Supplementary Information

Contents of the supplementary information:

Experimental Section

All reagents were purchased from commercial sources and used without further purification. Copper(I) iodide (fine grey powder), thiophenol, iodobenzene, 2-iodotoluene, 4-iodotoluene, 1,10-phenanthroline, 1,4-di-*tert*-butylbenzene, *t*BuOK were purchased from ACROS. 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. Elemental analysis was performed on a Thermo CHNS-O analyzer (FlashEA 1112 series). High resolution ESI-MS were recorded using a Waters LCT Premier XE with a dual ionization ESCi® 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-S Coupling Reaction: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (18.0 mg, 0.10 mmol, 10 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (112.9 μL, 1.1 mmol) and iodobenzene (111.9 μL, 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 for diphenyl thioether: 87.6%. (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.12).

Copper(I)-Catalyzed C-S Coupling Reaction without Phen : In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL)

were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (112.9 μL, 1.1 mmol) and iodobenzene (111.9 μL, 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 for diphenyl thioether: 6.6%. (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.12).

Selective Copper(I)-Catalyzed C-S Coupling Reaction with Phen: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (18.0 mg, 0.10 mmol, 10 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (102.6 μL, 1.0 mmol), 4-iodotoluene (411 mg, 1.9 mmol) and 2-iodotoluene (239 μL, 1.9 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: 39% for 2-tolylphenyl thioether (**2a**) and 49.4% for 4-tolylphenyl thioether (**2b**). (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.08).

Selective Copper(I)-Catalyzed C-S Coupling Reaction without Phen: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (102.6 μL, 1.0 mmol), 4-iodotoluene (436 mg, 2.0 mmol) and 2-iodotoluene (254 μL, 2.0 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: 11.9% for 2-tolylphenyl thioether (**2a**) and 15.2% for 4-tolylphenyl thioether (**2b**). (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.08).

Procedure of Copper(I)-Catalyzed C-S Coupling Reaction with 10 mol% Phen for 3 hr: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (18.0 mg, 0.10 mmol, 10 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (112.9 μL, 1.1 mmol) and iodobenzene (111.9 μL, 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 3 h. GC yield for diphenyl thioether**:** 35.7%. (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.12).

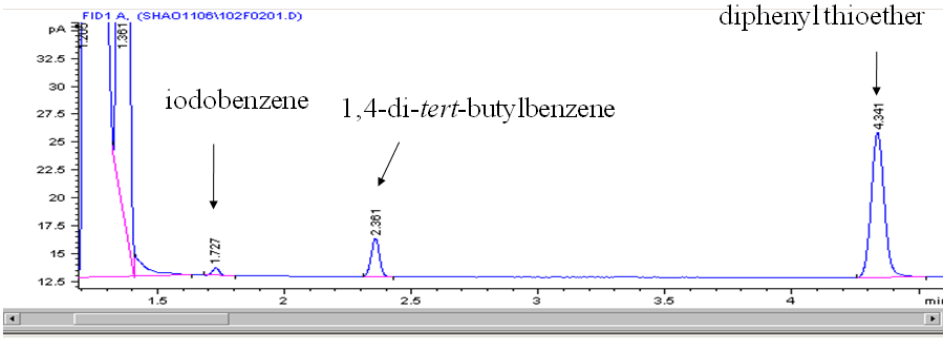
Procedure of Copper(I)-Catalyzed C-S Coupling Reaction with 20 mol% Phen for 3 hr: In a glove box, CuI (19.0 mg, 0.10 mmol, 10 mol%), 1,10-phenanthroline (36.0 mg, 0.20 mmol, 20 mol%), *t*BuOK (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (112.9 μL, 1.1 mmol) and iodobenzene (111.9 μL, 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 3 h. GC yield for diphenyl thioether**:** 63.1%. (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.12).

Procedure of Copper(I)-Catalyzed C-S Coupling Reaction with 30 mol% Phen for 3 hr: 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 (168.3 mg, 1.5 mmol), 1,4-di-*tert*-butylbenzene (19.0 mg, 0.10 mmol) and toluene (3 mL) were transferred to a Pyrex tube with a Teflon screw cap. Thiophenol (112.9 μL, 1.1 mmol) and iodobenzene (111.9 μL, 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 3 h. GC yield for diphenyl thioether**:** 67.2%. (1,4-di-*tert*-butylbenzene was used as the internal standard, correction factor: 1.12).

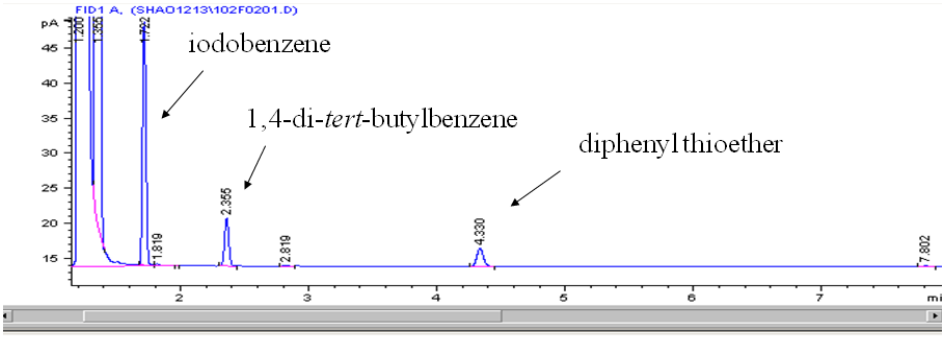
GC Data for Copper-Catalyzed C-S Cross-Coupling Reaction

1. Copper(I)-Catalyzed C-S Coupling Reaction



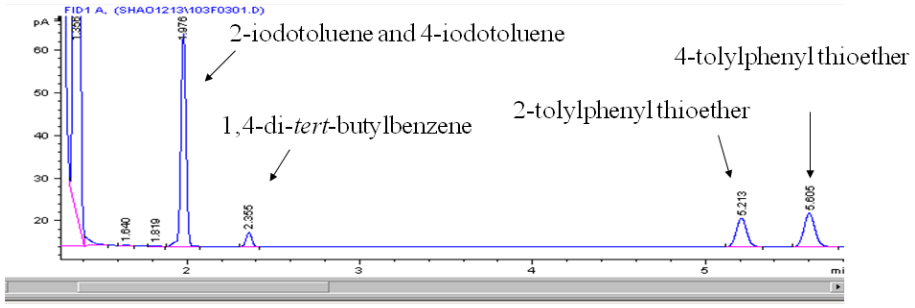
#	Time	Area	Height	Width	Area%	Symmetry
1	1.205	305023.2	153417.5	0.0312	99.635	0.26
2	1.361	1061.1	557.9	0.0312	0.347	1.143
3	1.727	1.2	6.4E-1	0.0307	0.000	1.093
4	2.361	7.8	3.4	0.0358	0.003	1.024
5	4.341	46.3	13	0.0557	0.015	0.897

2. Copper(I)-Catalyzed C- S Coupling Reaction without Phen



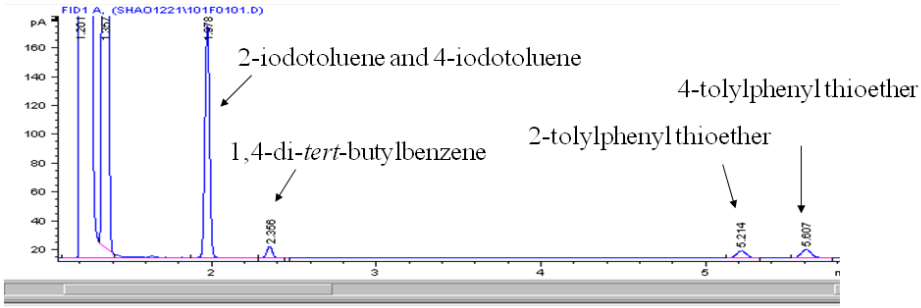
#	Time	Area	Height	Width	Area%	Symmetry
1	1.2	303551	158220.9	0.0299	99.272	0.138
2	1.355	2135	1131.1	0.031	0.698	0.931
3	1.722	65.5	34.7	0.03	0.021	0.909
4	1.819	4.7E-1	2E-1	0.0301	0.000	0.879
5	2.355	15.5	6.7	0.0369	0.005	0.988
6	2.819	2.7E-1	9.8E-2	0.0356	0.000	1.602
7	4.33	9.1	2.6	0.0551	0.003	0.925
8	7.802	4.9E-1	9.7E-2	0.0602	0.000	0.622

3. Selective Copper(I)-Catalyzed C-S Coupling Reaction with Phen:



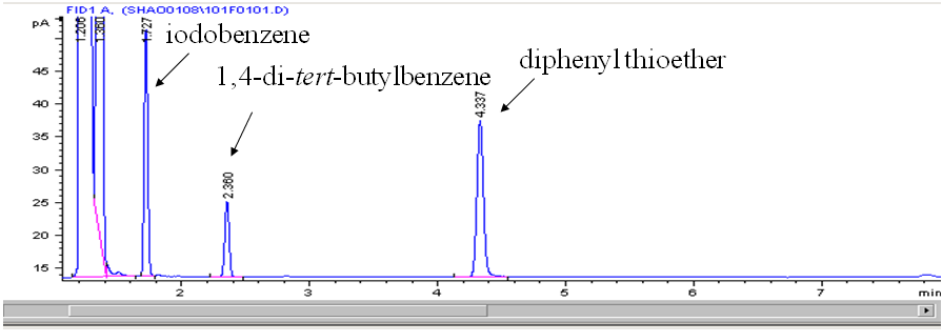
#	Time	Area	Height	Width	Area%	Symmetry
1	0.552	1.5E-1	8.5E-2	0.0222	0.000	0.503
2	1.2	309736.9	165570.6	0.0288	99.613	0.134
3	1.356	1028.5	541.7	0.0311	0.331	0.937
4	1.64	6.1E-1	2.3E-1	0.0332	0.000	0.812
5	1.819	3.8E-1	1.9E-1	0.0266	0.000	1.092
6	1.976	104.4	49.8	0.0334	0.034	1.003
7	2.355	7.6	3.3	0.0364	0.002	1.009
8	5.213	27.5	6.7	0.0639	0.009	0.991
9	5.605	34.8	7.8	0.0689	0.011	0.9

4. Selective Copper(I)-Catalyzed C-S Coupling Reaction without Phen:



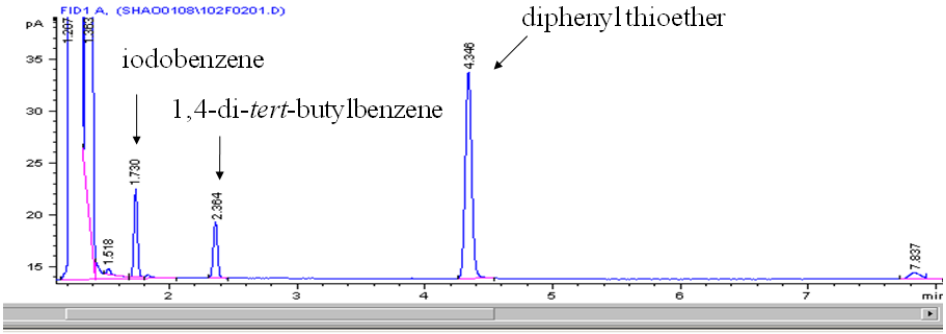
#	Time	Area	Height	Width	Area%	Symmetry
1	1.201	289531.2	160053.5	0.0286	99.040	0.147
2	1.357	2423.4	1310	0.0301	0.829	1.021
3	1.978	320.6	160.7	0.0318	0.110	0.982
4	2.356	18	7.9	0.036	0.006	1.006
5	5.214	19.9	4.9	0.0624	0.007	0.969
6	5.607	25.3	5.7	0.0697	0.009	0.89

5. Copper(I)-Catalyzed C-S Coupling Reaction with 10 mol% Phen for 3 hr:



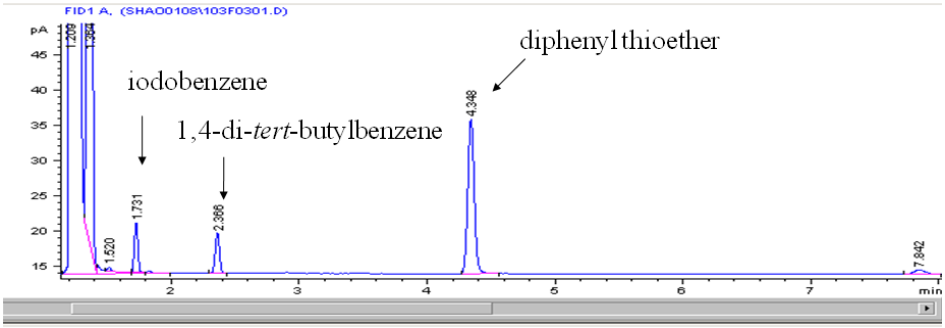
#	Time	Area	Height	Width	Area%	Symmetry
1	1.206	318682	153897.3	0.0322	98.997	0.249
2	1.36	3045.2	1528.8	0.0322	0.946	0.985
3	1.727	73.5	37.3	0.032	0.023	0.956
4	2.36	26.5	11.4	0.0371	0.008	1
5	4.337	84.5	23.8	0.0555	0.026	0.915

6. Copper(I)-Catalyzed C-S Coupling Reaction with 20 mol% Phen for 3 hr:



#	Time	Area	Height	Width	Area%	Symmetry
1	1.207	323119.2	166478.7	0.0306	99.482	0.212
2	1.363	1579.2	818.1	0.0315	0.486	1.014
3	1.518	1E0	5.9E-1	0.0269	0.000	1.1
4	1.73	16.3	8.4	0.0306	0.005	0.965
5	2.364	12.4	5.4	0.036	0.004	1.003
6	4.346	69.9	19.8	0.0542	0.022	0.931
7	7.837	4.1	6.2E-1	0.0852	0.001	0.882

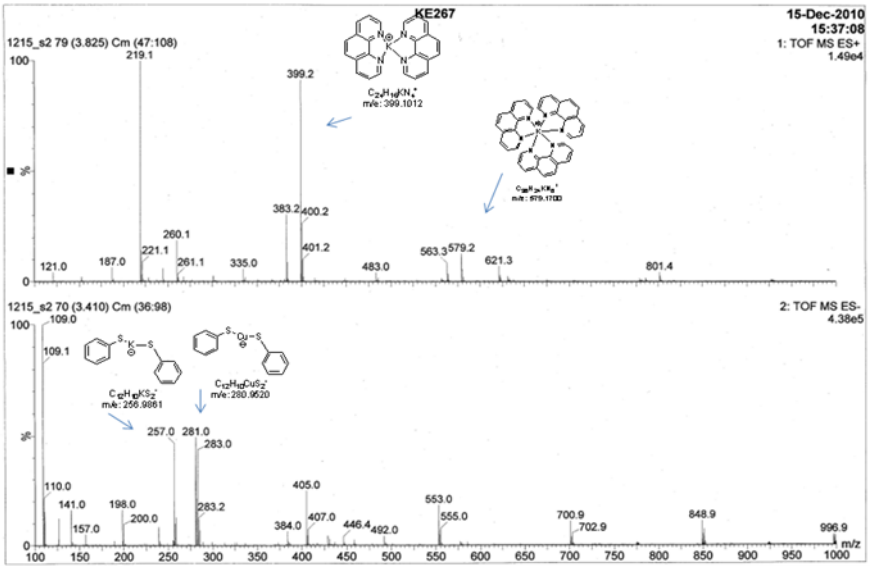
7. Copper(I)-Catalyzed C-S Coupling Reaction with 30 mol% Phen for 3 hr:



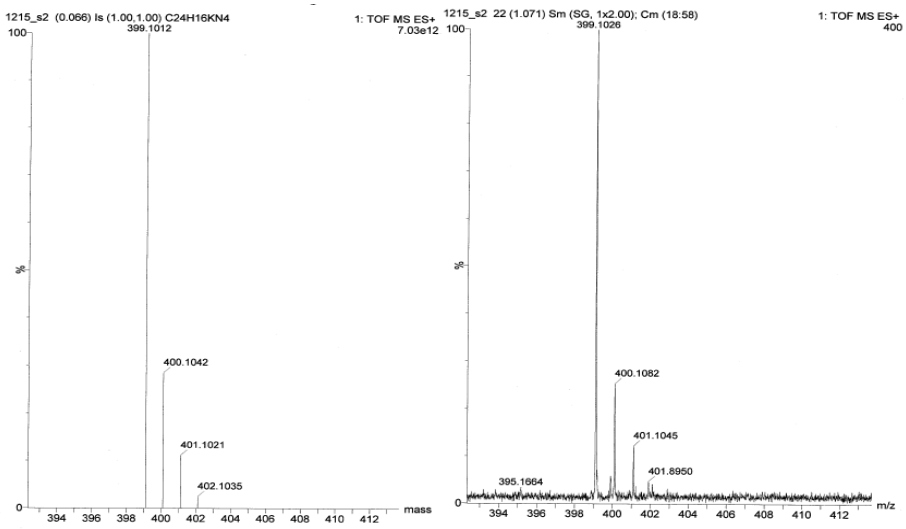
#	Time	Area	Height	Width	Area%	Symmetry
1	1.209	306057	151279.4	0.0316	99.438	0.253
2	1.364	1622	846	0.0314	0.527	1.053
3	1.52	8.1E-1	5.3E-1	0.0248	0.000	1.368
4	1.731	13.5	7	0.0305	0.004	0.995
5	2.366	12.9	5.6	0.0358	0.004	1.026
6	4.348	77.4	21.8	0.0555	0.025	0.923
7	7.842	3.6	5.6E-1	0.0907	0.001	0.916

In situ ESI-MS Spectra and Isotope Distribution of Intermediates

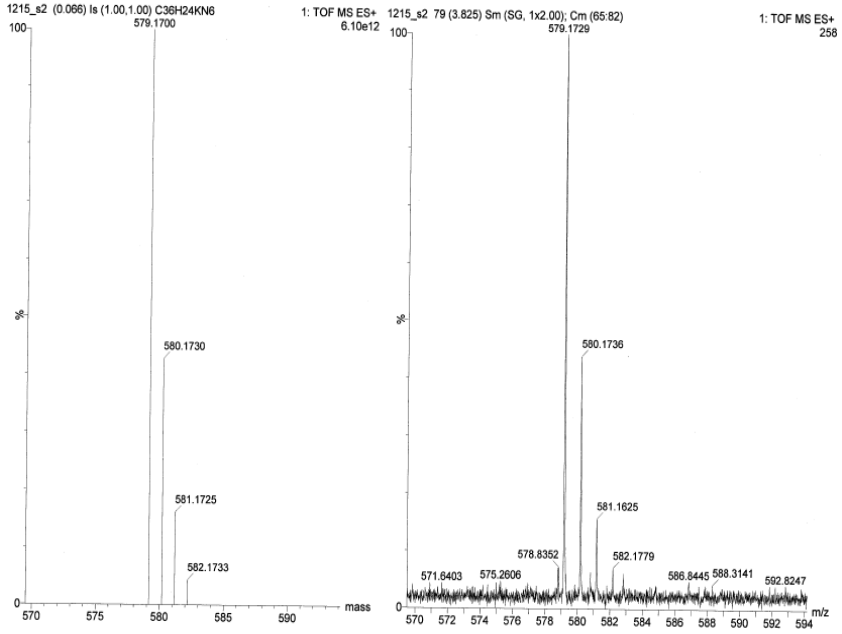
1. Experimental and theoretical isotopic distributions of $[K(phen)_2]^+$, $[K(phen)_3]^+$, $[K(SPh)_2]^-$ and $[Cu(SPh)_2]^-$ (from the ESI-MS spectra of the reaction solution taken during the reaction of thiophenol and iodobenzene with *t*BuOK in the presence of CuI and phen in toluene at room temperature).



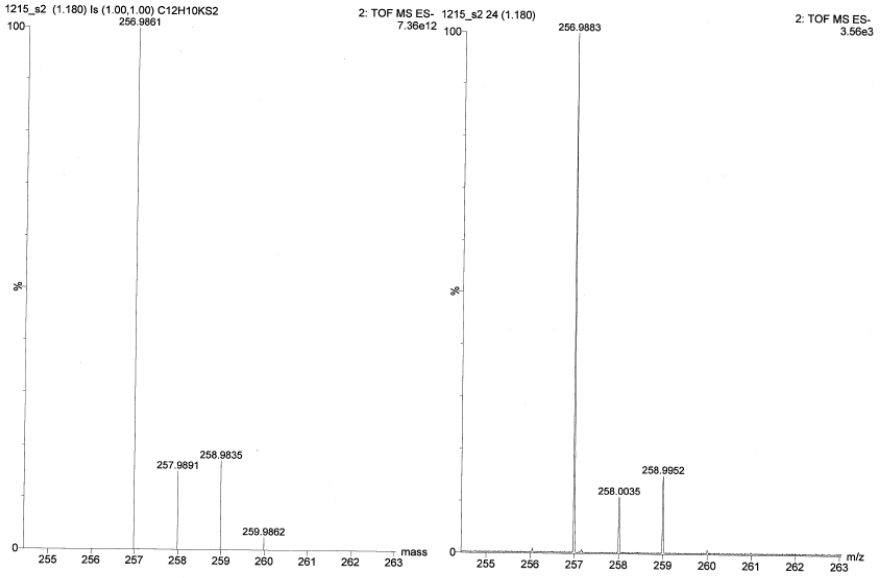
Theoretical isotopic distributions of $[K(phen)_2]^+$ Experimental isotopic distributions of $[K(phen)_2]^+$



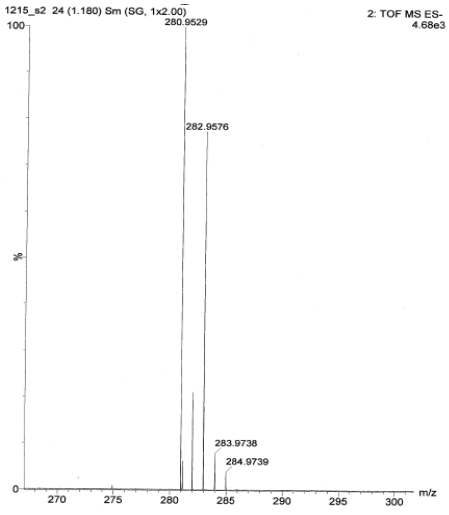
Theoretical isotopic distributions of $[K(phen)_3]^+$ **Experimental isotopic distributions of $[K(phen)_3]^+$**



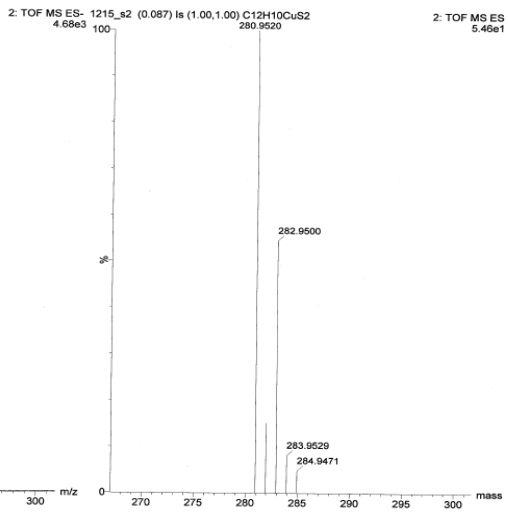
Theoretical isotopic distributions of $[K(SPh)_2]^-$ **Experimental isotopic distributions of $[K(SPh)_2]^-$**



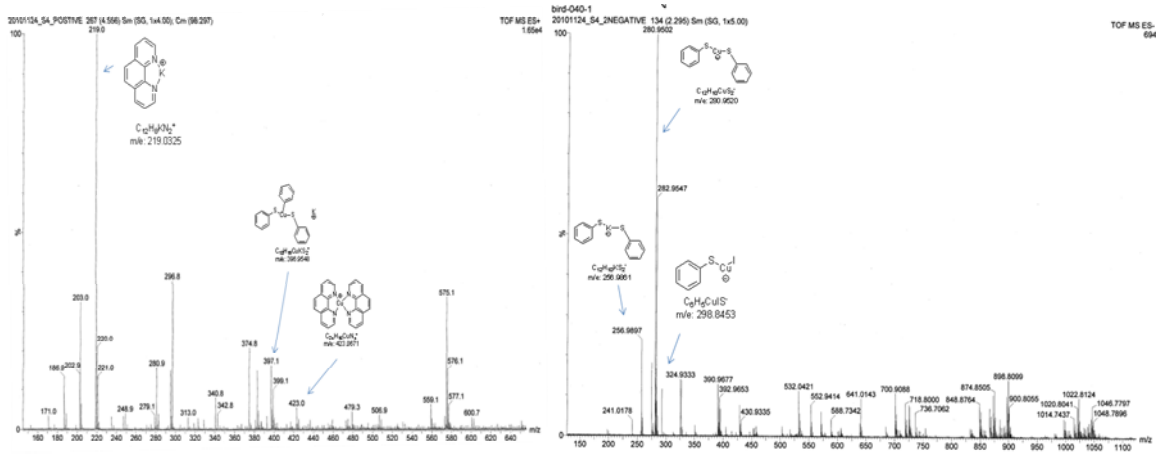
Theoretical isotopic distributions of $[Cu(SPh)_2]^-$



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

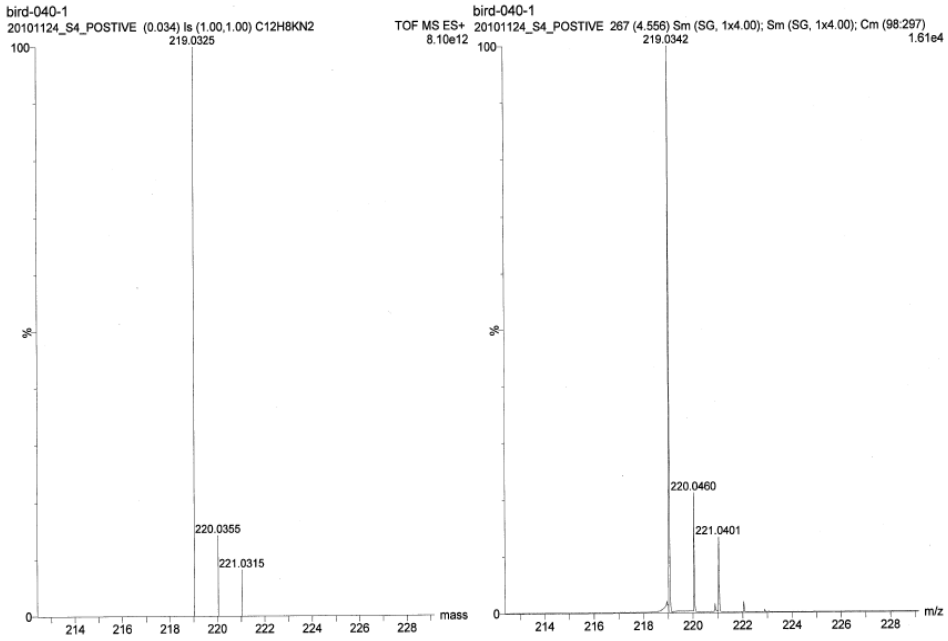


2. Experimental and theoretical isotopic distributions of $[K(phen)]^+$, $[Cu(SPh)_2(phenyl)K]^+$, $[Cu(phen)_2]^+$, $[K(SPh)_2]^-$, $[Cu(SPh)_2]^-$ and $[Cu(SPh)I]^-$ (from the ESI-MS spectra of the reaction solution during the reaction of thiophenol and iodobenzene with *t*BuOK in the presence of CuI and phen in toluene at 120 ^oC).

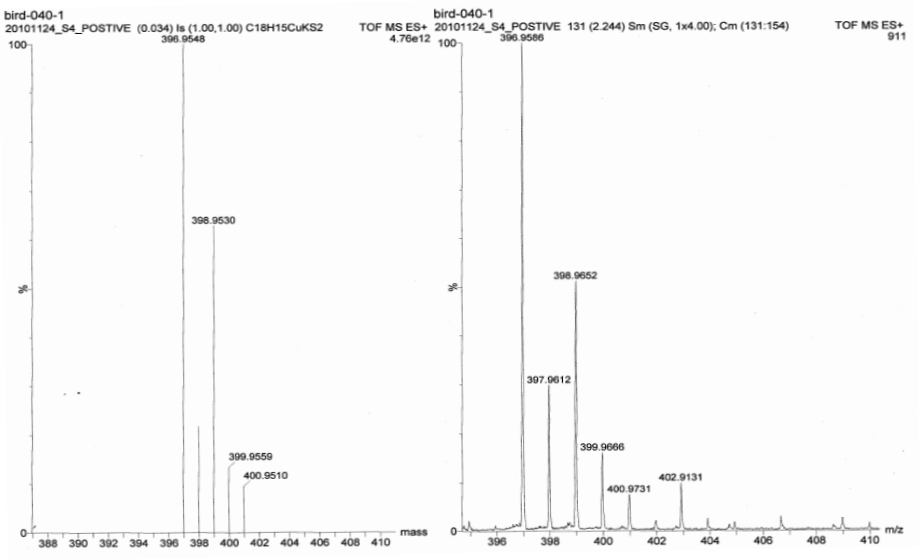


Theoretical isotopic distributions of [K(phen)]+

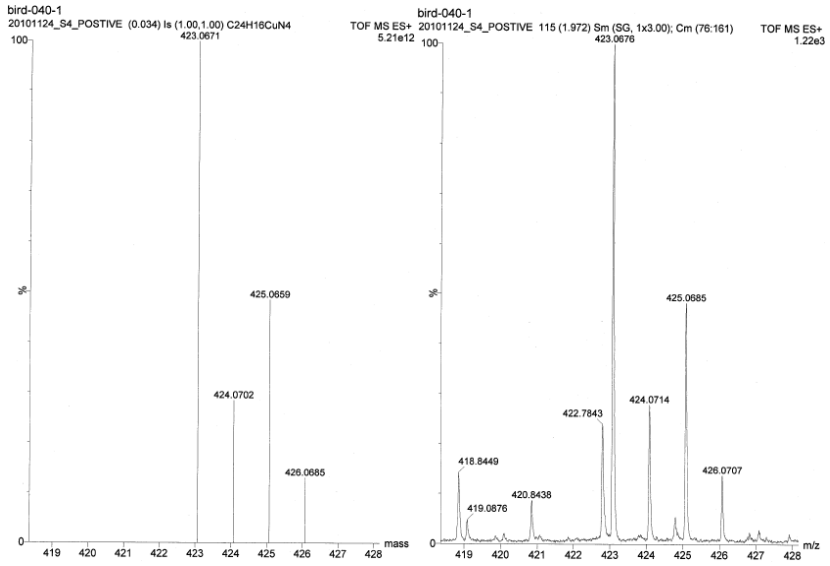
Experimental isotopic distributions of [K(phen)]+



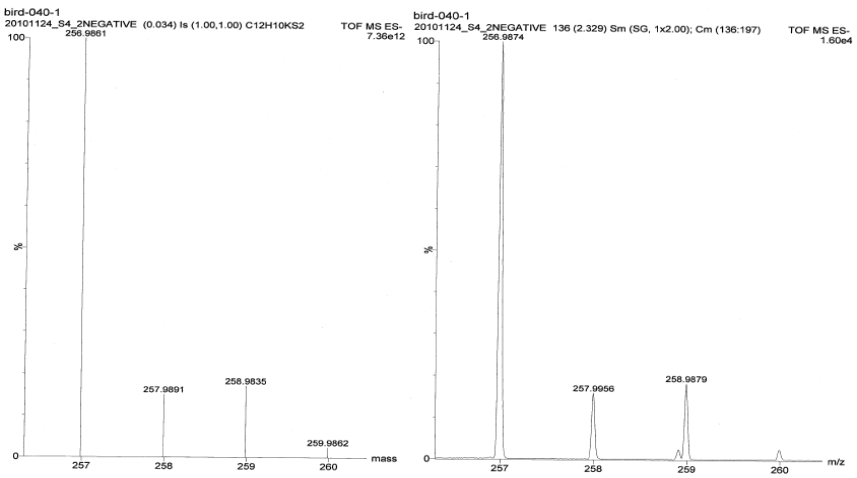
Theoretical isotopic distributions of $[Cu(SPh)_2(Ph)K]^+$ Experimental isotopic distributions of $[Cu(SPh)_2(Ph)K]^+$



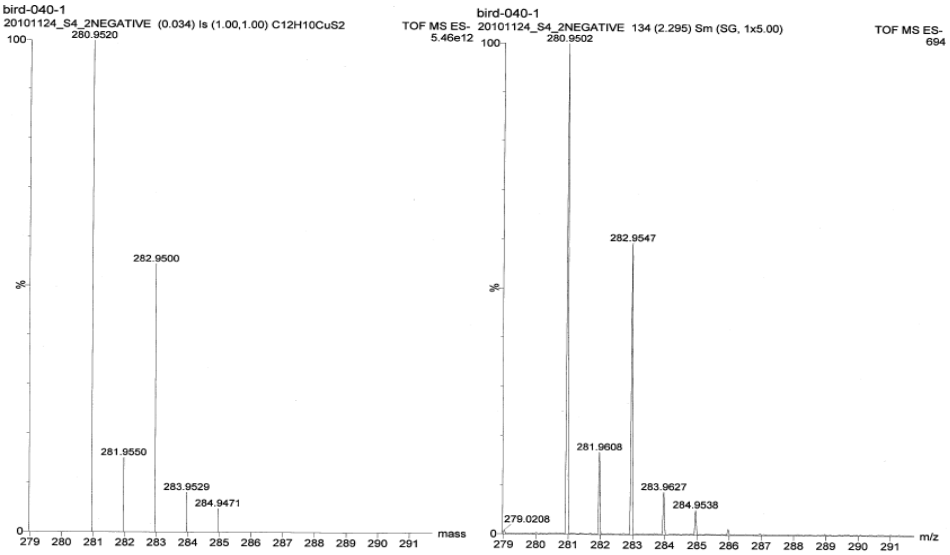
Theoretical isotopic distributions of $[Cu(phen)_2]^+$ Experimental isotopic distributions of $[Cu(phen)_2]^+$



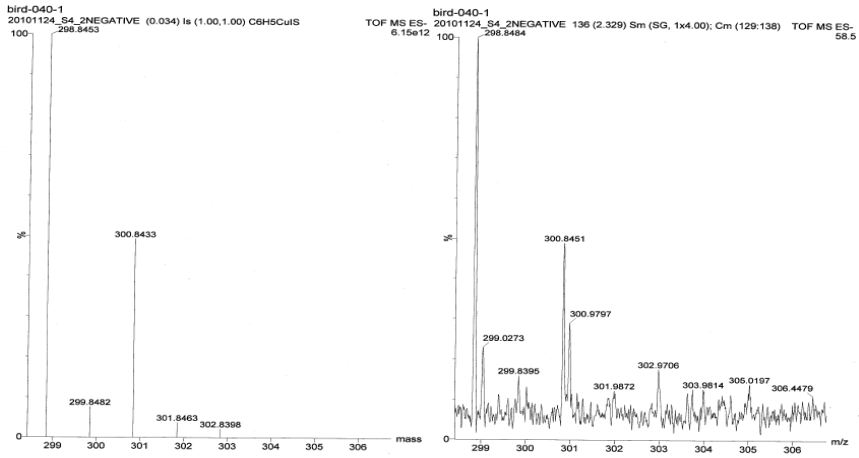
Theoretical isotopic distributions of $[K(SPh)_2]^-$ Experimental isotopic distributions of $[K(SPh)_2]^-$



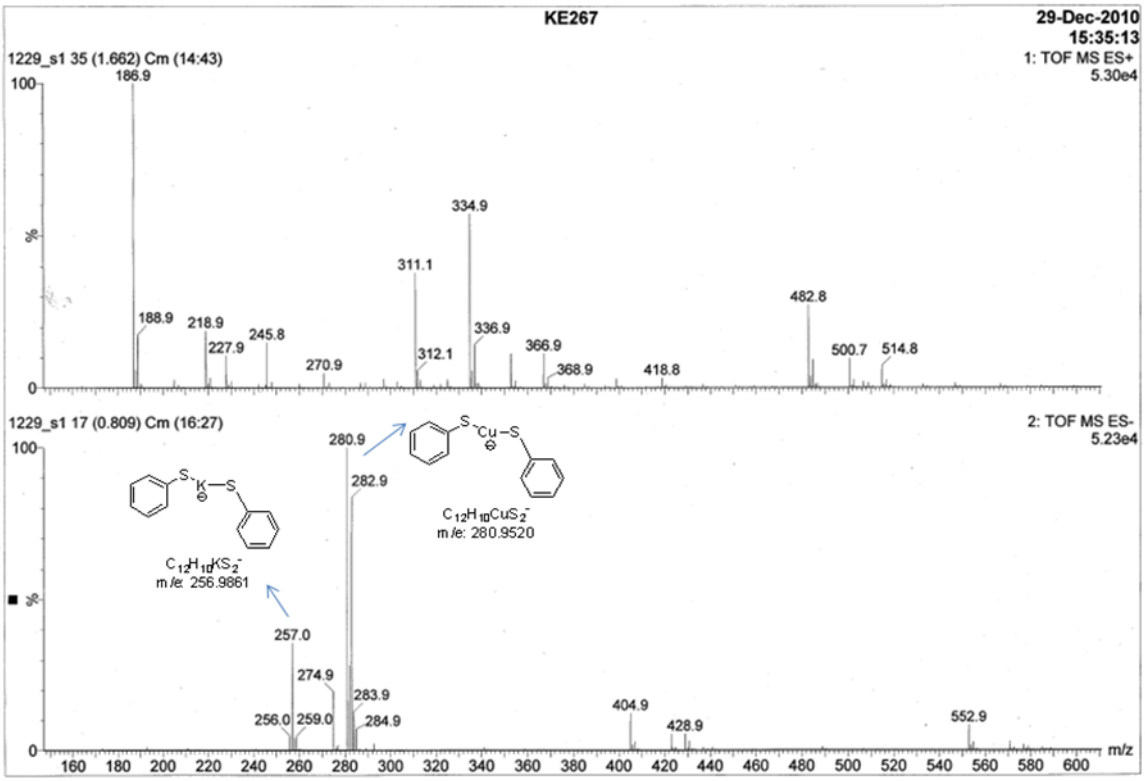
Theoretical isotopic distributions of $[Cu(SPh)_2]^-$ **Experimental isotopic distributions of $[Cu(SPh)_2]^-$**



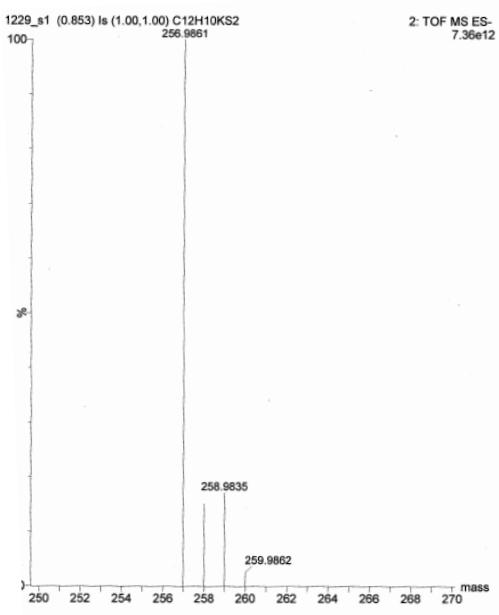
Theoretical isotopic distributions of $[Cu(SPh)I]^-$ **Experimental isotopic distributions of $[Cu(SPh)I]^-$**



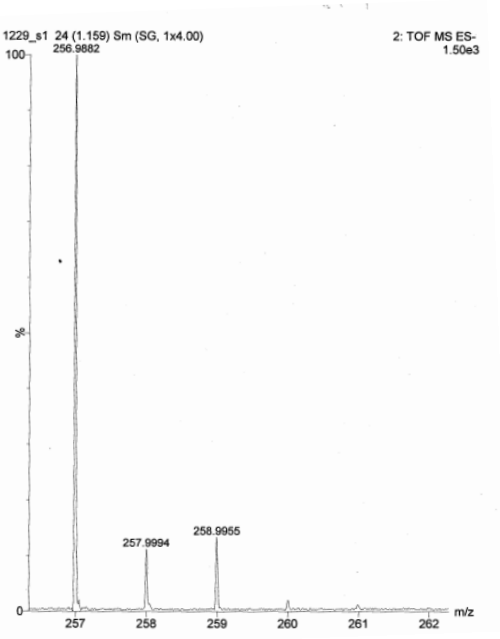
3. Experimental and theoretical isotopic distributions of $[K(SPh)_2]^-$ and $[Cu(SPh)_2]^-$ (from the ESI-MS spectra of the reaction solution during the reaction of thiophenol and iodobenzene with *t*BuOK in the presence of CuI in toluene at 120 ^oC).



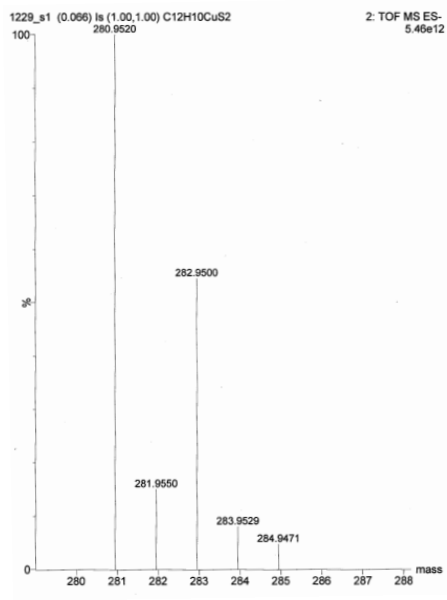
Theoretical isotopic distributions of $[K(SPh)_2]^-$



Experimental isotopic distributions of $[K(SPh)_2]^-$



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



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