

## Supplementary Information

### Possible Intermediates of Cu(Phen)-catalyzed C-O cross coupling of phenol with aryl bromide by *in situ* ESI-MS and EPR studies

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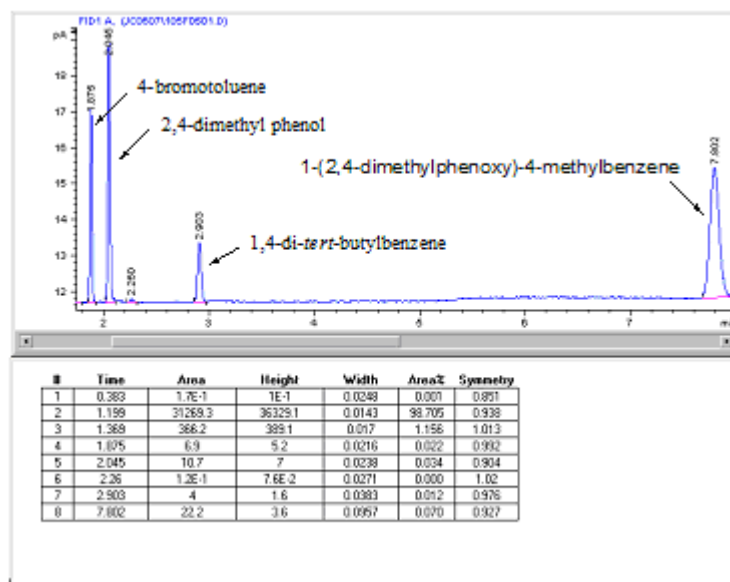
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## GC data for Copper-Catalyzed C-O Cross-Coupling Reaction

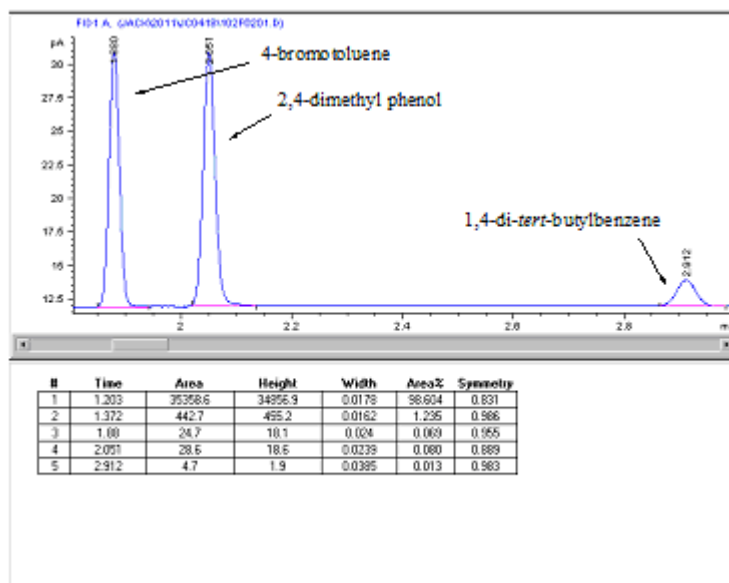
1. Copper-catalyzed C-O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by CuI/phen/K<sub>2</sub>CO<sub>3</sub>.

For 8 h

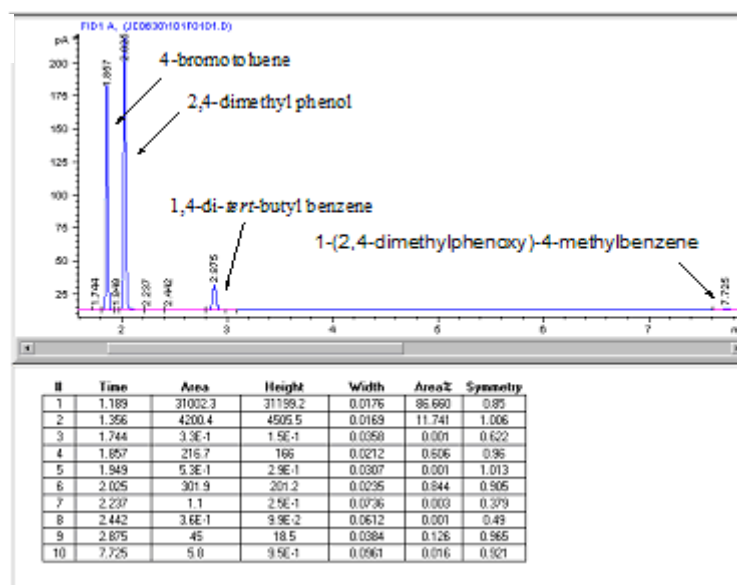


2. Copper-catalyzed C-O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by CuI/K<sub>2</sub>CO<sub>3</sub>.

For 8 h

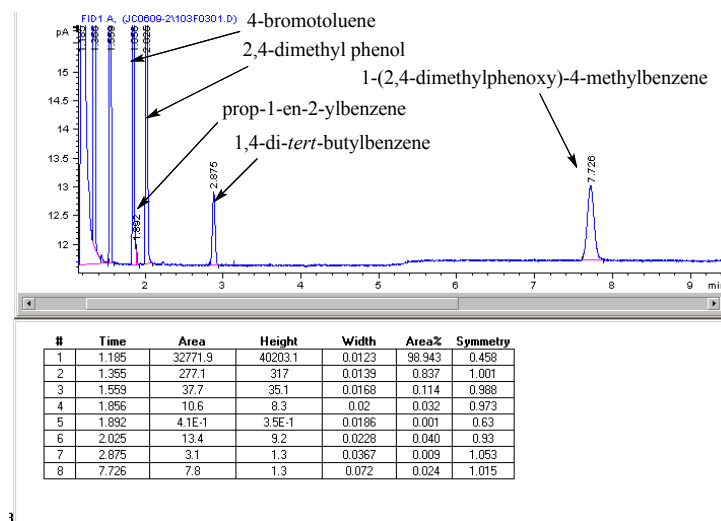


For 48 h

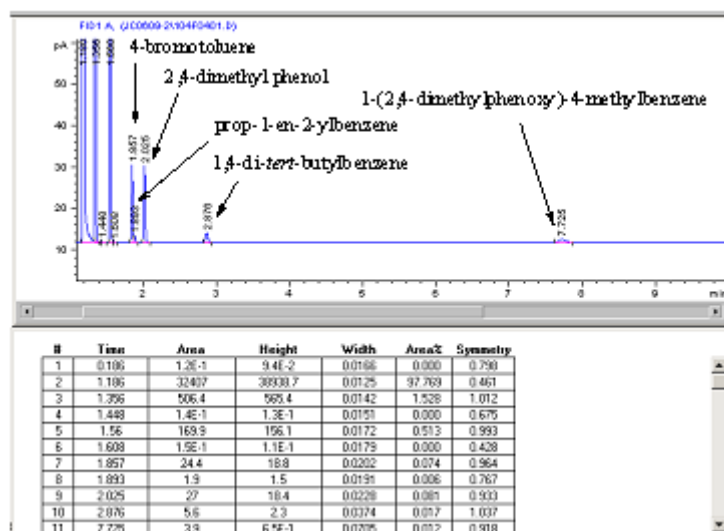


3. Copper-catalyzed C-O coupling reaction of 2,4-dimethyl phenol with 4-bromotoluene by  
 CuI/phen/K<sub>2</sub>CO<sub>3</sub>/Cumene.

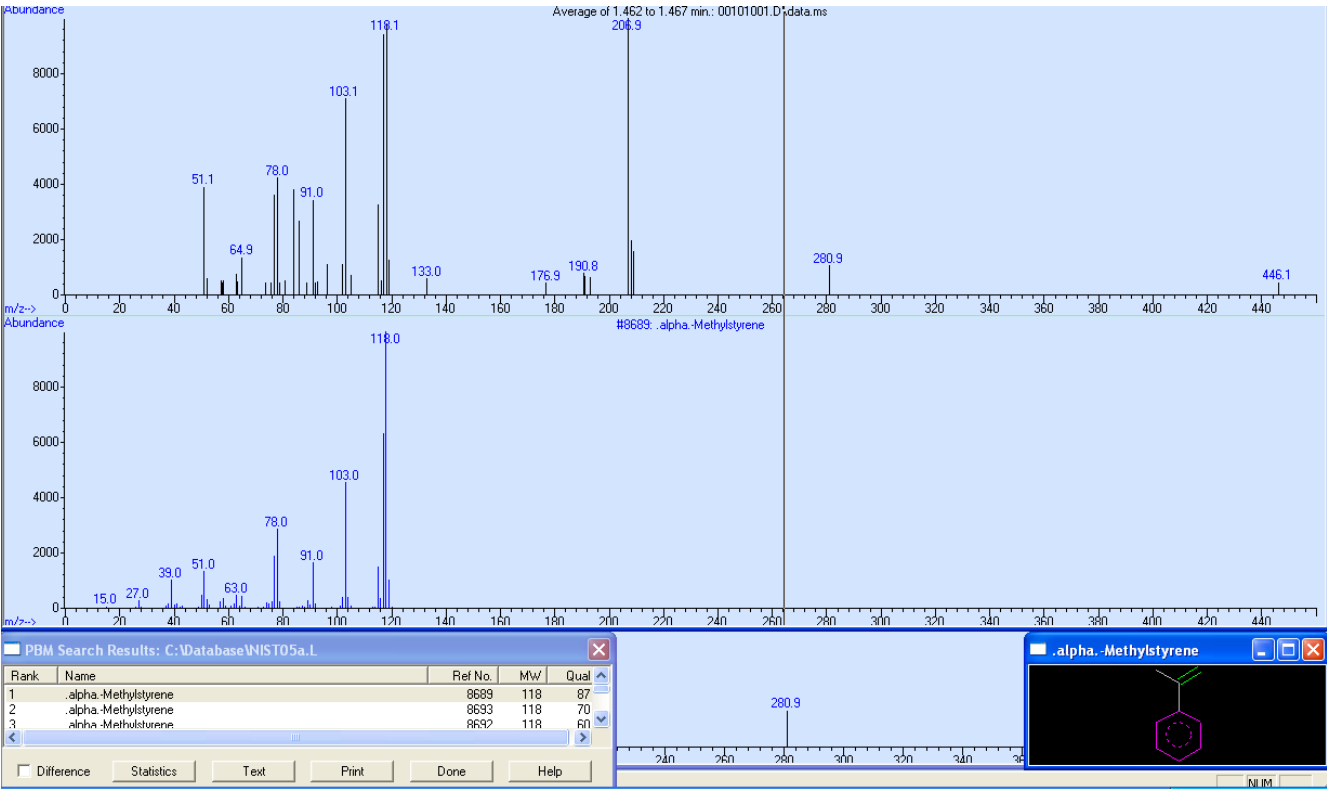
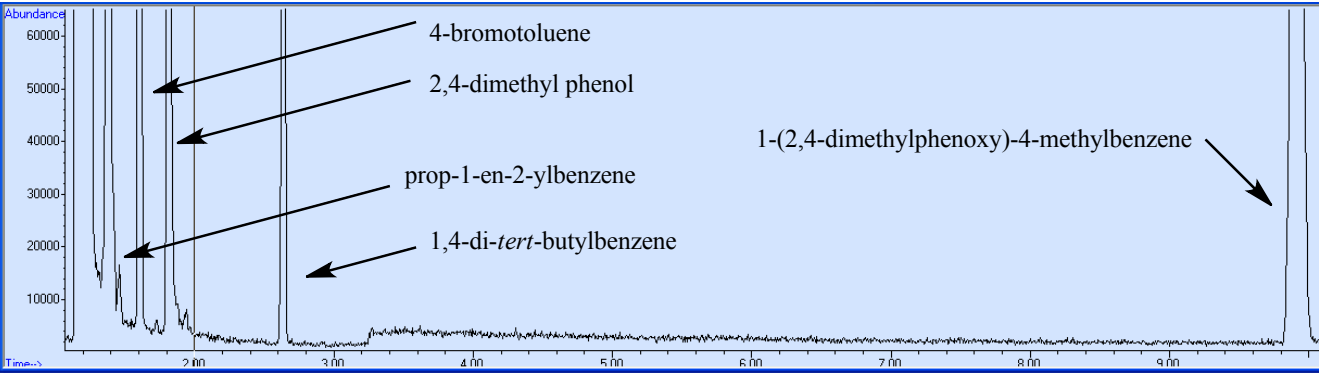
Cumene 20 mol%



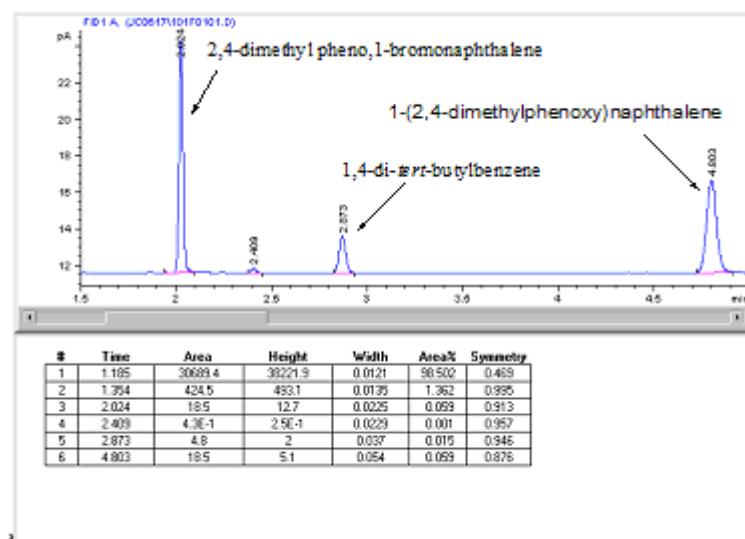
Cumene 50 mol%



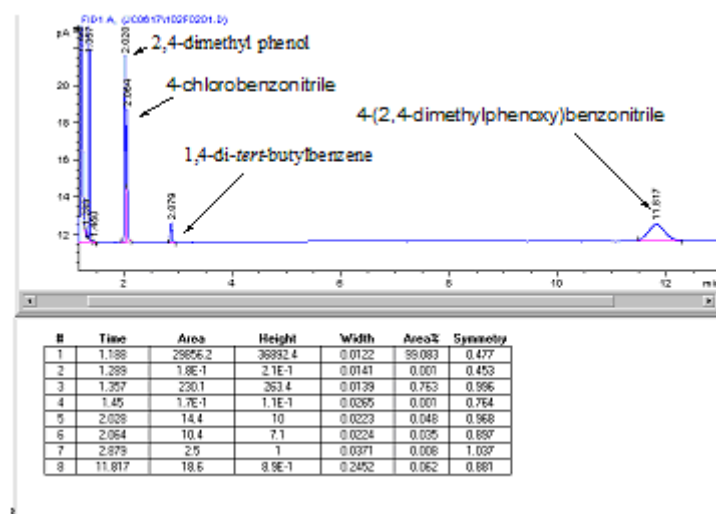
GC-MS data of prop-1-en-2-ylbenzene



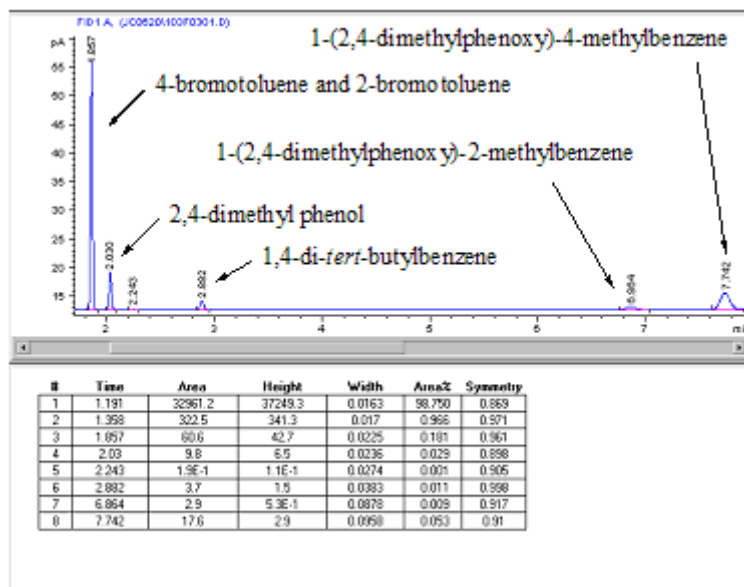
4. Copper-catalyzed C-O coupling reaction of 2,4-dimethyl phenol with 1-bromonaphthalene by CuI/phen/K<sub>2</sub>CO<sub>3</sub>.



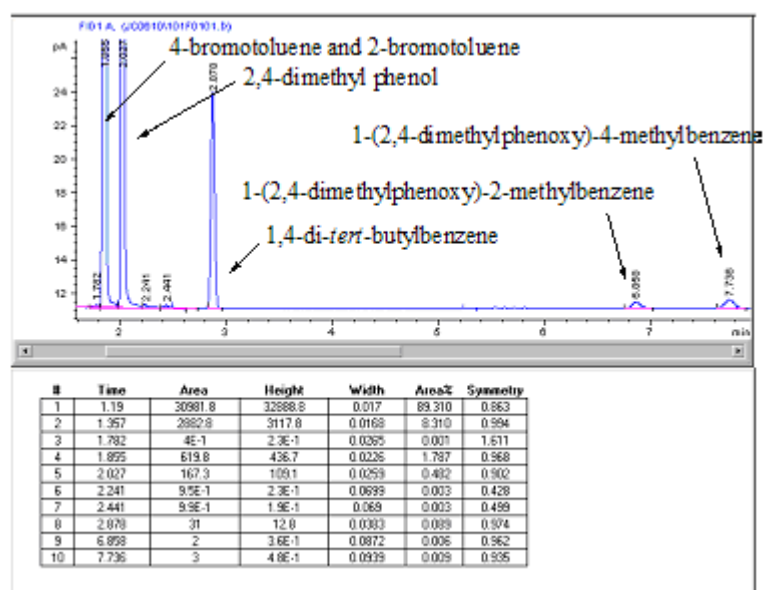
5. Copper-catalyzed C-O coupling reaction of 2,4-dimethyl phenol with 4-chlorobenzonitrile by CuI/phen/K<sub>2</sub>CO<sub>3</sub>.



6. Competitive catalytic C-O coupling of 2,4- dimethyl phenol with 4-bromotoluene and 2-bromotoluene by CuI/phen/K<sub>2</sub>CO<sub>3</sub>.



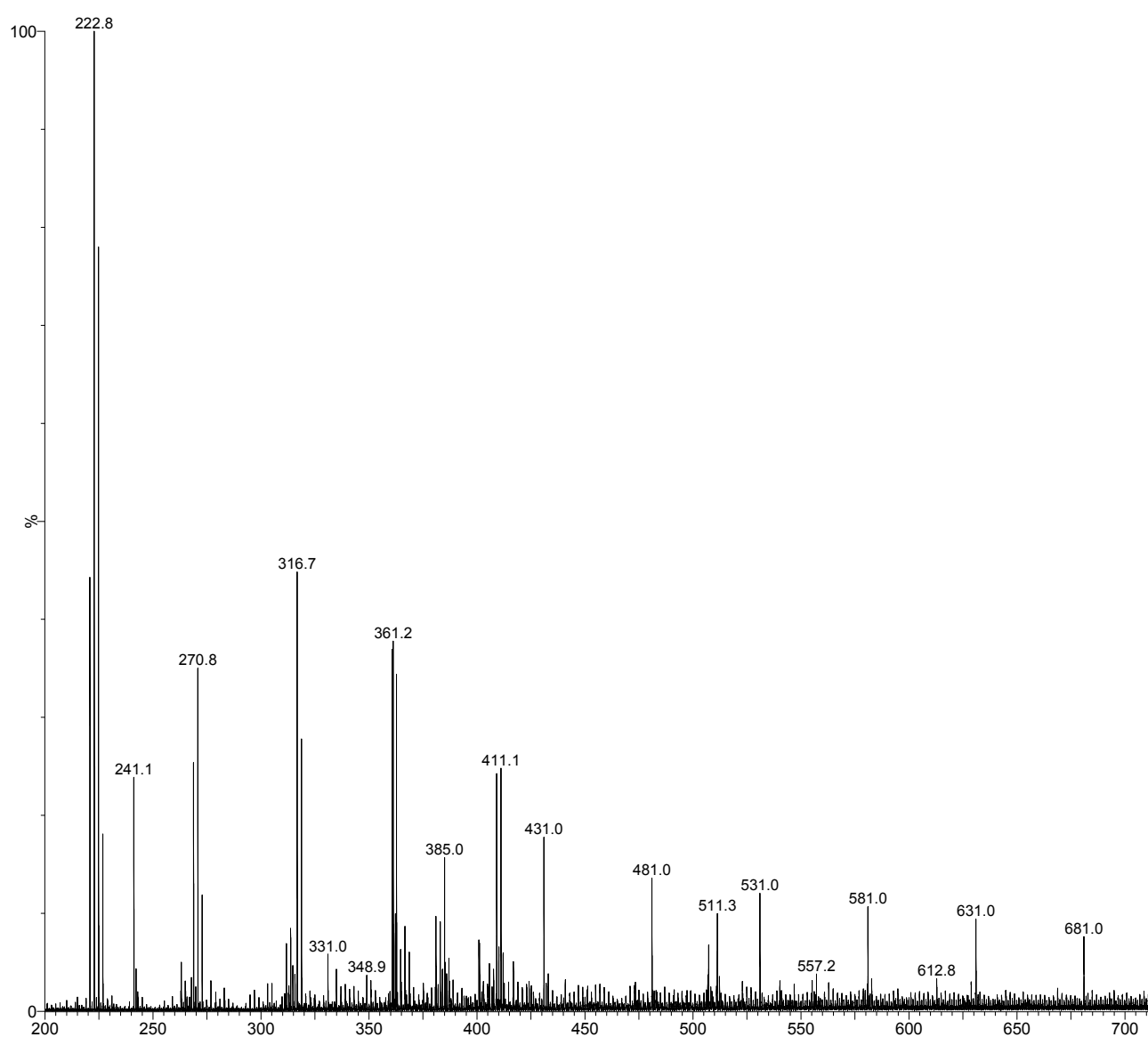
7. Competitive catalytic C-O coupling of 2, 4-dimethyl phenol with 4-bromotoluene and 2-bromotoluene by CuI/K<sub>2</sub>CO<sub>3</sub>.



## *In situ* ESI-MS Spectra and Isotope Distributions of Intermediates

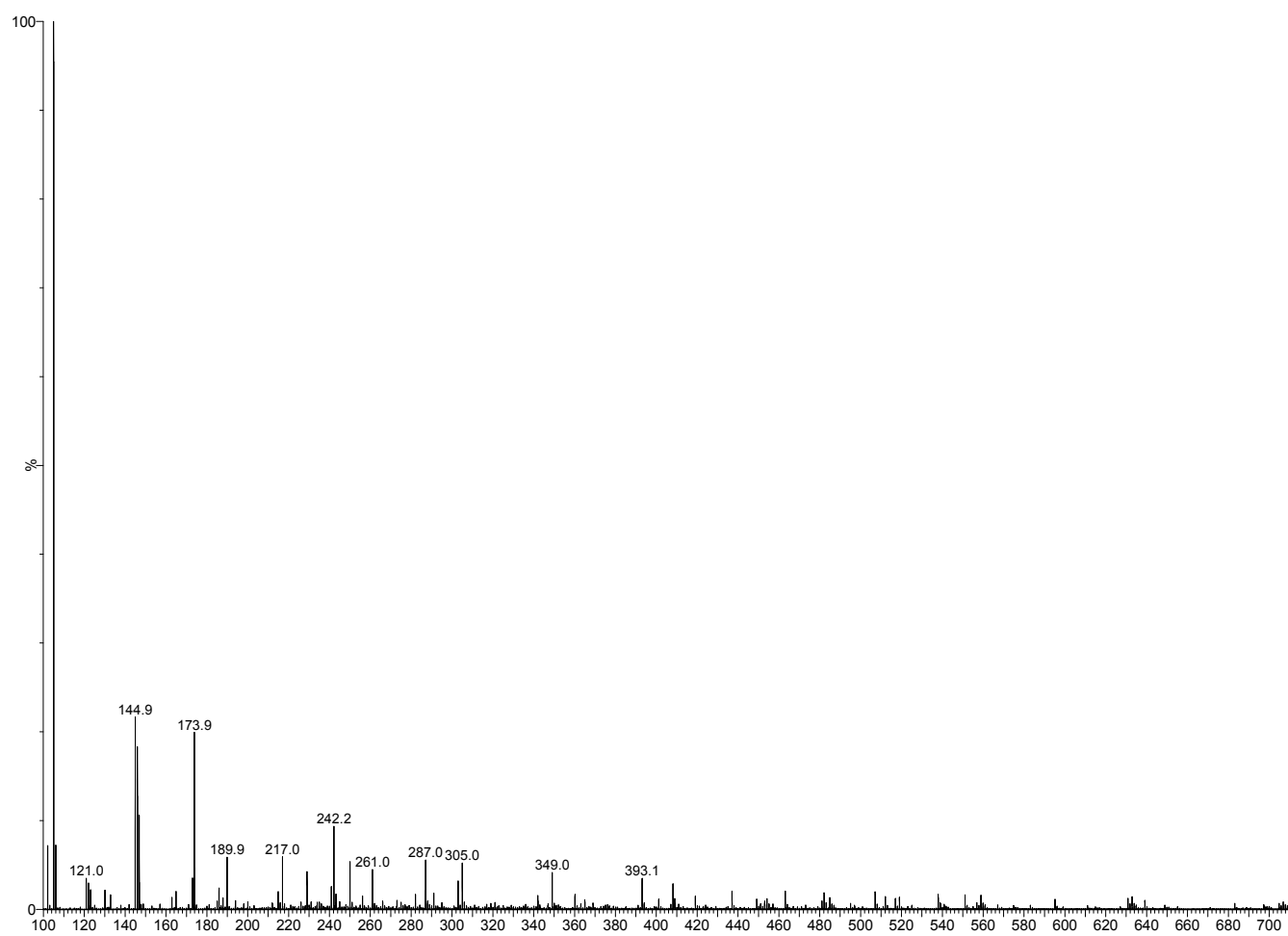
1. Experimental and simulated isotopic distributions of  $[\text{Cu}(\text{I})(2,4\text{-dimethylphenoxy})_2]^-$ ,  $\{\text{H}[\text{Cu}(\text{I})(\text{phen})(2,4\text{-dimethylphenoxy})]\}^+$ ,  $[\text{Cu}(\text{I})(\text{phen})(2,4\text{-dimethylphenoxy})(p\text{-tolyl})]^+$ ,  $[\text{Cu}(\text{phen})_2]^+$  and  $\{\text{K}[\text{Cu}(\text{I})(\text{phen})(2,4\text{-dimethylphenoxy})]\}^+$  (from the ESI-MS spectra of the C-O coupling reaction mixture of 2,4-dimethyl phenol and 4-bromotoluene catalyzed by CuI/phen/ $\text{K}_2\text{CO}_3$  in toluene at 120 °C)

ESI-MS(-) full mass

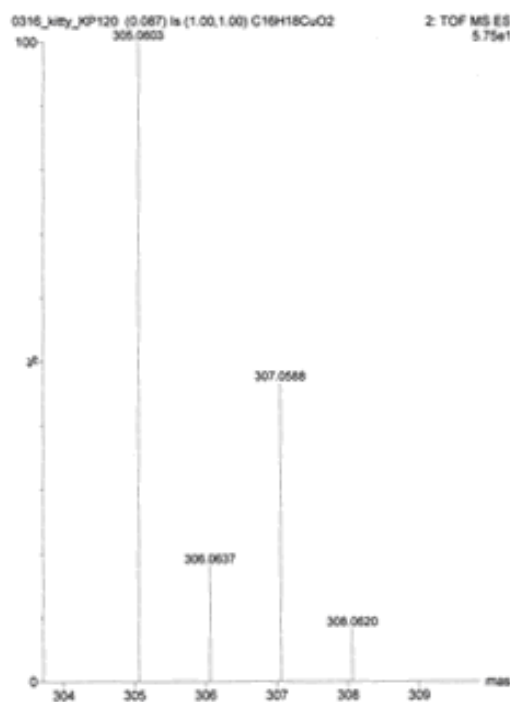




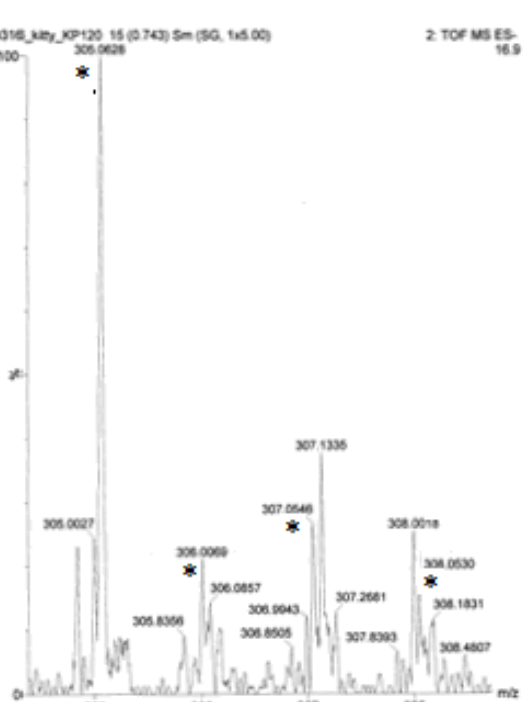
# ESI-MS(+) full mass



Simulated isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)<sub>2</sub>]<sup>-</sup>

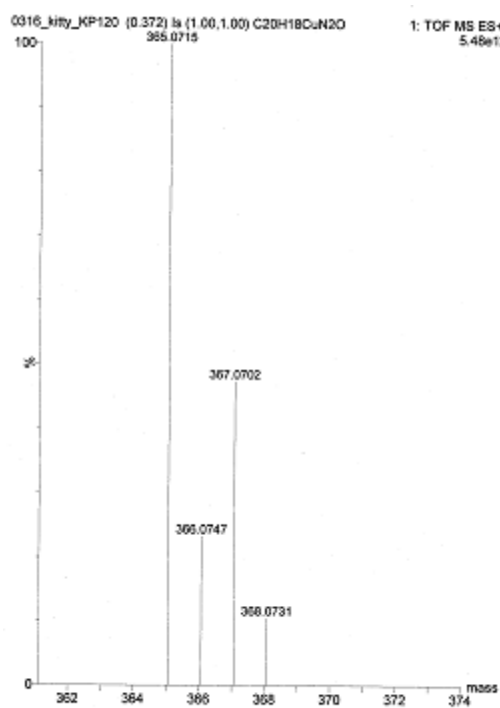


Experimental isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)<sub>2</sub>]<sup>-</sup>

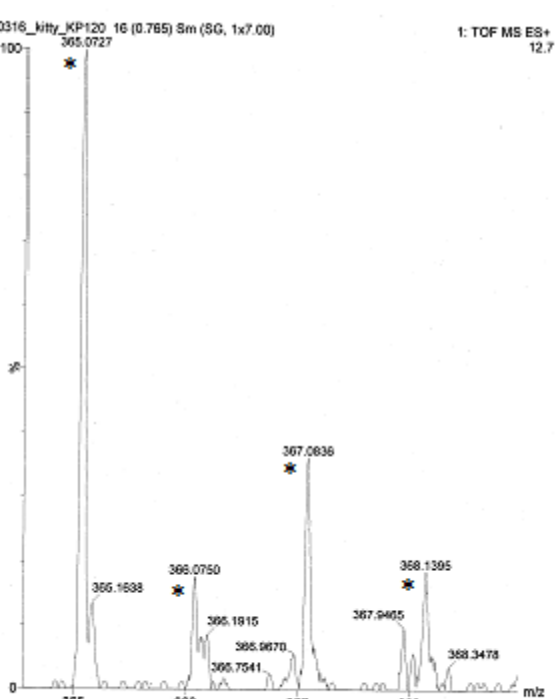


\* Signals of the compound

Simulated isotopic distributions of  
 $\{[Cu(I)(phen)(2,4\text{-dimethylphenoxy})]\}^+$



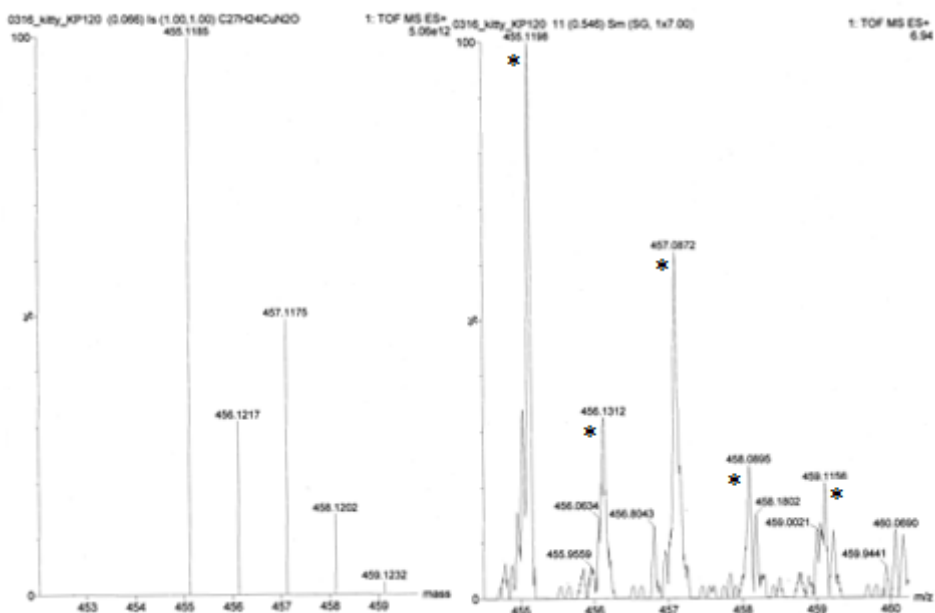
Experimental isotopic distributions of  
 $\{[Cu(I)(phen)(2,4\text{-dimethylphenoxy})]\}^+$



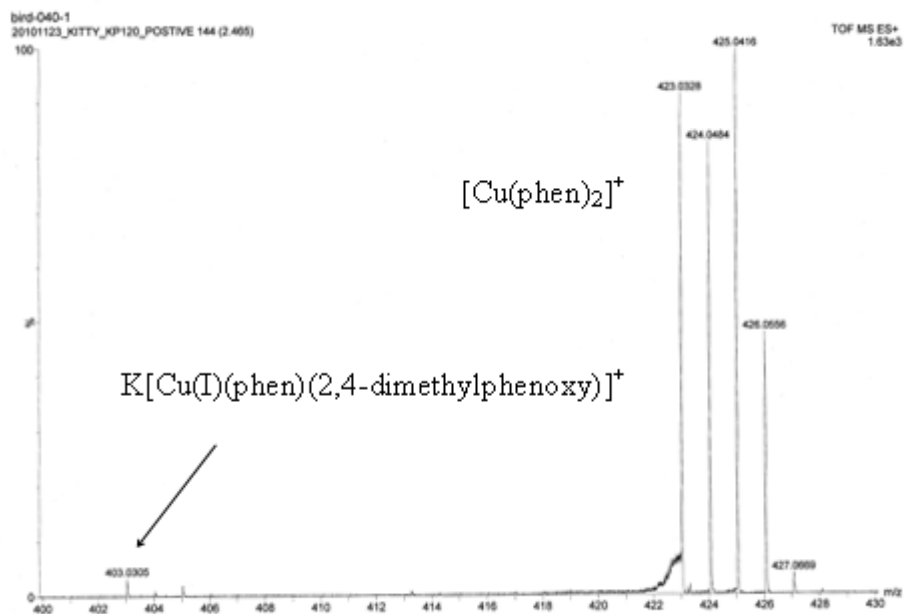
\*Signals of the compound

Simulated isotopic distributions of  
 $[\text{Cu(III)(phen)(2,4-dimethylphenoxy)(p-tolyl)}]^+$  or  
 $[\text{Cu(I)(phen)(1-(2,4-dimethylphenoxy)-4-methylbenzene)}]^+$

Experimental isotopic distributions of  
 $[\text{Cu(III)(phen)(2,4-dimethylphenoxy)(p-tolyl)}]^+$  or  
 $[\text{Cu(I)(phen)(1-(2,4-dimethylphenoxy)-4-methylbenzene)}]^+$

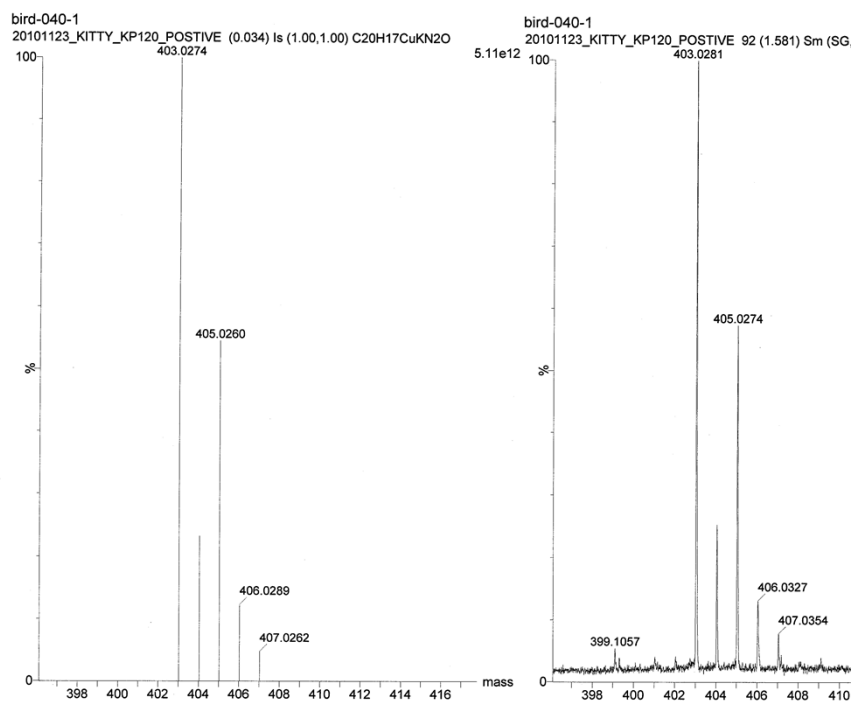


\* Signals of the compound



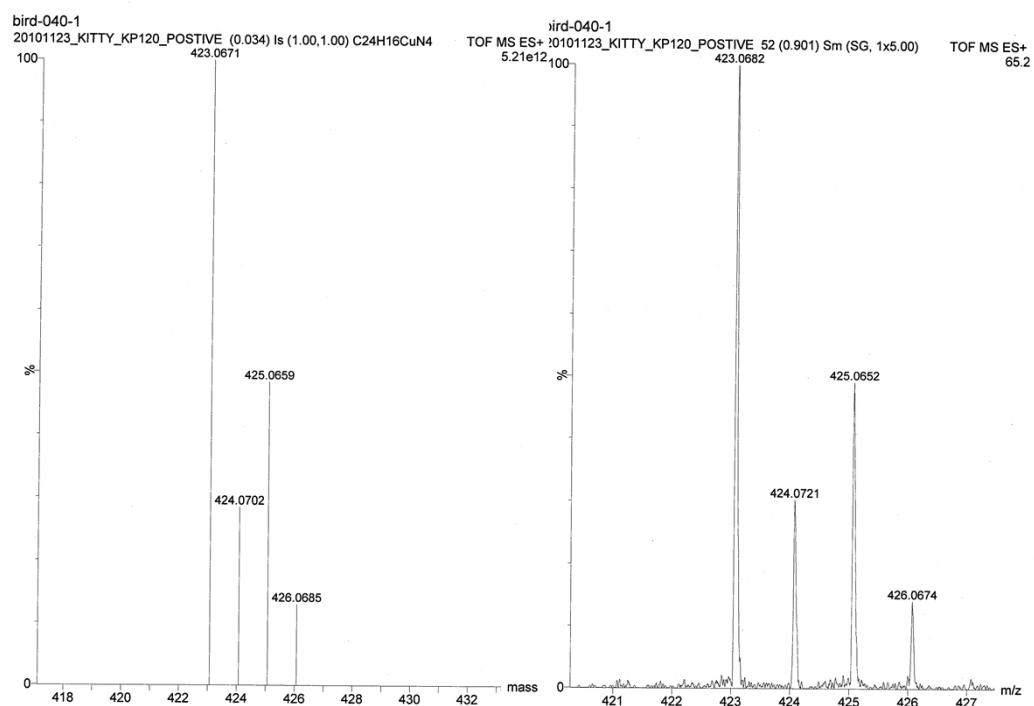
Simulated isotopic distributions of  
 $\{\text{K}[\text{Cu}(\text{I})(\text{phen})(2,4\text{-dimethylphenoxy})]\}^+$

Experimental isotopic distributions of  
 $\{\text{K}[\text{Cu}(\text{I})(\text{phen})(2,4\text{-dimethylphenoxy})]\}^+$



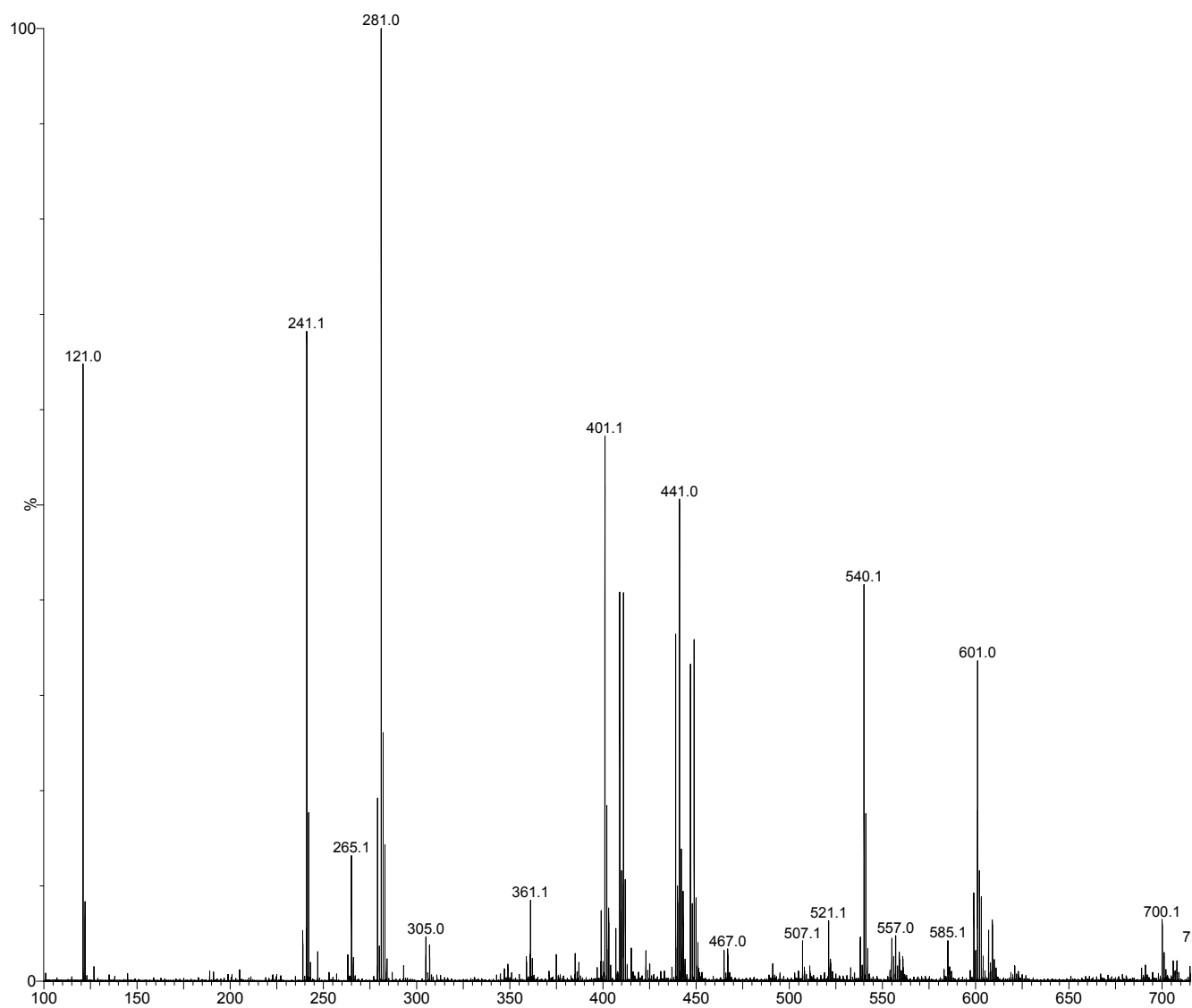
**Simulated isotopic distributions of  
[Cu(I)(phen)<sub>2</sub>]<sup>+</sup>**

**Experimental isotopic distributions of  
[Cu(I)(phen)<sub>2</sub>]<sup>+</sup>**

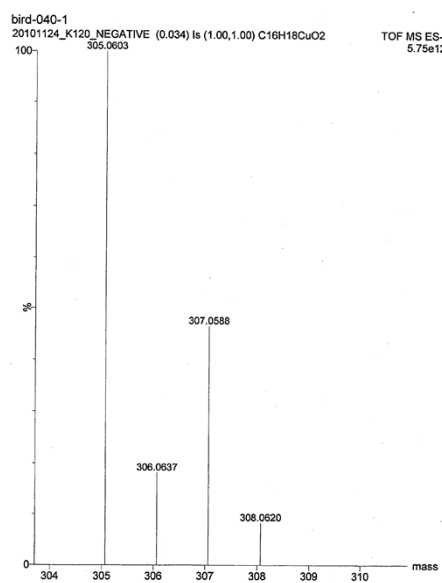


2. Experimental and theoretical isotopic distributions of  $[\text{Cu(I)(2,4-dimethylphenoxy)}_2]^-$  and  $[\text{Cu(I)(2,4-dimethylphenoxy)Br}]^-$ . (from the ESI-MS spectra of the C-O coupling reaction mixture of 2,4-dimethyl phenol and 4-bromotoluene catalyzed by  $\text{CuI/K}_2\text{CO}_3$  in toluene at 120 °C)

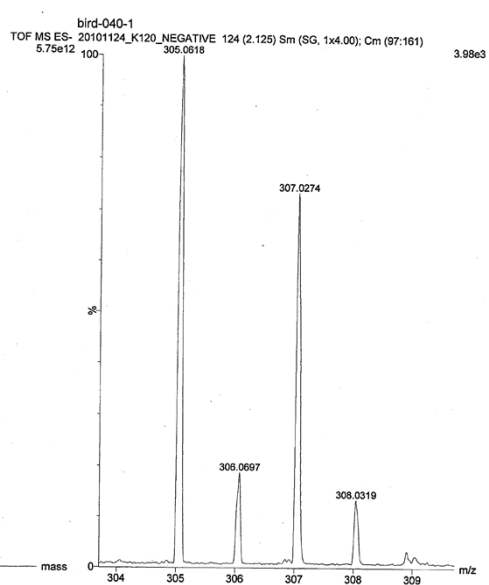
ESI-MS(-) full mass



**Simulated isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)<sub>2</sub>]<sup>-</sup>**



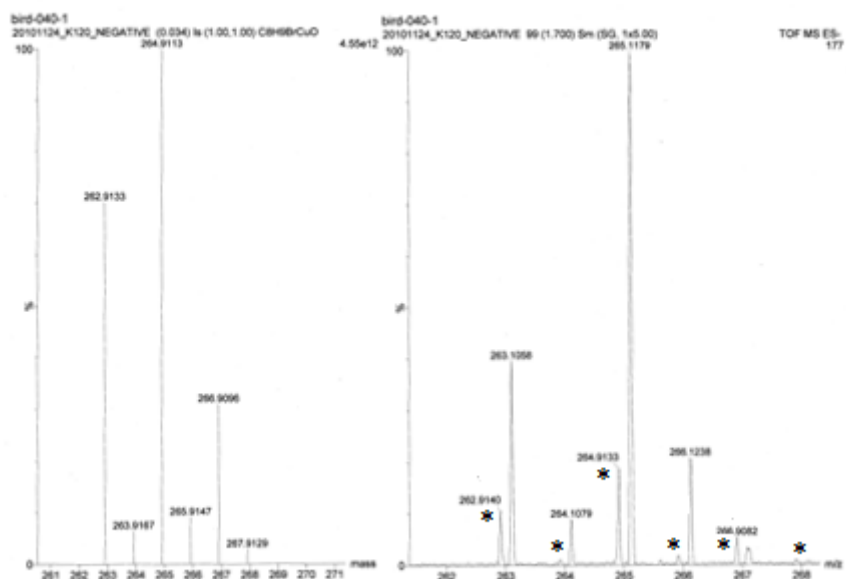
**Experimental isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)<sub>2</sub>]<sup>-</sup>**





Simulated isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)Br]<sup>-</sup>

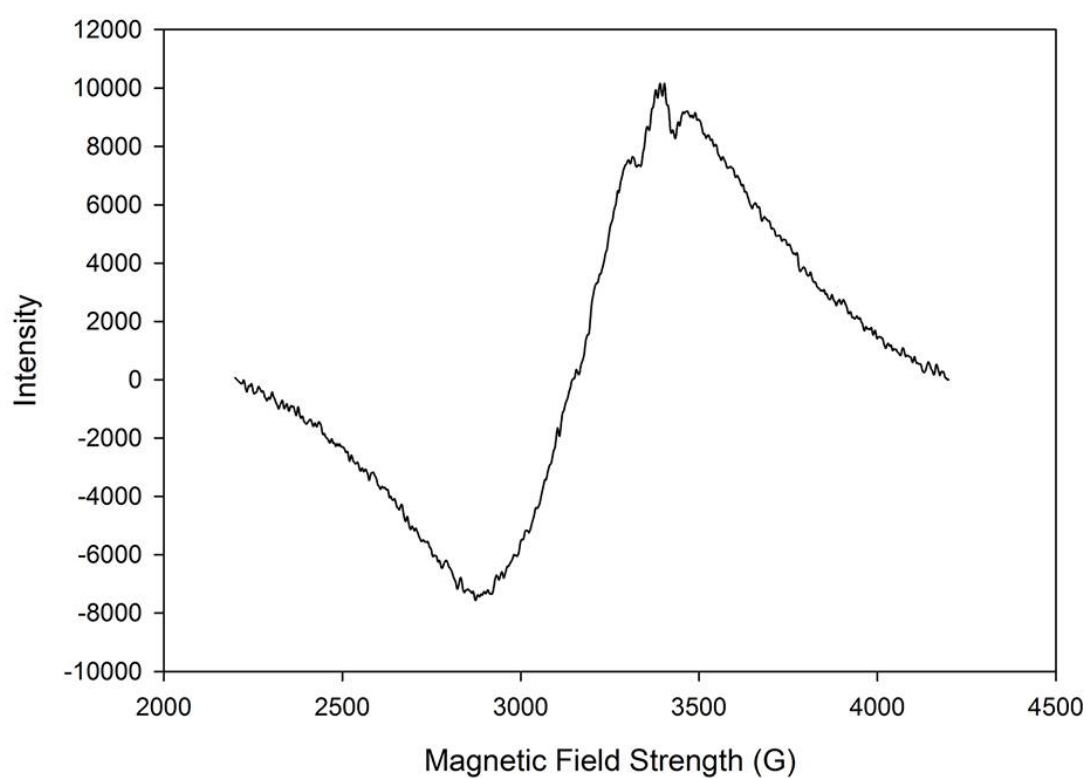
Experimental isotopic distributions of  
[Cu(I)(2,4-dimethylphenoxy)Br]<sup>-</sup>



\* Signals of the compound

## EPR spectra for Copper-Catalyzed C-O Cross-Coupling Reaction

Original



Calibrate

