Selective copper(II)-mediated oxidative coupling of a nucleophilic reagent to the para-methyl group of 2,4,6-trimethylphenol

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I. UV-vis studies

Sequential addition of Copper(II) chloride to a solution of 2,4,6-trimethylphenol/NaOMe.

For 0.5 eq of CuCl$_2$ added: Cu(OPh)$_2$(Solvent)$_n$

![Figure S1](image1.png)

![Figure S2](image2.png)
Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/(CuCl$_2$)$_2$. 

Figure S4

Figure S5
Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/(CuCl$_2$)$_2$/(bipyridine)$_2$. 
II. EPR studies

*Addition of various amounts of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/(CuCl)₂*

- $g_{\|} = 2.405\,$
- $g_{\perp} = 2.090$
III. Cyclovoltammetry

The electrochemical behavior of the complexes was investigated by cyclic voltammetry (CV), using an Autolab PGSTAT10 potentiostat in DMF-[n-(C₄H₉)₄N]PF₆ solvent-electrolyte couple versus Ag/Ag⁺ reference electrode under a nitrogen gas atmosphere at room temperature. A glassy carbon working electrode and a platinum plate (0.7 cm²) counter electrode were used for CV measurements. The cyclovoltammetric experiments were performed after mixing one equivalent of copper(II) chloride (0.004 M solution of in DMF) with one equivalent of the ligand (0.004 M solution in DMF). The voltage scan rate during the CV measurements was 100 mV/s.

<table>
<thead>
<tr>
<th>Compound</th>
<th>( E_a ) (V)</th>
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<tbody>
<tr>
<td>Cu(II)/Cu(I)</td>
<td>0.57</td>
</tr>
<tr>
<td>Cu(neo)</td>
<td>0.37</td>
</tr>
<tr>
<td>Cu(bipy)</td>
<td>0.18</td>
</tr>
</tbody>
</table>

N.B.: The voltammograms for Cu(neo) and Cu(bipy) show the presence of free CuCl₂, suggesting the formation of a [CuCl₂(ligand)₂] complex in solution.
IV. NMR spectra of the compounds VIc–h

4-(2-hydroxy-ethoxymethyl)-2,6-dimethylphenol (VIc)
1,2-bis(4-oxymethyl-2,6-dimethylphenol)ethane (Vid)
Bis-(4-hydroxy-3,5-dimethylbenzyl)-di-pyridin-2-yl-ammonium chloride (VIe)
3-(4-hydroxy-3,5-dimethylbenzyl)pentane-2,4-dione (VII)
2-(4-hydroxy-3,5-dimethylbenzyl)isoindole-1,3-dione (VIg)
4-(aminomethyl)-2,6-dimethylphenol (VIb)