

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.

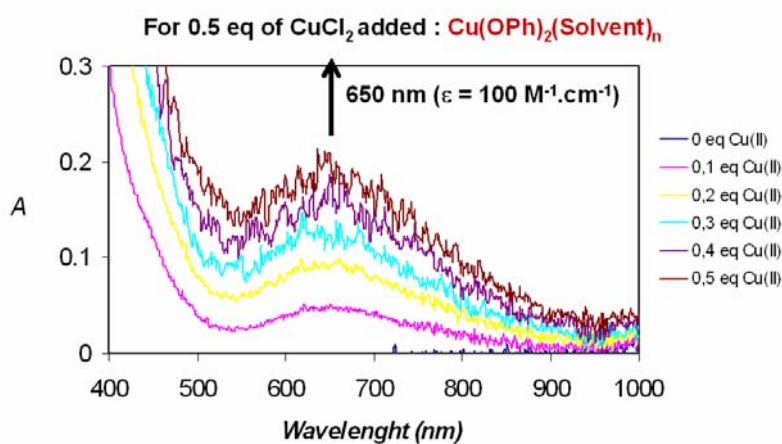


Figure S1

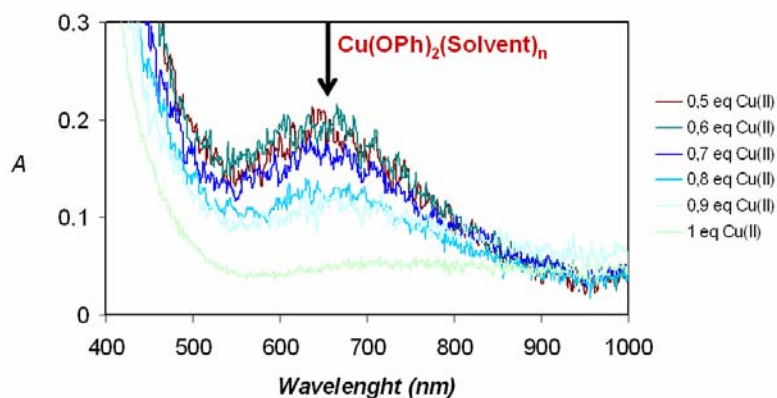


Figure S2

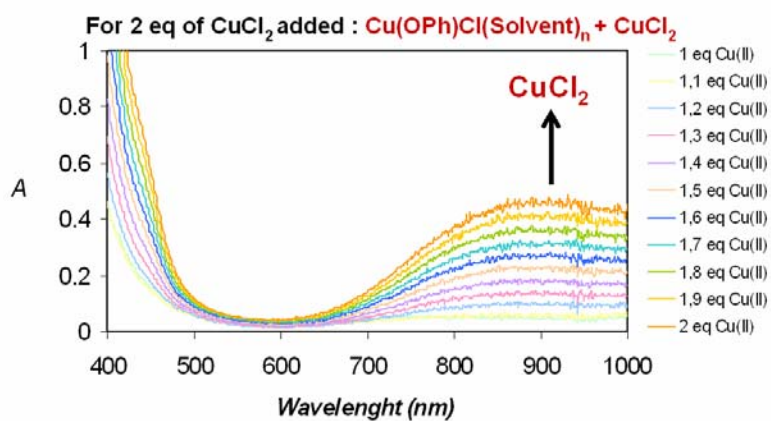


Figure S3

*Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/ $\text{NaOMe}/(\text{CuCl}_2)_2$ .*

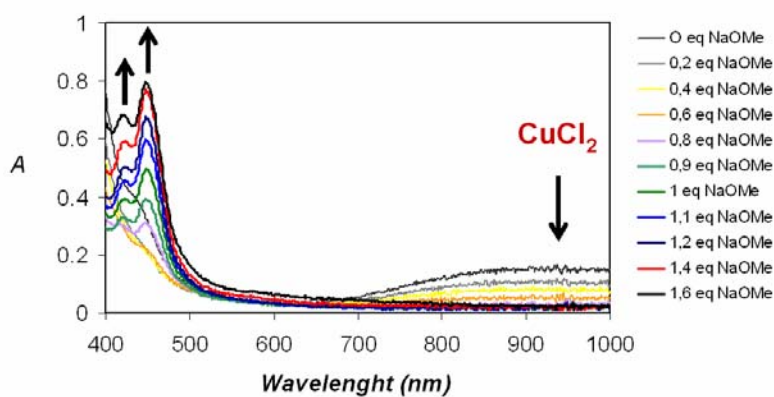


Figure S4

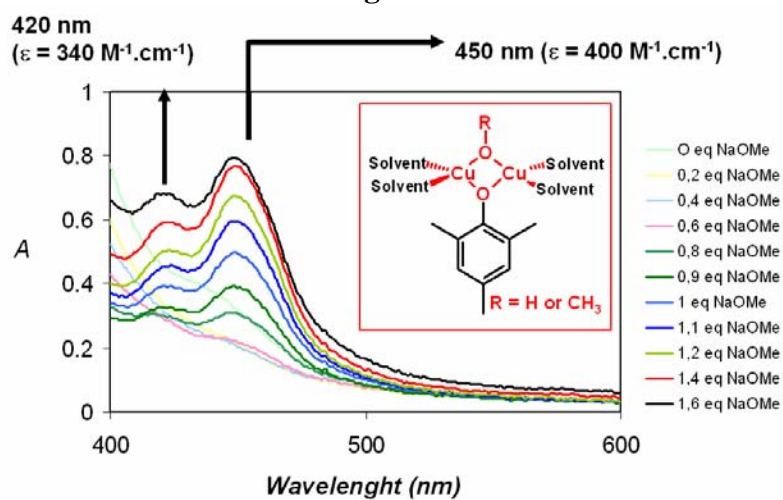
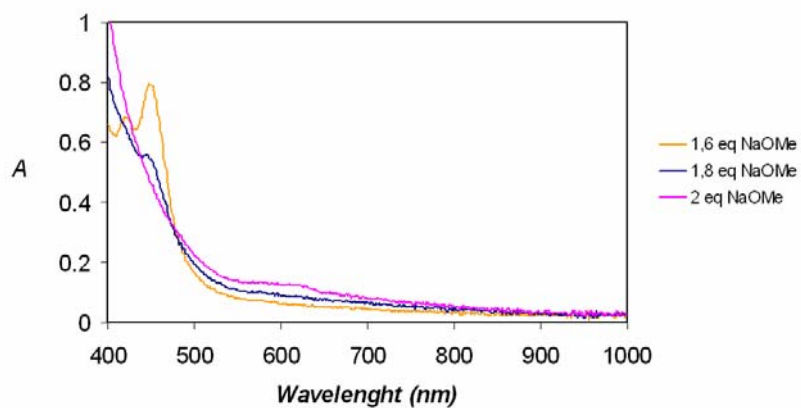
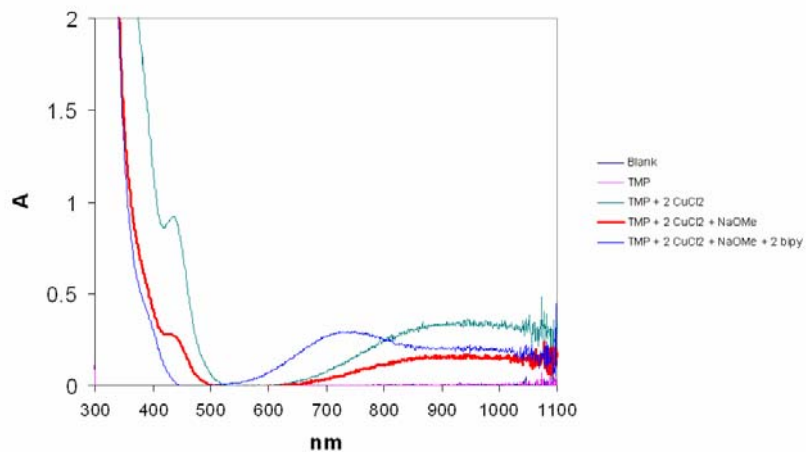


Figure S5

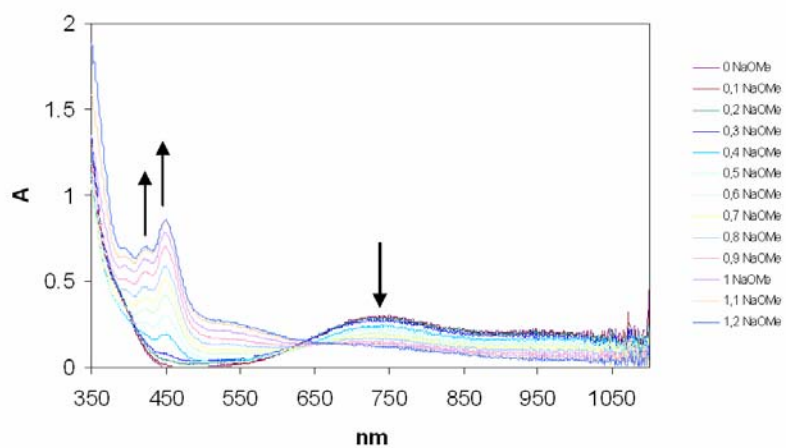


**Figure S6**

*Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/ $\text{NaOMe}/(\text{CuCl}_2)_2/(\text{bipyridine})_2$ .*



**Figure S7**



**Figure S8**

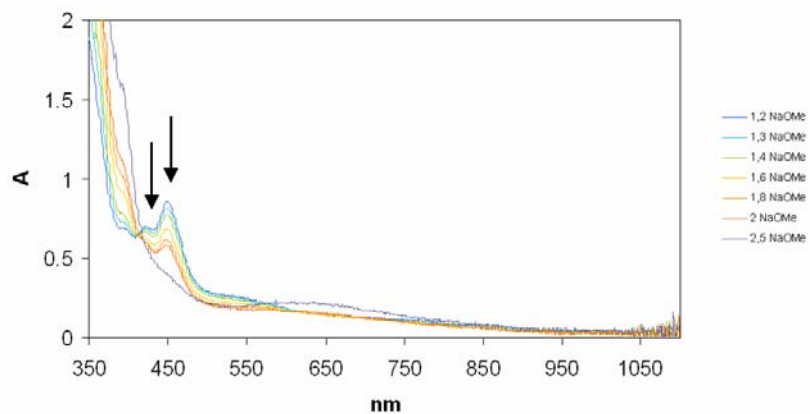


Figure S9

## II. EPR studies

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

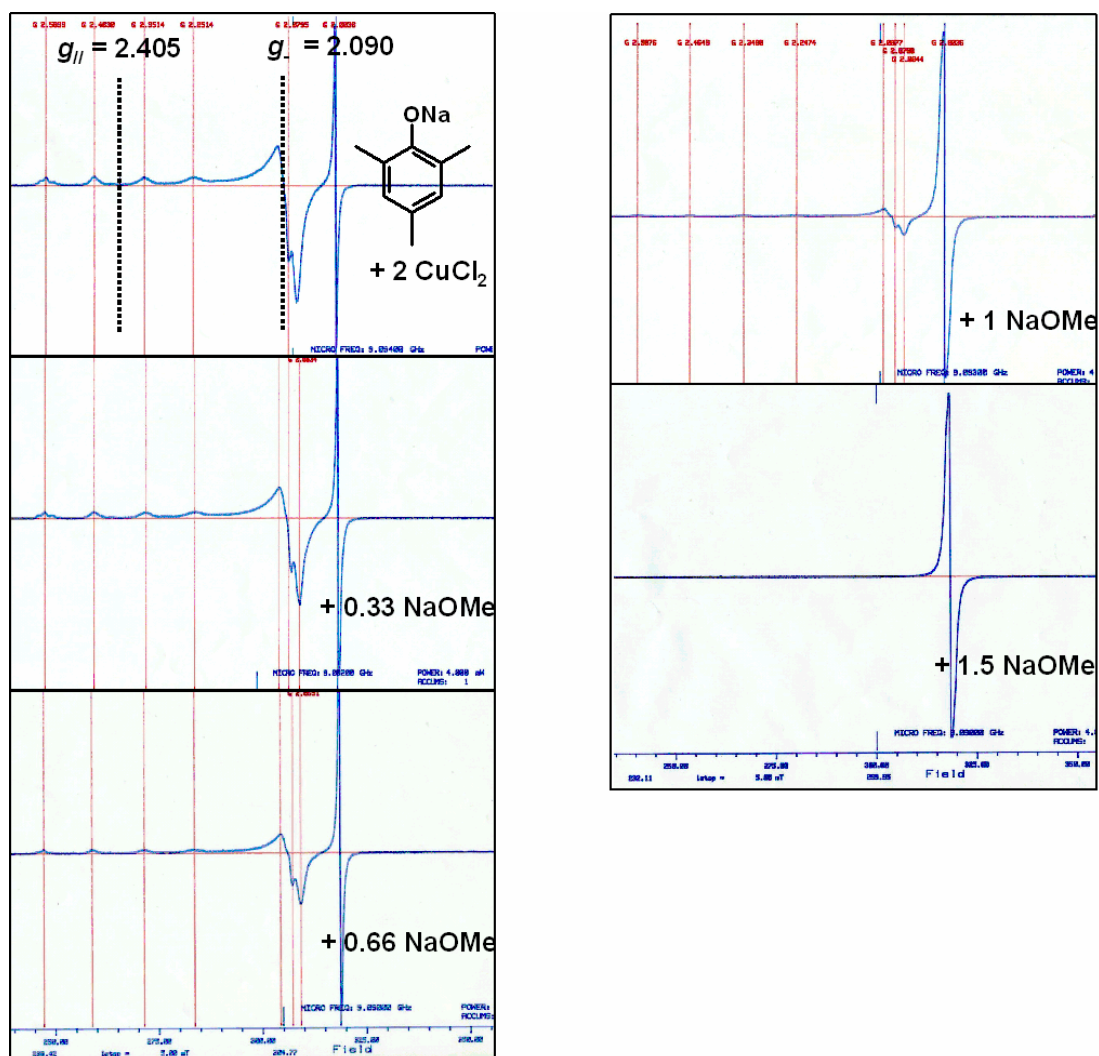
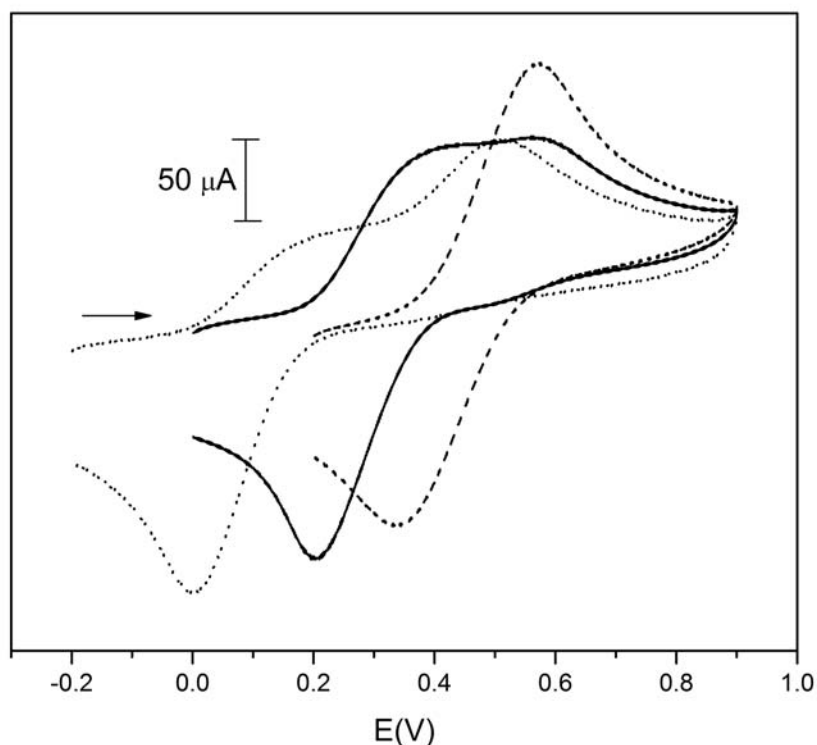


Figure S10

### III. Cyclovoltammetry



**Figure S11:** Cyclic voltammogram of 0.004 M  $\text{CuCl}_2^{\text{II/I}}$  (---),  $[\text{CuCl}_2(\text{neocuproine})_2]^{\text{II/I}}$  (—),  $[\text{CuCl}_2(\text{bipyridine})_2]^{\text{II/I}}$  (···) in DMF at room temperature vs.  $\text{Ag}/\text{Ag}^+$ .

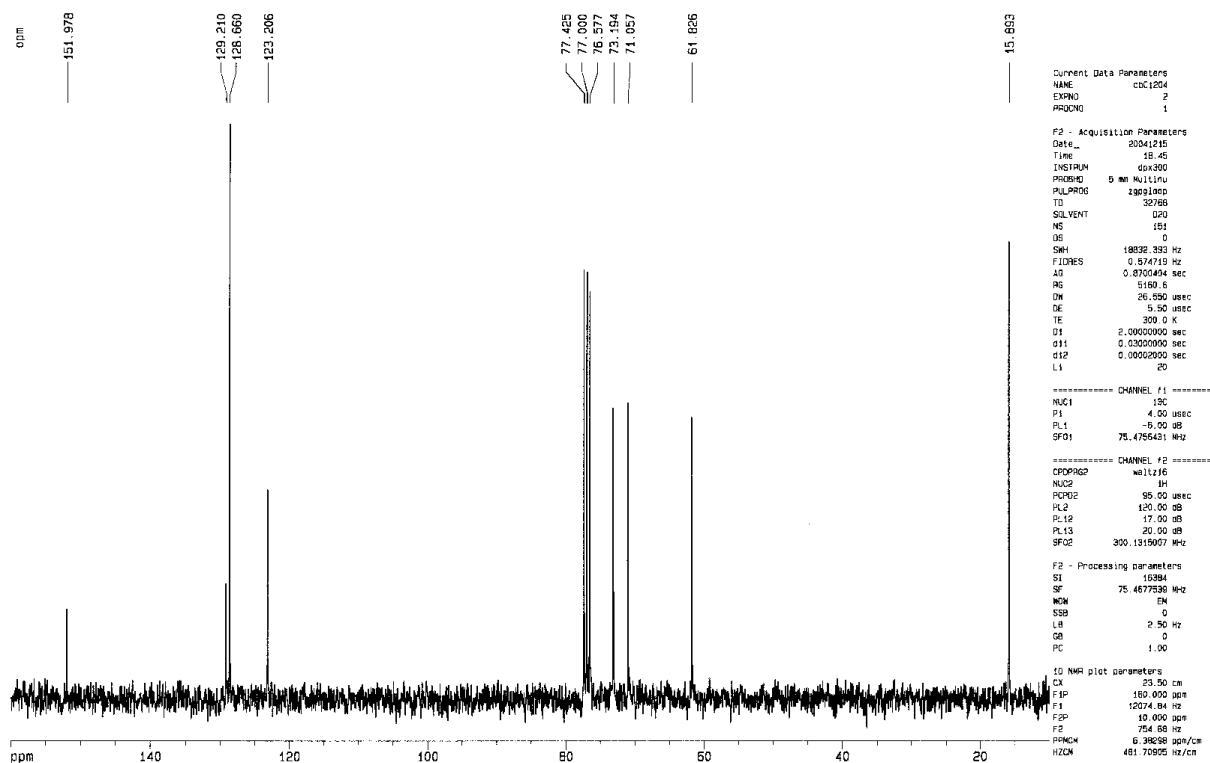
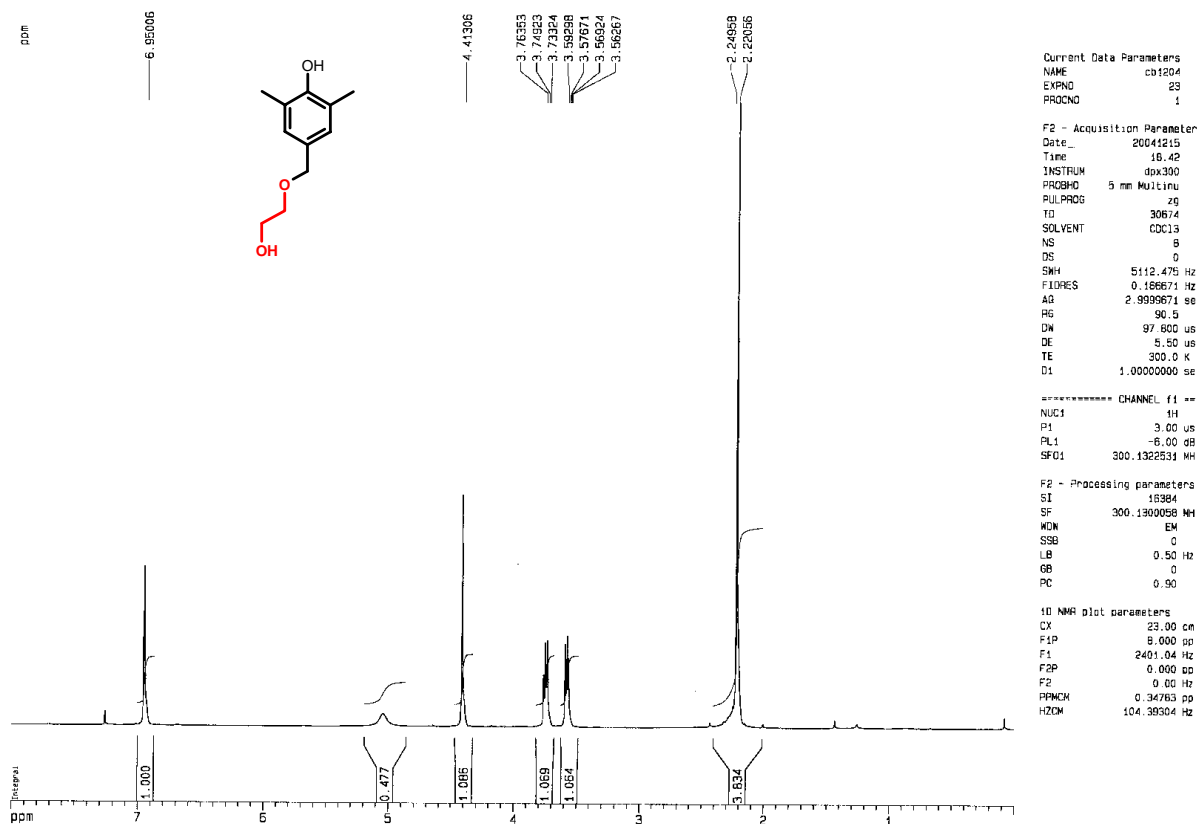
The electrochemical behavior of the complexes was investigated by cyclic voltammetry (CV), using an Autolab PGSTAT10 potentiostat in DMF- $[\text{n}-(\text{C}_4\text{H}_9)_4\text{N}]\text{PF}_6$  solvent-electrolyte couple versus  $\text{Ag}/\text{Ag}^+$  reference electrode under a nitrogen gas atmosphere at room temperature. A glassy carbon working electrode and a platinum plate ( $0.7 \text{ cm}^2$ ) counter electrode were used for CV measurements. The cyclic voltammetric 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.

Compound	$E_a$ (V)
Cu(II)/Cu(I)	0.57
Cu(neo)	0.37
Cu(bipy)	0.18

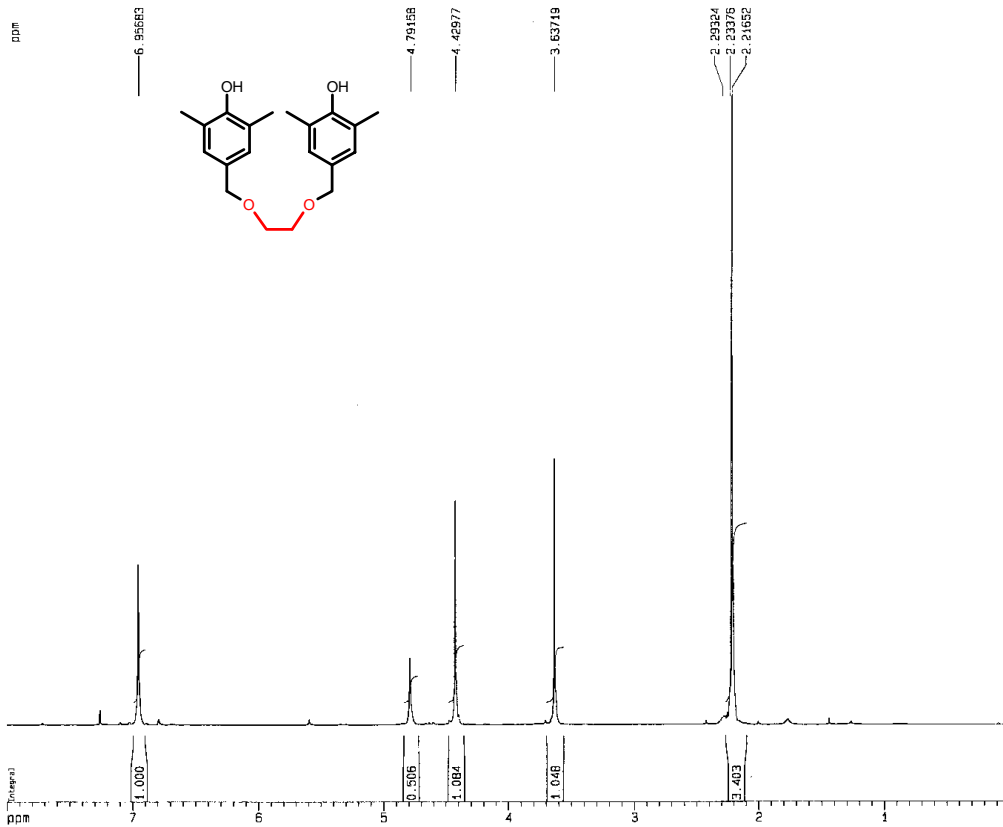
N.B.: The voltammograms for Cu(neo) and Cu(bipy) show the presence of free  $\text{CuCl}_2$ , suggesting the formation of a  $[\text{CuCl}_2(\text{ligand})_2]$  complex in solution.

# 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 (VIId)



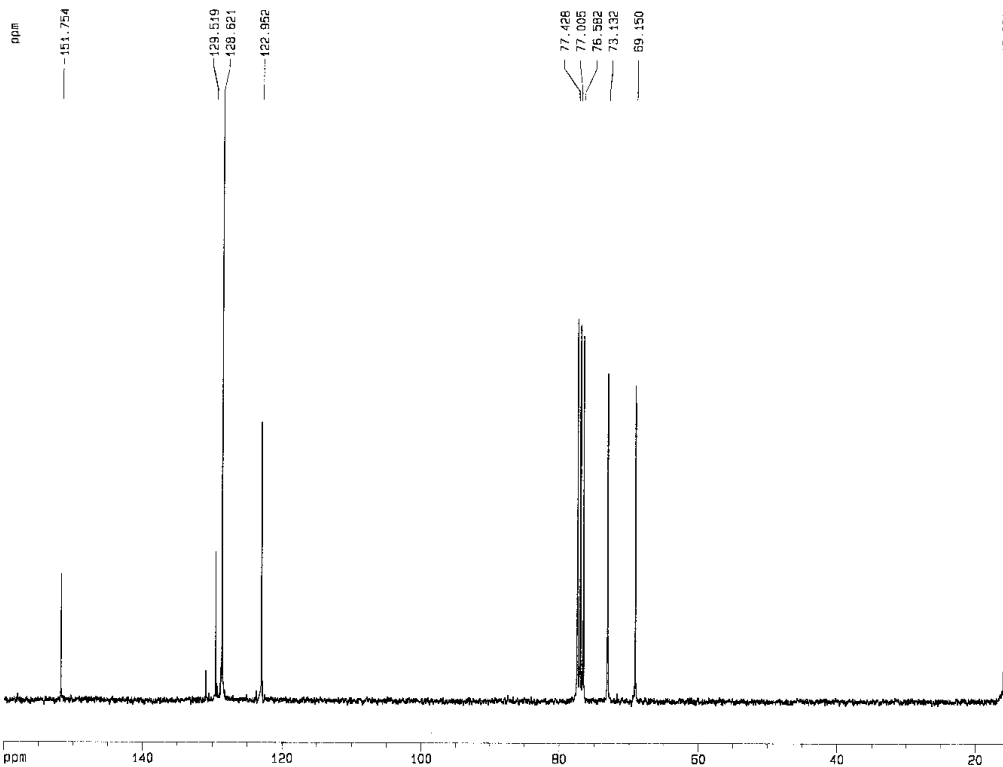
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 FIDRES 0.166871 Hz  
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 F2P 0.000 pp  
 F2 0.00 Hz  
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 HZCM 104.98304 Hz



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 DS 0  
 SMH 18892.393 Hz  
 FIDRES 0.514719 Hz  
 AQ 0.8720424 sec  
 RG 5180.6  
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 d12 0.00000000 sec  
 LI 20

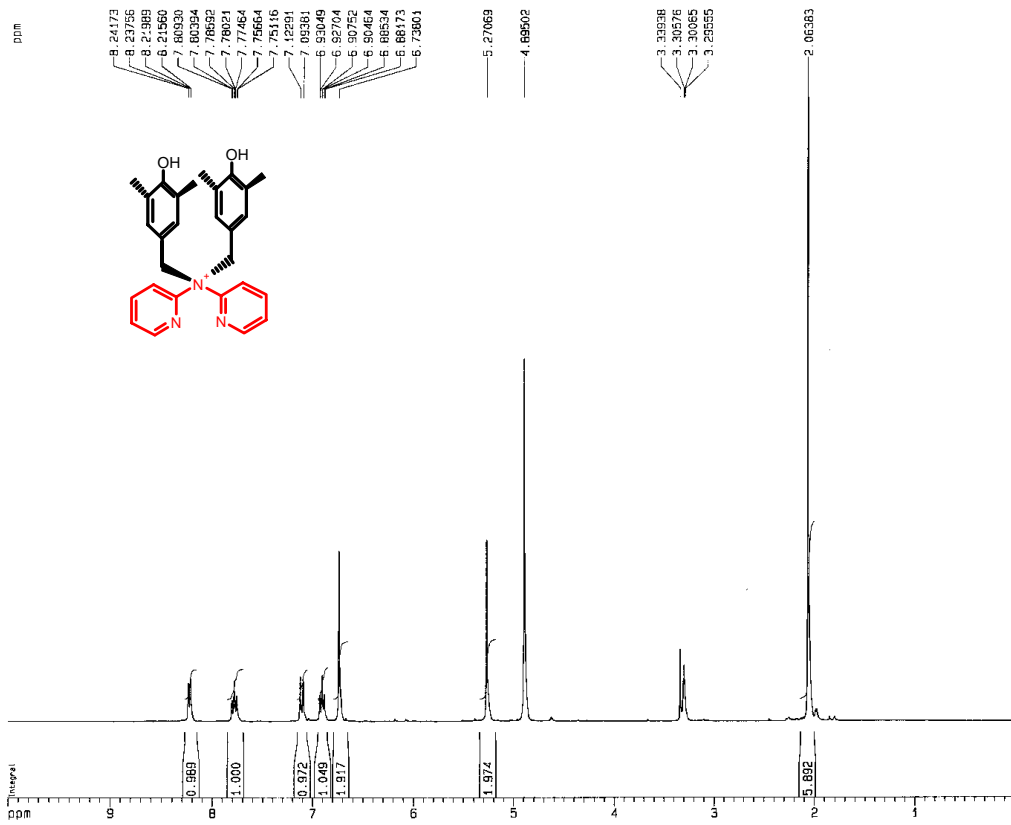
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 SFO2 300.1315007 MHz

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 F2 754.66 Hz  
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Bis-(4-hydroxy-3,5-dimethylbenzyl)-di-pyridin-2-yl-ammonium chloride (VIe)



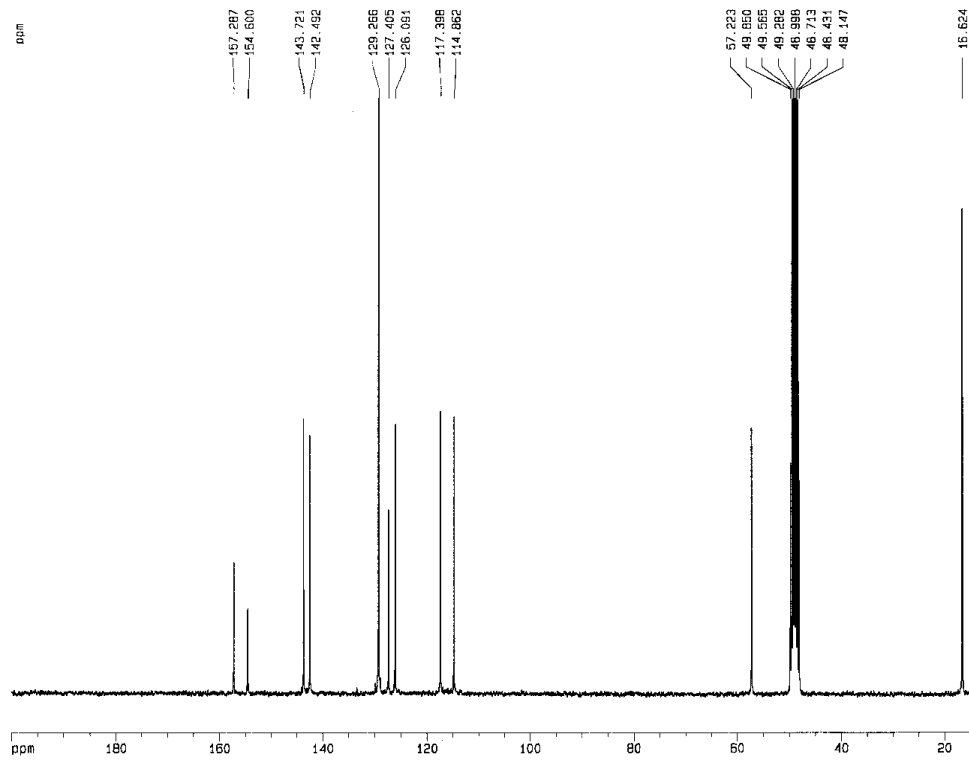
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 DS 0  
 SWH 5112.475 Hz  
 FIDRES 0.156671 Hz  
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 RG 128  
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 DE 5.50 us  
 TE 300.0 K  
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 AQ 0.8700404 sec  
 RG 5160.5  
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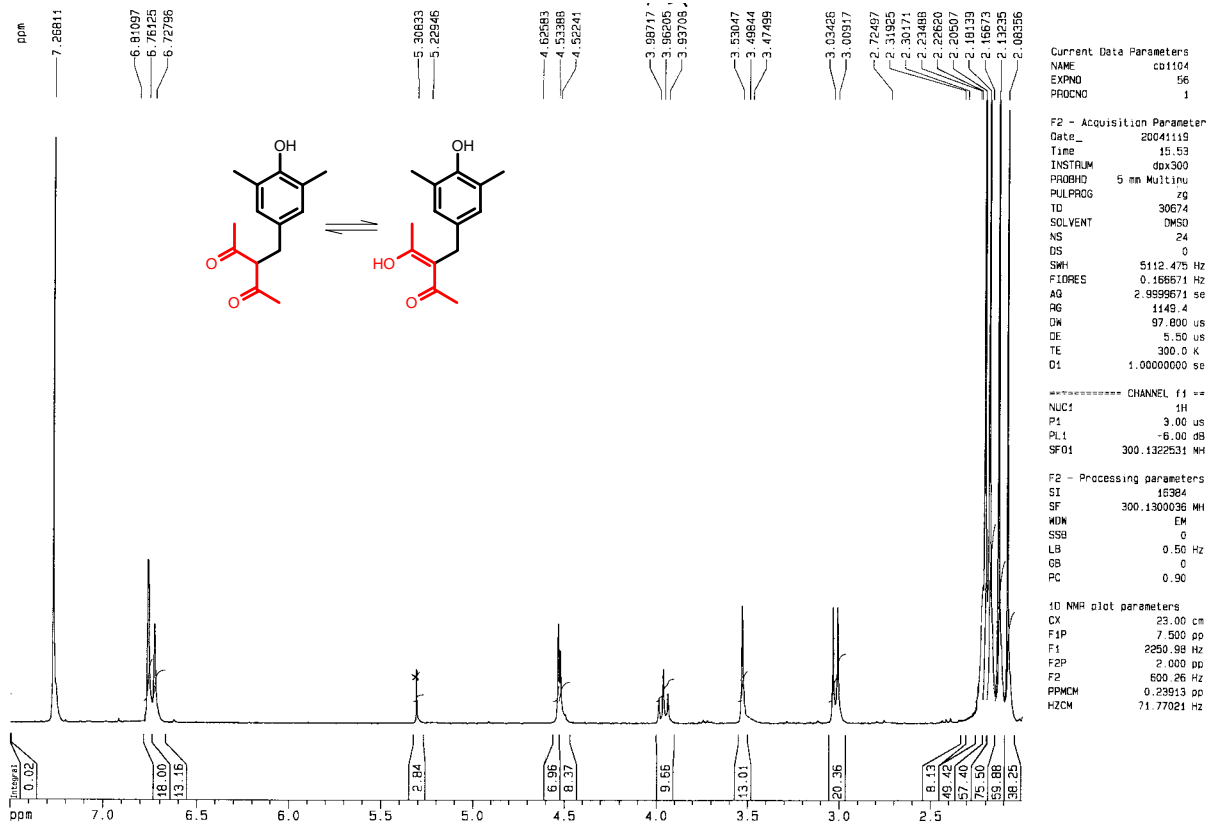
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3-(4-hydroxy-3,5-dimethylbenzyl)pentane-2,4-dione (VI)



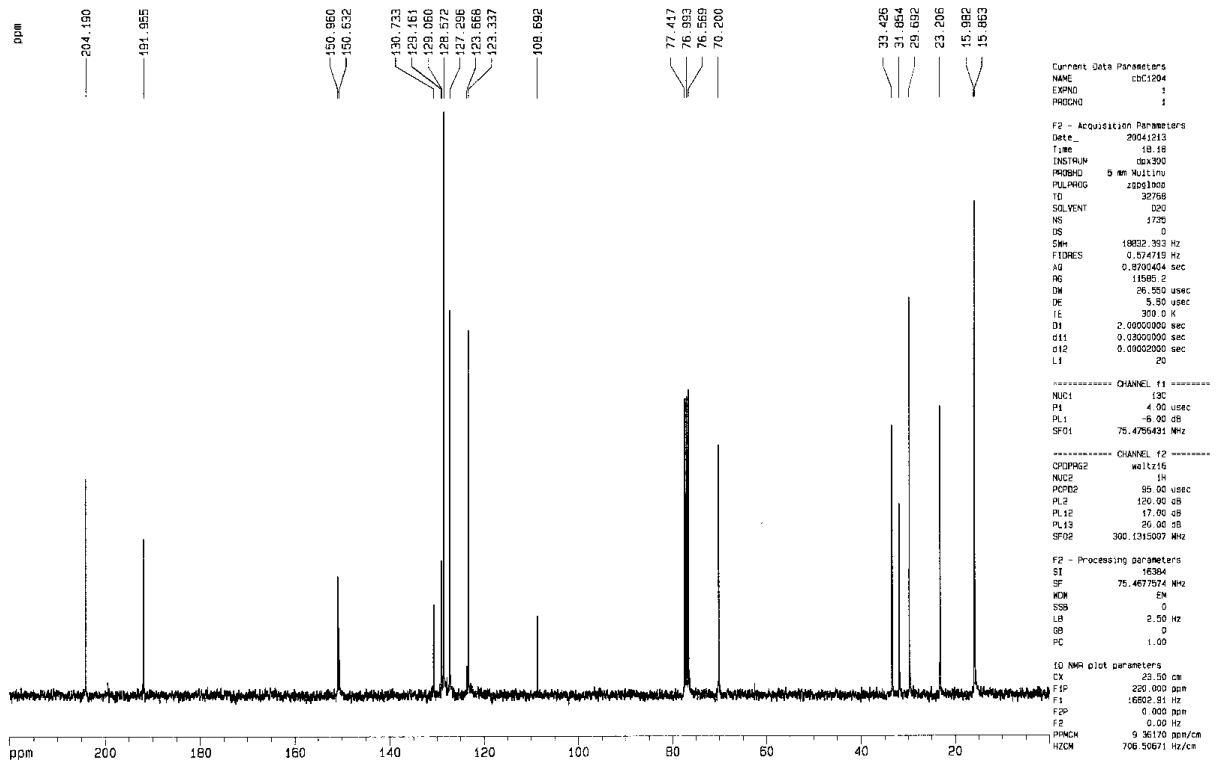
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 FIDRES 0.166571 Hz  
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 RG 1142.4  
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 TE 300.0 K  
 D1 1.00000000 se

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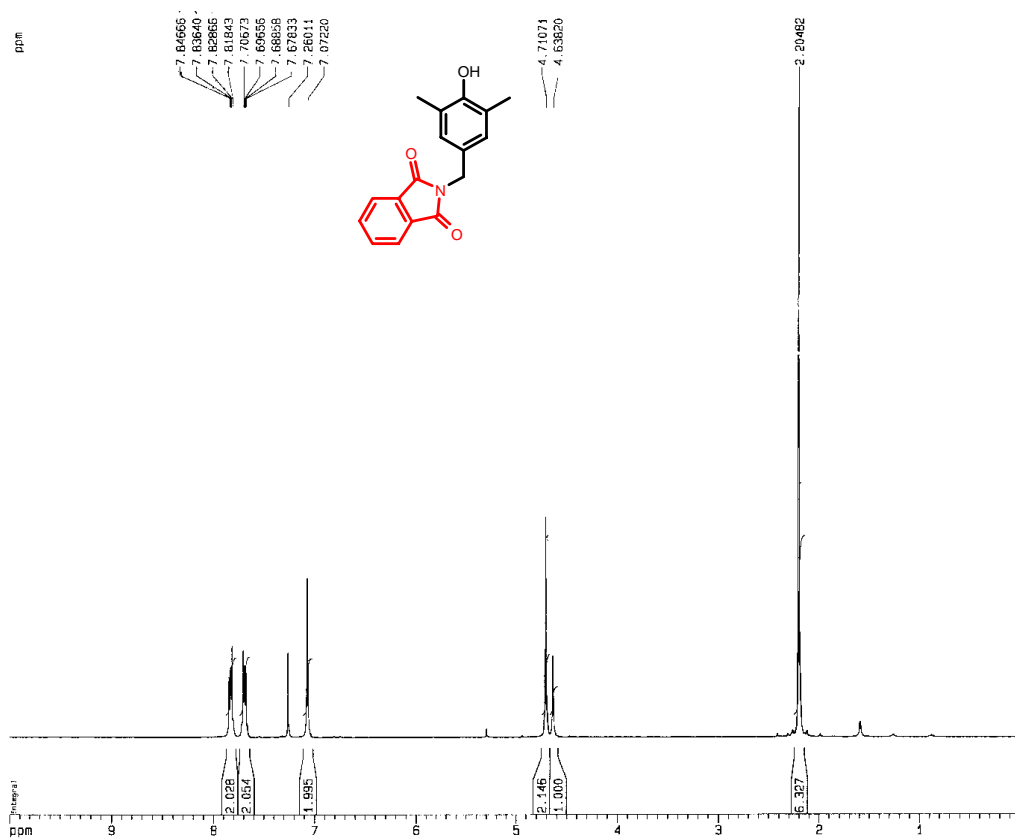
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2-(4-hydroxy-3,5-dimethylbenzyl)isoindole-1,3-dione (**VIg**)



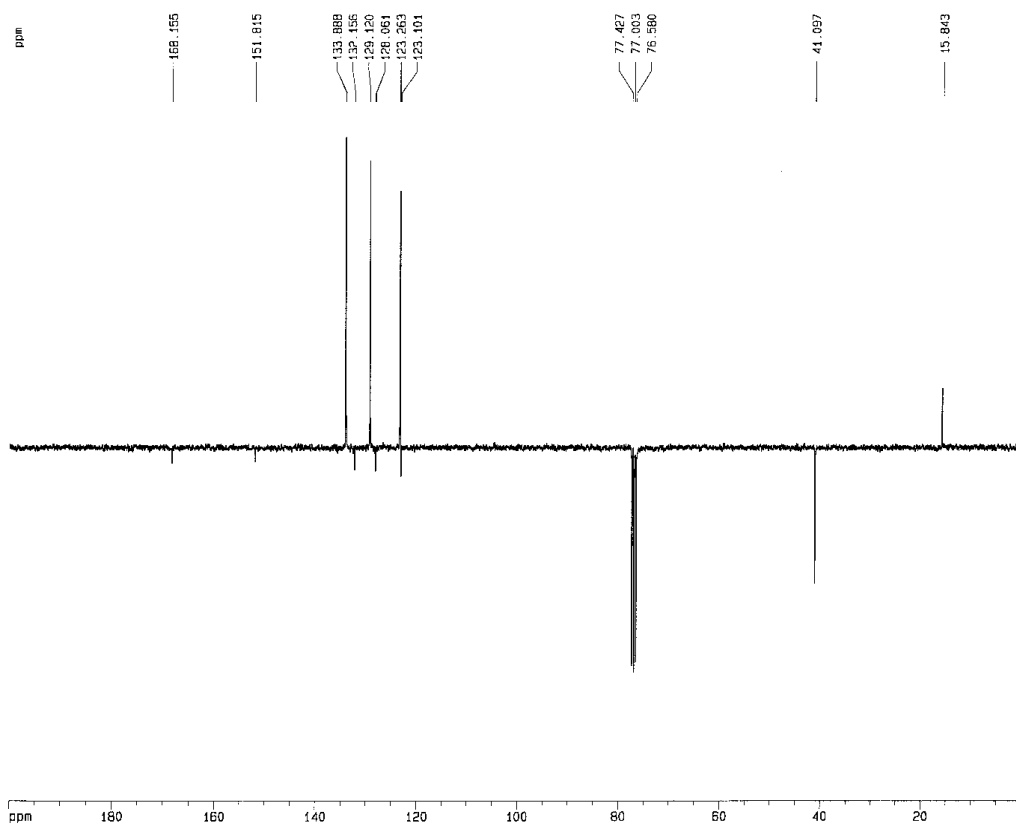
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 RG 456.1  
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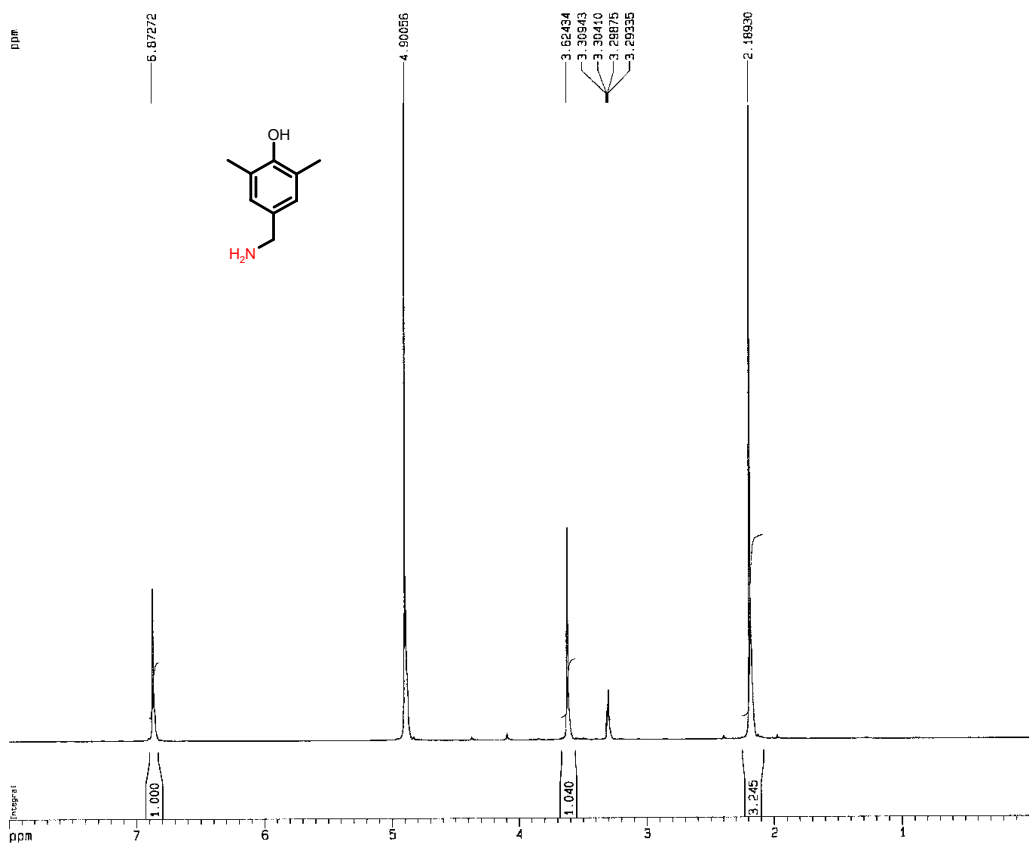
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 F2P 0.000 ppm  
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4-(aminomethyl)-2,6-dimethylphenol (VIIh)



```

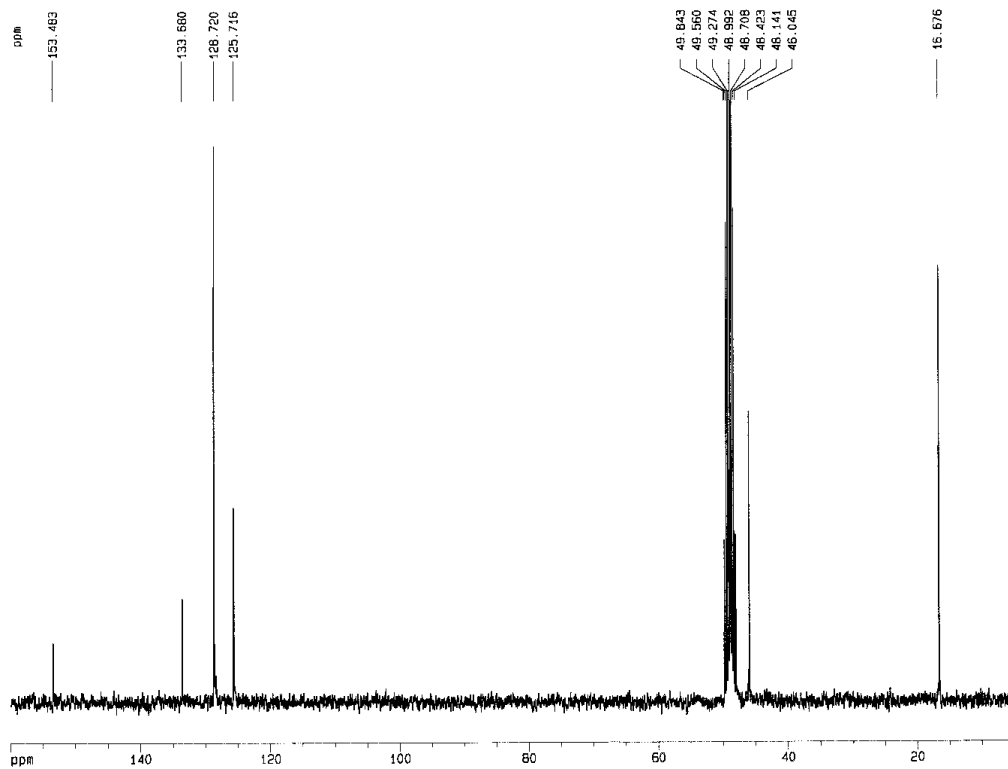
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TE            300.0 K
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L1            20

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1D NMR plot parameters
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