Supplementary Information Dalton Trans

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

Christophe Boldron, Seniz Özalp-Yaman, Patrick Gamez, Duncan M. Tooke, Anthony L. Spek and Jan Reedijk*

Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, P.O. Box 9502, 2300 RA Leiden, The Netherlands. Fax: 31 715274671; Tel: 31 715274459; E-mail: reedijk@chem.leidenuniv.nl

I. UV-vis studies

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

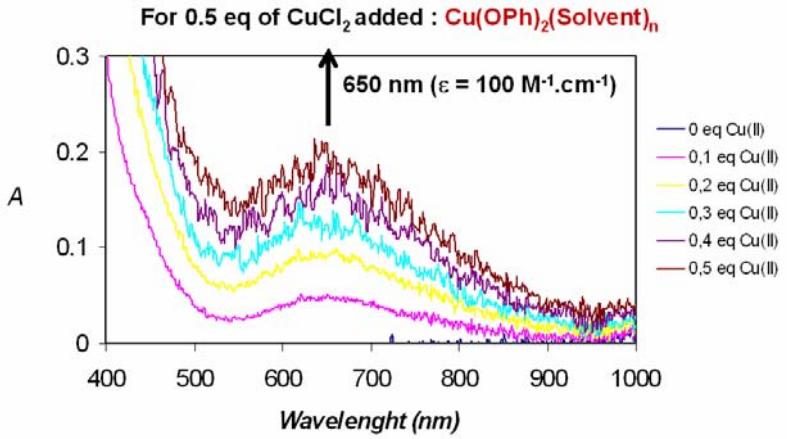


Figure S1

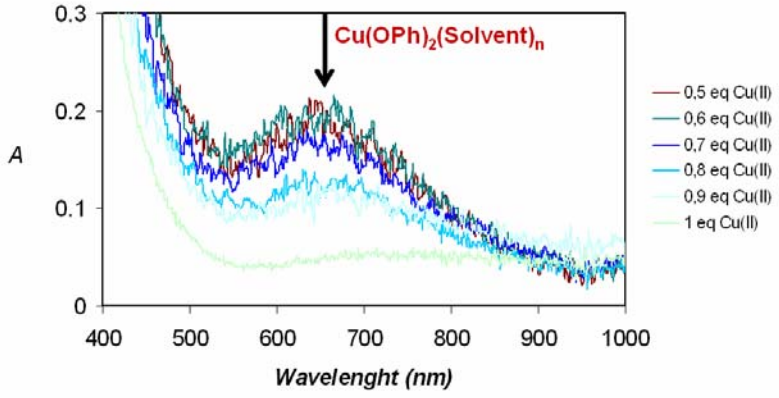


Figure S2

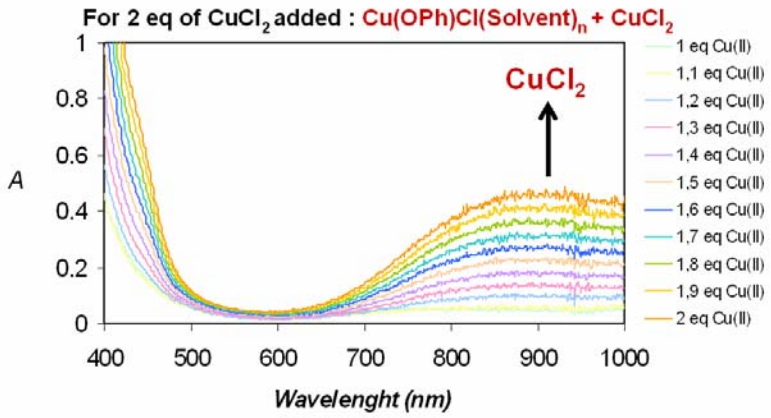


Figure S3

Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/$(CuCl_2)_2$.

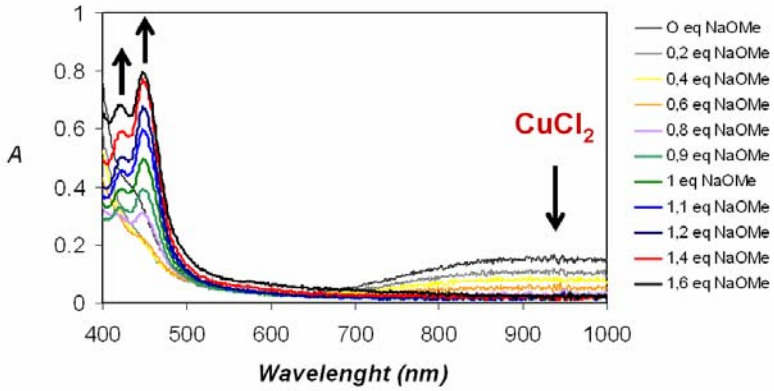


Figure S4

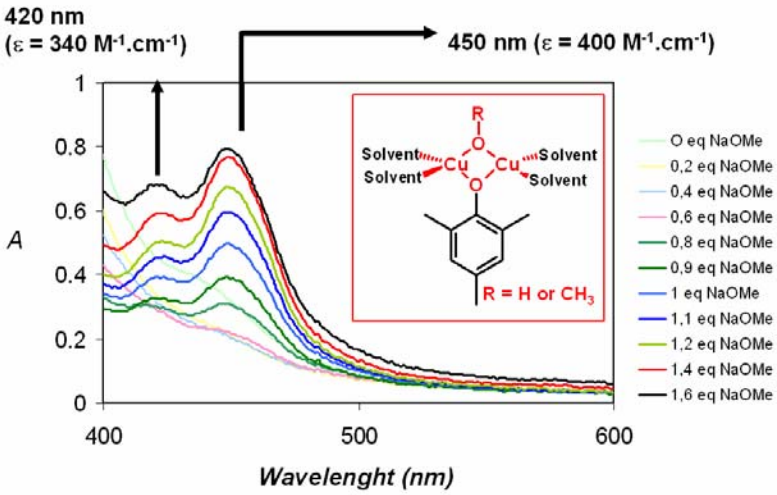


Figure S5

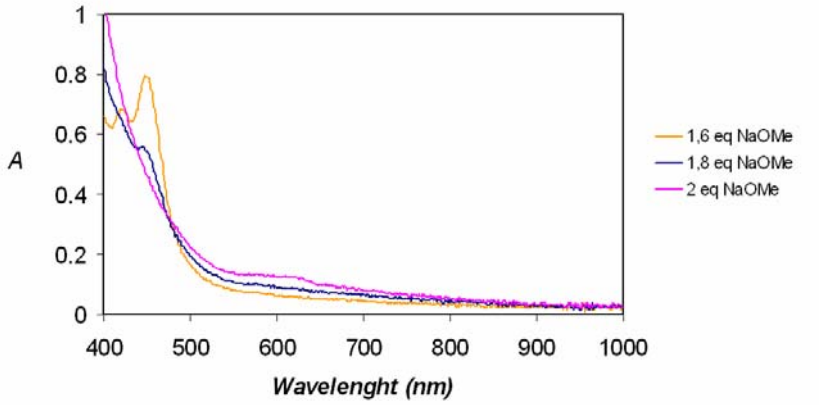


Figure S6

Sequential addition of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/$(CuCl_2)_2$/$(bipyridine)_2$.

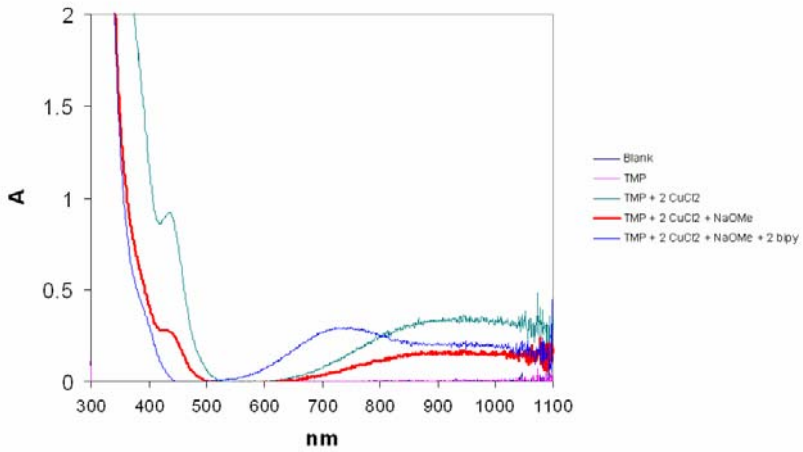


Figure S7

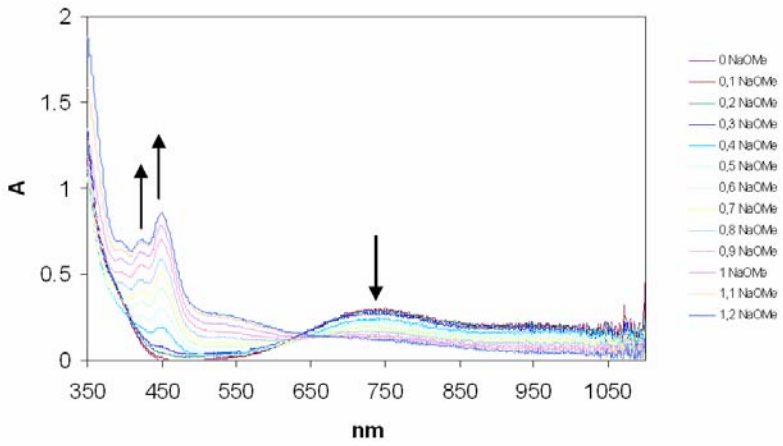


Figure S8

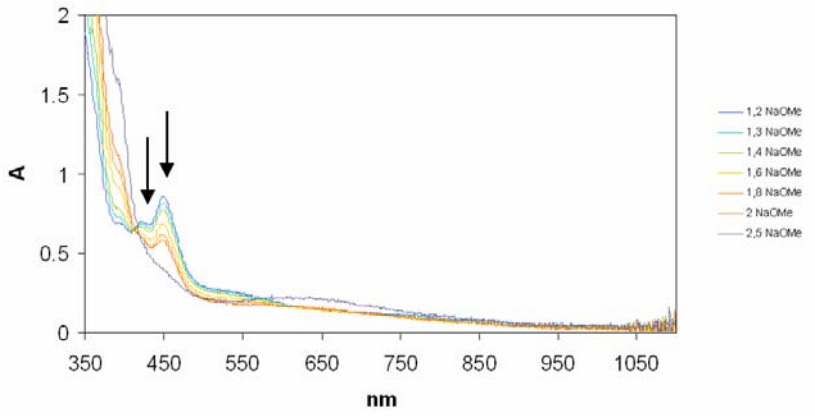


Figure S9

II. EPR studies

Addition of various amounts of sodium methoxide to a solution of 2,4,6-trimethylphenol/NaOMe/$(CuCl_2)_2$

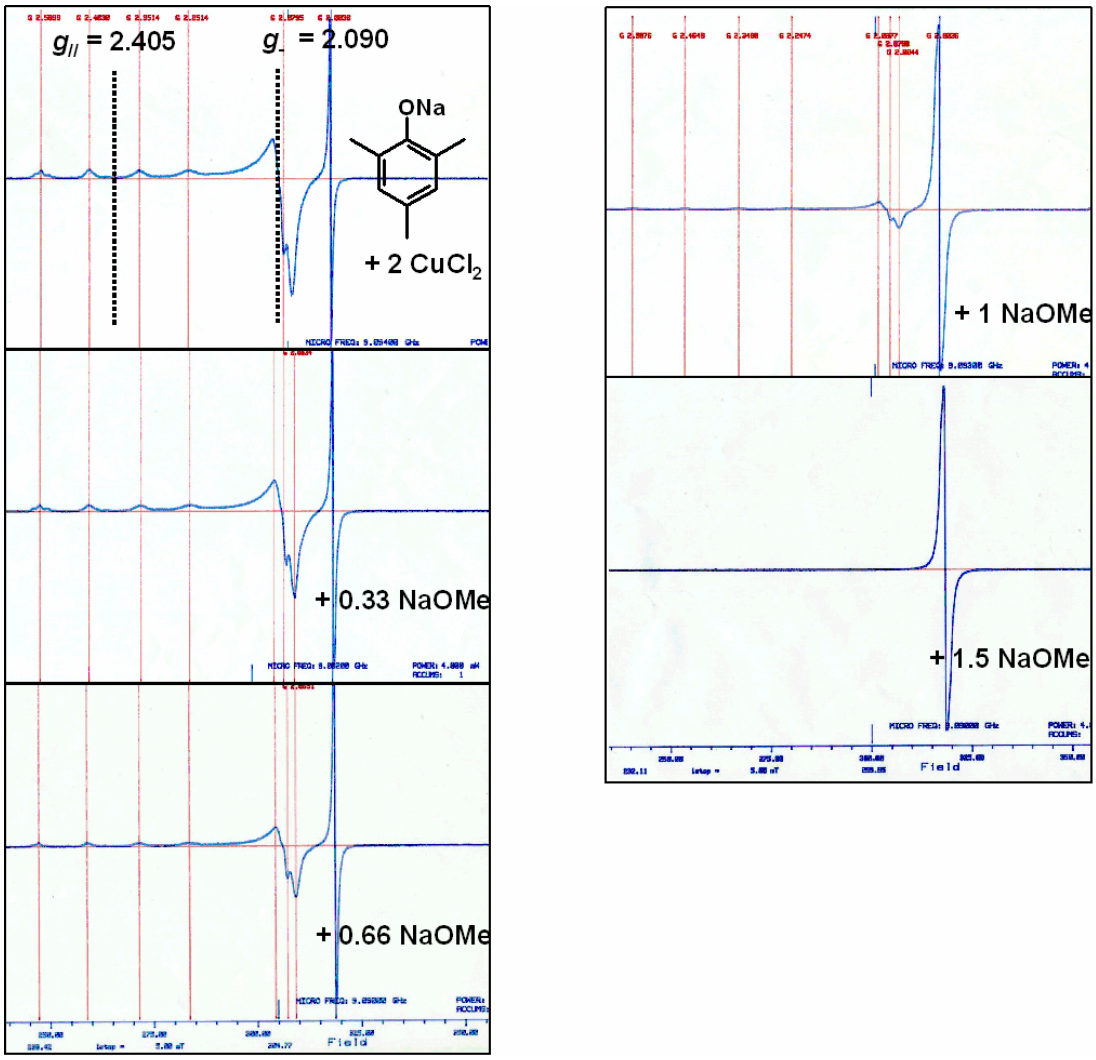


Figure S10

III. Cyclovoltammetry

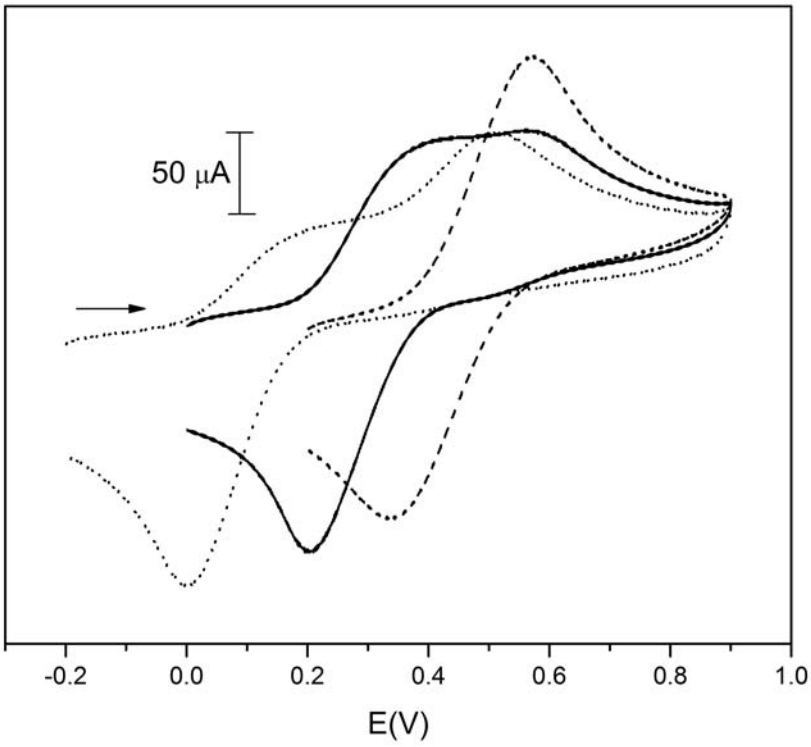


Figure S11: Cyclic voltammogram of 0.004 M $CuCl_2^{II/I}$ (---), $[CuCl_2(neocuproine)_2]^{II/I}$ (—), $[CuCl_2(bipyridine)_2]^{II/I}$ (···) in DMF at room temperature *vs.* Ag/Ag^+.

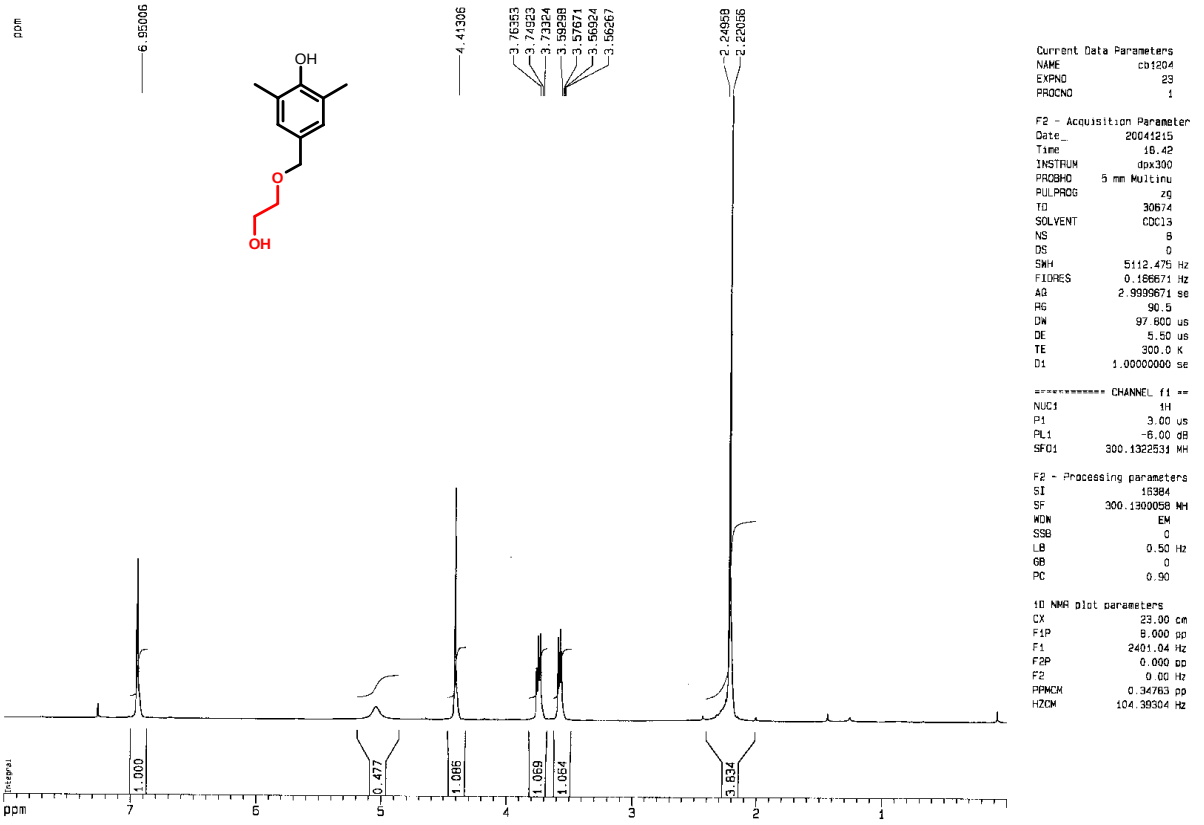
The electrochemical behavior of the complexes was investigated by cyclic voltammetry (CV), using an Autolab PGSTAT10 potantiostat in DMF-$[n\text{-}(C_4H_9)_4N]PF_6$ solvent-electrolyte couple versus Ag/Ag^+ reference electrode under a nitrogen gas atmosphere at room temperature. A glassy carbon working electrode and a platinum plate (0.7 cm^2) 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.

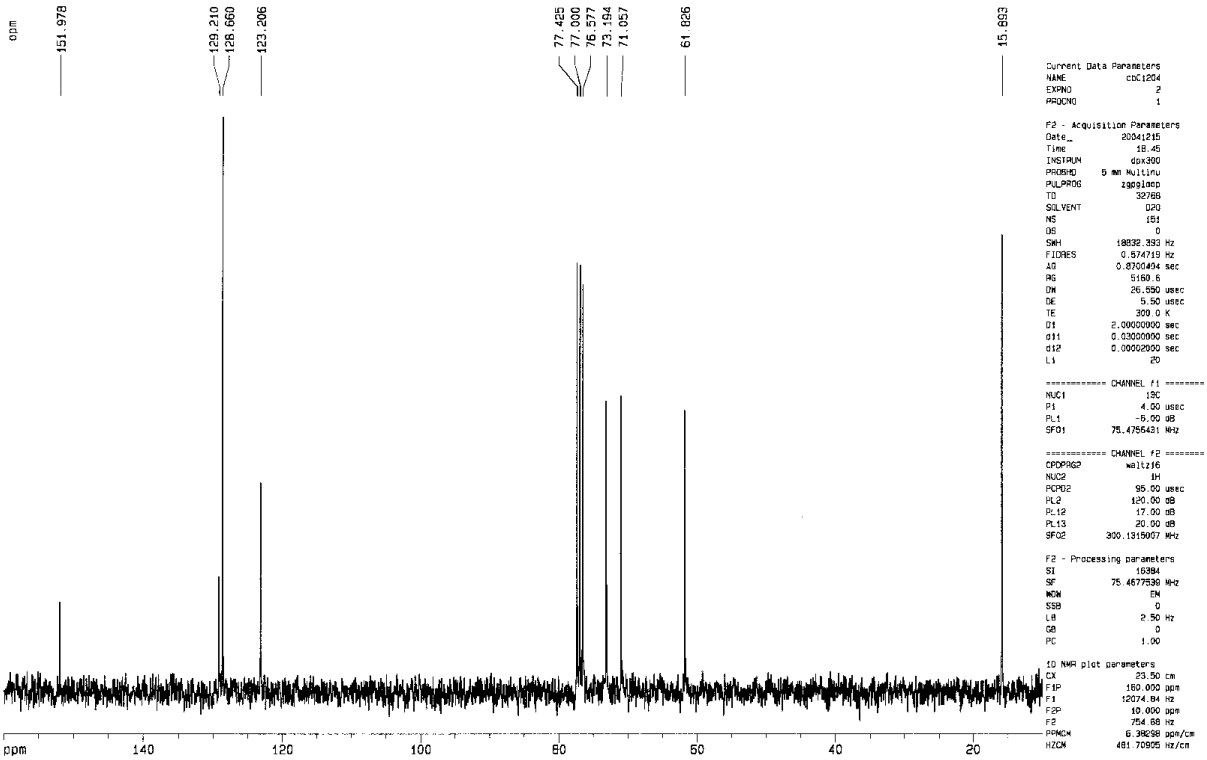
Compound	E_a (V)
Cu(II)/Cu(I)	0.57
Cu(neo)	0.37
Cu(bipy)	0.18

N.B.: The voltammograms for Cu(neo) and Cu(bipy) show the presence of free $CuCl_2$, suggesting the formation of a $[CuCl_2(ligand)_2]$ complex in solution.

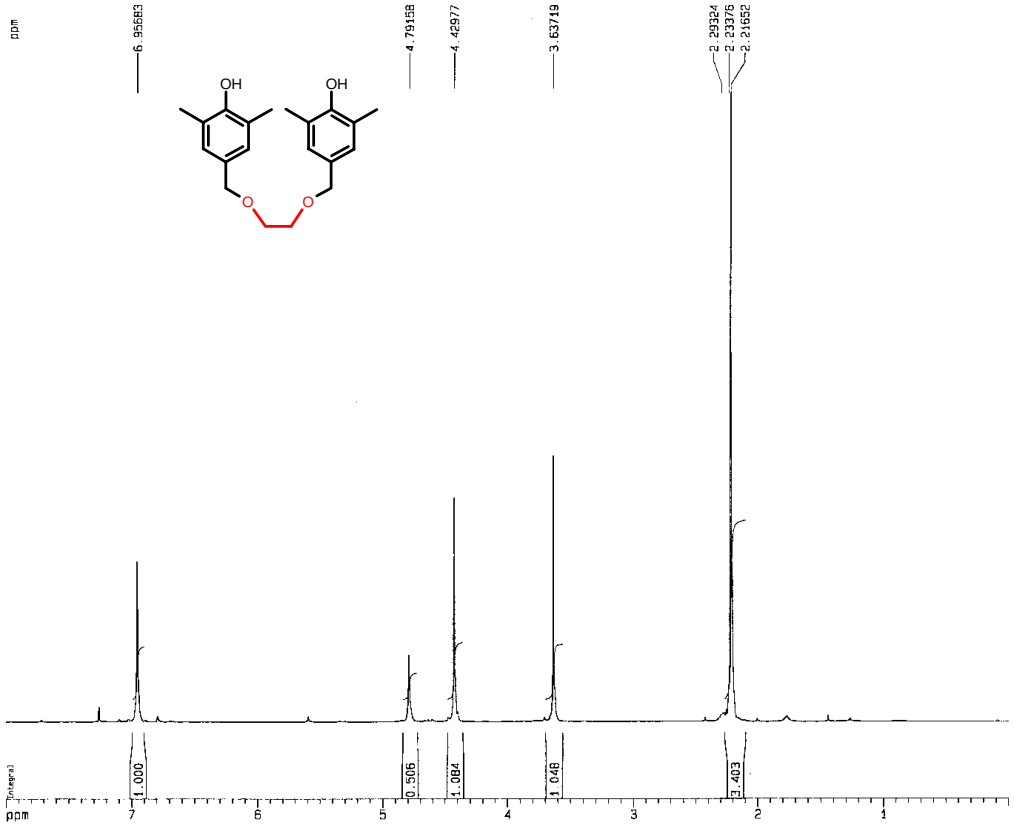
IV. NMR spectra of the compounds VIc–h

4-(2-hydroxy-ethoxymethyl)-2,6-dimethylphenol (**VIc**)





1,2-bis(4-oxymethyl-2,6-dimethylphenol)ethane (**VId**)

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TE                  300.0 K
D1                1.00000000 se

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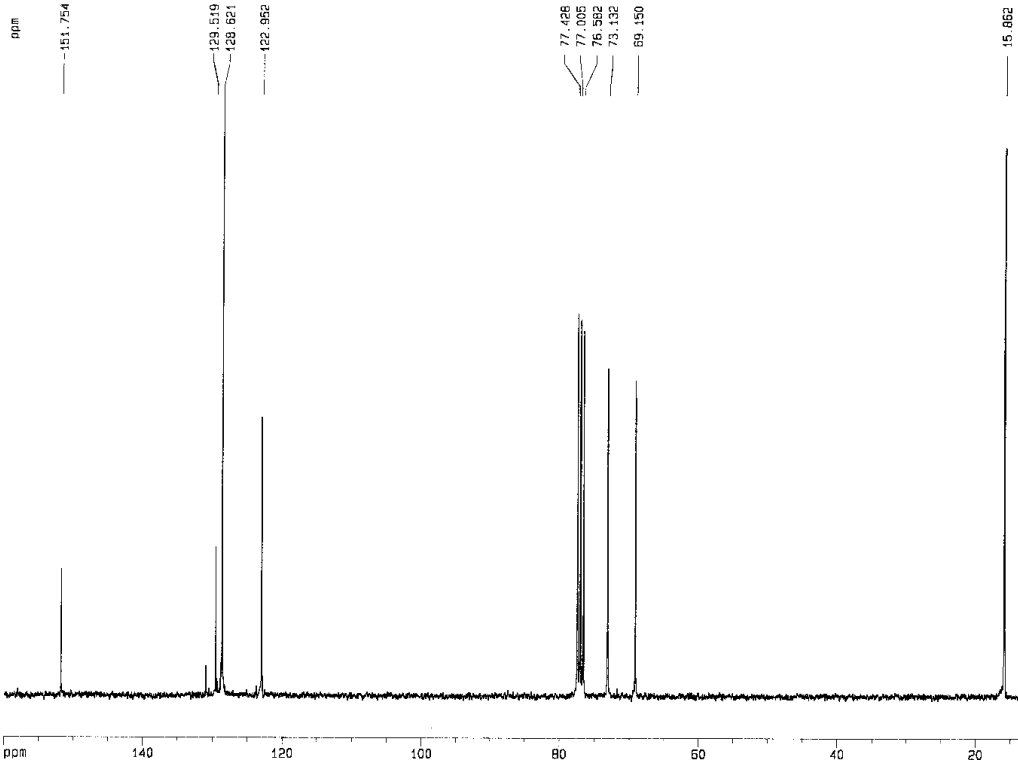


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F2 - Processing parameters
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1D NMR plot parameters
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F2                   754.66 Hz
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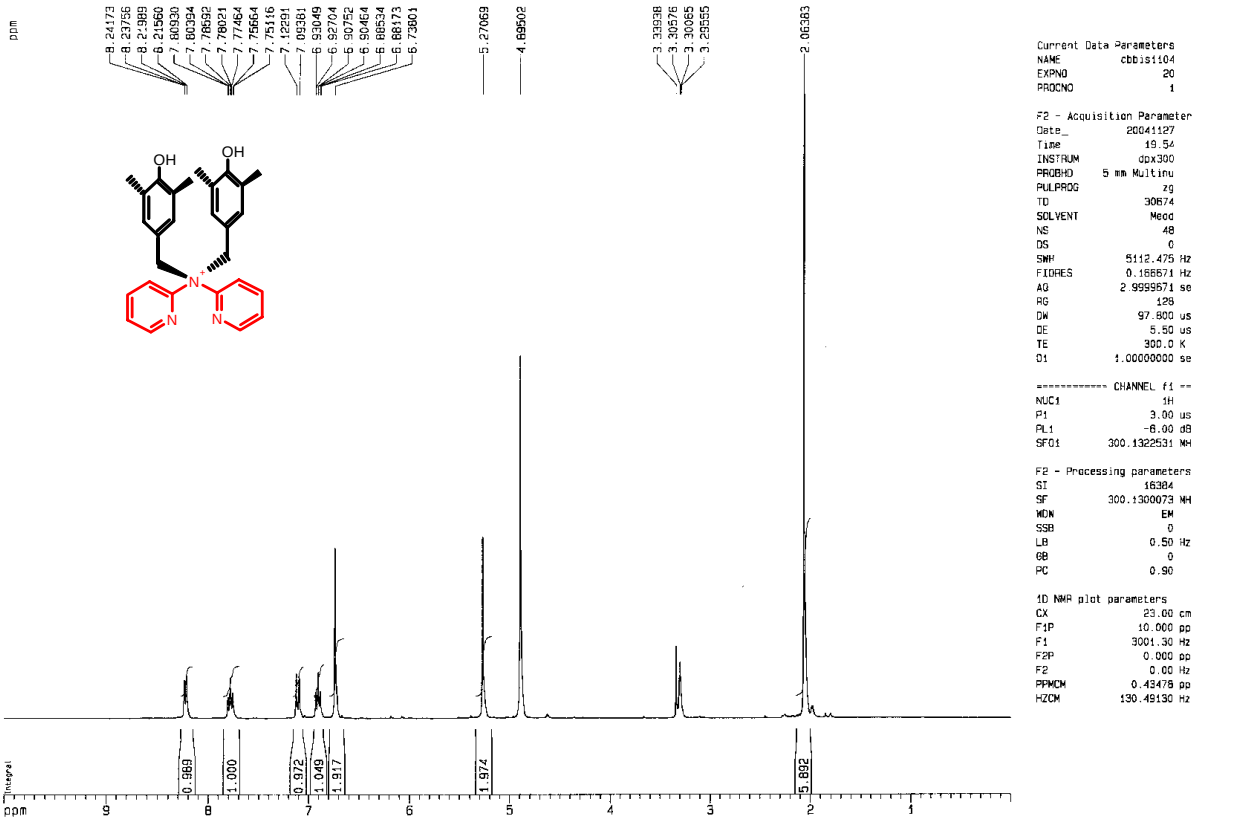
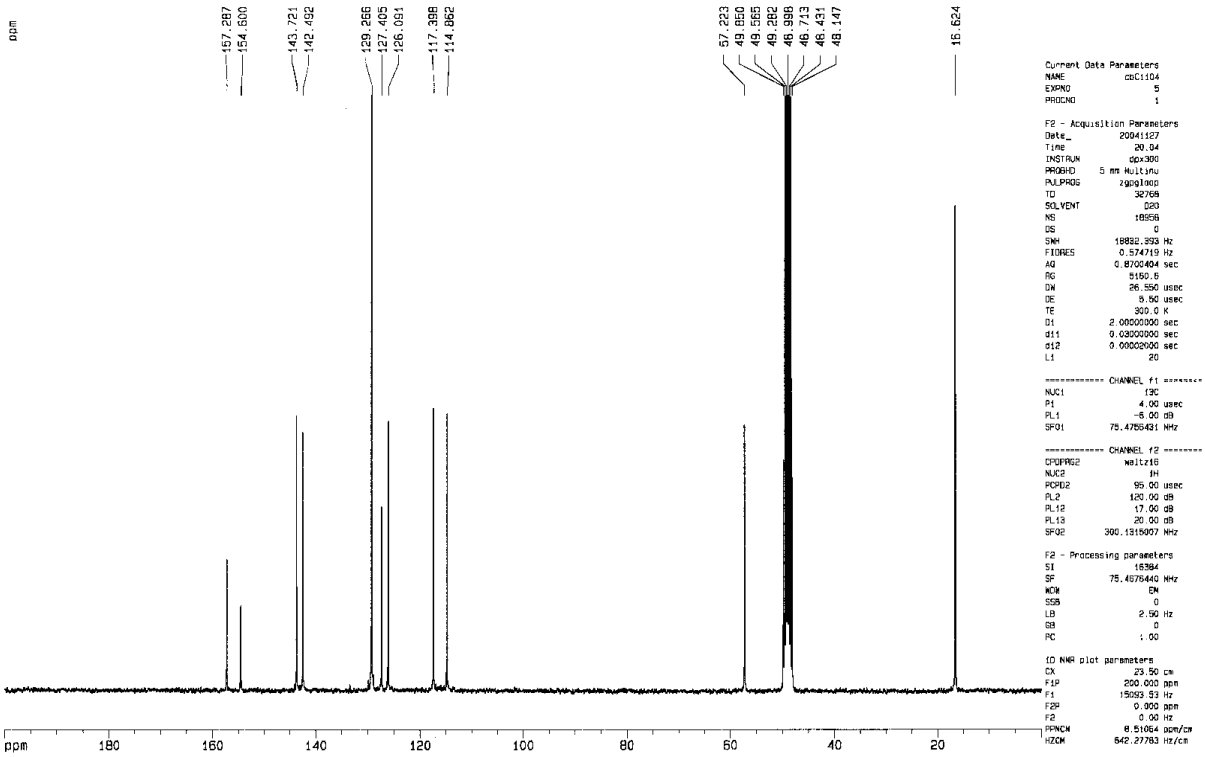
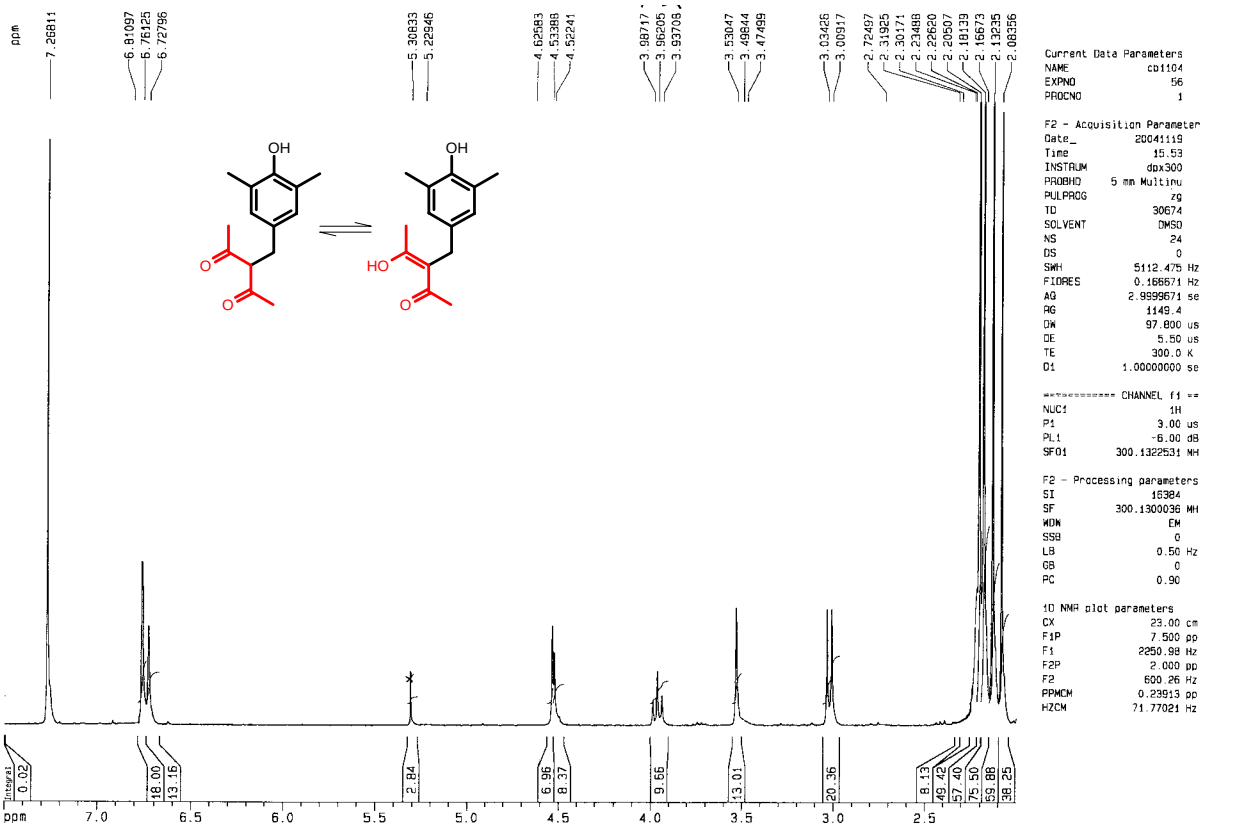
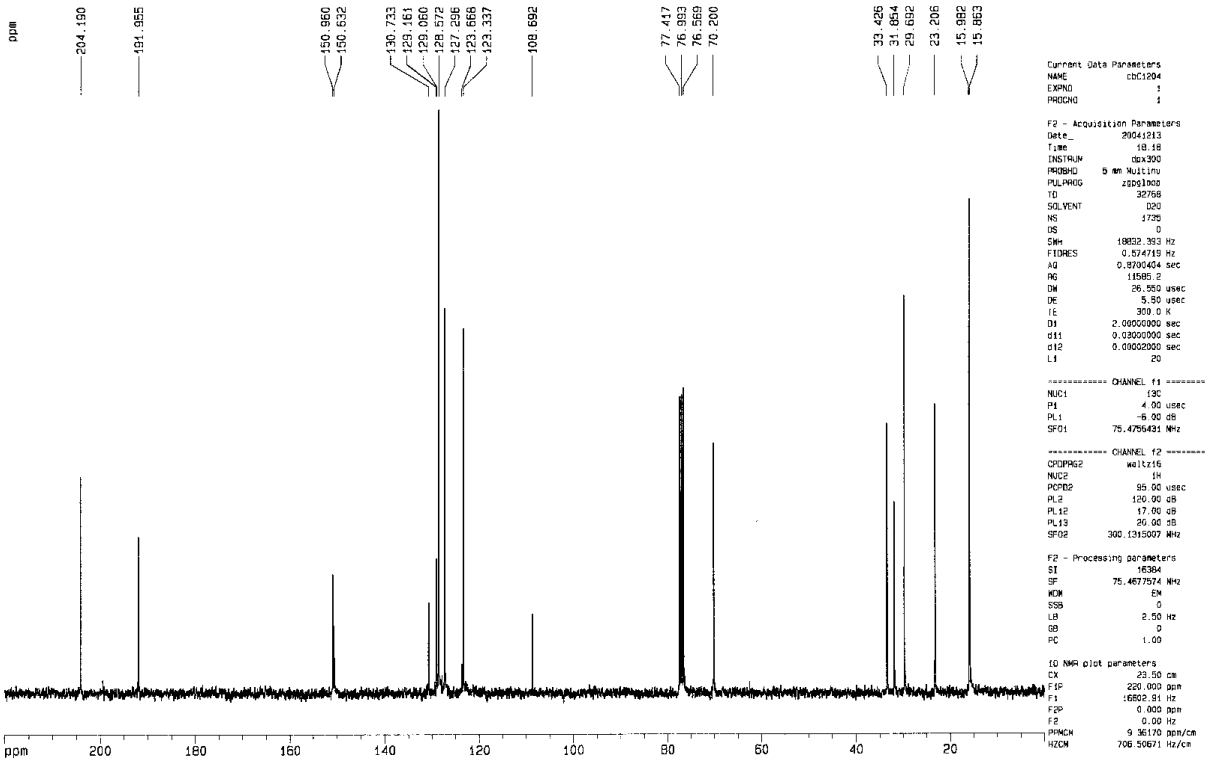
Bis-(4-hydroxy-3,5-dimethylbenzyl)-di-pyridin-2-yl-ammonium chloride (**VIe**)



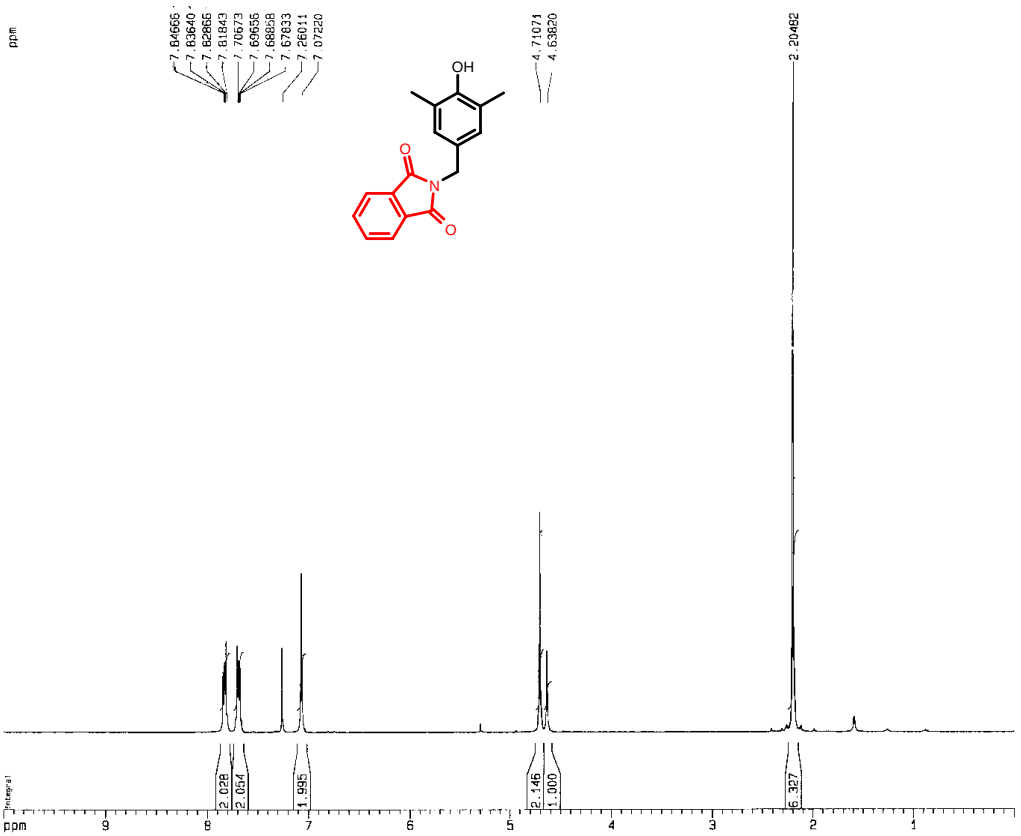


3-(4-hydroxy-3,5-dimethylbenzyl)pentane-2,4-dione (**VIf**)





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

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TE                   300.0 K
D1                   1.00000000 se

============ CHANNEL f1 ==
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PL1                  -6.00 dB
SFO1            300.1322531 MH

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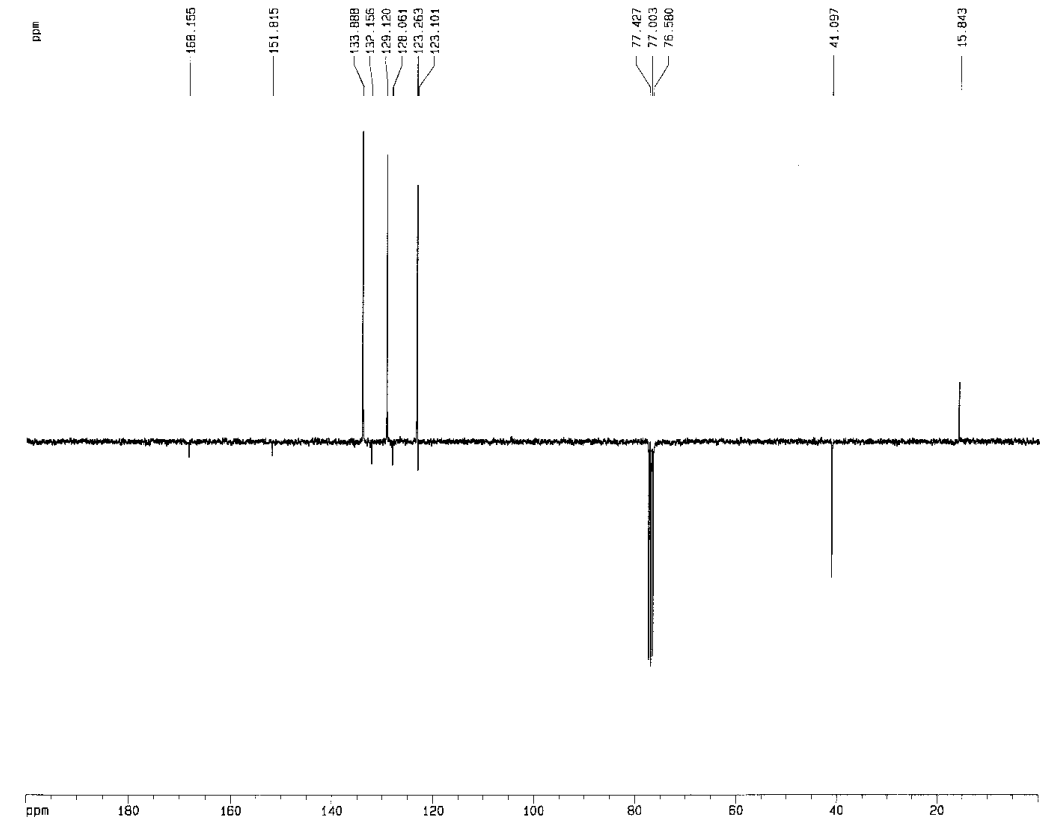


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DE                   5.50 usec
TE                   300.0 K
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CNST11               1.0000000
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D13                  0.00000300 sec
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p2                   17.80 usec
PL1                  -6.00 dB
SFO1            75.4758431 MHz

========== CHANNEL f2 =====
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NUC2                      1H
PCPD2                95.00 usec
PL2                  120.00 dB
PL12                 17.00 dB
SFO2            300.1315007 MHz

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4-(aminomethyl)-2,6-dimethylphenol (**VIh**)