Supporting Information for

Highly Active Copper-N-Heterocyclic Carbene Catalysts for the Synthesis of Phenols

Olivier Songis, Pierre Boulens, Callum G. M. Benson and Catherine S. J. Cazin*

EaStCHEM School of Chemistry, University of St Andrews, St Andrews, KY16 9ST, UK.

Fax: (+)44 (0) 1334 463 808

E-mail: cc111@st-andrews.ac.uk

Contents

General information

All reactions were performed under inert atmosphere using standard Schlenk line and glovebox techniques. Solvents were dispensed from a solvent purification system. All other reagents were used without further purification. ^{1}H and ^{13}C-{^{1}H} Nuclear Magnetic Resonance (NMR) spectra were recorded on a Bruker AVANCE 400 spectrometer using the residual solvent peak as reference ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.16 ppm) at 298K. Elemental analyses were performed by the London Metropolitan University Service. All complexes of the type **[**CuCl(NHC)] were prepared by reaction of Cu_2O with the corresponding imidazolium chloride.[1] All these complexes was analysed by NMR and their purity was ascertained by elemental analysis (CHN). All other compounds were purchased and used as received.

Catalysis

Procedure for Table 1

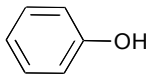
A vial was charged with a stirring bar, iodobenzene (204.1 mg, 1 mmol) and the base (3 mmol). The vial was flushed with argon and a solution of the catalyst (250 µL, 0.01-0.05 mol% from a stock solution of **1**-**4** dissolved in 2 mL of DMSO) was added. 250 µL of DMSO and 500 µL of water were finally added and the mixture was stirred at 130°C for 24 hours. The reaction mixture was then allowed to cool to room temperature, acidified with aqueous HCl (50 mL, HCl 0.1N), and extracted with dichloromethane (3x50 mL). The organic extracts were combined, dried with $MgSO_4$ and concentrated under reduced pressure. The conversion was determined by gas chromatography.

Procedure for Table 2

A vial was charged with a stirring bar, the substrate (1 mmol) and caesium hydroxide (488.6 mg, 3 mmol). The vial was flushed with argon and a solution of [CuCl(SIPr)] (**4**) (250 μL, from a stock solution of catalyst **4** dissolved in 2 mL of DMSO) was added. 250 μL of DMSO and 500 μL of water were finally added and the mixture was stirred at the appropriate temperature for 24 hours. The reaction mixture was then allowed to cool to room temperature, acidified with dilute aqueous HCl (50 mL, HCl 0.1N), and extracted with dichloromethane (3x50 mL). The organic extracts were combined, dried with $MgSO_4$ and concentrated under reduced pressure. The crude material was purified column chromatography (SiO_2).

Hydroxylation products

Phenol (Table 2, Entry 1)[2]



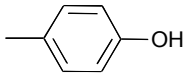
Eluent: C_5H_{10}/EtOAc (8/2).

Title compound obtained as a colourless solid (88%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 5.80 (br s, 1H, OH), 6.83 (d, *J* = 8.0 Hz, 2H, CH), 6.92 (m, 1H, CH), 7.23 (m, 2H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 115.5, 121.0, 129.8, 155.4.

p-Cresol (Table 2, Entry 2)[2]



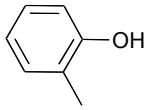
Eluent C_5H_{10}/EtOAc (8/2).

Title compound obtained as a colourless solid (82%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 2.22 (s, 3H, CH_3), 5.91 (br s, 1H, OH), 6.69 (d, *J* = 8.0 Hz, 2H, CH), 6.96 (d, *J* = 8.0 Hz, 2H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 20.5, 115.2, 130.1, 130.2, 153.2.

o-Cresol (Table 2, Entry 3)[3]



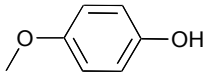
Eluent C_5H_{10}/EtOAc (7/3).

Title compound obtained as colourless oil (91%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 2.28 (s, 3H, CH_3), 5.16 (br s, 1H, OH), 6.78 (d, *J* = 8.0 Hz, 1H, CH), 6.87 (t, *J* = 8.0 Hz, 1H, CH), 7.08-7.16 (m, 2H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 15.8, 115.0, 120.8, 124.0, 127.19, 131.15, 153.8.

p-Hydroxyanisole (Table 2, Entry 4)[2]



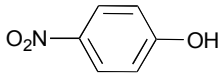
Eluent C_5H_{10}/EtOAc (7/3).

Title compound obtained as a colourless solid (92%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 3.77 (s, 3H, CH_3), 5.33 (br s, 1H, OH), 6.75-6.81 (m, 4H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 56.0, 115.0, 116.2, 149.6, 153.7.

p-Nitrophenol (Table 2, Entry 5)[2]



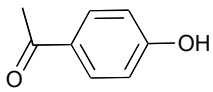
Eluent C_5H_{10}/EtOAc (5/5).

Title compound obtained as a yellow solid (80%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 6.37 (br s, 1H, OH), 6.93 (d, J = 9.0 Hz, 2H, CH), 8.17 (d, J = 9.0 Hz, 2H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 115.8, 126.4, 161.7.

p-Hydroxyacetophenone (Table 2, Entry 6)[2]



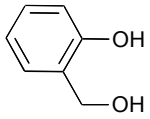
Eluent C_5H_{10}/EtOAc (8/2).

Title compound obtained as a yellow solid (63%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 2.59 (s, 3H, CH_3), 6.94 (d, J = 9.0 Hz, 2H, CH), 7.69 (br s, 1H, OH), 7.90 (d, J = 9.0 Hz, 2H, CH).

^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 26.4, 115.7, 129.7, 131.4, 161.5, 198.7.

2-Hydroxybenzylalcohol (Table 2, Entry 7)[4]



Eluent C_5H_{10}/EtOAc (6/4).

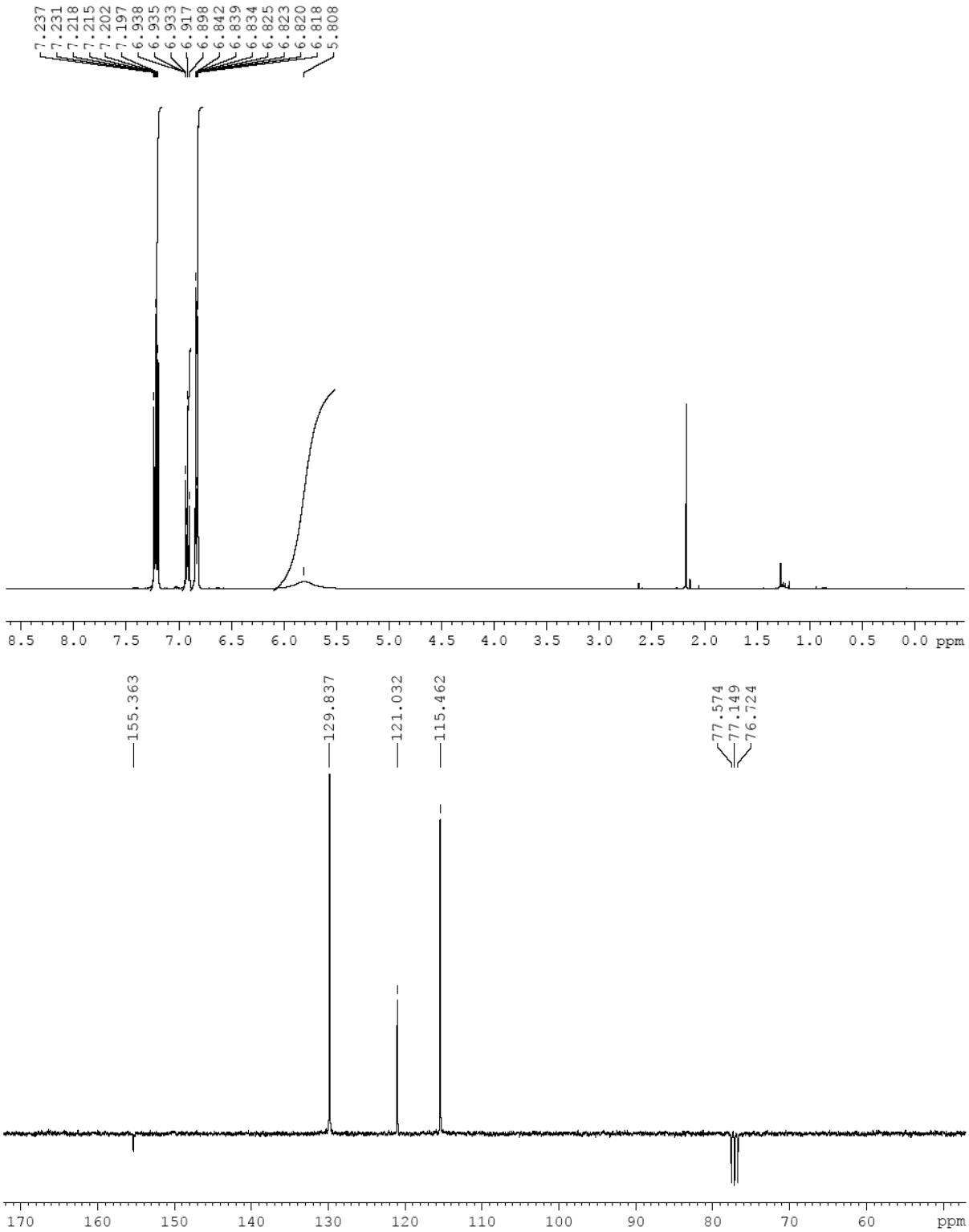
Title compound obtained as a yellow solid (58%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) = 4.83 (s, 2H, CH_2), 6.85 (t, J = 8.0 Hz, 1H, CH), 6.87 (d, J = 7.5 Hz, 1H, CH), 7.03 (d, J = 7.5 Hz, 1H, CH), 7.2 (t, J = 7.5 Hz, 1H, CH).

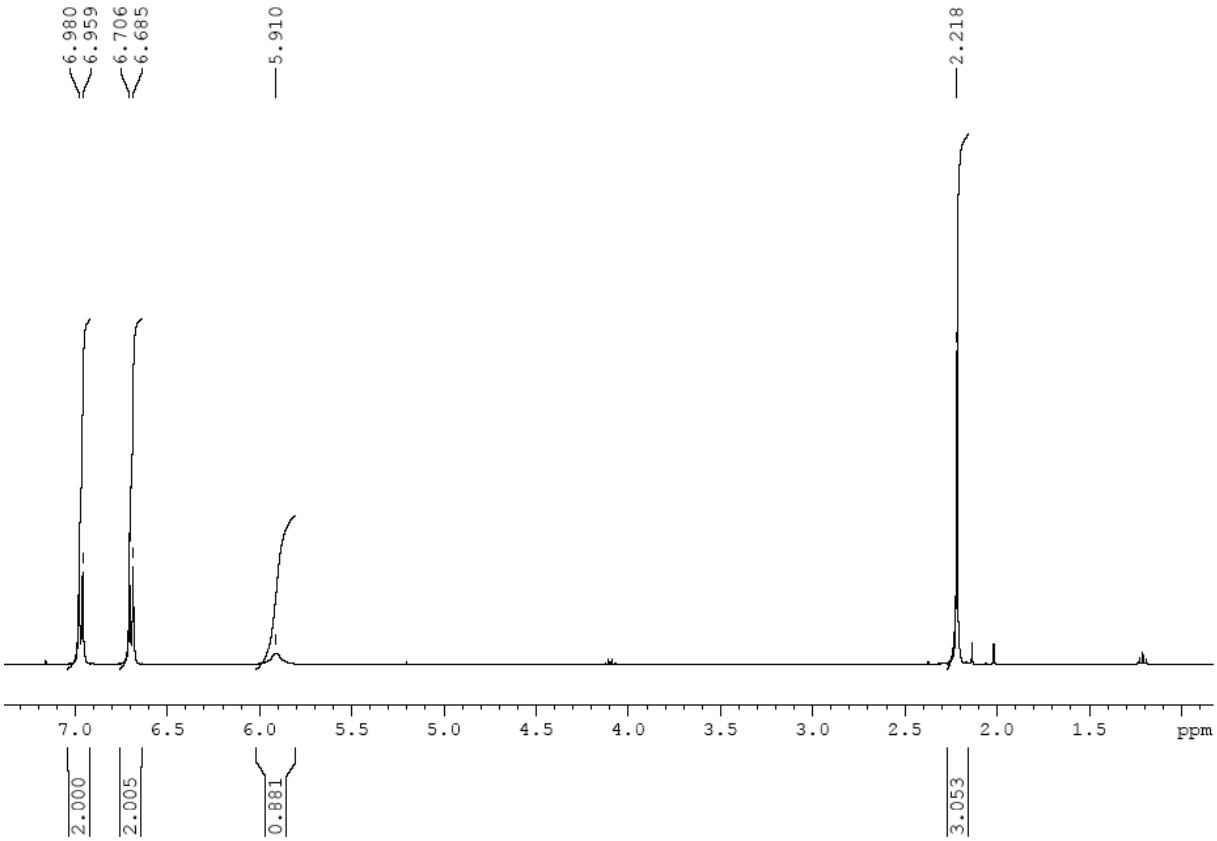
^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ (ppm) = 64.6, 116.6, 120.3, 124.9, 128.1, 129.6, 156.0.

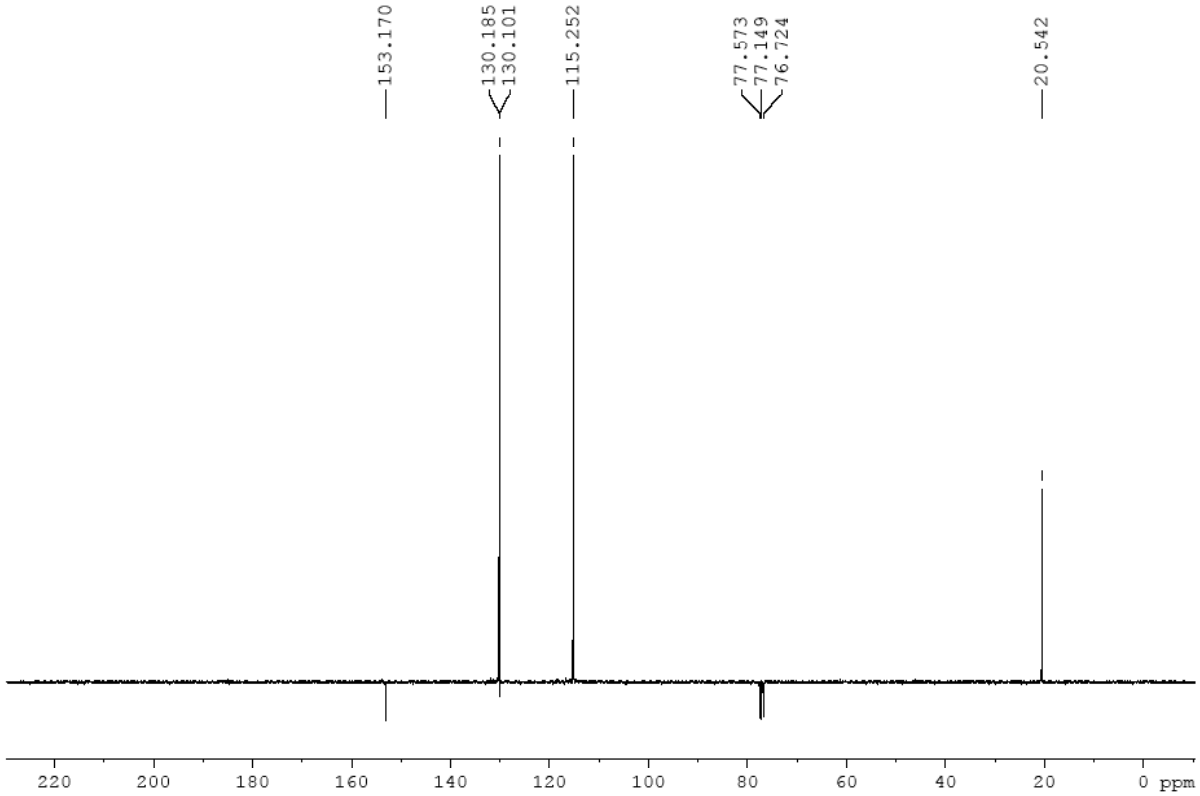
^{1}H and ^{13}C-{^{1}H} NMR spectra of hydroxylation products

Phenol (Table 2, Entry 1)[2]

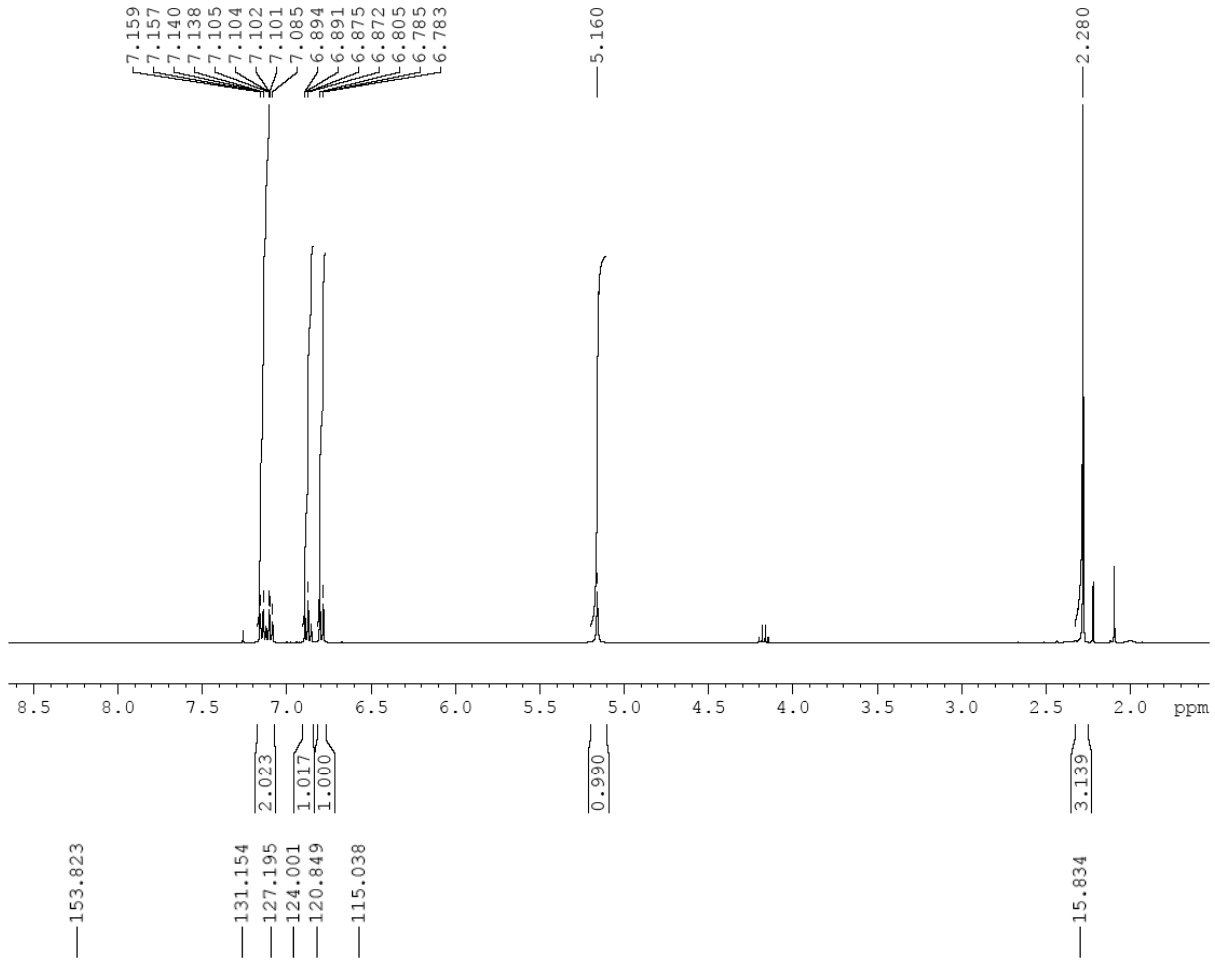


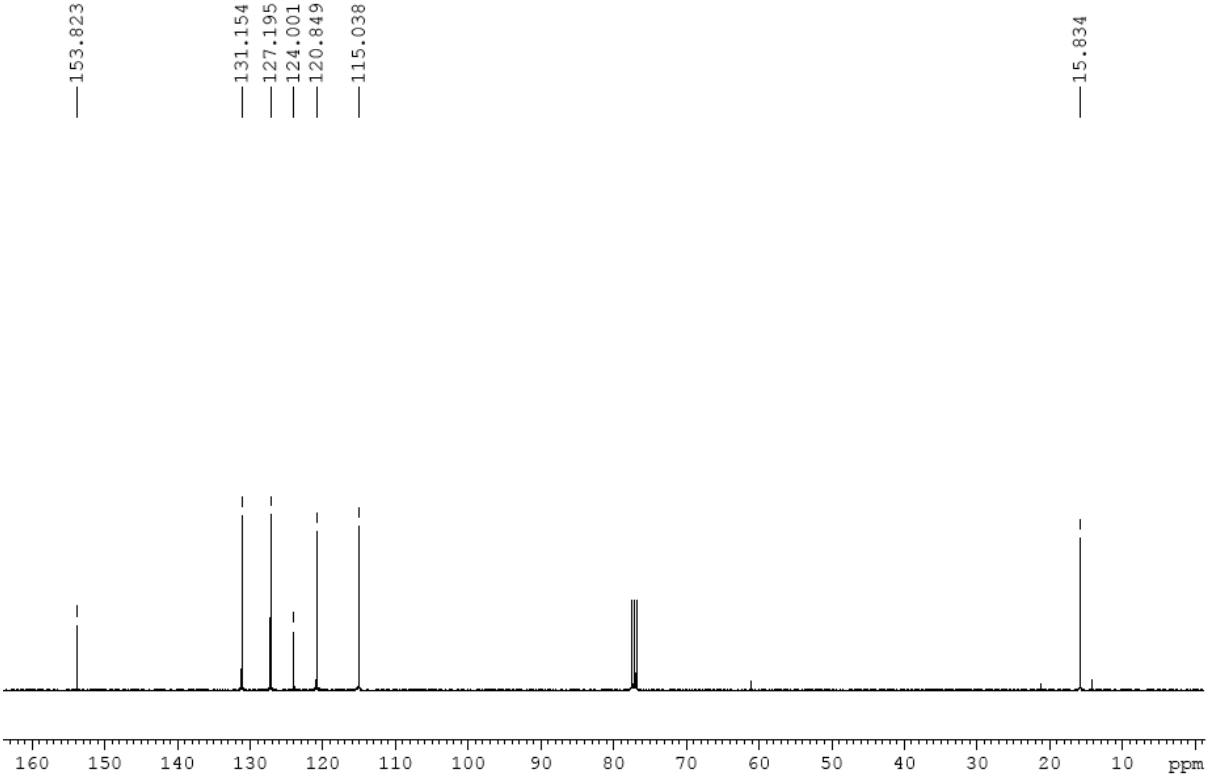
p-Cresol (Table 2, Entry 2)[2]



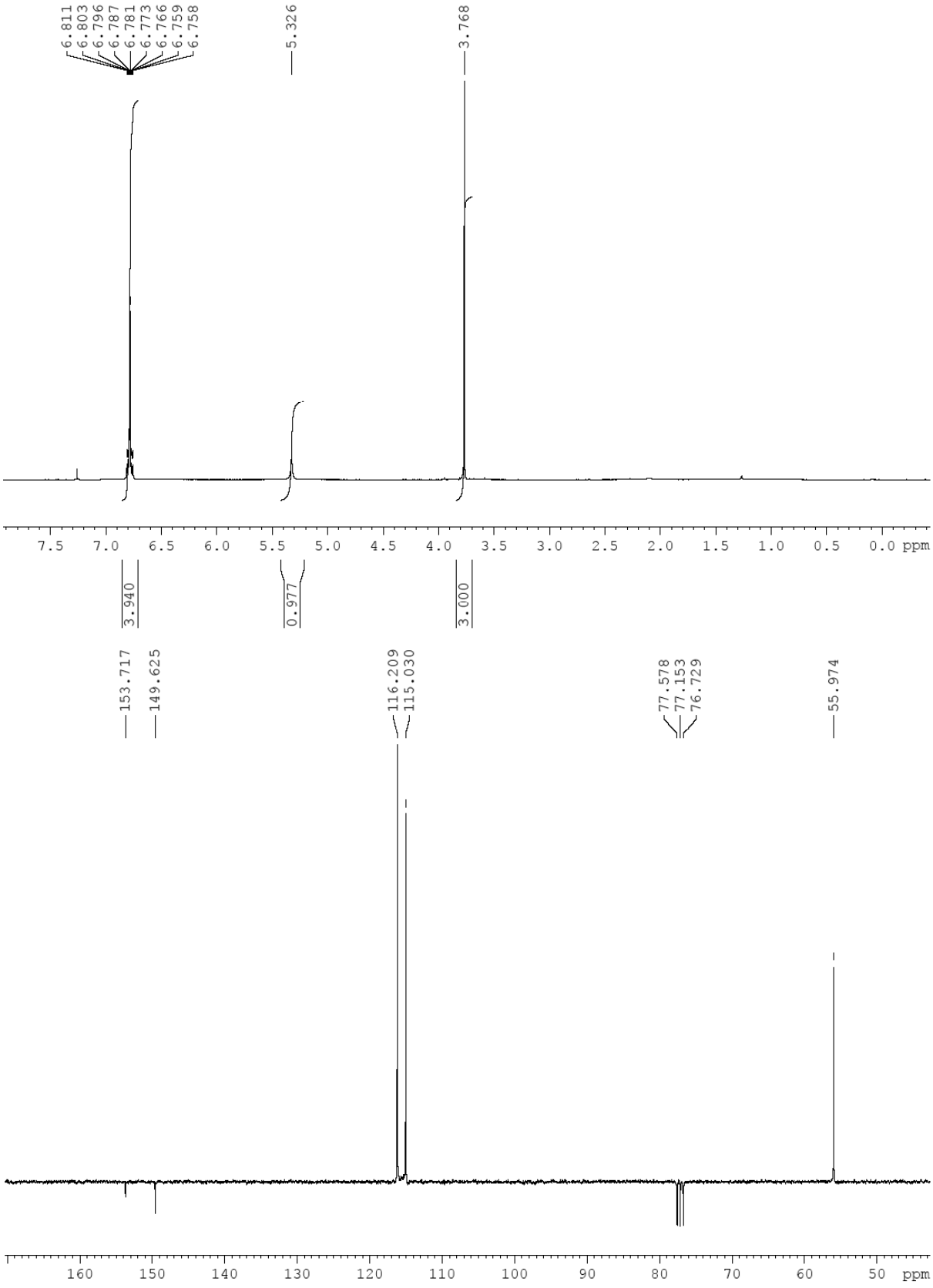


o-Cresol (Table 2, Entry 3)[3]

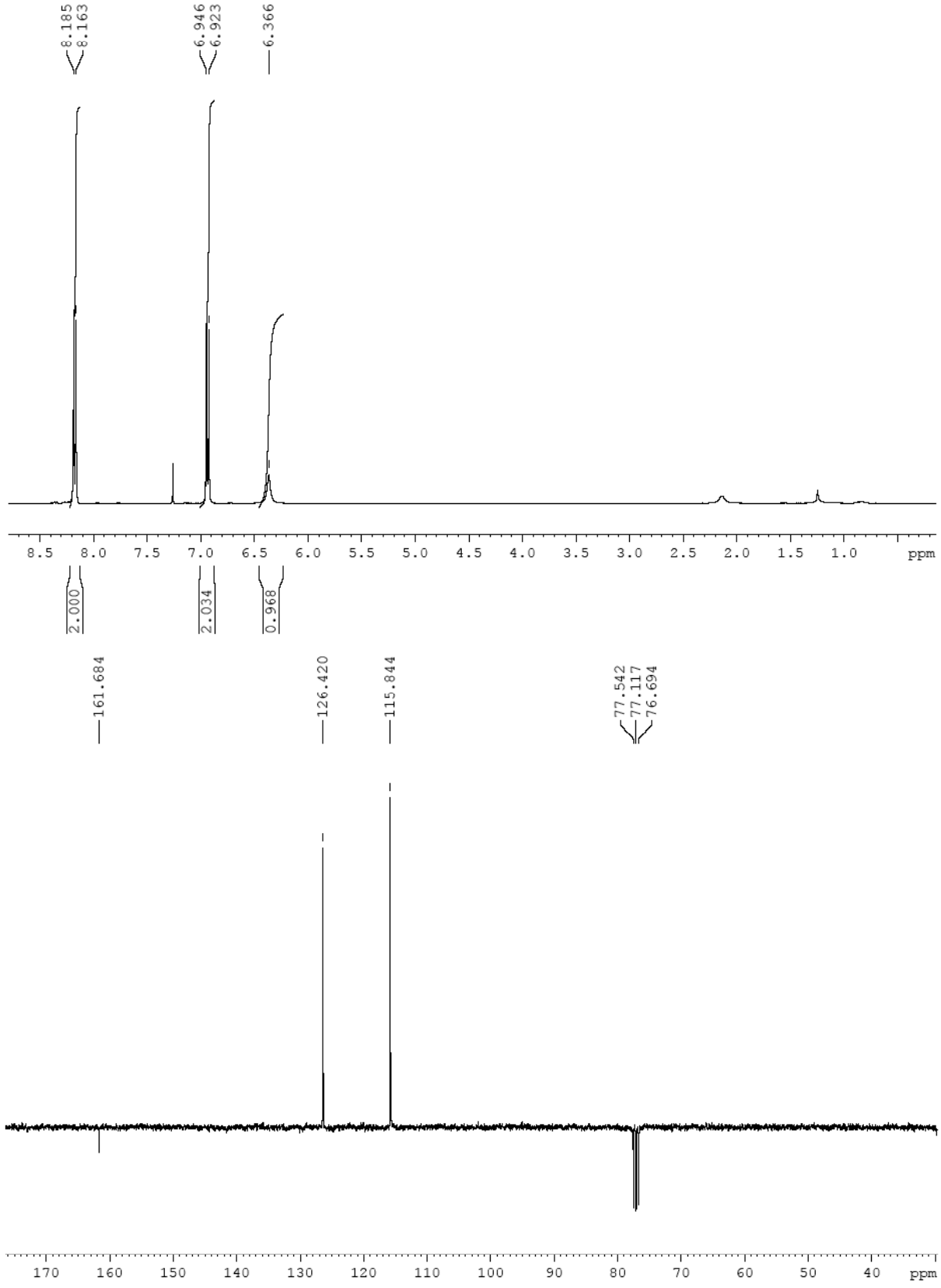




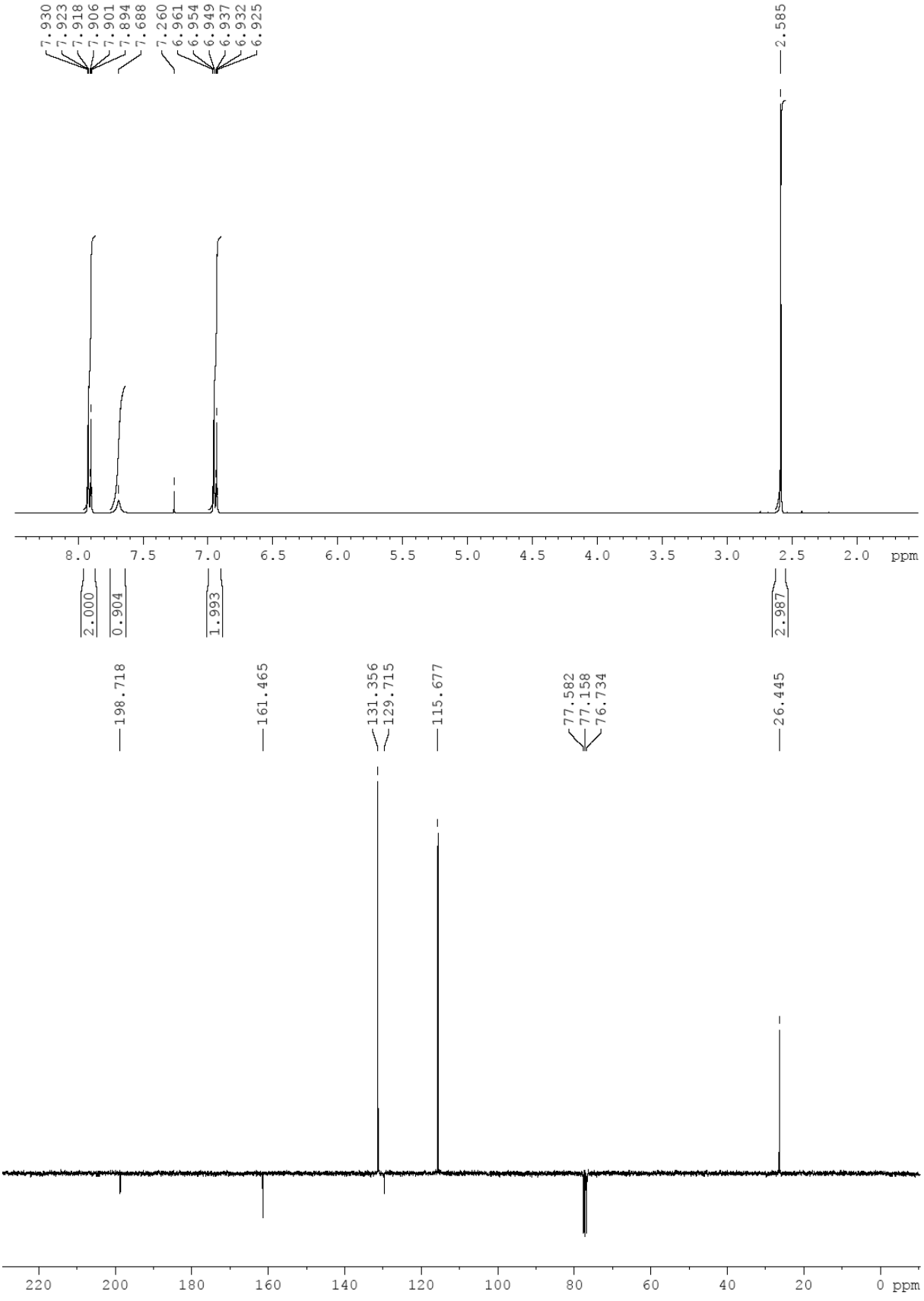
p-Hydroxyanisole (Table 2, Entry 4)[2]



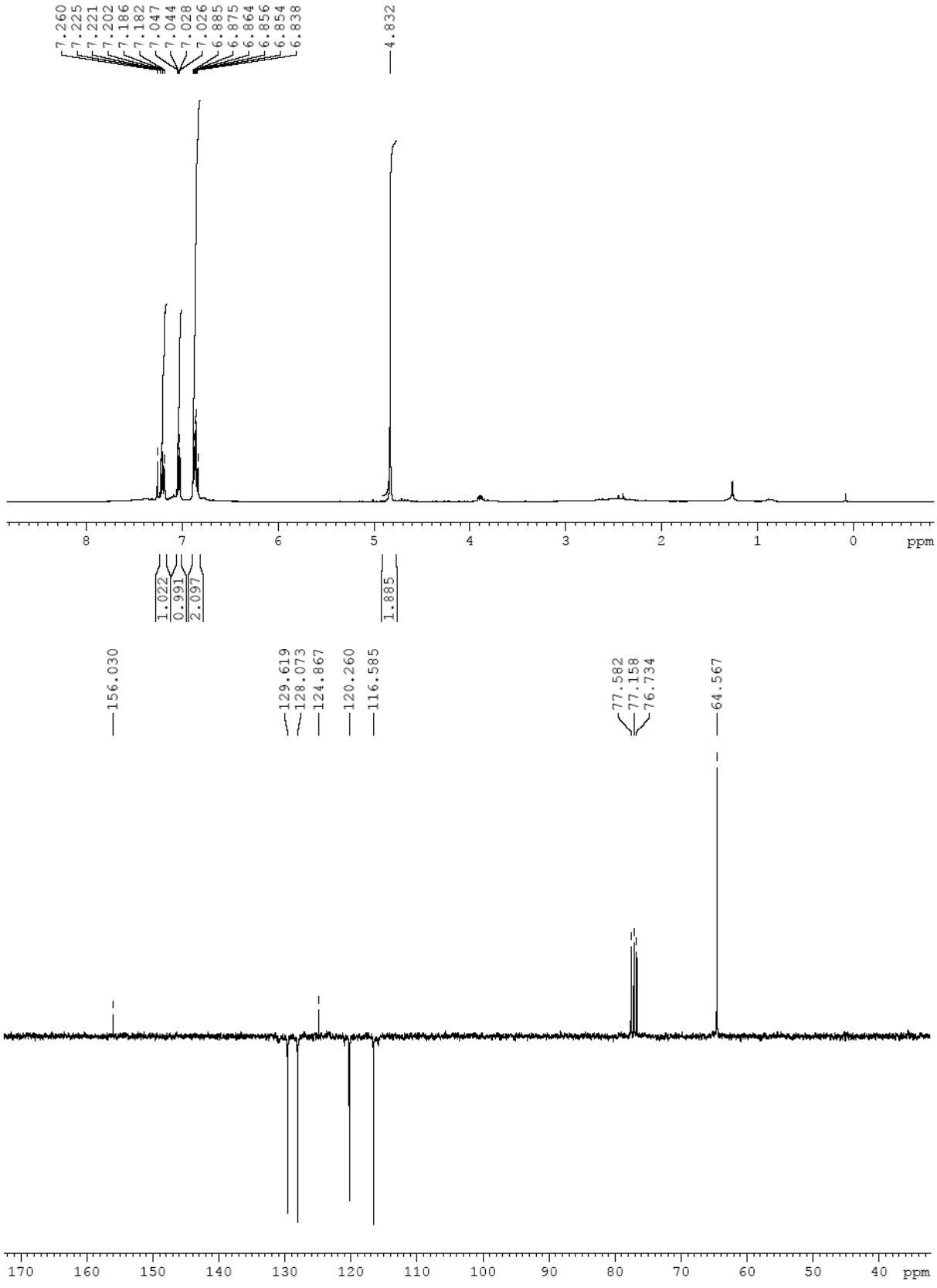
p-Nitrophenol (Table 2, Entry 5)[2]



p-Hydroxyacetophenone (Table 2, Entry 6)[2]



p-Hydroxybenzylalcohol (Table 2, Entry 7)[4]



References

1. Citadelle, C. A.; Le Nouy, E.; Bisaro, F.; Slawin, A. M. Z. and Cazin, C. S. J. *Dalton Trans*., **2010**, *39*, 4489.

2. Zhao, D.; Wu, N.; Zhang, S.; Xi, P.; Su, X.; Lan, J. and J. You, *Angew. Chem. Int. Ed.* **2009**, *48*, 8729.

3. Tlili, A.; Xia, N.; Monnier, F. and Taillefer, M. *Angew. Chem., Int. Ed. Engl.* **2009**, *48*, 8725.

4. NMR data were compared with Aldrich commercial compound data.