

# **Dramatic Synergistic Effects between Hydroquinone and Resorcinol Derivatives for the Organocatalyzed Reduction of Dioxygen by Diethylhydroxylamine**

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# **SUPPORTING INFORMATION**

## Synthesis of 5.

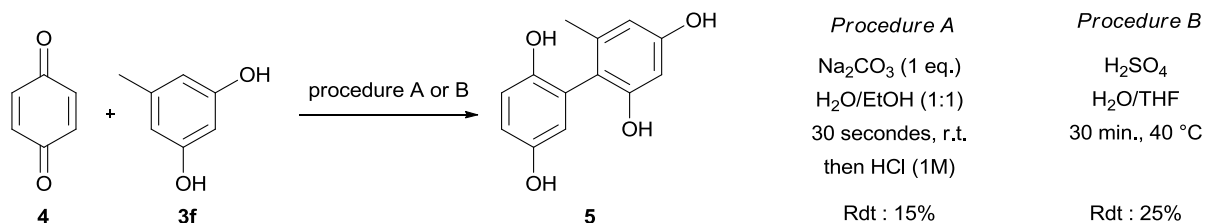
Orcinol monohydrate **3f** was purchased by Sigma Aldrich. Benzoquinone **4** was sublimed before used.

TLC was performed on 60F<sub>254</sub> silica gel plates and visualized with a UV lamp (254 nm), and KMnO<sub>4</sub>/K<sub>2</sub>CO<sub>3</sub>/AcOH aqueous solution with heating. SDS silica 60A C.C. (35-70 μM) was used for chromatography.

Infrared spectra were recorded on a Nicolet 380 FT-IR (Thermo Electron Corporation).

NMR spectra were recorded on a Bruker 300 apparatus and calibrated relative to residual solvent peaks (CD<sub>3</sub>OD : 3.31 ppm for <sup>1</sup>H NMR and 49.00 for <sup>13</sup>C NMR; DMSO-*d*<sub>6</sub> : 2.50 ppm for <sup>1</sup>H NMR and 39.52 for <sup>13</sup>C NMR).

High resolution mass spectra were performed by the "Centre Universitaire de Mesures et d'Analyses, Université Lille 2", on Exactive (Thermo Fischer Scientific).



### Procedure A:

To a solution of orcinol monohydrate (142 mg, 1.00 mmol) and sodium carbonate (106 mg, 1.00 mmol) in water (15 mL) degassed with argon, was added in one portion a degassed ethanol solution (5 mL) of *para*-benzoquinone (108 mg, 1.00 mmol). After 30 seconds, the brown solution was acidified by aqueous HCl (1M, 20 mL) and extracted with ethylacetate (3 x 20 mL). The combined organic fractions were washed with brine, dried over sodium sulfate and filtrated. After evaporation of the solvents, crude product was purified through silica gel chromatography (50/50 PE/EtOAc) to give the desired product (35 mg, 0.15 mmol, 15%). Further elution with EtOAc/MeOH 9:1 gave 115 mg of polymeric material.

**R<sub>f</sub>** : 0.33 (PE/EtOAc 1:1).

**m.p.** = not clear, decomposition

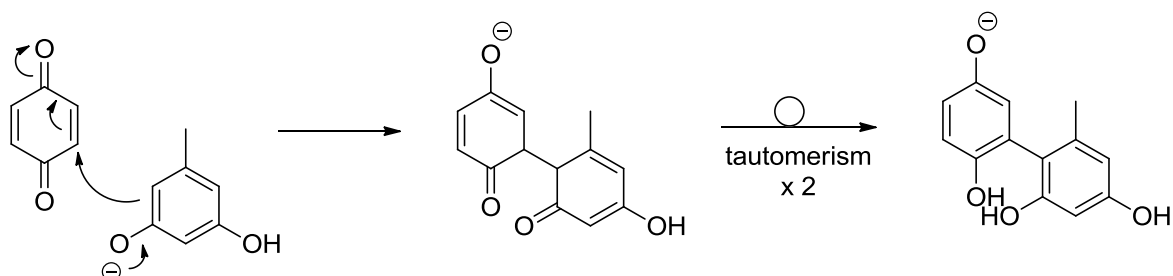
**IR** (ATR-FTIR, cm<sup>-1</sup>): 3326, 1622, 1586, 1482, 1445, 1197, 1149, 831, 810, 783, 726.

**<sup>1</sup>H NMR** (CD<sub>3</sub>OD, 300 MHz): 6.73 (d, *J* = 8.7 Hz, 1H), 6.63 (dd, *J* = 8.6 Hz, 3.0 Hz, 1H), 6.48 (d, *J* = 3.0 Hz, 1H), 6.27-6.22 (m, 2H), 1.98 (s, 3H).

$^{13}\text{C}$  NMR ( $\text{CD}_3\text{OD}$ , 75.5 MHz): 158.3 (C), 156.6 (C), 151.2 (C), 149.0 (C), 140.3 (C), 126.3 (C), 119.6 (CH), 117.9 (C), 117.3 (CH), 116.0 (CH), 109.6 (CH), 101.2 (CH), 20.5 ( $\text{CH}_3$ ).

HRMS:  $[\text{M}-\text{H}]^-$   $\text{C}_{13}\text{H}_{11}\text{O}_4$  calcd : 231.0652; found : 231.0660 (3.54 ppm).

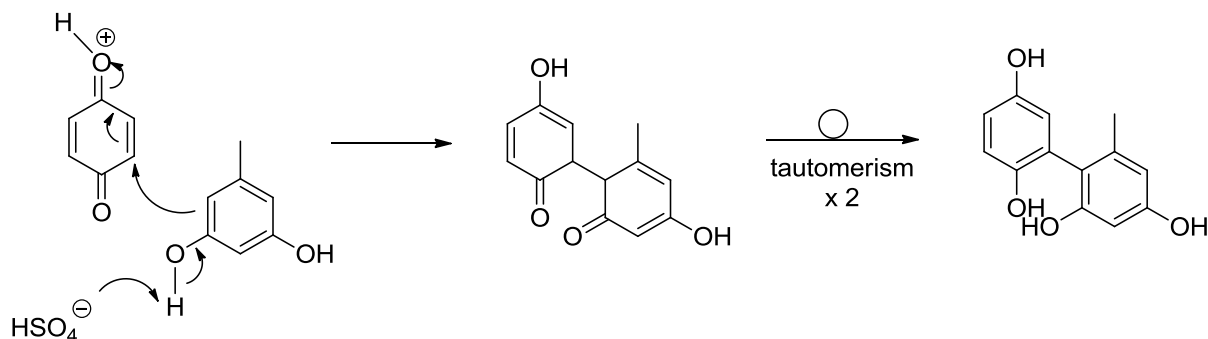
### Proposed mechanism:



### Procedure B (adapted from Stjernström's work on benzoquinone and resorcinol)<sup>1</sup>:

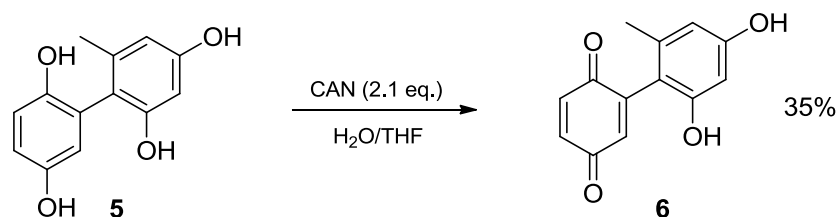
To an aqueous solution of sulfuric acid (10% v/v, 40 mL) and orcinol monohydrate (2.84 g, 20.0 mmol) was added in one portion a solution of benzoquinone (2.38 g, 22 mmol) in THF (40 mL). After stirring at 40°C for 30 minutes, the mixture was neutralized by an aqueous solution of sodium hydrogen carbonate (200 mL). The product was extracted by 3 portions of ethyl acetate (100 mL). The combined organic fractions were washed with sodium dithionite solution then brine, dried over sodium sulfate and filtrated. After evaporation of solvents, the product was purified through silica gel chromatography (50/50 PE/EtOAc) to give the desired product (1.18 g, 5.09 mmol, 25%).  $^1\text{H}$  NMR was in agreement to one of the product obtained following the first procedure.

### Proposed mechanism:



<sup>1</sup> N. E. Stjernstrom, *Ark. Kemi*, 1963, **6**, 57.

## Synthesis of 6.



To a solution of cerium ammonium nitrate (2.76 g, 5.04 mmol) in water (12 mL) was added in one portion a solution of product **5** (557 mg, 2.40 mmol) in THF (12 mL). After stirring for one hour at room temperature, the product was extracted by 3 portions of ethyl acetate (20 mL). The combined organic fractions were washed with brine, dried over sodium sulfate and filtrated. After evaporation of the solvents, the product was purified through silica gel chromatography (60/40 PE/EtOAc) to give the desired product (196 mg, 0.85 mmol, 35%) as red solid.

**R<sub>f</sub>**: 0.32 (PE/EtOAc 6:4).

**m.p.** = not clear, decomposition.

**IR** (ATR-FTIR, cm<sup>-1</sup>): 3375, 1647, 1587, 1457, 1340, 1282, 1254, 1150, 1094, 1053, 916, 836.

**<sup>1</sup>H NMR** (DMSO-*d*<sub>6</sub>, 300 MHz): 9.36 (s, 1H, OH), 9.29 (s, 1H, OH), 6.97-6.90 (m, 2H), 6.66 (d, *J* = 2.1 Hz, 1H), 6.17-6.15 (m, 2H), 1.96 (s, 3H).

**<sup>13</sup>C NMR** (DMSO-*d*<sub>6</sub>, 75.5 MHz): 188.0 (C), 186.4 (C), 158.4 (C), 155.9 (C), 145.6 (C), 137.7 (C), 137.2 (CH), 136.3 (CH), 135.5 (CH), 112.1 (C), 108.1 (CH), 100.0 (CH), 20.0 (CH<sub>3</sub>).

**HRMS**: [M+H]<sup>+</sup> C<sub>13</sub>H<sub>11</sub>O<sub>4</sub> calcd : 231.0652; found : 231.0654 (0.8 ppm).

## Measurements of dioxygen reduction:

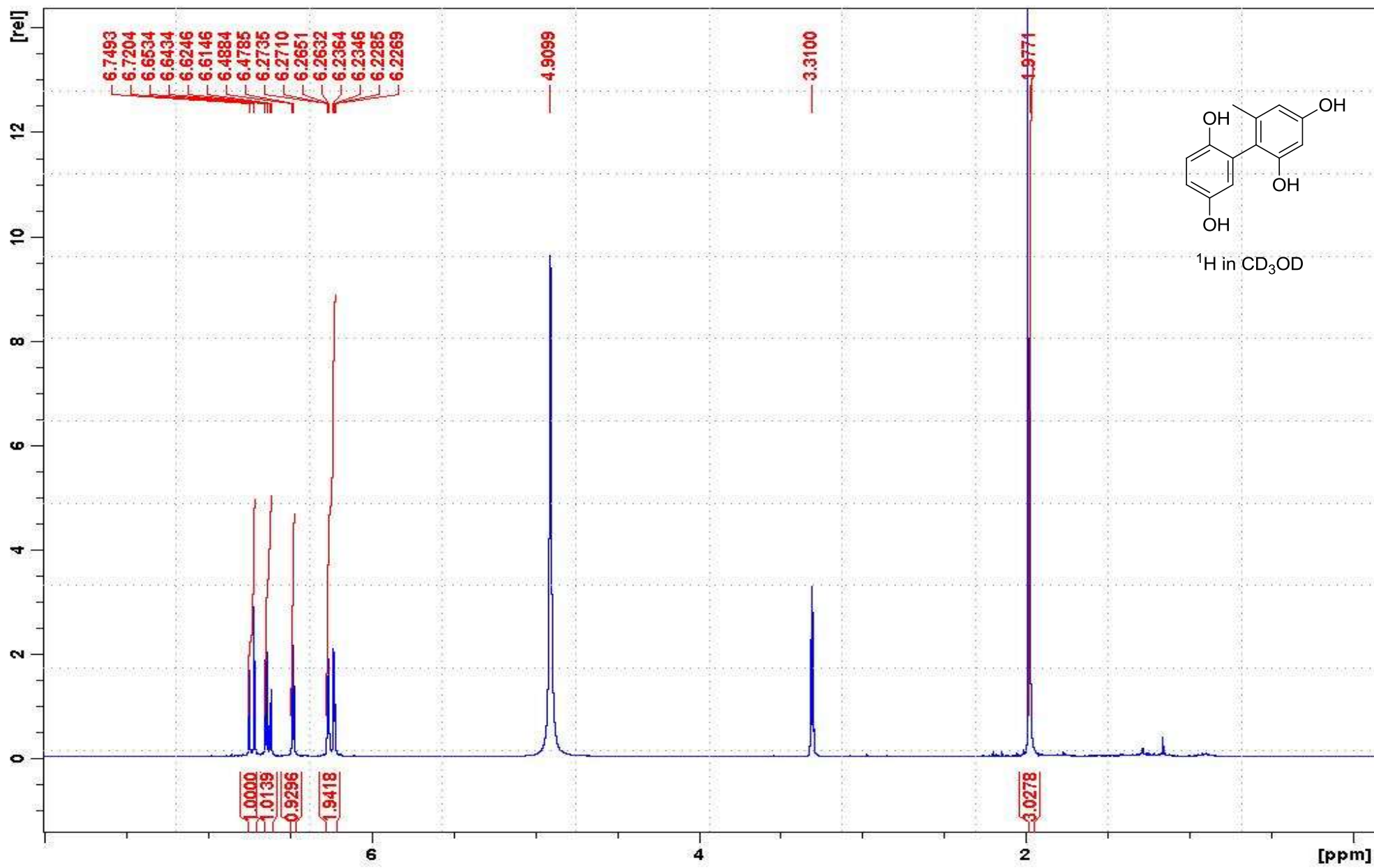
The concentration of dioxygen dissolved in water was followed by luminescence extinction using a LDO-Hach HQ30 apparatus.

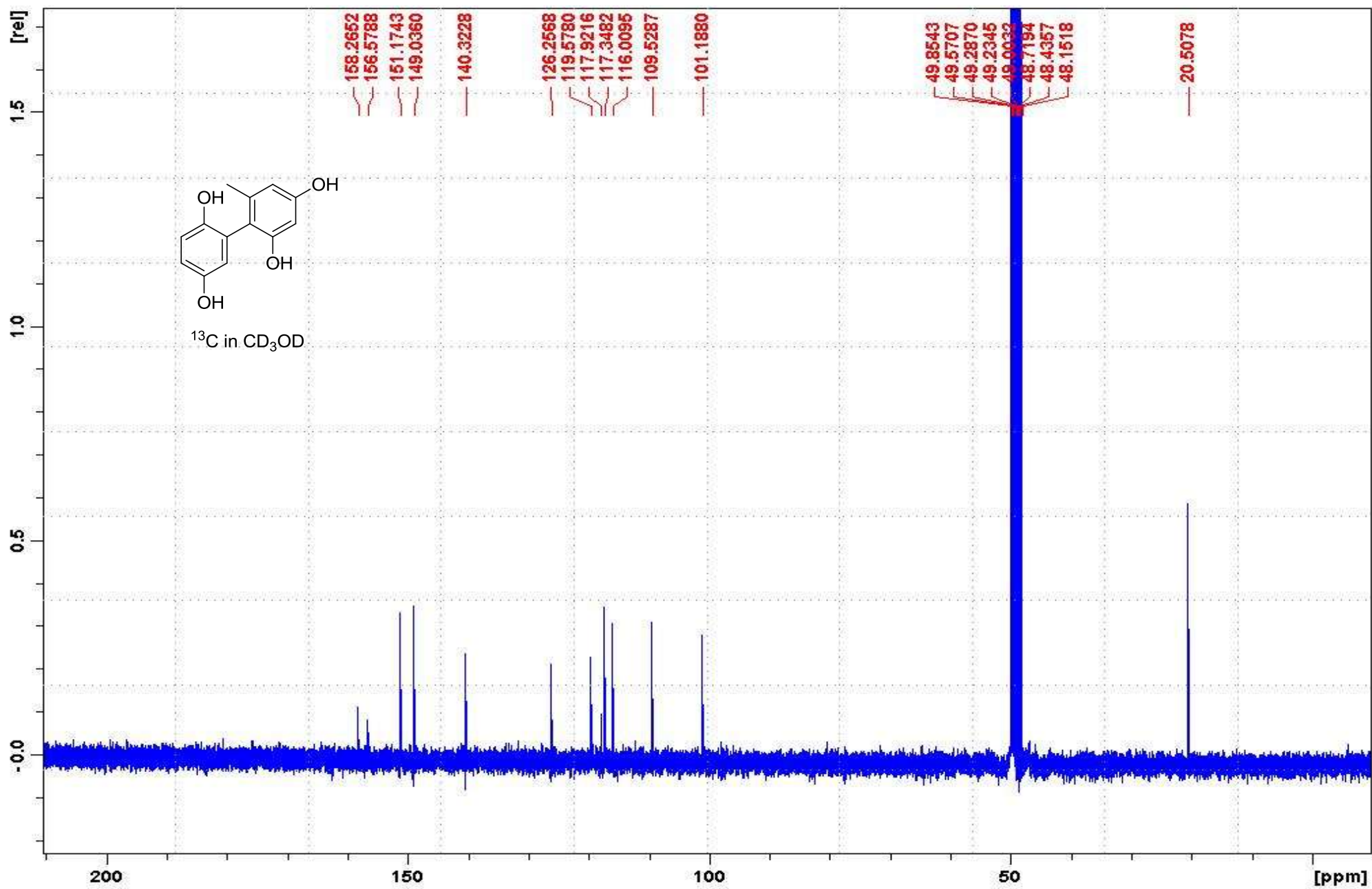
Water was purified by a Millipore® apparatus Simplicity 185 and collected at the resistivity of 18.2 MΩ.cm.

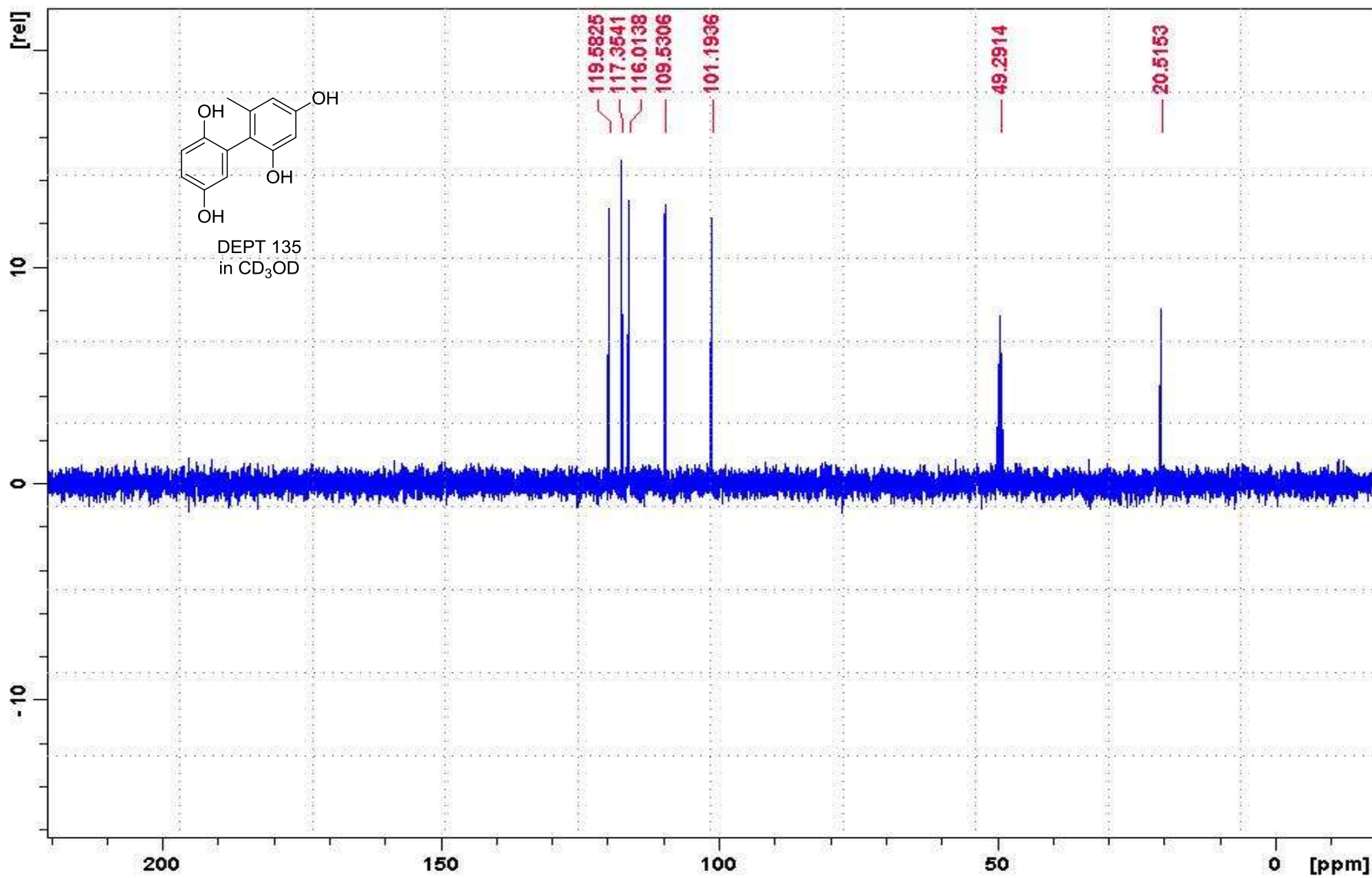
In an erlenmeyer of 250 mL, 285 mL of a buffered solution of sodium hydrogenocarbonate (10 mM) and sodium carbonate (16 mM) was introduced to fill it completely once closed by the electrode. The amount of dissolved dioxygen was adjusted to 0.28 mmol.l<sup>-1</sup> by bubbling dioxygen or argon. Diethylhydroxylamine (23 μL, 0.84 mM) was first introduced followed after a few minutes of stirring, by, if any, the co-catalyst, then after 5 minutes, the catalyst.

The catalysts and the co-catalysts were introduced by syringe once diluted in ethanol (1 mg/mL for 1 μM concentrations, 10 mg/mL for 16 μM concentrations, 2 mg/L for **5** and **6**) with the required volume.

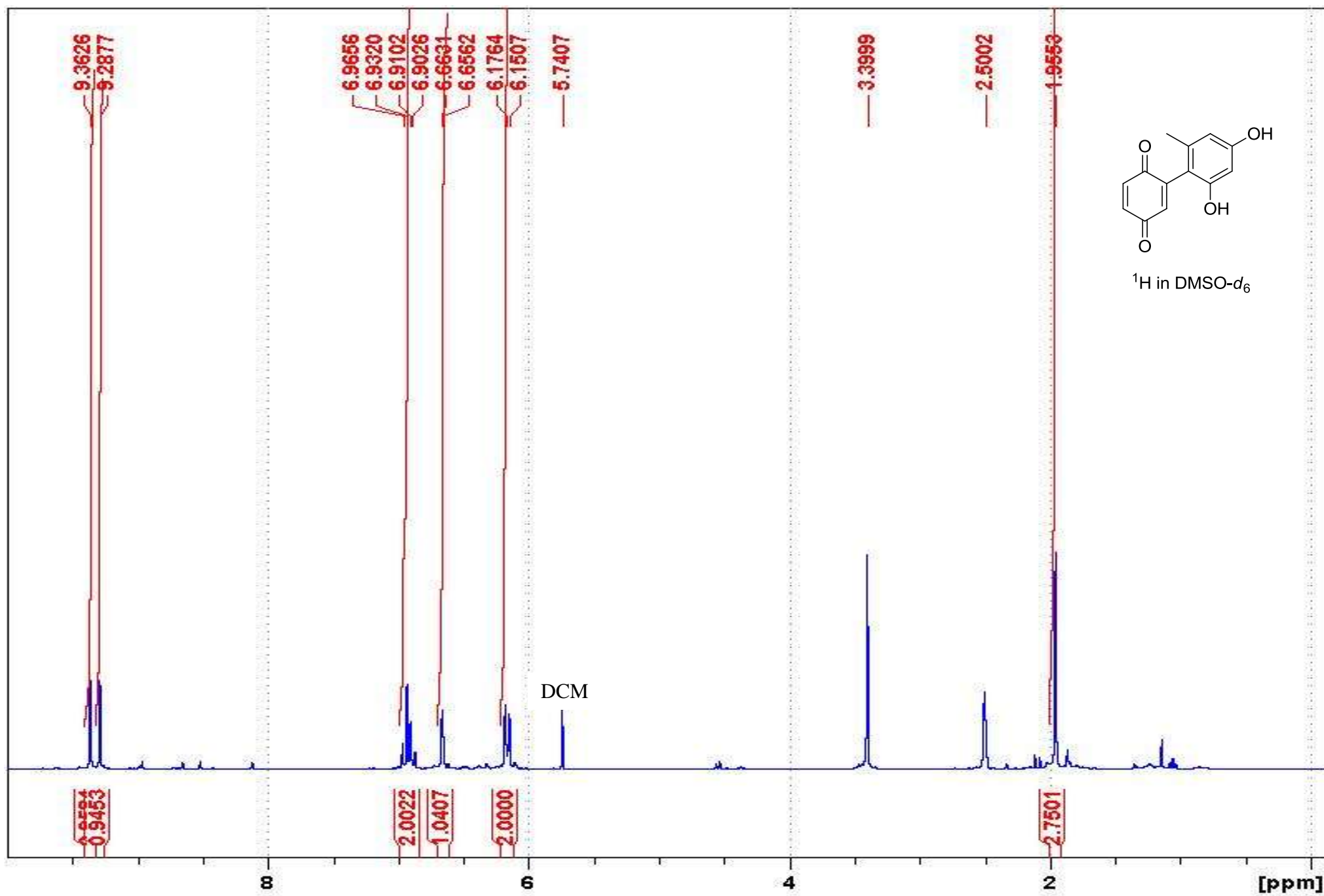
In case of the mixture of pyrogallol with hydroquinone, the solutions were transferred out with the same syringe and injected together.

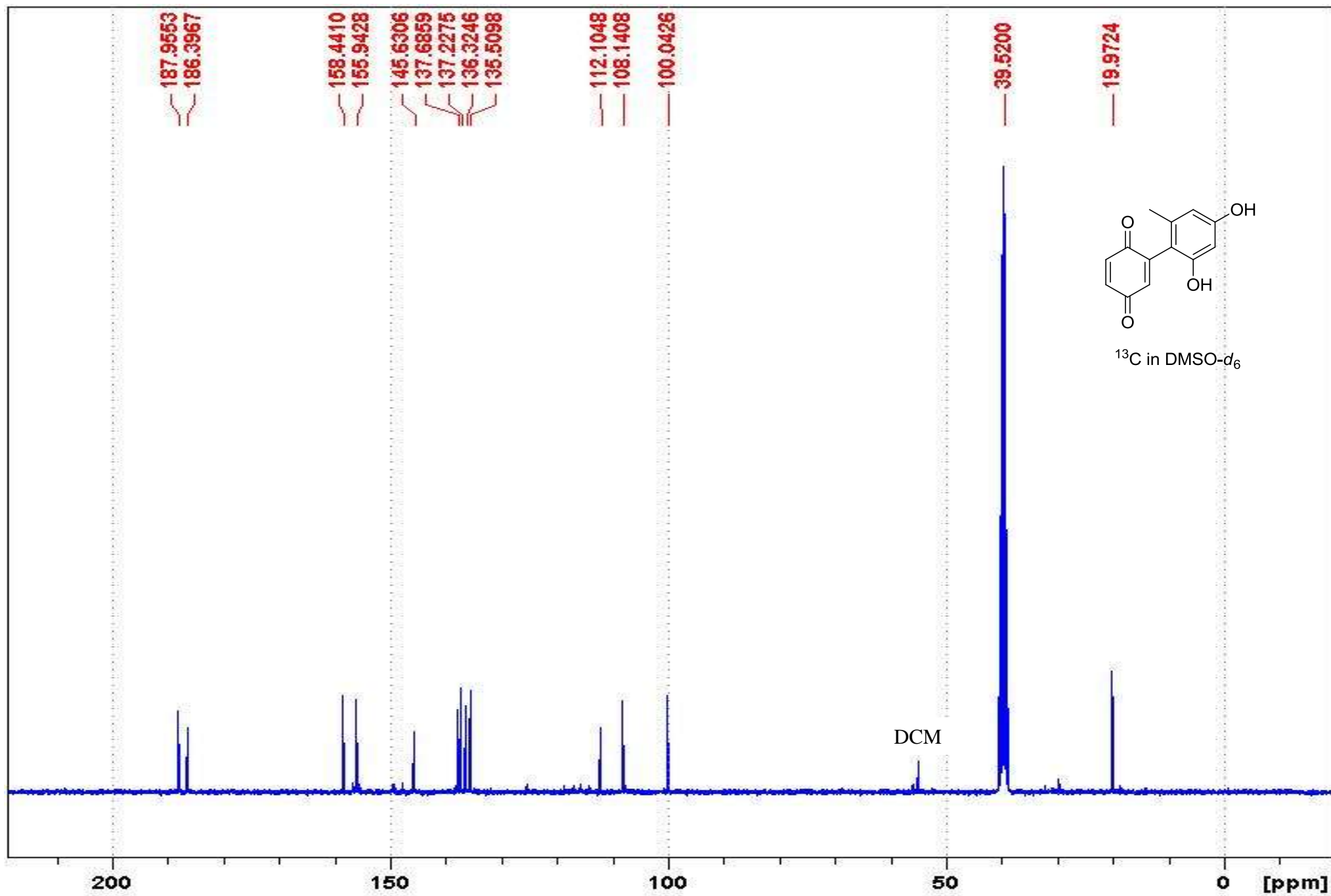


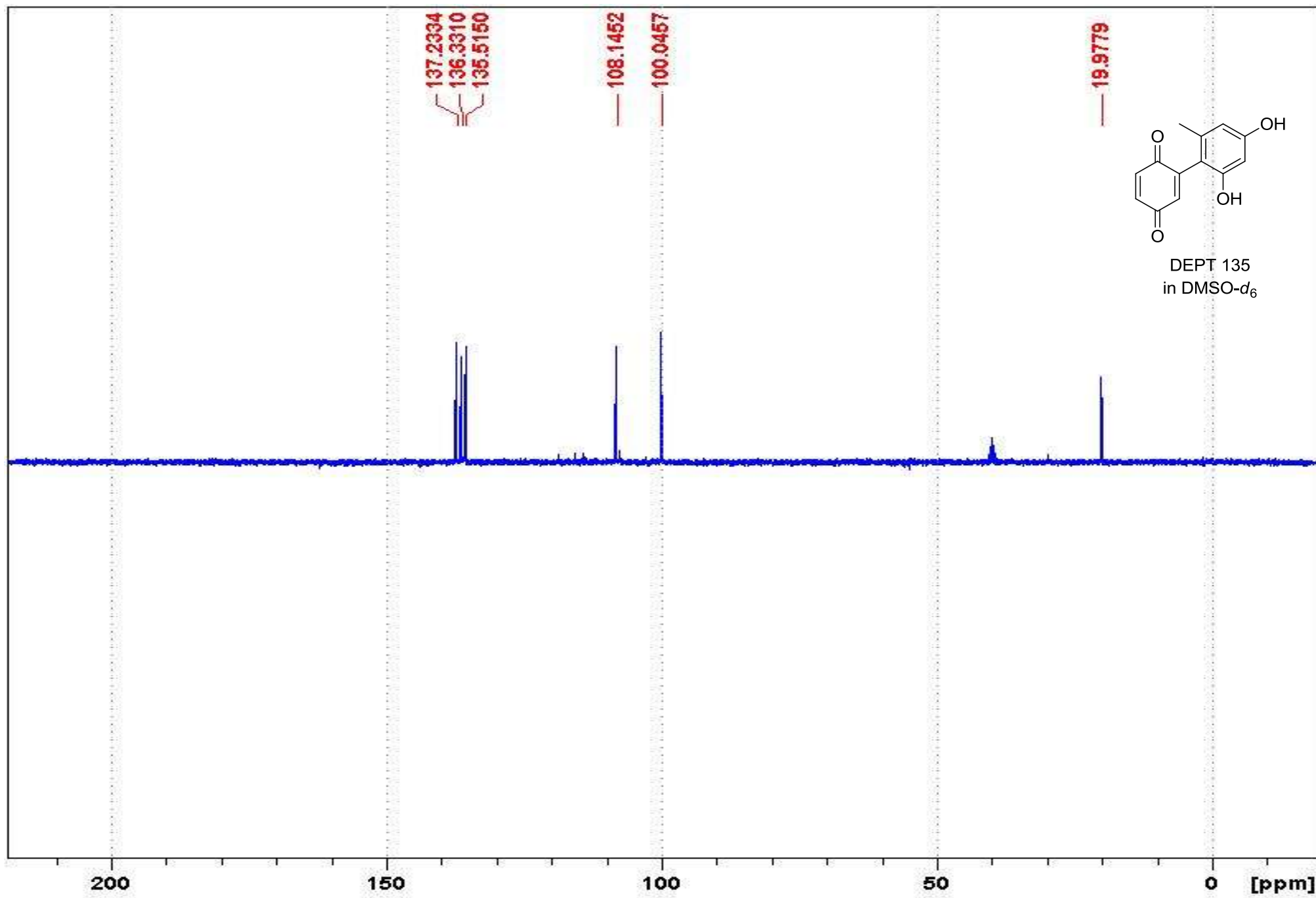




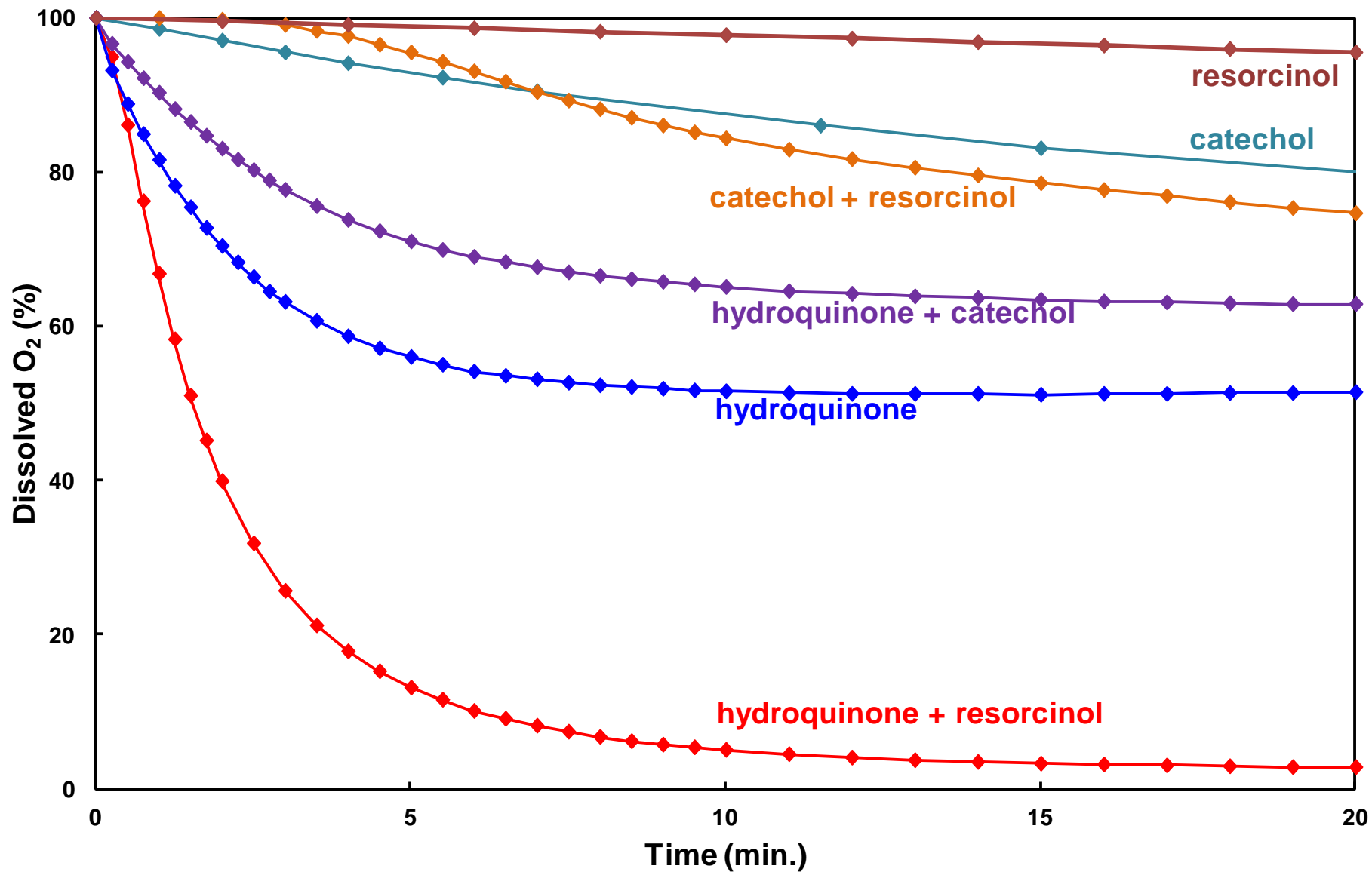




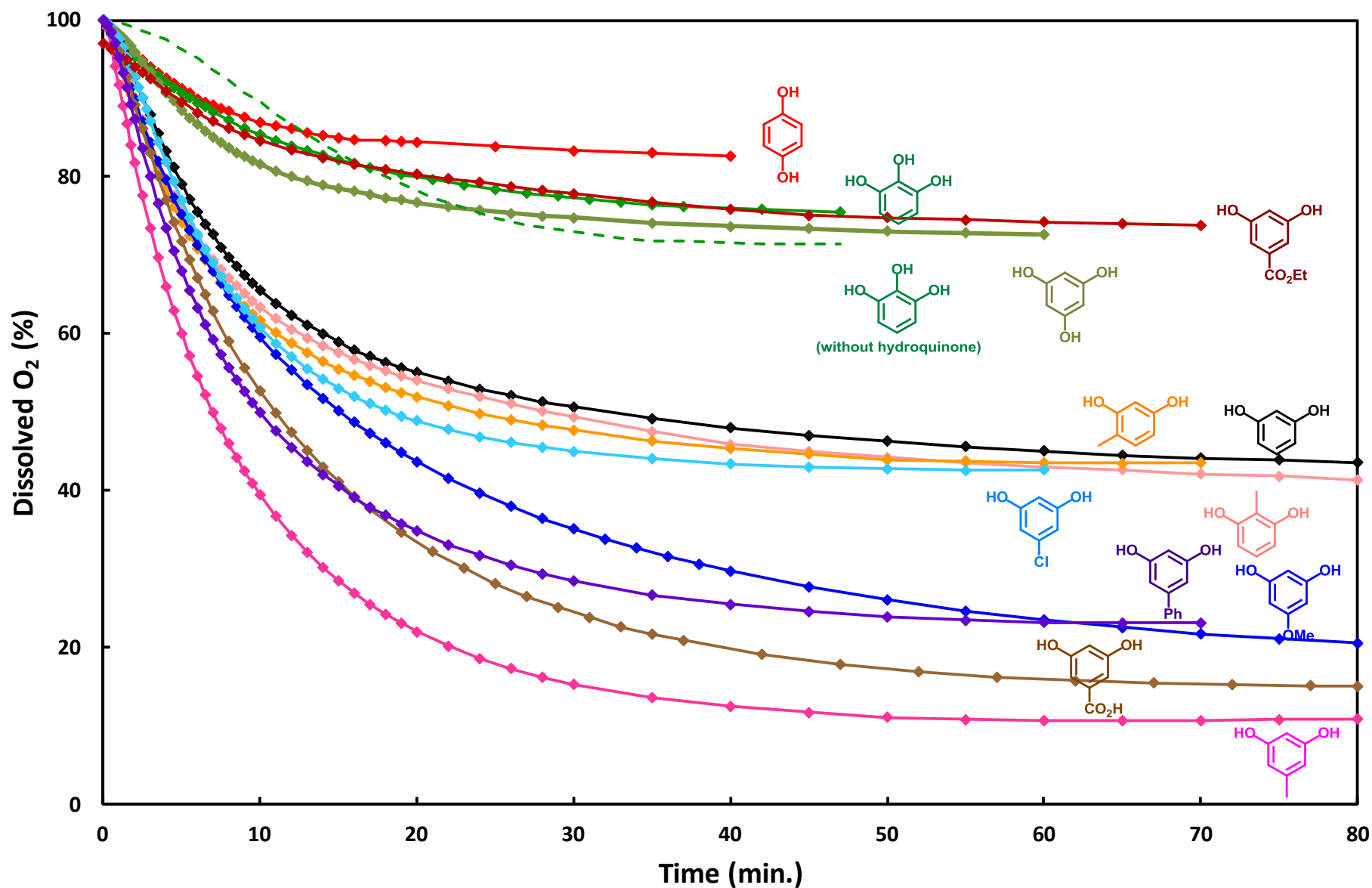




Dioxygen reduction by DEHA in water in the presence of several catalysts, alone or pairwise in 1:1 ratio.  
Conditions:  $[O_2]_0 \approx 0.28$  mM,  $[DEHA]_0 = 0.84$  mM,  $[catalyst] = 16$   $\mu$ M,  $[NaHCO_3] = 10$  mM,  $[Na_2CO_3] = 16$  mM, 25 °C.



Dioxygen reduction by DEHA in water in the presence of hydroquinone and several resorcinol derivatives as co-catalysts  
Conditions:  $[O_2]_0 \approx 0.28$  mM,  $[DEHA]_0 = 0.84$  mM,  $[\text{hydroquinone}] = 1$   $\mu\text{M}$ ,  $[\text{co-catalysts}] = 1$   $\mu\text{M}$ ,  $[\text{NaHCO}_3] = 10$  mM,  $[\text{Na}_2\text{CO}_3] = 16$  mM, 25 °C.



Dioxygen reduction by DEHA in water in the presence of several catalysts, with or without orcinol.  
Conditions:  $[O_2]_0 \approx 0.28$  mM,  $[DEHA]_0 = 0.84$  mM,  $[catalyst] = 1$   $\mu$ M,  $[orcinol] = 1$   $\mu$ M,  
 $[NaHCO_3] = 10$  mM,  $[Na_2CO_3] = 16$  mM, 25 °C.

