

# *Supporting Information*

## **Conversion of Simple Cyclohexanones into Catechols**

Yu-Feng Liang,<sup>†,§</sup> Xinyao Li,<sup>†,§</sup> Xiaoyang Wang,<sup>†</sup> Miancheng Zou,<sup>†</sup> Conghui Tang,<sup>†</sup> Yujie Liang,<sup>†</sup>  
Song Song,<sup>†</sup> and Ning Jiao<sup>\*,†,‡</sup>

<sup>†</sup>State Key Laboratory of Natural and Biomimetic Drugs, School of Pharmaceutical Sciences, Peking University, Xue Yuan Rd. 38, Beijing 100191, China

<sup>‡</sup>State Key Laboratory of Elemento-Organic Chemistry, Nankai University, Weijin Road 94, Tianjin 300071, China

<sup>§</sup>These authors contributed equally.

E-mail: jiaoning@pku.edu.cn

Fax: (+86)10-82805297

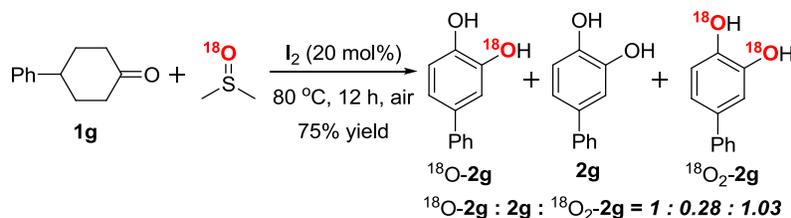
## **Table of Contents**

<b>General Remarks</b>	S2
<b>[<sup>18</sup>O]-Labeling Experiments</b>	S2
<b>Proposed Mechanism for O-Exchange of Catechol with H<sub>2</sub>O</b>	S6
<b>Reaction Result of 4-Phenyl-4-cyanocyclohexanone</b>	S6
<b>Reaction Kinetic Profile</b>	S9
<b>The Effect of Radical Inhibitors</b>	S9
<b>Experimental Section</b>	S10
<b>Analytical Data for Products</b>	S13
<b>Details of Calculation and Discussion</b>	S25
<b>References</b>	S35
<b><sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra</b>	S37

## General Remarks

I<sub>2</sub> was purchased from Sigma-Aldrich Chemical Company. DMSO, CH<sub>3</sub>NO<sub>2</sub> and other solvents were purchased from Beijing Chemical Works and used as received without further purification. Analysis of the crude reaction mixture was done on an Agilent 7890 GC System with an Agilent 5975 Mass Selective Detector. Products were purified by flash chromatography or by preparative thin-layer chromatography on silica gel. <sup>1</sup>H-NMR spectra were recorded on Bruker AVIII-400 spectrometers. Chemical shifts (in ppm) were calibrated with CDCl<sub>3</sub> (tetramethylsilane, δ = 0 ppm) or CD<sub>3</sub>SOCD<sub>3</sub> (dimethyl sulfoxide, δ = 2.50 ppm). <sup>13</sup>C-NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl<sub>3</sub> (δ = 77.00 ppm) or CD<sub>3</sub>SOCD<sub>3</sub> (dimethyl sulfoxide, δ = 39.50 ppm). Mass spectra were recorded using a PE SCLEX QSTAR spectrometer. High resolution mass spectra were obtained with a Bruker APEX IV Fourier transform ion cyclotron resonance mass spectrometer using electrospray ionization (ESI). Fourier-transform infrared (FTIR) spectra were obtained with a Nicolet Nexus 470 Fourier transform infrared spectrometer.

## [<sup>18</sup>O]-Labeling Experiments



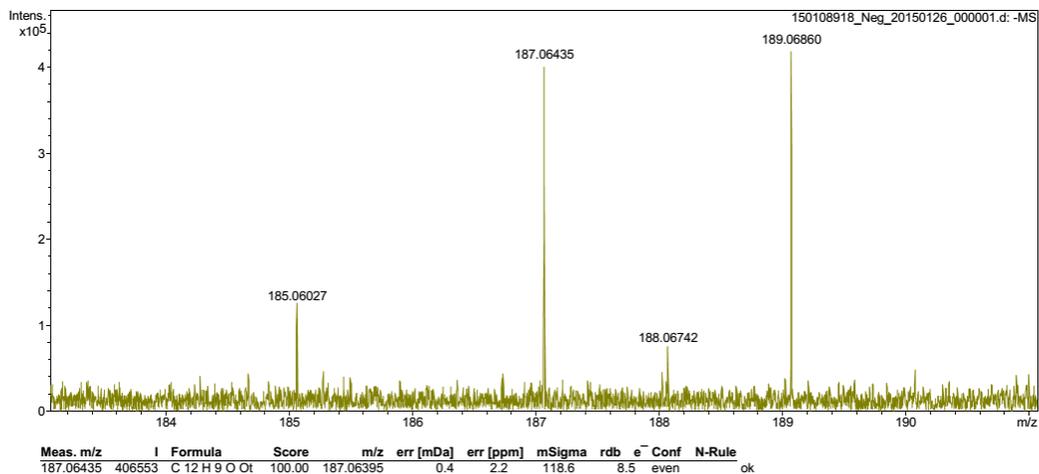
Reaction conditions: **1g** (44 mg, 0.25 mmol), I<sub>2</sub> (13 mg, 20 mol%), [<sup>18</sup>O]-DMSO (0.5 mL) and a stir bar were added to a 20 mL reaction tube under air. The mixture was stirred at 80 °C for 12 h as monitored by TLC. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3×5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to get the desired product [<sup>18</sup>O]-**2g** (35 mg, 75% yield). The <sup>18</sup>O was determined in product **2g** by HRMS. Three products were detected on the base of HRMS analysis: <sup>18</sup>O-**2g**, **2g** and <sup>18</sup>O<sub>2</sub>-**2g**, with the ratio 1:0.28:1.03. **2g**: HRMS *m/z* (ESI) calcd. for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub> (M - H)<sup>-</sup> 185.0608, found 185.0603. <sup>18</sup>O-**2g**: HRMS *m/z* (ESI) calcd. for C<sub>12</sub>H<sub>9</sub>O<sup>18</sup>O (M - H)<sup>-</sup> 187.0640, found 187.0644. <sup>18</sup>O<sub>2</sub>-**2g**: HRMS *m/z* (ESI) calcd. for C<sub>12</sub>H<sub>9</sub><sup>18</sup>O<sub>2</sub> (M - H)<sup>-</sup> 189.0693, found 189.0686.

Peking University Mass Spectrometry Sample Analysis Report

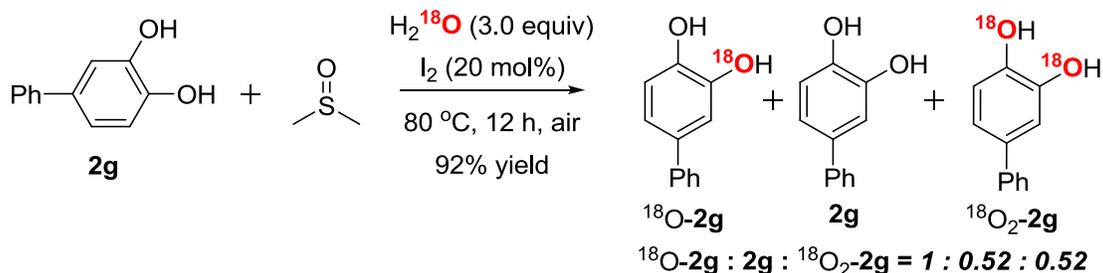
Analysis Info

Analysis Name 150108918\_Neg\_20150126\_000001.d  
 Sample lyf-11-8  
 Comment ESI Negative

Acquisition Date 1/26/2015 9:27:57 AM  
 Instrument Bruker Apex IV FTMS  
 Operator Peking University



When 3.0 equiv of H<sub>2</sub><sup>18</sup>O was added into the reaction of **2g** under the standard conditions, the three products could also be isolated with the ratio 1:0.52:0.52 on the base of HRMS analysis (see below).



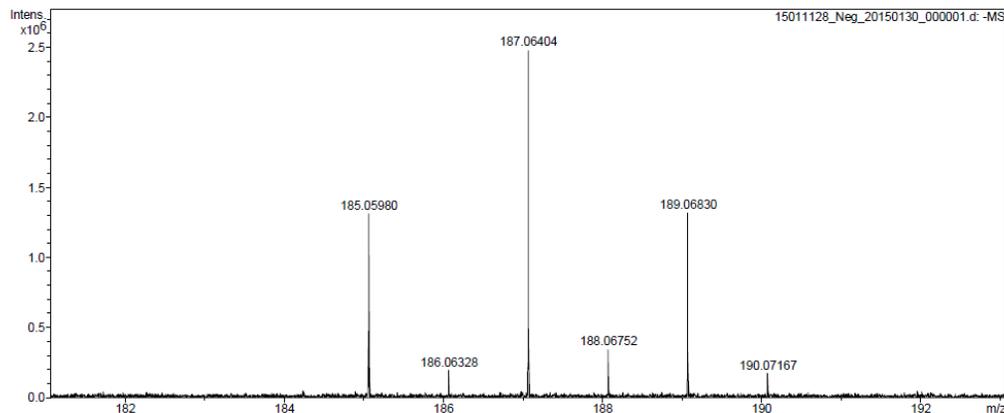
Reaction conditions: **2g** (47 mg, 0.25 mmol), I<sub>2</sub> (13 mg, 20 mol%), DMSO (0.5 mL), H<sub>2</sub><sup>18</sup>O (15 mg, 3.0 equiv) and a stir bar were added to a 20 mL reaction tube under air. The mixture was stirred at 80 °C for 12 h as monitored by TLC. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL), washed with water (5 mL), extracted with ethyl acetate (3×5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to get the product [<sup>18</sup>O]-**2g** (43 mg, 92% yield). The <sup>18</sup>O was determined in product **2g** by HRMS. Three products were detected on the base of HRMS analysis: <sup>18</sup>O-**2g**, **2g** and <sup>18</sup>O<sub>2</sub>-**2g**, with the ratio 1:0.52:0.52.

Peking University Mass Spectrometry Sample Analysis Report

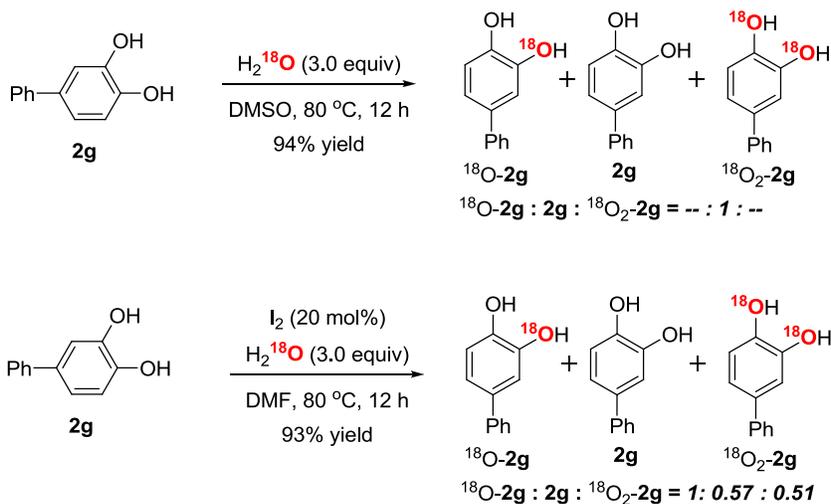
Analysis Info

Analysis Name 15011128\_Neg\_20150130\_000001.d  
 Sample lyf-11-9-2  
 Comment ESI Negative

Acquisition Date 1/30/2015 3:14:58 PM  
 Instrument Bruker Apex IV FTMS  
 Operator Peking University



Meas. m/z	I	Formula	Score	m/z	err [mDa]	err [ppm]	mSigma	rdb	e <sup>-</sup> Conf	N-Rule
185.05980	1315840	C 12 H 9 O 2	100.00	185.05971	0.1	0.5	5.7	8.5	even	ok
187.06404	2490848	C 12 H 9 O O t	100.00	187.06395	0.1	0.5	5.7	8.5	even	ok
189.06830	1326126	C 12 H 9 O t 2	100.00	189.06820	0.1	0.5	5.7	8.5	even	ok



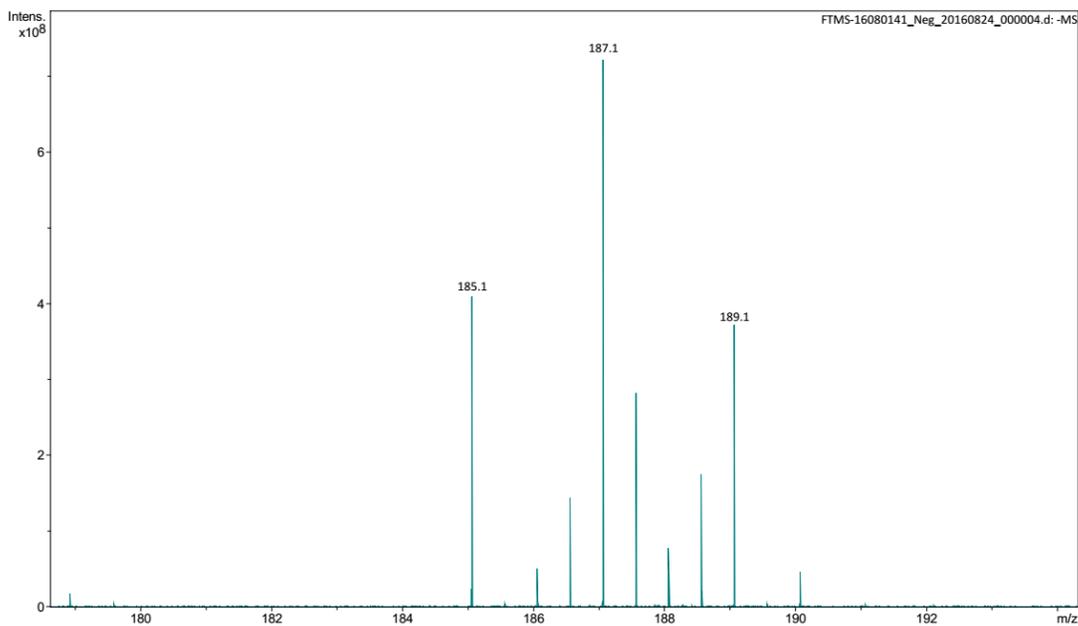
Moreover, there was no O-isotope exchange without I<sub>2</sub> catalyst, indicating that the O-isotope exchange between catechol and H<sub>2</sub>O should be completed in the presence of I<sub>2</sub> catalyst. In addition, the O-isotope exchange experiment in DMF solvent could also occur smoothly. The products  $^{18}\text{O}$ -2g, 2g and  $^{18}\text{O}_2$ -2g were detected, with the ratio 1:0.57:0.51, almost the same with in DMSO solvent (1:0.52:0.52), which indicated that DMSO is not required for the O-isotope exchange.

## Peking University Mass Spectrometry Analysis Report

### Analysis Info

Analysis Name FTMS-16080141\_Neg\_20160824\_000004.d  
 Sample lxy-9-128  
 Comment

Acquisition Date 8/24/2016 11:28:17 AM  
 Instrument Bruker Solarix XR FTMS  
 Operator Peking University

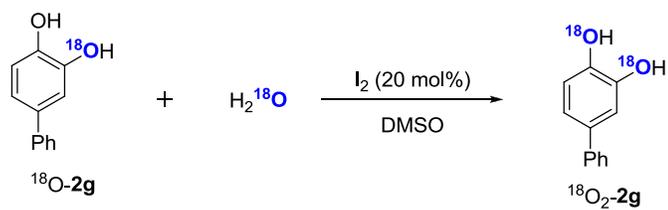
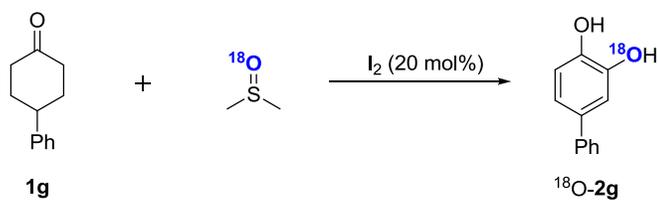


Bruker Compass DataAnalysis 4.4

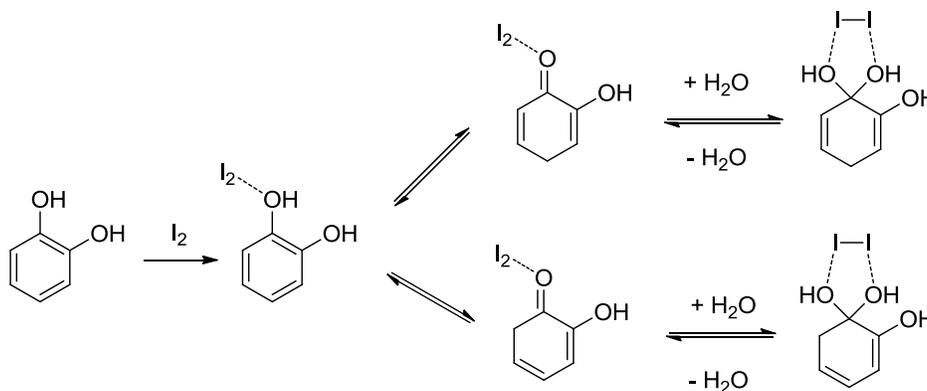
printed: 8/24/2016 11:29:04 AM

Page 1 of 1

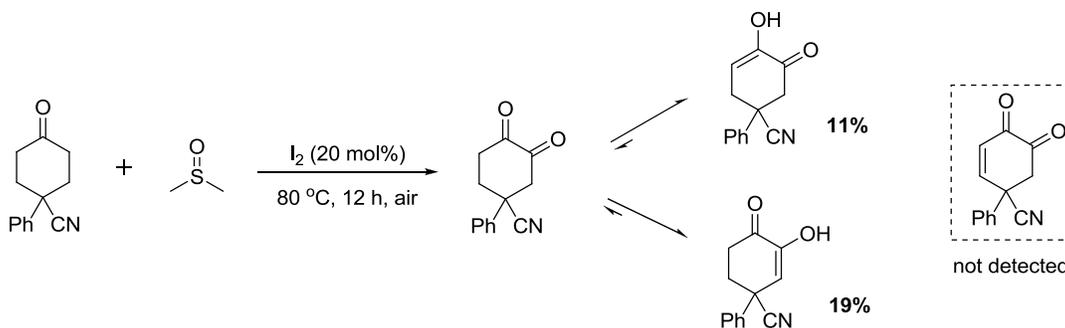
The above  $^{18}\text{O}$ -labeling experiments suggest that the additional oxygen atom in catechol product is original form DMSO, and the O-isotope exchange products are probably generated from exchange with  $\text{H}_2^{18}\text{O}$ , which was the byproduct in the  $^{18}\text{O}$ -DMSO oxidative regeneration of iodine catalyst.



## Proposed Mechanism for O-Exchange of Catechol with H<sub>2</sub>O

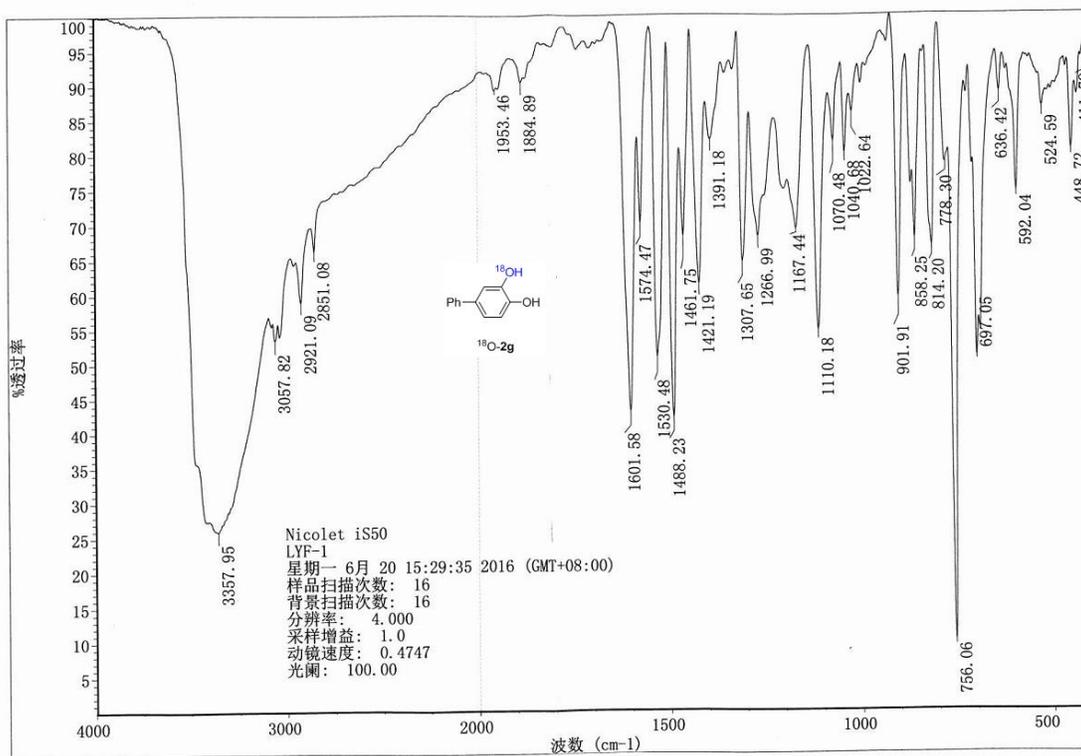
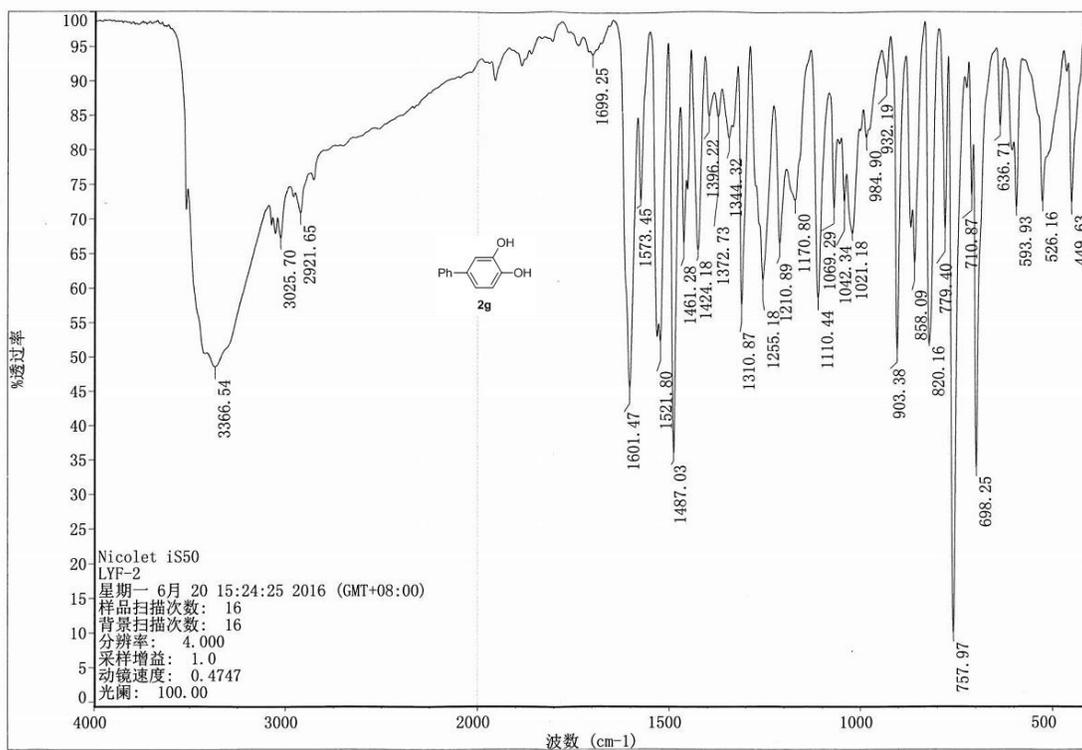


## Reaction Result of 4-Phenyl-4-cyanocyclohexanone

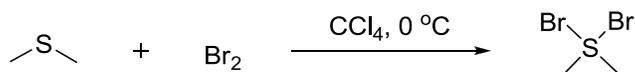


To gain additional insight into the scope and the mechanism of the present catalytic system, the reaction of 4-phenyl-4-cyanocyclohexanone under our standard conditions was investigated. The reaction afforded 30% yield of corresponding cyclohexane-1,2-dione product, which converted to the corresponding enol. This result further demonstrated that the corresponding cyclohexane-1,2-dione is a key intermediate for the catechol formation. The further iodization and HI elimination product, 4,5-dioxo-1-phenylcyclohex-2-enecarbonitrile, was not detected in the reaction, probably because of the easy decomposition character under the standard conditions.

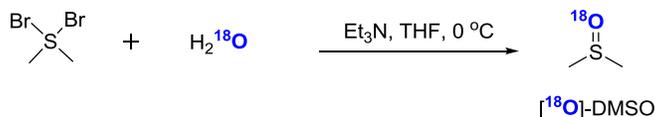
We also have done well to compare the IR spectra of the parent and the  $^{18}\text{O}$ -catechol from the labeling experiment. However, we didn't find any difference between the parent and the  $^{18}\text{O}$ -catechol in IR spectra.



## Preparation of [<sup>18</sup>O]-DMSO

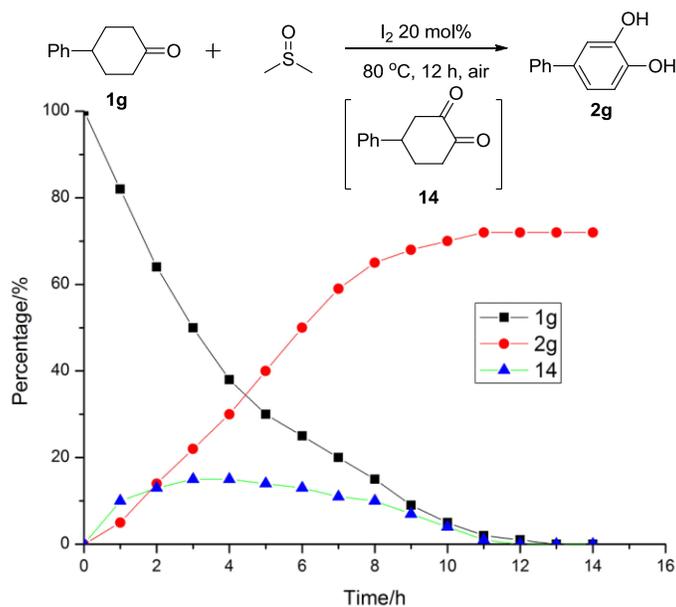


Preparation of dimethylsulfur dibromide:<sup>1</sup> Bromine (7.2 ml, 132 mmol) was added dropwise over 40 min to a vigorously stirred, ice-cooled solution of dimethyl sulfide (9.68 ml, 132 mmol) in carbon tetrachloride (120 ml). After being stirred for 2 h, the resulting yellowish orange crystals were removed by filtration and washed with cold carbon tetrachloride. After drying *in vacuo*, 27.2 g of dimethylsulfur dibromide was obtained. Recrystallization from carbon tetrachloride gave dimethylsulfur dibromide as yellow solid.



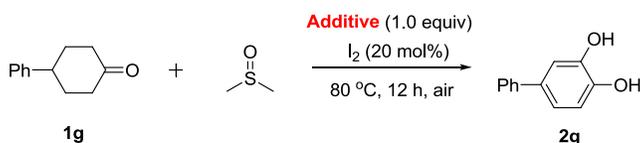
Preparation of [<sup>18</sup>O]-DMSO:<sup>1,2</sup> Solid dimethylsulfur dibromide (20.0 g, 90 mmol) was added portionwise over 15 min to a vigorously stirred solution of triethylamine (25.2 mL, 180 mmol, freshly distilled from sodium hydroxide) and <sup>18</sup>O-labeled water (97 atom % <sup>18</sup>O) (0.80 mL, 44 mmol) in 60 mL of tetrahydrofuran (freshly distilled from sodium metal). The temperature of the reaction was maintained at 0 °C by occasional cooling in ice. The precipitate of triethylamine hydrobromide was removed by centrifugation and washed twice with ether. The combined yellow supernatant and washings were dried on high vacuum pressure pump at room temperature (15 mm) to remove the solvent giving rise to 1.6 g of a brownish black liquid.

## Reaction Kinetic Profile

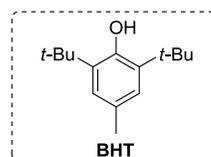
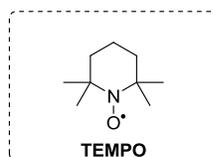
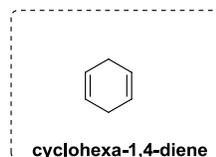
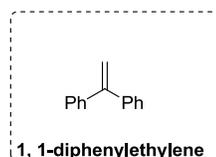


Reaction conditions: **1g** (0.5 mmol),  $\text{I}_2$  (20 mol %), DMSO (1 mL), under air, at 80 °C for the indicated time. All the reactions for different reaction time were set up independently. The yields of **1g** and 1,2-cyclohexanedione intermediate **14** were determined by GC-MS with diphenyl as internal standard, and the product **2g** was isolated by column to give isolated yield because **2g** could not be detected by GC-MS for its easy decomposition in detector.

## The Effect of Radical Inhibitors<sup>a</sup>



Additive	Yield of <b>2g</b> <sup>[b]</sup>
none	72%
1, 1-diphenylethylene	72%
cyclohexa-1,4-diene	74%
TEMPO	41%
BHT	37%

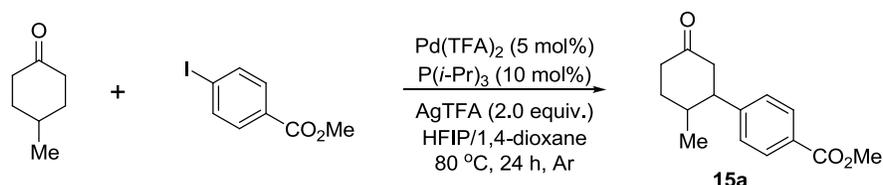


<sup>a</sup> Reaction conditions: **1g** (0.5 mmol), Additive (1.0 equiv),  $\text{I}_2$  (20 mol%), DMSO (1 mL) was stirred at 80 °C for 12 h. <sup>b</sup> Isolated yields.

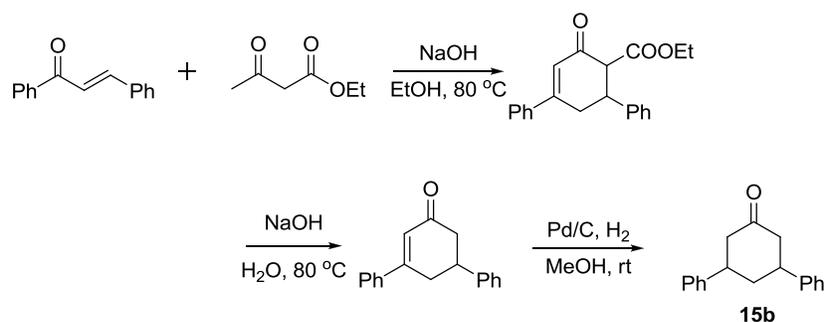
The reactions performed smoothly in the presence of 1,1-diphenylethylene, cyclohexa-1,4-diene, TEMPO and BHT, producing the desired product **2g** in 72%, 74%, 41% and 37% yield respectively, which indicate that a radical process might not be involved in the present reaction system.

## Experimental Section

### 1) Preparation of Multi-substituted Cyclohexanones

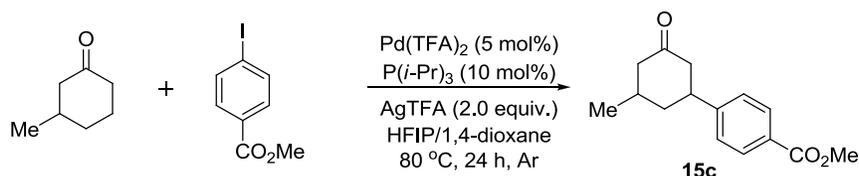


Substrates methyl 4-(2-methyl-5-oxocyclohexyl)benzoate **15a** was prepared according to the literature<sup>3</sup>: A flame-dried 50 mL Schlenk flask was charged with methyl 4-iodobenzoate (1.57 g, 6.0 mmol), 4-methylcyclohexanone (1.84 mL, 15 mmol), Pd(TFA)<sub>2</sub> (100 mg, 0.30 mmol) and AgTFA (2.65 g, 12 mmol). The flask was then transferred to glove-box under N<sub>2</sub>. 7.5 mL of HFIP and 1,4-dioxane were added to the flask (15 mL solvent in total, 0.4 M concentration). P(*i*-Pr)<sub>3</sub> (114 μL, 0.60 mmol) was then added to the mixture. The flask was sealed with a rubber cap and heated in an oil bath at 80 °C for 24 hours under stirring. The mixture was then allowed to cool to room temperature and passed through a small plug of silica gel, eluted with diethyl ether. The solvent was removed *in vacuo* and flash column chromatography of the residue afforded the product **15a** as a white solid.

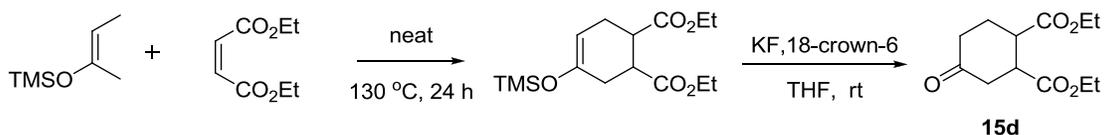


Substrates 3,5-diphenylcyclohexanone **15b** was prepared according to the literature<sup>4</sup>: To a 100 mL three-necked, round-bottomed flask was added chalcone (10 mmol), ethyl acetoacetate (12 mmol, 1.2 equiv), NaOH (0.29 g), and anhydrous ethanol (10 ml). The reaction was heated in an oil bath to reflux with vigorous stirring for an appropriate time until TLC indicated complete disappearance of the starting material (2-5 h). Then 80 ml

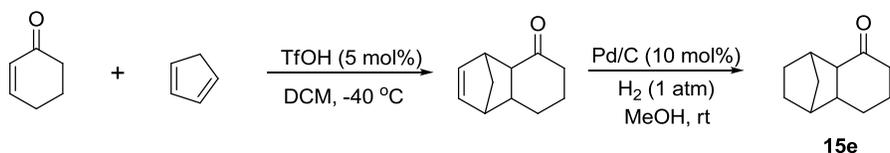
water was added. And Then NaOH (1.44 g) was following added and continued to reflux (2-5 h). After cooling a period of time, the solution was washed with saturated aqueous NaHCO<sub>3</sub> solution to neutral, dried. The crude product was purified by flash column chromatography to yield 3,5-diphenylcyclohexenone. And then 3,5-diphenylcyclohexenone (5 mmol) was placed in a 50 ml flask and immersed in 30 ml methanol, followed by Pd/C (10% wt). The reaction mixture was stirred at ambient temperature with hydrogen at atmospheric pressure (using hydrogen filled balloons). On completion, the reaction mixture was filtered. The solvent was removed in vacuo and the crude product was purified by silica gel chromatography to afford **15b** as a white solid.



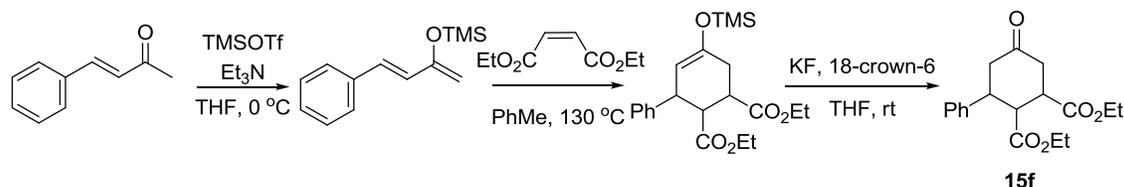
Substrates methyl 4-(3-methyl-5-oxocyclohexyl)benzoate **15c** was prepared according to the literature<sup>3</sup>: A flame-dried 50 mL Schlenk flask was charged with methyl 4-iodobenzoate (1.57 g, 6.0 mmol), 3-methylcyclohexanone (1.84 mL, 15 mmol), Pd(TFA)<sub>2</sub> (100 mg, 0.30 mmol) and AgTFA (2.65 g, 12 mmol). The flask was then transferred to glove-box under N<sub>2</sub>. 7.5 mL of HFIP and 1,4-dioxane were added to the flask (15 mL solvent in total, 0.4 M concentration). P(*i*-Pr)<sub>3</sub> (114 μL, 0.60 mmol) was then added to the mixture. The flask was sealed with a rubber cap and heated in an oil bath at 80 °C for 24 hours under stirring. The mixture was then allowed to cool to room temperature and passed through a small plug of silica gel, eluted with diethyl ether. The solvent was removed *in vacuo* and flash column chromatography of the residue afforded the product **15c** as a white solid.



Substrates diethyl 4-oxocyclohexane-1,2-dicarboxylate **15d** was prepared according to the literature<sup>5</sup>: 2-Trimethylsilyloxy-1,3-butadiene (9.35 g, 66 mmol) and diethyl fumarate (5.67 g, 33 mmol) were heated neat at 130 °C for 24 h. Direct short-path distillation afforded the adduct diethyl 4-(trimethylsilyloxy)cyclohex-4-ene-1,2-dicarboxylate as a colorless oil. Hydrolysis of diethyl 4-(trimethylsilyloxy)cyclohex-4-ene-1,2-dicarboxylate occurred in 5 h at 25 °C using potassium fluoride dihydrate (2.0 equiv.) and 18-crown-6 (1.0 equiv.) in THF to afford **15d** as a colorless oil.

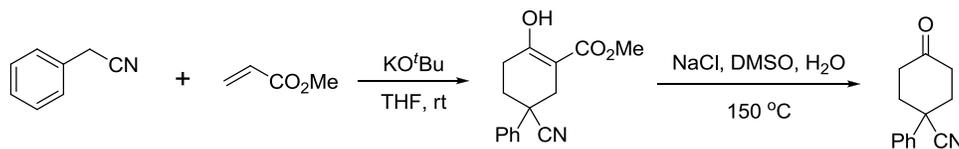


Substrate 1,4-methanonaphthalen-5-(1*H*)-one **15e** was prepared according to the literature<sup>6</sup>: To a solution of triflic anhydride (0.1M in CH<sub>2</sub>Cl<sub>2</sub>, 0.0275 equiv) and CH<sub>2</sub>Cl<sub>2</sub>, a solution of H<sub>2</sub>O (0.5M in CH<sub>2</sub>Cl<sub>2</sub>) is added. The solution is cooled to -40 °C and a solution of the 2-cyclohexene-1-one (91.2 mg, 0.949 mmol, 1.00 equiv), and cyclopentadiene (0.157 mL, 1.90 mmol, 2.00 equiv) in CH<sub>2</sub>Cl<sub>2</sub> is added dropwise. The reaction mixture is stirred for 5.5 h and subsequently quenched by the addition of saturated aqueous NaHCO<sub>3</sub> solution (2 mL). The phases are separated and the aqueous phase is extracted with diethyl ether. The combined organic phases are washed with brine and dried over anhydrous MgSO<sub>4</sub>. After evaporation of solvents under reduced pressure, the resulting residue is purified by flash column chromatography on silica gel affording 1,4-methanonaphthalen-5-(1*H*)-one. And then 1,4-methanonaphthalen-5-(1*H*)-one was placed in a 50 ml flask and immersed in 30 ml methanol, followed by Pd/C (10% wt). The reaction mixture was stirred at ambient temperature with hydrogen at atmospheric pressure (using hydrogen filled balloons). On completion, the reaction mixture was filtered. The solvent was removed in vacuo and the crude product was purified by silica gel chromatography to afford **15e** as colorless oil.



Substrates diethyl 5-oxo-3-phenylcyclohexane-1,2-dicarboxylate **15f** was prepared according to the literature<sup>5</sup>: 4-Phenylbut-3-en-2-one (730 mg 5.0 mmol) was dissolved in 12 mL of THF and triethylamine (1.9 mL, 13.2 mmol) was added. The solution was cooled to 0 °C and trimethylsilyl triflate (0.97 mL, 5.6 mmol) was added slowly. After the reaction was stirred at 0 °C for 1.5 h, 10 mL of a pH 7.0 buffer solution, and 20 mL of ether were added, and the mixture was allowed to warm to room temperature. The organic solution was washed with 3 x 10 mL of the buffer solution, and the combined aqueous layers were washed with 1 x 20 mL ether. The combined organic layers were dried over anhydrous magnesium sulfate, filtered, and evaporated in vacuo to yield trimethyl(4-phenylbuta-1,3-dien-2-yloxy)silane as a pale yellow oil. And then trimethyl(4-phenylbuta-1,3-dien-2-yloxy)silane (3 mmol) and diethyl fumarate (3 mmol) were heated in toluene (3 mL) at 130 °C for 24 h. Direct short-path distillation afforded the adduct diethyl 3-phenyl-5-(trimethylsilyloxy) cyclohex-4-ene-1,2-dicarboxylate as a colorless oil. Hydrolysis of diethyl 3-phenyl-5-(trimethylsilyloxy)cyclohex-4-ene-1,2-dicarboxylate occurred in 5 h at 25 °C using potassium fluoride dihydrate (2.0 equiv.)

and 18-crown-6 (1.0 equiv.) in THF to afford **15f** as a white solid.

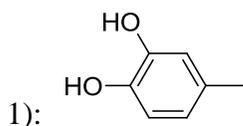


Substrates 4-phenyl-4-cyanocyclohexanone was prepared according to the literature<sup>7</sup>: To a solution of 2-phenylacetonitrile (10 mmol) and methyl acrylate (20 mmol) in THF (30 mL) was added solid *t*-BuOK (30 mmol). After being stirred for 3 h at 25 °C, the reaction mixture was acidified with aqueous 3 N HCl and extracted with EtOAc (20 mL × 3). The organic layers were combined, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided methyl 5-cyano-2-hydroxy-5-phenylcyclohex-1-enecarboxylate. And then a mixture of methyl 5-cyano-2-hydroxy-5-phenylcyclohex-1-enecarboxylate (6 mmol), NaCl (6 mmol) and DMSO/H<sub>2</sub>O (10 ml : 0.1 mL) was heated to 150 °C for 6 h. The reaction was then cooled to 25 °C and diluted with H<sub>2</sub>O and EtOAc. The aqueous layer was extracted with EtOAc (20 mL × 3) and the combined organic layers were washed with brine, dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated *in vacuo*. Purification of the crude product by flash chromatography on silica gel provided 4-phenyl-4-cyanocyclohexanone as white solid.

## 2) General Procedure

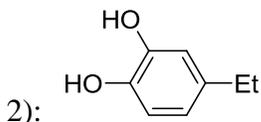
**1a** (56 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL) were added to a 25 mL tube with a magnetic bar. The mixture was stirred open to air at 80 °C for 12 h. After cooling down to room temperature, the solution was diluted with ethyl acetate (10 mL) and washed with 0.1 mol/L Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) aqueous solution, extracted with ethyl acetate (3 × 5 mL), and evaporated under vacuum. The crude reaction mixture was purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1) to get the desired catechol product **2a**.

## Analytical Data for Products

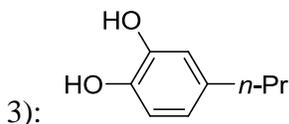


**4-Methylbenzene-1,2-diol (2a)**.<sup>8</sup> The reaction of 4-methylcyclohexanone **1a** (56 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 38 mg (62%) of **2a** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl

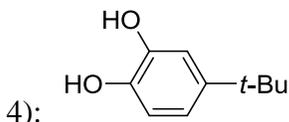
acetate = 5:1). **2a**: white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.74 (d,  $J = 8.0$  Hz, 1 H), 6.67 (s, 1 H), 6.59 (d,  $J = 8.0$  Hz, 1 H), 5.52 (brs, 1 H), 5.40 (brs, 1 H), 2.21 (s, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.1, 140.9, 131.1, 121.5, 116.2, 115.3, 20.6 ppm; MS (70 ev):  $m/z$  (%): 77.1 (70), 106.1 (60), 123.0 (100), 124.1 ( $\text{M}^+$ , 90).



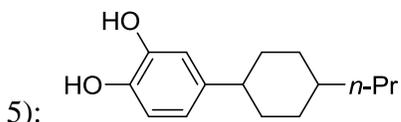
**4-Ethylbenzene-1,2-diol (2b)**.<sup>9</sup> The reaction of 4-ethylcyclohexanone **1b** (63 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 45 mg (65%) of **2b** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2b**: white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  8.65 (brs, 1 H), 8.55 (brs, 1 H), 6.62 (d,  $J = 8.0$  Hz, 1 H), 6.57 (d,  $J = 2.0$  Hz, 1 H), 6.42 (dd,  $J = 2.0, 8.0$  Hz, 1 H), 2.41 (d,  $J = 7.6$  Hz, 2 H), 1.09 (t,  $J = 7.6$  Hz, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CD}_3\text{SOCD}_3$ ):  $\delta$  145.0, 143.0, 134.6, 118.2, 115.4, 115.1, 27.5, 15.9 ppm; MS (70 ev):  $m/z$  (%): 77.0 (60), 122.9 (100), 138.1 ( $\text{M}^+$ , 80).



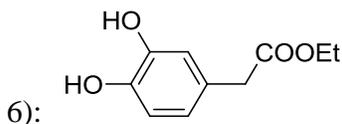
**4-Propylbenzene-1,2-diol (2c)**.<sup>10</sup> The reaction of 4-propylcyclohexanone **1c** (70 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 46 mg (60%) of **2c** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2c**: white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.68 (d,  $J = 8.0$  Hz, 1 H), 6.61 (d,  $J = 1.6$  Hz, 1 H), 6.52 (dd,  $J = 1.6, 8.0$  Hz, 1 H), 5.50 (brs, 1 H), 5.40 (brs, 1 H), 2.37 (t,  $J = 7.2$  Hz, 2 H), 1.53-1.44 (m, 2 H), 0.82 (t,  $J = 7.2$  Hz, 3 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  143.2, 141.4, 136.0, 120.9, 115.6, 115.2, 37.2, 24.5, 13.6 ppm; MS (70 ev):  $m/z$  (%): 55.1 (100), 123.1 (75), 152.1 ( $\text{M}^+$ , 20).



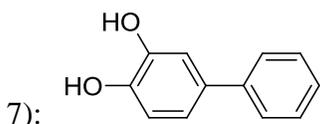
**4-Tert-butylbenzene-1,2-diol (2d)**.<sup>8</sup> The reaction of 4-*tert*-butylcyclohexanone **1d** (78 mg, 0.5 mmol),  $\text{I}_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 48 mg (58%) of **2d** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2d**: white solid;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  6.91 (d,  $J = 2.0$  Hz, 1 H), 6.83-6.77 (m, 2 H), 5.21 (brs, 1 H), 5.14 (brs, 1 H), 1.25 (s, 9 H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.8, 142.9, 140.8, 117.7, 114.9, 113.0, 34.1, 31.4 ppm; MS (70 ev):  $m/z$  (%): 77.1 (50), 123.0 (70), 150.9 (100), 166.1 ( $\text{M}^+$ , 70).



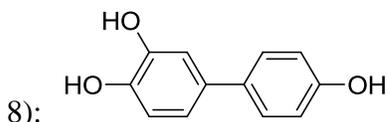
**4-(4-Propylcyclohexyl)benzene-1,2-diol (2e).** The reaction of 4'-propylbi(cyclohexan)-4-one **1e** (112 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 50 mg (43%) of **2e** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2e**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 8.63 (brs, 1 H), 8.56 (brs, 1 H), 6.61 (d, *J* = 8.0 Hz, 1 H), 6.57 (d, *J* = 2.0 Hz, 1 H), 6.43 (dd, *J* = 2.0, 8.0 Hz, 1 H), 2.27-2.17 (m, 1 H), 1.78-1.72 (m, 4 H), 1.35-1.26 (m, 5 H), 1.19-1.13 (m, 2 H), 1.02-0.96 (m, 2 H), 0.86 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 144.9, 143.1, 138.4, 117.0, 115.3, 114.0, 43.2, 39.3, 36.5, 34.2, 33.2, 19.5, 14.3 ppm; HRMS *m/z* (ESI) calcd for C<sub>15</sub>H<sub>23</sub>O<sub>2</sub> (M + H)<sup>+</sup>, 235.1693, found 235.1691.



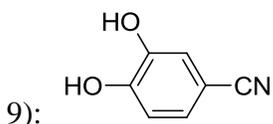
**Ethyl 2-(3,4-dihydroxyphenyl)acetate (2f).**<sup>11</sup> The reaction of ethyl 2-(4-oxocyclohexyl)acetate **1f** (93 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 40 mg (41%) of **2f** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2f**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.75-6.72 (m, 2 H), 6.64 (d, *J* = 8.4 Hz, 1 H), 6.23 (brs, 1 H), 5.98 (brs, 1 H), 4.16 (q, *J* = 7.2 Hz, 2 H), 3.49 (s, 2 H), 1.26 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 173.1, 143.7, 143.0, 126.1, 121.6, 116.2, 115.3, 61.2, 40.6, 14.0 ppm; HRMS *m/z* (ESI) calcd for C<sub>10</sub>H<sub>13</sub>O<sub>4</sub> (M + H)<sup>+</sup>, 197.0808, found 197.0809.



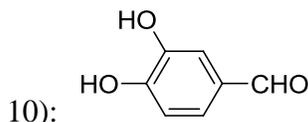
**Biphenyl-3,4-diol (2g).**<sup>8</sup> The reaction of 4-phenylcyclohexanone **1g** (88 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 69 mg (74%) of **2g** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2g**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.06 (brs, 1 H), 9.04 (brs, 1 H), 7.51 (d, *J* = 7.6 Hz, 2 H), 7.38 (t, *J* = 7.6 Hz, 2 H), 7.25 (t, *J* = 7.2 Hz, 1 H), 7.04 (d, *J* = 2.0 Hz, 1 H), 6.93 (dd, *J* = 2.0, 8.0 Hz, 1 H), 6.82 (d, *J* = 8.4 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 145.6, 145.2, 140.4, 131.6, 128.8, 126.3, 125.9, 117.6, 116.0, 113.9 ppm; HRMS *m/z* (ESI) calcd for C<sub>12</sub>H<sub>9</sub>O<sub>2</sub> (M - H)<sup>-</sup>, 185.0597, found 185.0506.



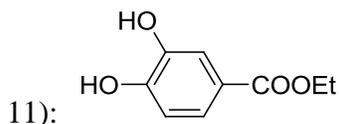
**Biphenyl-3,4,4'-triol (2h).**<sup>12</sup> The reaction of 4-(4-hydroxyphenyl)cyclohexanone **1h** (95 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 74 mg (73%) of **2h** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2h**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.37 (brs, 1 H), 8.91 (brs, 1 H), 8.88 (brs, 1 H), 7.33 (d, *J* = 8.8 Hz, 2 H), 6.96 (d, *J* = 1.2 Hz, 1 H), 6.84-6.77 (m, 4 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 156.2, 145.5, 144.3, 131.9, 131.5, 127.0, 117.0, 116.1, 115.6, 113.5 ppm; HRMS *m/z* (ESI) calcd for C<sub>12</sub>H<sub>11</sub>O<sub>3</sub> (M + H)<sup>+</sup>, 203.0703, found 203.0701.



**3,4-Dihydroxybenzonitrile (2i).**<sup>8</sup> The reaction of 4-oxocyclohexanecarbonitrile **1i** (62 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 58 mg (86%) of **2i** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 3:1). **2i**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 10.16 (brs, 1 H), 9.71 (brs, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 7.06 (s, 1 H), 6.85 (d, *J* = 8.0 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 150.6, 145.9, 124.9, 119.7, 118.4, 116.4, 110.9; MS (70 ev): *m/z* (%): 52.1 (70), 89.1 (70), 135.0 (M<sup>+</sup>, 100).

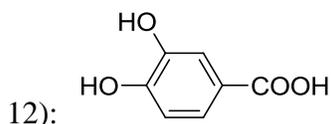


**3,4-Dihydroxybenzaldehyde (2j).**<sup>8</sup> The reaction of 4-oxocyclohexanecarbaldehyde **1j** (63 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 56 mg (81%) of **2j** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2j**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 10.11 (brs, 1 H), 9.69 (s, 1 H), 9.55 (brs, 1 H), 7.26 (dd, *J* = 1.6, 8.0 Hz, 1 H), 7.23 (d, *J* = 2.0 Hz, 1 H), 6.90 (d, *J* = 8.0 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 191.1, 152.1, 145.9, 128.8, 124.5, 115.5, 114.3 ppm; MS (70 ev): *m/z* (%): 81.1 (70), 109.1 (80), 137.1 (100), 138.1 (M<sup>+</sup>, 95).

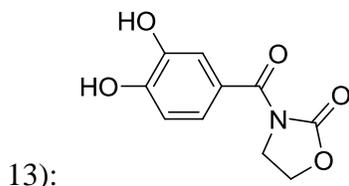


**Ethyl 3,4-dihydroxybenzoate (2k).**<sup>8</sup> The reaction of ethyl 4-oxocyclohexanecarboxylate

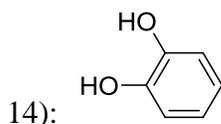
**1k** (85 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 76 mg (84%) of **2k** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2k**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.74 (brs, 1 H), 9.33 (brs, 1 H), 7.36 (d, *J* = 2.0 Hz, 1 H), 7.31 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 1.27 (d, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 165.6, 150.3, 145.0, 121.7, 120.8, 116.2, 115.2, 59.9, 14.2 ppm; HRMS *m/z* (ESI) calcd for C<sub>9</sub>H<sub>11</sub>O<sub>4</sub> (M + H)<sup>+</sup>, 183.0652, found 183.0652.



**Ethyl 3,4-dihydroxybenzoate (2l)**.<sup>10</sup> The reaction of 4-oxocyclohexanecarboxylic acid **1l** (71 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 65 mg (84%) of **2l** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2l**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 12.29 (brs, 1 H), 9.64 (brs, 1 H), 9.27 (brs, 1 H), 7.34 (d, *J* = 2.0 Hz, 1 H), 7.30 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 167.4, 150.0, 144.9, 122.0, 121.7, 116.6, 115.2 ppm; HRMS *m/z* (ESI) calcd for C<sub>7</sub>H<sub>7</sub>O<sub>4</sub> (M + H)<sup>+</sup>, 155.0339, found 155.0338.

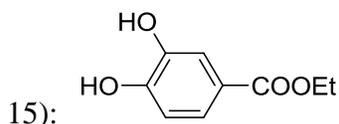


**3-(3,4-Dihydroxybenzoyl)oxazolidin-2-one (2m)**. The reaction of 3-(4-oxocyclohexanecarbonyl)oxazolidin-2-one **1m** (106 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 79 mg (71%) of **2a** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 3:1). **2a**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.49 (brs, 2 H), 7.07 (d, *J* = 2.0 Hz, 1 H), 7.04 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.75 (d, *J* = 8.0 Hz, 1 H), 4.40 (t, *J* = 7.6 Hz, 2 H), 3.99 (d, *J* = 7.6 Hz, 2 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 168.6, 153.5, 149.7, 144.3, 123.8, 122.1, 116.8, 114.5, 62.5, 43.9 ppm; HRMS *m/z* (ESI) calcd for C<sub>10</sub>H<sub>9</sub>NNaO<sub>5</sub> (M + Na)<sup>+</sup>, 246.0373, found 246.0372.

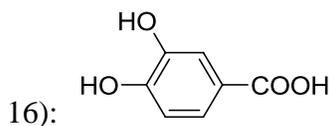


**Catechol (2n)**.<sup>8</sup> The reaction of 4-hydroxycyclohexanone **1n** (57 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 35 mg (63%) of **2n** purified

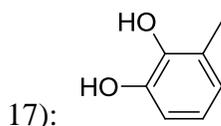
by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). The reaction of 4-methoxycyclohexanone **1o** (65 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 35 mg (63%) of **2a**. The reaction of 4-oxocyclohexyl pivalate **1p** (100 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 50 mg (91%) of **2a**. **2a**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 8.78 (s, 2 H), 6.73-6.70 (m, 2 H), 6.60-6.57 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 145.3, 119.2, 115.7 ppm.



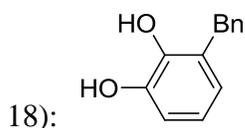
**Ethyl 3,4-dihydroxybenzoate (2k)**.<sup>8</sup> The reaction of ethyl 3-oxocyclohexanecarboxylate **1q** (85 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 48 mg (53%) of **2k** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2k**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.74 (brs, 1 H), 9.33 (brs, 1 H), 7.36 (d, *J* = 2.0 Hz, 1 H), 7.31 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.80 (d, *J* = 8.4 Hz, 1 H), 4.21 (q, *J* = 7.2 Hz, 2 H), 1.27 (d, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 165.6, 150.3, 145.0, 121.7, 120.8, 116.2, 115.2, 59.9, 14.2 ppm.



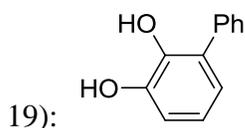
**Ethyl 3,4-dihydroxybenzoate (2l)**.<sup>10</sup> The reaction of 3-oxocyclohexanecarboxylic acid **1r** (71 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 49 mg (63%) of **2l** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2l**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 12.29 (brs, 1 H), 9.64 (brs, 1 H), 9.27 (brs, 1 H), 7.34 (d, *J* = 2.0 Hz, 1 H), 7.30 (dd, *J* = 2.0, 8.4 Hz, 1 H), 6.79 (d, *J* = 8.4 Hz, 1 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 167.4, 150.0, 144.9, 122.0, 121.7, 116.6, 115.2 ppm.



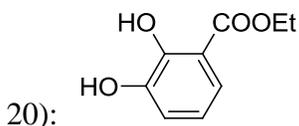
**3-Methylbenzene-1,2-diol (2s)**.<sup>8</sup> The reaction of 2-methylcyclohexanone **1s** (56 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 10 mg (16%) of **2s** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2s**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 6.70 (s, 3 H), 5.11 (s, 2 H), 2.25 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 143.0, 142.0, 124.5, 122.9, 120.2, 112.9, 15.4 ppm; MS (70 ev): *m/z* (%): 57.2 (100), 71.2 (80), 85.2 (70), 124.2 (M<sup>+</sup>, 60).



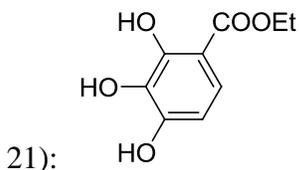
**3-Benzylbenzene-1,2-diol (2t).**<sup>13</sup> The reaction of 2-benzylcyclohexanone **1t** (95 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 21 mg (21%) of **2t** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2t**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.22 (brs, 1 H), 8.22 (brs, 1 H), 7.25-7.18 (m, 4 H), 7.13 (t, *J* = 6.8 Hz, 1 H), 6.63 (dd, *J* = 2.0, 7.6 Hz, 1 H), 6.55-6.49 (m, 2 H), 3.84 (s, 2 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 144.9, 143.0, 141.4, 128.5, 128.1, 128.0, 125.5, 120.7, 118.6, 113.3, 35.2 ppm; HRMS *m/z* (ESI) calcd for C<sub>13</sub>H<sub>12</sub>NaO<sub>2</sub> (M + Na)<sup>+</sup>, 223.0730, found 223.0729.



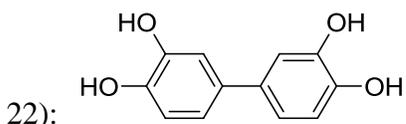
**Biphenyl-2,3-diol (2u).**<sup>14</sup> The reaction of 2-phenylcyclohexanone **1u** (88 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 21 mg (23%) of **2u** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2u**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 9.47 (brs, 1 H), 8.25 (brs, 1 H), 7.51 (d, *J* = 7.2 Hz, 2 H), 7.37 (t, *J* = 7.2 Hz, 2 H), 7.31-7.25 (m, 1 H), 6.78 (d, *J* = 6.4 Hz, 1 H), 6.70-6.67 (m, 2 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 145.5, 142.5, 138.7, 128.9, 128.3, 127.7, 126.3, 120.5, 119.1, 114.2 ppm; HRMS *m/z* (ESI) calcd for C<sub>12</sub>H<sub>11</sub>O<sub>2</sub> (M + H)<sup>+</sup>, 187.0754, found 187.0753.



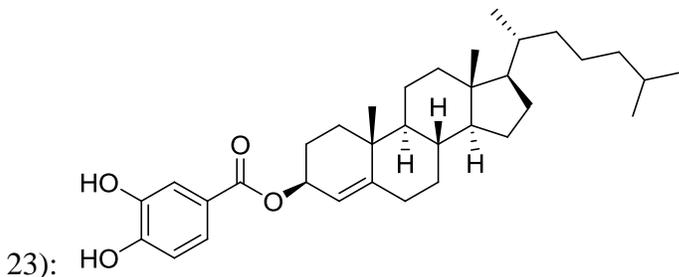
Ethyl 2,3-dihydroxybenzoate (**2v**).<sup>15</sup> The reaction of ethyl 2-oxocyclohexanecarboxylate **1v** (85 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 38 mg (62%) of **2v** and 55 mg (56%) of **2v'** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2v**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 10.99 (s, 1 H), 7.38 (dd, *J* = 1.6, 8.4 Hz, 1 H), 7.10 (dd, *J* = 1.6, 8.0 Hz, 1 H), 6.79 (t, *J* = 8.0 Hz, 1 H), 5.73 (s, 1 H), 4.41 (q, *J* = 7.2 Hz, 2 H), 1.41 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.9, 149.6, 141.5, 125.1, 120.4, 120.0, 111.2, 61.8, 14.1 ppm; MS (70 ev): *m/z* (%): 105.1 (80), 136.1 (100), 182.1 (M<sup>+</sup>, 25).



**Ethyl 2,3,4-trihydroxybenzoate (2v').**<sup>16</sup> The reaction of ethyl 2-oxocyclohexanecarboxylate **1v** (85 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 38 mg (62%) of **2v** and 55 mg (56%) of **2v'** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2v'**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 11.13 (s, 1 H), 7.36 (dd, *J* = 0.8, 9.2 Hz, 1 H), 6.51 (d, *J* = 9.2 Hz, 1 H), 6.05 (brs, 2 H), 4.38 (q, *J* = 7.2 Hz, 2 H), 1.39 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 170.2, 149.5, 149.2, 130.9, 121.9, 107.3, 105.8, 61.2, 14.1 ppm; MS (70 ev): *m/z* (%): 110.1 (20), 152.1 (100), 198.1 (M<sup>+</sup>, 30); HRMS *m/z* (ESI) calcd for C<sub>9</sub>H<sub>9</sub>O<sub>5</sub> (M - H)<sup>-</sup>, 197.0445, found 197.0453.

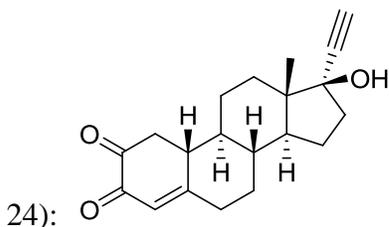


**Biphenyl-3,3',4,4'-tetraol (3).**<sup>17</sup> The reaction of bi(cyclohexane)-4,4'-dione **6** (97 mg, 0.5 mmol), I<sub>2</sub> (52 mg, 40 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 55 mg (51%) of **3** purified by column chromatography on silica gel (eluent: CHCl<sub>2</sub> / CH<sub>3</sub>OH = 20:1). **3**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 8.90 (brs, 2 H), 8.83 (brs, 2 H), 6.88 (s, 2 H), 6.77-6.72 (m, 4 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 145.3, 144.2, 132.0, 116.8, 115.9, 113.4 ppm; HRMS *m/z* (ESI) calcd for C<sub>12</sub>H<sub>11</sub>O<sub>4</sub> (M + H)<sup>+</sup>, 219.0652, found 219.0651.

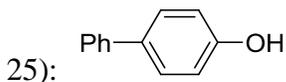


**(3S,8S,9S,10R,13R,14S,17R)-10,13-Dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 3,4-dihydroxybenzoate (8).** The reaction of (3S,8S,9S,10R,13R,14S,17R)-10,13-dimethyl-17-((R)-6-methylheptan-2-yl)-2,3,6,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-oxocyclohexanecarboxylate **7** (206 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 196 mg (75%) of **8** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **8**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.59 (brs, 1 H), 9.15 (brs, 1 H), 7.32 (s, 1 H), 7.25 (d, *J* = 6.4 Hz, 1 H), 6.73 (d, *J* = 5.2 Hz, 1 H), 5.30 (m, 1 H), 4.59 (m, 1 H), 2.33 (m, 2 H), 1.97-1.79 (m, 6 H), 1.47-0.81 (m, 31 H), 0.62 (m, 4 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 164.8, 157.1, 150.1, 144.8, 139.4, 121.6, 121.0, 116.2, 115.0, 73.1, 56.1, 55.7, 49.4, 41.7, 37.8, 36.5, 36.0, 35.8, 35.7, 35.4, 31.3, 27.7, 27.4, 25.1, 23.6, 22.4, 22.2, 20.5, 18.8, 18.4, 16.8, 11.5 ppm; HRMS *m/z* (ESI) calcd for C<sub>34</sub>H<sub>50</sub>NaO<sub>4</sub> (M

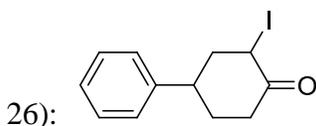
+ Na)<sup>+</sup>, 545.3601, found 545.3609.



**(8R,9S,10R,13S,14S,17R)-17-ethynyl-17-hydroxy-13-methyl-7,8,9,11,12,13,14,15,16,17-decahydro-1H-cyclopenta[a]phenanthrene-2,3(6H,10H)-dione (10)**. The reaction of norethindrone **9** (150 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 70 mg (45%) of **10** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **10**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 6.17 (s, 1 H), 5.36 (s, 1 H), 2.63-2.54 (m, 1 H), 2.46-2.31 (m, 4 H), 2.22-2.15 (m, 1 H), 2.09-2.04 (m, 1 H), 1.92-1.81 (m, 2 H), 1.76-1.55 (m, 6 H), 1.26-1.17 (m, 4 H), 0.78 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 199.8, 199.6, 155.1, 126.5, 88.6, 77.9, 75.2, 49.1, 46.4, 44.8, 44.2, 42.3, 38.5, 37.3, 37.2, 31.9, 27.6, 25.4, 22.2, 12.5 ppm; HRMS *m/z* (ESI) calcd for C<sub>20</sub>H<sub>25</sub>O<sub>3</sub> (M + H)<sup>+</sup>, 313.1798, found 313.1797.

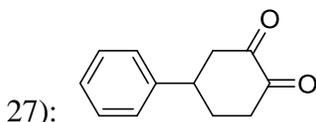


**4-Phenylphenol (12)**.<sup>18</sup> The reaction of 4-phenylcyclohex-2-enone **11** (86 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 80 mg (94%) of **12** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **12**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.53 (t, *J* = 6.8 Hz, 2 H), 7.47 (d, *J* = 8.8 Hz, 2 H), 7.41 (t, *J* = 7.2 Hz, 2 H), 7.30 (t, *J* = 7.2 Hz, 1 H), 6.90 (t, *J* = 8.8 Hz, 2 H), 4.82 (brs, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 154.9, 140.7, 134.0, 128.7, 128.3, 126.7, 115.6 ppm; MS (70 ev): *m/z* (%): 115.1 (20), 141.1 (20), 170.1 (M<sup>+</sup>, 100).

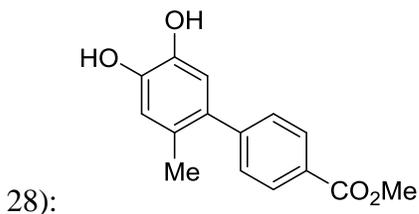


**2-Iodo-4-phenylcyclohexanone (13)**. Prepared according to the literature<sup>19</sup>: the reaction of 4-phenylcyclohexanone **1g** (1.74 g, 10 mmol), I<sub>2</sub> (1.4 g, 55 mol%), SeO<sub>2</sub> (610 mg, 55 mol%), AcOH (10 mL), at 70 °C for 3 h, afforded 630 mg (21%) of **13** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 30:1). **13**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.28-7.24 (m, 2 H), 7.19-7.15 (m, 3 H), 4.67-4.45 (m, 1 H), 3.52-3.38 (m, 2 H), 2.38-2.32 (m, 2 H), 2.19-2.06 (m, 2 H), 1.95-1.84 (m, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 204.7, 143.4, 128.7, 126.9, 126.8, 42.7, 38.6,

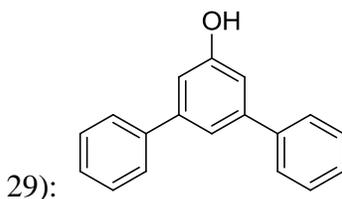
34.8, 33.4, 29.7 ppm; HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{13}INaO$  ( $M + Na$ )<sup>+</sup>, 322.9903, found 322.9898.



**4-Phenylcyclohexane-1,2-dione (14)**. The reaction of 4-phenylcyclohexanone **1g** (870 mg, 5 mmol),  $I_2$  (260 mg, 20 mol%), DMSO (10 mL), at 80 °C for 4 h, afforded 132 mg (14%) of **14** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **14**: white solid;  $^1H$  NMR (400 MHz,  $CDCl_3$ ):  $\delta$  7.36-7.21 (m, 5 H), 6.18-6.10 (m, 1.69 H), 3.88-3.70 (m, 0.54 H), 3.48-3.30 (m, 0.42 H), 2.82-2.74 (m, 0.79 H), 2.64-2.52 (m, 2.18 H), 2.35-2.29 (m, 0.70 H), 2.05-1.96 (m, 0.71 H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ ):  $\delta$  195.0, 194.5, 147.1, 147.0, 143.4, 142.6, 128.6, 127.3, 127.0, 126.9, 126.5, 121.0, 117.0, 43.0, 41.6, 41.4, 35.1, 32.9, 31.9 ppm; HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{13}O_2$  ( $M + H$ )<sup>+</sup>, 189.0910, found 189.0906; HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{12}NaO_2$  ( $M + Na$ )<sup>+</sup>, 211.0730, found 211.0727; HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{11}O_2$  ( $M - H$ )<sup>-</sup>, 187.0765, found 187.0759.

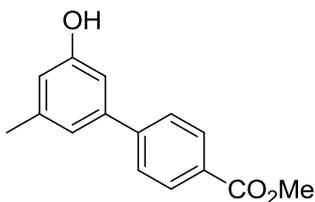


**Methyl 4',5'-dihydroxy-2'-methyl-[1,1'-biphenyl]-4-carboxylate (2w)**. The reaction of methyl 4-(2-methyl-5-oxocyclohexyl)benzoate **15a** (123 mg, 0.5 mmol),  $I_2$  (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 43 mg (33%) of **2w** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **2w**: white solid;  $^1H$  NMR: (400 MHz,  $CD_3SOCD_3$ )  $\delta$  8.98 (s, 1 H), 8.85 (s, 1 H), 7.97 (d,  $J = 8.0$  Hz, 2 H), 7.41 (d,  $J = 8.0$  Hz, 2 H), 6.69 (s, 1 H), 6.45 (s, 1 H), 3.86 (s, 3H), 2.08 (s, 3H);  $^{13}C$  NMR: (100 MHz,  $CD_3SOCD_3$ )  $\delta$  186.2, 146.6, 145.1, 143.3, 130.8, 129.4, 129.0, 127.4, 125.2, 117.8, 116.8, 52.0, 19.3; HRMS  $m/z$  (ESI) calcd for  $C_{15}H_{13}O_4$  ( $M - H$ )<sup>-</sup>, 257.0814, found 257.0813.

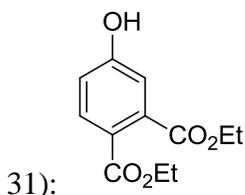


**[1,1':3',1''-Terphenyl]-5'-ol (16b)**.<sup>18</sup> The reaction of 3,5-diphenylcyclohexanone **15b**

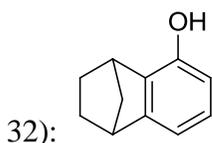
(125 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 105 mg (85%) of **16b** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **16b**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.60-7.57 (m, 4 H), 7.44-7.42 (m, 7 H), 7.03 (s, 2 H), 5.20 (s, 1 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 156.1, 143.4, 140.7, 128.8, 127.6, 127.2, 119.0, 113.1 ppm; MS (70 ev): m/z (%): 246.1 (M<sup>+</sup>, 90).



**Methyl 3'-hydroxy-5'-methyl-[1,1'-biphenyl]-4-carboxylate (16c).** The reaction of methyl 4-(3-methyl-5-oxocyclohexyl)benzoate **15c** (123 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 48 mg (40%) of **16c** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **16c**: white solid; <sup>1</sup>H NMR (400 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 8.08 (d, *J* = 8.0 Hz, 2 H), 7.62 (d, *J* = 8.0 Hz, 2 H), 7.01 (s, 1 H), 6.90 (s, 1 H), 6.70 (s, 1 H), 5.07 (s, 1 H), 3.94 (s, 3 H), 2.37 (s, 3 H); <sup>13</sup>C NMR (100 MHz, CD<sub>3</sub>SOCD<sub>3</sub>): δ 156.0, 145.4, 141.5, 140.3, 130.0, 128.9, 127.0, 120.7, 115.8, 111.4, 52.1, 21.4 ppm; MS (70 ev): m/z (%): 242.1 (M<sup>+</sup>, 80).

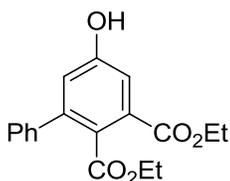


**Diethyl 4-hydroxyphthalate (16d).**<sup>20</sup> The reaction of diethyl 4-oxocyclohexane-1,2-dicarboxylate **15d** (121 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 73 mg (61%) of **16d** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 5:1). **16d**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 7.89 (s, 1 H), 7.73 (d, *J* = 8.4 Hz, 1 H), 7.02 (d, *J* = 2.8 Hz, 1 H), 6.92 (dd, *J* = 2.4 Hz, 8.8 Hz, 1 H), 4.36 (q, *J* = 7.2 Hz, 2 H), 4.31 (q, *J* = 7.2 Hz, 2 H), 1.34 (dt, *J* = 7.2 Hz, 6 H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 169.3, 167.0, 159.6, 135.8, 131.8, 121.4, 117.1, 115.3, 62.1, 61.5, 14.0, 13.9 ppm; MS (70 ev): m/z (%): 238 (100) [M<sup>+</sup>].

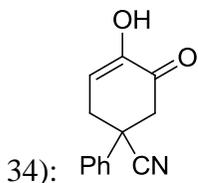


**1,4-Methanonaphthalen-5-ol (16e).** The reaction of 1,4-methanonaphthalen-5-(1*H*)-one

(83 mg, 0.3 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1 mL), at 80 °C for 12 h, afforded 20 mg (25%) of **16e** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **16e**: white solid; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 12.05 (s, 1H), 7.62 (s, 1H), 7.56 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.34 (d, *J* = 8.4 Hz, 1H), 6.79 (dd, *J* = 17.6, 10.8 Hz, 1H), 5.73 (d, *J* = 17.6 Hz, 1H), 5.25 (d, *J* = 11.2 Hz, 1H), 2.90 (t, *J* = 7.8 Hz, 2H), 2.76 (t, *J* = 7.8 Hz, 2H), 1.46-1.66 (m, 8H), 1.02 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 150.7, 148.6, 132.4, 126.8, 113.5, 113.0, 49.1, 44.0, 39.1, 27.0, 26.4; HRMS *m/z* (ESI) calcd for C<sub>11</sub>H<sub>11</sub>O [M - H]<sup>-</sup> 159.0815, found: 159.0811.

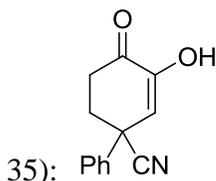


**Diethyl 5-hydroxybiphenyl-2,3-dicarboxylate (16f)**. The reaction of diethyl 5-oxo-3-phenylcyclohexane-1,2-dicarboxylate **15f** (95.4 mg, 0.3 mmol), I<sub>2</sub> (15.6 mg, 20 mol%), DMSO (0.6 mL), at 80 °C for 12 h, afforded 55.3 mg (59%) of **16f** purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1). **16f**: white solid <sup>1</sup>H NMR: (400 MHz, CDCl<sub>3</sub>) δ 7.42 (brs, 1 H), 7.34 (d, *J* = 2.4 Hz, 1 H), 7.33-7.28 (m, 3 H), 7.27-7.23 (m, 2 H), 6.88 (d, *J* = 2.8 Hz, 1 H), 4.27 (q, *J* = 7.2 Hz, 2 H), 4.07 (q, *J* = 7.2 Hz, 2 H), 1.29 (t, *J* = 7.2 Hz, 3 H), 1.00 (t, *J* = 7.2 Hz, 3 H); <sup>13</sup>C NMR: (100 MHz, CDCl<sub>3</sub>) δ 170.0, 166.2, 156.7, 142.5, 139.2, 130.4, 128.4, 128.1, 127.7, 126.3, 120.7, 115.8, 61.8, 61.6, 13.9, 13.5; MS (EI) *m/z* 314.1 (100) [M]<sup>+</sup>.



**4-Hydroxy-5-oxo-1-phenylcyclohex-3-enecarbonitrile**. The reaction of 4-phenyl-4-cyanocyclohexanone (100 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 12 mg (11%) of 4-hydroxy-5-oxo-1-phenylcyclohex-3-enecarbonitrile and 20 mg (19%) of 3-hydroxy-4-oxo-1-phenylcyclohex-2-enecarbonitrile purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) and then further separated by recycling preparative HPLC. 4-Hydroxy-5-oxo-1-phenylcyclohex-3-enecarbonitrile: pale yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.45-7.42 (m, 2 H), 7.38 (t, *J* = 7.0 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 1 H), 6.30 (s, 1 H), 6.05 (d, *J* = 1.5 Hz, 1 H), 2.92-2.85 (m, 1 H), 2.68-2.62 (m, 1 H), 2.56-2.51 (m, 1 H), 2.31-2.25 (m, 1 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 192.9, 148.3, 138.8, 129.3, 128.7, 125.8, 119.7, 115.0, 43.0, 38.1, 33.3 ppm; HRMS *m/z* (ESI) calcd for C<sub>13</sub>H<sub>11</sub>N

NaO<sub>2</sub> (M + Na)<sup>+</sup>, 236.0682, found 236.0678.



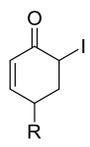
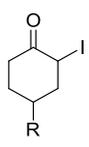
**3-Hydroxy-4-oxo-1-phenylcyclohex-2-enecarbonitrile.** The reaction of 4-phenyl-4-cyanocyclohexanone (100 mg, 0.5 mmol), I<sub>2</sub> (26 mg, 20 mol%), DMSO (1.0 mL), at 80 °C for 12 h, afforded 12 mg (11%) of 4-hydroxy-5-oxo-1-phenylcyclohex-3-enecarbonitrile and 20 mg (19%) of 3-hydroxy-4-oxo-1-phenylcyclohex-2-enecarbonitrile purified by column chromatography on silica gel (eluent: petroleum ether / ethyl acetate = 10:1) and then further separated by recycling preparative HPLC. 3-Hydroxy-4-oxo-1-phenylcyclohex-2-enecarbonitrile: pale yellow solid; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ 7.43-7.41 (m, 2 H), 7.38 (t, *J* = 7.0 Hz, 2 H), 7.32 (t, *J* = 7.5 Hz, 1 H), 6.07 (dd, *J* = 5.5, 1.5 Hz, 1 H), 5.99 (s, 1 H), 3.14-3.05 (m, 2 H), 3.02-2.92 (m, 2 H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>): δ 190.1, 147.3, 137.0, 129.4, 128.9, 125.6, 121.5, 113.4, 45.7, 44.0, 35.6 ppm; HRMS *m/z* (ESI) calcd for C<sub>13</sub>H<sub>11</sub>N NaO<sub>2</sub> (M + Na)<sup>+</sup>, 236.0682, found 236.0685.

## Details of Calculation and Discussion

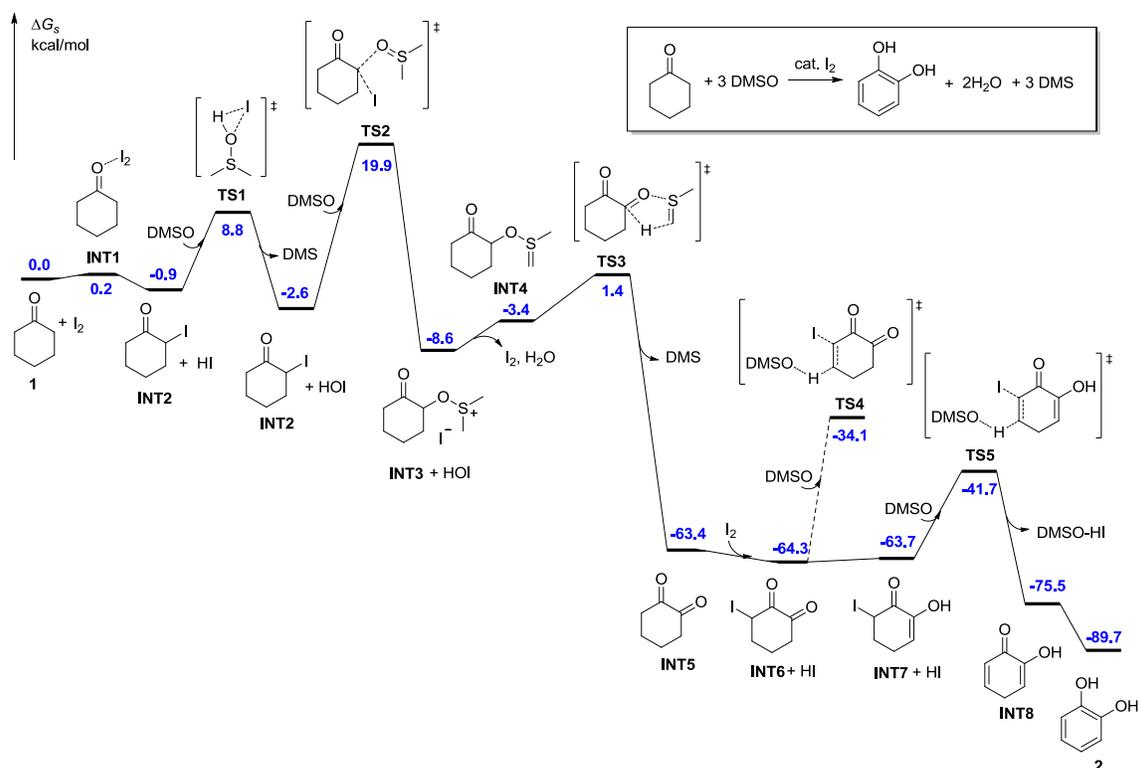
All of the DFT calculations were performed with the Gaussian 09 program package.<sup>21</sup> The geometry optimization of all the minima involved were performed at the M06-2X level of theory<sup>22</sup> with the 6-31G(d,p) basis set for lighter atoms (H, C, O, and S) and the LANL2DZ basis set for I atom.<sup>23</sup> The structures of the reactants, intermediates, transition states, and products were fully optimized without any restriction. The vibrational frequencies were computed at the same level to check whether each optimized structure is an energy minimum or a transition state and to evaluate its zero-point vibrational energy (ZPVE) and thermal corrections at 298 K. IRC calculations<sup>24</sup> were used to confirm that the transition states found from the optimization calculations connect the related reactants and products. Single-point solvent calculations (with 6-311+G(d,p)/SDD basis set) were performed at the optimized gas-phase geometries for all the intermediates and transition states, using the SMD<sup>25</sup> approach as implemented in Gaussian 09, employing DMSO as a solvent. Through the same approach full optimization, without any restriction, was carried out for the model reactions. The reported energies are Gibbs free energies in DMSO solution ( $\Delta G_s$ ).

Our calculation further confirms the chemoselectivity for the benzenediol and phenol formation also has universality, in which cyclohexenone is favour to deliver phenol, while cyclohexanone tends to give benzenediol (Table S1).

**Table S1.** DFT-computed Gibbs free energies in DMSO solution ( $\Delta G_s$ ) for chemoselectivity between phenol and benzenediol.

	R	TSa-S <sub>N</sub> 2	TSe-S <sub>N</sub> 2	TSa-E 2	TSe-E 2		R	TSa-S <sub>N</sub> 2 2	TSe-S <sub>N</sub> 2	TSa-E2	TSe-E 2
	Ph	31.3	27.5	22.1	27.2		Ph	27.6	20.1	27.9	23.3
	Me	28.4	27.3	20.9	24.0		Me	24.2	20.5	26.2	24.0
	H	27.7		20.9			H	22.6		24.5	

Although the mechanism is not completely clear yet, the whole energy profiles of cyclohexanone **1** as a model system were calculated to better understand the transformation process (Figure S1). Initially, electrophilic iodization of cyclohexanones by the iodine catalyst occurs to afford  $\alpha$ -iodo cyclohexanones **INT2** along with HI. This process is facile and slightly exergonic. Then HI could be oxidized by DMSO through transition state TS1 with O atom transfer from DMSO to HI. It requires an activation free energy of only 9.7 kcal/mol to form HOI exergonicly. When **INT2** was formed, it undergoes the key step of S<sub>N</sub>2 reaction with DMSO via **TS2** with an activation free energy of 22.5 kcal/mol to provide intermediates **INT3**. Deprotonation of **INT3** with HOI affords **INT4**, which undergoes H-transfer with the release of DMS through transition state **TS3** to complete Kornblum oxidation process. This step is facile with an activation free energy of only 10.0 kcal/mol and highly exergonic to deliver **INT5**. After further  $\alpha$ -iodization of **INT5**, the formed **INT6** directly undergoes HI elimination with the assistance of DMSO as a base through **TS4** requiring energy barrier of 30.2 kcal/mol. However, after **INT6** tautomerizes to **INT7**, the energy barrier of the HI elimination process of **INT7** via **TS5** is only 22.0 kcal/mol, indicating that it is facile to transform to **INT8**. Further isomerization of **INT8** affords stable catechol product **2** exergonicly.



**Figure S1.** DFT-computed whole energy profiles for I<sub>2</sub>-catalyzed conversion of cyclohexanone to catechol

## DFT-computed energies of all stationary points

**Table S2.** Sum of electronic and thermal enthalpies ( $H$ , in Hartree), sum of electronic and thermal free energies ( $G$ , in Hartree), thermal correction to Gibbs free energy ( $CGFE$ , in Hartree), electronic energy in DMSO ( $E_s$ , in Hartree), and free energies in DMSO ( $G_s$ , in Hartree).

Structure	$H$	$G$	$CGFE$	$E_s$	$G_s$
DMSO	-552.981406	-553.016036	0.052300	-553.163659	-553.111359
11-I	-550.011329	-550.065801	0.158957	-550.413706	-550.254749
TSa-E2-11	-1102.952436	-1103.022104	0.229451	-1103.560276	-1103.330825
TSe-E2-11	-1102.952697	-1103.024158	0.225917	-1103.548617	-1103.322700
TSa-S <sub>N</sub> 2-11	-1102.963395	-1103.031327	0.233666	-1103.549967	-1103.316301
TSe-S <sub>N</sub> 2-11	-1102.964322	-1103.033400	0.232489	-1103.554816	-1103.322327
1g-I	-551.203923	-551.258853	0.182630	-551.630357	-551.447727
TSa-E2-1g	-1104.150484	-1104.220705	0.251247	-1104.765885	-1104.514638

<b>TSe-E2-1g</b>	-1104.155763	-1104.226921	0.249645	-1104.771623	-1104.521978
<b>TSa-S<sub>N</sub>2-1g</b>	-1104.167654	-1104.233560	0.259987	-1104.775111	-1104.515124
<b>TSe- S<sub>N</sub>2-1g</b>	-1104.167445	-1104.237223	0.255907	-1104.783041	-1104.527134
<b>ene-1a-I</b>	-358.40603	-358.451429	0.11143	-358.7015974	-358.5901674
<b>TSa-E2-ene-1a</b>	-911.34633	-911.408468	0.180139	-911.8483407	-911.6682017
<b>TSe-E2—ene-1a</b>	-911.34707	-911.409048	0.179776	-911.8430666	-911.6632906
<b>TSa-S<sub>N</sub>2-ene-1a</b>	-911.35669	-911.417309	0.184358	-911.840637	-911.656279
<b>TSe- S<sub>N</sub>2-ene-1a</b>	-911.35807	-911.418645	0.184248	-911.8422883	-911.6580403
<b>1a-I</b>	-359.59998	-359.646288	0.134359	-359.917999	-359.78364
<b>TSa-E2-1a</b>	-912.54686	-912.608612	0.202861	-913.0561035	-912.8532425
<b>TSe-E2-1a</b>	-912.54762	-912.610005	0.202331	-913.0590114	-912.8566804
<b>TSa-S<sub>N</sub>2-1a</b>	-912.56224	-912.623016	0.208071	-913.0645636	-912.8564926
<b>TSe-S<sub>N</sub>2-1a</b>	-912.56231	-912.623438	0.208099	-913.0704464	-912.8623474
<b>ene-1-I</b>	-319.139335	-319.181505	0.084949	-319.3962414	-319.311292
<b>TS-E2-ene-1</b>	-872.0795	-872.138635	0.153227	-872.5425845	-872.389358
<b>TS-S<sub>N</sub>2-ene-1</b>	-872.091252	-872.148183	0.158312	-872.5367478	-872.378436
<b>1-I</b>	-320.332559	-320.375734	0.108215	-320.6120637	-320.503849
<b>TS-E2-1</b>	-873.280369	-873.339811	0.175149	-873.7513237	-873.576175
<b>TS-S<sub>N</sub>2-1</b>	-873.296453	-873.353625	0.18228	-873.7615172	-873.579237
<b>15-I</b>	-398.868233	-398.91761	0.160922	-399.2248929	-399.0639709
<b>TS-E2-15</b>	-951.81902	-951.885882	0.226539	-952.3667282	-952.1401892
<b>TS-S<sub>N</sub>2-15</b>	-951.826103	-951.889641	0.234828	-952.3680802	-952.1332522
<b>1</b>	-309.586122	-309.624338	0.121712	-309.8408856	-309.7191736
<b>I<sub>2</sub></b>	-22.659239	-22.689014	-0.025459	-22.7337929	-22.7592519
<b>INT1</b>	-332.262304	-332.316794	0.111507	-332.5896311	-332.4781241
<b>HI</b>	-11.913058	-11.936496	-0.015056	-11.9609918	-11.9760478

<b>INT2</b>	-320.332559	-320.375734	0.108215	-320.6120637	-320.5038487
<b>TS1</b>	-564.873815	-564.91812	0.055626	-565.1275571	-565.0719311
<b>HOI</b>	-87.061229	-87.090173	-0.012169	-87.1458195	-87.1579885
<b>TS2</b>	-873.296453	-873.353625	0.18228	-873.7615172	-873.5792372
<b>INT3</b>	-873.335225	-873.39461	0.182546	-873.8072242	-873.6246782
<b>INT4</b>	-861.366047	-861.41707	0.174784	-861.764823	-861.590039
<b>TS3</b>	-861.349787	-861.400551	0.171194	-861.7535193	-861.5823253
<b>INT5</b>	-383.58464	-383.624176	0.10168	-383.8551288	-383.7534488
<b>H<sub>2</sub>O</b>	-76.357585	-76.379007	0.00409	-76.4291955	-76.4251055
<b>DMS</b>	-477.842422	-477.875104	0.049928	-477.9821239	-477.9321959
<b>INT6</b>	-394.329735	-394.374999	0.087246	-394.6252859	-394.5380399
<b>TS4</b>	-947.280368	-947.340368	0.15622	-947.7575975	-947.6013775
<b>INT7</b>	-394.335982	-394.380156	0.089315	-394.6264898	-394.5371748
<b>TS5</b>	-947.279069	-947.339249	0.158031	-947.7714385	-947.6134075
<b>INT8</b>	-382.395814	-382.433808	0.079572	-382.6388736	-382.5593016
<b>2</b>	-382.418226	-382.456124	0.080188	-382.6621528	-382.5819648
<b>DMSO-HI</b>	-564.924859	-564.967741	0.057048	-565.1650131	-565.1079651

---

The coordinates of all stationary points (Å)

#### DMSO

S	-0.00007400	0.23580200	-0.44355300
O	-0.00100200	1.48717000	0.38714800
C	1.34587700	-0.80691800	0.18202700
H	1.32005900	-1.78457400	-0.30438600
H	2.28156900	-0.29863900	-0.05308300
H	1.24410700	-0.90320600	1.26539000
C	-1.34493000	-0.80845100	0.18195100
H	-2.28108200	-0.30109800	-0.05332200
H	-1.31805800	-1.78621500	-0.30414800
H	-1.24308100	-0.90424000	1.26535300

#### 11-I

C	1.64991800	-1.74099600	-0.01522500
C	1.11697200	-1.07807800	1.25308000
C	0.42555500	0.24494400	0.96737300
C	2.23382700	0.56206600	-0.80204600
C	2.38113800	-0.76525200	-0.89059200
H	0.45381400	-1.75088800	1.80221900
H	1.96457500	-0.84514400	1.91264000
H	2.78805700	1.24773300	-1.43466800
H	3.05871600	-1.17506900	-1.63638400

H	0.09062900	0.75920300	1.86710500
C	1.30301600	1.19167600	0.16159800
O	1.23854100	2.39161600	0.31584400
I	-1.43504500	-0.05856900	-0.16488100
H	0.82015700	-2.17713400	-0.58945800
H	2.31057700	-2.57365300	0.24538700

**TSa-E2-11**

C	-0.65209800	-1.46979600	0.24106100
C	-0.21266800	-0.51800700	-0.84539200
C	0.84134700	0.32786200	-0.62942800
C	0.55228300	0.02248400	1.85349400
C	-0.27728400	-0.99884100	1.61925400
H	-1.08766100	1.01030400	-0.50285100
H	-0.47810300	-0.79796900	-1.86206500
H	-0.06024300	-2.39209400	0.07659300
H	0.82255300	0.33512800	2.85677900
H	-0.69706200	-1.56288200	2.44939900
H	1.26881600	0.92424900	-1.43037800
C	1.07740300	0.84210200	0.74416100
O	1.46974400	1.99513800	0.92318000
I	3.32040800	-1.04464800	-0.25684000
S	-0.75798300	3.17568600	-0.54224700
O	-1.62405600	1.87296000	-0.22379300
C	-2.01561900	4.17347200	-1.34672200
H	-1.62159800	5.18240400	-1.48342100
H	-2.21793300	3.71773500	-2.31608600
H	-2.91630600	4.17873800	-0.73157900
C	-0.68508800	3.98366200	1.05533700
H	-0.00629100	3.38076600	1.66049400
H	-0.26323000	4.97947100	0.90332800
H	-1.69241100	4.03226500	1.47098500
C	-2.12432300	-1.82236100	0.12954000
C	-2.53060000	-2.99244600	-0.51102600
C	-3.09731500	-0.95367800	0.63160100
C	-3.88388000	-3.29169800	-0.64956800
H	-1.77987300	-3.67461400	-0.90143400
C	-4.44952300	-1.25141400	0.49723500
H	-2.78516400	-0.04022600	1.13391500
C	-4.84655700	-2.42252400	-0.14476500
H	-4.18524300	-4.20743100	-1.14835700

H	-5.19500200	-0.57104700	0.89732400
H	-5.90112600	-2.65713200	-0.24796600

**TSe-E2-11**

C	0.58147000	-1.61376900	0.46631500
C	-0.10496700	-0.87060800	-0.67179000
C	-0.63087900	0.40111200	-0.49197500
C	-0.41091600	0.11980900	1.99459200
C	0.35819200	-0.95696300	1.80281000
H	-1.59208400	-1.35844200	-0.49471000
H	0.18879100	-1.17626500	-1.67378300
H	-0.58500800	0.54291700	2.97837300
H	0.85798900	-1.42476500	2.64842100
H	-1.12705400	0.90855800	-1.31248200
C	-1.15193800	0.72058300	0.86781800
O	-2.22701200	1.29146900	1.02091100
I	0.98864400	2.60464500	-0.33085300
S	-3.74260300	-0.73630400	-0.54545900
O	-2.60115300	-1.78687200	-0.24021600
C	-4.93157100	-1.78025900	-1.39721800
H	-5.84787900	-1.20924800	-1.55956200
H	-4.48860100	-2.05434400	-2.35487100
H	-5.12065700	-2.67145400	-0.79697800
C	-4.56282400	-0.55957100	1.03900100
H	-3.89576900	0.04293900	1.65711500
H	-5.50390600	-0.03013100	0.87579100
H	-4.72844600	-1.55435200	1.45515000
H	0.14480100	-2.62342100	0.54070800
C	2.06614900	-1.81809200	0.19496000
C	2.55581600	-3.08241200	-0.13261500
C	2.94889800	-0.73627000	0.25199100
C	3.90942800	-3.26976000	-0.40250000
H	1.87309800	-3.92790000	-0.17621900
C	4.30020600	-0.92389300	-0.02008900
H	2.57219700	0.25514500	0.49257000
C	4.78437200	-2.18915100	-0.34644800
H	4.27851000	-4.25906200	-0.65480200
H	4.97470700	-0.07463400	0.02032800
H	5.83953900	-2.33215500	-0.55713500

**TSa-S<sub>N</sub>2-11**

C	-0.44037700	-1.97362600	0.10488400	C	0.88486900	-0.43720200	1.72511700
C	0.33859400	-1.18476100	-0.97726200	H	1.07990500	0.50741200	-1.05483400
C	0.74501500	0.20149400	-0.53054200	H	0.49680200	-1.04164200	-1.65070400
C	0.79406900	-0.65517100	1.84491900	H	-0.47966600	0.64137500	2.94717300
C	0.15967100	-1.77151500	1.47430100	H	1.62238500	-0.55643500	2.51588000
H	1.23697900	-1.74050200	-1.24113200	H	-1.57106000	0.35580800	-1.24278400
H	-0.26929900	-1.08313200	-1.88019100	C	-1.32024800	0.30023500	0.95888400
H	-0.32230000	-3.03400400	-0.15122500	O	-2.50890200	0.34467700	1.25302800
H	1.18562800	-0.51216900	2.84652900	I	-0.51771000	2.84224800	-0.34643500
H	0.01883400	-2.57083800	2.19844400	S	-3.12089200	-1.81233900	-0.46019600
H	1.10262300	0.93207000	-1.24081800	O	-1.56168600	-1.74067000	-0.45284400
C	0.90041600	0.50566300	0.93066400	C	-3.38615200	-3.31506100	-1.41990700
O	0.89943800	1.66136900	1.33281900	H	-4.44661700	-3.57364500	-1.39373700
I	3.51313400	-0.17058200	-0.28952800	H	-3.07896400	-3.10085700	-2.44357900
S	-1.26558900	2.37804500	-0.39672500	H	-2.77261300	-4.11457800	-1.00178800
O	-1.03625300	0.85748100	-0.63337500	C	-3.56242700	-2.44605900	1.16477400
C	-2.78339800	2.60041900	-1.34529400	H	-3.38962900	-1.62947100	1.86519100
H	-3.20439500	3.58628400	-1.13865100	H	-4.61750000	-2.72709000	1.15315600
H	-2.52119800	2.51514500	-2.39978300	H	-2.92520300	-3.30386200	1.38712000
H	-3.46900000	1.79797800	-1.06121200	H	0.83832700	-2.12195400	0.44545200
C	-1.98124700	2.49639000	1.25146100	C	2.70634400	-1.13256700	0.15919200
H	-1.17537300	2.28101500	1.95270800	C	3.35503100	-2.32448500	-0.15785800
H	-2.35313400	3.51312400	1.39455400	C	3.45271700	0.04755400	0.23620500
H	-2.78367400	1.75945900	1.32572400	C	4.72836800	-2.34330200	-0.39321000
C	-1.94486300	-1.69917000	0.07664700	H	2.78053900	-3.24559000	-0.21870700
C	-2.62326800	-1.08282800	1.12771200	C	4.82334300	0.03106700	0.00381800
C	-2.66926300	-2.05447200	-1.06440700	H	2.94773500	0.98235200	0.47543300
C	-3.98567900	-0.80370500	1.02994900	C	5.46471600	-1.16586400	-0.31149800
H	-2.07660600	-0.79878000	2.02193900	H	5.22203900	-3.27856600	-0.63790600
C	-4.02593100	-1.76937400	-1.17183900	H	5.39191400	0.95342300	0.06613900
H	-2.15912200	-2.55290500	-1.88586100	H	6.53445700	-1.17864500	-0.49363700
C	-4.69117500	-1.13506800	-0.12391700				
H	-4.49821600	-0.32959400	1.86271700				
H	-4.56711900	-2.04847200	-2.07049700				
H	-5.75215700	-0.91902500	-0.19984500				

### TSe-S<sub>N</sub>2-11

C	1.21121500	-1.08931400	0.39991200
C	0.51247700	-0.38097200	-0.77973400
C	-0.90252500	0.02704000	-0.45851700
C	-0.25026700	0.22196300	1.97363600

### 1g-I

C	-0.88343900	-0.10579200	0.37072500
C	-0.22844700	0.01662100	-1.02208000
C	1.20926800	0.50370800	-0.98211200
H	-0.30749300	-0.93326500	-1.55791400
H	-0.78922900	0.75435800	-1.61459400
H	1.67297100	0.55196900	-1.96711600
C	1.31941400	1.87631600	-0.32513600
O	2.23338100	2.62422100	-0.57212000

I	2.51396700	-0.89188300	0.10406000	H	-2.74169400	3.22622300	-2.18732600
H	-0.53682800	-1.04992800	0.80453300	H	-3.74552900	3.09271300	-0.71189000
C	-2.38509500	-0.21628100	0.19664700	C	-1.81737100	3.09133800	1.40181600
C	-2.97715300	-1.47412700	0.06462800	H	-1.05237700	2.60275300	2.00724700
C	-3.19942500	0.91548700	0.10139500	H	-1.75145800	4.17545100	1.51444900
C	-4.34594800	-1.60204400	-0.15282600	H	-2.81938300	2.72277100	1.62695600
H	-2.35513900	-2.36326900	0.13683000	C	-1.82870400	-1.88475400	-0.17157100
C	-4.56887000	0.79305500	-0.11446900	C	-2.62744000	-1.84089400	-1.32194100
H	-2.76271400	1.90622200	0.20294100	C	-2.46787000	-2.00637300	1.06288500
C	-5.14686500	-0.46724600	-0.24262600	C	-4.01243500	-1.90977400	-1.24317100
H	-4.78737900	-2.58907800	-0.24815200	H	-2.14979200	-1.75644400	-2.29544200
H	-5.18555200	1.68392700	-0.17988300	C	-3.85863600	-2.07170300	1.14810300
H	-6.21480200	-0.56393100	-0.40877000	H	-1.88443800	-2.05955300	1.97608900
C	0.16043800	2.24779000	0.58197300	C	-4.63682000	-2.02151500	-0.00184500
H	-0.59826900	2.71497000	-0.06193200	H	-4.60680200	-1.88380200	-2.15145500
H	0.50862500	3.01928100	1.27212800	H	-4.33093500	-2.16931100	2.12094500
C	-0.42566900	1.03635000	1.31500700	H	-5.71861200	-2.07875600	0.06460100
H	0.33994500	0.64607400	1.99246200				
H	-1.26069200	1.35566000	1.94450800				

**TSa-E2-1g**

C	-0.31176800	-1.79430600	-0.32850500
C	0.09687100	-0.53469100	-1.10225900
C	0.98813300	0.38177400	-0.55315400
H	-1.02633300	0.50804300	-0.74138100
H	0.05485500	-0.59884900	-2.18816500
H	-0.01507100	-2.65104600	-0.94903600
H	1.29232700	1.25263900	-1.12565300
C	0.86721300	0.61374600	0.91491300
O	0.84482200	1.75113700	1.36396700
I	3.59404900	-0.28932200	-0.27473900
C	0.52073800	-0.58791500	1.76919000
H	-0.45660000	-0.35440300	2.21231600
H	1.24001400	-0.63352100	2.59235200
C	0.49149400	-1.89634400	0.97738700
H	0.11168300	-2.71154900	1.60049800
H	1.52055300	-2.14882800	0.71216100
S	-1.43457200	2.67690400	-0.30022000
O	-1.87767900	1.16414100	-0.39617300
C	-2.81327200	3.47646200	-1.12876400
H	-2.72978700	4.55654100	-0.99346600

**TSe-E2-1g**

C	0.75281100	-1.33204100	0.59619900
C	0.00682900	-0.73538100	-0.59966000
C	-0.65809600	0.47780800	-0.49779600
H	-1.40464900	-1.37649100	-0.41902800
H	0.34272200	-1.05430900	-1.58483300
H	-1.16052200	0.90623000	-1.35932900
C	-1.28976500	0.77842500	0.81926900
O	-2.43703100	1.20044300	0.87289300
I	0.79226300	2.80206900	-0.29776600
C	-0.56096200	0.29058800	2.05459400
H	-1.22788800	-0.45409900	2.51196400
H	-0.48914400	1.12725200	2.75532000
C	0.80788800	-0.31513200	1.75286700
H	1.21181000	-0.80170400	2.64575300
H	1.49819500	0.48671900	1.47577100
S	-3.61173900	-1.07760800	-0.64400500
O	-2.36541600	-1.90475500	-0.13617400
C	-4.56497900	-2.37003500	-1.44947400
H	-5.53725200	-1.96446000	-1.73614600
H	-4.00999400	-2.67196400	-2.33779000
H	-4.67246400	-3.21236200	-0.76454100
C	-4.58553900	-0.86139000	0.84691800

H	-4.04734500	-0.13046000	1.45213700
H	-5.56216900	-0.46664500	0.55907100
H	-4.67470600	-1.82789800	1.34518300
H	0.22397900	-2.23129200	0.95054800
C	2.15361000	-1.75344600	0.20227800
C	2.63996600	-3.02038700	0.52003000
C	2.98970800	-0.85120800	-0.46458000
C	3.94004300	-3.38858000	0.17924600
H	1.99443100	-3.72513800	1.03901300
C	4.28698000	-1.21825000	-0.80617800
H	2.61704500	0.14437100	-0.70597900
C	4.76552600	-2.48783200	-0.48585200
H	4.30557200	-4.37896900	0.43271600
H	4.92729600	-0.50936700	-1.32165300
H	5.77843900	-2.77171600	-0.75342700

**TSa-S<sub>N</sub>2-1g**

C	-0.27205500	-1.82860500	-0.69667100
C	0.41225400	-0.67842900	-1.46867400
C	0.75498900	0.51037600	-0.59539800
H	1.33594500	-1.05698100	-1.90721400
H	-0.20237800	-0.31190900	-2.29377600
H	-0.21710500	-2.70356400	-1.35787000
H	1.20313400	1.39484800	-1.02330600
C	0.74863800	0.40210100	0.90662100
O	0.64944700	1.41455500	1.58177800
I	3.50092900	-0.02238400	-0.14989100
S	-1.49416100	2.41212800	0.12149500
O	-0.98199400	1.24528900	-0.77645200
C	-2.94184700	2.89995200	-0.83736800
H	-3.50603100	3.65275300	-0.28332500
H	-2.57943600	3.31636900	-1.77711600
H	-3.53878800	2.00430300	-1.02249800
C	-2.36833000	1.60241300	1.47419500
H	-1.61095100	1.25393800	2.17589400
H	-3.01760200	2.33725100	1.95551400
H	-2.94468500	0.77008700	1.05879900
C	0.61144800	-0.97253300	1.53598900
H	-0.31484600	-0.92012400	2.12123300
H	1.42903200	-1.08482800	2.25244300
C	0.57547800	-2.13998900	0.54624400

H	0.21712000	-3.04269100	1.04995100
H	1.59495900	-2.35290800	0.21294900
C	-1.76064500	-1.62063900	-0.40495300
C	-2.34623400	-2.04869300	0.78992800
C	-2.61148000	-1.07223900	-1.37473500
C	-3.71432900	-1.90466700	1.02673200
H	-1.73675500	-2.51030600	1.55897800
C	-3.97594500	-0.93038200	-1.14981400
H	-2.20268500	-0.73899800	-2.32299400
C	-4.53697600	-1.33698600	0.06123800
H	-4.13198000	-2.24649300	1.96864000
H	-4.60695400	-0.50924700	-1.92749200
H	-5.60208100	-1.22803100	0.23889800

**TSe-S<sub>N</sub>2-1g**

C	1.50130800	0.03501900	0.43537700
C	0.54892500	-0.25427000	-0.73789600
C	-0.91606500	-0.06185700	-0.40537400
H	0.80737800	0.36815400	-1.59629500
H	0.67052800	-1.30027500	-1.04213900
H	1.58018100	1.12364900	0.53369700
H	-1.60069500	0.24218500	-1.18730600
C	-1.40336000	0.17441300	1.01022000
O	-2.59859300	0.07973200	1.23745600
I	-0.76780300	2.83284700	-0.36983700
S	-2.94359900	-2.05220600	-0.54395400
O	-1.39761600	-1.82243500	-0.41851200
C	-2.96866900	-3.55271900	-1.53948600
H	-3.99473000	-3.91965900	-1.60641800
H	-2.60209500	-3.28446300	-2.53039400
H	-2.31093600	-4.29371100	-1.08274300
C	-3.43101200	-2.75862900	1.03731600
H	-3.42170000	-1.93918500	1.75551100
H	-4.43581800	-3.17357400	0.93560600
H	-2.70853100	-3.53203100	1.30467400
C	-0.36946900	0.25216200	2.11466300
H	-0.84128000	-0.14879700	3.01585900
H	-0.14112300	1.30613200	2.29726100
C	0.90741900	-0.50801600	1.74222100
H	0.68432000	-1.57823100	1.63043900
H	1.63969900	-0.41651500	2.54966200

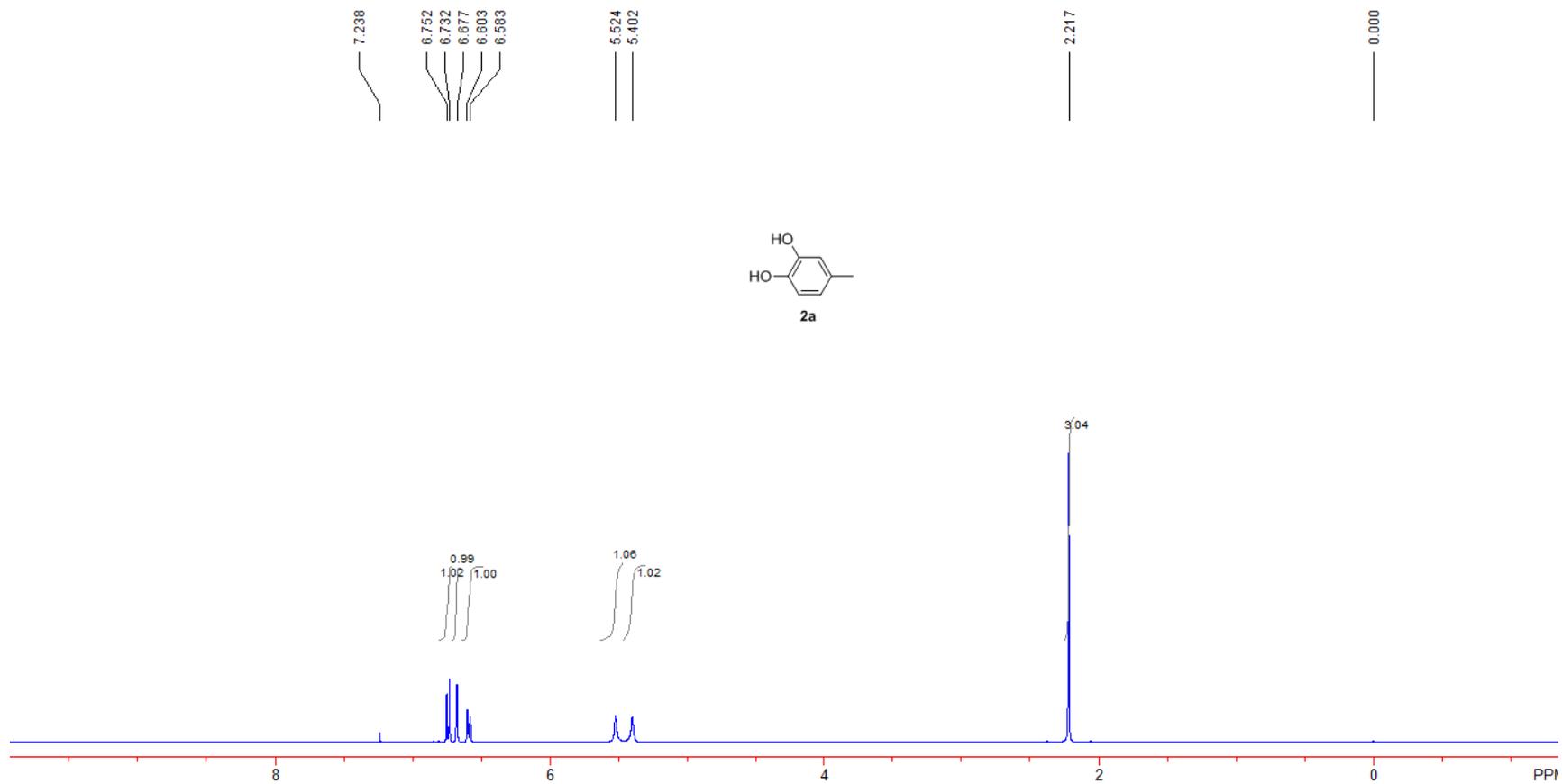
C	2.88162000	-0.51658900	0.15000400	H	0.69721200	2.57438900	1.82702000
C	3.10702700	-1.89423500	0.06310300	H	-0.12666300	-1.37390200	0.69814300
C	3.96235900	0.34700200	-0.03340800	C	-0.13404900	0.02004700	-0.98442300
C	4.37874800	-2.39420000	-0.19607400	O	-0.74905200	-0.73209200	-1.72808600
H	2.27838600	-2.58553200	0.19987300	I	2.66621900	-1.04556100	-0.05840900
C	5.23750200	-0.14894100	-0.29493600	C	0.23078600	1.42949400	-1.40025600
H	3.79794800	1.41955800	0.02719300	H	-0.71544600	1.90347000	-1.70467700
C	5.44976000	-1.52152700	-0.37584400	H	0.85756200	1.36830500	-2.29550300
H	4.53575500	-3.46672600	-0.25778600	C	0.89971500	2.24864800	-0.29613900
H	6.06440300	0.54009700	-0.43513300	H	1.89333400	1.81907600	-0.13058300
H	6.44257000	-1.91071500	-0.57780000	S	-3.18277900	-0.84174800	-0.01625700
<b>15-I</b>				O	-2.71130100	0.55435800	0.54319900
C	-1.57535400	1.28842800	-0.26522200	C	-4.78593400	-1.00141700	0.77885700
C	-0.73862900	1.22799200	1.02376700	H	-5.29914500	-1.87346500	0.36885200
C	0.12257200	-0.02511600	1.09783900	H	-4.60334500	-1.14307900	1.84415800
H	-1.43562300	1.10096800	1.86855200	H	-5.35869400	-0.08823000	0.61044200
H	0.73130500	-0.06778300	2.00192000	C	-3.71058700	-0.46102400	-1.68838600
C	-0.72361900	-1.29201500	1.02050200	H	-2.79760600	-0.28239300	-2.25841100
O	-0.36246600	-2.32240200	1.53490700	H	-4.23719200	-1.33195100	-2.08441100
I	1.63115600	-0.12355100	-0.50524700	H	-4.35668900	0.41762400	-1.65699900
H	-0.99175000	1.79137200	-1.04566700	C	-0.10842200	0.31577300	2.85622100
C	-2.06506800	-1.13530400	0.32712000	H	0.93187200	0.37000700	3.20389000
H	-2.79313100	-0.83847100	1.09750400	H	-0.70080900	1.01389300	3.45584400
H	-2.37311700	-2.11937100	-0.03557600	H	-0.46588100	-0.70023400	3.04798900
C	-2.04267400	-0.08762200	-0.79141800	C	1.04654300	3.70939200	-0.70775300
H	-1.31527300	-0.42992400	-1.53692700	H	1.55433400	4.28570000	0.07112100
H	-2.44641900	1.92607200	-0.06947500	H	1.62866200	3.80244100	-1.62917700
C	-3.40281700	0.01635700	-1.47607200	H	0.06512200	4.16716900	-0.87951800
H	-3.38134400	0.76914100	-2.26963700	<b>TS-S<sub>N</sub>2-15</b>			
H	-3.69931100	-0.93765700	-1.92108900	C	0.16666500	2.33412000	0.87213300
H	-4.17453100	0.30960600	-0.75543100	C	0.03425600	0.98653400	1.59834100
C	0.03336900	2.51960400	1.26378900	C	-0.32133900	-0.11348600	0.61369900
H	-0.65241200	3.37080200	1.29327500	H	-0.84242400	1.03608000	2.25350000
H	0.57973000	2.48669500	2.21080000	H	-0.83014200	2.68645400	0.57107600
H	0.75365300	2.69201100	0.45877000	H	0.56882400	3.07279500	1.57498900
<b>TS-E2-15</b>				H	-0.42850600	-1.13271300	0.96593500
C	0.11864500	2.11251800	1.01654000	C	-0.23481600	0.07183400	-0.88349700
C	-0.16234000	0.66000700	1.38992100	O	-0.87420600	-0.67439300	-1.61344100
C	0.06695900	-0.33457000	0.44871900	I	2.22451000	-1.27703600	-0.12994600
H	-1.61697800	0.49518300	0.91556900	S	-3.07310400	-0.85433400	0.01660300
H	-0.81986200	2.68735300	0.95133800	O	-2.17386300	0.24383900	0.66931300

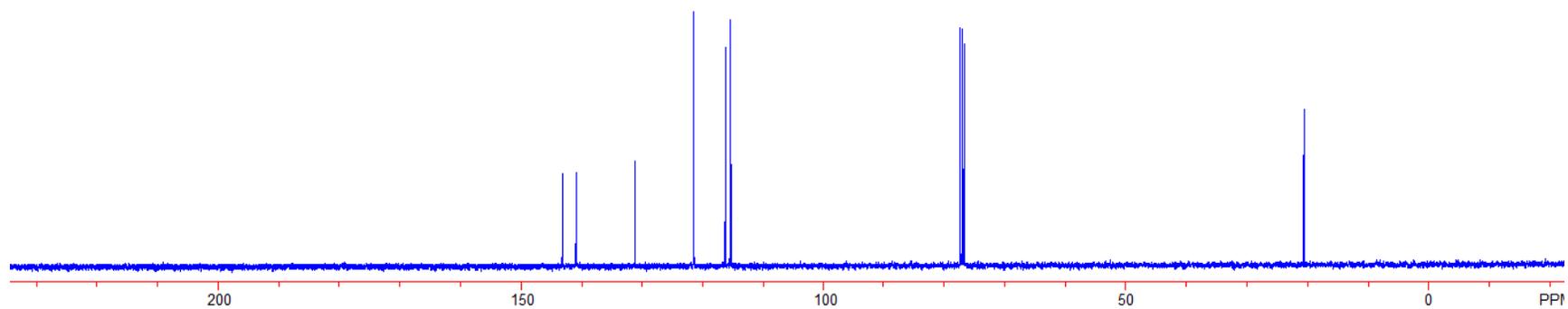
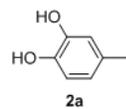
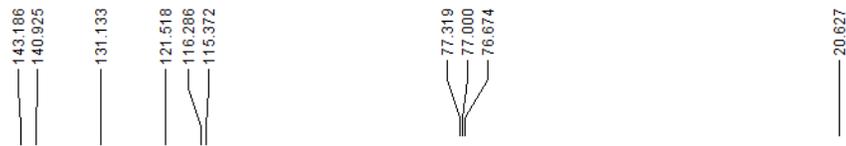
C	-4.53661000	-0.74315500	1.06455500	C	1.04978300	2.25093800	-0.37556600
H	-5.32296300	-1.37633900	0.64866300	H	2.00650500	1.78828100	-0.10538600
H	-4.25086800	-1.10353600	2.05279300	C	1.31965900	3.63581800	-0.95752800
H	-4.85557000	0.29868200	1.12218500	H	1.87122800	4.25921800	-0.24801200
C	-3.74581500	-0.07646800	-1.46059400	H	1.90667900	3.57001900	-1.87821400
H	-2.93187700	-0.04443300	-2.18414000	H	0.37848700	4.14642700	-1.19345600
H	-4.57144100	-0.68665900	-1.83245400	C	1.22813600	0.70039800	2.51668300
H	-4.08393000	0.92674300	-1.19447200	H	1.19515000	1.40263400	3.35546300
C	0.36310400	1.36085300	-1.41330300	H	1.19424400	-0.31787900	2.91116800
H	-0.49075400	1.90701000	-1.84416400	H	2.17790800	0.81373900	1.99363200
H	1.02650400	1.10583100	-2.24411300				

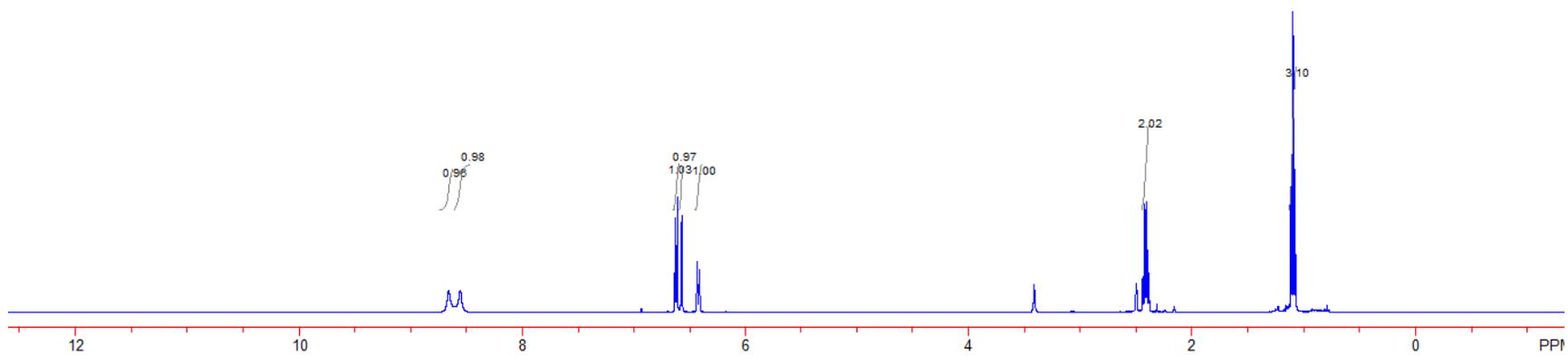
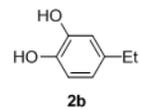
## References:

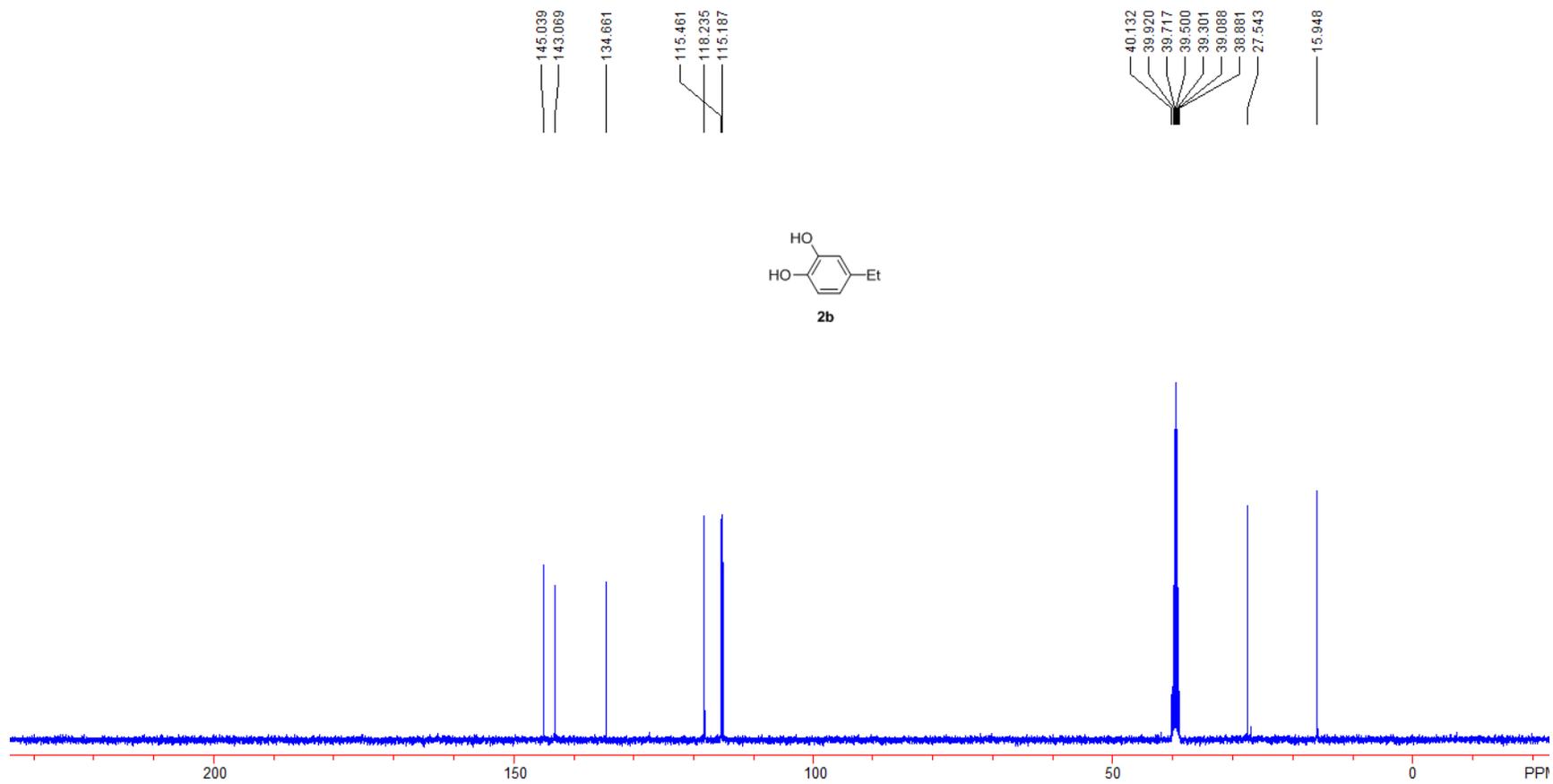
- (1) Fenselau, A. H.; Moffatt, J. G. *J. Am. Chem. Soc.* **1966**, *88*, 1762.
- (2) Mupparapu, N.; Khan, S.; Battula, S.; Kushwaha, M.; Gupta, A. P.; Ahmed, Q. N.; Vishwakarma, R. A. *Org. Lett.* **2014**, *16*, 1152.
- (3) Huang, Z.; Dong, G. *J. Am. Chem. Soc.* **2013**, *135*, 17747.
- (4) Zhang, J.; Jiang, Q.; Yang, D.; Zhao, X.; Dong, Y.; Liu, R. *Chem. Sci.* **2015**, *6*, 4674.
- (5) a) Jung, M. E.; Nishimura, N.; Novack, A. R. *J. Am. Chem. Soc.* **2005**, *127*, 11206. b) Jung, M. E.; McCombs, C. A.; Takeda, Y.; Pan, Y.-G. *J. Am. Chem. Soc.* **1981**, *103*, 6677.
- (6) Schmidt, R. K.; M $\ddot{u}$ ther, K.; M $\ddot{u}$ ck-Lichtenfeld, C.; Grimme, S.; Oestreich, M. *J. Am. Chem. Soc.* **2012**, *134*, 4421.
- (7) DeGraffenreid, M. R.; Bennett, S.; Caille, S.; Turiso, F. G.-L.; Hungate, R. W.; Julian, L. D.; Kaizerman, J. A.; McMinn, D. L.; Rew, Y.; Sun, D.; Yan, X.; Powers, J. P. *J. Org. Chem.* **2007**, *72*, 7455.
- (8) Huang, C.; Ghavtadze, N.; Chattopadhyay, B.; Gevorgyan, V. *J. Am. Chem. Soc.* **2011**, *133*, 17630.
- (9) Subrizi, F.; Crucianelli, M.; Grossi, V.; Passacantando, M.; Pesci, L.; Saladino, R. *ACS Catal.* **2014**, *4*, 810.
- (10) Moridani, M. Y.; Siraki, A.; Chevaldina, T.; Scobie, H.; O'Brien, P. J. *Chem. Biol. Interact.* **2004**, *147*, 297.
- (11) Kanie, K.; Nishii, M.; Yasuda, T.; Taki, T.; Ujiie, S.; T. Kato, *J. Mater. Chem.* **2001**, *11*, 2875.
- (12) Sietmann, R.; Hammer, E.; Moody, J.; Cerniglia, C. E.; Schauer, F. *Arch. Microbiol.* **2000**, *174*, 353.

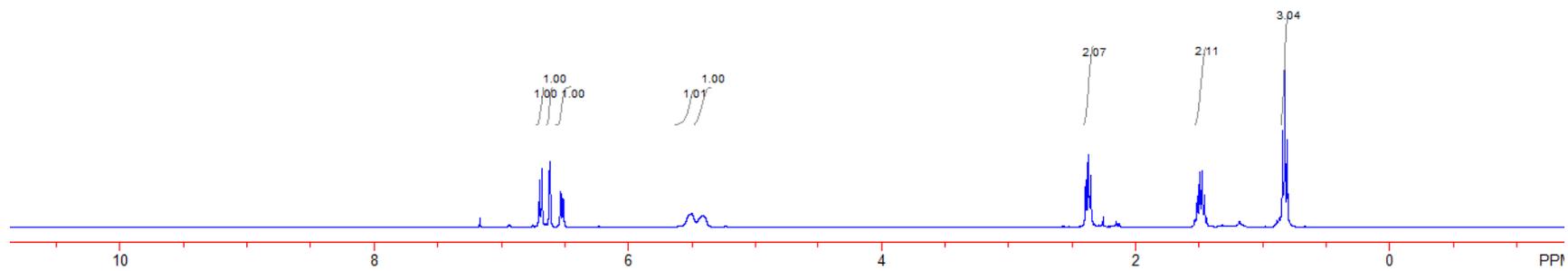
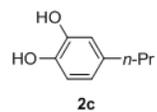
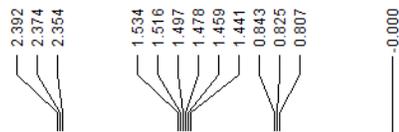
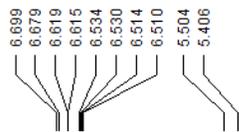
- (13) Nakai, Y.; Yamada, F. *Org. Magn. Reson.* **1978**, *11*, 607.
- (14) Nerdinger, S.; Kendall, C.; Cai, X.; Marchart, R.; Riebel, P.; Johnson, M. R.; Yin, C.-F.; Hénaff, N.; Eltis, L. D.; Snieckus, V. *J. Org. Chem.* **2007**, *72*, 5960.
- (15) Sher, M.; Dang, T. H. T.; Ahmed, Z.; Rashid, M. A.; Fischer, C.; Langer, P. *J. Org. Chem.* **2007**, *72*, 6284.
- (16) Parmar, V. S.; Kumar, A.; Bisht, K. S.; Mukherjee, S.; Prasad, A. K.; Sharma, S. K.; Wengel, J.; Olsen, C. E. *Tetrahedron* **1997**, *53*, 2163.
- (17) Stevens, C. B.; Hanna Jr., J. M.; Lammi, R. K. *Bioorg. Med. Chem. Lett.* **2013**, *23*, 1703.
- (18) Izawa, Y.; Pun, D.; Stahl, S. S. *Science* **2011**, *333*, 209.
- (19) Bekaert, A.; Barberan, O.; Gervais, M.; Brion, J.-D. *Tetrahedron Lett.* **2000**, *41*, 2903.
- (20) Lin, W.; Baron, O.; Knochel, P. *Org. Lett.* **2006**, *8*, 5673.
- (21) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Revision A.01, Gaussian, Inc., Wallingford CT, 2009.
- (22) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Account* **2008**, *120*, 215.
- (23) (a) Hay, J. P.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299. (b) Friesner, R. A.; Murphy, R. B.; Beachy, M. D.; Ringlanda, M. N.; Pollard, W. T.; Dunietz, B. D.; Cao, Y. X. *J. Phys. Chem. A* **1999**, *103*, 1913.
- (24) (a) Fukui, K. *J. Phys. Chem.* **1970**, *74*, 4161. (b) Gonzalez, C.; Schlegel, H. B. *J. Chem. Phys.* **1989**, *90*, 2154. (c) Gonzalez, C.; Schlegel, H. B. *J. Phys. Chem.* **1990**, *94*, 5523.
- (25) Marenich, A. V.; Cramer, C. J.; Truhlar, D. G. *J. Phys. Chem. B* **2009**, *113*, 6378.

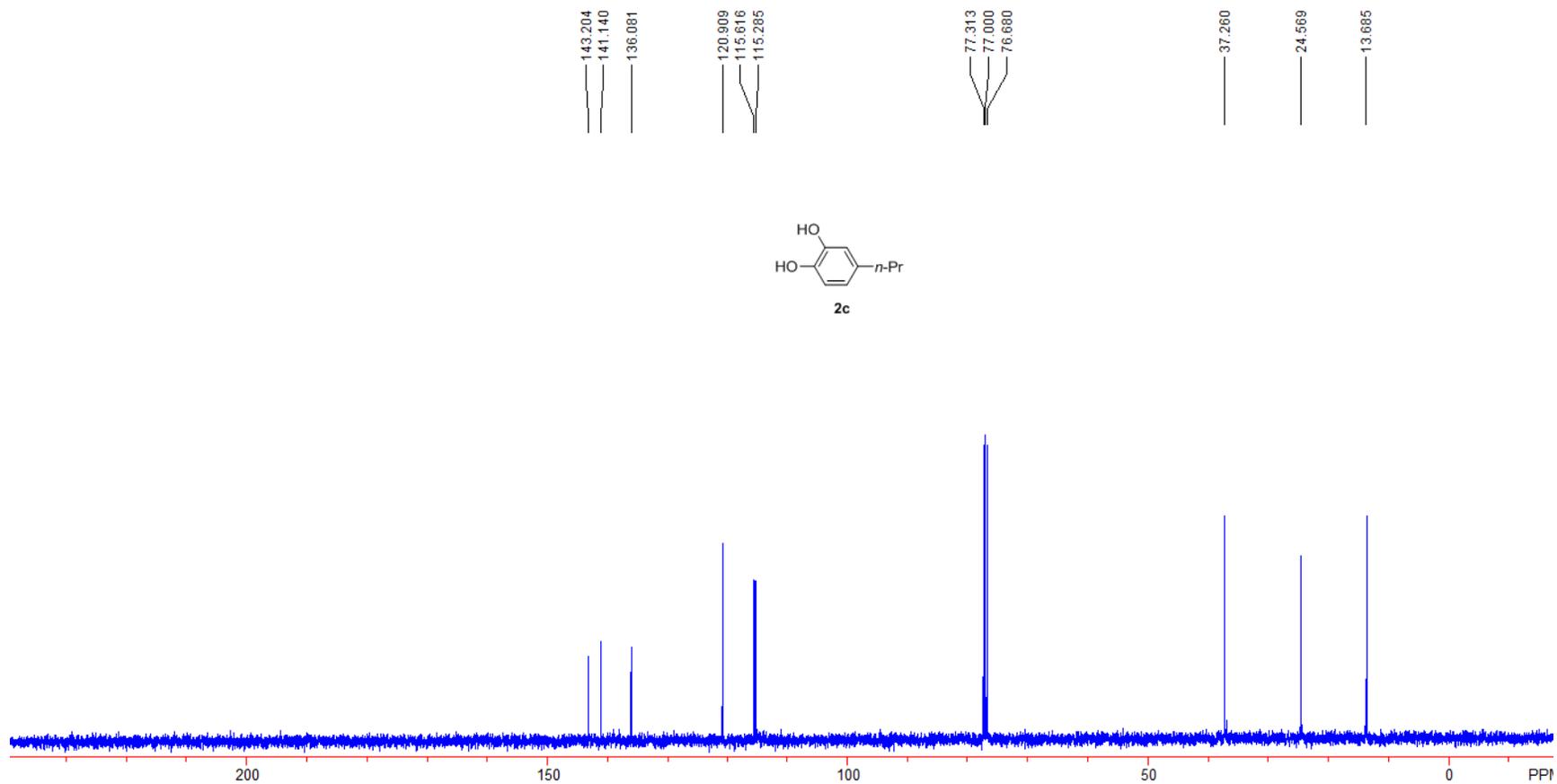


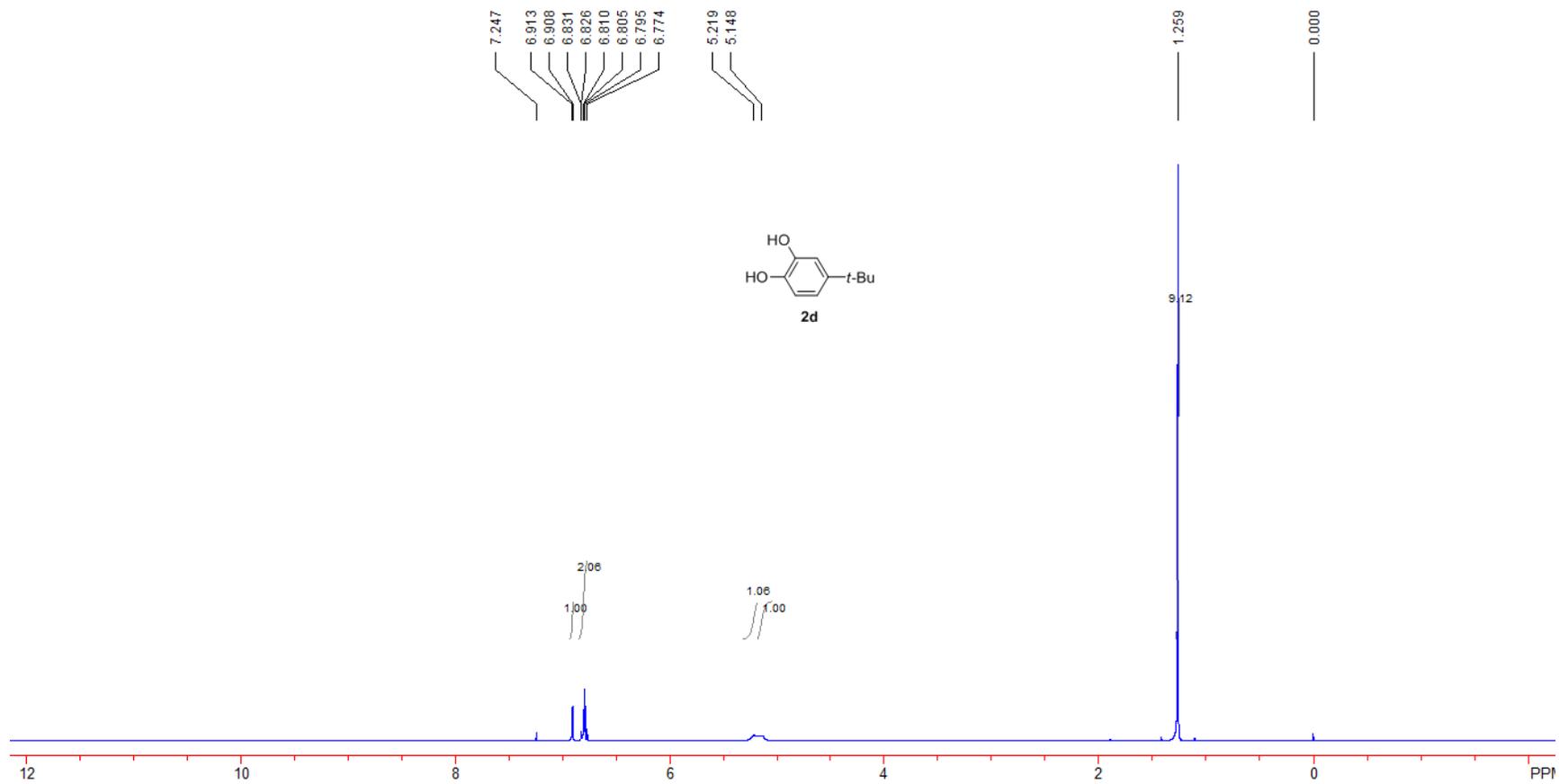


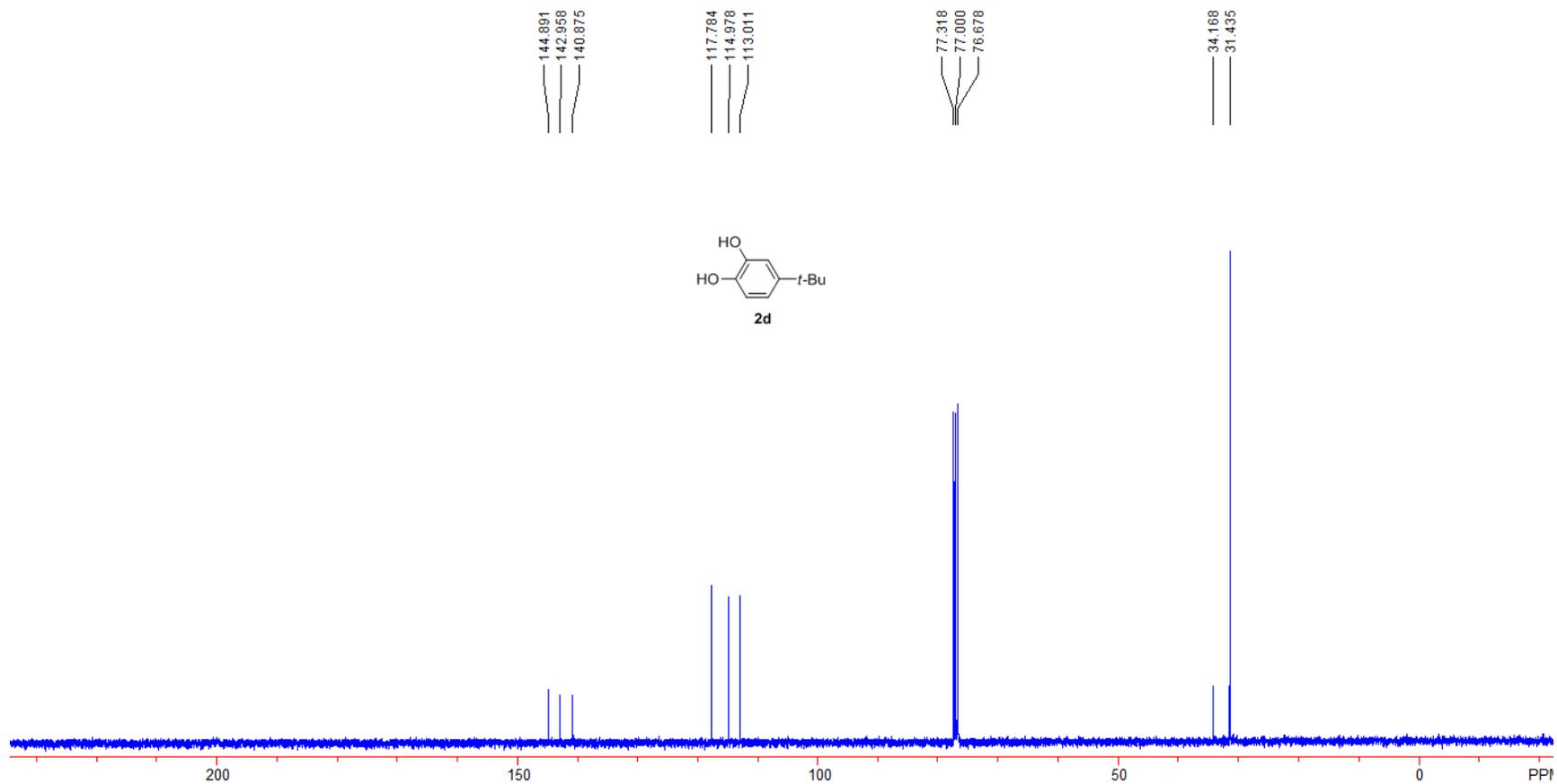










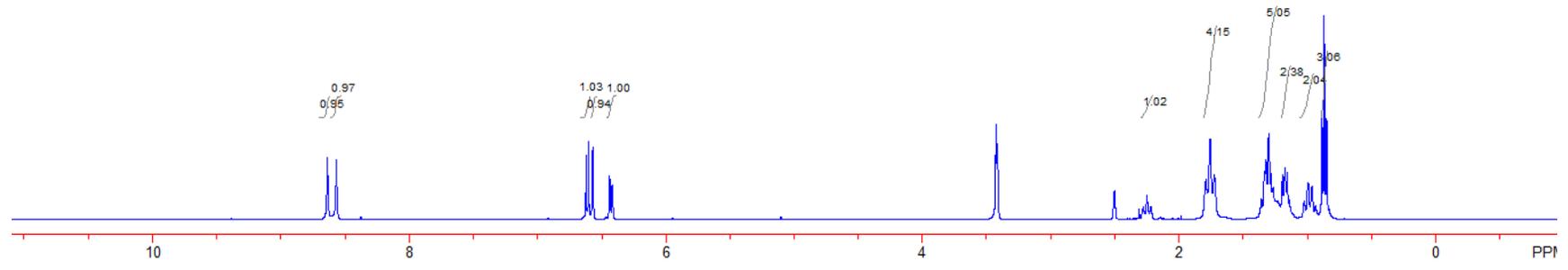
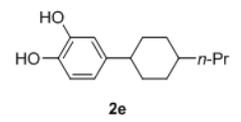


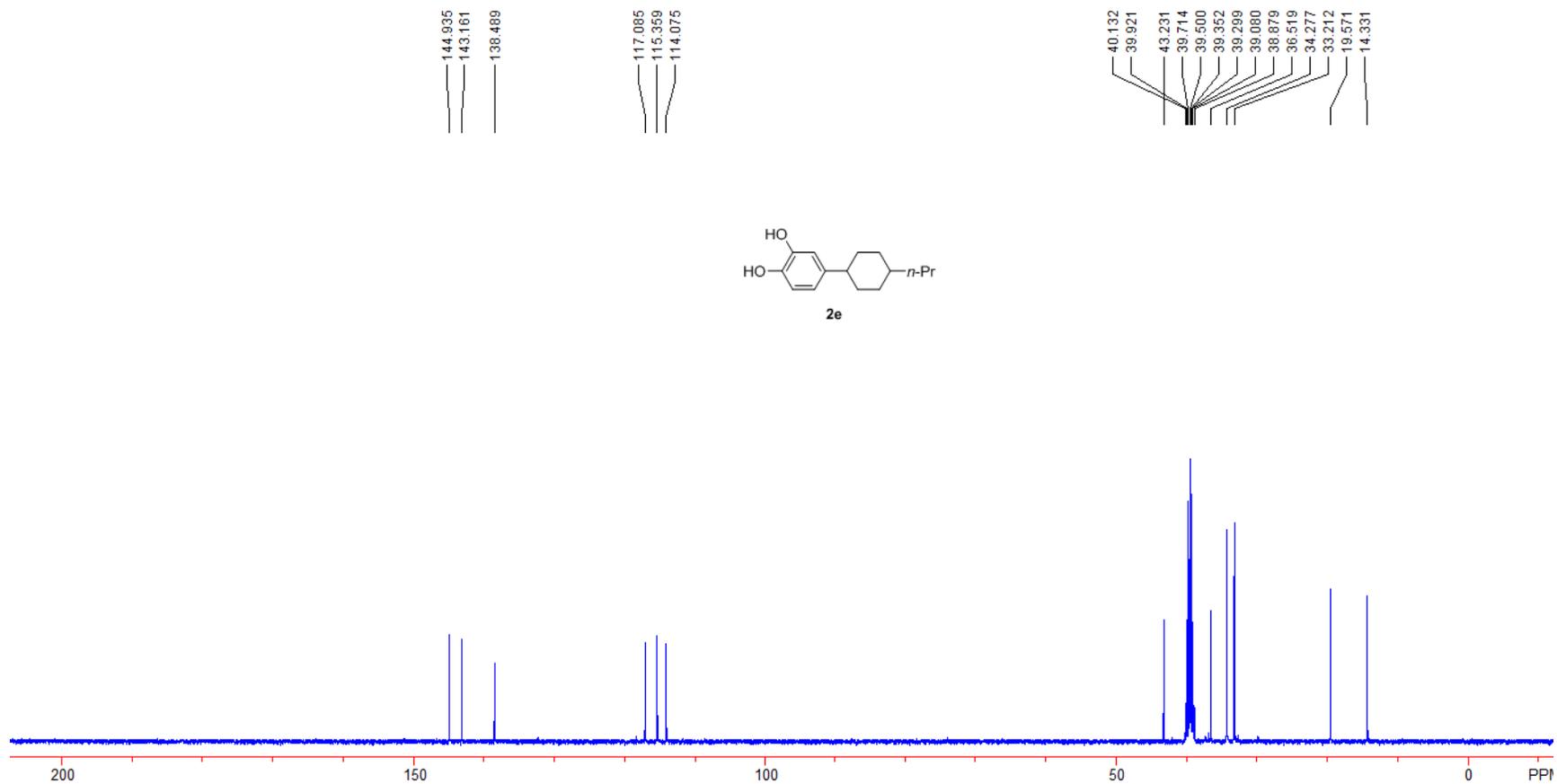
8.638  
8.567

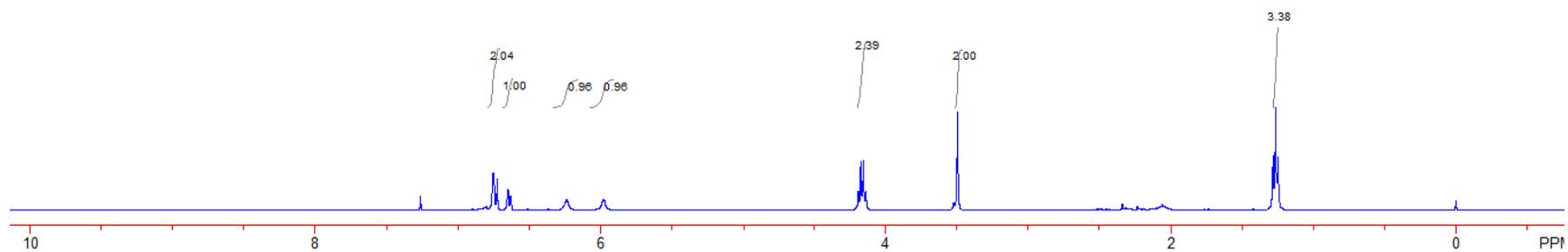
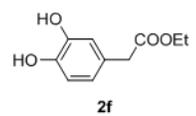
6.623  
6.603  
6.574  
6.569  
6.441  
6.436  
6.420  
6.416

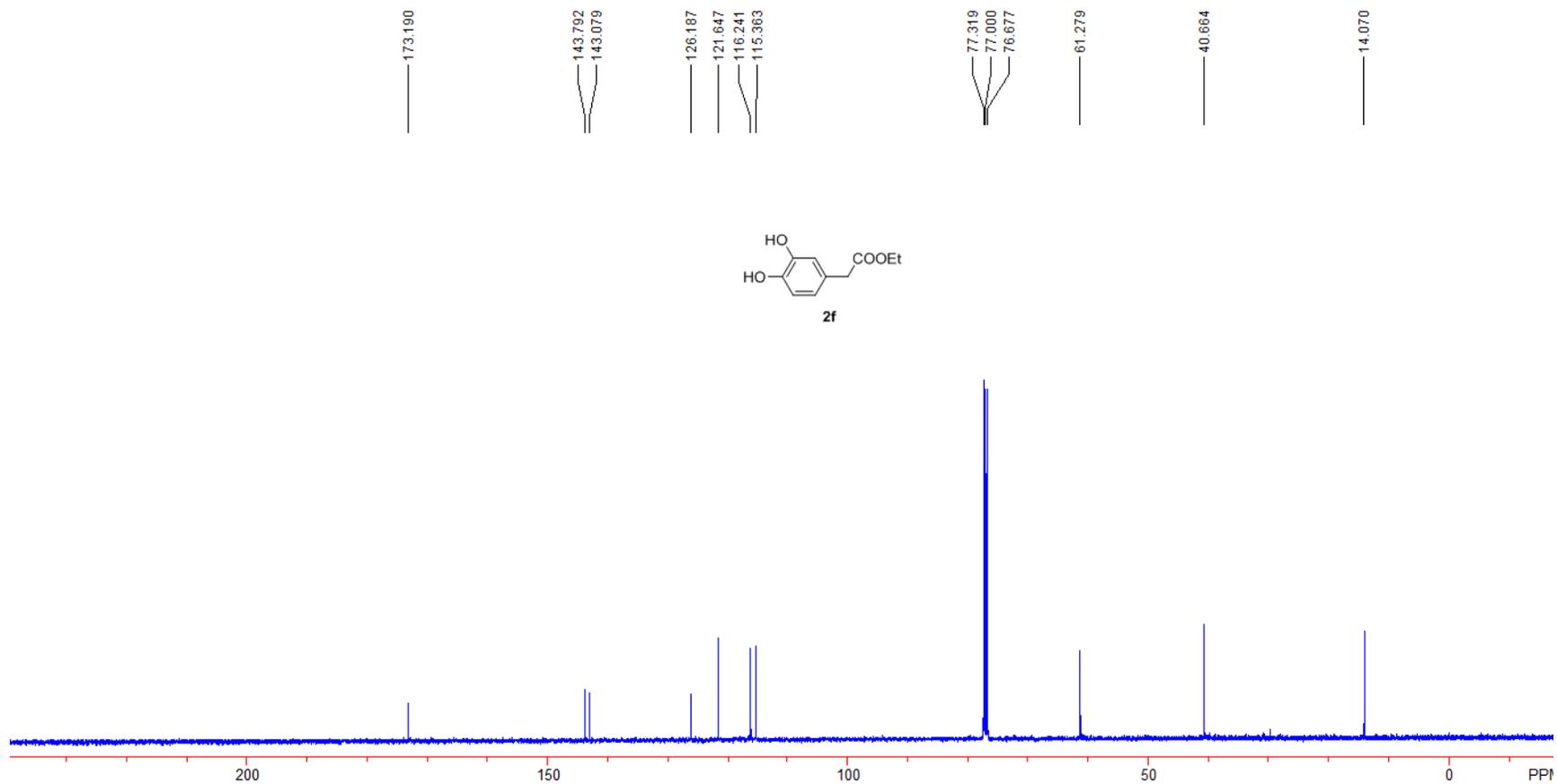
3.424

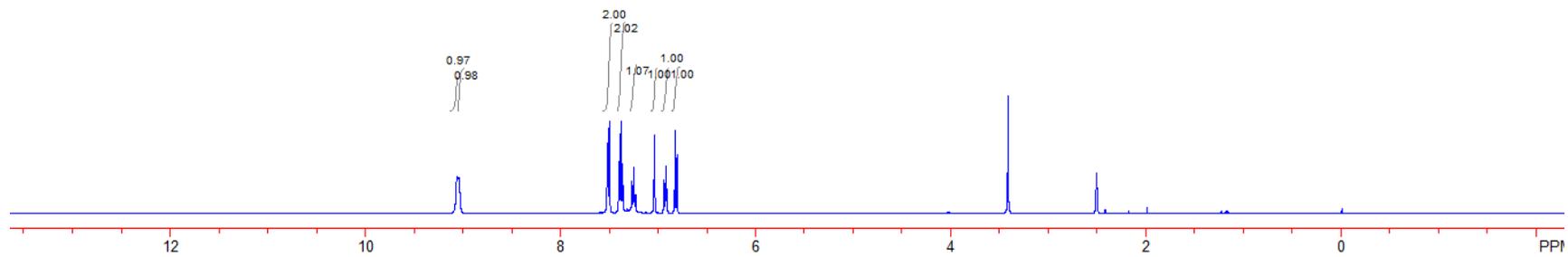
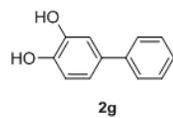
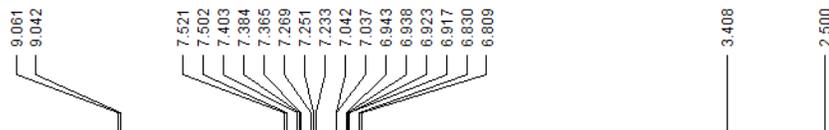
2.277  
2.247  
2.500  
2.217  
1.788  
1.756  
1.723  
1.355  
1.320  
1.289  
1.261  
1.262  
1.192  
1.179  
1.154  
1.139  
1.020  
0.994  
0.961  
0.884  
0.866  
0.848

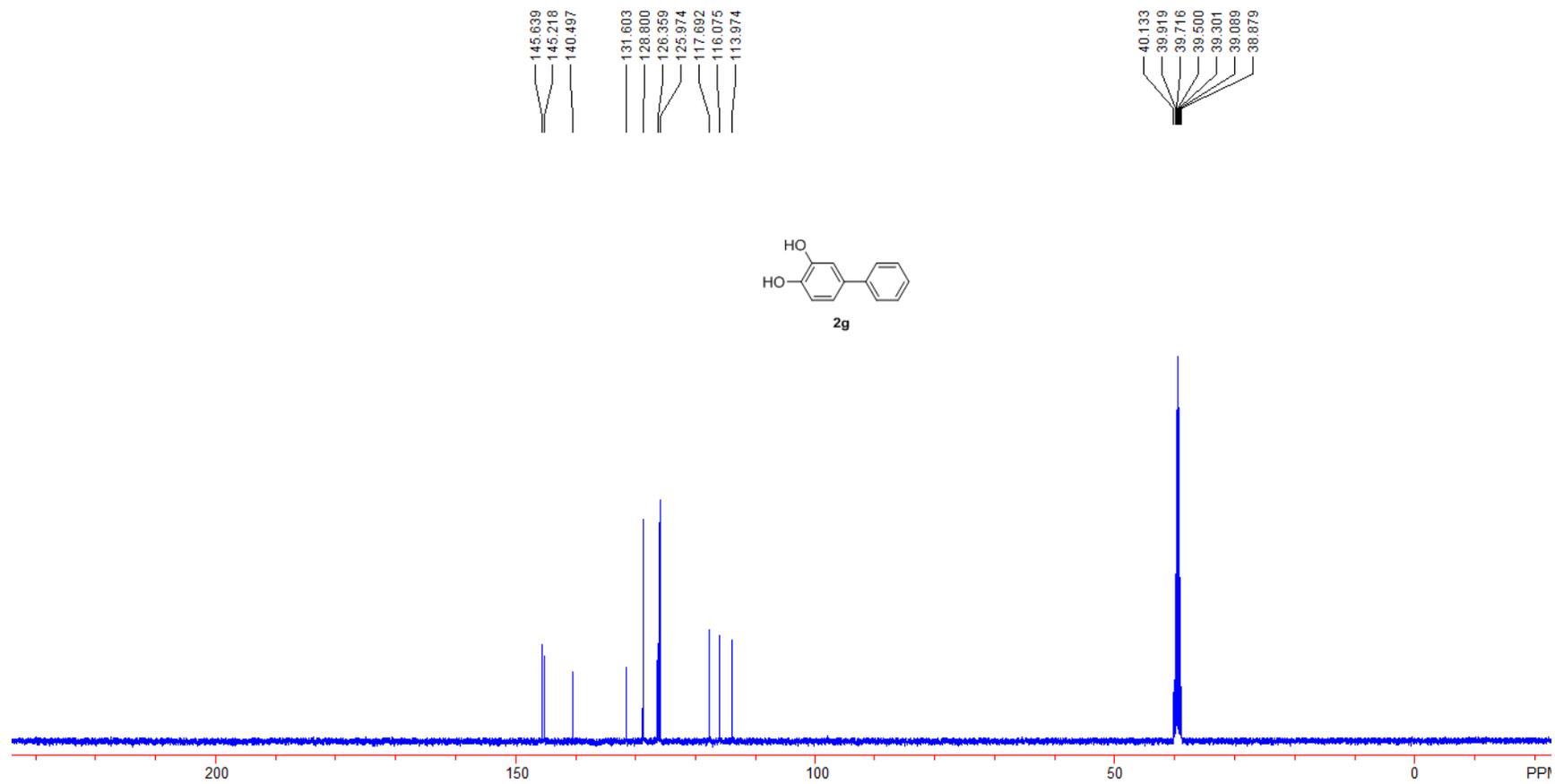


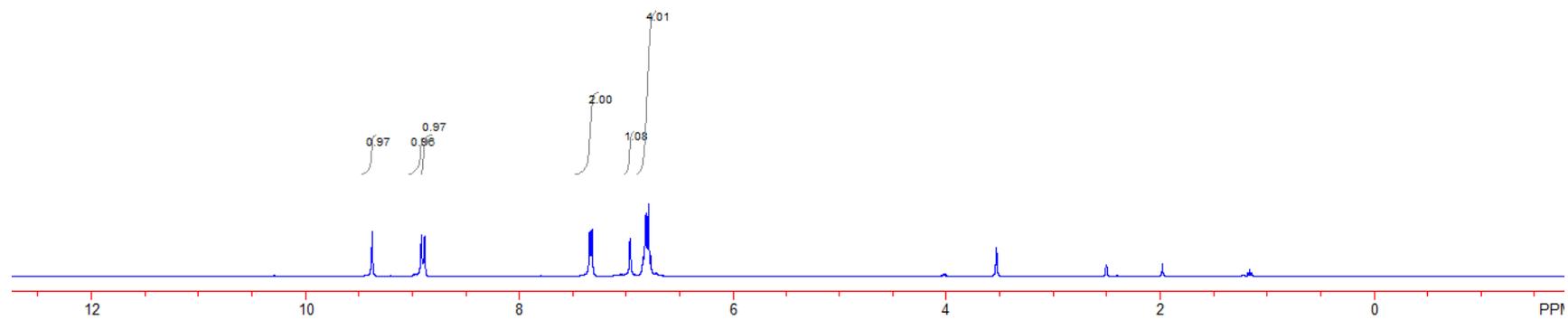
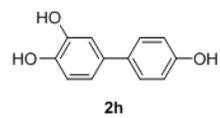
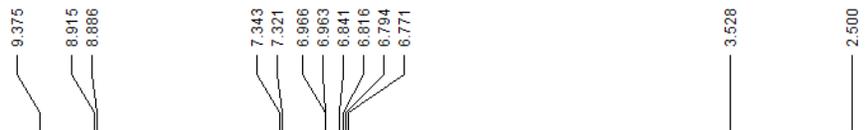


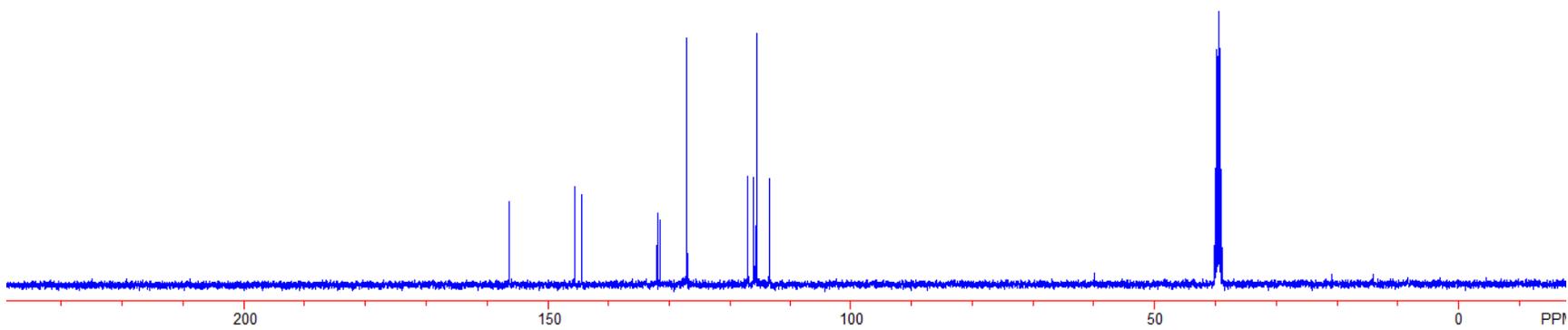
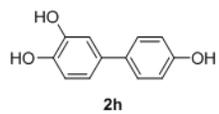


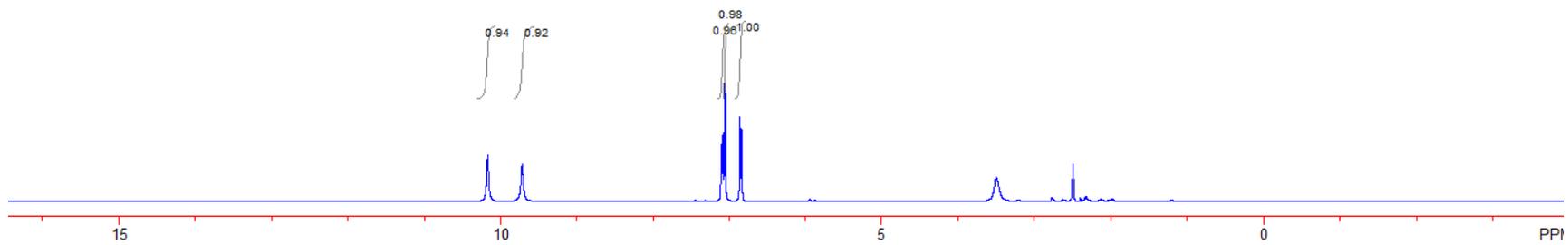
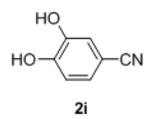
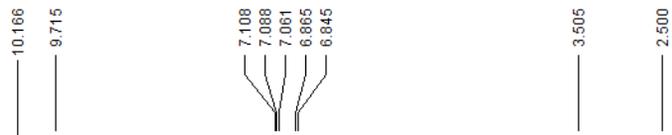










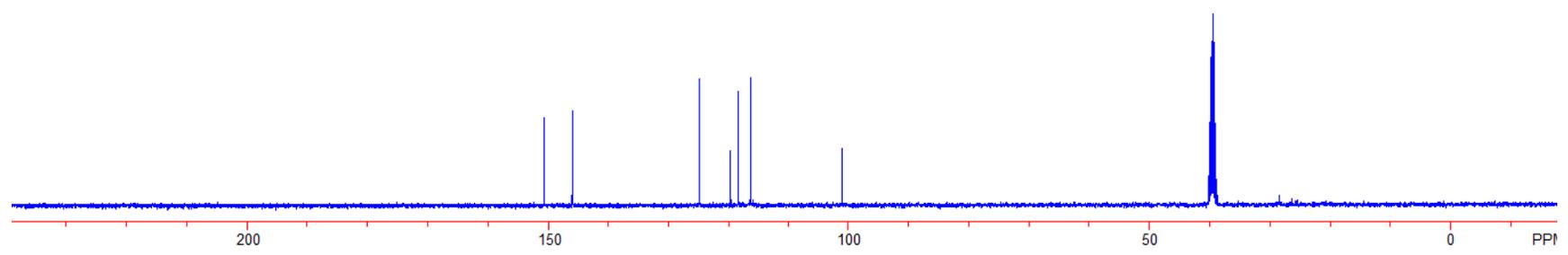
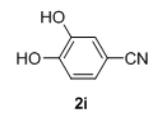


150.631  
145.993

124.901  
119.712  
118.429  
116.412

100.978

39.912  
39.712  
39.500  
39.289  
39.082

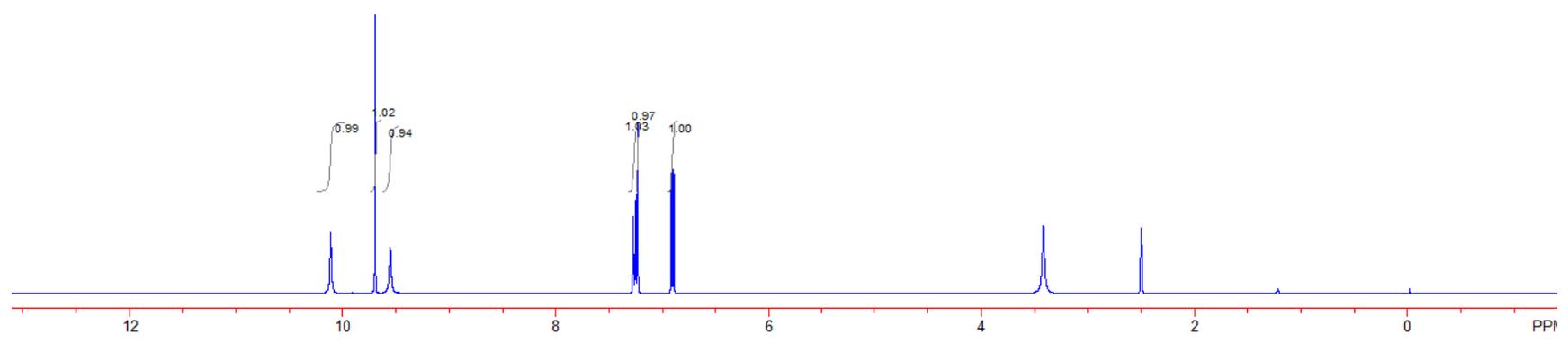
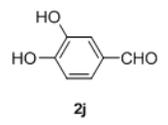


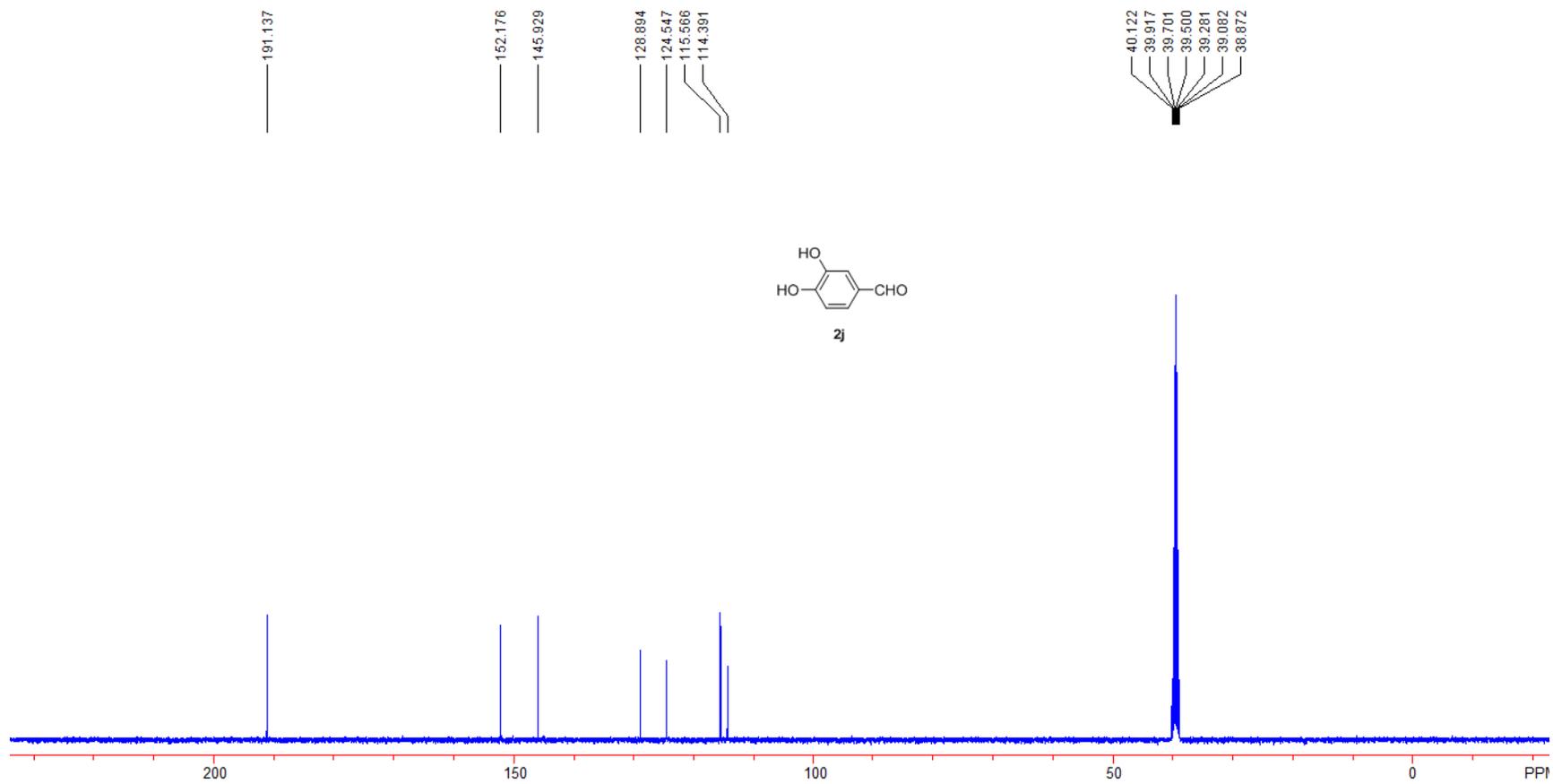
10.111  
9.694  
9.553

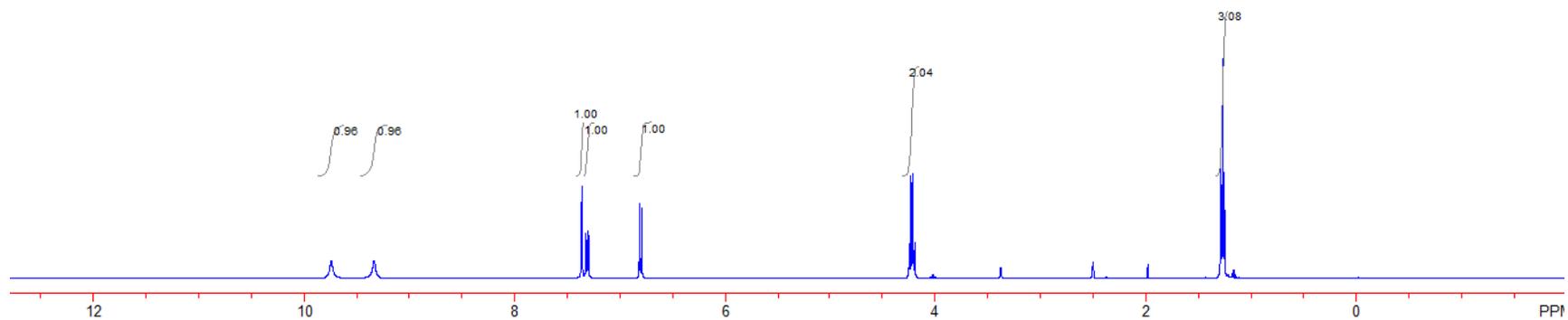
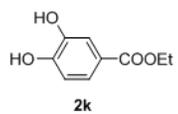
7.277  
7.273  
7.257  
7.253  
7.236  
7.231  
6.916  
6.896

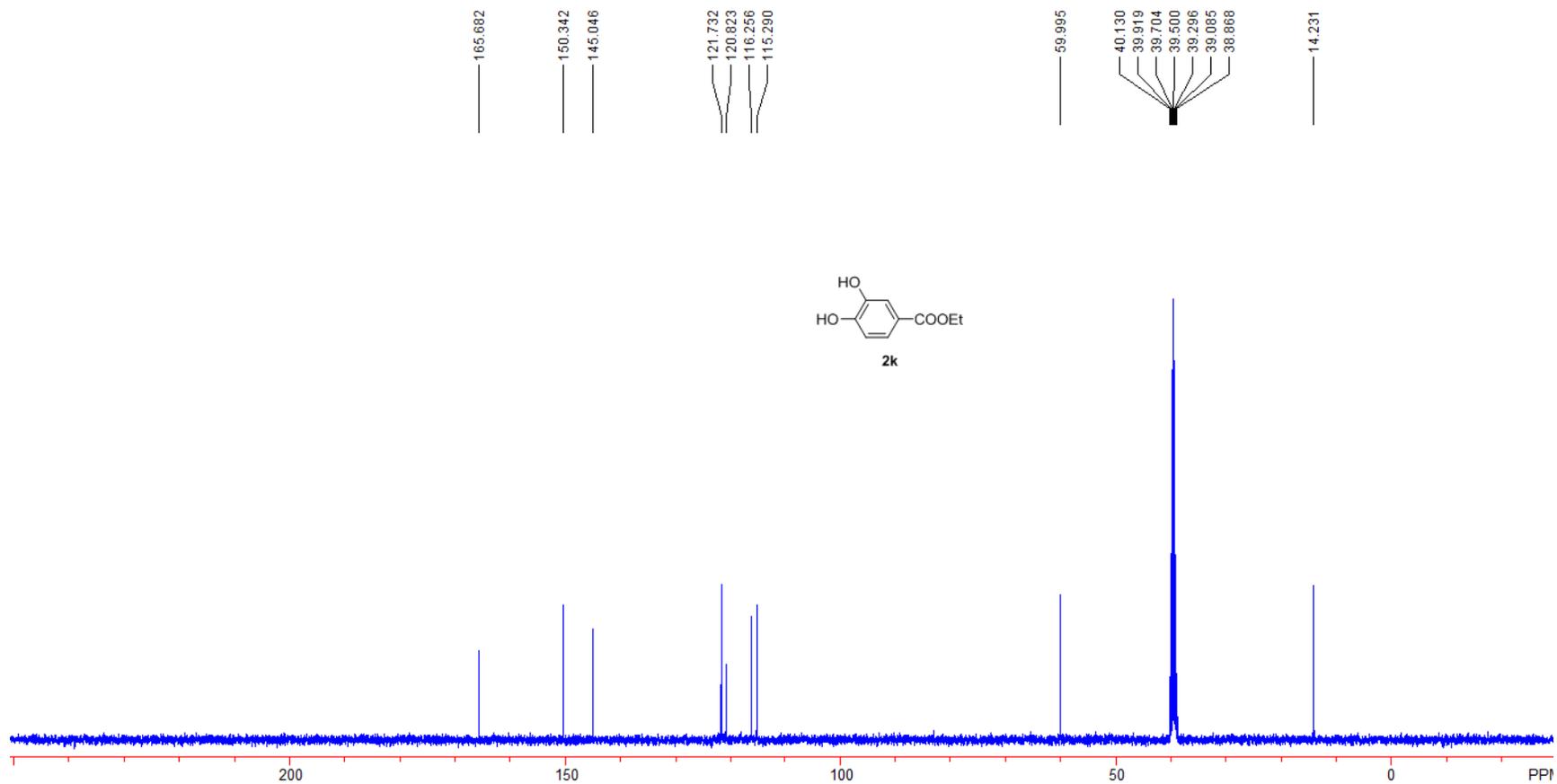
3.417

2.500









12.293

9.645

9.270

7.352

7.347

7.315

7.310

7.294

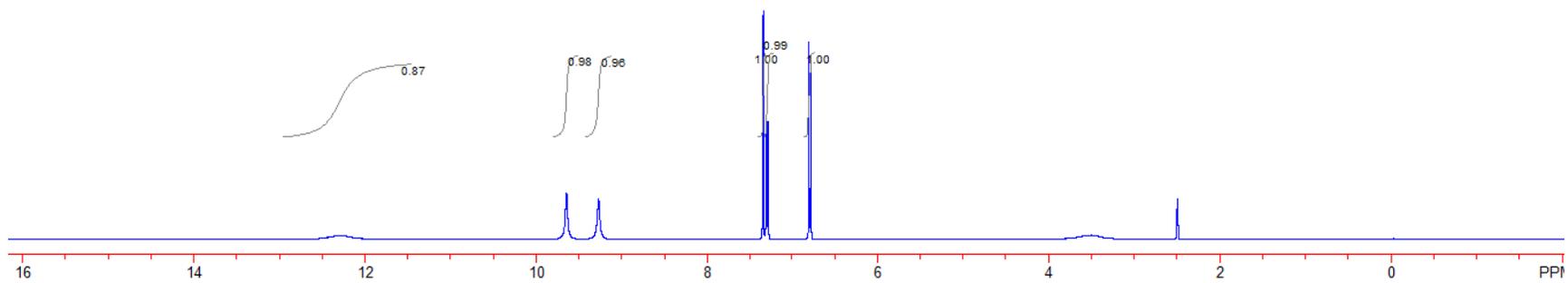
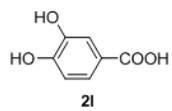
7.289

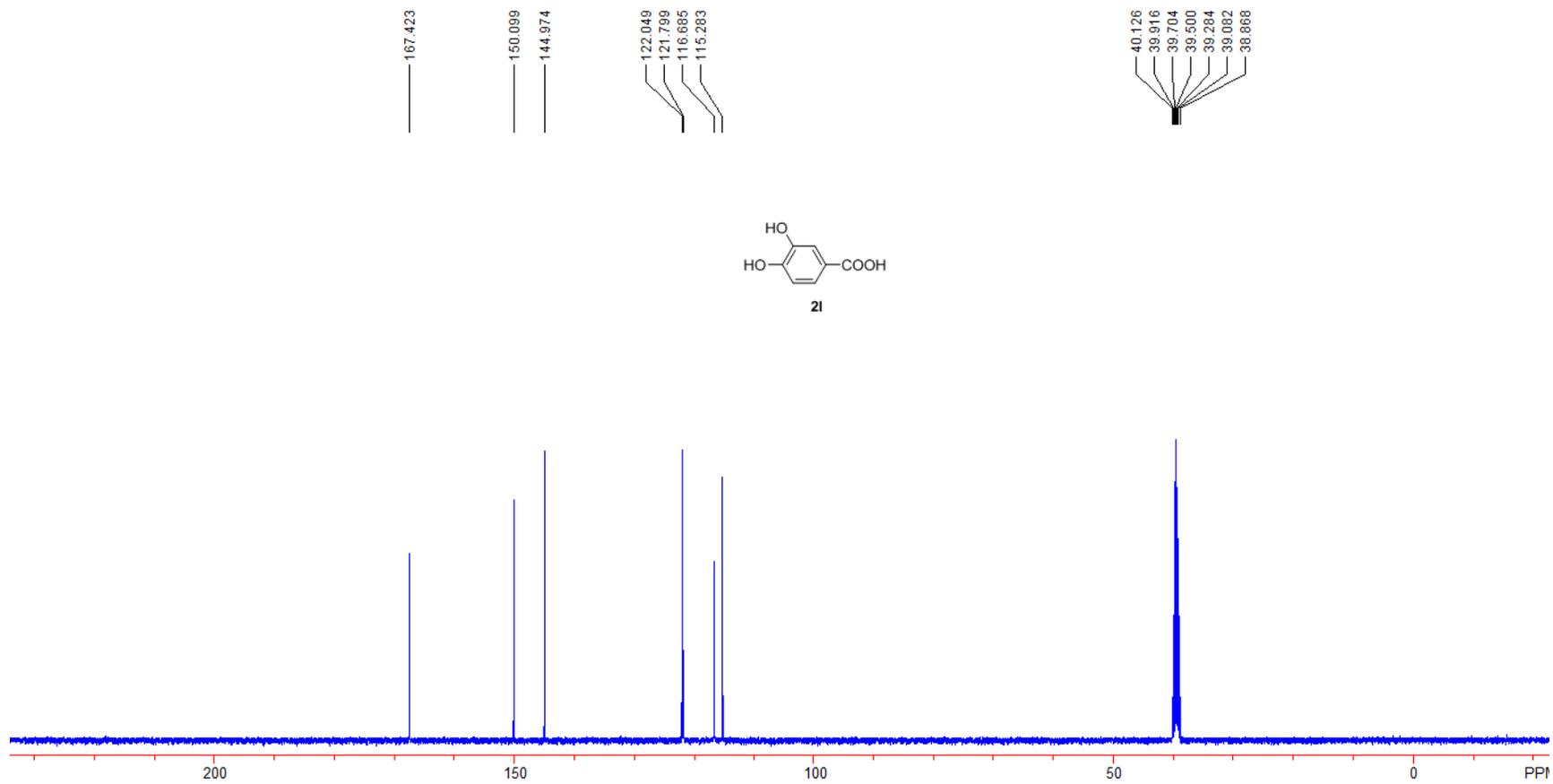
6.801

6.780

3.517

2.500





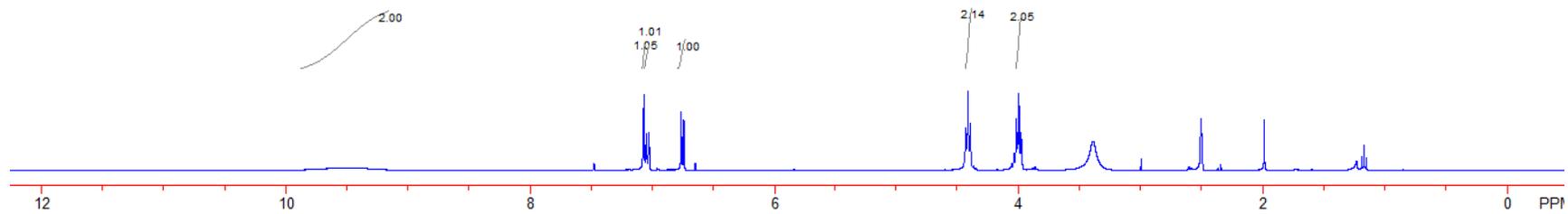
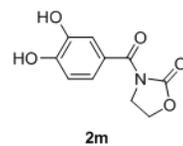
9.492

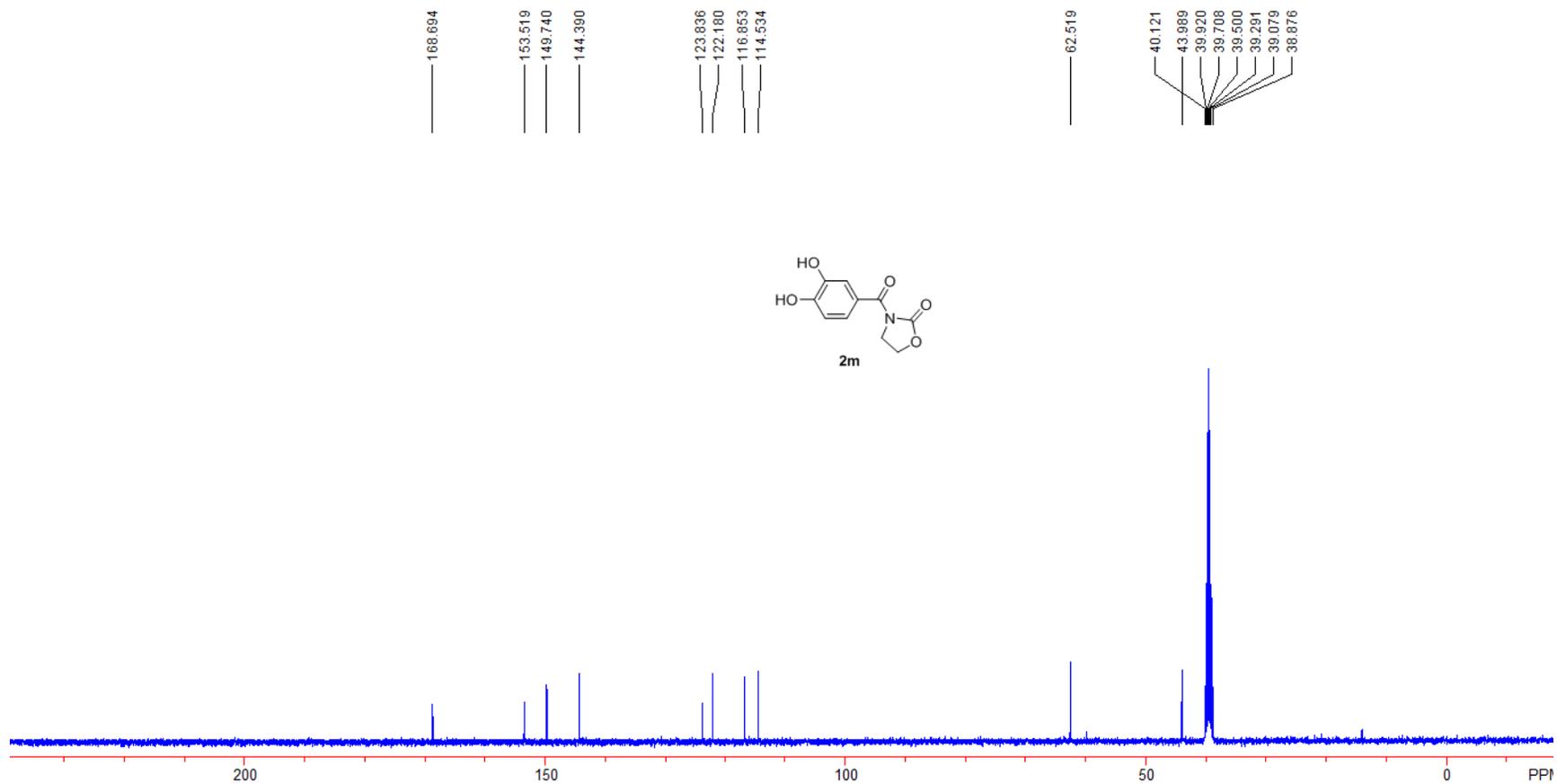
7.074  
7.069  
7.051  
7.046  
7.030  
7.025  
6.763  
6.743

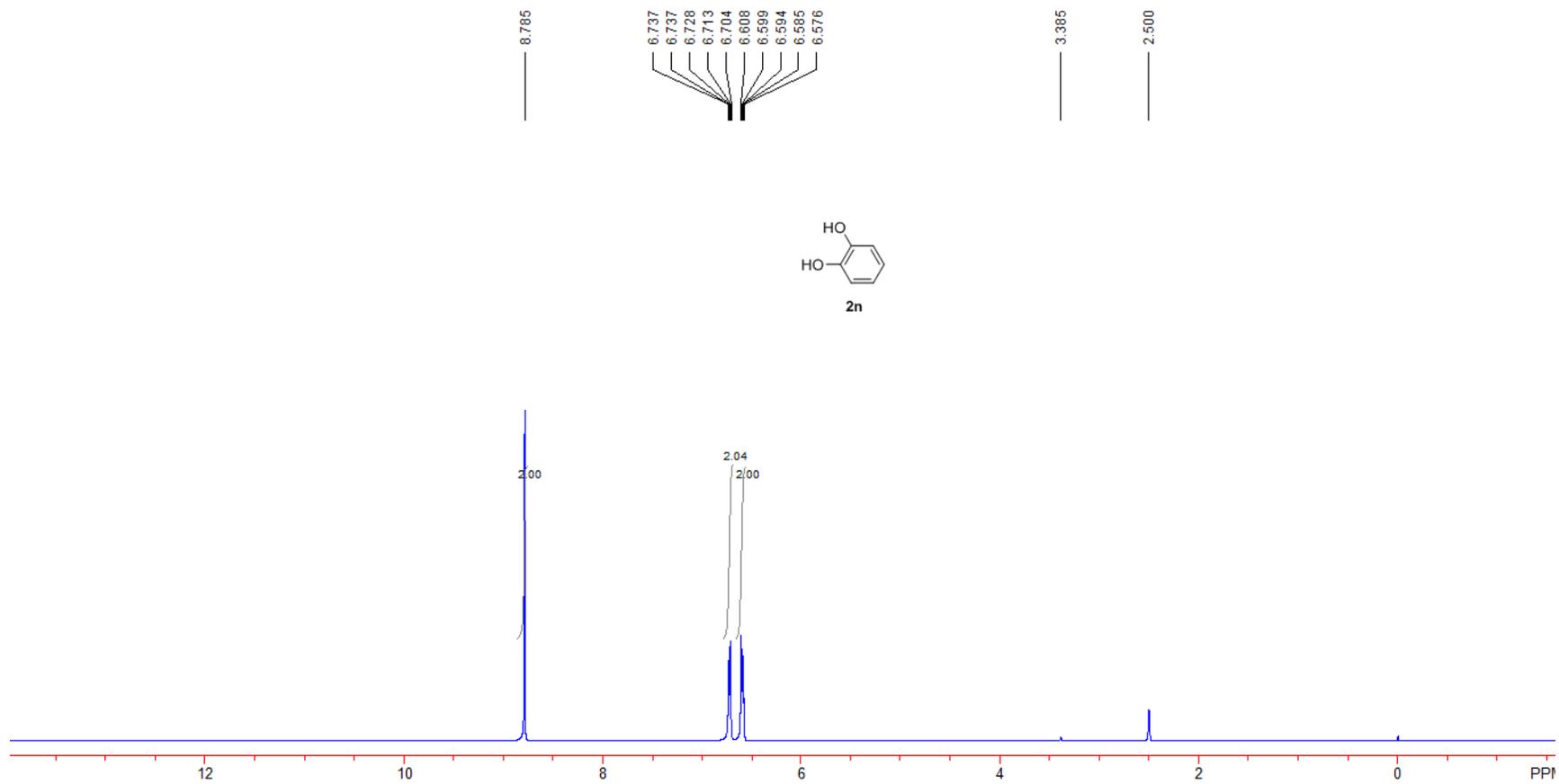
4.427  
4.408  
4.389  
4.011  
3.992  
3.973

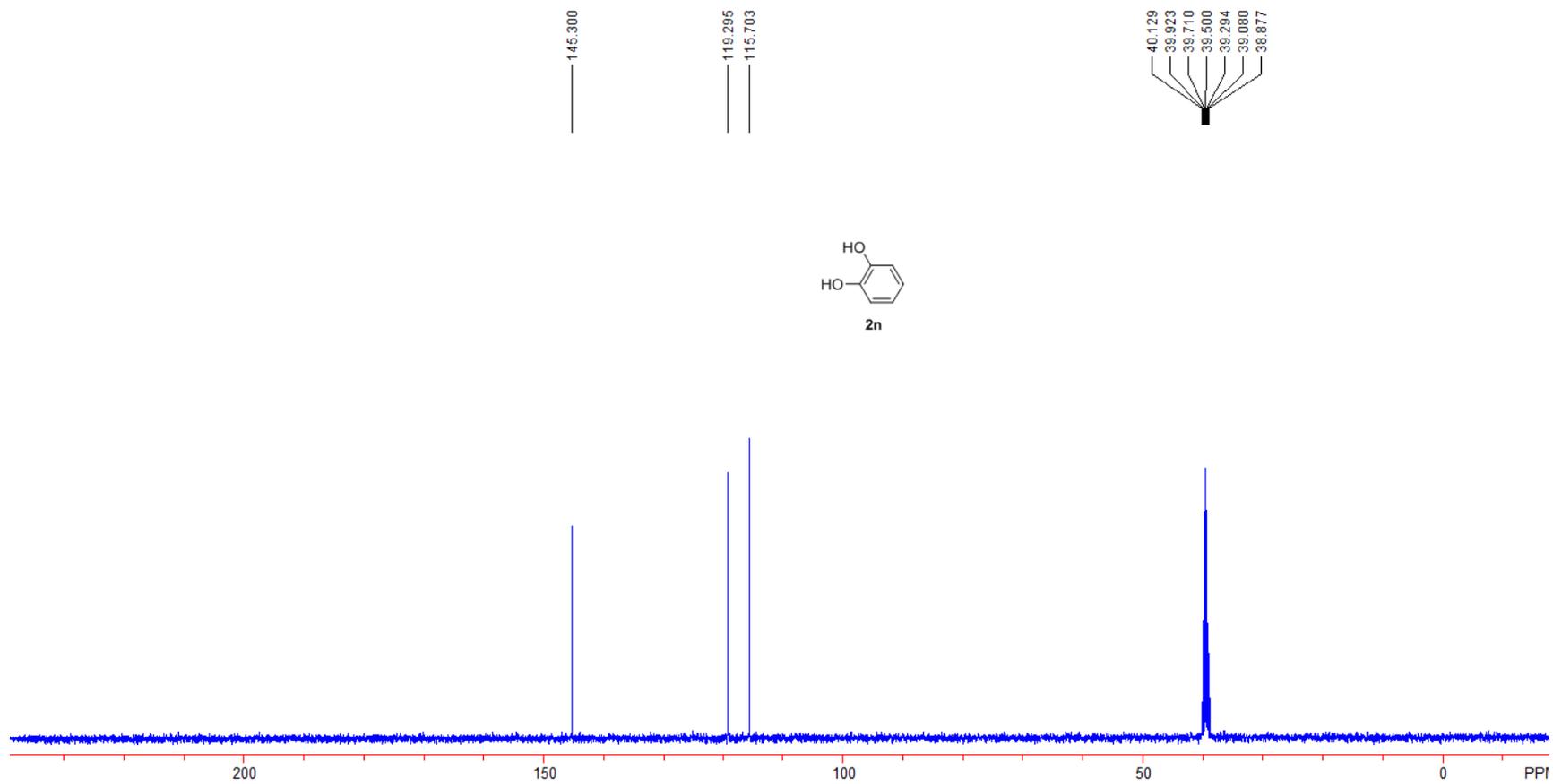
3.384

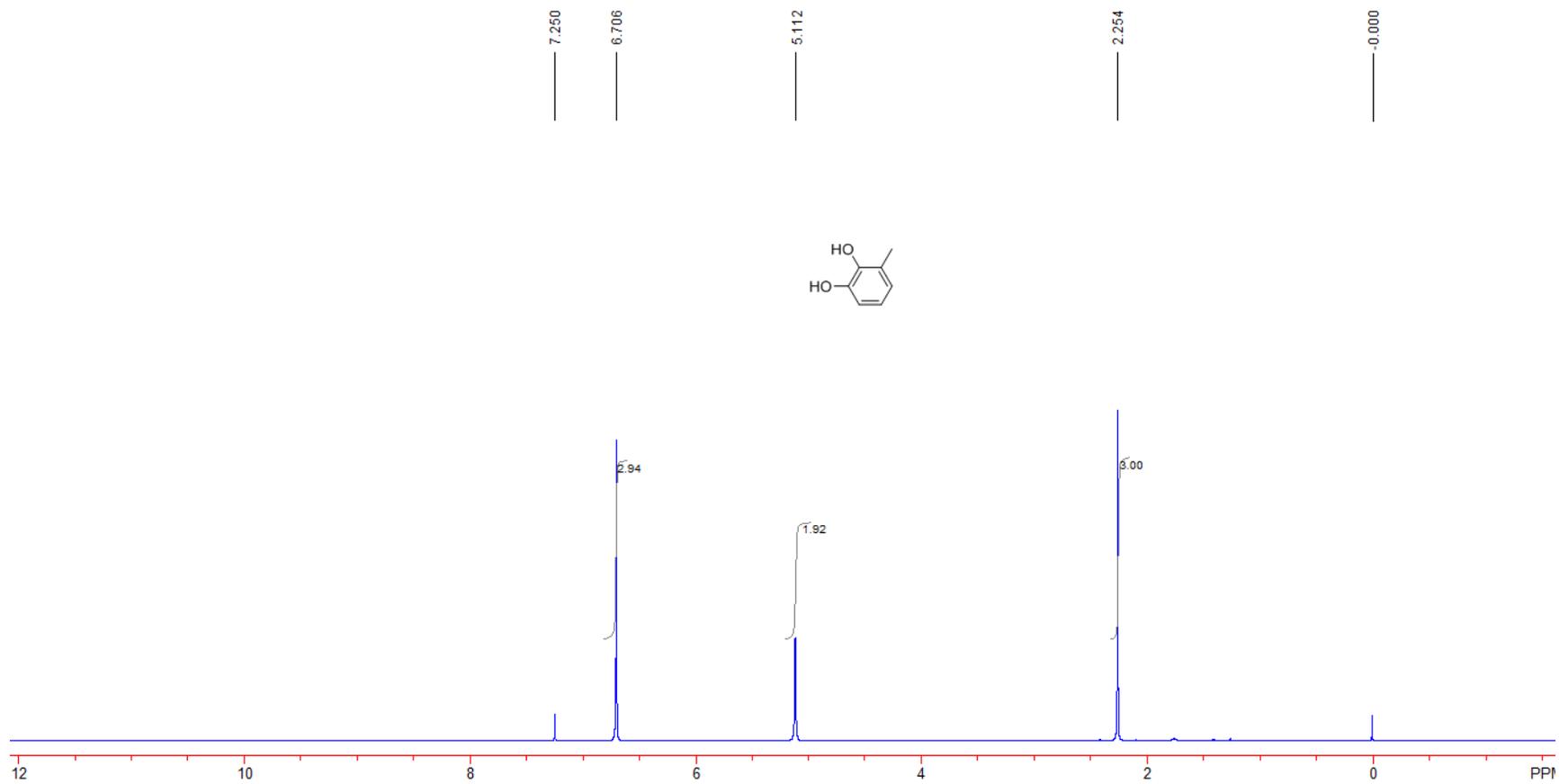
2.500

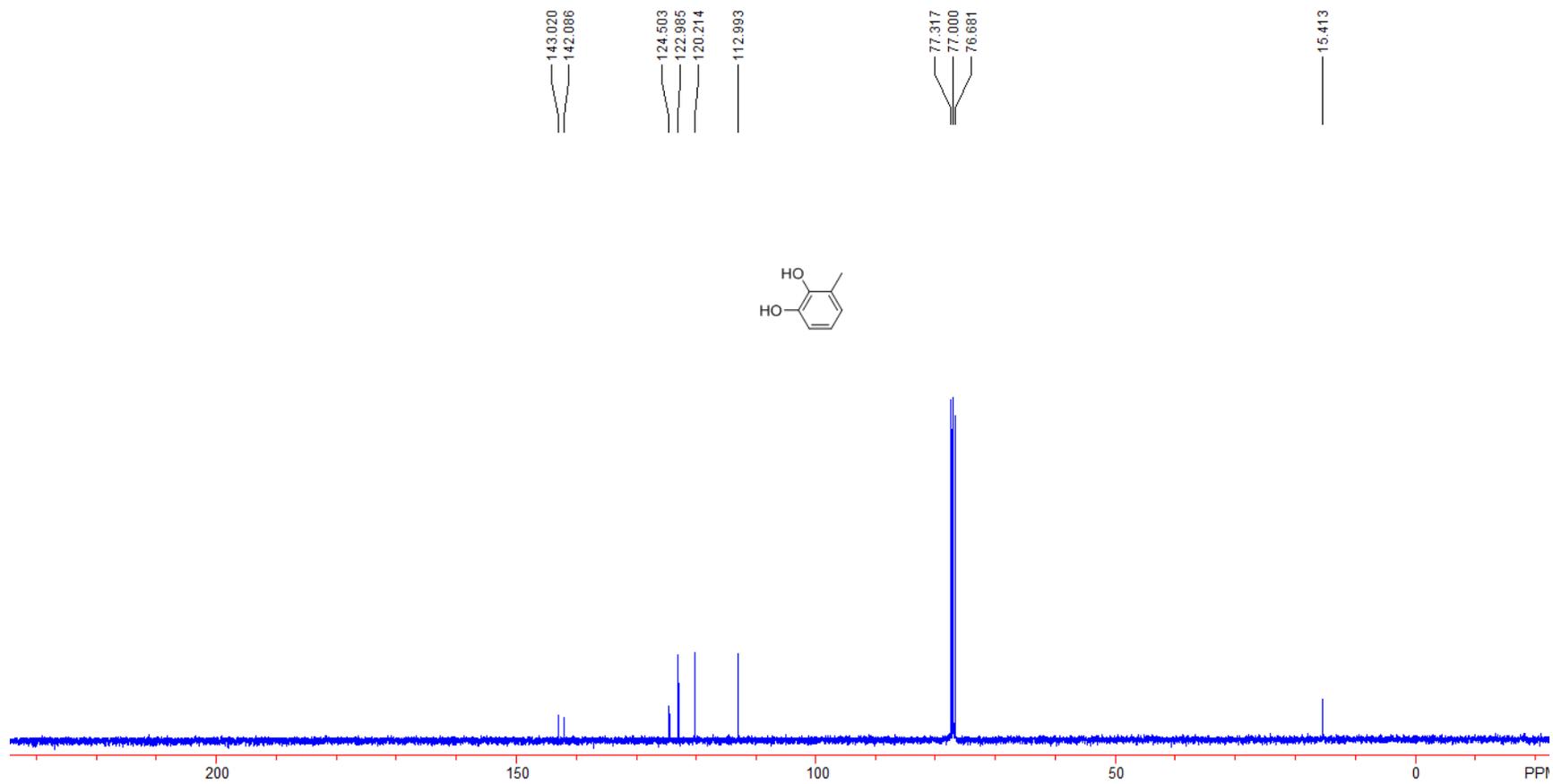


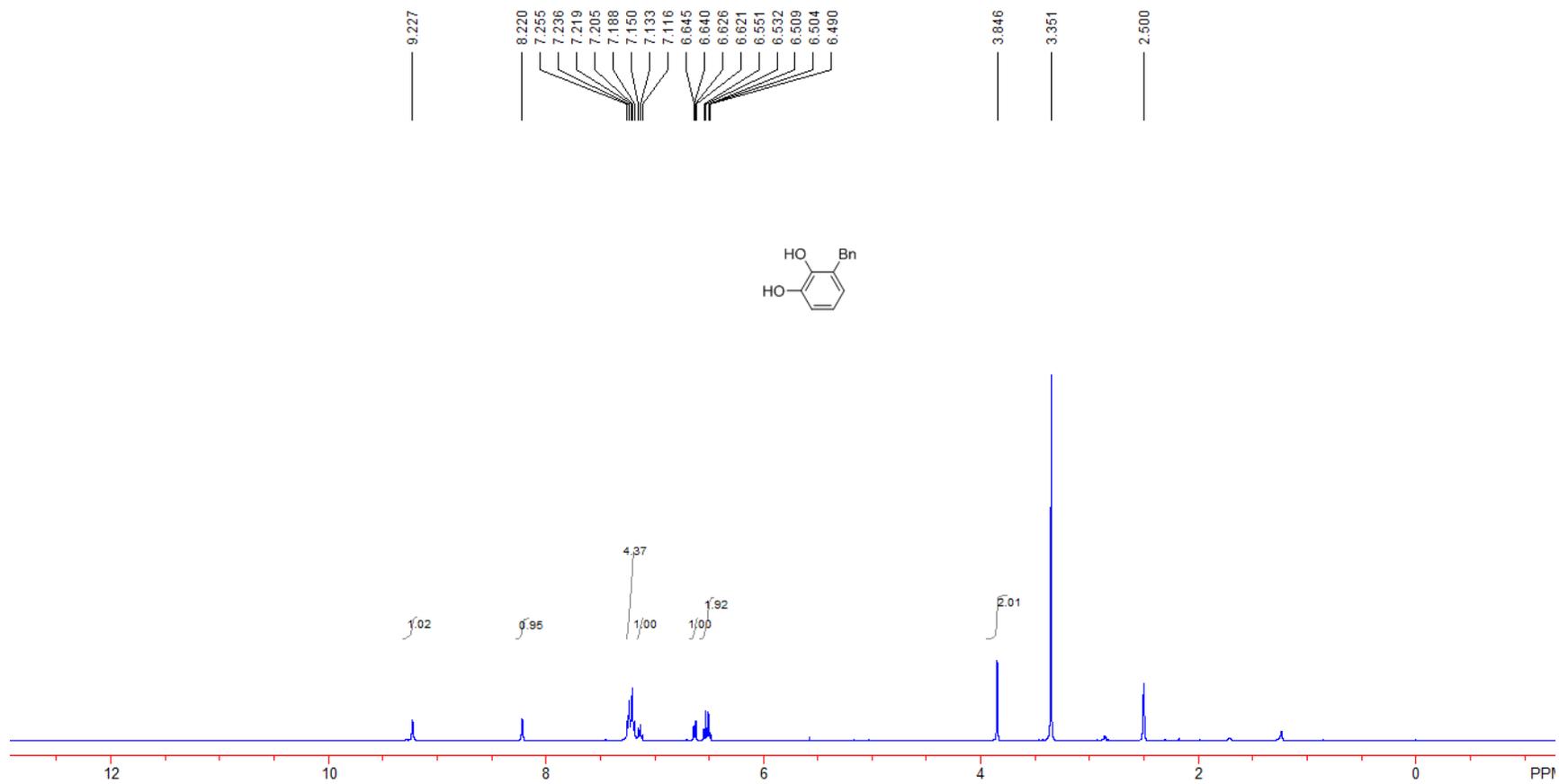


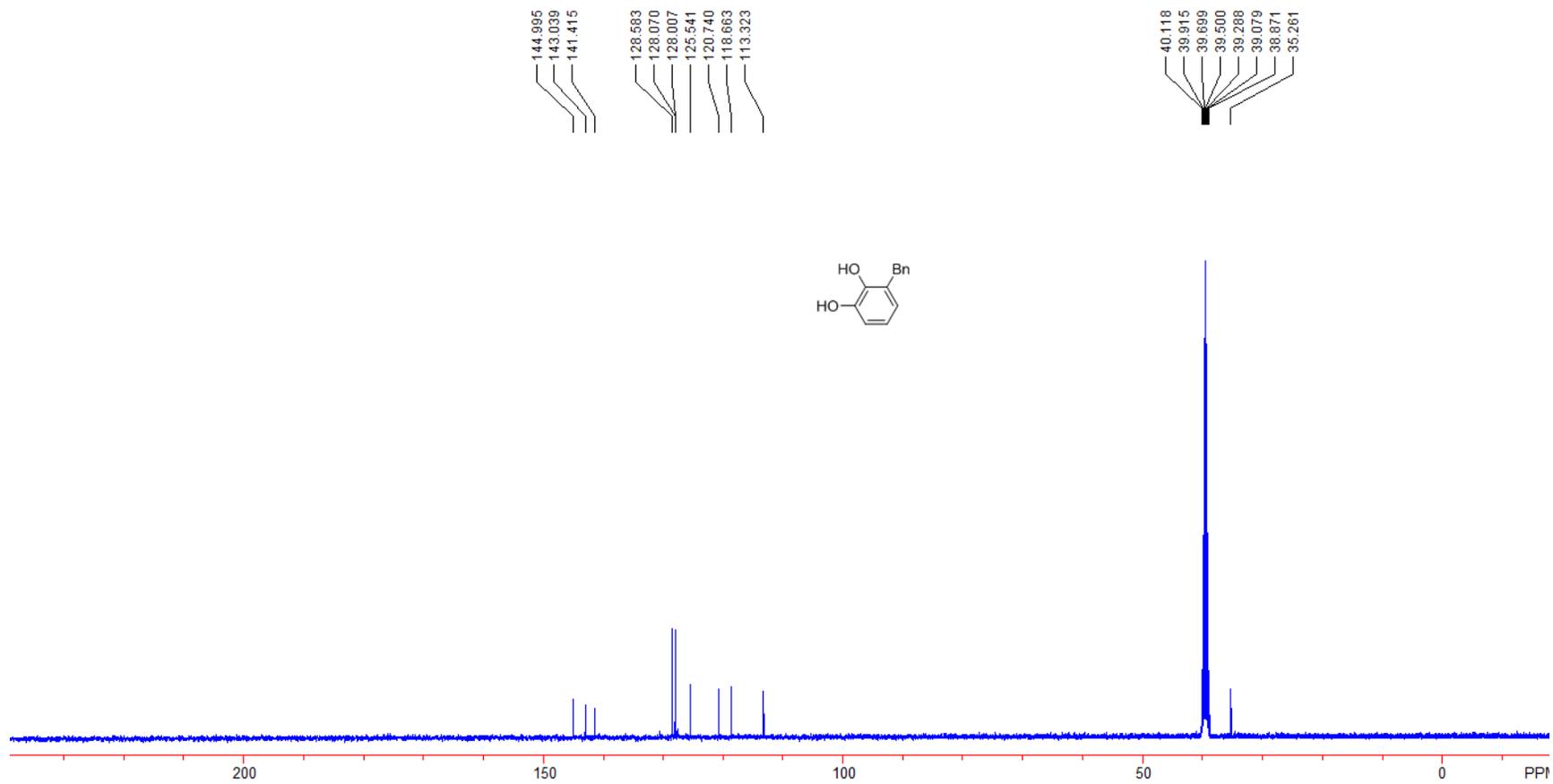


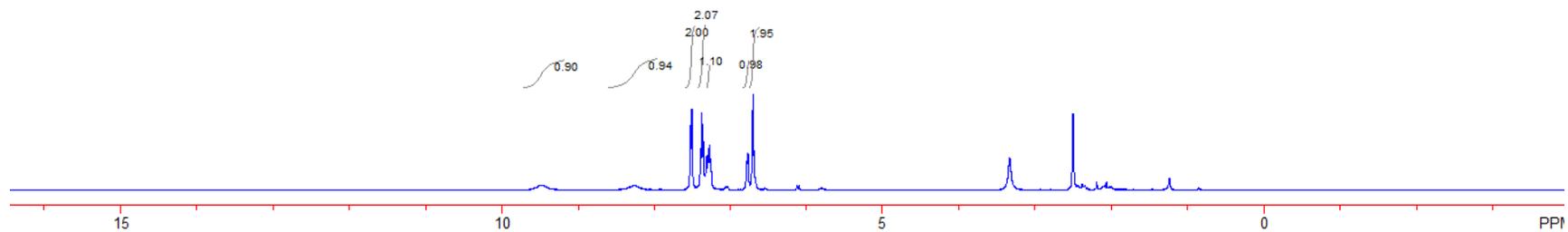
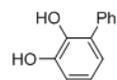
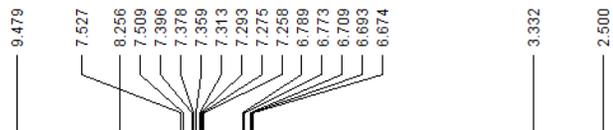


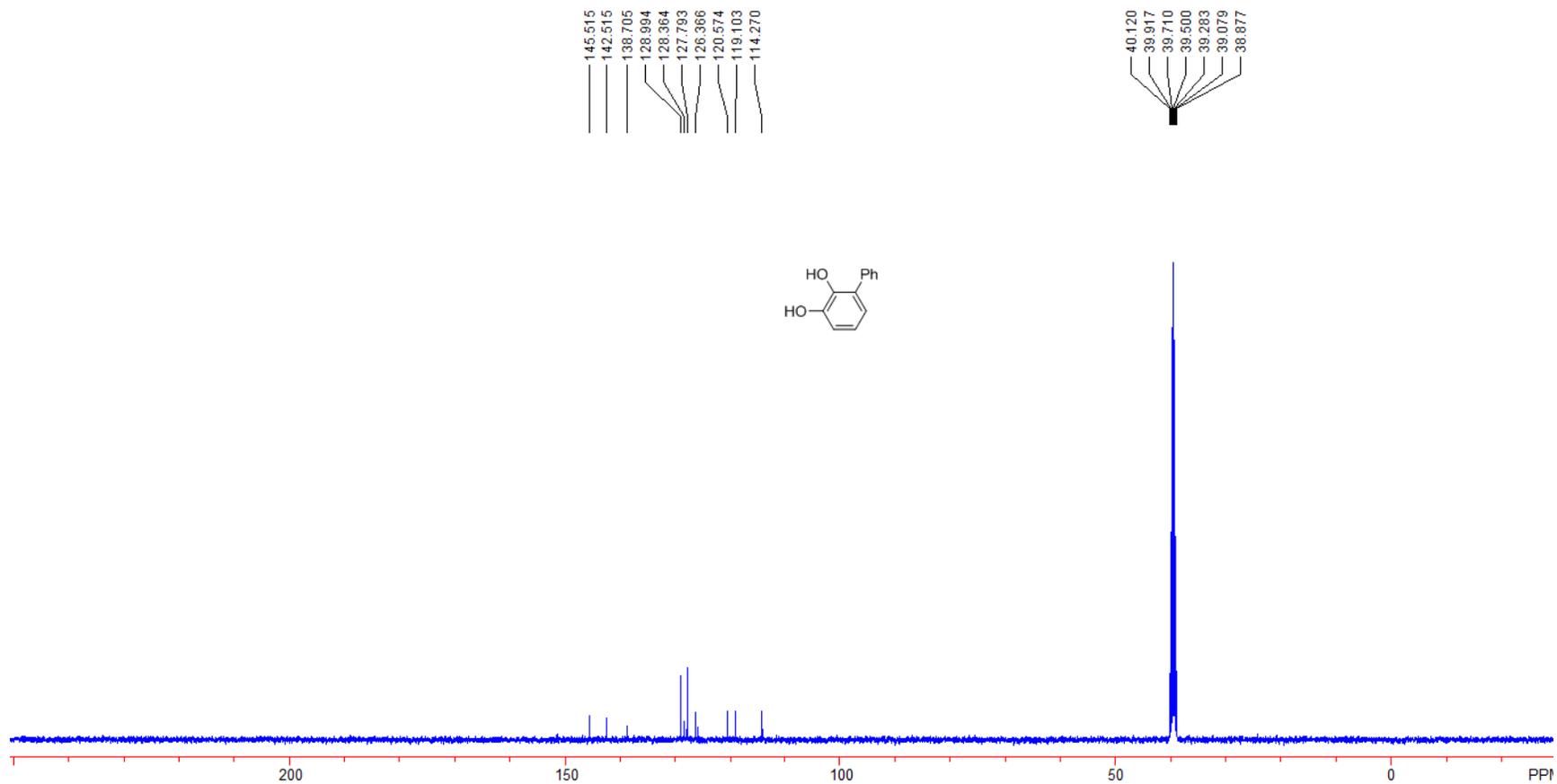


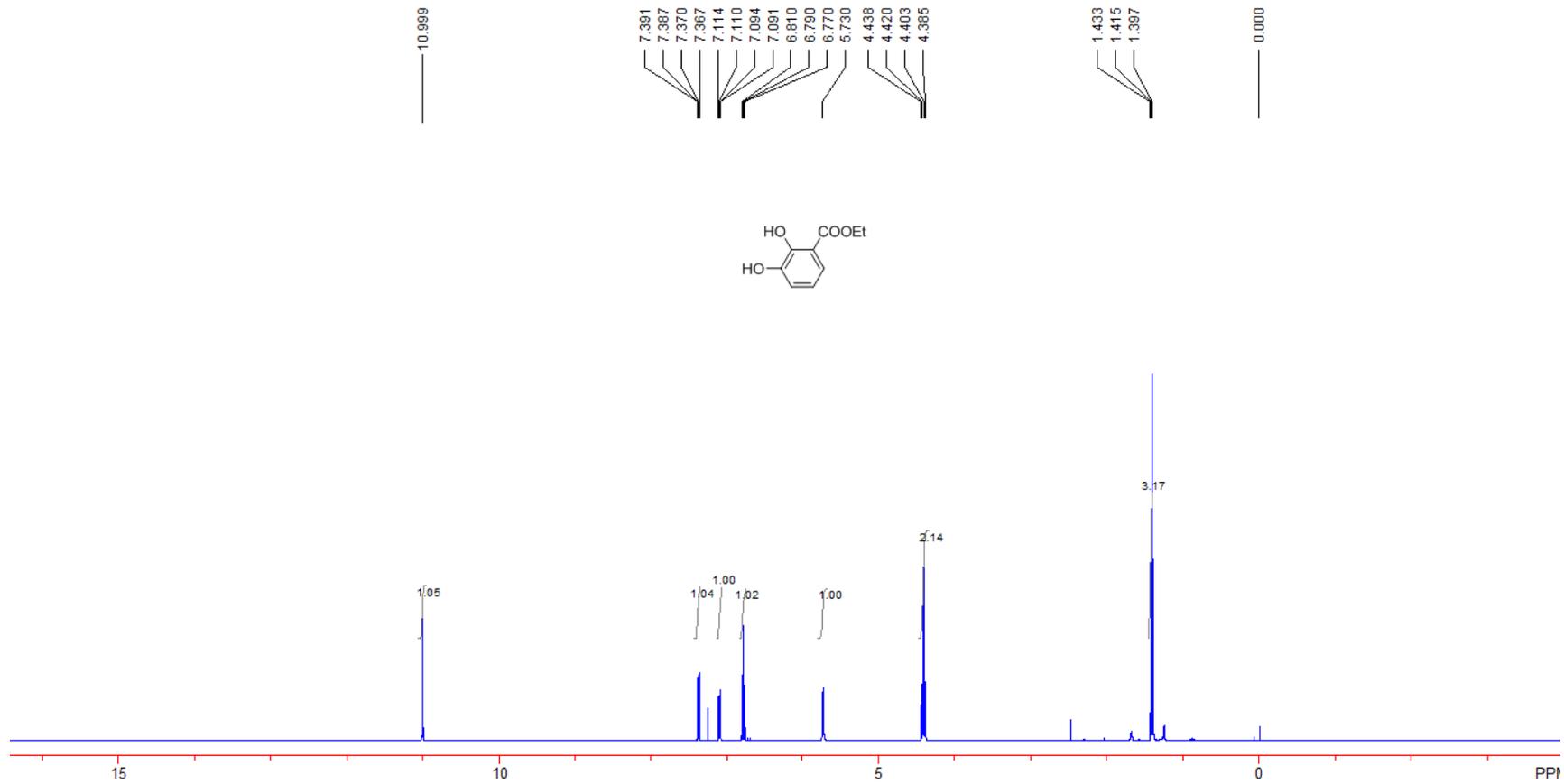


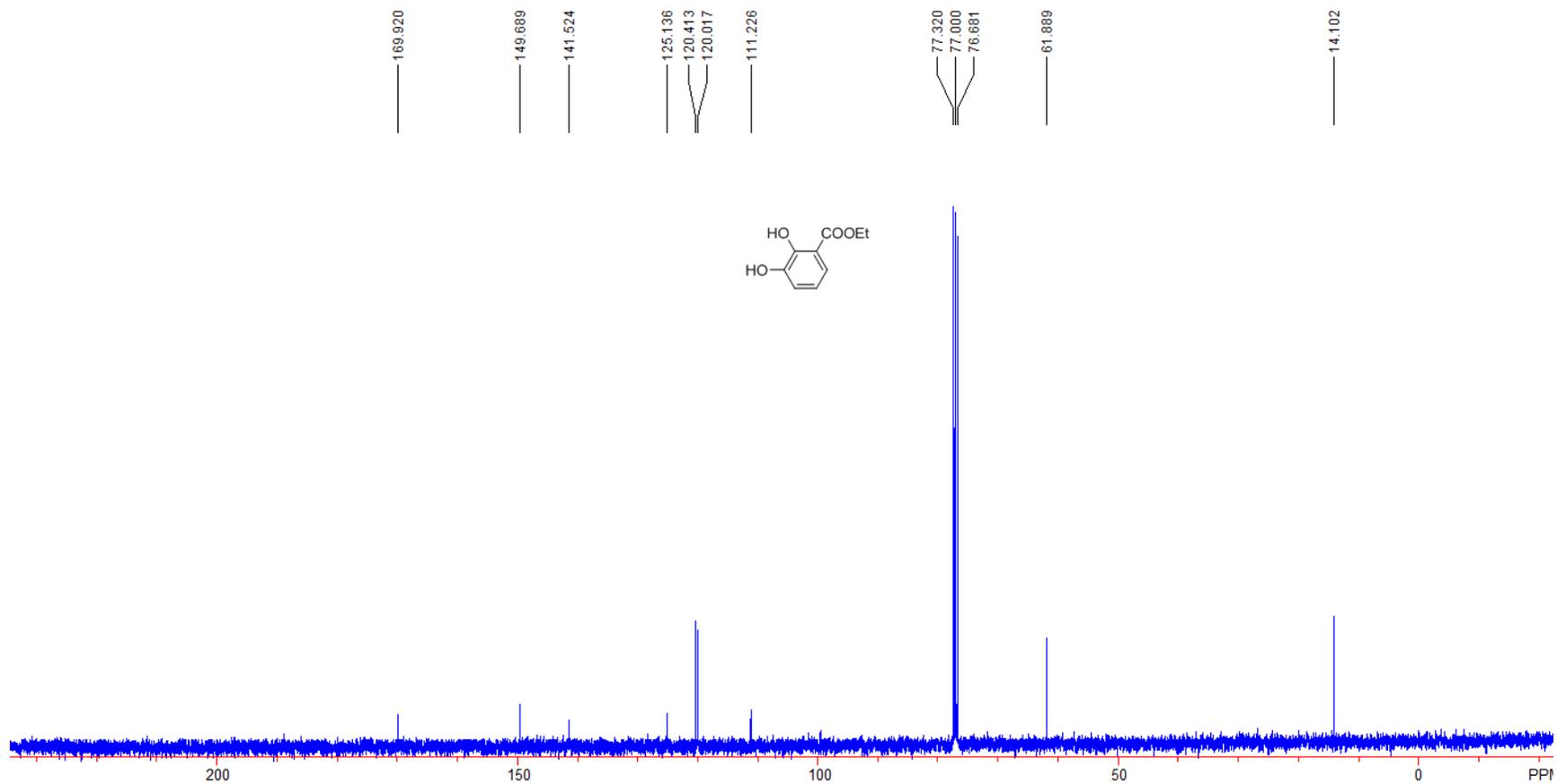


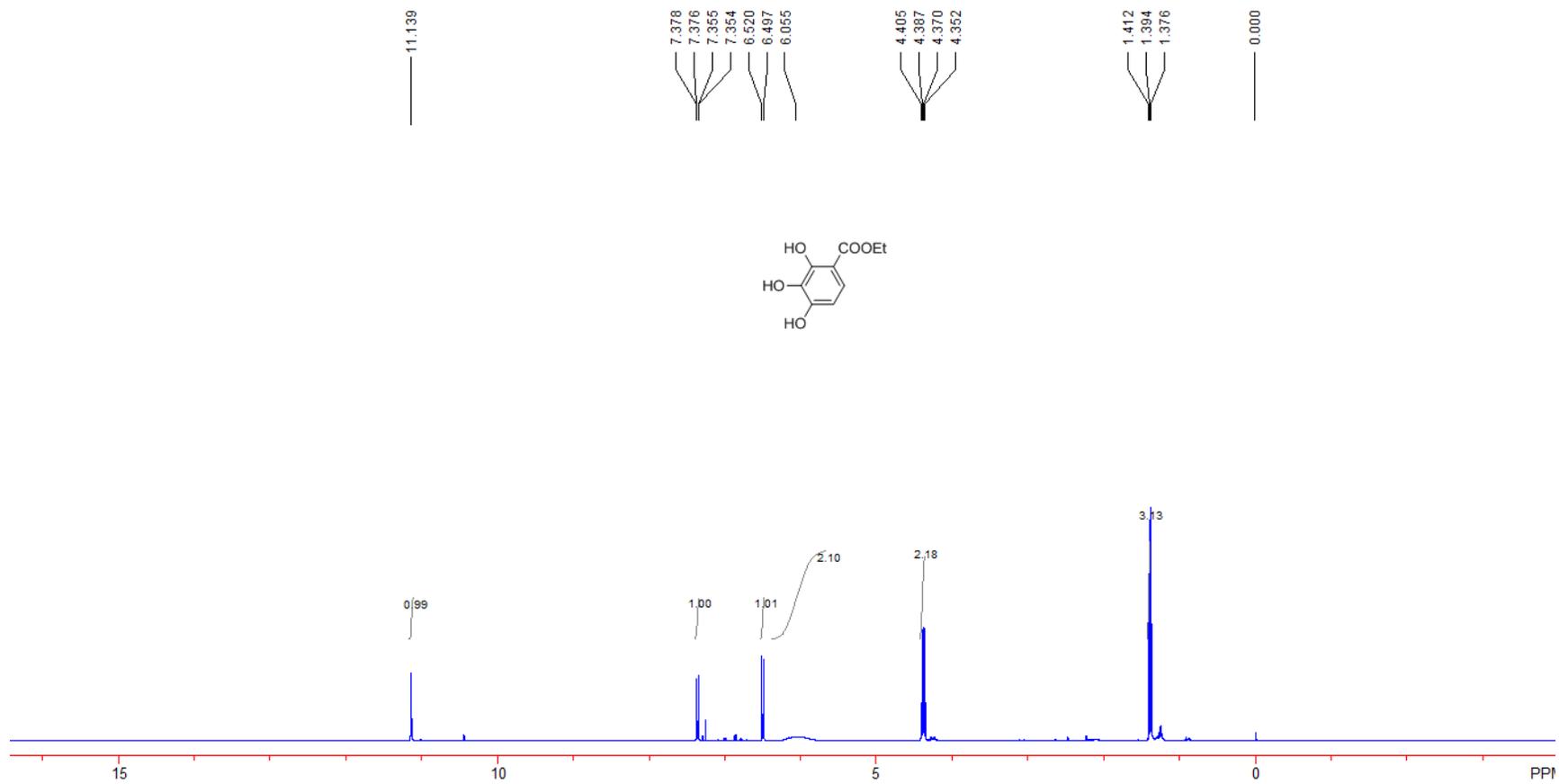


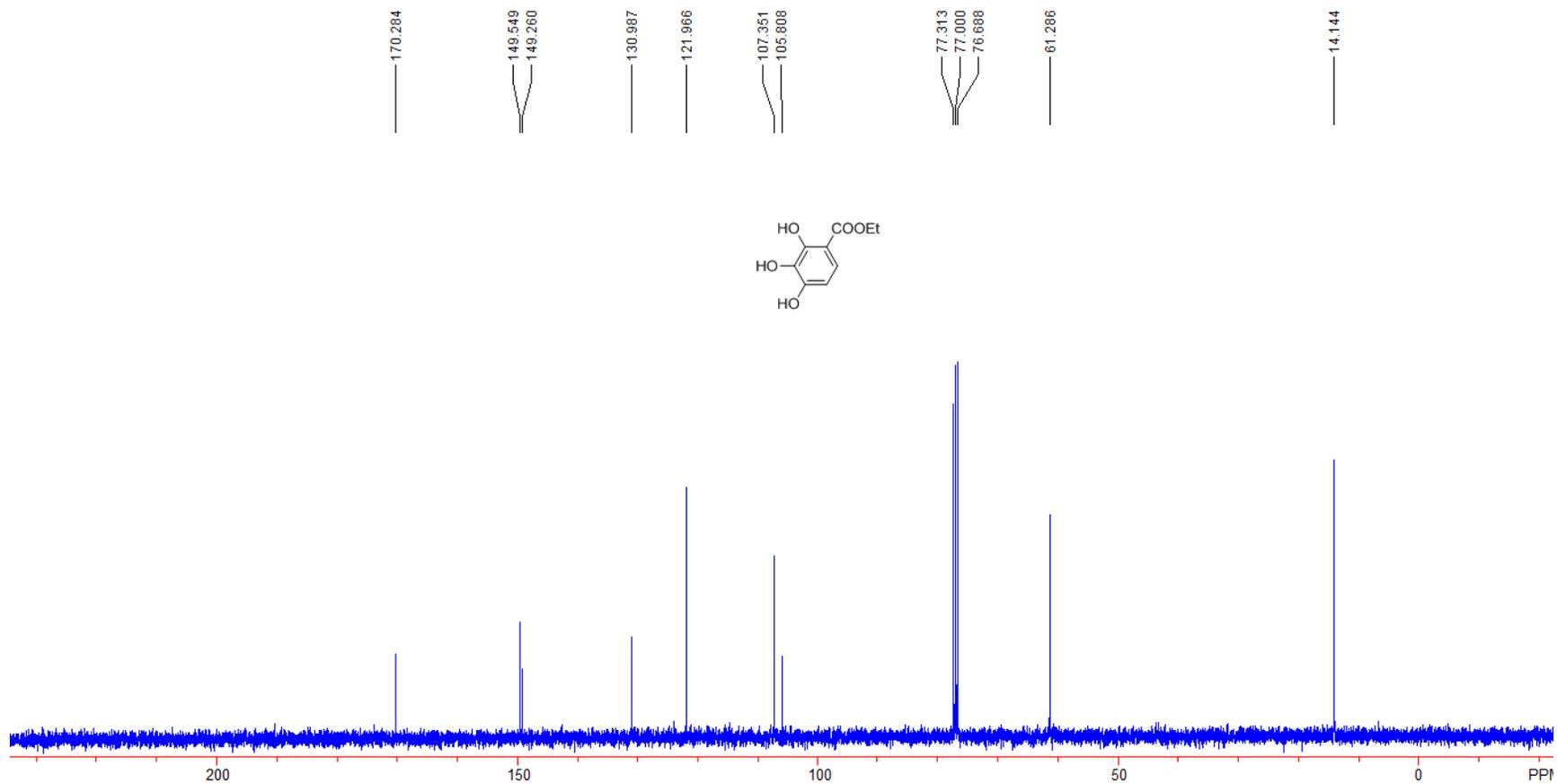


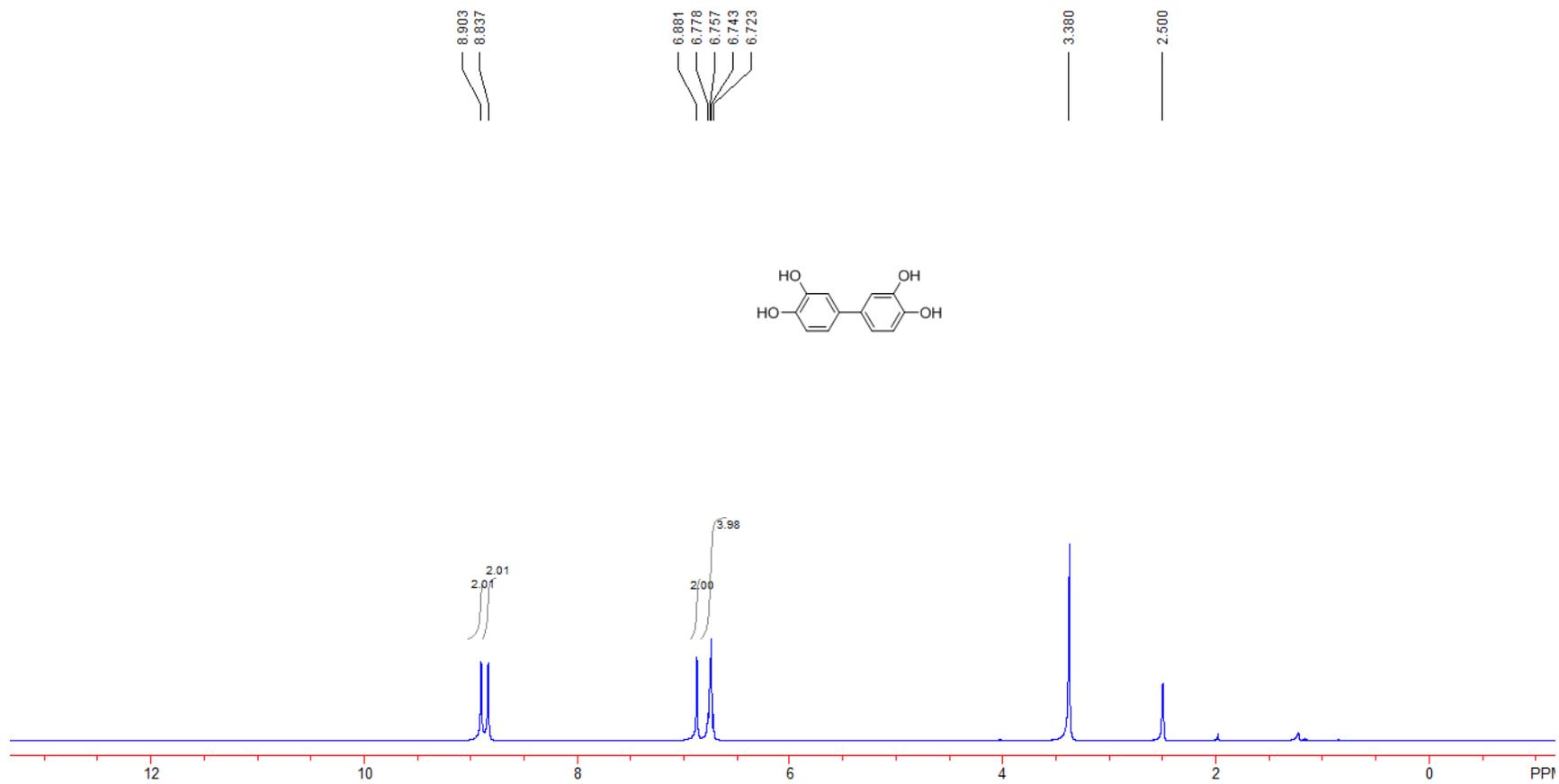


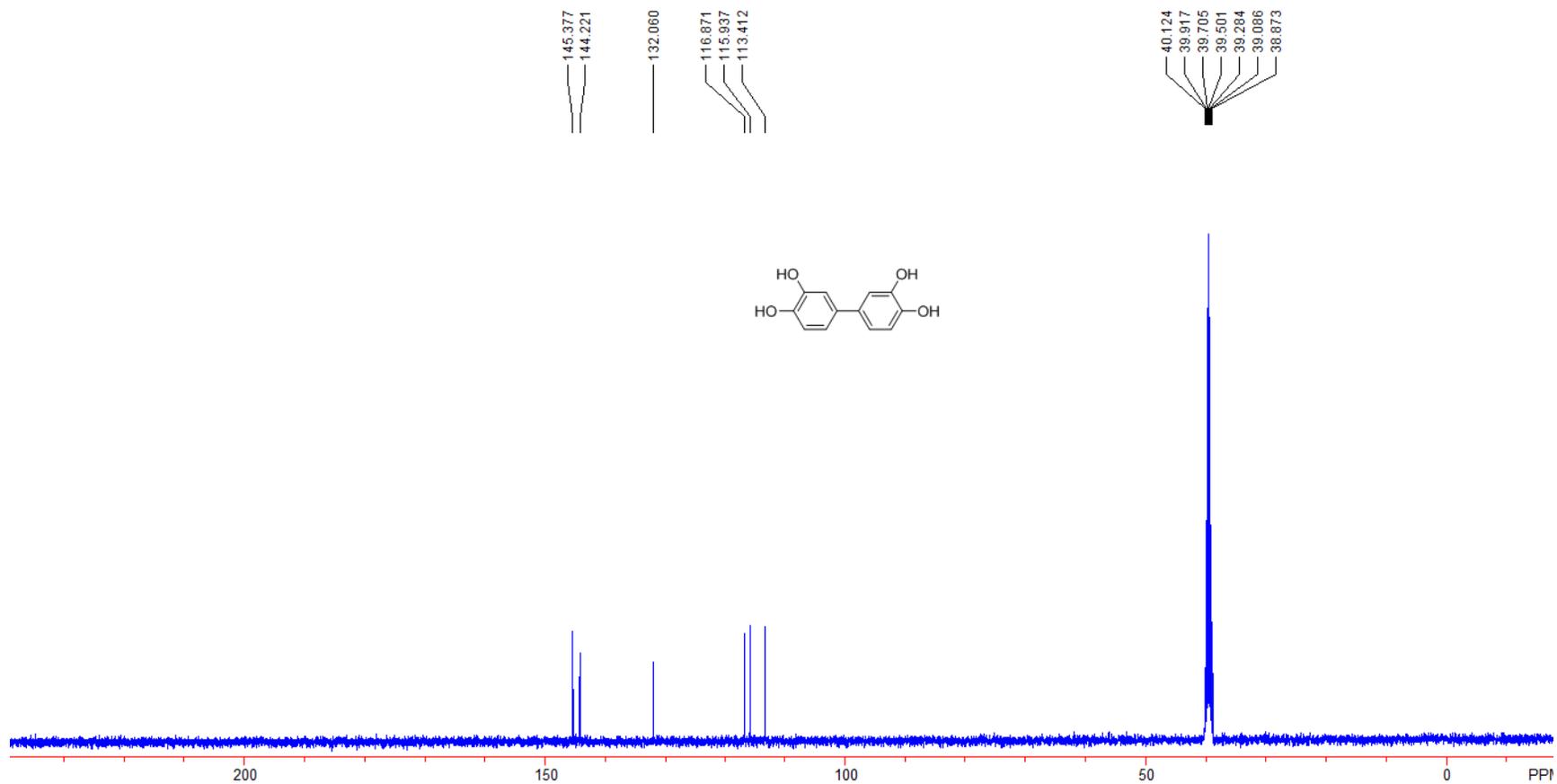


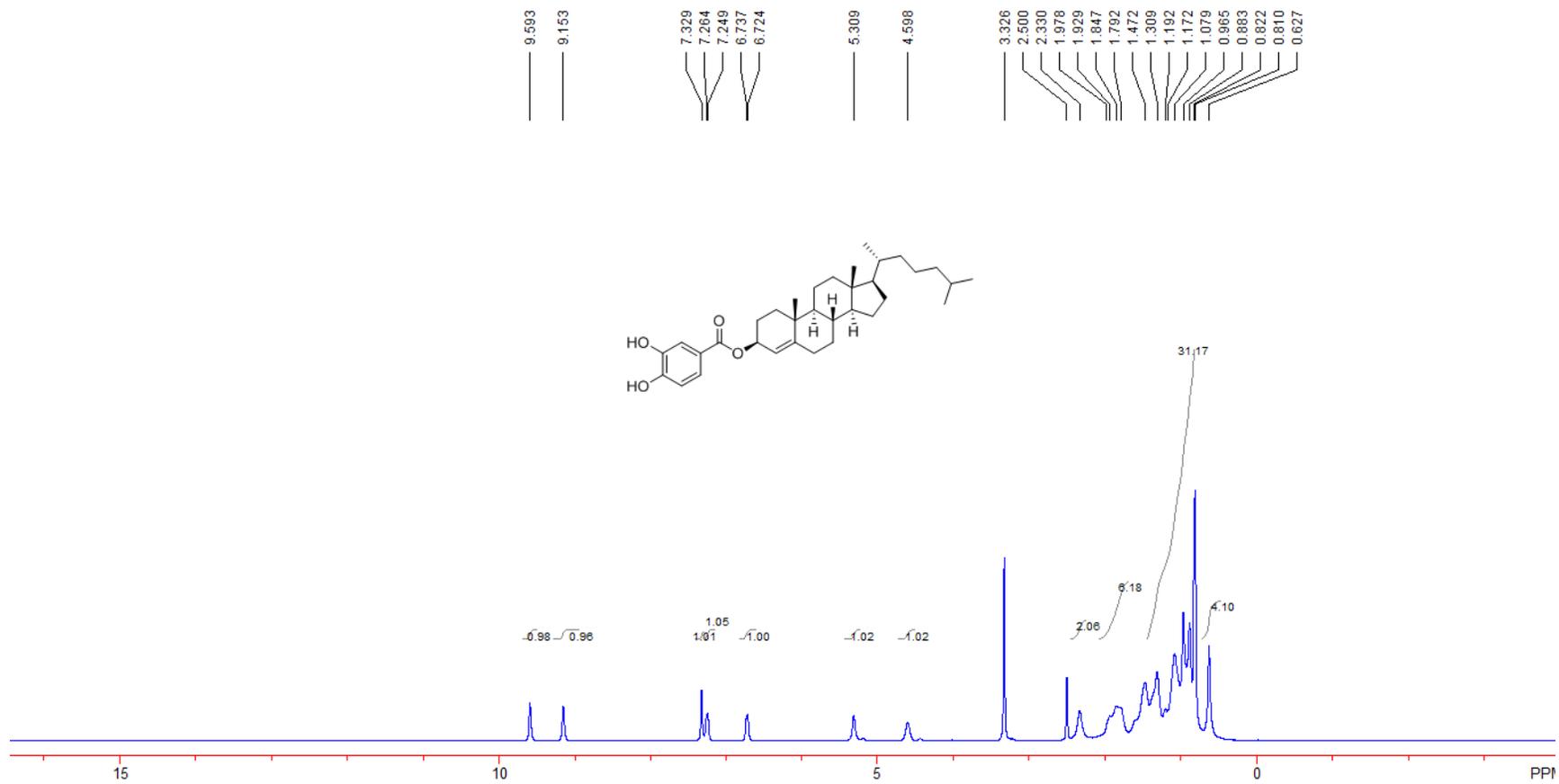


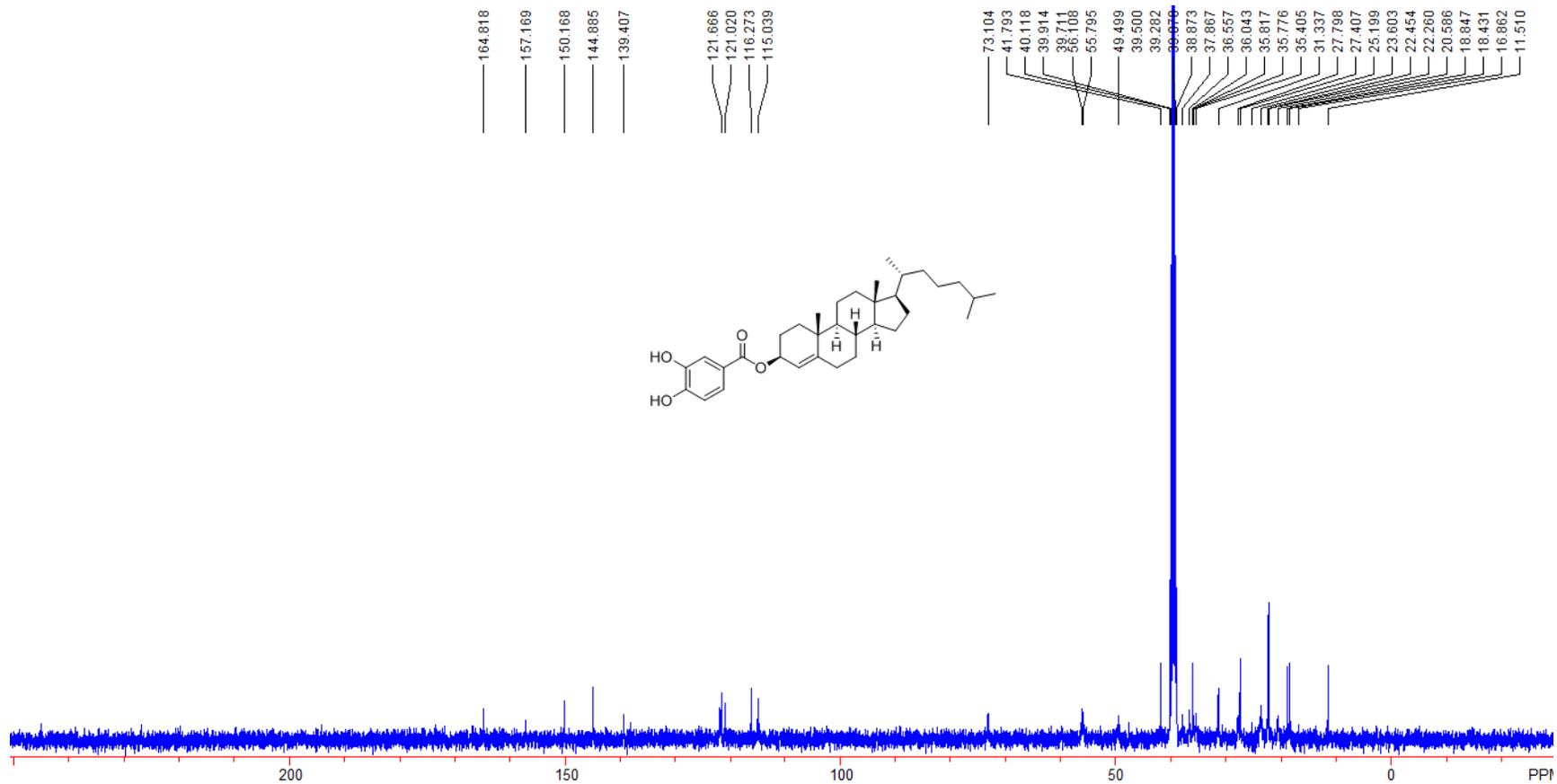


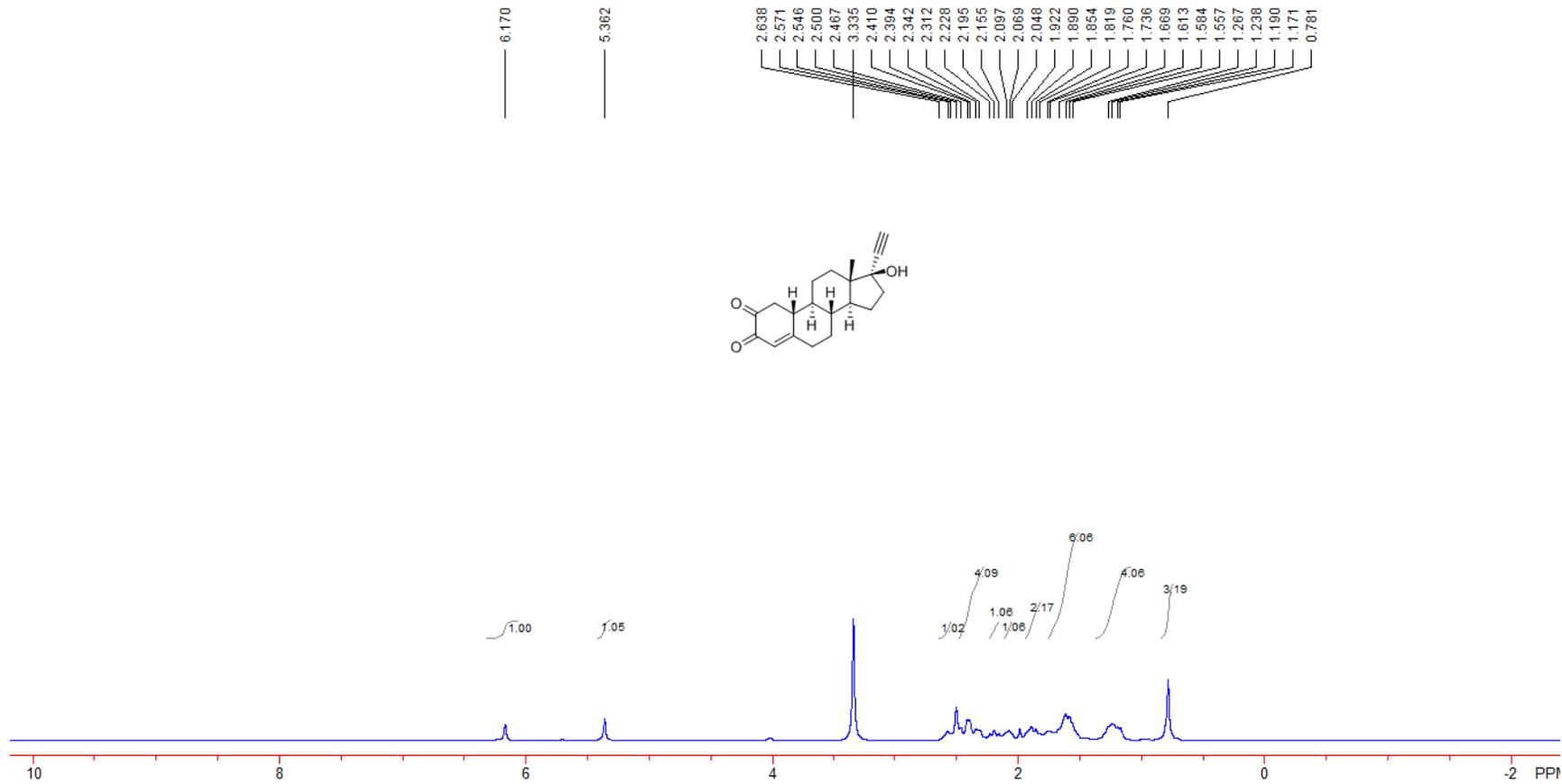


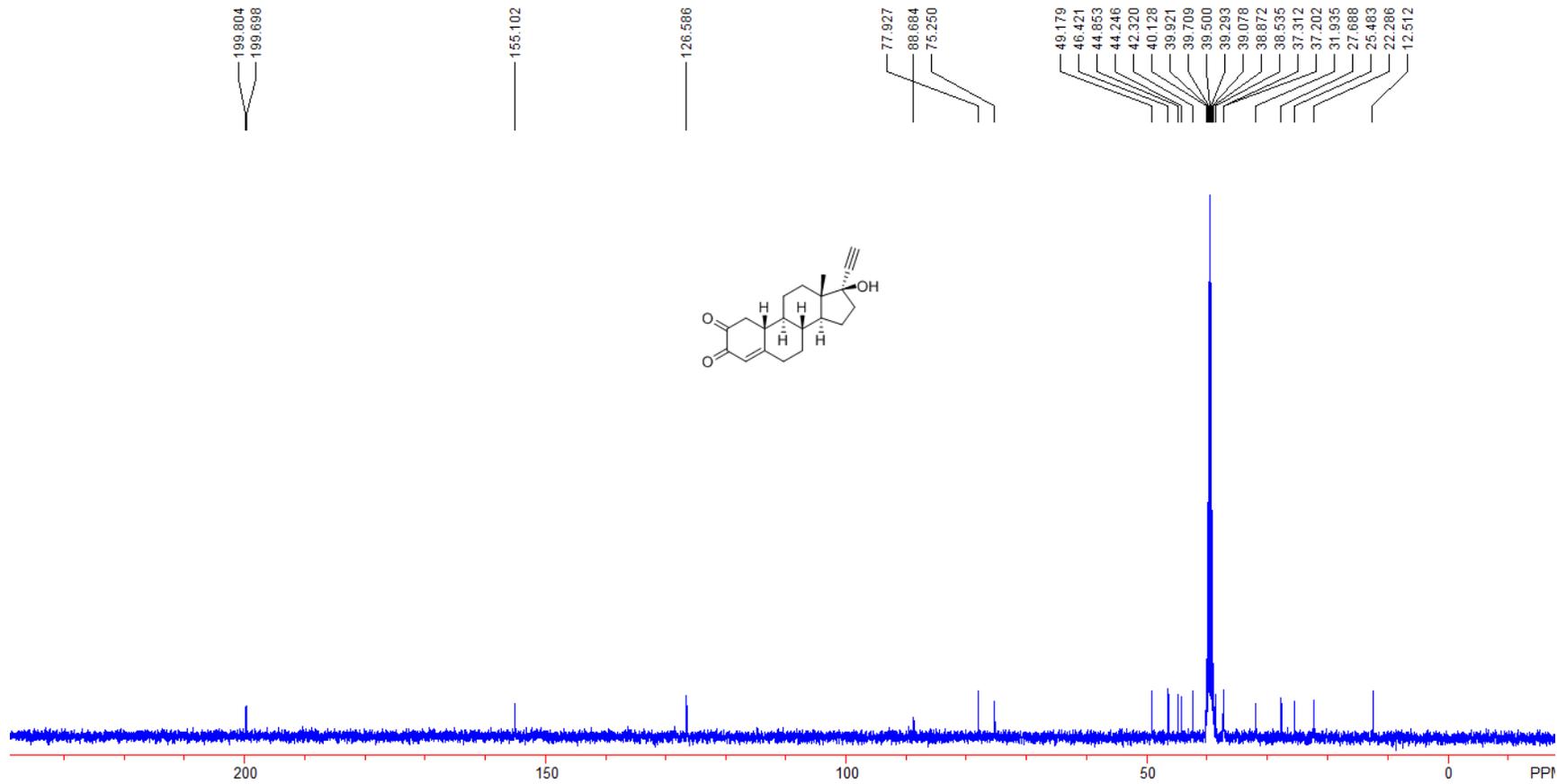


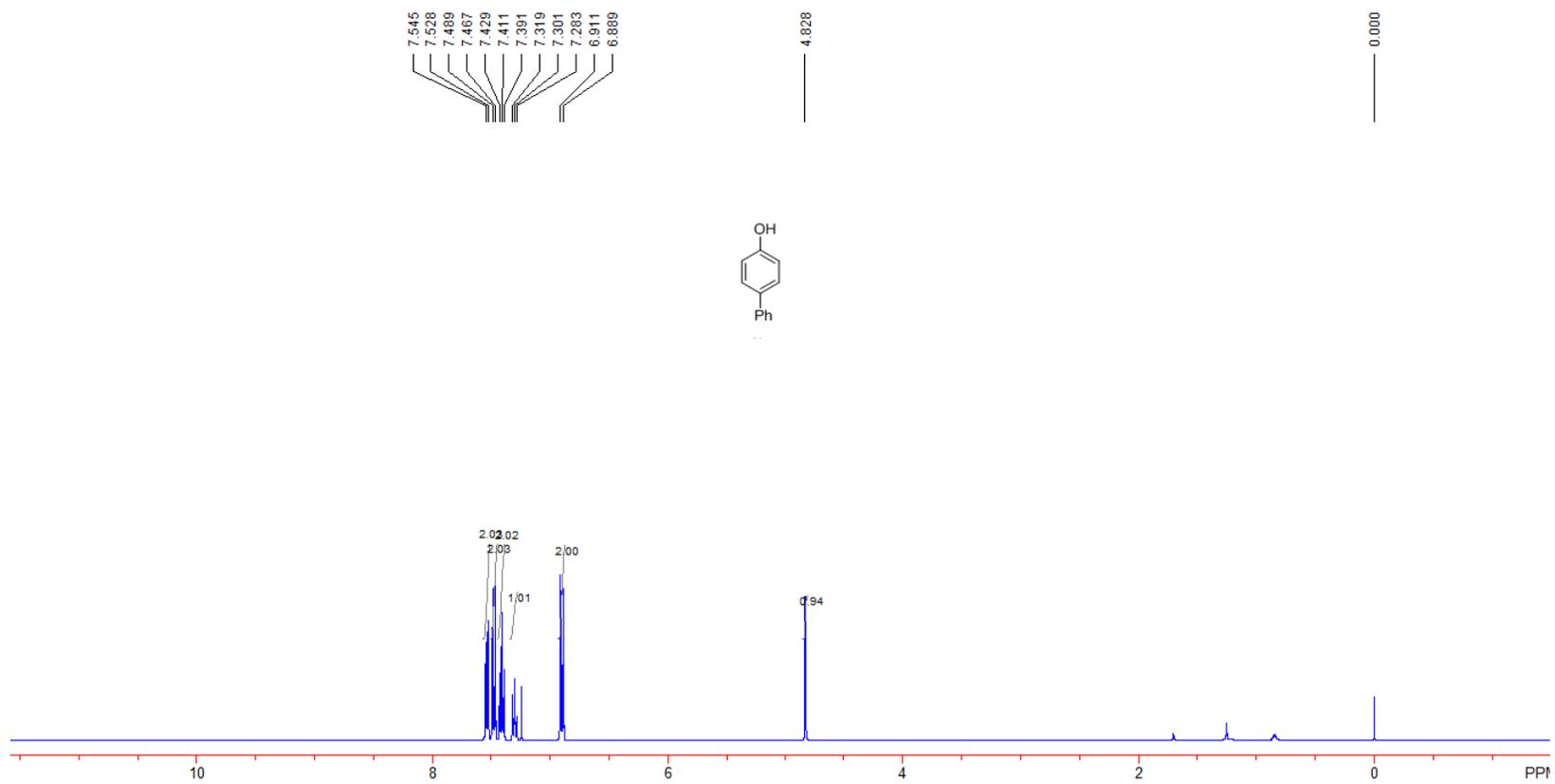


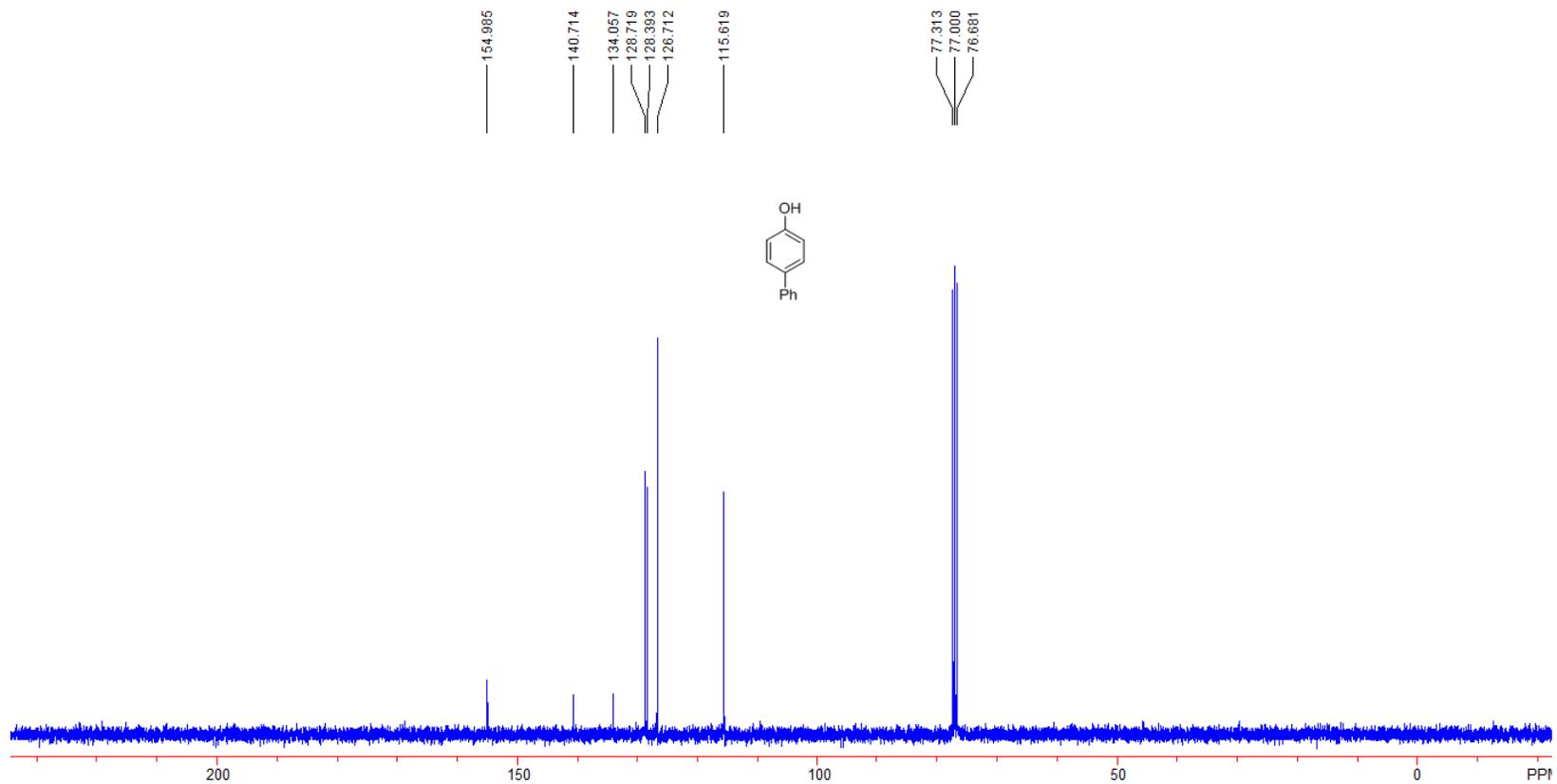


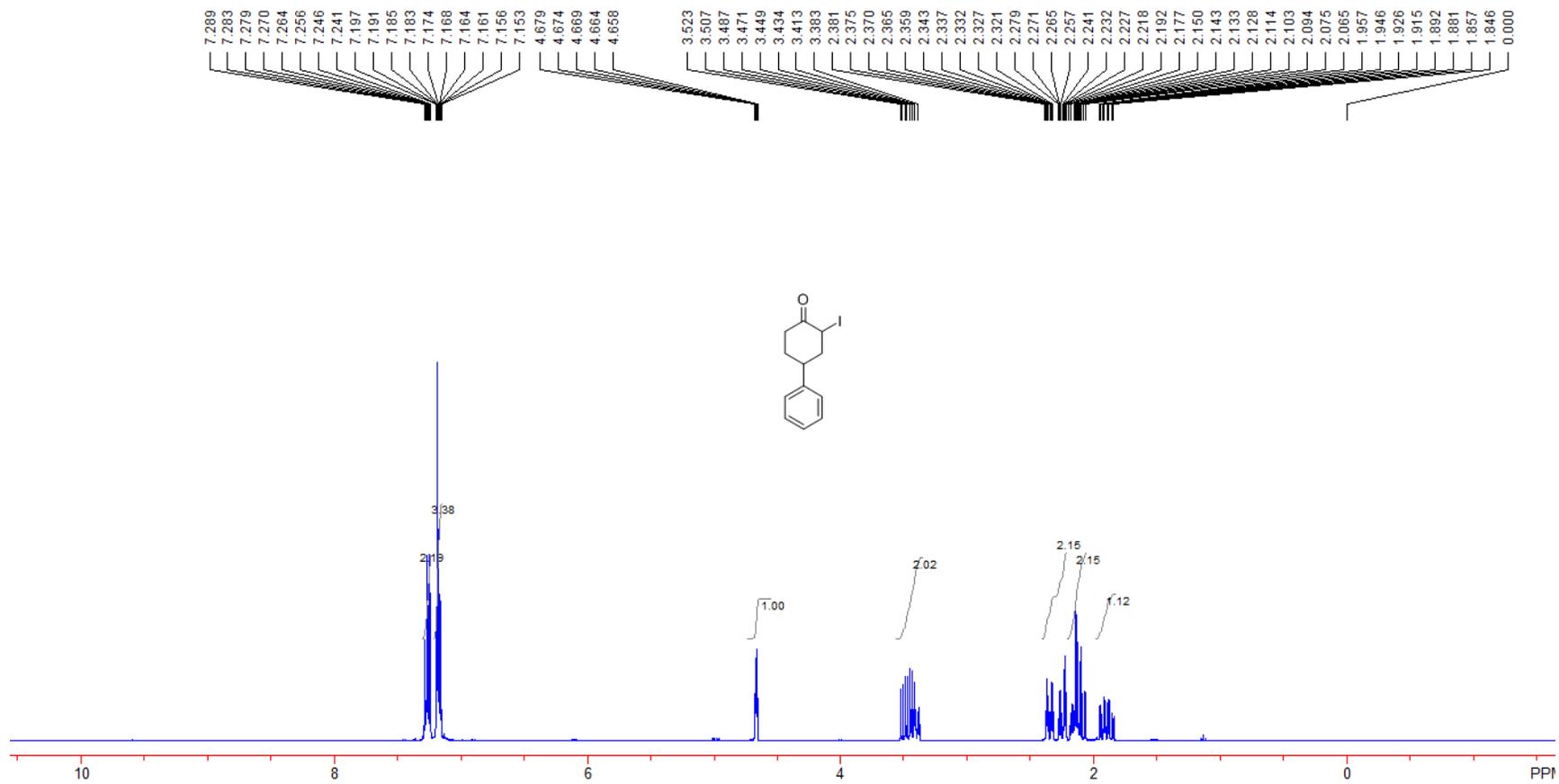


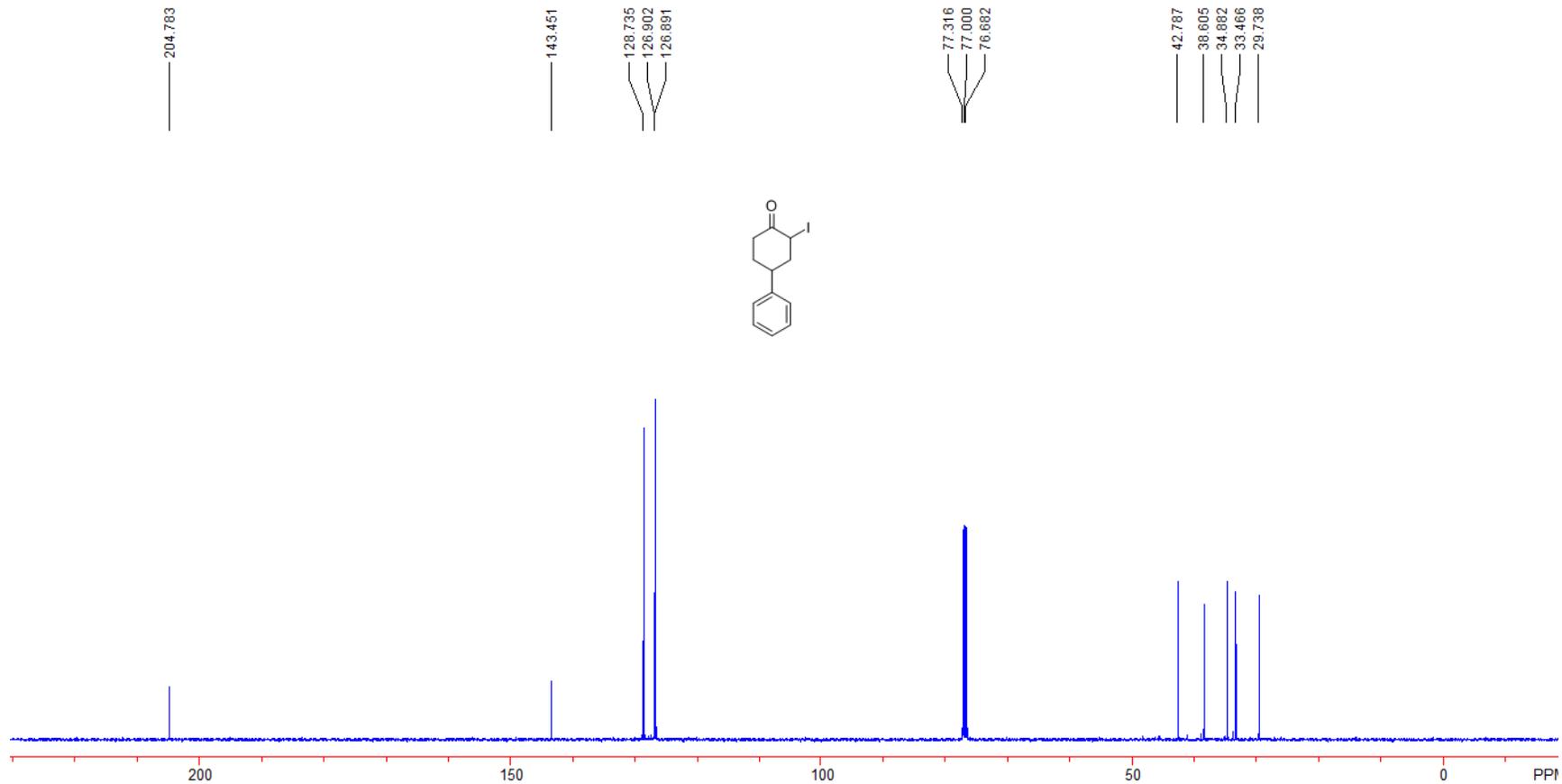


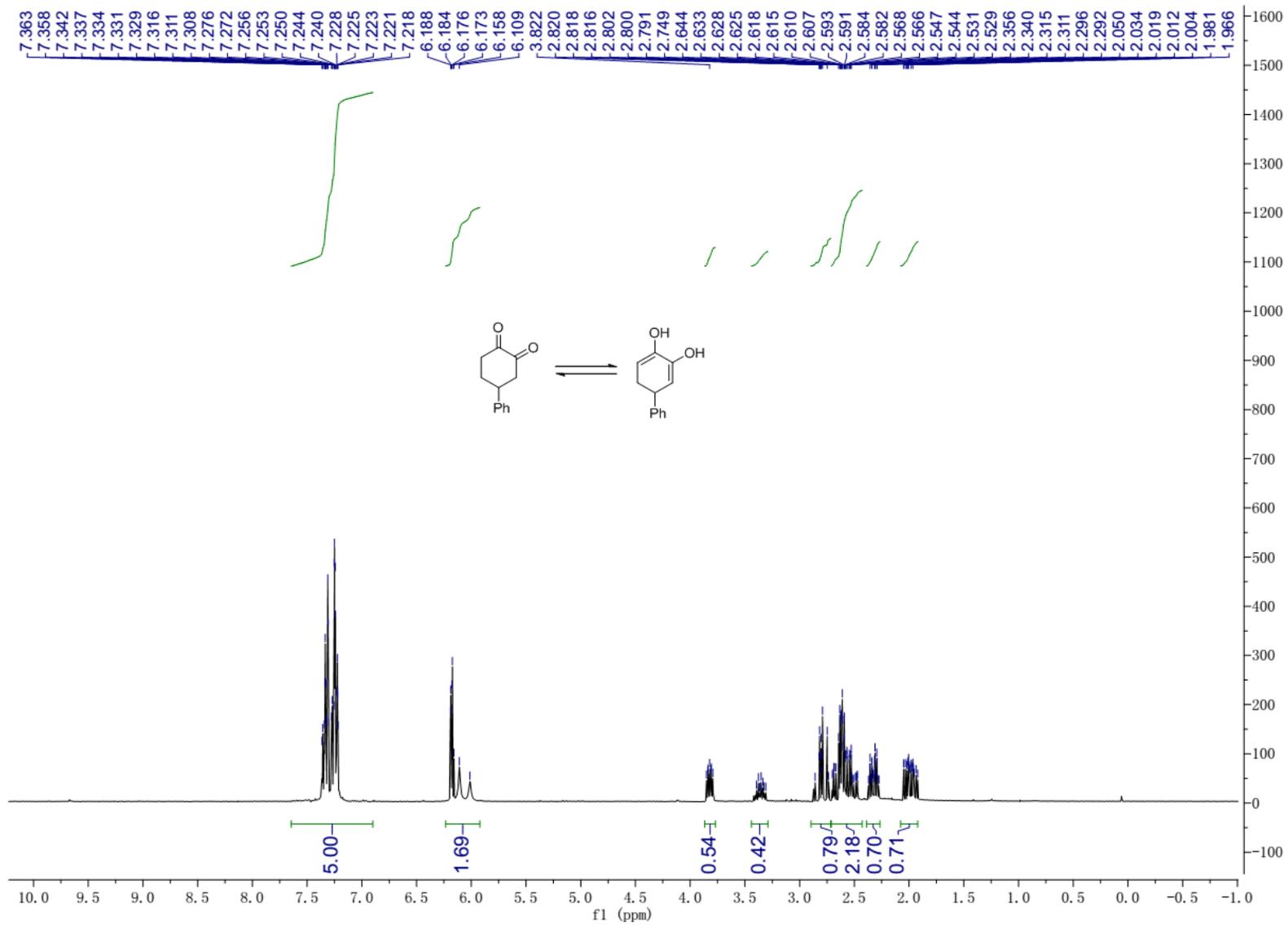


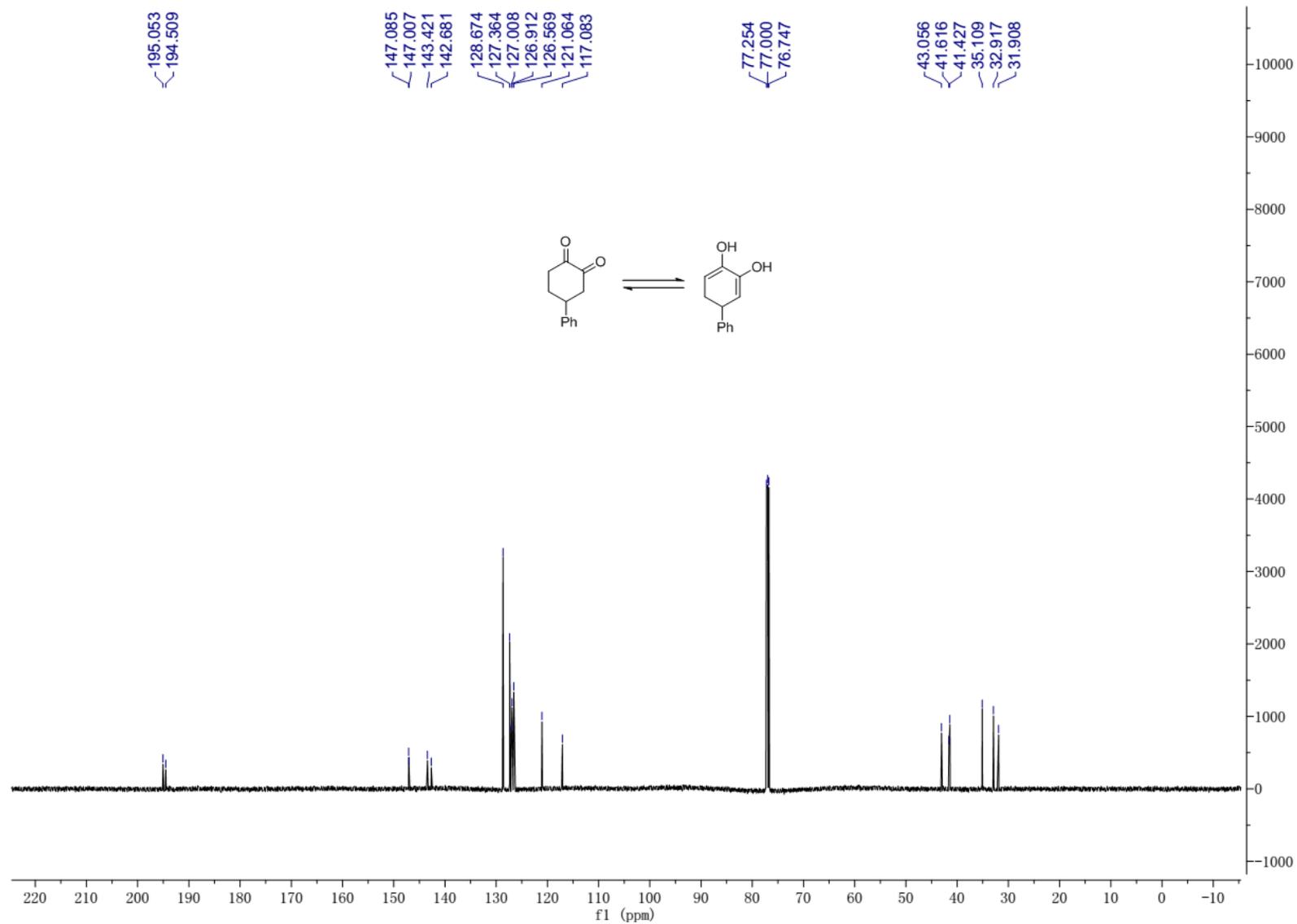


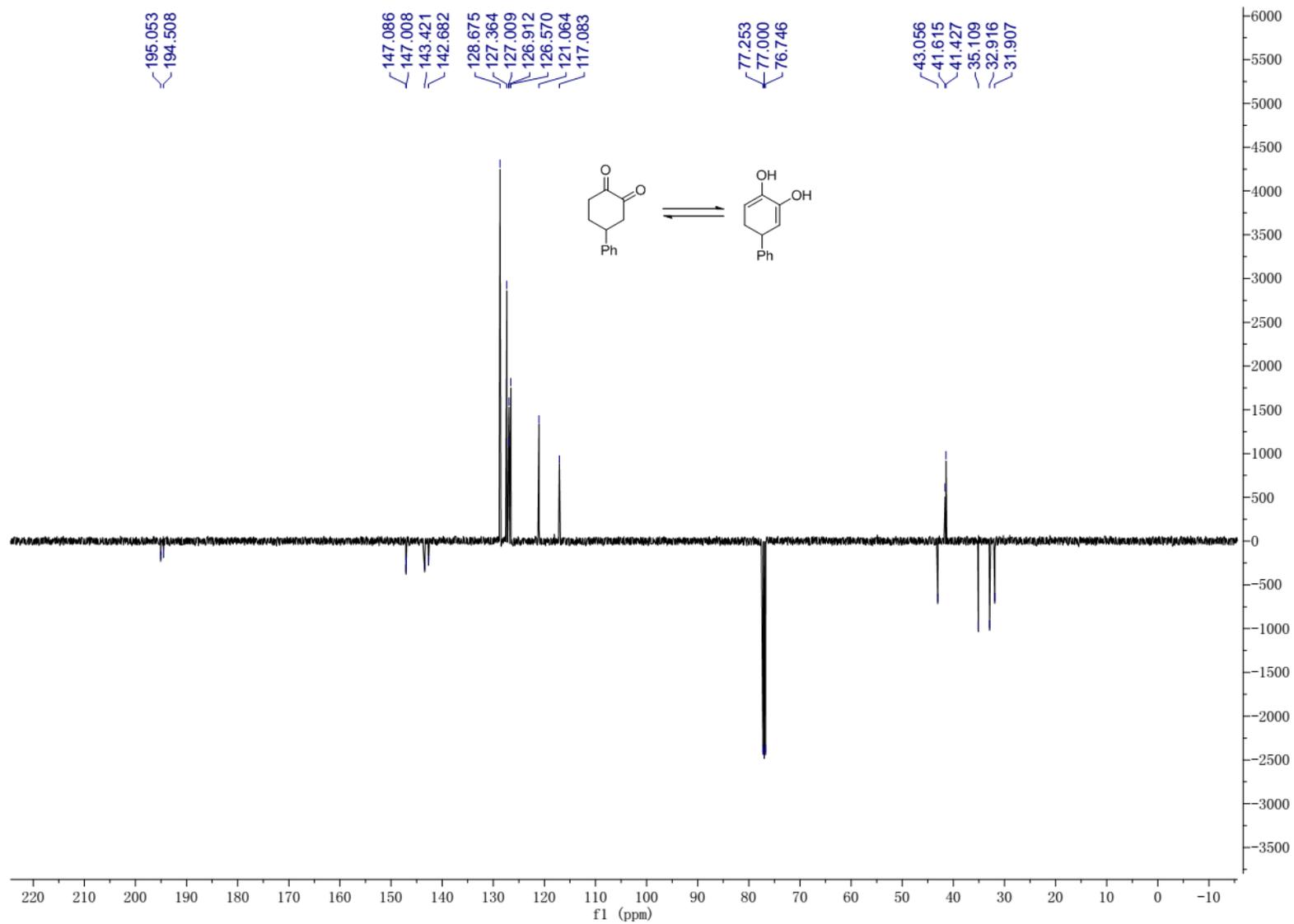




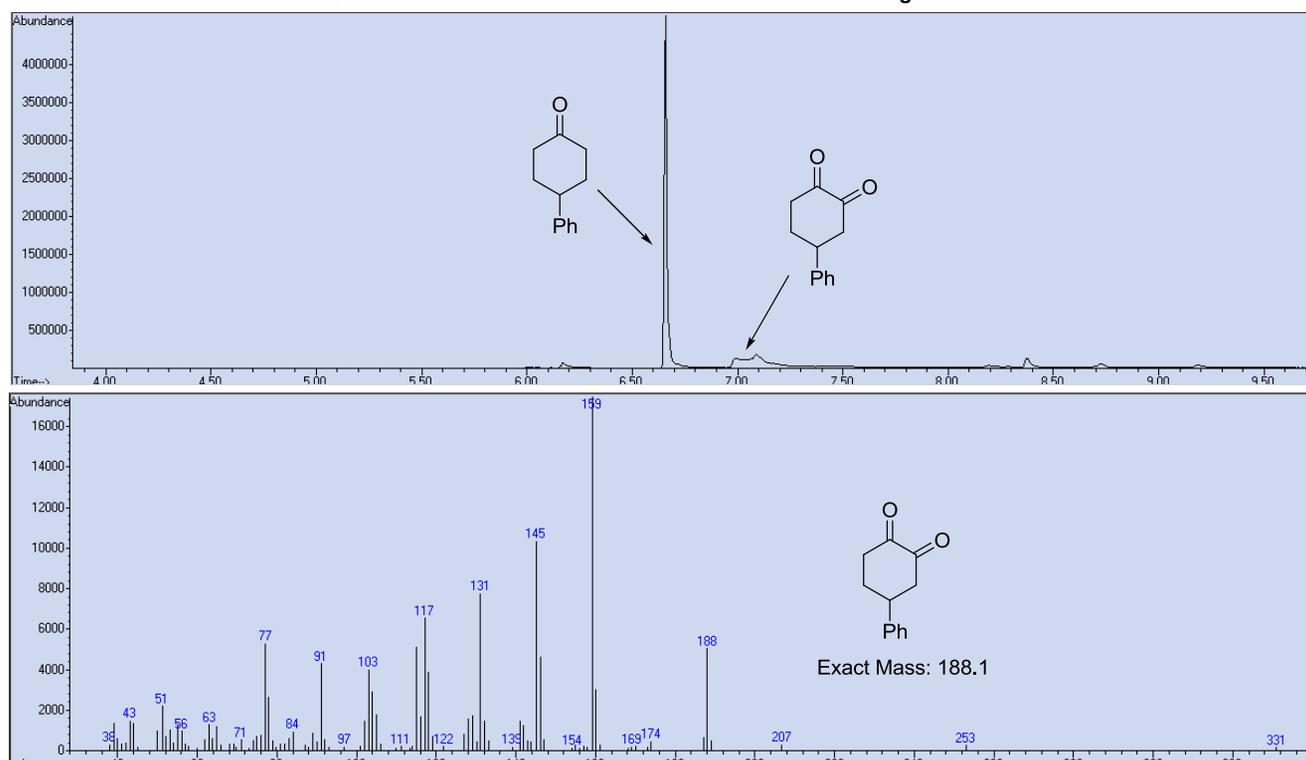
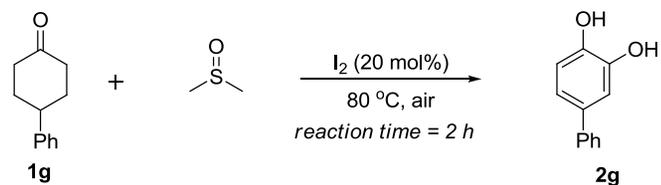




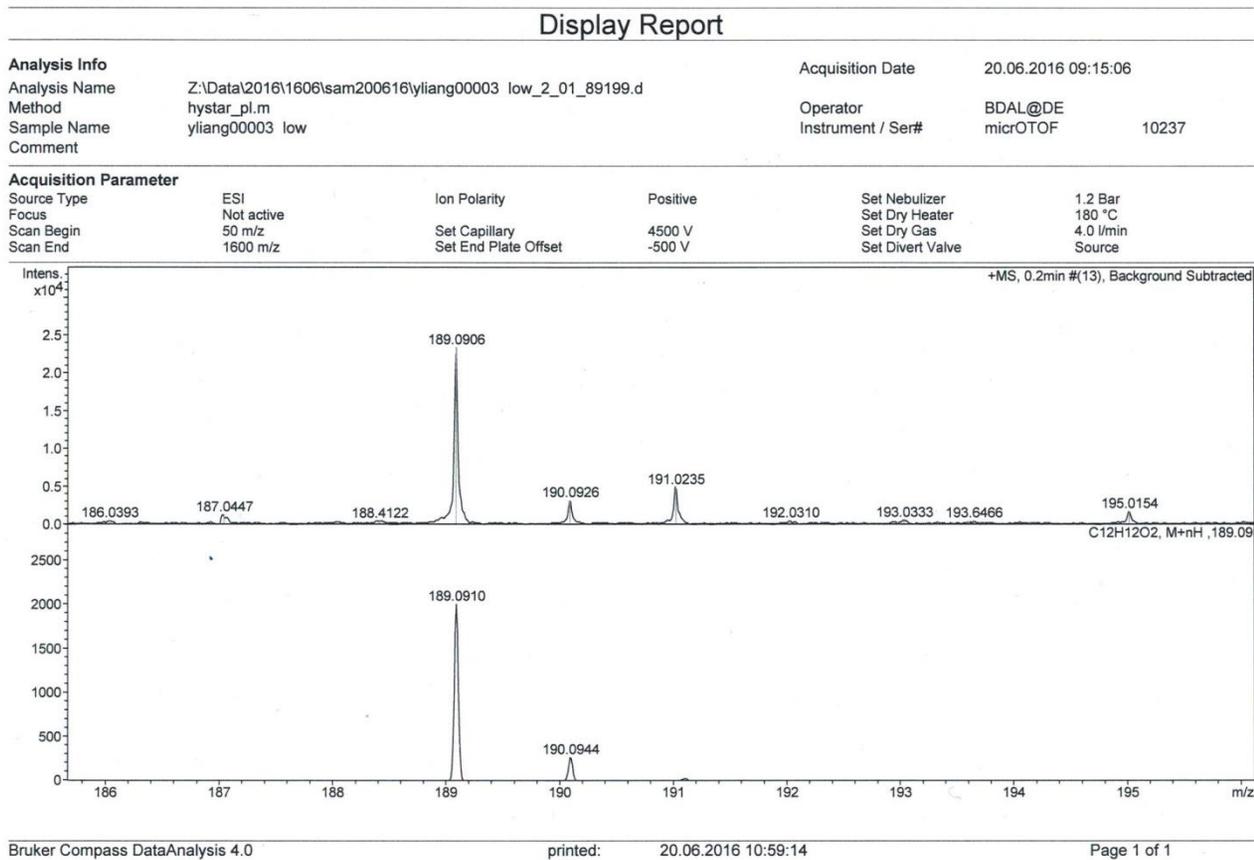




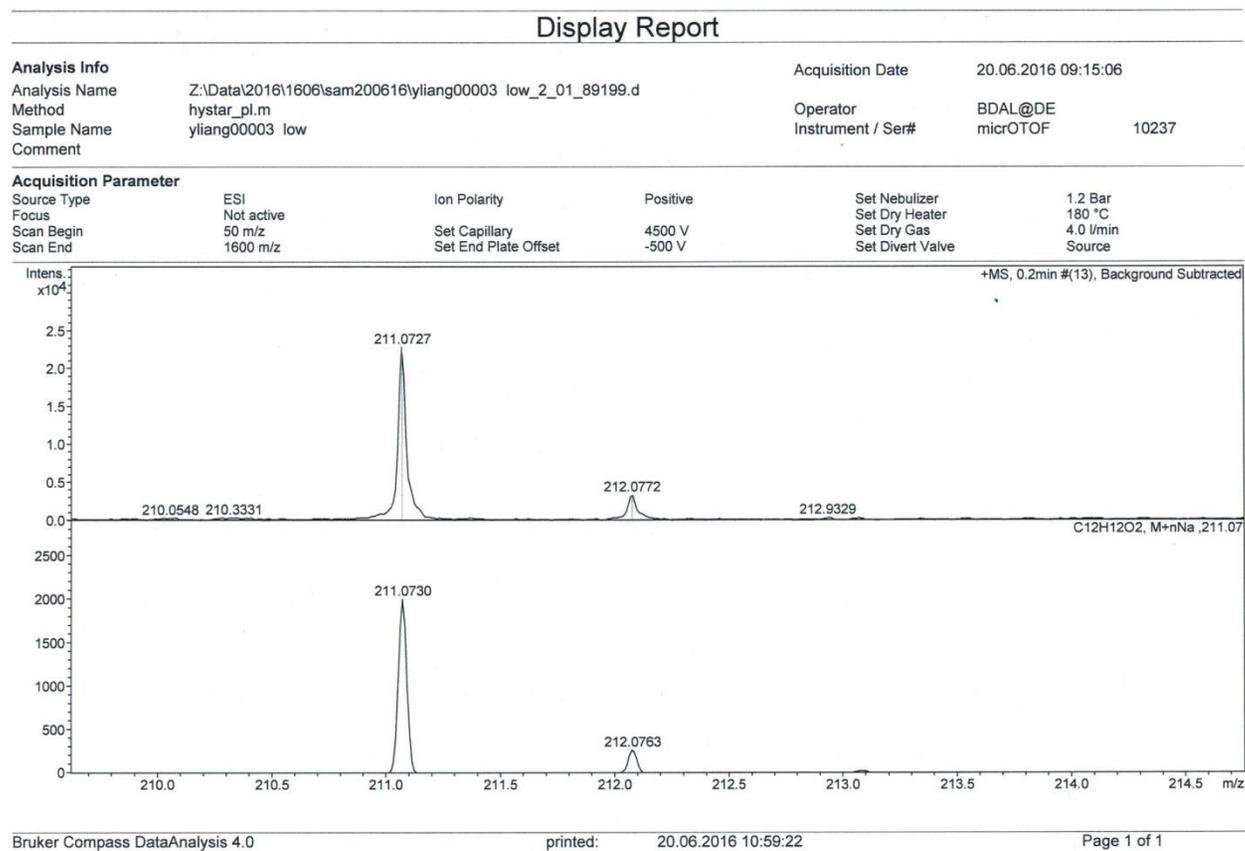
GC-MS analysis of reaction mixture at the reaction time of 2 h. (Note that the catechol product could not be detected by GCMS probably because of its easy decomposition character under high temperature in the detector)



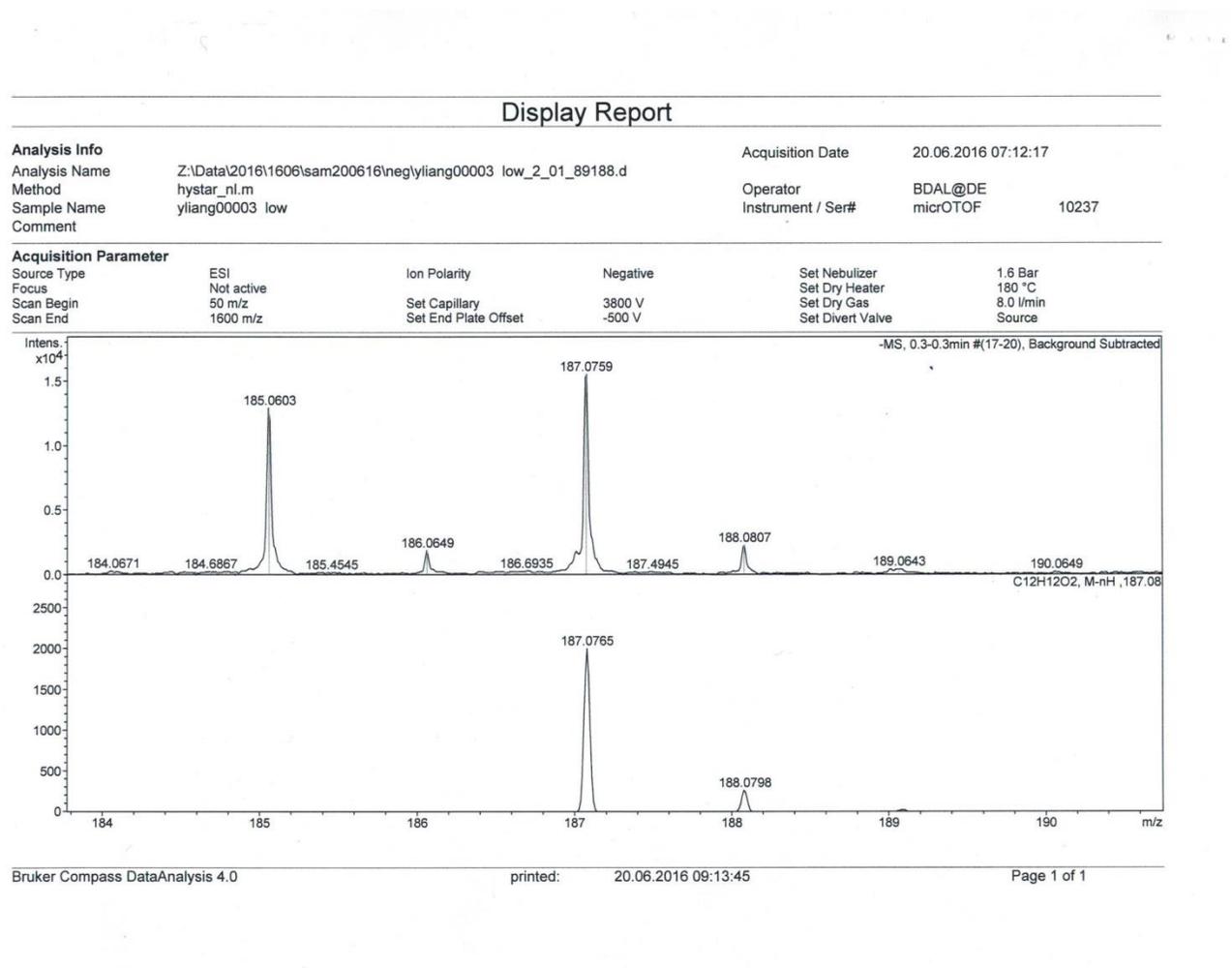
HRMS of 4-phenylcyclohexane-1,2-dione **14**: HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{13}O_2$  ( $M + H$ )<sup>+</sup>, 189.0910, found 189.0906.

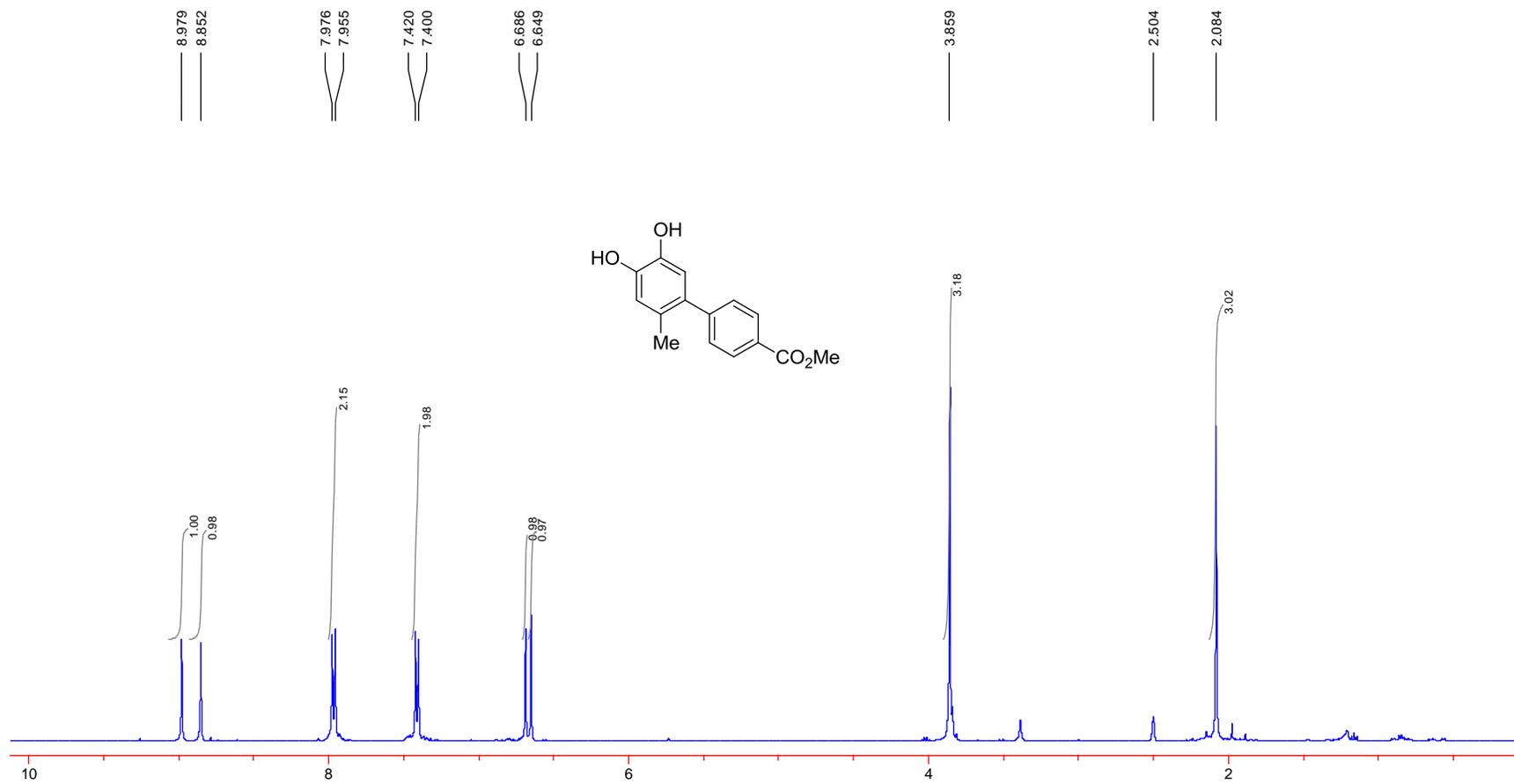


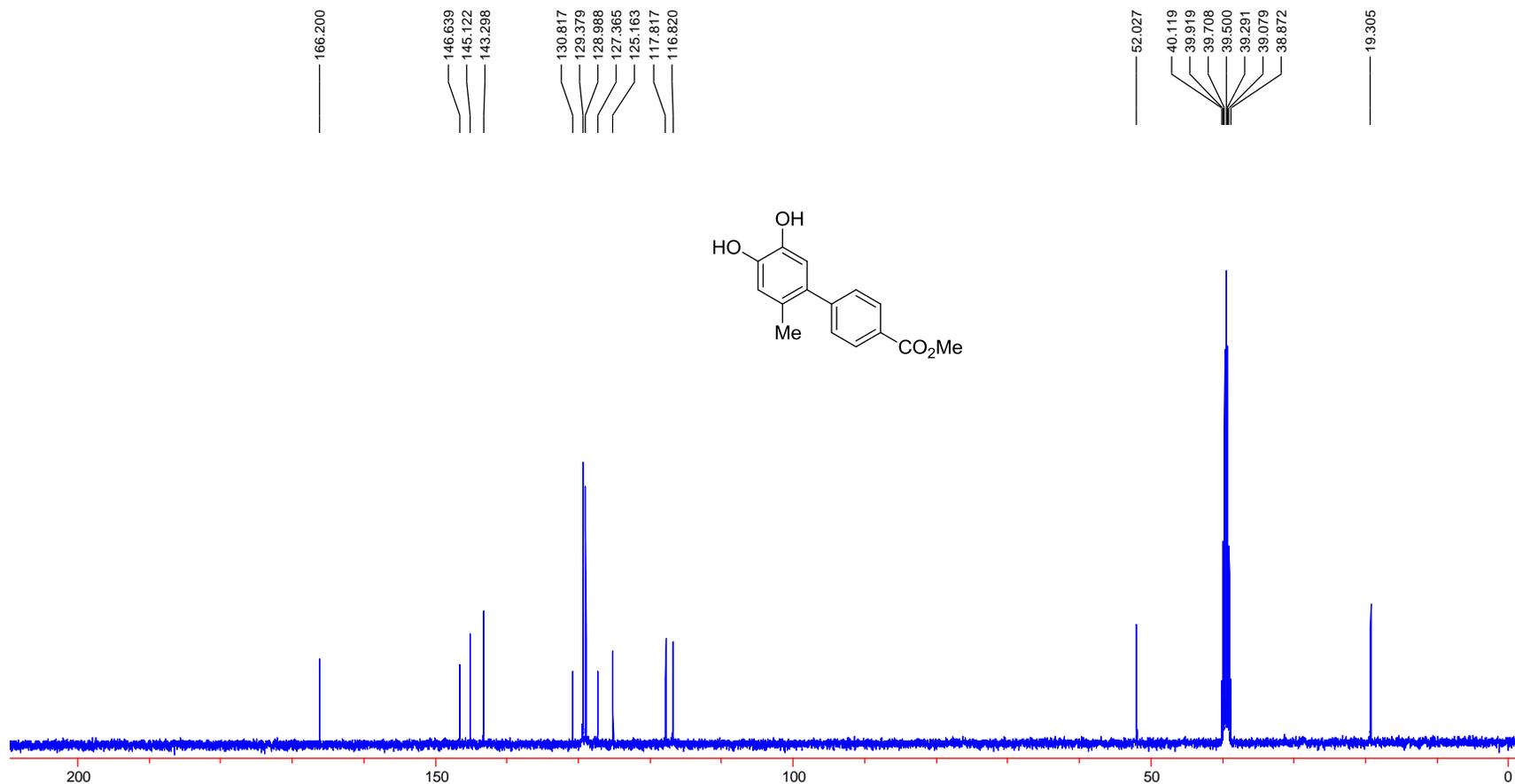
HRMS of 4-phenylcyclohexane-1,2-dione **14**: HRMS  $m/z$  (ESI) calcd for  $C_{12}H_{12}NaO_2$  ( $M + Na$ )<sup>+</sup>, 211.0730, found 211.0727.



HRMS of 4-phenylcyclohexane-1,2-dione **14**: the corresponding enol could also be detected as (M - H)<sup>-</sup>: HRMS *m/z* (ESI) calcd for C<sub>12</sub>H<sub>11</sub>O<sub>2</sub> (M - H)<sup>-</sup>, 187.0765, found 187.0759.

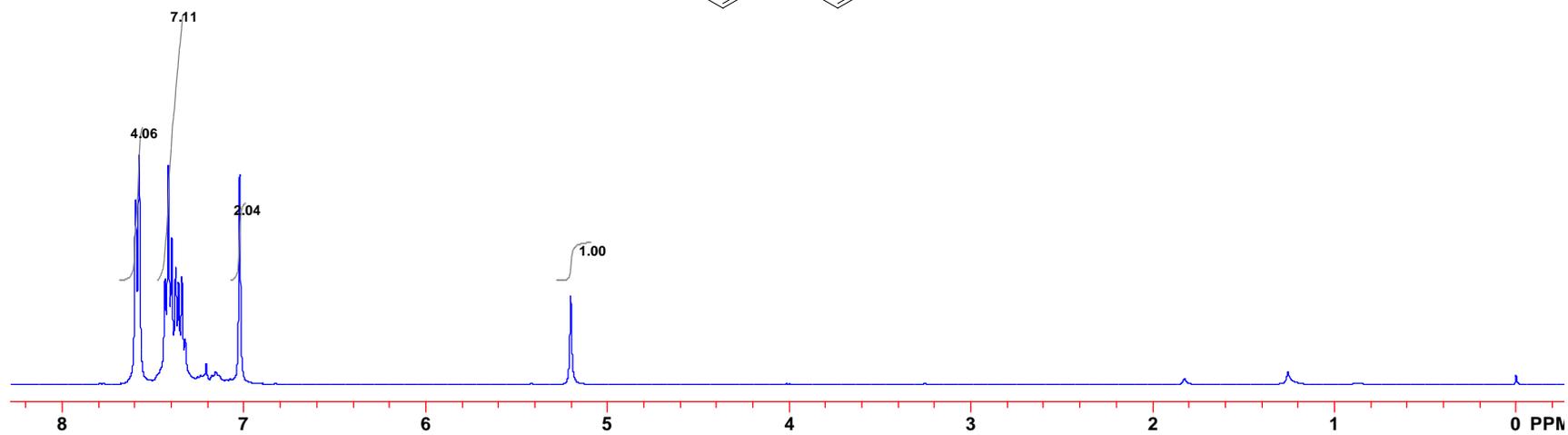
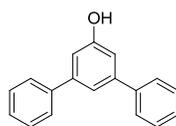


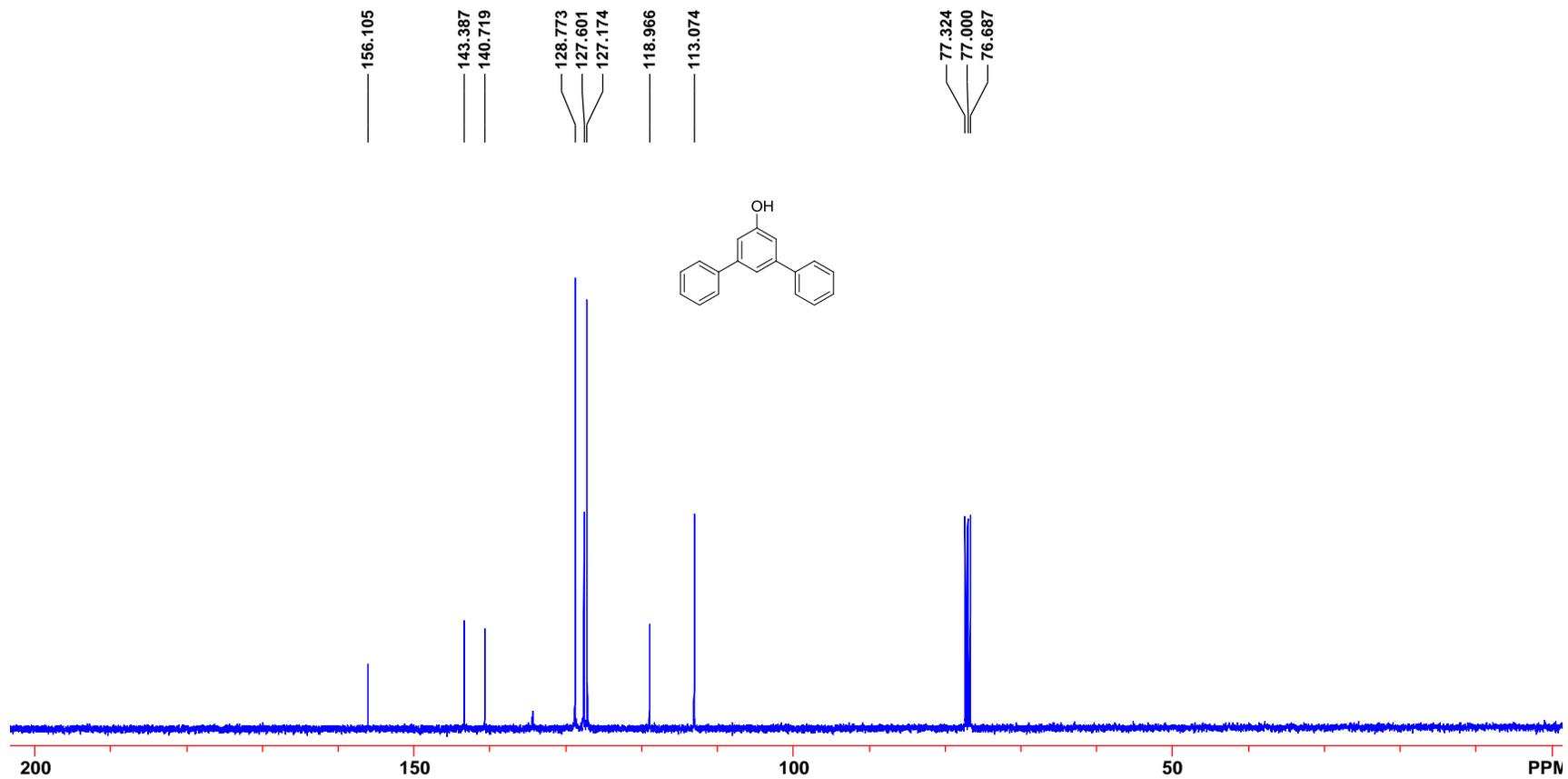


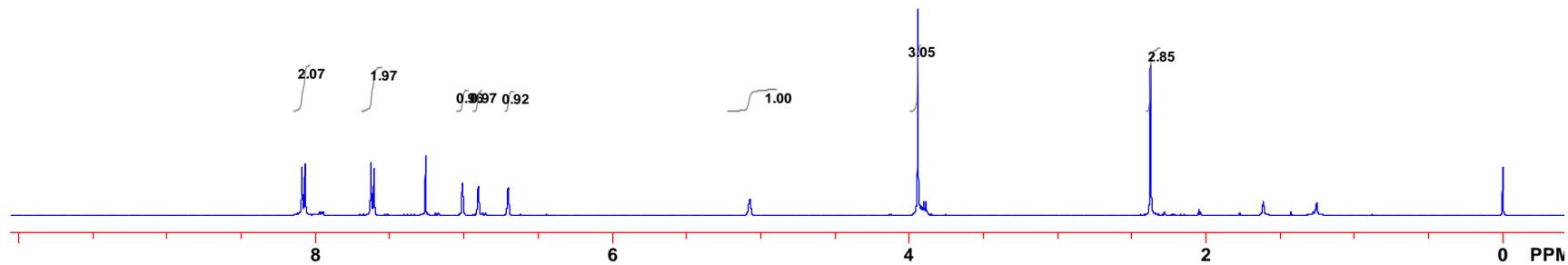
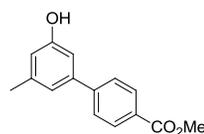
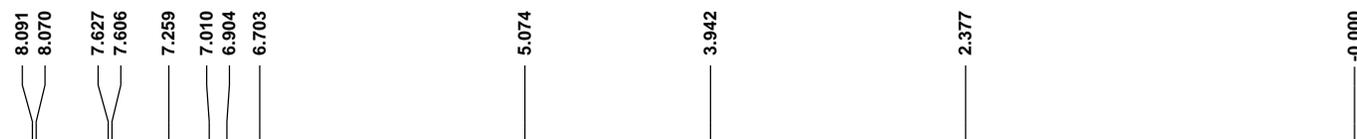


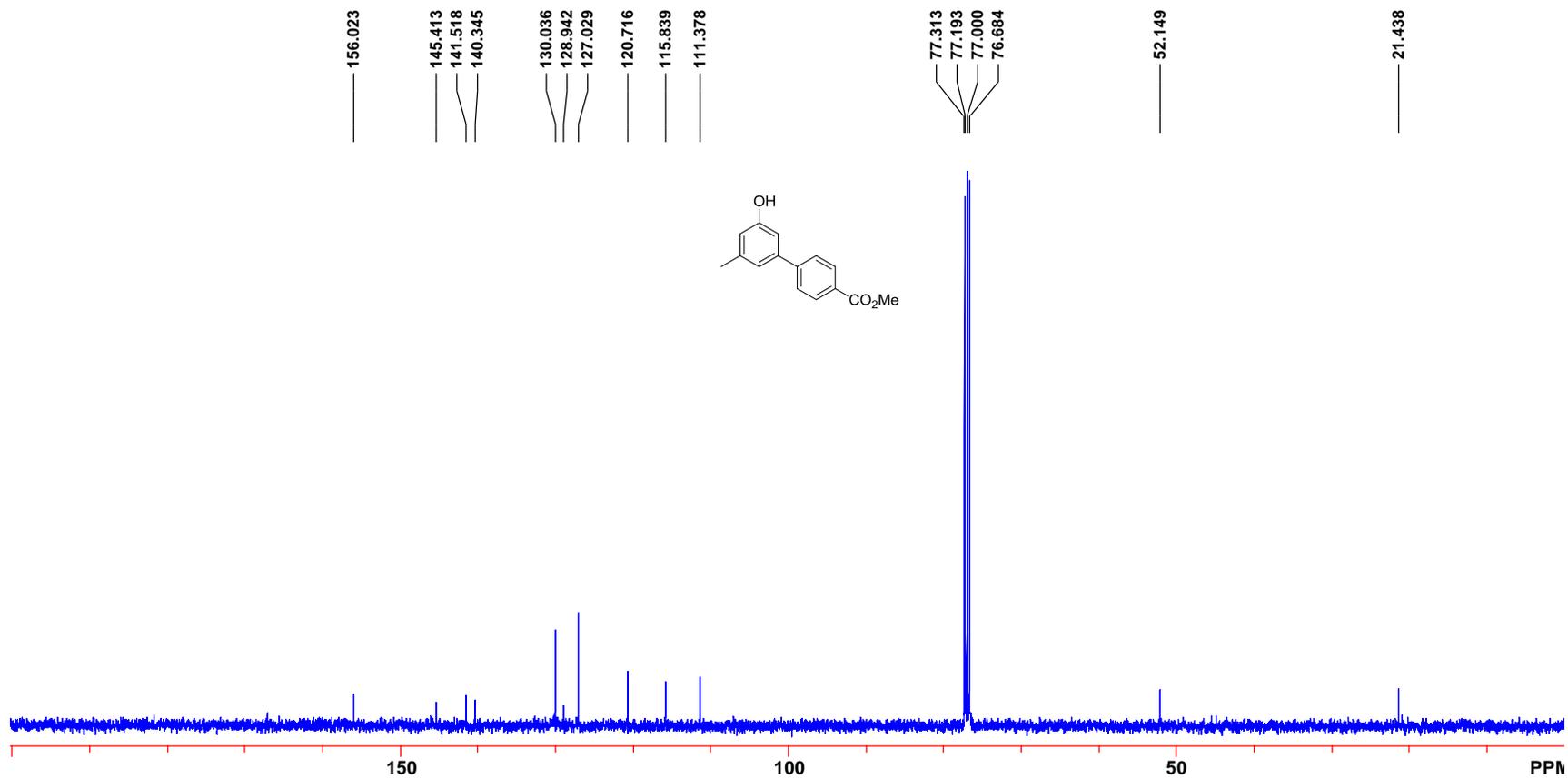
7.596  
7.577  
7.434  
7.416  
7.398  
7.376  
7.360  
7.342  
7.324  
7.025

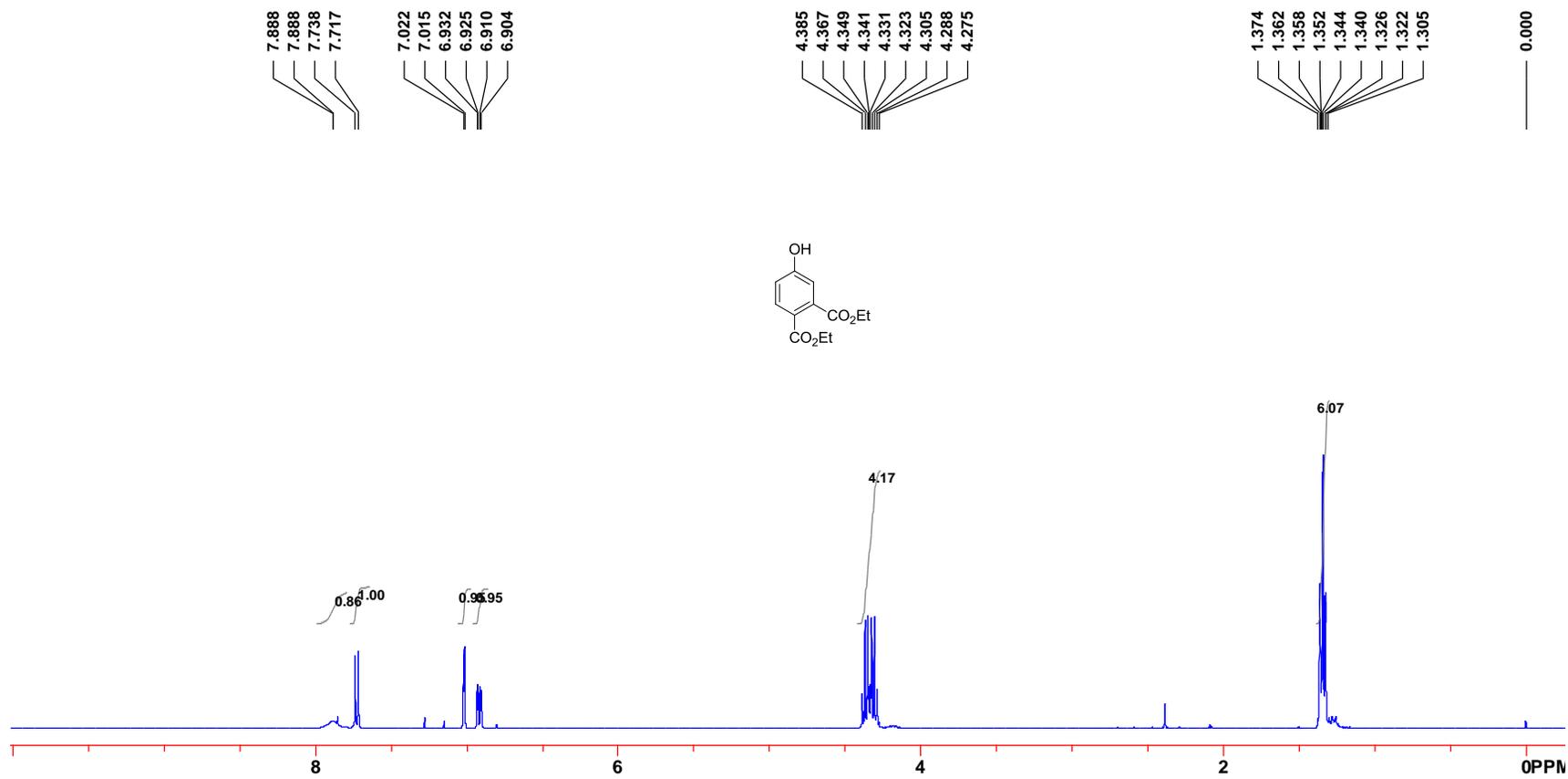
5.203

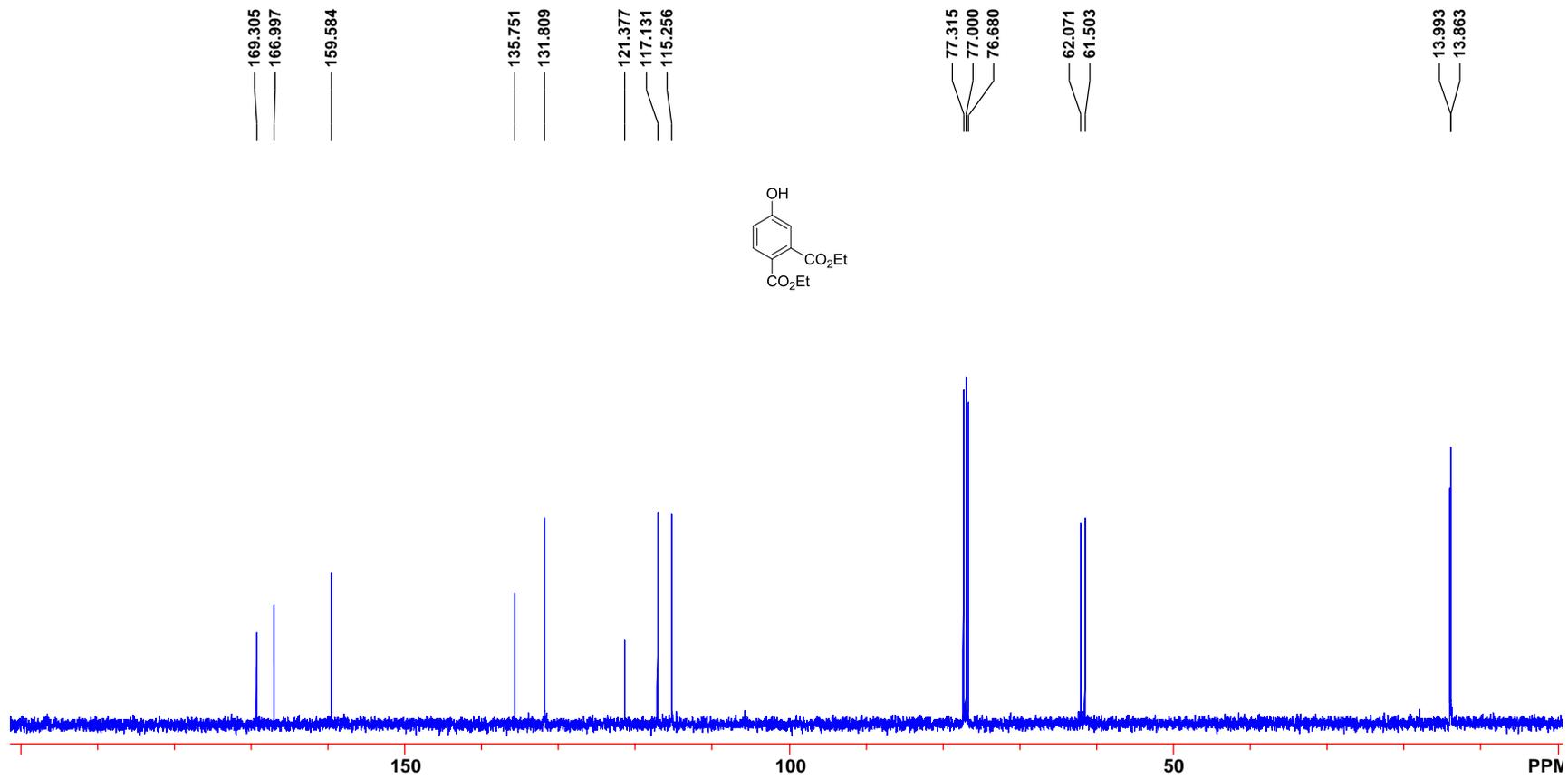










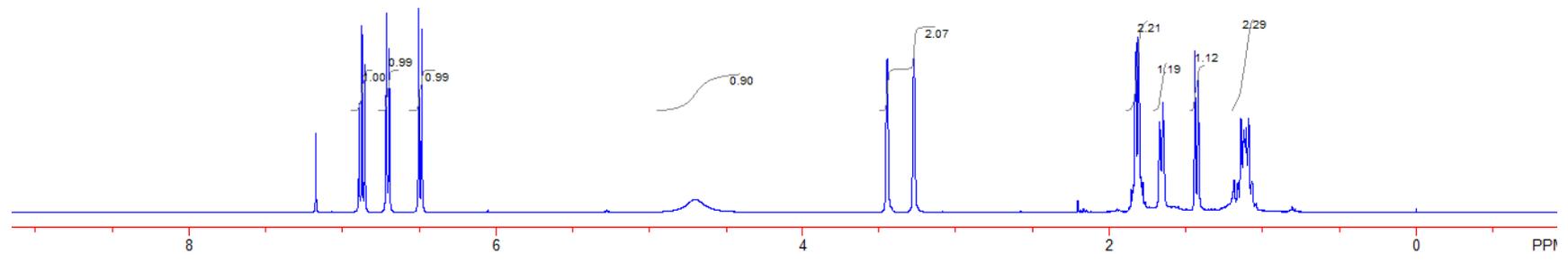
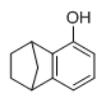


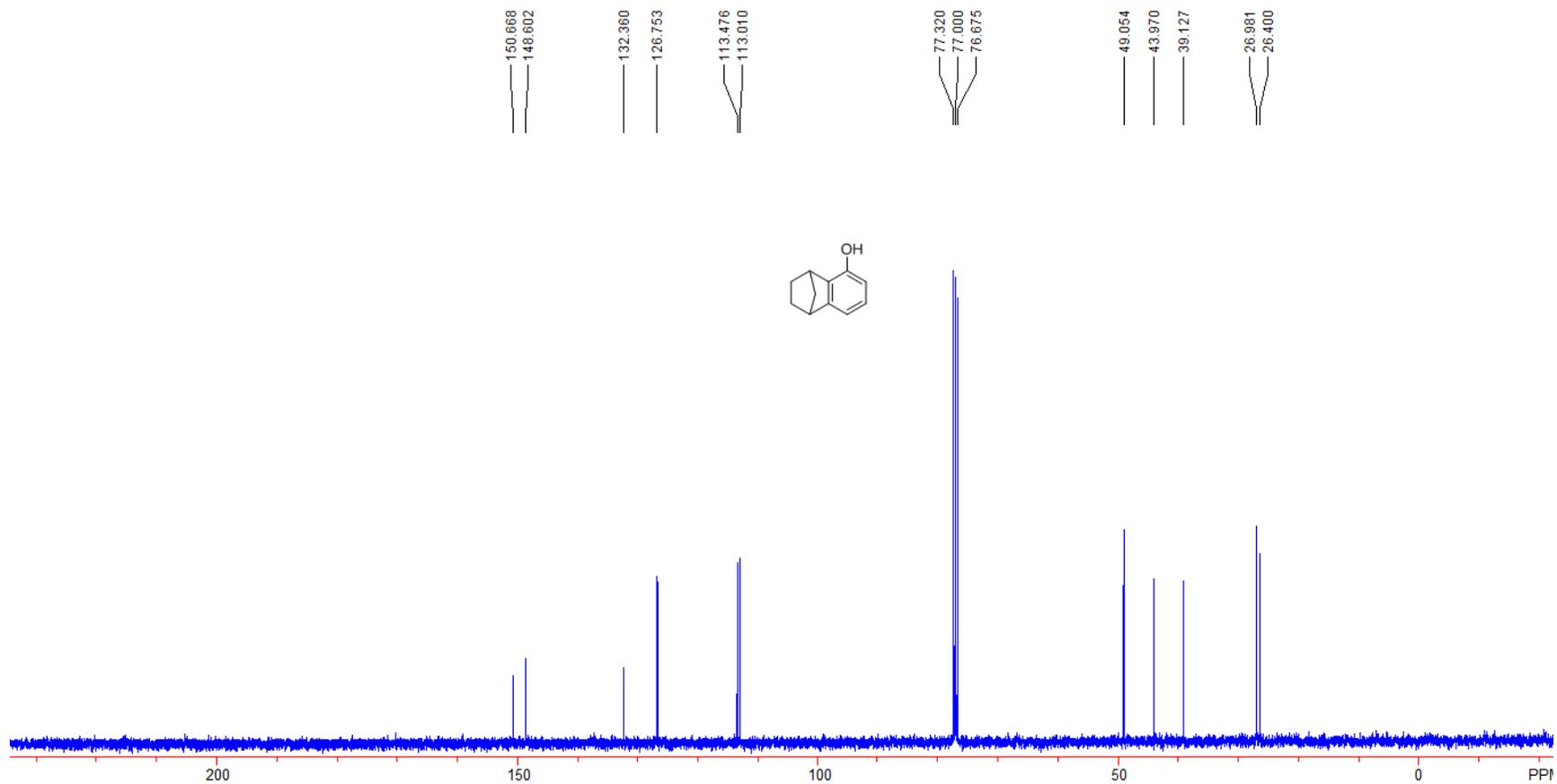
7.173  
6.892  
6.874  
6.854  
6.714  
6.696  
6.504  
6.483

4.710

3.444  
3.268

1.854  
1.825  
1.808  
1.779  
1.673  
1.669  
1.664  
1.652  
1.647  
1.642  
1.439  
1.417  
1.184  
1.159  
1.141  
1.123  
1.112  
1.090  
1.067  
1.048  
-0.000

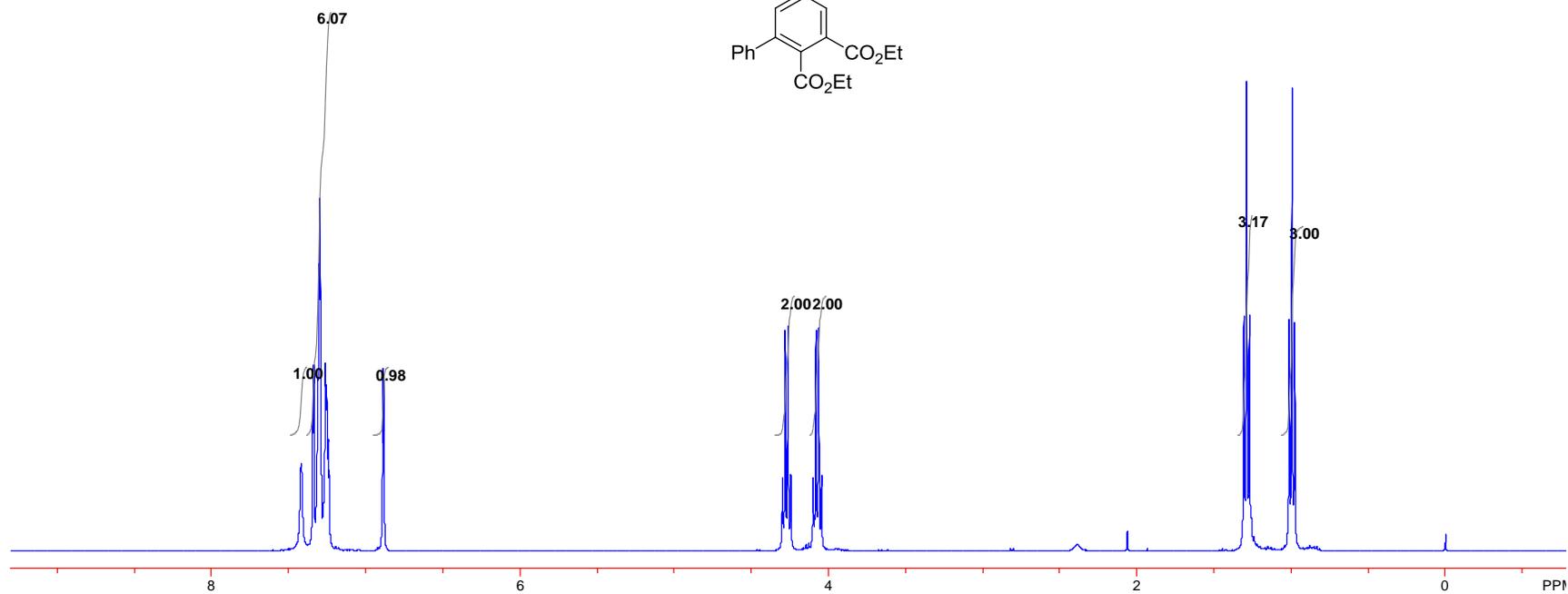
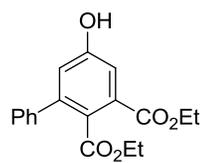


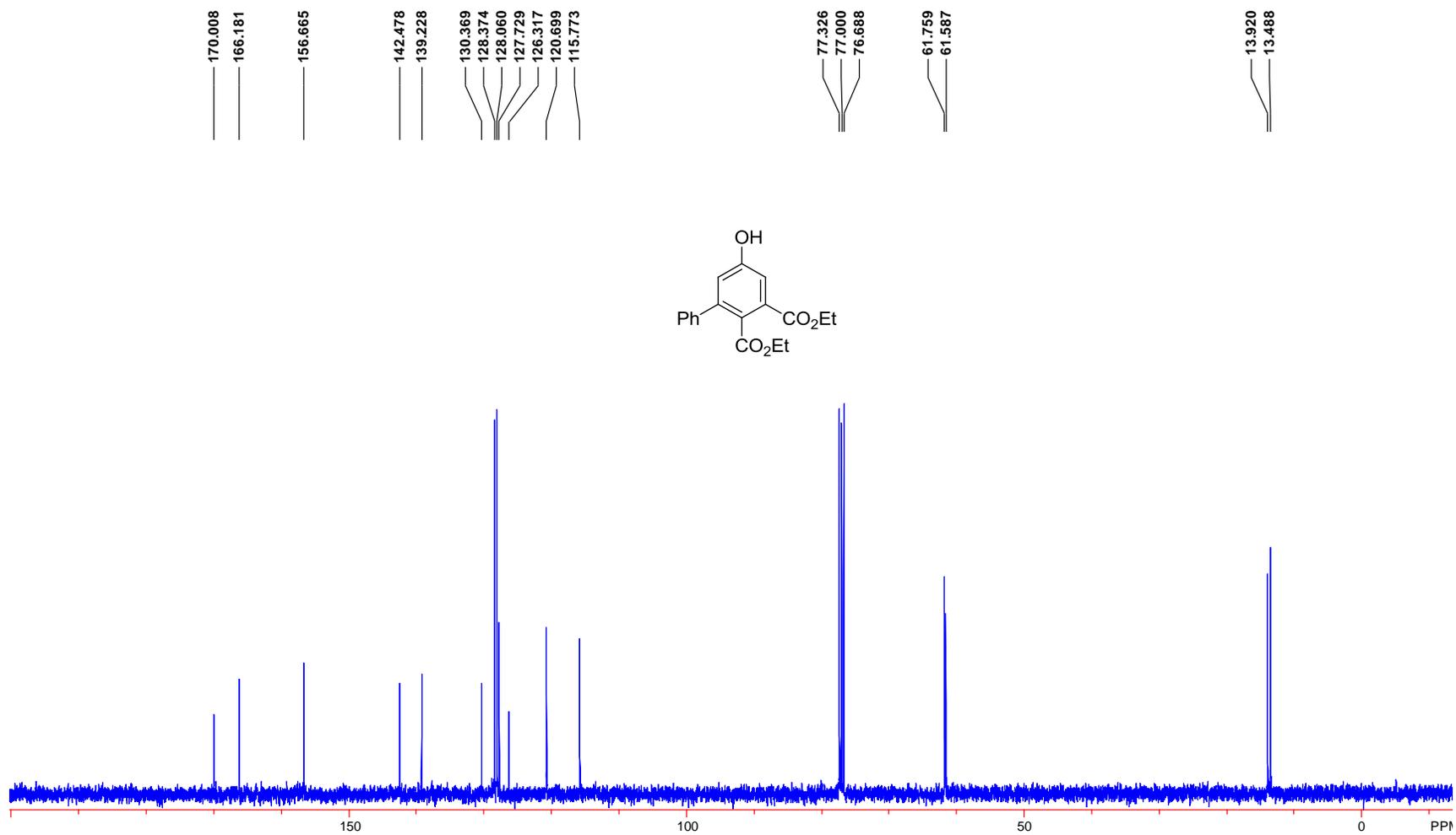


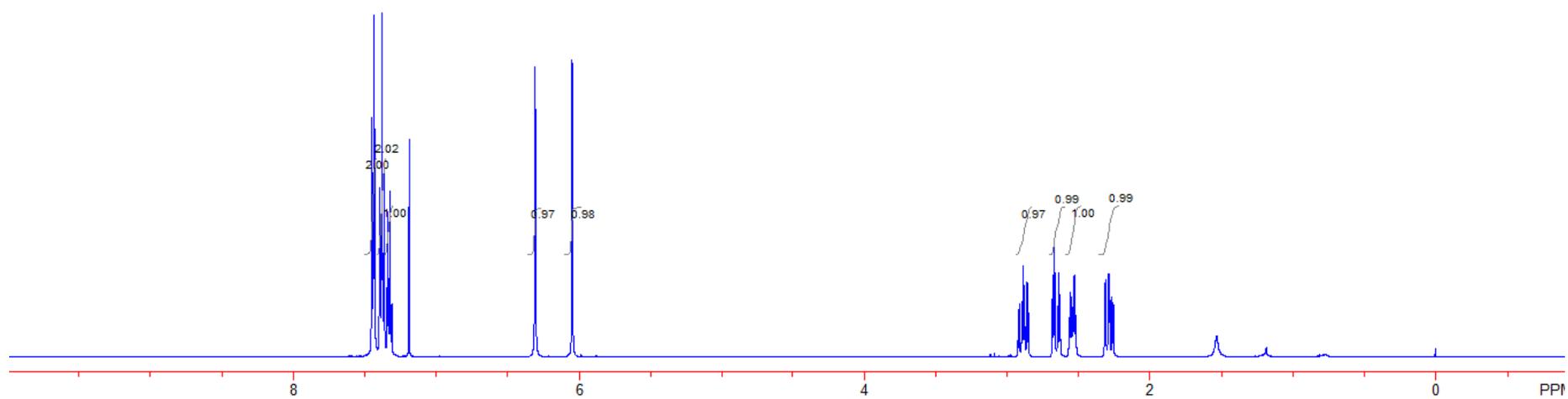
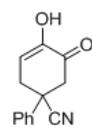
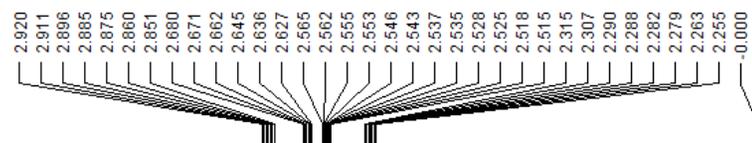
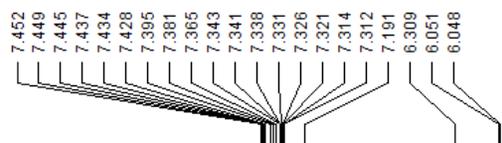
7.417  
7.341  
7.335  
7.311  
7.302  
7.295  
7.261  
7.252  
7.243  
7.237  
6.888  
6.882

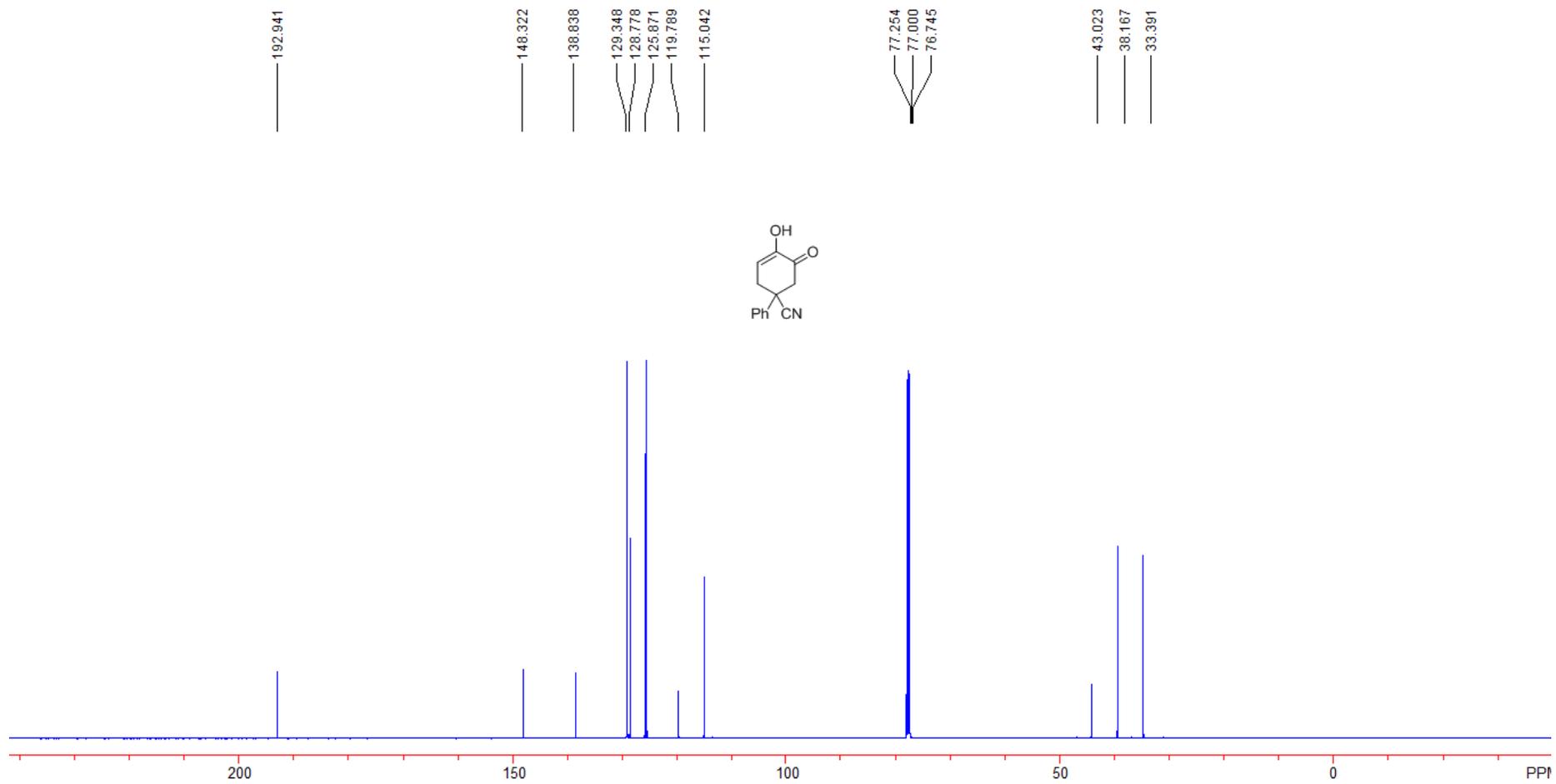
4.297  
4.279  
4.261  
4.244  
4.098  
4.080  
4.062  
4.045

1.307  
1.289  
1.271  
1.013  
0.995  
0.977









7.435  
7.432  
7.428  
7.416  
7.411  
7.395  
7.381  
7.365  
7.342  
7.327  
7.313  
7.190  
6.082  
6.074  
6.071  
6.063  
5.991

3.146  
3.143  
3.143  
3.112  
3.110  
3.083  
3.050  
3.026  
3.023  
3.014  
3.012  
2.990  
2.987  
2.978  
2.976  
2.972  
2.964  
2.936  
2.928

-0.000

