

## Supporting Information

### Kolbe-Schmitt Type Reaction under Ambient Conditions Mediated by Organic Base

Yuta Sadamitsu, Akira Okumura, Kodai Saito, and Tohru Yamada\*

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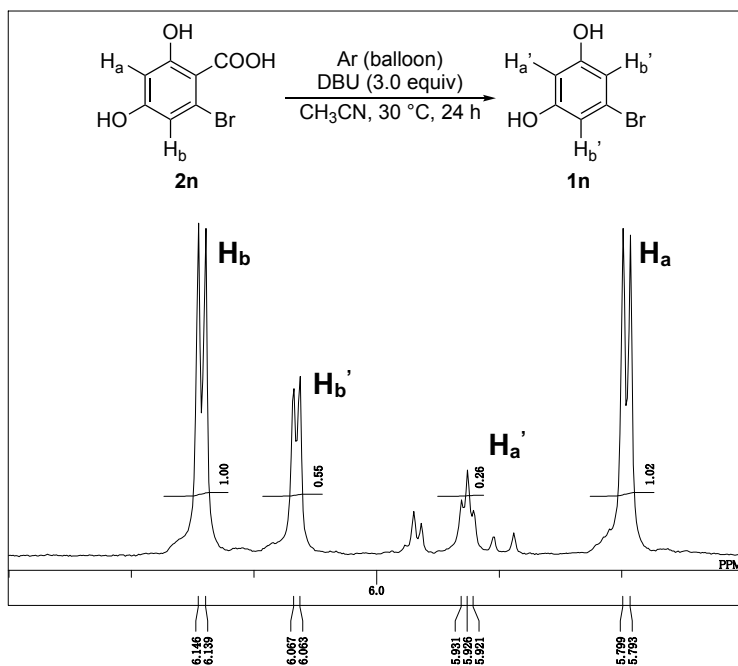
## 1. General

$^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded with a JEOL model AL-400, alpha-400 or ECX-400 spectrometer using  $\text{CD}_3\text{CN}$ , Acetone- $d_6$  or  $\text{DMSO}-d_6$  as the solvent. IR spectra were measured with a Thermo Electron Corporation model NICOLET 6700 FT-IR spectrometer. Melting points were measured with a Stanford Research Systems MPA100. ESI high resolution mass spectra were obtained using a Waters LCT Premier XE mass spectrometer. Column chromatography was conducted on silica gel (CHROMATOREX PSQ 100B Fuji Silysia). DBU was purchased from Tokyo Chemical Industry Co., Ltd., and used without further purification. Dehydrated  $\text{CH}_3\text{CN}$  was purchased from FUJIFILM Wako Pure Chemical Co..

## 2. Supporting results & discussion

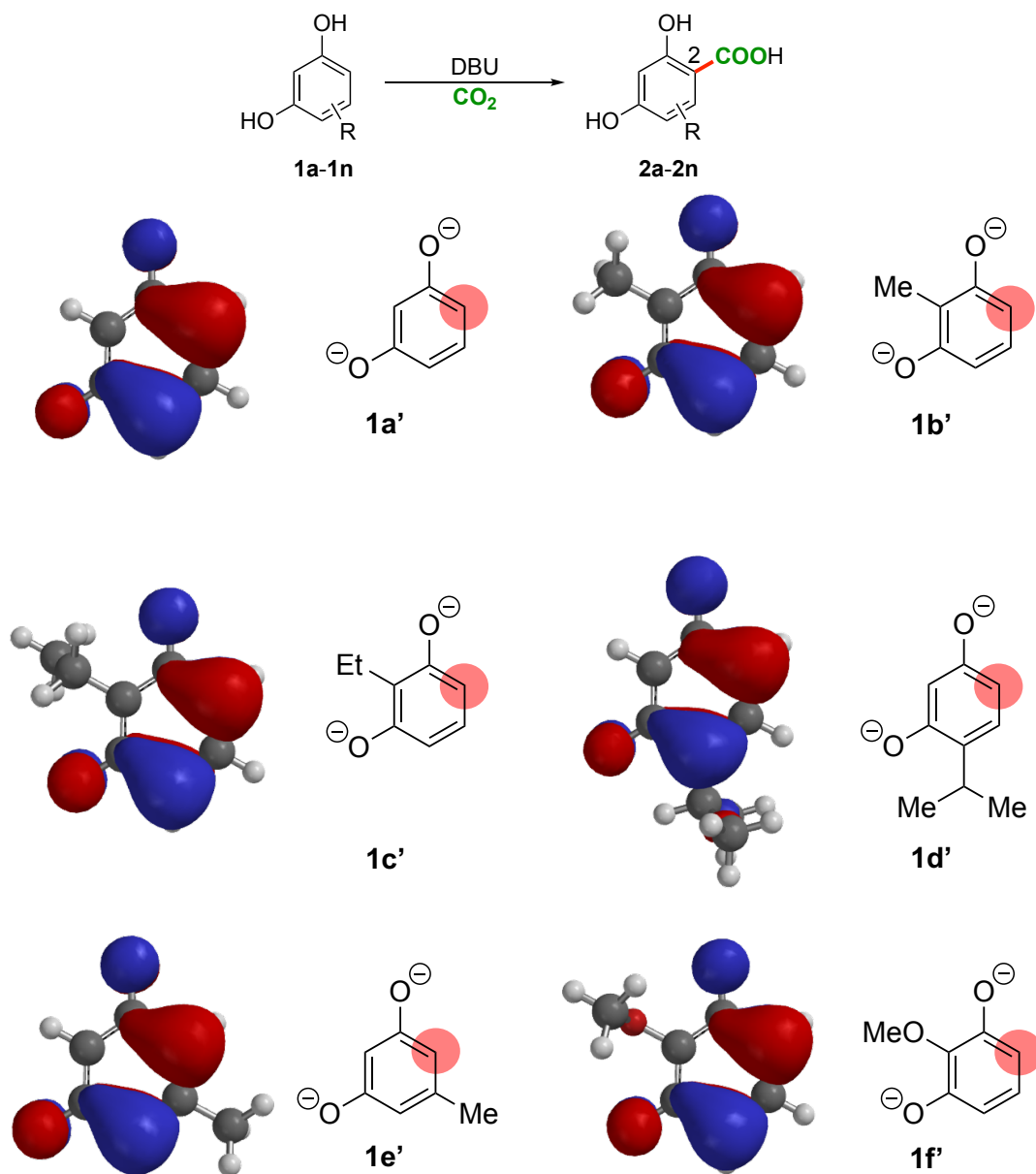
### 2.1 Confirmation of decarboxylation of **2n**

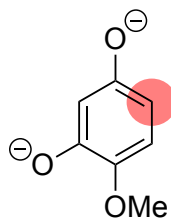
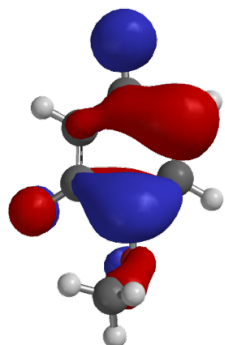
When the resorcinol **1n** was treated with 3 equiv of DBU in  $\text{CH}_3\text{CN}$  under 2 MPa of  $\text{CO}_2$  atmosphere at  $30\text{ }^\circ\text{C}$ , the carboxylated product **2n** was not observed. On the other hand, when the salicylic acid **2n** was employed for this reaction condition under Ar atmosphere, the decarboxylation proceeded to afford the resorcinol **1n** (20% conversion, detected by  $^1\text{H}$  NMR). It suggested that the reaction rate of decarboxylation of **2n** was faster than that of carboxylation of **1n**.



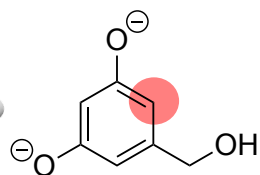
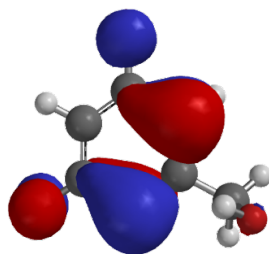
## 2.2 Molecular orbital of HOMO of resorcinol dianion **1a'-1q'** (B3LYP/6-311++G\*\*)

The HOMO of dianions of resorcinols **1a'-1q'** were calculated at the level of B3LYP/6-311++G\*\*.

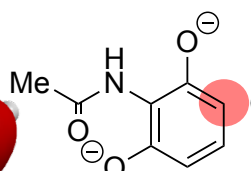
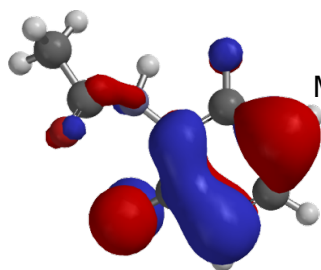




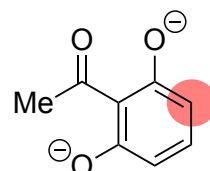
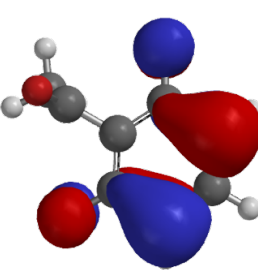
**1g'**



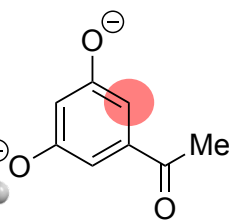
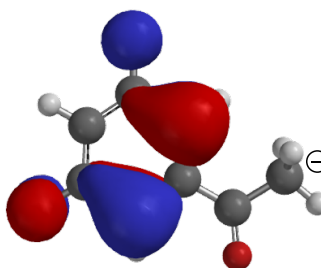
**1h'**



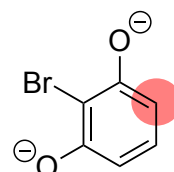
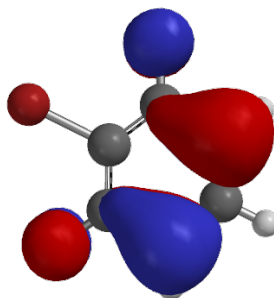
**1i'**



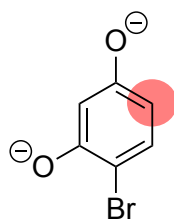
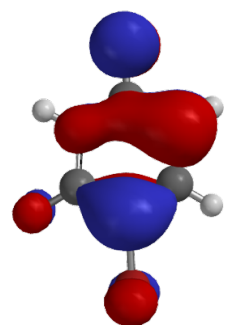
**1j'**



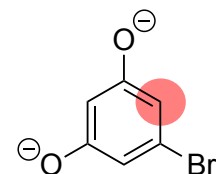
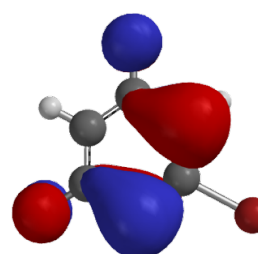
**1k'**



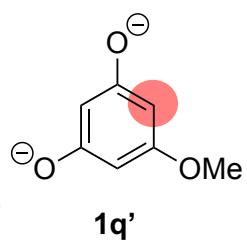
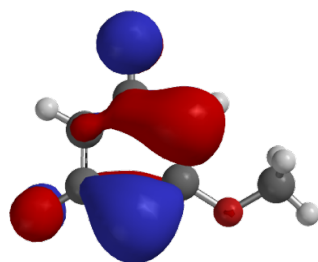
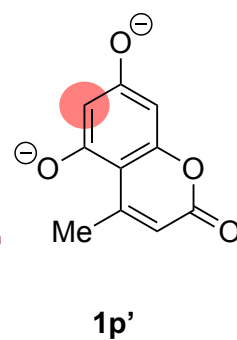
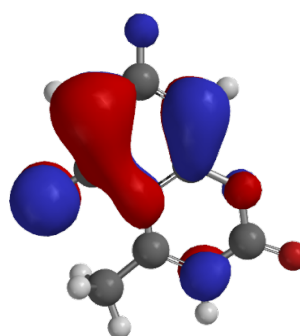
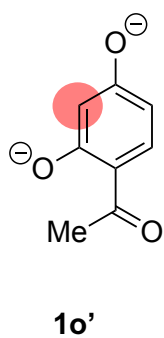
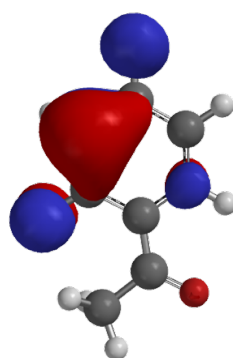
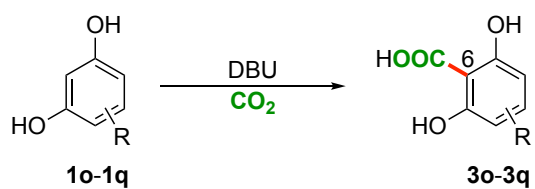
**1l'**



**1m'**



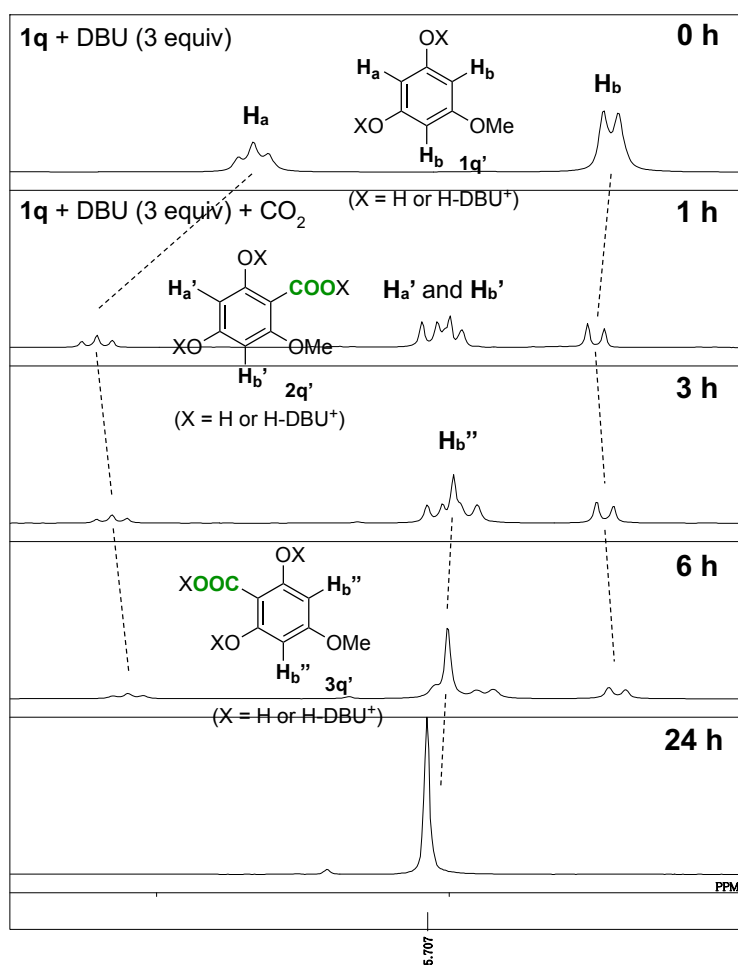
**1n'**



The carboxylation site of **1q** was not matched with the site predicted by the theoretical calculation. Please see the detail at the next section (S6).

## 2.3 Examination and consideration of the site-selectivity of **1q**

According to the HOMO of dianion **1q'** computed by theoretical calculation, the carboxylation should occur at the 2-position of resorcinol **1q**. However, when **1q** was employed for this reaction, only 6-carboxylated product **3q** was obtained. In order to elucidate this reason, time course experiment of the carboxylation reaction of **1q** using  $^1\text{H}$  NMR was conducted. When 3 equiv of DBU was added to **1q**,  $\text{H}_b$  was observed in the lowest chemical shift. It suggested that the  $\text{H}_b$  (2-position) is the most reactive site. After 2 MPa of  $\text{CO}_2$  was purged and the reaction was stirred for 1 h, the two doublet peaks appeared. Those could be signals of 2-carboxylated product **2q**. Thus, it indicated that carboxylation at  $\text{C}_b$  was faster than that of  $\text{C}_a$ . After furthermore reaction, one singlet peak area was increased and former two doublet peaks were diminished. The singlet peak was assigned as the signal of 6-carboxylated product **3q**. It indicated that 2-carboxylated product **2q** is not thermodynamically stable and decarboxylation proceeded. Therefore, **3q** was finally obtained.





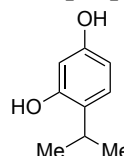
Resorcinol **1d** was prepared by the following procedure<sup>1,3,4</sup>. Under N<sub>2</sub> atmosphere, 2',4'-dihydroxy acetophenone (760.8 mg, 5.0 mmol), and K<sub>2</sub>CO<sub>3</sub> (2.07 g, 15 mmol) were dissolved into DMF (3.1 mL). To the solution, iodomethane (0.78 mL, 12.5 mmol) was added. After being stirred for 16 h at room temperature, the reaction was diluted by water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=20:1) to afford the acetophenone **S1** (826.7 mg, 92%).

Under N<sub>2</sub> atmosphere, the acetophenone **S1** (826.7 mg, 4.6 mmol) was dissolved into THF (9.2 mL). After cooling at 0 °C, MeMgBr (6.9 mL, 6.9 mmol, 1.0 M solution in THF) was added dropwise, and the reaction was warmed to room temperature. The reaction was quenched by sat. NH<sub>4</sub>Cl aq., and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=5:1) to afford the benzyl alcohol **S2** (806.8 mg, 90%).

Under N<sub>2</sub> atmosphere, the benzyl alcohol **S2** (392.5 mg, 2.0 mmol) was dissolved into TFA (6.7 mL). To the solution, triethylsilane (0.92 mL, 5.8 mmol) was added dropwise. After being stirred for 3 h at room temperature, the reaction was neutralized by sat. NaHCO<sub>3</sub> aq., and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=50:1) to afford the desired dimethoxybenzene **S3** (266.6 mg, 74%).

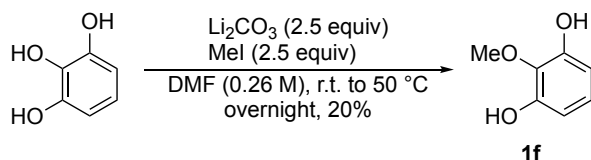
Under N<sub>2</sub> atmosphere, dimethoxybenzene **S3** (855.3 mg, 4.7 mmol) was dissolved into DCM (4.7 mL). After cooling at 0 °C, BBr<sub>3</sub> (11.3 mL, 11.3 mmol, 1.0 M solution in DCM) was added dropwise, and the reaction was warmed to room temperature. The reaction was quenched by water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the resorcinol **1d** (424.1 mg, 59%).

#### 4-isopropylbenzene-1,3-diol (**1d**)<sup>5</sup>

 Pale brown solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 1.08 (d, *J* = 6.8 Hz, 6H), 3.05 (sept, *J* = 6.8 Hz, 1H), 6.13 (dd, *J* = 2.4, 8.4 Hz, 1H), 6.24 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 8.4 Hz, 1H), 8.89 (bs, 1H), 9.01 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 22.9, 25.8, 102.4, 105.9, 124.8, 126.1, 155.0, 155.8.



### 3.1.3 The preparation of **1f**<sup>6</sup>

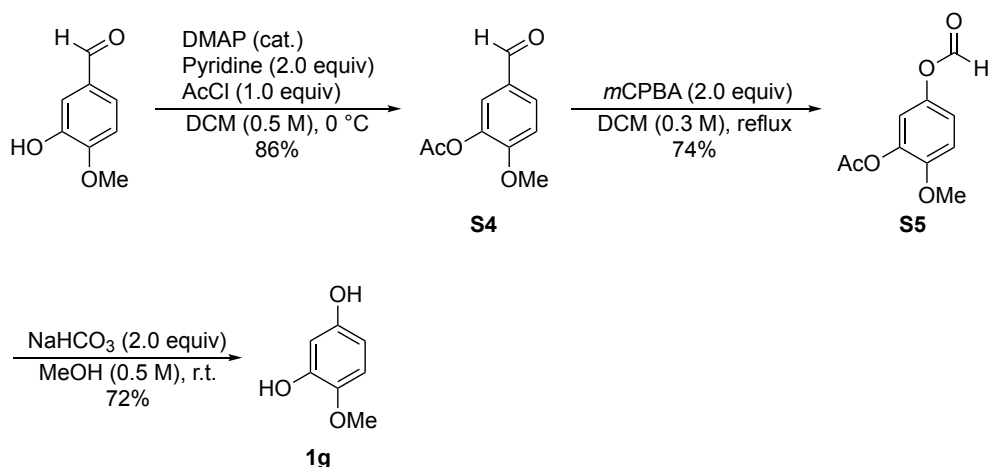


Resorcinol **1f** was prepared by the following procedure<sup>6</sup>. Under  $\text{N}_2$  atmosphere, pyrogallol (630.6 mg, 5.0 mmol), and  $\text{Li}_2\text{CO}_3$  (923.6 mg, 12.5 mmol) were dissolved into  $\text{DMF}$  (19 mL). To the solution, iodomethane (0.78 mL, 12.5 mmol) was added and the reaction mixture was stirred at  $50\text{ }^\circ\text{C}$  overnight. The reaction was diluted by water, and extracted three times with  $\text{EtOAc}$ . The combined organic layer was dried over  $\text{Na}_2\text{SO}_4$ , and the solvent was removed under reduced pressure. The residue was purified by column chromatography ( $\text{SiO}_2$ , eluent: hexane: $\text{EtOAc}$ =5:1 to 3:1) to afford the resorcinol **1f** (138.9 mg, 20%).

### 2-methoxybenzene-1,3-diol (**1f**)<sup>6</sup>

White solid;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 3.65$  (s, 3H), 6.26 (d,  $J = 8.4$  Hz, 2H), 6.65 (t,  $J = 8.4$  Hz, 1H), 8.99 (s, 2H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta = 59.8, 107.4, 123.5, 135.7, 151.0$ .

### 3.1.4 The preparation of **1g**<sup>7,8</sup>



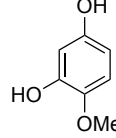
Resorcinol **1g** was prepared by the following procedure<sup>7,8</sup>. Under  $\text{N}_2$  atmosphere, isovanillin (1.52 g, 10 mmol),  $\text{DMAP}$  (2 pieces, cat.), and  $\text{pyridine}$  (1.6 mL, 20 mmol) were dissolved into  $\text{DCM}$  (20 mL). After cooling at  $0\text{ }^\circ\text{C}$ ,  $\text{AcCl}$  (0.71 mL, 12.5 mmol) was added

dropwise. The reaction was quenched by water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the benzaldehyde **S4** (1.66 g, 86%).

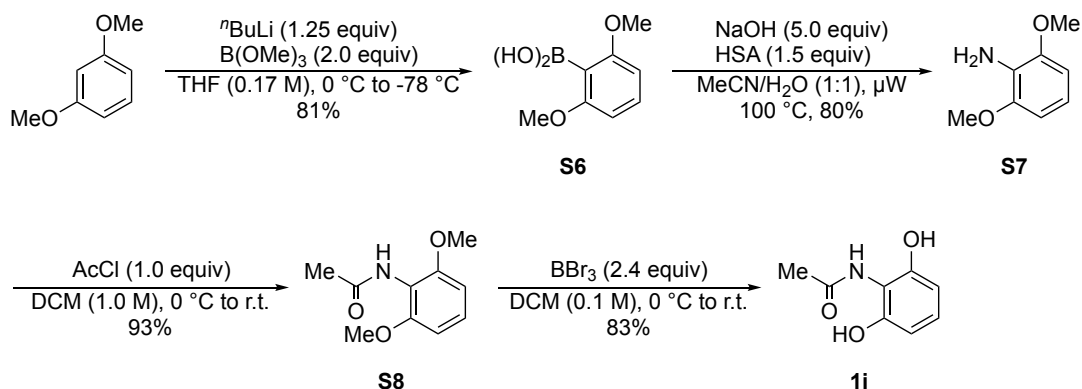
Under N<sub>2</sub> atmosphere, the benzaldehyde **S4** (918.6 g, 4.7 mmol) and *m*CPBA (2.33 g, 9.5 mmol, contains ca. 30% water) were dissolved into DCM (16 mL), and the reaction was refluxed. The reaction was quenched by sat. NaHSO<sub>3</sub> aq., and extracted three times with DCM, and washed with sat. NaHCO<sub>3</sub> aq.. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=5:1) to afford the methoxybenzene **S5** (732.3 mg, 74%).

The methoxybenzene **S5** (732.3 mg, 3.5 mmol) and NaHCO<sub>3</sub> (588.1 mg, 7.0 mmol) were dissolved into MeOH (7 mL), and the reaction was stirred at room temperature. The reaction was diluted with water and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the resorcinol **1g** (348.8 g, 72%).

#### 4-methoxybenzene-1,3-diol (**1g**)<sup>9</sup>

 White solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 3.63 (s, 3H), 6.10 (dd, *J* = 2.8 Hz, 8.4 Hz, 1H), 6.26 (d, *J* = 2.8 Hz, 1H), 6.67 (d, *J* = 8.4 Hz, 1H), 8.76 (s, 1H), 8.81 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 55.6, 103.8, 104.9, 114.2, 140.7, 147.5, 151.9.

### 3.1.5 The preparation of **1i**<sup>10,11</sup>



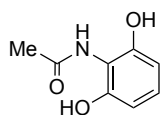
Resorcinol **1i** was prepared by the following procedure<sup>10,11</sup>. Under N<sub>2</sub> atmosphere, 1,3-dimethoxybenzene (1.3 mL, 10 mmol) was dissolved into THF (59 mL). The reaction was cooled at 0 °C, and <sup>n</sup>BuLi (0.92 mL, 8.0 mmol, 1.57 M solution in *n*-hexane) was added, dropwise. After being stirred for 4 h at 0 °C, the reaction was cooled at -78 °C, and B(OMe)<sub>3</sub> (2.2 mL, 20 mmol) was added. After stirred overnight at room temperature, the reaction was quenched with 1 N HCl aq., and stirred for 1 h. The reaction mixture was extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the desired phenyl boronic acid **S6** (1.48 g, 81%).

To the vial, the aryl boronic acid **S6** (364.0 mg, 2.0 mmol), Hydroxylamine-*O*-sulfonic acid (339.3 mg, 3.0 mmol), MeCN (10 mL), and NaOH (10 mmol, 10 mL, 1 N solution in H<sub>2</sub>O) were added. The vial tube was sealed and heated with microwave at 100 °C for 1 h. After the reaction was cooled to room temperature, the reaction mixture was extracted three times with Et<sub>2</sub>O. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=5:1) to afford the desired aniline **S7** (244.7 mg, 80%).

Under N<sub>2</sub> atmosphere, the aniline **S7** (408.6 mg, 2.7 mmol) was dissolved into DCM (3 mL). The reaction was cooled at 0 °C, and AcCl (0.19 mL, 2.7 mmol) was added, dropwise. After stirred overnight at room temperature, the reaction was quenched with water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=1:1) to afford the desired amide **S8** (484.3 mg, 93%).

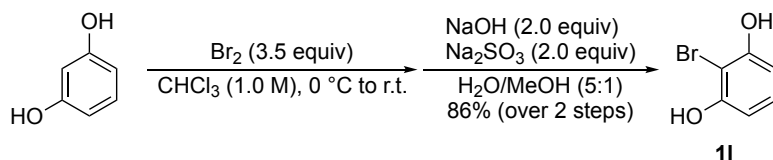
Under N<sub>2</sub> atmosphere, amide **S3** (484.3 mg, 2.5 mmol) was dissolved into DCM (25 mL). After cooling at 0 °C, BBr<sub>3</sub> (6.0 mL, 6.0 mmol, 1.0 M solution in DCM) was added dropwise, and the reaction was warmed at room temperature. The reaction was quenched by water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=2:1) to afford the resorcinol **1i** (344.1 mg, 83%).

#### *N*-(2,6-dihydroxyphenyl)acetamide (**1i**)<sup>12</sup>



Pale brown solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 2.10 (s, 3H), 6.34 (d, *J* = 7.6 Hz, 2H), 6.86 (d, *J* = 7.6 Hz, 1H), 9.24-9.51 (m, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 22.8, 107.6, 114.1, 126.7, 152.1, 170.4.

### 3.1.6 The preparation of **11**<sup>13</sup>

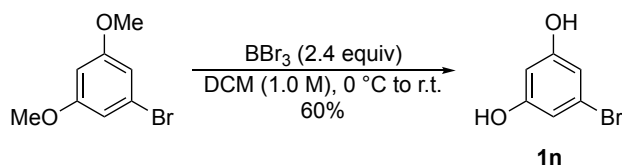


Resorcinol **11** was prepared by the following literature<sup>13</sup>. Under N<sub>2</sub> atmosphere, resorcinol (220.2 mg, 2.0 mmol) was dissolved into CHCl<sub>3</sub> (2.0 mL). After cooling at 0 °C, Br<sub>2</sub> (0.36 mL, 7.0 mmol) was added dropwise, and the reaction was warmed at room temperature. After being stirred, the solvent was removed, and the crude was dissolved into MeOH (0.8 mL). To the reaction, NaOH (160.0 mg, 4.0 mmol), Na<sub>2</sub>SO<sub>3</sub> (504.2 mg, 4.0 mmol), and water (4 mL) was added and stirred for 1 h. The reaction was quenched by 1 N HCl aq., and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the resorcinol **11** (325.0 mg, 86%)

### 2-bromobenzene-1,3-diol (**11**)<sup>14</sup>

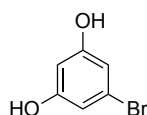
White solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 6.39 (d, *J* = 8.4 Hz, 2H), 6.91 (t, *J* = 8.4 Hz, 1H), 9.96 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 98.0, 106.8, 128.0, 155.5.

### 3.1.7 The preparation of **1n**<sup>4</sup>



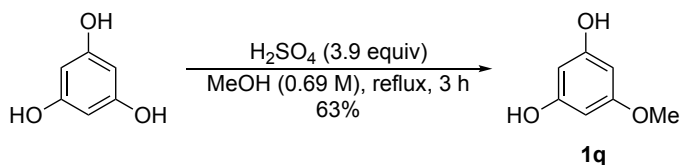
Resorcinol **1n** was prepared by the following procedure<sup>4</sup>. Under N<sub>2</sub> atmosphere, 5-bromo-1,3-dimethoxybenzene (1.09 g, 5.0 mmol) was dissolved into DCM (5 mL). After cooling at 0 °C, BBr<sub>3</sub> (12 mL, 12 mmol, 1.0 M solution in DCM) was added dropwise, and the reaction was warmed at room temperature. The reaction was quenched by water, and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=3:1) to afford the resorcinol **1n** (562.8 mg, 60%)

### 5-bromobenzene-1,3-diol (**1n**)<sup>4</sup>



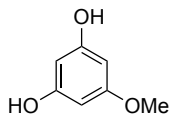
Pale brown solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 6.19 (t, *J* = 2.0 Hz, 1H), 6.38 (d, *J* = 2.0 Hz, 2H), 9.69 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 101.8, 109.4, 121.8, 159.3.

### 3.1.8 The preparation of **1q**<sup>15</sup>



Resorcinol **1q** was prepared by the following literature<sup>15</sup>. Under N<sub>2</sub> atmosphere, phloroglucinol (630.6 mg, 5.0 mmol) was dissolved into MeOH (7 mL). To the reaction, H<sub>2</sub>SO<sub>4</sub> (1.0 mL, 19.5 mmol) was added dropwise, and the reaction was refluxed for 3 h. The reaction was quenched by sat. NaHCO<sub>3</sub> aq., and extracted three times with EtOAc. The combined organic layer was dried over Na<sub>2</sub>SO<sub>4</sub>, and the solvent was removed under reduced pressure. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=4:1 to 2:1) to afford the resorcinol **1n** (442.7 mg, 63%)

### 5-methoxybenzene-1,3-diol (**1q**)<sup>16</sup>



White solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 3.60 (s, 3H), 5.78 (s, 2H), 5.81 (s, 1H), 9.19 (s, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 54.7, 92.6, 95.5, 159.1, 161.2.

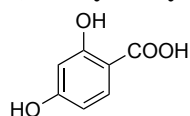
## 3.2 Procedure for Kolbe-Schmitt reaction on resorcinols

The reaction was performed using a pressure test tube equipped with a stirring bar in a 30 mL autoclave. To a solution of resorcinol **1a** (11.0 mg, 0.100 mmol) in dry CH<sub>3</sub>CN (1.0 mL) in a pressure test tube was added DBU (44.9 μL, 0.300 mmol). The pressure test tube containing the reaction mixture was placed in the autoclave. CO<sub>2</sub> (2.0 MPa) was charged and the reaction mixture was stirred at 30 °C for 24 h. After the CO<sub>2</sub> was carefully vented, 1 M HCl aq. (ca. 3.0 mL) was added to the mixture. The resulting mixture was extracted with ethyl acetate three times and volatile materials were removed under reduced pressure. The residue was purified by flash silica-gel column chromatography (eluent: EtOAc:AcOH=99:1, v/v) to afford **2a** (15.4 mg, 0.999 mmol) in >99% as a white solid.

The larger scale reaction was carried out as follows. The reaction was performed using

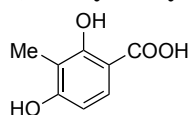
a 1 L three necked round bottom flask. To a solution of resorcinol **1a** (11.0 g, 0.100 mol) in dry CH<sub>3</sub>CN (500 mL) in a flask was added DBU (44.9 mL, 0.300 mol). CO<sub>2</sub> (balloon) was charged and the reaction mixture was stirred at room temperature for 28 h. After the CO<sub>2</sub> balloon was removed, 1 M HCl aq. (ca. 500 mL) was added to the mixture. The resulting mixture was extracted with ethyl acetate several times (checked by TLC) and volatile materials were removed under reduced pressure. The residue was purified by recrystallization (hexane/EtOAc) to afford **2a** (12.9 g, 0.838 mol) in 84% as a white solid.

### 2,4-dihydroxybenzoic acid (**2a**)<sup>17</sup>



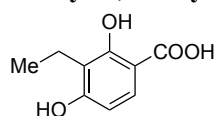
White solid; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 6.25 (d, *J* = 2.4 Hz, 1H), 6.33 (dd, *J* = 2.4 Hz, 8.8 Hz, 1H), 7.60 (d, *J* = 8.8 Hz, 1H), 10.42 (bs, 1H), 11.40 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 102.4, 104.5, 108.1, 132.1, 163.5, 164.2, 172.1.

### 2,4-dihydroxy-3-methylbenzoic acid (**2b**)



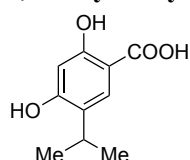
The reaction was carried out with **1b** (12.4 mg, 0.1 mmol), DBU (44.9 μL, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (16.0 mg, 95%); mp 182 °C (decomp.)(lit.<sup>18</sup>, 213-214 °C, decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 1.95 (s, 3H), 6.39 (d, *J* = 8.4 Hz, 1H), 7.48 (d, *J* = 8.4 Hz, 1H), 10.29 (s, 1H), 11.72 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 7.9, 103.9, 107.0, 110.2, 128.5, 161.4, 161.6, 172.6.; IR (KBr): 3426, 1645, 1622, 1504, 1420, 1300, 1084, 781; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>8</sub>H<sub>9</sub>O<sub>4</sub><sup>+</sup>, 169.0495; found, m/z 169.0498.

### 3-ethyl-2,4-dihydroxybenzoic acid (**2c**)



The reaction was carried out with **1c** (13.8 mg, 0.1 mmol), DBU (44.9 μL, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (18.2 mg, quant); mp 167 °C (decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 1.01 (t, *J* = 7.2 Hz, 3H), 2.52 (q, *J* = 7.2 Hz, 2H), 6.39 (d, *J* = 8.8 Hz, 1H), 7.48 (d, *J* = 8.8 Hz, 1H), 10.22 (s, 1H), 11.71 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 13.3, 15.6, 104.0, 107.2, 116.5, 128.7, 161.2, 161.3, 172.6; IR (KBr): 3415, 1621, 1423, 1278, 1098, 792; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>11</sub>O<sub>4</sub><sup>+</sup>, 183.0652; found, m/z 183.0657.

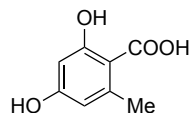
### 2,4-dihydroxy-5-isopropylbenzoic acid (**2d**)<sup>19</sup>



The reaction was carried out with **1d** (15.2 mg, 0.1 mmol), DBU (44.9 μL, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (16.6 mg, 85%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>): δ = 1.11 (d, *J* = 7.2 Hz, 6H), 3.06 (sept, *J* = 7.2 Hz, 1H), 6.31 (s, 1H), 7.48 (s, 1H), 10.34 (s, 1H), 11.30 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>): δ = 22.5, 25.8, 102.0, 103.8, 126.7, 127.4,

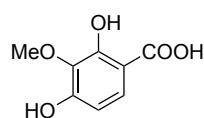
161.3, 161.4, 172.1.

#### 2,4-dihydroxy-6-methylbenzoic acid (**2e**)<sup>20</sup>



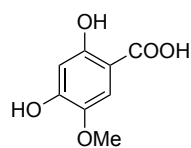
The reaction was carried out with **1e** (12.4 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 40 °C for 24 h; White solid (16.0 mg, 95%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.46 (s, 3H), 6.16 (d, *J* = 2.4 Hz, 1H), 6.21 (d, *J* = 2.4 Hz, 1H), 10.10 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 23.5, 100.5, 104.9, 111.1, 143.0, 162.0, 164.5, 173.4.

#### 2,4-dihydroxy-3-methoxybenzoic acid (**2f**)<sup>21</sup>



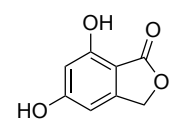
The reaction was carried out with **1f** (14.0 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (15.2 mg, 83%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 3.69 (s, 3H), 6.33 (d, *J* = 9.2 Hz, 1H), 7.36 (d, *J* = 9.2 Hz, 1H), 9.91 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 59.8, 105.3, 107.8, 125.7, 134.8, 156.2, 156.4, 172.3.

#### 2,4-dihydroxy-5-methoxybenzoic acid (**2g**)



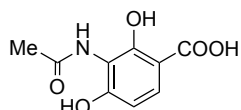
The reaction was carried out with **1g** (14.0 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (17.9 mg, 97%); mp 174 °C (decomp.)(lit.<sup>22</sup>, 201 °C, decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 3.69 (s, 3H), 6.32 (s, 1H), 7.14 (s, 1H), 10.31 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 56.3, 102.8, 103.5, 112.2, 141.4, 154.5, 158.0, 172.1; IR (KBr): 3488, 1654, 1624, 1259, 1171, 1025, 868; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>8</sub>H<sub>9</sub>O<sub>5</sub><sup>+</sup>, 185.0444; found, m/z 185.0458.

#### 5,7-dihydroxyisobenzofuran-1(3H)-one (**2h**)



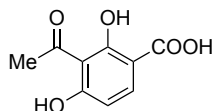
The reaction was carried out with **1h** (14.0 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; Pale purple solid (15.2 mg, 92%); mp 221 °C (decomp.)(lit., 253-260, decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 5.10 (s, 2H), 6.28 (d, *J* = 1.2 Hz, 1H), 6.33 (d, *J* = 1.2 Hz, 1H), 10.30-10.59 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 68.1, 100.2, 102.2, 102.9, 151.5, 158.2, 164.6, 168.5; IR (KBr): 3358, 3213, 1717, 1617, 1487, 1351, 1217, 1167, 1053; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>7</sub>O<sub>4</sub><sup>+</sup>, 167.3339; found, m/z 167.3338.

### 3-acetamido-2,4-dihydroxybenzoic acid (2i)



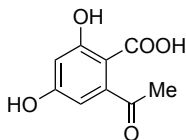
The reaction was carried out with **1i** (16.7 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (18.9 mg, 90%); mp 169 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.01 (s, 3H), 6.42 (d, *J* = 8.8 Hz, 1H), 7.55 (d, *J* = 8.8 Hz, 1H), 9.04 (s, 1H), 10.21 (s, 1H), 11.81 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 22.8, 104.5, 107.9, 112.8, 129.0, 159.0, 159.3, 169.2, 172.3; IR (KBr): 3385, 1660, 1617, 1426, 1267, 1241, 756; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>10</sub>O<sub>5</sub>N<sup>+</sup>, 212.0553; found, m/z 212.0555.

### 3-acetyl-2,4-dihydroxybenzoic acid (2j)



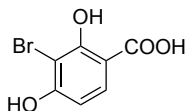
The reaction was carried out with **1j** (15.2 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 40 °C for 24 h; White solid (14.5 mg, 74%); mp 159 °C (decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.62 (s, 3H), 6.44 (d, *J* = 8.8 Hz, 1H), 7.84 (d, *J* = 8.8 Hz, 1H), 12.88 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 32.3, 104.1, 108.3, 111.4, 135.8, 164.1, 166.2, 171.9, 203.5; IR (KBr): 3437, 2843, 1629, 1585, 1480, 1451, 1261, 1235; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>O<sub>5</sub><sup>+</sup>, 197.0444; found, m/z 197.0446.

### 2-acetyl-4,6-dihydroxybenzoic acid (2k)



The reaction was carried out with **1k** (15.2 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 40 °C for 24 h; White solid (13.7 mg, 70%); mp 153 °C (decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 1.59 (s, 3H), 6.31 (s, 1H), 6.32 (s, 1H), 7.43 (bs, 1H), 10.47-10.55 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 26.5, 100.5, 103.3, 103.4, 103.6, 155.1, 157.8, 164.8, 166.0; IR (KBr): 3458, 3251, 1726, 1618, 1268, 1216, 1167, 1154; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>O<sub>5</sub><sup>+</sup>, 197.0444; found, m/z 197.0446.

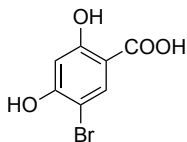
### 3-bromo-2,4-dihydroxybenzoic acid (2l)<sup>24</sup>



The reaction was carried out with **1l** (18.9 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (21.5 mg, 92%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 6.54 (d, *J* = 8.8 Hz, 1H), 7.63 (d, *J* = 8.8 Hz, 1H), 11.22 (bs, 1H), 12.28 (bs, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 97.2, 105.2, 107.5, 130.2, 160.2, 160.7, 172.0.

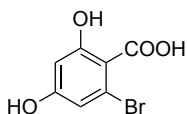


### 5-bromo-2,4-dihydroxybenzoic acid (**2m**)<sup>25</sup>



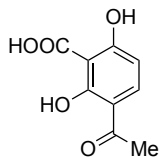
The reaction was carried out with **1m** (18.9 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 30 °C for 24 h; White solid (21.9 mg, 94%); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 6.47 (s, 1H), 7.81 (s, 1H), 10.58-11.94 (m, 2H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 99.8, 103.4, 106.2, 134.1, 160.2, 162.3, 170.9.

### 2-bromo-4,6-dihydroxybenzoic acid (**2n**)



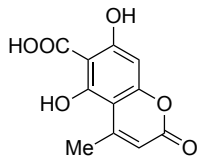
The reaction was carried out with **1n** (18.9 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 40 °C for 24 h; White solid (4.6 mg, 20%); mp 131 °C (decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 6.29 (d, *J* = 2.4 Hz, 1H), 6.47 (d, *J* = 2.4 Hz, 1H), 10.01 (s, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 102.0, 111.0, 114.6, 119.9, 158.1, 159.8, 168.3; IR (KBr): 3855, 3646, 1644, 1595, 1454, 1269, 1169, 854; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>7</sub>H<sub>6</sub>O<sub>4</sub>Br<sup>+</sup>, 232.9444; found, *m/z* 232.9453.

### 3-acetyl-2,6-dihydroxybenzoic acid (**3o**)



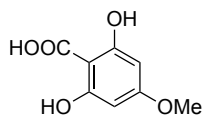
The reaction was carried out with **1o** (15.2 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in DMF at 100 °C for 48 h. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: hexane:EtOAc=1:1 to EtOAc:AcOH=99:1); White solid (8.4 mg, 43%); mp 185 °C (decomp.)(lit.<sup>26</sup>, 245-246, decomp.); <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.46 (s, 3H), 6.15 (d, *J* = 9.2 Hz, 1H), 7.60 (d, *J* = 9.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 31.6, 103.4, 106.5, 115.7, 133.6, 165.6, 167.8, 175.6, 195.4; IR (KBr): 3245, 3439, 1650, 1610, 1408, 1368, 1256, 604; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>9</sub>H<sub>9</sub>O<sub>5</sub><sup>+</sup>, 197.0444; found, *m/z* 197.0437.

### 5,7-dihydroxy-4-methyl-2-oxo-2H-chromene-6-carboxylic acid (**3p**)



The reaction was carried out with **1p** (19.2 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in CH<sub>3</sub>CN at 50 °C for 24 h. The residue was purified by column chromatography (SiO<sub>2</sub>, eluent: EtOAc:AcOH=50:1); Pale yellow solid (19.3 mg, 82%); mp 103 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 2.48 (s, 3H), 5.78 (s, 1H), 6.00-6.03 (m, 1H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  = 23.3, 93.0, 99.7, 101.3, 107.9, 155.8, 158.1, 160.0, 164.4, 165.4, 175.0; IR (KBr): 3408, 2933, 1686, 1604, 1391, 1369, 1263, 559; HRMS (ESI): [M+H]<sup>+</sup> calcd for C<sub>11</sub>H<sub>9</sub>O<sub>6</sub><sup>+</sup>, 237.0394; found, *m/z* 237.0373.

### 2,6-dihydroxy-4-methoxybenzoic acid (3q)



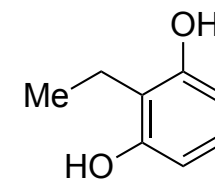
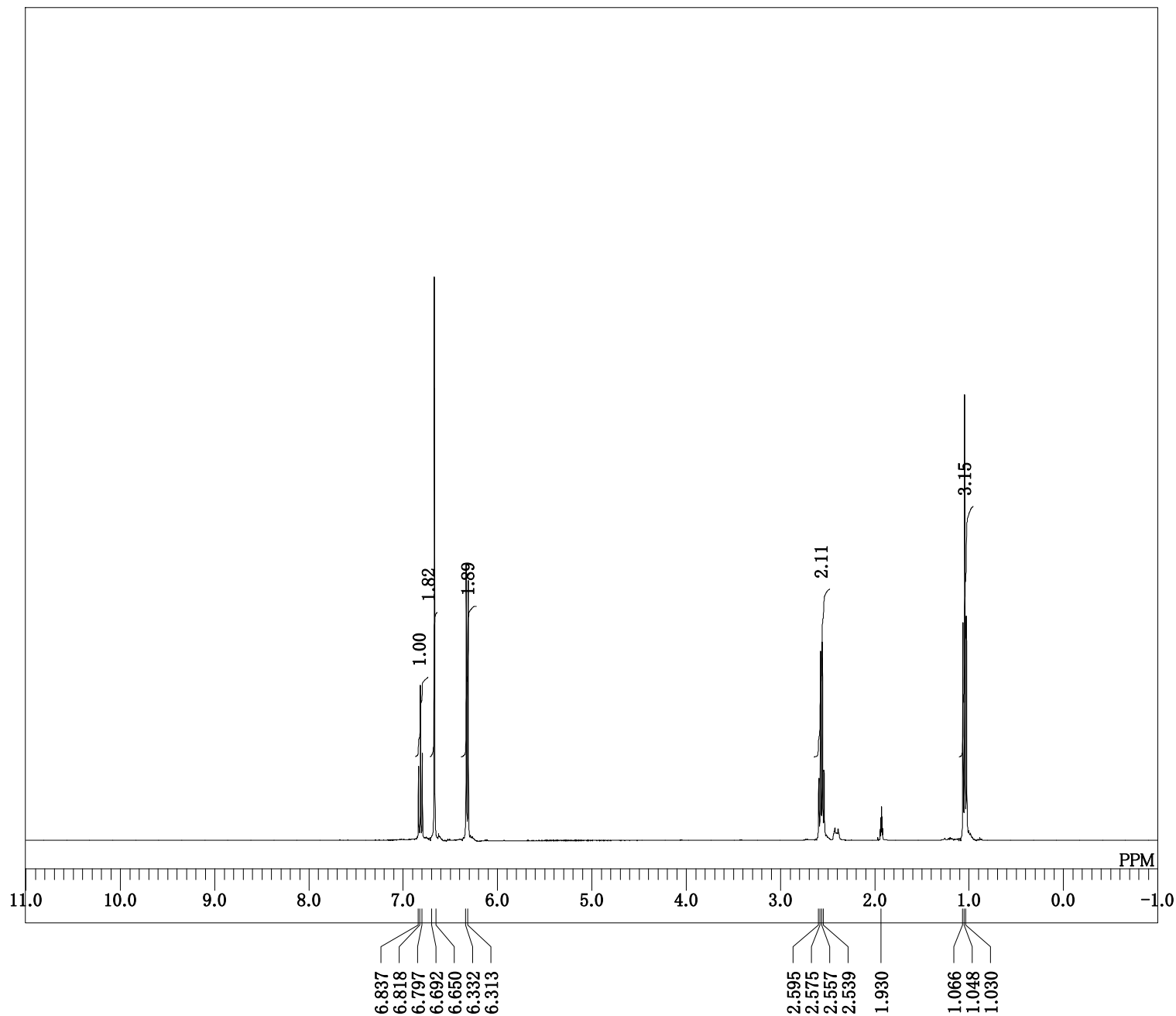
The reaction was carried out with **1q** (14.0 mg, 0.1 mmol), DBU (44.9  $\mu$ L, 0.3 mmol) in  $\text{CH}_3\text{CN}$  at 30  $^\circ\text{C}$  for 24 h; White solid (18.4 mg, quant); mp 132  $^\circ\text{C}$  (decomp.);  $^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ ):  $\delta$  = 3.72 (s, 3H), 5.80 (s, 2H), 12.69 (bs, 1H);  $^{13}\text{C}$  NMR (100 MHz, DMSO- $d_6$ ):  $\delta$  = 54.7, 91.0, 92.7, 95.5, 159.0, 161.1; IR (KBr): 3555, 3493, 3442, 1655, 1591, 1372, 1159; HRMS (ESI):  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_8\text{H}_9\text{O}_5^+$ , 185.0444; found,  $m/z$  185.0469.

### References

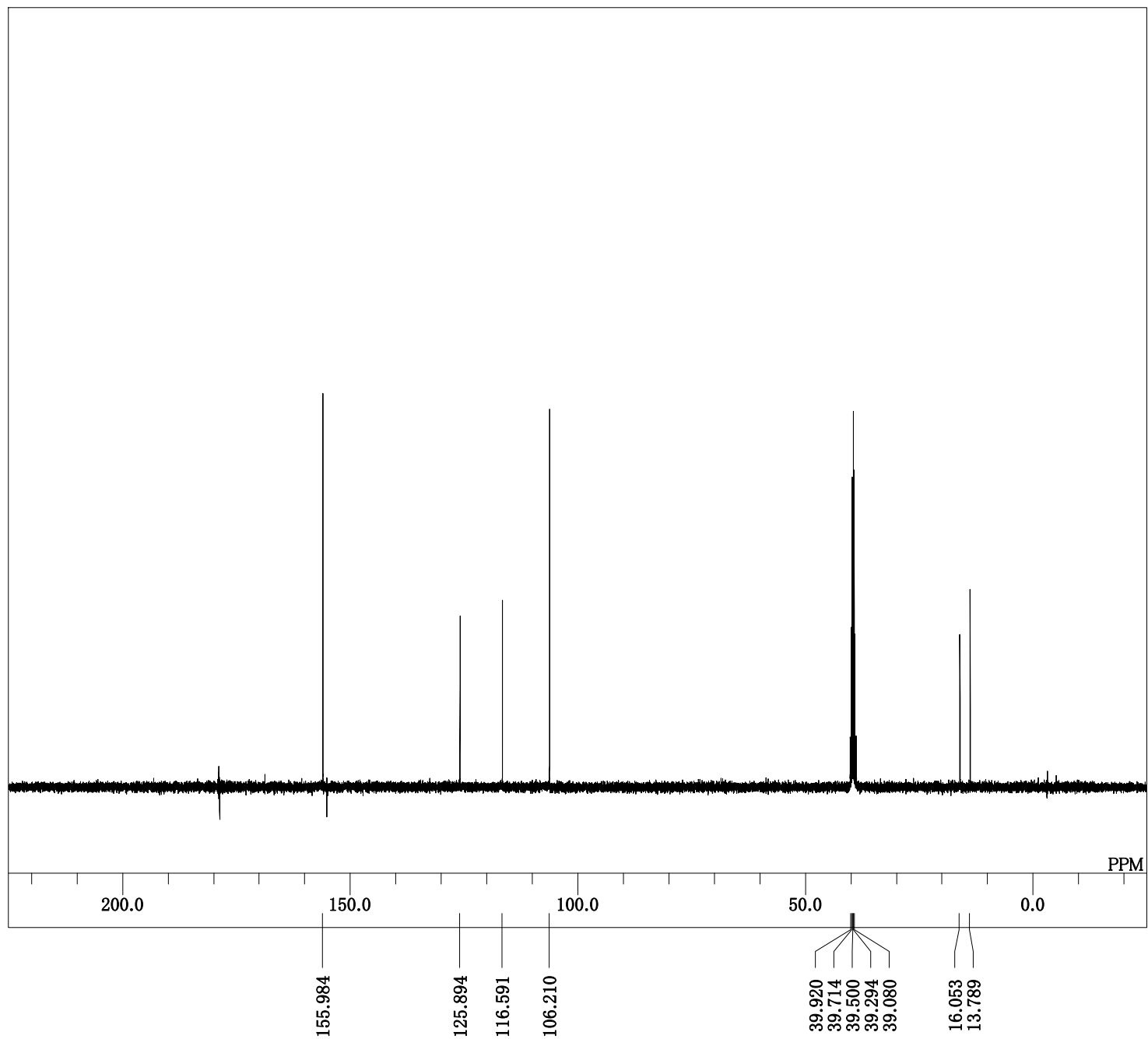
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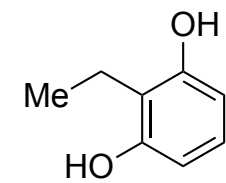
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**1c**

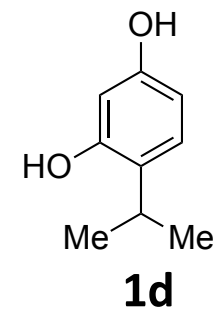
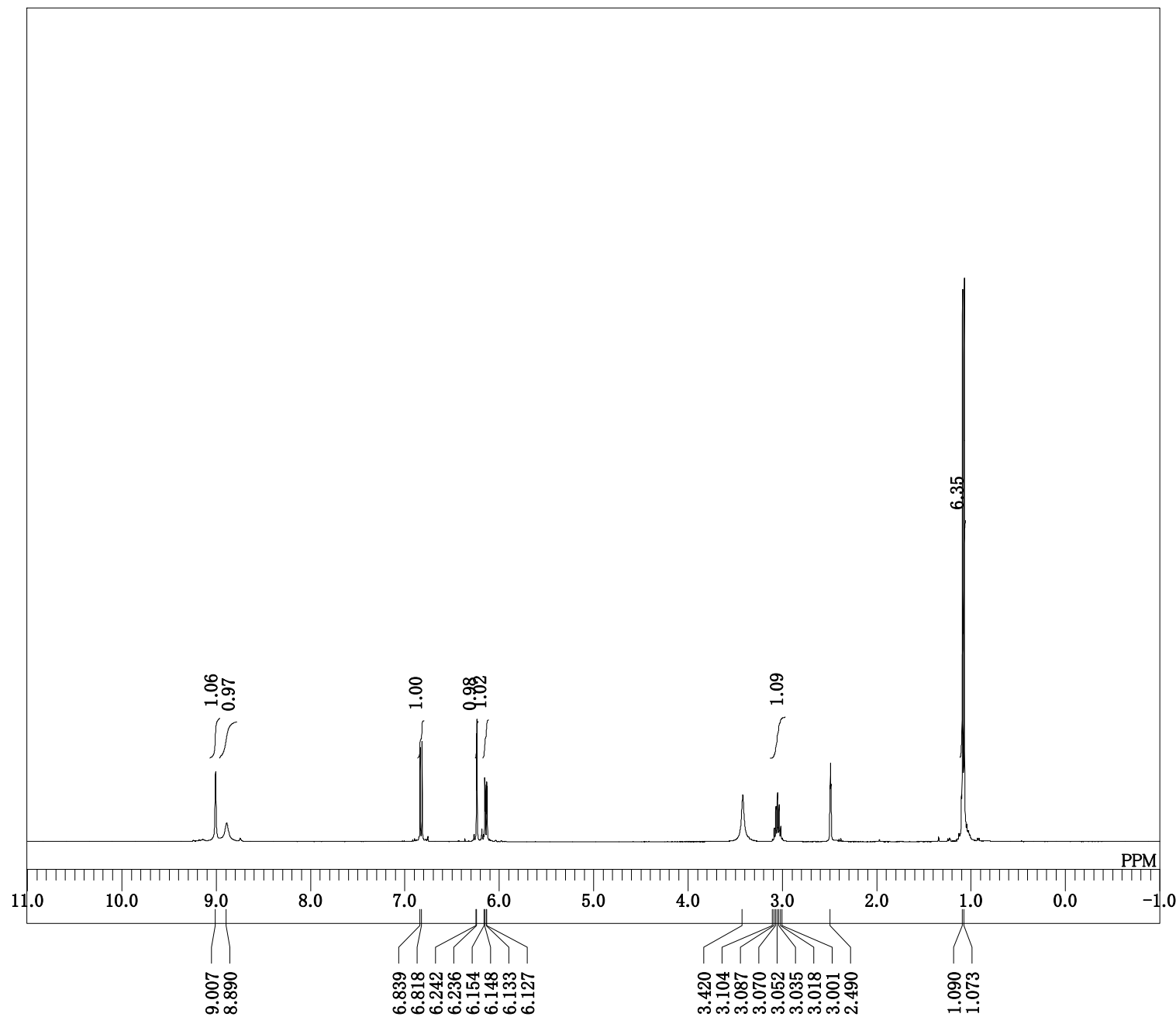


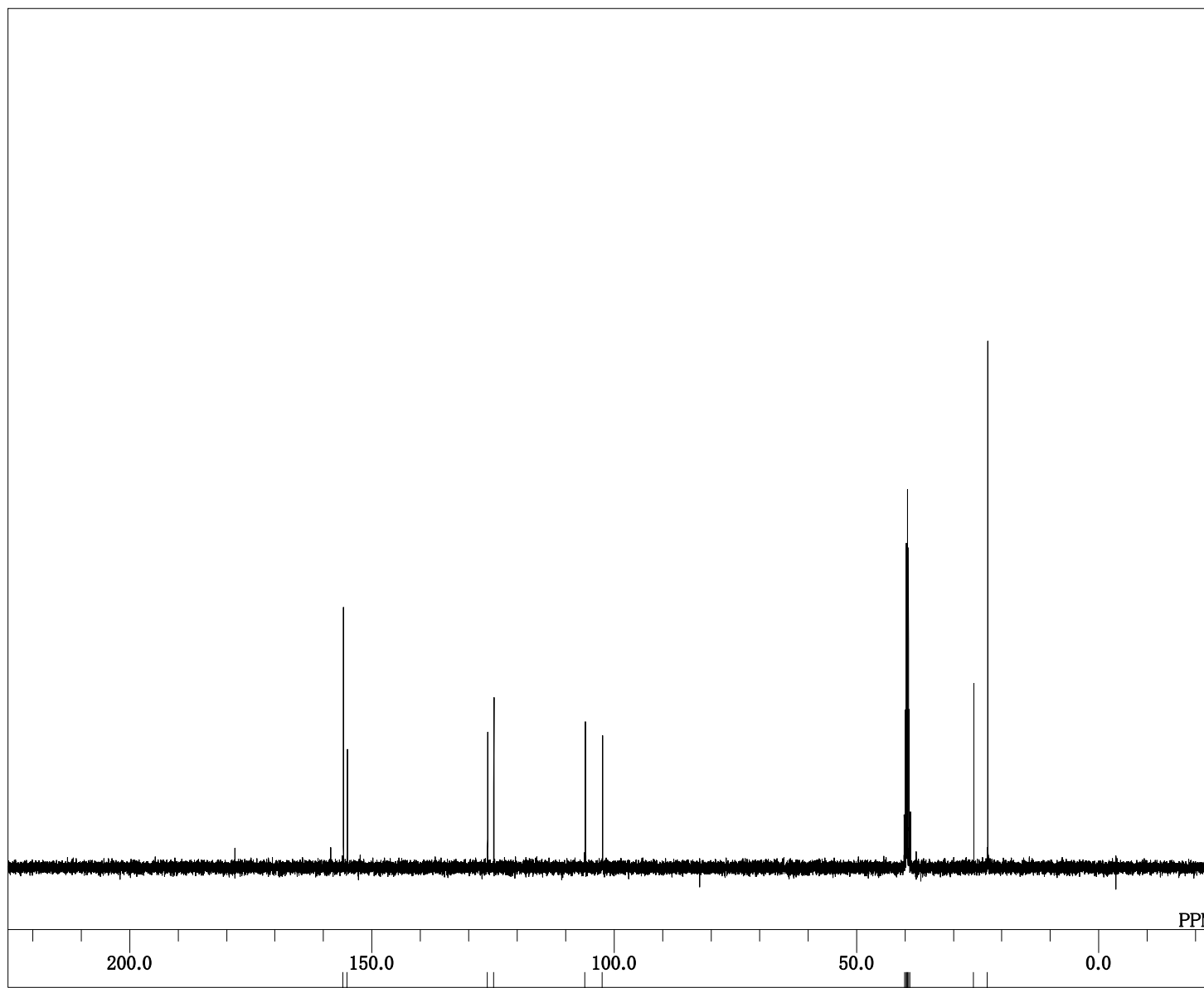
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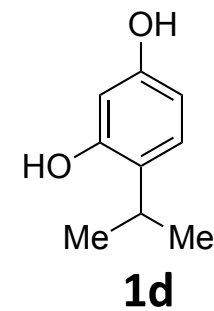
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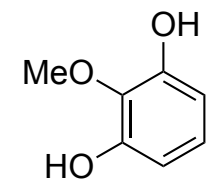
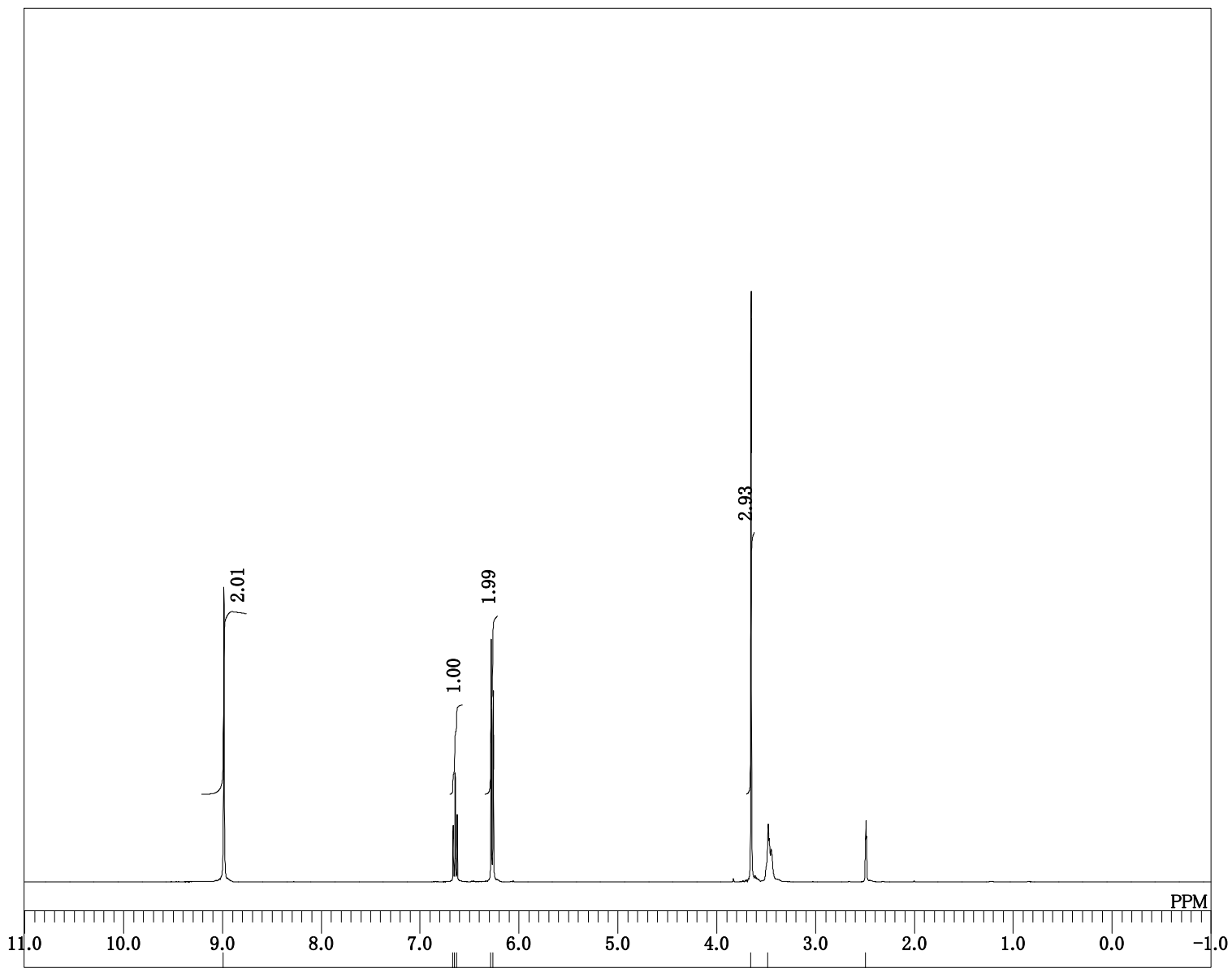




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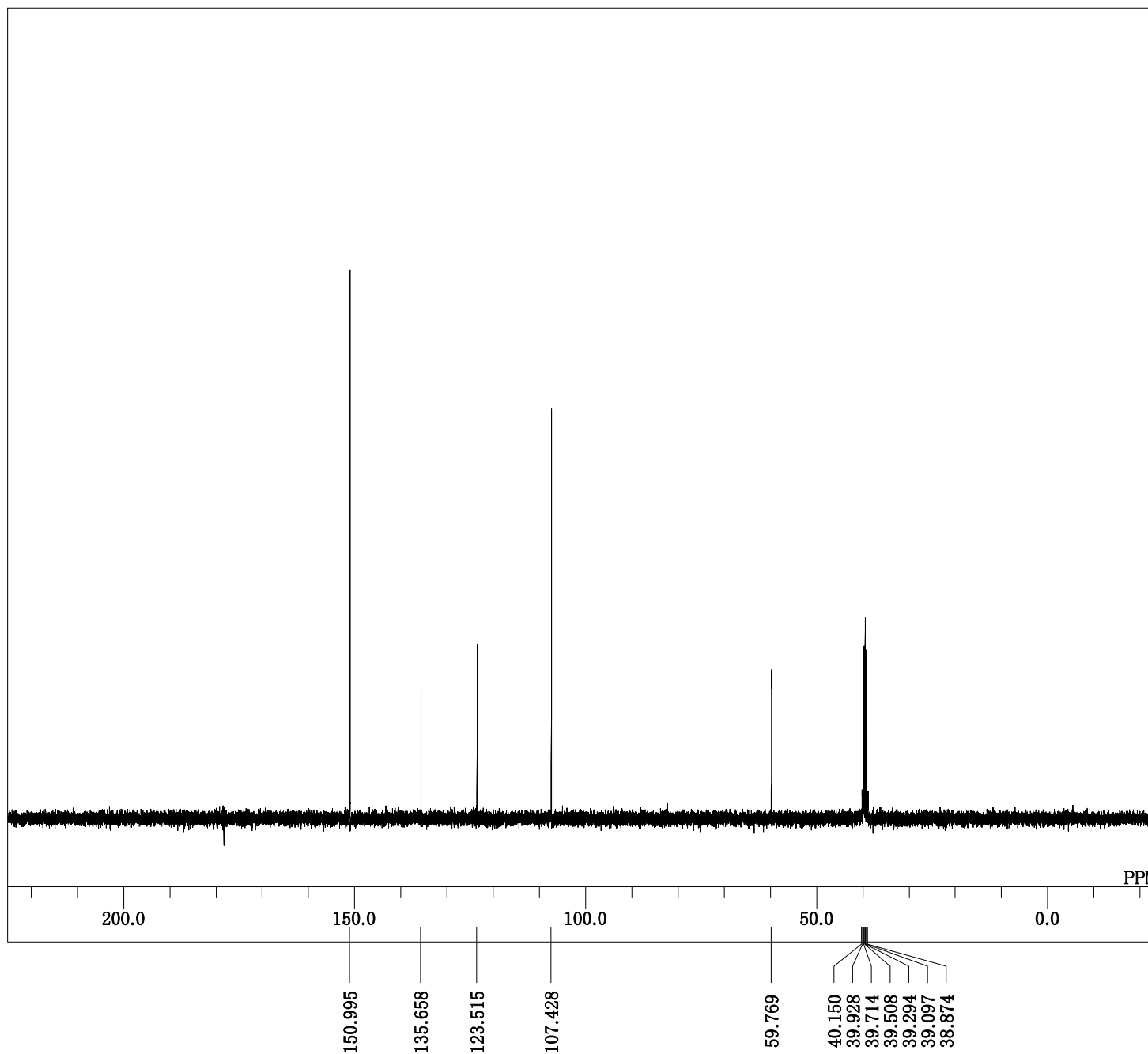


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RGAIN 11

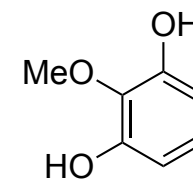


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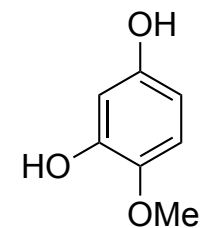
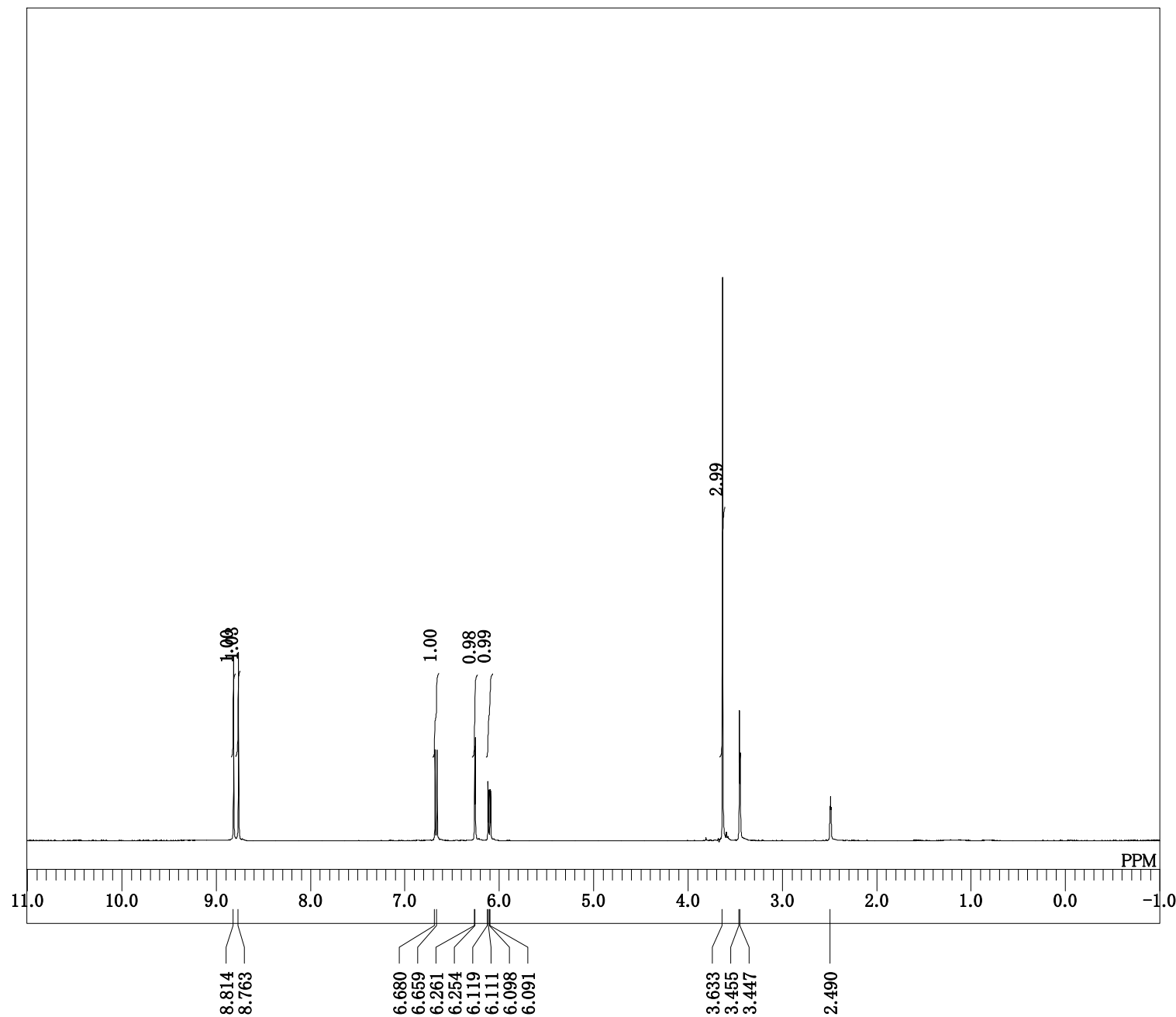


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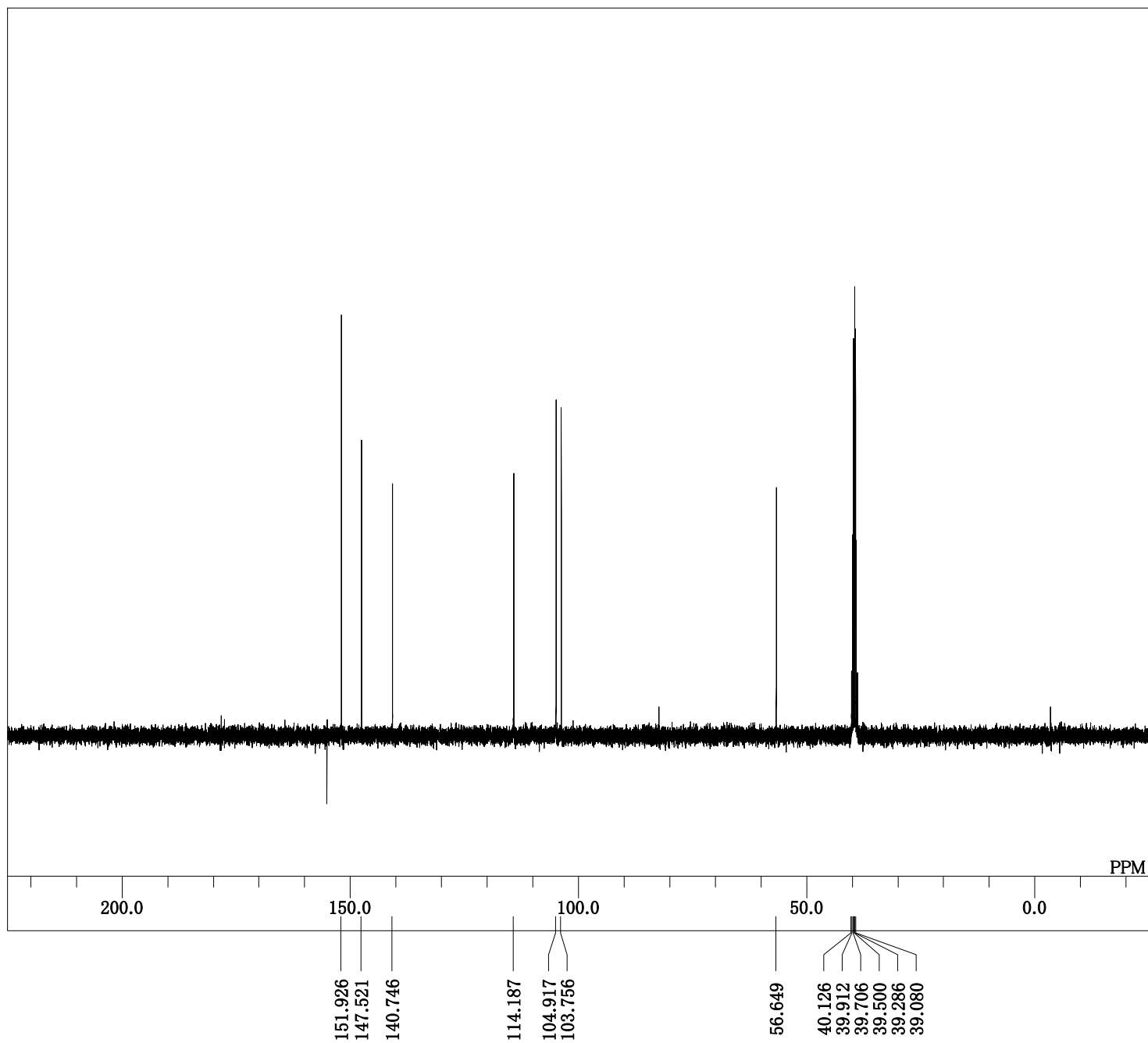


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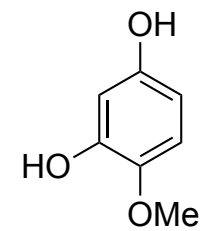
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 RGAIN 11



**1g**

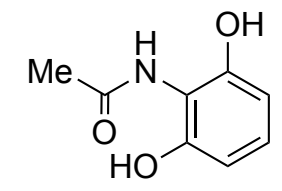
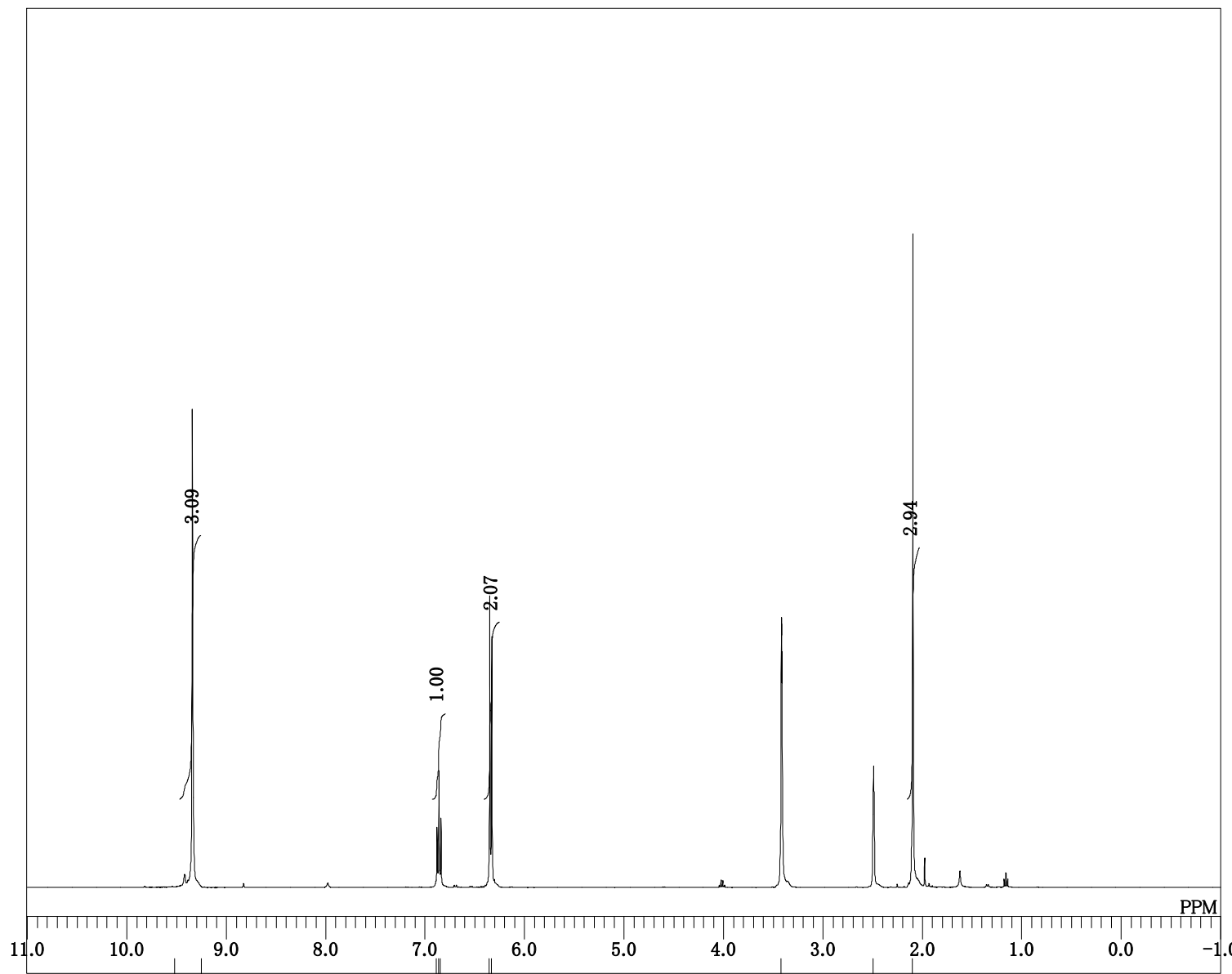


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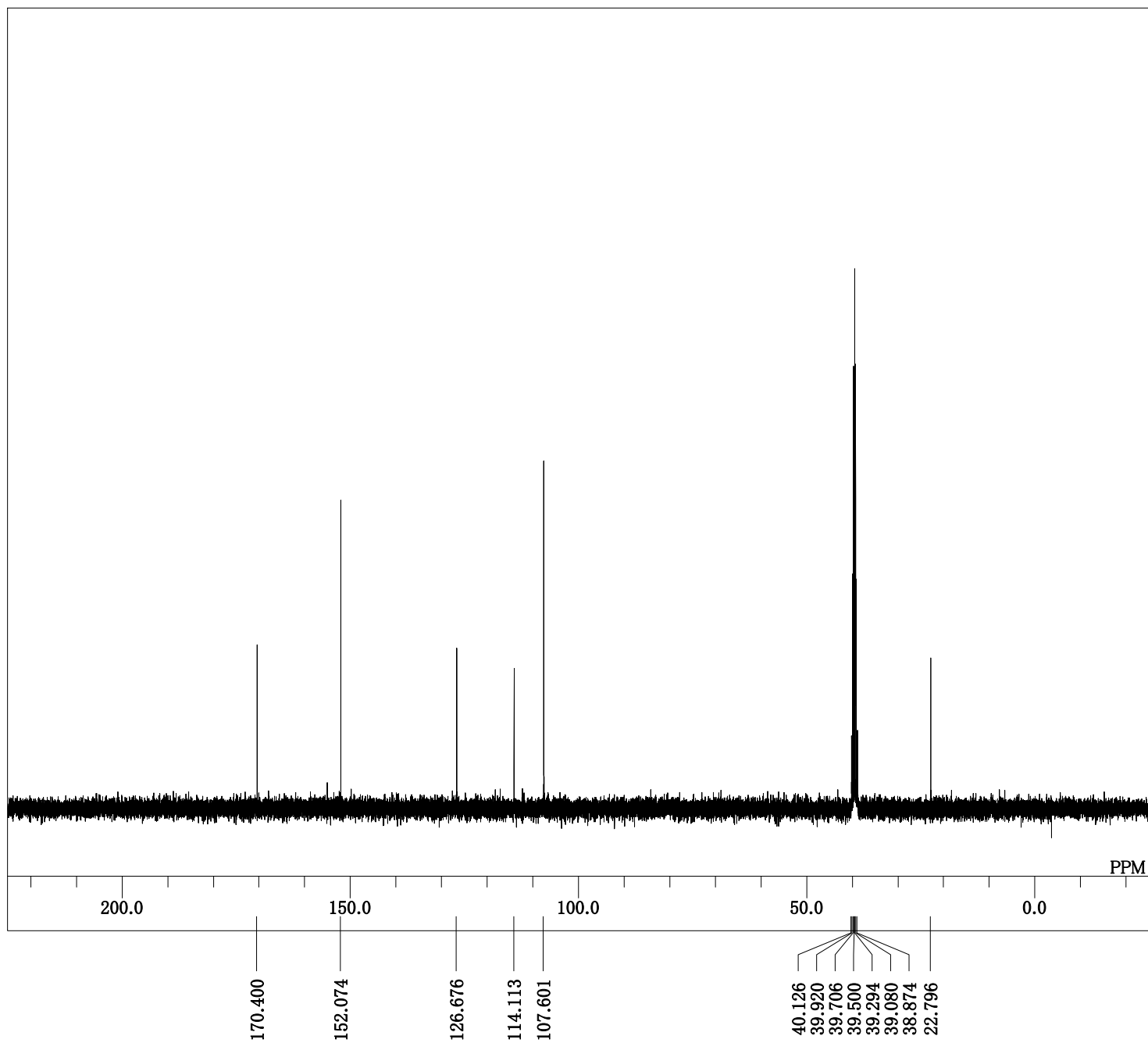


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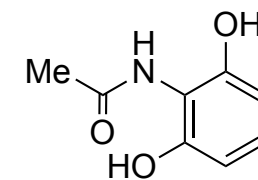
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RGAIN 12



**1i**

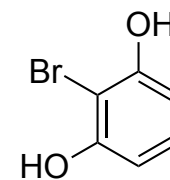
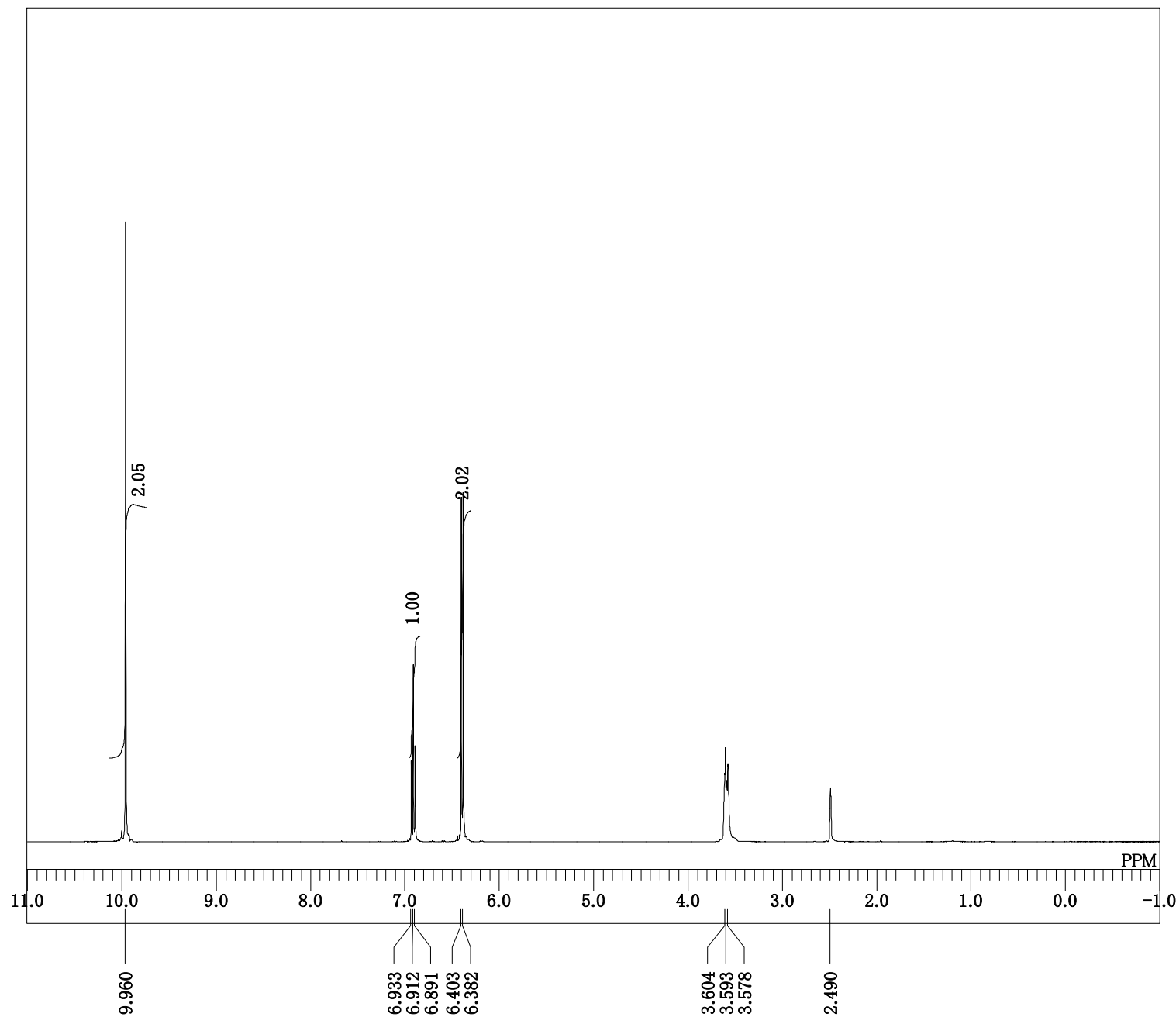


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 RGAIN 23

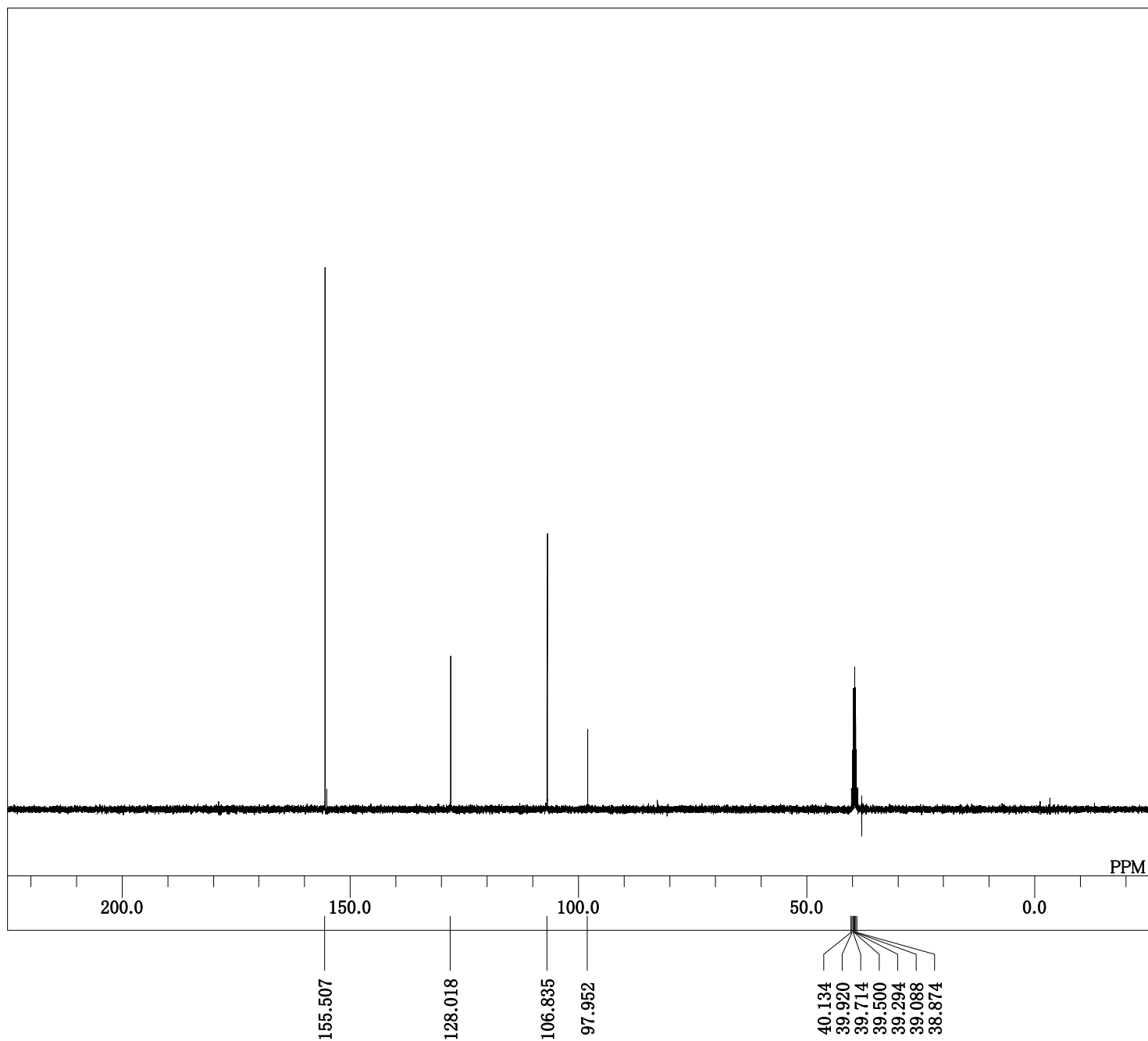


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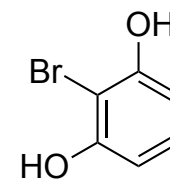
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RGAIN 11



11

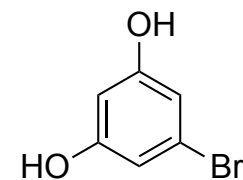
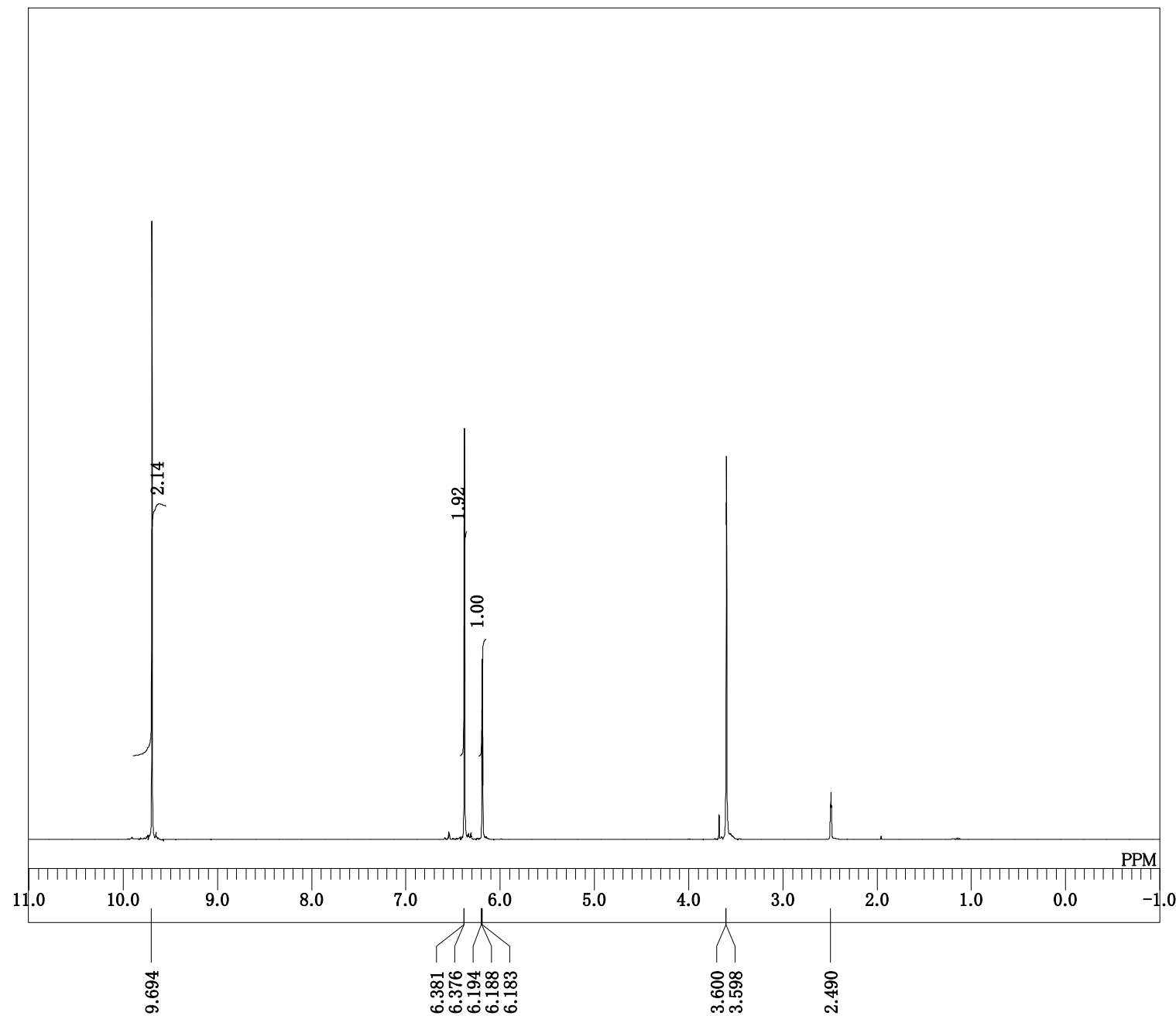


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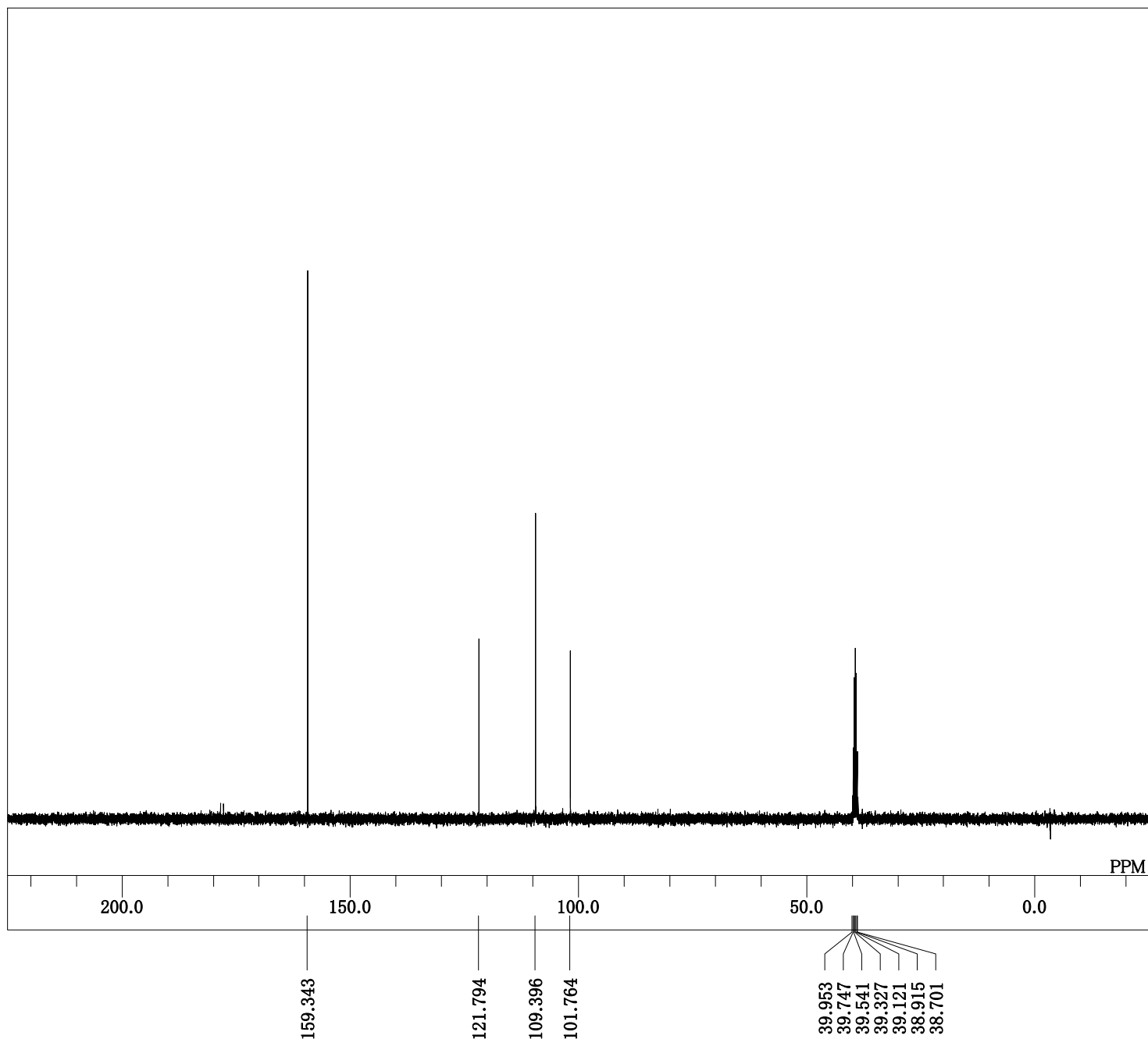
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RGAIN 12

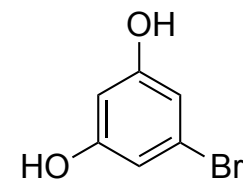


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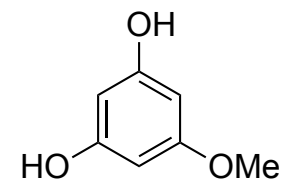
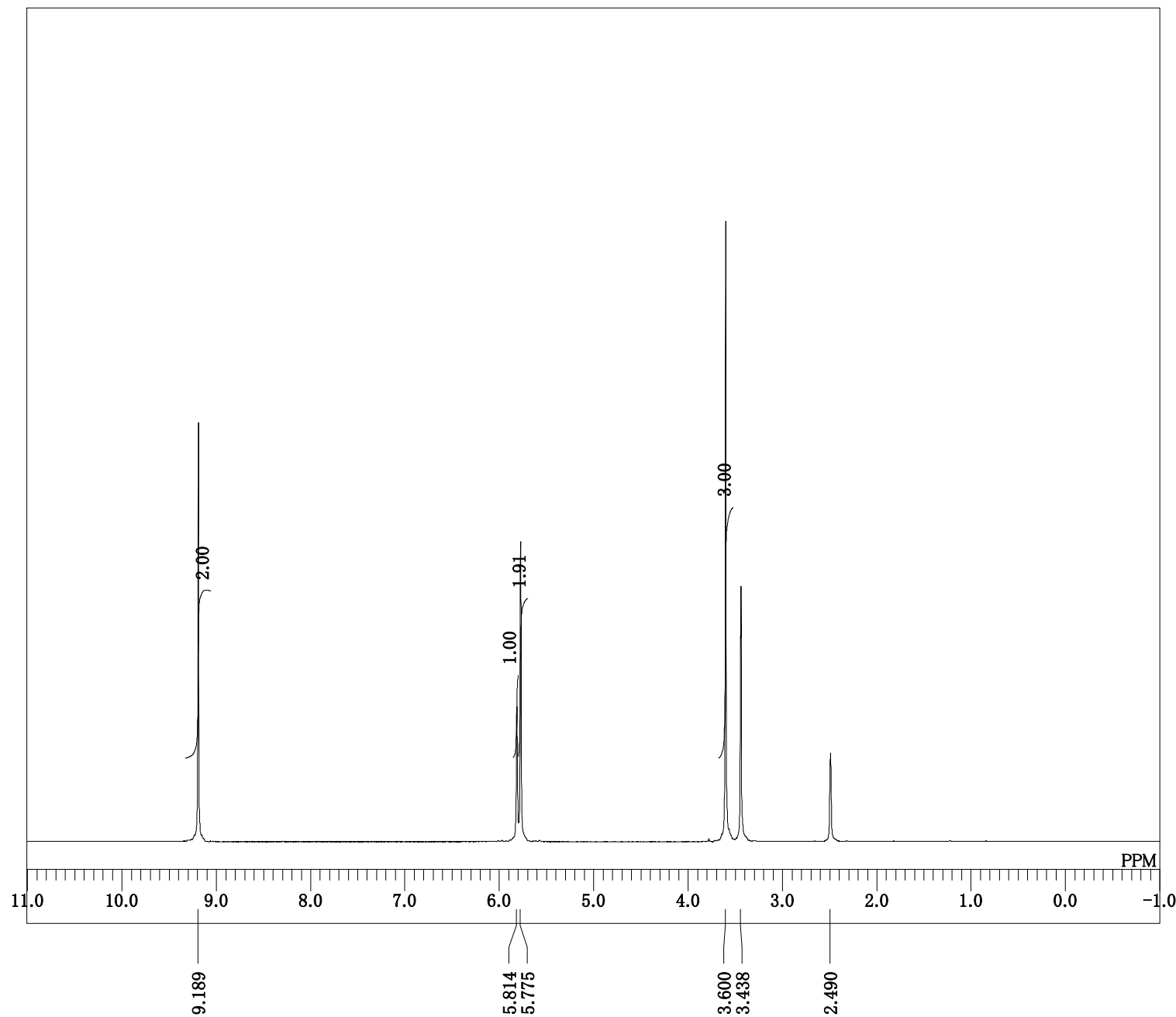


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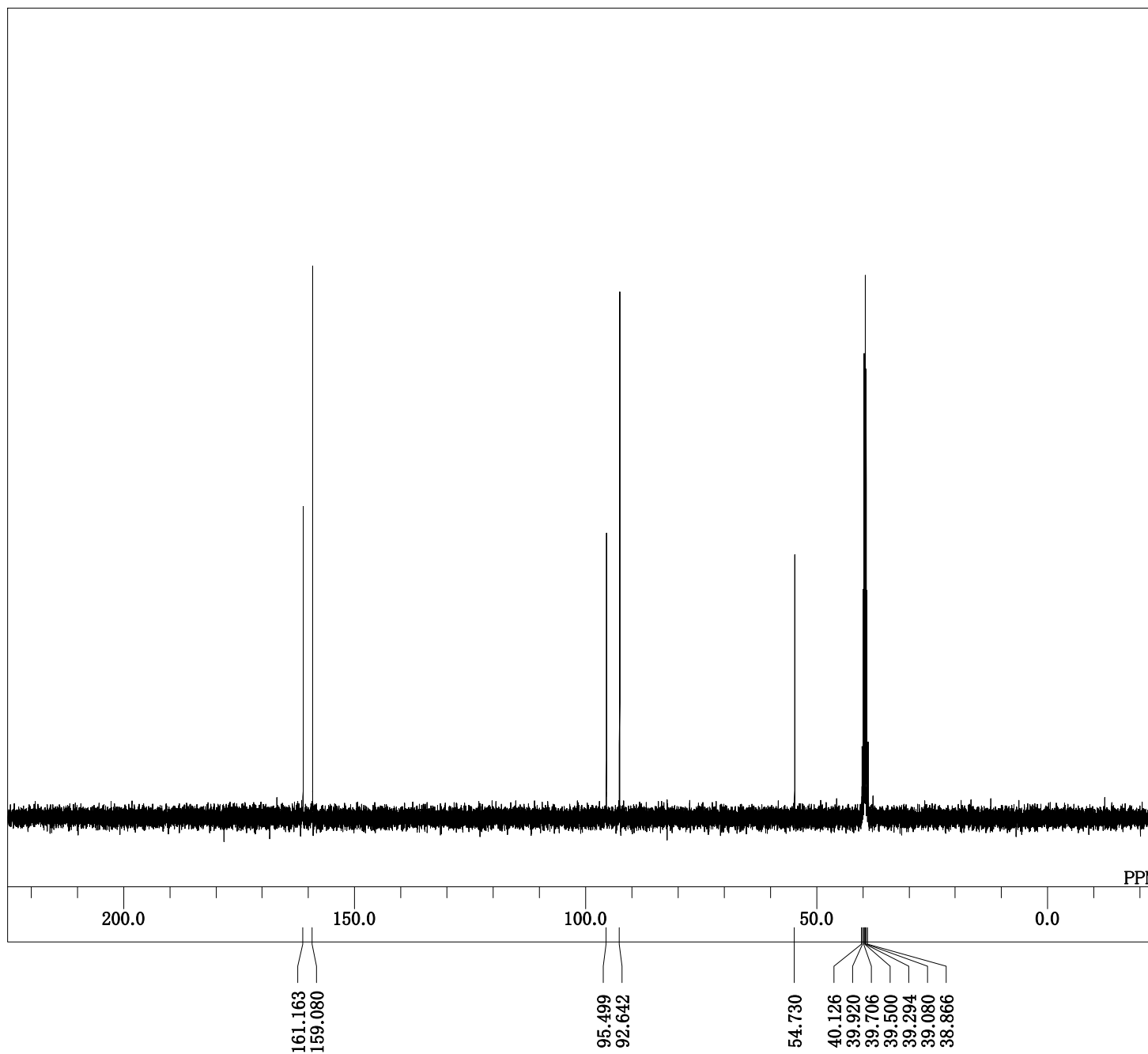


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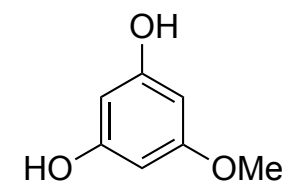
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RGAIN 13



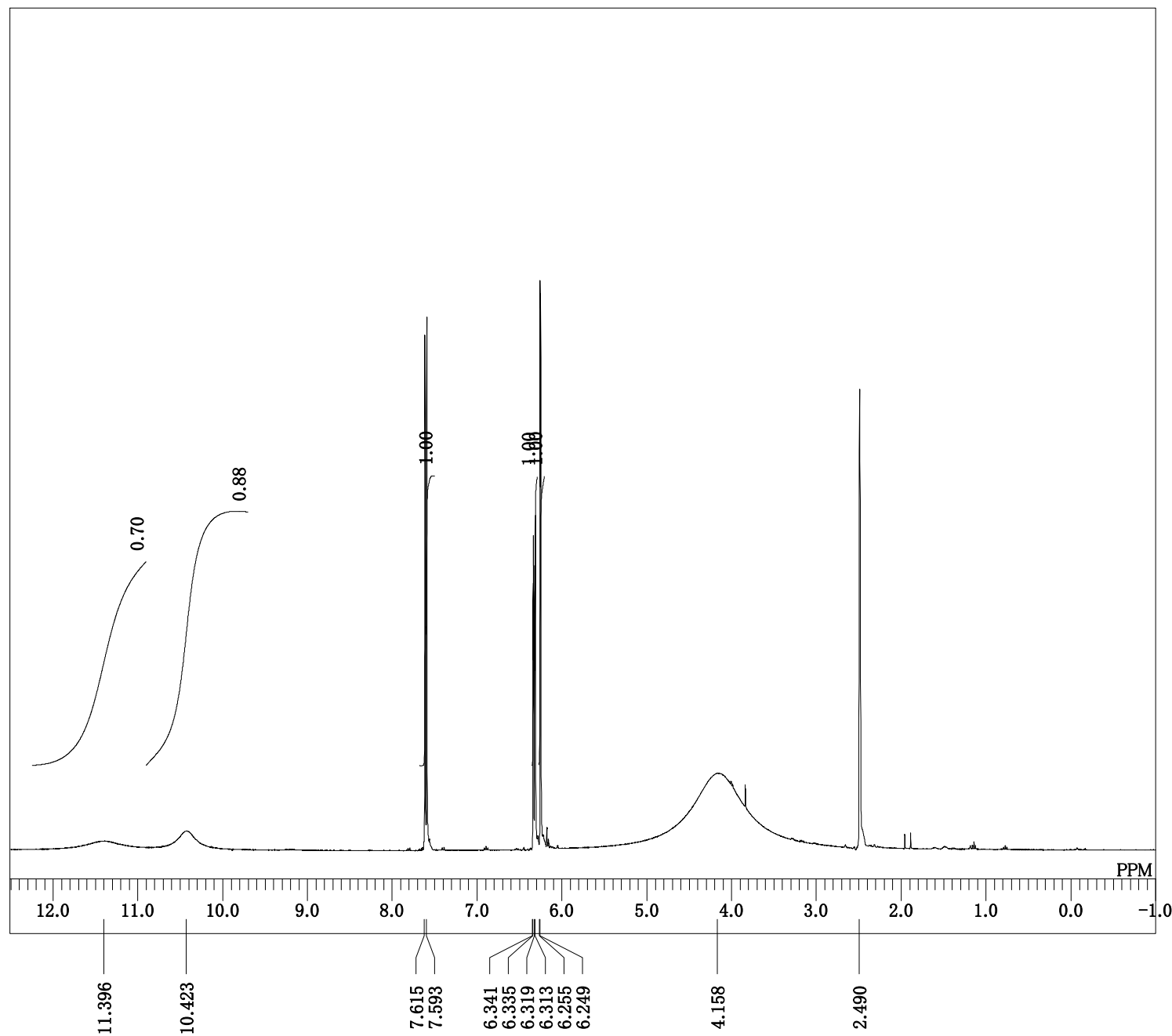
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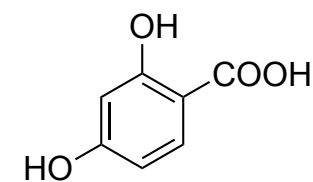
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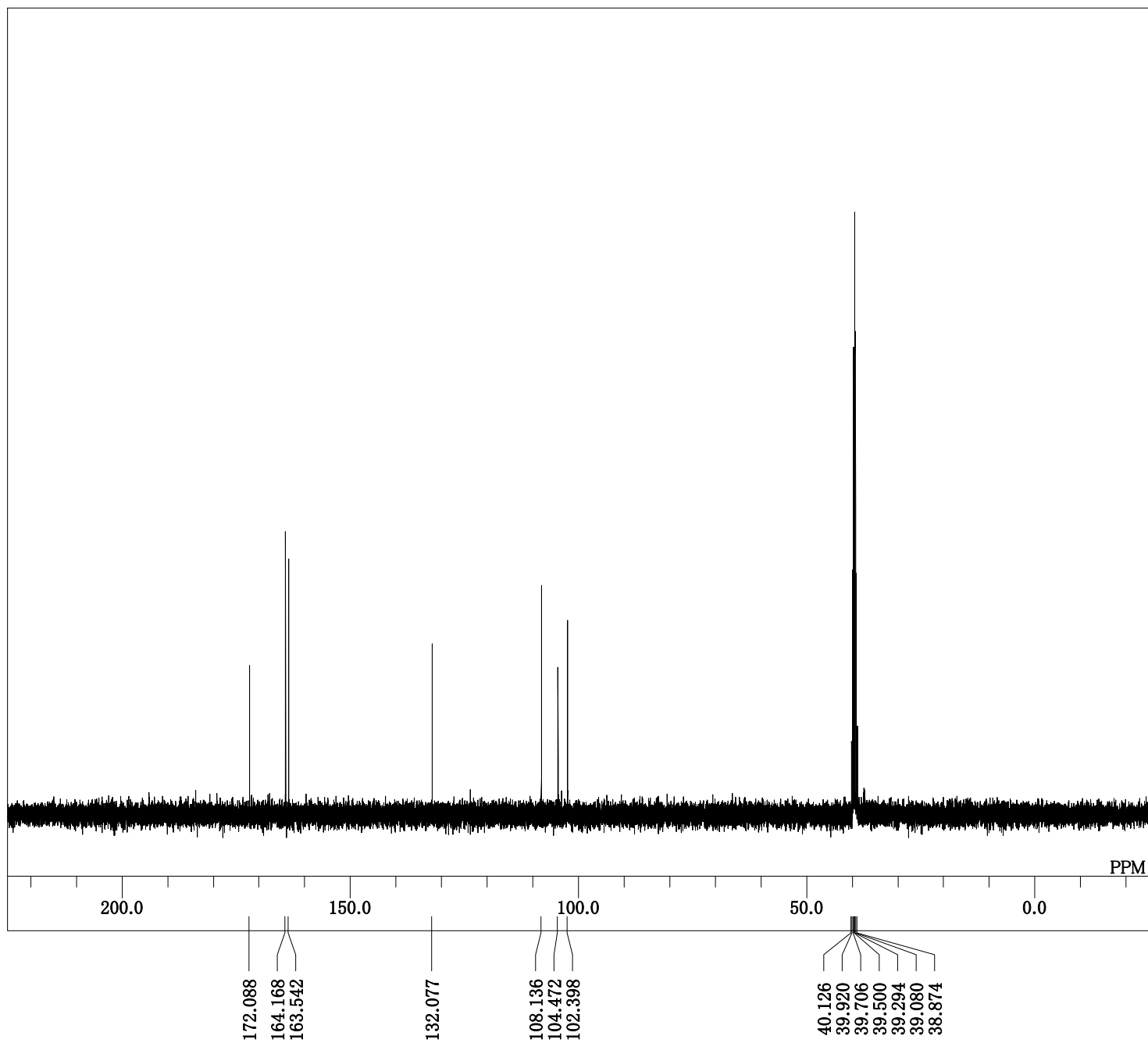
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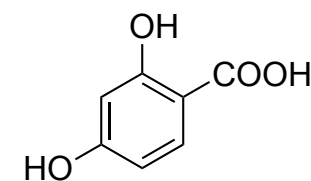
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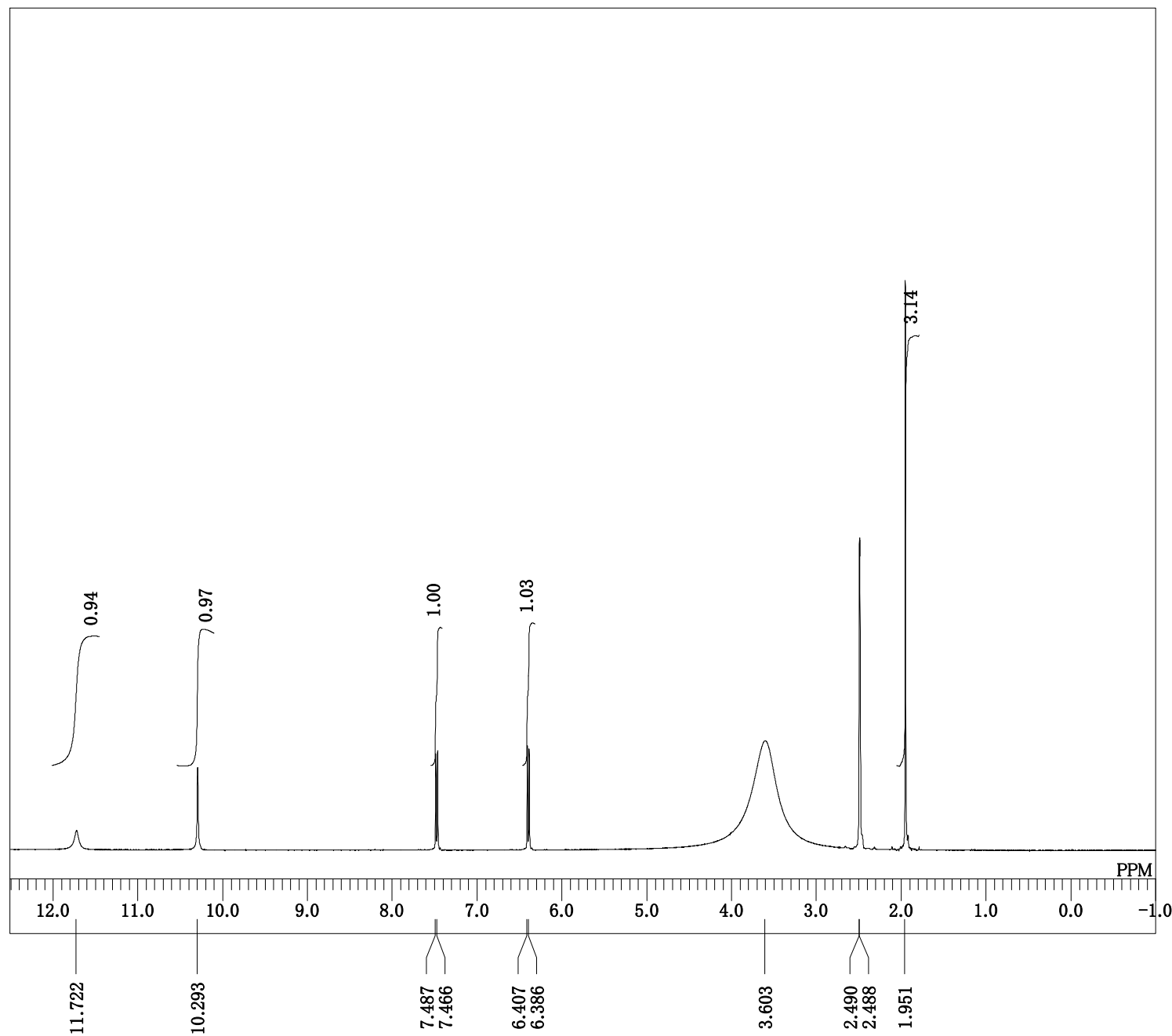
**2a**



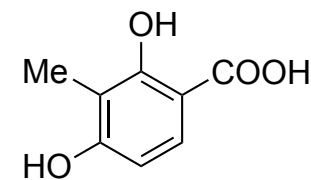
DFILE 20180628 Kolbe\_pro\_model]  
 COMNT  
 DATIM Thu Jun 28 10:56:36 2018  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 32  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 23



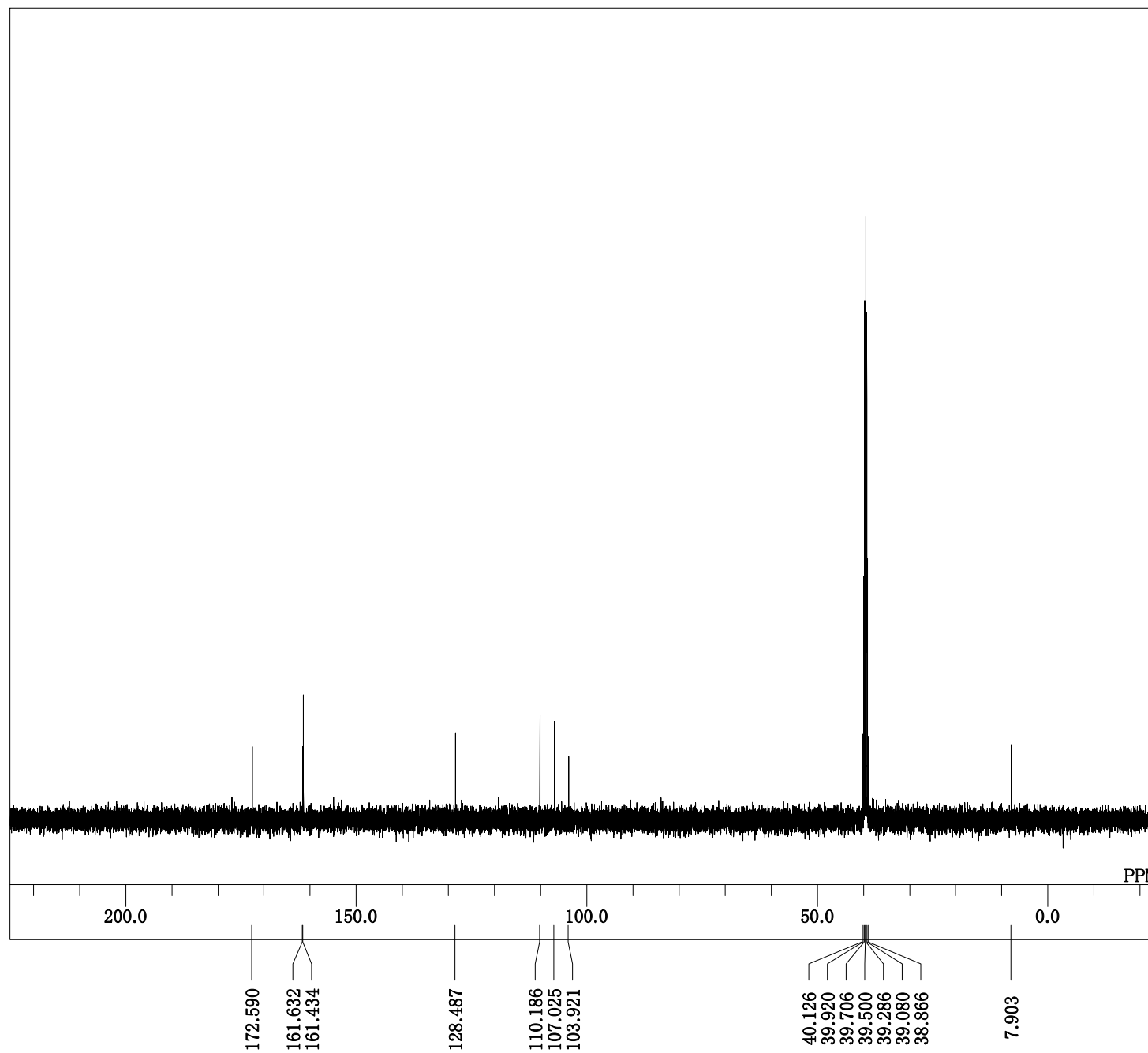
2a



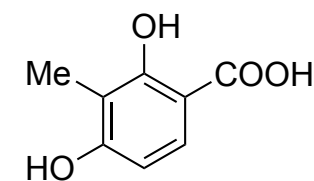
DFILE 20180628 Kolbe\_pro\_2Me.nc  
 COMNT  
 DATIM Thu Jun 28 11:04:58 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 12



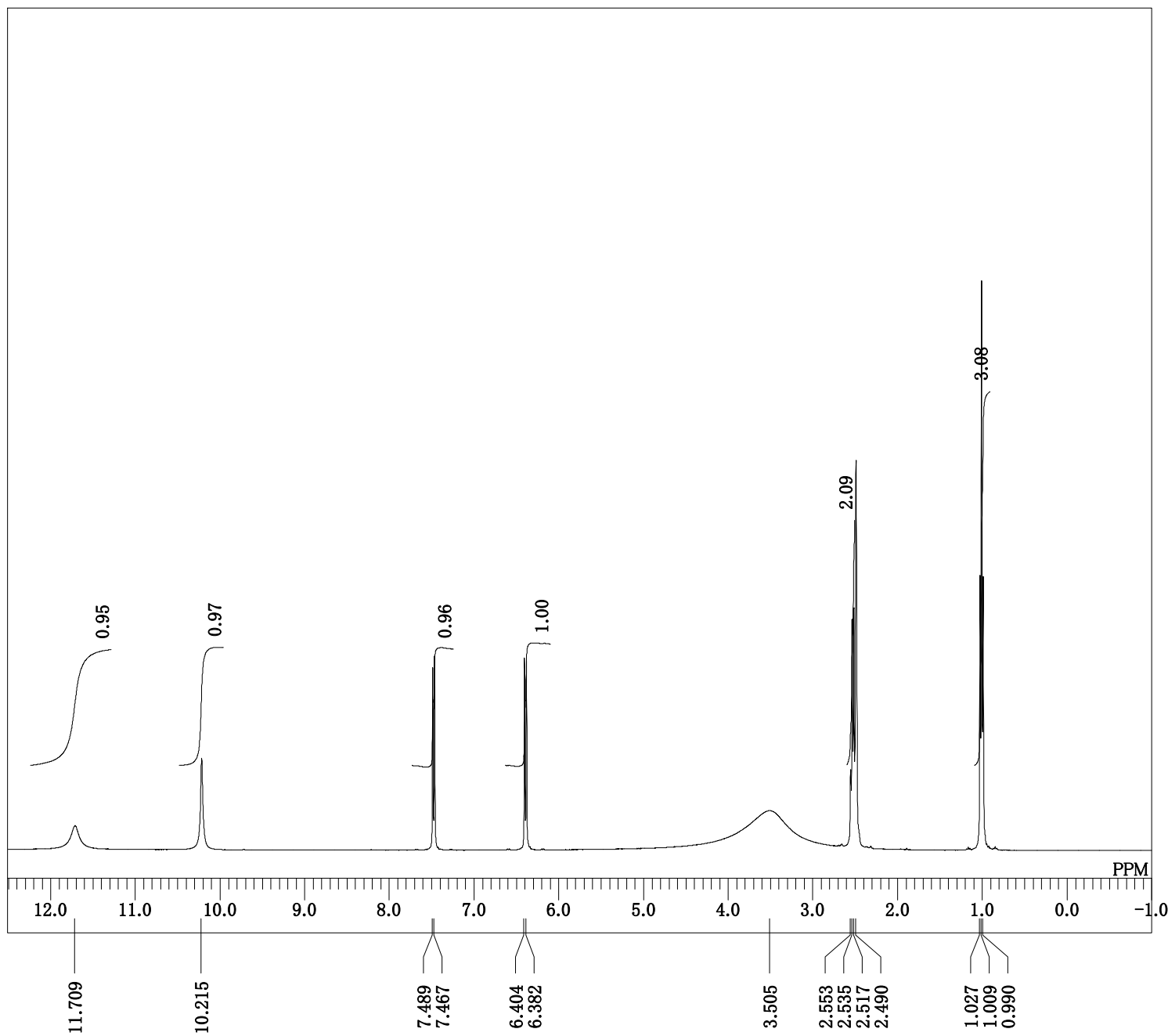
**2b**



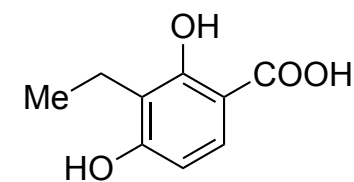
DFILE 20180628 Kolbe\_pro\_2Me.bc  
 COMNT  
 DATIM Thu Jun 28 11:13:20 2018  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 64  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 23



**2b**

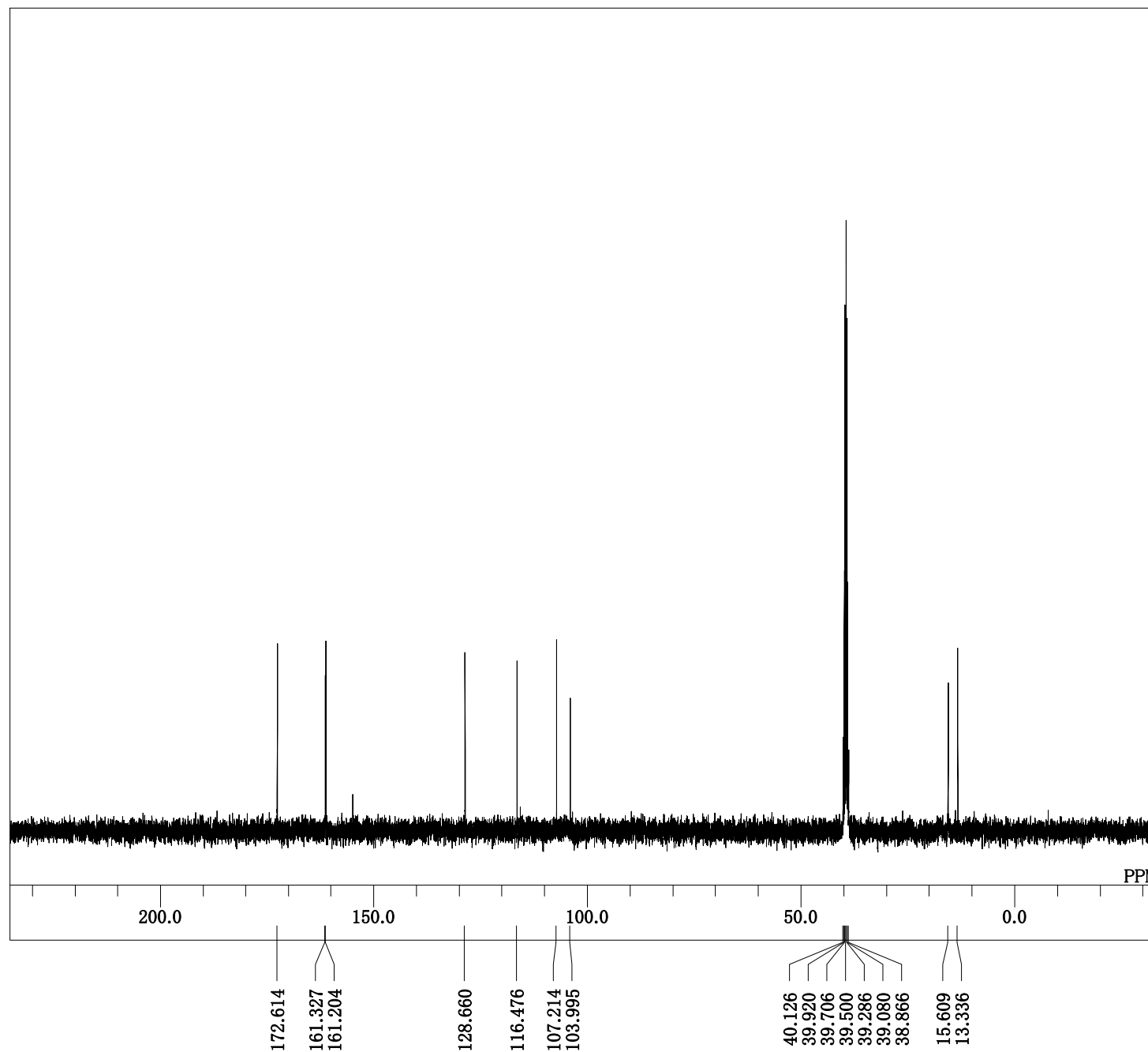


DFILE 20180517 pro-2Et.als  
 COMNT auto  
 DATIM Thu May 17 21:39:15 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP -39.9 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.92 Hz  
 RGAIN 13

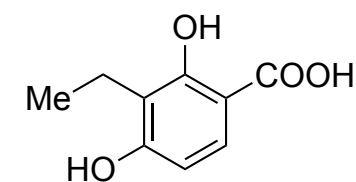


**2c**

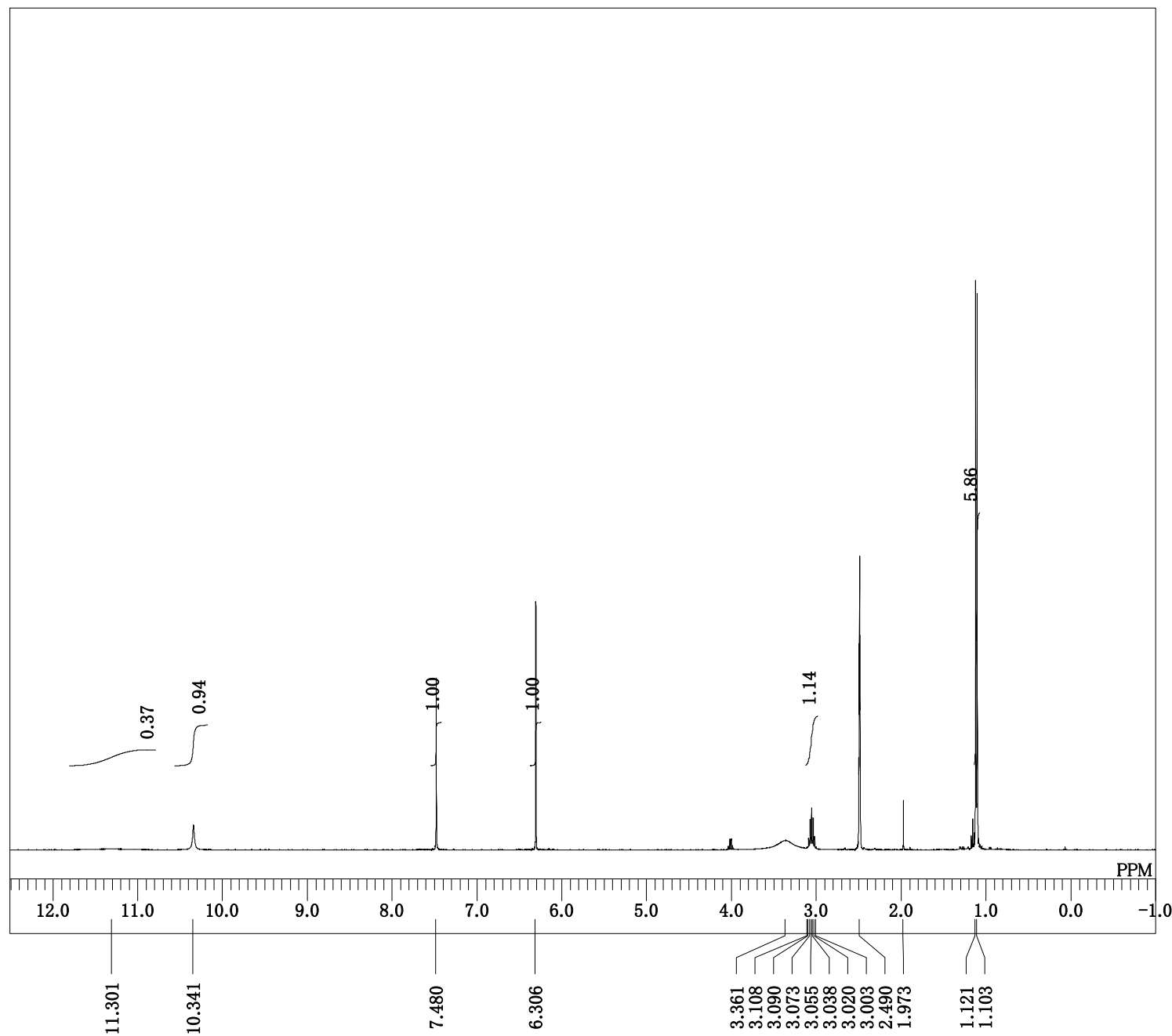




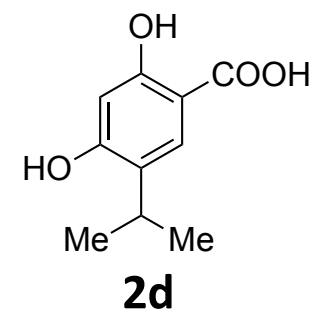
DFILE 20180517 pro-2Et\_bcm.als  
 COMNT auto  
 DATIM Thu May 17 21:47:55 2018  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 32  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC 1H  
 CTEMP -19.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.92 Hz  
 RGAIN 22

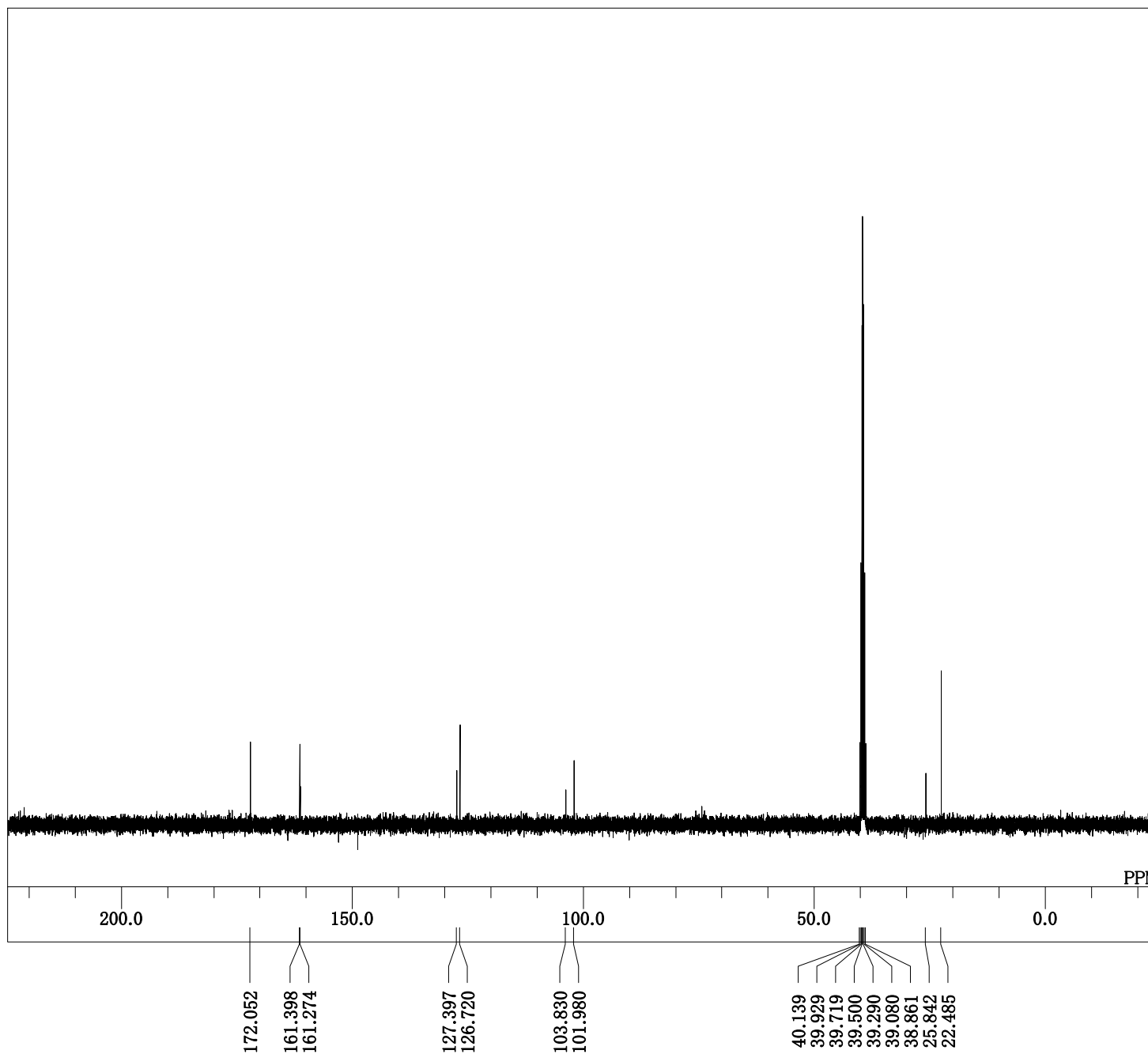


**2c**

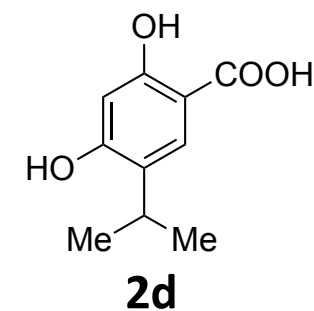


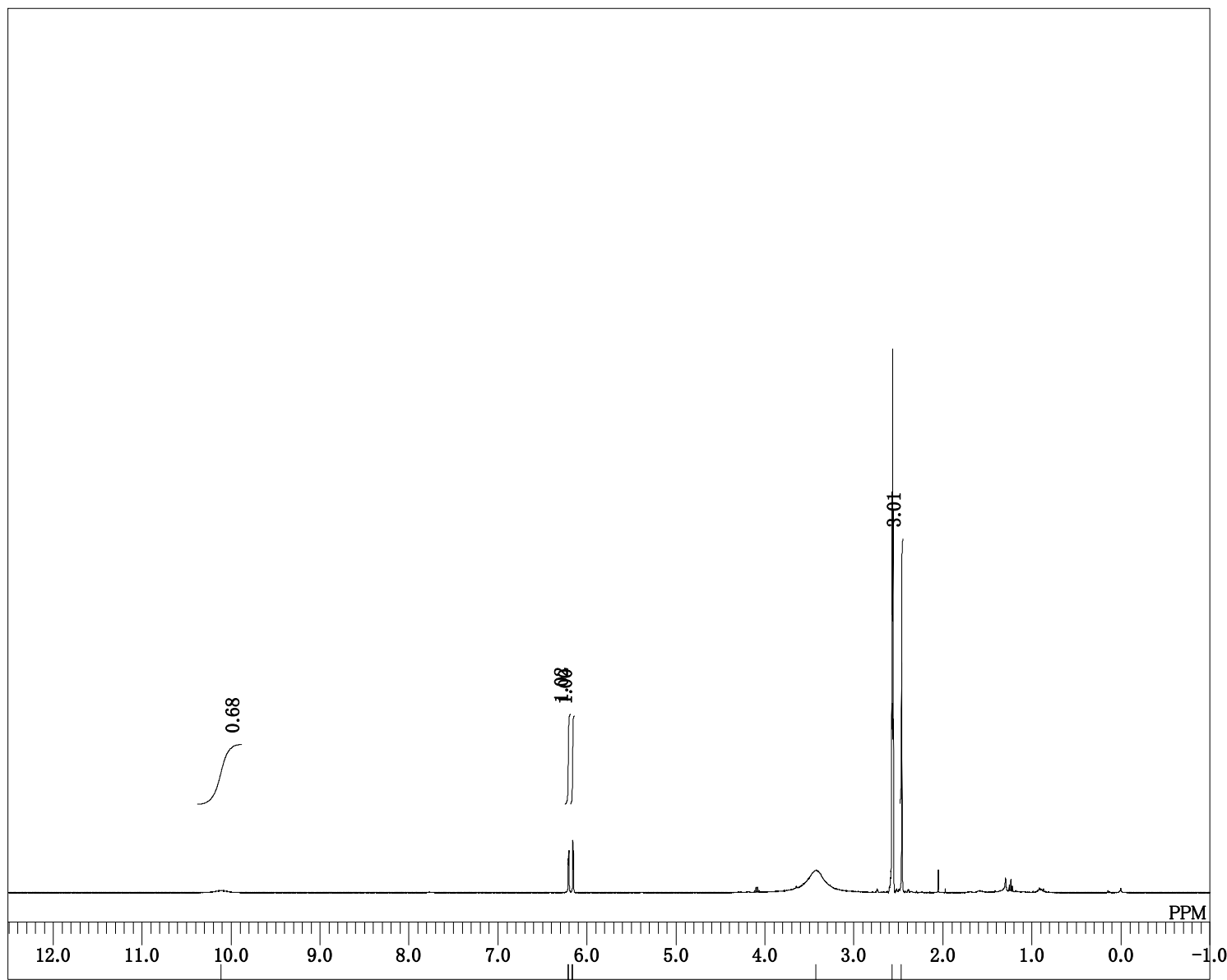
DFILE 20180331 4-ipr-prod(ao277)  
 COMNT single\_pulse  
 DATIM 2018-03-31 18:25:53  
 OBNUC 1H  
 EXMOD single\_pulse.ex2  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 26214  
 FREQU 5882.26 Hz  
 SCANS 16  
 ACQTM 4.4564 sec  
 PD 3.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.0 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 42



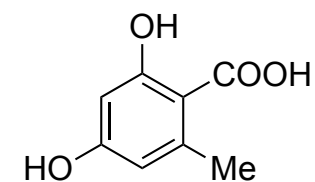


DFILE 20180331 4-ipr-prod(ao277)  
 COMNT single pulse decoupled gate  
 DATIM 2018-03-31 18:36:48  
 OBNUC <sup>13</sup>C  
 EXMOD single\_pulse\_dec  
 OBFRQ 98.52 MHz  
 OBSET 4.64 KHz  
 OBFIN 8.74 Hz  
 POINT 26214  
 FREQU 24630.17 Hz  
 SCANS 128  
 ACQTM 1.0643 sec  
 PD 2.0000 sec  
 PW1 3.00 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 21.3 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 48

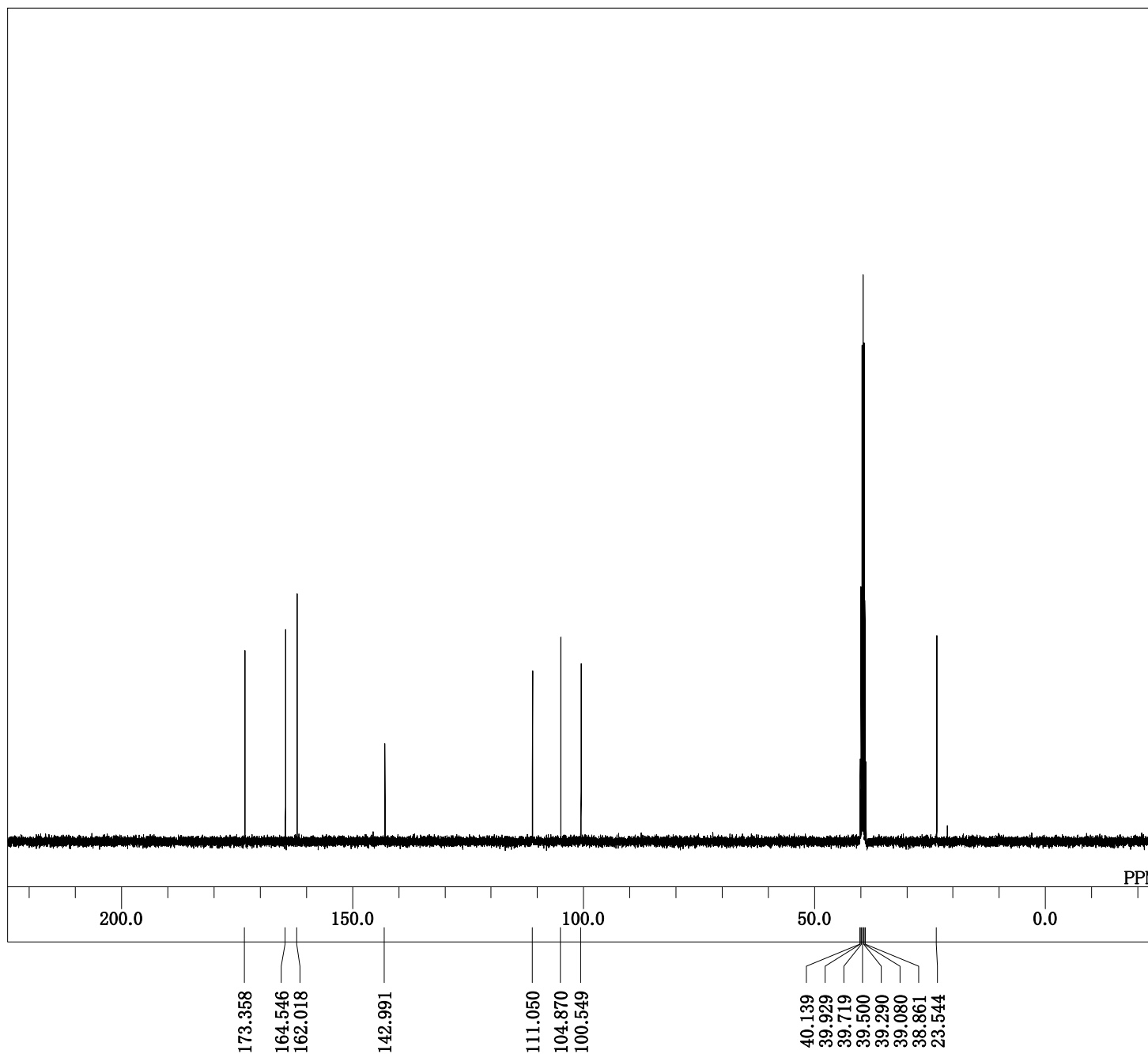




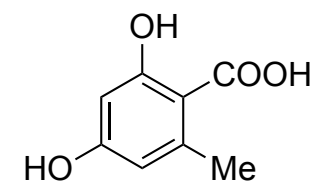
DFILE 20180404 5-methyl-prod(ac)  
 COMNT single\_pulse  
 DATIM 2018-04-04 17:58:35  
 OBNUC 1H  
 EXMOD single\_pulse.ex2  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 26214  
 FREQU 5882.26 Hz  
 SCANS 16  
 ACQTM 4.4564 sec  
 PD 3.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.4 c  
 SLVNT DMSO  
 EXREF 0.00 ppm  
 BF 0.12 Hz  
 RGAIN 46



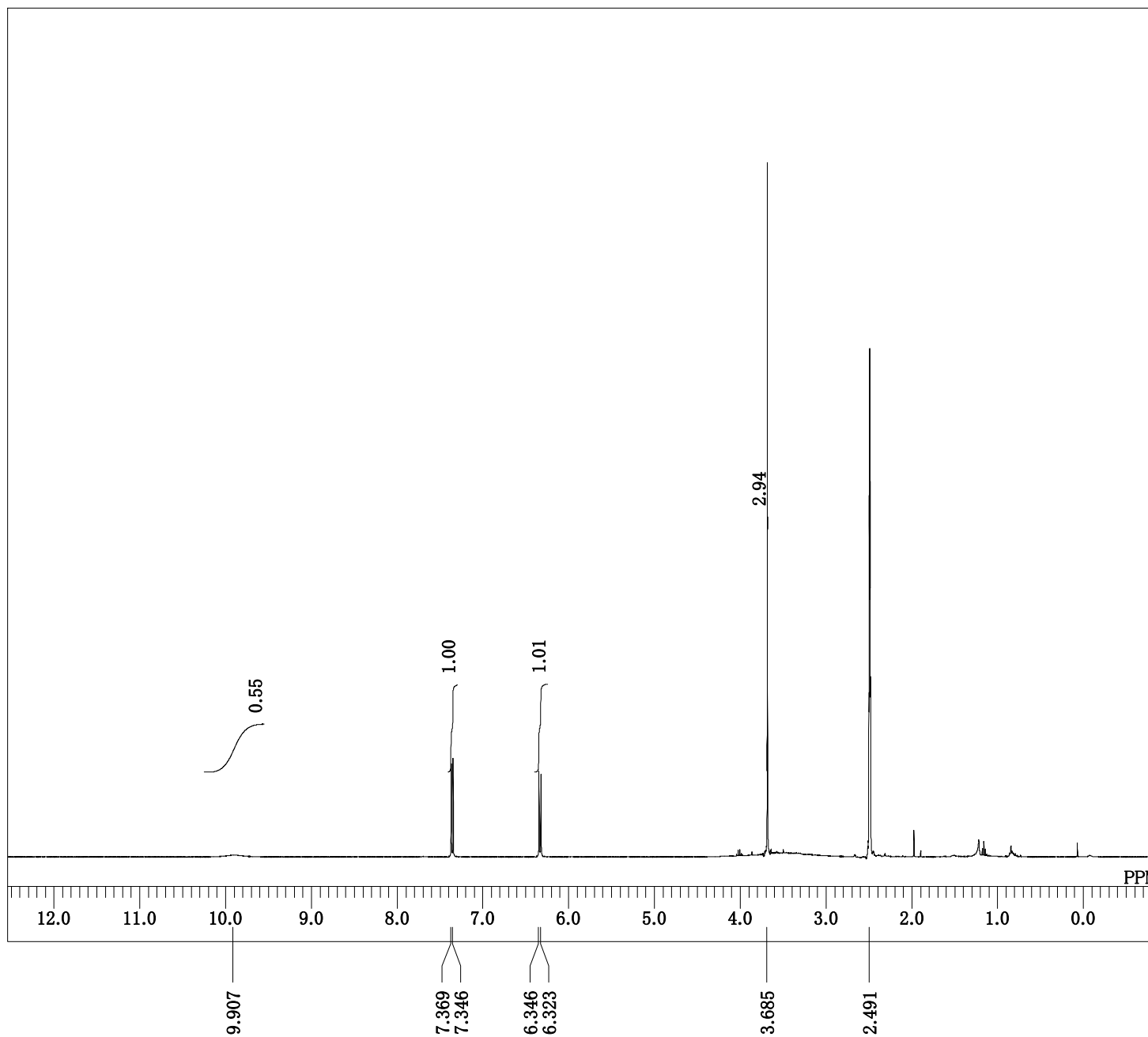
2e



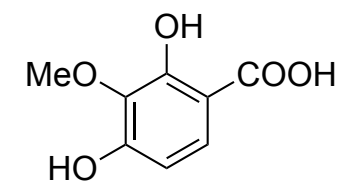
DFILE 20180421 5-methyl-prod(ac  
 COMNT single pulse decoupled gate  
 DATIM 2018-04-21 15:35:21  
 OBNUC <sup>13</sup>C  
 EXMOD single\_pulse\_dec  
 OBFRQ 98.52 MHz  
 OBSET 4.64 KHz  
 OBFIN 8.74 Hz  
 POINT 26214  
 FREQU 24630.17 Hz  
 SCANS 256  
 ACQTM 1.0643 sec  
 PD 2.0000 sec  
 PW1 3.00 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 21.4 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 40



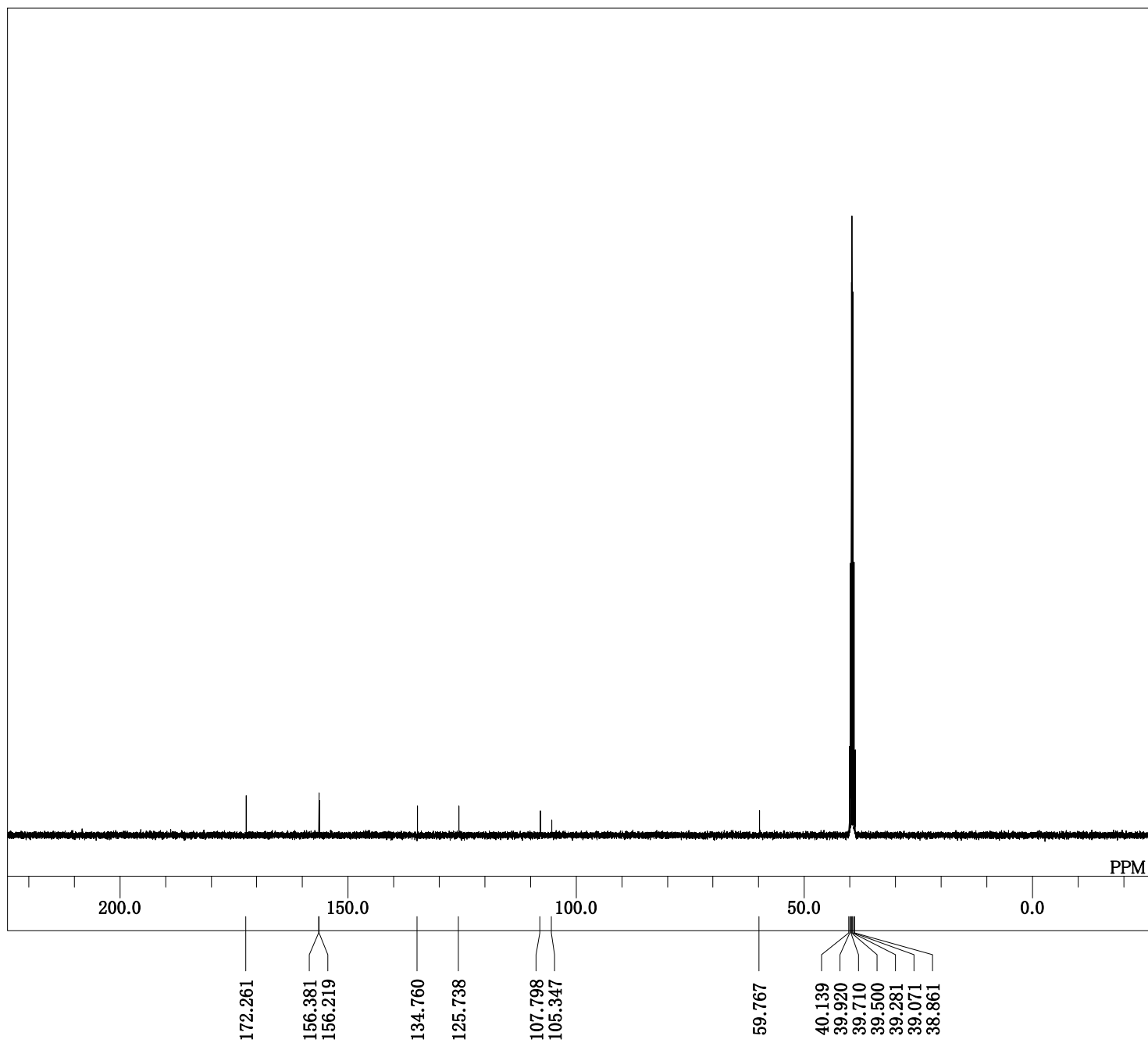
2e



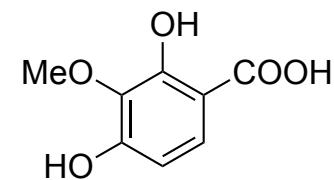
DFILE 20180404 2-methoxy-prod(  
 COMNT single\_pulse  
 DATIM 2018-04-04 17:33:02  
 OBNUC 1H  
 EXMOD single\_pulse.ex2  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 26214  
 FREQU 5882.26 Hz  
 SCANS 16  
 ACQTM 4.4564 sec  
 PD 3.0000 sec  
 PW1 5.55 usec  
 IRNUC 1H  
 CTEMP 21.2 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 44



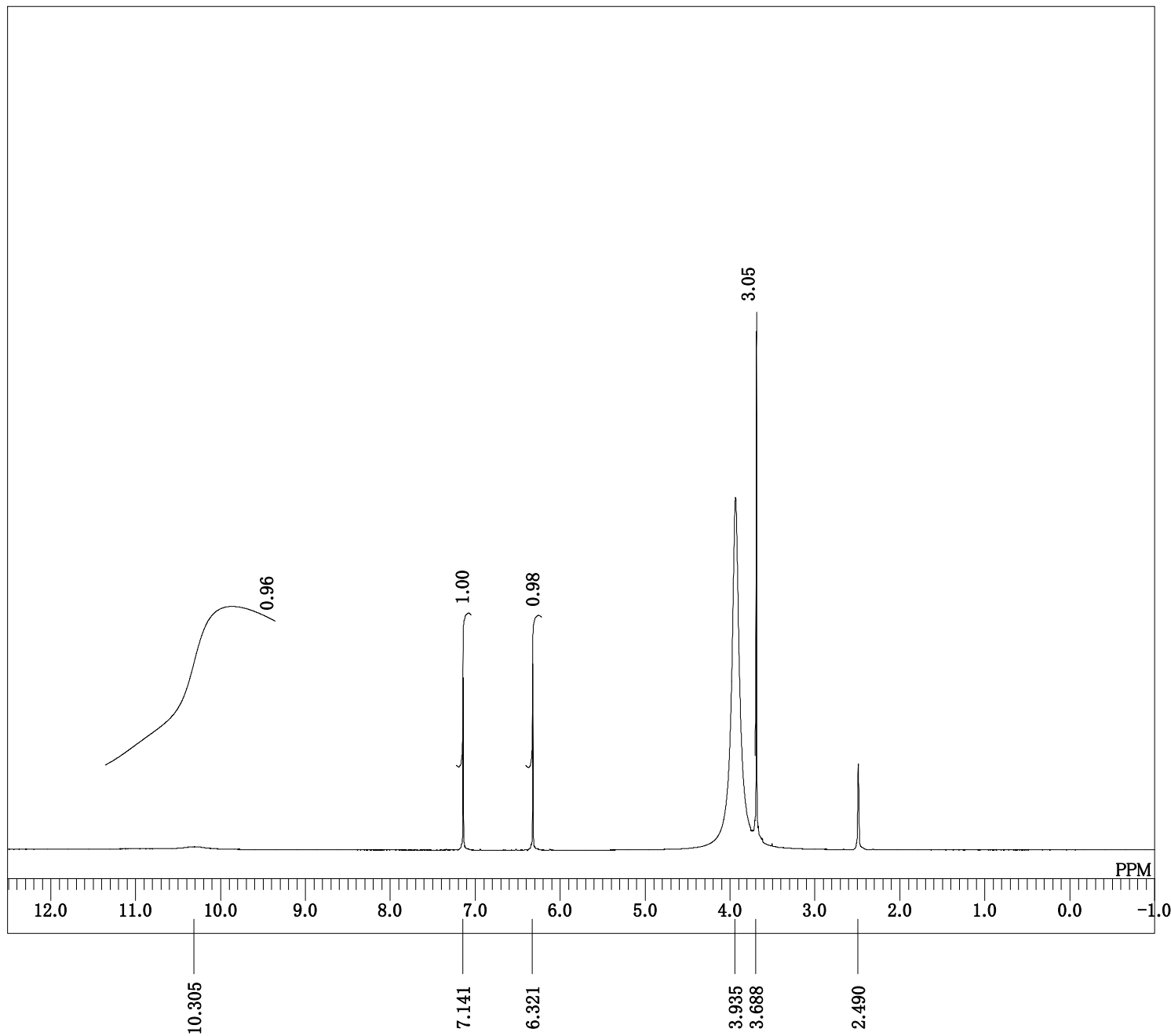
**2f**



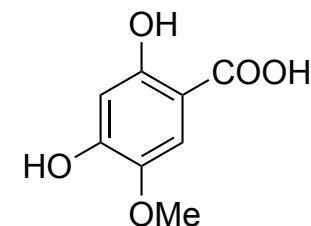
DFILE 20180404 2-methoxy-prod(  
 COMNT single pulse decoupled gate  
 DATIM 2018-04-14 17:08:10  
 OBNUC <sup>13</sup>C  
 EXMOD single\_pulse\_dec  
 OBFRQ 98.52 MHz  
 OBSET 4.64 KHz  
 OBFIN 8.74 Hz  
 POINT 26214  
 FREQU 24630.17 Hz  
 SCANS 1024  
 ACQTM 1.0643 sec  
 PD 2.0000 sec  
 PW1 3.00 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 21.7 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 44



**2f**

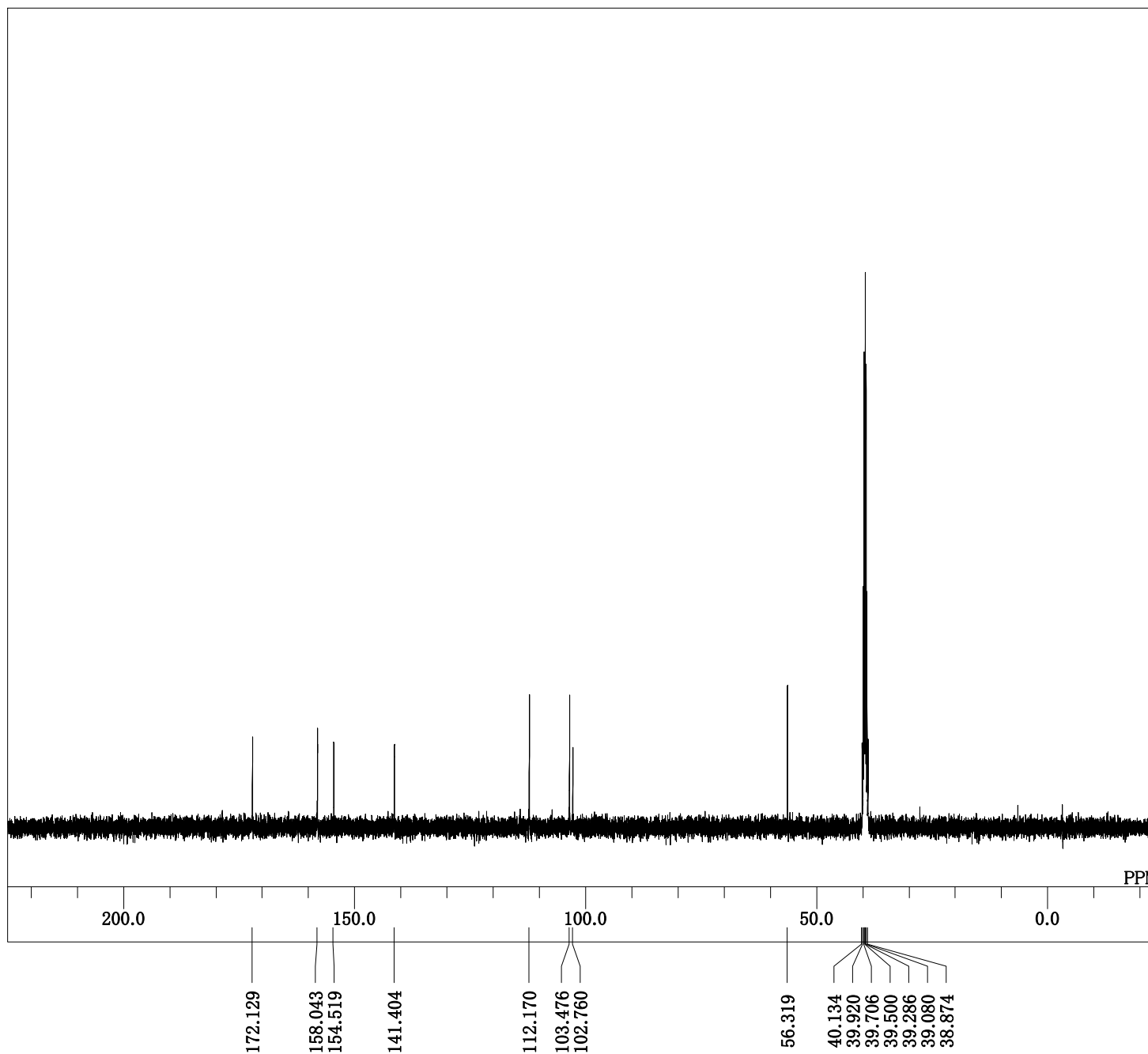


DFILE 20181108 4OMe\_pro\_non.ak  
 COMNT auto  
 DATIM Thu Nov 08 17:21:31 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.52 Hz  
 RGAIN 9

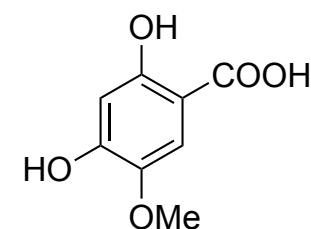


**2g**

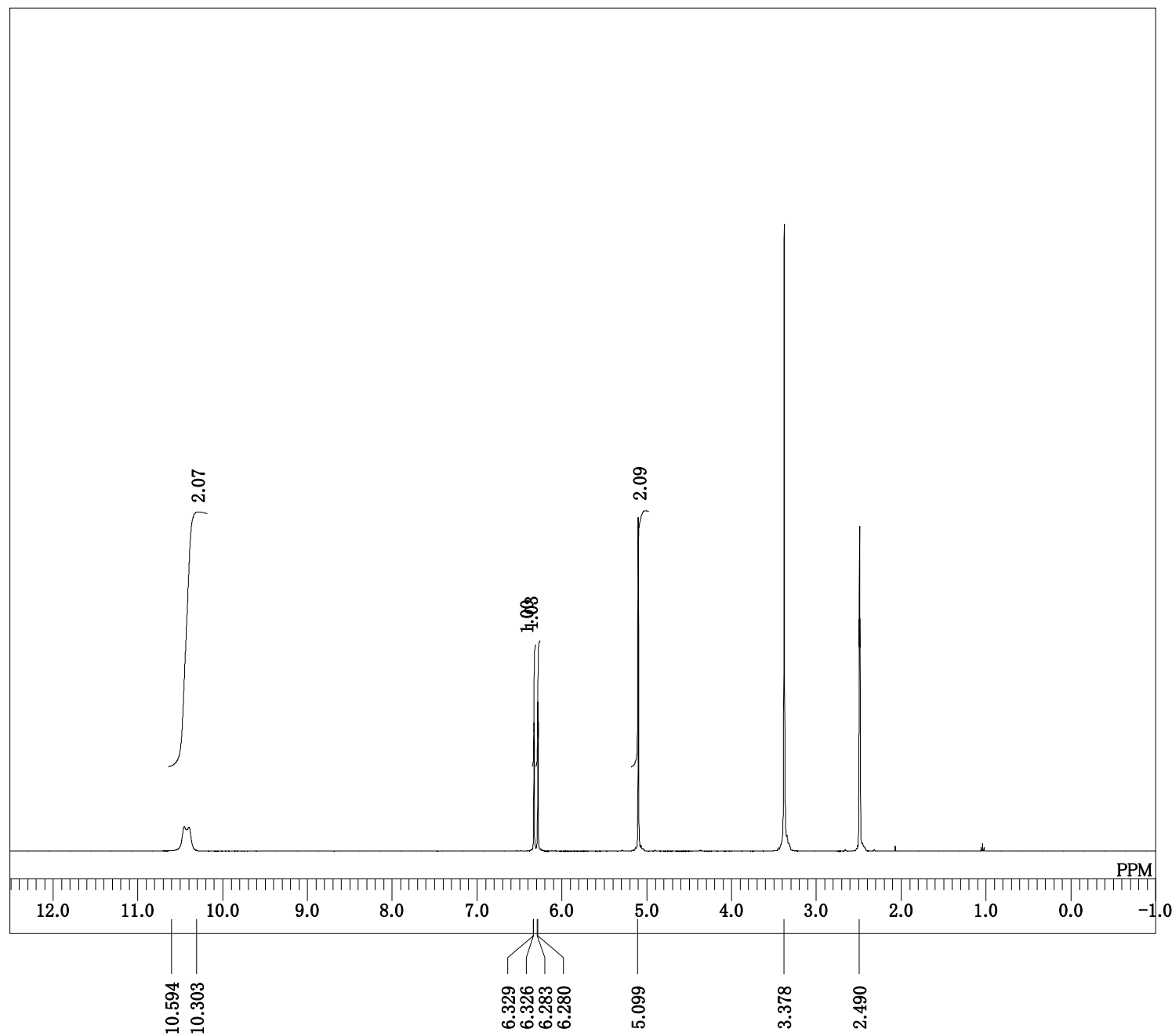




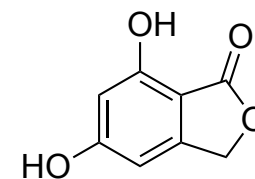
DFILE 20181108 4OMe\_pro\_bcm.al  
 COMNT auto  
 DATIM Thu Nov 08 17:36:55 2018  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 100  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.52 Hz  
 RGAIN 22



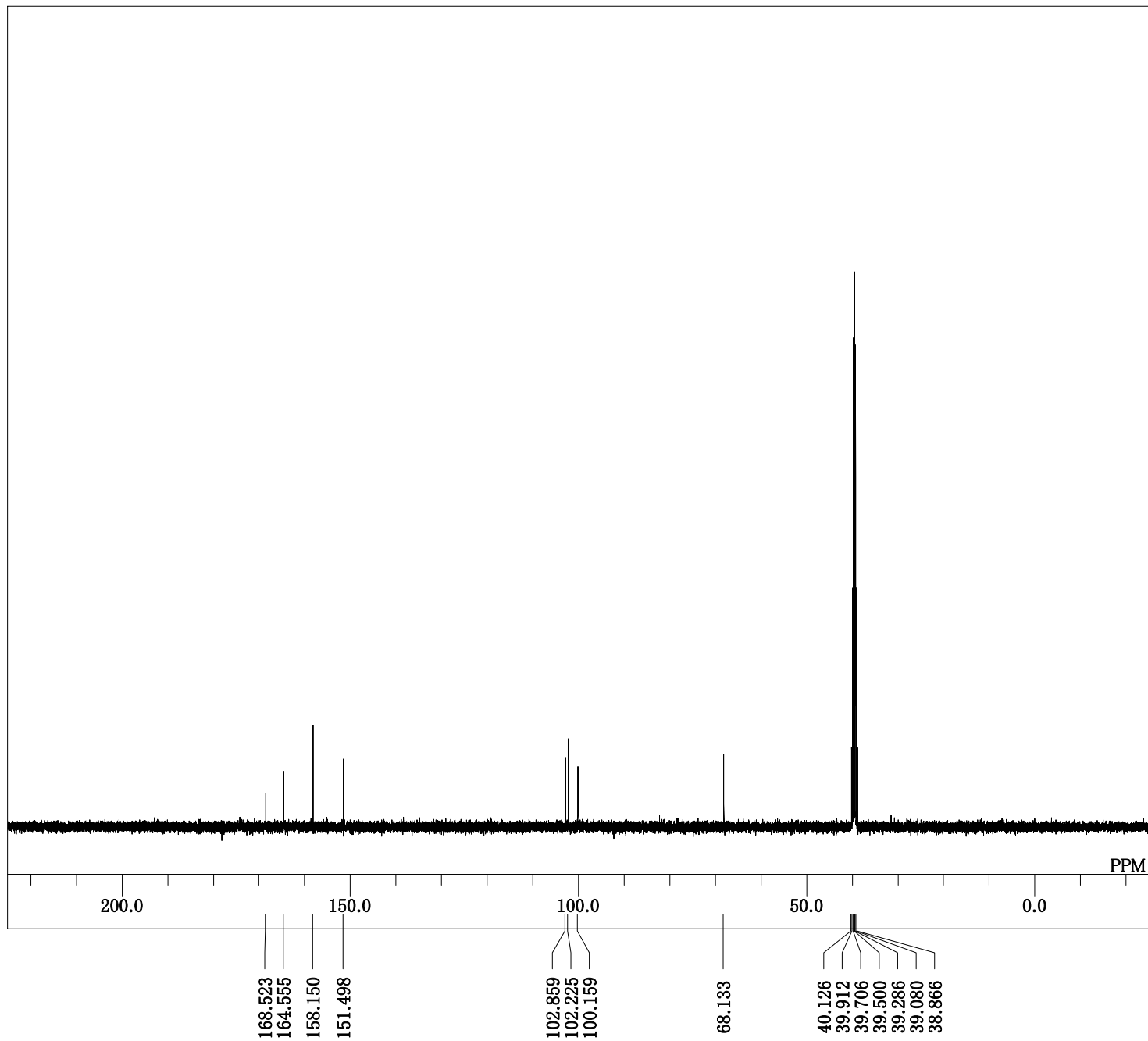
**2g**



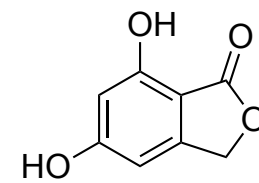
DFILE 20181108 5hydroxymethyl\_p  
 COMNT auto  
 DATIM Fri Nov 09 20:17:03 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 14



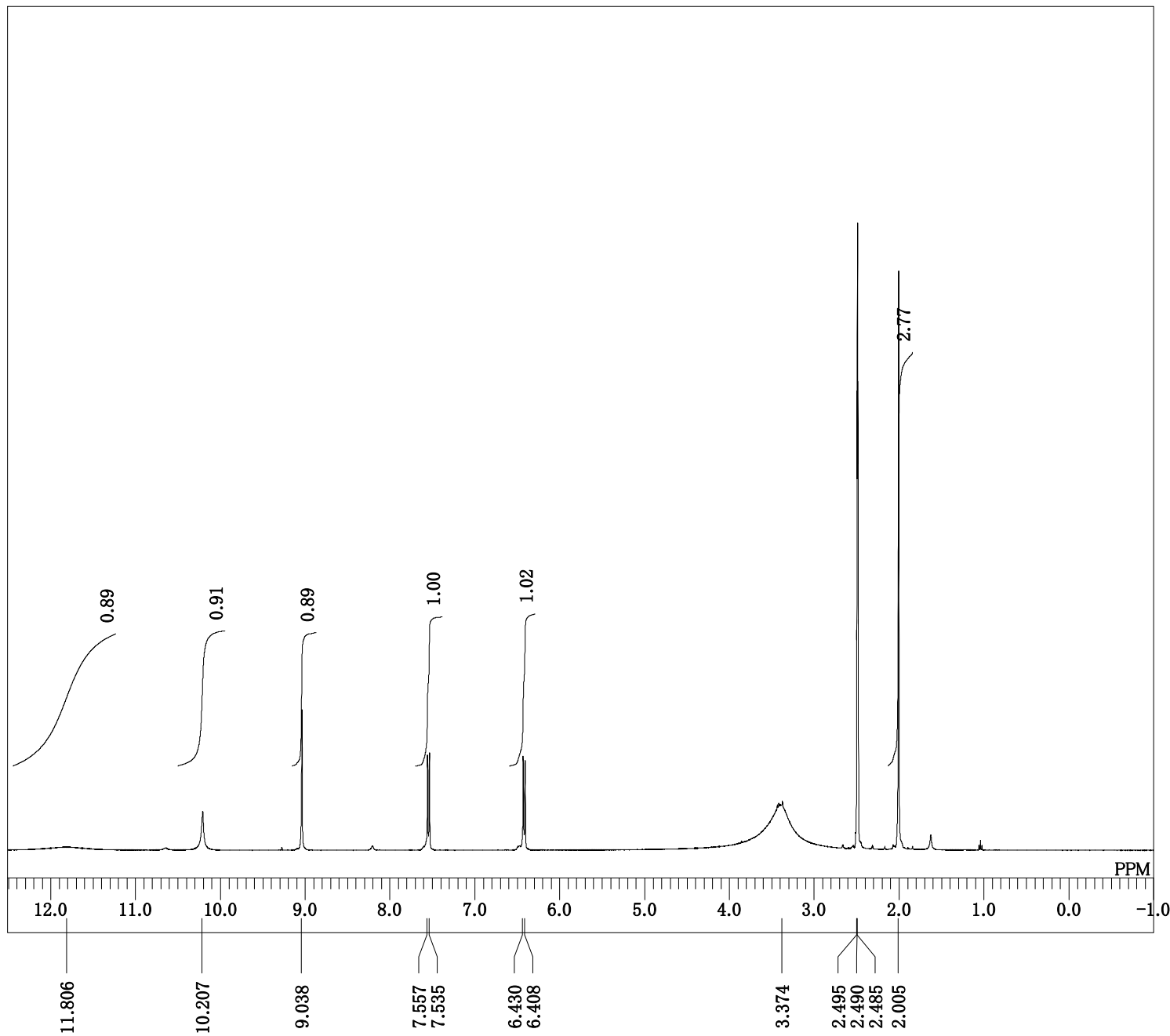
**2h**



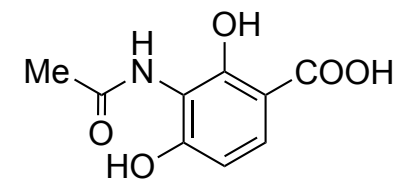
DFILE 20181108 5hydroxymethyl\_p  
 COMNT auto  
 DATIM Fri Nov 09 20:26:50 2018  
 OBNUC <sup>13</sup>C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 64  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 22



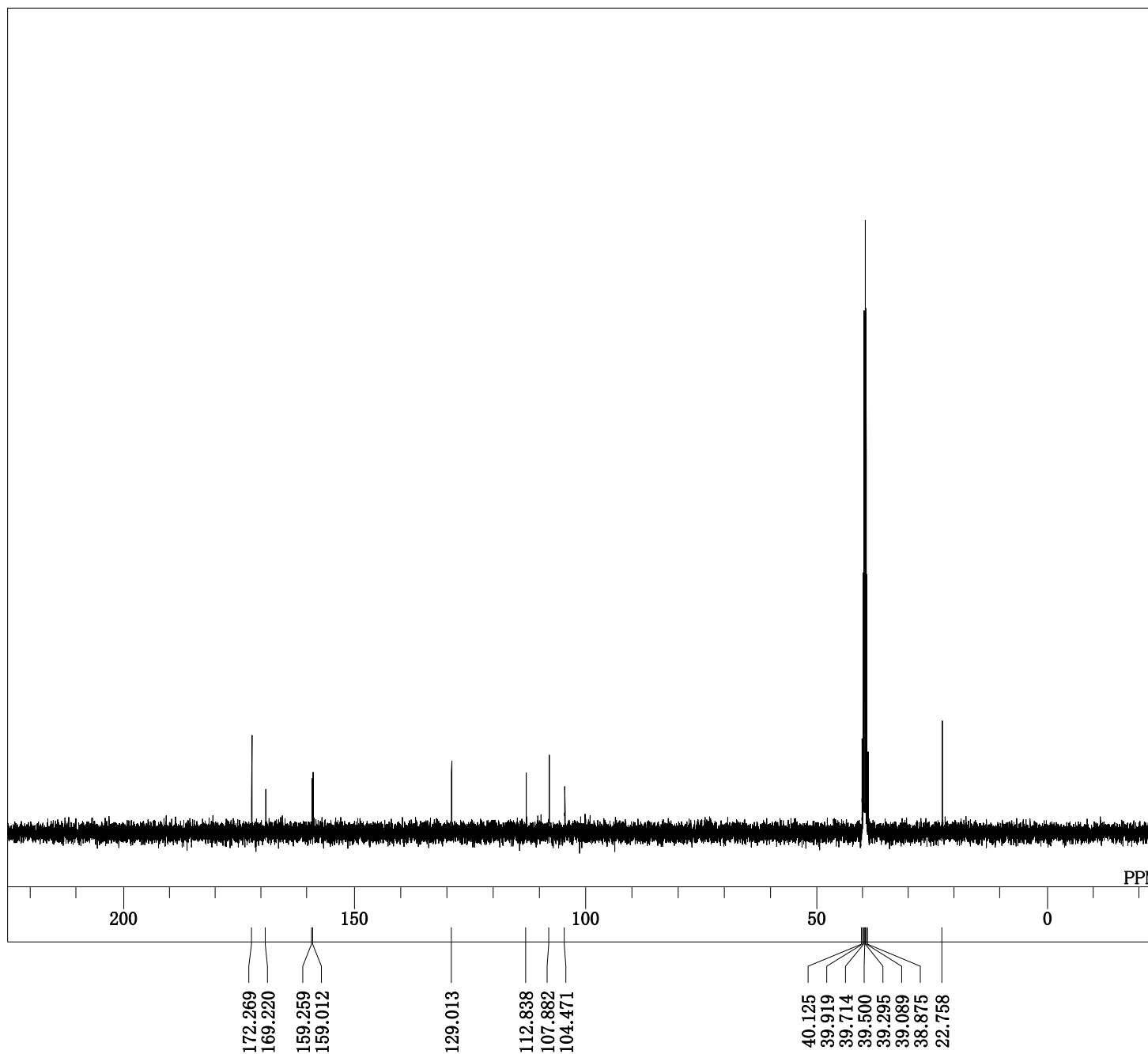
**2h**



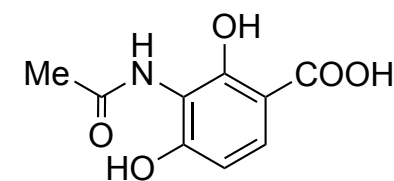
DFILE 20190426 kolbe\_pro\_amide.r  
 COMNT single\_pulse  
 DATIM 2019-04-26 17:17:25  
 OBNUC 1H  
 EXMOD single\_pulse.ex2  
 OBFRQ 391.78 MHz  
 OBSET 8.51 KHz  
 OBFIN 3.34 Hz  
 POINT 32768  
 FREQU 7352.94 Hz  
 SCANS 8  
 ACQTM 4.4564 sec  
 PD 3.0000 sec  
 PW1 5.90 usec  
 IRNUC 1H  
 CTEMP 21.1 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 40



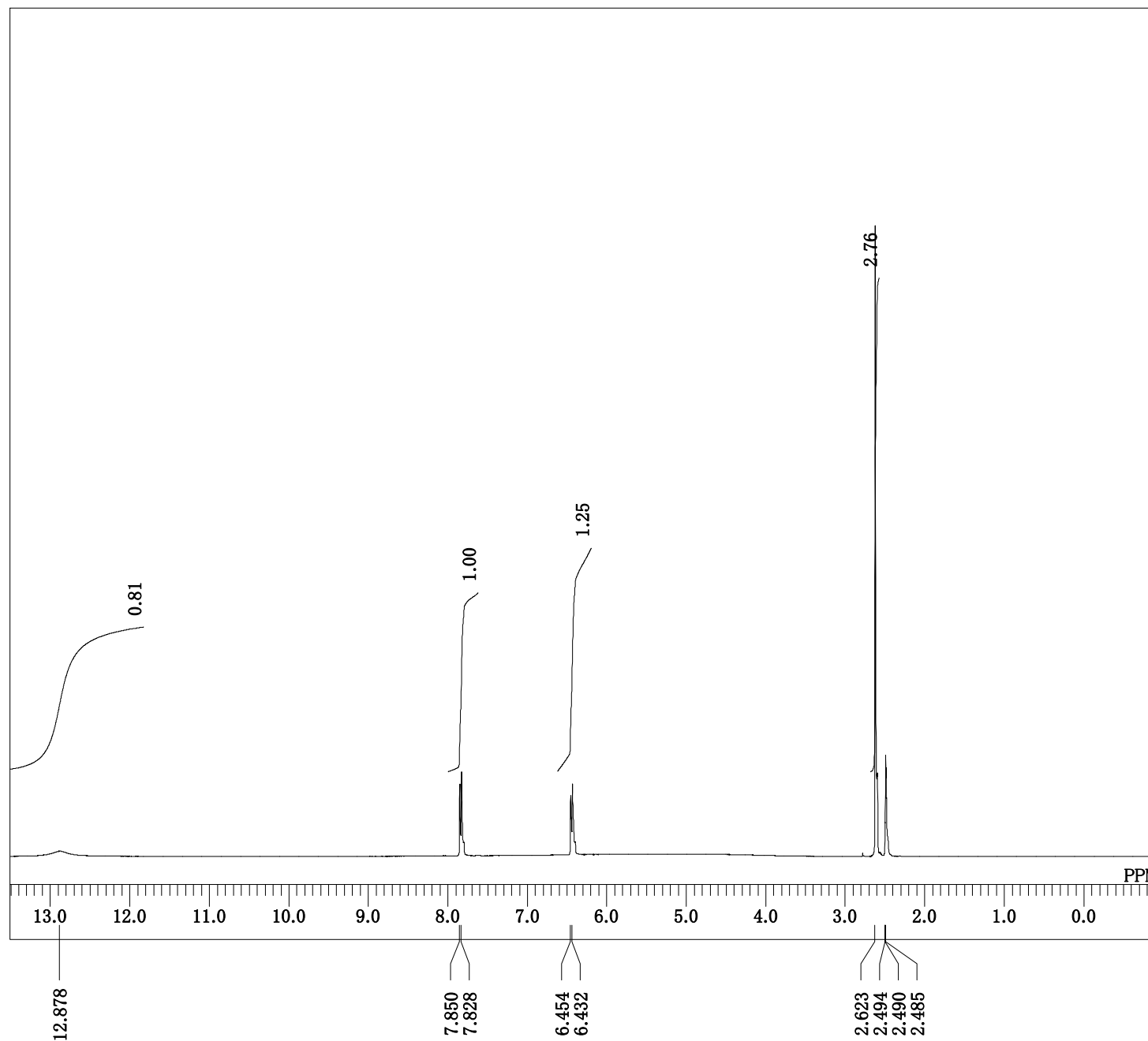
**2i**



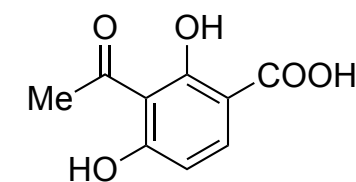
DFILE 20190426 kolbe\_pro\_2amide.  
 COMNT  
 DATIM Fri Apr 26 20:20:27 2019  
 OBNUC 13C  
 EXMOD SINGL  
 OBFRQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 128  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC 1H  
 CTEMP 23.1 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 33



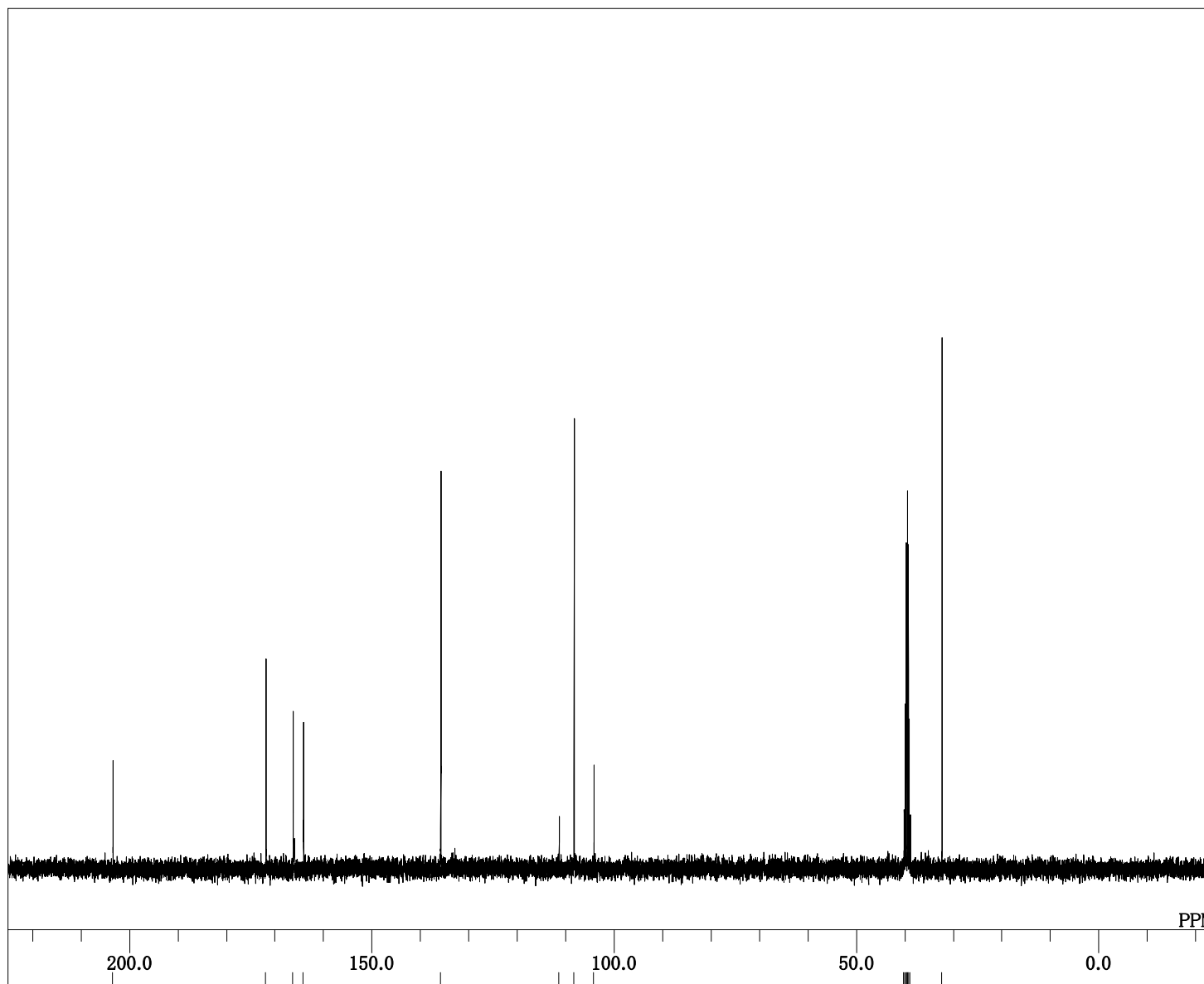
**2i**



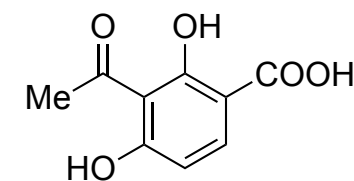
DFILE 20190427 kolbe\_pro\_2Ac\_no  
 COMNT  
 DATIM Sat Apr 27 13:34:53 2019  
 OBNUC 1H  
 EXMOD SINGL  
 OBFRQ 400.05 MHz  
 OBSET 0.00 KHz  
 OBFIN 130800.00 Hz  
 POINT 16384  
 FREQU 8000.00 Hz  
 SCANS 8  
 ACQTM 2.0480 sec  
 PD 2.0000 sec  
 PW1 5.30 usec  
 IRNUC 1H  
 CTEMP 69.7 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.62 Hz  
 RGAIN 18



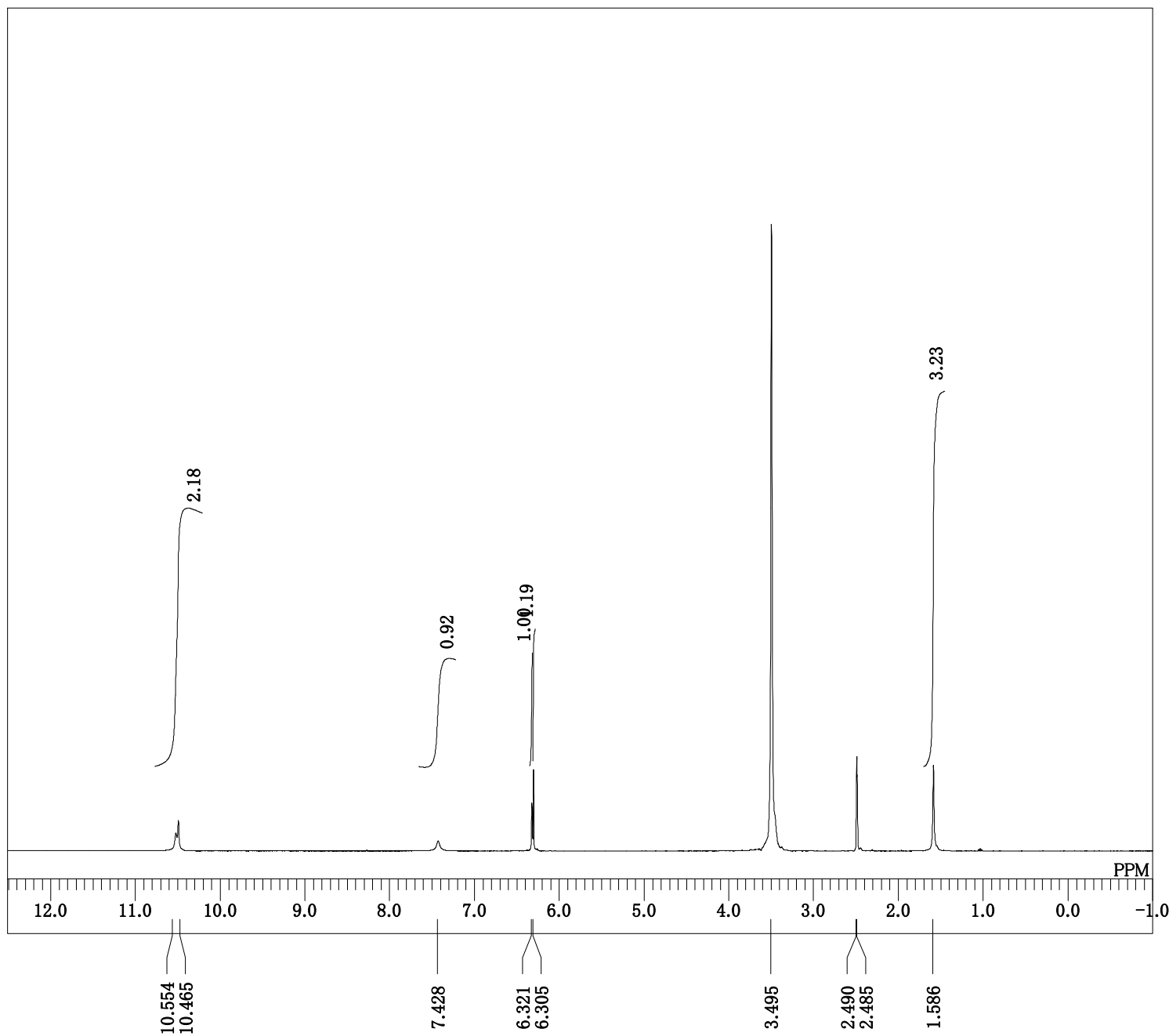
**2j**



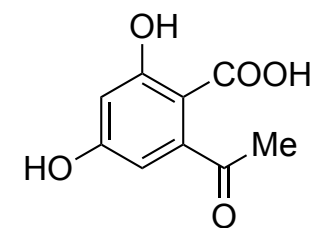
DFILE 20190427 kolbe\_pro\_2Ac\_bci  
 COMNT  
 DATIM Sat Apr 27 14:40:41 2019  
 OBNUC 13C  
 EXMOD SINGL  
 OBFRQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 200  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC 1H  
 CTEMP 69.7 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 32



2j

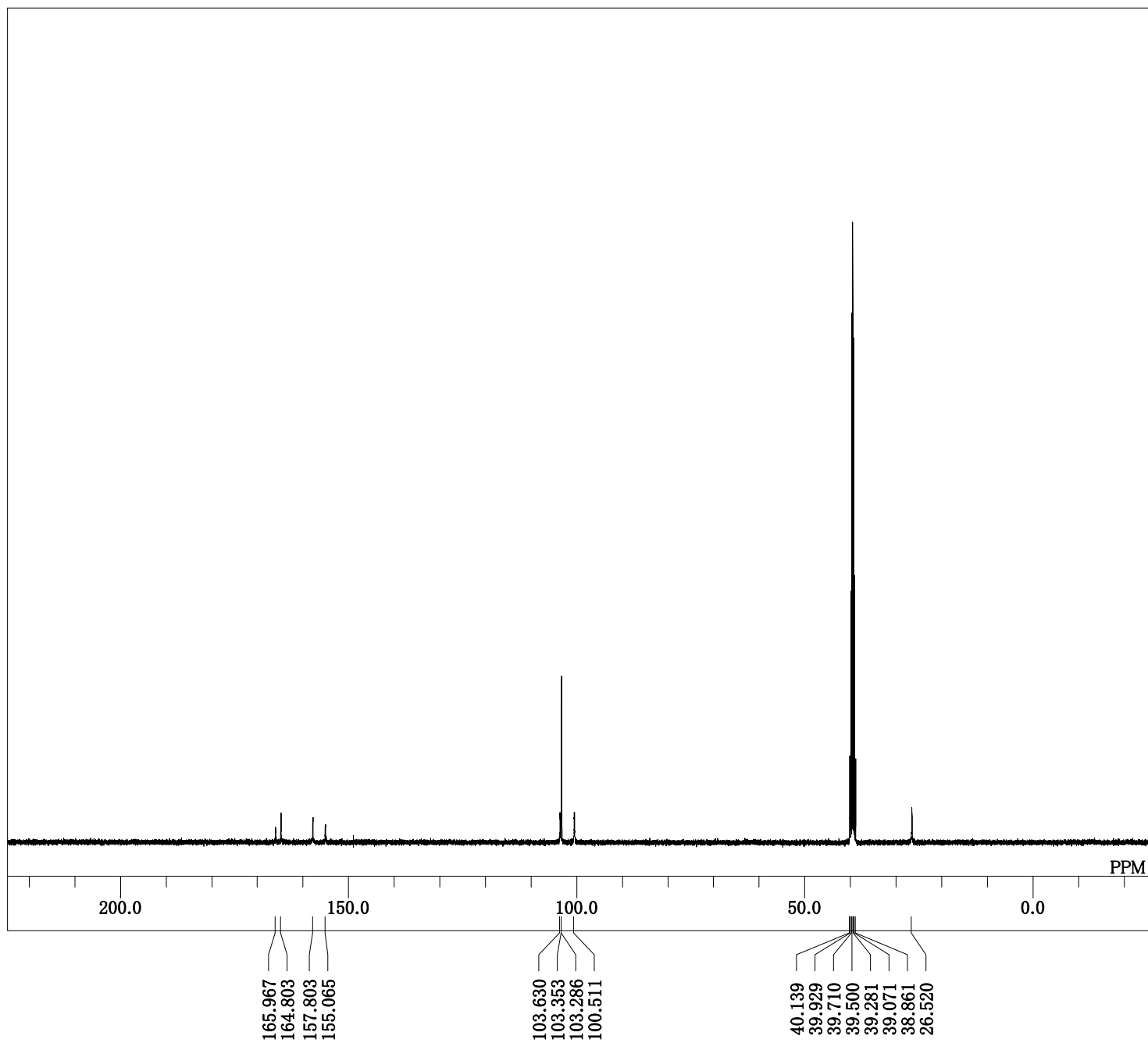


DFILE 20180628 Kolbe\_pro\_5Ac\_no  
 COMNT  
 DATIM Thu Jun 28 11:19:36 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 11

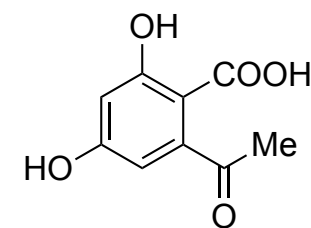


**2k**



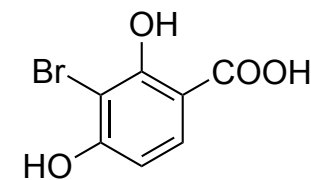
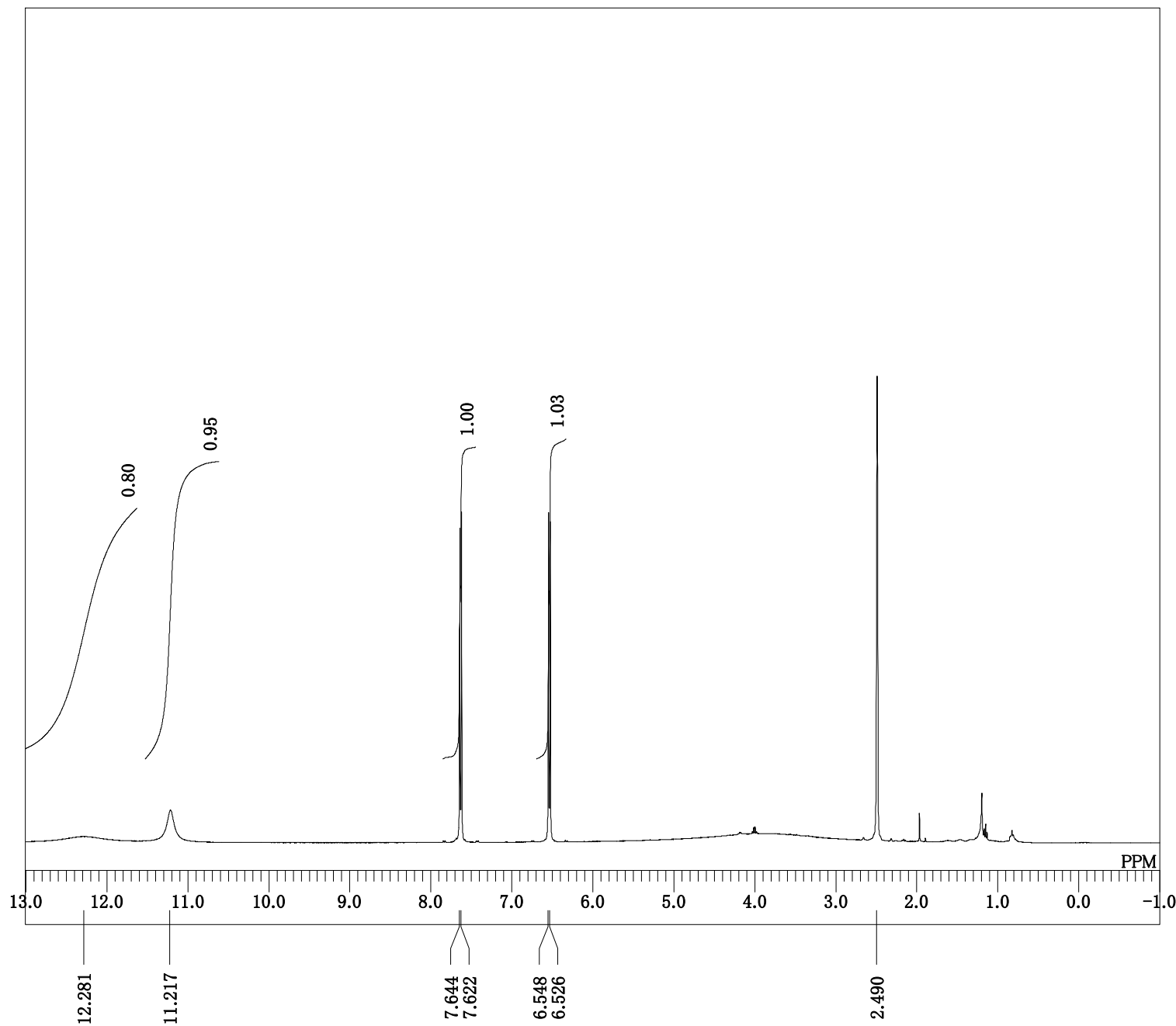


DFILE 201805015 pro\_5\_Ac\_bcm-1.  
 COMNT single pulse decoupled gate  
 DATIM 2018-05-15 16:03:24  
 OBNUC <sup>13</sup>C  
 EXMOD single\_pulse\_dec  
 OBFRQ 98.52 MHz  
 OBSET 4.64 KHz  
 OBFIN 8.74 Hz  
 POINT 32768  
 FREQU 30788.18 Hz  
 SCANS 1024  
 ACQTM 1.0643 sec  
 PD 2.0000 sec  
 PW1 3.83 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 21.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 42

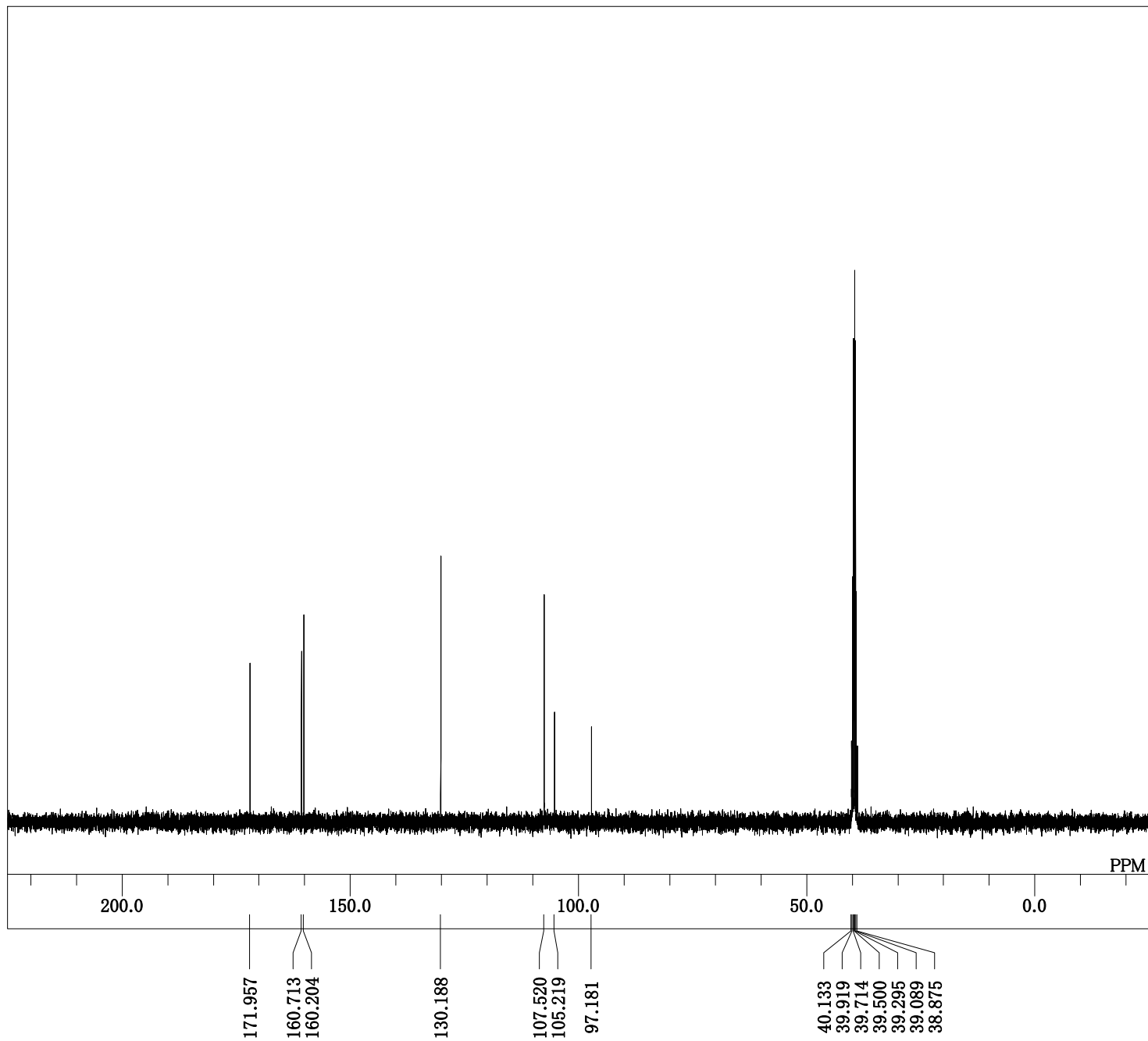


**2k**

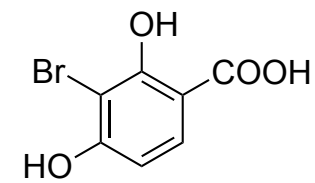
DFILE 20190426 kolbe\_pro\_2Br\_nor  
COMNT  
DATIM Fri Apr 26 20:30:41 2019  
OBNUC 1H  
EXMOD SINGL  
OBFRQ 400.05 MHz  
OBSET 0.00 KHz  
OBFIN 130800.00 Hz  
POINT 16384  
FREQU 8000.00 Hz  
SCANS 8  
ACQTM 2.0480 sec  
PD 2.0000 sec  
PW1 5.30 usec  
IRNUC 1H  
CTEMP 22.9 c  
SLVNT DMSO  
EXREF 2.49 ppm  
BF 0.62 Hz  
RGAIN 19



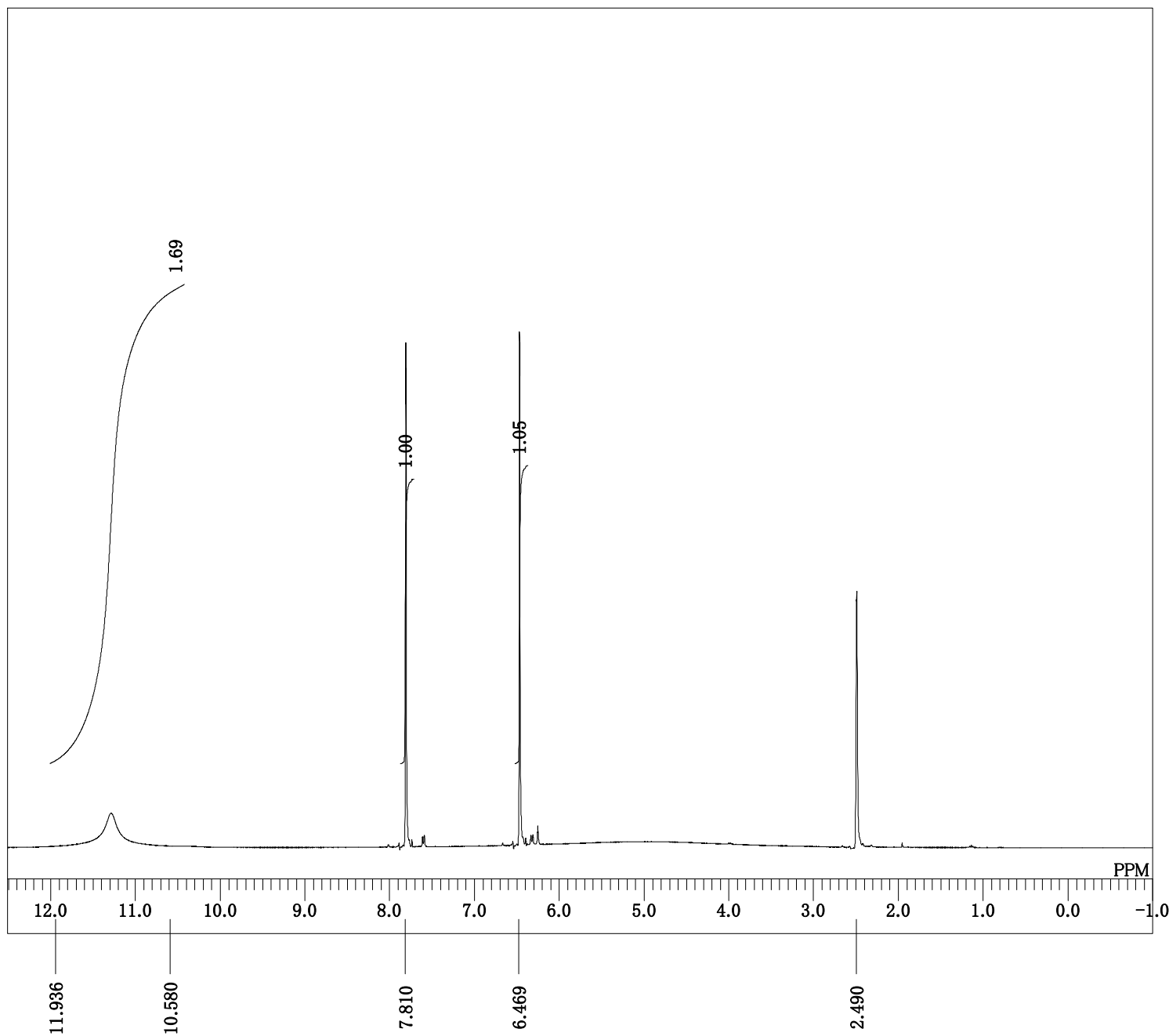
21



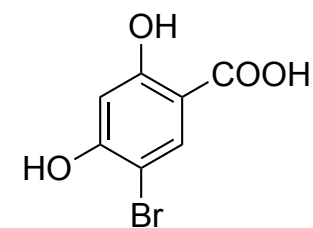
DFILE 20190426 kolbe\_pro\_2Br\_bcr  
 COMNT  
 DATIM Fri Apr 26 20:29:15 2019  
 OBNUC 13C  
 EXMOD SINGL  
 OBFRQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 64  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC 1H  
 CTEMP 23.0 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 32



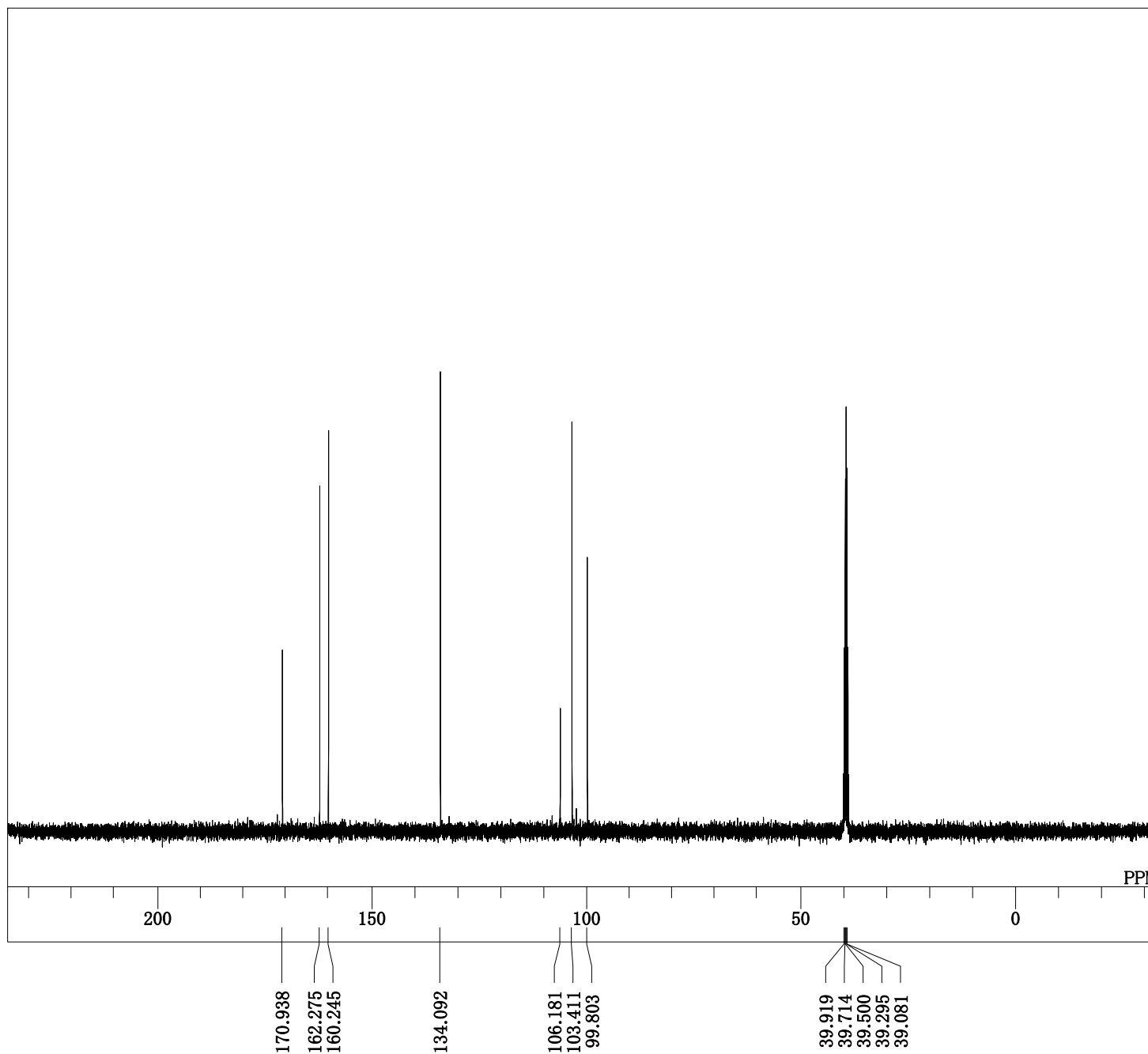
2I



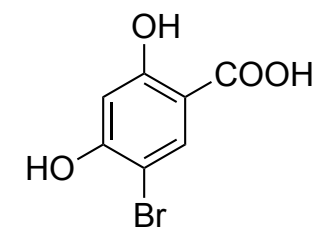
DFILE 20190423 kolbe\_pro\_4Br.als  
 COMNT auto  
 DATIM Mon Apr 22 19:58:14 2019  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 14



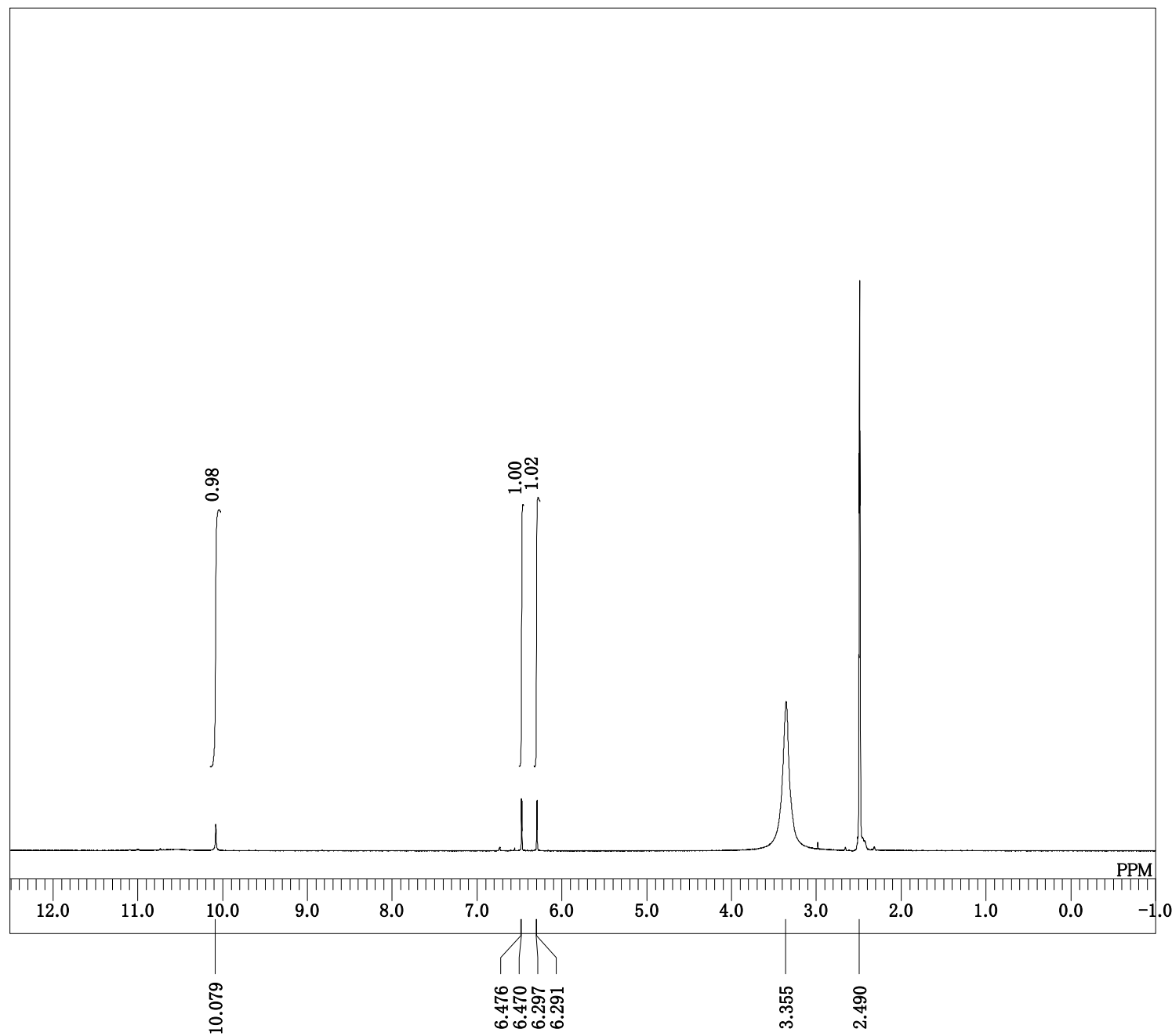
**2m**



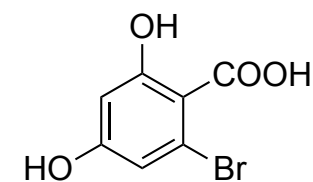
DFILE 20190427 kolbe\_pro\_4Br\_bcr  
 COMNT  
 DATIM Sat Apr 27 13:11:56 2019  
 OBNUC 13C  
 EXMOD SINGL  
 OBFRQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 64  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC 1H  
 CTEMP 22.6 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 32



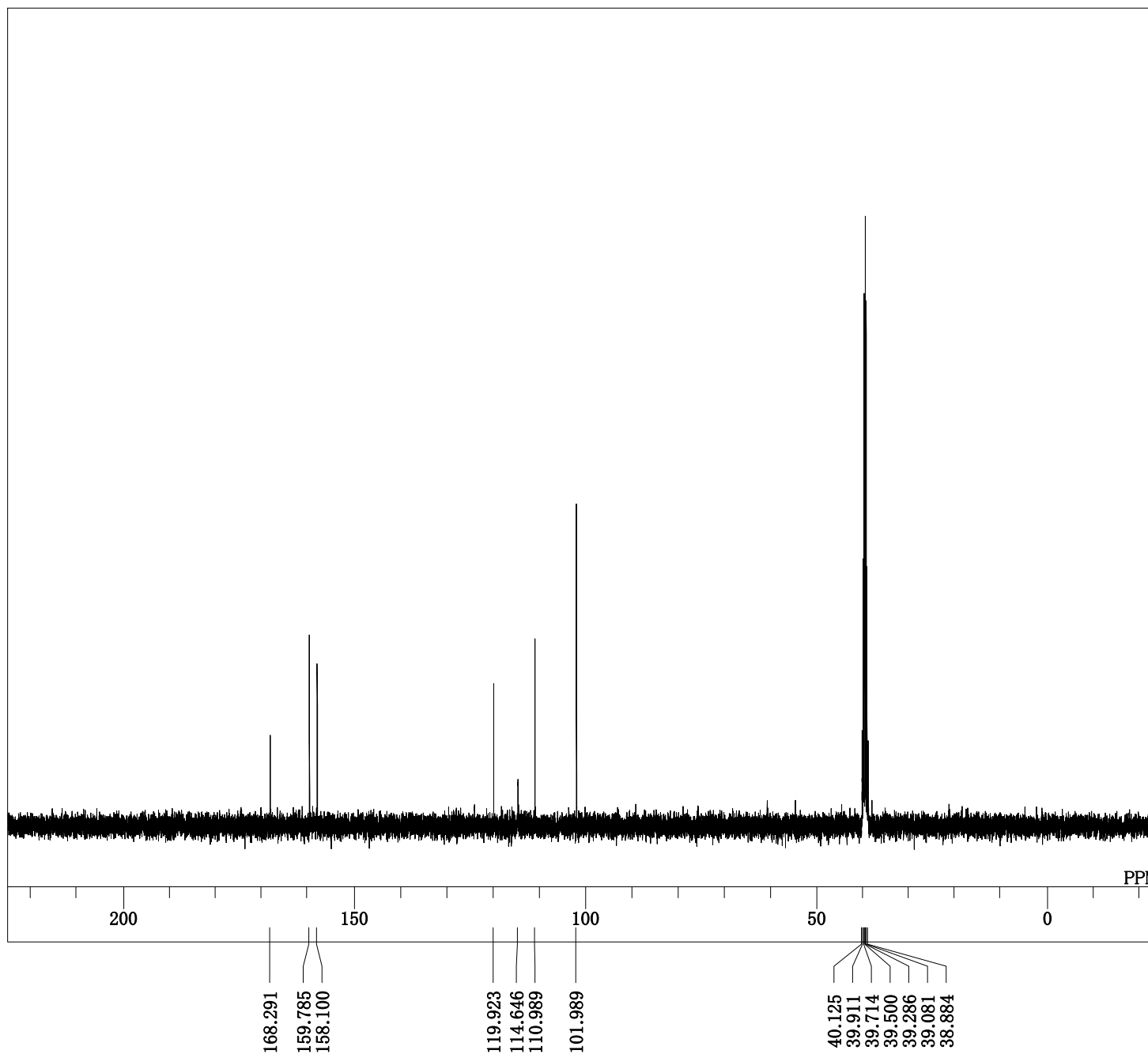
**2m**



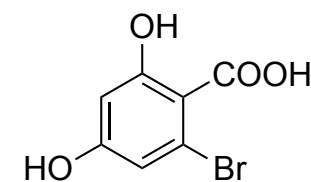
DFILE 20180904 5Br\_pro\_recry.als  
 COMNT auto  
 DATIM Tue Sep 04 15:36:56 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 25.7 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 17



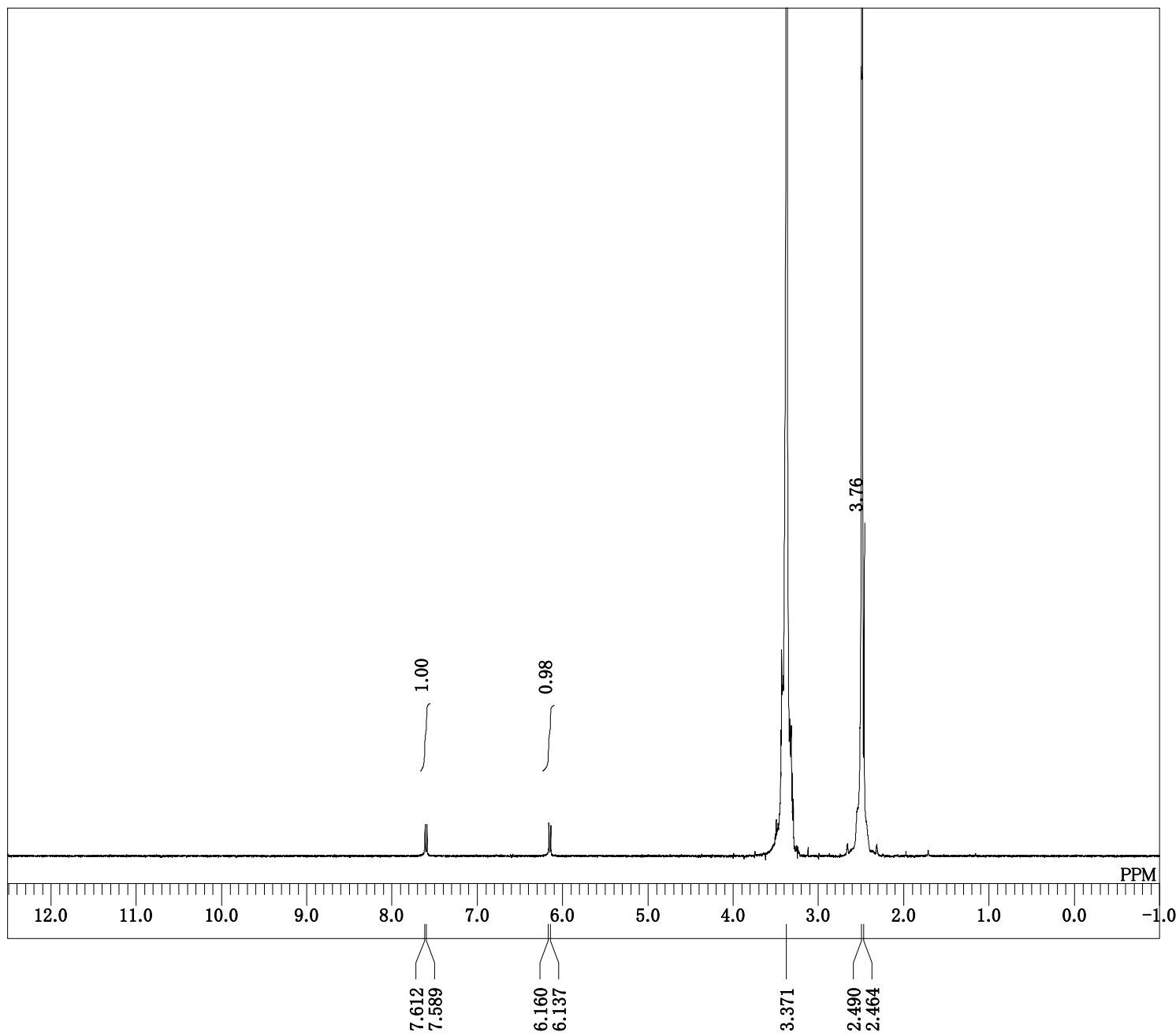
**2n**



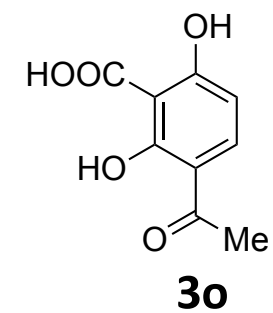
DFILE 20190426 kolbe\_pro\_5Br\_bcr  
 COMNT  
 DATIM Fri Apr 26 19:47:37 2019  
 OBNUC <sup>13</sup>C  
 EXMOD SINGL  
 OBFRQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 128  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 22.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 32



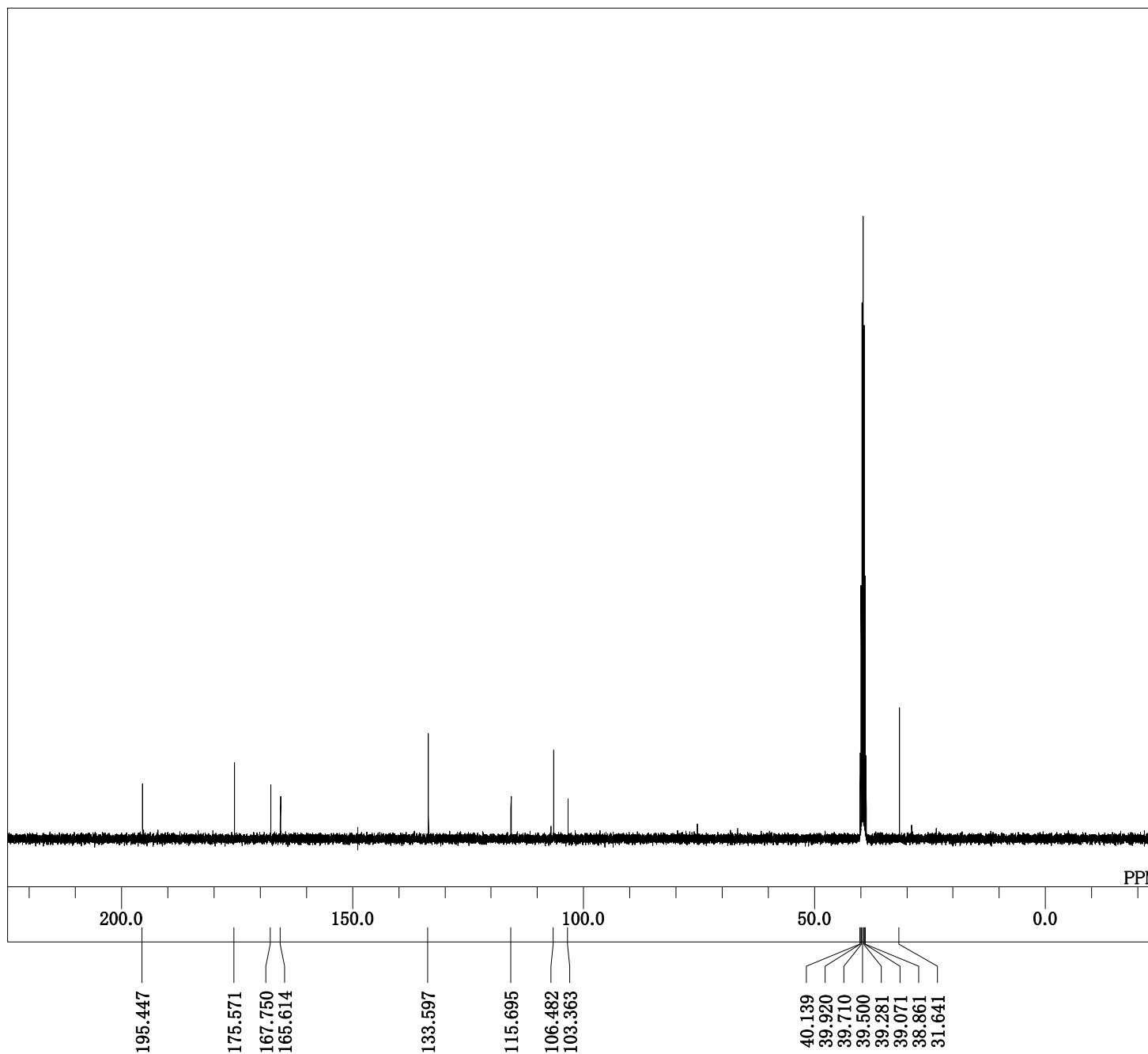
**2n**



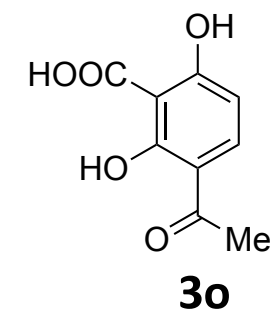
DFILE 20190427 resorcinol-4-OAc  
 COMNT auto  
 DATIM Sat Apr 27 15:57:16 2019  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP 6348.8 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 15

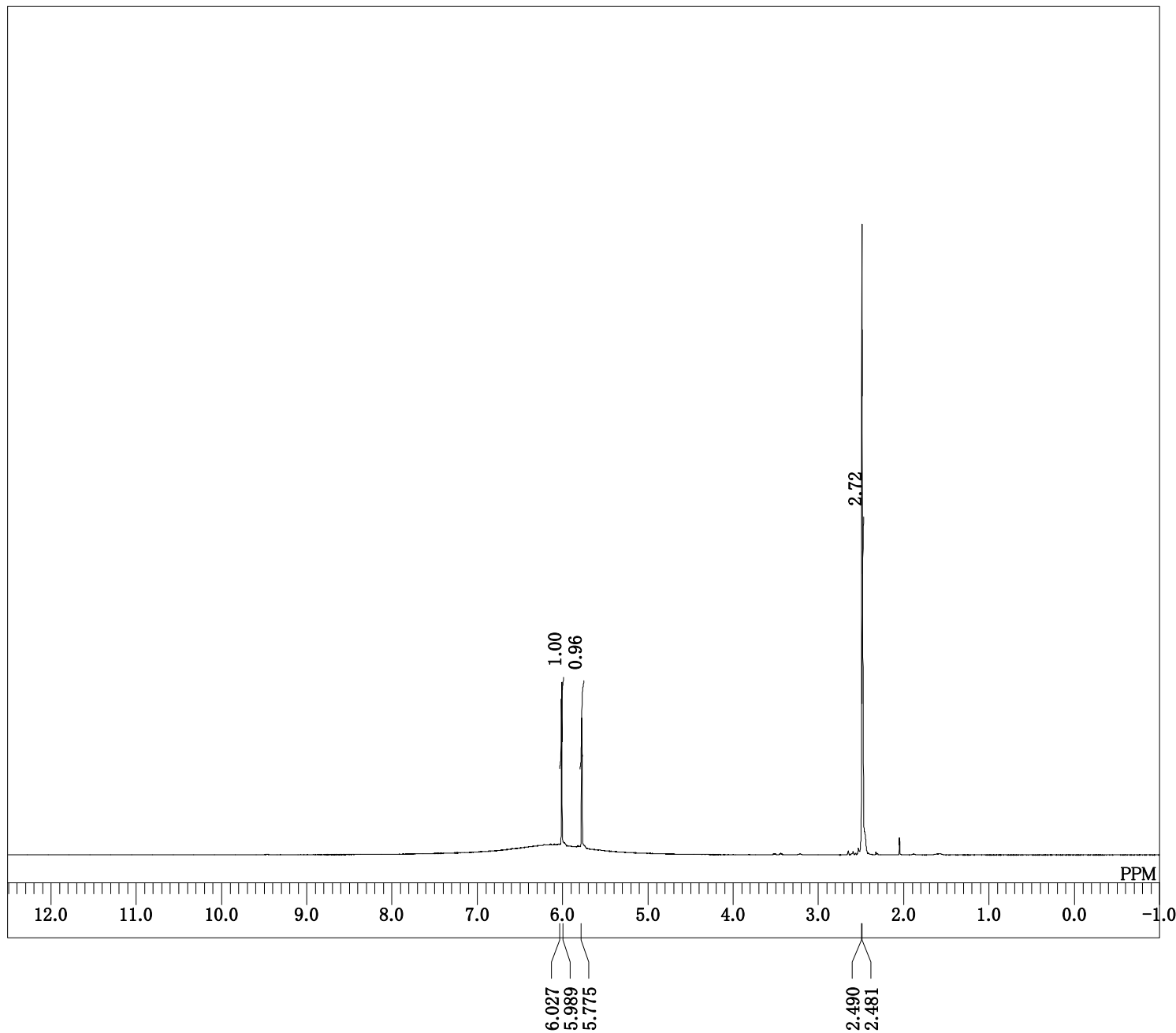




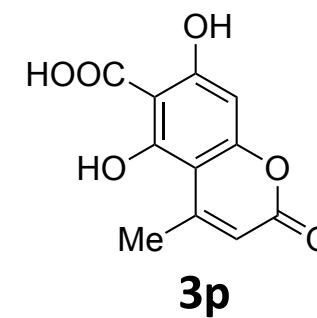


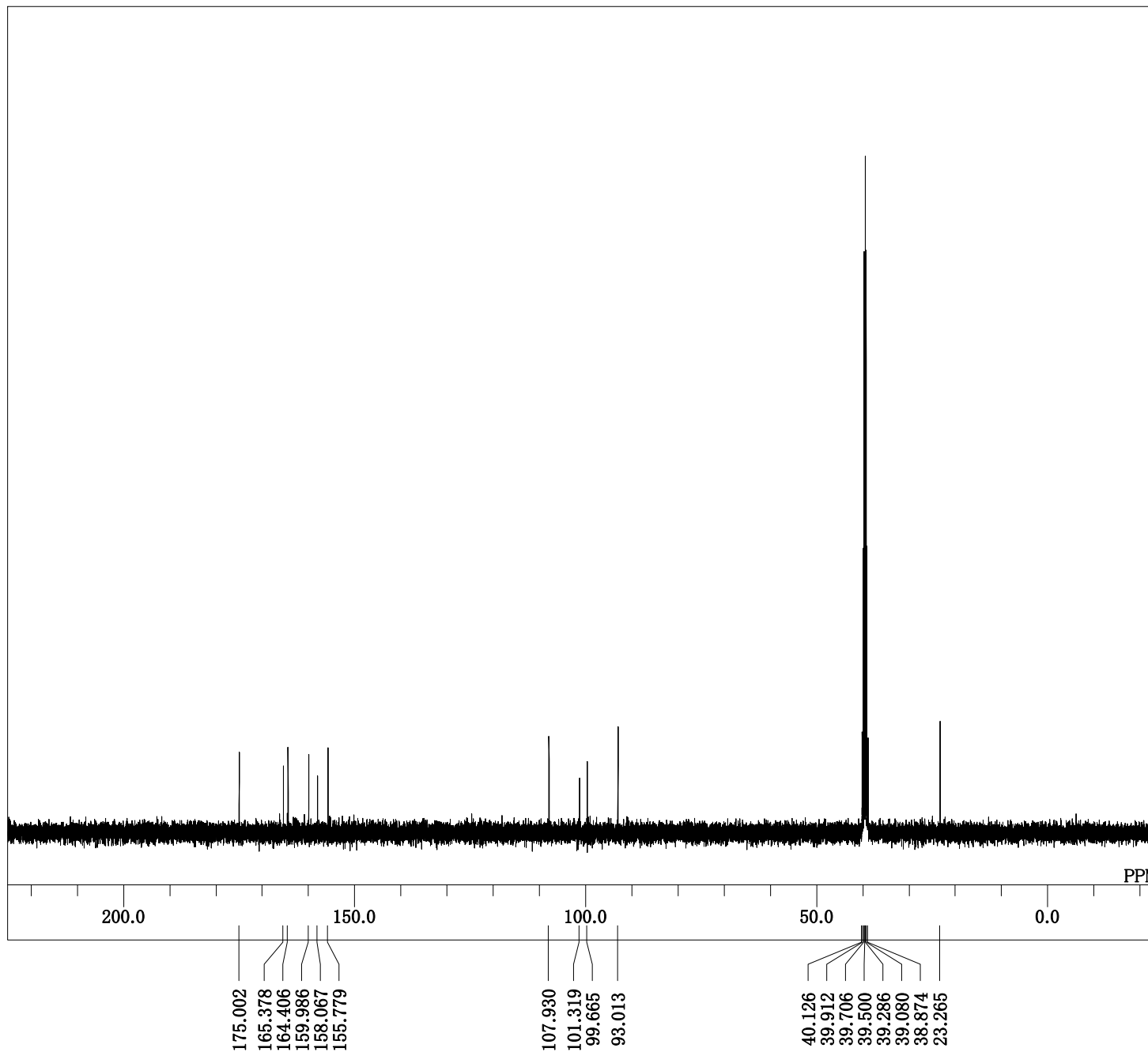
DFILE 20180507 4-acetyl-prod(ao:  
 COMNT single pulse decoupled gate  
 DATIM 2018-05-07 20:12:18  
 OBNUC <sup>13</sup>C  
 EXMOD single\_pulse\_dec  
 OBFREQ 98.52 MHz  
 OBSET 4.64 KHz  
 OBFIN 8.74 Hz  
 POINT 26214  
 FREQU 24630.17 Hz  
 SCANS 512  
 ACQTM 1.0643 sec  
 PD 2.0000 sec  
 PW1 3.00 usec  
 IRNUC <sup>1</sup>H  
 CTEMP 21.4 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 50



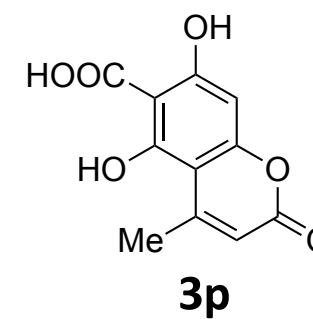


DFILE 20180724 coumarin\_pro.als  
 COMNT  
 DATIM Tue Jul 24 14:27:55 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP -59.5 c  
 SLVNT DMSO  
 EXREF 2.49 ppm  
 BF 0.12 Hz  
 RGAIN 14

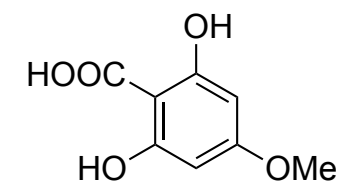
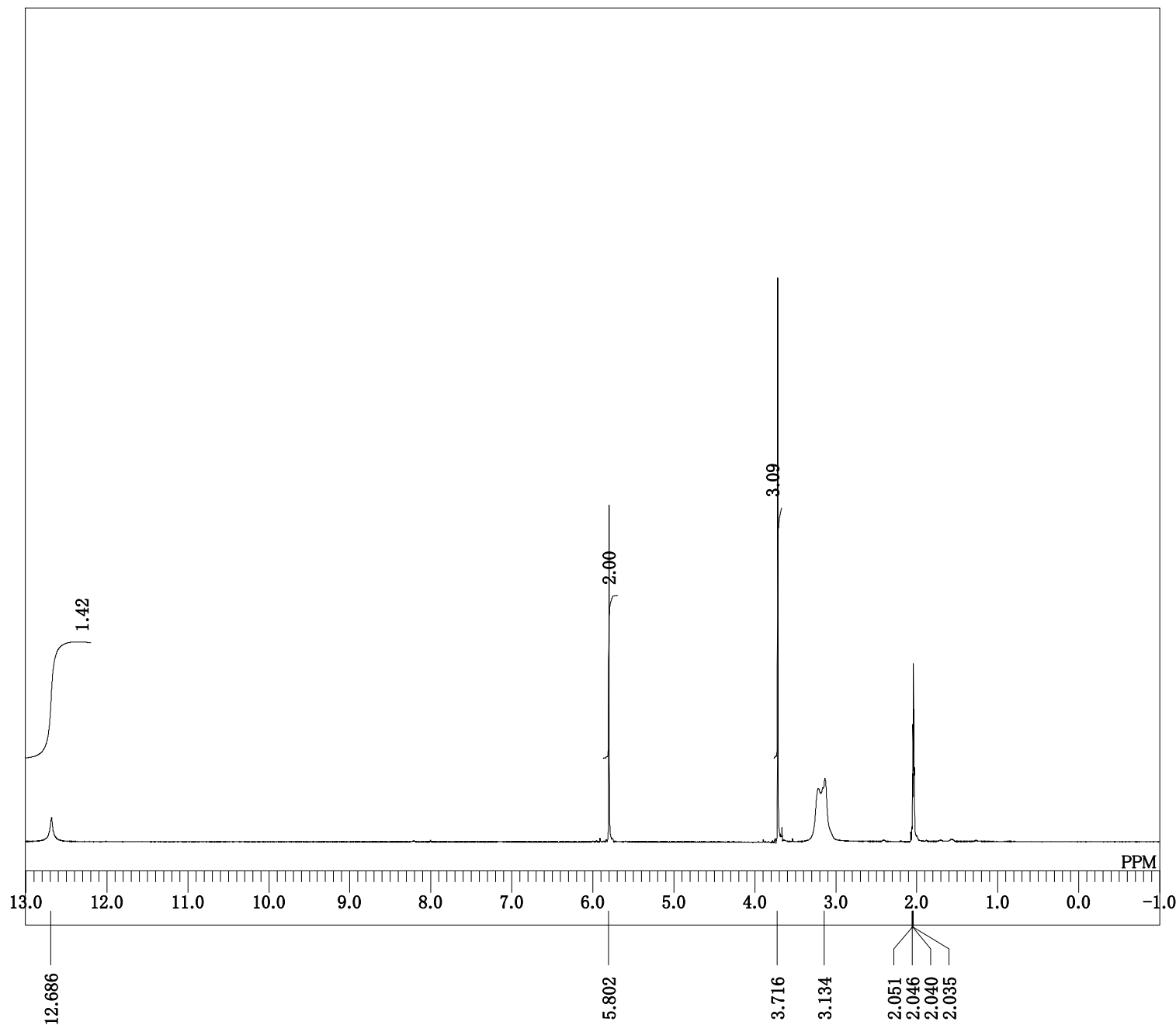




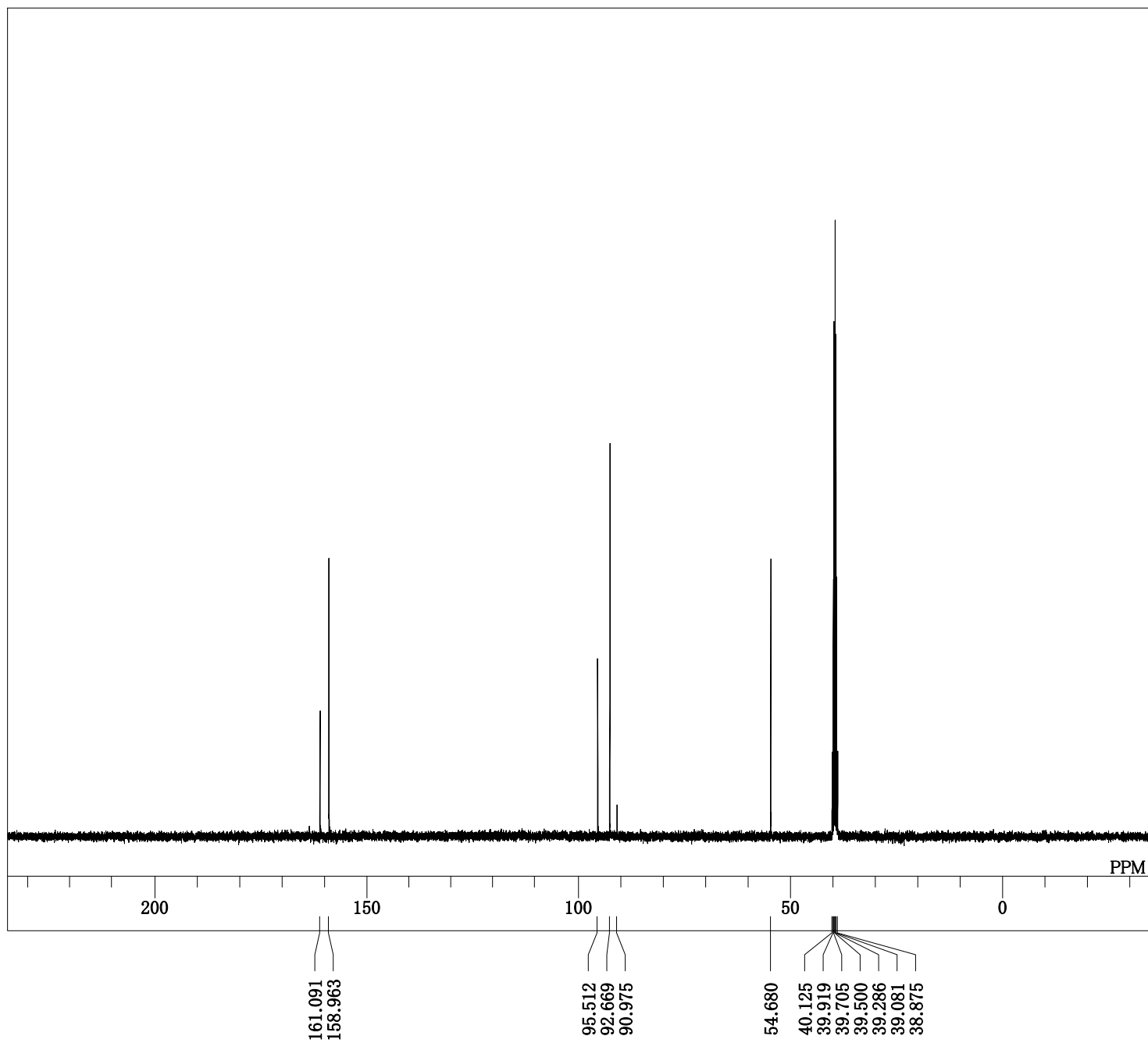
DFILE 20180724 coumarin\_pro\_bcr  
 COMNT  
 DATIM Tue Jul 24 14:40:37 2018  
 OBNUC 13C  
 EXMOD BCM  
 OBFRQ 100.40 MHz  
 OBSET 125.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 32768  
 FREQU 27118.64 Hz  
 SCANS 128  
 ACQTM 1.2083 sec  
 PD 3.0000 sec  
 PW1 4.70 usec  
 IRNUC 1H  
 CTEMP -81.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.12 Hz  
 RGAIN 22



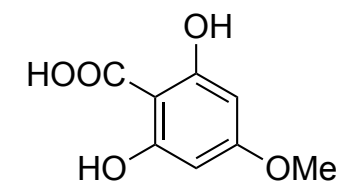
DFILE 20180515 pro\_5\_OMe.als  
 COMNT auto  
 DATIM Tue May 15 13:58:43 2018  
 OBNUC 1H  
 EXMOD NON  
 OBFRQ 399.65 MHz  
 OBSET 124.00 KHz  
 OBFIN 10500.00 Hz  
 POINT 16384  
 FREQU 7992.01 Hz  
 SCANS 8  
 ACQTM 2.0500 sec  
 PD 2.0000 sec  
 PW1 6.60 usec  
 IRNUC 1H  
 CTEMP -9.4 c  
 SLVNT ACETN  
 EXREF 2.04 ppm  
 BF 0.12 Hz  
 RGAIN 18



**3q**



DFILE 20190427 kolbe\_pro\_5OMe\_1  
 COMNT  
 DATIM Sat Apr 27 15:25:33 2019  
 OBNUC 13C  
 EXMOD SINGL  
 OBFREQ 100.50 MHz  
 OBSET 0.00 KHz  
 OBFIN 135159.00 Hz  
 POINT 32768  
 FREQU 27100.27 Hz  
 SCANS 736  
 ACQTM 1.2091 sec  
 PD 1.0000 sec  
 PW1 4.80 usec  
 IRNUC 1H  
 CTEMP 39.8 c  
 SLVNT DMSO  
 EXREF 39.50 ppm  
 BF 0.62 Hz  
 RGAIN 32



**3q**