

## Supporting Information

### Synthesis of polysubstituted 4-aminopyrazoles and 4-hydroxypyrazoles from vinyl azides and hydrazines

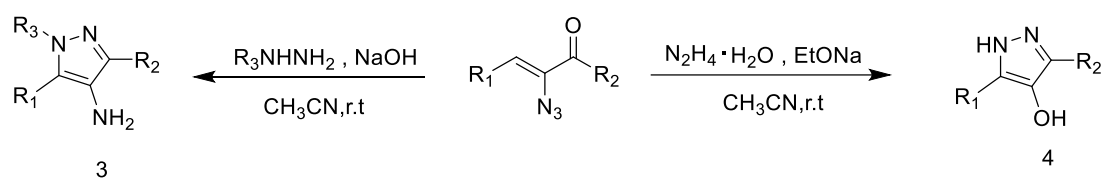
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## 1. General Information:

All solvents were purified according to standard methods prior to use. Melting points were recorded on a BÜCHI B-540 melting point apparatus. NMR spectra were recorded for  $^1\text{H}$  NMR at 500 MHz or 400 MHz and  $^{13}\text{C}$  NMR at 125 MHz. For  $^1\text{H}$  NMR, tetramethylsilane (TMS) served as internal standard ( $\delta=0$ ) and data are reported as follows: chemical shift, integration, multiplicity (s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet), and coupling constant(s) in Hertz. For  $^{13}\text{C}$  NMR, TMS ( $\delta=0$ ) or DMSO ( $\delta=40.45$ ) was used as internal standard and spectra were obtained with complete proton decoupling. LC-MS and HRMS data was obtained using Agilent Technologies 6224 TOF LC/MS. The starting material vinyl azides **1** were prepared according to literature methods.<sup>1</sup> The starting material **2** were commercially available.

## 2. General Procedure for the Synthesis of 3 and 4:

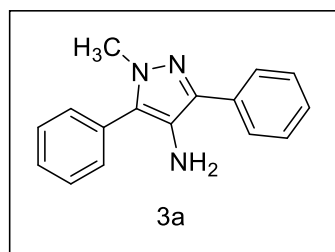
Procedure for the Synthesis of 3:

A mixture of vinyl azides (0.4 mmol), hydrazines (wt 80% , 0.4mmol) ,NaOH(0.8mmol) was stirred in  $\text{CH}_3\text{CN}$  2 mL at rt for 8 hours. After the completeness of the reaction, the reaction was diluted with water and extracted three times with ethyl acetate. The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , concentrated and purified by flash chromatography (PE/EtOAc) on silica gel to afford 3a-3n.

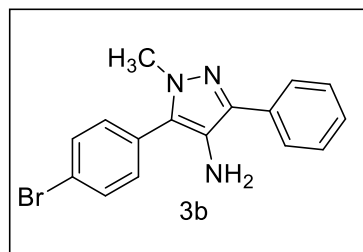
Procedure for the Synthesis of 4:

A mixture of vinyl azides (0.4 mmol), hydrazine hydrate (4 mmol) ,NaOEt(0.8mmol) was stirred in  $\text{CH}_3\text{CN}$  2 mL at rt for 5 hours. After the completeness of the reaction, the reaction was diluted with water and extracted three times with ethyl acetate. The combined organic extracts were washed with brine, dried over  $\text{Na}_2\text{SO}_4$ , concentrated and purified by flash chromatography (DCM/MeOH) on silica gel to afford 4a-4l.

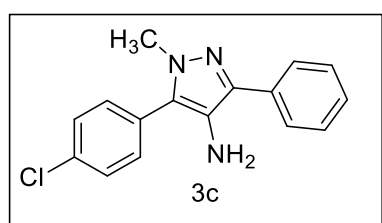
### 3. Characterization Data of 3 and 4:



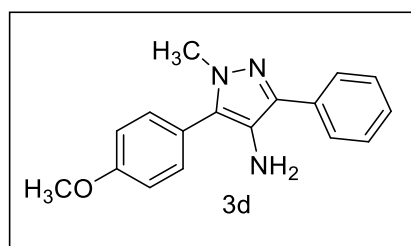
Yellow solid; mp 80.4-81.1 °C; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.83 (m, 2H), 7.58 – 7.52 (m, 2H), 7.50 – 7.44 (m, 5H), 7.37 – 7.32 (m, 1H), 3.83 (s, 3H), 3.14 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.75, 133.49, 131.47, 129.66, 129.35, 129.19, 128.79, 128.41, 127.16, 126.70, 124.45, 37.58. HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>15</sub>N<sub>3</sub> [M+H]<sup>+</sup>:250.1344. Found: 250.1346.



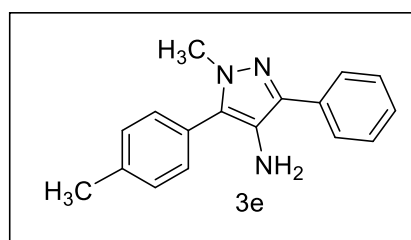
Light yellow solid; mp 138.5-139.6 °C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.82 (d, J = 7.2 Hz, 2H), 7.73 (d, J = 8.4 Hz, 2H), 7.47 (d, J = 8.4 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 3.80 (s, 2H), 3.73 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.97, 133.32, 132.43, 130.88, 130.20, 128.80, 128.62, 127.27, 126.73, 124.68, 122.61, 37.58. HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>14</sub>BrN<sub>3</sub> [M+H]<sup>+</sup>:328.0445. Found: 328.0447.



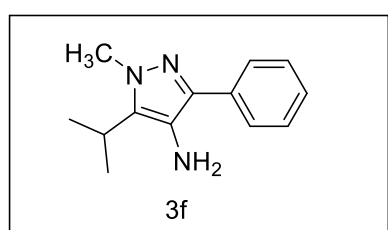
Yellow solid; mp 125.1-126.0 °C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.84 – 7.79 (m, 2H), 7.63 – 7.58 (m, 2H), 7.56 – 7.51 (m, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.4 Hz, 1H), 3.85 (s, 2H), 3.73 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.87, 134.46, 133.26, 130.63, 130.20, 129.50, 128.85, 128.06, 127.30, 126.72, 124.66, 37.60. HRMS (ESI) m/z calcd for C<sub>16</sub>H<sub>14</sub>ClN<sub>3</sub> [M+H]<sup>+</sup>:284.0955. Found: 284.0954.



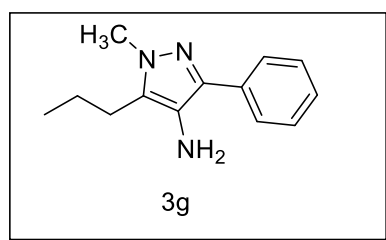
Yellow solid; mp 143.5-144.4 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.81 (d, J = 7.2 Hz, 2H), 7.44 (t, J = 7.6 Hz, 2H), 7.34 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 7.4 Hz, 1H), 7.05 (d, J = 8.6 Hz, 2H), 3.87 (s, 3H), 3.78 (s, 3H), 3.01 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.68, 139.69, 133.68, 131.45, 130.75, 128.73, 127.05, 126.65, 124.29, 121.83, 114.63, 55.38, 37.40. HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub>O [M+H]<sup>+</sup>:280.1453. Found: 280.1449.



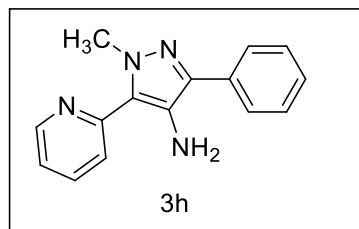
Yellow solid; mp 91.5-92.4 °C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.83 (d, J = 7.3 Hz, 2H), 7.42 (t, J = 7.7 Hz, 2H), 7.39 (d, J = 8.4 Hz, 2H), 7.36 (d, J = 8.2 Hz, 2H), 7.28 (t, J = 7.4 Hz, 1H), 3.72 (s, 3H), 3.68 (s, 2H), 2.39 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 139.73, 138.36, 133.64, 131.59, 129.87, 129.25, 128.74, 127.07, 126.68, 124.35, 37.50, 21.35. HRMS (ESI) m/z calcd for C<sub>17</sub>H<sub>17</sub>N<sub>3</sub> [M+H]<sup>+</sup>:264.1513. Found: 264.1511.



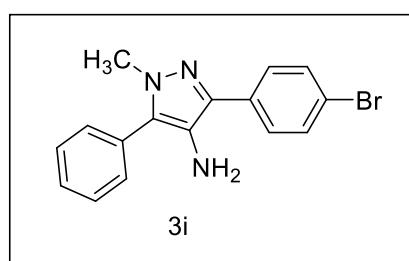
Liquid; <sup>1</sup>H NMR (500 MHz, DMSO) δ 7.74 (m, 2H), 7.37 (m, 2H), 7.23 (m, 1H), 3.75 (s, 3H), 3.59 (s, 2H), 3.24 – 3.05 (m, 1H), 1.30 (d, J = 7.2 Hz, 6H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 140.92, 135.64, 133.55, 128.69, 127.05, 122.48, 37.46, 25.32, 20.62. HRMS (ESI) m/z calcd for C<sub>13</sub>H<sub>17</sub>N<sub>3</sub> [M+H]<sup>+</sup>:216.1504. Found: 216.1505.



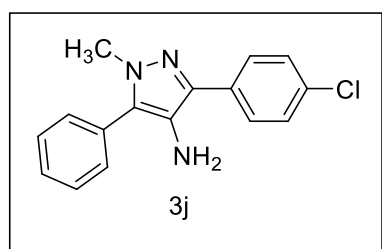
Orange solid; mp 74.3.6-75.4 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 – 7.73 (m, 2H), 7.47 – 7.40 (m, 2H), 7.34 – 7.29 (m, 1H), 3.82 (s, 3H), 2.85 (s, 2H), 2.61 (t,  $J = 7.6$  Hz, 3H), 1.72 – 1.58 (m, 2H), 1.03 (t,  $J = 7.4$  Hz, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  140.43, 133.74, 131.94, 128.67, 126.99, 126.77, 123.11, 36.64, 25.64, 21.99, 13.90. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{13}\text{H}_{17}\text{N}_3$   $[\text{M}+\text{H}]^+$ :216.1503. Found: 216.1505.



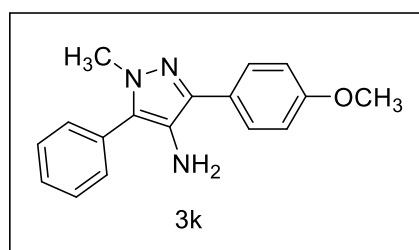
Liquid;  $^1\text{H NMR}$  (500 MHz, DMSO)  $\delta$  8.72 (d,  $J = 4.4$  Hz, 1H), 7.94 (t,  $J = 7.2$  Hz, 1H), 7.82 (d,  $J = 7.7$  Hz, 2H), 7.73 (d,  $J = 7.9$  Hz, 1H), 7.44 (t,  $J = 7.6$  Hz, 2H), 7.37 – 7.33 (m, 1H), 7.30 (t,  $J = 7.4$  Hz, 1H), 4.63 (s, 2H), 4.00 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  150.21, 149.81, 139.36, 136.69, 133.35, 128.80, 128.37, 127.92, 127.20, 126.82, 121.98, 121.32, 39.32. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{14}\text{N}_4$   $[\text{M}+\text{H}]^+$ :251.1298. Found: 251.1289.



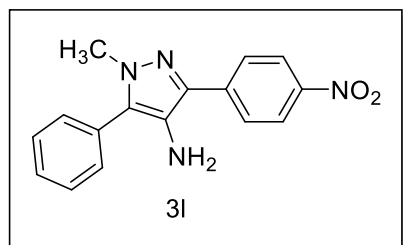
Light yellow solid; mp 118.7-119.2 °C;  $^1\text{H NMR}$  (500 MHz, DMSO)  $\delta$  7.82 (d,  $J = 8.5$  Hz, 2H), 7.60 (d,  $J = 8.5$  Hz, 2H), 7.56 (t,  $J = 7.5$  Hz, 2H), 7.49 (d,  $J = 7.0$  Hz, 2H), 7.45 (t,  $J = 7.3$  Hz, 1H), 3.78 (s, 2H), 3.73 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.73, 132.57, 131.91, 131.83, 129.45, 129.36, 129.23, 128.55, 128.14, 124.49, 120.94, 37.60. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{BrN}_3$   $[\text{M}+\text{H}]^+$ :328.0448. Found: 328.0447.



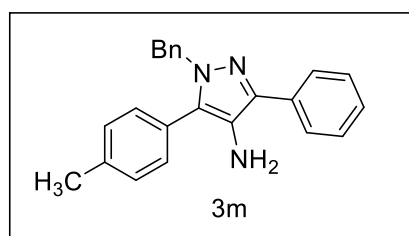
Light yellow solid; mp 102.8-104.0 °C;  $^1\text{H NMR}$  (500 MHz, DMSO)  $\delta$  7.91 – 7.86 (m, 2H), 7.56 (t,  $J = 7.5$  Hz, 2H), 7.51 – 7.43 (m, 5H), 3.80 (s, 2H), 3.73 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  138.72, 132.81, 132.06, 131.89, 129.43, 129.36, 129.25, 128.91, 128.57, 127.84, 124.42, 37.62. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{14}\text{ClN}_3$   $[\text{M}+\text{H}]^+$ :284.0958. Found: 284.0954.



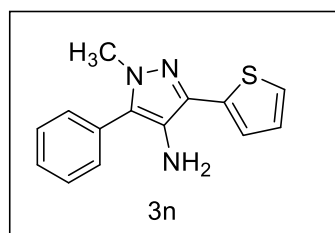
Liquid;  $^1\text{H NMR}$  (500 MHz, DMSO)  $\delta$  7.75 (d,  $J = 8.7$  Hz, 2H), 7.55 (t,  $J = 7.6$  Hz, 2H), 7.49 (d,  $J = 7.2$  Hz, 2H), 7.44 (t,  $J = 7.2$  Hz, 1H), 6.99 (d,  $J = 8.7$  Hz, 2H), 3.85 (s, 2H), 3.79 (s, 3H), 3.72 (s, 3H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.86, 139.81, 131.54, 129.76, 129.33, 129.14, 128.34, 128.02, 126.09, 123.96, 114.20, 55.30, 37.46. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{17}\text{H}_{17}\text{N}_3\text{O}$   $[\text{M}+\text{H}]^+$ :280.1455. Found: 280.1448.



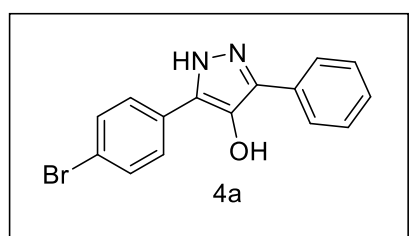
Yellow solid; mp 140.1-140.9 °C;  $^1\text{H NMR}$  (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.31 – 8.26 (m, 2H), 8.10 – 8.04 (m, 2H), 7.57 (t,  $J = 7.5$  Hz, 2H), 7.50 (t,  $J = 4.7$  Hz, 1H), 7.45 – 7.42 (m, 2H), 3.83 (s, 3H), 3.17 (s, 2H).  $^{13}\text{C NMR}$  (125 MHz,  $\text{CDCl}_3$ )  $\delta$  146.30, 140.33, 137.52, 132.61, 129.42, 129.37, 128.90, 126.51, 125.55, 124.12, 37.82. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{16}\text{H}_{15}\text{N}_4\text{O}_2$   $[\text{M}+\text{H}]^+$ :295.1194. Found: 295.1193.



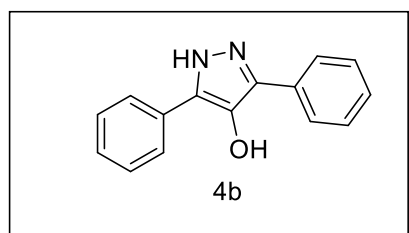
Light yellow solid; mp 168.6-169.3 °C;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.85 (d,  $J = 7.2$  Hz, 1H), 7.44 (t,  $J = 7.6$  Hz, 1H), 7.31 (t,  $J = 7.4$  Hz, 1H), 7.26 – 7.16 (m, 4H), 7.05 (d,  $J = 6.6$  Hz, 1H), 5.25 (s, 1H), 3.06 (s, 1H), 2.39 (s, 2H).  $^{13}\text{C}$  NMR (125 MHz, DMSO)  $\delta$  140.32, 138.47, 138.21, 134.06, 132.54, 130.11, 129.66, 128.90, 128.87, 127.67, 127.23, 127.03, 126.75, 126.68, 53.26, 21.34. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{21}\text{N}_3$   $[\text{M}+\text{H}]^+$ : 340.1812. Found: 340.1815.



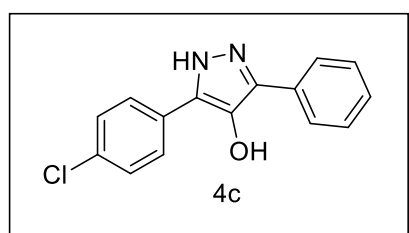
Orange solid; mp 83.4-85.0 °C;  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  7.57 – 7.53 (m, 2H), 7.51 – 7.48 (m, 2H), 7.47 – 7.43 (m, 2H), 7.42 (dt,  $J = 3.7, 1.9$  Hz, 1H), 7.11 (dd,  $J = 5.1, 3.6$  Hz, 1H), 3.86 (s, 2H), 3.70 (s, 3H).  $^{13}\text{C}$  NMR (126 MHz,  $\text{CDCl}_3$ )  $\delta$  135.72, 135.44, 131.76, 129.34, 129.23, 128.58, 127.58, 123.98, 123.95, 123.21, 37.62. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 256.0906. Found: 256.0908.



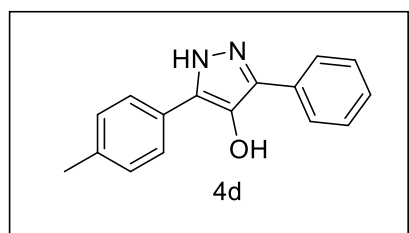
Light yellow solid; mp 222.6-223.3 °C;  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  12.98 (s, 1H), 8.43 (s, 1H), 7.90 (m, 4H), 7.65 (m, 2H), 7.39 (m, 3H).  $^{13}\text{C}$  NMR (125 MHz, Acetone)  $\delta$  135.62, 131.44, 128.53, 127.69, 127.27, 125.84, 120.29. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{BrN}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 315.0129. Found: 315.0128.



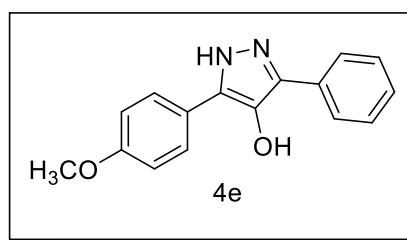
Light yellow solid; mp 236.2-237.2 °C;  $^1\text{H}$  NMR (500 MHz, DMSO)  $\delta$  12.87 (s, 1H), 8.30 (s, 1H), 7.94 (m, 4H), 7.45 (m, 4H), 7.31 (t,  $J = 6.7$  Hz, 2H).  $^{13}\text{C}$  NMR (125 MHz, Acetone)  $\delta$  135.52, 131.83, 128.40, 127.02, 125.86. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 237.1023. Found: 237.1022.



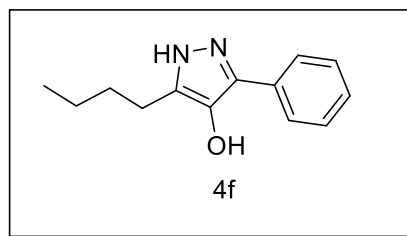
Deep yellow solid; mp 228.0-229.4 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  12.95 (s, 1H), 8.41 (s, 1H), 7.93 (m, 5H), 7.48 (m, 4H), 7.32 (m, 1H).  $^{13}\text{C}$  NMR (125 MHz, Acetone)  $\delta$  135.59, 132.13, 131.11, 128.52, 128.45, 127.37, 127.24, 125.83. HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{11}\text{ClN}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 271.0636. Found: 271.0635.



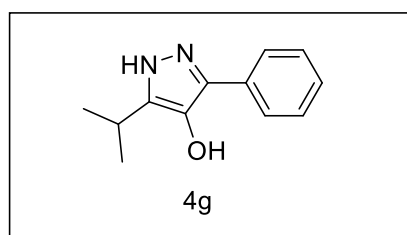
Light yellow solid; mp 240.0-241.0 °C;  $^1\text{H}$  NMR (400 MHz, DMSO)  $\delta$  12.80 (s, 1H), 8.23 (s, 1H), 7.89 (m, 4H), 7.43 (m, 2H), 7.33 – 7.21 (m, 3H), 2.33 (s, 3H). HRMS (ESI)  $m/z$  calcd for  $\text{C}_{15}\text{H}_{12}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$ : 251.1182. Found: 251.1184.



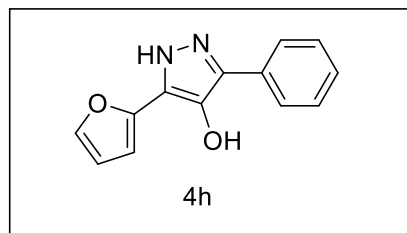
Deep yellow solid; mp 220.6-221.4°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.74 (s, 1H), 8.18 (s, 1H), 7.88 (m, 4H), 7.44 (m, 2H), 7.30 (t, *J* = 7.1 Hz, 1H), 7.03 (m, 2H), 3.80 (s, 3H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 159.02, 134.88, 128.37, 127.19, 126.92, 125.81, 113.84, 54.67. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 267.1134. Found: 267.1135.



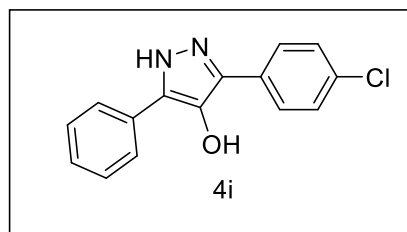
Light yellow solid; mp 211.9-212.9°C; <sup>1</sup>H NMR (400 MHz, DMSO) δ 12.13 (s, 1H), 7.89 (s, 3H), 7.37 (t, *J* = 7.3 Hz, 2H), 7.21 (t, *J* = 7.2 Hz, 1H), 2.57 – 2.52 (m, 2H), 1.57 (dt, *J* = 15.2, 7.5 Hz, 2H), 1.33 (dd, *J* = 14.6, 7.3 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 135.69, 132.88, 128.18, 126.38, 125.40, 30.96, 23.43, 22.21, 13.24. HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>16</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 217.1346. Found: 217.1344.



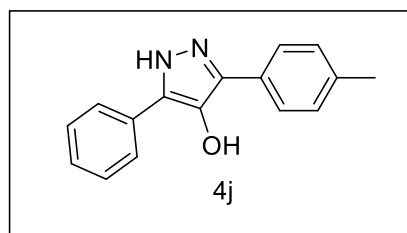
Brown solid; mp 184.4-185.5°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.17 (s, 1H), 7.88 (m, 2H), 7.81 (s, 1H), 7.38 (t, *J* = 7.1 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 3.13 – 3.03 (m, 1H), 1.23 (d, *J* = 7.0 Hz, 6H). HRMS (ESI) *m/z* calcd for C<sub>12</sub>H<sub>14</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 203.1183. Found: 203.1185.



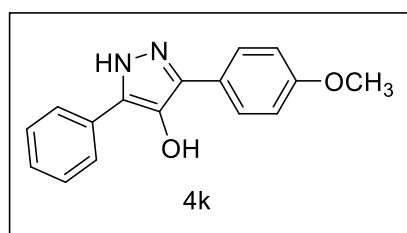
Black solid; mp 189.7-190.5°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.93 (s, 1H), 8.38 (s, 1H), 7.92 (m, 2H), 7.73 (m, 1H), 7.45 (t, *J* = 7.3 Hz, 2H), 7.31 (t, *J* = 7.3 Hz, 1H), 6.77 (d, *J* = 3.1 Hz, 1H), 6.61 (m, 1H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 141.49, 135.04, 128.42, 127.07, 125.66, 111.19, 105.89. HRMS (ESI) *m/z* calcd for C<sub>13</sub>H<sub>10</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 227.0283. Found: 227.0285.



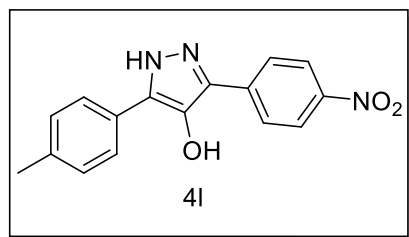
Light yellow solid; mp 230.0-231.2°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.96 (s, 1H), 8.42 (s, 1H), 7.94 (m, 4H), 7.39 (m, 5H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 135.61, 132.13, 128.52, 128.45, 127.37, 127.24, 125.83. HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>11</sub>ClN<sub>2</sub>O [M+H]<sup>+</sup>: 271.0635. Found: 271.0633.



Light yellow solid; mp 242.1-242.9°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.80 (s, 1H), 8.22 (s, 1H), 8.02 – 7.70 (m, 4H), 7.29 (m, 5H), 2.35 (s, 3H). HRMS (ESI) *m/z* calcd for C<sub>15</sub>H<sub>12</sub>N<sub>2</sub>O [M+H]<sup>+</sup>: 251.1183. Found: 251.1184.

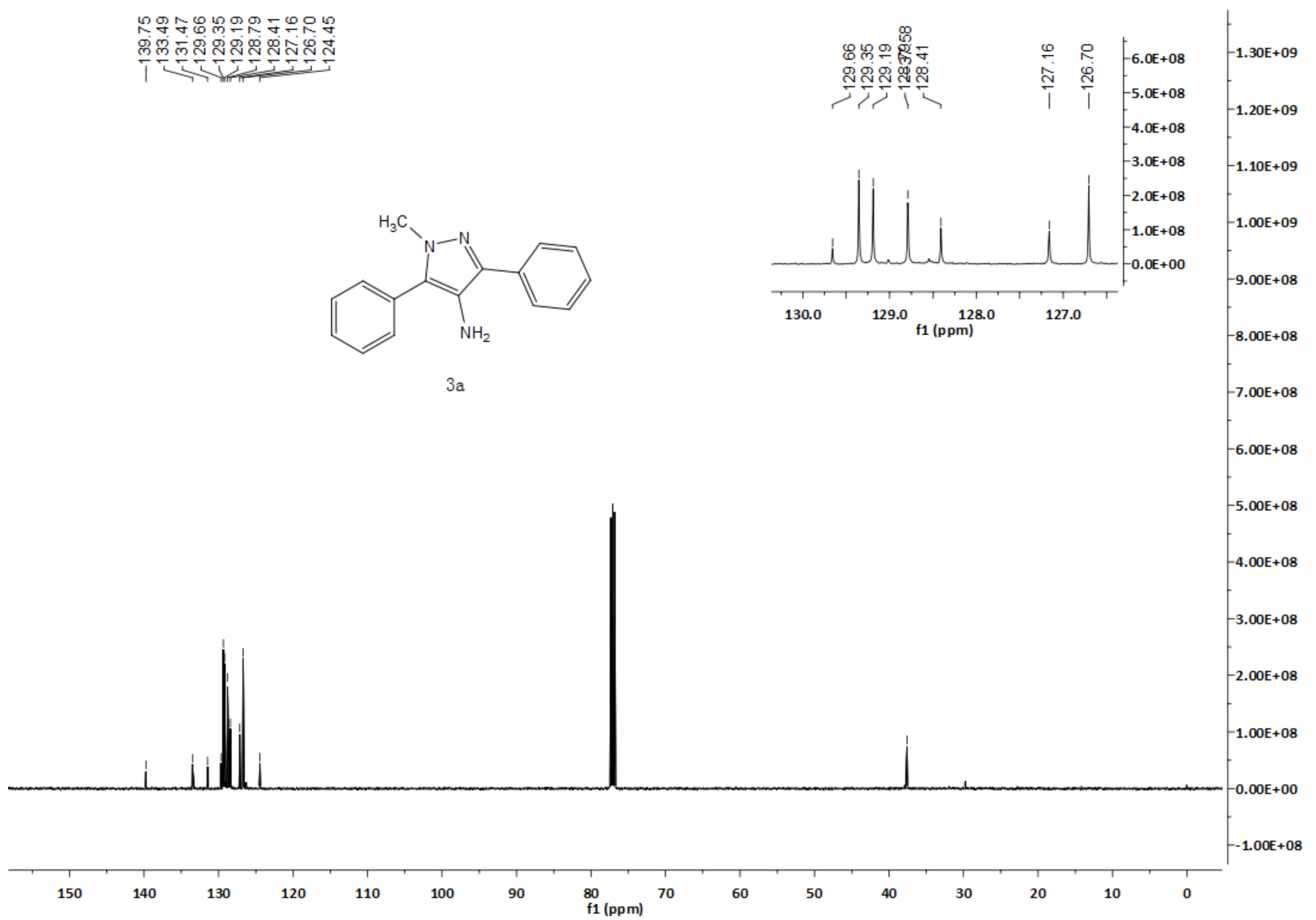
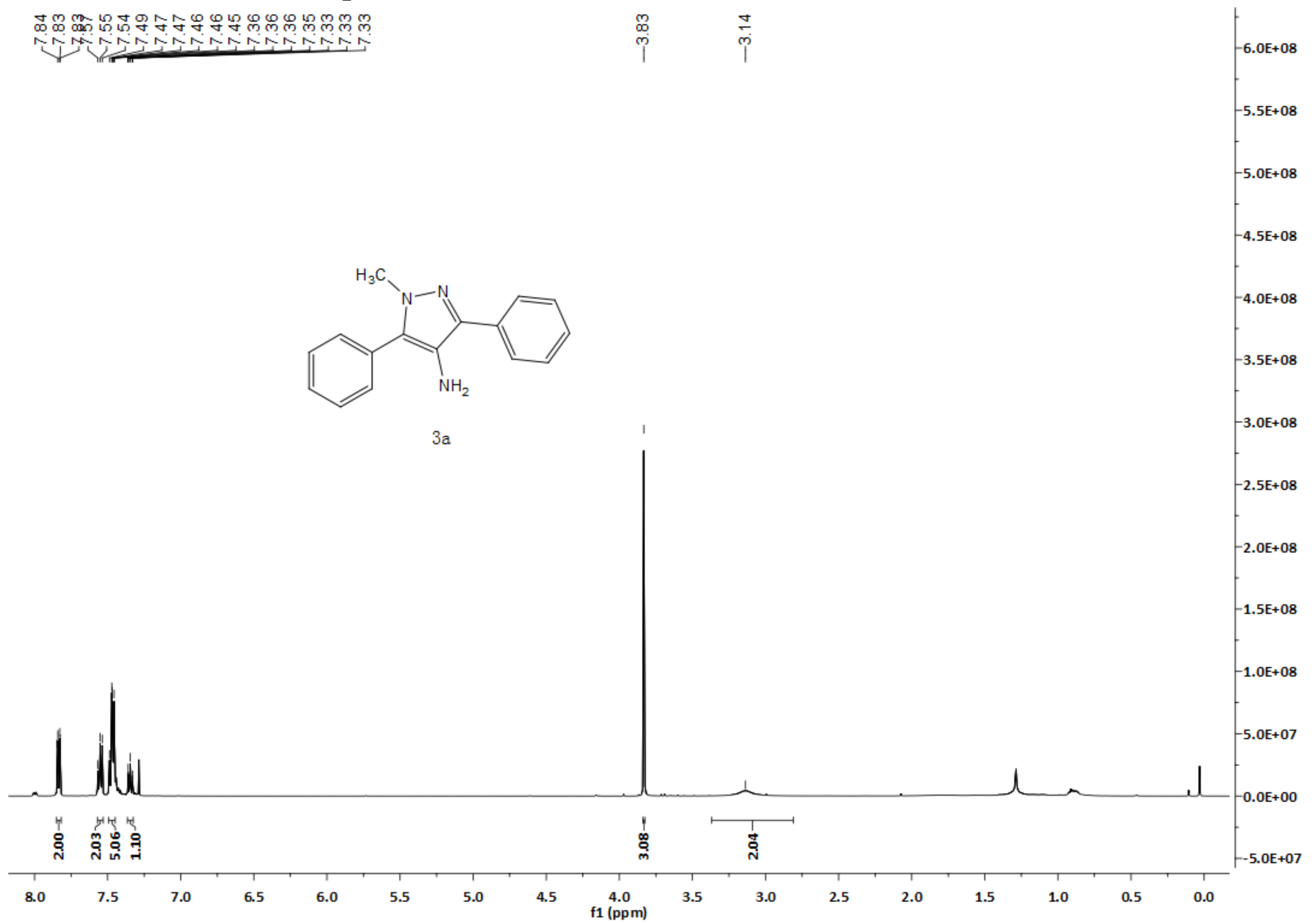


Deep yellow solid; mp 208.6-210.4°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 12.73 (s, 1H), 8.17 (s, 1H), 7.93 (d, *J* = 3.4 Hz, 2H), 7.86 (d, *J* = 6.5 Hz, 2H), 7.44 (t, *J* = 7.6 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.03 (d, *J* = 8.4 Hz, 2H), 3.80 (s, 1H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 159.03, 134.79, 128.37, 127.19, 126.93, 125.82, 113.85, 54.67. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> [M+H]<sup>+</sup>: 267.1136. Found: 267.1133.

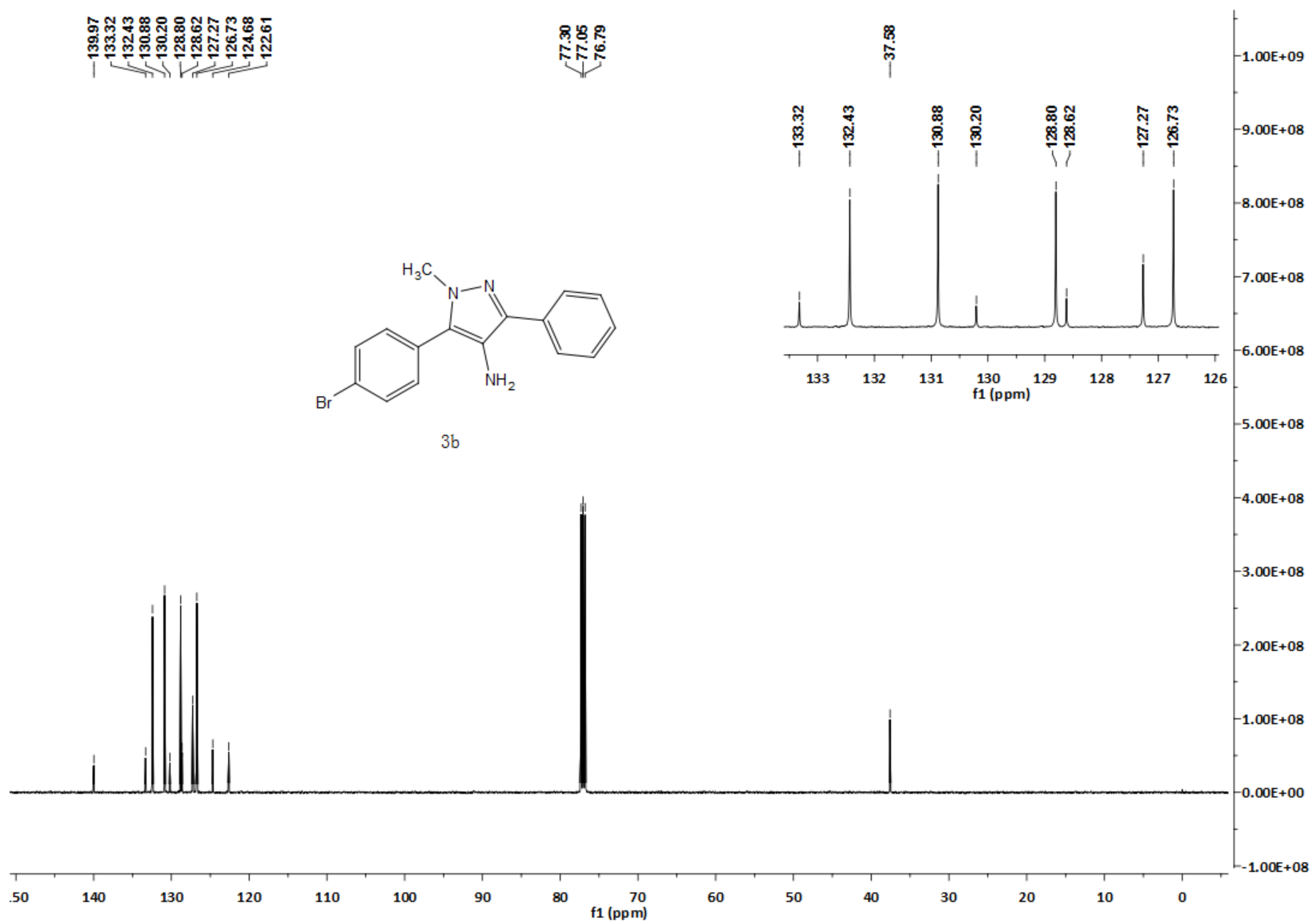
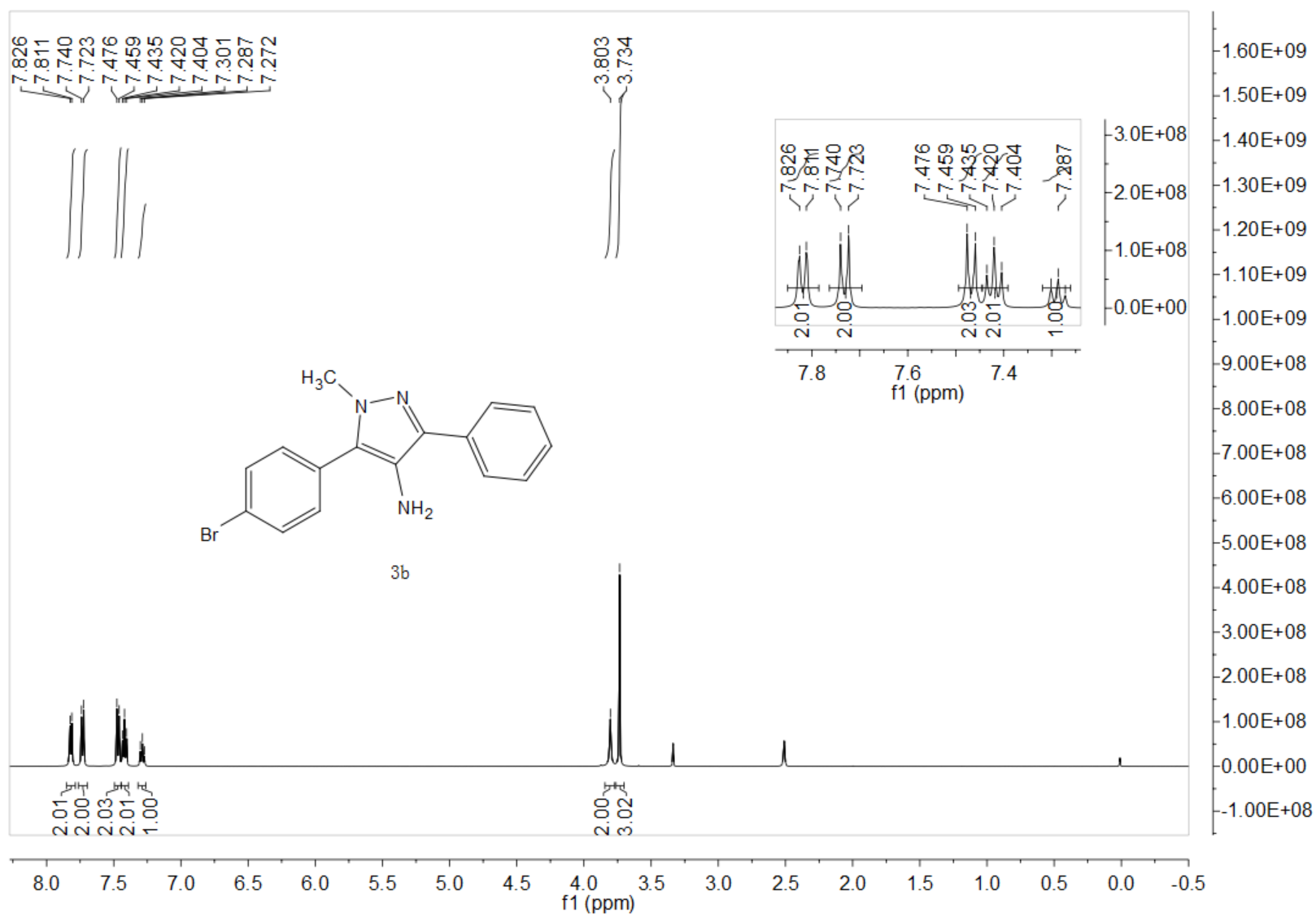


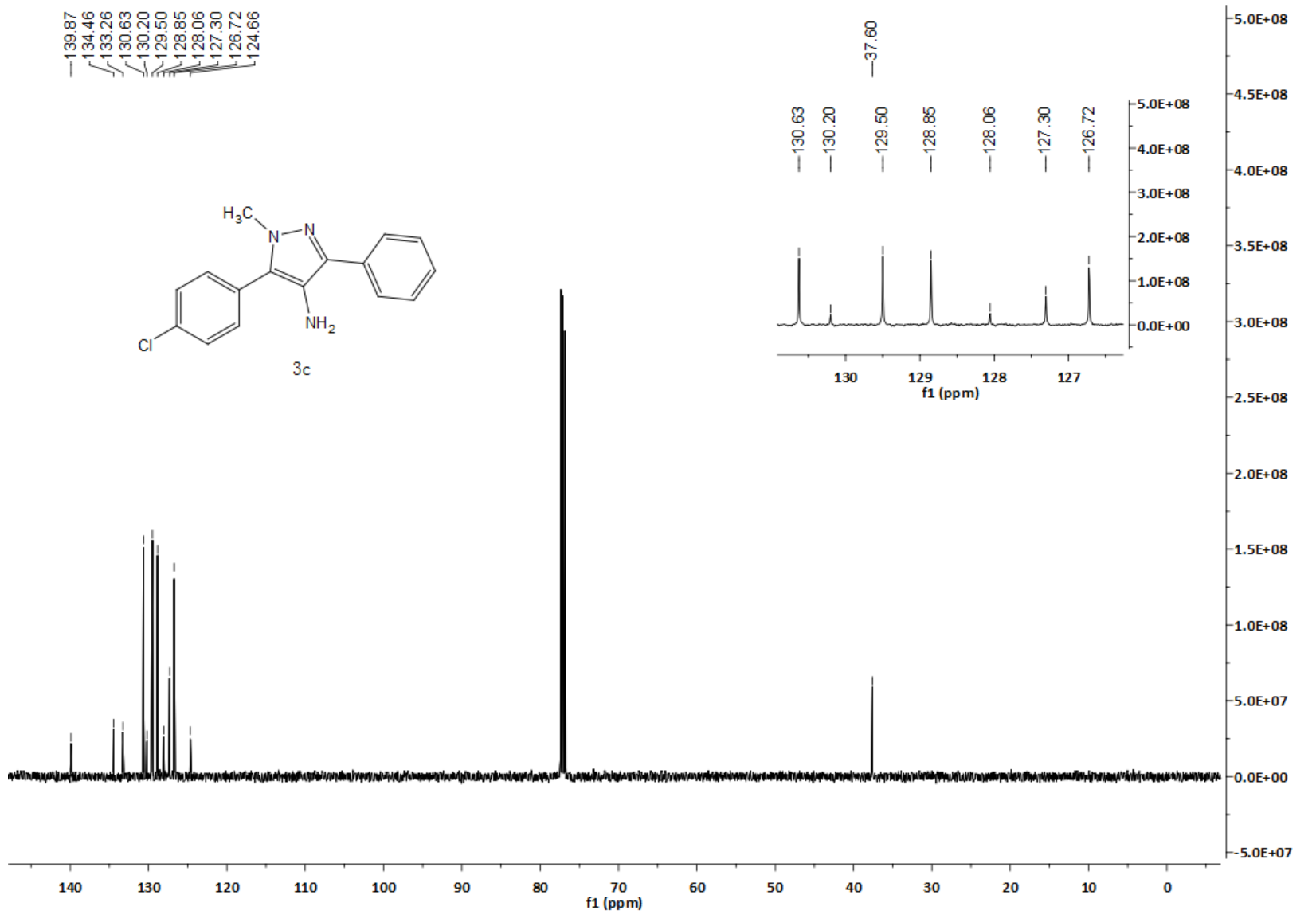
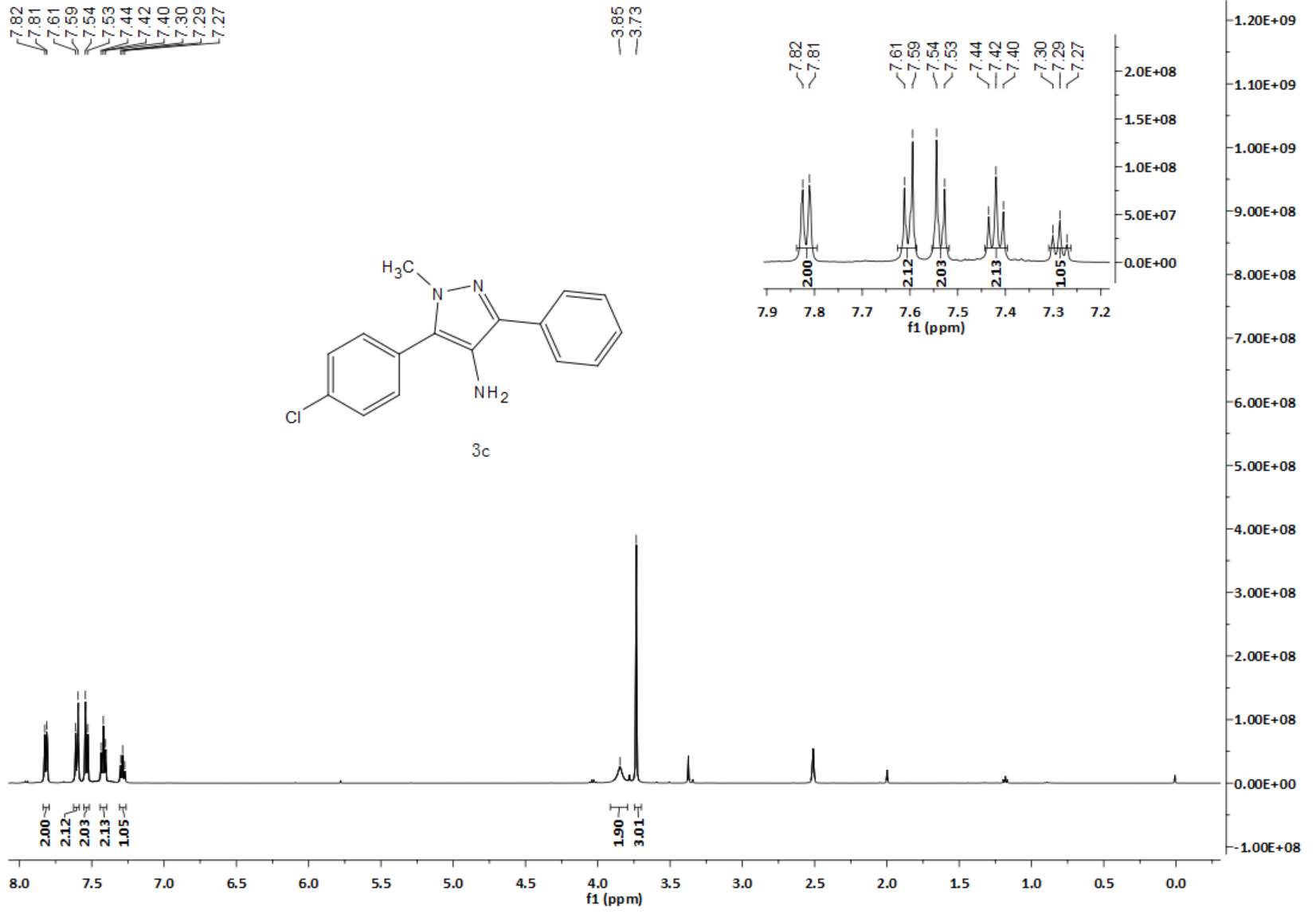
Yellow solid; mp >250°C; <sup>1</sup>H NMR (500 MHz, DMSO) δ 13.18 (s, 1H), 8.69 (s, 1H), 8.32 (d, *J* = 8.9 Hz, 2H), 8.24 (d, *J* = 7.8 Hz, 2H), 7.78 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 3H). <sup>13</sup>C NMR (125 MHz, Acetone) δ 146.35, 137.34, 136.32, 129.28, 126.13, 125.88, 125.57, 123.65, 20.35. HRMS (ESI) *m/z* calcd for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 296.1037. Found: 296.1036.

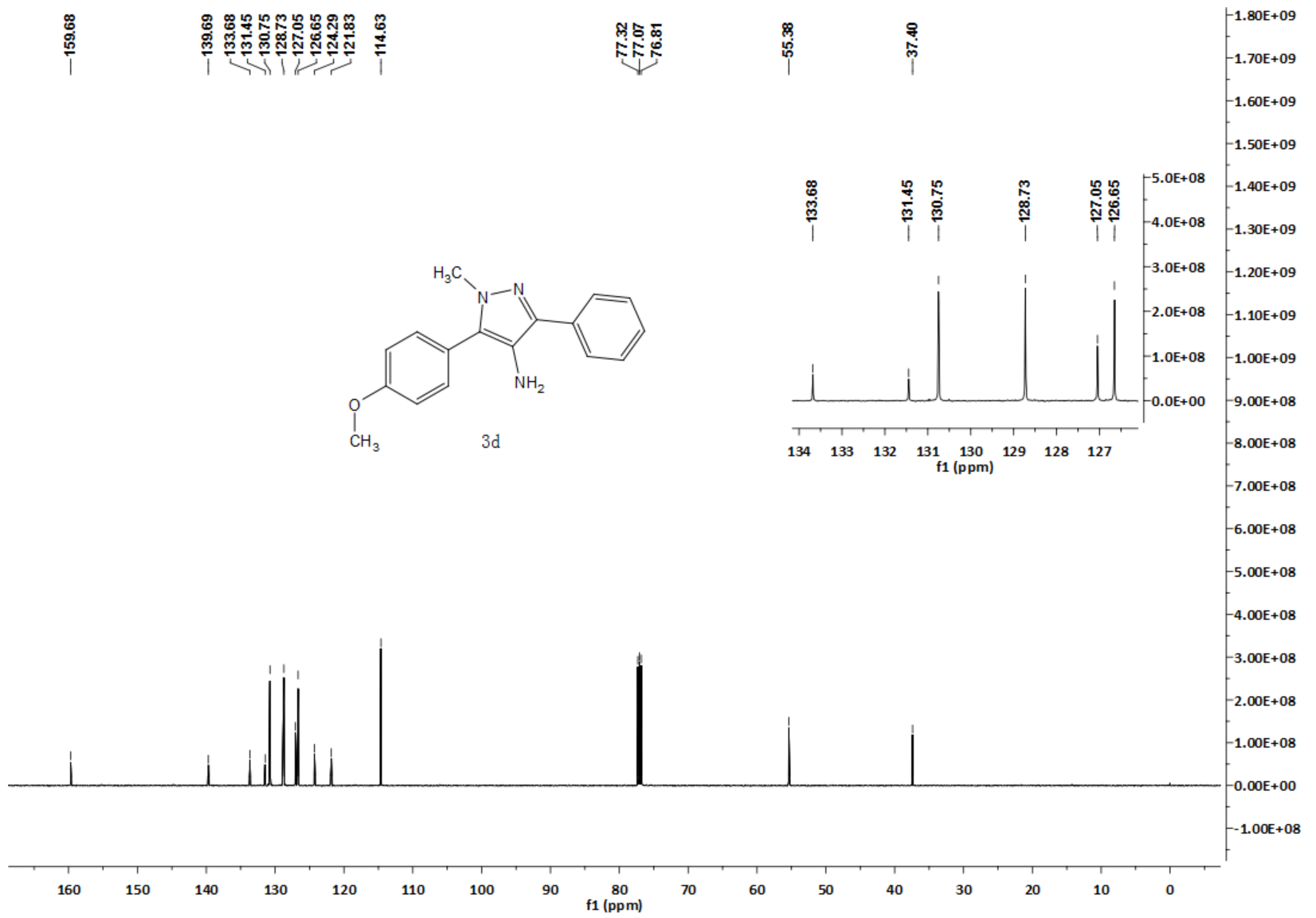
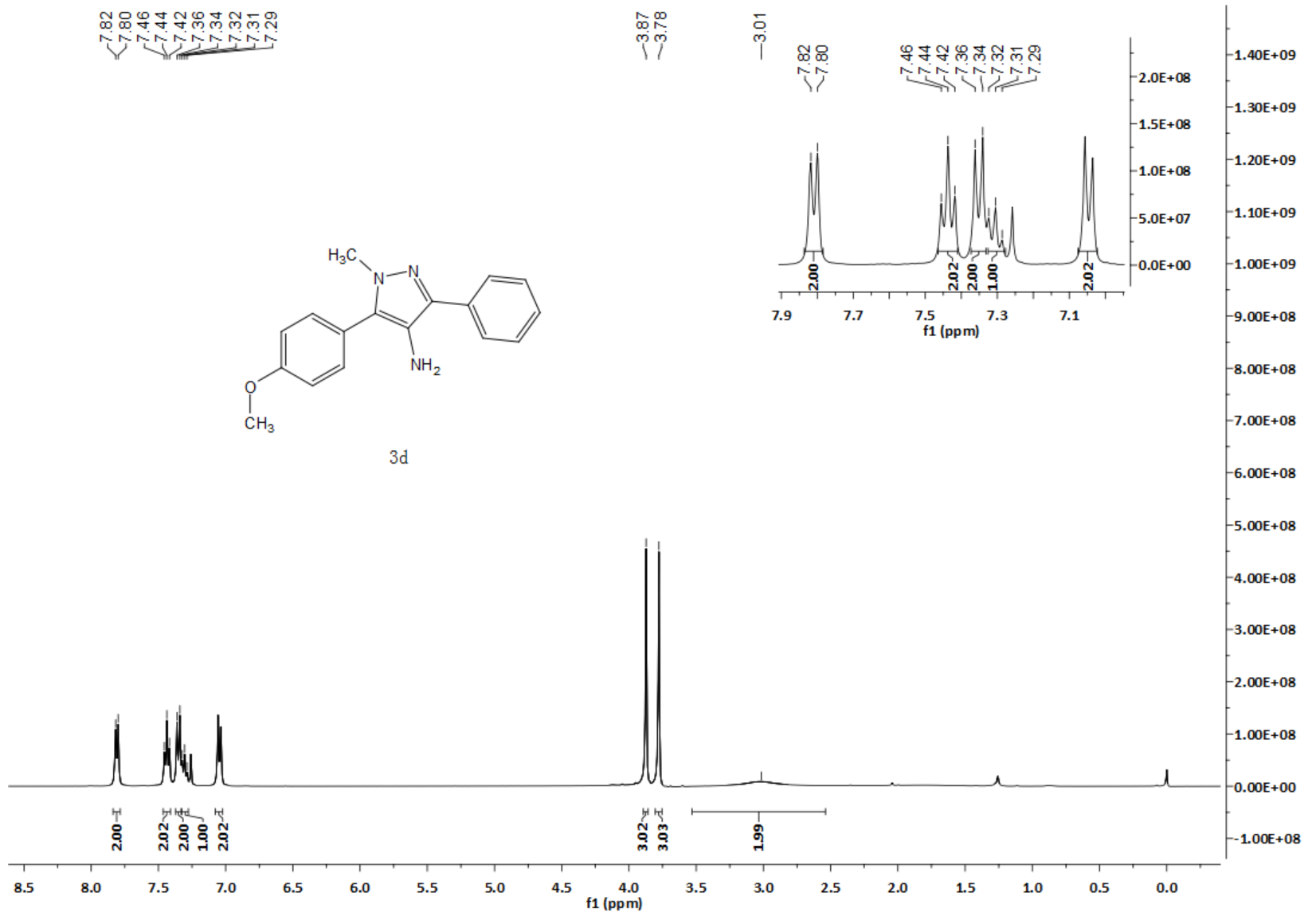
4. <sup>1</sup>H NMR and <sup>13</sup>C NMR Spectra :

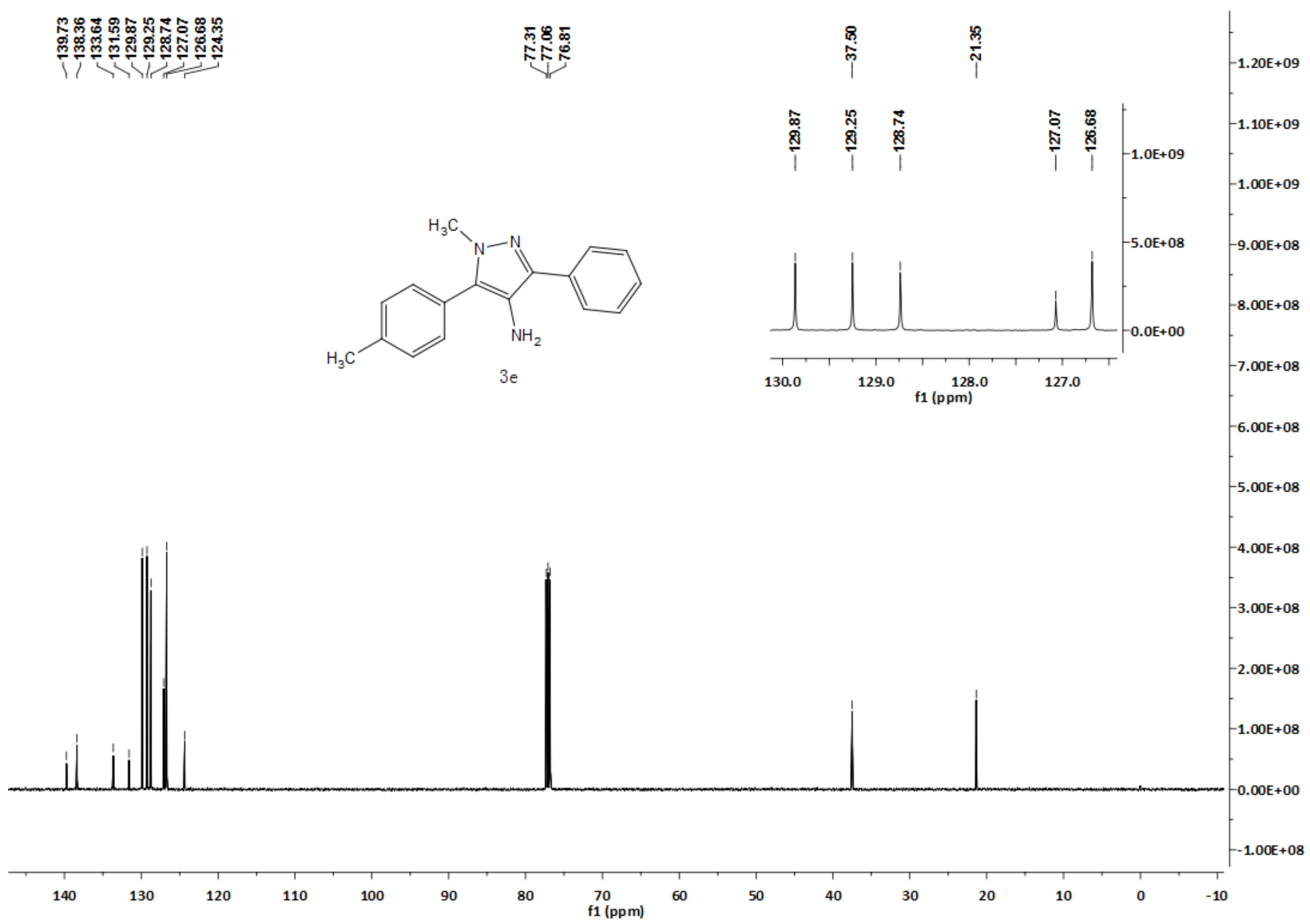
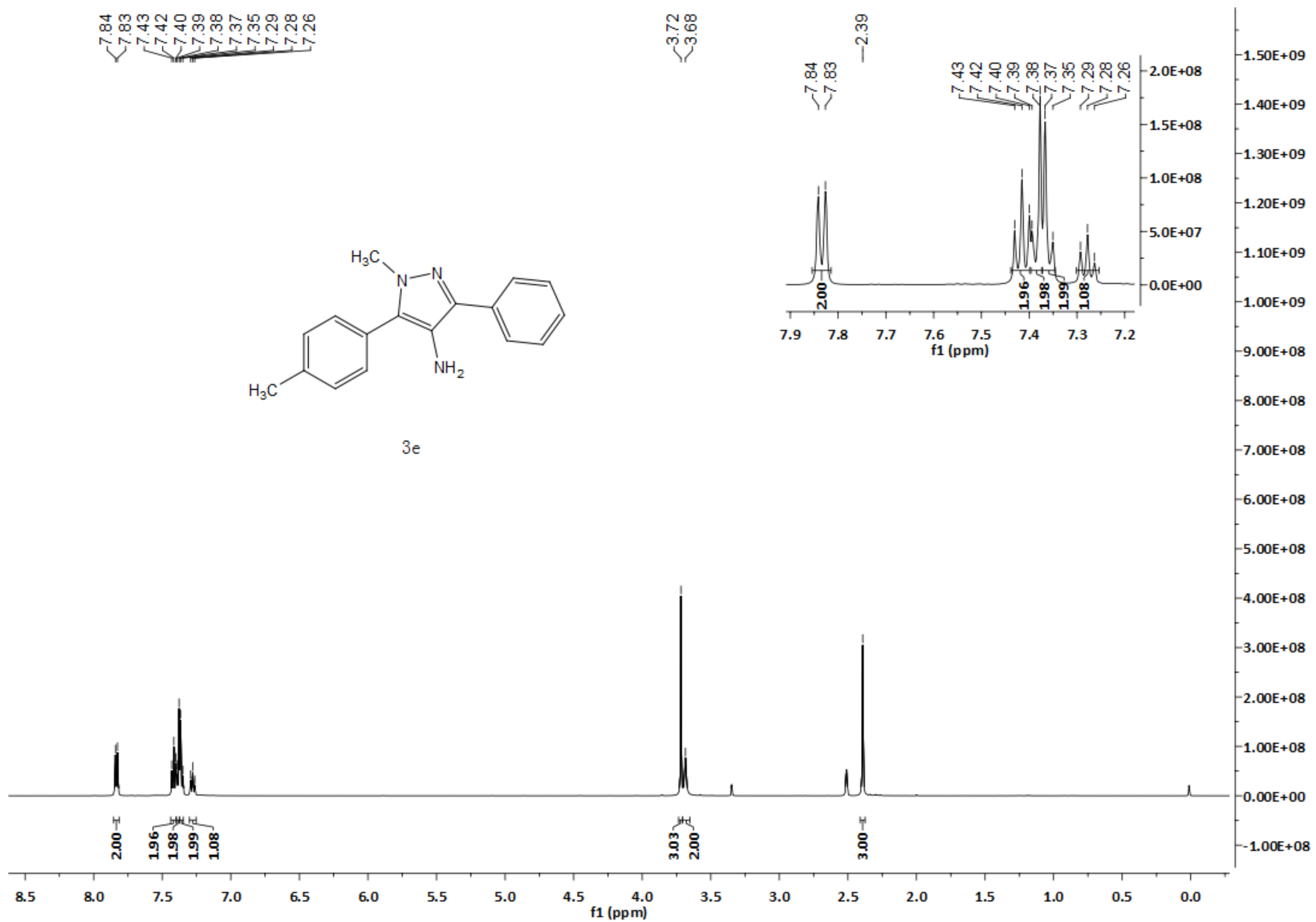


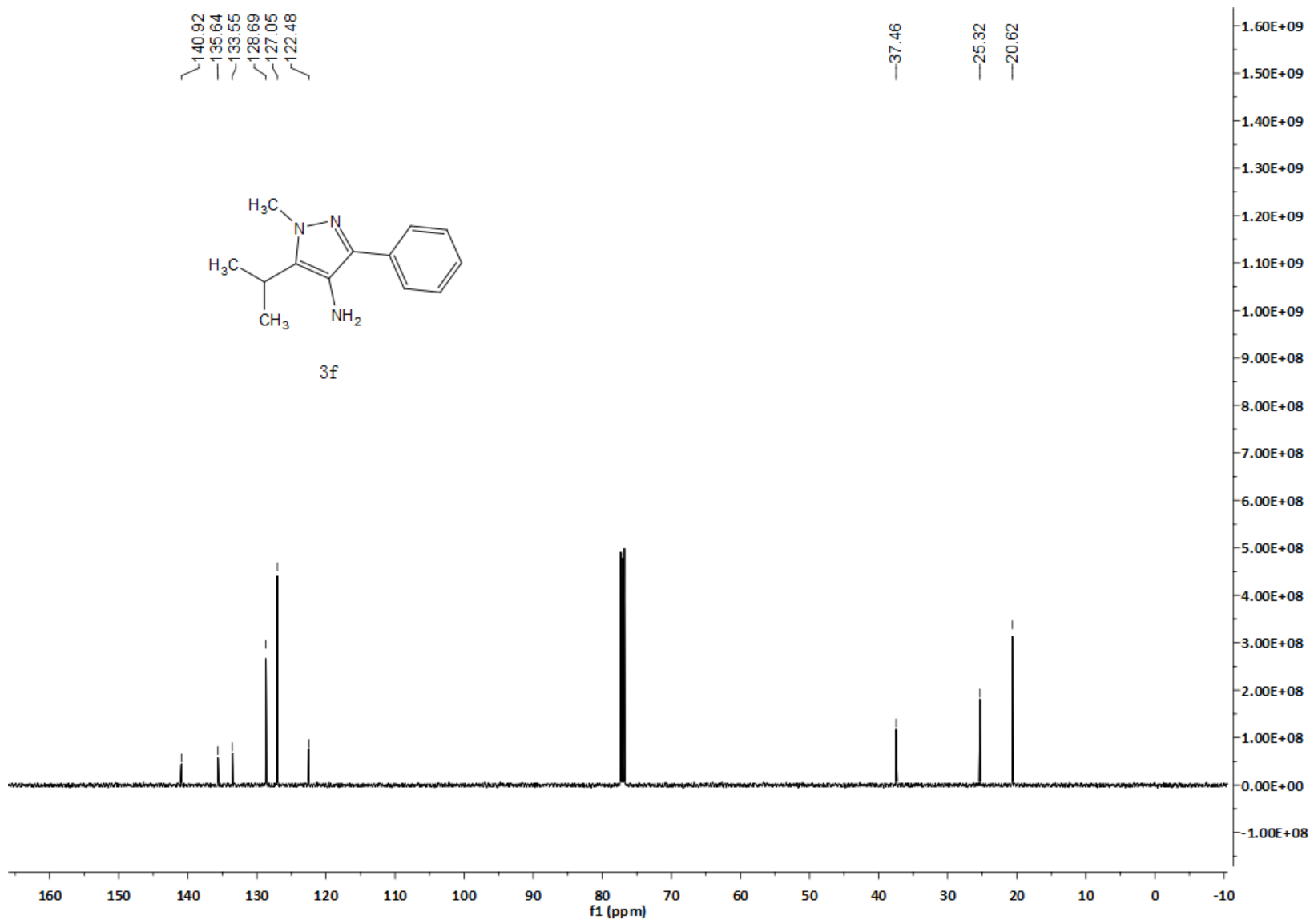
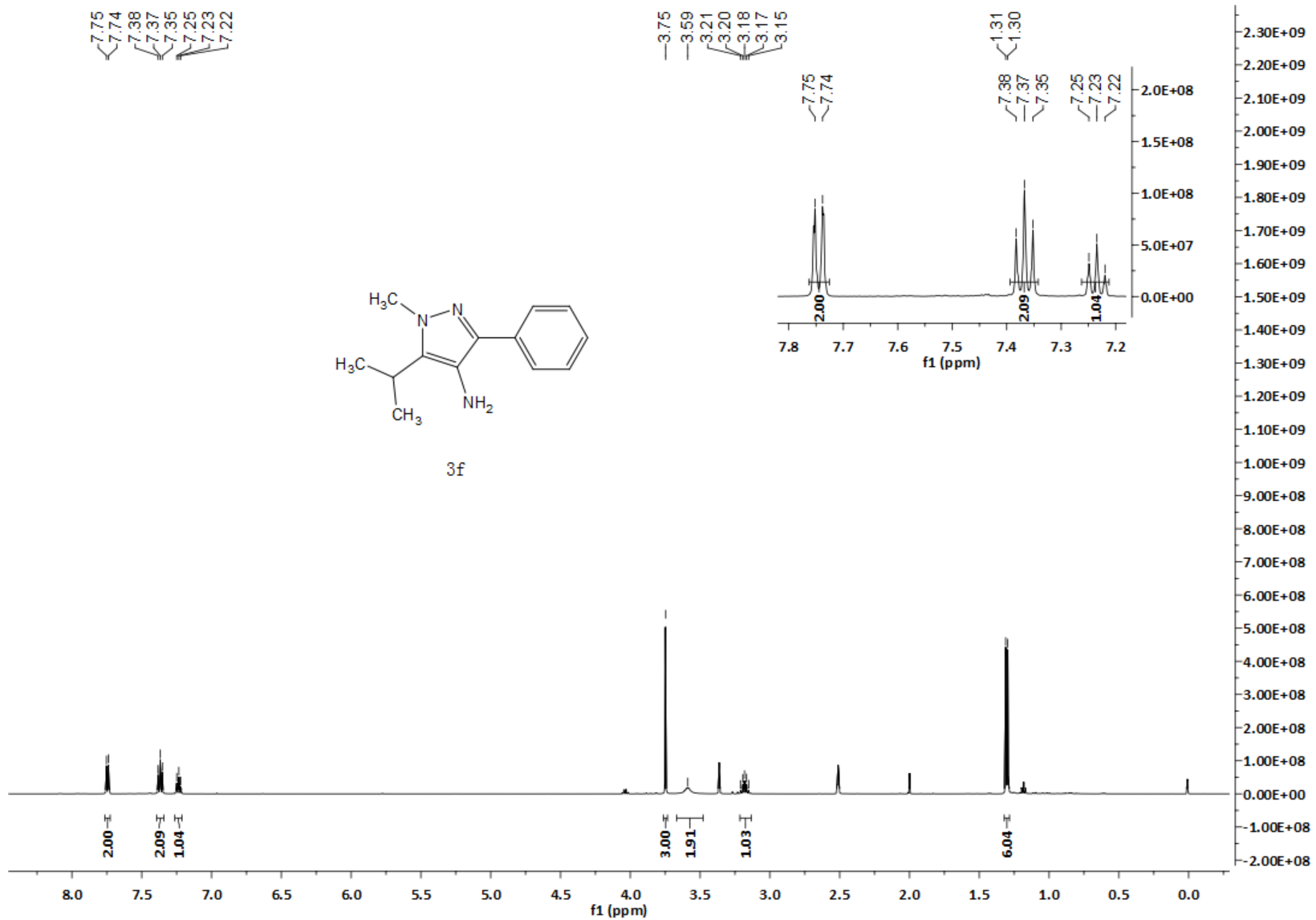


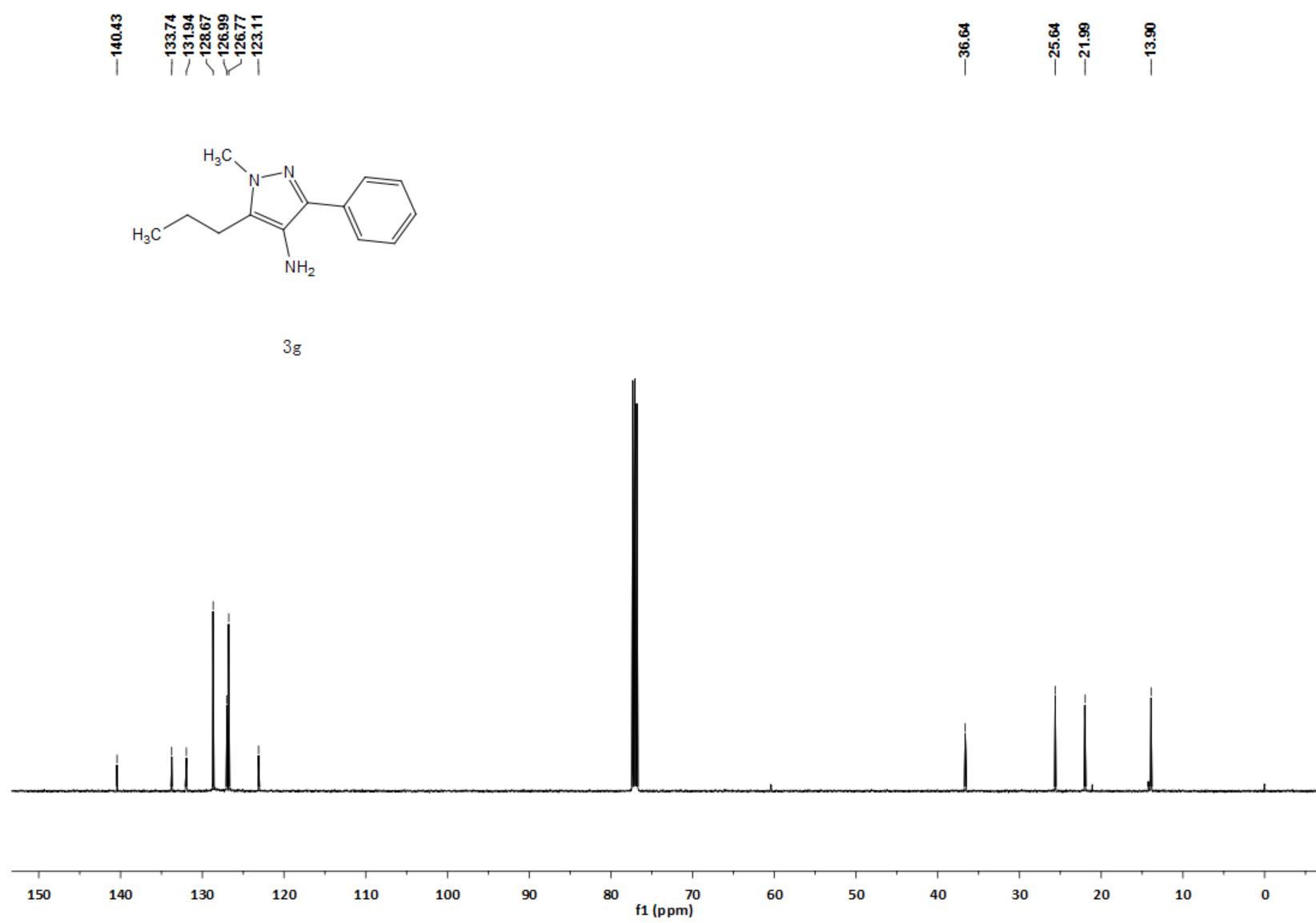
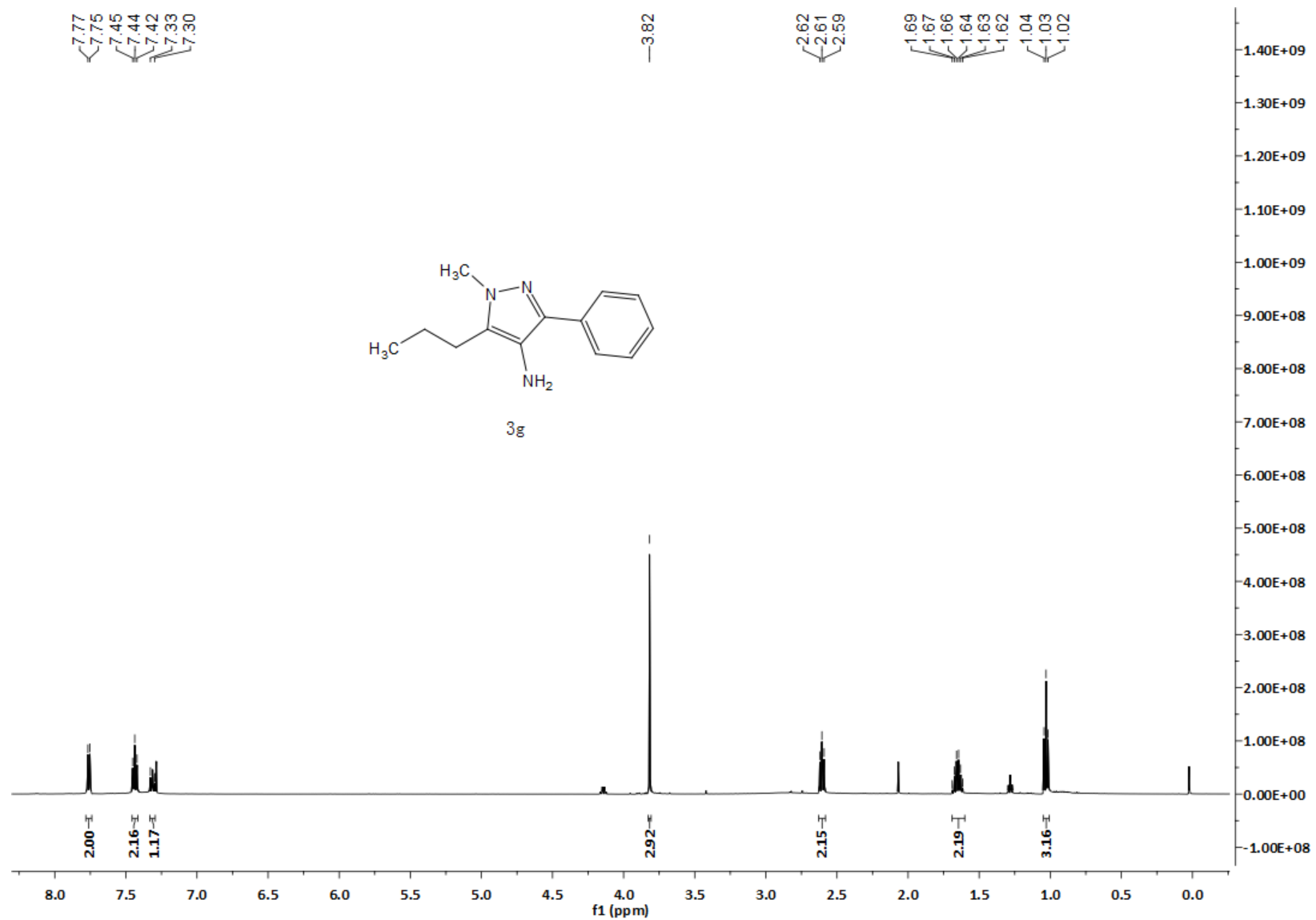


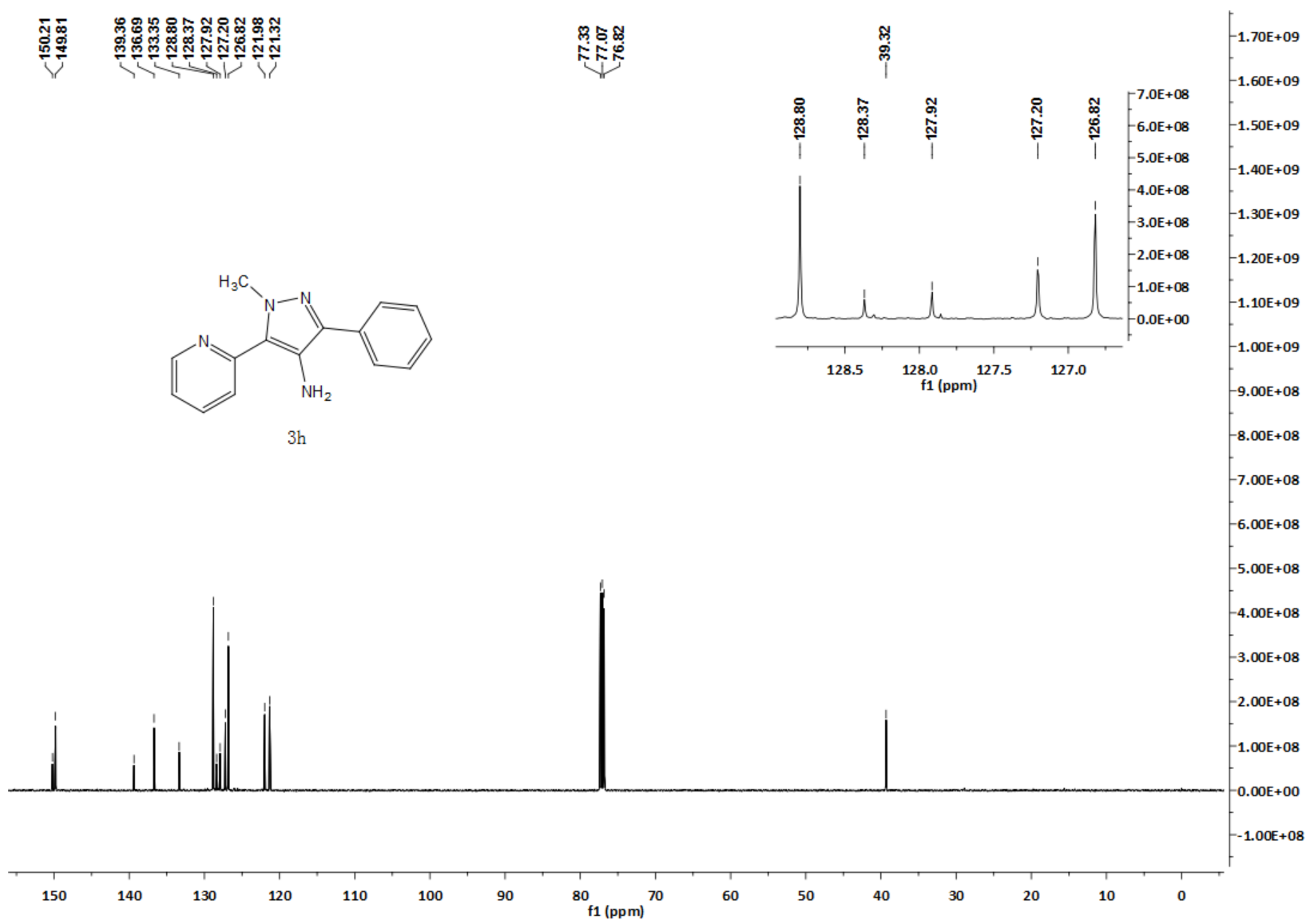
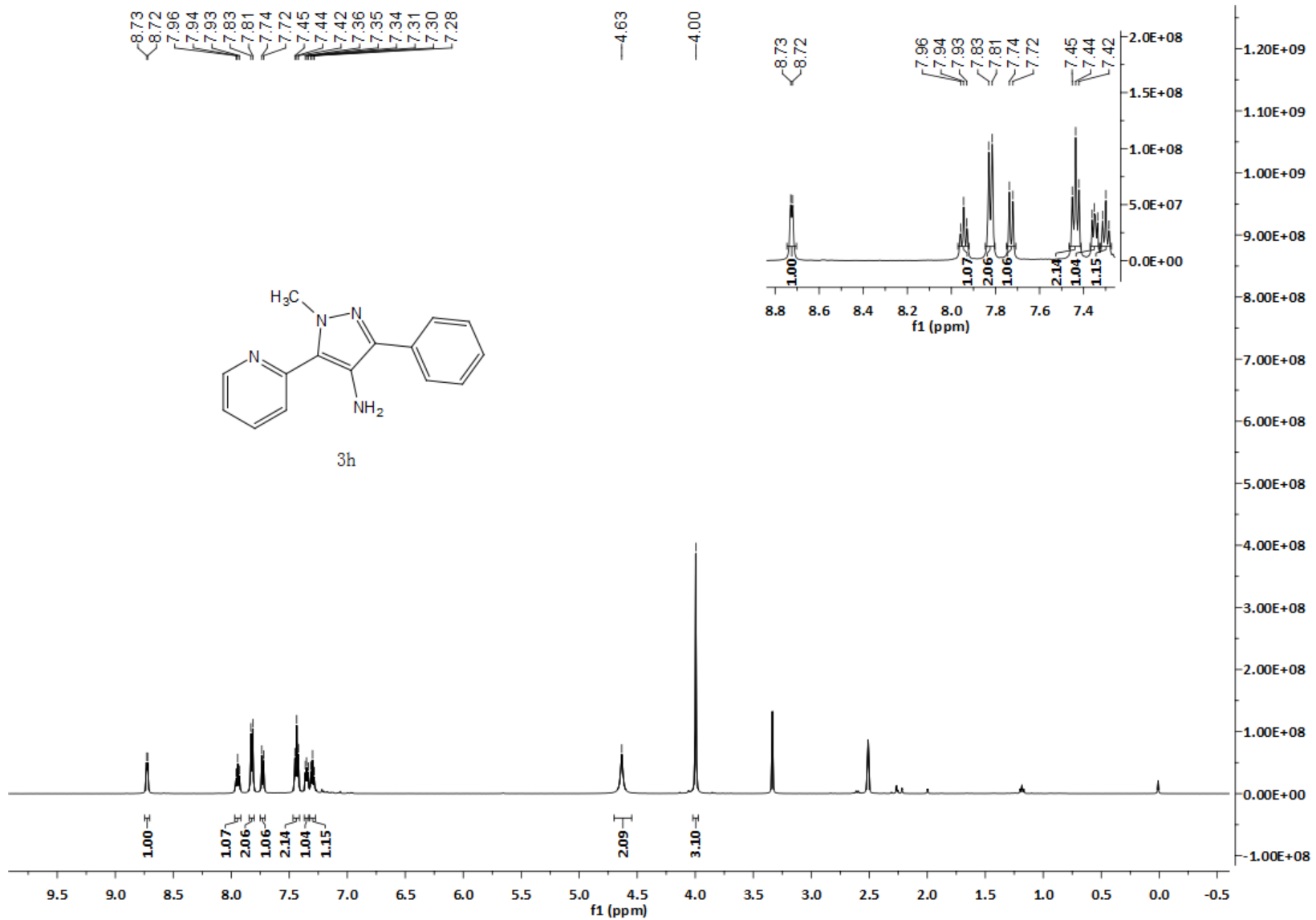


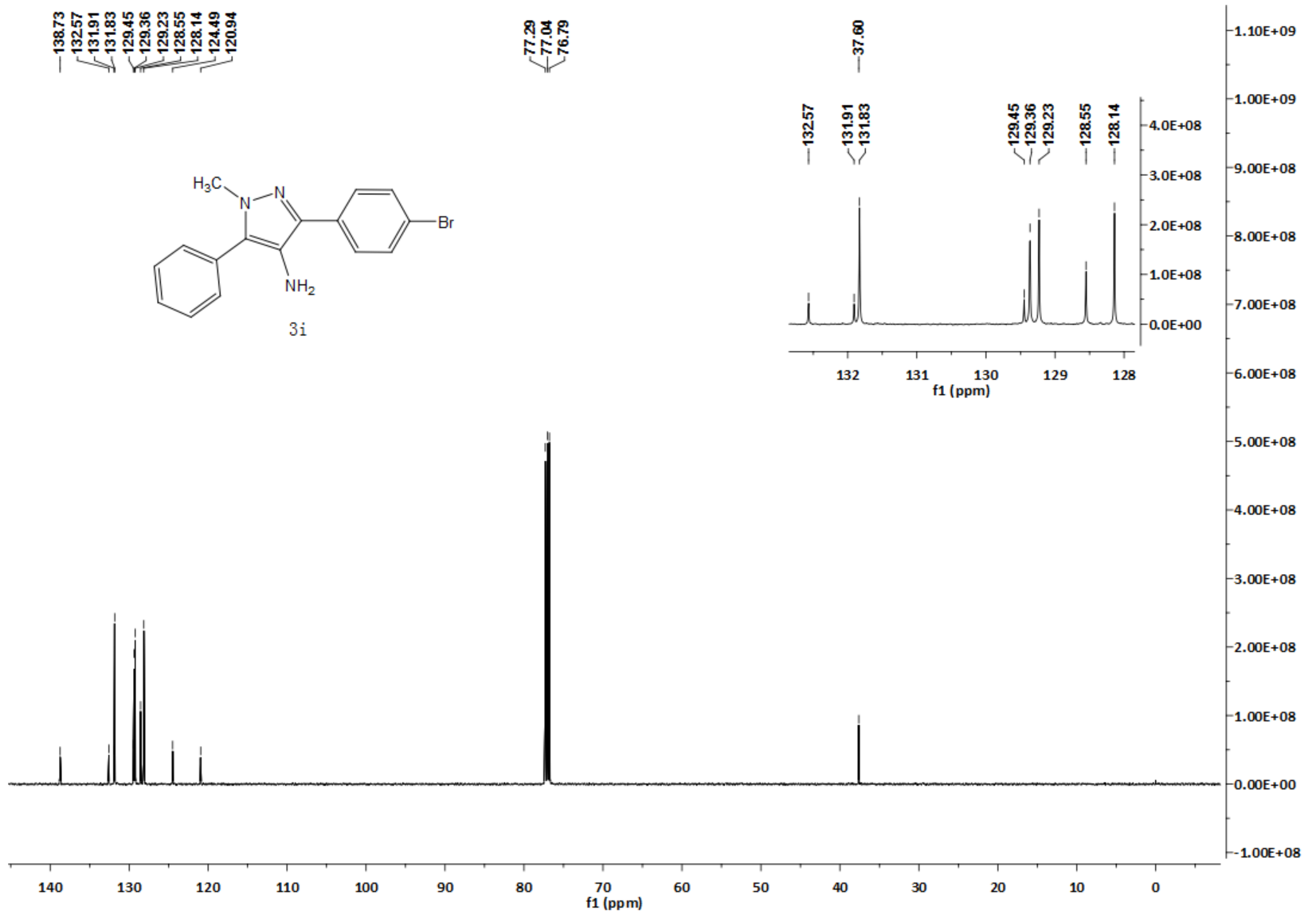
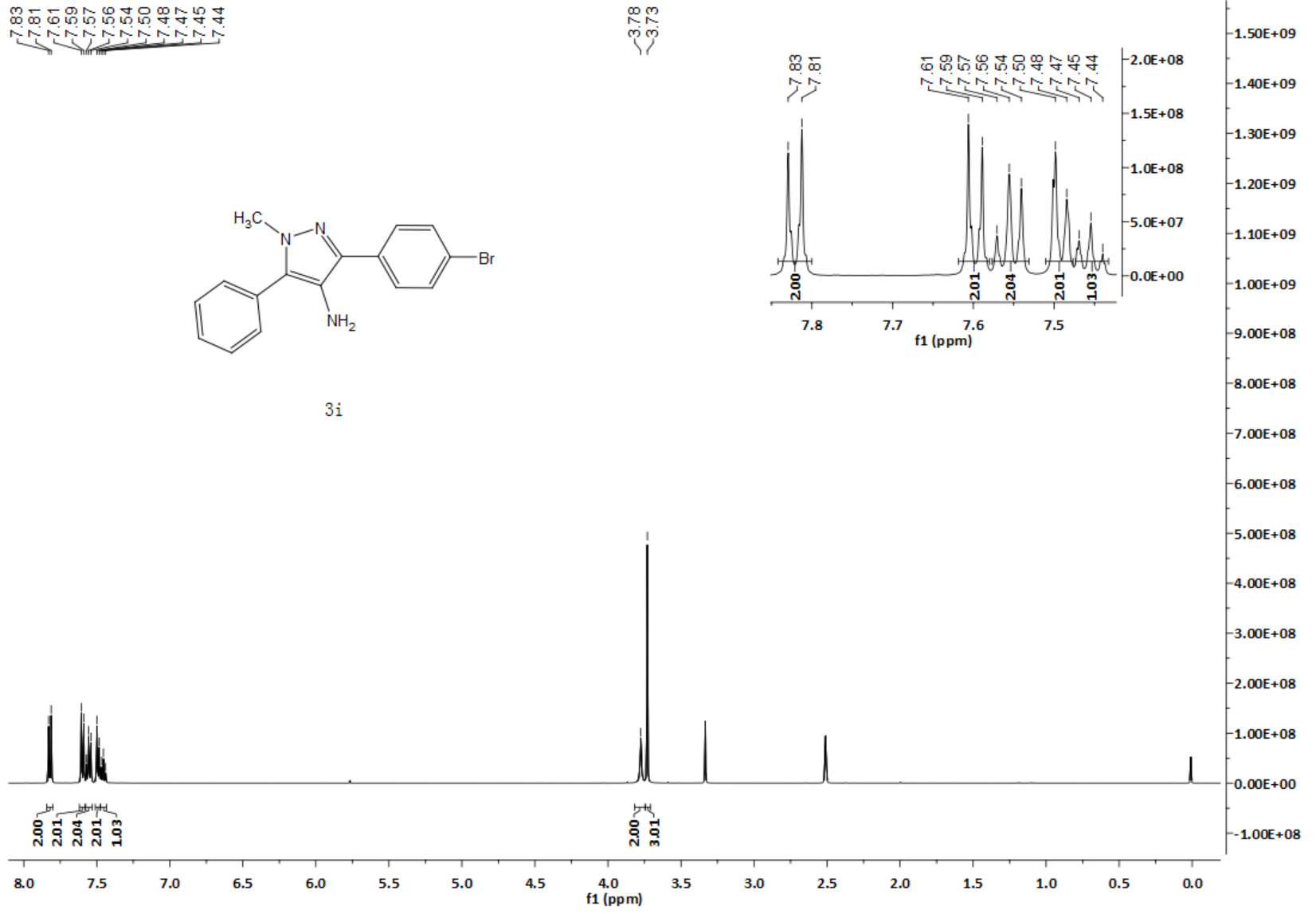




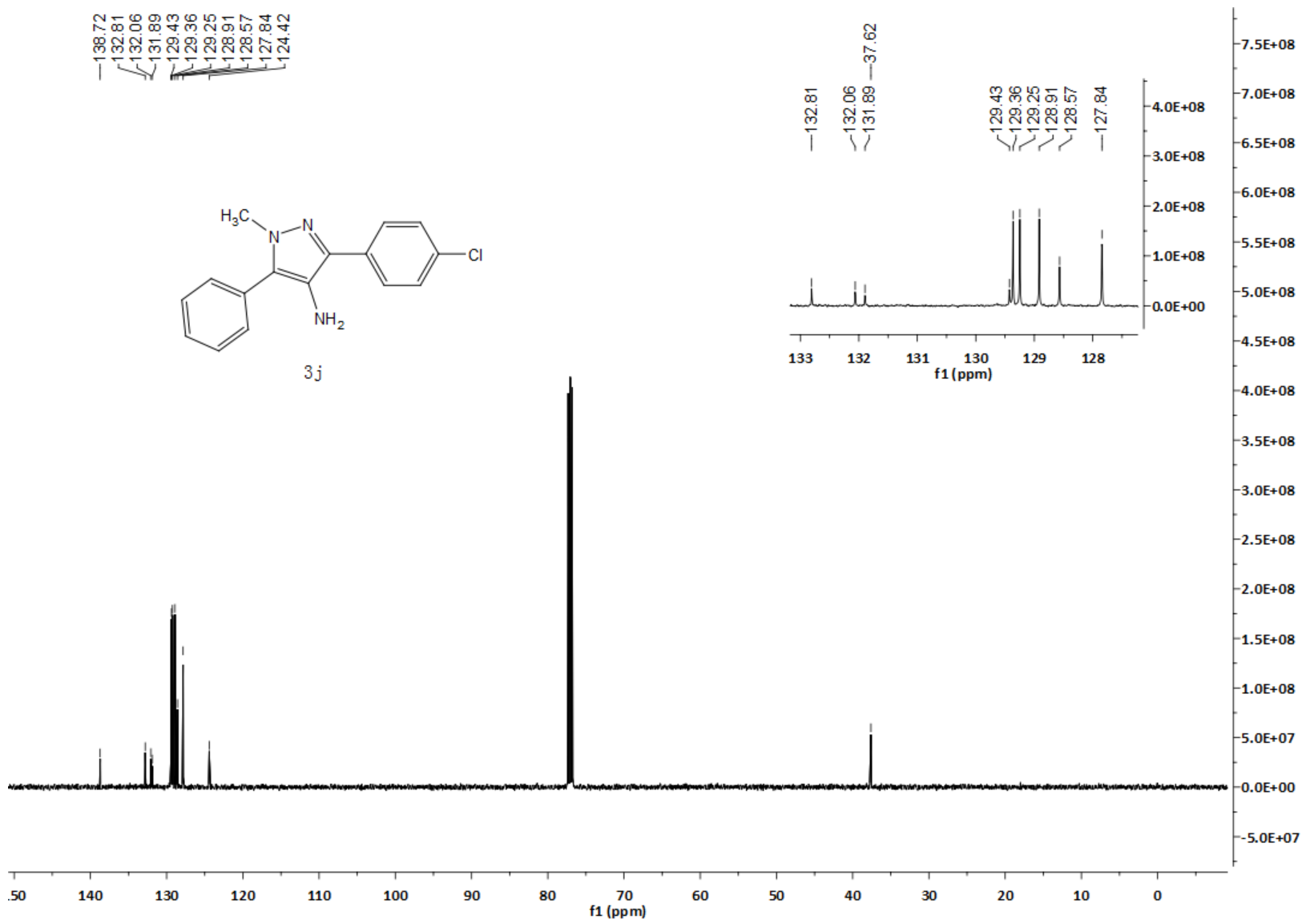
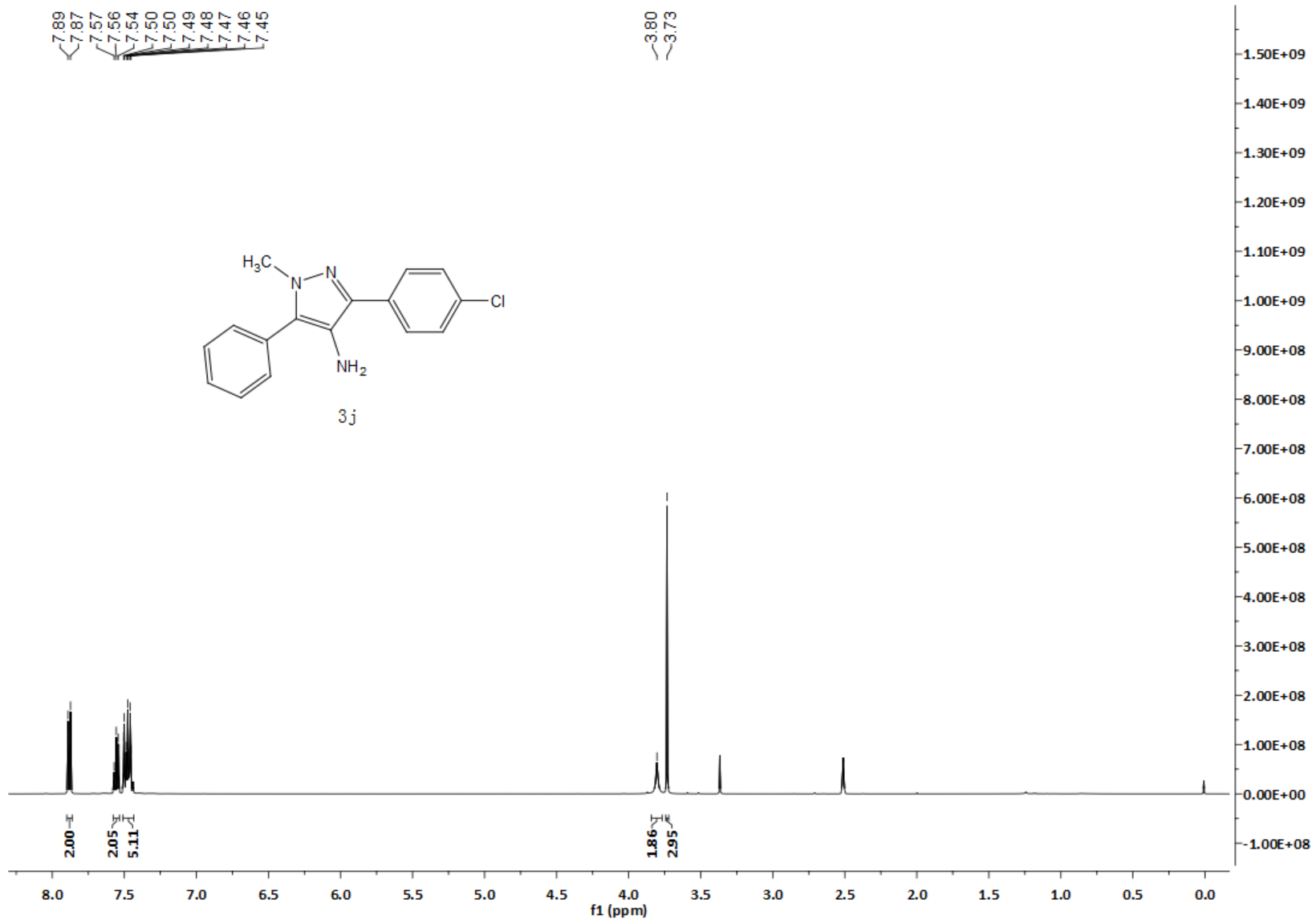


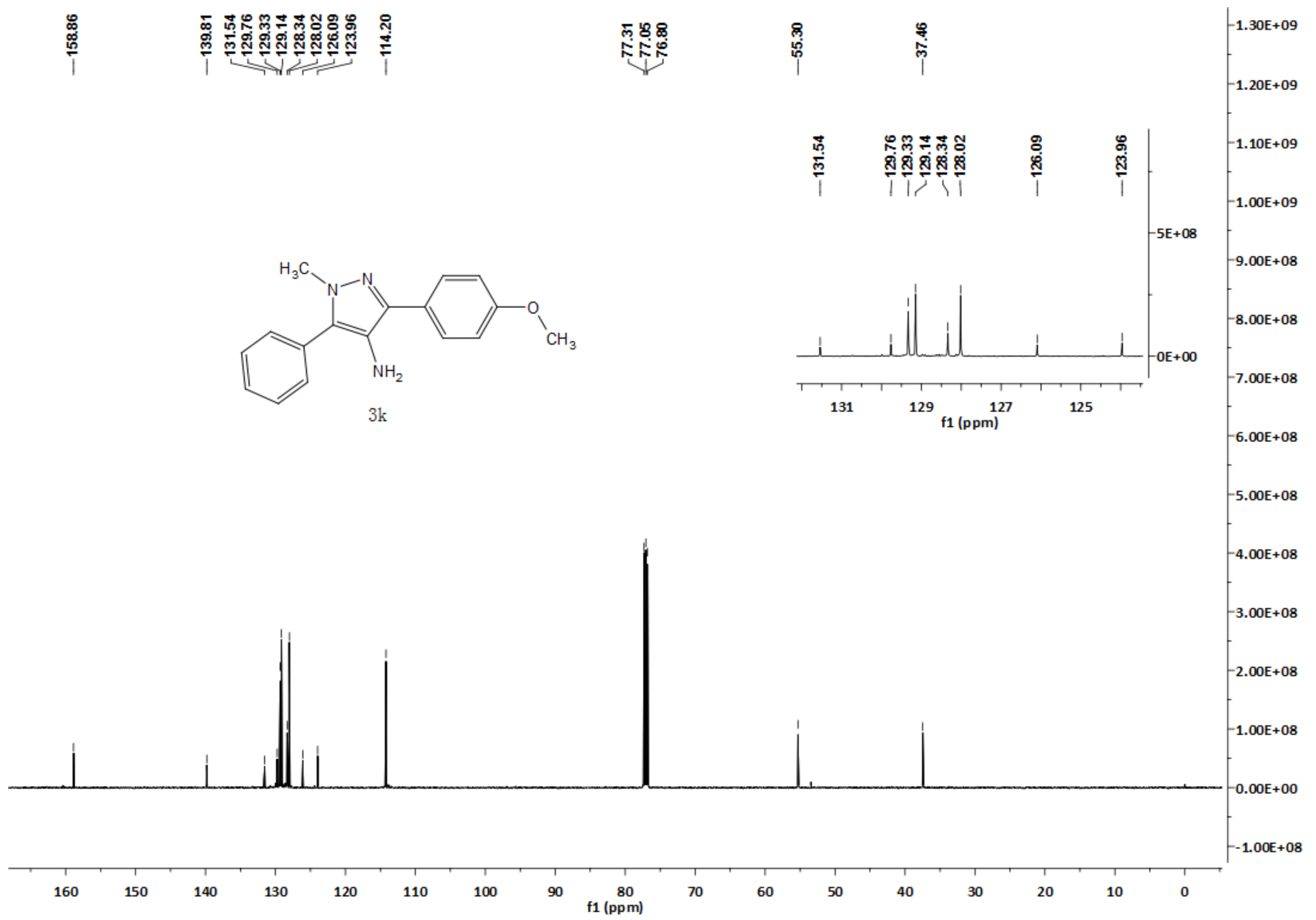
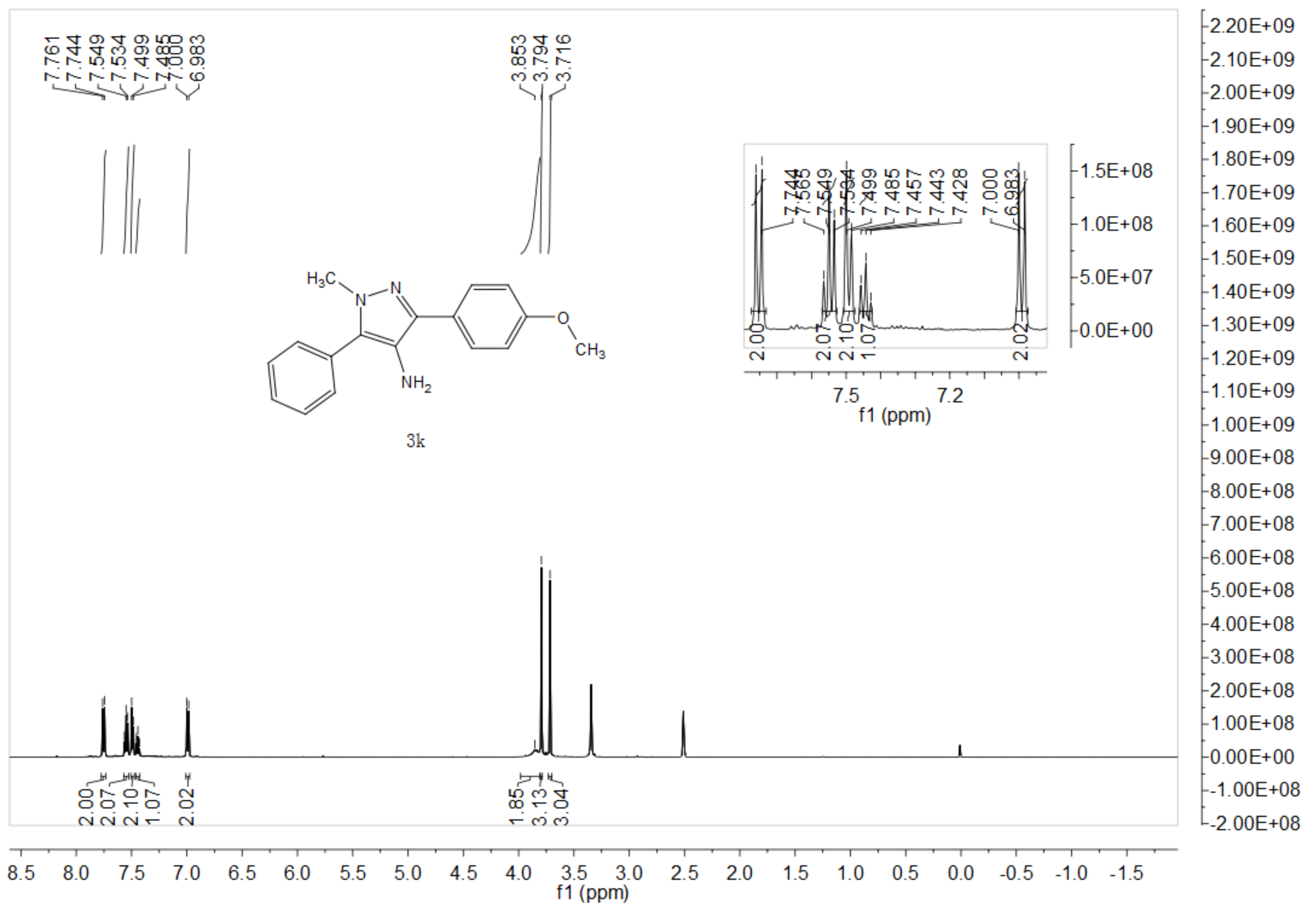


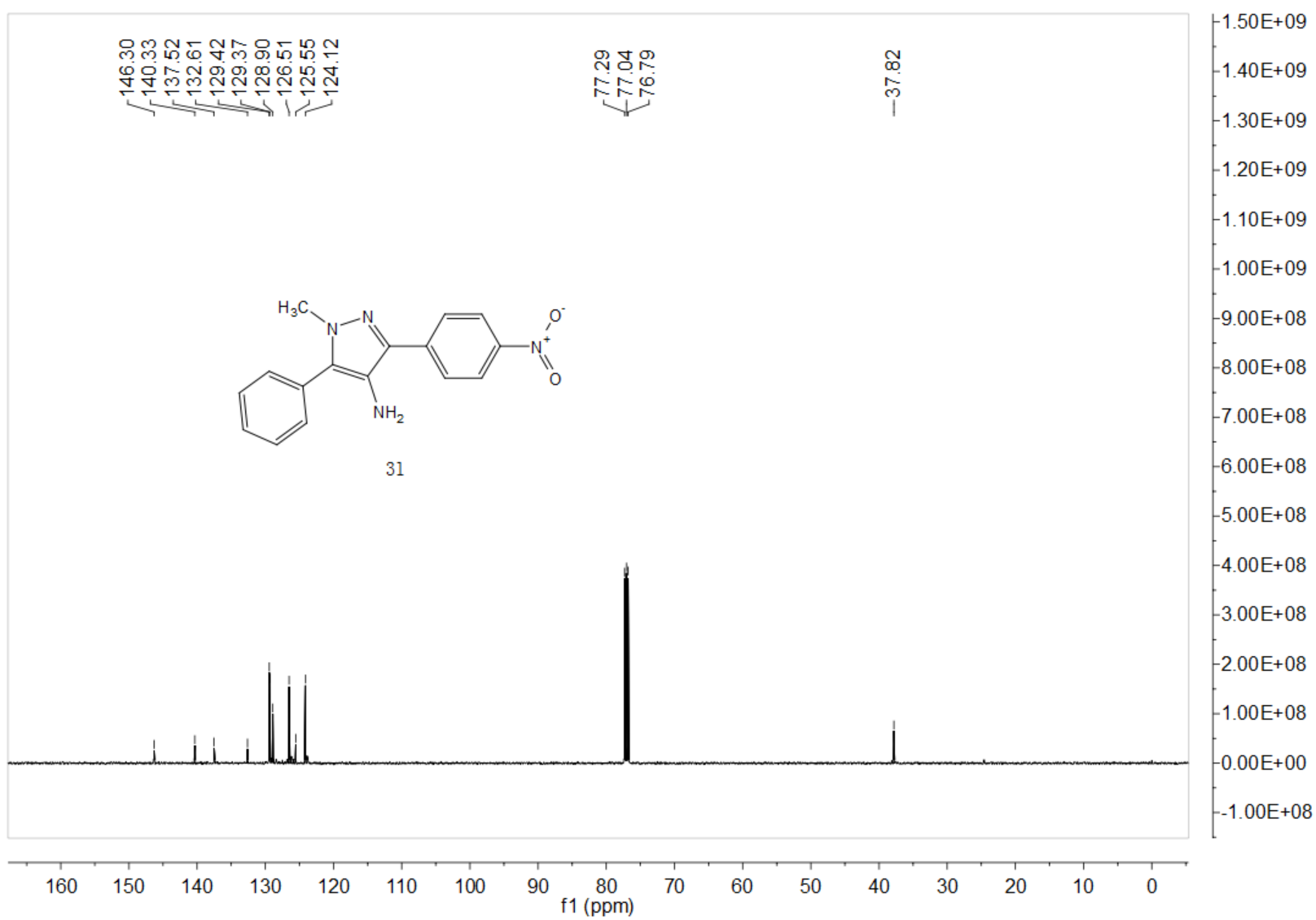
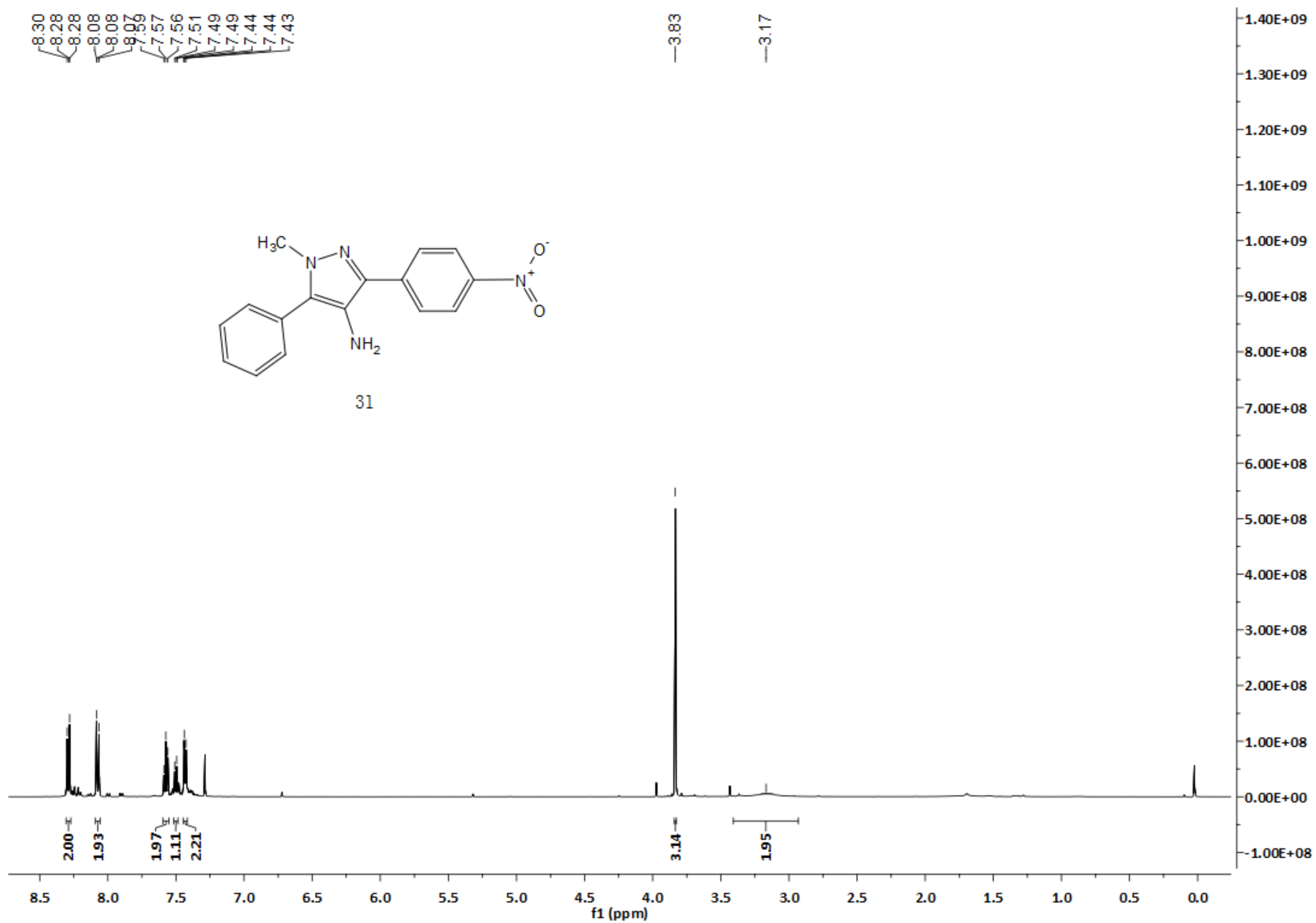


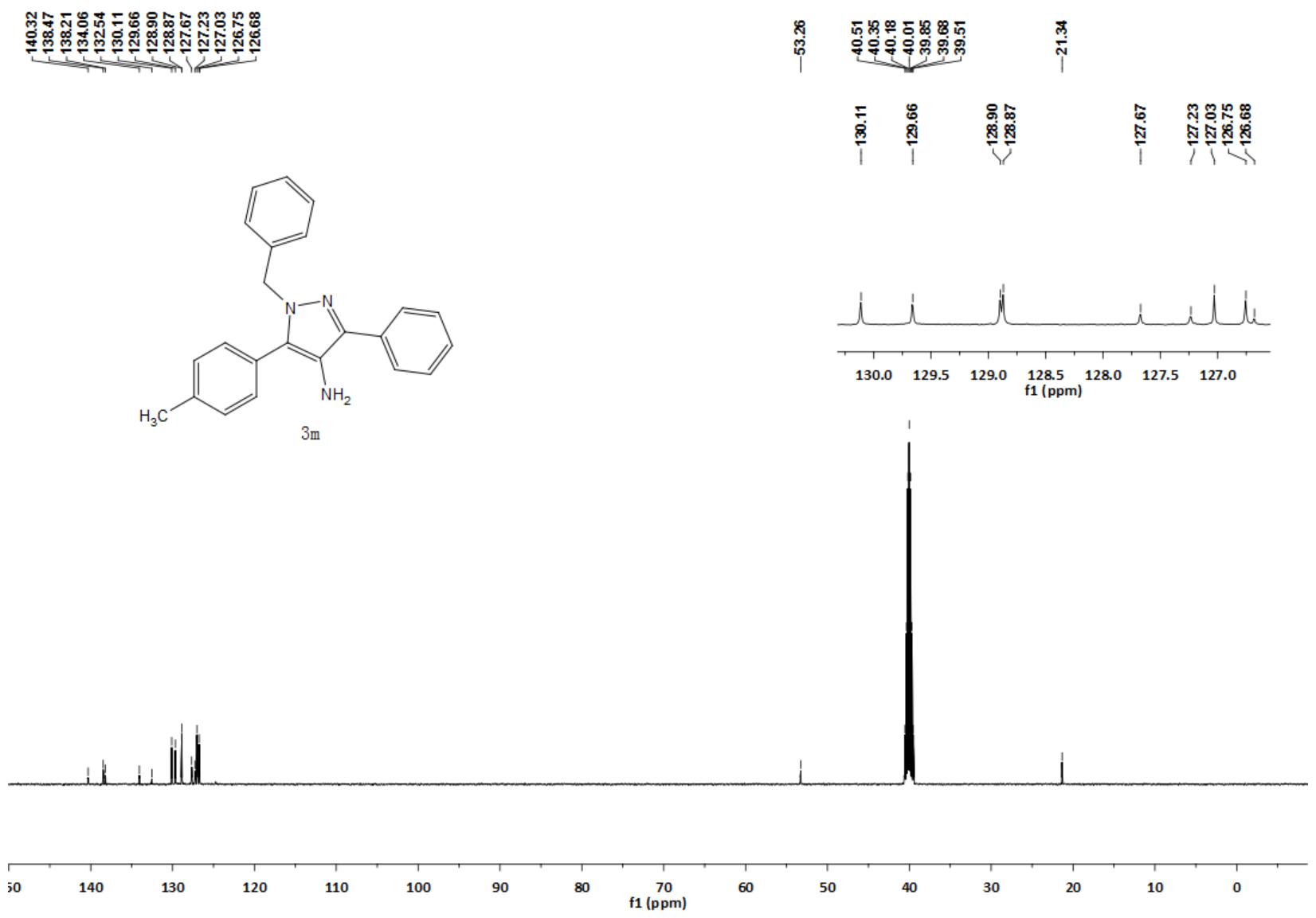
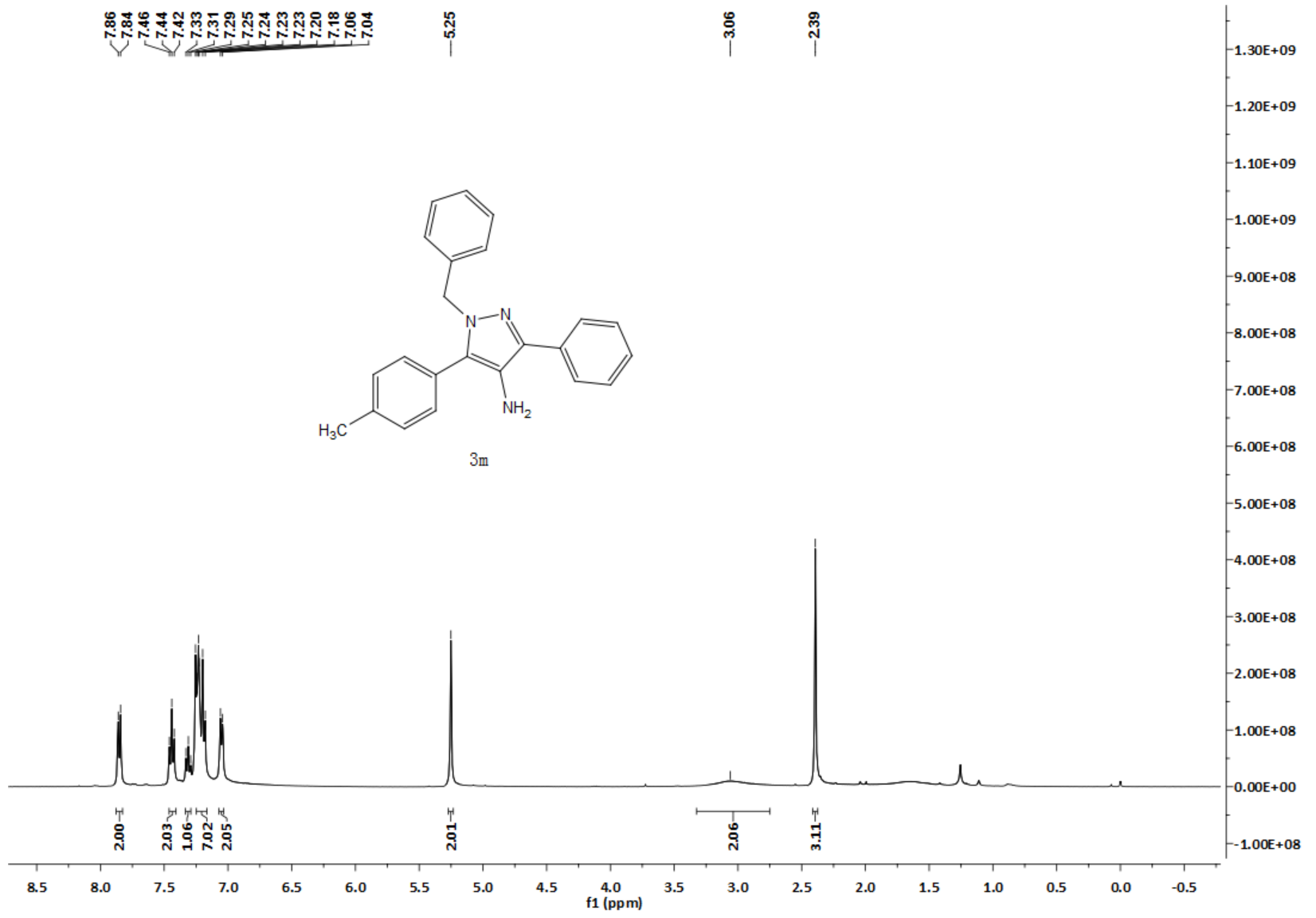


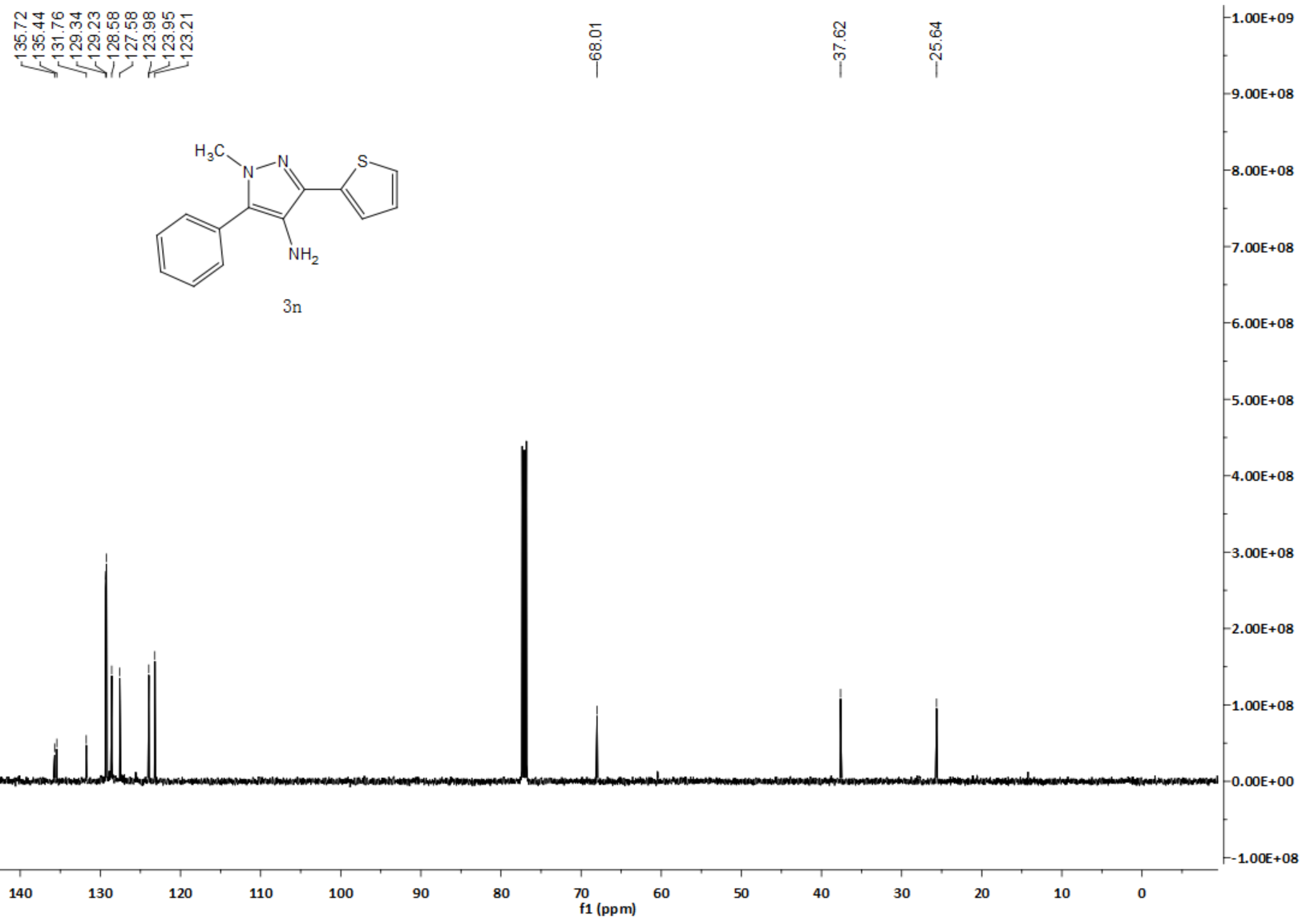
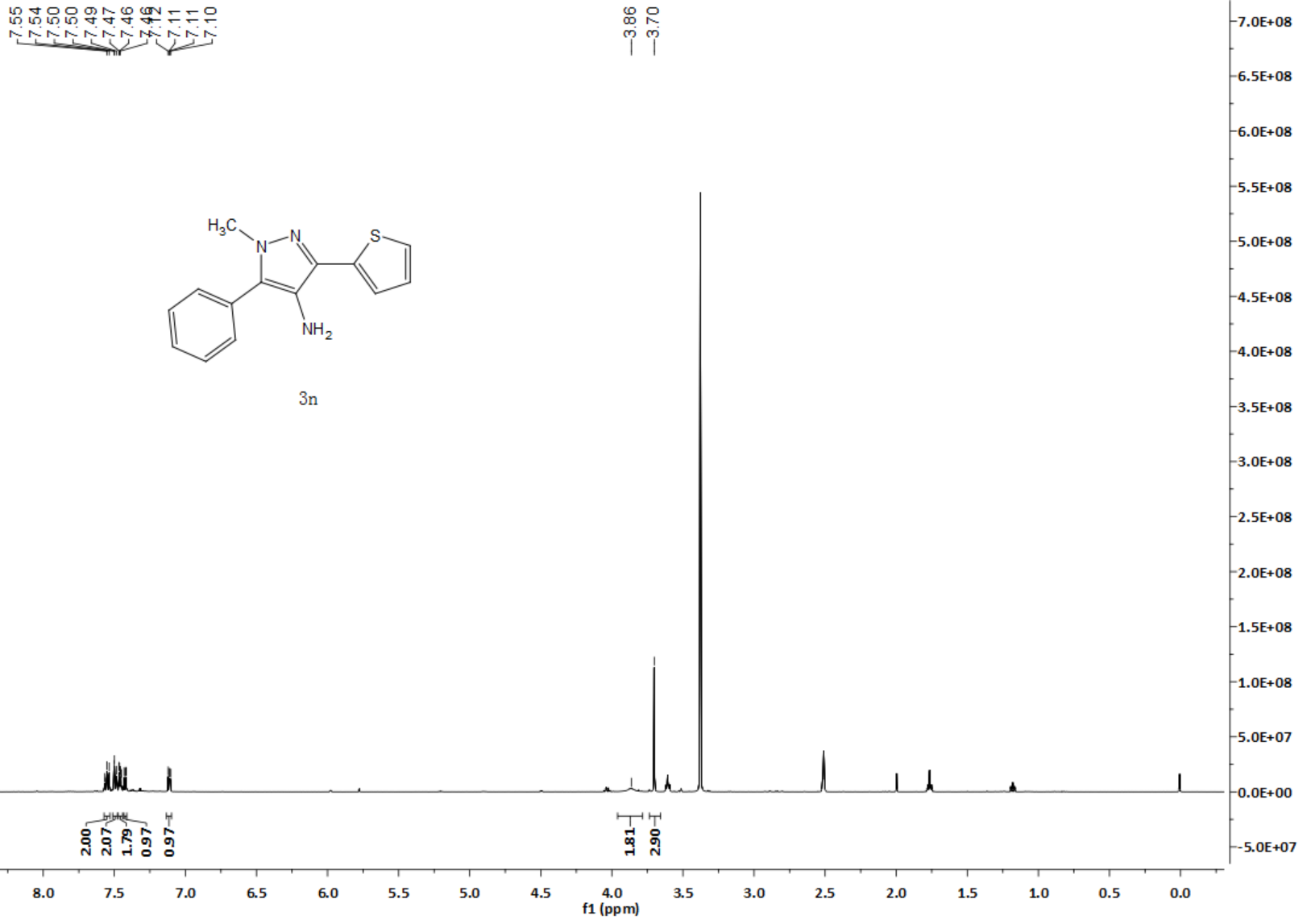


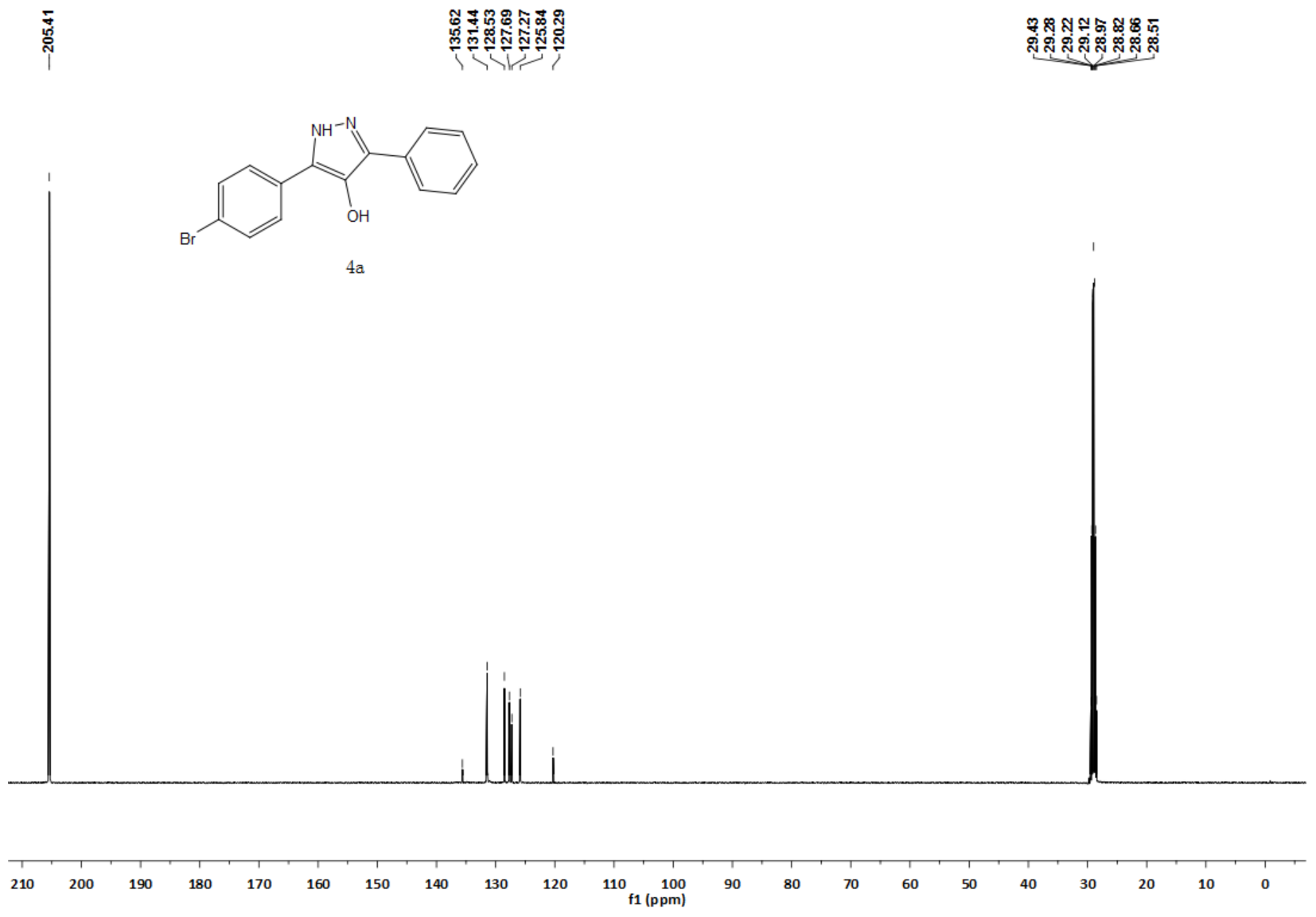
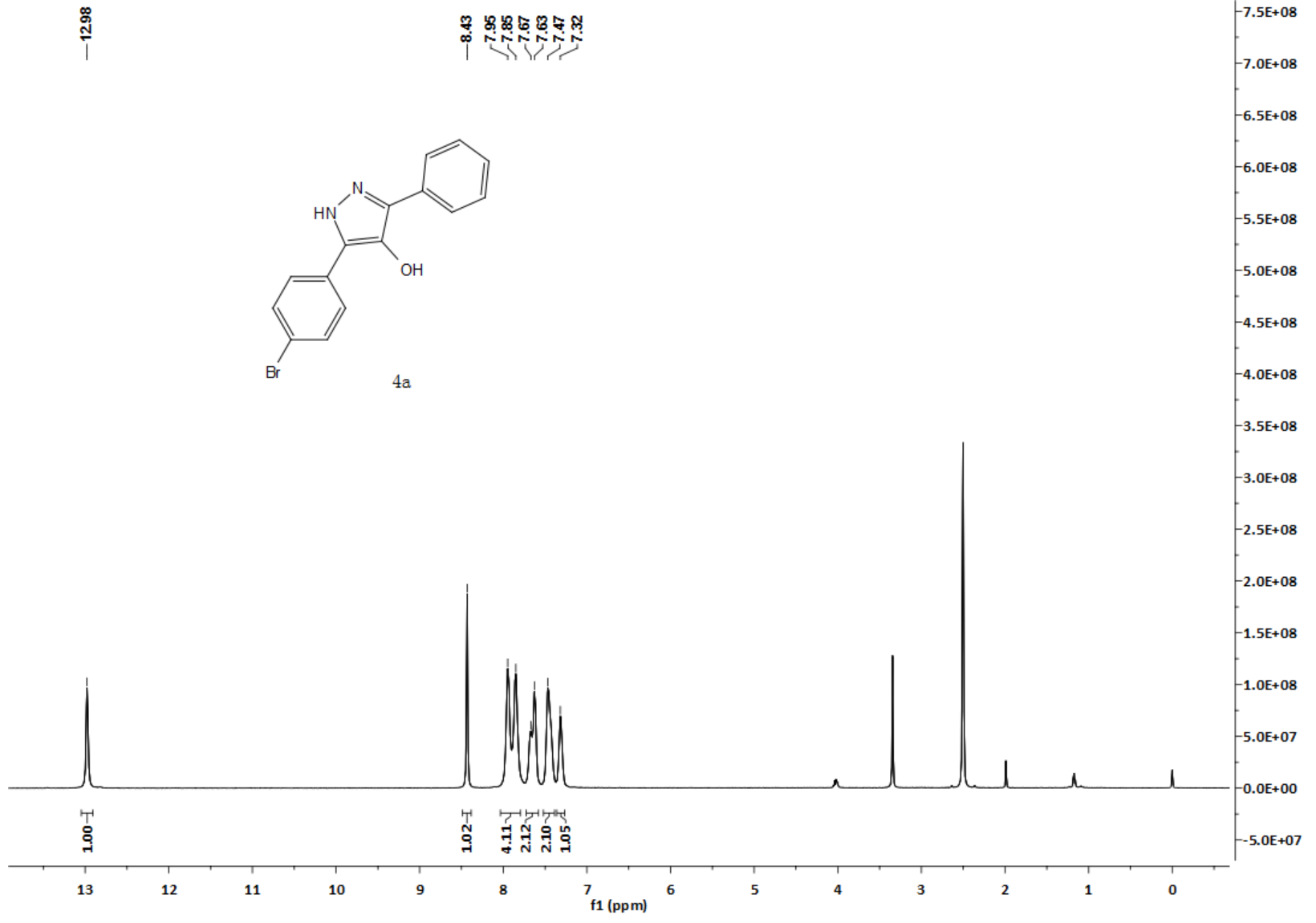


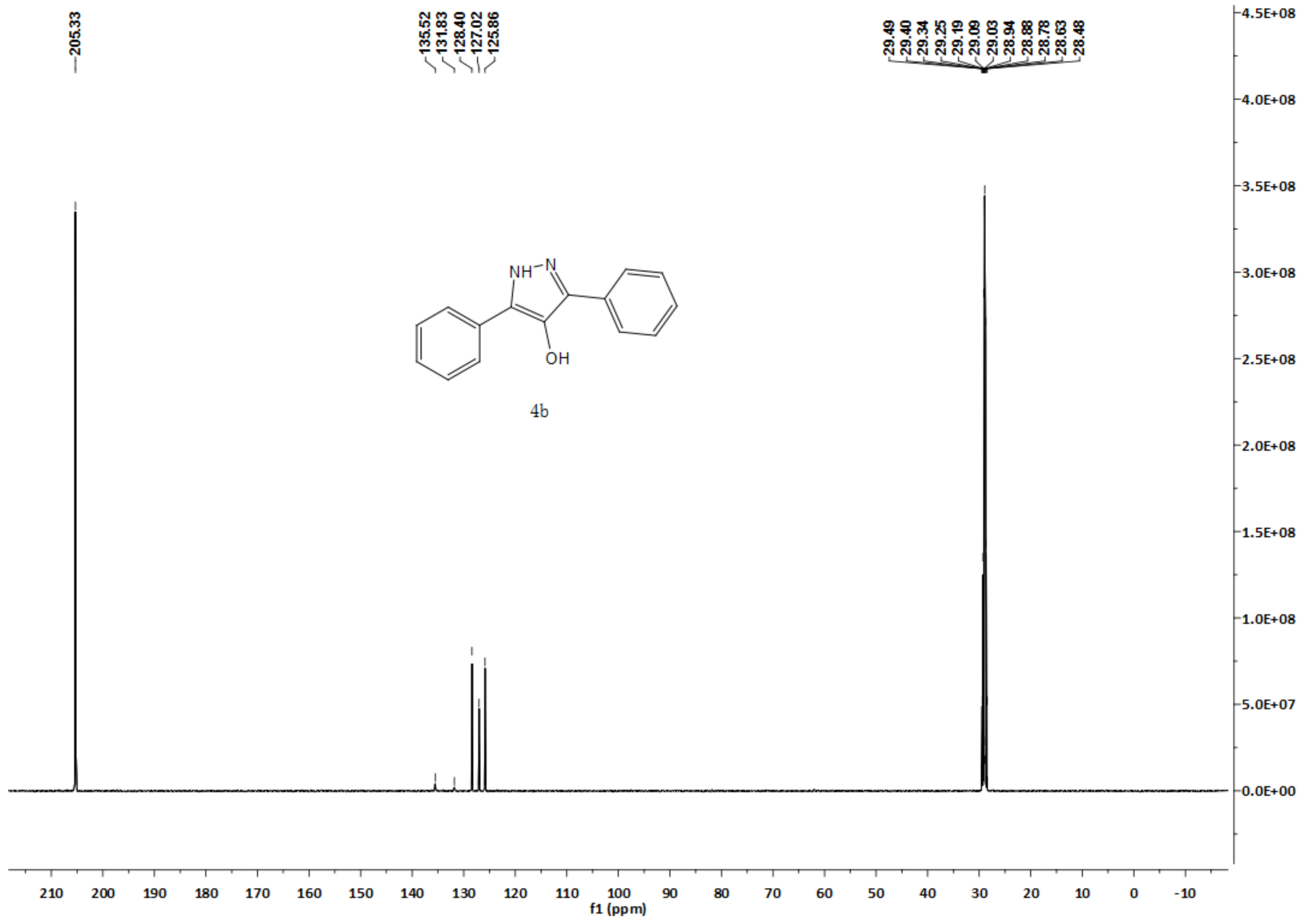
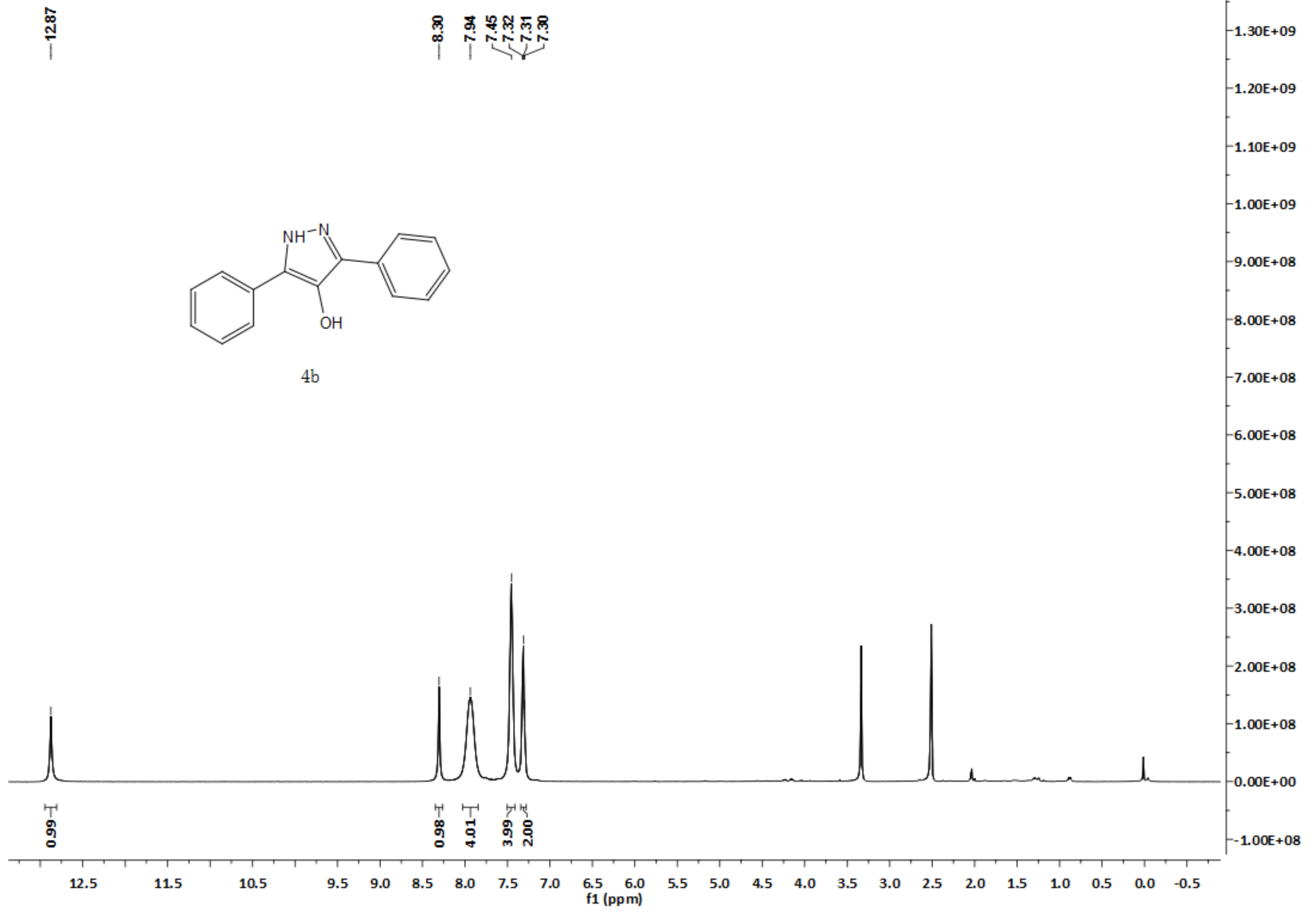


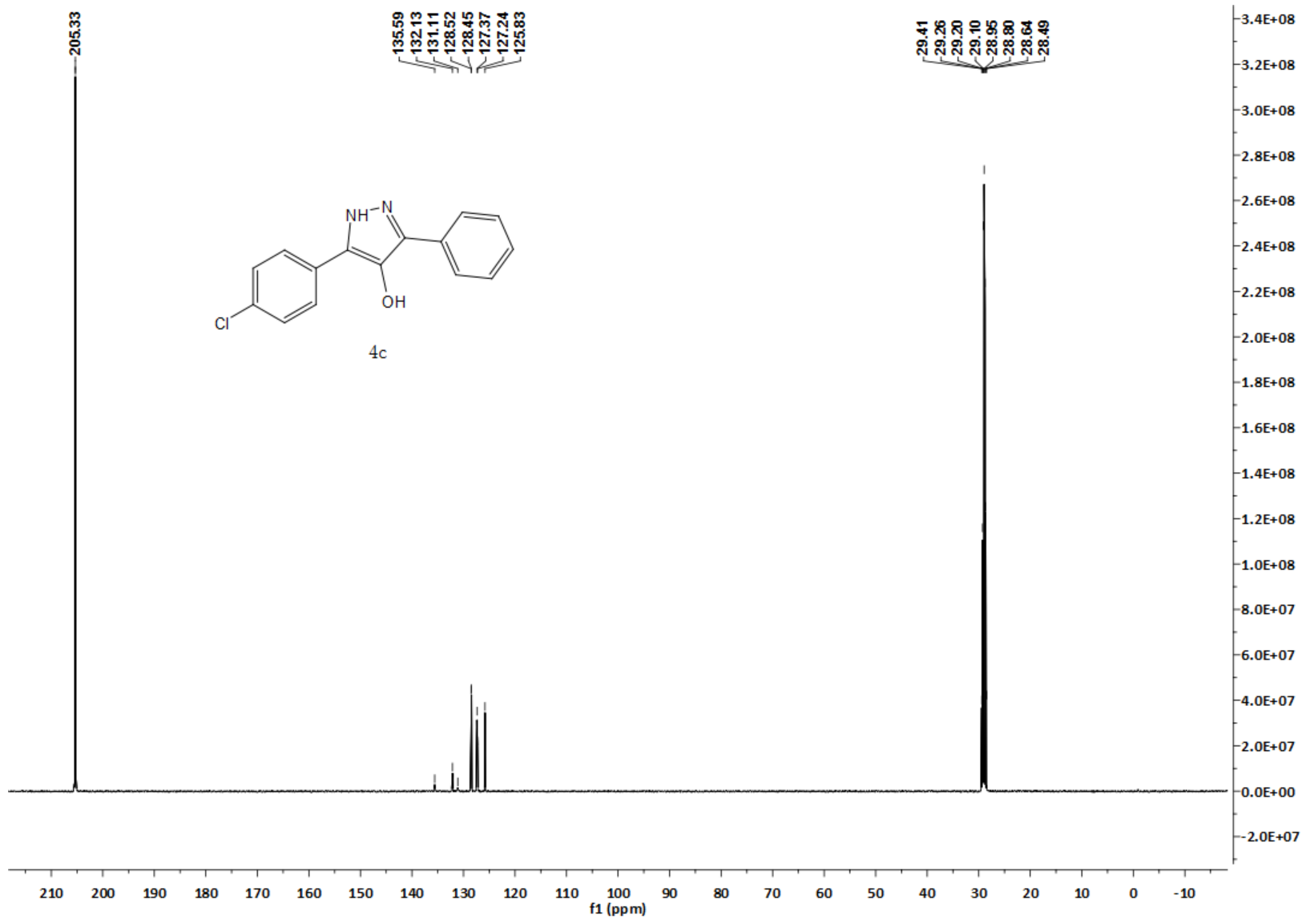
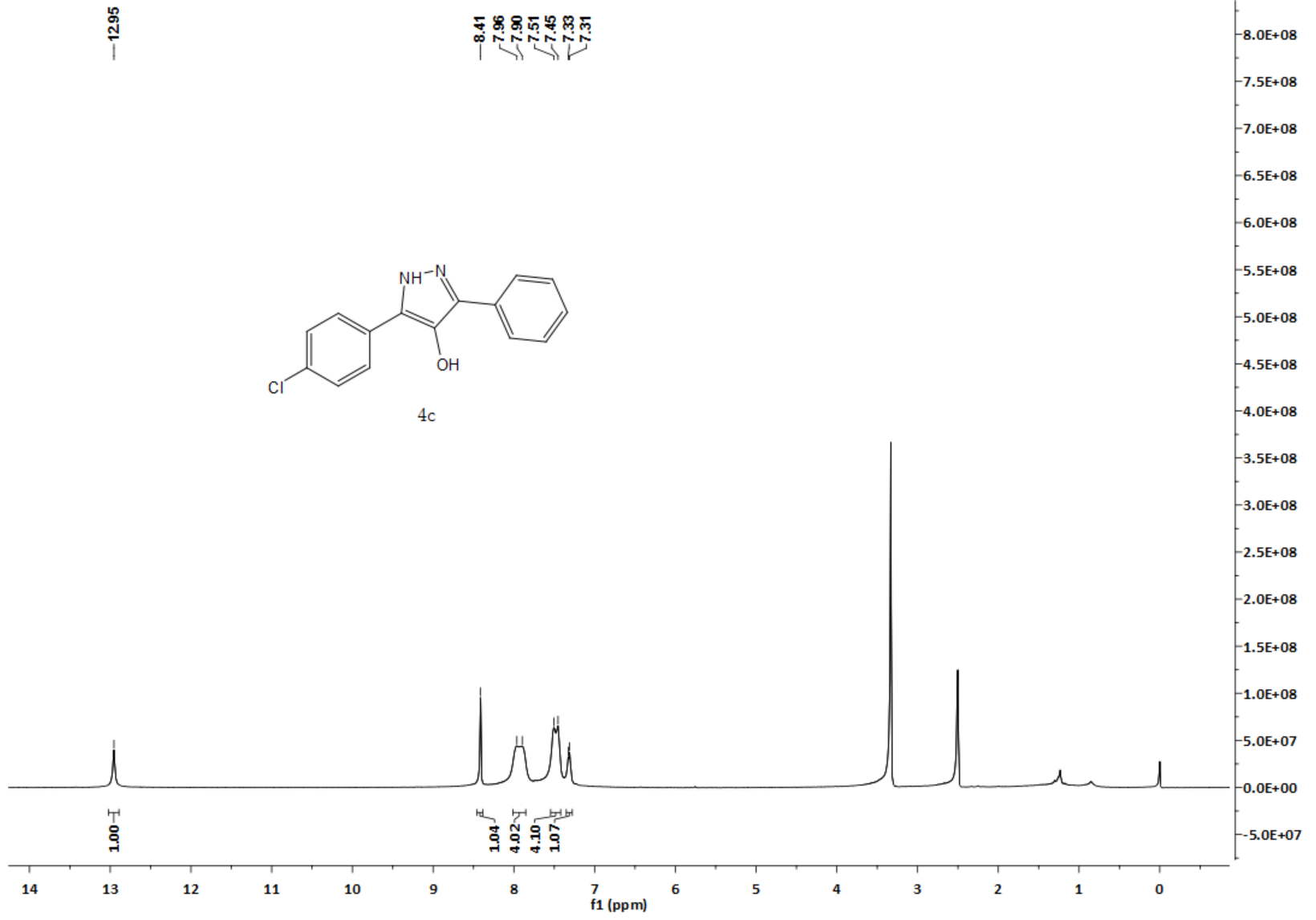




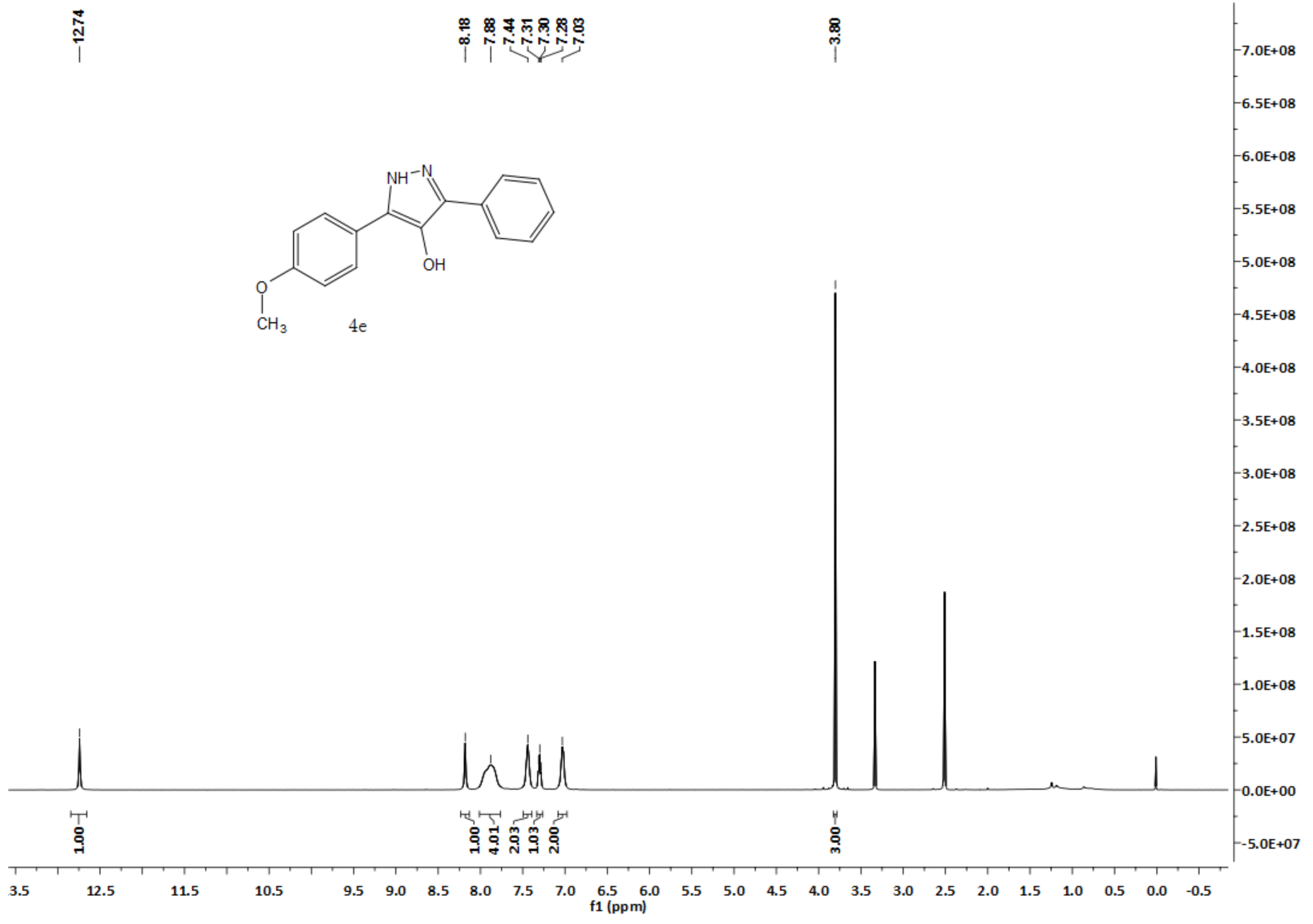
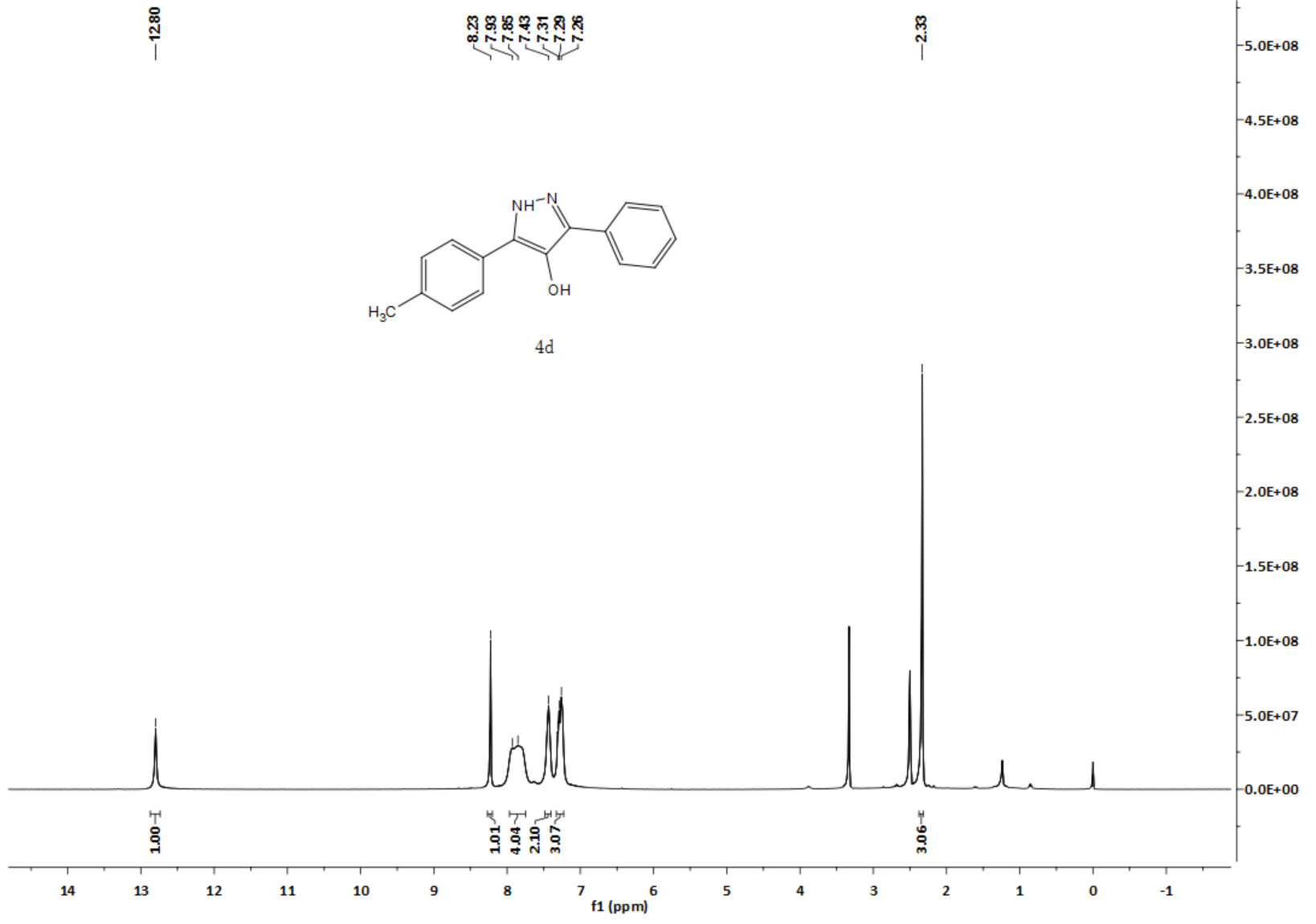


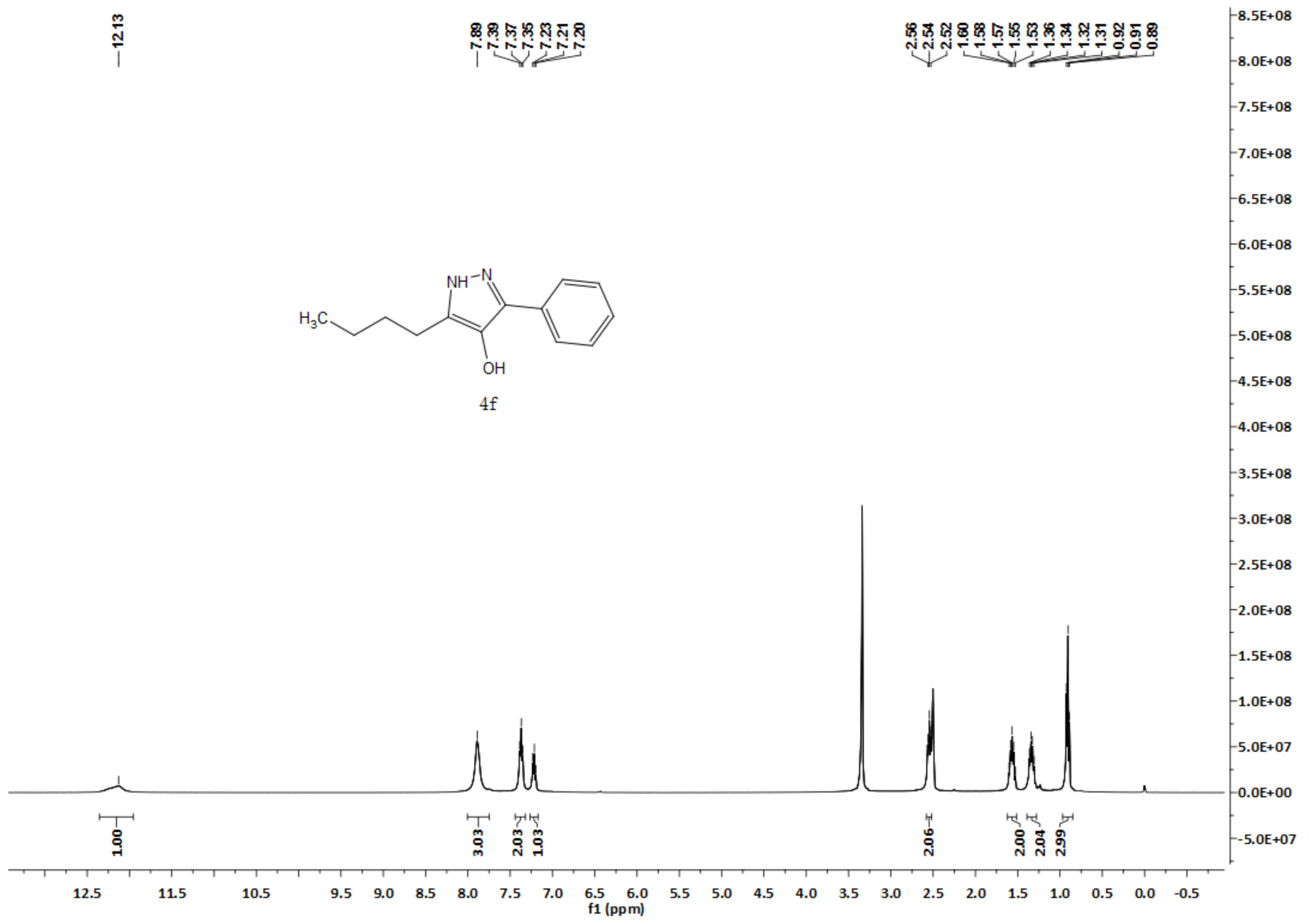
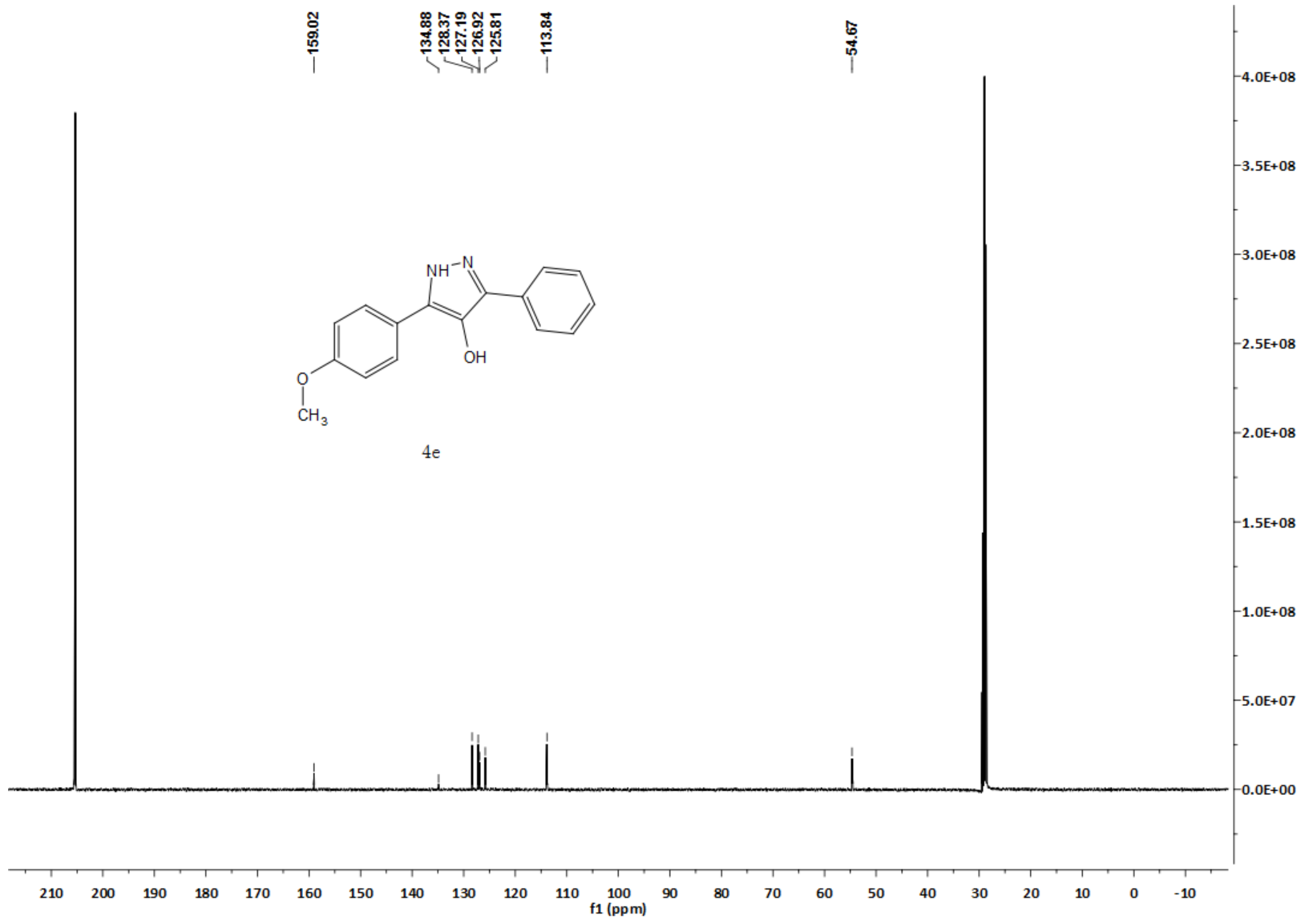


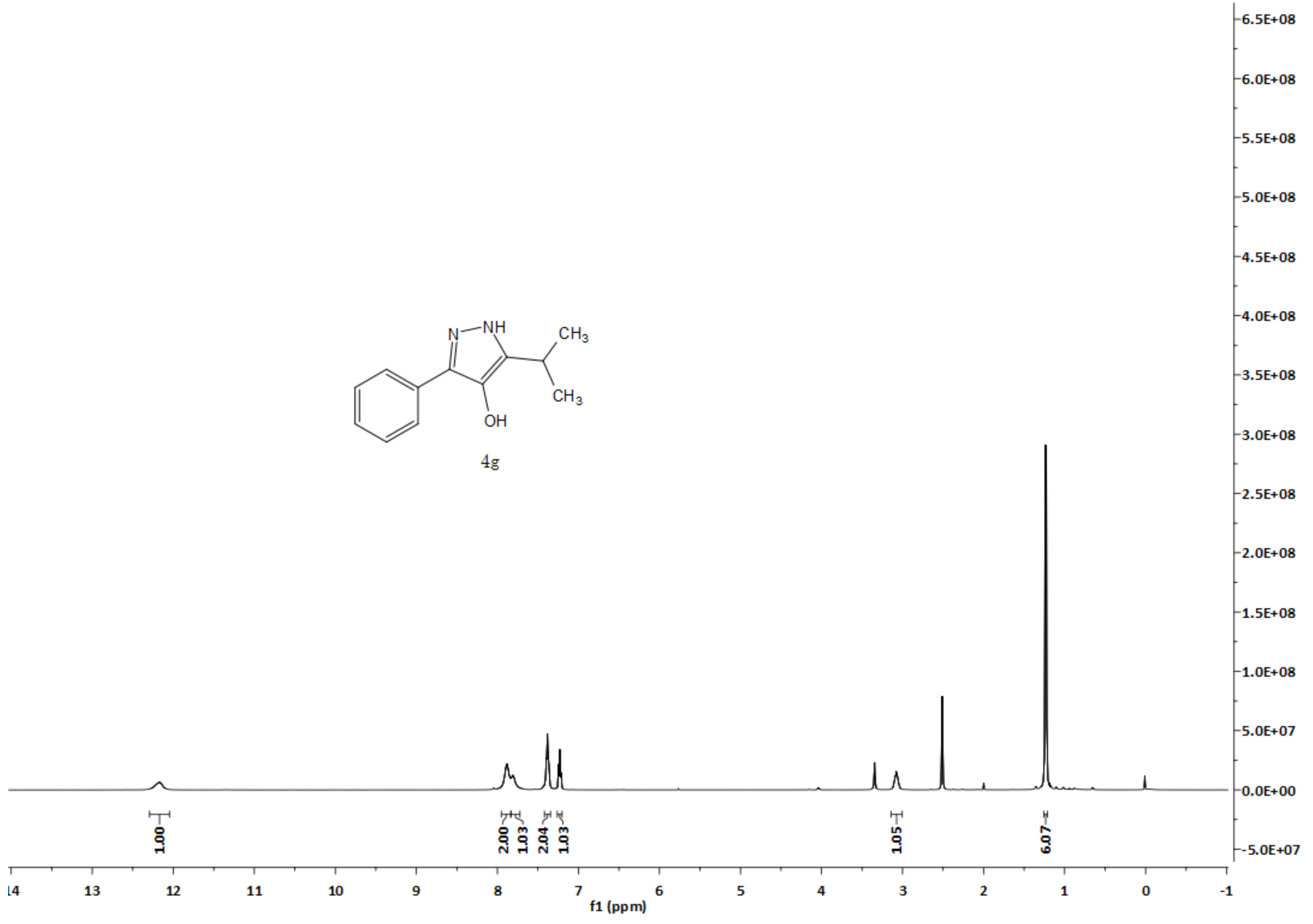
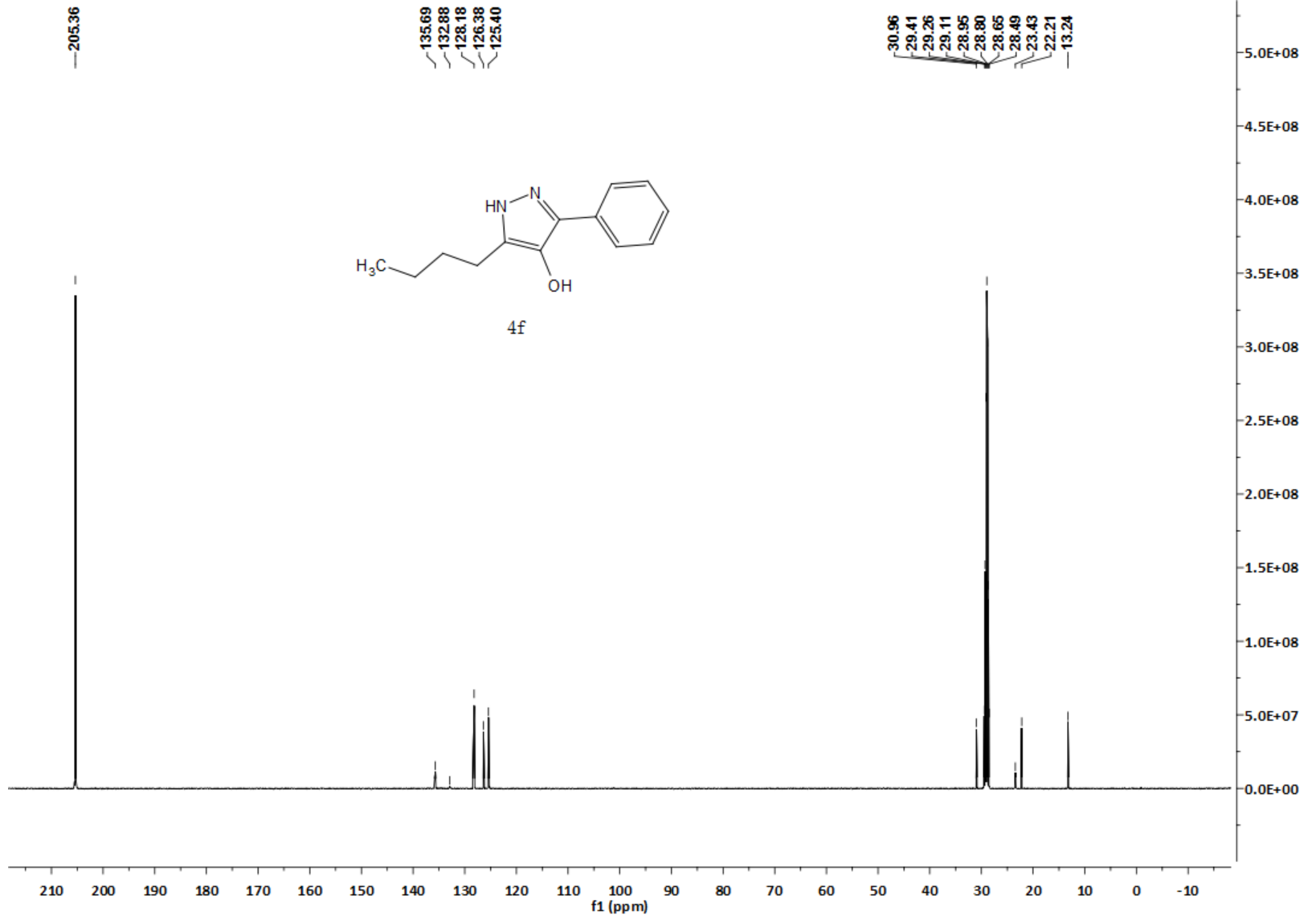


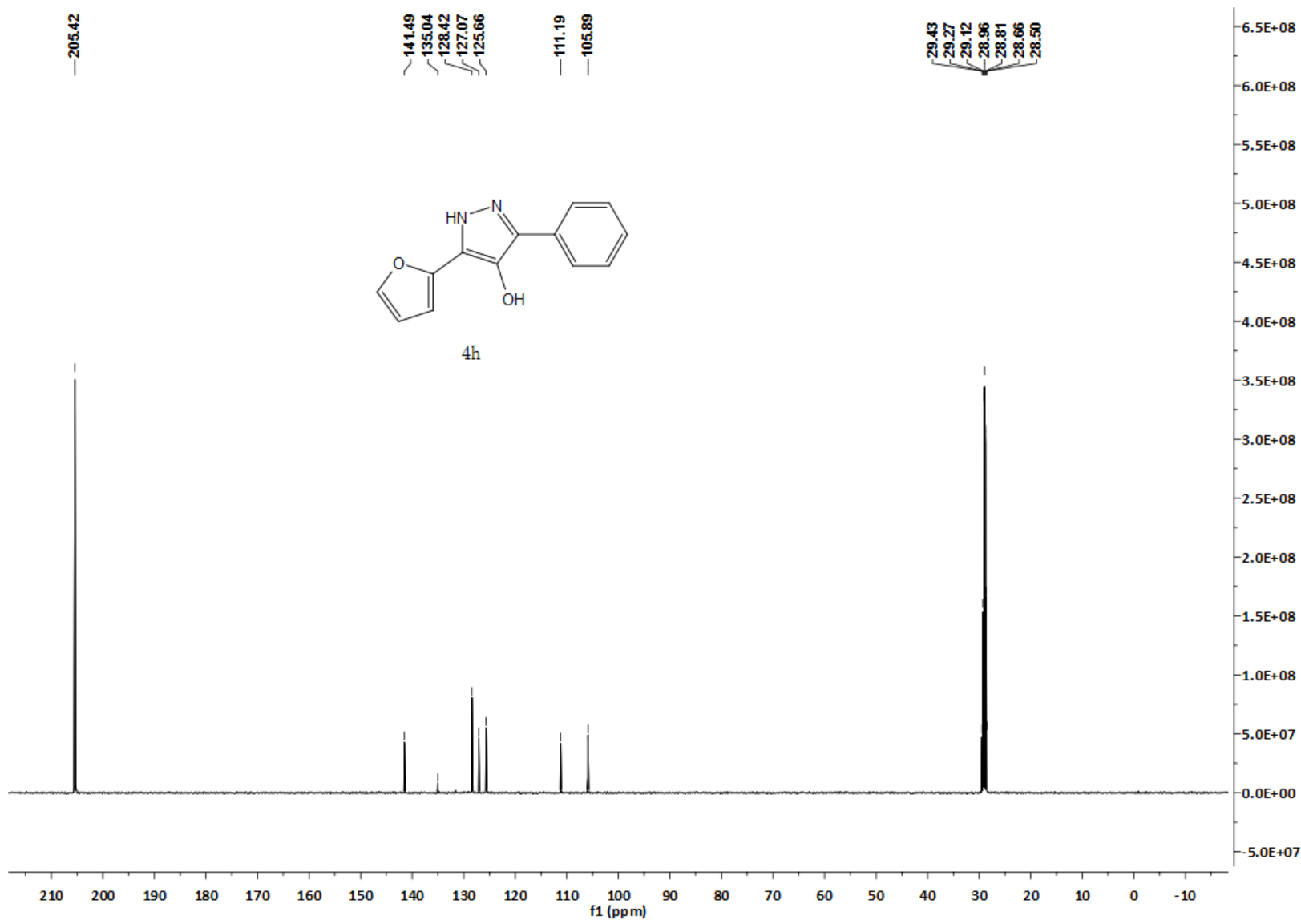
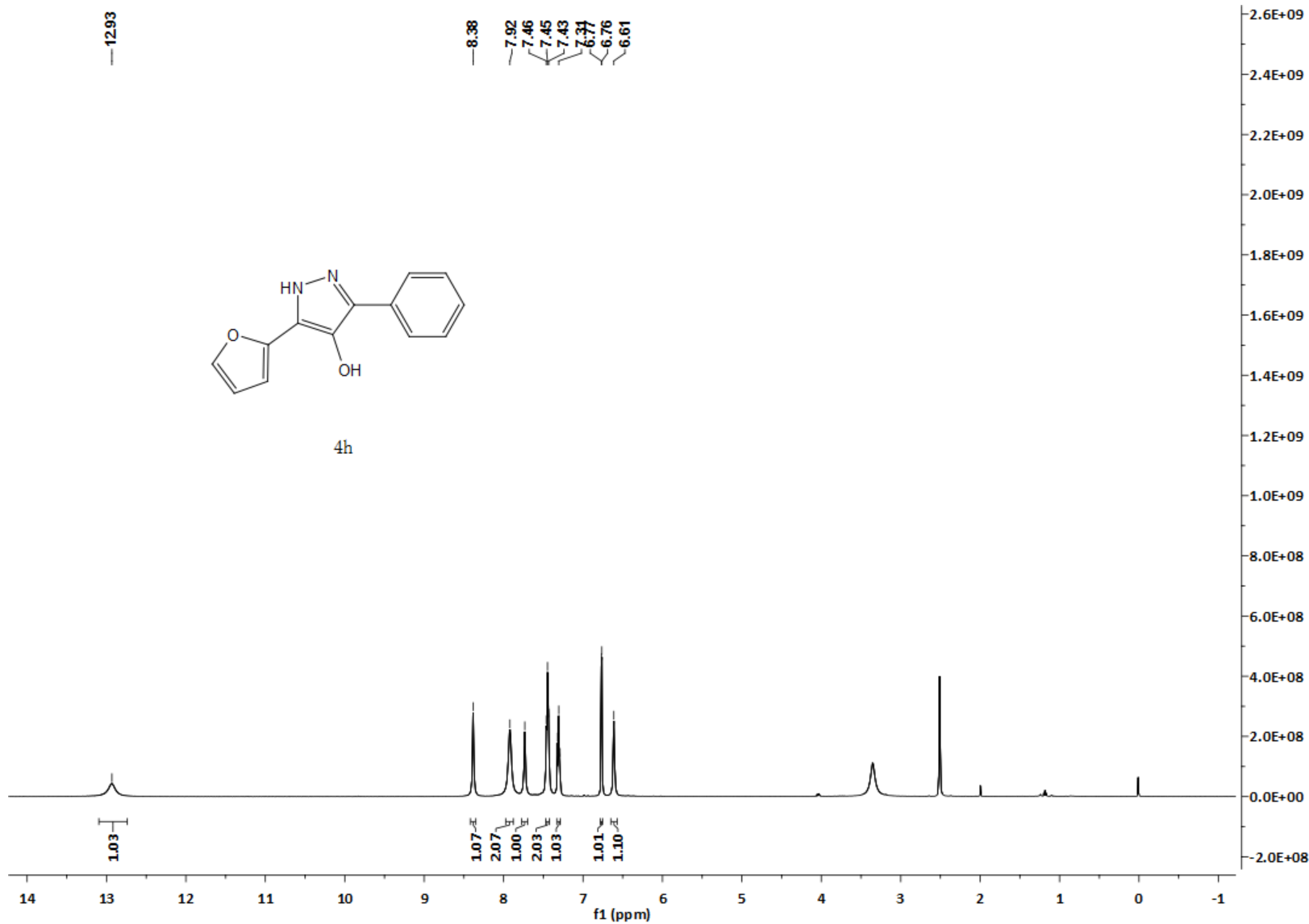


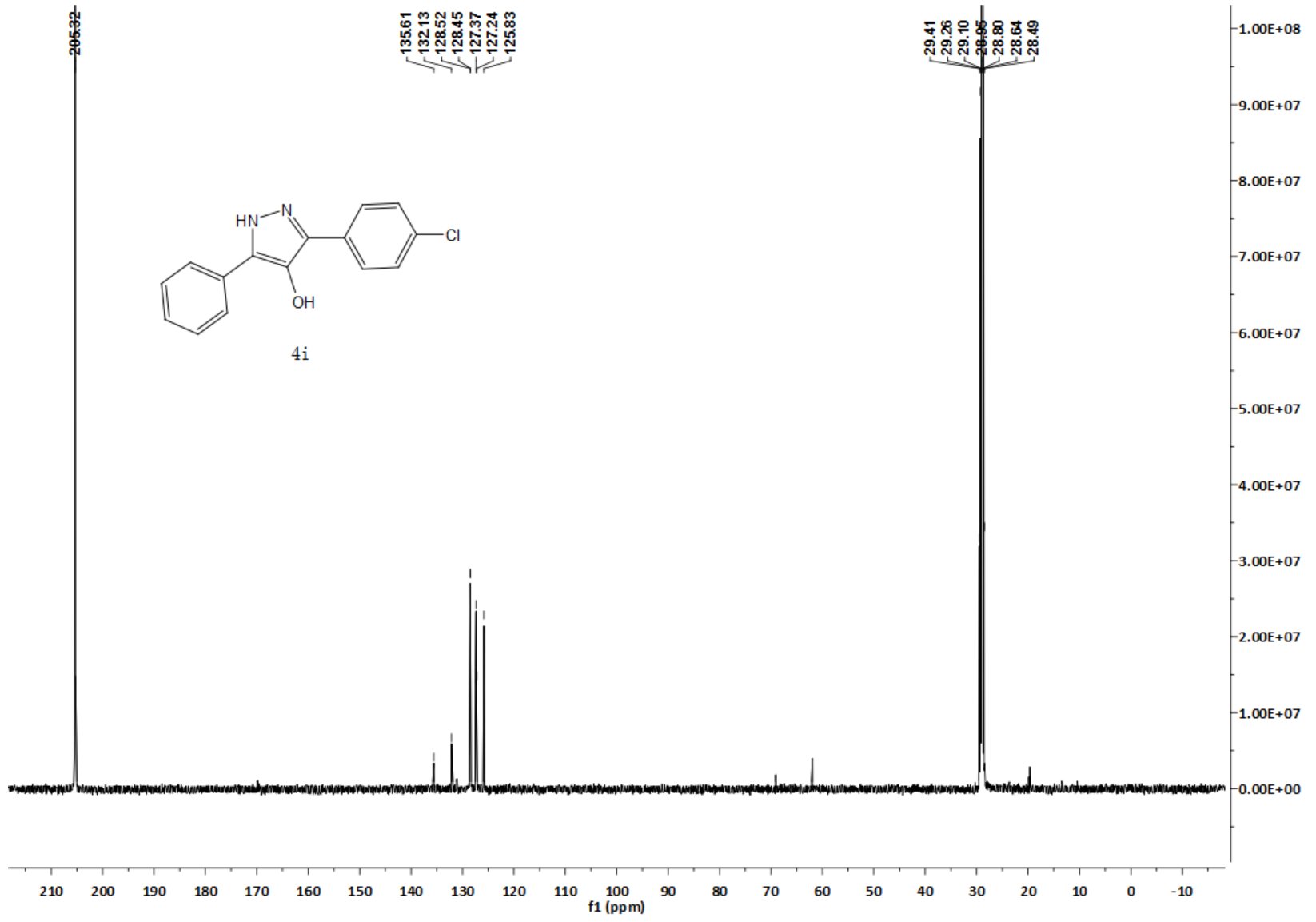
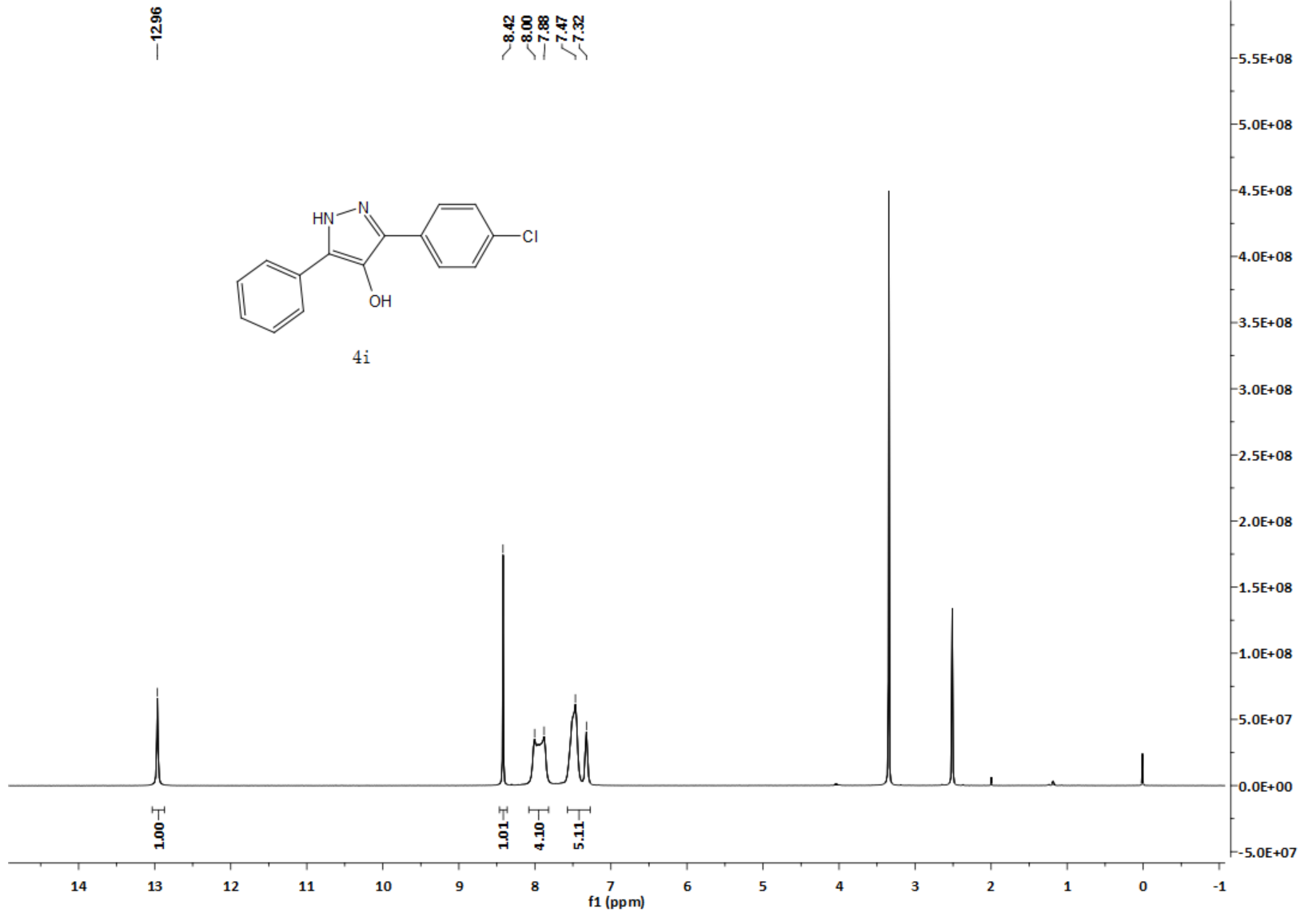




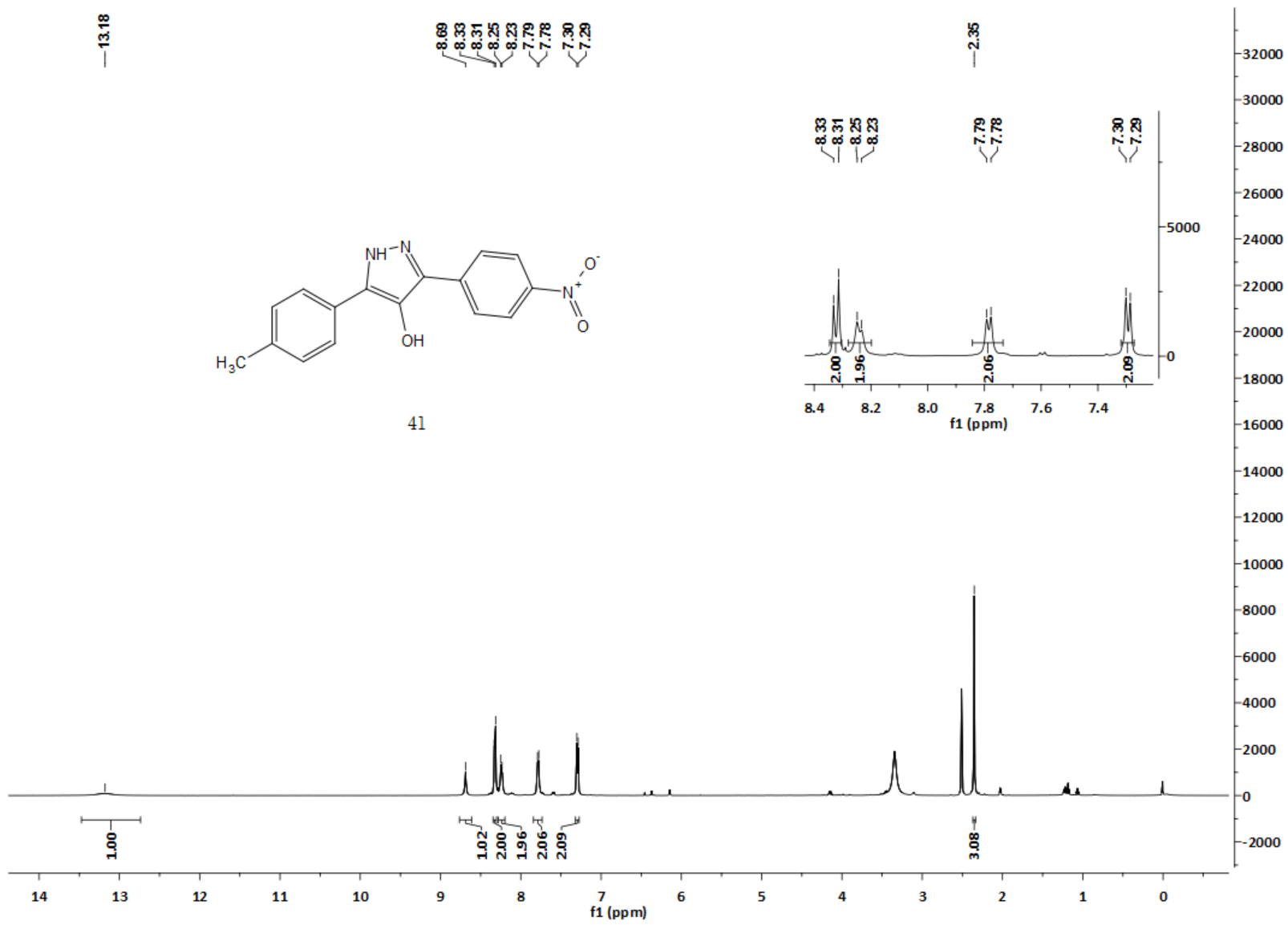
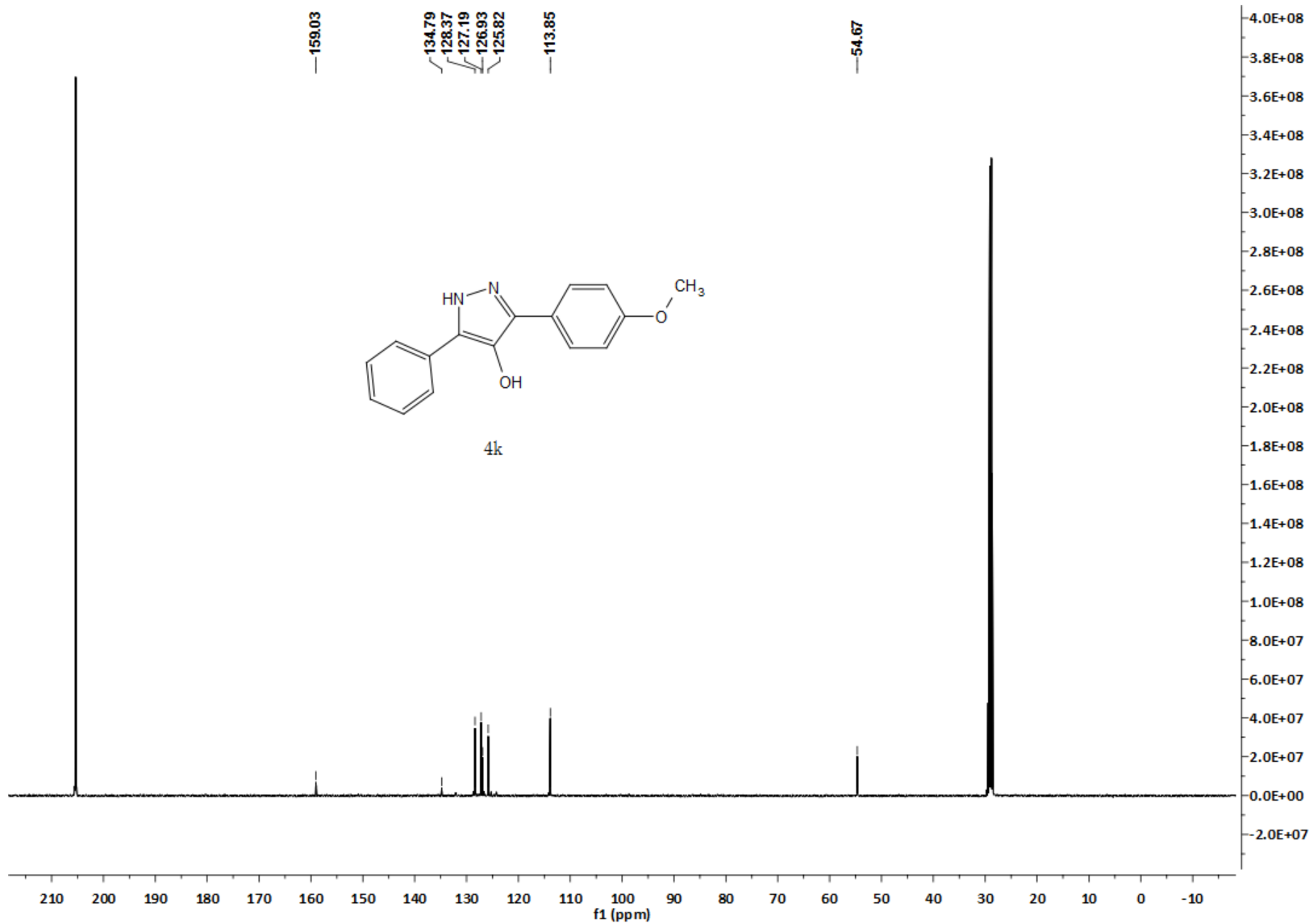


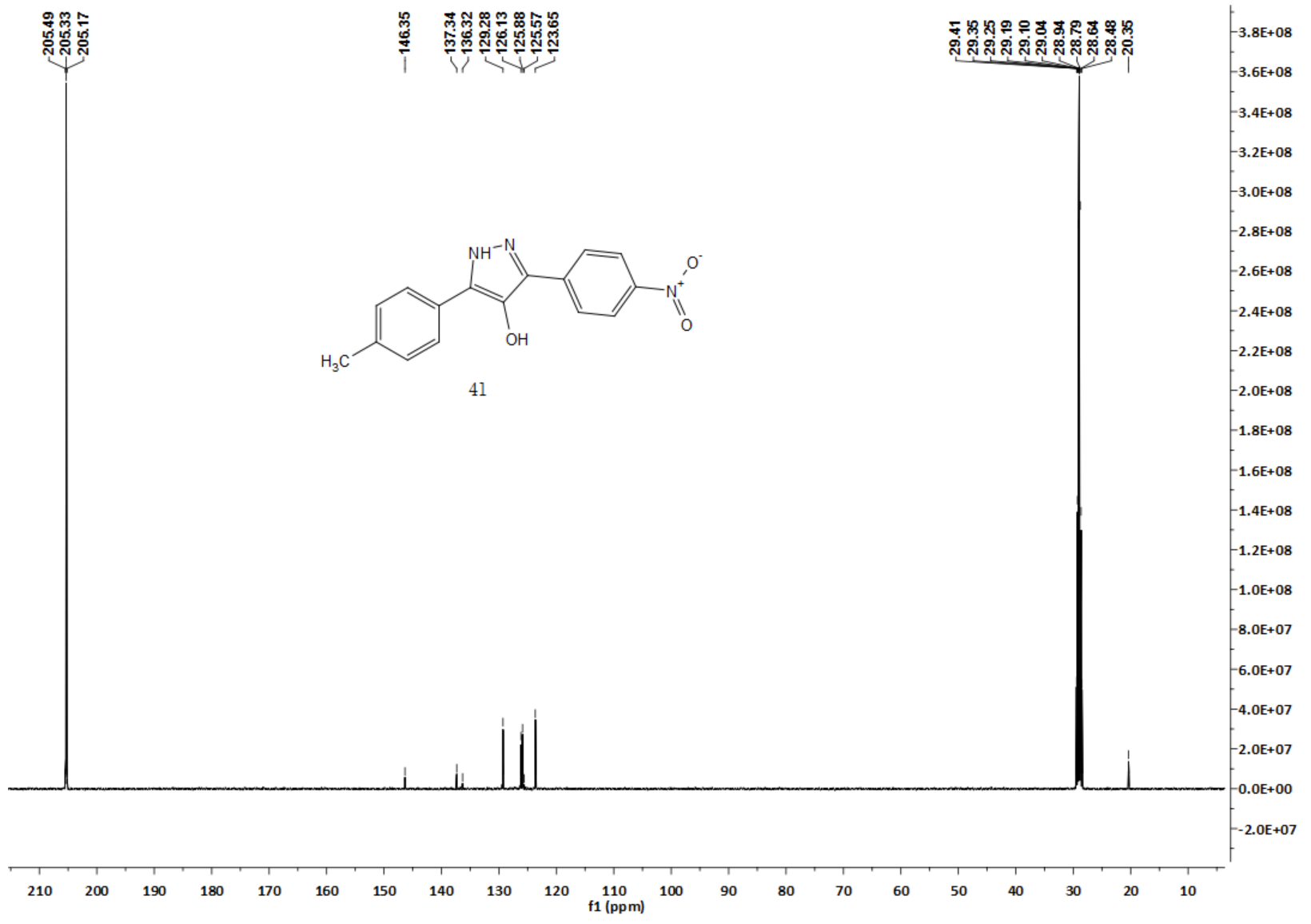






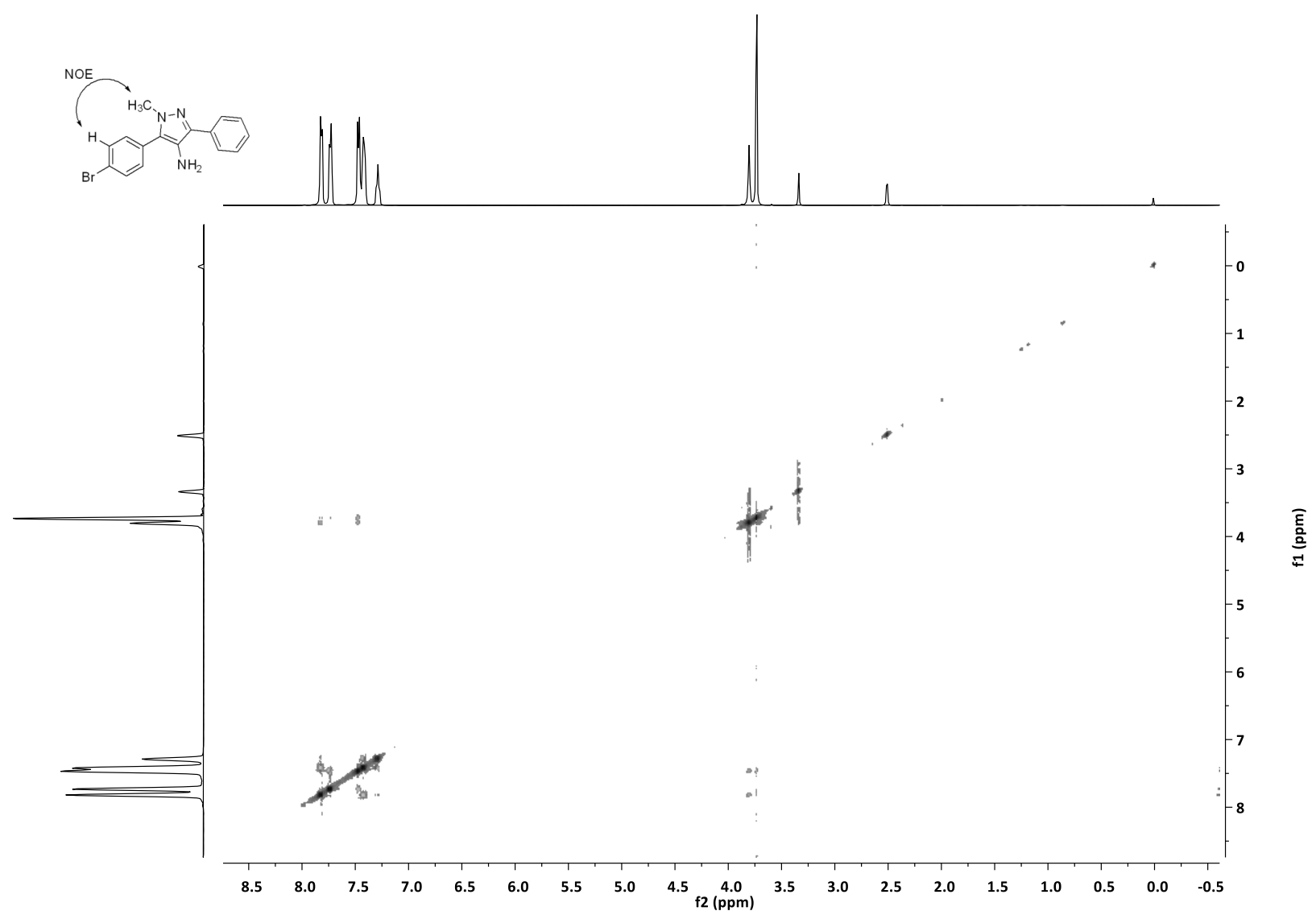


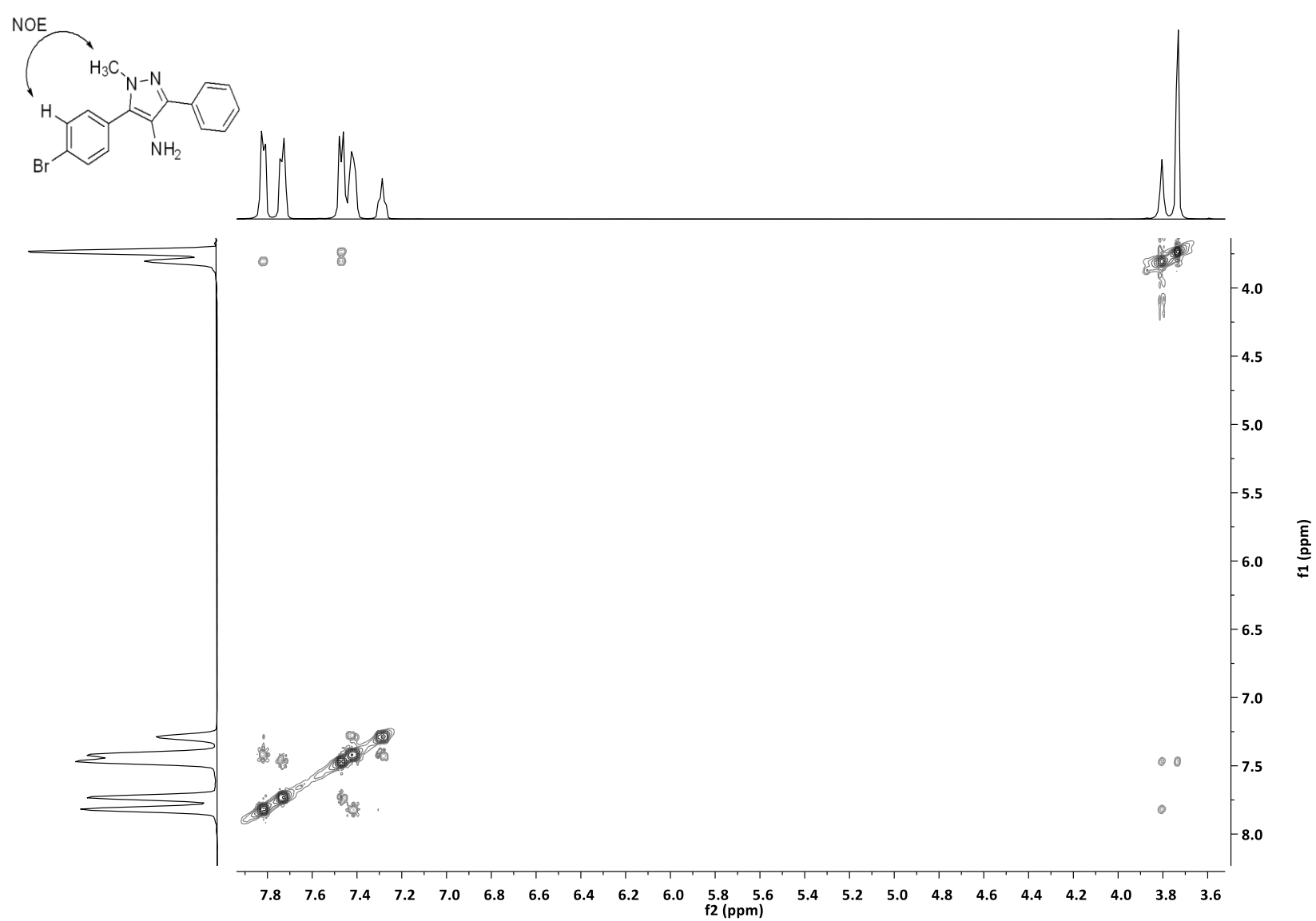






## 5. NOESY of 3b





## 6. X-ray crystallography Data of 4d

Single crystals of compound **3c** were measured on a Rigaku RAXIS-RAPID single-crystal diffractometer. The recrystallization solvent of **4d** was MeOH.

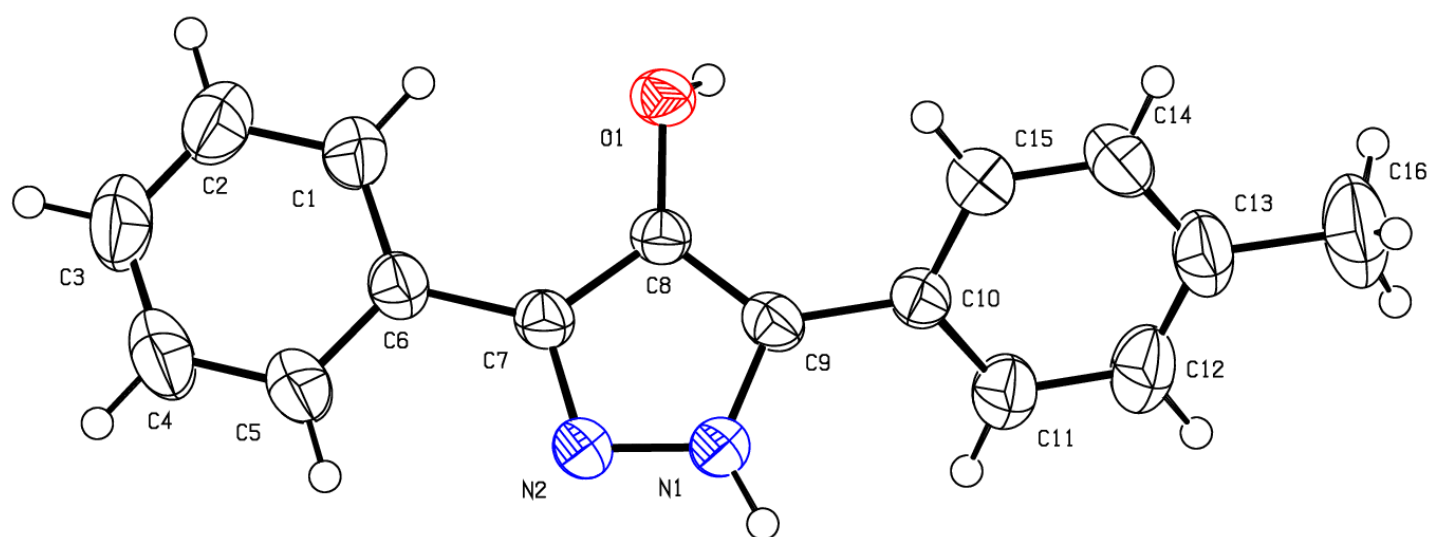


Figure S1 X-ray crystal structure of **4d**

Formula moiety	C16 H14 N2 O
Formula sum	C16 H14 N2 O
Formula weight	250.29
Temperature	293 K
Crystal system	monoclinic
Space group	P 21/c
Unit cell dimensions	a=13.1976(17) Å b=10.5014(8) Å c=9.8453(11) Å alpha = 90 deg. beta = 108.284(14) deg. gamma = 90 deg.
Volume	1295.6(3) Å <sup>3</sup>
Z	4
Calculated density	1.283 g/cm <sup>3</sup>
Absorption coefficient	0.082 mm <sup>-1</sup>
F(000)	528.0
Crystal size	0.42 x 0.36 x 0.2 mm
Theta range for data collection	3.2448 to 29.4437
Reflections collected / unique	6148 /2359 [R(int) = 0.0378]
Data / restraints / parameters	2359/0/178
Goodness-of-fit on F2	1.043
Final R indices [Fo > 4sig(Fo)]	R1 = 0.0488, wR2 = 0.1109
R indices (all data)	R1 = 0.0769 , wR2 = 0.1267

## Reference:

- 1 (a) Gilchrist, T. L.; Mendonca, R. *ARKIVOC*. **2000**, 769; (b) Liu, L.; Liebeskind, S. *J. Am. Chem. Soc.* **2008**, *130*, 6918; (c) Khazaei, M. A. *Synthesis* **2009**, *21*, 3672; (d) Kowalski, C. J.; Weber, A. E.; Fields, K. W. *J. Org. Chem.*, **1982**, *47*, 5088; (e) Chiba, S.; Wang, Y. F.; Lapointe, G.; Narasaka, K. *Org. Lett.* **2008**, *10*, 313.