

## Supporting information

### Radical Generation from Electroreduction of Aryl and Benzyl Ammonium Salts: Synthesis of Organoboronates

Xianqiang Kong,<sup>[a][b]</sup> Long Lin,<sup>[b]</sup> Qianjin Chen,<sup>[b]</sup> and Bo Xu\*<sup>[b]</sup>

<sup>a</sup> School of Chemical Engineering and Materials, Changzhou Institute of Technology, No. 666 Liaohe Road, Changzhou 213032, China

<sup>b</sup> Key Lab of Science and Technology of Eco-Textile, Ministry of Education, College of Chemistry, Chemical Engineering and Biotechnology, Donghua University, Shanghai, 201620, China. E-mail: bo.xu@dhu.edu.cn

## Table of Contents

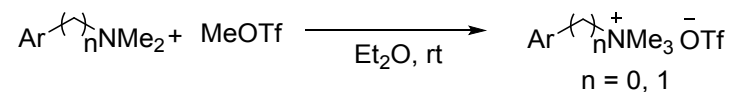
|   |      |
|---|------|
| Supporting information .....  | S1   |
| 1. General .....  | S3   |
| 2. General Procedure for Preparation of Ammonium Triflates <b>1</b> . ..... | S3   |
| 3. General Procedure for Cleavage of the C–N Bonds. ....                    | S5   |
| 4. Phenyl Radical Trapping Experiments .....                                | S25  |
| 5. Copies of NMR spectra .....  | S26  |
| 6. References .....   | S118 |

## 1. General

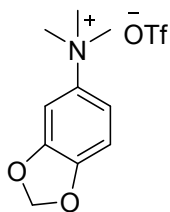
Commercial reagents and solvents were obtained from the commercial providers and used without further purification. The products were purified using a commercial flash chromatography system or a regular glass column. TLC was developed on silica gel 60 F254 glass plates.  $^1\text{H}$  NMR (400 MHz),  $^{13}\text{C}$  NMR (100 MHz),  $^1\text{H}$  NMR (600 MHz),  $^{13}\text{C}$  NMR (150 MHz) and  $^{19}\text{F}$  NMR (565 MHz) spectra were recorded on a Bruker NMR apparatus. The chemical shifts are reported in  $\delta$  (ppm) values ( $^1\text{H}$  and  $^{13}\text{C}$  NMR relative to  $\text{CHCl}_3$ ,  $\delta$  7.26 ppm for  $^1\text{H}$  NMR and  $\delta$  77.0 ppm for  $^{13}\text{C}$  NMR). Or alternatively,  $^1\text{H}$  NMR chemical shifts were referenced to tetramethylsilane signal (0 ppm). Multiplicities are recorded by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants ( $J$ ), are reported in Hertz (Hz). Commercial reagents were used without any further purification.

## 2. General Procedure for Preparation of Ammonium Triflates 1.

Ammonium Triflates **1** were prepared according to reported synthetic procedures.<sup>[1]</sup>

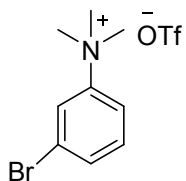


Dimethylamine (5 mmol, 1.0 equiv) was dissolved in  $\text{Et}_2\text{O}$  (10 mL). MeOTf (6.5 mmol, 1.3 equiv) was added dropwise at 0 °C. After complete addition, the reaction mixture was stirred for an additional 15–60 min at 0 °C. The solution was concentrated and washed with  $\text{Et}_2\text{O}$  ( $2 \times 20$  mL). The resulting compounds were dried under vacuum to give a salt.



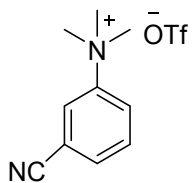
2p

(Benzo[d][1,3]dioxol-5-yl-dimethyl-4-azanylmethyl)trifluoromethanesulfonate (**2p**), 1.46 g, 90% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  7.70 (d,  $J = 2.8$  Hz, 1H), 7.39 (dd,  $J = 8.8, 2.8$  Hz, 1H), 7.11 (d,  $J = 8.7$  Hz, 1H), 6.18 (s, 2H), 3.54 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  148.8, 148.5, 141.7, 114.4, 108.4, 103.2, 102.7, 57.2. HRMS (ESI): calcd. for  $\text{C}_{10}\text{H}_{13}\text{NO}_2$  ( $[\text{M}-\text{OTf}]^+$ ) 179.0941, found 179.0967.



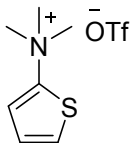
2q

(3-Cyanophenyl)dimethyl-4-azanylmethyl trifluoromethanesulfonate (**2q**), 1.67 g, 92% yield.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.28 – 8.24 (m, 1H), 7.99 (dd,  $J = 8.5, 2.6$  Hz, 1H), 7.82 (dd,  $J = 7.9, 1.7$  Hz, 1H), 7.61 (t,  $J = 8.3$  Hz, 1H), 3.61 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  148.71, 133.66, 132.30, 124.33, 123.03, 120.34, 56.92. HRMS (ESI): calcd. for  $\text{C}_9\text{H}_{12}\text{BrN}$  ( $[\text{M}-\text{OTf}]^+$ ) 213.0148, found 213.0157.



2s

((3-Cyanophenyl)dimethyl-14-azanylmethyl)trifluoromethanesulfonate (**2s**), 1.67 g, 92% yield.  $^1\text{H}$  NMR (400 MHz, DMSO- $d_6$ )  $\delta$  8.58 (dd,  $J$  = 2.8, 1.3 Hz, 1H), 8.34 (dd,  $J$  = 8.7, 2.8 Hz, 1H), 8.10 (dt,  $J$  = 7.8, 1.0 Hz, 1H), 7.87 (t,  $J$  = 8.2 Hz, 1H), 3.64 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz, DMSO)  $\delta$  147.9, 134.4, 131.8, 126.3, 125.6, 118.0, 113.3, 56.9. HRMS (ESI): calcd. for  $\text{C}_{10}\text{H}_{12}\text{N}_2$  ( $[\text{M}-\text{OTf}]^+$ ) 160.0995, found 160.0999.



**2u**

(Dimethyl(thiophen-2-yl)-14-azanylmethyl)trifluoromethanesulfonate (**2u**), 1.23 g, 85% yield.  $^1\text{H}$  NMR (300 MHz, DMSO- $d_6$ )  $\delta$  8.09 (dd,  $J$  = 3.1, 1.7 Hz, 1H), 7.86 (dd,  $J$  = 5.4, 3.1 Hz, 1H), 7.68 (dd,  $J$  = 5.4, 1.7 Hz, 1H), 3.58 (s, 9H).  $^{13}\text{C}$  NMR (101 MHz, DMSO)  $\delta$  145.8, 129.8, 121.2, 119.2, 57.3. HRMS (ESI): calcd. for  $\text{C}_7\text{H}_{11}\text{NS}$  ( $[\text{M}-\text{OTf}]^+$ ) 141.0607, found 141.0639.

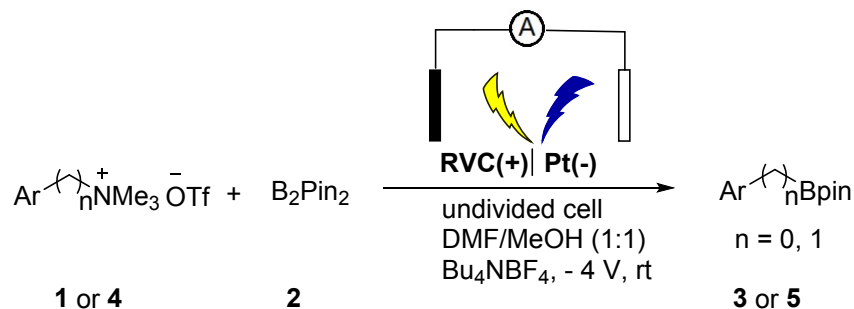
### 3. General Procedure for Cleavage of the C–N Bonds.



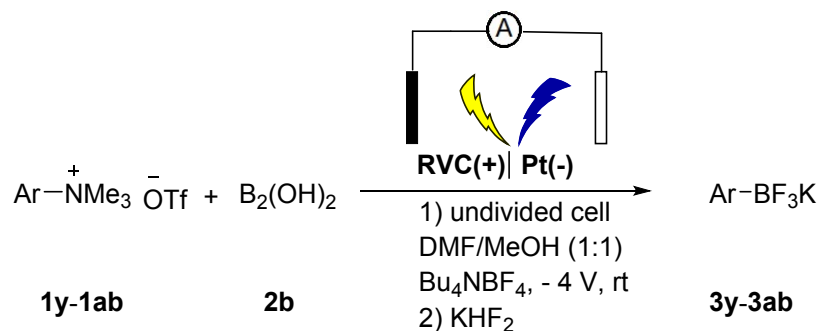
Reticulated Vitreous Carbon (RVC, Left) and Pt(Right)



Current controlled electrolysis ( ElectraSyn 2.0 apparatus, IKA)

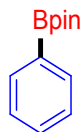


**General procedure A.** An undivided cell was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 0.5 cm × 0.5 cm), and Pt cathode (1 cm × 0.2cm) and connected to a DC regulated power supply. To the cell was added benzenaminium trifluoromethanesulfonate **1** (0.2 mmol), bis-(pinacolato)diboron **2a** (0.3 mmol, 76 mg) and 4 mL of 0.1 M n-Bu<sub>4</sub>NBF<sub>4</sub>/(DMF:MeOH = 1:1). The mixture was electrolyzed using V = -4 V at 30 °C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete (witnessed by the disappearance of **1** or **4**), the solvent was removed under reduced pressure. The product was then extracted with DCM (3×20 mL), dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether/EtOAc (v : v = 50 : 1) as eluent to afford the desired pure product.



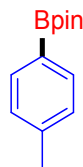
**General procedure B.** An undivided cell was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 0.5 cm × 0.5 cm) and Pt cathode (1 cm × 0.2cm) and connected to a DC regulated power supply. To the cell was added benzenaminium trifluoromethanesulfonate **1** (0.2 mmol), tetrahydroxydiboron **2b** (0.3 mmol, 27 mg) and 4 mL of 0.1 M n-Bu<sub>4</sub>NBF<sub>4</sub>/(DMF:MeOH = 1:1). The mixture was electrolyzed using V = -4 V at 30

°C under magnetic stirring. When TLC analysis indicated that the electrolysis was complete, the solvent was removed under reduced pressure. Dissolve the crude product in dichloromethane, filter to remove inorganic salts, and concentrate. MeOH was added to dilute the crude product. Saturated KHF<sub>2</sub> (4.5 M) was added dropwise via a syringe. The resulting slurry was stirred for 3 hours, concentrated. The dried solids were triturated with hot acetone and filtered to remove inorganic salts. The resulting filtrate was concentrated to a minimal volume, and Et<sub>2</sub>O was added to afford the desired pure product.



**3a**

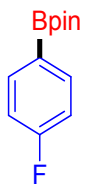
4,4,5,5-Tetramethyl-2-phenyl-1,3,2-dioxaborolane (**3a**), 33.1 mg, 81% yield. R<sub>f</sub> = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.81 (d, *J* = 7.8 Hz, 2H), 7.44 (t, *J* = 6.8 Hz, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 1.32 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 134.83, 131.33, 127.78, 83.80, 24.95. HRMS (ESI): calcd. for C<sub>12</sub>H<sub>18</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 205.1400, found 205.1403.



**3b**

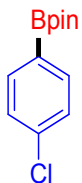


4,4,5,5-Tetramethyl-2-(p-tolyl)-1,3,2-dioxaborolane (**3b**), 36.2 mg, 83% yield. Rf = 0.2 (5:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.71 (d, *J* = 7.6 Hz, 2H), 7.18 (d, *J* = 7.6 Hz, 2H), 2.36 (s, 3H), 1.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 141.42, 134.86, 128.56, 83.64, 24.89, 21.76. HRMS (ESI): calcd. for C<sub>13</sub>H<sub>20</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>) 219.1556, found 219.1552.



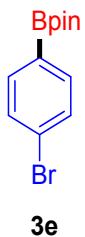
**3c**

2-(4-Fluorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3c**), 37.7 mg, 85% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.84 – 7.75 (m, 2H), 7.10 – 7.00 (m, 2H), 1.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 165.08 (d, *J* = 251.5 Hz), 136.96 (d, *J* = 9.1 Hz), 114.82 (d, *J* = 20.2 Hz), 83.89, 24.84. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -108.36--108.41(m). HRMS (ESI): calcd. for C<sub>12</sub>H<sub>17</sub>BF<sub>2</sub>O<sub>2</sub> ([M+H]<sup>+</sup>) 223.1306, found 223.1310.

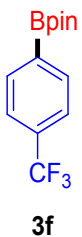


**3d**

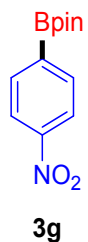
2-(4-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3d**), 40.0 mg, 84% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.73 (d,  $J = 8.2$  Hz, 2H), 7.34 (d,  $J = 8.3$  Hz, 2H), 1.33 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.55, 136.14, 128.01, 84.01, 24.87. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BClO}_2$  ( $[\text{M}+\text{H}]^+$ ) 239.1010, found 239.1015.



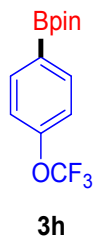
2-(4-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3e**), 47.9 mg, 85% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.66 (d,  $J = 8.0$  Hz, 2H), 7.49 (d,  $J = 8.2$  Hz, 2H), 1.32 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.38, 130.98, 126.26, 84.02, 24.91. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BBrO}_2$  ( $[\text{M}+\text{H}]^+$ ) 283.0505, found 283.0502.



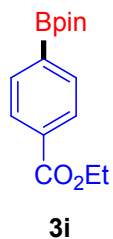
4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)phenyl)-1,3,2-dioxaborolane (**3f**), 43.5 mg, 80% yield. Rf = 0.5 (50:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.93 (d,  $J$  = 7.7 Hz, 2H), 7.61 (d,  $J$  = 7.7 Hz, 2H), 1.35 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.05, 132.87 (q,  $J$  = 32 Hz), 124.15 (q,  $J$  = 270.0 Hz), 124.30 (q,  $J$  = 4.0 Hz), 84.26, 24.79. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{17}\text{BF}_3\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ): 273.1274, found 273.1277.



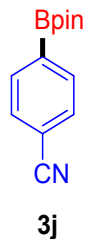
4,4,5,5-Tetramethyl-2-(4-nitrophenyl)-1,3,2-dioxaborolane (**3g**), 35.4 mg, 71% yield. Rf = 0.2 (30:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.19 (d,  $J$  = 8.6 Hz, 2H), 7.96 (d,  $J$  = 8.5 Hz, 2H), 1.37 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.85, 135.67, 122.41, 84.64, 24.88. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BNO}_4$  ( $[\text{M}+\text{H}]^+$ ): 250.1251, found 250.1250.



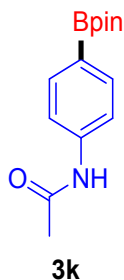
4,4,5,5-Tetramethyl-2-(4-(trifluoromethoxy)phenyl)-1,3,2-dioxaborolane (**3h**), 43.8 mg, 76% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.84 (d,  $J = 8.3$  Hz, 2H), 7.20 (d,  $J = 7.8$  Hz, 2H), 1.34 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  151.69, 151.67, 136.54, 119.87, 84.07, 24.83.  $^{19}\text{F}$  NMR (377 MHz,  $\text{CDCl}_3$ )  $\delta$  -57.60. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{17}\text{BF}_3\text{O}_3$  ( $[\text{M}+\text{H}]^+$ ): 289.1223, found 289.1226.



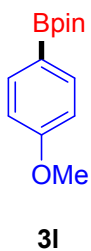
ethyl 4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzoate (**3i**), 43.6 mg, 79% yield.  $R_f = 0.2$  (30:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.03 (d,  $J = 8.2$  Hz, 2H), 7.87 (d,  $J = 8.1$  Hz, 2H), 4.38 (q,  $J = 7.1$  Hz, 2H), 1.39 (t,  $J = 7.1$  Hz, 3H), 1.35 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  166.60, 134.63, 132.67, 128.54, 84.13, 60.99, 24.87, 14.32. HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{22}\text{BO}_4$  ( $[\text{M}+\text{H}]^+$ ): 277.1611, found 277.1615.



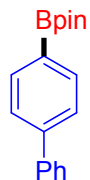
4-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**3j**), 35.7 mg, 78% yield.  $R_f = 0.2$  (10:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.87 (d,  $J = 8.0$  Hz, 2H), 7.61 (d,  $J = 8.0$  Hz, 2H), 1.33 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  135.11, 131.09, 118.80, 114.52, 84.47, 24.86. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{17}\text{BNO}_2$  ( $[\text{M}+\text{H}]^+$ ): 230.1352, found 230.1350.



N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)acetamide (**3k**), 39.67 mg, 76% yield. Rf = 0.2 (10:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 8.1 Hz, 2H), 7.46 (s, 1H), 2.17 (s, 3H), 1.33 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.42, 140.60, 135.81, 118.56, 83.76, 24.87, 24.78. HRMS (ESI): calcd. for C<sub>14</sub>H<sub>21</sub>BNO<sub>3</sub> ([M+H]<sup>+</sup>): 262.1614, found 262.1614.

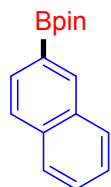


2-(4-Methoxyphenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3l**), 37.4 mg, 80% yield. Rf = 0.2 (30:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.71 (m, 1H), 6.93 – 6.83 (m, 1H), 3.81 (s, 2H), 1.33 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 162.17, 136.54, 113.33, 83.56, 55.09, 24.88. HRMS (ESI) calcd for C<sub>13</sub>H<sub>20</sub>BO<sub>3</sub> ([M+H]<sup>+</sup>): 235.1506, found 235.1509.



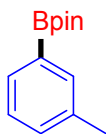
**3m**

2-([1,1'-Biphenyl]-4-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4m**), 45.9 mg, 82% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.89 (d,  $J = 8.1$  Hz, 2H), 7.61 (d,  $J = 7.6$  Hz, 4H), 7.43 (t,  $J = 7.5$  Hz, 2H), 7.34 (t,  $J = 7.3$  Hz, 1H), 1.35 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.94, 141.07, 135.32, 128.82, 127.61, 127.28, 126.52, 83.86, 24.94. HRMS (ESI): calcd. for  $\text{C}_{18}\text{H}_{22}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ): 281.1713, found 281.1714.



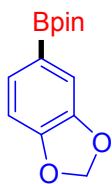
**3n**

4,4,5,5-Tetramethyl-2-(naphthalen-2-yl)-1,3,2-dioxaborolane (**3n**), 40.7 mg, 80% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  8.39 (d,  $J = 4.4$  Hz, 1H), 7.86 (d,  $J = 6.0$  Hz, 2H), 7.83 – 7.73 (m, 2H), 7.44 (d,  $J = 7.1$  Hz, 2H), 1.34 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.41, 136.39, 135.18, 135.16, 132.95, 130.56, 130.54, 128.76, 127.83, 127.12, 127.09, 125.93, 83.99, 25.03. HRMS (ESI): calcd for  $\text{C}_{16}\text{H}_{20}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ): 255.1556, found 255.1558.



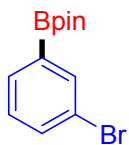
**3o**

4,4,5,5-Tetramethyl-2-(m-tolyl)-1,3,2-dioxaborolane (**4o**), 35.8 mg, 82% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.67 – 7.57 (m, 2H), 7.25 (d,  $J = 4.5$  Hz, 2H), 2.34 (s, 3H), 1.33 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.12, 135.43, 132.10, 131.89, 127.76, 83.74, 24.93, 21.33. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{20}\text{BO}_2$  ( $[\text{M}+\text{H}]^+$ ): 219.1556, found 219.1561.



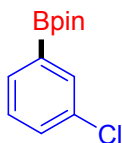
**3p**

2-(Benzo[d][1,3]dioxol-5-yl)-4,4,5,5-Tetramethyl-1,3,2-dioxaborolane (**3p**), 41.3 mg, 83% yield.  $R_f = 0.2$  (30:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.35 (d,  $J = 7.7$  Hz, 1H), 7.24 (s, 1H), 6.82 (d,  $J = 7.7$  Hz, 1H), 5.93 (s, 2H), 1.32 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz, Chloroform)  $\delta$  150.20, 147.23, 129.75, 113.96, 108.30, 100.74, 83.70, 24.86. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{18}\text{BO}_4$  ( $[\text{M}+\text{H}]^+$ ): 249.1298, found 249.1300.



**3q**

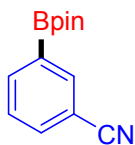
2-(3-Bromophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3q**), 46.3 mg, 82% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.93 (s, 1H), 7.71 (d,  $J$  = 7.3 Hz, 1H), 7.61 – 7.55 (m, 1H), 7.23 (t,  $J$  = 7.7 Hz, 1H), 1.34 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.50, 134.19, 133.11, 129.51, 122.47, 84.16, 24.88. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BBrO}_2$  ( $[\text{M}+\text{H}]^+$ ): 283.0505, found 283.0509.



**3r**

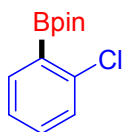
2-(3-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3r**), 39.0 mg, 82% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.78 (s, 1H), 7.67 (d,  $J$  = 7.3 Hz, 1H), 7.44 – 7.40 (m, 1H), 7.29 (t,  $J$  = 7.7 Hz, 1H), 1.34 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  134.59, 134.05, 132.68, 131.28, 129.22, 84.15, 24.88. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BClO}_2$  ( $[\text{M}+\text{H}]^+$ ): 239.1010, found 239.1014.





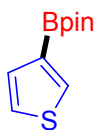
**3s**

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)benzonitrile (**3s**), 33.0 mg, 72% yield. Rf = 0.2 (30:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  8.09 (s, 1H), 8.01 (d,  $J$  = 7.5 Hz, 1H), 7.72 (d,  $J$  = 6.5 Hz, 1H), 7.47 (t,  $J$  = 7.6 Hz, 1H), 1.35 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.75, 138.41, 134.39, 128.40, 118.83, 112.09, 84.49, 24.87. HRMS (ESI): calcd. for  $\text{C}_{13}\text{H}_{17}\text{BNO}_2$  ( $[\text{M}+\text{H}]^+$ ): 230.1352, found 230.1357.



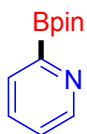
**3t**

2-(2-Chlorophenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4t**), 34.7 mg, 73% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc),  $^1\text{H}$  NMR (400 MHz, Chloroform- $d$ )  $\delta$  7.67 (s, 1H), 7.38 – 7.29 (m, 2H), 7.22 (td,  $J$  = 7.5, 2.3 Hz, 1H), 1.37 (s, 12H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.54, 136.41, 131.83, 129.38, 125.80, 84.15, 24.80. HRMS (ESI): calcd. for  $\text{C}_{12}\text{H}_{17}\text{BClO}_2$  ( $[\text{M}+\text{H}]^+$ ): 239.1010, found 239.1013.



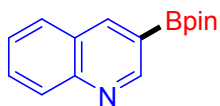
**3u**

4,4,5,5-Tetramethyl-2-(thiophen-3-yl)-1,3,2-dioxaborolane (**4u**), 29.4 mg, 70% yield.  $R_f = 0.2$  (10:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.94 – 7.90 (m, 1H), 7.41 (d,  $J = 4.8$  Hz, 1H), 7.32 (dd,  $J = 4.8, 2.7$  Hz, 1H), 1.32 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  136.51, 132.08, 125.36, 83.65, 24.88. HRMS (ESI): calcd. for  $\text{C}_{10}\text{H}_{16}\text{BO}_2\text{S}$  ( $[\text{M}+\text{H}]^+$ ): 211.0964, found 211.0971.



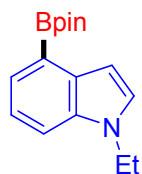
**3v**

2-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)pyridine (**4v**), 26.7 mg, 65% yield.  $R_f = 0.2$  (10:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  8.95 (s, 1H), 8.67 (dd,  $J = 5.0, 1.8$  Hz, 1H), 8.06 (d,  $J = 7.5$  Hz, 1H), 7.28 (ddd,  $J = 7.5, 4.9, 1.0$  Hz, 1H), 1.35 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  155.43, 151.92, 142.21, 123.06, 84.19, 24.84. HRMS (ESI): calcd. for  $\text{C}_{11}\text{H}_{17}\text{BNO}_2$  ( $[\text{M}+\text{H}]^+$ ): 206.1352, found 206.1358.



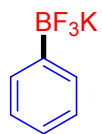
**3w**

3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)quinoline (**3w**), 27.5 mg, 54% yield.  $R_f = 0.2$  (5:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  9.22 (d,  $J = 1.3$  Hz, 1H), 8.63 (s, 1H), 8.12 (d,  $J = 8.5$  Hz, 1H), 7.83 (d,  $J = 8.1$  Hz, 1H), 7.73 (t,  $J = 7.6$  Hz, 1H), 7.52 (t,  $J = 7.5$  Hz, 1H), 1.39 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  154.75, 149.39, 144.25, 130.51, 129.31, 128.38, 127.54, 126.47, 84.30, 24.89. HRMS (ESI): calcd. for  $\text{C}_{15}\text{H}_{19}\text{BNO}_2$  ( $[\text{M}+\text{H}]^+$ ): 256.1509, found 256.1512.



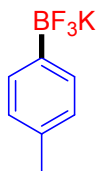
**3x**

1-Ethyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1H-indole (**3x**), 33.2 mg, 61% yield. R<sub>f</sub> = 0.2 (5:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 8.16 (s, 1H), 7.65 (d, *J* = 8.3 Hz, 1H), 7.33 (d, *J* = 8.3 Hz, 1H), 7.08 (d, *J* = 3.2 Hz, 1H), 6.50 (d, *J* = 3.2 Hz, 1H), 4.15 (q, *J* = 7.3 Hz, 2H), 1.43 (t, *J* = 7.3 Hz, 3H), 1.36 (s, 12H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 137.70, 129.00, 128.46, 127.49, 127.18, 108.69, 101.85, 83.41, 40.98, 24.94, 15.47. HRMS (ESI): calcd. for C<sub>16</sub>H<sub>23</sub>BNO<sub>2</sub> ([M+H]<sup>+</sup>): 272.1822, found 272.1827.



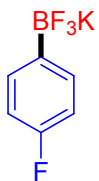
**3y**

Trifluoro(phenyl)-14-borane, potassium salt (**3y**), 32.6 mg, 89% yield. <sup>1</sup>H NMR (400 MHz, Acetone-d<sub>6</sub>) δ 7.49 (d, *J* = 7.2 Hz, 2H), 7.11 (t, *J* = 7.2 Hz, 2H), 7.08 – 7.01 (m, 1H). <sup>13</sup>C NMR (100 MHz, Acetone) δ 131.56, 126.20, 125.09. HRMS (ESI): calcd. for C<sub>6</sub>H<sub>5</sub>BF<sub>3</sub> ([M-K]<sup>-</sup>): 145.0436, found 145.0439.



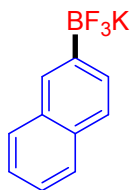
**3z**

Trifluoro(p-tolyl)-l4-borane, potassium salt (**3z**),<sup>2</sup> 33.6 mg, 85% yield. <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>) δ 7.38 (d, *J* = 7.4 Hz, 2H), 6.94 (d, *J* = 7.4 Hz, 2H), 2.24 (s, 3H). <sup>13</sup>C NMR (100 MHz, Acetone) δ 133.72, 131.64, 131.62, 126.96, 20.52.



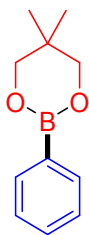
**3aa**

Trifluoro(p-tolyl)-l4-borane, potassium salt (**3aa**),<sup>2</sup> 32.6 mg, 81% yield. <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>) δ 7.58 – 7.42 (m, 2H), 6.92 – 6.73 (m, 2H). <sup>13</sup>C NMR (100 MHz, Acetone) δ 163.10, 160.72, 133.18, 112.89, 112.71. <sup>19</sup>F NMR (376 MHz, Acetone) δ -119.37, -142.04.



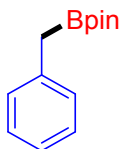
**3ab**

Trifluoro(naphthalen-2-yl)-14-borane, potassium salt (**3ab**),<sup>2</sup> 35.6 mg, 76% yield. <sup>1</sup>H NMR (300 MHz, Acetone-d<sub>6</sub>) δ 7.97 (s, 1H), 7.79 – 7.68 (m, 3H), 7.64 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.28 (m, 2H). <sup>13</sup>C NMR (100 MHz, Acetone) δ 133.52, 132.80, 130.92, 130.06, 127.70, 127.29, 125.11, 124.32, 123.94.



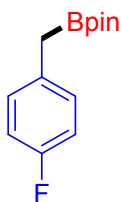
**3ac**

5,5-Dimethyl-2-phenyl-1,3,2-dioxaborinane (**3ac**), 31.5 mg, 83% yield. *R*<sub>f</sub> = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.80 (d, *J* = 7.8 Hz, 2H), 7.45 – 7.38 (m, 1H), 7.38 – 7.30 (m, 2H), 3.75 (s, 4H), 1.00 (s, 6H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 133.91, 130.75, 127.64, 72.35, 31.93, 21.96. HRMS (ESI): calcd. For C<sub>11</sub>H<sub>16</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>): 191.1243, found 191.1247.



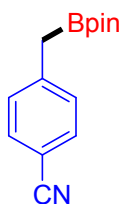
**5a**

2-Benzyl-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5a**), 24.9 mg, 61% yield. R<sub>f</sub> = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.23 (t, *J* = 7.5 Hz, 2H), 7.18 (d, *J* = 7.5 Hz, 2H), 7.11 (t, *J* = 7.1 Hz, 1H), 2.29 (s, 2H), 1.22 (s, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 138.67, 129.04, 128.31, 124.89, 83.45, 24.78. HRMS (ESI): calcd. for C<sub>13</sub>H<sub>20</sub>BO<sub>2</sub> ([M+H]<sup>+</sup>): 219.1556, found 219.1554.



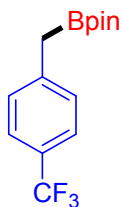
**5b**

2-(4-Fluorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5b**), 22.6 mg, 51% yield. R<sub>f</sub> = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.15 – 7.09 (m, 2H), 6.91 (t, *J* = 8.6 Hz, 2H), 2.25 (s, 2H), 1.22 (s, 12H). <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 160.80 (d, *J* = 240.0 Hz), 134.13 (d, *J* = 3.0 Hz), 130.20 (d, *J* = 7.5 Hz), 114.94 (d, *J* = 21.2 Hz), 83.5, 24.70. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -119.35. HRMS (ESI): calcd. for C<sub>13</sub>H<sub>19</sub>BFO<sub>2</sub> ([M+H]<sup>+</sup>): 237.1462, found 237.1465.



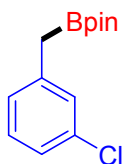
**5c**

4-((4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)methyl)benzonitrile (**5c**), 21.1 mg, 46% yield. R<sub>f</sub> = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 7.9 Hz, 2H), 2.36 (s, 2H), 1.23 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 145.01, 132.03, 129.70, 119.32, 108.66, 83.80, 24.70. HRMS (ESI): calcd. for C<sub>14</sub>H<sub>19</sub>BNO<sub>2</sub> ([M+H]<sup>+</sup>): 244.1509, found 244.1512.



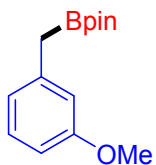
**5d**

4,4,5,5-Tetramethyl-2-(4-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (**5d**), 26.7 mg, 49% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.48 (d, *J* = 7.9 Hz, 2H), 7.28 (d, *J* = 7.9 Hz, 2H), 2.35 (s, 2H), 1.23 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 143.15 (q, *J* = 30 Hz), 129.18, 125.14 (q, *J* = 60.0 Hz), 83.70, 24.68. <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -62.19. HRMS (ESI): calcd. for C<sub>14</sub>H<sub>19</sub>BF<sub>3</sub>O<sub>2</sub> ([M+H]<sup>+</sup>): 287.1430, found 287.1432.



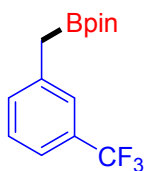
**5e**

2-(3-Chlorobenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5e**), 19.9 mg, 42% yield. Rf = 0.2 (50:1 Petroleum Ether/EtOAc), <sup>1</sup>H NMR (400 MHz, Chloroform-d) δ 7.17 (d, *J* = 2.4 Hz, 1H), 7.13 (d, *J* = 7.6 Hz, 1H), 7.07 (ddt, *J* = 13.9, 7.4, 1.6 Hz, 2H), 2.26 (s, 2H), 1.23 (s, 12H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 140.79, 133.92, 129.42, 129.07, 127.21, 125.08, 83.62, 24.72. HRMS (ESI): calcd. for C<sub>13</sub>H<sub>19</sub>BClO<sub>2</sub> ([M+H]<sup>+</sup>): 253.1167, found 253.1171.



**5f**

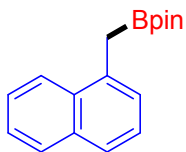
2-(3-Methoxybenzyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**5f**), 22.0 mg, 47% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.15 (t,  $J = 7.8$  Hz, 1H), 6.84 – 6.73 (m, 2H), 6.67 (dd,  $J = 8.4, 2.6$  Hz, 1H), 3.78 (s, 3H), 1.23 (s, 13H).  $^{13}\text{C NMR}$  (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.53, 140.21, 129.17, 121.53, 114.61, 110.43, 83.46, 55.08, 24.74. HRMS (ESI): calcd. for  $\text{C}_{14}\text{H}_{22}\text{BO}_3$  ( $[\text{M}+\text{H}]^+$ ): 249.1662, found 249.1661.



**5g**

4,4,5,5-Tetramethyl-2-(3-(trifluoromethyl)benzyl)-1,3,2-dioxaborolane (**5g**), 28.3 mg, 52% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (400 MHz, Chloroform- $d$ )  $\delta$  7.44 (d,  $J = 2.2$  Hz, 1H), 7.40 – 7.30 (m, 3H), 2.34 (s, 2H), 1.23 (s, 12H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.70, 132.41 (t,  $J = 3.0$  Hz), 130.54 (q,  $J = 48.0$  Hz), 125.66 (q,  $J = 4.5$  Hz), 121.76 (q,  $J = 4.5$  Hz), 83.68, 24.65.  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -62.59. HRMS (ESI): calcd for  $\text{C}_{14}\text{H}_{19}\text{BF}_3\text{O}_2$  ( $[\text{M}+\text{H}]^+$ ): 287.1430, found 287.1438.

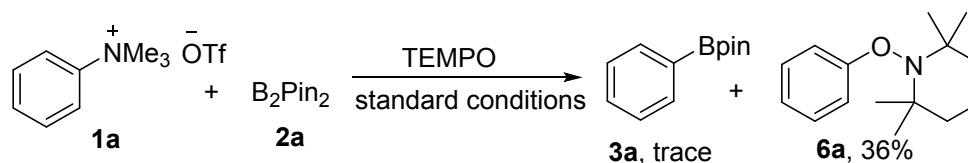




**5h**

4,4,5,5-Tetramethyl-2-(naphthalen-1-ylmethyl)-1,3,2-dioxaborolane (**5h**),<sup>3</sup> 26.8 mg, 50% yield.  $R_f = 0.2$  (50:1 Petroleum Ether/EtOAc),  $^1\text{H NMR}$  (300 MHz, Chloroform- $d$ )  $\delta$  8.00 (dd,  $J = 8.1, 1.5$  Hz, 1H), 7.85 – 7.77 (m, 1H), 7.68 – 7.62 (m, 1H), 7.49 – 7.43 (m, 2H), 7.38 – 7.32 (m, 2H), 2.69 (s, 2H), 1.19 (s, 12H).  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ )  $\delta$  135.62, 133.78, 132.45, 128.52, 126.47, 125.79, 125.38, 125.35, 124.54, 83.56, 24.69.

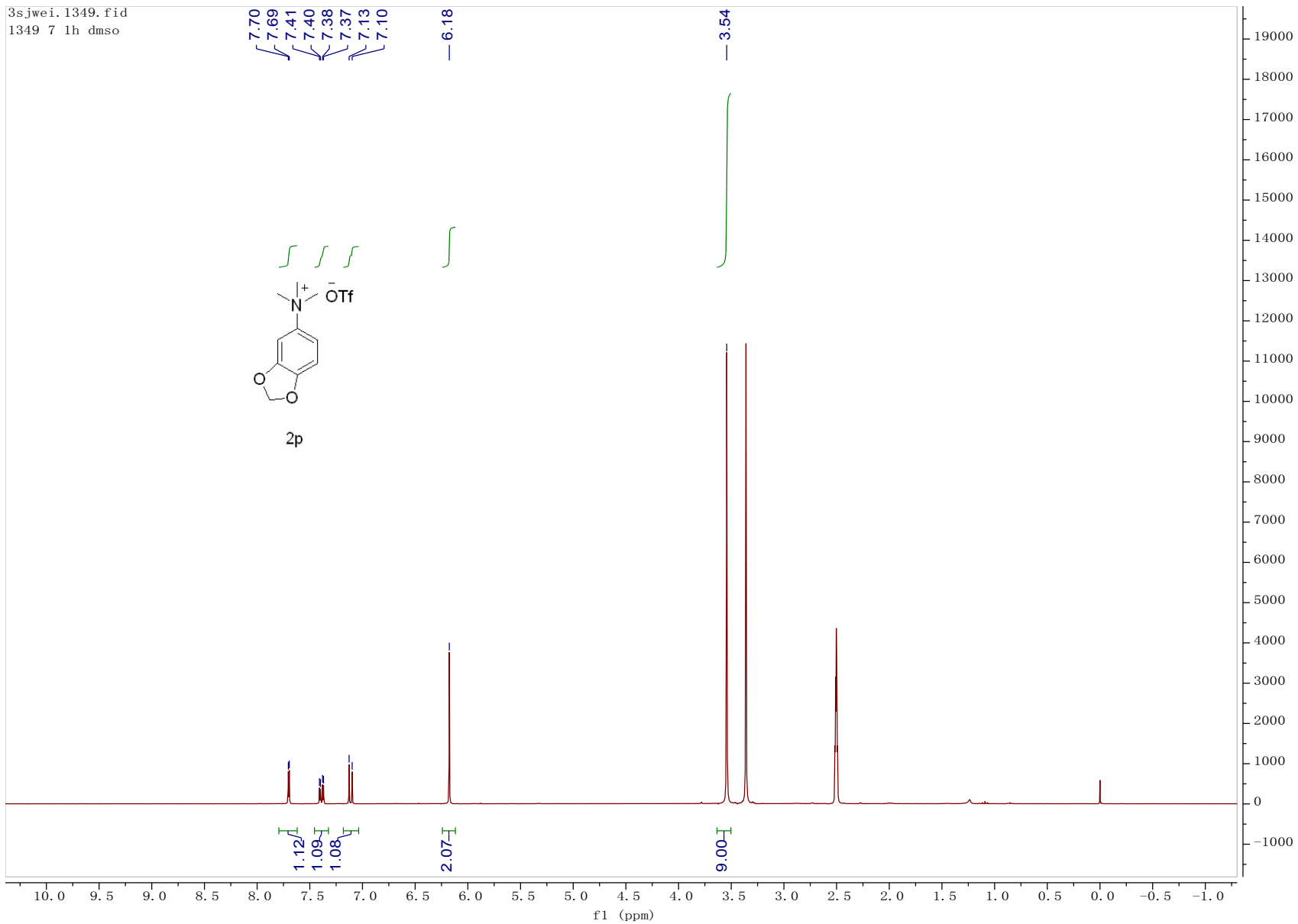
#### 4. Phenyl Radical Trapping Experiments

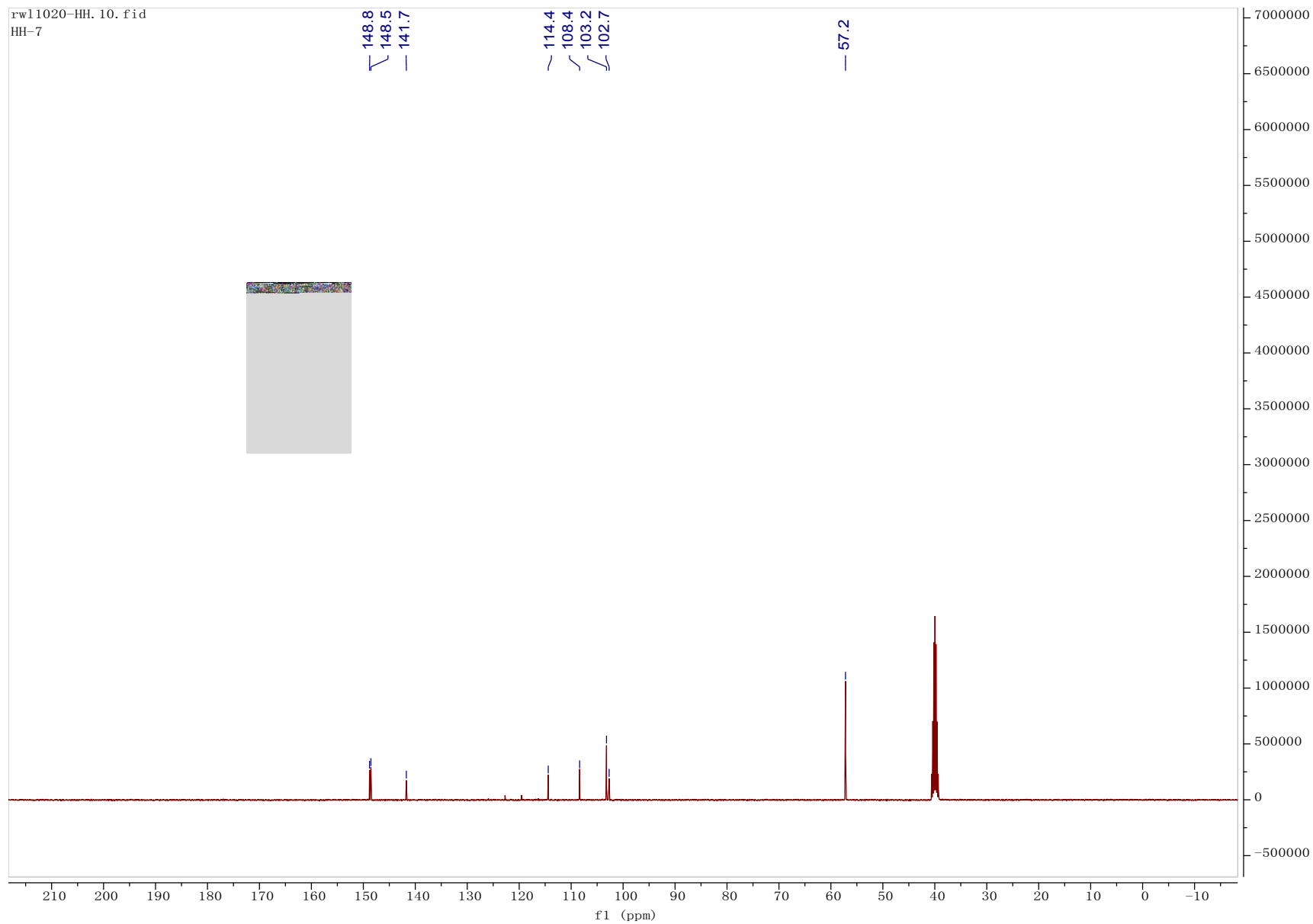


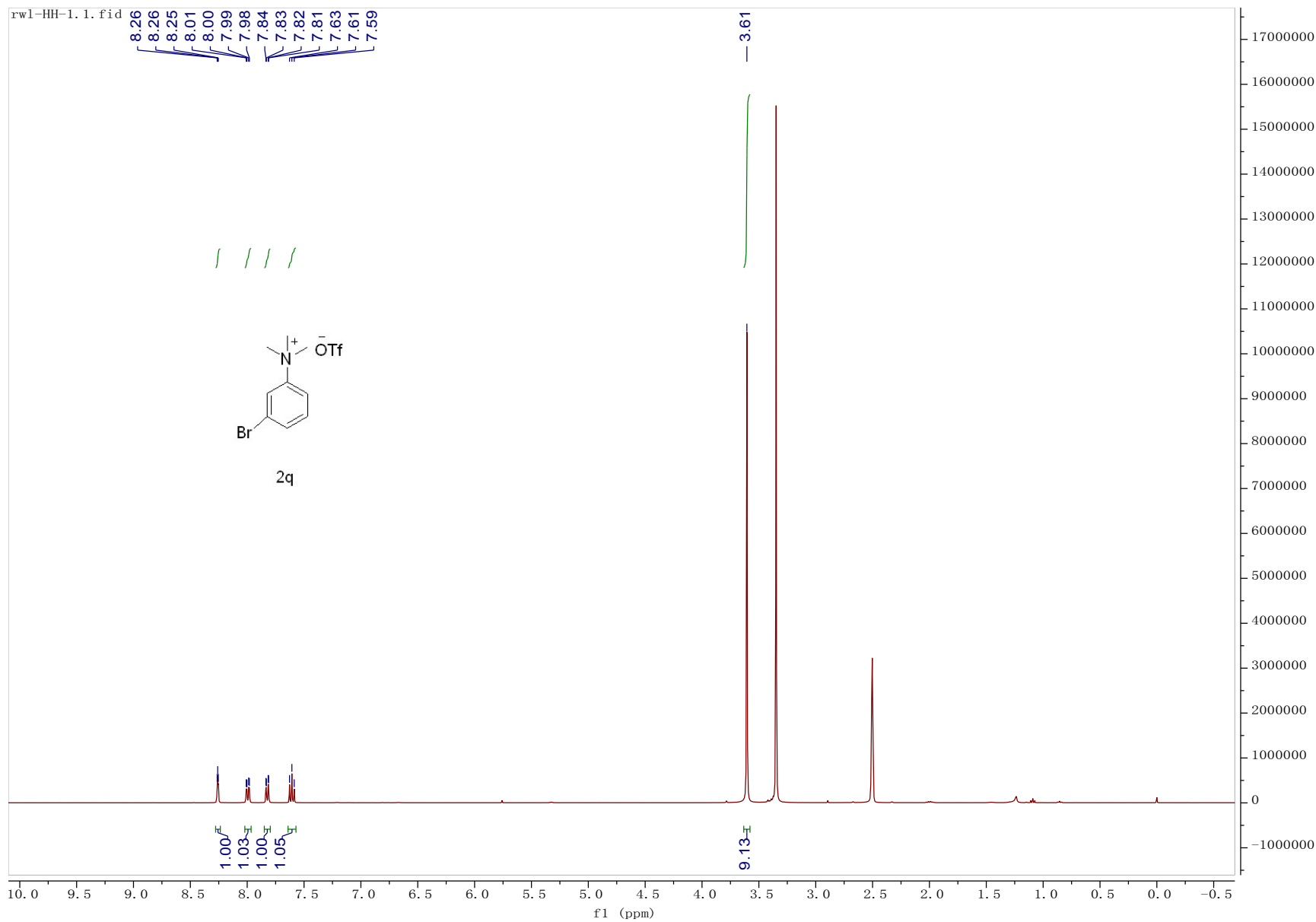
An undivided cell was equipped with a reticulated vitreous carbon (RVC) anode (100 PPI, 0.5 cm  $\times$  0.5 cm) and Pt cathode (1 cm  $\times$  0.2cm) and connected to a DC regulated power supply. To the cell was added benzenaminium trifluoromethanesulfonate **1a** (0.2 mmol, 57mg), bis-(pinacolato)diboron **2a** (0.3 mmol, 76 mg), 2,2,6,6-Tetramethylpiperidinoxy (0.4 mmol, 62.4 mg) and 4 mL of 0.1 M  $n\text{-Bu}_4\text{NBF}_4/(\text{DMF}:\text{MeOH} = 1:1)$ . The mixture was electrolyzed using  $V = -4$  V at 30  $^\circ\text{C}$  under magnetic stirring. When TLC analysis indicated that the electrolysis was complete, the solvent was removed under reduced pressure. The product was then extracted with DCM (3 $\times$ 20 mL), dried over  $\text{Na}_2\text{SO}_4$ , and concentrated in vacuo. The residue was purified by column chromatography on silica gel using a mixture of petroleum ether as eluent to afford the desired pure product **6a** 16.8 mg, 36%.<sup>4</sup>  $^1\text{H NMR}$  (300 MHz, Chloroform- $d$ )  $\delta$  7.18 (dd,  $J = 4.6, 2.6$  Hz, 4H), 6.82 (d,  $J = 4.1$  Hz, 1H), 1.67 – 1.47 (m, 5H), 1.43 – 1.32 (m, 1H), 1.22 (s, 6H), 1.01 (s, 6H).  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  163.74, 128.85, 120.10, 114.03, 60.45, 39.96, 32.81, 20.64, 17.26.

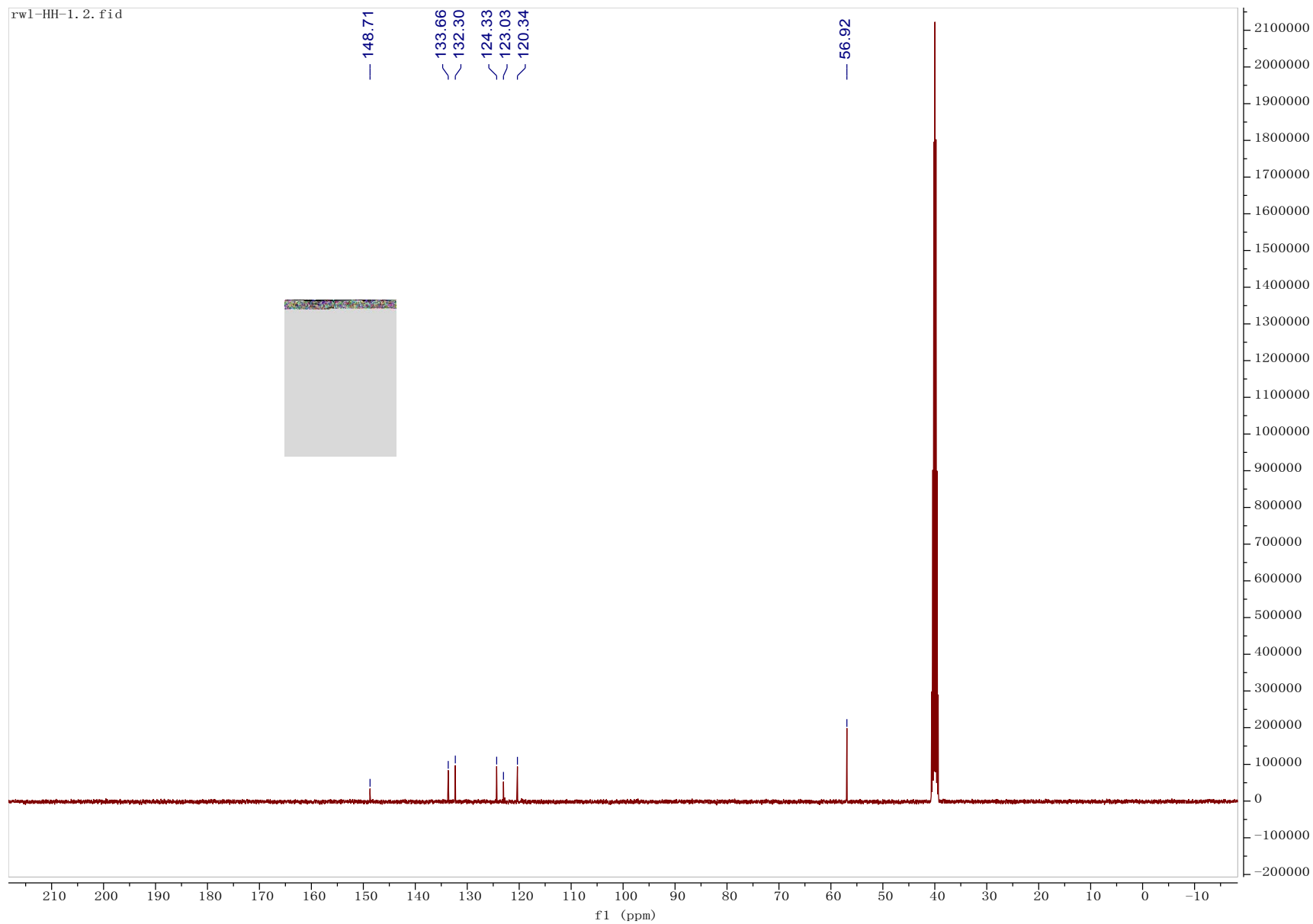
## **5. Copies of NMR spectra**

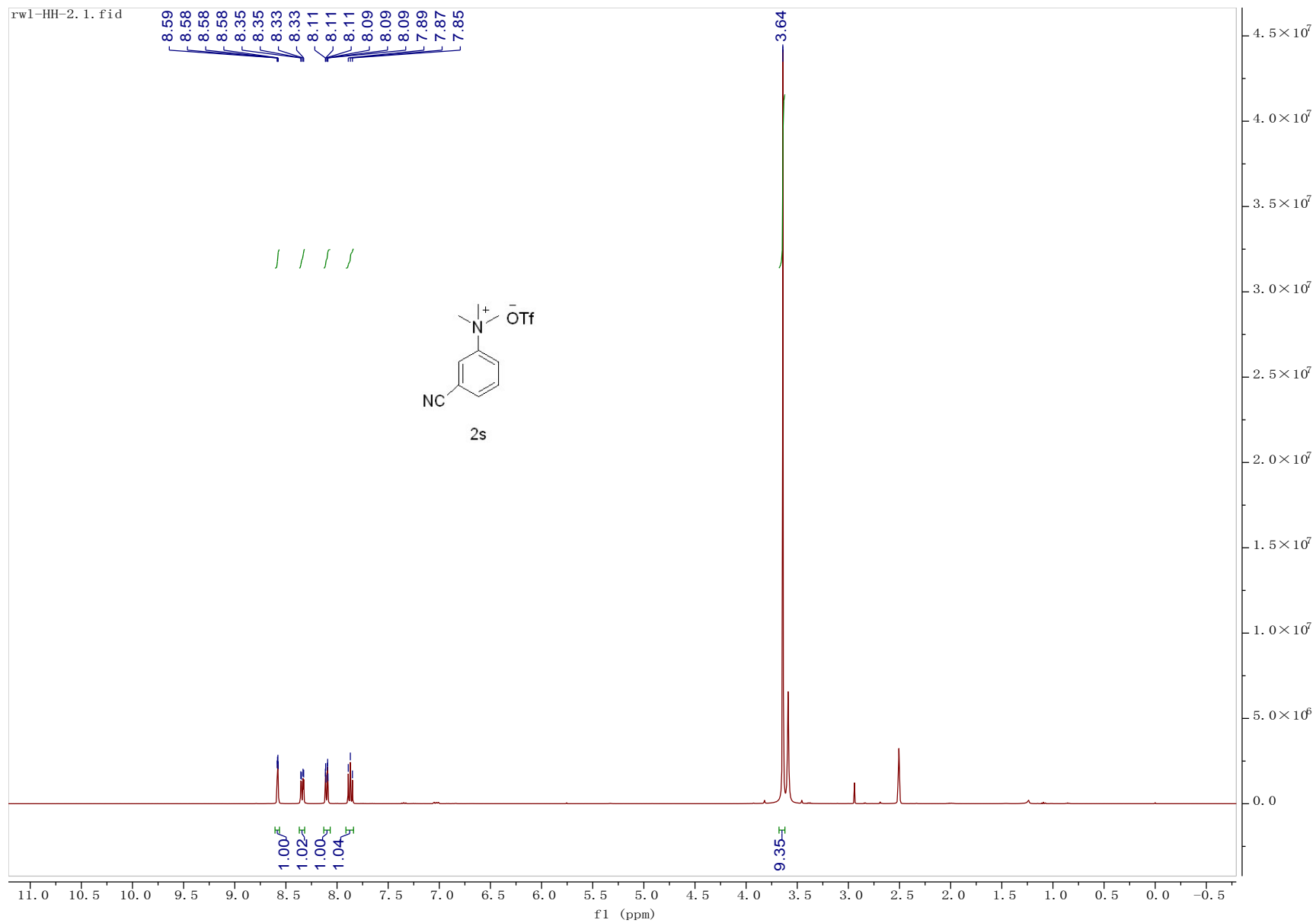
3sjwei.1349.fid  
1349 7 1h dmso

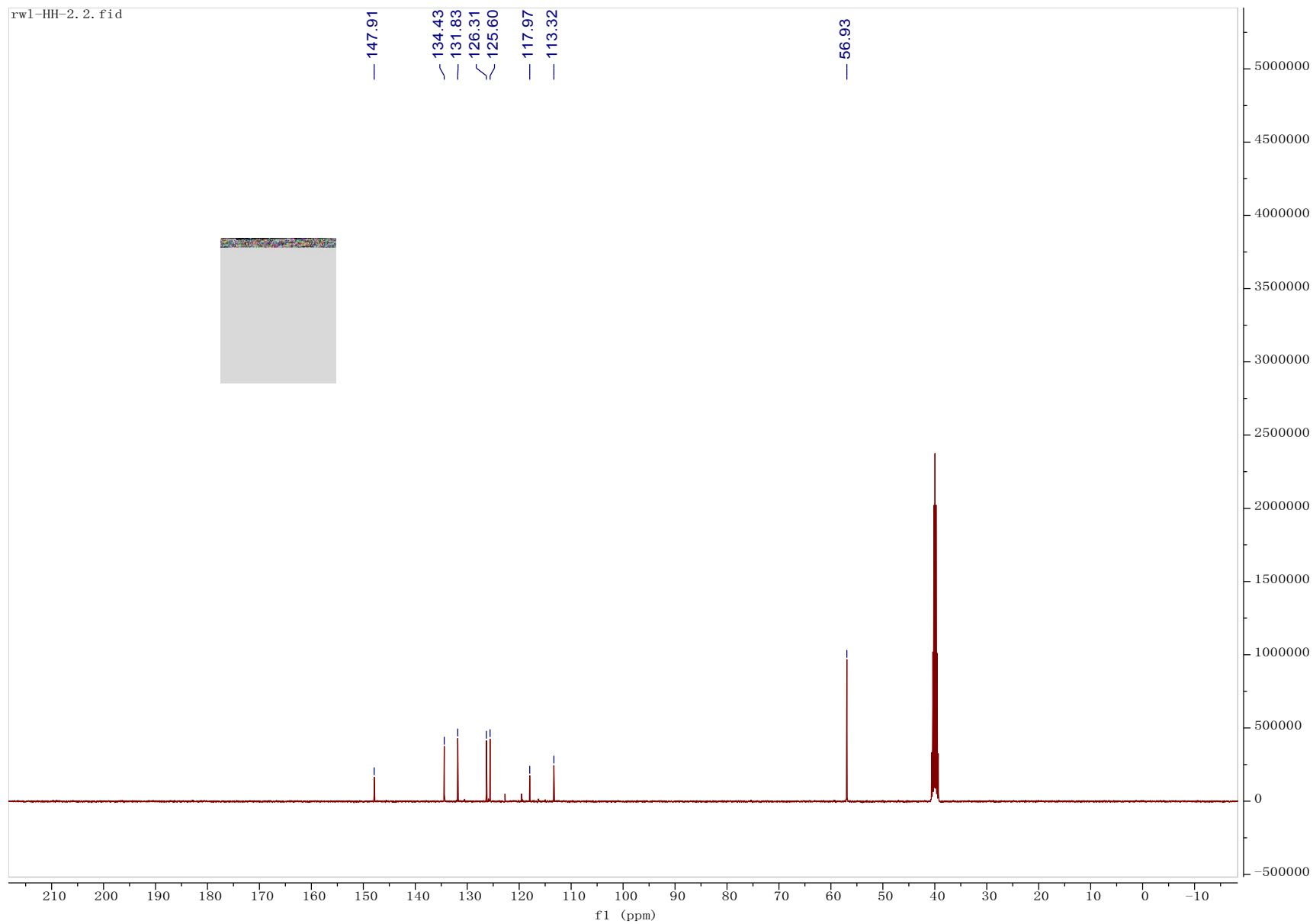




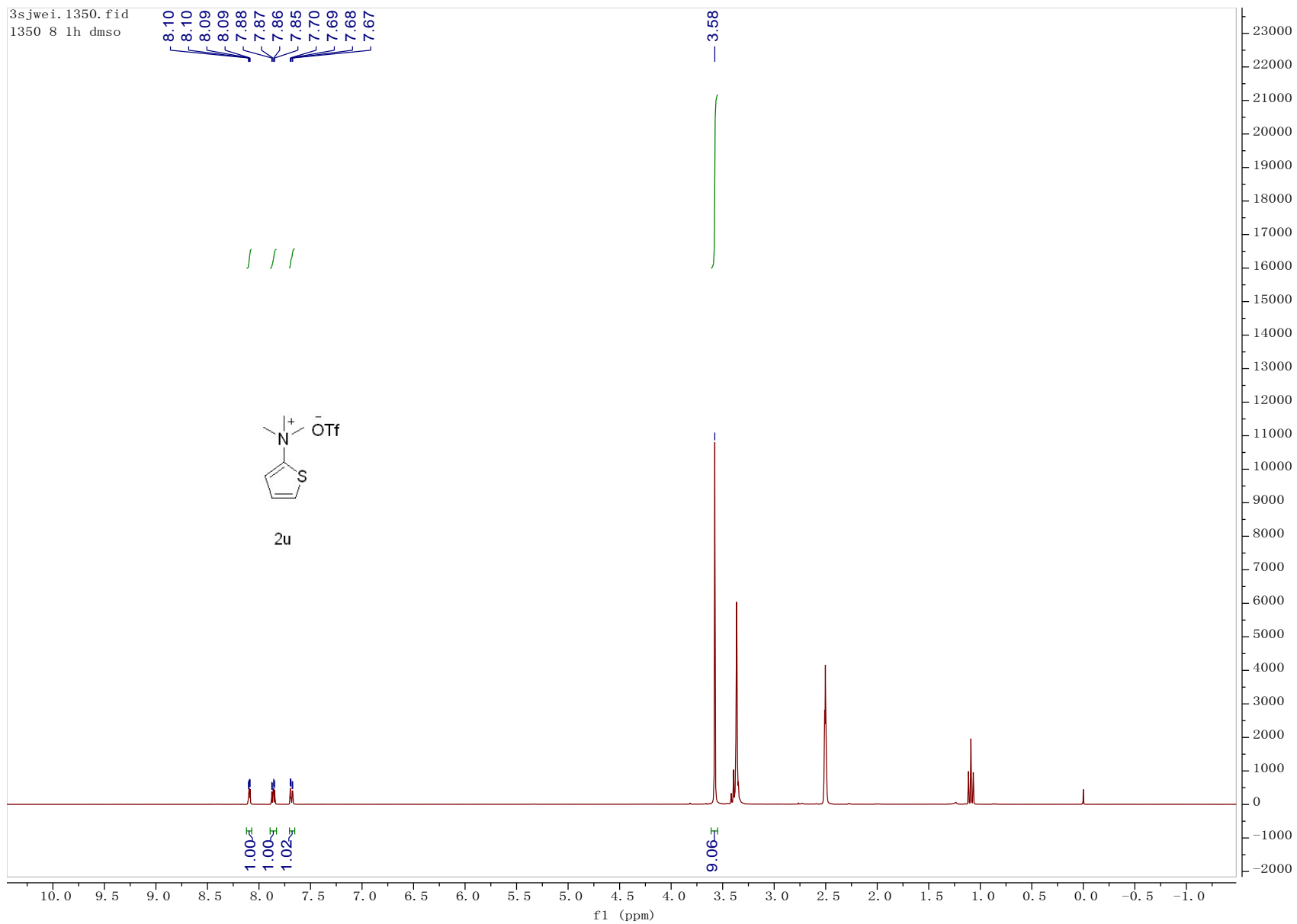




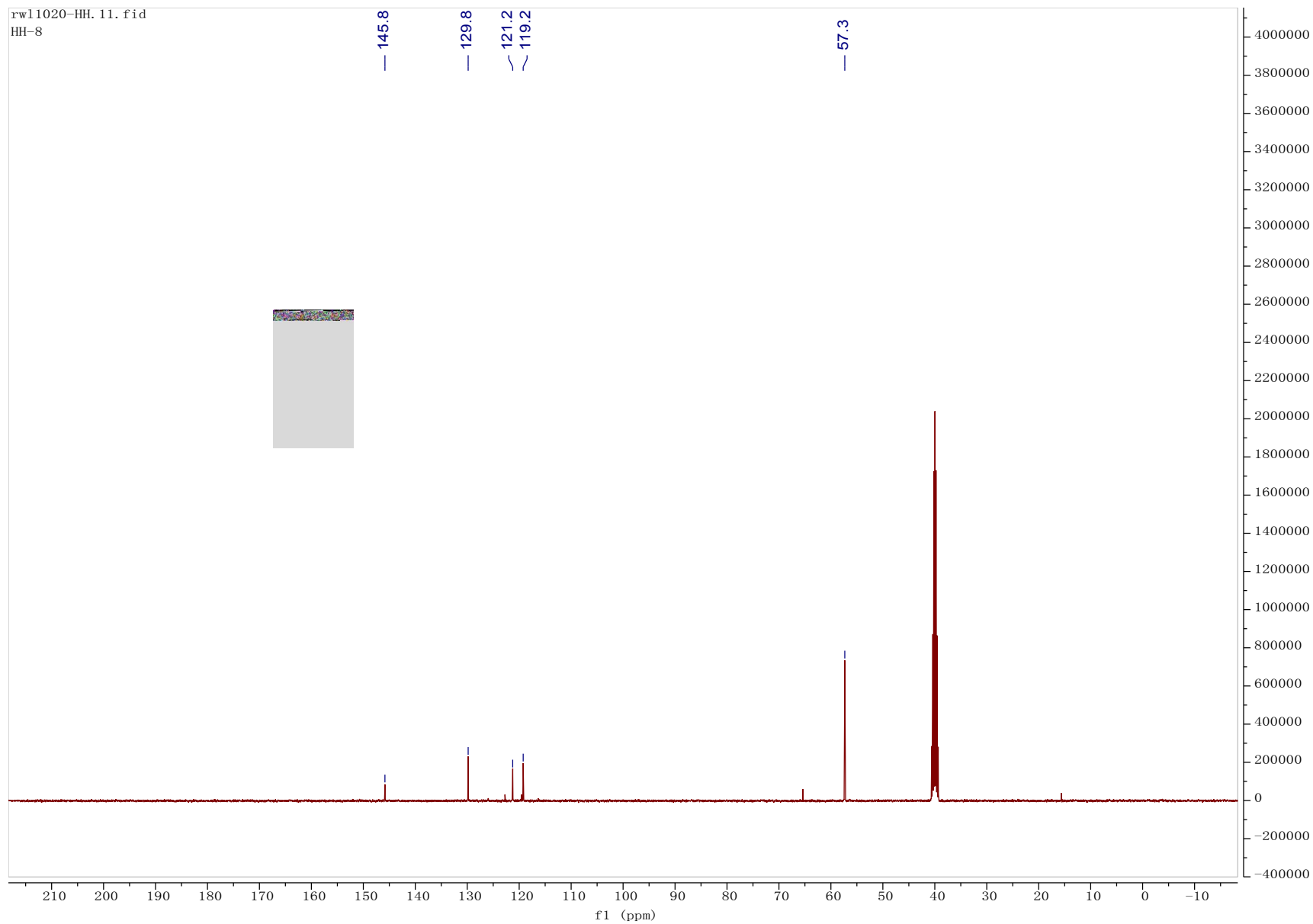


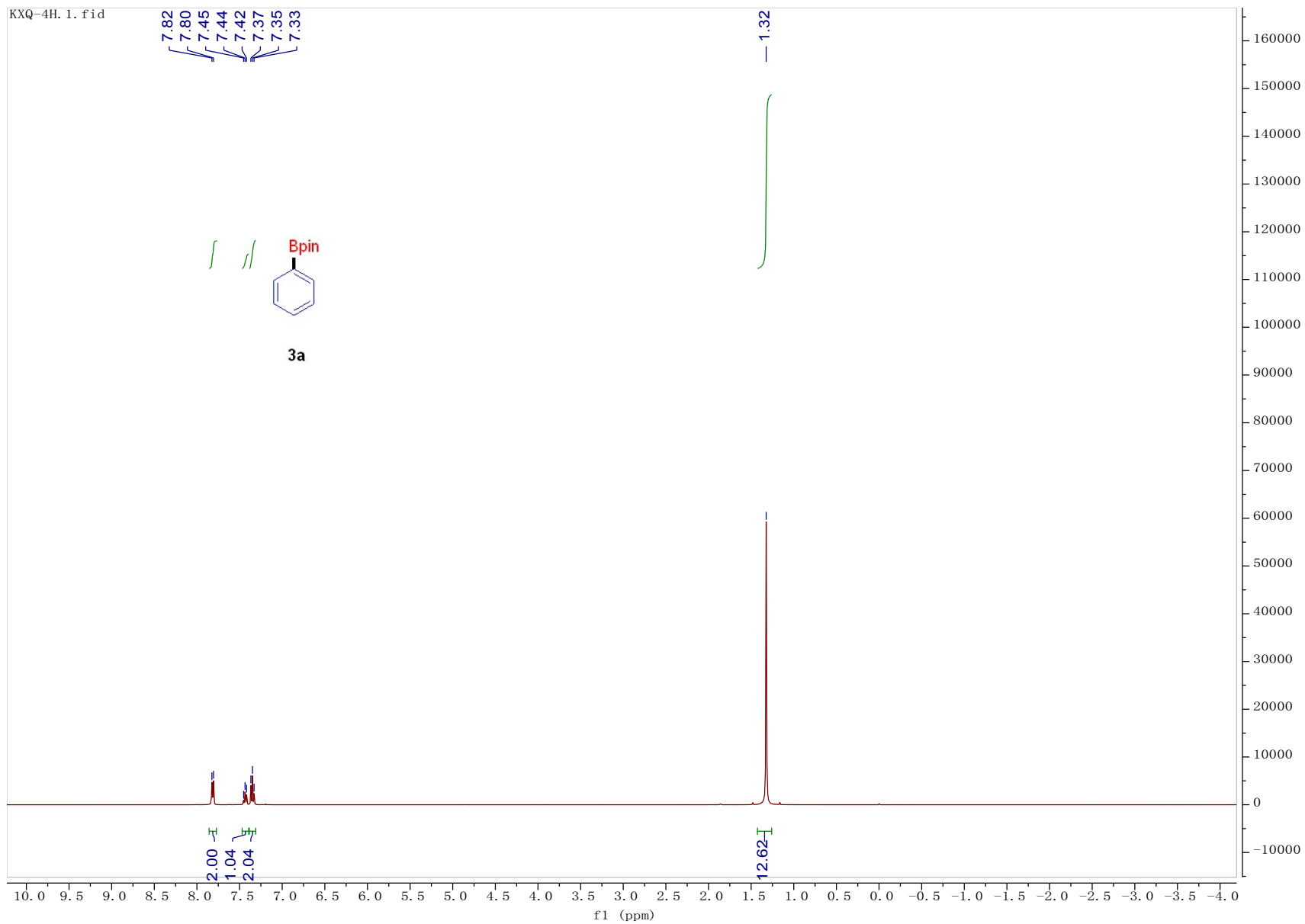


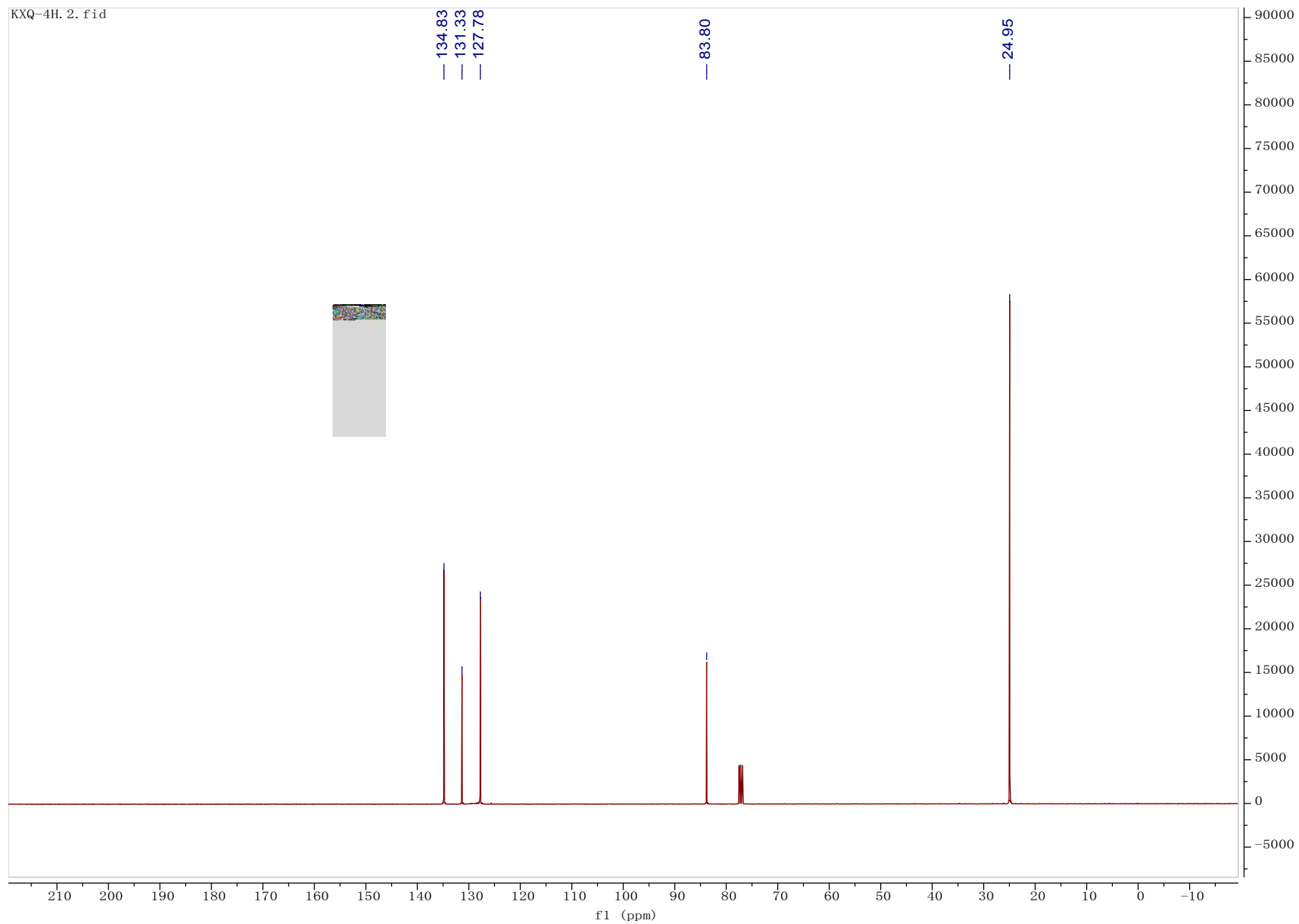




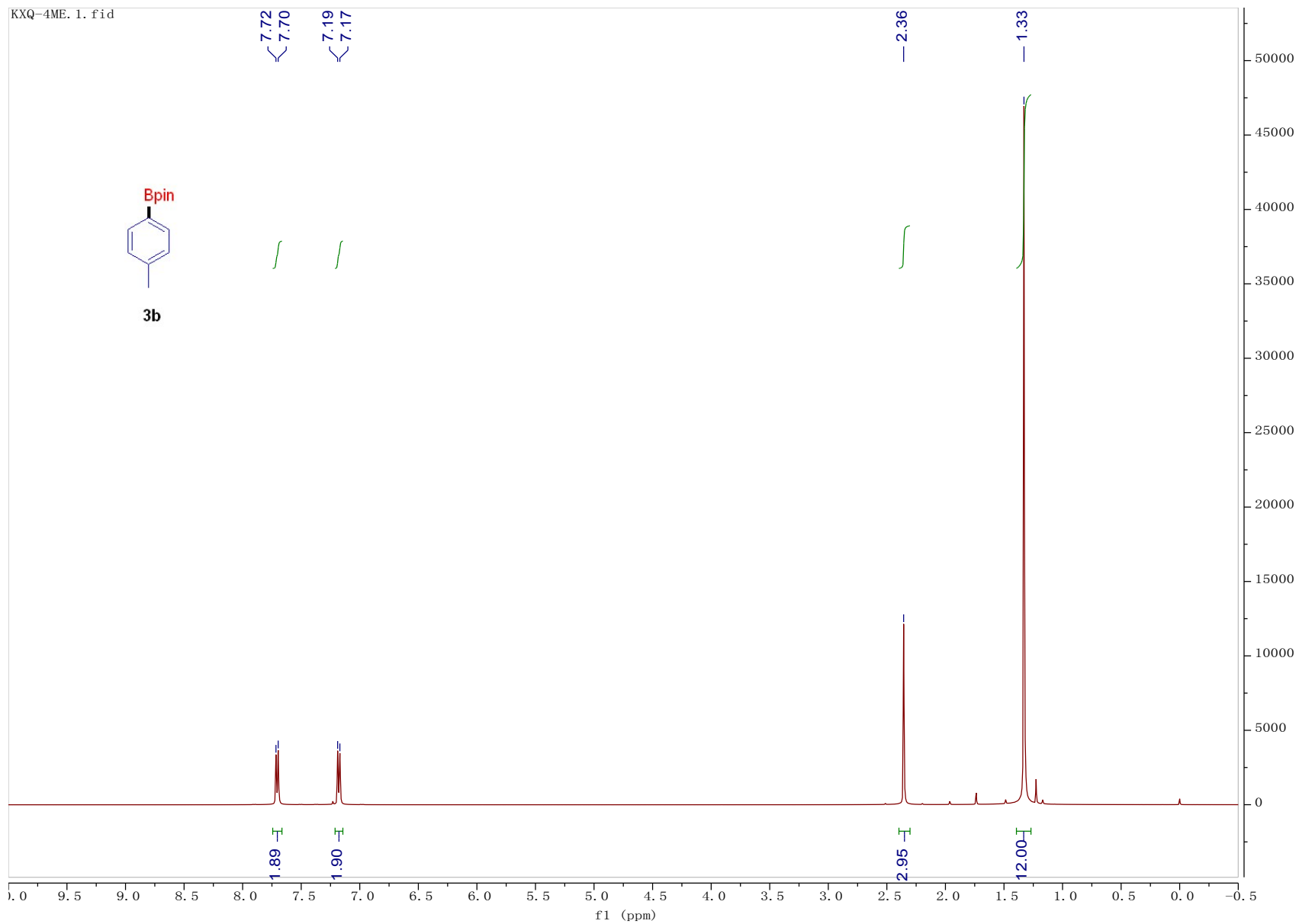
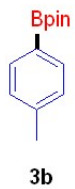
rw11020-HH. 11. fid  
HH-8



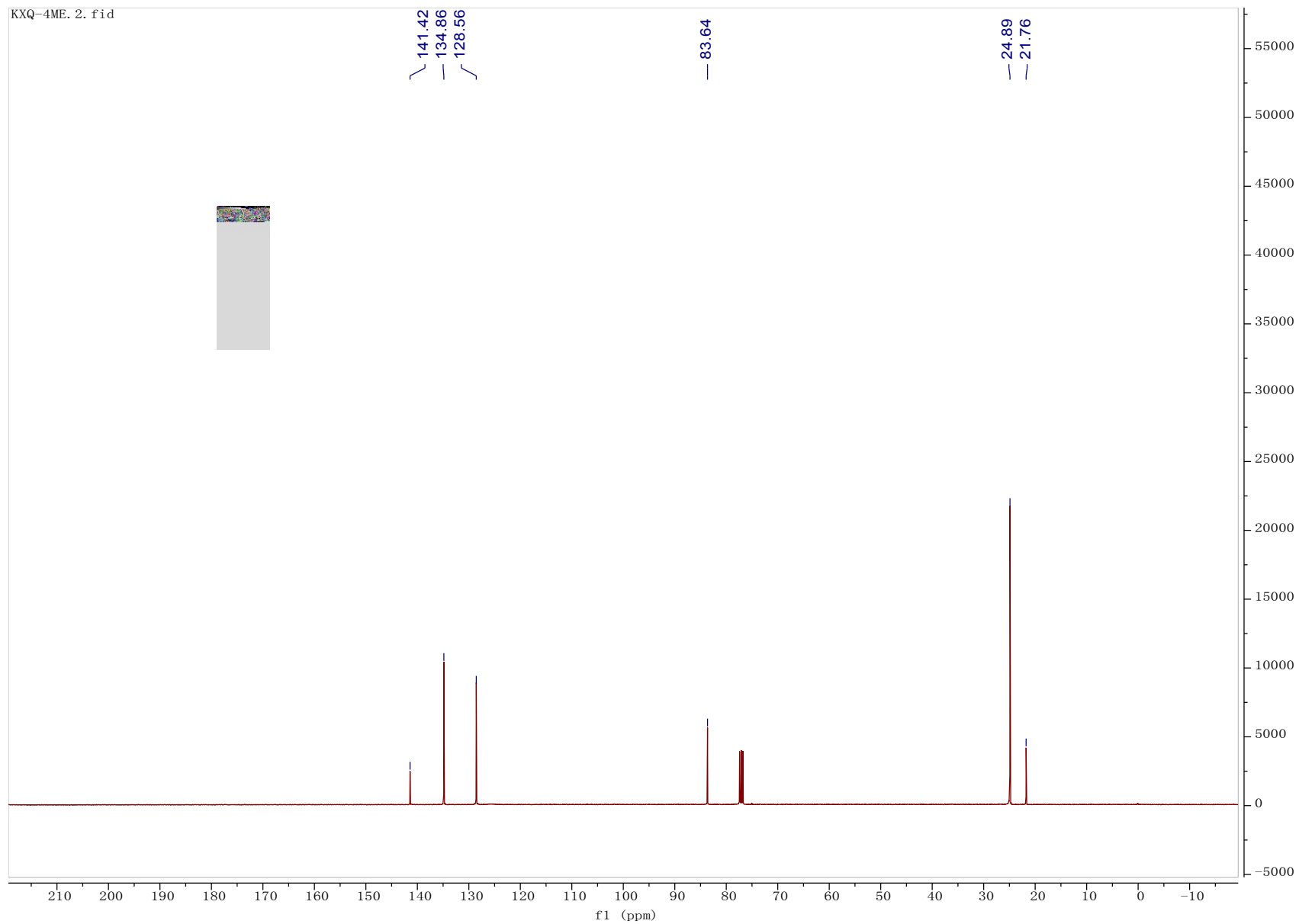




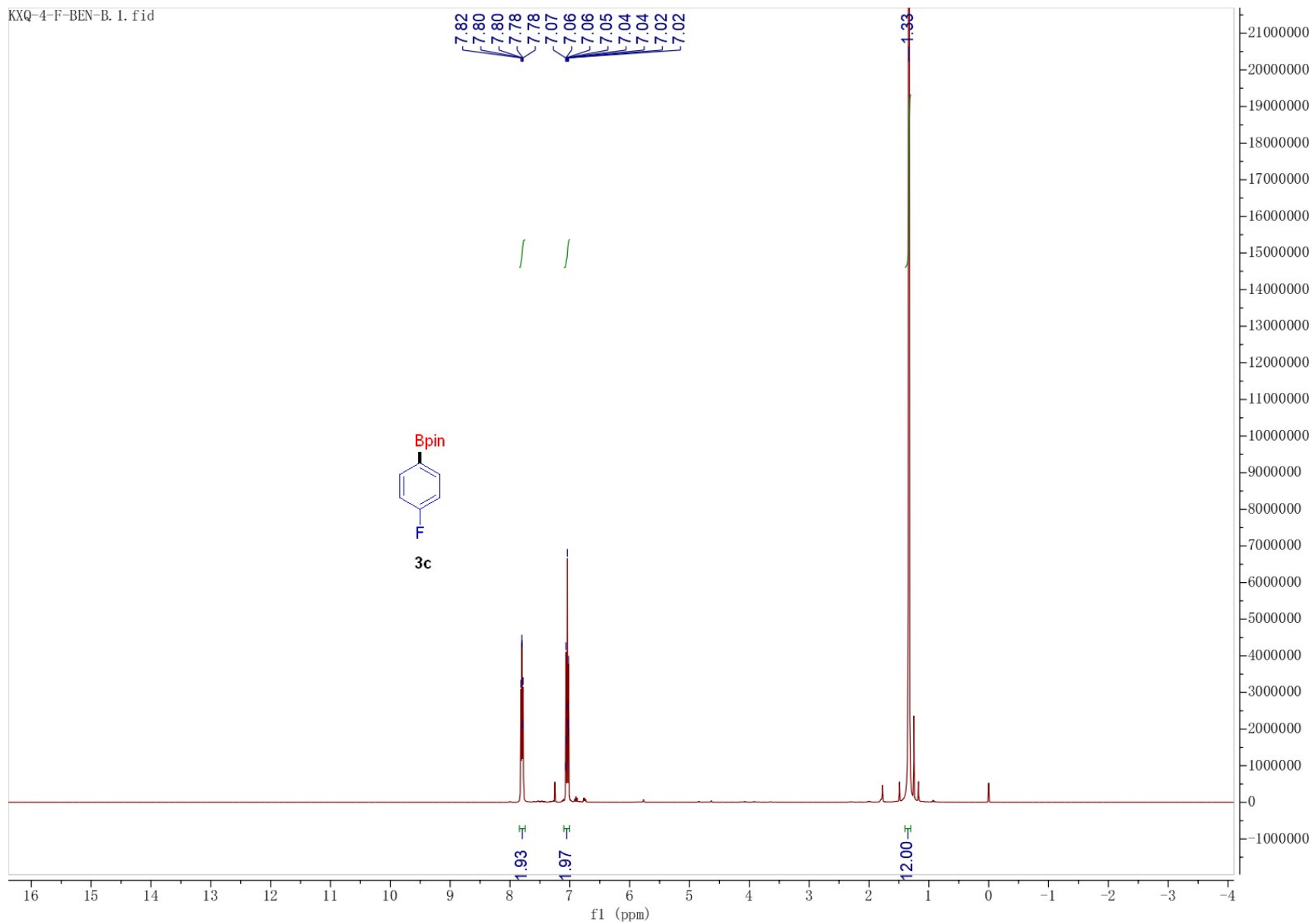
KXQ-4ME. 1. fid

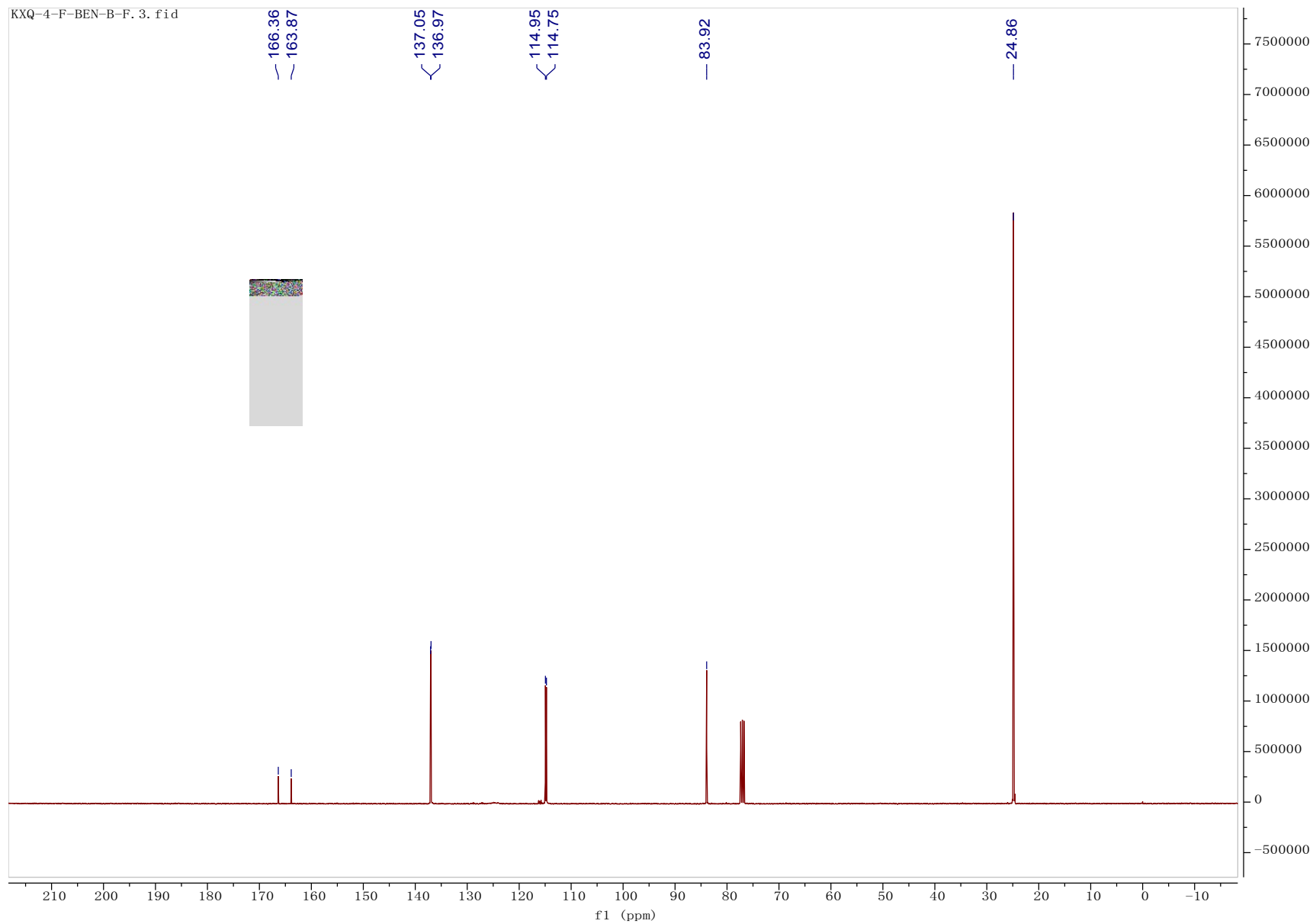


KXQ-4ME. 2. fid



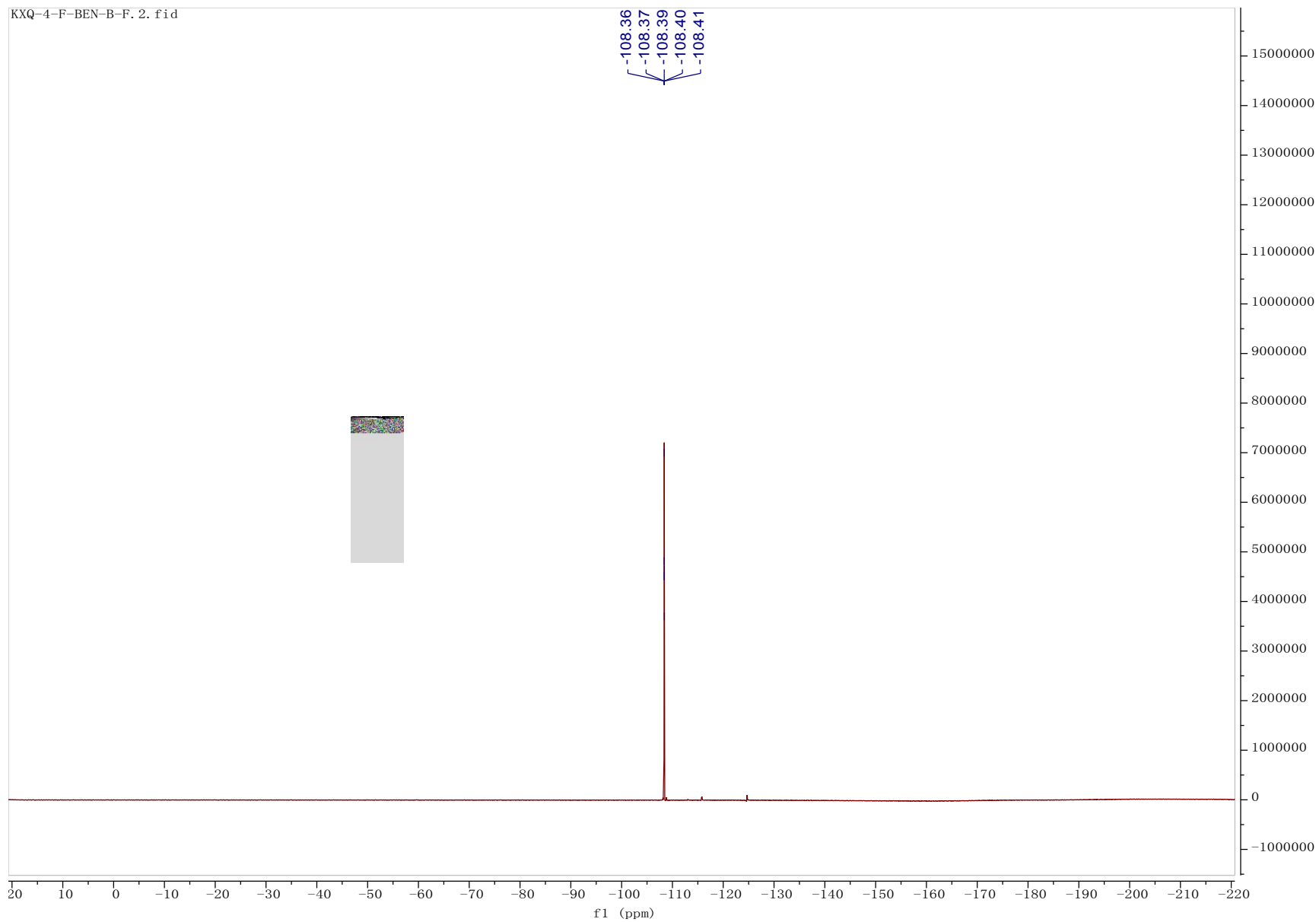
KXQ-4-F-BEN-B. 1. fid



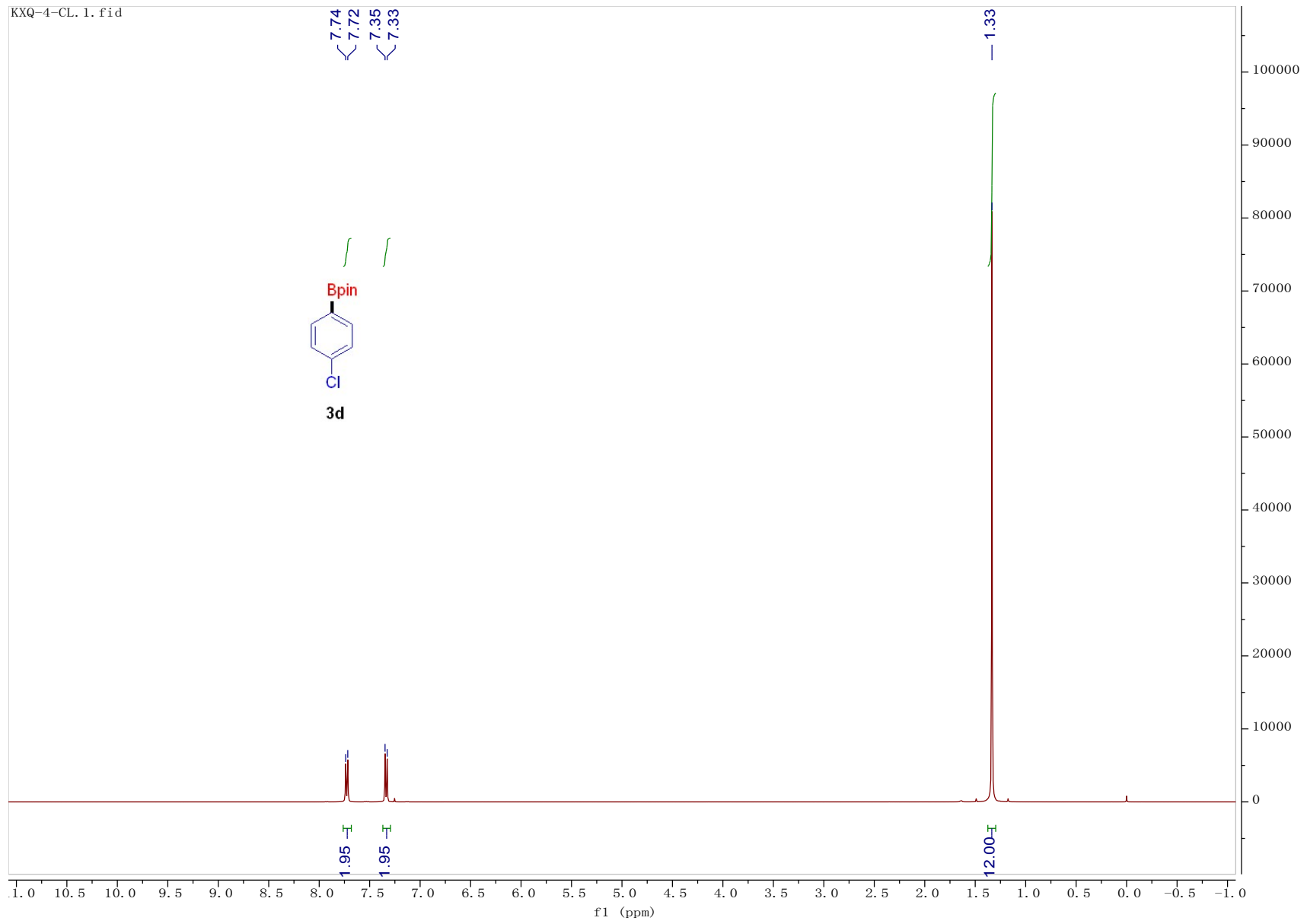


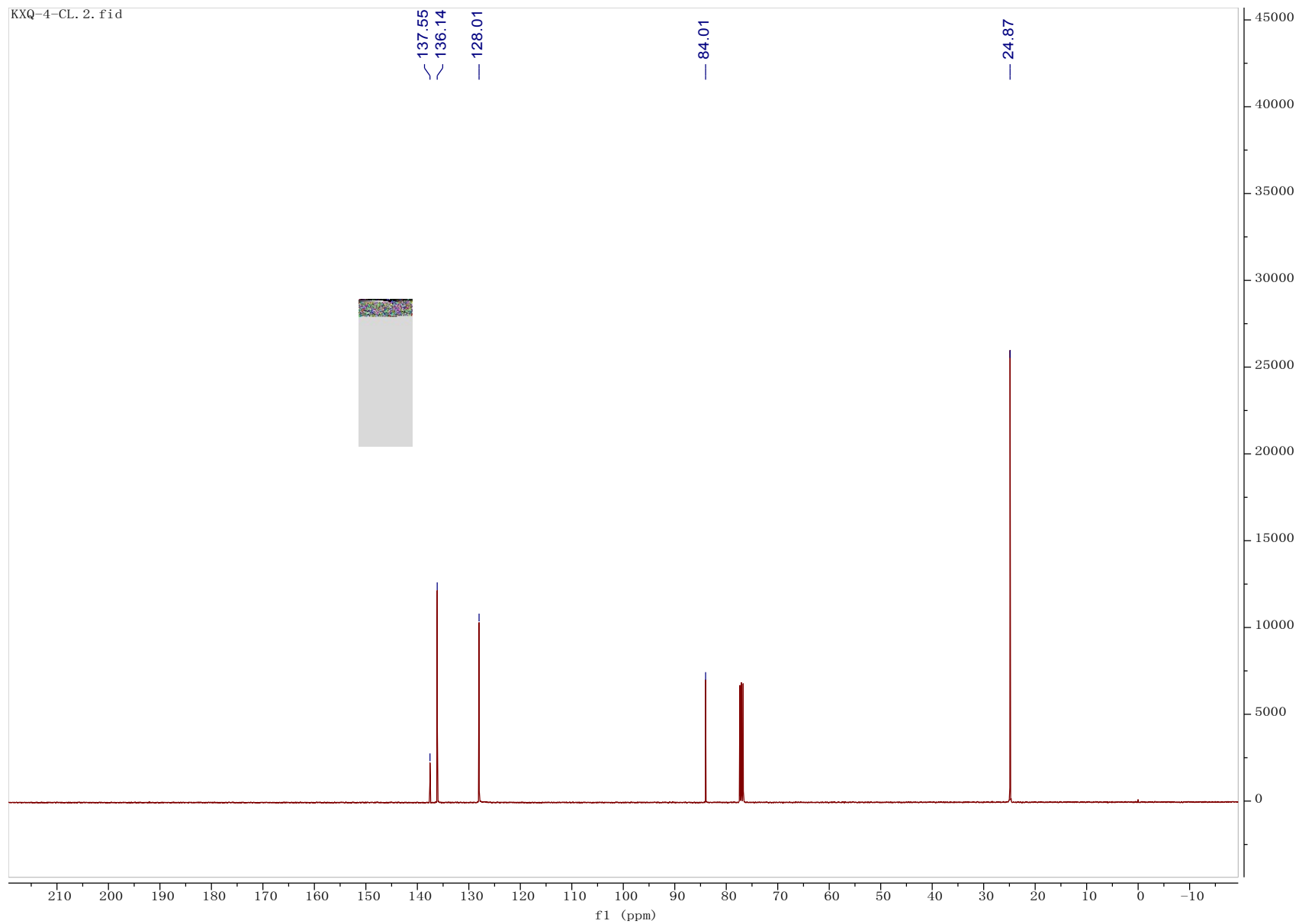


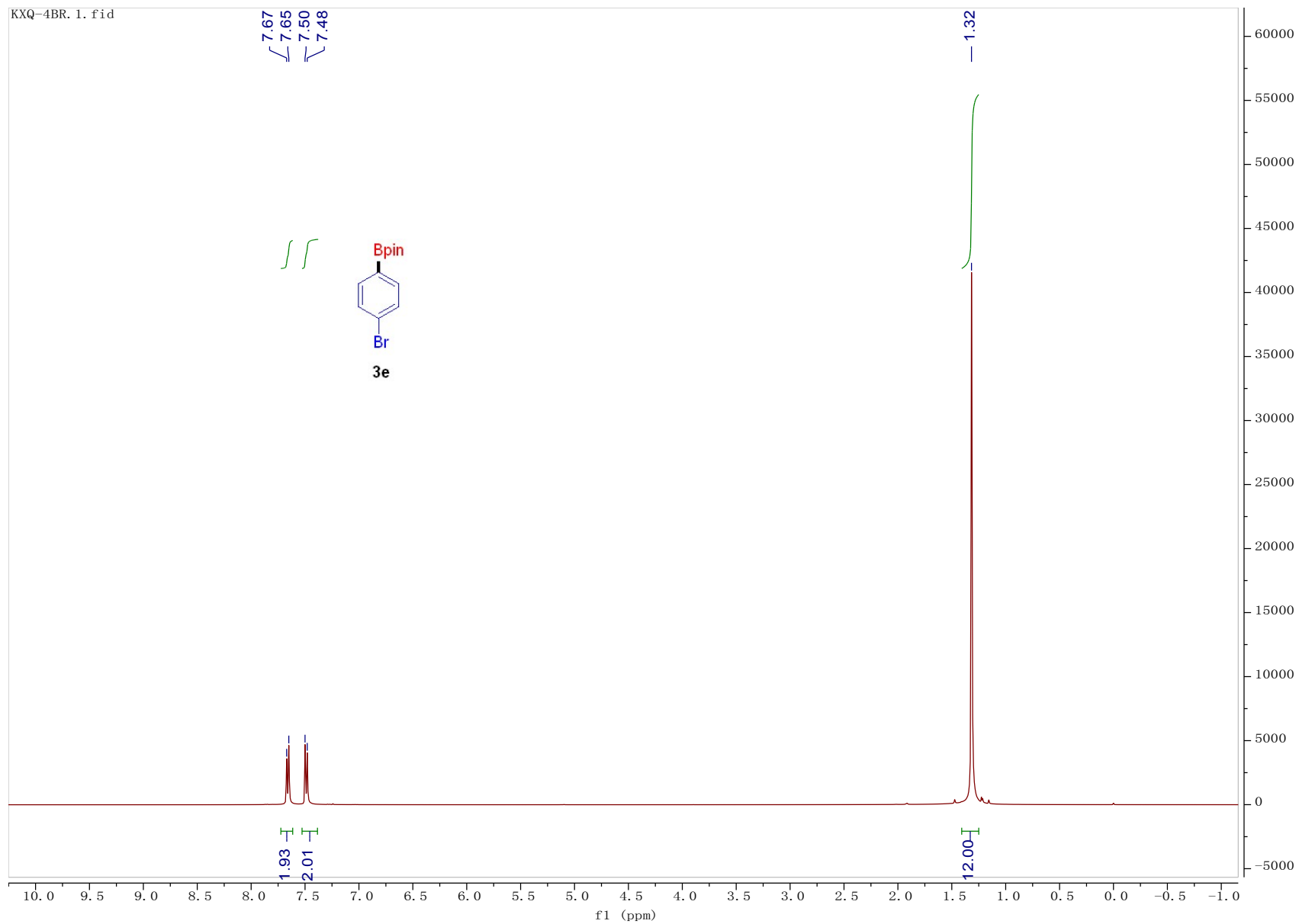
KXQ-4-F-BEN-B-F. 2. fid



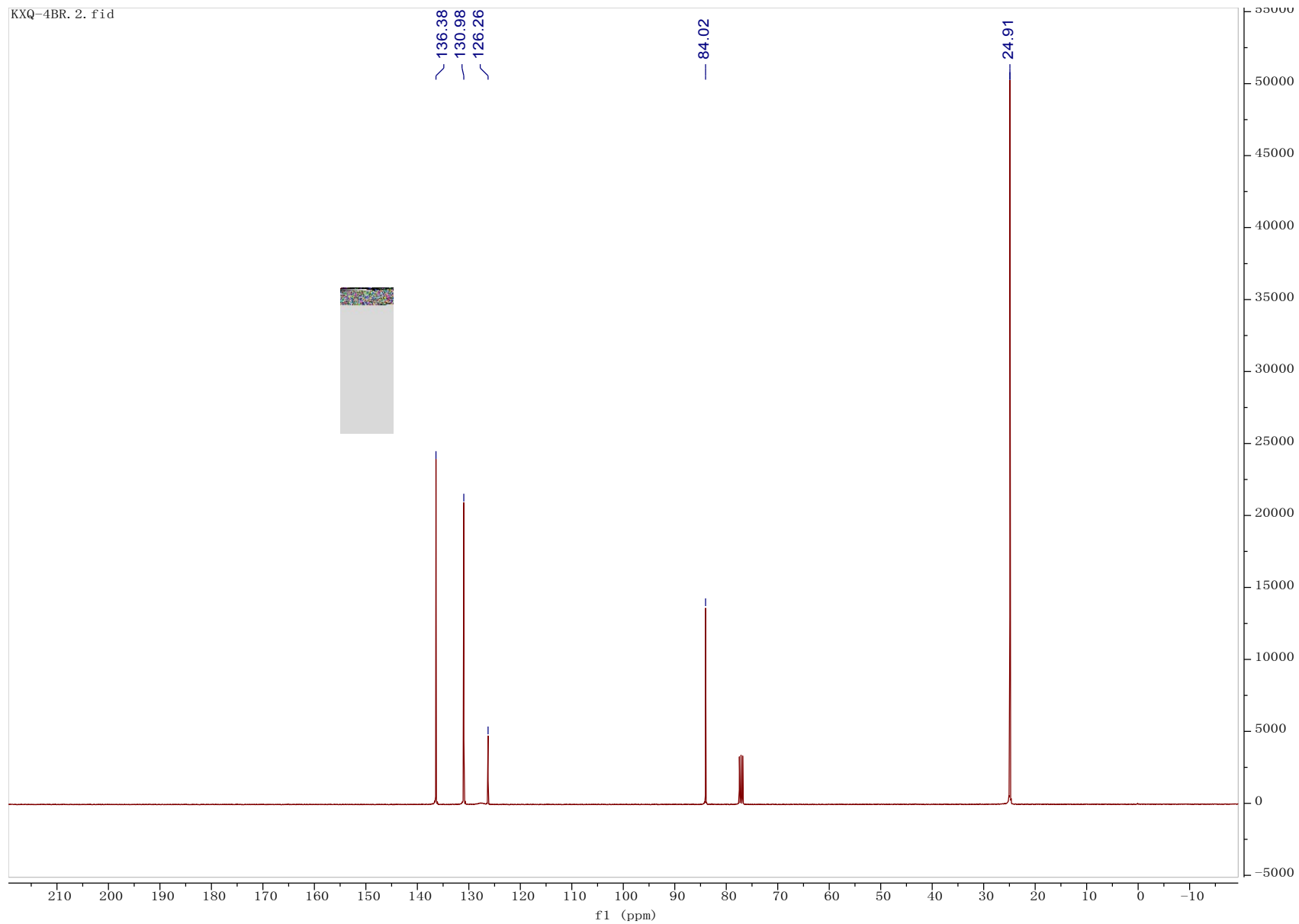
KXQ-4-CL. 1. fid

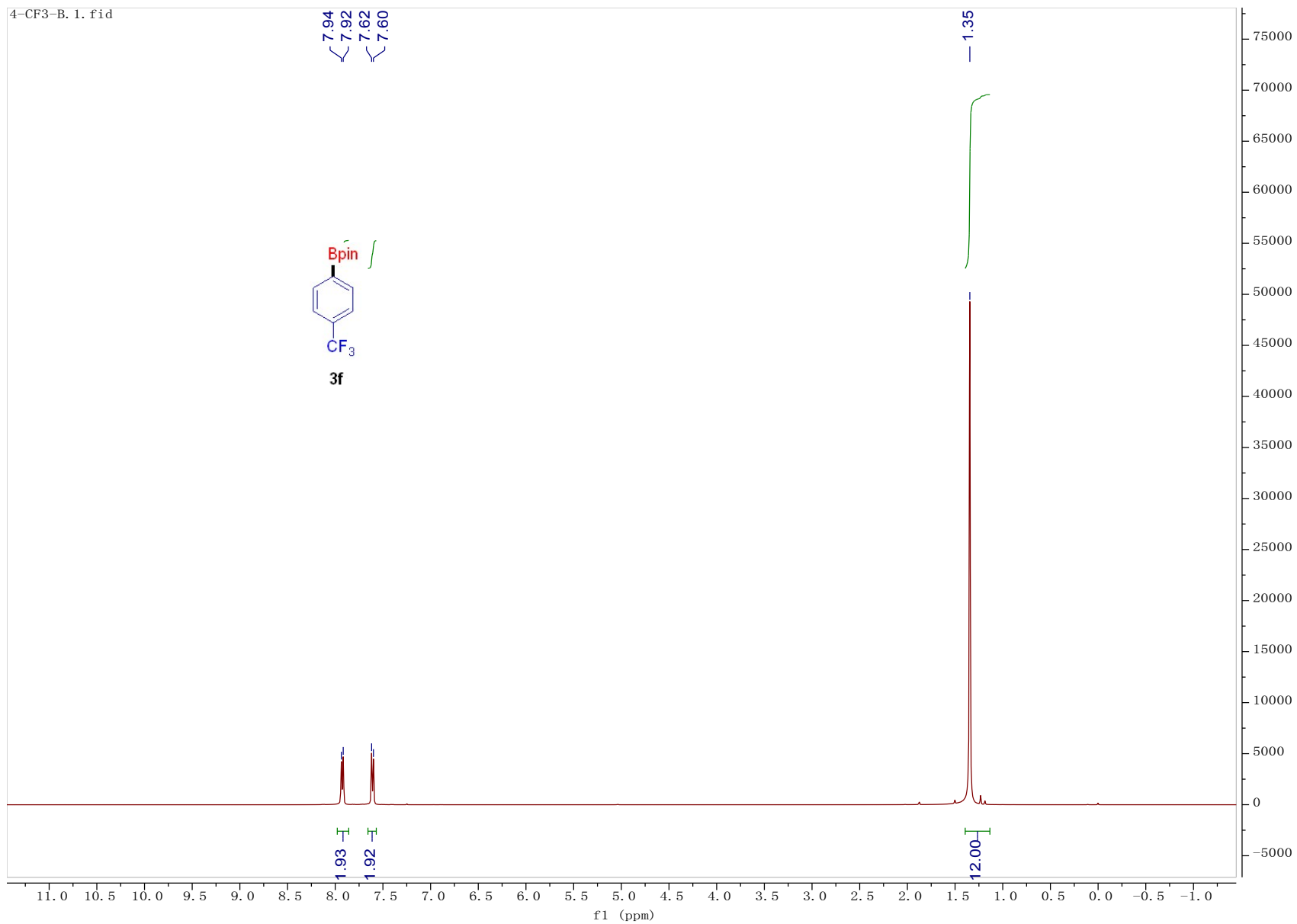


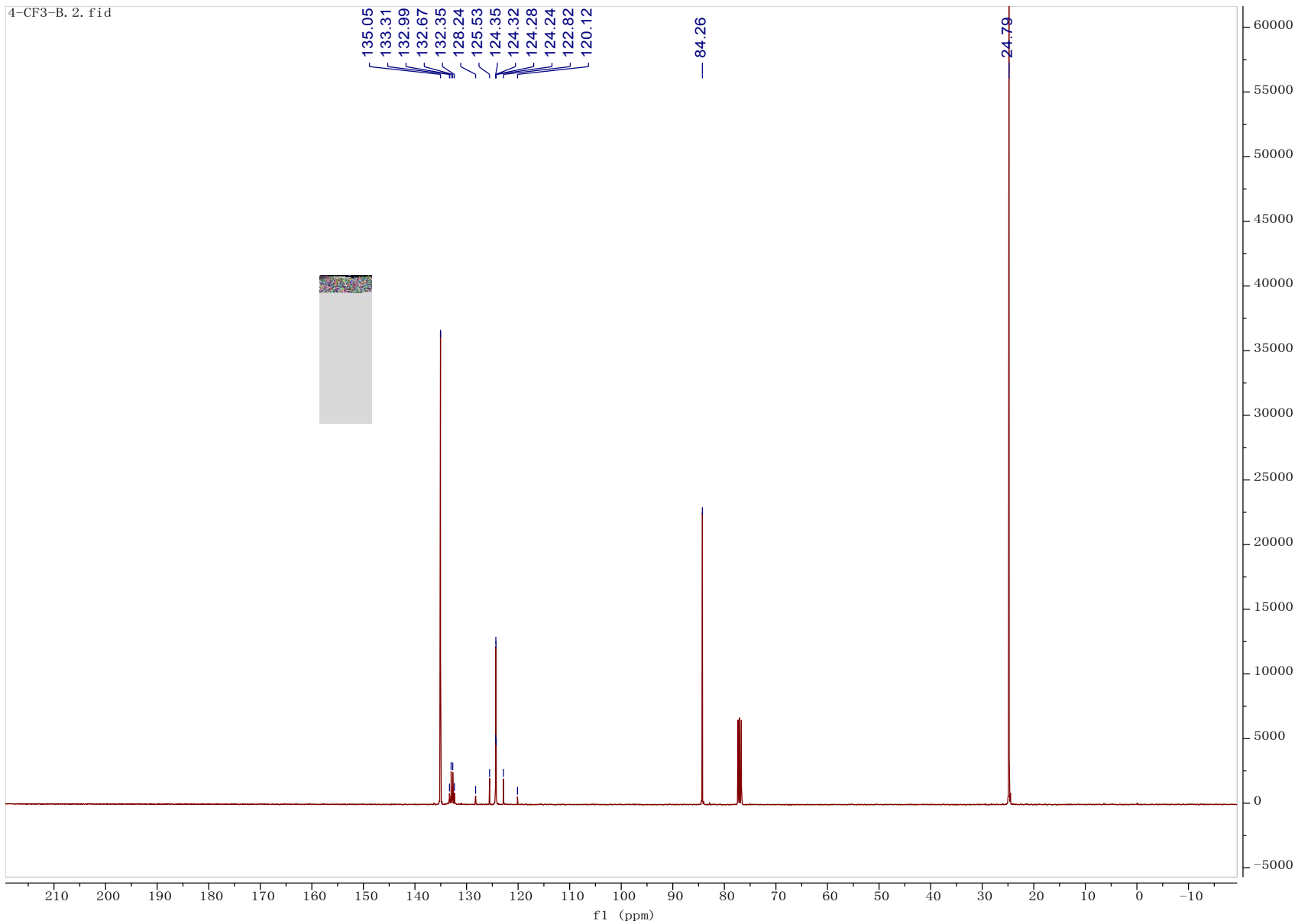




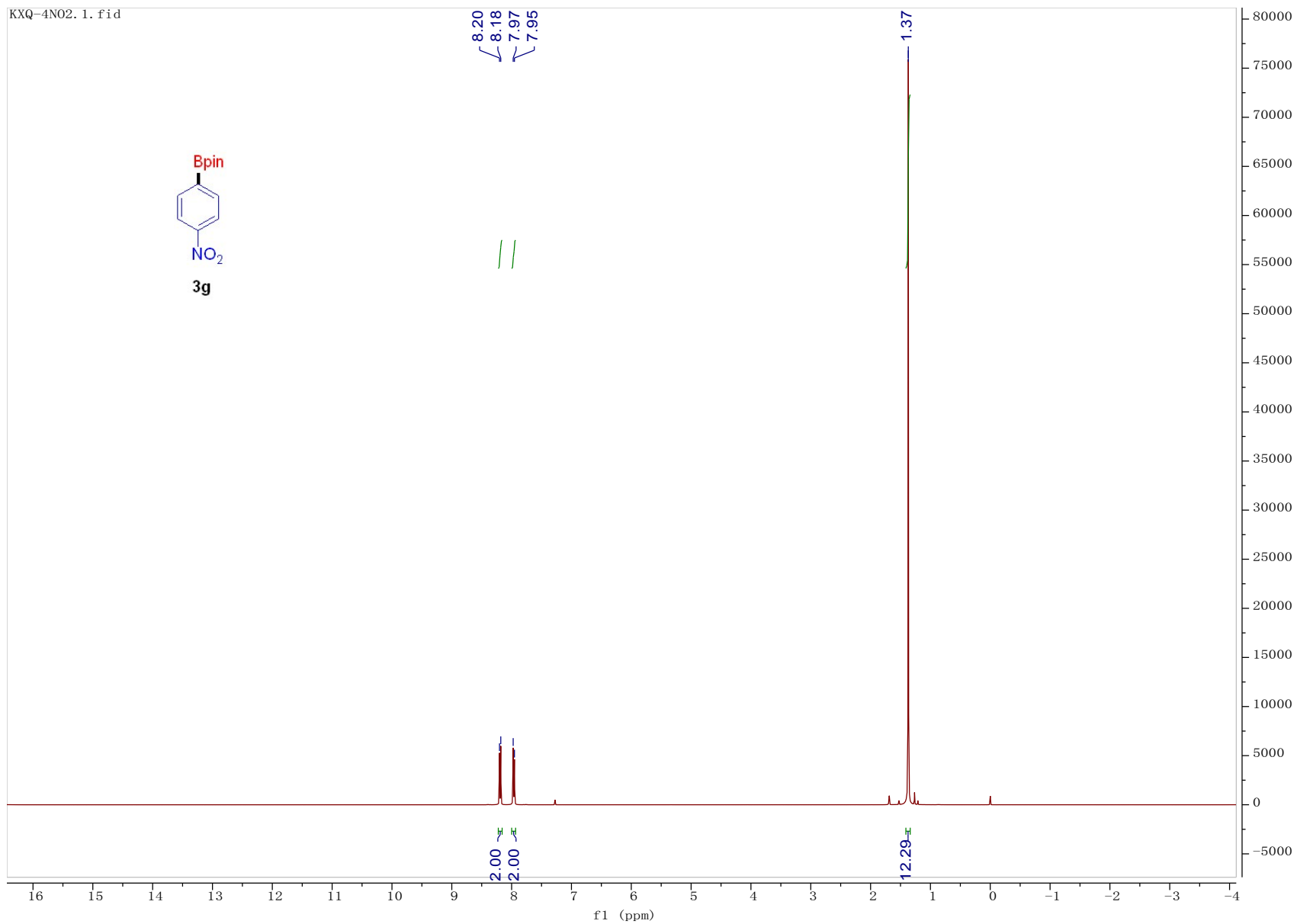
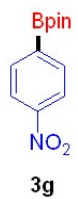
KXQ-4BR. 2. fid



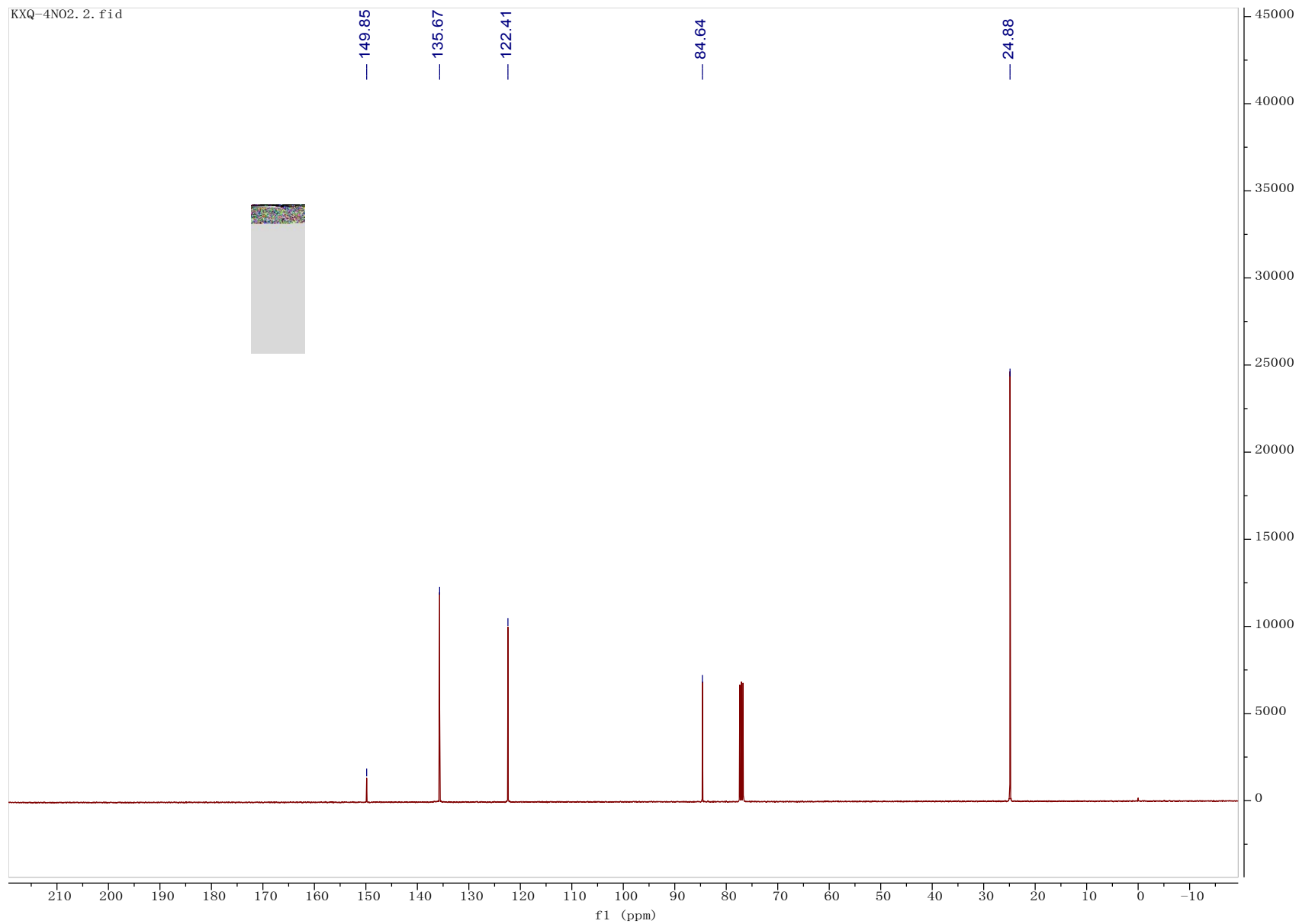




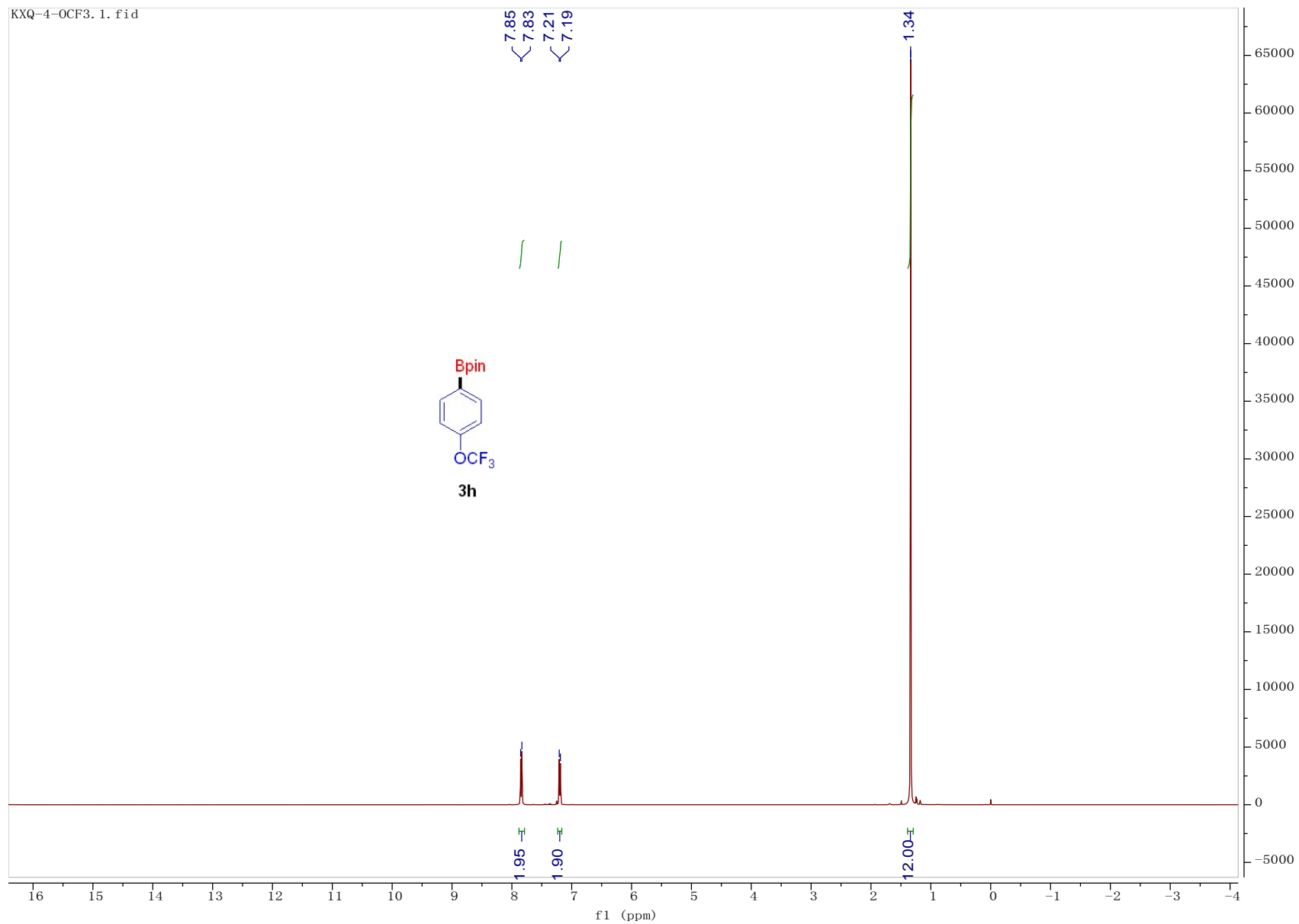
KXQ-4NO2.1.fid



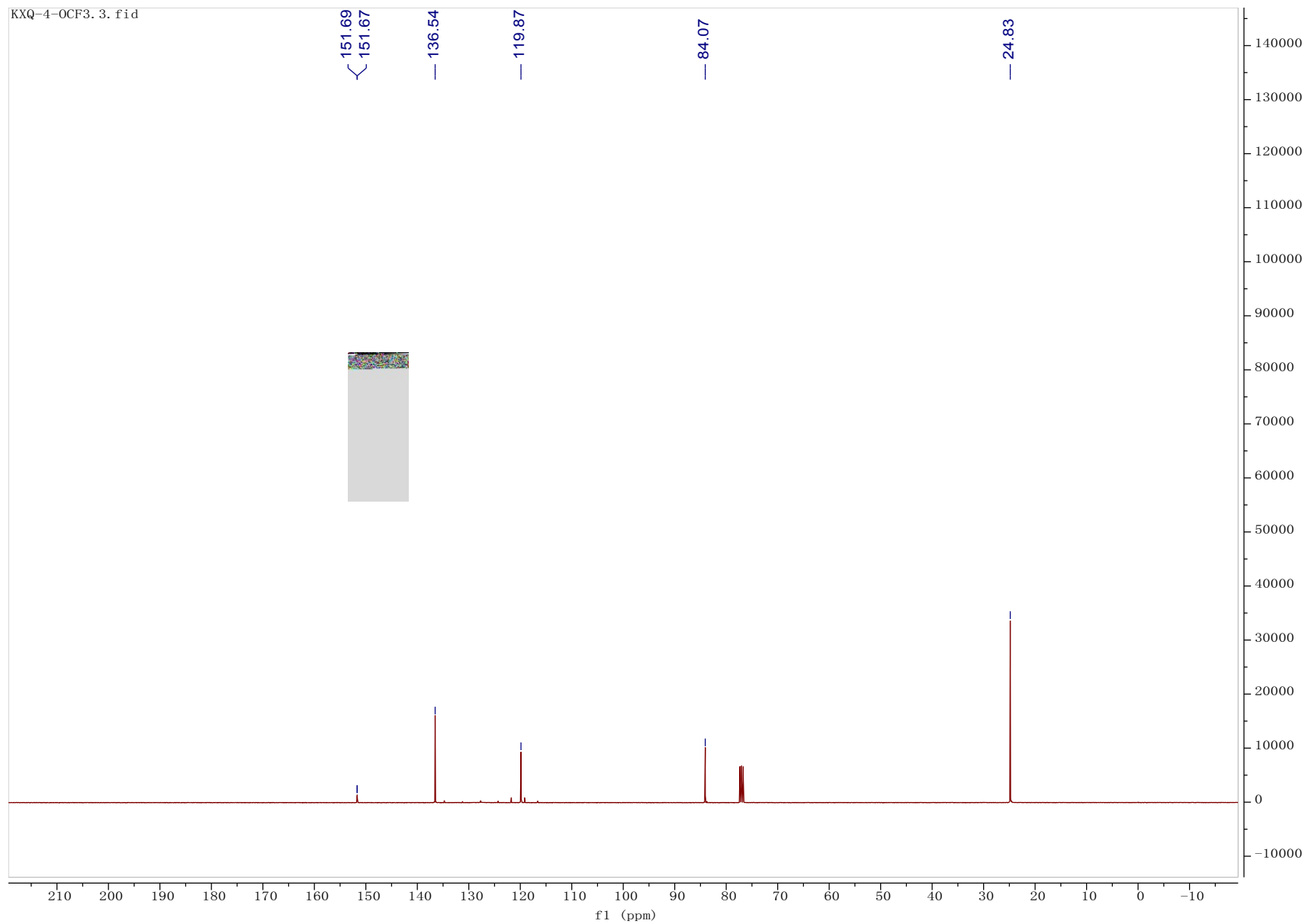




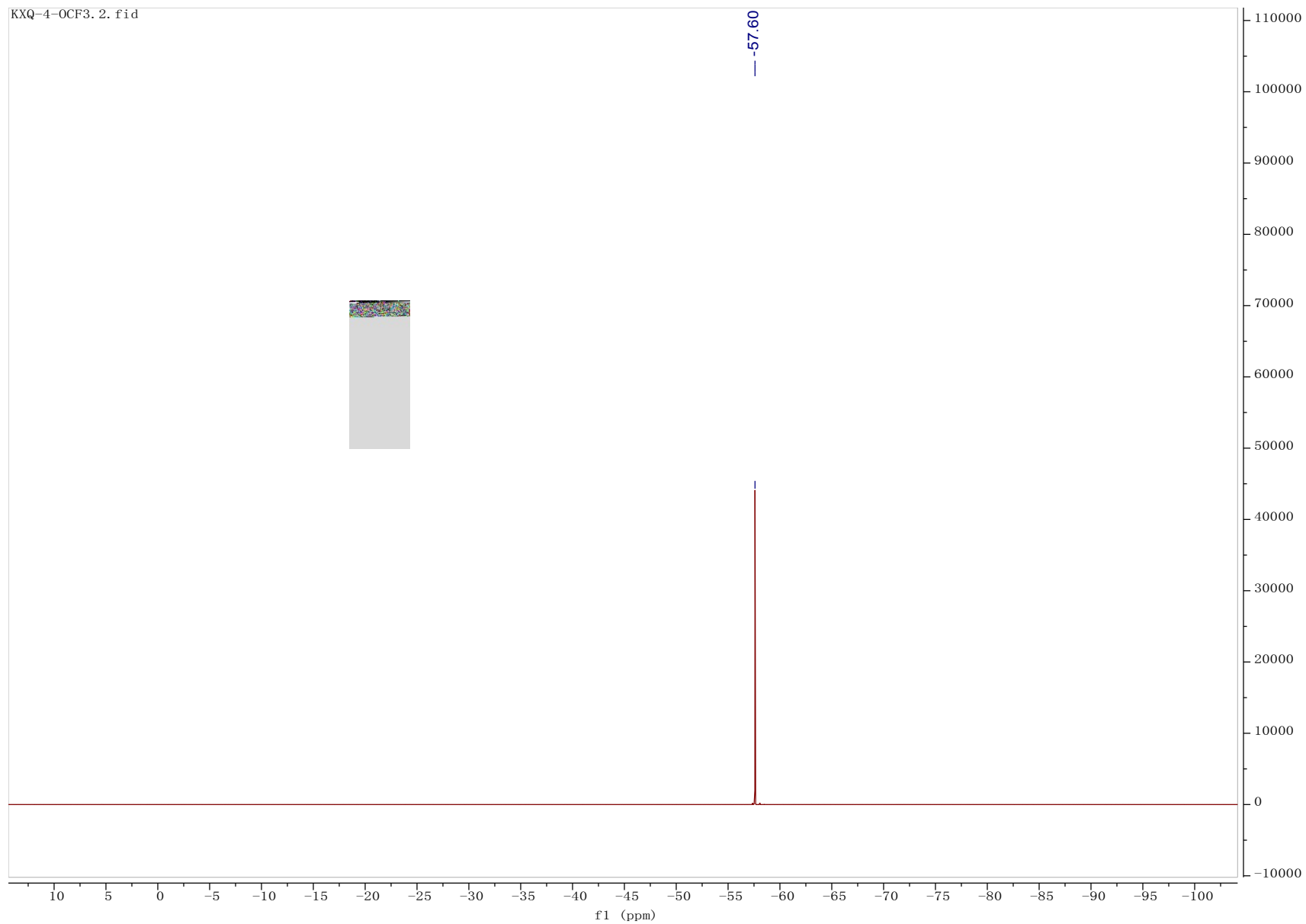
KXQ-4-OCF3. 1. fid



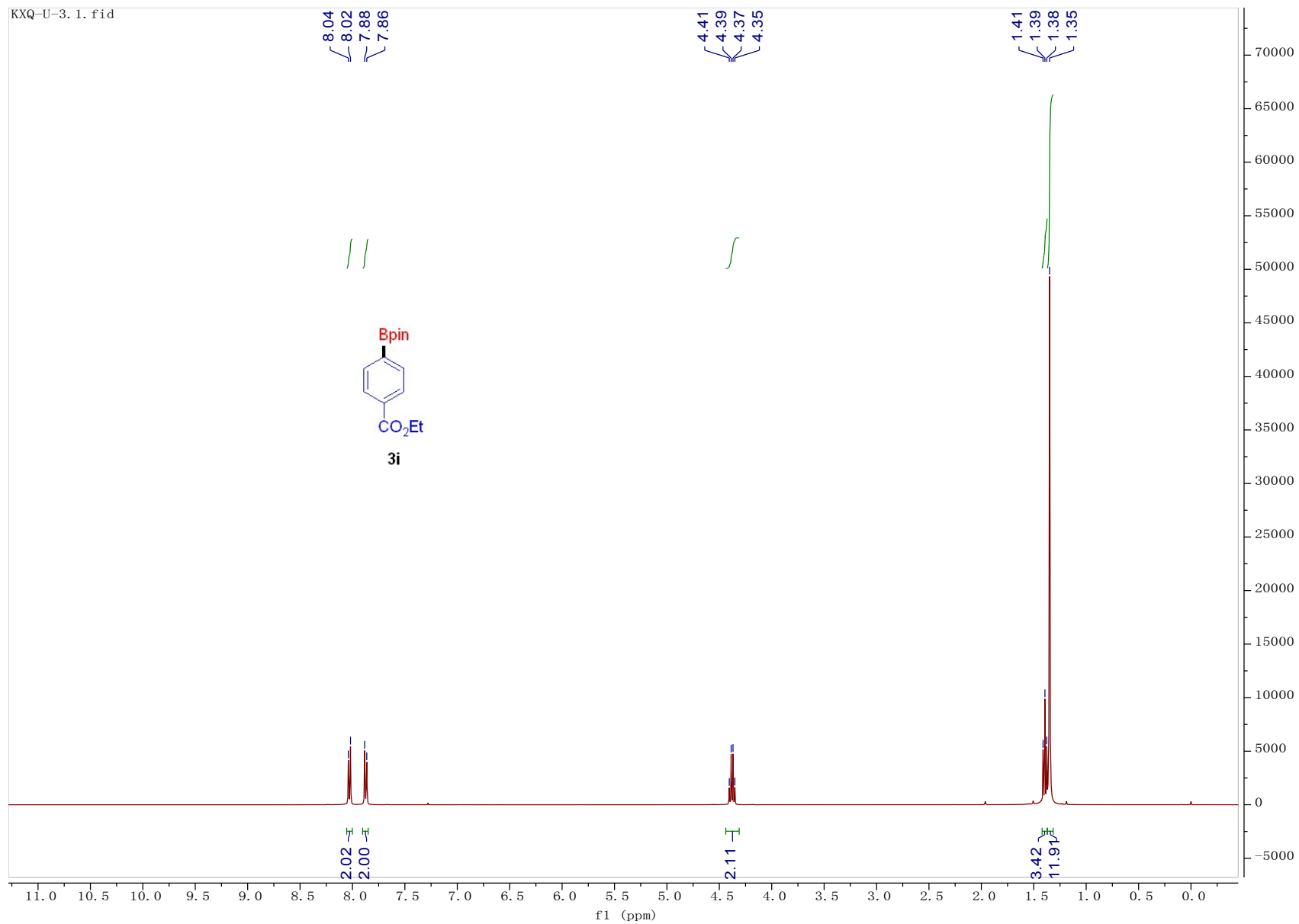
KXQ-4-OCF3. 3. fid

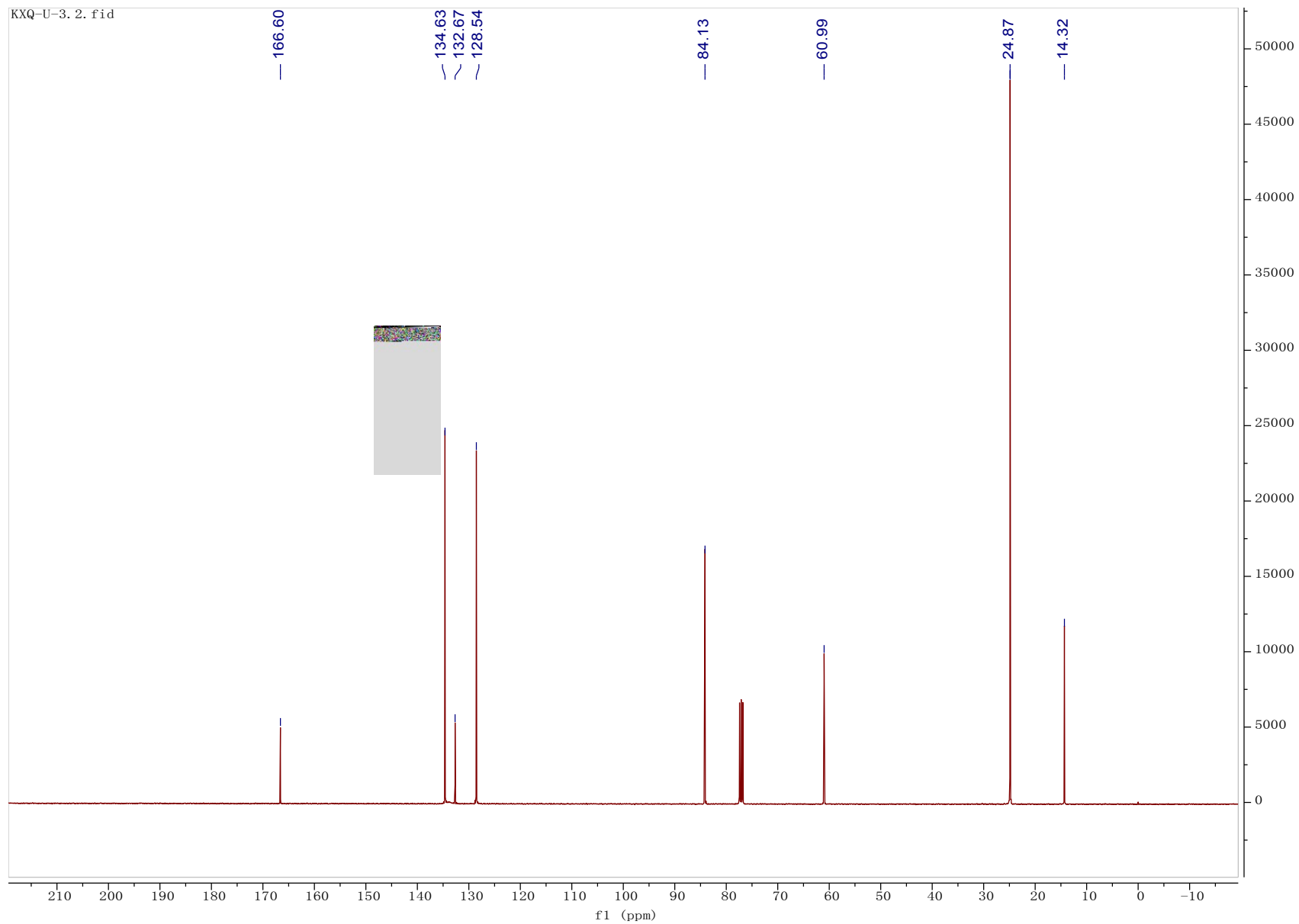


KXQ-4-OCF3. 2. fid

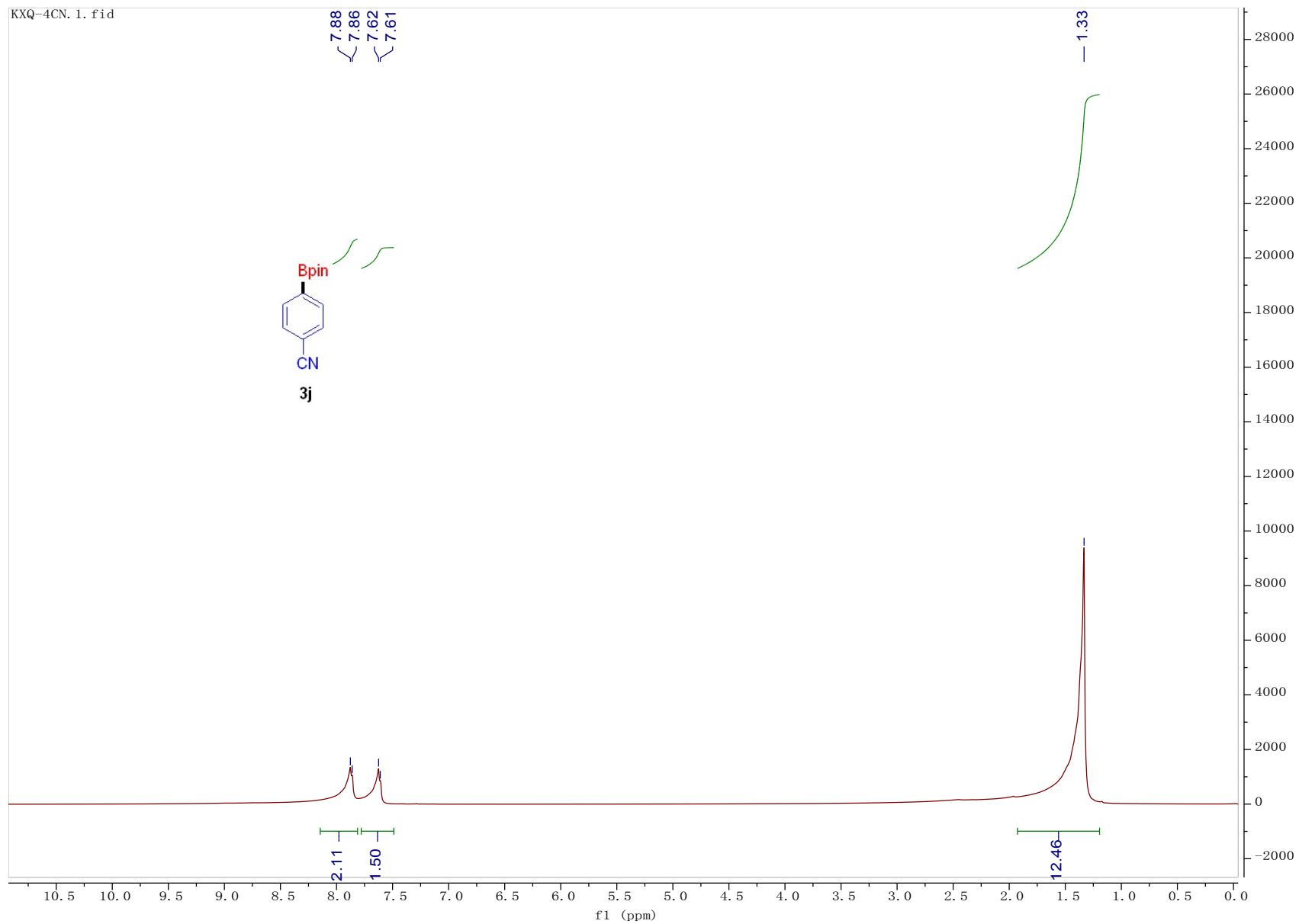


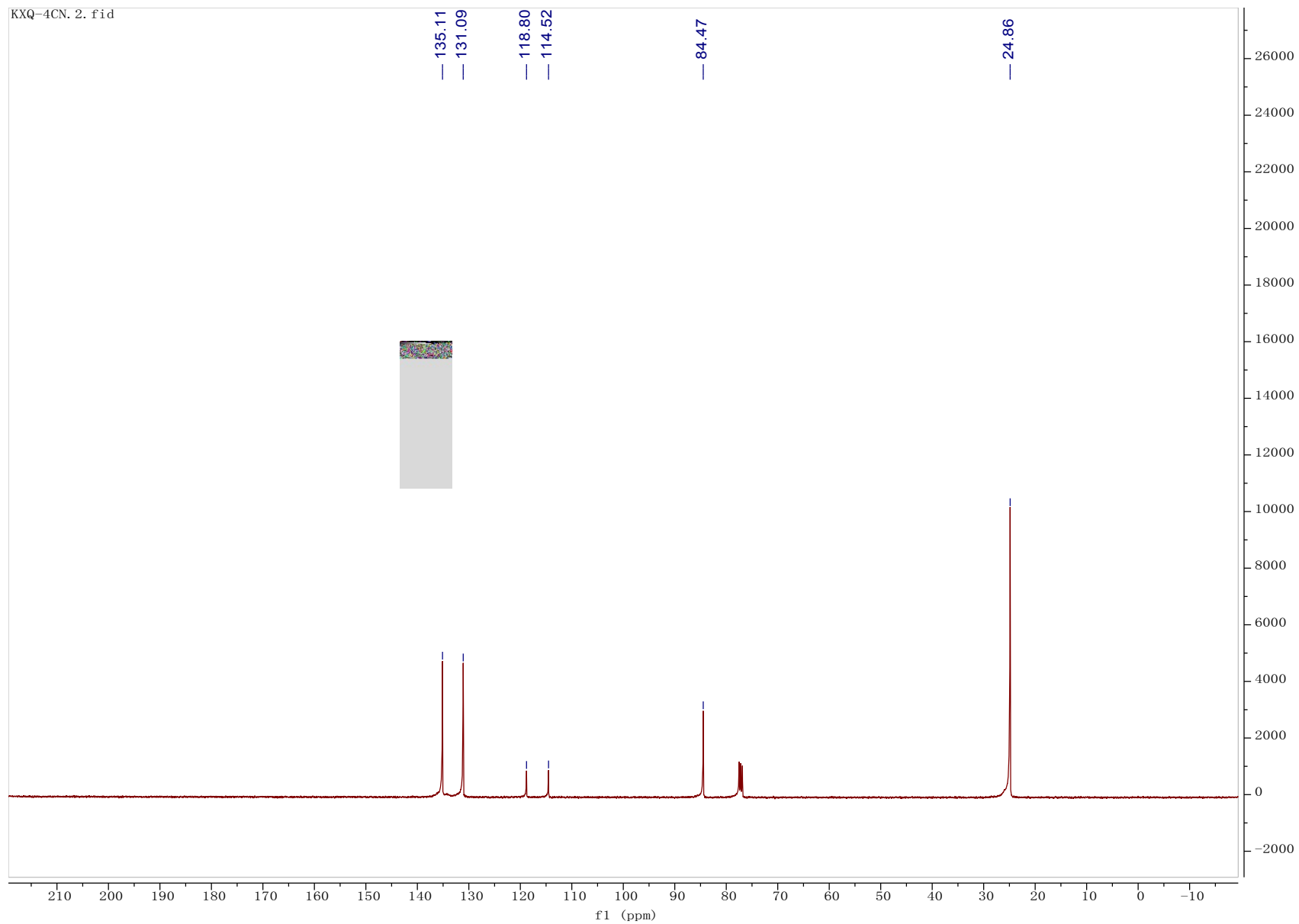
KXQ-U-3.1.fid





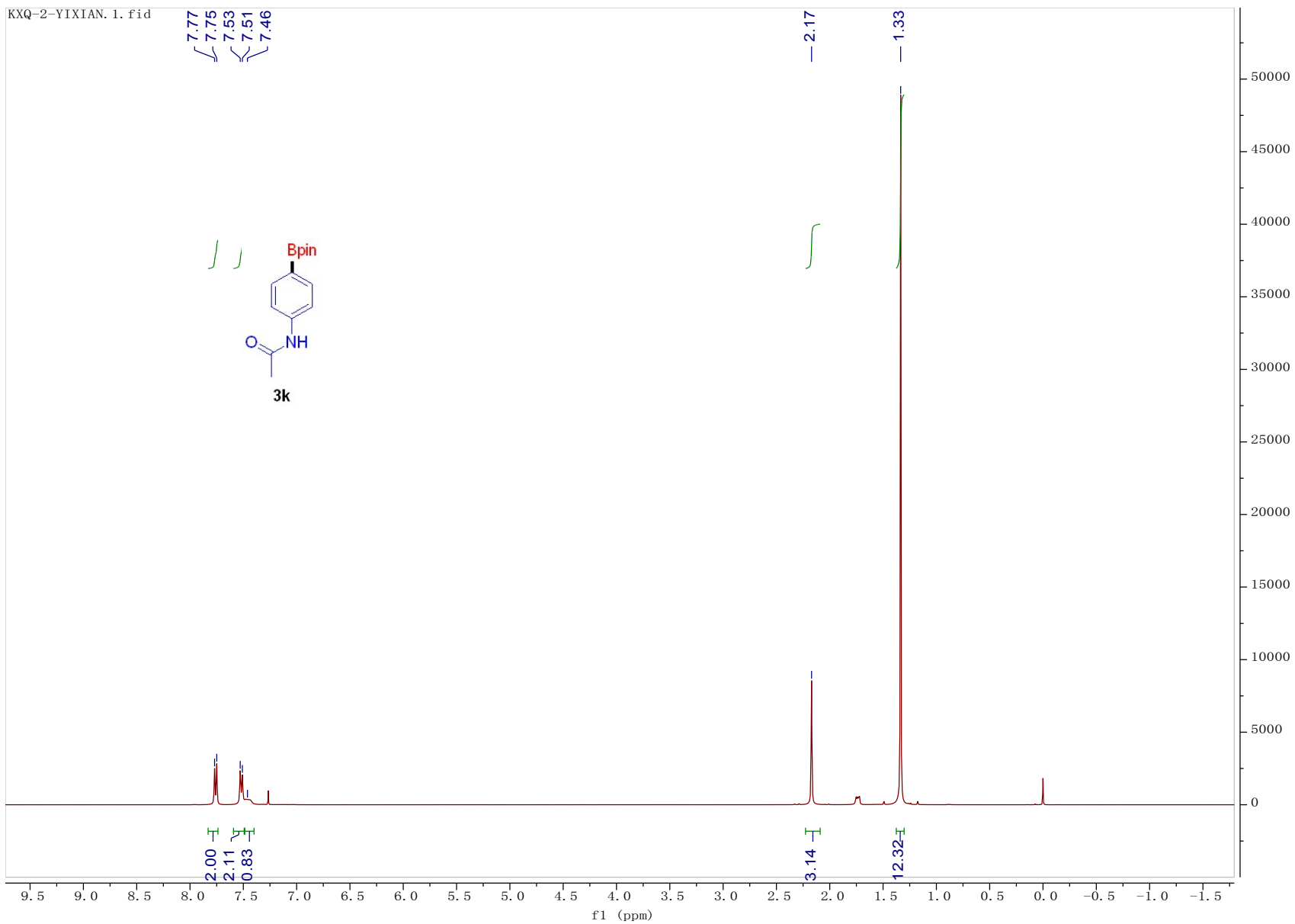
KXQ-4CN. 1. fid

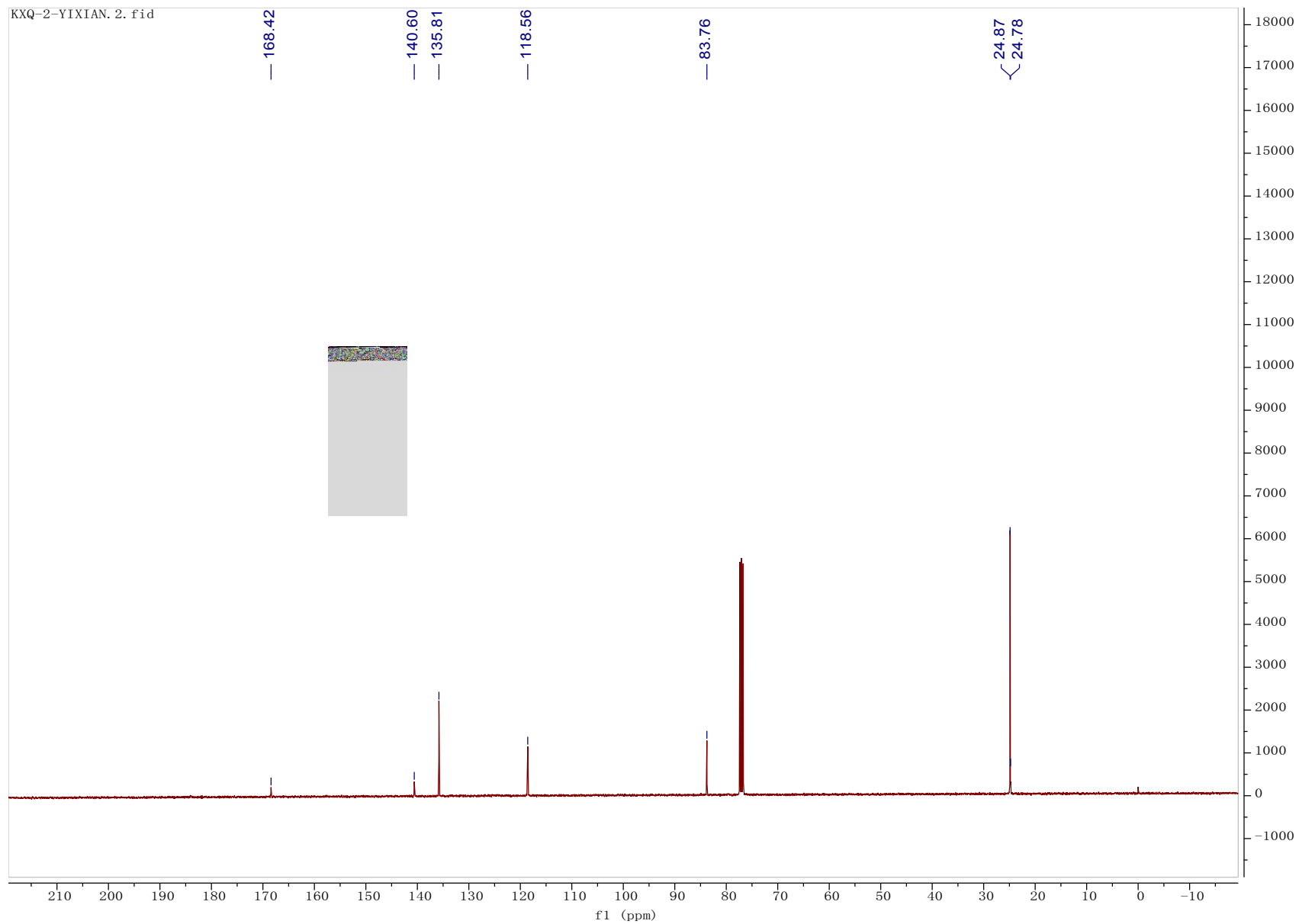




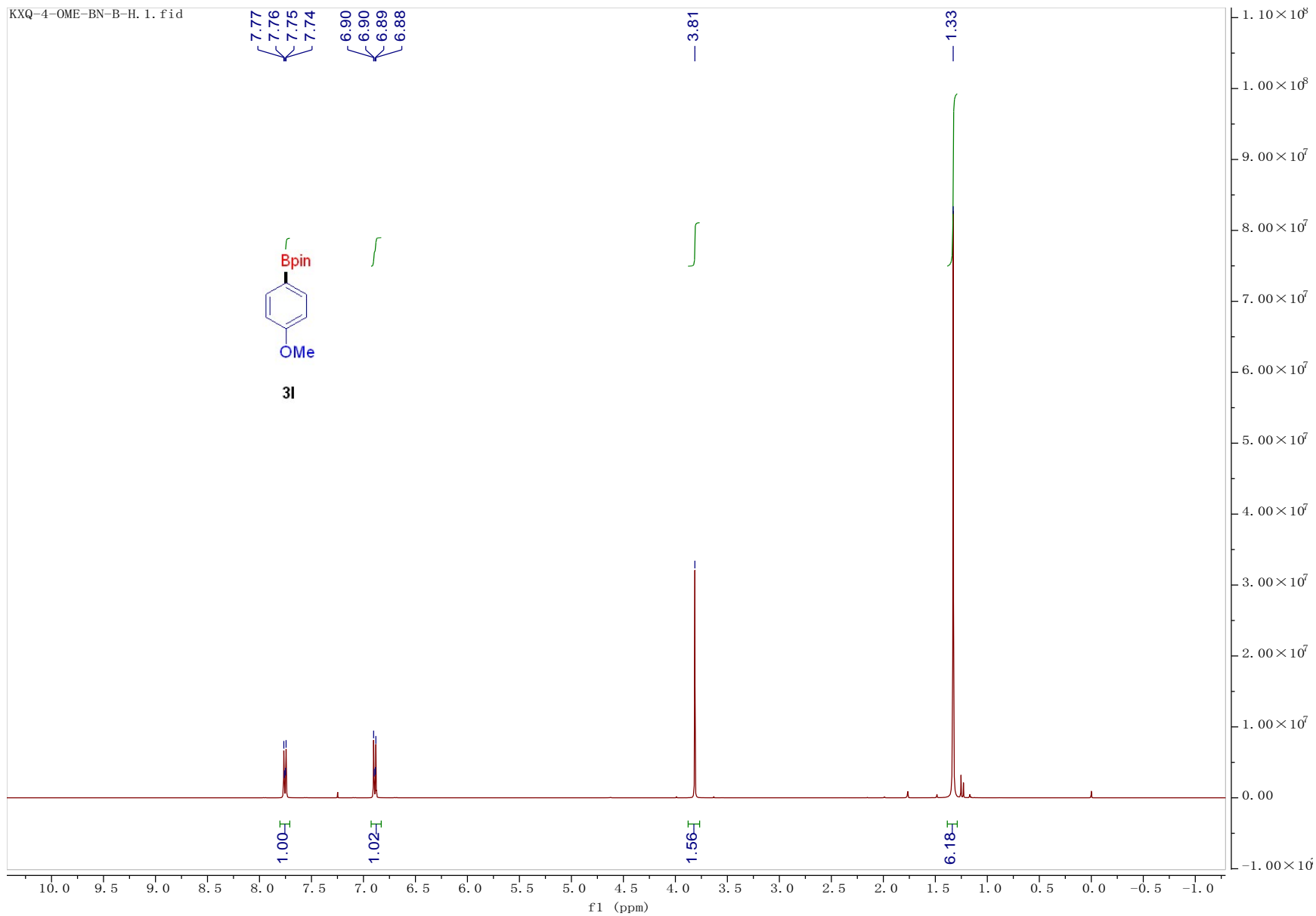


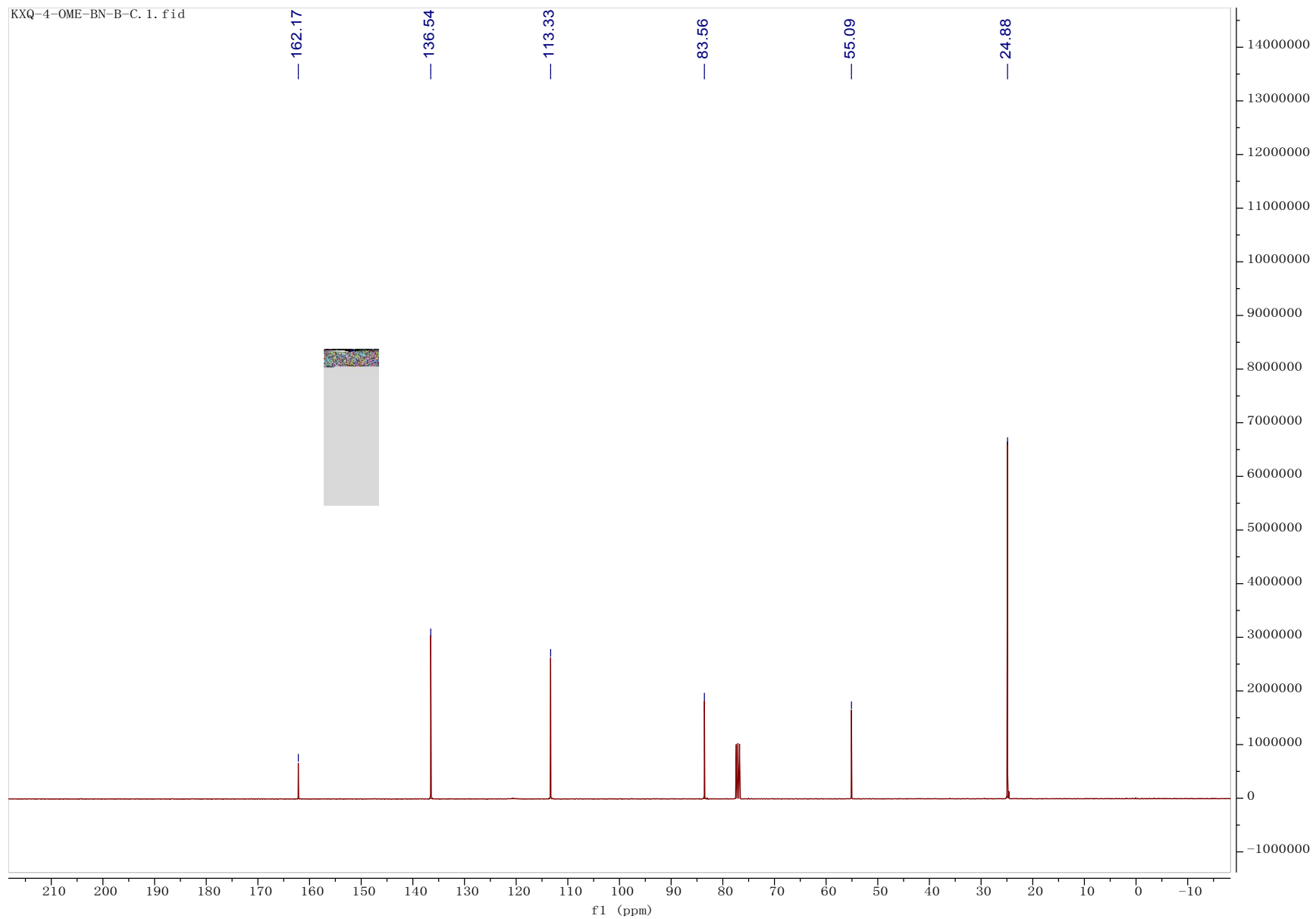
KXQ-2-YIXIAN. 1. fid

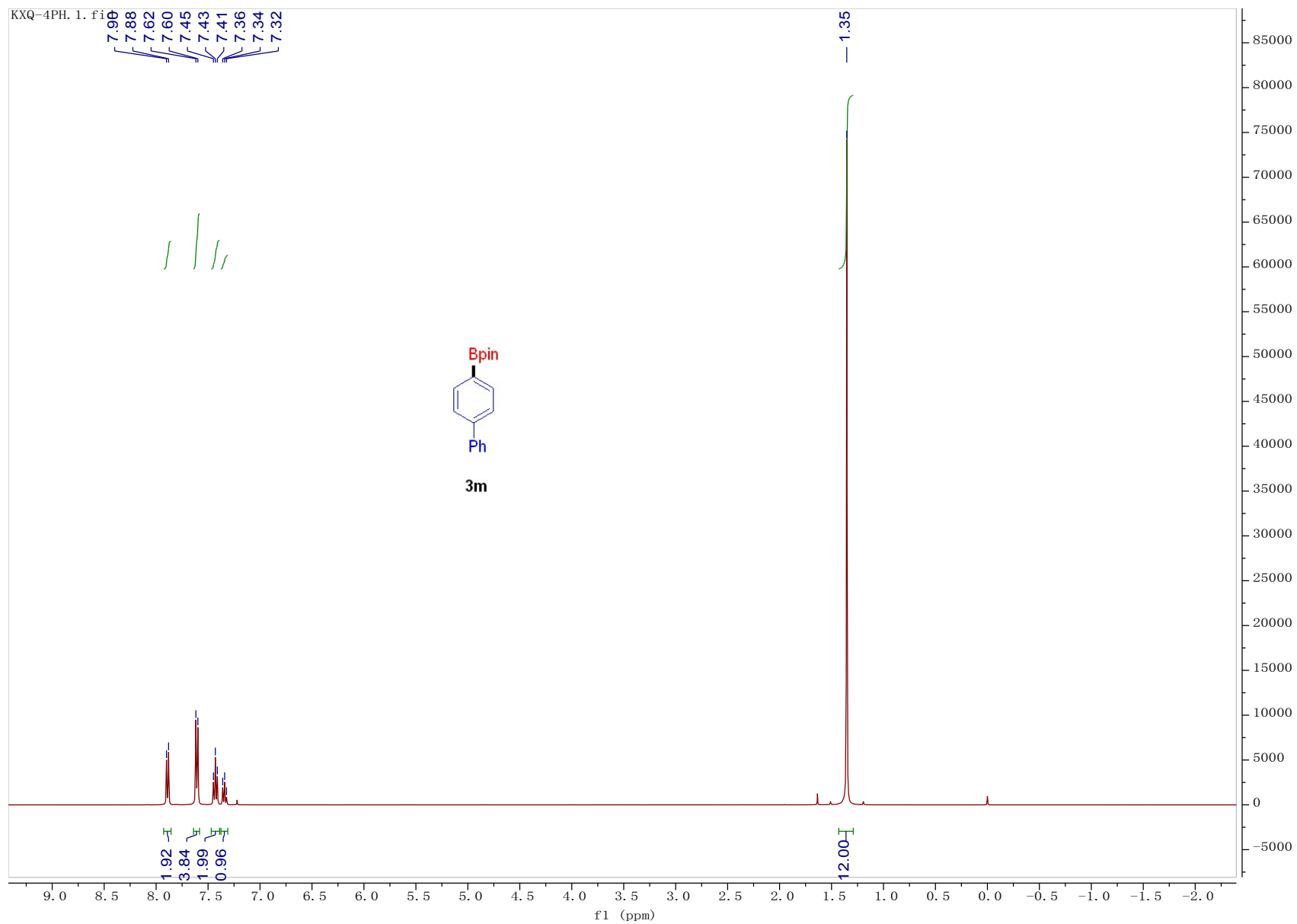




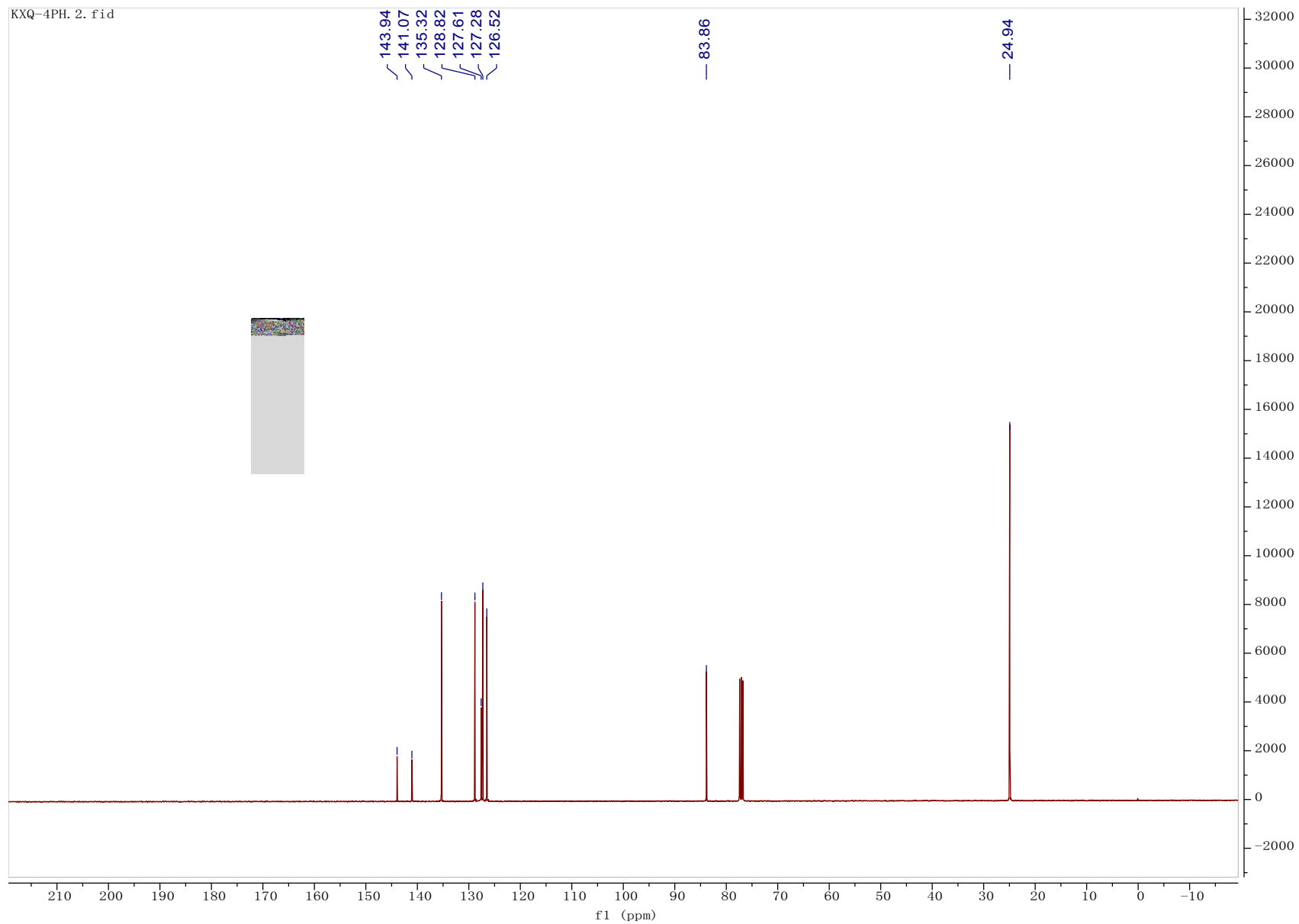


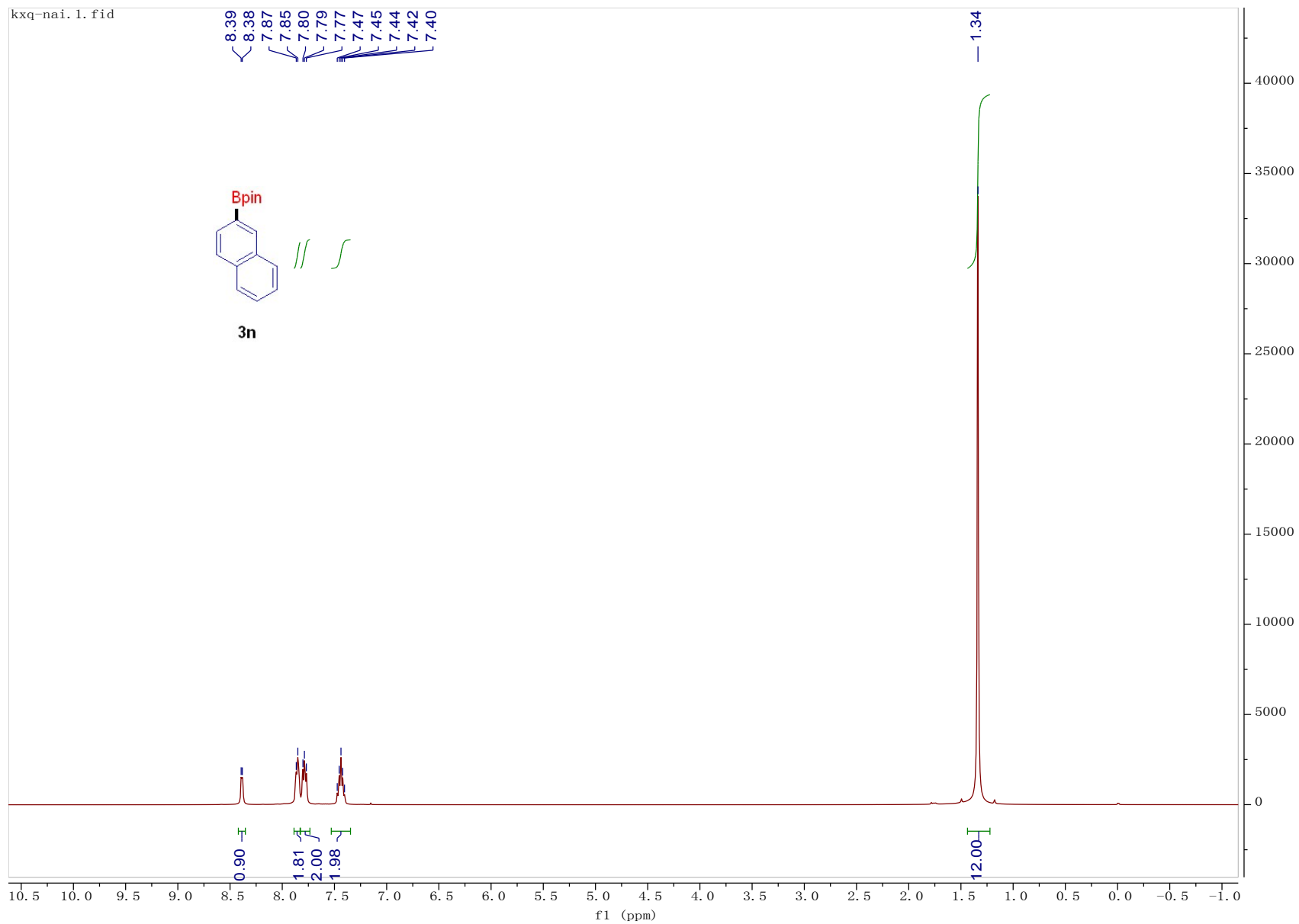




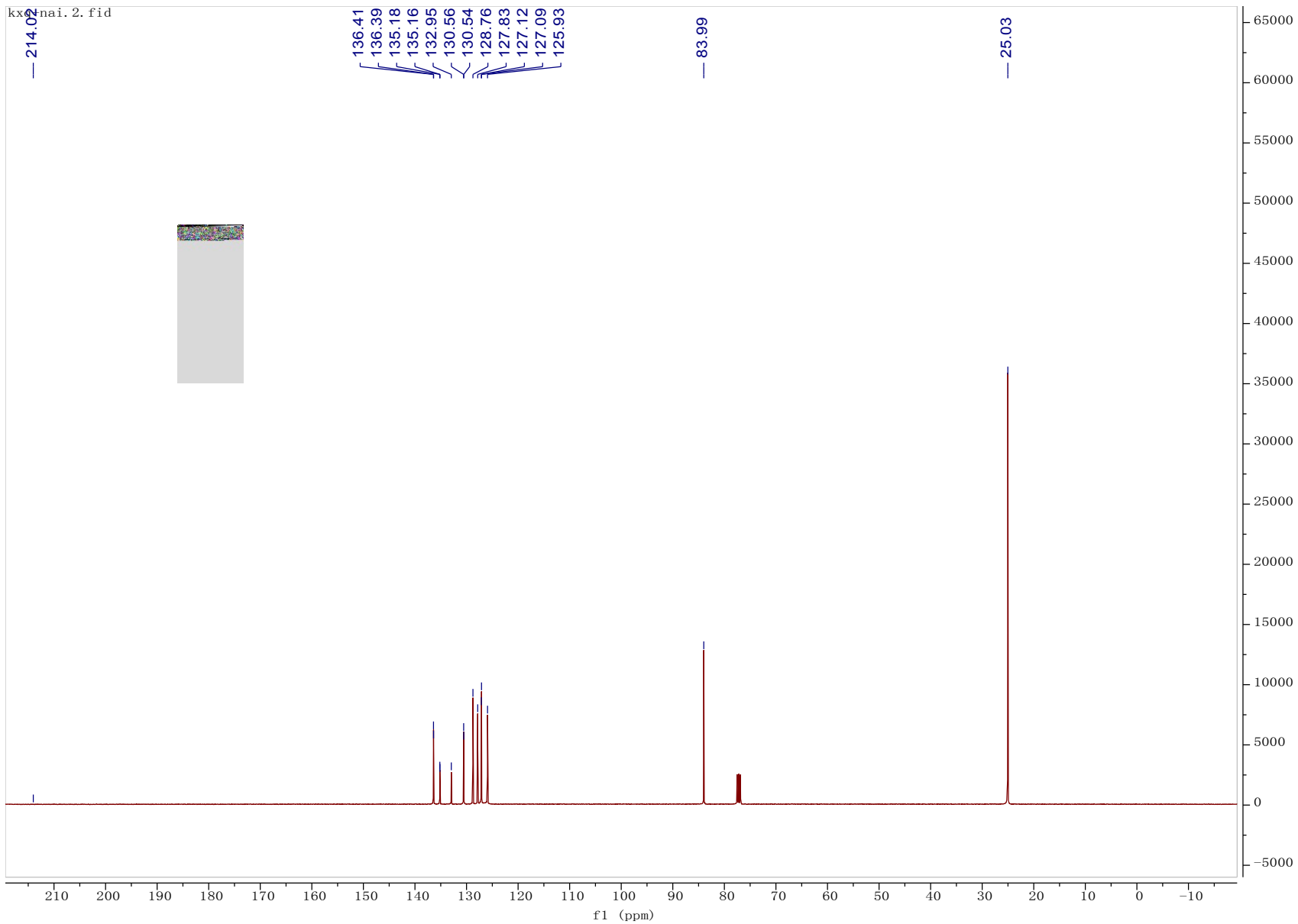


KXQ-4PH. 2. fid

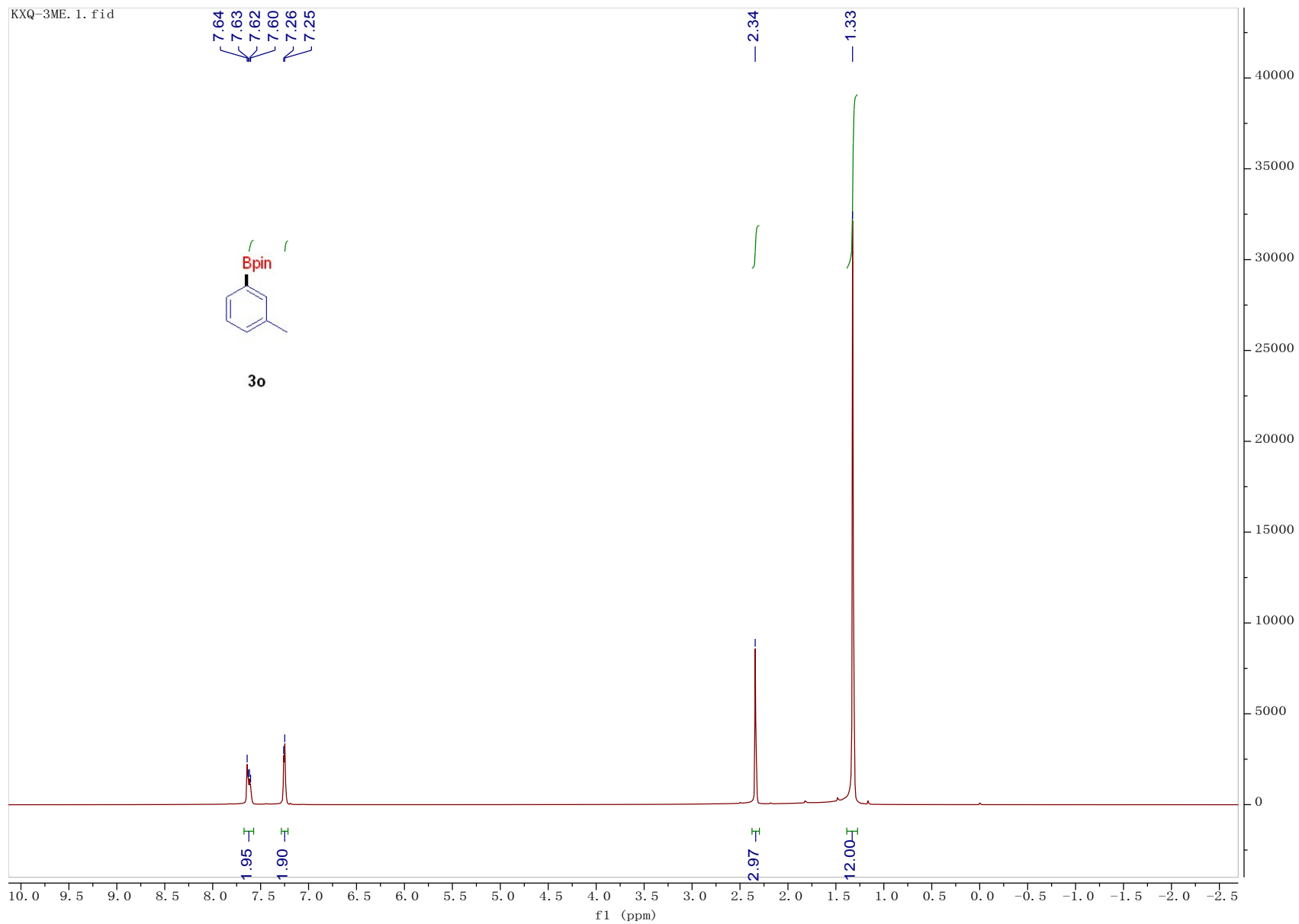




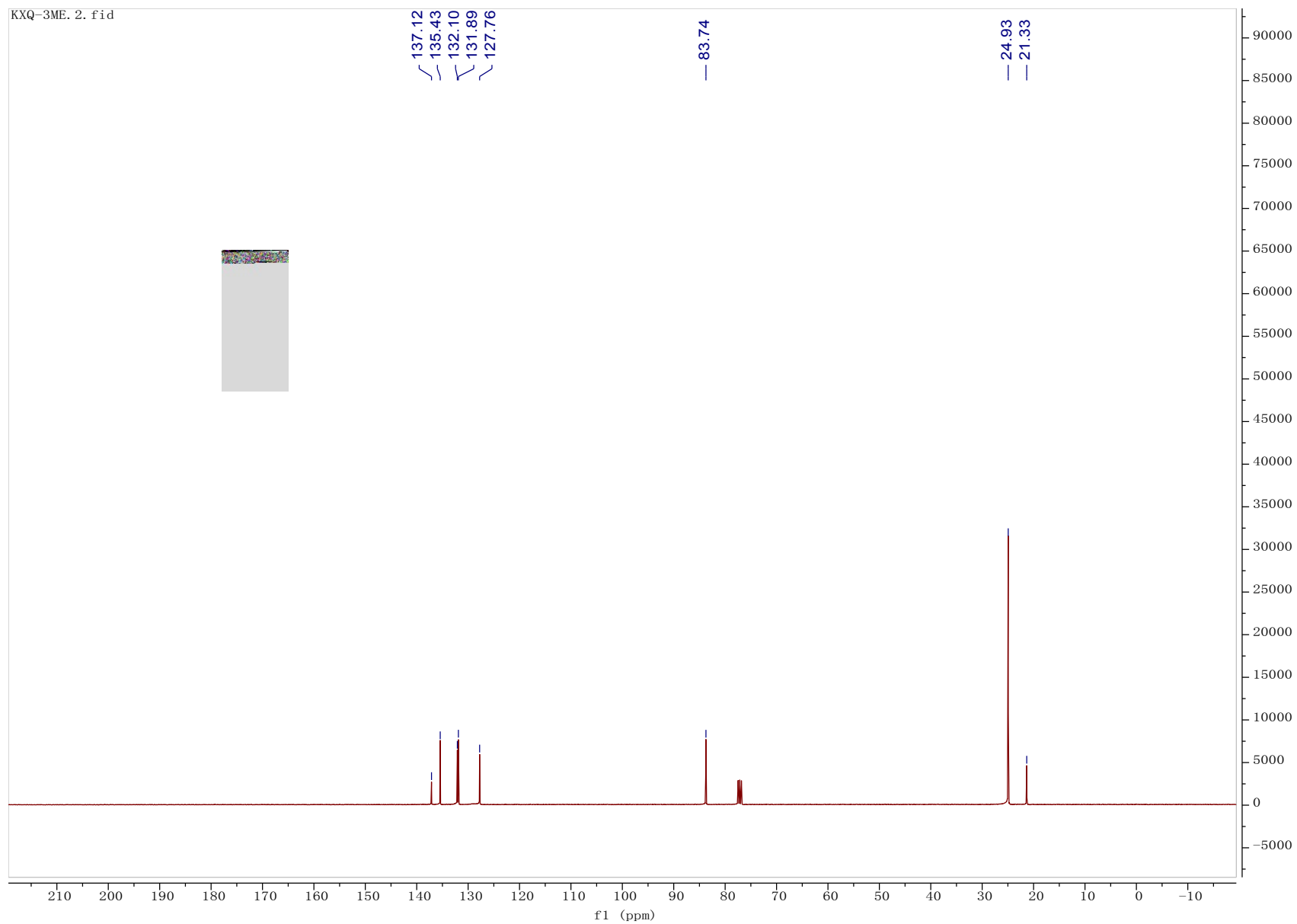


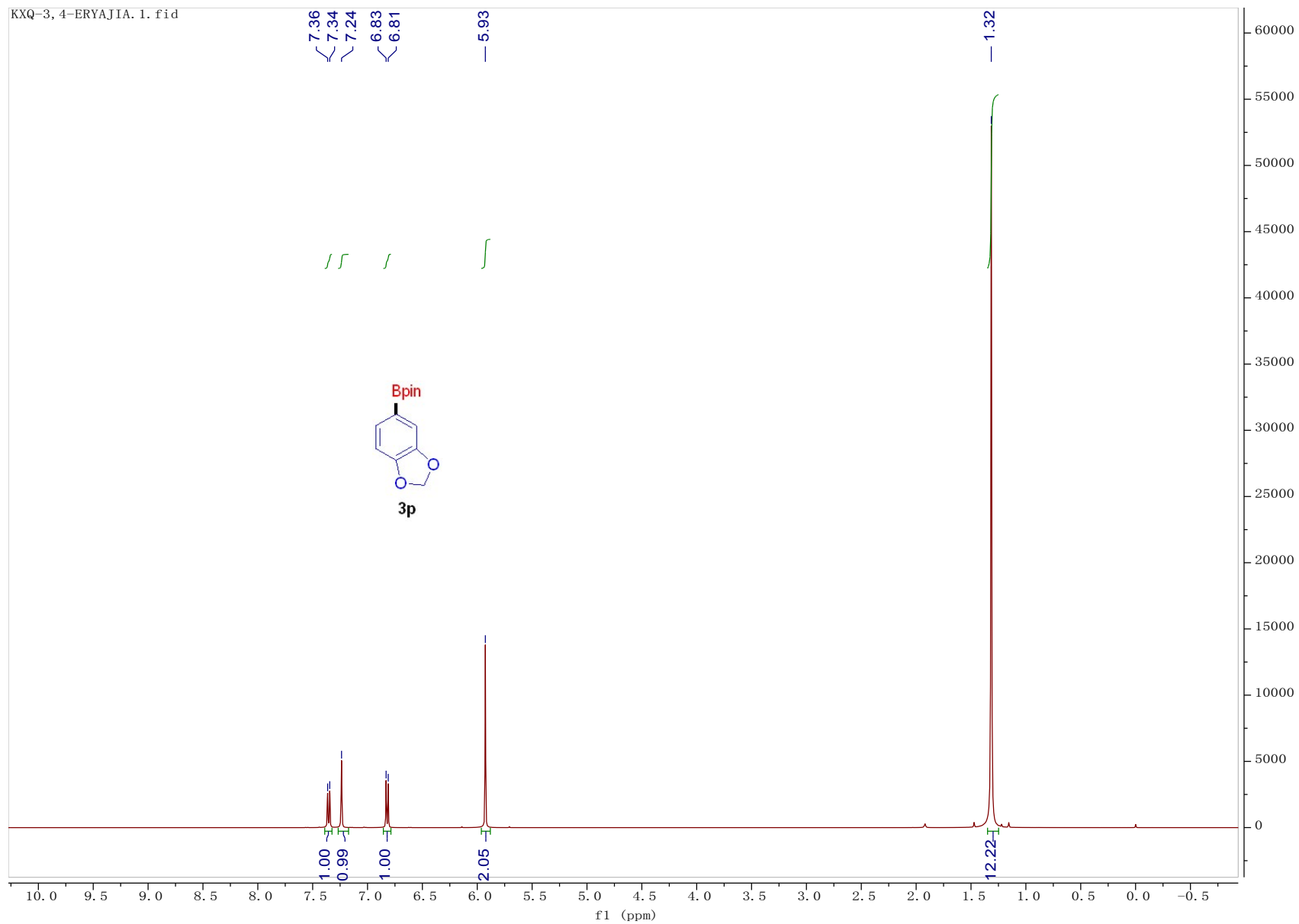


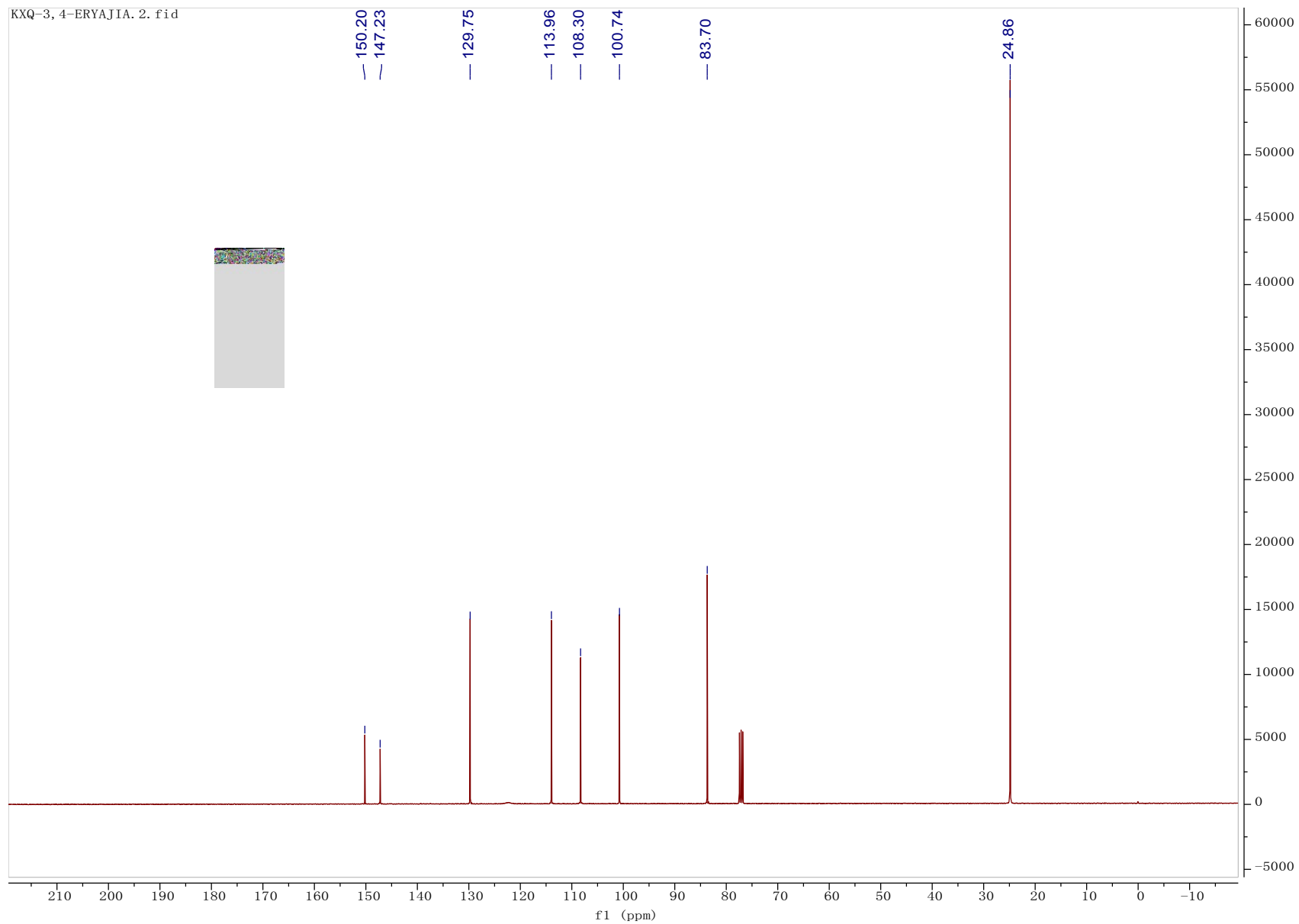
KXQ-3ME. 1. fid



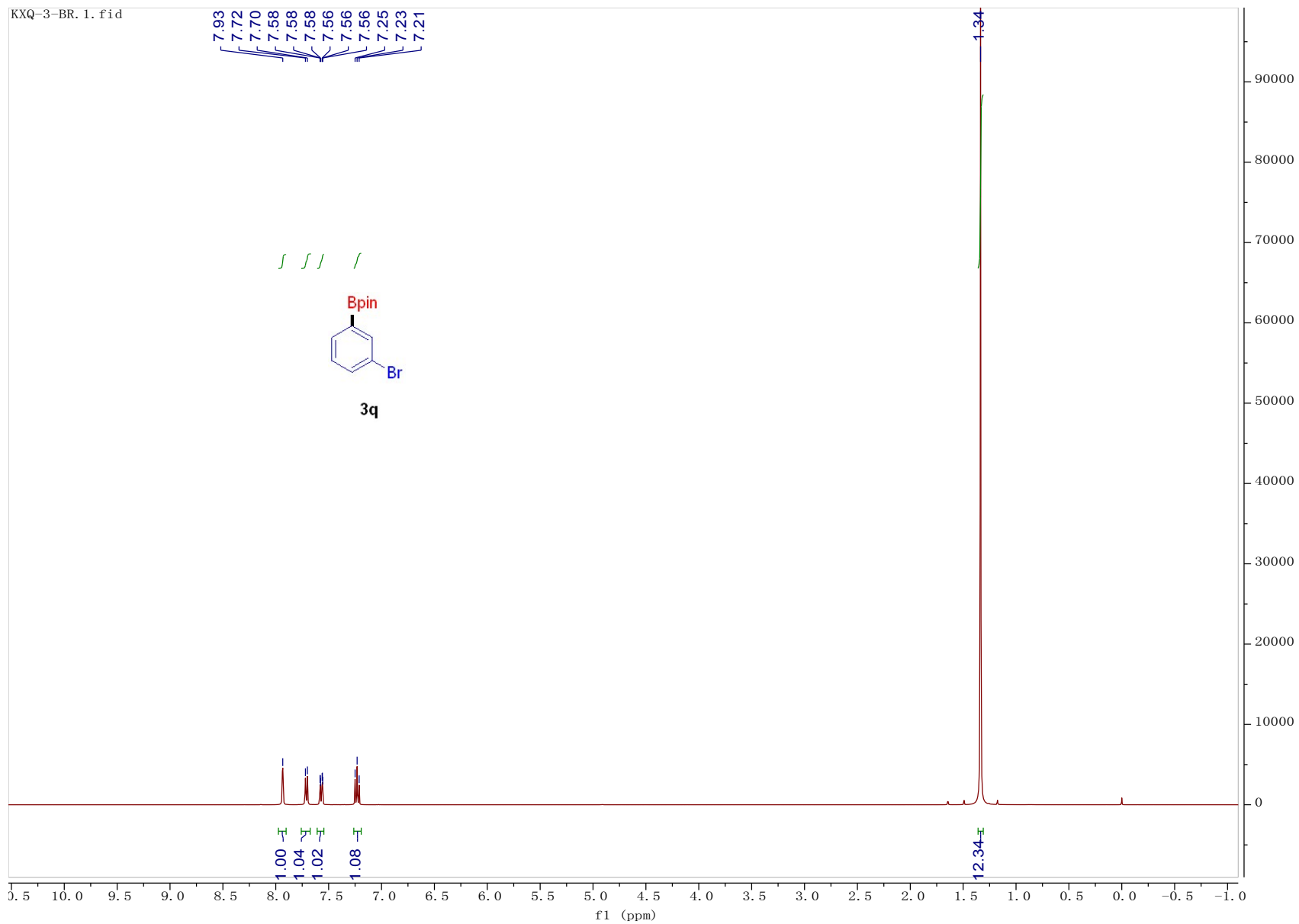
KXQ-3ME. 2. fid



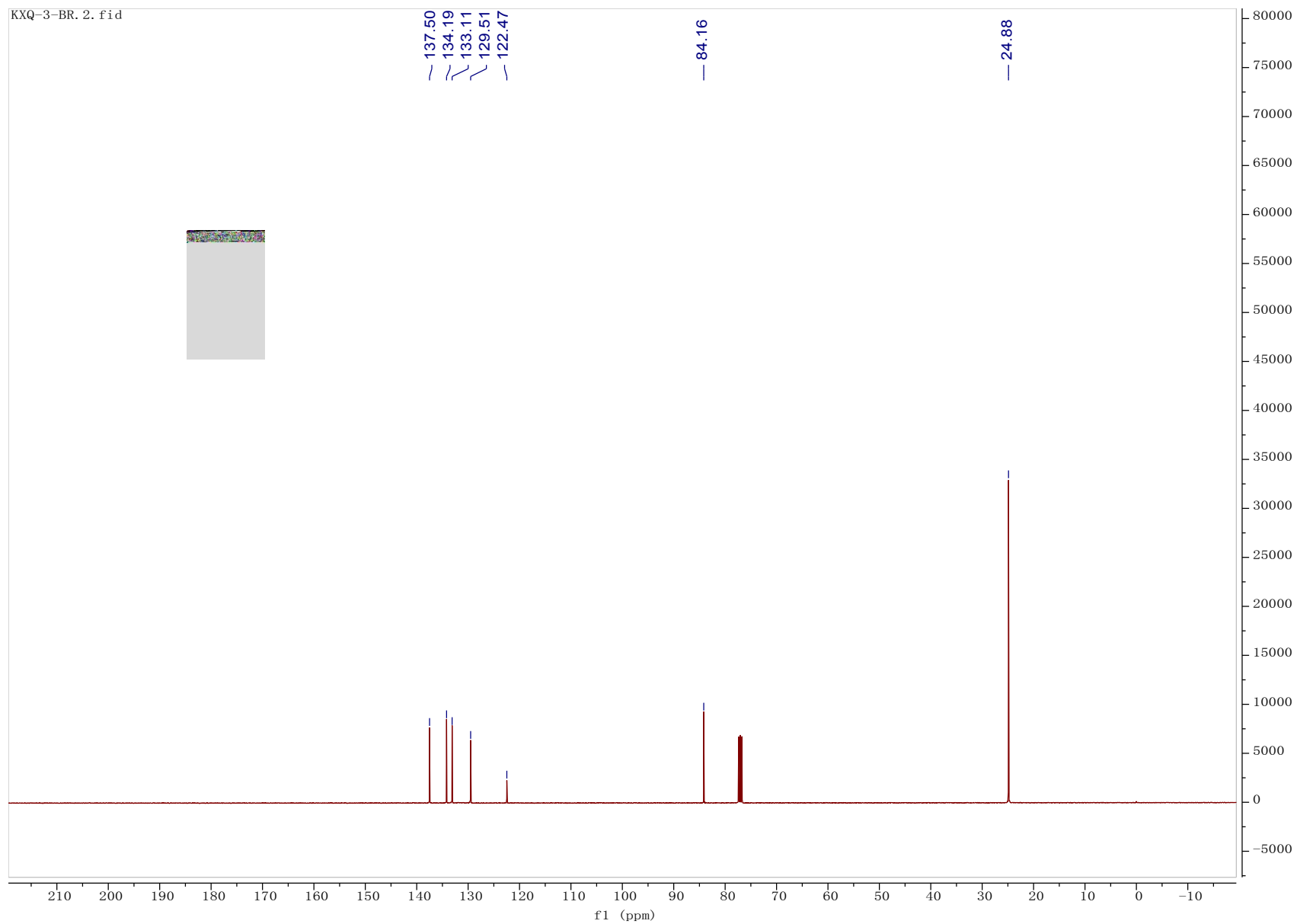


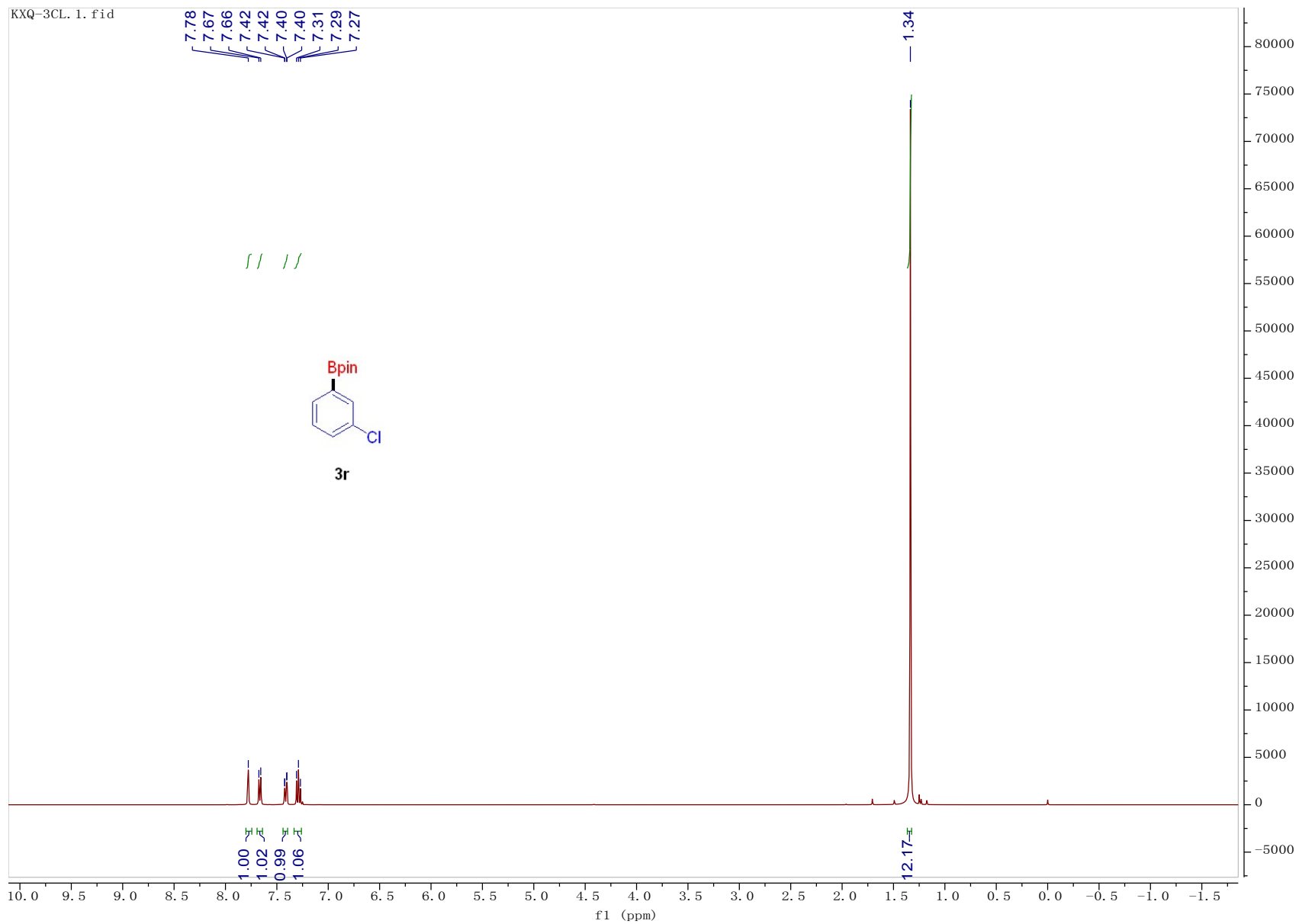


KXQ-3-BR.1.fid



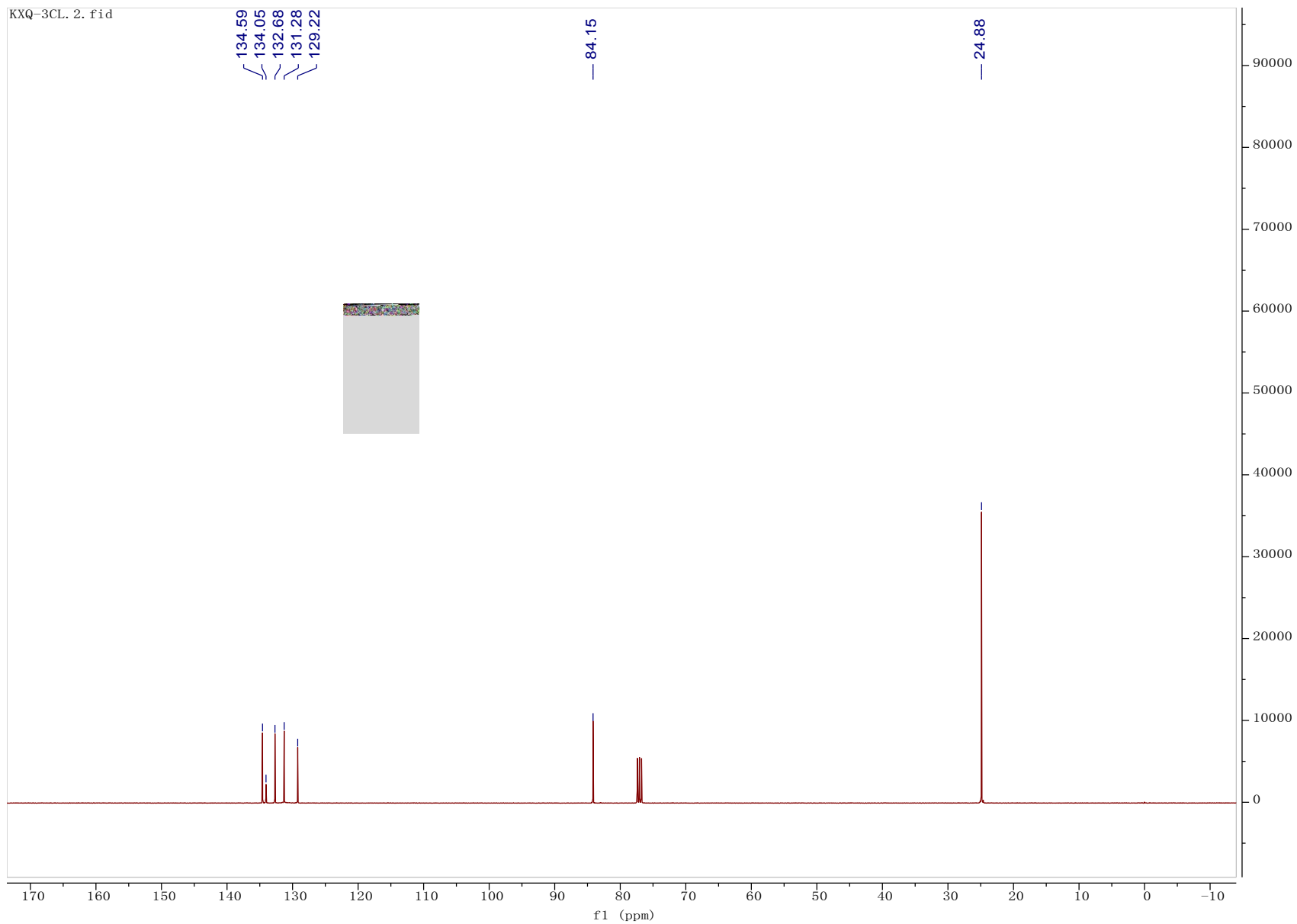
KXQ-3-BR. 2. fid



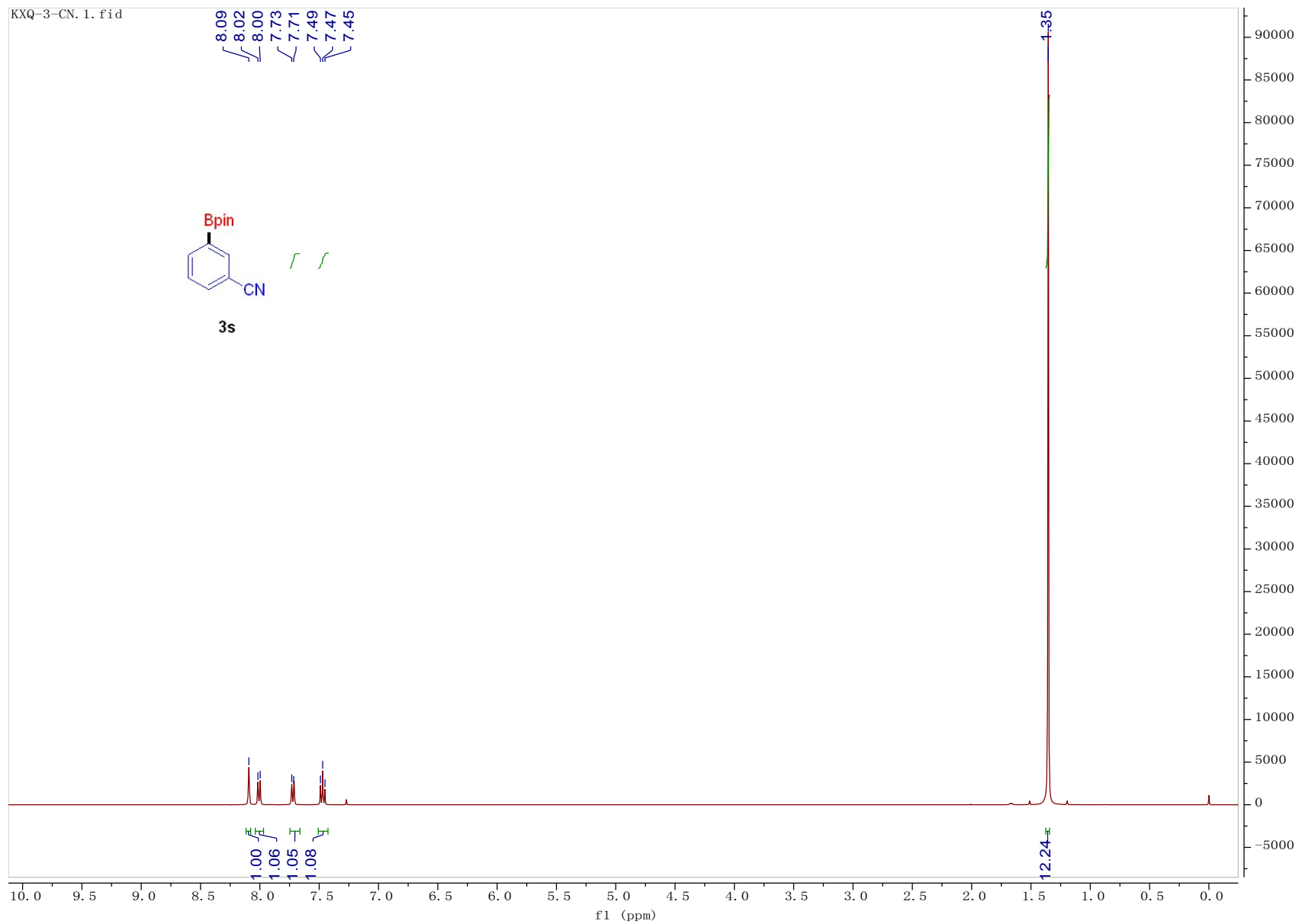




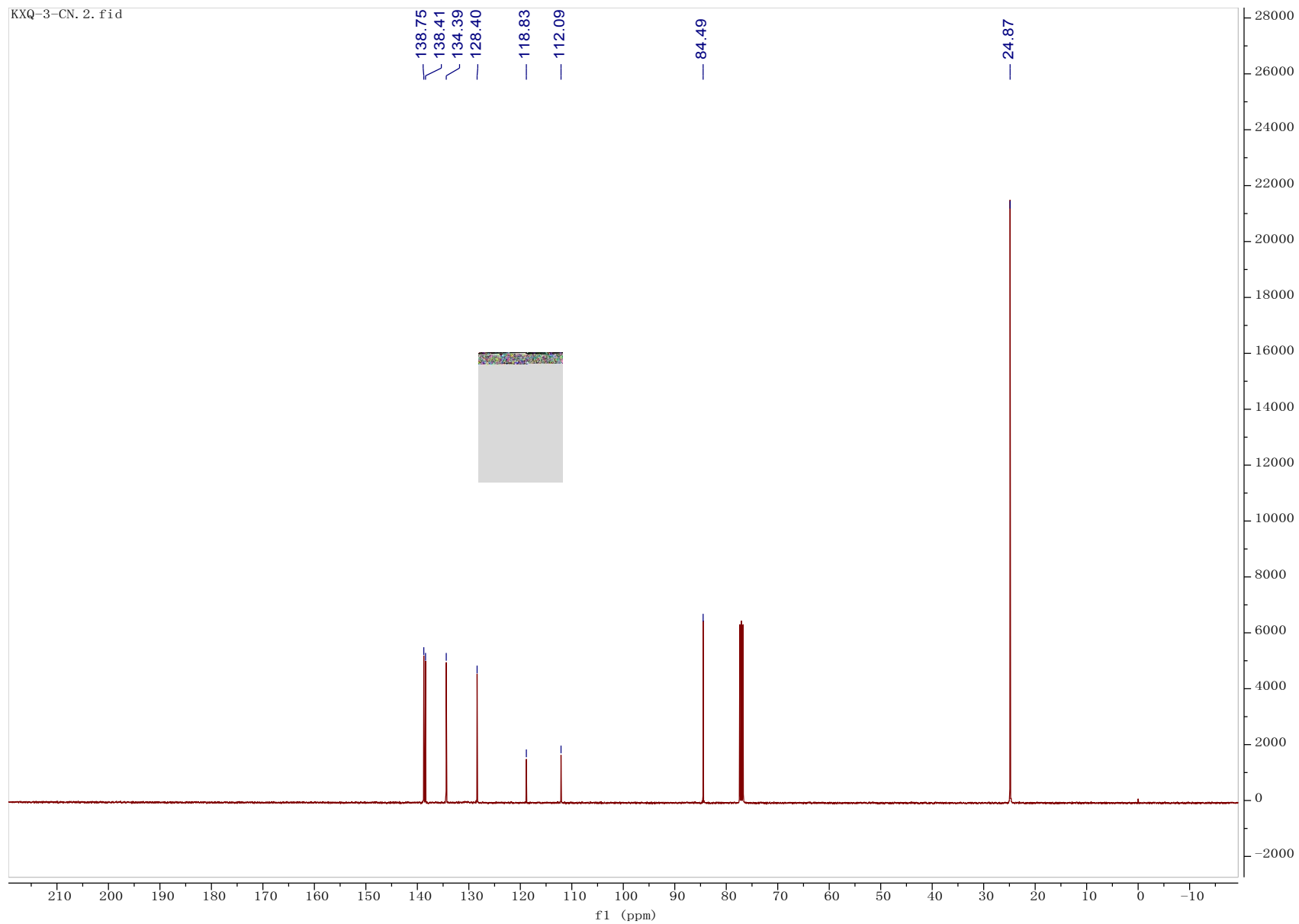
KXQ-3CL. 2. fid

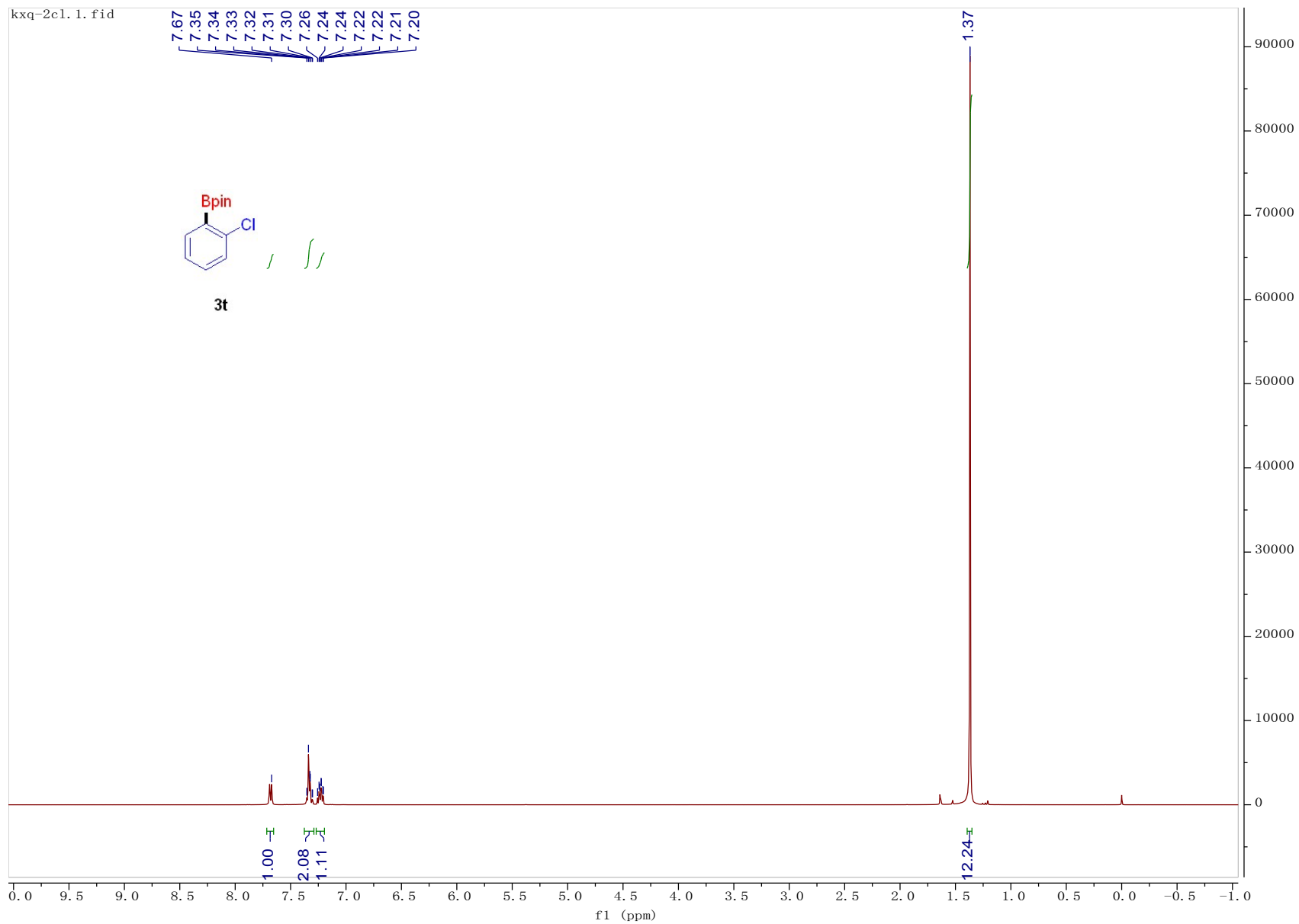


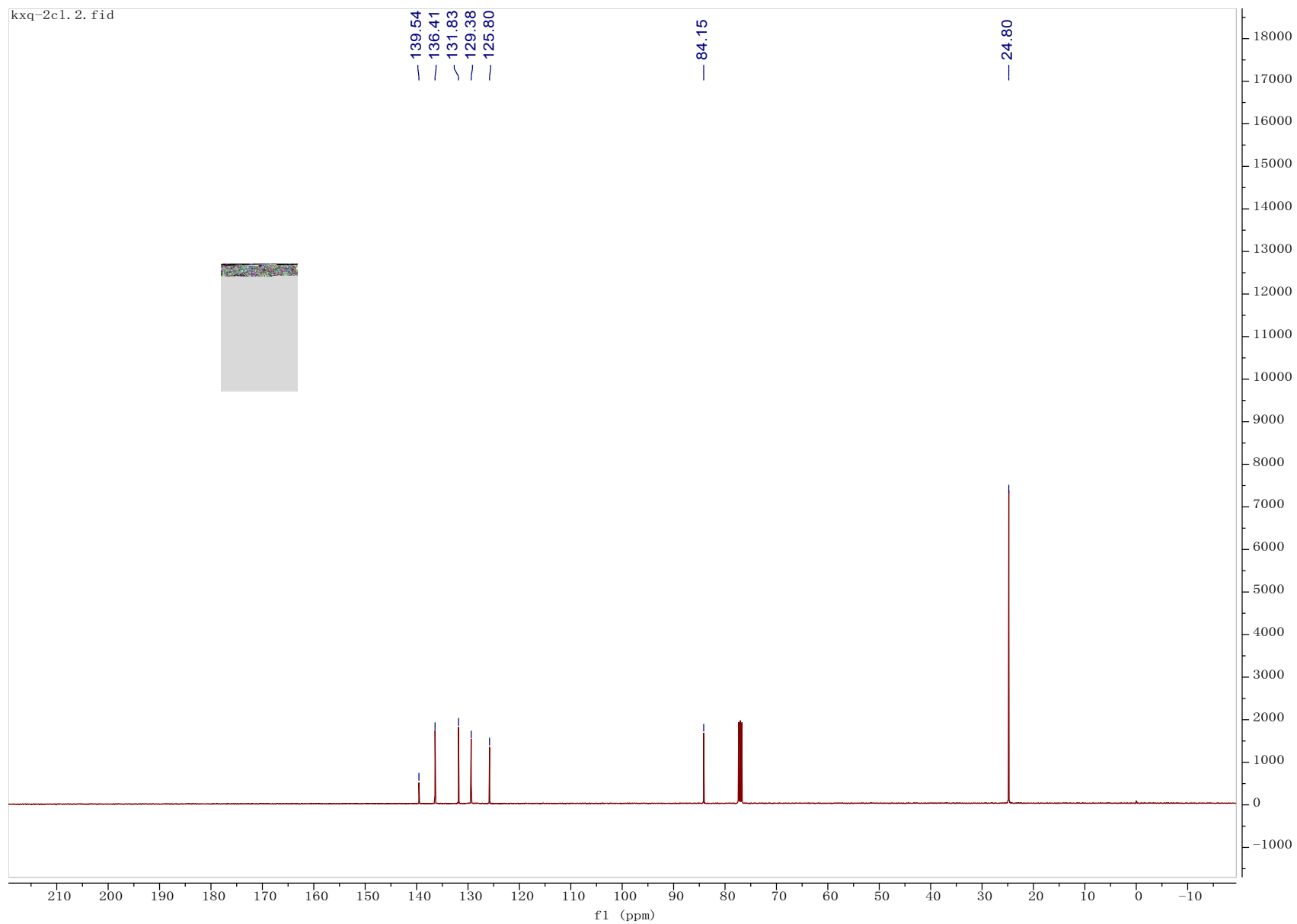
KXQ-3-CN.1.fid



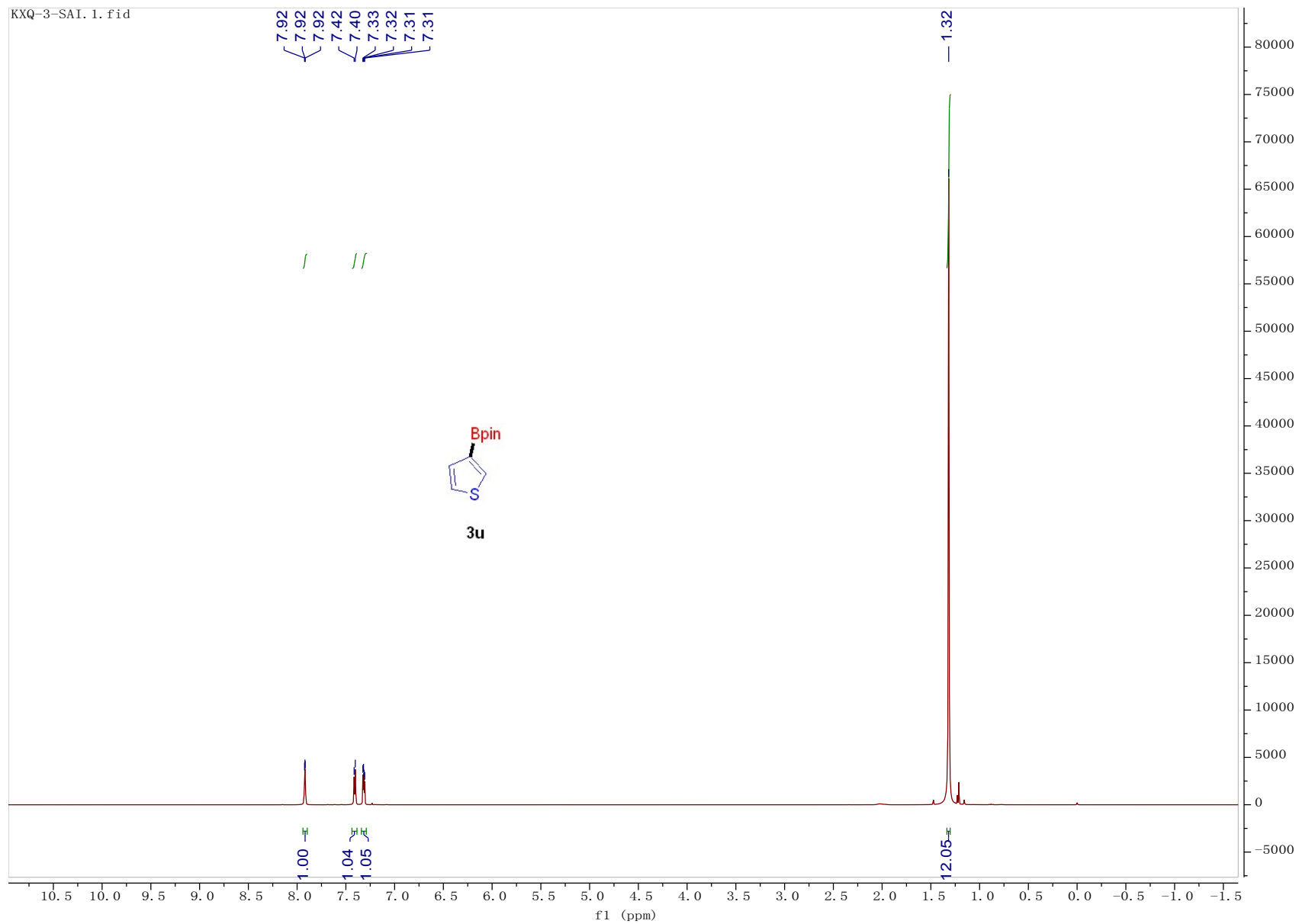
KXQ-3-CN. 2. fid



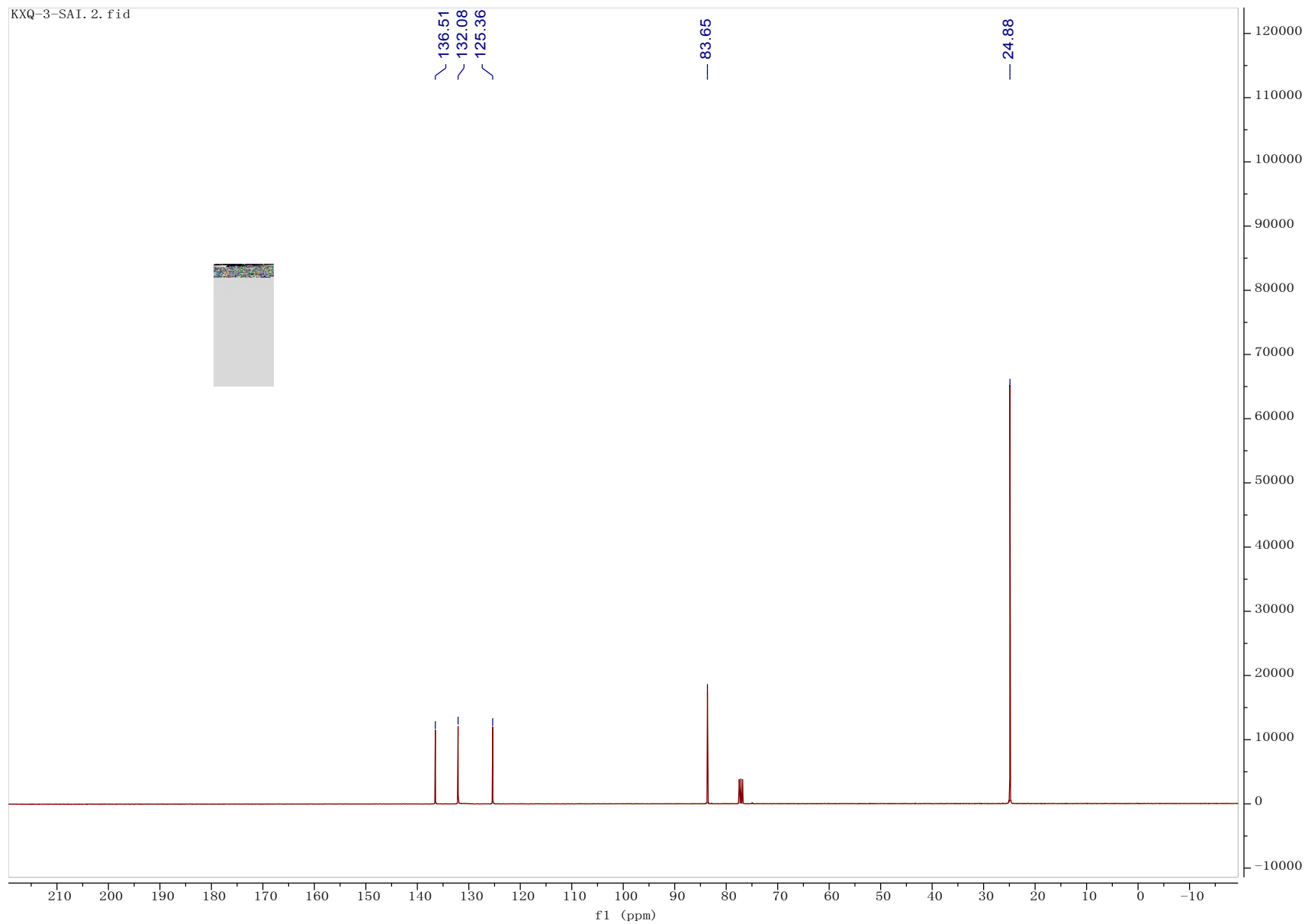


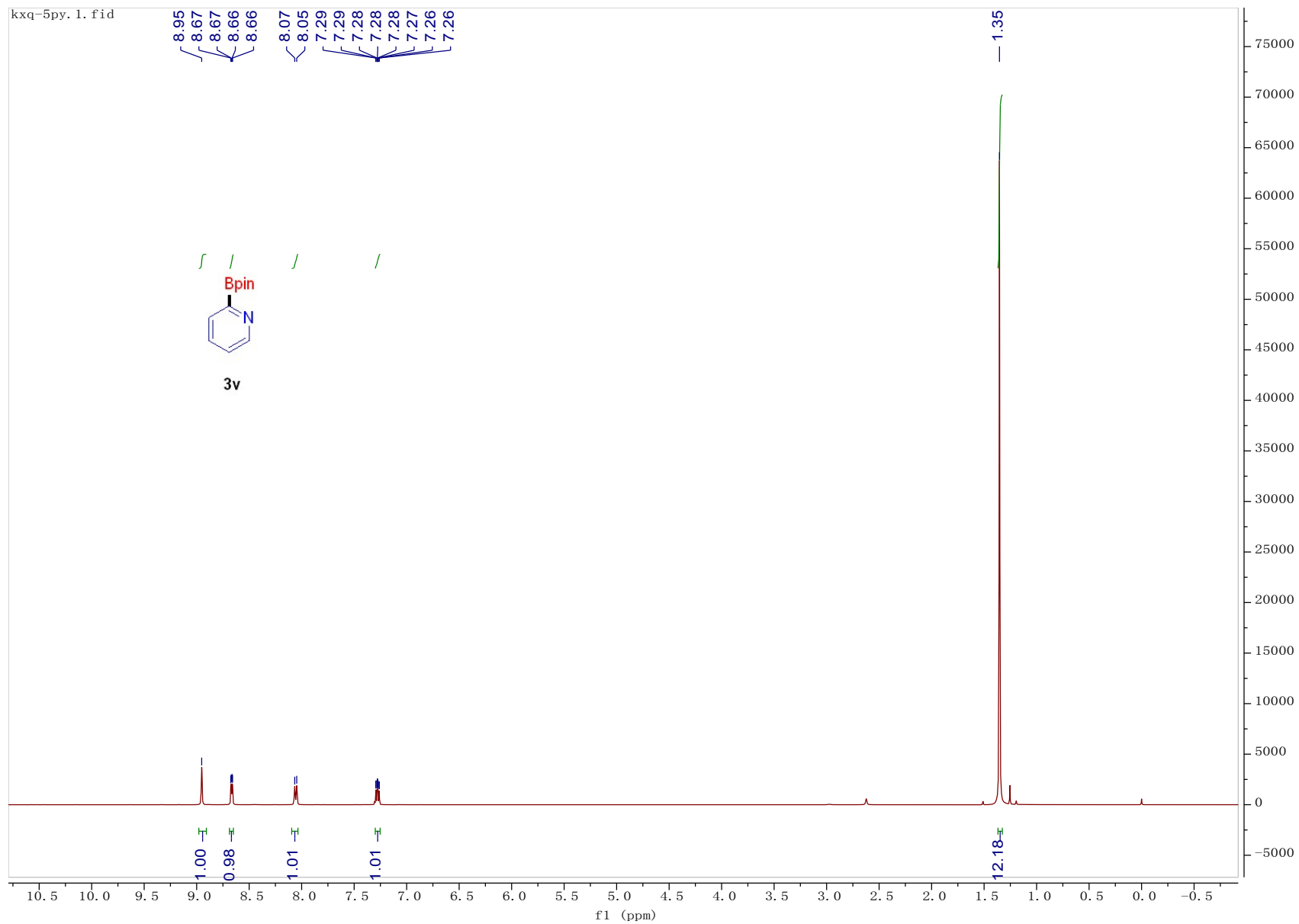


KXQ-3-SAI. 1. fid

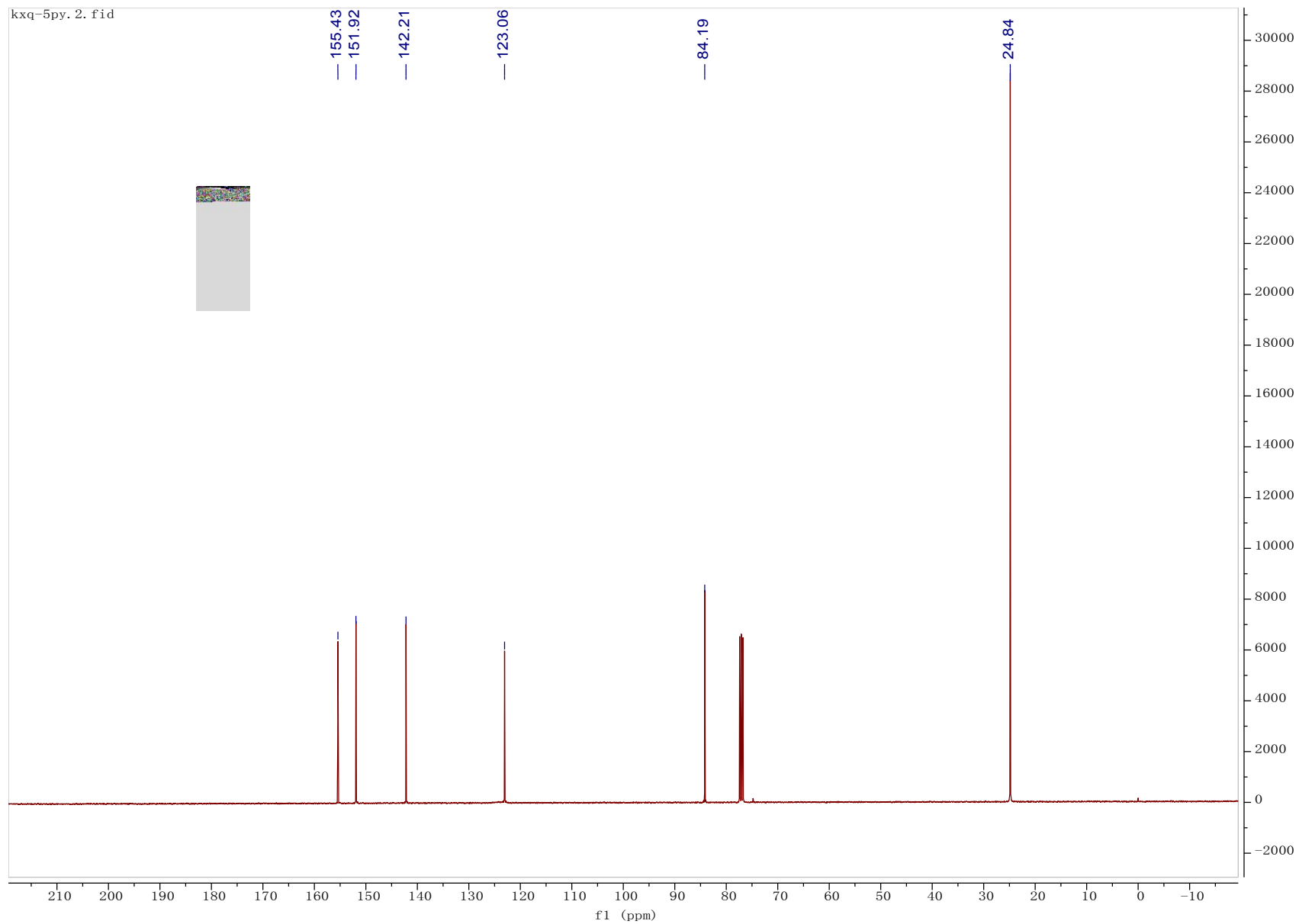


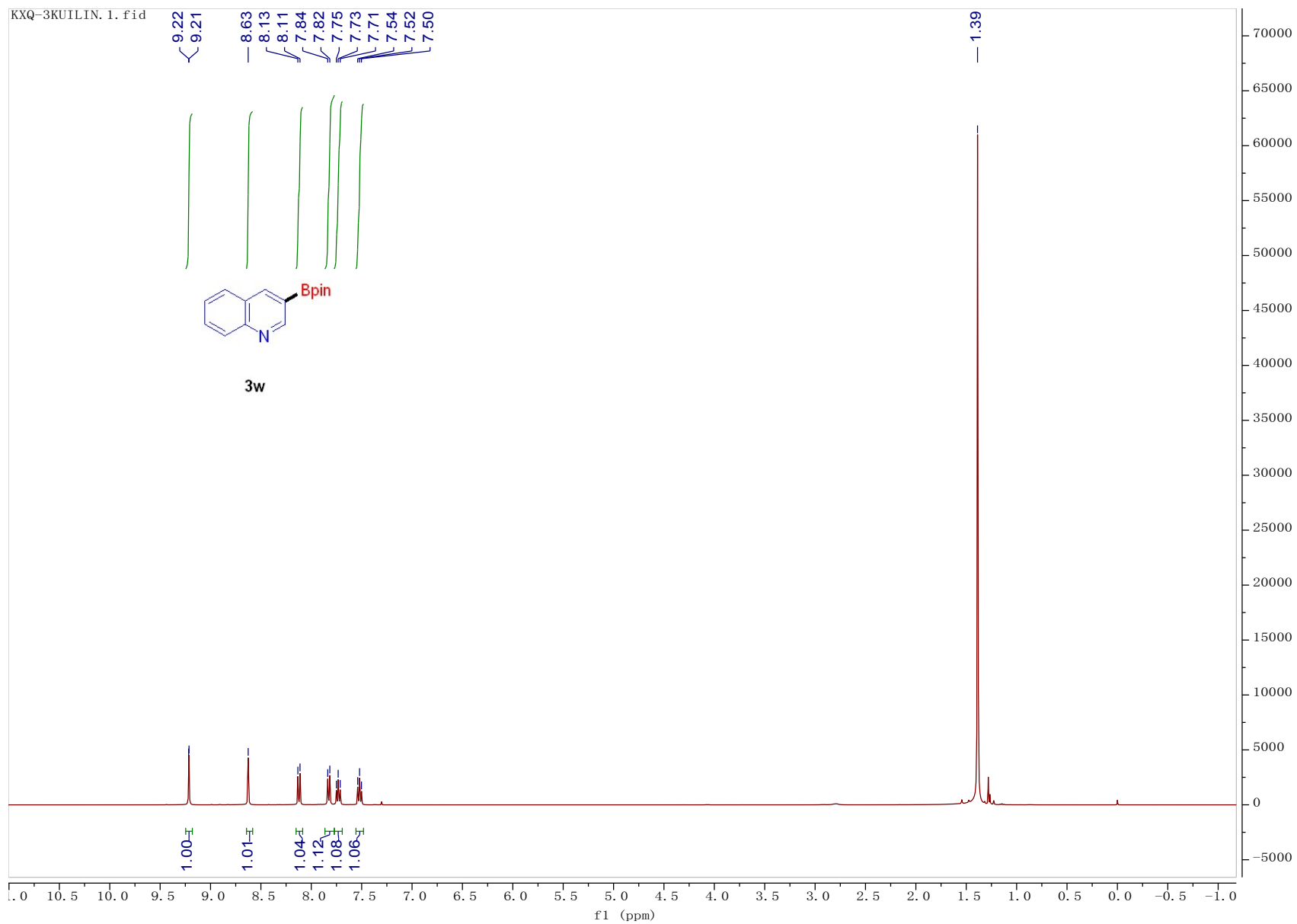
KXQ-3-SAI. 2. fid



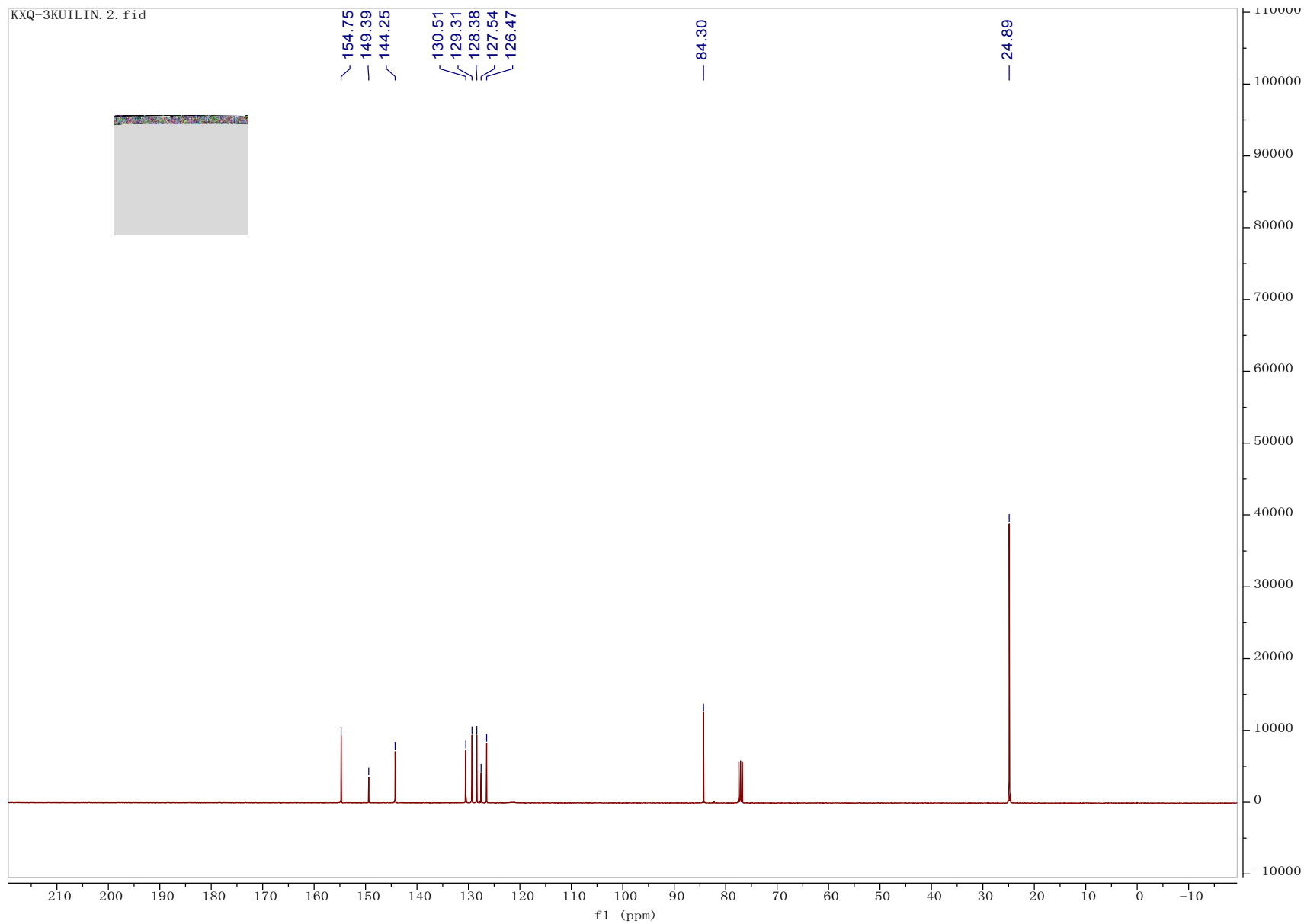




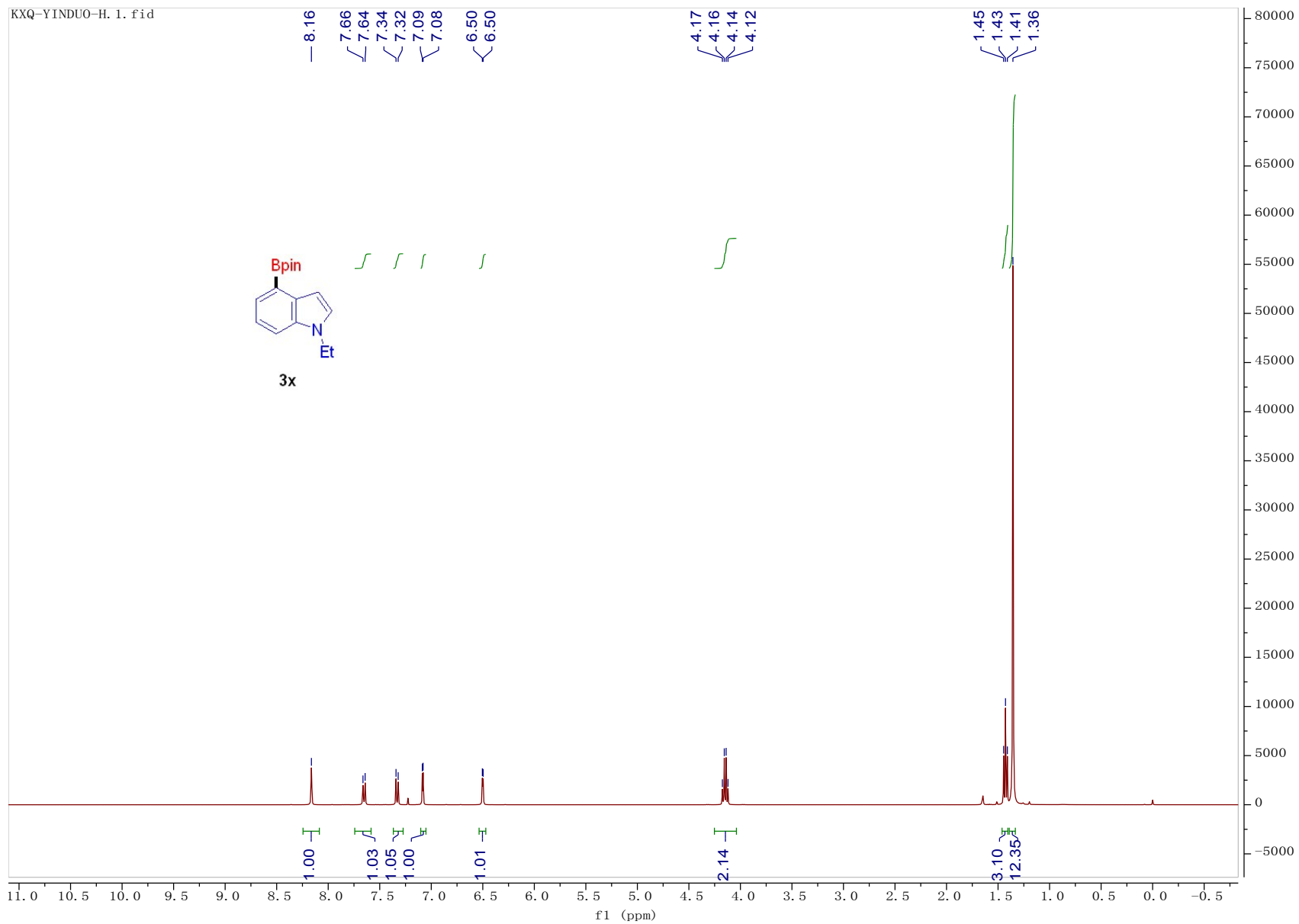




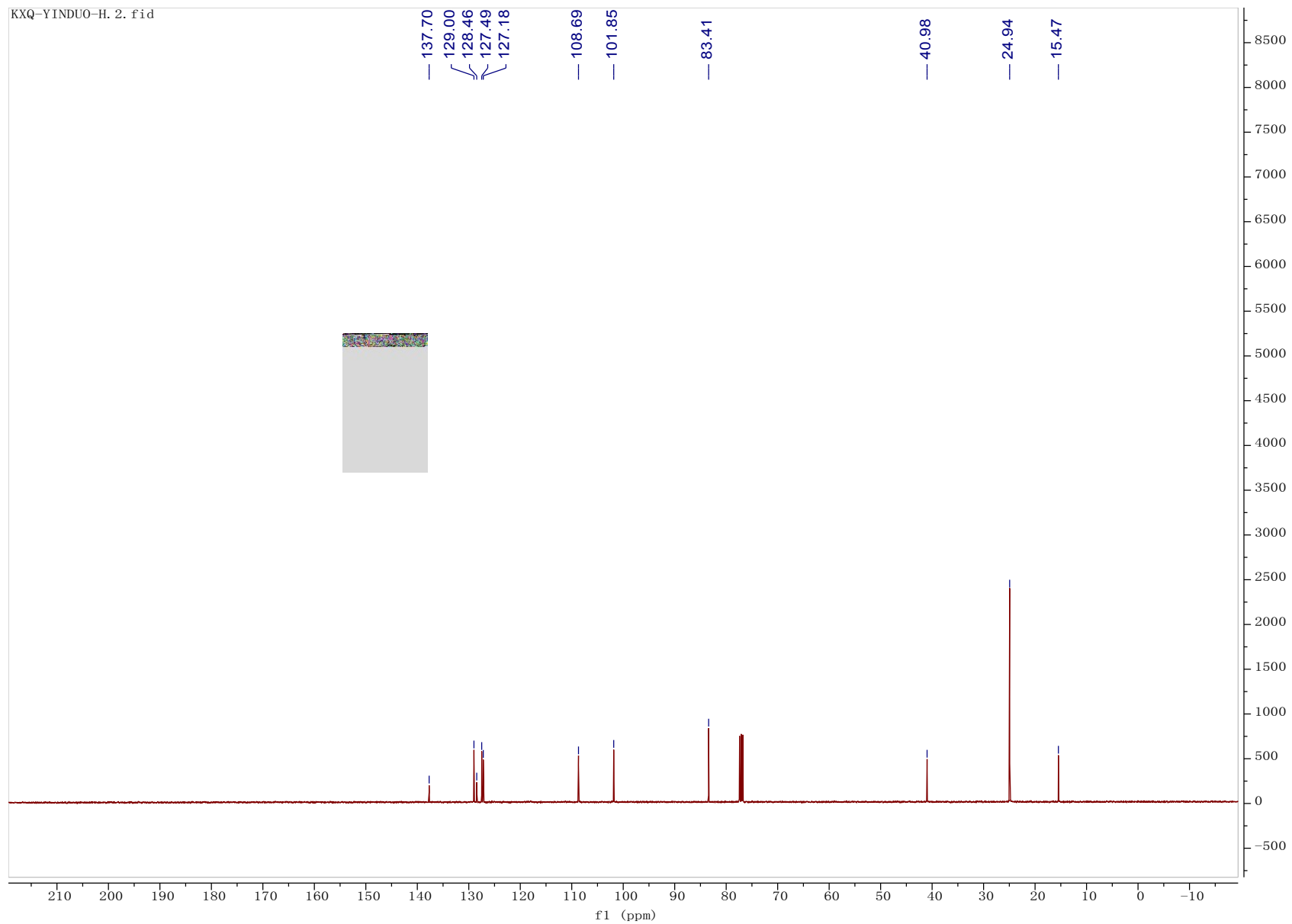
KXQ-3KUILIN. 2. fid

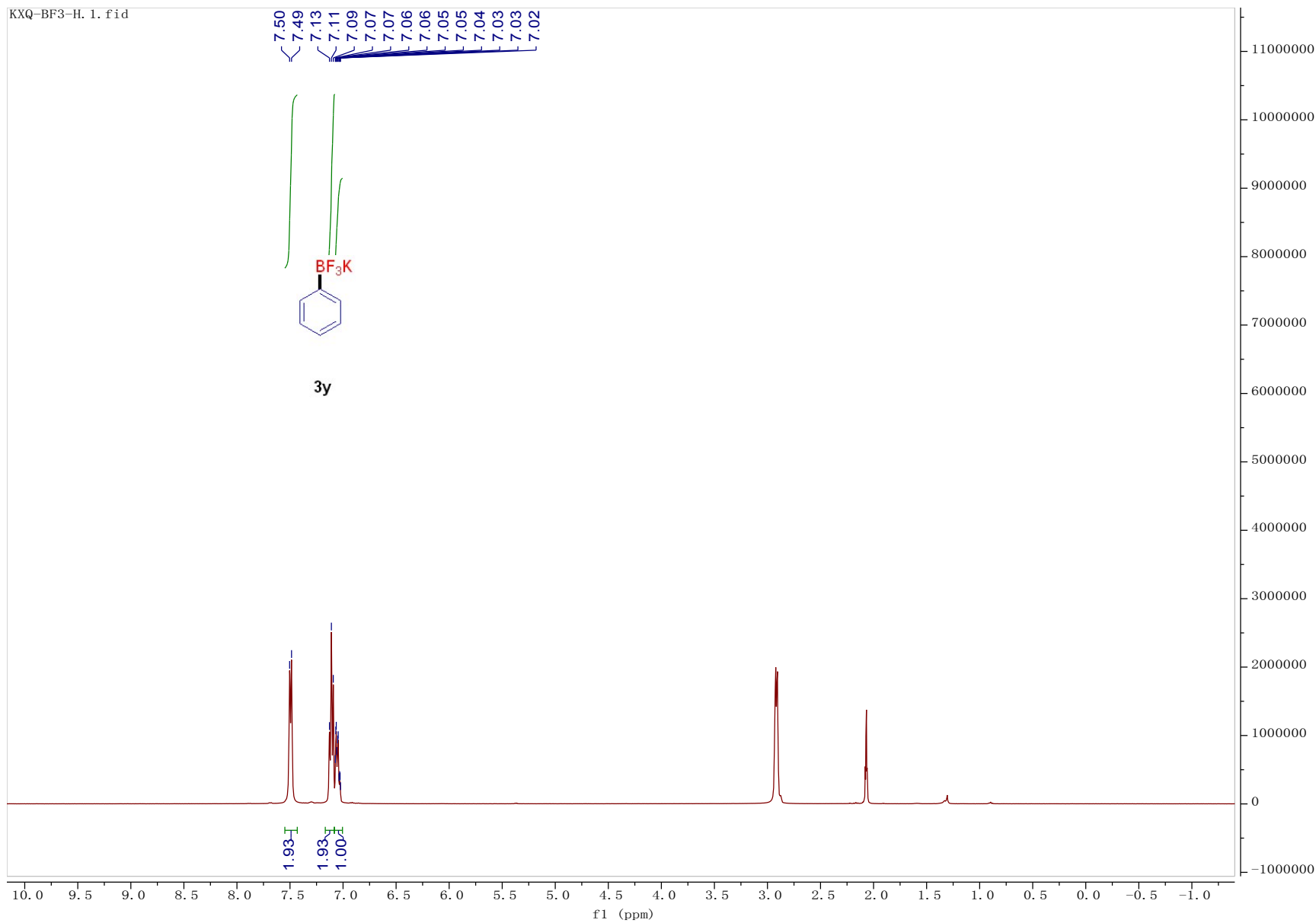


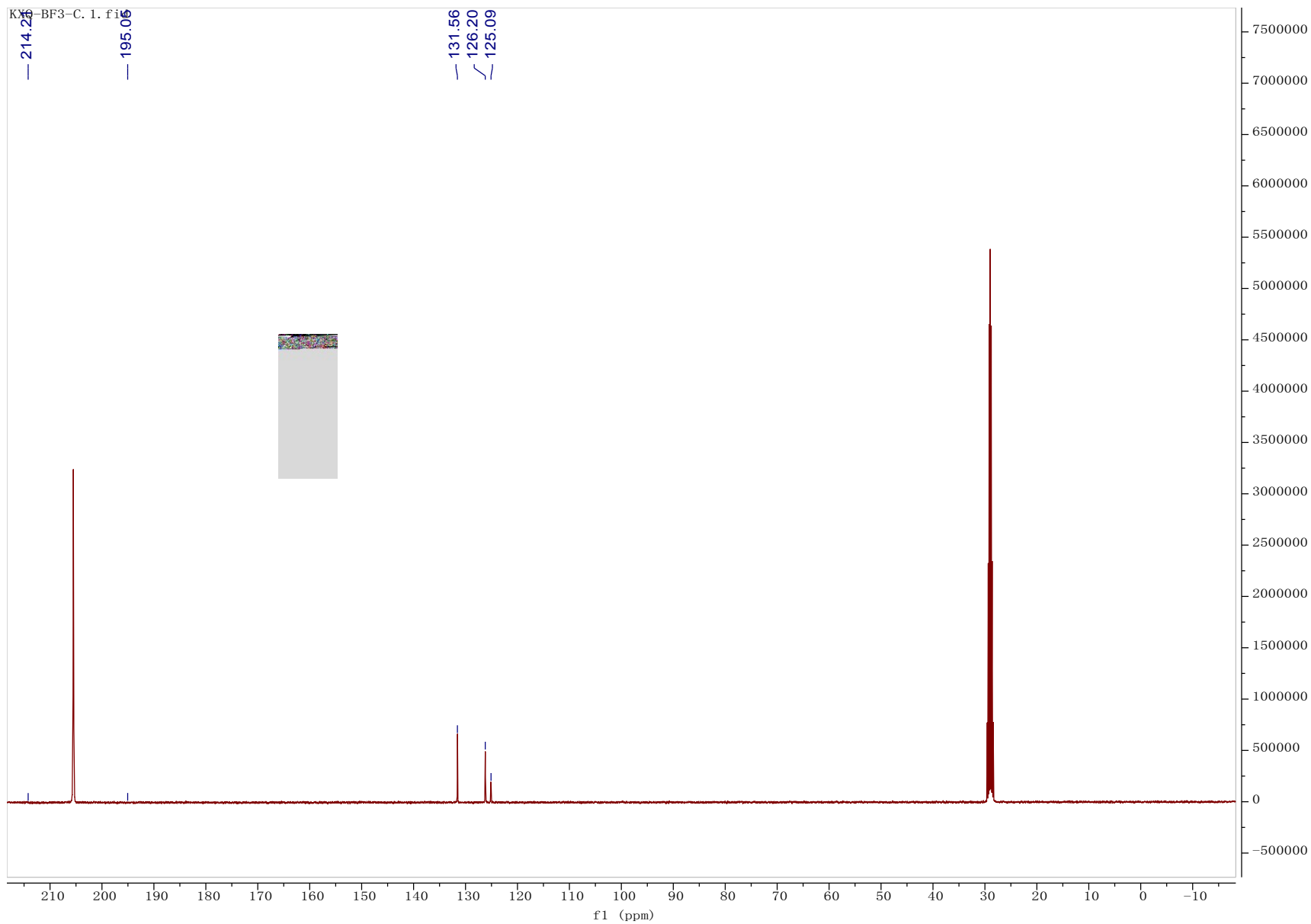
KXQ-YINDUO-H. 1. fid



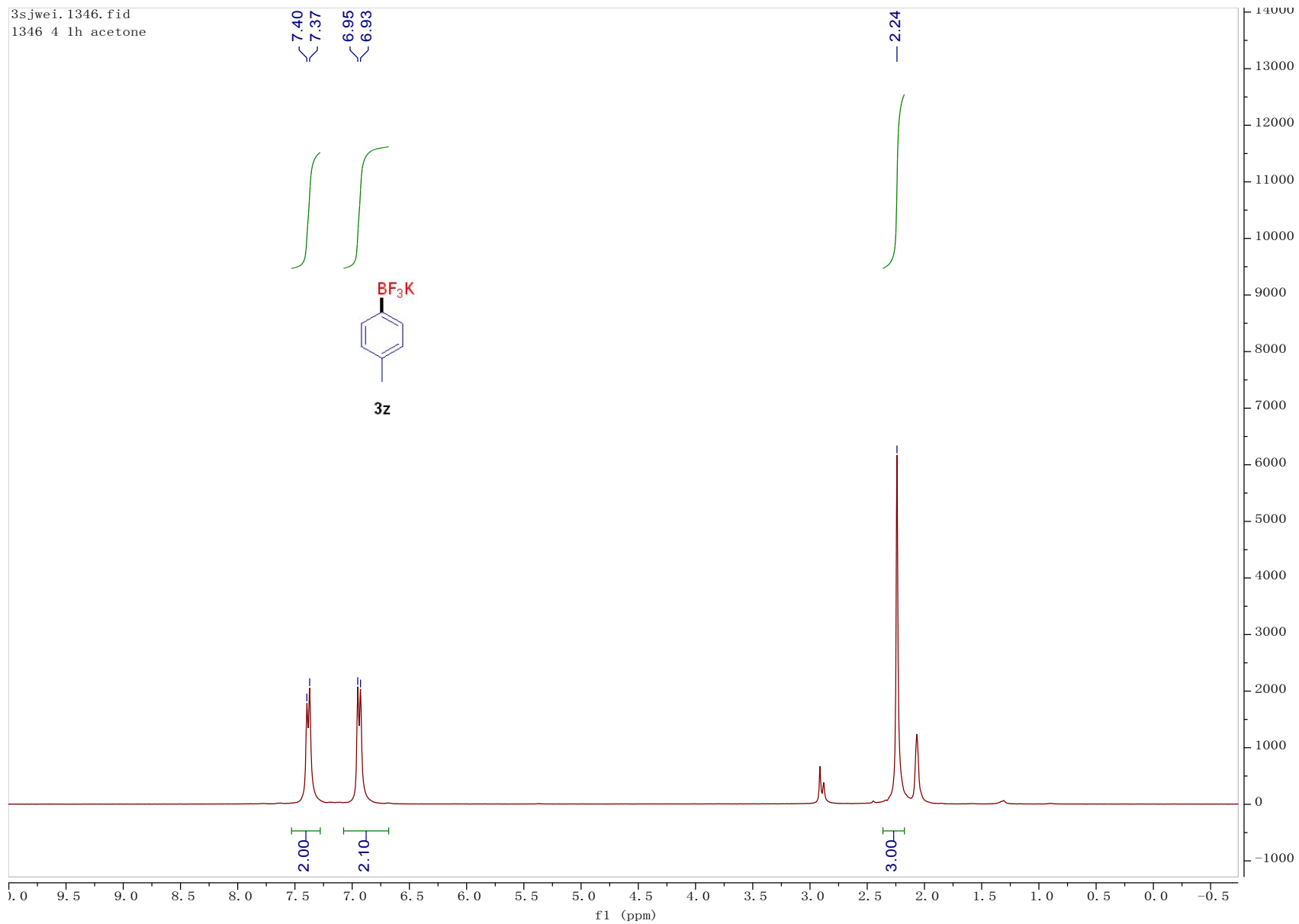
KXQ-YINDUO-H. 2. fid





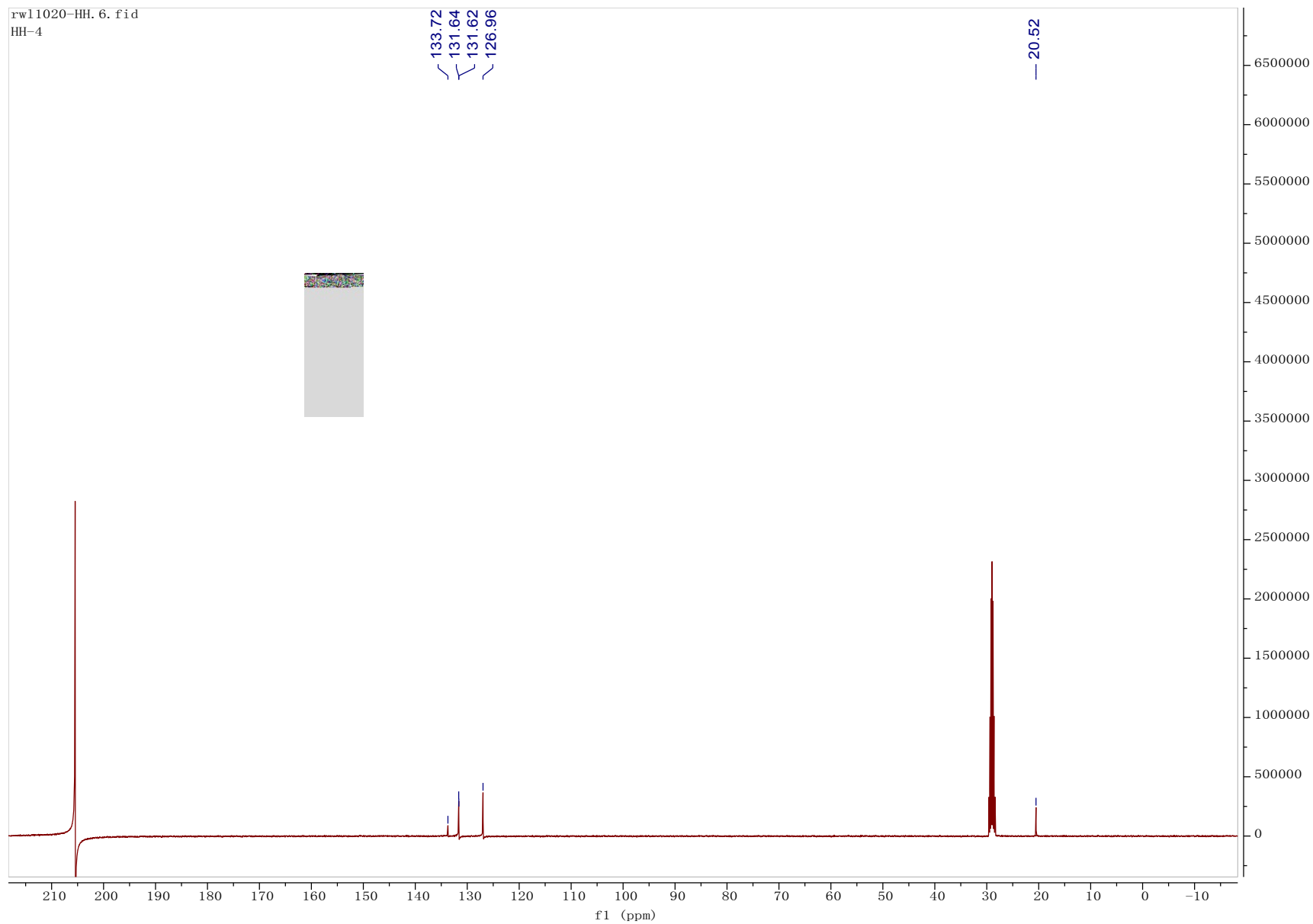


3sjwei.1346.fid  
1346 4 1h acetone

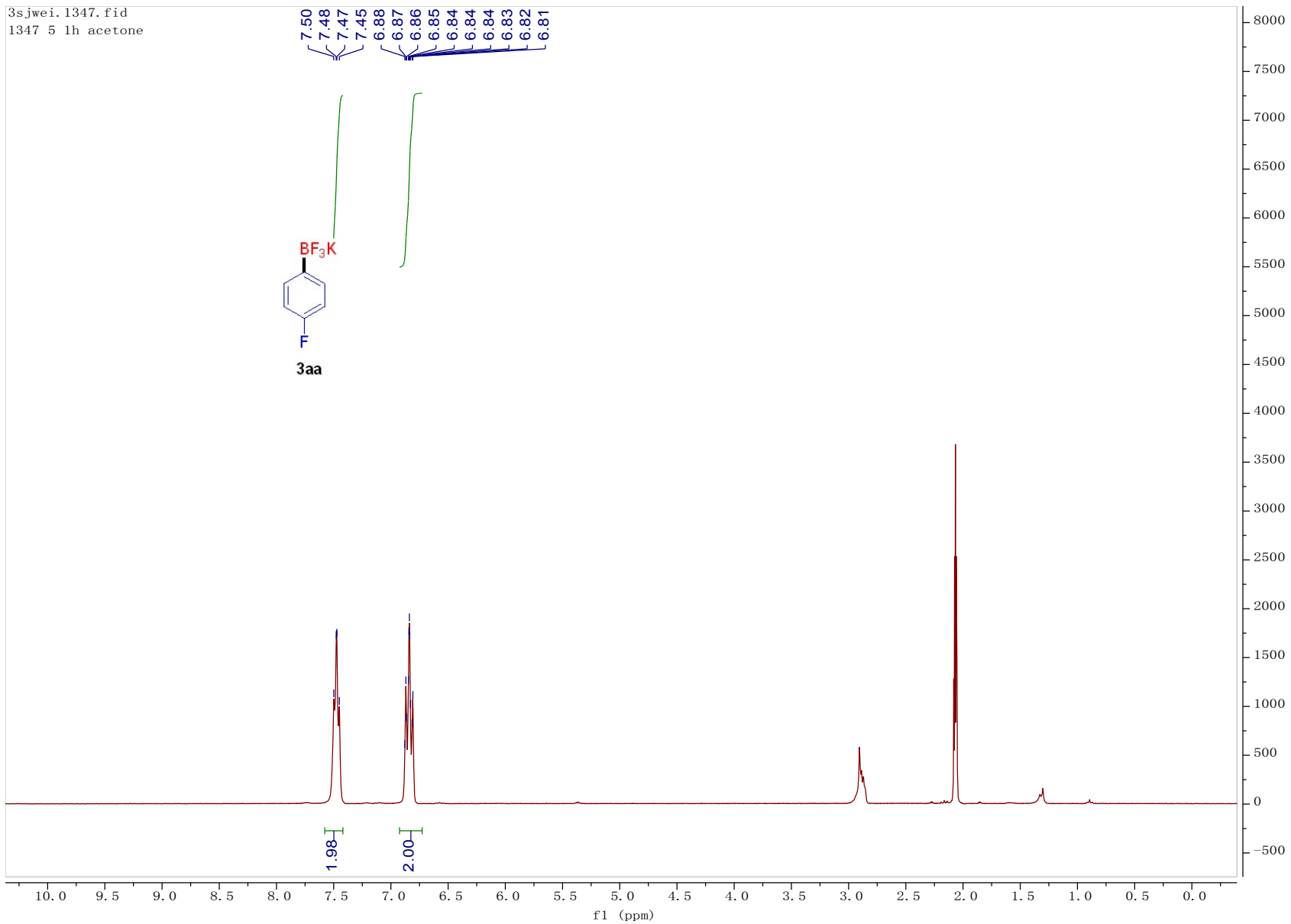
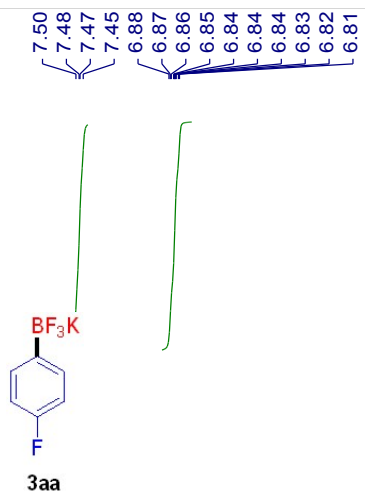




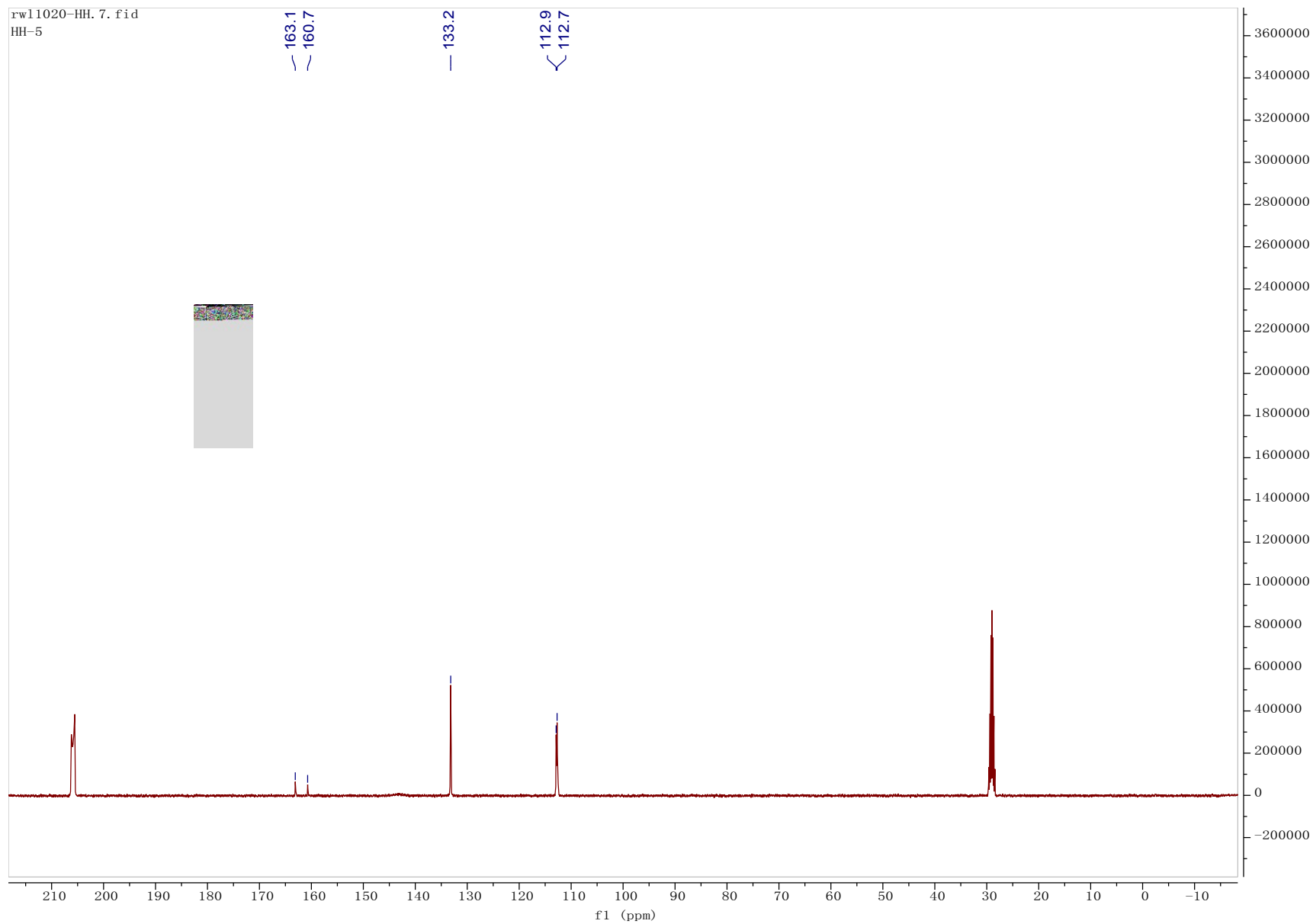
rw11020-HH. 6. fid  
HH-4



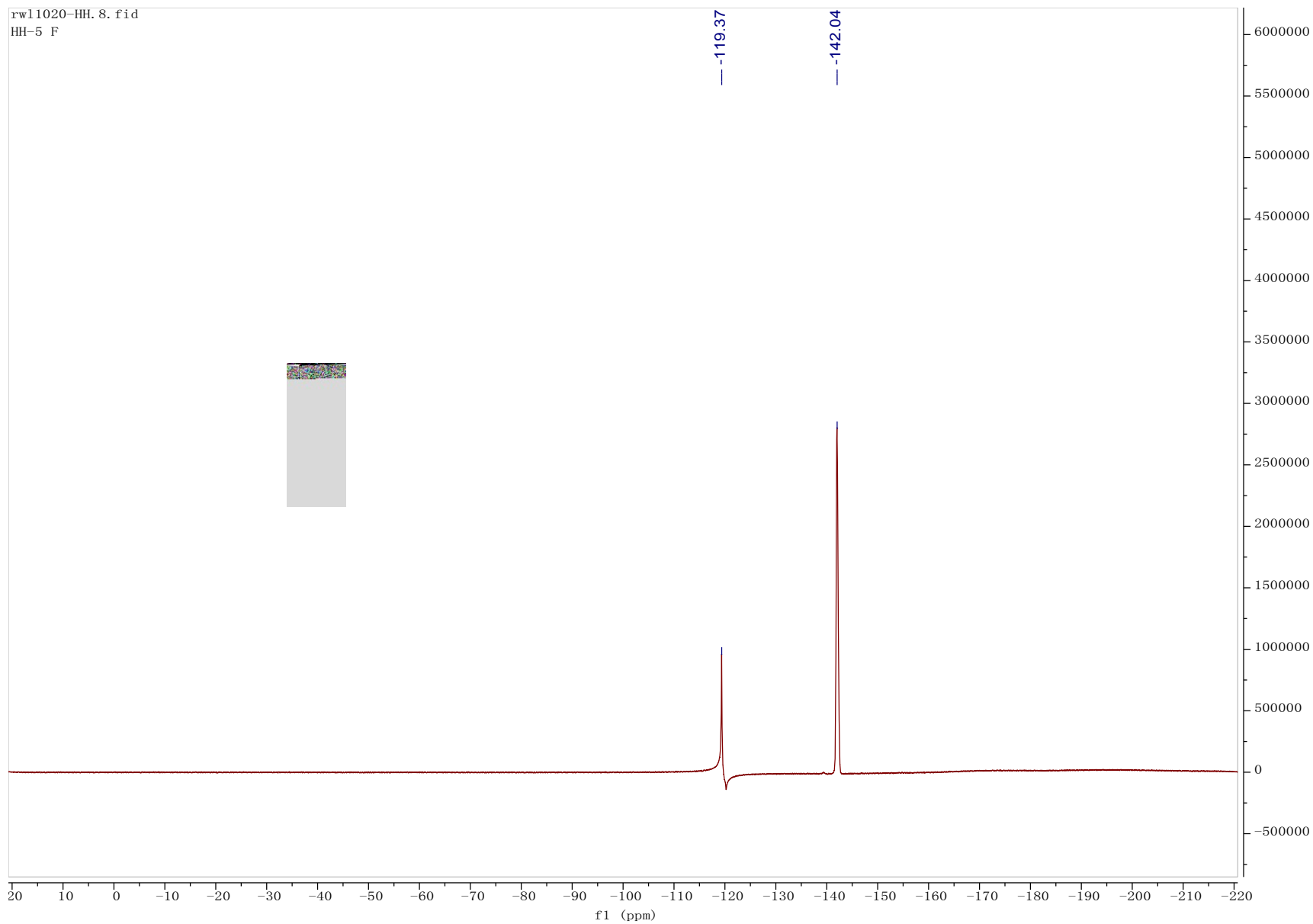
3sjwei.1347.fid  
1347 5 1h acetone



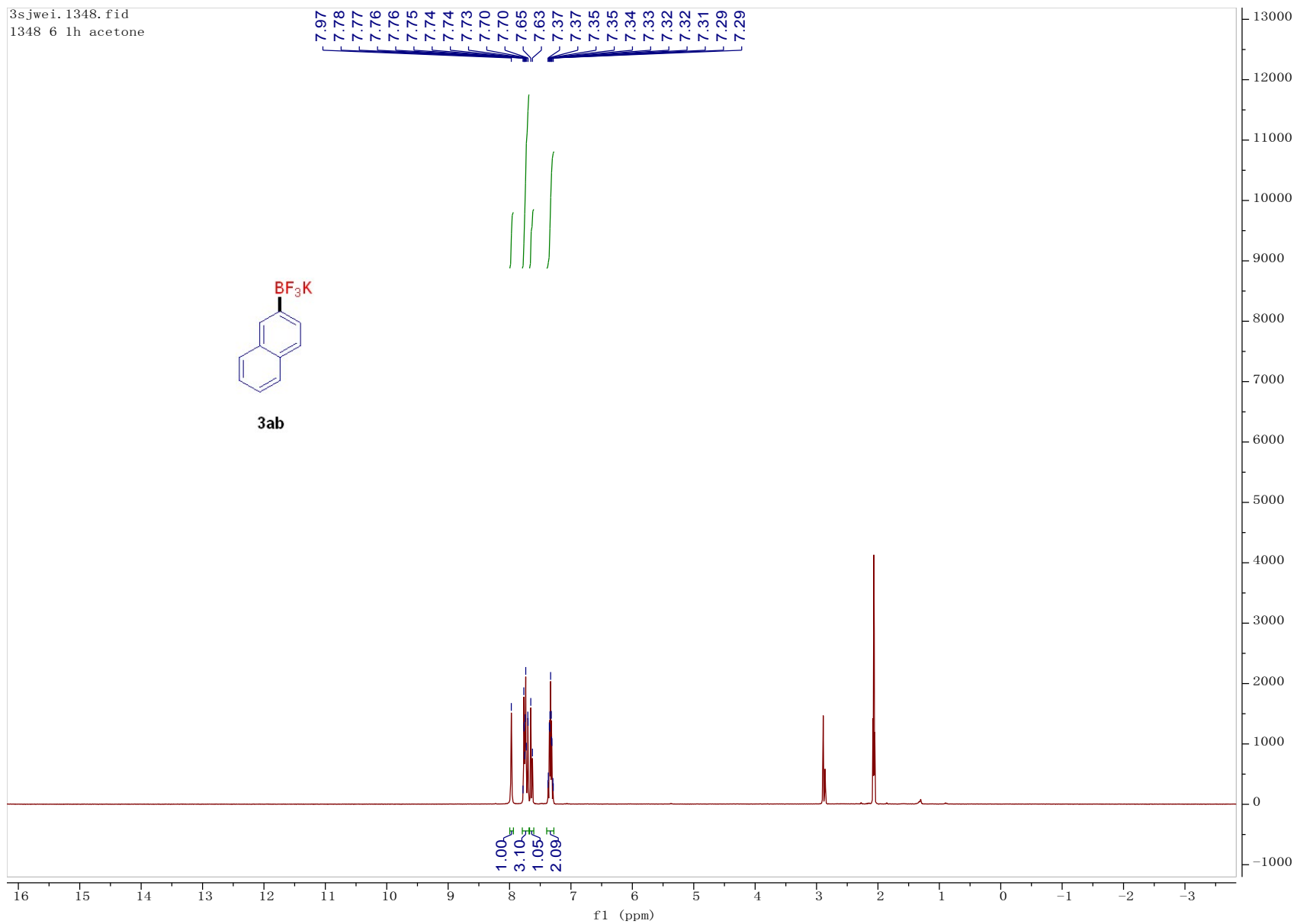
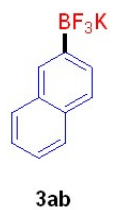
rw11020-HH. 7. fid  
HH-5



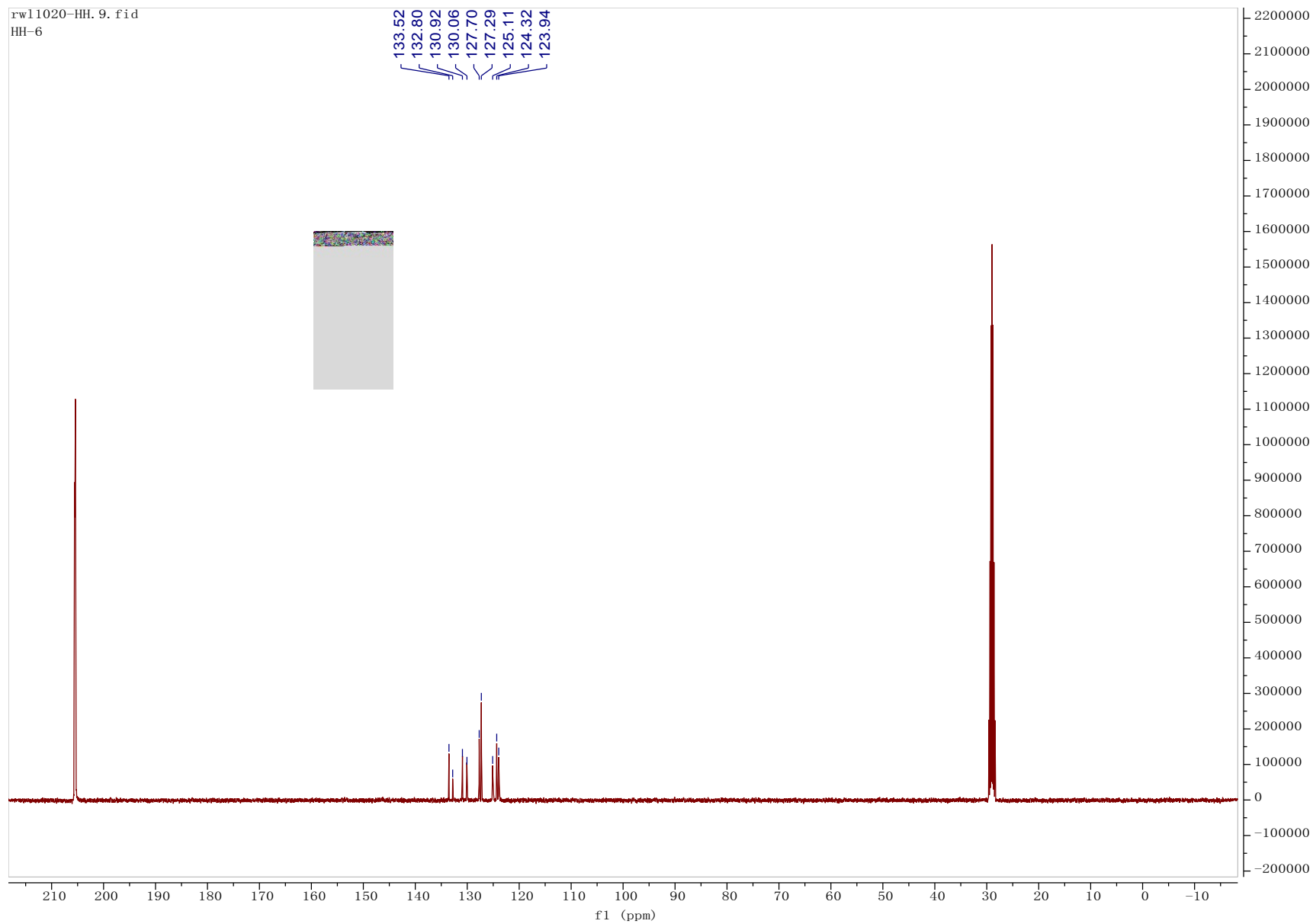
rw11020-HH. 8. fid  
HH-5 F



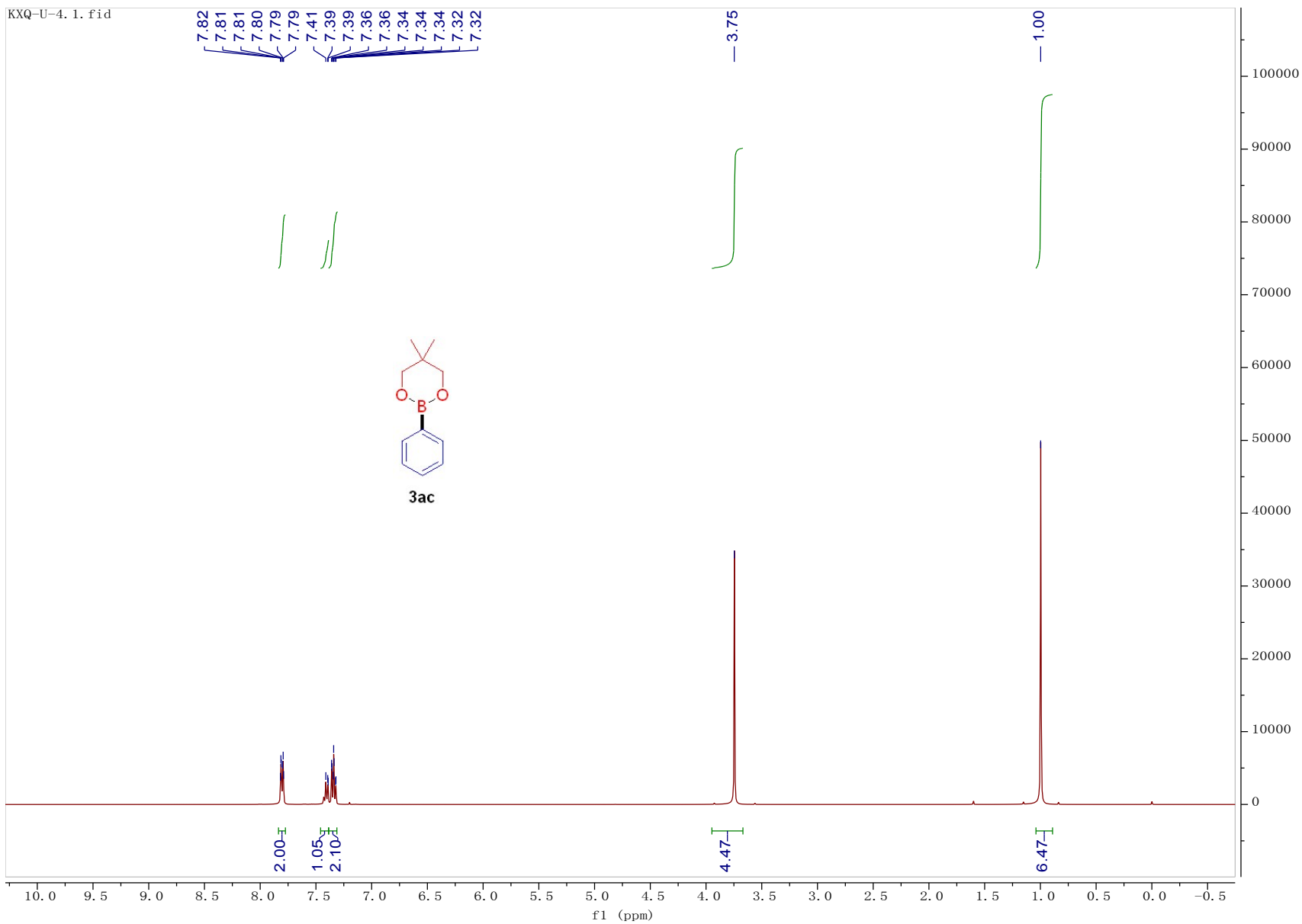
3sjwei.1348.fid  
1348 6 lh acetone

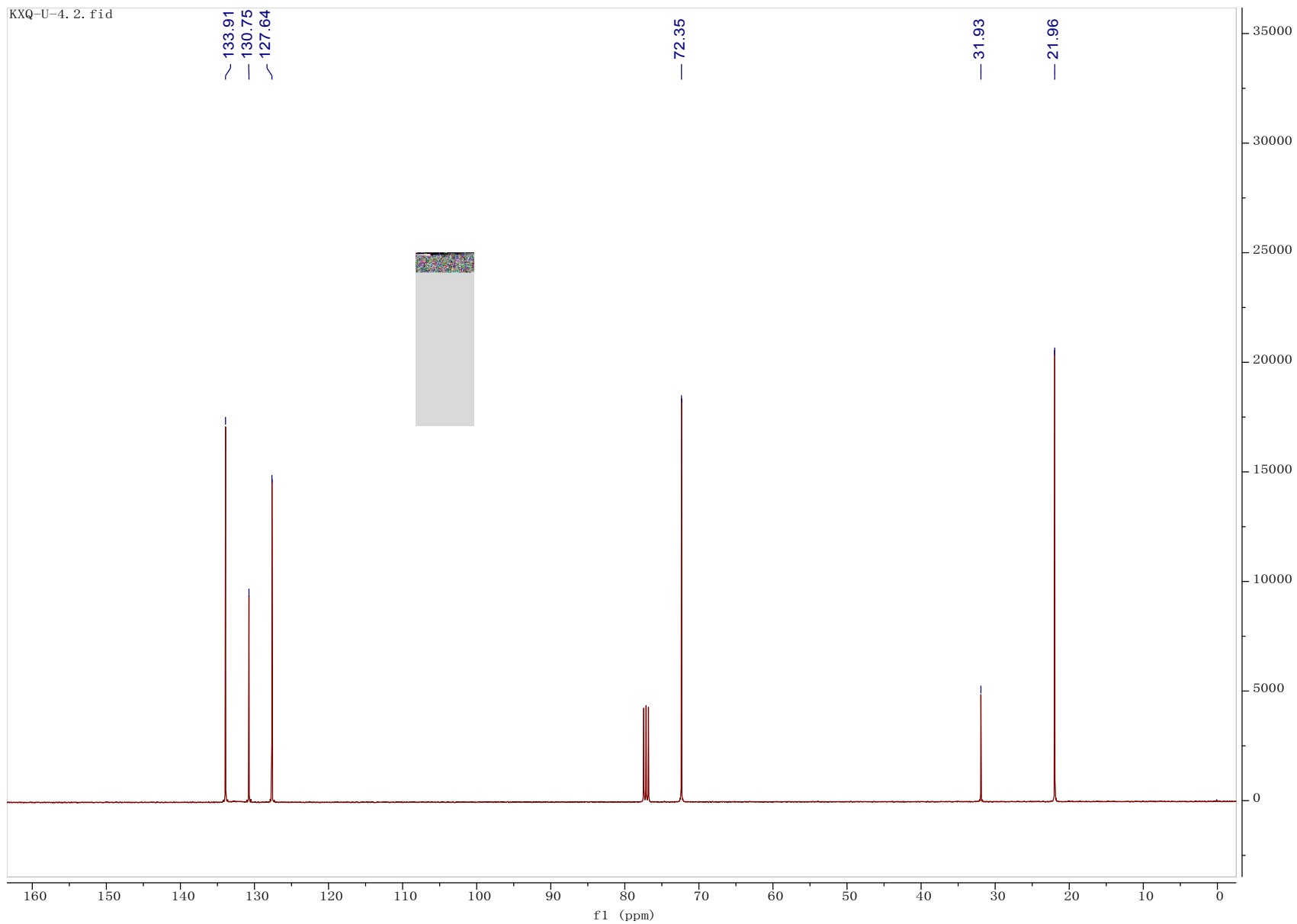


rw11020-HH. 9. fid  
HH-6



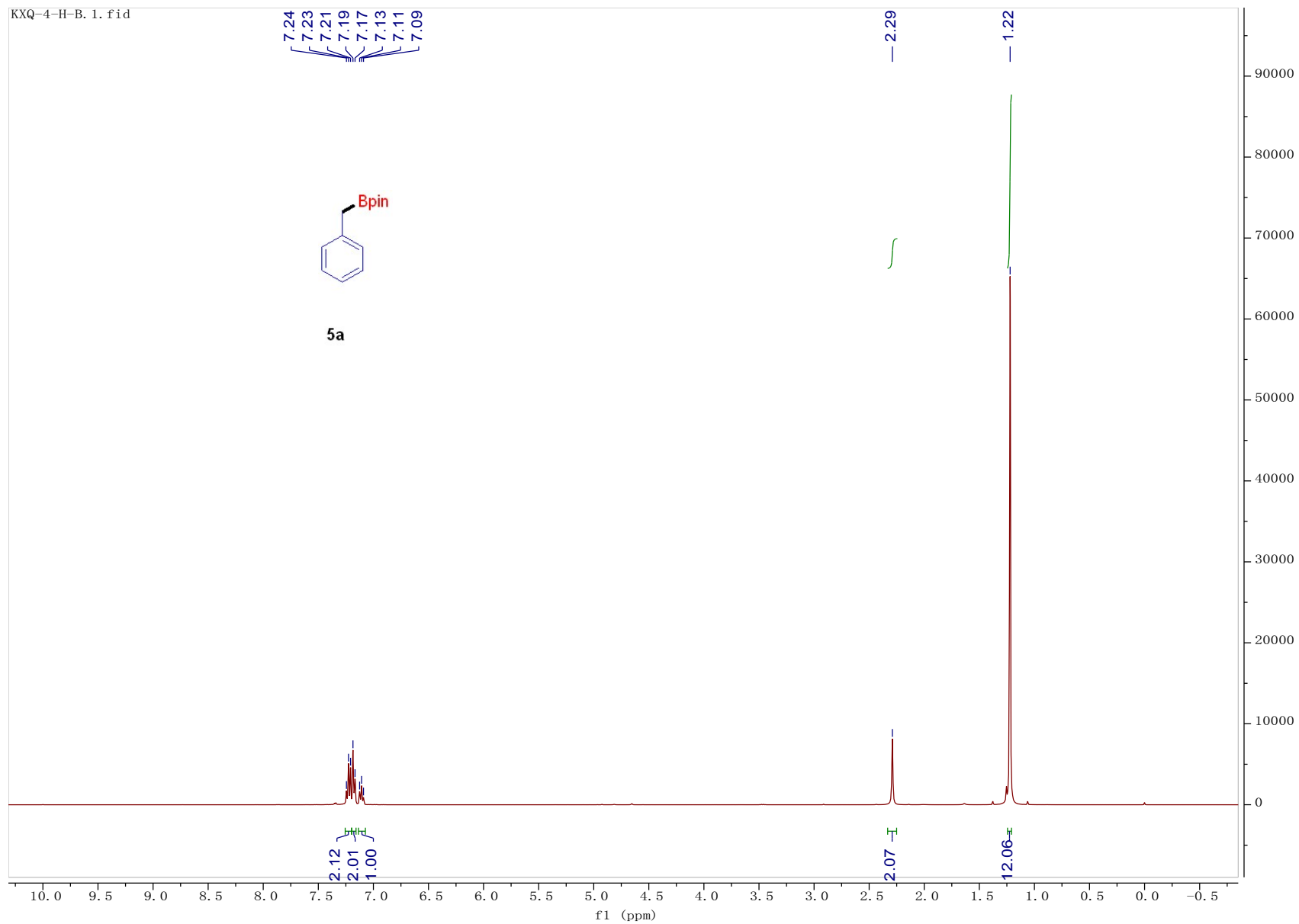
KXQ-U-4.1.fid

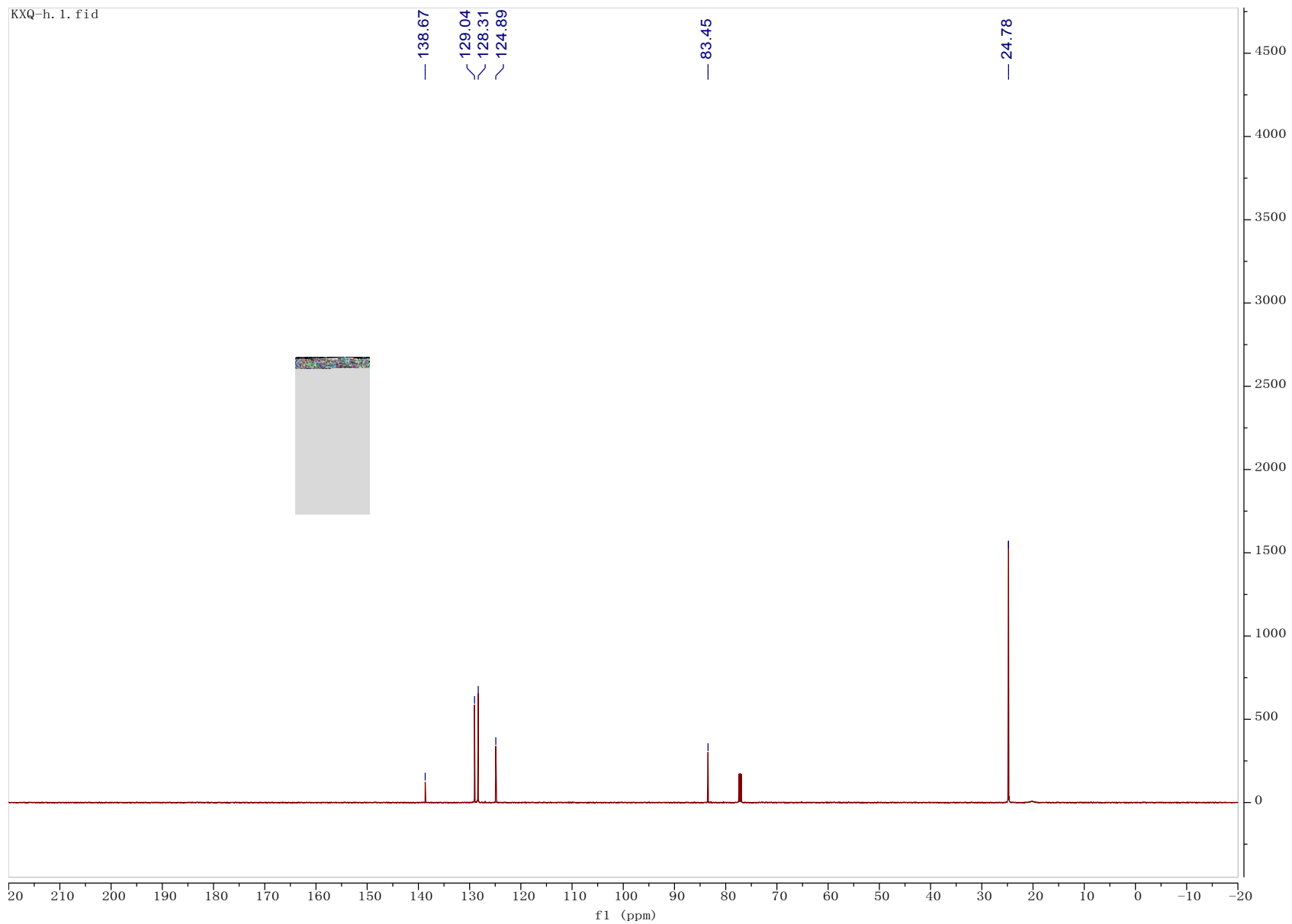




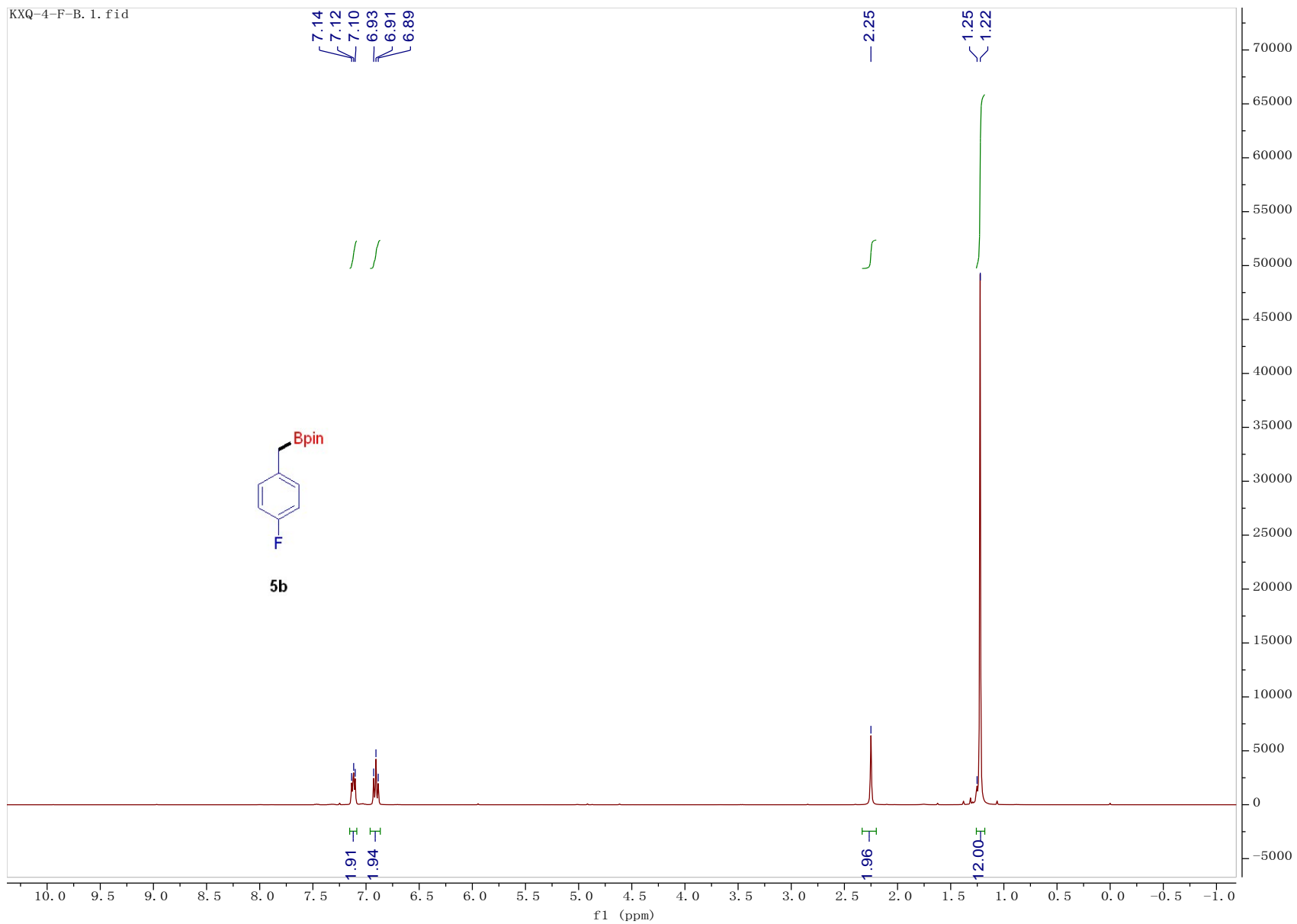


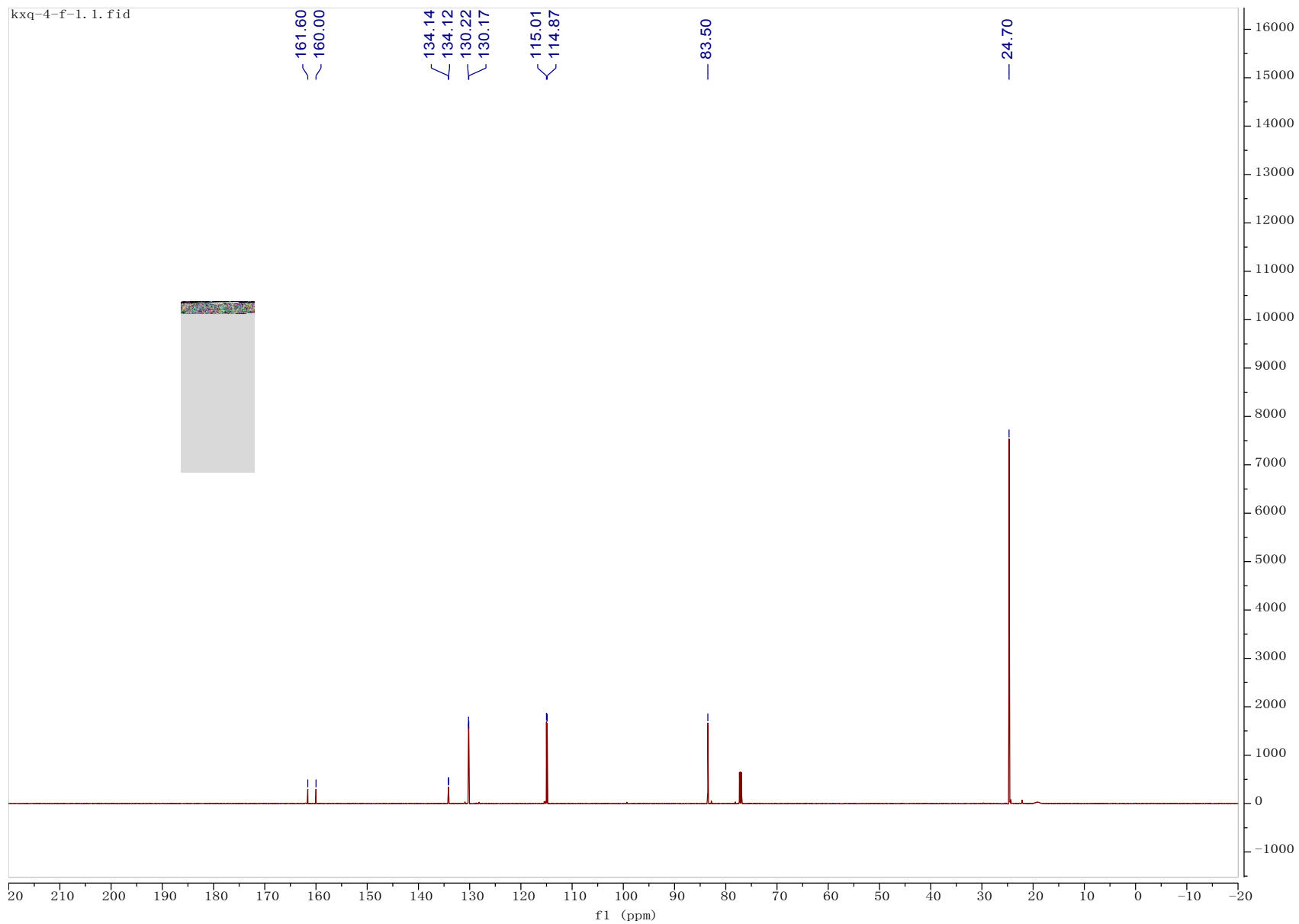
KXQ-4-H-B. 1. fid



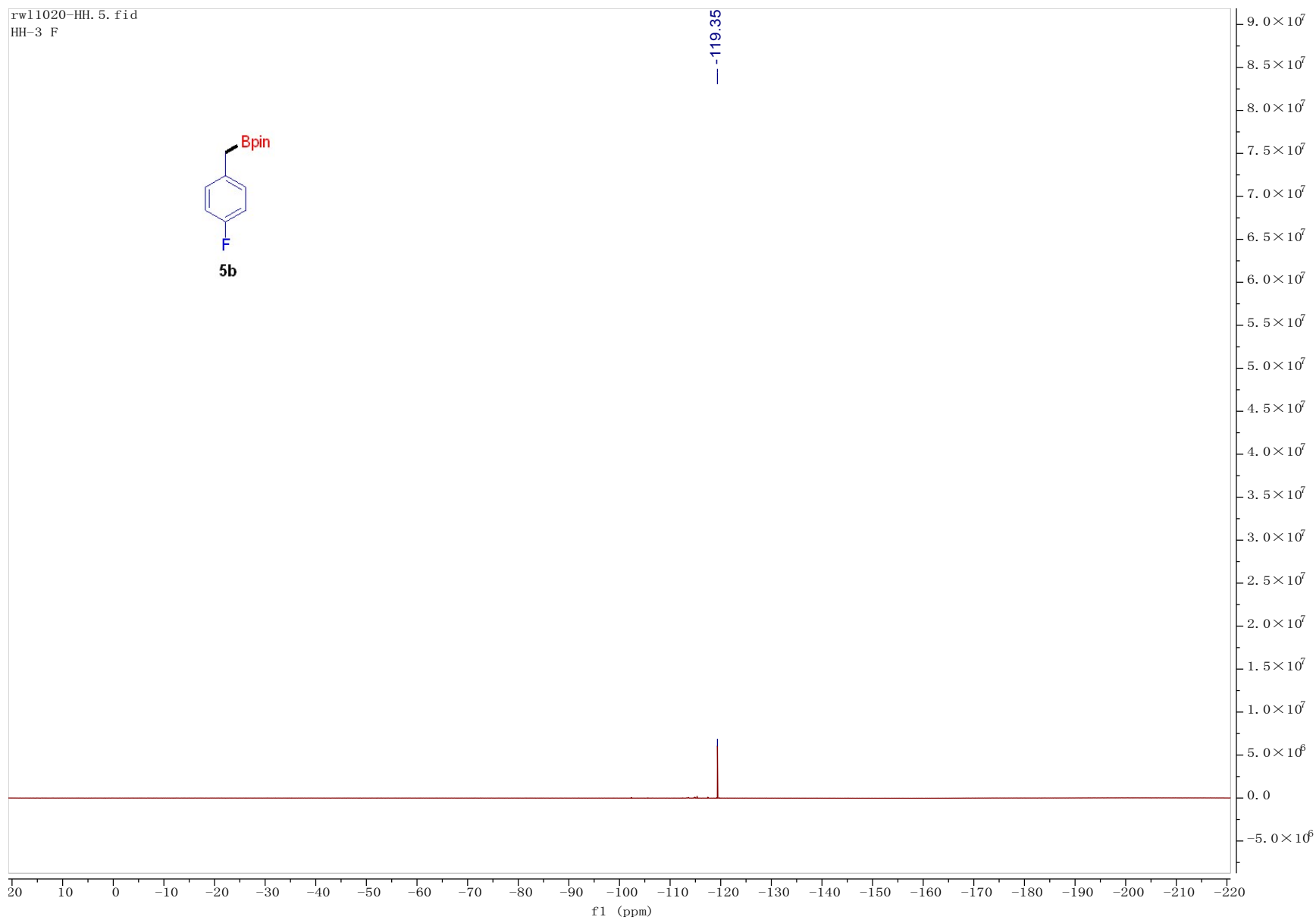
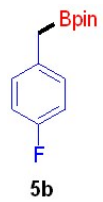


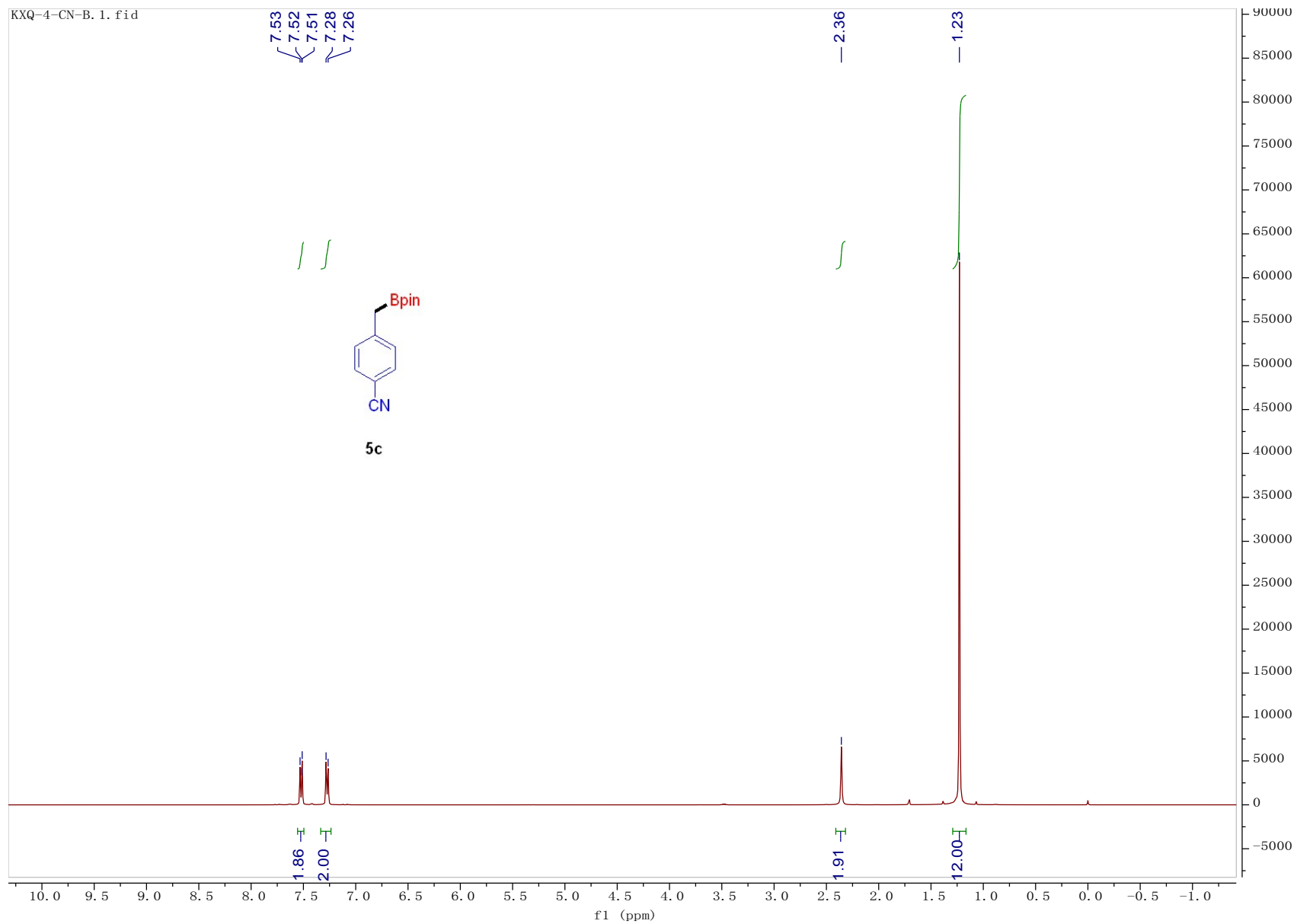
KXQ-4-F-B. 1. fid



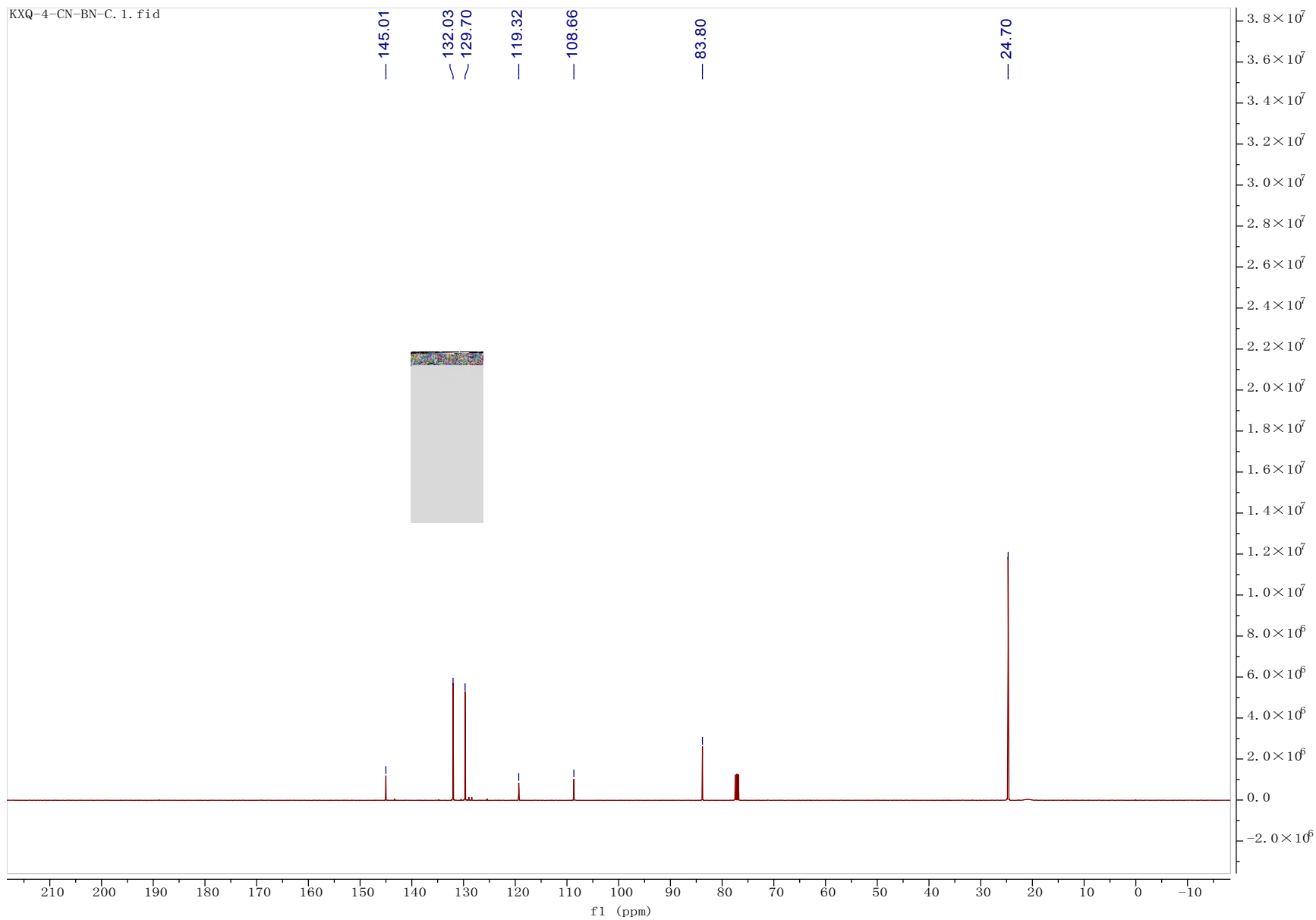


rw11020-HH. 5. fid  
HH-3 F

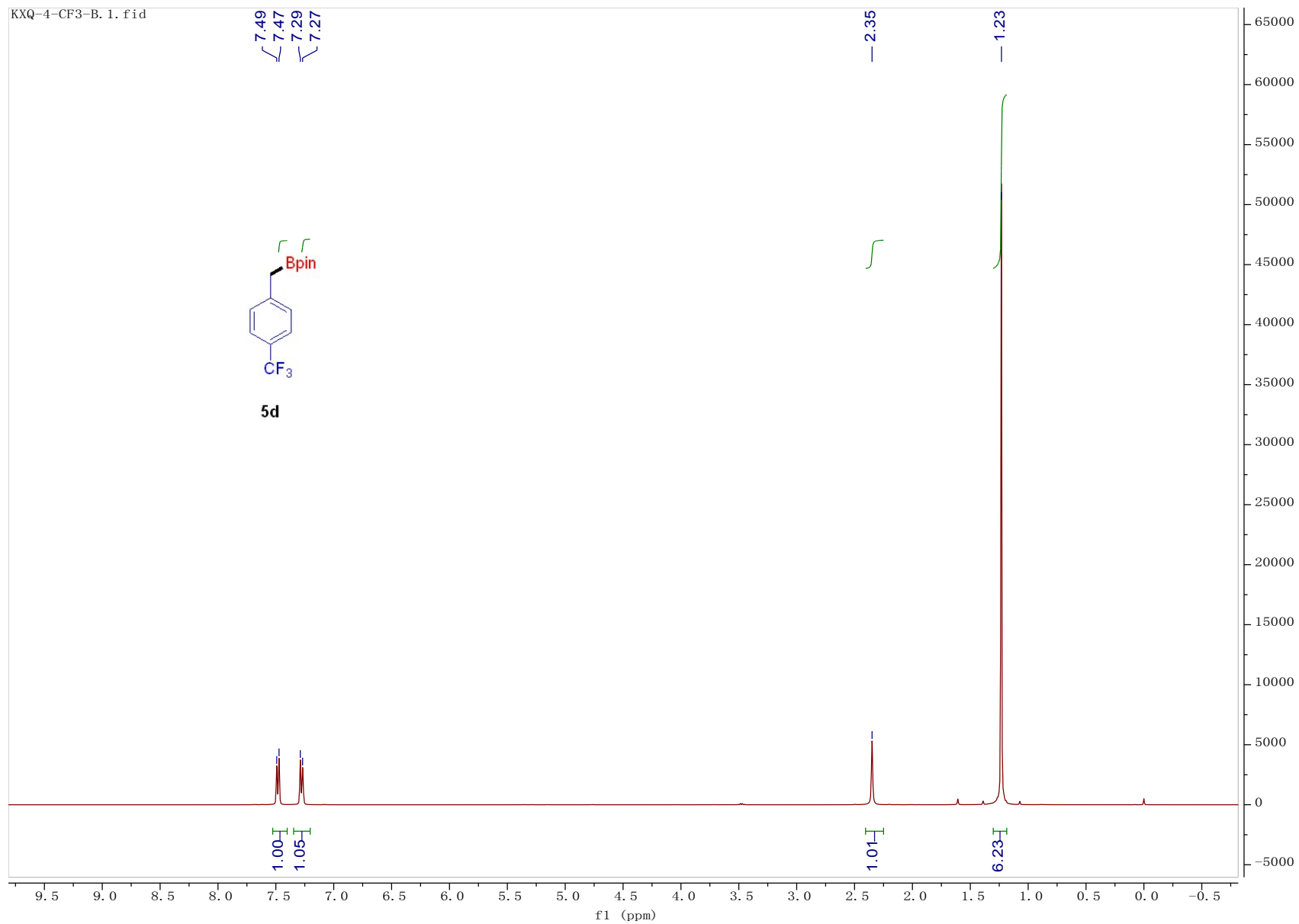




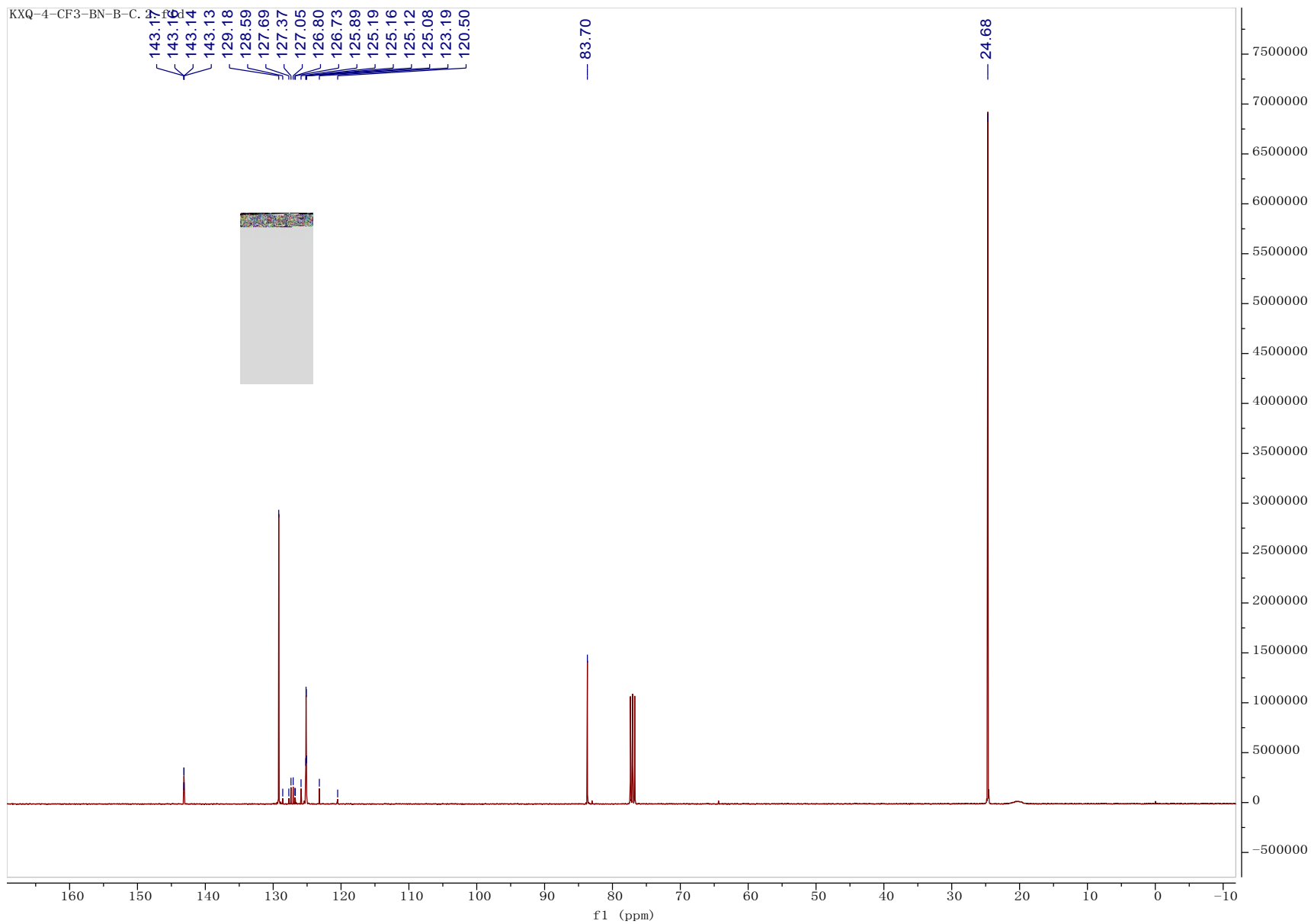
KXQ-4-CN-BN-C. 1. fid

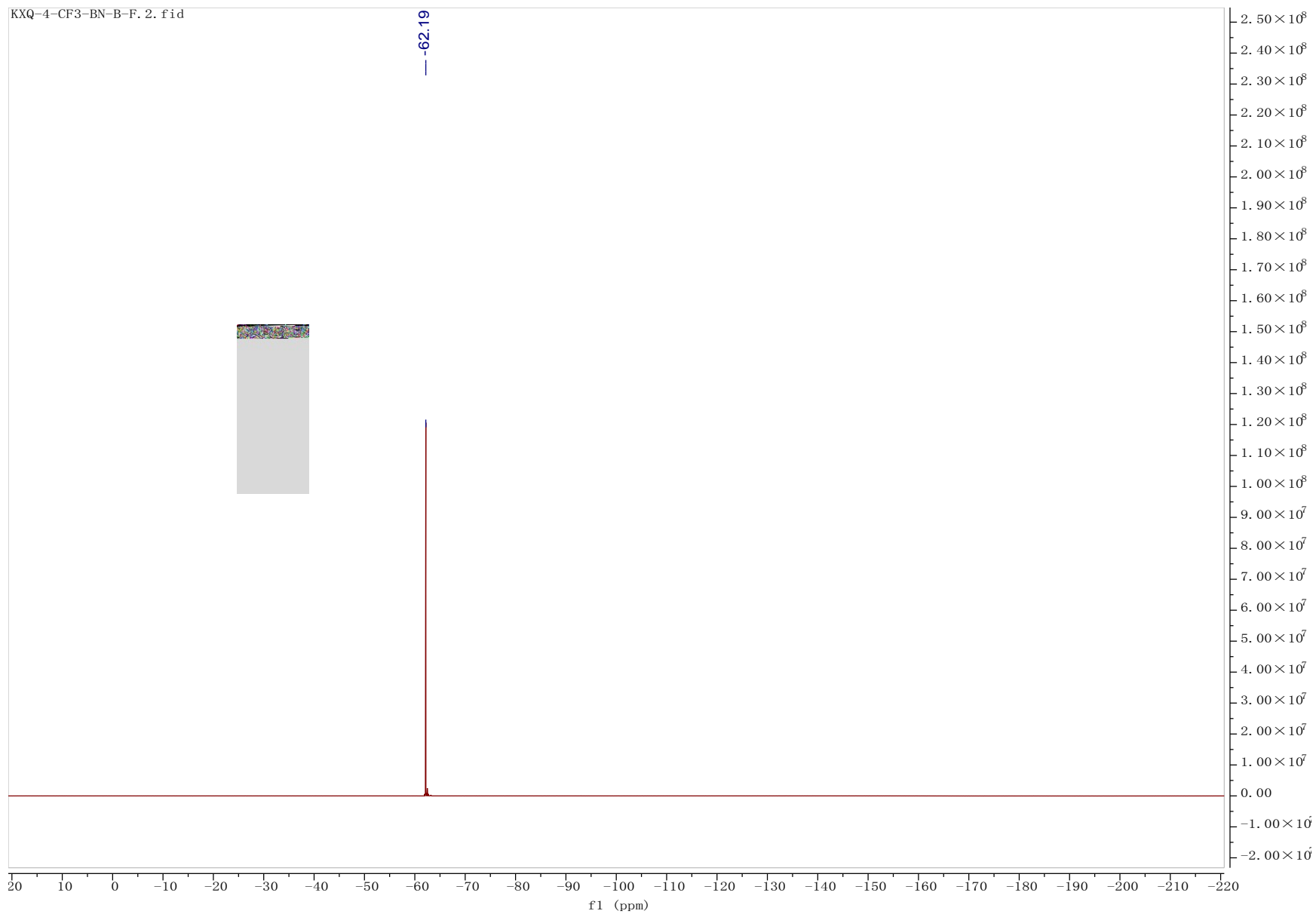


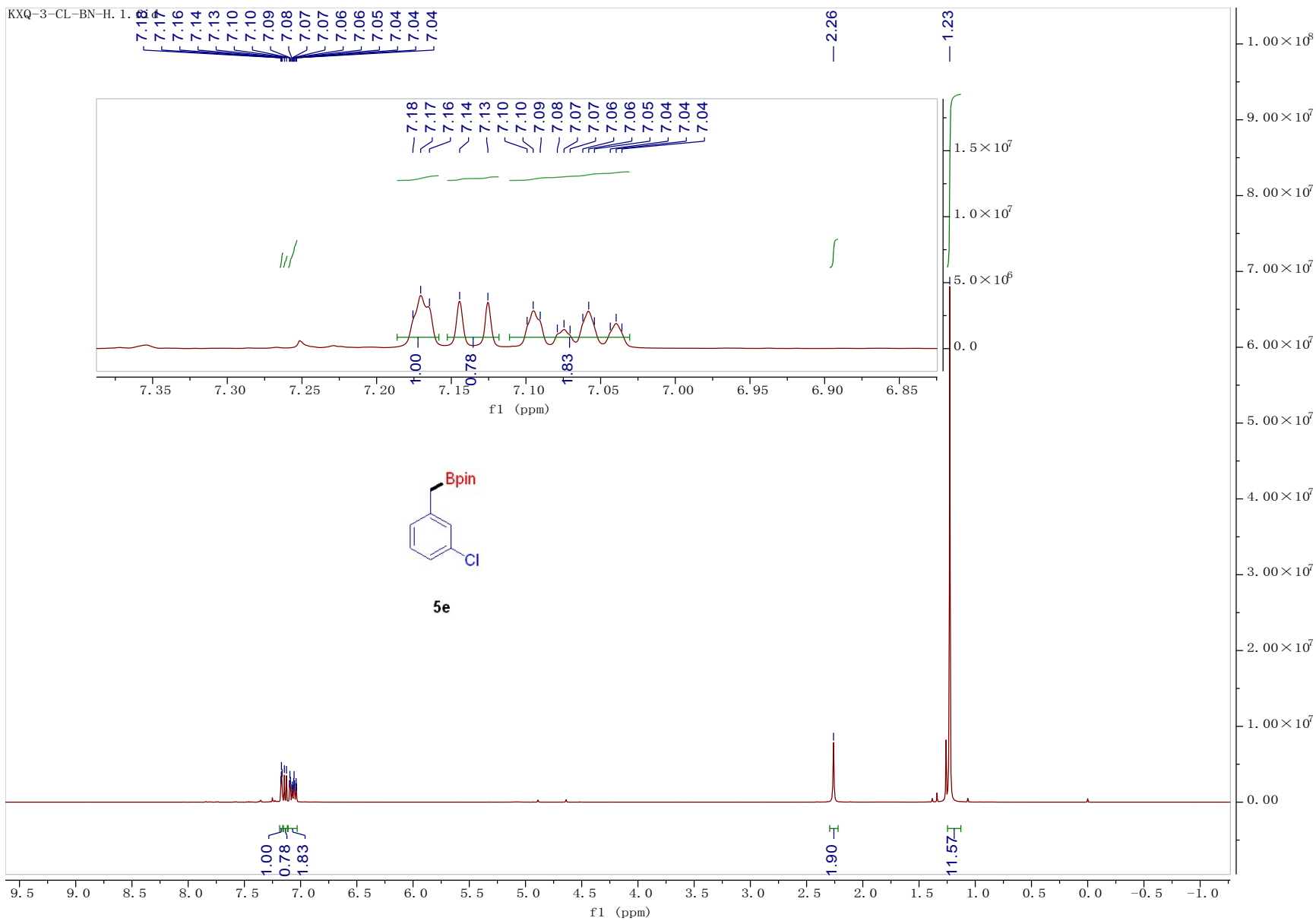
KXQ-4-CF3-B. 1. fid

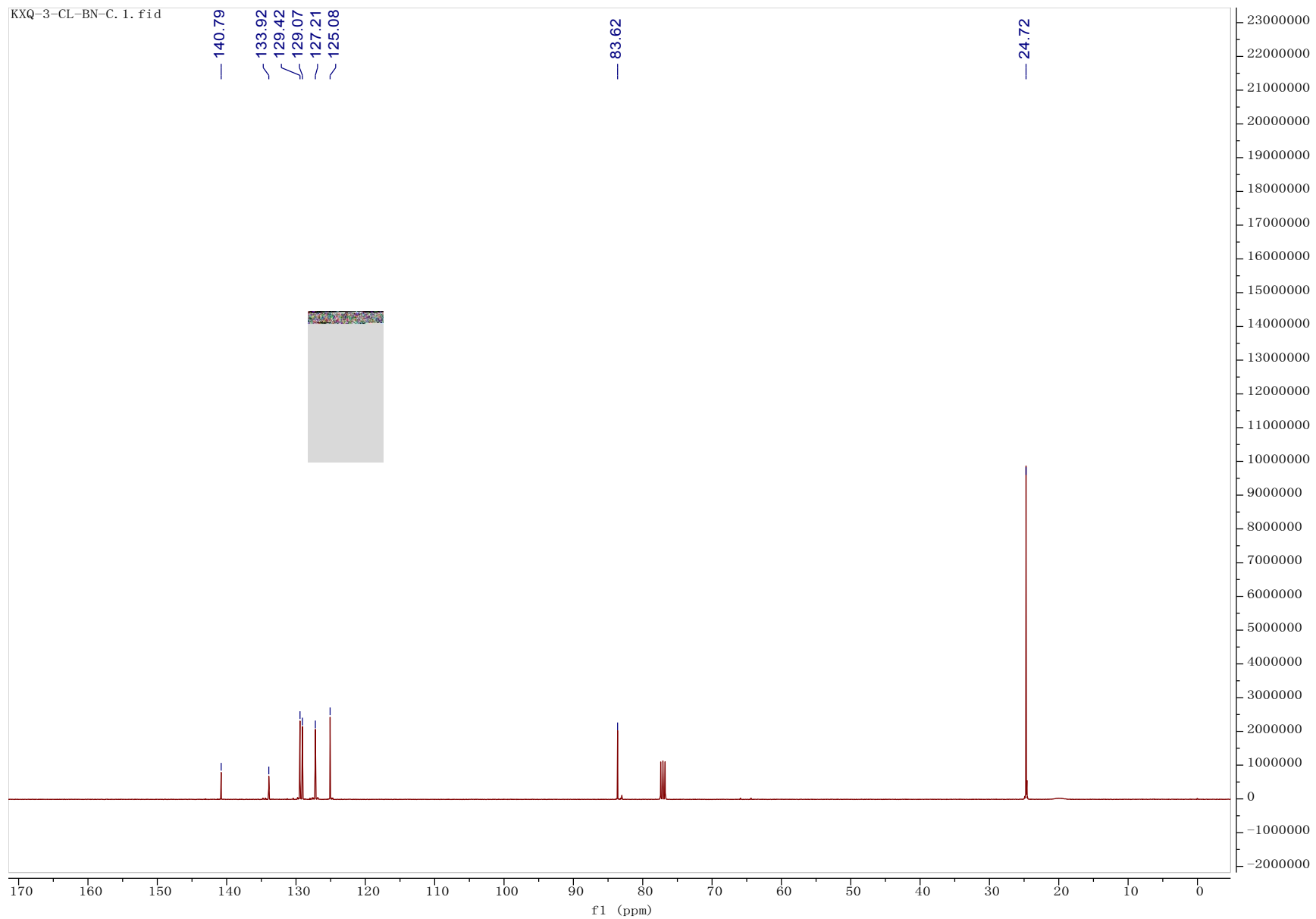




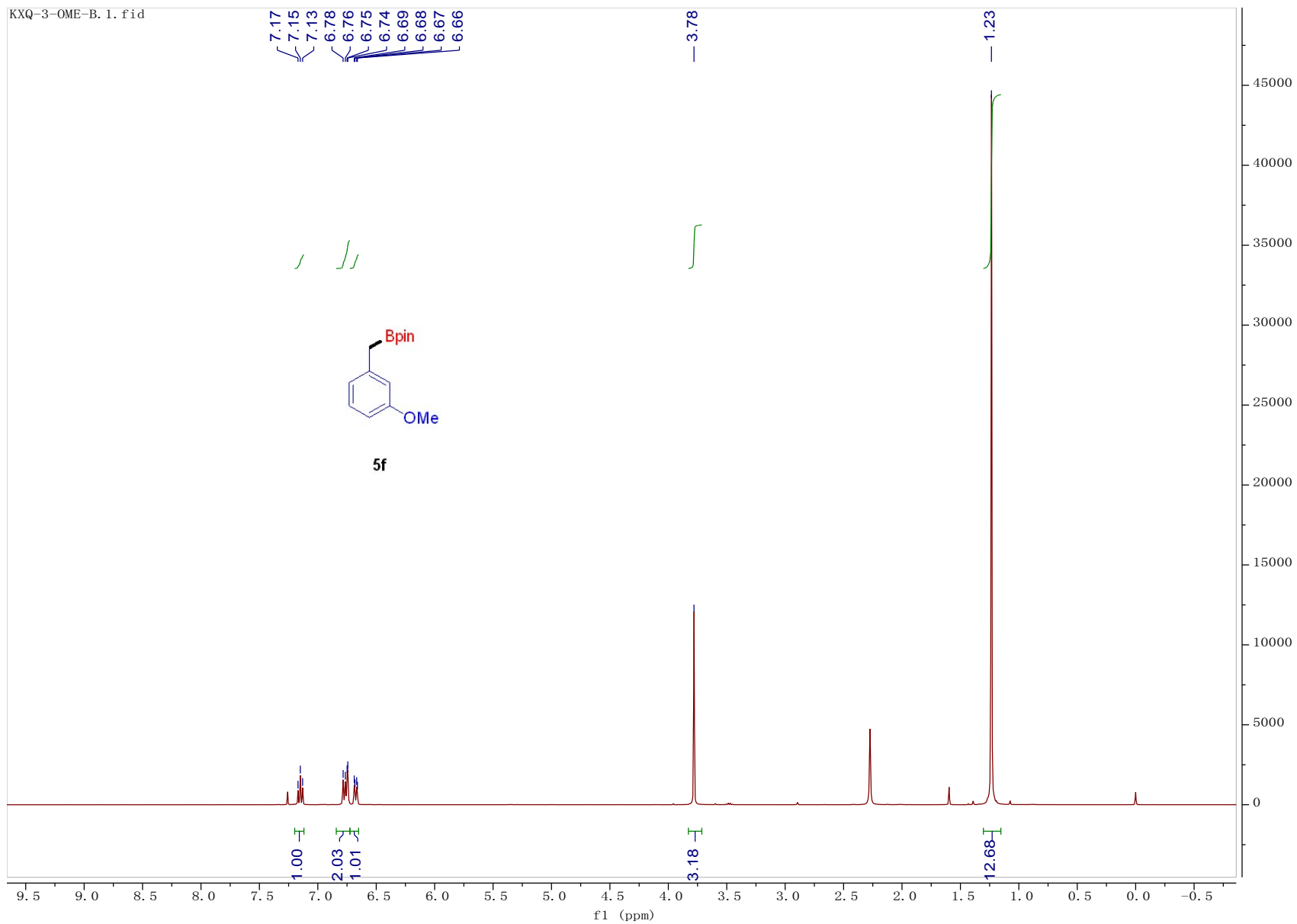


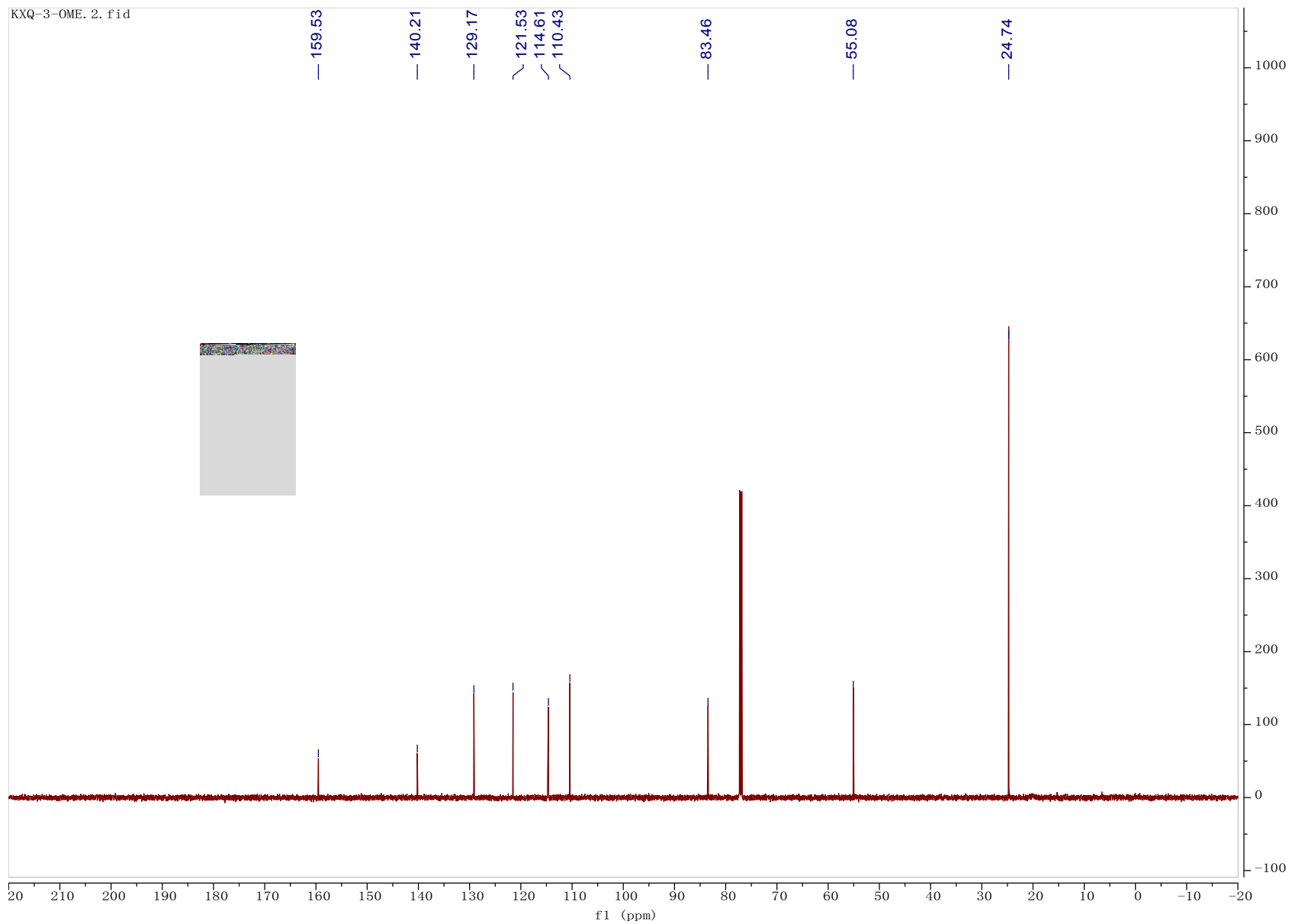


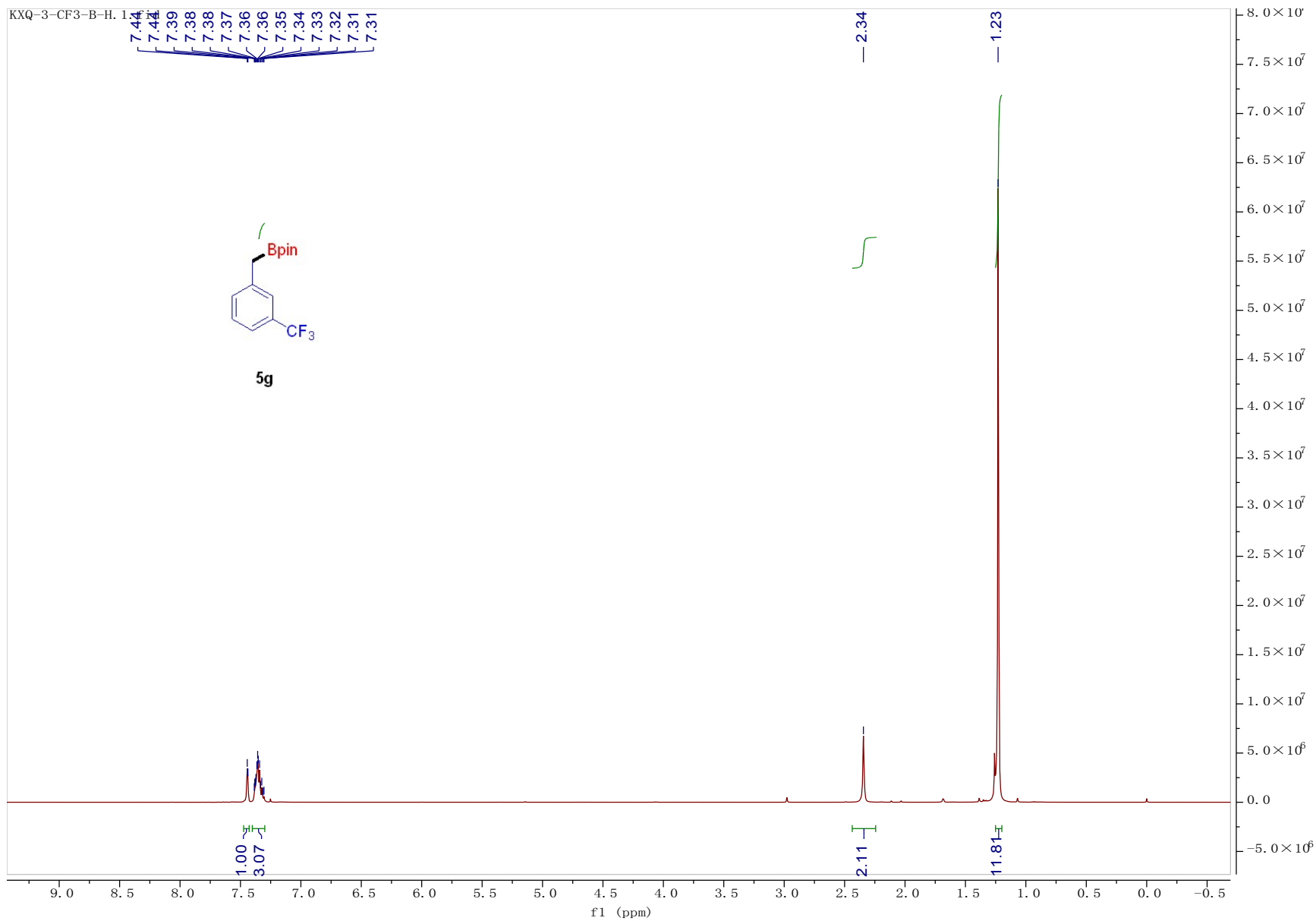


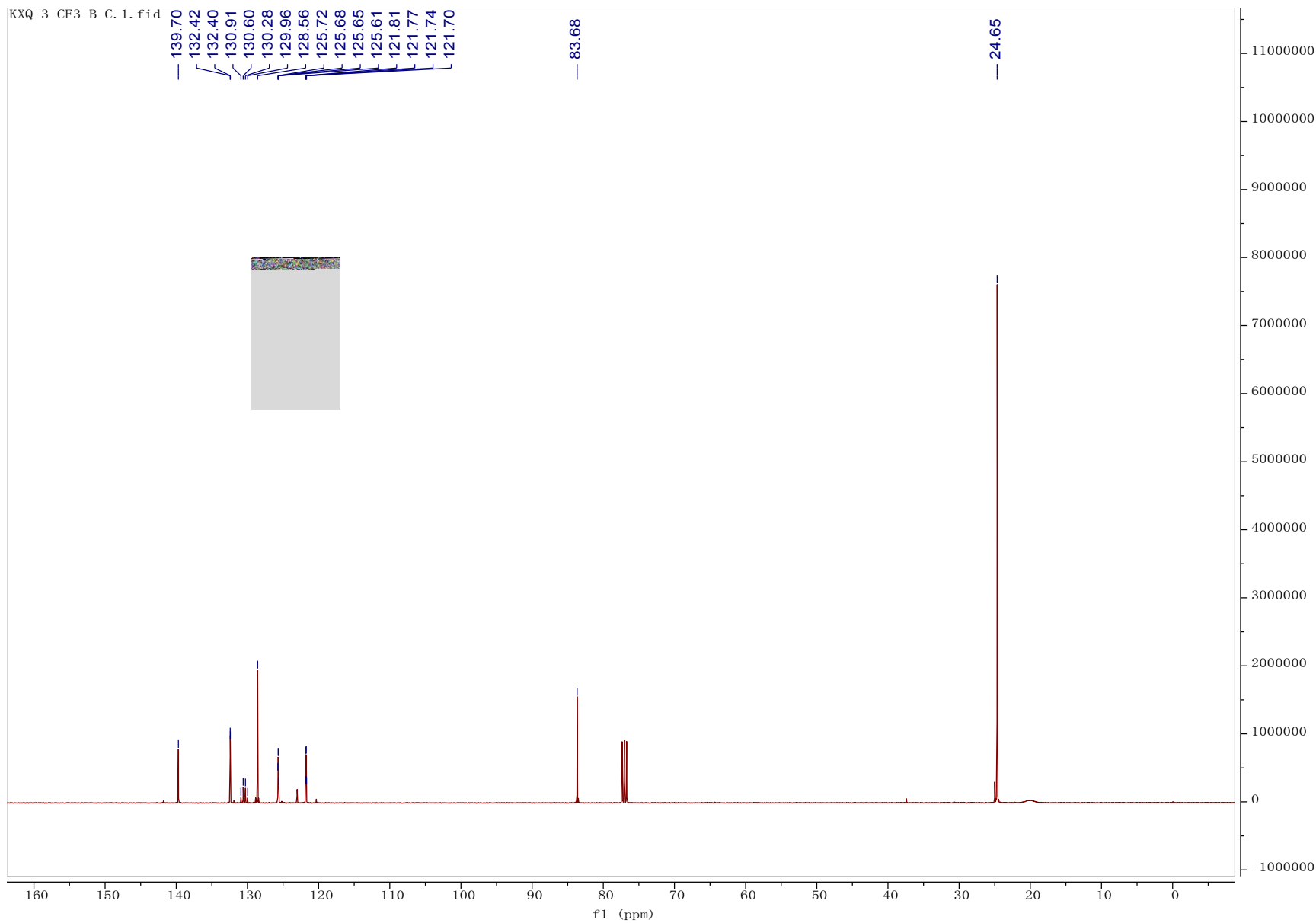


KXQ-3-OMe-B. 1. fid

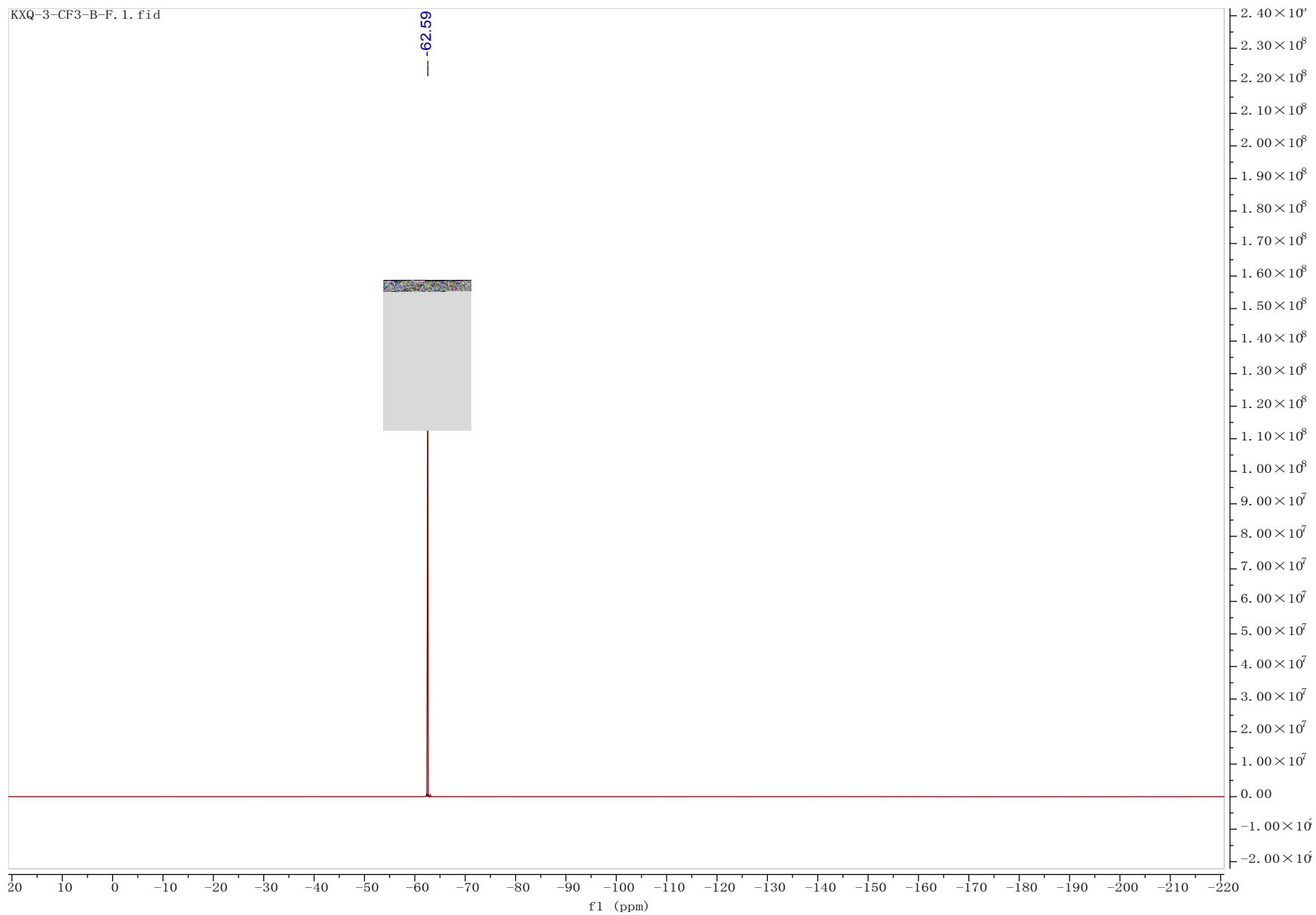


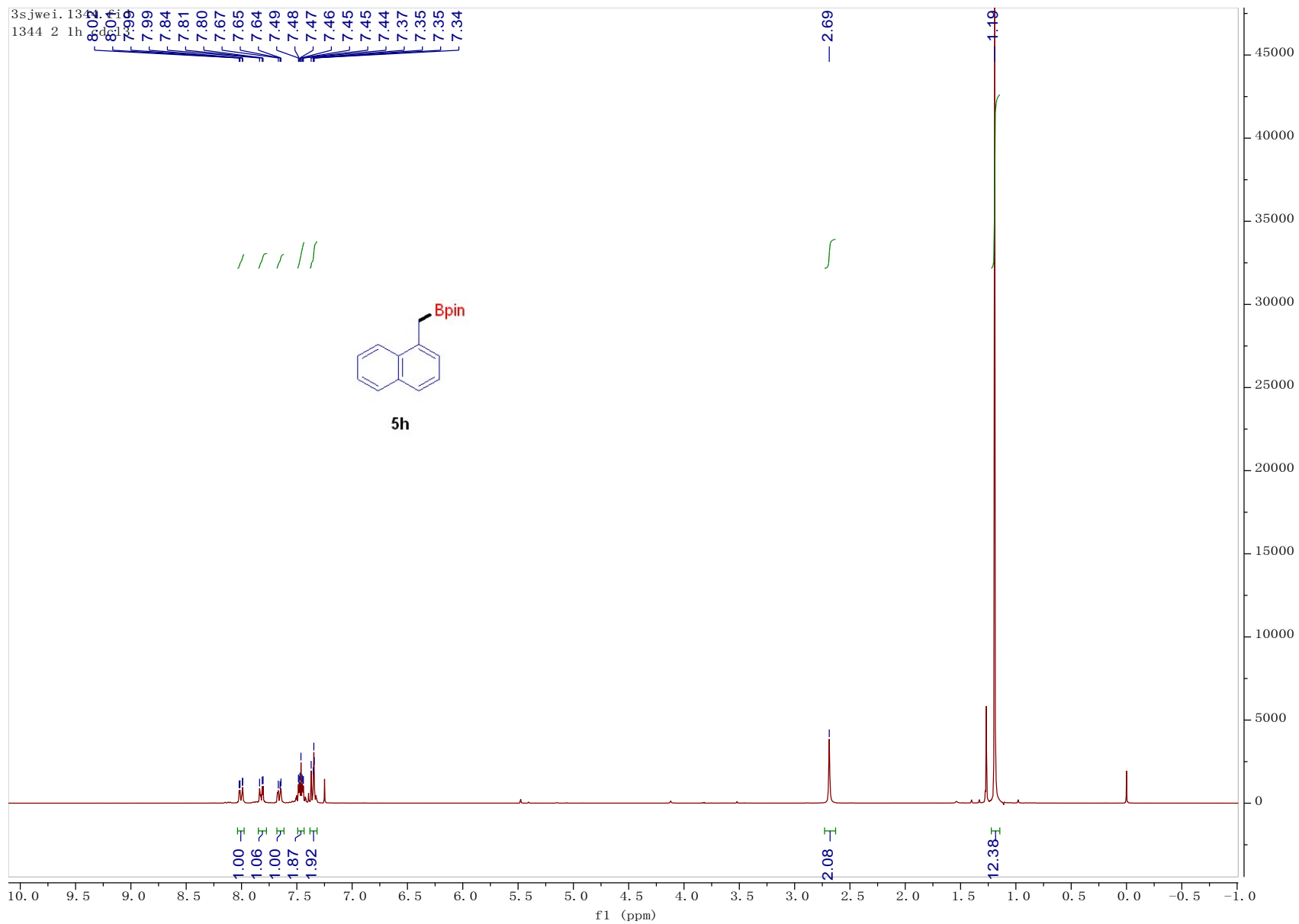




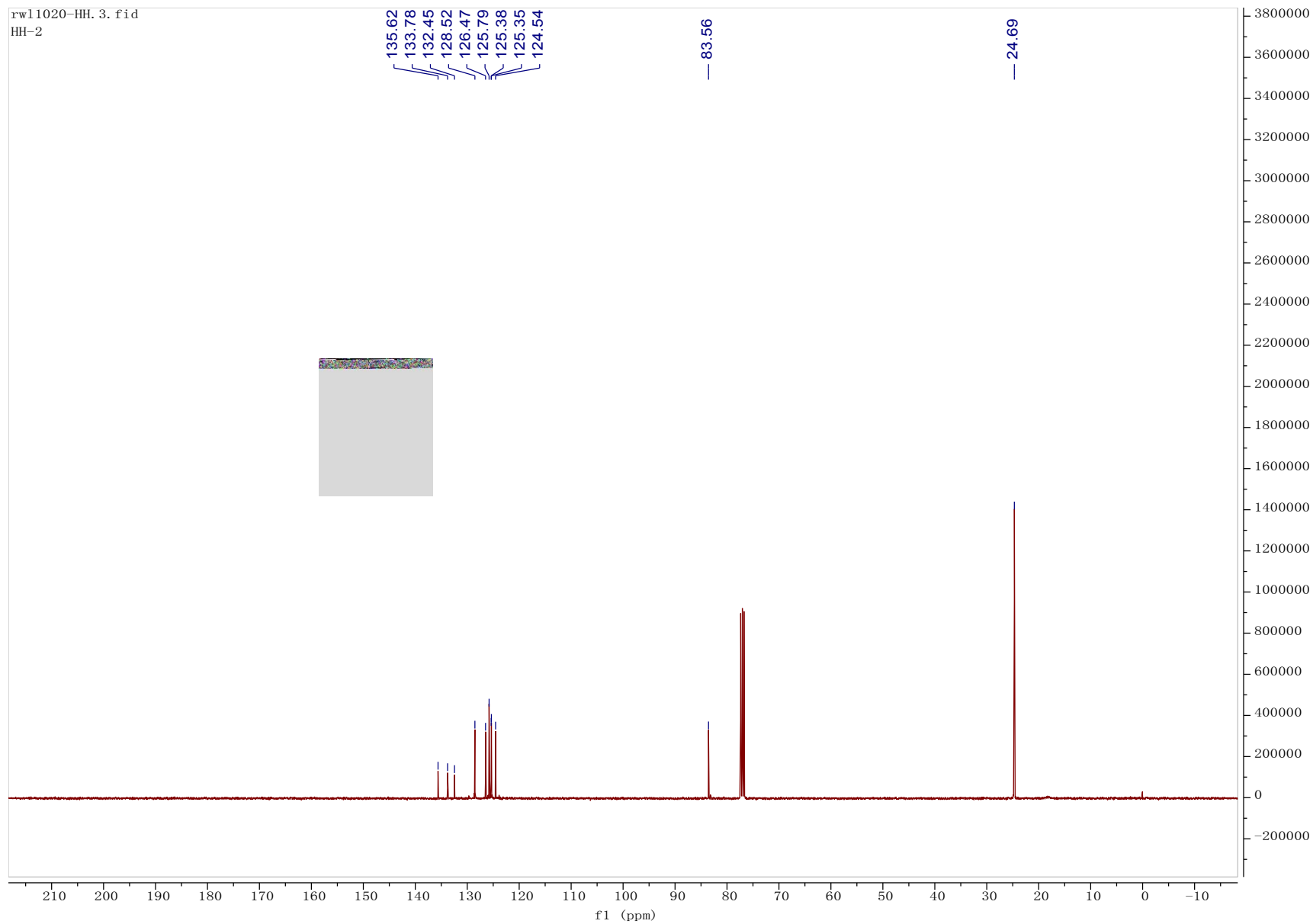




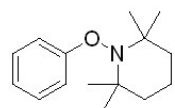




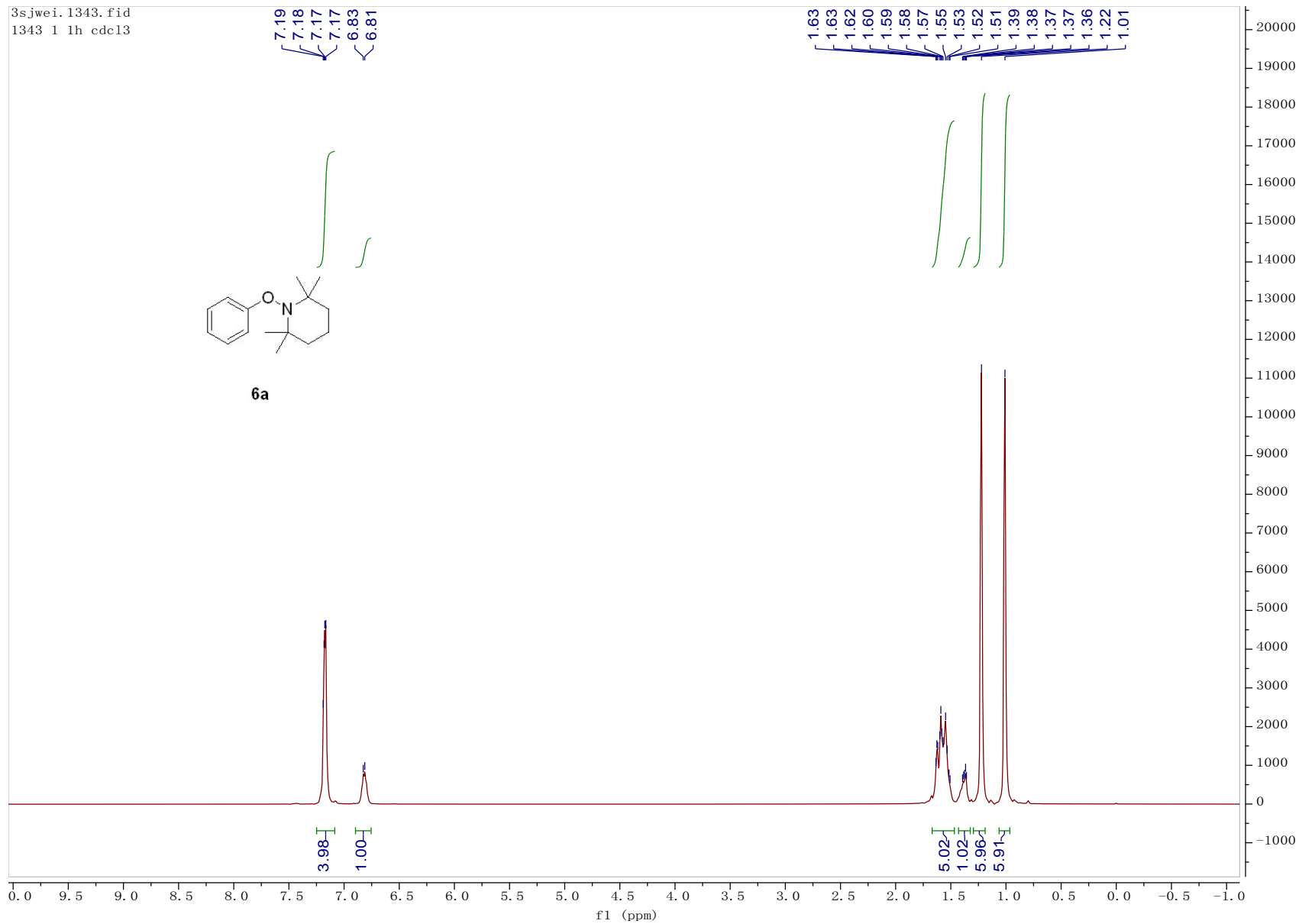
rw11020-HH.3.fid  
HH-2



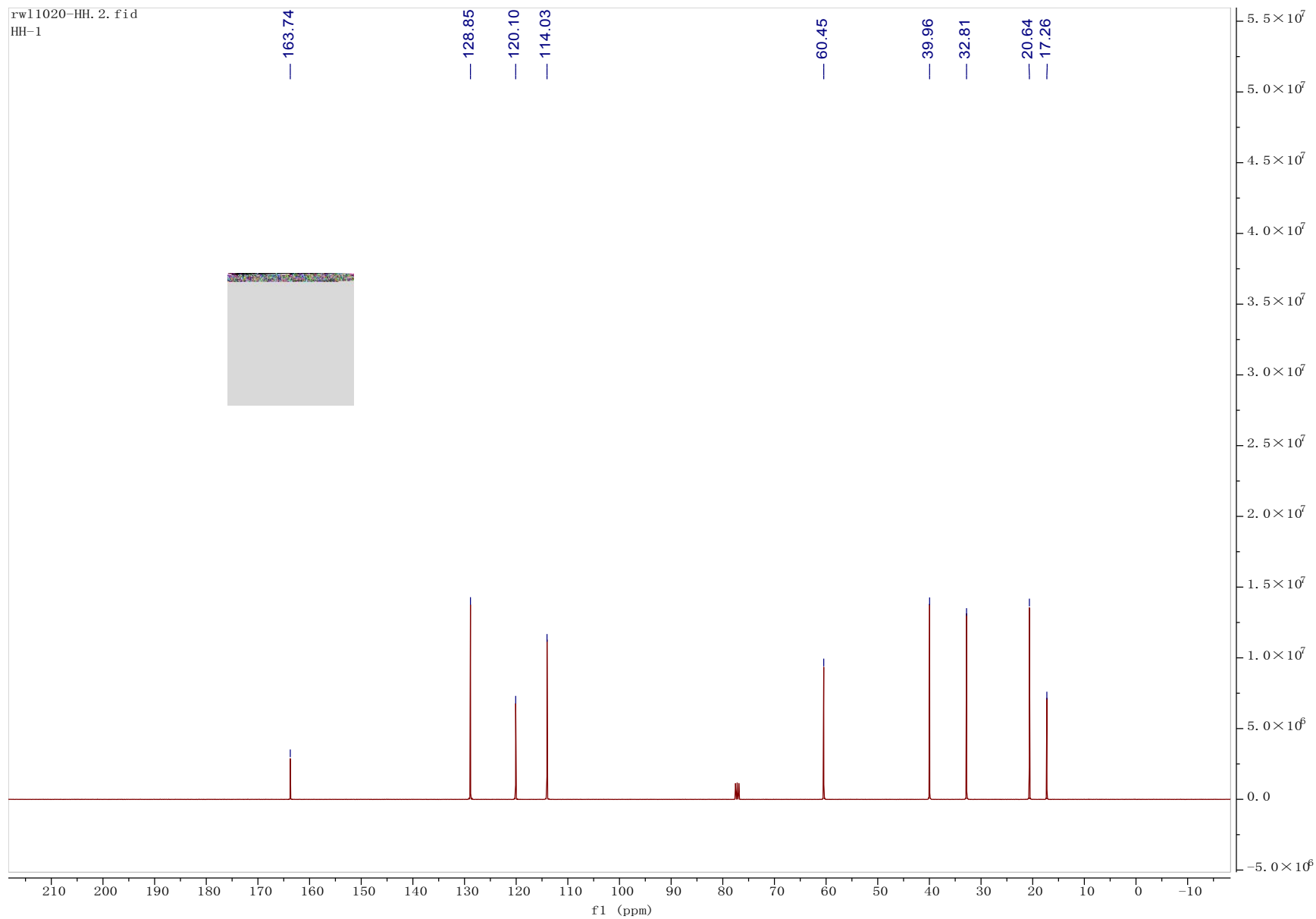
3sjwei.1343.fid  
1343 1 1h cdc13



6a



rw11020-HH. 2. fid  
HH-1



## 6. References

- [1] (a) Maity, P.; Shacklady-McAtee, D. M.; Yap, G. P. A.; Sirianni, E. R.; Watson, M. P. *J. Am. Chem. Soc.* **2013**, *135*, 280. (b) Shacklady-McAtee, D. M.; Roberts, K. M.; Basch, C. H.; Song, Y. G.; Watson, M. P. *Tetrahedron*. **2014**, *70*, 4257. (c) Zhang, Q.; Zhang, X. Q.; Wang, Z. X. *Dalton Trans.* **2012**, *41*, 10453. (d) Yang, X.; Wang, Z. X. *Organometallics* **2014**, *33*, 5863. (e) Zhang, X. Q.; Wang, Z. X. *Org. Biomol. Chem.* **2014**, *12*, 1448.
- [2] Dyga, M., Hayrapetyan, D, R. K. Rit and L. J. Gooßen, Electrochemical ipso-thiocyanation of arylboron compounds, *Adv. Synth. Catal.*, **2019**, *361*, 3548.
- [3] Hu, J, Sun, J, Cai, H, Pu, X, Zhang, Y and Shi, Z, Nickel-Catalyzed Borylation of Aryl- and Benzyltrimethylammonium Salts via C–N Bond Cleavage, *J. Org. Chem.*, **2016**, *81*, 14.
- [4] Hartmann, M.; Li, Y.; Studer, A. Transition-Metal-Free Oxyarylation of Alkenes with Aryl Diazonium Salts and TEMPO<sup>Na</sup>. *J. Am. Chem. Soc.* **2012**, *134*, 16516.