

# Gold-Catalyzed Highly Regio- and Enantioselective Vinylcarbene Insertion into O-H Bonds of 2-Pyridones

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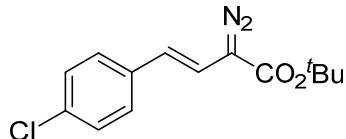
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## General Information

All of the reactions were carried out in flame-dried tubes under argon atmosphere. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used.  $^1\text{H}$  NMR were recorded on Bruker 300 MHz, 400 MHz or 500 MHz spectrometer and  $^{13}\text{C}$  NMR were recorded on Bruker 75 MHz, 100 MHz or 125MHz spectrometer in  $\text{CDCl}_3$ . HRMS were performed on Agilent 6540 Q-TOF mass spectrometer (ESI). Melting points were determined on a SGW X-4B melting point apparatus. Chiral HPLC were performed on Agilent 1260 using a Chiraldak ID column. Optical rotations were recorded on Rudolph Autopol IV polarimeter. 2-pyridones were commercial available. The gold catalysts<sup>[1]</sup> and NaBARf<sup>[2]</sup> were prepared according to the literature procedures.

## Preparation of substrates

All of the diazo compounds were prepared according to the literature procedures.<sup>[3]</sup> The unreported diazo compounds were showing as below.

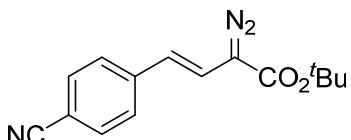


### *tert-butyl (E)-4-(4-chlorophenyl)-2-diazobut-3-enoate:*

A red solid (yield: 70 %), mp: 46-48 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26 (s, 4H), 6.43 (d,  $J = 16.0$  Hz, 1H), 6.12 (d,  $J = 16.0$  Hz, 1H), 1.53 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  164.20, 135.57, 132.45, 128.84, 126.91, 121.21, 112.83, 82.48, 28.35.

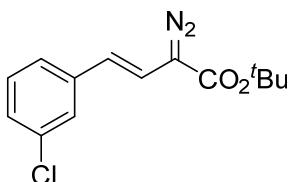
HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{16}\text{ClO}_2 [\text{M}+\text{H}-\text{N}_2]^+$ : 251.0834, found: 251.0838.



### *tert-butyl (E)-4-(4-cyanophenyl)-2-diazobut-3-enoate:*

A red solid (yield: 69 %), mp: 84-86 °C.

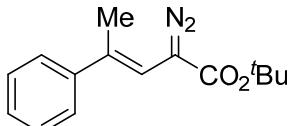
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.56 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 6.63 (d, *J* = 16.0 Hz, 1H), 6.17 (d, *J* = 16.0 Hz, 1H), 1.57 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 163.58, 141.51, 132.52, 126.03, 120.30, 119.08, 116.74, 109.75, 82.87, 28.32. HRMS (ESI) calcd. for C<sub>15</sub>H<sub>16</sub>NO<sub>2</sub>[M+H-N<sub>2</sub>]<sup>+</sup>: 242.1176, found: 242.1179.



**tert-butyl (E)-4-(3-chlorophenyl)-2-diazobut-3-enoate:**

Red oil (yield: 75 %).

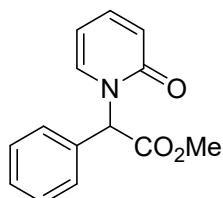
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.33-7.30 (m, 1H), 7.24-7.11 (m, 3H), 6.48 (d, *J* = 16.0 Hz, 1H), 6.10 (d, *J* = 16.0 Hz, 1H), 1.54 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 164.04, 138.91, 134.65, 129.87, 126.75, 125.67, 123.88, 120.94, 113.85, 82.53, 28.35. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>16</sub>ClO<sub>2</sub>[M+H-N<sub>2</sub>]<sup>+</sup>: 251.0834, found: 251.0838.



**tert-butyl (E)-2-diazo-4-phenylpent-3-enoate:**

Red oil (yield: 70 %).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.43-7.26 (m, 5H), 5.96 (d, *J* = 3.0 Hz, 1H), 2.07 (d, *J* = 3.0 Hz, 3H), 1.52 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.84, 142.79, 133.68, 128.40, 127.19, 125.77, 109.65, 82.04, 28.35, 16.94. HRMS (ESI) calcd. for C<sub>15</sub>H<sub>19</sub>O<sub>2</sub>[M+H-N<sub>2</sub>]<sup>+</sup>: 231.1380, found: 231.1383.

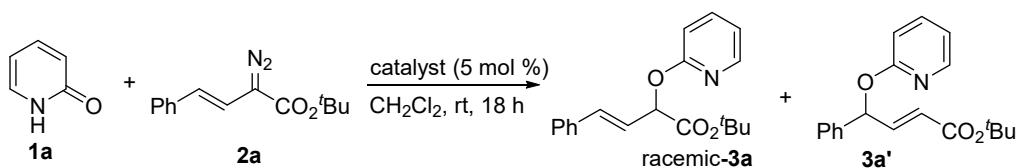


**methyl 2-(2-oxopyridin-1(2H)-yl)-2-phenylacetate (6):**

To a mixture of 2-pyridone (100 mg) and K<sub>2</sub>CO<sub>3</sub> (174 mg) in DMF (5 mL) was added methyl 2-bromo-2-phenylacetate (289 mg). The mixture was stirred at room temperature for 5 h. The solvent was removed under vacuum; the residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20-1:10) to give **6** (230 mg, yield: 90 %) as a white solid; mp: 92-94 °C.

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>): δ 7.51-7.40 (m, 3H), 7.39-7.29 (m, 3H), 7.05 (dd, *J* = 6.0, 3.0 Hz, 1H), 6.70 (s, 1H), 6.63-6.58 (m, 1H), 6.14-6.05 (m, 1H), 3.83 (s, 3H); <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>): δ 169.76, 162.60, 139.77, 135.47, 133.08, 129.53, 129.43, 120.14, 105.92, 61.48, 52.92. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>14</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 244.0968, found: 244.0965.

## Initial investigation of Scheme 2



Xantphos(AuNTf<sub>2</sub>)<sub>2</sub>: 78% yield of racemic-3a  
Cu(OTf)<sub>2</sub>: 17% yield of racemic-3a  
Rh<sub>2</sub>(OAc)<sub>4</sub>: 9% yield of racemic-3a  
AgNTf<sub>2</sub>: 75% yield of 3a'

### 1. Using Xantphos(AuNTf<sub>2</sub>) as catalyst:

To a schlenk tube was added Xantphos(AuNTf<sub>2</sub>)<sub>2</sub> (38.4 mg, 0.025 mmol), **1a** (57 mg, 0.6 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) under argon atmosphere, then a solution of **2a** (122 mg, 0.5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was added via syringe pump over 30 min at RT. The resulting mixture was stirred at RT for 18 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:20) to afford product racemic-**3a** (121 mg, yield: 78 %) as a white solid, mp: 103-105 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.09 (m, 1H), 7.62 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 4.0 Hz, 2H), 7.38-7.27 (m, 3H), 6.92 (d, *J* = 12.0 Hz, 3H), 6.42 (dd, *J* = 16.0, 8.0 Hz, 1H), 5.77 (d, *J* = 8.0 Hz,

1H), 1.44 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.23, 162.25, 146.46, 138.86, 136.35, 133.87, 128.63, 128.16, 126.80, 122.87, 117.45, 111.19, 81.95, 74.84, 27.98. HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{22}\text{NO}_3$  [ $\text{M}+\text{H}]^+$ : 312.1594, found: 312.1596.

## 2. Using $\text{Cu}(\text{OTf})_2$ as catalyst:

To a schlenk tube was added  $\text{Cu}(\text{OTf})_2$  (9 mg, 0.025 mmol), **1a** (57 mg, 0.6 mmol) and dry  $\text{CH}_2\text{Cl}_2$  (2.5 mL) under argon atmosphere, then a solution of **2a** (122 mg, 0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2.5 mL) was added via syringe pump over 30 min at RT. The resulting mixture was stirred at RT for 18 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:20) to afford product racemic-**3a** (26 mg, yield: 17 %) as a white solid, mp: 103-105 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13-8.09 (m, 1H), 7.62 (t,  $J$  = 8.0 Hz, 1H), 7.44 (d,  $J$  = 4.0 Hz, 2H), 7.38-7.27 (m, 3H), 6.92 (d,  $J$  = 12.0 Hz, 3H), 6.42 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 5.77 (d,  $J$  = 8.0 Hz, 1H), 1.44 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.23, 162.25, 146.46, 138.86, 136.35, 133.87, 128.63, 128.16, 126.80, 122.87, 117.45, 111.19, 81.95, 74.84, 27.98. HRMS (ESI) calcd. for  $\text{C}_{19}\text{H}_{22}\text{NO}_3$  [ $\text{M}+\text{H}]^+$ : 312.1594, found: 312.1596.

## 3. Using $\text{Rh}_2(\text{OAc})_4$ as catalyst:

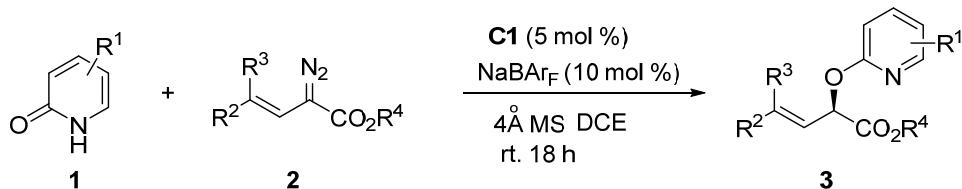
To a schlenk tube was added  $\text{Rh}_2(\text{OAc})_4$  (11 mg, 0.025 mmol), **1a** (57 mg, 0.6 mmol) and dry  $\text{CH}_2\text{Cl}_2$  (2.5 mL) under argon atmosphere, then a solution of **2a** (122 mg, 0.5 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (2.5 mL) was added via syringe pump over 30 min at RT. The resulting mixture was stirred at RT for 18 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:20) to afford product racemic-**3a** (14 mg, yield: 9 %) as a white solid, mp: 103-105 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.13-8.09 (m, 1H), 7.62 (t,  $J$  = 8.0 Hz, 1H), 7.44 (d,  $J$  = 4.0 Hz, 2H), 7.38-7.27 (m, 3H), 6.92 (d,  $J$  = 12.0 Hz, 3H), 6.42 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 5.77 (d,  $J$  = 8.0 Hz, 1H), 1.44 (s, 9H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  169.23, 162.25, 146.46, 138.86, 136.35, 133.87, 128.63, 128.16, 126.80, 122.87, 117.45, 111.19, 81.95, 74.84, 27.98. HRMS (ESI)

calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 312.1594, found: 312.1596.

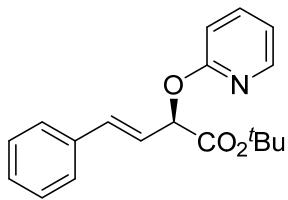
#### 4. Using AgNTf<sub>2</sub> as catalyst:

To a schlenk tube was added AgNTf<sub>2</sub> (9.7 mg, 0.025 mmol), **1a** (57 mg, 0.6 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) under argon atmosphere, then a solution of **2a** (122 mg, 0.5 mmol) in dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) was added via syringe pump over 30 min at RT. The resulting mixture was stirred at RT for 18 h. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:20) to afford product **3a'** (117 mg, yield: 75 %) as colorless oil. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 – 8.08 (m, 1H), 7.61 – 7.53 (m, 1H), 7.45 (d, *J* = 7.3 Hz, 2H), 7.40 – 7.28 (m, 3H), 7.05 (dd, *J* = 15.6, 4.8 Hz, 1H), 6.88 – 6.80 (m, 3H), 6.02 (dd, *J* = 15.6, 1.5 Hz, 1H), 1.46 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.62, 162.33, 146.79, 145.24, 138.87, 138.74, 128.65, 128.17, 127.38, 122.86, 117.28, 111.53, 80.60, 74.67, 28.10. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 312.1594, found: 312.1598.

#### General procedure for table 2



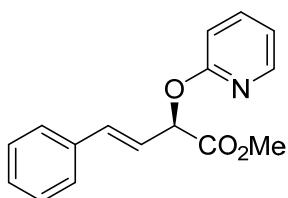
A 10 mL schlenk tube was charged with **C1** (41.92 mg, 0.025 mmol), NaBAr<sub>F</sub> (44.30 mg, 0.05 mmol), **1** (0.6 mmol) and 4 Å MS (47 mg) under argon atmosphere, then dry DCE (2.5 mL) was added. The mixture was stirred at room temperature for 15 min; then a solution of **2** (0.5 mmol) in dry DCE (2.5 mL) was added via syringe pump over 40 min. The resulting mixture was for 18 h at room temperature. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:60-1:10) to afford product **3**.



**tert-butyl (R,E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3a):**

A white solid (124 mg, 80 %), mp: 103-105 °C. 94 % ee, determined by HPLC: Chiralpak ID Column, EtOH/hexane = 10/90, 1.0 mL/min, 254 nm;  $t_R$  = 4.59 min (major) and 4.21 min (minor).  $[\alpha]_D^{22} = +52.2$  ( $c = 0.1$ , CHCl<sub>3</sub>).

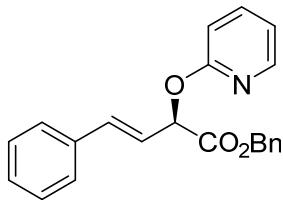
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.09 (m, 1H), 7.62 (t,  $J = 8.0$  Hz, 1H), 7.44 (d,  $J = 4.0$  Hz, 2H), 7.38-7.27 (m, 3H), 6.92 (d,  $J = 12.0$  Hz, 3H), 6.42 (dd,  $J = 16.0, 8.0$  Hz, 1H), 5.77 (d,  $J = 8.0$  Hz, 1H), 1.44 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.23, 162.25, 146.46, 138.86, 136.35, 133.87, 128.63, 128.16, 126.80, 122.87, 117.45, 111.19, 81.95, 74.84, 27.98. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>22</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 312.1594, found: 312.1596.



**methyl (R,E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3b):**

Yellow oil (113 mg, 84 %). 48 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 7.10 min (major) and 4.97 min (minor).  $[\alpha]_D^{22} = +15.0$  ( $c = 0.1$ , CHCl<sub>3</sub>).

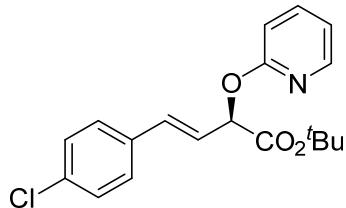
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.10 (m, 1H), 7.66-7.60 (m, 1H), 7.44 (d,  $J = 8.0$  Hz, 2H), 7.37-7.26 (m, 3H), 6.97-6.89 (m, 3H), 6.43 (dd,  $J = 16.0, 4.0$  Hz, 1H), 5.93 (d,  $J = 8.0$  Hz, 1H), 3.78 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.75, 162.09, 146.62, 138.99, 135.96, 134.45, 128.66, 128.35, 126.84, 122.29, 117.64, 111.24, 74.28, 52.50. HRMS (ESI) calcd. for C<sub>16</sub>H<sub>16</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 270.1125, found: 270.1128.



**benzyl (R,E)-4-phenyl-2-(pyridin-2-yloxy)but-3-enoate (3c):**

Colorless oil (134mg, 78%). 96 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 8.88 min (major) and 7.28 min (minor).  $[\alpha]_D^{22} = +35.1$  ( $c = 0.3$ , CHCl<sub>3</sub>).

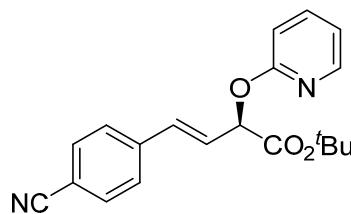
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.04 (s, 1H), 7.62 (t,  $J$  = 8.0 Hz, 1H), 7.42 (d,  $J$  = 8.0 Hz, 2H), 7.38-7.27 (m, 8H), 6.96-6.88 (m, 3H), 6.44 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 5.93 (d,  $J$  = 8.0 Hz, 1H), 5.23 (q,  $J$  = 24.0 Hz, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  170.17, 162.06, 146.56, 138.97, 135.97, 135.65, 134.61, 128.67, 128.50, 128.36, 128.21, 128.11, 126.86, 122.18, 117.65, 111.18, 74.53, 66.86. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>20</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 346.1438, found: 346.1440.



**tert-butyl (R,E)-4-(4-chlorophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3d):**

A white solid (129 mg, 75 %), mp: 90-91 °C. 86 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 6.45 min (major) and 5.09 min (minor).  $[\alpha]_D^{22} = +35.9$  ( $c = 0.14$ , CHCl<sub>3</sub>).

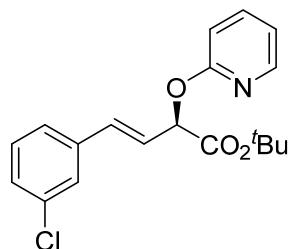
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  8.12-8.09 (m, 1H), 7.65-7.58(m, 1H), 7.38-7.27 (m, 4H), 6.94-6.83 (m, 3H), 6.39 (dd,  $J$  = 16.0, 4.0 Hz, 1H), 5.78 (dd,  $J$  = 8.0, 4.0 Hz, 1H), 1.44 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  169.01, 162.22, 146.46, 138.87, 134.81, 133.81, 132.44, 128.80, 127.98, 123.64, 117.50, 111.15, 82.05, 74.60, 27.97. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>21</sub>ClNO<sub>3</sub> [M+H]<sup>+</sup>: 346.1204, found: 346.1208.



**tert-butyl (*R,E*)-4-(4-cyanophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3e):**

A white solid (137 mg, 82 %), mp: 85-87 °C. 93 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 14.01 min (major) and 11.34 min (minor). [α]<sub>D</sub><sup>22</sup> = +39.5 (c = 0.1, CHCl<sub>3</sub>).

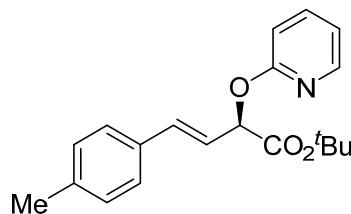
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.08 (m, 1H), 7.63 (d, J = 8.0 Hz, 3H), 7.51 (d, J = 8.0 Hz, 2H), 6.97-6.88 (m, 3H), 6.55 (dd, J = 16.0, 4.0 Hz, 1H), 5.85 (d, J = 4.0 Hz, 1H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.57, 162.05, 155.59, 146.47, 140.77, 138.98, 132.47, 131.46, 127.23, 127.04, 117.67, 111.36, 111.11, 82.38, 74.20, 27.96. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 337.1547, found: 337.1545.



**tert-butyl (*R,E*)-4-(3-chlorophenyl)-2-(pyridin-2-yloxy)but-3-enoate (3f):**

A white solid (140 mg, 81%), mp: 87-89 °C. 92 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 7.39 min (major) and 6.24 min (minor). [α]<sub>D</sub><sup>22</sup> = -20.3 (c = 0.1, CHCl<sub>3</sub>).

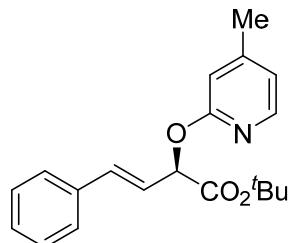
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12-8.09 (m, 1H), 7.65-7.59 (m, 1H), 7.42 (s, 1H), 7.32-7.25 (m, 3H), 6.94-6.83 (m, 3H), 6.44 (dd, J = 16.0, 4.0 Hz, 1H), 5.79 (d, J = 4.0 Hz, 1H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.91, 162.18, 146.46, 138.90, 138.17, 134.58, 132.17, 129.85, 128.05, 126.68, 124.99, 124.53, 117.54, 111.16, 82.13, 74.46, 27.97. HRMS (ESI) calcd. for C<sub>19</sub>H<sub>21</sub>ClNO<sub>3</sub> [M+H]<sup>+</sup>: 346.1204, found: 346.1208.



**tert-butyl (R,E)-2-(pyridin-2-yloxy)-4-(p-tolyl)but-3-enoate (3g):**

A white solid (91 mg, 56 %), mp: 83-85 °C. 87 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 7.33 min (major) and 7.03 min (minor). [α]<sub>D</sub><sup>22</sup> = +20.5 (c = 0.1, CHCl<sub>3</sub>).

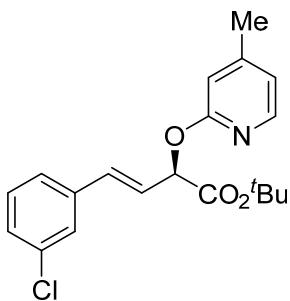
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13-8.08 (m, 1H), 7.65-7.57 (m, 1H), 7.34 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 8.0 Hz, 2H), 6.93-6.84 (m, 3H), 6.38 (d, J = 8.0 Hz, 1H), 5.75 (d, J = 8.0 Hz, 1H), 2.35 (s, 3H), 1.44 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.55, 162.35, 146.44, 138.77, 133.89, 131.56, 129.29, 126.70, 121.83, 117.77, 117.36, 111.18, 81.70, 74.96, 28.02, 21.09. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 326.1751, found: 326.1752.



**tert-butyl (R,E)-2-((4-methylpyridin-2-yl)oxy)-4-phenylbut-3-enoate (3h):**

A white solid (122 mg, 75 %), mp: 79-81 °C. 93 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 30/70, 1.0 mL/min, 254 nm; t<sub>R</sub> = 11.29 min (major) and 4.73 min (minor). [α]<sub>D</sub><sup>22</sup> = +32.5 (c = 0.1, CHCl<sub>3</sub>).

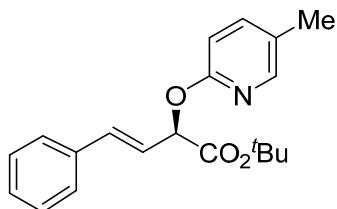
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.96 (d, J = 5.2 Hz, 1H), 7.46-7.42 (m, 2H), 7.37-7.25 (m, 3H), 6.91 (dd, J = 16.0, 0.8 Hz, 1H), 6.75-6.71 (m, 2H), 6.41 (dd, J = 16.0, 6.5 Hz, 1H), 5.78 (dd, J = 6.5, 1.4 Hz, 1H), 2.31 (s, 3H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.31, 162.62, 150.21, 145.97, 136.36, 133.72, 128.60, 128.09, 126.78, 123.08, 119.01, 111.24, 81.86, 74.73, 27.98, 20.96. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 326.1751, found: 326.1755.



**tert-butyl (R,E)-4-(3-chlorophenyl)-2-((4-methylpyridin-2-yl)oxy)but-3-enoate (3i):**

A white solid (144 mg, 80 %), mp: 89-91 °C. 91 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 6.78 min (major) and 4.91 min (minor). [α]<sub>D</sub><sup>22</sup> = +34.9 (c = 0.1, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.97-7.93 (m, 1H), 7.41 (s, 1H), 7.31–7.21 (m, 3H), 6.84 (dd, J = 12.0, 4.0 Hz, 1H), 6.75–6.71 (m, 2H), 6.42 (dd, J = 16.0, 8.0 Hz, 1H), 5.79 (dd, J = 8.0, 4.0 Hz, 1H), 2.31 (s, 3H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.99, 162.50, 150.29, 145.97, 138.23, 134.58, 132.03, 129.83, 128.00, 126.67, 124.97, 124.70, 119.10, 111.20, 82.05, 74.35, 27.98, 20.96. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>23</sub>ClNO<sub>3</sub> [M+H]<sup>+</sup>: 360.1361, found: 360.1364.

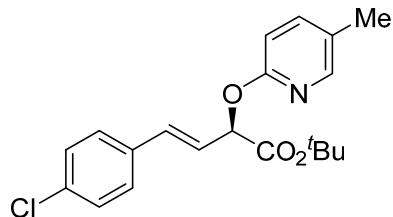


**tert-butyl (R,E)-2-((5-methylpyridin-2-yl)oxy)-4-phenylbut-3-enoate (3j):**

A white solid (123 mg, 76 %), mp: 83-85 °C. 89 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 8.43 min (major) and 7.97 min (minor). [α]<sub>D</sub><sup>22</sup> = +36.8 (c = 0.1, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90 (s, 1H), 7.43 (d, J = 7.7 Hz, 3H), 7.36-7.24 (m, 3H), 6.87 (dd, J = 30.9, 12.2 Hz, 2H), 6.41 (dd, J = 16.0, 6.5 Hz, 1H), 5.73 (d, J = 6.5 Hz, 1H), 2.24 (s, 3H), 1.45 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 169.34, 160.56, 145.84, 139.87, 136.34, 133.72, 128.58, 128.07, 126.76, 123.10, 110.49, 100.64,

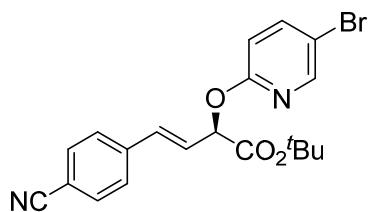
81.82, 74.74, 27.98, 17.44. HRMS (ESI) calcd. for  $C_{20}H_{24}NO_3$  [M+H]<sup>+</sup>: 326.1751, found: 326.1752.



**tert-butyl(R,E)-4-(4-chlorophenyl)-2-((5-methylpyridin-2-yl)oxy)but-3-enoate (3k):**

A white solid (131 mg, 73 %), mp: 87-89 °C. 90 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 6.76 min(major) and 6.03 min (minor). [α]<sub>D</sub><sup>22</sup> = +31.5 (c = 0.1, CHCl<sub>3</sub>).

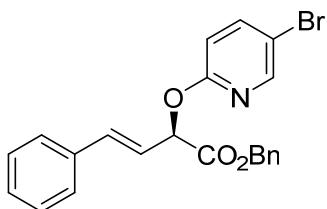
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.89 (s, 1H), 7.43 (dd, *J* = 8.4, 2.3 Hz, 1H), 7.35 (d, *J* = 8.5 Hz, 2H), 7.30 (d, *J* = 8.5 Hz, 2H), 6.89-6.79 (m, 2H), 6.39 (dd, *J* = 16.0, 6.3 Hz, 1H), 5.74 (dd, *J* = 6.3, 1.4 Hz, 1H), 2.24 (s, 3H), 1.44 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.16, 160.47, 145.85, 139.93, 134.86, 133.76, 132.31, 128.78, 127.97, 126.47, 123.81, 110.46, 81.97, 74.52, 27.99, 17.45. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>23</sub>ClNO<sub>3</sub> [M+H]<sup>+</sup>: 360.1361, found: 360.1358.



**tert-butyl (R,E)-2-((5-bromopyridin-2-yl)oxy)-4-(4-cyanophenyl)but-3-enoate (3l):**

A white solid (169 mg, 82 %), mp: 133-135 °C. 96 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 6.88 min (major) and 5.84 min (minor). [α]<sub>D</sub><sup>22</sup> = +46.7 (c = 0.1, CHCl<sub>3</sub>).

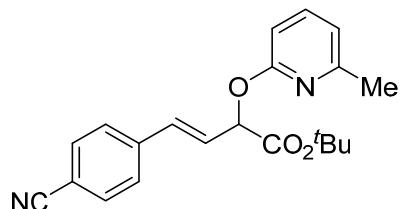
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (d, *J* = 4.0 Hz, 1H), 7.75-7.58 (m, 3H), 7.51 (d, *J* = 8.0 Hz, 2H), 6.96-6.82 (m, 2H), 6.52 (dd, *J* = 24.0, 8.0 Hz, 1H), 5.79-5.75 (m, 1H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.14, 160.87, 147.09, 141.63, 140.54, 132.49, 131.74, 127.24, 126.42, 118.80, 112.79, 112.73, 111.45, 82.66, 74.56, 27.96. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>20</sub>BrN<sub>2</sub>O<sub>3</sub> [M+H]<sup>+</sup>: 415.0652, found: 415.0653.



**benzyl (R,E)-2-((5-bromopyridin-2-yl)oxy)-4-phenylbut-3-enoate (3m):**

Colorless oil (148mg, 70%). 81 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 11.50 min (major) and 6.29 min (minor). [α]<sub>D</sub><sup>22</sup> = +28.8 (c = 0.1, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.02 (d, J = 2.3 Hz, 1H), 7.69 (dd, J = 8.7, 2.4 Hz, 1H), 7.40 (d, J = 7.2 Hz, 2H), 7.37-7.24 (m, 8H), 6.90 (d, J = 16.0 Hz, 1H), 6.83 (d, J = 8.7 Hz, 1H), 6.39 (dd, J = 16.0, 6.8 Hz, 1H), 5.85 (d, J = 6.2 Hz, 1H), 5.27 – 5.13 (m, 2H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 169.66, 160.93, 147.18, 141.53, 135.84, 135.47, 134.92, 128.67, 128.52, 128.45, 128.31, 128.21, 126.84, 121.73, 112.76, 112.73, 74.95, 66.98. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>19</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup>: 424.0543, found: 424.0538.

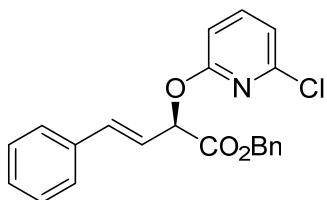


**tert-butyl (E)-4-(4-cyanophenyl)-2-((6-methylpyridin-2-yl)oxy)but-3-enoate (3n):**

A white solid (134 mg, 77 %), mp: 112-114 °C. 73 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm; t<sub>R</sub> = 19.94 min (major) and 13.01 min (minor). [α]<sub>D</sub><sup>22</sup> = +8.8 (c = 0.15, CHCl<sub>3</sub>).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.63 (d, J = 12.0Hz, 2H), 7.54-7.48 (m, 3H), 6.94 (d, J = 16.0 Hz, 1H), 6.73 (dd, J = 20.0, 8.0Hz, 2H), 6.55 (dd, J = 16.0, 8.0 Hz, 1H), 5.80 (d, J = 4.0 Hz, 1H), 2.40 (s, 3H), 1.45 (s, 9H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.71, 161.40, 155.80, 140.85, 139.18, 132.46, 131.42, 127.22, 127.19, 118.86, 116.63,

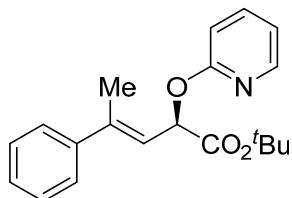
111.31, 107.53, 82.11, 74.15, 28.00, 23.93. HRMS (ESI) calcd. for  $C_{21}H_{23}N_2O_3$   $[M+H]^+$ : 351.1703, found: 351.1704.



**benzyl (R,E)-2-((6-chloropyridin-2-yl)oxy)-4-phenylbut-3-enoate (3o):**

Colorless oil (134 mg, 71 %). 64 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 14.27 min (major) and 6.67 min (minor).  $[\alpha]_D^{22} = +16.5$  ( $c = 0.15$ , CHCl<sub>3</sub>).

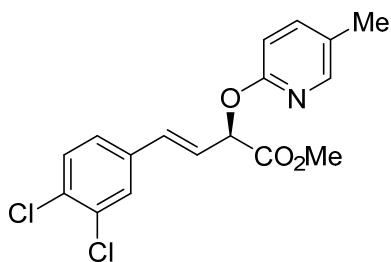
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  7.57 (t,  $J$  = 8.0 Hz, 1H), 7.43 - 7.28 (m, 10H), 6.96-6.88 (m, 2H), 6.84 (d,  $J$  = 8.0 Hz, 1H), 6.39 (dd,  $J$  = 16.0, 8.0 Hz, 1H), 5.93 (d,  $J$  = 8.0 Hz, 1H), 5.30 (d,  $J$  = 12.4 Hz, 1H), 5.18 (d,  $J$  = 12.0 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>)  $\delta$  169.58, 161.68, 148.03, 141.10, 135.77, 135.43, 135.15, 128.67, 128.57, 128.48, 128.28, 128.10, 126.86, 121.48, 117.40, 109.34, 74.95, 67.12. HRMS (ESI) calcd. for C<sub>22</sub>H<sub>19</sub>ClNO<sub>3</sub>  $[M+H]^+$ : 380.1048, found: 380.1049.



**tert-butyl (R,E)-4-phenyl-2-(pyridin-2-yloxy)pent-3-enoate (3p):**

a white solid (83 mg, 51 %), mp: 90-92 °C. 43 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 8.80 min (major) and 6.44 min (minor).  $[\alpha]_D^{22} = +17.3$  ( $c = 0.1$ , CHCl<sub>3</sub>).

<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  8.14-8.10 (m, 1H), 7.64-7.56 (m, 1H), 7.49-7.42 (m, 2H), 7.38-7.28 (m, 3H), 6.92-6.85 (m, 2H), 6.02-5.92 (m, 2H), 2.28 (d,  $J$  = 0.7 Hz, 3H), 1.43 (s, 9H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  169.60, 162.52, 146.44, 142.54, 141.69, 138.72, 128.31, 127.68, 126.04, 121.51, 117.27, 111.18, 81.62, 72.47, 27.98, 17.16. HRMS (ESI) calcd. for C<sub>20</sub>H<sub>24</sub>NO<sub>3</sub>  $[M+H]^+$ : 326.1751, found: 326.1752.



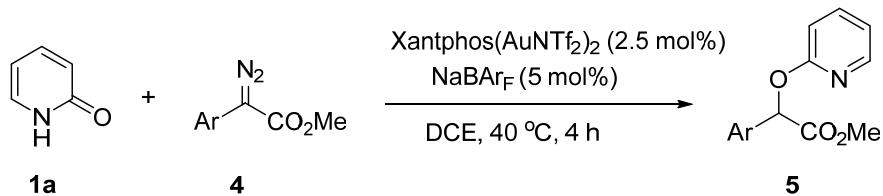
*methyl (R,E)-4-(3,4-dichlorophenyl)-2-((5-methylpyridin-2-yl)oxy)but-3-enoate (3q):*

A yellow solid (144 mg, 82 %), mp: 105-107 °C. 90 % ee, determined by HPLC: Chiralpak ID Column, i-PrOH/hexane = 50/50, 1.0 mL/min, 254 nm;  $t_R$  = 11.93 min (major) and 11.23 min (minor).  $[\alpha]_D^{22} = +42.3$  ( $c = 0.1$ ,  $\text{CHCl}_3$ ).

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.88 (m, 1H), 7.51-7.36 (m, 3H), 7.24 (dd,  $J = 12.0, 4.0$  Hz, 1H), 6.86-6.78 (m, 2H), 6.42 (dd,  $J = 20.0, 8.0$  Hz, 1H), 5.92 (dd,  $J = 8.0, 4.0$  Hz, 1H), 3.77 (s, 3H), 2.24 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.45, 160.13, 146.01, 140.12, 136.12, 132.77, 131.92, 131.42, 130.54, 128.49, 126.82, 125.93, 124.59, 110.47, 73.65, 52.57, 17.45. HRMS (ESI) calcd. for  $\text{C}_{17}\text{H}_{16}\text{Cl}_2\text{NO}_3$  [ $\text{M}+\text{H}]^+$ : 352.0502, found: 352.0505.

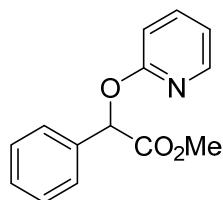
## Control experiments for Scheme 3

### 1. General procedure for Scheme 3-a



A 10 mL schlenk tube was charged with Xantphos( $\text{AuNTf}_2$ )<sub>2</sub> (19.2 mg, 0.0125 mmol), NaBAr<sub>F</sub> (22.1 mg, 0.025 mmol) and **1a** (0.6 mmol) under argon atmosphere, then dry DCE (2.5 mL) was added. The mixture was stirred at room temperature for 15 min; then a solution of **4** (0.5 mmol) in dry DCE (2.5 mL) was added via syringe pump over 40 min. After addition, the mixture was stirred for 4 h at 40 °C. The mixture was concentrated under vacuum; the crude residue was purified by column

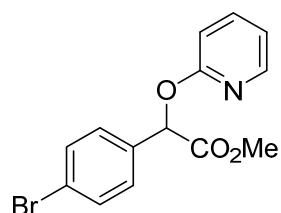
chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:30-1:10) to afford product **5**.



**methyl 2-phenyl-2-(pyridin-2-yloxy)acetate (5a):**

Colorless oil (111 mg, 91 %).

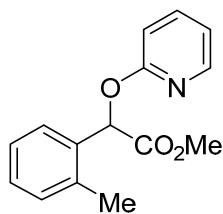
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14-8.10 (m, 1H), 7.64-7.57 (m, 3H), 7.44-7.34 (m, 3H), 6.92 (d, *J* = 12.0 Hz, 1H), 6.91-6.87 (m, 1H), 6.23 (s, 1H), 3.71 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.89, 162.35, 146.62, 138.94, 135.15, 128.97, 128.74, 127.70, 117.63, 111.34, 75.58, 52.41. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>14</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 244.0968, found: 244.0965.



**methyl 2-(4-bromophenyl)-2-(pyridin-2-yloxy)acetate (5b):**

Colorless oil (138 mg, 86 %).

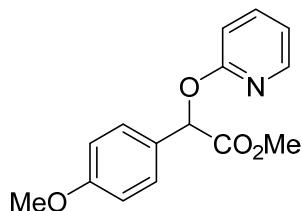
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 4.0 Hz, 1H), 7.63 (t, *J*=8.0 Hz, 1H), 7.52 (q, *J*=16.0 Hz, 4H), 6.95-6.90(m, 2H), 6.20 (s, 1H), 3.72 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.46, 162.07, 146.62, 139.04, 134.20, 131.88, 129.28, 123.10, 117.80, 111.29, 74.83, 52.57. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>13</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup>: 322.0073, found: 322.0077.



*methyl 2-(pyridin-2-yloxy)-2-(o-tolyl)acetate (5c):*

Colorless oil (114 mg, 89 %).

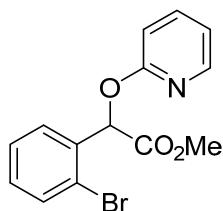
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.11 (d,  $J = 4.0$  Hz, 1H), 7.61-7.53 (m, 2H), 7.28-7.17 (m, 3H), 6.88 (d,  $J = 8.0$  Hz, 2H), 6.51 (s, 1H), 3.70 (s, 3H), 2.50 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.11, 162.47, 146.64, 138.93, 137.04, 133.74, 130.75, 128.95, 127.99, 126.39, 117.58, 111.34, 72.43, 52.34, 19.57. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{16}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 258.1125, found: 258.1127.



*methyl 2-(4-methoxyphenyl)-2-(pyridin-2-yloxy)acetate (5d):*

Colorless oil (121 mg, 89 %).

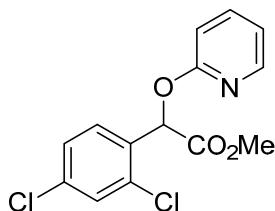
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.12 (d,  $J = 4.0$  Hz, 1H), 7.61 (t,  $J = 8.0$  Hz, 1H), 7.52 (d,  $J = 12.0$  Hz, 2H), 6.96-6.88 (m, 4H), 6.16 (s, 1H), 3.82 (s, 3H), 3.72 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.11, 162.41, 160.15, 146.61, 138.90, 129.16, 127.22, 117.55, 114.17, 111.33, 75.20, 55.35, 52.38. HRMS (ESI) calcd. for  $\text{C}_{15}\text{H}_{16}\text{NO}_4$   $[\text{M}+\text{H}]^+$ : 274.1074, found: 274.1078.



*methyl 2-(2-bromophenyl)-2-(pyridin-2-yloxy)acetate (5e):*

Colorless oil (139 mg, 87 %).

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.14 (d, *J* = 4.0 Hz, 1H), 7.67-7.58 (m, 3H), 7.39-7.33 (m, 1H), 7.27-7.20 (m, 1H), 6.95-6.86 (m, 2H), 6.77 (s, 1H), 3.75 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.43, 162.18, 146.71, 138.96, 135.05, 133.19, 130.49, 129.66, 127.85, 124.39, 117.75, 111.16, 74.35, 52.55. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>13</sub>BrNO<sub>3</sub> [M+H]<sup>+</sup>: 322.0073, found: 322.0069.

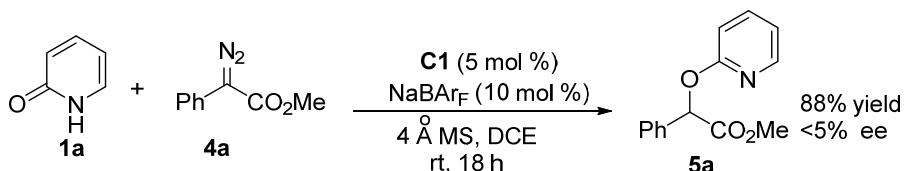


*methyl 2-(2,4-dichlorophenyl)-2-(pyridin-2-yloxy)acetate (5f):*

A white solid (140 mg, 91 %), mp: 87-89 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.13 (d, *J* = 8.0 Hz, 1H), 7.62 (t, *J* = 12.0 Hz, 2H), 7.46 (s, 1H), 7.33-7.24 (m, 1H), 6.96-6.86 (m, 2H), 6.75 (s, 1H), 3.75 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 170.04, 161.96, 146.68, 139.05, 135.49, 134.85, 132.08, 130.40, 129.66, 127.60, 117.89, 111.15, 71.36, 52.66. HRMS (ESI) calcd. for C<sub>14</sub>H<sub>12</sub>Cl<sub>2</sub>NO<sub>3</sub> [M+H]<sup>+</sup>: 312.0189, found: 312.0186.

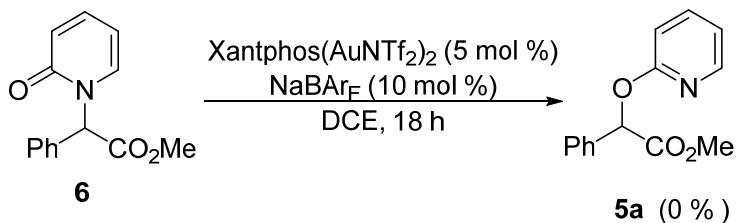
## 2. Control experiments for Scheme 3-b



A 10 mL schlenk tube was charged with **C1** (41.92 mg, 0.025 mmol), NaBAr<sub>F</sub> (44.30 mg, 0.05 mmol), **1a** (57 mg, 0.6 mmol) and 4Å MS (47 mg) under argon atmosphere, then dry DCE (2.5 mL) was added. The mixture was stirred at room temperature for 15 min; then a solution of **4a** (88 mg, 0.5 mmol) in dry DCE (2.5 mL) was added via syringe pump over 40 min. The resulting mixture was for 18 h at room temperature. The mixture was concentrated under vacuum; the crude residue was purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:60-1:10) to afford product **5a** (107 mg, yield: 88 %) as colorless oil. <sup>1</sup>H NMR (400 MHz,

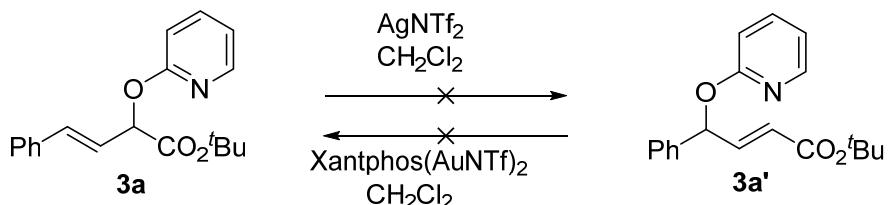
$\text{CDCl}_3$ )  $\delta$  8.14-8.10 (m, 1H), 7.64-7.57 (m, 3H), 7.44-7.34 (m, 3H), 6.92 (d,  $J$  = 12.0 Hz, 1H), 6.91-6.87 (m, 1H), 6.23 (s, 1H), 3.71 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.89, 162.35, 146.62, 138.94, 135.15, 128.97, 128.74, 127.70, 117.63, 111.34, 75.58, 52.41. HRMS (ESI) calcd. for  $\text{C}_{14}\text{H}_{14}\text{NO}_3$   $[\text{M}+\text{H}]^+$ : 244.0968, found: 244.0965.

### 3. Control experiments for Scheme 3-c



A 10 mL schlenk tube was charged with Xantphos( $\text{AuNTf}_2$ )<sub>2</sub> (15.3 mg, 0.01 mmol), NaBAr<sub>F</sub> (18.2 mg, 0.02 mmol), **6** (50 mg, 0.2 mmol) under argon atmosphere, then dry DCE (2.5 mL) was added. The mixture was stirred under argon atmosphere for 18h. The reaction was concentrated and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether= 1:20-1:10) to recover compound **6** (48 mg).

### 4. Control experiments for Scheme 3-d



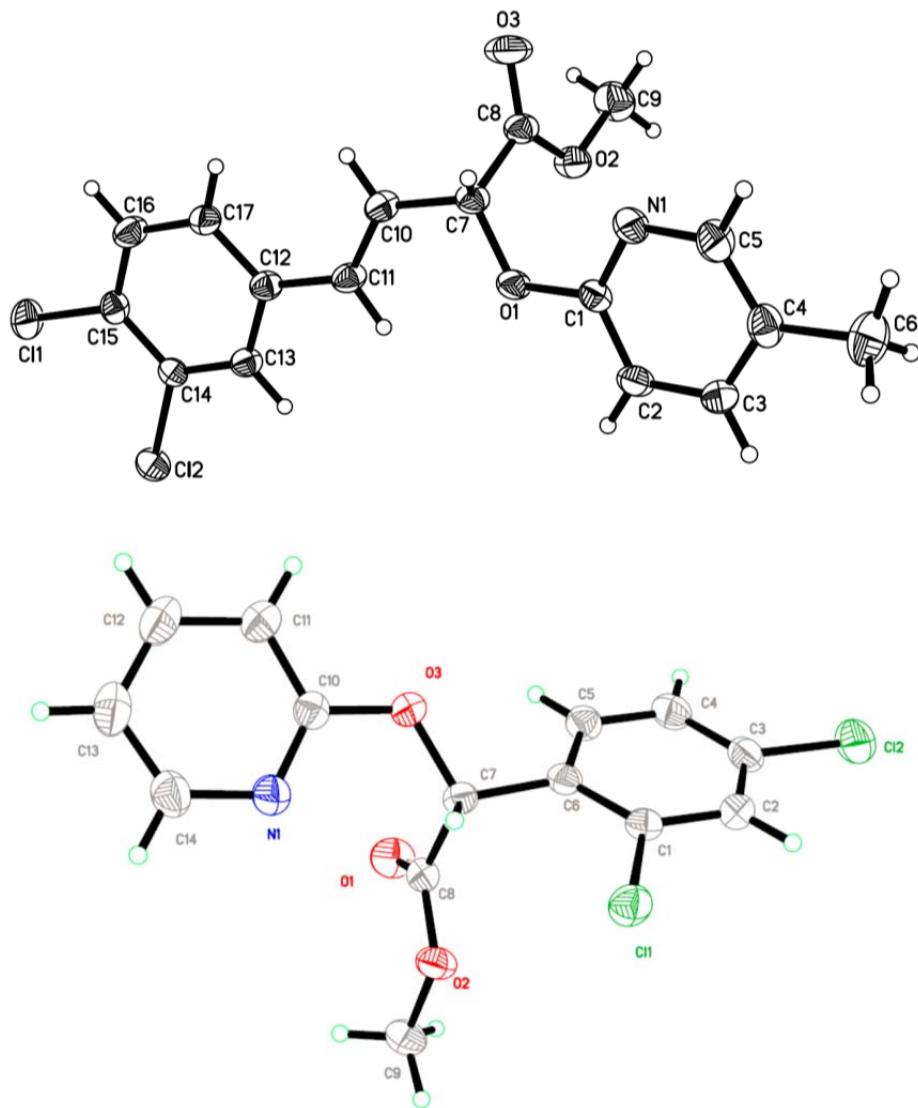
To a schlenk tube was added AgNTf<sub>2</sub> (1.9 mg, 0.005 mmol), **3a** (31 mg, 0.1 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (2.5 mL) under argon atmosphere. The resulting mixture was stirred at RT for 18 h. The mixture was concentrated under vacuum and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:20) to recovered **3a** (30 mg).

To a schlenk tube was added Xantphos( $\text{AuNTf}_2$ )<sub>2</sub> (7.6 mg, 0.005 mmol), **3a'** (31 mg, 0.1 mmol) and dry CH<sub>2</sub>Cl<sub>2</sub> (2 mL) under argon atmosphere; the resulting solution was

stirred at RT for 18 h. The mixture was concentrated under vacuum and purified by column chromatography (silica gel, eluted with EtOAc: Petroleum ether=1:15) to recovered **3a'** (30.5 mg).

## X-ray structure of **3q** and **5f**

The crystal structures have been deposited at the Cambridge Crystallographic Data Centre (CCDC 1445774, **3q**) and (CCDC 1445775, **5f**). The data can be obtained free of charge via the internet at [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).



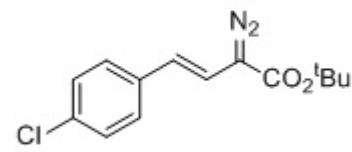
## References:

- [1] (a) Huang, L.; Yang, H.-B.; Zhang, D.-H.; Zhang, Zh.; Tang, X.-Y.; Xu, Q.; Shi, M.

*Angew. Chem. Int. Ed.* **2013**, *52*, 6767. (b) Handa, S.; Lippincott, D. J.; Aue, D. H.; Lipshutz, B. H. *Angew. Chem. Int. Ed.* **2014**, *53*, 10658. (c) LaLonde, R. L.; Wang, Z. J.; Mba, M.; Lackner, A. D.; Toste, F. D. *Angew. Chem. Int. Ed.* **2010**, *49*, 598. (d) Deák, A.; Megyes, T.; Tárkányi, G.; Király, P.; Biczók, L.; Pálinkás, G.; Stang, P. J. *J. Am. Chem. Soc.* **2006**, *128*, 12668.

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[3] (a) Manning, J. R.; Davies, H. M. L. *J. Am. Chem. Soc.* **2008**, *130*, 8602. (b) Manning, J. R.; Davies, H. M. L. *Org. Synth.* **2007**, *84*, 334. (c) Davies, H. M. L.; Yang, J.; Manning, J. R. *Tetrahedron: Asymmetry* **2006**, *17*, 665. (d) Davies, H. M. L.; Smith, H. D.; Hu, B.; Klenzak, S. M.; Hegner, F. J. *J. Org. Chem.* **1992**, *57*, 6900. (e) Wang, H.; Guptill, D. M.; Varela-Alvarez, A.; Musaev, D. G.; Davies, H. M. L. *Chem. Sci.* **2013**, *4*, 2844.



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~6.41  
~6.14  
~6.10

—1.53

4.41

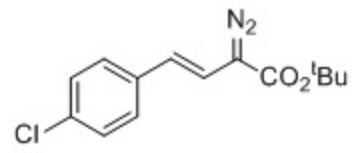
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1.00

9.00

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f1 (ppm)



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— 132.45  
— 128.84  
— 126.91  
— 121.21

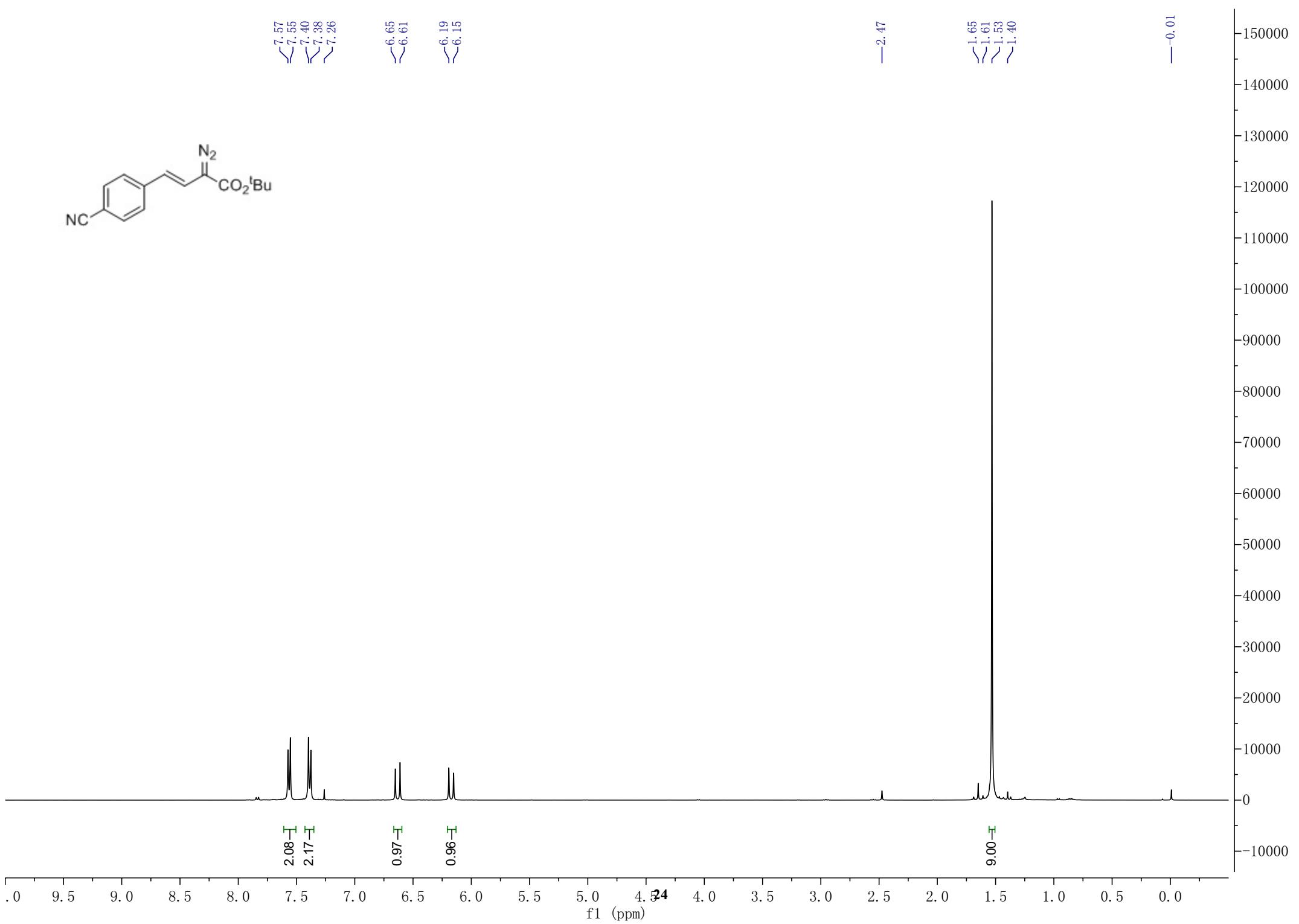
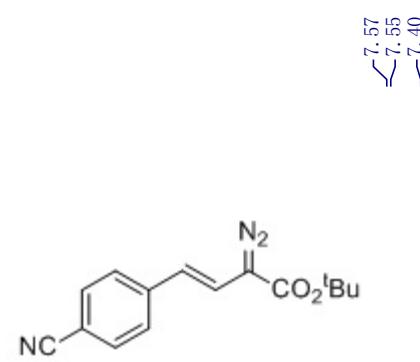
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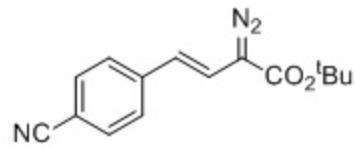
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— 28.35

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f1 (ppm)





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—141.51

—132.52

—126.03

~120.30

~119.08

~116.74

—109.75

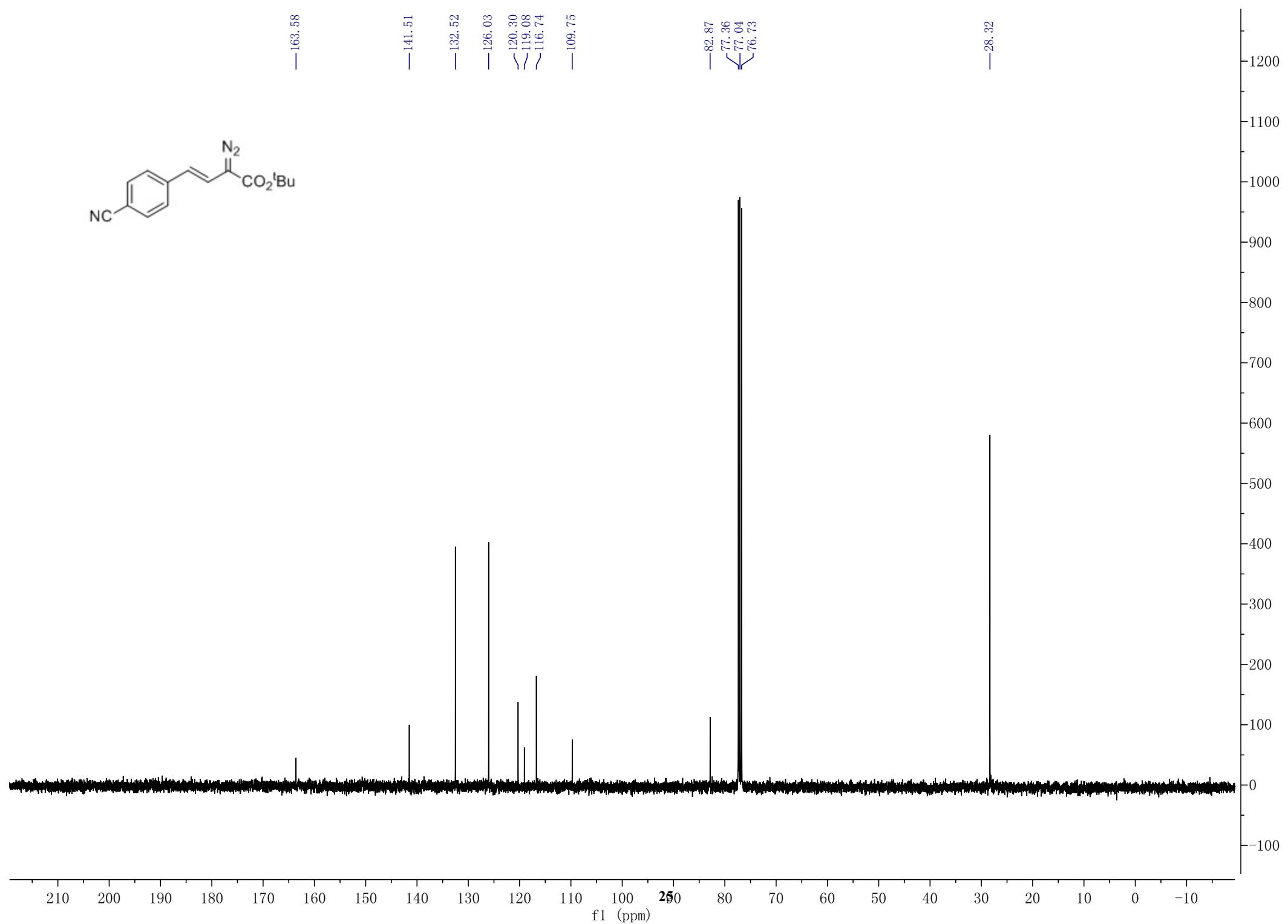
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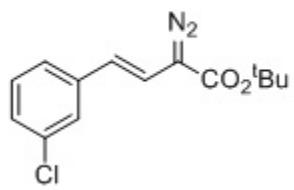
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—76.73

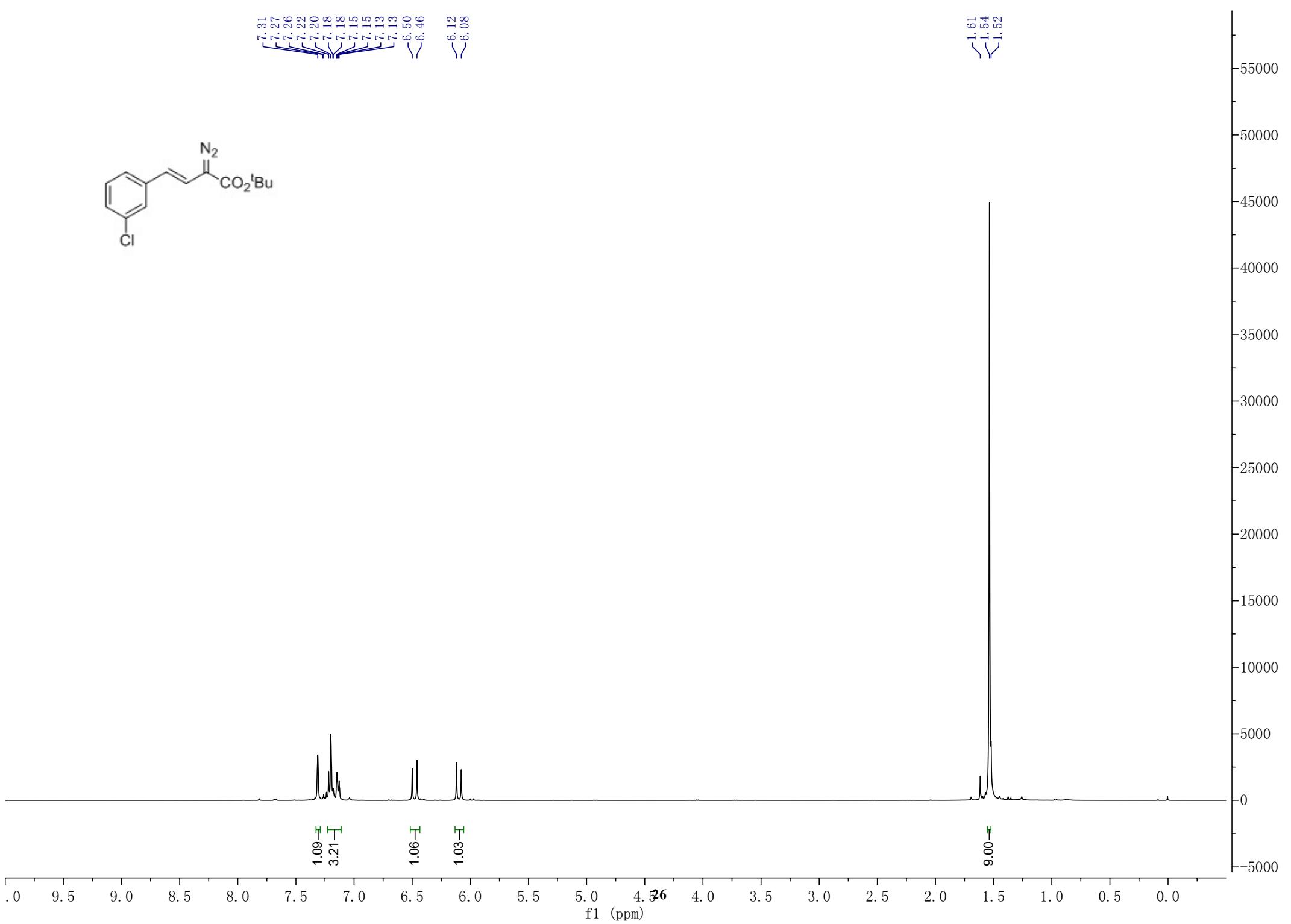
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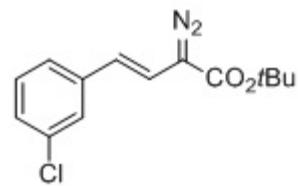




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7.22  
7.20  
7.18  
7.18  
7.15  
7.15  
7.13  
7.13  
6.50  
~6.46  
~6.12  
~6.08

1.61  
1.54  
1.52





— 164.04

~138.91  
~134.65  
129.87  
126.75  
125.67  
~123.88  
~120.94

— 113.85

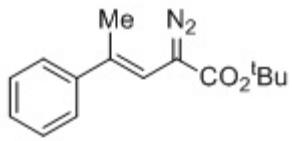
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77.41  
77.09  
76.77

— 28.35

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10

f1 (ppm)

1900  
1800  
1700  
1600  
1500  
1400  
1300  
1200  
1100  
1000  
900  
800  
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500  
400  
300  
200  
100  
0  
-100  
-200

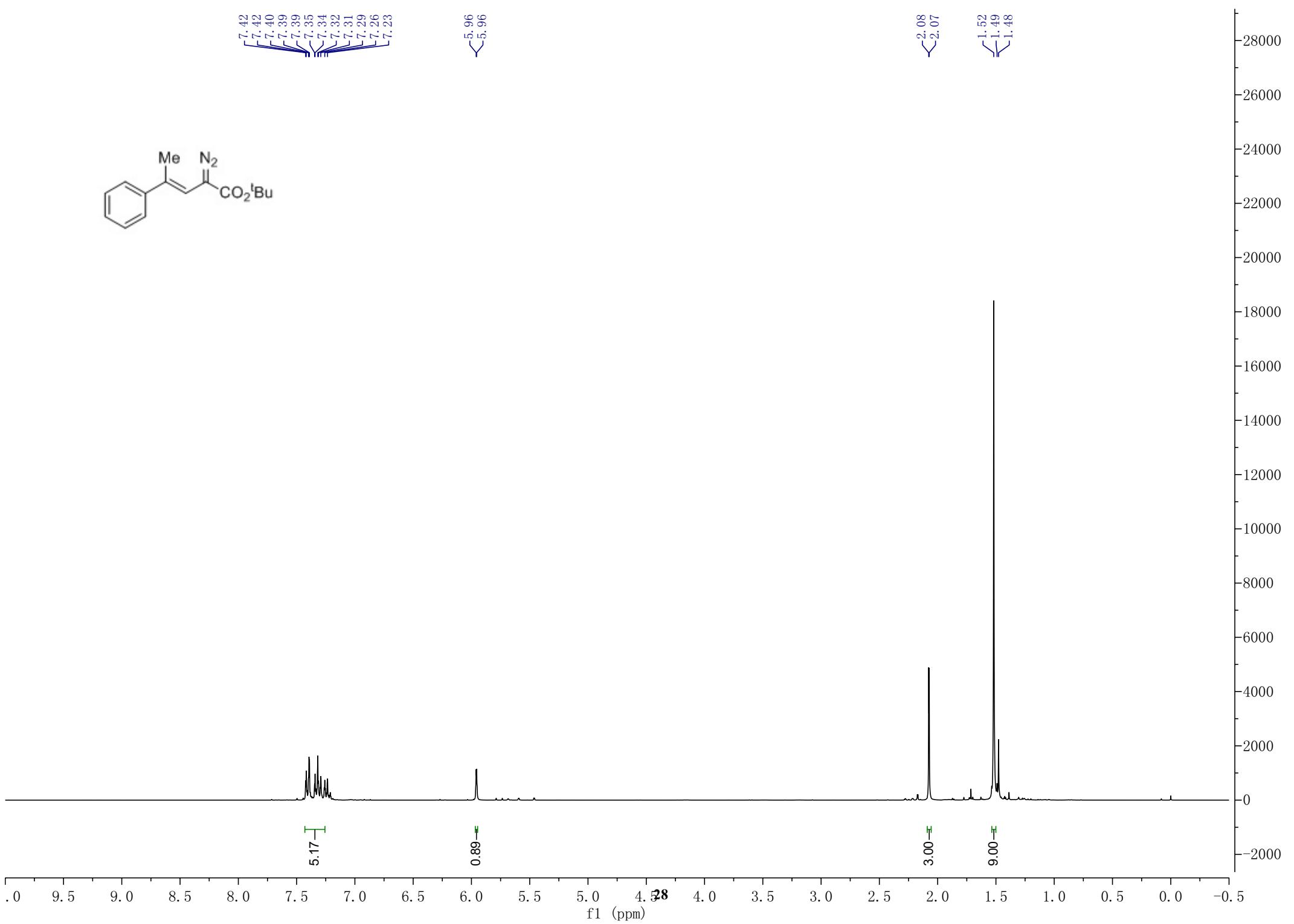


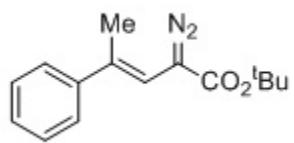
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7.23

5.96  
5.96

2.08  
2.07

1.52  
1.49  
1.48





—165.84

—142.79

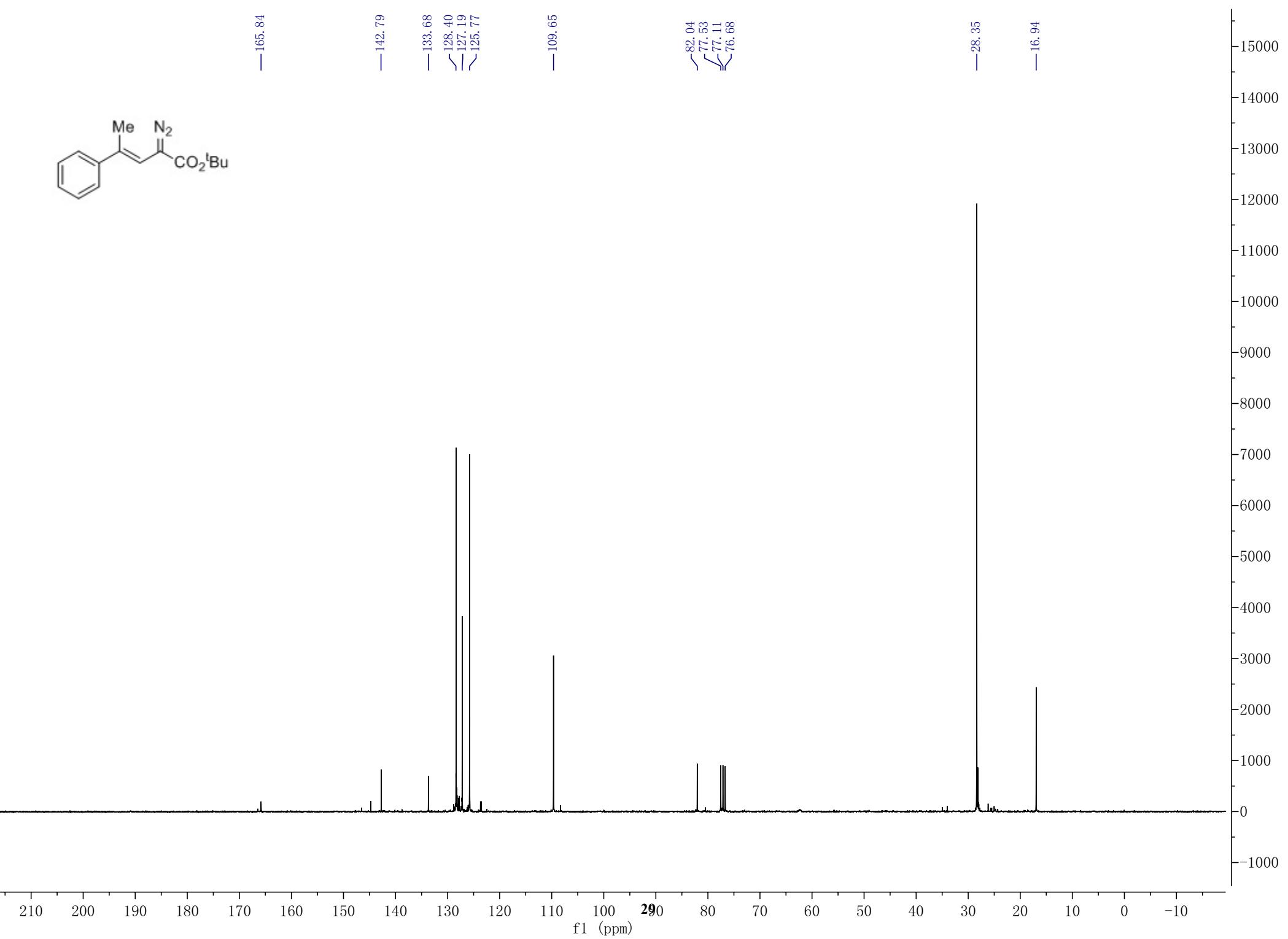
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—28.35

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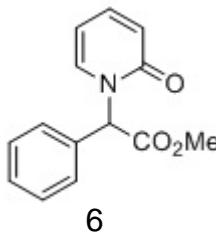


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7.31  
7.31  
7.30

7.06  
7.04  
7.04  
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6.07

3.83

0.00



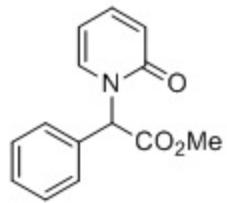
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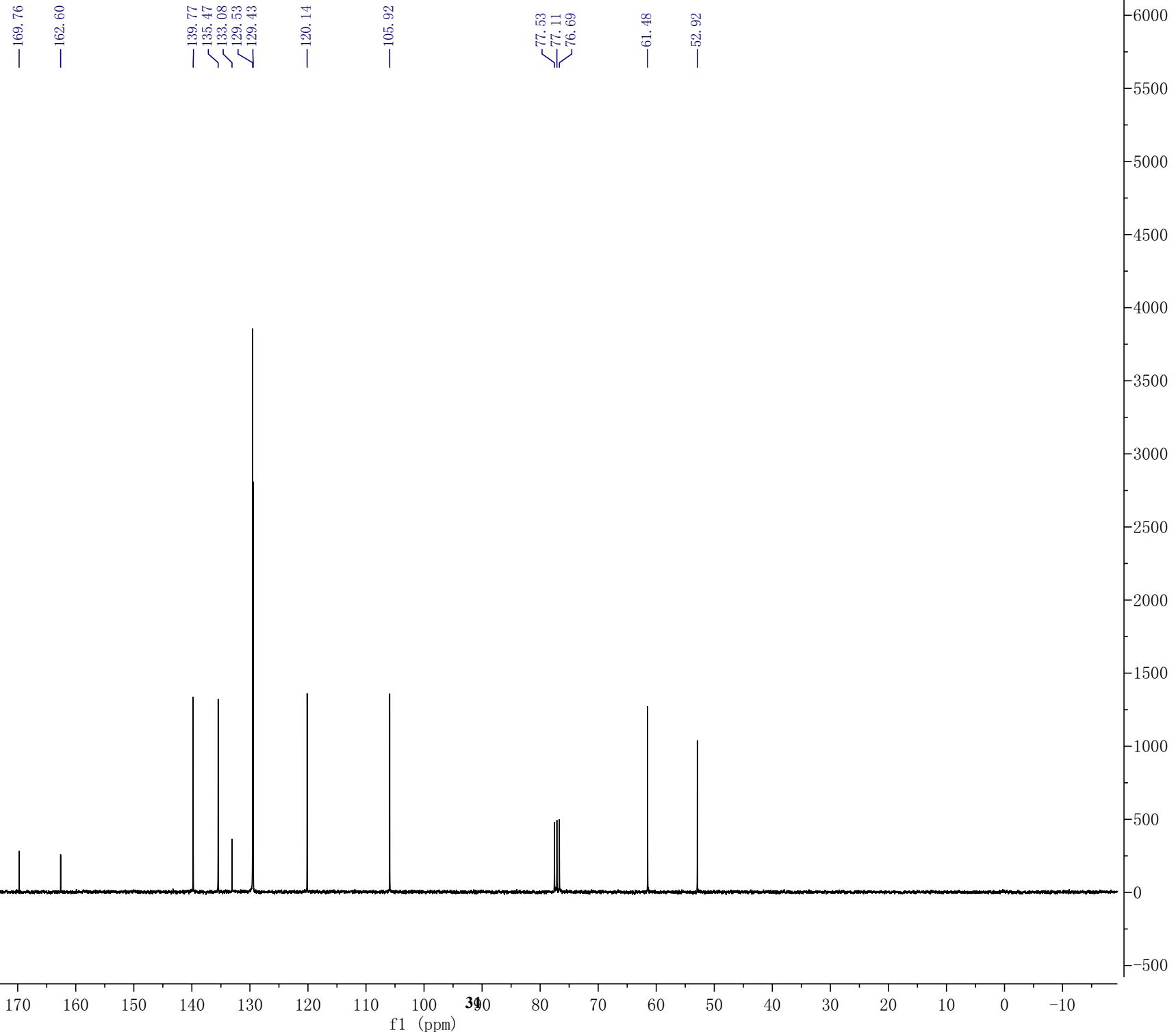
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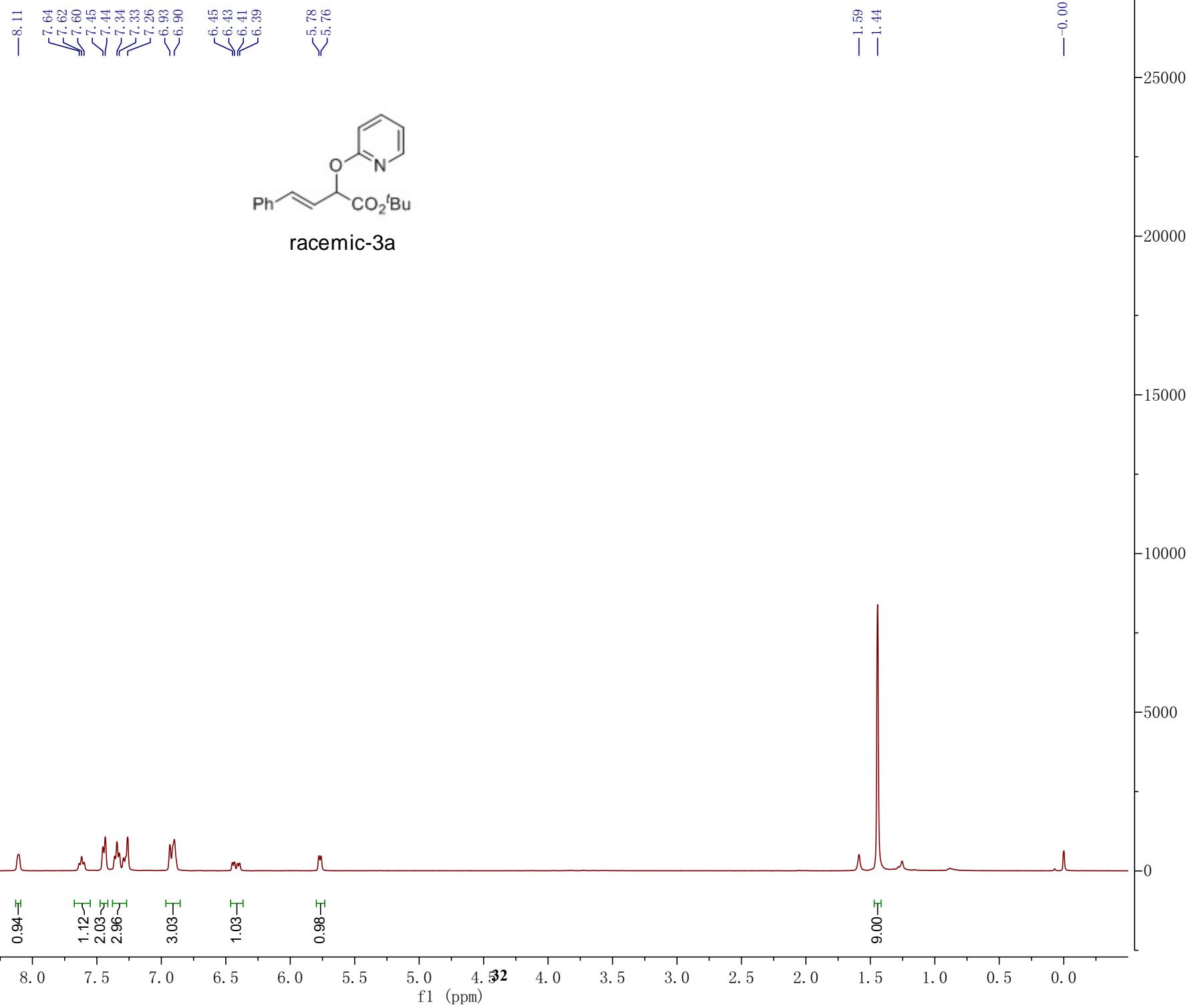
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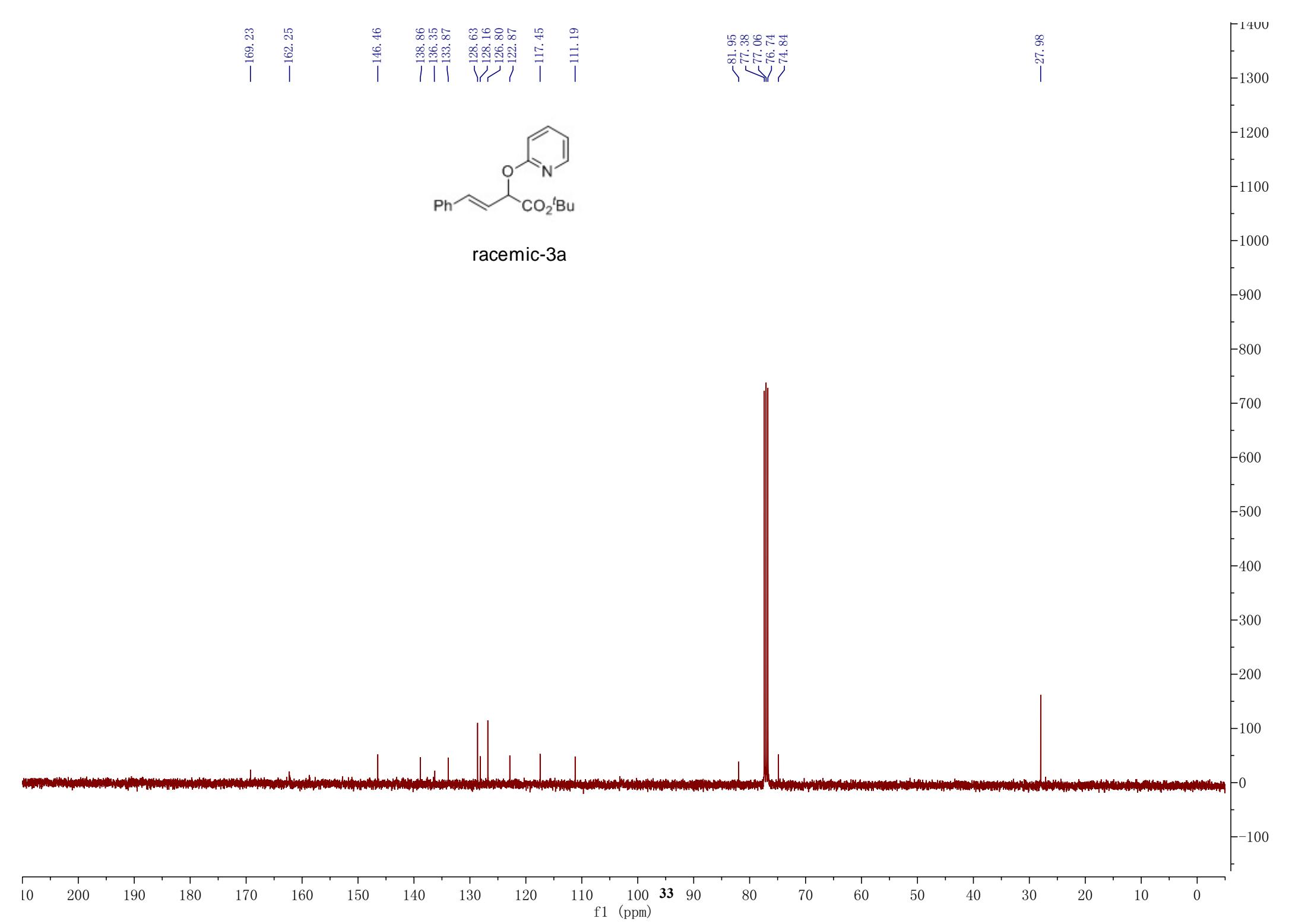
f1 (ppm)

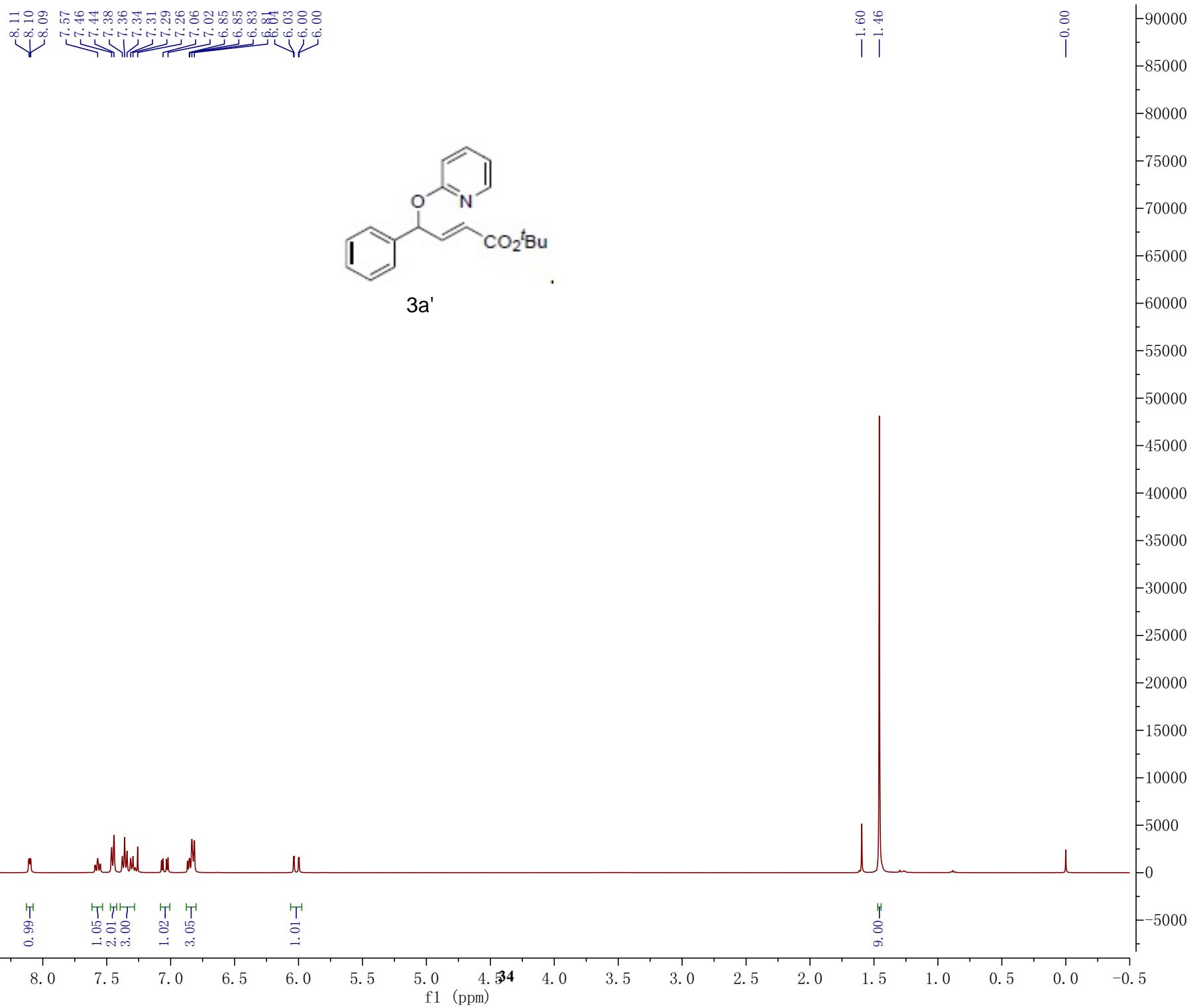


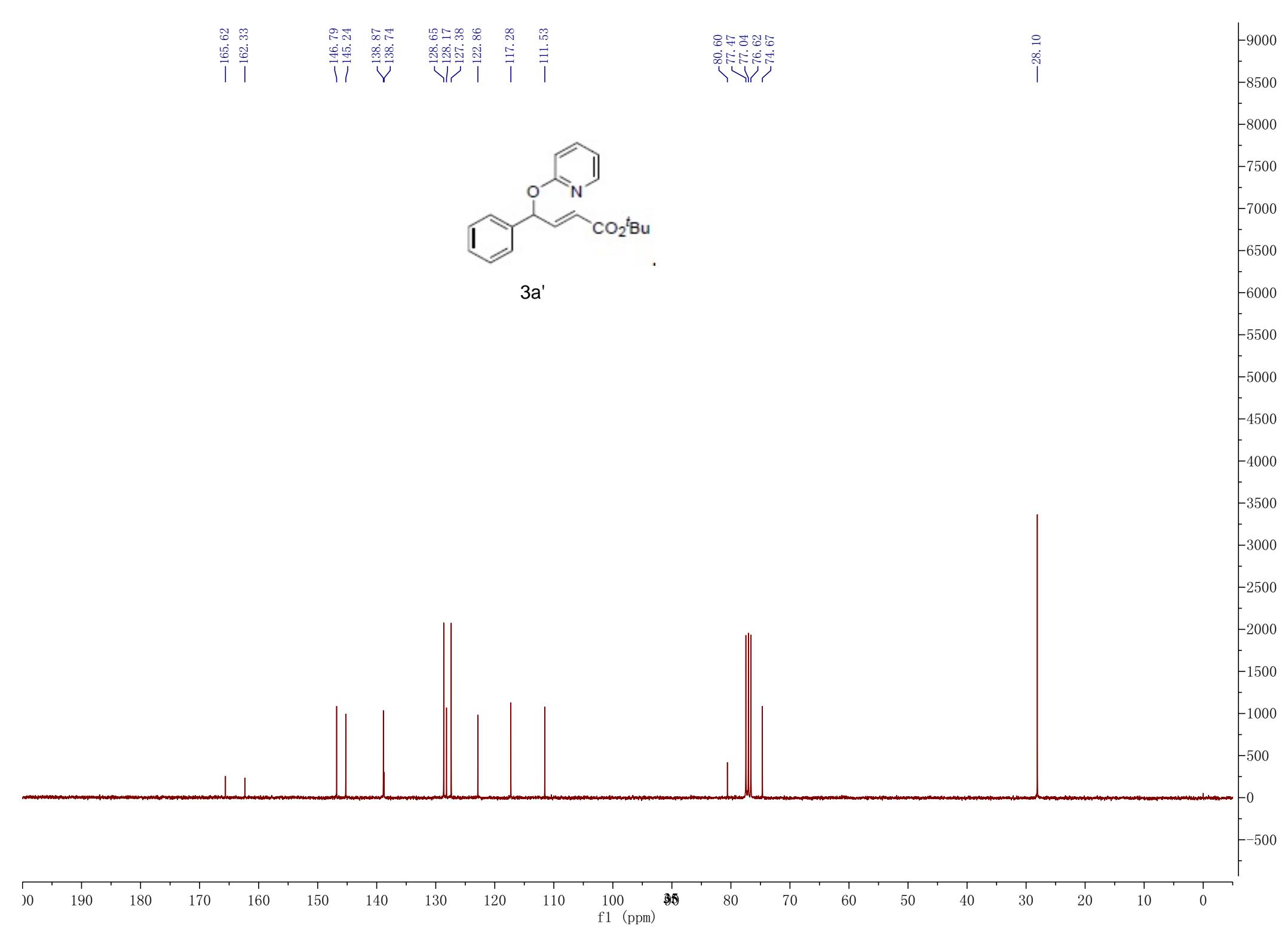
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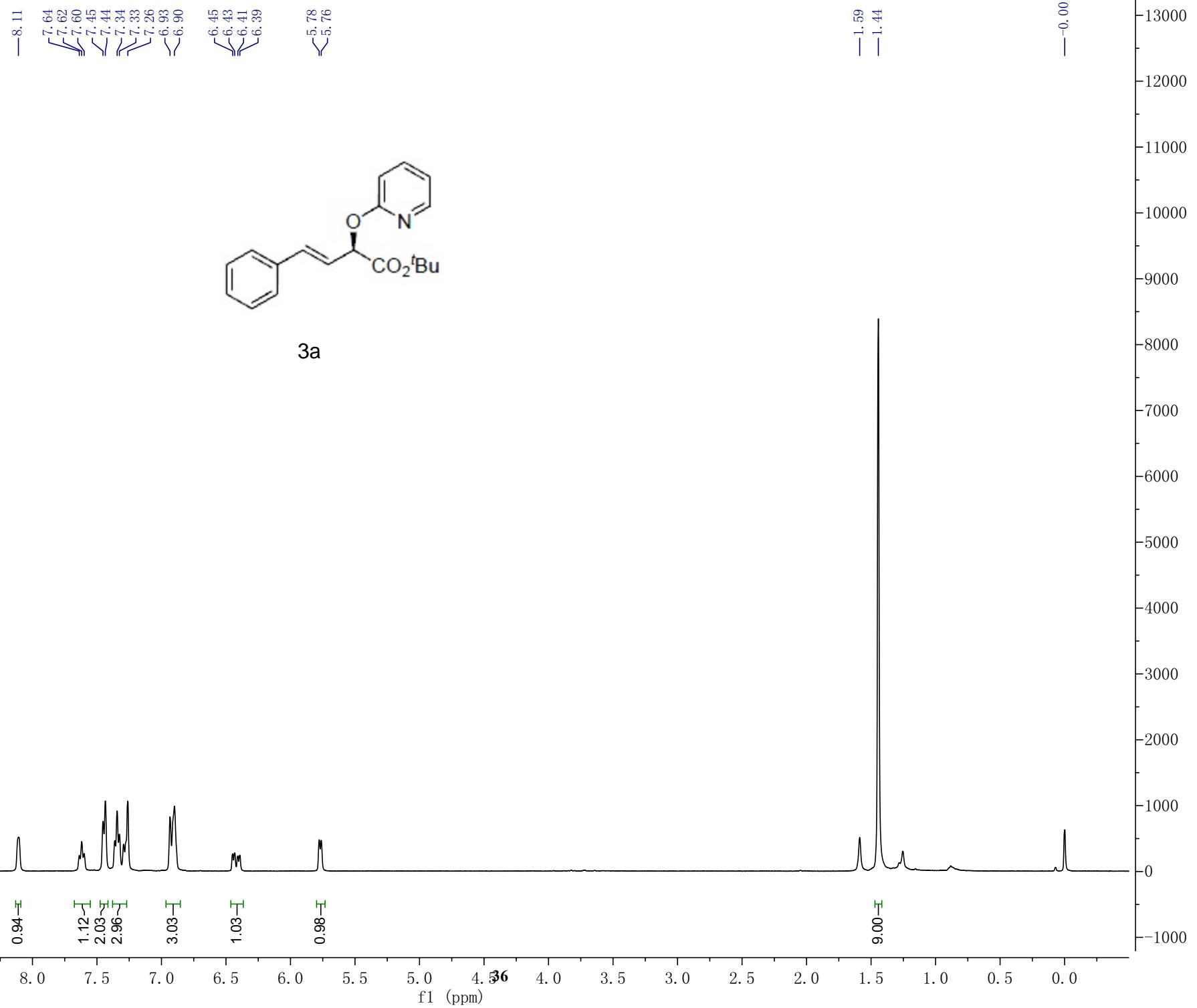


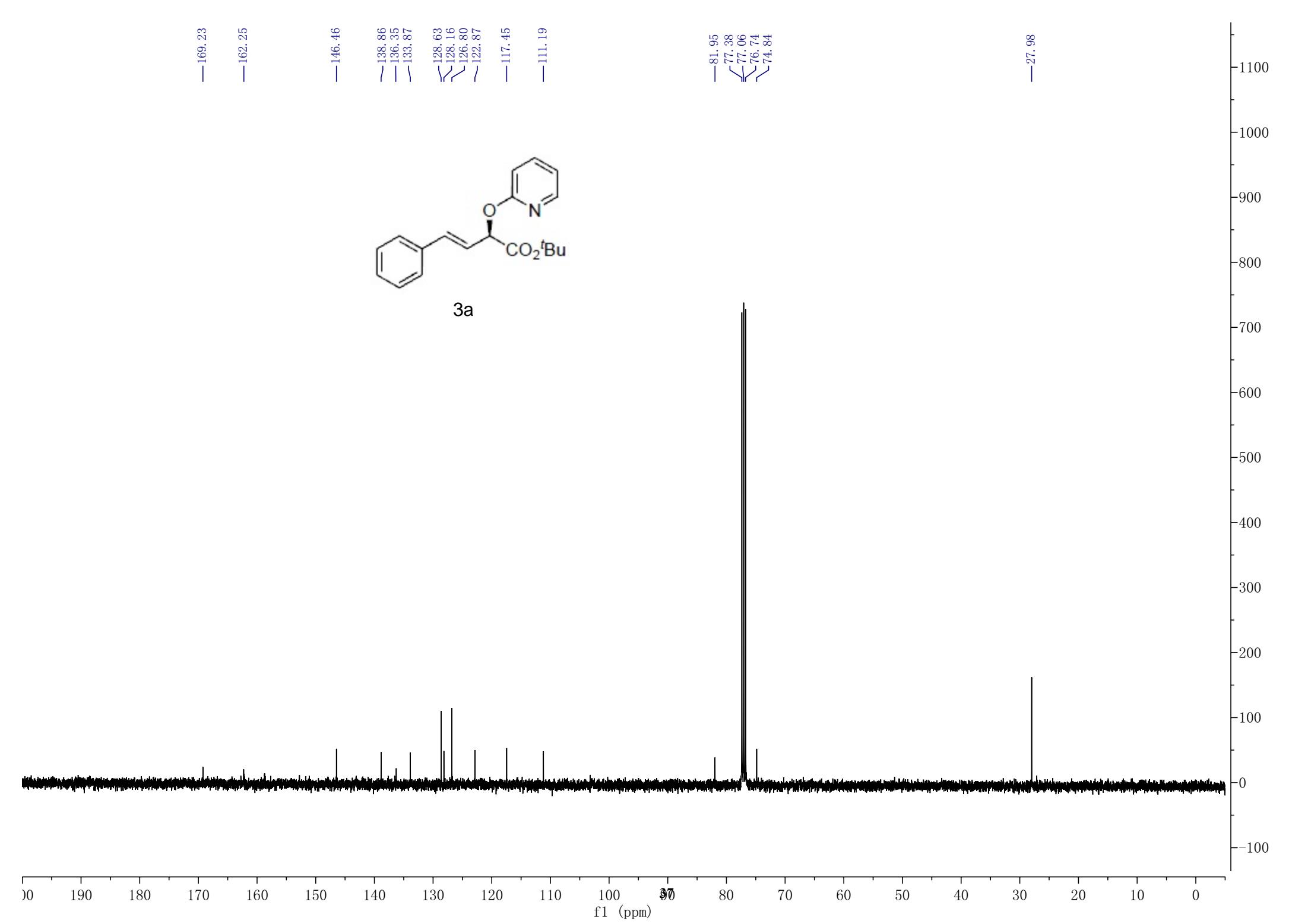




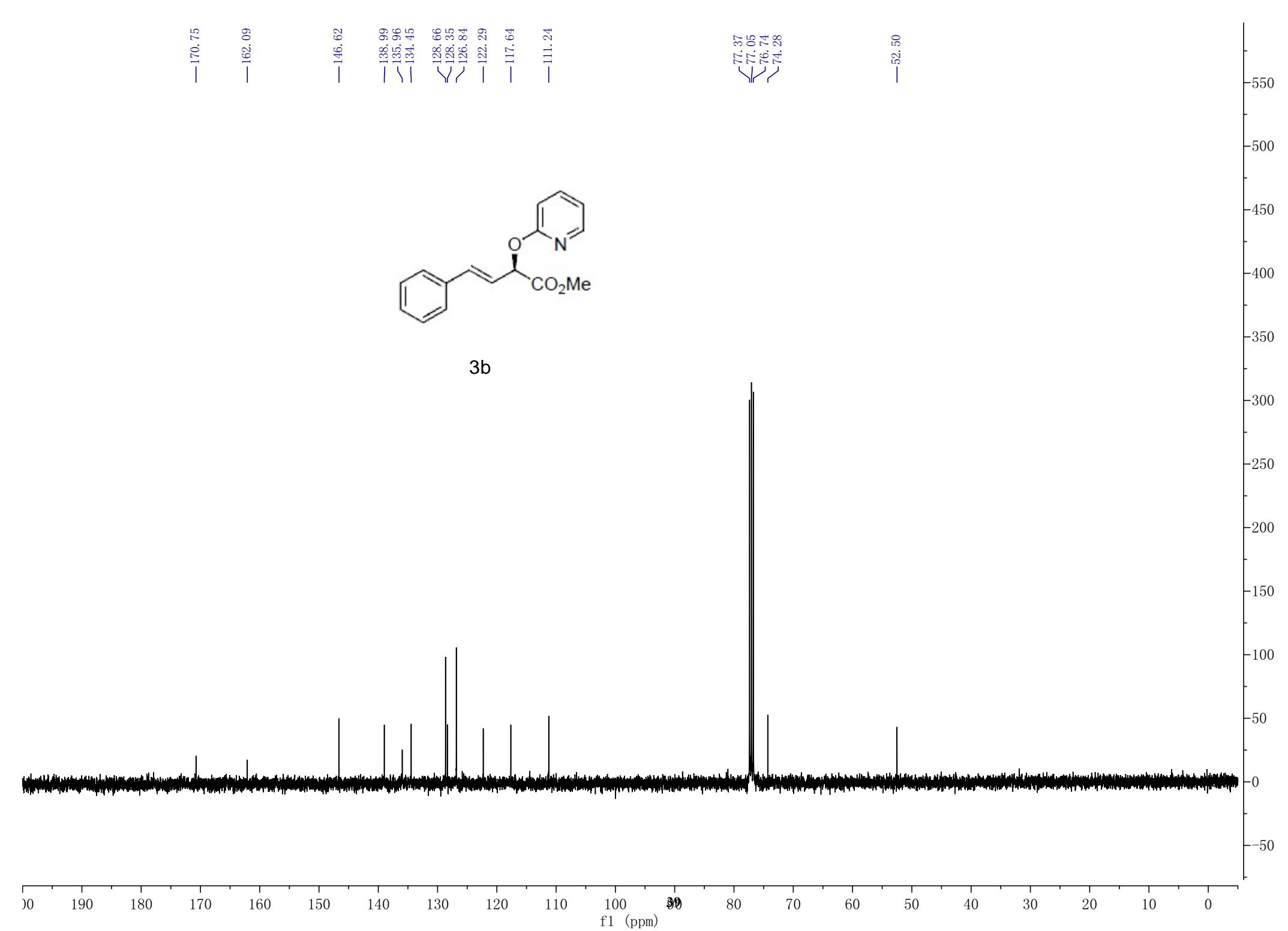


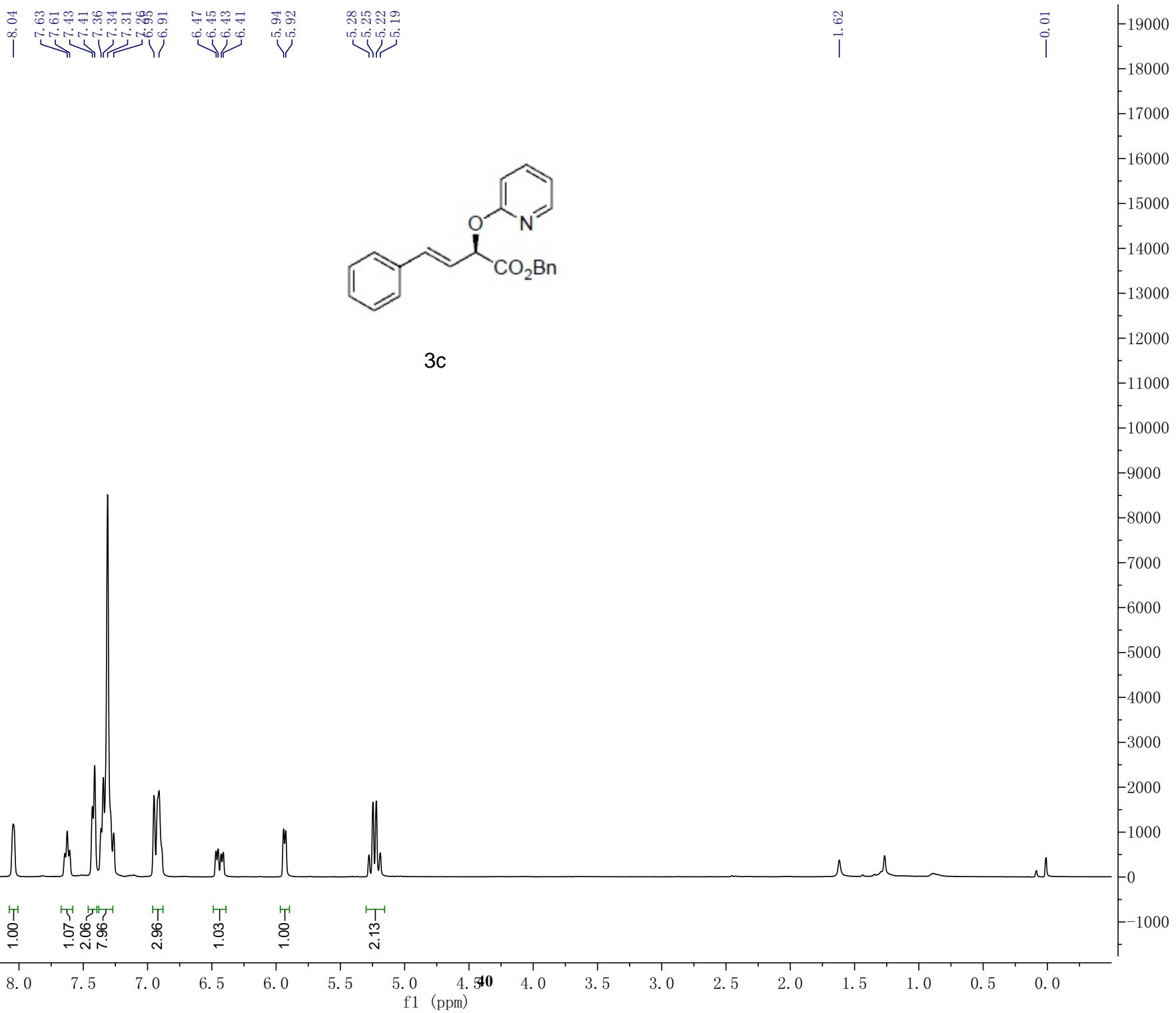


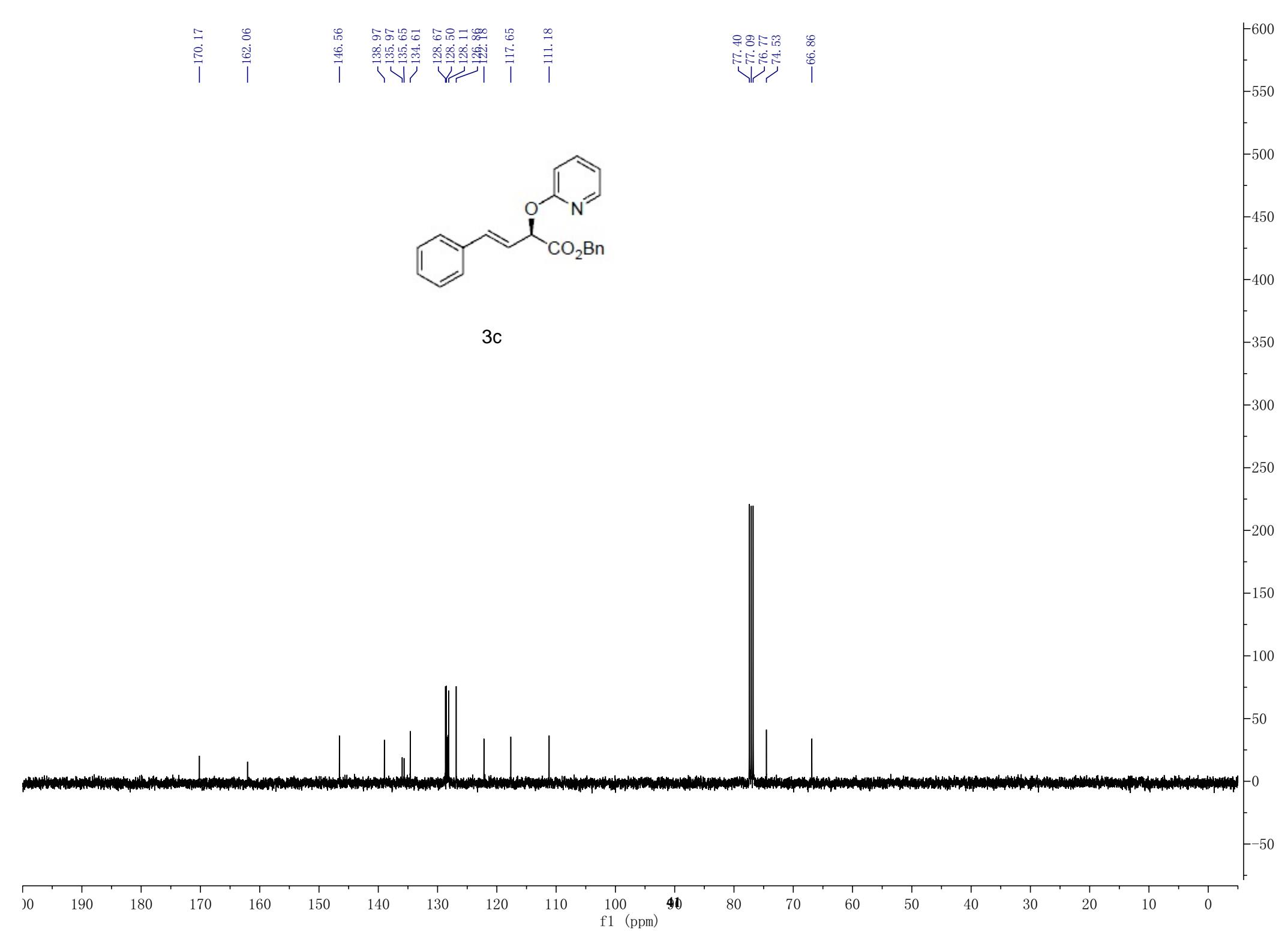




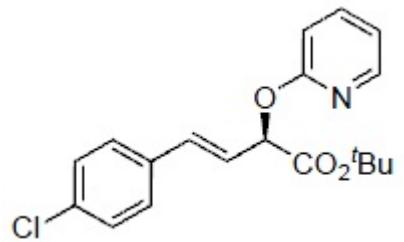




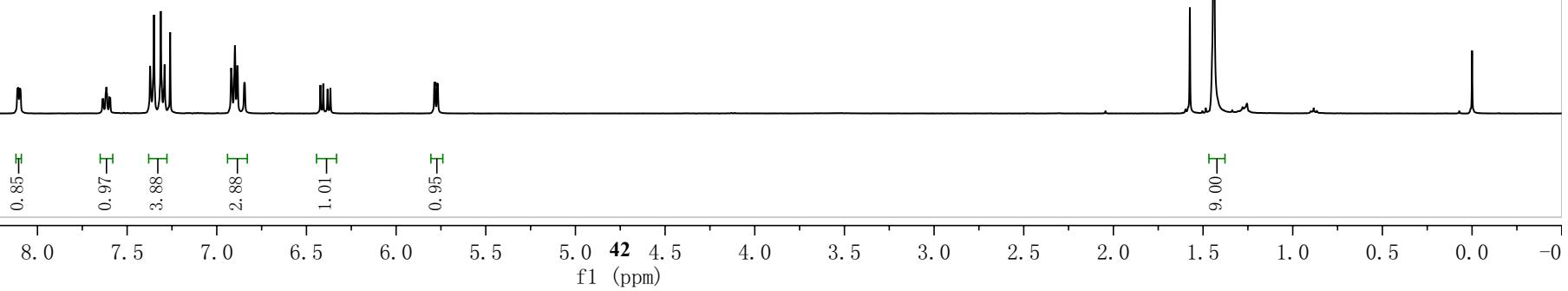


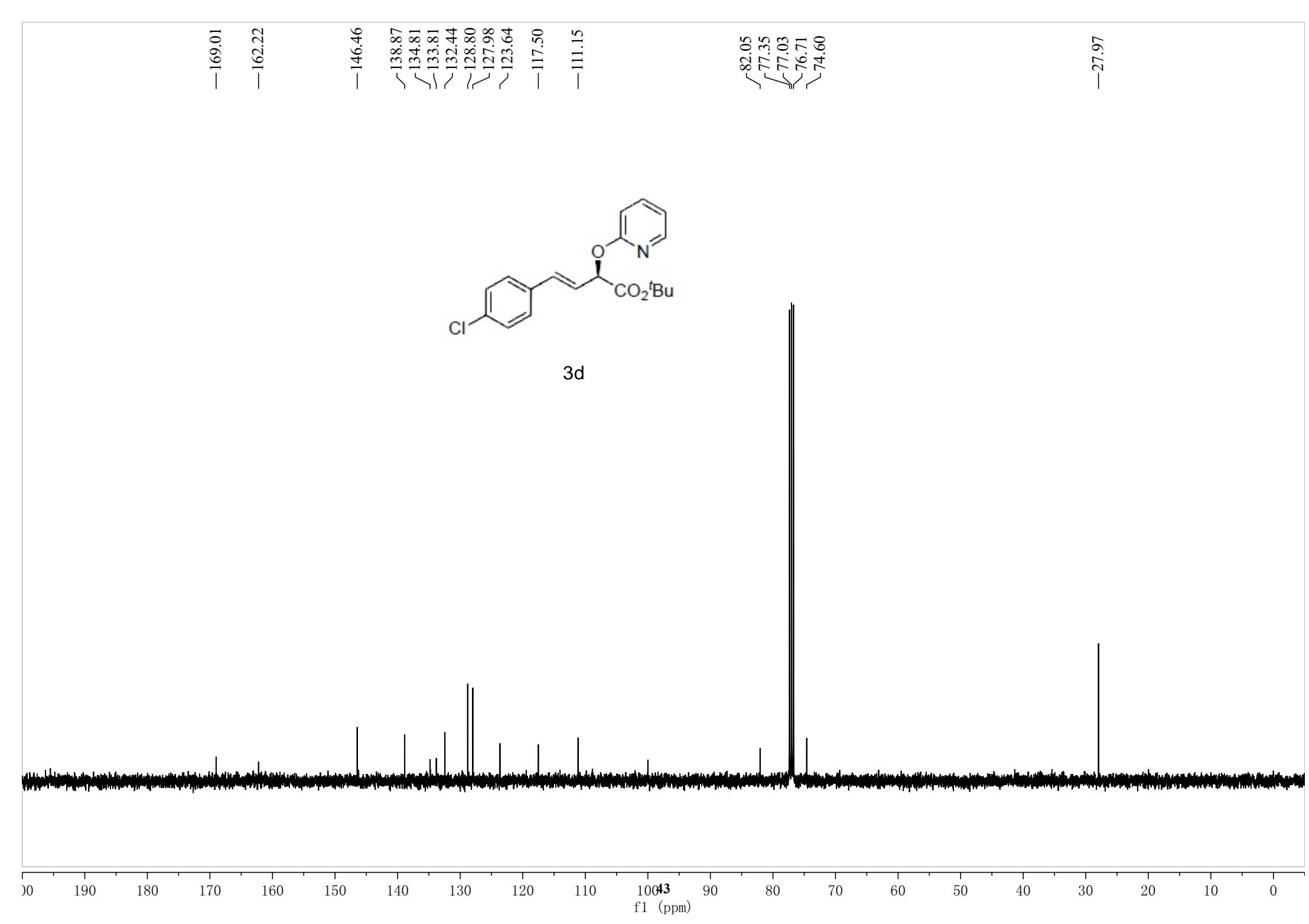


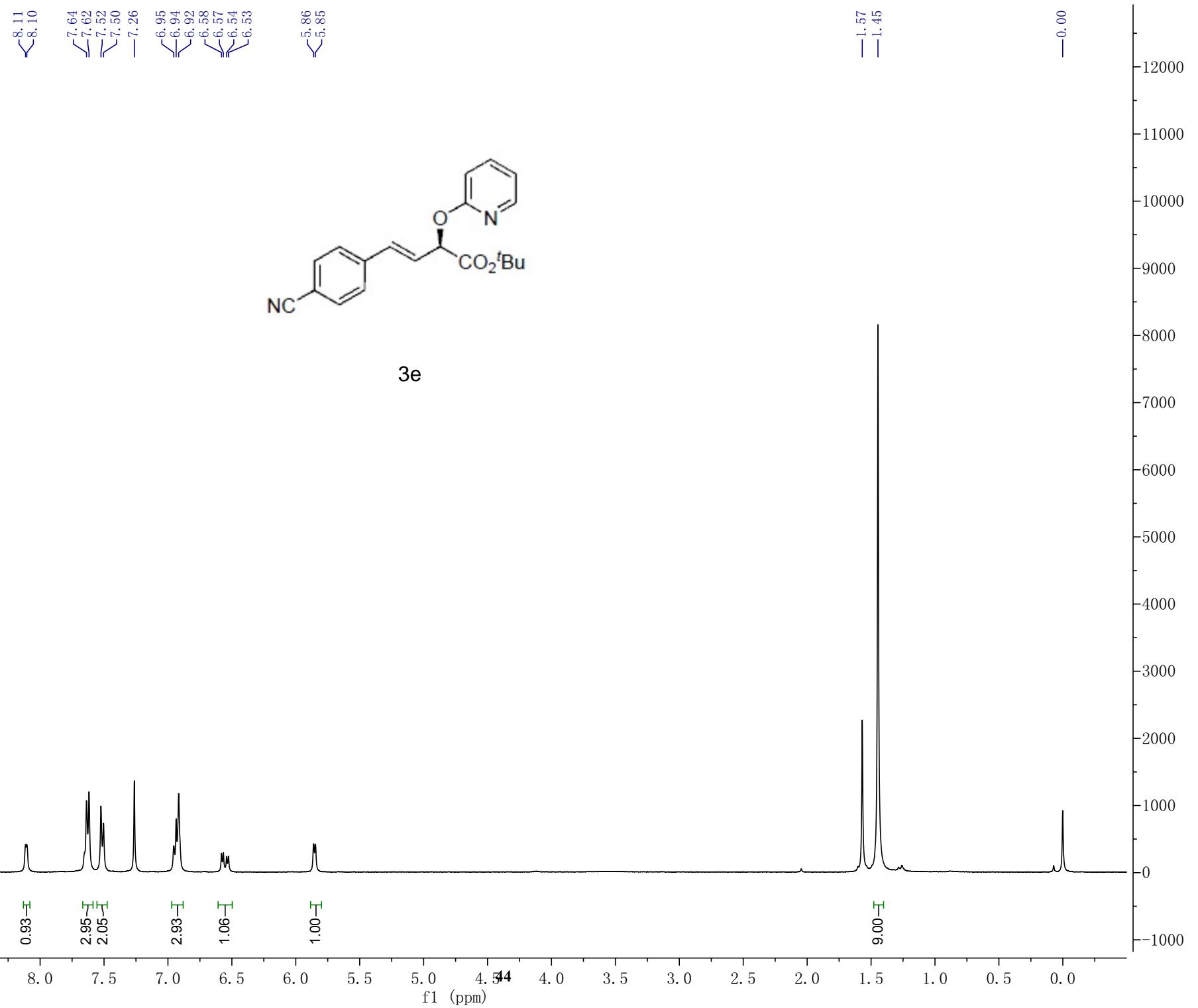
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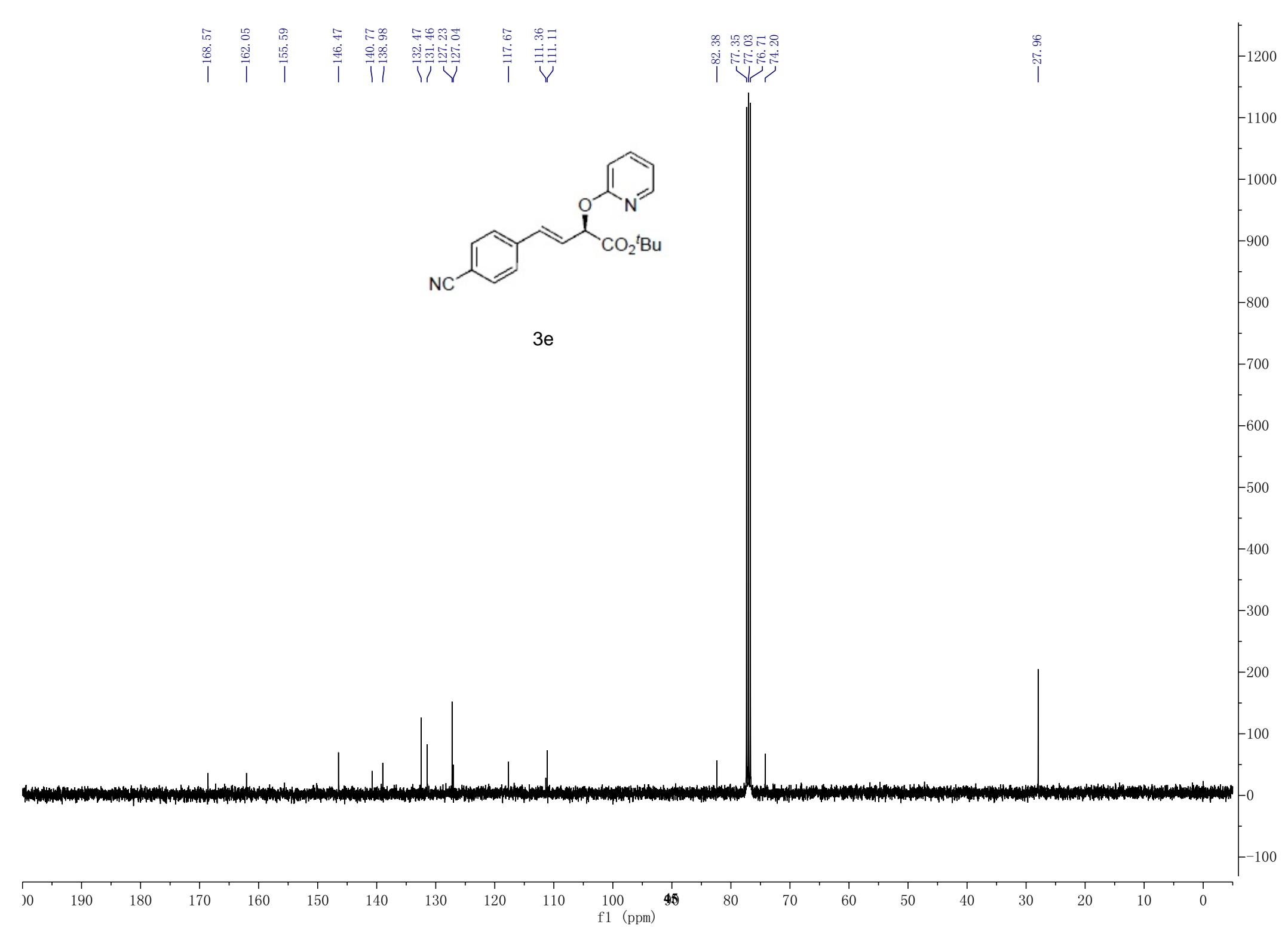


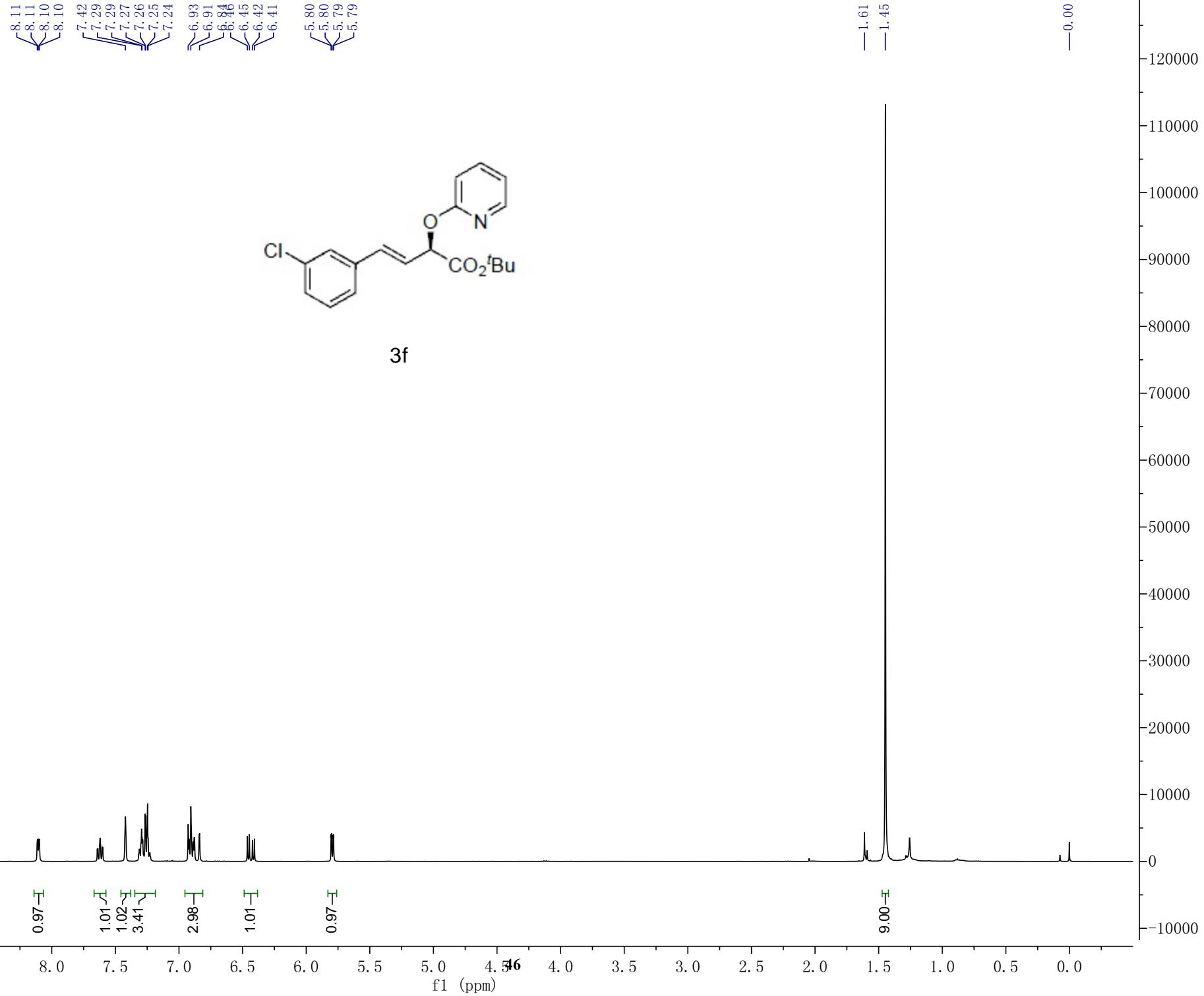
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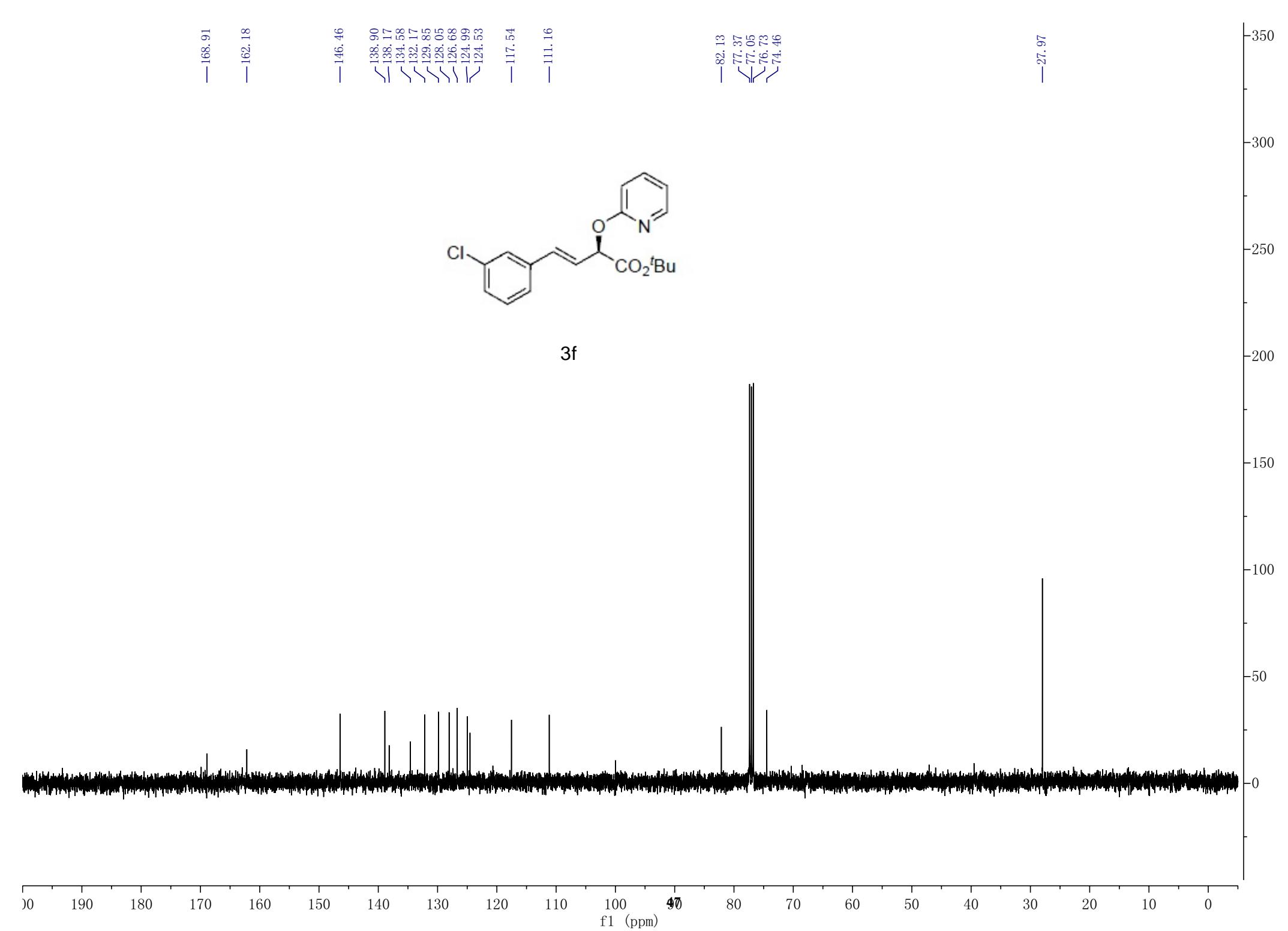


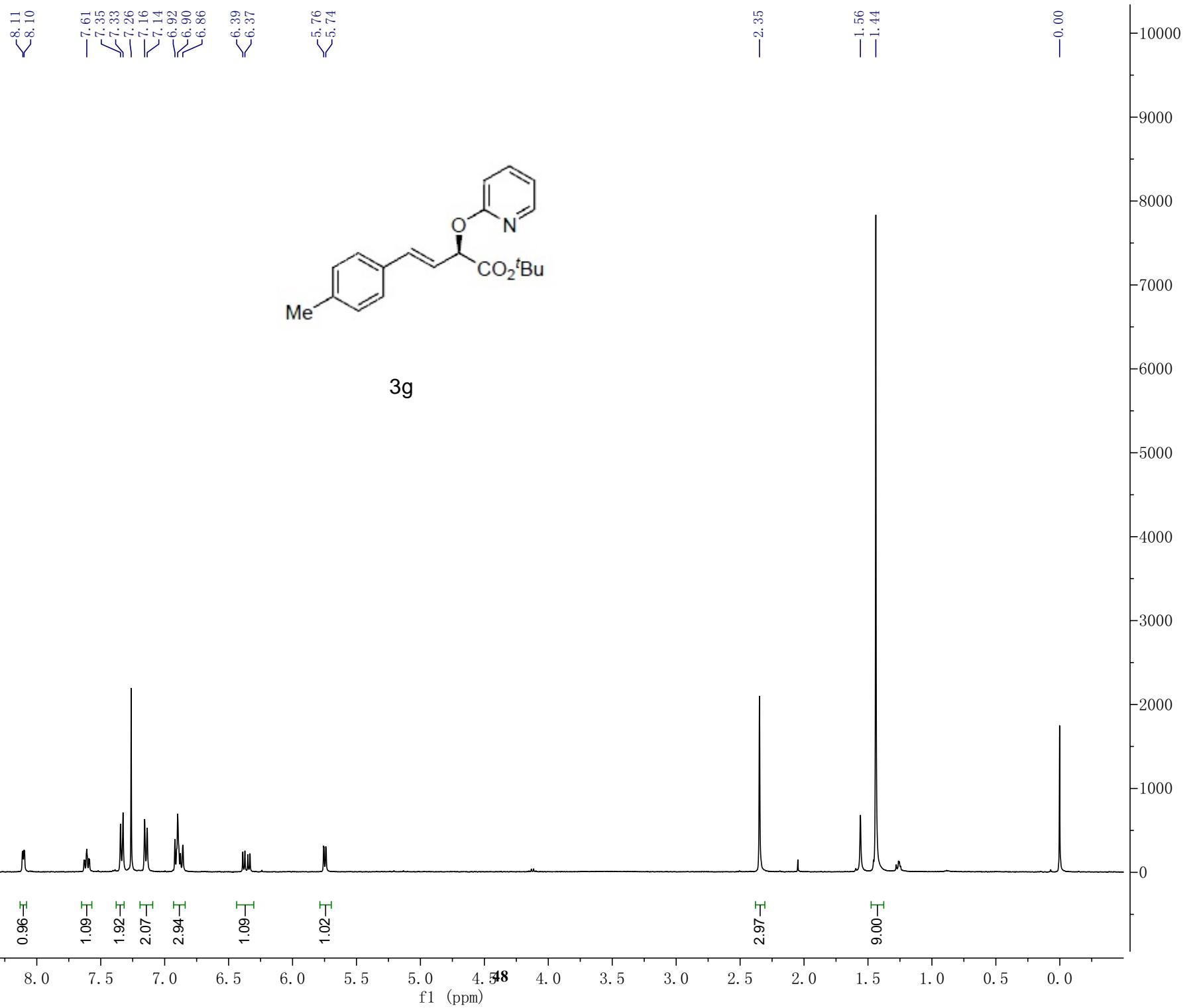


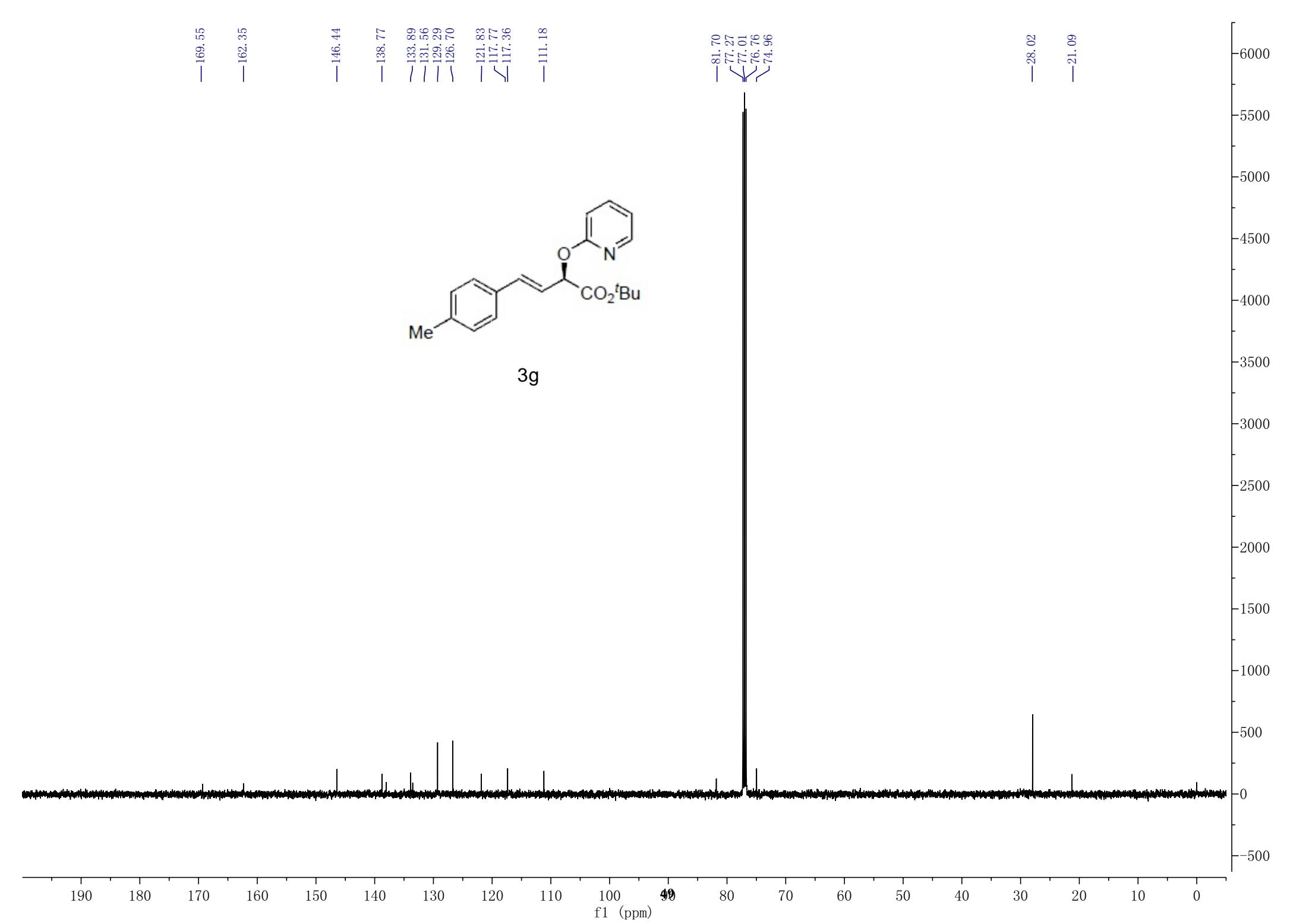


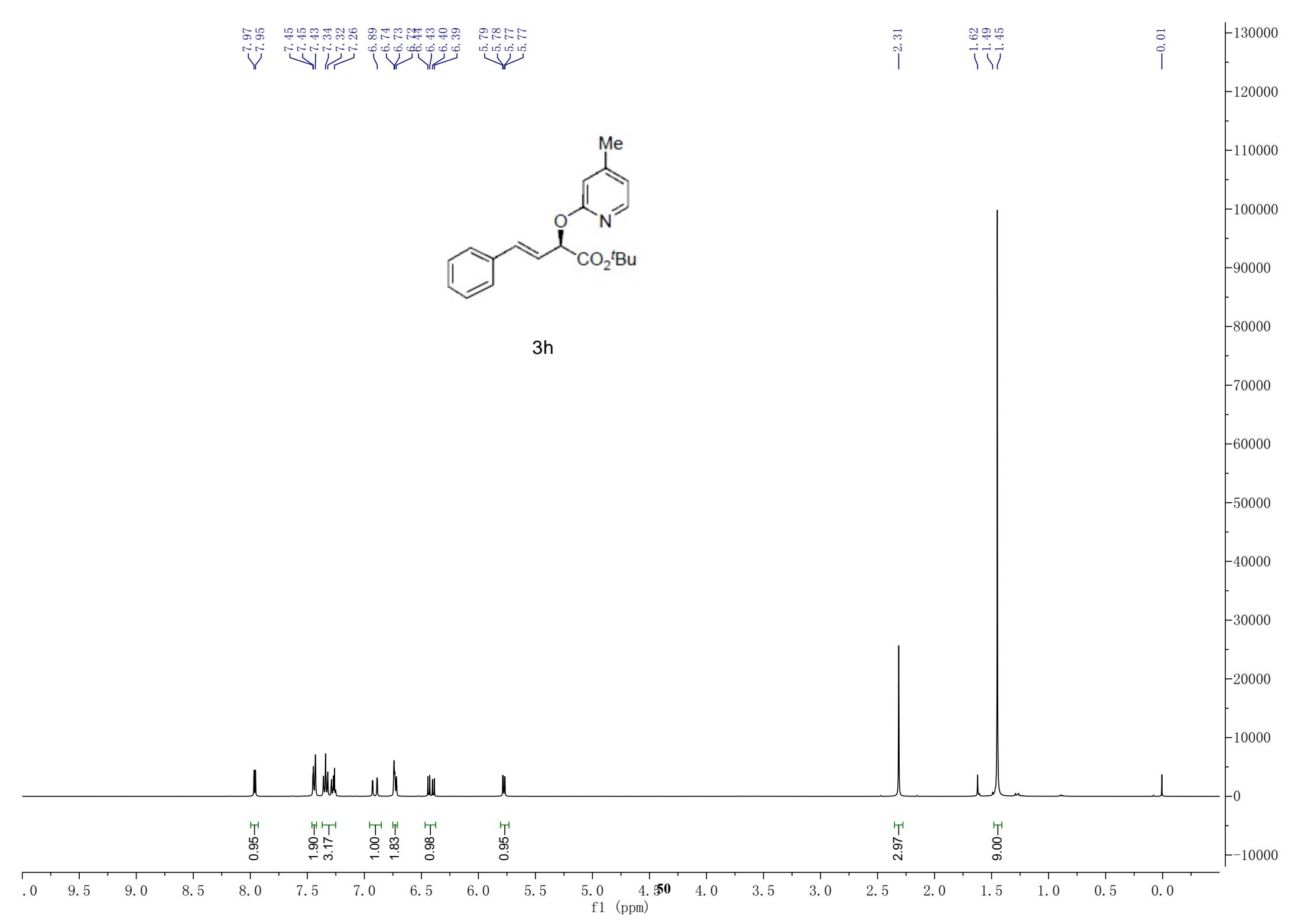


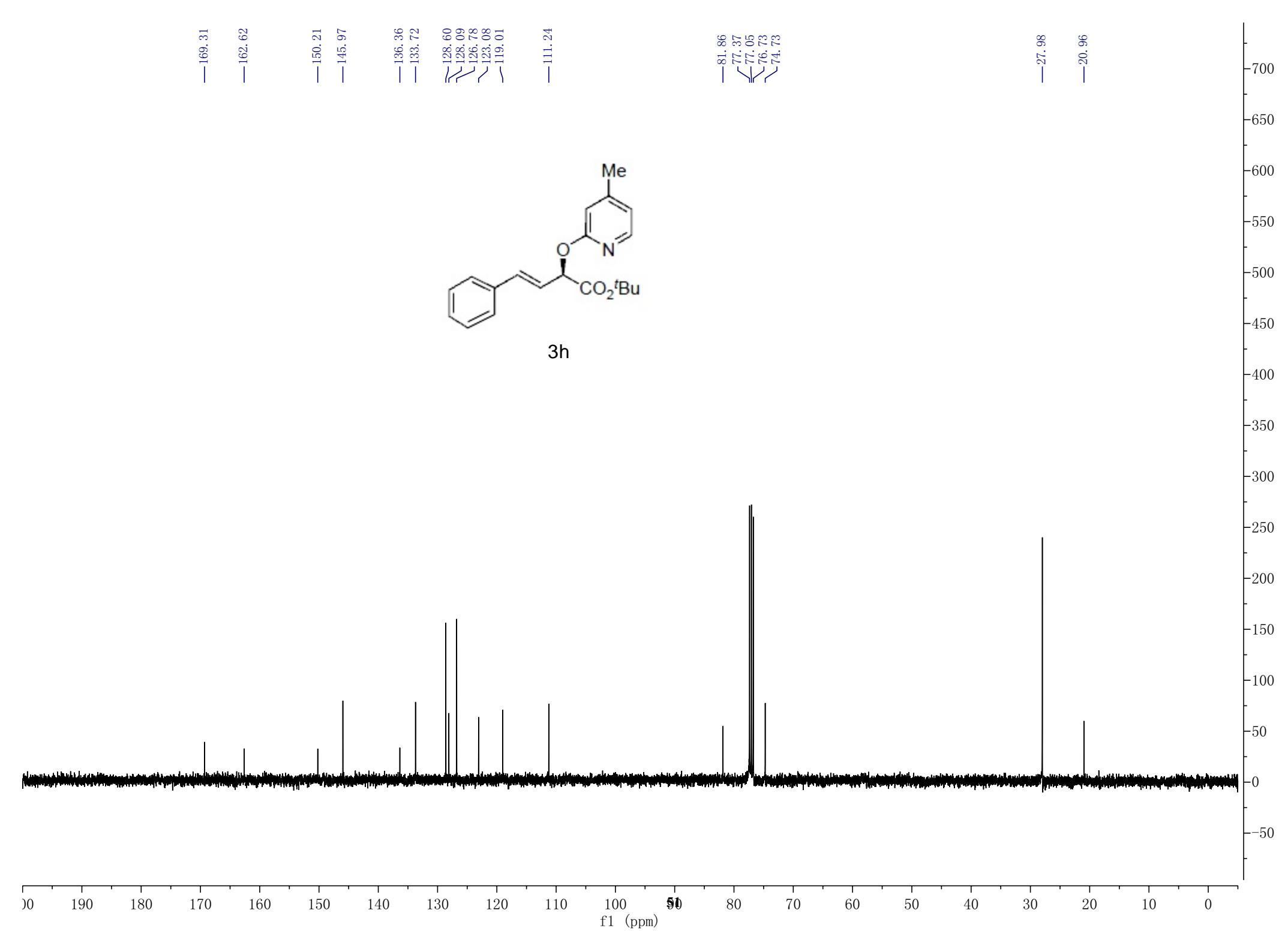




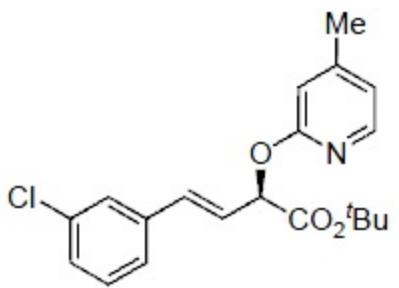




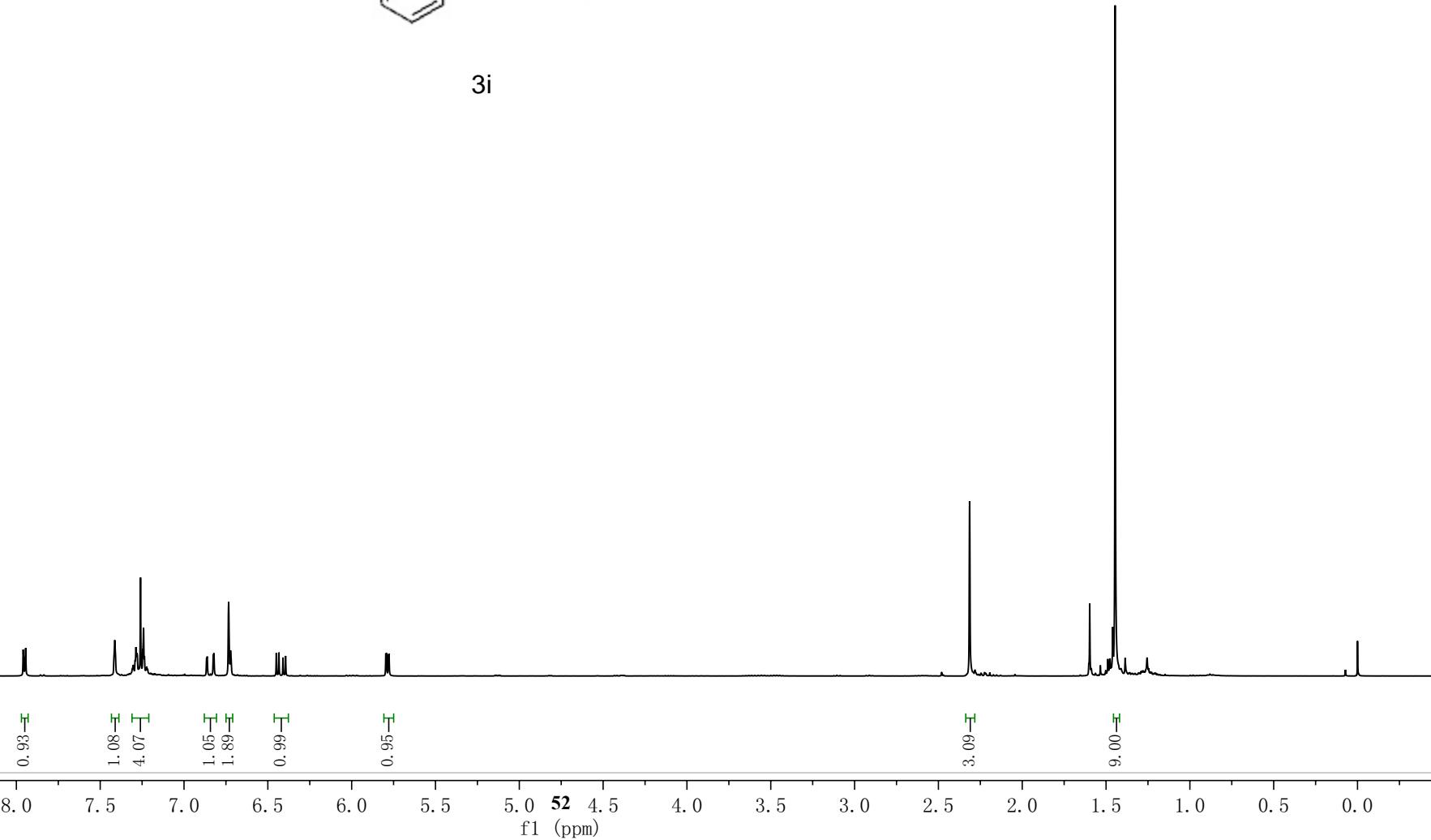




<7.96  
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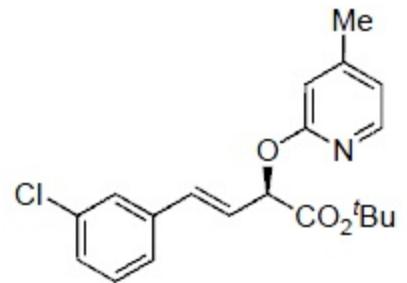
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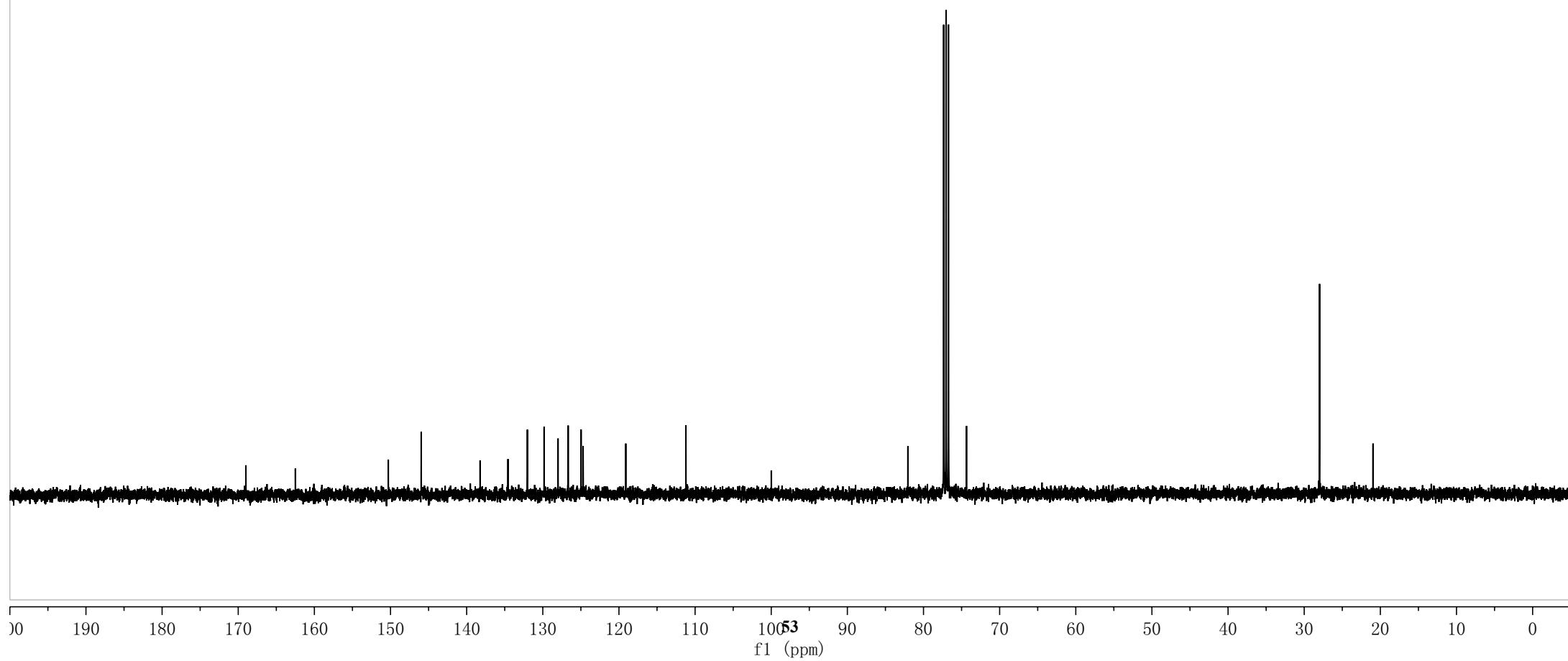
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—111.20

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77.04  
76.72  
74.35

—27.98  
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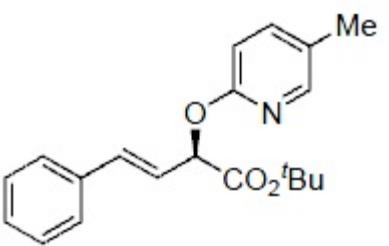


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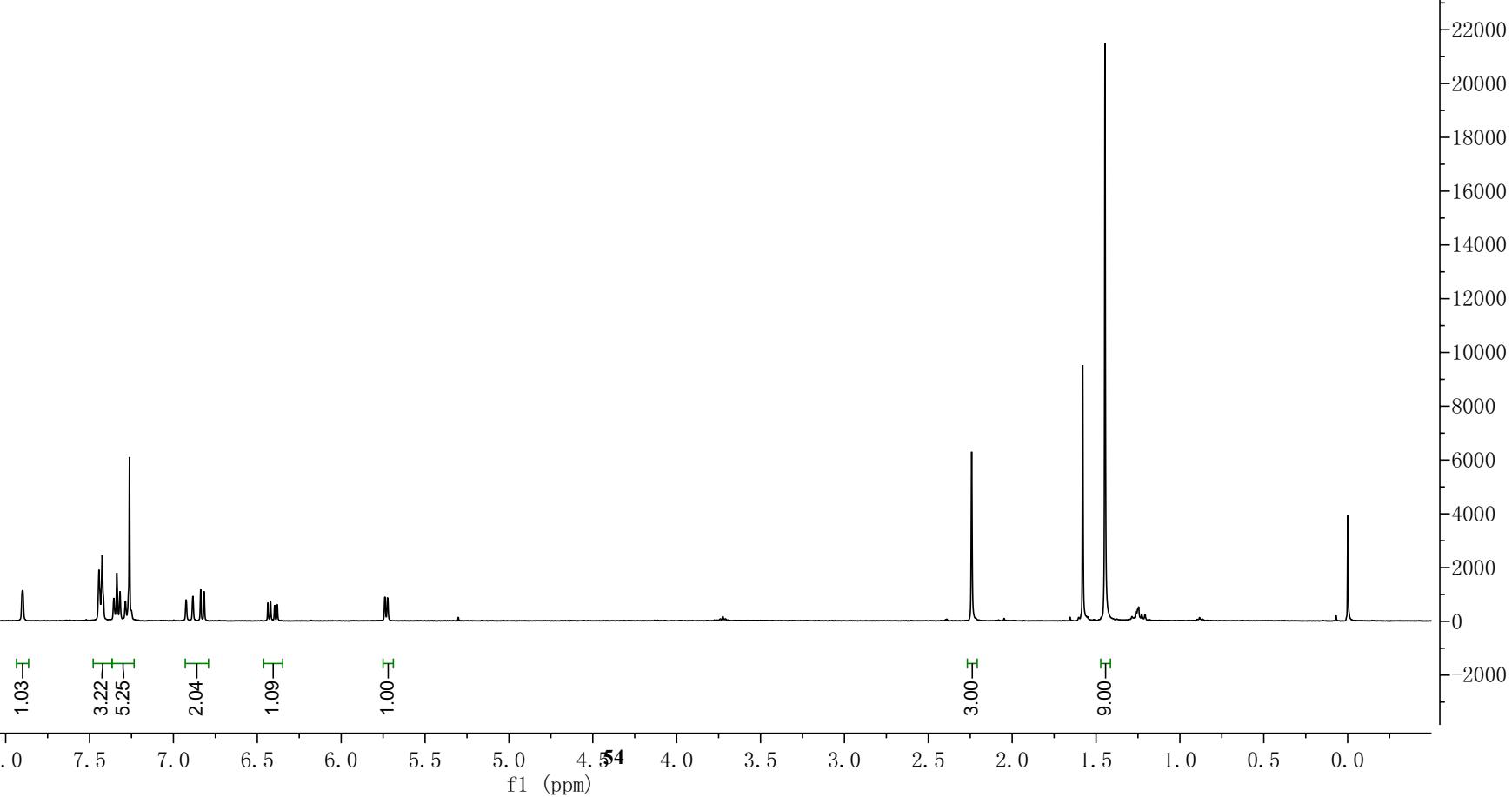


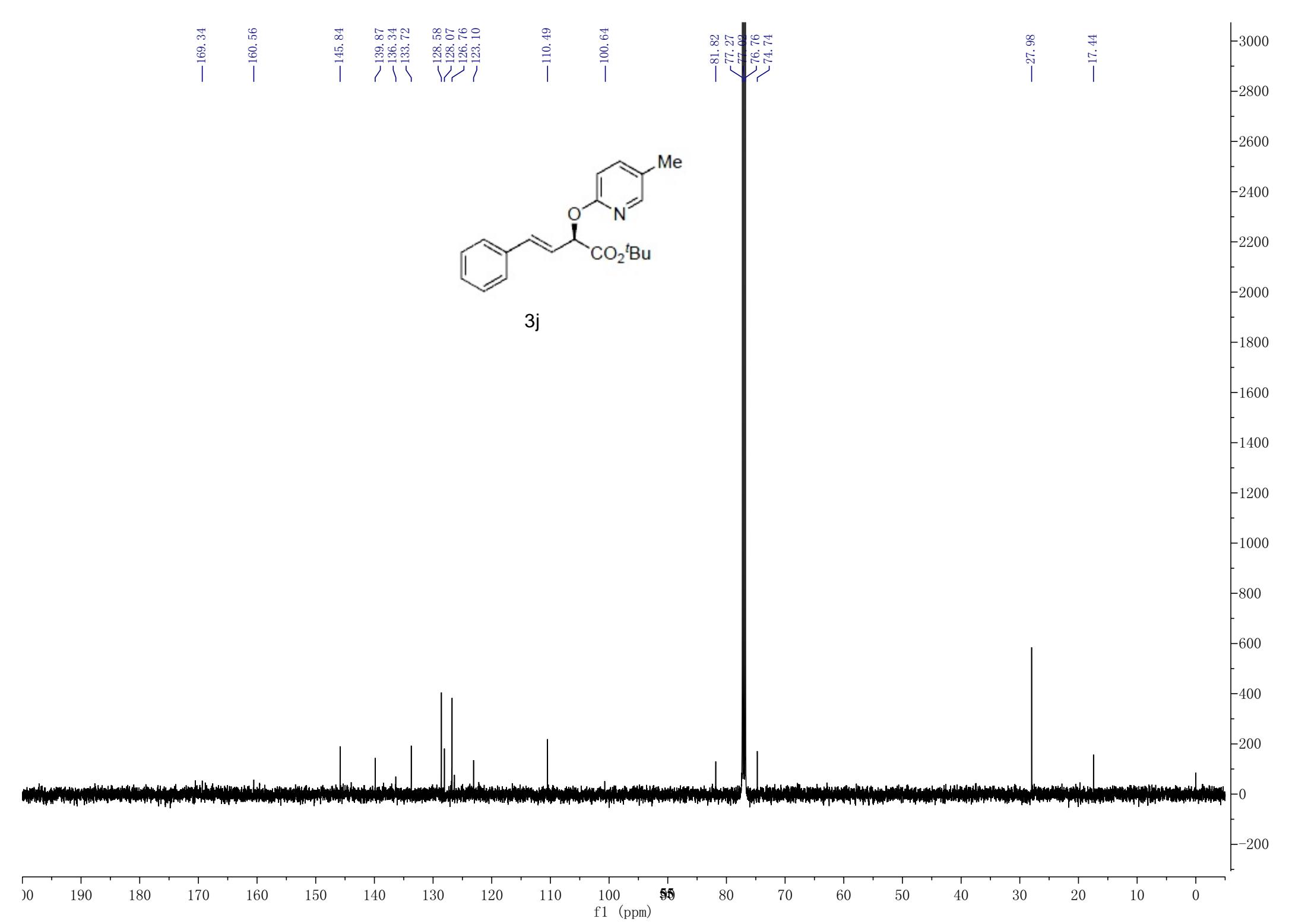
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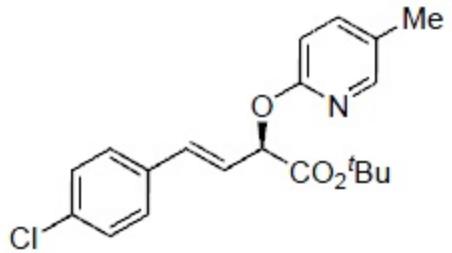


3j

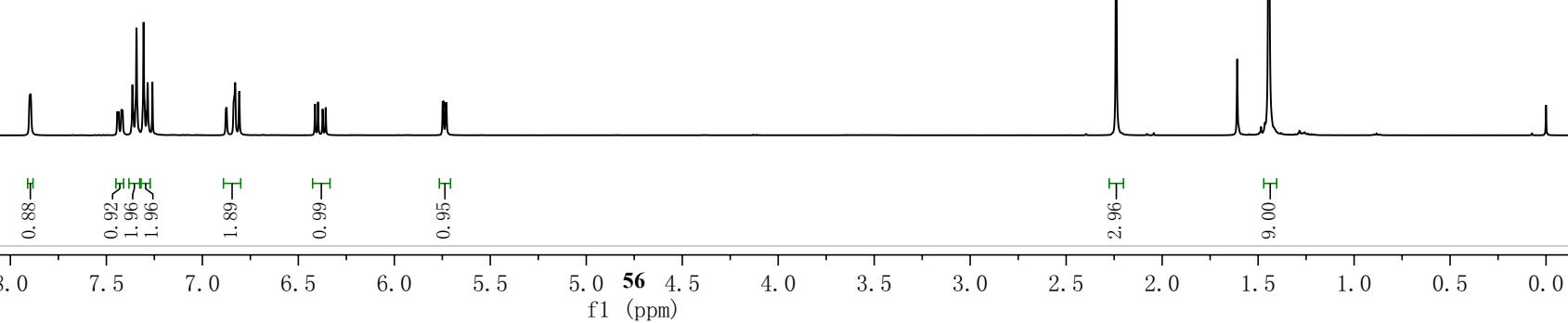


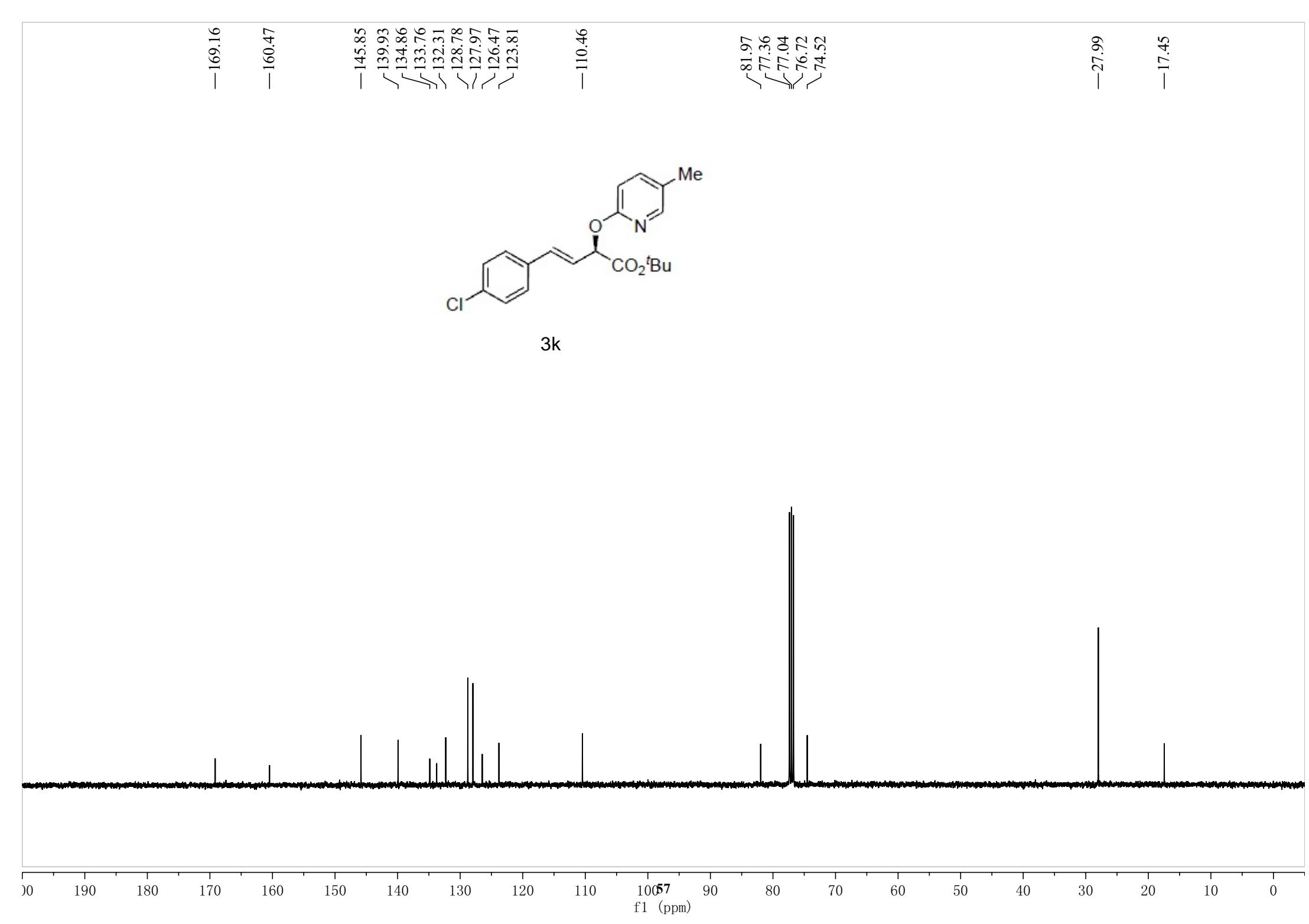


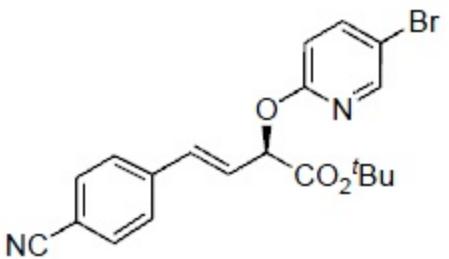
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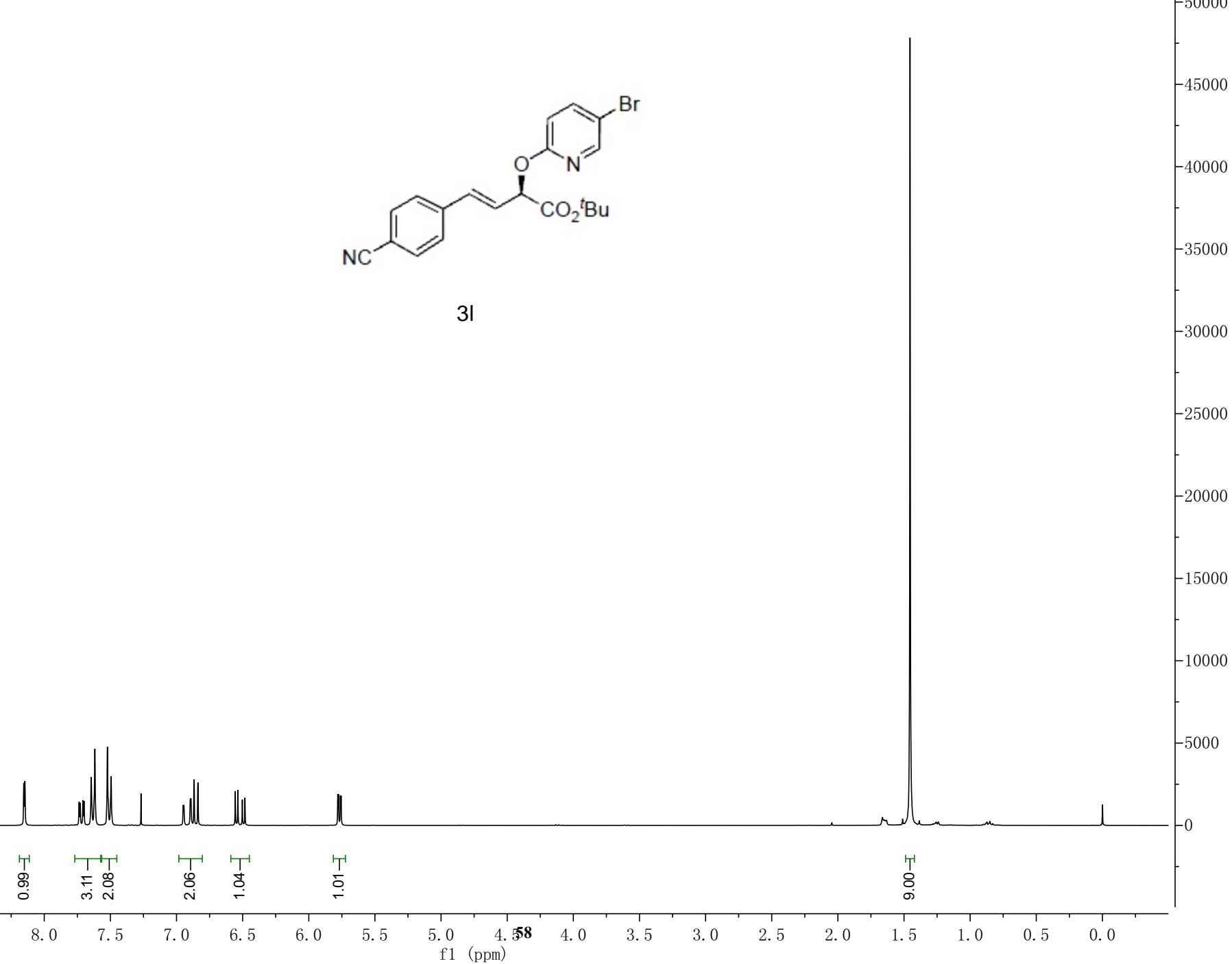
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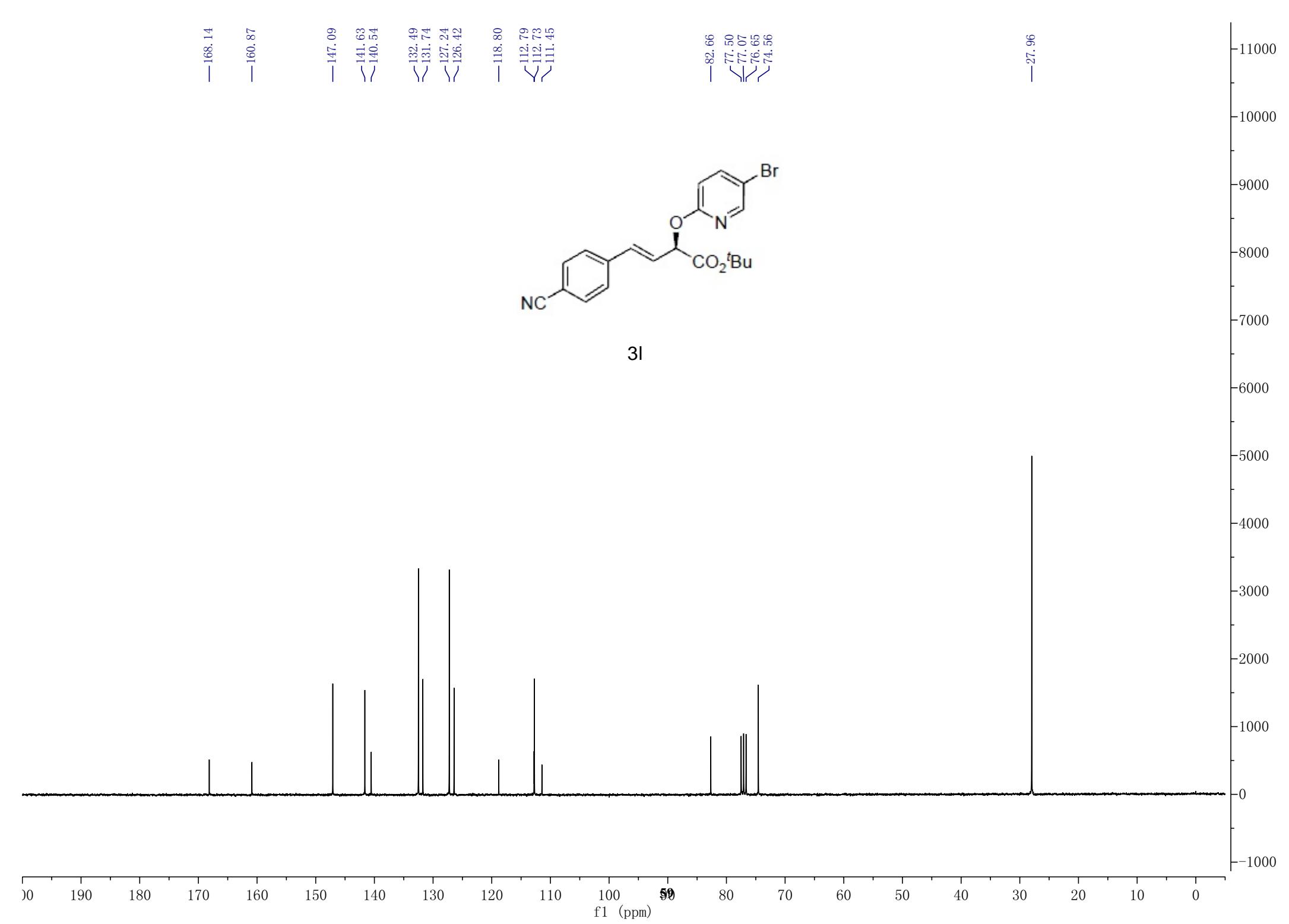




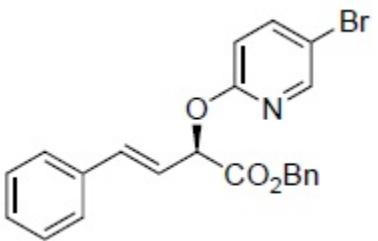


**3l**

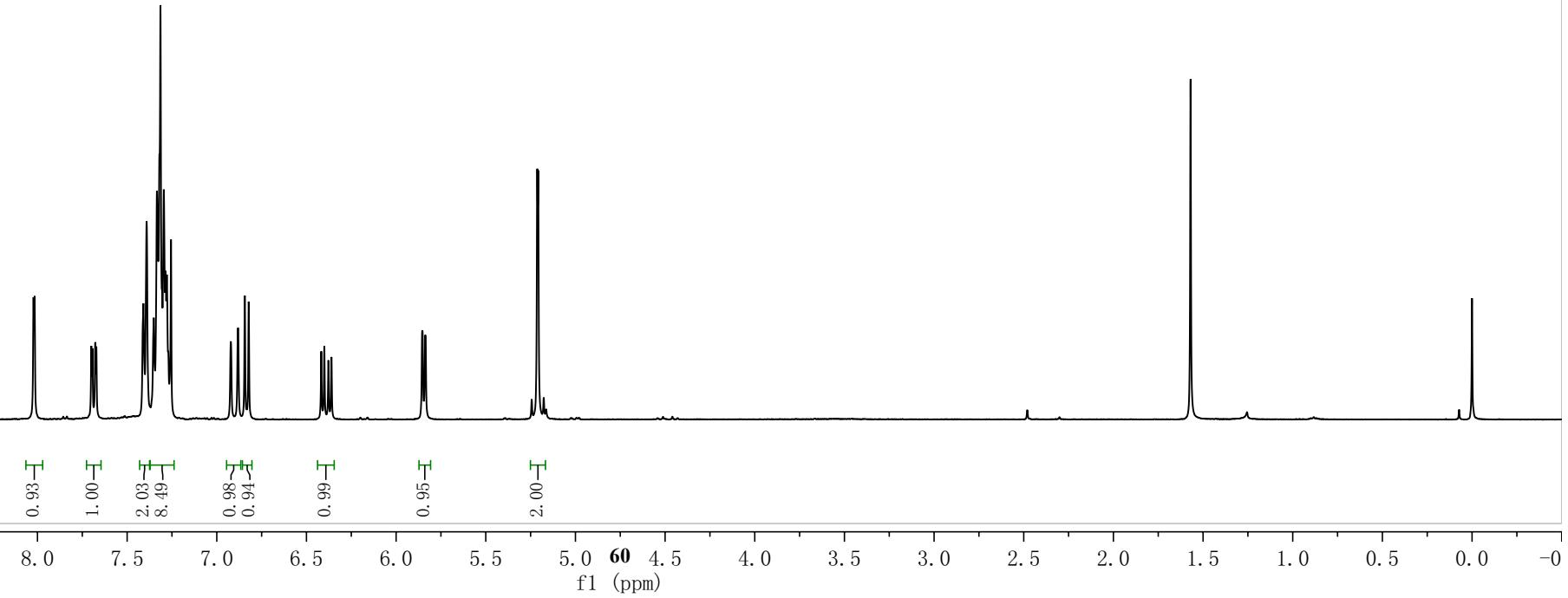


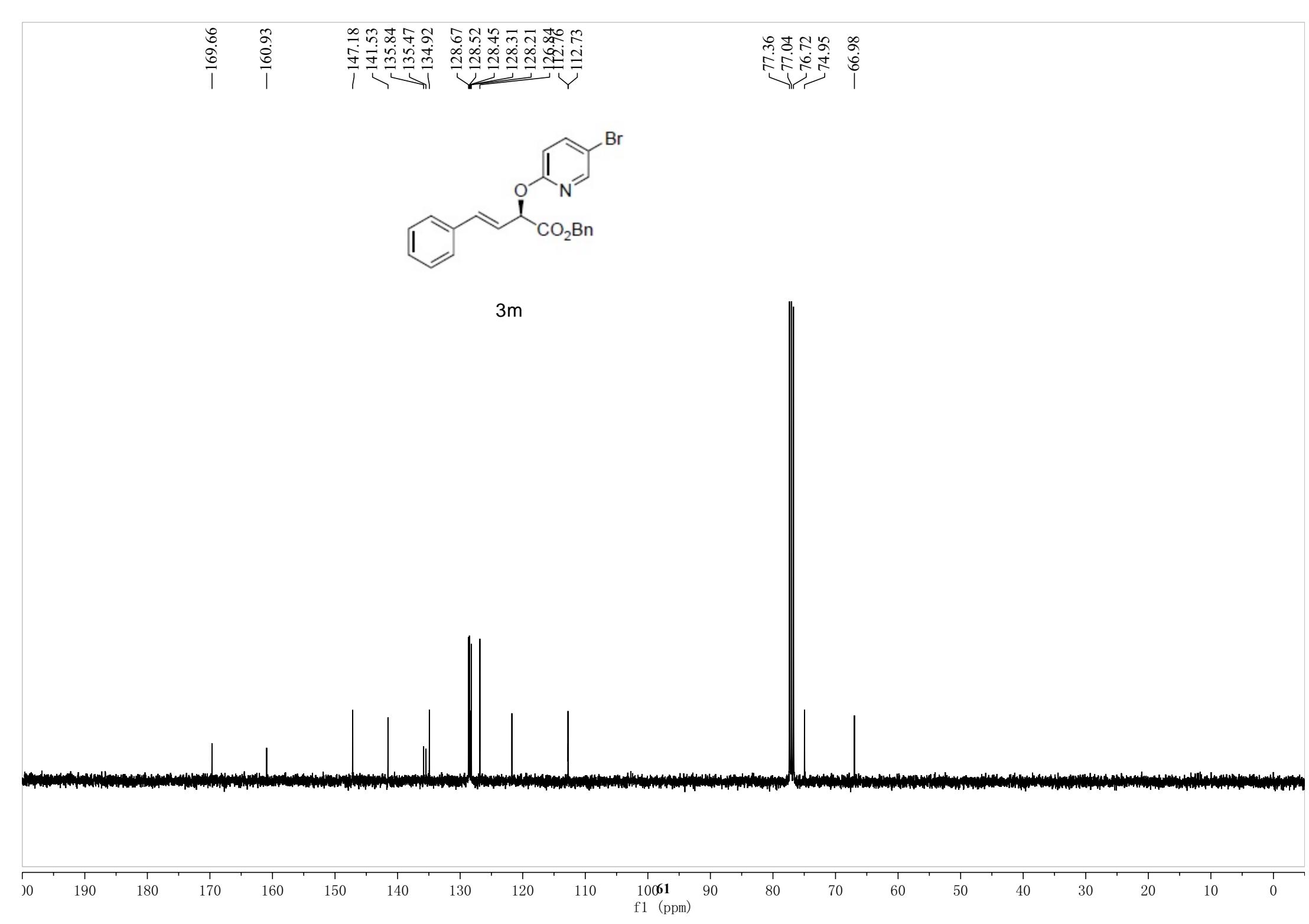


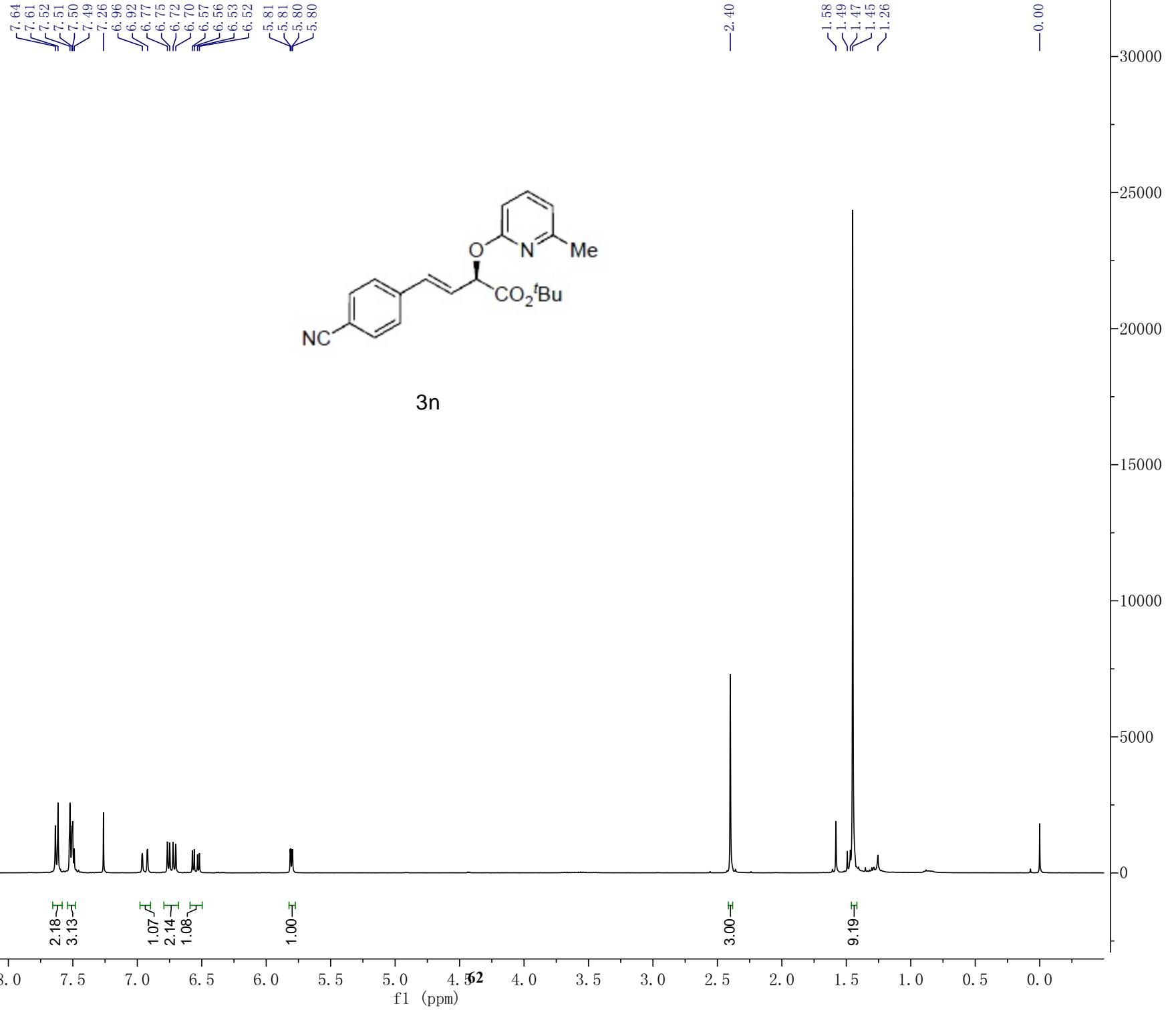
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—0.00

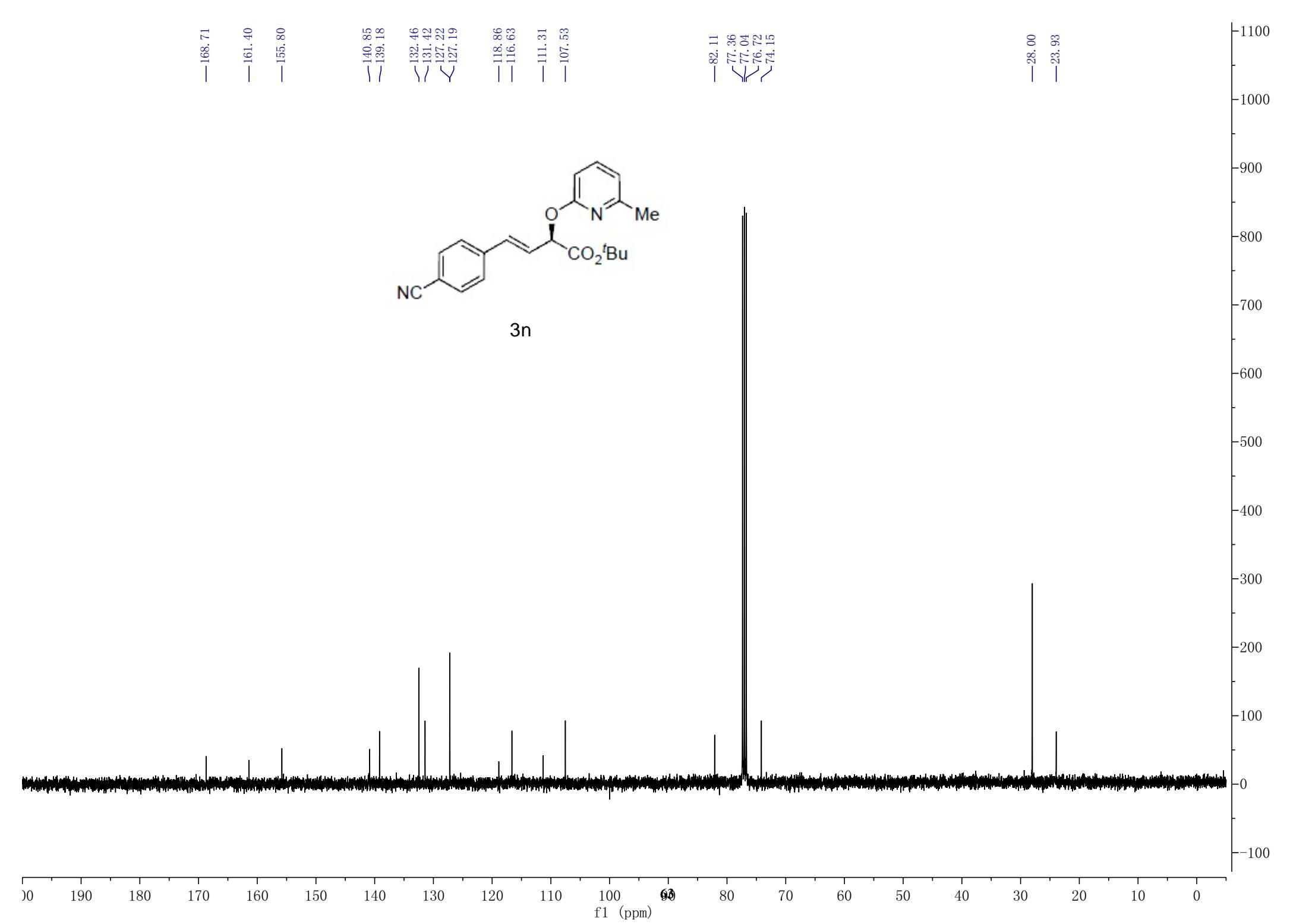


3m





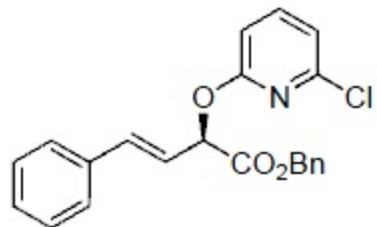




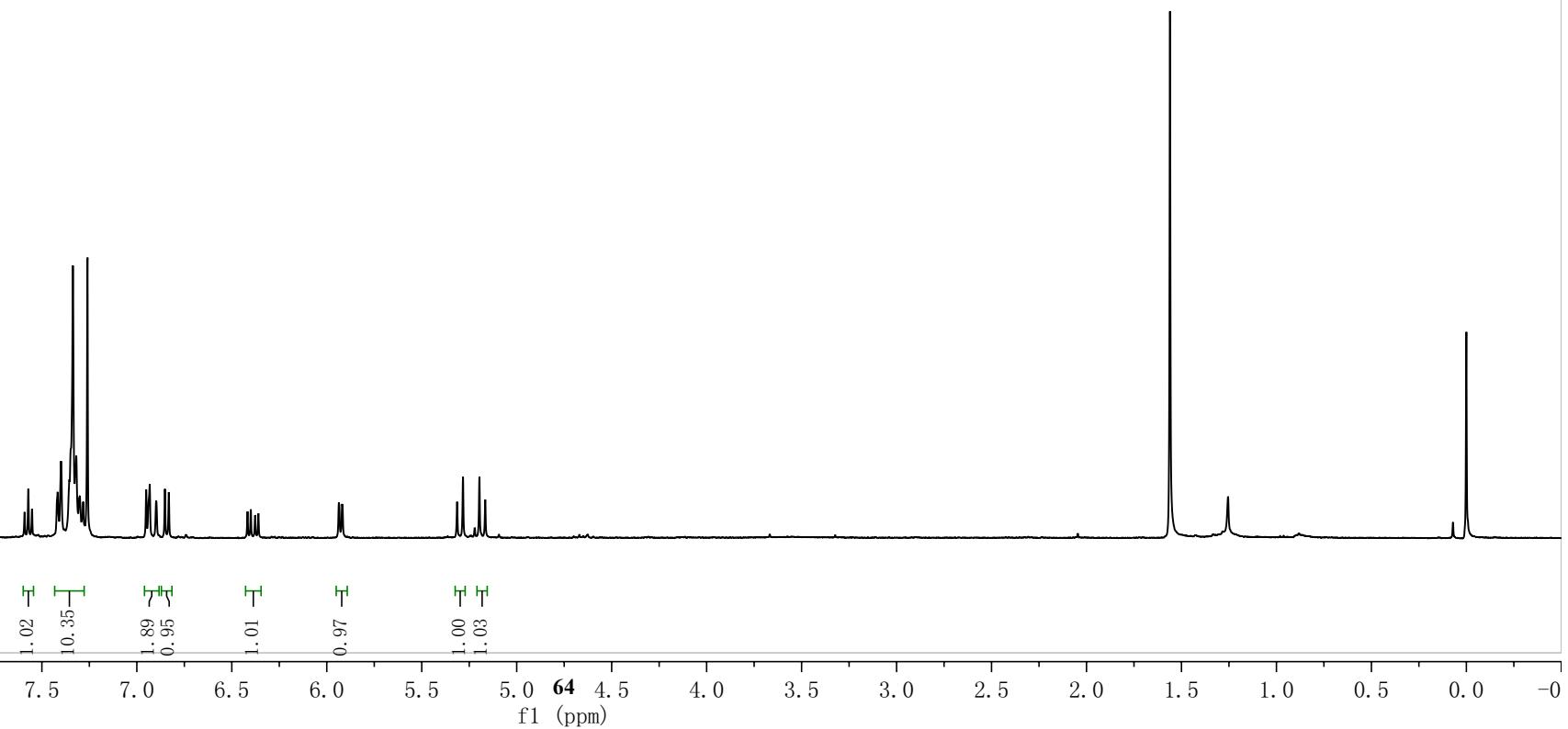
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6.93  
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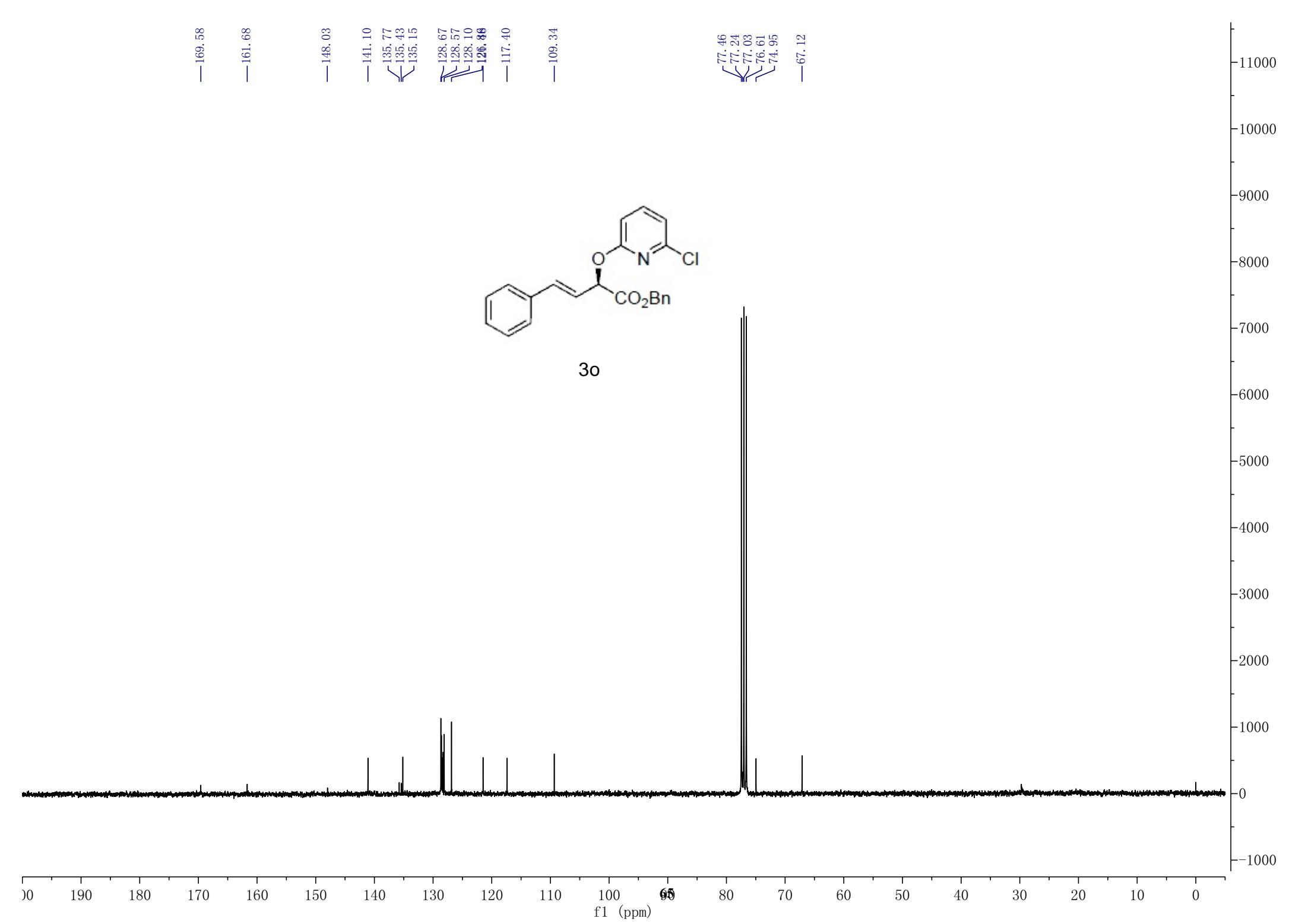
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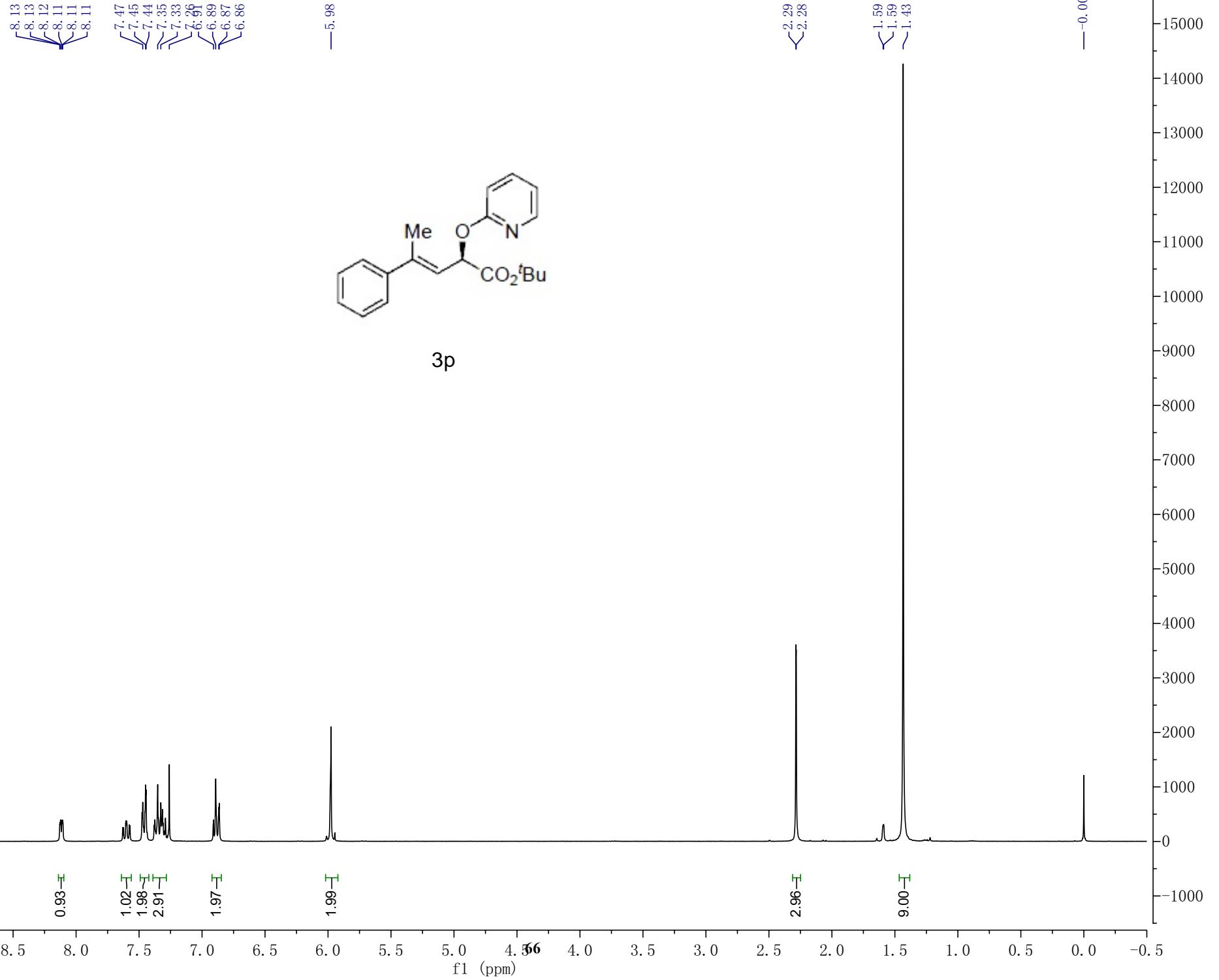
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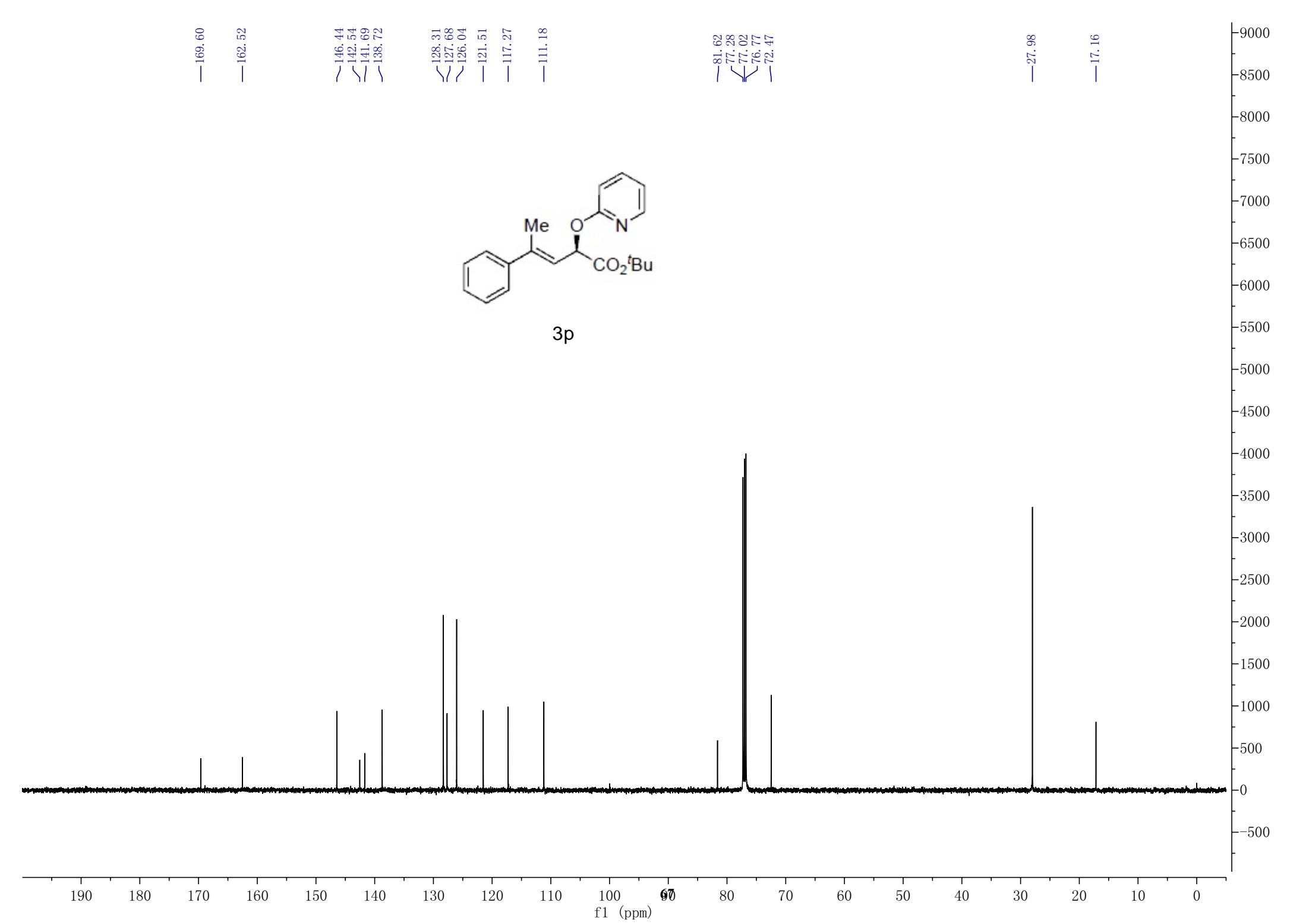


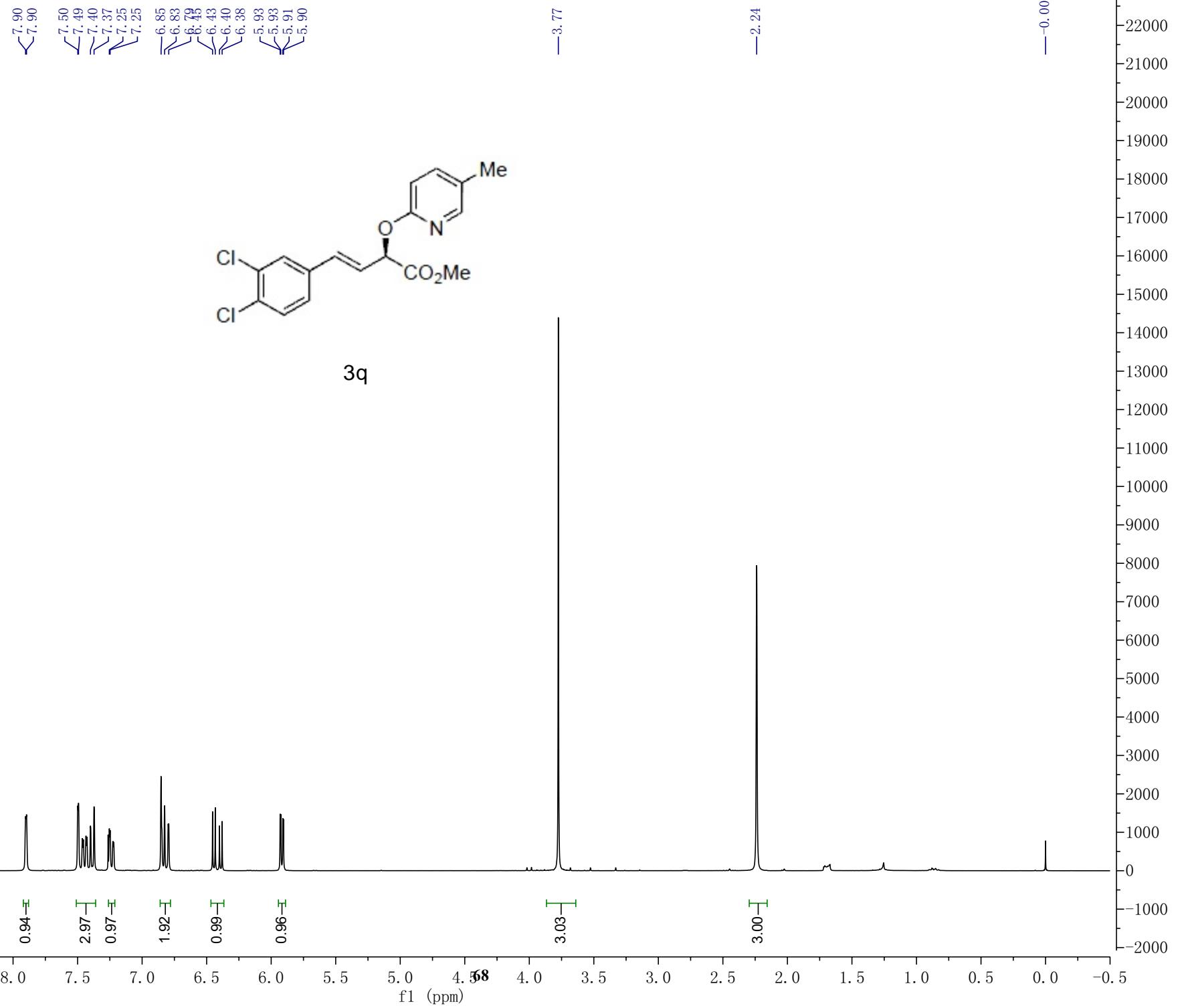
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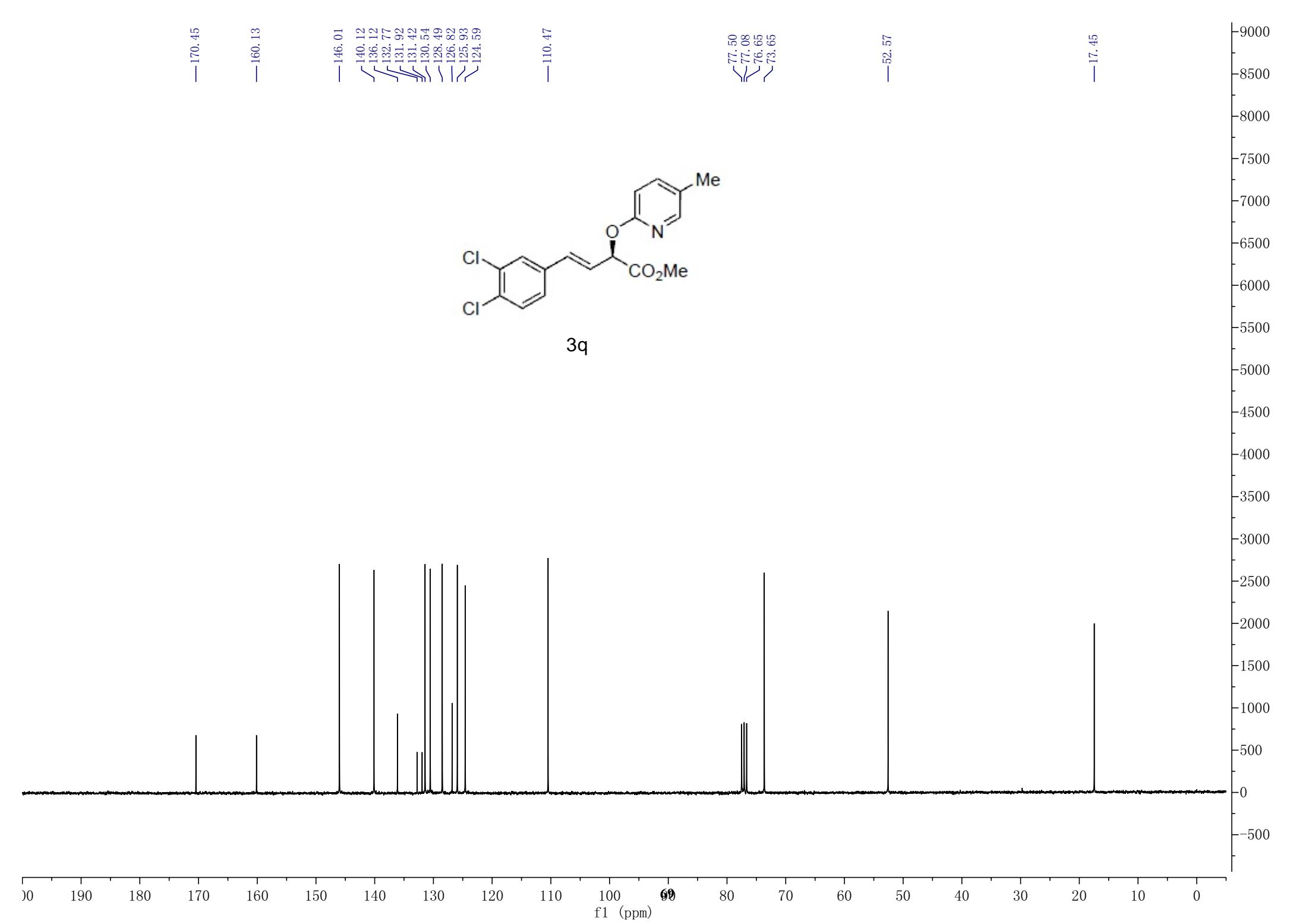


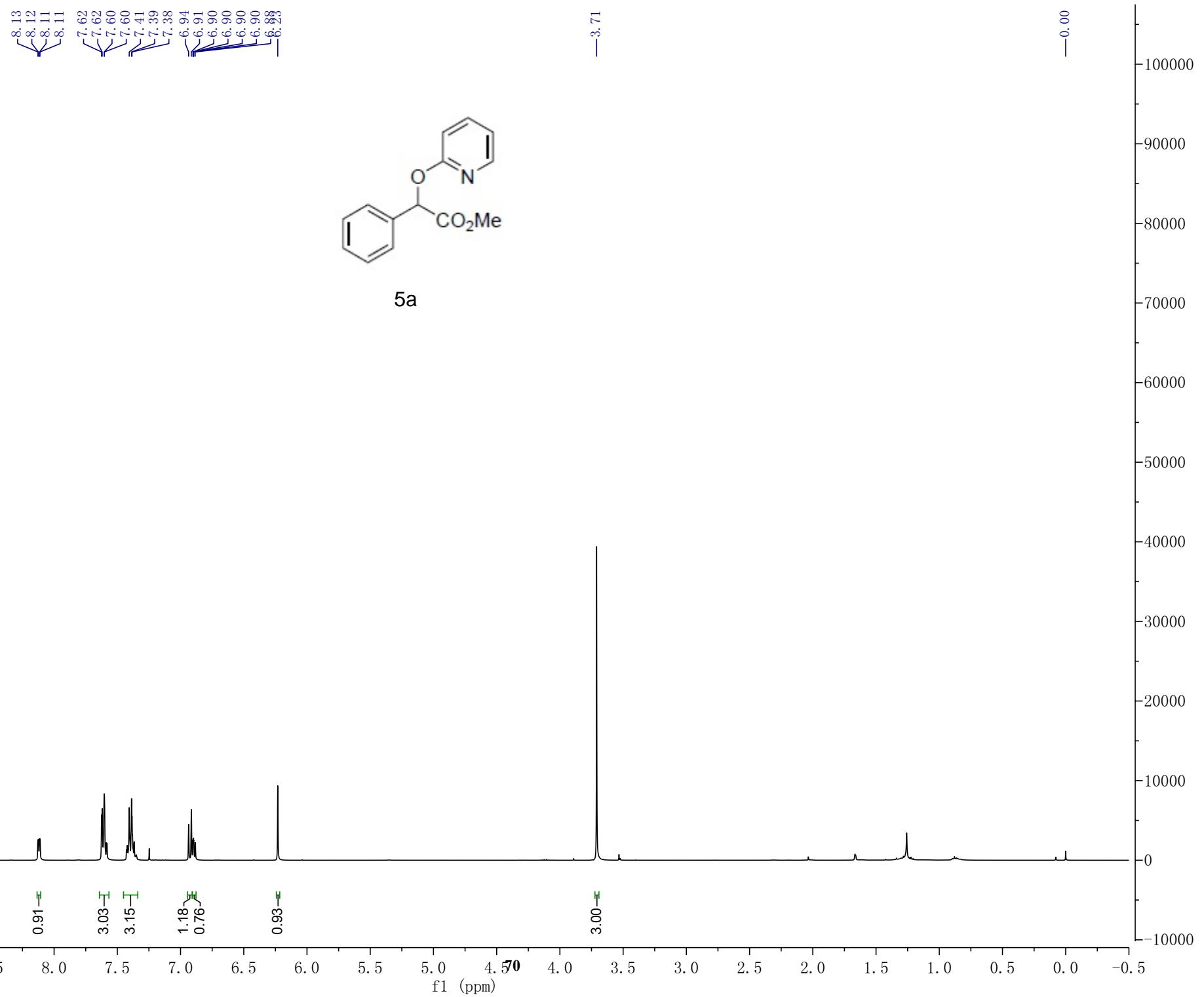


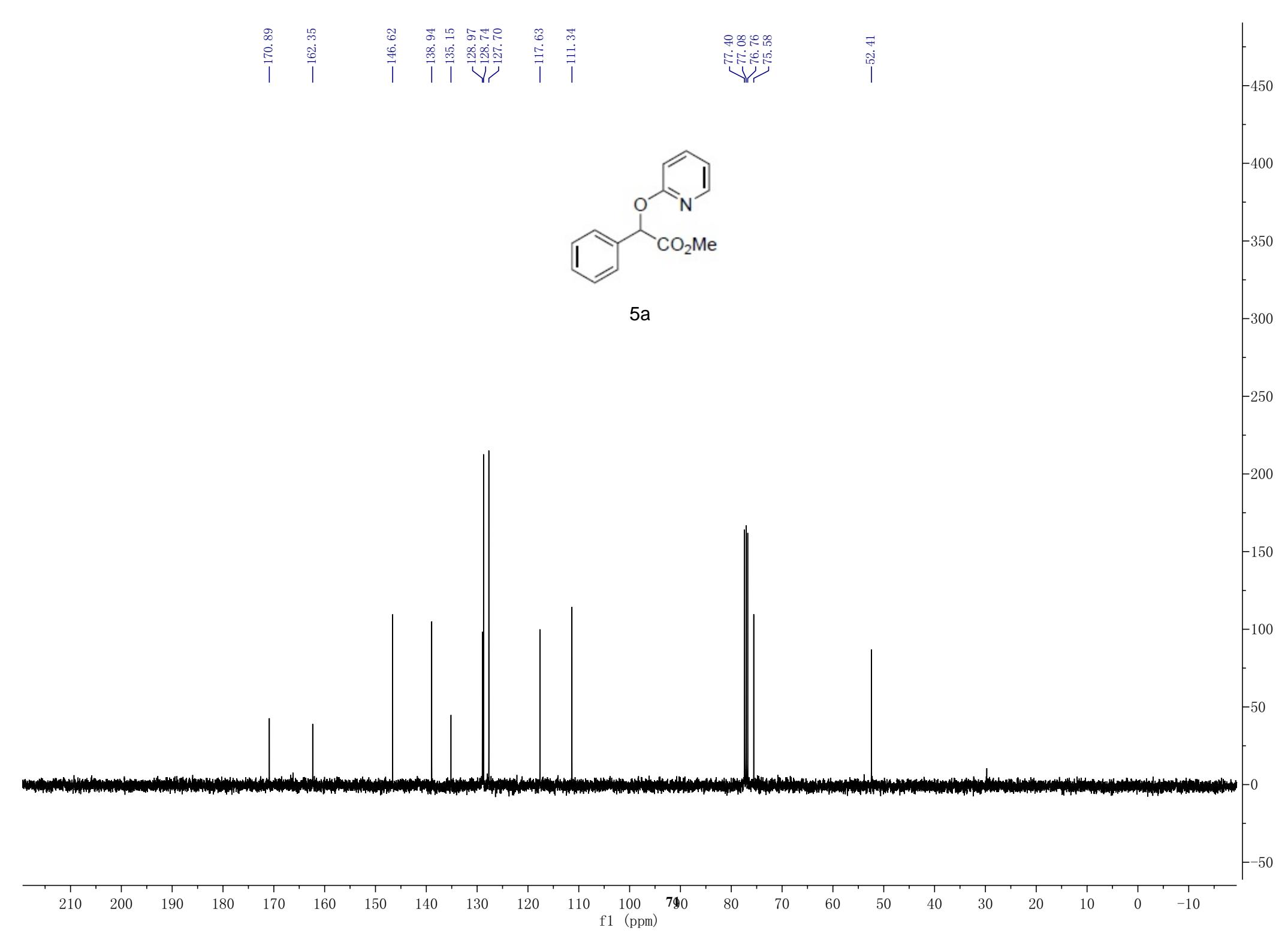


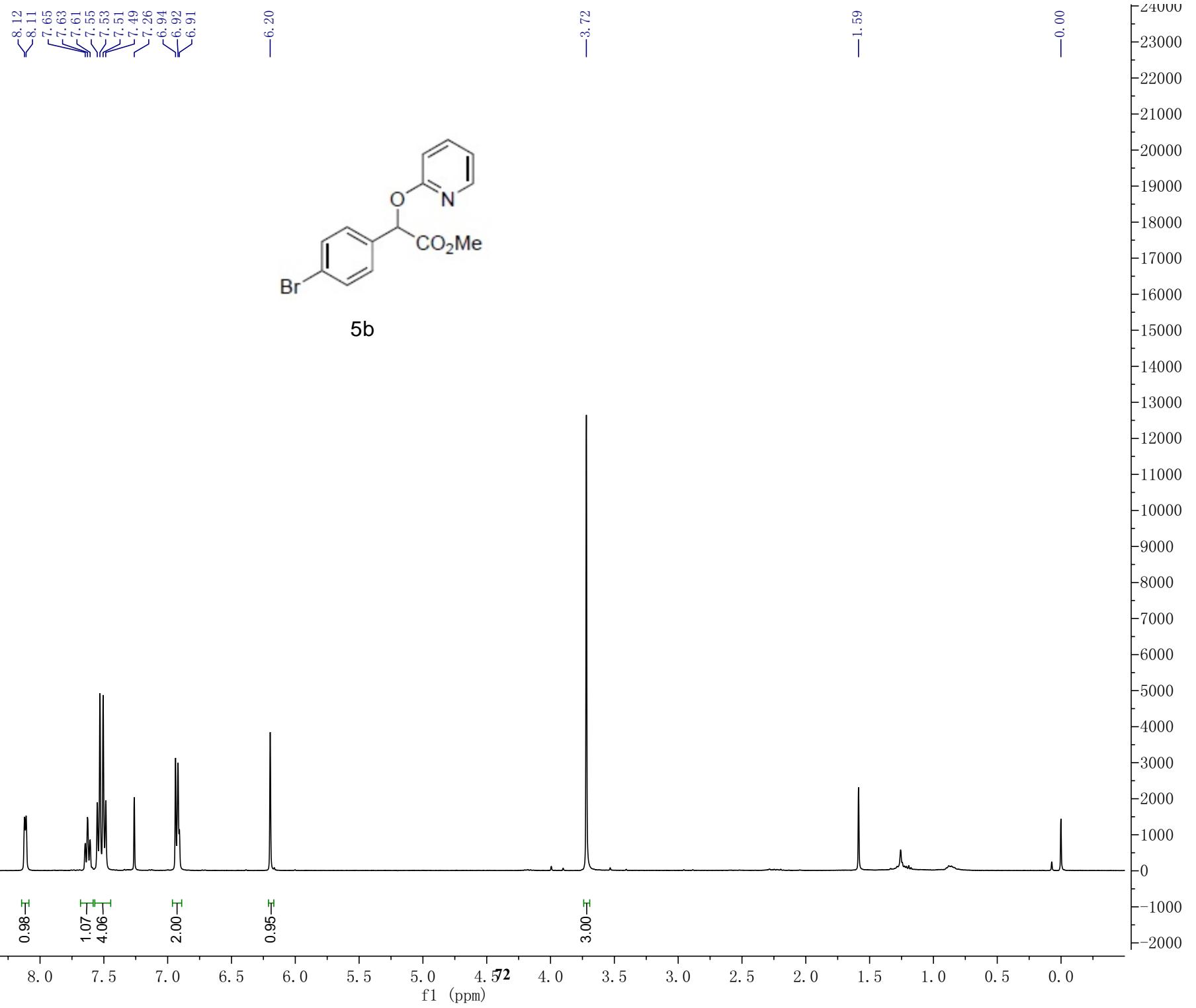


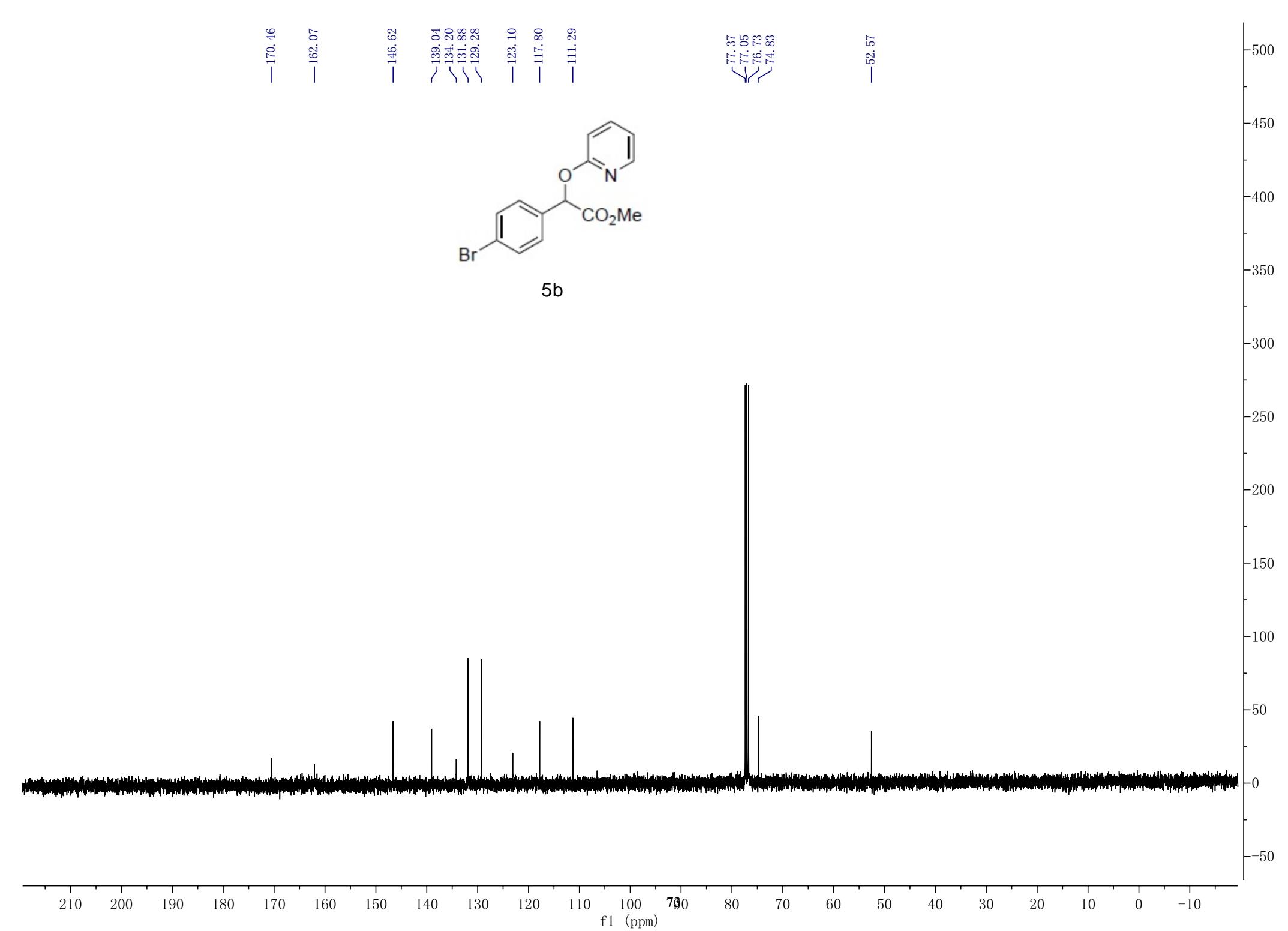


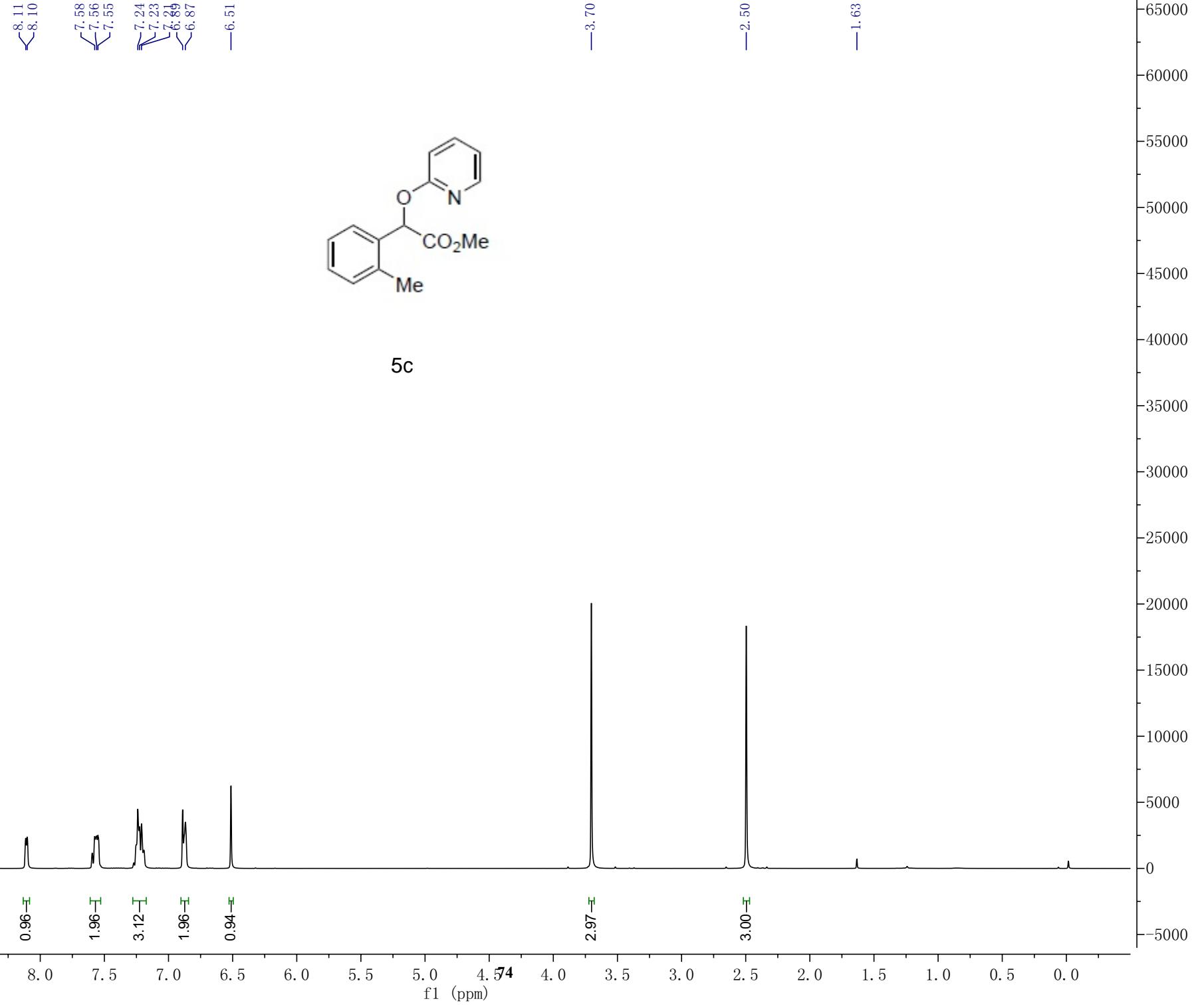


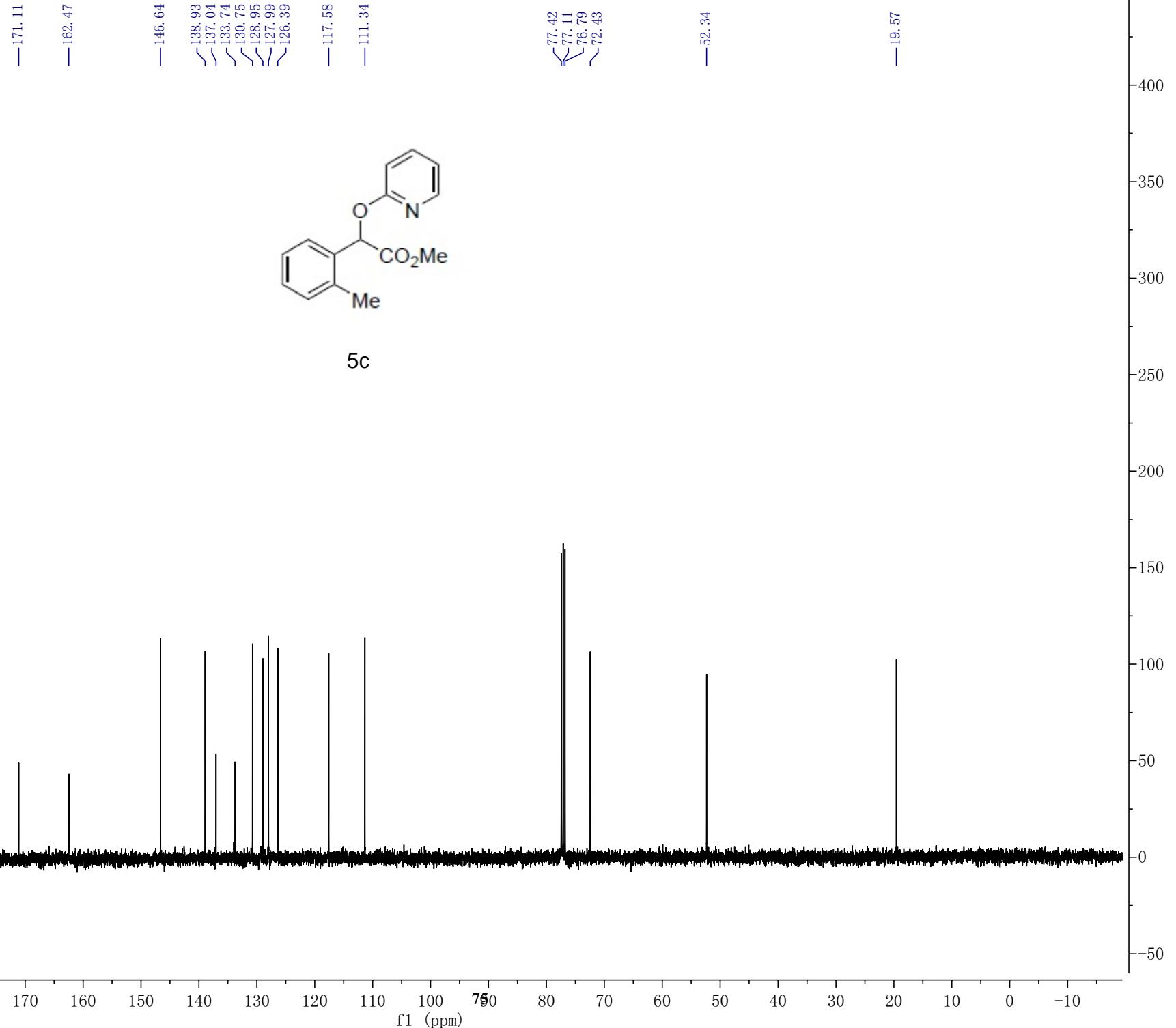


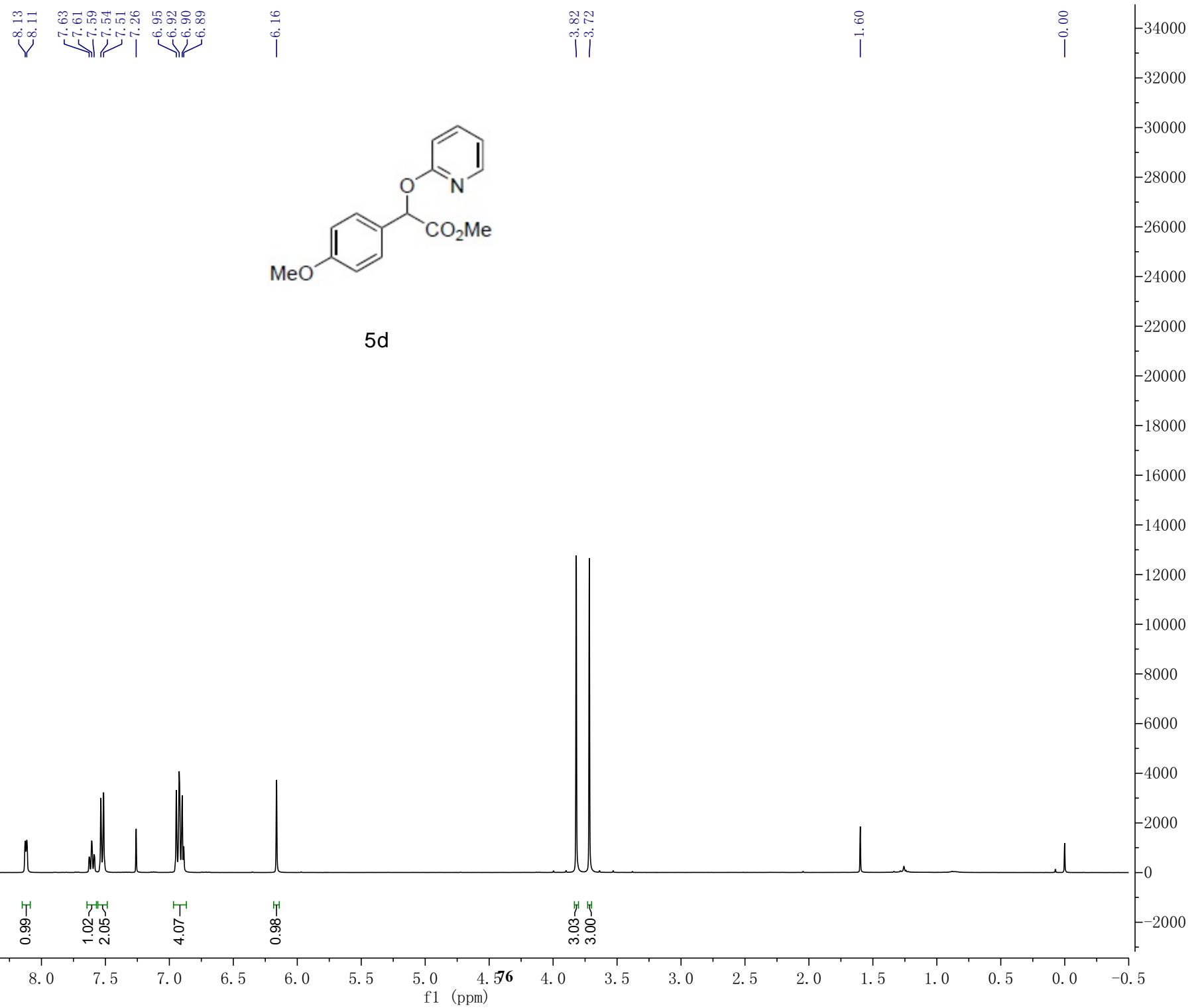


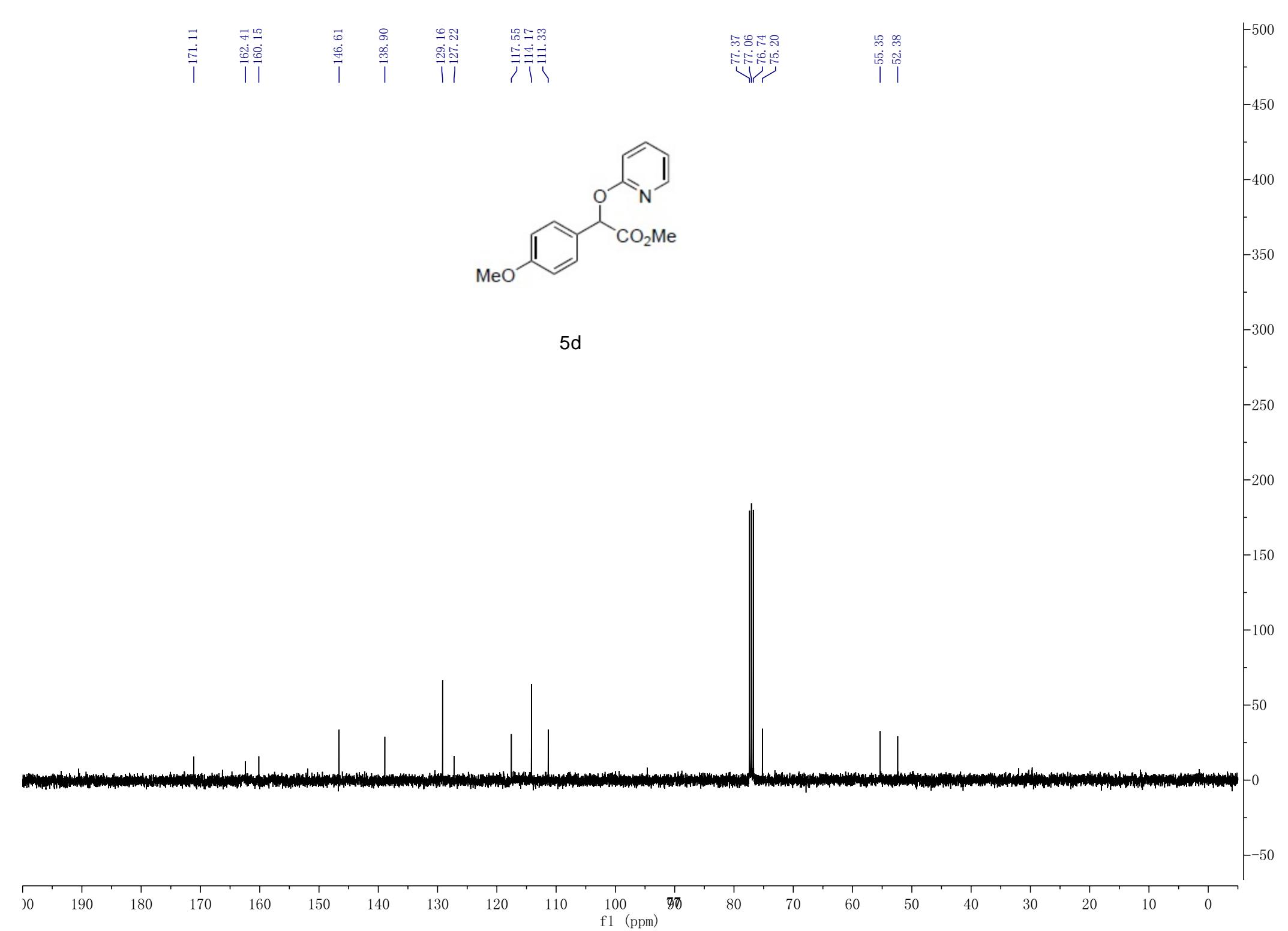


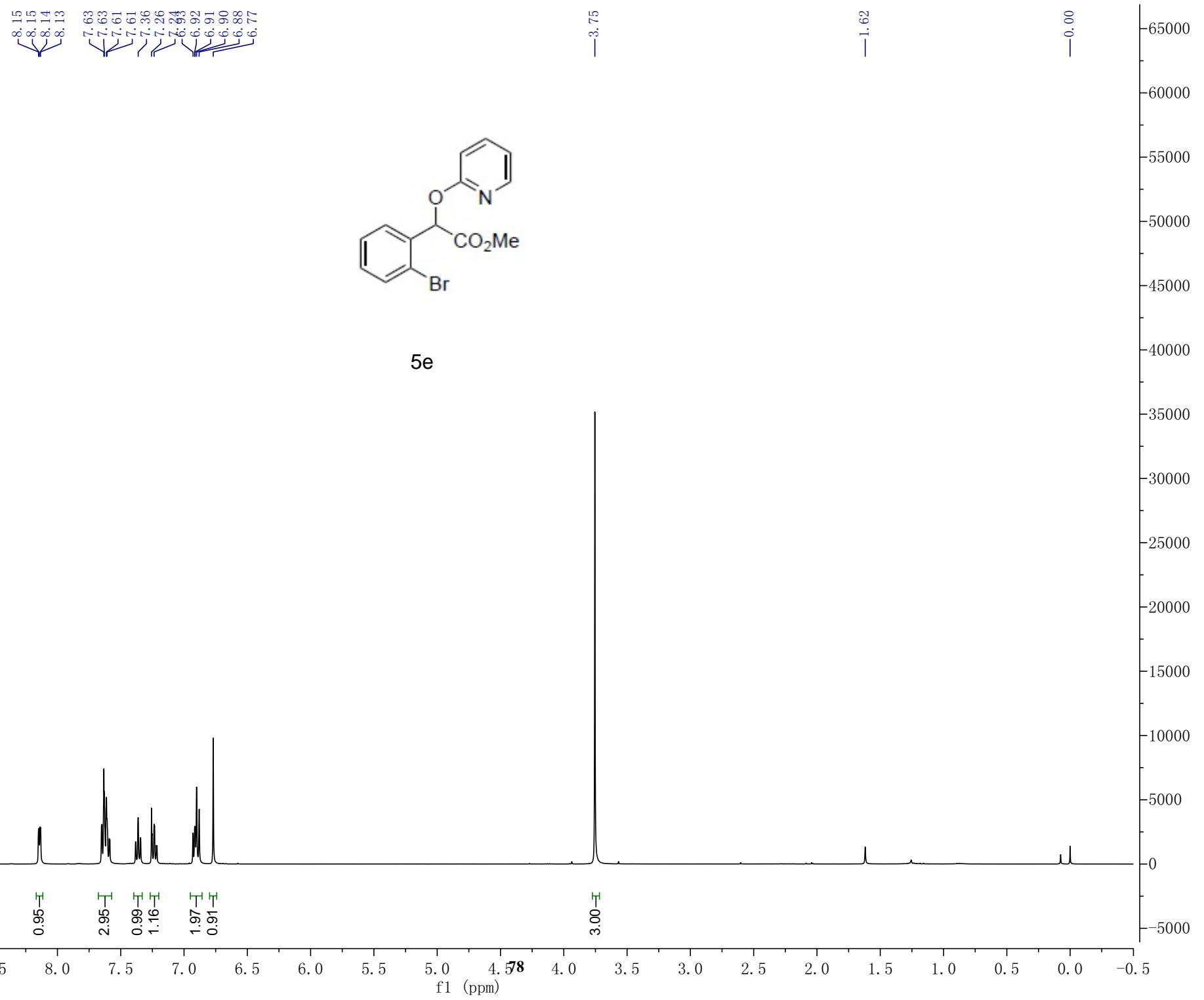


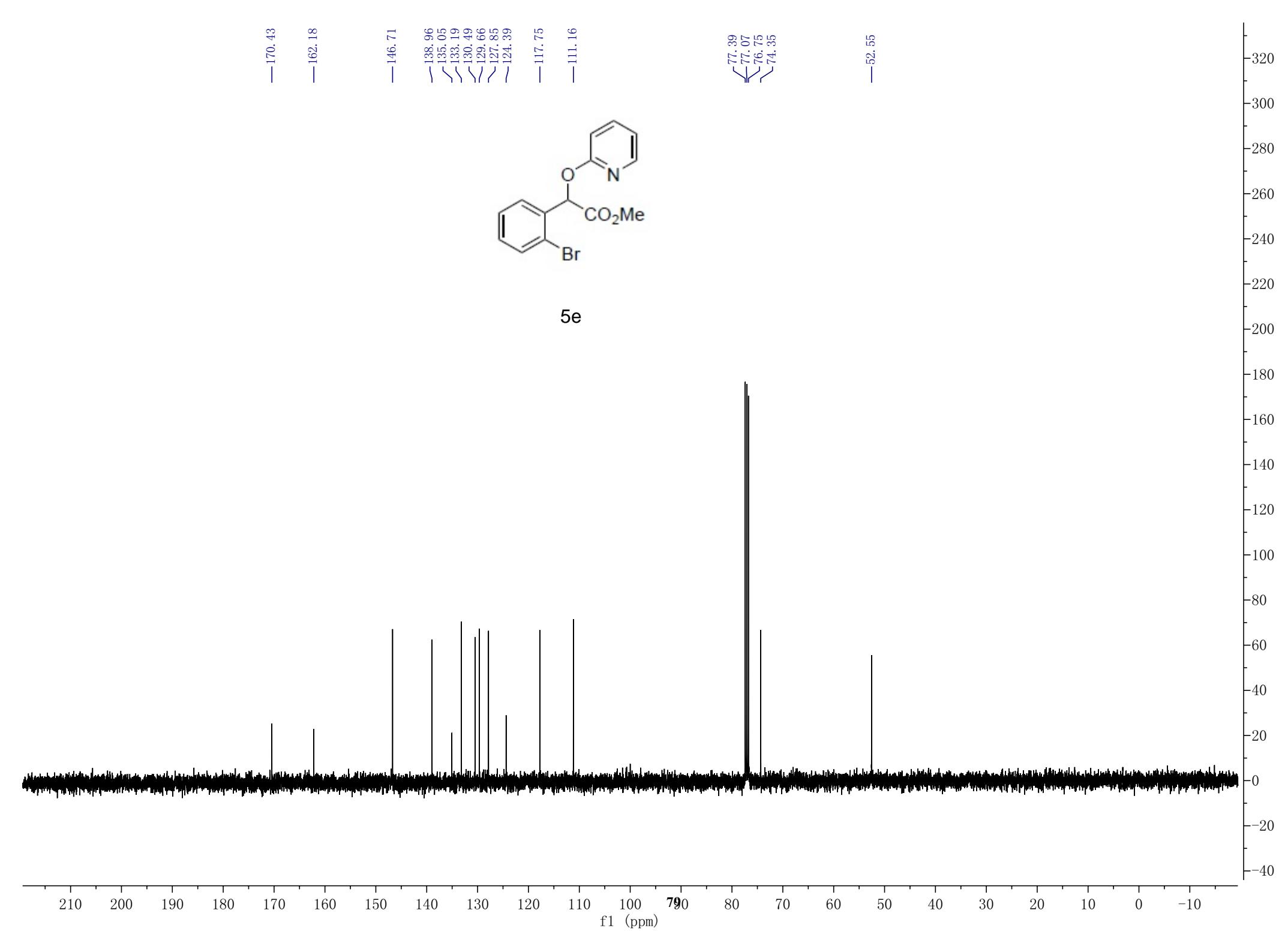


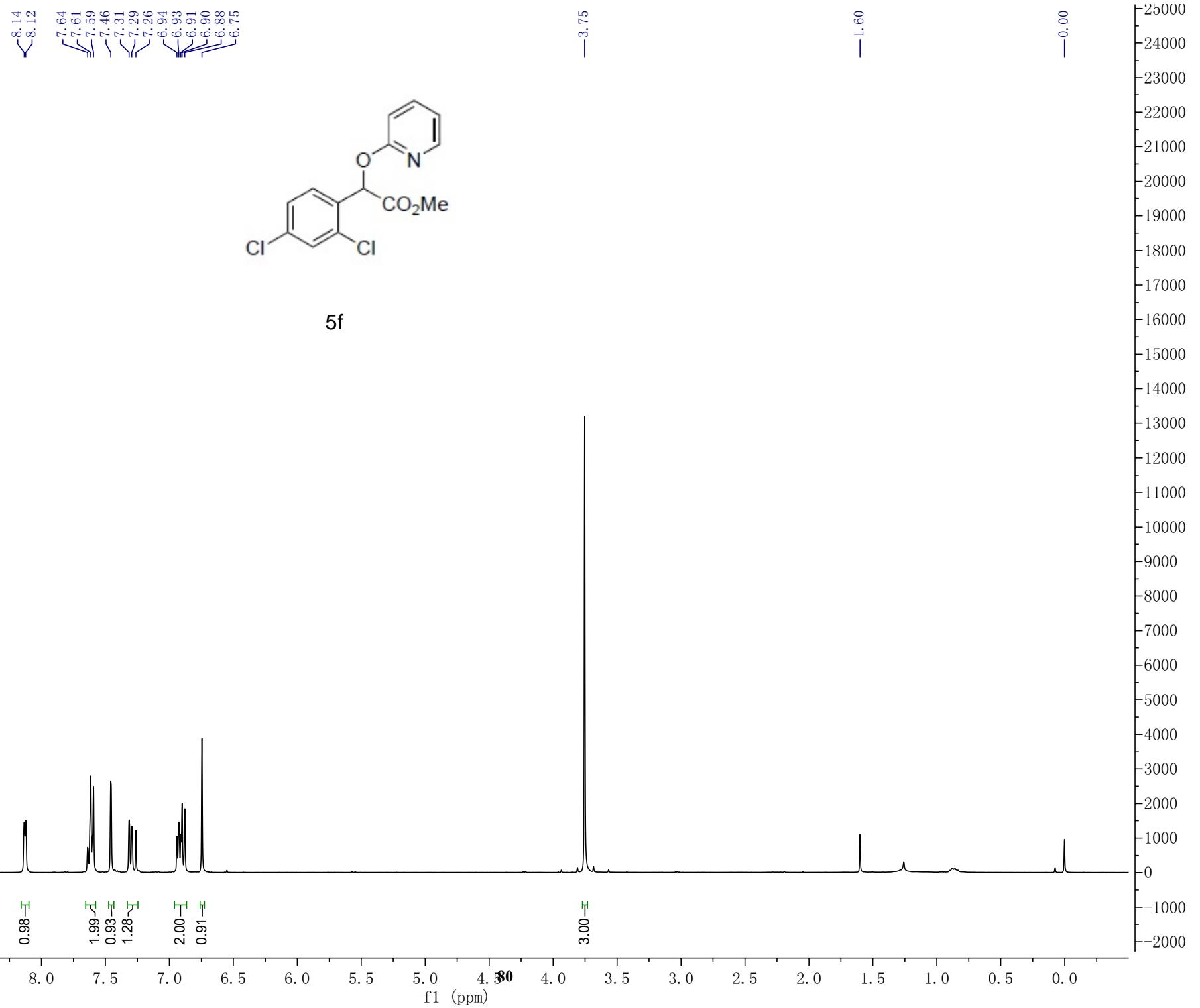


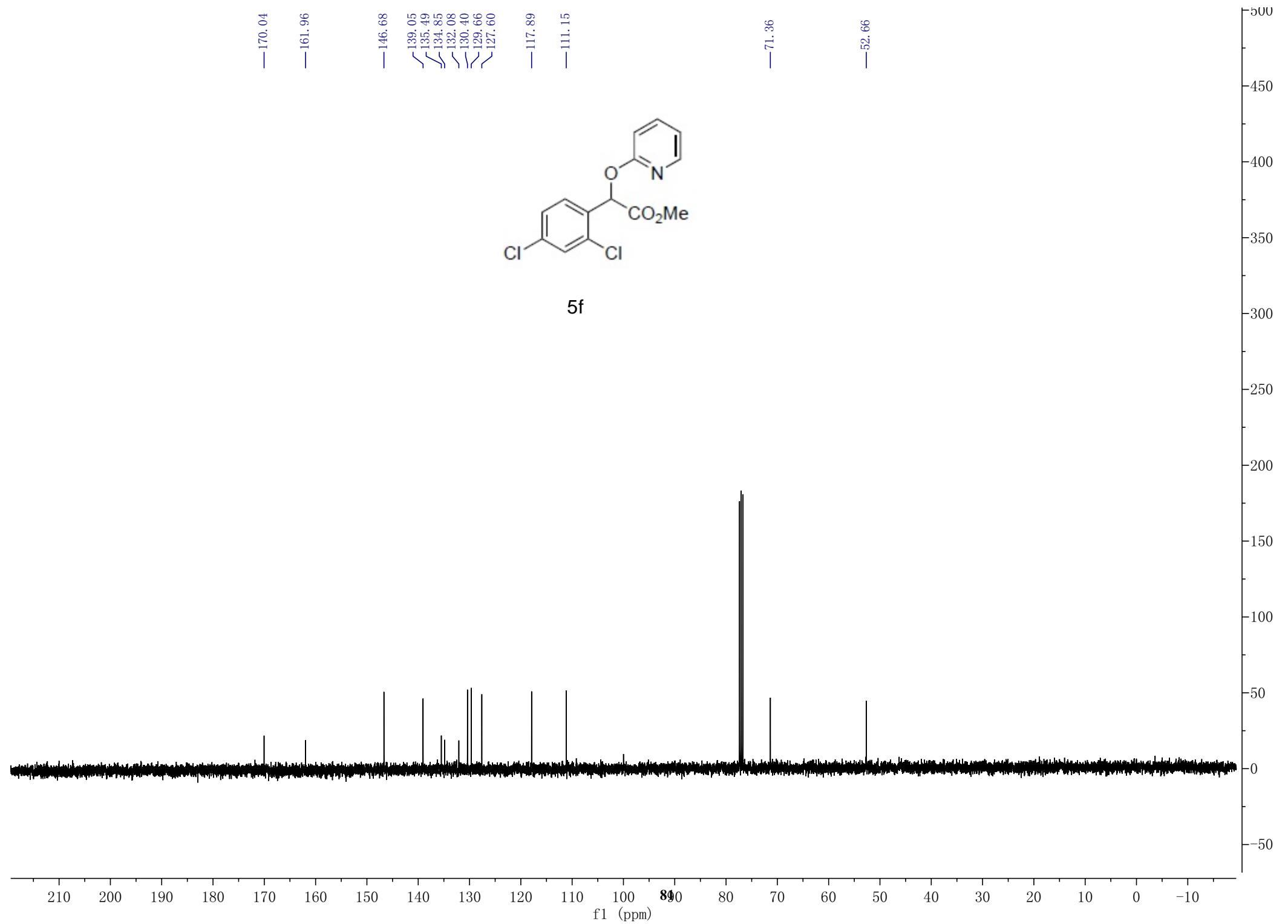


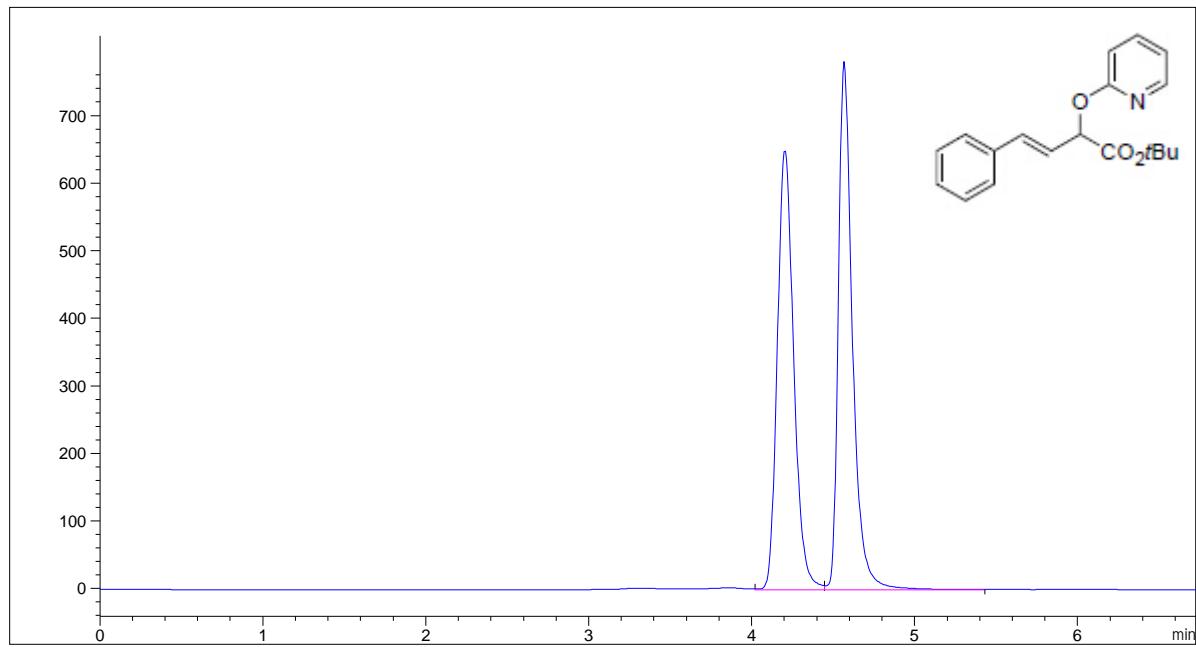






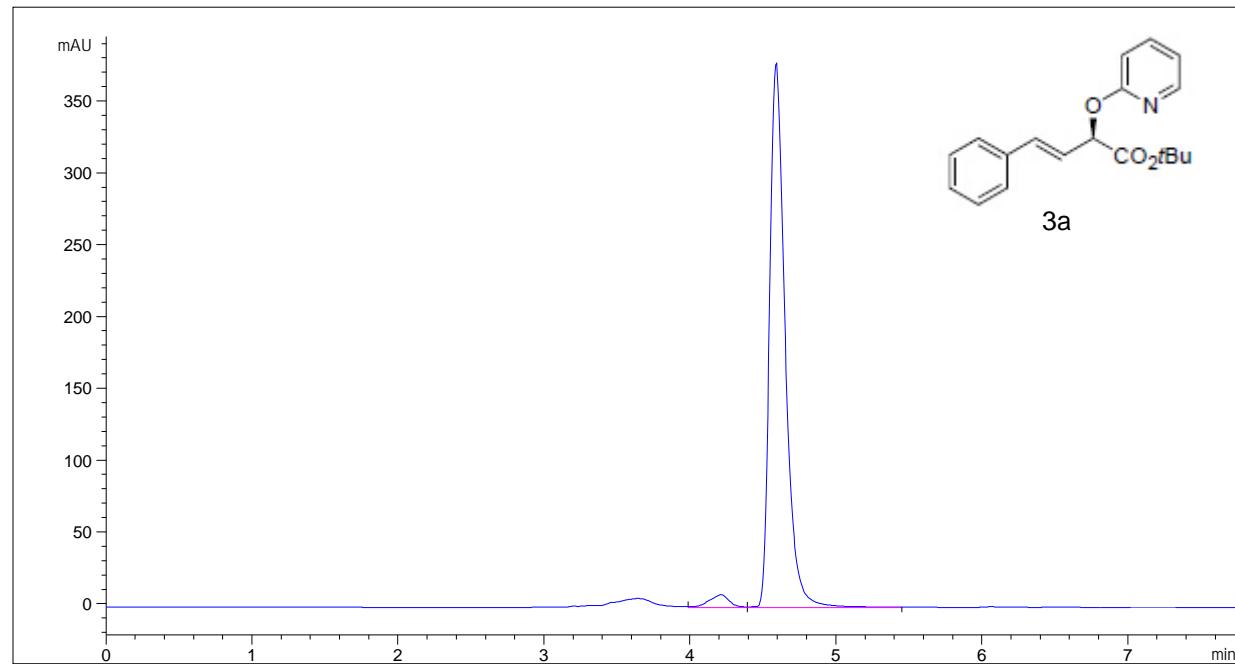






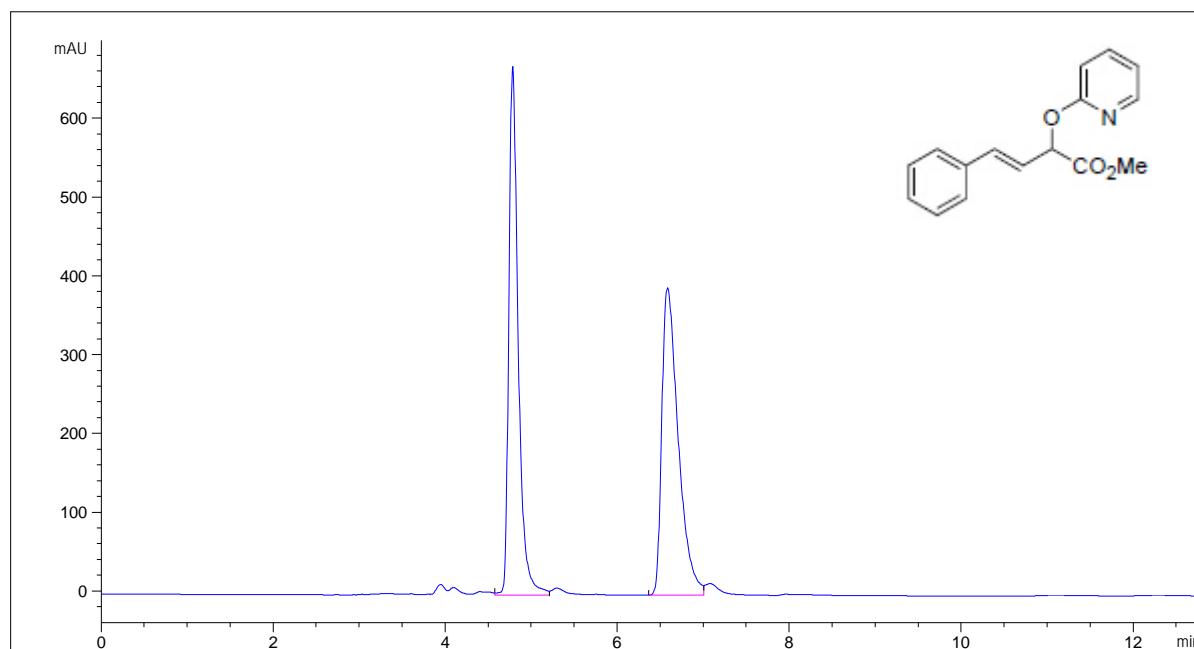
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.204	VV	0.1097	4554.21387	49.2453 ?	
2	4.568	VV	0.0921	4693.80908	50.7547 ?	



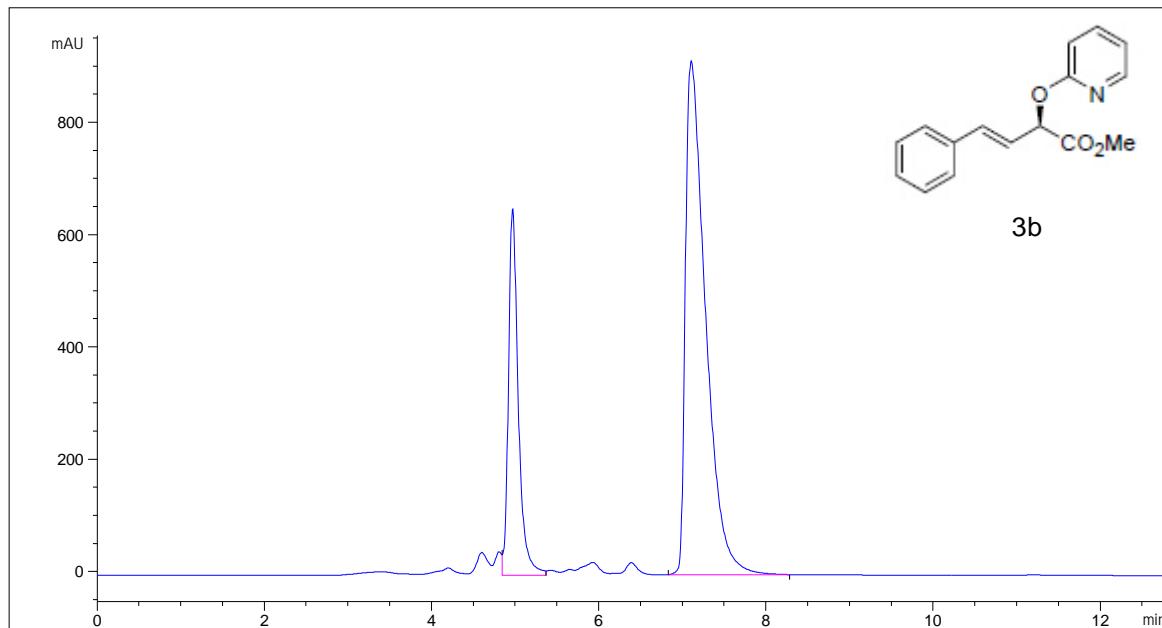
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.213	VV	0.1390	84.16236	2.9145 ?	
2	4.592	VV	0.1143	2803.54639	97.0855 ?	



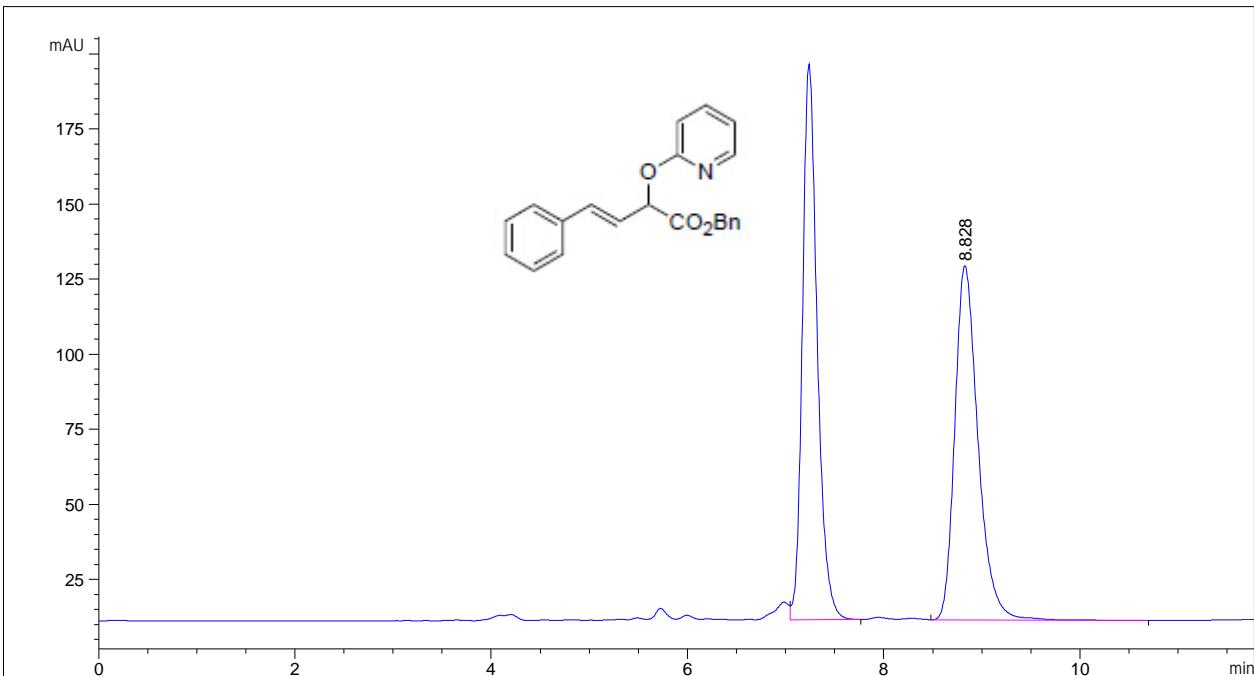
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.786	VV	0.1150	5114.83984	49.6402	?
2	6.587	BV	0.2012	5188.98291	50.3598	?



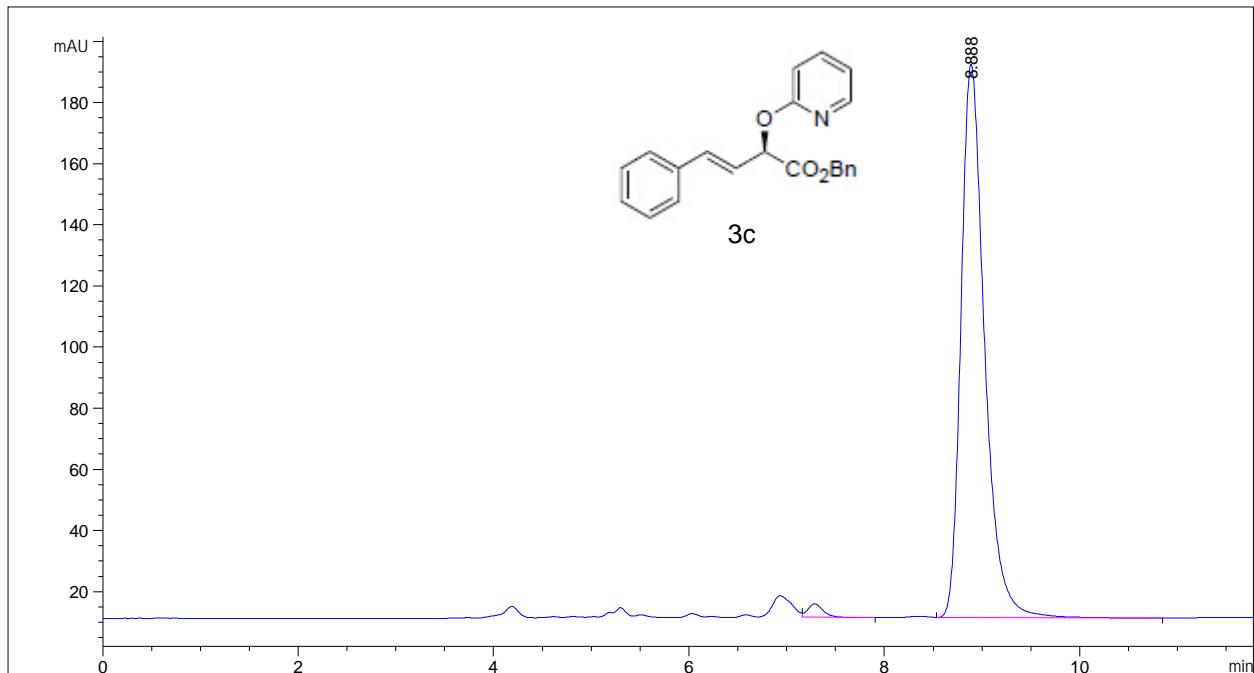
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峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.971	VV	0.1238	5364.01270	25.9108	?
2	7.108	BB	0.2515	1.53378e4	74.0892	?



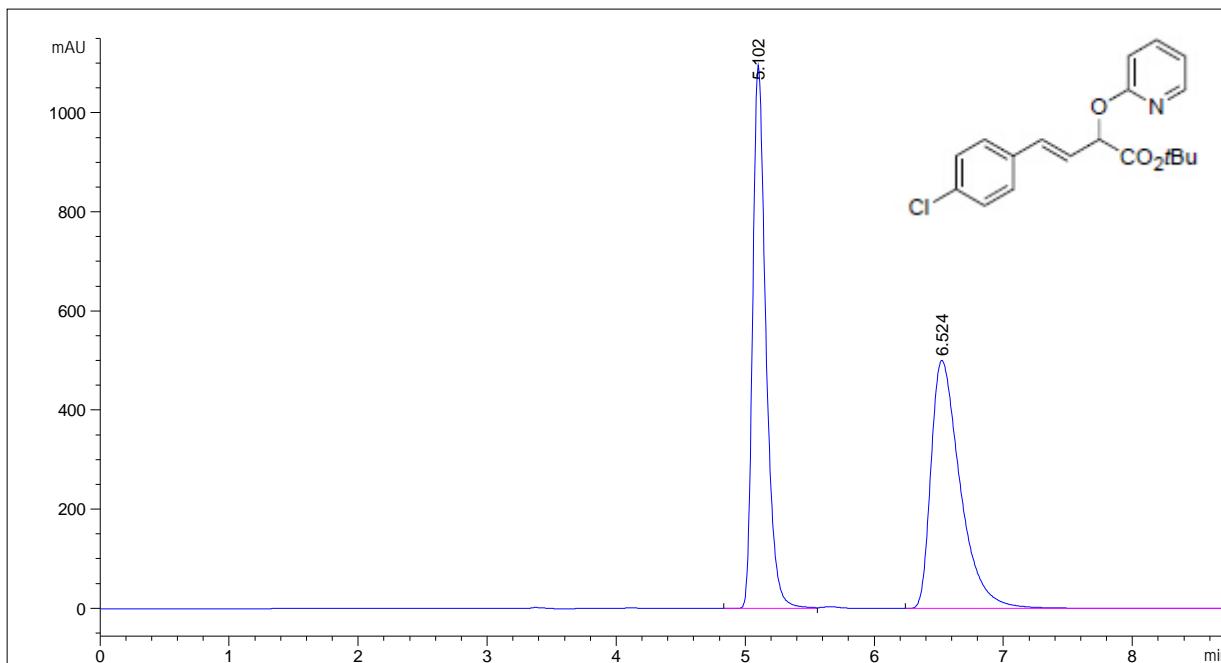
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.240	VB	0.1607	1945.29553	184.95264	50.0923
2	8.828	VB	0.2497	1938.12756	117.95007	49.9077



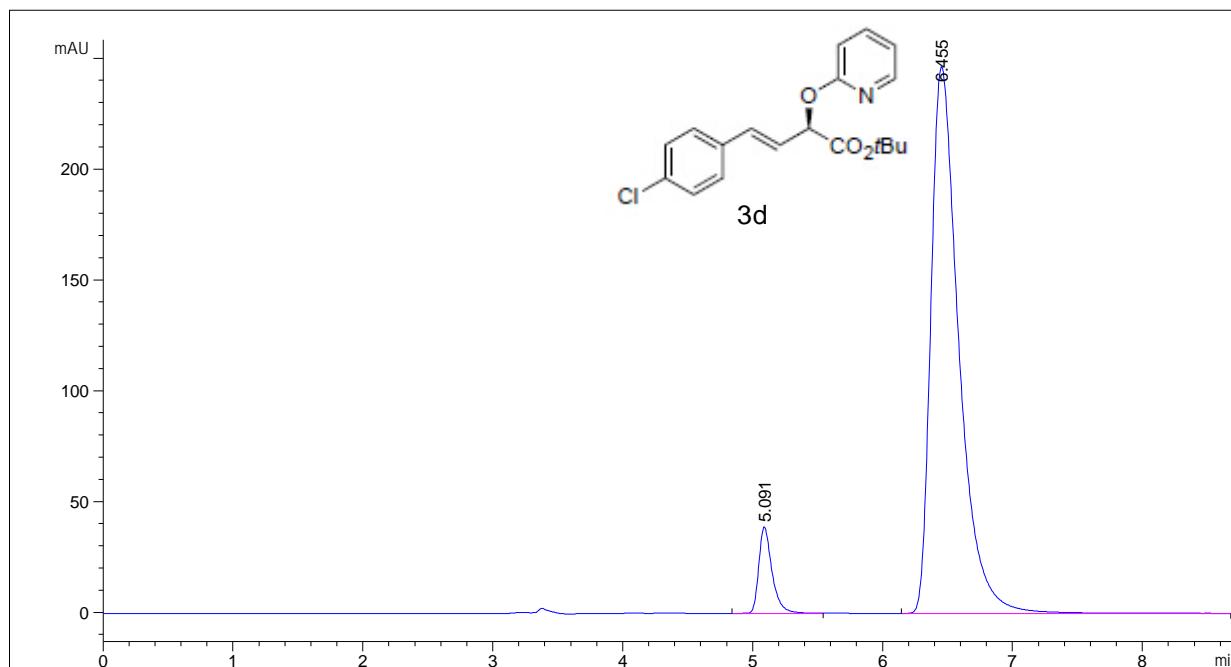
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.287	VB	0.1624	48.24669	4.45405	1.5660
2	8.888	VB	0.2534	3032.69482	181.03250	98.4340



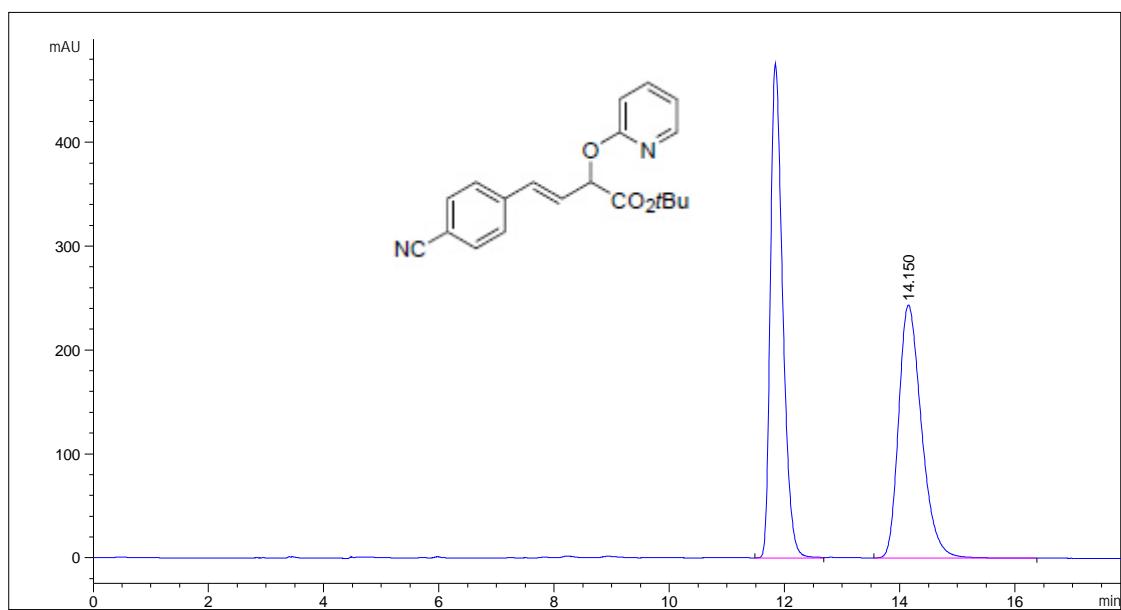
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.102	BV	0.1094	7845.29736	1097.05273	49.7765
2	6.524	BBA	0.2383	7915.75732	500.96686	50.2235



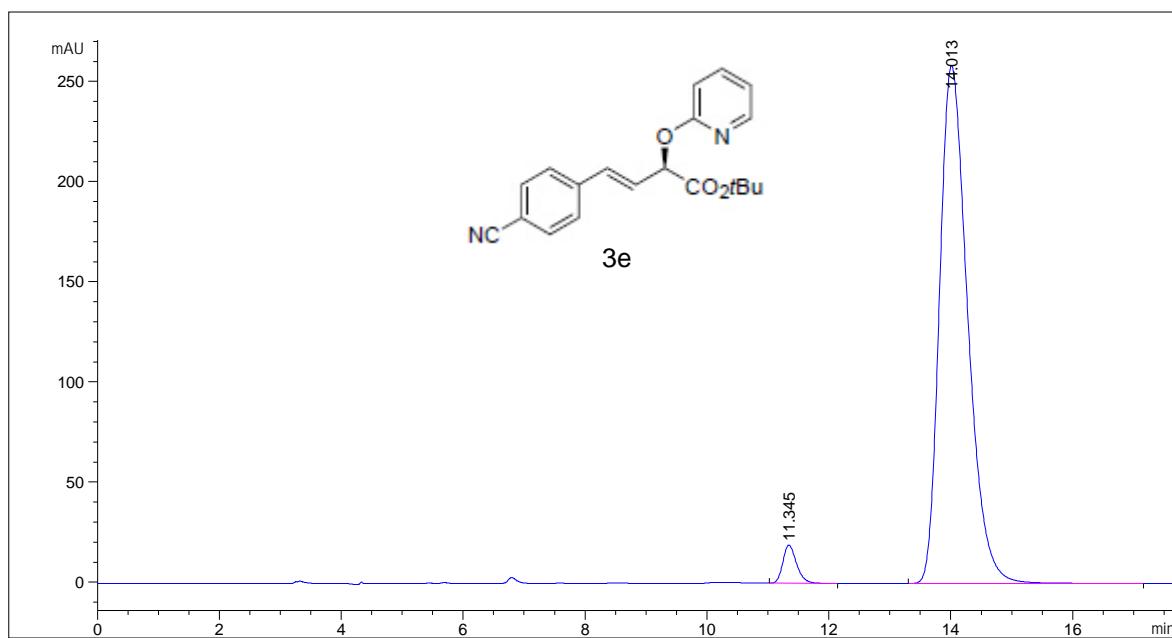
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.091	BV	0.1075	279.24249	39.03054	7.0437
2	6.455	BBA	0.2263	3685.21143	246.61336	92.9563



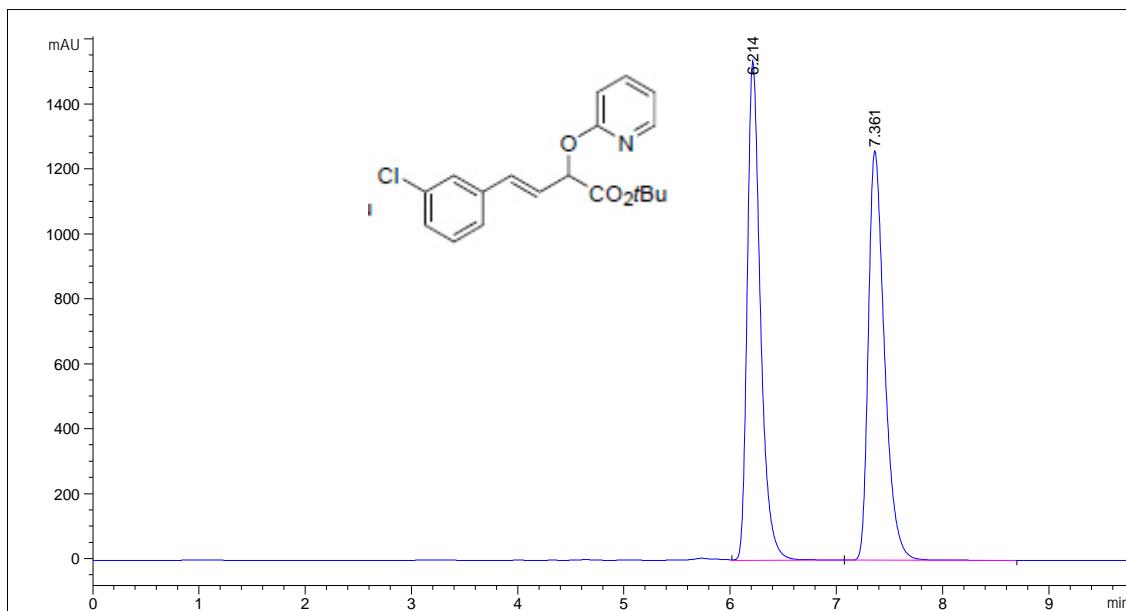
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.841	VV	0.2274	7072.94971	475.94724	51.3371
2	14.150	VB	0.4230	6704.50586	243.70515	48.6629



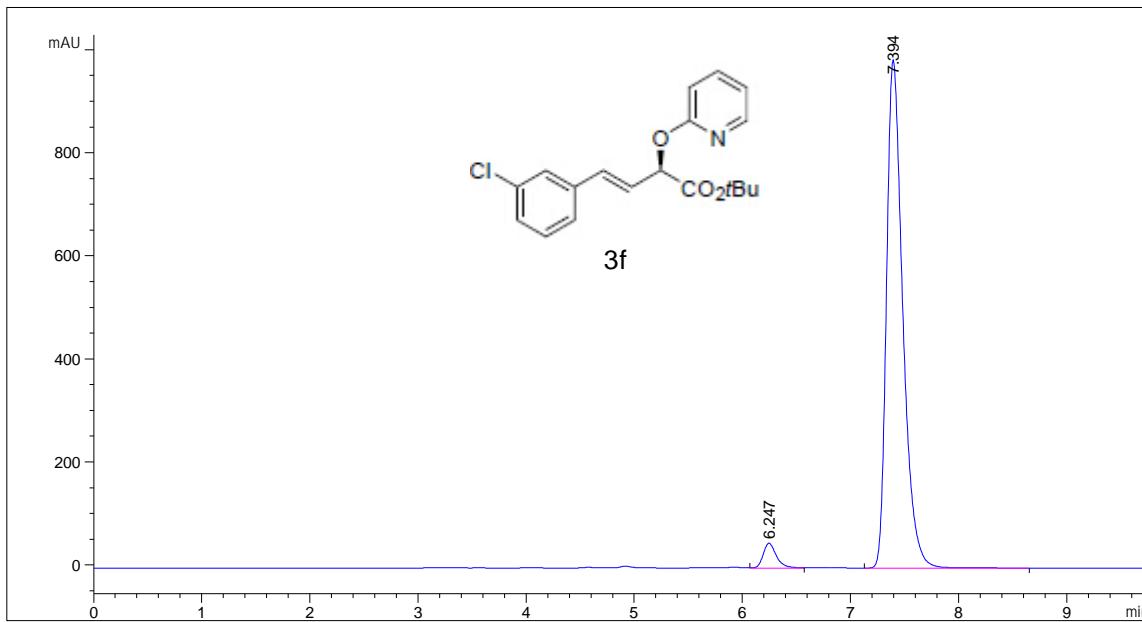
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.345	BB	0.2375	295.37354	18.98594	3.4520
2	14.013	BB	0.4929	8261.12207	258.49054	96.5480



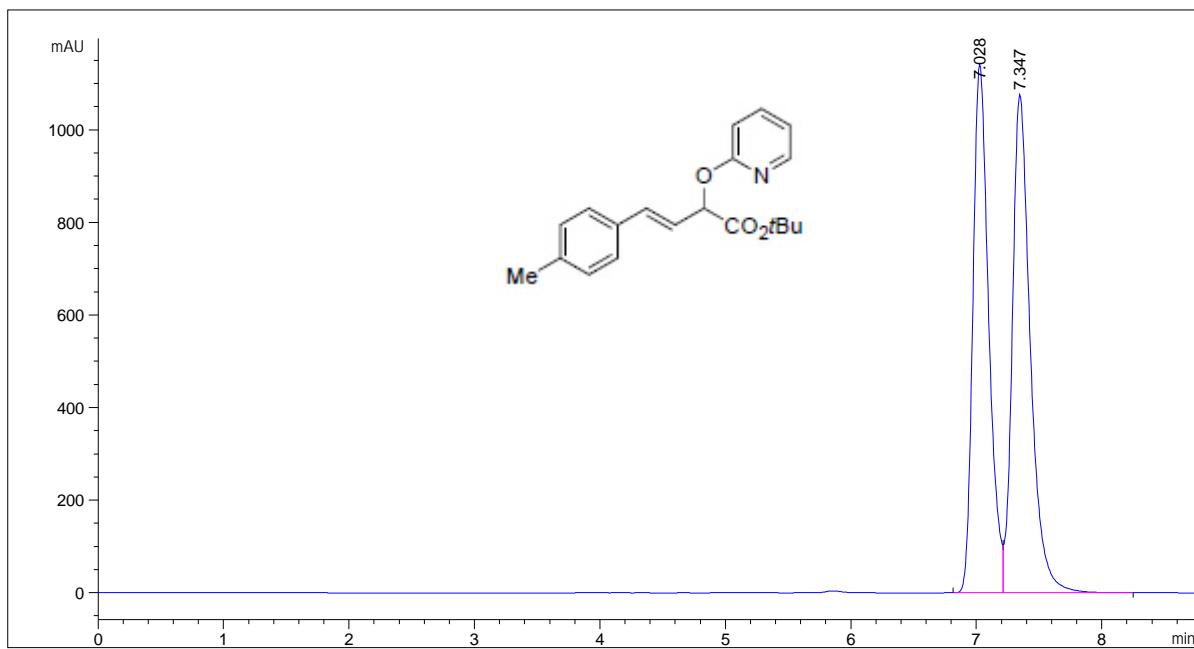
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.214	VB	0.1307	1.32551e4	1536.41089	50.0087
2	7.361	BB	0.1586	1.32505e4	1261.14319	49.9913



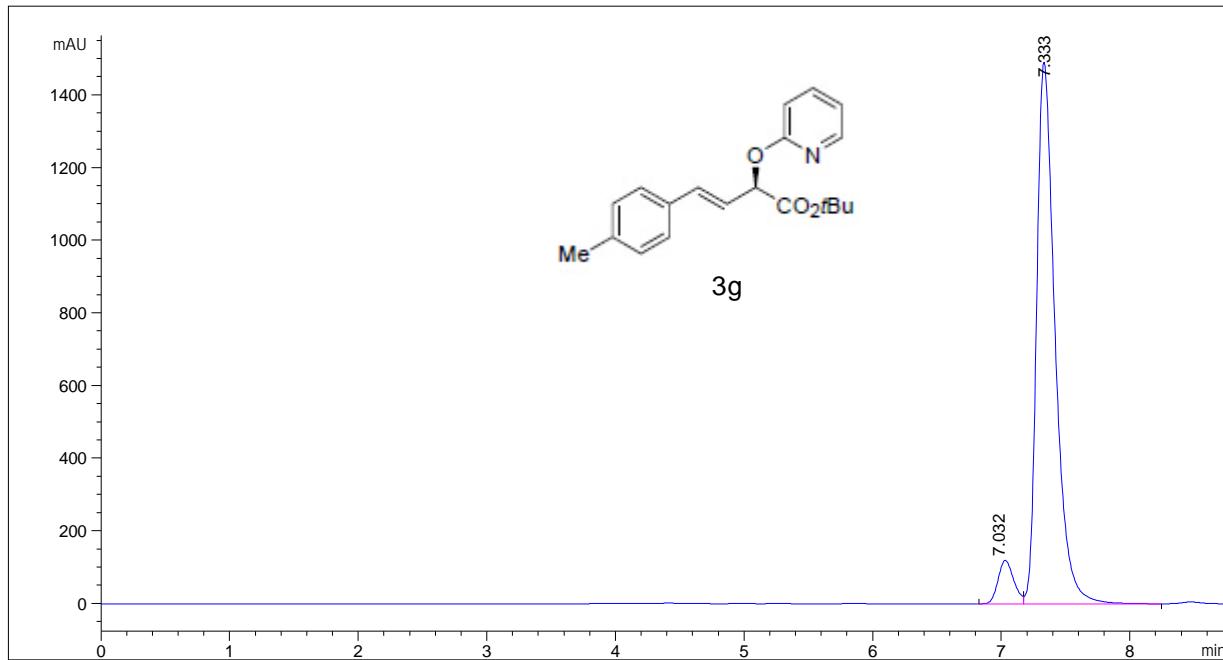
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰	保留时间	类型	峰宽	峰面积	峰高	峰面积
#	[min]		[min]	[mAU*s]	[mAU]	%
1	6.247	VV	0.1286	408.14822	48.27512	3.8284
2	7.394	BB	0.1573	1.02530e4	986.06055	96.1716



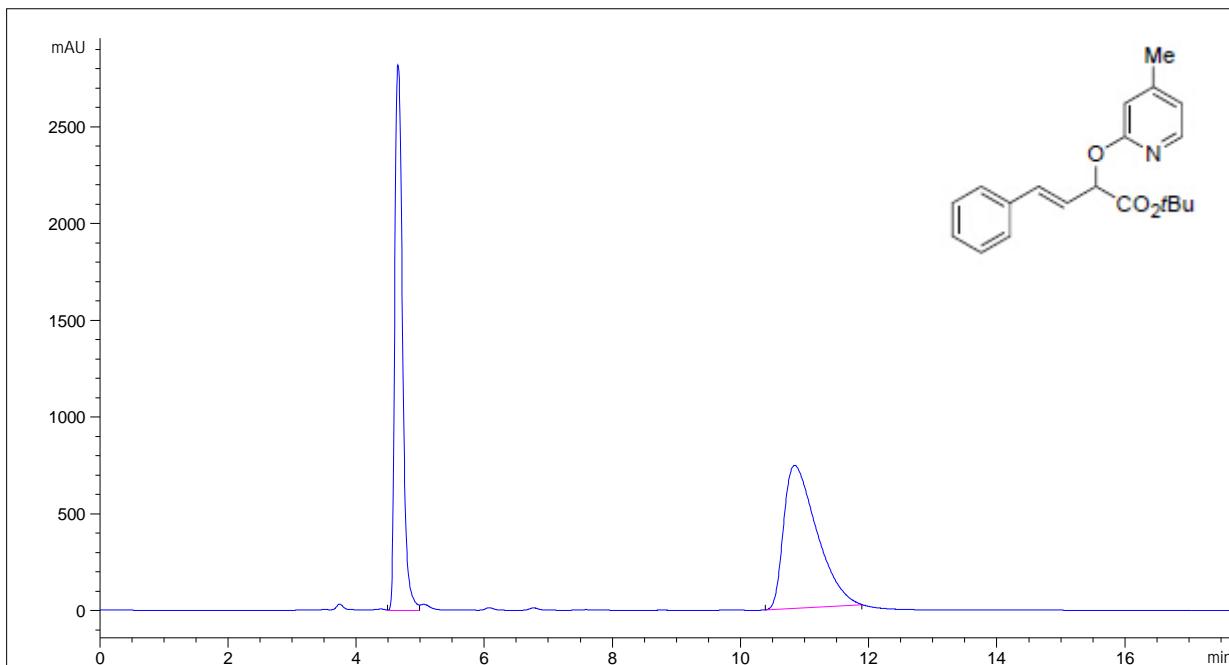
信号 1: DAD1 A, Sig=254, 4 Ref=off

#	峰保留时间 [min]	类型	峰宽 [min]	峰面积		峰高 [mAU]	峰面积 %
				[mAU*s]	[mAU]		
1	7.028	BV	0.1341	9993.36230	1141.35754	48.1298	
2	7.347	VB	0.1507	1.07700e4	1076.33447	51.8702	



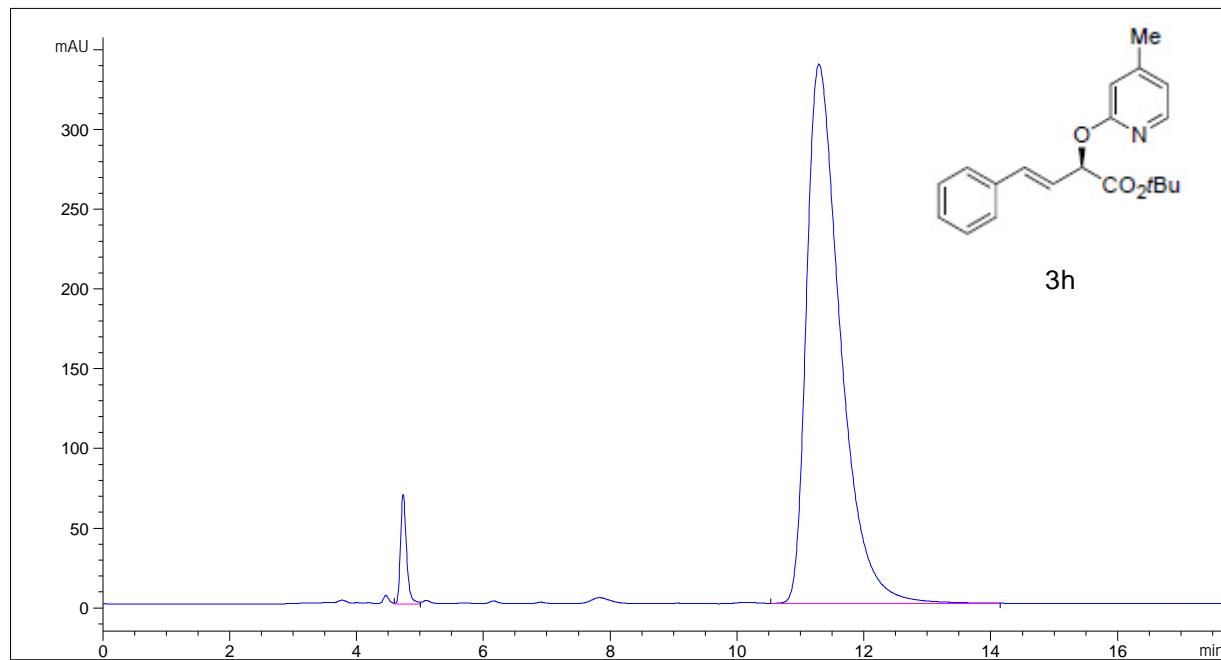
信号 1: DAD1 A, Sig=254, 4 Ref=off

#	峰保留时间 [min]	类型	峰宽 [min]	峰面积		峰高 [mAU]	峰面积 %
				[mAU*s]	[mAU]		
1	7.032	BV	0.1307	1013.22223	119.74002	6.3963	
2	7.333	VB	0.1500	1.48274e4	1490.65601	93.6037	



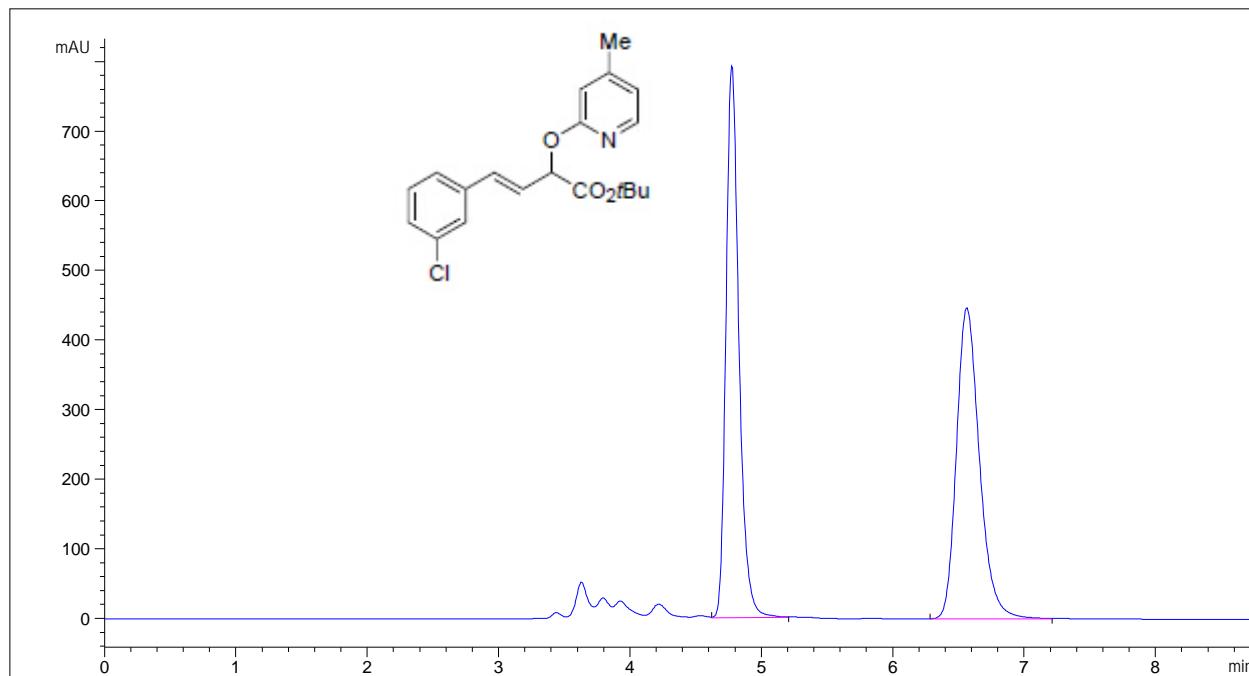
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.656	VV	0.1347	2.38079e4	47.3194	?
2	10.846	MM	0.5981	2.65053e4	52.6806	?



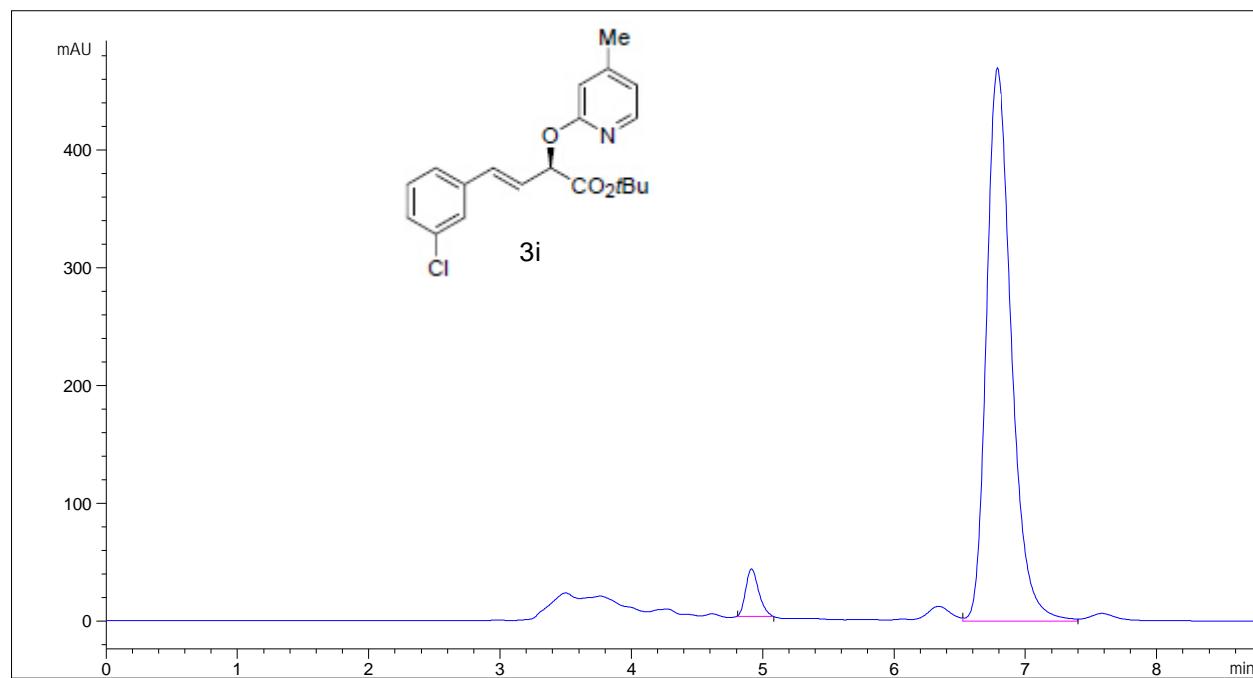
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.737	VV	0.1009	451.28976	3.4792	?
2	11.293	VB	0.5639	1.25197e4	96.5208	?



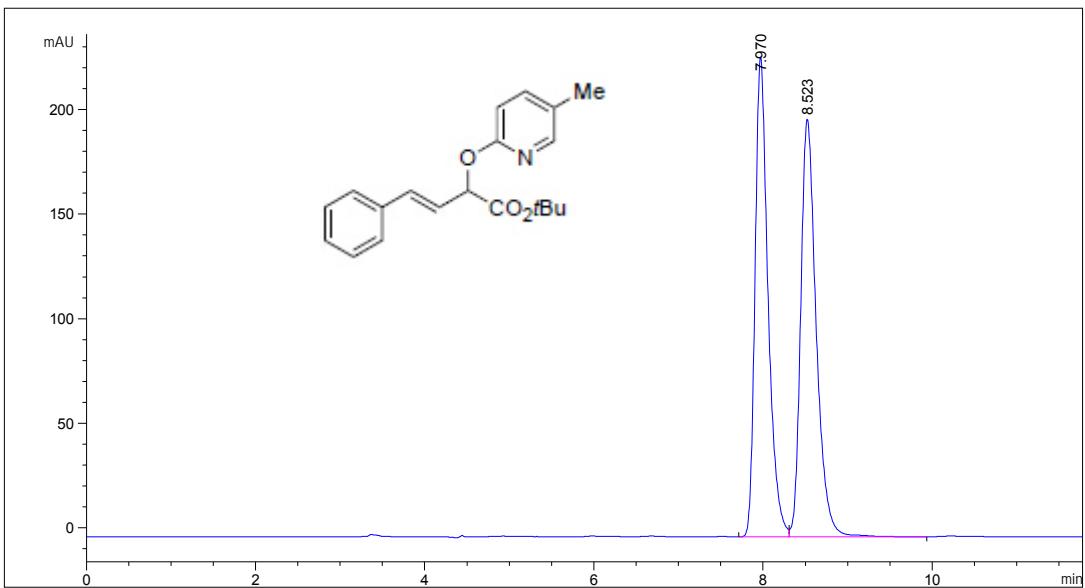
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.776	VB	0.1032	5386.93701	49.7907	?
2	6.564	BB	0.1859	5432.23340	50.2093	?



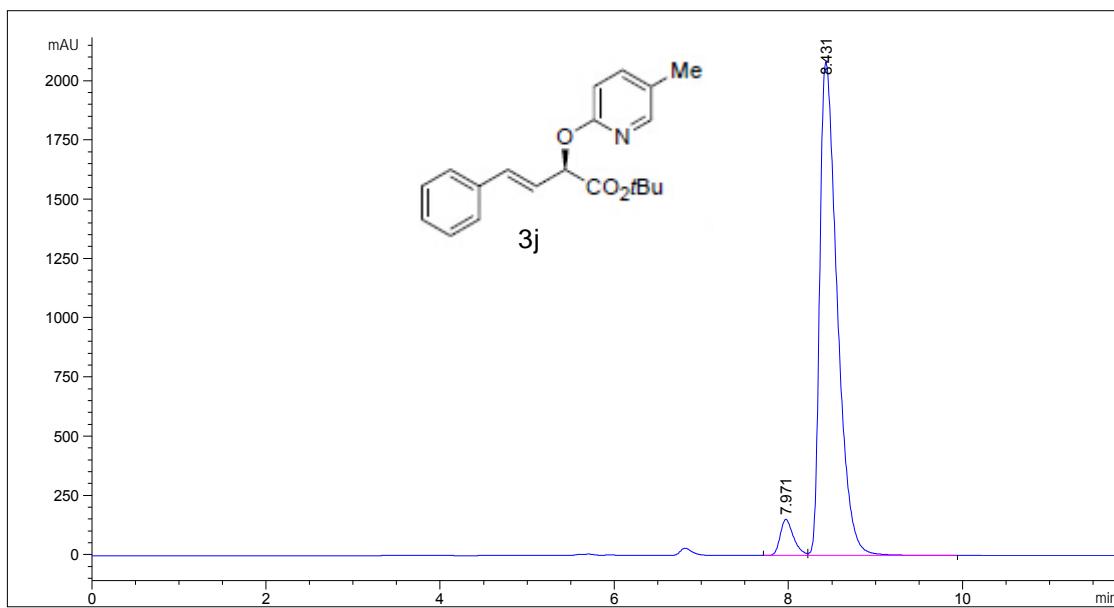
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	4.915	MM	0.1150	279.83853	4.3710	?
2	6.788	VV	0.2001	6122.29346	95.6290	?



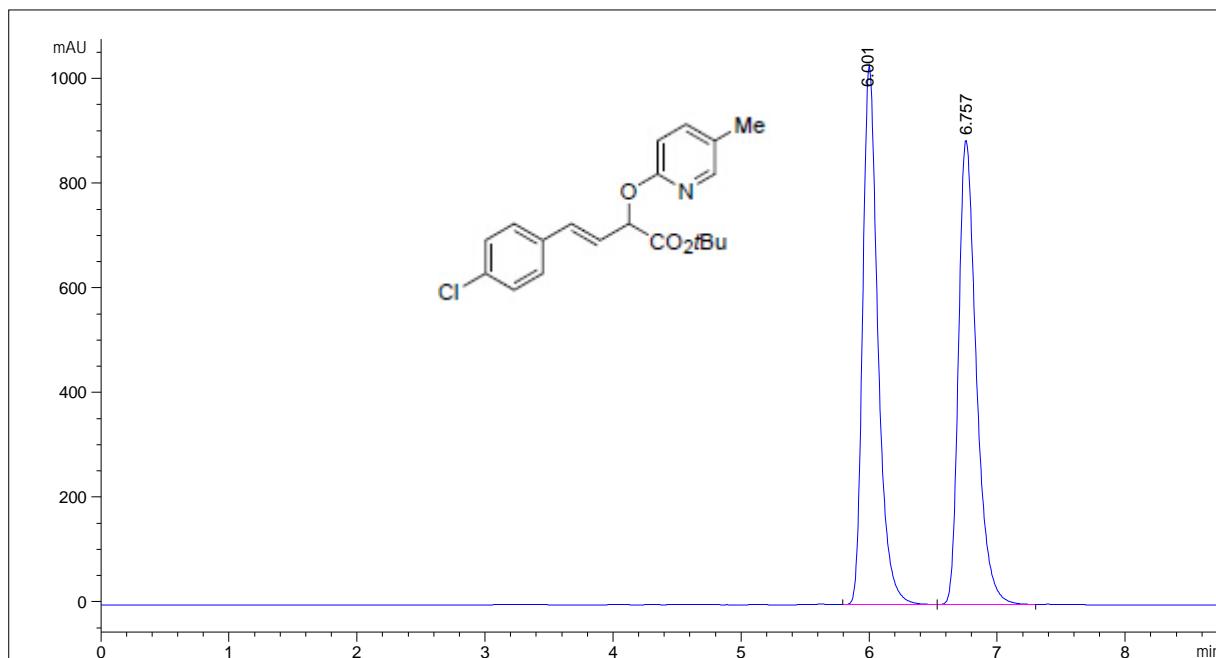
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.970	BV	0.1605	2444.94653	229.12538	49.0539
2	8.523	VV	0.1925	2539.25879	199.54655	50.9461



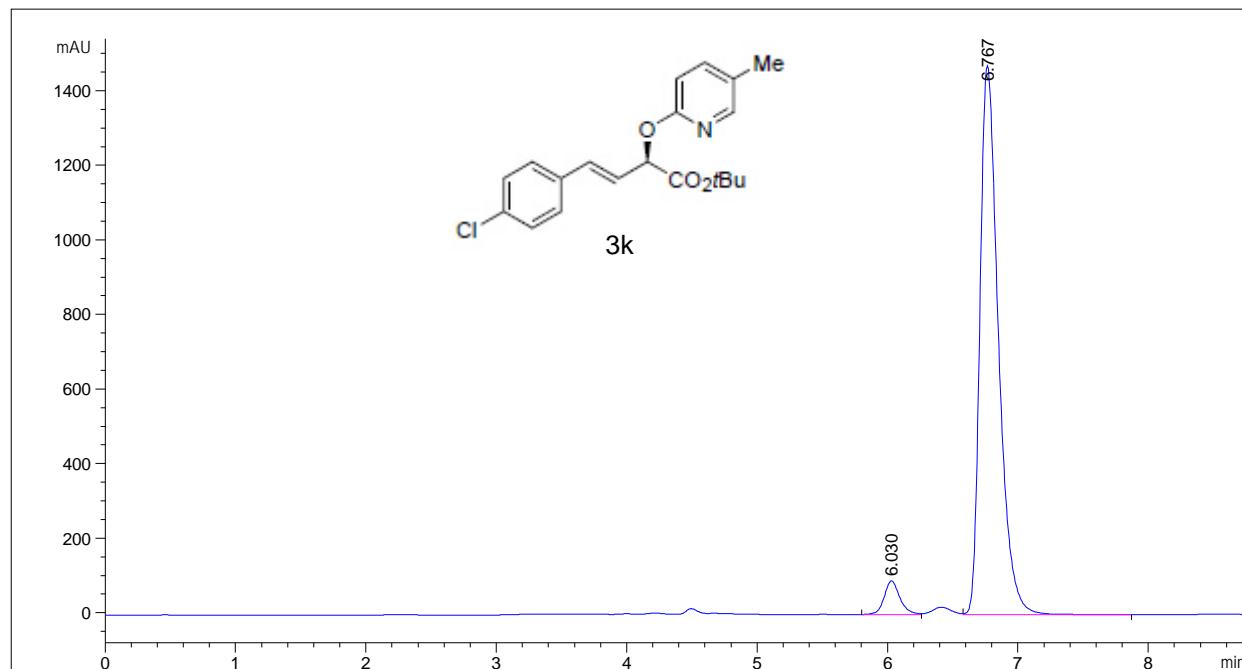
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.971	BV	0.1607	1633.17529	152.79597	5.3282
2	8.431	VV	0.2124	2.90182e4	2084.31592	94.6718



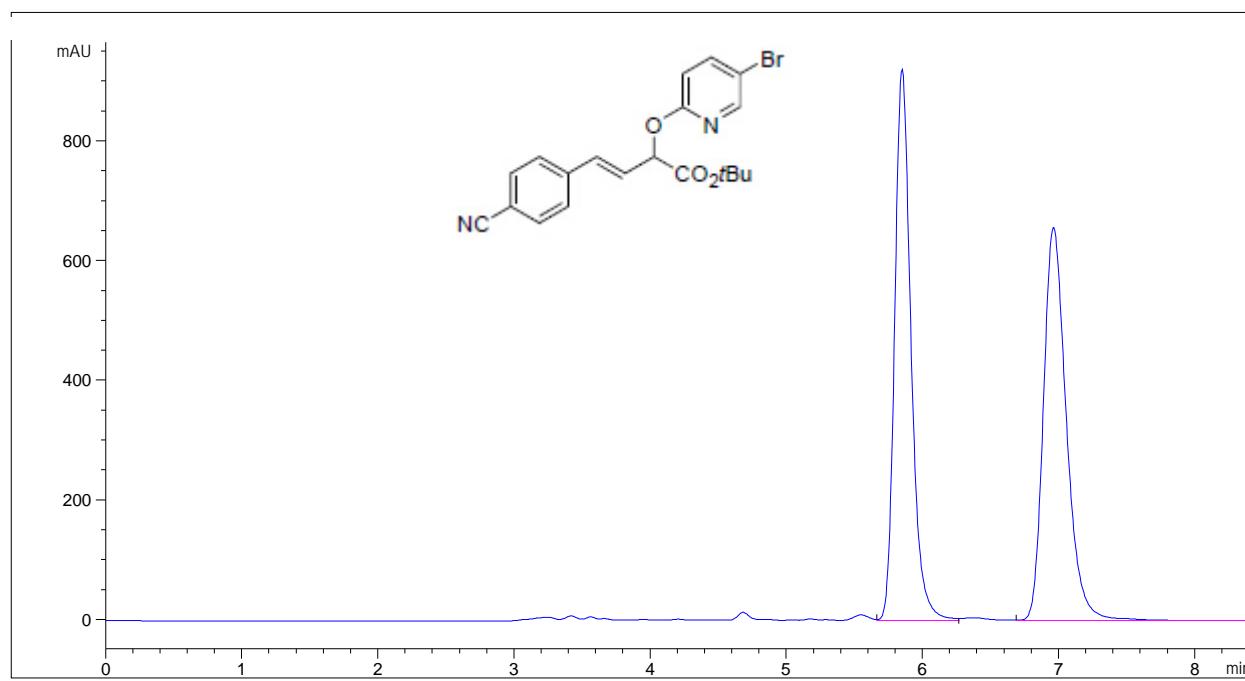
信号 1: DAD1 A, Si g=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.001	BB	0.1263	8508.05566	1030.35950	49.9660
2	6.757	BV	0.1460	8519.62988	887.48395	50.0340



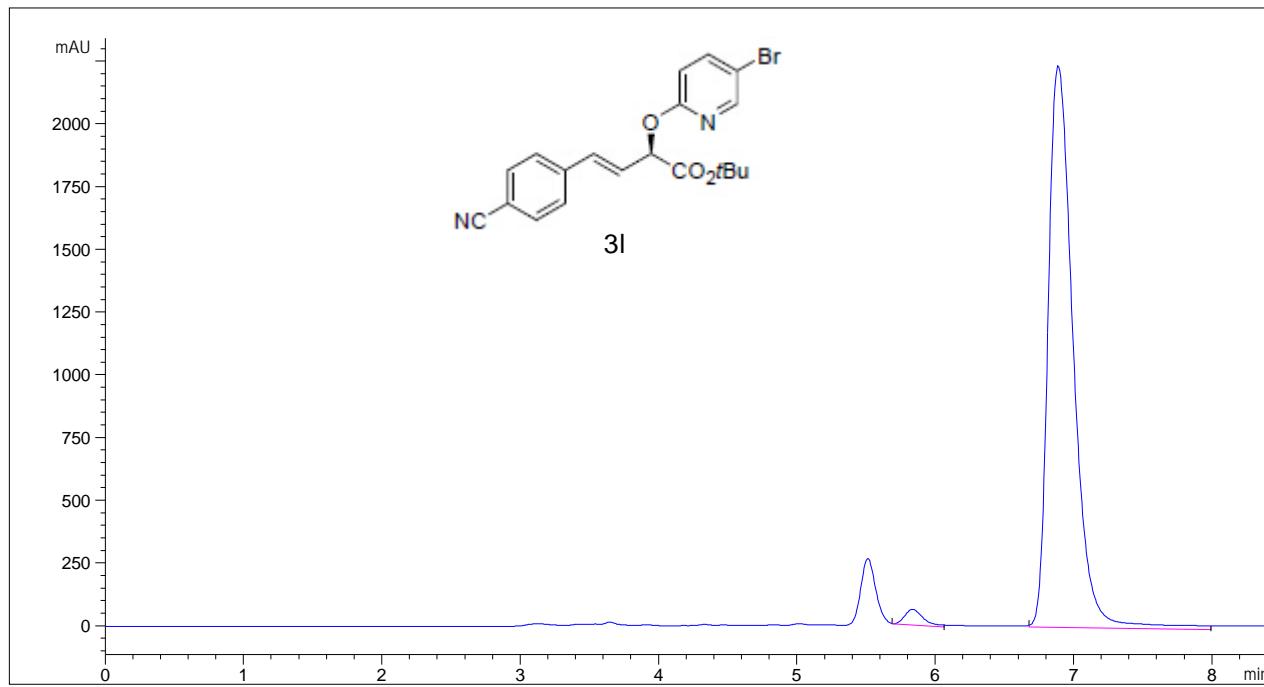
信号 1: DAD1 A, Si g=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.030	BV	0.1251	748.72327	89.94305	4.9478
2	6.767	VB	0.1480	1.43837e4	1471.47681	95.0522



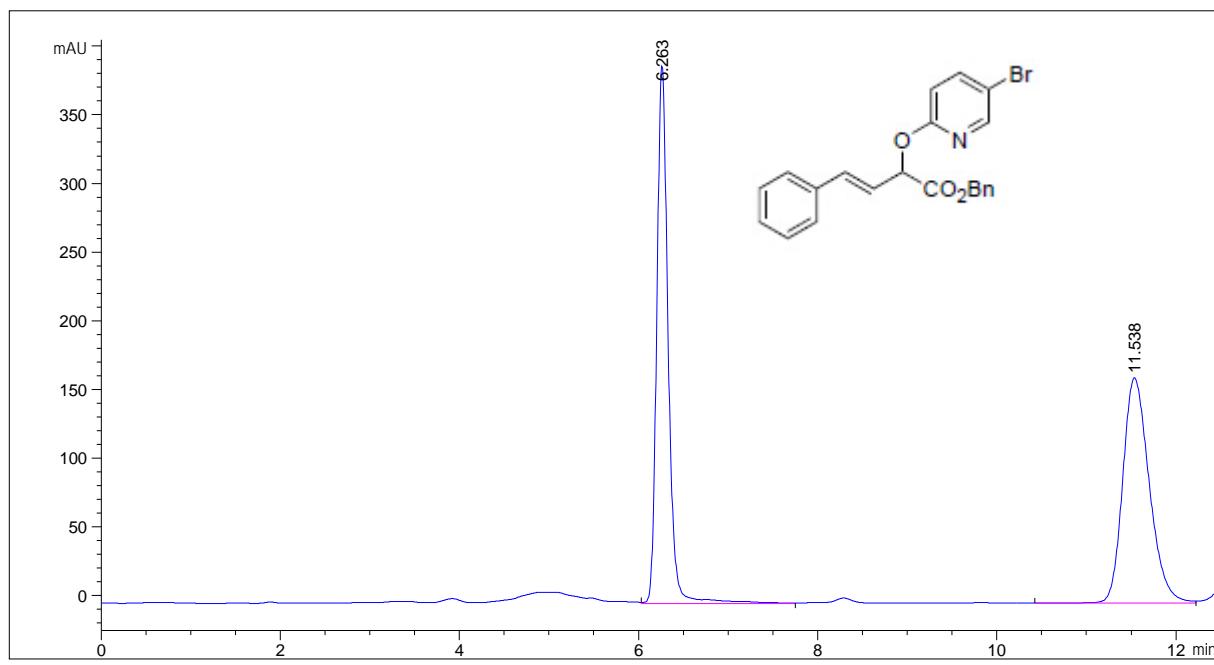
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	5.852	VW	0.1273	7691.66895	49.9460	o-Terphenyl
2	6.964	VB	0.1807	7708.30615	50.0540	?



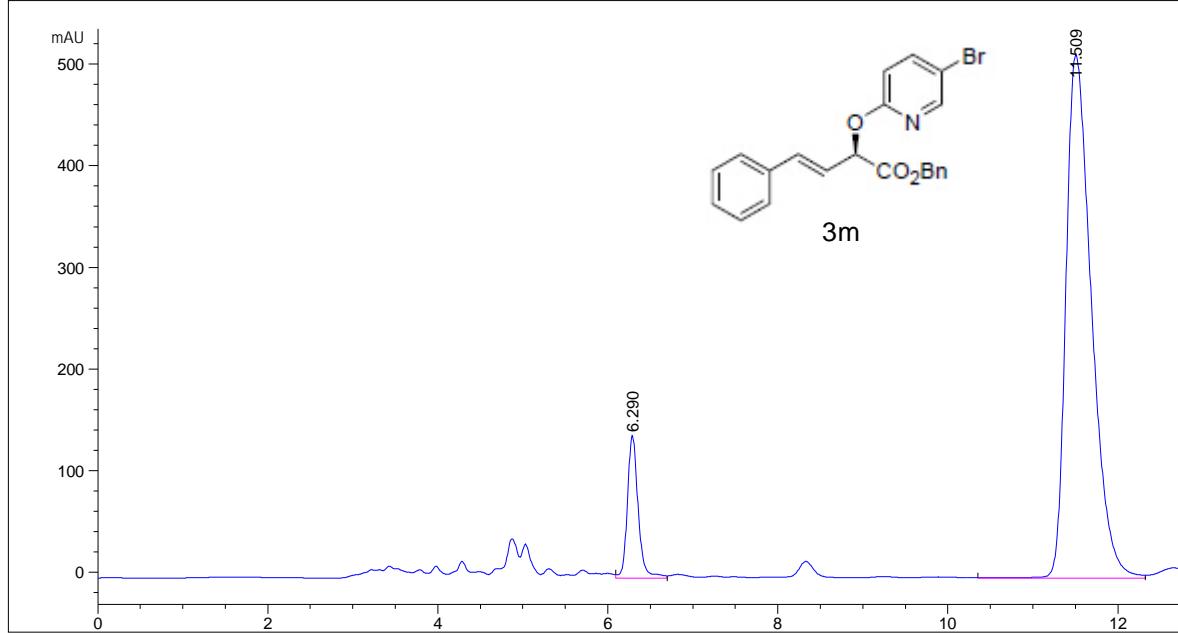
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	5.840	MM	0.1570	581.76593	2.0159	o-Terphenyl
2	6.889	MM	0.2105	2.82769e4	97.9841	?



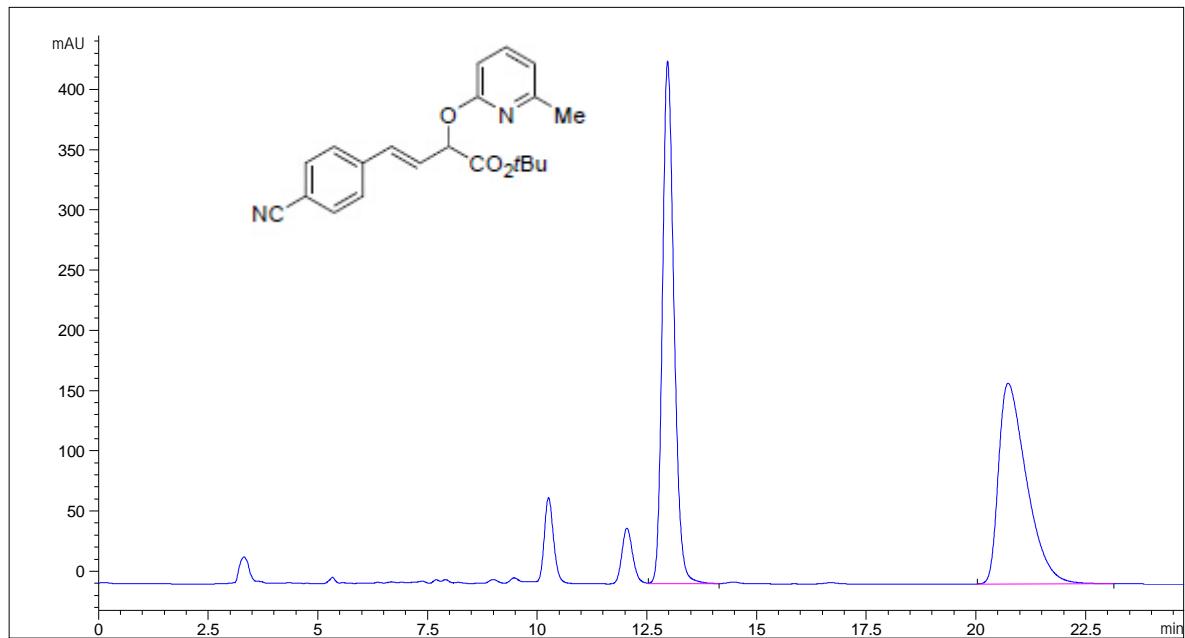
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.263	VB	0.1356	3468.80762	50.5708	?
2	11.538	VV	0.3212	3390.50659	49.4292	?



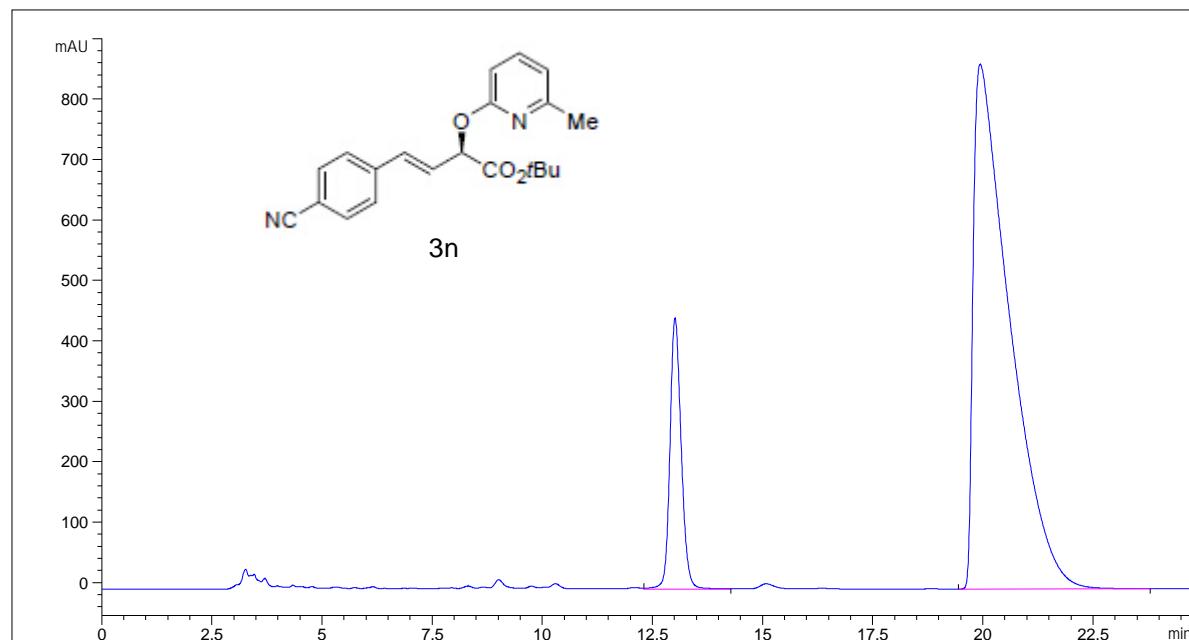
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.290	VV	0.1350	1234.60425	9.3527	?
2	11.509	VV	0.3225	1.06908e4	90.6473	?



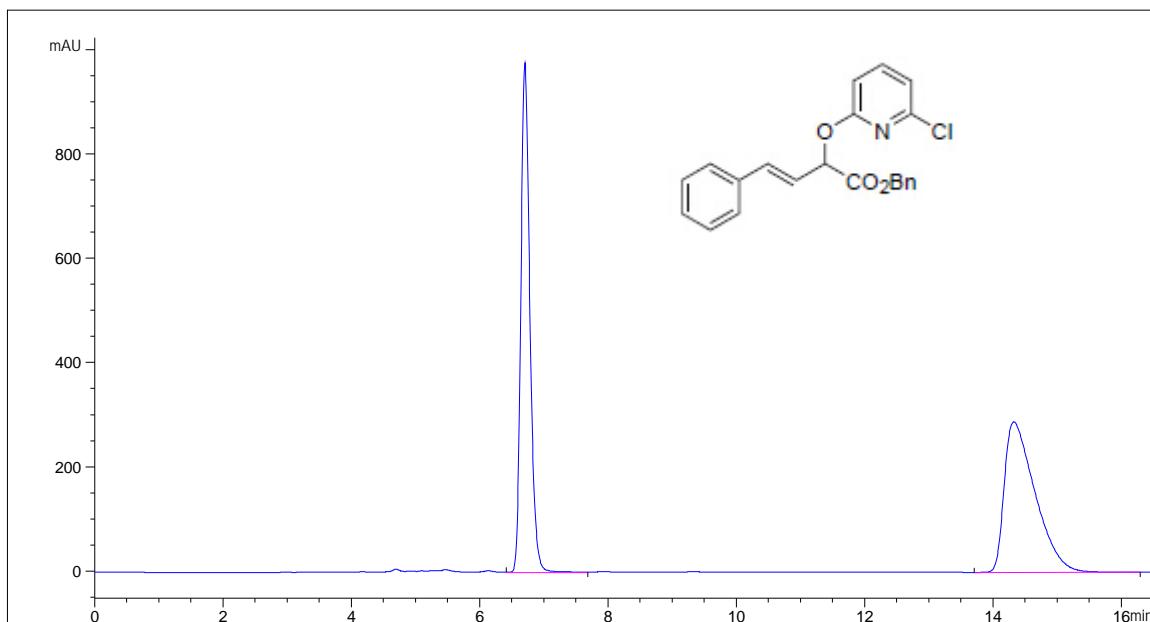
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	12.973	VV	0.2831	7992.72314	51.9296	?
2	20.736	BB	0.6781	7398.73975	48.0704	?



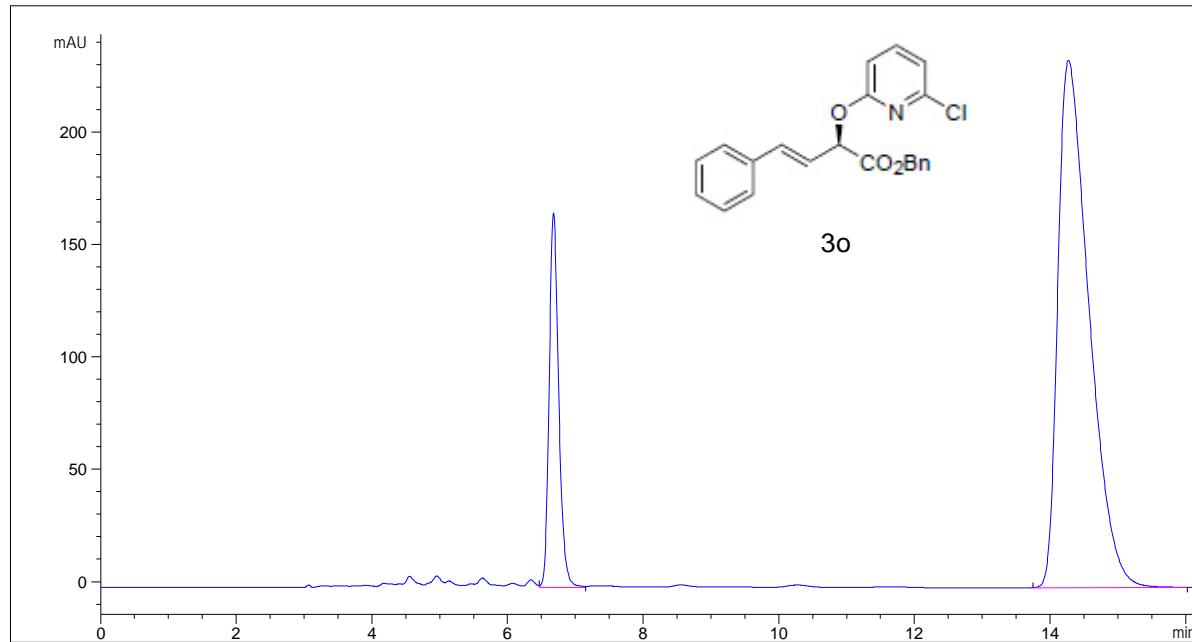
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	13.014	VV	0.2752	7955.31836	13.7476	?
2	19.944	BB	0.8230	4.99116e4	86.2524	?



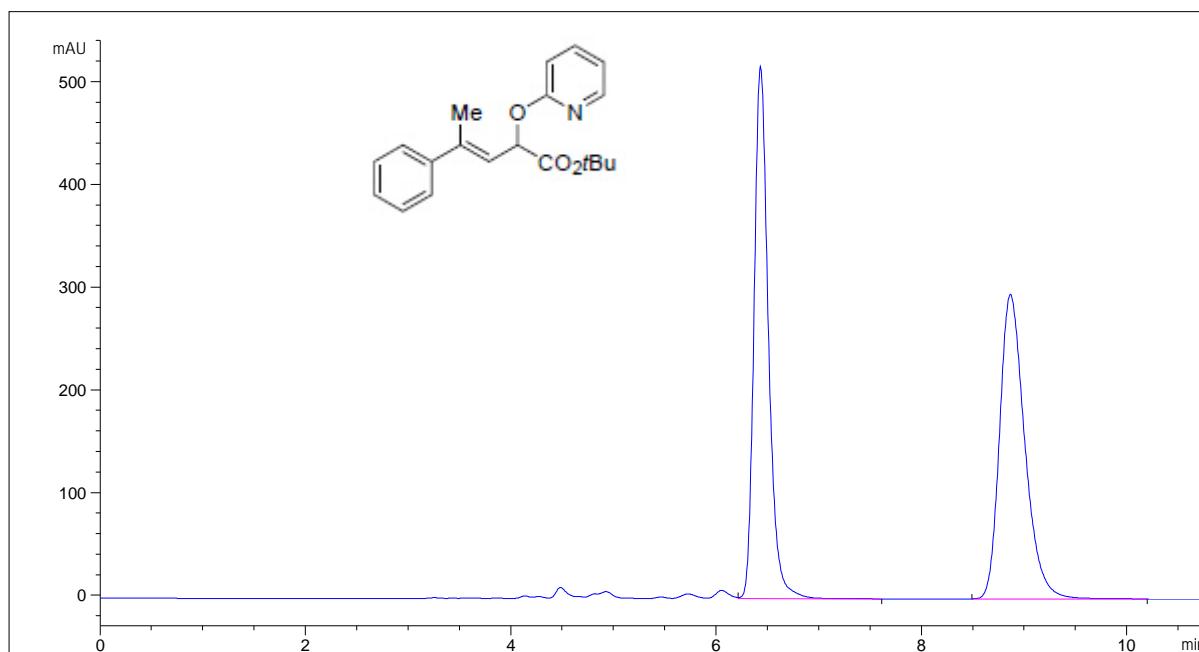
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.706	VB	0.1506	9602.67676	49.9357 ?	
2	14.326	VB	0.5068	9627.40820	50.0643 ?	



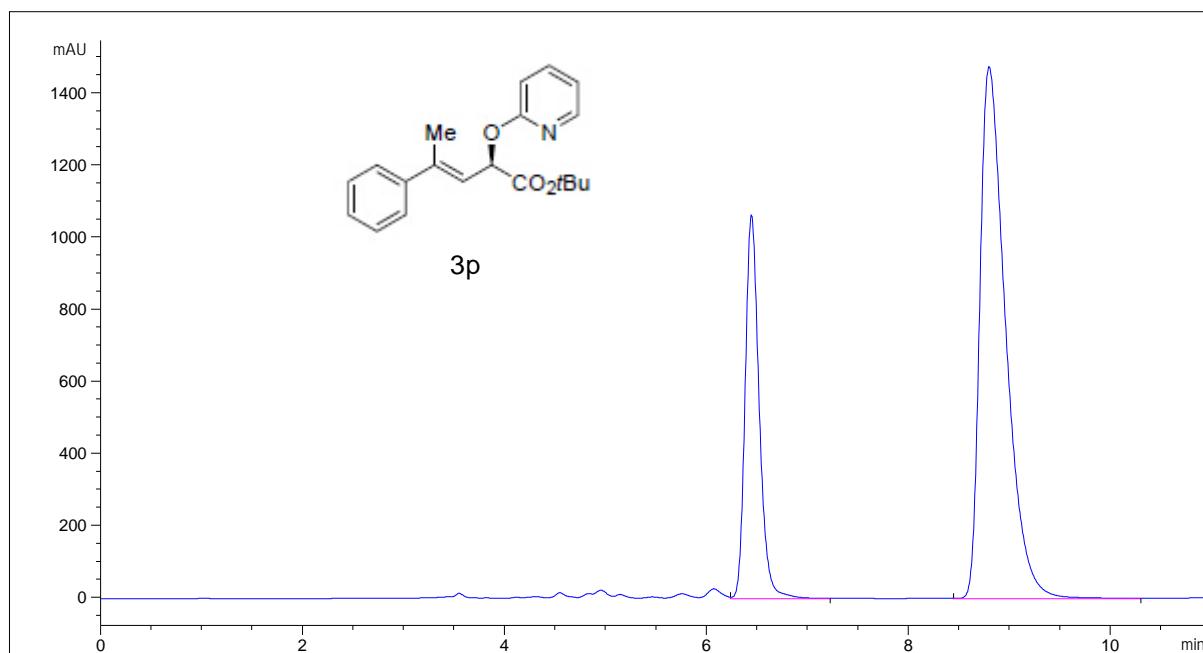
信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.679	VW	0.1507	1637.01379	17.9657 ?	
2	14.272	BB	0.4878	7474.87646	82.0343 ?	



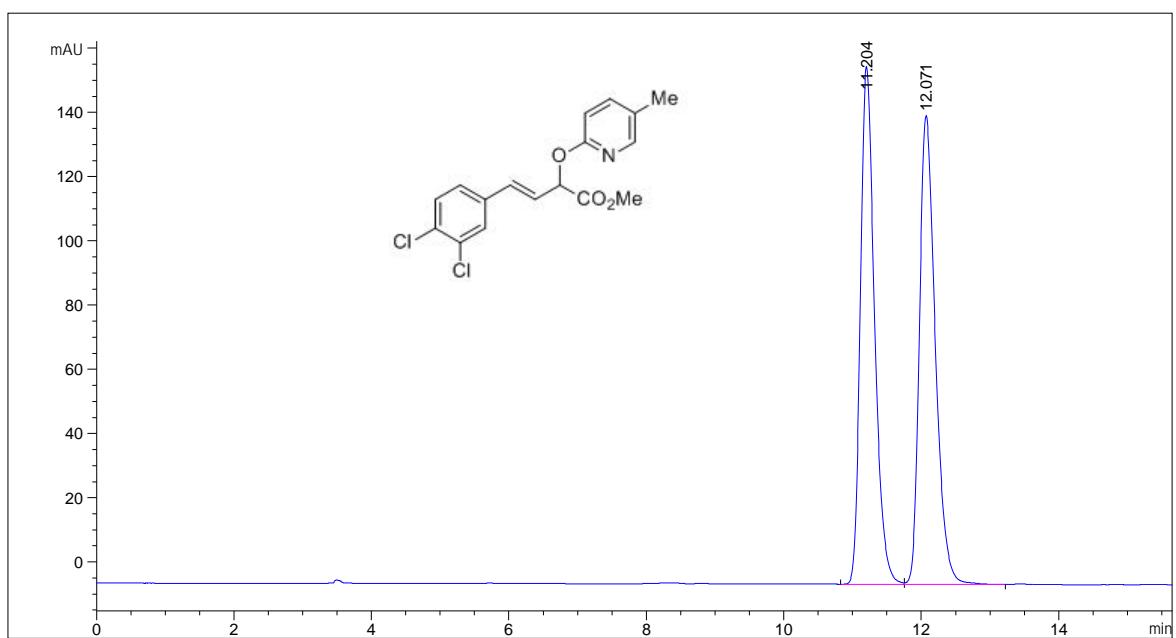
信号 1: DAD1 A, Si g=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.433	VB	0.1496	5044.84180	50.0212	?
2	8.867	BB	0.2604	5040.56250	49.9788	?



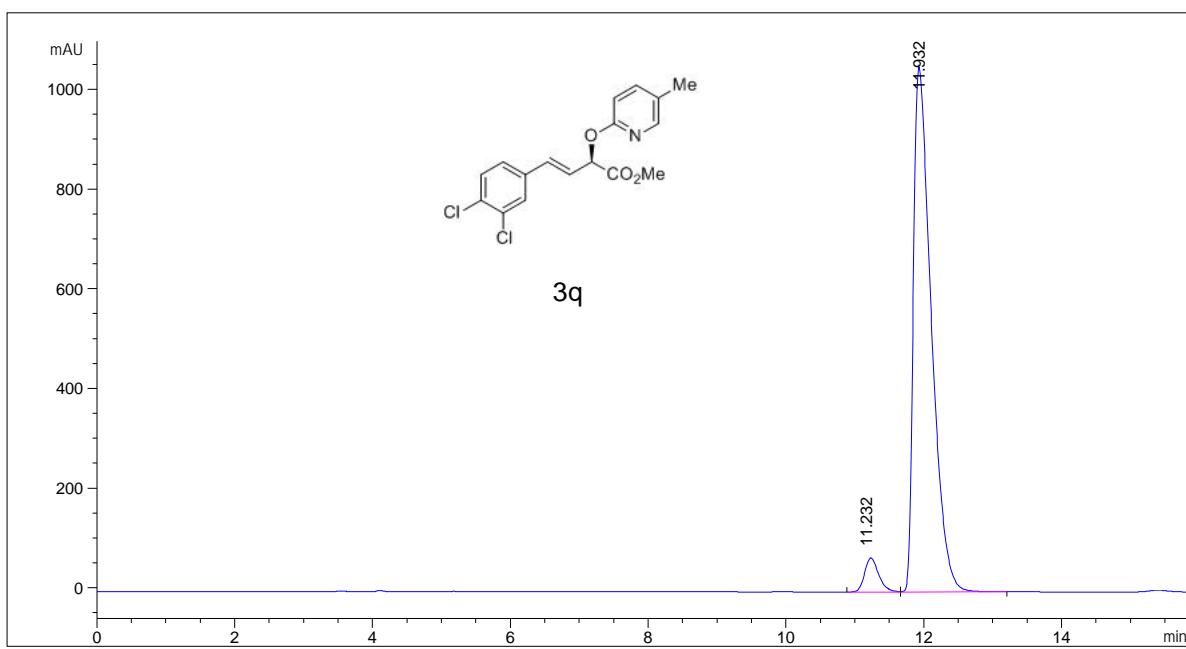
信号 1: DAD1 A, Si g=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰面积 %	名称
1	6.448	VV	0.1488	1.02979e4	28.2676	?
2	8.802	VB	0.2706	2.61321e4	71.7324	?



信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.204	BV	0.2187	2303.74854	161.23346	49.5767
2	12.071	VV	0.2453	2343.09302	145.98354	50.4233



信号 1: DAD1 A, Sig=254, 4 Ref=off

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.232	BV	0.2173	966.39264	68.19072	4.8593
2	11.932	VB	0.2736	1.89210e4	1053.05518	95.1407