

# Supporting Information

## **AlCl<sub>3</sub>-CATALYZED CYCLIZATION OF $\beta$ -KETO DERIVATIVES WITH IN SITU GENERATED ENAMINES UNDER SOLVENT-FREE HIGH SPEED BALL MILLING: AN EFFICIENT ONE-POT ACCESS TO POLYSUBSTITUTED 1,4-DIHYDROPYRIDINES**

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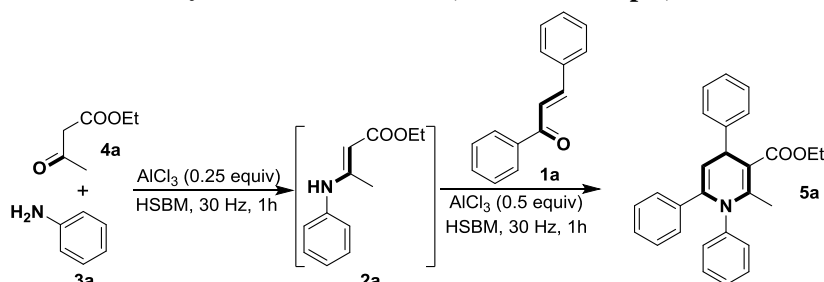
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## 1. Experimental Section

### 1.1 General Information

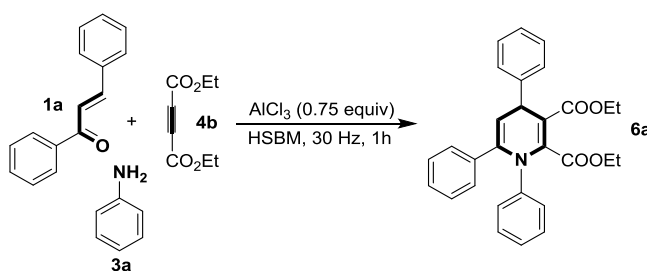
Chalcones **1** and enamine **2a** were prepared according to reported procedures.<sup>1,2</sup> All other chemical reagents were obtained from commercial suppliers and used without further purification. The mixer mill MM 400 (Retsch GmbH, Germany) was used for all ball-milling reactions, and the reaction vessels are titanium-alloyed jars lined with PTFE (neat volume: 4 mL) or stainless jars (neat volume: 25 mL). The milling balls are titanium-alloyed of 6.0 mm in diameter or stainless of 8.0 mm in diameter. Analytical thin-layer chromatography was performed on glass plates pre-coated with silica gel impregnated with a fluorescent indicator (254 nm), and the plates were visualized by exposure to ultraviolet light. Column chromatography was performed on silica gel using EtOAc/petroleum ether as the eluent. Melting points were determined on a XT-4 binocular microscope (Beijing Tech Instrument Co., China) and are uncorrected. <sup>1</sup>H NMR spectra were recorded on a Bruker AV300, AV400 or AV500 NMR instrument. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ 7.26). <sup>13</sup>C NMR spectra were recorded on an NMR instrument operated at 125 MHz or 100 MHz with complete proton decoupling. Chemical shifts are reported in parts per million with the solvent resonance as the internal standard (CDCl<sub>3</sub>, δ 77.16). HR-MS were recorded on a Bruker MicroTOF-QII mass instrument (ESI).

### 1.2 General Procedure for the Synthesis of Product 5 (5a as an Example)



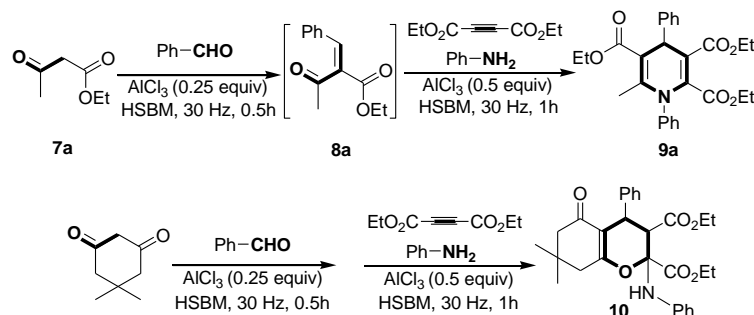
Aniline (**3a**, 0.55 mmol), ethyl acetoacetate (**4a**, 0.55 mmol), AlCl<sub>3</sub> (0.125 mmol), together with two titanium-alloyed balls of 6.0 mm in diameter, were introduced into a titanium-alloyed jar lined with PTFE (4 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 30 minutes. After the vessels were opened, chalcone (**1a**, 0.5 mmol) and AlCl<sub>3</sub> (0.25 mmol) were added into the two parallel jars, respectively. The vessels were sealed again and continued to vibrate for 60 minutes (30 Hz). The resulted mixtures were combined and directly loaded on silica gel chromatography column for purification with EtOAc/petroleum ether as the eluent, affording the desired product **5a** as white solid.

### 1.3 General Procedure for the Synthesis of Product 6 (6a as an Example)



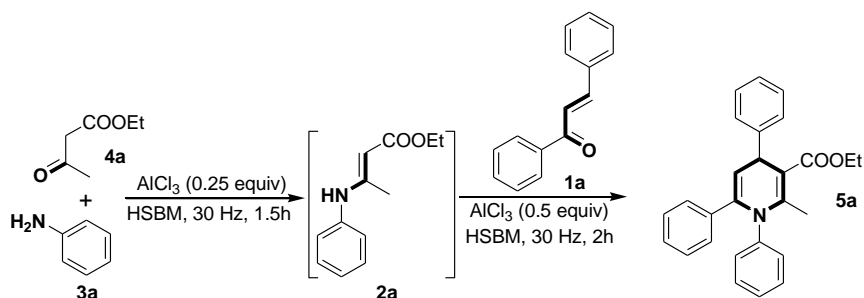
Chalcone (**1a**, 0.5 mmol), aniline (**3a**, 0.55 mmol), diethyl acetylenedicarboxylate (**4b**, 0.55 mmol) and  $\text{AlCl}_3$  (0.375 mmol), together with two titanium-alloyed balls of 6.0 mm in diameter, were introduced into a titanium-alloyed jar lined with PTFE (4 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 60 minutes. The resulted mixtures were combined and directly loaded on silica gel chromatography column for purification with EtOAc/petroleum ether as the eluent, affording the desired product **6a** as white solid.

#### 1.4 General Procedure for the Synthesis of Product 9 and 10 (9a as an Example)



Ethyl acetoacetate (**7a**, 0.5 mmol), benzaldehyde (0.55 mmol) and  $\text{AlCl}_3$  (0.125 mmol), together with two titanium-alloyed balls of 6.0 mm in diameter, were introduced into a titanium-alloyed jar lined with PTFE (4 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 30 minutes. After the vessels were opened, aniline (0.55 mmol), diethyl acetylenedicarboxylate (0.55 mmol) and  $\text{AlCl}_3$  (0.25 mmol) were added into the two parallel jars, respectively. The vessels were sealed again and continued to vibrate for 60 minutes (30 Hz). The resulted mixtures were combined and directly loaded on silica gel chromatography column for purification with EtOAc/petroleum ether as the eluent, affording the desired product **9a** as white solid.

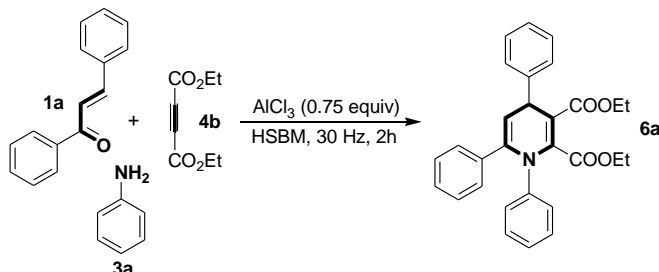
#### 1.5 Gram Scale Synthesis of Product 5a



Aniline (**3a**, 5.5 mmol, 0.512 g), ethyl acetoacetate (**4a**, 5.5 mmol, 0.716 g),  $\text{AlCl}_3$  (1.25 mmol, 0.166 g), together with two stainless balls of 8.0 mm in diameter, were introduced into a stainless jar (25 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 90 minutes. After the vessels were opened, chalcone (**1a**, 5.0 mmol, 1.04 g) and

AlCl<sub>3</sub> (2.5 mmol, 0.333 g) were added into the two parallel jars, respectively. The vessels were sealed again and continued to vibrate for 120 minutes (30 Hz). The resulted mixtures were combined and directly loaded on silica gel chromatography column for purification with EtOAc/petroleum ether as the eluent, affording 3.16 g of the desired product **5a** as white solid (80%).

### 1.6 Gram Scale Synthesis of Product **6a**

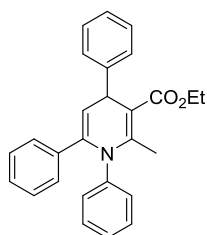


Chalcone (**1a**, 5.0 mmol, 1.04 g), aniline (**3a**, 5.5 mmol, 0.512 g), diethyl acetylenedicarboxylate (**4b**, 5.5 mmol, 0.936 g) and AlCl<sub>3</sub> (3.75 mmol, 0.500 g), together with two stainless balls of 8.0 mm in diameter, were introduced into a stainless jar (25 mL). The same mixture was also introduced into a second parallel jar. The two reaction vessels were sealed with screw caps, fixed on the vibration arms of a ball-milling apparatus (mixer mill MM400, Retsch GmbH, Haan, Germany) and were vibrated vigorously at a rate of 1800 rounds per minute (30 Hz) at room temperature for 120 minutes. The resulted mixtures were combined and directly loaded on silica gel chromatography column for purification with EtOAc/petroleum ether as the eluent, affording 3.66 g of the desired product **6a** as white solid (81%).

### 1.7 References

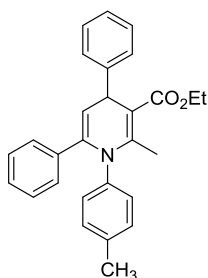
- [1] Zhang, Z.; Dong, Y.-W.; Wang, G.-W. *Chem. Lett.* **2003**, *32*, 966.
- [2] Liu, J.-Y.; Cao, G.-E.; Xu, W.; Cao, J.; Wang, W.-L. *Appl. Organometal. Chem.* **2010**, *24*, 685.

## 2. Spectroscopic Data for Products



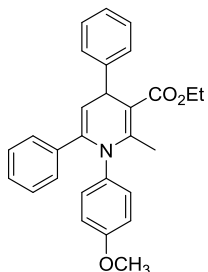
### Ethyl 2-methyl-1,4,6-triphenyl-1,4-dihydropyridine-3-carboxylate (**5a**)

White solid, m.p. 85-87 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49-7.47 (m, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (tt, *J* = 7.2, 1.4 Hz, 1H), 7.20-7.16 (m, 2H), 7.12-7.06 (m, 8H), 5.14 (d, *J* = 6.0 Hz, 1H), 4.79 (d, *J* = 6.0 Hz, 1H), 4.07 (qd, *J* = 7.2, 2.4 Hz, 2H), 2.22 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.0, 149.7, 148.5, 142.0, 140.1, 137.4, 130.7, 129.3, 128.7, 128.5, 127.7, 127.5, 127.3 (2C), 126.2, 110.3, 102.9, 59.7, 40.7, 19.2, 14.3; HRMS (ESI-TOF) *m/z* calcd for C<sub>27</sub>H<sub>26</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 396.1964, found 396.1958.



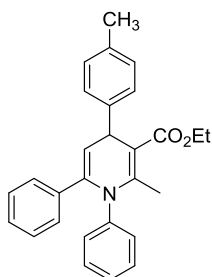
**Ethyl 2-methyl-4,6-diphenyl-1-(p-tolyl)-1,4-dihydropyridine-3-carboxylate (5b)**

White solid, m.p. 102-104 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45 (d, *J* = 7.5 Hz, 2H), 7.38-7.33 (m, 2H), 7.24-7.22 (m, 1H), 7.06 (brs, 5H), 6.97-6.91 (m, 4H), 5.11 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.05 (q, *J* = 6.9 Hz, 2H), 2.22 (s, 3H), 2.19 (s, 3H), 1.15 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ (ppm) 169.4, 150.4, 148.8, 140.5, 139.6, 137.8, 137.4, 130.6, 129.6 (2C), 128.8, 128.0, 127.8, 127.6, 126.5, 110.6, 102.9, 59.9, 40.9, 21.4, 19.5, 14.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 410.2120, found 410.2123.



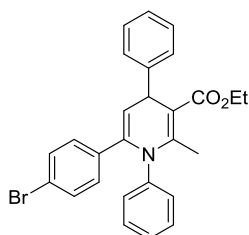
**Ethyl 1-(4-methoxyphenyl)-2-methyl-4,6-diphenyl-1,4-dihydropyridine-3-carboxylate (5c)**

Slightly yellow solid, m.p. 108-110 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.47 (d, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 7.07 (brs, 5H), 6.97 (dt, *J* = 8.8, 2.8 Hz, 2H), 6.68 (dt, *J* = 9.2, 2.8 Hz, 2H), 5.11 (d, *J* = 6.0 Hz, 1H), 4.78 (d, *J* = 6.0 Hz, 1H), 4.06 (qd, *J* = 7.2, 2.2 Hz, 2H), 3.70 (s, 3H), 2.20 (s, 3H), 1.16 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.0, 158.3, 150.3, 148.6, 140.4, 137.5, 134.7, 131.5, 129.3, 128.5, 127.7, 127.5, 127.3, 126.2, 113.8, 110.1, 102.6, 59.6, 55.4, 40.6, 19.1, 14.3; HRMS (ESI-TOF) *m/z* calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>3</sub> [M+H]<sup>+</sup> 426.2069, found 426.2066.



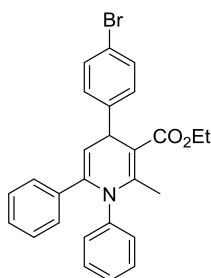
**Ethyl 2-methyl-1,6-diphenyl-4-(p-tolyl)-1,4-dihydropyridine-3-carboxylate (5d)**

White solid, m.p. 89-91 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.37 (d, *J* = 8.0 Hz, 2H), 7.20-7.16 (m, 4H), 7.12-7.03 (m, 8H), 5.13 (d, *J* = 6.0 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 4.12-4.03 (m, 2H), 2.36 (s, 3H), 2.20 (s, 3H), 1.19 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 169.1, 149.5, 145.6, 142.0, 140.1, 137.5, 135.7, 130.7, 129.3, 129.2, 128.7, 127.6, 127.5, 127.3 (2C), 110.5, 103.1, 59.7, 40.2, 21.2, 19.2, 14.4; HRMS (ESI-TOF) *m/z* calcd for C<sub>28</sub>H<sub>28</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 410.2120, found 410.2115.



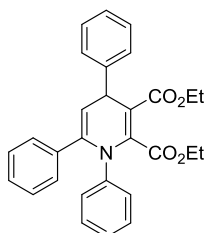
**Ethyl 6-(4-bromophenyl)-2-methyl-1,4-diphenyl-1,4-dihydropyridine-3-carboxylate (5e)**

Slightly yellow solid, m.p. 101-103 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45-7.43 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.25-7.12 (m, 6H), 7.07-7.04 (m, 2H), 6.93 (dt, *J* = 8.4, 2.1 Hz, 2H), 5.12 (d, *J* = 6.0 Hz, 1H), 4.76 (d, *J* = 6.0 Hz, 1H), 4.05 (qd, *J* = 7.2, 2.2 Hz, 2H), 2.20 (s, 3H), 1.14 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 168.9, 149.6, 148.2, 141.8, 139.1, 136.4, 130.8 (2C), 130.6, 128.9, 128.6, 127.7, 127.6, 126.3, 121.5, 110.9, 103.1, 59.7, 40.7, 19.1, 14.3; HRMS (ESI-TOF) *m/z* calcd for C<sub>27</sub>H<sub>25</sub>Br NO<sub>2</sub> [M+H]<sup>+</sup> 474.1069, found 474.1073.



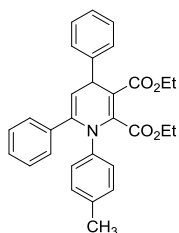
**Ethyl 4-(4-bromophenyl)-2-methyl-1,6-diphenyl-1,4-dihydropyridine-3-carboxylate (5f)**

White solid, m.p. 147-149 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.48 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.33 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.19-7.16 (m, 2H), 7.12-7.02 (m, 8H), 5.08 (d, *J* = 6.0 Hz, 1H), 4.74 (d, *J* = 6.0 Hz, 1H), 4.11-4.03 (m, 2H), 2.20 (s, 3H), 1.16 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 168.8, 150.0, 147.6, 141.7, 140.4, 137.2, 131.6, 130.6, 129.4, 129.3, 128.7, 127.6, 127.5, 127.4, 120.0, 109.7, 102.2, 59.8, 40.2, 19.2, 14.4; HRMS (ESI-TOF) *m/z* calcd for C<sub>27</sub>H<sub>25</sub>Br NO<sub>2</sub> [M+H]<sup>+</sup> 474.1069, found 474.1074.



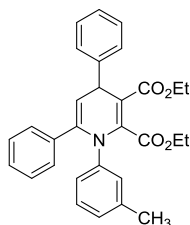
**Diethyl 1,4,6-triphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6a)**

White solid, m.p. 85-87 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.15-7.14 (m, 4H), 7.12-7.03 (m, 6H), 5.14 (d, *J* = 5.6 Hz, 1H), 4.75 (d, *J* = 5.2 Hz, 1H), 4.03 (qd, *J* = 7.2, 1.2 Hz, 2H), 4.01-3.89 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 164.9, 147.3, 145.5, 140.5, 139.2, 136.1 (2C overlapped), 130.1, 129.1, 128.6 (2C), 128.0, 127.8, 127.7, 126.6, 110.8, 102.3, 61.6, 60.3, 39.9, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>28</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 454.2018, found 454.2019.



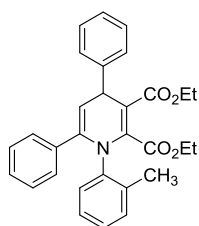
**Diethyl 4,6-diphenyl-1-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6b)**

White solid, m.p. 102-104 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49 (d, *J* = 7.6 Hz, 2H), 7.38 (t, *J* = 7.4 Hz, 2H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.09-7.05 (m, 5H), 7.02 (d, *J* = 8.4 Hz, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 5.12 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.2 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.98-3.89 (m, 2H), 2.20 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.99 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 164.9, 147.3, 145.6, 139.2, 137.7, 137.6, 136.1, 129.7, 129.1, 129.0, 128.5, 127.9, 127.6, 127.5, 126.5, 110.7, 102.0, 61.5, 60.2, 39.8, 21.0, 14.0, 13.5; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 468.2175, found 468.2167.



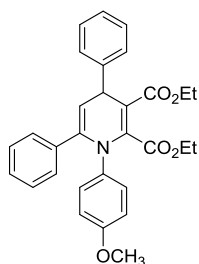
**Diethyl 4,6-diphenyl-1-(m-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6c)**

Slightly yellow solid, m.p. 101-103 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49 (d, *J* = 6.8 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.25 (t, *J* = 7.6 Hz, 1H), 7.08-7.05 (m, 5H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.90 (d, *J* = 7.6 Hz, 1H), 5.13 (d, *J* = 5.6 Hz, 1H), 4.75 (d, *J* = 5.6 Hz, 1H), 4.03 (qd, *J* = 7.2, 1.4 Hz, 2H), 4.01-3.89 (m, 2H), 2.20 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H), 0.97 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.8, 165.0, 147.4, 145.6, 140.3, 139.2, 138.4, 136.2, 130.6, 129.1, 128.6, 128.5, 128.3, 128.0, 127.7 (2C), 127.0, 126.6, 110.8, 102.2, 61.6, 60.3, 39.9, 21.2, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 468.2175, found 468.2170.



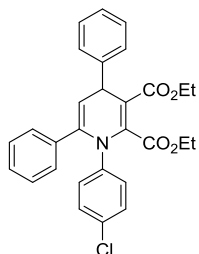
**Diethyl 4,6-diphenyl-1-(o-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6d)**

Slightly yellow solid, m.p. 51-53 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (t, *J* = 8.4 Hz, 2H), 7.40-7.34 (m, 3H), 7.24-7.21 (m, 1H), 7.15 (d, *J* = 8.0 Hz, 1H), 7.07-7.02 (m, 6H), 6.98 (t, *J* = 7.6 Hz, 1H), 5.04 (d, *J* = 5.6 Hz, 0.66H), 5.00 (d, *J* = 4.4 Hz, 0.34H), 4.85 (d, *J* = 5.2 Hz, 0.66H), 4.80 (d, *J* = 4.4 Hz, 0.34H), 4.04-3.81 (m, 4H), 2.34 (s, 2H), 2.19 (s, 1H), 1.07 (t, *J* = 7.2 Hz, 2H), 1.05 (t, *J* = 7.2 Hz, 1H), 0.91 (t, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 1H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 167.0, 166.9, 164.6, 164.5, 148.0, 147.7, 145.2, 145.0, 138.9, 138.8, 138.5 (2C), 138.2, 135.9, 135.6, 132.3, 132.2, 130.7, 130.5, 129.3, 129.0, 128.9, 128.8, 128.5 (2C), 128.3, 128.1, 128.0, 127.8, 127.6, 127.4 (2C), 126.4 (2C), 125.7 (2C), 110.1, 109.7, 100.7, 100.0, 61.5, 61.4, 61.2 (2C), 40.4, 40.1, 27.0, 18.6, 18.2, 14.1, 14.0, 13.5; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 468.2175, found 468.2172.



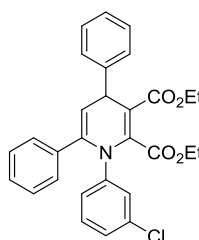
**Diethyl 1-(4-methoxyphenyl)-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6e)**

White solid, m.p. 95-97 °C; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (d, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.5 Hz, 2H), 7.27 (d, *J* = 6.0 Hz, 1H), 7.06-7.14 (m, 7H), 6.67 (d, *J* = 8.7 Hz, 2H), 5.11 (d, *J* = 5.4 Hz, 1H), 4.75 (d, *J* = 5.4 Hz, 1H), 3.95-4.08 (m, 4H), 3.71 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 164.9, 158.7, 147.5, 145.8, 139.4, 136.1, 133.0, 131.3, 129.1, 128.6, 128.0, 127.7 (2C), 126.5, 113.6, 110.5, 101.9, 61.6, 60.3, 55.4, 39.8, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 484.2124, found 484.2129.



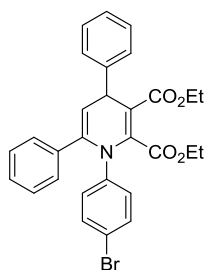
**Diethyl 1-(4-chlorophenyl)-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6f)**

Slightly yellow solid, m.p. 84-86 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.46 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.2 Hz, 1H), 7.14-7.05 (m, 9H), 5.16 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.5 Hz, 1H), 4.05-3.94 (m, 4H), 1.09 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.5, 164.8, 147.0, 145.1, 139.2, 138.9, 135.8, 133.6, 131.3, 129.0, 128.8, 128.7, 128.0, 127.9 (2C), 126.7, 111.2, 103.1, 61.8, 60.4, 39.8, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>ClNO<sub>4</sub> [M+H]<sup>+</sup> 488.1629, found 488.1636.



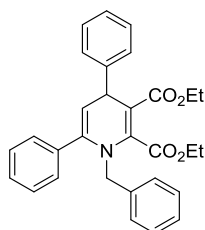
**Diethyl 1-(3-chlorophenyl)-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6g)**

Slightly yellow solid, m.p. 80-82 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.46 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19-7.08 (m, 9H), 5.18 (d, *J* = 5.6 Hz, 1H), 4.75 (d, *J* = 5.6 Hz, 1H), 4.09-3.97 (m, 4H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.04 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.5, 164.8, 146.9, 145.0, 141.8, 138.8, 135.7, 134.1, 130.1, 129.6, 128.9, 128.7, 128.3, 128.1, 128.0 (2C), 127.9, 126.7, 111.4, 103.3, 61.9, 60.5, 39.9, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>ClNO<sub>4</sub> [M+H]<sup>+</sup> 488.1629, found 488.1632.



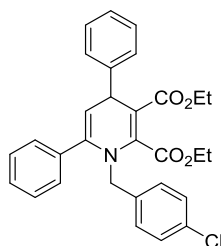
**Diethyl 1-(4-bromophenyl)-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6h)**

Slightly yellow solid, m.p. 85-87 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.46 (dd, *J* = 8.2, 1.4 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.28 (dt, *J* = 8.8, 2.4 Hz, 2H), 7.25-7.23 (m, 1H), 7.06-7.11 (m, 5H), 7.03 (dt, *J* = 8.8, 2.4 Hz, 2H), 5.17 (d, *J* = 5.2 Hz, 1H), 4.75 (d, *J* = 5.2 Hz, 1H), 4.04 (qd, *J* = 7.2, 1.4 Hz, 2H), 3.94-4.05 (m, 2H), 1.10 (t, *J* = 7.0 Hz, 3H), 1.03 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.5, 164.9, 147.0, 145.1, 139.7, 138.8, 135.8, 131.8, 131.6, 129.0, 128.7, 128.0 (2C), 127.9, 126.7, 121.7, 111.3, 103.2, 61.9, 60.5, 39.8, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 532.1123, found 532.1133.



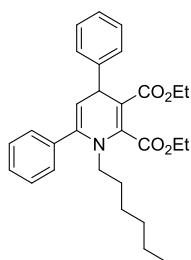
**Diethyl 1-benzyl-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6i)**

White solid, m.p. 83-85 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.34-7.35 (m, 3H), 7.19-7.28 (m, 5H), 7.12-7.13 (m, 3H), 6.97-7.02 (m, 4H), 5.06 (d, *J* = 6.4 Hz, 1H), 4.58 (d, *J* = 6.4 Hz, 1H), 4.52 (d, *J* = 15.6 Hz, 1H), 4.33-4.47 (m, 2H), 4.31 (d, *J* = 15.2 Hz, 1H), 4.08 (q, *J* = 7.2 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 3H), 1.17 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 165.9, 145.8, 145.5, 139.8, 136.8, 135.7, 128.9, 128.7, 128.6, 128.5 (2C overlapped), 128.3, 128.2, 127.9, 126.3, 112.4, 104.8, 62.3, 60.5, 51.8, 39.3, 14.3, 14.0; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 468.2175, found 468.2169.



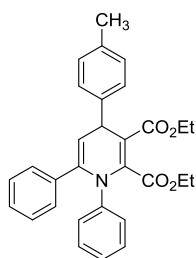
**Diethyl 1-(4-chlorobenzyl)-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6j)**

White solid, m.p. 89-91 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.38-7.36 (m, 3H), 7.29-7.27 (m, 2H), 7.18-7.15 (m, 5H), 6.98 (d, *J* = 2.0 Hz, 1H), 6.97-6.96 (m, 1H), 6.91 (dt, *J* = 8.4, 2.2 Hz, 2H), 5.11 (d, *J* = 6.4 Hz, 1H), 4.60 (d, *J* = 6.4 Hz, 1H), 4.49 (d, *J* = 15.6 Hz, 1H), 4.48-4.35 (m, 2H), 4.27 (d, *J* = 15.6 Hz, 1H), 4.10 (q, *J* = 7.2 Hz, 2H), 1.38 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 165.6, 164.9, 144.6, 144.2, 138.6, 134.5, 134.2, 132.8, 129.1, 127.8, 127.7 (2C), 127.6, 127.2, 127.1, 125.5, 111.7, 104.4, 61.4, 59.6, 50.0, 38.0, 13.2, 13.1; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>ClNO<sub>4</sub> [M+H]<sup>+</sup> 502.1785, found 502.1781.



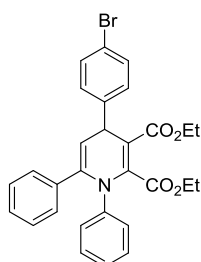
**Diethyl 1-hexyl-4,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6k)**

Slightly yellow solid, m.p. 56-58 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.39 (d, *J* = 6.8 Hz, 2H), 7.35-7.29 (m, 7H), 7.22 (t, *J* = 7.2 Hz, 1H), 5.08 (d, *J* = 6.4 Hz, 1H), 4.64 (d, *J* = 6.4 Hz, 1H), 4.46 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.35 (dq, *J* = 10.8, 7.2 Hz, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 3.30 (ddd, *J* = 15.0, 9.6, 5.8 Hz, 1H), 3.09 (ddd, *J* = 15.0, 9.6, 5.4 Hz, 1H), 1.52-1.48 (m, 1H), 1.44-1.35 (m, 1H), 1.40 (t, *J* = 7.2 Hz, 3H), 1.16 (t, *J* = 7.0 Hz, 3H), 1.11 (t, *J* = 7.4 Hz, 2H), 1.02-0.96 (m, 4H), 0.78 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 165.9, 146.9, 145.9, 139.7, 135.7, 128.8, 128.4 (3C), 127.8, 126.4, 111.5, 103.0, 62.1, 60.3, 48.5, 39.0, 31.2, 30.2, 26.2, 22.4, 14.2, 14.1, 14.0; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>36</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 462.2644, found 462.2653.



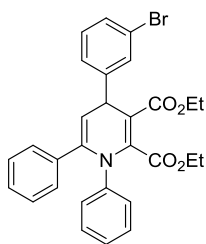
**Diethyl 1,6-diphenyl-4-(p-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6l)**

White solid, m.p. 104-106 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.40 (d, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 7.17-7.15 (m, 4H), 7.10-7.05 (m, 6H), 5.14 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 1H), 4.05 (q, *J* = 7.2 Hz, 2H), 4.01-3.90 (m, 2H), 2.37 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 165.0, 145.3, 144.5, 140.5, 139.1, 136.1 (2C), 130.1, 129.3, 129.1, 128.6, 127.9, 127.8, 127.7 (2C), 111.0, 102.5, 61.6, 60.3, 39.4, 21.2, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 468.2175, found 468.2172.



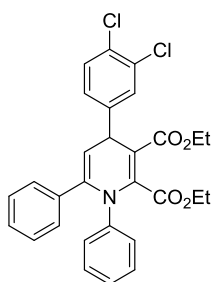
**Diethyl 4-(4-bromophenyl)-1,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6m)**

white solid, m.p. 99-101 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.3 Hz, 2H), 7.17-7.10 (m, 5H), 7.06 (brs, 5H), 5.09 (d, *J* = 5.2 Hz, 1H), 4.73 (d, *J* = 5.6 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.00-3.87 (m, 2H), 1.11 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.5, 164.7, 146.4, 145.7, 140.2, 139.5, 135.8, 131.7, 130.1, 129.7, 129.1, 128.6, 128.0, 127.8 (2C), 120.4, 110.1, 101.7, 61.7, 60.4, 39.4, 14.2, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 532.1123, found 532.1128.



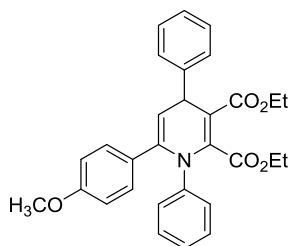
**Diethyl 4-(3-bromophenyl)-1,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6n)**

white solid, m.p. 98-100 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.61 (s, 1H), 7.44 (d, *J* = 7.6 Hz, 1H), 7.37 (d, *J* = 8.0 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.14-7.06 (m, 10H), 5.09 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.07-3.88 (m, 4H), 1.13 (t, *J* = 7.0 Hz, 3H), 0.94 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 164.6, 149.5, 145.7, 140.1, 139.7, 135.7, 131.1, 130.3, 130.1, 129.6, 129.1, 128.6, 128.0, 127.8, 127.7, 126.6, 122.7, 109.9, 101.5, 61.7, 60.4, 39.6, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 532.1123, found 532.1126.



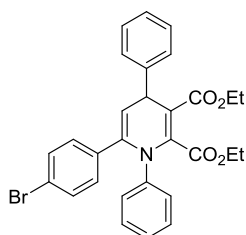
**Diethyl 4-(3,4-dichlorophenyl)-1,6-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6o)**

white solid, m.p. 79-81 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.56 (d, *J* = 2.0 Hz, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.2, 1.8 Hz, 1H), 7.16-7.07 (m, 10H), 5.07 (d, *J* = 5.2 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.10-4.03 (m, 2H), 4.01-3.87 (m, 2H), 1.15 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.3, 164.5, 147.5, 145.8, 140.0, 139.9, 135.6, 132.5, 130.7, 130.5, 130.1, 129.9, 129.1, 128.7, 128.1, 128.0, 127.8, 127.4, 109.4, 101.2, 61.8, 60.6, 39.2, 14.2, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>26</sub>Cl<sub>2</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 522.1239, found 522.1248.



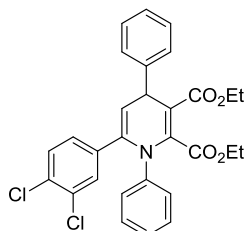
**Diethyl 6-(4-methoxyphenyl)-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6p)**

Slightly yellow solid, m.p. 84-86 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (dd, *J* = 8.0, 1.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.25 (tt, *J* = 7.4, 1.4 Hz, 1H), 7.17-7.10 (m, 5H), 7.01 (dt, *J* = 8.8, 2.4 Hz, 2H), 6.58 (dt, *J* = 9.2, 2.6 Hz, 2H), 5.11 (d, *J* = 5.6 Hz, 1H), 4.75 (d, *J* = 5.6 Hz, 1H), 4.04 (dd, *J* = 7.2, 1.2 Hz, 2H), 4.02-3.90 (m, 2H), 3.66 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 165.0, 158.9, 147.4, 145.5, 140.6, 138.8, 130.3, 130.1, 128.6 (2C), 128.5, 127.9, 127.8, 126.5, 113.1, 110.2, 102.2, 61.6, 60.3, 55.1, 39.9, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>30</sub>NO<sub>5</sub> [M+H]<sup>+</sup> 484.2124, found 484.2125.



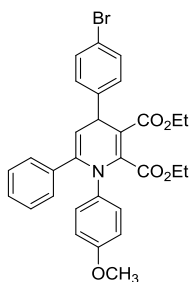
**Diethyl 6-(4-bromophenyl)-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6q)**

Slightly yellow solid, m.p. 95-97 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.47 (d, *J* = 7.2 Hz, 2H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.24 (t, *J* = 7.4 Hz, 1H), 7.18 (d, *J* = 6.8 Hz, 2H), 7.17-7.14 (m, 4H), 7.12 (dt, *J* = 8.3, 1.9 Hz, 1H), 6.95 (d, *J* = 8.8 Hz, 2H), 5.13 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.02 (qd, *J* = 7.2, 1.6 Hz, 2H), 4.00-3.88 (m, 2H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 164.7, 147.0, 145.3, 140.2, 138.1, 135.0, 130.9, 130.5, 129.8, 128.7, 128.6, 128.0, 127.8, 126.6, 121.8, 111.3, 102.6, 61.6, 60.3, 39.8, 14.0, 13.5; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>27</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 532.1123, found 532.1126.



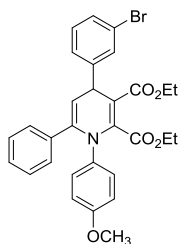
**Diethyl 6-(3,4-dichlorophenyl)-1,4-diphenyl-1,4-dihydropyridine-2,3-dicarboxylate (6r)**

Slightly yellow solid, m.p. 75-77 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.46 (d, *J* = 7.2 Hz, 2H), 7.39 (t, *J* = 7.6 Hz, 2H), 7.28-7.11 (m, 9H), 5.17 (d, *J* = 5.6 Hz, 1H), 4.74 (d, *J* = 5.6 Hz, 1H), 4.05-3.89 (m, 4H), 1.09 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 164.8, 146.8, 145.4, 140.2, 137.2, 136.1, 132.0, 131.9, 130.7, 129.8, 129.7, 129.0, 128.8, 128.3, 128.1, 127.9, 126.8, 112.1, 102.9, 61.8, 60.5, 39.8, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>26</sub>Cl<sub>2</sub>NO<sub>4</sub> [M+H]<sup>+</sup> 522.1239, found 522.1250.



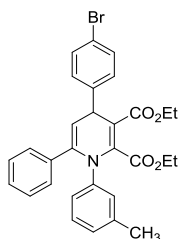
**Diethyl 4-(4-bromophenyl)-1-(4-methoxyphenyl)-6-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (6s)**

Slightly yellow solid, m.p. 92-94 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (dt, *J* = 8.4, 2.2 Hz, 2H), 7.36 (dt, *J* = 8.4, 2.1 Hz, 2H), 7.07-7.09 (m, 5H), 7.03 (d, *J* = 8.8 Hz, 2H), 6.64 (dt, *J* = 8.8, 2.8 Hz, 2H), 5.05 (d, *J* = 5.6 Hz, 1H), 4.71 (d, *J* = 5.6 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.01-3.91 (m, 2H), 3.68 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.5, 164.7, 158.8, 146.6, 146.0, 139.8, 135.9, 132.8, 131.7, 131.3, 129.6, 129.2, 127.8 (2C), 120.4, 113.7, 109.7, 101.4, 61.7, 60.4, 55.4, 39.4, 14.2, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup> 562.1229, found 562.1236.



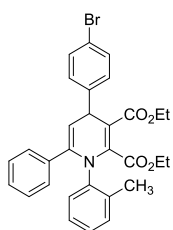
**Diethyl 4-(3-bromophenyl)-1-(4-methoxyphenyl)-6-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (6t)**

White solid, m.p. 85-87 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.61 (s, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 7.37 (d, *J* = 7.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.08 (brs, 5H), 7.05 (d, *J* = 8.4 Hz, 2H), 6.65 (d, *J* = 8.4 Hz, 2H), 5.05 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 5.2 Hz, 1H), 4.07-3.93 (m, 4H), 3.68 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.00 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 164.6, 158.7, 149.6, 146.0, 139.9, 135.8, 132.6, 131.2, 131.0, 130.2, 129.5, 129.1, 127.7 (2C), 126.6, 122.6, 113.6, 109.5, 101.2, 61.6, 60.3, 55.3, 39.5, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>BrNO<sub>5</sub> [M+H]<sup>+</sup> 562.1229, found 562.1234.



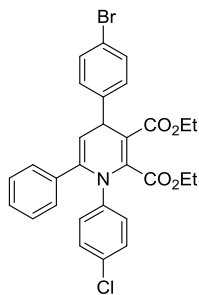
**Diethyl 4-(4-bromophenyl)-6-phenyl-1-(m-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6u)**

Slightly yellow solid, m.p. 81-83 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.49 (dt, *J* = 8.8, 1.9 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.07-7.03 (m, 5H), 7.01 (t, *J* = 7.6 Hz, 1H), 6.92 (s, 1H), 6.90 (t, *J* = 7.6 Hz, 2H), 5.07 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 4.00-3.88 (m, 2H), 2.19 (s, 3H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.96 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 164.6, 146.4, 145.7, 140.1, 139.5, 138.4, 135.9, 131.7, 130.5, 129.6, 129.0, 128.6, 128.3, 127.7, 127.6, 127.0, 120.3, 110.0, 101.5, 61.6, 60.3, 39.4, 21.1, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 546.1280, found 546.1284.



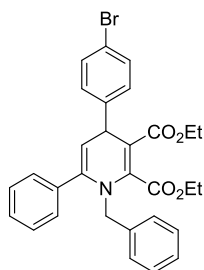
**Diethyl 4-(4-bromophenyl)-6-phenyl-1-(o-tolyl)-1,4-dihydropyridine-2,3-dicarboxylate (6v)**

White solid, m.p. 121-123 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.52-7.46 (m, 2H), 7.39-7.31 (m, 2H), 7.15-6.90 (m, 9H), 4.99 (d, *J* = 5.2 Hz, 0.66H), 4.95 (d, *J* = 4.4 Hz, 0.34H), 4.82 (d, *J* = 5.6 Hz, 0.66H), 4.78 (d, *J* = 4.4 Hz, 0.34H), 4.06-4.00 (m, 2H), 3.95-3.80 (m, 2H), 2.30 (s, 2H), 2.17 (s, 1H), 1.09 (t, *J* = 7.2 Hz, 2H), 1.08 (t, *J* = 7.2 Hz, 1H), 0.93-0.88 (m, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.7, 166.6, 164.3, 164.2, 147.1, 146.7, 145.3, 145.2, 139.2, 138.9, 138.8, 138.6, 138.3, 138.0, 135.6, 135.4, 132.2, 131.6, 131.5, 130.7, 130.5, 129.8, 129.6, 129.2, 129.0, 128.8, 127.9, 127.8, 127.5, 127.4, 125.8, 125.7, 120.3, 120.2, 109.4, 109.0, 100.2, 99.5, 61.6, 61.5, 60.3 (2C), 39.9, 39.6, 18.6, 18.2, 14.1 (2C), 13.5; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 546.1280, found 546.1283.



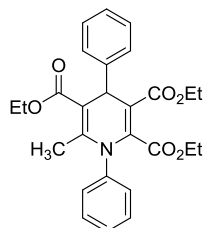
**Diethyl 4-(4-bromophenyl)-1-(4-chlorophenyl)-6-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (6w)**

Slightly yellow solid, m.p. 87-89 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.50 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.14-7.03 (m, 9H), 5.11 (d, *J* = 5.6 Hz, 1H), 4.72 (d, *J* = 5.6 Hz, 1H), 4.04 (q, *J* = 7.2 Hz, 2H), 4.04-3.94 (m, 2H), 1.12 (t, *J* = 7.2 Hz, 3H), 1.02 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.3, 164.6, 146.1, 145.3, 139.2, 138.9, 135.5, 133.8, 131.8, 131.3, 129.6, 129.0, 128.9, 128.1, 128.0, 120.5, 110.5, 102.5, 61.9, 60.6, 39.3, 14.1, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>26</sub>BrClNO<sub>4</sub> [M+H]<sup>+</sup> 566.0734, found 566.0741.



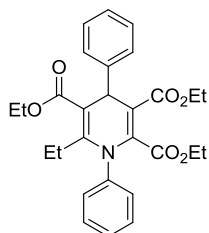
**Diethyl 1-benzyl-4-(4-bromophenyl)-6-phenyl-1,4-dihydropyridine-2,3-dicarboxylate (6x)**

White solid, m.p. 90-92 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.38-7.37 (m, 3H), 7.29-7.28 (m, 3H), 7.25-7.20 (m, 4H), 6.97 (d, *J* = 7.2 Hz, 2H), 6.83 (d, *J* = 8.4 Hz, 2H), 5.04 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 6.4 Hz, 1H), 4.53 (d, *J* = 15.6 Hz, 1H), 4.48-4.38 (m, 2H), 4.29 (d, *J* = 15.6 Hz, 1H), 4.09 (q, *J* = 7.2 Hz, 2H), 1.37 (t, *J* = 7.0 Hz, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 166.4, 165.7, 145.6, 144.8, 140.2, 136.6, 135.4, 131.2, 130.0, 128.9, 128.8, 128.6 (2C), 128.1, 120.2, 111.9, 104.6, 62.4, 60.6, 51.8, 38.7, 14.3, 14.0; HRMS (ESI-TOF) *m/z* calcd for C<sub>30</sub>H<sub>29</sub>BrNO<sub>4</sub> [M+H]<sup>+</sup> 546.1280, found 546.1283.



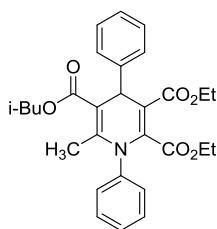
**Triethyl 6-methyl-1,4-diphenyl-1,4-dihydropyridine-2,3,5-tricarboxylate (9a)**

White solid, m.p. 72-74 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45-7.41 (m, 5H), 7.34-7.26 (m, 4H), 7.22-7.19 (m, 1H), 5.12 (s, 1H), 4.12 (q, *J* = 7.2 Hz, 2H), 4.10-4.06 (m, 2H), 3.94-3.79 (m, 2H), 2.07 (s, 3H), 1.23 (t, *J* = 7.0 Hz, 3H), 1.18 (t, *J* = 7.0 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 167.7, 165.9, 164.1, 146.4, 146.1, 142.7, 138.7, 130.8, 129.4, 129.2, 128.3, 128.1, 126.7, 106.5, 105.4, 61.7, 60.7, 60.3, 38.5, 18.0, 14.3, 14.1, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>27</sub>H<sub>30</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 464.2073, found 464.2065.



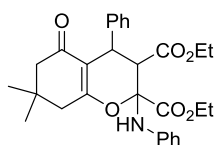
**Triethyl 6-ethyl-1,4-diphenyl-1,4-dihydropyridine-2,3,5-tricarboxylate (9b)**

White solid, m.p. 89-91 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45-7.41 (m, 5H), 7.34-7.30 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.13 (s, 1H), 4.13 (q, *J* = 7.2 Hz, 2H), 4.10 (qd, *J* = 7.2, 2.8 Hz, 2H), 3.94-3.78 (m, 2H), 2.71-2.62 (m, 1H), 2.47-2.38 (m, 1H), 1.24 (t, *J* = 7.2 Hz, 3H), 1.19 (t, *J* = 7.2 Hz, 3H), 0.95 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 167.1, 165.9, 164.2, 152.4, 146.2, 143.1, 138.4, 130.9, 129.4, 129.2, 128.3, 128.0, 126.7, 105.8, 105.6, 61.7, 60.7, 60.2, 38.2, 23.0, 14.3, 14.2, 13.6 (2C); HRMS (ESI-TOF) *m/z* calcd for C<sub>28</sub>H<sub>32</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 478.2230, found 478.2226.



**2,3-diethyl 5-isobutyl 6-methyl-1,4-diphenyl-1,4-dihydropyridine-2,3,5-tricarboxylate (9c)**

White solid, m.p. 95-97 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.45-7.41 (m, 5H), 7.34-7.26 (m, 4H), 7.21 (t, *J* = 7.2 Hz, 1H), 5.16 (s, 1H), 4.11 (q, *J* = 7.2 Hz, 2H), 3.94-3.78 (m, 4H), 2.10 (s, 3H), 1.95-1.88 (m, 1H), 1.20 (t, *J* = 7.2 Hz, 3H), 0.91 (t, *J* = 7.2 Hz, 3H), 0.90-0.86 (m, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 167.8, 165.9, 164.1, 146.7, 146.0, 142.6, 138.7, 130.8, 129.4, 129.2, 128.4, 127.9, 126.7, 106.3, 105.5, 70.6, 61.7, 60.7, 38.3, 27.9, 19.3 (2C), 18.1, 14.2, 13.6; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>34</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 492.2386, found 492.2382.

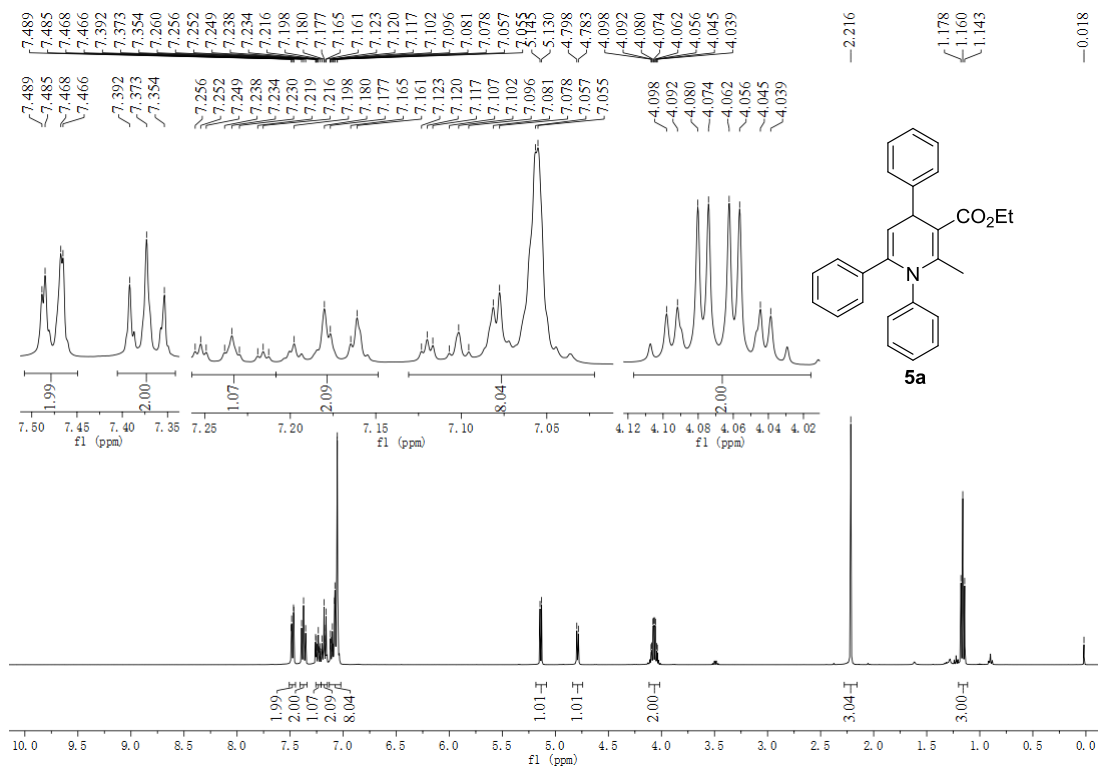


**Diethyl 7,7-dimethyl-5-oxo-4-phenyl-2-(phenylamino)-3,4,6,8-hexahydro-2H-chromene-2,3-dicarboxylate (10)**

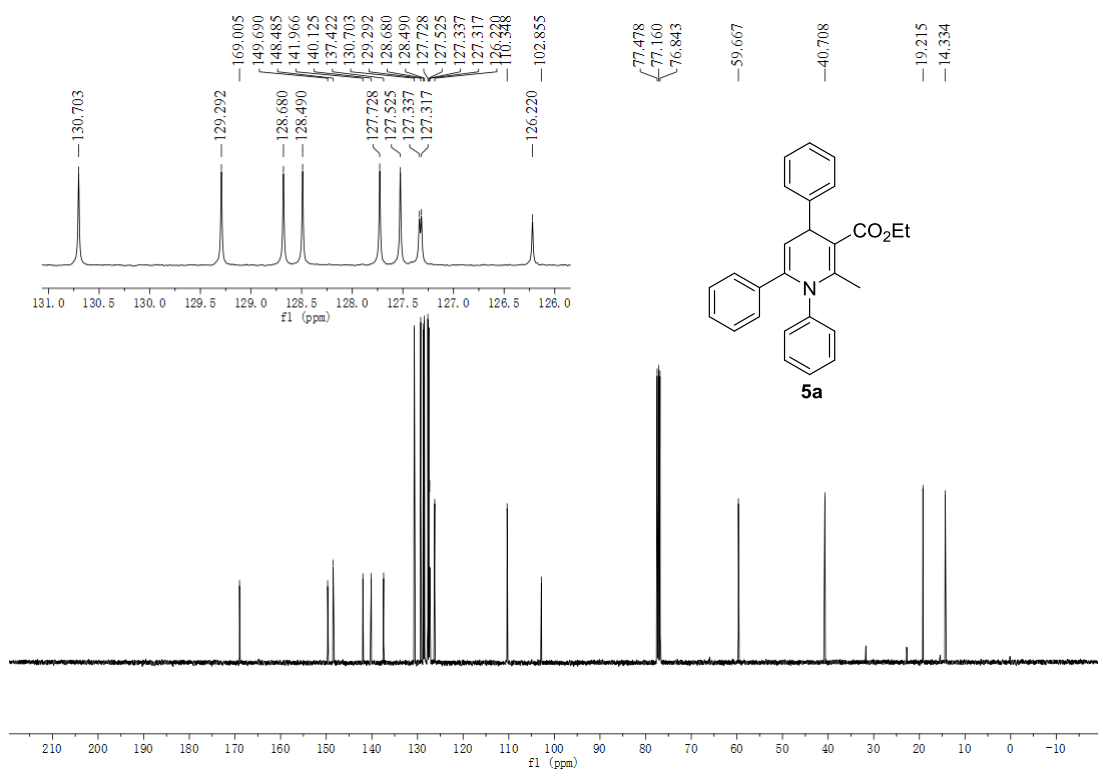
White solid, m.p. 158-160 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ (ppm) 7.27-7.23 (m, 2H), 7.20-7.13 (m, 5H), 6.87-6.83 (m, 3H), 5.67 (s, 1H), 4.19 (d, *J* = 11.6 Hz, 1H), 4.12-4.04 (m, 2H), 3.98-3.94 (m, 1H), 3.92-3.85 (m, 1H), 3.14 (d, *J* = 10.4 Hz, 1H), 2.62 (d, *J* = 18.0 Hz, 1H), 2.36 (dd, *J* = 17.6, 2.4 Hz, 1H), 2.17 (s, 2H), 1.16 (s, 3H), 1.03 (t, *J* = 7.2 Hz, 3H), 1.02 (s, 3H), 0.94 (t, *J* = 7.2 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ (ppm) 196.0, 171.2, 168.1, 166.5, 143.7, 141.2, 129.2, 128.6, 127.3, 126.9, 120.5, 115.7, 113.4, 87.8, 62.5, 61.8, 54.1, 50.8, 42.1, 39.2, 31.8, 29.4, 27.6, 14.0, 13.7; HRMS (ESI-TOF) *m/z* calcd for C<sub>29</sub>H<sub>34</sub>NO<sub>6</sub> [M+H]<sup>+</sup> 492.2386, found 492.2388.

### 3. Copies of NMR Spectra for Products

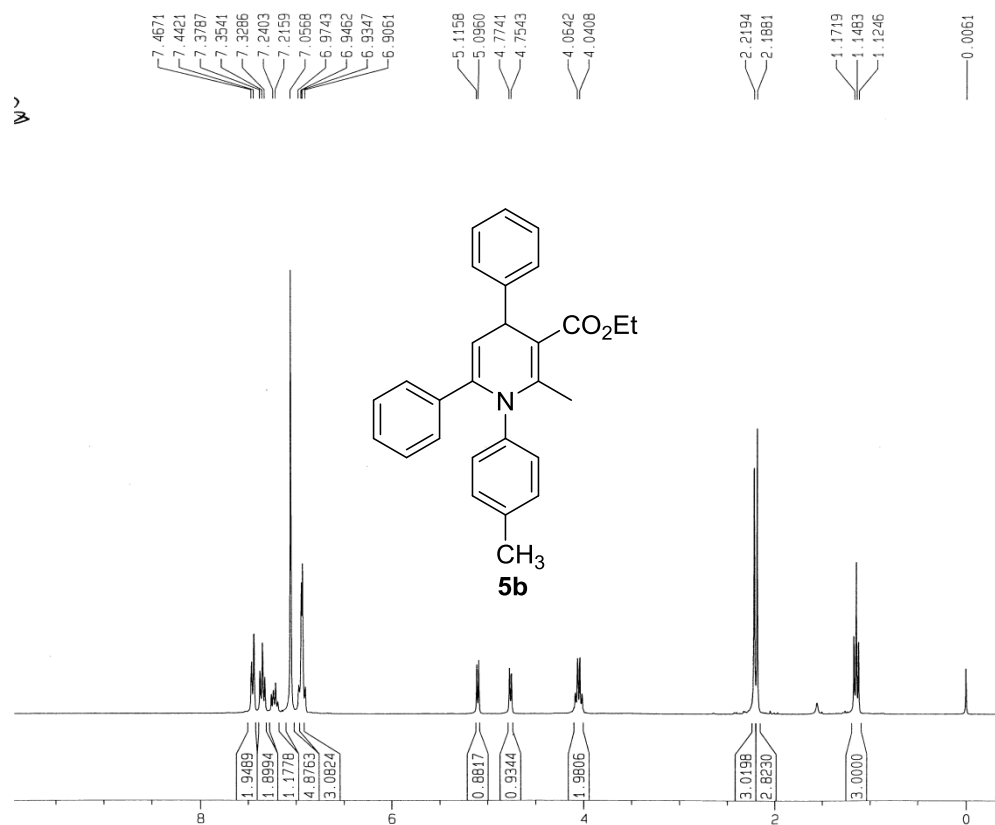
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )



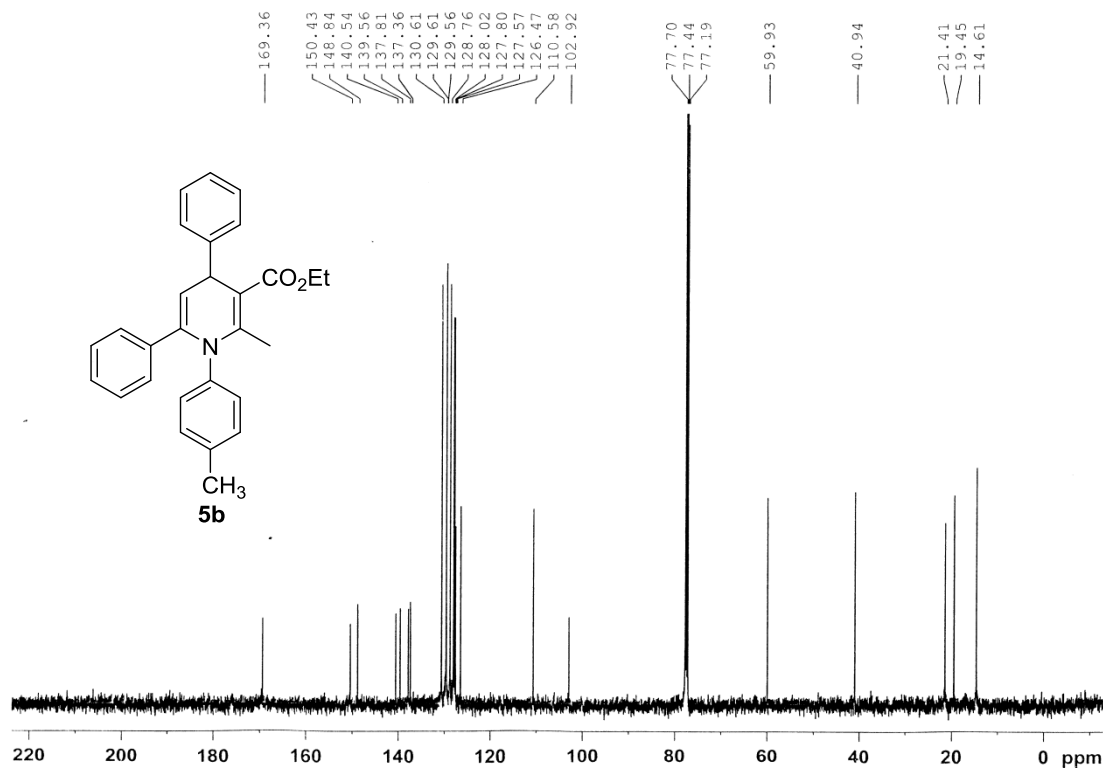
$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )



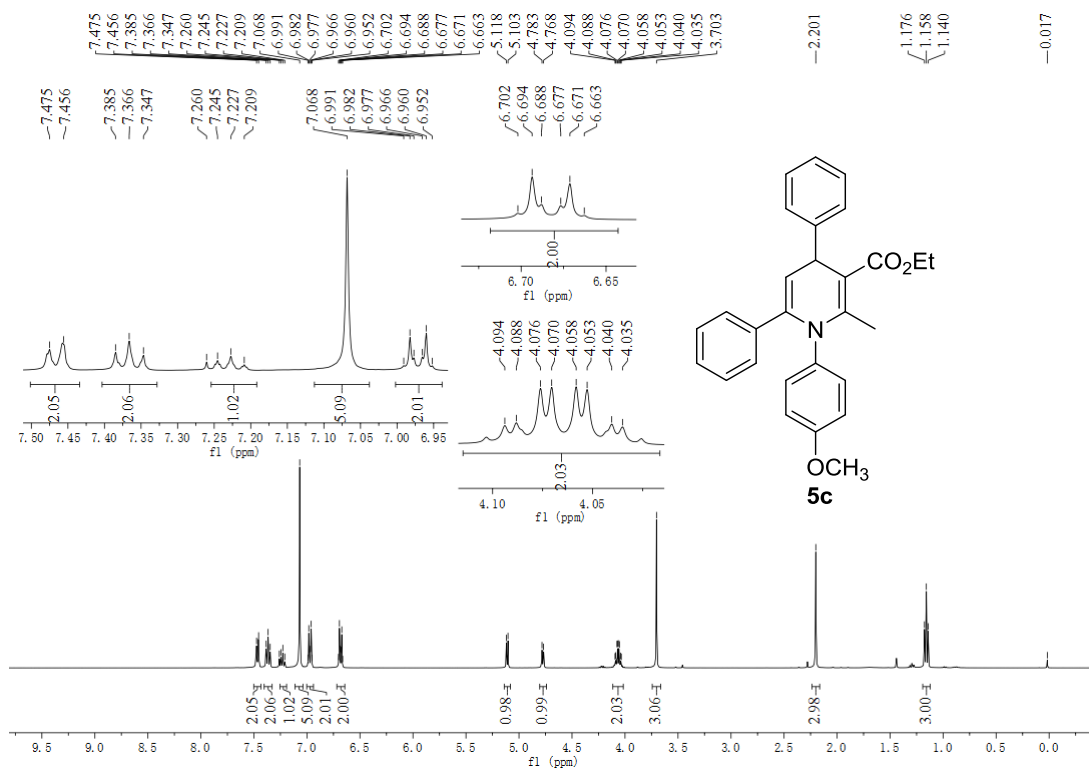
<sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)



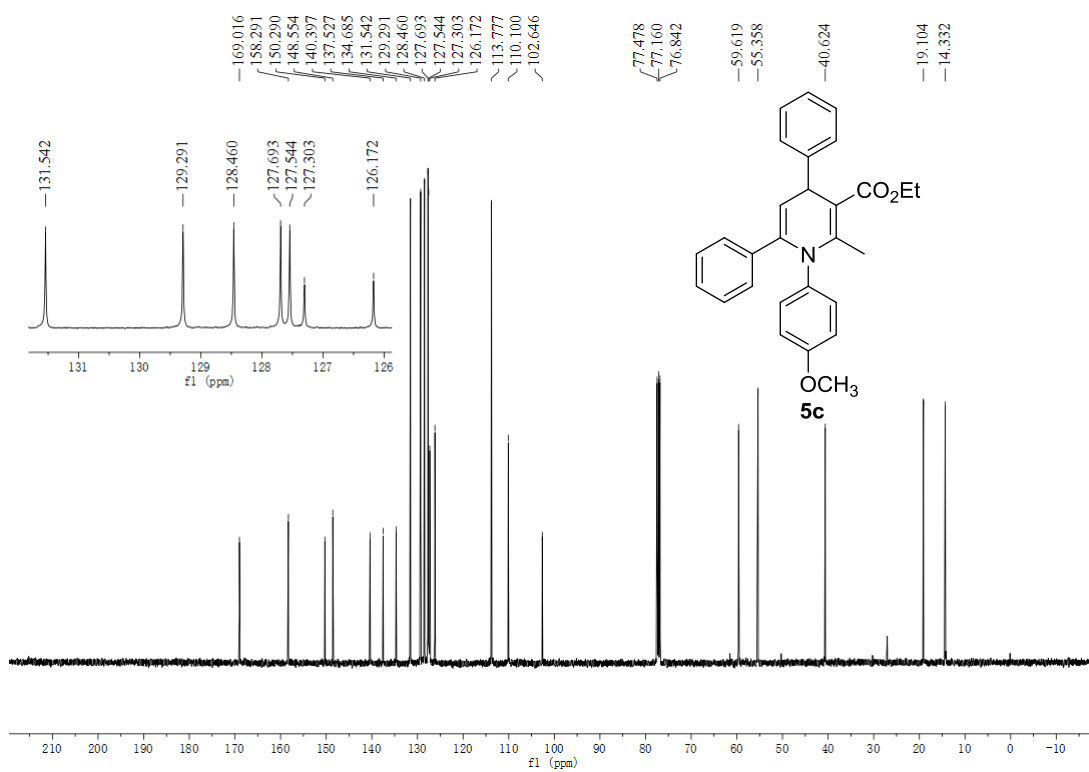
<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)



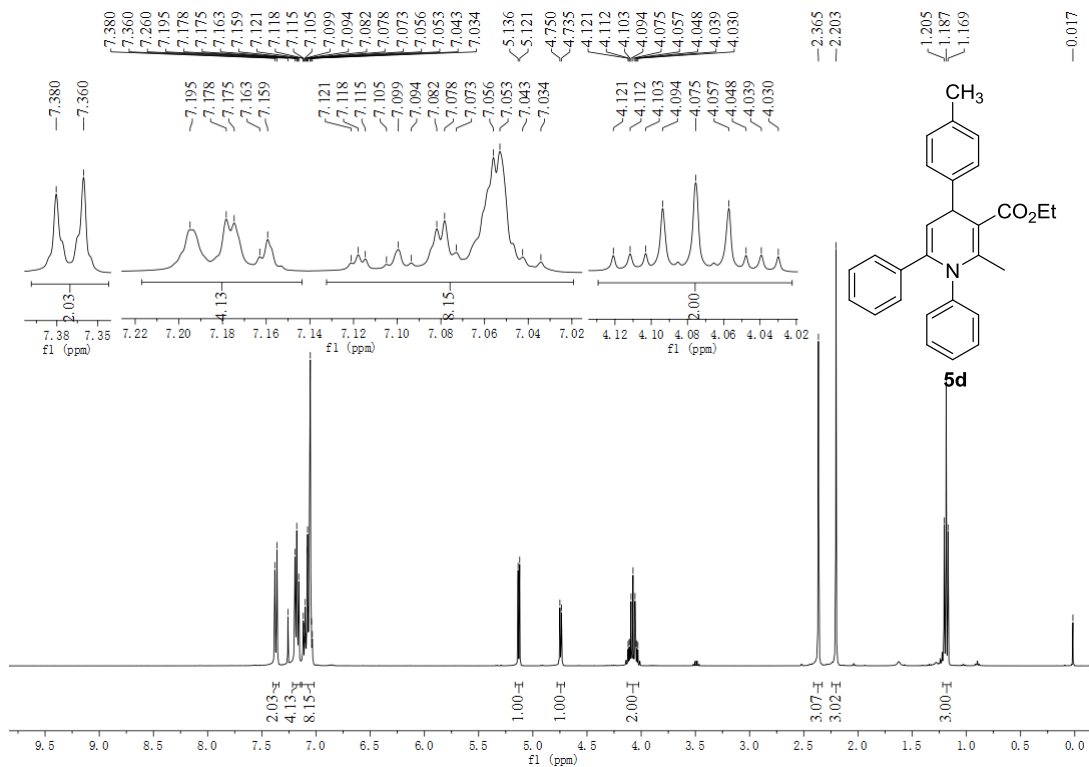
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



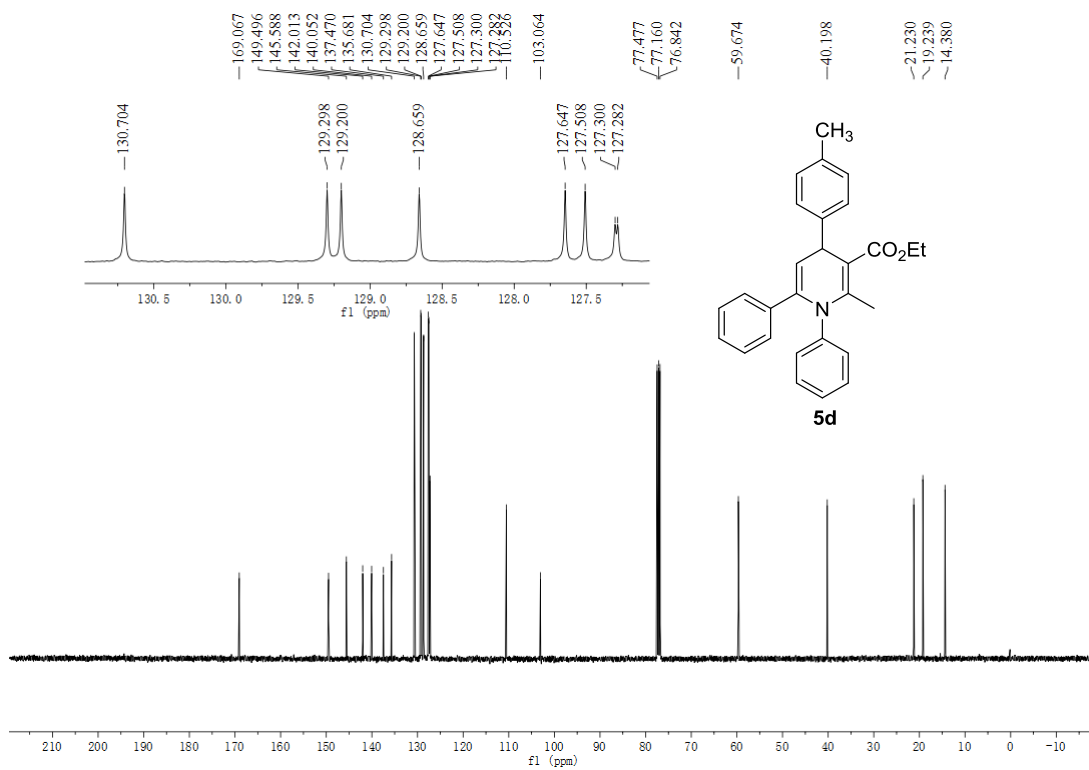
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



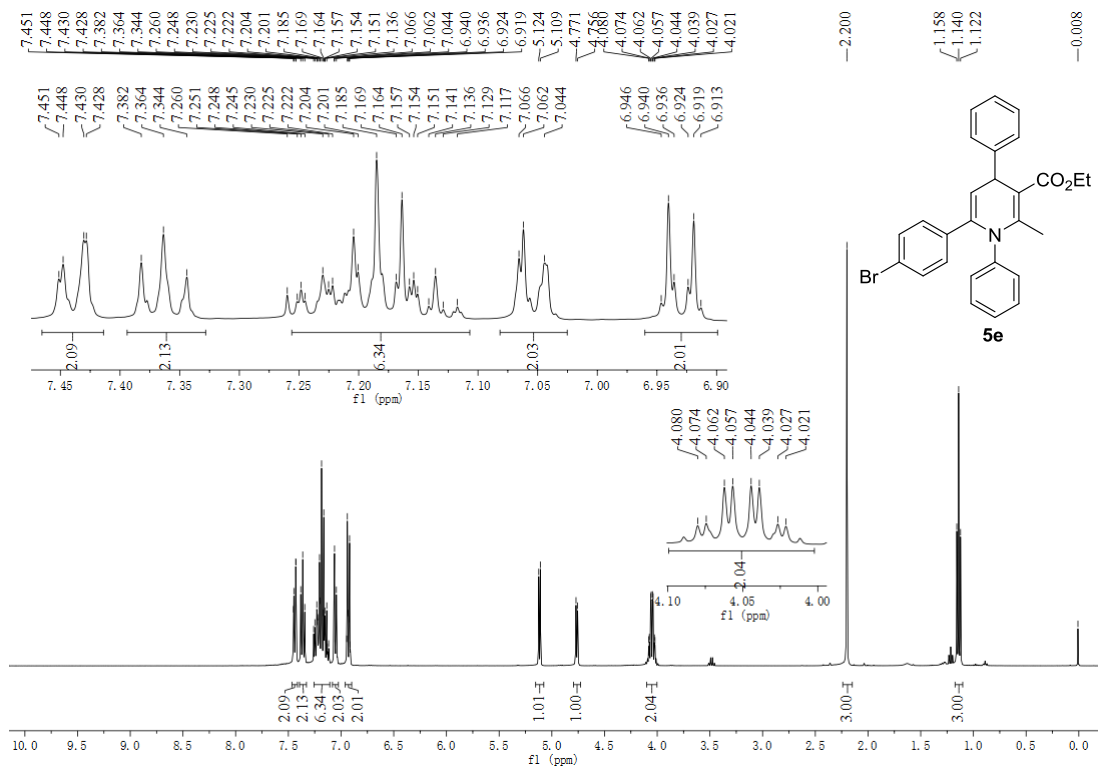
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



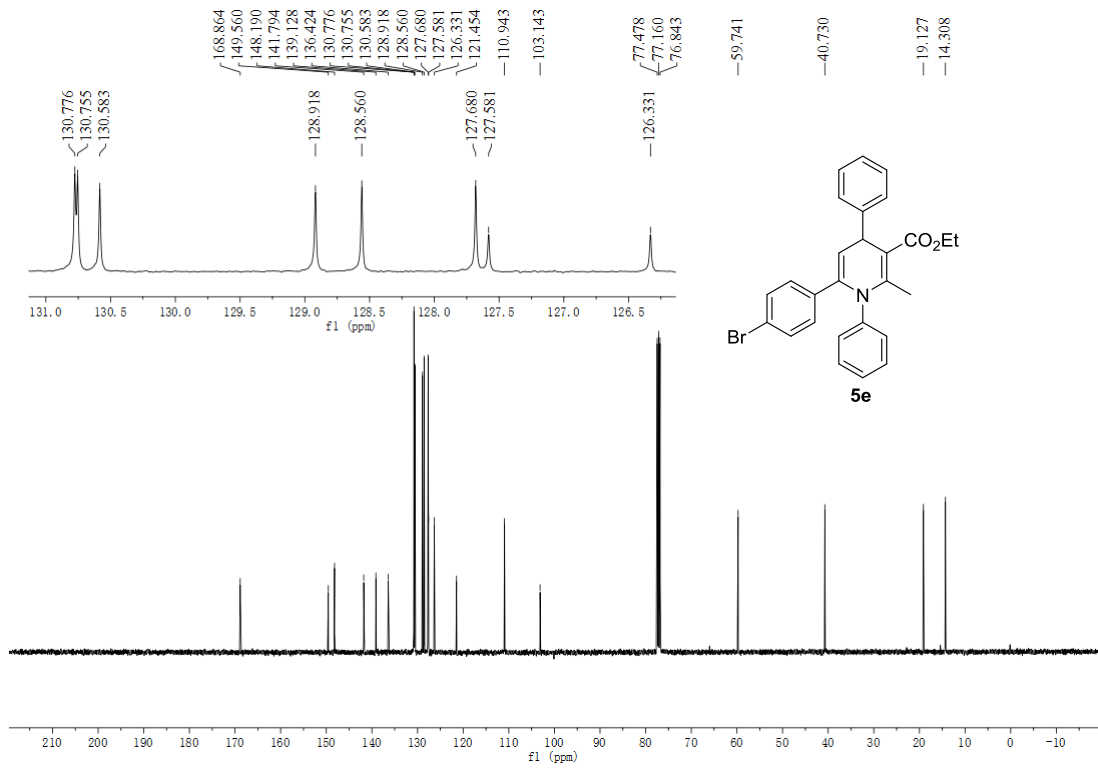
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



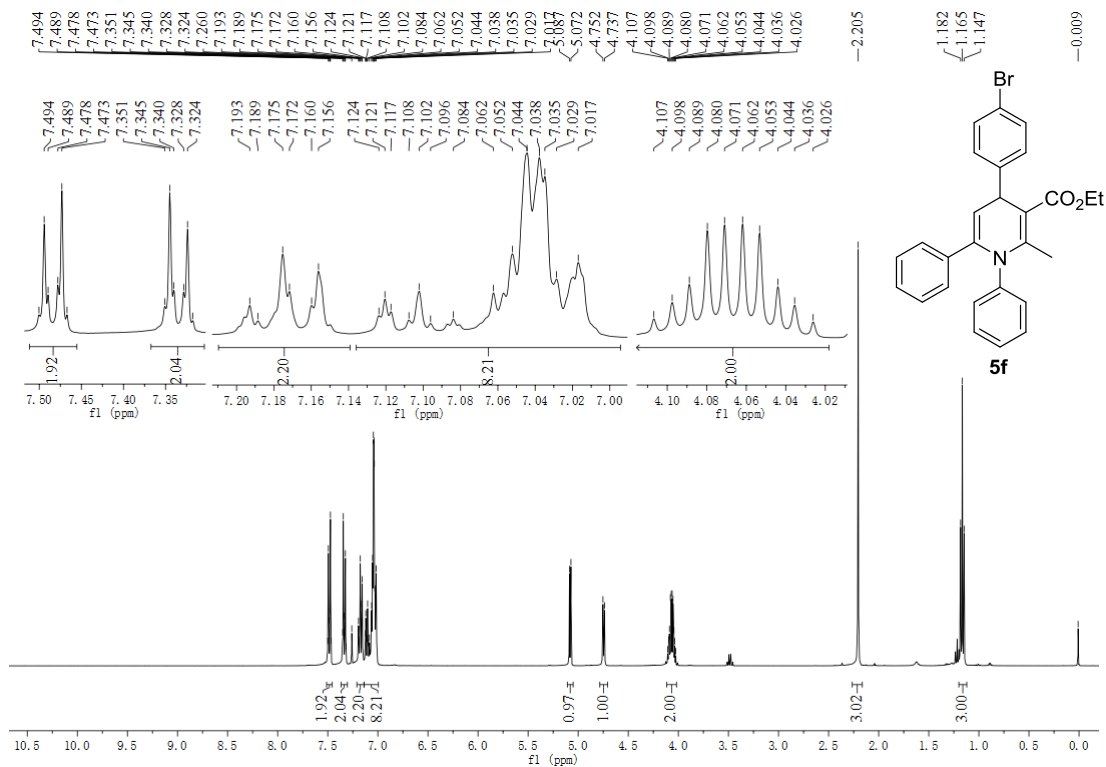
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



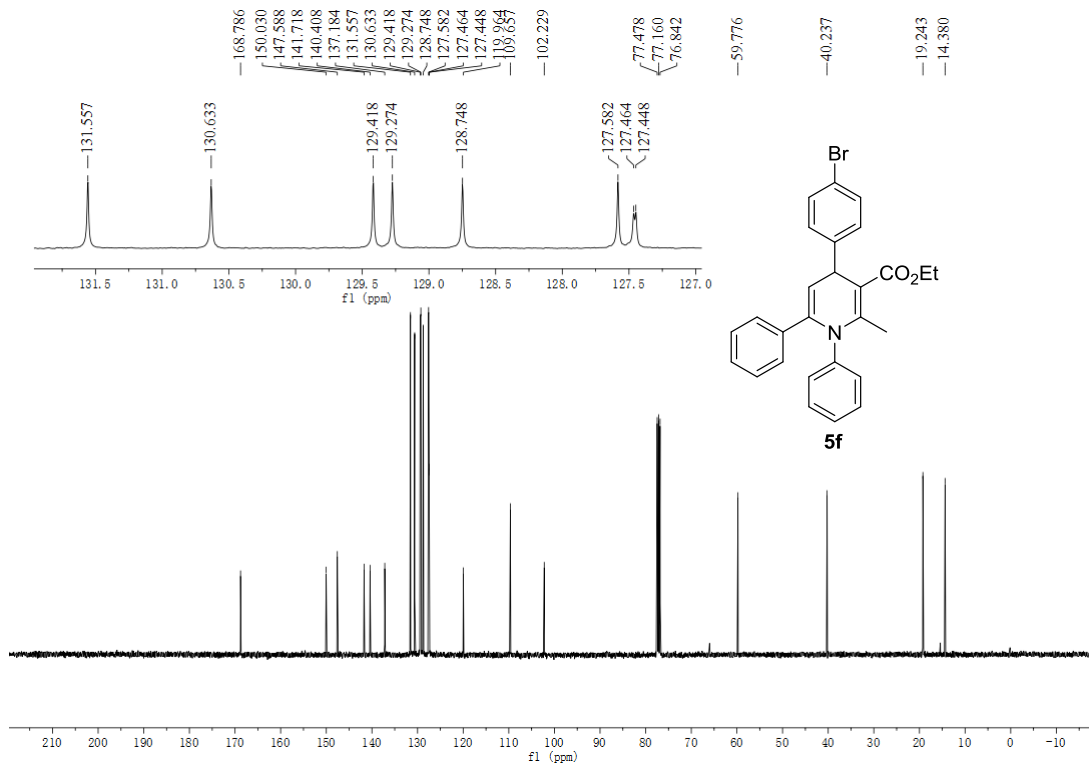
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



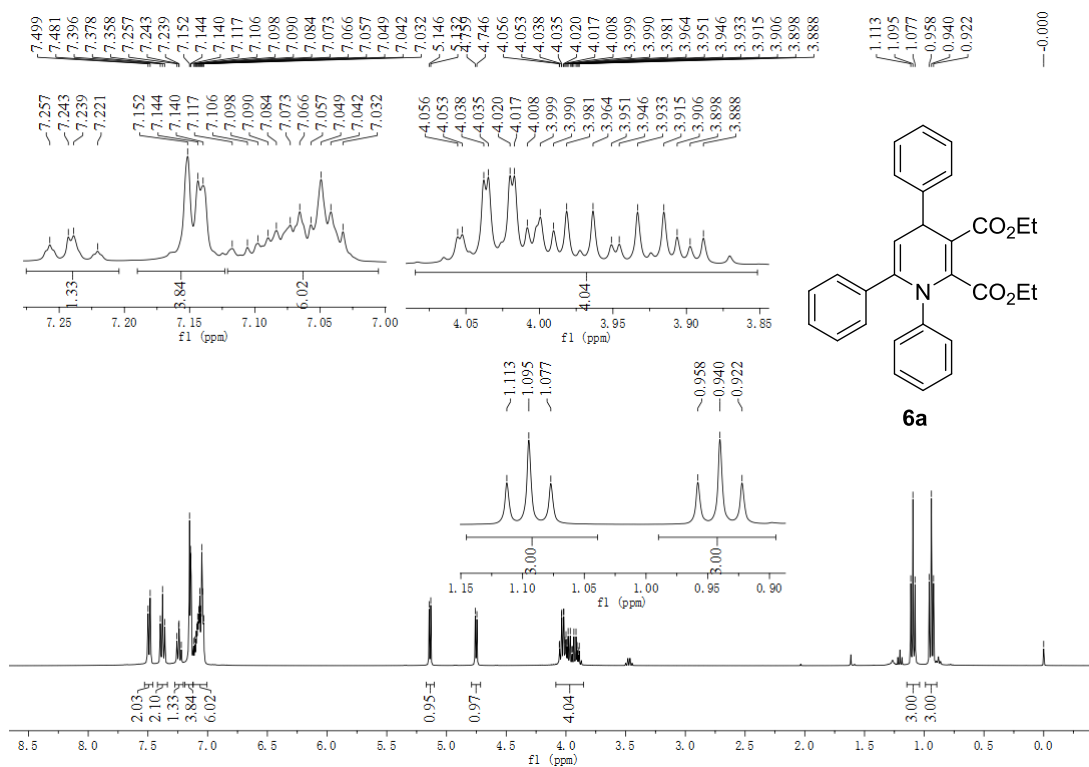
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



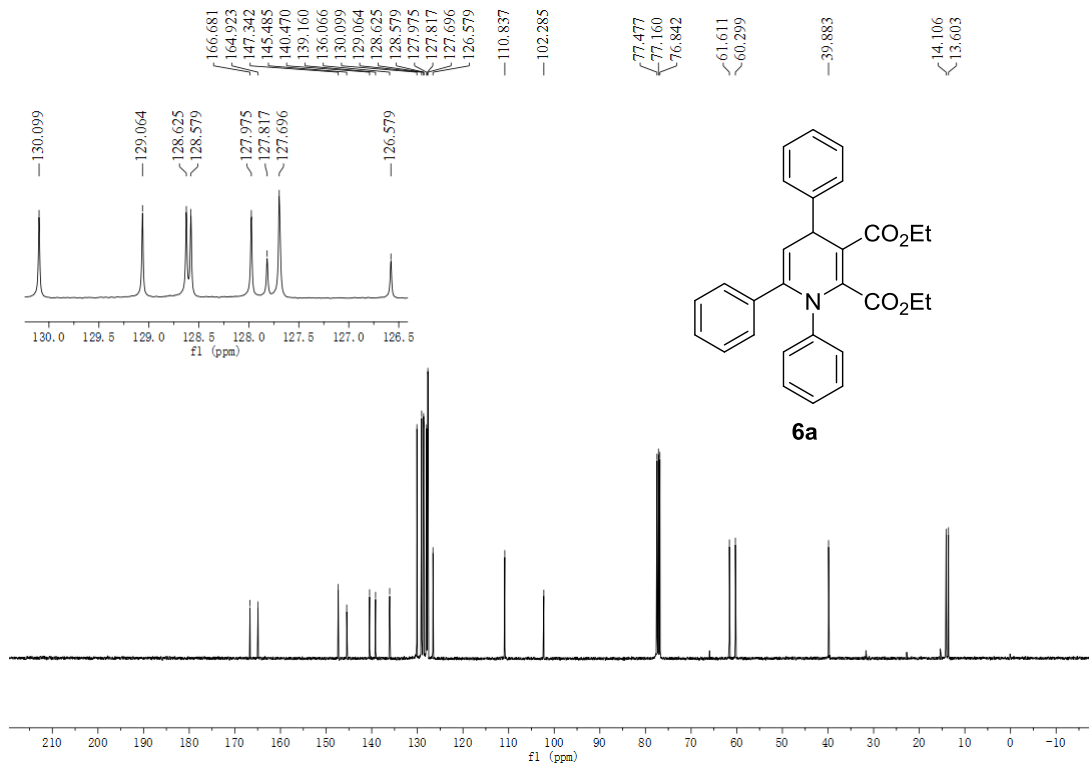
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



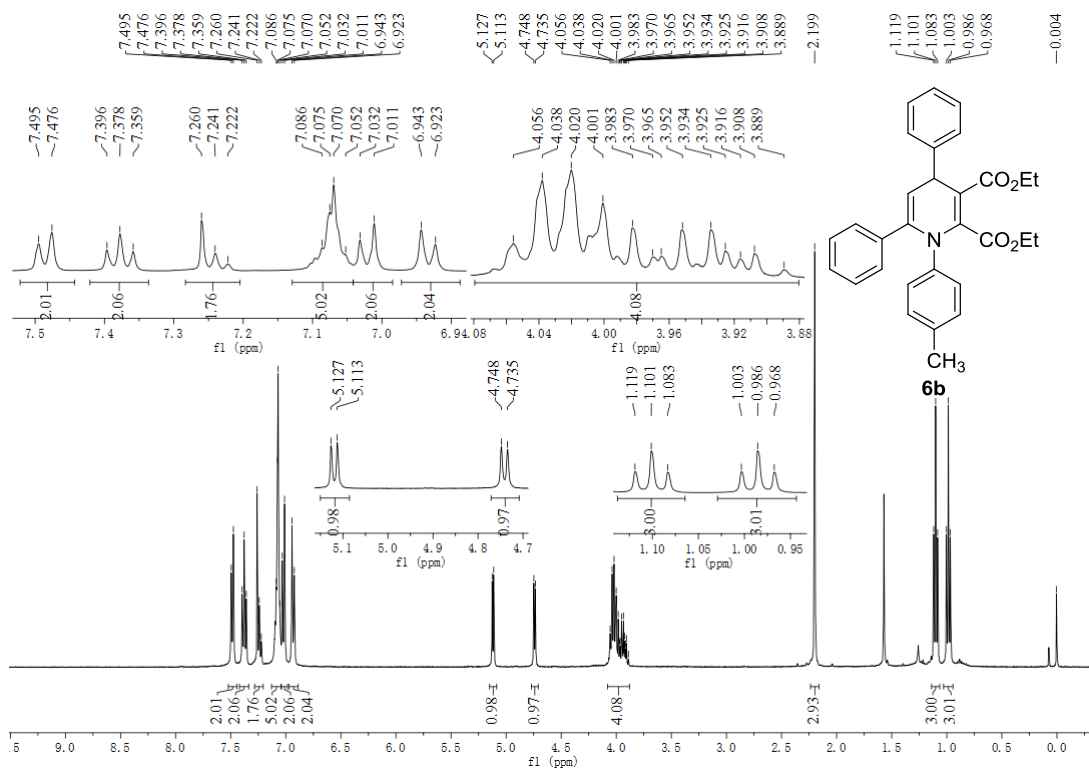
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



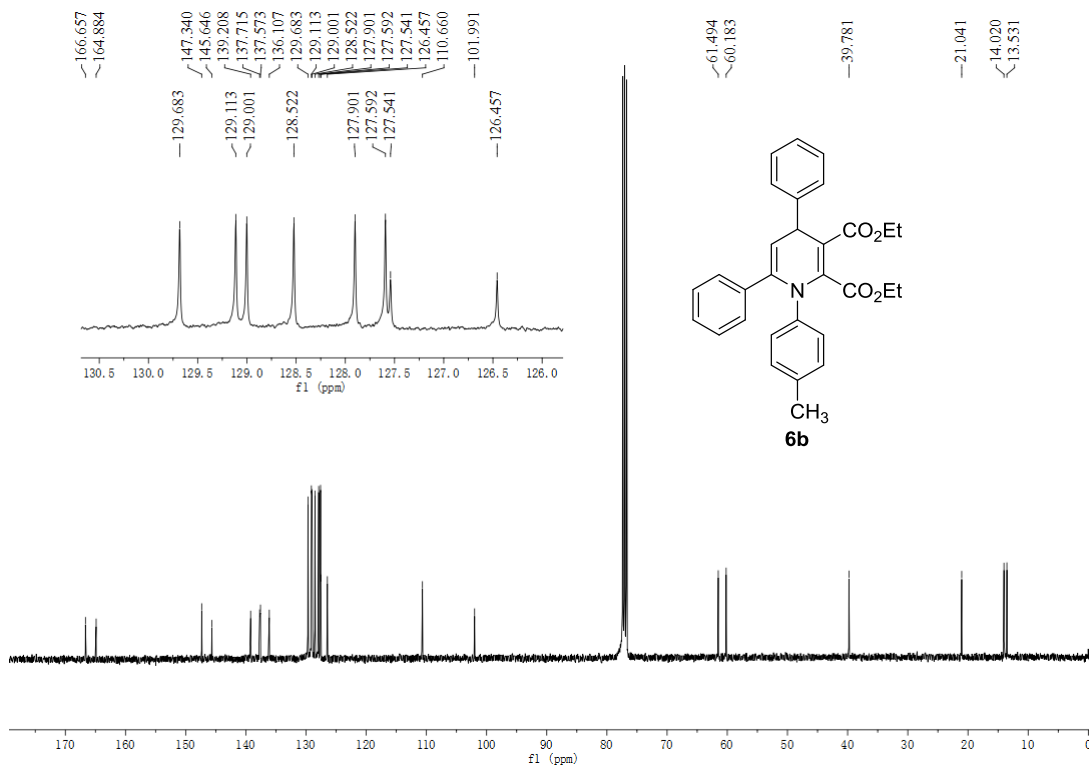
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



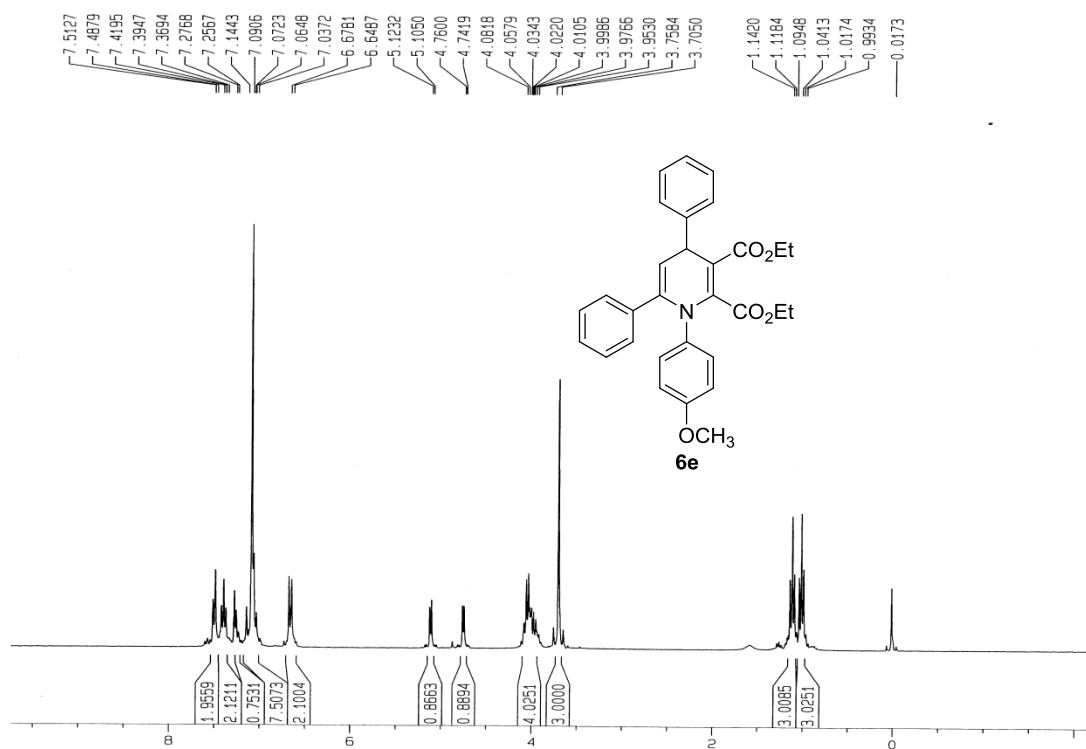
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



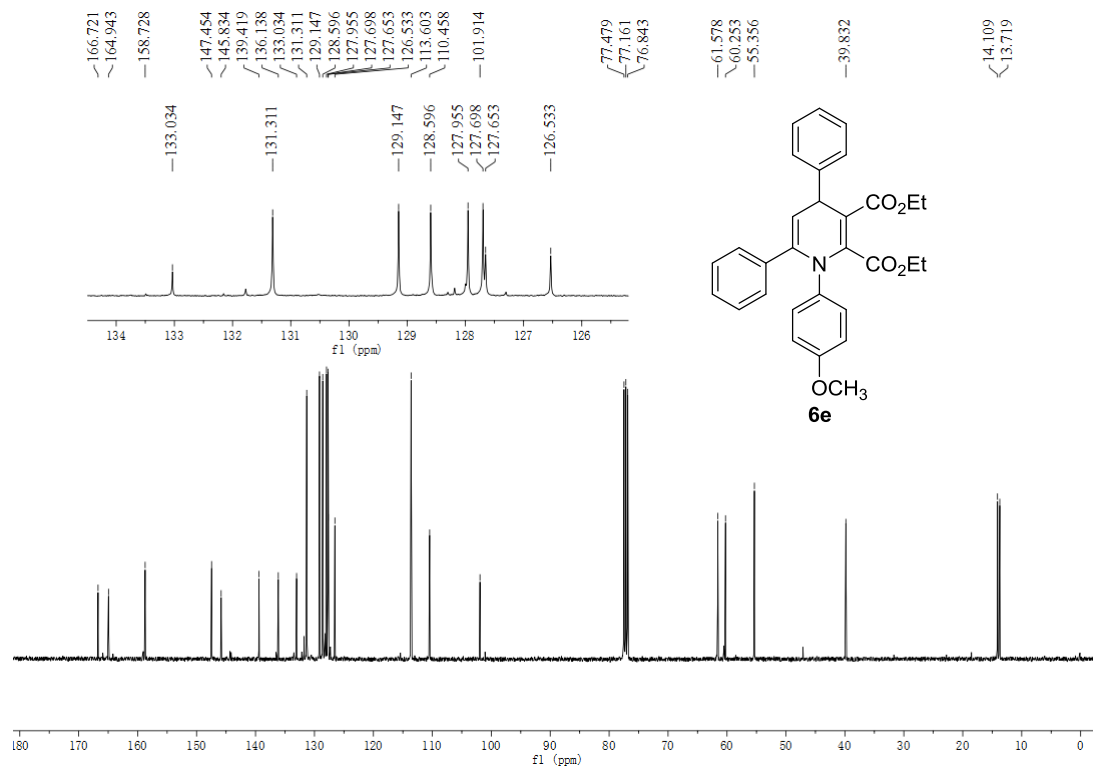
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



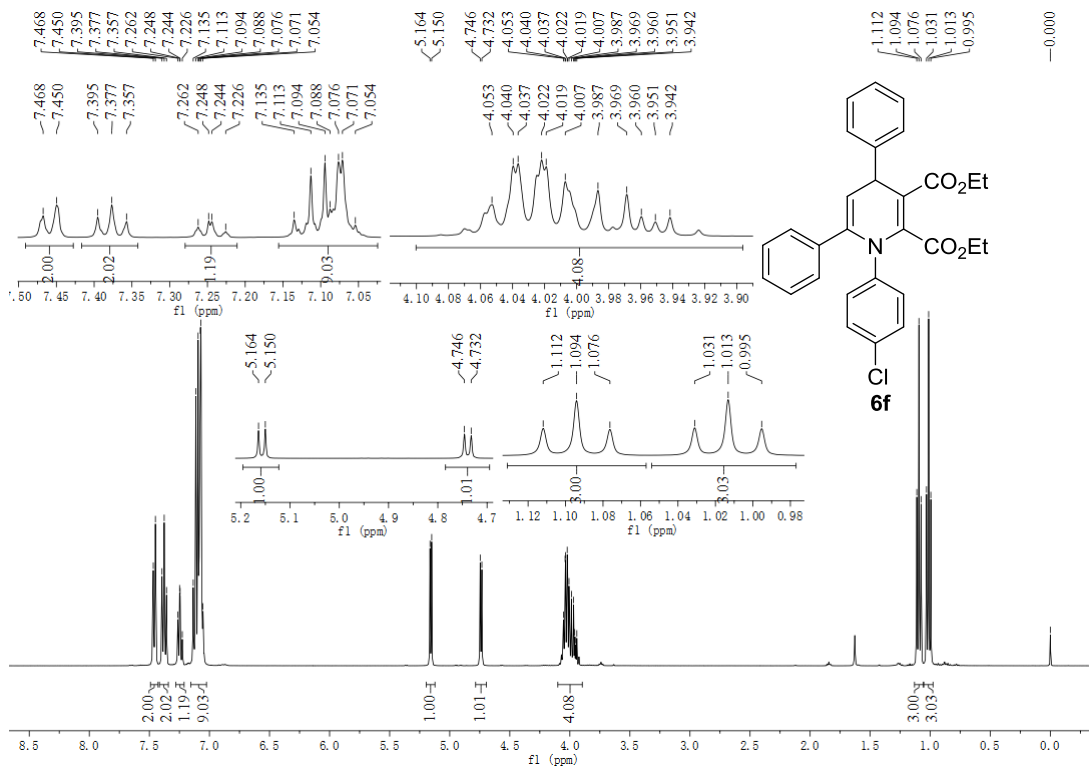




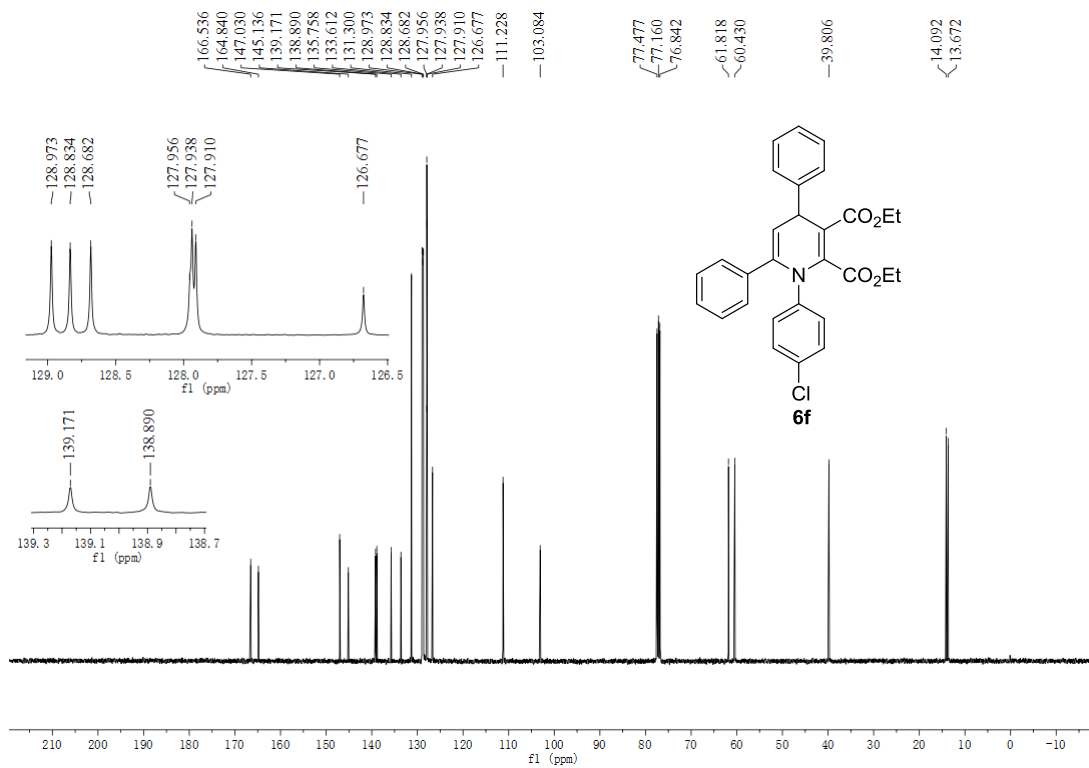
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



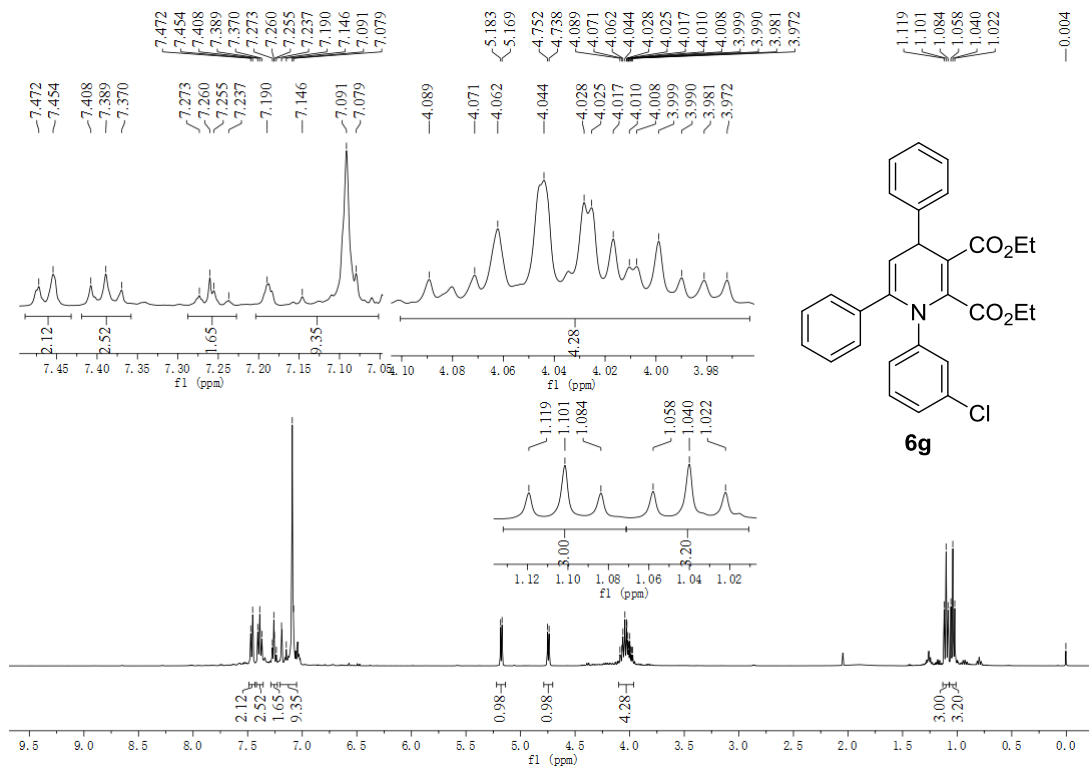
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



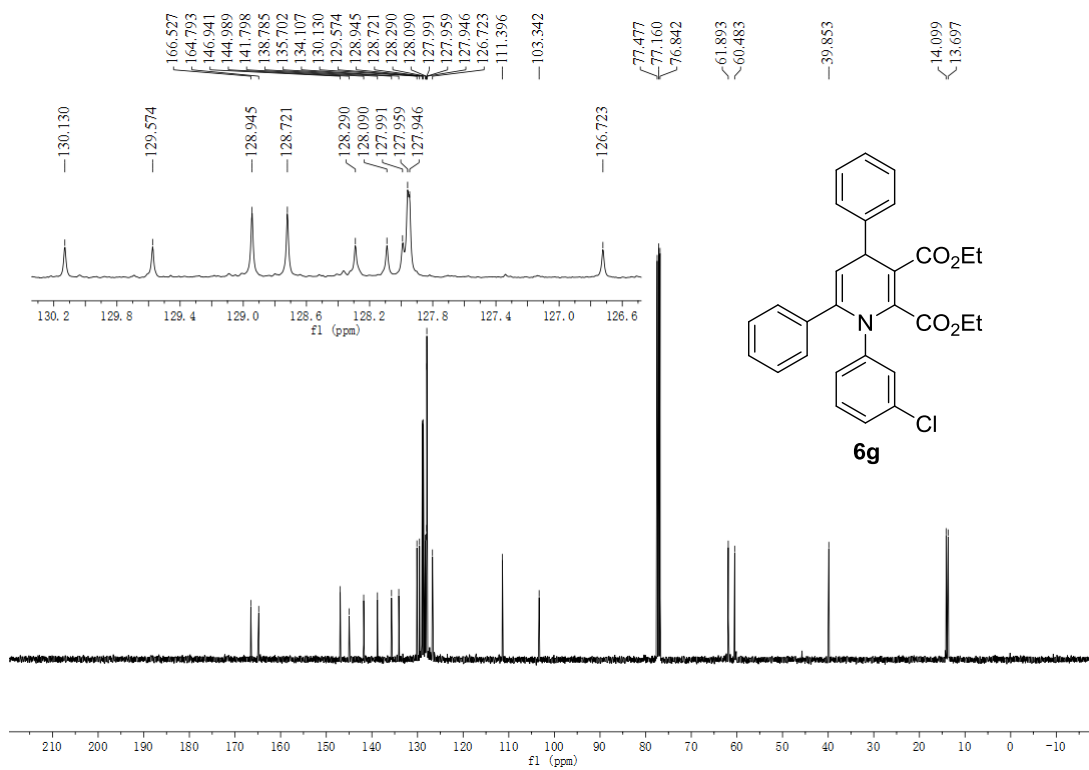
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



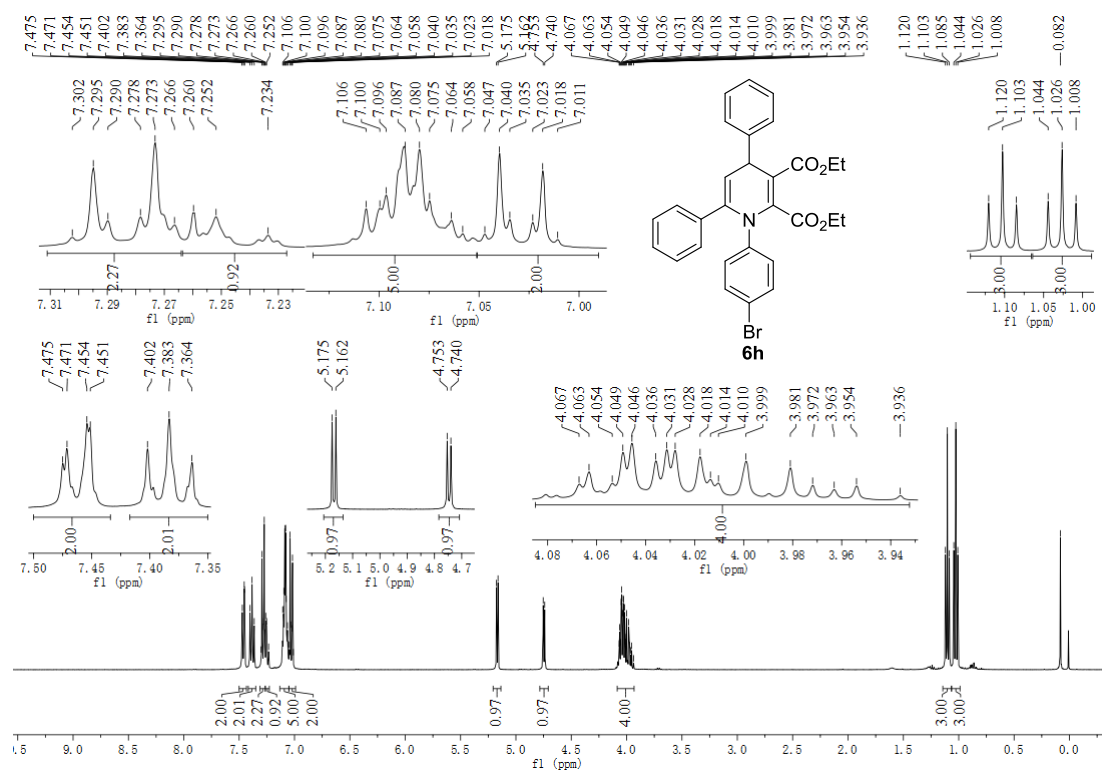
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



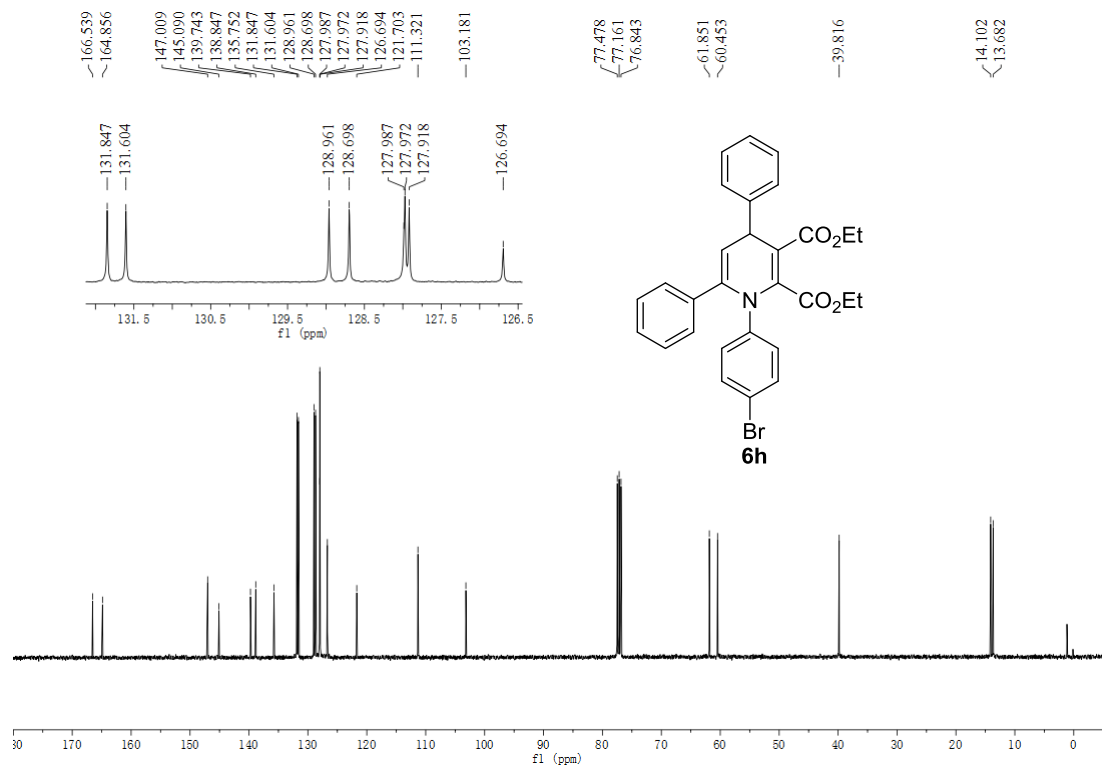
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



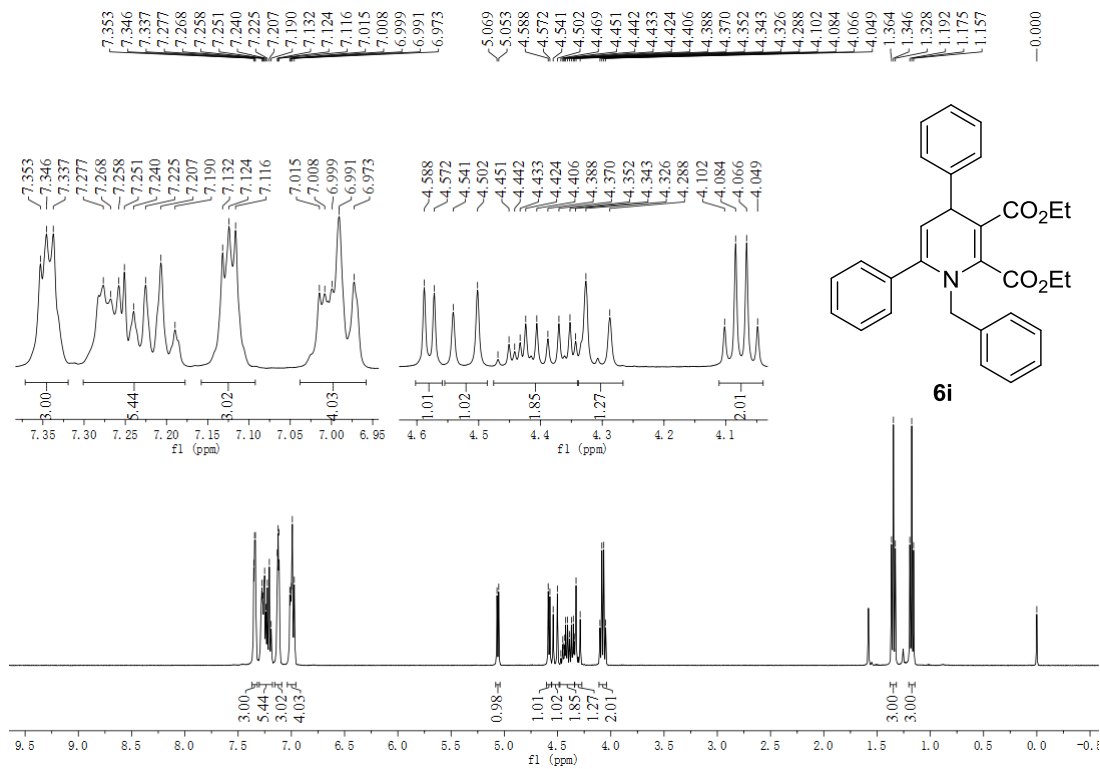
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



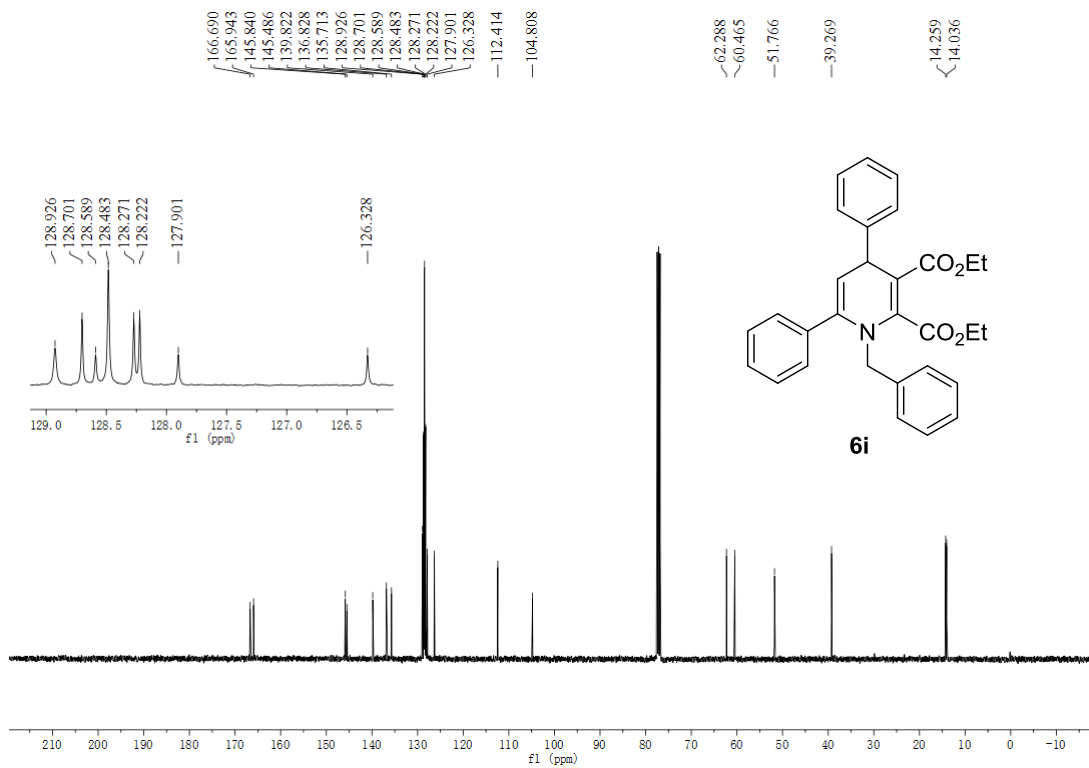
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



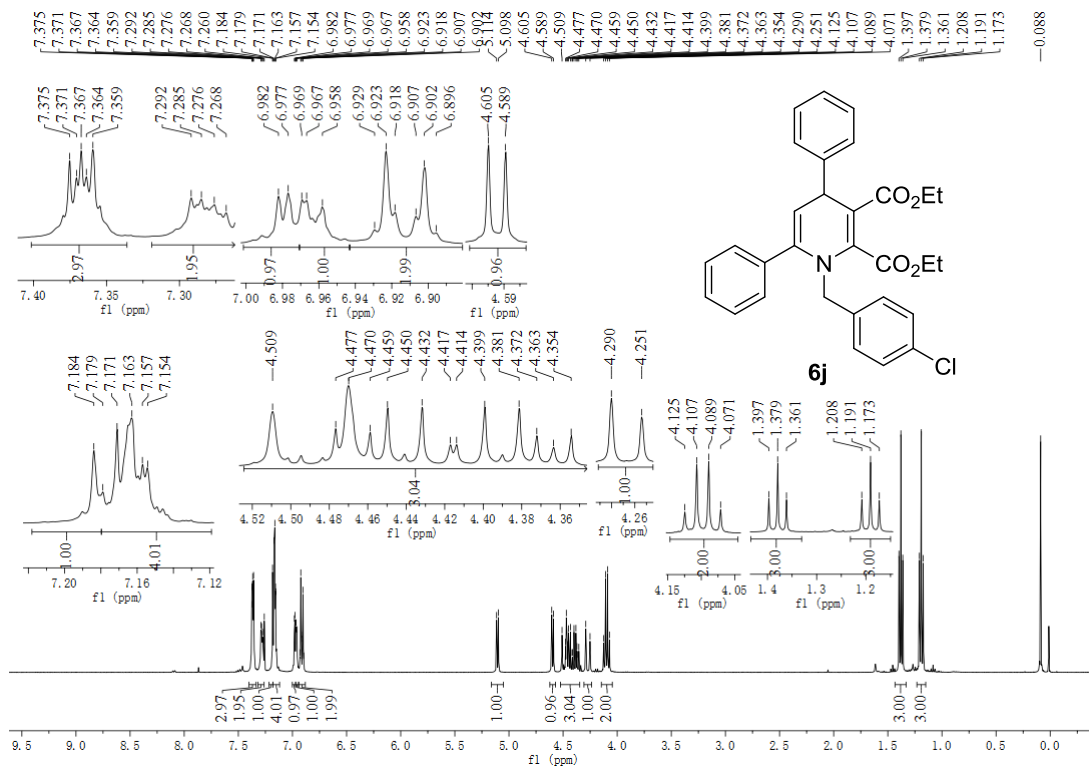
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



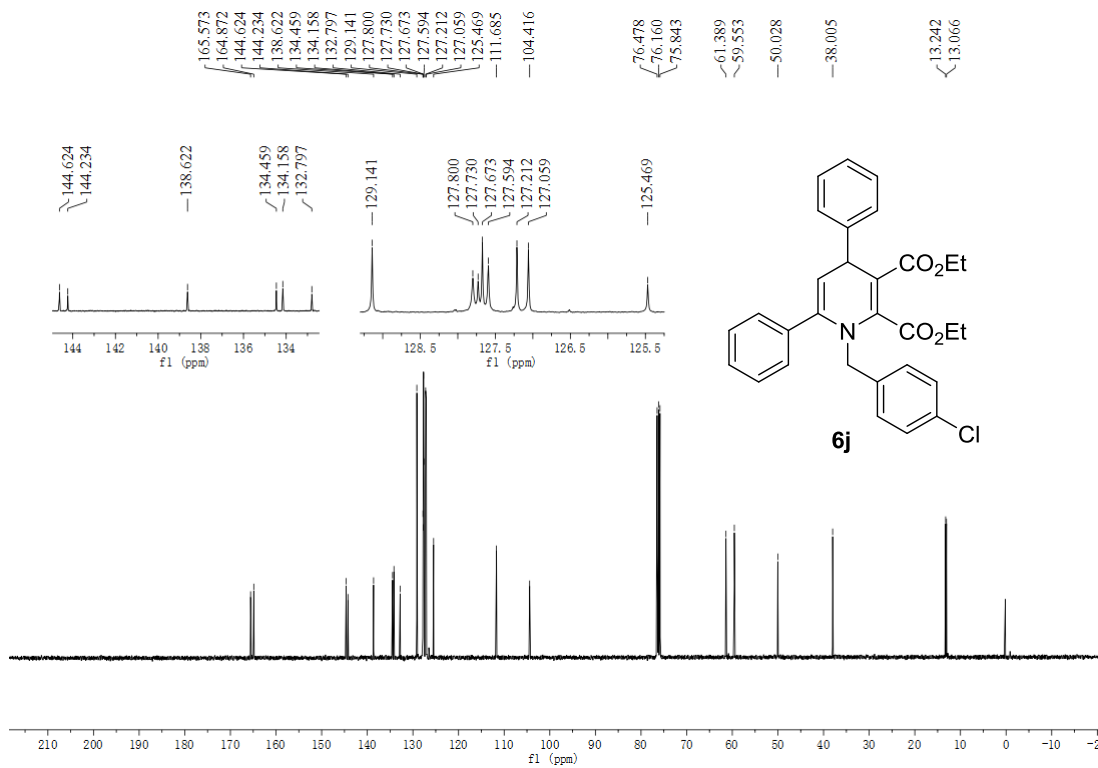
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

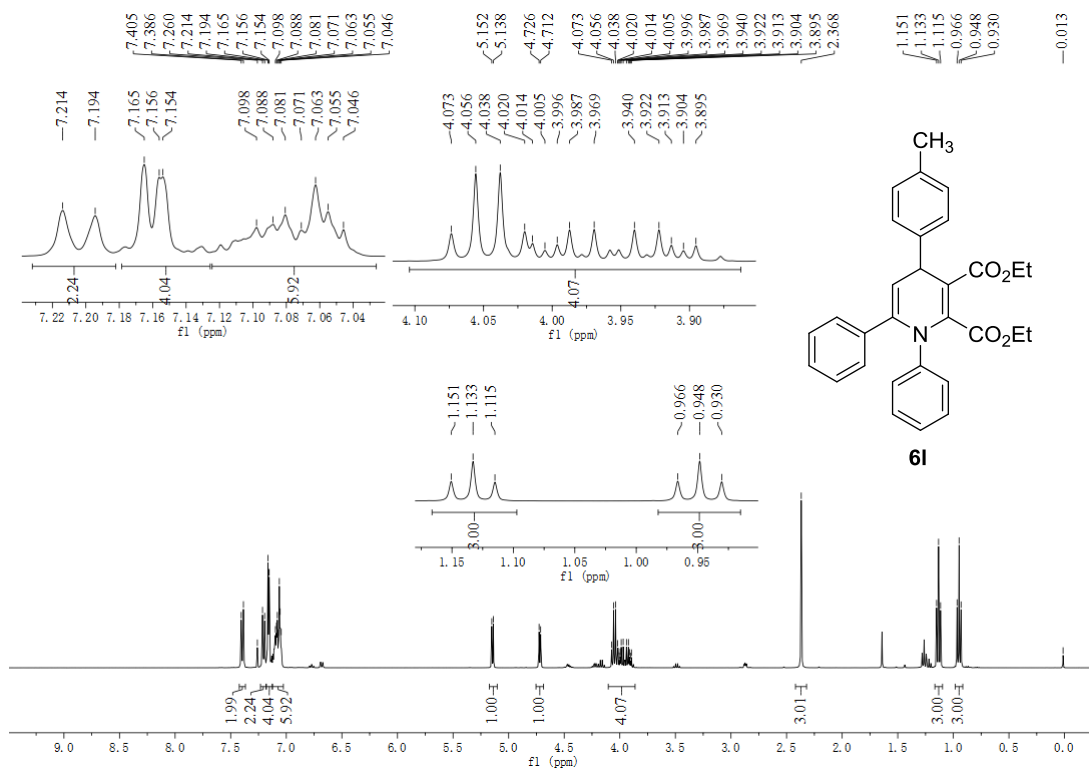


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

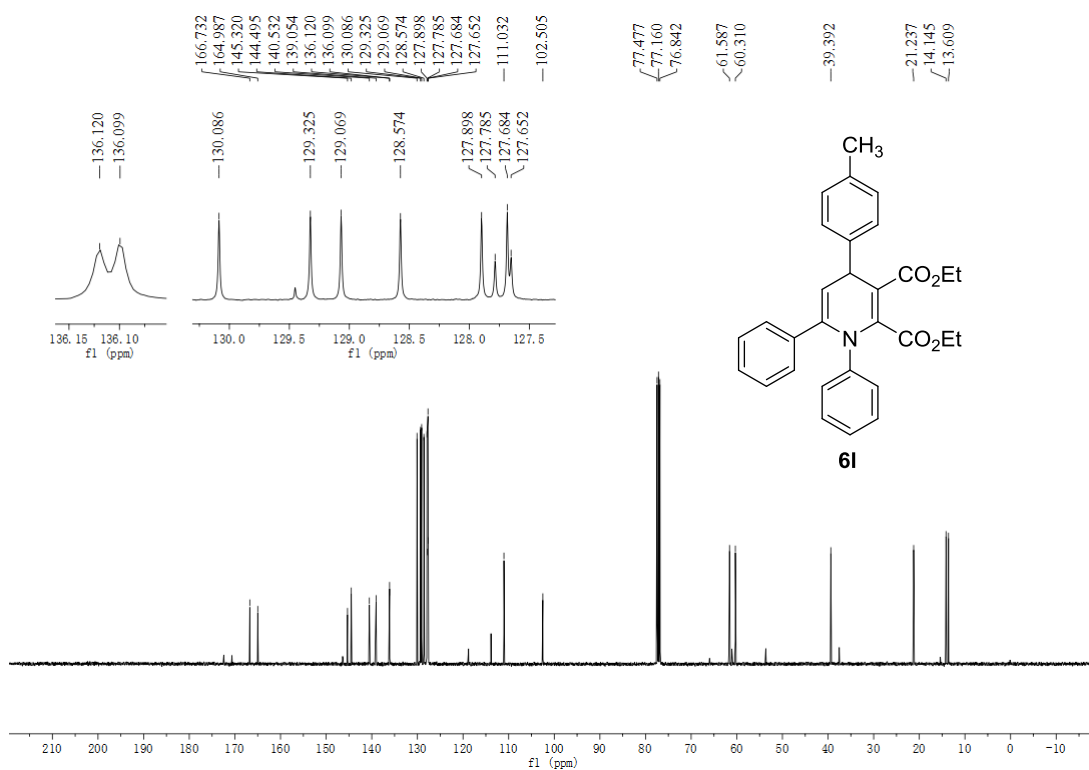


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

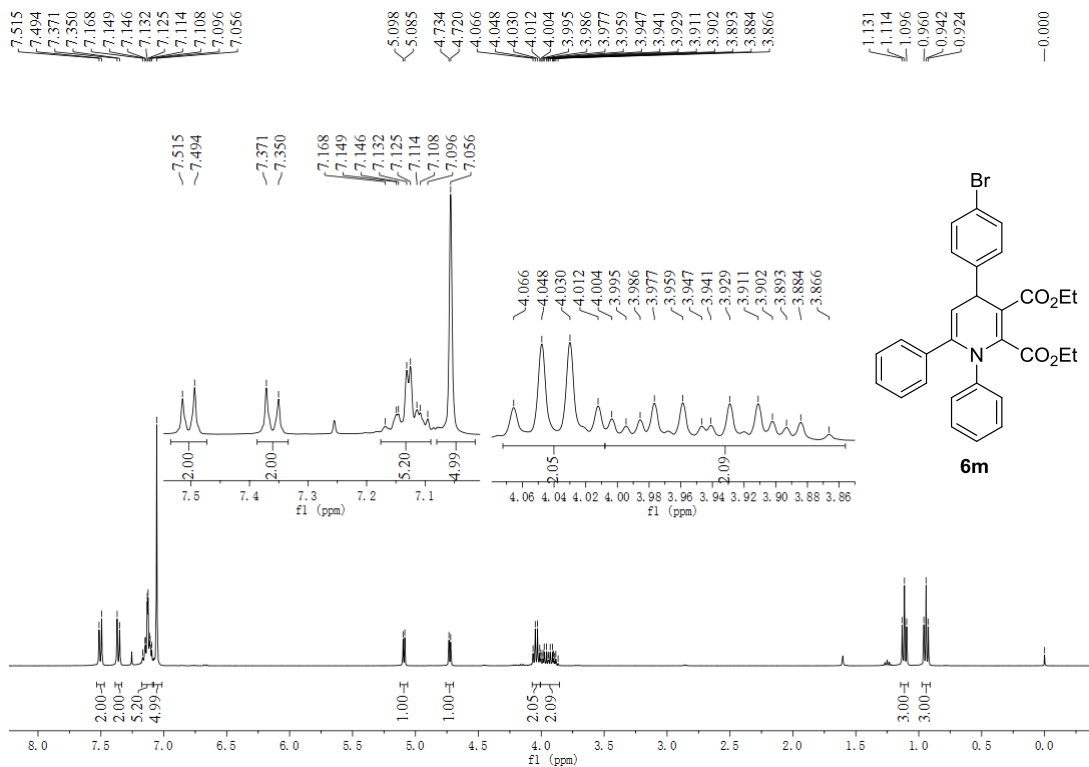




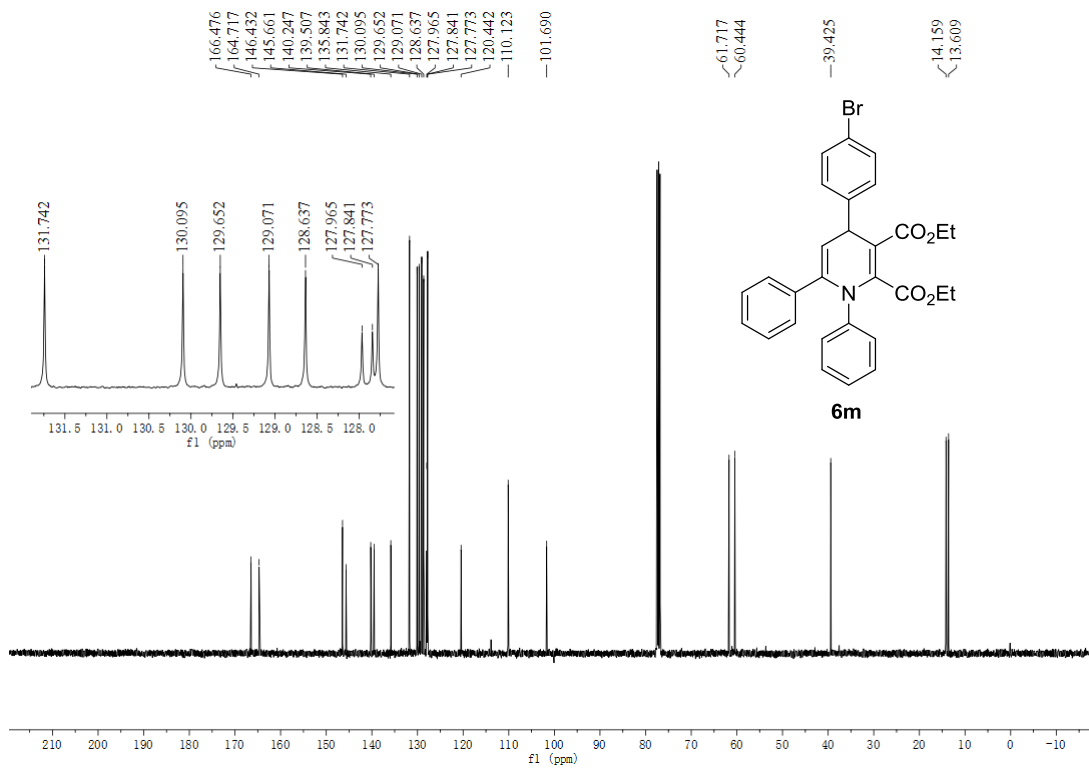
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



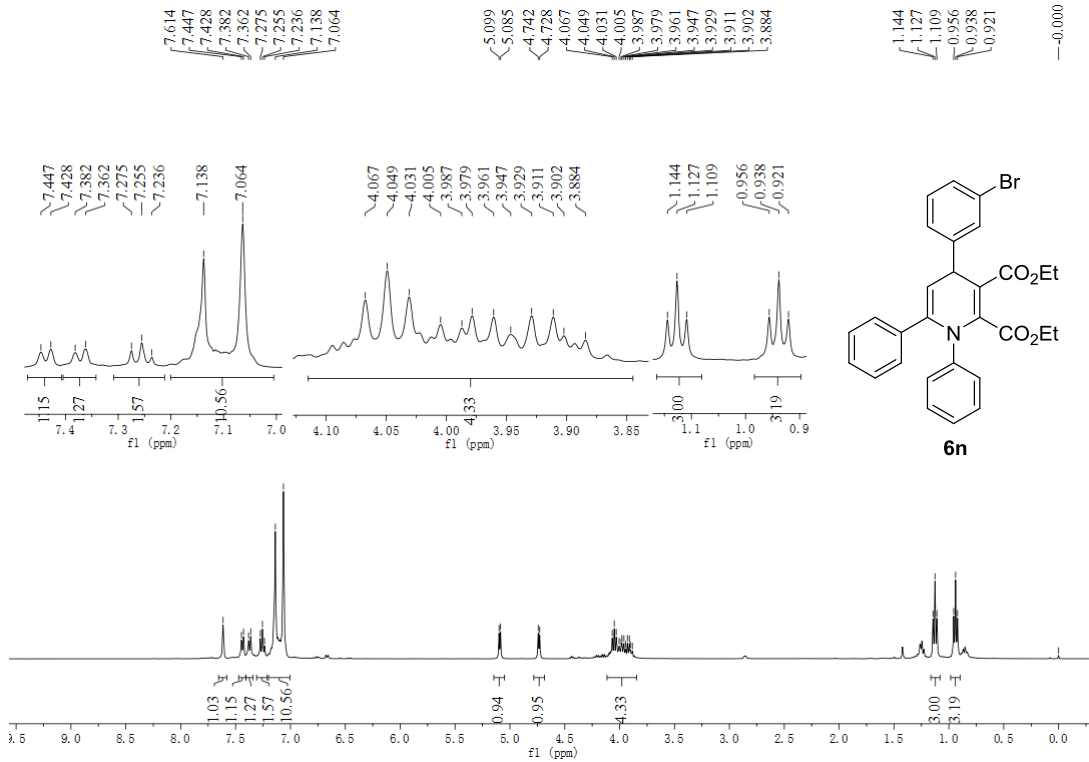
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



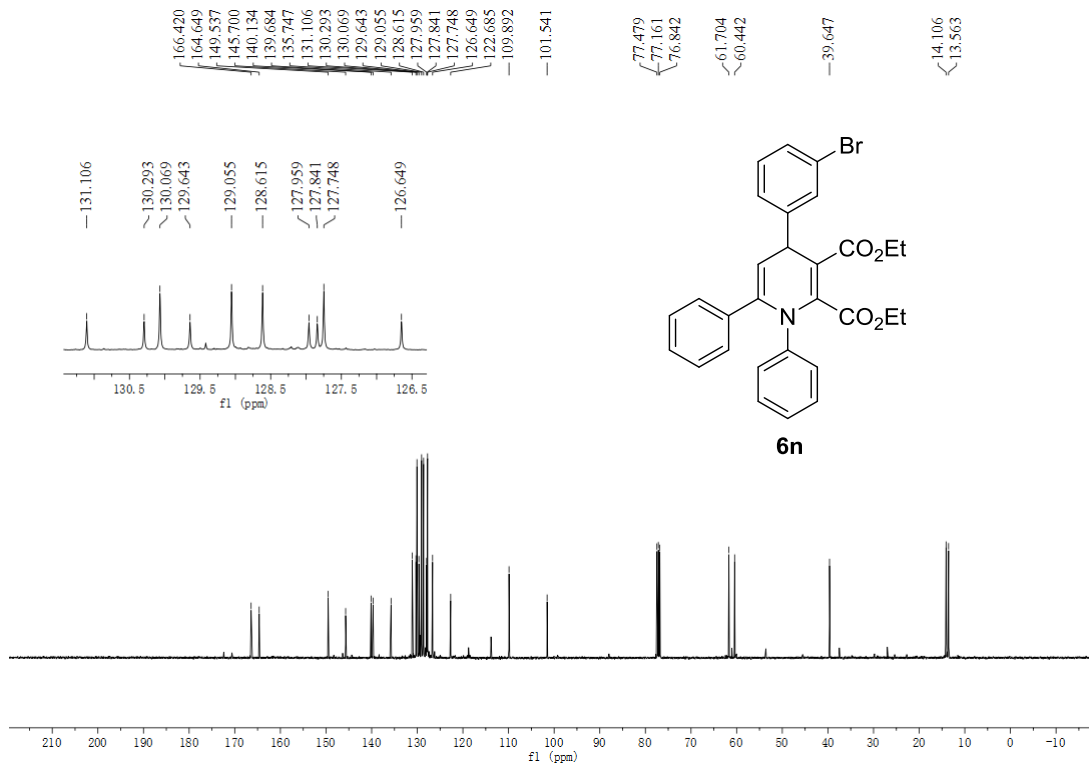
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



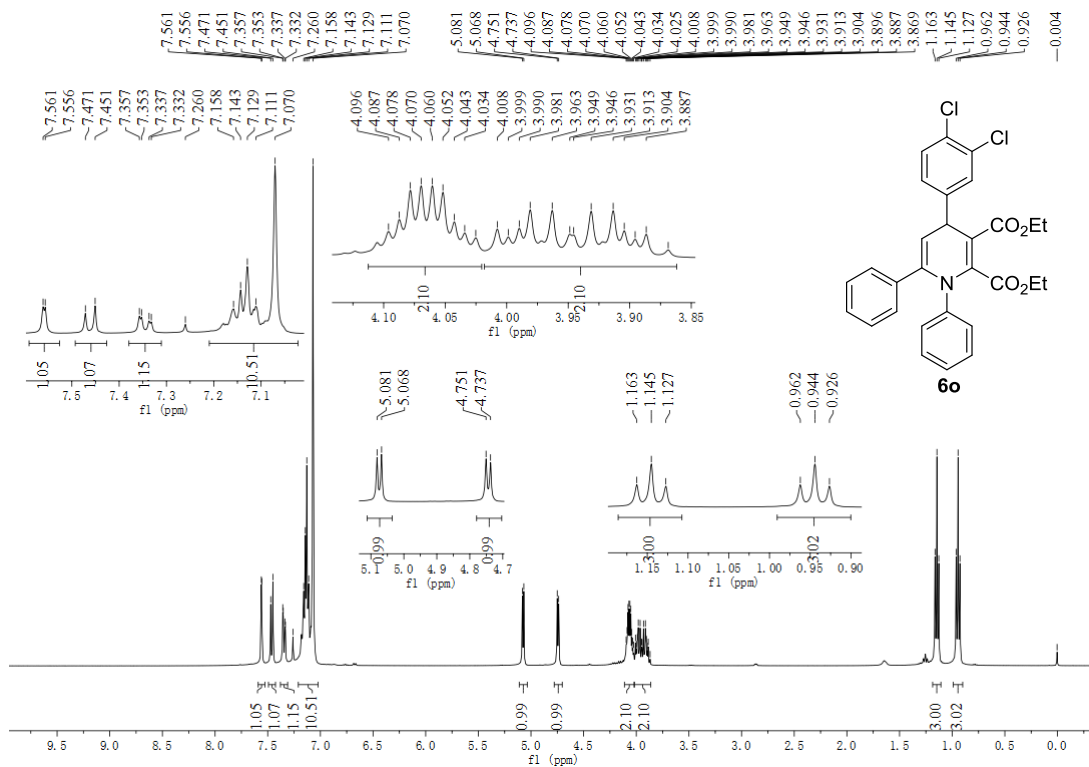
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



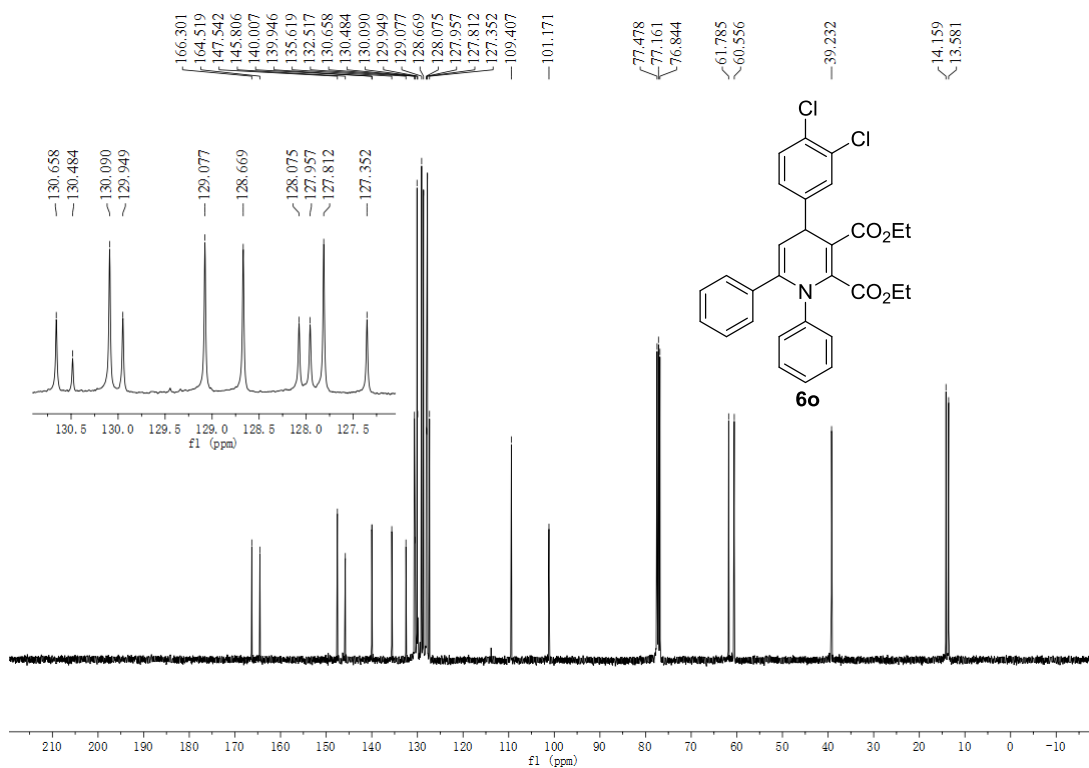
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



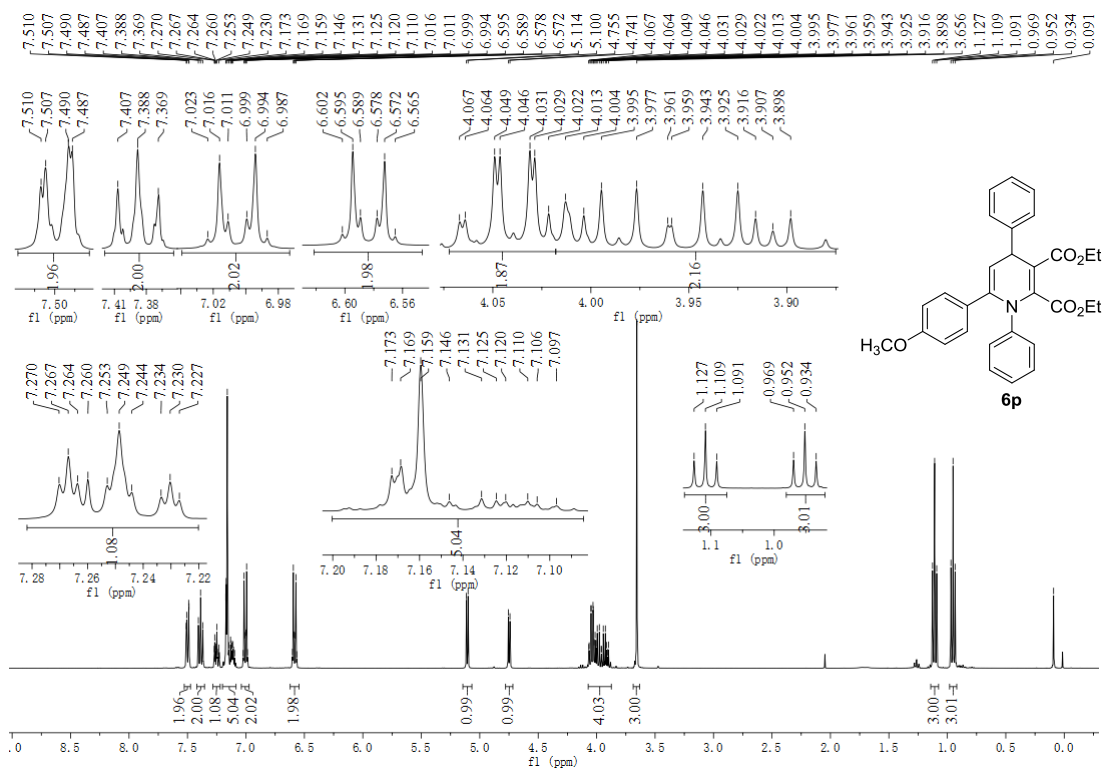
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



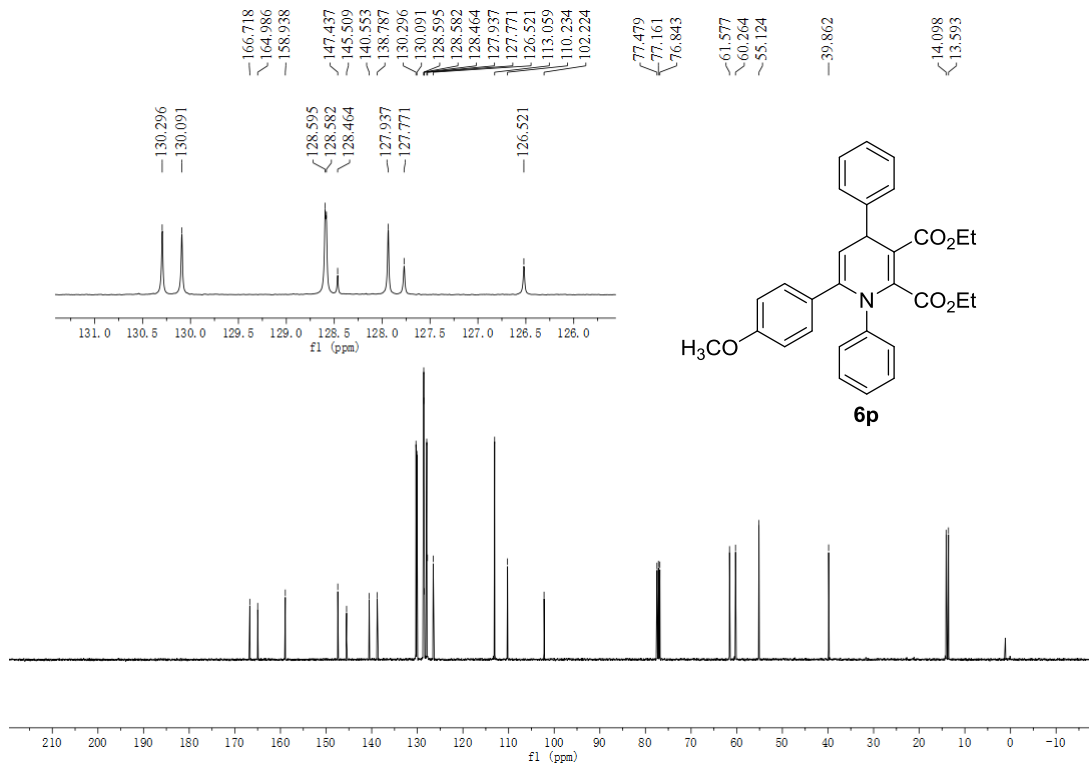
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



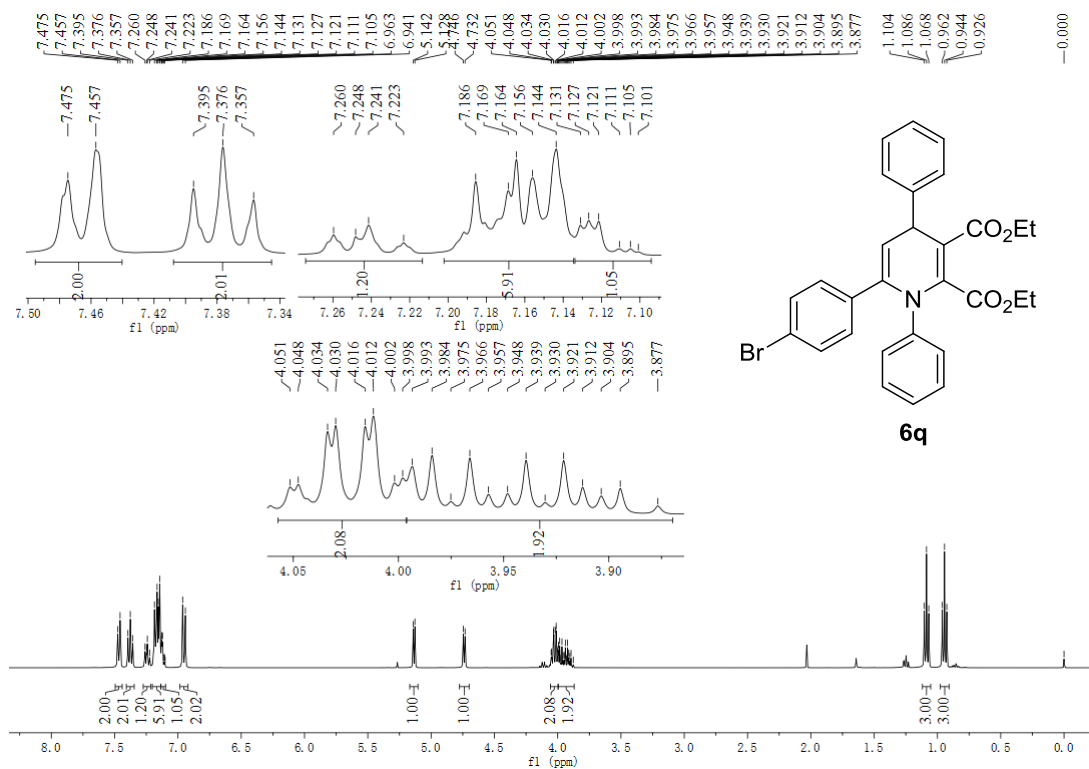
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



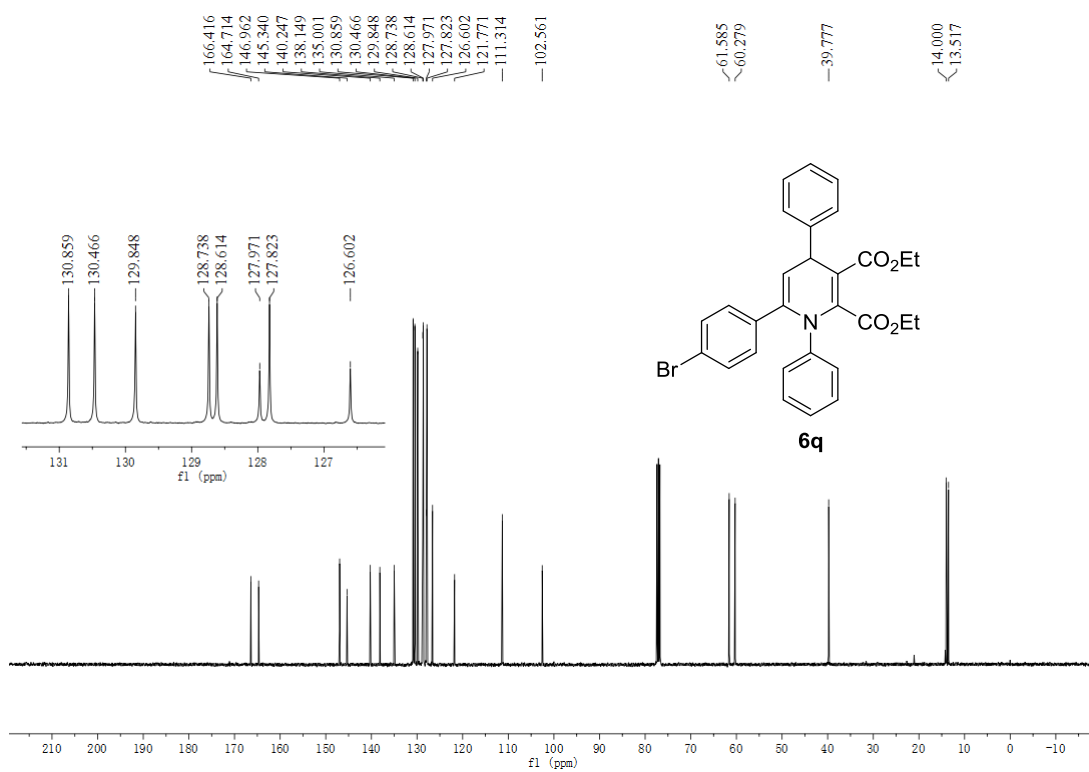
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



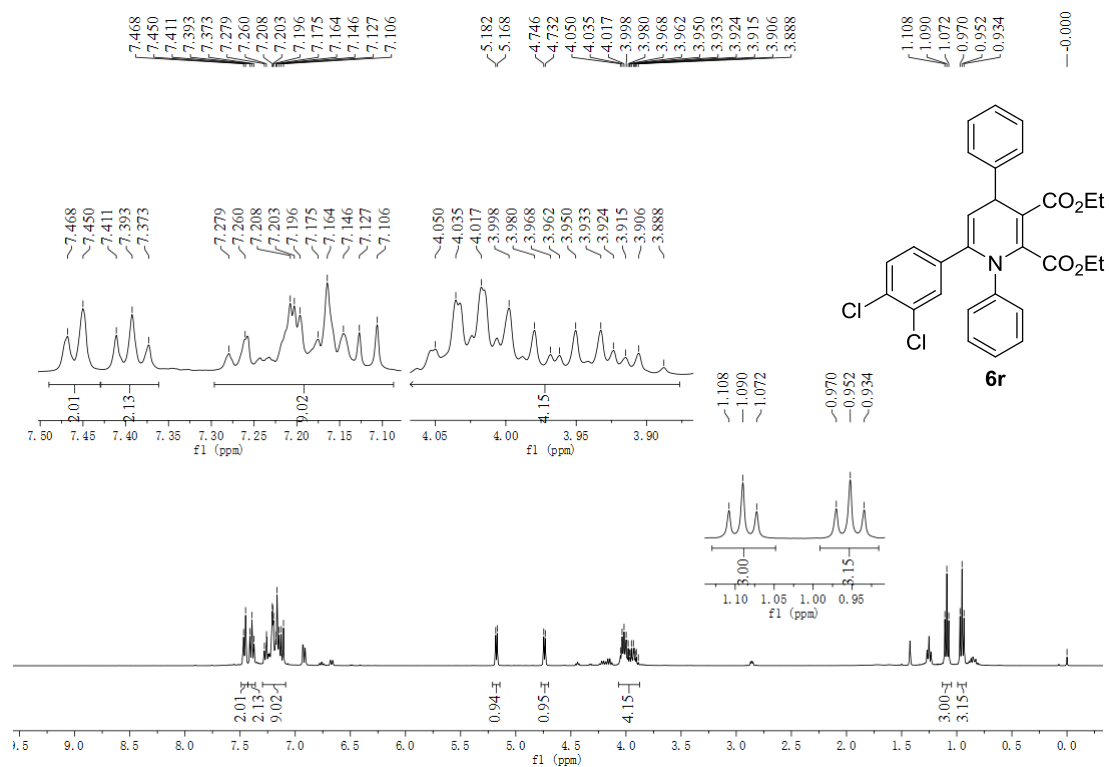
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



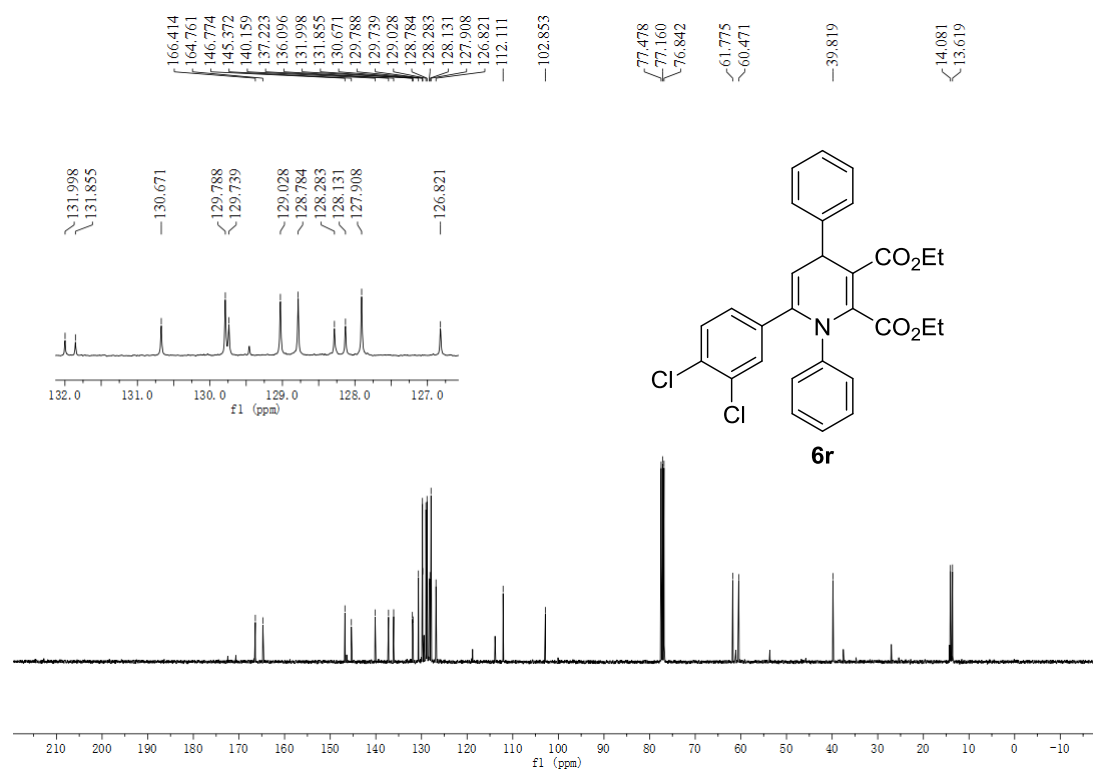
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



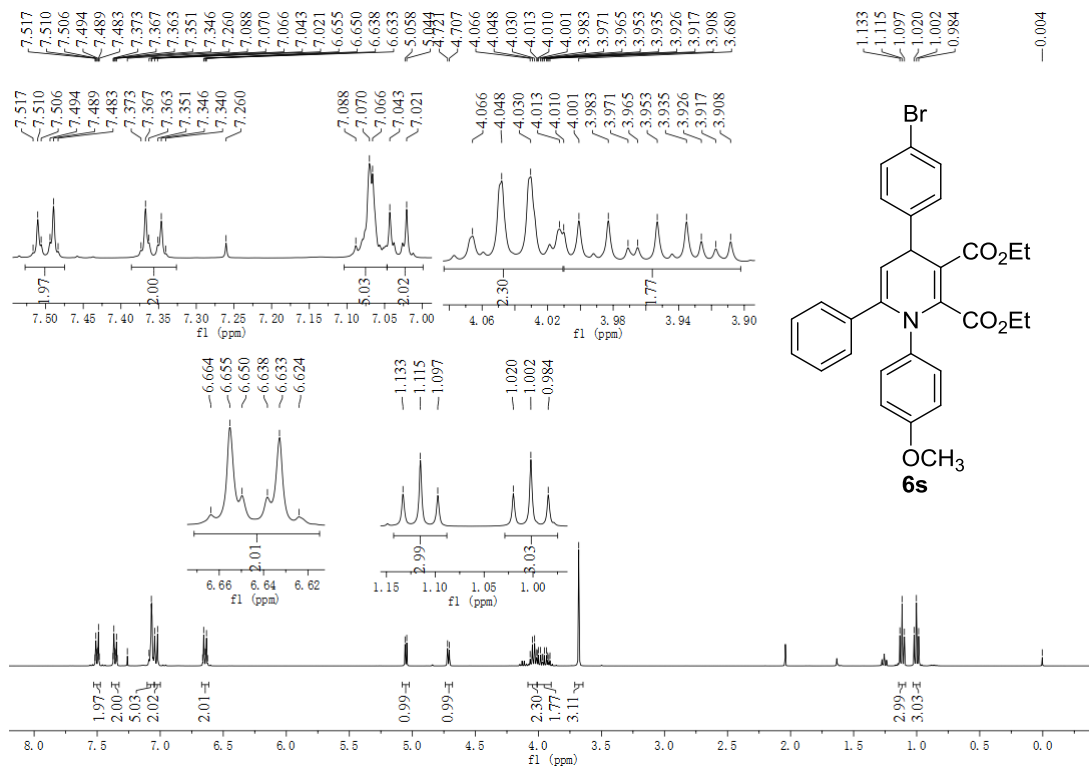
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



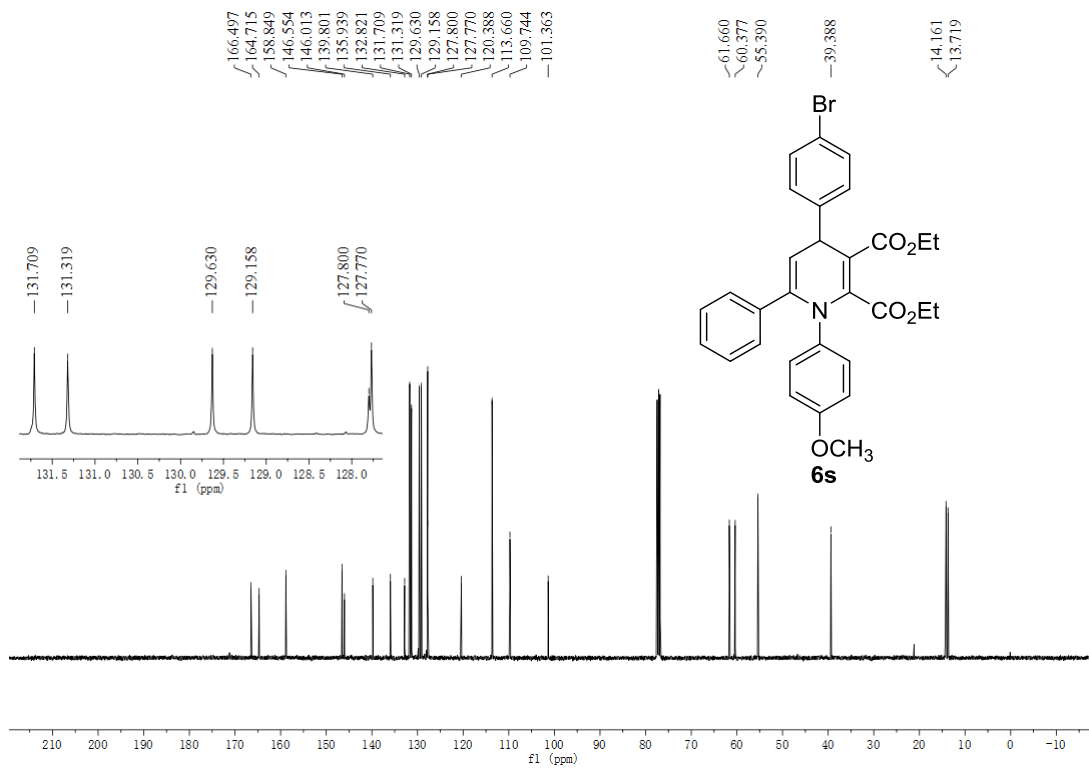
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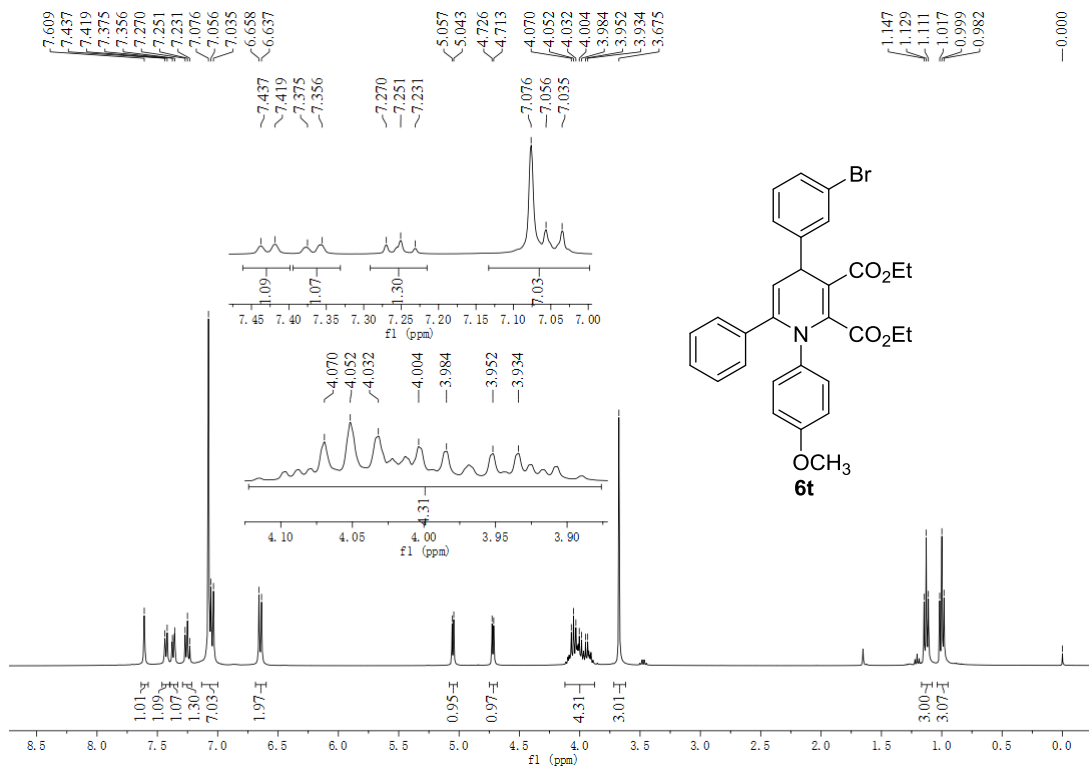
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)



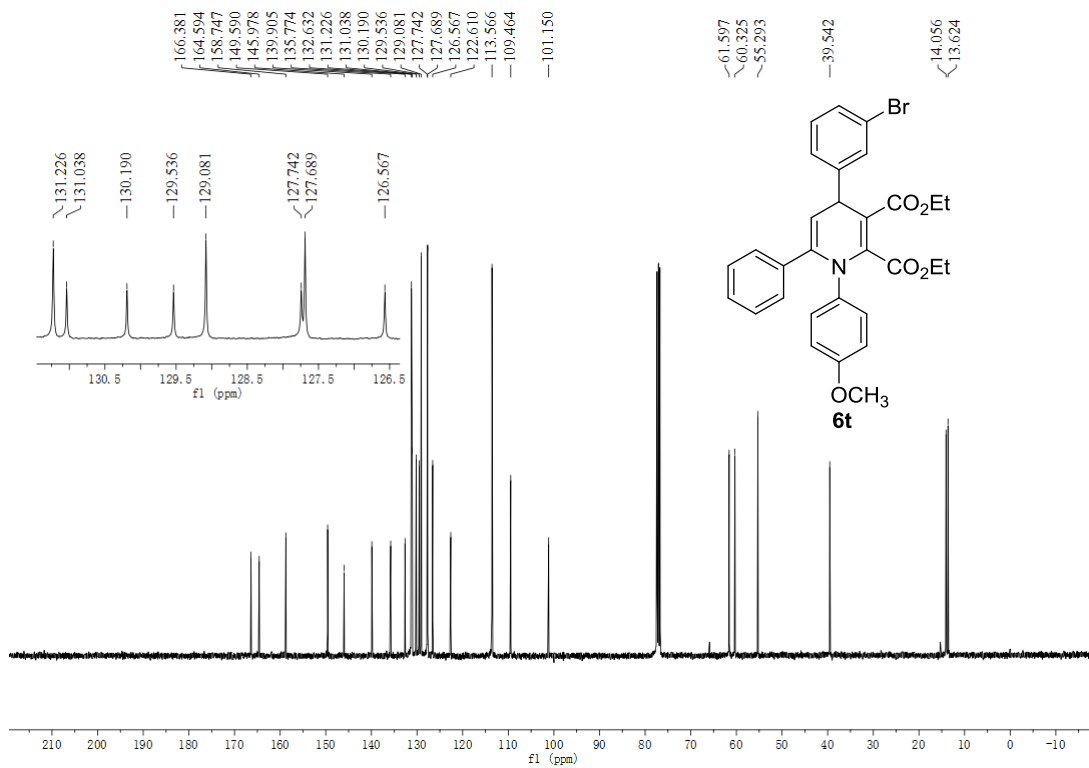
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



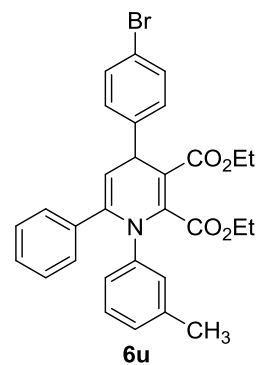
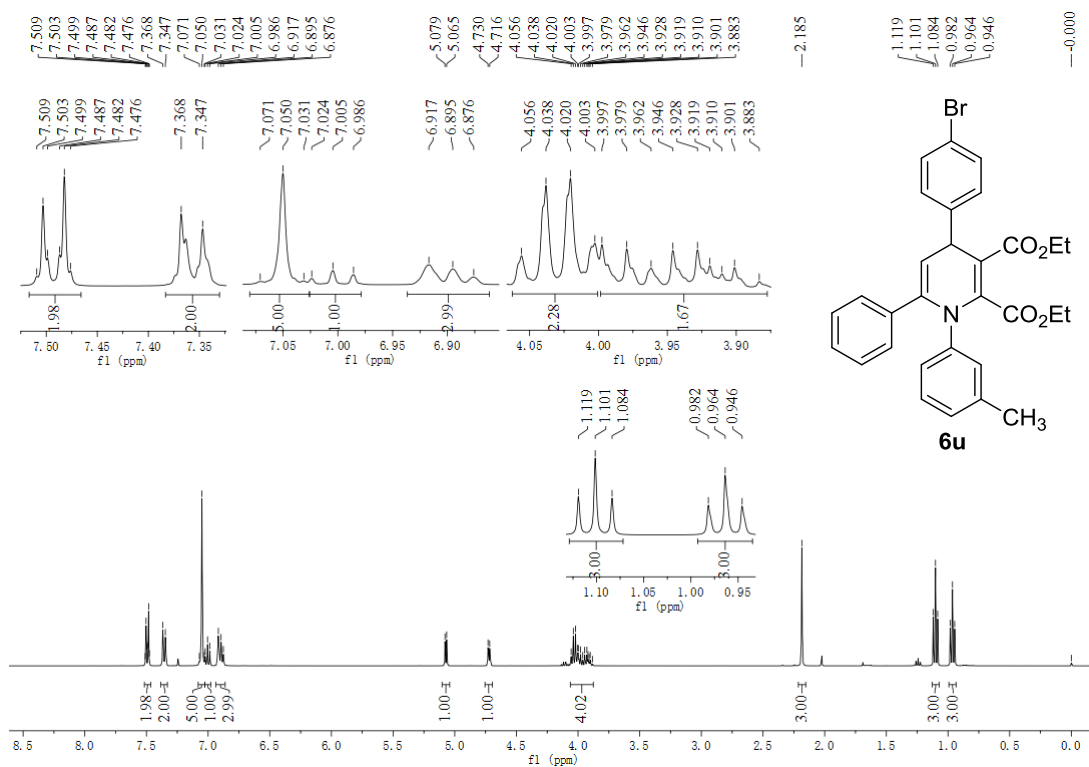
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



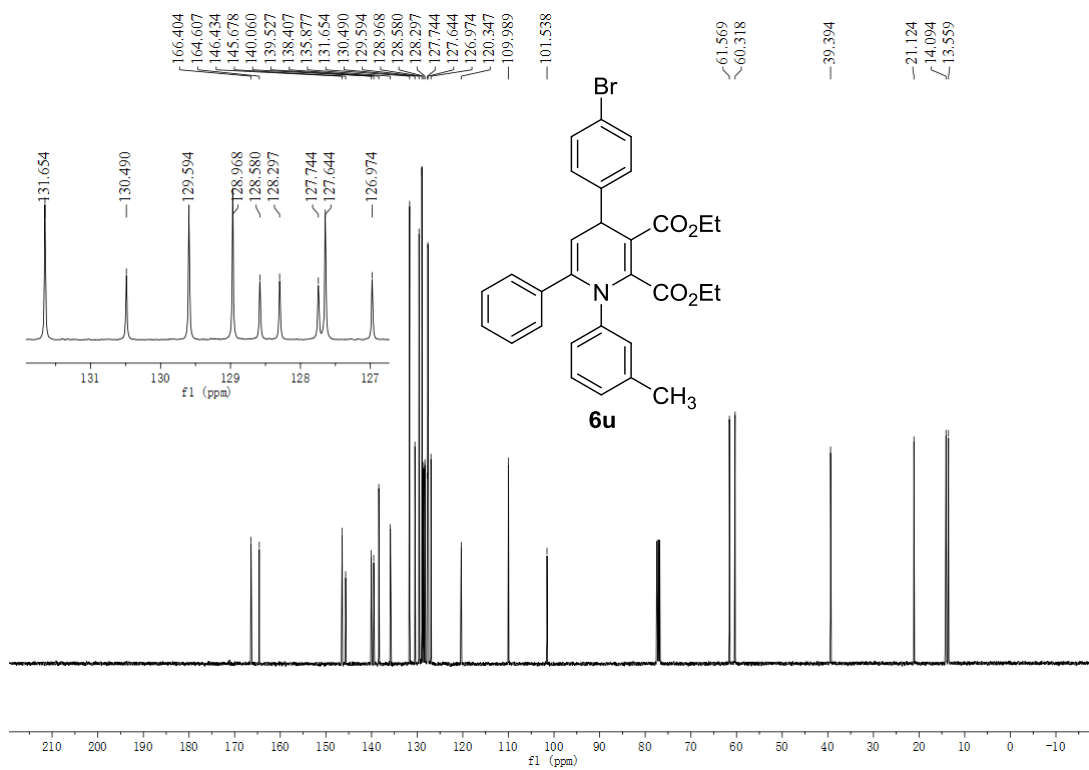
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

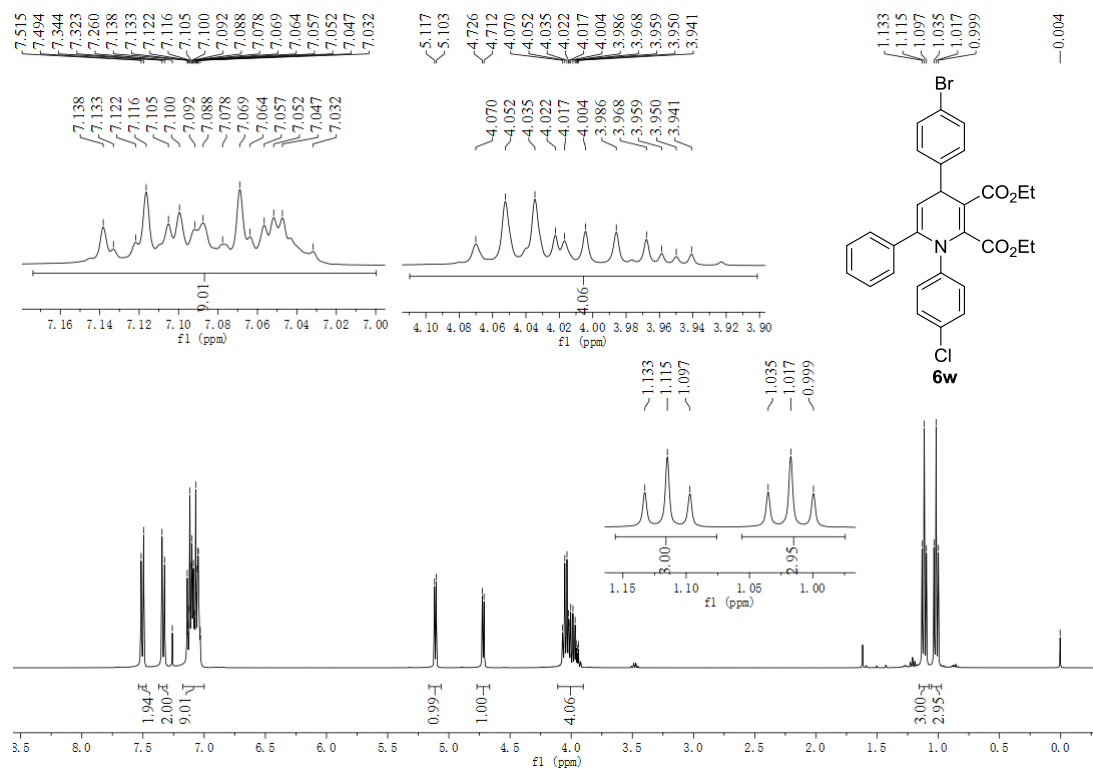


**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

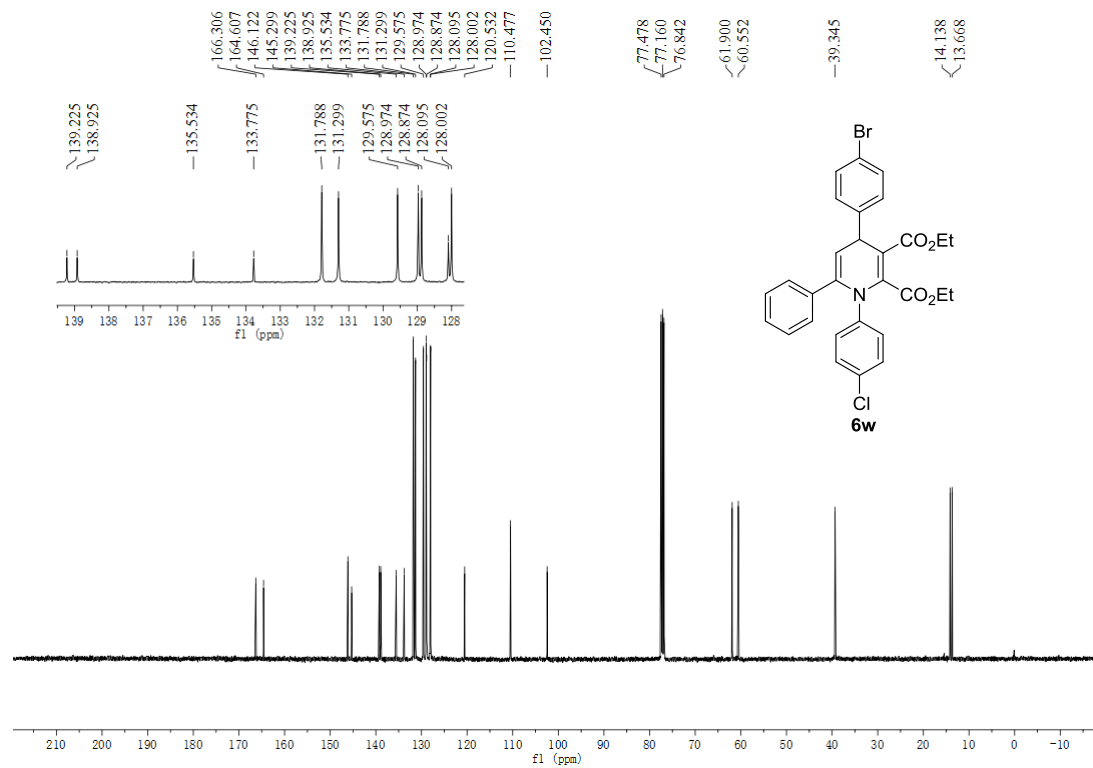


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**

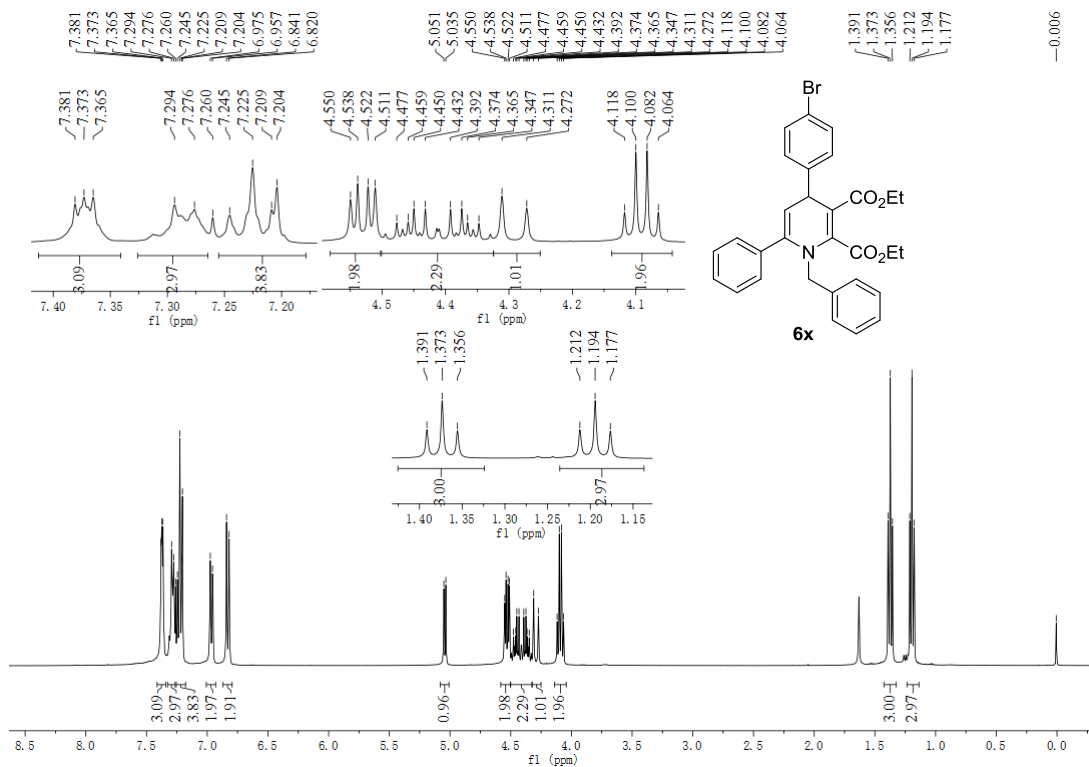




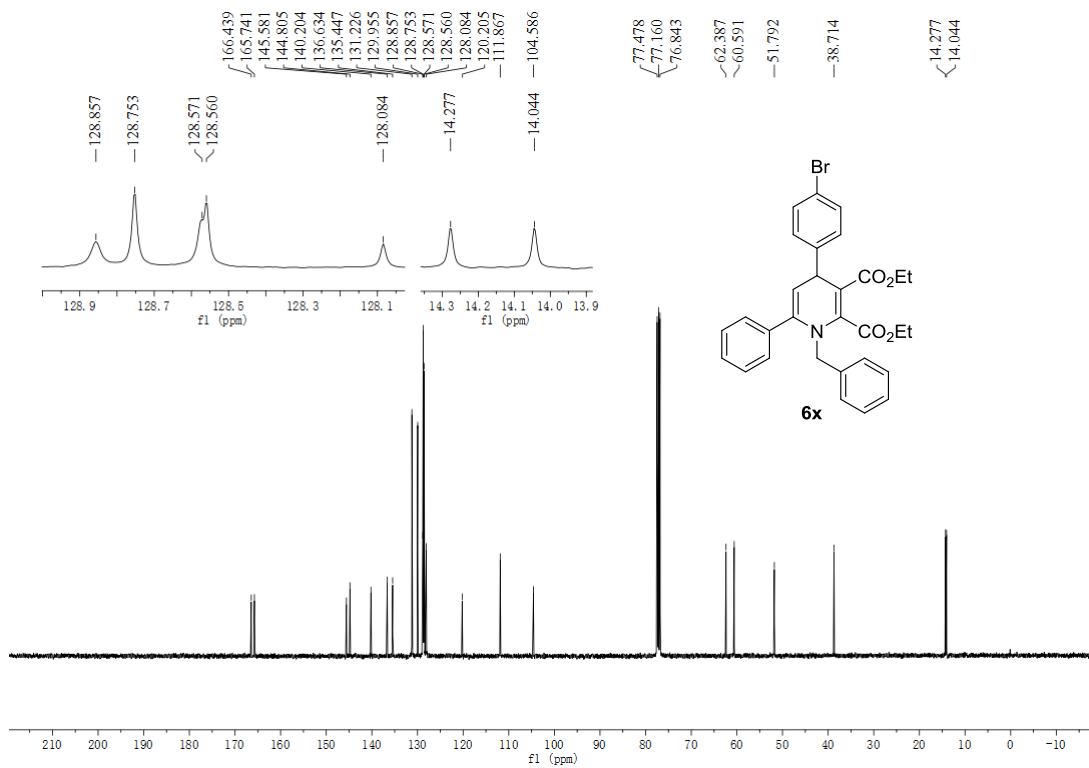
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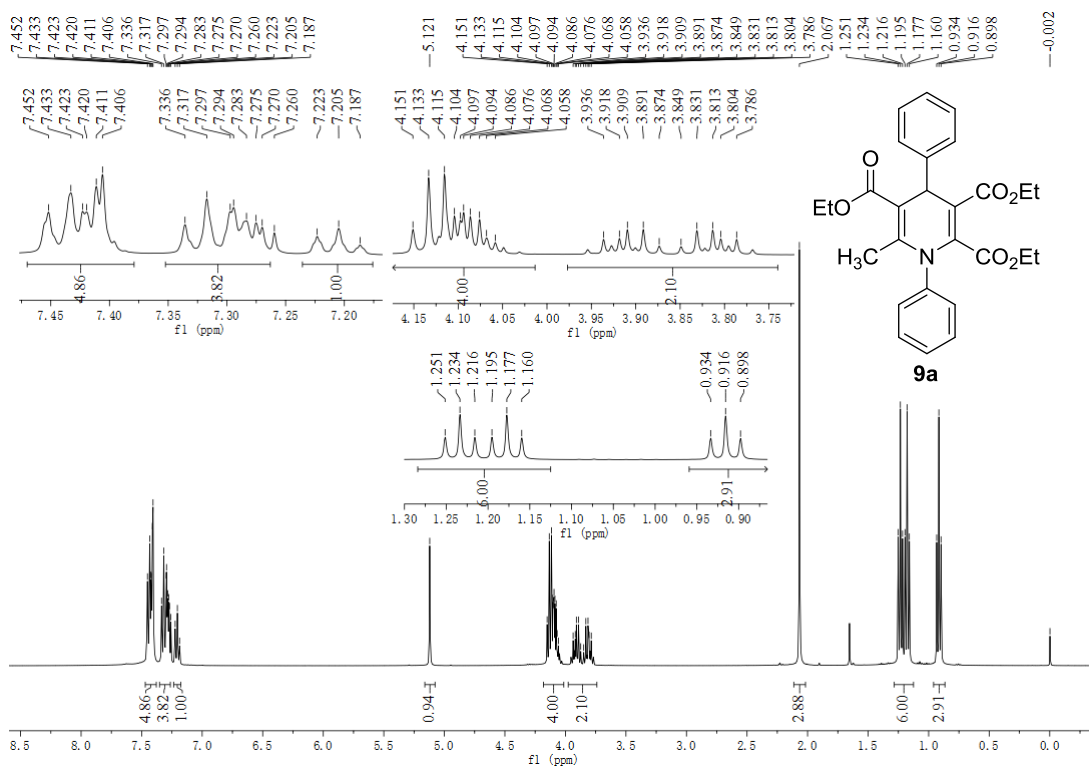
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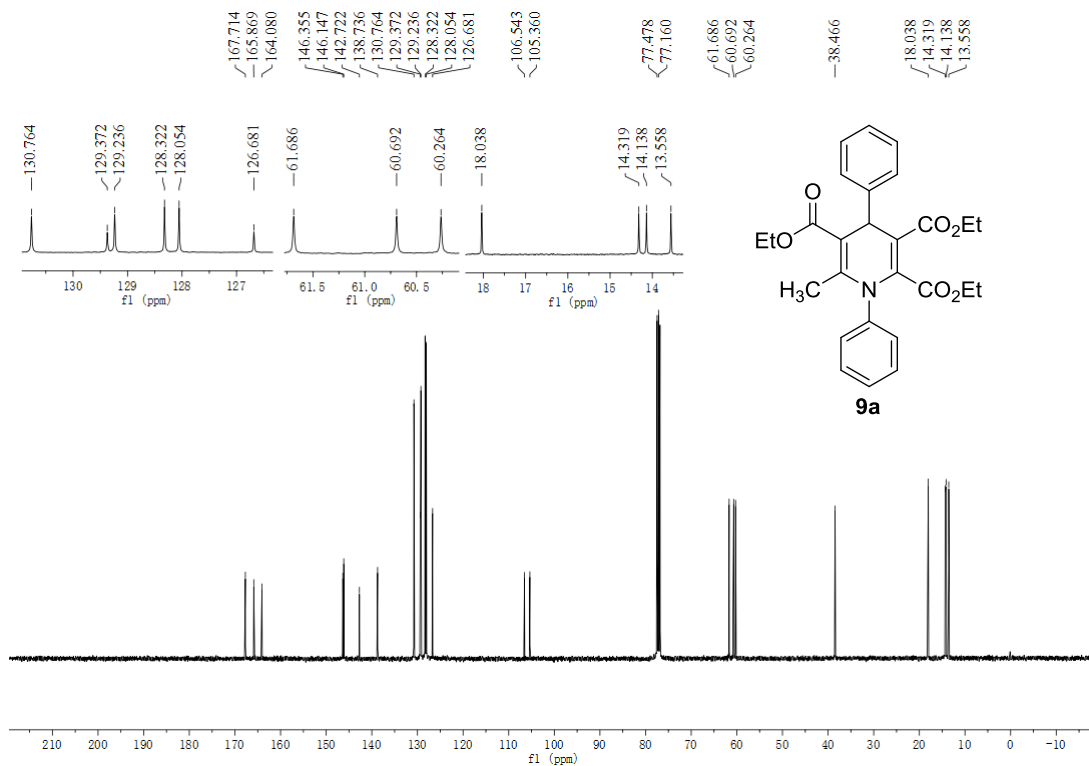
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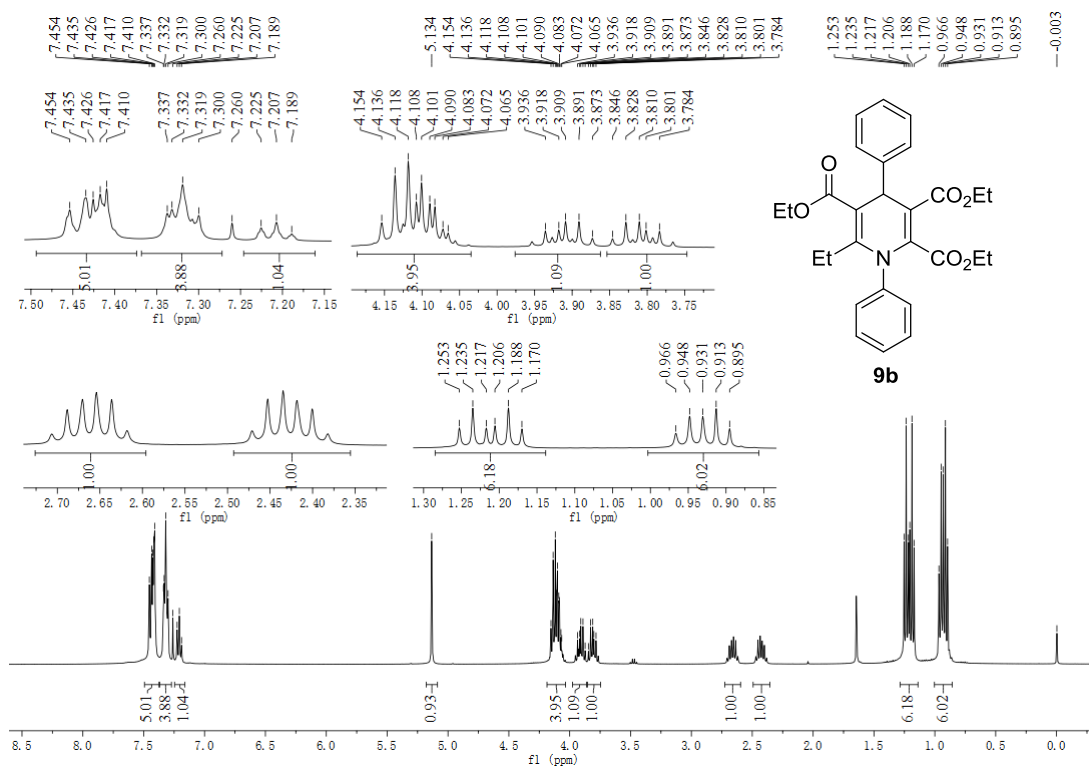
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



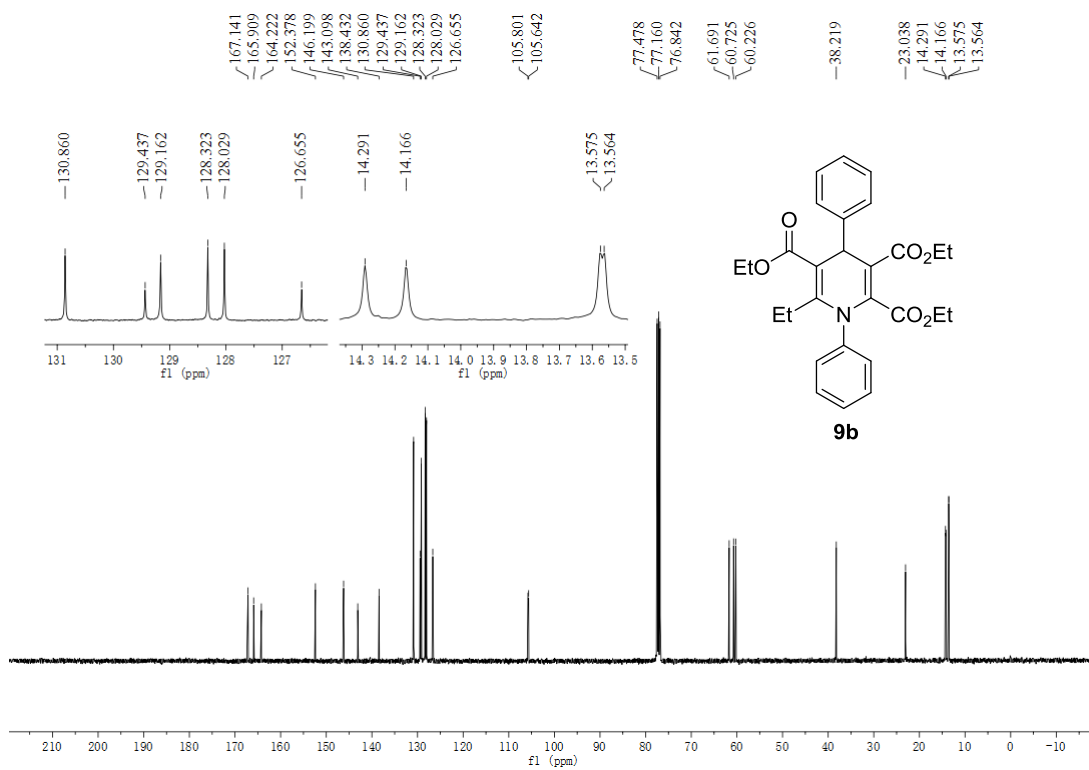
**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



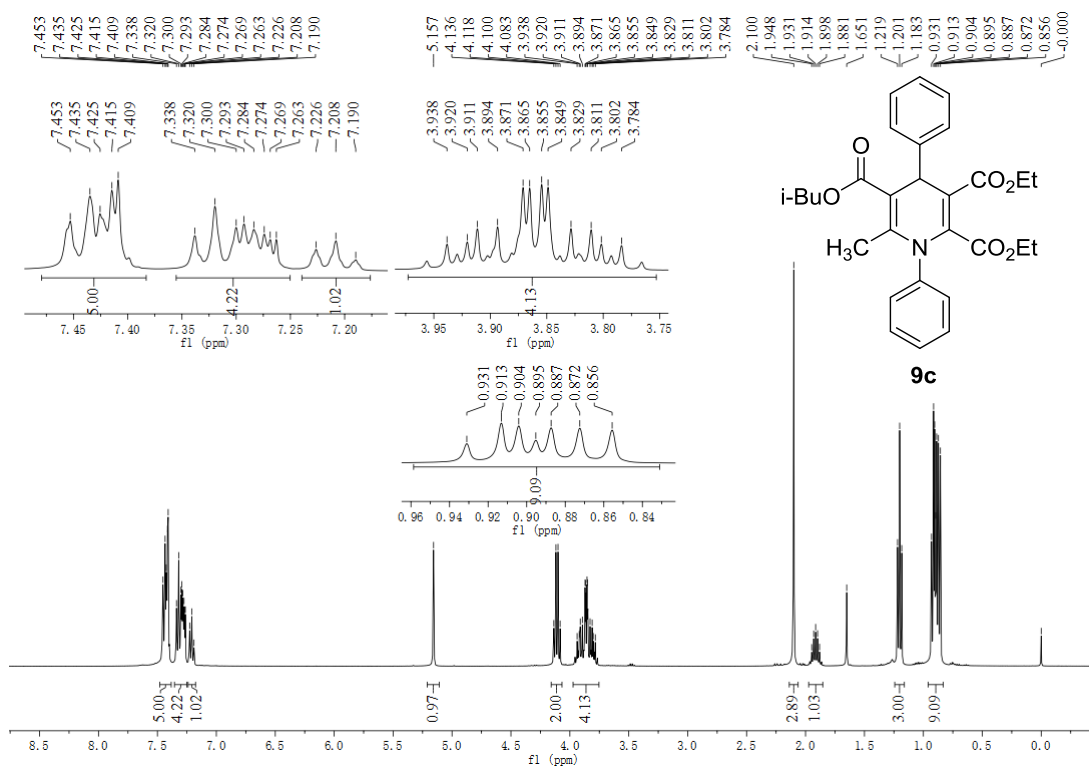
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



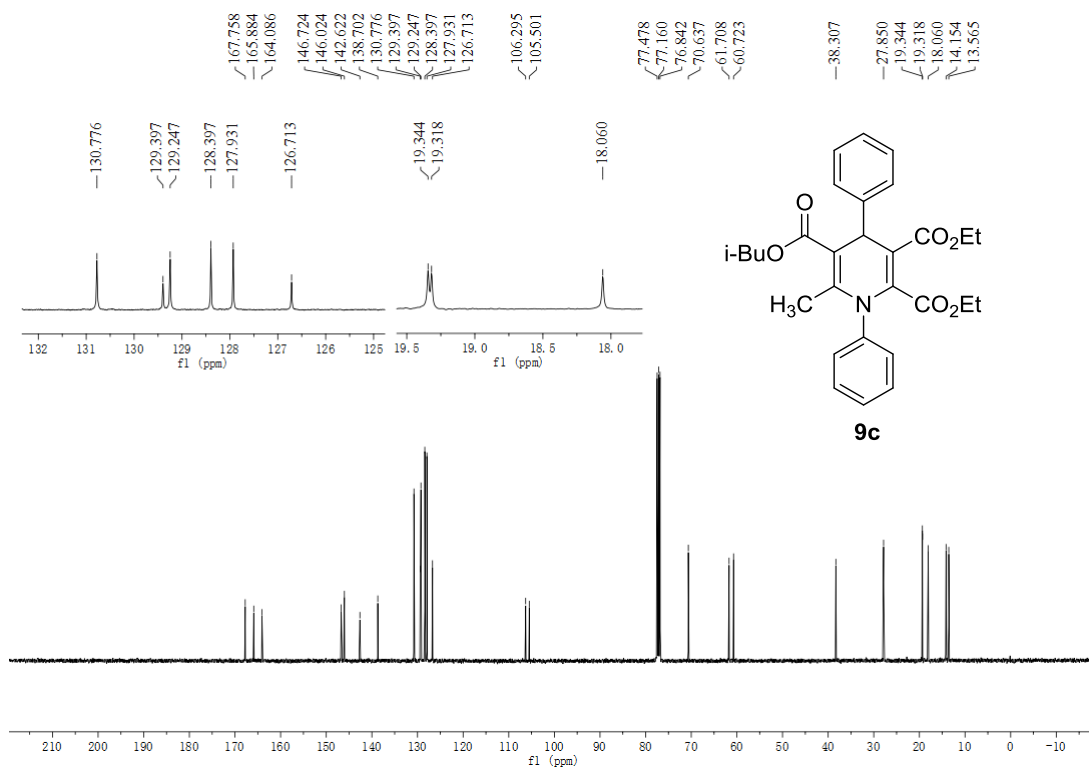
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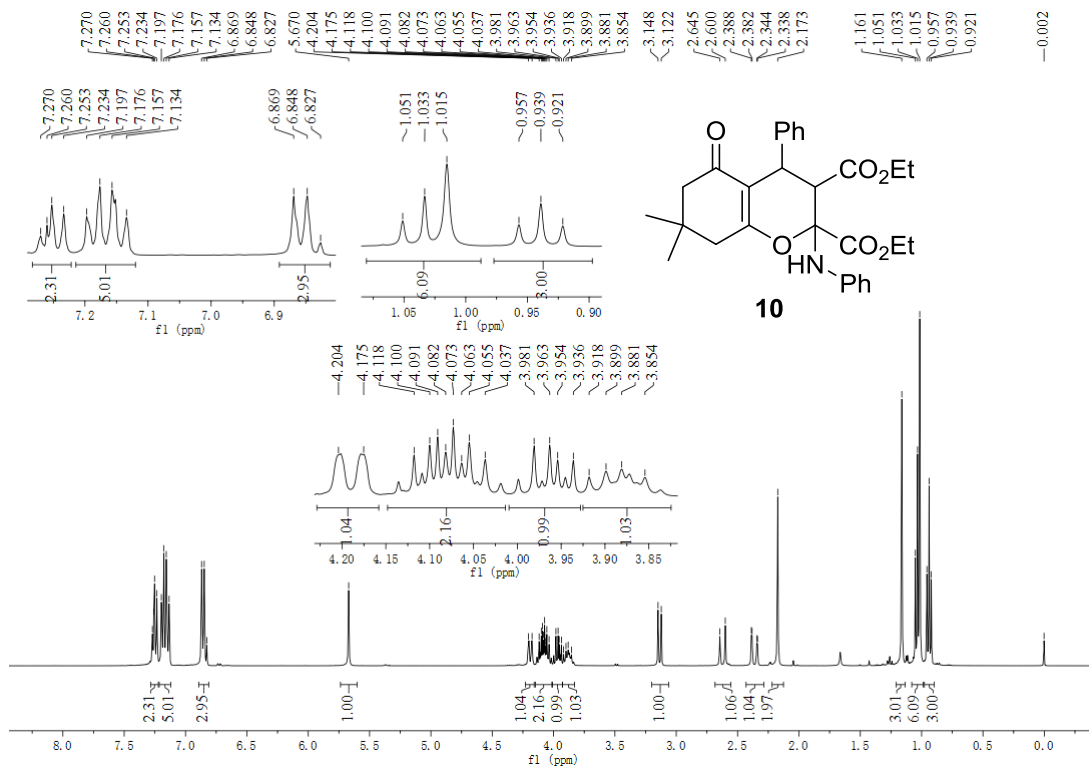
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)**



**<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)**

