

# Supporting Information

## Aroylchlorination of 1,6-Dienes *via* a Photoredox Catalytic Atom-Transfer Radical Cyclization Process

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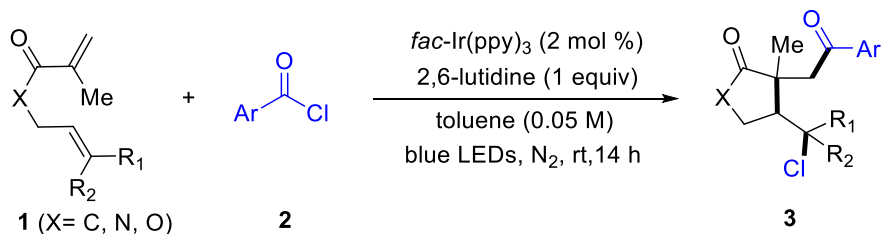
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## 1. General Information

All glassware was thoroughly oven-dried. Chemicals and solvents were either purchased from commercial suppliers or purified by standard techniques. Thin-layer chromatography (TLC) plates were visualized by exposure to ultraviolet light and/or staining with phosphomolybdic acid followed by heating on a hot plate. Flash chromatography was carried out using silica gel (200-300 mesh).  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AM-400 (400 MHz). The spectra were recorded in  $\text{CDCl}_3$  as solvent at room temperature,  $^1\text{H}$  and  $^{13}\text{C}$  NMR chemical shifts are reported in ppm relative to the residual solvent peak. The residual solvent signals were used as references and the chemical shifts were converted to the TMS scale ( $\text{CDCl}_3$ :  $\delta_{\text{H}} = 0$  ppm,  $\delta_{\text{C}} = 77.00$  ppm). Data for  $^1\text{H}$  NMR are reported as follows: chemical shift ( $\delta$  ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for  $^{13}\text{C}$  NMR are reported as chemical shift. HRMS were performed on a Bruker Apex II mass instrument (ESI).

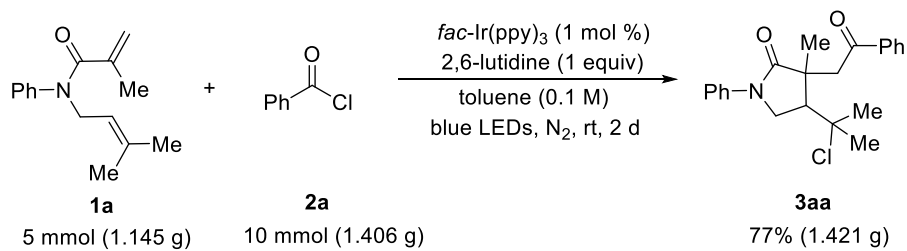
## 2. General Procedure for the Synthesis of Product 3 and Analytic Data

### 2.1 General procedure for the synthesis of product 3



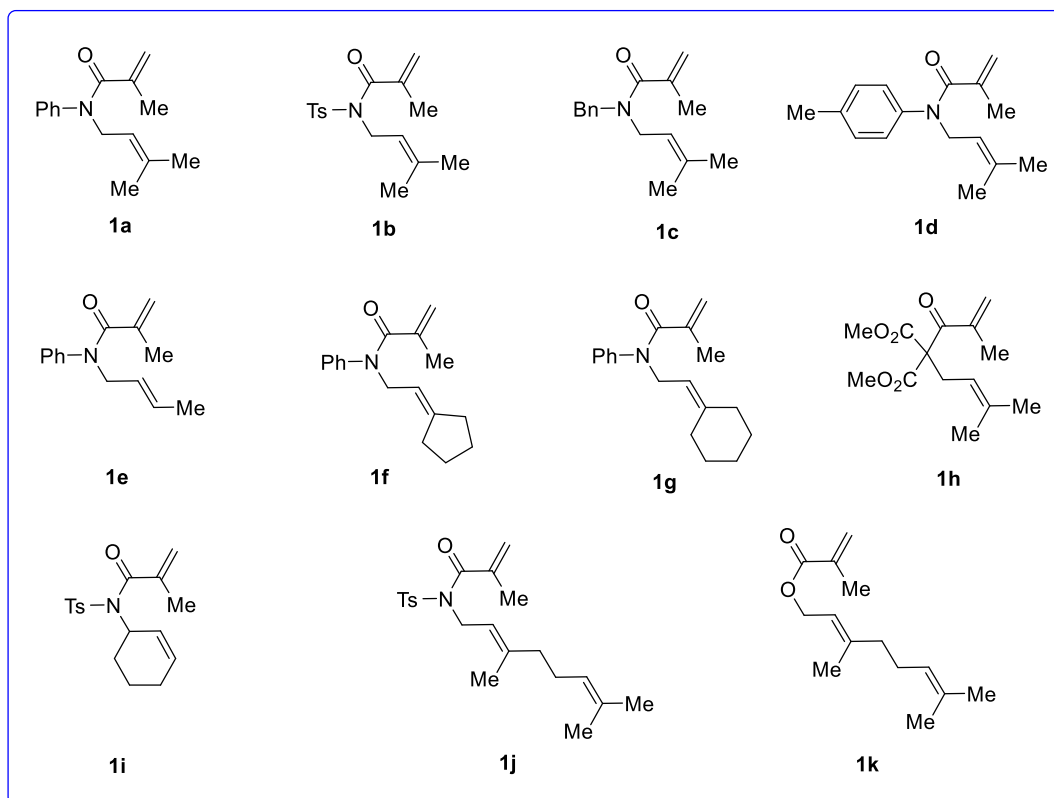
A mixture of 1,6-dienes **1** (0.1 mmol), *fac*-Ir(ppy)<sub>3</sub> (2 mol %), 2,6-lutidine (12  $\mu$ L, 1 equiv) and toluene (2 mL) was degassed by three cycles of freeze-pump-thaw. Acyl chloride **2** (0.2 mmol) was added and the mixture was stirred under nitrogen atmosphere at room temperature while irradiated by blue LEDs for 14 hours. After completion of the reaction, the crude mixture was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 8:1–3:1) to furnish the desired product **3** as described.

## 2.2 Procedure for scale-up preparation of 3aa

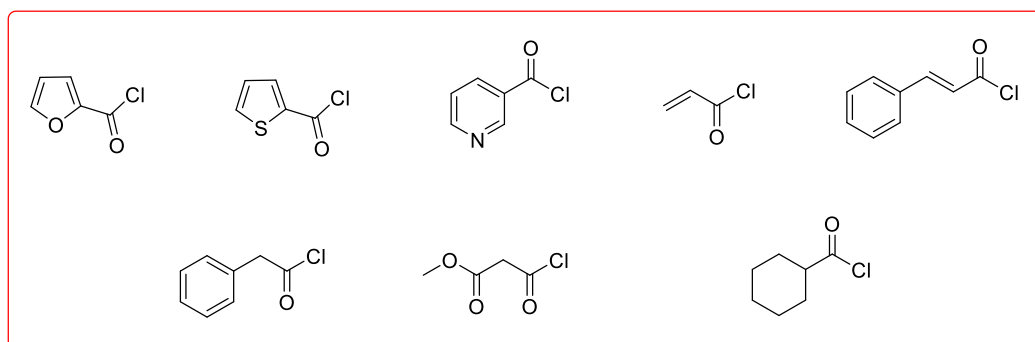


Benzoyl chloride **2a** (10 mmol, 1.406 g, 2 equiv) and 2,6-lutidine (5 mmol, 1.2 mL, 1 equiv) were added to a solution of substrate **1a** (5 mmol, 1.145 g, 1 equiv) and photocatalyst *fac*-Ir(ppy)<sub>3</sub> (32.5 mg, 1 mol %) in dry toluene (50 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then placed in the irradiation apparatus equipped with a 2\*3 W blue LEDs strip. The resulting mixture was stirred at room temperature for 2 days. After completion of the reaction, the reaction mixture was concentrated under reduced pressure, and the resulting crude mixture was purified by flash column chromatography on silica gel (petroleum ether/EtOAc = 4:1) to afford the desired product **3aa** (yield 77%, 1.421g).

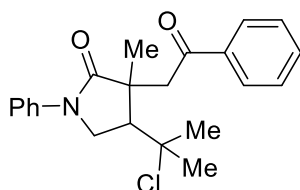
### 2.3 Successful substrates of 1,6-dienes



### 2.4 Unsuccessful substrates of chlorides



## 2.5 Analytic data of products



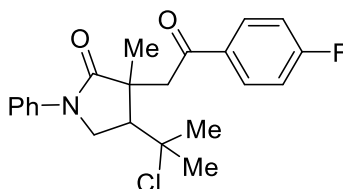
### 4-(2-Chloropropan-2-yl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylpyrrolidin-2-one (3aa)

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3aa**. White solid, 31.4 mg, 85% yield, mp = 148–150 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01–7.92 (m, 2H), 7.70 (d, *J* = 7.7 Hz, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.07–3.93 (m, 2H), 3.61 (q, *J* = 18.5 Hz, 2H), 3.30 (dd, *J* = 10.0, 8.3 Hz, 1H), 1.73 (s, 3H), 1.68 (s, 3H), 1.46 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.87, 176.66, 139.46, 136.89, 133.24, 128.74, 128.54, 127.94, 124.46, 120.05, 70.20, 48.02, 47.61, 47.40, 45.62, 33.39, 32.34, 20.62.

HRMS (ESI) for C<sub>22</sub>H<sub>25</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 370.1568, found 370.1567.



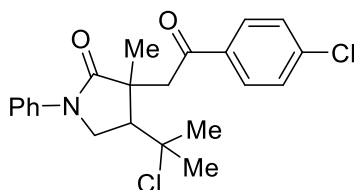
### 4-(2-Chloropropan-2-yl)-3-(2-(4-fluorophenyl)-2-oxoethyl)-3-methyl-1-phenylpyrrolidin-2-one (3ab)

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3ab**. White solid, 31.0 mg, 80% yield, mp = 132–134 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.03–7.99 (m, 2H), 7.70–7.67 (m, 2H), 7.42–7.34 (m, 2H), 7.19–7.10 (m, 3H), 4.04–3.94 (m, 2H), 3.57 (q, *J* = 18.4 Hz, 2H), 3.31 (dd, *J* = 10.0, 8.3 Hz, 1H), 1.73 (s, 3H), 1.69 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.36, 176.60, 165.86 (d, *J* = 256.5 Hz), 139.42, 133.37 (d, *J* = 2.9 Hz), 130.67 (d, *J* = 9.4 Hz), 128.80, 124.56, 120.07, 115.79, 115.57, 70.15, 48.04, 47.66, 47.50, 45.50, 33.30, 32.47, 20.66.

HRMS (ESI) for C<sub>22</sub>H<sub>24</sub>ClFNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 388.1474, found 388.1476.



### 3-(2-(4-Chlorophenyl)-2-oxoethyl)-4-(2-chloropropan-2-yl)-3-methyl-1-phenylpyrrolidin-2-one (3ac)

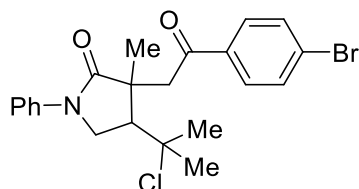
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3ac**. White solid, 35.5 mg, 88% yield, mp = 120–122 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (d, *J* = 8.5 Hz, 2H), 7.69 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 8.5 Hz, 2H), 7.38 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.05–3.93 (m, 2H), 3.56 (q, *J* = 18.4 Hz,

2H), 3.29 (dd,  $J = 9.9, 8.4$  Hz, 1H), 1.72 (s, 3H), 1.69 (s, 3H), 1.45 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.75, 176.54, 161.24, 141.35, 139.75, 139.36, 135.18, 131.82, 129.40, 128.88, 128.79, 127.03, 124.57, 120.04, 70.10, 48.00, 47.62, 47.47, 45.52, 33.25, 32.48, 20.62.

HRMS (ESI) for  $\text{C}_{22}\text{H}_{24}\text{Cl}_2\text{NO}_2$   $[\text{M}+\text{H}]^+$  calcd. 404.1179, found 404.1178.



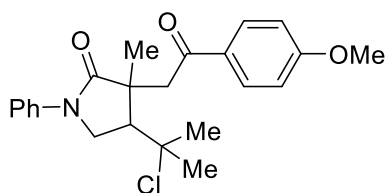
**3-(2-(4-Bromophenyl)-2-oxoethyl)-4-(2-chloropropan-2-yl)-3-methyl-1-phenylpyrrolidin-2-one (3ad)**

Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 4:1) afforded **3ad**. White solid, 34.4 mg, 77% yield, mp = 120–122 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.5$  Hz, 2H), 7.68 (d,  $J = 8.1$  Hz, 2H), 7.60 (d,  $J = 8.5$  Hz, 2H), 7.38 (t,  $J = 7.9$  Hz, 2H), 7.16 (t,  $J = 7.4$  Hz, 1H), 4.04–3.93 (m, 2H), 3.56 (q,  $J = 18.5$  Hz, 2H), 3.28 (dd,  $J = 9.8, 8.5$  Hz, 1H), 1.72 (s, 3H), 1.69 (s, 3H), 1.45 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.83, 176.41, 139.28, 135.47, 131.77, 129.41, 128.69, 128.38, 124.45, 119.93, 70.06, 47.89, 47.53, 47.35, 45.39, 33.13, 32.37, 20.52.

HRMS (ESI) for  $\text{C}_{22}\text{H}_{24}\text{BrClNO}_2$   $[\text{M}+\text{H}]^+$  calcd. 448.0673, found 448.0671.



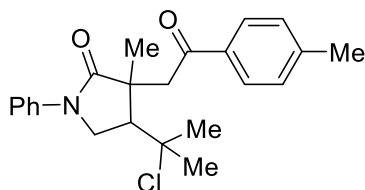
**4-(2-Chloropropan-2-yl)-3-(2-(4-methoxyphenyl)-2-oxoethyl)-3-methyl-1-phenylpyrrolidin-2-one (3ae)**

Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 3:1) afforded **3ae**. White solid, 24.0 mg, 60% yield, mp = 96–98 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97–7.92 (m, 2H), 7.70 (d,  $J = 7.7$  Hz, 2H), 7.38–7.34 (m, 2H), 7.13 (t,  $J = 7.4$  Hz, 1H), 6.91–6.88 (m, 2H), 3.98 (dt,  $J = 17.6, 9.4$  Hz, 2H), 3.82 (s, 3H), 3.55 (q,  $J = 18.3$  Hz, 2H), 3.29 (dd,  $J = 9.9, 8.4$  Hz, 1H), 1.70 (s, 3H), 1.65 (s, 3H), 1.43 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.21, 176.77, 163.50, 139.38, 131.97, 130.14, 129.85, 128.61, 124.30, 119.93, 113.59, 70.25, 55.30, 47.91, 47.49, 47.32, 45.12, 33.35, 32.13, 20.51.

HRMS (ESI) for  $\text{C}_{23}\text{H}_{27}\text{ClNO}_3$   $[\text{M}+\text{H}]^+$  calcd. 400.1674, found 400.1675.



**4-(2-Chloropropan-2-yl)-3-methyl-3-(2-oxo-2-(p-tolyl)ethyl)-1-phenylpyrrolidin-2-one (3af)**

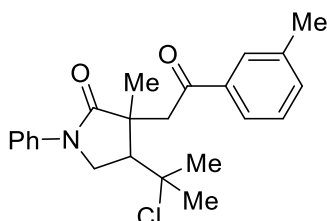
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3af**.

White solid, 29.1 mg, 76% yield, mp = 122–124 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90–7.85 (m, 2H), 7.72–7.68 (m, 2H), 7.40–7.35 (m, 2H), 7.27–7.26 (m, 1H), 7.24 (d, *J* = 0.6 Hz, 1H), 7.17–7.12 (m, 1H), 4.06–3.93 (m, 2H), 3.57 (dd, *J* = 39.5, 18.4 Hz, 2H), 3.29 (dd, *J* = 10.0, 8.3 Hz, 1H), 2.41 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.46, 176.75, 144.09, 139.51, 134.45, 129.23, 128.74, 128.08, 124.43, 120.05, 70.25, 48.02, 47.59, 47.39, 45.51, 33.48, 32.29, 21.59, 20.64.

HRMS (ESI) for C<sub>23</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 384.1725, found 384.1723.



#### 4-(2-Chloropropan-2-yl)-3-methyl-3-(2-oxo-2-(m-tolyl)ethyl)-1-phenylpyrrolidin-2-one (**3ag**)

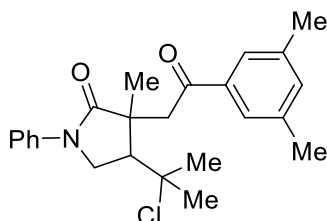
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3ag**.

White solid, 29.9 mg, 78% yield, mp = 108–110 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.78–7.76 (m, 2H), 7.72–7.69 (m, 2H), 7.40–7.32 (m, 4H), 7.18–7.11 (m, 1H), 4.00 (dt, *J* = 17.6, 9.4 Hz, 2H), 3.59 (q, *J* = 18.6 Hz, 2H), 3.30 (dd, *J* = 10.0, 8.3 Hz, 1H), 2.41 (s, 3H), 1.73 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.92, 176.61, 139.38, 138.20, 136.76, 133.92, 128.62, 128.35, 128.33, 125.05, 124.30, 119.91, 70.18, 47.89, 47.48, 47.24, 45.57, 33.32, 32.19, 21.21, 20.51.

HRMS (ESI) for C<sub>23</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 384.1725, found 384.1727.



#### 4-(2-Chloropropan-2-yl)-3-(2-(3,5-dimethylphenyl)-2-oxoethyl)-3-methyl-1-phenylpyrrolidin-2-one (**3ah**)

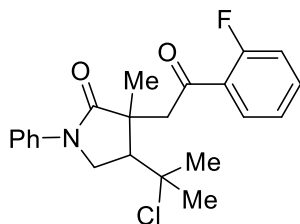
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3ah**.

White solid, 29.4 mg, 74% yield, mp = 130–132 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.70 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.57 (s, 2H), 7.41–7.34 (m, 2H), 7.20 (s, 1H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.00 (dt, *J* = 17.6, 9.4 Hz, 2H), 3.57 (q, *J* = 18.6 Hz, 2H), 3.30 (dd, *J* = 9.9, 8.3 Hz, 1H), 2.36 (s, 6H), 1.73 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.07, 176.63, 139.39, 138.01, 136.82, 134.77, 128.59, 125.62, 124.26, 119.91, 70.20, 47.90, 47.48, 47.22, 45.63, 33.35, 32.15, 21.08, 20.49.

HRMS (ESI) for C<sub>24</sub>H<sub>29</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 398.1881, found 398.1882.



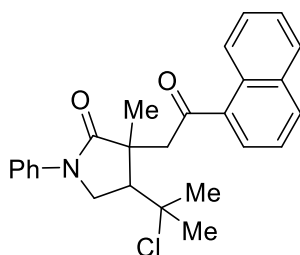
**4-(2-Chloropropan-2-yl)-3-(2-(2-fluorophenyl)-2-oxoethyl)-3-methyl-1-phenylpyrrolidin-2-one (3ai)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 3:1) afforded **3ai**.  
White solid, 32.1 mg, 83% yield, mp = 82–84 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.86 (td, *J* = 7.7, 1.8 Hz, 1H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.55–7.49 (m, 1H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.22 (t, *J* = 7.6 Hz, 1H), 7.20–7.11 (m, 2H), 4.07–3.95 (m, 2H), 3.61 (qd, *J* = 19.3, 2.7 Hz, 2H), 3.27 (dd, *J* = 10.0, 8.4 Hz, 1H), 1.75 (s, 3H), 1.69 (s, 3H), 1.43 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 196.07, 176.62, 161.74 (d, *J* = 255.5 Hz), 139.39, 134.67 (d, *J* = 9.1 Hz), 130.48 (d, *J* = 2.5 Hz), 128.67, 125.39 (d, *J* = 12.9 Hz), 124.40, 124.37, 119.95, 116.69, 116.45, 70.17, 50.46, 47.93, 47.67, 47.39, 33.49, 32.08, 20.43.

HRMS (ESI) for C<sub>22</sub>H<sub>24</sub>ClFNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 388.1471, found 388.1473.



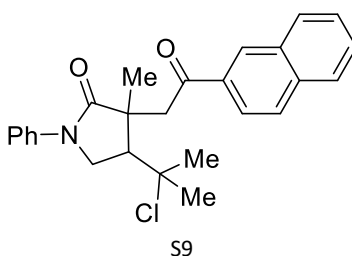
**4-(2-Chloropropan-2-yl)-3-methyl-3-(2-(naphthalen-1-yl)-2-oxoethyl)-1-phenylpyrrolidin-2-one (3aj)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 5:1) afforded **3aj**.  
White solid, 30.6 mg, 73% yield, mp = 60–62 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.52 (d, *J* = 8.4 Hz, 1H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.92 (d, *J* = 7.1 Hz, 1H), 7.86 (d, *J* = 7.6 Hz, 1H), 7.72 (d, *J* = 8.3 Hz, 2H), 7.59–7.46 (m, 3H), 7.39 (t, *J* = 7.9 Hz, 2H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.02 (p, *J* = 9.3 Hz, 2H), 3.66 (q, *J* = 18.5 Hz, 2H), 3.49 (dd, *J* = 9.8, 8.4 Hz, 1H), 1.77 (s, 3H), 1.72 (s, 3H), 1.44 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 202.64, 176.62, 139.49, 136.20, 133.88, 132.50, 129.93, 128.79, 128.37, 127.87, 127.09, 126.44, 125.57, 124.54, 124.30, 120.17, 70.21, 49.14, 48.09, 47.91, 47.76, 33.39, 32.53, 20.61.

HRMS (ESI) for C<sub>26</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 420.1725, found 420.1723.



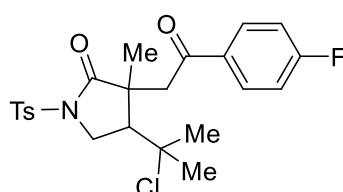
**4-(2-Chloropropan-2-yl)-3-methyl-3-(2-(naphthalen-2-yl)-2-oxoethyl)-1-phenylpyrrolidin-2-one (3ak)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 5:1) afforded **3ak**.  
White solid, 29.7 mg, 71% yield, mp = 62–64 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.51 (s, 1H), 8.02 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.97 (d, *J* = 8.0 Hz, 1H), 7.90–7.85 (m, 2H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.62–7.53 (m, 2H), 7.38 (t, *J* = 8.0 Hz, 2H), 7.15 (t, *J* = 7.4 Hz, 1H), 4.02 (dt, *J* = 17.6, 9.4 Hz, 2H), 3.75 (q, *J* = 18.4 Hz, 2H), 3.35 (dd, *J* = 9.9, 8.3 Hz, 1H), 1.74 (s, 3H), 1.69 (s, 3H), 1.50 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.85, 176.78, 139.50, 135.67, 134.25, 132.45, 129.72, 129.61, 128.80, 128.55, 128.46, 127.75, 126.80, 124.53, 123.67, 120.13, 70.25, 48.11, 47.72, 47.56, 45.74, 33.46, 32.40, 20.71.

**HRMS (ESI)** for C<sub>26</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 420.1725, found 420.1724.



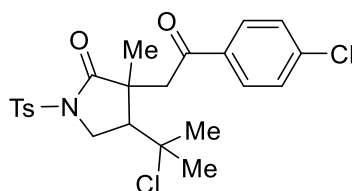
**4-(2-Chloropropan-2-yl)-3-(2-(4-fluorophenyl)-2-oxoethyl)-3-methyl-1-tosylpyrrolidin-2-one (3bb)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3bb**.  
White solid, 33.9 mg, 73% yield, mp = 180–182 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97 (d, *J* = 8.4 Hz, 2H), 7.90–7.82 (m, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 7.13–7.06 (m, 2H), 4.15 (dd, *J* = 9.8, 8.5 Hz, 1H), 3.87 (t, *J* = 10.0 Hz, 1H), 3.58 (d, *J* = 18.6 Hz, 1H), 3.30 (d, *J* = 18.6 Hz, 1H), 3.10 (dd, *J* = 10.2, 8.5 Hz, 1H), 2.45 (s, 3H), 1.63 (s, 3H), 1.61 (s, 3H), 1.28 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.21, 176.40, 165.84 (d, *J* = 256.5 Hz), 144.93, 134.94, 132.68 (d, *J* = 2.9 Hz), 130.54 (d, *J* = 9.4 Hz), 129.49, 127.95, 115.76, 115.54, 69.31, 47.47, 47.23, 46.18, 45.40, 32.86, 32.54, 21.60, 19.91.

**HRMS (ESI)** for C<sub>23</sub>H<sub>26</sub>ClFNO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 466.1250, found 466.1249.



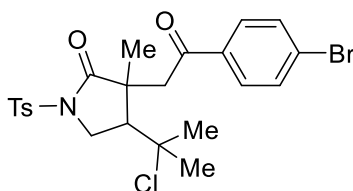
**3-(2-(4-Chlorophenyl)-2-oxoethyl)-4-(2-chloropropan-2-yl)-3-methyl-1-tosylpyrrolidin-2-one (3bc)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3bc**.  
White solid, 36.1 mg, 75% yield, mp = 178–180 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.97 (d, *J* = 8.1 Hz, 2H), 7.77 (d, *J* = 8.4 Hz, 2H), 7.39 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8.0 Hz, 2H), 4.15 (t, *J* = 9.1 Hz, 1H), 3.87 (t, *J* = 10.0 Hz, 1H), 3.58 (d, *J* = 18.6 Hz, 1H), 3.30 (d, *J* = 18.6 Hz, 1H), 3.08 (t, *J* = 9.3 Hz, 1H), 2.45 (s, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.27 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.68, 176.38, 145.00, 140.00, 135.01, 134.63, 129.55, 129.31, 128.93, 128.05, 69.28, 47.56, 47.30, 46.23, 45.50, 32.83, 32.70, 21.68, 19.99.

HRMS (ESI) for  $\text{C}_{23}\text{H}_{26}\text{Cl}_2\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 482.0954, found 482.0952.



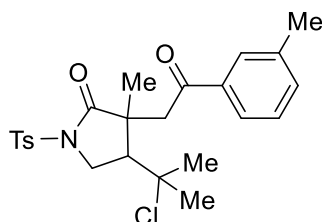
**3-(2-(4-Bromophenyl)-2-oxoethyl)-4-(2-chloropropan-2-yl)-3-methyl-1-tosylpyrrolidin-2-one (3bd)**

Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 4:1) afforded **3bd**. White solid, 36.8 mg, 70% yield, mp = 172–174 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (d,  $J$  = 8.3 Hz, 2H), 7.69 (d,  $J$  = 8.6 Hz, 2H), 7.56 (d,  $J$  = 8.5 Hz, 2H), 7.35 (d,  $J$  = 8.1 Hz, 2H), 4.15 (t,  $J$  = 9.1 Hz, 1H), 3.87 (t,  $J$  = 10.0 Hz, 1H), 3.58 (d,  $J$  = 18.7 Hz, 1H), 3.29 (d,  $J$  = 18.6 Hz, 1H), 3.08 (dd,  $J$  = 10.1, 8.6 Hz, 1H), 2.45 (s, 3H), 1.62 (s, 3H), 1.61 (s, 3H), 1.27 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  195.88, 176.36, 145.00, 135.00, 131.92, 129.55, 129.39, 128.75, 128.03, 69.26, 47.53, 47.28, 46.21, 45.46, 32.82, 32.69, 21.68, 19.98.

HRMS (ESI) for  $\text{C}_{23}\text{H}_{26}\text{BrClNO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 526.0449, found 526.0450.



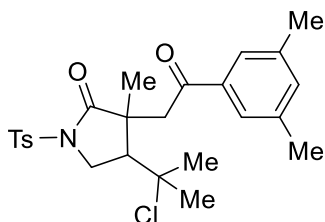
**4-(2-Chloropropan-2-yl)-3-methyl-3-(2-oxo-2-(m-tolyl)ethyl)-1-tosylpyrrolidin-2-one (3bg)**

Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 4:1) afforded **3bg**. White solid, 30.0 mg, 65% yield, mp = 184–186 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J$  = 8.3 Hz, 2H), 7.63–7.60 (m, 2H), 7.36–7.33 (m, 3H), 7.30 (t,  $J$  = 7.8 Hz, 1H), 4.15 (dd,  $J$  = 9.6, 8.6 Hz, 1H), 3.89 (t,  $J$  = 10.0 Hz, 1H), 3.60 (d,  $J$  = 18.7 Hz, 1H), 3.31 (d,  $J$  = 18.7 Hz, 1H), 3.10 (dd,  $J$  = 10.1, 8.6 Hz, 1H), 2.45 (s, 3H), 2.38 (s, 3H), 1.62 (s, 3H), 1.60 (s, 3H), 1.28 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.95, 176.51, 144.87, 138.36, 136.31, 135.04, 134.20, 129.51, 128.43, 128.37, 128.02, 125.04, 69.37, 47.45, 47.24, 46.24, 45.66, 33.04, 32.49, 21.65, 21.26, 19.98.

HRMS (ESI) for  $\text{C}_{24}\text{H}_{29}\text{ClNO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 462.1500, found 462.1499.



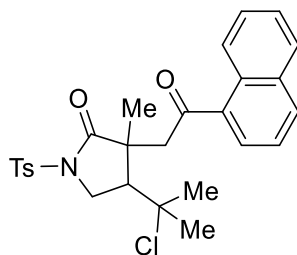
**4-(2-Chloropropan-2-yl)-3-(2-(3,5-dimethylphenyl)-2-oxoethyl)-3-methyl-1-tosylpyrrolidin-2-one (3bh)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3bh**. White solid, 29.5 mg, 62% yield, mp = 180–182 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.42 (s, 2H), 7.35 (d, *J* = 7.1 Hz, 2H), 7.18 (s, 1H), 4.14 (t, *J* = 8.7 Hz, 1H), 3.89 (t, *J* = 9.8 Hz, 1H), 3.58 (d, *J* = 18.6 Hz, 1H), 3.30 (d, *J* = 18.7 Hz, 1H), 3.09 (t, *J* = 8.9 Hz, 1H), 2.45 (s, 3H), 2.33 (s, 6H), 1.62 (s, 3H), 1.60 (s, 3H), 1.28 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.12, 176.55, 144.85, 138.18, 136.35, 135.08, 135.02, 129.50, 128.01, 125.62, 69.39, 47.41, 47.21, 46.24, 45.73, 33.09, 32.45, 21.65, 21.15, 19.98.

HRMS (ESI) for C<sub>25</sub>H<sub>31</sub>ClNO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 476.1657, found 476.1654.



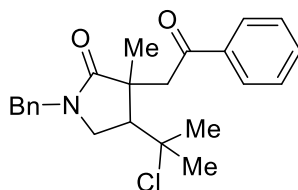
**4-(2-Chloropropan-2-yl)-3-methyl-3-(2-(naphthalen-1-yl)-2-oxoethyl)-1-tosylpyrrolidin-2-one (3bj)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 5:1) afforded **3bj**. White solid, 33.8 mg, 68% yield, mp = 180–182 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.28–8.22 (m, 1H), 8.04 (d, *J* = 8.3 Hz, 2H), 7.97 (d, *J* = 8.2 Hz, 1H), 7.87–7.83 (m, 1H), 7.81–7.77 (m, 1H), 7.56–7.50 (m, 2H), 7.47–7.42 (m, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 4.19 (dd, *J* = 9.7, 8.8 Hz, 1H), 3.94 (t, *J* = 10.0 Hz, 1H), 3.73 (d, *J* = 18.9 Hz, 1H), 3.39 (d, *J* = 18.9 Hz, 1H), 3.22 (dd, *J* = 10.1, 8.7 Hz, 1H), 2.46 (s, 3H), 1.69 (s, 3H), 1.66 (s, 3H), 1.32 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 201.14, 176.52, 144.89, 135.02, 134.85, 133.83, 132.98, 129.85, 129.44, 128.35, 128.13, 127.81, 127.29, 126.44, 125.46, 124.18, 69.42, 48.91, 47.76, 47.43, 46.30, 32.72, 21.70, 20.01.

HRMS (ESI) for C<sub>27</sub>H<sub>29</sub>ClNO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 498.1500, found 498.1497.



### 1-Benzyl-4-(2-chloropropan-2-yl)-3-methyl-3-(2-oxo-2-phenylethyl)pyrrolidin-2-one (3ca)

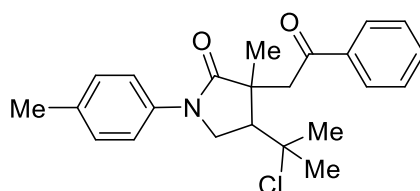
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 3:1) afforded **3ca**.

White solid, 28.7 mg, 75% yield, mp = 90–92 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46–7.43 (m, 2H), 7.39–7.35 (m, 4H), 7.31–7.28 (m, 1H), 4.64 (d, *J* = 14.9 Hz, 1H), 4.51 (d, *J* = 14.9 Hz, 1H), 3.56 (q, *J* = 18.4 Hz, 2H), 3.37 (p, *J* = 9.3 Hz, 2H), 3.18 (t, *J* = 9.0 Hz, 1H), 1.62 (s, 3H), 1.54 (s, 3H), 1.41 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.01, 177.49, 136.96, 136.36, 133.12, 129.84, 128.64, 128.47, 127.91, 127.85, 127.41, 70.33, 48.16, 46.61, 46.25, 46.12, 45.25, 33.10, 32.39, 20.79.

HRMS (ESI) for C<sub>23</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 384.1725, found 384.1724.



### 4-(2-Chloropropan-2-yl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-(p-tolyl)pyrrolidin-2-one (3da)

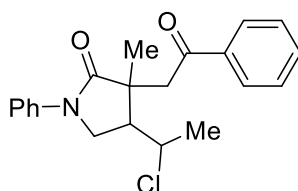
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 4:1) afforded **3da**.

White solid, 29.5 mg, 77% yield, mp = 114–116 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.00–7.95 (m, 2H), 7.59–7.54 (m, 3H), 7.48–7.44 (m, 2H), 7.18 (d, *J* = 8.3 Hz, 2H), 3.97 (dt, *J* = 17.6, 9.4 Hz, 2H), 3.59 (q, *J* = 18.5 Hz, 2H), 3.31 (dd, *J* = 9.9, 8.3 Hz, 1H), 2.33 (s, 3H), 1.72 (s, 3H), 1.68 (s, 3H), 1.45 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.91, 176.44, 136.95, 136.93, 134.10, 133.21, 129.26, 128.53, 127.94, 120.11, 70.28, 48.12, 47.65, 47.33, 45.57, 33.38, 32.34, 20.81, 20.63.

HRMS (ESI) for C<sub>23</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 384.1725, found 384.1729.



### 4-(1-Chloroethyl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylpyrrolidin-2-one (3ea)

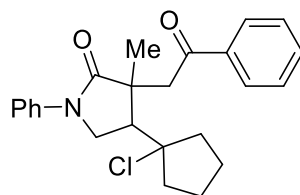
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 6:1) afforded **3ea**.

White solid, 24.9 mg, 70% yield, mp = 98–100 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.95 (d, *J* = 7.6 Hz, 2H), 7.67 (d, *J* = 7.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.46–7.42 (m, 2H), 7.38–7.34 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.25–4.18 (m, 1H), 4.08 (dd, *J* = 9.9, 8.4 Hz, 1H), 3.72 (dd, *J* = 10.6, 8.5 Hz, 1H), 3.54 (d, *J* = 18.2 Hz, 1H), 3.33 (d, *J* = 18.2 Hz, 1H), 3.09 (q, *J* = 8.9 Hz, 1H), 1.59 (d, *J* = 6.5 Hz, 3H), 1.26 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.21, 176.61, 139.22, 136.74, 133.28, 128.69, 128.53, 127.87, 124.48, 119.99, 58.22, 49.98, 46.16, 45.23, 44.74, 24.81, 18.08.

HRMS (ESI) for C<sub>21</sub>H<sub>23</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 356.1412, found 356.1415.



**4-(1-Chlorocyclopentyl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylpyrrolidin-2-one (3fa)**

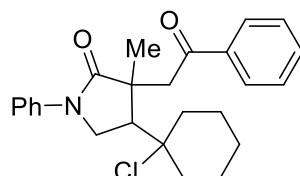
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 6:1) afforded **3fa**.

White solid, 26.1 mg, 66% yield, mp = 132–134 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01–7.95 (m, 2H), 7.70 (d, *J* = 7.8 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.48–7.43 (m, 2H), 7.39–7.35 (m, 2H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.03 (t, *J* = 9.4 Hz, 1H), 3.93 (t, *J* = 8.9 Hz, 1H), 3.66 (d, *J* = 18.5 Hz, 1H), 3.52 (d, *J* = 18.5 Hz, 1H), 3.35 (t, *J* = 8.9 Hz, 1H), 2.27–2.10 (m, 2H), 2.04–1.96 (m, 2H), 1.88–1.70 (m, 4H), 1.49 (s, 3H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 198.02, 176.86, 139.49, 136.86, 133.26, 128.75, 128.55, 127.98, 124.41, 120.02, 81.93, 48.35, 47.58, 46.96, 45.74, 42.50, 41.72, 22.65, 22.30, 21.05.

HRMS (ESI) for C<sub>24</sub>H<sub>27</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 396.1725, found 396.1724.



**4-(1-Chlorocyclohexyl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-phenylpyrrolidin-2-one (3ga)**

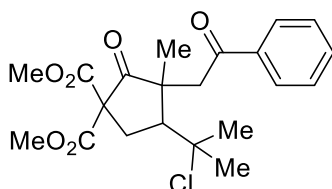
Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 6:1) afforded **3ga**.

White solid, 29.4 mg, 72% yield, mp = 108–110 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.3 Hz, 2H), 7.70 (d, *J* = 7.9 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.47–7.43 (m, 2H), 7.38–7.34 (m, 2H), 7.13 (t, *J* = 7.4 Hz, 1H), 4.13 (t, *J* = 9.7 Hz, 1H), 3.94 (t, *J* = 8.7 Hz, 1H), 3.59 (d, *J* = 1.4 Hz, 2H), 3.30 (dd, *J* = 9.8, 8.5 Hz, 1H), 2.20 (d, *J* = 13.4 Hz, 1H), 2.01 (d, *J* = 12.4 Hz, 1H), 1.80–1.73 (m, 2H), 1.65 (d, *J* = 13.2 Hz, 1H), 1.58–1.53 (m, 4H), 1.49 (s, 3H), 1.18–1.08 (m, 1H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 197.86, 176.79, 139.52, 136.79, 133.21, 128.67, 128.51, 127.91, 124.30, 119.92, 75.41, 47.70, 47.27, 47.25, 45.90, 39.94, 38.60, 24.83, 21.63, 21.26, 21.12.

HRMS (ESI) for C<sub>25</sub>H<sub>29</sub>ClNO<sub>2</sub> [M+H]<sup>+</sup> calcd. 410.1881, found 410.1888.



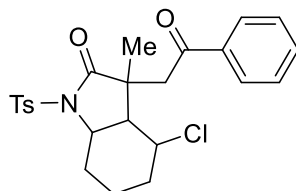
**Dimethyl 4-(2-chloropropan-2-yl)-3-methyl-2-oxo-3-(2-oxo-2-phenylethyl)cyclopentane-1,1-dicarboxylate (3ha)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 5:1) afforded **3ha**.

White solid, 25.7 mg, 63% yield, mp = 120–122 °C.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.90–7.86 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.45–7.41 (m, 2H), 4.00–3.93 (m, 4H), 3.79 (s, 3H), 3.45 (d, *J* = 18.8 Hz, 1H), 3.21 (dd, *J* = 12.8, 5.9 Hz, 1H), 2.83

(dd,  $J = 12.7, 5.9$  Hz, 1H), 2.42 (t,  $J = 12.8$  Hz, 1H), 1.69 (s, 3H), 1.68 (s, 3H), 1.36 (s, 3H).  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  209.06, 196.74, 168.94, 165.62, 135.94, 133.47, 128.54, 128.07, 71.10, 66.90, 53.59, 53.26, 51.73, 49.33, 48.61, 33.55, 32.89, 32.63, 19.86.  
HRMS (ESI) for  $\text{C}_{21}\text{H}_{26}\text{ClO}_6$   $[\text{M}+\text{H}]^+$  calcd. 409.1412, found 409.1414.



#### 4-Chloro-3-methyl-3-(2-oxo-2-phenylethyl)-1-tosyloctahydro-2H-indol-2-one (3ia)

Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 3:1) afforded **3ia**.  
28.0 mg, 61% yield, dr = 1.5:1.

(*Major diastereomer*) White solid, mp = 140–142 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.3$  Hz, 2H), 7.76–7.70 (m, 2H), 7.54 (t,  $J = 7.4$  Hz, 1H), 7.42–7.38 (m, 2H), 7.34 (d,  $J = 8.1$  Hz, 2H), 4.57–4.50 (m, 1H), 4.36–4.31 (m, 1H), 3.52 (d,  $J = 18.4$  Hz, 1H), 3.22 (d,  $J = 18.4$  Hz, 1H), 2.95 (dd,  $J = 9.6, 7.2$  Hz, 1H), 2.66–2.55 (m, 1H), 2.46 (s, 3H), 2.07–1.95 (m, 1H), 1.94–1.76 (m, 3H), 1.59–1.53 (m, 1H), 1.34 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  196.52, 176.93, 144.70, 136.21, 135.13, 133.33, 129.20, 128.68, 128.46, 127.77, 56.58, 56.43, 46.97, 46.58, 45.16, 30.60, 28.02, 21.63, 17.74.

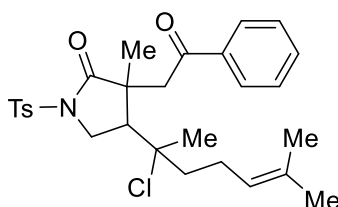
HRMS (ESI) for  $\text{C}_{24}\text{H}_{27}\text{ClNO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 460.1344, found 460.1342.

(*Minor diastereomer*) White solid, mp = 116–118 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.3$  Hz, 2H), 7.87 (d,  $J = 7.4$  Hz, 2H), 7.56 (t,  $J = 7.4$  Hz, 1H), 7.46–7.42 (m, 2H), 7.34 (d,  $J = 8.1$  Hz, 2H), 4.58–4.52 (m, 1H), 4.13–4.08 (m, 1H), 3.74 (d,  $J = 18.7$  Hz, 1H), 3.27 (d,  $J = 18.7$  Hz, 1H), 2.64 (t,  $J = 8.2$  Hz, 1H), 2.45 (s, 3H), 2.26–2.21 (m, 1H), 2.16–2.06 (m, 1H), 1.91–1.83 (m, 1H), 1.81–1.71 (m, 2H), 1.65–1.59 (m, 1H), 1.36 (s, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  197.30, 177.38, 144.90, 136.41, 135.73, 133.39, 129.47, 128.61, 128.17, 127.94, 57.40, 55.26, 50.70, 46.47, 43.12, 31.96, 26.51, 25.78, 21.65, 17.92.

HRMS (ESI) for  $\text{C}_{24}\text{H}_{27}\text{ClNO}_4\text{S}$   $[\text{M}+\text{H}]^+$  calcd. 460.1344, found 460.1351.



#### 4-(2-Chloro-6-methylhept-5-en-2-yl)-3-methyl-3-(2-oxo-2-phenylethyl)-1-tosylpyrrolidin-2-one (3ja)

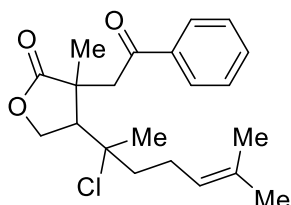
Purification by flash column chromatography ( $\text{SiO}_2$ , petroleum ether/EtOAc = 3:1) afforded **3ja**.  
White solid, 24.7 mg, 48% yield, mp = 102–104 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 8.3$  Hz, 2H), 7.83 (d,  $J = 7.4$  Hz, 2H), 7.55 (t,  $J = 7.4$  Hz, 1H), 7.44–7.40 (m, 2H), 7.35 (d,  $J = 8.1$  Hz, 2H), 5.01 (t,  $J = 7.0$  Hz, 1H), 4.18–4.11 (m, 1H), 3.95 (t,  $J = 10.0$  Hz, 1H), 3.52 (d,  $J = 18.6$  Hz, 1H), 3.34 (d,  $J = 18.6$  Hz, 1H), 3.17 (dd,  $J = 10.0,$

8.5 Hz, 1H), 2.45 (s, 3H), 2.13–1.98 (m, 2H), 1.82–1.69 (m, 2H), 1.65 (s, 3H), 1.59 (s, 3H), 1.53 (s, 3H), 1.29 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 196.61, 176.47, 144.86, 136.26, 135.04, 133.44, 132.90, 129.50, 128.55, 127.98, 127.84, 122.33, 73.38, 47.38, 46.15, 45.96, 45.53, 44.54, 28.05, 25.54, 22.91, 21.64, 20.38, 17.56.

**HRMS (ESI)** for C<sub>28</sub>H<sub>35</sub>ClNO<sub>4</sub>S [M+H]<sup>+</sup> calcd. 516.1970, found 516.1969.



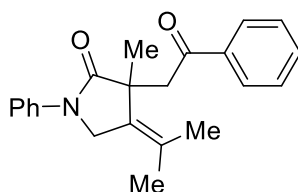
**4-(2-Chloro-6-methylhept-5-en-2-yl)-3-methyl-3-(2-oxo-2-phenylethyl)dihydrofuran-2(3H)-one (3ka)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 8:1) afforded **3ka**. Colorless oil, 25.0 mg, 65% yield.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.98–7.89 (m, 2H), 7.62–7.55 (m, 1H), 7.49–7.45 (m, 2H), 5.33 (td, *J* = 7.0, 1.1 Hz, 1H), 5.08–5.05 (m, 1H), 4.71 (d, *J* = 7.1 Hz, 2H), 4.02 (d, *J* = 17.8 Hz, 1H), 3.69 (d, *J* = 17.8 Hz, 1H), 2.10–2.00 (m, 4H), 1.93 (s, 3H), 1.68 (s, 3H), 1.66 (s, 3H), 1.58 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 195.38, 170.26, 142.79, 136.05, 133.53, 131.64, 128.63, 127.92, 123.68, 117.58, 64.33, 62.94, 50.41, 39.40, 27.33, 26.19, 25.59, 17.61, 16.42.

**HRMS (ESI)** for C<sub>21</sub>H<sub>27</sub>ClNaO<sub>3</sub> [M+Na]<sup>+</sup> calcd. 385.1541, found 385.1542.



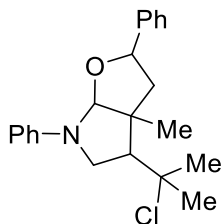
**3-Methyl-3-(2-oxo-2-phenylethyl)-1-phenyl-4-(propan-2-ylidene)pyrrolidin-2-one (4aa)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 6:1) afforded **4aa**. White solid, 28.3 mg, 85% yield, mp = 122–124 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.94–7.86 (m, 2H), 7.78–7.75 (m, 2H), 7.55–7.50 (m, 1H), 7.46–7.35 (m, 4H), 7.16 (t, *J* = 7.4 Hz, 1H), 4.55 (d, *J* = 13.0 Hz, 1H), 4.39 (d, *J* = 13.1 Hz, 1H), 3.83 (d, *J* = 18.1 Hz, 1H), 3.64 (d, *J* = 18.1 Hz, 1H), 1.76 (s, 3H), 1.64 (s, 3H), 1.51 (s, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 197.49, 177.91, 139.53, 136.53, 133.00, 128.79, 128.48, 128.26, 127.89, 124.84, 124.48, 120.44, 52.15, 46.82, 46.67, 24.52, 21.17, 20.14.

**HRMS (ESI)** for C<sub>22</sub>H<sub>24</sub>NO<sub>2</sub> [M+H]<sup>+</sup> calcd. 334.1802, found 334.1801.



**4-(2-Chloropropan-2-yl)-3a-methyl-2,6-diphenylhexahydro-2H-furo[2,3-b]pyrrole (5aa)**

Purification by flash column chromatography (SiO<sub>2</sub>, petroleum ether/EtOAc = 8:1) afforded **5aa**.

White solid, 29.1 mg, 82% yield, mp = 146–148 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.45–7.39 (m, 2H), 7.38–7.34 (m, 2H), 7.30–7.24 (m, 3H), 6.91 (d, *J* = 7.8 Hz, 2H), 6.82 (t, *J* = 7.3 Hz, 1H), 5.25 (dd, *J* = 10.8, 5.0 Hz, 1H), 5.17 (s, 1H), 3.82 (dd, *J* = 8.9, 7.4 Hz, 1H), 3.59 (dd, *J* = 11.0, 9.0 Hz, 1H), 2.82 (dd, *J* = 11.0, 7.3 Hz, 1H), 2.69 (dd, *J* = 12.9, 5.1 Hz, 1H), 1.82 (s, 3H), 1.79 (s, 3H), 1.42 (s, 3H).

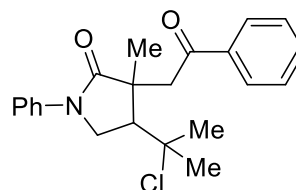
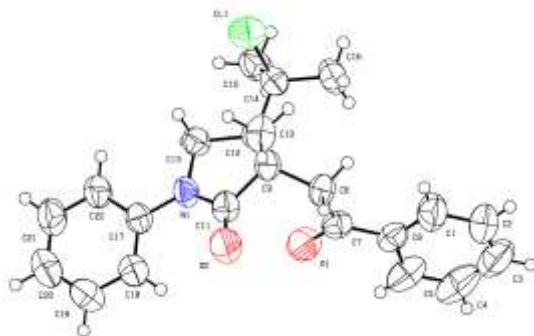
**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 146.56, 141.78, 129.13, 128.39, 127.57, 126.01, 118.30, 113.36, 104.13, 79.37, 70.22, 53.45, 53.37, 50.10, 49.14, 34.18, 32.62, 21.05.

**HRMS (ESI)** for C<sub>22</sub>H<sub>27</sub>ClNO [M+H]<sup>+</sup> calcd. 356.1776, found 356.1775.

### 3. X-Ray Crystallographic Data

#### 3.1 X-Ray Crystallographic Data of Product 3aa

The crystal structure **3aa** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1950320**.



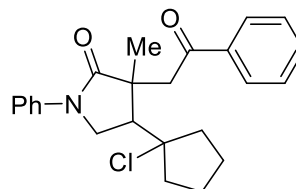
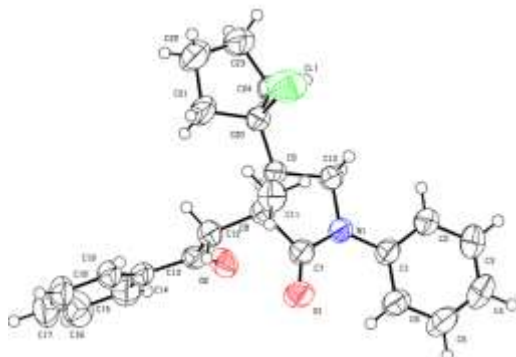
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Bond precision:	C-C = 0.0046 Å	Wavelength=0.71073	
Cell:	a=10.3573(8)	b=10.8597(6)	c=17.9457(13)
	alpha=90	beta=106.439(8)	gamma=90
Temperature:	293 K		
	Calculated	Reported	
Volume	1936.0(2)	1936.0(3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C <sub>22</sub> H <sub>24</sub> Cl N O <sub>2</sub>	C <sub>22</sub> H <sub>24</sub> Cl N O <sub>2</sub>	
Sum formula	C <sub>22</sub> H <sub>24</sub> Cl N O <sub>2</sub>	C <sub>22</sub> H <sub>24</sub> Cl N O <sub>2</sub>	
Mr	369.87	369.87	
Dx, g cm <sup>-3</sup>	1.269	1.269	
Z	4	4	
Mu (mm <sup>-1</sup> )	0.213	0.213	
F000	784.0	784.0	
F000'	784.89		
h,k,lmax	12,13,22	12,13,22	
Nref	3817	3808	
Tmin,Tmax	0.964,0.975	0.796,1.000	
Tmin'	0.964		
Correction method=	# Reported T Limits: Tmin=0.796 Tmax=1.000		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.998	Theta(max)= 26.020	
R(reflections)=	0.0555( 2190)	wR2(reflections)= 0.1495( 3808)	
S =	1.045	Npar= 238	

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### 3.2 X-Ray Crystallographic Data of product 3fa

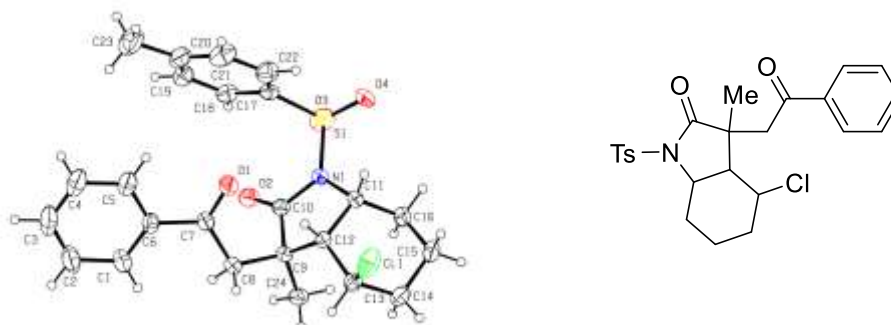
The crystal structure **3fa** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1950366**.



Bond precision:	C-C =0.0066 Å	Wavelength=1.54184	
Cell:	a=10.3245(5)	b=19.2615(7)	c=11.3211(5)
	alpha=90	beta=111.645(5)	gamma=90
Temperature:	296 K		
	Calculated	Reported	
Volume	2092.62(17)	2092.64(15)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>2</sub>	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>2</sub>	
Sum formula	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>2</sub>	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>2</sub>	
Mr	395.91	395.91	
Dx, g cm <sup>-3</sup>	1.257	1.257	
Z	4	4	
Mu (mm <sup>-1</sup> )	1.758	1.758	
F <sub>000</sub>	840.0	840.0	
F <sub>000</sub> '	843.61		
h,k,lmax	12,22,13	12,22,13	
Nref	3701	3598	
Tmin,Tmax	0.779,0.782	0.647,1.000	
Tmin'	0.706		
Correction method=	# Reported T Limits: Tmin= 0.647 Tmax=1.000		
AbsCorr =	MULTI-SCAN		
Data completeness=	0.972	Theta(max)= 66.600	
R(reflections)=	0.0795( 3021)	wR2(reflections)= 0.2411( 3598)	
S =	1.135	Npar= 254	

### 3.3 X-Ray Crystallographic Data of product 3ia

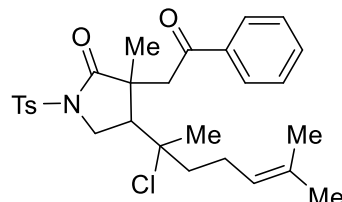
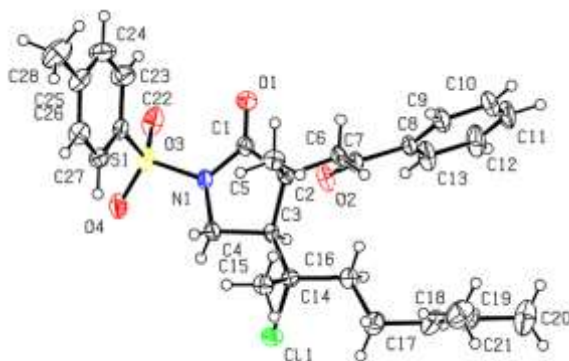
The crystal structure **3ia** (*major diastereomer*) has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1828303**.



Bond precision:	C-C = 0.0034 Å	Wavelength=0.71073	
Cell:	a=8.8275(9)	b=11.6249(9)	c=12.1060(13)
	alpha=86.125(7)	beta=69.758(10)	gamma=77.426(8)
Temperature:	295 K		
	Calculated	Reported	
Volume	1137.6(2)	1137.60(19)	
Space group	P -1	P -1	
Hall group	-P 1	-P 1	
Moiety formula	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>4</sub> S	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>4</sub> S	
Sum formula	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>4</sub> S	C <sub>24</sub> H <sub>26</sub> Cl N O <sub>4</sub> S	
Mr	459.97	459.97	
D <sub>x</sub> , g cm <sup>-3</sup>	1.343	1.343	
Z	2	2	
Mu (mm <sup>-1</sup> )	0.290	0.290	
F <sub>000</sub>	484.0	484.0	
F <sub>000</sub> '	484.75		
h,k,l <sub>max</sub>	10,14,14	10,14,14	
N <sub>ref</sub>	4473	4466	
T <sub>min</sub> , T <sub>max</sub>	0.943, 0.960	0.849, 1.000	
T <sub>min</sub> '	0.935		
Correction method= # Reported T Limits: T <sub>min</sub> =0.849 T <sub>max</sub> =1.000			
AbsCorr = MULTI-SCAN			
Data completeness=	0.998	Theta(max)= 26.020	
R(reflections)=	0.0451( 3396)	wR2(reflections)= 0.1089( 4466)	
S =	1.049	N <sub>par</sub> = 282	

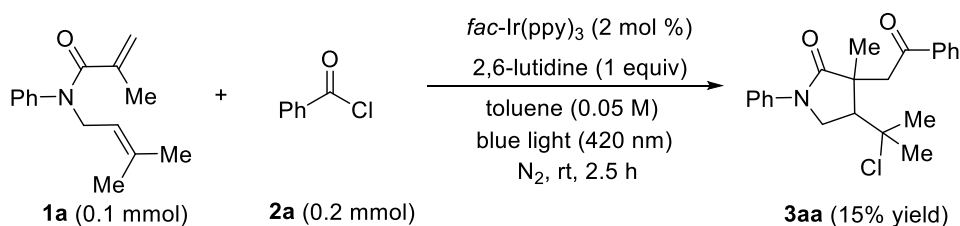
### 3.4 X-Ray Crystallographic Data of product 3ja

The crystal structure **3ja** has been deposited at the Cambridge Crystallographic Data Centre and allocated the deposition number: **CCDC 1950434**.



Bond precision:	C-C = 0.0037Å	Wavelength= 0.71073	
Cell:	a= 12.6990(3)	b= 27.2511(8)	c= 15.4722(5)
	alpha=90	beta= 90.051(3)	gamma=90
Temperature:	173 K		
	Calculated	Reported	
Volume	5354.3(3)	5354.3(3)	
Space group	P 21/c	P 1 21/c 1	
Hall group	-P 2ybc	-P 2ybc	
Moiety formula	C <sub>28</sub> H <sub>34</sub> Cl N O <sub>4</sub> S	2(C <sub>28</sub> H <sub>34</sub> Cl N O <sub>4</sub> S)	
Sum formula	C <sub>28</sub> H <sub>34</sub> Cl N O <sub>4</sub> S	C <sub>56</sub> H <sub>68</sub> Cl <sub>2</sub> N <sub>2</sub> O <sub>8</sub> S <sub>2</sub>	
Mr	516.07	1032.14	
D <sub>x</sub> , g cm <sup>-3</sup>	1.280	1.280	
Z	8	4	
Mu (mm <sup>-1</sup> )	0.254	0.254	
F <sub>000</sub>	2192.0	2192.0	
F <sub>000</sub> '	2195.06		
h,k,lmax	15,33,19	15,33,19	
Nref	10553	10390	
Tmin,Tmax	0.958,0.970	0.576,1.000	
Tmin'	0.953		
Correction method= # Reported T Limits:	Tmin= 0.576 Tmax=1.000		
AbsCorr = MULTI-SCAN			
Data completeness= 0.985	Theta(max)= 26.020		
R(reflections)= 0.0510( 7275)	wR2(reflections)= 0.1241( 10390)		
S = 1.042	Npar= 670		

#### 4. Measurement of Quantum Yield



According to the procedure of related literature<sup>1-2</sup> and our previous studies<sup>3</sup>, the photon flux of the LED was determined by standard ferrioxalate actinometry.

Determination of the reaction quantum yield at 420 nm and quantum yield measurement was performed in an oven-dried 20 mL quartz vial with a magnetic stirring bar. Acyl chloride **2a** (0.2 mmol) and 2, 6-lutidine (0.1 mmol) were added to a solution of substrate **1a** (0.1 mmol) and photocatalyst *fac*-Ir(ppy)<sub>3</sub> (2 mol %) in dry toluene (2 mL) at room temperature. The mixture was degassed by three cycles of freeze-pump-thaw and then irradiated in Parallel Light Reactor (WP-TEC-1020) for for 9000 s (2.5 h). The reaction mixture was concentrated under reduced pressure, and the resulting mixture was rapid filtered by flash column chromatography on silica gel. The crude yield of the product **3aa** was determined by <sup>1</sup>H NMR based on a 1,3,5-trimethoxybenzene standard and the final yield was 15% (1.5\*10<sup>-5</sup> mol). The reaction quantum yield ( $\Phi$ ) was determined using eq 2, where the photon flux is 2.38\*10<sup>-9</sup> E s<sup>-1</sup> (determined by our previous studies as described<sup>3a</sup>), *t* is the reaction time (9000 s) and *f* is the fraction of incident light absorbed by the reaction mixture, determined using eq 1 (*A* >3 indicating that the fraction of light absorbed is >0.999).

$$f = 1 - 10^{-A(420 \text{ nm})} \quad (\text{eq 1})$$

$\Phi$  = Mole number for product/Mole number for absorption of photons

$$\Phi = \frac{\text{Mol product}}{\text{flux} * t * f} = \frac{\text{Mol product}}{\text{flux} * t * f} = 0.7 \quad (\text{eq 2})$$

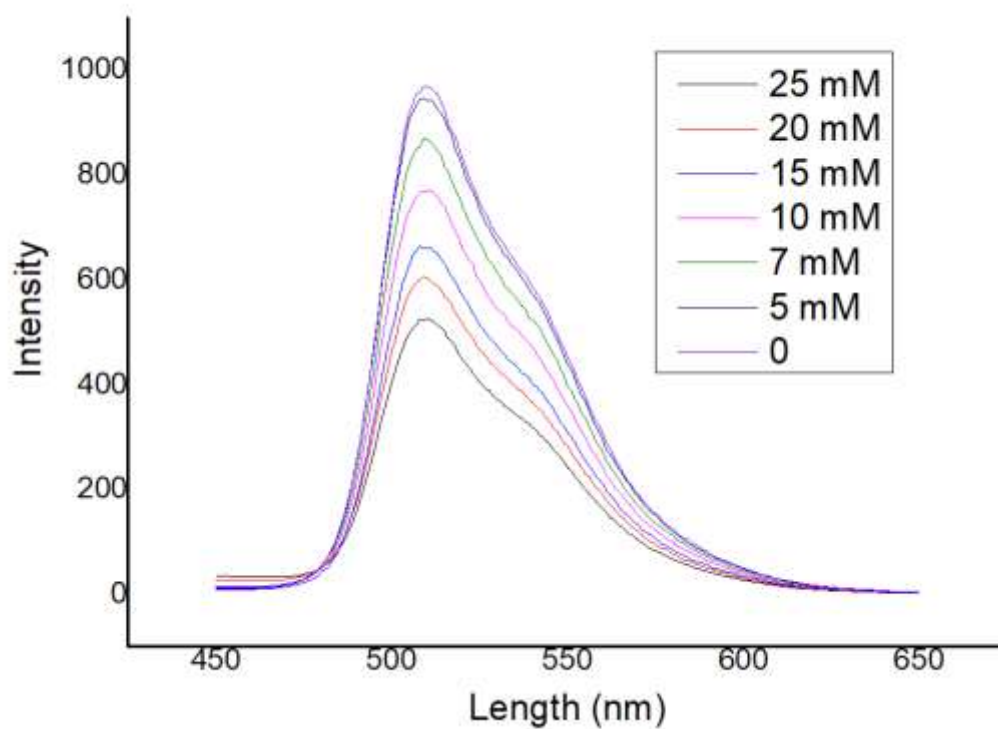
We calculated the quantum yield ( $\Phi$ ) of the model reaction of **1a** with **2a** to be 0.7. This result shows that the reaction does not support the radical chain growth process.

#### References

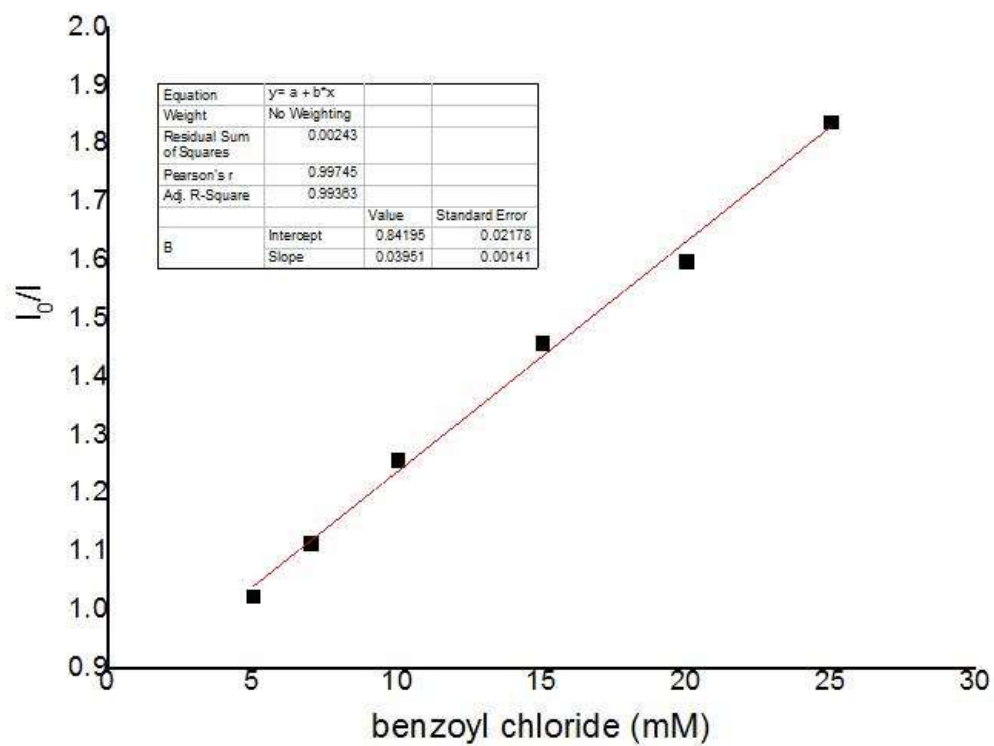
- (1) Cismesia, M. A.; Yoon, T. P. *Chem. Sci.* **2015**, *6*, 5426.
- (2) (a) Garza-Sanchez, R. A.; Tlahuext-Aca, A.; Tavakoli, G.; Glorius, F. *ACS catal.* **2017**, *7*, 4057. (b) Klauck, F. J. R.; James, M. J.; Glorius, F. *Angew. Chem., Int. Ed.* **2017**, *56*, 12336.
- (3) (a) Mo, J.-N.; Yu, W.-L.; Chen, J.-Q.; Hu, X.-Q.; Xu, P.-F. *Org. Lett.* **2018**, *20*, 4471. (b) Liu, D.; Jiao, M.-J.; Feng, Z.-T.; Wang, X.-Z.; Xu, G.-Q.; Xu, P.-F. *Org. Lett.* **2018**, *20*, 5700. (c) Wei, Y.-L.; Chen, J.-Q.; Sun, B.; Xu, P.-F. *Chem. Commun.* **2019**, *55*, 5922.

## 5. Stern-Volmer Experiments

According to the procedure of related literature<sup>1</sup>, Stern-Volmer fluorescence quenching experiments were run with freshly prepared solutions of 0.1 mM *fac*-Ir(ppy)<sub>3</sub> in toluene at room temperature. The solutions were irradiated at 375 nm and fluorescence was measured from 450 nm to 650 nm. Control experiments show that excited state of *fac*-Ir(ppy)<sub>3</sub> was only quenched by benzoyl chloride.



**Fig. S1.** Fluorescence quenching data with *fac*-Ir(ppy)<sub>3</sub> and variable benzoyl chloride.



**Fig. S2.** Stern-Volmer plot of *fac*-Ir(ppy)<sub>3</sub> and variable benzoyl chloride.

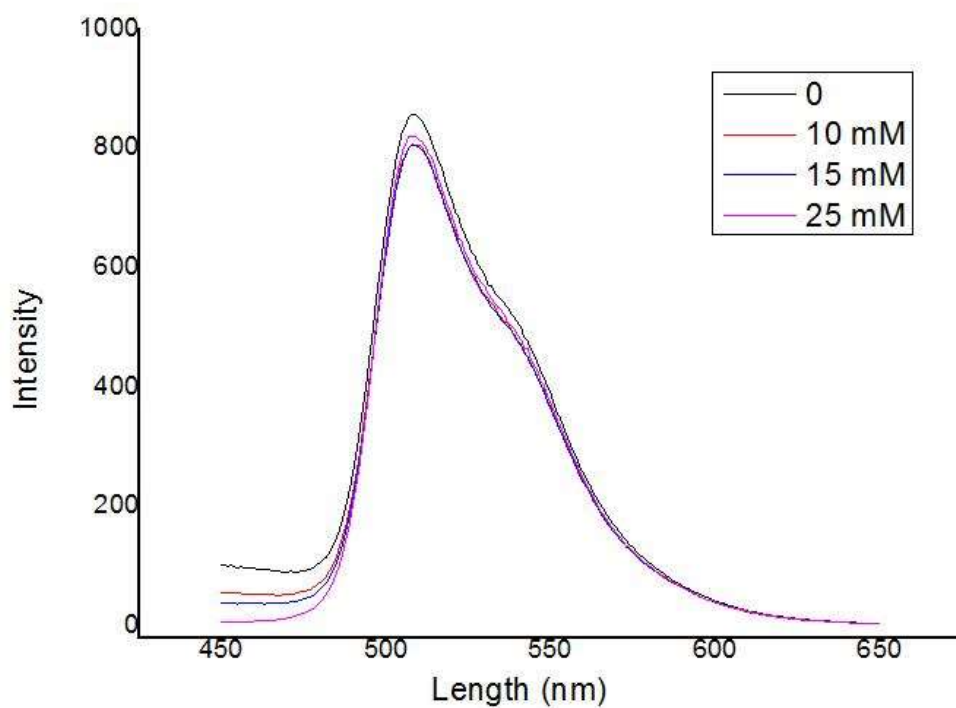


Fig. S3. Fluorescence quenching date with *fac*-Ir(ppy)<sub>3</sub> and variable substrate-1a.

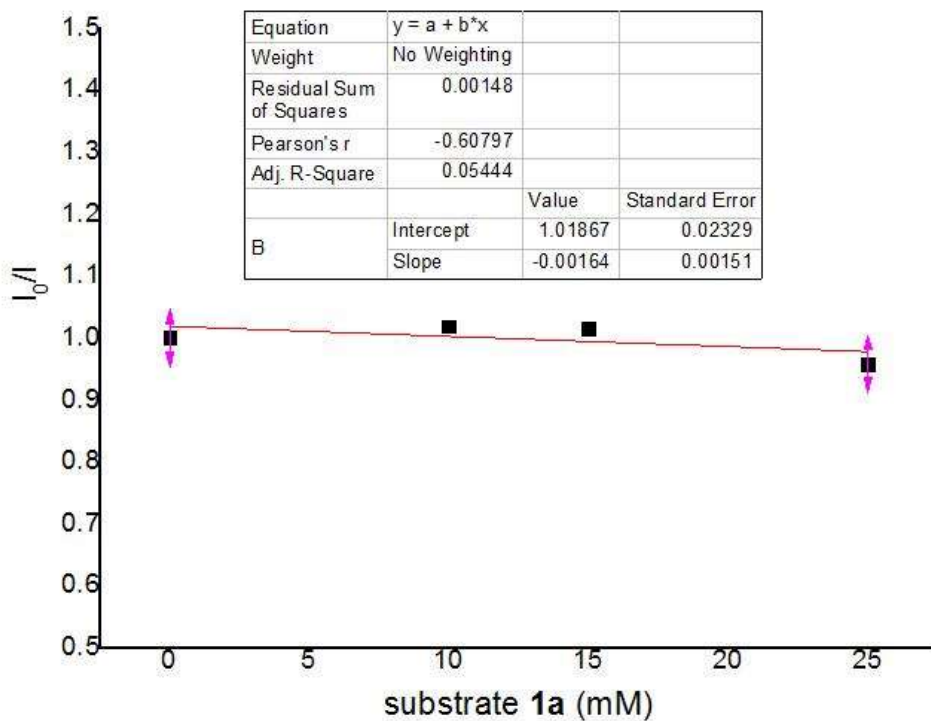
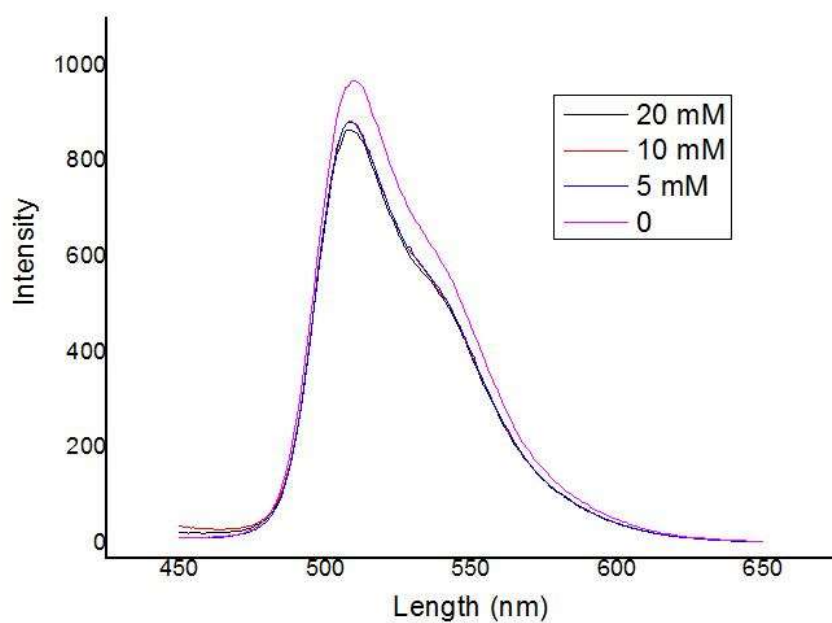
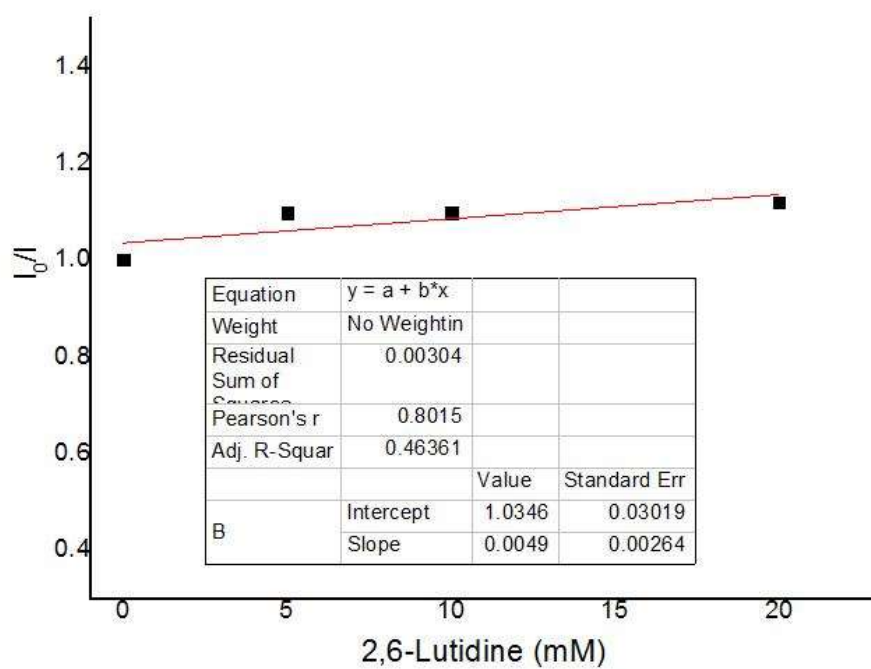


Fig. S4. Stern-Volmer plot of *fac*-Ir(ppy)<sub>3</sub> and variable substrate-1a.



**Fig. S5.** Fluorescence quenching data with *fac*-Ir(ppy)<sub>3</sub> and variable 2,6-lutidine.



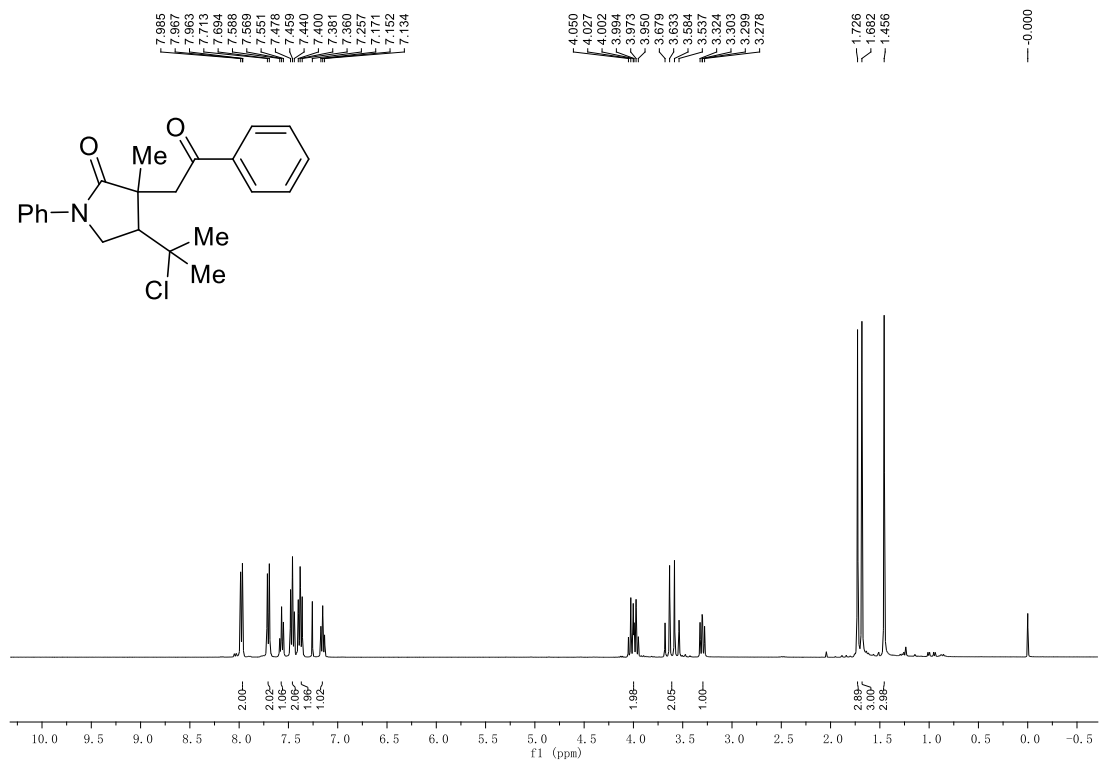
**Fig. S6.** Stern-Volmer plot of *fac*-Ir(ppy)<sub>3</sub> and variable 2,6-lutidine.

## References

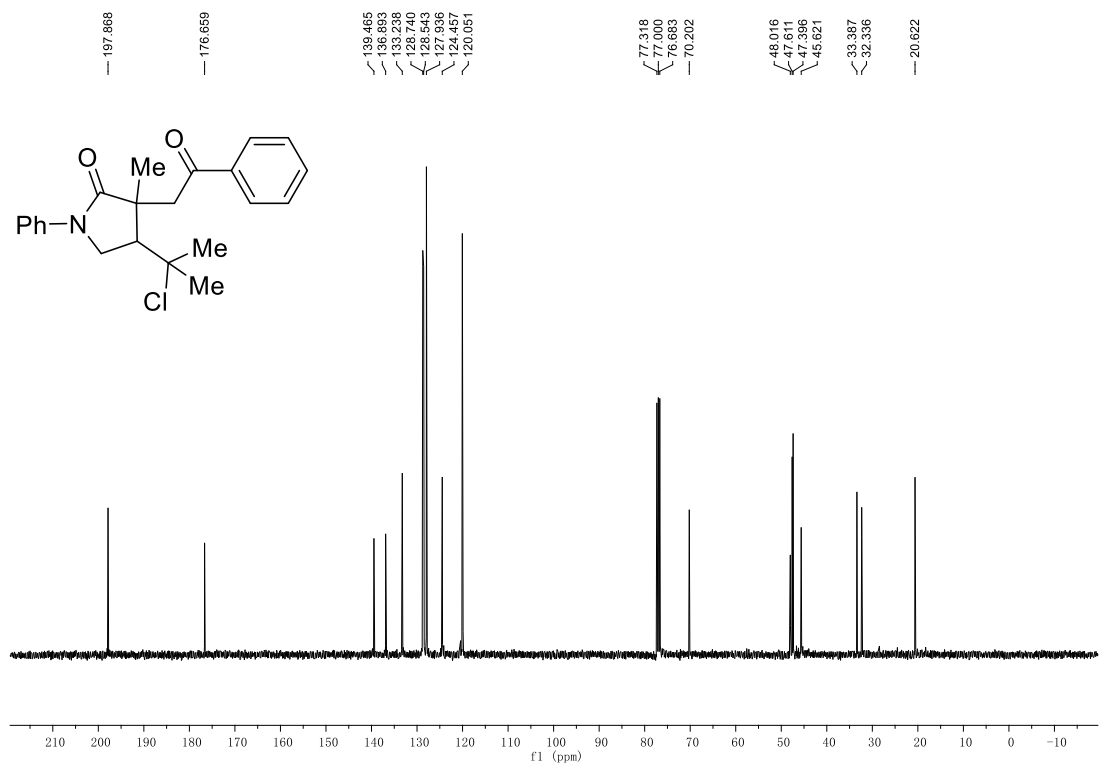
- (1) Triandafillidi, I.; Kokotou, M. G.; Kokotos, C. G. *Org. Lett.* **2018**, *20*, 36–39.

## 6. NMR Spectra of New Compounds

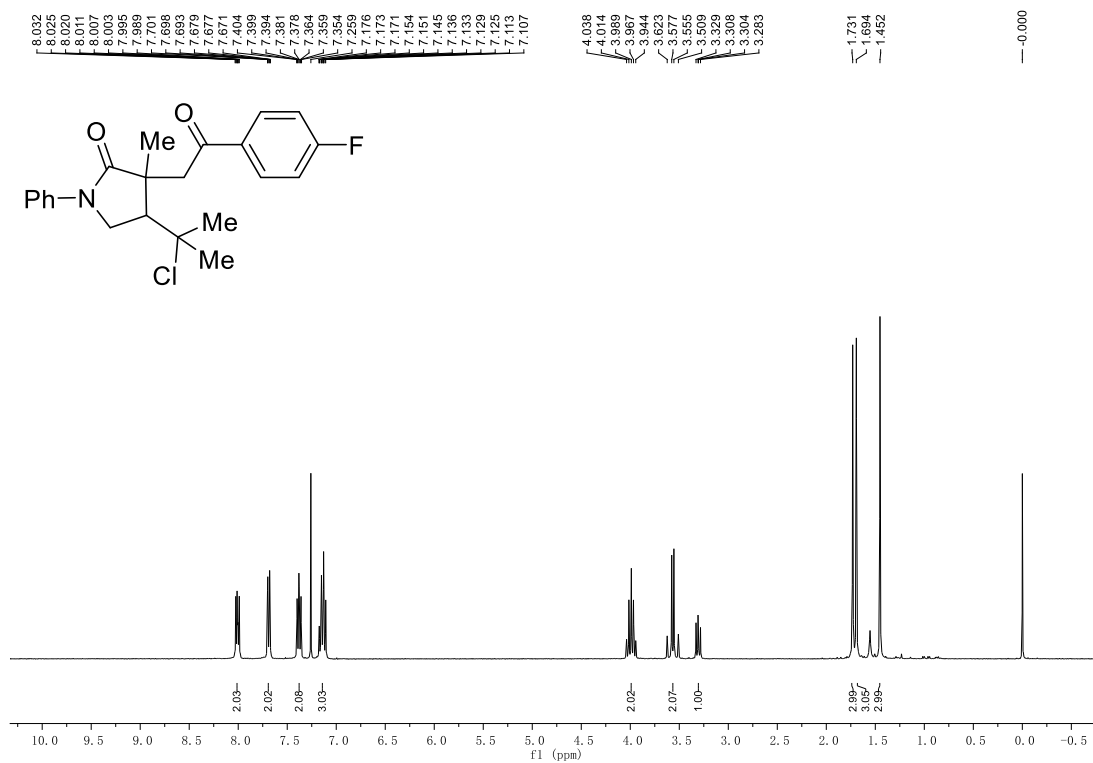
$^1\text{H}$  NMR of **3aa** in  $\text{CDCl}_3$



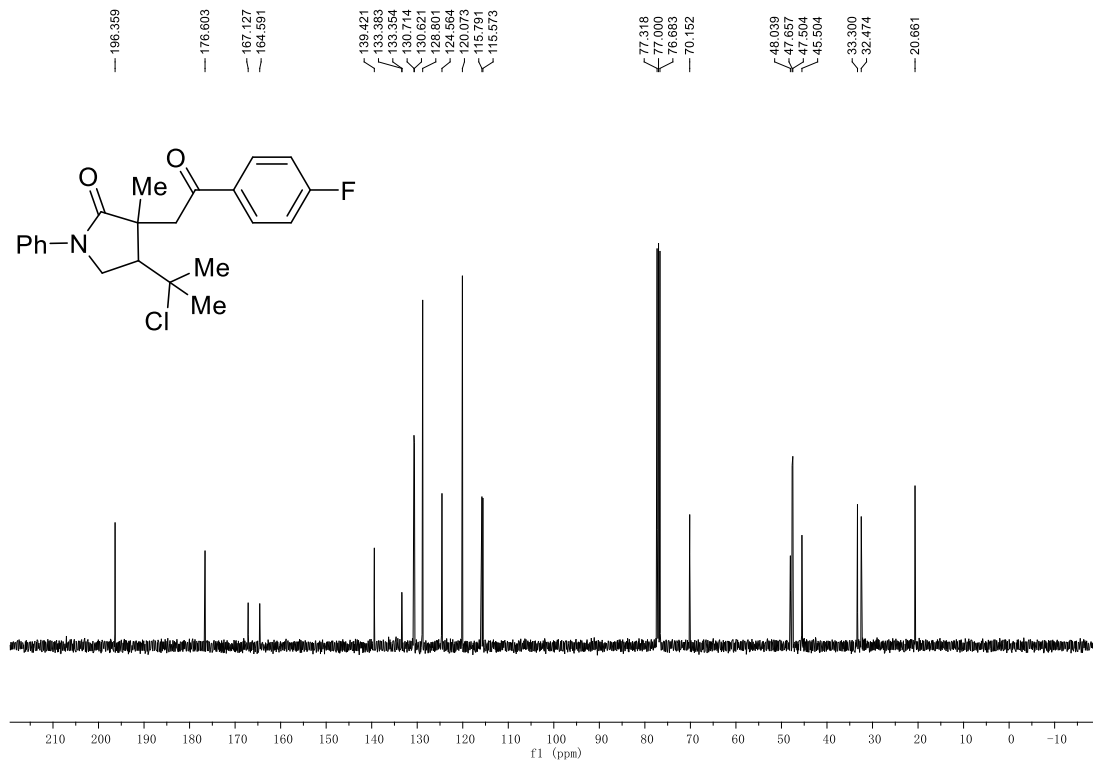
$^{13}\text{C}$  NMR of **3aa** in  $\text{CDCl}_3$



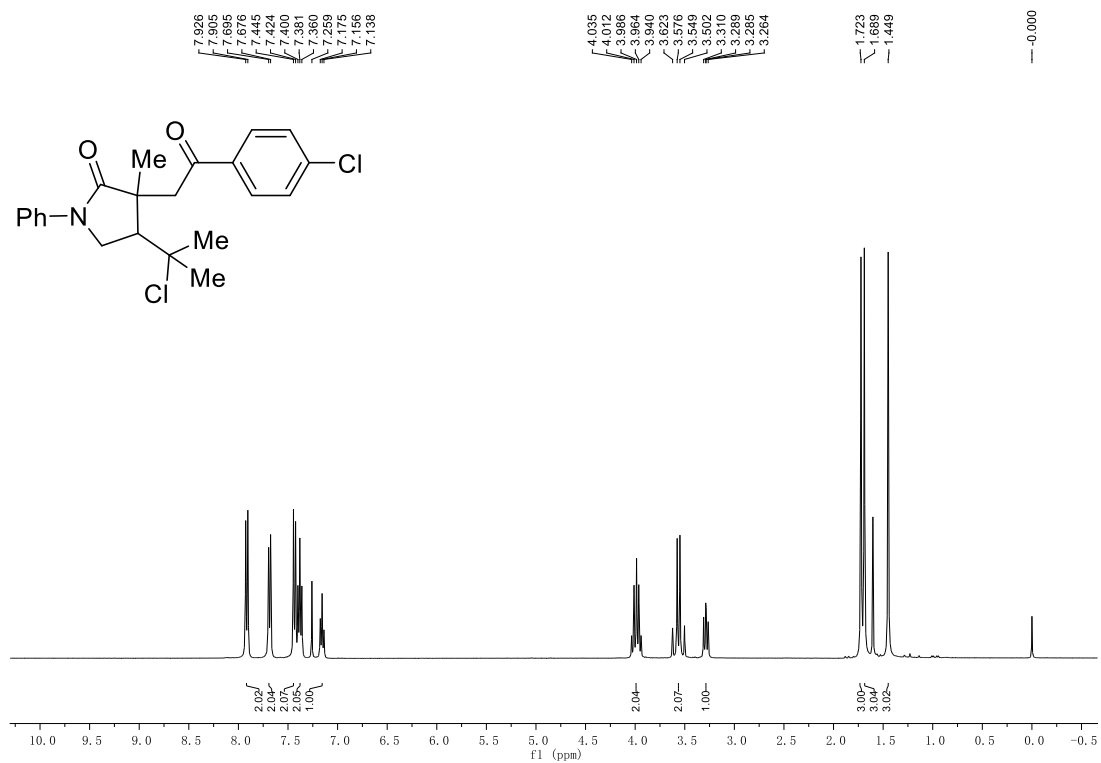
$^1\text{H}$  NMR of **3ab** in  $\text{CDCl}_3$



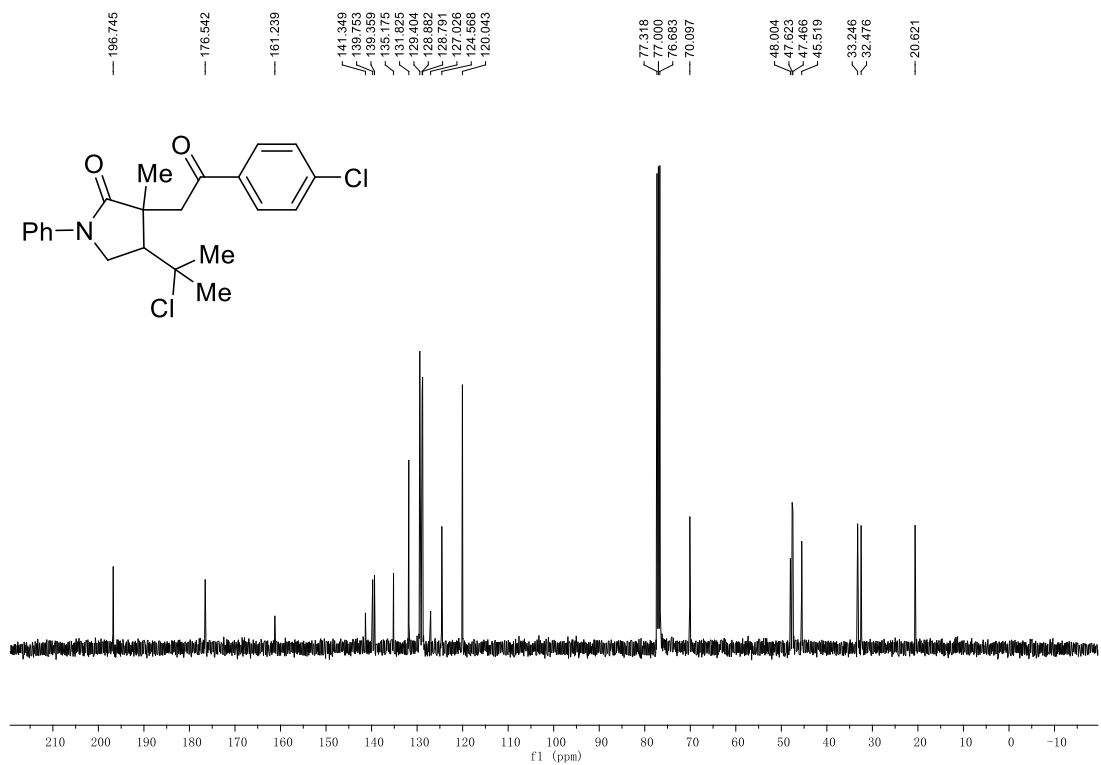
$^{13}\text{C}$  NMR of **3ab** in  $\text{CDCl}_3$



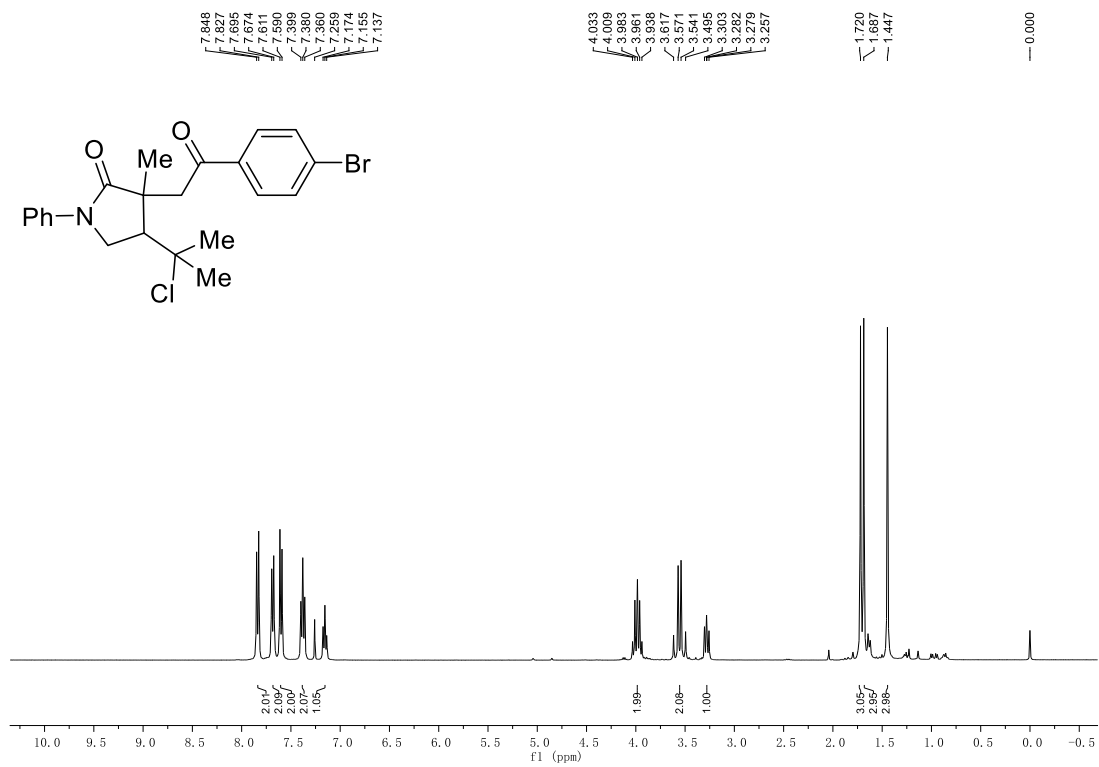
<sup>1</sup>H NMR of **3ac** in CDCl<sub>3</sub>



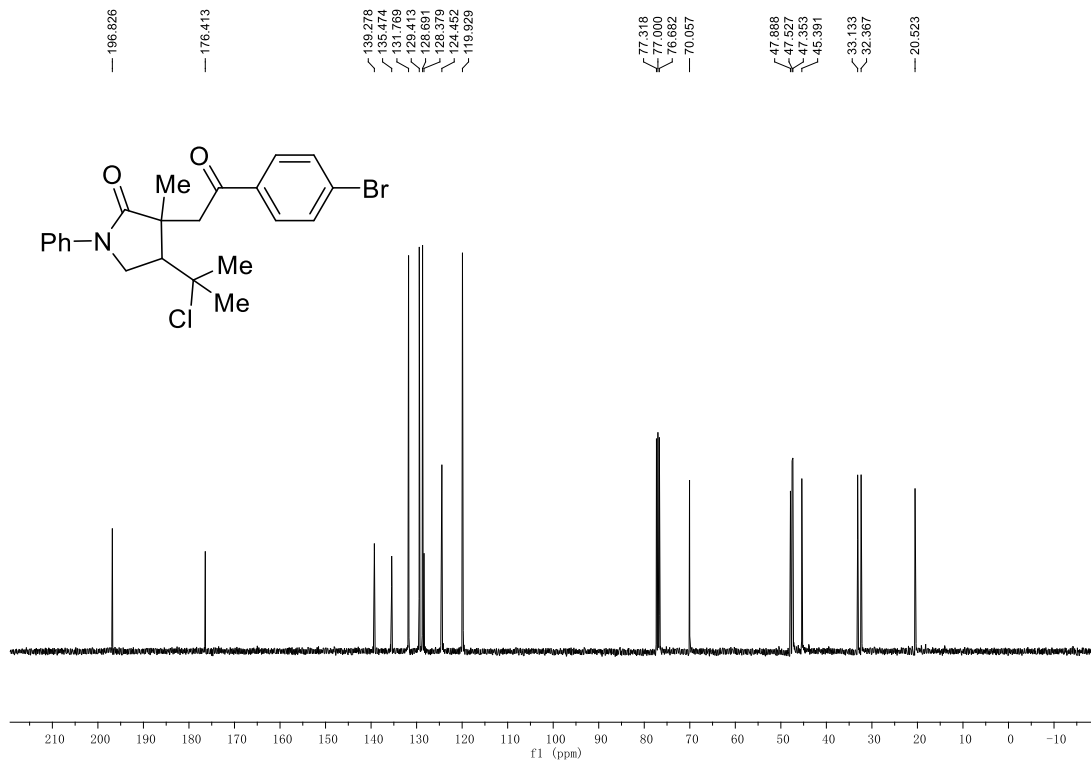
<sup>13</sup>C NMR of **3ac** in CDCl<sub>3</sub>



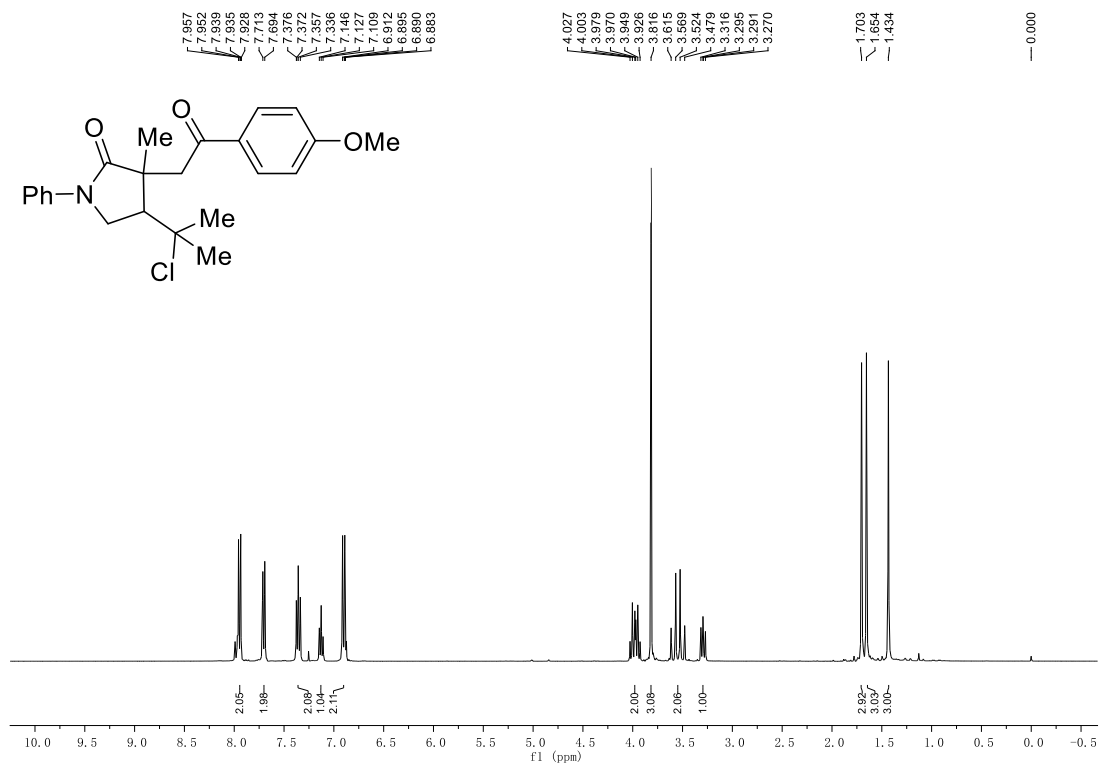
$^1\text{H}$  NMR of **3ad** in  $\text{CDCl}_3$



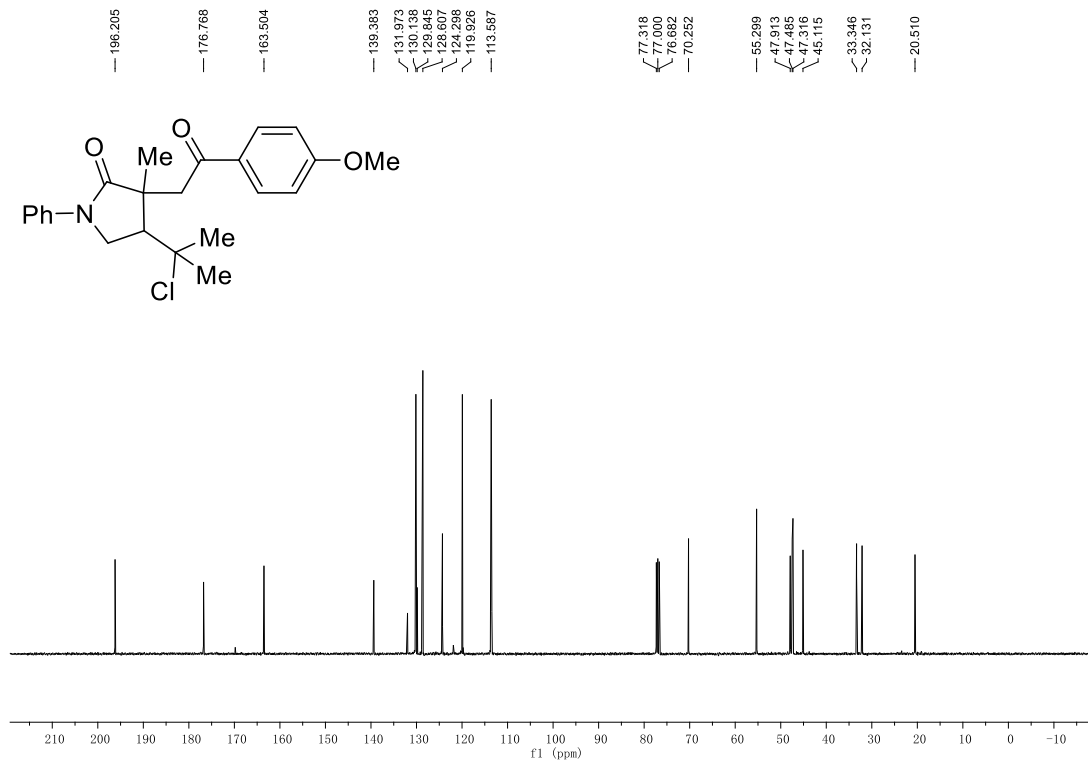
$^{13}\text{C}$  NMR of **3ad** in  $\text{CDCl}_3$



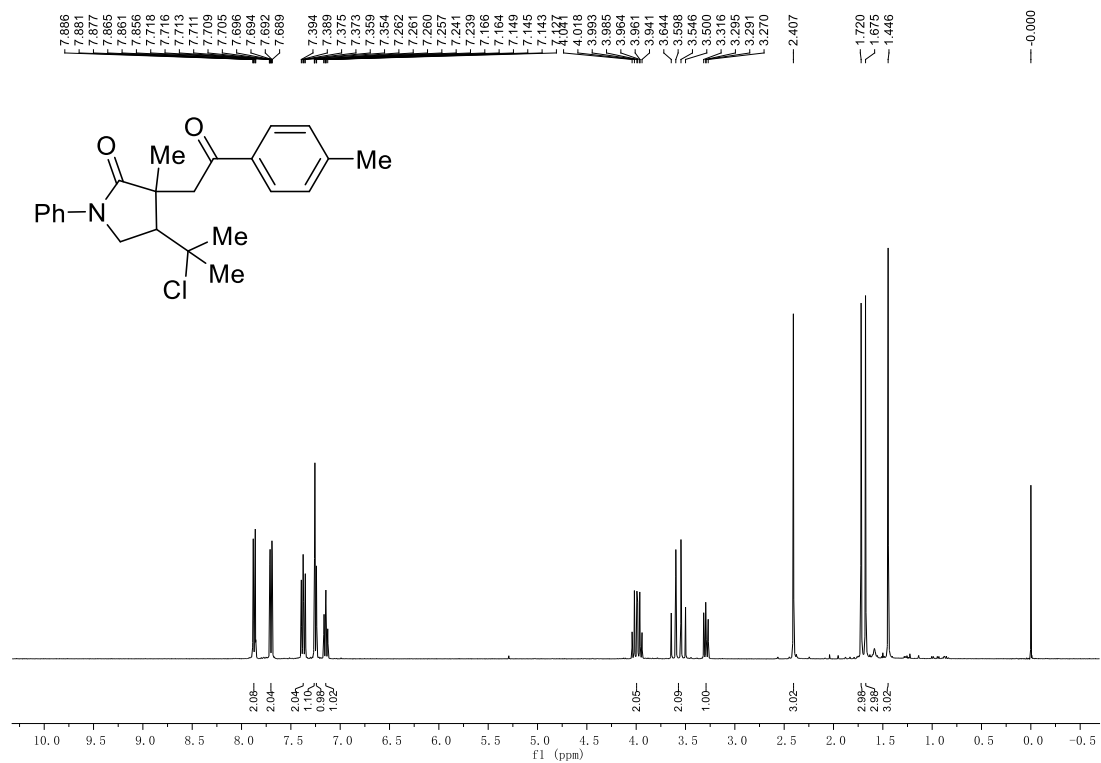
<sup>1</sup>H NMR of **3ae** in CDCl<sub>3</sub>



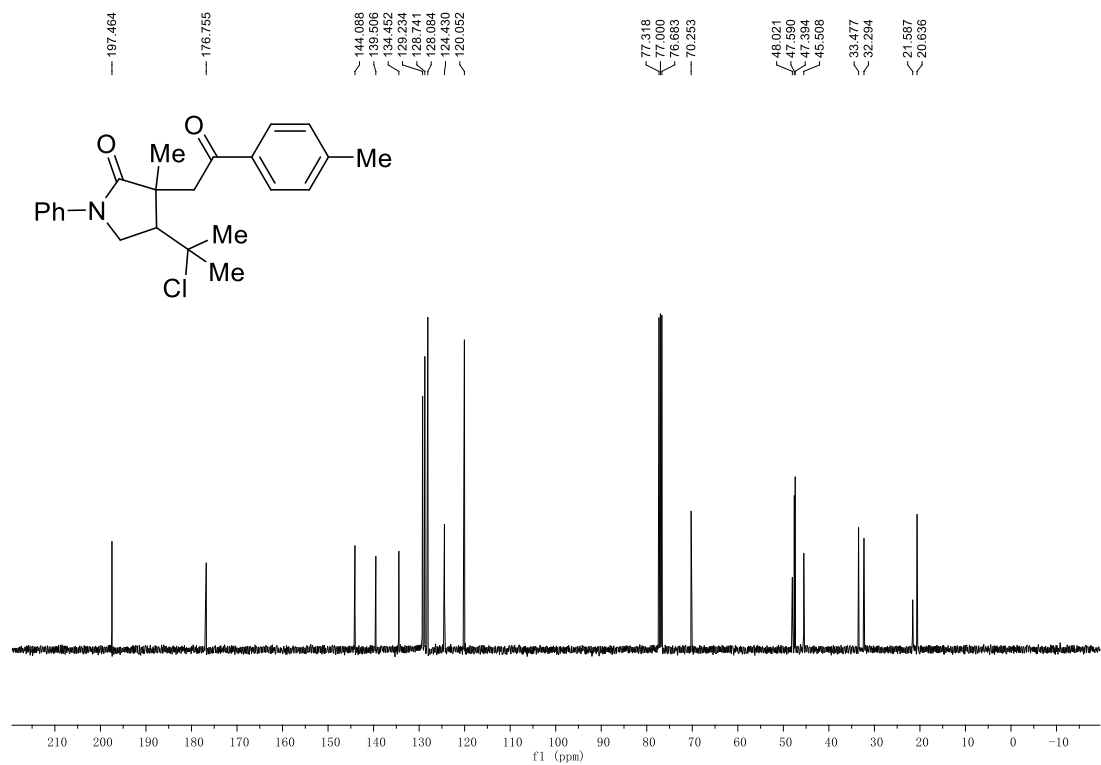
<sup>13</sup>C NMR of **3ae** in CDCl<sub>3</sub>



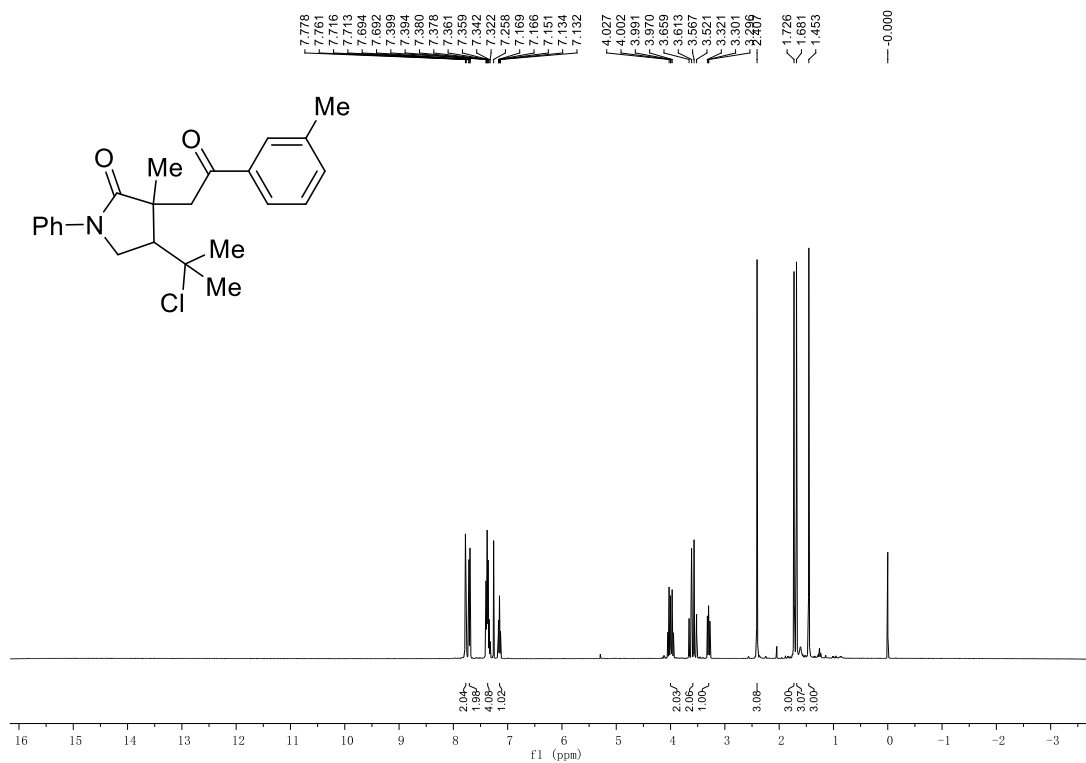
$^1\text{H}$  NMR of **3af** in  $\text{CDCl}_3$



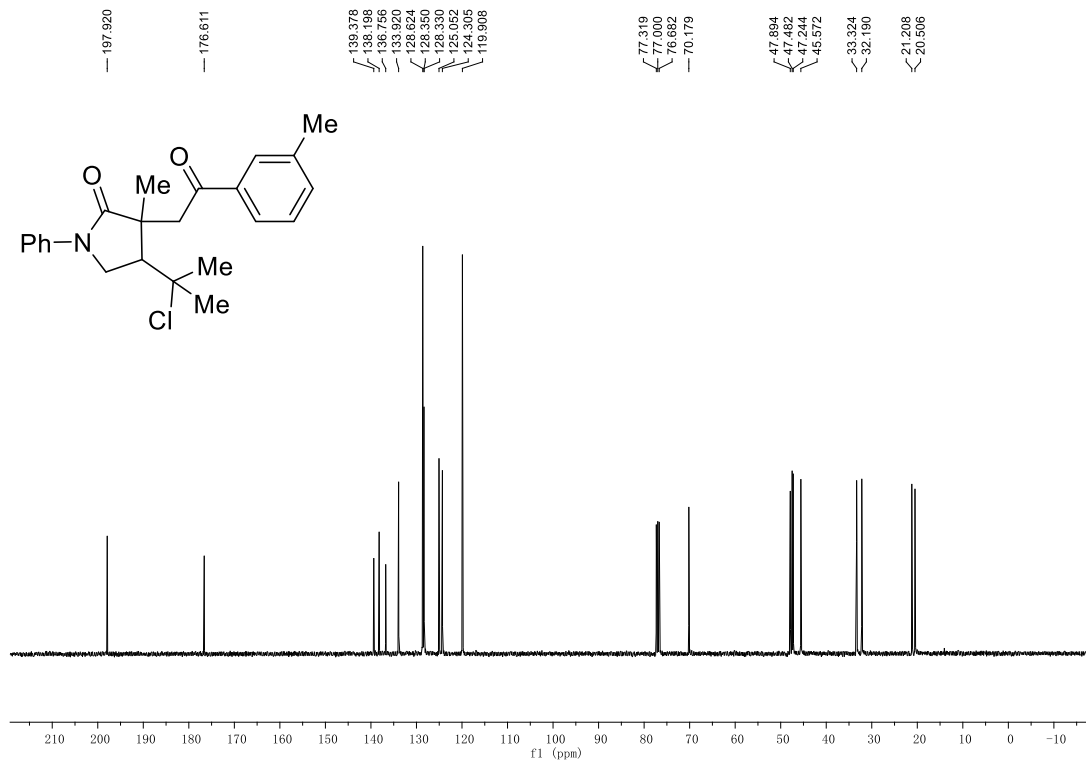
$^{13}\text{C}$  NMR of **3af** in  $\text{CDCl}_3$



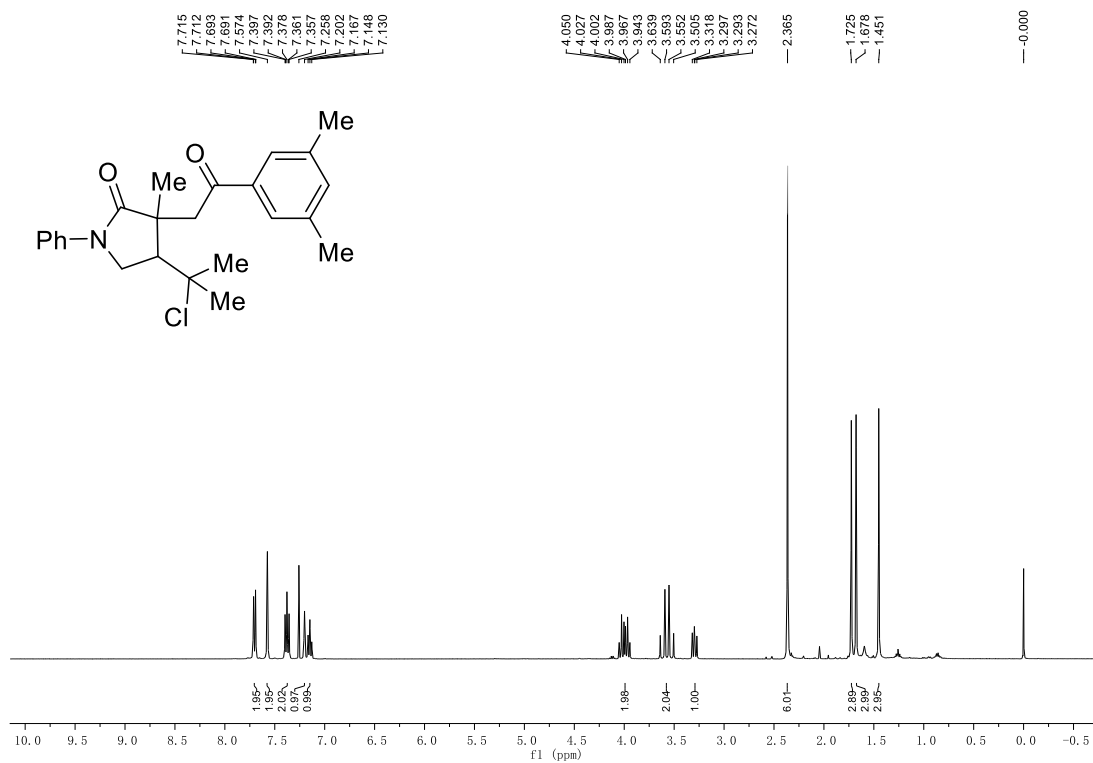
$^1\text{H}$  NMR of **3ag** in  $\text{CDCl}_3$



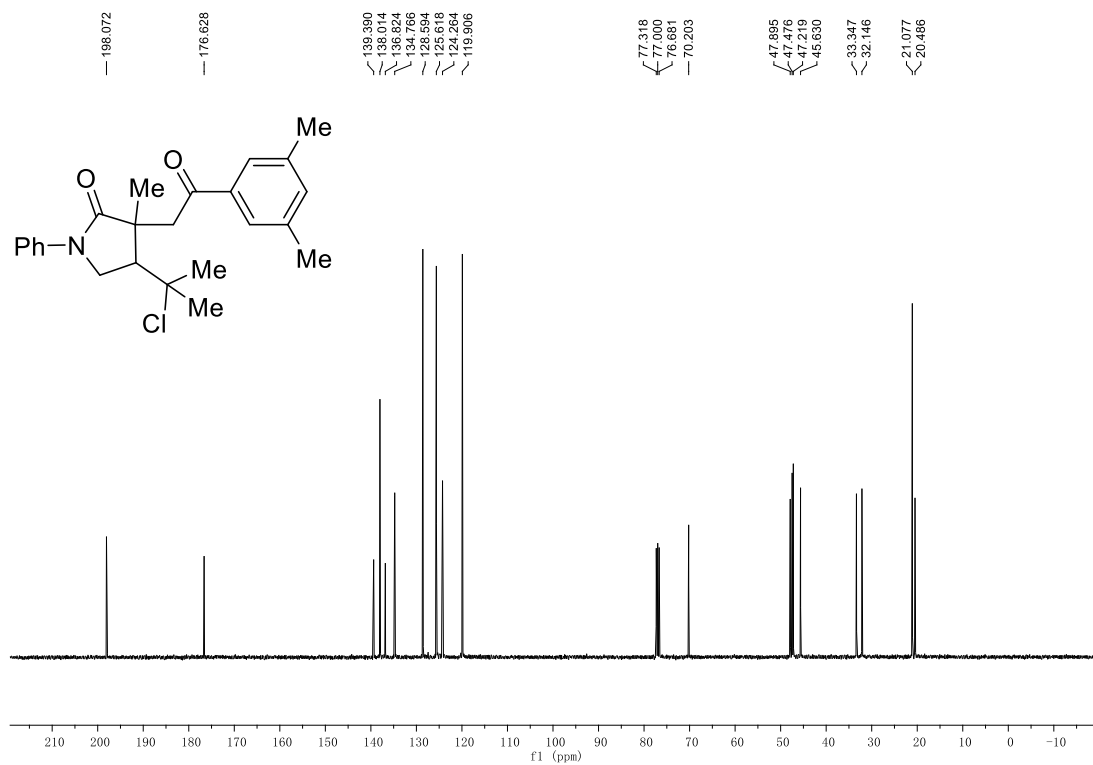
$^{13}\text{C}$  NMR of **3ag** in  $\text{CDCl}_3$



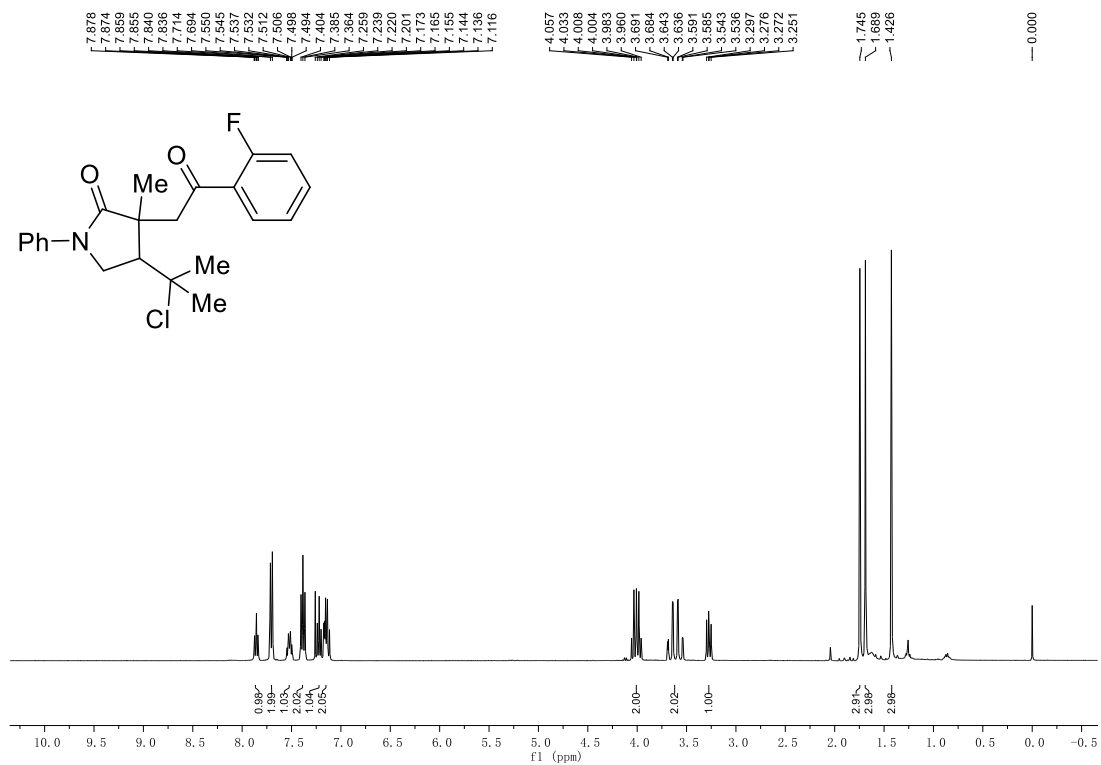
$^1\text{H}$  NMR of **3ah** in  $\text{CDCl}_3$



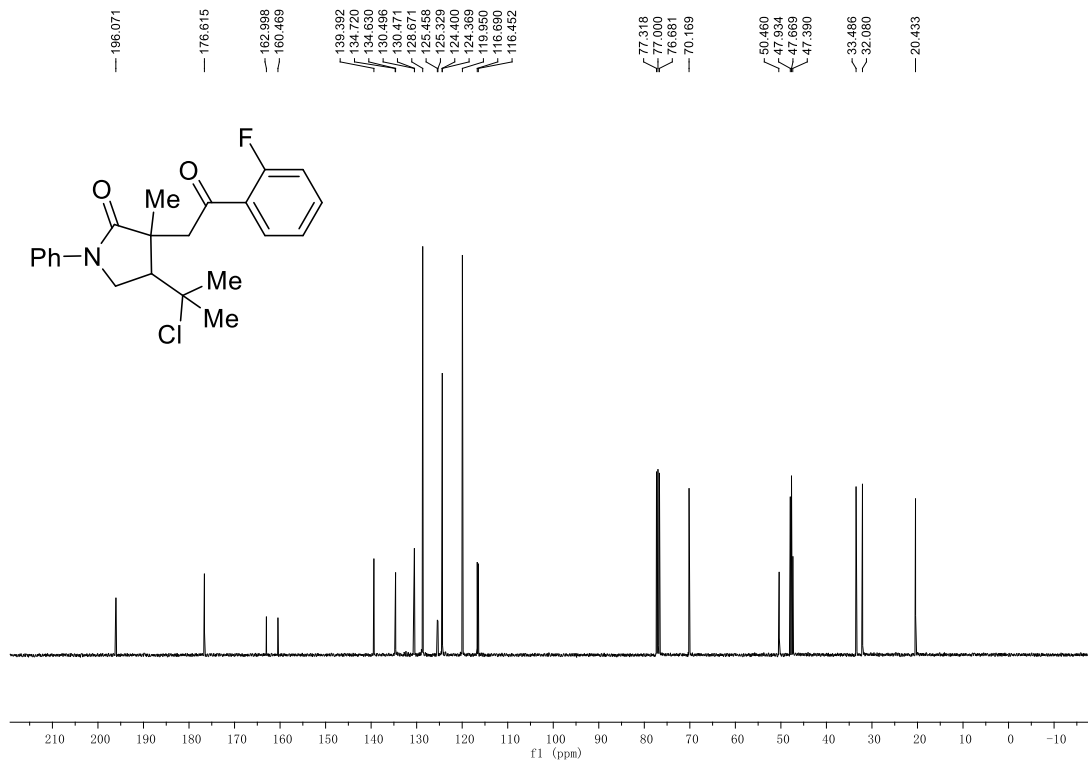
$^{13}\text{C}$  NMR of **3ah** in  $\text{CDCl}_3$



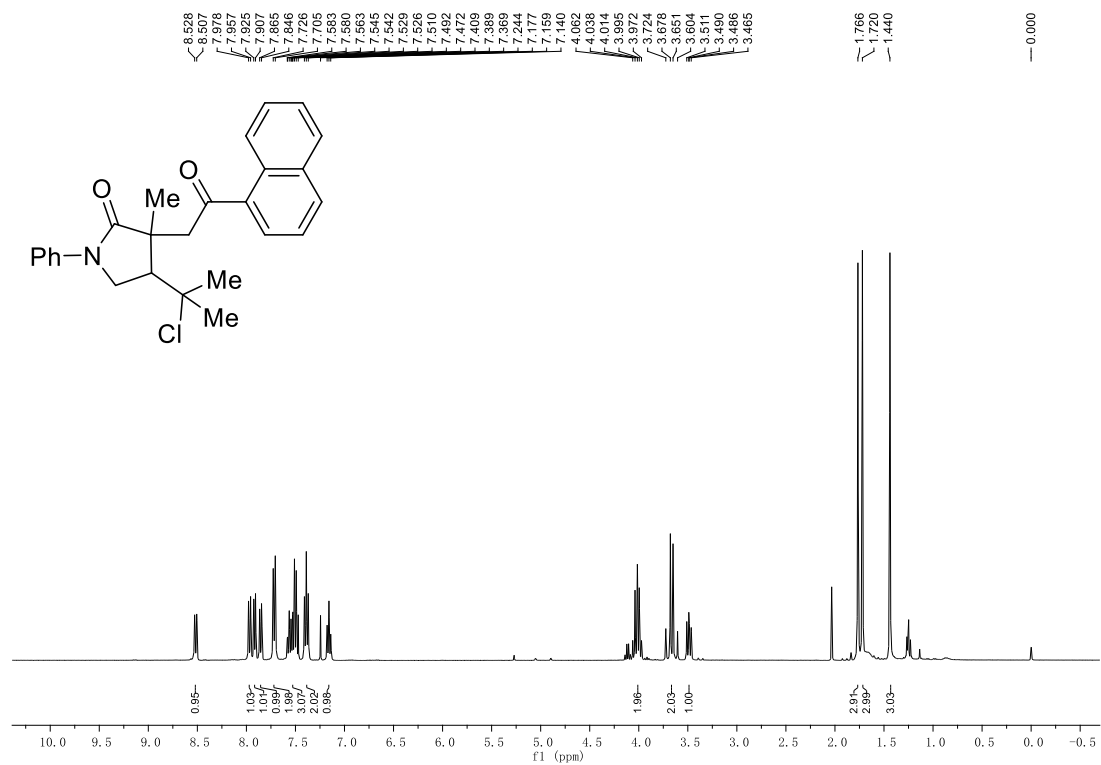
<sup>1</sup>H NMR of **3ai** in CDCl<sub>3</sub>



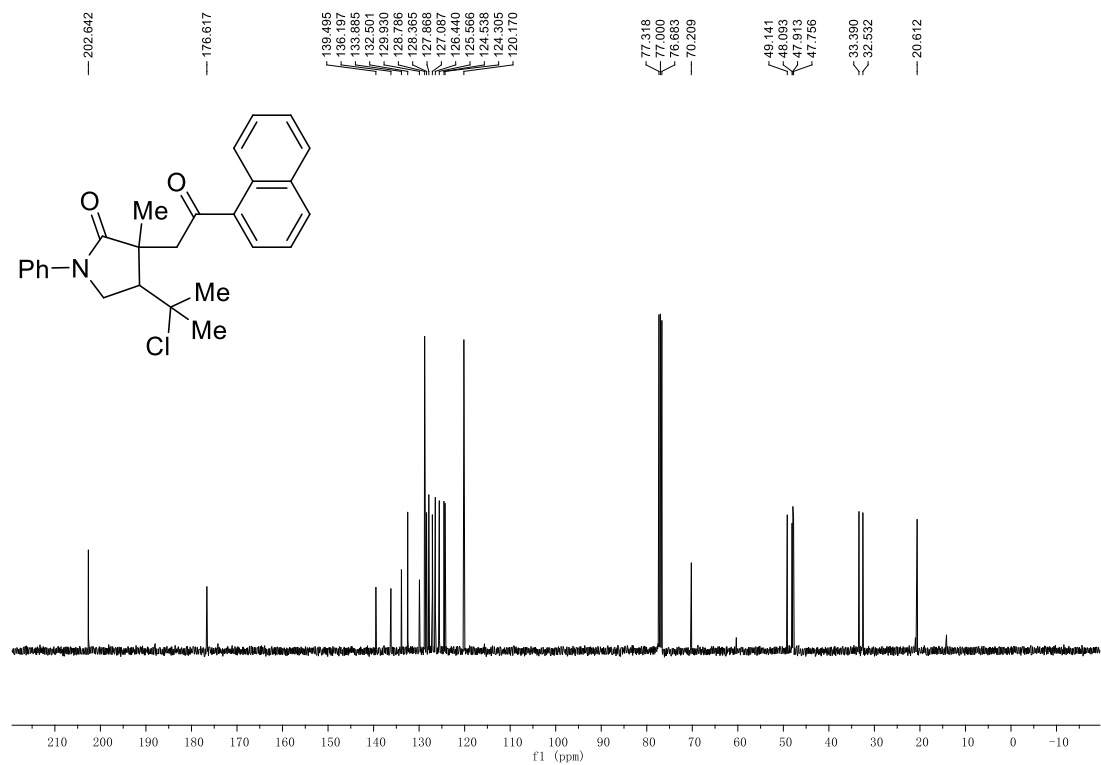
<sup>13</sup>C NMR of **3ai** in CDCl<sub>3</sub>



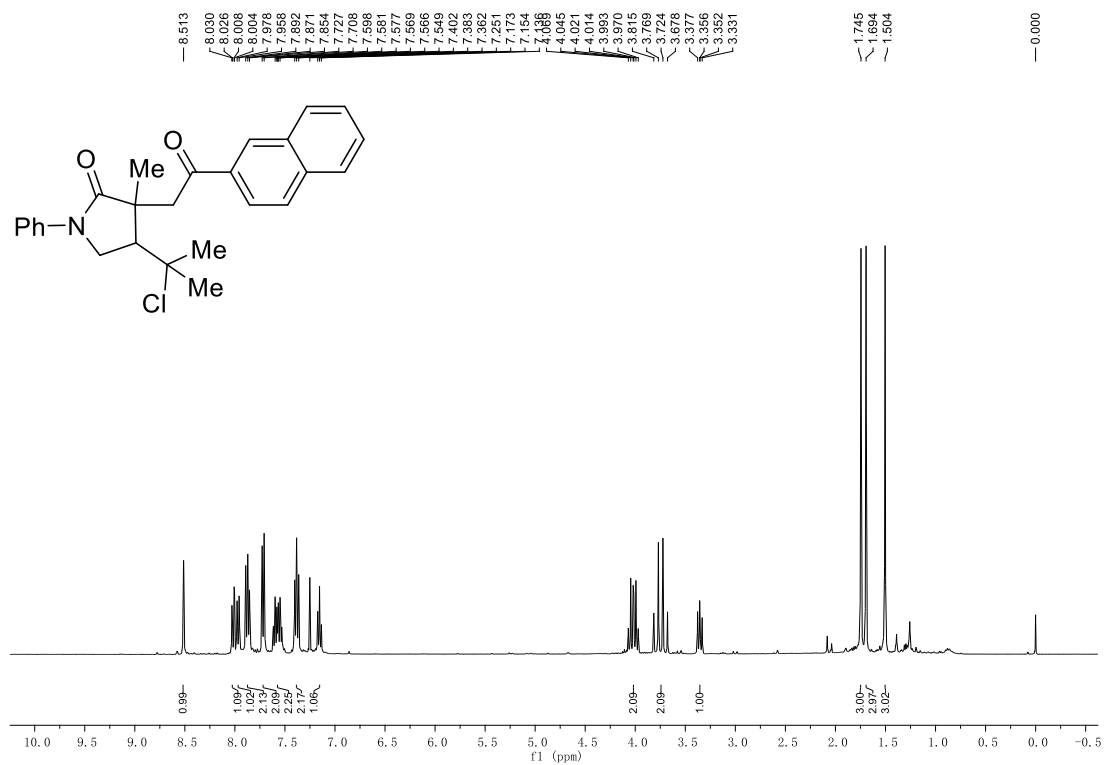
<sup>1</sup>H NMR of **3aj** in CDCl<sub>3</sub>



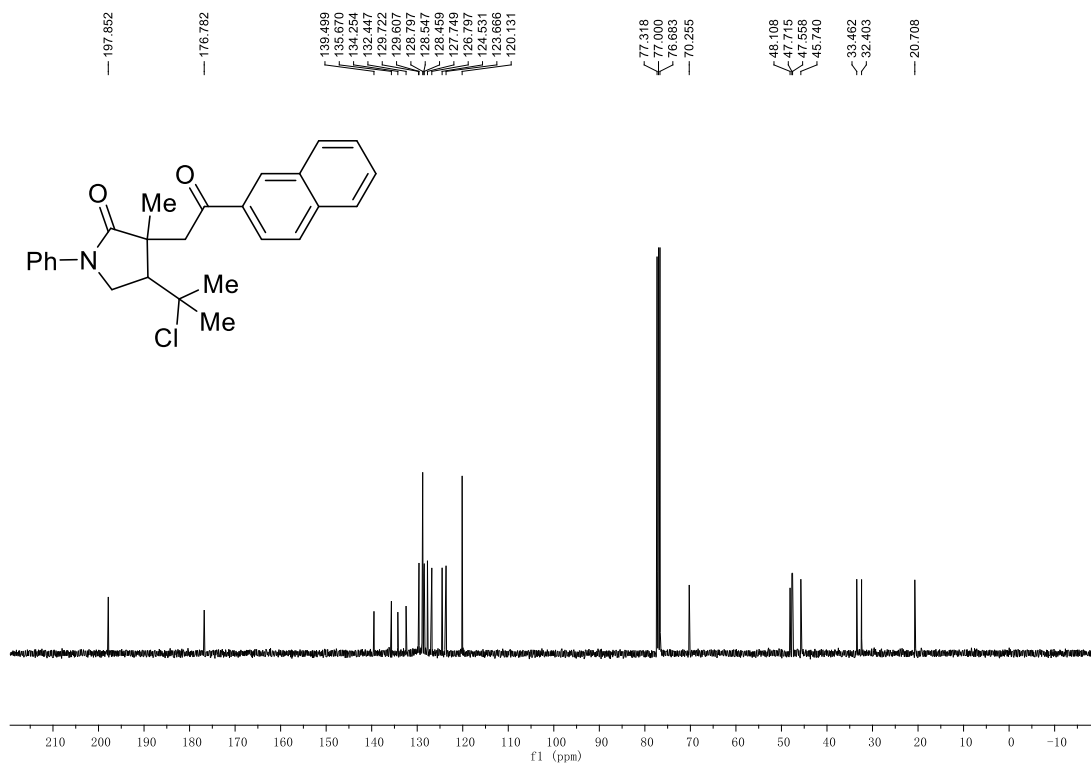
<sup>13</sup>C NMR of **3aj** in CDCl<sub>3</sub>



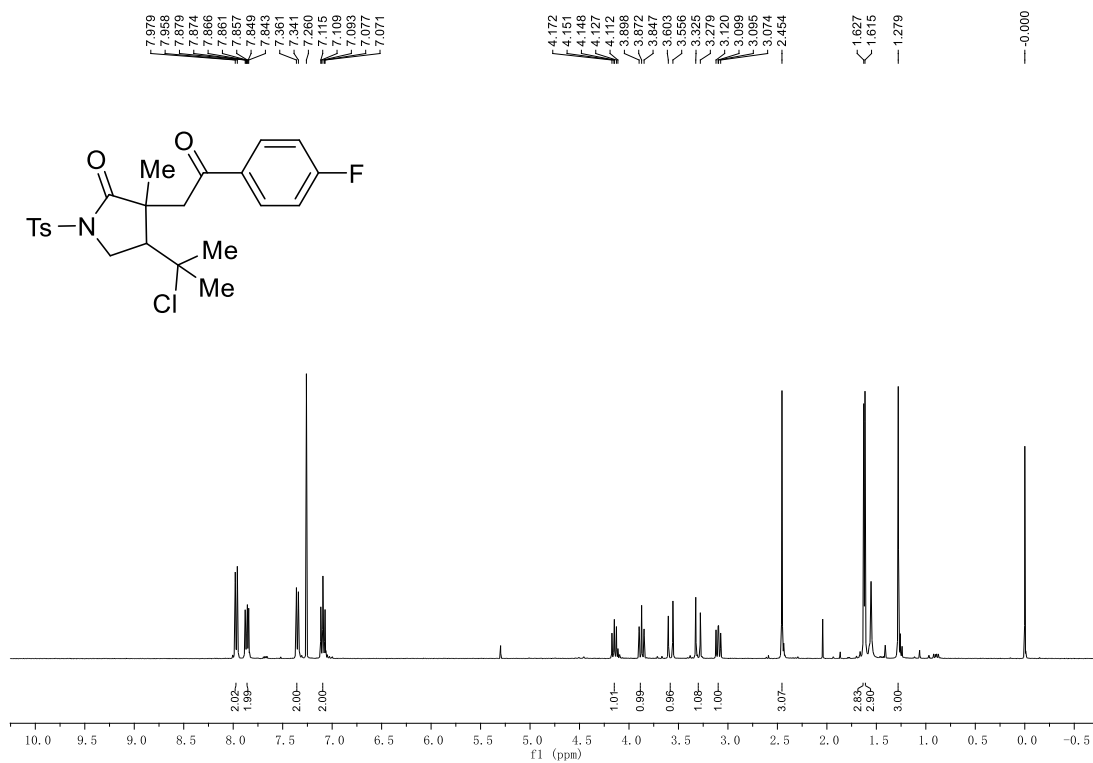
<sup>1</sup>H NMR of **3ak** in CDCl<sub>3</sub>



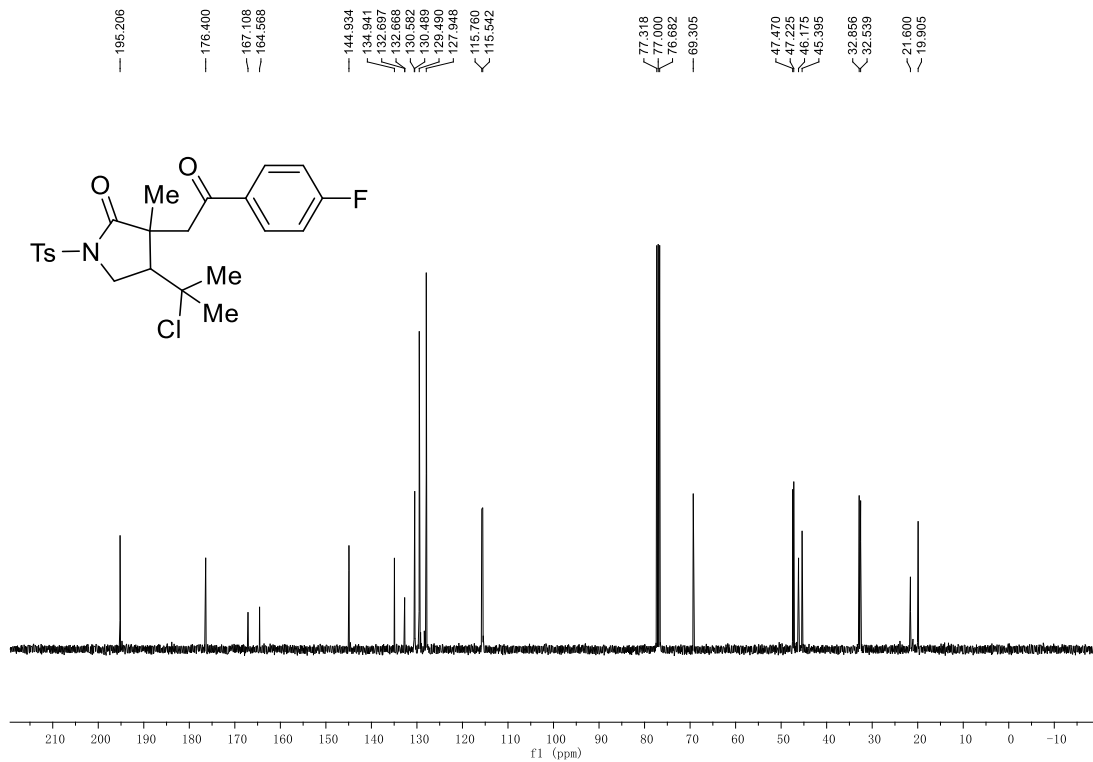
<sup>13</sup>C NMR of **3ak** in CDCl<sub>3</sub>



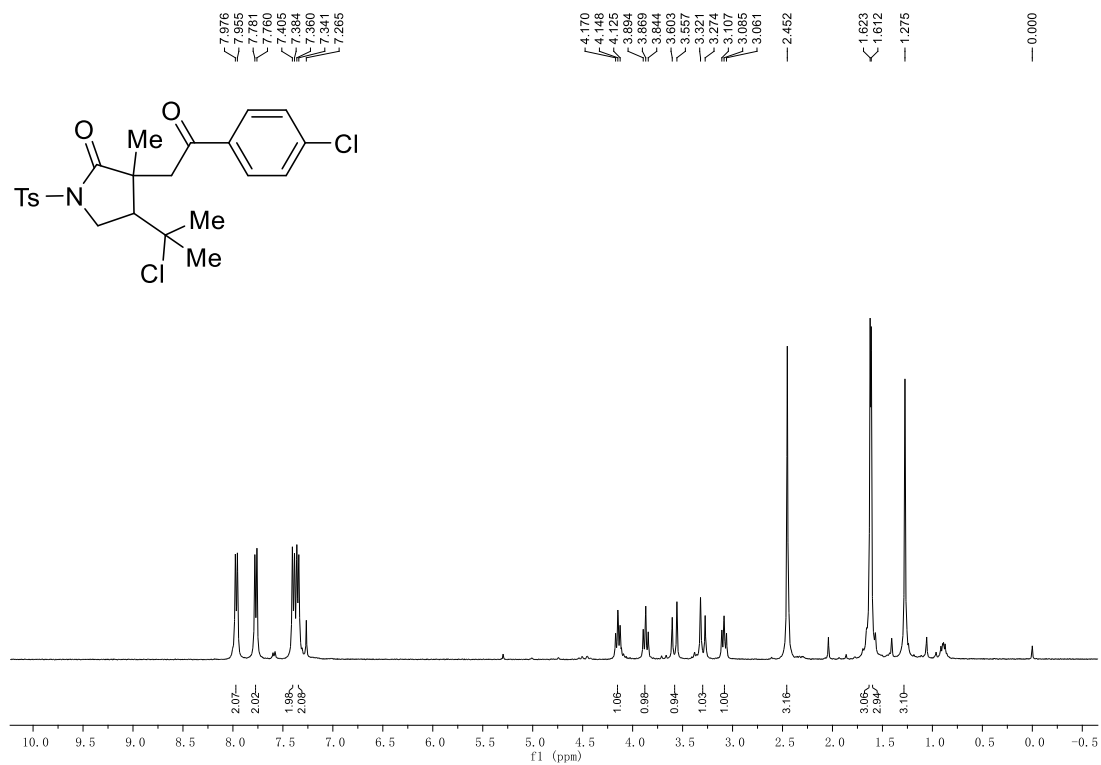
$^1\text{H}$  NMR of **3bb** in  $\text{CDCl}_3$



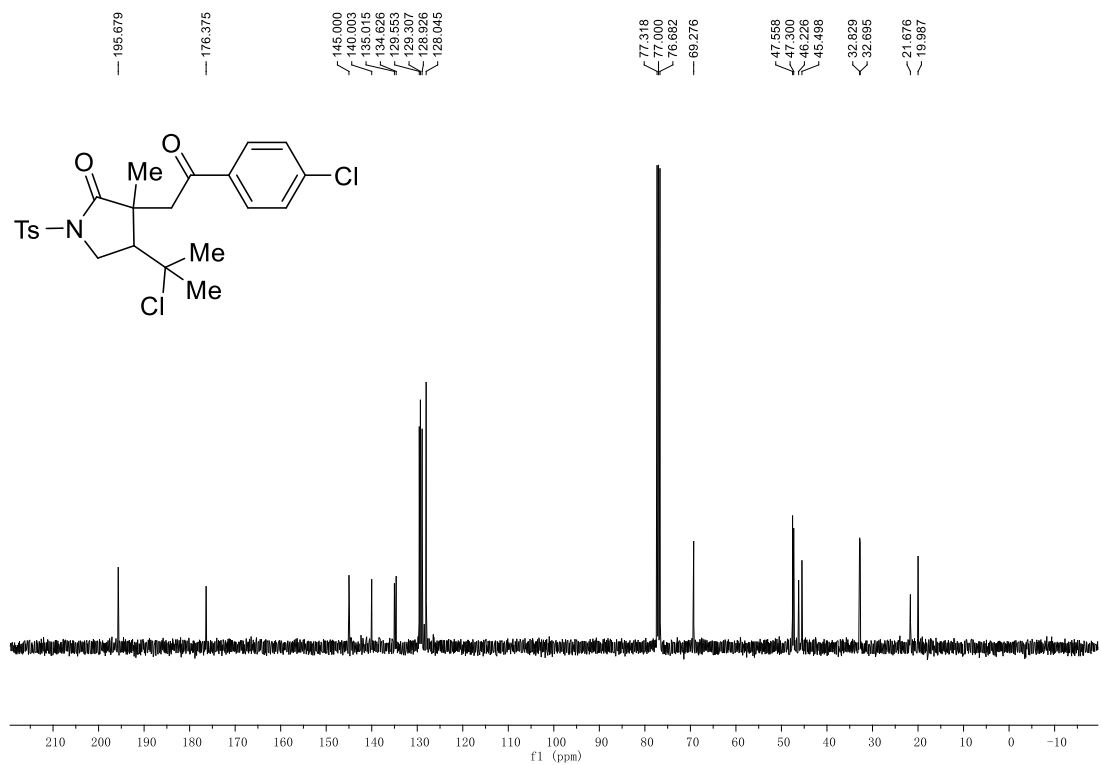
$^{13}\text{C}$  NMR of **3bb** in  $\text{CDCl}_3$



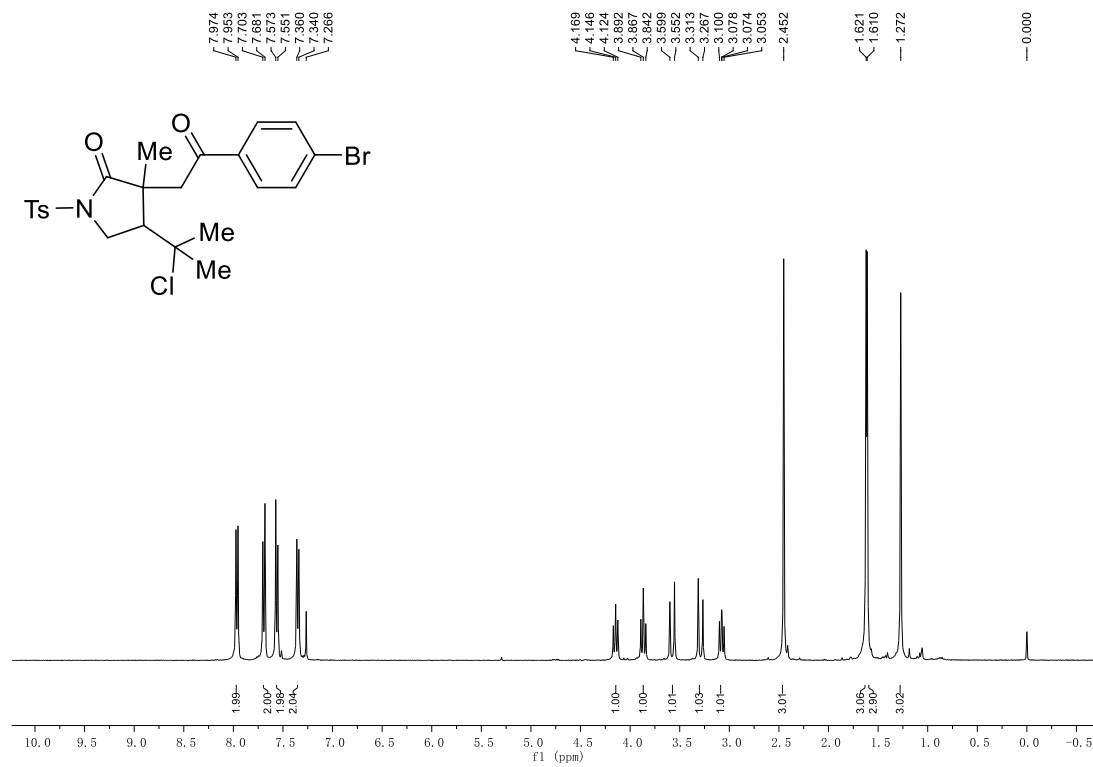
<sup>1</sup>H NMR of **3bc** in CDCl<sub>3</sub>



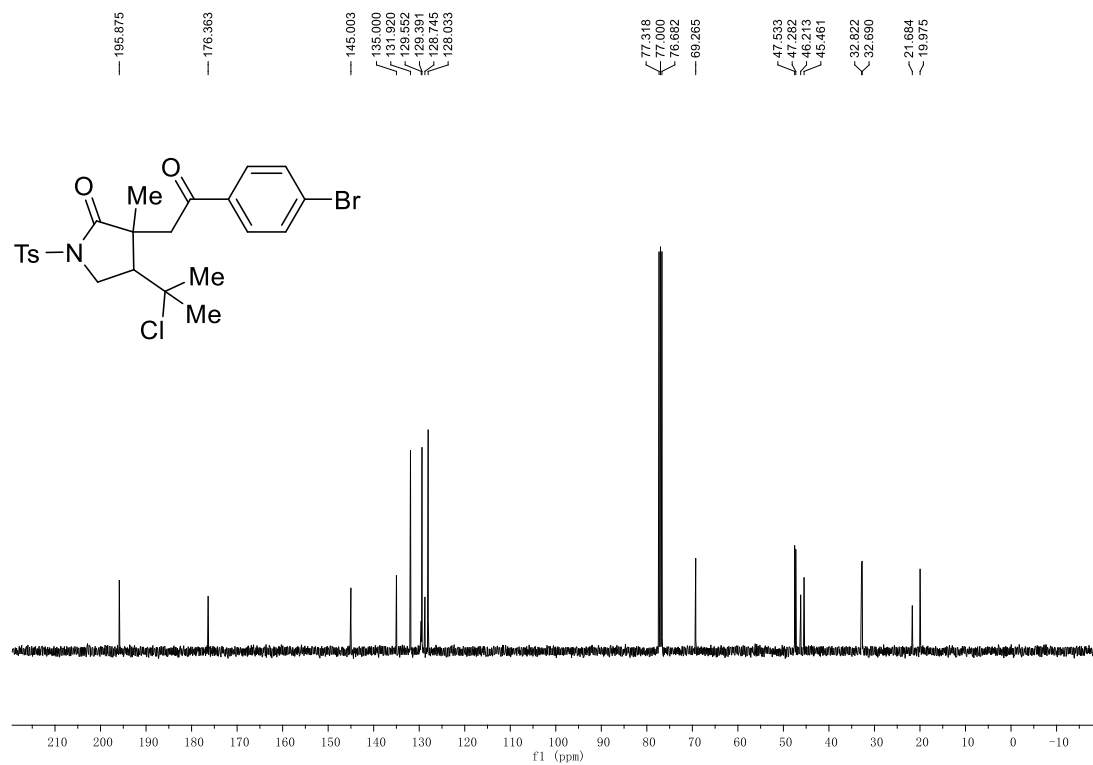
<sup>13</sup>C NMR of **3bc** in CDCl<sub>3</sub>



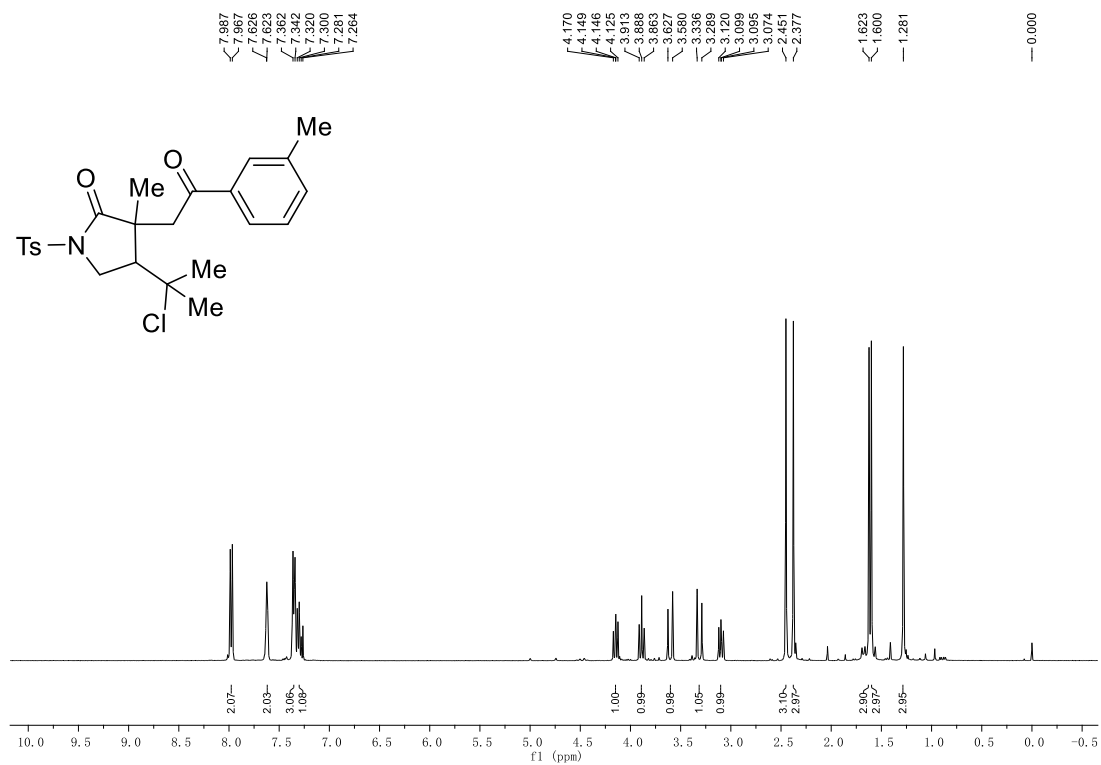
<sup>1</sup>H NMR of **3bd** in CDCl<sub>3</sub>



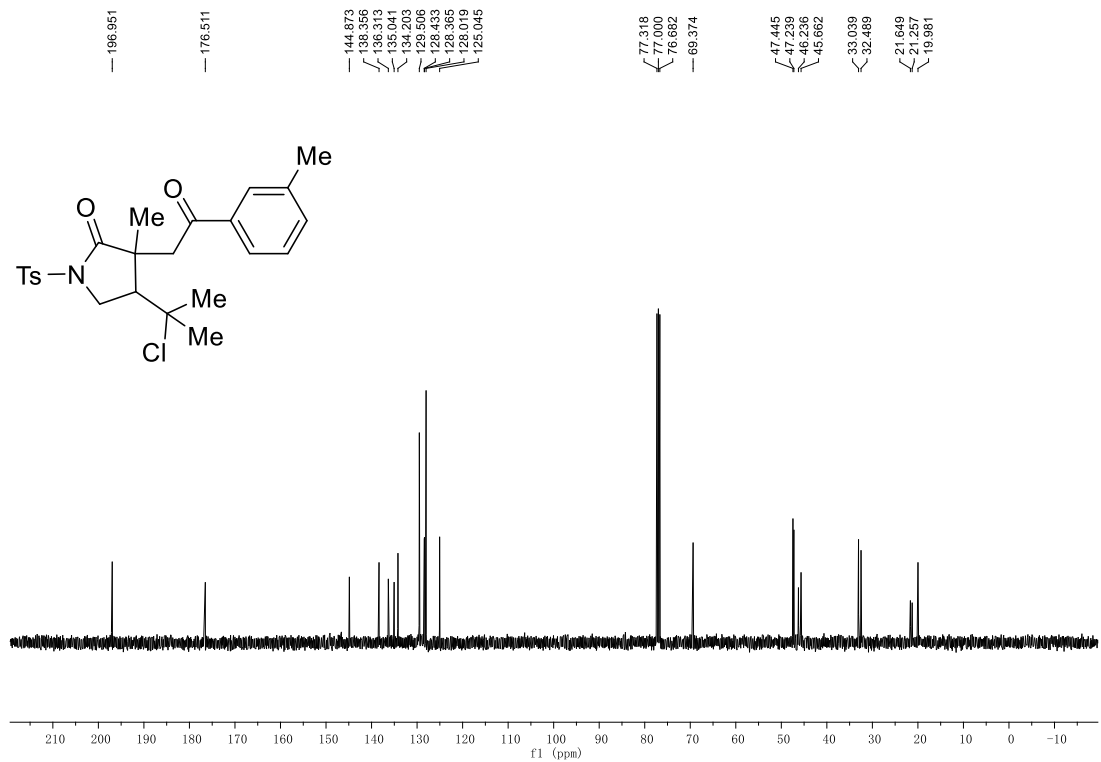
<sup>13</sup>C NMR of **3bd** in CDCl<sub>3</sub>



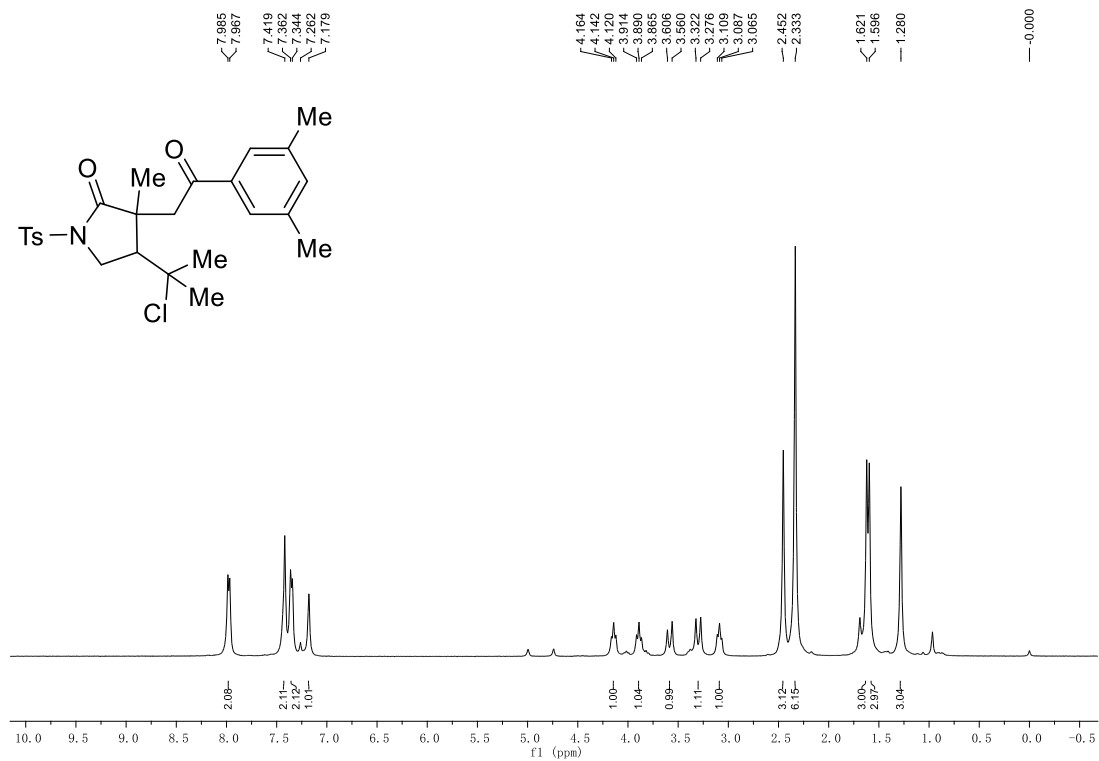
$^1\text{H}$  NMR of **3bg** in  $\text{CDCl}_3$



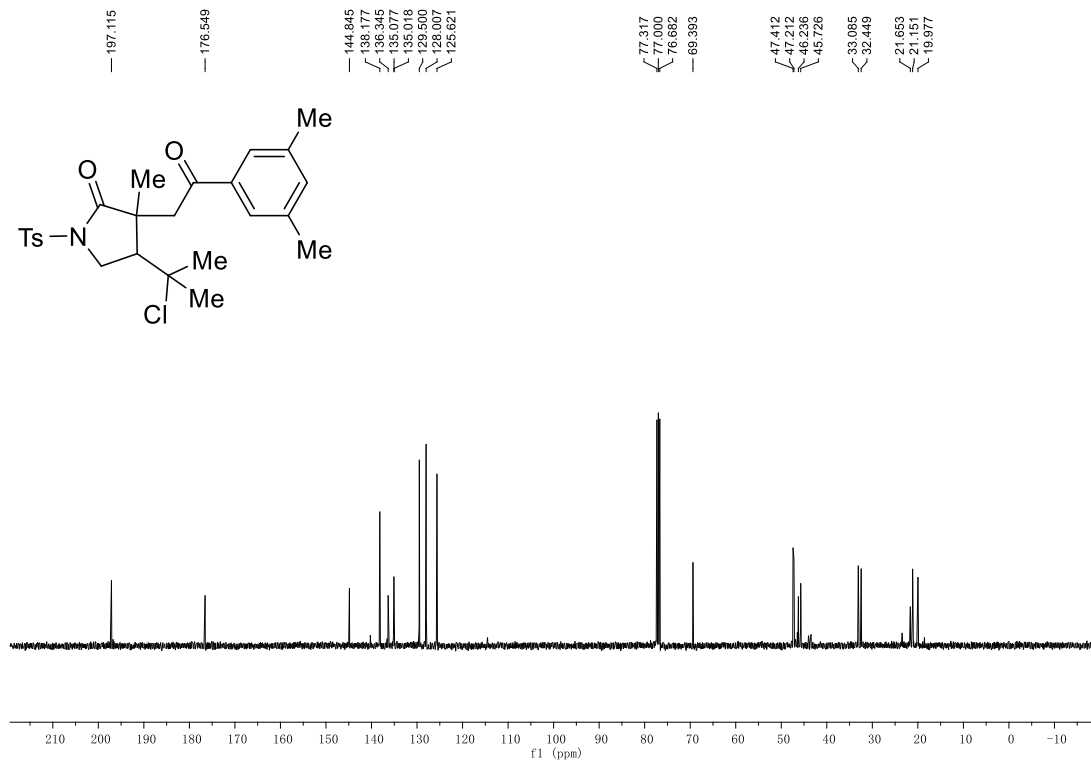
$^{13}\text{C}$  NMR of **3bg** in  $\text{CDCl}_3$



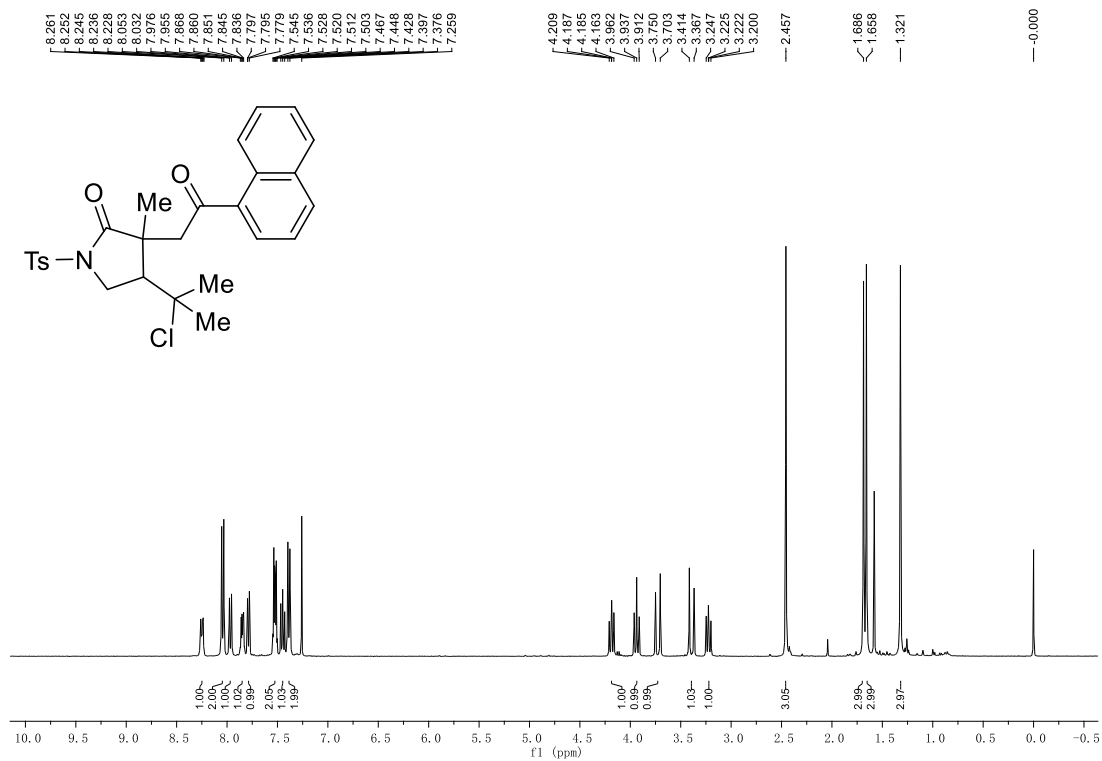
$^1\text{H}$  NMR of **3bh** in  $\text{CDCl}_3$



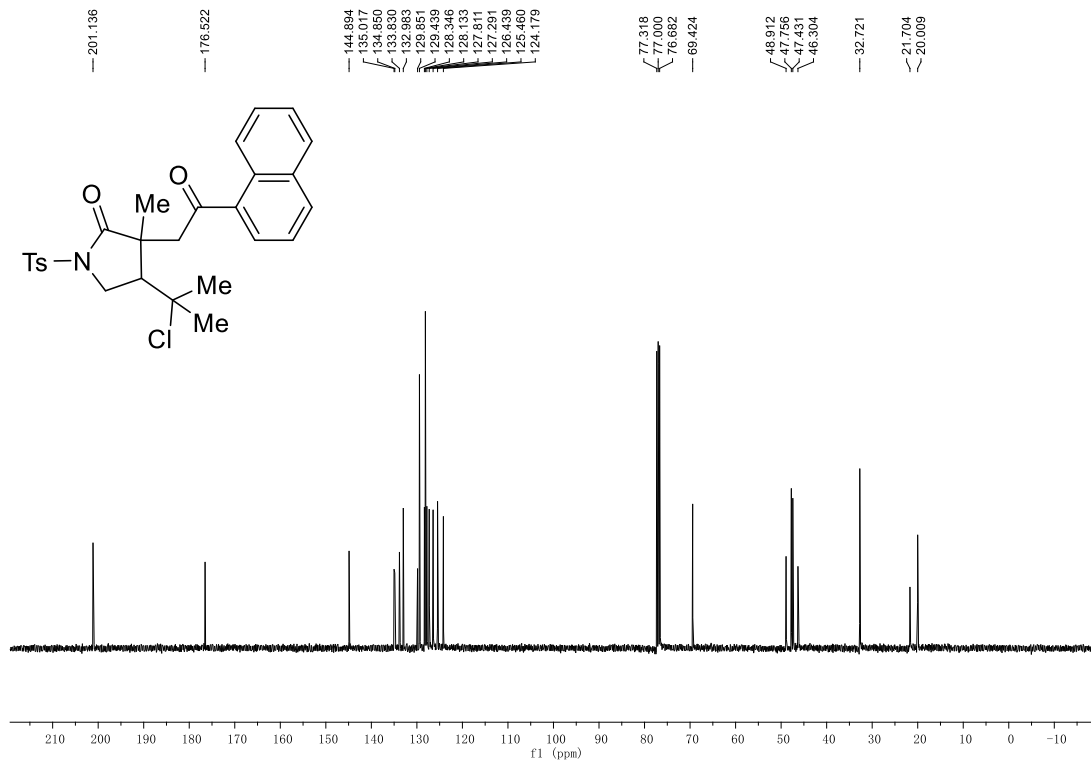
$^{13}\text{C}$  NMR of **3bh** in  $\text{CDCl}_3$



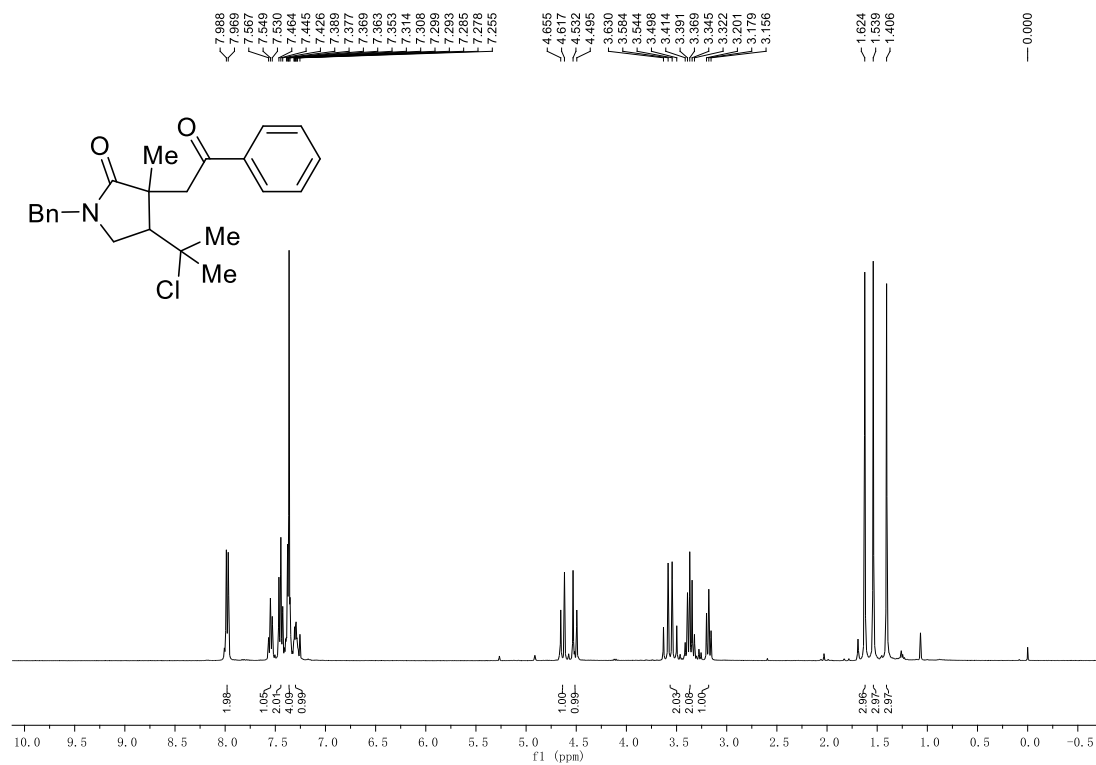
<sup>1</sup>H NMR of **3bj** in CDCl<sub>3</sub>



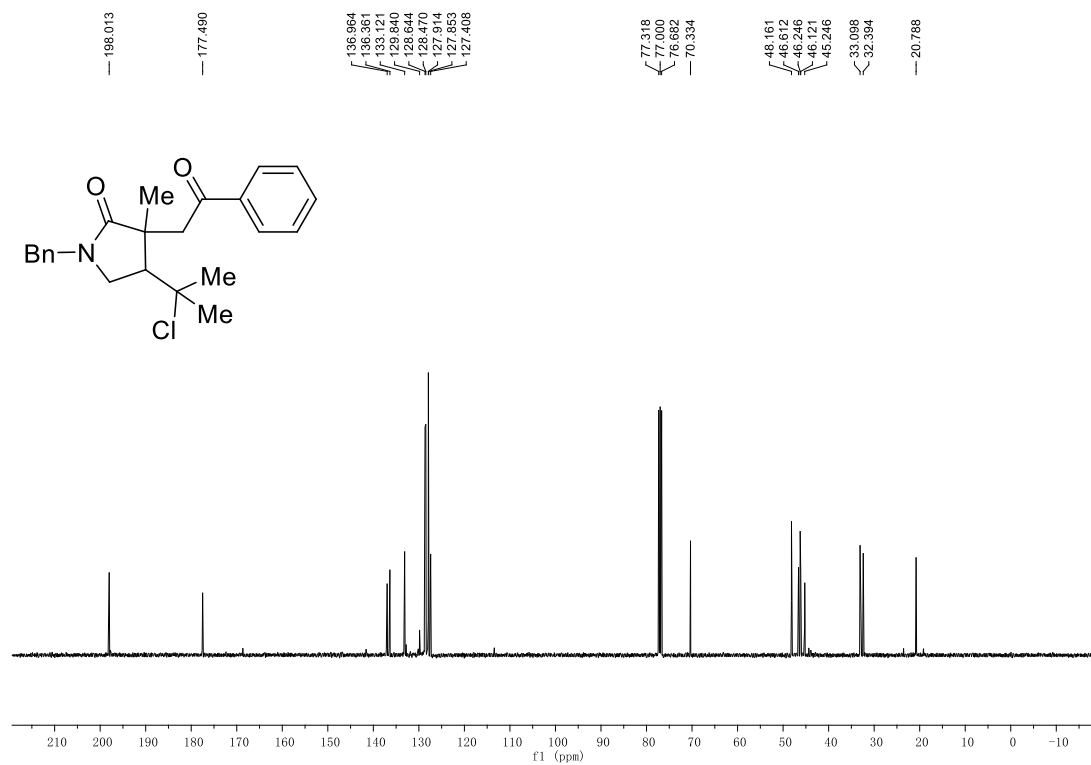
<sup>13</sup>C NMR of **3bj** in CDCl<sub>3</sub>



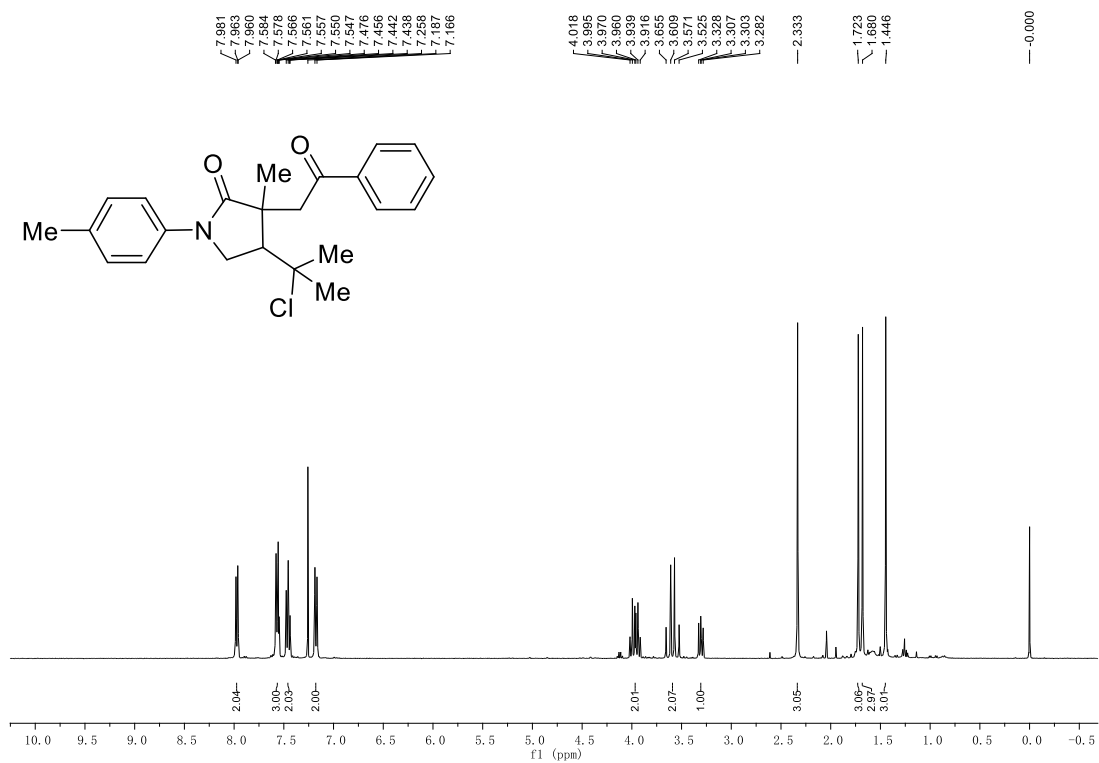
$^1\text{H}$  NMR of **3ca** in  $\text{CDCl}_3$



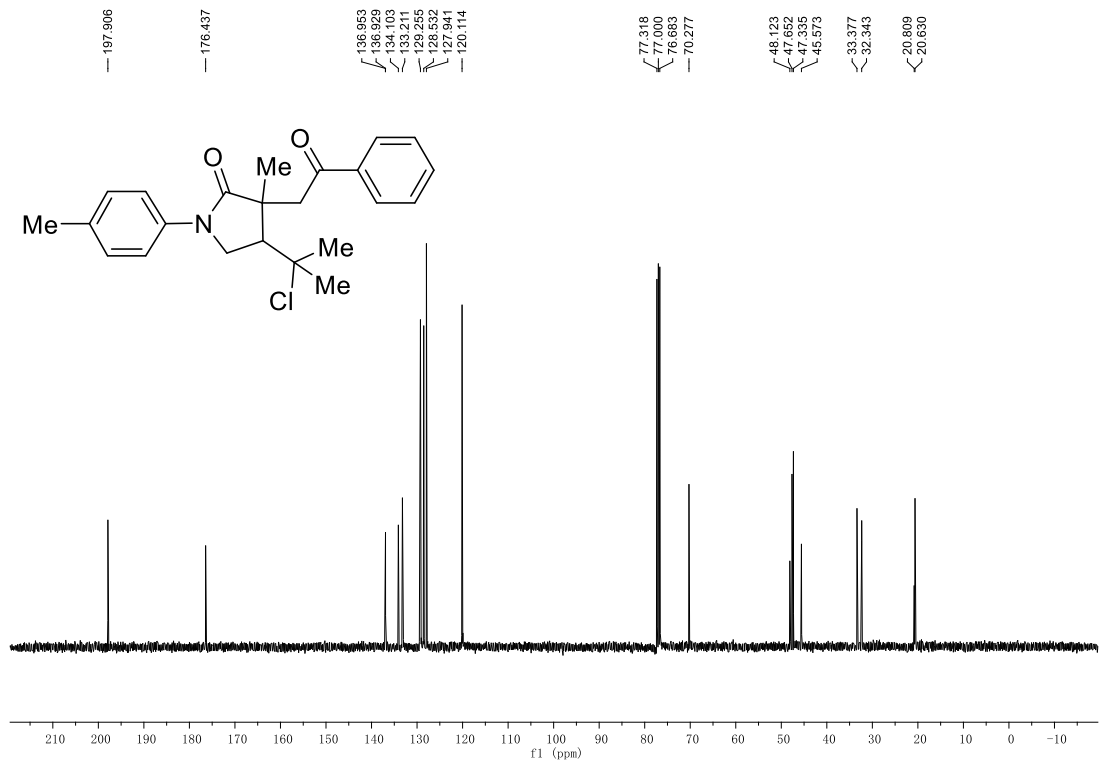
$^{13}\text{C}$  NMR of **3ca** in  $\text{CDCl}_3$



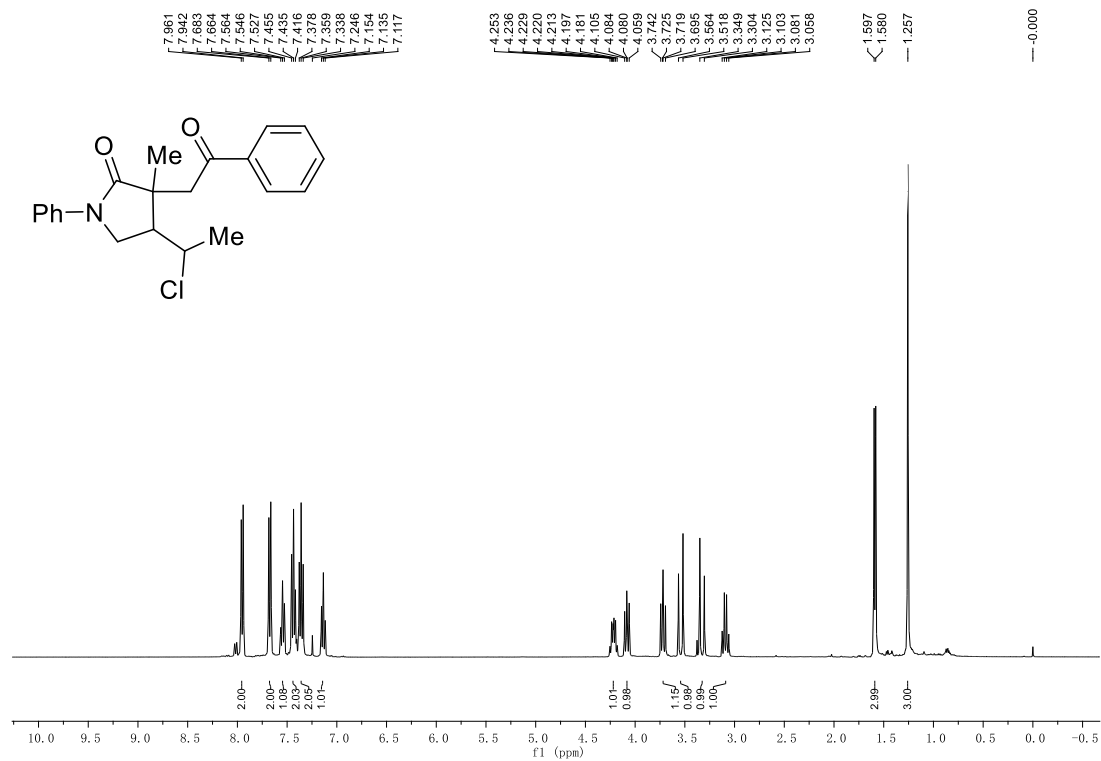
$^1\text{H}$  NMR of **3da** in  $\text{CDCl}_3$



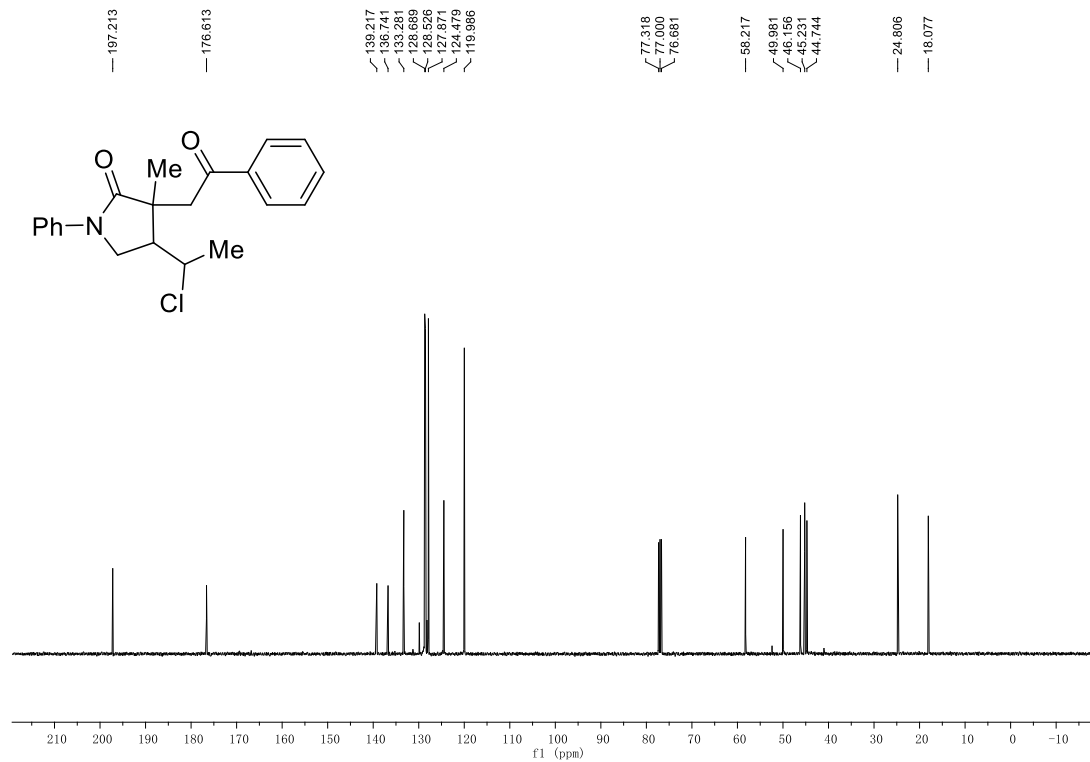
$^{13}\text{C}$  NMR of **3da** in  $\text{CDCl}_3$



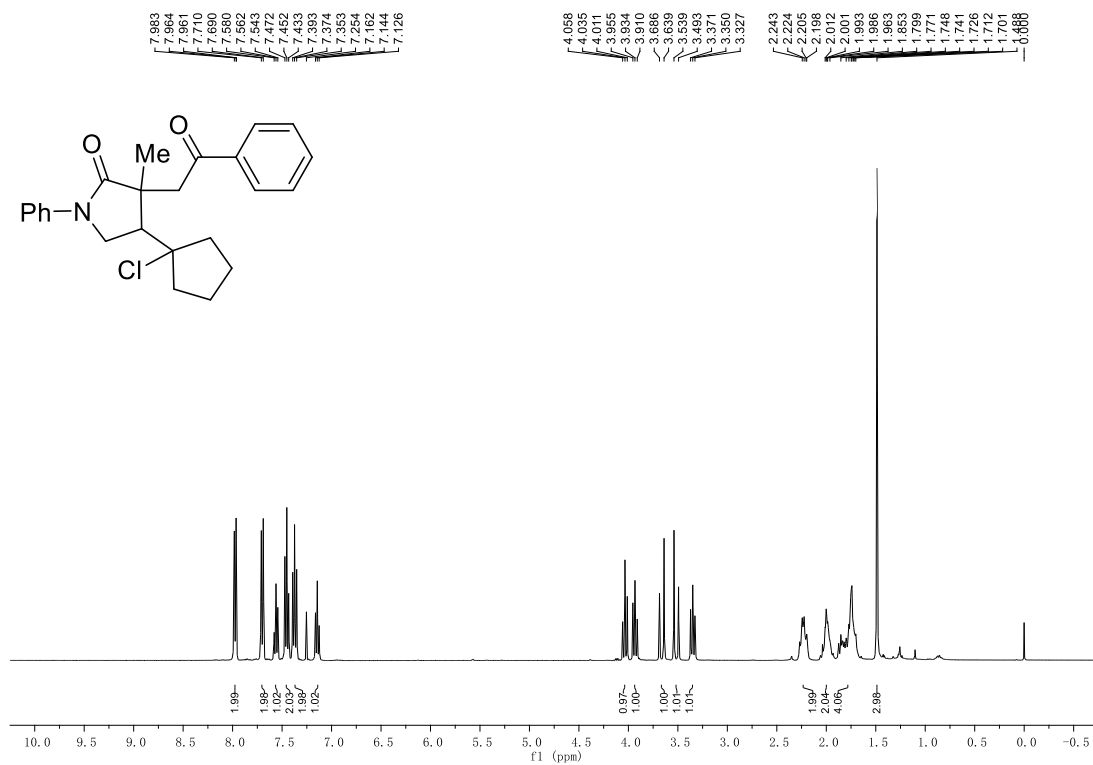
<sup>1</sup>H NMR of **3ea** in CDCl<sub>3</sub>



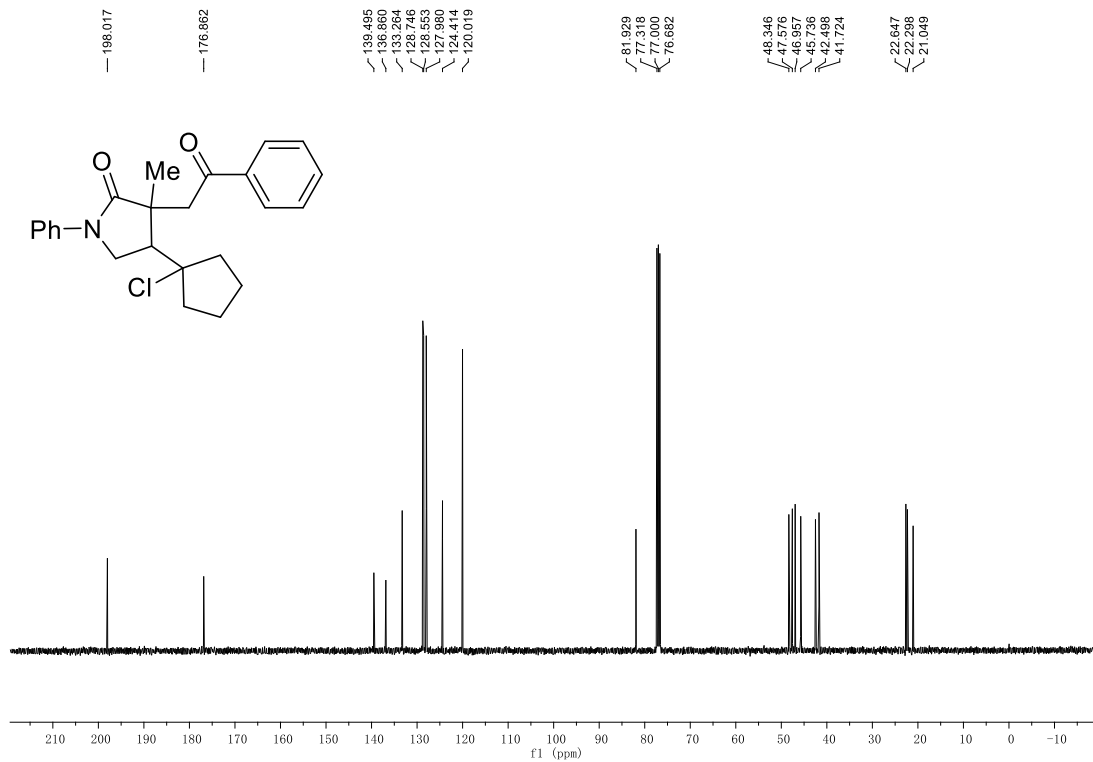
<sup>13</sup>C NMR of **3ea** in CDCl<sub>3</sub>



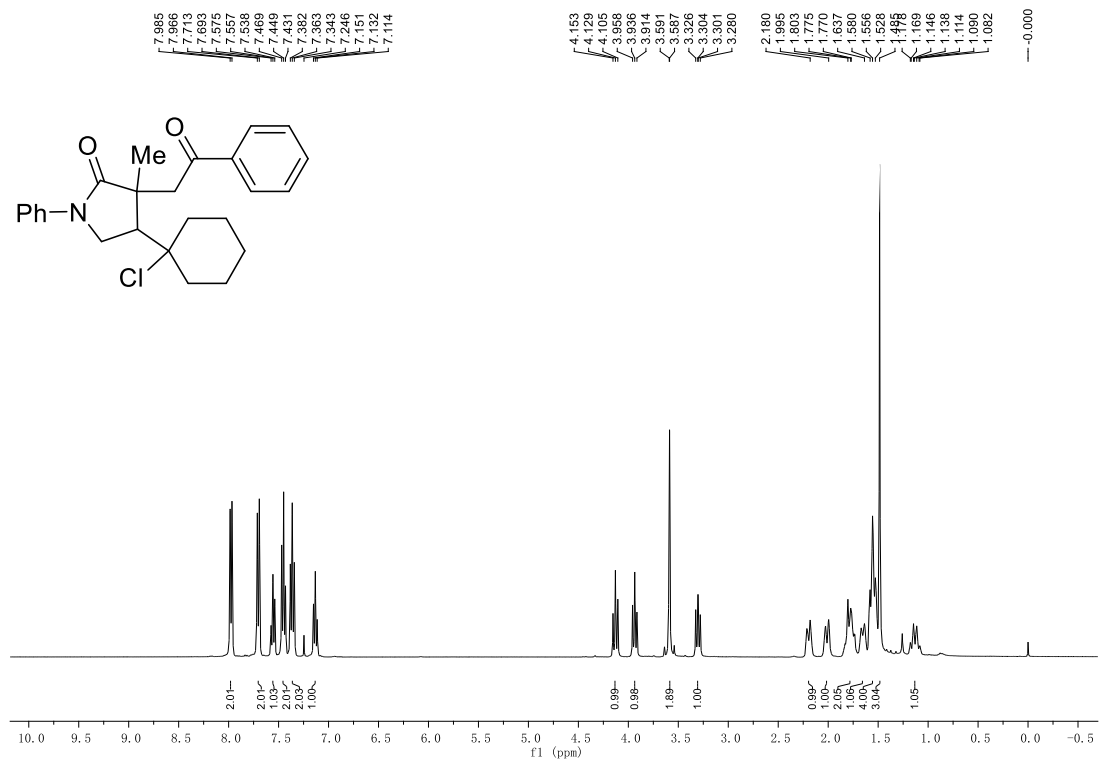
$^1\text{H}$  NMR of **3fa** in  $\text{CDCl}_3$



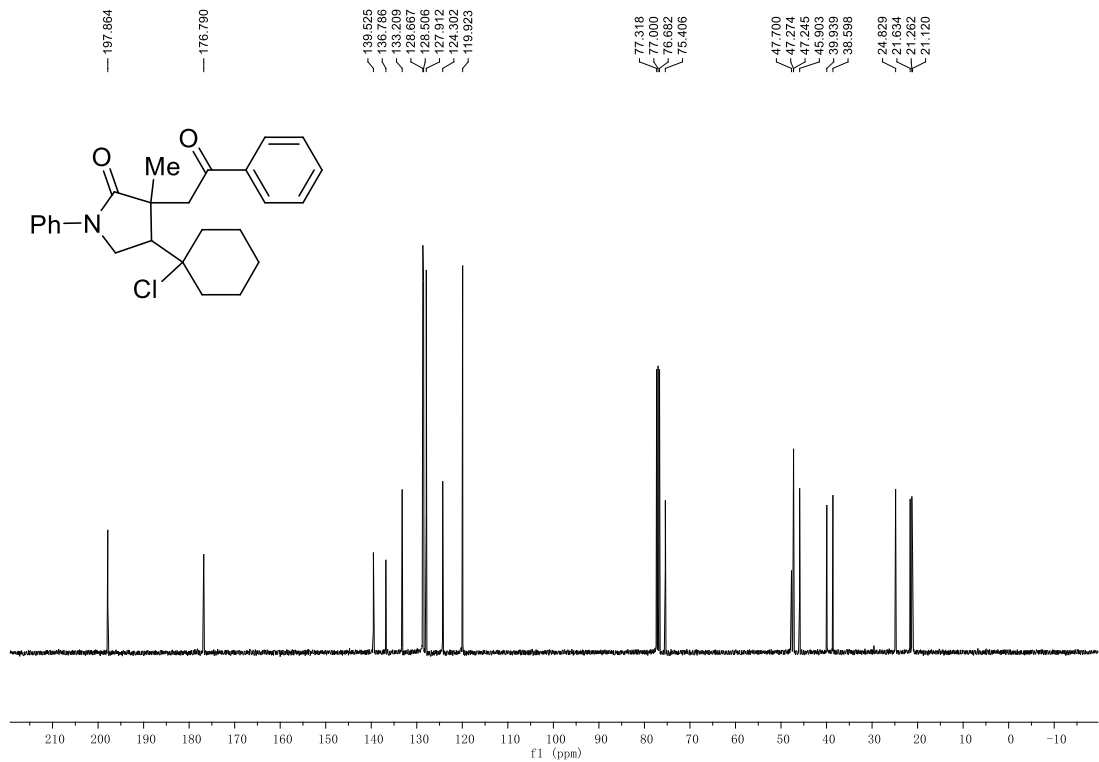
$^{13}\text{C}$  NMR of **3fa** in  $\text{CDCl}_3$



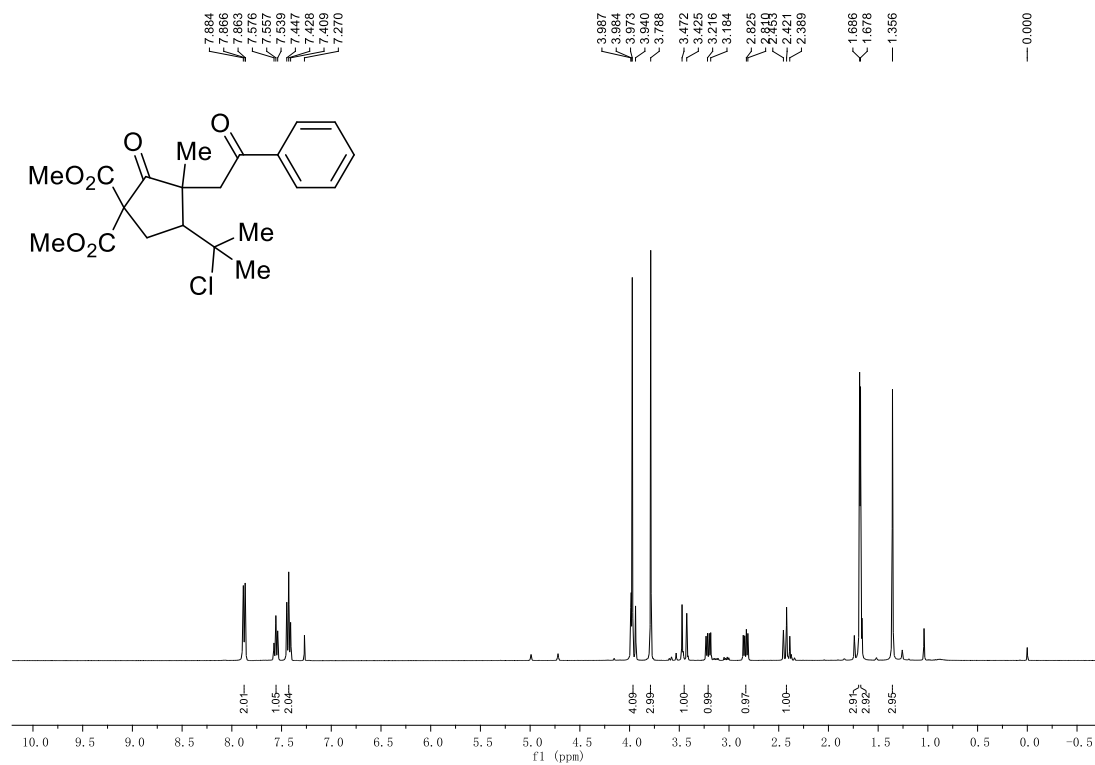
$^1\text{H}$  NMR of **3ga** in  $\text{CDCl}_3$



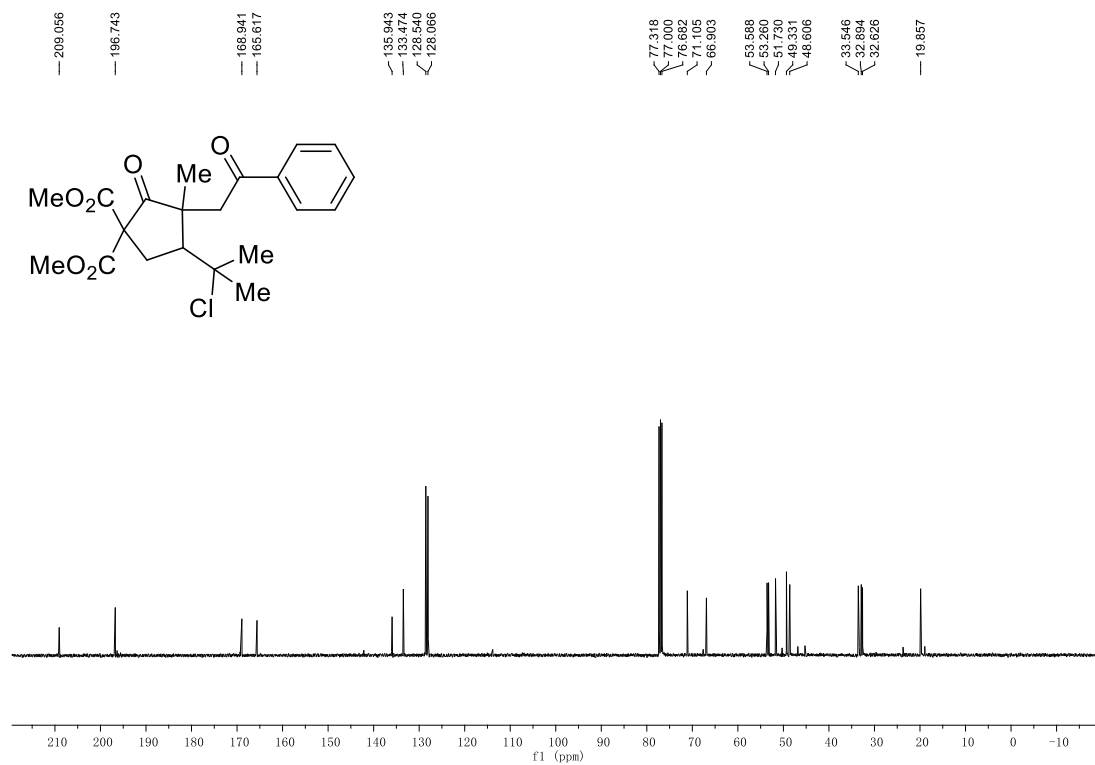
$^{13}\text{C}$  NMR of **3ga** in  $\text{CDCl}_3$



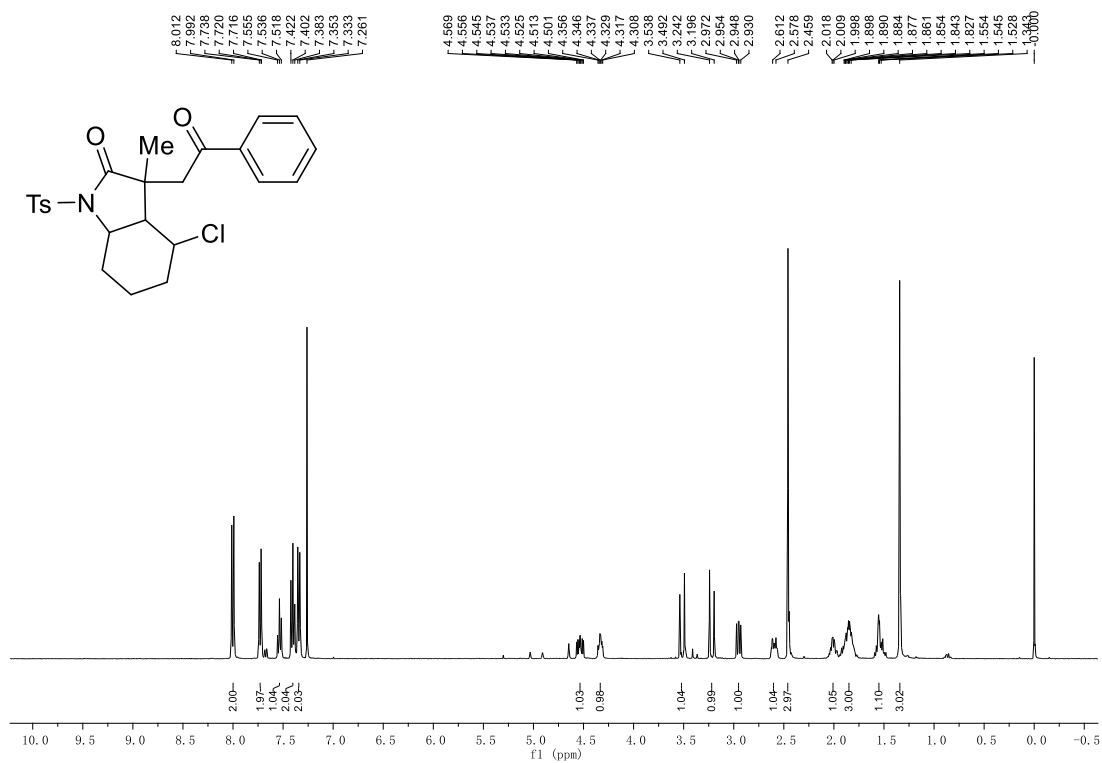
<sup>1</sup>H NMR of **3ha** in CDCl<sub>3</sub>



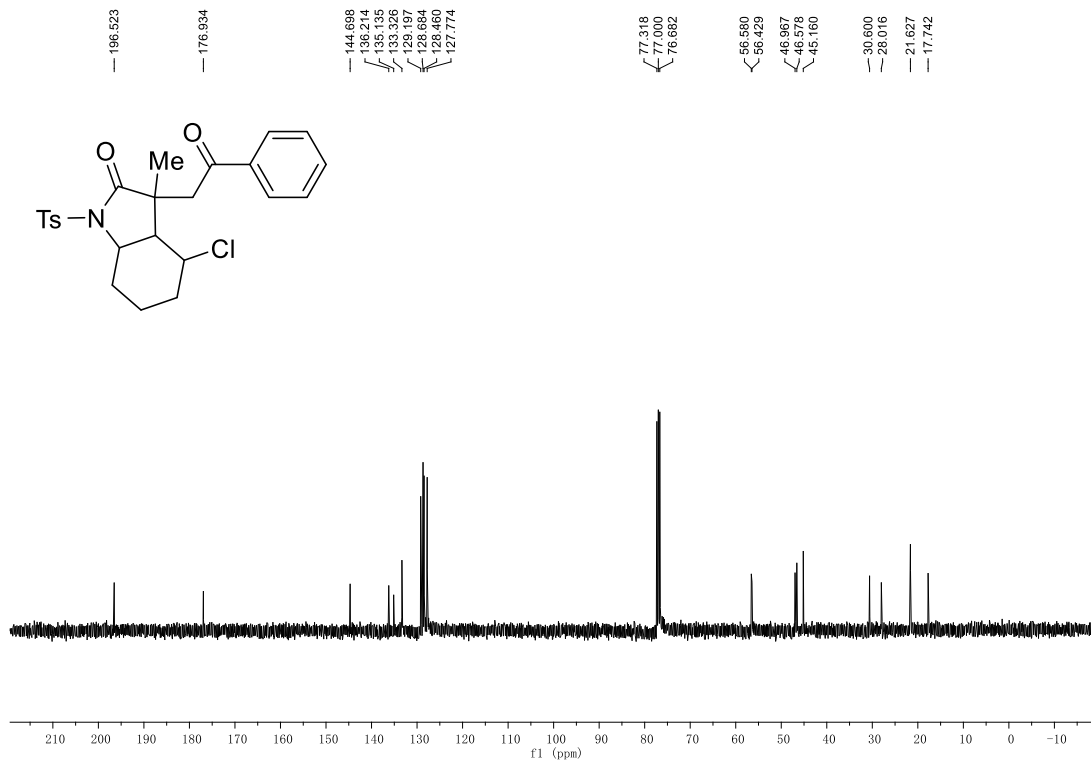
<sup>13</sup>C NMR of **3ha** in CDCl<sub>3</sub>



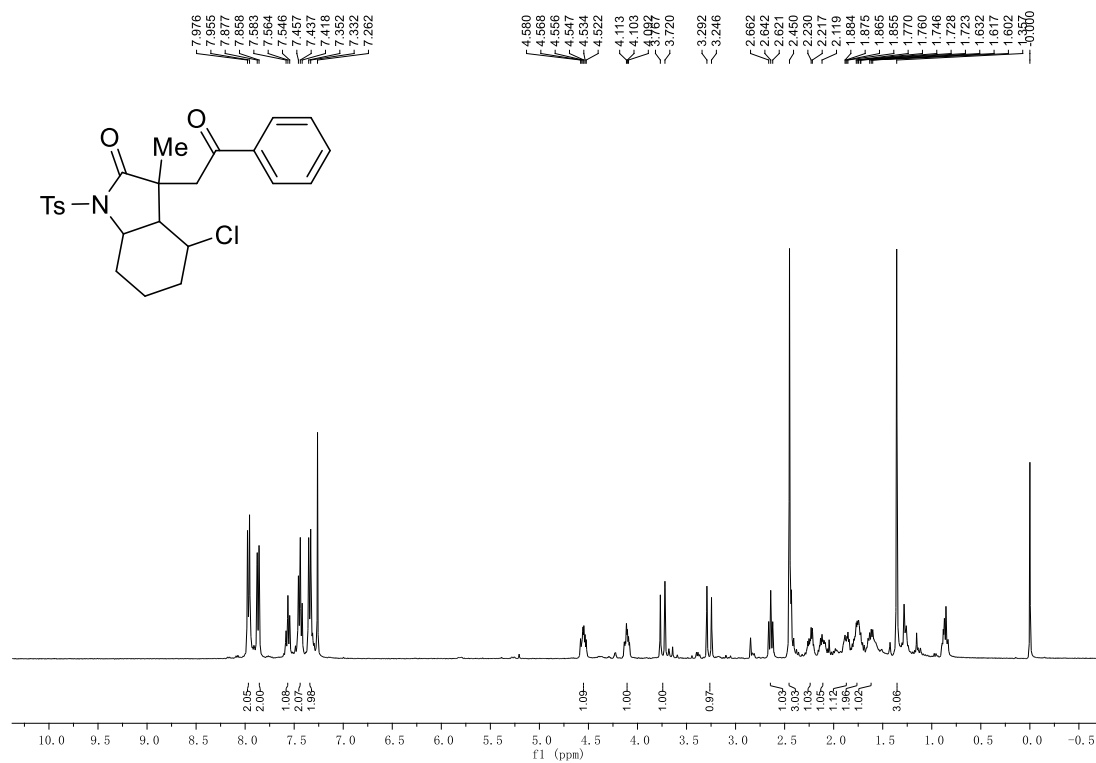
$^1\text{H}$  NMR of **3ia** (*Major diastereomer*) in  $\text{CDCl}_3$



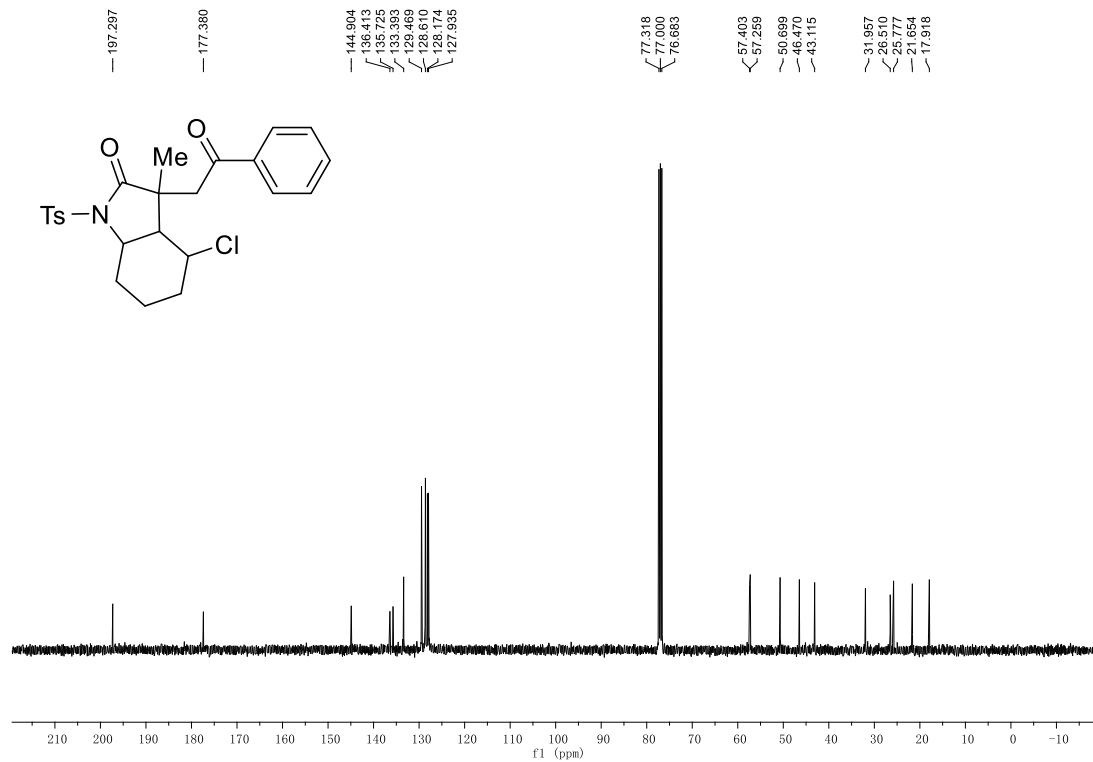
$^{13}\text{C}$  NMR of **3ia** (*Major diastereomer*) in  $\text{CDCl}_3$



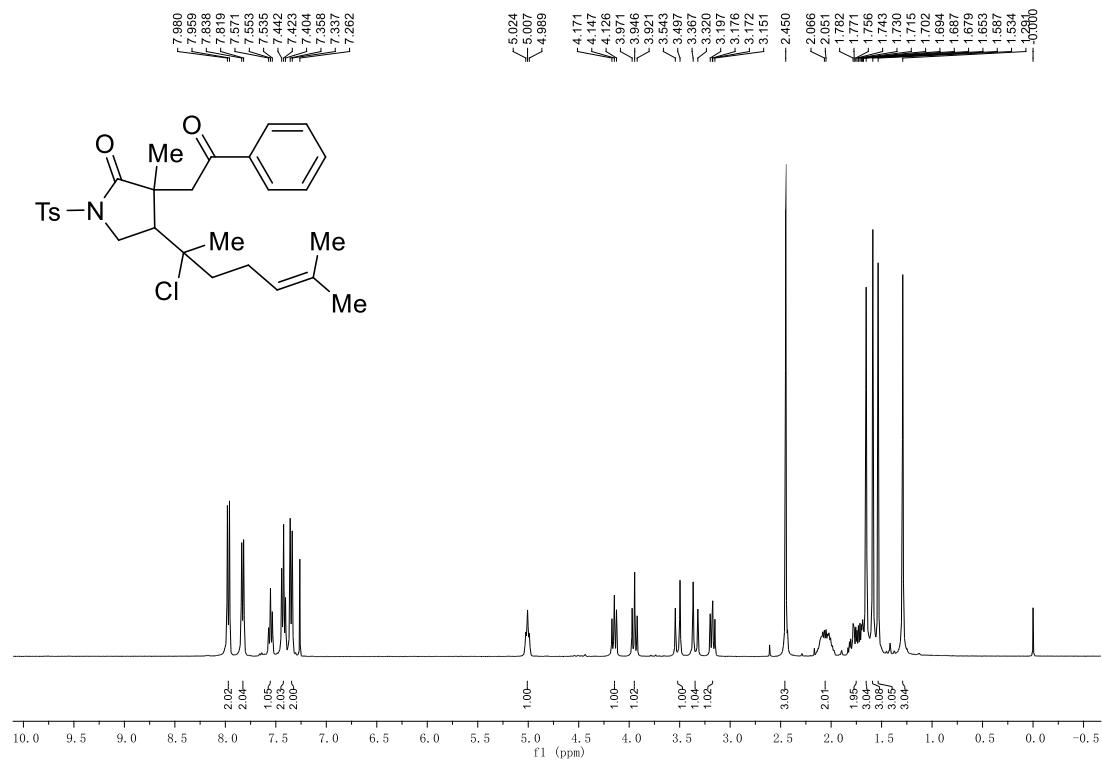
$^1\text{H}$  NMR of **3ia'** (*Minor diastereomer*) in  $\text{CDCl}_3$



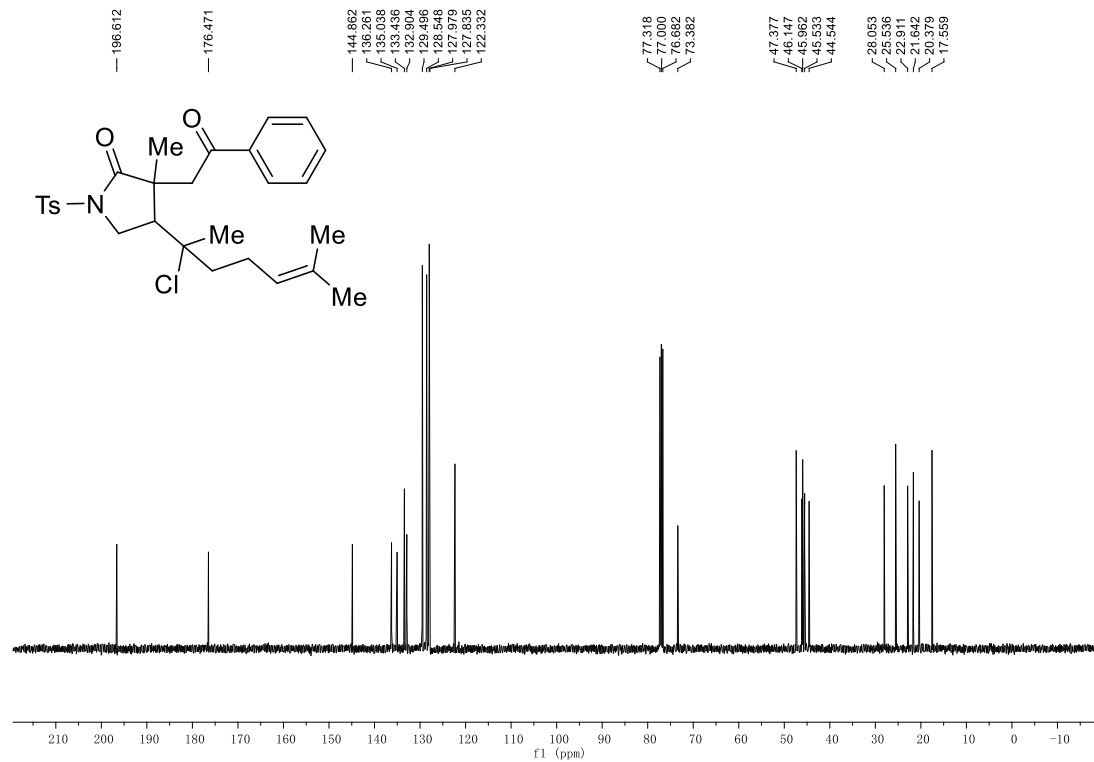
$^{13}\text{C}$  NMR of **3ia'** (*Minor diastereomer*) in  $\text{CDCl}_3$



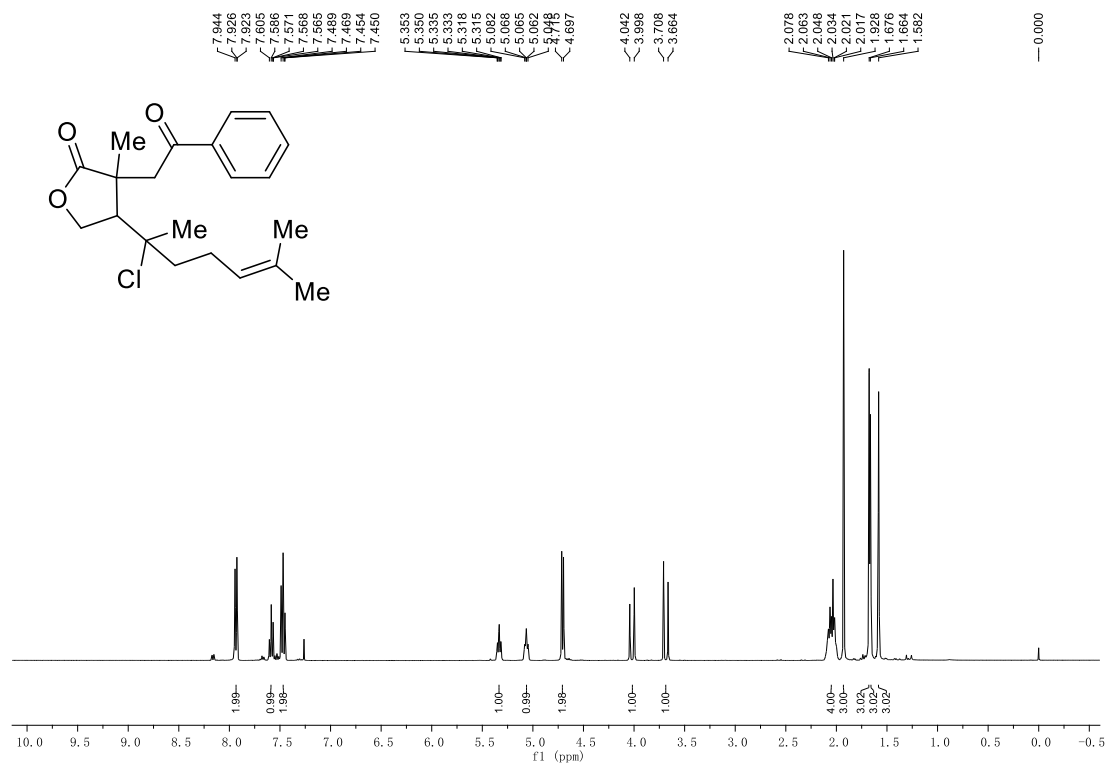
$^1\text{H}$  NMR of **3ja** in  $\text{CDCl}_3$



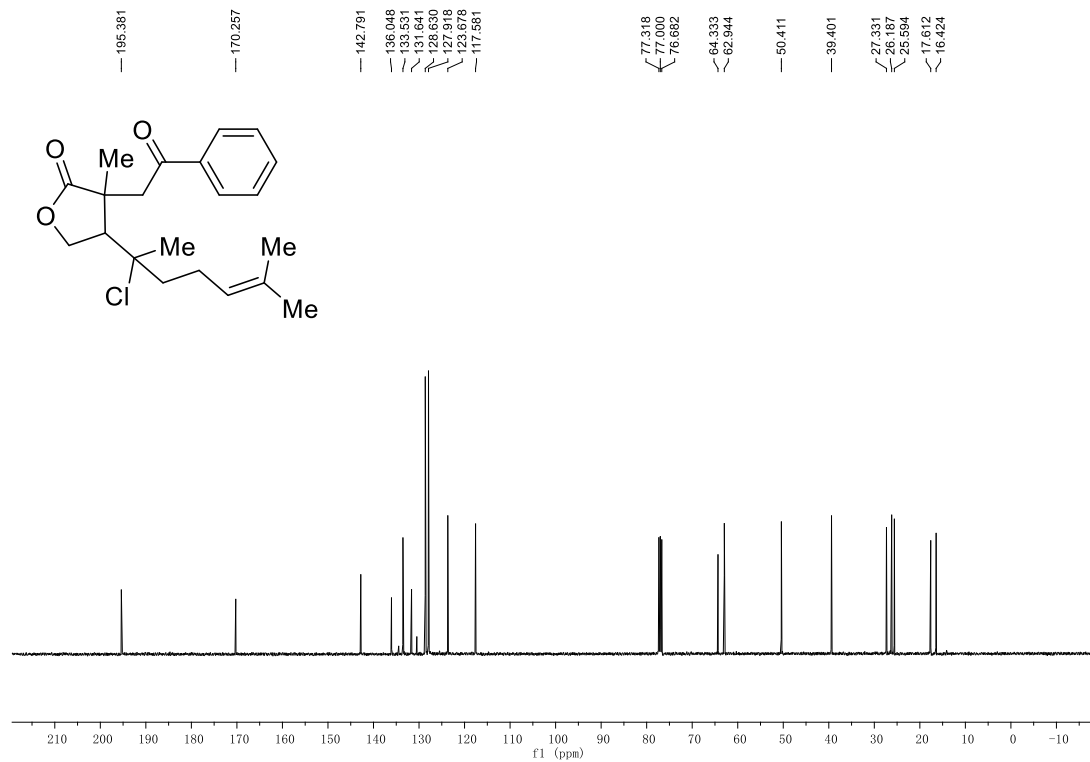
$^{13}\text{C}$  NMR of **3ja** in  $\text{CDCl}_3$



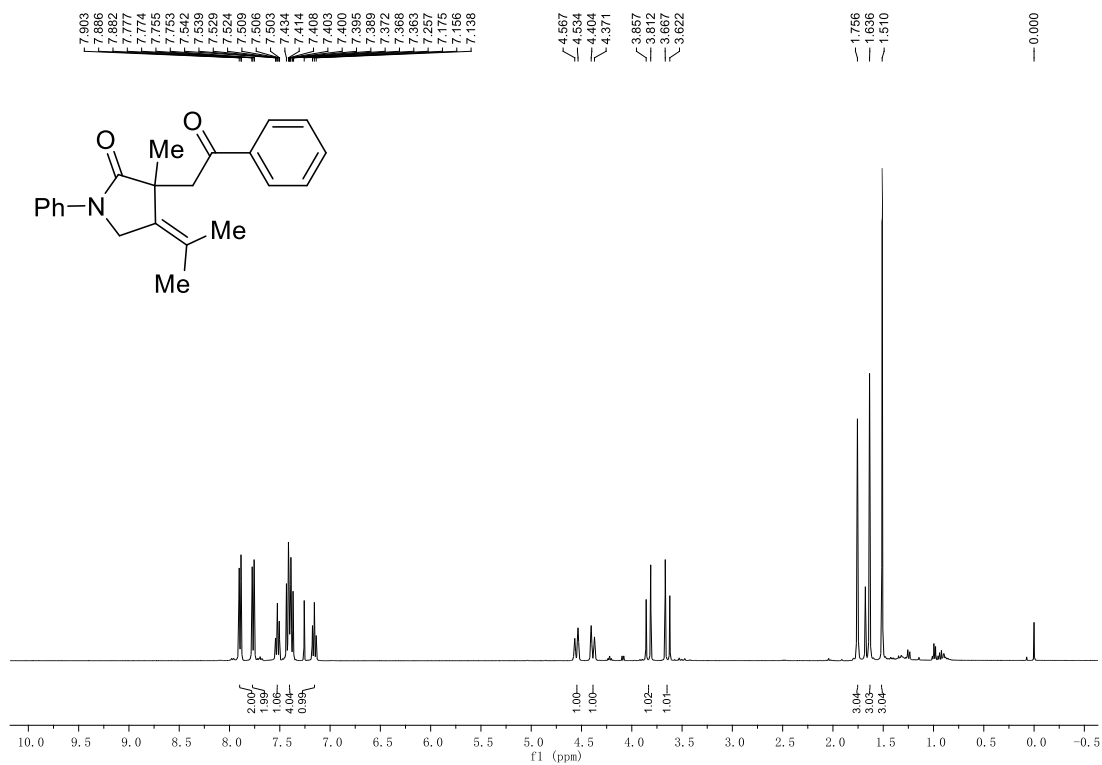
<sup>1</sup>H NMR of **3ka** in CDCl<sub>3</sub>



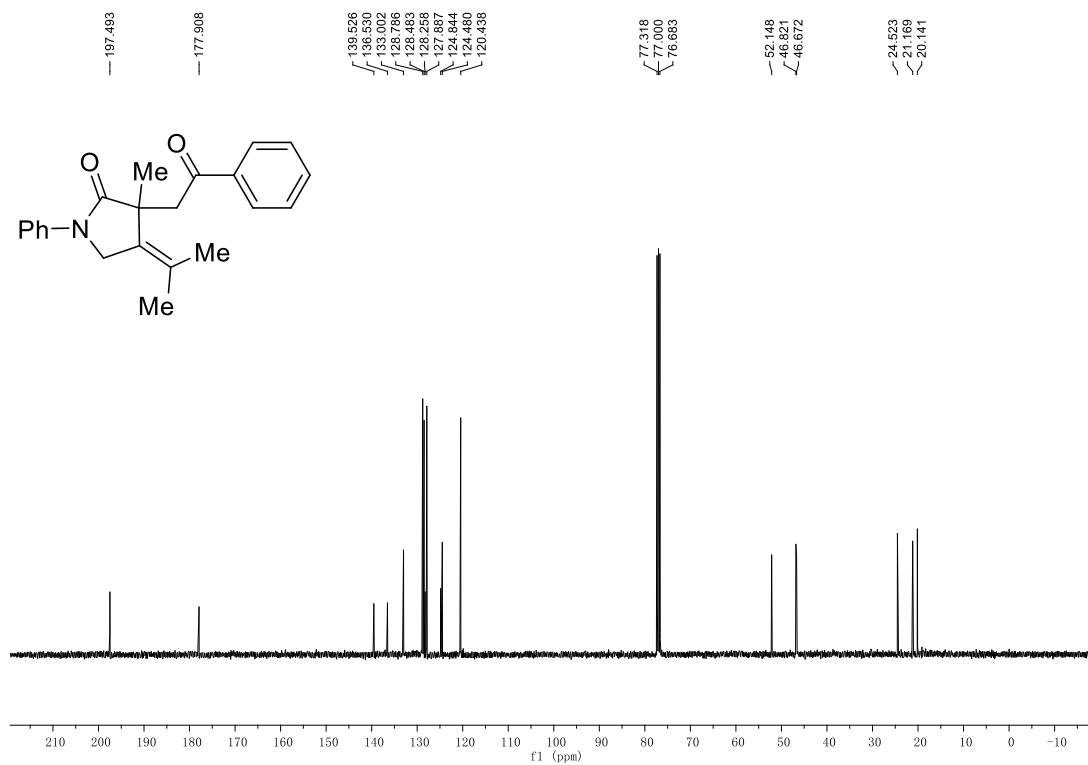
<sup>13</sup>C NMR of **3ka** in CDCl<sub>3</sub>



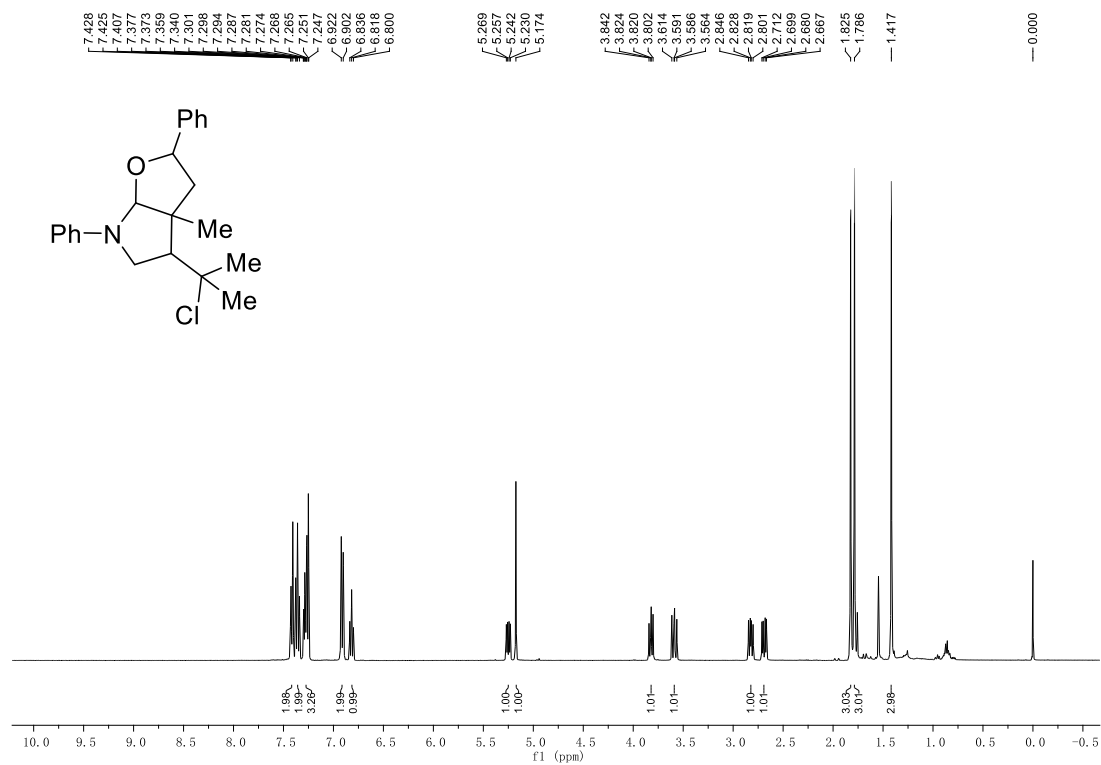
<sup>1</sup>H NMR of **4aa** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **4aa** in CDCl<sub>3</sub>



<sup>1</sup>H NMR of **5aa** in CDCl<sub>3</sub>



<sup>13</sup>C NMR of **5aa** in CDCl<sub>3</sub>

