

# **Palladium-catalyzed decarboxylative [4+2] cycloaddition of $\delta$ -vinylvalerolactones for the synthesis of spirocyclohexane compounds**

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## **Supporting Information**

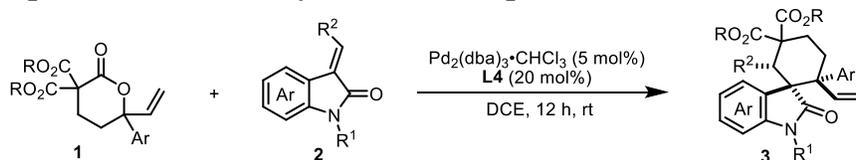
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## 1. General information

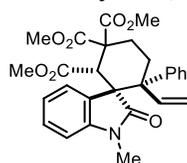
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  and  $\text{DMSO-}d_6$ .  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ( $\text{CDCl}_3$  at 7.26 ppm,  $\text{DMSO-}d_6$  at 2.50 ppm,  $\text{Acetone-}d_6$  at 2.05 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ( $\text{CDCl}_3$  at 77.20 ppm,  $\text{DMSO-}d_6$  at 39.51 ppm,  $\text{Acetone-}d_6$  at 29.84 ppm and 206.26 ppm). Data for  $^{19}\text{F}$  NMR were reported in terms of chemical shift ( $\delta$ , ppm). The enantiomeric excesses were determined by chiral HPLC analysis. HPLC analysis was performed on Shimadzu SCL-10AVP HPLC systems consisting of the followings: pump, LC-10AD; detector, SPD-10A measured at 254 nm. HRMS was recorded on Bruker Q TOF. Optical rotations were measured with a Perkin-Elmer-341 polarimeter. Melting points were recorded on a Büchi Melting Point B-545.

## 2. General procedures for the synthesis of compounds 3



Under argon atmosphere, an oven-dried Schlenk tube was added  $\text{Pd}_2(\text{dba})_3\cdot\text{CHCl}_3$  (0.005 mmol, 5.2 mg, 5 mol%), **L4** (0.02 mmol, 4.7 mg, 20 mol%) was added along with  $\delta$ -vinylvalerolactones **1**<sup>[1]</sup> (0.1 mmol) and 3-alkenyloxindoles **2**<sup>[2]</sup> (0.12 mmol) and DCE (1.0 mL). The reaction was stirred at room temperature for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give the corresponding cycloadducts **3**.

### Trimethyl 1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (**3a**)



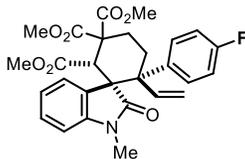
The product **3a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 95% yield; >20:1 dr; m.p. 194.3-195.1 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 7.5 Hz, 1H), 7.24 – 7.17 (m, 1H), 7.07 – 6.92 (m, 3H), 6.92 – 6.82 (m, 2H), 6.60 (d,  $J$  = 7.9 Hz, 2H), 6.37 (d,  $J$  = 7.8 Hz, 1H), 5.35 (d,  $J$  = 11.0 Hz, 1H), 4.79 (d,  $J$  = 17.3 Hz, 1H), 4.31 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.55 (td,  $J$  = 13.7, 3.3 Hz, 1H), 3.43 (s, 3H), 2.71 (dt,  $J$  = 13.8, 3.5 Hz, 1H), 2.42 (s, 3H), 2.32 (td,  $J$  = 13.9, 3.2 Hz, 1H), 1.68 (dt,  $J$  = 13.4, 3.5 Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 173.5, 170.3, 169.2, 145.4, 141.3, 140.8, 130.8, 128.6, 128.5, 126.7, 126.4, 122.3, 121.3, 118.6, 107.5, 57.2, 55.2, 53.4, 52.8, 52.2, 50.6, 48.7, 28.4, 28.1, 25.3;

HRMS (ESI-TOF) calcd. for  $\text{C}_{28}\text{H}_{30}\text{NO}_7$   $[\text{M} + \text{H}]^+$  492.2017; found: 492.2019.

**Trimethyl 2-(4-fluorophenyl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3b)**



The product **3b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 95% yield; >20:1 dr; m.p. 205.4-205.9 °C;

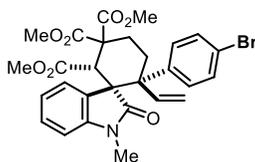
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.35 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.26 – 7.17 (m, 1H), 7.03 – 6.90 (m, 2H), 6.59 (d, *J* = 8.2 Hz, 4H), 6.41 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.35 (dd, *J* = 10.9, 0.9 Hz, 1H), 4.82 – 4.68 (m, 1H), 4.30 (s, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.51 (td, *J* = 13.6, 3.3 Hz, 1H), 3.43 (s, 3H), 2.70 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.50 (s, 3H), 2.29 (td, *J* = 13.9, 3.2 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.2, 173.5, 170.3, 169.2, 161.6 (d, *J* = 246.2 Hz), 145.3, 141.3, 136.6 (d, *J* = 3.3 Hz), 130.6, 130.5 (d, *J* = 7.8 Hz), 128.8, 122.4, 121.5, 118.7, 113.1 (d, *J* = 20.8 Hz), 107.6, 57.2, 55.1, 53.4, 52.9, 52.2, 50.3, 48.7, 29.0, 28.1, 25.4;

**<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)** δ -116.2;

**HRMS (ESI-TOF)** calcd. for C<sub>28</sub>H<sub>29</sub>FNO<sub>7</sub> [M + H]<sup>+</sup> 510.1923; found: 510.1925.

**Trimethyl 2-(4-bromophenyl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3c)**



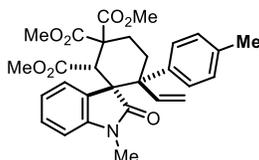
The product **3c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 249.7-250.4 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.10 – 6.97 (m, 3H), 6.93 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.45 (dd, *J* = 16.5, 7.9 Hz, 3H), 5.35 (d, *J* = 10.9 Hz, 1H), 4.74 (d, *J* = 17.3 Hz, 1H), 4.30 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.55 – 3.46 (m, 1H), 3.43 (s, 3H), 2.70 (dt, *J* = 14.0, 3.6 Hz, 1H), 2.50 (s, 3H), 2.29 (td, *J* = 13.9, 3.1 Hz, 1H), 1.63 (dt, *J* = 13.3, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.0, 173.5, 170.3, 169.2, 145.3, 141.0, 140.0, 130.6, 130.5, 129.4, 128.8, 122.4, 121.5, 121.0, 118.9, 107.8, 57.2, 55.0, 53.4, 52.9, 52.3, 50.5, 48.7, 28.7, 28.1, 25.4;

**HRMS (ESI-TOF)** calcd. for C<sub>28</sub>H<sub>29</sub><sup>79</sup>BrNO<sub>7</sub> [M + H]<sup>+</sup> 570.1122; found: 570.1124; calcd. for C<sub>28</sub>H<sub>29</sub><sup>81</sup>BrNO<sub>7</sub> [M + H]<sup>+</sup> 572.1106; found: 572.1108.

**Trimethyl 1'-methyl-2'-oxo-2-(p-tolyl)-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3d)**



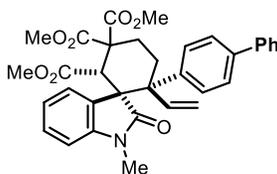
The product **3d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 98% yield; >20:1 dr; m.p. 213.4-214.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.35 (d, *J* = 7.4 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.03 – 6.89 (m, 2H), 6.72 (d, *J* = 8.0 Hz, 2H), 6.48 (d, *J* = 7.9 Hz, 2H), 6.39 (d, *J* = 7.7 Hz, 1H), 5.33 (d, *J* = 10.9 Hz, 1H), 4.79 (d, *J* = 17.3 Hz, 1H), 4.29 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.52 (td, *J* = 13.7, 3.3 Hz, 1H), 3.43 (s, 3H), 2.70 (dt, *J* = 13.9, 3.6 Hz, 1H), 2.45 (s, 3H), 2.31 (td, *J* = 13.9, 3.2 Hz, 1H), 2.17 (s, 3H), 1.66 (dt, *J* = 13.5, 3.6 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.3, 173.6, 170.4, 169.3, 145.4, 141.4, 137.8, 136.2, 130.9, 128.5, 127.1, 122.4, 121.3, 118.4, 107.5, 57.3, 55.3, 53.4, 52.9, 52.2, 50.3, 48.7, 28.5, 28.1, 25.4, 20.9;

**HRMS (ESI-TOF)** calcd. for C<sub>29</sub>H<sub>32</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 506.2174; found: 506.2175.

**Trimethyl 2-([1,1'-biphenyl]-4-yl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3e)**



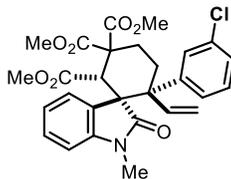
The product **3e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 209.9-210.4 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.51 – 7.44 (m, 2H), 7.38 (dd, *J* = 8.4, 6.9 Hz, 3H), 7.33 – 7.16 (m, 4H), 7.06 – 6.94 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.38 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.39 (dd, *J* = 10.9, 1.0 Hz, 1H), 4.86 (dd, *J* = 17.3, 1.0 Hz, 1H), 4.34 (s, 1H), 3.87 (s, 3H), 3.83 (s, 3H), 3.59 (td, *J* = 13.6, 13.0, 2.7 Hz, 1H), 3.45 (s, 3H), 2.74 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.45 (s, 3H), 2.35 (td, *J* = 13.9, 3.1 Hz, 1H), 1.76 – 1.71 (m, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.2, 173.6, 170.4, 169.3, 145.4, 141.2, 140.7, 140.0, 139.3, 130.8, 129.1, 128.8, 128.7, 127.3, 126.9, 124.9, 122.4, 121.4, 118.7, 107.6, 57.3, 55.3, 53.4, 52.9, 52.2, 50.6, 48.7, 28.5, 28.1, 25.4;

**HRMS (ESI-TOF)** calcd. for C<sub>34</sub>H<sub>34</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 568.2330; found: 568.2333.

**Trimethyl 2-(3-chlorophenyl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3f)**



The product **3f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 74% yield; >20:1 dr; m.p. 188.8-189.2 °C;

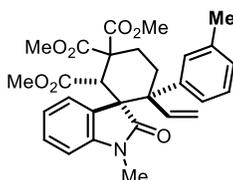
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.36 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.29 – 7.25 (m, 1H), 7.07 – 6.99 (m, 2H), 6.98 – 6.88 (m, 2H), 6.69 (d, *J* = 6.9 Hz, 1H), 6.46 (d, *J* = 7.8 Hz, 1H), 6.35 (s, 1H), 5.38 (d, *J* =

11.0 Hz, 1H), 4.77 (d,  $J = 17.5$  Hz, 1H), 4.32 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.54 – 3.46 (m, 1H), 3.45 (s, 3H), 2.72 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.50 (s, 3H), 2.30 (td,  $J = 13.9, 3.2$  Hz, 1H), 1.70 – 1.65 (m, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.0, 173.5, 170.3, 169.2, 145.3, 143.1, 140.9, 132.3, 130.4, 129.3, 129.0, 127.7, 126.9, 126.7, 122.3, 121.6, 119.2, 107.7, 57.2, 55.1, 53.5, 52.9, 52.3, 50.8, 48.7, 28.6, 28.1, 25.5;

HRMS (ESI-TOF) calcd. for  $\text{C}_{28}\text{H}_{29}^{35}\text{ClNO}_7$  [ $\text{M} + \text{H}$ ] $^+$  526.1628; found: 526.1630; calcd. for  $\text{C}_{28}\text{H}_{29}^{37}\text{ClNO}_7$  [ $\text{M} + \text{H}$ ] $^+$  528.1612; found: 528.1615.

**Trimethyl 1'-methyl-2'-oxo-2-(m-tolyl)-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3g)**



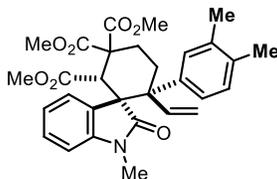
The product **3g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 179.9-180.6 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (dd,  $J = 7.5, 1.2$  Hz, 1H), 7.26 – 7.18 (m, 1H), 7.05 – 6.81 (m, 4H), 6.58 (d,  $J = 7.3$  Hz, 1H), 6.42 – 6.35 (m, 1H), 6.16 (s, 1H), 5.34 (d,  $J = 10.8$  Hz, 1H), 4.79 (d,  $J = 17.4$  Hz, 1H), 4.31 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.52 (td,  $J = 13.7, 3.3$  Hz, 1H), 3.43 (s, 3H), 2.71 (dt,  $J = 13.8, 3.5$  Hz, 1H), 2.43 (s, 3H), 2.32 (td,  $J = 13.9, 3.2$  Hz, 1H), 1.99 (s, 3H), 1.68 (dt,  $J = 13.4, 3.5$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 173.6, 170.4, 169.3, 145.5, 141.3, 140.7, 135.5, 131.0, 129.8, 128.5, 127.3, 126.3, 125.3, 122.3, 121.2, 118.6, 107.3, 57.2, 55.3, 53.4, 52.8, 52.2, 50.6, 48.6, 28.3, 28.1, 25.3, 21.4;

HRMS (ESI-TOF) calcd. for  $\text{C}_{29}\text{H}_{32}\text{NO}_7$  [ $\text{M} + \text{H}$ ] $^+$  506.2174; found: 506.2175.

**Trimethyl 2-(3,4-dimethylphenyl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3h)**



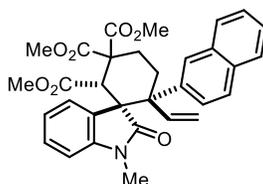
The product **3h** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 233.4-233.7 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (dd,  $J = 7.4, 1.1$  Hz, 1H), 7.25 – 7.19 (m, 1H), 7.04 – 6.98 (m, 1H), 6.92 (dd,  $J = 17.4, 11.0$  Hz, 1H), 6.72 (d,  $J = 8.0$  Hz, 1H), 6.48 (d,  $J = 8.6$  Hz, 1H), 6.38 (d,  $J = 7.7$  Hz, 1H), 6.12 (s, 1H), 5.33 (d,  $J = 10.8$  Hz, 1H), 4.80 (d,  $J = 17.3$  Hz, 1H), 4.30 (s, 1H), 3.84 (s,

3H), 3.81 (s, 3H), 3.50 (td,  $J = 13.7, 3.3$  Hz, 1H), 3.43 (s, 3H), 2.70 (dt,  $J = 13.8, 3.5$  Hz, 1H), 2.42 (s, 3H), 2.31 (td,  $J = 13.9, 3.2$  Hz, 1H), 2.08 (s, 3H), 1.90 (s, 3H), 1.67 (dt,  $J = 13.4, 3.5$  Hz, 1H);  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 173.6, 170.5, 169.3, 145.6, 141.4, 138.2, 134.7, 134.1, 131.1, 130.1, 128.4, 127.7, 125.7, 122.3, 121.2, 118.4, 107.3, 57.3, 55.3, 53.4, 52.8, 52.2, 50.3, 48.6, 28.2, 28.1, 25.3, 19.7, 19.2;

HRMS (ESI-TOF) calcd. for  $\text{C}_{30}\text{H}_{34}\text{NO}_7$   $[\text{M} + \text{H}]^+$  520.2330; found: 520.2331.

**Trimethyl 1'-methyl-2-(naphthalen-2-yl)-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3i)**



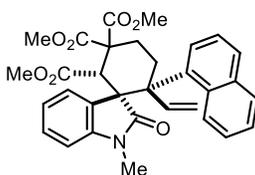
The product **3i** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);  
White solid; 94% yield; >20:1 dr; m.p. 230.1-230.6 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.63 (dd,  $J = 7.0, 2.1$  Hz, 1H), 7.60 – 7.52 (m, 1H), 7.44 (dd,  $J = 7.5, 1.2$  Hz, 1H), 7.39 – 7.20 (m, 5H), 7.11 – 6.99 (m, 2H), 6.50 (d,  $J = 5.7$  Hz, 1H), 6.27 (d,  $J = 8.0$  Hz, 1H), 5.38 (dd,  $J = 10.9, 0.9$  Hz, 1H), 4.76 (d,  $J = 17.4$  Hz, 1H), 4.39 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.71 (td,  $J = 13.6, 3.2$  Hz, 1H), 3.45 (s, 3H), 2.79 (dt,  $J = 13.8, 3.5$  Hz, 1H), 2.38 (td,  $J = 13.9, 3.2$  Hz, 1H), 2.20 (s, 3H), 1.81 (dt,  $J = 13.2, 3.5$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 173.6, 170.4, 169.3, 145.4, 141.4, 138.5, 132.2, 132.1, 130.9, 128.6, 128.4, 127.7, 127.1, 126.9, 125.8, 125.4, 125.1, 122.3, 121.4, 118.9, 107.6, 57.3, 55.2, 53.4, 52.9, 52.2, 50.8, 48.7, 28.9, 28.2, 25.2;

HRMS (ESI-TOF) calcd. for  $\text{C}_{32}\text{H}_{32}\text{NO}_7$   $[\text{M} + \text{H}]^+$  542.2174; found: 542.2174.

**Trimethyl 1'-methyl-2-(naphthalen-1-yl)-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3j)**



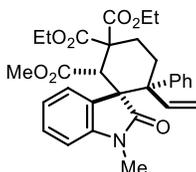
The product **3j** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);  
White solid; 54% yield; >20:1 dr; m.p. 224.8-225.4 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 – 7.61 (m, 1H), 7.56 (d,  $J = 7.6$  Hz, 1H), 7.44 (dd,  $J = 7.5, 1.2$  Hz, 1H), 7.38 – 7.21 (m, 5H), 7.10 – 7.00 (m, 2H), 6.50 (d,  $J = 7.3$  Hz, 1H), 6.27 (d,  $J = 7.7$  Hz, 1H), 5.38 (d,  $J = 11.5$  Hz, 1H), 4.77 (d,  $J = 17.3$  Hz, 1H), 4.39 (s, 1H), 3.87 (s, 3H), 3.84 (s, 3H), 3.71 (td,  $J = 13.2, 12.7, 2.8$  Hz, 1H), 3.45 (s, 3H), 2.79 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.37 (td,  $J = 13.9, 3.2$  Hz, 1H), 2.20 (s, 3H), 1.81 (dt,  $J = 13.3, 3.5$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.2, 173.6, 170.4, 169.3, 145.5, 141.4, 138.5, 132.2, 132.2, 130.9, 128.7, 128.5, 127.7, 127.2, 126.9, 125.9, 125.4, 125.2, 122.4, 121.5, 118.9, 107.6, 57.3, 55.3, 53.4, 52.9, 52.2, 50.9, 48.8, 28.9, 28.3, 25.2;

HRMS (ESI-TOF) calcd. for  $\text{C}_{32}\text{H}_{32}\text{NO}_7$   $[\text{M} + \text{H}]^+$  542.2174; found: 542.2177.

**5,5-Diethyl 6-methyl -1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3k)**



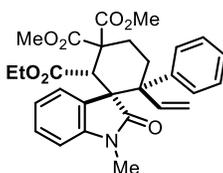
The product **3k** was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1); White solid; 82% yield; >20:1 dr; m.p. 160.5-161.4 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.36 (d,  $J$  = 7.4 Hz, 1H), 7.24 – 7.18 (m, 1H), 7.06 – 6.86 (m, 5H), 6.61 (d,  $J$  = 7.8 Hz, 2H), 6.37 (d,  $J$  = 7.7 Hz, 1H), 5.34 (d,  $J$  = 11.0 Hz, 1H), 4.78 (d,  $J$  = 17.3 Hz, 1H), 4.42 – 4.16 (m, 5H), 3.55 (td,  $J$  = 13.7, 3.3 Hz, 1H), 3.42 (s, 3H), 2.73 (dt,  $J$  = 13.8, 3.5 Hz, 1H), 2.43 (s, 3H), 2.30 (td,  $J$  = 13.9, 3.2 Hz, 1H), 1.67 (dt,  $J$  = 13.4, 3.5 Hz, 1H), 1.30 (t,  $J$  = 7.1 Hz, 3H), 1.24 (t,  $J$  = 7.2 Hz, 3H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 173.2, 170.3, 168.7, 145.4, 141.4, 140.9, 131.0, 128.7, 128.5, 126.7, 126.4, 122.4, 121.3, 118.5, 107.4, 62.2, 61.5, 57.0, 55.2, 51.8, 50.7, 48.6, 28.5, 28.2, 25.3, 14.2, 14.0.

HRMS (ESI-TOF) calcd. for  $\text{C}_{30}\text{H}_{34}\text{NO}_7$   $[\text{M} + \text{H}]^+$  520.2330; found: 520.2317.

**6-Ethyl 5,5-dimethyl 1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3l)**



The product **3k** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 88% yield; >20:1 dr; m.p. 187.0-187.7 °C;

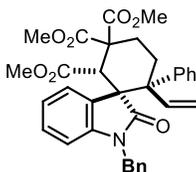
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.37 (d,  $J$  = 7.4 Hz, 1H), 7.23 – 7.18 (m, 1H), 7.04 – 6.85 (m, 5H), 6.60 (d,  $J$  = 7.8 Hz, 2H), 6.35 (d,  $J$  = 7.7 Hz, 1H), 5.34 (d,  $J$  = 11.0 Hz, 1H), 4.78 (d,  $J$  = 17.4 Hz, 1H), 4.28 (s, 1H), 3.89 (q,  $J$  = 7.2 Hz, 2H), 3.81 (d,  $J$  = 8.0 Hz, 6H), 3.54 (td,  $J$  = 13.7, 3.3 Hz, 1H), 2.70 (dt,  $J$  = 13.8, 3.5 Hz, 1H), 2.41 (s, 3H), 2.32 (td,  $J$  = 13.9, 3.2 Hz, 1H), 1.68 (dt,  $J$  = 13.4, 3.5 Hz, 1H), 0.96 (t,  $J$  = 7.1 Hz, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.1, 173.4, 169.8, 169.2, 145.3, 141.3, 140.9, 130.9, 128.6, 128.5, 126.7, 126.3, 122.4, 121.3, 118.5, 107.4, 61.0, 57.2, 55.2, 53.2, 52.6, 50.6, 48.7, 28.4, 28.1, 25.2, 13.6;

HRMS (ESI-TOF) calcd. for  $\text{C}_{29}\text{H}_{32}\text{NO}_7$   $[\text{M} + \text{H}]^+$  506.2174; found: 506.2178.

**Trimethyl 1'-benzyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate**

**(3m)**



The product **3l** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

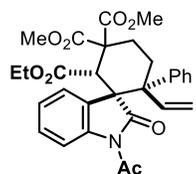
White solid; 91% yield; >20:1 dr; m.p. 220.5-221.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.41 (dd, *J* = 7.5, 1.2 Hz, 1H), 7.20 – 6.92 (m, 9H), 6.81 (dd, *J* = 6.8, 2.9 Hz, 2H), 6.69 (d, *J* = 7.8 Hz, 2H), 6.24 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.37 (d, *J* = 11.8 Hz, 1H), 4.77 (d, *J* = 17.2 Hz, 1H), 4.38 (d, *J* = 16.0 Hz, 1H), 4.37 (s, 1H), 3.99 (d, *J* = 16.2 Hz, 1H), 3.83 (s, 3H), 3.81 (s, 3H), 3.62 (td, *J* = 13.7, 3.4 Hz, 1H), 3.37 (s, 3H), 2.77 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.37 (td, *J* = 13.9, 3.2 Hz, 1H), 1.74 (dt, *J* = 13.5, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.6, 173.5, 170.2, 169.2, 145.0, 141.5, 141.2, 136.1, 131.0, 129.0, 128.5, 128.4, 127.1, 127.0, 126.9, 126.8, 122.6, 121.6, 118.7, 108.8, 57.4, 55.0, 53.4, 52.7, 52.1, 50.6, 49.4, 43.9, 28.8, 28.1;

**HRMS (ESI-TOF)** calcd. for C<sub>34</sub>H<sub>34</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 568.2330; found: 568.2329.

**6-Ethyl 5,5-dimethyl 1'-acetyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3n)**



The product **3m** was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1);

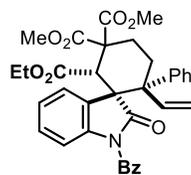
White solid; 83% yield; >20:1 dr; m.p. 212.4-212.9 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.90 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.43 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.32 – 7.26 (m, 1H), 7.21 – 7.16 (m, 1H), 7.10 – 7.05 (m, 1H), 7.00 – 6.86 (m, 3H), 6.60 (d, *J* = 7.5 Hz, 2H), 5.35 (d, *J* = 10.6 Hz, 1H), 4.78 (d, *J* = 17.3 Hz, 1H), 4.33 (s, 1H), 3.94 – 3.76 (m, 2H), 3.82 (s, 3H), 3.81 (s, 3H), 3.37 (td, *J* = 13.8, 3.3 Hz, 1H), 2.75 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.33 (td, *J* = 13.9, 3.1 Hz, 1H), 2.13 (s, 3H), 1.77 (dt, *J* = 13.5, 3.4 Hz, 1H), 0.98 (t, *J* = 7.1 Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 177.7, 173.0, 169.9, 169.7, 169.2, 141.9, 140.5, 139.5, 129.9, 129.0, 128.6, 127.7, 127.0, 124.2, 122.3, 119.0, 116.1, 61.4, 57.3, 55.3, 53.4, 52.7, 51.2, 49.7, 29.0, 28.0, 26.0, 13.6;

**HRMS (ESI-TOF)** calcd. for C<sub>30</sub>H<sub>32</sub>NO<sub>8</sub> [M + H]<sup>+</sup> 534.2123; found: 534.2124.

**6-Ethyl 5,5-dimethyl 1'-benzoyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3o)**



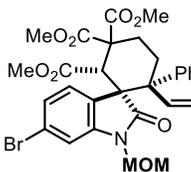
The product **3n** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 118.7-119.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 – 7.42 (m, 3H), 7.39 – 7.27 (m, 5H), 7.23 – 7.14 (m, 2H), 7.07 – 6.93 (m, 3H), 6.60 (d, *J* = 7.5 Hz, 2H), 5.36 (d, *J* = 10.9 Hz, 1H), 4.76 (d, *J* = 17.3 Hz, 1H), 4.36 (s, 1H), 4.01 (dq, *J* = 11.0, 7.1 Hz, 1H), 3.89 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.82 (s, 3H), 3.60 (s, 3H), 3.30 (td, *J* = 13.8, 3.3 Hz, 1H), 2.70 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.32 (td, *J* = 13.9, 3.1 Hz, 1H), 1.73 – 1.67 (m, 1H), 1.05 (t, *J* = 7.1 Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 175.5, 173.1, 169.9, 168.9, 168.5, 142.2, 140.8, 139.5, 134.6, 132.2, 130.4, 129.5, 129.1, 128.9, 127.6, 127.0, 123.9, 122.7, 118.8, 114.5, 61.5, 57.2, 55.2, 53.3, 52.6, 51.3, 50.1, 29.0, 28.1, 13.7;

**HRMS (ESI-TOF)** calcd. for C<sub>35</sub>H<sub>34</sub>NO<sub>8</sub> [M + H]<sup>+</sup> 596.2279; found: 596.2282.

**Trimethyl 6'-bromo-1'-(methoxymethyl)-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3p)**



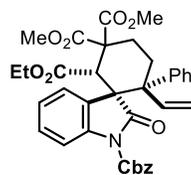
The product **3o** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 163.8-164.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.27 (d, *J* = 8.0 Hz, 1H), 7.20 (dd, *J* = 8.0, 1.8 Hz, 1H), 7.09 – 7.04 (m, 1H), 7.02 – 6.95 (m, 2H), 6.90 (dd, *J* = 17.3, 10.9 Hz, 1H), 6.83 (d, *J* = 1.8 Hz, 1H), 6.80 – 6.54 (m, 2H), 5.37 (d, *J* = 11.0 Hz, 1H), 4.78 (d, *J* = 17.2 Hz, 1H), 4.46 (d, *J* = 11.1 Hz, 1H), 4.30 (s, 1H), 4.07 (d, *J* = 11.2 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 3.55 – 3.46 (m, 1H), 3.45 (s, 3H), 2.97 (s, 3H), 2.74 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.31 (td, *J* = 13.9, 3.2 Hz, 1H), 1.71 (dt, *J* = 13.4, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.8, 173.2, 170.0, 169.0, 145.5, 140.7, 140.3, 129.6, 128.8, 127.2, 126.8, 124.9, 123.8, 122.5, 119.2, 112.6, 71.4, 57.2, 56.1, 55.3, 53.5, 52.6, 52.3, 50.6, 49.2, 28.8, 28.0;

**HRMS (ESI-TOF)** calcd. for C<sub>29</sub>H<sub>31</sub><sup>79</sup>BrNO<sub>8</sub> [M + H]<sup>+</sup> 600.1228; found: 600.1224; calcd. for C<sub>29</sub>H<sub>31</sub><sup>81</sup>BrNO<sub>8</sub> [M + H]<sup>+</sup> 602.1212; found: 602.1209.

**1'-Benzyl 6-ethyl 5,5-dimethyl 2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3q)**



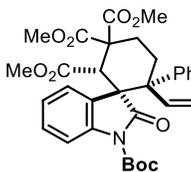
The product **3p** was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1); White solid; 99% yield; >20:1 dr; m.p. 110.2-110.9 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.54 (d, *J* = 8.1 Hz, 1H), 7.47 – 7.30 (m, 6H), 7.29 – 7.24 (m, 1H), 7.19 – 7.12 (m, 1H), 6.98 – 6.88 (m, 2H), 6.87 – 6.76 (m, 2H), 6.75 – 6.34 (m, 2H), 5.36 (d, *J* = 11.0 Hz, 1H), 5.21 – 5.01 (m, 2H), 4.81 (d, *J* = 17.3 Hz, 1H), 4.32 (s, 1H), 4.01 – 3.75 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.41 (td, *J* = 13.7, 3.2 Hz, 1H), 2.75 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.33 (td, *J* = 13.9, 3.1 Hz, 1H), 1.73 (dd, *J* = 8.4, 4.8 Hz, 1H), 0.96 (t, *J* = 7.1 Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.7, 173.2, 169.8, 169.0, 149.8, 141.2, 140.5, 139.5, 135.4, 129.8, 128.9, 128.7, 128.4, 128.2, 128.0, 127.1, 126.8, 123.8, 122.4, 119.0, 114.8, 67.6, 61.4, 57.3, 55.4, 53.4, 52.8, 51.2, 49.5, 28.8, 28.0, 13.5;

**HRMS (ESI-TOF)** calcd. for C<sub>36</sub>H<sub>36</sub>NO<sub>9</sub> [M + H]<sup>+</sup> 626.2385; found: 626.2388.

**1'-(Tert-butyl) 5,5,6-trimethyl 2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3r)**



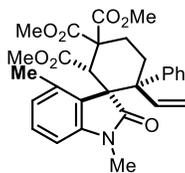
The product **3q** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 91% yield; >20:1 dr; m.p. 214.4-215.1 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.44 – 7.37 (m, 2H), 7.28 – 7.23 (m, 1H), 7.16 – 7.11 (m, 1H), 7.08 – 7.03 (m, 1H), 7.00 – 6.87 (m, 3H), 6.63 (s, 2H), 5.36 (d, *J* = 11.1 Hz, 1H), 4.80 (d, *J* = 17.2 Hz, 1H), 4.32 (s, 1H), 3.86 (s, 3H), 3.83 (s, 3H), 3.46 (s, 3H), 3.45 – 3.36 (m, 1H), 2.74 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.32 (td, *J* = 13.9, 3.2 Hz, 1H), 1.72 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.40 (s, 9H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.9, 173.4, 170.4, 169.0, 147.8, 141.5, 140.7, 139.9, 129.5, 128.8, 128.7, 127.1, 126.8, 123.4, 122.3, 118.9, 114.7, 83.1, 57.3, 55.3, 53.5, 53.1, 52.4, 51.1, 49.4, 28.7, 28.0, 28.0;

**HRMS (ESI-TOF)** calcd. for C<sub>32</sub>H<sub>35</sub>NNaO<sub>9</sub> [M + Na]<sup>+</sup> 600.2205; found: 600.2227.

**Trimethyl 1',4'-dimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3s)**



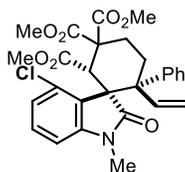
The product **3r** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 44% yield; >20:1 dr; m.p. 166.5-167.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.15 – 7.07 (m, 1H), 7.06 – 7.00 (m, 1H), 6.99 – 6.90 (m, 2H), 6.86 (dd, *J* = 17.6, 11.1 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.76 – 6.51 (m, 2H), 6.20 (d, *J* = 7.7 Hz, 1H), 5.32 (d, *J* = 11.1 Hz, 1H), 4.90 (d, *J* = 17.6 Hz, 1H), 4.80 (s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.54 (td, *J* = 14.0, 3.5 Hz, 1H), 3.48 (s, 3H), 2.74 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.61 (s, 3H), 2.40 (td, *J* = 14.0, 3.2 Hz, 1H), 2.34 (s, 3H), 1.74 (dt, *J* = 13.8, 3.4 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.0, 173.9, 170.8, 169.4, 146.1, 141.6, 140.8, 133.6, 128.2, 127.9, 127.8, 126.8, 126.5, 126.0, 116.7, 105.9, 58.7, 57.4, 53.4, 52.8, 52.3, 51.0, 47.2, 28.1, 25.9, 25.2, 21.6;

**HRMS (ESI-TOF)** calcd. for C<sub>29</sub>H<sub>32</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 506.2174; found: 506.2174.

**Trimethyl 4'-chloro-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3t)**



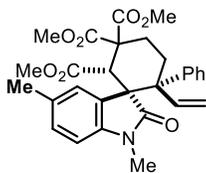
The product **3s** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 54% yield; >20:1 dr; m.p. 198.5-199.3 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.37 (dd, *J* = 17.3, 11.0 Hz, 1H), 7.16 – 7.09 (m, 1H), 7.08 – 7.02 (m, 1H), 7.01 – 6.90 (m, 3H), 6.72 (s, 2H), 6.23 (dd, *J* = 7.7, 1.0 Hz, 1H), 5.37 (s, 1H), 5.34 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 17.3 Hz, 1H), 3.85 (s, 3H), 3.84 (s, 3H), 3.53 (s, 3H), 3.48 (dd, *J* = 13.8, 3.3 Hz, 1H), 2.72 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.37 (td, *J* = 13.9, 3.2 Hz, 1H), 2.35 (s, 3H), 1.68 (t, *J* = 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 175.4, 173.7, 171.2, 169.5, 147.5, 142.4, 140.7, 130.0, 129.5, 128.5, 127.0, 127.0, 126.5, 124.3, 117.5, 106.5, 59.1, 57.2, 53.5, 52.9, 52.8, 52.5, 46.3, 28.0, 25.5;

**HRMS (ESI-TOF)** calcd. for C<sub>28</sub>H<sub>29</sub><sup>35</sup>ClNO<sub>7</sub> [M + H]<sup>+</sup> 526.1628; found: 526.1629; calcd. for C<sub>28</sub>H<sub>29</sub><sup>37</sup>ClNO<sub>7</sub> [M + H]<sup>+</sup> 528.1612; found: 528.1614.

**Trimethyl 1',5'-dimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3u)**



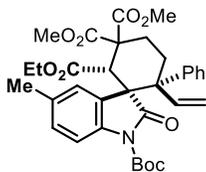
The product **3t** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 204.9-205.5°C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.17 (d, *J* = 1.7 Hz, 1H), 7.07 – 6.87 (m, 5H), 6.61 (d, *J* = 7.8 Hz, 2H), 6.26 (d, *J* = 7.8 Hz, 1H), 5.35 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 17.3 Hz, 1H), 4.28 (s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.55 (td, *J* = 13.7, 3.3 Hz, 1H), 3.45 (s, 3H), 2.70 (dt, *J* = 13.8, 3.5 Hz, 1H), 2.40 (s, 3H), 2.37 (s, 3H), 2.36 – 2.26 (m, 1H), 1.71 – 1.66 (m, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 176.1, 173.7, 170.5, 169.3, 143.1, 141.5, 141.0, 130.8, 130.6, 128.9, 128.7, 126.7, 126.4, 123.4, 118.5, 107.2, 57.3, 55.3, 53.4, 52.9, 52.3, 50.6, 48.8, 28.4, 28.2, 25.4, 21.5;

**HRMS (ESI-TOF)** calcd. for C<sub>29</sub>H<sub>32</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 506.2174; found: 506.2176.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 5'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3v)**



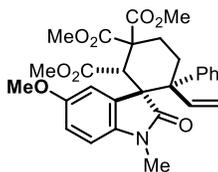
The product **3u** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 97% yield; >20:1 dr; m.p. 187.3-188.1 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.28 (d, *J* = 8.1 Hz, 1H), 7.19 (s, 1H), 7.05 (d, *J* = 7.7 Hz, 2H), 7.00 – 6.88 (m, 3H), 6.82 – 6.40 (m, 2H), 5.36 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 17.3 Hz, 1H), 4.26 (s, 1H), 3.99 – 3.79 (m, 2H), 3.84 (s, 3H), 3.83 (s, 3H), 3.42 (td, *J* = 13.8, 3.2 Hz, 1H), 2.73 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.39 (s, 3H), 2.32 (td, *J* = 13.9, 3.1 Hz, 1H), 1.73 (dd, *J* = 13.6, 3.5 Hz, 1H), 1.39 (s, 9H), 0.99 (t, *J* = 7.2 Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.9, 173.5, 169.9, 169.0, 148.0, 140.9, 140.0, 139.2, 132.8, 129.5, 129.2, 128.8, 127.1, 126.8, 123.1, 118.6, 114.4, 82.8, 61.3, 57.3, 55.3, 53.3, 52.8, 51.1, 49.5, 28.6, 28.1, 28.0, 21.4, 13.5;

**HRMS (ESI-TOF)** calcd. for C<sub>34</sub>H<sub>40</sub>NO<sub>9</sub> [M + H]<sup>+</sup> 606.2698; found: 606.2690.

**Trimethyl 5'-methoxy-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3w)**



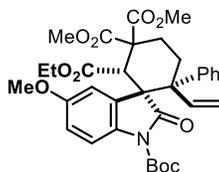
The product **3v** was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1); White solid; 96% yield; >20:1 dr; m.p. 167.3-167.8 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.05 – 6.88 (m, 5H), 6.74 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 2H), 6.27 (d, *J* = 8.4 Hz, 1H), 5.35 (d, *J* = 11.0 Hz, 1H), 4.79 (d, *J* = 17.3 Hz, 1H), 4.26 (s, 1H), 3.84 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.56 (td, *J* = 13.7, 3.3 Hz, 1H), 3.45 (s, 3H), 2.70 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.40 (s, 3H), 2.31 (td, *J* = 13.9, 3.2 Hz, 1H), 1.67 (dt, *J* = 13.3, 3.4 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 175.8, 173.6, 170.4, 169.2, 155.0, 141.1, 140.8, 139.2, 132.2, 128.8, 126.8, 126.4, 118.7, 111.9, 111.0, 107.5, 57.3, 55.9, 55.6, 53.4, 52.9, 52.3, 50.7, 48.8, 28.6, 28.1, 25.4;

**HRMS (ESI-TOF)** calcd. for C<sub>29</sub>H<sub>32</sub>NO<sub>8</sub> [M + H]<sup>+</sup> 522.2123; found: 522.2125.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 5'-methoxy-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3x)**



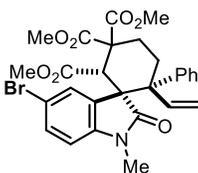
The product **3w** was purified by flash column chromatography (petroleum ether/ethyl acetate = 2:1); White solid; 83% yield; >20:1 dr; m.p. 106.7-107.4 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.32 (dd, *J* = 9.0, 1.3 Hz, 1H), 7.07 – 7.02 (m, 1H), 6.99 – 6.85 (m, 4H), 6.78 – 6.74 (m, 1H), 6.65 (d, *J* = 7.6 Hz, 2H), 5.35 (d, *J* = 11.0 Hz, 1H), 4.80 (d, *J* = 17.2 Hz, 1H), 4.24 (s, 1H), 3.97 – 3.79 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.81 (s, 3H), 3.41 (td, *J* = 13.8, 3.2 Hz, 1H), 2.72 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.30 (td, *J* = 13.9, 3.1 Hz, 1H), 1.70 (dt, *J* = 13.5, 3.5 Hz, 1H), 1.37 (s, 9H), 1.01 (t, *J* = 7.1 Hz, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 174.7, 173.4, 169.8, 169.0, 156.0, 148.0, 140.6, 139.8, 135.2, 131.0, 128.9, 127.1, 126.8, 118.9, 115.2, 112.2, 110.0, 82.8, 61.4, 57.3, 55.8, 55.5, 53.3, 52.9, 51.2, 49.5, 28.8, 28.0, 13.6;

**HRMS (ESI-TOF)** calcd. for C<sub>34</sub>H<sub>40</sub>NO<sub>10</sub> [M + H]<sup>+</sup> 622.2647; found: 622.2641.

**Trimethyl 5'-bromo-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3y)**



The product **3x** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 92% yield; >20:1 dr; m.p. 217.5-217.9 °C;

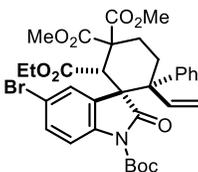
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.47 (d, *J* = 1.9 Hz, 1H), 7.34 (dd, *J* = 8.3, 1.9 Hz, 1H), 7.02 (d, *J* = 7.3 Hz, 1H), 6.99 – 6.90 (m, 2H), 6.86 (dd, *J* = 17.3, 11.0 Hz, 1H), 6.65 (d, *J* = 7.8 Hz, 2H), 6.25 (d, *J* = 8.2 Hz, 1H), 5.41 (d, *J* = 11.0 Hz, 1H), 4.82 (d, *J* = 17.3 Hz, 1H), 4.25 (s, 1H), 3.84 (s, 3H), 3.82 (s,

3H), 3.53 (dd,  $J = 13.7, 3.3$  Hz, 1H), 3.47 (s, 3H), 2.70 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.40 (s, 3H), 2.30 (td,  $J = 13.9, 3.2$  Hz, 1H), 1.67 (dt,  $J = 13.4, 3.6$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  175.7, 173.4, 170.3, 169.1, 144.6, 140.6, 140.4, 133.1, 131.4, 128.6, 127.0, 126.6, 125.5, 119.3, 113.9, 108.8, 57.2, 55.5, 53.5, 52.9, 52.4, 50.8, 48.7, 28.6, 28.0, 25.4;

HRMS (ESI-TOF) calcd. for  $\text{C}_{28}\text{H}_{29}^{79}\text{BrNO}_7$  [ $\text{M} + \text{H}$ ] $^+$  570.1122; found: 570.1124; calcd. for  $\text{C}_{28}\text{H}_{29}^{81}\text{BrNO}_7$  [ $\text{M} + \text{H}$ ] $^+$  572.1106; found: 572.1110.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 5'-bromo-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3z)**



The product **3y** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

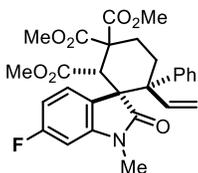
White solid; 95% yield; >20:1 dr; m.p. 193.8-194.2 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.50 (d,  $J = 1.9$  Hz, 1H), 7.40 – 7.29 (m, 2H), 7.10 – 6.94 (m, 3H), 6.83 (dd,  $J = 17.3, 11.0$  Hz, 1H), 6.78 – 6.49 (m, 2H), 5.41 (d,  $J = 10.9$  Hz, 1H), 4.83 (d,  $J = 17.2$  Hz, 1H), 4.22 (s, 1H), 4.00 – 3.85 (m, 2H), 3.83 (s, 6H), 3.38 (td,  $J = 13.8, 3.3$  Hz, 1H), 2.73 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.30 (td,  $J = 14.0, 3.1$  Hz, 1H), 1.75 – 1.69 (m, 1H), 1.38 (s, 9H), 1.04 (t,  $J = 7.1$  Hz, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.9, 173.2, 169.8, 168.9, 147.7, 140.7, 140.1, 139.4, 132.0, 131.6, 128.8, 127.4, 127.0, 125.3, 119.5, 116.3, 116.2, 83.5, 61.6, 57.2, 55.4, 53.4, 52.9, 51.3, 49.4, 28.9, 28.0, 28.0, 13.6;

HRMS (ESI-TOF) calcd. for  $\text{C}_{33}\text{H}_{37}^{79}\text{BrNO}_9$  [ $\text{M} + \text{H}$ ] $^+$  670.1647; found: 670.1650; calcd. for  $\text{C}_{33}\text{H}_{37}^{81}\text{BrNO}_9$  [ $\text{M} + \text{H}$ ] $^+$  672.1632; found: 672.1643.

**Trimethyl 6'-fluoro-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3aa)**



The product **3z** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

White solid; 96% yield; >20:1 dr; m.p. 197.6-198.2 °C;

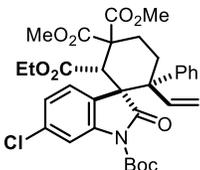
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29 (dd,  $J = 8.3, 5.2$  Hz, 1H), 7.07 – 7.01 (m, 1H), 6.99 – 6.84 (m, 3H), 6.76 – 6.53 (m, 3H), 6.12 (dd,  $J = 9.0, 2.3$  Hz, 1H), 5.37 (d,  $J = 11.0$  Hz, 1H), 4.81 (d,  $J = 17.3$  Hz, 1H), 4.28 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.51 (td,  $J = 13.7, 3.3$  Hz, 1H), 3.45 (s, 3H), 2.70 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.41 (s, 3H), 2.30 (td,  $J = 13.9, 3.2$  Hz, 1H), 1.68 (dt,  $J = 13.5, 3.5$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.5, 173.5, 170.4, 169.2, 163.5 (d,  $J = 245.2$  Hz), 147.1 (d,  $J = 11.6$  Hz), 141.0, 140.6, 128.6, 127.0, 126.6, 126.3 (d,  $J = 2.9$  Hz), 123.2 (d,  $J = 9.7$  Hz), 119.0, 107.3 (d,  $J = 22.3$  Hz), 96.4 (d,  $J = 27.3$  Hz), 57.3, 55.0, 53.4, 52.9, 52.3, 50.7, 48.8, 28.5, 28.1, 25.5;

$^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  $\delta$  -111.8;

HRMS (ESI-TOF) calcd. for  $\text{C}_{28}\text{H}_{29}\text{FNO}_7$   $[\text{M} + \text{H}]^+$  510.1923; found: 510.1925.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 6'-chloro-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3ab)**



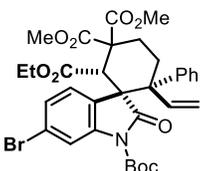
The product **3aa** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 97% yield; >20:1 dr; m.p. 106.8-107.2 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.49 (d,  $J = 2.0$  Hz, 1H), 7.32 (d,  $J = 8.1$  Hz, 1H), 7.14 – 7.05 (m, 2H), 7.04 – 6.93 (m, 2H), 6.85 (dd,  $J = 17.3, 11.0$  Hz, 1H), 6.65 (d,  $J = 6.3$  Hz, 2H), 5.37 (d,  $J = 11.0$  Hz, 1H), 4.82 (d,  $J = 17.3$  Hz, 1H), 4.25 (s, 1H), 4.00 – 3.73 (m, 2H), 3.83 (s, 3H), 3.81 (s, 3H), 3.38 (td,  $J = 13.8, 3.3$  Hz, 1H), 2.73 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.29 (td,  $J = 14.0, 3.1$  Hz, 1H), 1.76 – 1.69 (m, 1H), 1.39 (s, 9H), 1.02 (t,  $J = 7.1$  Hz, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.2, 173.2, 169.8, 169.0, 147.7, 142.5, 140.4, 139.5, 134.4, 128.8, 128.3, 127.3, 127.0, 123.4, 123.2, 119.3, 115.3, 83.6, 61.5, 57.3, 55.2, 53.4, 52.9, 51.2, 49.4, 28.8, 28.0, 28.0, 13.6;

HRMS (ESI-TOF) calcd. for  $\text{C}_{33}\text{H}_{36}^{35}\text{ClINNaO}_9$   $[\text{M} + \text{Na}]^+$  648.1971; found: 648.1995; calcd. for  $\text{C}_{33}\text{H}_{36}^{37}\text{ClINNaO}_9$   $[\text{M} + \text{Na}]^+$  650.1960; found: 650.1989.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 6'-bromo-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3ac)**



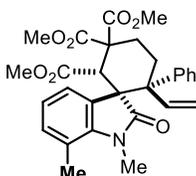
The product **3ab** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 165.8-166.4 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.66 (d,  $J = 1.5$  Hz, 1H), 7.28 (d,  $J = 2.1$  Hz, 2H), 7.12 – 6.98 (m, 3H), 6.86 (dd,  $J = 17.3, 11.0$  Hz, 1H), 6.66 (d,  $J = 7.7$  Hz, 2H), 5.37 (d,  $J = 11.0$  Hz, 1H), 4.82 (d,  $J = 17.2$  Hz, 1H), 4.26 (s, 1H), 3.99 – 3.85 (m, 2H), 3.84 (s, 3H), 3.82 (s, 3H), 3.39 (td,  $J = 13.8, 3.2$  Hz, 1H), 2.74 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.30 (td,  $J = 13.9, 3.1$  Hz, 1H), 1.73 – 1.67 (m, 1H), 1.40 (s, 9H), 1.04 (t,  $J = 7.2$  Hz, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 173.2, 169.8, 168.9, 147.7, 142.6, 140.3, 139.5, 128.8, 128.8, 127.3, 127.0, 126.3, 123.5, 122.4, 119.3, 118.0, 83.6, 61.5, 57.2, 55.2, 53.4, 52.9, 51.2, 49.3, 28.8, 28.0, 28.0, 13.6;

HRMS (ESI-TOF) calcd. for  $\text{C}_{33}\text{H}_{37}^{79}\text{BrNO}_9$   $[\text{M} + \text{H}]^+$  670.1647; found: 670.1653; calcd. for  $\text{C}_{33}\text{H}_{37}^{81}\text{BrNO}_9$   $[\text{M} + \text{H}]^+$  672.1632; found: 672.1638.

**Trimethyl 1',7'-dimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3ad)**



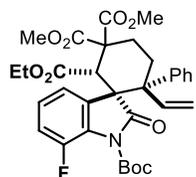
The product **3ac** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 93% yield; >20:1 dr; m.p. 213.4-214.3 °C;

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.18 (dd,  $J = 7.3, 1.4$  Hz, 1H), 7.10 – 7.02 (m, 1H), 7.00 – 6.85 (m, 5H), 6.55 (s, 2H), 5.31 (d,  $J = 11.0$  Hz, 1H), 4.76 (d,  $J = 17.3$  Hz, 1H), 4.29 (s, 1H), 3.85 (s, 3H), 3.81 (s, 3H), 3.53 (td,  $J = 13.7, 3.3$  Hz, 1H), 3.46 (s, 3H), 2.70 (dt,  $J = 13.9, 3.6$  Hz, 1H), 2.66 (s, 3H), 2.30 (td,  $J = 13.9, 3.2$  Hz, 1H), 2.19 (s, 3H), 1.66 (dt,  $J = 13.3, 3.5$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 173.6, 170.5, 169.3, 143.2, 141.2, 140.8, 132.1, 131.1, 128.8, 126.8, 126.2, 121.1, 120.2, 119.1, 118.4, 57.3, 54.7, 53.4, 52.9, 52.2, 50.9, 48.6, 28.7, 28.5, 28.1, 18.9;

HRMS (ESI-TOF) calcd. for  $\text{C}_{29}\text{H}_{32}\text{NO}_7$   $[\text{M} + \text{H}]^+$  506.2174; found: 506.2176.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 7'-fluoro-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3ae)**



The product **3ad** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 59% yield; >20:1 dr; m.p. 224.8-225.6 °C;

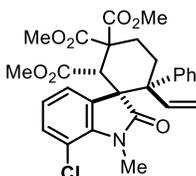
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.22 (d,  $J = 7.5$  Hz, 1H), 7.11 (dq,  $J = 8.1, 4.4, 3.7$  Hz, 2H), 7.01 (dd,  $J = 9.0, 6.6$  Hz, 3H), 6.94 (dd,  $J = 17.3, 11.0$  Hz, 1H), 6.70 (d,  $J = 7.8$  Hz, 2H), 5.36 (d,  $J = 10.9$  Hz, 1H), 4.79 (d,  $J = 17.3$  Hz, 1H), 4.25 (s, 1H), 3.96 – 3.74 (m, 2H), 3.80 (s, 6H), 3.44 (td,  $J = 13.8, 3.3$  Hz, 1H), 2.74 (dt,  $J = 14.0, 3.6$  Hz, 1H), 2.31 (td,  $J = 13.9, 3.1$  Hz, 1H), 1.70 (dt,  $J = 13.6, 3.5$  Hz, 1H), 1.33 (s, 9H), 0.97 (t,  $J = 7.1$  Hz, 3H);

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  174.1, 173.2, 169.5, 168.7, 148.7 (d,  $J = 251.1$  Hz), 146.4, 140.8, 139.8, 133.2 (d,  $J = 2.5$  Hz), 128.8 (d,  $J = 9.2$  Hz), 128.6, 127.6, 127.3, 124.6 (d,  $J = 7.2$  Hz), 119.1, 118.6 (d,  $J = 3.3$  Hz), 117.1 (d,  $J = 21.2$  Hz), 83.4, 61.4, 57.3, 56.0, 53.4, 52.8, 51.2, 49.8, 28.8, 28.1, 27.5, 13.5;

<sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>) δ -118.8;

HRMS (ESI-TOF) calcd. for C<sub>33</sub>H<sub>37</sub>FNO<sub>9</sub> [M + H]<sup>+</sup> 610.2447; found: 610.2465.

**Trimethyl 7'-chloro-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3af)**



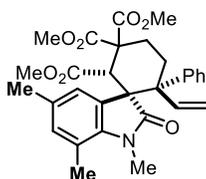
The product **3ae** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 96% yield; >20:1 dr; m.p. 244.8-245.1 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.24 (dd, J = 7.4, 1.1 Hz, 1H), 7.18 – 7.06 (m, 2H), 7.05 – 6.95 (m, 2H), 6.95 – 6.90 (m, 1H), 6.90 – 6.79 (m, 1H), 6.71 – 6.44 (m, 2H), 5.34 (d, J = 11.0 Hz, 1H), 4.78 (d, J = 17.3 Hz, 1H), 4.29 (s, 1H), 3.84 (s, 3H), 3.81 (s, 3H), 3.52 (dd, J = 13.7, 3.4 Hz, 1H), 3.47 (s, 3H), 2.76 (s, 3H), 2.71 (dt, J = 13.9, 3.4 Hz, 1H), 2.29 (td, J = 13.9, 3.2 Hz, 1H), 1.66 (dt, J = 13.4, 3.5 Hz, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.5, 173.4, 170.4, 169.2, 141.3, 140.7, 140.2, 133.6, 130.8, 128.5, 127.2, 126.5, 121.9, 120.6, 118.9, 115.2, 57.2, 55.2, 53.4, 52.9, 52.3, 51.0, 48.7, 28.7, 28.6, 28.0;

HRMS (ESI-TOF) calcd. for C<sub>28</sub>H<sub>29</sub><sup>35</sup>ClNO<sub>7</sub> [M + H]<sup>+</sup> 526.1628; found: 526.1629; calcd. for C<sub>28</sub>H<sub>29</sub><sup>37</sup>ClNO<sub>7</sub> [M + H]<sup>+</sup> 528.1612; found: 528.1612.

**Trimethyl 1',5',7'-trimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3ag)**



The product **3af** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 50% yield; >20:1 dr; m.p. 230.6-231.2 °C;

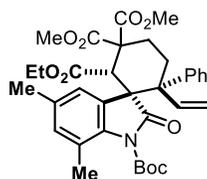
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.08 – 7.02 (m, 1H), 7.01 – 6.86 (m, 4H), 6.75 (s, 1H), 6.57 (d, J = 6.7 Hz, 2H), 5.32 (d, J = 10.6 Hz, 1H), 4.76 (d, J = 17.3 Hz, 1H), 4.25 (s, 1H), 3.85 (s, 3H), 3.82 (s, 3H), 3.57 – 3.50 (m, 1H), 3.47 (s, 3H), 2.70 (dt, J = 13.8, 3.4 Hz, 1H), 2.63 (s, 3H), 2.36 – 2.25 (m, 1H), 2.31 (s, 3H), 2.15 (s, 3H), 1.69 – 1.65 (m, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.9, 173.8, 170.6, 169.4, 141.4, 141.0, 140.8, 132.7, 131.2, 130.4, 128.8, 126.7, 126.2, 121.1, 118.7, 118.3, 57.3, 54.8, 53.4, 52.9, 52.3, 50.8, 48.7, 28.7, 28.5, 28.2, 21.2, 18.8;

HRMS (ESI-TOF) calcd. for C<sub>30</sub>H<sub>34</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 520.2330; found: 520.2330.

**1'-(Tert-butyl) 6-ethyl 5,5-dimethyl 5',7'-dimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-**

### 1,3'-indoline]-1',5,5,6-tetracarboxylate (**3ah**)



The product **3ag** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 71% yield; >20:1 dr; m.p. 153.4-154.2 °C;

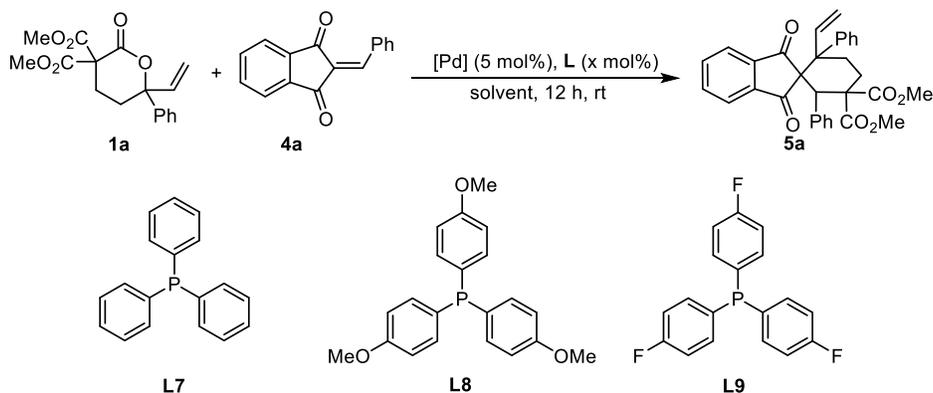
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.10 – 7.01 (m, 2H), 6.99 – 6.83 (m, 4H), 6.62 (d, *J* = 7.8 Hz, 2H), 5.32 (d, *J* = 11.7 Hz, 1H), 4.74 (d, *J* = 18.2 Hz, 1H), 4.23 (s, 1H), 3.94 – 3.73 (m, 2H), 3.81 (s, 3H), 3.76 (s, 3H), 3.42 (td, *J* = 13.7, 3.4 Hz, 1H), 2.73 (dt, *J* = 13.7, 3.5 Hz, 1H), 2.34 (s, 3H), 2.33 – 2.23 (m, 1H), 1.89 (s, 3H), 1.71 (dt, *J* = 13.5, 3.4 Hz, 1H), 1.38 (s, 9H), 0.93 (t, *J* = 7.1 Hz, 3H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 175.3, 173.4, 169.7, 169.2, 148.3, 141.2, 140.1, 137.9, 132.6, 132.1, 130.8, 128.9, 127.0, 126.9, 122.9, 120.9, 118.3, 83.0, 61.2, 57.4, 55.3, 53.3, 52.5, 50.8, 49.9, 28.8, 28.2, 27.8, 21.3, 19.6, 13.5;

HRMS (ESI-TOF) calcd. for C<sub>35</sub>H<sub>42</sub>NO<sub>9</sub> [M + H]<sup>+</sup> 620.2855; found: 620.2851.

### 3. Optimization of reaction conditions

**Table 1.** Optimization of the reaction conditions for Pd-catalyzed [4+2] cycloaddition of δ-vinylvalerolactones **1a** and 2-benzylideneindan-1,3-diones **4a**<sup>[3]</sup>

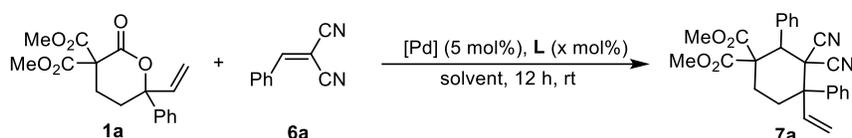


entry	[Pd]	L(x mol%)	solvent	dr <sup>b</sup>	yield (%) <sup>c</sup>
1	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L4</b> (20 mol%)	DCE	--	--
2	PdCl <sub>2</sub>	<b>L4</b> (10 mol%)	DCE	--	--
3	Pd(PPh <sub>3</sub> ) <sub>4</sub>	--	DCE	10:1	59
4	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L1</b> (10 mol%)	DCE	20:1	29
5	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L2</b> (10 mol%)	DCE	20:1	50
6	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L3</b> (10 mol%)	DCE	20:1	61
7	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L4</b> (10 mol%)	DCE	20:1	62
8	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L5</b> (10 mol%)	DCE	20:1	68
9	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L6</b> (10 mol%)	DCE	20:1	60
10	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L7</b> (10 mol%)	DCE	4:1	69

11	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	DCE	12:1	81
12	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L9</b> (10 mol%)	DCE	20:1	52
13	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	THF	5:1	64
14	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	DMF	6:1	77
15	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	MeOH	-	-
16	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	Toluene	4:1	50
17	Pd(PPh <sub>3</sub> ) <sub>4</sub>	<b>L8</b> (10 mol%)	DCM	6:1	77

<sup>a</sup>Unless otherwise noted, the reaction was carried out with **1a** (0.1 mmol), **4a** (0.12 mmol), [Pd] (5 mol%), ligand (x mol%) in 1.0 mL of solvent at room temperature for 12 h under Ar. <sup>b</sup>Determined by NMR analysis. <sup>c</sup>Isolated yield.

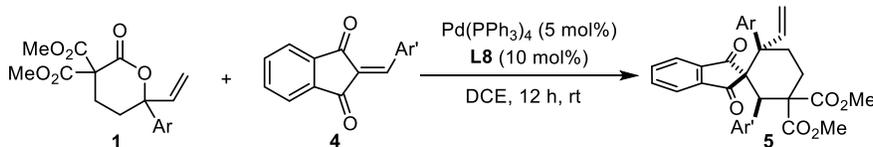
**Table 2.** Optimization of the reaction conditions for Pd-catalyzed [4+2] cycloaddition of  $\delta$ -vinylvalerolactones **1a** and 2-benzylidenemalononitriles **6a**<sup>[4]</sup>



entry	[Pd]	L	solvent	dr <sup>b</sup>	yield (%) <sup>c</sup>
1	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L4</b>	DCE	20:1	78
2	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L3</b>	DCE	20:1	91
3	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L5</b>	DCE	20:1	26
4	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L6</b>	DCE	20:1	45

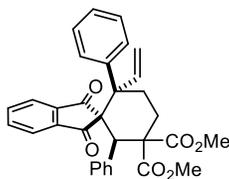
<sup>a</sup>Unless otherwise noted, the reaction was carried out with **1a** (0.1 mmol), **6a** (0.12 mmol), [Pd] (5 mol%), ligand (20 mol%) in 1.0 mL of solvent at room temperature for 12 h under Ar. <sup>b</sup>Determined by NMR analysis. <sup>c</sup>Isolated yield.

#### 4. General procedures for the synthesis of compounds **5**



Under argon atmosphere, an oven-dried Schlenk tube was added Pd(PPh<sub>3</sub>)<sub>4</sub> (0.005 mmol, 5.8 mg, 5 mol%), **L8** (0.01 mmol, 3.5 mg, 10 mol%) was added along with  $\delta$ -vinylvalerolactones **1** (0.1 mmol) and 2-benzylideneindan-1,3-diones **4** (0.12 mmol) and DCE (1.0 mL). The reaction was stirred at room temperature for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give the corresponding cycloadducts **5**.

#### Dimethyl 1',3'-dioxo-2,6-diphenyl-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (**5a**)



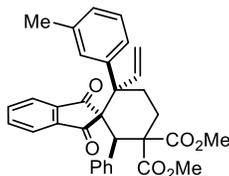
The product **5a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 81% yield; dr = 12:1; m.p. 236.6-237.4 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 (dd, *J* = 17.6, 11.1 Hz, 1H), 7.41 (s, 4H), 7.09 – 6.71 (m, 10H), 5.47 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 4.60 (s, 1H), 3.83 (s, 3H), 3.62 (s, 3H), 3.51 (td, *J* = 13.3, 3.2 Hz, 1H), 2.75 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.40 (td, *J* = 13.6, 3.1 Hz, 1H), 1.95 (dt, *J* = 13.7, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.8, 201.1, 172.7, 170.4, 143.4, 143.1, 142.8, 142.1, 136.5, 134.8, 132.3, 129.0, 127.3, 127.2, 126.9, 126.7, 122.3, 122.0, 117.9, 63.1, 58.5, 53.0, 51.9, 51.8, 49.2, 29.8, 29.7;

**HRMS (ESI-TOF)** calcd. for C<sub>32</sub>H<sub>29</sub>O<sub>6</sub> [M + H]<sup>+</sup> 509.1959; found: 509.1975.

**Dimethyl 1',3'-dioxo-6-phenyl-2-(m-tolyl)-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (**5b**)**



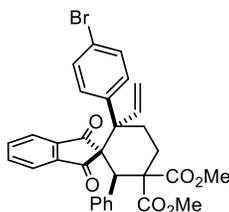
The product **5b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 80% yield; dr = 15:1; m.p. 202.1-202.9 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 – 7.40 (m, 5H), 7.10 – 6.78 (m, 6H), 6.74 – 6.65 (m, 2H), 6.54 (d, *J* = 7.5 Hz, 1H), 5.45 (d, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 17.6 Hz, 1H), 4.60 (s, 1H), 3.82 (s, 3H), 3.62 (s, 3H), 3.47 (td, *J* = 13.6, 3.2 Hz, 1H), 2.74 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.39 (td, *J* = 13.6, 3.0 Hz, 1H), 2.01 – 1.94 (m, 1H), 1.93 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.8, 201.1, 172.7, 170.4, 143.5, 143.0, 142.7, 141.9, 136.7, 136.7, 134.6, 134.6, 132.3, 130.0, 127.3, 127.3, 127.1, 126.9, 125.8, 122.3, 121.7, 117.8, 63.3, 58.5, 53.0, 51.8, 51.7, 49.0, 29.8, 29.5, 21.2;

**HRMS (ESI-TOF)** calcd. for C<sub>33</sub>H<sub>31</sub>O<sub>6</sub> [M + H]<sup>+</sup> 523.2116; found: 523.2140.

**Dimethyl 2-(4-bromophenyl)-1',3'-dioxo-6-phenyl-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (**5c**)**



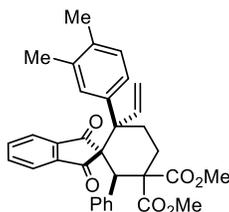
The product **5c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 81% yield; dr = 9:1; m.p. 198.8-199.6 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.54 – 7.40 (m, 5H), 7.08 – 6.82 (m, 9H), 5.46 (d, *J* = 11.0 Hz, 1H), 4.91 (d, *J* = 17.6 Hz, 1H), 4.58 (s, 1H), 3.82 (s, 3H), 3.61 (s, 3H), 3.46 (td, *J* = 13.6, 3.2 Hz, 1H), 2.74 (dt, *J* = 13.7, 3.6 Hz, 1H), 2.36 (td, *J* = 13.6, 3.0 Hz, 1H), 1.90 (dt, *J* = 13.5, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.6, 200.9, 172.5, 170.3, 143.1, 142.7, 142.3, 141.7, 136.2, 135.1, 135.1, 132.3, 130.8, 130.3, 127.3, 126.9, 122.5, 122.0, 120.9, 118.2, 62.9, 58.3, 53.0, 51.9, 51.4, 49.2, 30.0, 29.8;

**HRMS (ESI-TOF)** calcd. for C<sub>32</sub>H<sub>28</sub><sup>79</sup>BrO<sub>6</sub> [M + H]<sup>+</sup> 587.1064; found: 587.1074; calcd. for C<sub>32</sub>H<sub>28</sub><sup>81</sup>BrO<sub>6</sub> [M + H]<sup>+</sup> 589.1049; found: 589.1060.

**Dimethyl 2-(3,4-dimethylphenyl)-1',3'-dioxo-6-phenyl-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (5d)**



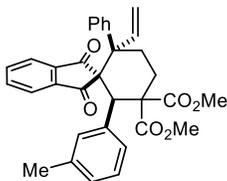
The product **5d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 86% yield; dr = 8:1; m.p. 196.2-197.2 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.51 – 7.38 (m, 5H), 7.13 – 6.84 (m, 5H), 6.73 (dd, *J* = 8.0, 2.2 Hz, 1H), 6.62 (d, *J* = 2.2 Hz, 1H), 6.56 (d, *J* = 8.0 Hz, 1H), 5.44 (d, *J* = 11.1 Hz, 1H), 4.96 (d, *J* = 17.6 Hz, 1H), 4.59 (s, 1H), 3.81 (s, 3H), 3.62 (s, 3H), 3.44 (td, *J* = 13.7, 3.2 Hz, 1H), 2.74 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.39 (td, *J* = 13.6, 3.1 Hz, 1H), 1.94 (dt, *J* = 13.7, 3.5 Hz, 1H), 1.87 (s, 3H), 1.83 (s, 3H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.8, 201.1, 172.7, 170.5, 143.5, 142.7, 142.0, 140.4, 136.8, 135.2, 134.8, 134.4, 134.3, 132.2, 130.5, 128.6, 127.1, 126.9, 126.0, 122.3, 121.7, 117.6, 63.5, 58.5, 52.9, 51.8, 51.5, 49.0, 29.8, 29.5, 19.5, 19.0;

**HRMS (ESI-TOF)** calcd. for C<sub>34</sub>H<sub>33</sub>O<sub>6</sub> [M + H]<sup>+</sup> 537.2272; found: 537.2273.

**Dimethyl 1',3'-dioxo-2-phenyl-6-(*m*-tolyl)-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (5e)**



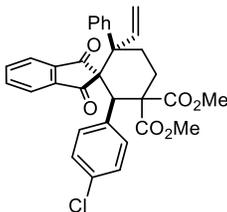
The product **5e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 73% yield; dr = 9:1; m.p. 84.6-85.3 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.52 (dd, *J* = 17.6, 11.1 Hz, 1H), 7.42 (s, 4H), 7.01 – 6.96 (m, 2H), 6.92 – 6.60 (m, 7H), 5.46 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 17.5 Hz, 1H), 4.56 (s, 1H), 3.80 (s, 3H), 3.62 (s, 3H), 3.50 (td, *J* = 13.4, 3.1 Hz, 1H), 2.75 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.41 (td, *J* = 13.6, 3.1 Hz, 1H), 2.14 – 1.85 (m, 4H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.8, 201.1, 172.7, 170.3, 143.3, 143.1, 142.8, 142.1, 136.4, 134.7, 134.7, 133.2, 129.0, 127.8, 127.3, 126.6, 122.2, 122.0, 117.8, 63.0, 58.6, 52.9, 51.8, 51.7, 49.1, 29.8, 29.6, 21.3;

**HRMS (ESI-TOF)** calcd. for C<sub>33</sub>H<sub>31</sub>O<sub>6</sub> [M + H]<sup>+</sup> 523.2116; found: 523.2129.

**Dimethyl 6-(4-chlorophenyl)-1',3'-dioxo-2-phenyl-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (5f)**



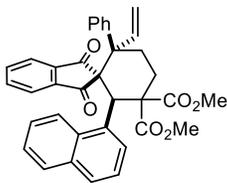
The product **5f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 70% yield; dr = 20:1; m.p. 226.4-227.3 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.53 – 7.38 (m, 5H), 7.10 – 6.62 (m, 9H), 5.46 (d, *J* = 11.1 Hz, 1H), 4.95 (d, *J* = 17.6 Hz, 1H), 4.57 (s, 1H), 3.85 (s, 3H), 3.62 (s, 3H), 3.49 (td, *J* = 13.6, 3.1 Hz, 1H), 2.74 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.36 (td, *J* = 13.6, 3.1 Hz, 1H), 1.95 (dt, *J* = 13.7, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.7, 201.0, 172.5, 170.2, 143.3, 142.9, 142.6, 141.8, 135.0, 135.0, 134.9, 133.7, 133.1, 128.9, 127.4, 127.0, 126.8, 122.4, 122.2, 118.1, 63.1, 58.2, 53.1, 52.0, 51.7, 48.3, 29.8, 29.6;

**HRMS (ESI-TOF)** calcd. for C<sub>32</sub>H<sub>27</sub><sup>35</sup>ClNaO<sub>6</sub> [M + Na]<sup>+</sup> 565.1388; found: 565.1409; calcd. for C<sub>32</sub>H<sub>27</sub><sup>35</sup>ClNaO<sub>6</sub> [M + Na]<sup>+</sup> 567.1376; found: 567.1392.

**Dimethyl 6-(naphthalen-1-yl)-1',3'-dioxo-2-phenyl-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (5g)**



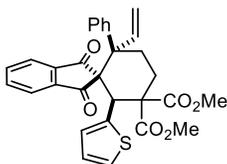
The product **5g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); Yellow solid; 55% yield; dr = 5:1; m.p. 245.2-245.8 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.61 (d, *J* = 8.9 Hz, 1H), 7.78 – 7.63 (m, 3H), 7.48 – 7.31 (m, 5H), 7.26 – 7.17 (m, 2H), 7.06 – 6.94 (m, 2H), 6.92 – 6.67 (m, 4H), 5.57 (d, *J* = 11.1 Hz, 1H), 5.51 (s, 1H), 5.06 (d, *J* = 17.6 Hz, 1H), 3.91 (s, 3H), 3.67 (td, *J* = 13.5, 3.2 Hz, 1H), 3.22 (s, 3H), 2.84 (dt, *J* = 13.9, 3.6 Hz, 1H), 2.67 (td, *J* = 13.7, 3.0 Hz, 1H), 2.06 (dt, *J* = 13.7, 3.5 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 203.0, 200.5, 172.1, 170.2, 143.4, 143.2, 143.0, 142.2, 134.7, 134.6, 133.7, 133.1, 131.9, 131.0, 128.9, 128.6, 128.5, 127.3, 126.7, 125.7, 125.2, 125.0, 123.3, 122.2, 122.0, 118.1, 64.1, 58.0, 52.7, 52.1, 52.0, 41.9, 30.3, 29.5;

**HRMS (ESI-TOF)** calcd. for C<sub>36</sub>H<sub>31</sub>O<sub>6</sub> [M + H]<sup>+</sup> 559.2116; found: 559.2134.

**Dimethyl 1',3'-dioxo-2-phenyl-6-(thiophen-2-yl)-2-vinyl-1',3'-dihydrospiro[cyclohexane-1,2'-indene]-5,5-dicarboxylate (**5h**)**



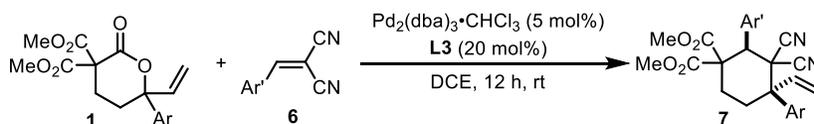
The product **5h** was purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1); White solid; 95% yield; dr = 3:1; m.p. 248.6-249.3 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.55 – 7.36 (m, 5H), 7.03 – 6.95 (m, 2H), 6.88 (dd, *J* = 4.6, 1.7 Hz, 1H), 6.82 – 6.71 (m, 3H), 6.52 (d, *J* = 4.7 Hz, 2H), 5.46 (d, *J* = 11.1 Hz, 1H), 5.00 – 4.89 (m, 2H), 3.83 (s, 3H), 3.71 (s, 3H), 3.43 (td, *J* = 13.6, 3.1 Hz, 1H), 2.75 (dt, *J* = 13.6, 3.5 Hz, 1H), 2.34 (td, *J* = 13.5, 3.0 Hz, 1H), 1.93 (dt, *J* = 13.7, 3.4 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 202.1, 200.5, 172.6, 170.0, 143.3, 142.9, 142.9, 141.8, 138.9, 134.8, 134.8, 130.3, 129.0, 127.4, 126.8, 125.3, 124.9, 122.3, 122.0, 118.1, 63.7, 58.8, 53.2, 52.0, 51.9, 43.5, 29.9, 29.5;

**HRMS (ESI-TOF)** calcd. for C<sub>30</sub>H<sub>27</sub>O<sub>6</sub>S [M + H]<sup>+</sup> 515.1523; found: 515.1532.

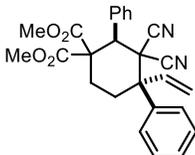
**5. General procedures for the synthesis of compounds 7**



Under argon atmosphere, an oven-dried Schlenk tube was added Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub> (0.005 mmol, 5.2 mg, 5 mol%), **L3** (0.02 mmol, 3.6 mg, 20 mol%) was added along with δ-vinylvalerolactones **1** (0.1 mmol) and 2-benzylidenemalononitriles **6** (0.12 mmol) and DCE (1.0 mL). The reaction was

stirred at room temperature for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give the corresponding cycloadducts **7**.

#### Dimethyl 3,3-dicyano-2,4-diphenyl-4-vinylcyclohexane-1,1-dicarboxylate (**7a**)



The product **7a** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

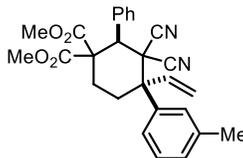
White solid; 91% yield; >20:1 dr; m.p. 219.3-219.9 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.72 – 7.59 (m, 4H), 7.45 – 7.31 (m, 6H), 6.59 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.73 (d, *J* = 11.2 Hz, 1H), 5.39 (d, *J* = 17.5 Hz, 1H), 4.16 (s, 1H), 3.80 (s, 3H), 3.63 (s, 3H), 3.17 (td, *J* = 15.7, 14.7, 3.6 Hz, 1H), 2.64 (dt, *J* = 12.8, 3.1 Hz, 1H), 2.37 – 2.21 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.7, 168.9, 140.9, 137.0, 135.0, 131.2, 129.1, 128.7, 128.5, 128.4, 128.0, 120.7, 114.3, 113.8, 58.4, 53.3, 52.4, 51.4, 50.1, 49.4, 29.3, 27.6;

**HRMS (ESI-TOF)** calcd. for C<sub>26</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 429.1809; found: 429.1821.

#### Dimethyl 3,3-dicyano-2-phenyl-4-(*m*-tolyl)-4-vinylcyclohexane-1,1-dicarboxylate (**7b**)



The product **7b** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

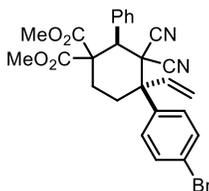
White solid; 96% yield; >20:1 dr; m.p. 135.2-136.1 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.62 (dd, *J* = 6.9, 3.0 Hz, 2H), 7.44 (d, *J* = 6.5 Hz, 2H), 7.38 – 7.31 (m, 3H), 7.27 (dd, *J* = 9.0, 7.7 Hz, 1H), 7.15 (d, *J* = 7.5 Hz, 1H), 6.56 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.70 (d, *J* = 11.2 Hz, 1H), 5.37 (d, *J* = 17.6 Hz, 1H), 4.14 (s, 1H), 3.79 (s, 3H), 3.62 (s, 3H), 3.19 – 3.08 (m, 1H), 2.62 (dt, *J* = 12.8, 3.1 Hz, 1H), 2.37 (s, 3H), 2.33 – 2.22 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.7, 169.0, 140.9, 138.0, 137.1, 135.0, 131.2, 129.4, 129.0, 128.9, 128.3, 128.0, 125.5, 120.5, 114.3, 113.8, 58.4, 53.3, 52.4, 51.3, 50.1, 49.3, 29.3, 27.5, 21.8;

**HRMS (ESI-TOF)** calcd. for C<sub>27</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 443.1966; found: 443.1979.

#### Dimethyl 4-(4-bromophenyl)-3,3-dicyano-2-phenyl-4-vinylcyclohexane-1,1-dicarboxylate (**7c**)



The product **7c** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

White solid; 93% yield; >20:1 dr; m.p. 145.6-146.4 °C;

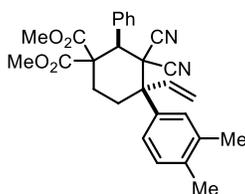
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.62 (dd, *J* = 6.9, 2.9 Hz, 2H), 7.52 (s, 4H), 7.35 (dd, *J* = 4.9, 1.8 Hz, 3H), 6.55 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.74 (d, *J* = 11.2 Hz, 1H), 5.38 (d, *J* = 17.5 Hz, 1H), 4.14 (s, 1H), 3.79 (s, 3H), 3.63 (s, 3H), 3.22 – 3.01 (m, 1H), 2.63 (dt, *J* = 15.7, 3.9 Hz, 1H), 2.27 (td, *J* = 14.2, 13.1, 3.3 Hz, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.6, 168.9, 140.0, 136.6, 134.8, 131.6, 131.2, 130.2, 129.2, 128.1, 123.2, 121.2, 114.1, 113.6, 58.2, 53.4, 52.5, 51.2, 50.0, 49.2, 29.3, 27.7;

**HRMS (ESI-TOF)** calcd. for C<sub>26</sub>H<sub>24</sub><sup>79</sup>BrN<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 507.0914; found: 507.0936; calcd. for C<sub>26</sub>H<sub>24</sub><sup>81</sup>BrN<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 509.0897; found: 509.0909.

#### Dimethyl 3,3-dicyano-4-(3,4-dimethylphenyl)-2-phenyl-4-vinylcyclohexane-1,1-dicarboxylate

(7d)



The product **7d** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

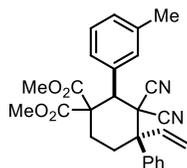
White solid; 95% yield; dr > 20:1; m.p. 157.5-158.5 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.62 (dd, *J* = 6.7, 3.0 Hz, 2H), 7.42 – 7.27 (m, 5H), 7.14 (d, *J* = 7.9 Hz, 1H), 6.56 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.68 (d, *J* = 11.2 Hz, 1H), 5.36 (d, *J* = 17.6 Hz, 1H), 4.13 (s, 1H), 3.78 (s, 3H), 3.61 (s, 3H), 3.21 – 3.04 (m, 1H), 2.61 (dt, *J* = 15.7, 4.2 Hz, 1H), 2.35 – 2.19 (m, 8H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.7, 169.0, 138.5, 137.2, 137.2, 136.6, 135.1, 131.2, 129.7, 129.4, 129.0, 128.0, 125.7, 120.2, 114.4, 113.9, 58.4, 53.3, 52.4, 51.1, 50.1, 49.5, 29.4, 27.5, 20.2, 19.5;

**HRMS (ESI-TOF)** calcd. for C<sub>28</sub>H<sub>29</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 457.2122; found: 457.2124.

#### Dimethyl 3,3-dicyano-4-phenyl-2-(m-tolyl)-4-vinylcyclohexane-1,1-dicarboxylate (7e)



The product **7e** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1);

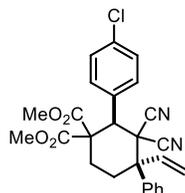
White solid; 89% yield; >20:1 dr; m.p. 144.6-145.3 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.71 – 7.61 (m, 2H), 7.47 – 7.31 (m, 5H), 7.25 – 7.20 (m, 1H), 7.15 (d, *J* = 7.6 Hz, 1H), 6.58 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.71 (d, *J* = 11.2 Hz, 1H), 5.37 (d, *J* = 17.6 Hz, 1H), 4.11 (s, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 3.24 – 3.05 (m, 1H), 2.62 (dt, *J* = 12.0, 2.4 Hz, 1H), 2.35 (s, 3H), 2.33 – 2.19 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.7, 169.0, 141.0, 137.5, 137.1, 134.9, 132.0, 129.8, 128.7, 128.4, 128.1, 127.9, 120.6, 114.3, 113.8, 58.4, 53.3, 52.3, 51.4, 50.0, 49.4, 29.3, 27.5, 21.7;

**HRMS (ESI-TOF)** calcd. for C<sub>27</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 443.1966; found: 443.1976.

**Dimethyl 2-(4-chlorophenyl)-3,3-dicyano-4-phenyl-4-vinylcyclohexane-1,1-dicarboxylate (7f)**



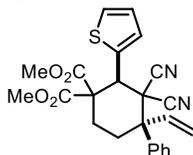
The product **7f** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 88% yield; >20:1 dr; m.p. 182.1-183.0 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.71 – 7.54 (m, 4H), 7.44 – 7.30 (m, 5H), 6.56 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.73 (d, *J* = 11.2 Hz, 1H), 5.39 (d, *J* = 17.6 Hz, 1H), 4.15 (s, 1H), 3.80 (s, 3H), 3.64 (s, 3H), 3.23 – 3.10 (m, 1H), 2.64 (dt, *J* = 13.8, 3.6 Hz, 1H), 2.38 – 2.12 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.6, 168.7, 140.7, 136.8, 135.1, 133.5, 132.6, 128.8, 128.5, 128.3, 128.3, 120.8, 114.1, 113.6, 58.2, 53.5, 52.6, 51.4, 49.5, 49.2, 29.3, 27.5;

**HRMS (ESI-TOF)** calcd. for C<sub>26</sub>H<sub>24</sub><sup>35</sup>ClN<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 463.1420; found: 463.1428; calcd. for C<sub>26</sub>H<sub>24</sub><sup>37</sup>ClN<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 465.1402; found: 465.1416.

**Dimethyl 3,3-dicyano-4-phenyl-2-(thiophen-3-yl)-4-vinylcyclohexane-1,1-dicarboxylate (7g)**



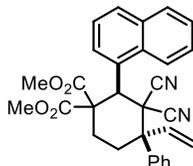
The product **7g** was purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1); White solid; 90% yield; >20:1 dr; m.p. 193.4-193.9 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.67 – 7.60 (m, 2H), 7.49 (dd, *J* = 3.1, 1.4 Hz, 1H), 7.43 – 7.32 (m, 4H), 7.29 – 7.25 (m, 1H), 6.56 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.71 (d, *J* = 11.2 Hz, 1H), 5.36 (d, *J* = 17.6 Hz, 1H), 4.39 (s, 1H), 3.78 (s, 3H), 3.67 (s, 3H), 3.21 – 3.03 (m, 1H), 2.62 (dt, *J* = 13.8, 3.8 Hz, 1H), 2.32 – 2.15 (m, 2H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.8, 168.8, 140.9, 137.0, 135.0, 129.2, 128.7, 128.5, 128.3, 127.3, 124.7, 120.7, 114.2, 113.7, 58.3, 53.4, 52.6, 51.2, 49.6, 45.8, 29.1, 27.6;

**HRMS (ESI-TOF)** calcd. for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O<sub>4</sub>S [M + H]<sup>+</sup> 435.1374; found: 435.1383.

**Dimethyl 3,3-dicyano-2-(naphthalen-1-yl)-4-phenyl-4-vinylcyclohexane-1,1-dicarboxylate (7h)**



The product **7h** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 43% yield; >20:1 dr; m.p. 228.6-229.5 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.29 – 8.12 (m, 2H), 7.89 (d, *J* = 8.1 Hz, 2H), 7.72 – 7.62 (m, 3H), 7.55 – 7.48 (m, 2H), 7.44 – 7.32 (m, 3H), 6.73 (dd, *J* = 17.6, 11.2 Hz, 1H), 5.85 (d, *J* = 11.2 Hz, 1H), 5.52 (d, *J* = 17.6 Hz, 1H), 5.14 (s, 1H), 3.89 (s, 3H), 3.43 – 3.34 (m, 1H), 3.30 (s, 3H), 2.70 (dt, *J* = 14.2, 3.6 Hz, 1H), 2.52 (td, *J* = 13.8, 3.5 Hz, 1H), 2.39 (dt, *J* = 14.8, 3.6 Hz, 1H);

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 170.4, 169.4, 141.0, 137.3, 134.0, 133.0, 130.6, 130.2, 129.5, 128.8, 128.7, 128.5, 128.4, 126.6, 125.6, 124.7, 122.8, 120.8, 114.3, 113.7, 57.7, 53.1, 52.6, 51.6, 51.0, 42.0, 29.9, 27.6;

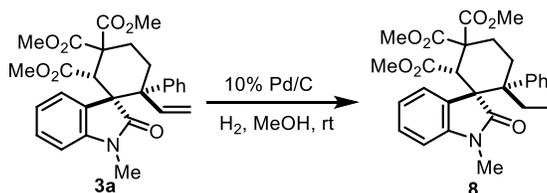
**HRMS (ESI-TOF)** calcd. for C<sub>30</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub> [M + H]<sup>+</sup> 479.1966; found: 479.1964.

## 6. Scale-up experiment

Under argon atmosphere, an oven-dried Schlenk tube was added Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub> (5 mol%), **L4** (20 mol%) was added along with δ-vinylvalerolactones **1a** (2.5 mmol, 1.0 equiv) and 3-alkenyloxindoles **2a** (3.0 mmol, 1.2 equiv) and DCE (25 mL). The reaction was stirred at room temperature for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give the corresponding cycloadducts **3a** (1.22 g, >20:1 dr, 99% yield).

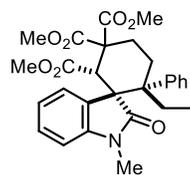
## 7. Synthetic transformations of products

### 7.1 The procedure for the synthesis of compound 8



To a stirring solution of **3a** (49.2 mg, 0.10 mmol, 1.0 equiv) in MeOH (2.0 mL) was slowly added 10% Pd/C (20 mg) at room temperature. The resulting mixture was stirred at room temperature in an atmosphere of hydrogen gas for 4 hours. The mixture was filtered and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 3:1) to give **8** as a white solid (48.9 mg, >20:1 dr, 99% yield).

### Trimethyl 2-ethyl-1'-methyl-2'-oxo-2-phenylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (**8**)

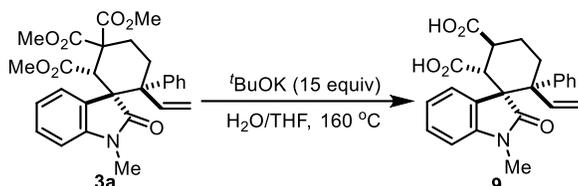


The product **8** was purified by flash column chromatography (petroleum ether/ethyl acetate = 3:1); White solid; 99% yield; >20:1 dr; m.p. 210.7-211.6 °C;

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.43 – 7.10 (m, 4H), 7.07 – 6.98 (m, 2H), 6.75 (d, *J* = 8.2 Hz, 1H), 6.40 (dd, *J* = 7.8, 1.0 Hz, 1H), 5.89 (d, *J* = 7.8 Hz, 1H), 4.27 (s, 1H), 3.85 (s, 3H), 3.83 (s, 3H), 3.42 (s,

3H), 3.31 (td,  $J = 14.3, 3.6$  Hz, 1H), 2.77 (dt,  $J = 13.9, 3.5$  Hz, 1H), 2.41 (s, 3H), 2.33 – 2.04 (m, 3H), 1.67 (dt,  $J = 14.2, 3.4$  Hz, 1H), 0.54 (t,  $J = 7.2$  Hz, 3H);  
 $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  176.8, 173.8, 170.6, 169.3, 145.5, 139.6, 130.4, 128.4, 127.6, 126.7, 126.6, 123.4, 120.8, 107.5, 57.2, 56.4, 53.4, 52.9, 52.1, 48.4, 46.1, 27.3, 25.2, 23.7, 21.0, 7.8;  
 HRMS (ESI-TOF) calcd. for  $\text{C}_{28}\text{H}_{32}\text{NO}_7$   $[\text{M} + \text{H}]^+$  494.2174; found: 494.2192.

## 7.2 The procedure for the synthesis of compound 9



To a stirring solution of **3a** (49.2 mg, 0.10 mmol, 1.0 equiv) in THF :  $\text{H}_2\text{O} = 10:1$  (1.1 mL) was slowly added  $t\text{BuOK}$  (168.3 mg, 1.5 mmol, 15 equiv). The resulting mixture was stirred at  $160^\circ\text{C}$  for 24 hours. After concentrated in vacuo, the residue was acidified with conc. HCl until the pH of the solution become 1. The layers were separated, and the aqueous layer was extracted with EtOAc three times. The combined organic layers were washed with water, then brine, and dried over  $\text{Na}_2\text{SO}_4$ . After  $\text{Na}_2\text{SO}_4$  was filtered off, the collected filtrate was concentrated in vacuo. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 1:1) to give **9** as a white solid (38.3 mg, >20:1 dr, 94% yield).

### 1'-Methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,6-dicarboxylic acid (**9**)



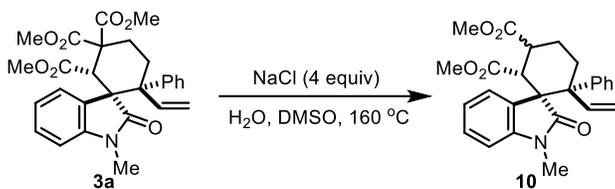
The product **9** was purified by flash column chromatography (petroleum ether/ethyl acetate = 1:1);  
 White solid; 94% yield; >20:1 dr; m.p.  $234.4\text{--}235.3^\circ\text{C}$ ;

$^1\text{H}$  NMR (400 MHz, Acetone- $d_6$ )  $\delta$  7.71 (d,  $J = 7.5$  Hz, 1H), 7.26 – 7.15 (m, 2H), 7.09 – 7.00 (m, 2H), 6.95 – 6.89 (m, 2H), 6.76 – 6.71 (m, 2H), 6.51 (d,  $J = 7.8$  Hz, 1H), 5.40 (d,  $J = 11.0$  Hz, 1H), 4.84 (d,  $J = 17.4$  Hz, 1H), 3.95 (td,  $J = 12.3, 4.4$  Hz, 1H), 3.75 – 3.66 (m, 2H), 2.47 (s, 3H), 2.22 – 2.07 (m, 2H), 1.79 (dt,  $J = 13.1, 3.4$  Hz, 1H);

$^{13}\text{C}$  NMR (101 MHz, Acetone- $d_6$ )  $\delta$  176.0, 176.0, 172.8, 145.6, 142.8, 142.7, 130.0, 129.3, 129.1, 127.2, 127.1, 125.8, 121.9, 118.0, 108.2, 56.4, 51.1, 48.9, 41.1, 30.6, 25.7, 25.5;

HRMS (ESI-TOF) calcd. for  $\text{C}_{24}\text{H}_{24}\text{NO}_5$   $[\text{M} + \text{H}]^+$  406.1649; found: 406.1645.

## 7.3 The procedure for the synthesis of compound 10



**3a** (49.2 mg, 0.10 mmol, 1.0 equiv) and NaCl (23.4 mg, 0.4 mmol, 4.0 equiv) and H<sub>2</sub>O (0.1 ml) in 2 mL DMSO was stirred for 24 h at 160°C. After 24 h, the reaction mixture was then cooled to room temperature. The reaction mixture was quenched with H<sub>2</sub>O, and extracted with 3 × 5.0 mL EtOAc. The combined organic layers were washed with saturated aqueous NaCl, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ ethyl acetate = 5:1) to give **10** as a white solid (32.5 mg, 3:2 dr, 75% yield).

**Dimethyl 1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,6-dicarboxylate**  
(**10**)



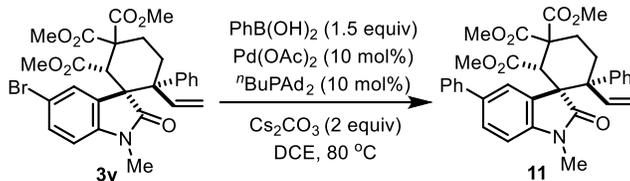
The product **10** was purified by flash column chromatography (petroleum ether/ethyl acetate = 5:1); White solid; 75% yield; dr = 3:2; m.p. 188.6-189.5 °C;

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.48 (dd, J = 7.5, 1.2 Hz, 1H), 7.25 – 7.18 (m, 1H), 7.07 – 6.90 (m, 5H), 6.83 – 6.65 (m, 2H), 6.39 (d, J = 7.8 Hz, 1H), 5.37 (d, J = 11.0 Hz, 1H), 4.89 (d, J = 17.4 Hz, 1H), 4.00 (td, J = 12.4, 4.4 Hz, 1H), 3.74 – 3.58 (m, 5H), 3.24 (s, 3H), 2.54 (s, 3H), 2.20 (dq, J = 13.6, 3.9 Hz, 1H), 2.10 (td, J = 13.2, 3.4 Hz, 1H), 1.82 (dt, J = 13.2, 3.4 Hz, 1H);

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.5, 172.1, 171.5, 145.5, 141.5, 141.4, 130.9, 128.5, 128.4, 126.6, 126.5, 122.5, 121.3, 118.2, 107.5, 55.0, 52.1, 52.1, 50.7, 46.8, 40.5, 28.0, 25.3, 21.8;

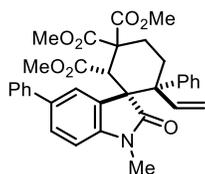
HRMS (ESI-TOF) calcd. for C<sub>26</sub>H<sub>28</sub>NO<sub>5</sub> [M + H]<sup>+</sup> 434.1962; found: 434.1972.

#### 7.4 The procedure for the synthesis of compound 11



Under argon atmosphere, an oven-dried Schlenk tube was added **3y** (57.0 mg, 0.10 mmol, 1.0 equiv), phenylboronic acid (18.3 mg, 0.15 mmol, 1.5 equiv.), Pd(OAc)<sub>2</sub> (2.2 mg, 0.01 mmol, 10 mol%), Cs<sub>2</sub>CO<sub>3</sub> (65.2 mg, 0.2 mmol, 2.0 equiv.), <sup>t</sup>BuPAD<sub>2</sub> (3.6 mg, 0.012 mmol, 12 mol%), and DCE (2.0 mL). The reaction was stirred at 80 °C for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give **11** as a white solid (53.0 mg, >20:1 dr, 93% yield).

**Trimethyl 1'-methyl-2'-oxo-2,5'-diphenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (11)**



The product **11** was purified by flash column chromatography (petroleum ether/ethyl acetate = 4:1); White solid; 93% yield; >20:1 dr; m.p. 223.8-224.6 °C;

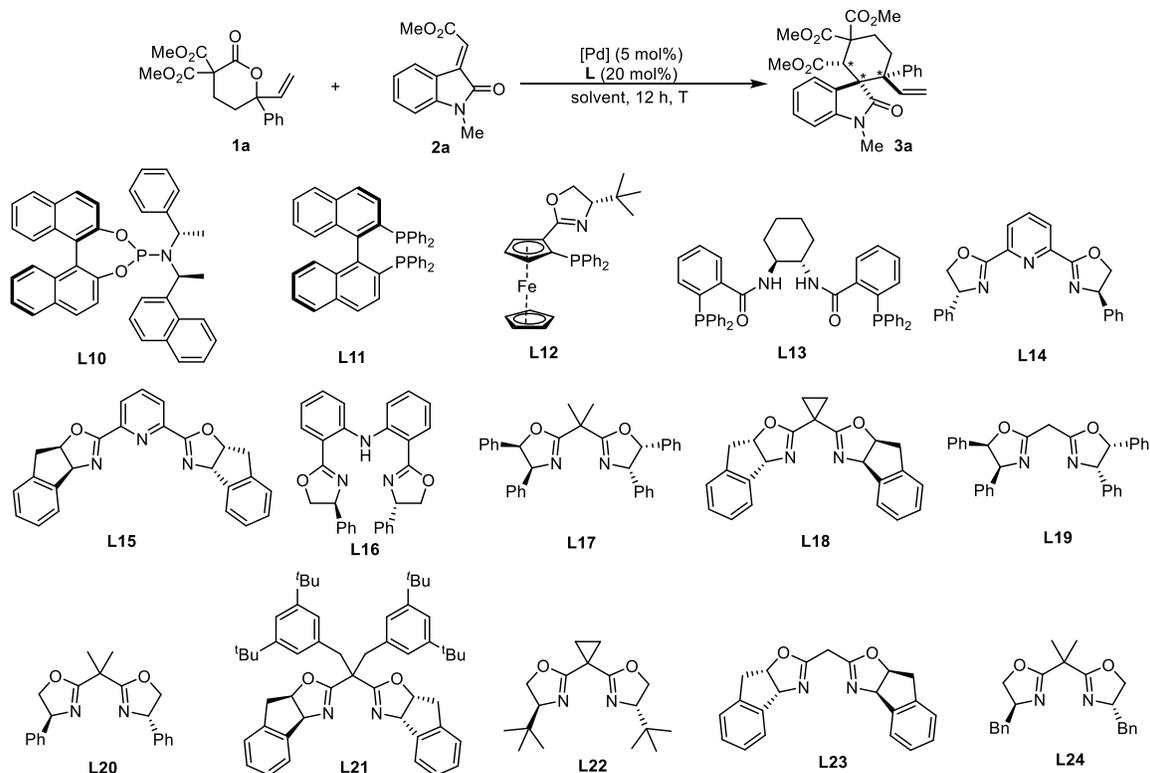
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.72 – 7.55 (m, 3H), 7.55 – 7.41 (m, 3H), 7.40 – 7.31 (m, 1H), 7.10 – 7.00 (m, 2H), 6.98 – 6.88 (m, 2H), 6.68 (d, *J* = 7.8 Hz, 2H), 6.46 (d, *J* = 8.1 Hz, 1H), 5.43 (d, *J* = 11.0 Hz, 1H), 4.84 (d, *J* = 17.3 Hz, 1H), 4.38 (s, 1H), 3.88 (s, 3H), 3.83 (s, 3H), 3.59 (td, *J* = 13.7, 3.3 Hz, 1H), 3.46 (s, 3H), 2.75 (dt, *J* = 13.9, 3.5 Hz, 1H), 2.48 (s, 3H), 2.36 (td, *J* = 14.0, 3.2 Hz, 1H), 1.74 – 1.68 (m, 1H);

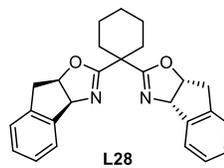
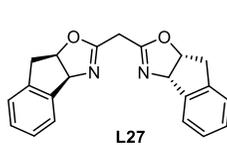
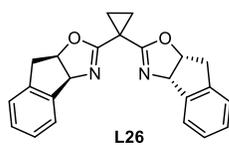
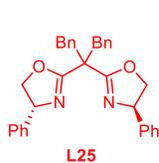
<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 176.2, 173.5, 170.4, 169.2, 144.9, 141.2, 141.2, 140.6, 134.6, 131.4, 128.9, 128.7, 127.5, 127.0, 127.0, 126.9, 126.5, 121.2, 118.8, 107.7, 57.3, 55.4, 53.4, 52.9, 52.3, 50.8, 48.7, 28.6, 28.1, 25.5;

HRMS (ESI-TOF) calcd. for C<sub>34</sub>H<sub>34</sub>NO<sub>7</sub> [M + H]<sup>+</sup> 568.2330; found: 568.2350.

## 8. Investigation on asymmetric [4+2] cycloaddition

**Table 3.** Optimization of the reaction conditions for investigation on asymmetric [4+2] cycloaddition

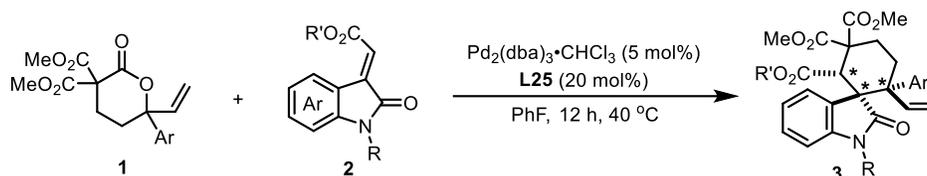




entry	[Pd]	L	solvent	T/°C	dr <sup>b</sup>	yield (%) <sup>c</sup>	er <sup>d</sup>	
1	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>NO</b>	DCE	50	--	--	--
2	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L10</b>	DCE	50	--	--	--
3	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L11</b>	DCE	50	--	--	--
4	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L12</b>	DCE	50	--	--	--
5	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L13</b>	DCE	50	--	--	--
6	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L14</b>	DCE	50	--	--	--
7	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L15</b>	DCE	50	--	--	--
8	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L16</b>	DCE	50	--	--	--
9	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L17</b>	DCE	50	>20:1	42	57:43
10	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L18</b>	DCE	50	--	--	--
11	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L19</b>	DCE	50	--	--	--
12	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L20</b>	DCE	50	>20:1	14	56:44
13	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L21</b>	DCE	50	>20:1	11	68:32
14	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L22</b>	DCE	50	--	--	--
15	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L23</b>	DCE	50	--	--	--
16	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L24</b>	DCE	50	>20:1	23	60:40
17	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	DCE	50	>20:1	38	71:29
18	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L26</b>	DCE	50	>20:1	15	57:43
19	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L27</b>	DCE	50	--	--	--
20	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L28</b>	DCE	50	>20:1	24	59:41
21	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L29</b>	DCE	50	>20:1	34	50:50
22	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L30</b>	DCE	50	>20:1	24	52:48
23	Pd <sub>2</sub> (dba) <sub>3</sub>		<b>L25</b>	DCE	50	>20:1	35	67:33
24	PdCl <sub>2</sub>		<b>L25</b>	DCE	50	--	--	--
25	Pd(TFA) <sub>2</sub>		<b>L25</b>	DCE	50	--	--	--
26	Pd(OAc) <sub>2</sub>		<b>L25</b>	DCE	50	--	--	--
27	[Pd(Cl)(C <sub>3</sub> H <sub>5</sub> ) <sub>2</sub> ]		<b>L25</b>	DCE	50	--	--	--
28	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	DCM	50	>20:1	35	78:22
29	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	THF	50	>20:1	13	57:43
30	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	DMF	50	>20:1	8	76:24
31	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	MeOH	50	--	--	--
32	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	chlorobenzene	50	>20:1	34	80:20
33	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	fluorobenzene	50	>20:1	34	82:18
34	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	toluene	50	>20:1	18	82:18
35	Pd <sub>2</sub> (dba) <sub>3</sub>	CHCl <sub>3</sub>	<b>L25</b>	mesitylene	50	--	--	--

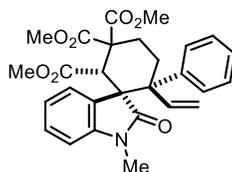
36	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L25</b>	fluorobenzene	0	--	--	--
37	Pd <sub>2</sub> (dba) <sub>3</sub> CHCl <sub>3</sub>	<b>L25</b>	fluorobenzene	30	>20:1	37	82.5:17.5
<b>38</b>	<b>Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub></b>	<b>L25</b>	<b>fluorobenzene</b>	<b>40</b>	<b>&gt;20:1</b>	<b>45</b>	<b>82:18</b>

<sup>a</sup>Unless otherwise noted, the reaction was carried out with **1a** (0.1 mmol), **2a** (0.12 mmol), [Pd] (5 mol%), ligand (20 mol%) in 1.0 mL of solvent for 12 h under Ar. <sup>b</sup>Determined by NMR analysis. <sup>c</sup>Isolated yield. <sup>d</sup>Determined by chiral HPLC analysis.



**General procedures for the asymmetric synthesis of compounds 3:** Under argon atmosphere, an oven-dried Schlenk tube was added Pd<sub>2</sub>(dba)<sub>3</sub> CHCl<sub>3</sub> (0.005 mmol, 5.2 mg, 5 mol%), **L25** (0.02 mmol, 9.7 mg, 20 mol%) was added along with  $\delta$ -vinylvalerolactones **1** (0.1 mmol) and 3-alkenyloxindoles **2** (0.12 mmol) and PhF (1.0 mL). The reaction was stirred at 40°C for 12 h. The reaction mixture was directly purified by silica gel column chromatography (petroleum ether/ ethyl acetate = 3:1) to give the corresponding cycloadducts **3**.

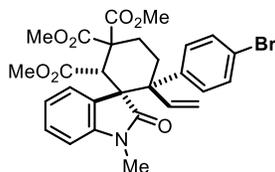
**Trimethyl 1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3a)**



45% yield; 82:18 er;  $[\alpha]_D^{20} = -47.1$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 8/92, flow rate 0.8 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 12.5$  min,  $t_{\text{minor}} = 14.3$  min).

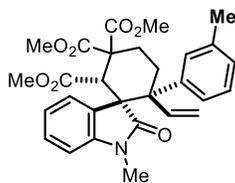
**Trimethyl 2-(4-bromophenyl)-1'-methyl-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3c)**



29% yield; 74.5:25.5 er;  $[\alpha]_D^{20} = -60.0$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 10/90, flow rate 1.0 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 7.9$  min,  $t_{\text{minor}} = 9.2$  min).

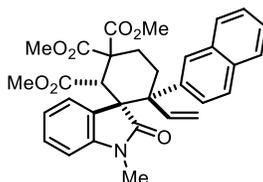
**Trimethyl 1'-methyl-2'-oxo-2-(m-tolyl)-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3g)**



45% yield; 79:21 er;  $[\alpha]_D^{20} = -37.7$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 10/90, flow rate 1.0 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 8.6$  min,  $t_{\text{minor}} = 9.7$  min).

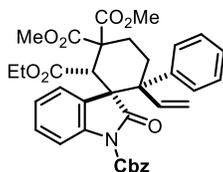
**Trimethyl 1'-methyl-2-(naphthalen-2-yl)-2'-oxo-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3i)**



50% yield; 77:23 er;  $[\alpha]_D^{20} = -66.1$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 10/90, flow rate 1.0 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 9.2$  min,  $t_{\text{minor}} = 10.6$  min).

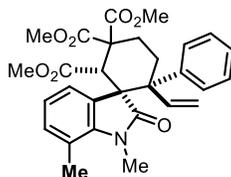
**1'-Benzyl 6-ethyl 5,5-dimethyl 2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-1',5,5,6-tetracarboxylate (3q)**



72% yield; 65:35 er;  $[\alpha]_D^{20} = -35.9$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 10/90, flow rate 1.0 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 9.2$  min,  $t_{\text{minor}} = 14.9$  min).

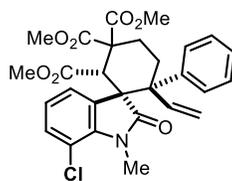
**Trimethyl 1',7'-dimethyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3ad)**



35% yield; 82.5:17.5 er;  $[\alpha]_D^{20} = -33.4$  (*c* 1.00, CH<sub>2</sub>Cl<sub>2</sub>);

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 10/90, flow rate 1.0 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 8.7$  min,  $t_{\text{minor}} = 9.9$  min).

**Trimethyl 7'-chloro-1'-methyl-2'-oxo-2-phenyl-2-vinylspiro[cyclohexane-1,3'-indoline]-5,5,6-tricarboxylate (3af)**

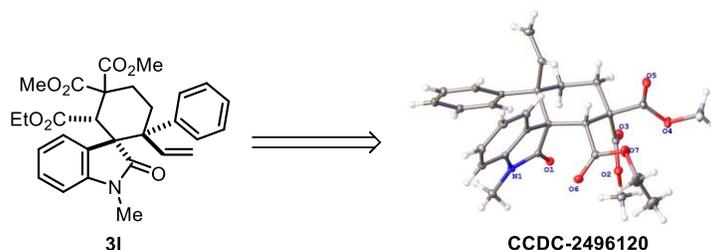


68% yield; 70:30 er;  $[\alpha]_D^{20} = -35.4$  ( $c$  1.00,  $\text{CH}_2\text{Cl}_2$ );

The ee was determined by HPLC (Chiralpak IC, EtOH/hexane = 8/92, flow rate 0.8 mL/min,  $\lambda = 254$  nm,  $t_{\text{major}} = 10.0$  min,  $t_{\text{minor}} = 11.0$  min).

## 9. X-ray crystal structure of compound 31

Single crystal of compound **31** was prepared from the mixture solvent of EtOH/ dichloromethane ( $V : V = 2/1$ ) at room temperature by slow evaporation of solvent. A suitable crystal was selected and on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 100.00(10) K during data collection. Using Olex2 [5], the structure was solved with the SHELXS [6] structure solution program using Direct Methods and refined with the SHELXL [7] refinement package using Least Squares minimisation.



ORTEP of **31** (at 50% level)

**Table 4 Crystal data and structure refinement for 3k (CCDC-2496120).**

Identification code	<b>31</b>
Empirical formula	$\text{C}_{29}\text{H}_{31}\text{NO}_7$
Formula weight	505.55
Temperature/K	100.00(10)
Crystal system	monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	10.23342(9)
$b/\text{\AA}$	10.91871(9)
$c/\text{\AA}$	22.88257(16)
$\alpha/^\circ$	90
$\beta/^\circ$	93.5134(7)
$\gamma/^\circ$	90
Volume/ $\text{\AA}^3$	2552.00(4)
$Z$	4
$\rho_{\text{calc}}/\text{cm}^3$	1.316

$\mu/\text{mm}^{-1}$	0.772
F(000)	1072.0
Crystal size/ $\text{mm}^3$	$0.14 \times 0.13 \times 0.12$
Radiation	Cu K $\alpha$ ( $\lambda = 1.54184$ )
2 $\Theta$ range for data collection/ $^\circ$	7.742 to 146.658
Index ranges	$-12 \leq h \leq 11, -13 \leq k \leq 13, -28 \leq l \leq 28$
Reflections collected	18836
Independent reflections	4975 [ $R_{\text{int}} = 0.0295, R_{\text{sigma}} = 0.0251$ ]
Data/restraints/parameters	4975/7/357
Goodness-of-fit on $F^2$	1.025
Final R indexes [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0423, wR_2 = 0.1135$
Final R indexes [all data]	$R_1 = 0.0457, wR_2 = 0.1167$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.54/-0.39

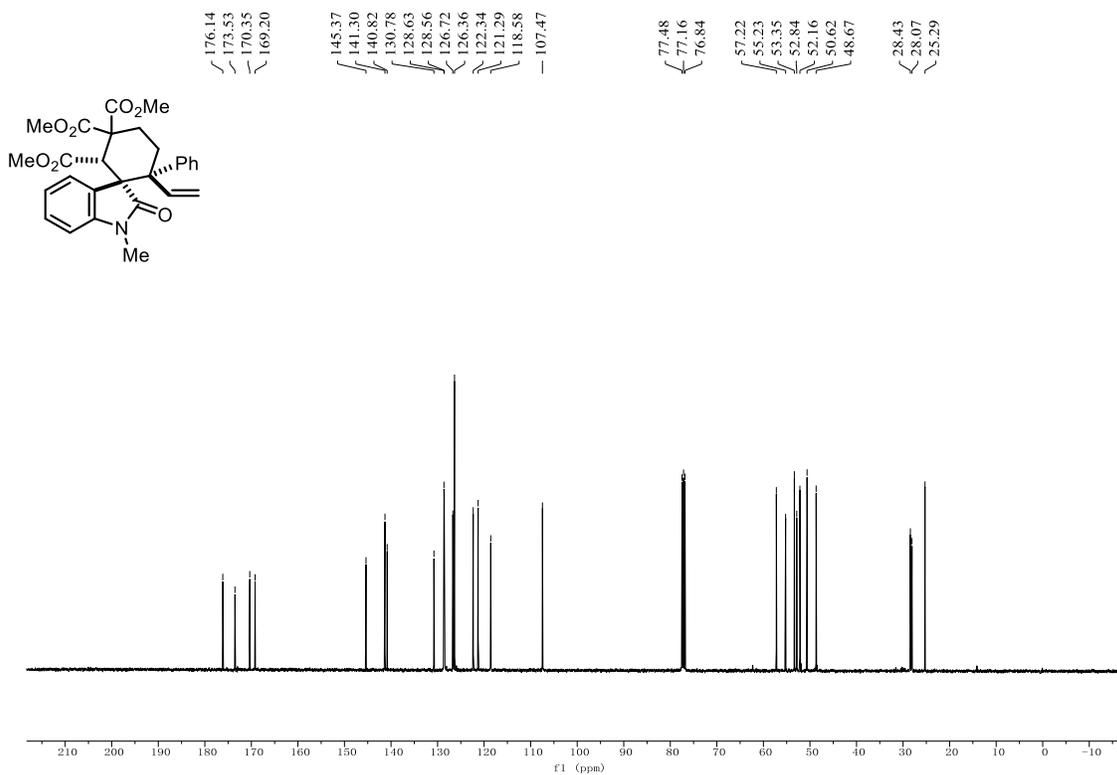
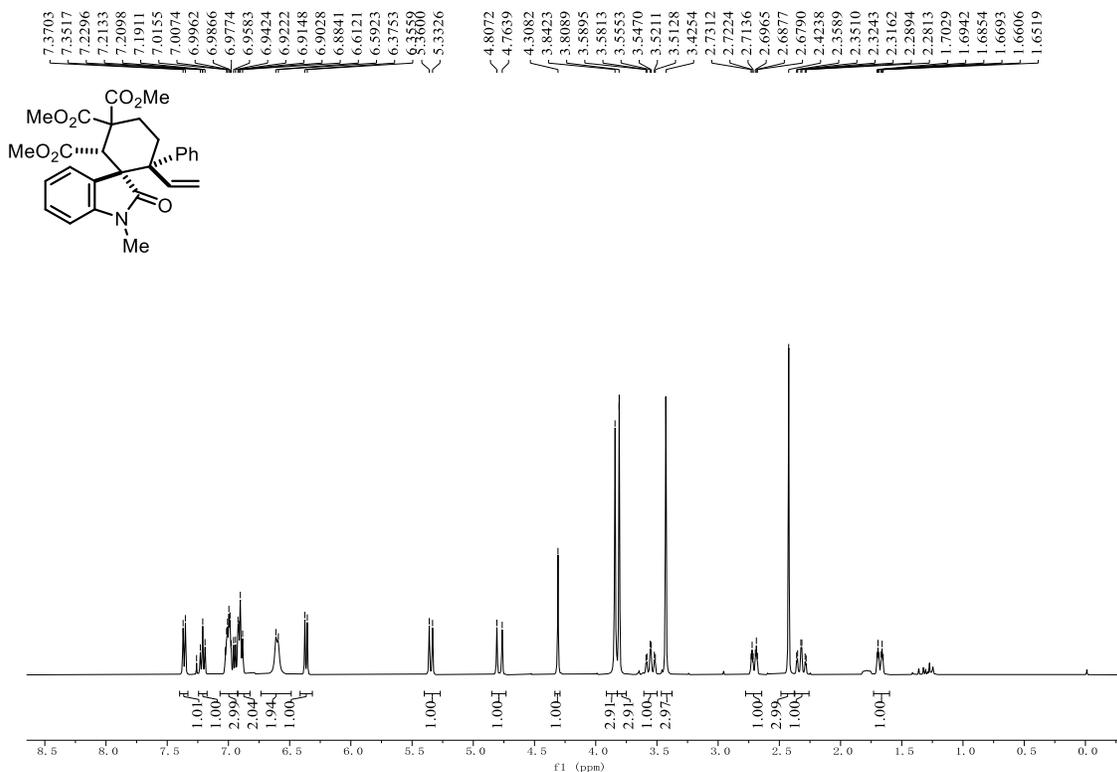
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## References:

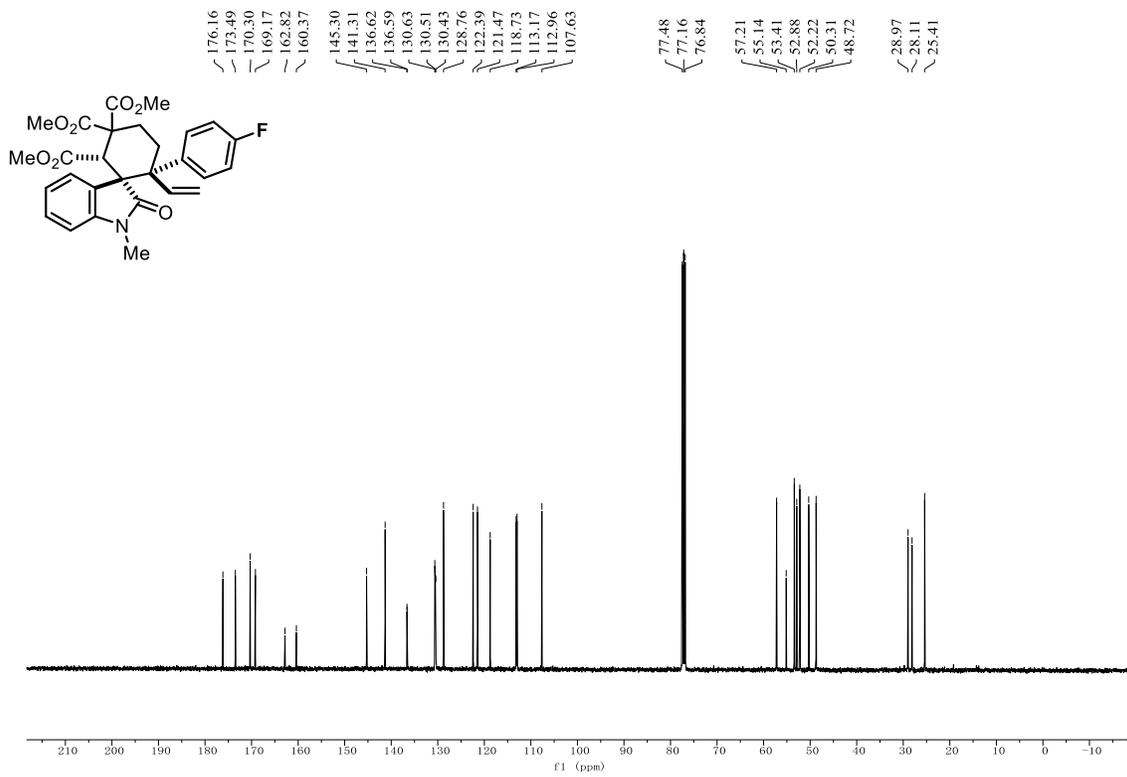
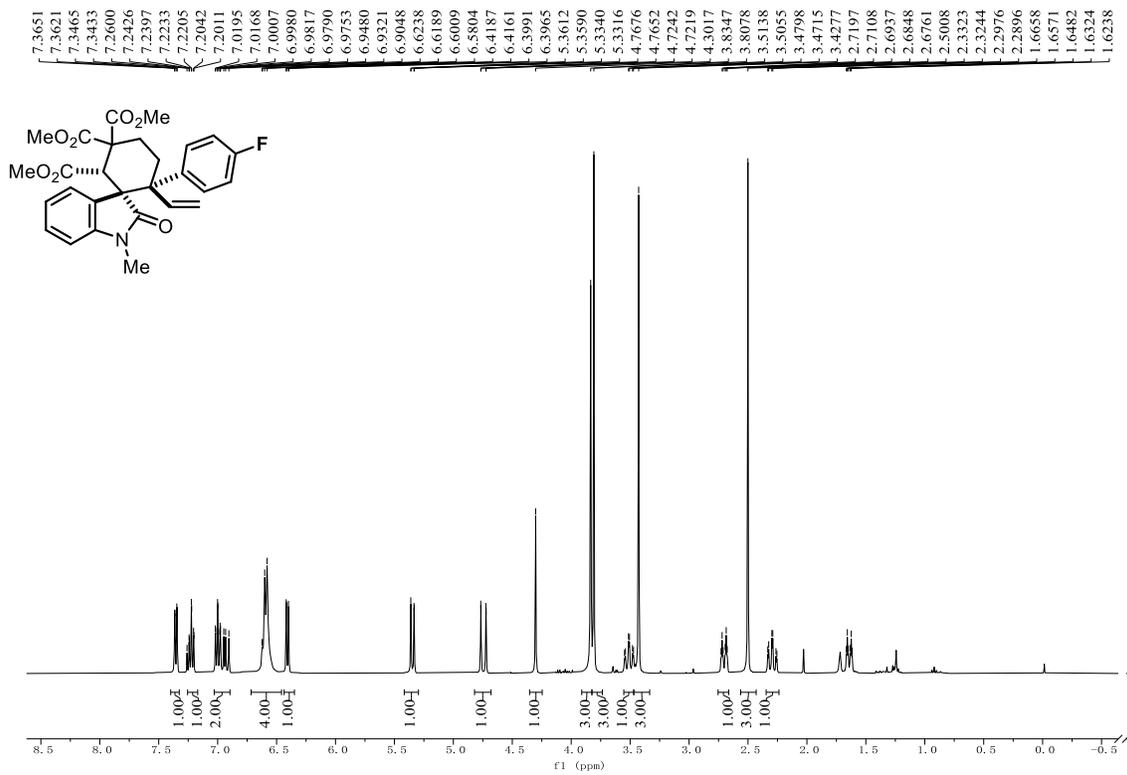
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- [6] Sheldrick, G. M. *Acta Cryst.* 2008, **A64**, 112-122.
- [7] Sheldrick, G. M. *Acta Cryst.* 2015, **C71**, 3-8.

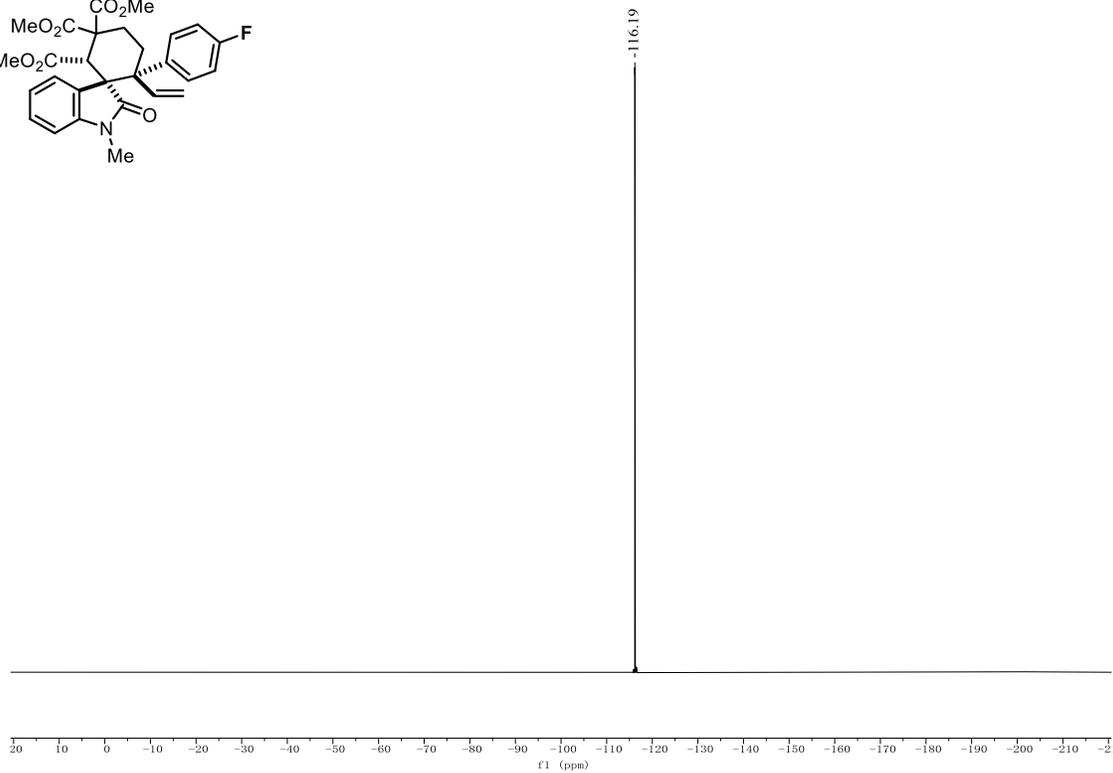
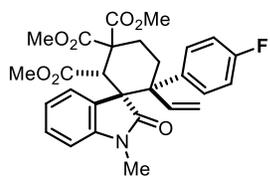
# 10. <sup>1</sup>H NMR, <sup>13</sup>C NMR and HPLC spectra for compounds 3, 5, 7, 8, 9, 10 and 11

## <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3a

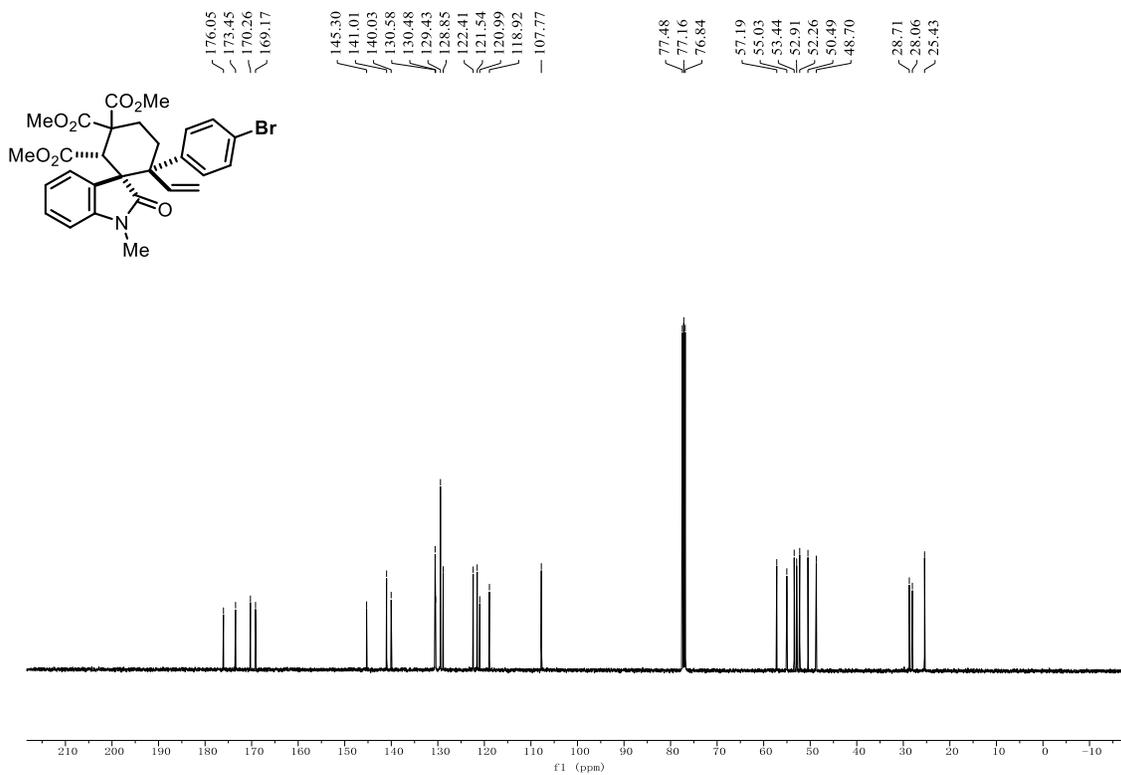
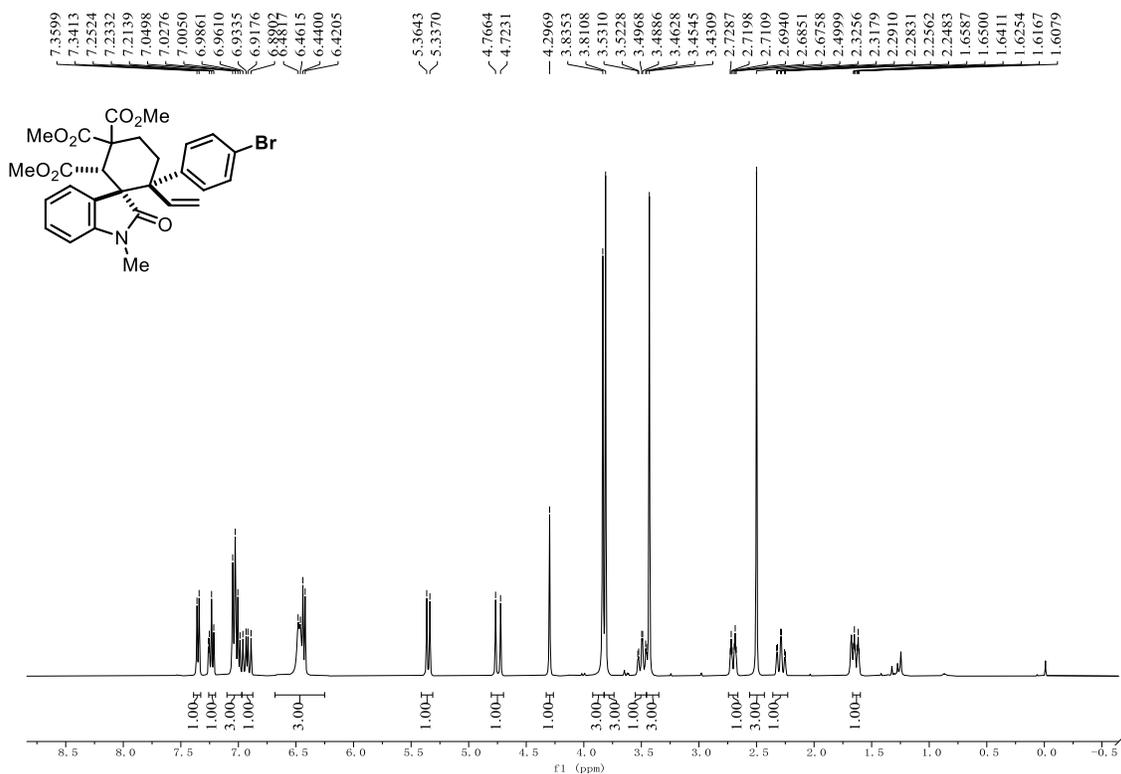


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ )  
of 3b**

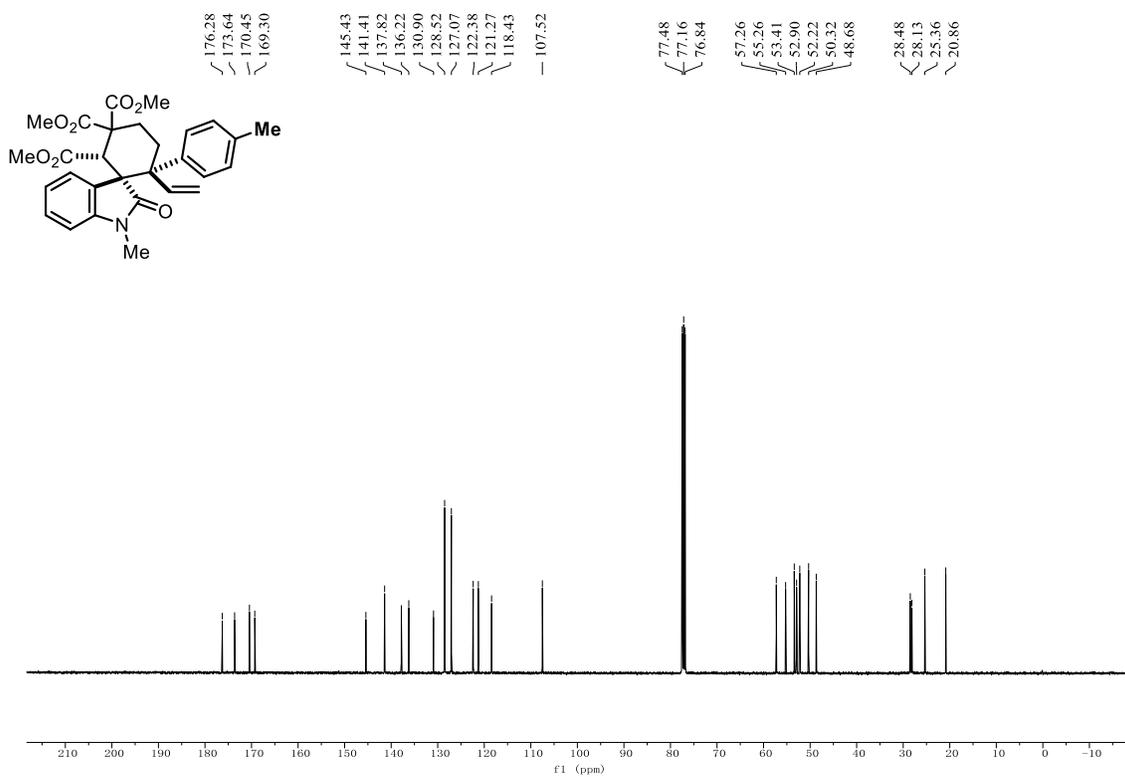
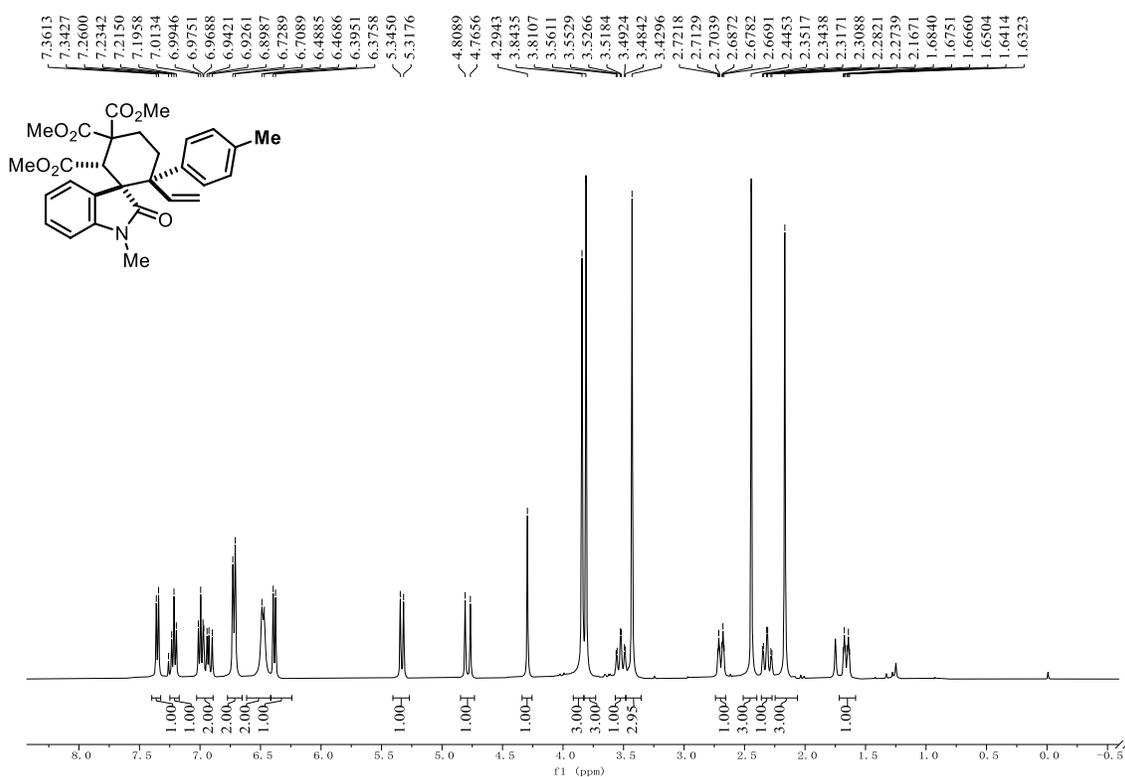




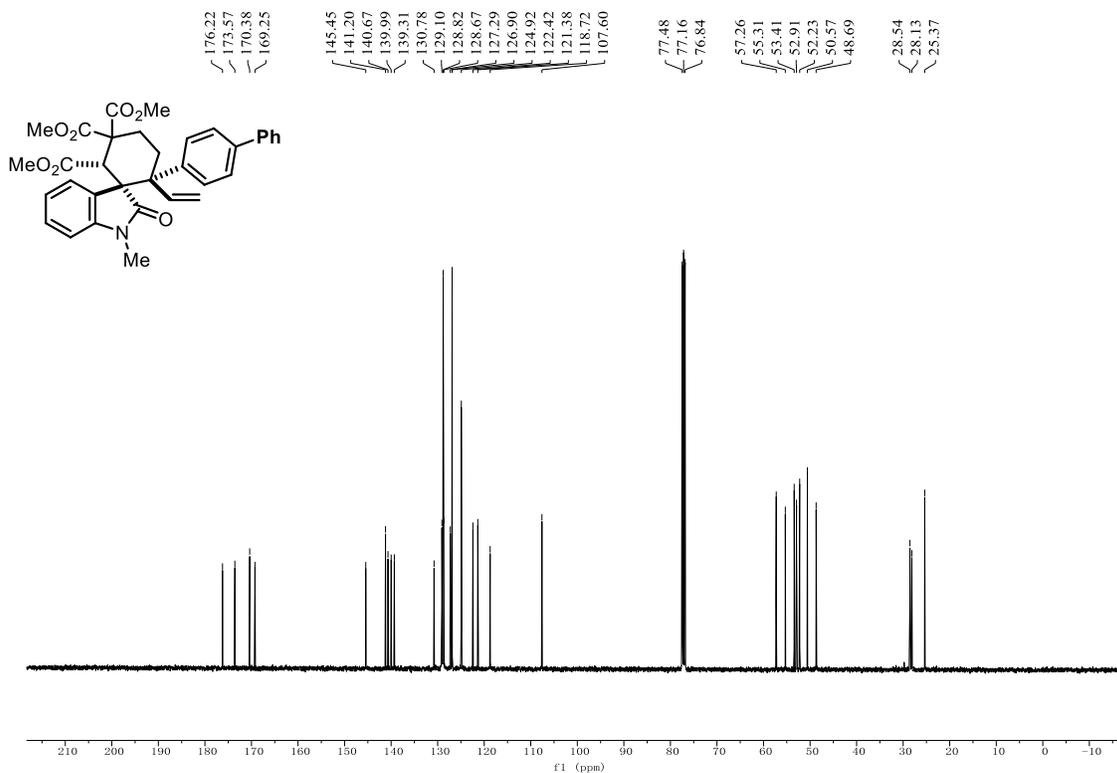
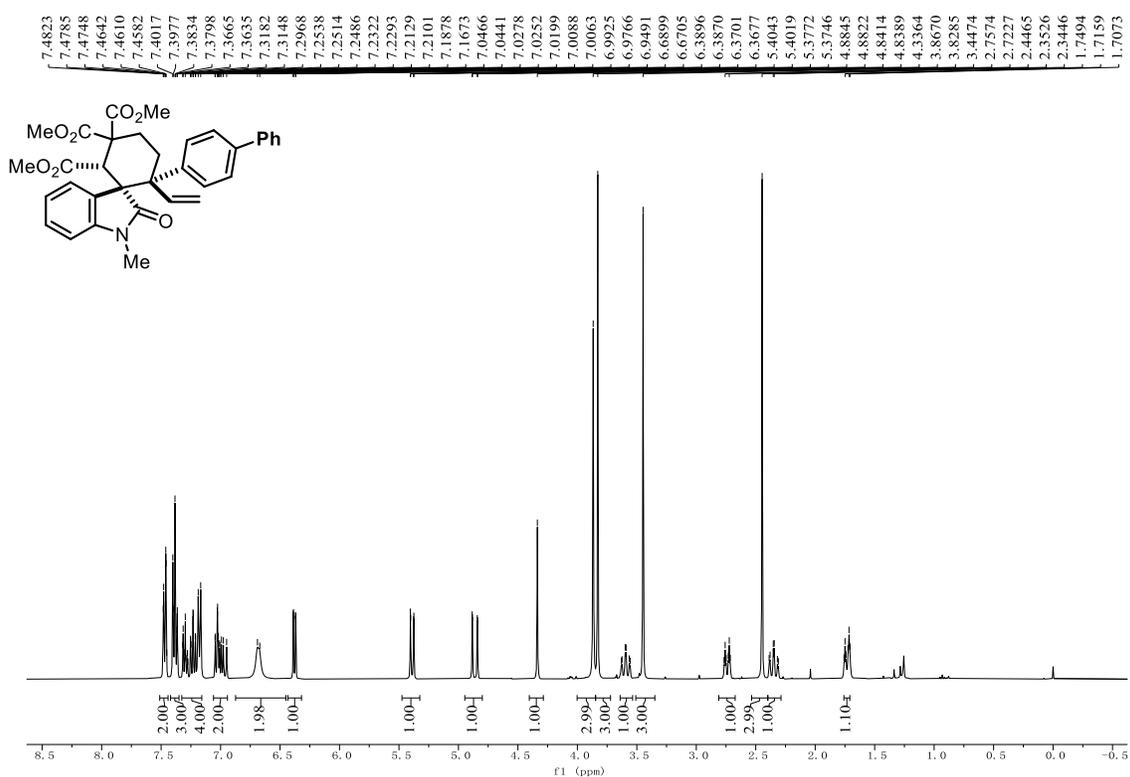
### $^1\text{H}$ NMR (400 MHz, $\text{CDCl}_3$ ) and $^{13}\text{C}$ NMR (101 MHz, $\text{CDCl}_3$ ) of 3c



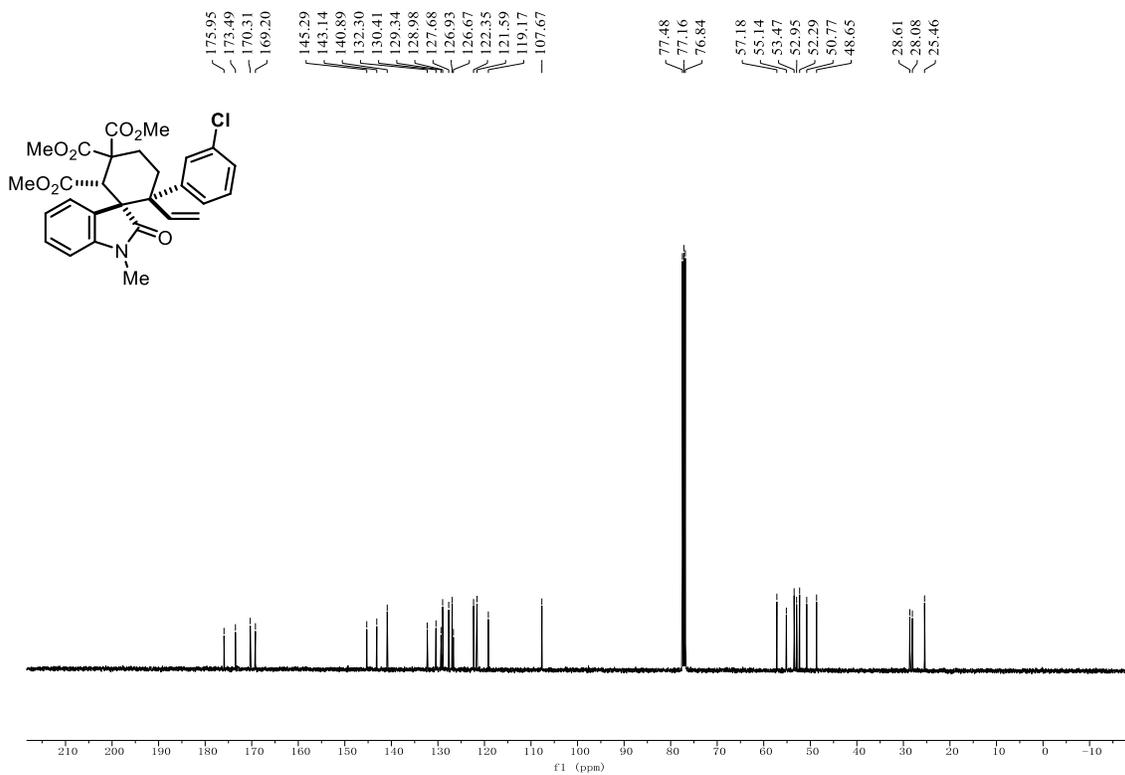
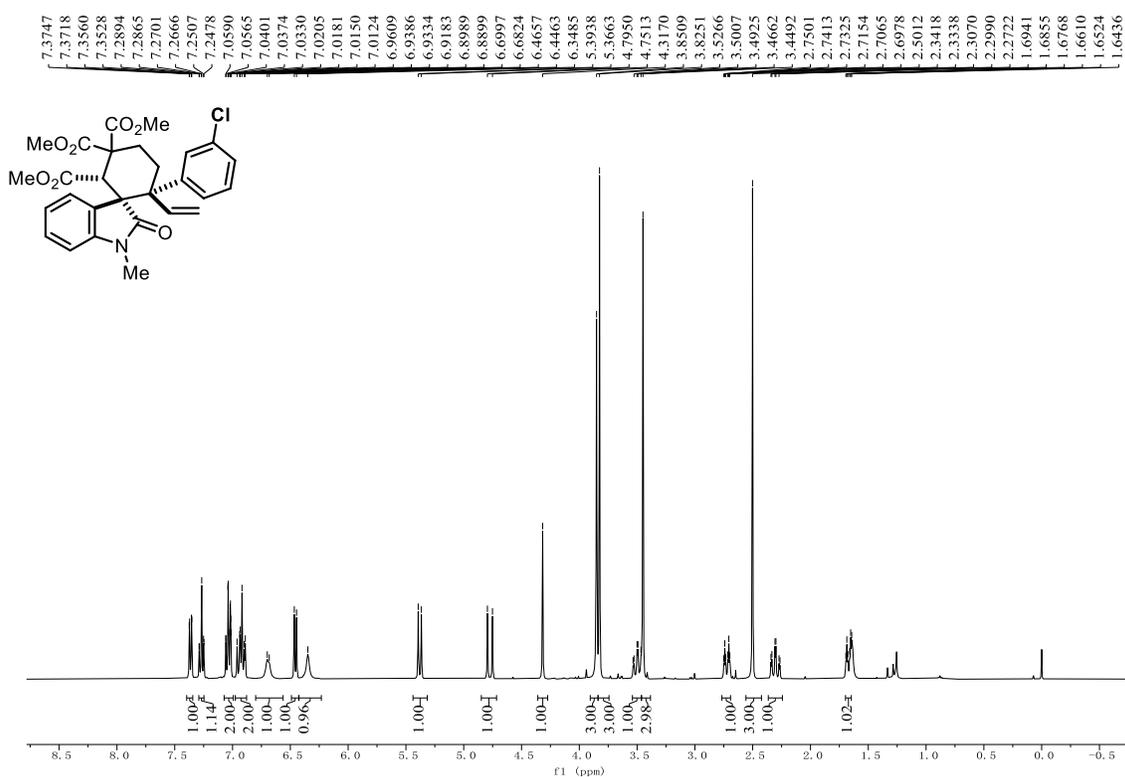
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3d**



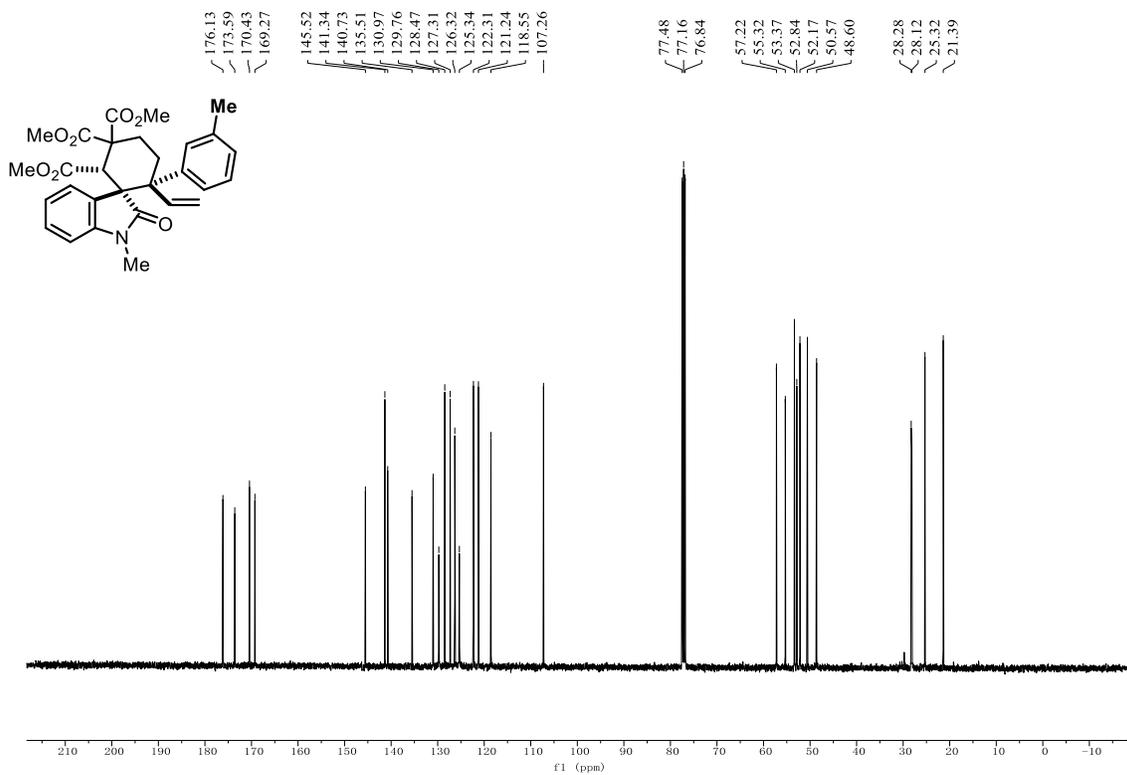
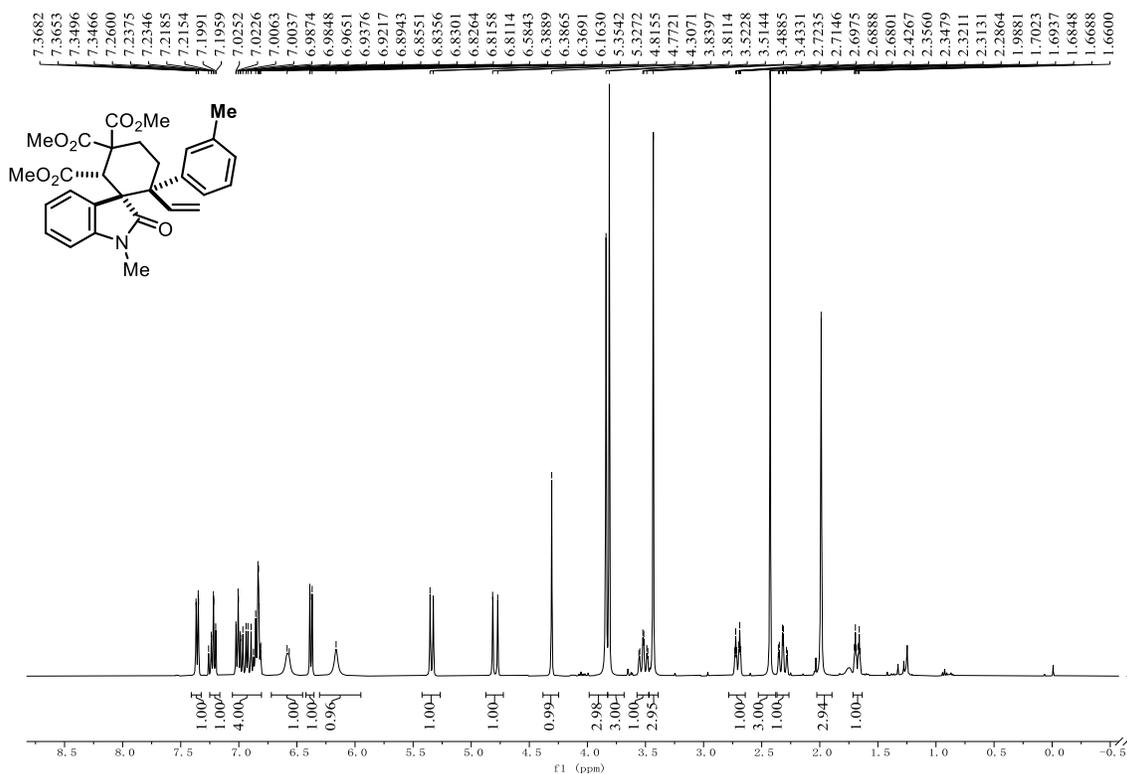
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3e**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3f**

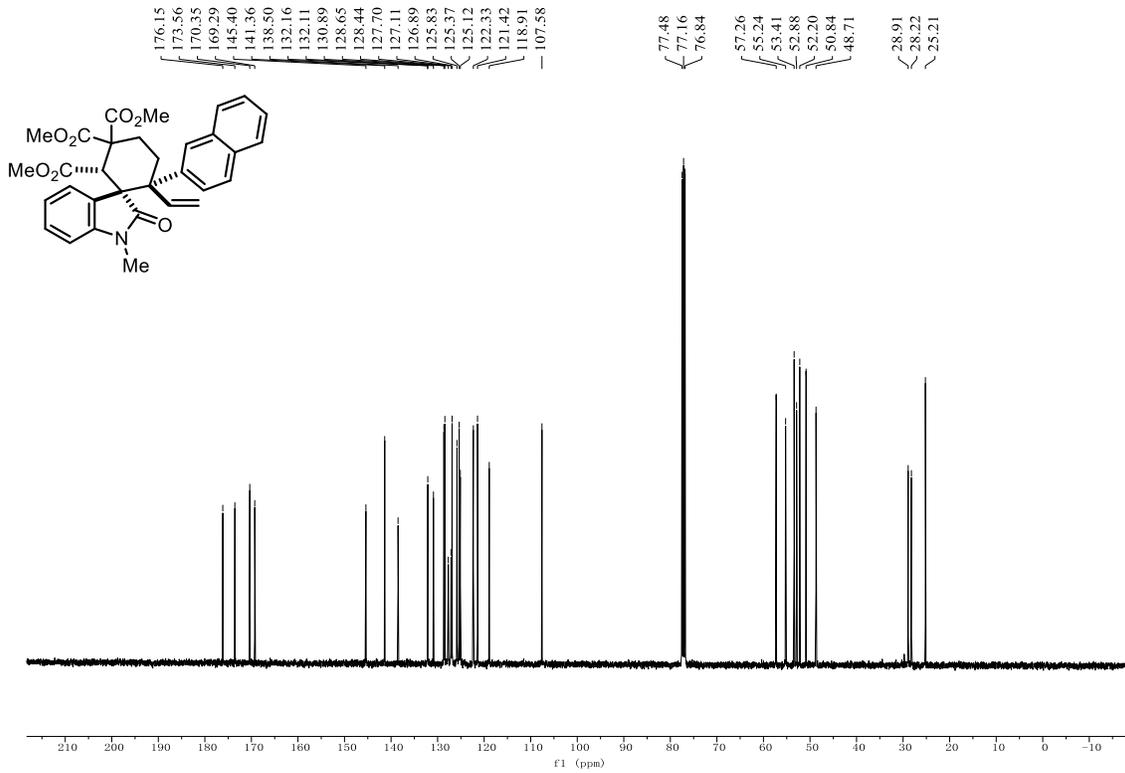
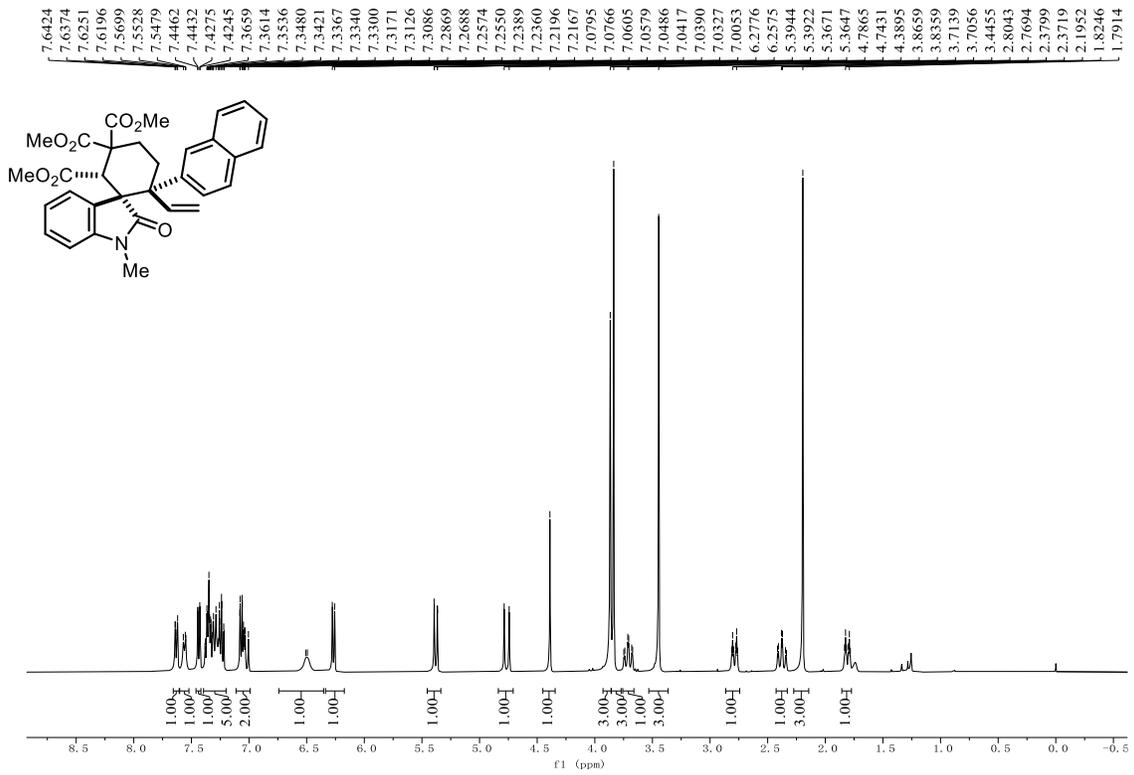


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3g**

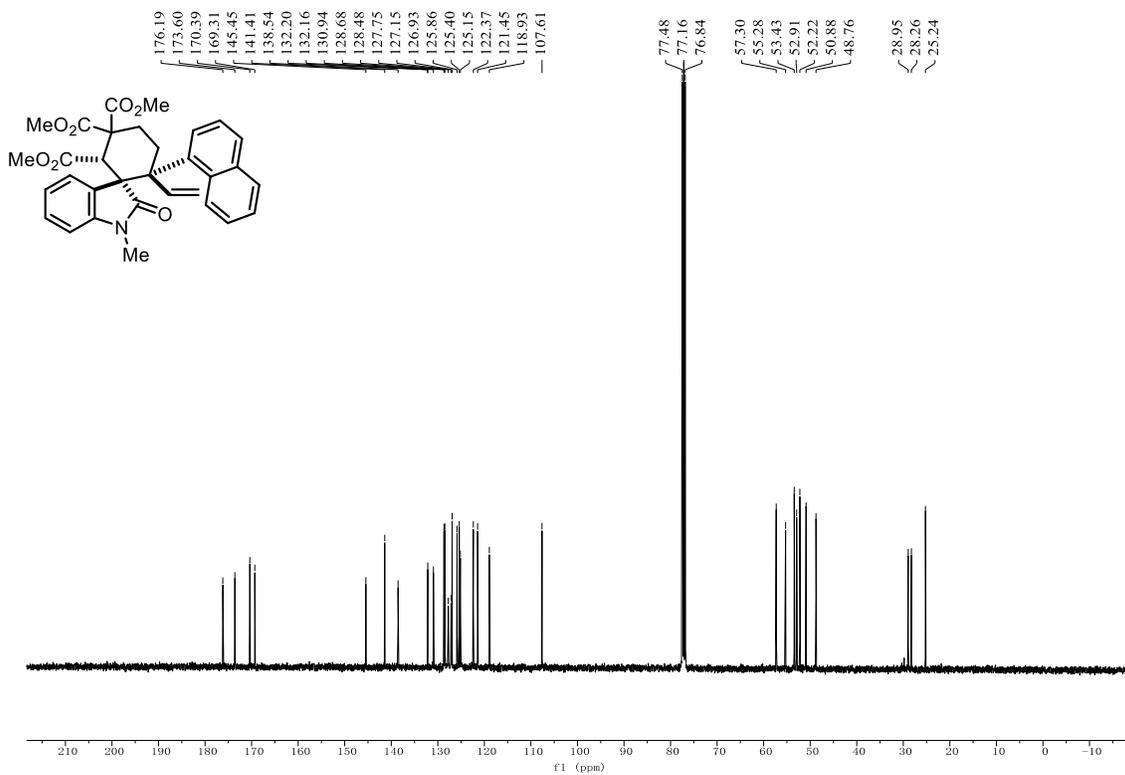
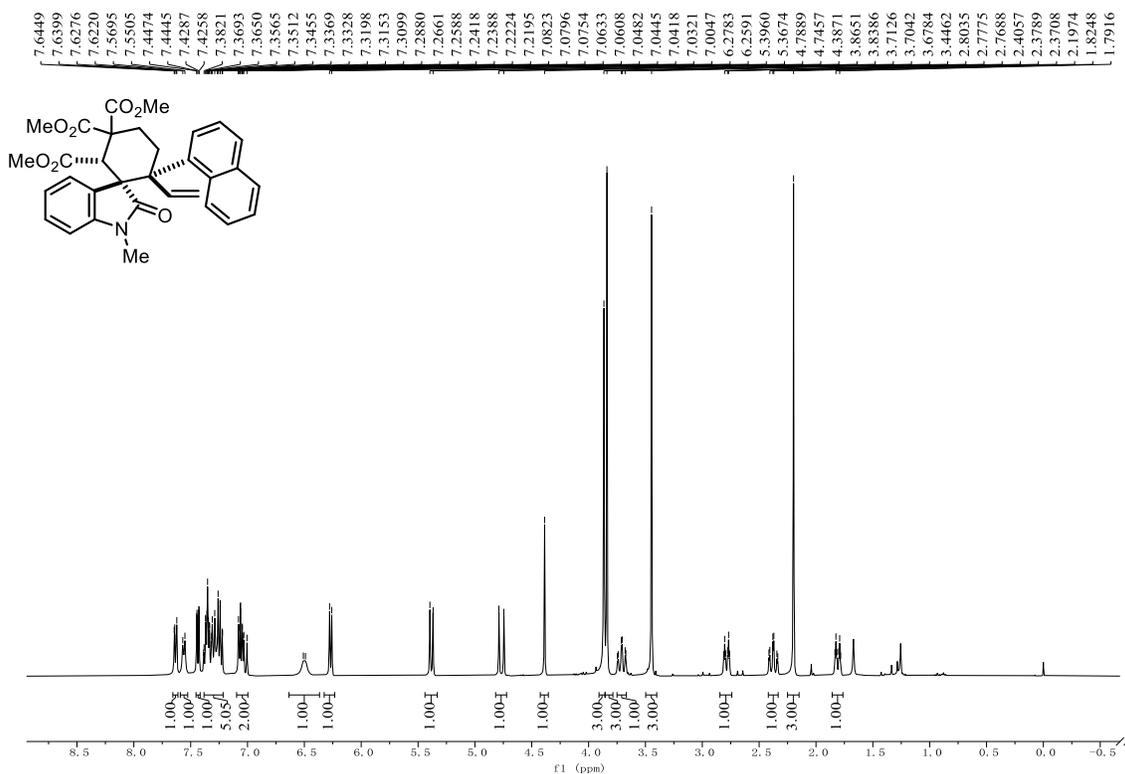




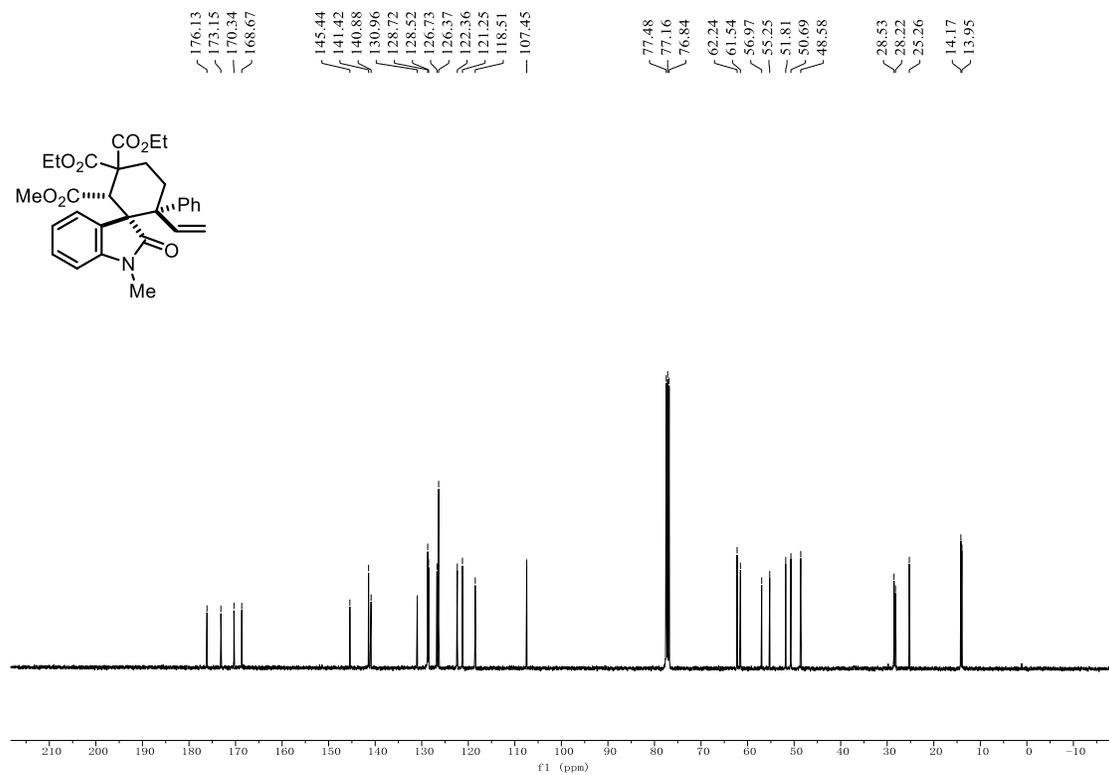
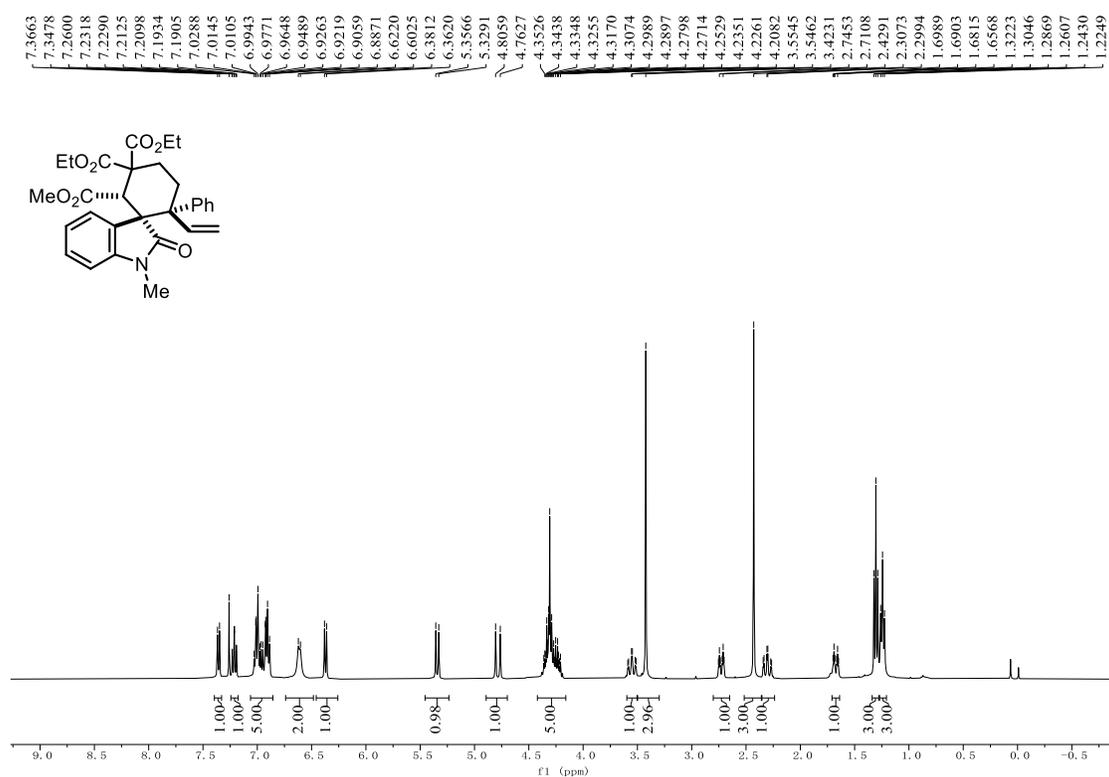
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3i**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3j**

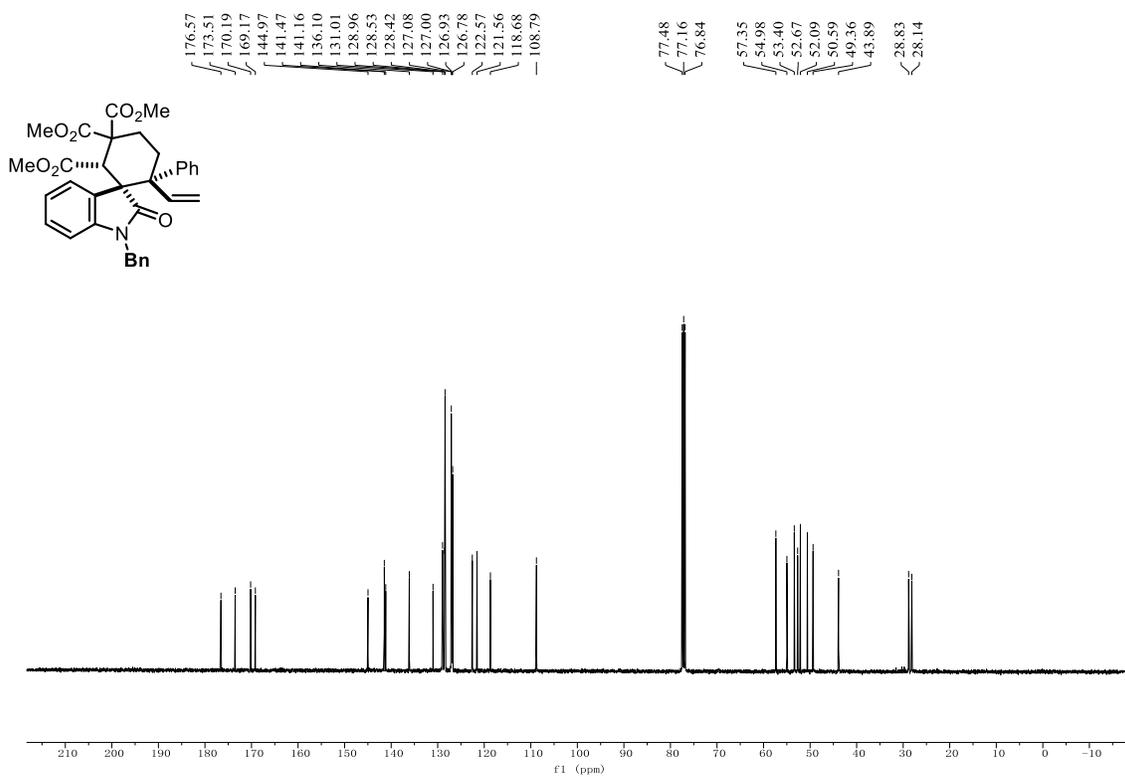
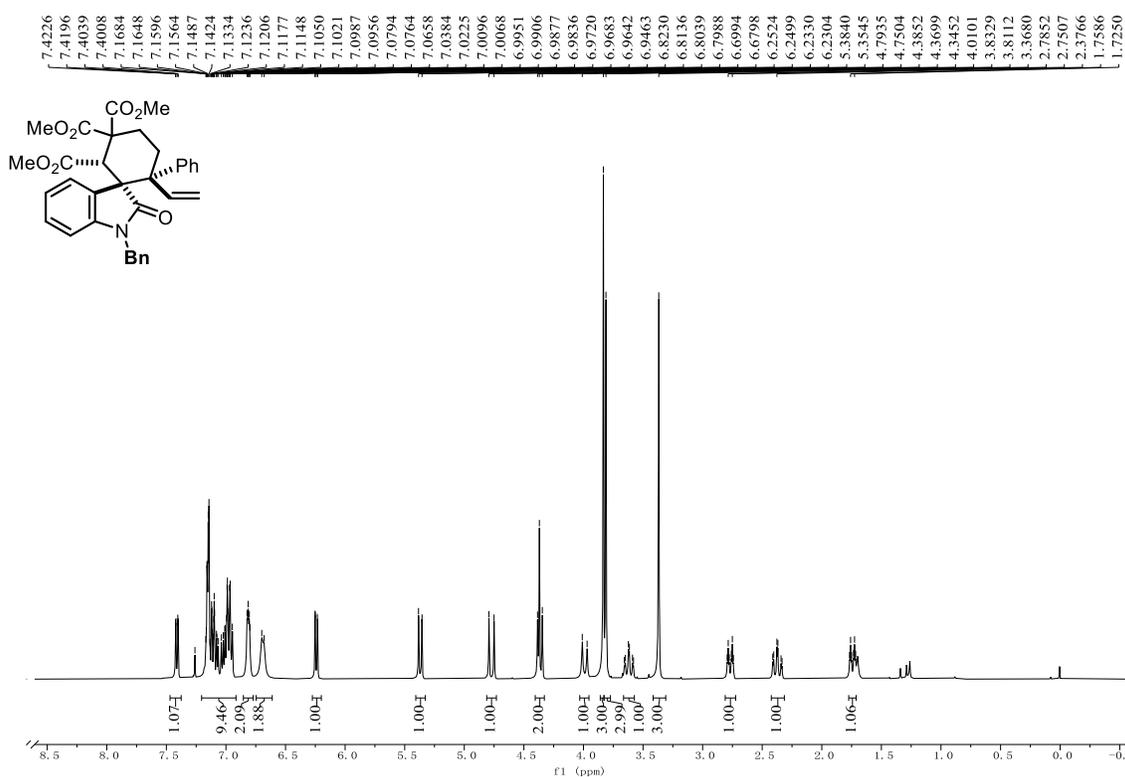


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3k**



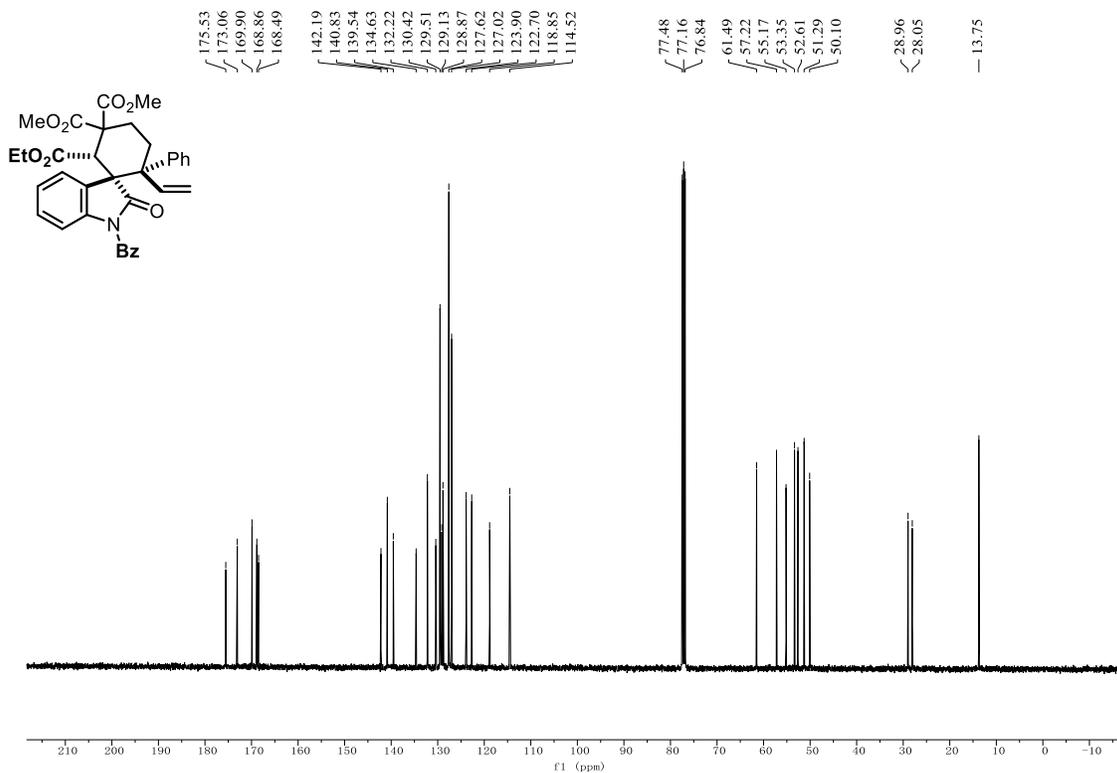
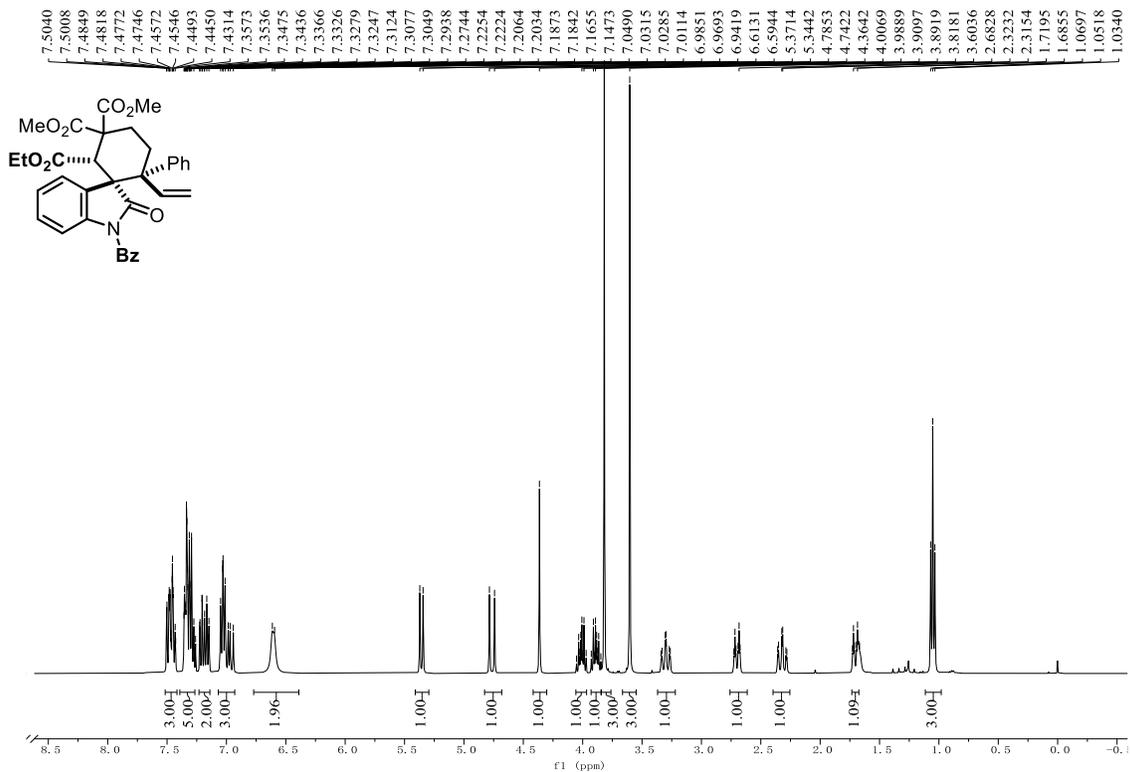


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3m**

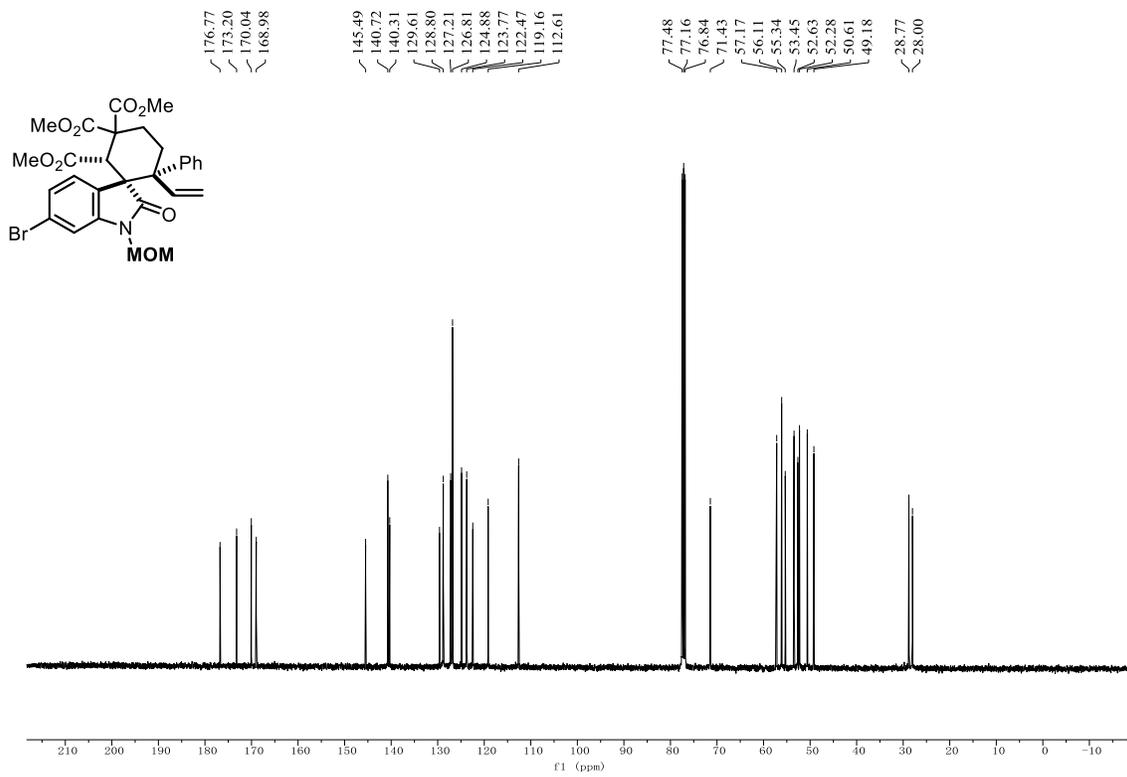
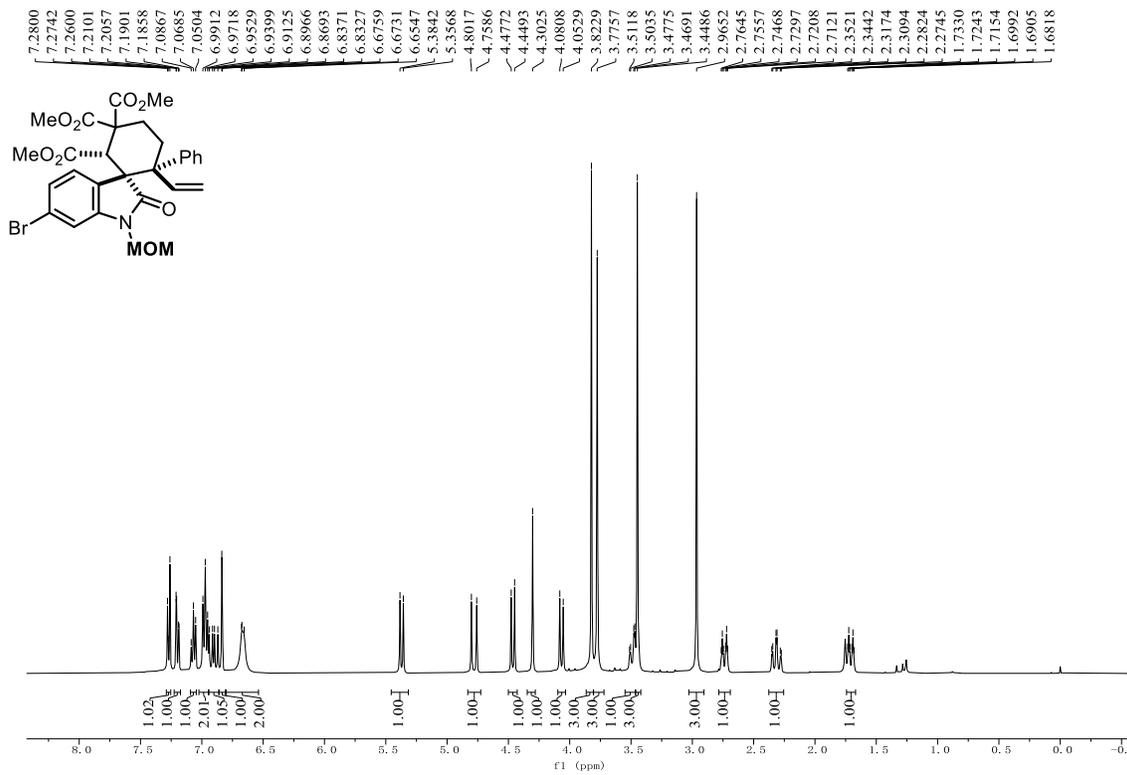




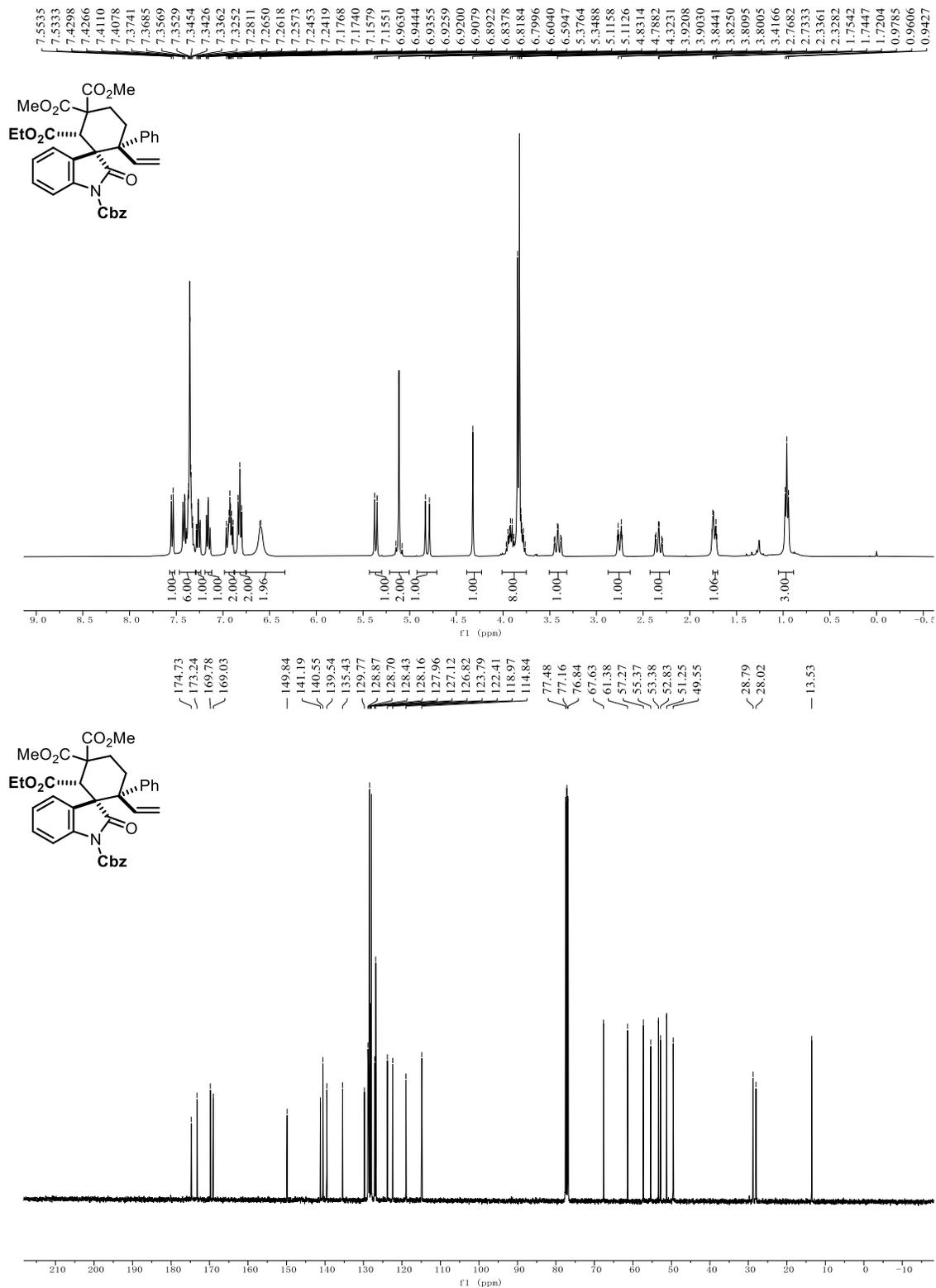
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3o**



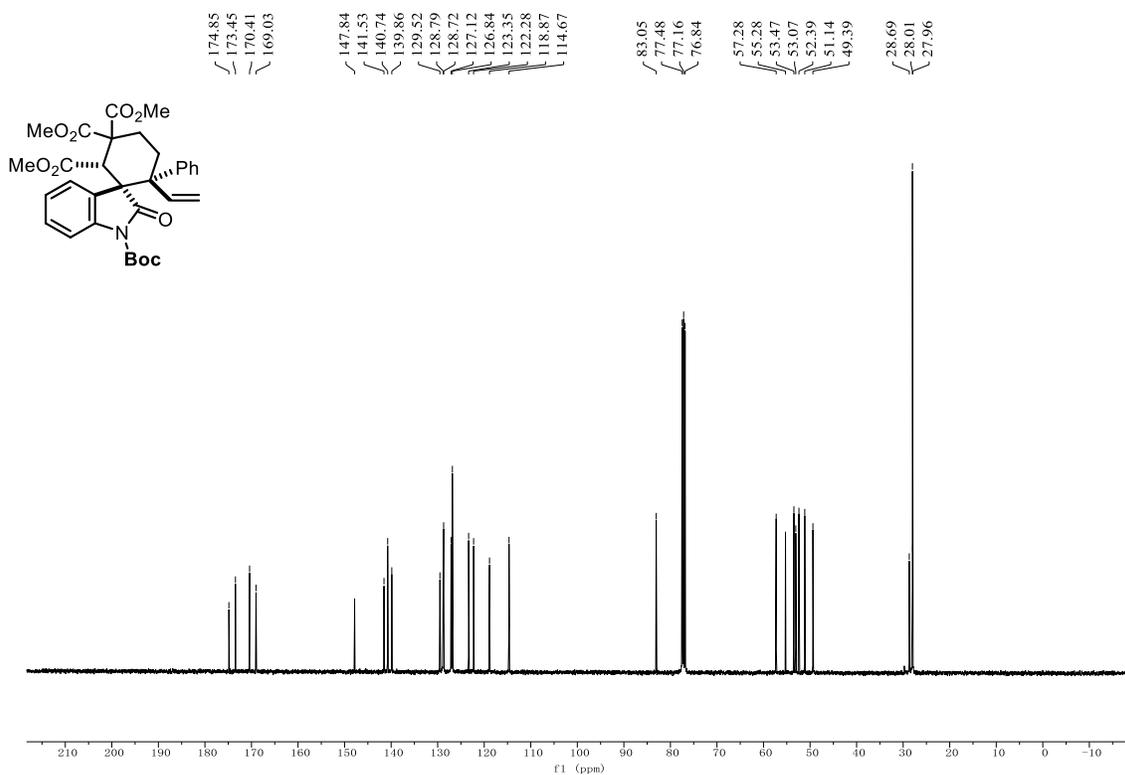
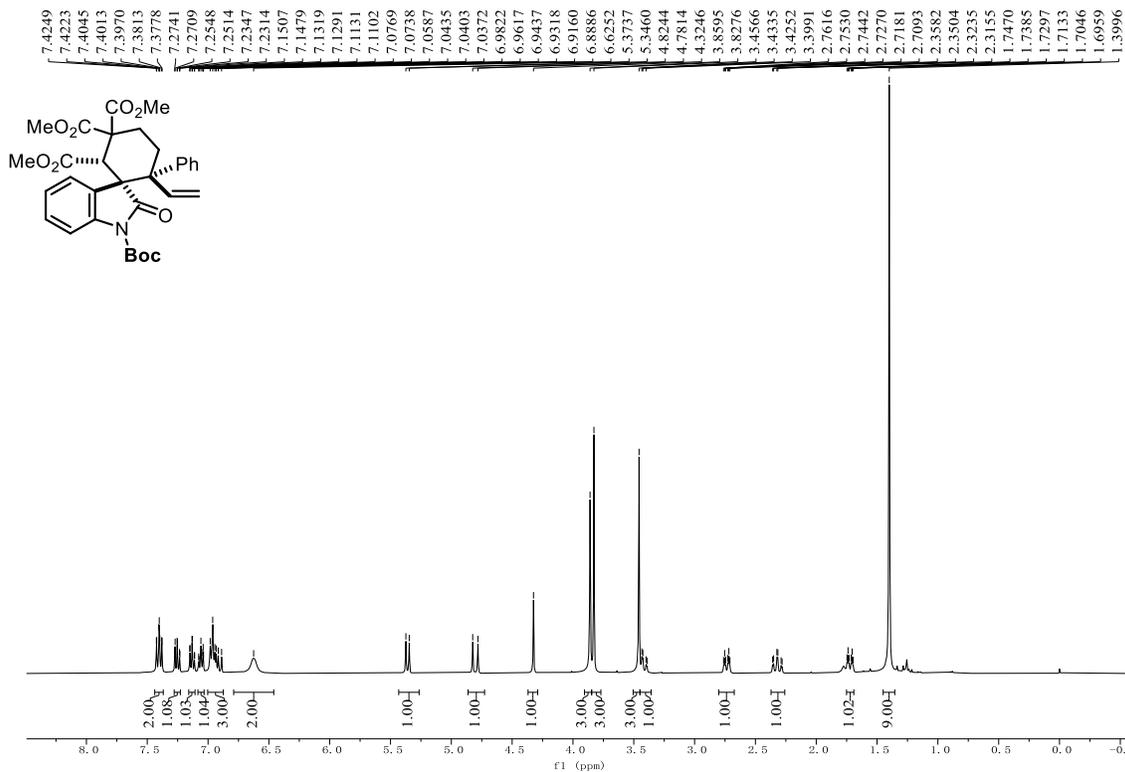
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3p****



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of **3q****

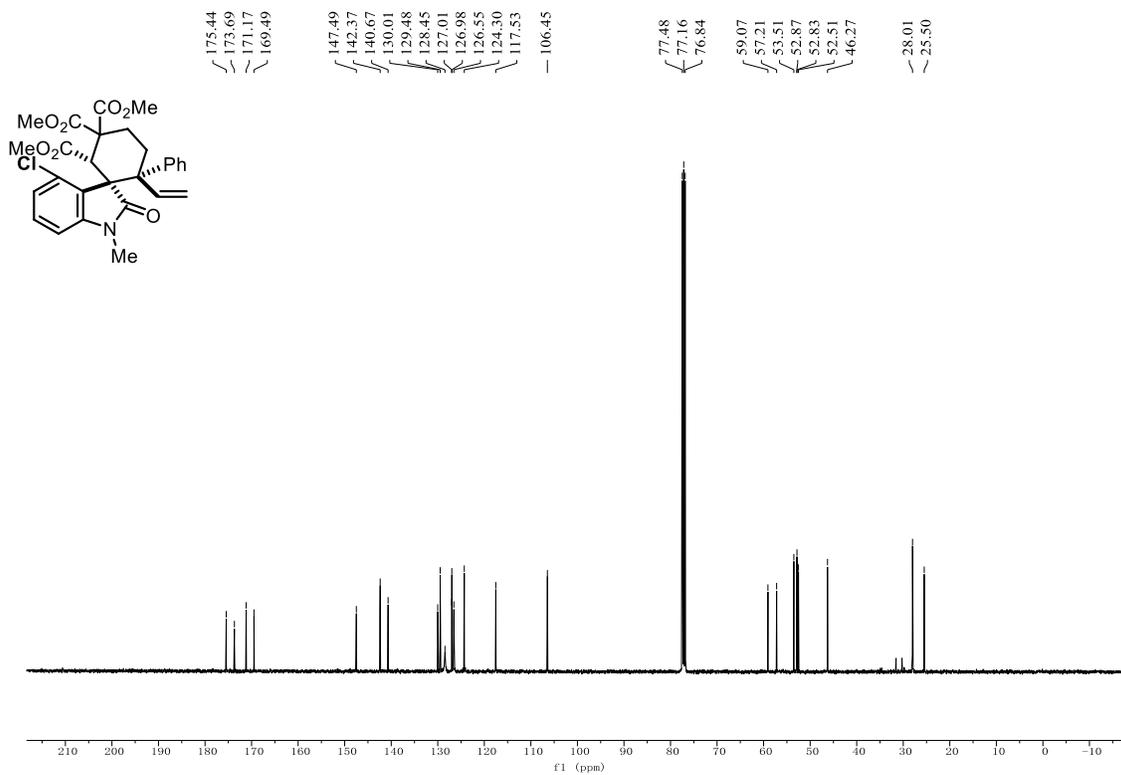
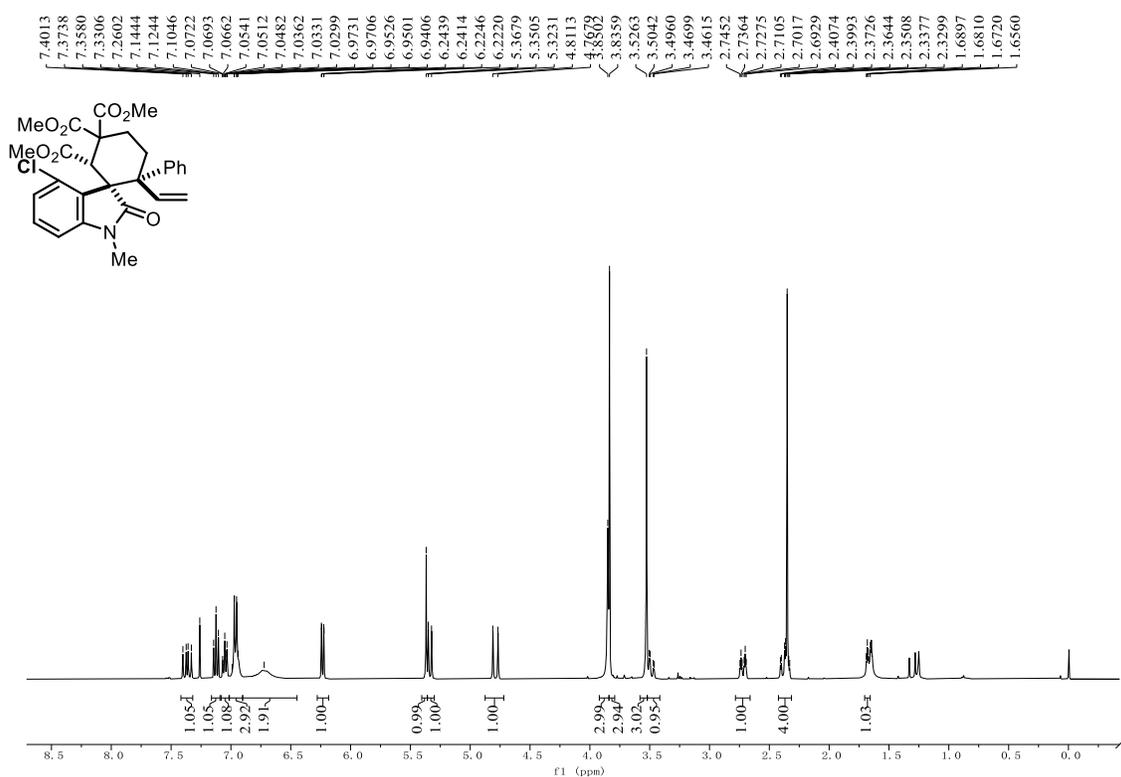


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3r**

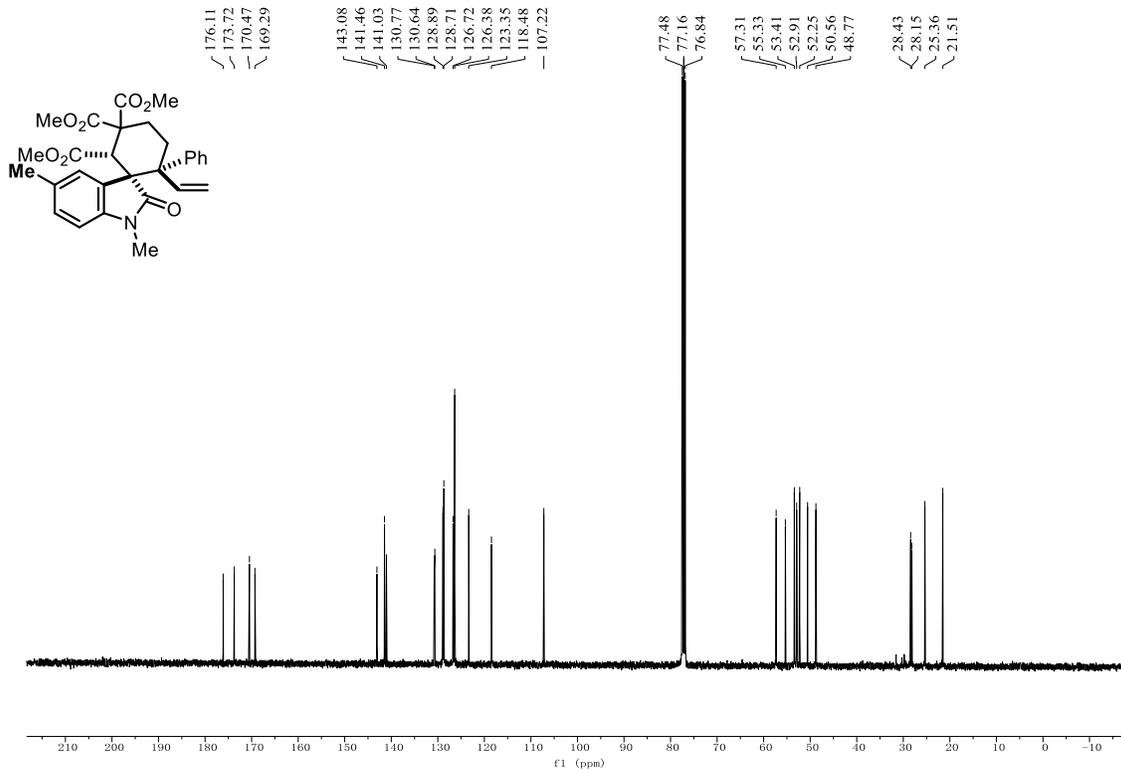
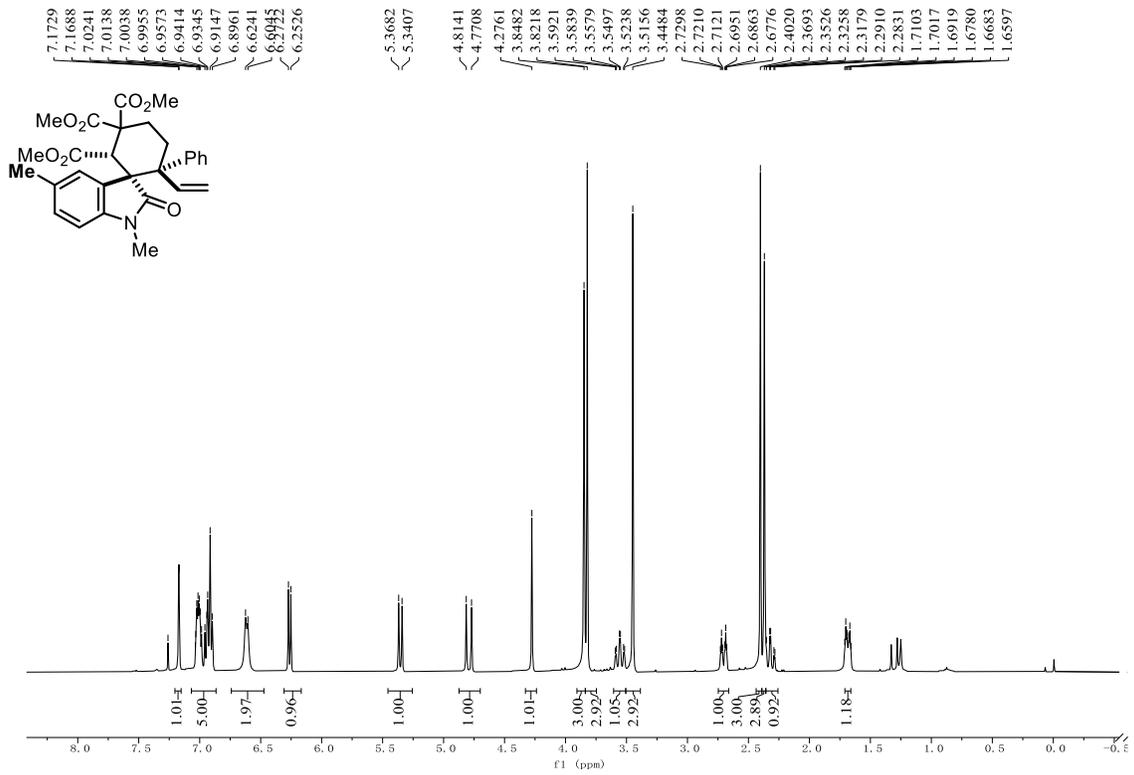




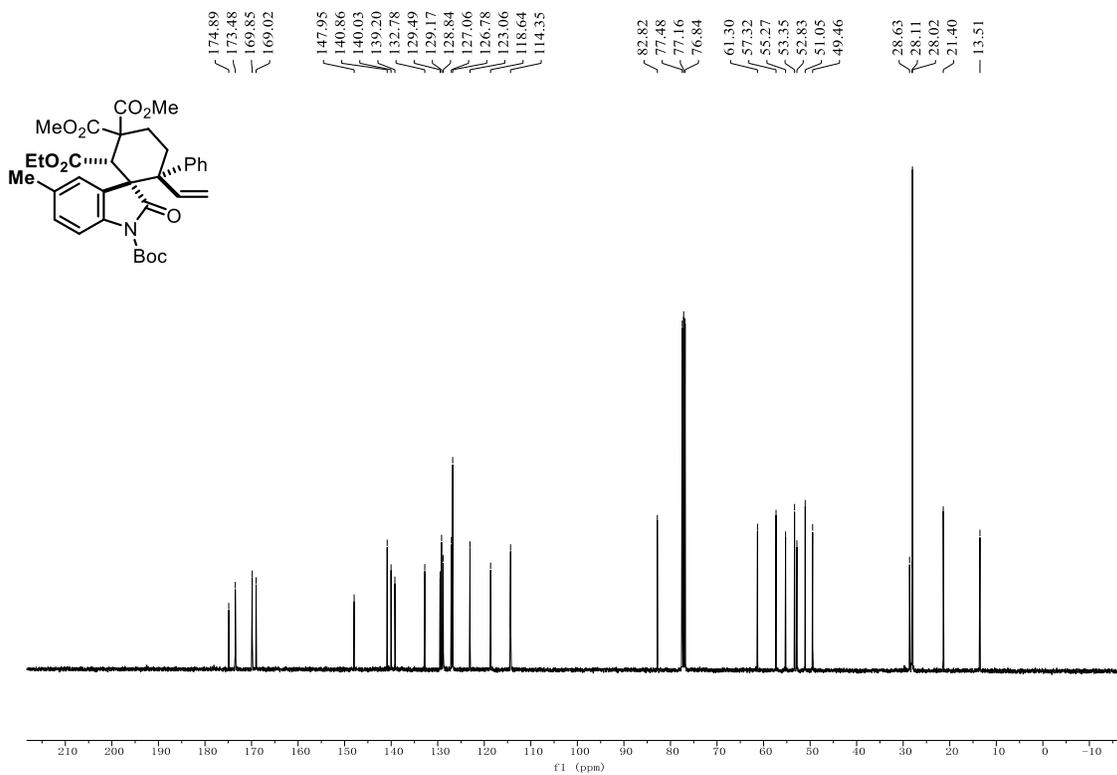
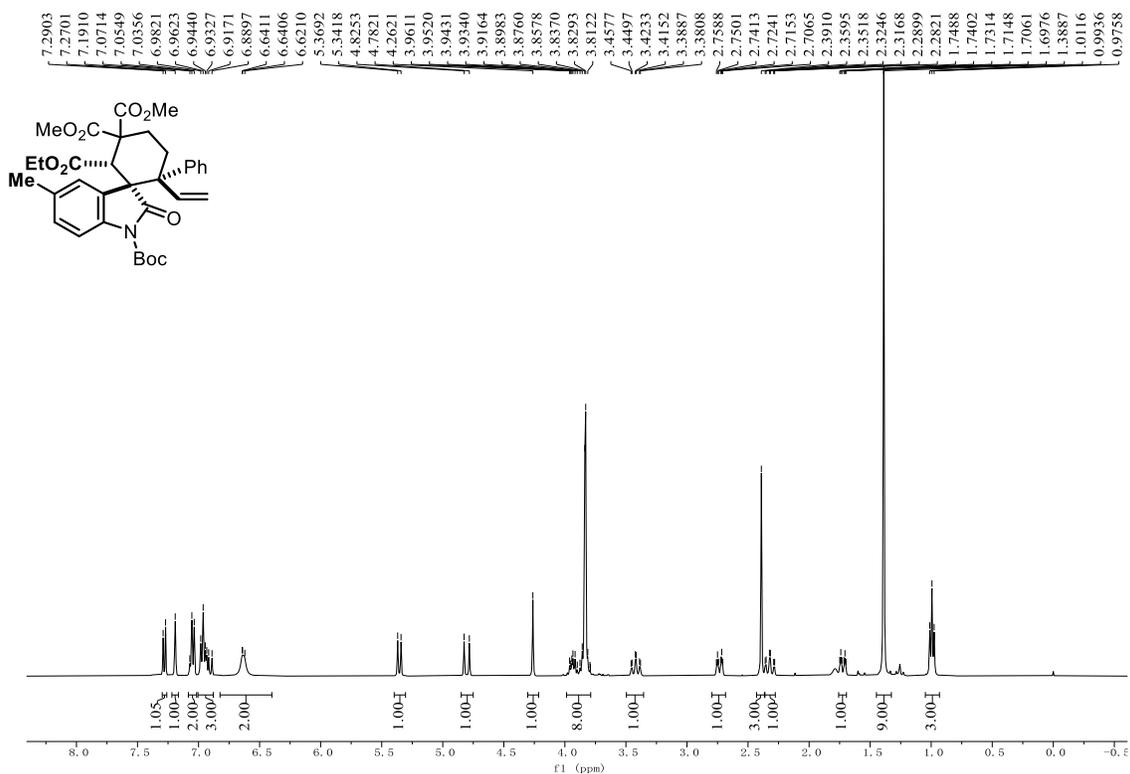
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3t



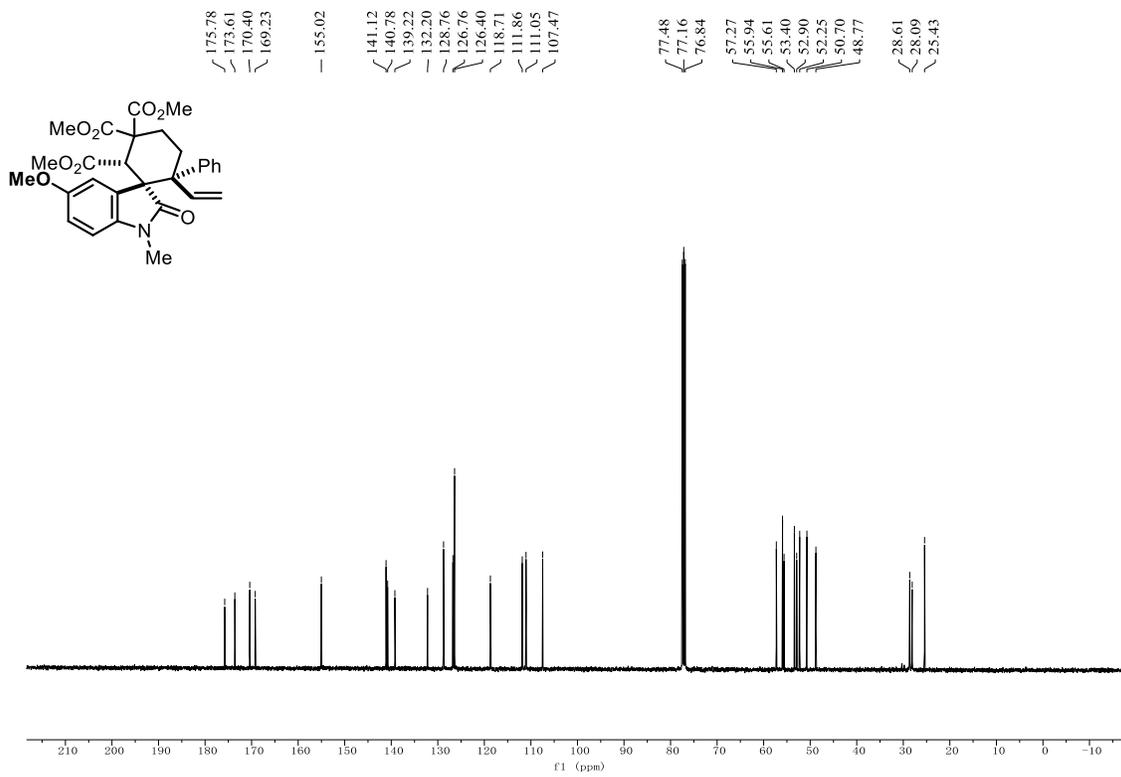
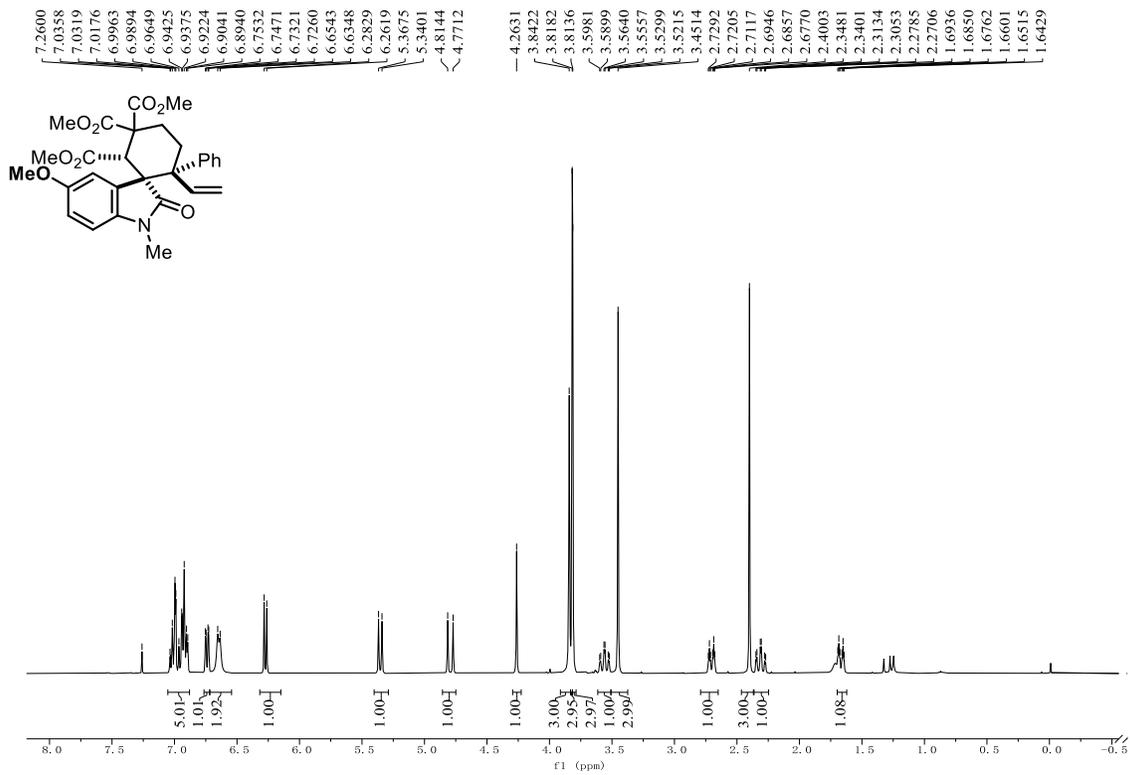
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3u**



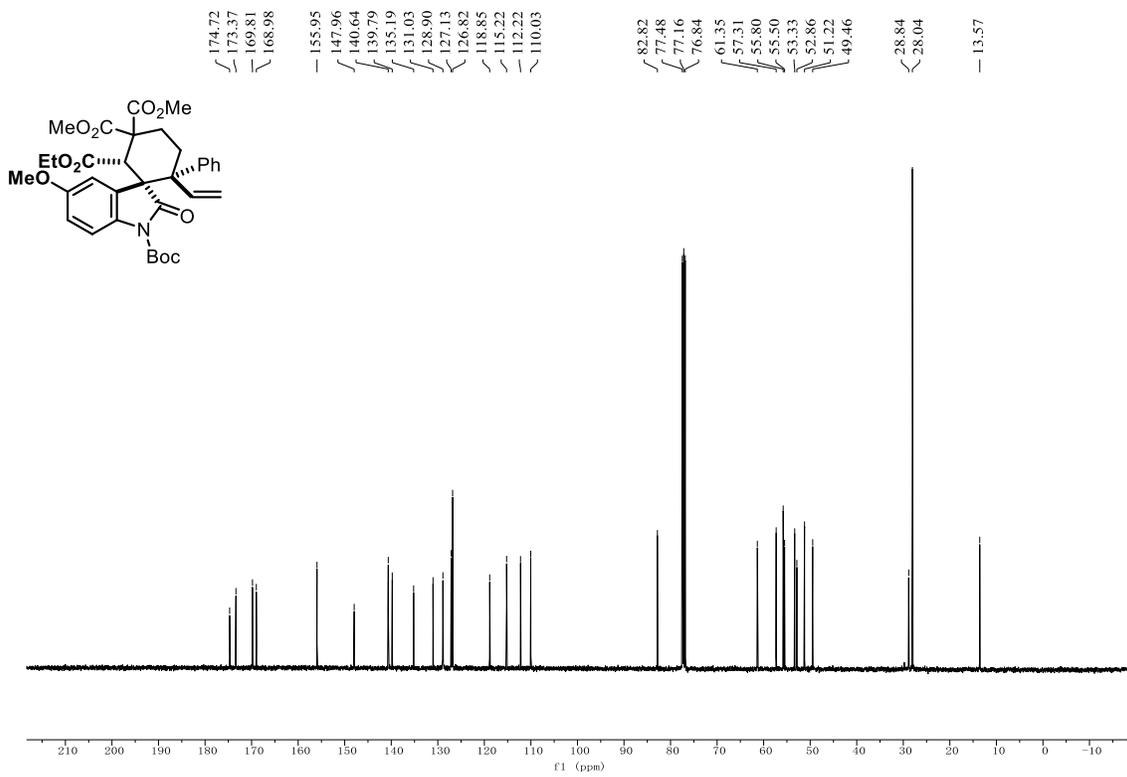
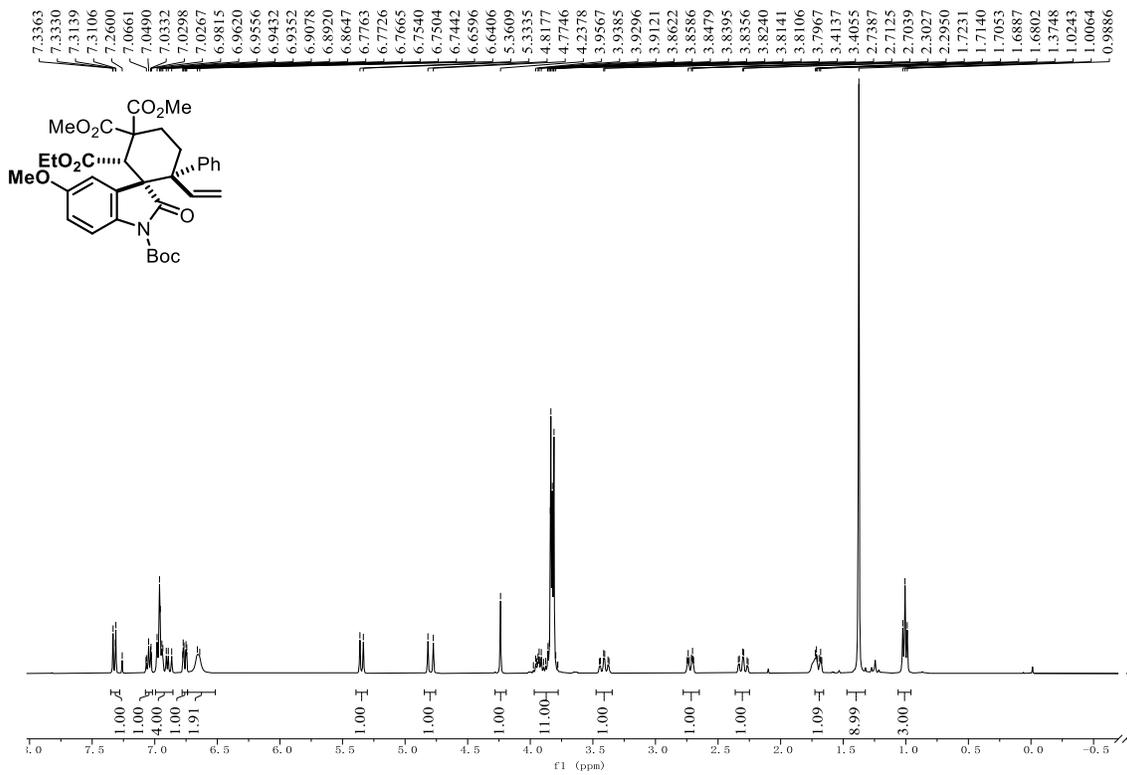
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3v**



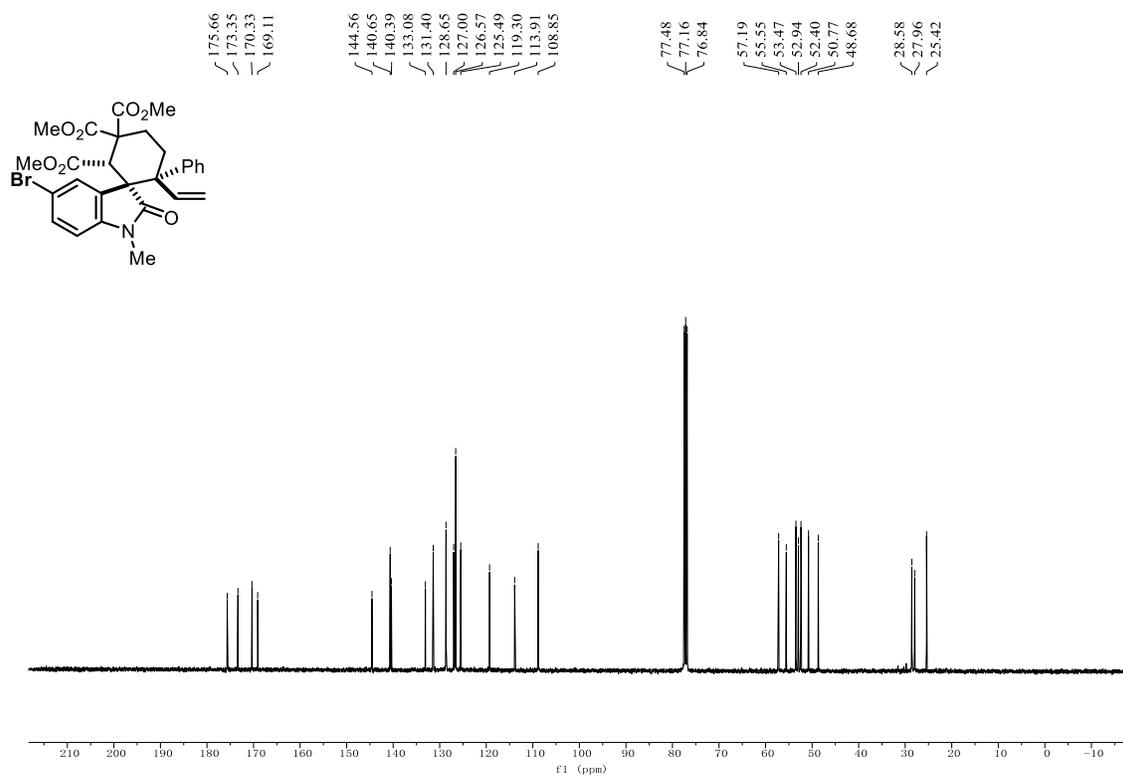
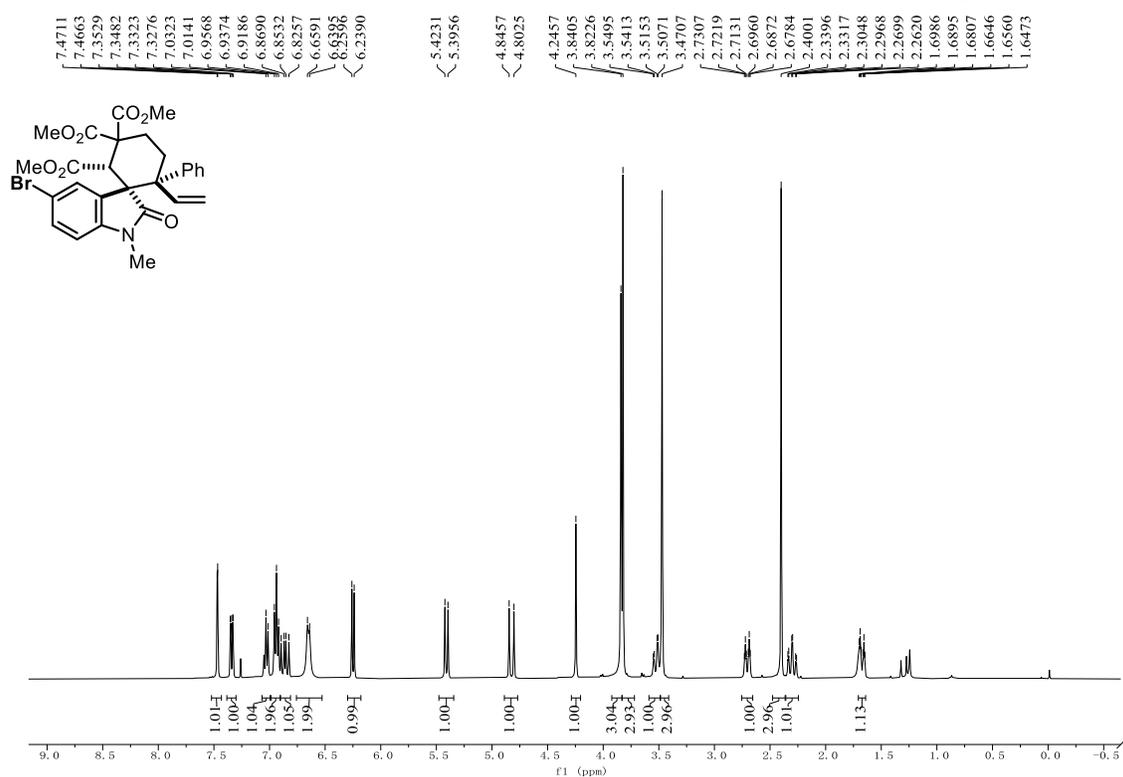
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3w**



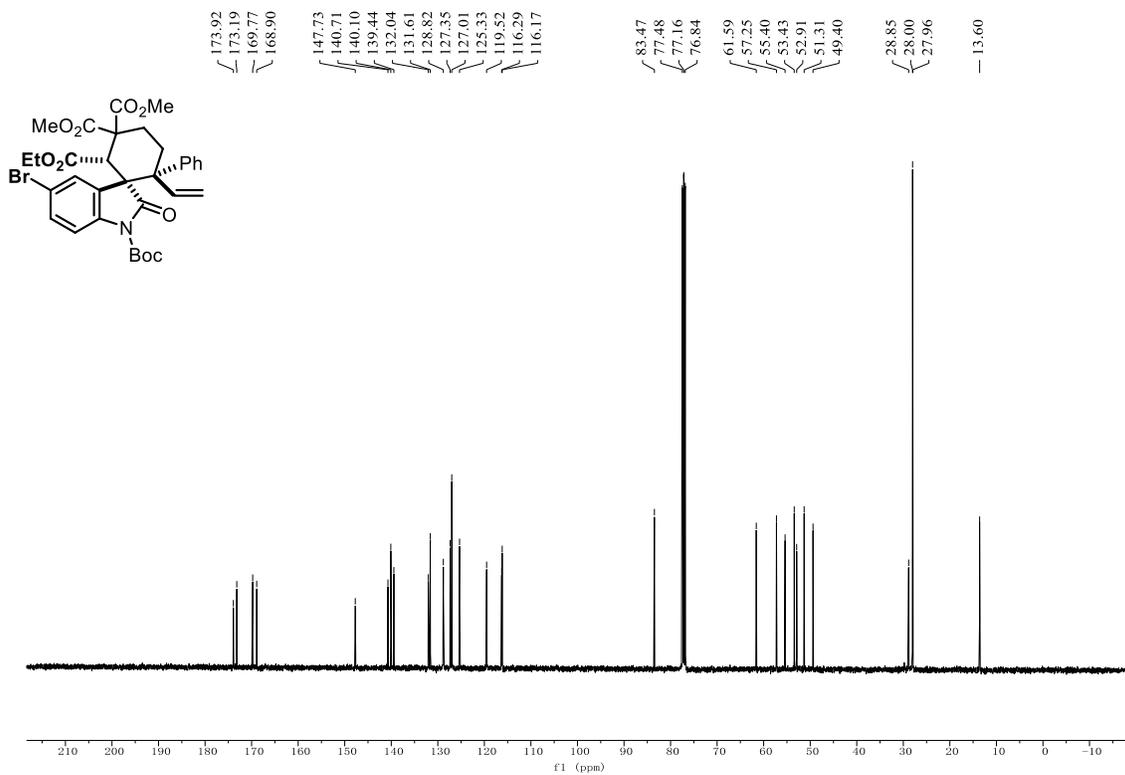
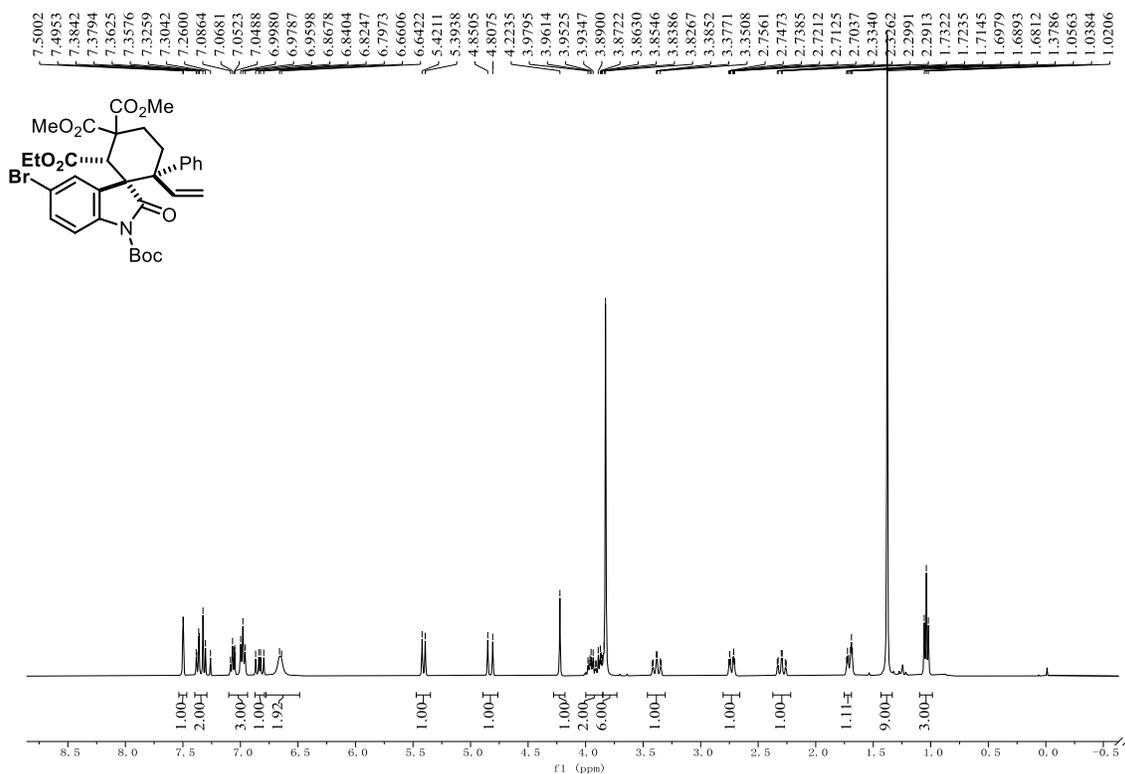
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3x**



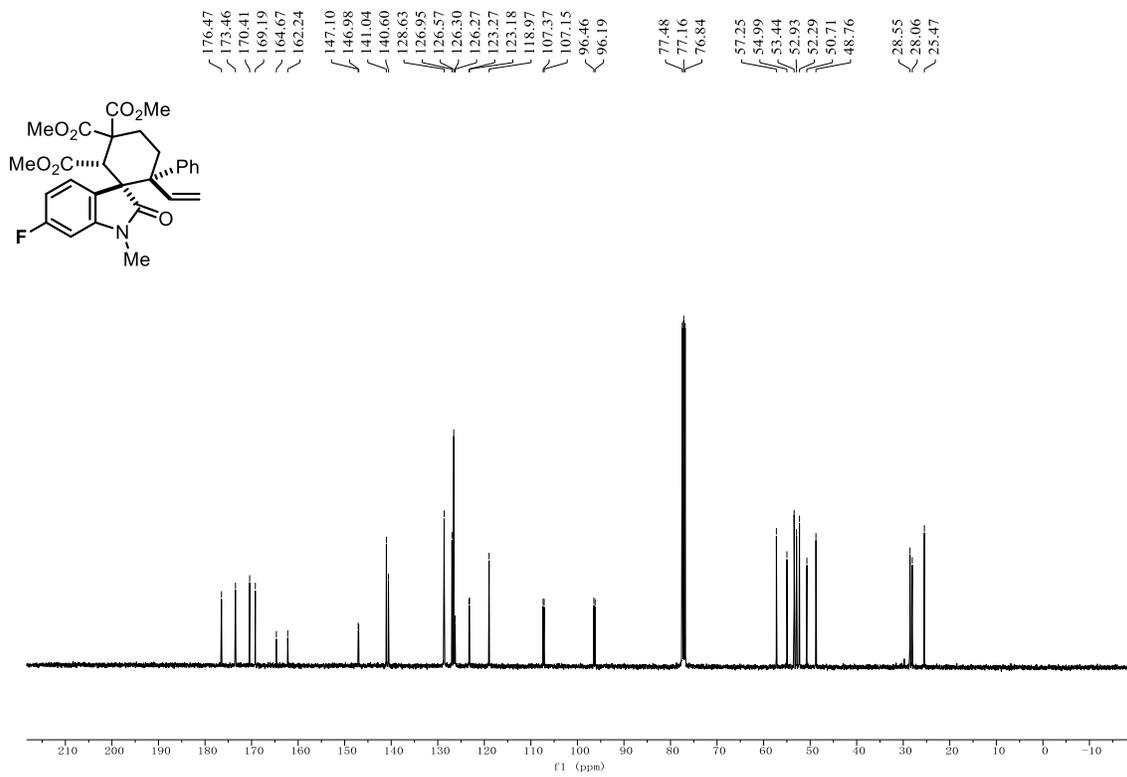
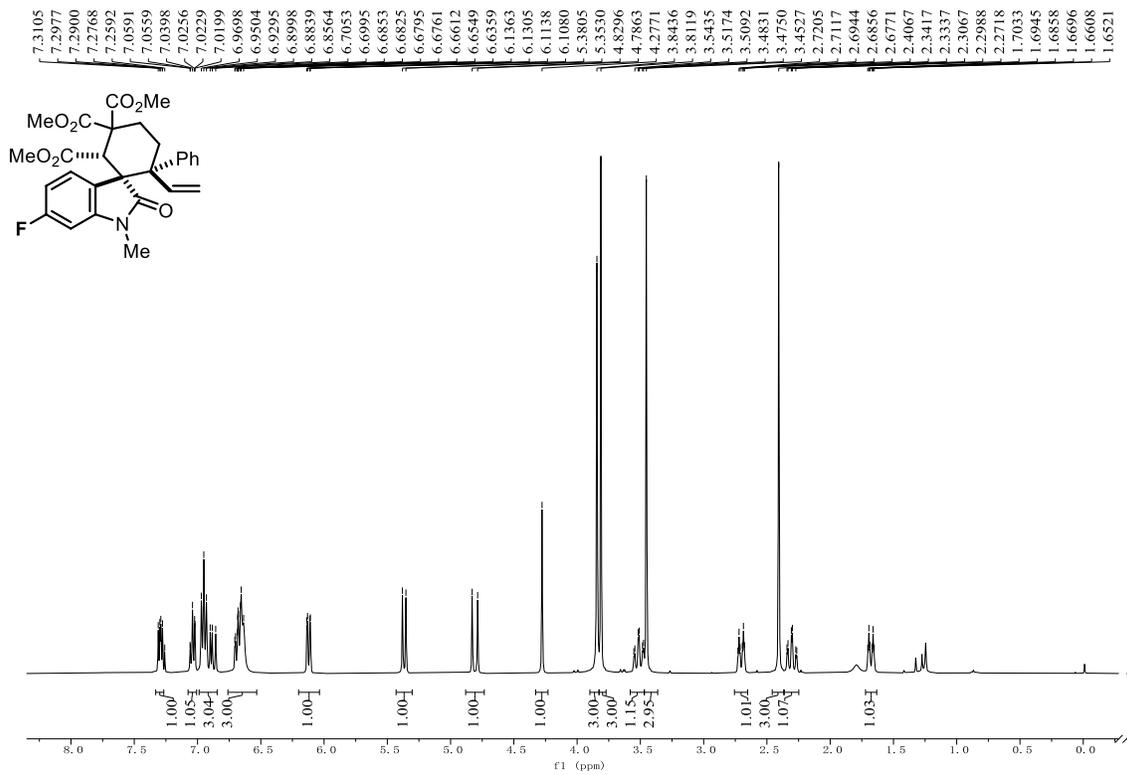
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3y**

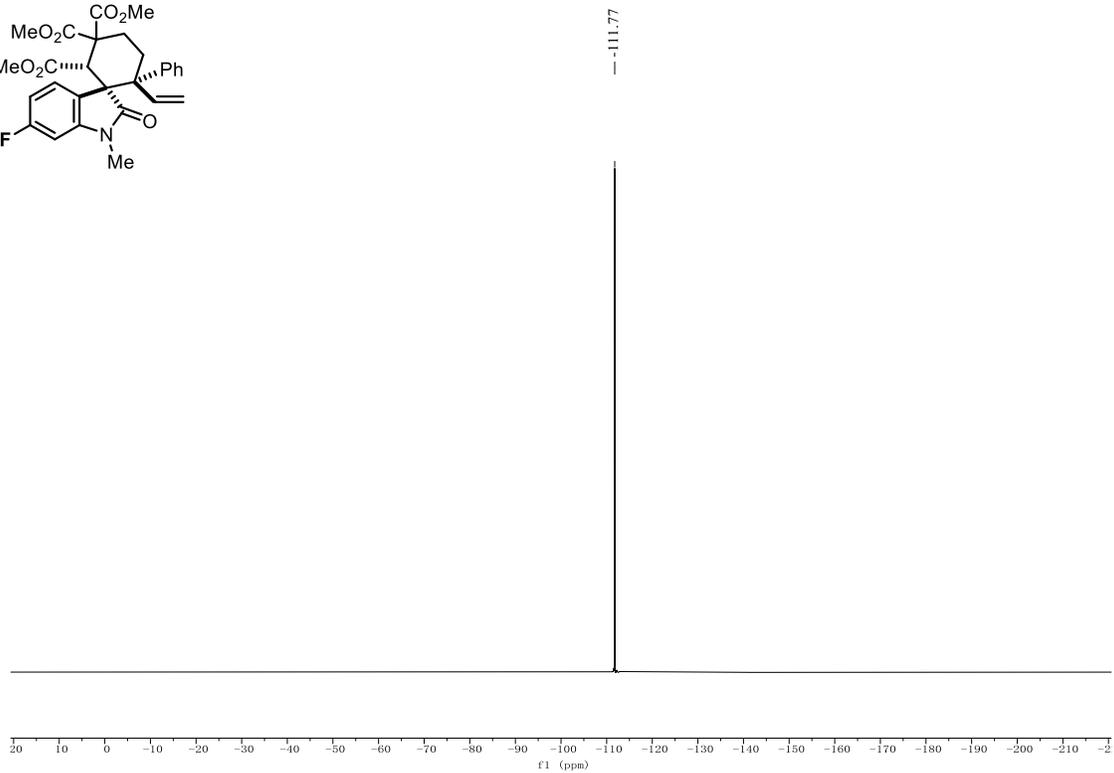
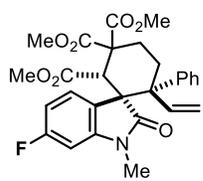


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3z**

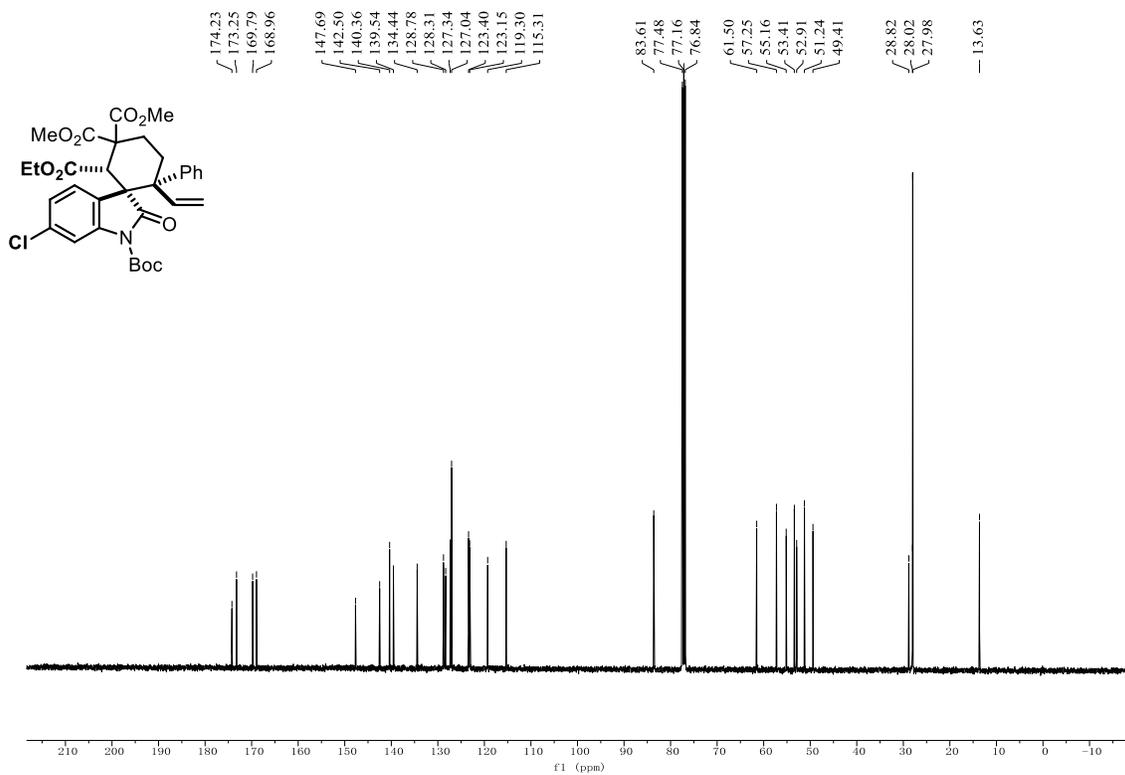
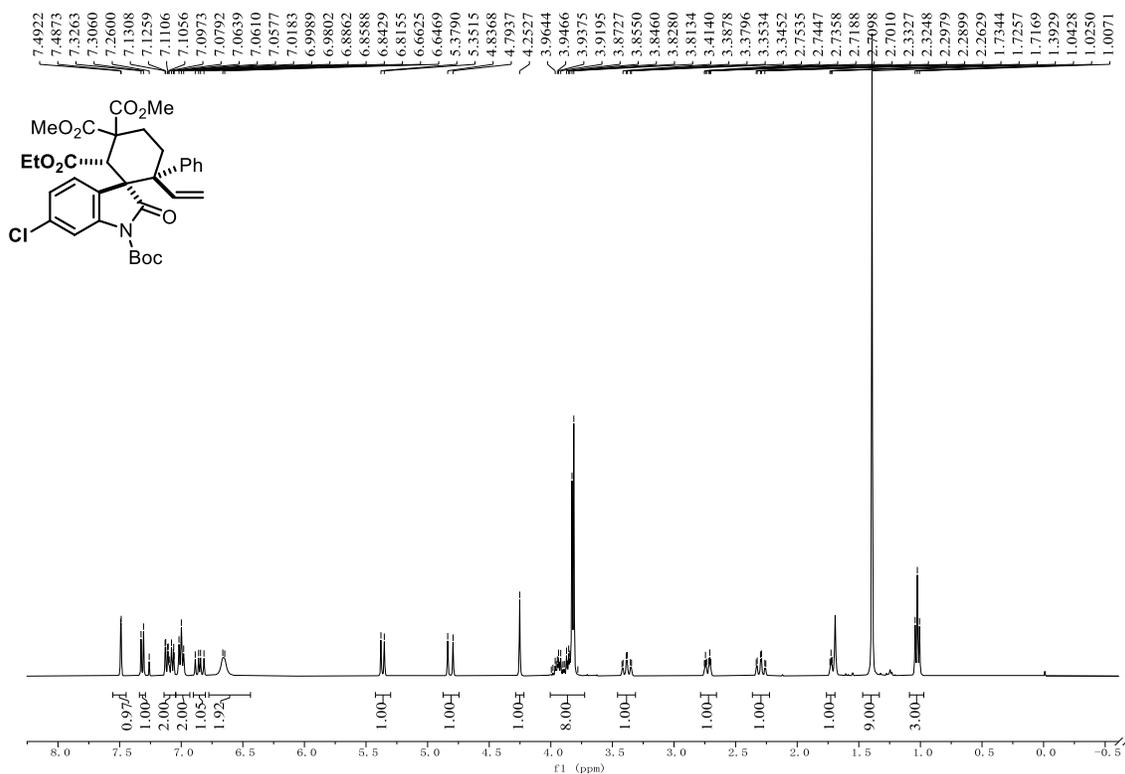


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) and  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ) of 3aa**

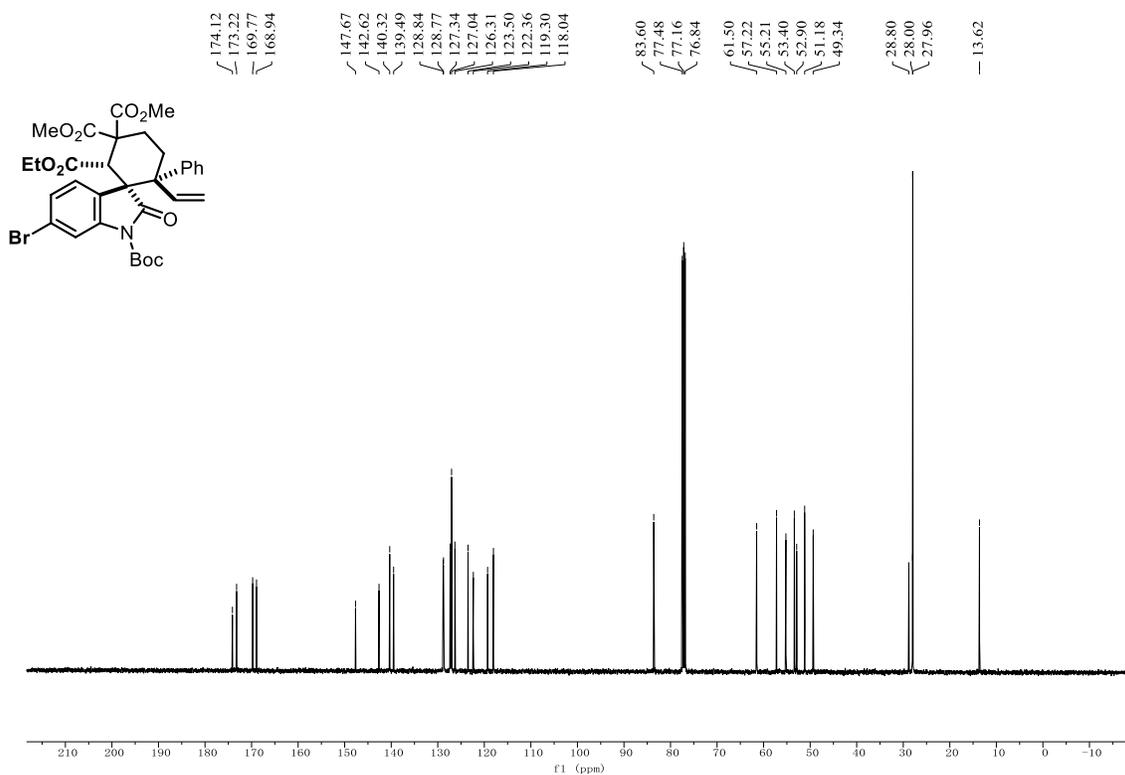
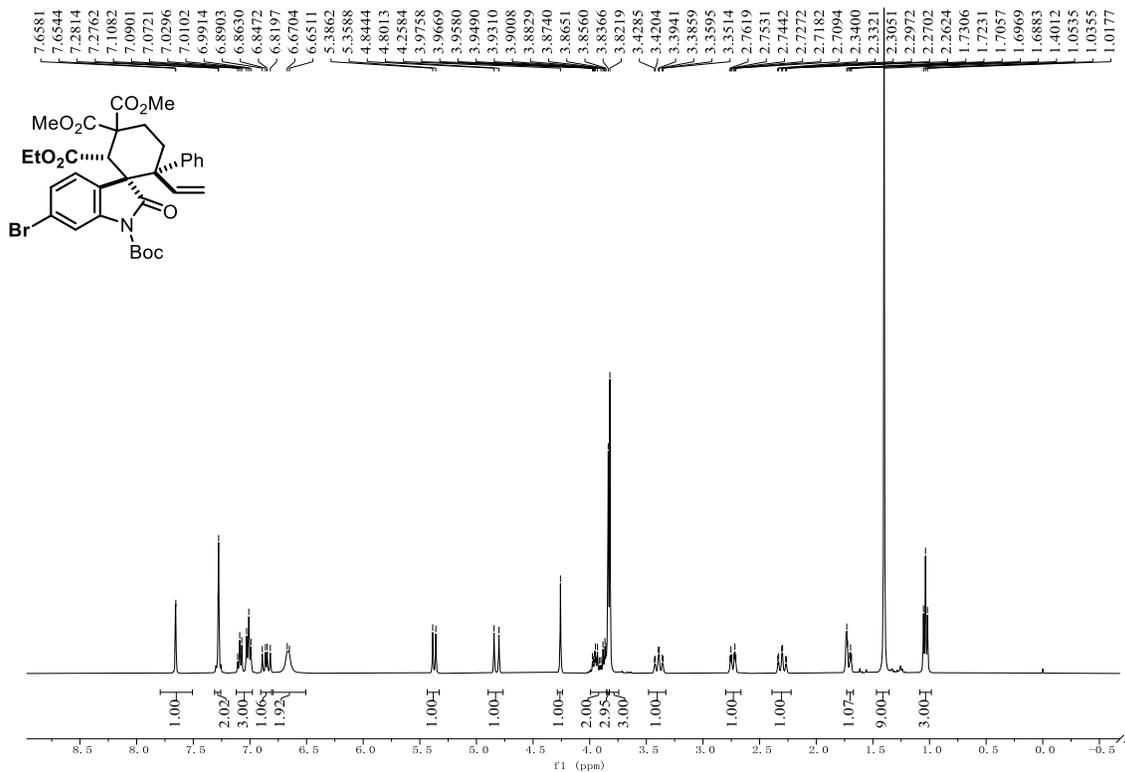




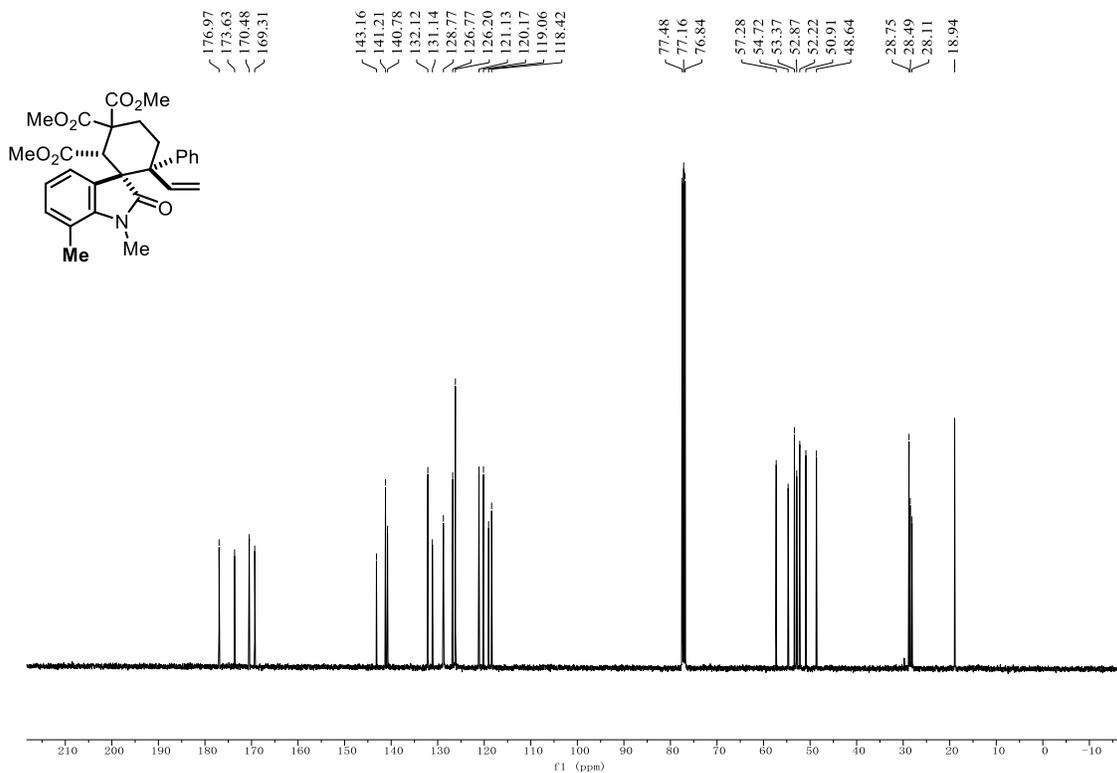
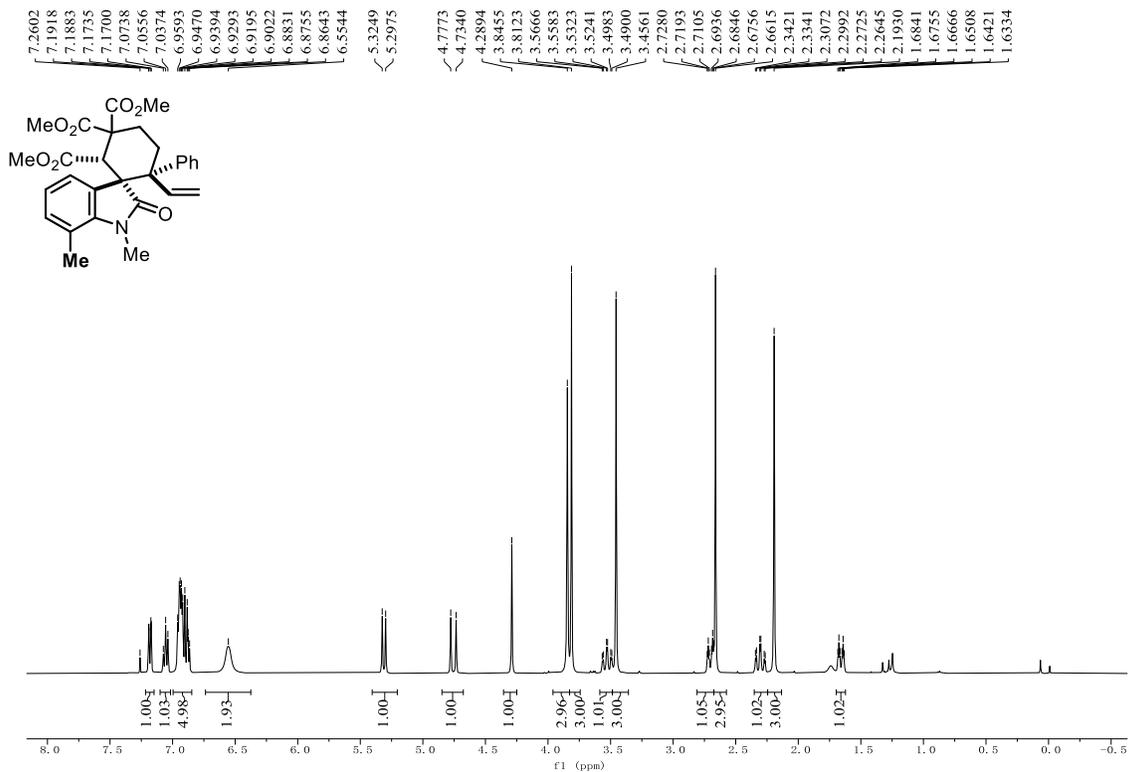
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3ab



**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3ac**

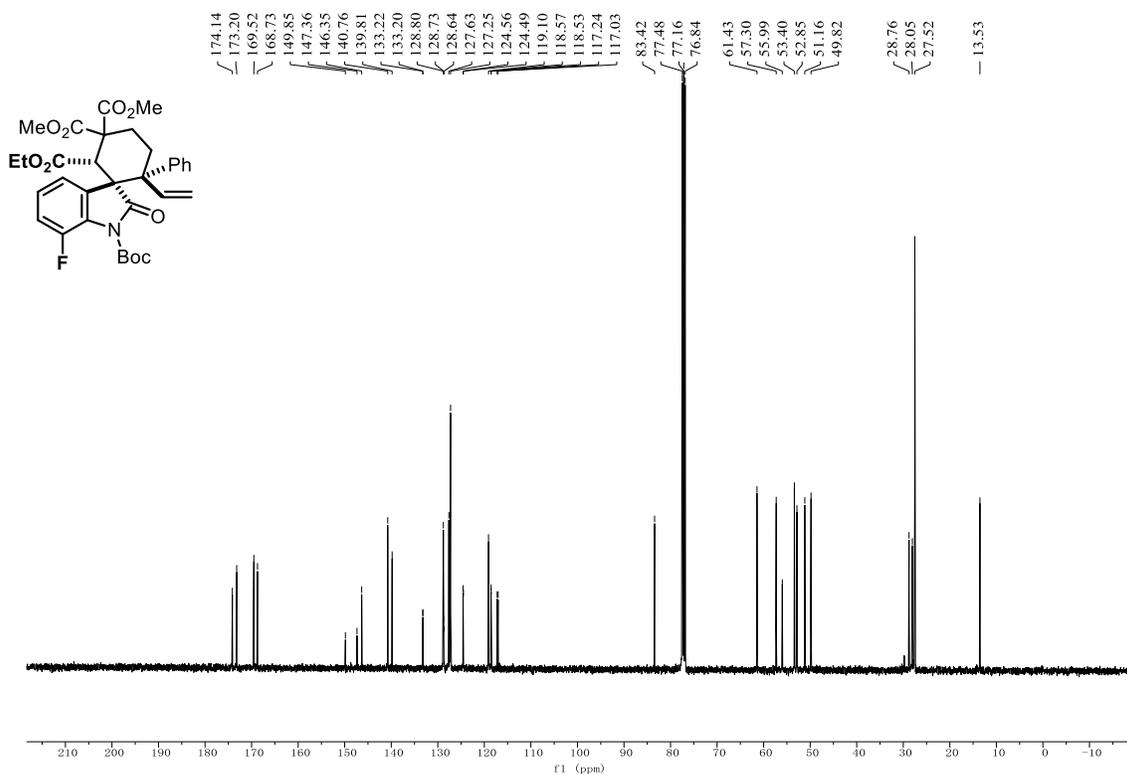
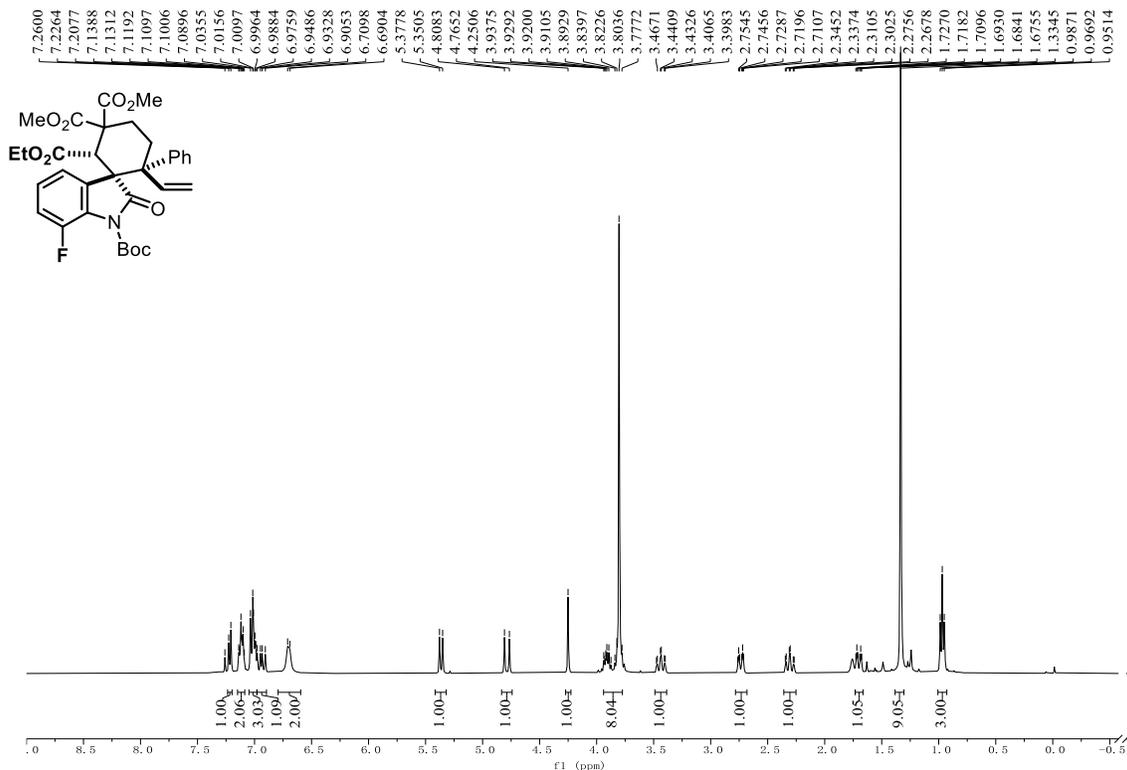


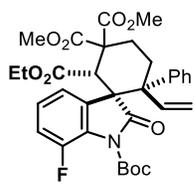
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3ad**



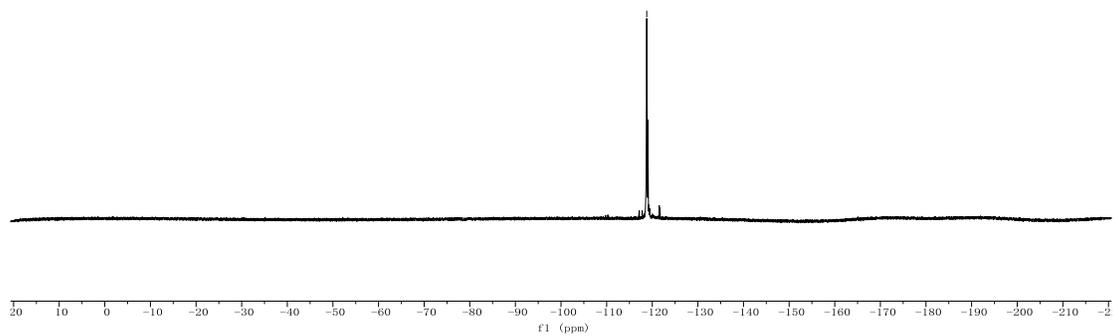
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) and <sup>19</sup>F NMR (376 MHz, CDCl<sub>3</sub>)

of 3ae

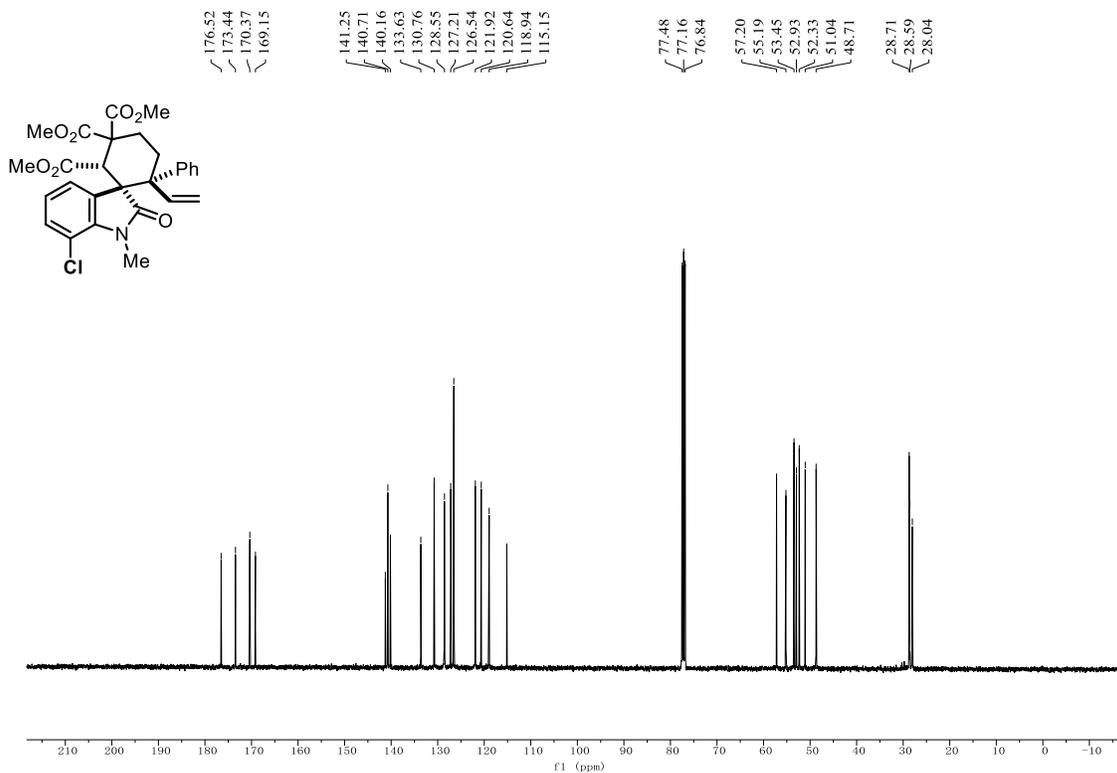
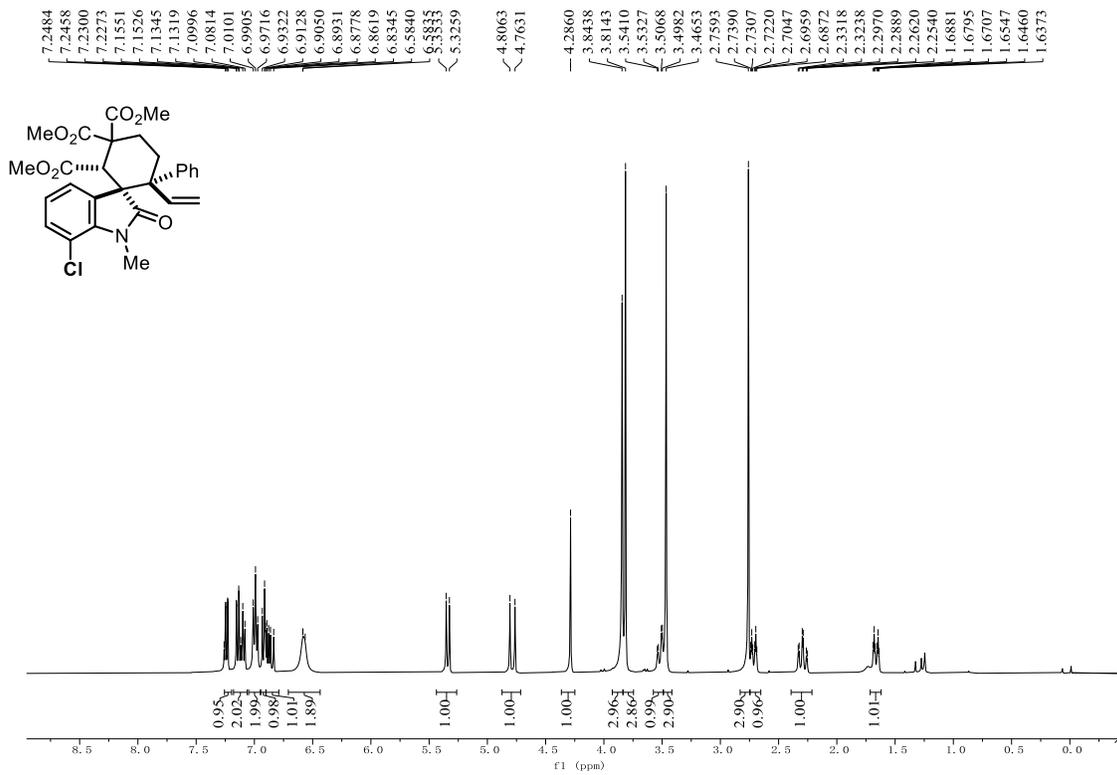




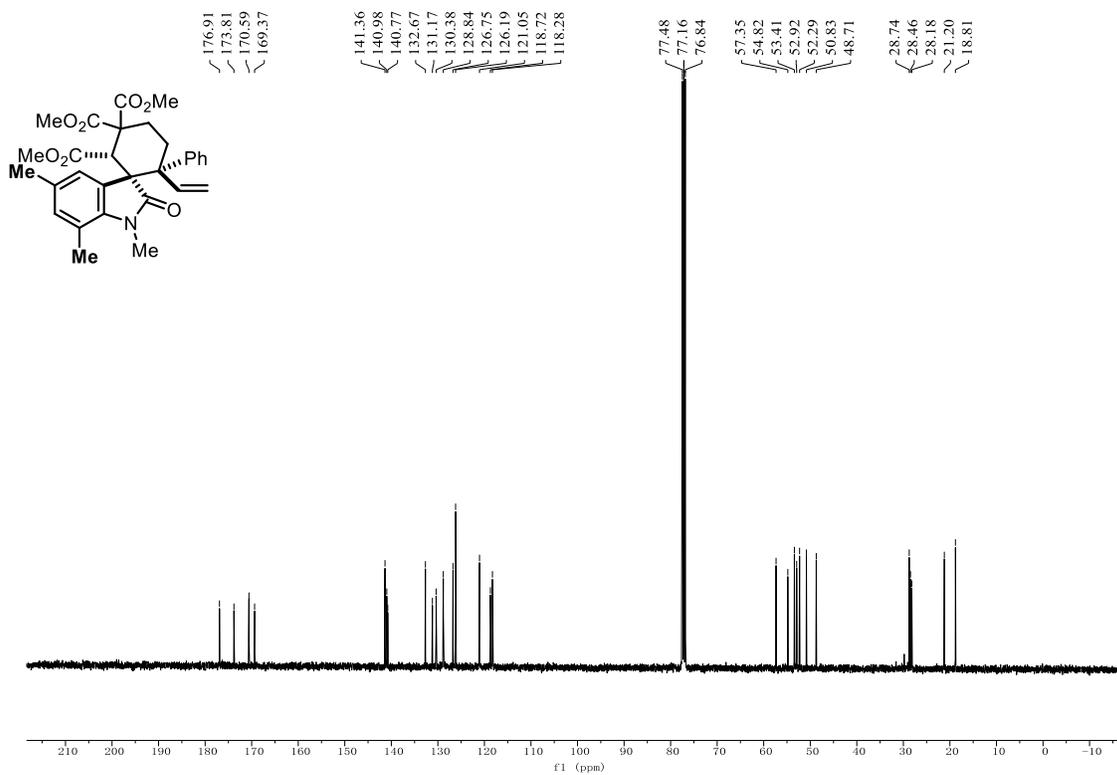
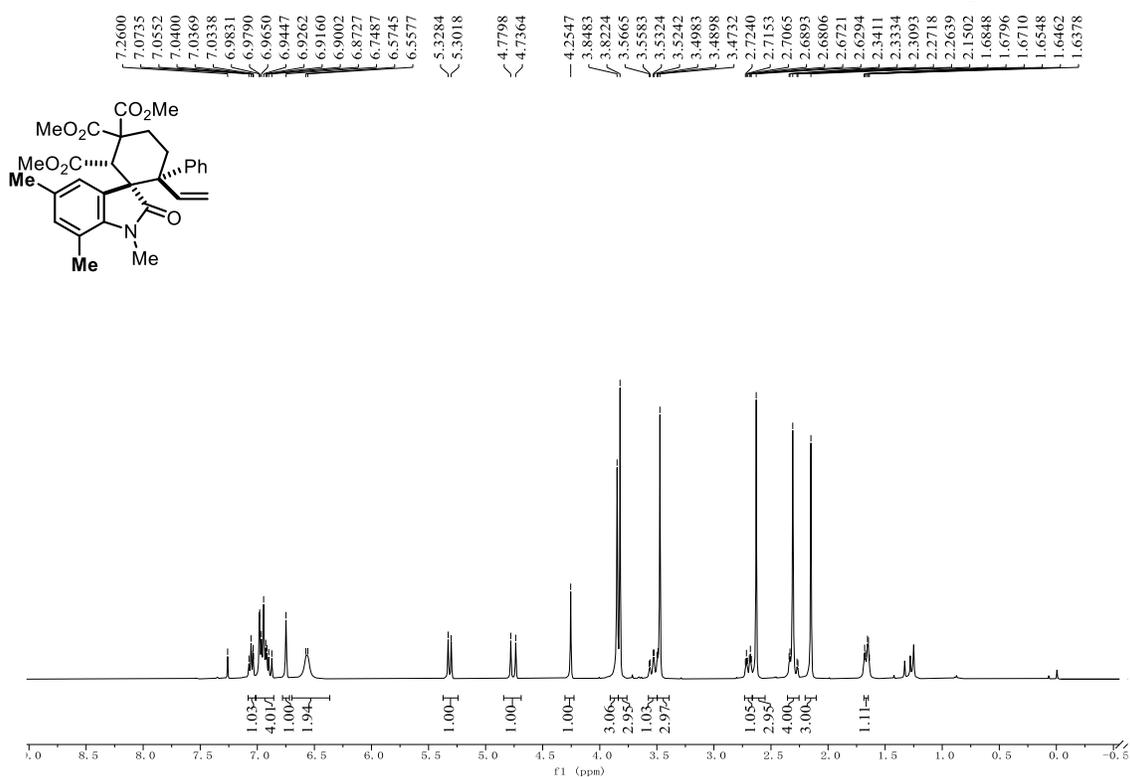
-118.79



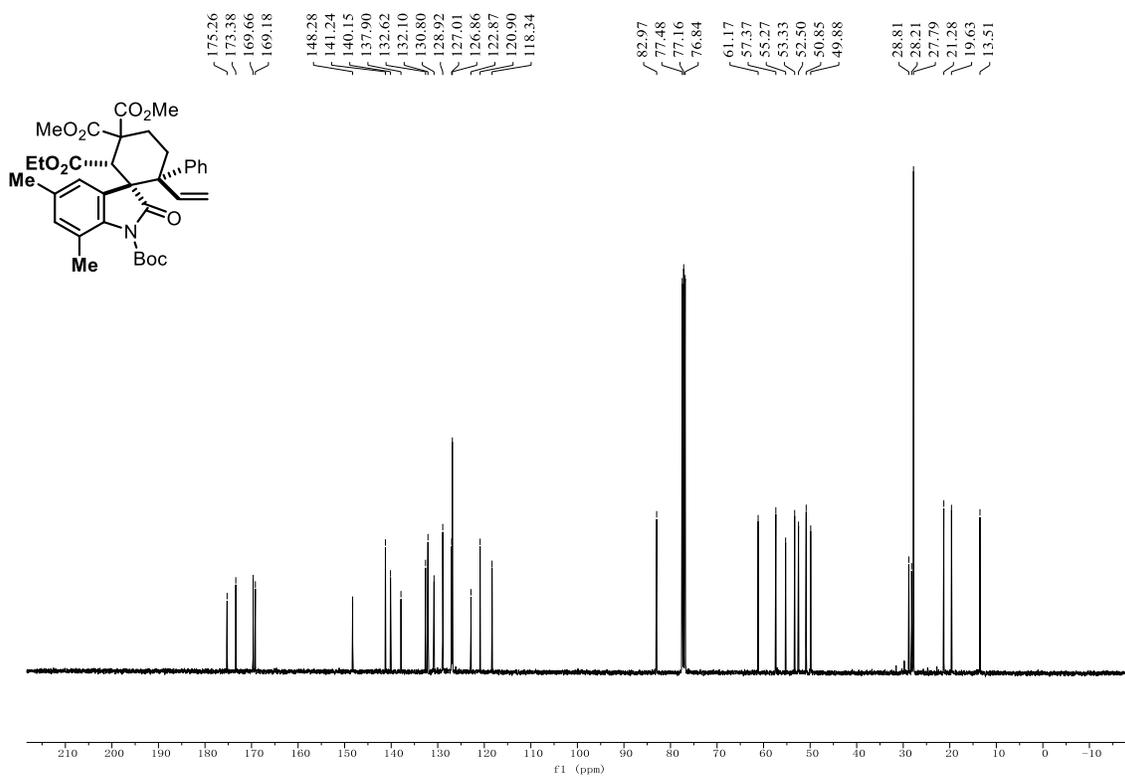
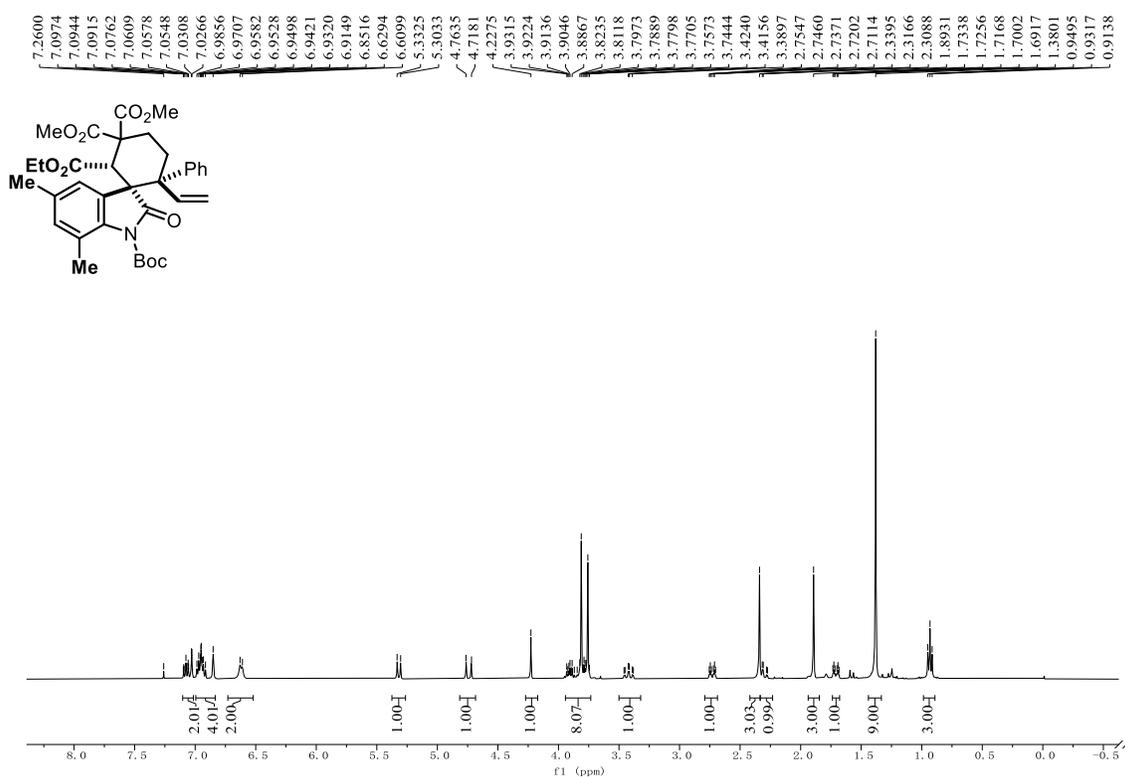
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 3af**



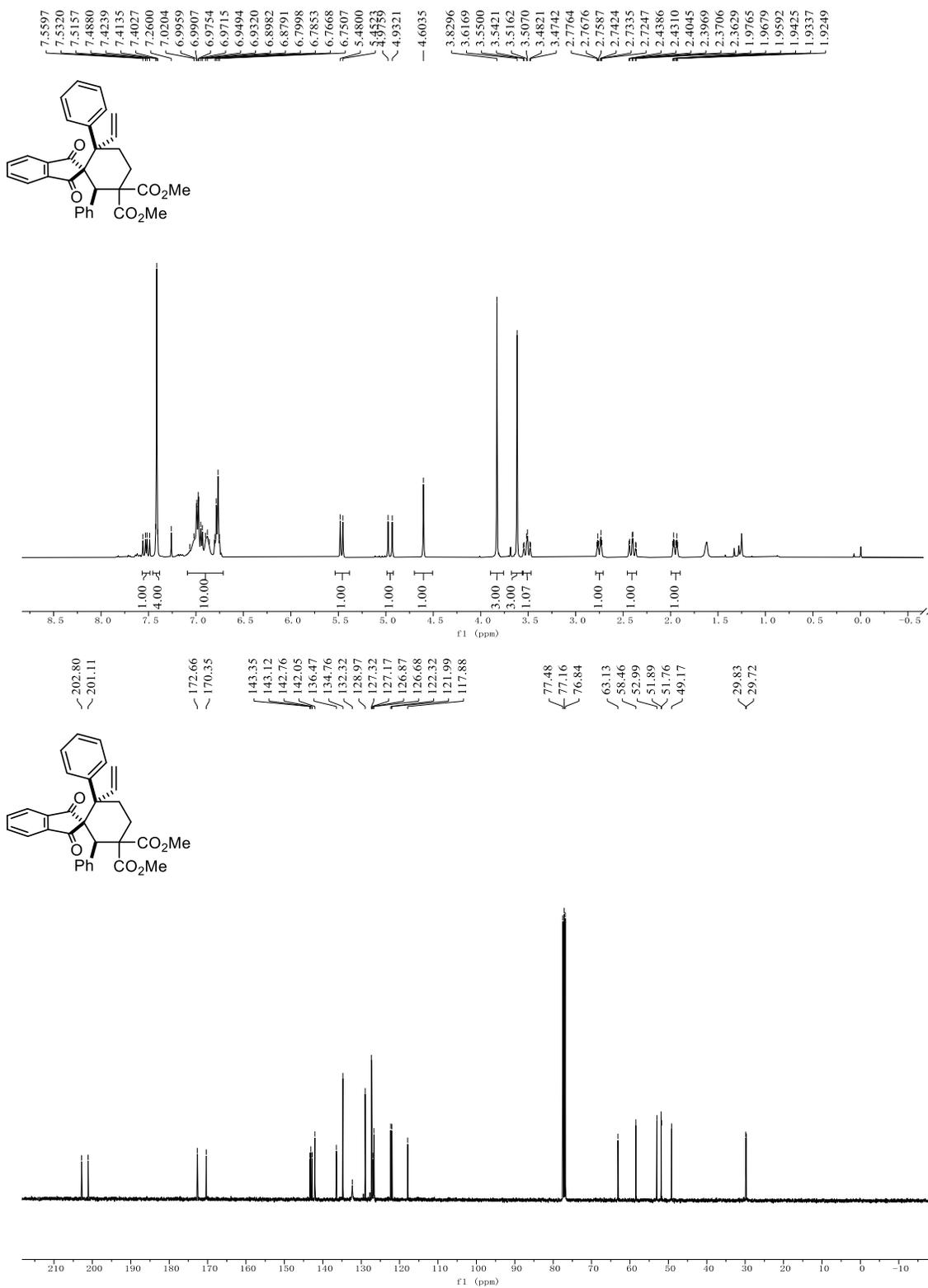
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3ag**



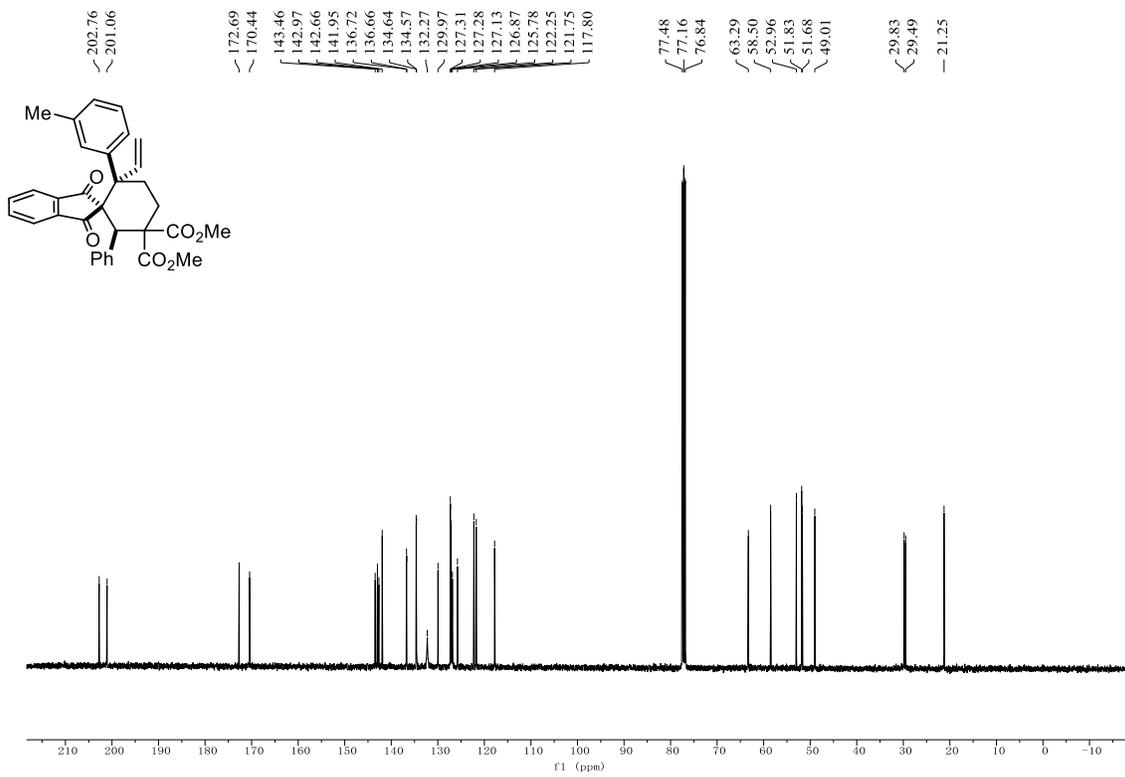
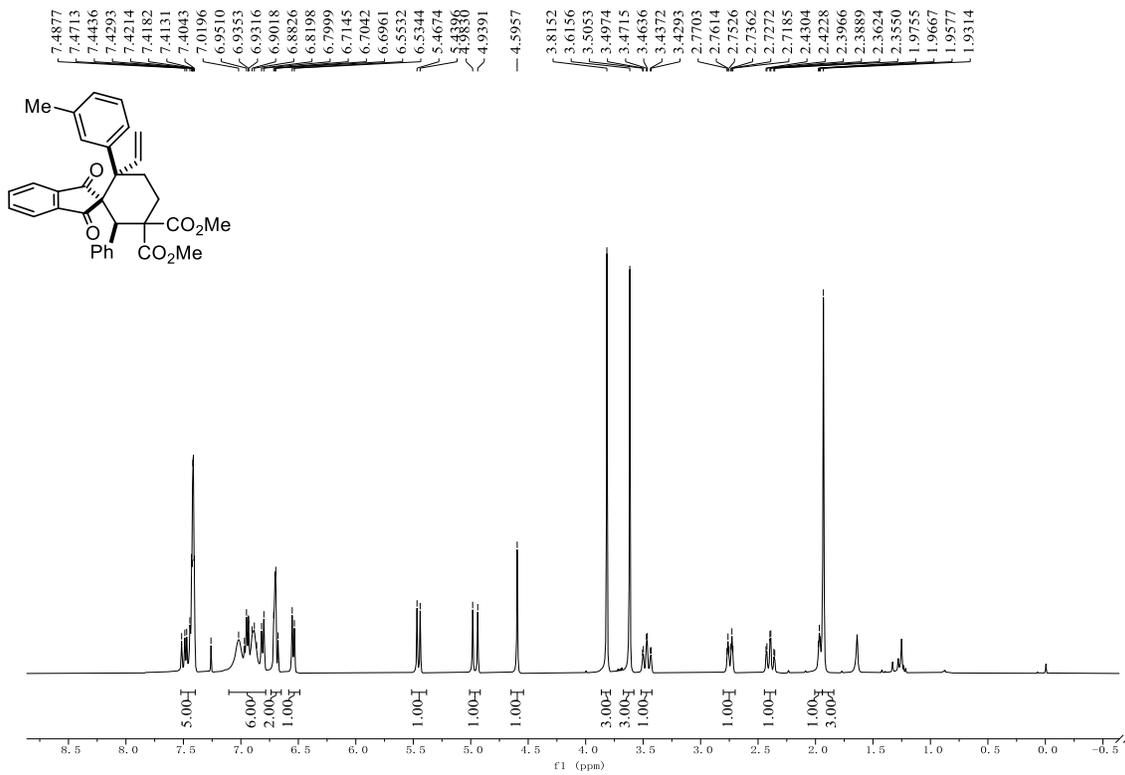
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 3ah

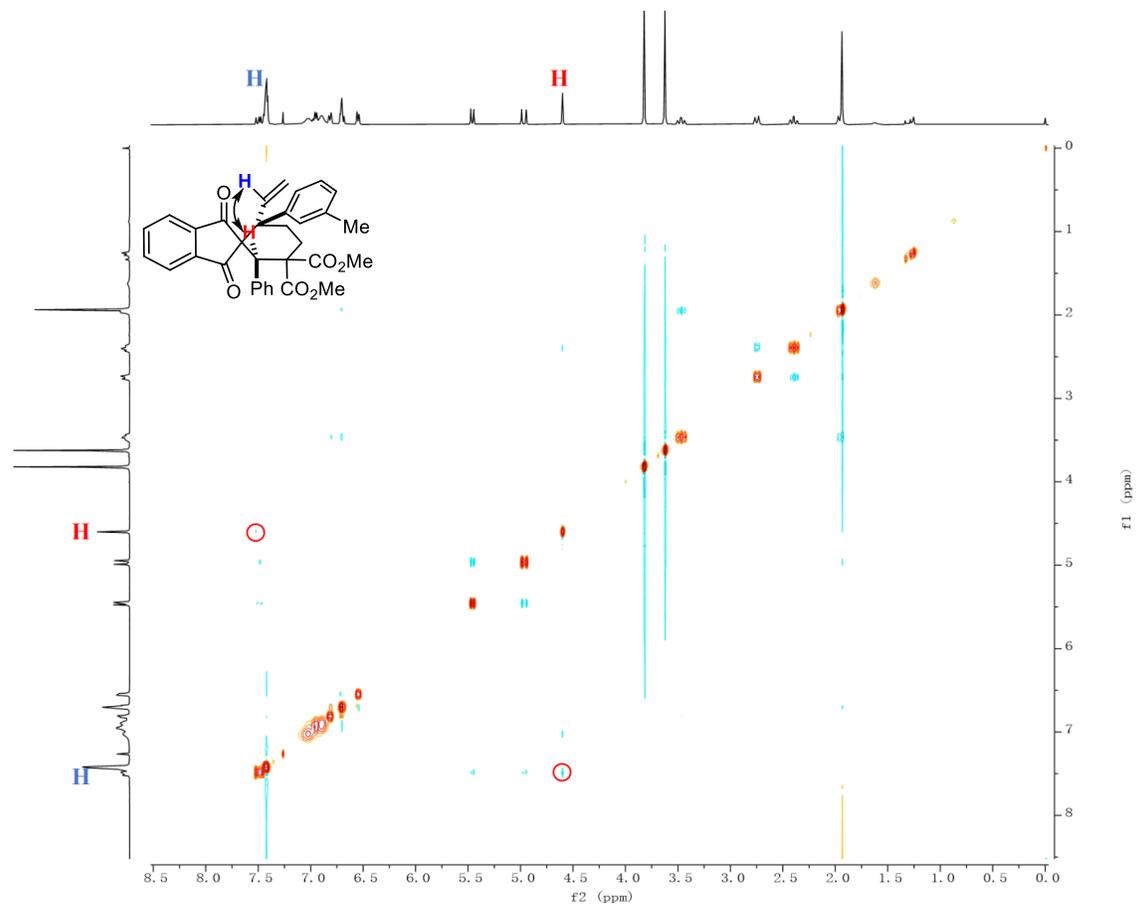


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 5a**

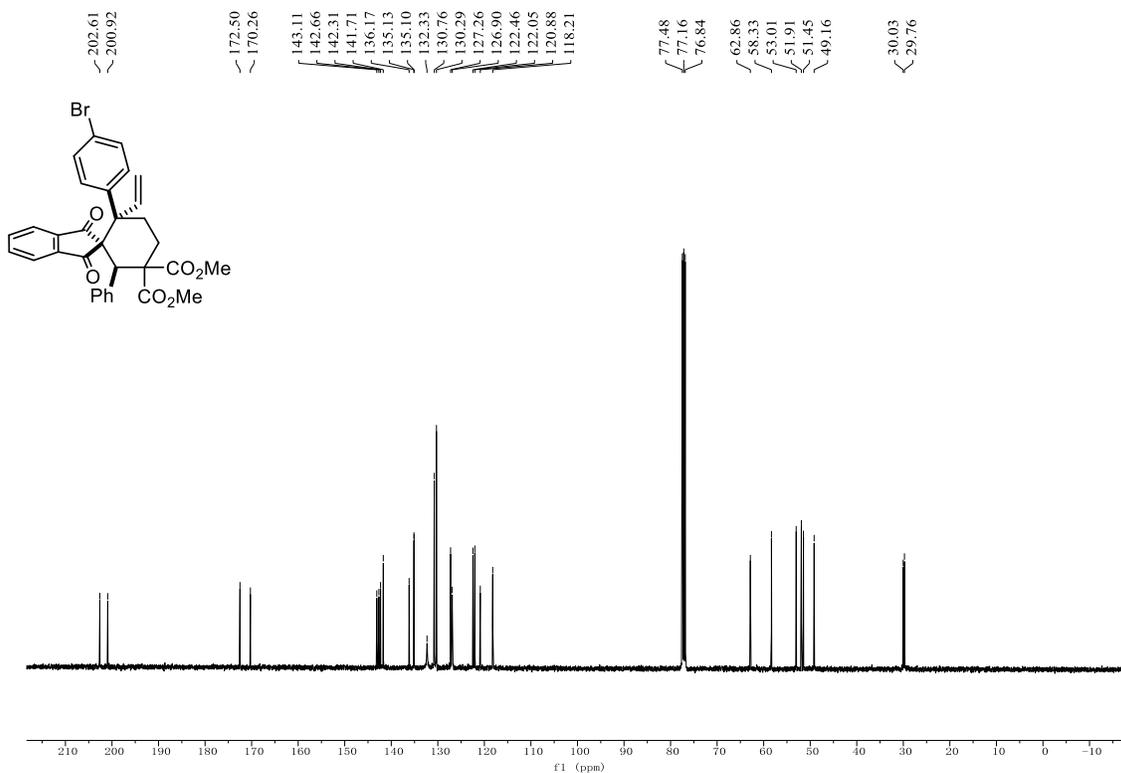
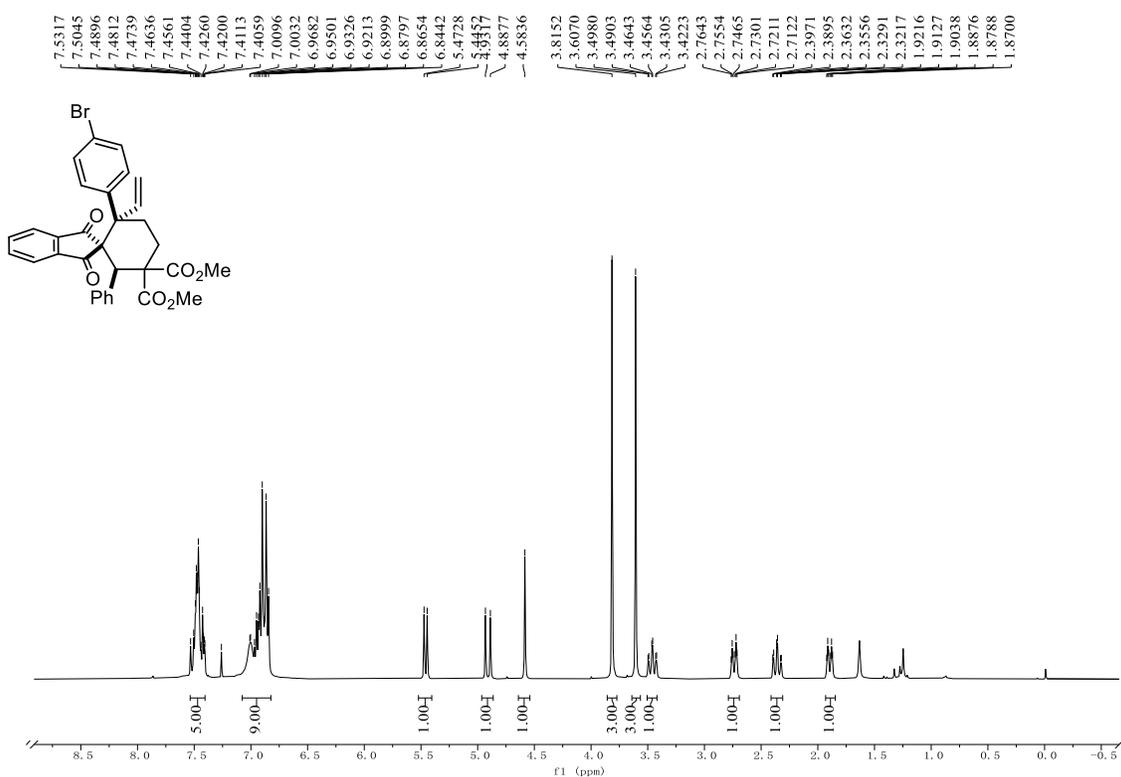


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ),  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) and the NOE result of 5b**

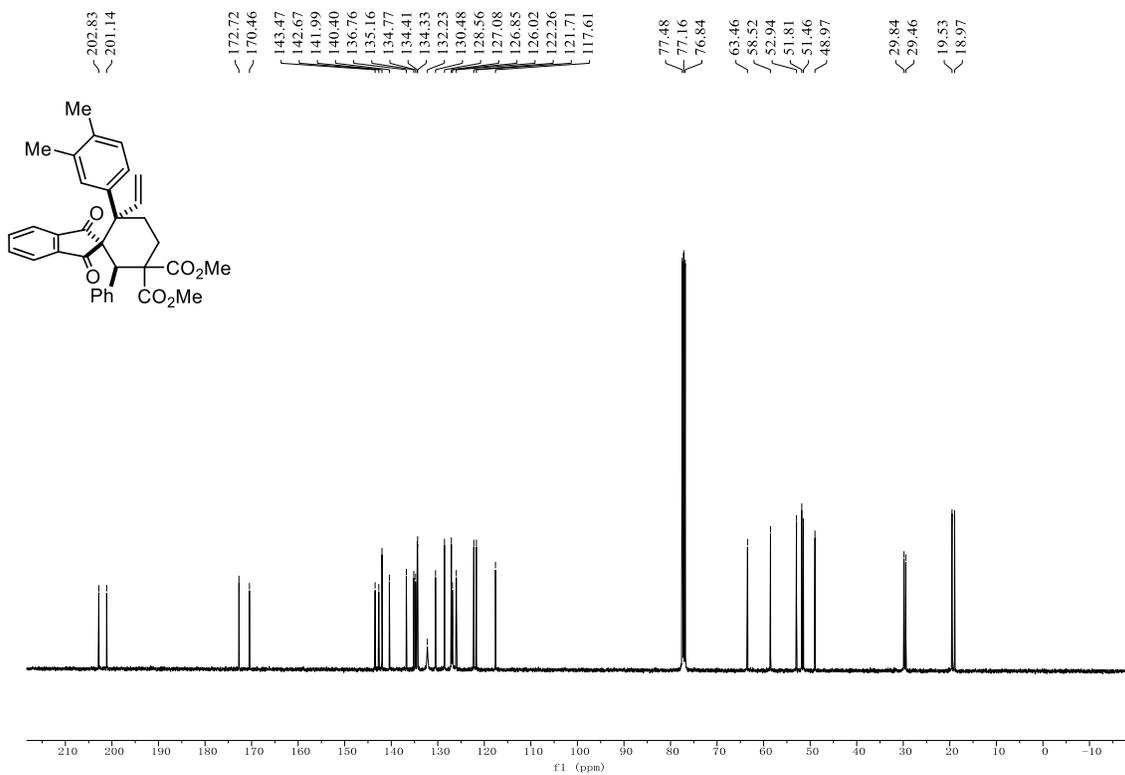
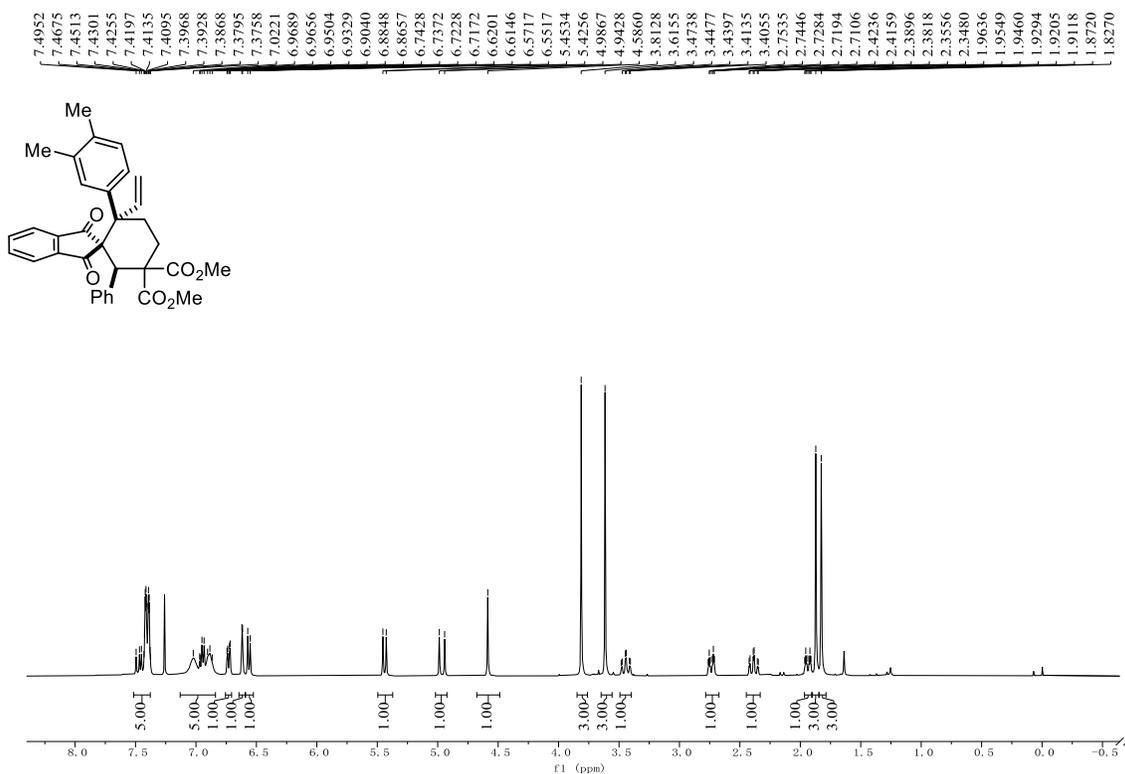




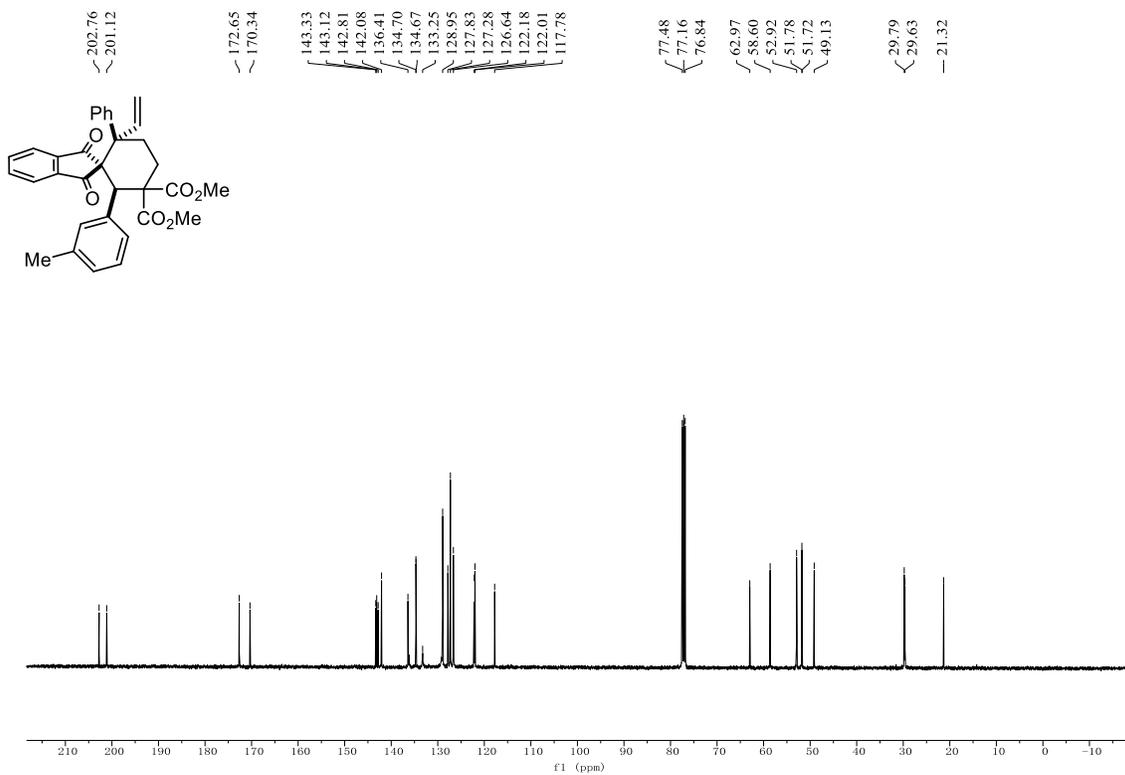
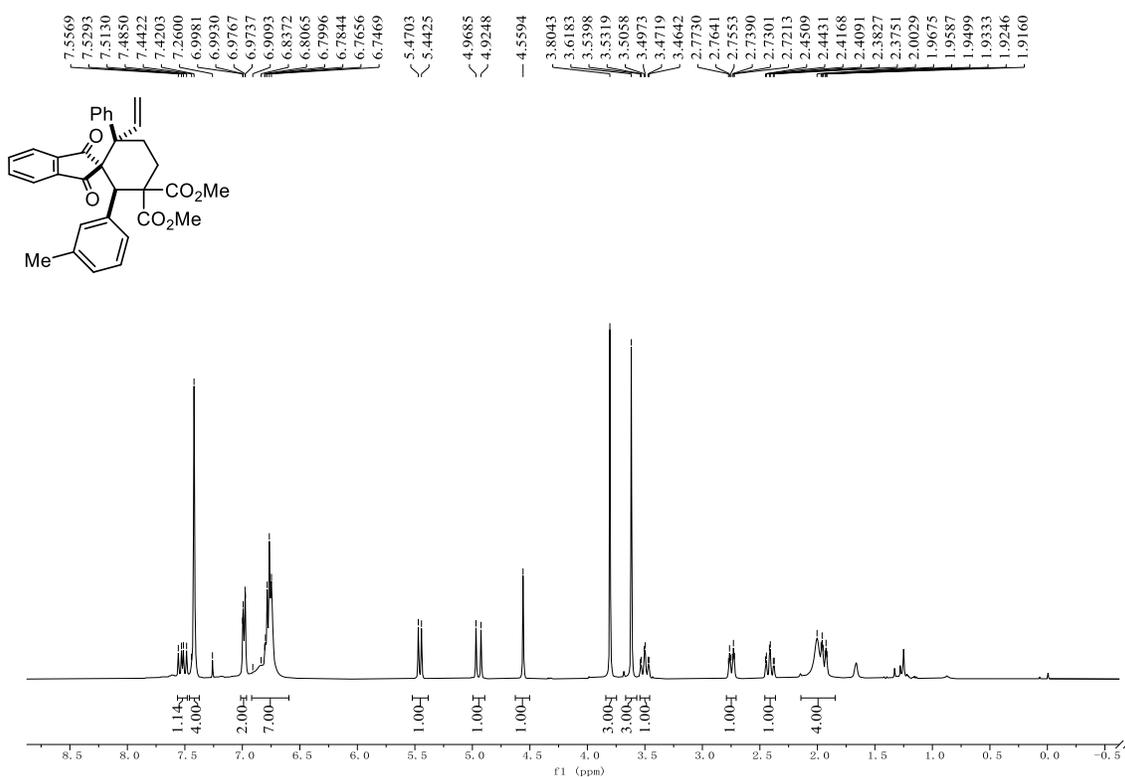
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 5c**



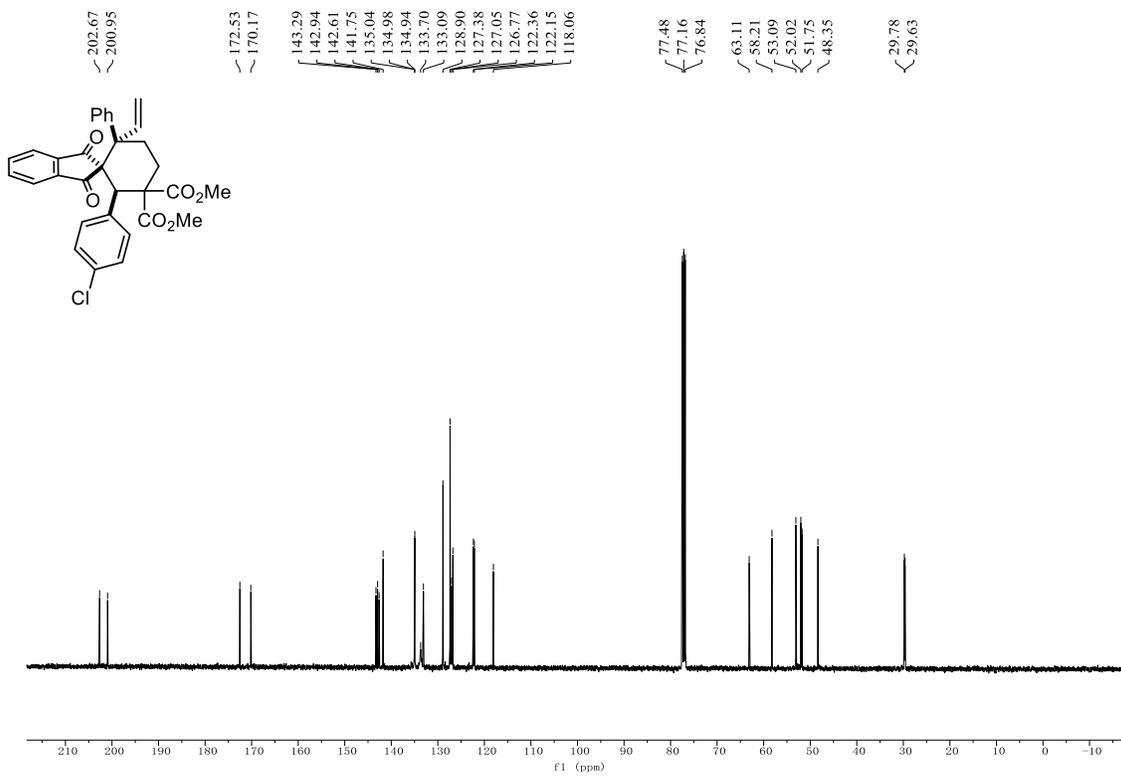
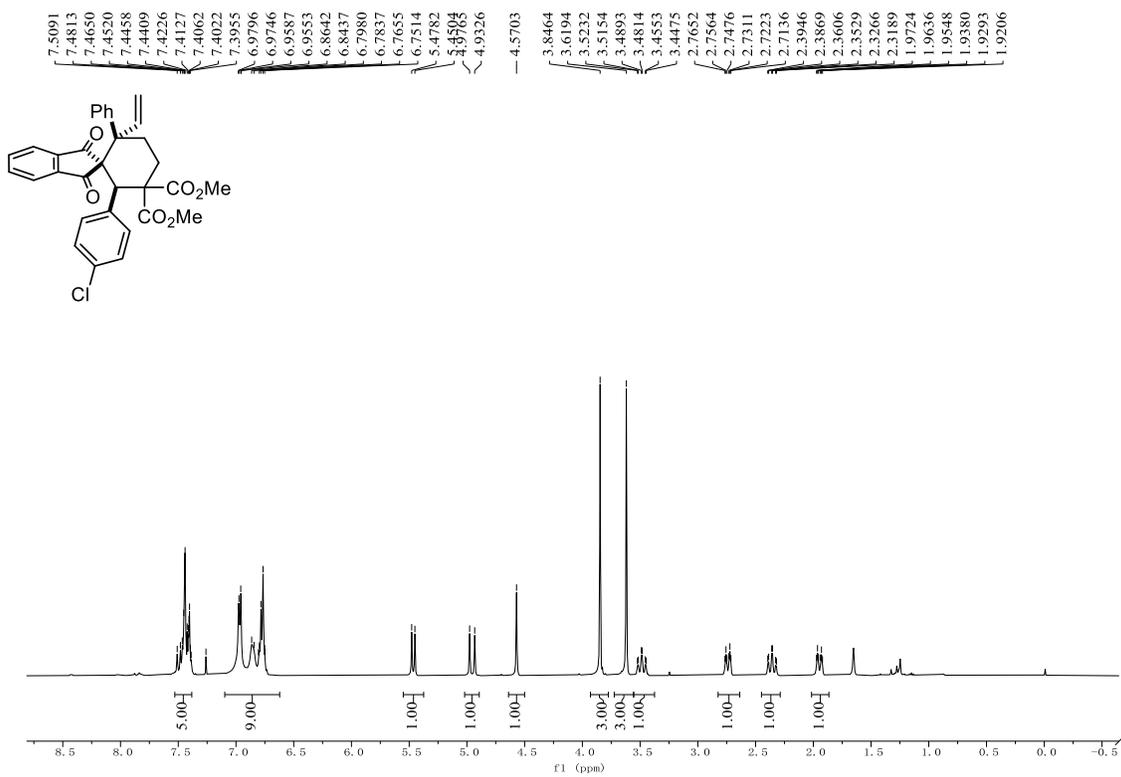
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 5d**



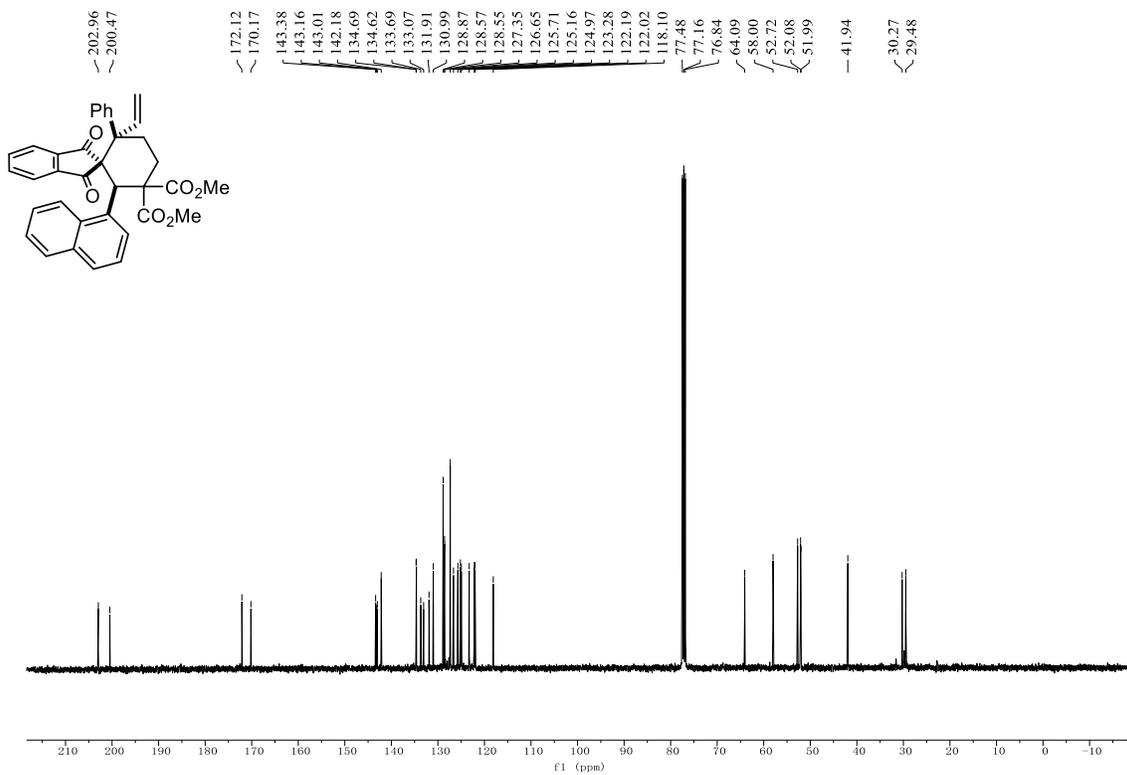
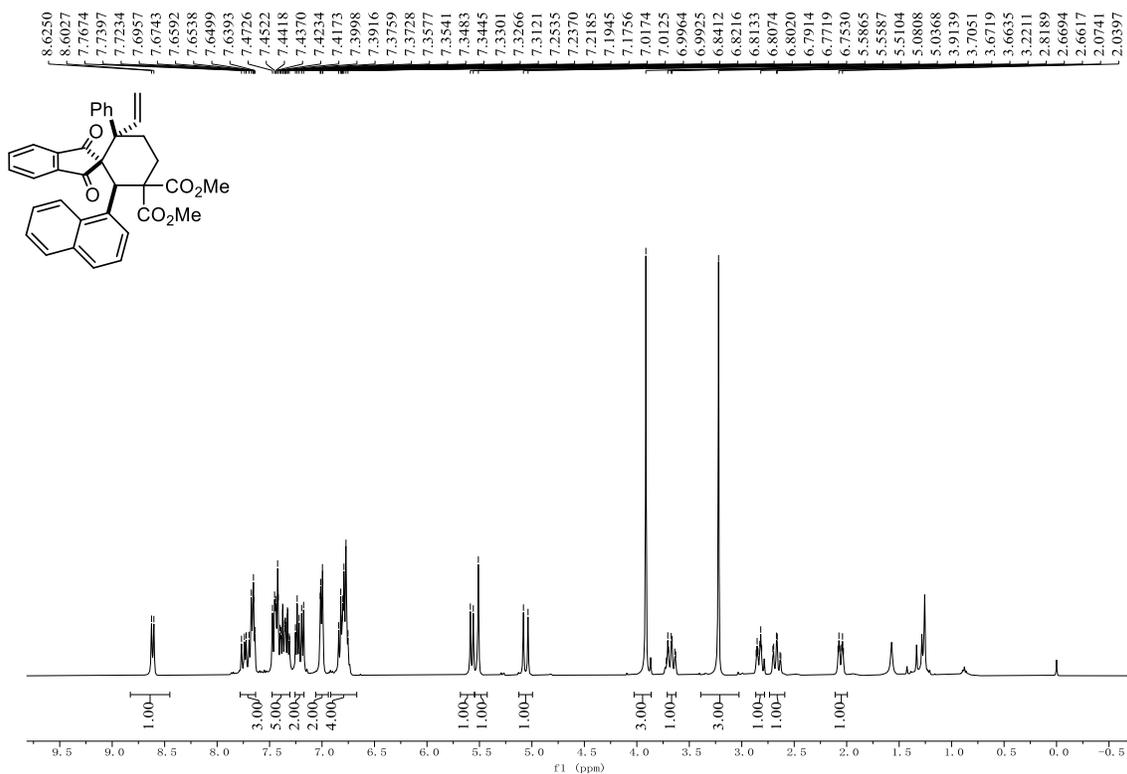
# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 5e



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 5f**

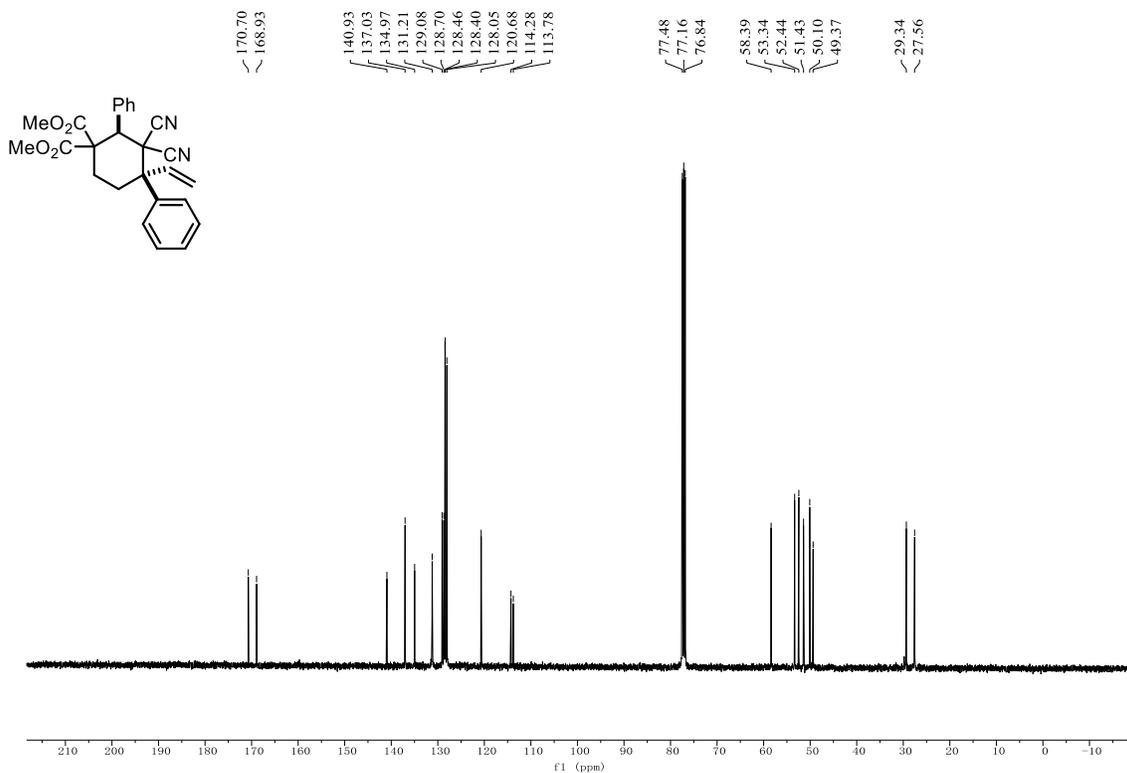
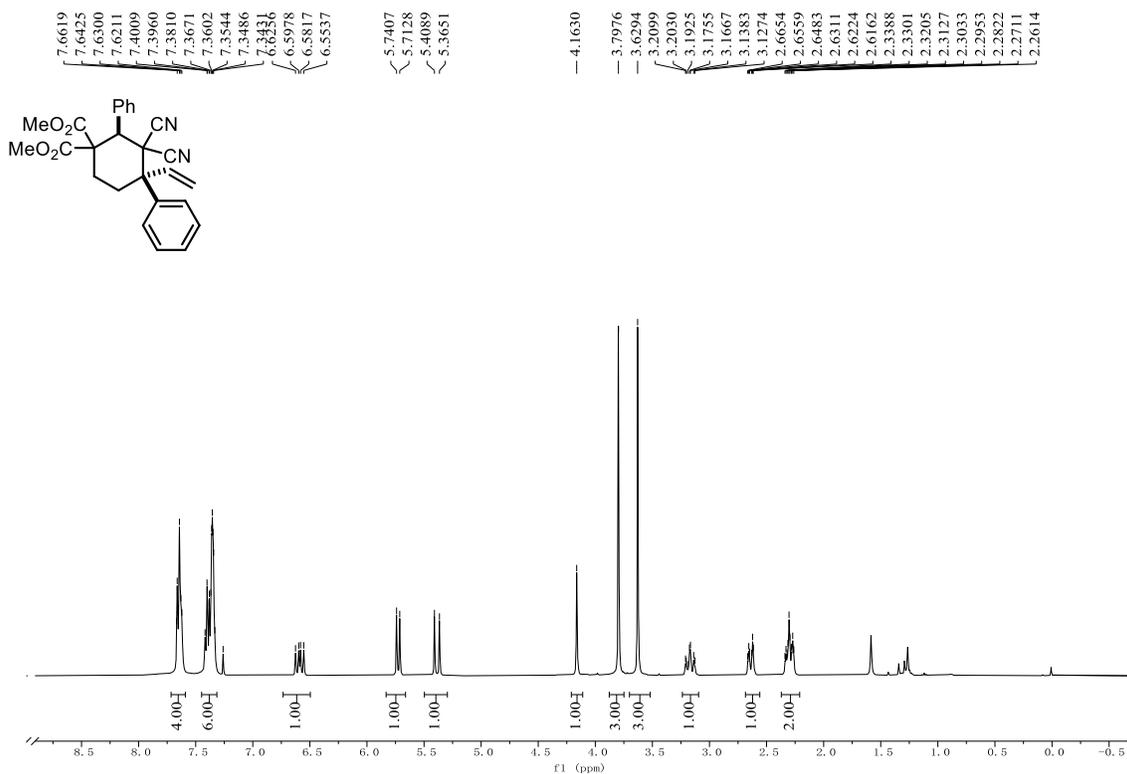


<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 5g

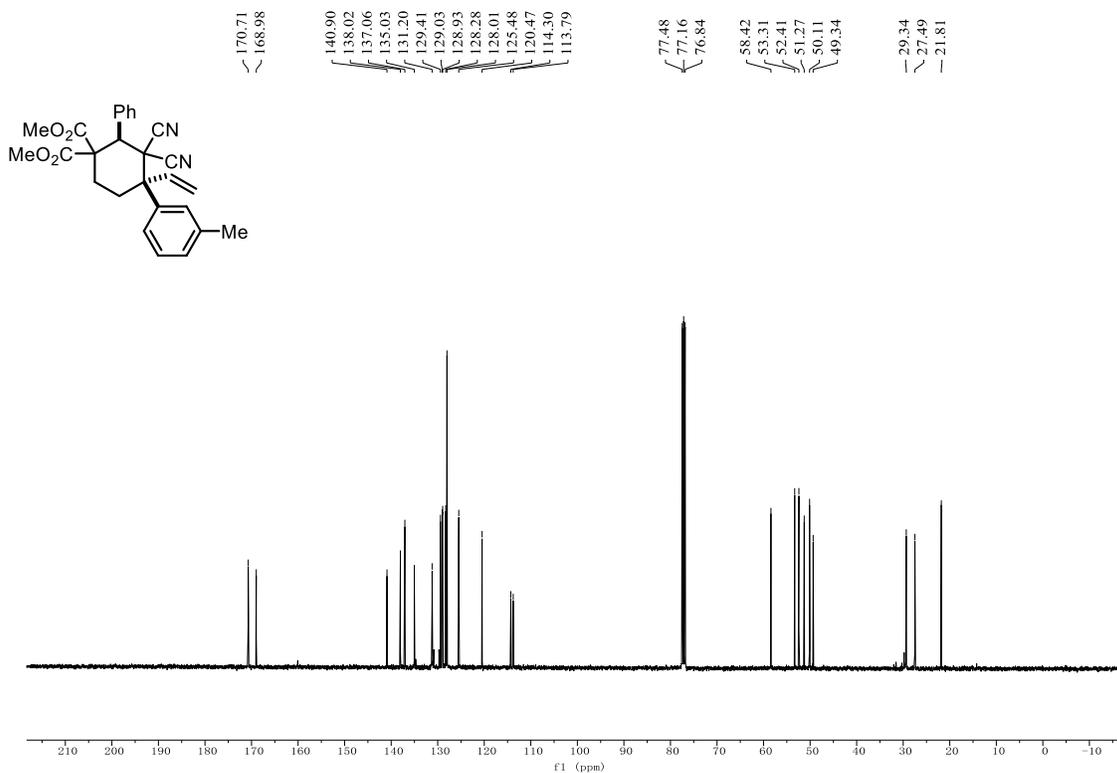
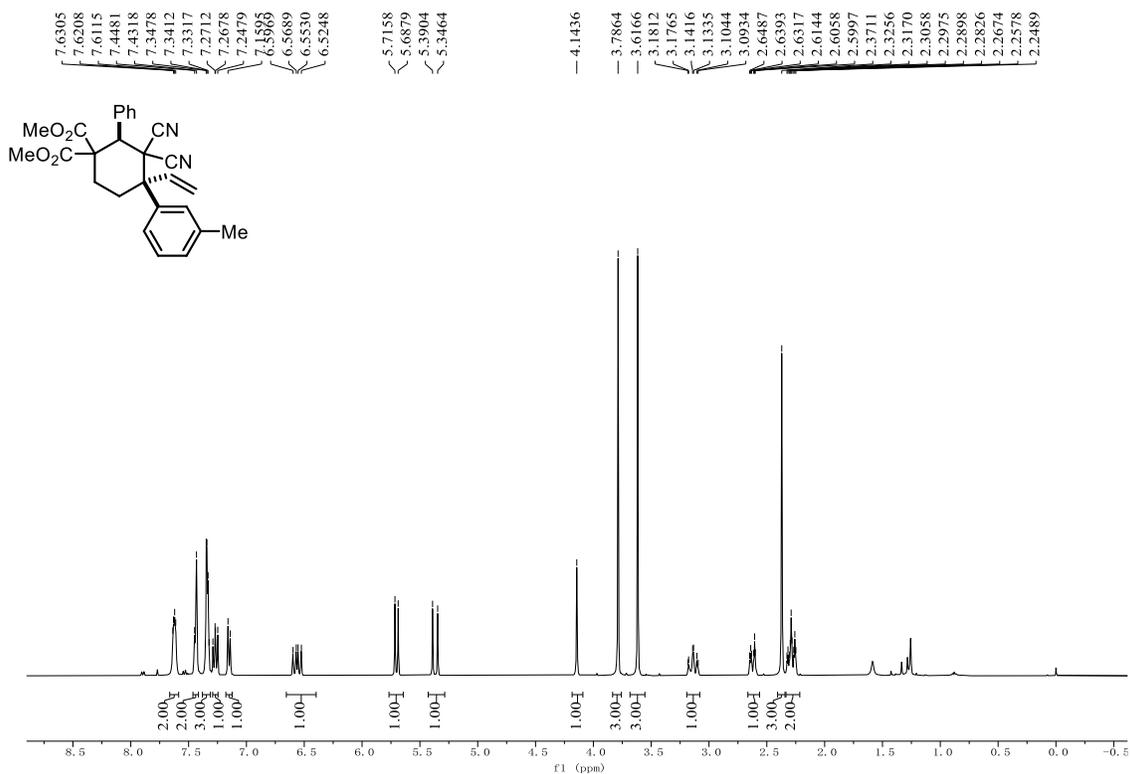


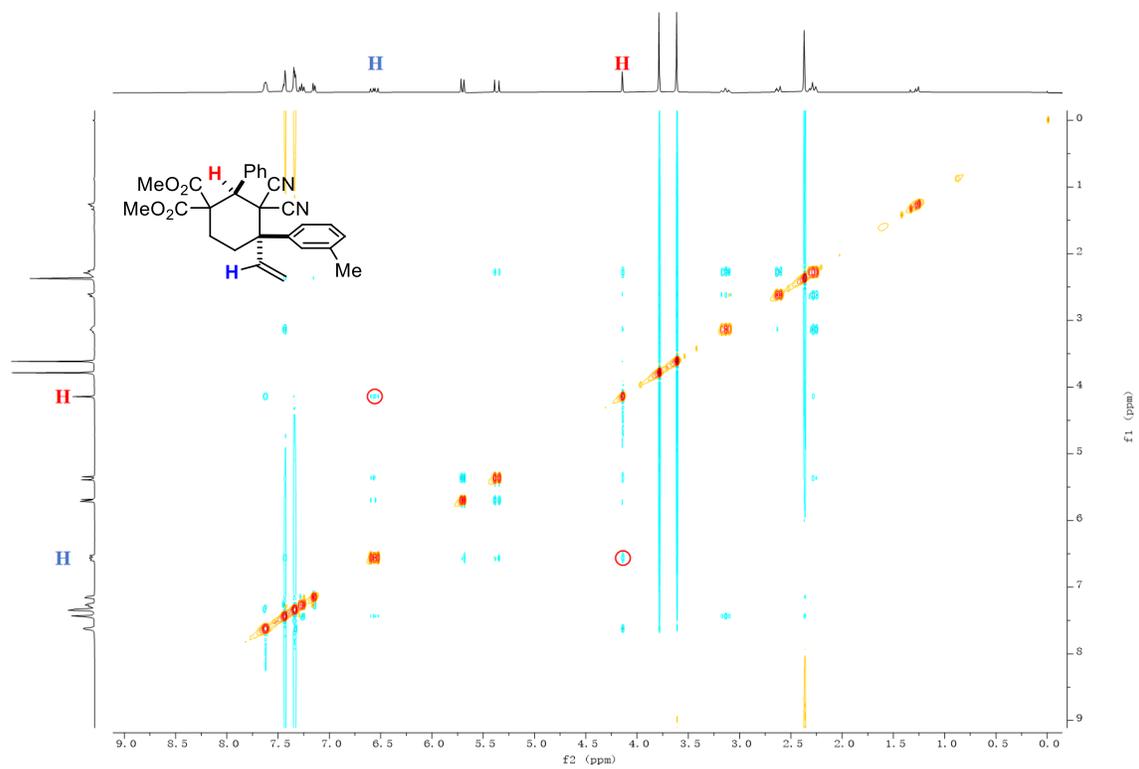


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7a**

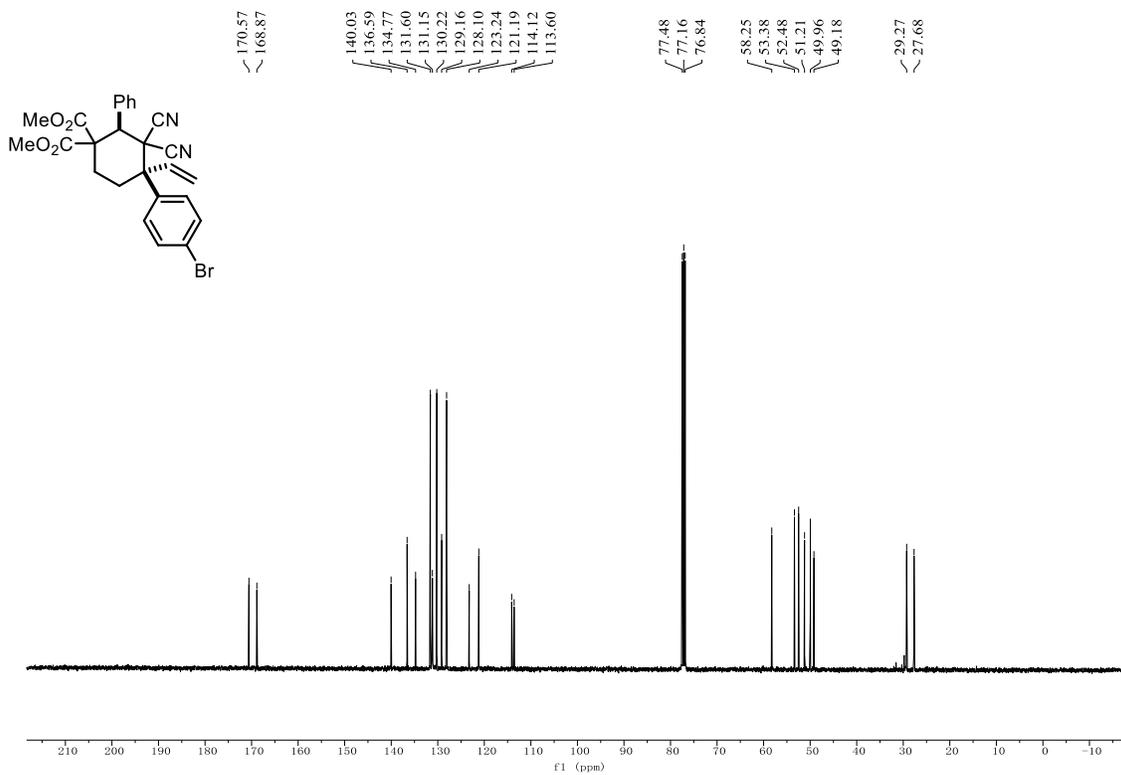
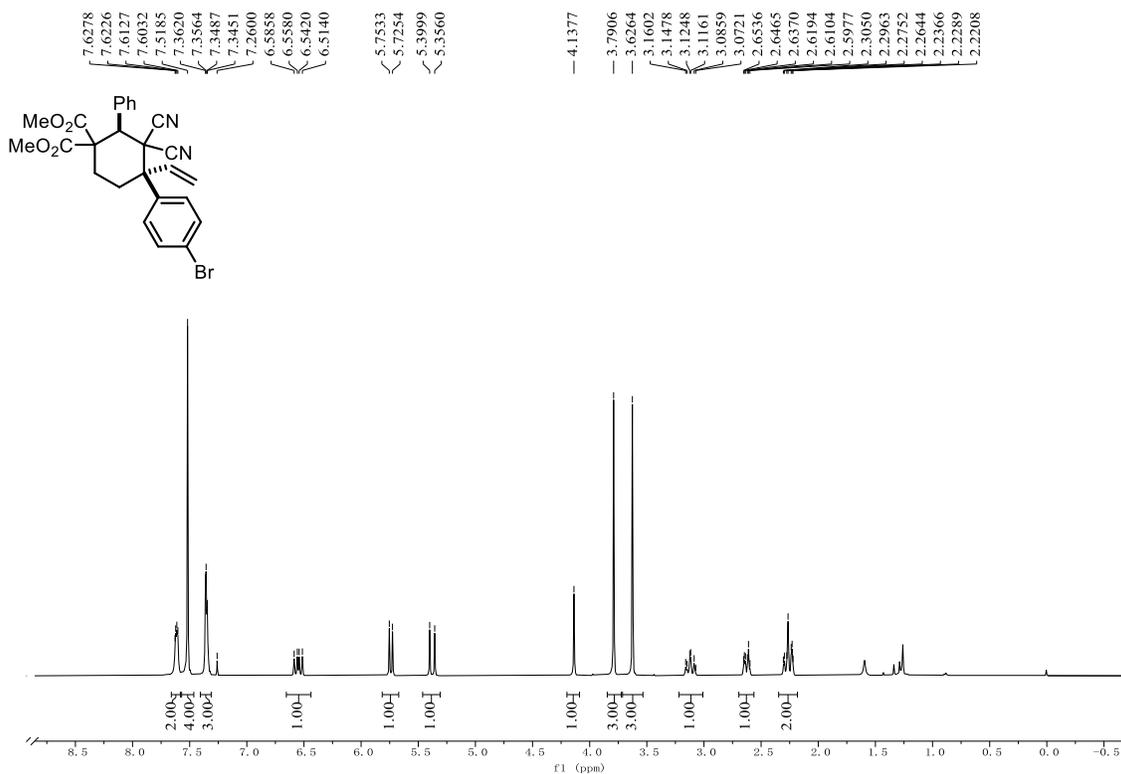


**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>), <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) and the NOE result of 7b**

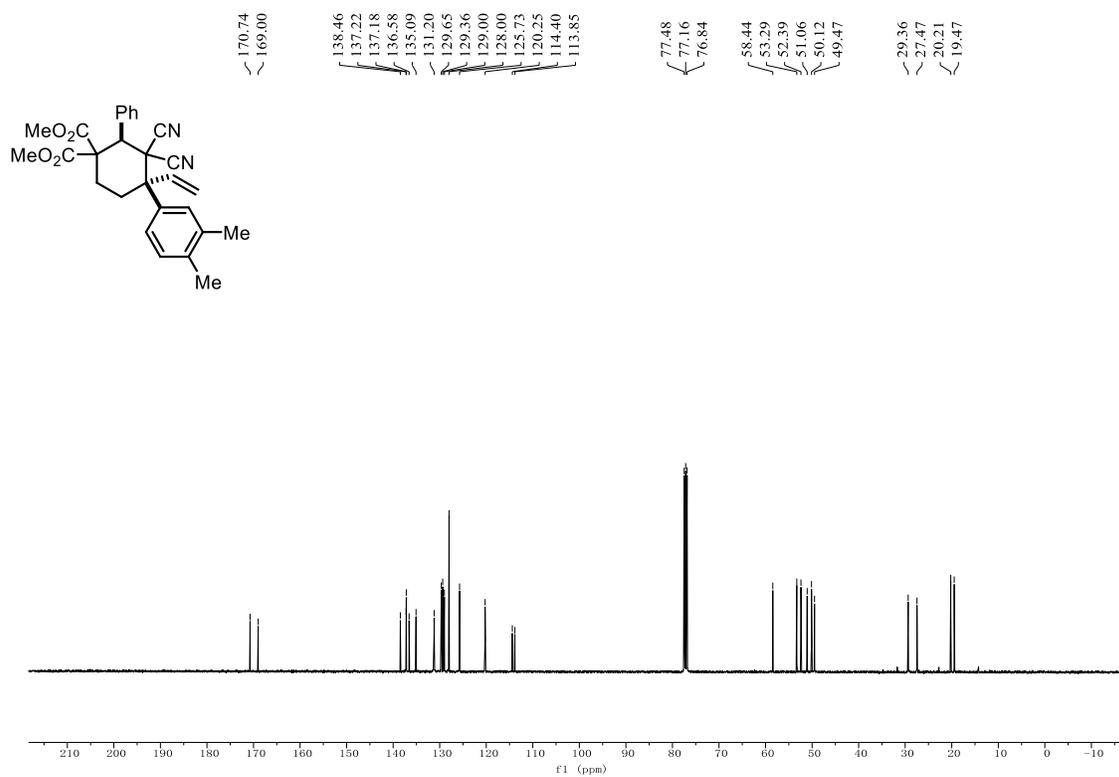
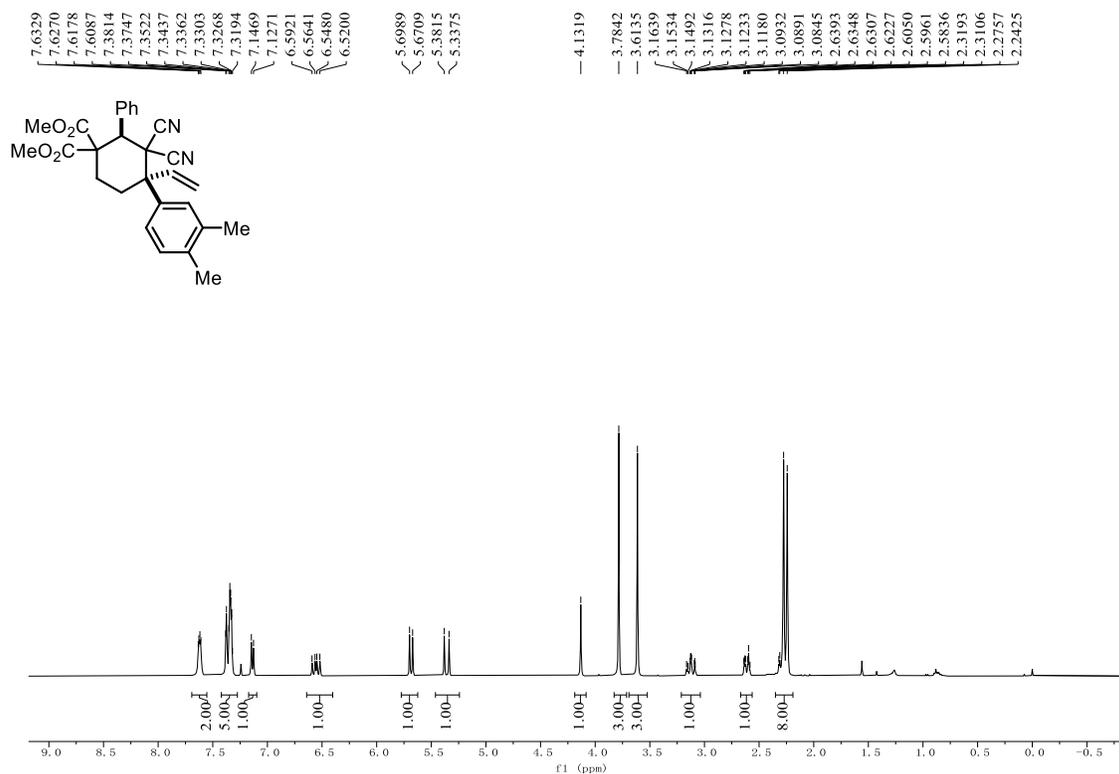




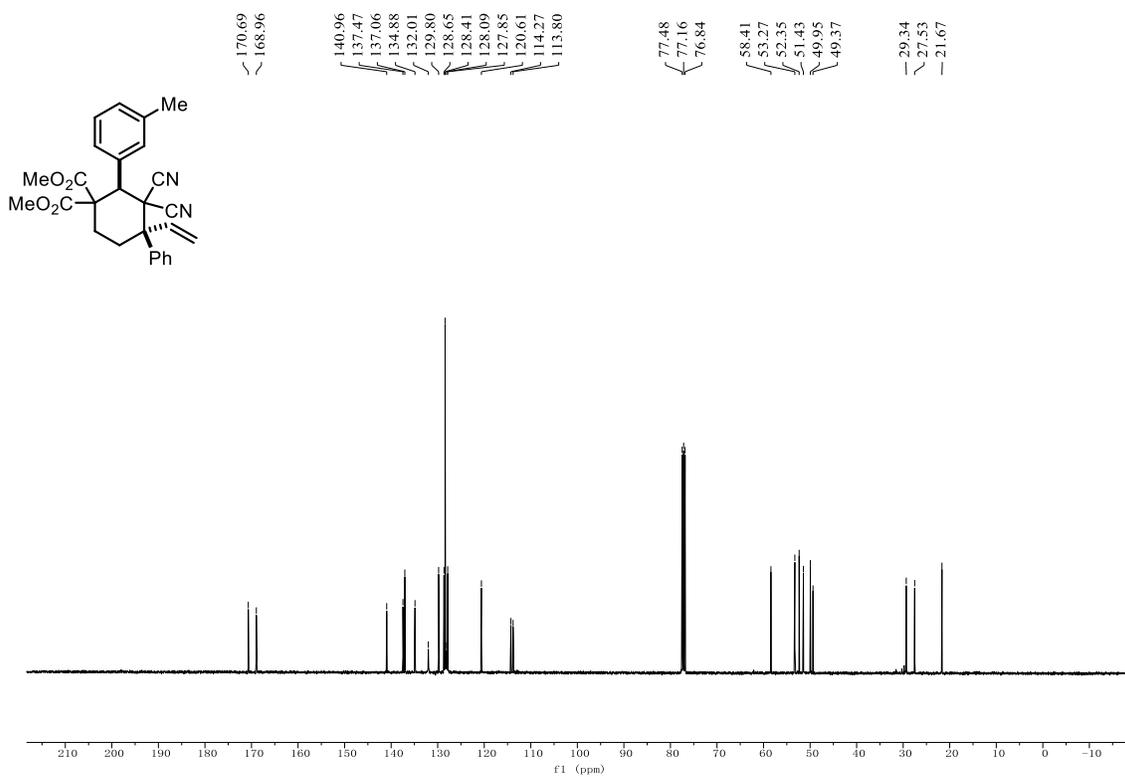
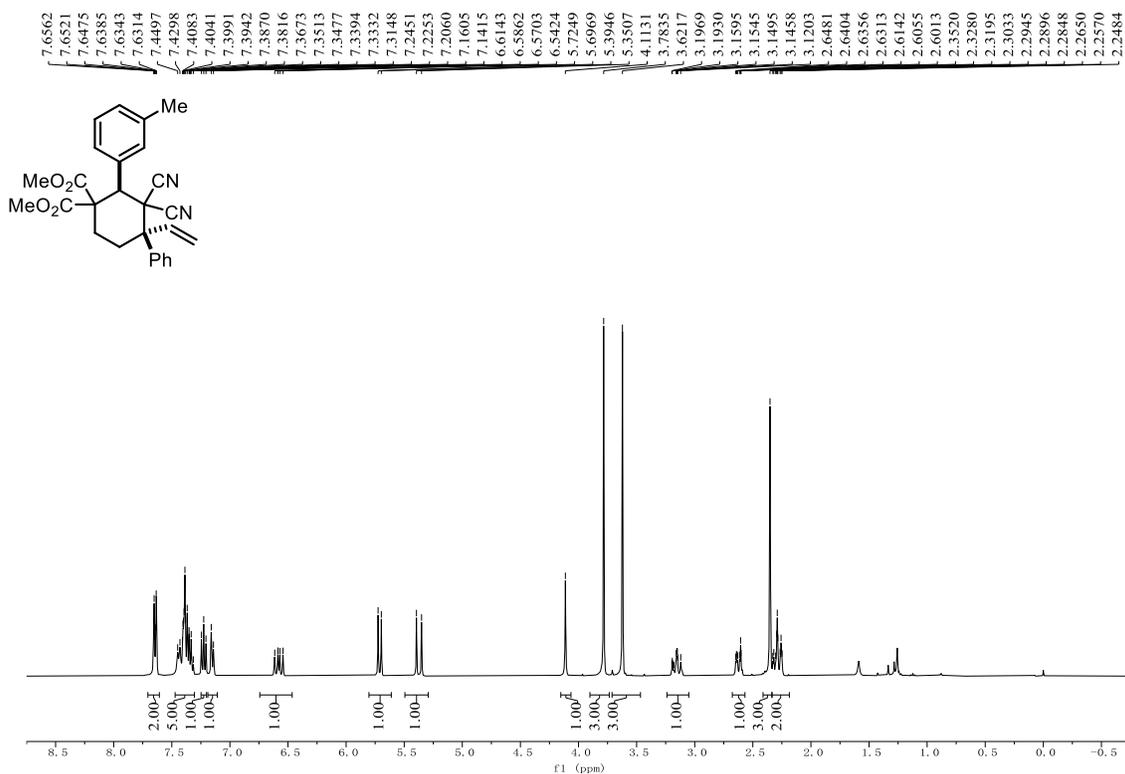
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7c**



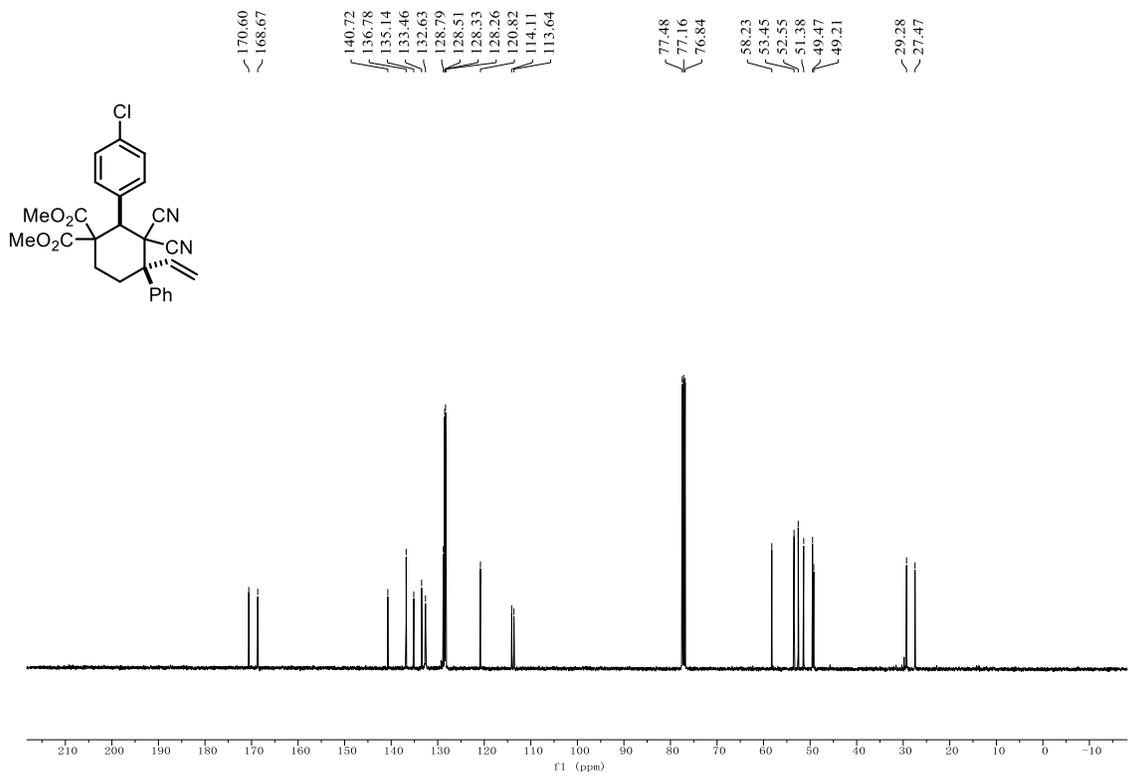
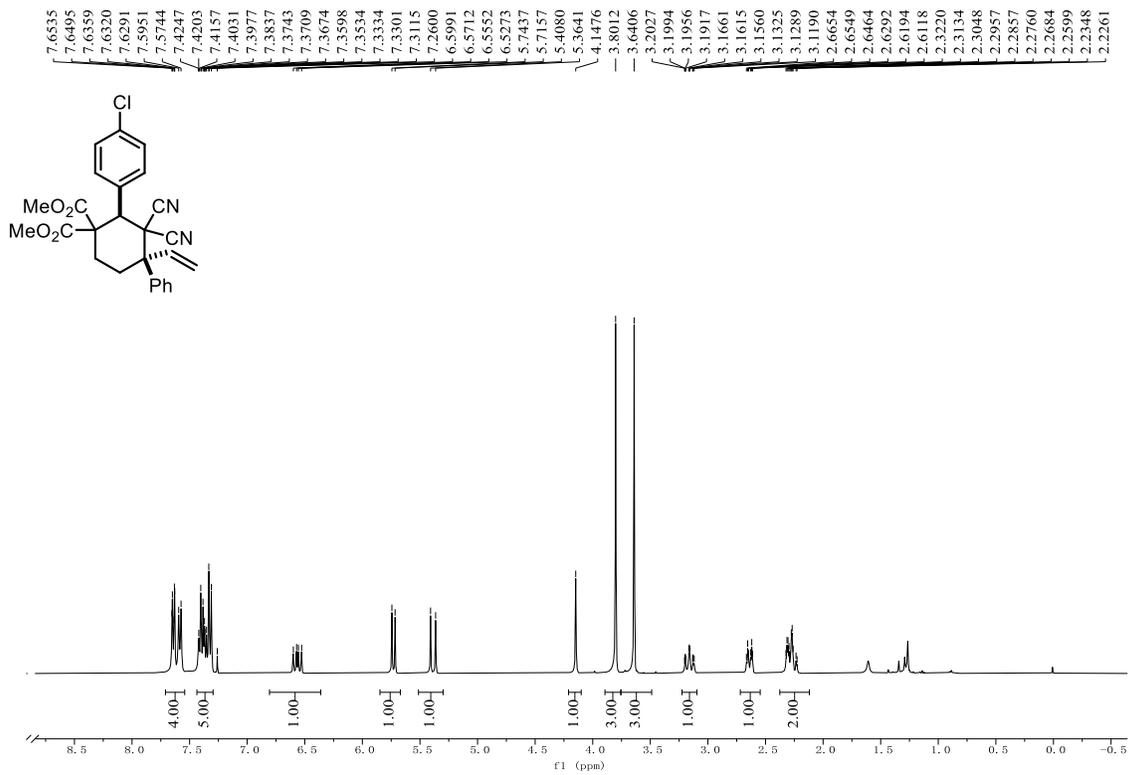
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7d**



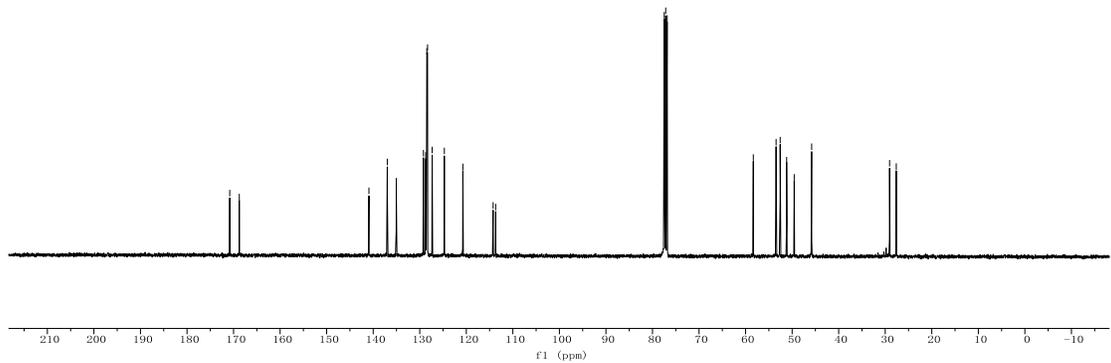
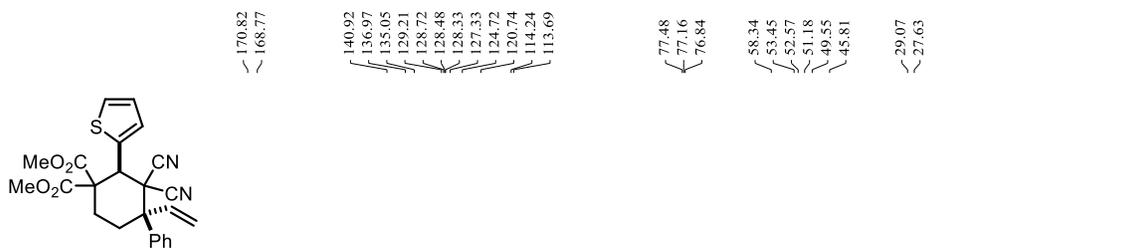
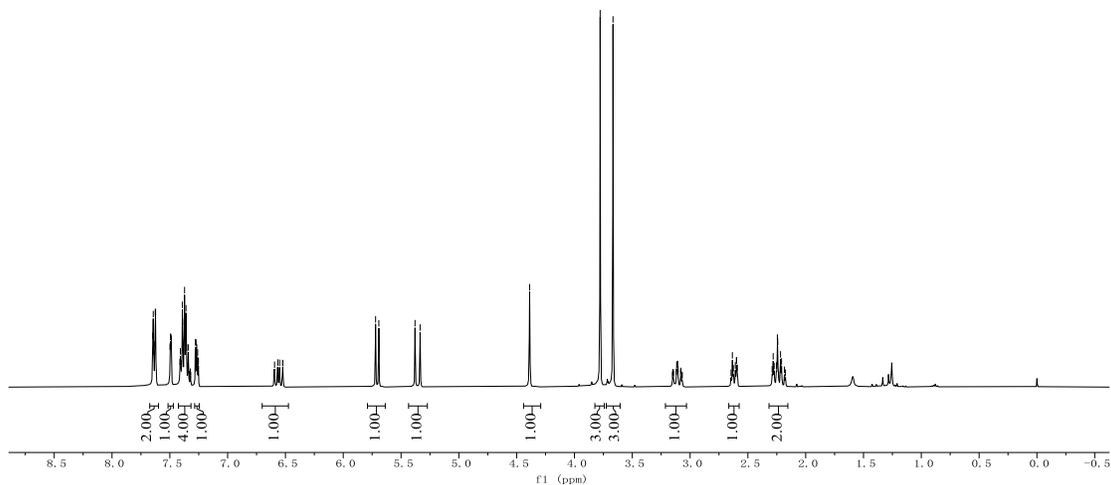
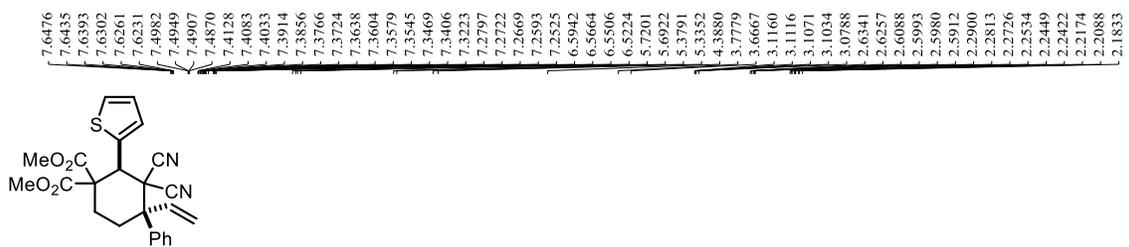
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7e**



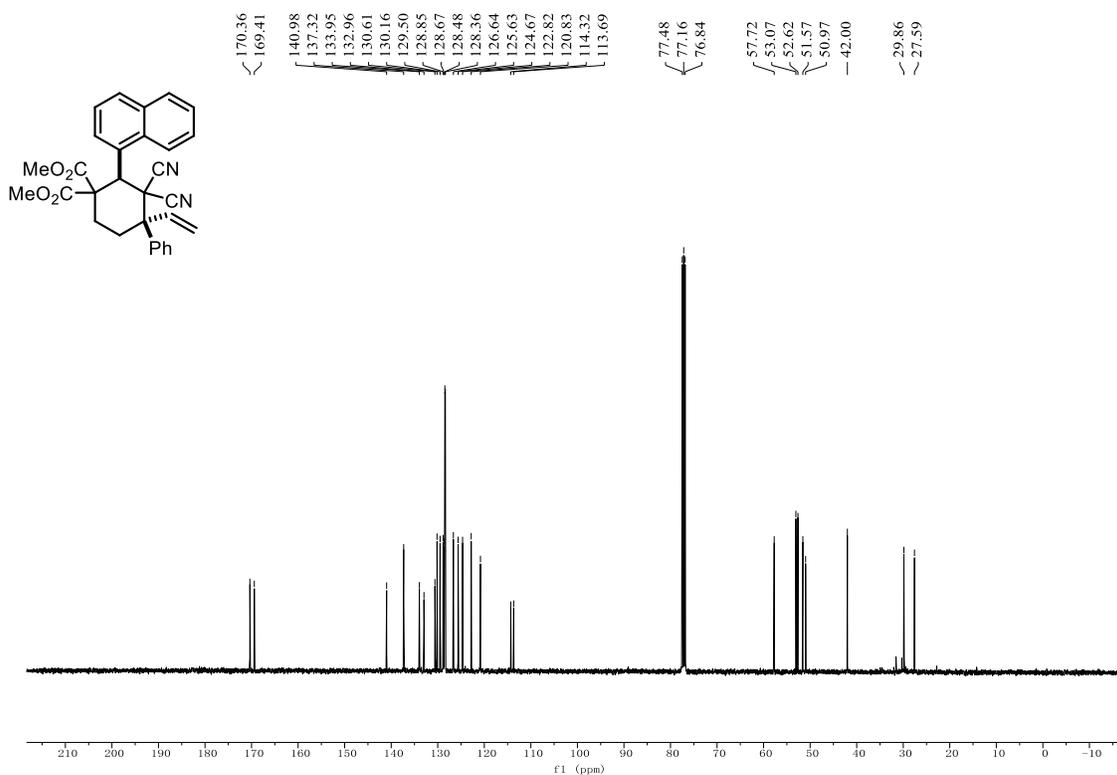
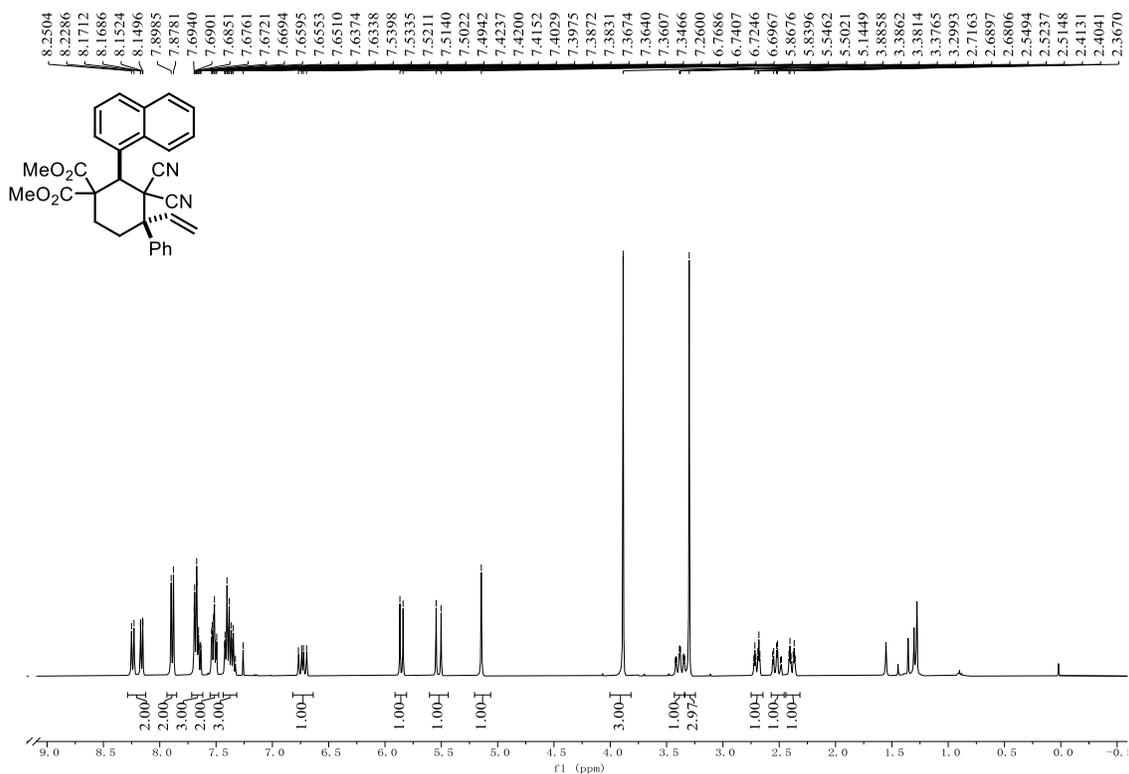
**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 7f**



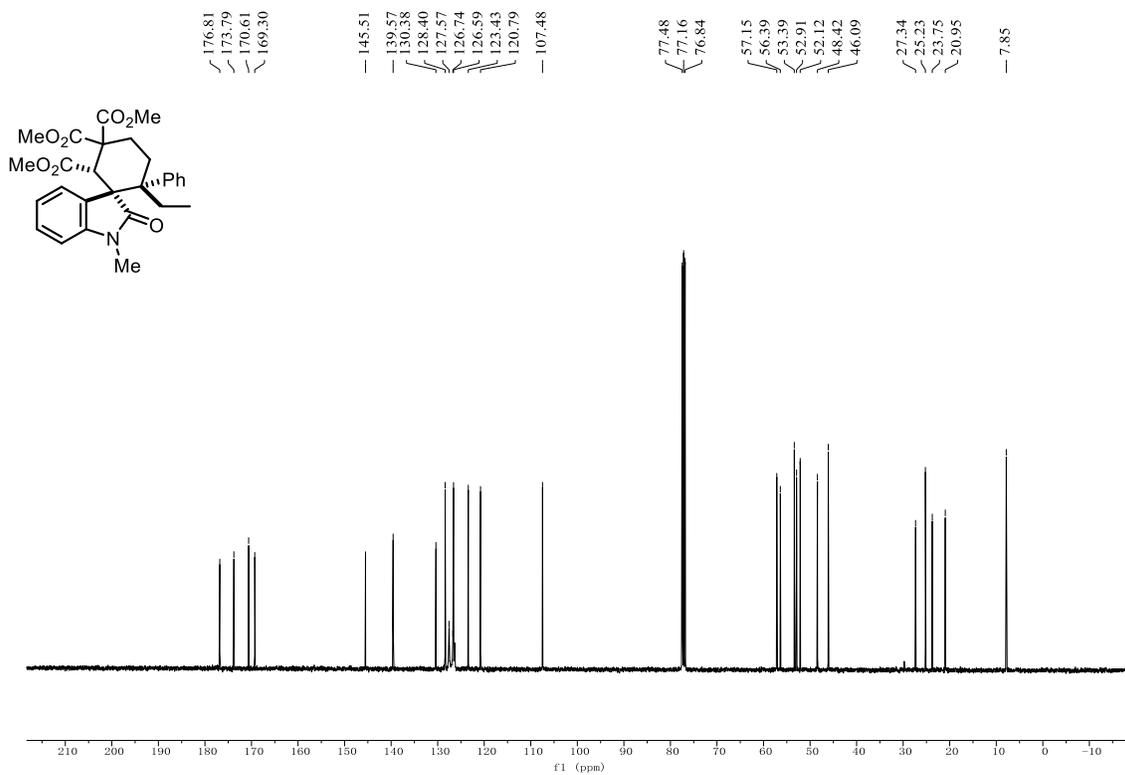
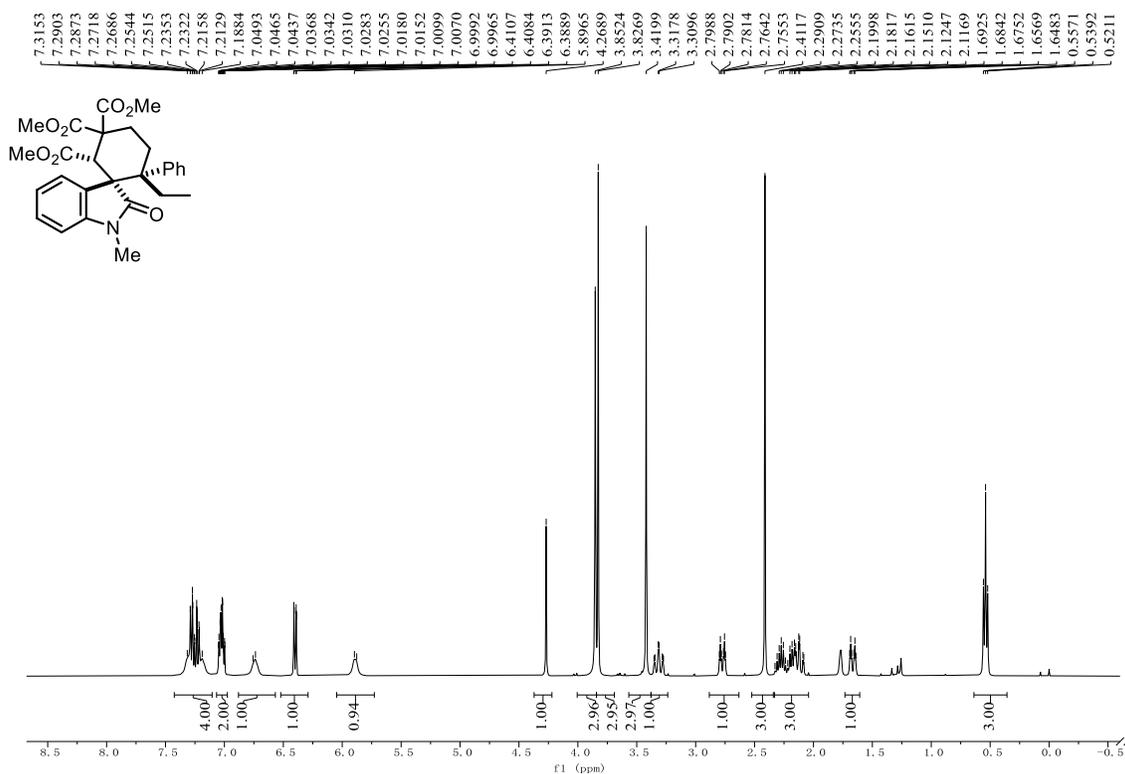
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7g**



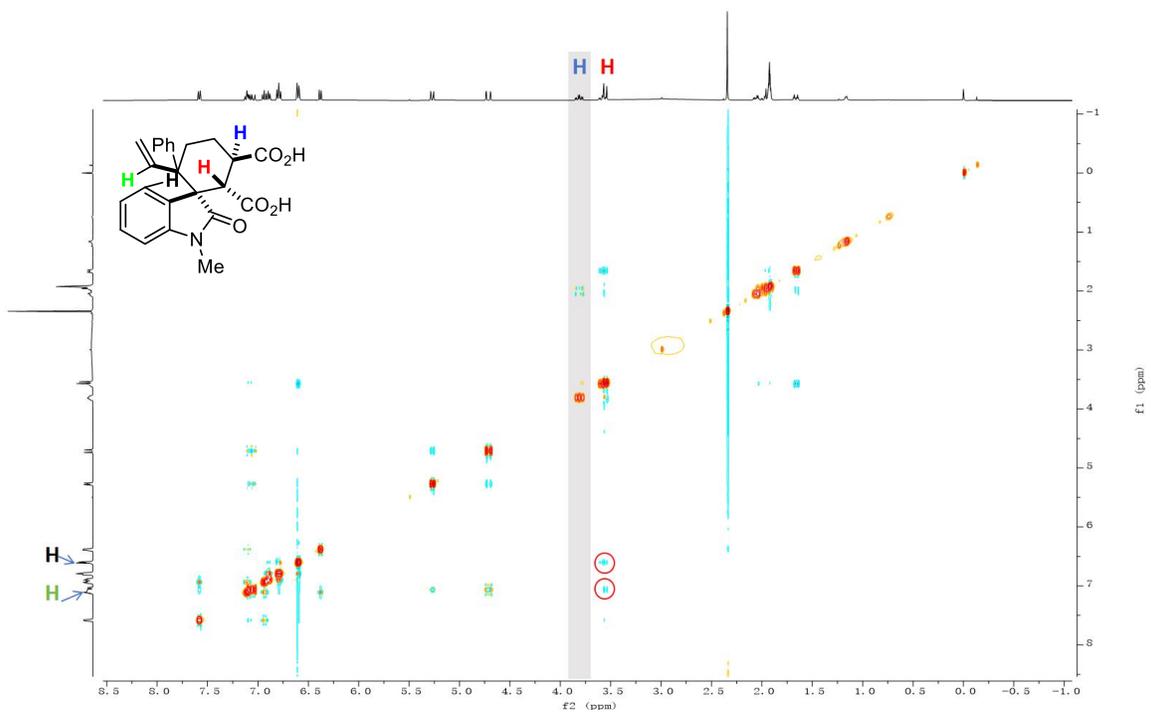
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 7h**



**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 8**

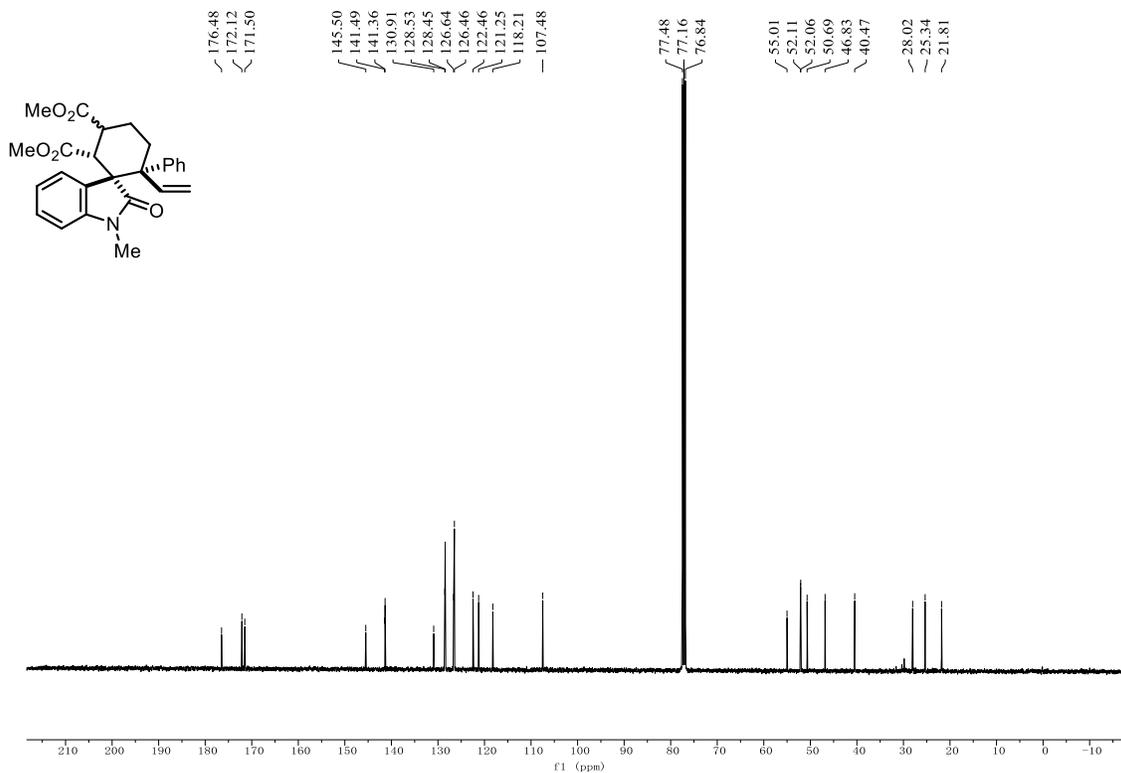
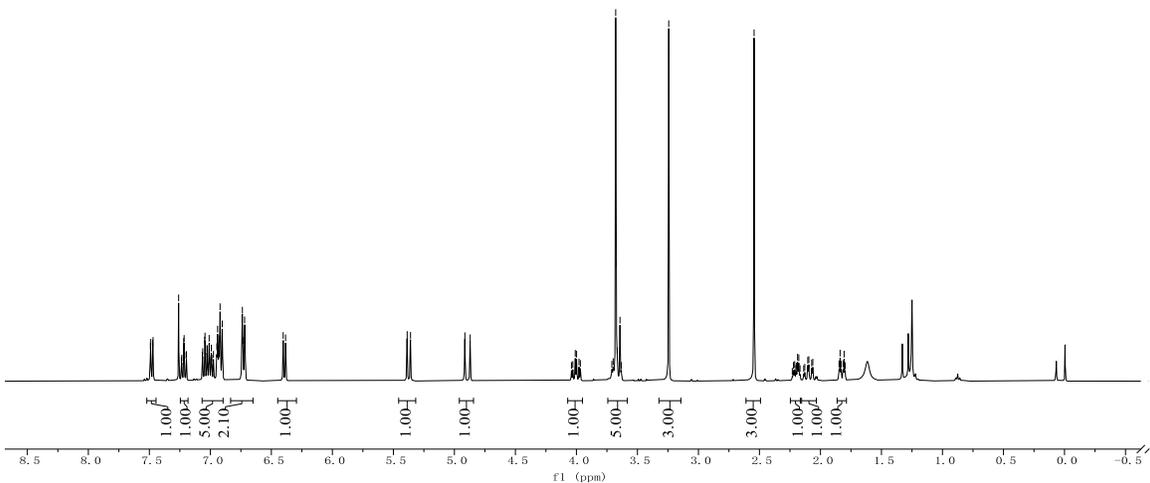
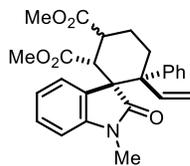




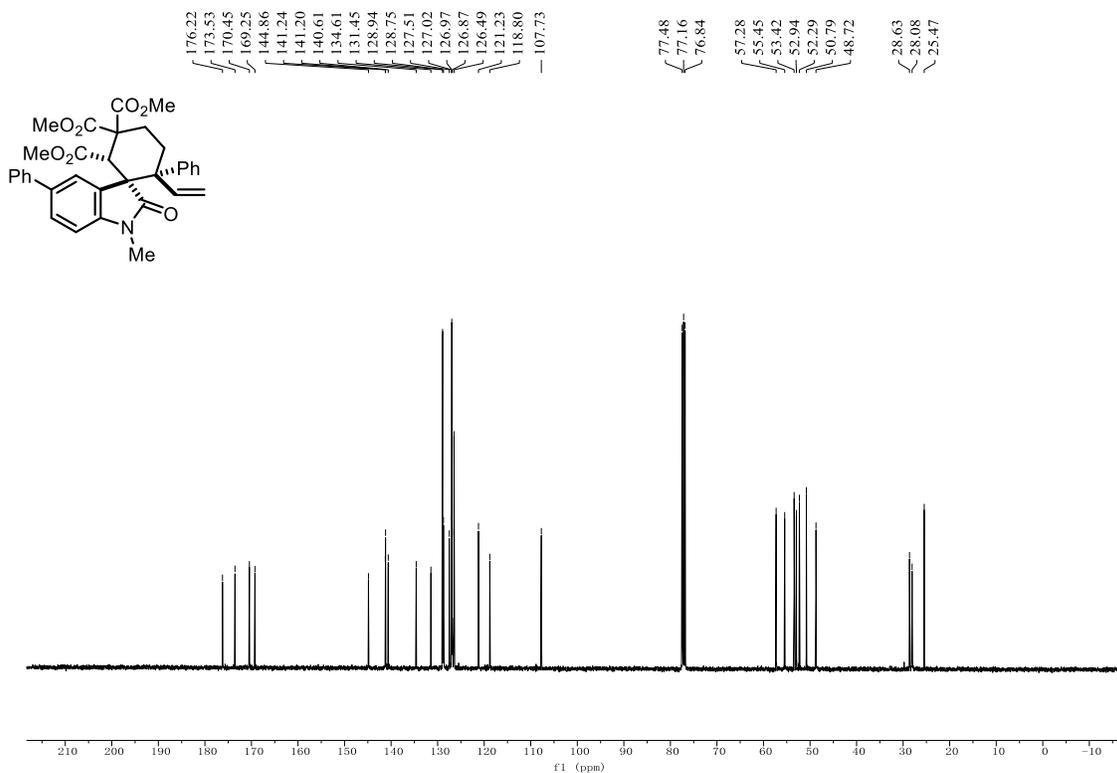
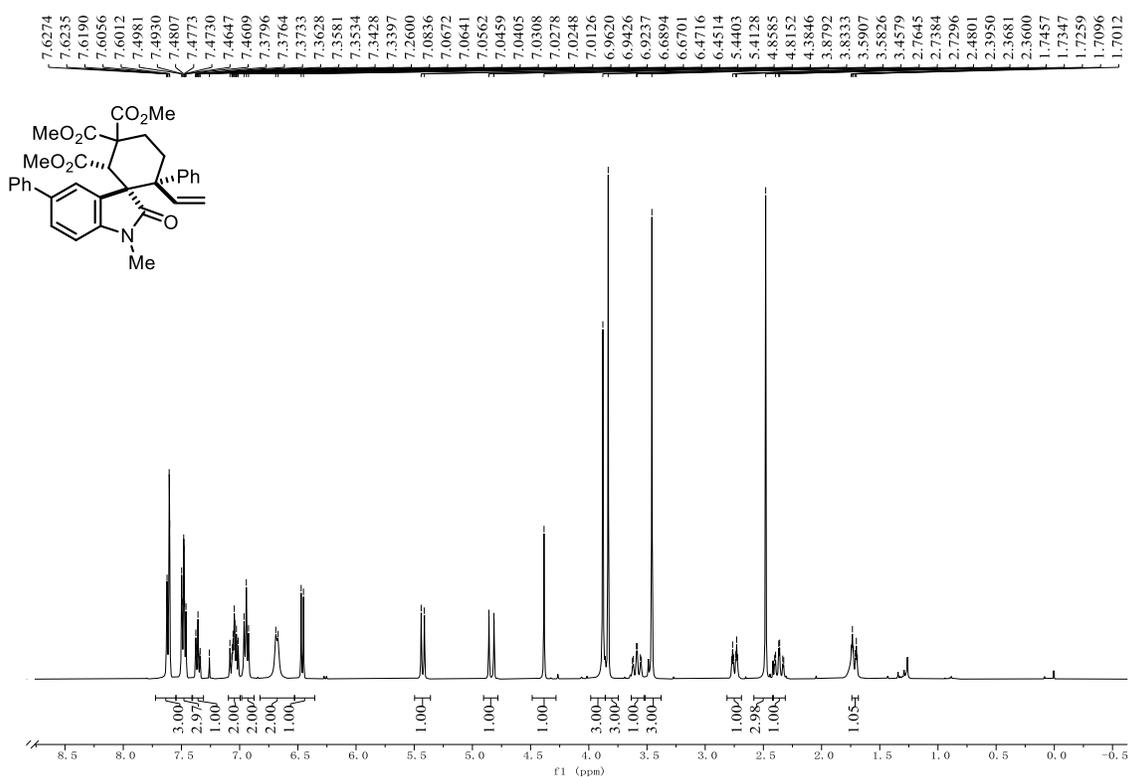


**$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ) and  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ) of 10**

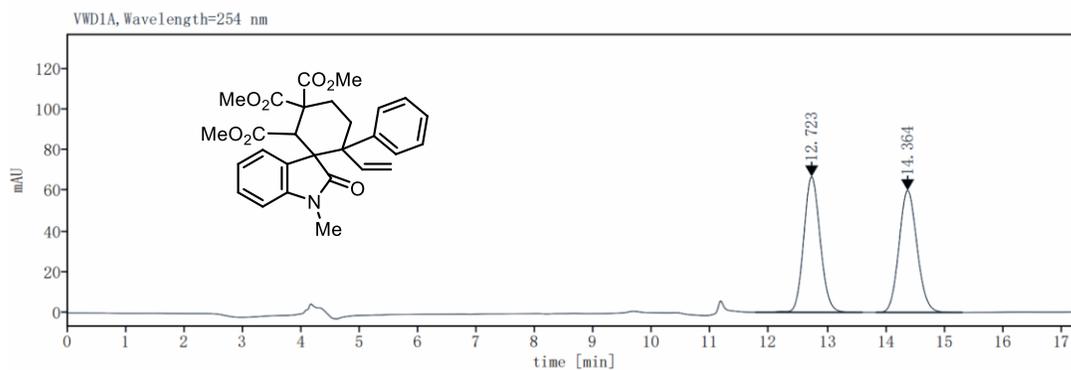
7.4915  
7.4885  
7.4728  
7.4698  
7.2600  
7.2373  
7.2343  
7.2181  
7.2150  
7.1987  
7.1958  
7.0656  
7.0629  
7.0466  
7.0439  
7.0279  
7.0250  
7.0099  
7.0050  
6.9952  
6.9919  
6.9885  
6.9745  
6.9470  
6.9406  
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6.9312  
6.9248  
6.9206  
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6.7375  
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6.7154  
6.4031  
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3.6431  
3.2435  
2.5439  
2.1874  
2.1776  
2.1038  
2.0953  
2.0713  
2.0628  
1.8391  
1.8062



# <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) and <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) of 11

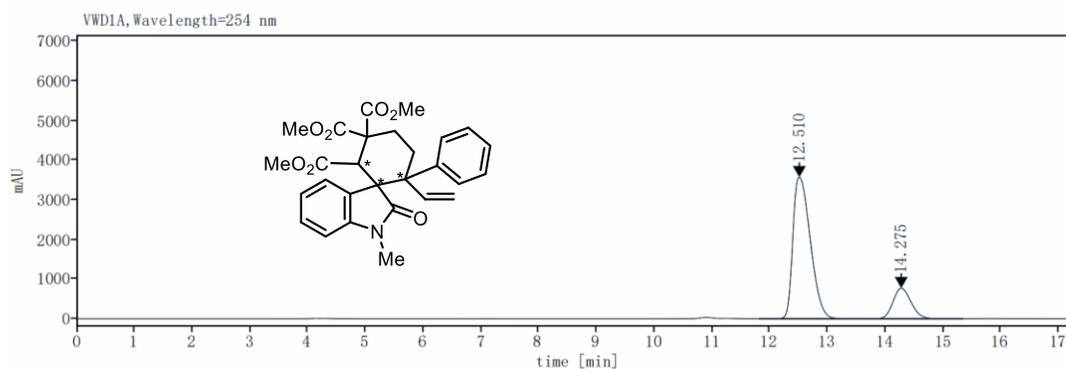


## HPLC spectra of 3a



Detector VWD1A, Wavelength=254 nm

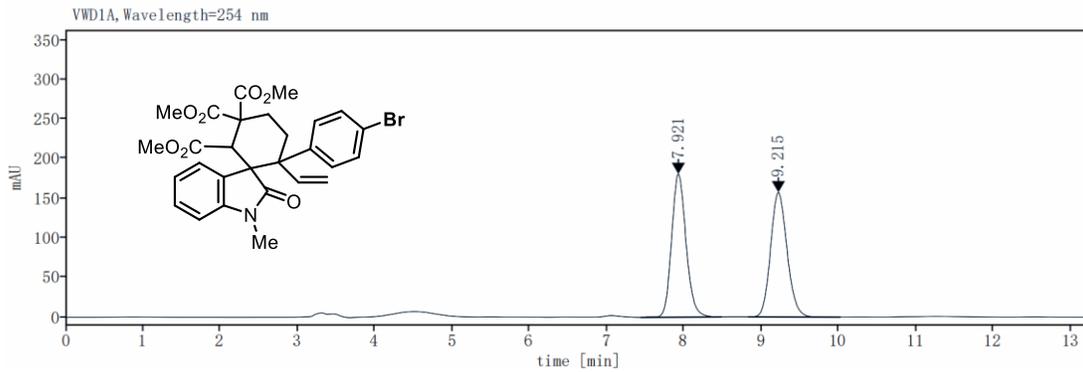
Peak	Ret. Time [min]	Area	Height	Area%
	12.723	1301.20	66.59	50.30
	14.364	1285.84	59.84	49.70
		2587.04		100.00



Detector VWD1A, Wavelength=254 nm

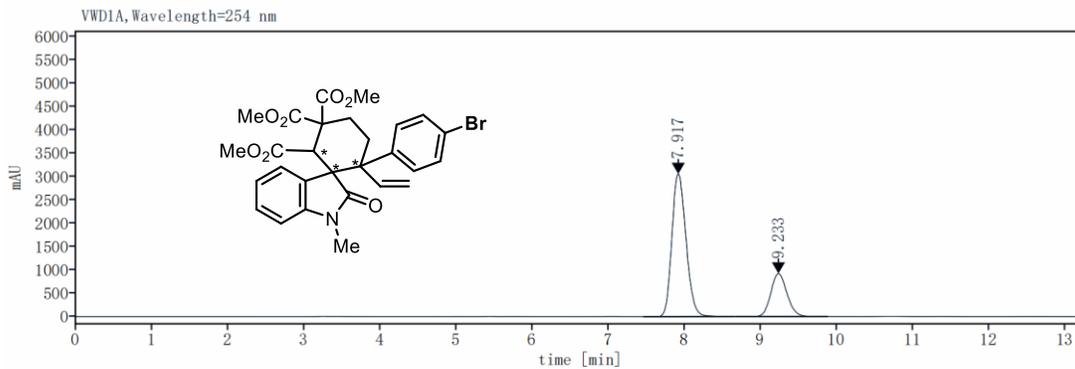
Peak	Ret. Time [min]	Area	Height	Area%
	12.510	75074.36	3573.01	81.75
	14.275	16758.48	772.97	18.25
		91832.84		100.00

### HPLC spectra of 3c



Detector VWD1A, Wavelength=254 nm

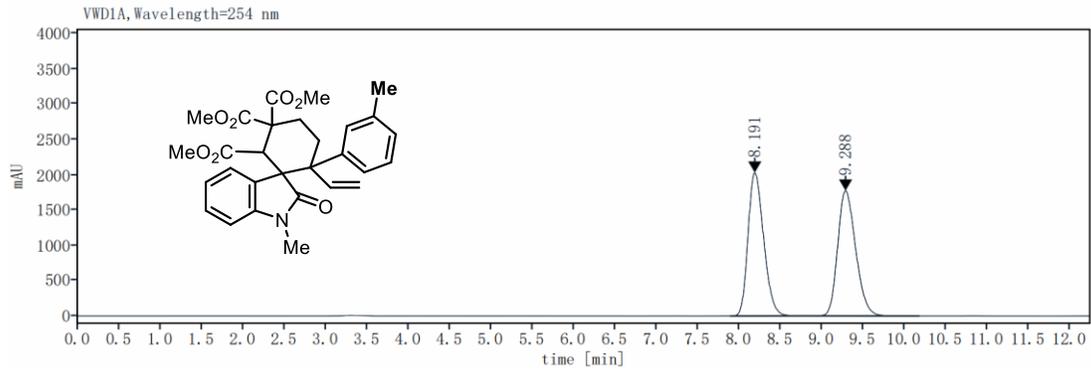
Peak	Ret.Time [min]	Area	Height	Area%
	7.921	2354.26	180.75	50.19
	9.215	2336.75	157.30	49.81
		4691.01		100.00



Detector VWD1A, Wavelength=254 nm

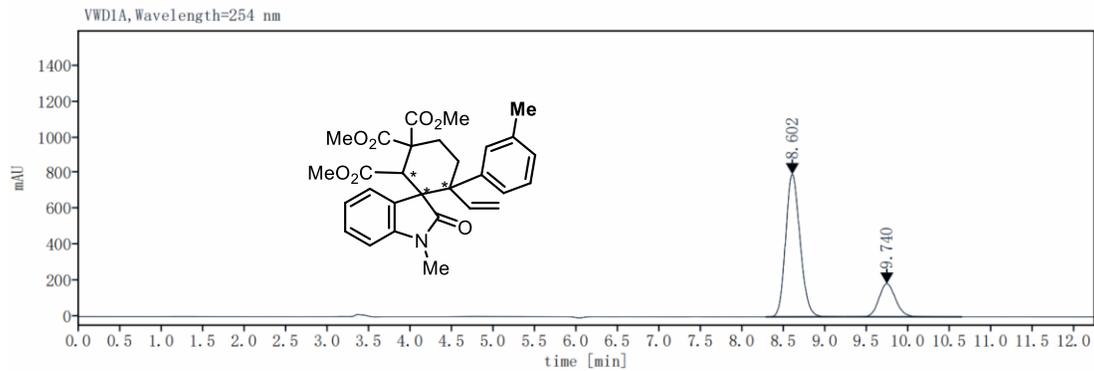
Peak	Ret.Time [min]	Area	Height	Area%
	7.917	39380.70	3058.73	74.39
	9.233	13558.30	921.60	25.61
		52939.01		100.00

## HPLC spectra of 3g



Detector VWD1A, Wavelength=254 nm

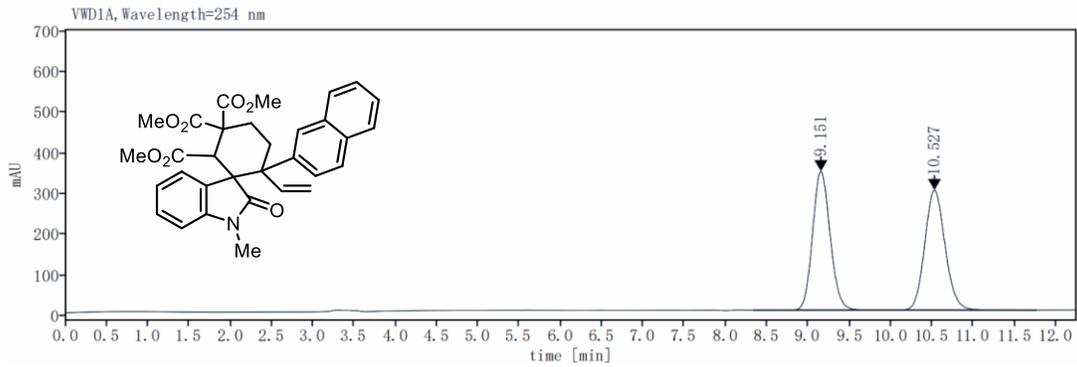
Peak	Ret. Time [min]	Area	Height	Area%
	8.191	26672.53	2028.71	49.85
	9.288	26835.86	1773.05	50.15
		53508.39		100.00



Detector VWD1A, Wavelength=254 nm

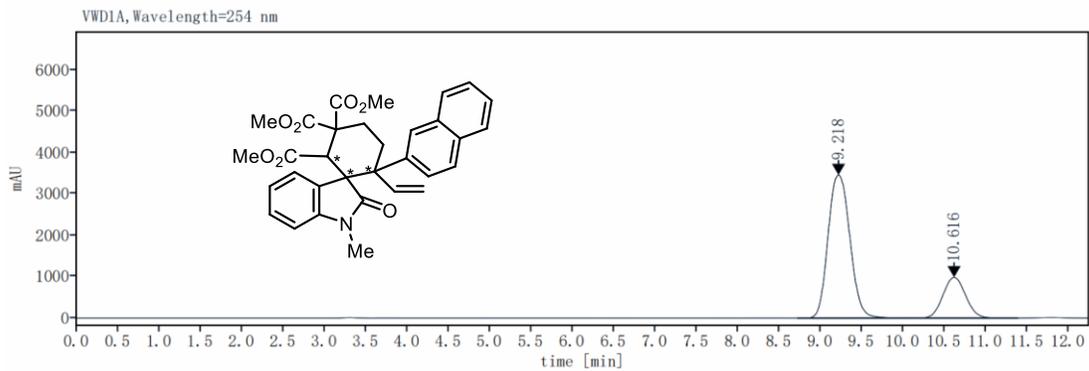
Peak	Ret. Time [min]	Area	Height	Area%
	8.602	9611.31	794.43	78.85
	9.740	2578.49	184.02	21.15
		12189.80		100.00

### HPLC spectra of 3i



Detector VWD1A, Wavelength=254 nm

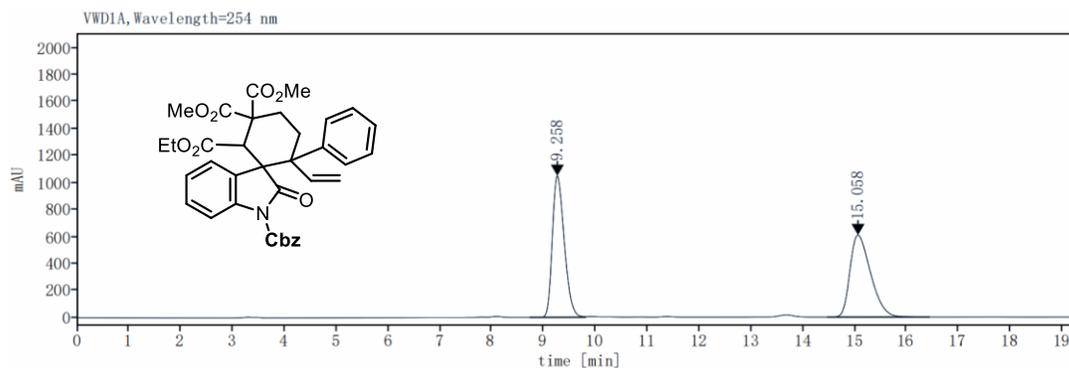
Peak	Ret.Time [min]	Area	Height	Area%
	9.151	5054.57	341.12	49.97
	10.527	5061.05	294.65	50.03
		10115.62		100.00



Detector VWD1A, Wavelength=254 nm

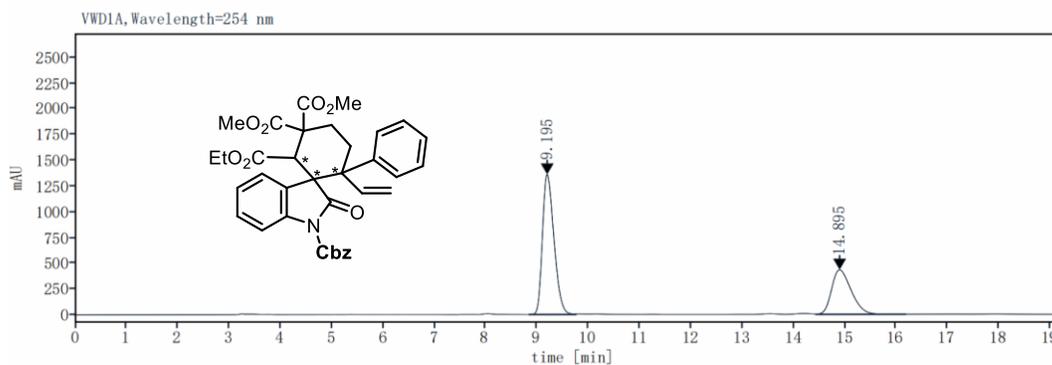
Peak	Ret.Time [min]	Area	Height	Area%
	9.218	63448.16	3461.13	77.17
	10.616	18774.75	984.01	22.83
		82222.91		100.00

## HPLC spectra of 3p



Detector VWD1A, Wavelength=254 nm

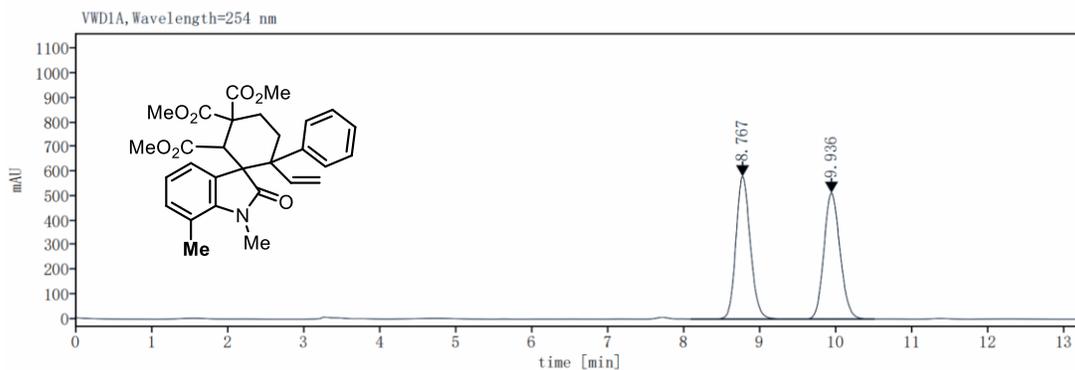
Peak	Ret. Time [min]	Area	Height	Area%
	9.258	16750.54	1048.01	49.91
	15.058	16813.72	607.22	50.09
		33564.26		100.00



Detector VWD1A, Wavelength=254 nm

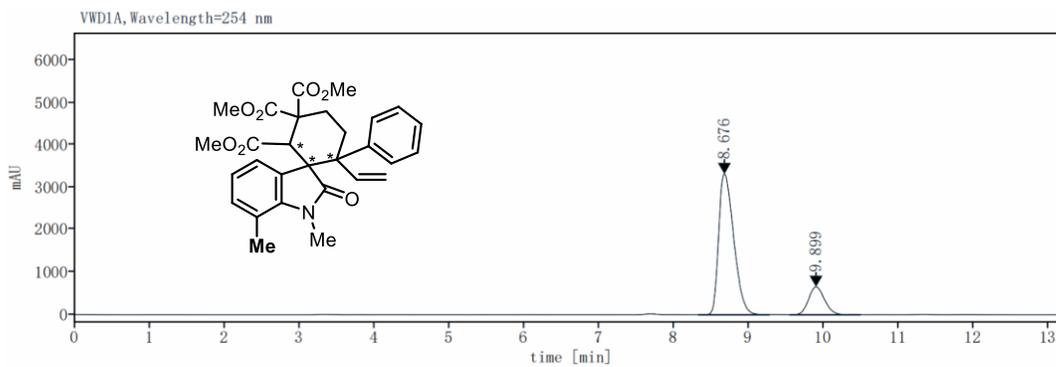
Peak	Ret. Time [min]	Area	Height	Area%
	9.195	21210.41	1358.86	64.99
	14.895	11427.87	432.12	35.01
		32638.27		100.00

## HPLC spectra of 3ac



Detector VWD1A, Wavelength=254 nm

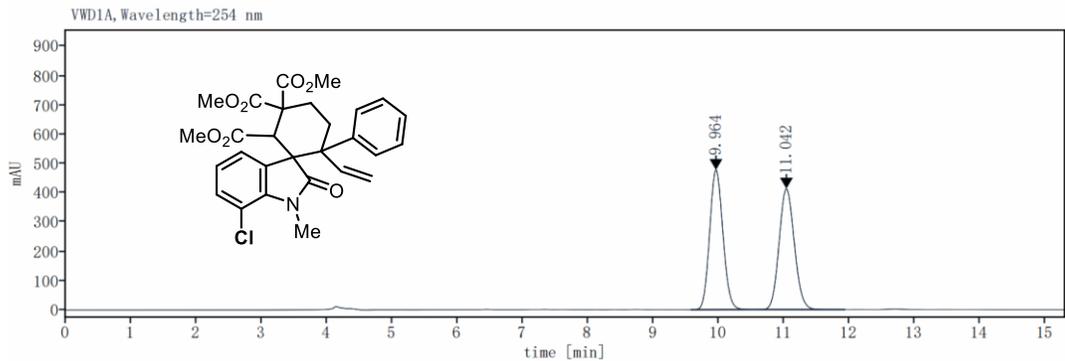
Peak	Ret. Time [min]	Area	Height	Area%
	8.767	7650.52	581.29	50.27
	9.936	7569.06	513.90	49.73
		15219.58		100.00



Detector VWD1A, Wavelength=254 nm

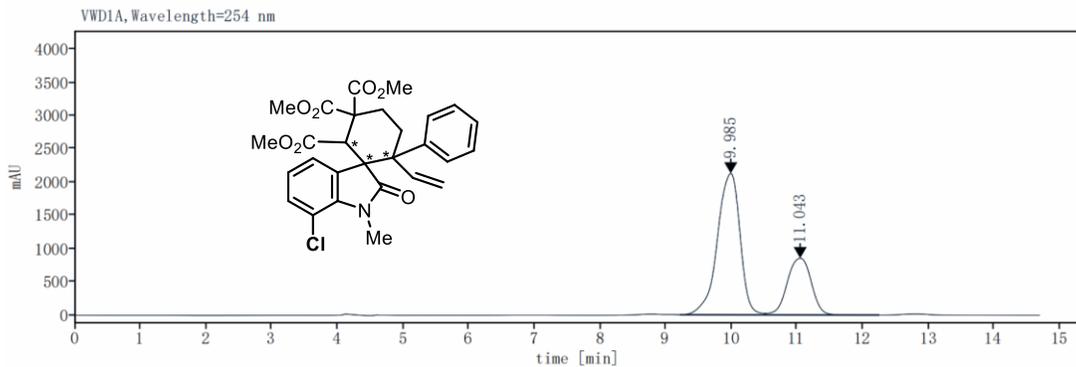
Peak	Ret. Time [min]	Area	Height	Area%
	8.676	46440.16	3318.73	82.54
	9.899	9826.20	659.38	17.46
		56266.36		100.00

### HPLC spectra of 3ae



Detector VWD1A, Wavelength=254 nm

Peak	Ret. Time [min]	Area	Height	Area%
	9.964	6746.95	476.88	50.15
	11.042	6707.43	412.67	49.85
		13454.38		100.00



Detector VWD1A, Wavelength=254 nm

Peak	Ret. Time [min]	Area	Height	Area%
	9.985	51141.97	2127.63	70.21
	11.043	21696.65	853.33	29.79
		72838.62		100.00