

## Supporting Information for

# Cu(II)-Catalyzed Highly Regio- and Stereoselective Construction of C-C Double Bonds: An Efficient Method for the Ketonization-Olefination of Indoles

Yun-Hong Bao, Pan-Pan Zhou, Jia-Yi Zhu, Wen-Bing Qin, Yu-Bo Kong

Zheng-Wang Chen, Shao-Bin Tang, Liang-Xian Liu\*

*Department of Chemistry and Chemical Engineering, Gannan Normal University, Ganzhou,*

*Jiangxi 341000, P. R. China*

*E-mail: lxliu@xmu.edu.cn*

### CONTENTS

1. General Methods and Materials .....	2
2. General Procedure and Spectroscopic Data of the Products <b>5-7</b> .....	2
3. Copies of <sup>1</sup> H, <sup>13</sup> C Spectra .....	14
4. X-ray Data of Compound <b>5j</b> .....	51
5. Reference.....	51

## 1. General Methods

Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were measured with a Nicolet Avatar 360 FT-IR spectrometer using film KBr pellet techniques.  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker spectrometers at 400 and 100 MHz, respectively. Chemical shifts were reported in ppm relative to TMS for  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra.  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$  was used as the NMR solvent. Mass spectra were recorded with Bruker Dalton Esquire 3000 plus LC-MS apparatus. Elemental analysis was carried out on a Perkin-Elmer 240B instrument. Silica gel (300-400 mesh) was used for flash column chromatography, eluting (unless otherwise stated) with an ethyl acetate/petroleum ether (PE) (60-90 °C) mixture.

## Materials

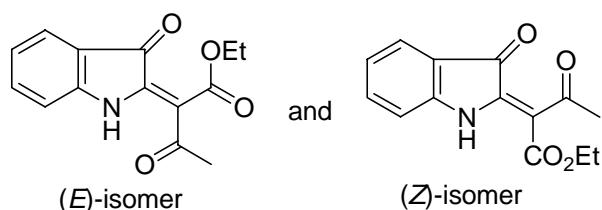
Commercially available starting materials and solvents were used as supplied, without further purification.

## 2. General Procedure for the Preparation of 5-7.

To a solution of indole (0.5 mmol),  $\beta$ -keto ester (1.0 mmol) and TEMPO (1.0 mmol) in toluene (0.6 mL) was added  $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$  (0.1 mmol) under atmosphere and the mixture was stirred at 80 or 85 °C for 20-24 h. The reaction mixture was concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: EtOAc/PE = 1:3) to yield the corresponding product.

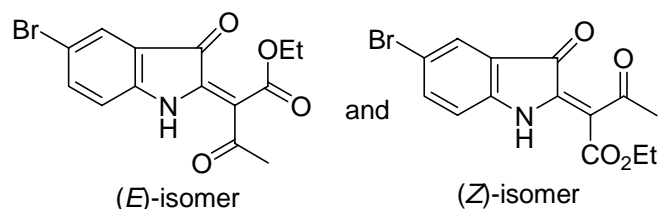
### Spectroscopic Data of the Products 5-7.

(*E*)- and (*Z*)-Ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)butanoate (**5a**)



With admixture (9%) of (*Z*)-isomer. Total yield: 94 mg, 73%. Red solid. IR (KBr)  $\nu_{\text{max}}$ : 3415, 1728, 1658, 1620, 1593, 1462, 1175, 1137  $\text{cm}^{-1}$ . MS (ESI): 260 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{13}\text{NO}_4$ : C, 64.86; H, 5.05; N, 5.40. Found C, 64.53; H, 5.39; N, 5.17. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.25 (s, 1H, NH), 7.64 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.51 (t,  $J = 7.6$  Hz, 1H, Ar-H), 7.03 (t,  $J = 7.6$  Hz, 1H, Ar-H), 6.95 (d,  $J = 7.8$  Hz, 1H, Ar-H), 4.45 (q,  $J = 7.1$  Hz, 2H,  $\text{OCH}_2$ ), 2.36 (s, 3H,  $\text{CH}_3$ ), 1.41 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.6, 187.3, 167.2, 152.4, 141.1, 137.5, 125.6, 122.7, 119.5, 112.2, 108.1, 62.2, 28.5, 13.8.

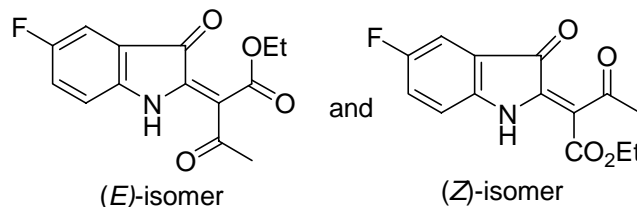
(*E*)- and (*Z*)-Ethyl 2-(5-bromo-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5b**)



With admixture (18%) of (*Z*)-isomer. Total yield: 89 mg, 53%. Red solid. IR (KBr)  $\nu_{\text{max}}$ : 3338, 1723, 1657, 1589, 1463, 1187, 1155  $\text{cm}^{-1}$ . MS (ESI): 338 ( $\text{M}+\text{H}^+$ , 100), 340 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{12}\text{BrNO}_4$ : C, 49.73; H, 3.58; N, 4.14. Found C, 50.04; H, 3.32; N, 4.06. Major

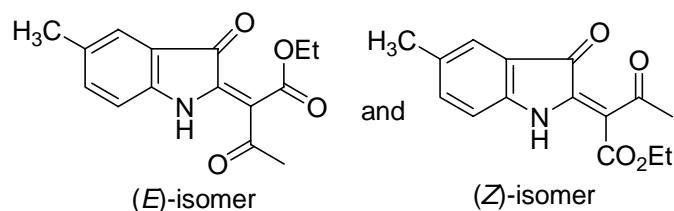
isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.25 (s, 1H, NH), 7.75 (d,  $J = 2.0$  Hz, 1H, Ar-H), 7.61 (dd,  $J = 8.3, 2.0$  Hz, 1H, Ar-H), 6.88 (d,  $J = 8.3$  Hz, 1H, Ar-H), 4.46 (q,  $J = 7.2$  Hz, 2H,  $\text{OCH}_2$ ), 2.37 (s, 3H,  $\text{CH}_3$ ), 1.41 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.6, 185.9, 166.7, 151.0, 140.5, 139.7, 128.3, 121.1, 115.2, 113.7, 108.2, 62.3, 28.5, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(5-fluoro-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5c**)



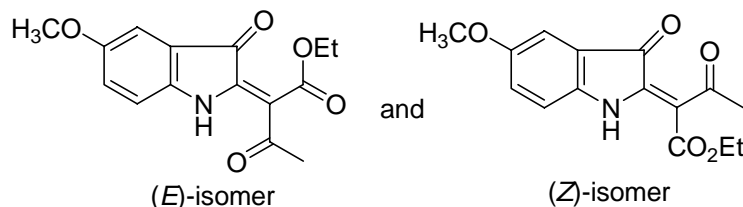
With admixture (14%) of (*Z*)-isomer. Total yield: 77 mg, 56%. Red solid. IR (KBr)  $\nu_{\text{max}}$ : 3414, 1723, 1657, 1621, 1593, 1487, 1178, 1124  $\text{cm}^{-1}$ . MS (ESI): 278 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{12}\text{FNO}_4$ : C, 60.65; H, 4.36; N, 5.05. Found C, 60.30; H, 4.61; N, 4.92. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.23 (s, 1H, NH), 7.30 (dd,  $J = 6.8, 2.6$  Hz, 1H, Ar-H), 7.23 (dt,  $J = 2.6, 8.6$  Hz, 1H, Ar-H), 6.92 (dd,  $J = 8.6, 3.6$  Hz, 1H, Ar-H), 4.44 (q,  $J = 7.2$  Hz, 2H,  $\text{OCH}_2$ ), 2.34 (s, 3H,  $\text{CH}_3$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.4, 186.6 (d,  $J = 3.1$  Hz), 166.9, 159.8, 157.4, 148.6 (d,  $J = 1.1$  Hz), 141.4, 124.3 (d,  $J = 24.9$  Hz), 120.2 (d,  $J = 7.7$  Hz), 113.1 (d,  $J = 7.7$  Hz), 111.8 (d,  $J = 24.2$  Hz), 62.3, 28.4, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(5-methyl-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5d**)



With admixture (16%) of (*Z*)-isomer. Total yield: 105 mg, 77%. Purple solid. IR (KBr)  $\nu_{\text{max}}$ : 3340, 1722, 1586, 1489, 1177  $\text{cm}^{-1}$ . MS (ESI): 274 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_4$ : C, 65.92; H, 5.53; N, 5.13. Found C, 66.01; H, 5.09; N, 4.97. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.19 (s, 1H, NH), 7.39 (s, 1H, Ar-H), 7.29 (t,  $J = 8.0$  Hz, 1H, Ar-H), 6.82 (d,  $J = 8.0$  Hz, 1H, Ar-H), 4.45 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2$ ), 2.34 (s, 3H,  $\text{CH}_3$ ), 2.29 (s, 3H,  $\text{CH}_3$ ), 1.41 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.4, 187.4, 167.3, 150.4, 141.5, 138.2, 132.5, 125.6, 119.6, 111.9, 107.7, 62.1, 28.4, 20.6, 13.8.

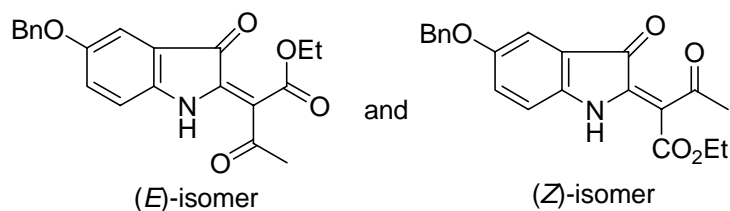
(*E*)- and (*Z*)-Ethyl 2-(5-methoxy-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5e**)



With admixture (17%) of (*Z*)-isomer. Total yield: 118 mg, 82%. Purple solid. IR (KBr)  $\nu_{\text{max}}$ : 3340, 1718, 1651, 1584, 1490, 1278, 1190, 1139  $\text{cm}^{-1}$ . MS (ESI): 290 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{15}\text{H}_{15}\text{NO}_5$ : C, 62.28; H, 5.23; N, 4.84. Found C, 61.89; H, 5.52; N, 5.09. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.13 (s, 1H, NH), 7.12 (s, 1H, Ar-H), 7.10 (d,  $J = 8.5$  Hz, 1H, Ar-H), 6.87

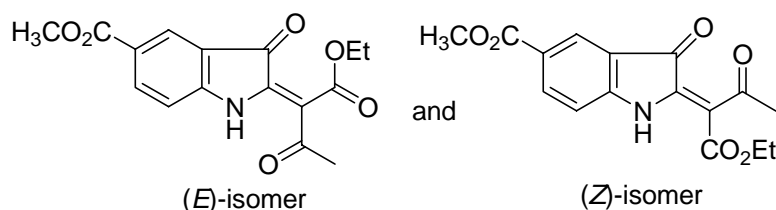
(d,  $J = 8.5$  Hz, 1H, Ar-H), 4.44 (q,  $J = 7.1$  Hz, 2H, OCH<sub>2</sub>), 3.79 (s, 3H, OCH<sub>3</sub>), 2.34 (s, 3H, CH<sub>3</sub>), 1.40 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.3, 187.5, 167.3, 155.8, 146.8, 141.9, 125.2, 119.9, 113.1, 108.3, 107.8, 62.2, 55.9, 28.4, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(5-benzyloxy-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5f**)



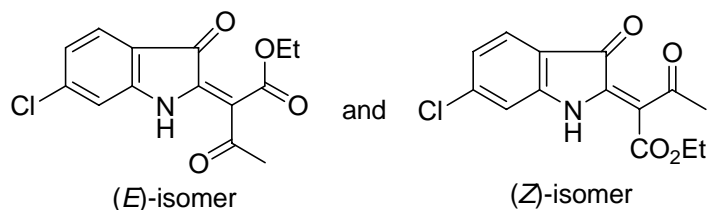
With admixture (12%) of (*Z*)-isomer. Total yield: 124 mg, 68%. Purple solid. IR (KBr)  $\nu_{\max}$ : 3357, 1705, 1643, 1568, 1492, 1193, 1135 cm<sup>-1</sup>. MS (ESI): 366 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>5</sub>: C, 69.03; H, 5.24; N, 3.83. Found C, 68.71; H, 5.59; N, 3.47. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.16 (s, 1H, NH), 7.44-7.33 (m, 5H, Ar-H), 7.19 (s, 1H, Ar-H), 7.16 (d,  $J = 8.5$  Hz, 1H, Ar-H), 6.87 (d,  $J = 8.5$  Hz, 1H, Ar-H), 5.04 (s, 2H, OCH<sub>2</sub>), 4.45 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 2.35 (s, 3H, CH<sub>3</sub>), 1.42 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.4, 187.4, 167.2, 154.9, 147.0, 141.9, 136.3, 128.7, 128.2, 127.7, 126.1, 120.0, 113.1, 109.8, 107.9, 70.8, 62.2, 28.4, 13.8.

(*E*)- and (*Z*)-Methyl 3-(1-ethoxy-1,3-dioxobutan-2-ylidene)-3-oxoindoline-5-carboxylate (**5g**)



With admixture (20%) of (*Z*)-isomer. Total yield: 82 mg, 52%. Orange solid. IR (KBr)  $\nu_{\max}$ : 3414, 1718, 1625, 1593, 1255, 1192, 1125 cm<sup>-1</sup>. MS (ESI): 318 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>6</sub>: C, 60.57; H, 4.77; N, 4.41. Found C, 60.53; H, 4.86; N, 4.37. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.40 (s, 1H, NH), 8.32 (s, 1H, Ar-H), 8.23 (dd,  $J = 8.4, 1.6$  Hz, 1H, Ar-H), 7.02 (d,  $J = 8.4$  Hz, 1H, Ar-H), 4.47 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 1.42 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.7, 186.2, 166.6, 165.7, 155.1, 140.7, 138.9, 127.4, 124.9, 119.5, 111.9, 109.5, 62.4, 52.3, 28.6, 13.8.

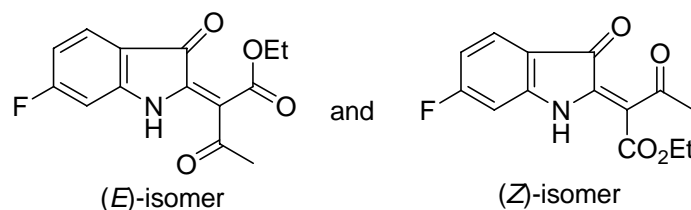
(*E*)- and (*Z*)-Ethyl 2-(6-chloro-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5h**)



With admixture (16%) of (*Z*)-isomer. Total yield: 98 mg, 67%. Orange solid. IR (KBr)  $\nu_{\max}$ : 3414, 1710, 1615, 1570, 1440, 1168 cm<sup>-1</sup>. MS (ESI): 294 (M+H<sup>+</sup>, 100), 296 (M+H<sup>+</sup>, 30). Anal calcd for C<sub>14</sub>H<sub>12</sub>ClNO<sub>4</sub>: C, 57.25; H, 4.12; N, 4.77. Found C, 56.89; H, 4.46; N, 4.51. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.26 (s, 1H, NH), 7.57 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.00 (dd,  $J = 8.0, 1.6$  Hz, 1H, Ar-H), 6.98 (s, 1H, Ar-H), 4.46 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 1.41 (t,

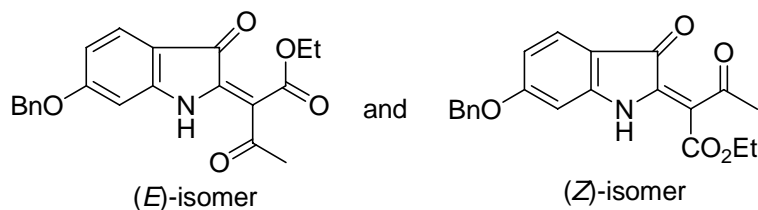
$J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.6, 185.7, 166.8, 153.1, 143.9, 140.9, 126.4, 123.1, 118.0, 112.7, 109.0, 62.3, 28.5, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(6-fluoro-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5i**)



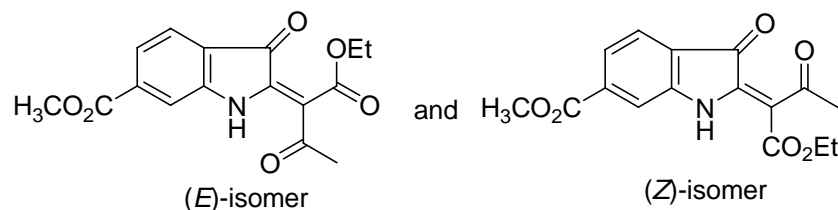
With admixture (11%) of (*Z*)-isomer. Total yield: 97 mg, 70%. Orange solid. IR (KBr)  $\nu_{\max}$ : 3276, 1715, 1651, 1619, 1573, 1449, 1187 cm<sup>-1</sup>. MS (ESI): 278 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>14</sub>H<sub>12</sub>FNO<sub>4</sub>: C, 60.65; H, 4.36; N, 5.05. Found C, 60.29; H, 4.67; N, 4.83. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.25 (s, 1H, NH), 7.64 (dd,  $J = 8.2, 5.6$  Hz, 1H, Ar-H), 6.75-6.64 (m, 2H, Ar-H), 4.45 (q,  $J = 7.1$  Hz, 2H, OCH<sub>2</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.6, 185.3, 168.9 (d,  $J = 258.7$  Hz), 166.8, 154.5 (d,  $J = 13.8$  Hz), 141.2, 127.9 (d,  $J = 12.0$  Hz), 116.0, 110.3 (d,  $J = 24.1$  Hz), 108.9, 100.2 (d,  $J = 27.4$  Hz), 62.3, 28.5, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(6-benzyloxy-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5j**)



With admixture (9%) of (*Z*)-isomer. Total yield: 155 mg, 85%. Red solid. IR (KBr)  $\nu_{\max}$ : 3317, 1713, 1621, 1586, 1453, 1187, 1141 cm<sup>-1</sup>. MS (ESI): 366 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>21</sub>H<sub>19</sub>NO<sub>5</sub>: C, 69.03; H, 5.24; N, 3.83. Found C, 69.34; H, 4.87; N, 3.75. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.15 (s, 1H, NH), 7.56 (d,  $J = 8.5$  Hz, 1H, Ar-H), 7.45-7.35 (m, 5H, Ar-H), 6.59 (dd,  $J = 8.5, 1.9$  Hz, 1H, Ar-H), 6.48 (d,  $J = 1.9$  Hz, 1H, Ar-H), 5.14 (s, 2H, OCH<sub>2</sub>), 4.45 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 2.35 (s, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.5, 184.9, 167.3, 166.9, 154.9, 142.5, 135.5, 128.8, 128.5, 127.5, 127.4, 113.0, 110.1, 108.1, 98.2, 70.7, 62.2, 28.4, 13.9.

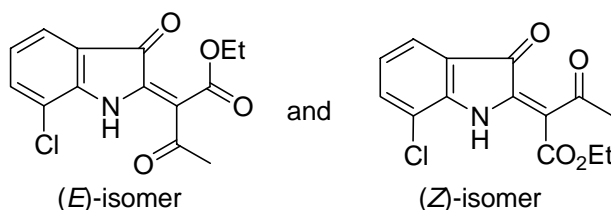
(*E*)- and (*Z*)-Methyl 3-(1-ethoxy-1,3-dioxobutan-2-ylidene)-3-oxoindoline-6-carboxylate (**5k**)



With admixture (25%) of (*Z*)-isomer. Total yield: 90 mg, 57%. Red solid. IR (KBr)  $\nu_{\max}$ : 3416, 1720, 1623, 1596, 1251, 1193, 1126 cm<sup>-1</sup>. MS (ESI): 318 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>16</sub>H<sub>15</sub>NO<sub>6</sub>: C, 60.57; H, 4.77; N, 4.41. Found C, 60.21; H, 5.02; N, 4.29. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.35 (s, 1H, NH), 7.72 (s, 1H, Ar-H), 7.71 (d,  $J = 8.7$  Hz, 1H, Ar-H), 7.64 (dd,  $J = 8.7, 1.0$  Hz, 1H, Ar-H), 4.47 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 3.97 (s, 3H, OCH<sub>3</sub>), 2.38 (s, 3H, CH<sub>3</sub>), 1.42 (t,

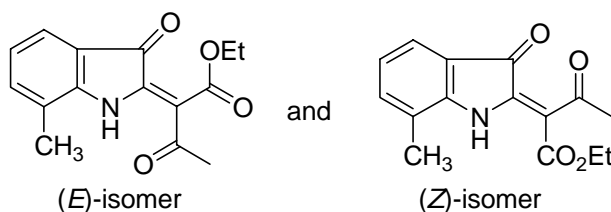
$J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.6, 186.9, 166.8, 165.6, 152.0, 140.7, 137.9, 125.4, 123.9, 122.5, 113.1, 108.7, 62.3, 52.7, 28.5, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(7-chloro-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5l**)



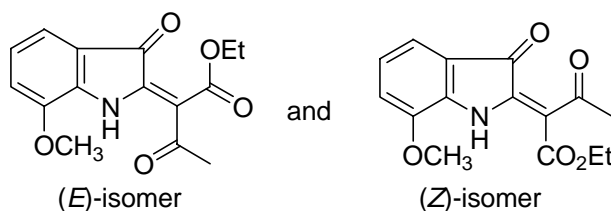
With admixture (28%) of (*Z*)-isomer. Total yield: 91 mg, 62%. Red solid. IR (KBr)  $\nu_{\max}$ : 3415, 1719, 1619, 1588, 1169, 1133 cm<sup>-1</sup>. MS (ESI): 294 (M+H<sup>+</sup>, 100), 296 (M+H<sup>+</sup>, 30). Anal calcd for C<sub>14</sub>H<sub>12</sub>ClNO<sub>4</sub>: C, 57.25; H, 4.12; N, 4.77. Found C, 57.03; H, 3.97; N, 5.02. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.30 (s, 1H, NH), 7.57 (d,  $J = 7.7$  Hz, 1H, Ar-H), 7.51 (dd,  $J = 7.7$ , 1.0 Hz, 1H, Ar-H), 6.99 (t,  $J = 7.7$  Hz, 1H, Ar-H), 4.46 (q,  $J = 7.1$  Hz, 2H, OCH<sub>2</sub>), 2.39 (s, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.4, 186.5, 166.6, 149.4, 140.2, 136.7, 123.8, 123.3, 121.2, 117.7, 109.5, 62.3, 28.6, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(7-methyl-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5m**)



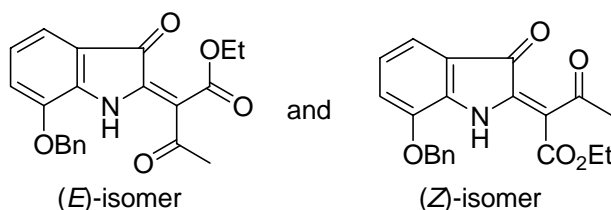
With admixture (11%) of (*Z*)-isomer. Total yield: 83 mg, 61%. Red solid. IR (KBr)  $\nu_{\max}$ : 3414, 1720, 1666, 1594, 1185 cm<sup>-1</sup>. MS (ESI): 274 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>4</sub>: C, 65.92; H, 5.53; N, 5.13. Found C, 66.25; H, 5.37; N, 4.79. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.21 (s, 1H, NH), 7.49 (d,  $J = 7.5$  Hz, 1H, Ar-H), 7.33 (d,  $J = 7.5$  Hz, 1H, Ar-H), 6.95 (t,  $J = 7.5$  Hz, 1H, Ar-H), 4.45 (q,  $J = 7.1$  Hz, 2H, OCH<sub>2</sub>), 2.37 (s, 3H, CH<sub>3</sub>), 2.31 (s, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.1$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.7, 187.6, 167.1, 150.1, 141.4, 138.4, 123.1, 122.7, 121.3, 119.2, 108.2, 62.2, 28.5, 15.3, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(7-methoxy-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5n**)



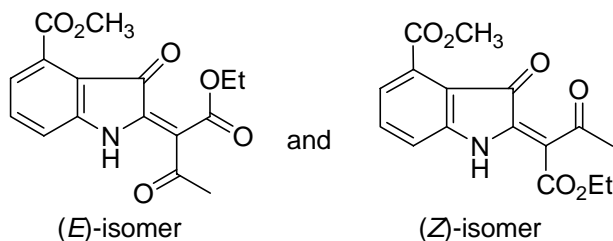
With admixture (10%) of (*Z*)-isomer. Total yield: 95 mg, 66%. Purple solid. IR (KBr)  $\nu_{\max}$ : 3415, 1710, 1644, 1622, 1184, 1124 cm<sup>-1</sup>. MS (ESI): 290 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>15</sub>H<sub>15</sub>NO<sub>5</sub>: C, 62.28; H, 5.23; N, 4.84. Found C, 62.50; H, 4.89; N, 4.92. Major isomer. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta$  10.08 (s, 1H, NH), 7.22 (d,  $J = 7.7$  Hz, 1H, Ar-H), 7.03 (d,  $J = 7.7$  Hz, 1H, Ar-H), 6.95 (t,  $J = 7.7$  Hz, 1H, Ar-H), 4.44 (q,  $J = 7.2$  Hz, 2H, OCH<sub>2</sub>), 3.92 (s, 3H, OCH<sub>3</sub>), 2.36 (s, 3H, CH<sub>3</sub>), 1.41 (t,  $J = 7.2$  Hz, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>):  $\delta$  197.1, 187.5, 167.2, 145.5, 142.4, 140.6, 123.1, 120.2, 118.4, 116.9, 108.5, 62.2, 55.8, 28.5, 13.8.

(*E*)- and (*Z*)-Ethyl 2-(7-benzyloxy-3-oxoindolin-2-ylidene)-3-oxobutanoate (**5o**)



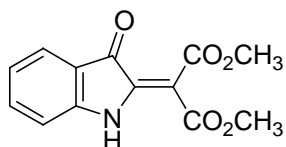
With admixture (12%) of (*Z*)-isomer. Total yield: 111 mg, 61%. Purple solid. IR (KBr)  $\nu_{\max}$ : 3437, 1716, 1659, 1626, 1582, 1451, 1185, 1143  $\text{cm}^{-1}$ . MS (ESI): 366 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{21}\text{H}_{19}\text{NO}_5$ : C, 69.03; H, 5.24; N, 3.83. Found C, 68.89; H, 5.46; N, 3.68. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.17 (s, 1H, NH), 7.46-7.37 (m, 5H, Ar-H), 7.25 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.18 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.92 (t,  $J = 7.8$  Hz, 1H, Ar-H), 5.19 (s, 2H,  $\text{OCH}_2$ ), 4.46 (q,  $J = 7.2$  Hz, 2H,  $\text{OCH}_2$ ), 2.36 (s, 3H,  $\text{CH}_3$ ), 1.42 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.6, 187.5, 167.2, 144.5, 142.7, 140.7, 135.8, 128.8, 128.6, 128.4, 127.4, 122.2, 120.3, 117.4, 108.6, 70.8, 62.2, 28.5, 13.8.

(*E*)- and (*Z*)-Methyl 3-(1-ethoxy-1,3-dioxobutan-2-ylidene)-3-oxoindoline-4-carboxylate (**5p**)



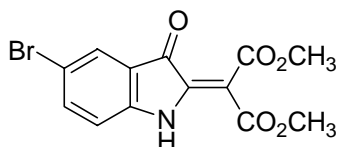
With admixture (18%) of (*Z*)-isomer. Total yield: 95 mg, 60%. Red solid. IR (KBr)  $\nu_{\max}$ : 3415, 1716, 1654, 1575, 1259, 1225, 1178  $\text{cm}^{-1}$ . MS (ESI): 318 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{16}\text{H}_{15}\text{NO}_6$ : C, 60.57; H, 4.77; N, 4.41. Found C, 60.25; H, 4.96; N, 4.13. Major isomer.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  10.37 (s, 1H, NH), 7.55 (t,  $J = 7.8$  Hz, 1H, Ar-H), 7.34 (dd,  $J = 7.8, 1.0$  Hz, 1H, Ar-H), 7.11 (d,  $J = 7.8$  Hz, 1H, Ar-H), 4.46 (q,  $J = 7.2$  Hz, 2H,  $\text{OCH}_2$ ), 3.96 (s, 3H,  $\text{OCH}_3$ ), 2.36 (s, 3H,  $\text{CH}_3$ ), 1.40 (t,  $J = 7.2$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  197.7, 184.3, 166.9, 165.8, 153.0, 140.4, 136.8, 131.2, 123.4, 116.7, 115.2, 108.7, 62.2, 52.7, 28.5, 13.8.

Dimethyl 2-(3-oxoindolin-2-ylidene)malonate (**6a**)



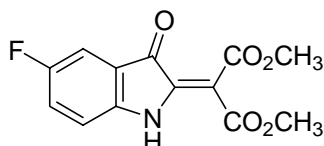
91 mg, 70% yield. Yellow solid, mp: 189-191  $^{\circ}\text{C}$  (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3347, 1745, 1686, 1610, 1192  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.20 (s, 1H, NH), 7.65 (d,  $J = 7.6$  Hz, 1H, Ar-H), 7.52 (t,  $J = 7.9$  Hz, 1H, Ar-H), 7.01 (t,  $J = 7.9$  Hz, 1H, Ar-H), 6.95 (d,  $J = 7.6$  Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.85 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.6, 166.4, 165.3, 152.1, 142.9, 137.7, 125.7, 122.3, 119.9, 111.9, 101.3, 53.1, 52.6. MS (ESI): 262 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{13}\text{H}_{11}\text{NO}_5$ : C, 59.77; H, 4.24; N, 5.36. Found C, 60.05; H, 3.97; N, 5.03.

Dimethyl 2-(5-bromo-3-oxoindolin-2-ylidene)malonate (**6b**)



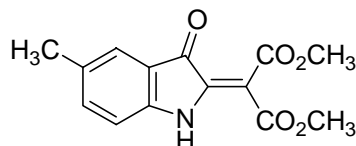
114 mg, 67% yield. Yellow solid, mp: 183-184 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3381, 1737, 1686, 1605, 1263, 1190  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.23 (s, 1H, NH), 7.75 (d,  $J$  = 2.0 Hz, 1H, Ar-H), 7.62 (dd,  $J$  = 8.5, 2.0 Hz, 1H, Ar-H), 6.88 (d,  $J$  = 8.5 Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.3, 166.2, 164.9, 150.8, 142.3, 140.0, 128.3, 121.4, 114.8, 113.5, 102.3, 53.2, 52.8. MS (ESI): 340 ( $\text{M}+\text{H}^+$ , 100), 342 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{13}\text{H}_{10}\text{BrNO}_5$ : C, 45.91; H, 2.96; N, 4.12. Found C, 45.82; H, 3.14; N, 3.89.

Dimethyl 2-(5-fluoro-3-oxoindolin-2-ylidene)malonate (**6c**)



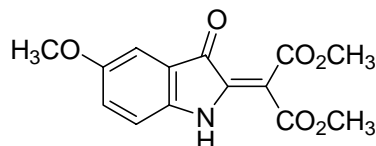
74 mg, 53% yield. Red solid, mp: 224-226 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3410, 1744, 1683, 1617, 1485, 1263, 1127  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.16 (s, 1H, NH), 7.34 (dd,  $J$  = 6.8, 2.4 Hz, 1H, Ar-H), 7.26 (dt,  $J$  = 2.6, 8.6 Hz, 1H, Ar-H), 6.93 (dd,  $J$  = 8.6, 2.6 Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.0, 166.2, 165.0, 145.7 (d,  $J$  = 243.5 Hz), 148.3, 143.2, 124.6 (d,  $J$  = 25.0 Hz), 120.5 (d,  $J$  = 7.6 Hz), 112.8 (d,  $J$  = 7.6 Hz), 111.8 (d,  $J$  = 24.1 Hz), 102.0, 53.2, 52.7. MS (ESI): 280 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{13}\text{H}_{10}\text{FNO}_5$ : C, 55.92; H, 3.61; N, 5.02. Found C, 55.75; H, 3.91; N, 4.83.

Dimethyl 2-(5-methyl-3-oxoindolin-2-ylidene)malonate (**6d**)



92 mg, 67% yield. Red solid, mp: 202-204 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3416, 1737, 1687, 1619, 1491, 1282, 1199  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.11 (s, 1H, NH), 7.43 (s, 1H, Ar-H), 7.32 (d,  $J$  = 8.1 Hz, 1H, Ar-H), 6.84 (d,  $J$  = 8.1 Hz, 1H, Ar-H), 3.99 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ), 2.32 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.7, 166.4, 165.4, 150.2, 148.3, 138.5, 132.0, 125.6, 119.9, 111.6, 100.7, 53.1, 52.5, 20.6. MS (ESI): 276 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{13}\text{NO}_5$ : C, 61.09; H, 4.76; N, 5.09. Found C, 60.81; H, 5.13; N, 4.93.

Dimethyl 2-(5-methoxy-3-oxoindolin-2-ylidene)malonate (**6e**)

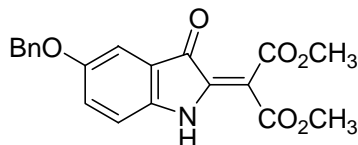


90 mg, 62% yield. Red solid, mp: 169-171 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3378, 1721, 1689, 1615, 1489, 1274, 1190, 1135  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.02 (s, 1H, NH), 7.13 (s, 1H, Ar-H), 7.11 (dd,  $J$  = 8.0, 2.5 Hz, 1H, Ar-H), 6.87 (dd,  $J$  = 8.0, 2.5 Hz, 1H, Ar-H), 3.94 (s, 3H,  $\text{OCH}_3$ ), 3.84 (s, 3H,  $\text{OCH}_3$ ), 3.79 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.8, 166.4, 165.4, 155.5, 146.8, 143.6, 125.7, 120.2, 112.8, 108.1, 101.0, 55.9, 53.1, 52.5. MS (ESI): 292 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{13}\text{NO}_6$ : C, 57.73; H, 4.50; N, 4.81. Found C, 57.41; H, 4.79; N,



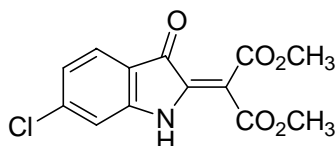
4.62.

Dimethyl 2-(5-benzyloxy-3-oxoindolin-2-ylidene)malonate (**6f**)



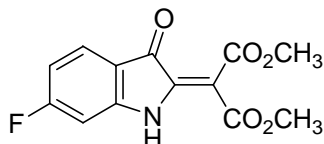
139 mg, 76% yield. Red solid, mp: 176-178 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3375, 1726, 1683, 1616, 1482, 1270, 1187, 1132  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.03 (s, 1H, NH), 7.45-7.33 (m, 5H, Ar-H), 7.21 (s, 1H, Ar-H), 7.19 (dd,  $J = 6.6, 2.6$  Hz, 1H, Ar-H), 6.87 (dd,  $J = 6.6, 2.6$  Hz, 1H, Ar-H), 5.04 (s, 2H,  $\text{OCH}_2$ ), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.85 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.7, 166.4, 165.4, 154.6, 146.9, 143.6, 136.3, 128.7, 128.2, 127.5, 126.6, 120.2, 112.8, 109.6, 101.0, 70.9, 53.1, 52.5. MS (ESI): 368 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}_6$ : C, 65.39; H, 4.66; N, 3.81. Found C, 65.07; H, 4.83; N, 3.58.

Dimethyl 2-(6-chloro-3-oxoindolin-2-ylidene)malonate (**6g**)



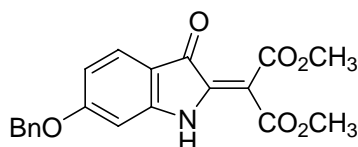
87 mg, 59% yield. Red solid, mp: 235-238 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3362, 1698, 1599, 1437, 1272, 1192  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.24 (s, 1H, NH), 7.59 (d,  $J = 8.0$  Hz, 1H, Ar-H), 7.00 (dd,  $J = 8.0, 1.6$  Hz, 1H, Ar-H), 6.98 (d,  $J = 1.6$  Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.87 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  184.1, 166.2, 164.9, 152.7, 144.1, 142.7, 126.5, 122.8, 118.4, 112.4, 102.5, 53.2, 52.7. MS (ESI): 296 ( $\text{M}+\text{H}^+$ , 100), 298 ( $\text{M}+\text{H}^+$ , 30). Anal calcd for  $\text{C}_{13}\text{H}_{10}\text{ClNO}_5$ : C, 52.81; H, 3.41; N, 4.74. Found C, 52.72; H, 3.60; N, 4.46.

Dimethyl 2-(6-fluoro-3-oxoindolin-2-ylidene)malonate (**6h**)



99 mg, 71% yield. Red solid, mp: 202-204 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3360, 1725, 1692, 1604, 1447, 1257, 1208, 1132  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.25 (s, 1H, NH), 7.67 (dd,  $J = 8.4, 5.5$  Hz, 1H, Ar-H), 6.72 (dt,  $J = 2.0, 8.8$  Hz, 1H, Ar-H), 6.67 (dd,  $J = 8.8, 2.0$  Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  183.6, 169.0 (d,  $J = 258.6$  Hz), 166.2, 164.9, 154.1 (d,  $J = 23.8$  Hz), 143.0, 128.0 (d,  $J = 12.2$  Hz), 116.3 (d,  $J = 1.6$  Hz), 110.0 (d,  $J = 23.9$  Hz), 102.2, 99.8 (d,  $J = 27.5$  Hz), 53.2, 52.7. MS (ESI): 280 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{13}\text{H}_{10}\text{FNO}_5$ : C, 55.92; H, 3.61; N, 5.02. Found C, 56.17; H, 3.29; N, 4.76.

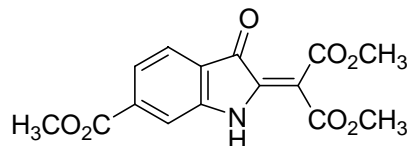
Dimethyl 2-(6-benzyloxy-3-oxoindolin-2-ylidene)malonate (**6i**)



97 mg, 53% yield. Red amorphous solid. IR (KBr)  $\nu_{\max}$ : 3382, 1733, 1688, 1610, 1453, 1276, 1247, 1206, 1151  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.12 (s, 1H, NH), 7.57 (d,  $J = 8.5$  Hz, 1H, Ar-H), 7.45-7.36 (m, 5H, Ar-H), 6.59 (dd,  $J = 8.5, 2.0$  Hz, 1H, Ar-H), 6.46 (d,  $J = 2.0$  Hz, 1H,

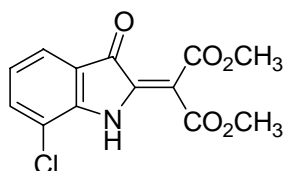
Ar-H), 5.15 (s, 2H, OCH<sub>2</sub>), 3.94 (s, 3H, OCH<sub>3</sub>), 3.84 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 183.3, 167.1, 166.4, 165.4, 154.6, 144.2, 135.5, 128.8, 128.5, 127.6, 127.5, 113.4, 109.9, 101.1, 97.9, 70.7, 53.1, 52.5. MS (ESI): 368 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>20</sub>H<sub>17</sub>NO<sub>6</sub>: C, 65.39; H, 4.66; N, 3.81. Found C, 65.48; H, 4.38; N, 3.50.

Dimethyl 2-(6-(methoxycarbonyl)-3-oxoindolin-2-ylidene)malonate (**6j**)



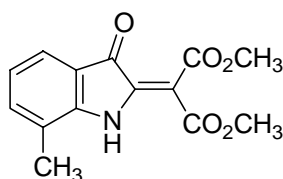
96 mg, 60% yield. Orange solid, mp: 154-156 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3414, 1712, 1698, 1615, 1442, 1277, 1214 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.33 (s, 1H, NH), 7.71 (dd, *J* = 8.0, 0.8 Hz, 1H, Ar-H), 7.68 (dd, *J* = 8.0, 0.8 Hz, 1H, Ar-H), 7.63 (s, 1H, Ar-H), 3.96 (s, 3H, OCH<sub>3</sub>), 3.95 (s, 3H, OCH<sub>3</sub>), 3.86 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 185.2, 166.1, 165.6, 164.9, 151.7, 142.4, 138.1, 125.4, 123.4, 122.8, 112.9, 102.2, 53.2, 52.8, 52.7. MS (ESI): 320 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>15</sub>H<sub>13</sub>NO<sub>7</sub>: C, 56.43; H, 4.10; N, 4.39. Found C, 56.69; H, 3.83; N, 4.10.

Dimethyl 2-(7-chloro-3-oxoindolin-2-ylidene)malonate (**6k**)



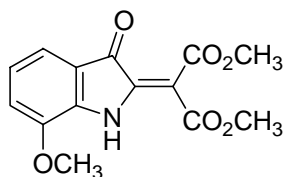
102 mg, 69% yield. Red solid, mp: 154-156 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3384, 1728, 1690, 1607, 1433, 1255, 1175 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.31 (s, 1H, NH), 7.59 (d, *J* = 7.7 Hz, 1H, Ar-H), 7.53 (dd, *J* = 7.7, 0.8 Hz, 1H, Ar-H), 6.99 (t, *J* = 7.7 Hz, 1H, Ar-H), 3.96 (s, 3H, OCH<sub>3</sub>), 3.89 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 184.9, 166.0, 164.7, 149.0, 142.0, 136.8, 123.8, 122.9, 121.5, 117.5, 103.1, 53.2, 52.8. MS (ESI): 296 (M+H<sup>+</sup>, 100), 298 (M+H<sup>+</sup>, 30). Anal calcd for C<sub>13</sub>H<sub>10</sub>ClNO<sub>5</sub>: C, 52.81; H, 3.41; N, 4.74. Found C, 52.92; H, 3.26; N, 4.33.

Dimethyl 2-(7-methyl-3-oxoindolin-2-ylidene)malonate (**6l**)



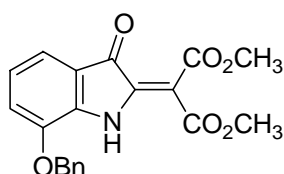
114 mg, 83% yield. Orange solid, mp: 190-191 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3394, 1725, 1693, 1603, 1442, 1273, 1183, 1129 cm<sup>-1</sup>. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 9.11 (s, 1H, NH), 7.49 (d, *J* = 7.5 Hz, Ar-H), 7.34 (d, *J* = 7.5 Hz, 1H, Ar-H), 6.93 (d, *J* = 7.5 Hz, 1H, Ar-H), 3.95 (s, 3H, OCH<sub>3</sub>), 3.87 (s, 3H, OCH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ 186.0, 166.6, 165.3, 150.9, 143.1, 138.6, 123.2, 122.3, 121.1, 119.4, 101.2, 53.2, 52.6, 15.3. MS (ESI): 276 (M+H<sup>+</sup>, 100). Anal calcd for C<sub>14</sub>H<sub>13</sub>NO<sub>5</sub>: C, 61.09; H, 4.76; N, 5.09. Found C, 60.98; H, 4.78; N, 4.88.

Dimethyl 2-(7-methoxy-3-oxoindolin-2-ylidene)malonate (**6m**)



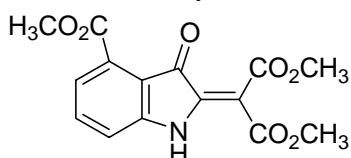
67 mg, 46% yield. Red solid, mp: 180-182 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3419, 1734, 1685, 1617, 1271, 1201, 1165  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.10 (s, 1H, NH), 7.23 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.04 (d,  $J = 7.8$  Hz, 1H, Ar-H), 6.93 (t,  $J = 7.8$  Hz, 1H, Ar-H), 3.94 (s, 3H,  $\text{OCH}_3$ ), 3.92 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.9, 166.2, 165.3, 145.4, 142.5, 142.3, 122.6, 120.4, 118.4, 117.0, 101.7, 55.8, 53.1, 52.5. MS (ESI): 292 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{14}\text{H}_{13}\text{NO}_6$ : C, 57.73; H, 4.50; N, 4.81. Found C, 58.07; H, 4.21; N, 4.52.

Dimethyl 2-(7-benzyloxy-3-oxoindolin-2-ylidene)malonate (**6n**)



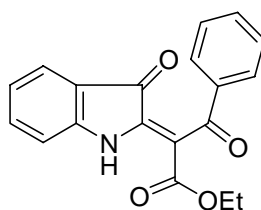
95 mg, 52% yield. Brown solid. mp: 122-124 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3417, 1743, 1685, 1615, 1445, 1273, 1190, 1156  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.13 (s, 1H, NH), 7.45-7.37 (m, 5H, Ar-H), 7.26 (d,  $J = 7.6$  Hz, 1H, Ar-H), 7.09 (d,  $J = 7.6$  Hz, 1H, Ar-H), 6.91 (t,  $J = 7.6$  Hz, 1H, Ar-H), 5.19 (s, 2H,  $\text{OCH}_2$ ), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.86 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.8, 166.2, 165.3, 144.5, 142.6, 142.5, 135.8, 128.8, 128.5, 127.5, 122.6, 120.7, 120.2, 117.5, 101.8, 70.9, 53.1, 52.5. MS (ESI): 368 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{20}\text{H}_{17}\text{NO}_6$ : C, 65.39; H, 4.66; N, 3.81. Found C, 65.05; H, 4.97; N, 3.52.

Dimethyl 2-(4-(methoxycarbonyl)-3-oxoindolin-2-ylidene)malonate (**6o**)

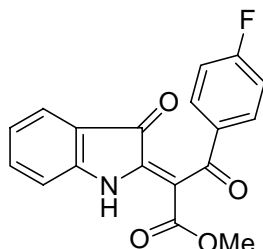


115 mg, 72% yield. Orange solid, mp: 185-187 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\max}$ : 3392, 1724, 1694, 1636, 1597, 1435, 1256, 1220, 1140  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.33 (s, 1H, NH), 7.54 (t,  $J = 7.8$  Hz, 1H, Ar-H), 7.30 (d,  $J = 7.8$  Hz, 1H, Ar-H), 7.10 (d,  $J = 7.8$  Hz, 1H, Ar-H), 3.95 (s, 3H,  $\text{OCH}_3$ ), 3.93 (s, 3H,  $\text{OCH}_3$ ), 3.82 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  182.7, 166.3, 165.8, 165.1, 152.8, 142.0, 137.0, 131.3, 122.9, 116.9, 115.1, 102.1, 53.2, 52.7, 52.6. MS (ESI): 320 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{15}\text{H}_{13}\text{NO}_7$ : C, 56.43; H, 4.10; N, 4.39. Found C, 56.35; H, 4.02; N, 4.16.

(Z)-Ethyl 3-oxo-2-(3-oxoindolin-2-ylidene)-3-phenylpropanoate (**7a**)

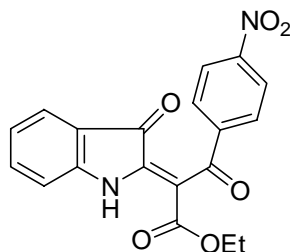


112 mg, 70% yield. Red solid, mp: 195-196 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3399, 1682, 1605, 1465, 1283, 1201, 1145  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.34 (s, 1H, NH), 7.99 (dd,  $J = 8.5, 1.4$  Hz, 2H, Ar-H), 7.59-7.43 (m, 5H, Ar-H), 6.95 (d,  $J = 8.8$  Hz, 2H, Ar-H), 4.21 (q,  $J = 7.1$  Hz, 2H,  $\text{OCH}_2$ ), 1.16 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.4, 186.1, 166.7, 152.6, 142.9, 137.6, 137.3, 133.4, 128.8, 128.6, 125.6, 122.0, 119.8, 112.0, 107.8, 61.6, 14.0. MS (ESI): 322 ( $\text{M}+\text{H}^+$ , 100). These assignments matched with those previously published.<sup>1</sup>  
(*Z*)-Methyl 3-(4-fluorophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate (**7b**)



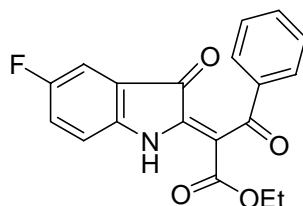
104 mg, 64% yield. Orange solid, mp: 171-172 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\max}$ : 3414, 1692, 1661, 1604, 1467, 1281, 1201, 1146  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.34 (s, 1H, NH), 8.02 (dt,  $J = 8.5, 2.0$  Hz, 2H, Ar-H), 7.53 (d,  $J = 7.6$  Hz, 1H, Ar-H), 7.50 (t,  $J = 7.6$  Hz, 1H, Ar-H), 7.13 (t,  $J = 8.5$  Hz, 2H, Ar-H), 6.98 (d,  $J = 8.5$  Hz, 1H, Ar-H), 6.95 (t,  $J = 8.5$  Hz, 1H, Ar-H), 3.74 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.8, 186.1, 167.1 (d,  $J = 34.6$  Hz), 164.7, 152.6, 143.0, 137.8, 133.7 (d,  $J = 2.6$  Hz), 131.5 (d,  $J = 9.5$  Hz), 125.6, 122.2, 119.7, 115.8 (d,  $J = 22.1$  Hz), 112.1, 106.8, 52.6. MS (ESI): 326 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{18}\text{H}_{12}\text{FNO}_4$ : C, 66.46; H, 3.72; N, 4.31. Found C, 66.13; H, 4.09; N, 4.11.

(*Z*)-Ethyl 3-(4-nitrophenyl)-3-oxo-2-(3-oxoindolin-2-ylidene)propanoate (**7c**)



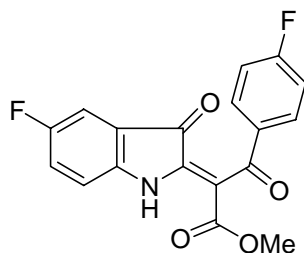
31 mg, 17% yield. Orange solid, mp: 192-194 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\max}$ : 3414, 1692, 1660, 1613, 1467, 1282, 1202, 1146  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.33 (s, 1H, NH), 8.32 (dt,  $J = 9.0, 2.0$  Hz, 2H, Ar-H), 8.14 (dt,  $J = 9.0, 2.0$  Hz, 2H, Ar-H), 7.58-7.52 (m, 2H, Ar-H), 7.03-6.97 (m, 2H, Ar-H), 4.25 (q,  $J = 7.1$  Hz, 2H,  $\text{OCH}_2$ ), 1.19 (t,  $J = 7.1$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.9, 186.2, 166.2, 152.6, 150.4, 143.5, 141.8, 138.0, 129.6, 125.8, 123.9, 122.5, 119.6, 112.1, 106.3, 61.9, 14.0. MS (ESI): 367 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{19}\text{H}_{14}\text{N}_2\text{O}_6$ : C, 62.30; H, 3.85; N, 7.65. Found C, 62.05; H, 4.17; N, 7.52.

(*Z*)-Ethyl 2-(5-fluoro-3-oxoindolin-2-ylidene)-3-oxo-3-phenylpropanoate (**7d**)



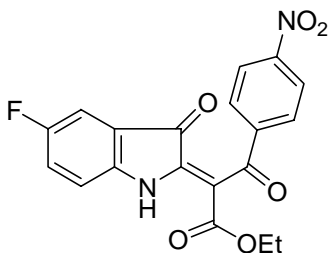
105 mg, 62% yield. Red solid, mp: 182-183 °C (from EtOAc/PE = 1:4). IR (KBr)  $\nu_{\max}$ : 3415, 1719, 1685, 1618, 1488, 1266, 1192, 1127  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.31 (s, 1H, NH), 7.98 (d,  $J = 7.3$  Hz, 2H, Ar-H), 7.59 (t,  $J = 7.3$  Hz, 1H, Ar-H), 7.47 (t,  $J = 7.6$  Hz, 2H, Ar-H), 7.26-7.15 (m, 2H, Ar-H), 6.93 (dd,  $J = 8.5, 3.5$  Hz, 1H, Ar-H), 4.22 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2$ ), 1.17 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  192.0, 185.5 (d,  $J = 3.1$  Hz), 166.6, 159.4, 157.0, 148.8, 143.2, 137.1, 133.5, 128.7 (d,  $J = 21.8$  Hz), 124.6 (d,  $J = 24.9$  Hz), 120.4 (d,  $J = 7.6$  Hz), 112.9 (d,  $J = 7.6$  Hz), 111.6 (d,  $J = 23.9$  Hz), 108.6, 61.7, 14.0. MS (ESI): 340 ( $\text{M}+\text{H}^+$ , 100). These assignments matched with those previously published.<sup>1</sup>

(Z)-Methyl 2-(5-fluoro-3-oxoindolin-2-ylidene)-3-(4-fluorophenyl)-3-oxopropanoate (**7e**)



117 mg, 68% yield. Red solid, mp: 206-208 °C (from EtOAc/PE = 1:2). IR (KBr)  $\nu_{\max}$ : 3414, 1718, 1680, 1618, 1487, 1263, 1127  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  9.30 (s, 1H, NH), 8.01 (dt,  $J = 8.6, 2.1$  Hz, 2H, Ar-H), 7.29-7.19 (m, 2H, Ar-H), 7.14 (dt,  $J = 2.1, 8.6$  Hz, 2H, Ar-H), 6.96 (dd,  $J = 8.6, 3.6$  Hz, 1H, Ar-H), 3.76 (s, 3H,  $\text{OCH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  190.4, 185.5 (d,  $J = 3.0$  Hz), 166.8, 166.1 (d,  $J = 255.7$  Hz), 152.9 (d,  $J = 243.2$  Hz), 148.8, 143.3, 133.6 (d,  $J = 2.8$  Hz), 131.4 (d,  $J = 9.5$  Hz), 124.7 (d,  $J = 25.0$  Hz), 120.3 (d,  $J = 7.6$  Hz), 115.8 (d,  $J = 22.1$  Hz), 113.0 (d,  $J = 7.4$  Hz), 111.8 (d,  $J = 23.9$  Hz), 107.6, 52.6. MS (ESI): 344 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{18}\text{H}_{11}\text{F}_2\text{NO}_4$ : C, 62.98; H, 3.23; N, 4.08. Found C, 62.83; H, 3.56; N, 3.94.

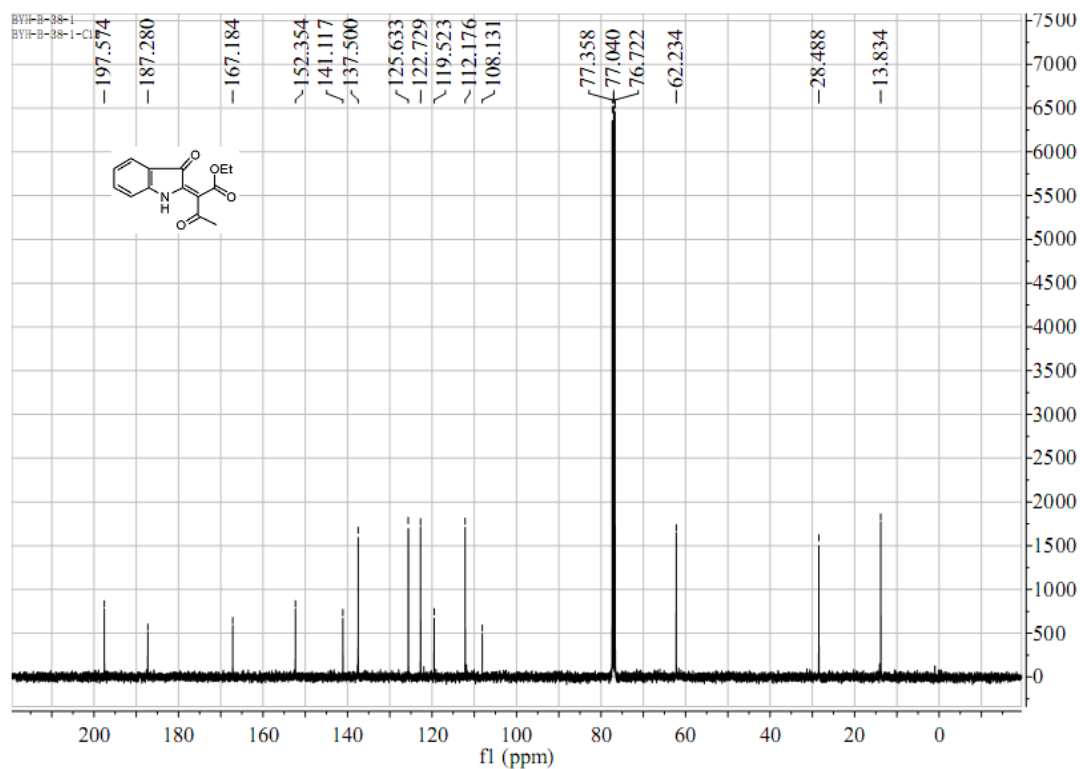
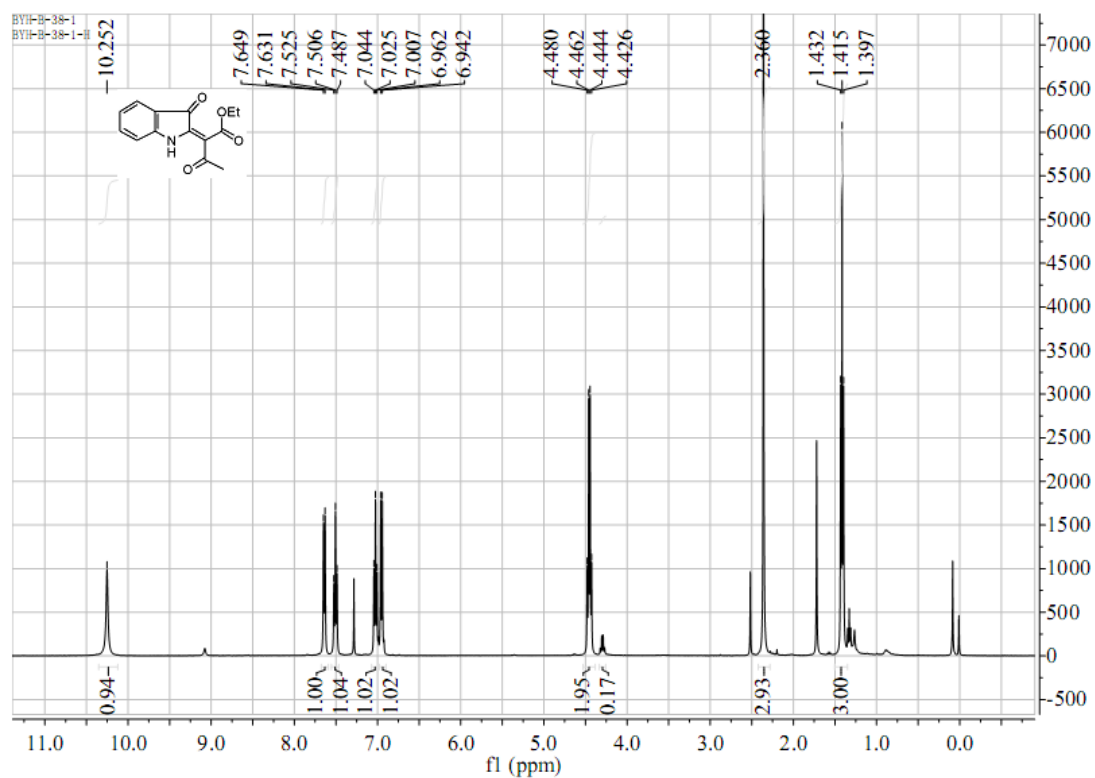
(Z)-Ethyl 2-(5-fluoro-3-oxoindolin-2-ylidene)-3-(4-nitrophenyl)-3-oxopropanoate (**7f**)



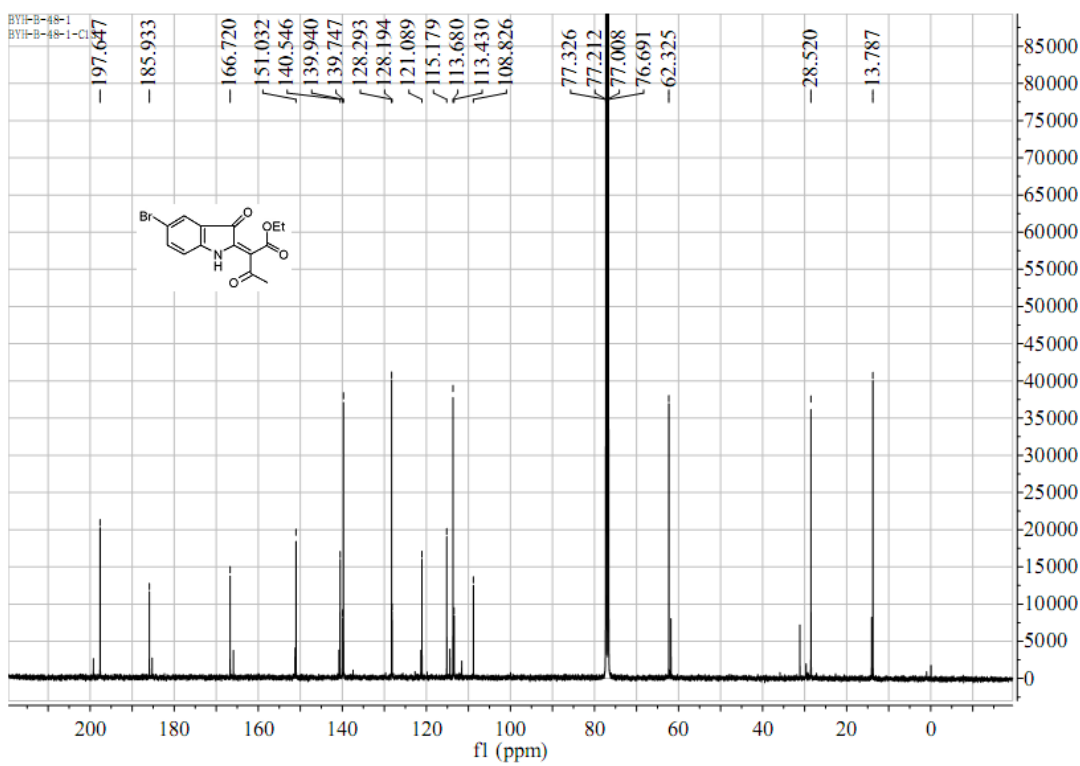
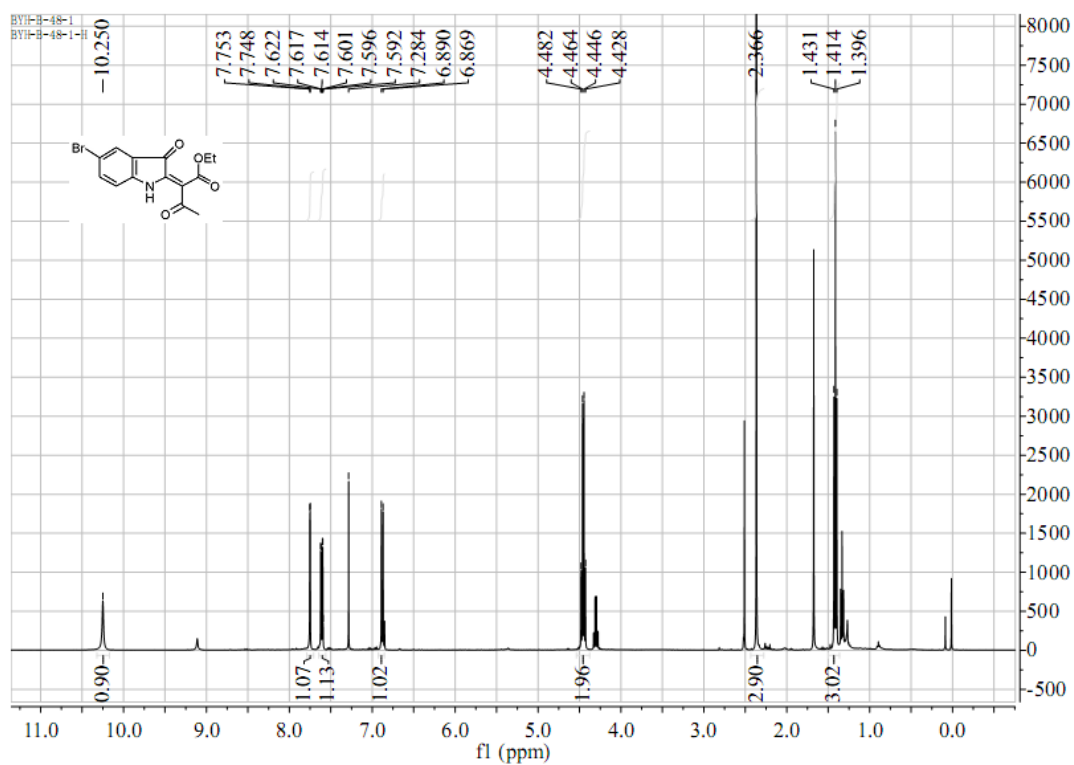
31 mg, 16% yield. Orange solid, mp: 241-243 °C (from EtOAc/PE = 1:3). IR (KBr)  $\nu_{\max}$ : 3379, 1723, 1669, 1606, 1487, 1219, 1187, 1129  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  10.66 (s, 1H, NH), 8.29 (d,  $J = 8.8$  Hz, 2H, Ar-H), 8.17 (d,  $J = 8.8$  Hz, 2H, Ar-H), 7.48 (dt,  $J = 2.5, 8.4$  Hz, 2H, Ar-H), 7.31 (dd,  $J = 8.4, 3.3$  Hz, 2H, Ar-H), 4.18 (q,  $J = 7.0$  Hz, 2H,  $\text{OCH}_2$ ), 1.08 (t,  $J = 7.0$  Hz, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ):  $\delta$  191.6, 187.0 (d,  $J = 3.2$  Hz), 165.0, 157.9 (d,  $J = 239.2$  Hz), 151.2, 150.5, 143.2, 141.8, 130.2, 125.5 (d,  $J = 24.7$  Hz), 124.4, 119.6 (d,  $J = 7.9$  Hz), 115.2 (d,  $J = 7.7$  Hz), 111.2 (d,  $J = 24.0$  Hz), 106.6, 61.5, 14.4. MS (ESI): 385 ( $\text{M}+\text{H}^+$ , 100). Anal calcd for  $\text{C}_{19}\text{H}_{13}\text{FN}_2\text{O}_6$ : C, 59.38; H, 3.41; N, 7.29. Found C, 59.61; H, 3.06; N, 6.93.

### 3. Copies of $^1\text{H}$ , $^{13}\text{C}$ NMR Spectra

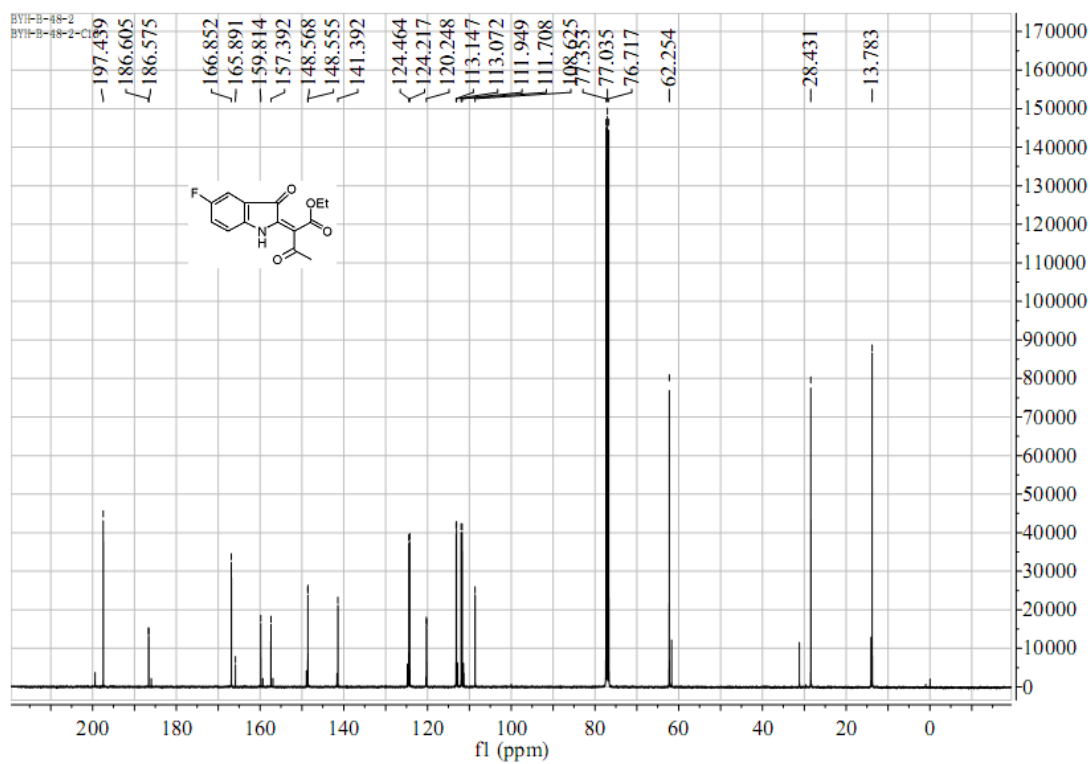
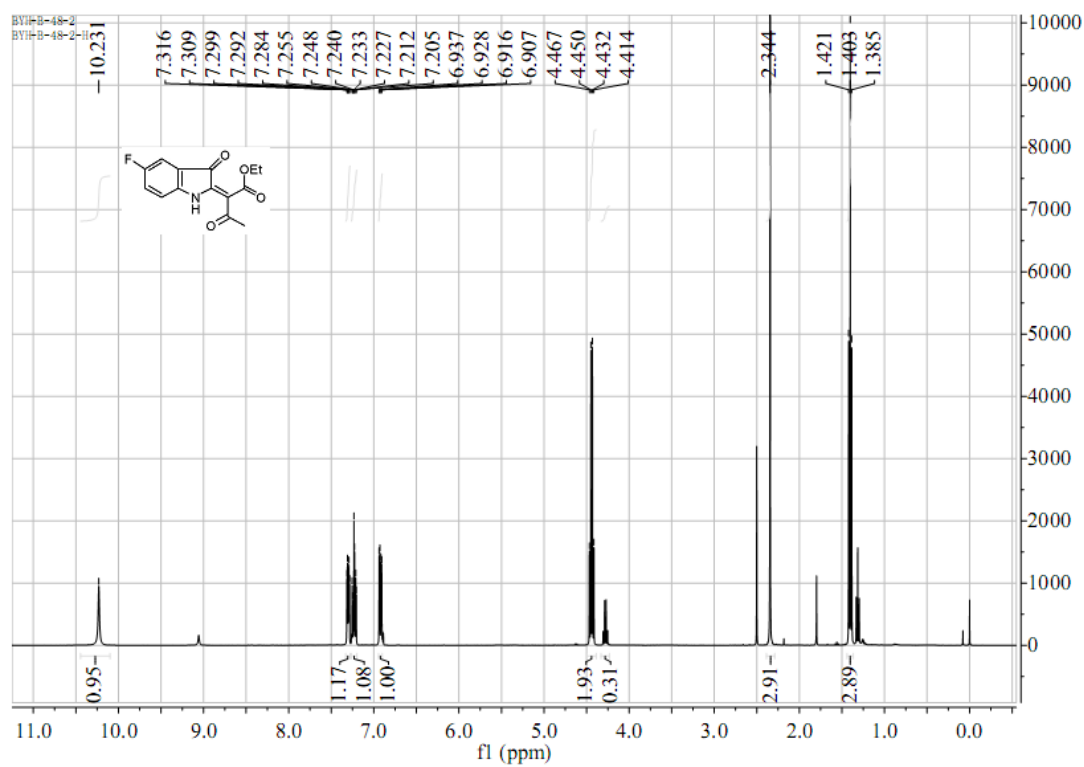
#### Compound 5a



Compound **5b**

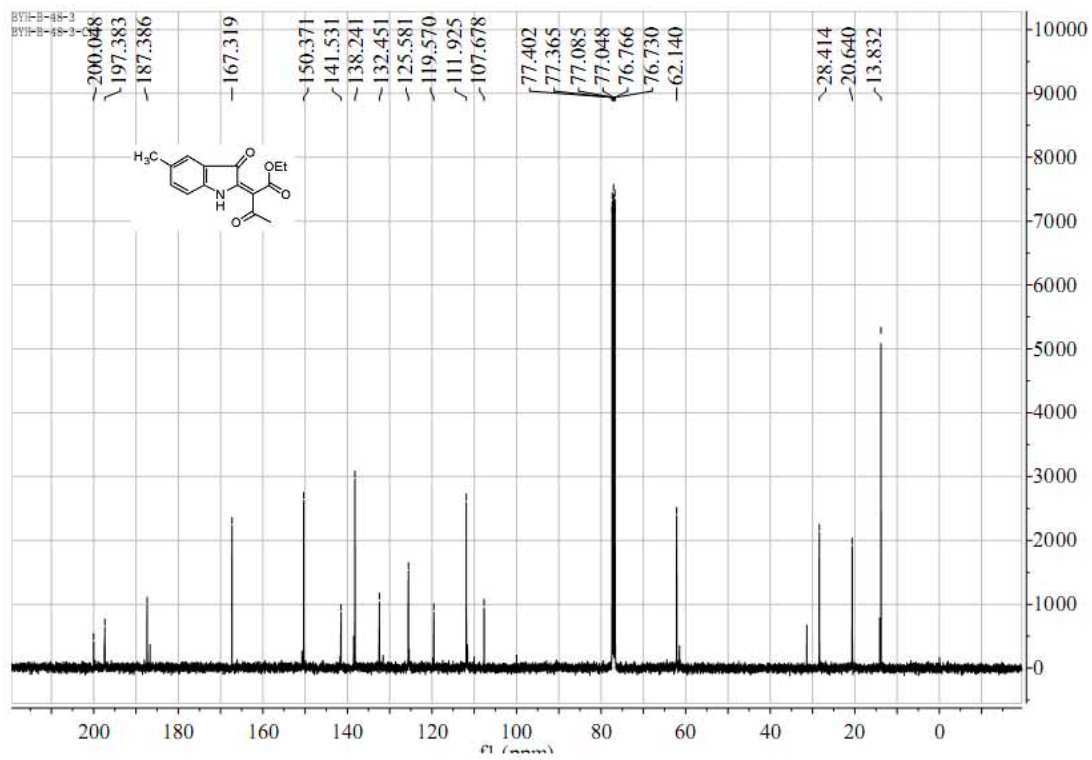
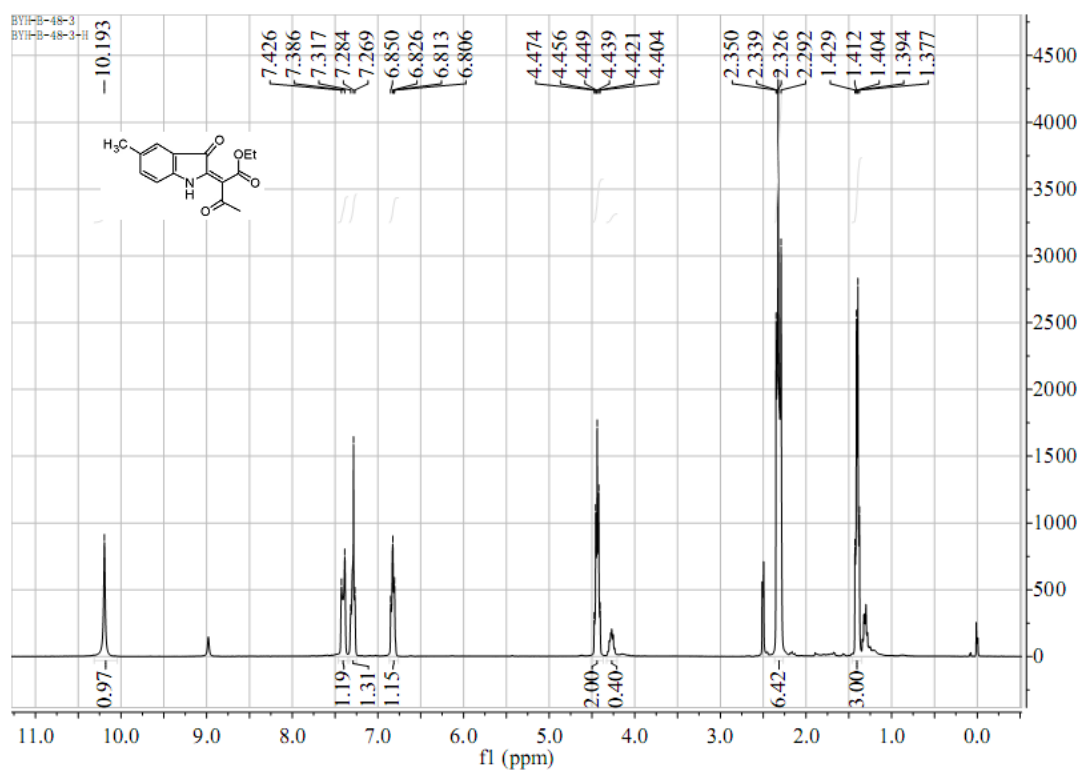


Compound 5c

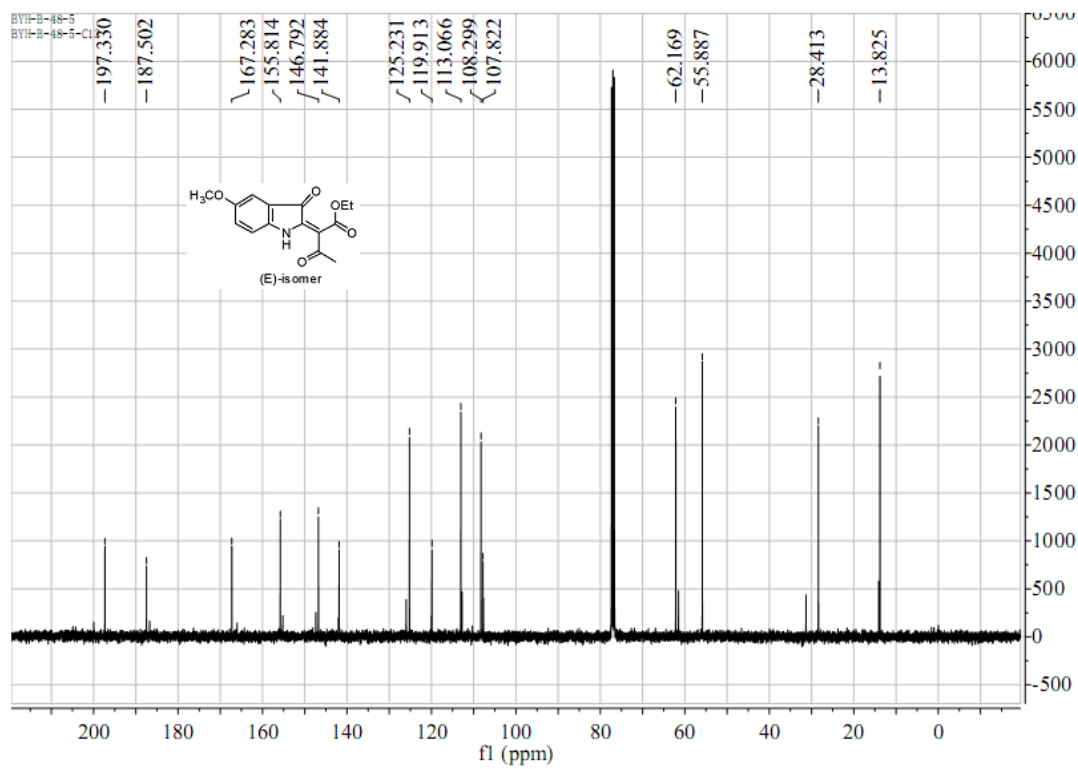
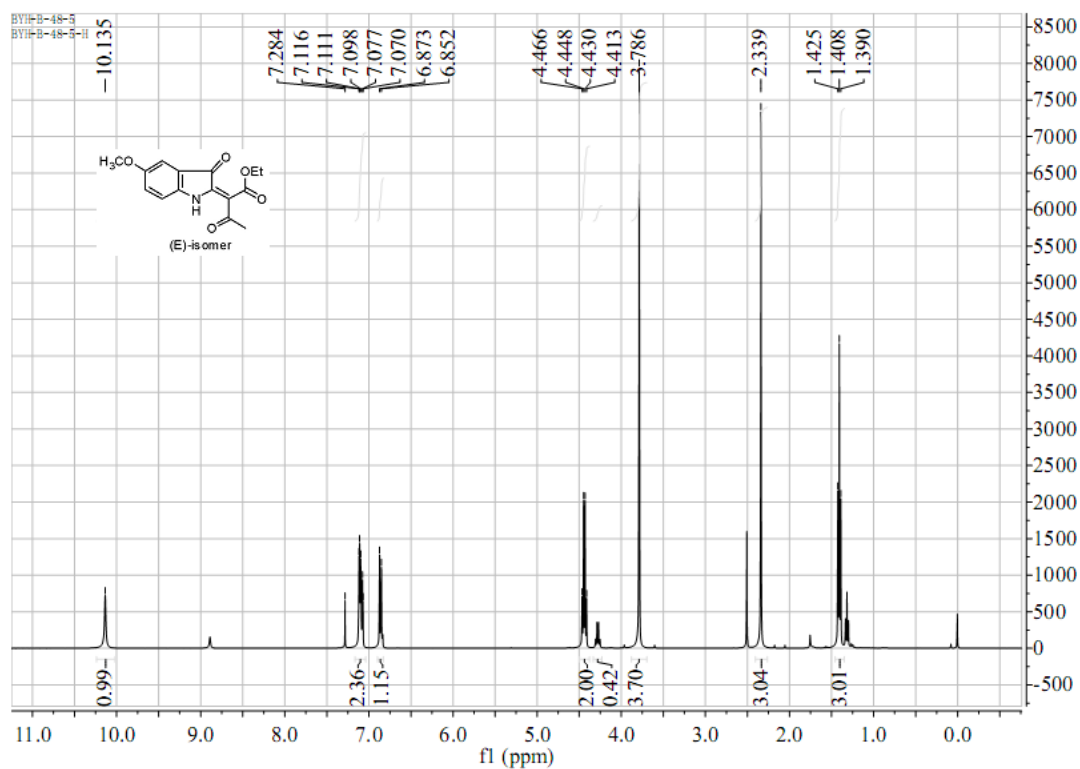




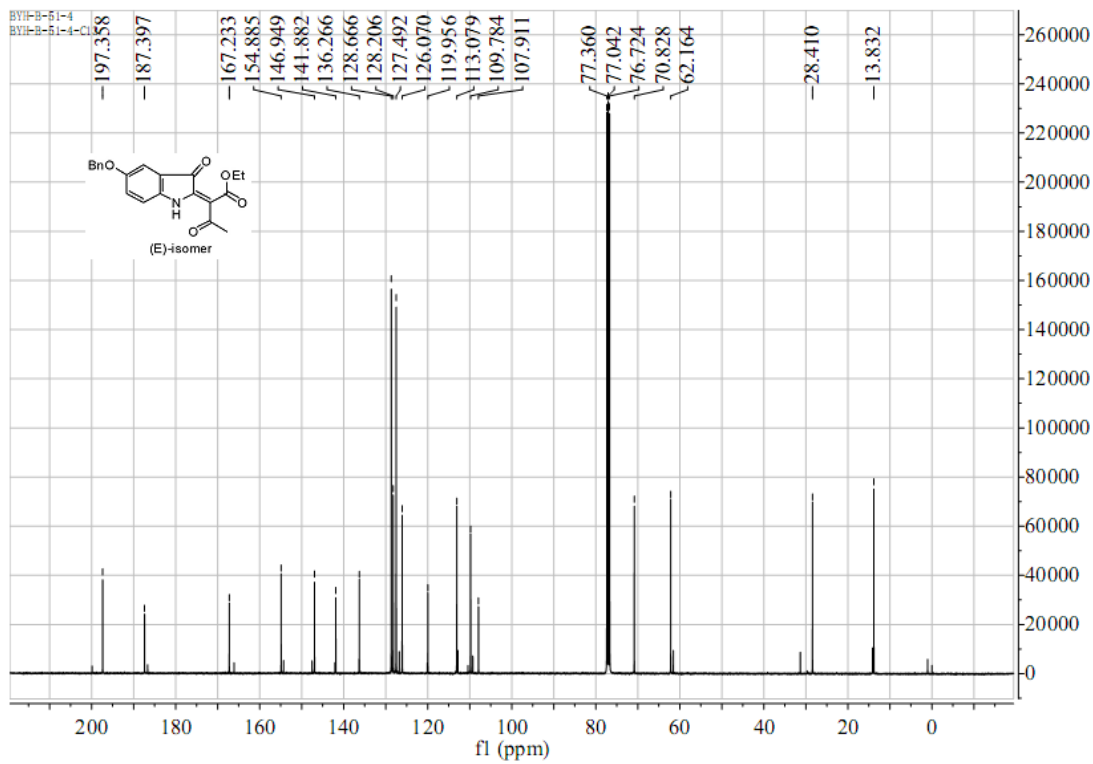
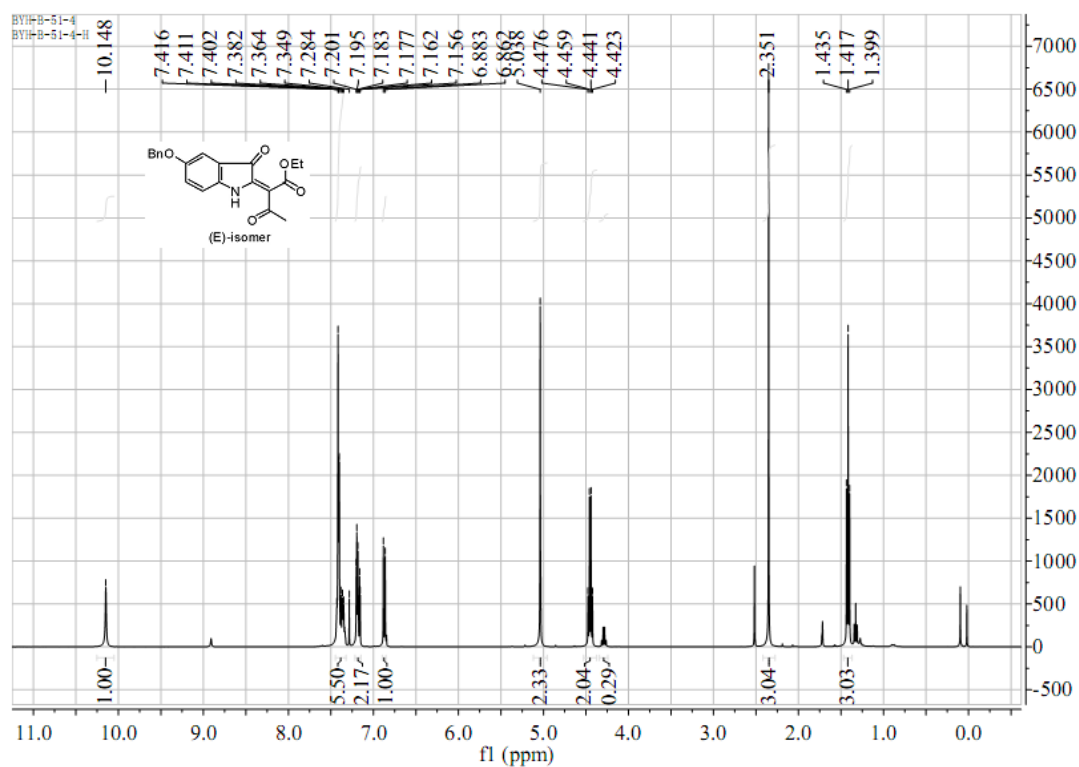
Compound 5d



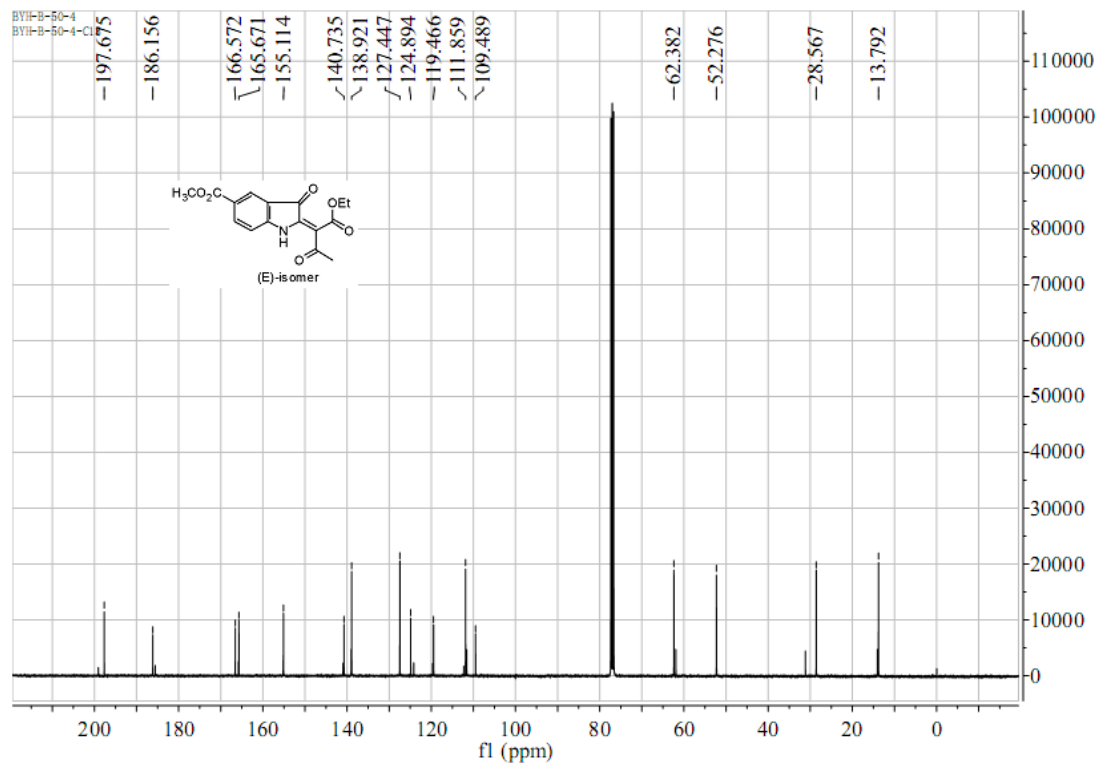
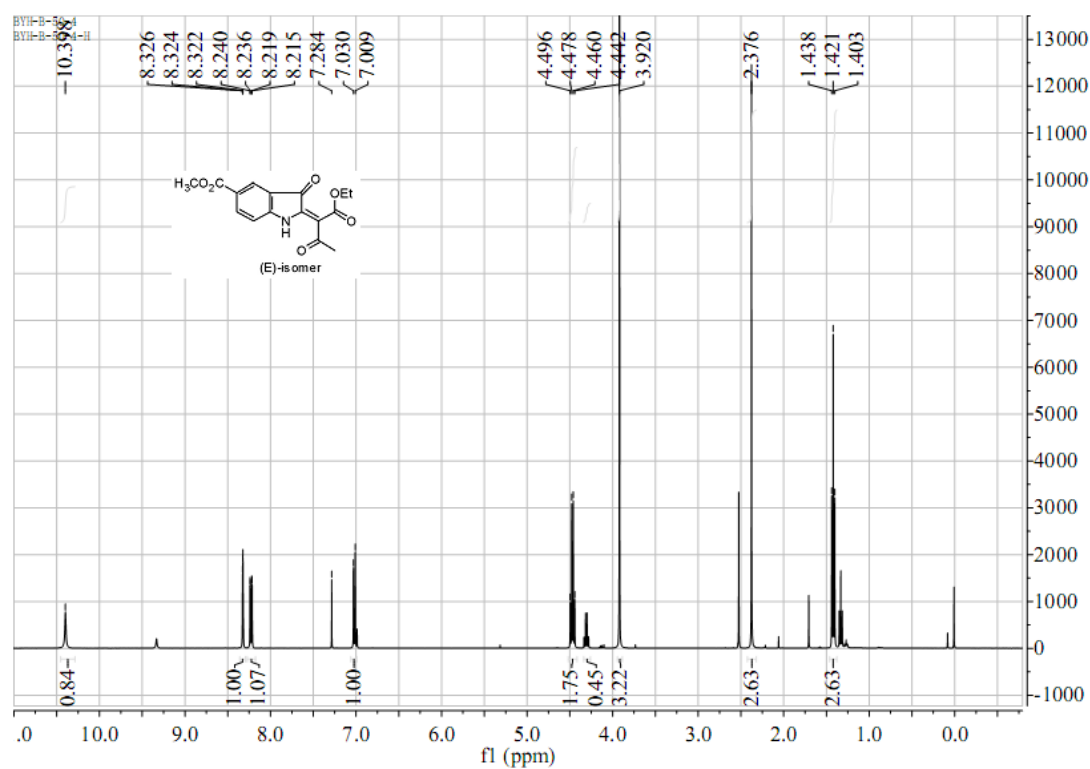
### Compound 5e



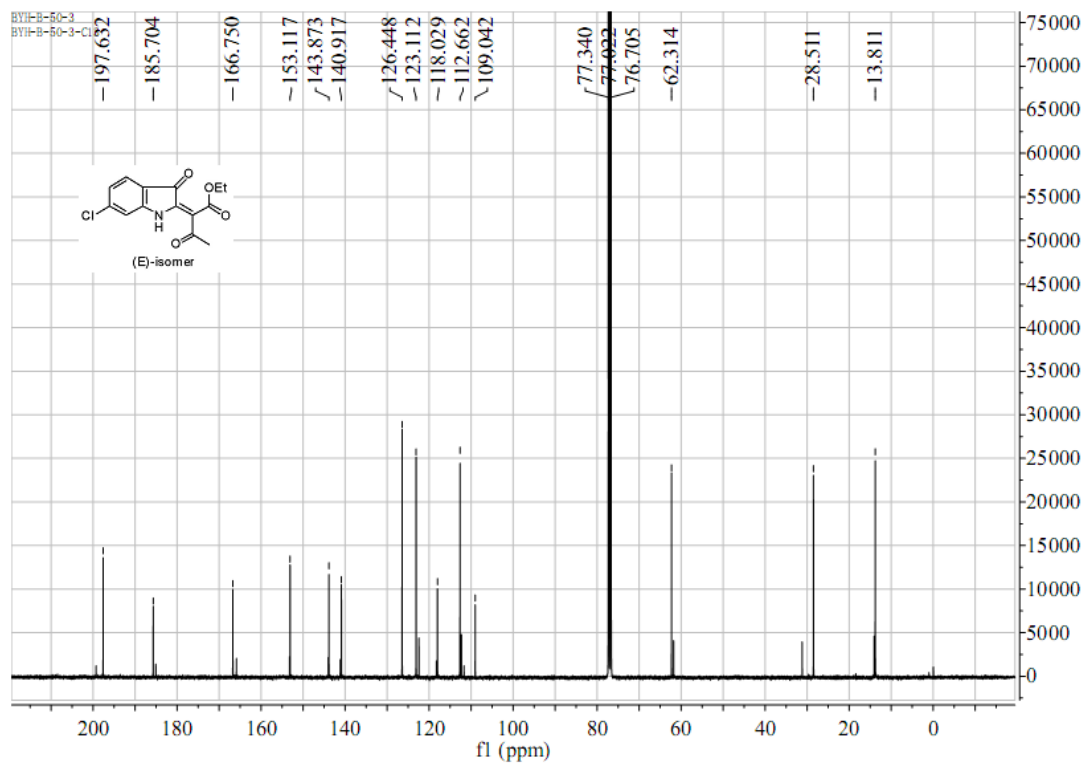
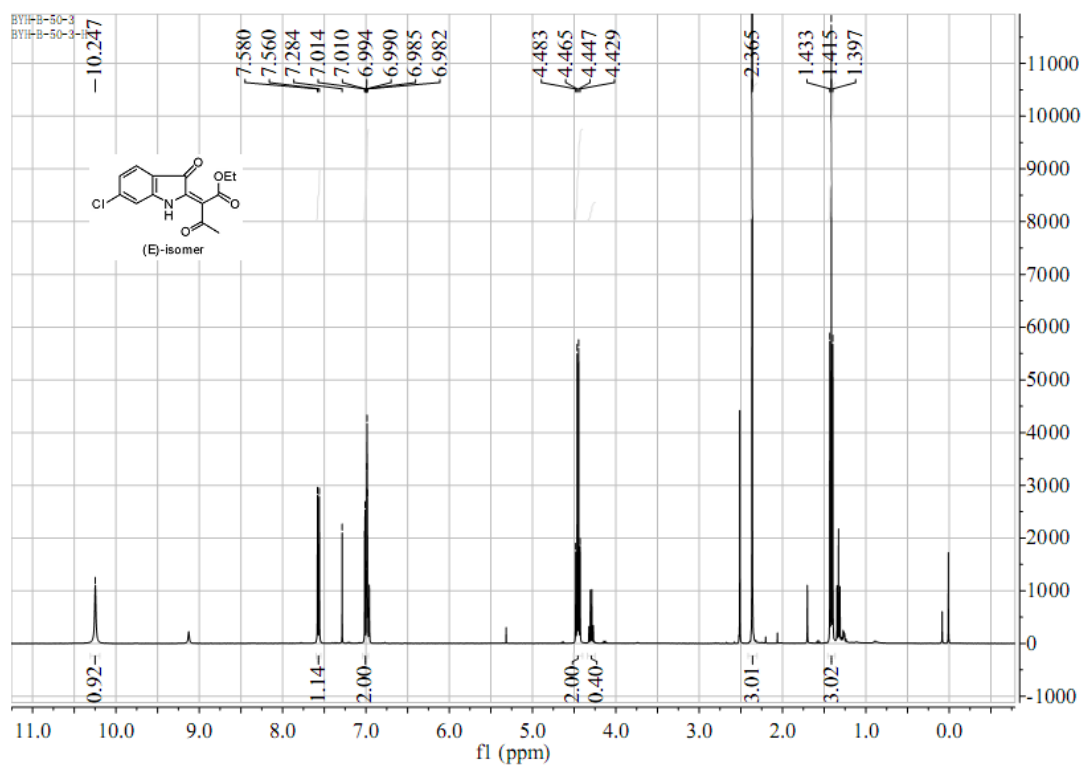
Compound **5f**



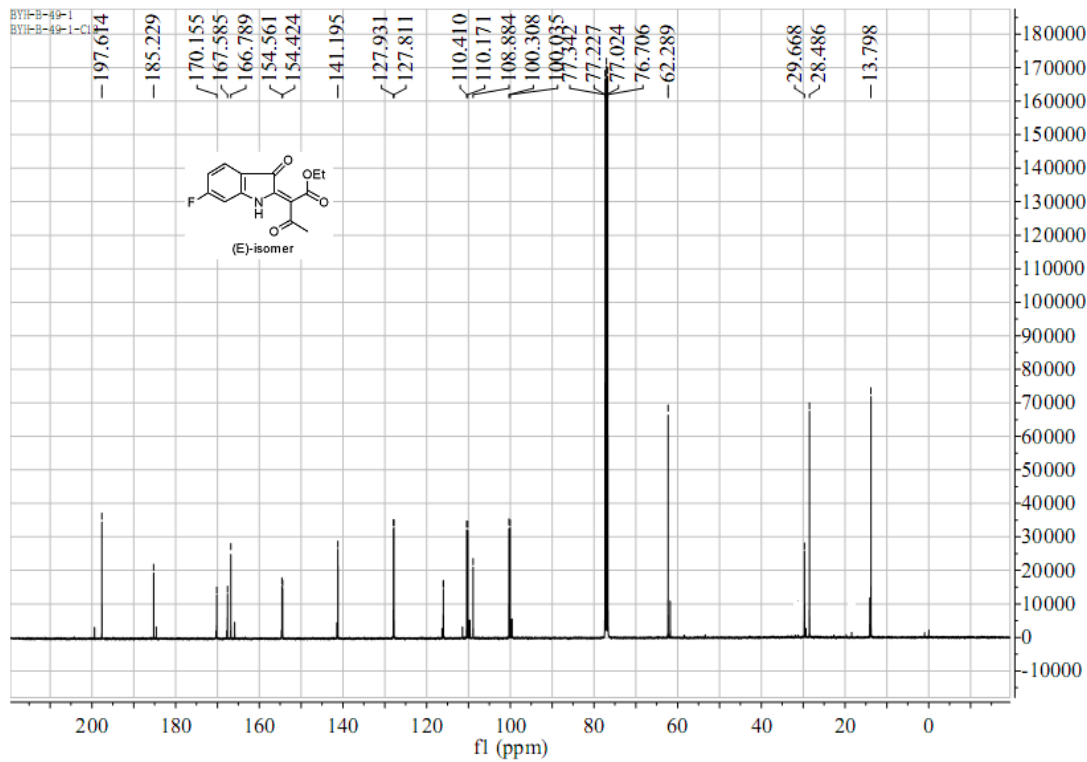
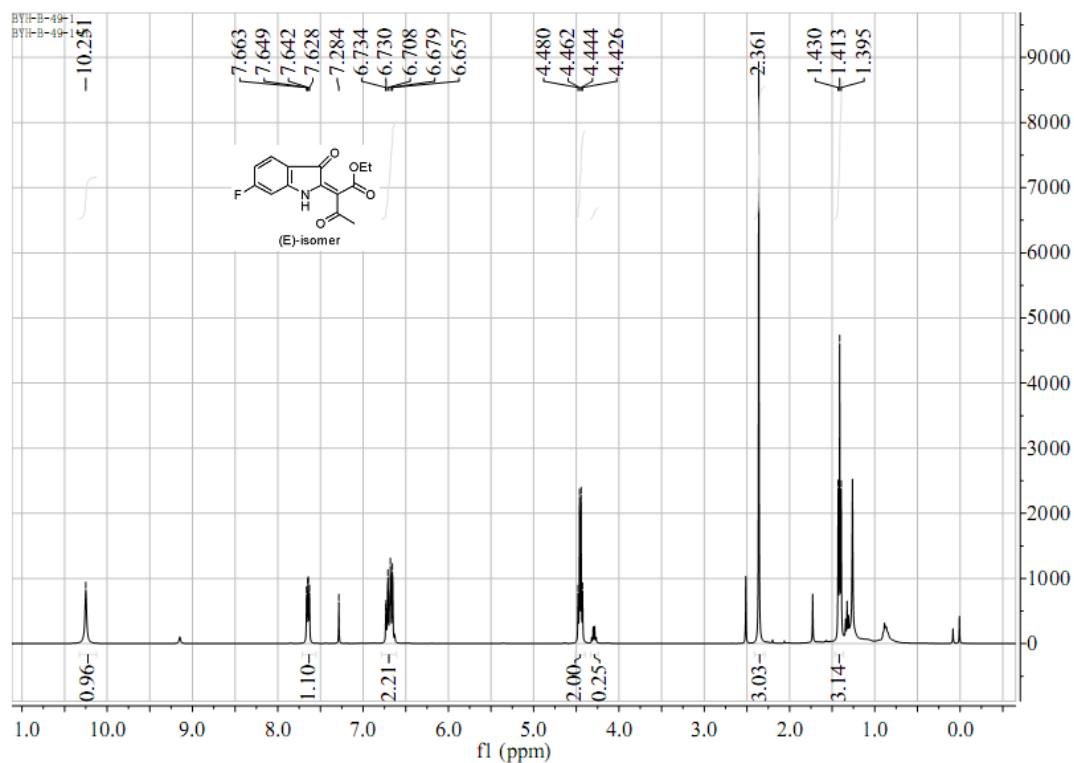
Compound **5g**



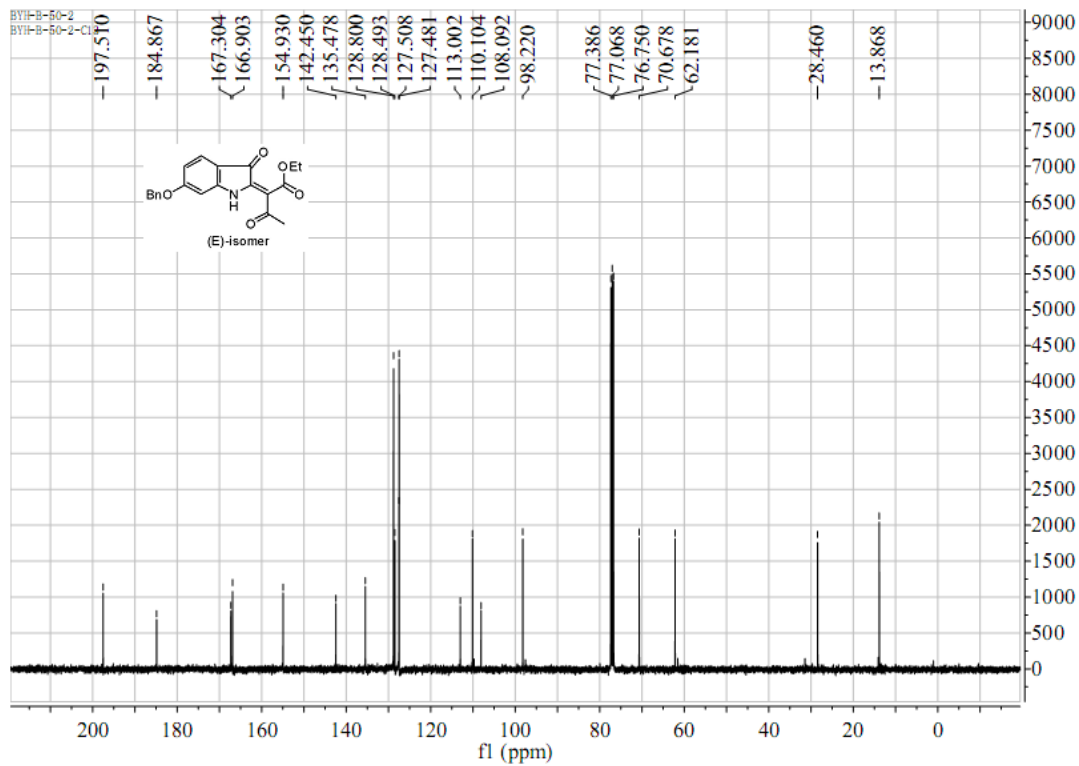
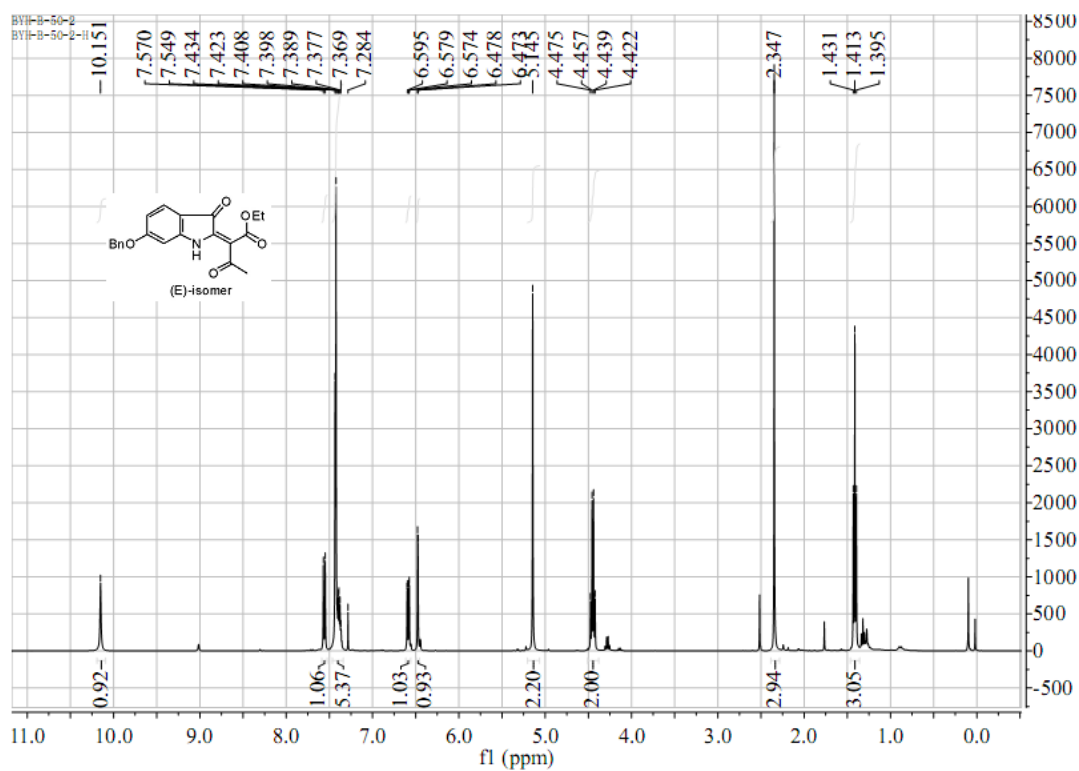
### Compound 5h



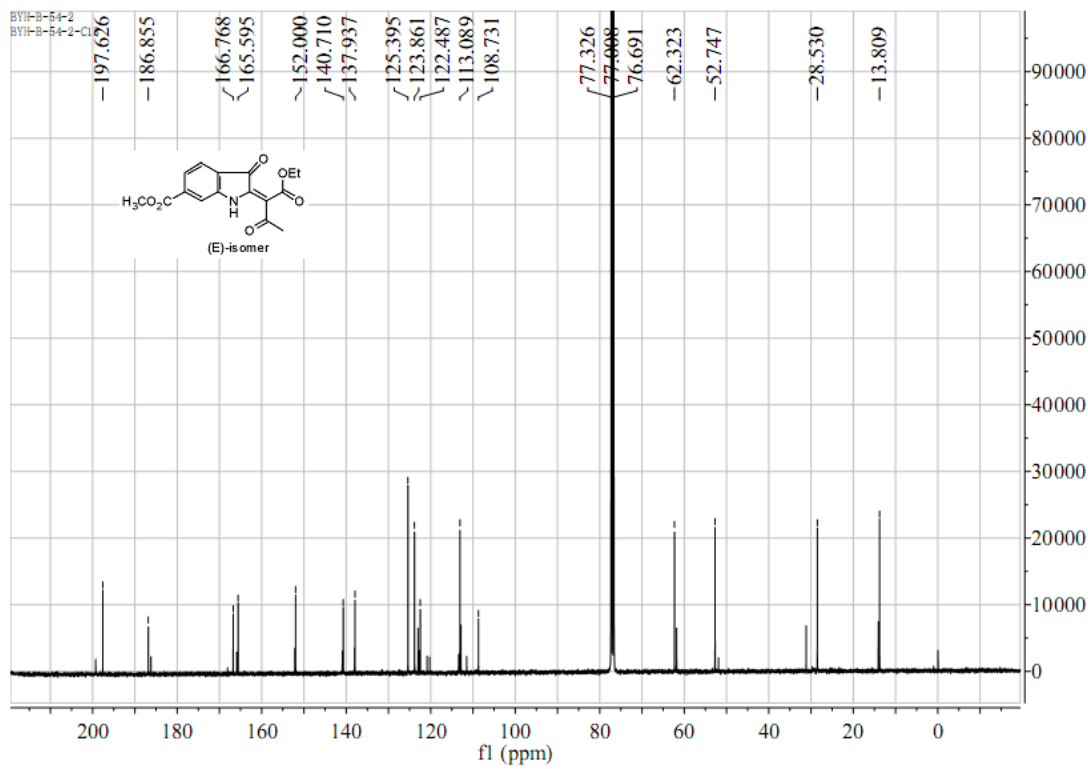
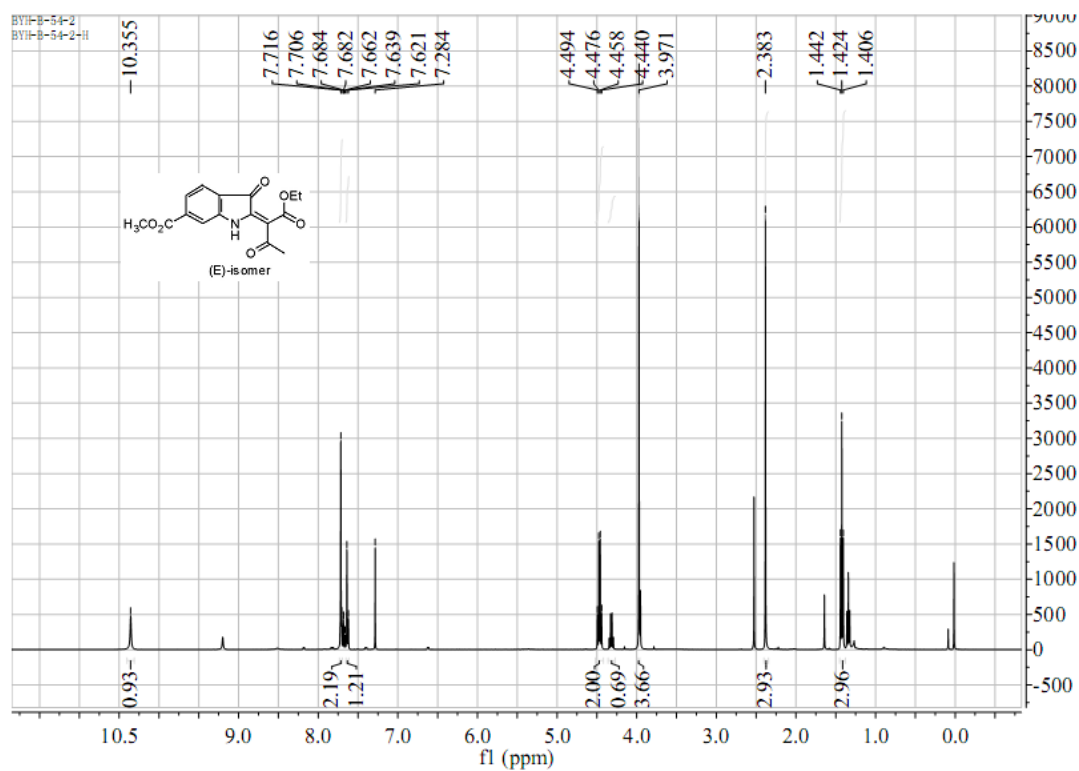
Compound **5i**



Compound 5j

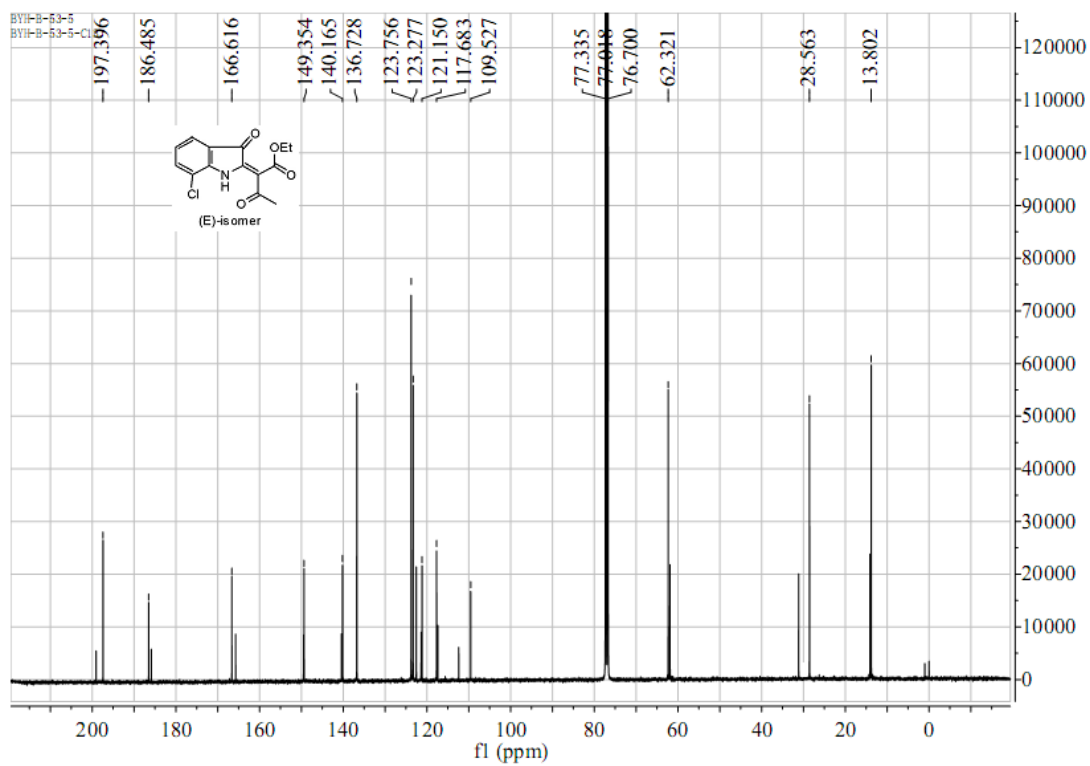
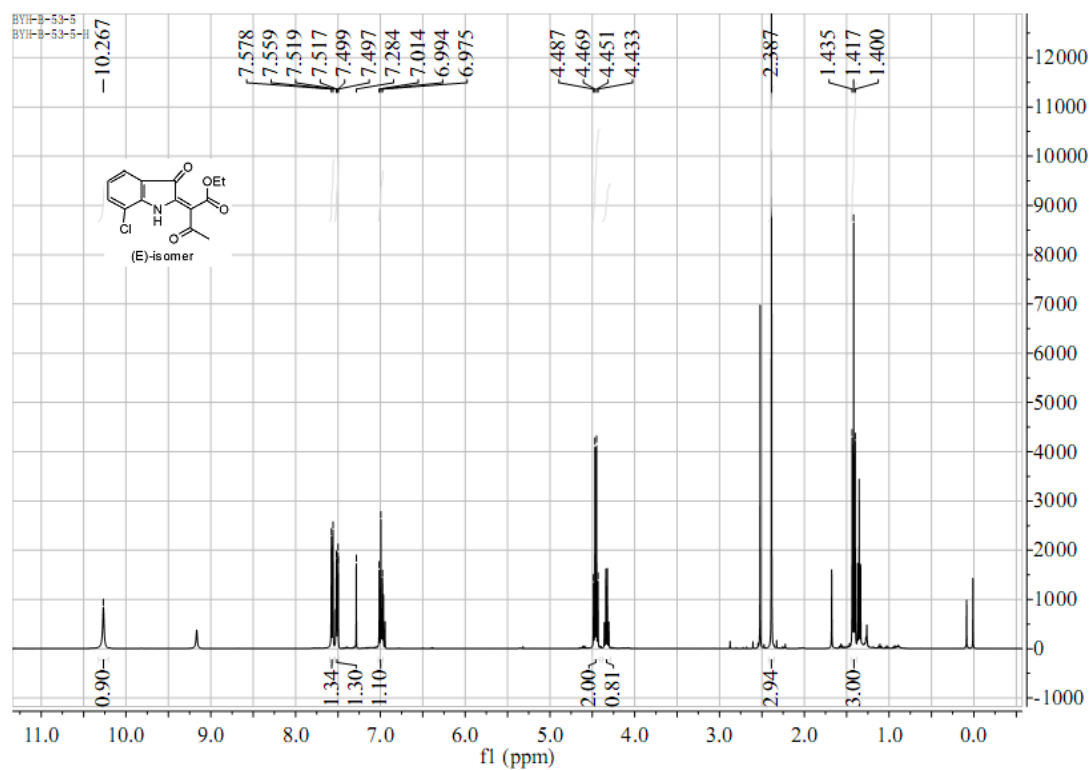


Compound **5k**

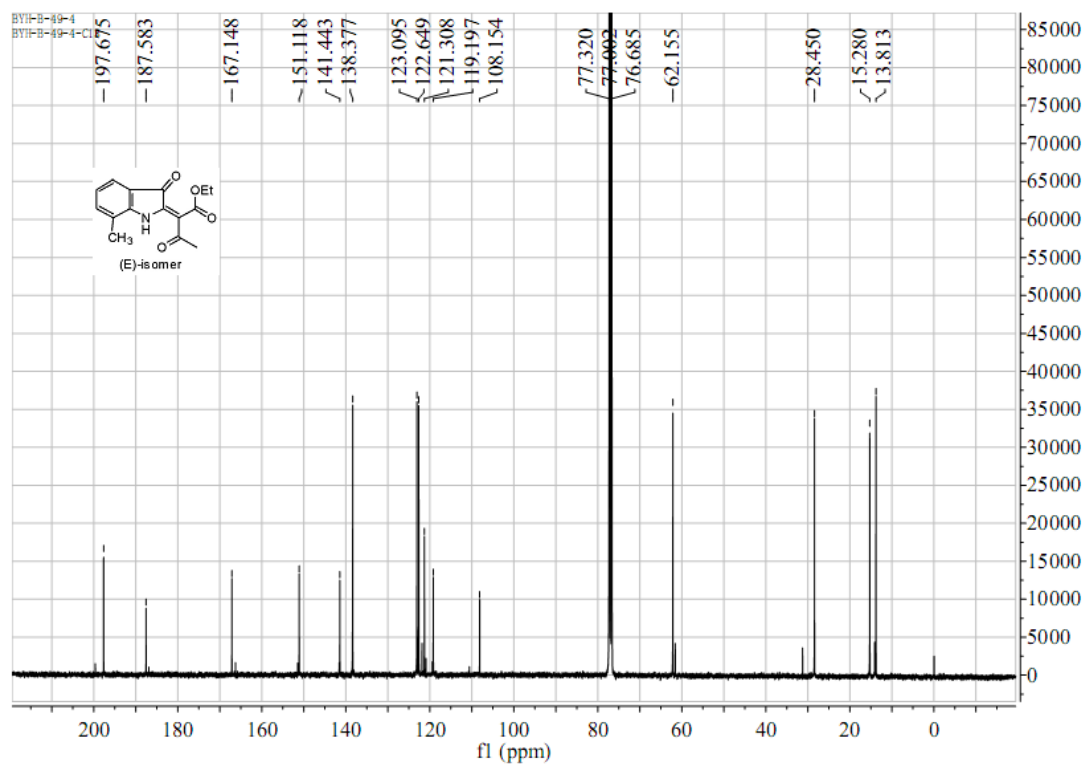
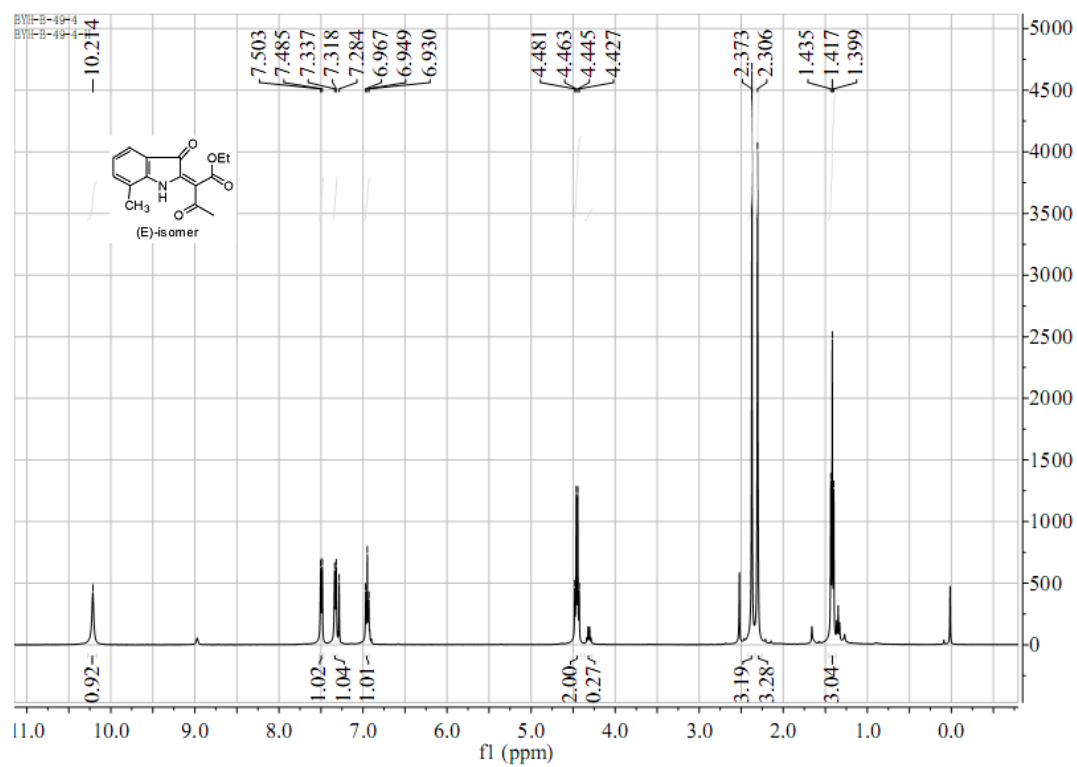




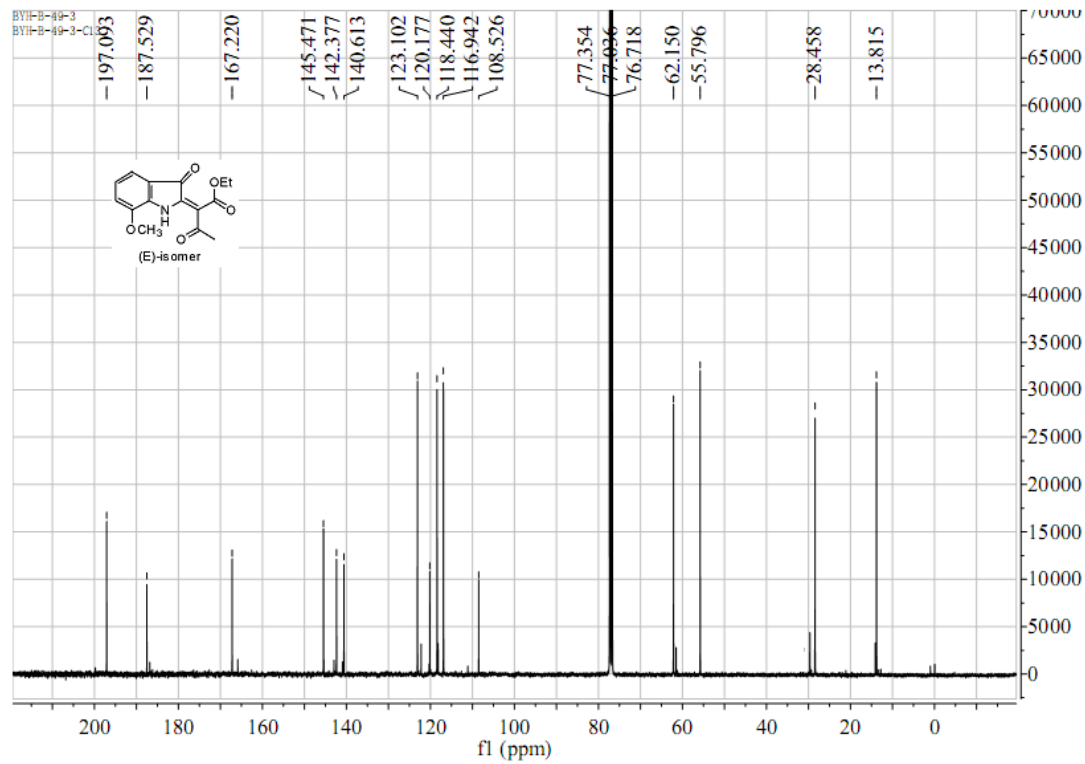
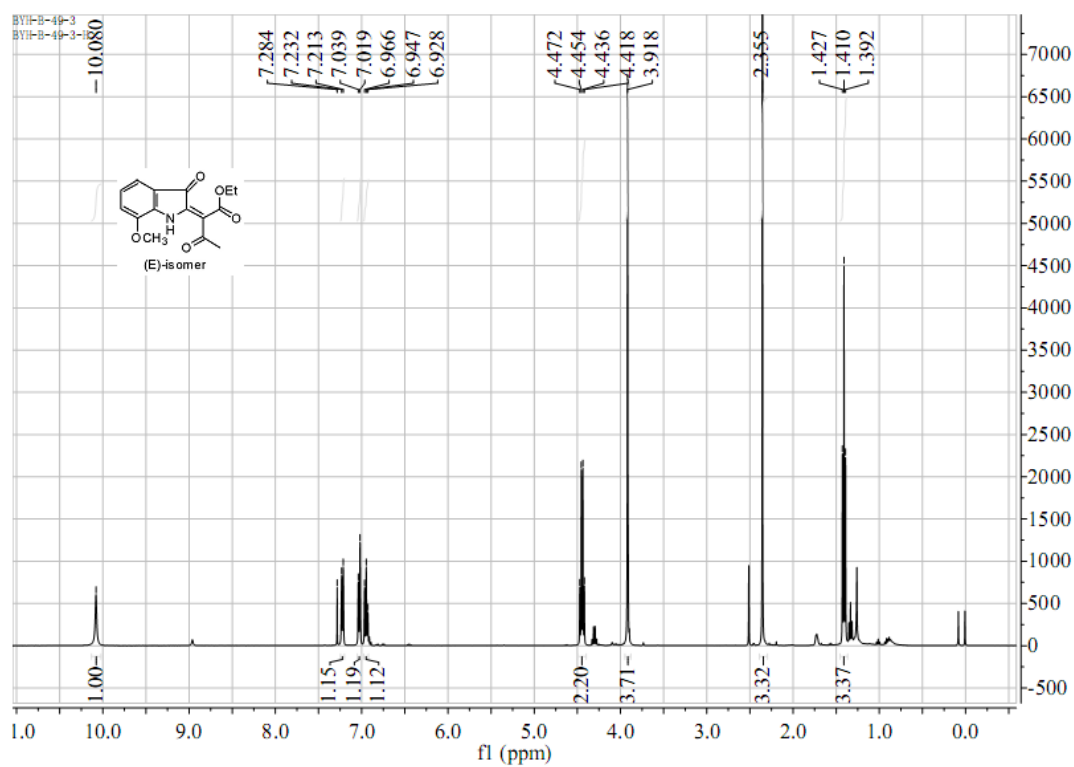
### Compound 51



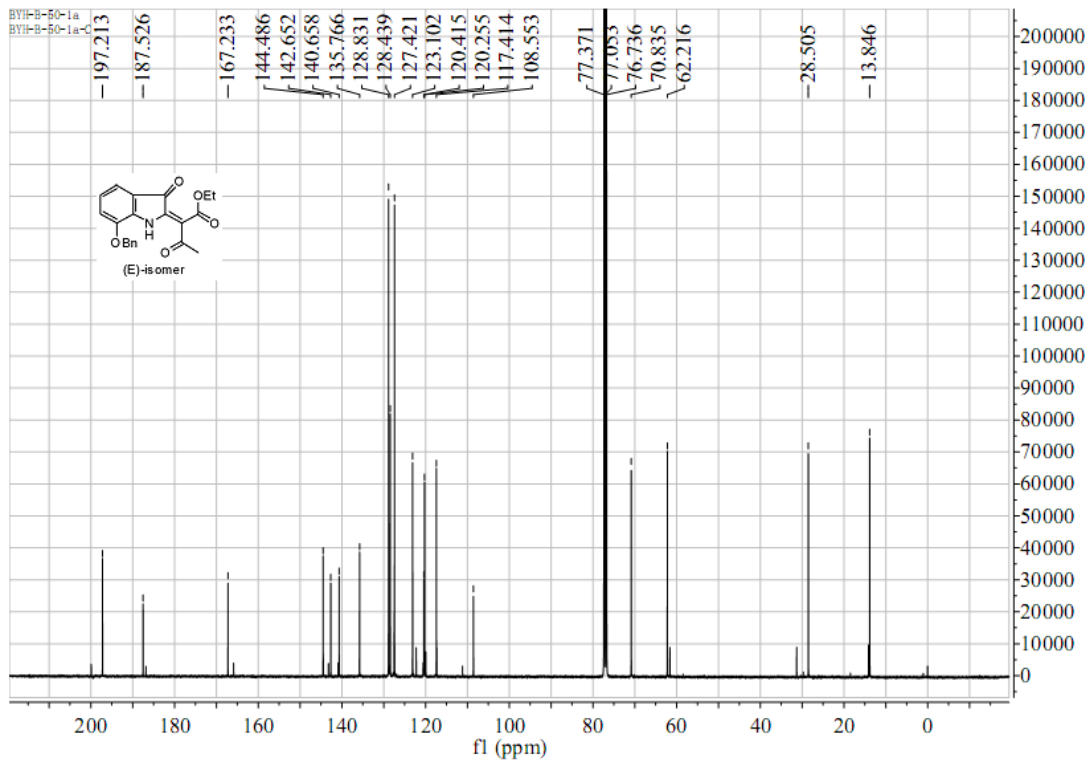
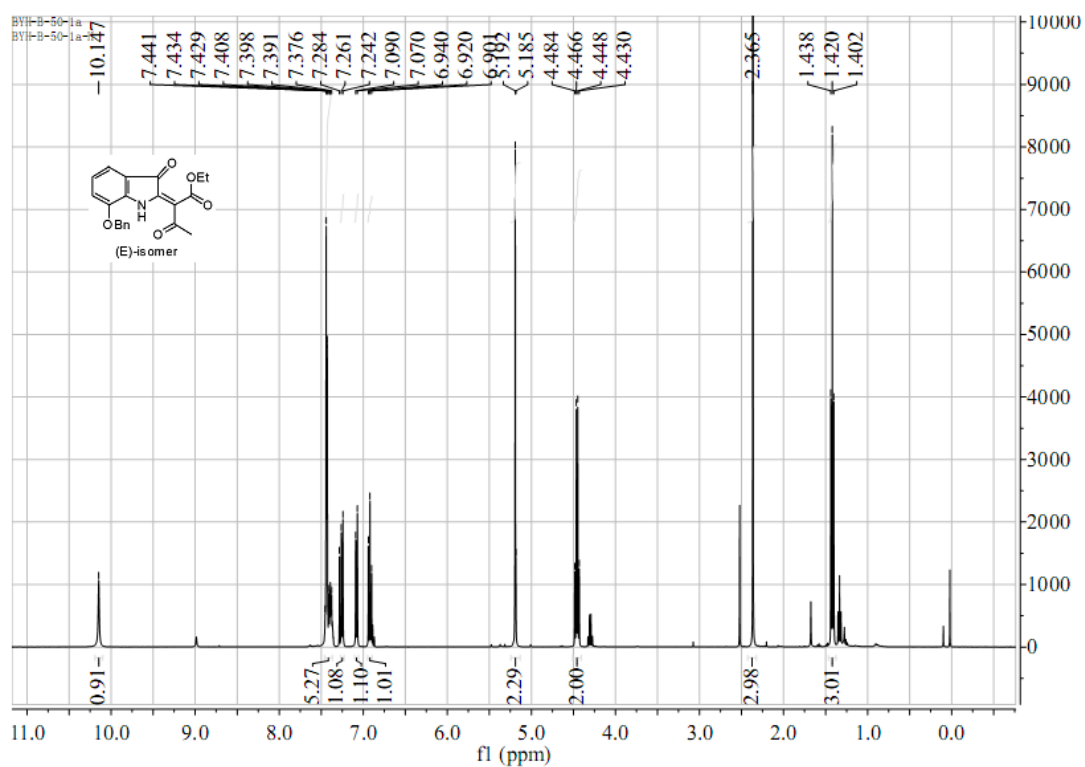
### Compound 5m



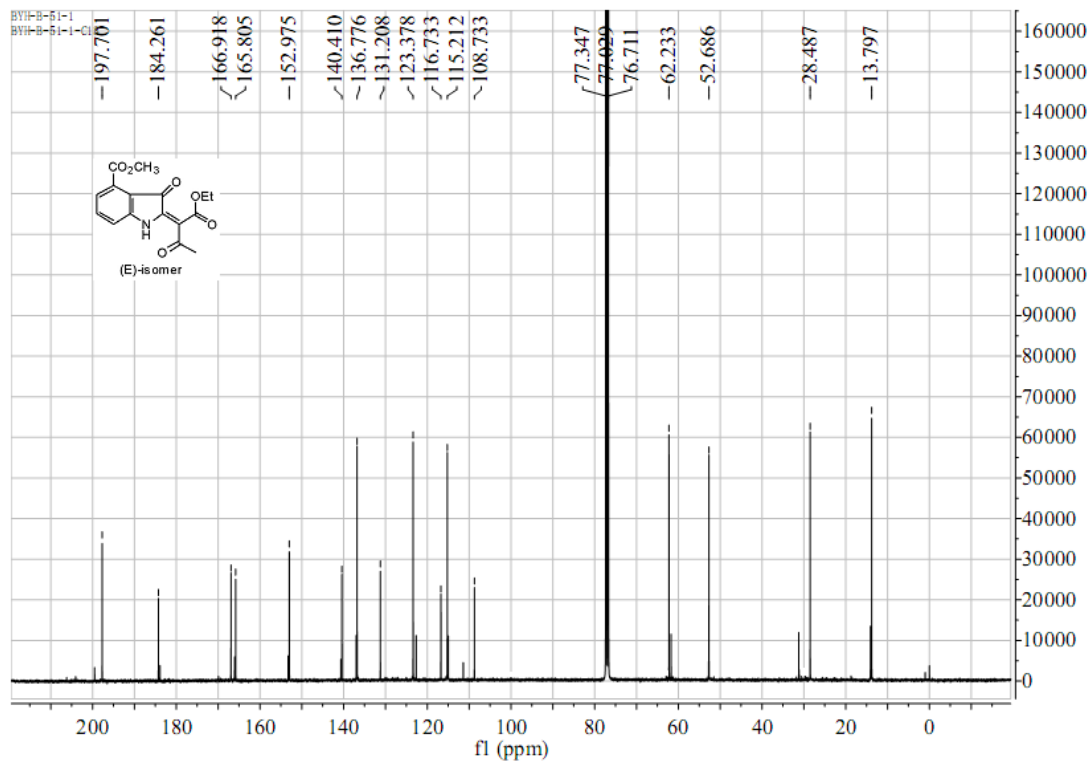
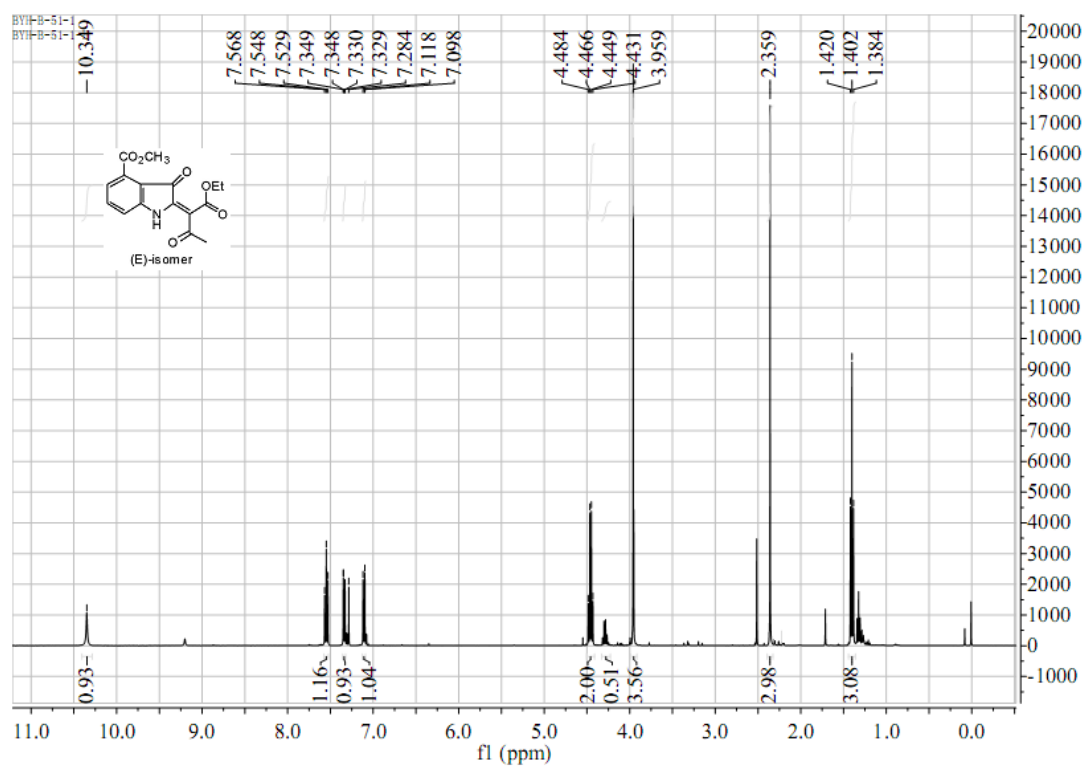
Compound **5n**



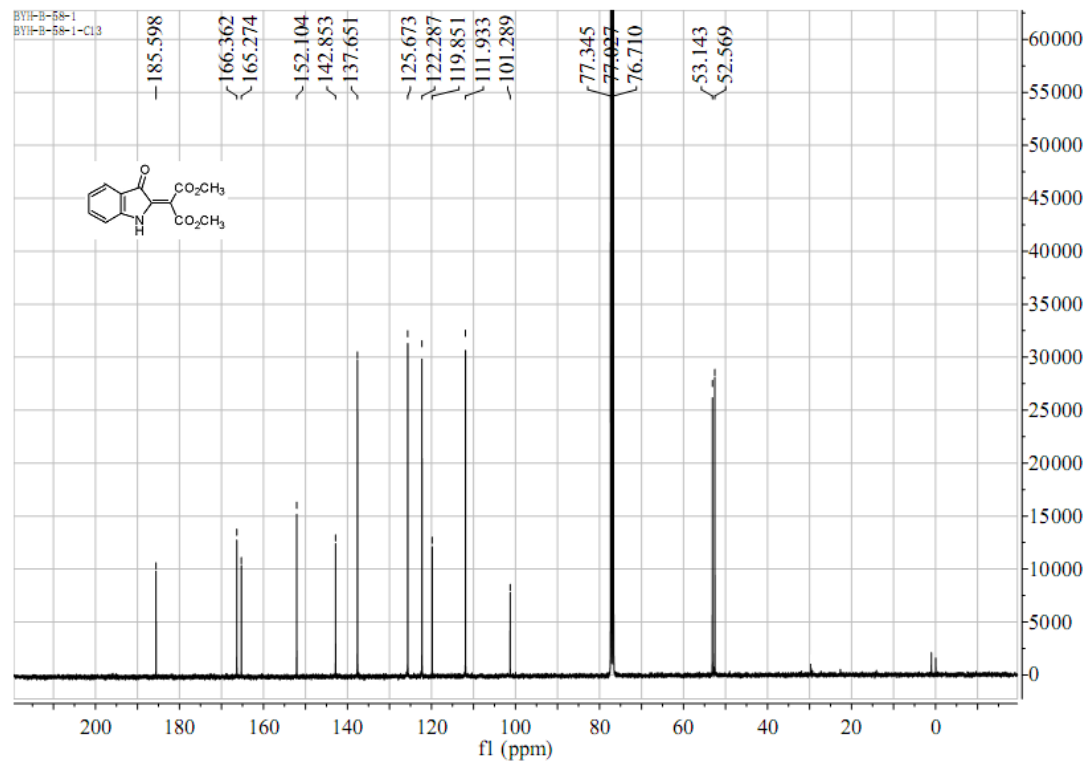
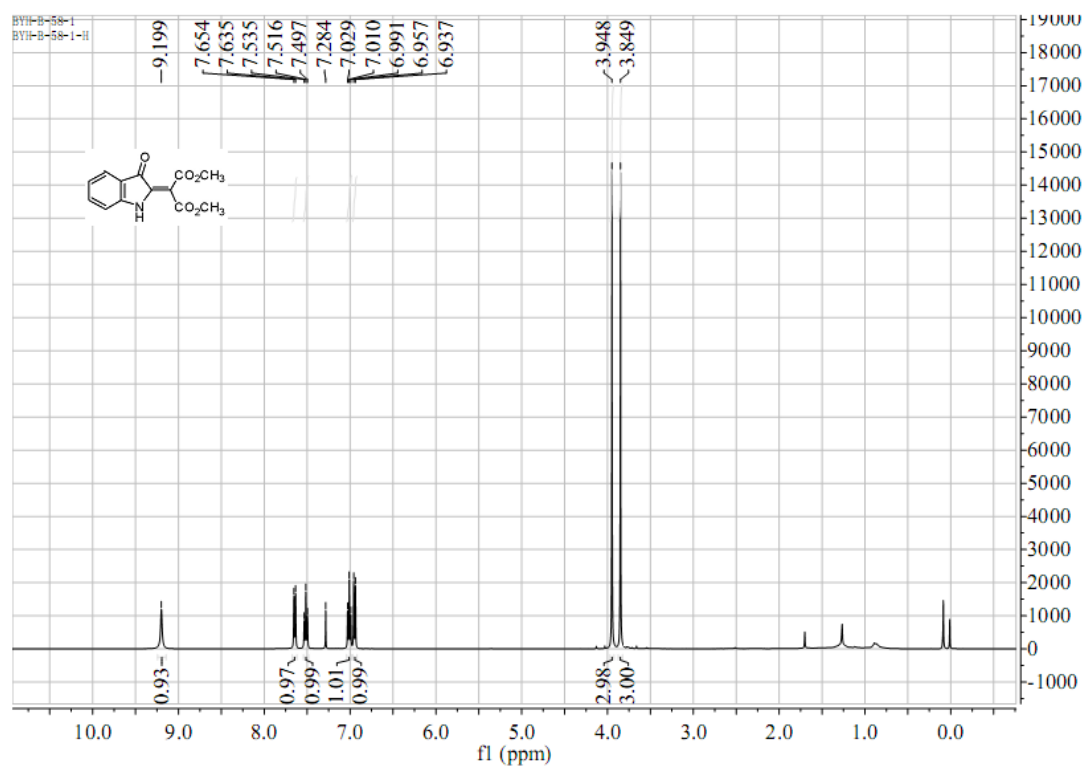
### Compound 5o



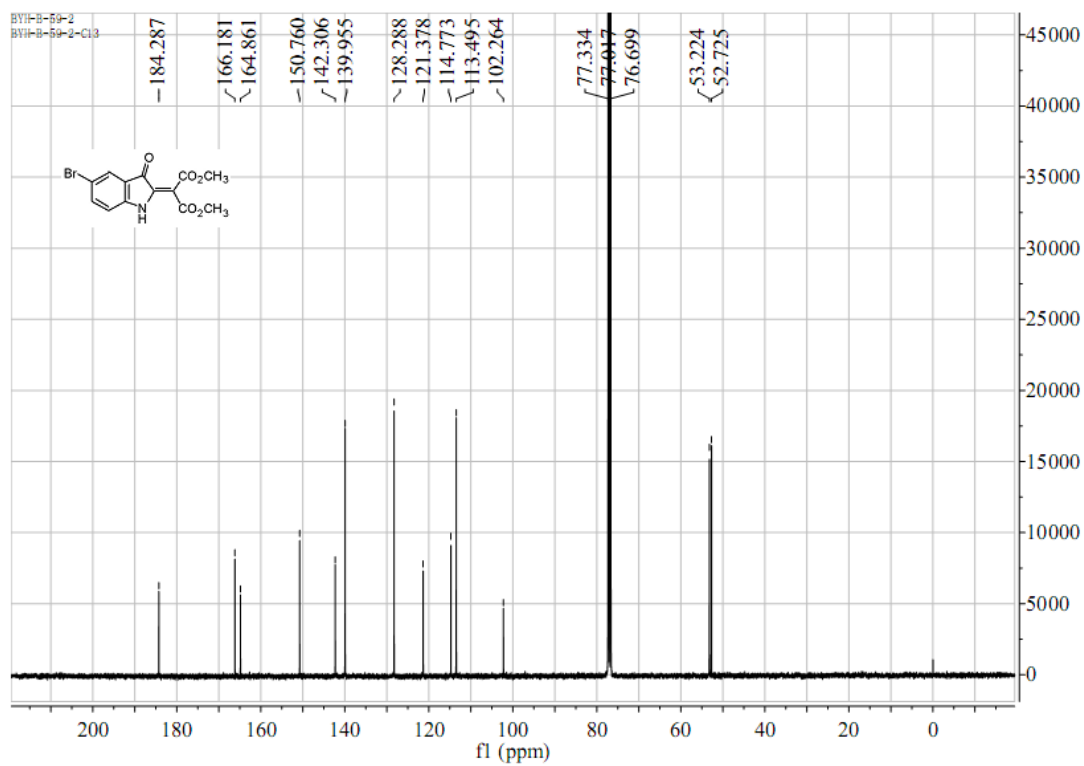
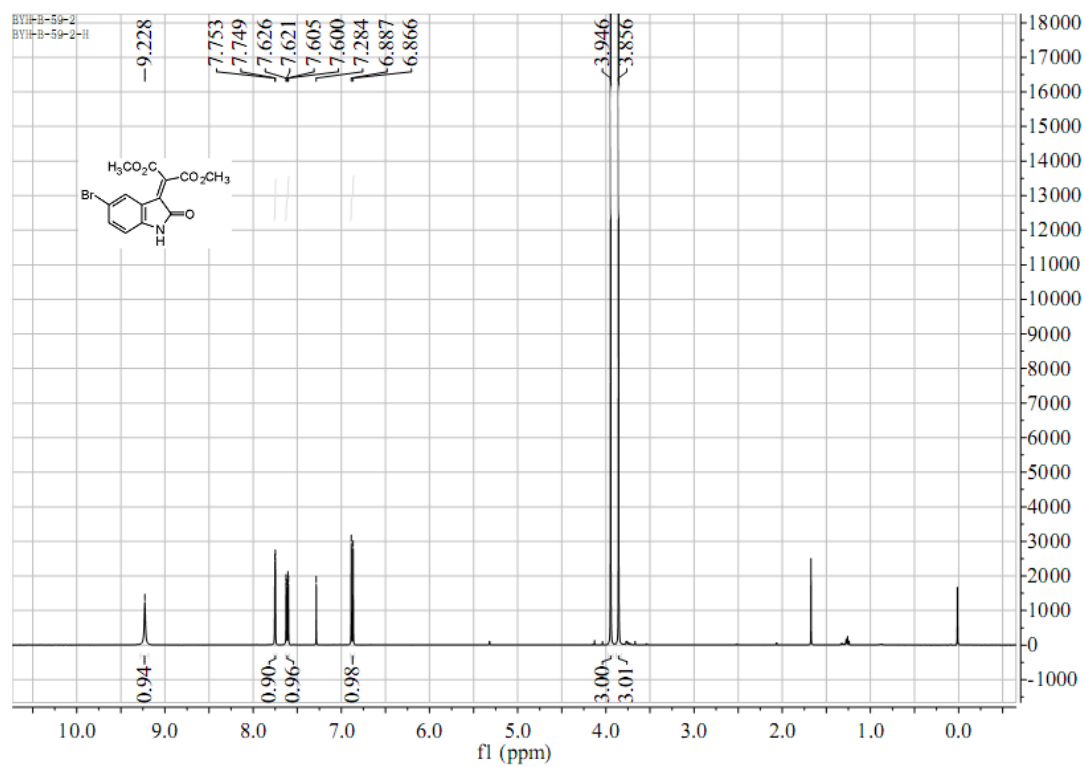
### Compound 5p



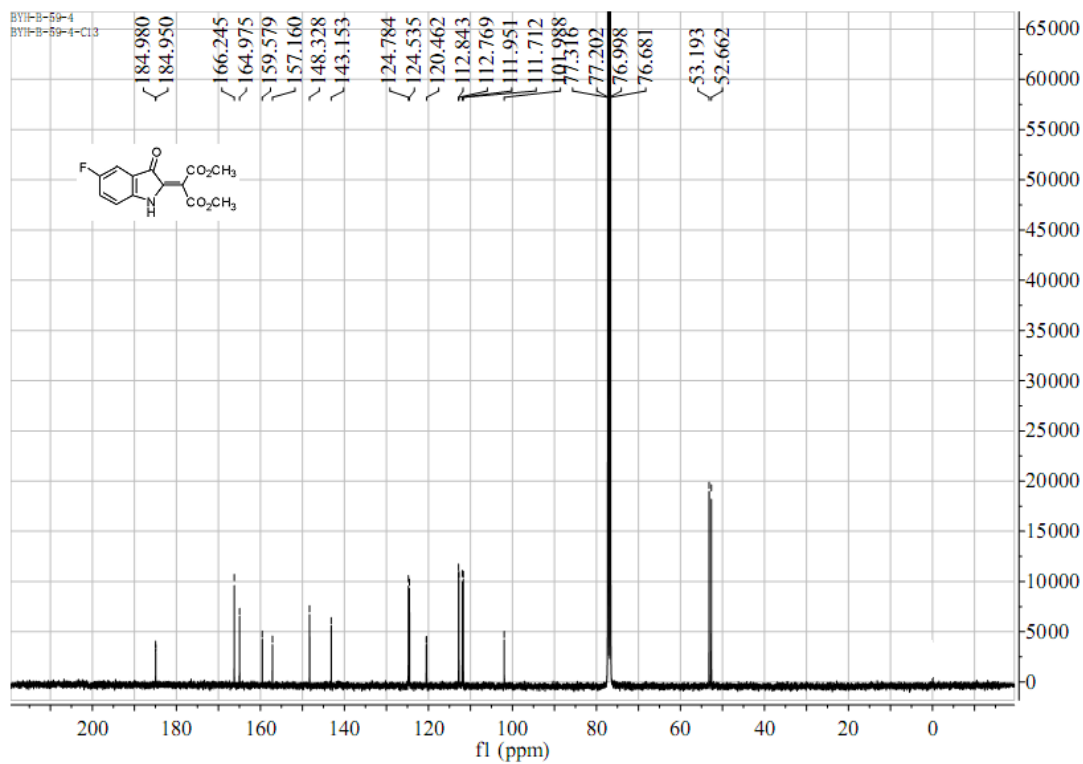
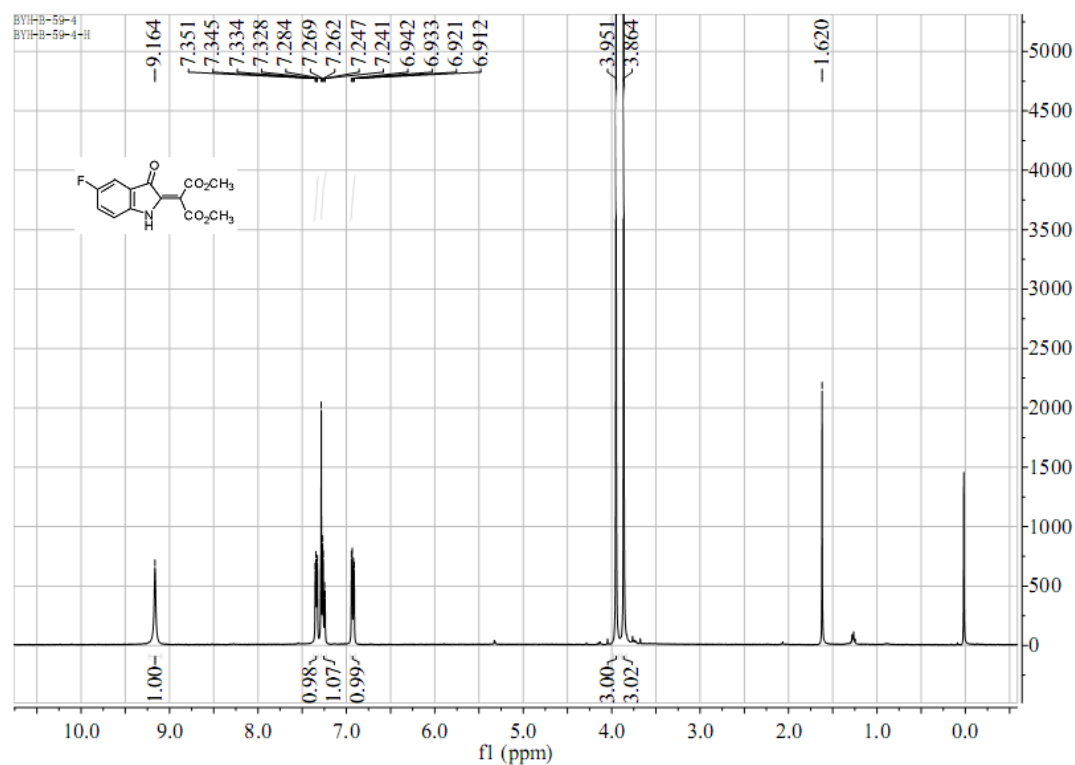
Compound 6a



### Compound 6b

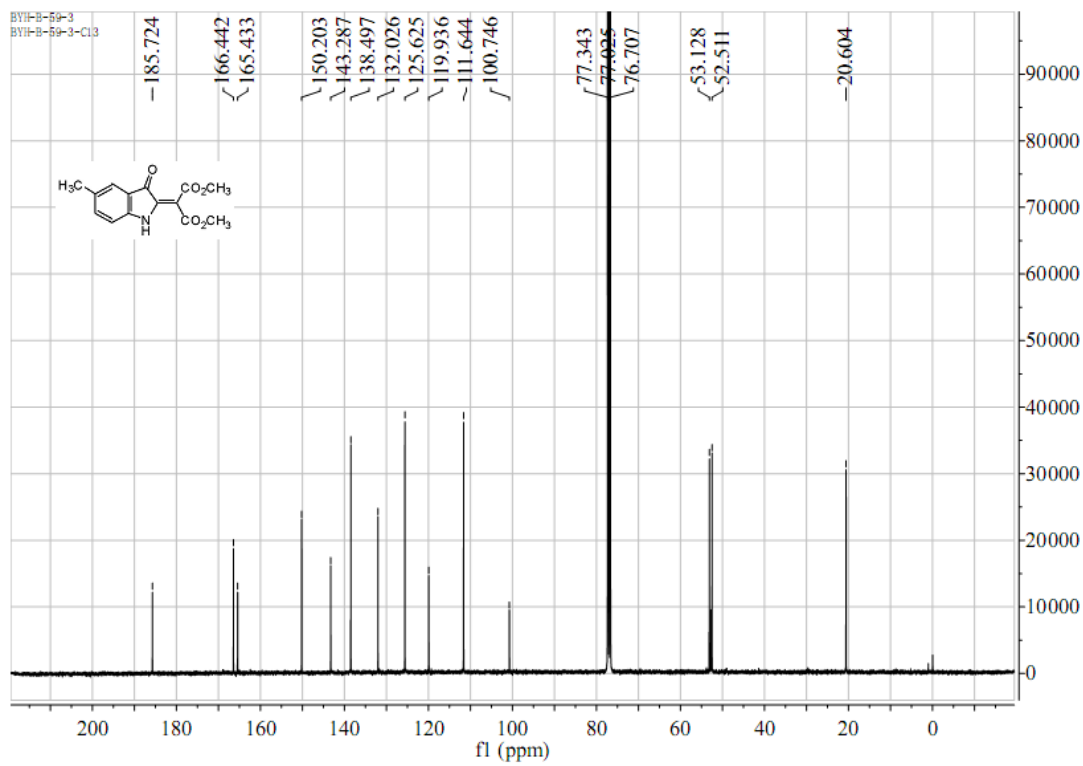
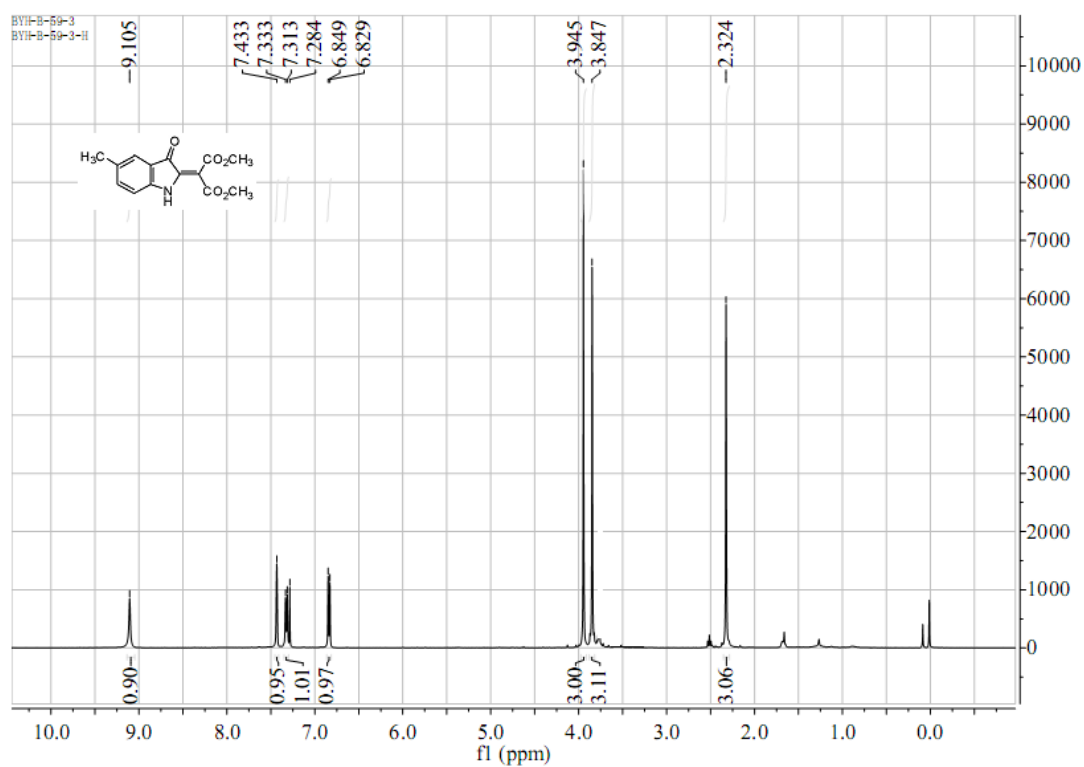


### Compound 6c

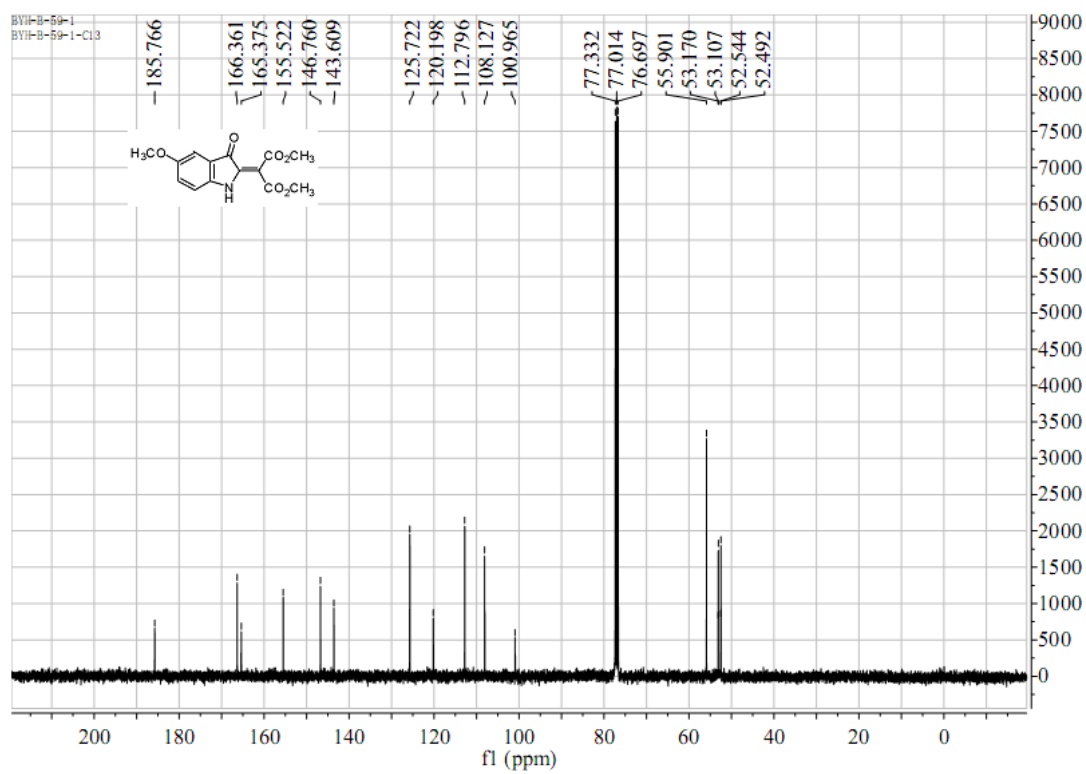
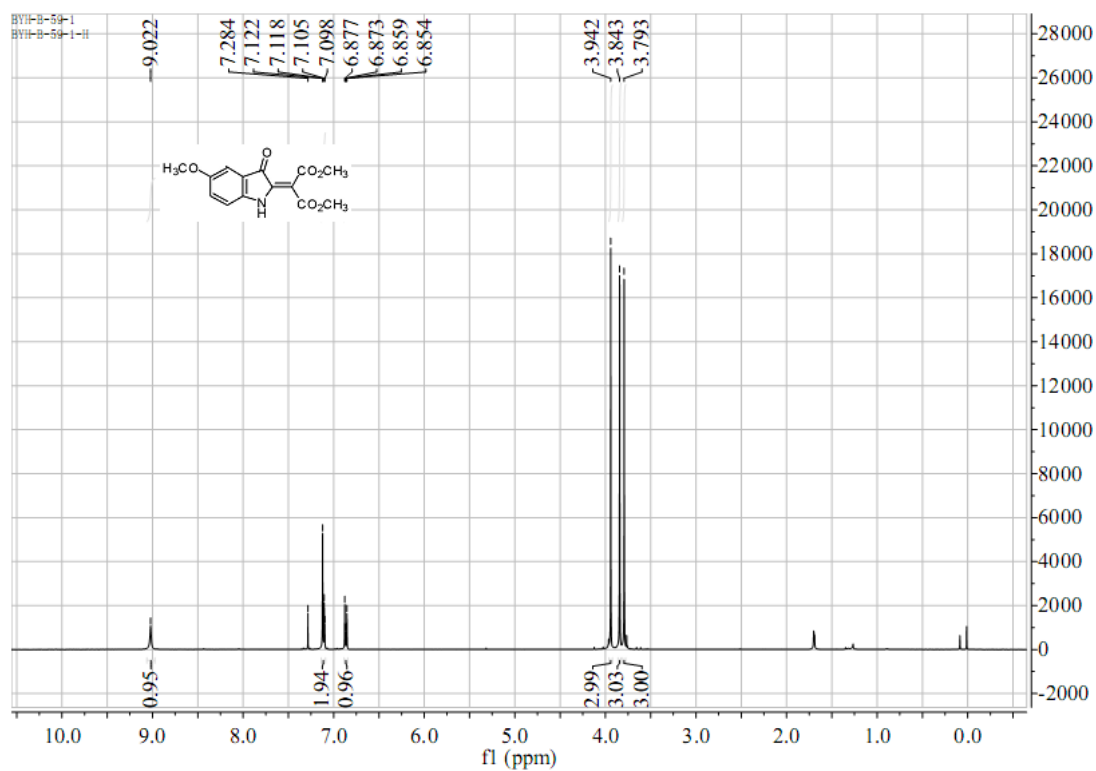




Compound **6d**

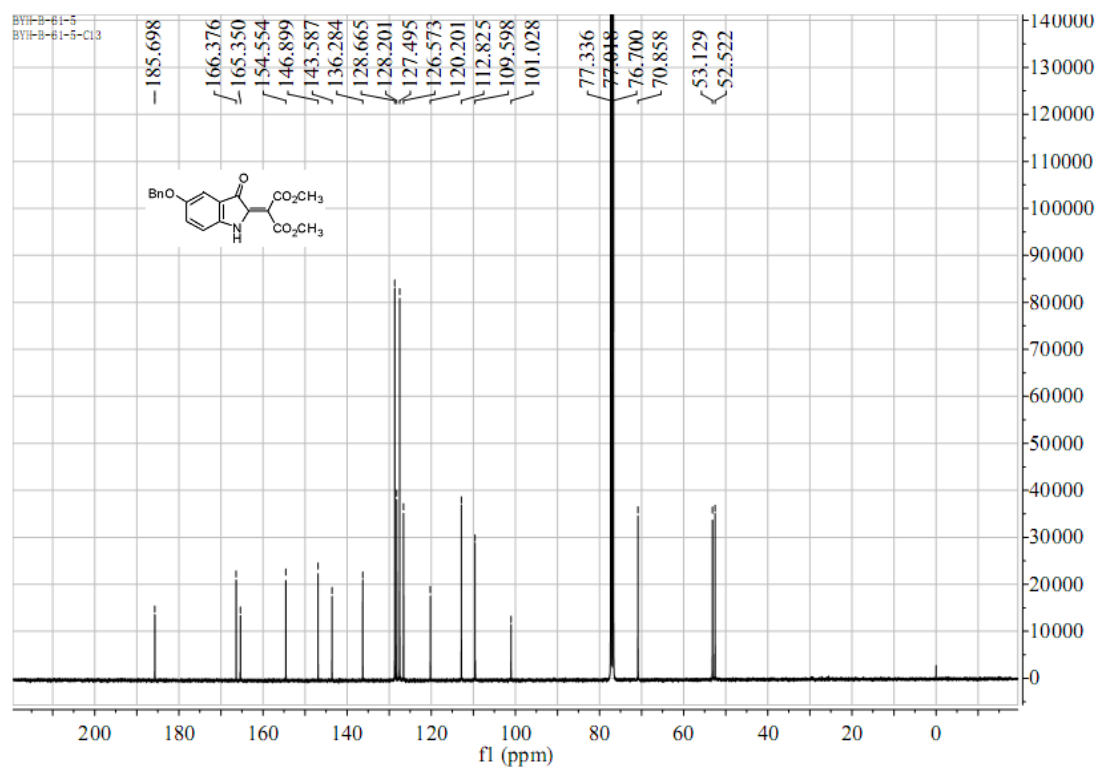
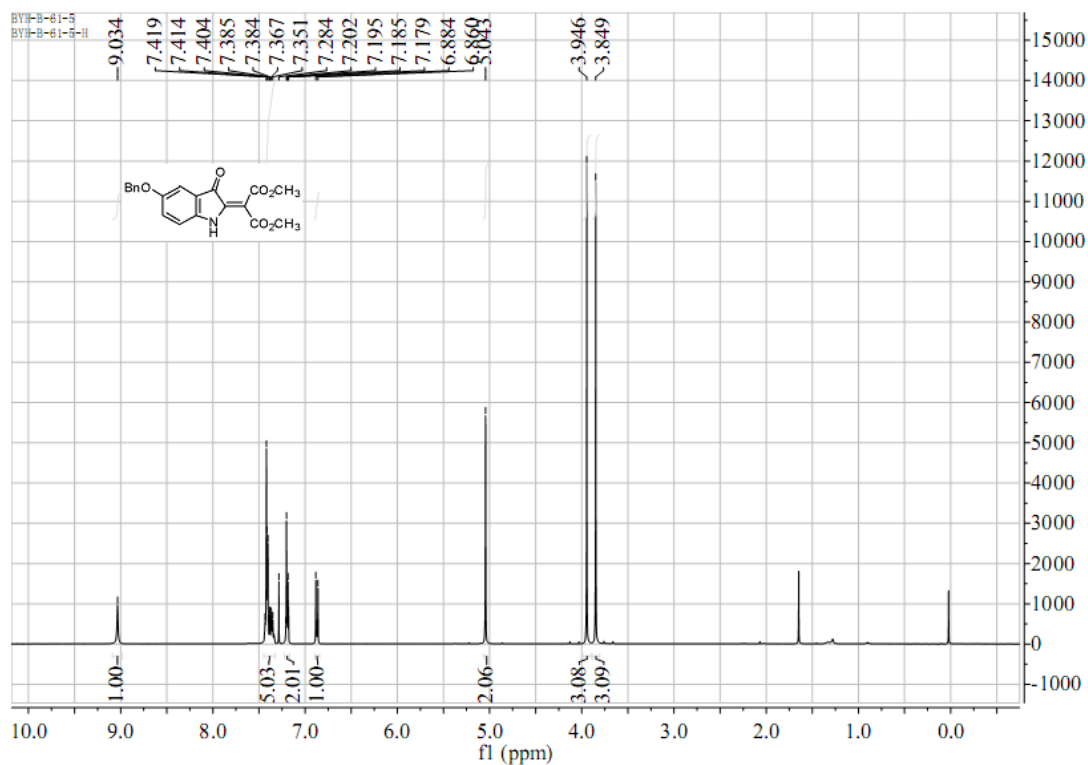


Compound 6e

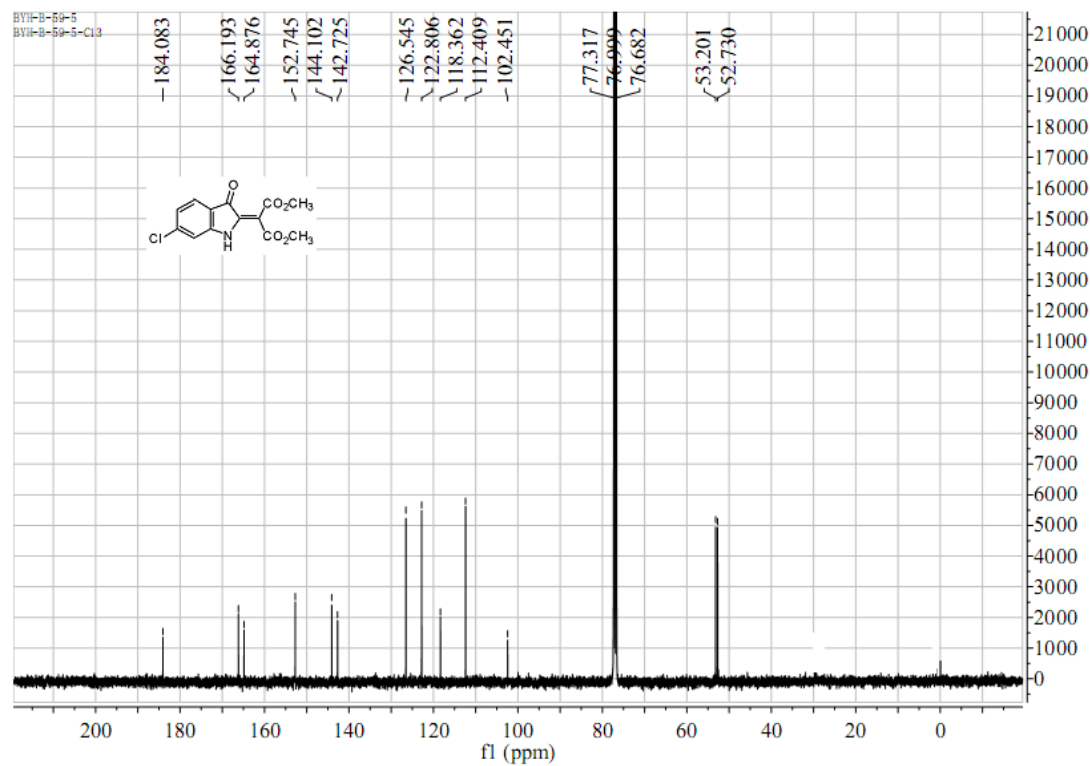
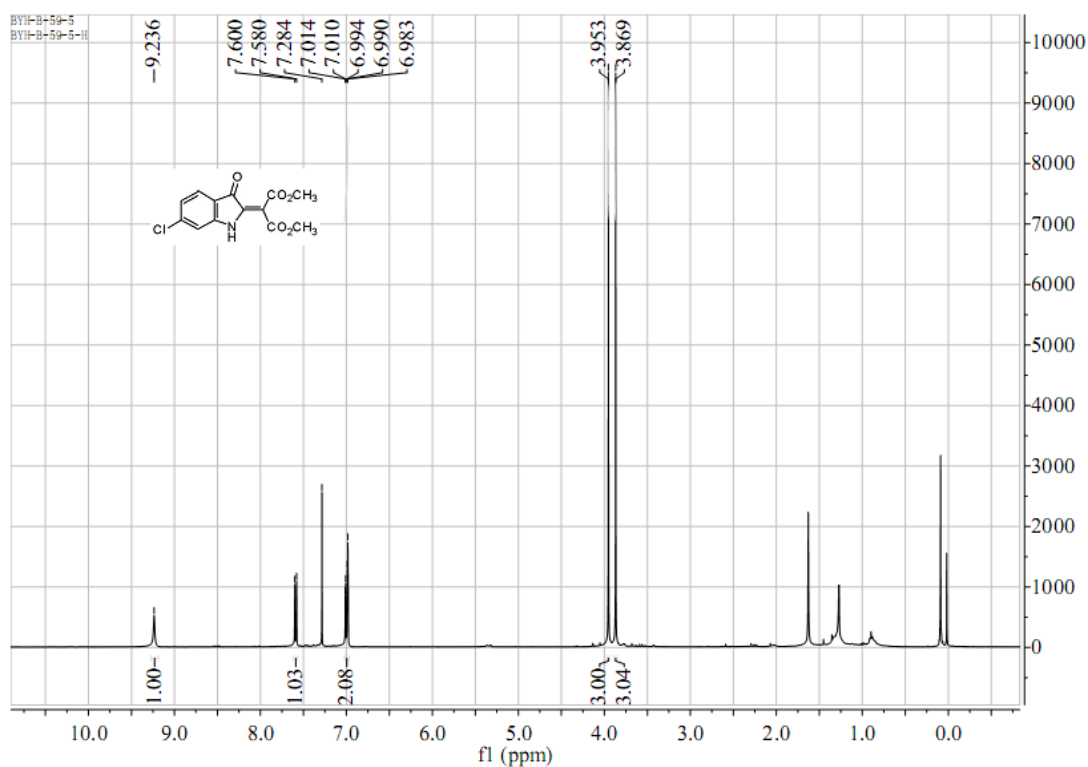


Compound

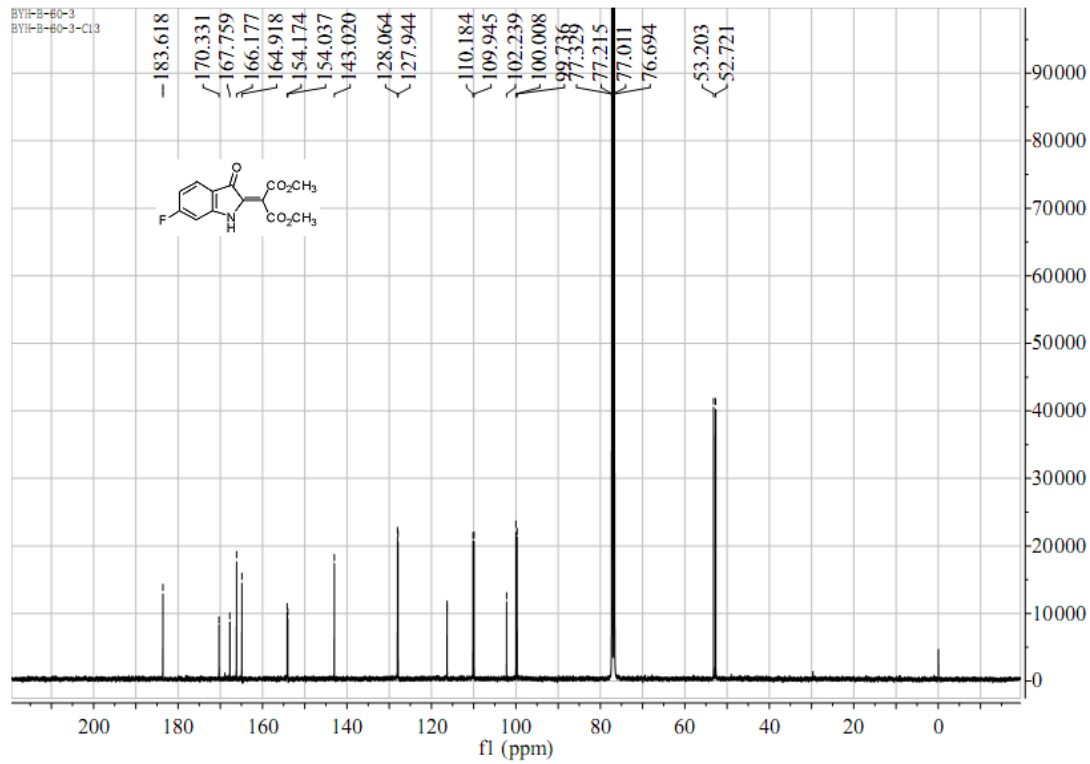
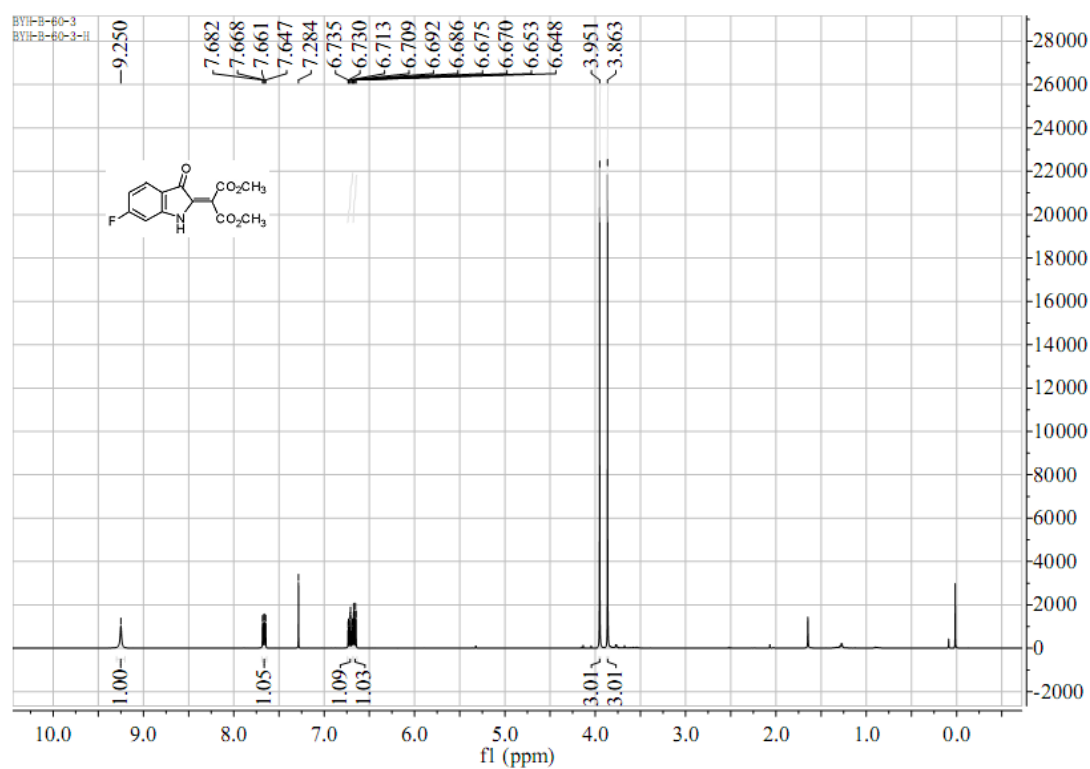
6f



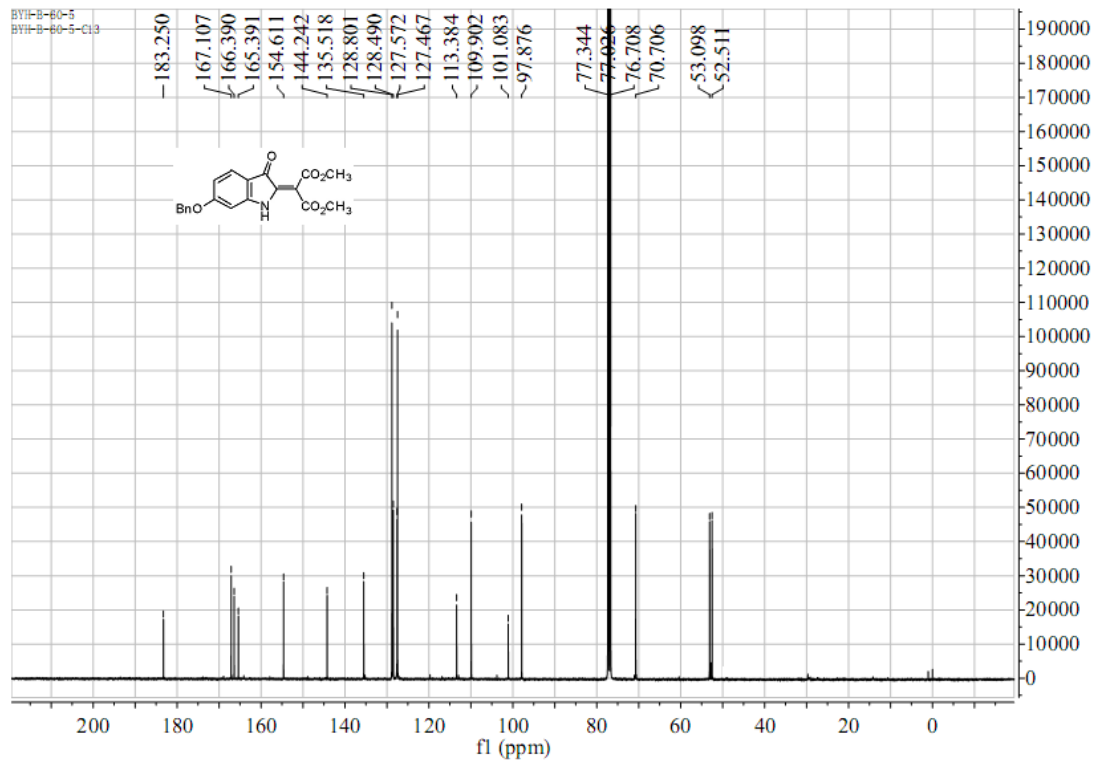
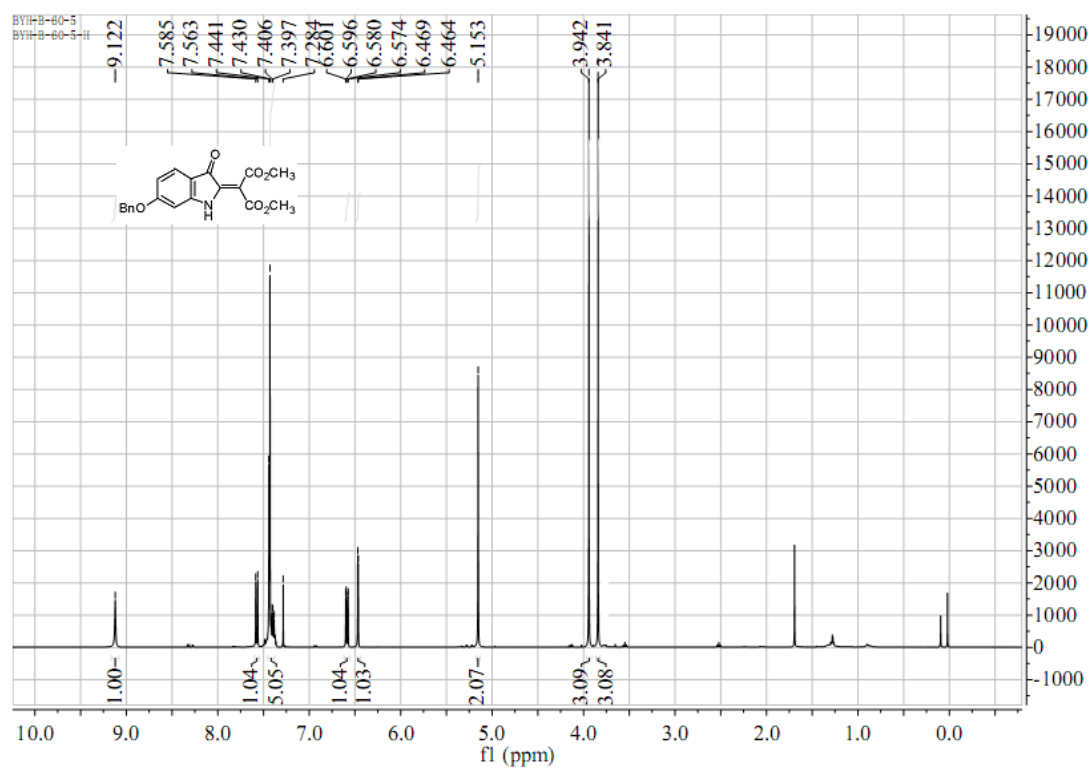
Compound **6g**



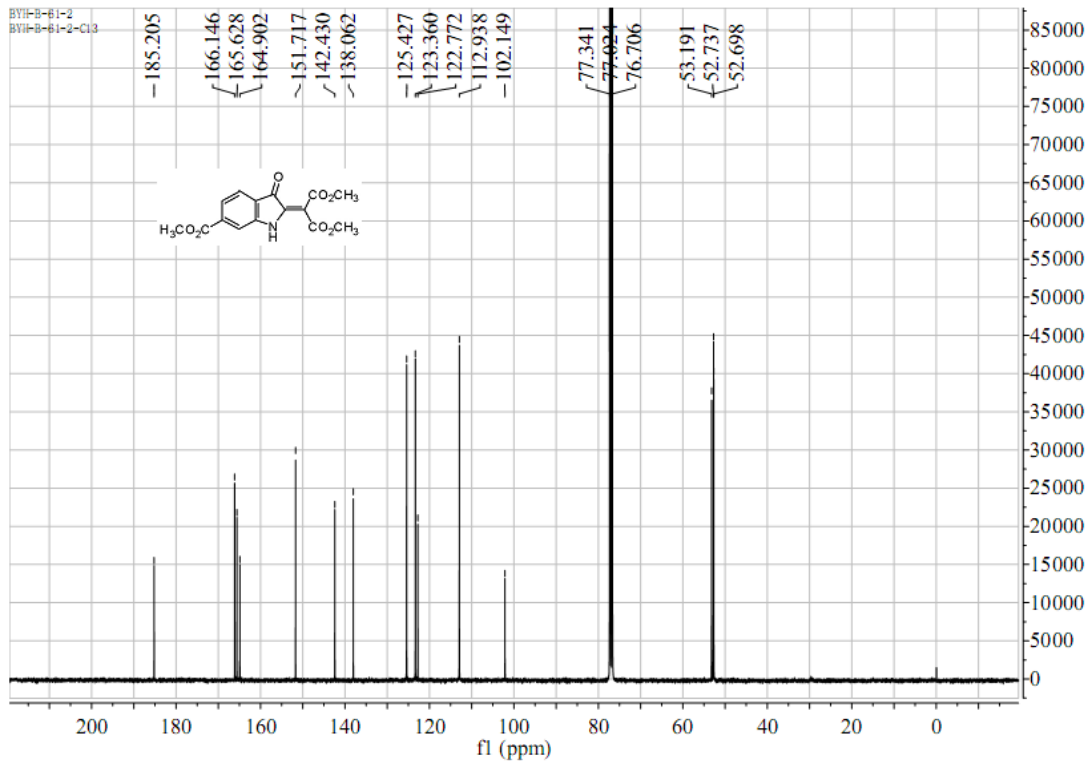
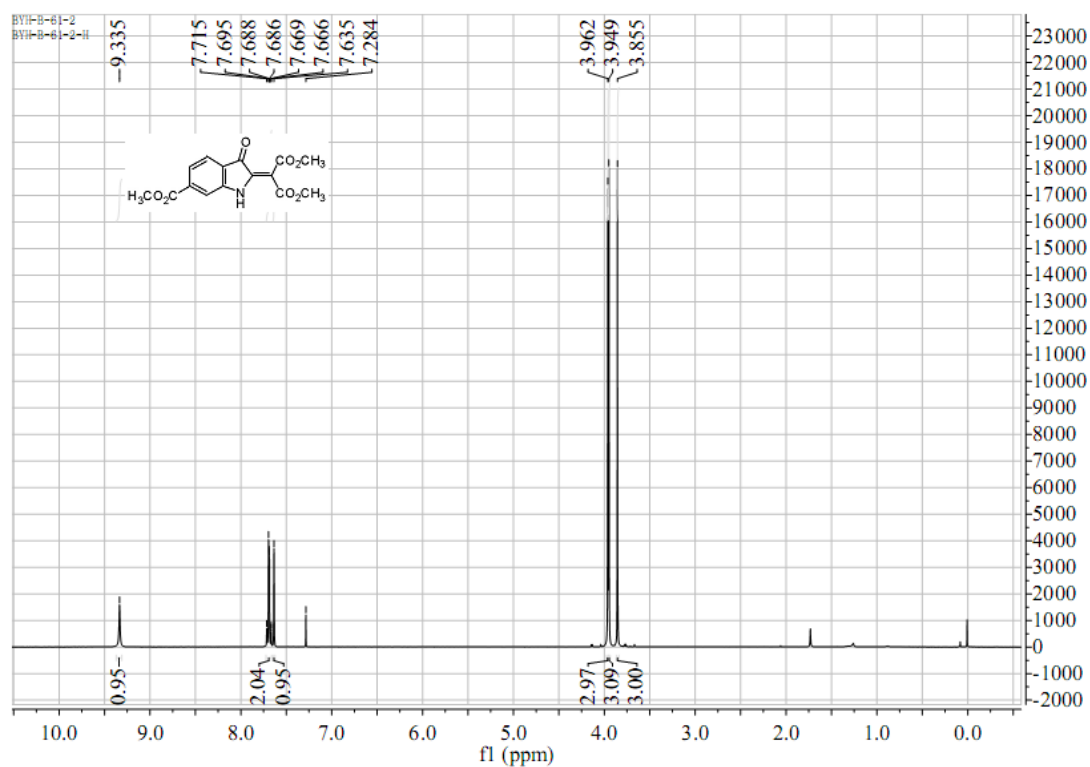
### Compound 6h



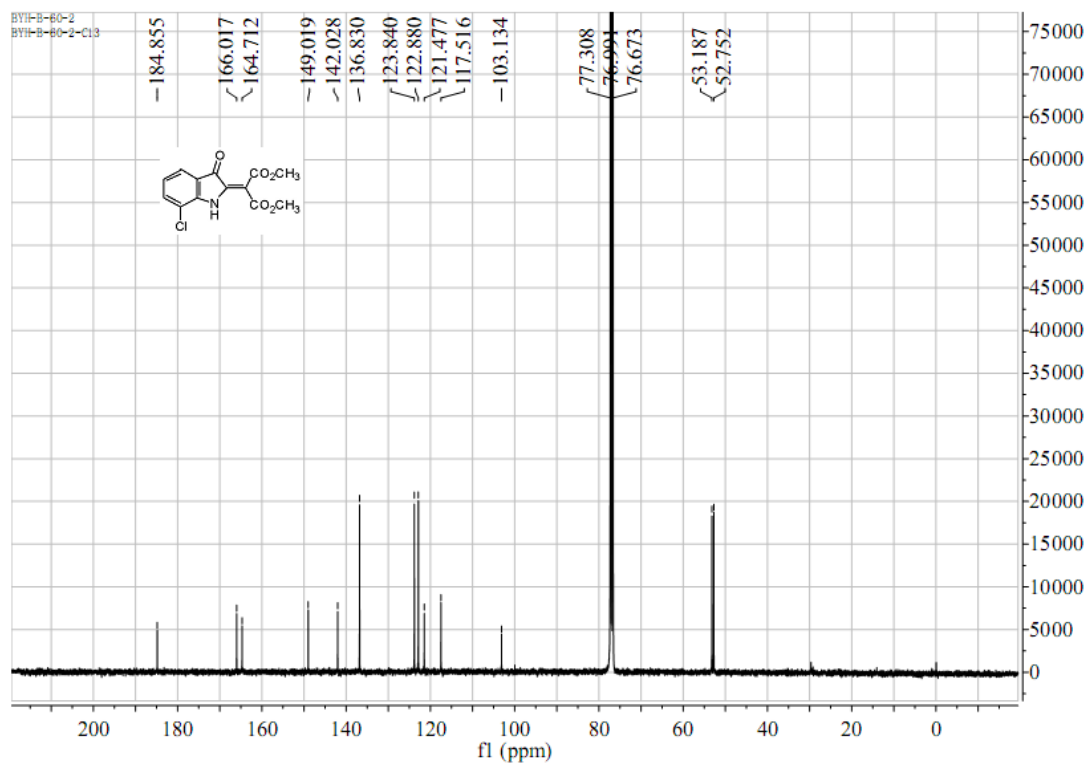
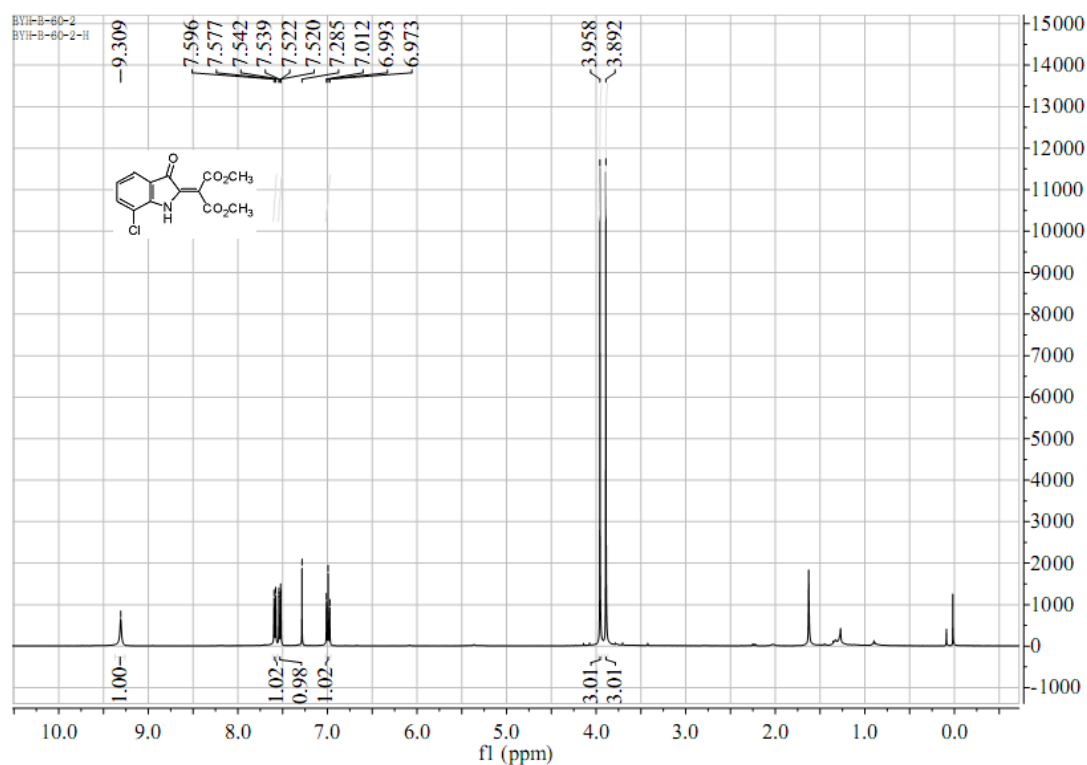
Compound **6i**



Compound 6j

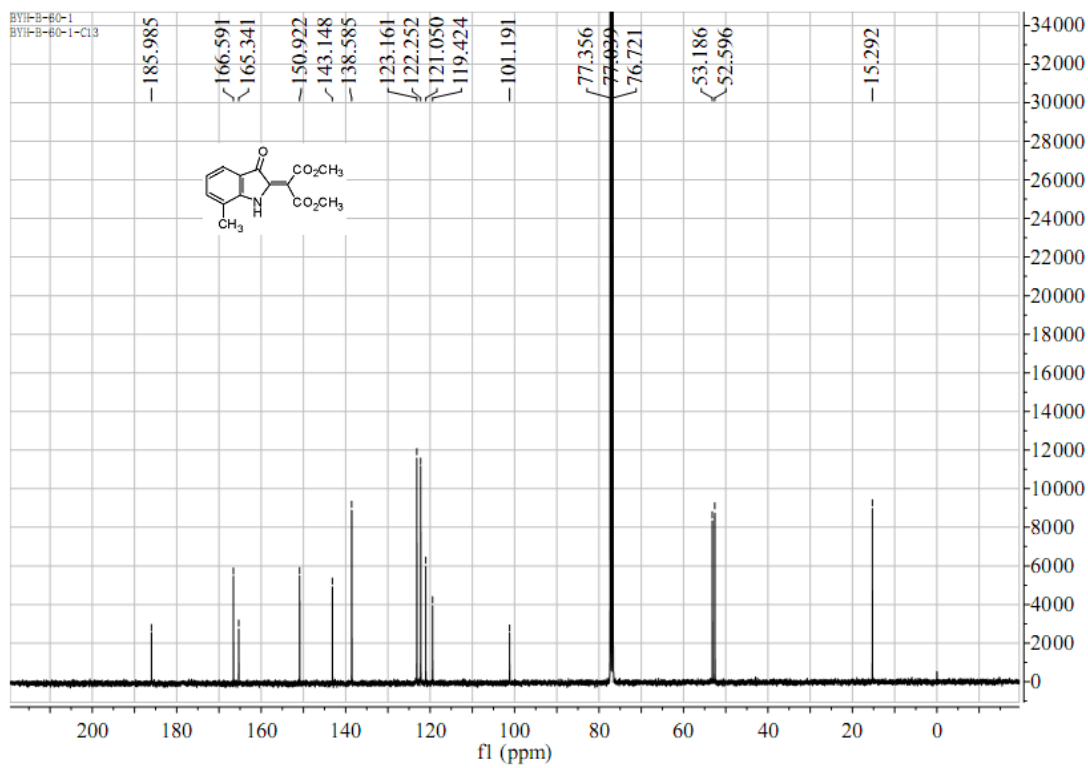
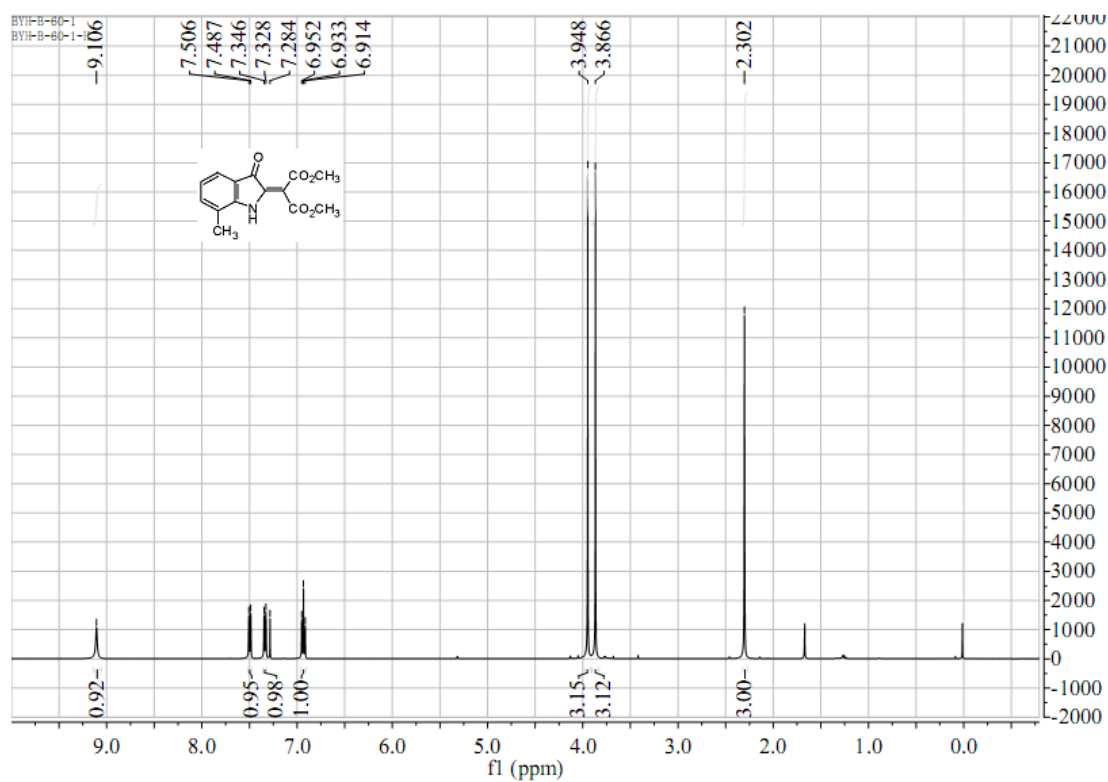


Compound **6k**

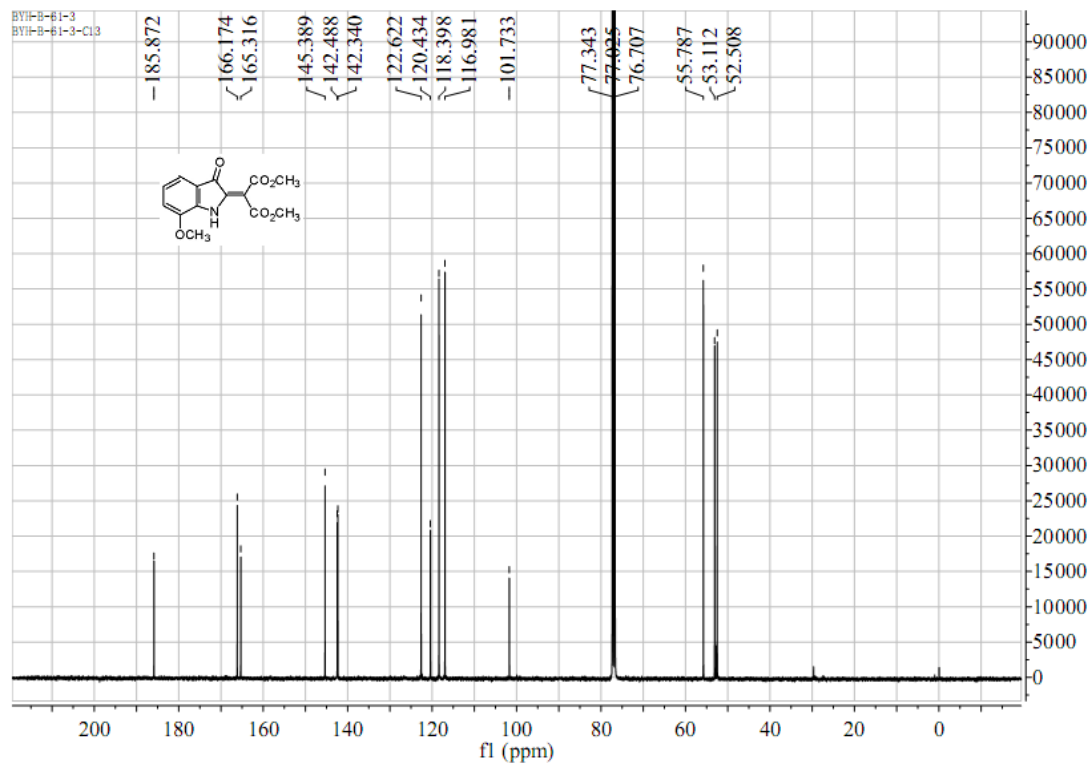
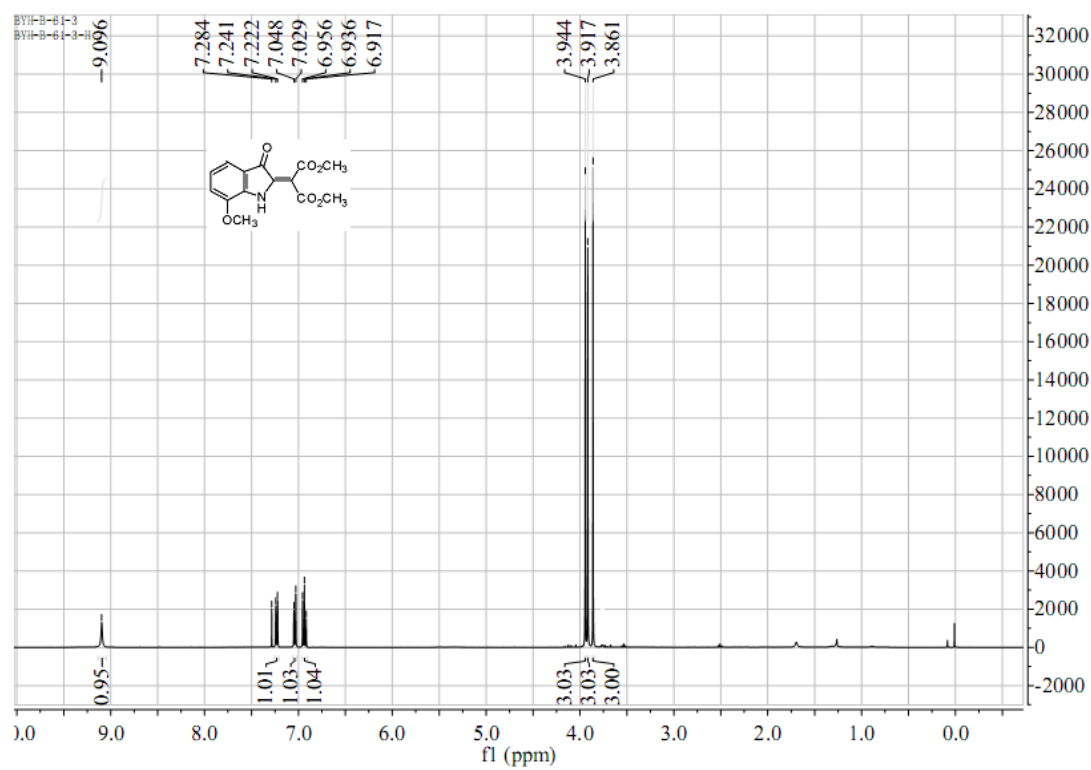




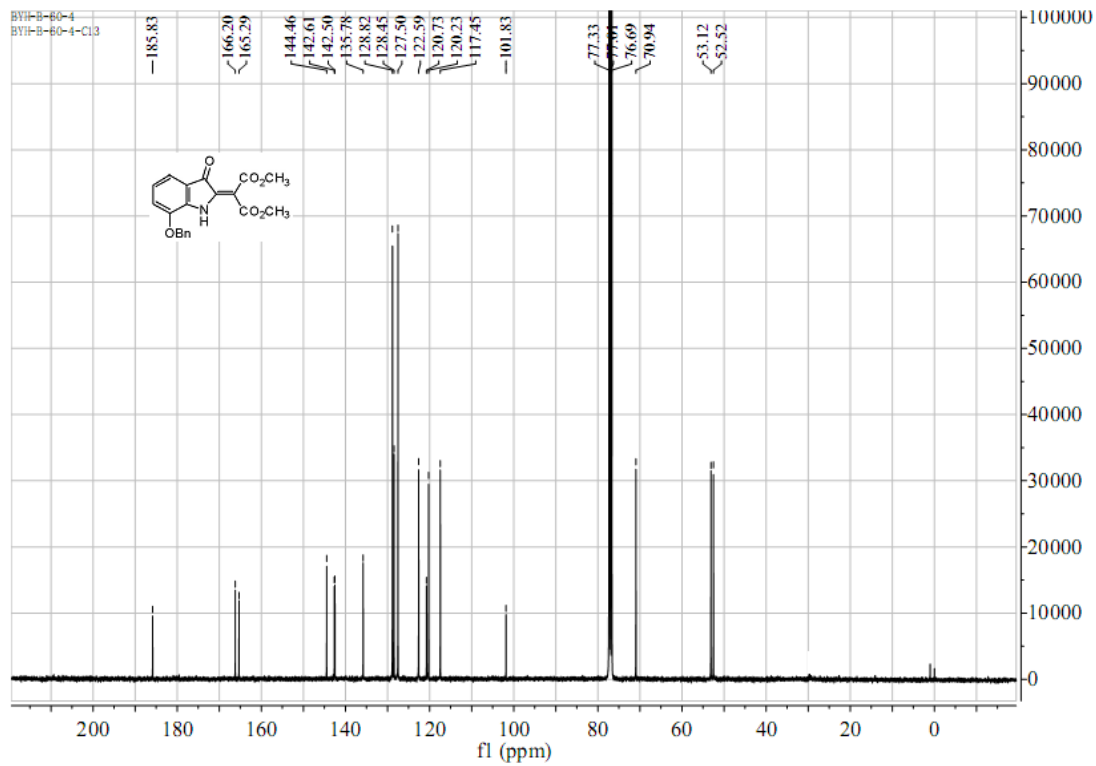
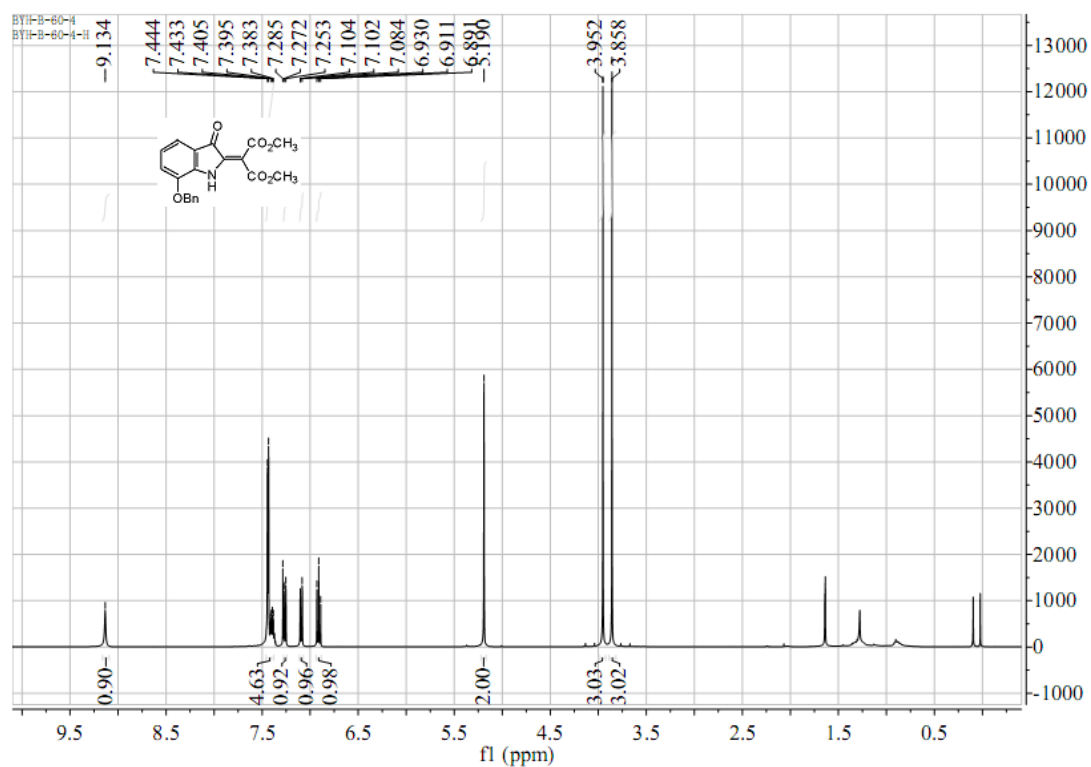
Compound **6l**



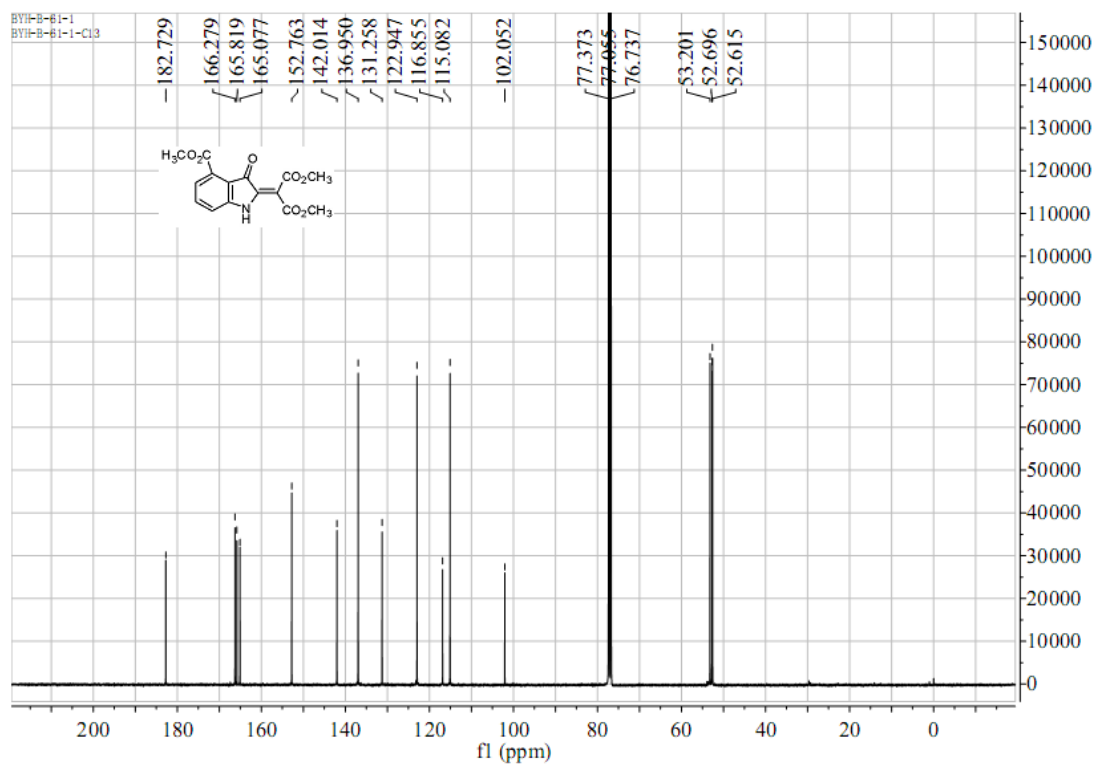
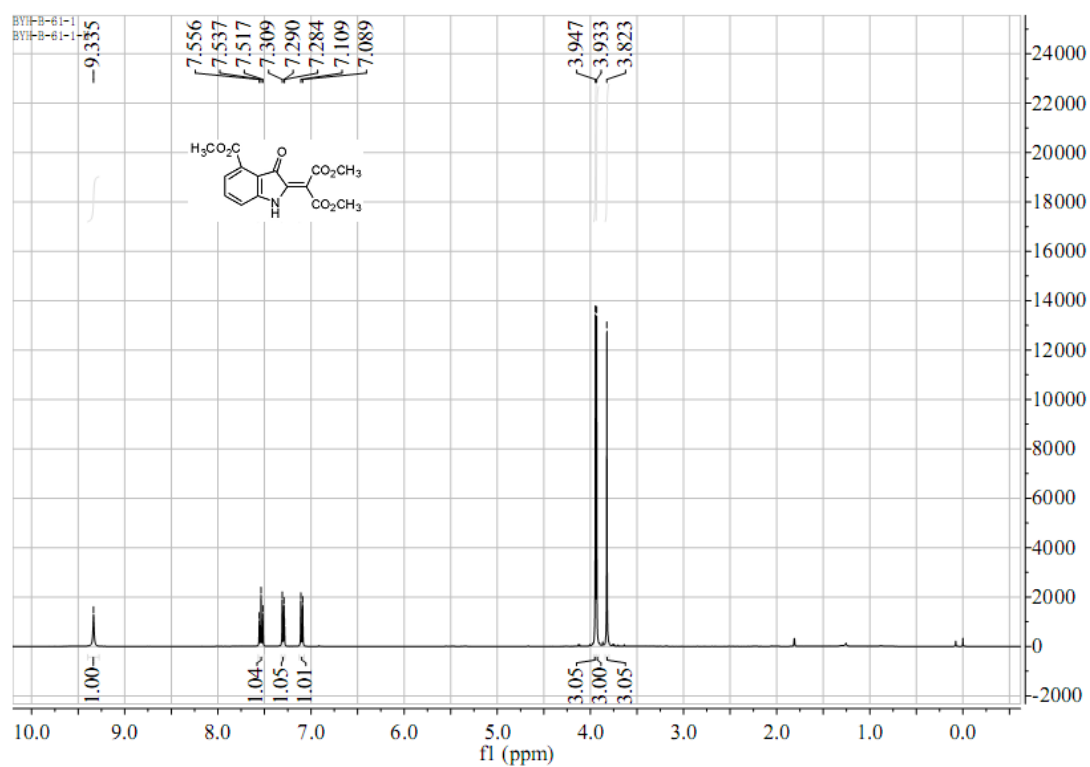
Compound **6m**



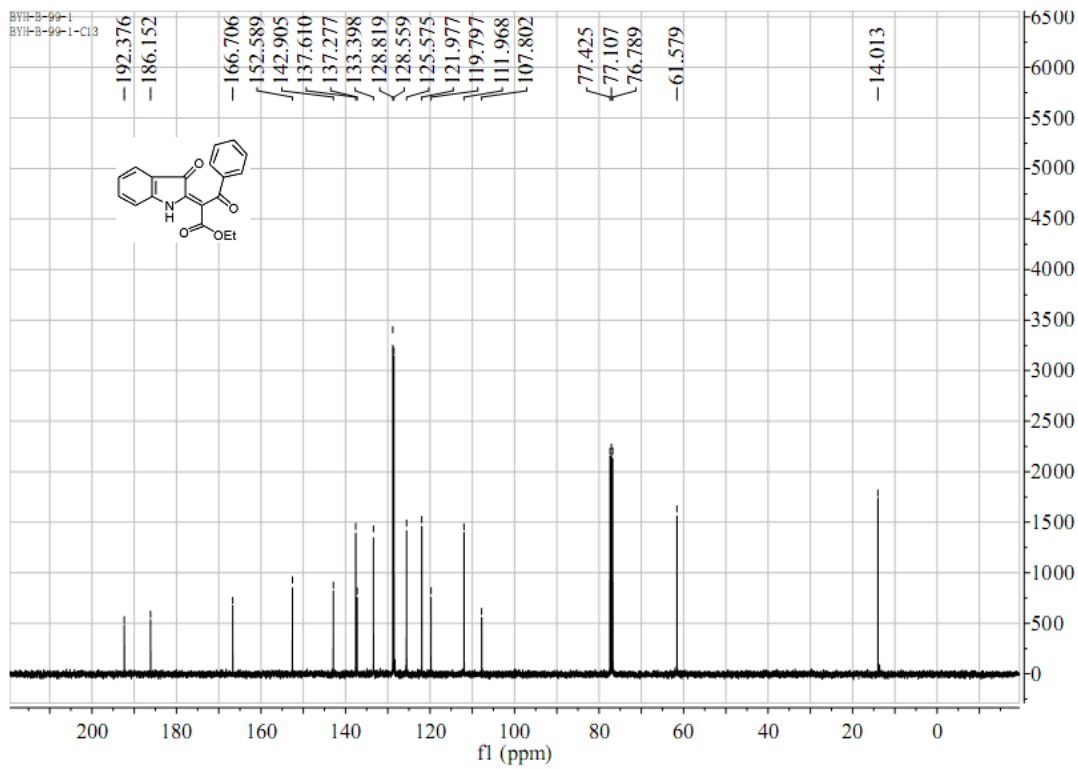
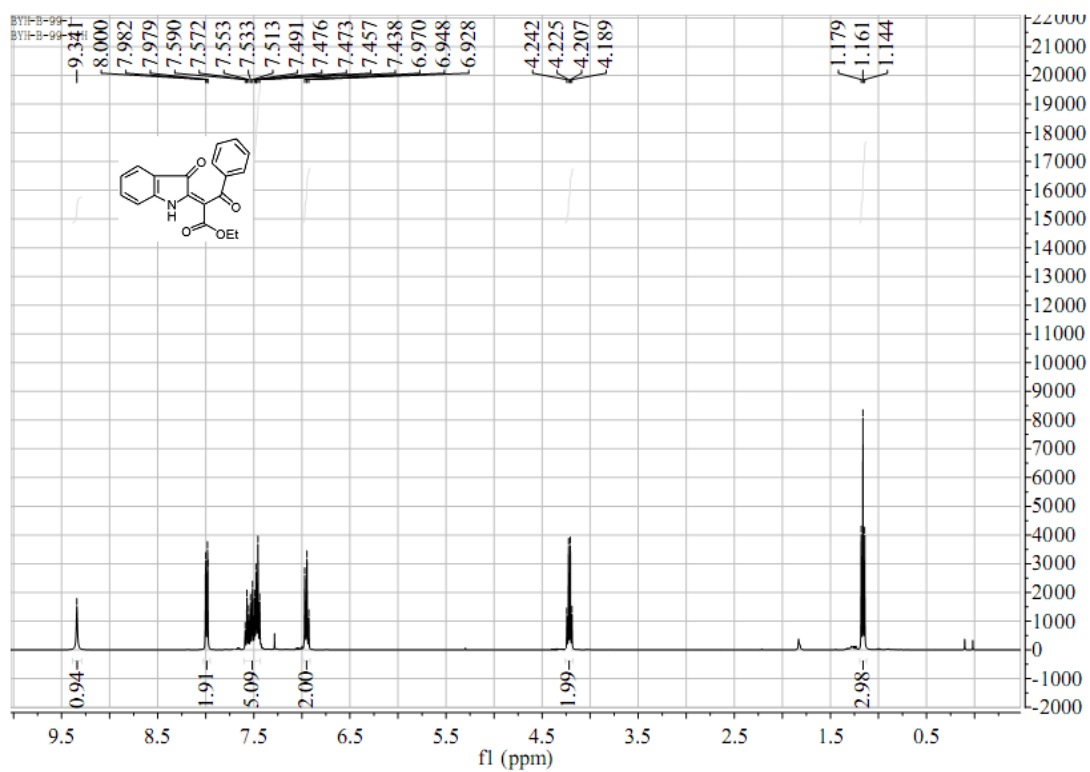
Compound **6n**



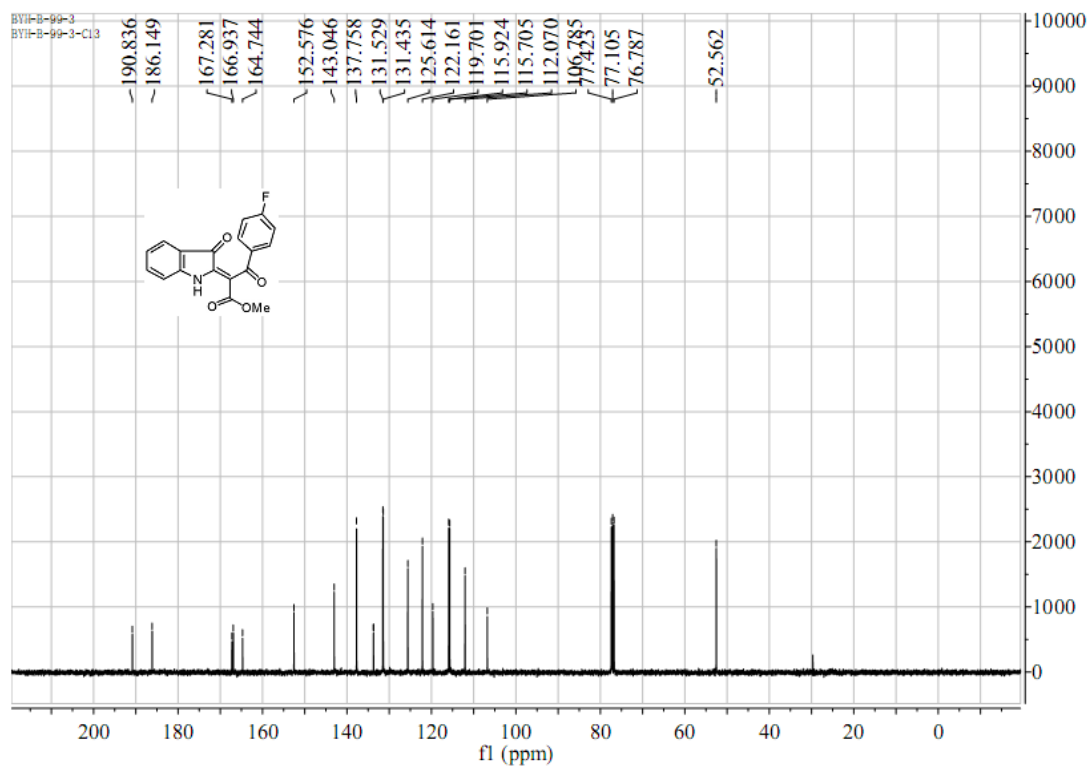
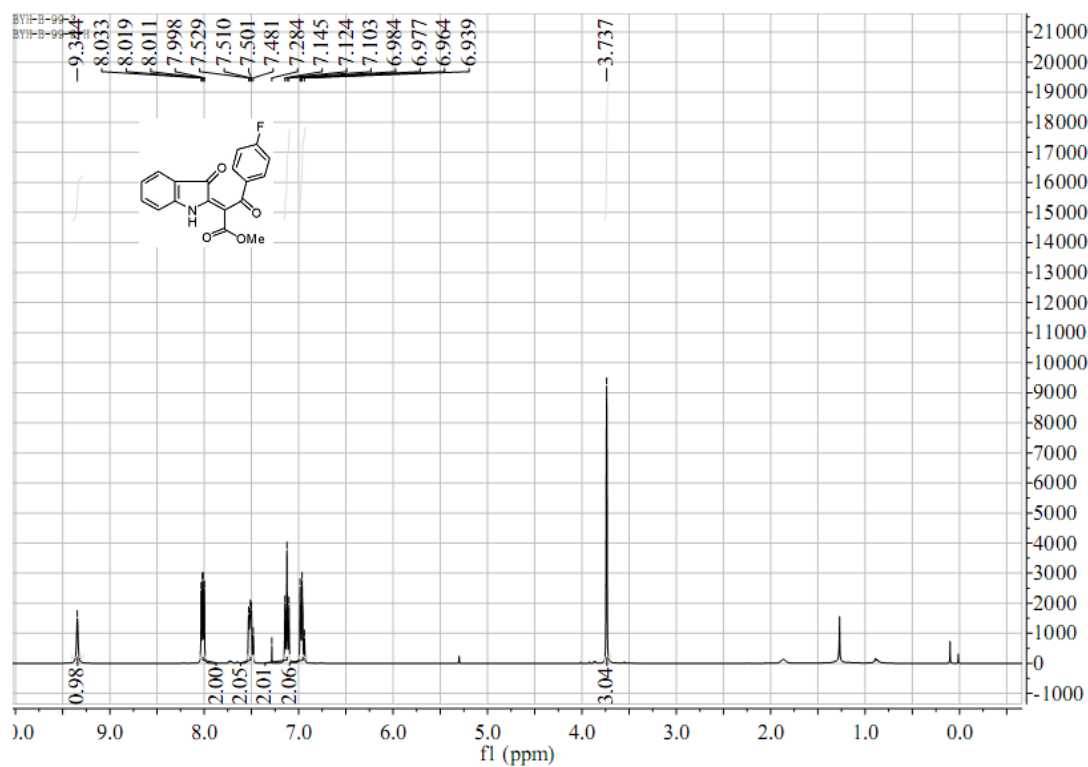
Compound 60



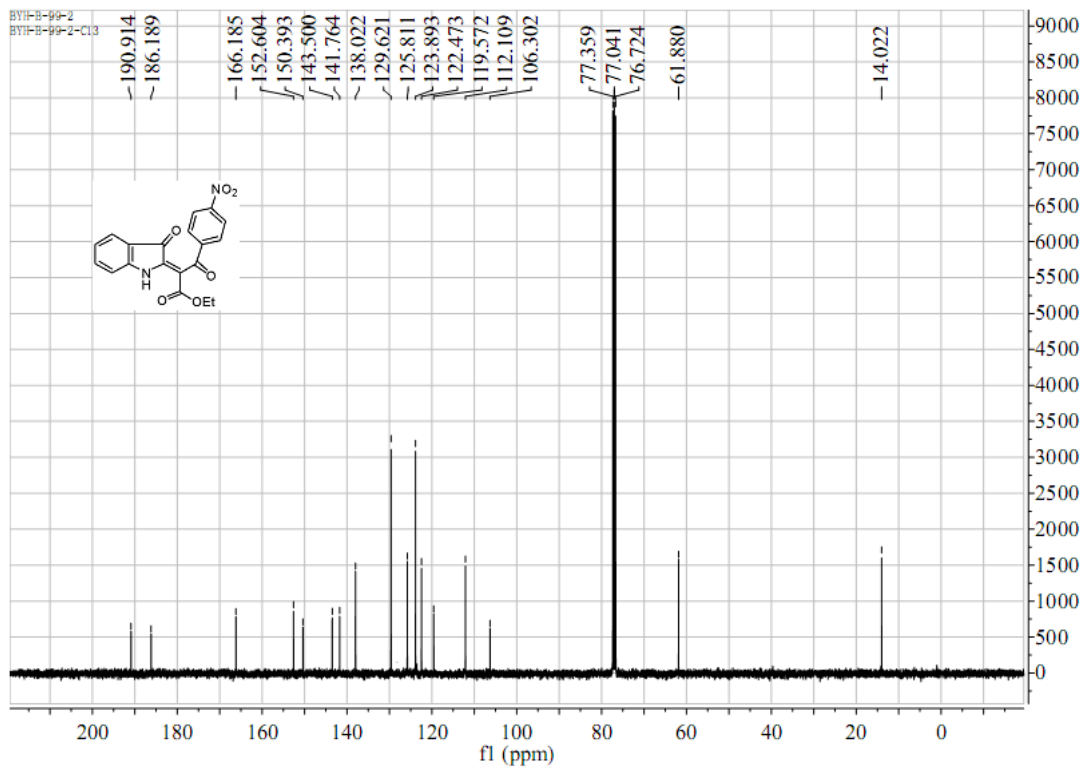
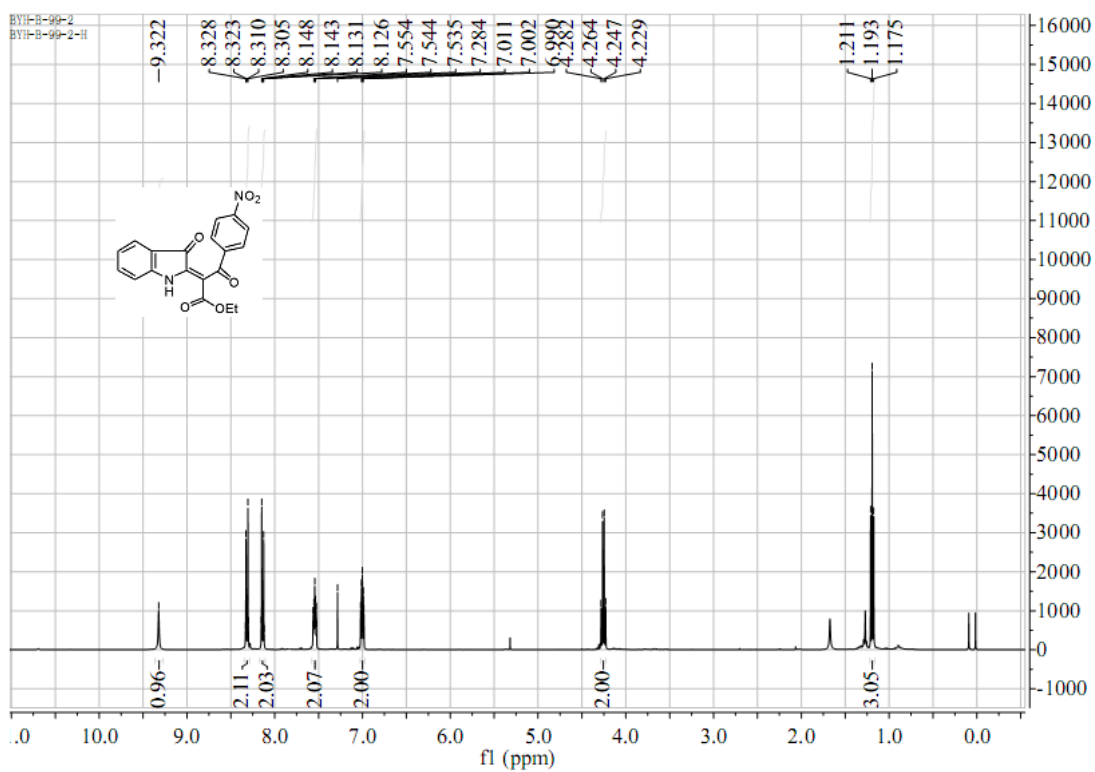
Compound 7a



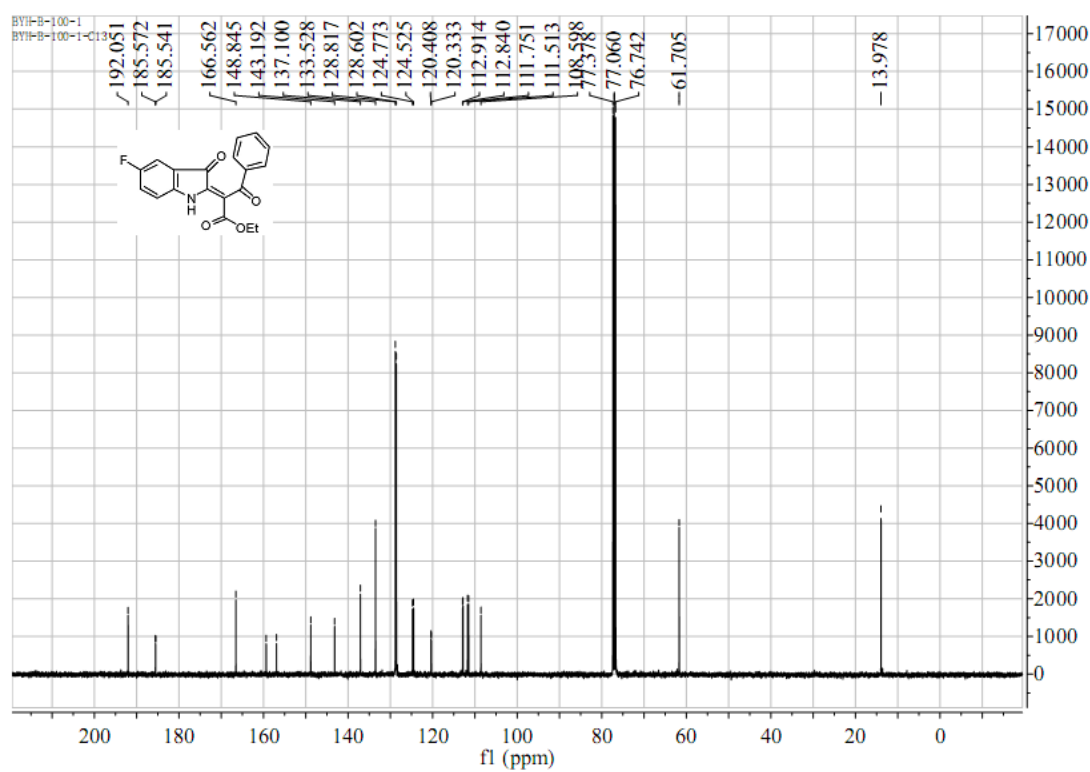
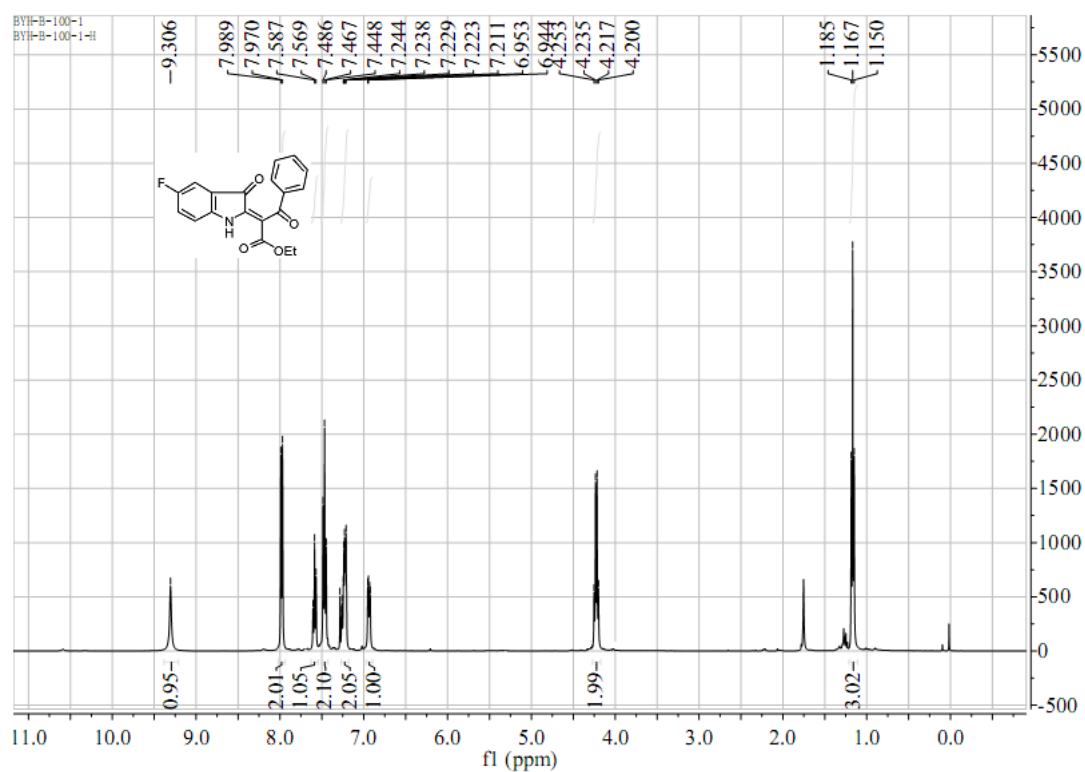
### Compound 7b



### Compound 7c

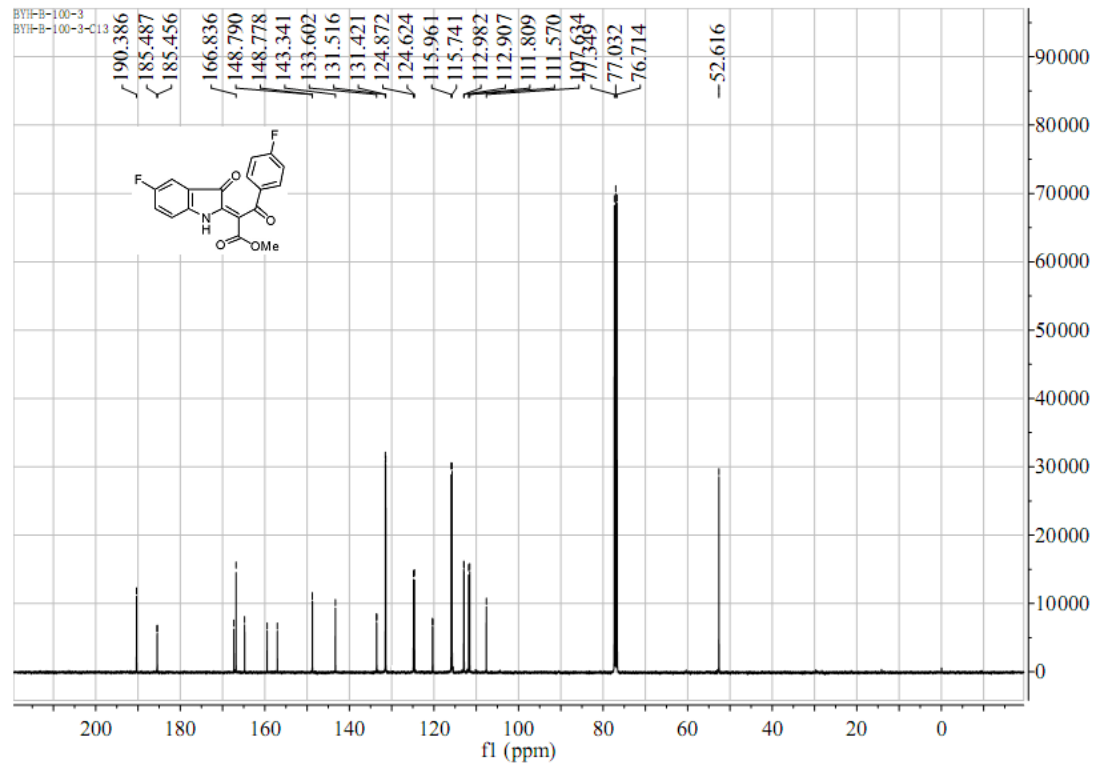
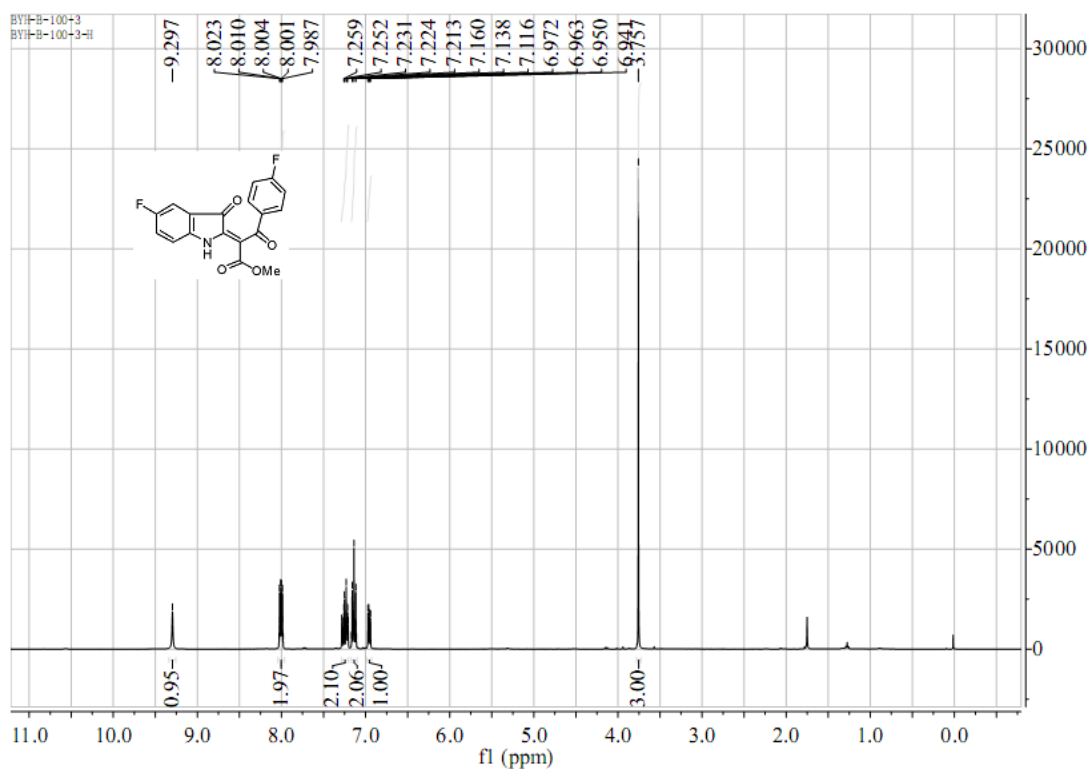


### Compound 7d

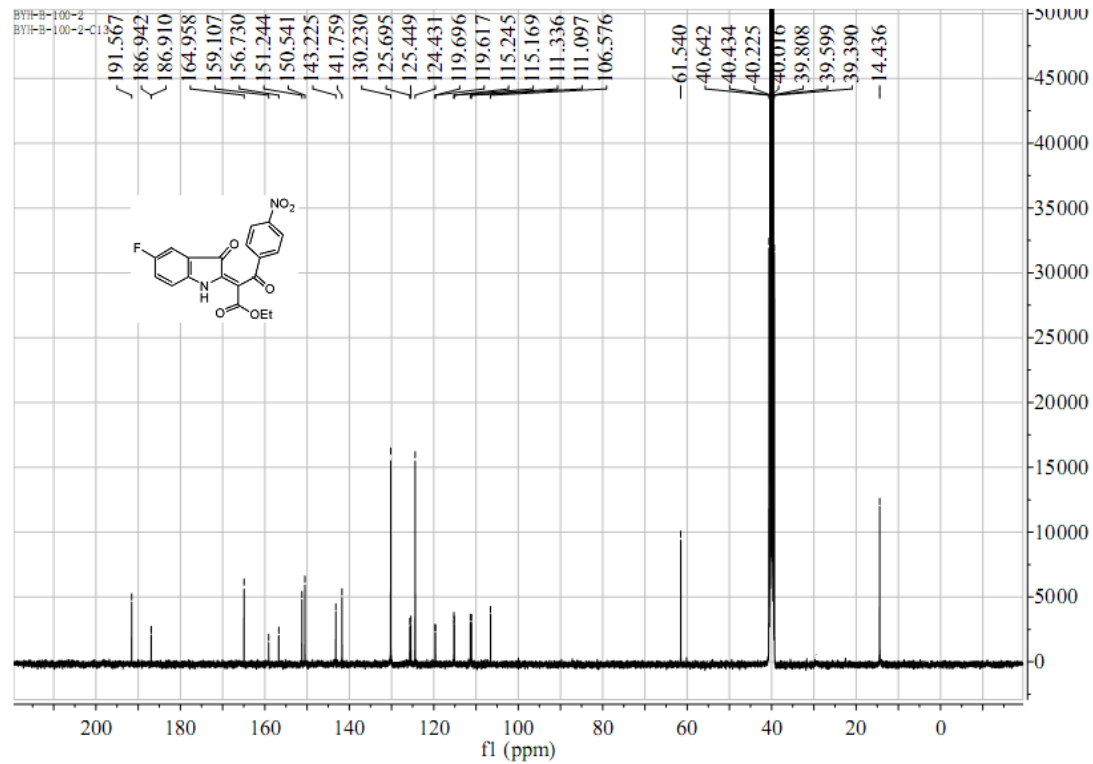
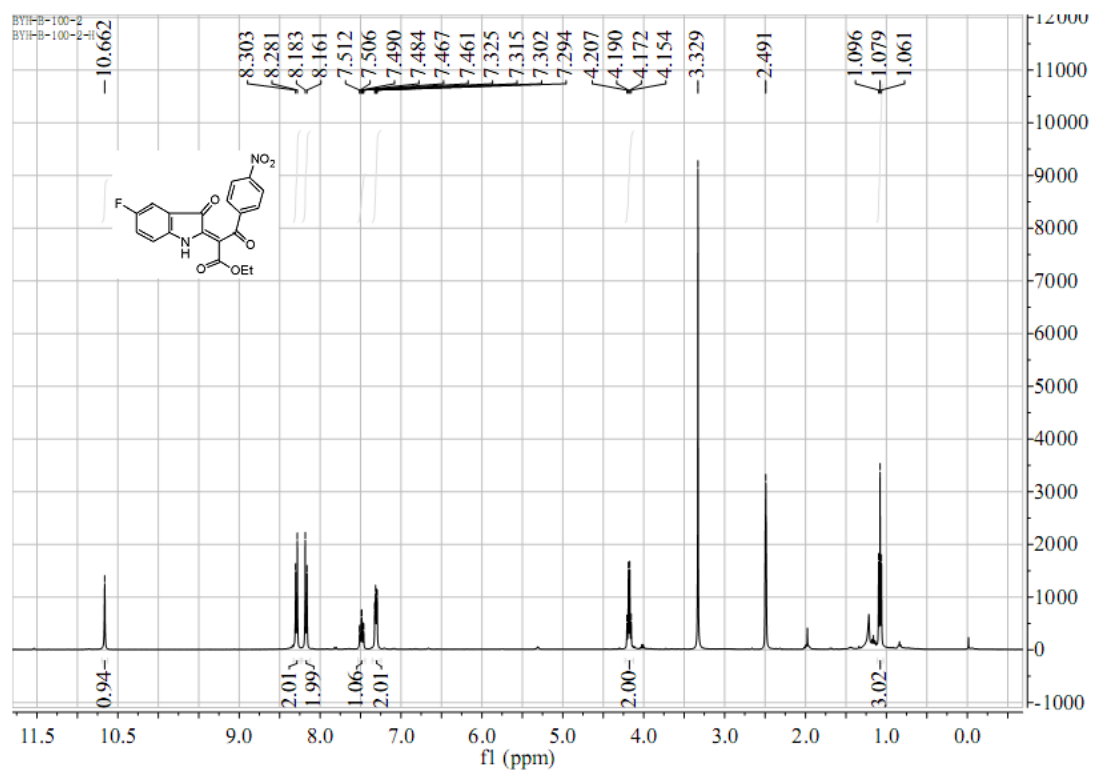




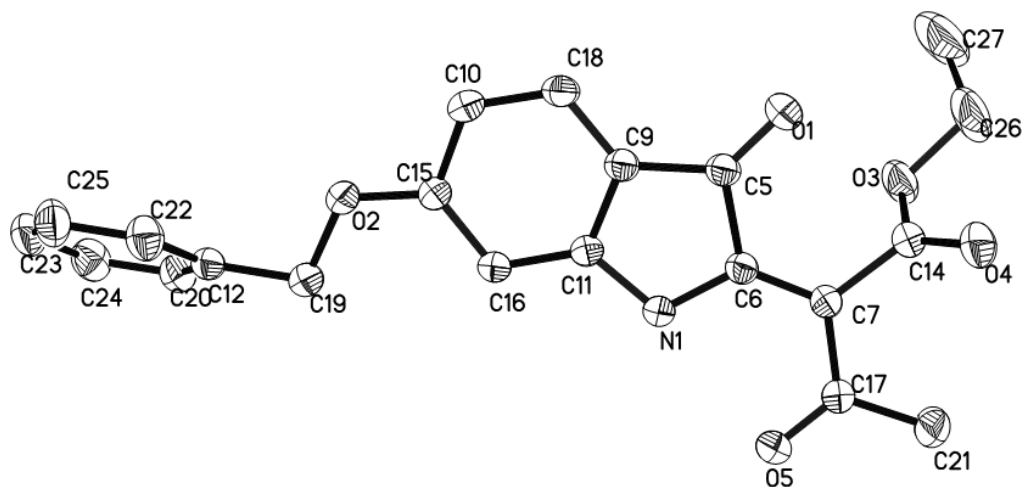
### Compound 7e



Compound **7f**



#### 4. X-ray Data of Compound 5j



**Figure 1.** ORTEP representation of the molecular structure of **5j** with H atoms omitted for clarity.

#### 5. Reference

1. W.-L. Wu, J. Xu, S.-J. Huang and W.-P. Su. *Chem. Commun.* **2011**, 47, 9660-9662.