

# Supplementary Materials: Rh(III)-Catalyzed, Highly Selectively Direct C–H Alkylation of Indoles with Diazo Compounds

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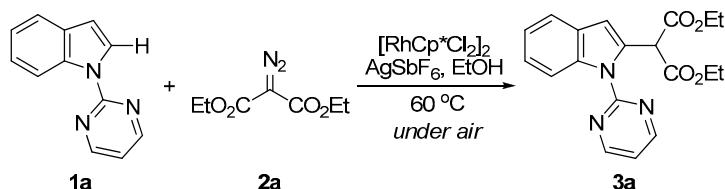
## General

Unless otherwise noted, all reactions were carried out under ambient atmosphere using standard Schlenk techniques. All chemicals were purchased from commercial suppliers and used without further purification. All the solvents were treated prior to use according to the standard methods. Flash column chromatography was performed using 200–300 mesh silica gel.

$^1\text{H}$  NMR spectra were recorded on 400 MHz spectrophotometers. Chemical shifts ( $\delta$ ) are reported in ppm from the solvent resonance as the internal standard ( $\text{CDCl}_3$ : 7.26 ppm). Data are reported as follows: Chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR spectra were recorded on 100 MHz spectrophotometers with complete proton decoupling spectrophotometers ( $\text{CDCl}_3$ : 77.0 ppm). High resolution mass spectral analysis (HRMS) was performed on Bruker micrOTOF-QII. Melting point was measured with Melting Point apparatus WPS-2. IR spectra were measured on a BRUKER TENSOR 27 FT-IR spectrometer.

*N*-pyrimidyl indole derivatives [1–3] were prepared according to the literature.

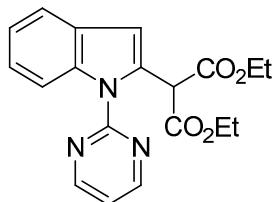
## Representative Procedure for the C–H Alkylation Reaction



A mixture of *N*-pyrimidyl indole **1a** (0.20 mmol, 1.0 equiv.), diazo compounds **2a** (0.24 mmol, 1.2 equiv),  $[\text{Cp}^*\text{RhCl}_2]_2$  (2.5 mg, 2 mol %), and  $\text{AgSbF}_6$  (6.8 mg, 10 mol %) were combined in  $\text{EtOH}$  (2.0 mL) in a dried 10 mL Schlenk tube. The mixture was stirred at  $50^\circ\text{C}$  for 6–18 h and monitored by TLC. After the reaction was finished, the volatiles were removed under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/ethyl acetate) to afford the desired product **3a** in 92% yield.

## Spectral Data of Compounds

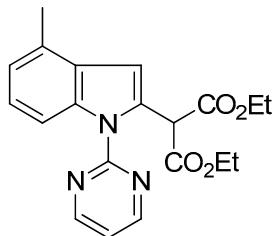
### diethyl 2-(1-(pyrimidin-2-yl)-1*H*-indol-2-yl)malonate [4]



Yield: 92%, white solid, m.p.  $72^\circ\text{C}$ – $73^\circ\text{C}$

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (d,  $J = 4.7$  Hz, 2H), 8.56 (d,  $J = 8.4$  Hz, 1H), 7.58 (d,  $J = 7.7$  Hz, 1H), 7.30 (d,  $J = 8.0$  Hz, 1H), 7.23 (d,  $J = 7.5$  Hz, 1H), 7.06 (d,  $J = 2.9$  Hz, 1H), 6.71 (s, 1H), 5.59 (s, 1H), 4.25 (q,  $J = 7.1$  Hz, 4H), 1.24 (t,  $J = 7.1$  Hz, 6H).

### diethyl 2-(4-methyl-1-(pyrimidin-2-yl)-1*H*-indol-2-yl)malonate



Yield: 93%, white solid, m.p. 105 °C–106 °C

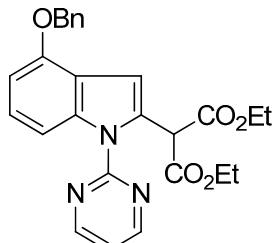
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 8.5 Hz, 1H), 7.24–7.18 (m, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 7.03 (d, *J* = 7.2 Hz, 1H), 6.74 (s, 1H), 5.58 (s, 1H), 4.26 (d, *J* = 7.1 Hz, 4H), 2.54 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.84, 158.01, 157.74, 136.65, 131.39, 129.94, 128.48, 123.99, 122.74, 116.73, 112.91, 107.71, 61.79, 54.37, 18.57, 14.09.

IR  $\nu$ : 2988, 1734, 1722, 1569, 1424, 1339, 1290, 1273, 1179, 1146, 901, 862, 799, 773 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 390.1424, found 390.1434.

**diethyl 2-(4-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 92%, white solid, m.p. 131 °C–132 °C

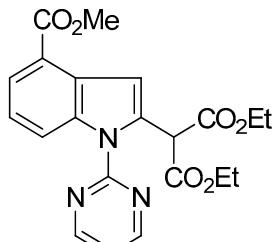
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.49 (d, *J* = 7.3 Hz, 2H), 7.39 (t, *J* = 7.4 Hz, 2H), 7.33 (d, *J* = 7.2 Hz, 1H), 7.20 (t, *J* = 8.2 Hz, 1H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.89 (s, 1H), 6.72 (d, *J* = 7.9 Hz, 1H), 5.54 (s, 1H), 5.21 (s, 2H), 4.24 (d, *J* = 7.1 Hz, 4H), 1.23 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.77, 158.05, 157.74, 151.96, 138.21, 137.37, 130.56, 128.52, 127.80, 127.36, 124.65, 116.83, 108.79, 106.53, 104.04, 70.05, 61.77, 54.37, 14.07.

IR  $\nu$ : 2949, 1730, 1642, 1563, 1496, 1231, 1152, 1106, 985, 910, 856, 803, 747 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>Na [M + Na<sup>+</sup>] 482.1686, found 482.1683.

**diethyl 2-(4-(methoxycarbonyl)-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 91%, white solid, m.p. 110 °C–111 °C

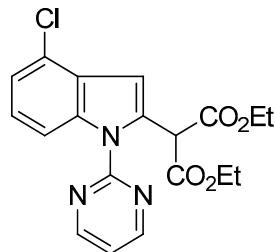
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.38 (d, *J* = 8.5 Hz, 1H), 7.20 (d, *J* = 8.0 Hz, 1H), 7.05 (dd, *J* = 18.4, 6.0 Hz, 2H), 6.74 (s, 1H), 5.58 (s, 1H), 4.25 (s, 4H), 2.54 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.83, 158.02, 157.73, 136.65, 131.39, 129.93, 128.48, 123.99, 122.74, 116.72, 112.91, 107.71, 61.78, 54.37, 18.56, 14.08.

IR  $\nu$ : 2998, 1746, 1701, 1572, 1429, 1354, 1276, 1182, 1139, 1023, 964, 816, 759, 632  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{21}\text{H}_{22}\text{N}_3\text{O}_6$  [ $\text{M} + \text{H}^+$ ] 412.1503, found 412.1507.

**diethyl 2-(4-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 87%, white solid, m.p. 107 °C–108 °C

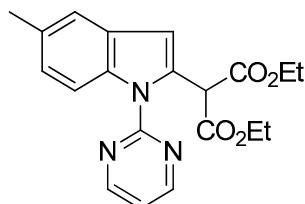
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (d,  $J = 8.4$  Hz, 1H), 8.71 (d,  $J = 4.8$  Hz, 2H), 8.02–7.97 (m, 1H), 7.41 (s, 1H), 7.35 (s, 1H), 7.14 (s, 1H), 5.57 (s, 1H), 4.27 (q,  $J = 7.1$  Hz, 4H), 1.26 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.51, 167.41, 157.85, 137.49, 134.14, 128.60, 125.43, 123.18, 121.54, 120.03, 117.24, 109.99, 61.87, 54.47, 51.83, 14.08.

IR  $\nu$ : 2982, 1731, 1570, 1420, 1339, 1290, 1273, 1238, 1149, 1027, 866, 756  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{ClN}_3\text{O}_4\text{Na}$  [ $\text{M} + \text{Na}^+$ ] 410.0878, found 410.0878.

**diethyl 2-(5-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 86%, white solid, m.p. 95 °C–95 °C

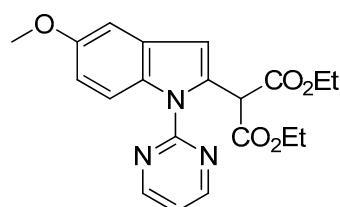
$^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 4.8$  Hz, 2H), 8.45 (d,  $J = 8.6$  Hz, 1H), 7.36 (s, 1H), 7.12 (dd,  $J = 8.6, 1.5$  Hz, 1H), 7.05 (t,  $J = 4.8$  Hz, 1H), 6.62 (s, 1H), 5.58 (s, 1H), 4.24 (q,  $J = 6.9$  Hz, 4H), 2.44 (s, 3H), 1.24 (s, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.81, 158.02, 157.67, 135.12, 132.09, 131.74, 129.08, 125.34, 120.43, 116.48, 115.25, 109.11, 61.74, 54.52, 21.31, 14.09.

IR  $\nu$ : 2969, 1718, 1643, 1570, 1567, 1426, 1375, 1248, 1064, 969, 794  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{21}\text{N}_3\text{O}_4\text{Na}$  [ $\text{M} + \text{Na}^+$ ] 390.1424, found 390.1428.

**diethyl 2-(5-methoxy-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 90%, white solid, m.p. 136 °C–136 °C

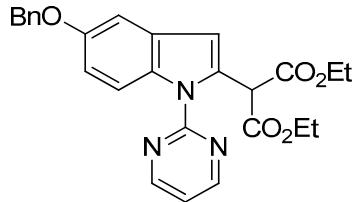
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 4.8$  Hz, 2H), 8.50 (d,  $J = 9.1$  Hz, 1H), 7.08–7.02 (m, 2H), 6.93 (dd,  $J = 9.1, 2.6$  Hz, 1H), 6.63 (s, 1H), 5.59 (s, 1H), 4.25 (d,  $J = 7.1$  Hz, 4H), 3.86 (s, 3H), 1.25 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.77, 157.66, 155.64, 132.62, 131.72, 129.60, 116.59, 116.47, 113.06, 109.22, 102.71, 61.77, 55.70, 54.57, 14.09.

IR  $\nu$ : 2975, 1737, 1612, 1569, 1424, 1339, 1301, 1253, 1141, 1021, 946, 854, 733  $\text{cm}^{-1}$ .

HRMS *m/z*: calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>5</sub>Na [M + Na<sup>+</sup>] 406.1373, found 406.1382.

**diethyl 2-(5-(benzyloxy)-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 94%, white solid, m.p. 106 °C–107 °C

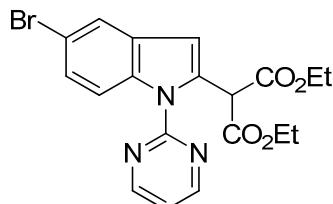
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.65 (d, *J* = 4.8 Hz, 2H), 8.51 (d, *J* = 9.1 Hz, 1H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.38 (t, *J* = 7.3 Hz, 2H), 7.32 (d, *J* = 7.1 Hz, 1H), 7.10 (s, 1H), 7.04 (dd, *J* = 8.7, 3.3 Hz, 2H), 6.61 (s, 1H), 5.59 (s, 1H), 5.12 (s, 2H), 4.25 (d, *J* = 7.1 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.76, 157.91, 157.66, 154.81, 137.47, 132.67, 131.91, 129.57, 128.55, 127.83, 127.51, 116.61, 116.49, 113.84, 109.25, 104.26, 70.61, 61.78, 54.57, 14.10.

IR *v*: 2976, 1724, 1611, 1430, 1380, 1348, 1220, 1174, 1027, 953, 837, 738 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>26</sub>H<sub>25</sub>N<sub>3</sub>O<sub>5</sub>Na [M + Na<sup>+</sup>] 482.1686, found 482.1676.

**diethyl 2-(5-bromo-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 93%, white solid, m.p. 104 °C–105 °C

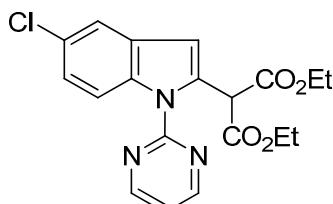
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.46 (d, *J* = 9.0 Hz, 1H), 7.70 (d, *J* = 1.9 Hz, 1H), 7.38 (dd, *J* = 9.0, 2.0 Hz, 1H), 7.12 (t, *J* = 4.8 Hz, 1H), 6.64 (s, 1H), 5.59 (s, 1H), 4.25 (d, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.48, 157.82, 135.52, 133.38, 130.51, 126.67, 123.10, 117.12, 117.07, 115.55, 108.47, 61.91, 54.34, 14.08.

IR *v*: 2924, 1722, 1640, 1569, 1550, 1425, 1311, 1247, 1172, 1083, 965, 807, 798 cm<sup>-1</sup>.

HRMS *m/z*: Calcd for C<sub>19</sub>H<sub>18</sub>BrN<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 454.0373, found 454.0396.

**diethyl 2-(5-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 92%, white solid, m.p. 112 °C–113 °C

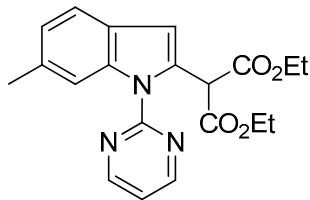
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 4.7 Hz, 2H), 8.51 (d, *J* = 8.9 Hz, 1H), 7.54 (d, *J* = 2.1 Hz, 1H), 7.24 (d, *J* = 2.2 Hz, 1H), 7.11 (s, 1H), 6.64 (s, 1H), 5.58 (s, 1H), 4.24 (dd, *J* = 7.1, 6.7 Hz, 4H), 1.24 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.50, 157.81, 135.19, 133.51, 129.94, 127.85, 124.02, 120.01, 117.05, 116.73, 108.59, 61.91, 54.38, 14.08.

IR *v*: 2988, 1720, 1570, 1425, 1378, 1308, 1247, 1173, 1112, 1037, 918, 797 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>19</sub>H<sub>19</sub>ClN<sub>3</sub>O<sub>4</sub> [M + H<sup>+</sup>] 388.1059, found 388.1038.

**diethyl 2-(6-methyl-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 90%, white solid, m.p. 119 °C–120 °C

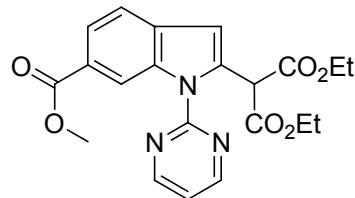
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.37 (s, 1H), 7.46 (d, *J* = 7.9 Hz, 1H), 7.11–7.04 (m, 2H), 6.65 (s, 1H), 5.55 (s, 1H), 4.24 (d, *J* = 7.1 Hz, 4H), 2.50 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.82, 158.01, 157.73, 137.18, 133.83, 131.41, 126.61, 123.90, 120.22, 116.61, 115.30, 109.20, 61.75, 54.39, 22.15, 14.08.

IR  $\nu$ : 2924, 1882, 1566, 1420, 1339, 1295, 1247, 1145, 1096, 1029, 863, 732 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>20</sub>H<sub>21</sub>N<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 390.1424, found 390.1430.

#### diethyl 2-(6-(methoxycarbonyl)-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate



Yield: 90%, white solid, m.p. 118 °C–119 °C

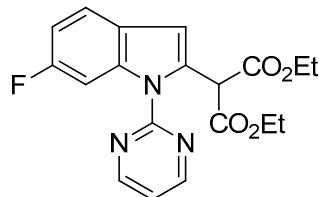
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.66 (d, *J* = 4.8 Hz, 2H), 8.50 (d, *J* = 9.1 Hz, 1H), 7.04 (d, *J* = 2.5 Hz, 2H), 6.93 (dd, *J* = 9.1, 2.6 Hz, 1H), 6.63 (s, 1H), 5.59 (s, 1H), 4.25 (d, *J* = 7.1 Hz, 4H), 3.86 (s, 3H), 1.25 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.76, 157.92, 157.65, 155.64, 132.63, 131.73, 129.60, 116.59, 116.46, 113.05, 109.22, 102.72, 61.76, 55.69, 54.57, 14.09.

IR  $\nu$ : 2969, 1757, 1717, 1574, 1422, 1352, 1269, 1174, 1044, 991, 918, 746 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>21</sub>H<sub>21</sub>N<sub>3</sub>O<sub>6</sub>Na [M + Na<sup>+</sup>] 434.1323, found 434.1319.

#### diethyl 2-(6-fluoro-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate



Yield: 89%, white solid, m.p. 98 °C–99 °C

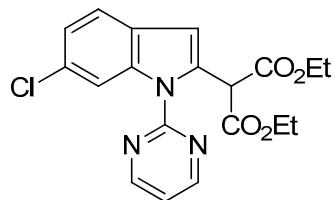
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.37 (dd, *J* = 11.3, 2.2 Hz, 1H), 7.49 (dd, *J* = 8.6, 5.6 Hz, 1H), 7.11 (t, *J* = 4.8 Hz, 1H), 7.00 (dd, *J* = 8.9, 2.3 Hz, 1H), 6.67 (s, 1H), 5.60 (s, 1H), 4.25 (d, *J* = 7.1 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 6H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.66, 157.83, 157.77, 136.83, 132.56, 132.52, 125.12, 121.17, 121.07, 116.95, 109.08, 103.05, 61.85, 54.45, 14.09.

IR  $\nu$ : 2997, 1730, 1571, 1475, 1421, 1348, 1294, 1246, 1154, 1021, 985, 805, 731 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>19</sub>H<sub>18</sub>FN<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 394.1174, found 394.1162.

#### diethyl 2-(6-chloro-1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate



Yield: 89%, white solid, m.p. 118 °C–119 °C

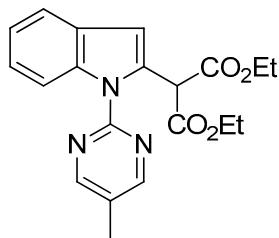
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (d,  $J = 4.8$  Hz, 2H), 8.64 (d,  $J = 1.4$  Hz, 1H), 7.48 (d,  $J = 8.3$  Hz, 1H), 7.21 (dd,  $J = 8.3, 1.8$  Hz, 1H), 7.12 (s, 1H), 6.68 (s, 1H), 5.59 (s, 1H), 4.25 (d,  $J = 7.1$  Hz, 4H), 1.25 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.54, 157.83, 157.71, 137.08, 132.89, 129.79, 127.30, 122.95, 121.29, 117.09, 115.75, 109.03, 61.89, 54.38, 14.08.

IR  $\nu$ : 2995, 1732, 1570, 1417, 1337, 1293, 1240, 1152, 1020, 860, 803, 736  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{ClN}_3\text{O}_4\text{Na}$  [M + Na $^+$ ] 410.0878, found 410.0876.

#### diethyl 2-(1-(5-methylpyrimidin-2-yl)-1H-indol-2-yl)malonate



Yield: 87%, white solid, m.p. 120 °C–121 °C

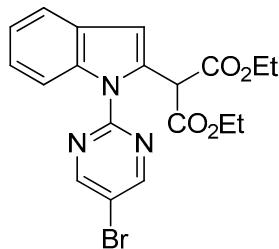
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.52 (s, 2H), 8.48 (d,  $J = 8.3$  Hz, 1H), 7.58 (d,  $J = 7.6$  Hz, 1H), 7.30–7.18 (m, 2H), 6.69 (s, 1H), 5.54 (s, 1H), 4.25 (d,  $J = 7.1$  Hz, 4H), 2.31 (s, 3H), 1.25 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.77, 157.76, 156.14, 136.75, 131.92, 128.68, 126.11, 123.71, 122.06, 120.60, 114.97, 108.60, 61.78, 54.16, 15.06, 14.10.

IR  $\nu$ : 3002, 1748, 1557, 1436, 1344, 1292, 1233, 1134, 1016, 853, 821, 746  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{20}\text{H}_{22}\text{N}_3\text{O}_4$  [M + H $^+$ ] 368.1605, found 368.1585.

#### diethyl 2-(1-(5-bromopyrimidin-2-yl)-1H-indol-2-yl)malonate



Yield: 88%, white solid, m.p. 114 °C–115 °C

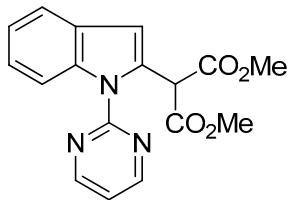
$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.70 (s, 2H), 8.49 (d,  $J = 8.3$  Hz, 1H), 7.58 (d,  $J = 7.6$  Hz, 1H), 7.35–7.28 (m, 1H), 7.25 (d,  $J = 6.9$  Hz, 1H), 6.72 (s, 1H), 5.51 (s, 1H), 4.25 (q,  $J = 7.1$  Hz, 4H), 1.26 (t,  $J = 7.1$  Hz, 6H).

$^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  167.56, 158.20, 156.16, 136.74, 131.96, 128.89, 124.18, 122.70, 120.77, 115.44, 114.11, 110.10, 61.90, 54.28, 14.11.

IR  $\nu$ : 2977, 1722, 1553, 1429, 1340, 1250, 1116, 1036, 968, 856, 790, 739  $\text{cm}^{-1}$ .

HRMS  $m/z$ : calcd for  $\text{C}_{19}\text{H}_{18}\text{BrN}_3\text{O}_4\text{Na}$  [M + Na $^+$ ] 454.0373, found 454.0363.

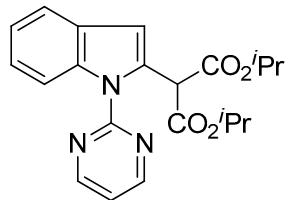
#### dimethyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate [5]



Yield: 90%, colorless oil.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.58 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.32 (s, 1H), 7.23 (s, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.69 (s, 1H), 5.59 (s, 1H), 3.77 (s, 6H).

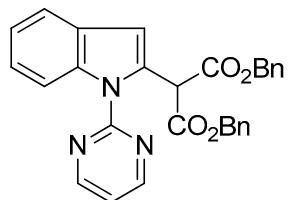
**diisopropyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate<sup>3</sup>**



Yield: 92%, white solid, m.p. 114 °C–115 °C

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.69 (d, *J* = 4.8 Hz, 2H), 8.55 (d, *J* = 8.3 Hz, 1H), 7.58 (d, *J* = 7.6 Hz, 1H), 7.31–7.21 (m, 2H), 7.08 (t, *J* = 4.8 Hz, 1H), 6.70 (s, 1H), 5.54 (s, 1H), 5.17–5.09 (m, 2H), 1.25 (dd, *J* = 6.0, 5.3 Hz, 12H).

**dibenzyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 91%, yellow oil.

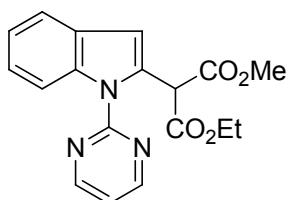
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 4.8 Hz, 2H), 7.51 (d, *J* = 7.7 Hz, 1H), 7.29 (s, 10H), 7.27 (d, *J* = 1.2 Hz, 1H), 7.23 (s, 1H), 7.22–7.18 (m, 1H), 6.87 (s, 1H), 6.57 (s, 1H), 5.62 (s, 1H), 5.26 (d, *J* = 12.2 Hz, 2H), 5.16 (d, *J* = 12.2 Hz, 2H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 167.43, 157.78, 157.50, 136.82, 135.37, 131.64, 128.80, 128.62, 128.53, 128.37, 123.99, 122.36, 120.64, 116.56, 115.60, 109.68, 67.44, 54.44.

IR *v*: 2964, 1737, 1568, 1425, 1341, 1225, 1140, 1004, 906, 807, 732 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>29</sub>H<sub>23</sub>N<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 500.1581, found 500.1552.

**1-ethyl 3-methyl 2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)malonate**



Yield: 88%, colorless oil.

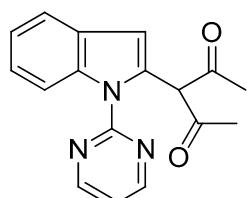
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (d, *J* = 4.8 Hz, 2H), 8.57 (d, *J* = 8.4 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.4 Hz, 1H), 7.23 (s, 1H), 7.09 (t, *J* = 4.8 Hz, 1H), 6.70 (s, 1H), 5.58 (s, 1H), 4.24 (q, *J* = 7.1 Hz, 2H), 3.77 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 168.29, 167.65, 157.76, 136.84, 131.94, 128.79, 124.00, 122.41, 120.66, 117.69, 116.77, 115.46, 109.44, 108.14, 61.89, 54.25, 52.84, 14.07.

IR  $\nu$ : 2984, 1736, 1567, 1423, 1296, 1241, 1147, 1026, 926, 857, 740 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>18</sub>H<sub>17</sub>N<sub>3</sub>O<sub>4</sub>Na [M + Na<sup>+</sup>] 362.1111, found 362.1102.

### 3-(1-(pyrimidin-2-yl)-1H-indol-2-yl)pentane-2,4-dione



Yield: 85%, white solid, m.p. 93 °C–95 °C

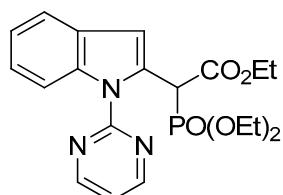
<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.72 (d, *J* = 4.8 Hz, 2H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.32 (s, 1H), 7.26 (d, *J* = 6.7 Hz, 1H), 7.13 (t, *J* = 4.8 Hz, 1H), 6.61 (s, 1H), 1.93 (s, 6H).

<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 191.99, 158.19, 157.59, 136.56, 134.89, 128.93, 123.69, 122.14, 120.55, 117.35, 114.06, 110.10, 107.59, 24.12.

IR  $\nu$ : 2924, 1721, 1645, 1620, 1562, 1419, 1342, 1294, 1213, 1154, 980, 857, 803, 746 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O<sub>2</sub>Na [M + Na<sup>+</sup>] 316.1056, found 316.1060.

### ethyl 2-(diethoxyphosphoryl)-2-(1-(pyrimidin-2-yl)-1H-indol-2-yl)acetate



Yield: 89%, yellow oil.

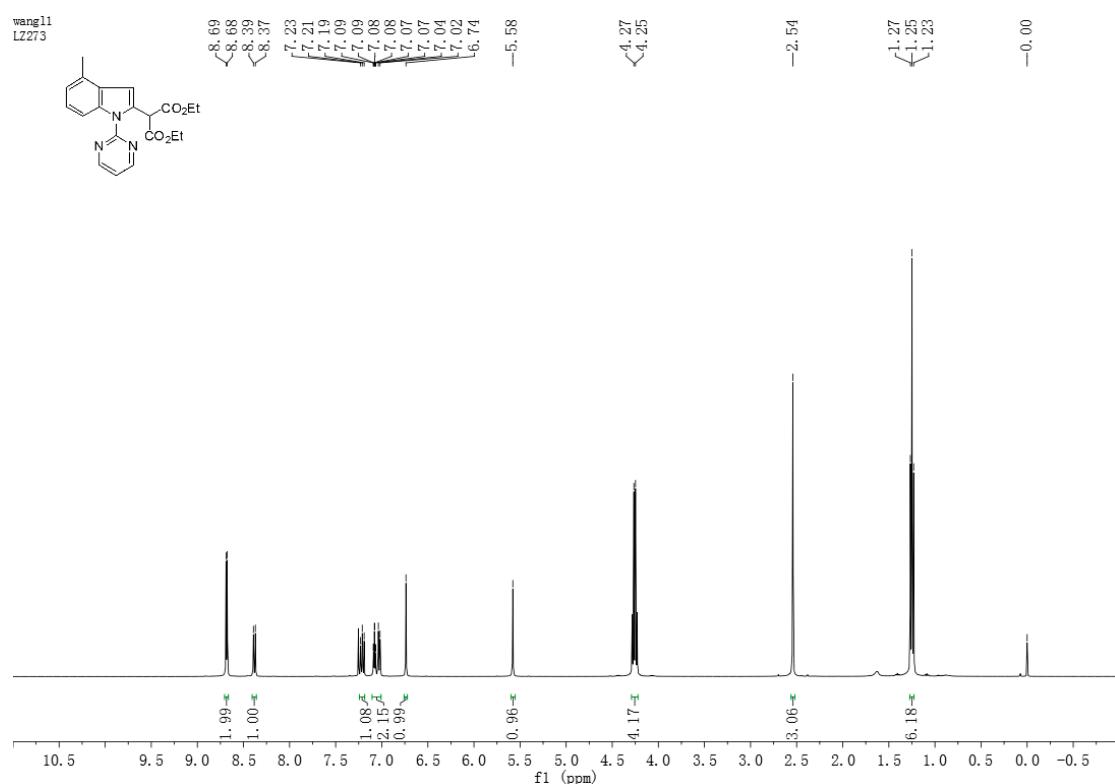
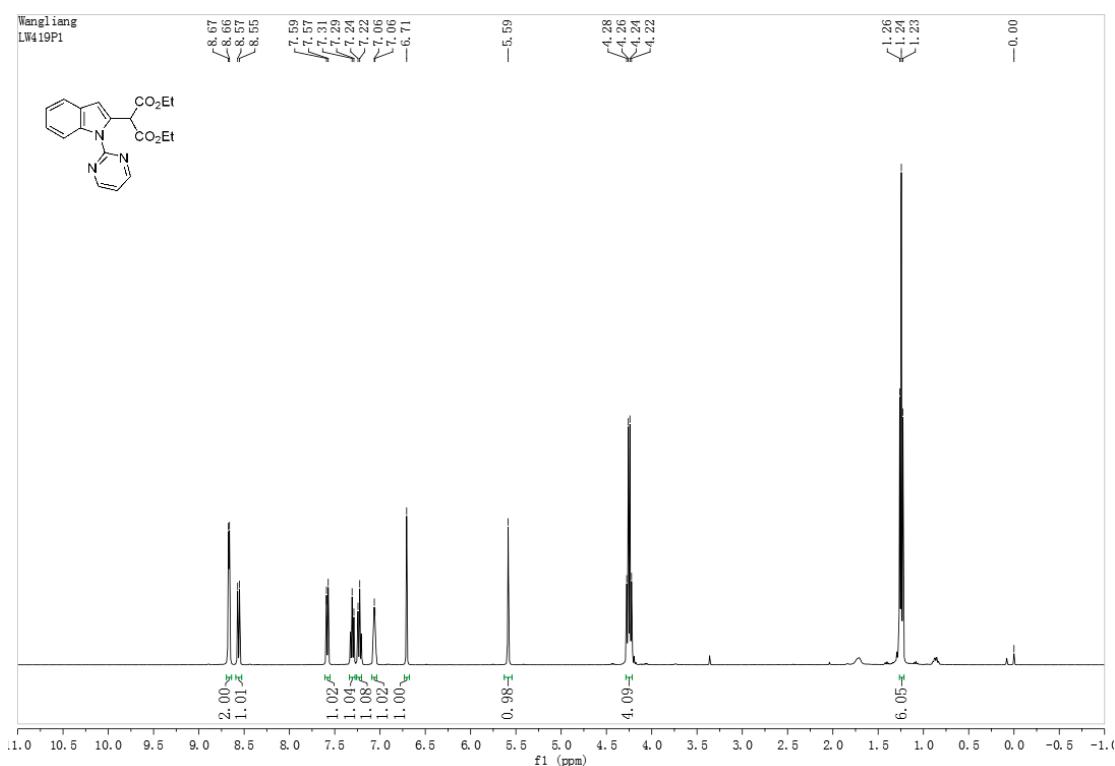
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.78 (d, *J* = 4.8 Hz, 2H), 8.31 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.27 (s, 1H), 7.24 – 7.19 (m, 2H), 7.15 (t, *J* = 4.8 Hz, 1H), 5.99 (d, *J* = 25.6 Hz, 1H), 4.27–4.20 (m, 2H), 4.10–4.03 (m, 3H), 1.26 (d, *J* = 7.1 Hz, 4H), 1.20 (dd, *J* = 7.0, 3.5 Hz, 6H).

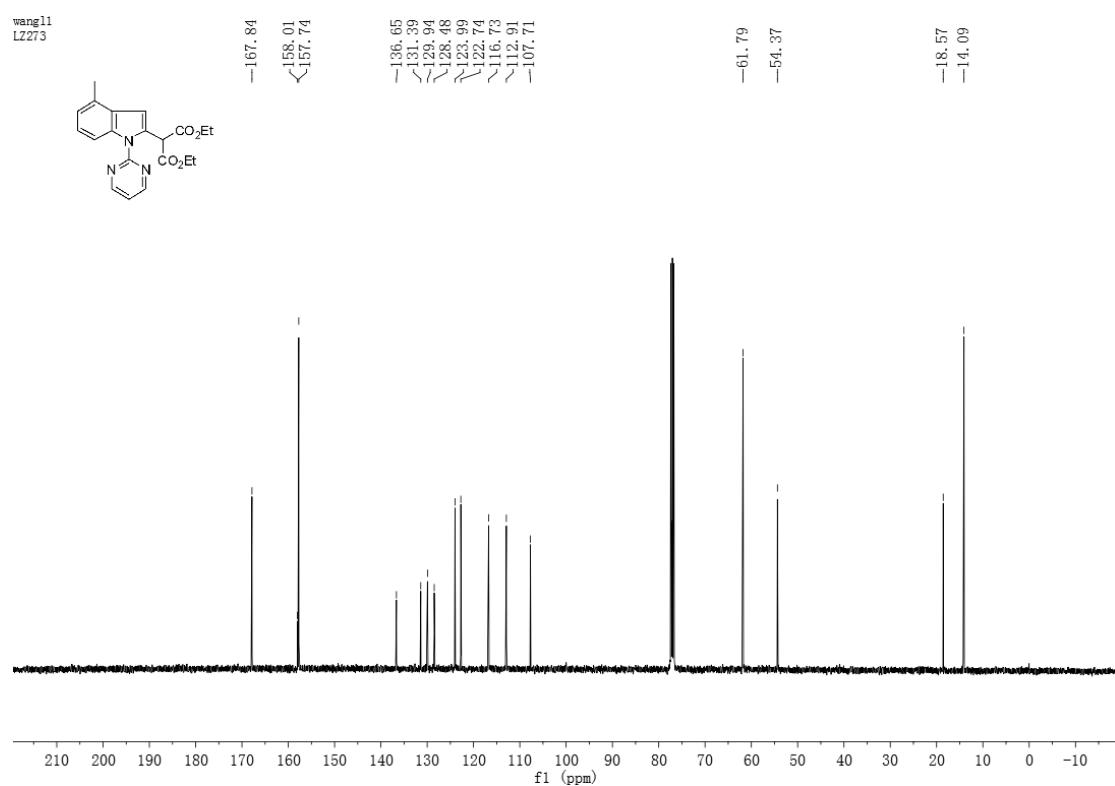
<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.06, 167.03, 158.12, 136.86, 129.62, 129.56, 128.81, 128.78, 123.70, 122.17, 120.77, 117.19, 114.31, 110.56, 110.50, 63.56, 63.49, 63.02, 62.95, 61.91, 46.26, 44.92, 29.71, 16.32, 16.27, 16.26, 14.09.

IR  $\nu$ : 2980, 1733, 1565, 1422, 1342, 1296, 1245, 1152, 1096, 1021, 962, 807, 733 cm<sup>-1</sup>.

HRMS *m/z*: calcd for C<sub>20</sub>H<sub>24</sub>N<sub>3</sub>O<sub>5</sub>PNa [M + Na<sup>+</sup>] 440.1346, found 440.1347.

**Figures S1–S60 are the NMR spectra and HRMS of compounds of 3a–v.**

**Figure S2.**  $^1\text{H}$  NMR spectrum of 3b.



**Figure S3.** <sup>13</sup>C NMR spectrum of 3b.

**Analysis Info**

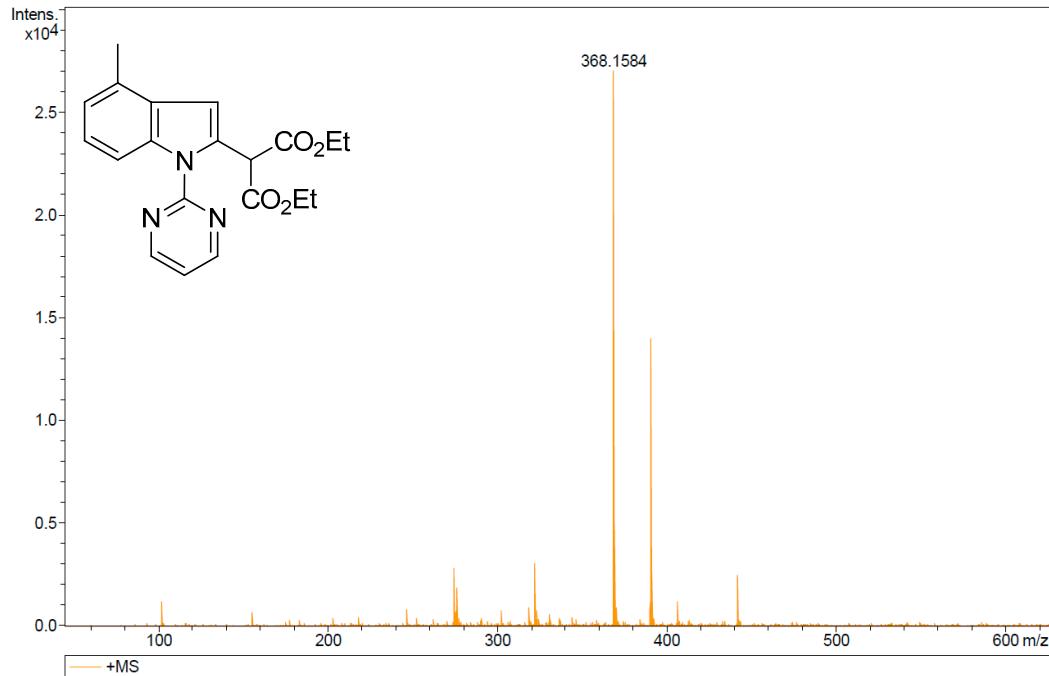
Analysis Name D:\Data\LY\B01000009.d  
 Method tune\_low.m  
 Sample Name B01  
 Comment

Acquisition Date 1/7/2016 9:40:16 PM

Operator BDAL@CN  
 Instrument / Ser# micrOTOF-Q II 10410

**Acquisition Parameter**

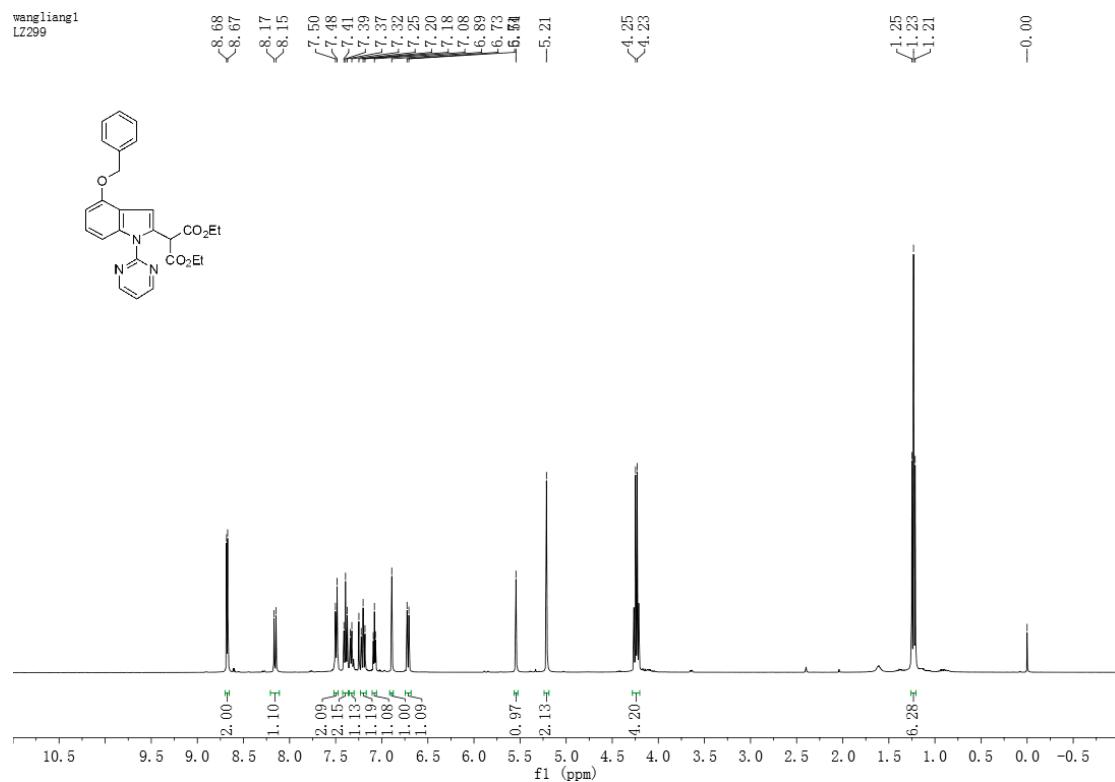
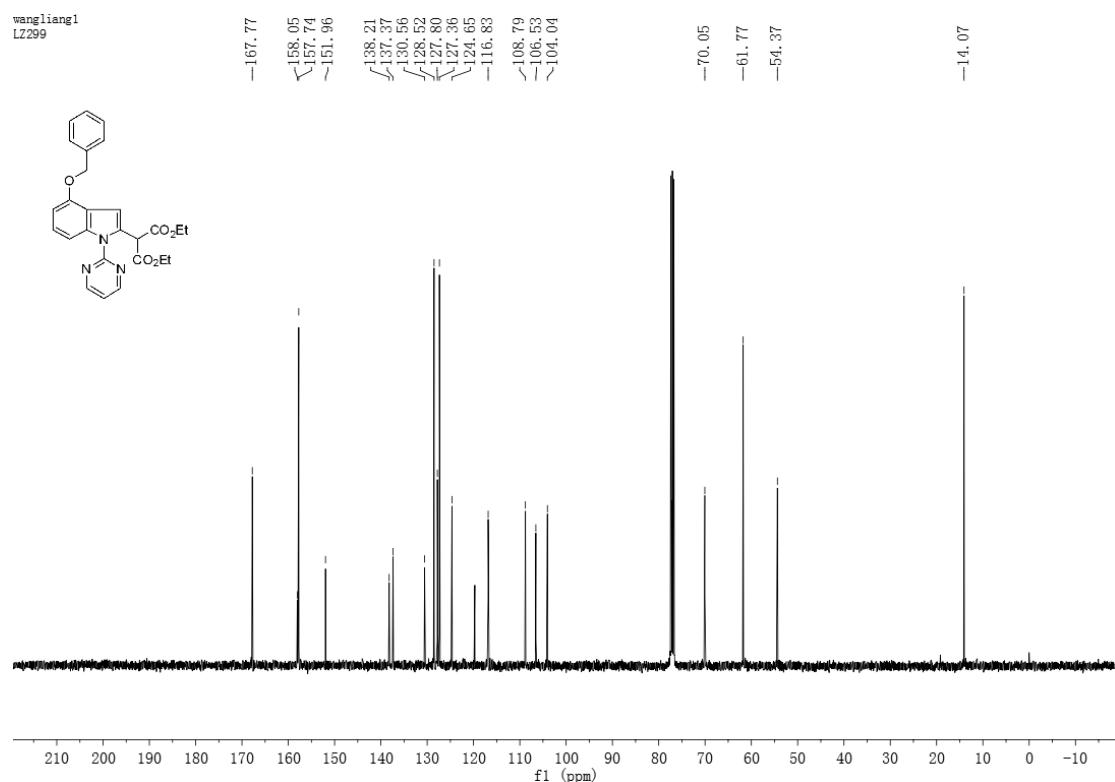
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	620 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

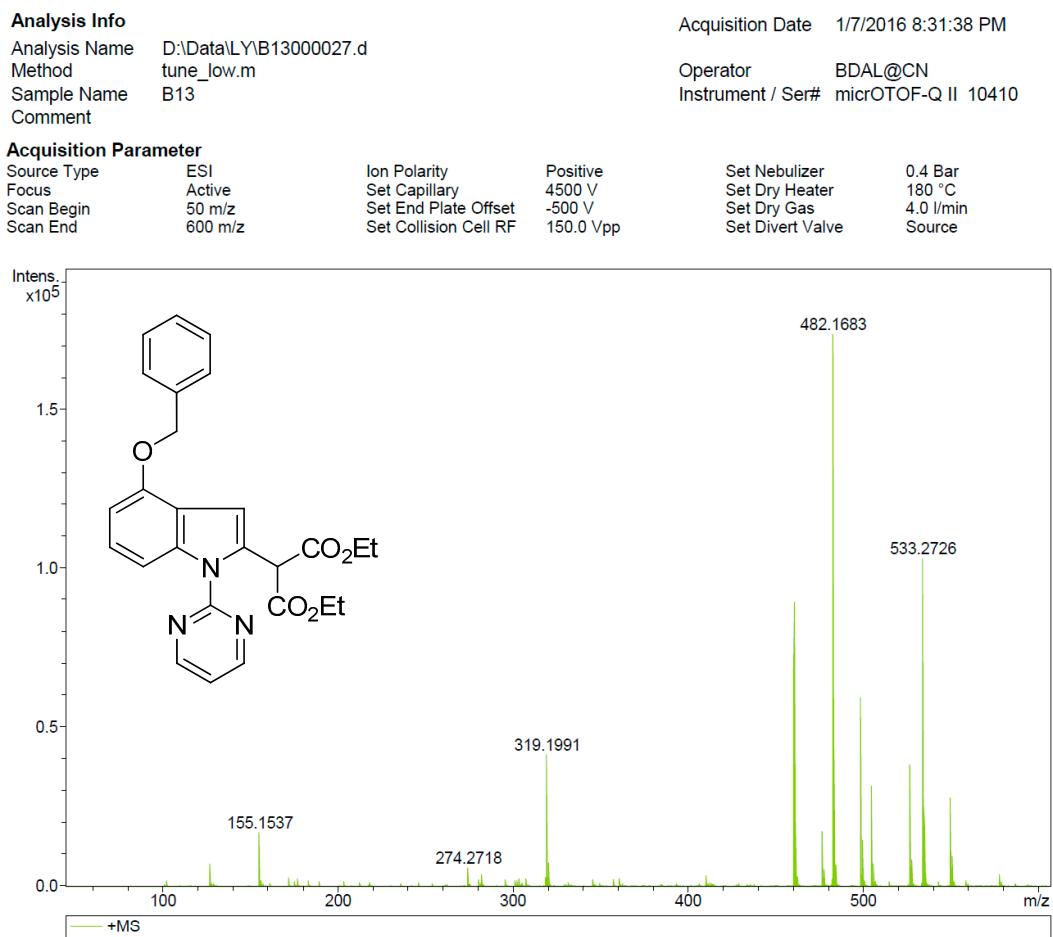
**Mass Spectrum List Report**

#	$m/z$	Res.	S/N	I	FWHM
1	368.1584	10553	32.2	27044	0.0349
2	390.1434	10523	22.4	14004	0.0371

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**Figure S4. HRMS of 3b.**

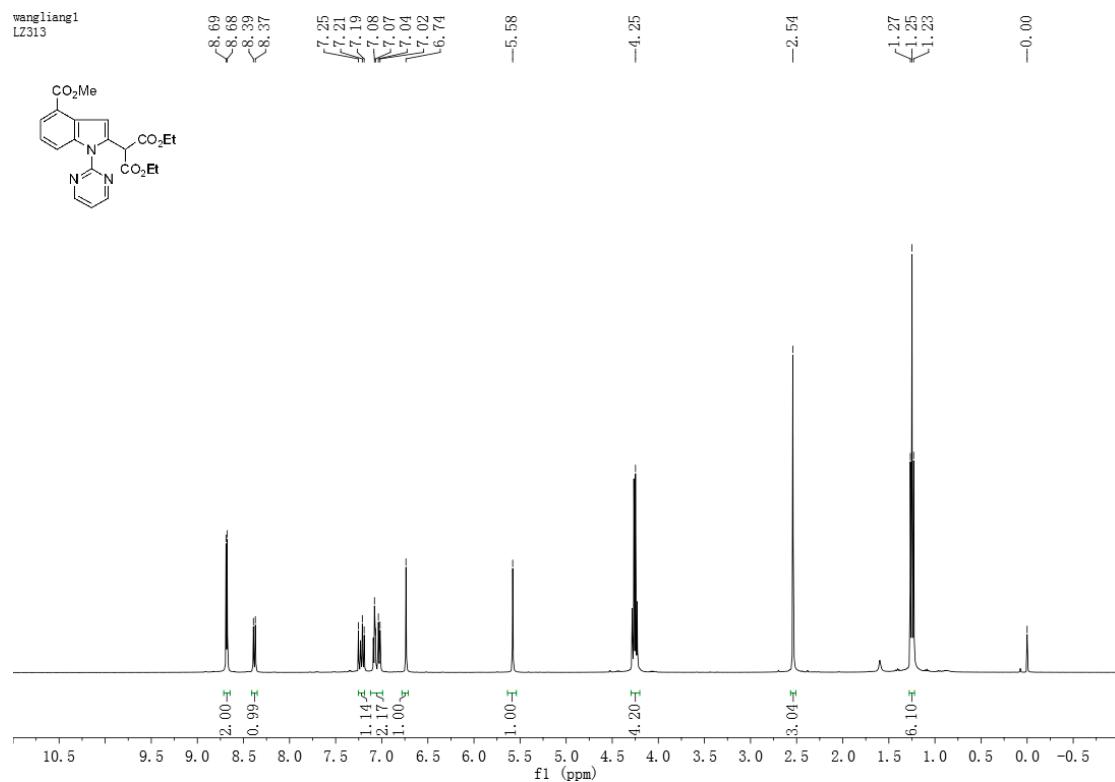
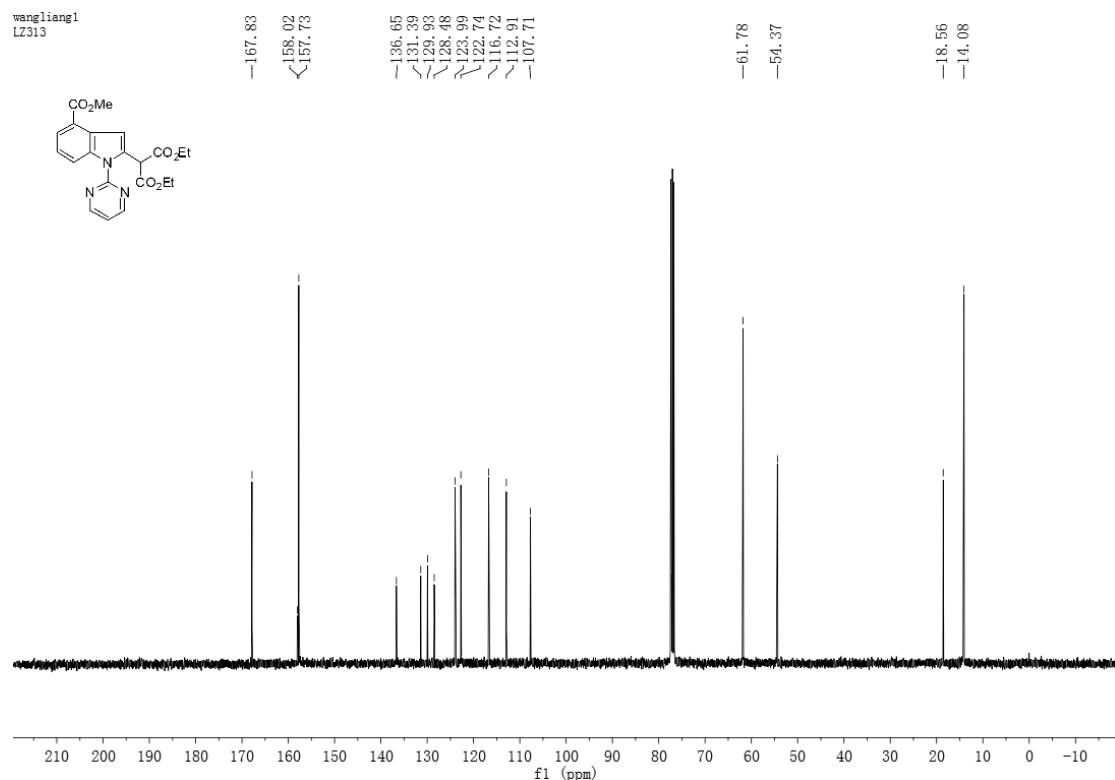
**Figure S5.**  $^1\text{H}$  NMR spectrum of **3c**.**Figure S6.**  $^{13}\text{C}$  NMR spectrum of **3c**.



### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	155.1537	9173	17.5	16940	0.0169
2	274.2718	9405	12.8	6064	0.0292
3	319.1991	11073	49.8	41368	0.0288
4	460.1838	13900	94.5	89404	0.0331
5	461.1874	11259	20.3	19780	0.0410
6	476.1797	11262	13.5	17432	0.0423
7	482.1683	14022	139.8	173572	0.0344
8	483.1693	11594	35.0	43096	0.0417
9	498.1602	12126	53.8	59400	0.0411
10	499.1654	11994	13.2	14448	0.0416
11	504.2114	12721	29.9	31488	0.0396
12	526.1941	11965	34.5	38368	0.0440
13	533.2726	14282	87.8	102928	0.0373
14	534.2774	11978	21.1	24980	0.0446
15	549.2713	11667	21.4	27924	0.0471

**Figure S7. HRMS of 3c.**

**Figure S8.**  $^1\text{H}$  NMR spectrum of **3d****Figure S9.**  $^{13}\text{C}$  NMR spectrum of **3d**.

**Analysis Info**

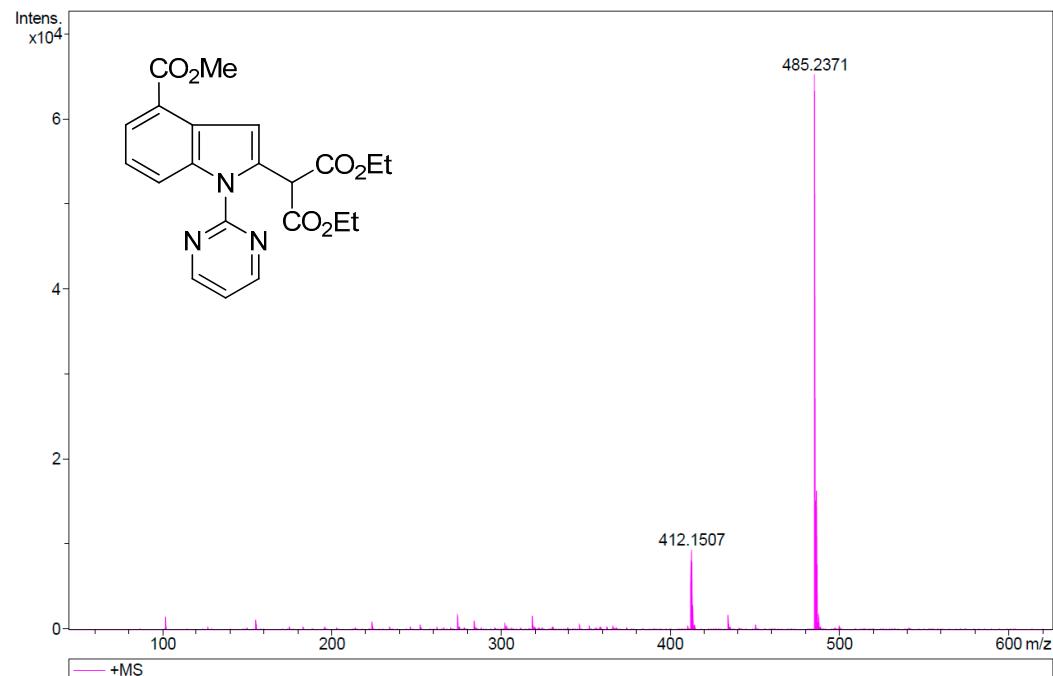
Analysis Name D:\Data\LY\B03000011.d  
 Method tune\_low.m  
 Sample Name B03  
 Comment

Acquisition Date 1/7/2016 9:27:40 PM

Operator BDAL@CN  
 Instrument / Ser# micrOTOF-Q II 10410

**Acquisition Parameter**

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	620 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

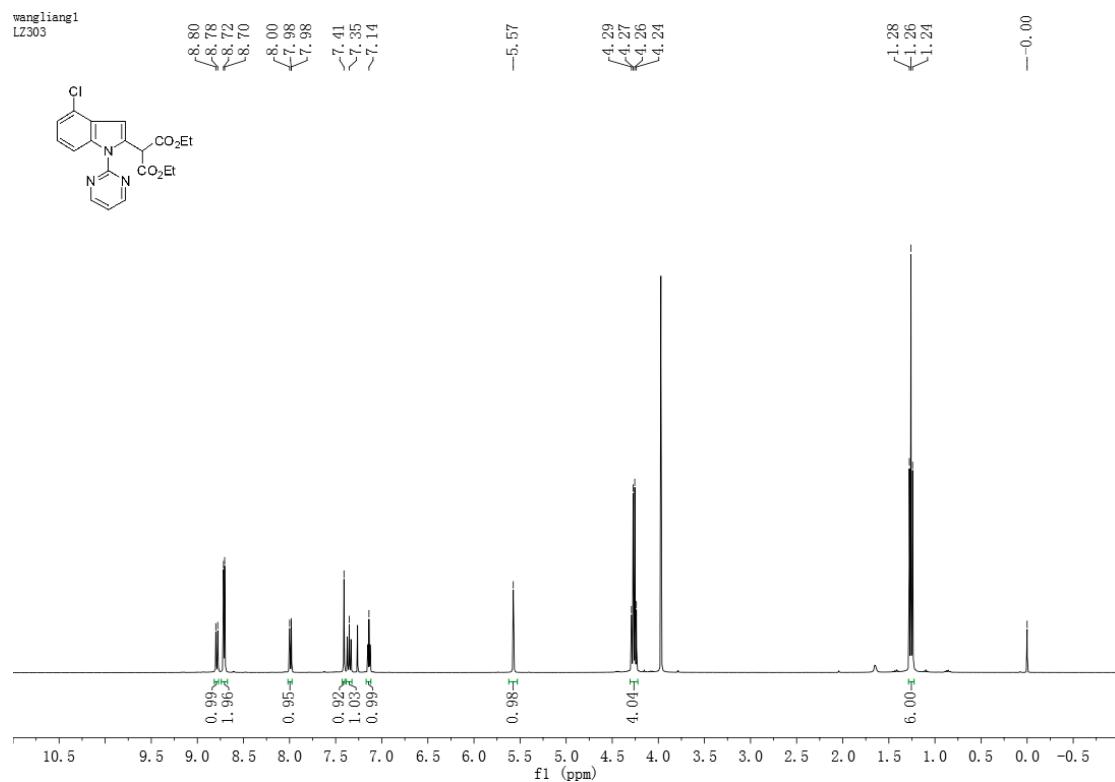
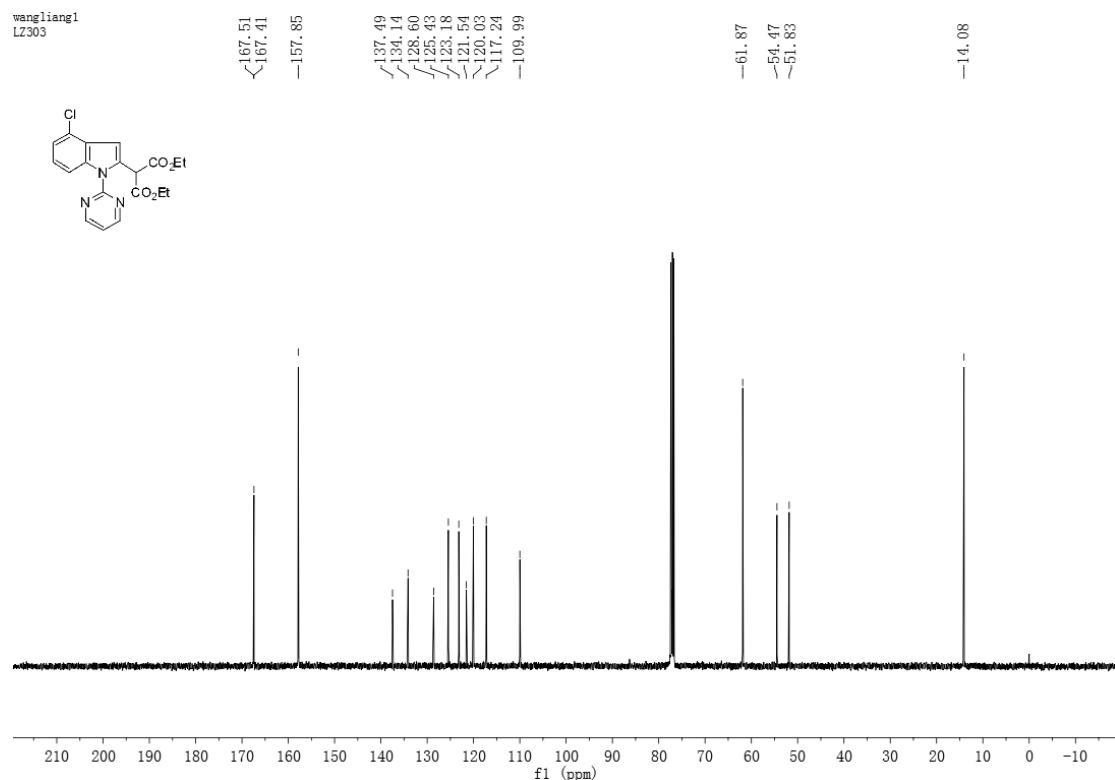
**Mass Spectrum List Report**

#	$m/z$	Res.	S/N	I	FWHM
1	412.1507	9012	16.8	9440	0.0457
2	485.2371	12648	55.5	65168	0.0384
3	486.2420	11322	13.6	16320	0.0429

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**Figure S10. HRMS of 3d.**

**Figure S11.**  $^1\text{H}$  NMR spectrum of 3e.**Figure S12.**  $^{13}\text{C}$  NMR spectrum of 3f.

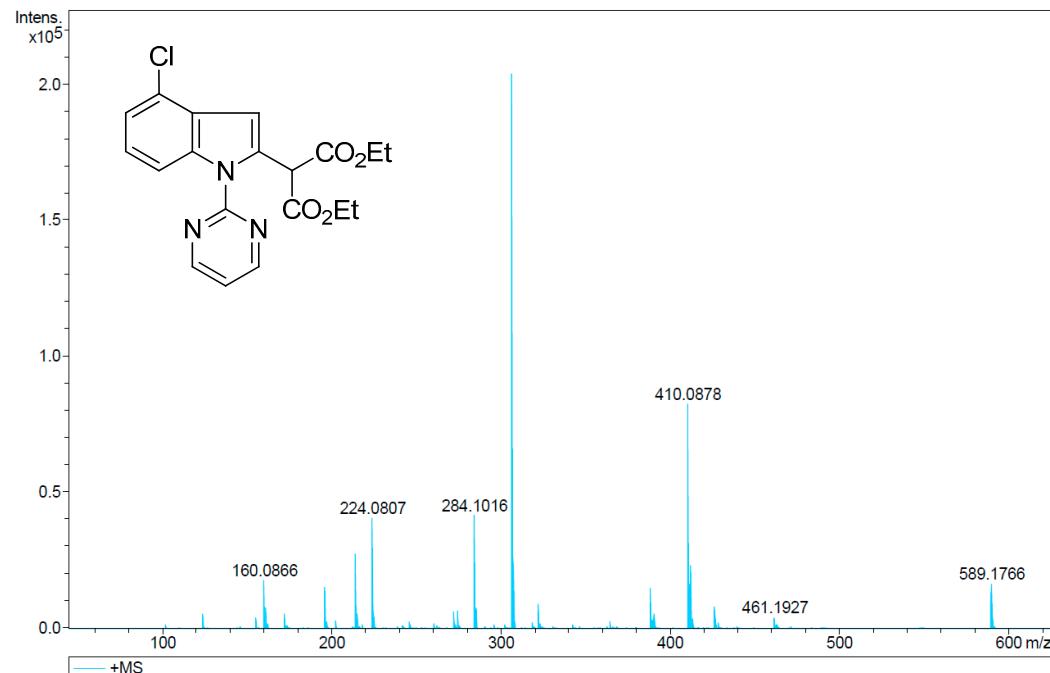
**Analysis Info**

Analysis Name D:\Data\LY\B04000007.d  
 Method tune\_low.m  
 Sample Name B04  
 Comment

Acquisition Date 1/7/2016 9:08:24 PM  
 Operator BDAL@CN  
 Instrument / Ser# micrOTOF-Q II 10410

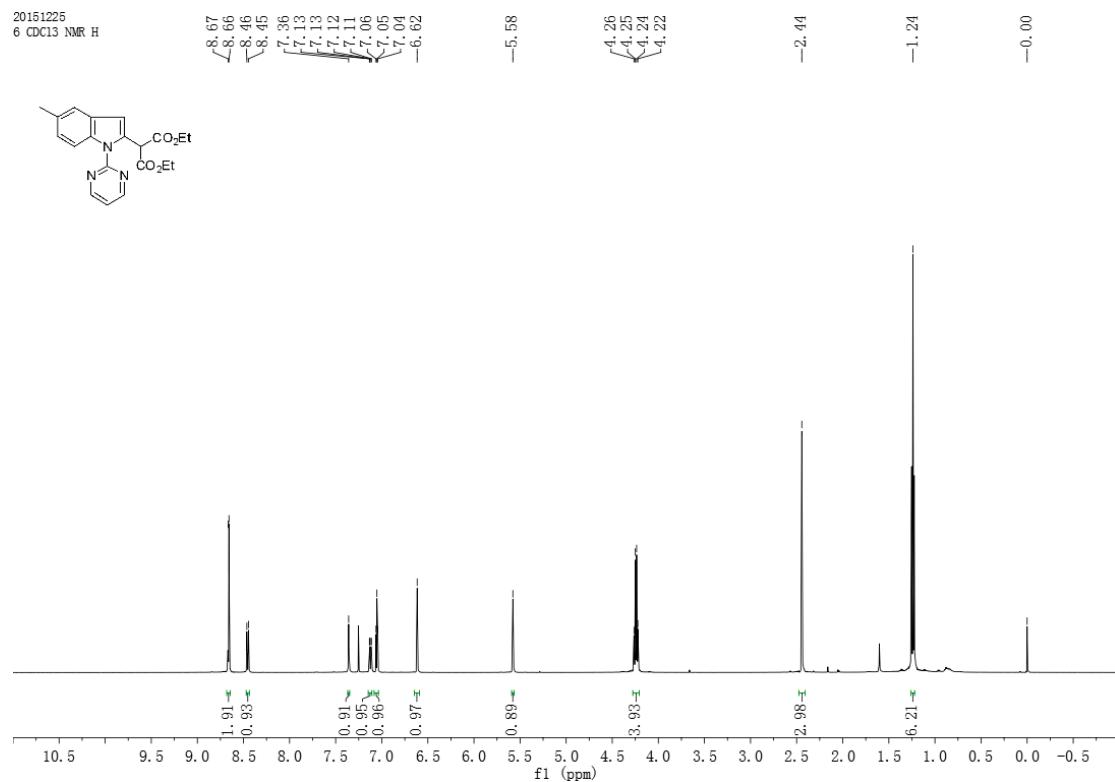
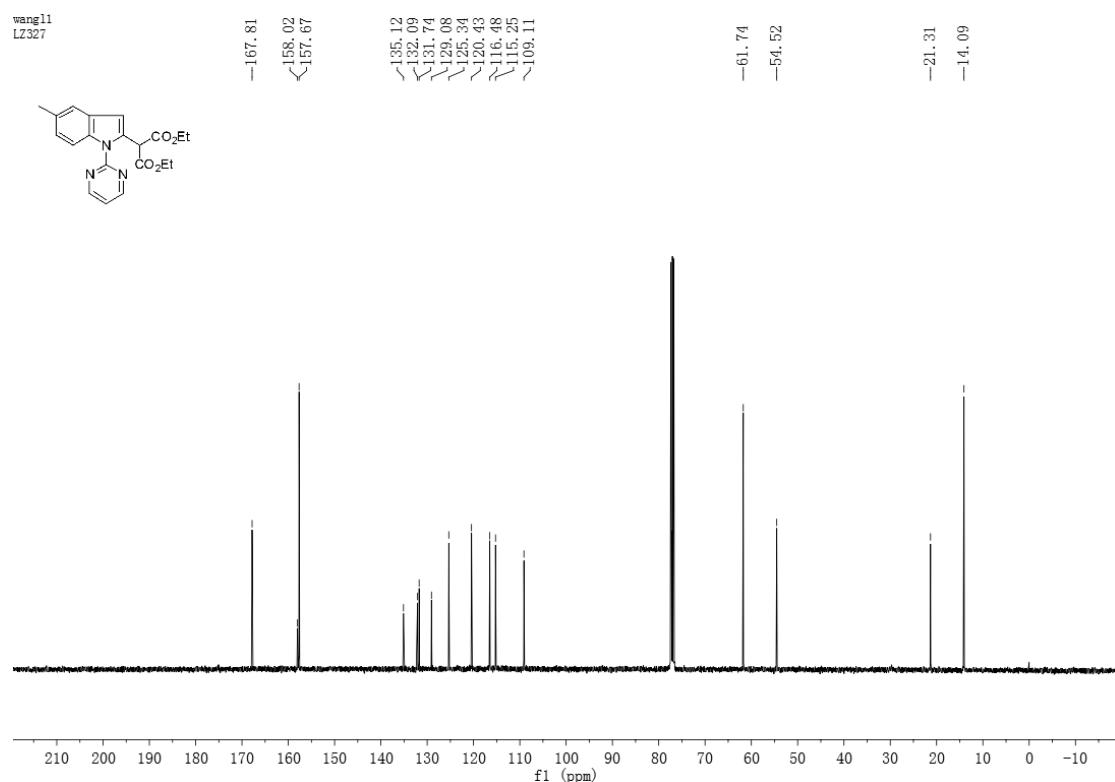
**Acquisition Parameter**

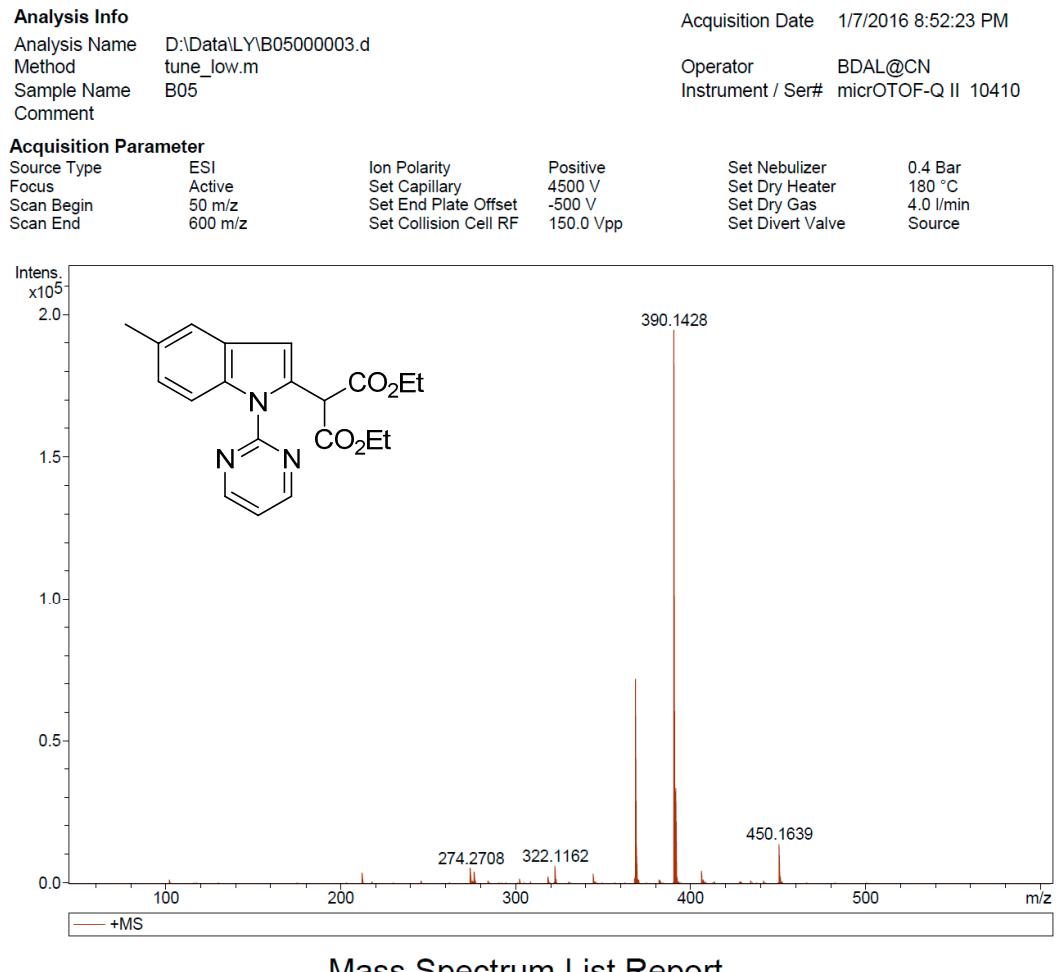
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	620 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

**Mass Spectrum List Report**

#	m/z	Res.	S/N	I	FWHM
1	160.0866	8860	17.3	17888	0.0181
2	196.0868	9307	13.8	15172	0.0211
3	214.0955	9302	21.8	27680	0.0230
4	224.0807	9102	33.3	40448	0.0246
5	284.1016	9328	35.0	41536	0.0305
6	307.0854	10159	23.1	27396	0.0302
7	322.0589	11087	11.5	9276	0.0290
8	388.1042	10160	18.9	14976	0.0382
9	410.0878	12185	73.6	82268	0.0337
10	411.0894	11632	14.4	16272	0.0353
11	412.0825	11089	20.3	23292	0.0372
12	461.1927	10257	12.0	4208	0.0450
13	589.1766	11324	68.9	16476	0.0520
14	590.1820	11234	17.8	4272	0.0525

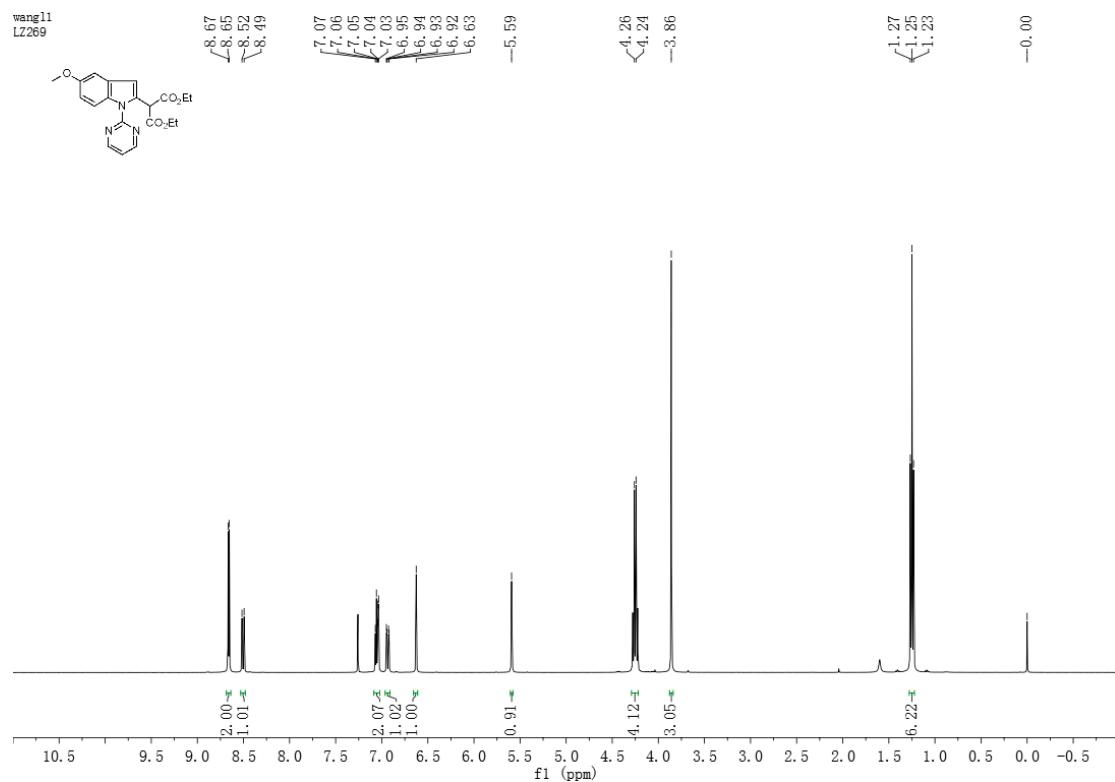
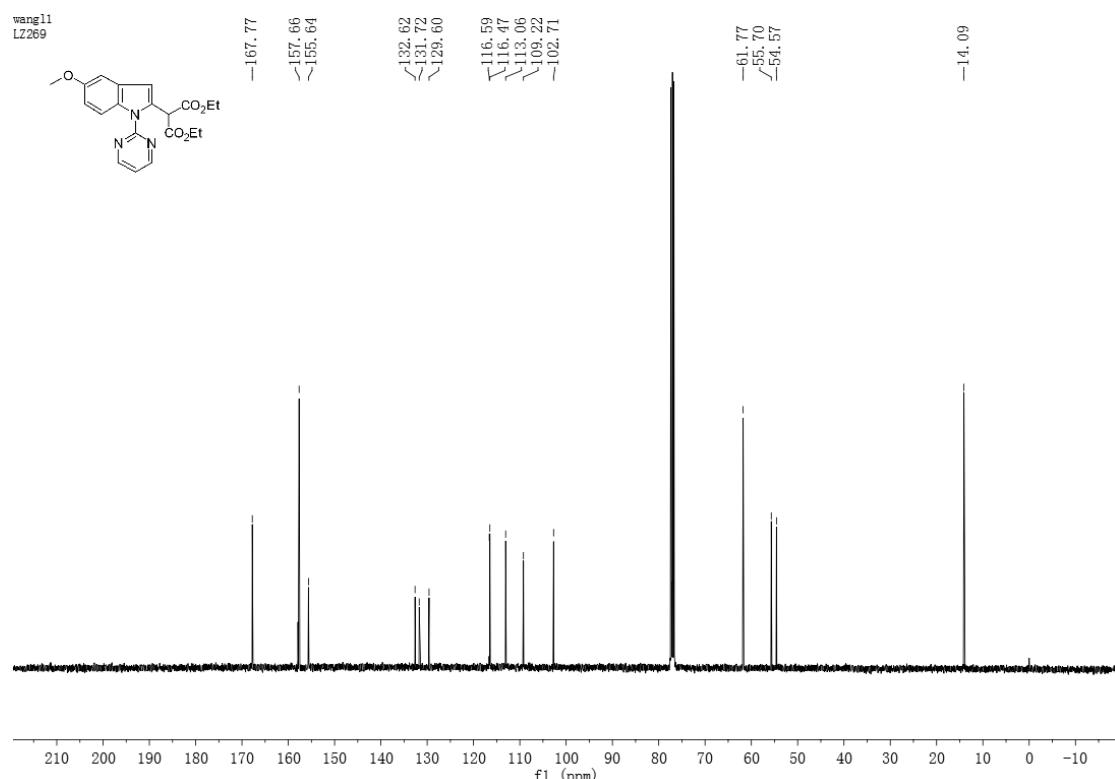
**Figure S13. HRMS of 3d.**

**Figure S14.** <sup>1</sup>H NMR spectrum of 3f.**Figure S15.** <sup>13</sup>C NMR spectrum of 3f.



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**Figure S16. HRMS of 3f.**

**Figure S17.** <sup>1</sup>H NMR spectrum of 3g.**Figure S18.** <sup>13</sup>C NMR spectrum of 3g.

**Analysis Info**

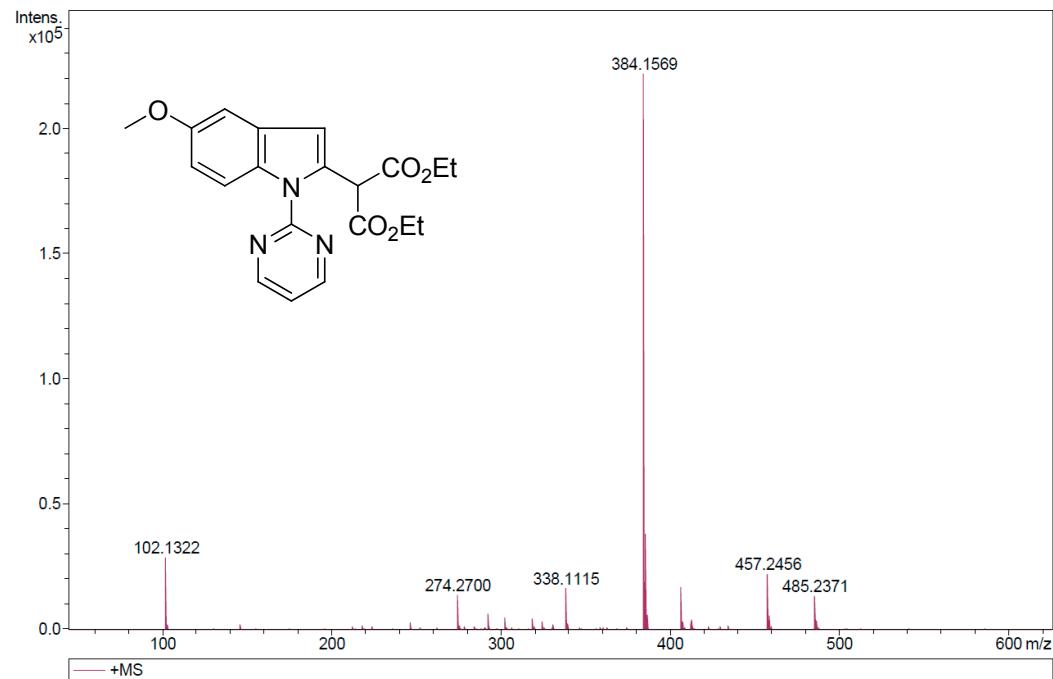
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 Sample Name B06  
 Comment

Acquisition Date 1/7/2016 9:37:09 PM

Operator BDAL@CN  
 Instrument / Ser# micrOTOF-Q II 10410

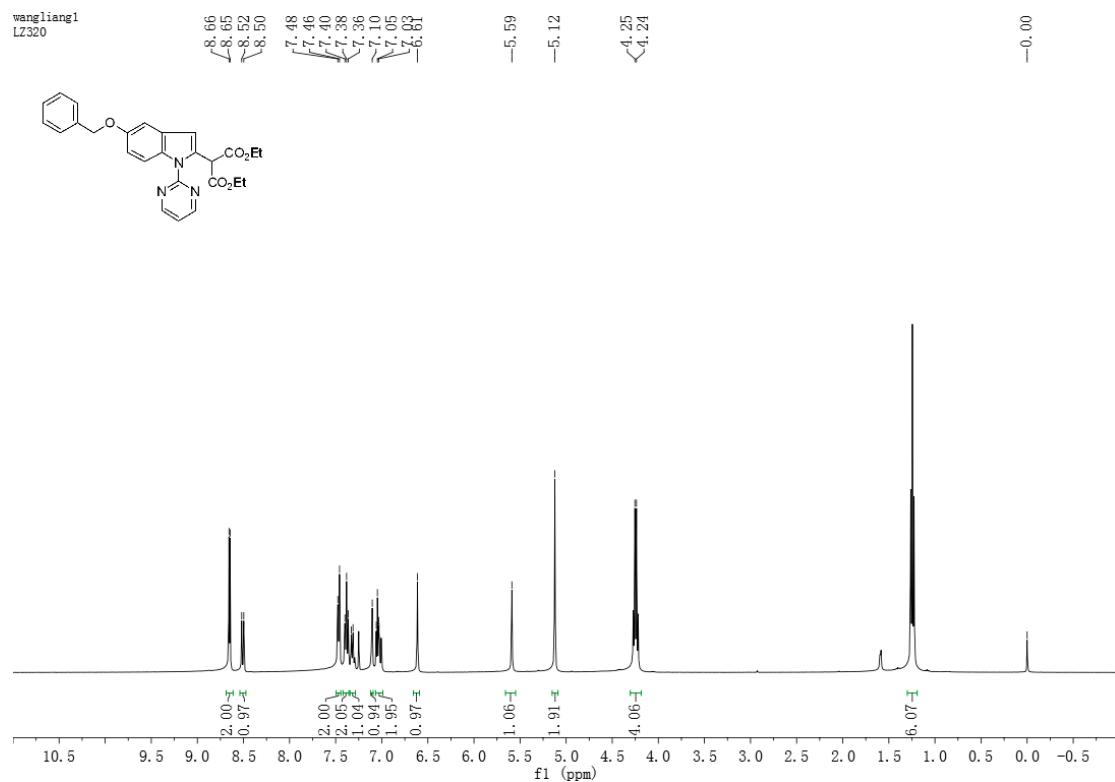
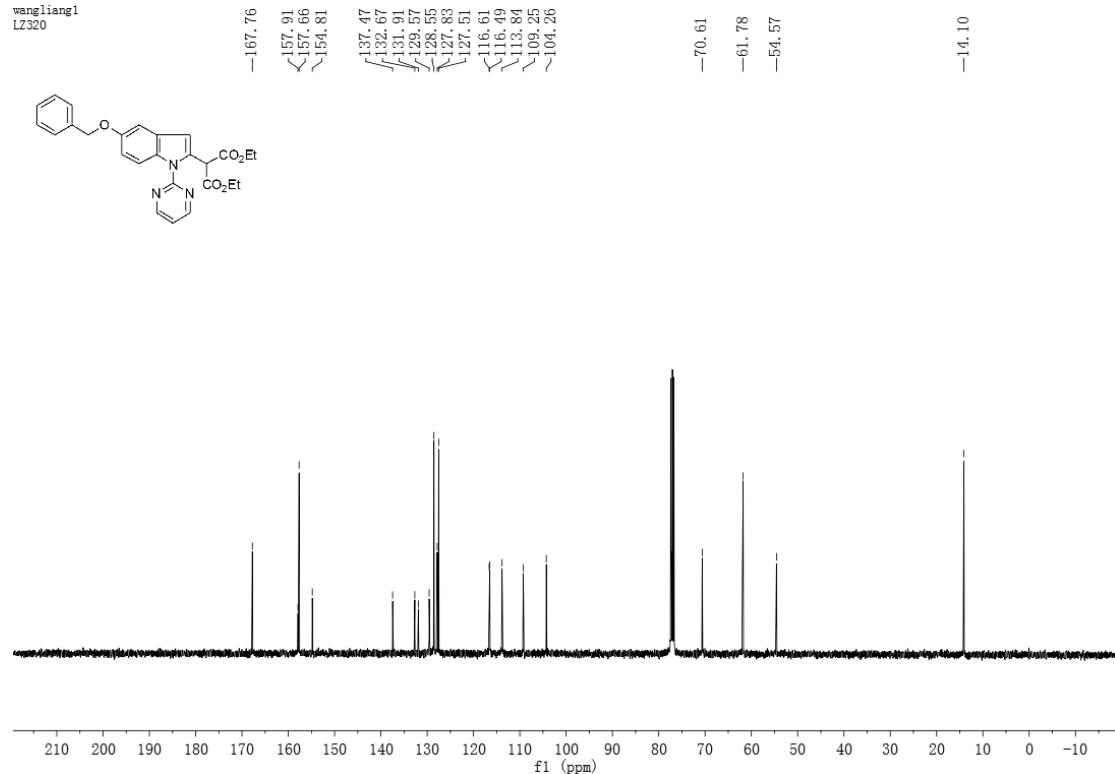
**Acquisition Parameter**

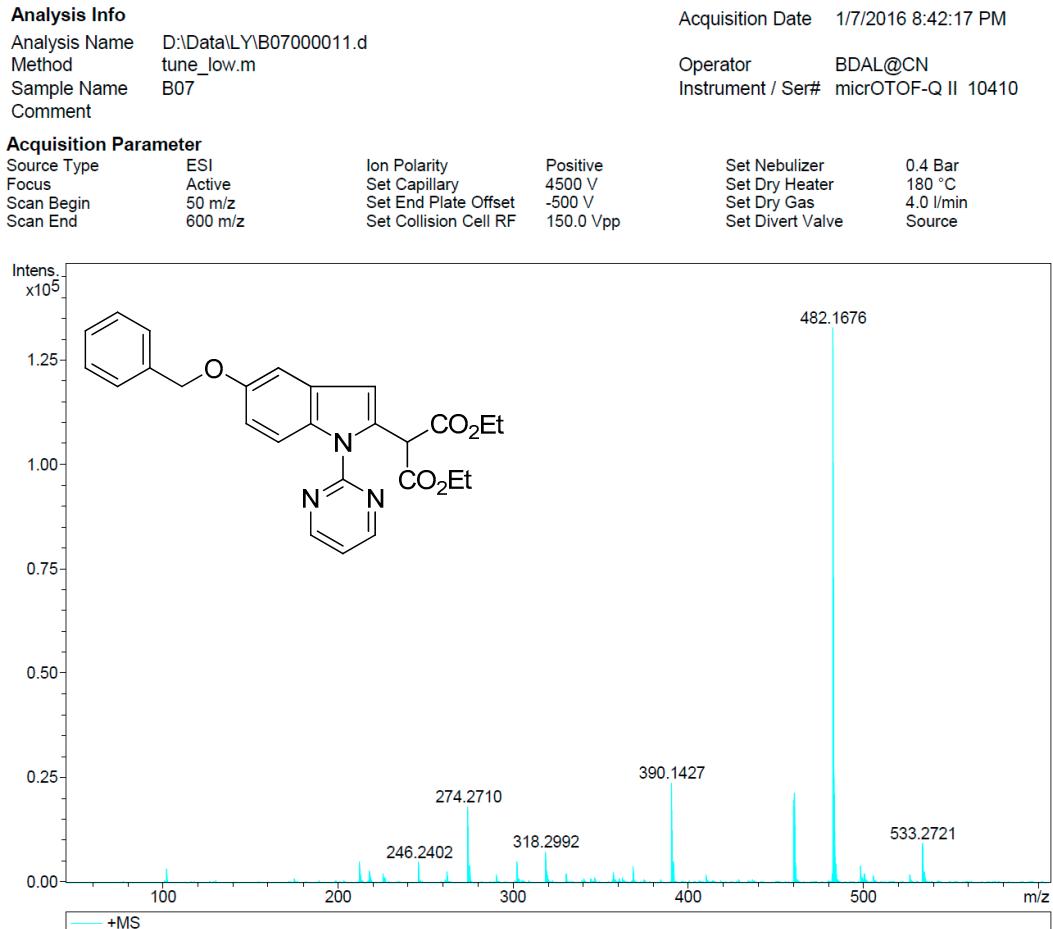
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	620 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

**Mass Spectrum List Report**

#	m/z	Res.	S/N	I	FWHM
1	102.1322	7834	14.6	28612	0.0130
2	274.2700	8835	24.6	13824	0.0310
3	292.0696	8502	12.5	6416	0.0344
4	338.1115	12452	27.1	16460	0.0272
5	384.1569	14787	268.8	221932	0.0260
6	385.1557	11523	46.9	38288	0.0334
7	406.1382	10579	26.9	16972	0.0384
8	457.2456	11297	35.1	22148	0.0405
9	485.2371	11129	32.5	13548	0.0436

**Figure S19. HRMS of 3g.**

**Figure S20.** <sup>1</sup>H NMR spectrum of 3h.**Figure S21.** <sup>13</sup>C NMR spectrum of 3h.



### Mass Spectrum List Report

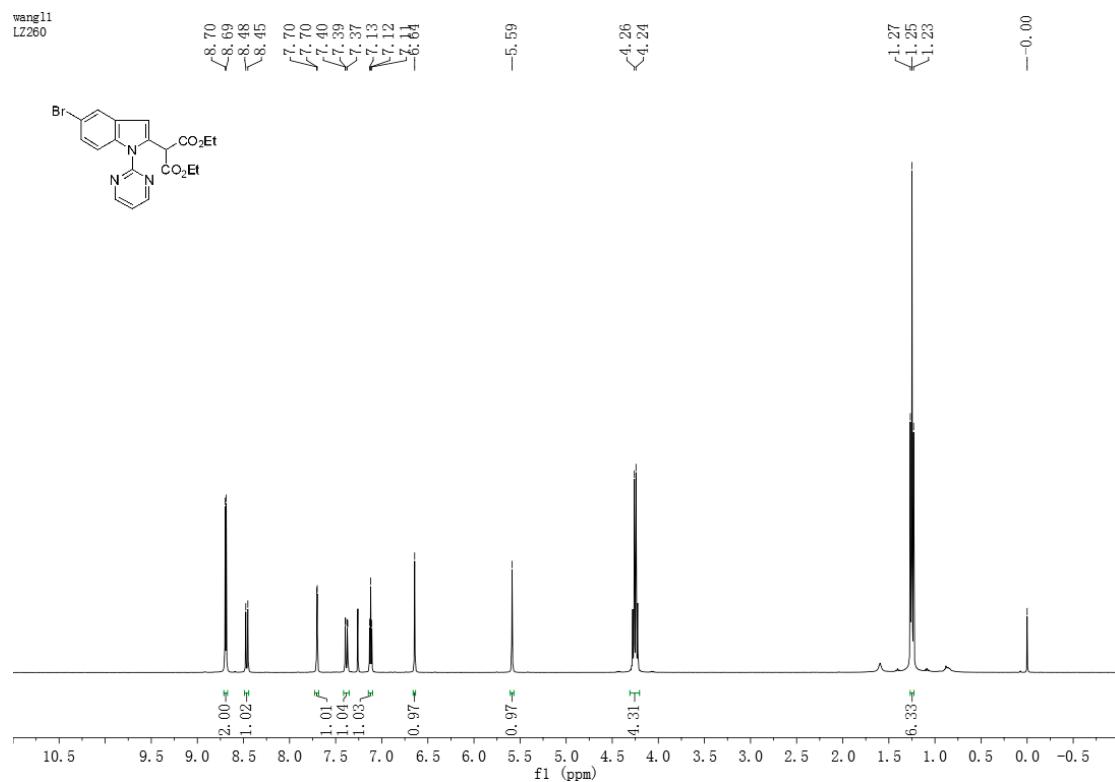
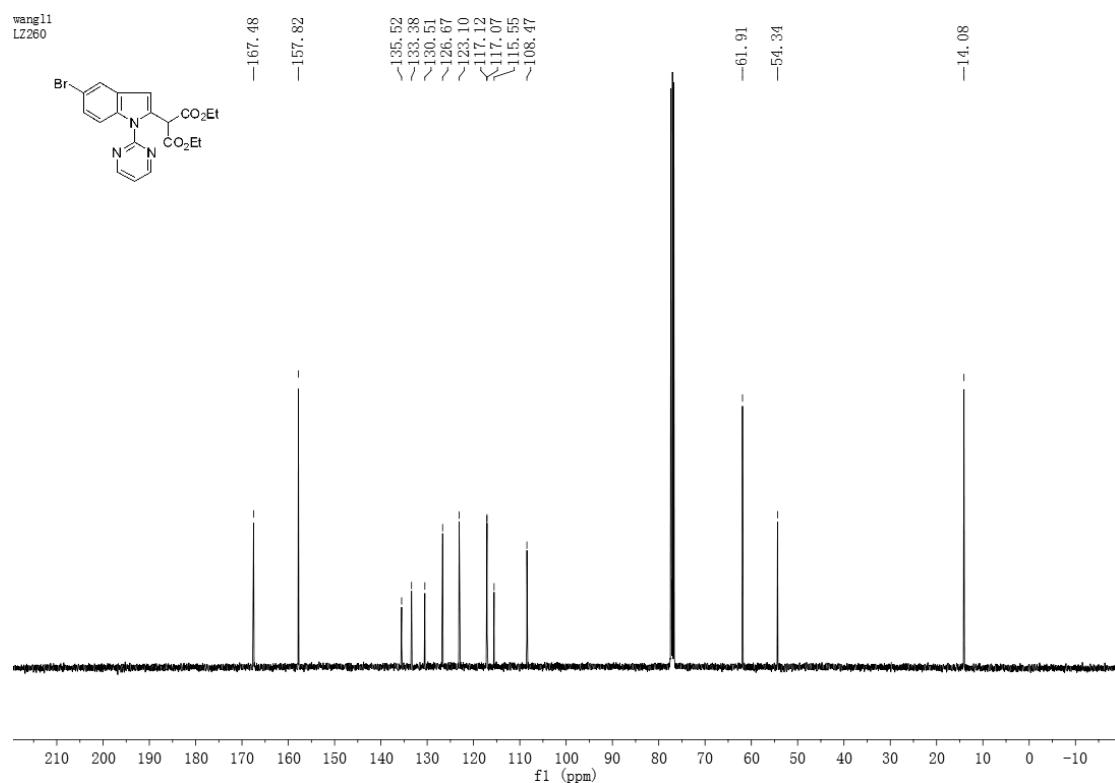
#	m/z	Res.	S/N	I	FWHM
1	246.2402	9948	10.9	4916	0.0248
2	274.2710	8620	32.7	18304	0.0318
3	318.2992	10851	14.8	7436	0.0293
4	390.1427	10451	47.7	23848	0.0373
5	391.1431	11446	10.0	5012	0.0342
6	460.1827	13160	32.7	21568	0.0350
7	482.1676	13749	172.6	132736	0.0351
8	483.1688	10680	35.2	26624	0.0452
9	533.2721	11380	26.3	9400	0.0469

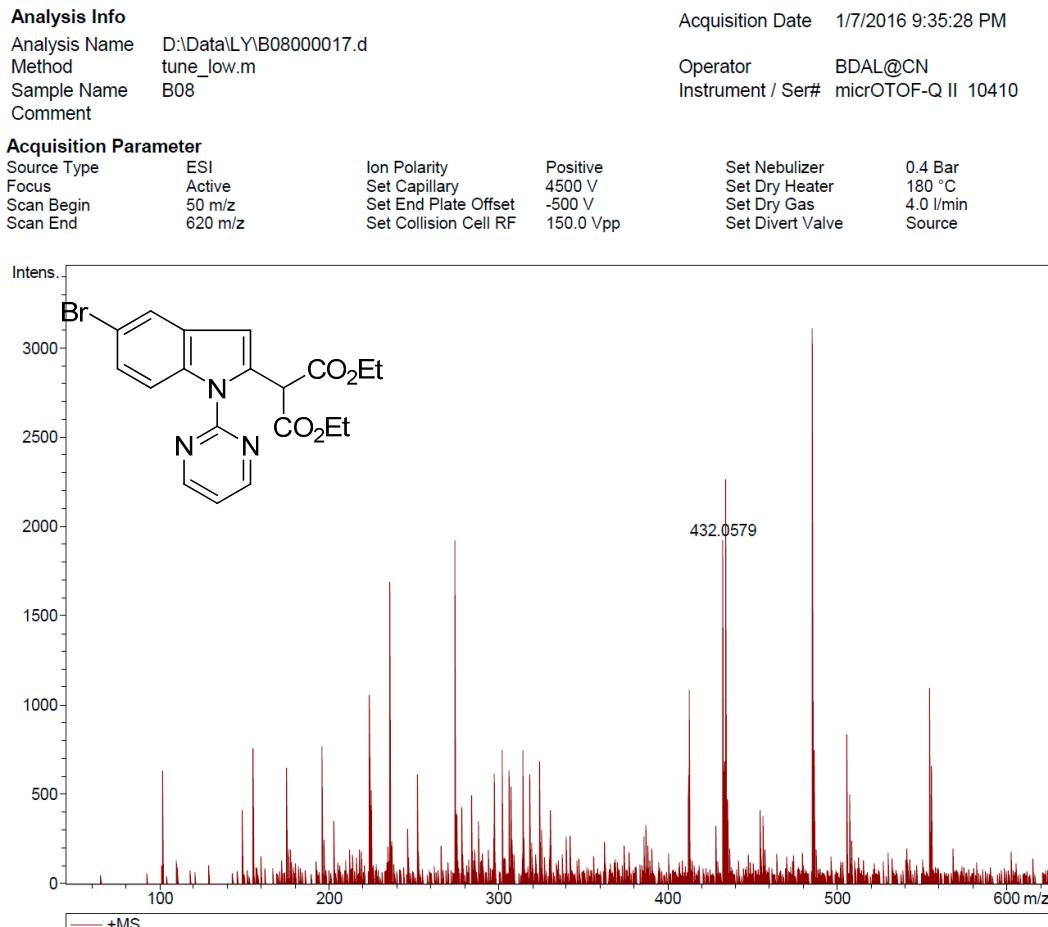
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**Figure S22. HRMS of 3h.**

**Figure S23.**  $^1\text{H}$  NMR spectrum of **3i**.**Figure S24.**  $^{13}\text{C}$  NMR spectrum of **3i**.



### Mass Spectrum List Report

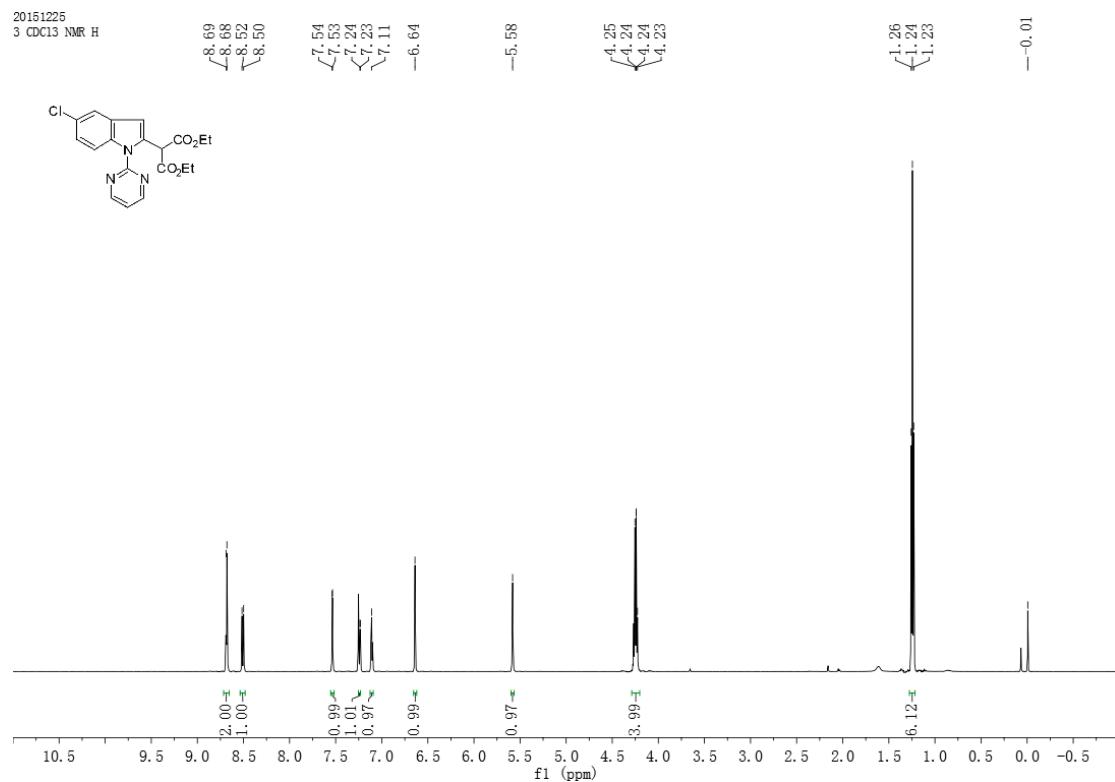
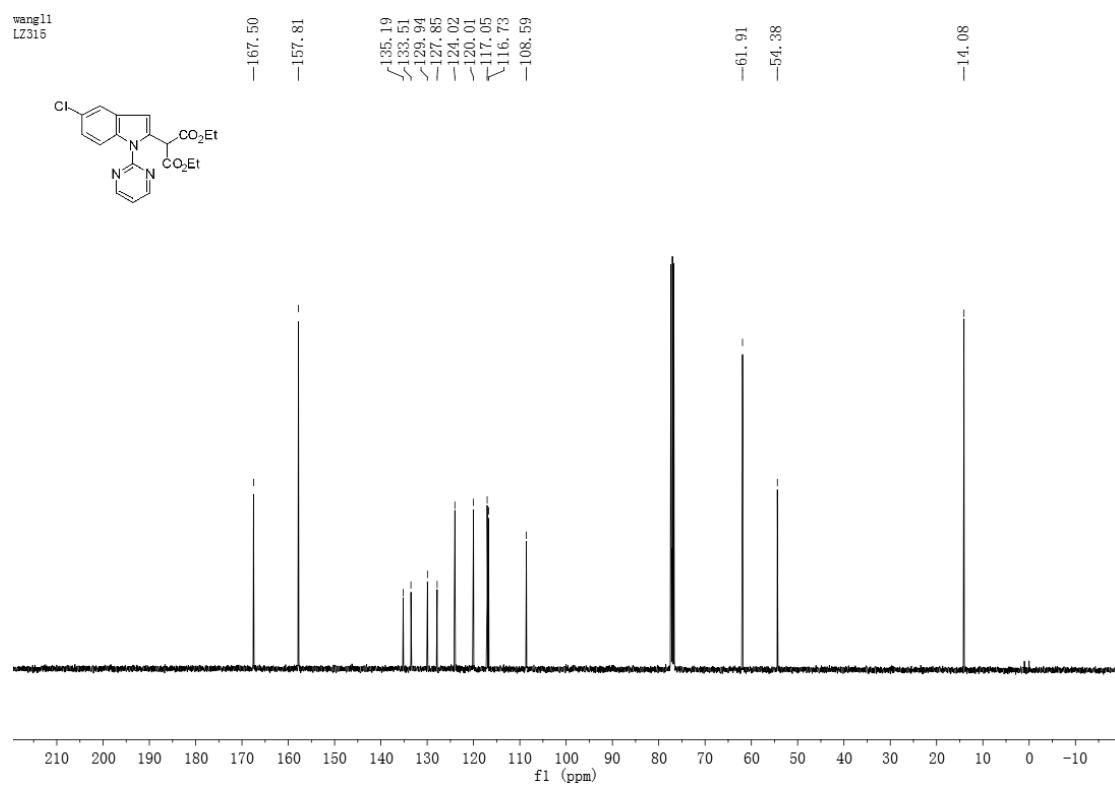
#	m/z	Res.	S/N	I	FWHM
1	432.0579	9149	6.2	1924	0.0472
2	454.0396	6033	1.0	412	0.0753

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**Figure S25.** HRMS of 3i.

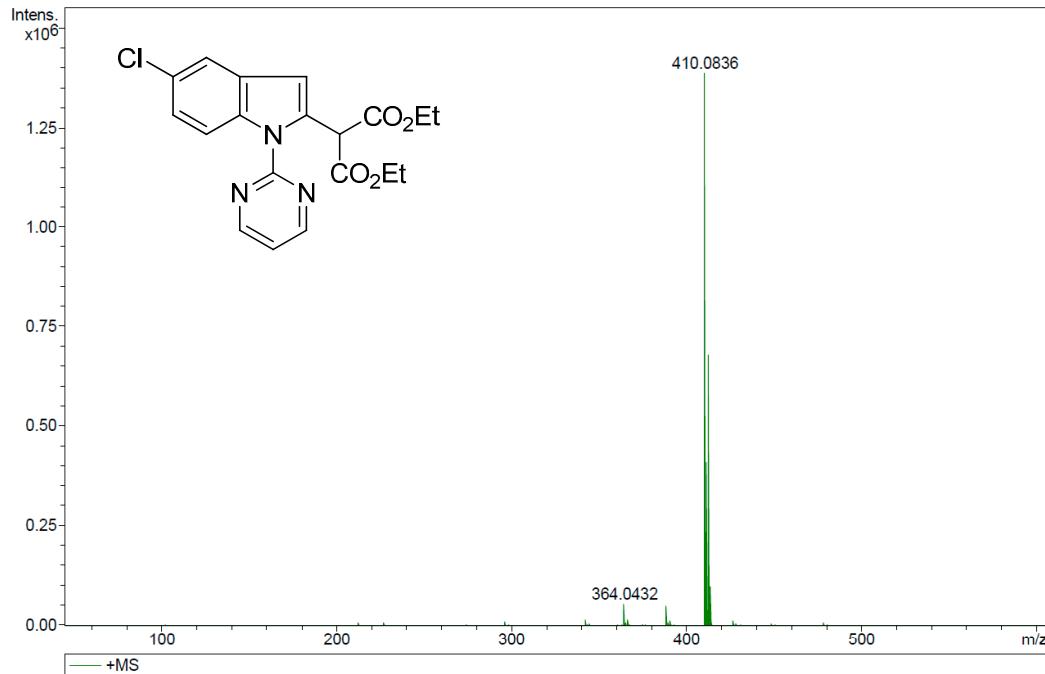
**Figure S26.** <sup>1</sup>H NMR spectrum of 3j**Figure S27.** <sup>13</sup>C NMR spectrum of 3j.

**Analysis Info**

Analysis Name	D:\Data\LY\B13000018.d	Acquisition Date	1/7/2016 8:29:52 PM
Method	tune_low.m	Operator	BDAL@CN
Sample Name	B13	Instrument / Ser#	micrOTOF-Q II 10410
Comment			

**Acquisition Parameter**

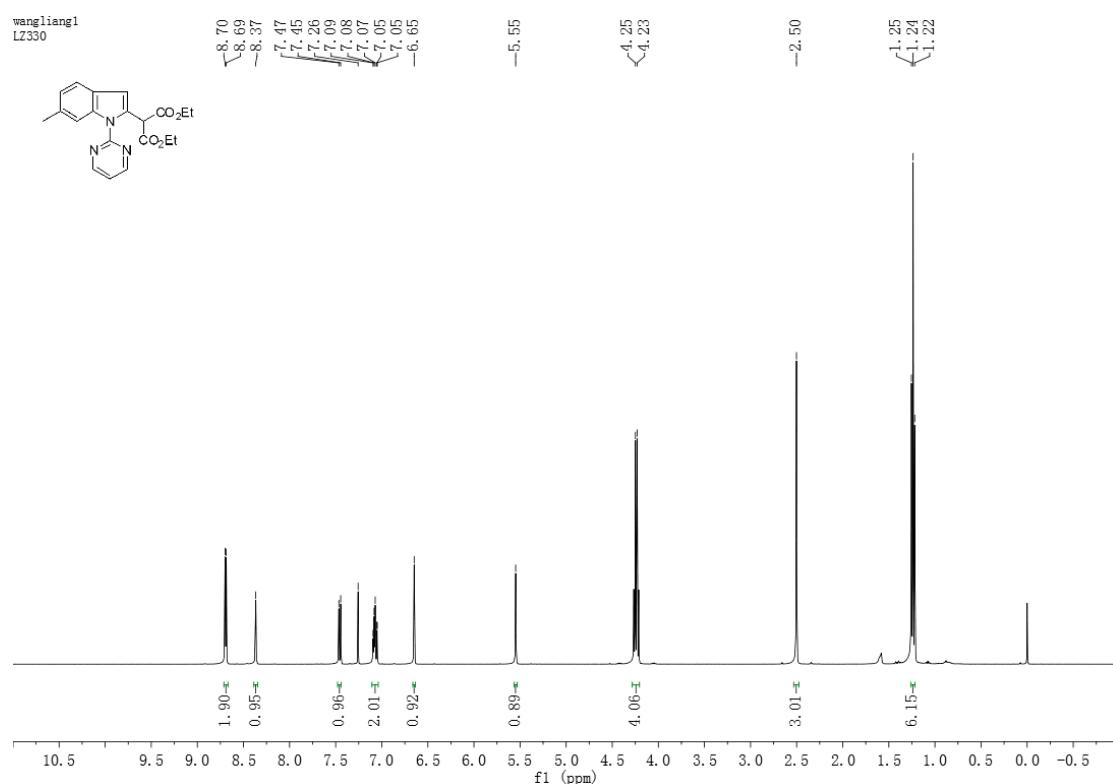
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source



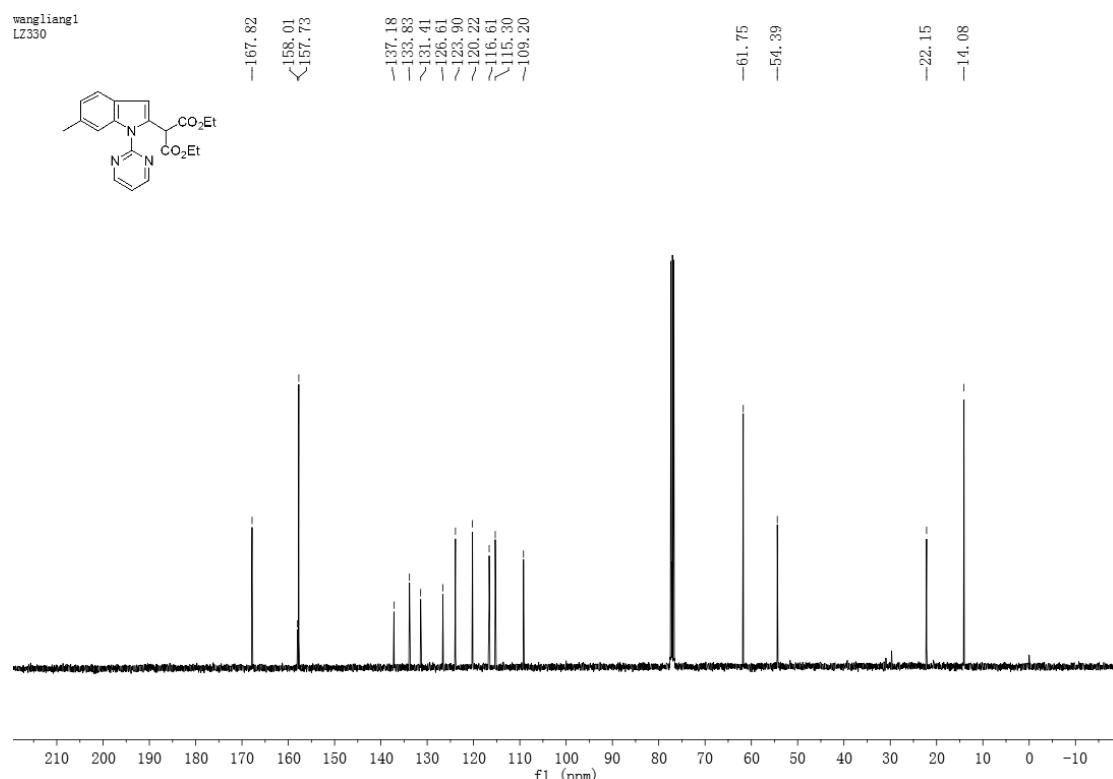
### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	212.1163	8192	23.8	7932	0.0259
2	226.9497	11645	25.8	8392	0.0195
3	296.0193	9343	24.7	11496	0.0317
4	342.0633	11573	24.9	16596	0.0296
5	364.0432	13167	59.4	55612	0.0276
6	366.0430	11666	14.2	14608	0.0314
7	388.1038	11750	24.4	50532	0.0330
8	410.0836	13676	678.5	1387080	0.0300
9	411.0898	14990	206.0	409548	0.0274
10	412.0848	17016	351.3	679204	0.0242
11	413.0882	12428	53.1	99652	0.0332
12	426.0615	10823	11.2	12960	0.0394
13	478.0733	10747	18.7	7448	0.0445

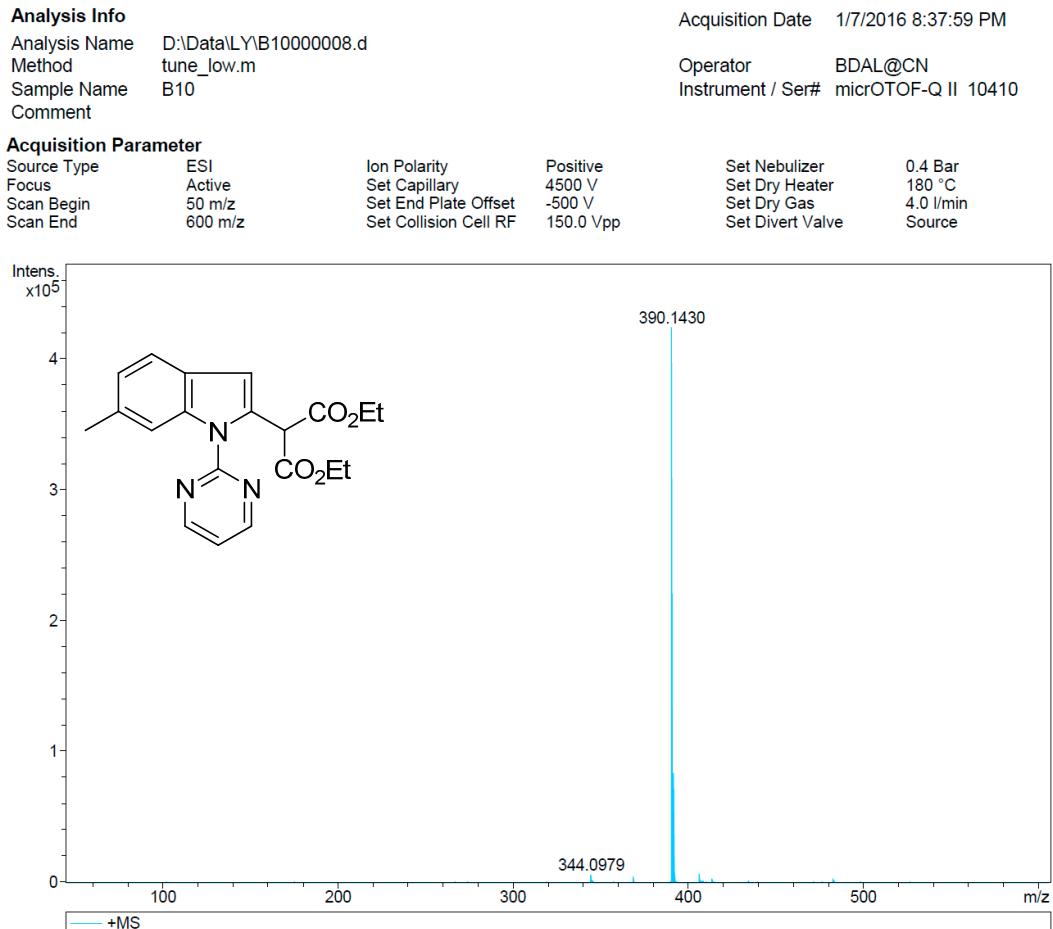
**Figure S28. HRMS of 3j.**



**Figure S29.**  $^1\text{H}$  NMR spectrum of 3k.



**Figure S30.**  $^{13}\text{C}$  NMR spectrum of 3k.

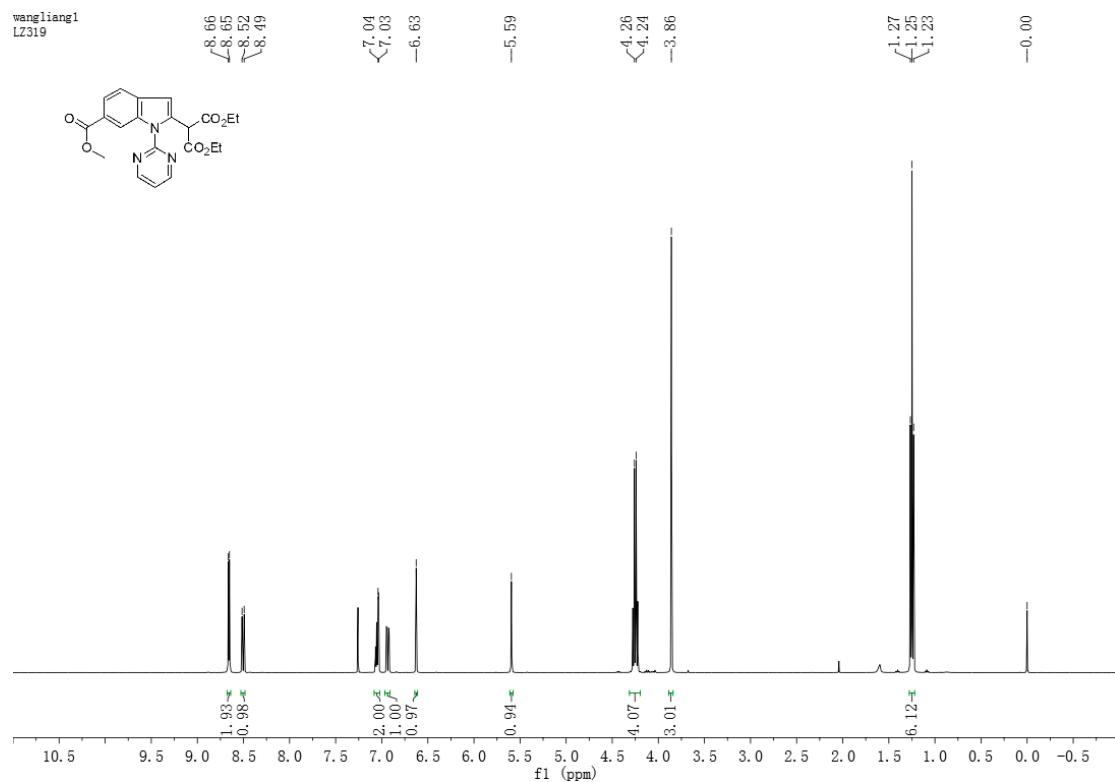
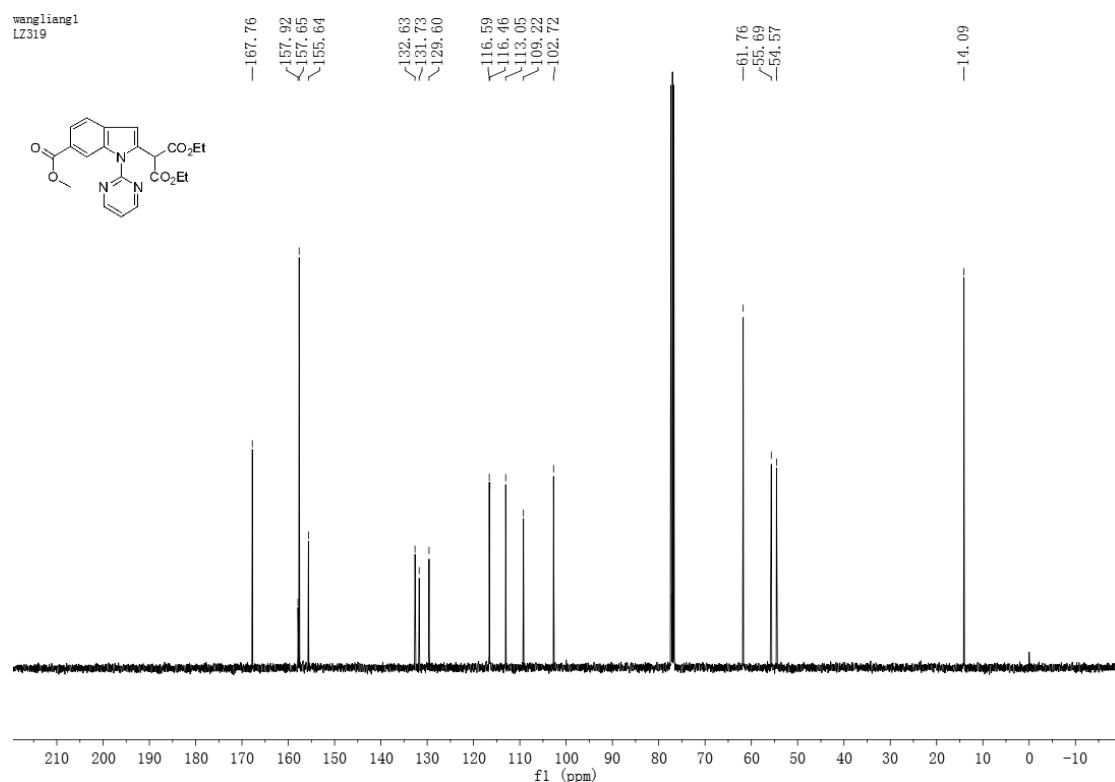


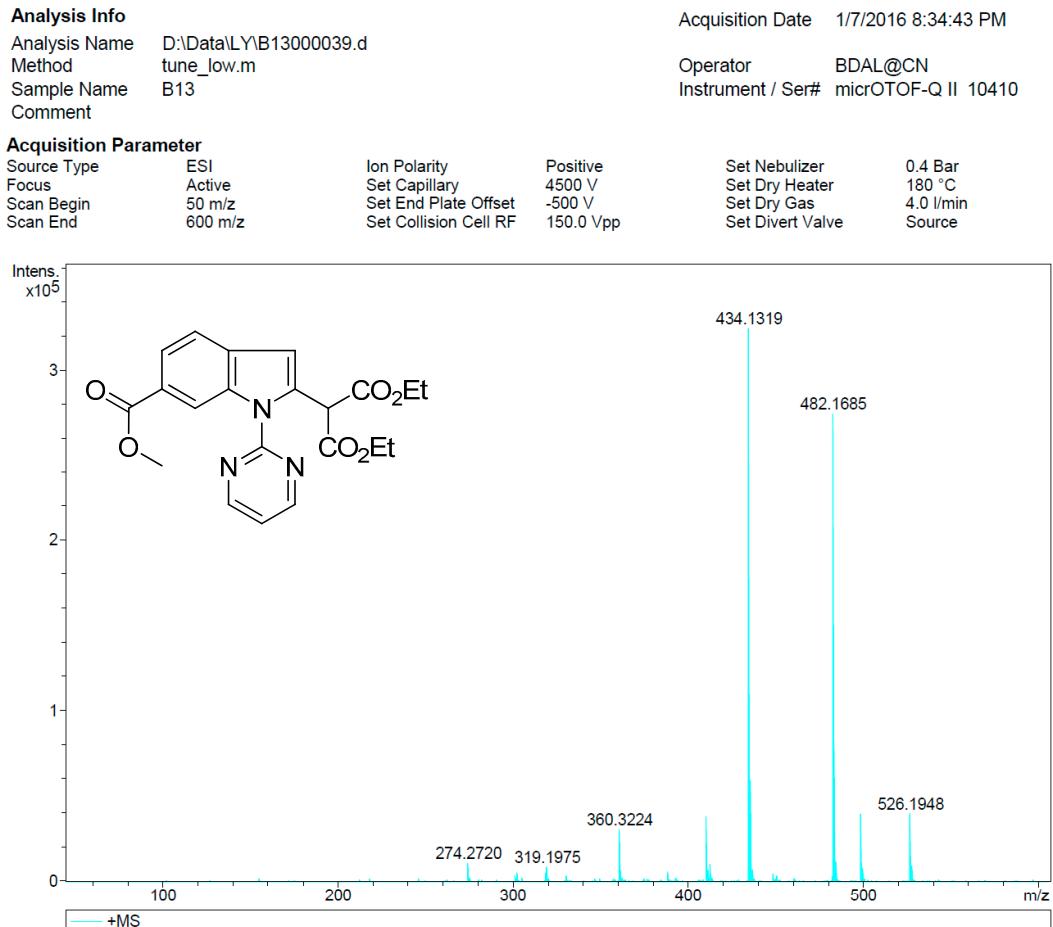
### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	344.0979	9538	16.3	6032	0.0361
2	390.1430	16092	349.9	424116	0.0242
3	391.1430	12562	67.4	83508	0.0311

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**Figure S31.** HRMS of 3k.

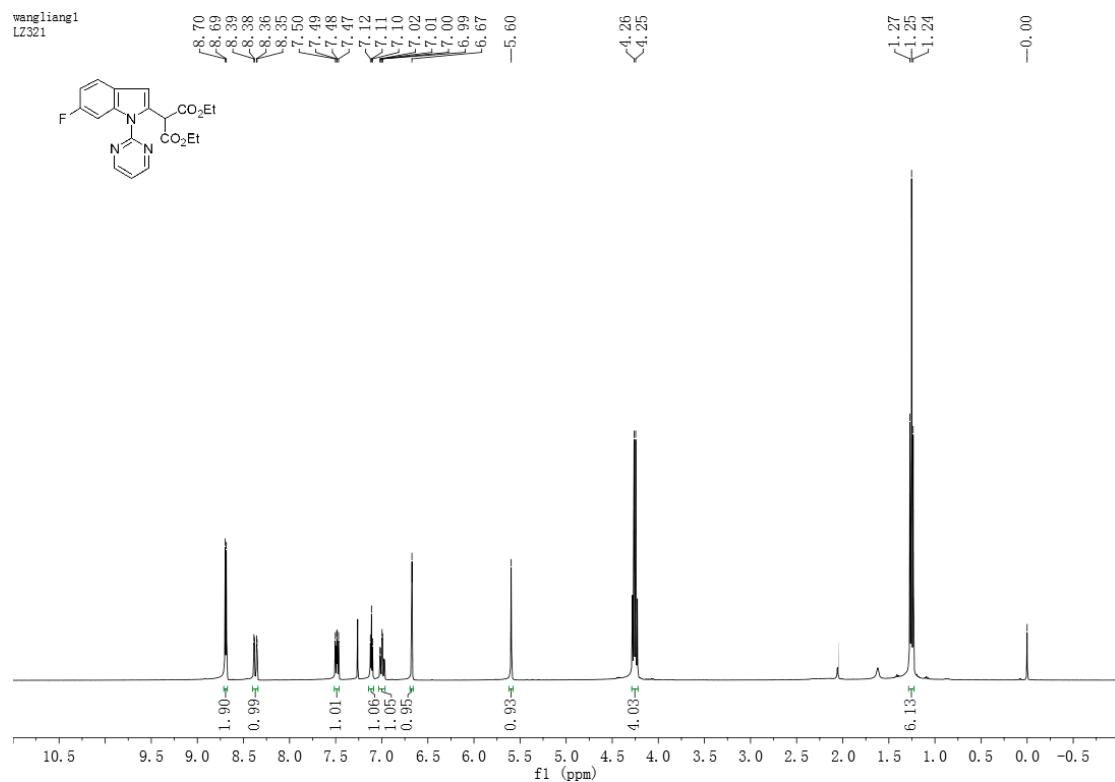
**Figure S32.**  $^1\text{H}$  NMR spectrum of 31.**Figure S33.**  $^{13}\text{C}$  NMR spectrum of 31.

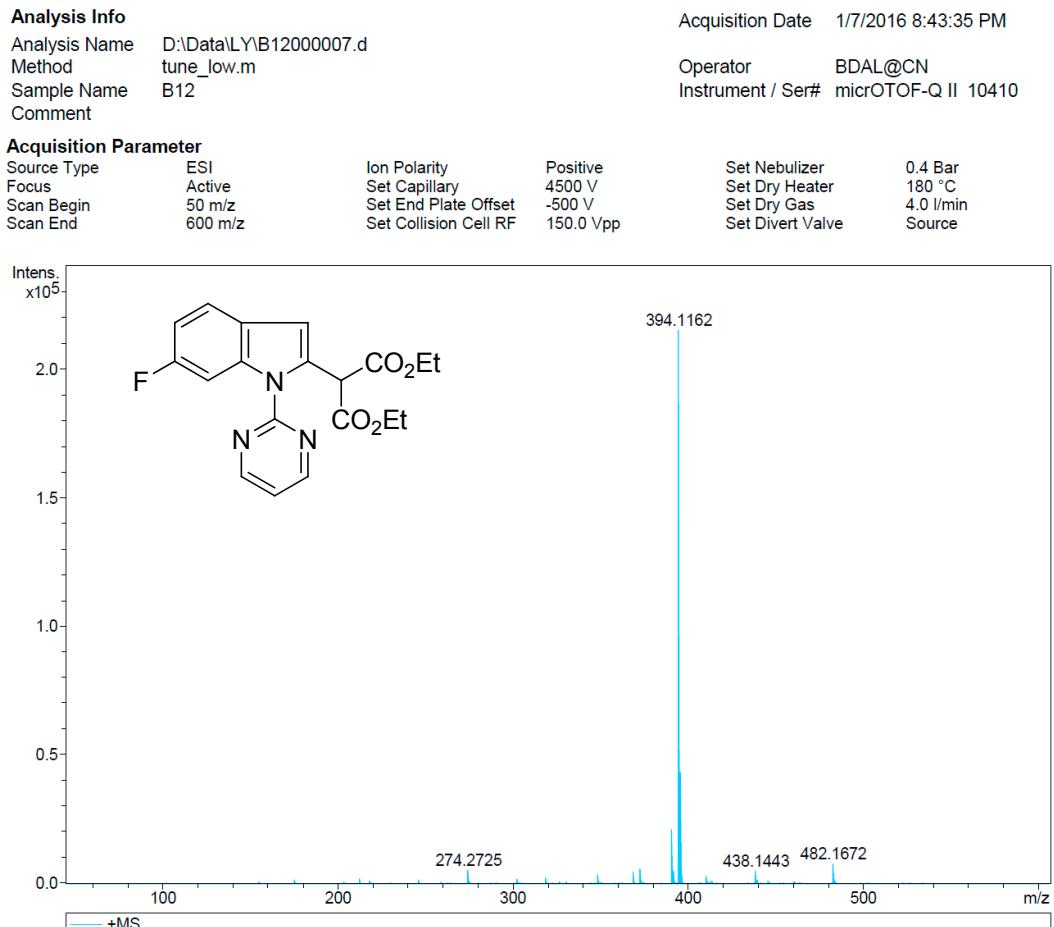


### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	274.2720	8833	20.2	10924	0.0310
2	319.1975	11001	15.4	8780	0.0290
3	360.3224	10540	38.3	30468	0.0342
4	410.0879	11660	37.2	37968	0.0352
5	434.1319	15243	237.0	324644	0.0285
6	435.1340	10900	42.8	59192	0.0399
7	482.1685	14444	285.9	274552	0.0334
8	483.1695	13690	86.6	82504	0.0353
9	484.1731	13014	12.3	11592	0.0372
10	498.1587	11957	47.1	39808	0.0417
11	499.1641	9731	10.1	8476	0.0513
12	526.1948	13098	66.6	40128	0.0402
13	527.1937	11091	16.2	9564	0.0475

**Figure S34.** HRMS of 31.





### Mass Spectrum List Report

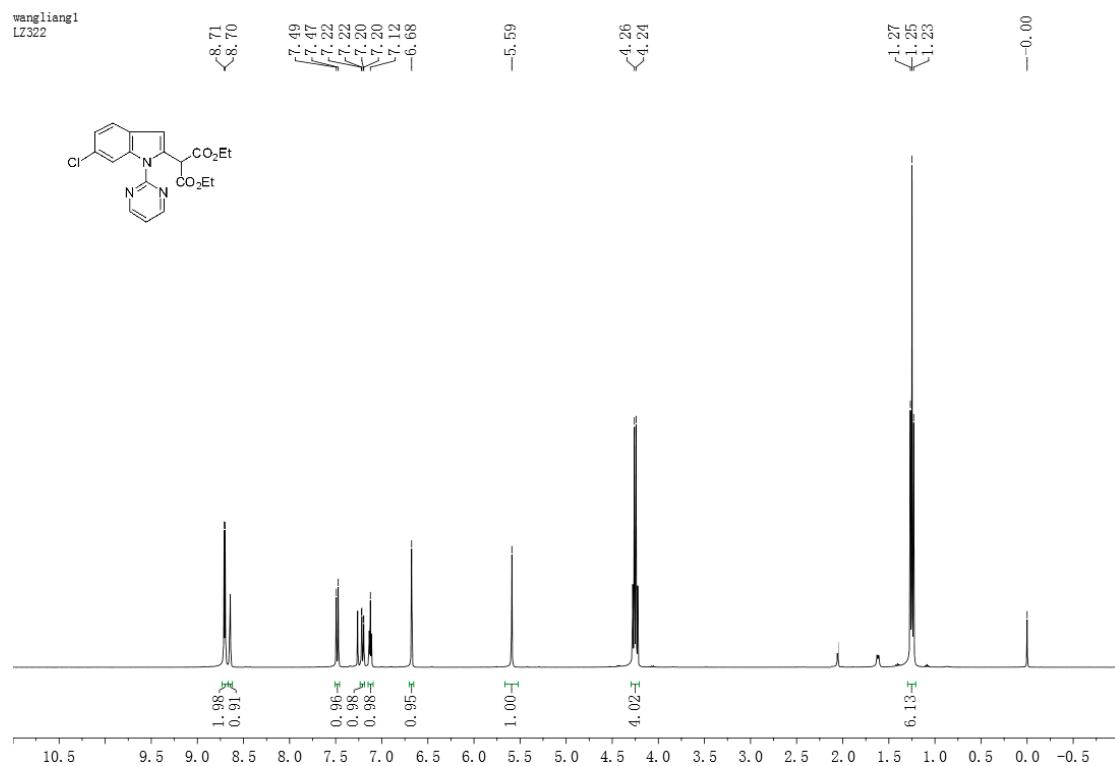
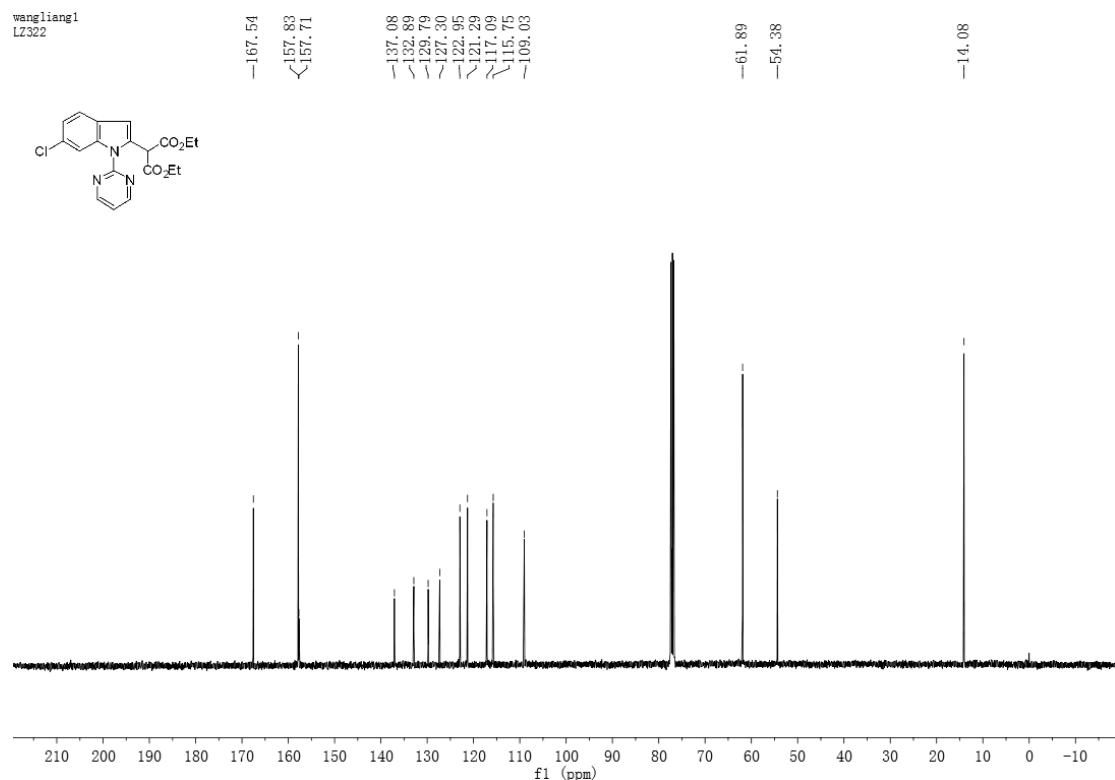
#	m/z	Res.	S/N	I	FWHM
1	274.2725	7958	13.5	5360	0.0345
2	390.1412	10366	18.6	21076	0.0376
3	394.1162	13001	177.4	215260	0.0303
4	395.1202	11672	35.0	43128	0.0339
5	438.1443	9855	12.9	5100	0.0445
6	482.1672	9362	19.9	7808	0.0515

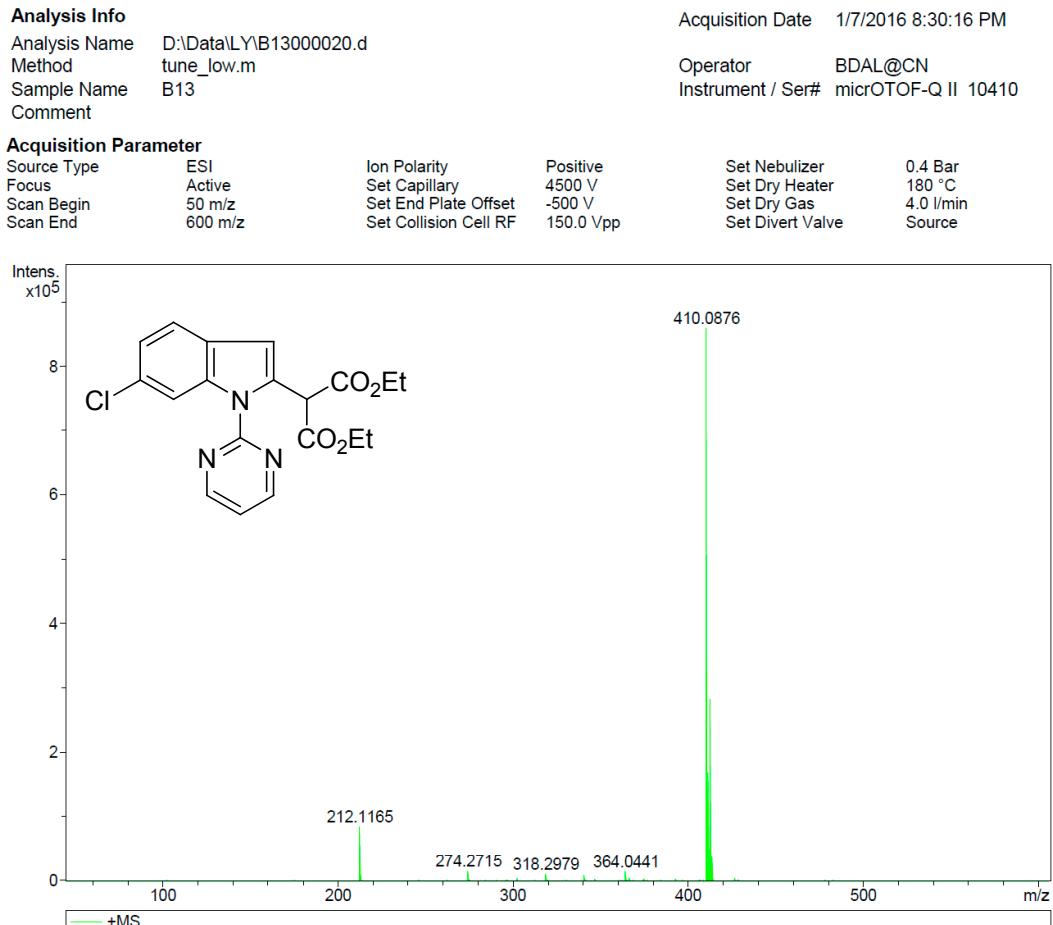
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**Figure S37.** HRMS of 3m.

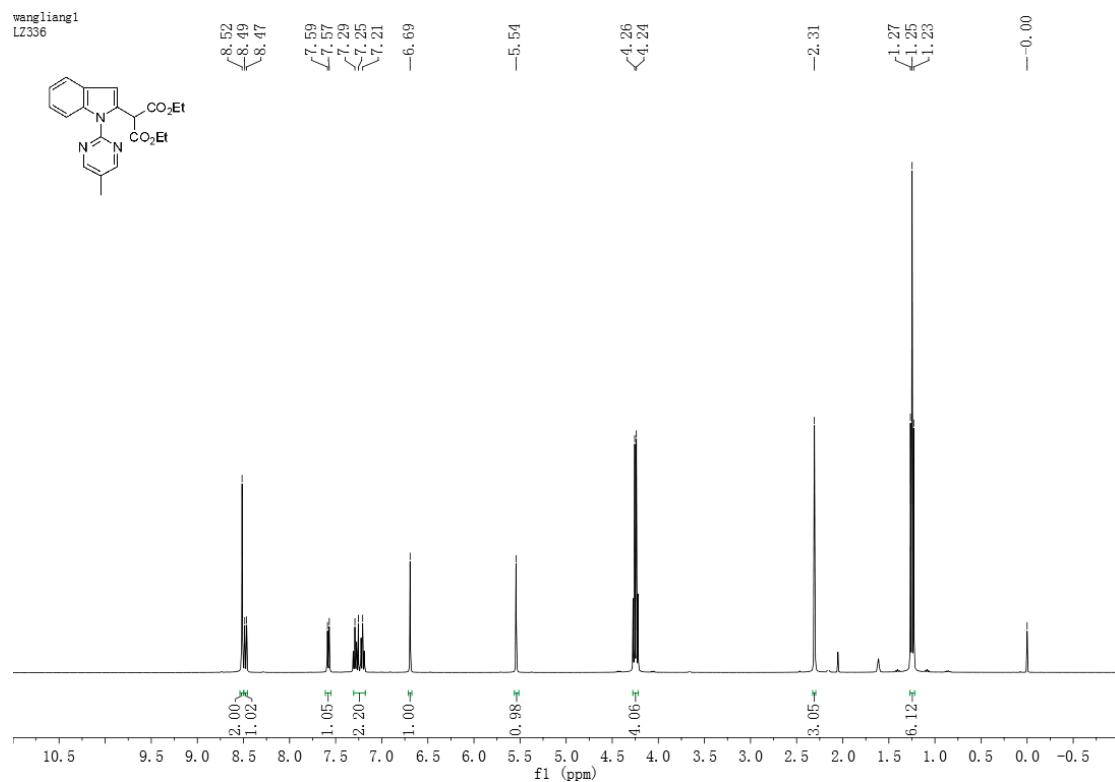
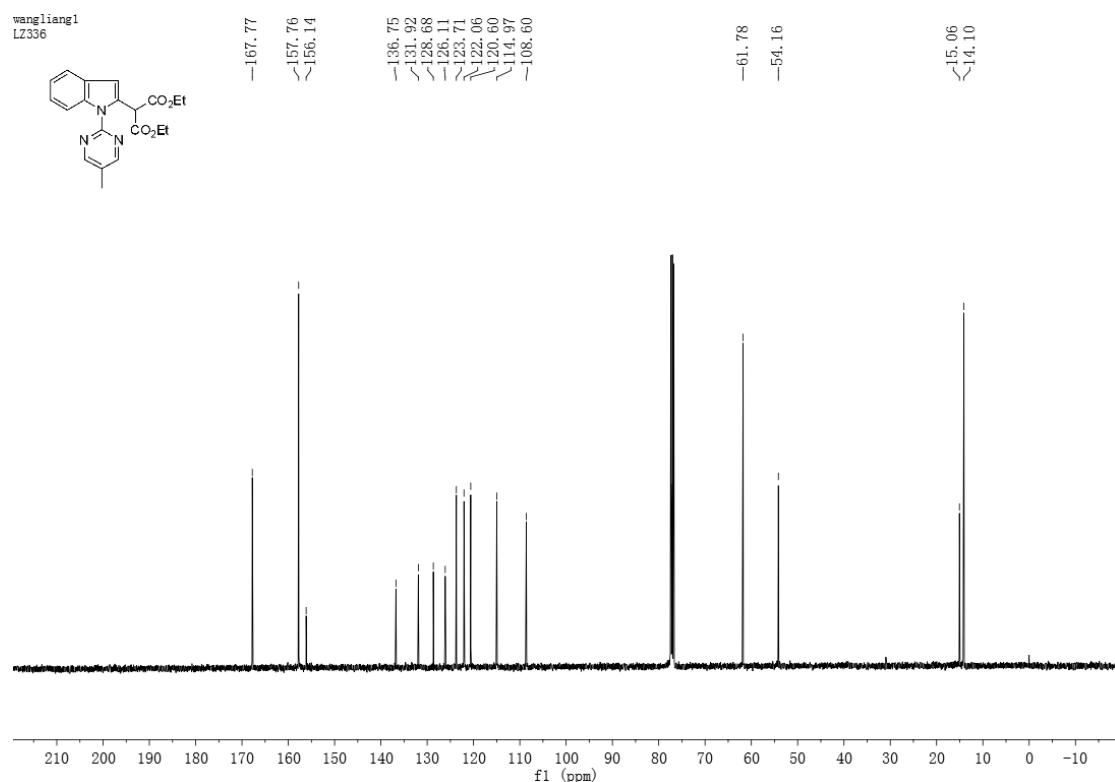
**Figure S38.**  $^1\text{H}$  NMR spectrum of 3n.**Figure S39.**  $^{13}\text{C}$  NMR spectrum of 3n.

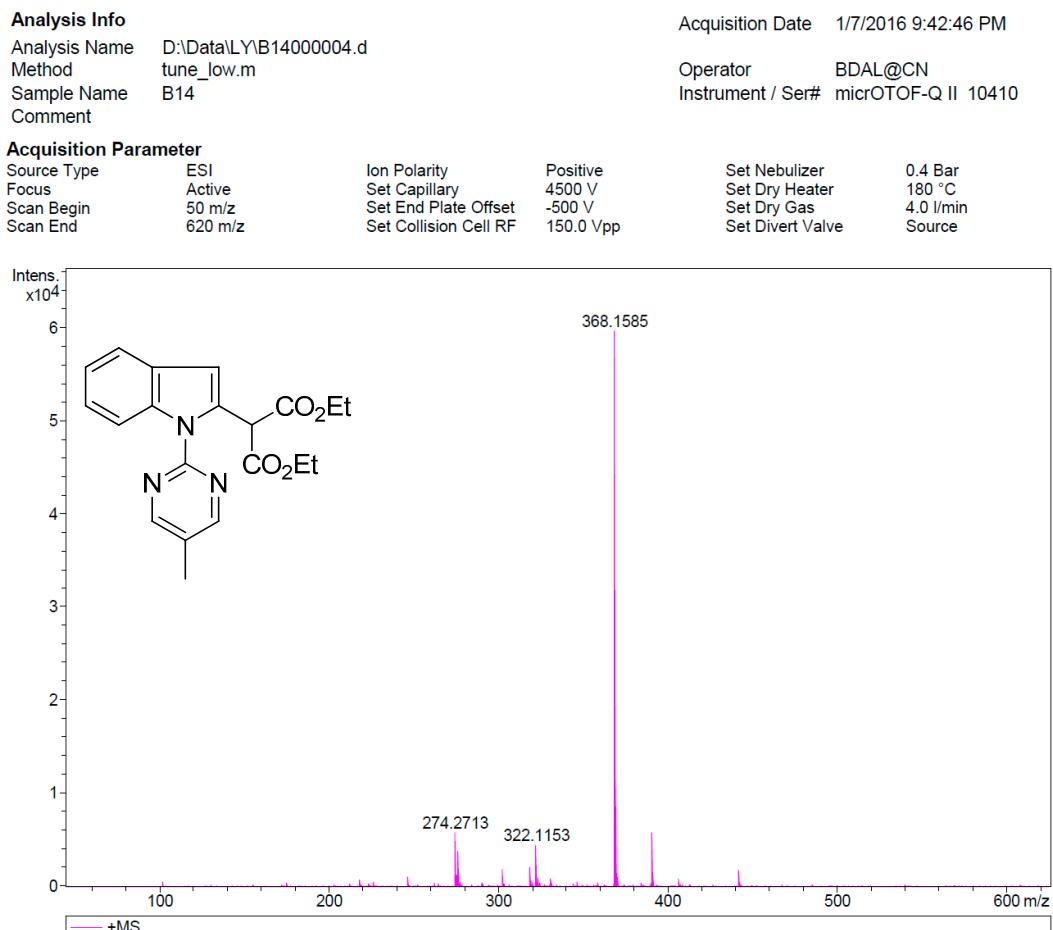


### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	212.1165	9604	122.1	86300	0.0221
2	213.1199	9096	14.6	10420	0.0234
3	274.2715	9683	32.7	16124	0.0283
4	318.2979	11597	19.2	11436	0.0274
5	340.2810	9139	15.2	9876	0.0372
6	364.0441	10386	19.8	15316	0.0351
7	410.0876	17137	553.0	859248	0.0239
8	411.0902	13349	112.4	170096	0.0308
9	412.0850	14952	193.0	284252	0.0276
10	413.0899	10872	26.6	38040	0.0380

**Figure S40. HRMS of 3n.**

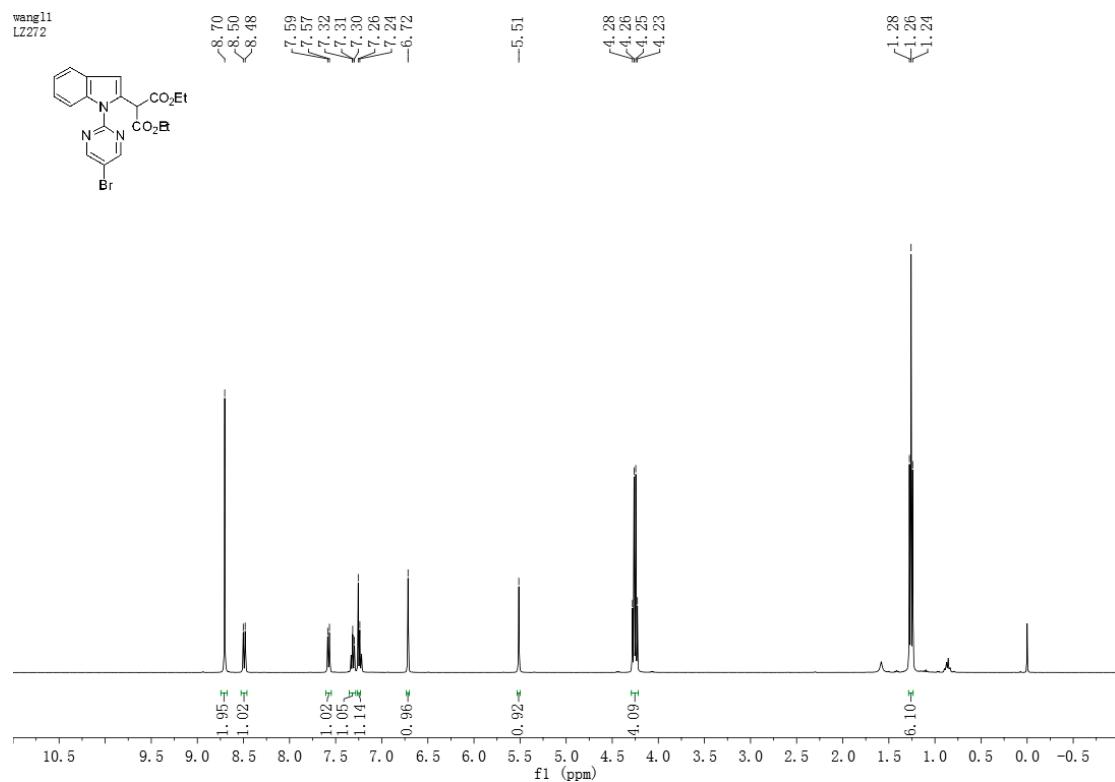
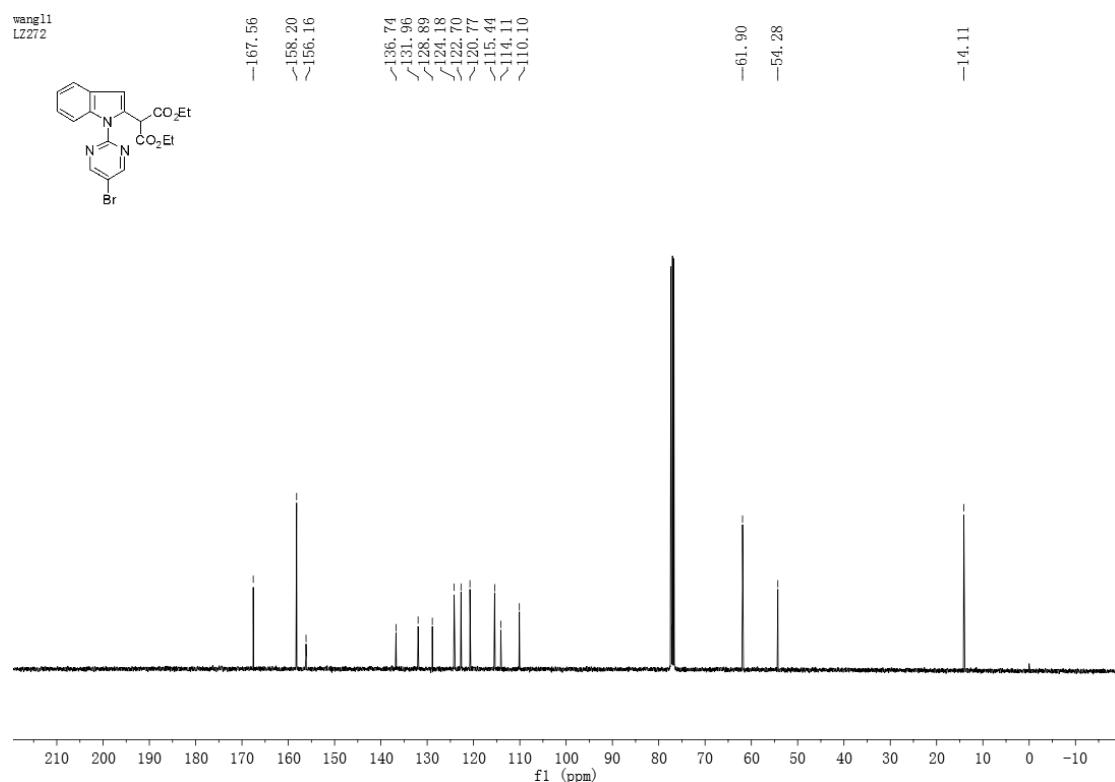
**Figure S41.**  $^1\text{H}$  NMR spectrum of **3o**.**Figure S42.**  $^{13}\text{C}$  NMR spectrum of **3o**.



### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	274.2713	8673	13.5	5800	0.0316
2	322.1153	11015	10.8	4496	0.0292
3	368.1585	11878	58.4	59584	0.0310
4	369.1657	10601	11.1	11496	0.0348

**Figure S43. HRMS of 3o.**

**Figure S44.** <sup>1</sup>H NMR spectrum of 3p.**Figure S45.** <sup>13</sup>C NMR spectrum of 3p.

**Analysis Info**

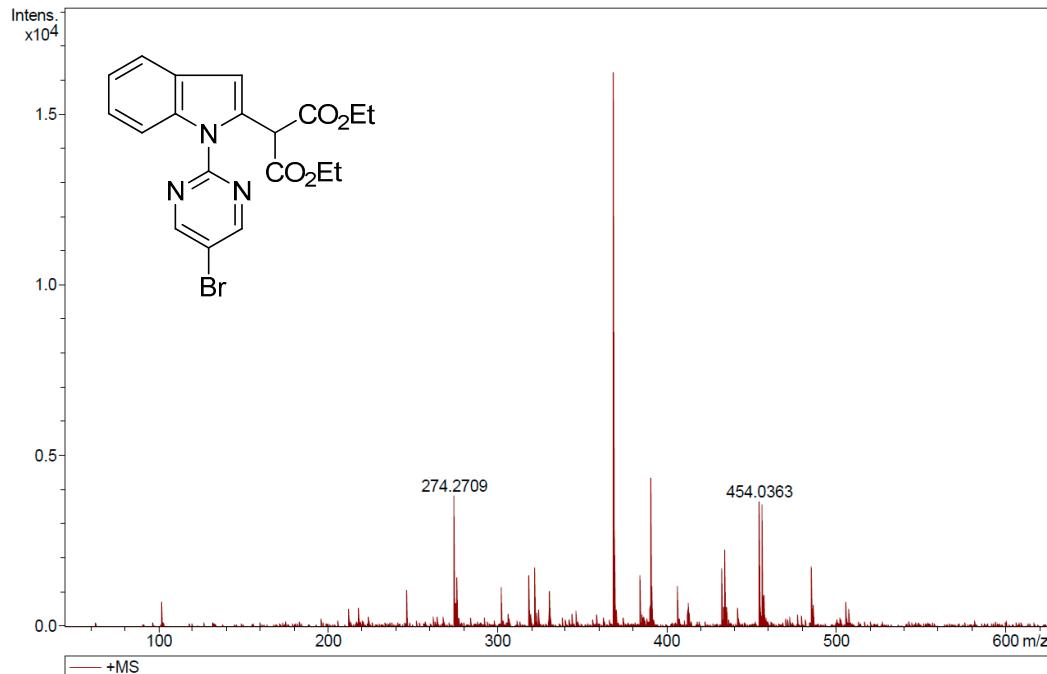
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 Method tune\_low.m  
 Sample Name B15  
 Comment

Acquisition Date 1/7/2016 9:47:54 PM

Operator BDAL@CN  
 Instrument / Ser# micrOTOF-Q II 10410

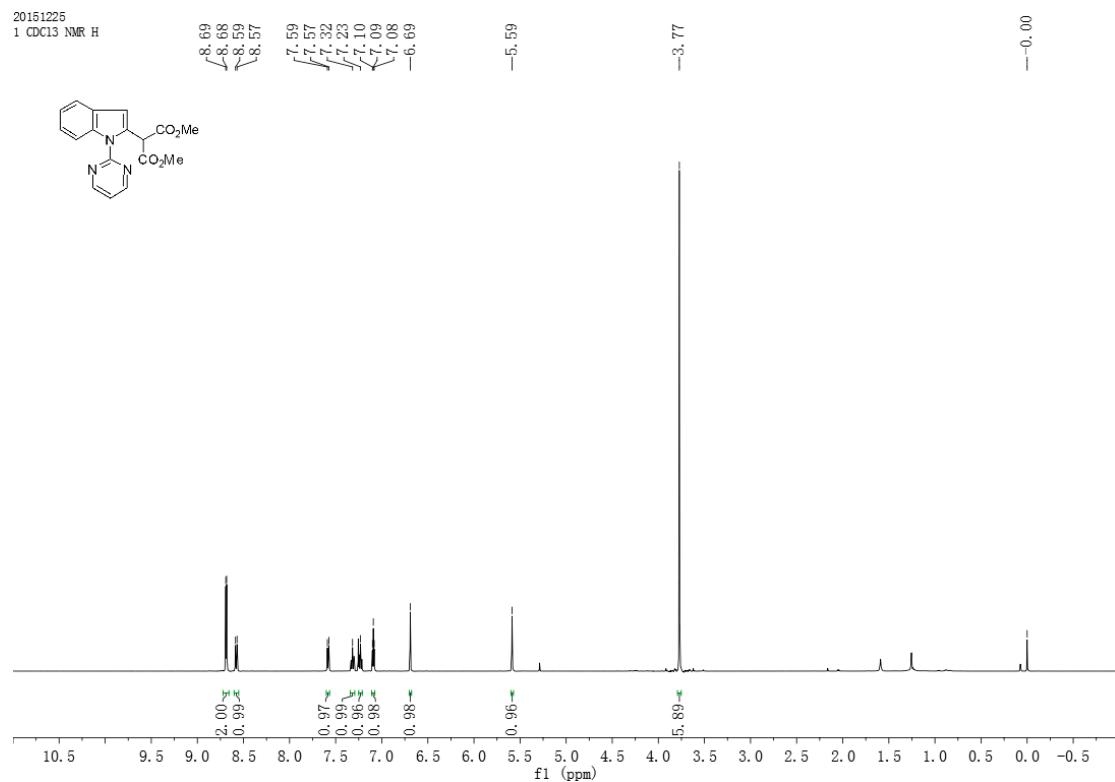
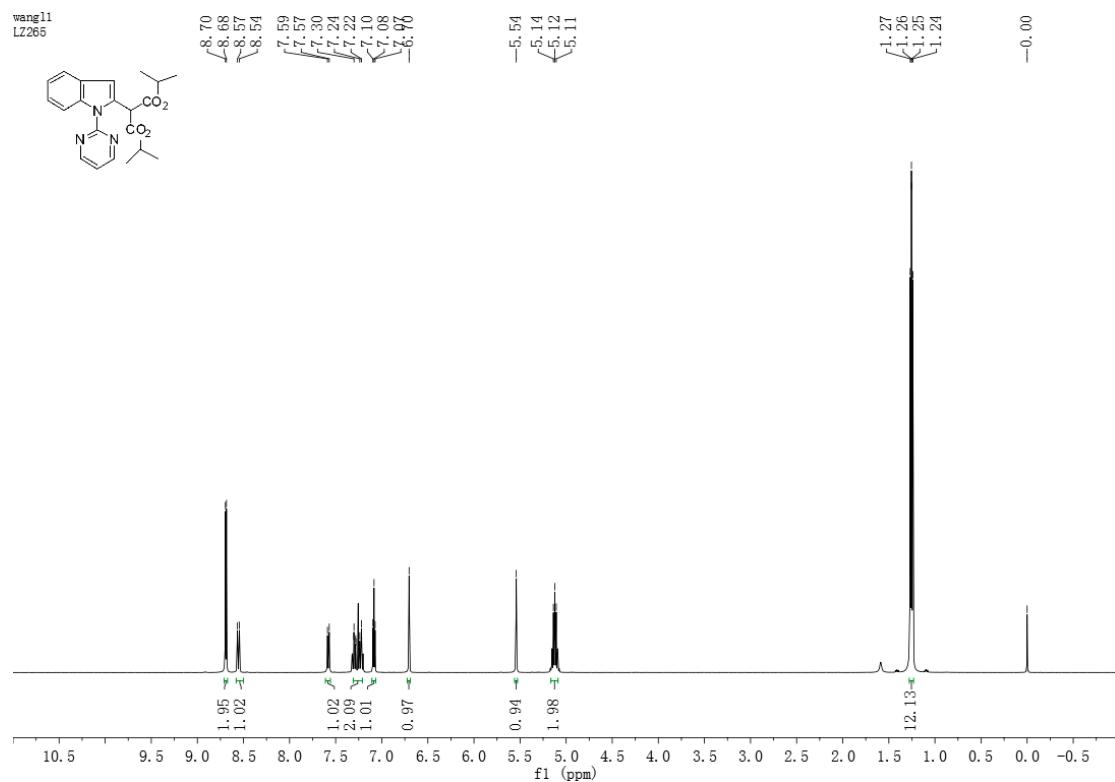
**Acquisition Parameter**

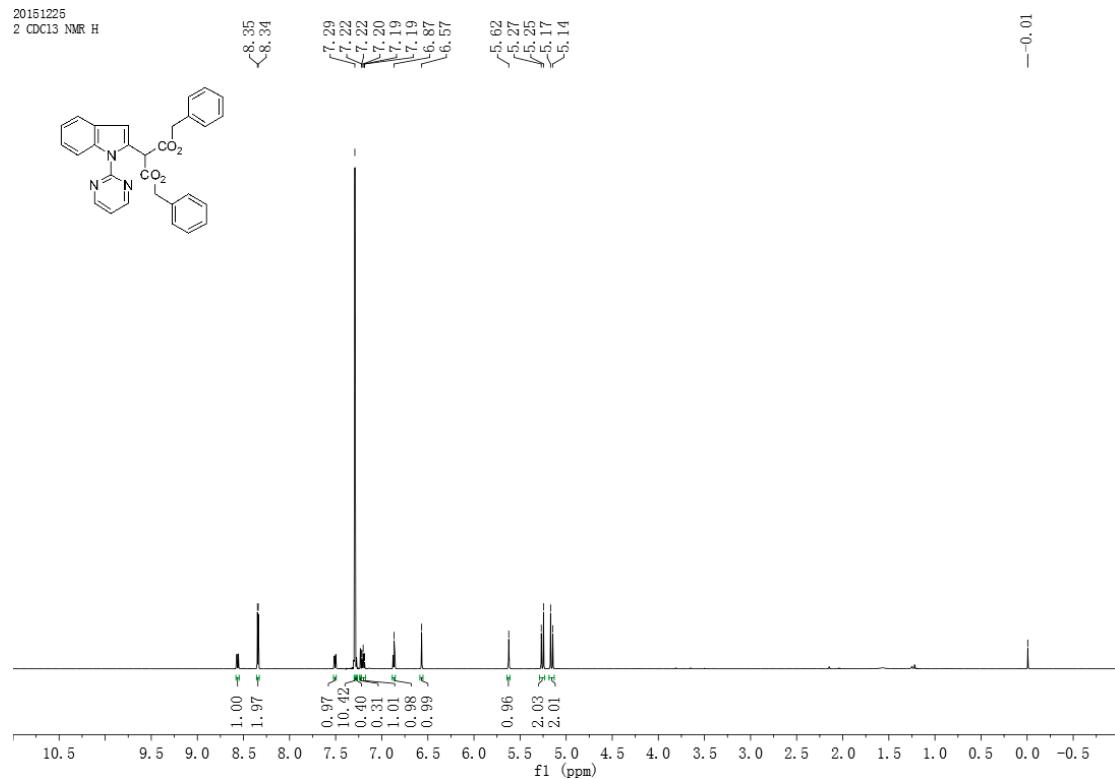
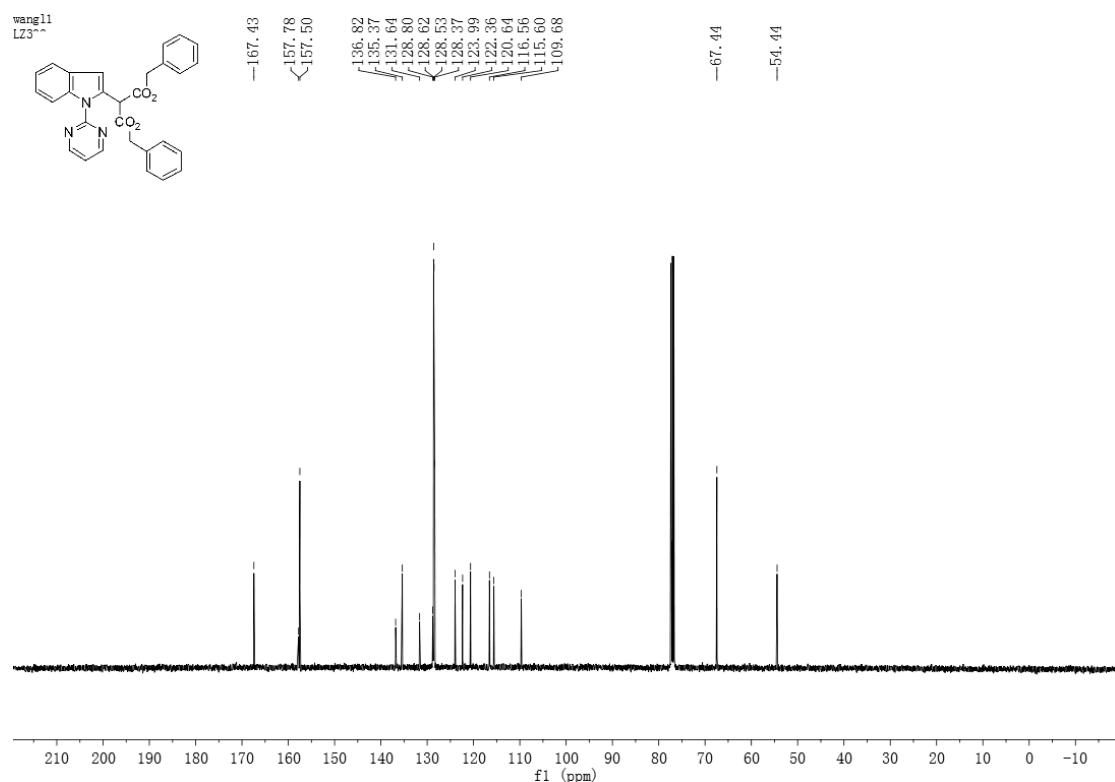
Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	620 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

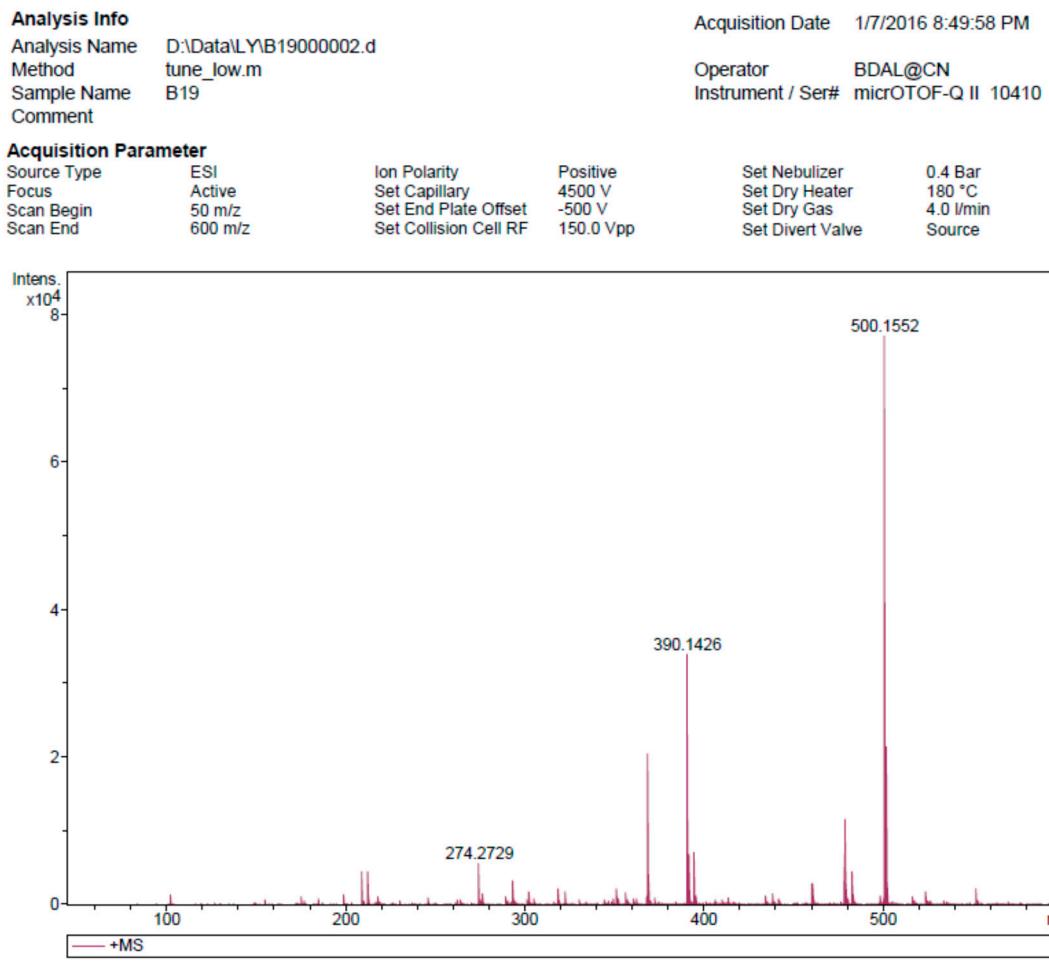
**Mass Spectrum List Report**

#	m/z	Res.	S/N	I	FWHM
1	274.2709	7586	10.3	3844	0.0362
2	432.0559	7918	3.6	1608	0.0546
3	454.0363	10561	6.2	3656	0.0430

**Figure S46.** HRMS of 3p.

**Figure S47.** <sup>1</sup>H NMR spectrum of 3q**Figure S48.** <sup>1</sup>H NMR spectrum of 3r.

**Figure S49.**  $^1\text{H}$  NMR spectrum of 3s.**Figure S50.**  $^{13}\text{C}$  NMR spectrum of 3s.



### Mass Spectrum List Report

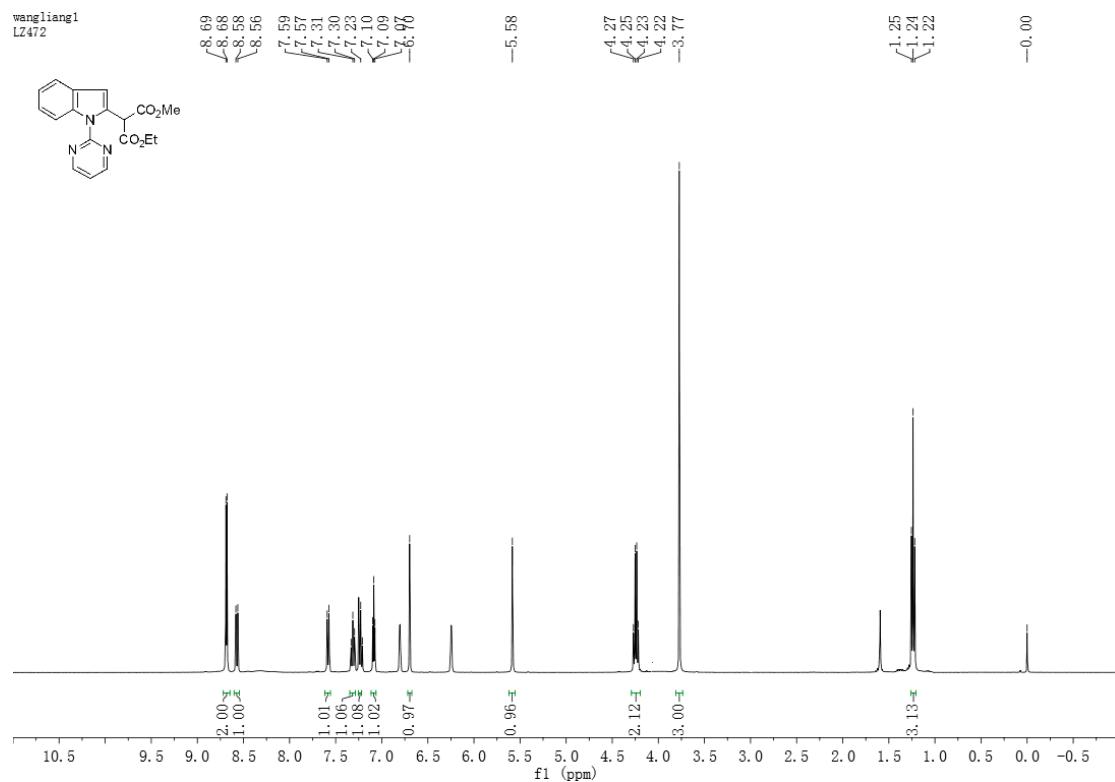
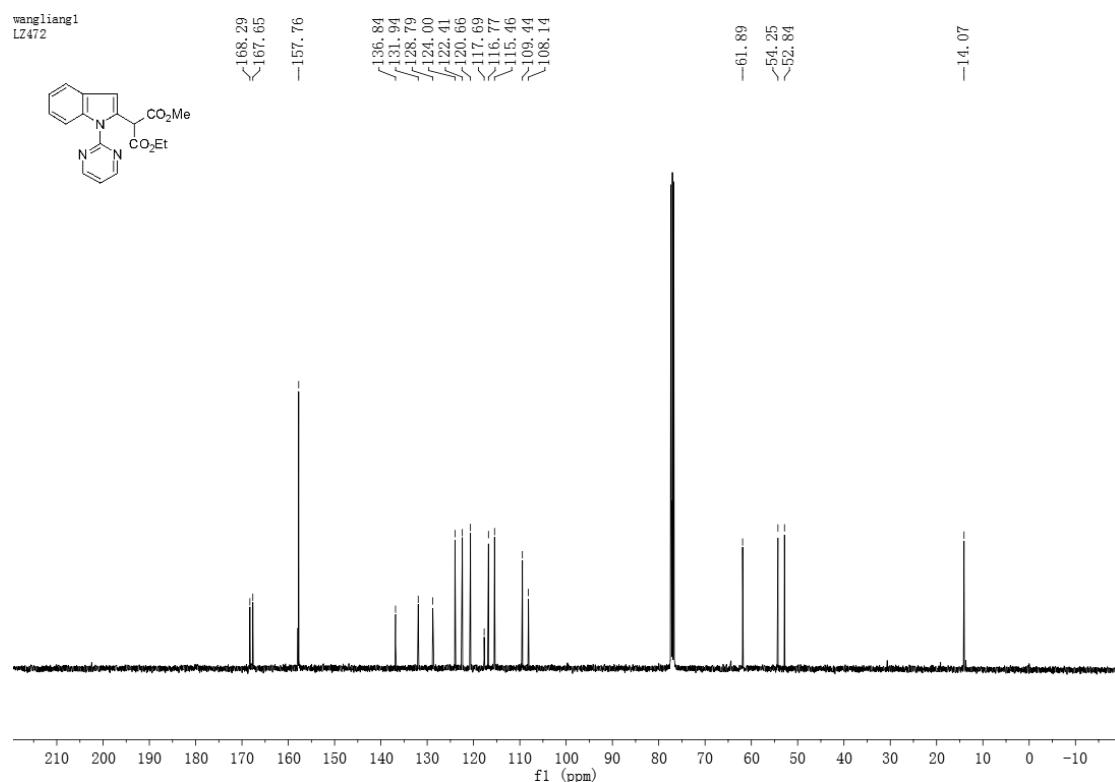
#	m/z	Res.	S/N	I	FWHM
1	274.2729	8297	12.6	5600	0.0331
2	368.1577	10984	30.5	20500	0.0335
3	390.1426	10813	45.8	33932	0.0361
4	478.1770	9548	18.5	11644	0.0501
5	500.1552	12829	76.9	77012	0.0390
6	501.1594	12267	21.1	21492	0.0409

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**Figure S51.** HRMS of 3s.

**Figure S52.**  $^1\text{H}$  NMR spectrum of **3t**.**Figure S53.**  $^{13}\text{C}$  NMR spectrum of **3t**.

## Formula Predictor Report - 1.lcd

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Data File: F:\miaohui\CESHI\jianghandaxue\1.lcd

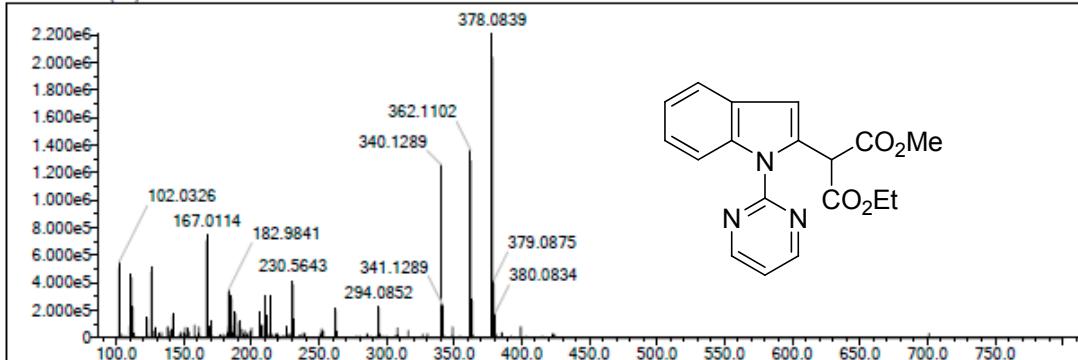
Elmt	Val.	Min	Max	Use Adduct												
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2H	1	0	0	18O	2	0	0	Cl	1	0	1	I	3	0	0	Na
B	3	0	0	F	1	0	1	Ni	2	0	0	10B	3	0	0	
C	4	0	70	Si	4	0	0	Cu	2	0	0					
N	3	0	7	P	3	0	1	Se	2	0	0					

Error Margin (mDa): 10.0  
HC Ratio: unlimited  
Max Isotopes: all  
MSn Iso RI (%): 75.00

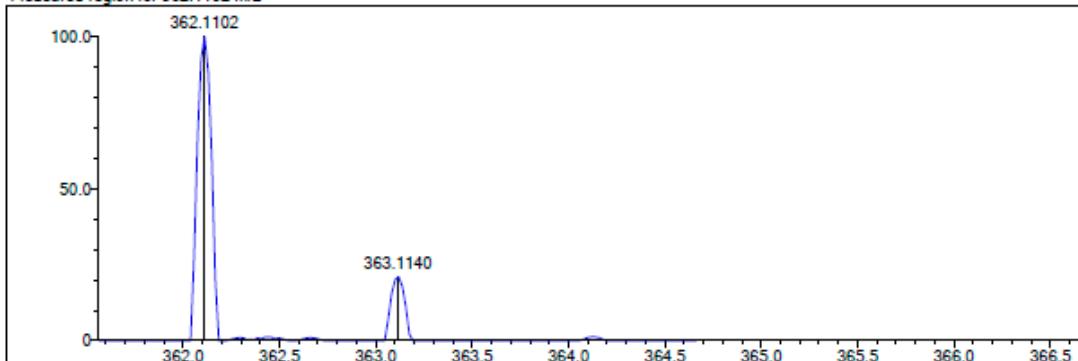
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Max Results: 800

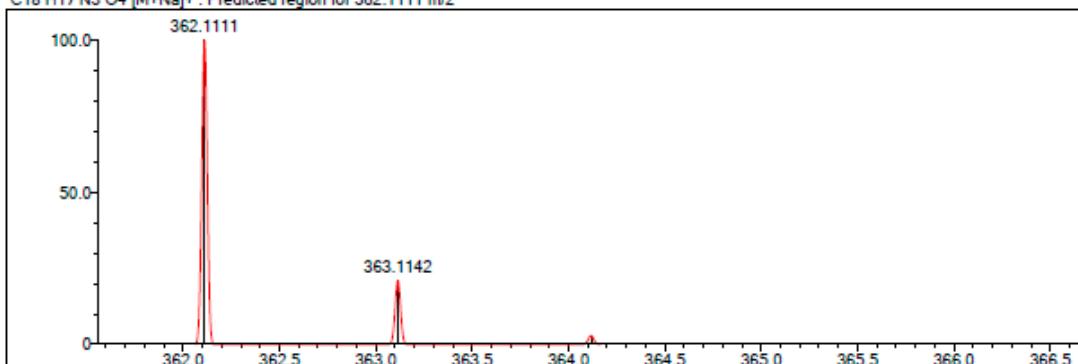
Event#: 1 MS(E+) Ret. Time : 2.200 -&gt; 2.200 Scan# : 441 -&gt; 441



Measured region for 362.1102 m/z

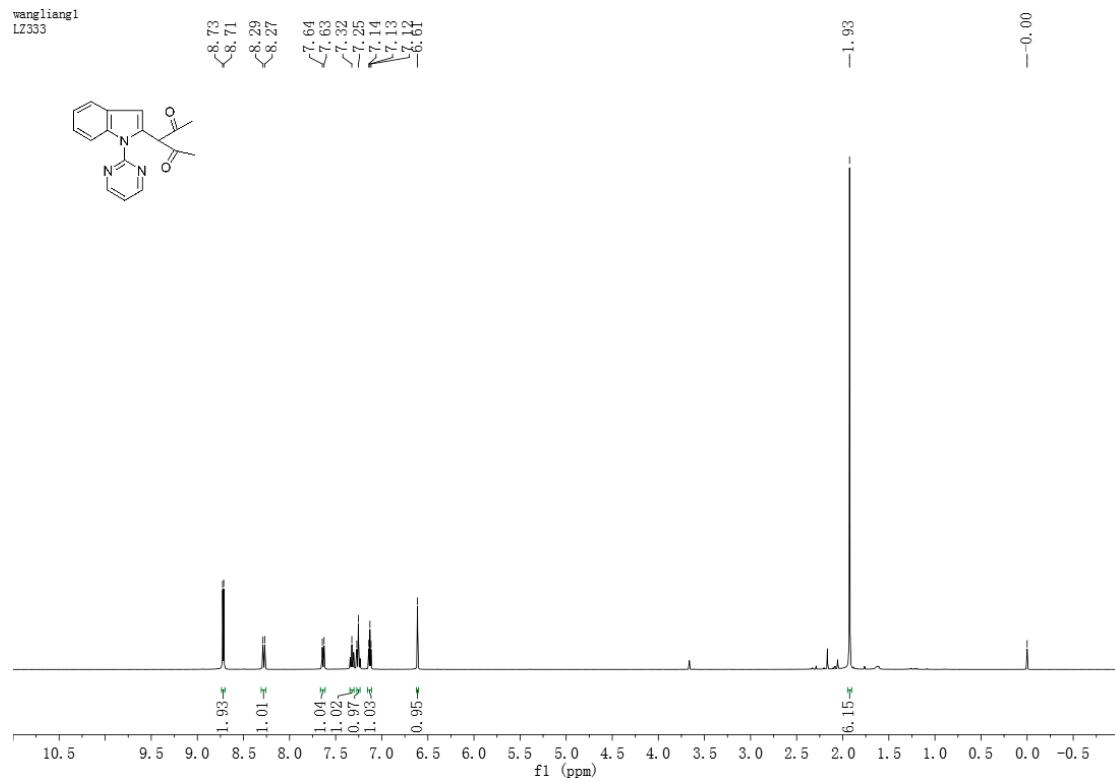
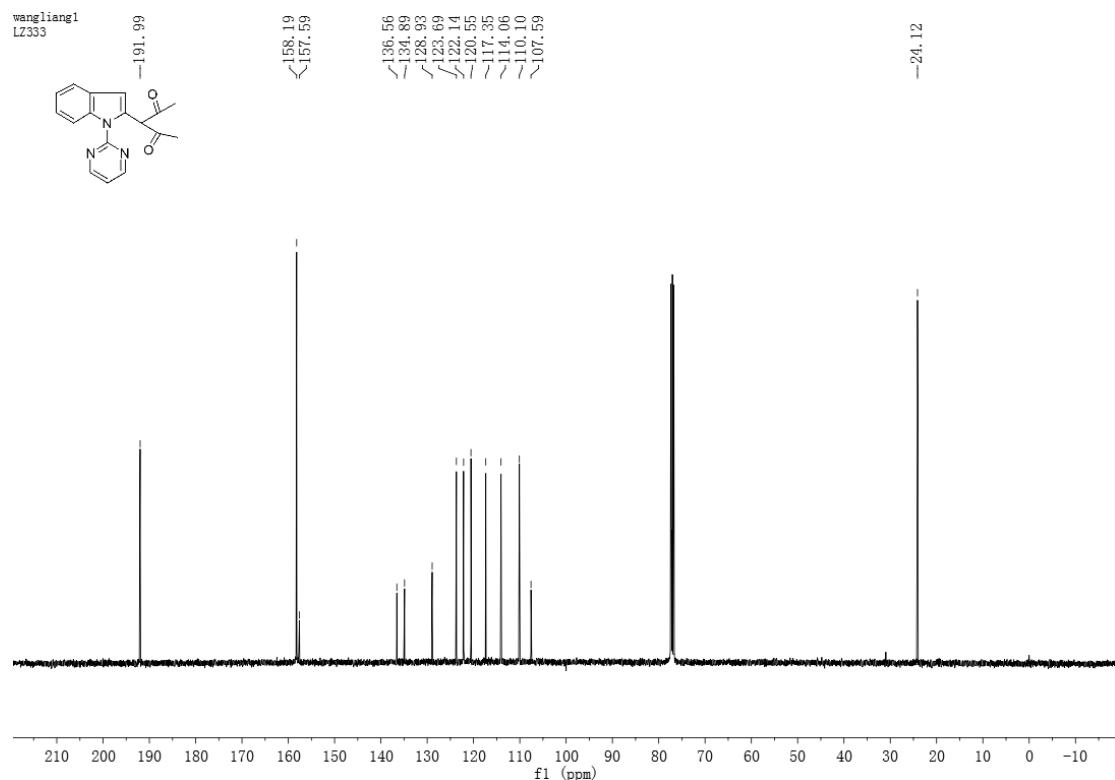


C18 H17 N3 O4 [M+Na]+ : Predicted region for 362.1111 m/z



Rank	Score	Formula (M)	Ion	Meas. m/z	Pred. m/z	Df. (mDa)	Df. (ppm)	Iso	DBE
2	75.87	C18 H17 N3 O4	[M+Na]+	362.1102	362.1111	-0.9	-2.49	78.80	12.0

Figure S54. HRMS of 3t.

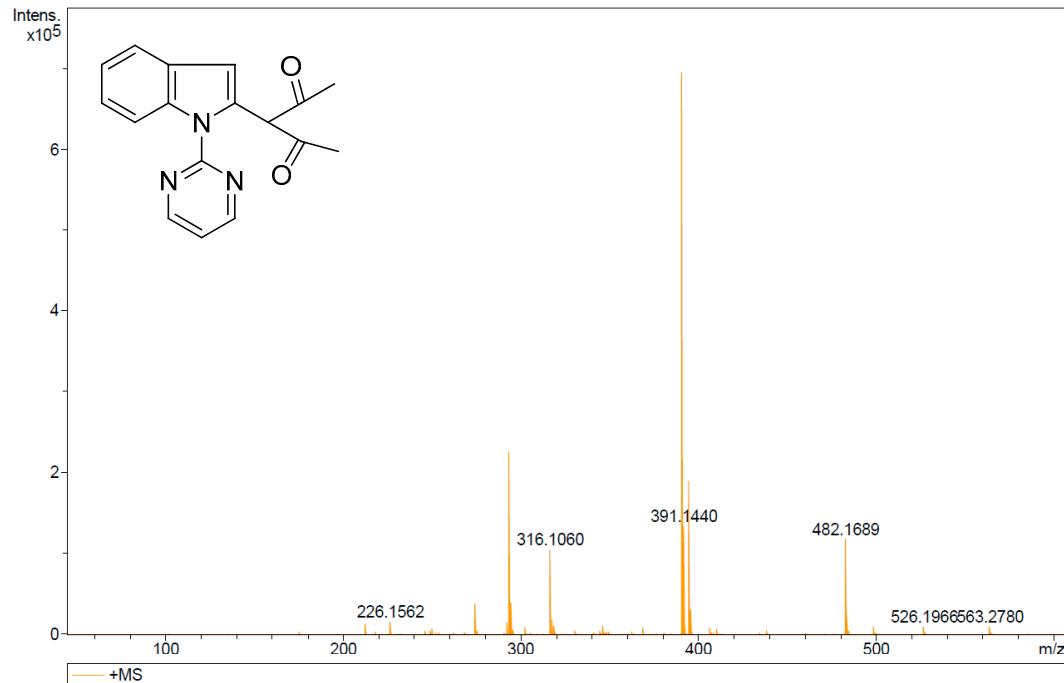
**Figure S55.** <sup>1</sup>H NMR spectrum of 3u.**Figure S56.** <sup>13</sup>C NMR spectrum of 3u.

**Analysis Info**

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Sample Name	B17	Instrument / Ser#	micrOTOF-Q II 10410
Comment			

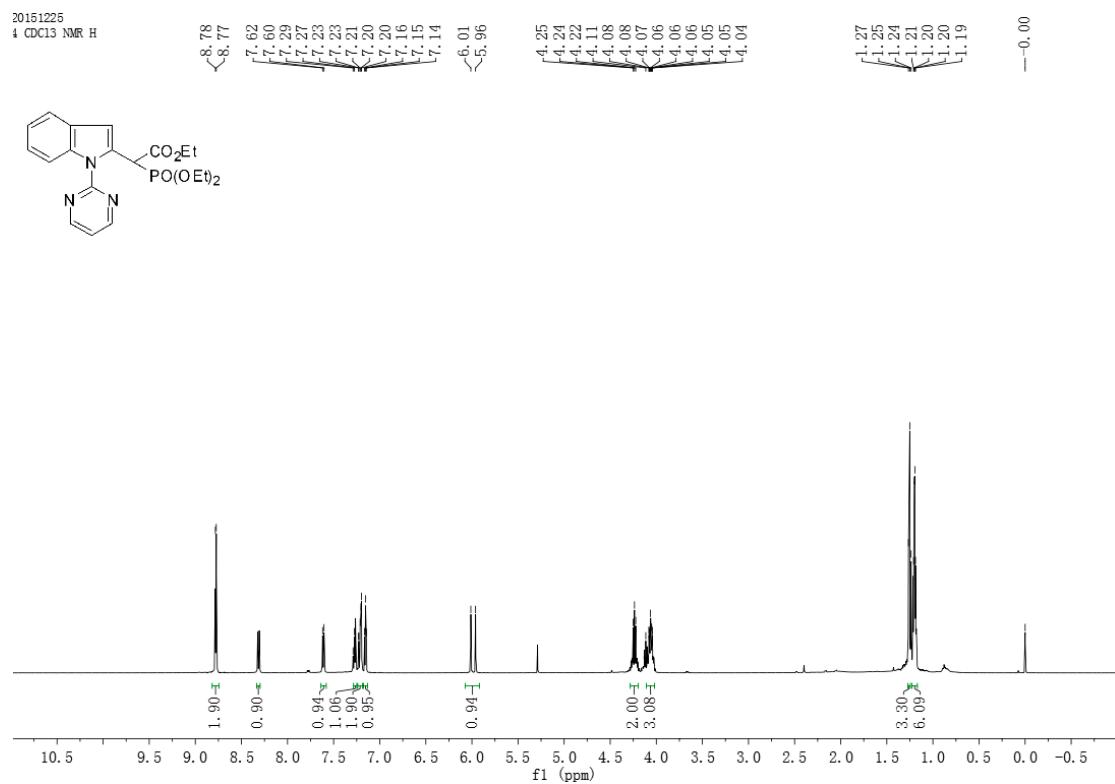
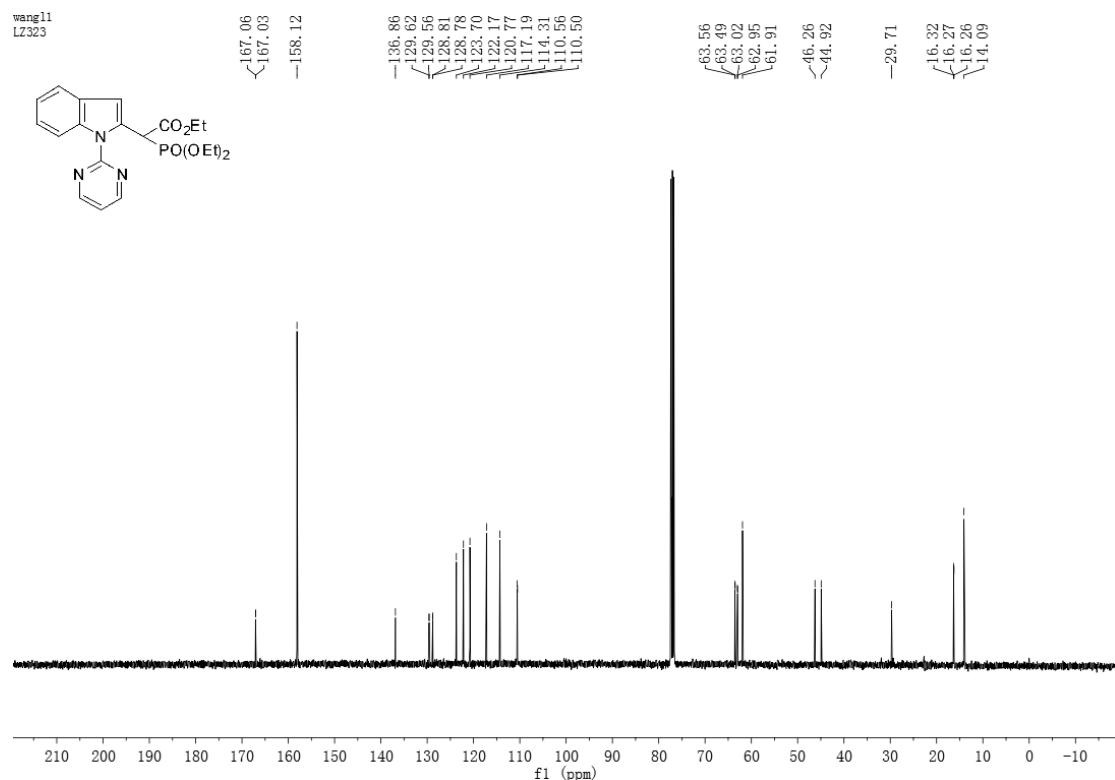
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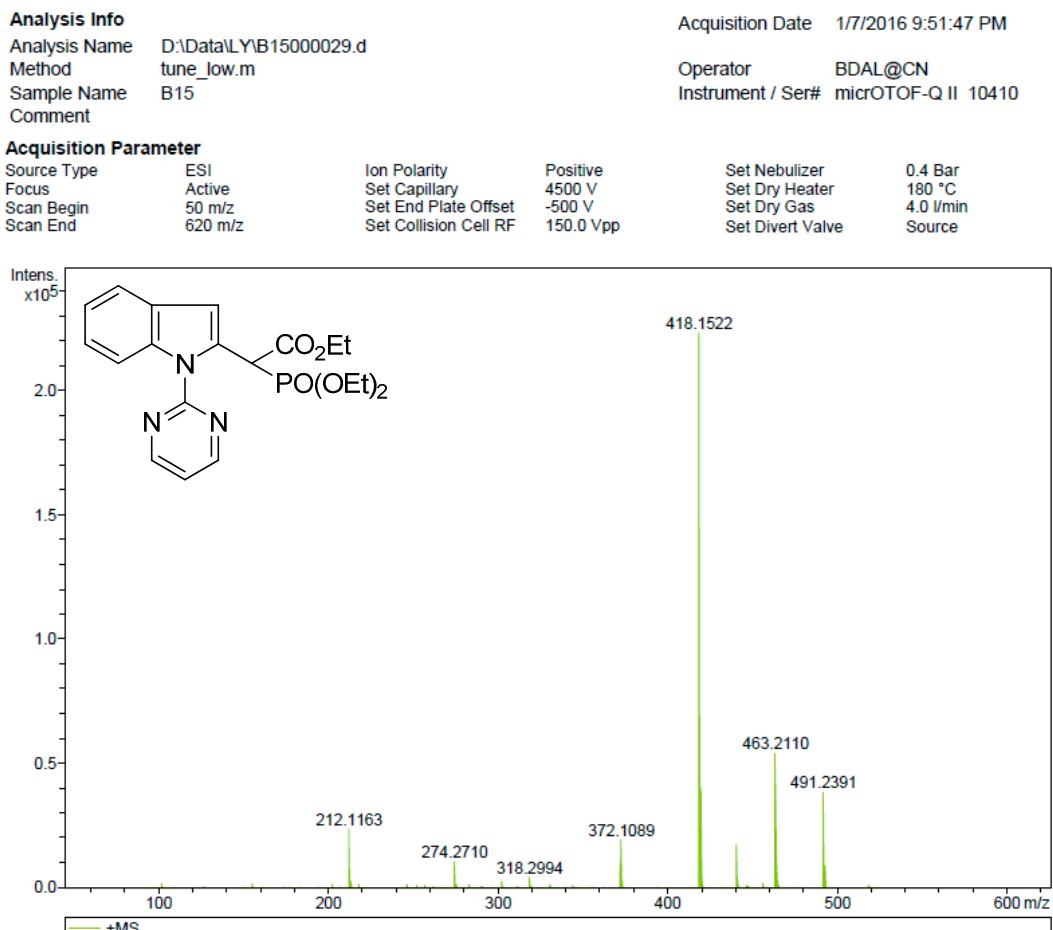
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Focus	Active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	600 m/z	Set Collision Cell RF	150.0 Vpp	Set Divert Valve	Source

**Mass Spectrum List Report**

#	$m/z$	Res.	S/N	I	FWHM
1	175.1239	9599	12.3	3728	0.0182
2	212.1154	9063	18.1	13952	0.0234
3	226.1562	10859	22.6	16508	0.0208
4	250.0943	10254	12.3	7800	0.0244
5	274.2720	9742	23.6	38352	0.0282
6	294.1319	9417	19.5	39684	0.0312
7	316.1060	11010	67.1	105256	0.0287
8	317.1067	10920	12.5	19292	0.0290
9	391.1440	12678	77.7	134352	0.0309
10	395.1215	10721	17.2	31700	0.0369
11	482.1689	13873	204.6	118036	0.0348
12	483.1684	11002	46.5	26636	0.0439
13	484.1739	14722	10.1	5720	0.0329
14	498.1595	8764	19.8	9976	0.0568
15	526.1966	9336	23.6	10648	0.0564
16	563.2780	10531	24.8	10360	0.0535

**Figure S57. HRMS of 3u.**

**Figure S58.** <sup>1</sup>H NMR spectrum of 3v.**Figure S59.** <sup>13</sup>C NMR spectrum of 3v.



### Mass Spectrum List Report

#	m/z	Res.	S/N	I	FWHM
1	212.1163	9028	40.9	23724	0.0235
2	274.2710	8977	22.9	10640	0.0306
3	318.2994	11519	11.6	4384	0.0276
4	372.1089	10525	59.3	19344	0.0354
5	373.1130	11814	10.9	3536	0.0316
6	418.1522	14316	341.3	223192	0.0292
7	419.1542	11919	60.4	40388	0.0352
8	440.1347	10577	18.0	17680	0.0416
9	463.2110	12671	61.8	54288	0.0366
10	464.2157	9764	10.9	9344	0.0475
11	491.2391	11900	123.5	38608	0.0413
12	492.2462	10544	29.6	9216	0.0467

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**Figure S60. HRMS of 3v.**

### References

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2. Shi, J.-J.; Zhou, B.; Yang, Y.-X.; Li, Y.-C. Rhodium-catalyzed regioselective amidation of indoles with sulfonyl azides via C–H bond activation. *Org. Biomol. Chem.* **2012**, *10*, 8953–8955.
3. Xu, S.; Huang, X.; Hong, X.; Xu, B. Palladium-assisted regioselective C–H cyanation of heteroarenes using isonitrile as cyanide source. *Org. Lett.* **2012**, *14*, 4614–4617.
4. Wang, L.; Li, Z.; Qu, X.; Peng, W.-M.; Hu, S.-Q.; Wang, H.-B. Sequential one-pot Rh(III)-catalyzed direct C2 and C7 alkylation of (hetero)aromatic C–H bonds of indoles. *Tetrahedron Lett.* **2015**, *56*, 6214–6218.
5. Liu, X.-G.; Zhang, S.-S.; Wu, J.-Q.; Li, Q.-J.; Wang, H.-G. Cp\*Co(III)-catalyzed direct functionalization of aromatic C–H bonds with  $\alpha$ -diazomalonates. *Tetrahedron Lett.* **2015**, *56*, 4093–4095.