

# Supporting Information

## Copper-catalyzed regioselective [3 + 2] annulation of malonate-tethered acyl oximes with isatins

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## Experimental section

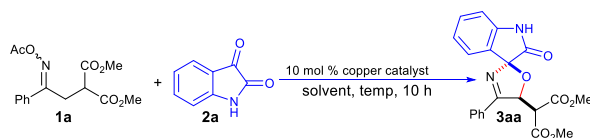
### General

Unless otherwise noted, all reactions were carried out without exclusion of air or moisture. All solvents and reagents were used without further purification as commercially available. Thin-layer chromatography (TLC) was performed on silica gel plates (60F–254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (300–400 mesh). NMR (400 MHz for  $^1\text{H}$  NMR, 100 MHz for  $^{13}\text{C}$  NMR) spectra were recorded in  $\text{CDCl}_3$  or DMSO with TMS as the internal standard. Chemical shifts are reported in ppm and coupling constants are given in Hz. Data for  $^1\text{H}$  NMR are recorded as follows: chemical shift (ppm), multiplicity (s, singlet; d, doublet; t, triplet; q, quarter; m, multiplet), coupling constant (Hz), integration. Data for  $^{13}\text{C}$  NMR are reported in terms of chemical shift ( $\delta$ , ppm). High-resolution mass spectra (HRMS) were obtained on an Agilent mass spectrometer using ESI-TOF (electrospray ionization time of flight).

All the acyl oximes were all known compounds and synthesized according to previously reported literature procedure.<sup>1</sup>

### Optimization table S1

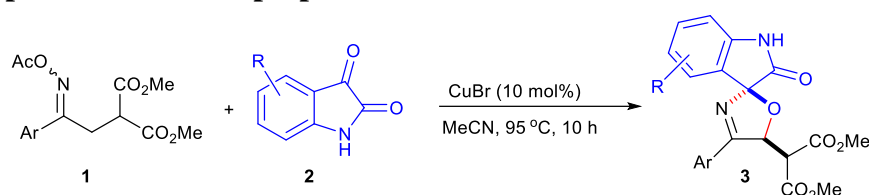
Copper-catalyzed [3 + 2] annulation of malonate-tethered acyl oximes with isatin **2a**<sup>a</sup>



Entry	Catalyst	Solvent	Temp (°C)	Yield (%) <sup>b</sup>
1	CuI	DCE	95	57
2	CuBr	DCE	95	68
3	CuCl	DCE	95	53
4	CuOAc	DCE	95	46
5	CuCl <sub>2</sub>	DCE	95	trace
6	CuBr <sub>2</sub>	DCE	95	trace
7	CuCN	DCE	95	trace
8	CuBr	THF	95	71
9	CuBr	toluene	95	57
10	CuBr	MeCN	95	75
11	CuBr	DMSO	95	39
12	CuBr	EA	95	42
13	CuBr	MeCN	80	71
14 <sup>b</sup>	CuBr	MeCN	105	72

<sup>a</sup>Reaction conditions: acetyl oxime **1a** (0.3 mmol), isatin **2a** (0.2 mmol), copper salt (10 mol%) in solvent (2 mL) for 10 h under  $\text{N}_2$ . <sup>b</sup>Isolated yields.

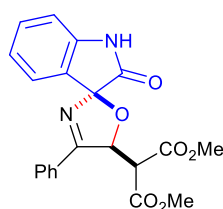
## General procedure for the preparation of 3



A mixture of acyl oximes **1** (0.30 mmol), isatins **2** (0.20 mmol), and CuBr (2.84 mg, 0.02 mmol) in CH<sub>3</sub>CN (2 mL) was stirred at 95 °C for 10 h under N<sub>2</sub> atmosphere until completion of the reaction as determined by TLC. After cooling to room temperature, ammonium hydroxide (10%, 10 mL) was added and the mixture was extracted with EtOAc (3 x 20 mL). The combined organic phase was dried over Na<sub>2</sub>SO<sub>4</sub>, filtered, and concentrated under reduced pressure. The residue was purified by column chromatography (PE: EA) to give the products **3**.

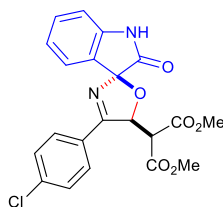
## Compounds characterization

### Dimethyl 2-(2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (**3aa**)



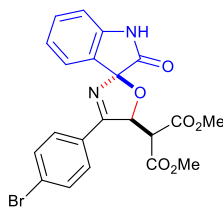
Prepared according to general procedure to afford **3aa** (59 mg, 75% yield) as a white solid; m.p. 186–187 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.11 (s, 1H), 7.65 (d, *J* = 6.9 Hz, 2H), 7.43–7.36 (m, 4H), 7.24–7.19 (m, 1H), 7.00 (t, *J* = 7.5 Hz, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.22 (d, *J* = 3.6 Hz, 1H), 4.04 (d, *J* = 3.7 Hz, 1H), 3.63 (s, 3H), 3.58 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 172.6, 166.9, 166.0, 141.4, 131.7, 131.2, 130.7, 128.8, 127.9, 126.5, 126.2, 123.4, 110.6, 84.3, 54.8, 52.9, 52.7; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>18</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 417.1063, Found 417.1061.

### Dimethyl 2-(4'-(4-chlorophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (**3ba**)

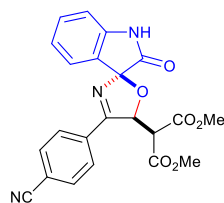


Prepared according to general procedure to afford **3ba** (65 mg, 76% yield) as a yellow solid; m.p. 170–171 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.16 (s, 1H), 7.60 (d, *J* = 8.6 Hz, 2H), 7.36–7.33 (m, 3H), 7.24–7.19 (m, 1H), 7.02–6.97 (m, 1H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 3.6 Hz, 1H), 4.01 (d, *J* = 3.6 Hz, 1H), 3.65 (s, 3H), 3.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.7, 171.6, 166.7, 165.9, 141.3, 137.8, 131.3, 129.4, 129.2, 129.1, 126.3, 126.2, 123.4, 110.7, 106.3, 84.2, 54.7, 52.9, 52.8; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>ClN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 451.0673, Found 451.0667.

### Dimethyl 2-(4'-(4-bromophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (**3ca**)

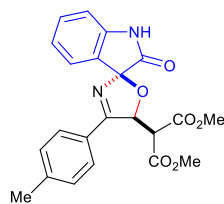


Prepared according to general procedure to afford **3ca** (74 mg, 78% yield) as a yellow solid; m.p. 158–159 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.24 (s, 1H), 7.55–7.49 (m, 4H), 7.33 (d, *J* = 7.4 Hz, 1H), 7.24–7.19 (m, 1H), 7.01–6.98 (m, 1H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.18 (d, *J* = 3.6 Hz, 1H), 4.00 (d, *J* = 3.6 Hz, 1H), 3.65 (s, 3H), 3.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.8, 171.7, 166.8, 165.9, 141.4, 132.1, 131.3, 129.6, 129.5, 126.4, 126.3, 126.2, 123.4, 110.7, 106.4, 84.2, 54.7, 52.9, 52.8; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 495.0168, Found 495.0166.

**Dimethyl 2-(4'-(4-cyanophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3da)**

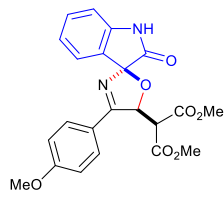
Prepared according to general procedure to afford **3da** (59 mg, 71% yield) as a yellow solid; m.p. 195–196 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.69–7.66 (m, 2H), 7.63 (s, 1H), 7.46–7.37 (m, 3H), 7.13–7.11 (m, 1H), 7.02–6.97 (m, 2H), 6.26 (d, *J* = 8.9 Hz, 1H), 4.34 (d, *J* = 8.9 Hz, 1H), 3.71 (s, 3H), 3.10 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.3, 172.9, 167.1, 166.3, 142.1, 132.2, 130.4, 128.7, 128.6, 126.7, 126.4, 125.7, 124.9, 113.9, 106.3, 84.9, 58.7, 53.1,

52.3; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>17</sub>N<sub>3</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 442.1015, Found 442.1012.

**Dimethyl 2-(2-oxo-4'-(p-tolyl)-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ea)**

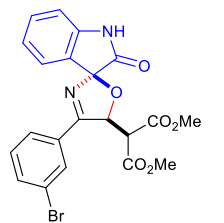
Prepared according to general procedure to afford **3ea** (68 mg, 83% yield) as a yellow solid; m.p. 202–203 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.34 (s, 1H), 7.55 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 1H), 7.21–7.16 (m, 3H), 6.98 (t, *J* = 7.6 Hz, 1H), 6.77 (d, *J* = 7.7 Hz, 1H), 6.20 (d, *J* = 3.6 Hz, 1H), 4.04 (d, *J* = 3.6 Hz, 1H), 3.63 (s, 3H), 3.59 (s, 3H), 2.31 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.3, 172.4, 166.9, 166.1, 142.2, 141.5, 131.2, 129.5, 127.9, 127.8,

126.6, 126.2, 123.3, 110.7, 106.4, 84.2, 54.9, 52.9, 52.7, 21.6; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 431.1219, Found 431.1212.

**Dimethyl 2-(4'-(4-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3fa)**

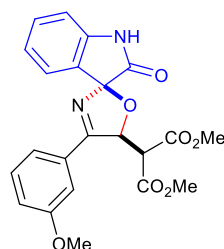
Prepared according to general procedure to afford **3fa** (65 mg, 77% yield) as a white solid; m.p. 193–195 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.44 (s, 1H), 7.63–7.60 (m, 2H), 7.36 (d, *J* = 7.3 Hz, 1H), 7.20–7.16 (m, 1H), 6.97 (t, *J* = 7.6 Hz, 1H), 6.87 (d, *J* = 8.6 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.19 (d, *J* = 3.6 Hz, 1H), 4.04 (d, *J* = 3.8 Hz, 1H), 3.76 (s, 3H), 3.63 (s, 3H), 3.59 (s, 3H);

<sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.4, 171.7, 166.9, 166.3, 162.3, 141.5, 131.1, 129.8, 126.7, 126.1, 123.3, 123.00, 114.2, 110.7, 106.3, 84.0, 55.4, 55.2, 52.9, 52.7; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 447.1168, Found 447.1163.

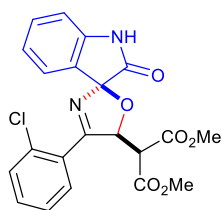
**Dimethyl 2-(4'-(3-bromophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ga)**

Prepared according to general procedure to afford **3ga** (60 mg, 64% yield) as a pale sticky oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.49 (s, 1H), 7.92–7.91 (m, 1H), 7.63–7.61 (m, 2H), 7.40 (d, *J* = 7.4 Hz, 1H), 7.35–7.26 (m, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.8 Hz, 1H), 6.25 (d, *J* = 3.7 Hz, 1H), 4.10 (d, *J* = 3.7 Hz, 1H), 3.74 (s, 3H), 3.69 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.8, 171.5, 166.7, 166.0, 141.4, 134.6, 132.7, 131.4, 130.9, 130.3, 126.5, 126.2, 126.1,

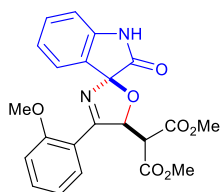
123.5, 122.9, 110.8, 106.3, 84.3, 54.7, 53.0, 52.9; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 495.0168, Found 495.0163.

**Dimethyl 2-(4'-(3-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ha)**

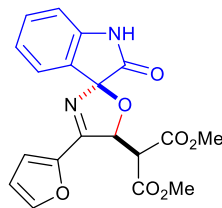
Prepared according to general procedure to afford **3ha** (53 mg, 63% yield) as a white solid; m.p. 187–188 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.08 (s, 1H), 7.29–7.13 (m, 4H), 7.15 (d, *J* = 7.4 Hz, 1H), 6.99–6.94 (m, 2H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.27 (d, *J* = 8.9 Hz, 1H), 4.39 (d, *J* = 8.9 Hz, 1H), 3.77 (s, 3H), 3.69 (s, 3H), 3.16 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.5, 172.8, 167.2, 166.5, 159.8, 141.0, 131.7, 131.3, 129.7, 126.8, 125.3, 123.4, 121.0, 119.0, 112.6, 110.6, 106.9, 84.8, 58.8, 55.5, 53.0, 52.3; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 447.1168, Found 447.1161.

**Dimethyl 2-(4'-(2-chlorophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ia)**

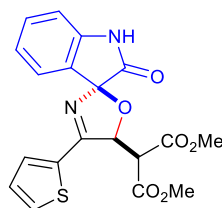
Prepared according to general procedure to afford **3ia** (51 mg, 59% yield) as a white solid; m.p. 160–162 °C; dr = 3:1; Major diastereomer: <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.97 (s, 1H), 6.05–6.03 (m, 1H), 5.75–5.71 (m, 2H), 5.69–5.55 (m, 3H), 5.36 (t, *J* = 7.6 Hz, 1H), 5.18 (d, *J* = 7.8 Hz, 1H), 4.78 (d, *J* = 3.7 Hz, 1H), 2.31 (d, *J* = 3.7 Hz, 1H), 2.02 (s, 3H), 1.91 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.7, 172.9, 166.8, 165.9, 141.6, 132.2, 132.0, 131.9, 131.4, 130.7, 130.1, 127.1, 126.4, 126.1, 123.3, 110.8, 105.9, 85.1, 53.6, 52.9, 52.7; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>ClN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 451.0673, Found 451.0669.

**Dimethyl 2-(4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ja)**

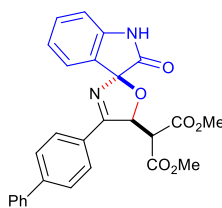
Prepared according to general procedure to afford **3ja** (56 mg, 66% yield) as a pale sticky oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.15 (s, 1H), 7.76–7.74 (m, 1H), 7.38–7.35 (m, 1H), 7.19–7.15 (m, 2H), 6.96–6.92 (m, 2H), 6.88 (d, *J* = 8.4 Hz, 1H), 6.79 (d, *J* = 7.5 Hz, 1H), 6.43–6.41 (m, 1H), 4.25–4.23 (m, 1H), 3.82 (d, *J* = 1.6 Hz, 3H), 3.68 (d, *J* = 1.8 Hz, 3H), 3.12 (d, *J* = 1.6 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.9, 172.4, 167.3, 166.5, 157.8, 141.0, 132.9, 131.3, 131.0, 127.0, 125.2, 123.3, 121.0, 120.4, 110.9, 110.6, 105.6, 86.2, 57.9, 55.4, 52.9, 52.0; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>20</sub>N<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 447.1168, Found 447.1159.

**Dimethyl 2-(4'-(furan-2-yl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ka)**

Prepared according to general procedure to afford **3ka** (44 mg, 57% yield) as a white solid; m.p. 205–207 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.77 (s, 1H), 8.05 (d, *J* = 1.2 Hz, 1H), 7.46–7.41 (m, 2H), 7.33–7.32 (m, 1H), 7.14–7.10 (m, 1H), 6.99 (d, *J* = 7.8 Hz, 1H), 6.81–6.79 (m, 1H), 5.92 (d, *J* = 3.1 Hz, 1H), 4.72 (d, *J* = 3.1 Hz, 1H), 3.77 (s, 3H), 3.71 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 173.6, 167.2, 166.7, 161.1, 147.5, 145.9, 143.0, 131.8, 126.7, 126.1, 122.9, 116.6, 113.1, 111.0, 105.9, 83.9, 54.0, 53.2, 52.9; HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 407.0855, Found 407.0847.

**Dimethyl 2-(2-oxo-4'-(thiophen-2-yl)-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3la)**

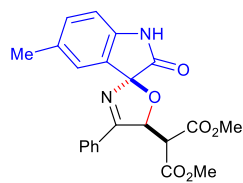
Prepared according to general procedure to afford **3la** (49 mg, 61% yield) as a white solid; m.p. 240–241 °C; <sup>1</sup>H NMR (400 MHz, DMSO-*d*<sub>6</sub>) δ 10.68 (s, 1H), 7.89–7.86 (m, 2H), 7.39–7.31 (m, 2H), 7.24–7.22 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.8 Hz, 1H), 6.00 (d, *J* = 3.0 Hz, 1H), 4.66 (d, *J* = 3.0 Hz, 1H), 3.70 (s, 3H), 3.60 (s, 3H); <sup>13</sup>C NMR (100 MHz, DMSO-*d*<sub>6</sub>) δ 173.7, 167.2, 166.8, 165.6, 143.0, 133.8, 132.7, 132.1, 131.8, 128.9, 126.7, 126.2, 122.9, 111.0, 105.4, 84.1, 54.2, 53.1, 52.8; HRMS (ESI): *m/z* calcd for C<sub>19</sub>H<sub>16</sub>N<sub>2</sub>NaO<sub>6</sub>S [M+Na]<sup>+</sup> 423.0627, Found 423.0625.

**Dimethyl 2-(4'-([1,1'-biphenyl]-4-yl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ma)**

Prepared according to general procedure to afford **3ma** (70 mg, 75% yield) as a yellow solid; m.p. 215–216 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.80 (s, 1H), 7.72 (d, *J* = 7.9 Hz, 2H), 7.57 (d, *J* = 8.0 Hz, 2H), 7.51 (d, *J* = 7.4 Hz, 2H), 7.36–7.33 (m, 3H), 7.29–7.26 (m, 1H), 7.16–7.12 (m, 1H), 6.96–6.93 (m, 1H), 6.75 (d, *J* = 7.7 Hz, 1H), 6.25 (s, 1H), 4.09 (d, *J* = 3.1 Hz, 1H), 3.61 (s, 3H), 3.57 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 174.4, 172.2, 167.0, 166.2, 144.4, 141.7, 139.9, 131.3, 129.5, 128.9, 128.5, 128.1, 127.5, 127.2, 126.6, 126.1, 123.3,

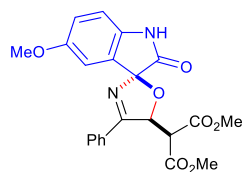
110.9, 106.6, 84.3, 54.9, 52.9, 52.7; HRMS (ESI):  $m/z$  calcd for  $C_{27}H_{22}N_2NaO_6$   $[M+Na]^+$  493.1376, Found 493.1373.

**Dimethyl 2-(5-methyl-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ab)**



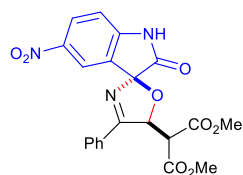
Prepared according to general procedure to afford **3ab** (67 mg, 82% yield) as a pale sticky oil;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  9.82 (s, 1H), 7.66–7.64 (m, 2H), 7.52–7.48 (m, 4H), 7.43–7.42 (m, 2H), 4.16 (d,  $J = 6.3$  Hz, 1H), 3.99 (d,  $J = 6.3$  Hz, 1H), 3.78 (s, 3H), 3.62 (s, 3H), 2.97 (s, 3H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $\delta$  171.2, 171.0, 170.5, 164.4, 163.9, 152.7, 141.1, 133.5, 130.8, 129.2, 129.0, 128.7, 128.6, 125.9, 125.2, 92.9, 56.0, 54.6, 53.5, 53.0, 52.4; HRMS (ESI):  $m/z$  calcd for  $C_{22}H_{20}N_2NaO_6$   $[M+Na]^+$  431.1219, Found 431.1216.

**Dimethyl 2-(5-methoxy-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ac)**



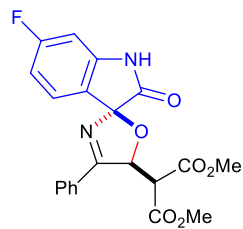
Prepared according to general procedure to afford **3ac** (67 mg, 79% yield) as a pale sticky oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.53 (s, 1H), 7.65–7.63 (m, 2H), 7.42–7.34 (m, 3H), 7.01 (d,  $J = 2.4$  Hz, 1H), 6.73–6.66 (m, 2H), 6.21 (d,  $J = 3.5$  Hz, 1H), 4.04 (d,  $J = 3.6$  Hz, 1H), 3.69 (s, 3H), 3.63 (s, 3H), 3.57 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  174.2, 172.5, 166.9, 166.0, 156.4, 134.7, 131.6, 130.6, 128.8, 128.0, 127.6, 116.3, 112.8, 111.3, 106.8, 84.3, 55.8, 54.7, 52.9, 52.7; HRMS (ESI):  $m/z$  calcd for  $C_{22}H_{20}N_2NaO_7$   $[M+Na]^+$  447.1168, Found 447.1165.

**Dimethyl 2-(5-nitro-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ad)**



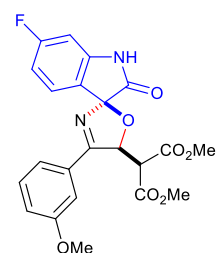
Prepared according to general procedure to afford **3ad** (60 mg, 68% yield) as a white solid; m.p. 163–165 °C;  $^1H$  NMR (400 MHz,  $DMSO-d_6$ )  $\delta$  11.48 (s, 1H), 8.37–8.29 (m, 2H), 7.72 (s, 2H), 7.52–7.44 (m, 3H), 7.13 (s, 1H), 6.51 (s, 1H), 4.16 (s, 1H), 3.66 (s, 3H), 3.20 (s, 3H);  $^{13}C$  NMR (100 MHz,  $DMSO-d_6$ )  $\delta$  173.9, 173.6, 166.7, 166.3, 148.6, 143.4, 132.4, 130.6, 129.4, 129.0, 128.9, 128.7, 128.5, 128.4, 121.8, 111.5, 105.9, 85.4, 58.1, 53.3, 52.7; HRMS (ESI):  $m/z$  calcd for  $C_{21}H_{17}N_3NaO_8$   $[M+Na]^+$  462.0913, Found 462.0908.

**Dimethyl 2-(6-fluoro-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ae)**



Prepared according to general procedure to afford **3ae** (59 mg, 71% yield) as a pale sticky oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.43 (s, 1H), 7.77–7.75 (m, 2H), 7.52–7.44 (m, 3H), 7.19–7.16 (m, 1H), 6.74–6.63 (m, 2H), 6.35 (d,  $J = 9.0$  Hz, 1H), 4.44 (d,  $J = 9.0$  Hz, 1H), 3.77 (s, 3H), 3.16 (s, 3H);  $^{13}C$  NMR (101 MHz,  $CDCl_3$ )  $\delta$  173.8, 173.2, 167.2, 166.4, 165.8 ( $J_{C-F} = 247.3$  Hz), 142.8 ( $J_{C-F} = 12.3$  Hz), 132.1, 130.4, 128.7, 128.6, 126.9 ( $J_{C-F} = 10.3$  Hz), 122.3 ( $J_{C-F} = 2.9$  Hz), 110.0 ( $J_{C-F} = 22.6$  Hz), 106.4, 99.6 ( $J_{C-F} = 27.5$  Hz), 84.8, 58.7, 53.1, 52.3; HRMS (ESI):  $m/z$  calcd for  $C_{21}H_{17}FN_2NaO_6$   $[M+Na]^+$  435.0968, Found 435.0966.

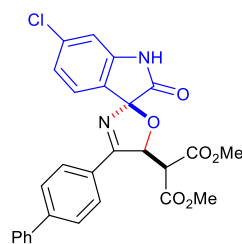
**Dimethyl 2-(6-fluoro-4'-(3-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3he)**



Prepared according to general procedure to afford **3he** (49 mg, 55% yield) as a pale sticky oil;  $^1H$  NMR (400 MHz,  $CDCl_3$ )  $\delta$  8.22 (s, 1H), 7.30–7.20 (m, 3H), 7.11–7.08 (m, 1H), 6.99–6.97 (m, 1H), 6.70–6.61 (m, 1H), 6.58–6.55 (m, 1H), 6.25 (d,  $J = 8.8$  Hz, 1H), 4.35 (d,  $J = 8.9$  Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.17 (s, 3H);  $^{13}C$  NMR (100 MHz,  $CDCl_3$ )  $\delta$  174.2, 172.6, 166.9, 166.1, 165.8 ( $J_{C-F} = 247.2$  Hz), 159.9, 143.2 ( $J_{C-F} = 12.6$  Hz), 131.7, 129.9, 128.0 ( $J_{C-F} = 10.1$  Hz), 122.1 ( $J_{C-F} = 2.9$  Hz), 120.2, 118.4, 112.6, 109.9 ( $J_{C-F} = 22.4$  Hz), 105.8, 99.5 ( $J_{C-F} = 27.4$  Hz), 84.3, 55.5, 54.5, 53.0, 52.7; HRMS (ESI):  $m/z$  calcd for

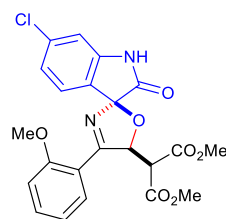
C<sub>22</sub>H<sub>19</sub>FN<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 465.1074, Found 465.1071.

**Dimethyl 2-(4'-([1,1'-biphenyl]-4-yl)-6-chloro-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3mf)**



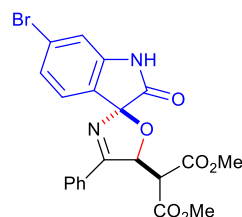
Prepared according to general procedure to afford **3mf** (81 mg, 80% yield) as a yellow solid; m.p. 215–216 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (s, 1H), 7.74 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.2 Hz, 2H), 7.56–7.54 (m, 2H), 7.41–7.30 (m, 4H), 6.99–6.97 (m, 1H), 6.81 (d, *J* = 1.7 Hz, 1H), 6.21 (d, *J* = 3.0 Hz, 1H), 4.09 (d, *J* = 3.4 Hz, 1H), 3.67 (s, 3H), 3.59 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.6, 172.4, 166.9, 166.0, 144.6, 142.5, 139.8, 136.9, 129.2, 128.9, 128.5, 128.2, 127.5, 127.2, 124.9, 123.5, 111.2, 105.8, 84.3, 54.5, 53.0, 52.8; HRMS (ESI): *m/z* calcd for C<sub>27</sub>H<sub>21</sub>ClN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 527.0986, Found 527.0982.

**Dimethyl 2-(6-chloro-4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jf)**



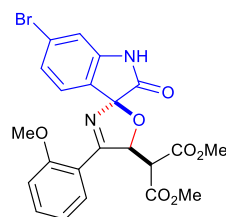
Prepared according to general procedure to afford **3jf** (52 mg, 58% yield) as a pale sticky oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.17 (s, 1H), 7.74–7.72 (m, 1H), 7.41–7.36 (m, 1H), 7.09–7.07 (m, 1H), 6.97–6.93 (m, 3H), 6.79 (d, *J* = 1.7 Hz, 1H), 6.41 (d, *J* = 7.7 Hz, 1H), 4.20 (d, *J* = 7.7 Hz, 1H), 3.83 (s, 3H), 3.69 (s, 3H), 3.15 (s, 3H); <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 173.7, 172.7, 167.2, 166.5, 157.8, 142.2, 136.7, 133.2, 131.2, 126.2, 125.4, 123.3, 121.1, 120.2, 111.3, 110.9, 105.0, 86.3, 57.8, 55.4, 52.9, 52.1; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>19</sub>ClN<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 481.0778, Found 481.0771.

**Dimethyl 2-(6-bromo-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ag)**

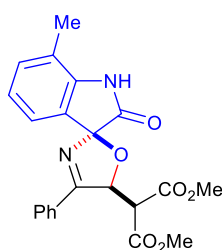


Prepared according to general procedure to afford **3ag** (72 mg, 76% yield) as a yellow solid; m.p. 187–189 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.84–7.81 (m, 2H), 7.69–7.67 (m, 2H), 7.41 (s, 1H), 7.27–7.23 (m, 1H), 7.14 (d, *J* = 7.4 Hz, 1H), 7.00–6.97 (m, 1H), 6.82 (d, *J* = 7.8 Hz, 1H), 6.28 (d, *J* = 8.5 Hz, 1H), 4.36 (d, *J* = 8.5 Hz, 1H), 3.70 (s, 3H), 3.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 172.4, 171.5, 166.8, 166.3, 140.8, 134.6, 132.3, 131.5, 129.3, 126.2, 125.3, 123.6, 115.4, 110.6, 84.8, 58.4, 53.2, 52.4; HRMS (ESI): *m/z* calcd for C<sub>21</sub>H<sub>17</sub>BrN<sub>2</sub>NaO<sub>6</sub> [M+Na]<sup>+</sup> 495.0168, Found 495.0159.

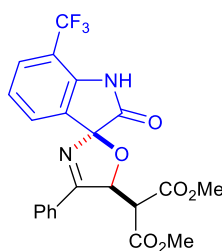
**Dimethyl 2-(6-bromo-4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jg)**



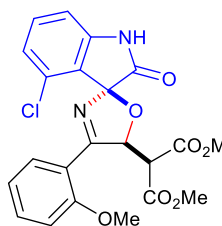
Prepared according to general procedure to afford **3jg** (60 mg, 60% yield) as a pale sticky oil; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.83 (s, 1H), 7.74 (d, *J* = 7.7 Hz, 1H), 7.40–7.36 (m, 1H), 7.19 (d, *J* = 1.8 Hz, 1H), 7.10–7.08 (m, 1H), 7.04–7.02 (m, 1H), 6.97–6.94 (m, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 6.41–6.39 (m, 1H), 4.20–4.18 (m, 1H), 3.83 (d, *J* = 1.5 Hz, 3H), 3.69 (d, *J* = 1.7 Hz, 3H), 3.14 (d, *J* = 1.7 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 173.4, 172.7, 167.2, 166.5, 157.8, 142.1, 133.1, 131.2, 126.5, 126.2, 125.9, 124.6, 121.1, 120.2, 113.9, 110.9, 104.9, 86.3, 57.8, 55.4, 52.9, 52.1; HRMS (ESI): *m/z* calcd for C<sub>22</sub>H<sub>19</sub>BrN<sub>2</sub>NaO<sub>7</sub> [M+Na]<sup>+</sup> 525.0273, Found 525.0268.

**Dimethyl 2-(7-methyl-2-oxo-4'-phenyl-5'-H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ah)**

Prepared according to general procedure to afford **3ah** (69 mg, 85% yield) as a pale sticky oil;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.77 (s, 1H), 7.65 (d,  $J = 7.0$  Hz, 2H), 7.41–7.34 (m, 3H), 7.21–7.17 (m, 1H), 7.05–7.03 (m, 1H), 6.92–6.88 (m, 1H), 6.21 (d,  $J = 3.8$  Hz, 1H), 4.03 (d,  $J = 3.8$  Hz, 1H), 3.60 (s, 3H), 3.57 (s, 3H), 2.14 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  174.6, 172.4, 166.9, 166.1, 140.1, 132.5, 131.6, 130.7, 128.8, 128.0, 126.1, 123.3, 123.2, 120.1, 106.9, 84.3, 55.0, 52.9, 52.7, 16.1; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{N}_2\text{NaO}_6$   $[\text{M}+\text{Na}]^+$  431.1219, Found 431.1205.

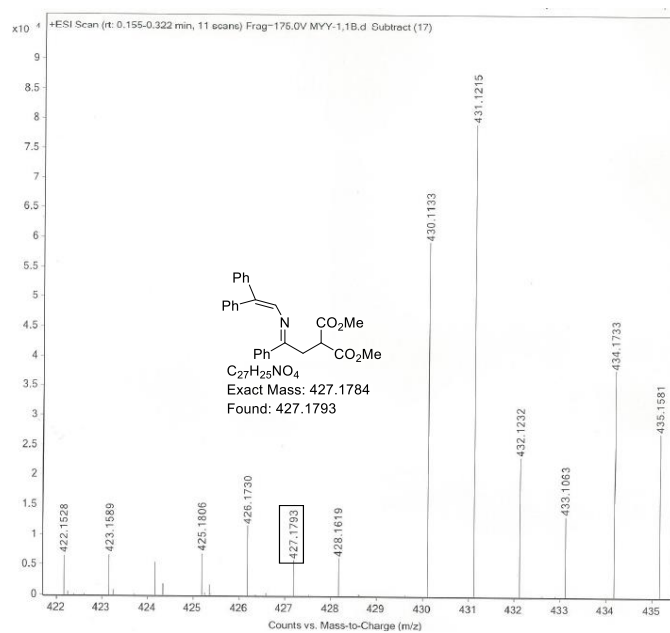
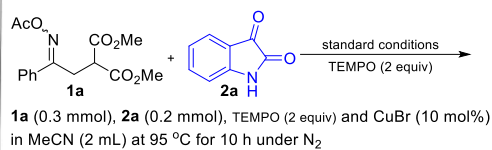
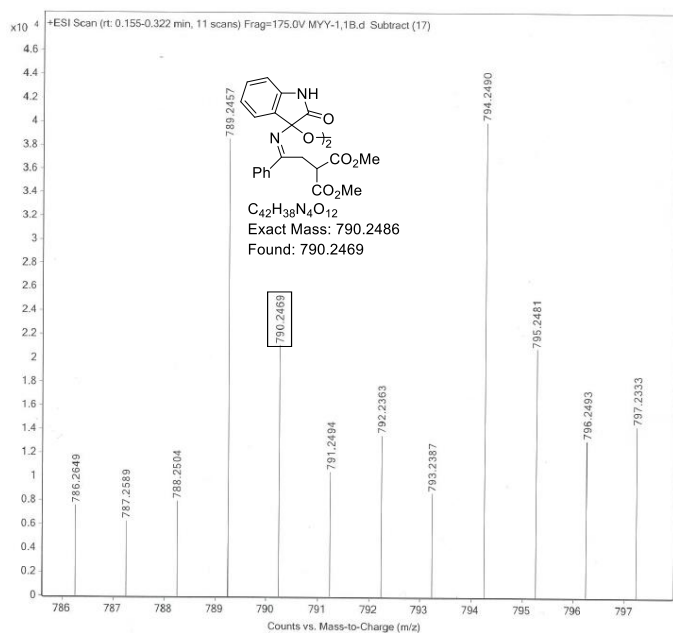
**Dimethyl 2-(2-oxo-4'-phenyl-7-(trifluoromethyl)-5'-H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ai)**

Prepared according to general procedure to afford **3ai** (68 mg, 74% yield) as a yellow solid; m.p. 218–220 °C;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.79 (s, 1H), 7.66–7.62 (m, 3H), 7.47–7.36 (m, 4H), 7.12 (t,  $J = 7.7$  Hz, 1H), 6.21 (d,  $J = 3.5$  Hz, 1H), 4.06 (d,  $J = 3.5$  Hz, 1H), 3.66 (s, 3H), 3.56 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.1, 172.8, 166.7, 166.0, 138.9 (d,  $J = 1.9$  Hz), 131.9, 130.3, 130.1, 128.9, 128.1, 127.9, 127.8 (q,  $J = 4.0$  Hz), 125.0 (q,  $J = 270.3$  Hz), 123.3, 112.9 (q,  $J = 33.1$  Hz), 104.8, 84.5, 54.3, 53.0, 52.7; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{17}\text{F}_3\text{N}_2\text{NaO}_6$   $[\text{M}+\text{Na}]^+$  485.0936, Found 485.0928.

**Dimethyl 2-(4-chloro-4'-(2-methoxyphenyl)-2-oxo-5'-H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jj)**

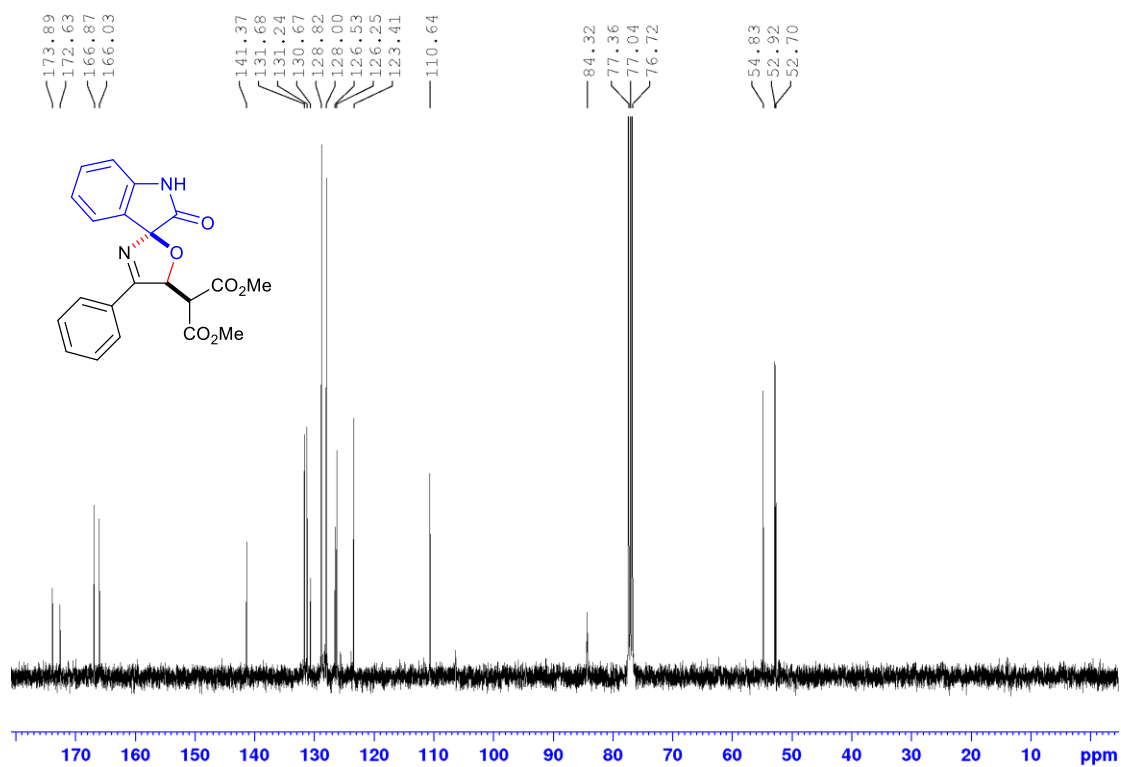
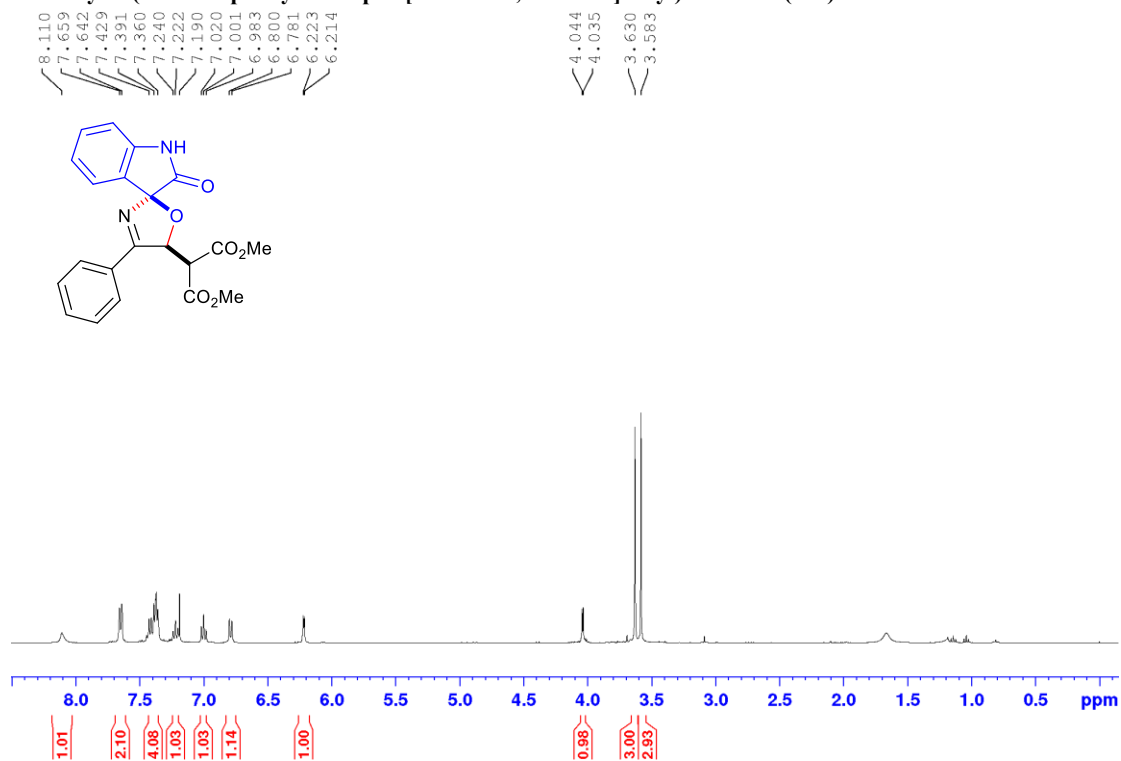
Prepared according to general procedure to afford **3jj** (67 mg, 73% yield) as a pale sticky oil; dr = 4:1; Major diastereomer:  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (s, 1H), 7.75–7.72 (m, 1H), 7.40–7.33 (m, 1H), 7.17–7.08 (m, 1H), 6.97–6.92 (m, 1H), 6.89–6.85 (m, 2H), 6.73–6.68 (m, 1H), 6.42–6.38 (m, 1H), 4.11 (d,  $J = 6.6$  Hz, 1H), 3.81 (m, 3H), 3.69 (m, 3H), 3.27 (m, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  173.6, 172.8, 166.9, 166.8, 157.9, 142.6, 133.0, 132.4, 132.0, 131.2, 124.2, 123.7, 121.1, 120.2, 111.1, 109.0, 105.3, 87.0, 56.9, 55.6, 52.9, 52.3; HRMS (ESI):  $m/z$  calcd for  $\text{C}_{22}\text{H}_{19}\text{ClN}_2\text{NaO}_7$   $[\text{M}+\text{Na}]^+$  481.0778, Found 481.0776.



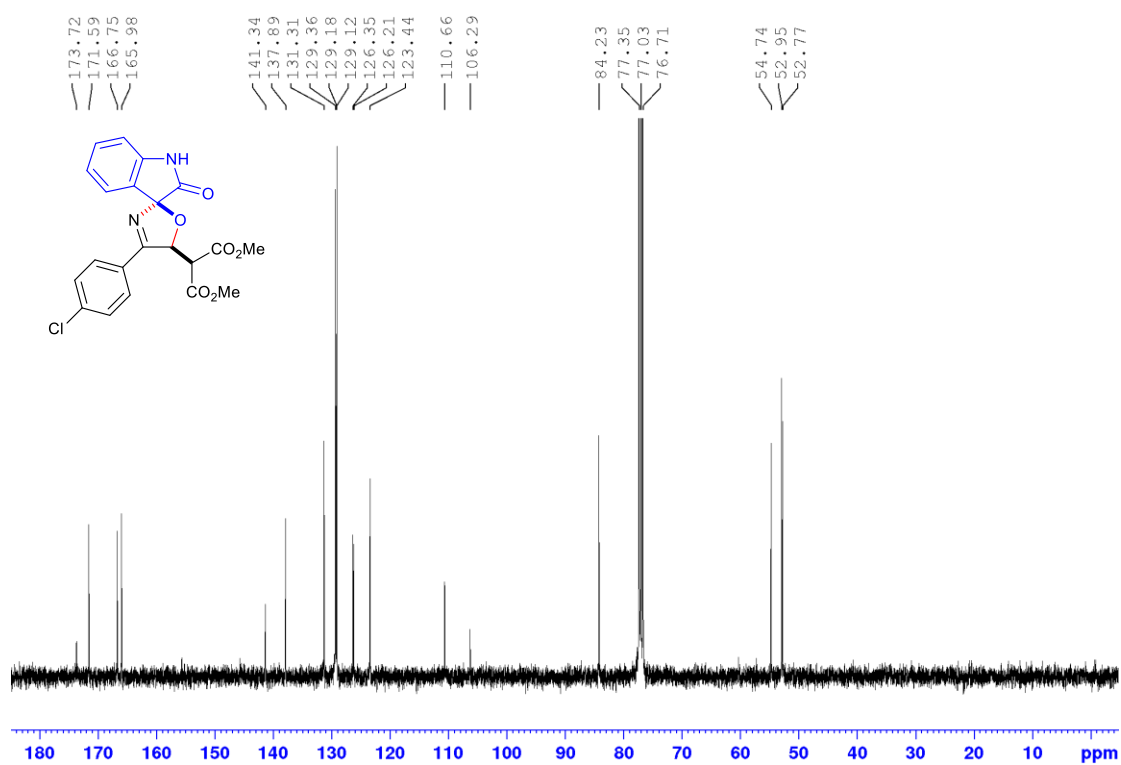
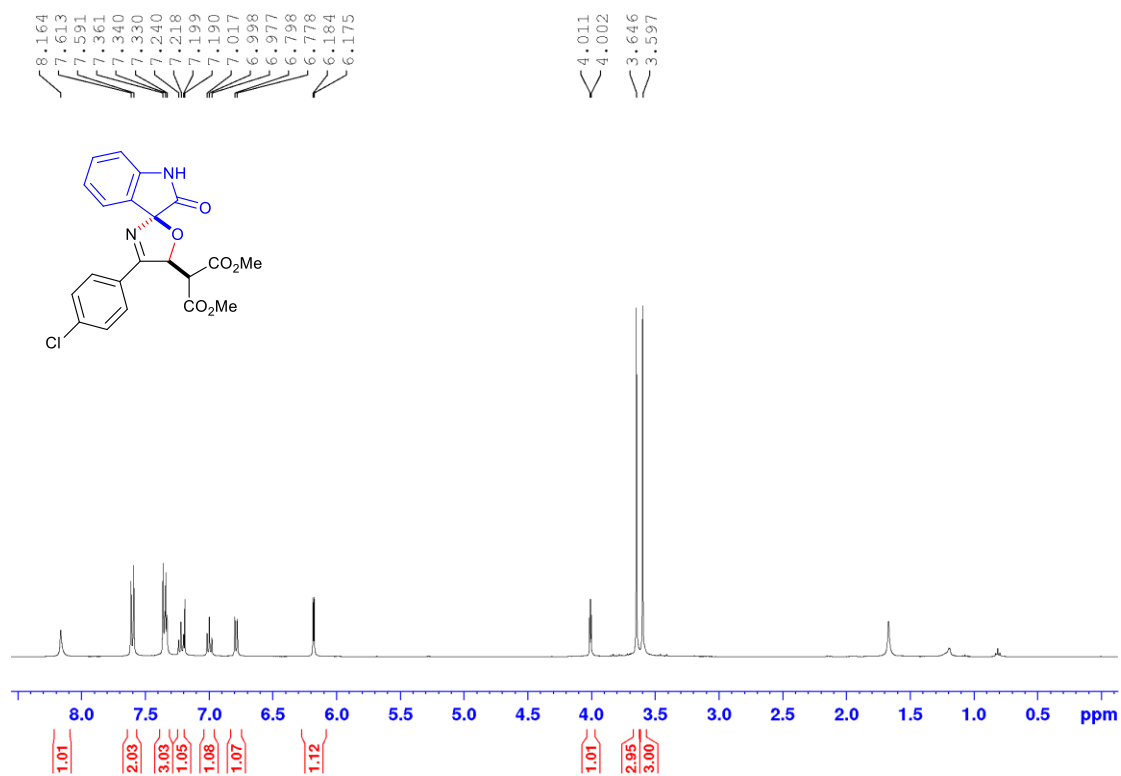


## NMR spectra of compounds

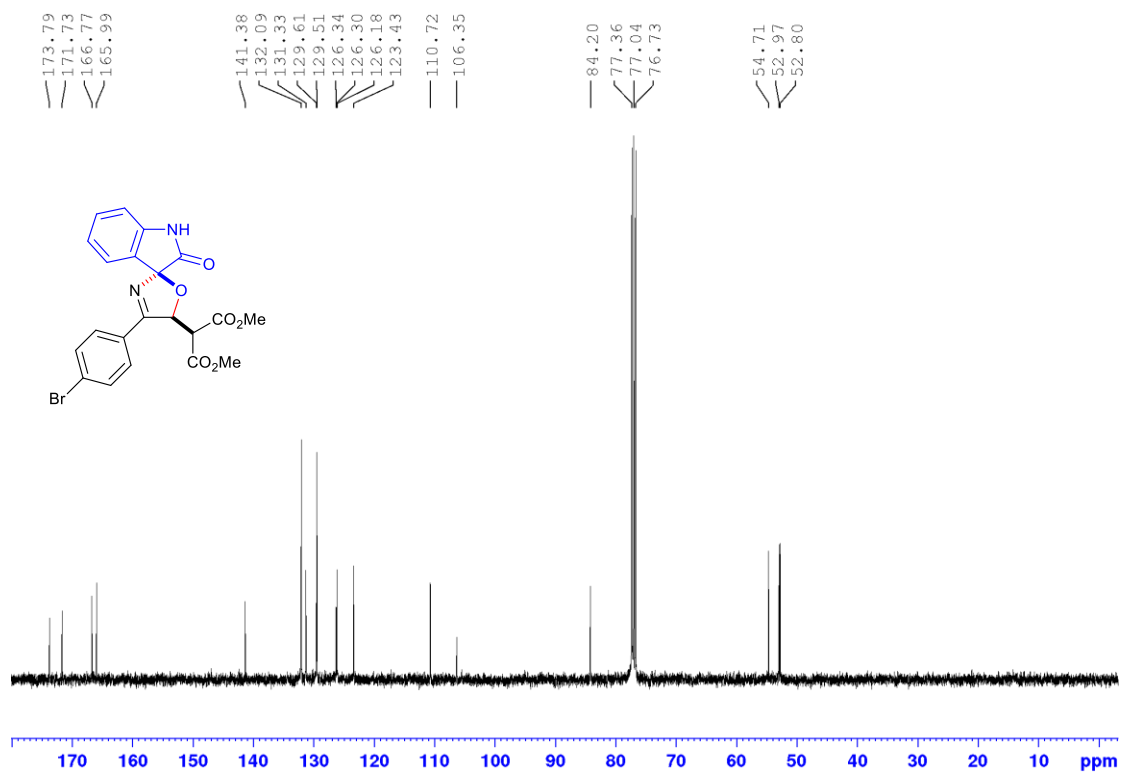
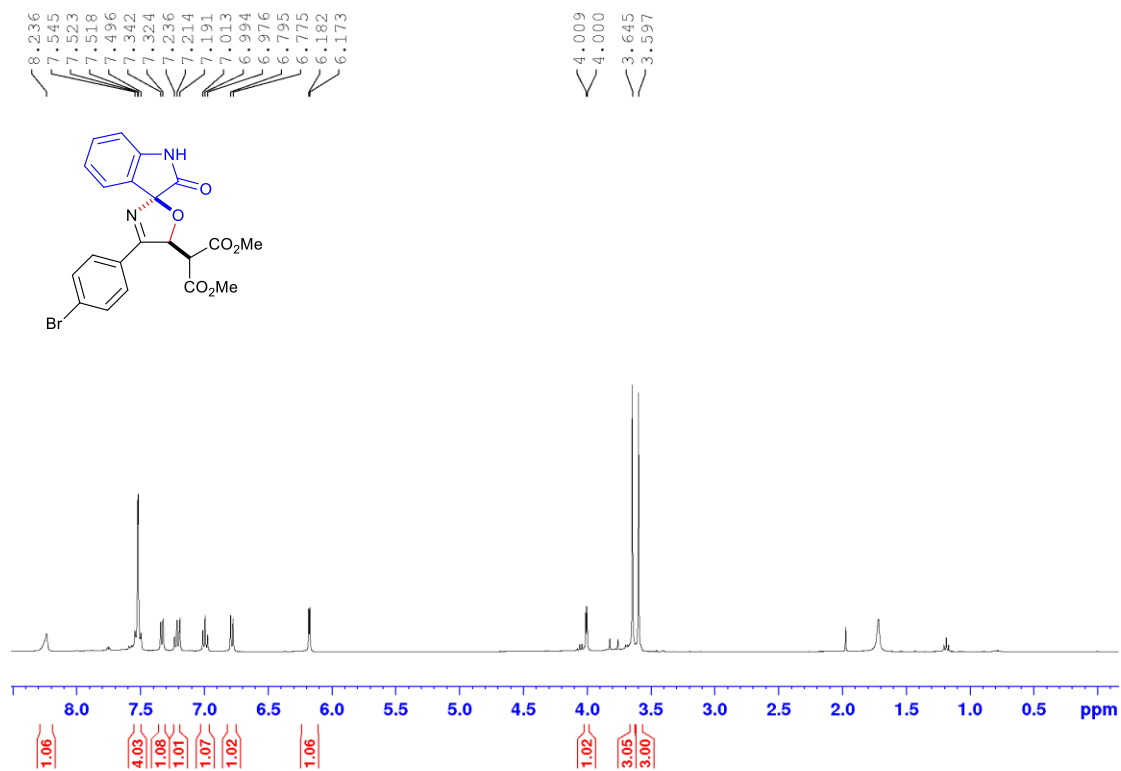
Dimethyl 2-(2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3aa)



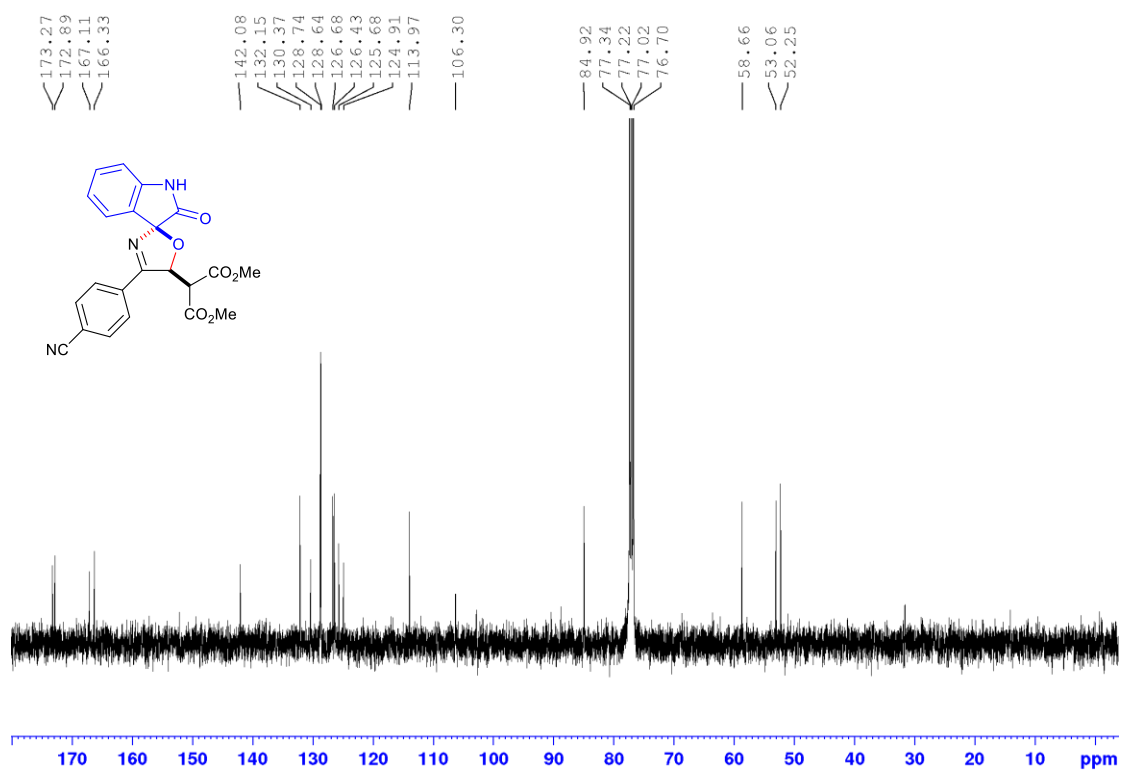
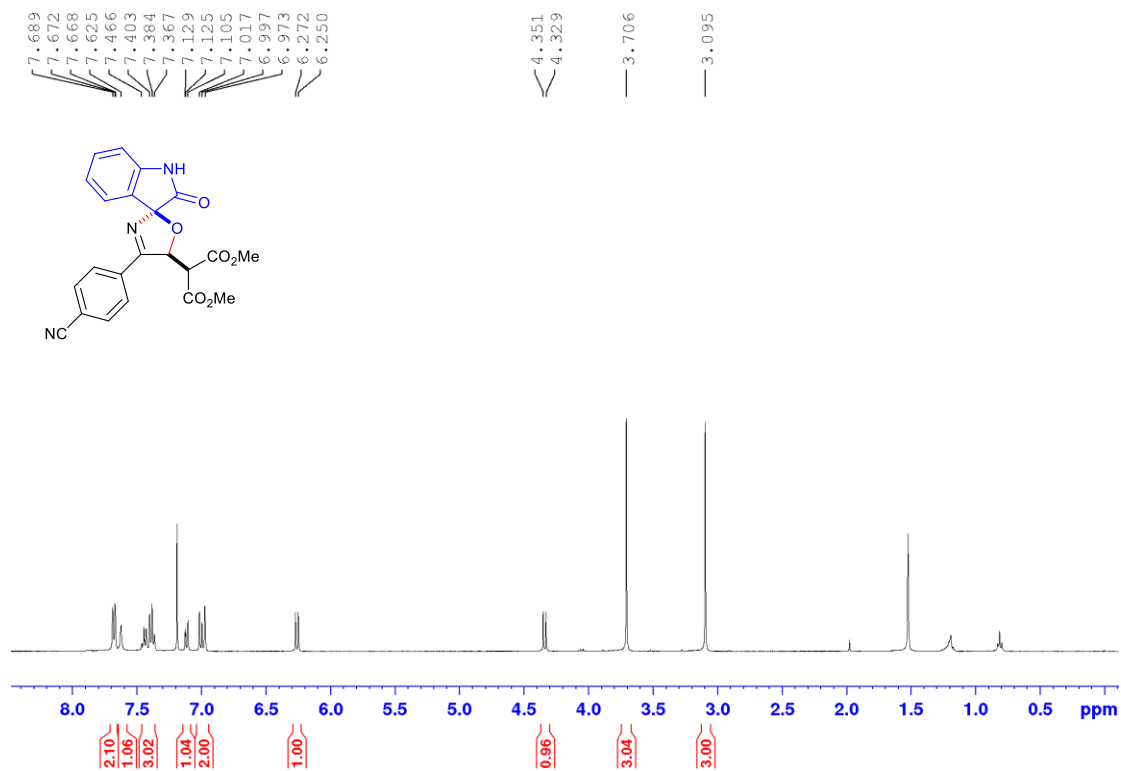
**Dimethyl 2-(4'-(4-chlorophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonat (3ba)**



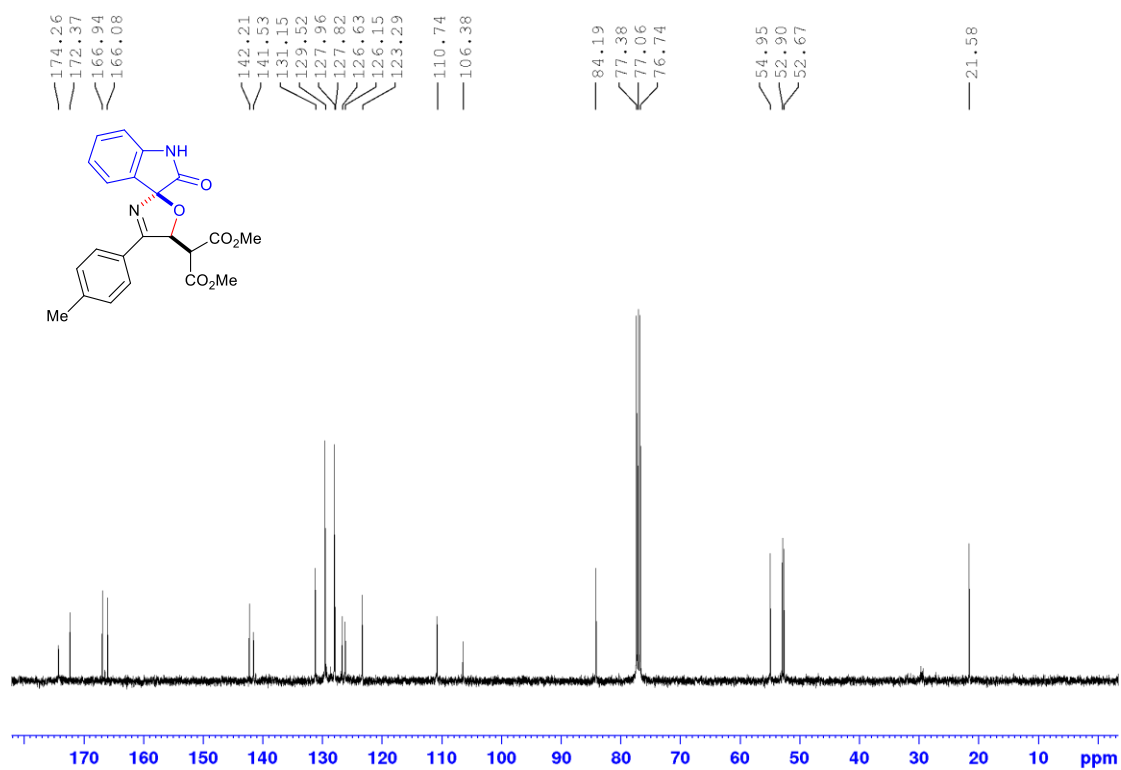
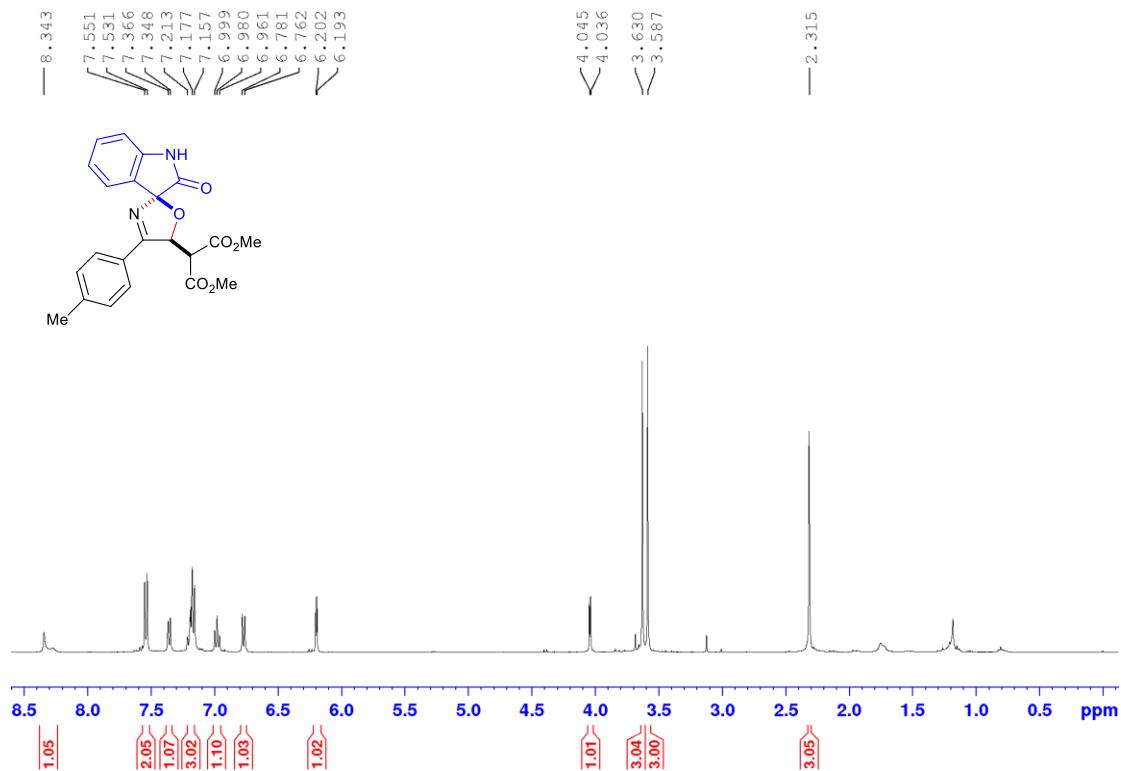
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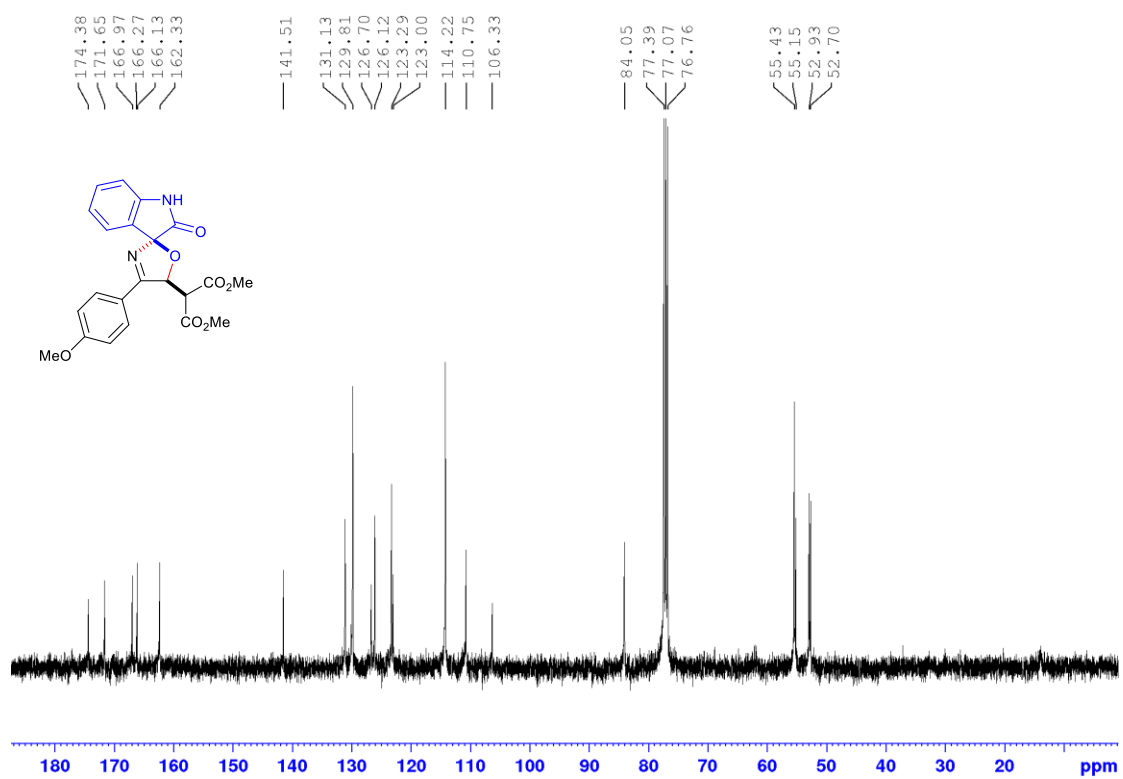
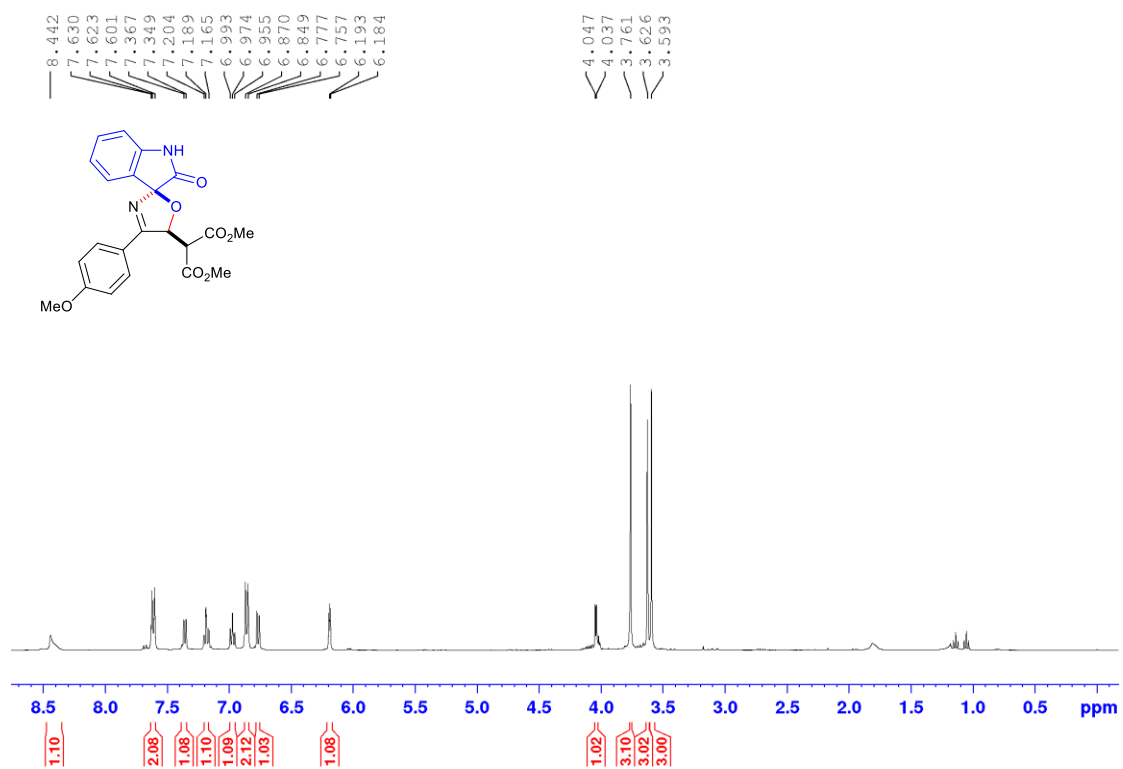
**Dimethyl 2-(4'-(4-cyanophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3da)**



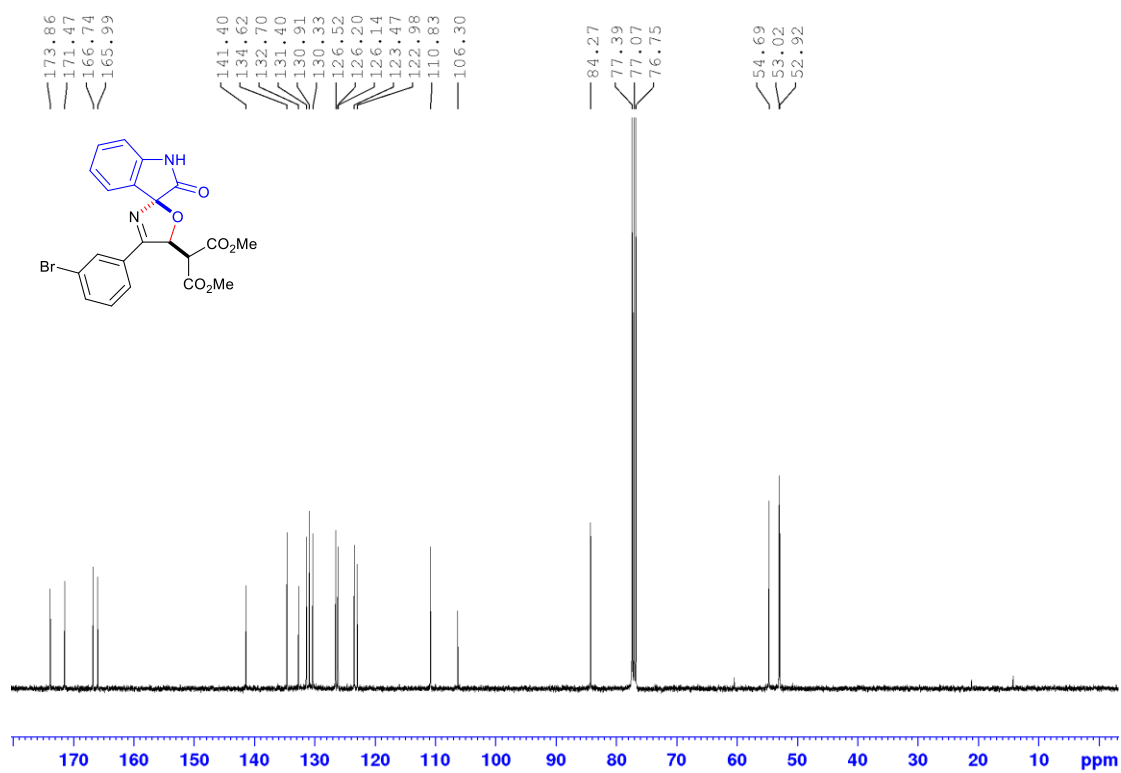
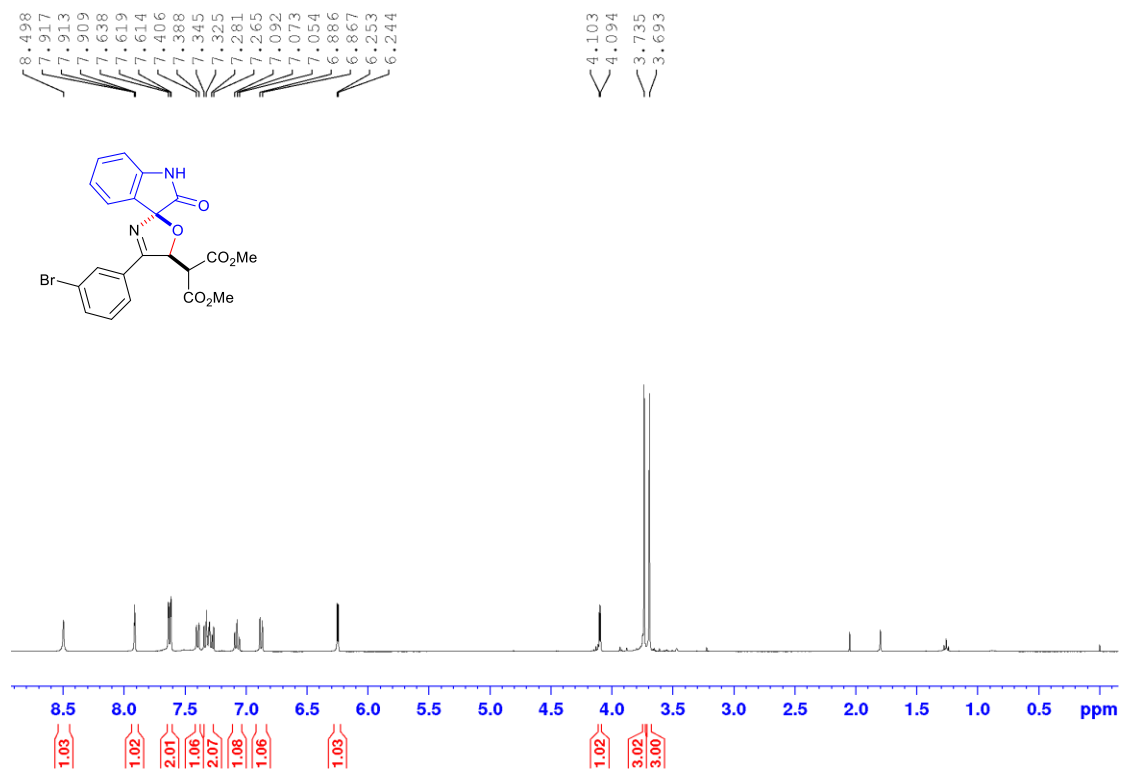
**Dimethyl 2-(2-oxo-4'-(p-tolyl)-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ea)**



Dimethyl 2-(4'-(4-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3fa)

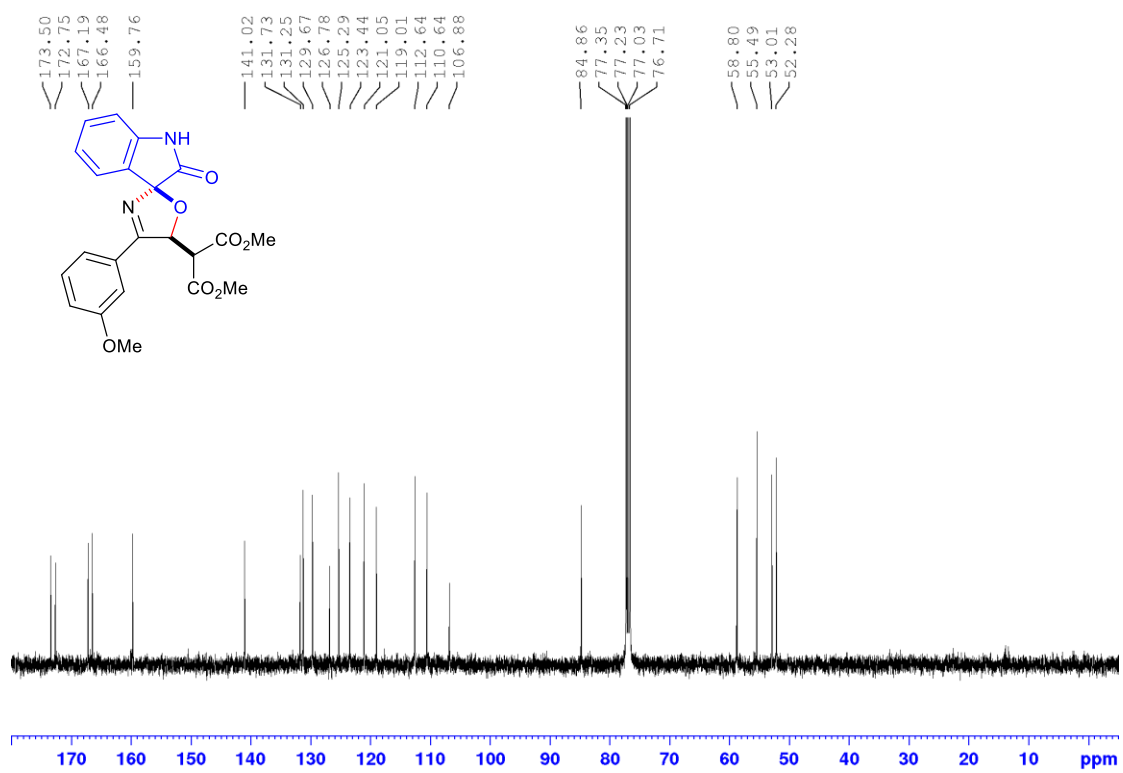
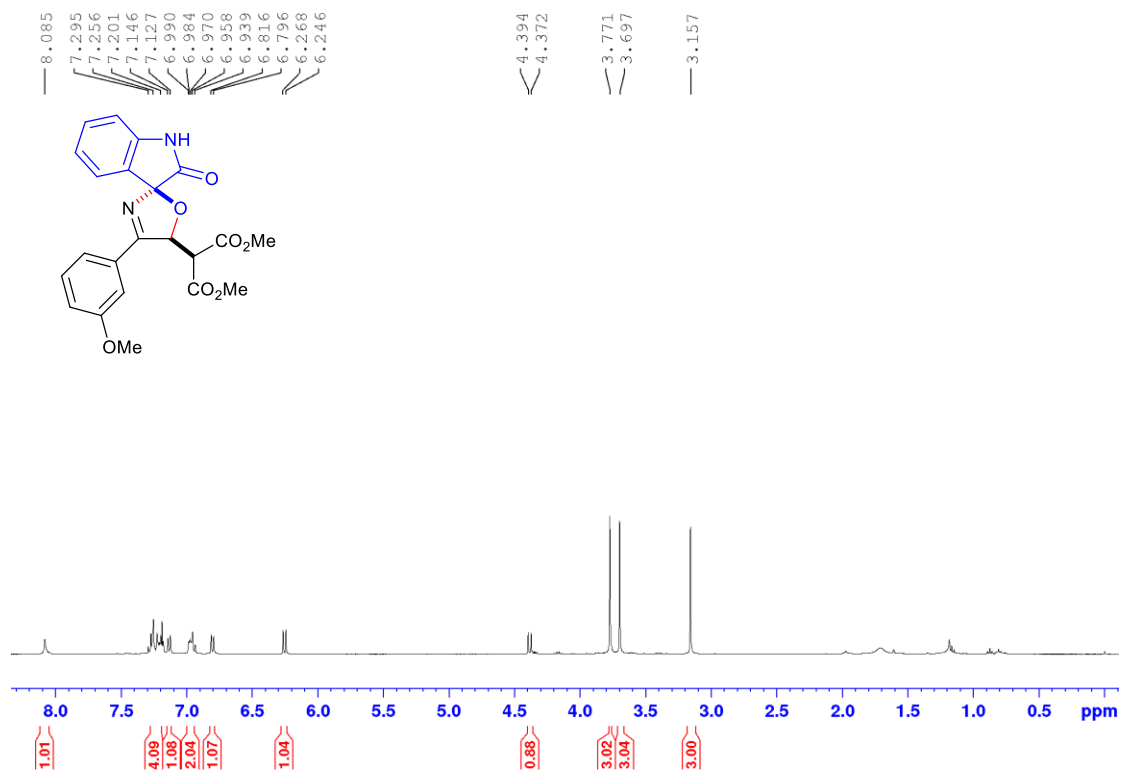


Dimethyl 2-(4'-(3-bromophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ga)

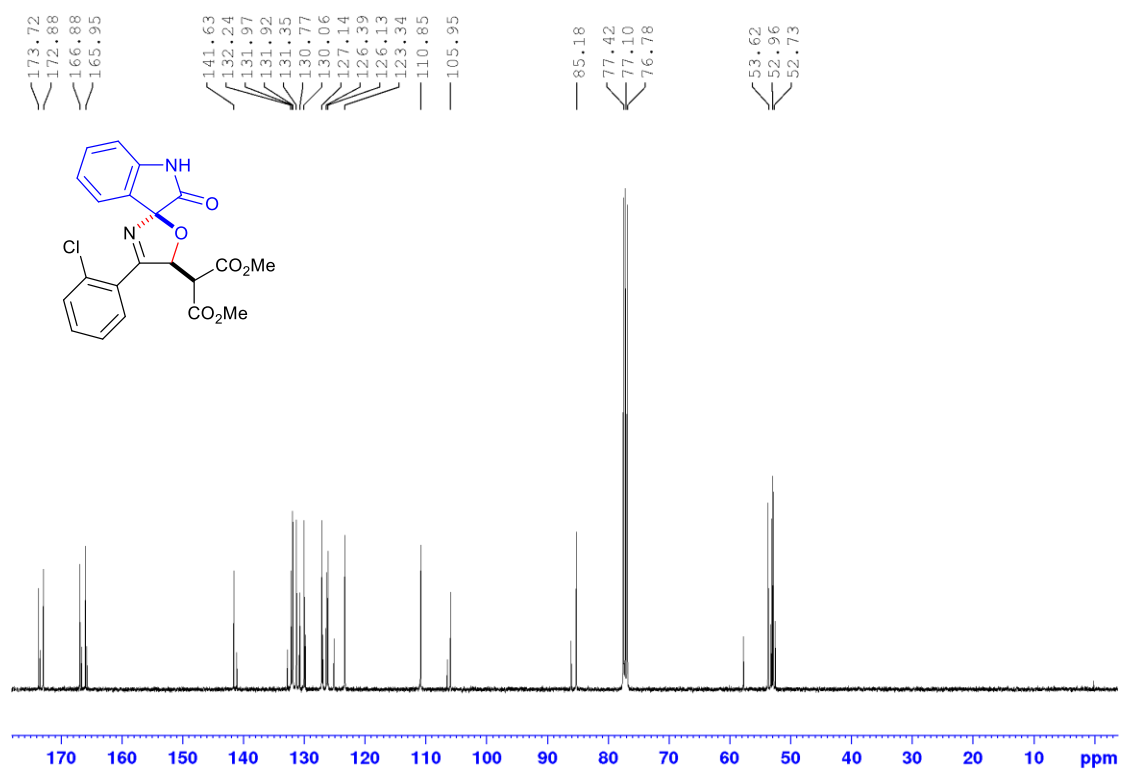
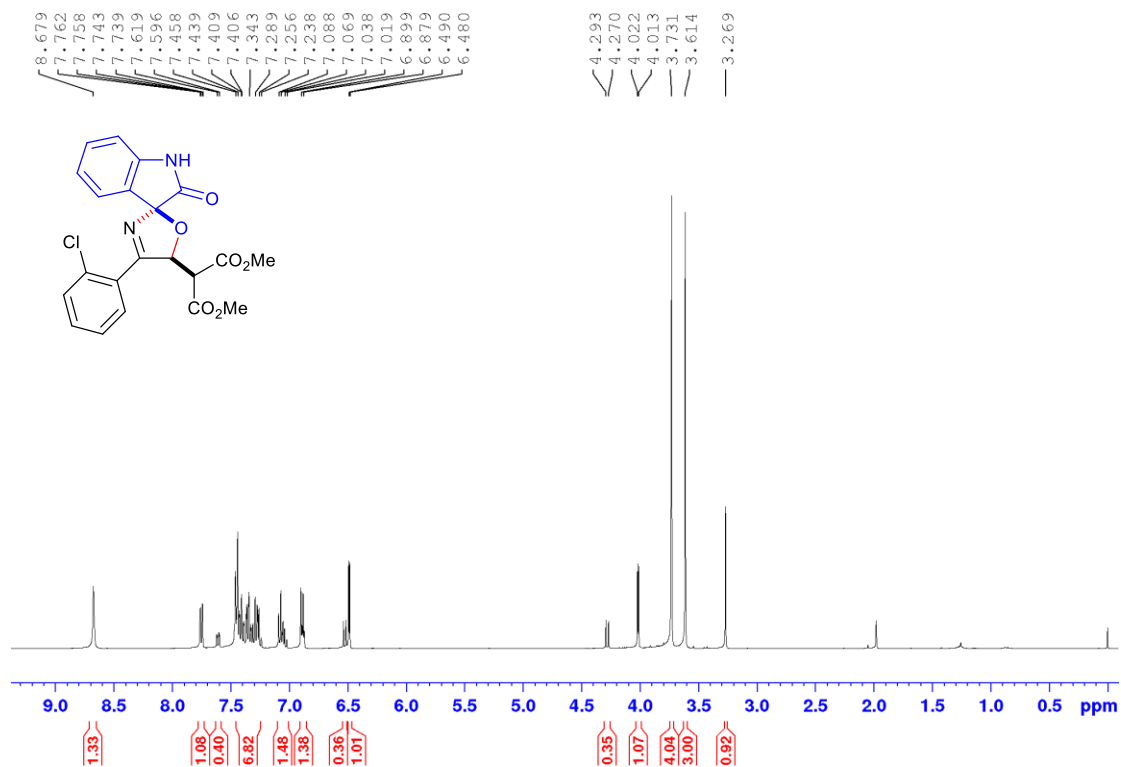




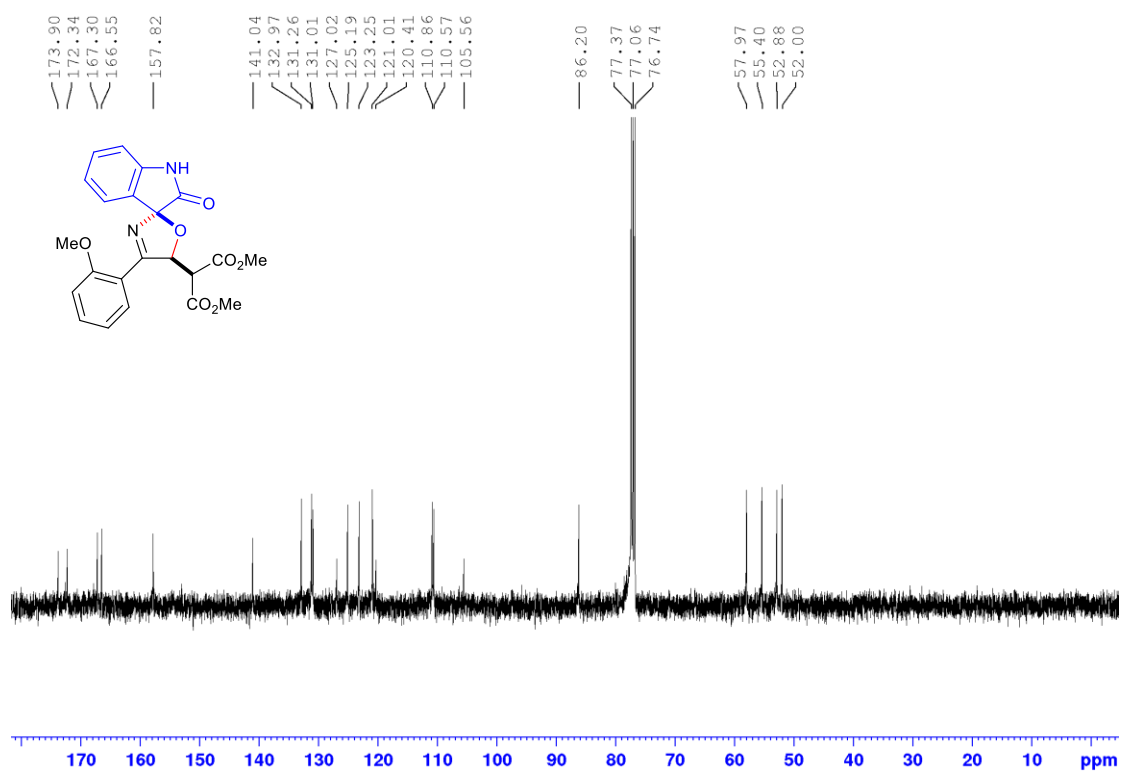
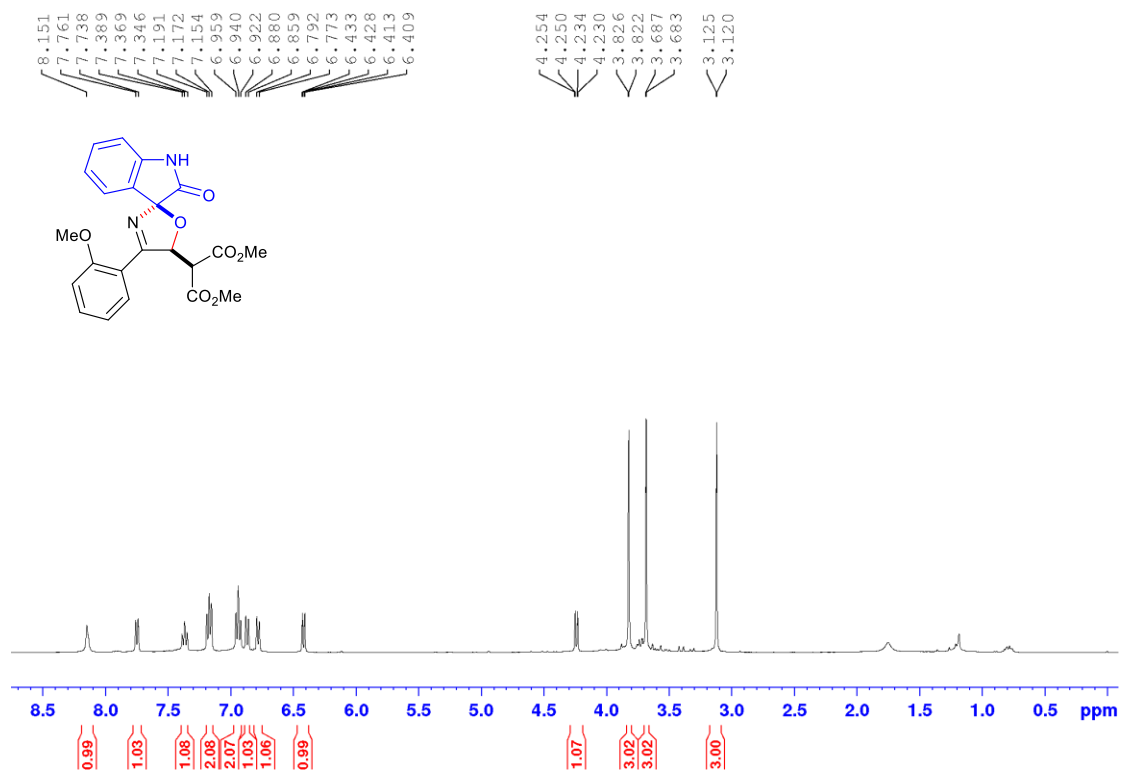
Dimethyl 2-(4'-(3-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ha)



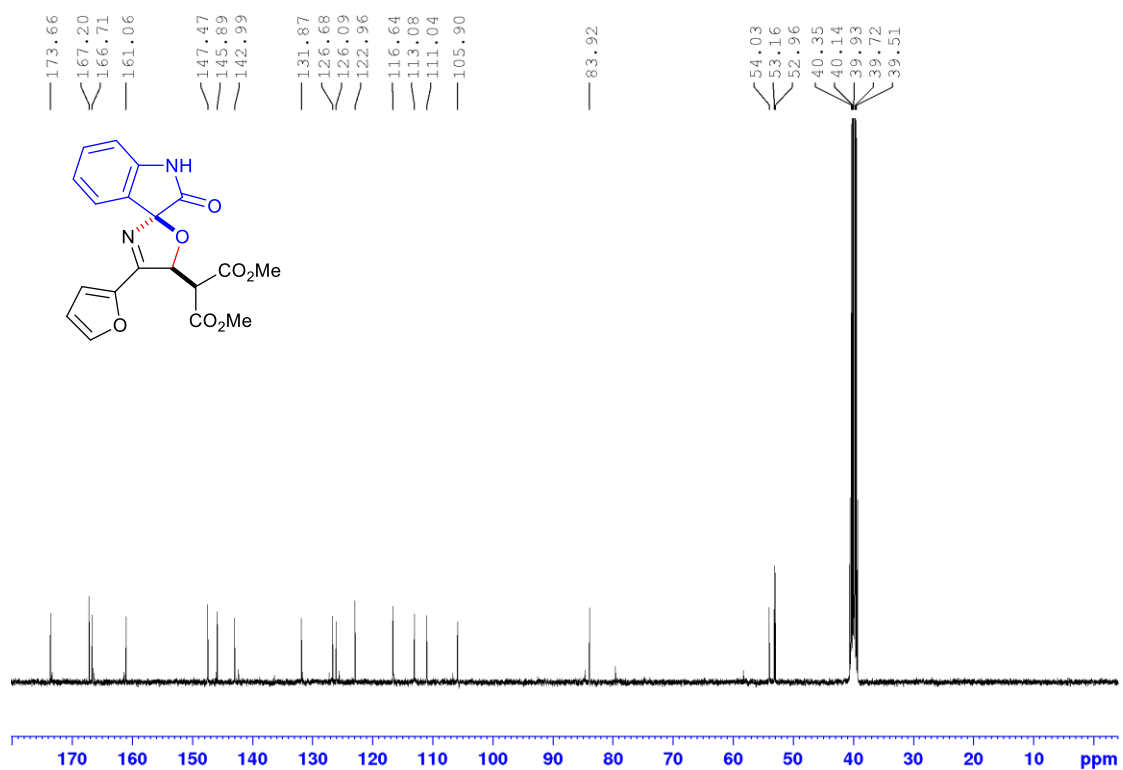
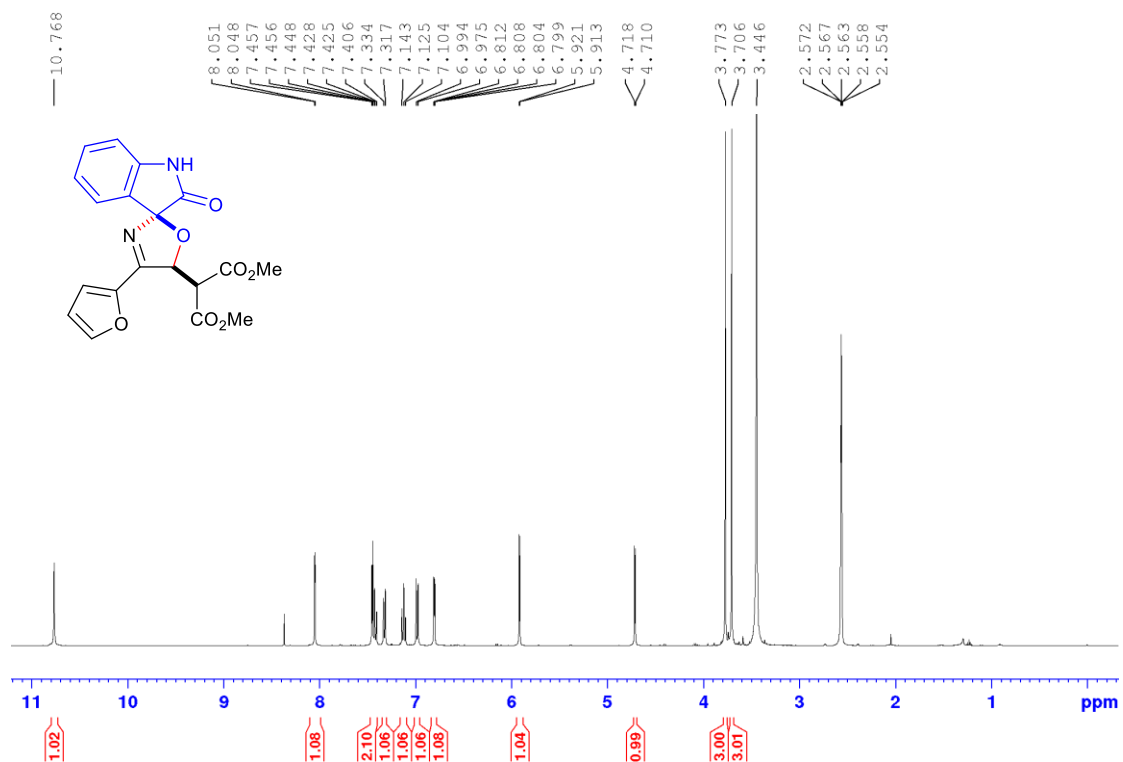
Dimethyl 2-(4'-(2-chlorophenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ia)



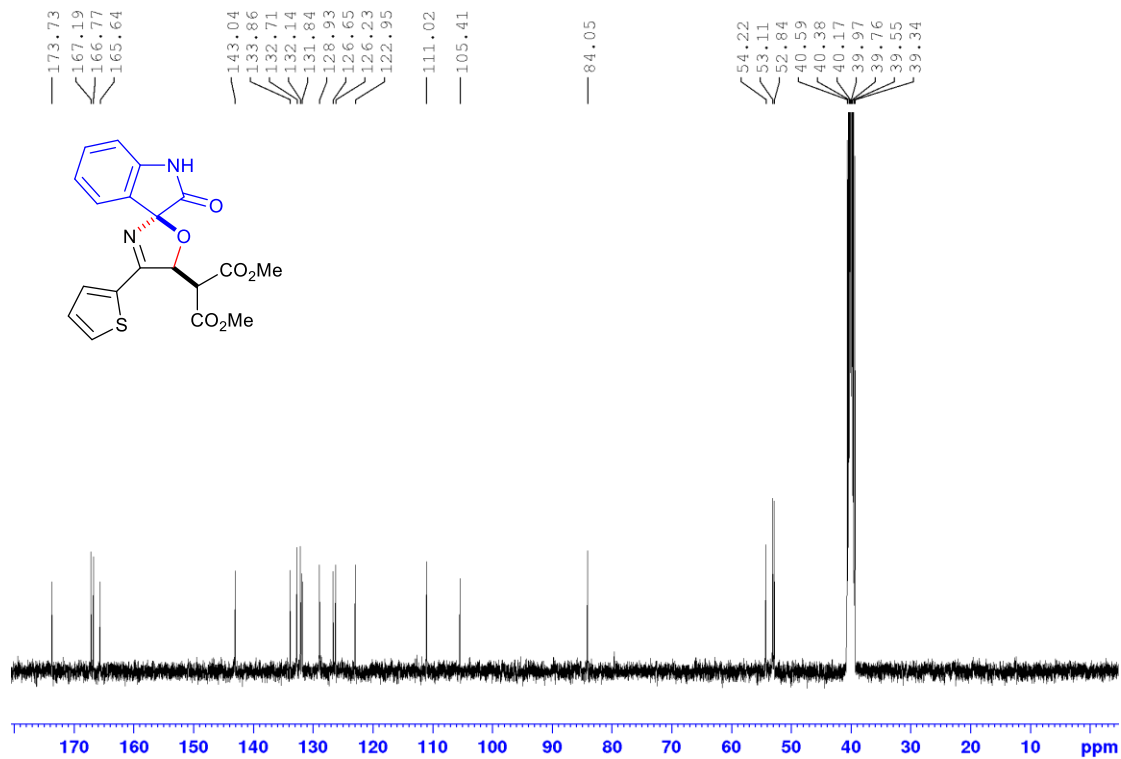
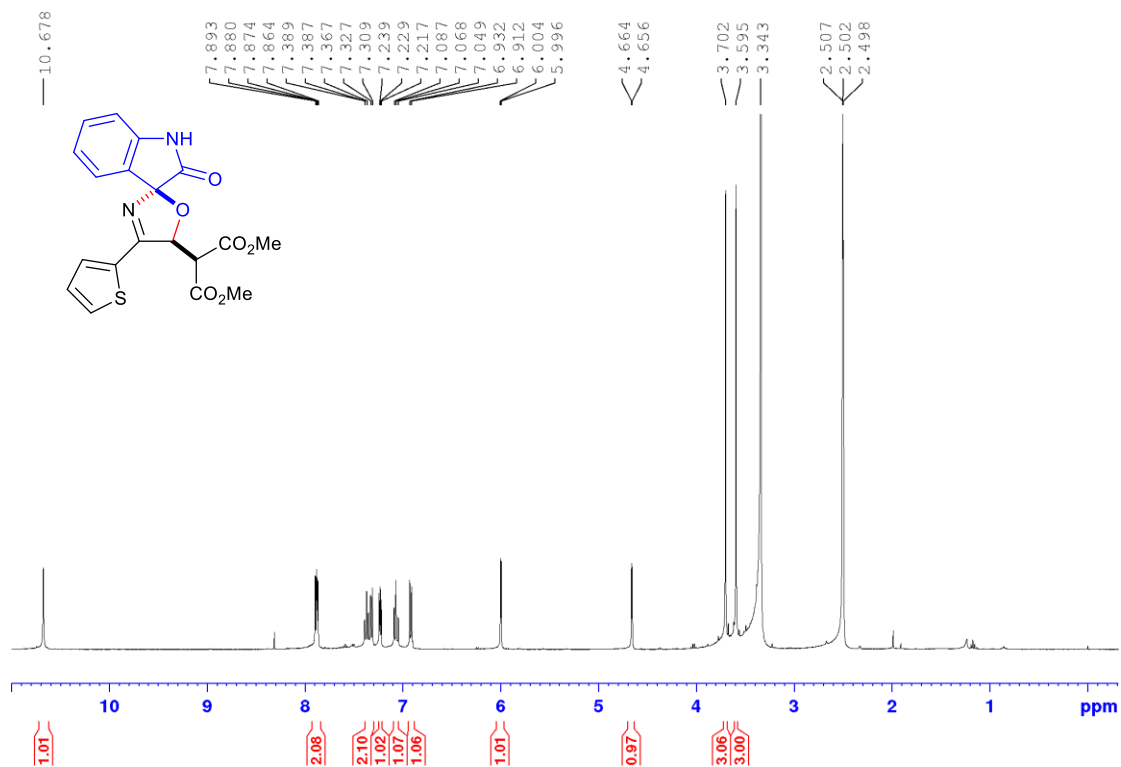
Dimethyl 2-(4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ja)



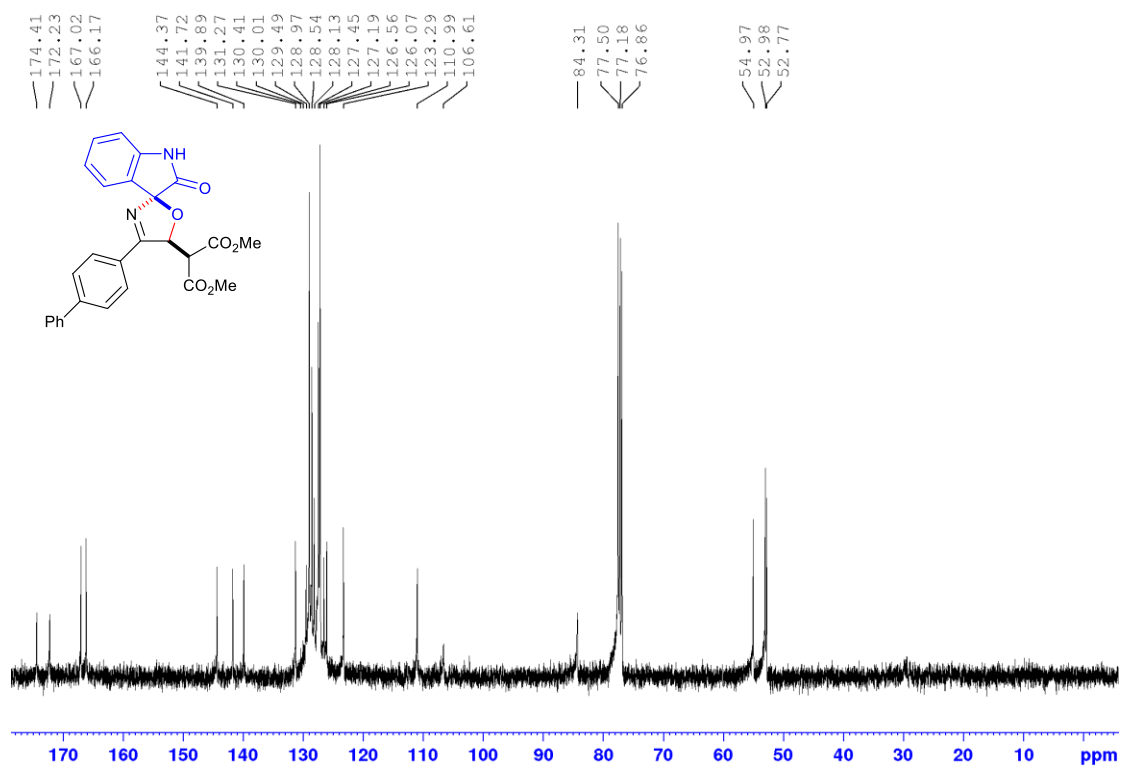
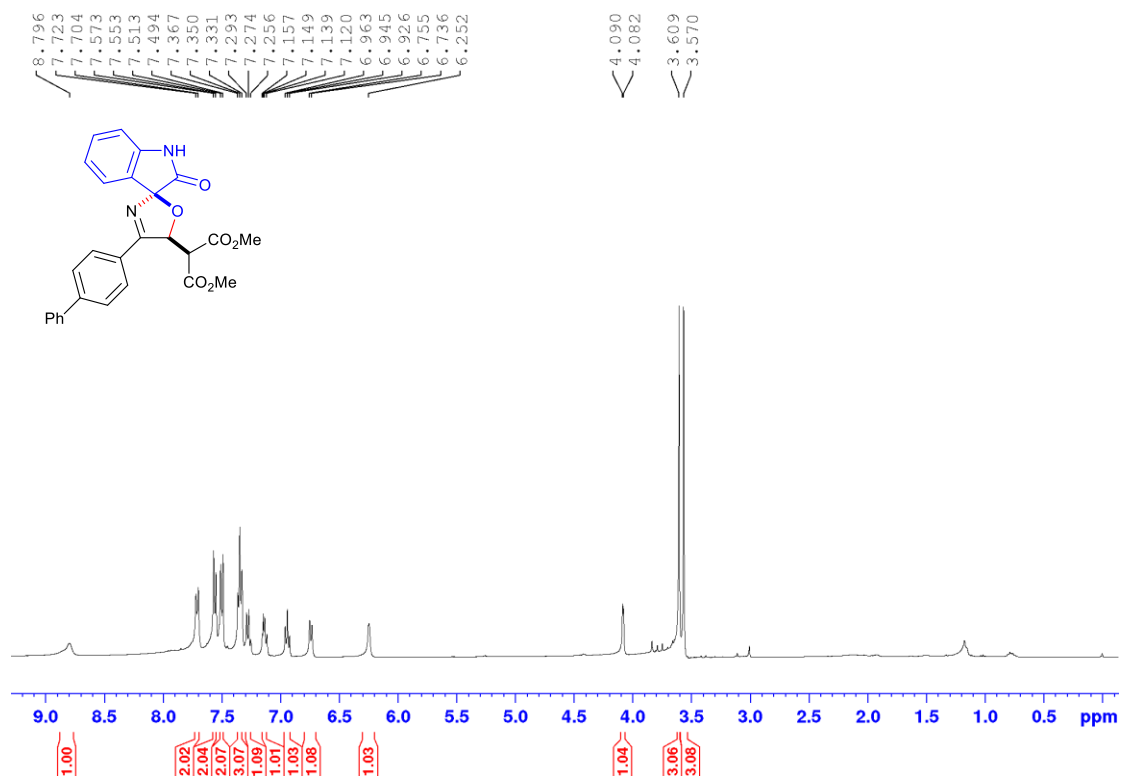
Dimethyl 2-(4'-(furan-2-yl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ka)



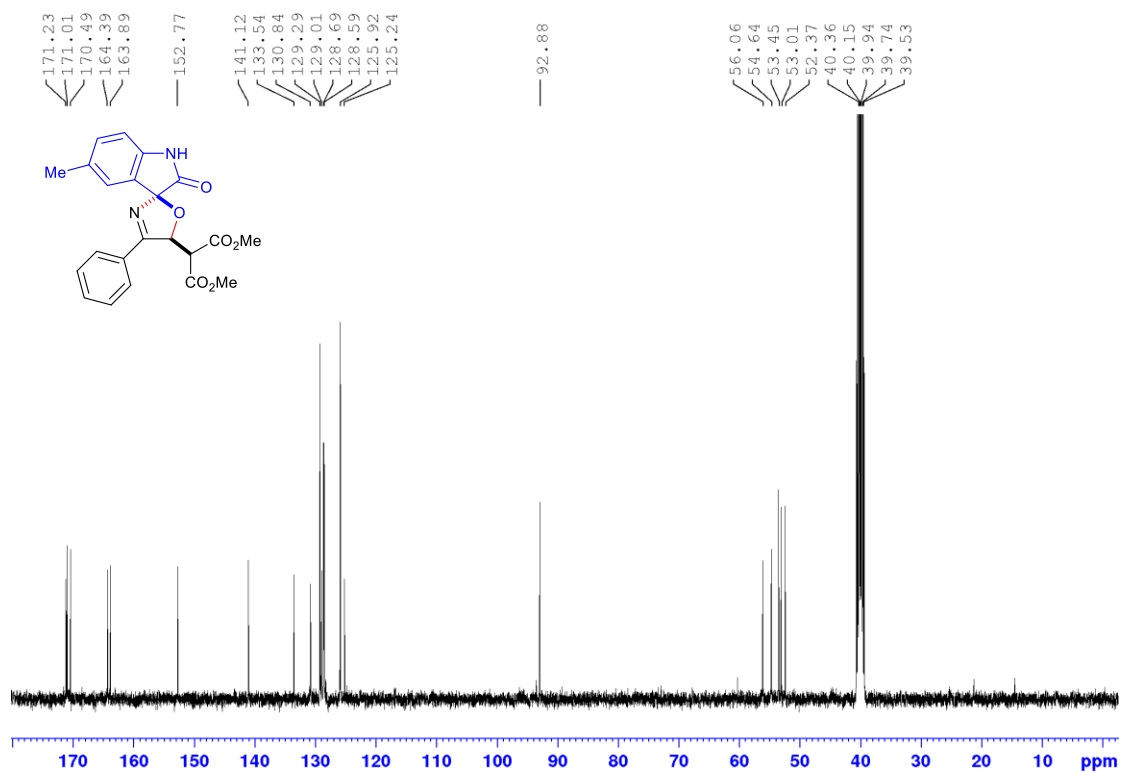
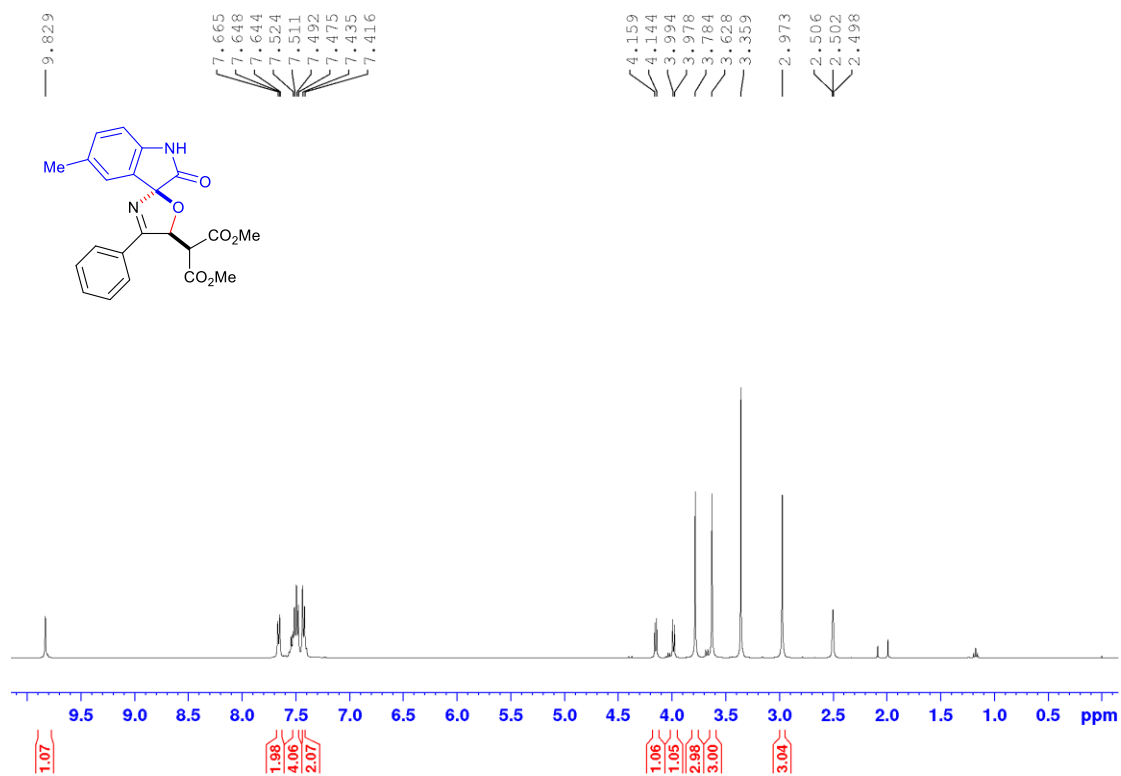
Dimethyl 2-(2-oxo-4'-(thiophen-2-yl)-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3la)



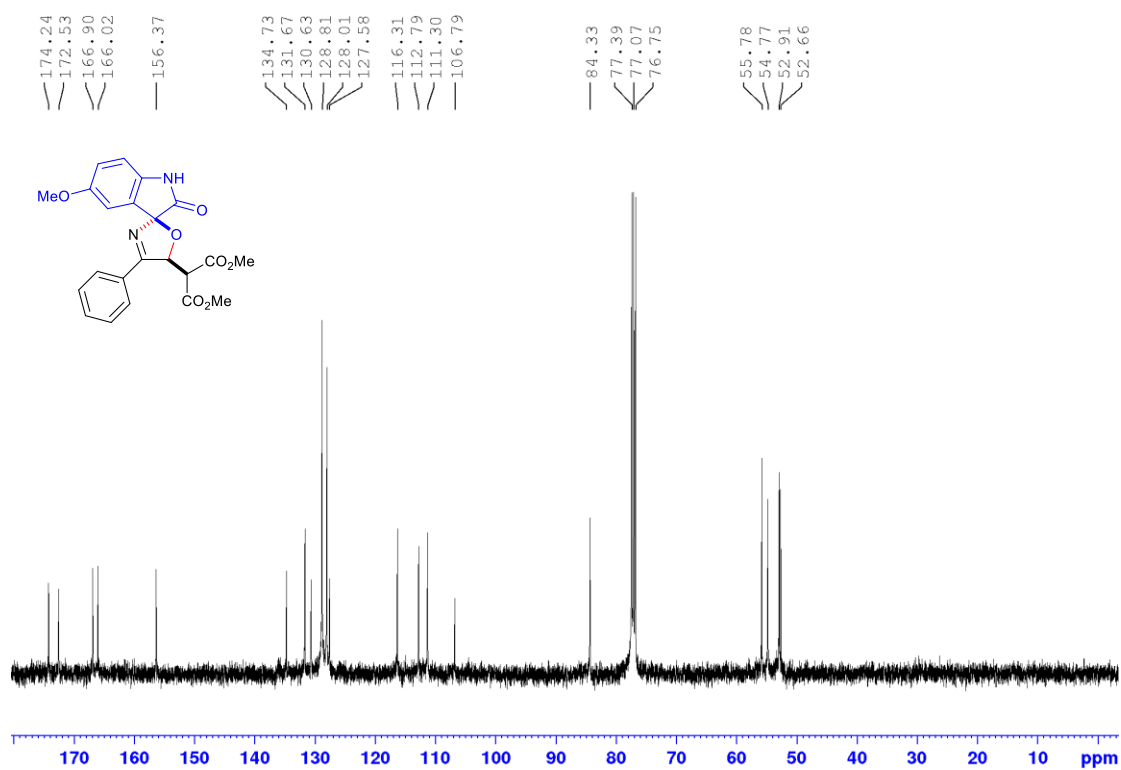
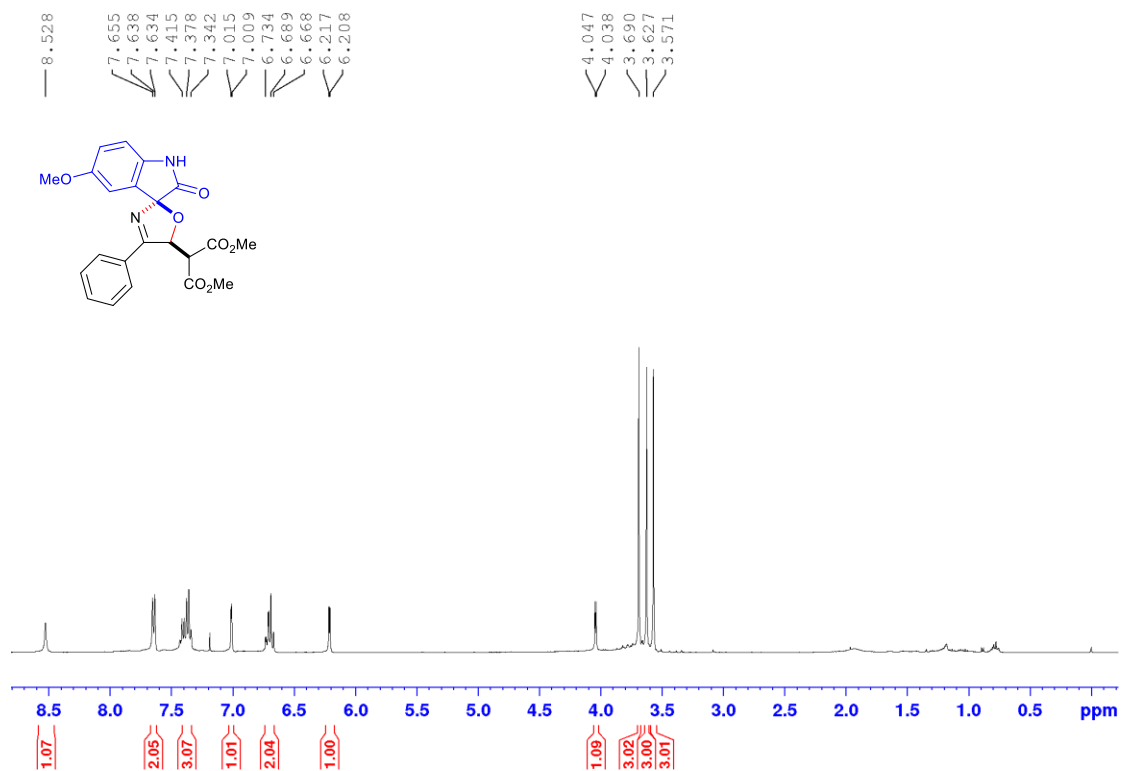
Dimethyl 2-(4'-([1,1'-biphenyl]-4-yl)-2-oxo-5'-H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ma)



**Dimethyl 2-(5-methyl-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ab)**

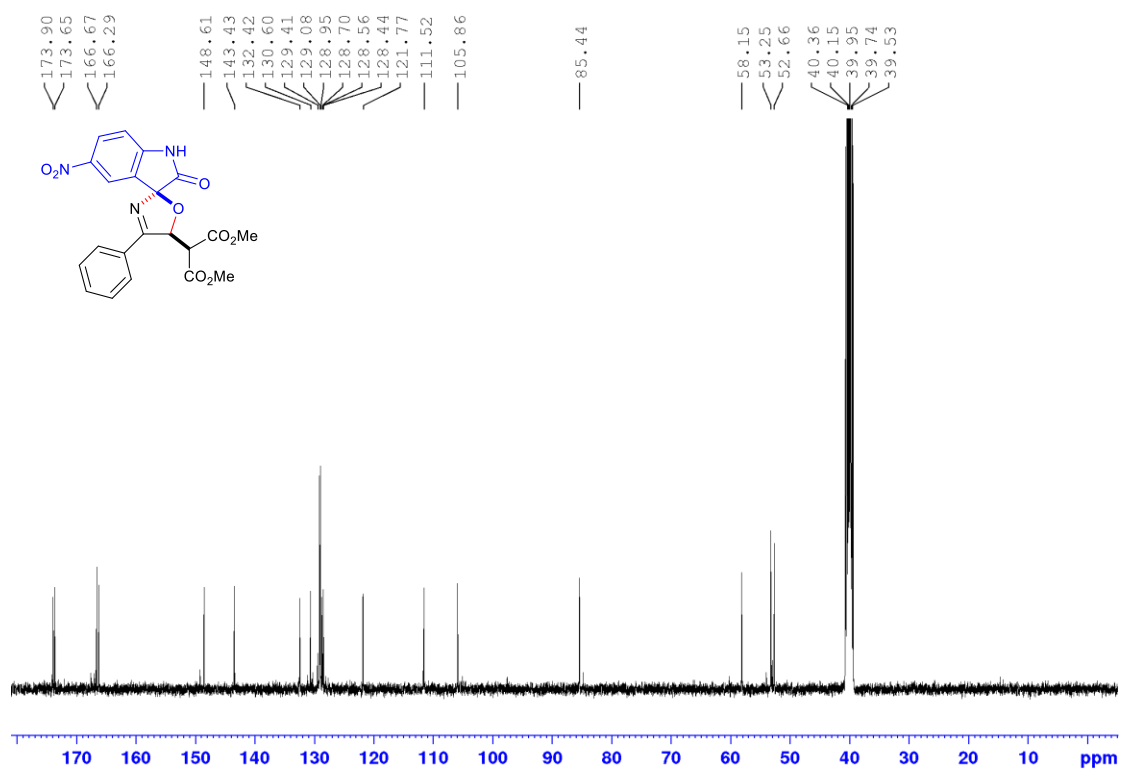
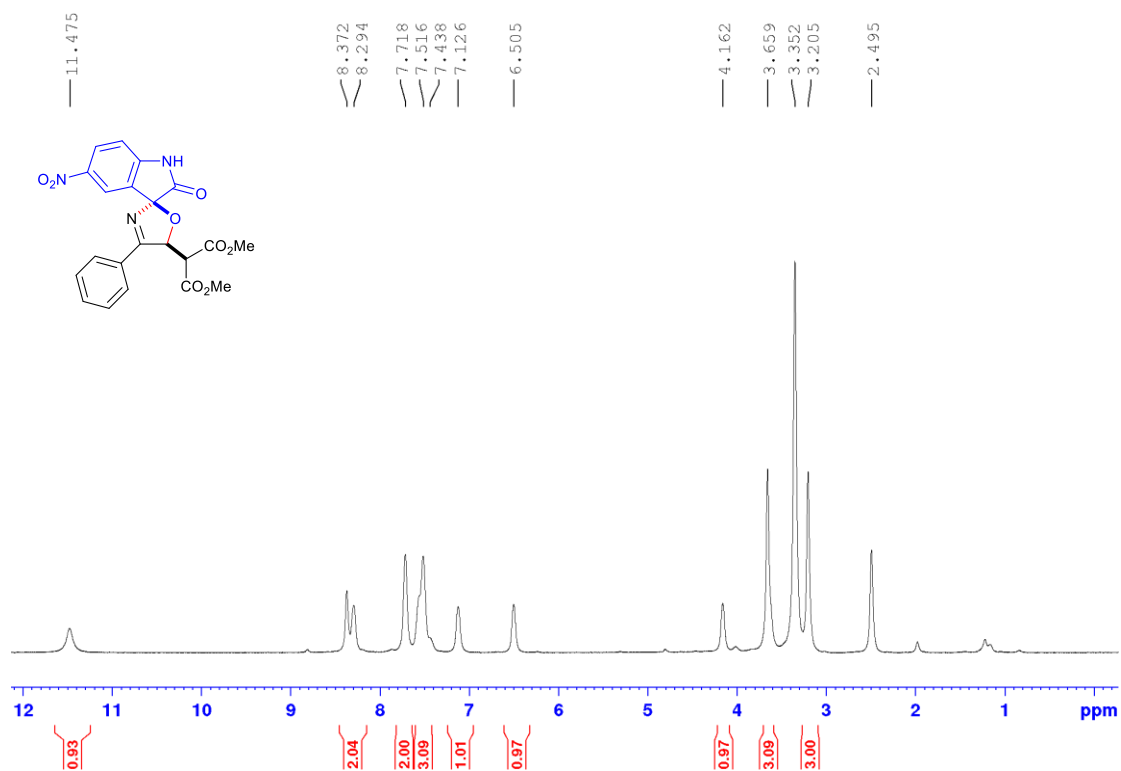


Dimethyl 2-(5-methoxy-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ac)

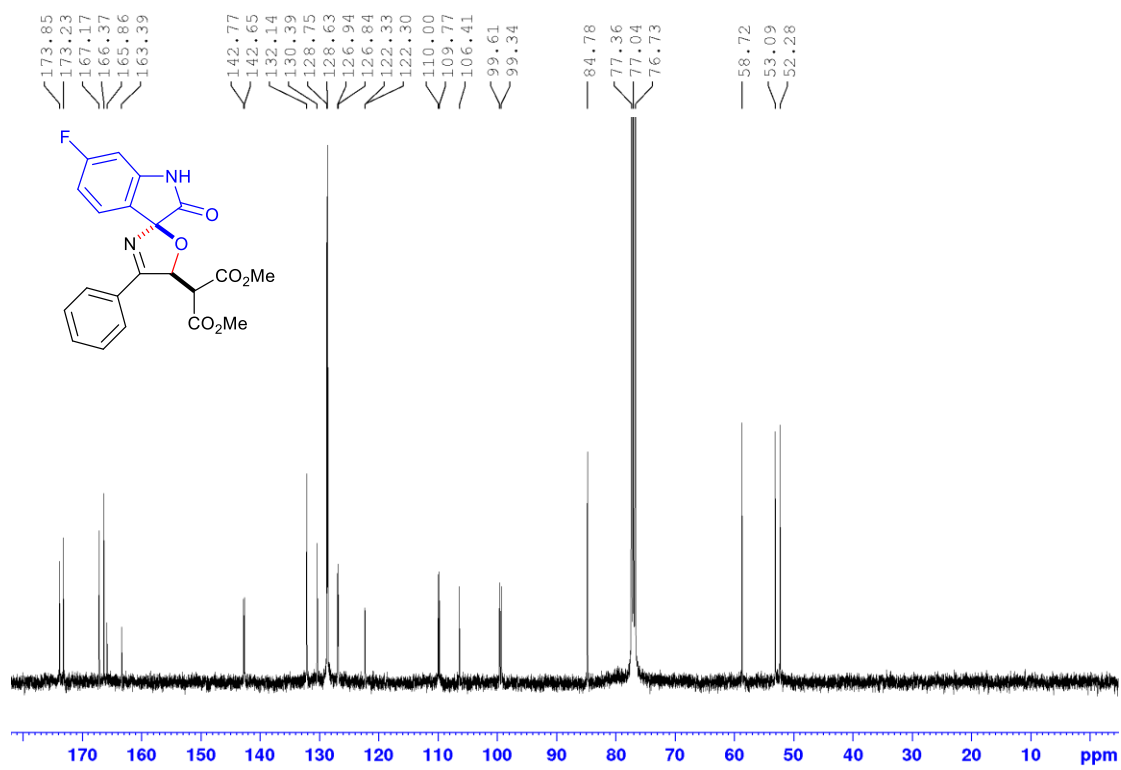
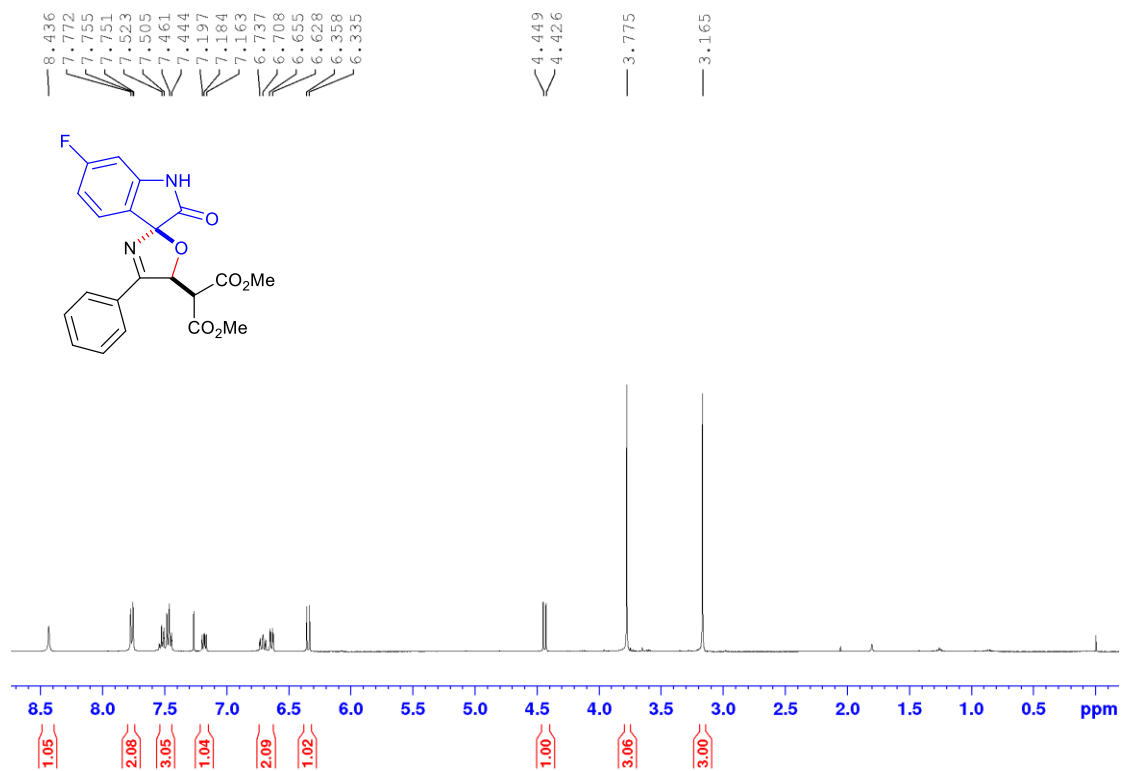




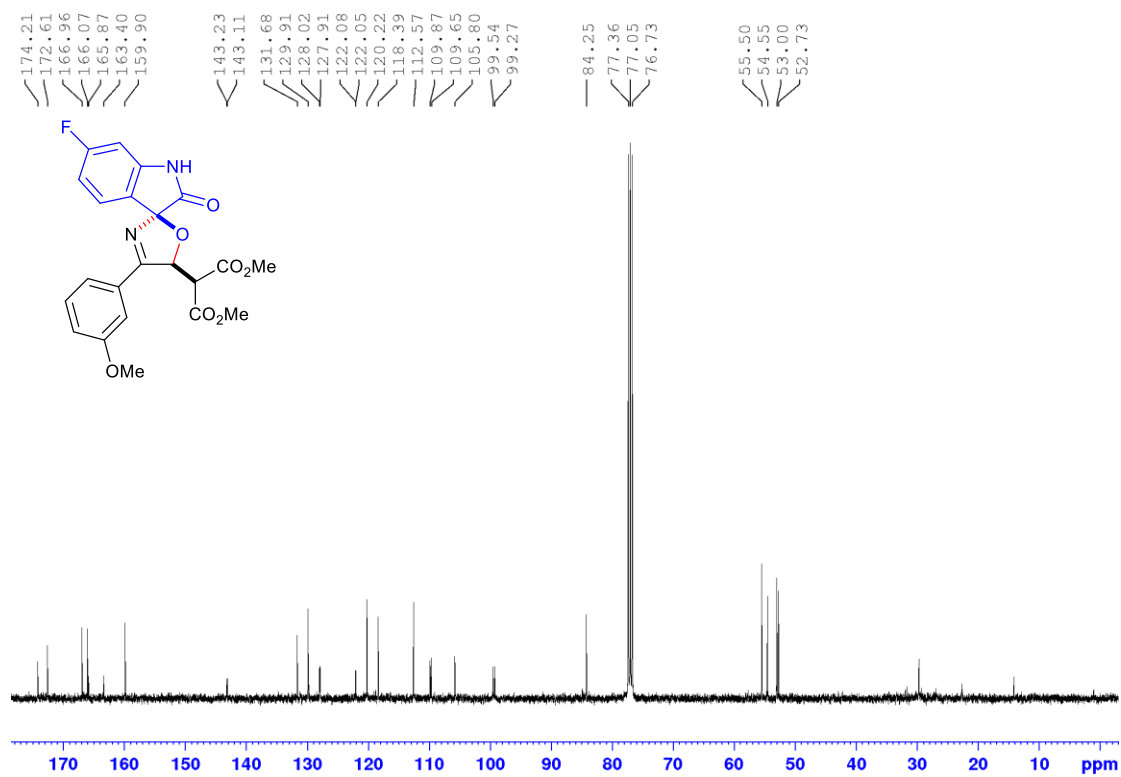
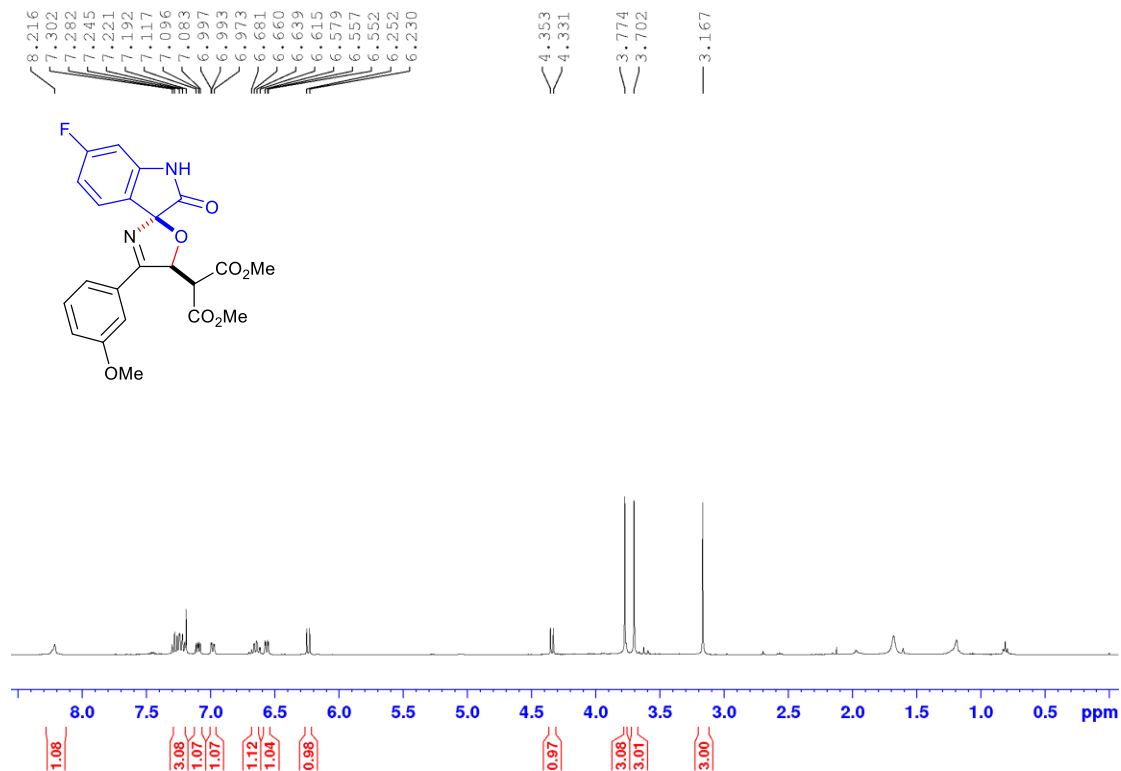
Dimethyl 2-(5-nitro-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ad)



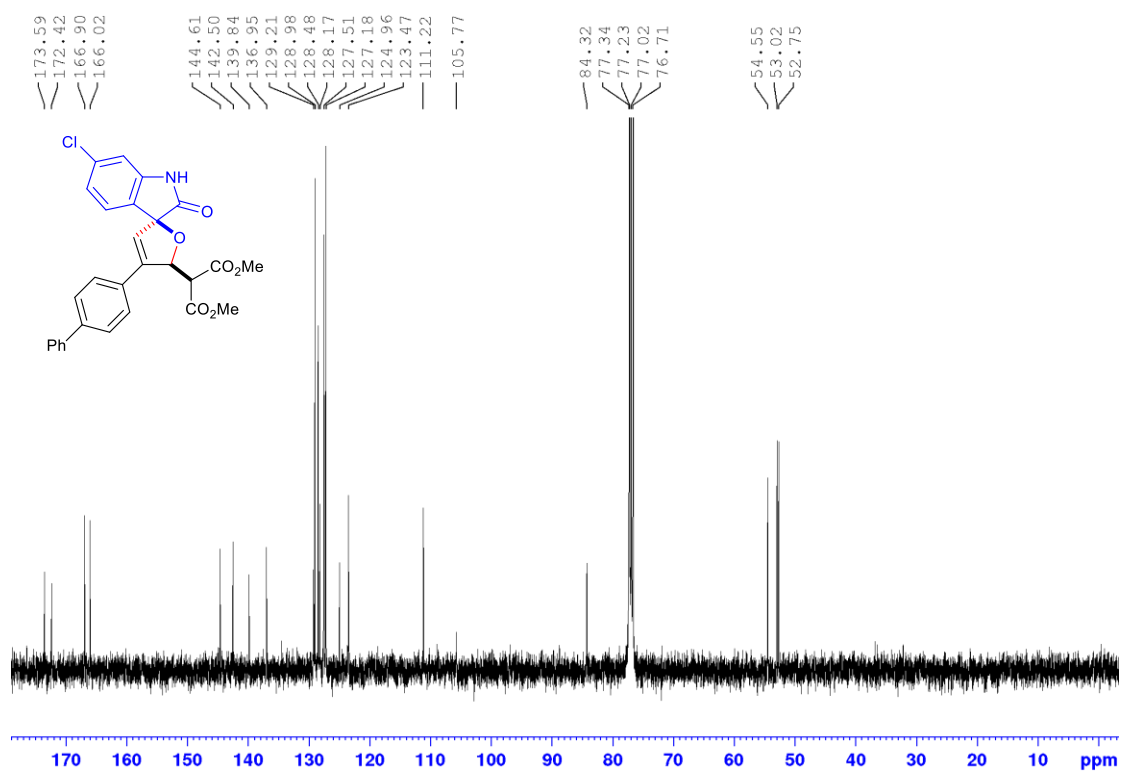
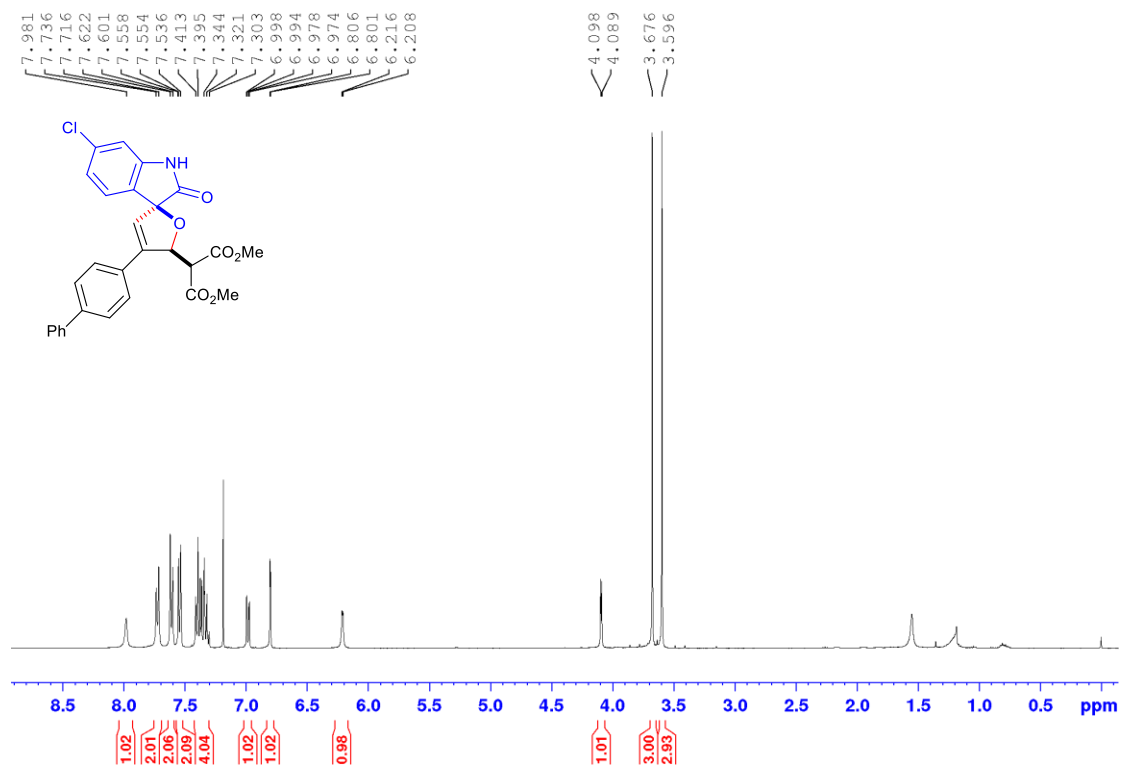
Dimethyl 2-(6-fluoro-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ae)



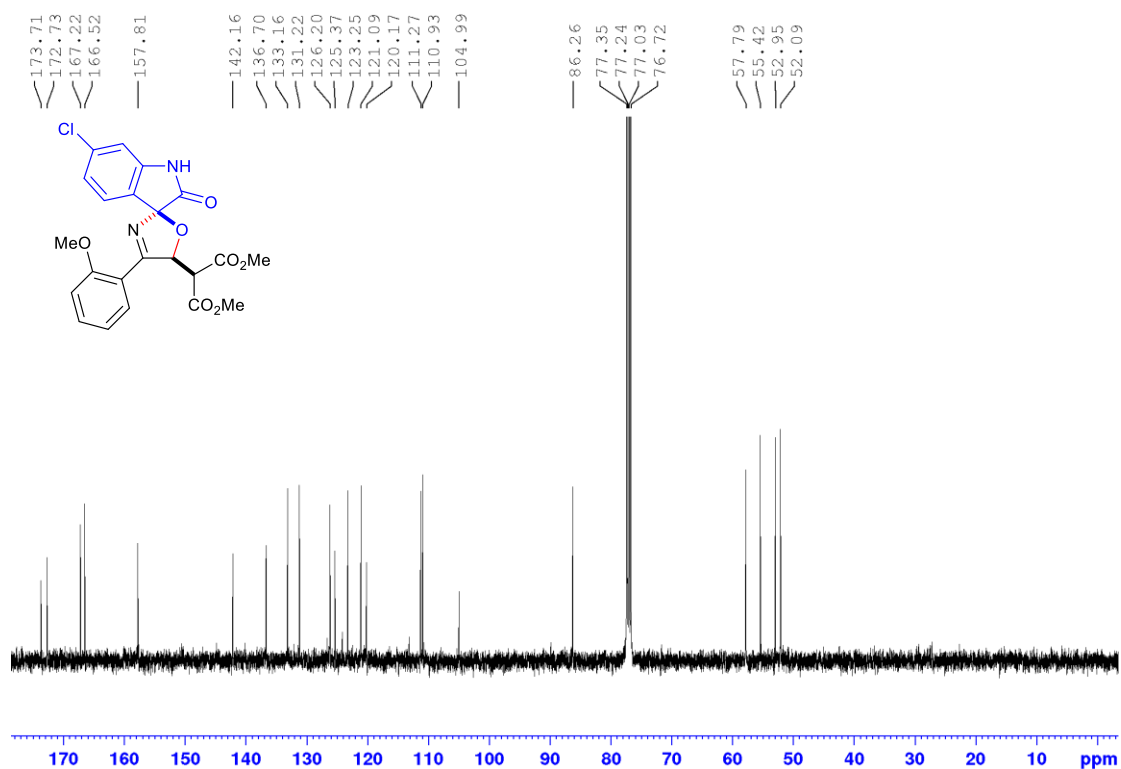
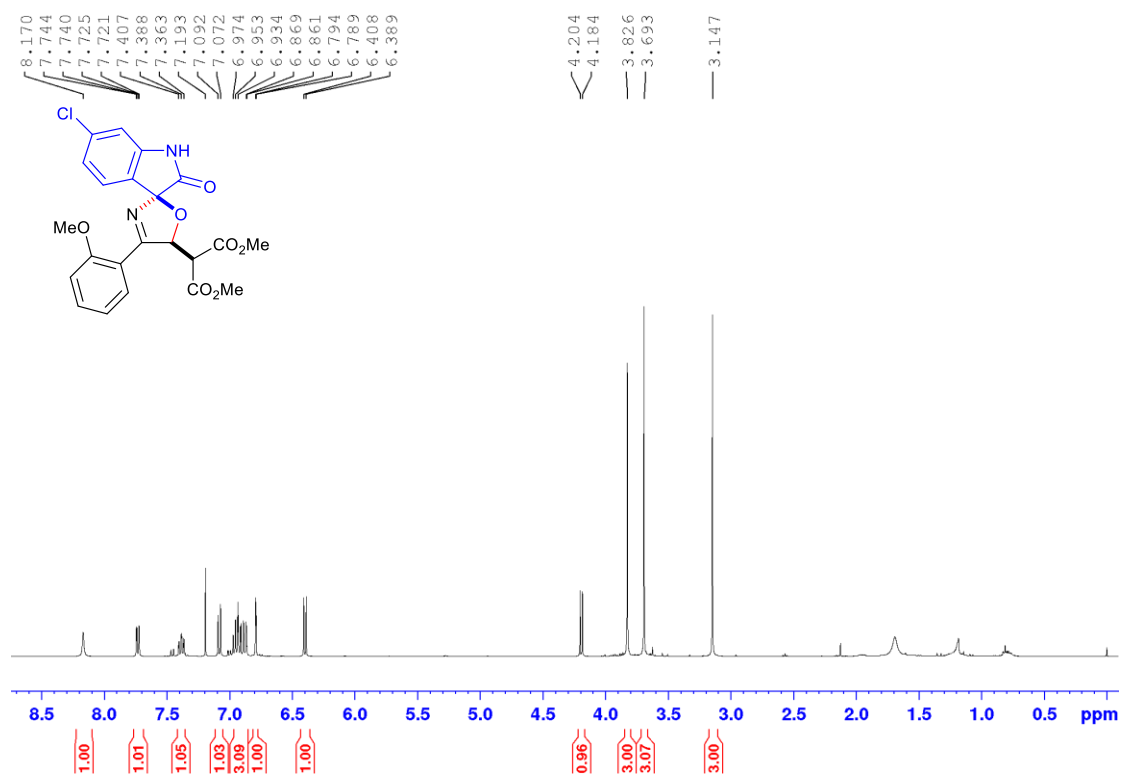
**Dimethyl 2-(6-fluoro-4'-(3-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3he)**



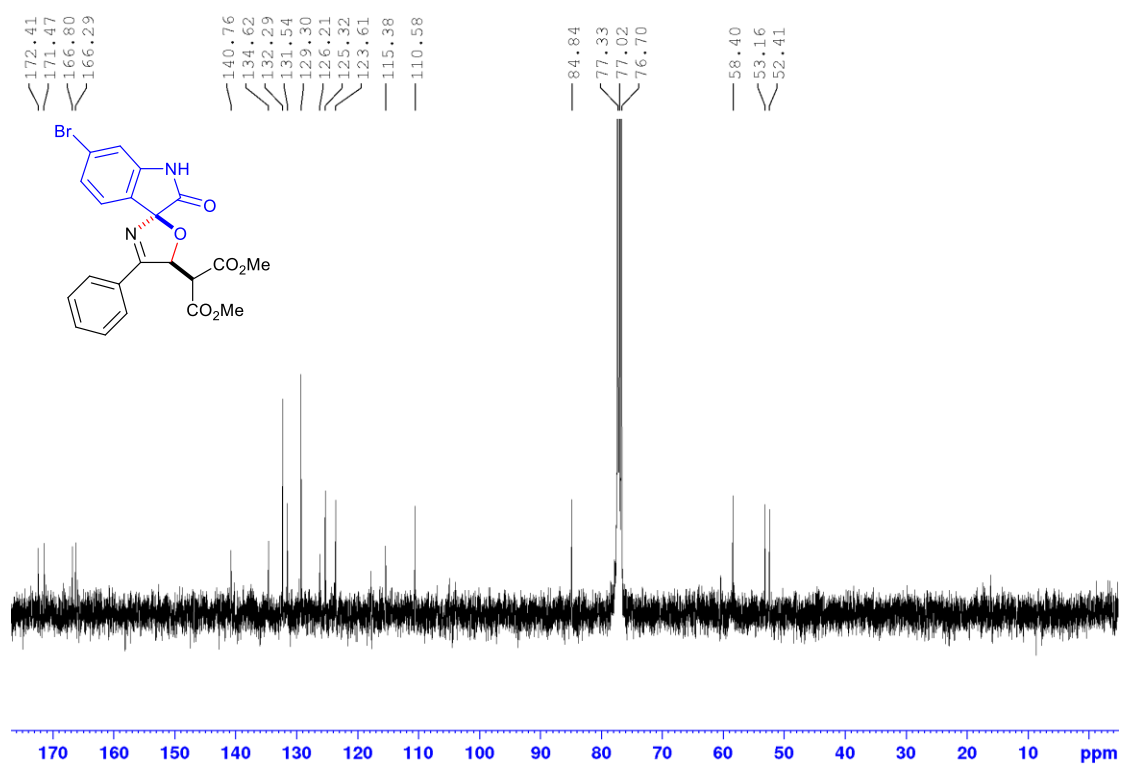
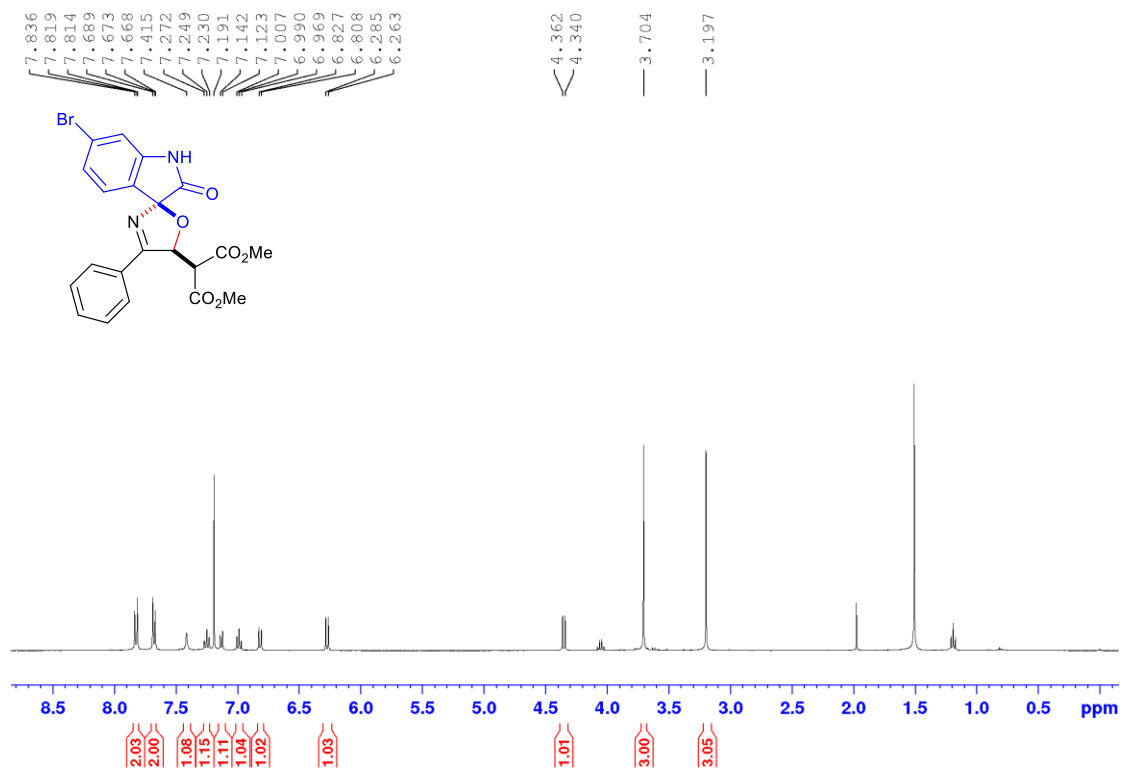
**Dimethyl 2-(4'-([1,1'-biphenyl]-4-yl)-6-chloro-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3mf)**



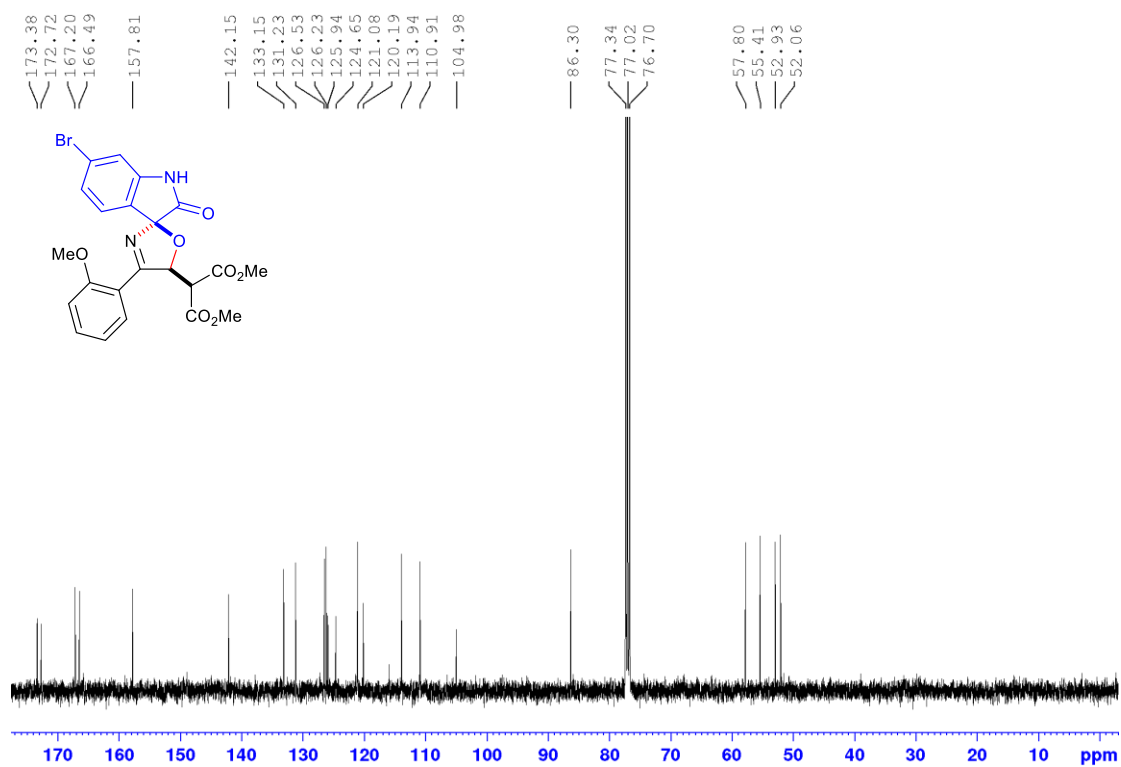
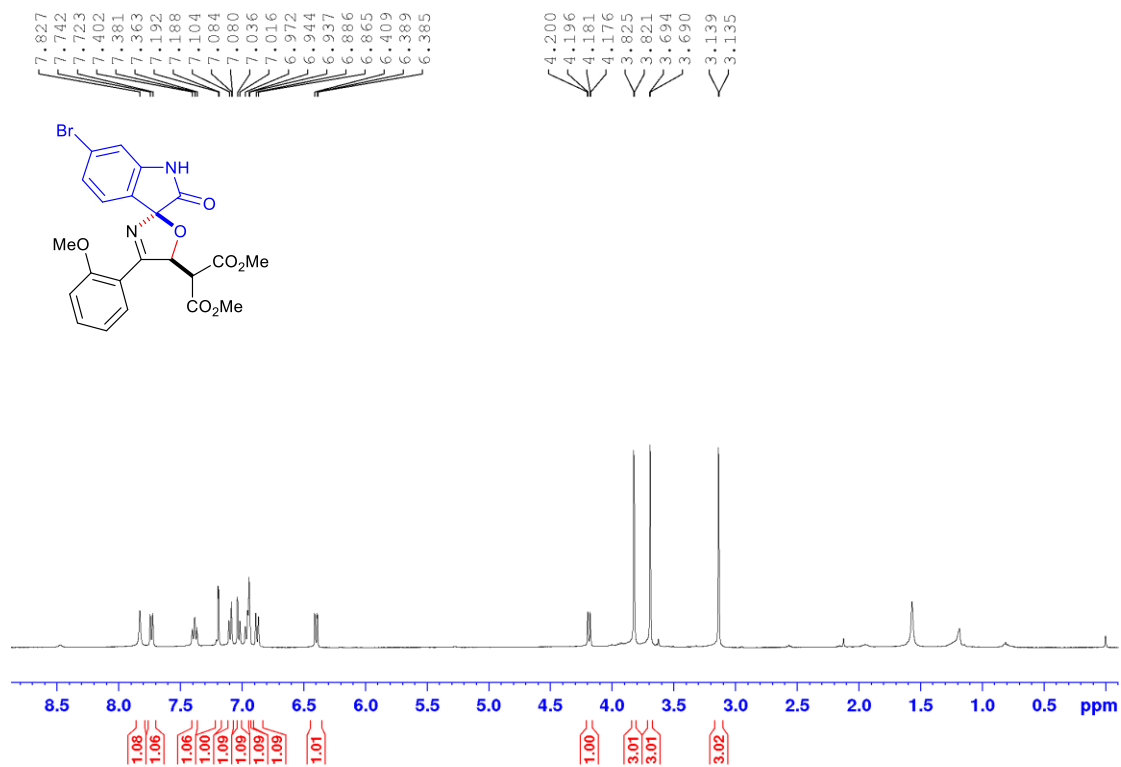
Dimethyl 2-(6-chloro-4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jf)



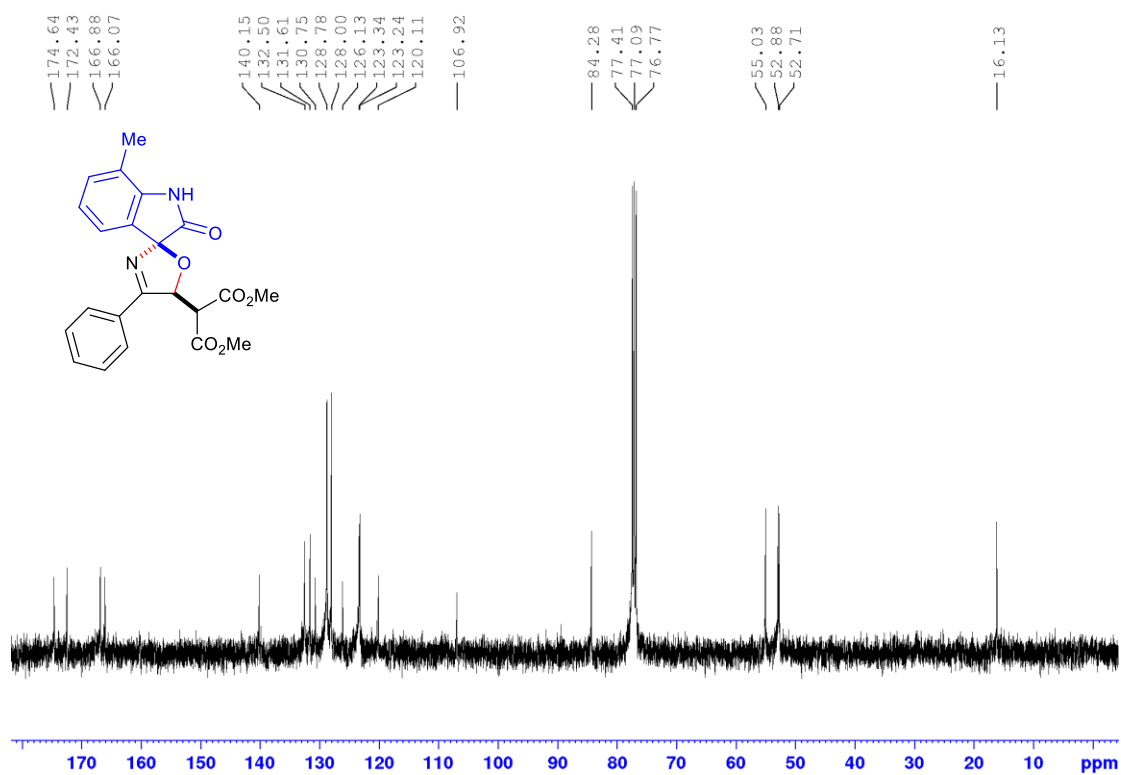
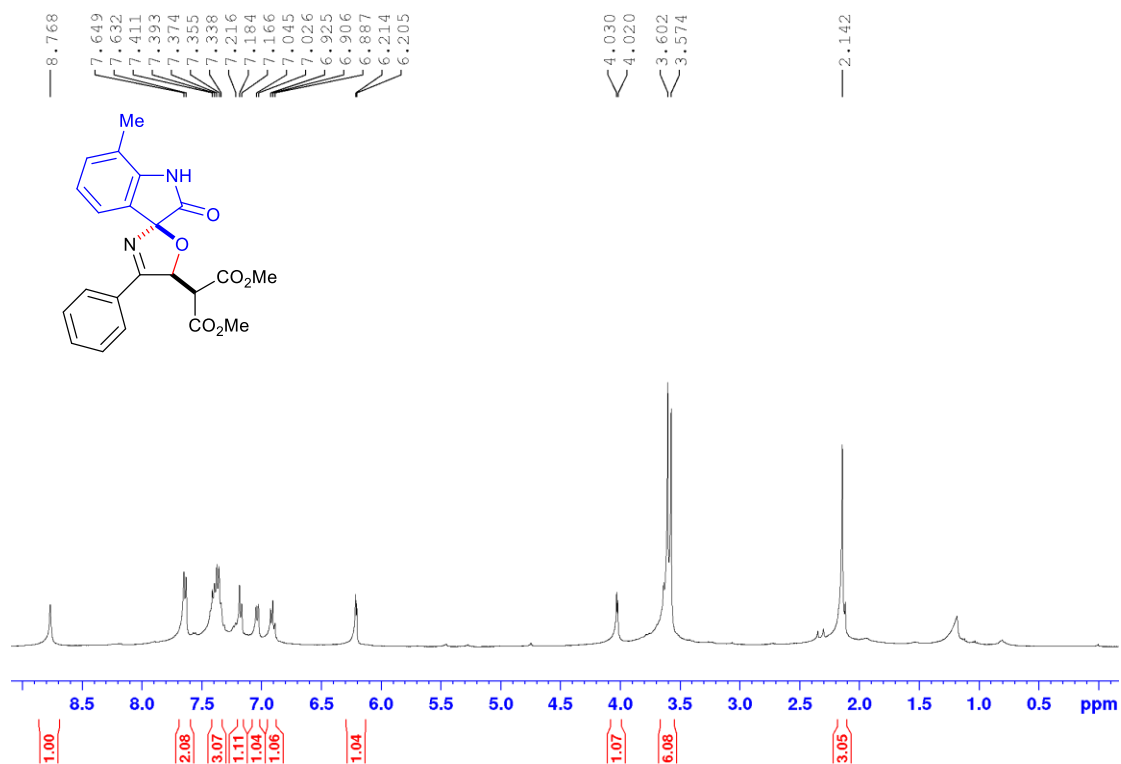
Dimethyl 2-(6-bromo-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ag)



Dimethyl 2-(6-bromo-4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jg)

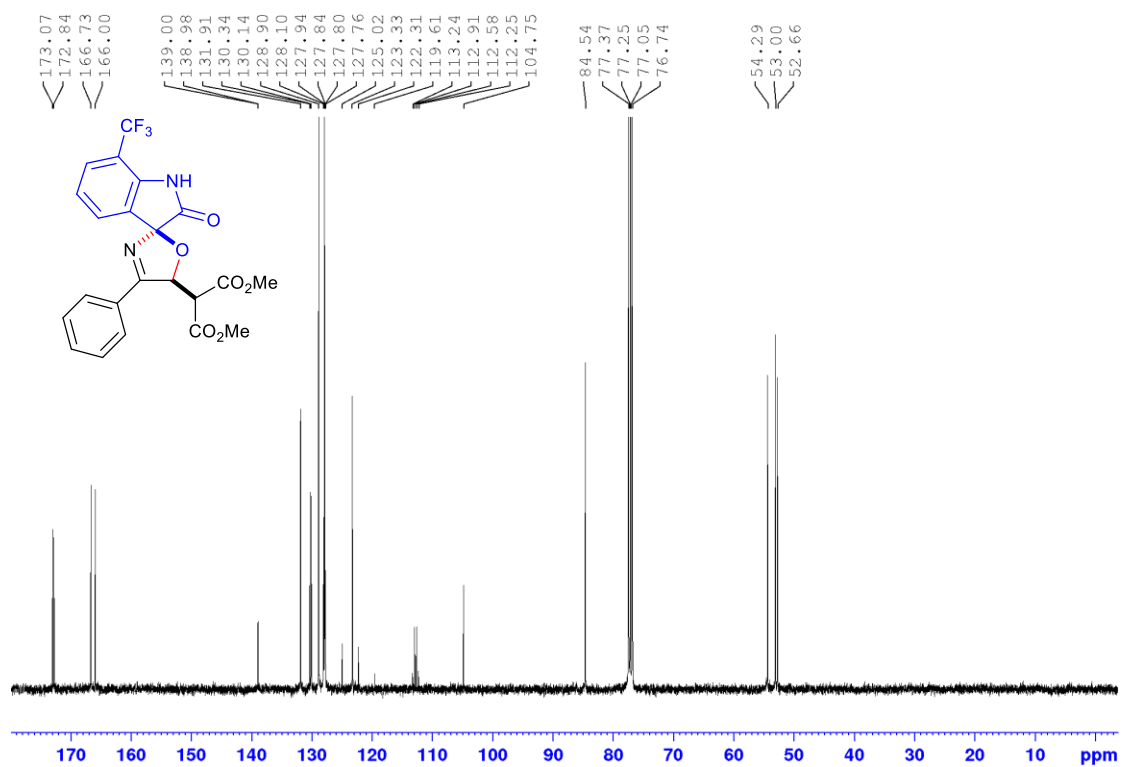
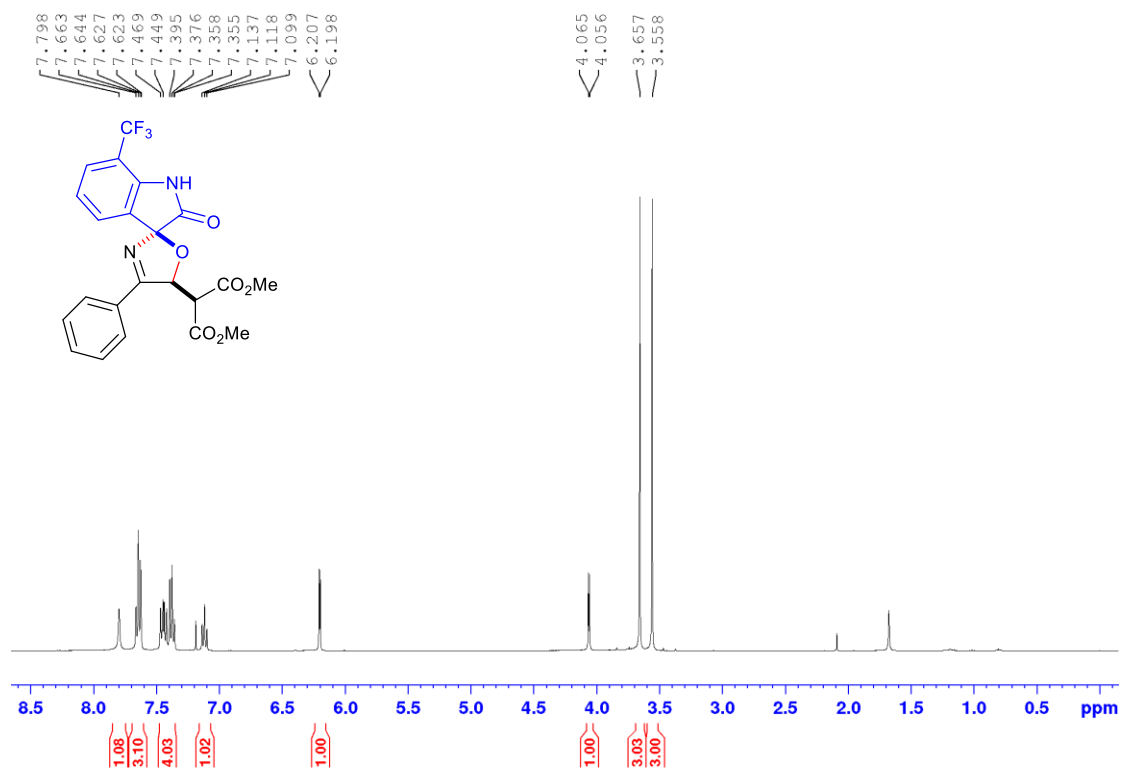


Dimethyl 2-(7-methyl-2-oxo-4'-phenyl-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ah)

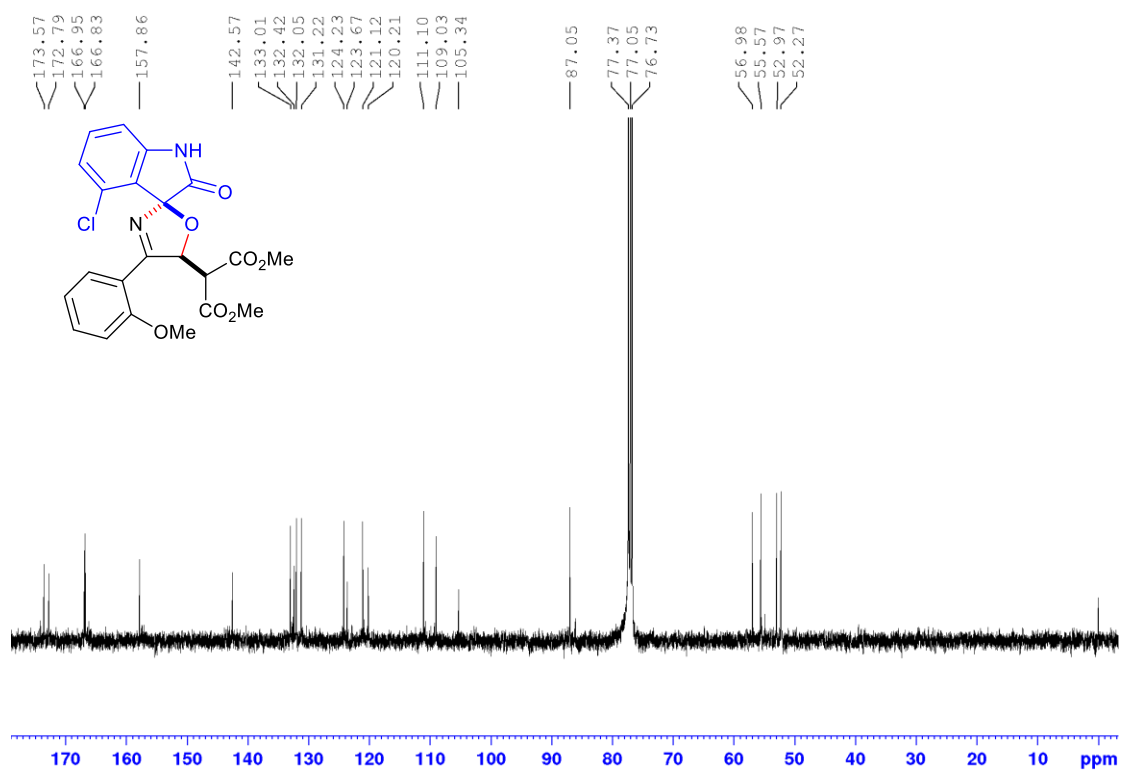
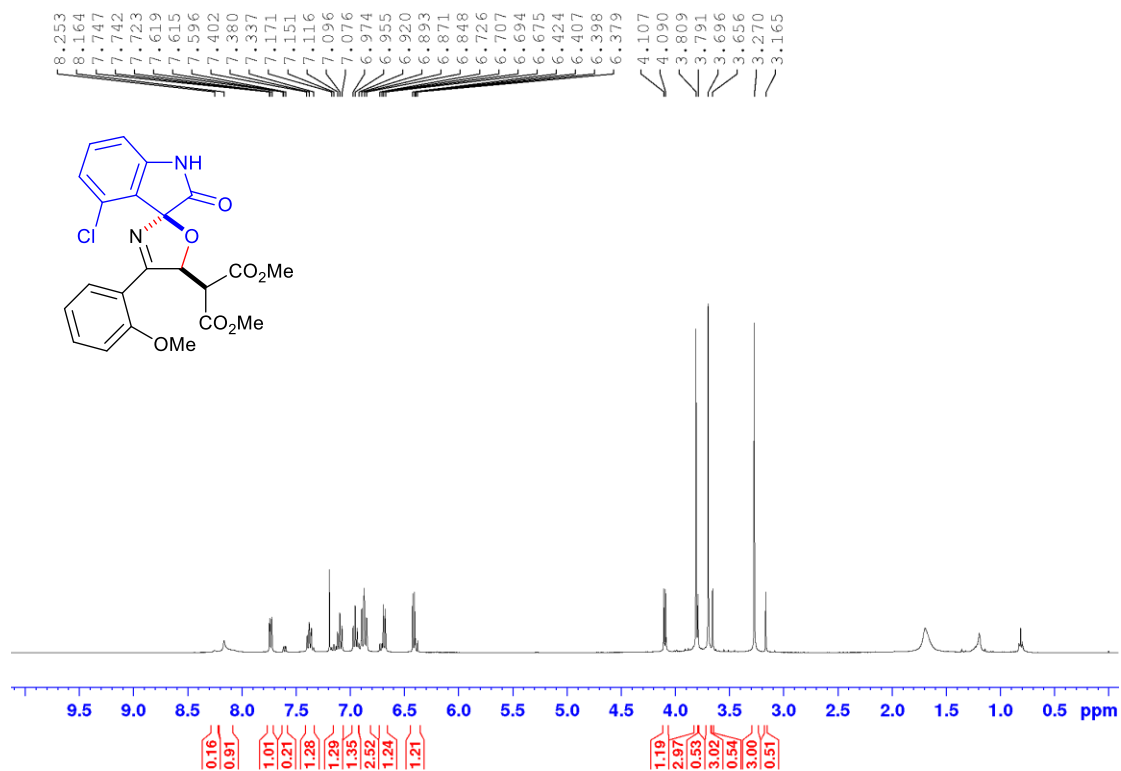




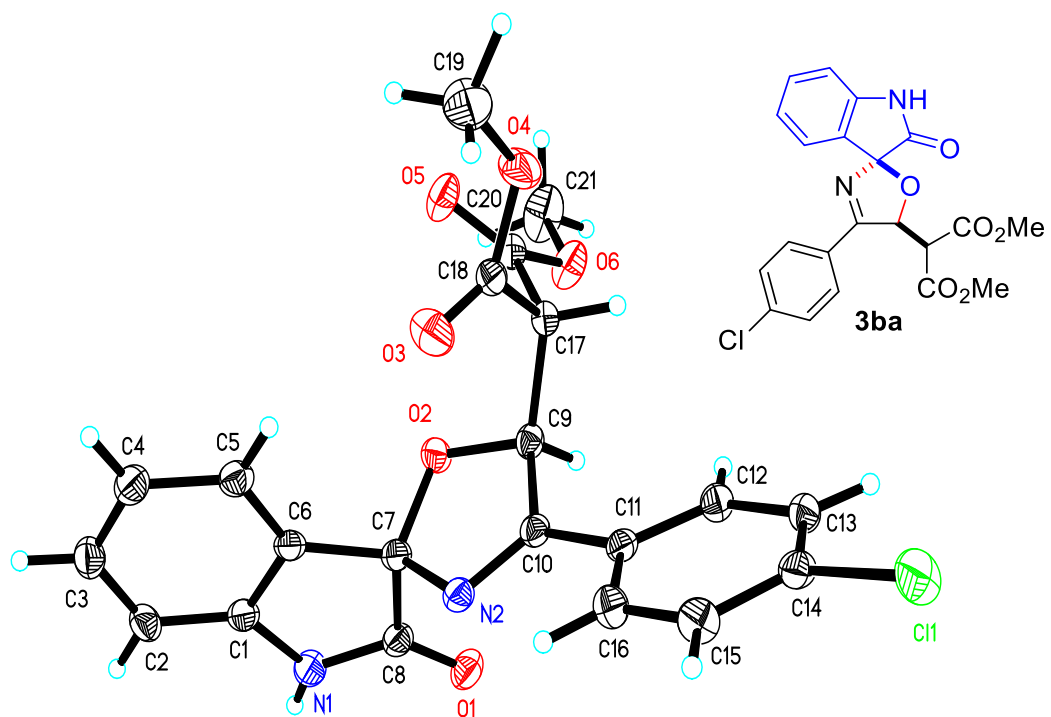
Dimethyl 2-(2-oxo-4'-phenyl-7-(trifluoromethyl)-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3ai)



**Dimethyl 2-(4-chloro-4'-(2-methoxyphenyl)-2-oxo-5'H-spiro[indoline-3,2'-oxazol]-5'-yl)malonate (3jj)**



## Crystal Structure and data for compound 3ba



Crystal data and structure refinement for compound **3ba**

Identification code	shelx	
Empirical formula	C <sub>21</sub> H <sub>17</sub> Cl N <sub>2</sub> O <sub>6</sub>	
Formula weight	428.82	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Trigonal	
Space group	R -3 :H	
Unit cell dimensions	a = 32.8416(15) Å	a = 90 °
	b = 32.8416(15) Å	b = 90 °
	c = 9.7790(5) Å	g = 120 °
Volume	9134.3(10) Å <sup>3</sup>	
Z	18	
Density (calculated)	1.403 Mg/m <sup>3</sup>	
Absorption coefficient	0.229 mm <sup>-1</sup>	
F(000)	3996	
Crystal size	0.180 x 0.150 x 0.120 mm <sup>3</sup>	
Theta range for data collection	2.528 to 27.534 °	
Index ranges	-29<=h<=42, -42<=k<=37, -12<=l<=12	
Reflections collected	16997	
Independent reflections	4662 [R(int) = 0.0720]	
Completeness to theta = 25.242?	99.7 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4538	
Refinement method	Full-matrix least-squares on F <sup>2</sup>	
Data / restraints / parameters	4662 / 0 / 278	
Goodness-of-fit on F <sup>2</sup>	1.017	
Final R indices [I>2sigma(I)]	R1 = 0.0510, wR2 = 0.1348	
R indices (all data)	R1 = 0.0759, wR2 = 0.1552	
Extinction coefficient	0.0013(2)	
Largest diff. peak and hole	1.040 and -0.327 e.Å <sup>-3</sup>	

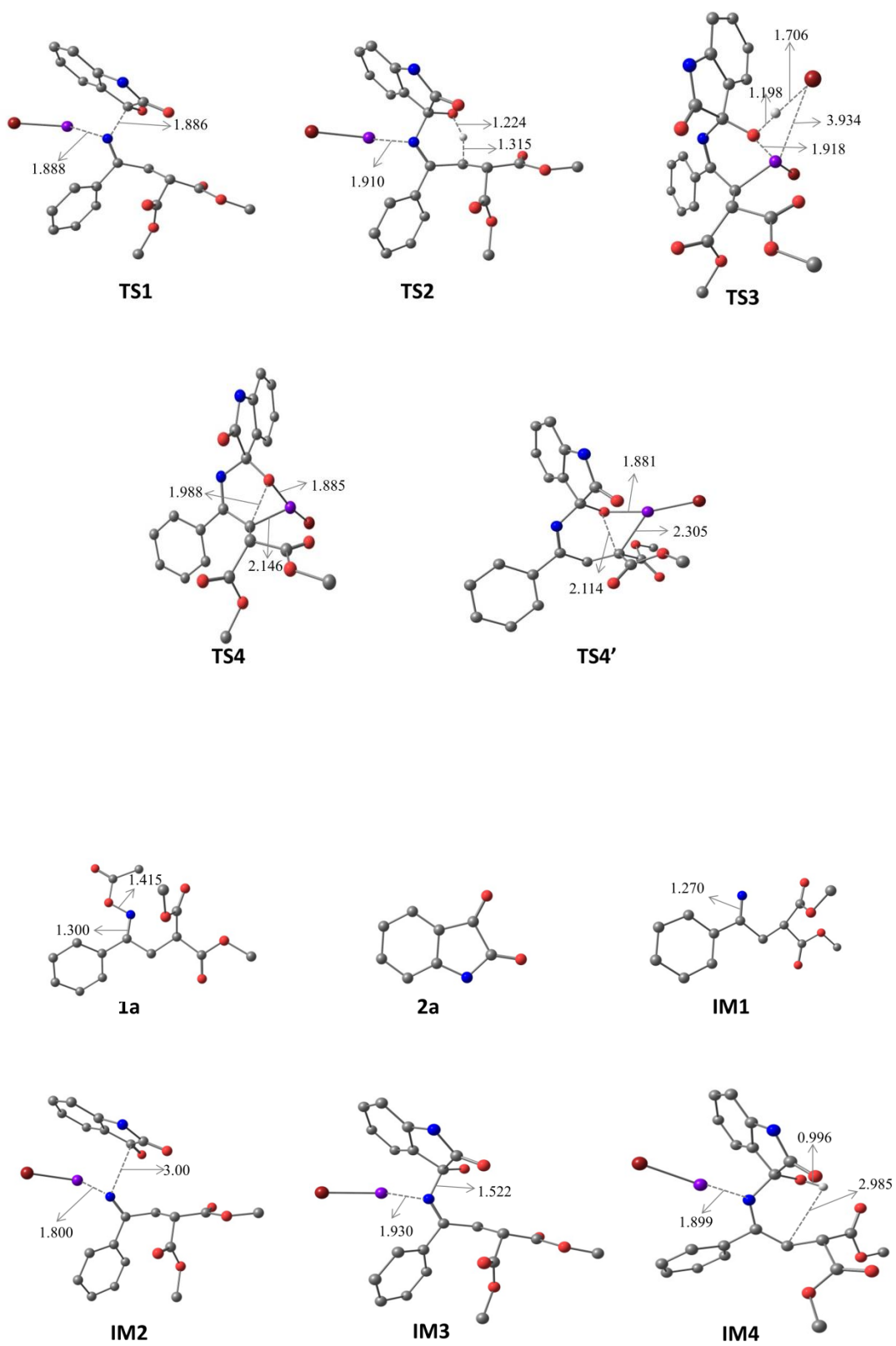
## Computational details

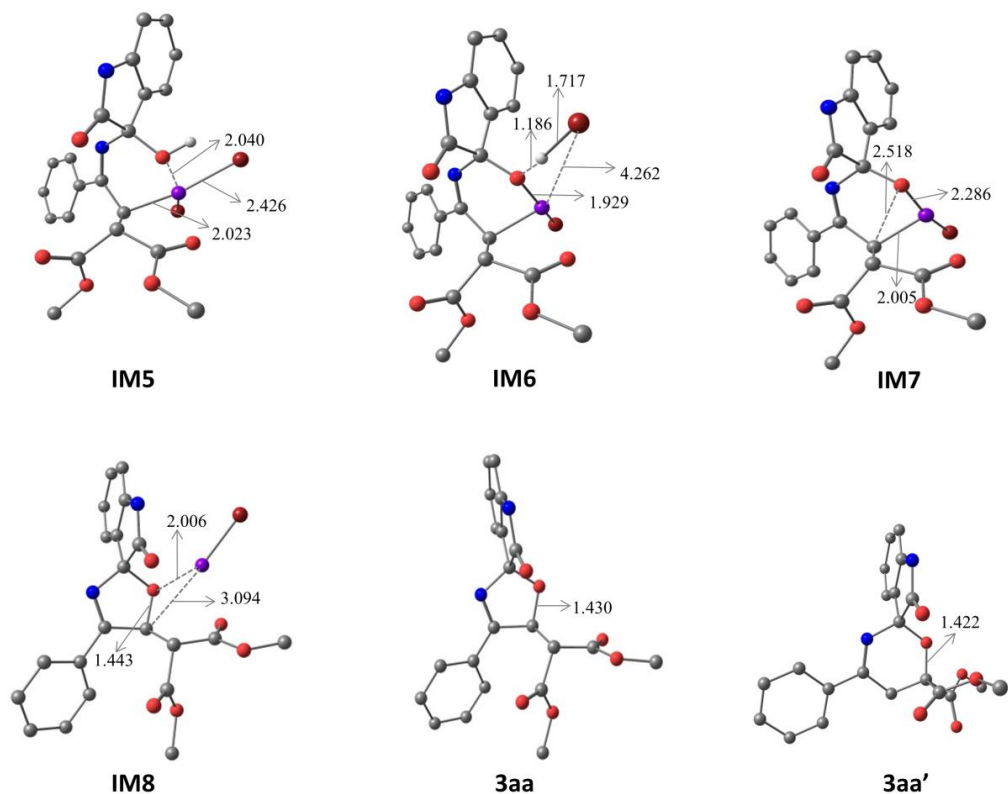
All calculations were performed with the Gaussian 16<sup>2</sup> program without symmetry restrictions. All molecules were using the BP86 functional<sup>3,4</sup> with def2-SVP<sup>5</sup> basis set and dispersion correction by Grimme with Becke-Johnson damping D3(BJ)<sup>6,7</sup>, the solvation effects of acetonitrile (an experimentally used solvent) were considered by SMD<sup>8</sup> solvation model (termed as BP86+D3(BJ)/def2-SVP (SMD, solvent= Acetonitrile)). The energetic results were then improved by the single-point at BP86/def2-TZVPP<sup>9,10</sup> levels with the solvation effects included. Therefore, all the energetics reported in this study is at the BP86+D3(BJ)/def2-TZVPP (SMD, solvent= Acetonitrile)//BP86+D3(BJ)/def2-SVP (SMD, solvent= Acetonitrile) level.

## References

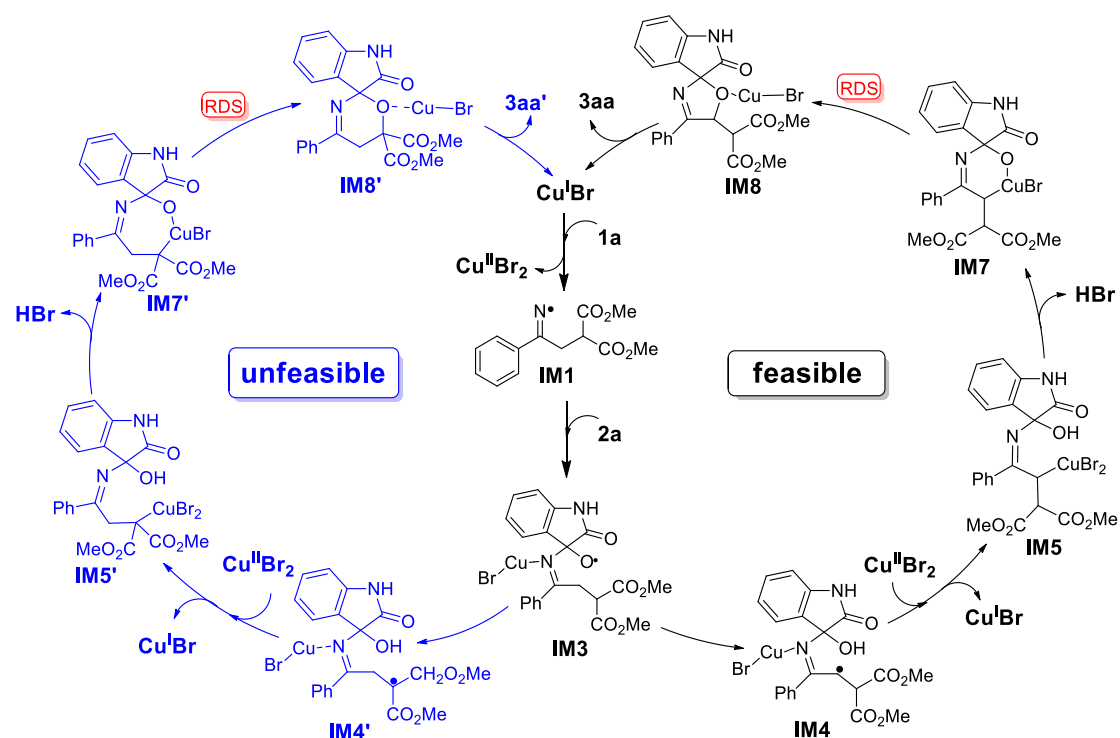
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## Optimized structures and the whole catalytic cycle





**Figure S1.** Optimized structures of intermediates and transition states according to scheme 5. The key bond distances are given in Å. Some hydrogen atoms are omitted for clarity (color code, C: gray, H: white, O: red, N: blue, Cu: purple, Br: dark red).



**Figure S2.** The proposed whole catalytic cycle of the two pathways.

## Coordinates and energies of the calculated structures

**Table S2.** Coordinates and energies (in hartree) of the calculated structures at the BP86+D3(BJ)/def2-TZVPP(SMD,solvent=Acetonitrile)//BP86+D3(BJ)/def2-SVP(SMD, solvent=Acetonitrile) level.

<b>1a</b>				H	0.361274	3.264450	-0.351704
E=-1088.437242				H	-0.024738	3.000622	-2.059521
G= -1088.196725				H	-0.439172	4.596708	-1.305170
N	-0.677146	0.937807	-0.491782				
C	-0.833739	-0.333679	-0.291441				
C	-2.112252	-1.050593	-0.032287				
C	-3.064974	-0.545813	0.885452				
C	-2.365813	-2.285537	-0.674692				
C	-4.243735	-1.260587	1.145828				
H	-2.872616	0.402712	1.405477				
C	-3.555786	-2.987401	-0.424286				
H	-1.634813	-2.691675	-1.390291				
C	-4.496903	-2.478503	0.487919				
H	-4.972186	-0.862026	1.869591				
H	-3.746192	-3.939890	-0.943588				
H	-5.427361	-3.032585	0.689686				
C	0.441263	-1.143071	-0.302378				
H	0.369906	-1.934953	-1.077043				
H	0.514367	-1.680536	0.667042				
C	1.720055	-0.331350	-0.548644				
H	1.665816	0.177584	-1.534305				
C	1.954715	0.781071	0.474209				
O	2.348647	1.906510	0.221606				
O	1.690234	0.337074	1.723718				
C	1.859736	1.298138	2.783336				
H	2.897557	1.687695	2.800582				
H	1.155078	2.145392	2.656774				
H	1.637808	0.758540	3.721937				
C	2.920434	-1.282641	-0.624706				
O	2.854730	-2.450165	-0.968852				
O	4.064941	-0.656658	-0.289351				
C	5.270248	-1.448881	-0.359004				
H	6.090173	-0.777961	-0.045598				
H	5.204833	-2.319895	0.323639				
H	5.442526	-1.807108	-1.393906				
O	-1.893959	1.660902	-0.483555				
C	-1.753067	3.009815	-0.777132				
O	-2.769419	3.673266	-0.730510				
C	-0.380787	3.505840	-1.138104				
				<b>2a</b>			
				E= -513.3241728			
				G= -513.2447678			
				C	0.000000	0.641229	0.000000
				C	0.675741	-0.611588	0.000000
				C	2.073219	-0.676102	0.000000
				C	2.781236	0.544784	0.000000
				C	2.122888	1.793718	0.000000
				C	0.718037	1.847724	0.000000
				C	-1.444803	0.360850	0.000000
				C	-1.553107	-1.215863	0.000000
				H	2.600508	-1.641567	0.000000
				H	3.882601	0.516698	0.000000
				H	2.713169	2.722559	0.000000
				H	0.180356	2.808833	0.000000
				H	0.015117	-2.660516	0.000000
				O	-2.410251	1.110190	0.000000
				O	-2.577240	-1.881720	0.000000
				N	-0.247299	-1.668896	0.000000
				<b>CuBr</b>			
				E= -4215.297424			
				G= -4215.321293			
				Cu	0.000000	0.000000	-1.233686
				Br	0.000000	0.000000	1.022197
				<b>CuBr2</b>			
				E= -6789.745039			
				G= -6789.775208			
				Cu	0.000000	0.000000	0.927923
				Br	0.000000	-1.911772	-0.384425
				Br	0.000000	1.911772	-0.384425
				<b>HBr</b>			
				E= -2575.039245			



G= -2575.052665				C	-2.433428	-1.234831	0.218098
Br	0.000000	0.000000	0.039965	O	-2.168786	-2.348817	-0.199790
H	0.000000	0.000000	-1.398789	O	-3.683891	-0.752955	0.352765
				C	-4.754914	-1.639588	-0.037197
<b>AcOCu</b>				H	-5.689805	-1.076807	0.135543
E= -1869.423243				H	-4.664218	-1.913915	-1.107502
G= -1869.405717				H	-4.742998	-2.560903	0.579169
O	0.244121	-0.829896	0.000239				
C	1.372308	-0.159405	-0.000117	<b>IM2</b>			
O	2.481318	-0.712731	-0.000115	E= -5588.528486			
C	1.252827	1.371081	-0.000042	G= -5588.238552			
H	0.677156	1.707102	-0.889050	N	-0.253875	0.298690	0.515765
H	0.685937	1.707056	0.894643	C	0.961267	0.486677	0.837466
H	2.251327	1.852416	-0.004509	C	1.524661	1.874325	0.919934
Cu	-1.419612	-0.006745	-0.000039	C	0.961772	2.902434	0.126513
				C	2.613151	2.173651	1.769427
				C	1.480503	4.202355	0.180156
<b>IM1</b>				H	0.123496	2.664664	-0.547081
E= -859.8299892				C	3.125141	3.480374	1.824710
G= -859.6357832				H	3.058072	1.391100	2.400425
N	0.854047	1.341398	1.321002	C	2.564154	4.495725	1.030382
C	1.123077	0.300662	0.644708	H	1.042033	4.991365	-0.450895
C	2.531721	-0.041787	0.251050	H	3.971286	3.704059	2.493021
C	3.593213	0.796074	0.670683	H	2.973609	5.517441	1.070334
C	2.820570	-1.182046	-0.531080	C	1.880375	-0.712852	1.045707
C	4.914853	0.497814	0.314946	H	1.283588	-1.582807	1.378461
H	3.366674	1.684377	1.280851	H	2.641146	-0.492733	1.818383
C	4.148473	-1.476525	-0.885478	C	2.572105	-1.083349	-0.283160
H	2.013976	-1.847410	-0.871461	H	1.801956	-1.387631	-1.018681
C	5.197107	-0.640717	-0.465037	C	3.328284	0.087927	-0.910570
H	5.732569	1.156428	0.647889	O	2.986906	0.684892	-1.916131
H	4.362411	-2.368212	-1.495567	O	4.418698	0.397127	-0.175333
H	6.236460	-0.875317	-0.744307	C	5.178237	1.540643	-0.617994
C	-0.001948	-0.634512	0.206280	H	5.631415	1.345036	-1.611003
H	0.216101	-1.650789	0.593683	H	4.530398	2.437317	-0.680776
H	0.022645	-0.705320	-0.900688	H	5.968813	1.691257	0.138800
C	-1.395733	-0.201953	0.674609	C	3.503120	-2.278733	-0.086707
H	-1.442075	-0.166099	1.783194	O	3.698239	-2.860807	0.965320
C	-1.804223	1.193738	0.194897	O	4.081998	-2.609432	-1.259943
O	-2.307491	2.063037	0.881849	C	5.005688	-3.717837	-1.223650
O	-1.555168	1.319864	-1.129133	H	5.383991	-3.830253	-2.255684
C	-1.895482	2.591306	-1.716861	H	5.843952	-3.506193	-0.529454
H	-2.980358	2.794977	-1.611170	H	4.490455	-4.645520	-0.902262
H	-1.322839	3.409285	-1.234569	C	-2.852252	-1.932341	1.068674
H	-1.623912	2.515068	-2.785319				

C	-3.165671	-1.945405	-0.320701	H	3.482310	2.979006	-1.033682
C	-4.421071	-1.543078	-0.782296	H	4.919161	3.058942	0.074124
C	-5.360456	-1.118354	0.180580	C	4.283686	-1.565984	0.467953
C	-5.062860	-1.096519	1.559865	O	4.514640	-1.882301	1.621731
C	-3.796918	-1.504588	2.014695	O	5.135040	-1.763244	-0.560117
C	-1.451384	-2.359517	1.207930	C	6.404030	-2.365702	-0.228124
C	-0.958844	-2.622836	-0.268531	H	6.961555	-2.440057	-1.179155
H	-4.658624	-1.535083	-1.855571	H	6.959653	-1.733029	0.493291
H	-6.353271	-0.785828	-0.160816	H	6.256178	-3.373932	0.208702
H	-5.823216	-0.751935	2.276933	C	-2.279526	-1.885620	0.538169
H	-3.537287	-1.487719	3.084634	C	-2.734822	-2.389811	-0.701541
H	-2.040313	-2.436179	-2.091881	C	-4.096005	-2.565460	-0.971916
O	-0.753480	-2.518428	2.199734	C	-5.010633	-2.228893	0.047448
O	0.152898	-2.998874	-0.617030	C	-4.575106	-1.740729	1.293911
N	-2.051176	-2.364418	-1.068860	C	-3.200189	-1.566093	1.549671
Cu	-1.825911	0.816998	-0.189391	C	-0.719889	-1.895263	0.578003
Br	-3.420023	2.078250	-1.211440	C	-0.429718	-2.418701	-0.974787
				H	-4.436298	-2.953442	-1.943540
<b>IM3</b>				H	-6.088574	-2.352943	-0.141204
E=	-5588.517259			H	-5.311647	-1.486886	2.071285
G=	-5588.226112			H	-2.847437	-1.191929	2.523780
N	-0.351140	-0.421709	0.482434	H	-1.734421	-3.090964	-2.474402
C	0.809369	0.118207	0.724673	O	-0.128890	-2.637329	1.456354
C	0.893756	1.588337	0.525257	O	0.672763	-2.568567	-1.469098
C	0.243050	2.172217	-0.591751	N	-1.643928	-2.670574	-1.541534
C	1.589304	2.418735	1.432759	Cu	-1.983769	0.526822	0.081891
C	0.269342	3.561416	-0.781187	Br	-3.770554	1.908003	-0.317644
H	-0.222117	1.520061	-1.348230				
C	1.603765	3.808721	1.243648	<b>TS1</b>			
H	2.098919	1.977821	2.302171	E=	-5588.512149		
C	0.942251	4.382548	0.140753	G=	-5588.220106		
H	-0.230740	4.001747	-1.657519	N	-0.355715	-0.414575	0.422516
H	2.134066	4.450828	1.963913	C	0.788437	0.122182	0.670310
H	0.963045	5.473828	-0.006516	C	0.876608	1.609569	0.539159
C	2.040787	-0.640415	1.150891	C	0.264983	2.239846	-0.571344
H	1.733382	-1.613738	1.573104	C	1.520752	2.395394	1.520100
H	2.577309	-0.053350	1.923022	C	0.288379	3.636970	-0.690760
C	3.000946	-0.903988	-0.032700	H	-0.188293	1.621659	-1.361790
H	2.506658	-1.596425	-0.743902	C	1.532754	3.793467	1.399339
C	3.338235	0.354469	-0.833483	H	1.997978	1.914429	2.387012
O	2.962544	0.587844	-1.968523	C	0.915602	4.416305	0.297640
O	4.092325	1.197377	-0.094273	H	-0.181944	4.117835	-1.562413
C	4.407204	2.465582	-0.704436	H	2.027818	4.402326	2.171862
H	5.076779	2.320833	-1.576676	H	0.932816	5.513708	0.205581

C	2.018781	-0.664034	1.067246	C	0.302085	2.558081	-0.331557
H	1.711955	-1.654911	1.449629	C	1.828564	2.402376	1.569202
H	2.548046	-0.118312	1.873863	C	0.491241	3.945773	-0.368171
C	2.990309	-0.871883	-0.117071	H	-0.332241	2.069921	-1.090237
H	2.528081	-1.571809	-0.840978	C	2.004835	3.794350	1.534023
C	3.289706	0.412511	-0.890478	H	2.352791	1.807212	2.330569
O	2.905261	0.657481	-2.020355	C	1.337649	4.569006	0.568400
O	4.017328	1.261342	-0.132831	H	-0.019892	4.543824	-1.138691
C	4.281704	2.557124	-0.708188	H	2.670632	4.276017	2.266825
H	4.941461	2.461455	-1.594451	H	1.484730	5.660088	0.538577
H	3.334877	3.048945	-1.006957	C	1.917266	-0.581607	1.014179
H	4.786155	3.142741	0.080976	H	1.237795	-1.683401	1.248273
C	4.293173	-1.500225	0.377408	H	2.469473	-0.304848	1.931755
O	4.533462	-1.820023	1.528293	C	2.819181	-0.909855	-0.163968
O	5.150532	-1.660397	-0.651770	H	2.214738	-1.374588	-0.974527
C	6.438347	-2.224306	-0.324220	C	3.429413	0.371518	-0.764022
H	7.002863	-2.260686	-1.273307	O	3.151916	0.832371	-1.854941
H	6.967742	-1.586798	0.412439	O	4.283226	0.934370	0.113799
H	6.323608	-3.245440	0.092121	C	4.876227	2.187780	-0.289568
C	-2.298173	-2.046036	0.588647	H	4.089288	2.919584	-0.558845
C	-2.618476	-2.252418	-0.778781	H	5.451131	2.543947	0.583756
C	-3.940446	-2.179708	-1.238248	H	5.551488	2.034853	-1.155601
C	-4.944167	-1.913615	-0.285709	C	3.921179	-1.887592	0.241338
C	-4.642203	-1.730031	1.078400	O	3.997481	-2.454315	1.317041
C	-3.307989	-1.792807	1.527908	O	4.790437	-2.050354	-0.774618
C	-0.790068	-2.219312	0.754955	C	5.890406	-2.955323	-0.535721
C	-0.321898	-2.617183	-0.726885	H	6.492330	-2.949553	-1.462087
H	-4.181279	-2.330221	-2.300990	H	6.501531	-2.607875	0.321435
H	-5.990693	-1.846451	-0.621496	H	5.515626	-3.977875	-0.328559
H	-5.452670	-1.526657	1.794459	C	-2.098033	-1.900077	0.742243
H	-3.051935	-1.649845	2.589249	C	-2.758694	-2.402208	-0.404047
H	-1.454275	-2.790827	-2.503192	C	-4.133767	-2.661117	-0.394763
O	-0.222650	-2.673850	1.769171	C	-4.832433	-2.411528	0.804105
O	0.798206	-2.948227	-1.083912	C	-4.180806	-1.918665	1.952893
N	-1.454197	-2.541490	-1.507250	C	-2.796241	-1.657898	1.928252
Cu	-2.023274	0.406515	0.090162	C	-0.635350	-1.662336	0.400810
Br	-3.729480	1.877168	-0.320529	C	-0.574113	-2.146159	-1.121342
				H	-4.647566	-3.039619	-1.290821
<b>TS2</b>				H	-5.916097	-2.605952	0.838481
E= -5588.501421				H	-4.757939	-1.733424	2.871744
G= -5588.211665				H	-2.271392	-1.267651	2.813954
N	-0.411448	-0.188522	0.358046	H	-2.083754	-2.930980	-2.380319
C	0.754469	0.301964	0.681101	O	0.218084	-2.360254	1.218078
C	0.959509	1.772304	0.647720	O	0.424136	-2.188180	-1.830289

N	-1.844901	-2.540835	-1.461722	C	-2.243265	-1.692610	1.852178
Cu	-2.009280	0.720341	-0.160869	C	-0.081226	-1.544173	0.318058
Br	-3.942768	1.779260	-0.707256	C	0.086123	-2.268451	-1.090207
<b>IM4</b>				H	-3.781621	-3.832134	-1.104196
E=	-5588.521709			H	-5.135866	-3.325437	0.958177
G=	-5588.226823			H	-4.167233	-1.984158	2.829806
N	-0.154745	-0.081739	0.110266	H	-1.811846	-1.085445	2.663019
C	0.823530	0.813058	0.408014	H	-1.251942	-3.434724	-2.225908
C	0.299879	2.190162	0.718565	O	0.838192	-1.972006	1.264446
C	-0.522049	2.863733	-0.214499	O	1.106548	-2.290415	-1.773402
C	0.596449	2.806862	1.950934	N	-1.102176	-2.882931	-1.373754
C	-1.049640	4.129083	0.091366	Cu	-1.925397	0.450081	-0.322963
H	-0.723690	2.408758	-1.198707	Br	-4.055522	0.997388	-0.911699
C	0.061999	4.071877	2.255127	<b>IM5</b>			
H	1.232944	2.283897	2.682260	E=	-8162.987632		
C	-0.764760	4.733193	1.329360	G=	-8162.692903		
H	-1.686224	4.644288	-0.645005	N	0.573673	1.465343	0.890489
H	0.288565	4.538823	3.226813	C	-0.574989	1.342827	0.283326
H	-1.184081	5.722705	1.570990	C	-1.201461	2.599955	-0.222015
C	2.212780	0.663692	0.413543	C	-0.396581	3.750898	-0.400435
H	1.721805	-2.241798	0.891586	C	-2.582921	2.677551	-0.515477
H	2.789008	1.515534	0.805561	C	-0.959592	4.947364	-0.862337
C	3.013444	-0.394834	-0.279879	H	0.678839	3.680426	-0.178894
H	2.357842	-1.102733	-0.838395	C	-3.145954	3.880102	-0.970969
C	3.965674	0.150364	-1.358592	H	-3.232686	1.802239	-0.370528
O	4.793931	-0.543414	-1.921396	C	-2.337122	5.016119	-1.149051
O	3.737160	1.445303	-1.630607	H	-0.320653	5.832750	-1.007517
C	4.545182	2.027886	-2.678224	H	-4.224654	3.928406	-1.186987
H	4.374910	1.500482	-3.638188	H	-2.778891	5.956733	-1.514351
H	4.220652	3.080937	-2.756262	C	-1.288923	0.064398	0.032390
H	5.620425	1.974464	-2.414743	H	-2.108875	0.147414	-0.694866
C	3.815187	-1.242148	0.706596	C	-1.688635	-0.776008	1.240681
O	3.470027	-2.368812	1.055251	H	-0.970016	-0.666413	2.081165
O	4.890892	-0.608777	1.172502	C	-3.046601	-0.294500	1.790945
C	5.693637	-1.319069	2.147439	O	-3.234919	0.090413	2.927403
H	6.504553	-0.624380	2.428575	O	-3.989581	-0.358820	0.830549
H	5.080994	-1.580321	3.032824	C	-5.318505	0.067727	1.210036
H	6.113644	-2.240979	1.698919	H	-5.298863	1.114093	1.574180
C	-1.499048	-1.975358	0.703584	H	-5.931314	-0.011048	0.294732
C	-2.049686	-2.745970	-0.342584	H	-5.722874	-0.592960	2.002609
C	-3.355593	-3.242481	-0.278962	C	-1.744541	-2.254256	0.875990
C	-4.102882	-2.951050	0.881244	O	-1.133099	-2.727833	-0.081653
C	-3.558841	-2.193937	1.936666	O	-2.480765	-2.967203	1.719576



C	2.537503	4.611205	-0.855115	Br	-3.608068	-2.061946	0.097122
H	0.520228	3.785599	-0.787421	Br	1.334089	0.440513	3.204851
C	4.349980	2.990934	-0.706588				
H	3.772759	0.912295	-0.542937	<b>IM7</b>			
C	3.915999	4.322929	-0.823233	E=	-5587.903381		
H	2.193264	5.654008	-0.939466	G=	-5587.616682		
H	5.425928	2.757793	-0.687751	N	-1.110235	0.969035	-0.887246
H	4.652282	5.139648	-0.887657	C	0.059187	1.164044	-0.348863
C	1.426393	-0.151577	0.007791	C	0.501966	2.577682	-0.148840
H	2.353626	-0.106408	0.600447	C	-0.446138	3.622438	-0.278746
C	1.328272	-1.408446	-0.831313	C	1.844741	2.908831	0.151857
H	0.498480	-1.343009	-1.565796	C	-0.059977	4.958632	-0.116271
C	2.619692	-1.587669	-1.664126	H	-1.489601	3.358413	-0.505571
O	2.639495	-1.681923	-2.873840	C	2.228503	4.250228	0.312774
O	3.696562	-1.622323	-0.860239	H	2.606981	2.122885	0.250614
C	4.977872	-1.806195	-1.510415	C	1.279848	5.278373	0.180120
H	5.142309	-1.014569	-2.267592	H	-0.809568	5.759690	-0.215425
H	5.732358	-1.738040	-0.707138	H	3.278715	4.490231	0.541001
H	5.019345	-2.801729	-1.995282	H	1.581835	6.329737	0.309475
C	1.069002	-2.653458	0.023104	C	0.984780	0.081244	0.085165
O	0.570552	-2.618090	1.146122	H	1.711262	0.378801	0.860974
O	1.399111	-3.768760	-0.614707	C	1.605878	-0.784009	-0.997005
C	1.125207	-5.021119	0.067564	H	0.889045	-0.940285	-1.830023
H	1.455869	-5.812969	-0.626742	C	2.835719	-0.080167	-1.605288
H	1.695634	-5.070441	1.015498	O	2.940317	0.239340	-2.772198
H	0.040647	-5.109976	0.273409	O	3.766804	0.139070	-0.655682
C	-2.480036	1.486004	-0.295454	C	4.981845	0.791867	-1.092303
C	-3.461813	1.550433	-1.305815	H	5.522299	0.149783	-1.816134
C	-4.641743	2.280992	-1.129003	H	4.749319	1.767352	-1.563655
C	-4.810551	2.951191	0.101297	H	5.588242	0.937496	-0.180967
C	-3.833407	2.891275	1.114402	C	1.993061	-2.167588	-0.469255
C	-2.645936	2.154596	0.916625	O	1.528499	-2.671936	0.547666
C	-1.331563	0.613728	-0.783372	O	2.864967	-2.770896	-1.275471
C	-1.868364	0.146740	-2.231443	C	3.274526	-4.111755	-0.906943
H	-5.407353	2.327163	-1.917676	H	3.982977	-4.431488	-1.691013
H	-5.730995	3.532234	0.269602	H	3.770391	-4.101681	0.083532
H	-3.997167	3.421079	2.065338	H	2.396048	-4.786101	-0.879332
H	-1.870952	2.097178	1.697849	C	-3.137103	-0.209540	-0.397068
H	-3.653597	0.611368	-3.236603	C	-4.021810	-0.382471	-1.482869
O	-1.129915	-0.558895	-0.020063	C	-5.410356	-0.322175	-1.314043
O	-1.287683	-0.632966	-2.966024	C	-5.896194	-0.080567	-0.011133
N	-3.059157	0.789537	-2.419062	C	-5.021259	0.092577	1.079164
H	-2.132281	-1.183640	0.082997	C	-3.623773	0.032791	0.887757
Cu	0.056208	-0.392632	1.492539	C	-1.698692	-0.346397	-0.898416

C	-1.940331	-0.660752	-2.467335	H	-0.183581	-5.038699	-0.657358
H	-6.094837	-0.458280	-2.164769	H	1.172215	-4.324315	0.309968
H	-6.984349	-0.028788	0.151861	C	1.640040	2.336903	-0.242597
H	-5.429154	0.276265	2.085188	C	2.680844	2.328324	0.713140
H	-2.927116	0.167670	1.731472	C	3.886115	2.999016	0.481850
H	-3.724798	-0.828041	-3.572483	C	4.021922	3.686033	-0.743265
O	-0.991461	-1.405832	-0.389771	C	2.989077	3.700554	-1.700801
O	-1.059197	-0.902885	-3.274576	C	1.779475	3.017142	-1.452512
N	-3.293325	-0.618037	-2.665321	C	0.506786	1.490763	0.278998
Cu	-0.137766	-1.121796	1.231362	C	1.066596	0.990172	1.682685
Br	0.337043	-0.593805	3.404264	H	4.697158	2.984964	1.224877

### IM8

E= -5587.94032

G= -5587.652316

N	-0.776872	2.103028	0.421551
C	-1.681153	1.317614	-0.075804
C	-3.117362	1.628264	-0.072832
C	-3.635342	2.521034	0.896888
C	-3.989998	1.056734	-1.029615
C	-5.002376	2.823292	0.916392
H	-2.948928	2.956770	1.638549
C	-5.357923	1.370404	-1.009275
H	-3.602003	0.379663	-1.804333
C	-5.867208	2.247302	-0.035179
H	-5.401061	3.508689	1.680594
H	-6.029328	0.928660	-1.761710
H	-6.942588	2.484593	-0.016446
C	-1.096180	0.015602	-0.621752
H	-1.377891	-0.203168	-1.670802
C	-1.375408	-1.203290	0.293427
H	-1.029026	-0.944410	1.316215
C	-2.855967	-1.575135	0.404737
O	-3.534110	-1.453780	1.406363
O	-3.297752	-2.071470	-0.770602
C	-4.688243	-2.462682	-0.811730
H	-4.872422	-3.301116	-0.110495
H	-5.338855	-1.607180	-0.542342
H	-4.880894	-2.782054	-1.851273
C	-0.561923	-2.402273	-0.186860
O	0.181047	-2.396495	-1.171357
O	-0.712454	-3.450014	0.625656
C	0.101983	-4.611400	0.324129
H	-0.098109	-5.334547	1.134026

H	4.961843	4.221157	-0.952064
H	3.127707	4.244415	-2.647699
H	0.965432	3.010751	-2.194031
H	2.924778	1.347373	2.615940
O	0.312932	0.325314	-0.595521
O	0.483895	0.243098	2.458365
N	2.300715	1.566710	1.832200
Cu	1.830330	-0.986518	-0.557069
Br	3.913660	-1.623719	0.028107

### 3aa

E= -1372.613174

G= -1372.320168

N	-1.041922	-1.239530	0.381871
C	0.134139	-1.056528	-0.129664
C	1.198879	-2.072158	-0.100436
C	1.204241	-3.055924	0.917606
C	2.216219	-2.084495	-1.083442
C	2.216557	-4.022686	0.959001
H	0.411158	-3.035095	1.680427
C	3.223678	-3.061744	-1.042130
H	2.215809	-1.337930	-1.890753
C	3.230199	-4.026998	-0.019754
H	2.221808	-4.776850	1.761711
H	4.008849	-3.067892	-1.814104
H	4.027290	-4.786444	0.016130
C	0.289439	0.337738	-0.728221
H	0.665473	0.342364	-1.772138
C	1.173383	1.272035	0.142836
H	0.620632	1.441649	1.089169
C	2.525763	0.684340	0.547652
O	2.781325	0.219391	1.643485
O	3.406068	0.752294	-0.475729

C	4.722072	0.219568	-0.215213	C	-2.191724	0.957490	-1.099555
H	5.239796	0.830645	0.551658	H	-2.237453	0.608243	-2.153697
H	4.654818	-0.829327	0.134732	H	-2.553027	2.005891	-1.128643
H	5.265264	0.271302	-1.175722	C	-3.110683	0.083682	-0.261156
C	1.383025	2.606798	-0.571321	H	-2.439916	-1.023920	-0.284365
O	1.159459	2.828372	-1.748044	C	-3.278831	0.490338	1.176170
O	1.873974	3.516188	0.295805	O	-4.119641	0.090518	1.963895
C	2.180602	4.815312	-0.254181	O	-2.331375	1.414011	1.508473
H	2.571086	5.415548	0.587242	C	-2.257379	1.772027	2.896449
H	2.945883	4.730756	-1.052206	H	-3.196583	2.255873	3.234267
H	1.269155	5.288834	-0.671553	H	-2.063091	0.871970	3.512586
C	-3.214527	-0.301275	-0.364829	H	-1.413908	2.481785	2.982145
C	-4.142006	0.122490	0.612874	C	-4.342167	-0.344326	-1.008848
C	-5.521754	-0.013304	0.419108	O	-4.596690	0.007506	-2.156330
C	-5.953542	-0.587462	-0.795884	O	-5.102574	-1.213167	-0.314410
C	-5.036725	-1.008769	-1.778046	C	-6.295970	-1.669491	-0.978708
C	-3.647885	-0.867224	-1.563189	H	-6.788149	-2.363329	-0.273028
C	-1.813974	-0.035537	0.148976	H	-6.970683	-0.819691	-1.208866
C	-2.095986	0.674248	1.541723	H	-6.047113	-2.197038	-1.922377
H	-6.239979	0.318297	1.183796	C	0.849927	-2.234104	-0.570778
H	-7.034032	-0.705136	-0.975555	C	1.466792	-2.819185	0.565488
H	-5.404603	-1.450219	-2.717098	C	2.644321	-3.567739	0.444594
H	-2.919385	-1.192593	-2.322369	C	3.183401	-3.724348	-0.846976
H	-3.921695	1.092465	2.527150	C	2.573119	-3.150775	-1.983233
O	-1.057849	0.818079	-0.723509	C	1.390163	-2.399336	-1.851983
O	-1.253467	1.140558	2.298565	C	-0.362470	-1.422224	-0.123814
N	-3.458676	0.670962	1.714431	C	-0.331192	-1.675687	1.462252
				H	3.127454	-4.012720	1.326704
<b>TS2'</b>				H	4.108672	-4.309116	-0.969568
E= -5588.505453				H	3.028116	-3.288778	-2.975936
G= -5588.213314				H	0.902698	-1.940345	-2.725801
N	0.013679	-0.003696	-0.314021	H	0.979574	-2.835791	2.659816
C	-0.734633	0.992387	-0.700039	O	-1.518414	-1.851141	-0.678575
C	-0.008579	2.285985	-0.808479	O	-1.149130	-1.261709	2.268248
C	1.284693	2.311256	-1.399663	N	0.736745	-2.509162	1.717572
C	-0.539020	3.472104	-0.253502	Cu	1.904053	0.250268	0.022156
C	2.038060	3.498547	-1.405398	Br	4.121303	0.424554	0.567507
H	1.648188	1.431470	-1.960404				
C	0.226038	4.648365	-0.251088	<b>IM4'</b>			
H	-1.533163	3.453581	0.216589	E= -5588.519311			
C	1.515621	4.662715	-0.819566	G= -5588.225748			
H	3.033273	3.507773	-1.875342	N	0.009096	0.017444	-0.386639
H	-0.183630	5.561824	0.207599	C	-0.766617	0.997116	-0.759166
H	2.108293	5.590927	-0.815220	C	-0.096303	2.320818	-0.869566



C	1.216726	2.400302	-1.405533	N	0.673900	-2.556549	1.575746
C	-0.723512	3.501468	-0.410186	Cu	1.882801	0.272030	0.062441
C	1.892142	3.631101	-1.449200	Br	4.037914	0.389497	0.805037
H	1.673617	1.514446	-1.880544				
C	-0.036635	4.724816	-0.441973	<b>IM5'</b>			
H	-1.734898	3.448357	0.018075	E=	-8162.973752		
C	1.272782	4.791871	-0.955323	G=	-8162.679311		
H	2.904397	3.679905	-1.879403	N	0.738390	1.660240	0.629872
H	-0.525610	5.632701	-0.055557	C	-0.531003	1.672214	0.857799
H	1.805718	5.755383	-0.982280	C	-1.295922	2.829666	0.315452
C	-2.226288	0.913547	-1.172525	C	-0.734809	3.575003	-0.750969
H	-2.290254	0.400309	-2.154640	C	-2.545485	3.230112	0.838765
H	-2.554510	1.958346	-1.376018	C	-1.403238	4.687337	-1.276152
C	-3.213772	0.275947	-0.242347	H	0.229916	3.246382	-1.163400
H	-2.215619	-1.643832	-0.320027	C	-3.209117	4.354239	0.320915
C	-3.245367	0.646406	1.184579	H	-3.010154	2.674562	1.665357
O	-4.082931	0.334532	2.021629	C	-2.644538	5.083499	-0.739811
O	-2.183887	1.461128	1.471889	H	-0.959060	5.248260	-2.113827
C	-2.009735	1.812951	2.849636	H	-4.177503	4.658756	0.748168
H	-2.886537	2.373458	3.234259	H	-3.172334	5.958086	-1.152423
H	-1.862368	0.901065	3.463230	C	-1.270990	0.586480	1.652248
H	-1.105623	2.448134	2.889147	H	-2.175249	1.032047	2.116749
C	-4.277743	-0.508896	-0.899176	H	-0.609252	0.265224	2.475776
O	-4.410409	-0.554058	-2.124768	C	-1.729130	-0.623424	0.867417
O	-5.073577	-1.196488	-0.049249	C	-1.607085	-1.927960	1.593474
C	-6.112582	-1.975103	-0.668031	O	-0.844351	-2.776526	1.082809
H	-6.645633	-2.478148	0.159335	O	-2.263288	-2.084658	2.714161
H	-6.812485	-1.325921	-1.233455	C	-2.089151	-3.350247	3.426012
H	-5.684860	-2.728168	-1.361967	H	-2.435301	-4.186229	2.788450
C	0.944757	-2.171272	-0.684680	H	-1.023253	-3.482653	3.692926
C	1.488949	-2.806072	0.457528	H	-2.713575	-3.262000	4.330908
C	2.685148	-3.527198	0.390208	C	-2.971487	-0.517663	0.024266
C	3.328927	-3.599989	-0.861965	O	-3.615410	0.501653	-0.139811
C	2.797099	-2.970522	-2.004502	O	-3.297902	-1.729006	-0.479173
C	1.593486	-2.240783	-1.921111	C	-4.437741	-1.765807	-1.361967
C	-0.305708	-1.409956	-0.268143	H	-4.550965	-2.822275	-1.663431
C	-0.402429	-1.764505	1.273940	H	-5.349886	-1.413523	-0.839996
H	3.110977	-4.007058	1.283512	H	-4.250650	-1.130515	-2.251021
H	4.274445	-4.159120	-0.942691	C	2.941039	0.736776	0.177779
H	3.327388	-3.043424	-2.966315	C	4.042721	1.046438	1.007210
H	1.173961	-1.731213	-2.802272	C	5.339417	1.149666	0.490209
H	0.839562	-2.946647	2.510085	C	5.503410	0.939378	-0.895799
O	-1.457290	-1.862617	-0.916182	C	4.408640	0.645568	-1.731362
O	-1.332009	-1.438543	2.000672	C	3.106743	0.545462	-1.195212

C	1.689549	0.691259	1.035443	O	-2.972204	-2.444399	-0.366458
C	2.249701	1.089230	2.470769	C	-3.917475	-2.785746	-1.399053
H	6.194088	1.392840	1.138905	H	-4.064411	-3.877786	-1.326578
H	6.513332	1.013746	-1.329520	H	-4.876769	-2.251762	-1.248675
H	4.568680	0.491649	-2.809647	H	-3.493779	-2.517124	-2.389565
H	2.238998	0.314225	-1.831720	C	2.180823	1.585630	-0.400580
H	4.228814	1.456988	3.117457	C	3.258430	2.238889	0.232410
O	1.185777	-0.671259	1.168059	C	4.384061	2.654186	-0.486039
O	1.579048	1.201401	3.485834	C	4.399737	2.394159	-1.872802
N	3.607759	1.233825	2.331992	C	3.325146	1.747625	-2.513795
H	1.864814	-1.279868	0.780101	C	2.195360	1.341286	-1.773225
Cu	-0.270682	-1.395971	-0.387509	C	1.136729	1.241200	0.648441
Br	1.502534	-2.683702	-1.321655	C	1.795614	1.840969	1.984786
Br	-0.725531	0.010925	-2.181461	H	5.222739	3.162464	0.012356
				H	5.274962	2.707255	-2.463727
<b>TS3'</b>				H	3.366476	1.557617	-3.597208
E= -8162.945097				H	1.347266	0.835677	-2.263341
G= -8162.65449				H	3.655784	2.782127	2.282676
N	-0.077266	1.935910	0.406312	O	1.005292	-0.166381	0.873976
C	-1.278106	1.611241	0.748705	O	1.290850	1.789881	3.093129
C	-2.374549	2.545859	0.383561	N	2.997552	2.374322	1.609293
C	-2.062027	3.702830	-0.375824	H	2.030500	-0.689923	0.829357
C	-3.717037	2.334656	0.774037	Cu	0.048870	-1.077901	-0.532554
C	-3.059951	4.616891	-0.730183	Br	3.542643	-1.563055	0.632418
H	-1.016411	3.863311	-0.677922	Br	-0.360122	-1.914306	-2.614357
C	-4.715311	3.257131	0.426385				
H	-4.005170	1.440855	1.345672	<b>IM6'</b>			
C	-4.392737	4.398568	-0.328492	E= -8162.945537			
H	-2.800248	5.507973	-1.323104	G= -8162.659525			
H	-5.755083	3.076740	0.740453	N	0.062657	1.873022	-0.385826
H	-5.179935	5.116581	-0.607869	C	1.227991	1.550842	-0.834607
C	-1.589843	0.332776	1.554233	C	2.341294	2.509763	-0.611308
H	-2.602471	0.433956	2.000603	C	2.093389	3.675920	0.157993
H	-0.871908	0.274741	2.392305	C	3.632194	2.319153	-1.155075
C	-1.576583	-0.944971	0.773616	C	3.103409	4.619879	0.371316
C	-1.138923	-2.189230	1.515161	H	1.087478	3.820628	0.579461
O	-0.244715	-2.917677	1.093139	C	4.641579	3.271798	-0.948857
O	-1.808948	-2.365452	2.648608	H	3.870399	1.422175	-1.743969
C	-1.458885	-3.538283	3.432134	C	4.383260	4.422881	-0.184222
H	-1.652760	-4.458160	2.846258	H	2.894101	5.518417	0.972841
H	-0.391052	-3.495229	3.722593	H	5.639636	3.108538	-1.384227
H	-2.108073	-3.502275	4.324144	H	5.179270	5.165971	-0.018503
C	-2.671864	-1.137936	-0.246898	C	1.473790	0.247746	-1.628839
O	-3.228121	-0.228257	-0.839294	H	2.442289	0.337416	-2.163938



H	0.103806	-2.571327	1.317100	H	1.438077	6.521842	0.855796
				H	1.939069	4.945665	2.728881
<b>TS4'</b>				H	1.644749	2.455638	2.406631
E= -5587.877025				H	-0.052019	3.314811	-2.707505
G= -5587.592087				O	-0.282499	0.722812	0.668135
N	1.966268	0.554508	-0.227973	O	-0.192870	0.655695	-2.374480
C	2.154517	-0.600034	0.318179	N	0.262632	2.877295	-1.833988
C	3.509397	-1.208683	0.192021	Cu	-1.923964	0.127659	-0.031053
C	4.617681	-0.367308	-0.074448	Br	-4.184957	-0.035404	-0.243499
C	3.726042	-2.600442	0.314090	H	1.404383	-2.399481	1.280839
C	5.905662	-0.902071	-0.205248				
H	4.442750	0.715030	-0.167981	<b>IM8'</b>			
C	5.017262	-3.135877	0.175363	E= -5587.929999			
H	2.880958	-3.283585	0.484550	G= -5587.644543			
C	6.110669	-2.290196	-0.080163	N	1.934132	1.090705	-0.099677
H	6.758716	-0.233442	-0.401982	C	2.693531	0.075851	0.165708
H	5.167448	-4.223454	0.262519	C	4.167711	0.284517	0.167621
H	7.123316	-2.711421	-0.183150	C	4.690851	1.556410	-0.172704
C	1.094334	-1.344539	1.124579	C	5.067093	-0.754502	0.504831
H	1.008671	-0.899278	2.135595	C	6.072653	1.780946	-0.180294
C	-0.257646	-1.381839	0.475774	H	3.986310	2.360920	-0.431398
C	-0.243312	-1.945034	-0.943425	C	6.452952	-0.525323	0.499684
O	0.745893	-2.449270	-1.445427	H	4.694514	-1.753186	0.775077
O	-1.445250	-1.843075	-1.520569	C	6.960279	0.739628	0.156629
C	-1.566069	-2.280107	-2.888522	H	6.464443	2.774359	-0.450472
H	-0.825281	-1.751524	-3.519039	H	7.140316	-1.343871	0.764849
H	-1.411128	-3.375259	-2.957540	H	8.047542	0.916426	0.150881
H	-2.594749	-2.015502	-3.189904	C	2.171597	-1.298336	0.528818
C	-1.349247	-1.960100	1.355625	H	2.389239	-1.477447	1.602299
O	-1.829594	-3.061601	1.134756	C	0.677354	-1.478361	0.262965
O	-1.615174	-1.188710	2.422014	C	0.397554	-2.102919	-1.142066
C	-2.693996	-1.640910	3.272638	O	1.209532	-2.715642	-1.803154
H	-3.644306	-1.623094	2.700643	O	-0.904838	-1.947226	-1.426872
H	-2.496497	-2.664017	3.647860	C	-1.365154	-2.404412	-2.717395
H	-2.736457	-0.921389	4.109130	H	-0.829042	-1.857784	-3.517176
C	0.981453	2.696423	0.351431	H	-1.198385	-3.494541	-2.822179
C	0.695311	3.591815	-0.703421	H	-2.443848	-2.168847	-2.740743
C	0.856133	4.973474	-0.548661	C	0.064606	-2.502907	1.250157
C	1.306216	5.438702	0.705264	O	0.633182	-3.525296	1.577143
C	1.588893	4.551658	1.762471	O	-1.172289	-2.139410	1.620903
C	1.426034	3.160258	1.589498	C	-1.922919	-3.067877	2.442945
C	0.729280	1.269834	-0.134285	H	-1.988694	-4.052377	1.940200
C	0.214188	1.526430	-1.613776	H	-1.437744	-3.178538	3.432163
H	0.637569	5.667345	-1.373949	H	-2.924371	-2.614248	2.545467

C	-0.269008	2.114846	0.391975	H	-6.729997	1.631510	-0.239628
C	-1.036177	2.692650	-0.644456	C	-1.048602	-1.057854	-0.945769
C	-1.919536	3.746794	-0.394961	H	-0.908200	-0.870508	-2.032353
C	-2.017509	4.210121	0.934000	C	0.282636	-1.525694	-0.343080
C	-1.256645	3.639963	1.973166	C	0.041109	-2.152626	1.062804
C	-0.367640	2.577595	1.704751	O	-1.045681	-2.254520	1.600454
C	0.537573	0.969416	-0.183990	O	1.203295	-2.597460	1.562716
C	0.122643	1.007808	-1.721609	C	1.148870	-3.138626	2.898274
H	-2.521423	4.188285	-1.202687	H	0.813603	-2.355050	3.605387
H	-2.708935	5.037234	1.159892	H	0.457304	-4.004029	2.942928
H	-1.357420	4.023915	2.999834	H	2.178798	-3.458578	3.138445
H	0.227776	2.115245	2.507032	C	0.851218	-2.658252	-1.217266
H	-1.240569	2.252992	-2.745948	O	0.263392	-3.722190	-1.334088
O	-0.036463	-0.241573	0.435840	O	1.998466	-2.338064	-1.821491
O	0.553044	0.256602	-2.585341	C	2.567971	-3.364264	-2.666561
N	-0.771803	2.036463	-1.859642	H	2.790293	-4.275177	-2.075366
Cu	-2.031922	-0.271454	0.263142	H	1.871272	-3.622409	-3.489132
Br	-4.228991	0.035991	-0.095649	H	3.500192	-2.934075	-3.074090
H	2.716207	-2.077299	-0.038093	C	1.536047	1.915695	-0.333180
				C	2.300853	2.541952	0.674795
				C	3.128900	3.634774	0.389081
<b>3aa'</b>				C	3.174279	4.084659	-0.947755
E= -1372.602158				C	2.418878	3.461568	-1.959720
G= -1372.309105				C	1.587054	2.362051	-1.652813
N	-0.652248	1.044477	0.262483	C	0.746399	0.770936	0.287527
C	-1.494676	0.224821	-0.279883	C	1.205920	0.845587	1.809581
C	-2.938282	0.589286	-0.273725	H	3.722010	4.120943	1.178063
C	-3.358731	1.765485	0.395065	H	3.817749	4.942401	-1.200280
C	-3.908327	-0.202147	-0.931631	H	2.477575	3.832707	-2.994550
C	-4.708892	2.135562	0.409099	H	0.992214	1.864351	-2.434655
H	-2.598384	2.377399	0.903186	H	2.552354	2.158731	2.780889
C	-5.262255	0.173751	-0.920899	O	1.217947	-0.455907	-0.293609
H	-3.613111	-1.118871	-1.462821	O	0.844108	0.103745	2.711295
C	-5.667649	1.340319	-0.250328	N	2.085534	1.899178	1.905337
H	-5.020440	3.050545	0.937691	H	-1.799803	-1.859980	-0.842191
H	-6.004959	-0.452210	-1.440197				