

# Lewis Base Promoted [4+2] Annulation of *o*-Acylamino-aryl MBH Carbonates with Isatin

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## Supporting Information

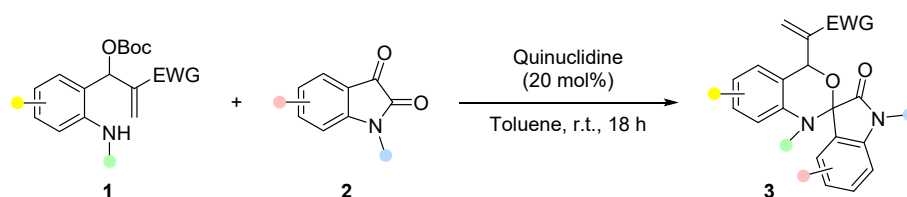
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## 1. General experimental information

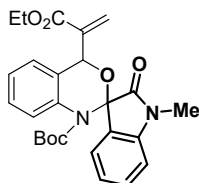
Reagents were purchased from commercial sources and were used as received unless mentioned otherwise. Reactions were monitored by TLC.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  or  $\text{DMSO-}d_6$ .  $^1\text{H}$  NMR chemical shifts are reported in ppm relative to tetramethylsilane (TMS) with the solvent resonance employed as the internal standard ( $\text{CDCl}_3$  at 7.26 ppm,  $\text{DMSO-}d_6$  at 2.50 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration.  $^{13}\text{C}$  NMR chemical shifts are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard ( $\text{CDCl}_3$  at 77.16 ppm,  $\text{DMSO-}d_6$  at 39.52 ppm). Melting points products were recorded on a Büchi Melting Point B-545. The HRMS were recorded by Thermo Scientific LTQ Orbitrap XL.

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



In an ordinary vial charged with a magnetic stirring bar, *o*-acylamino-aryl MBH carbonates **1** (0.12 mmol, 1.2 equiv), isatins **2** (0.1 mmol, 1.0 equiv), quinuclidine (0.02 mmol, 0.2 equiv) and Toluene (1 mL) was added, and then the mixture was stirred at r.t. for 18 h. the products **3** were isolated by flash chromatography on silica gel.

### tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3a)



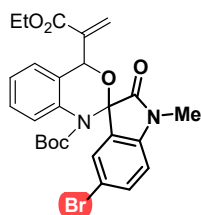
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (42.3 mg, 92% yield); m.p. 173.5-175.7 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.80 (dd,  $J = 8.3, 1.1$  Hz, 1H), 7.38 – 7.30 (m, 2H), 7.11 – 7.04 (m, 2H), 7.02 – 6.96 (m, 1H), 6.91 – 6.85 (m, 1H), 6.80 (d,  $J = 7.7$  Hz, 1H), 6.59 – 6.49 (m, 2H), 5.88 (d,  $J = 1.3$  Hz, 1H), 4.36 – 4.15 (m, 2H), 3.22 (s, 3H), 1.35 – 1.22 (m, 12H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 165.6, 151.2, 144.1, 138.0, 135.4, 134.5, 130.5, 129.3, 128.4, 128.0, 123.9, 123.7, 123.5, 123.1, 122.9, 108.3, 86.0, 83.0, 68.6, 61.3, 28.1, 26.4, 14.3.

HRMS (ESI) Calcd. for  $\text{C}_{26}\text{H}_{28}\text{N}_2\text{O}_6\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 487.18396; found: 487.18396.

### tert-butyl 5'-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3b)



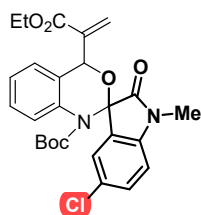
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (33.3 mg, 61% yield); m.p. 181.9-183.4 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.45 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.39 – 7.32 (m, 1H), 7.17 (d, *J* = 2.0 Hz, 1H), 7.13 – 7.06 (m, 1H), 6.91 – 6.84 (m, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 1.2 Hz, 1H), 6.48 (s, 1H), 5.89 (s, 1H), 4.34 – 4.18 (m, 2H), 3.20 (s, 3H), 1.33 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.0, 165.5, 151.2, 143.2, 137.9, 135.1, 134.2, 133.2, 130.3, 129.4, 128.1, 126.3, 124.0, 123.9, 123.6, 115.4, 109.9, 85.6, 83.4, 68.8, 61.3, 28.1, 26.5, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>27</sub>BrN<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 565.09447, 567.09242; found: 565.09491, 567.09277.

**tert-butyl 5'-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3c)**



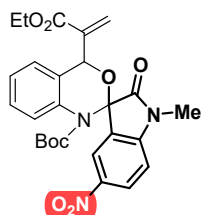
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (46.0 mg, 92% yield); m.p. 182.5-185.7 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.78 – 7.70 (m, 1H), 7.39 – 7.33 (m, 1H), 7.30 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.13 – 7.06 (m, 1H), 7.05 (d, *J* = 2.1 Hz, 1H), 6.92 – 6.85 (m, 1H), 6.74 (d, *J* = 8.3 Hz, 1H), 6.57 (d, *J* = 1.2 Hz, 1H), 6.49 (s, 1H), 5.89 (t, *J* = 1.3 Hz, 1H), 4.35 – 4.19 (m, 2H), 3.21 (s, 3H), 1.33 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.1, 165.5, 151.2, 142.7, 137.9, 135.1, 134.2, 130.3, 130.0, 129.4, 128.2, 128.1, 124.0, 123.9, 123.6, 123.5, 109.4, 85.7, 83.3, 68.8, 61.3, 28.1, 26.5, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 521.14499, 523.14203; found: 521.14551, 523.14282.

**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-5'-nitro-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3d)**



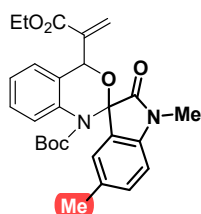
It was purified by flash chromatography (petroleum ether /EtOAc, 3:1) to afford white solid (32.0 mg, 63% yield); m.p. 199.2-199.8 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.32 (dd, *J* = 8.7, 2.3 Hz, 1H), 7.94 (d, *J* = 2.3 Hz, 1H), 7.69 (d, *J* = 8.2 Hz, 1H), 7.43 – 7.33 (m, 1H), 7.18 – 7.08 (m, 1H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.59 (d, *J* = 1.2 Hz, 1H), 6.48 (s, 1H), 5.89 (t, *J* = 1.2 Hz, 1H), 4.34 – 4.20 (m, 2H), 3.30 (s, 3H), 1.36 (s, 9H), 1.30 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.6, 165.4, 151.3, 149.8, 143.7, 137.6, 134.7, 133.7, 129.7, 129.2, 128.4, 127.6, 124.3, 124.2, 123.7, 119.2, 108.1, 85.0, 83.8, 69.1, 61.4, 28.2, 26.8, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>27</sub>N<sub>3</sub>O<sub>8</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 532.16904; found: 532.16937.

**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',5'-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3e)**



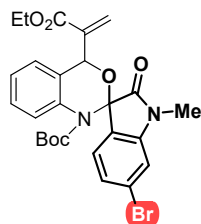
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (31.7 mg, 66% yield); m.p. 176.9-179.3 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.81 (d, *J* = 8.2 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.15 – 7.04 (m, 2H), 6.88 (d, *J* = 7.1 Hz, 2H), 6.69 (d, *J* = 7.9 Hz, 1H), 6.59 – 6.46 (m, 2H), 5.89 (s, 1H), 4.35 – 4.15 (m, 2H), 3.19 (s, 3H), 2.26 (s, 3H), 1.29 (d, *J* = 3.8 Hz, 12H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.5, 165.6, 151.3, 141.7, 138.0, 135.5, 134.5, 132.5, 130.6, 129.2, 128.3, 127.9, 123.9, 123.6, 123.5, 108.1, 86.1, 82.9, 68.6, 61.2, 28.1, 26.3, 21.1, 14.3.

**HRMS (ESI)** Calcd. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 501.19961; found: 501.19992.

**tert-butyl 6-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3f)**



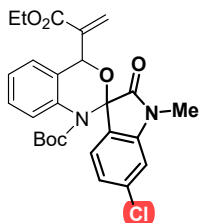
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (26.5 mg, 49% yield); m.p. 189.5-193.4 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.73 (d, *J* = 8.1 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.13 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.11 – 7.05 (m, 1H), 6.96 (d, *J* = 1.7 Hz, 1H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.90 – 6.85 (m, 1H), 6.56 (d, *J* = 1.2 Hz, 1H), 6.47 (s, 1H), 5.87 (t, *J* = 1.2 Hz, 1H), 4.36 – 4.18 (m, 2H), 3.20 (s, 3H), 1.33 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.3, 165.5, 151.2, 145.5, 137.9, 135.2, 134.3, 129.3, 128.1, 127.4, 125.7, 124.4, 124.2, 124.0, 123.9, 123.5, 111.9, 85.6, 83.3, 68.8, 61.3, 28.2, 26.5, 14.3.

**HRMS (ESI)** Calcd. for  $C_{26}H_{27}BrN_2O_6Na^+$   $[M+Na]^+$ : 565.09447, 567.09242; found: 565.09497, 567.09302.

**tert-butyl 6'-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3g)**



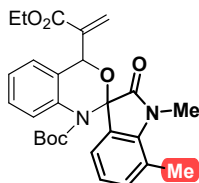
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (37.1 mg, 74% yield); m.p. 179.8-182.2 °C.

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.73 (d,  $J$  = 8.2 Hz, 1H), 7.38 – 7.31 (m, 1H), 7.11 – 7.05 (m, 1H), 7.01 – 6.95 (m, 2H), 6.91 – 6.85 (m, 1H), 6.81 (d,  $J$  = 1.6 Hz, 1H), 6.56 (d,  $J$  = 1.3 Hz, 1H), 6.48 (s, 1H), 5.87 (t,  $J$  = 1.3 Hz, 1H), 4.34 – 4.17 (m, 2H), 3.21 (s, 3H), 1.33 (s, 9H), 1.29 (t,  $J$  = 7.1 Hz, 3H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  172.4, 165.5, 151.2, 145.4, 137.9, 136.3, 135.2, 134.3, 129.3, 128.1, 126.8, 124.1, 124.0, 123.9, 123.5, 122.7, 109.2, 85.5, 83.3, 68.8, 61.3, 28.1, 26.5, 14.3.

**HRMS (ESI)** Calcd. for  $C_{26}H_{27}ClN_2O_6Na^+$   $[M+Na]^+$ : 521.14499, 523.14203; found: 521.14539, 523.14276.

**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',7'-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3h)**



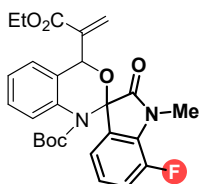
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (41.4 mg, 86% yield); m.p. 177.9-179.7 °C.

**$^1H$  NMR (400 MHz,  $CDCl_3$ )**  $\delta$  7.79 (d,  $J$  = 8.2 Hz, 1H), 7.38 – 7.30 (m, 1H), 7.11 – 7.00 (m, 2H), 6.91 (dd,  $J$  = 7.4, 1.7 Hz, 1H), 6.89 – 6.83 (m, 2H), 6.55 (d,  $J$  = 1.3 Hz, 1H), 6.52 (s, 1H), 5.88 (t,  $J$  = 1.4 Hz, 1H), 4.38 – 4.13 (m, 2H), 3.50 (s, 3H), 2.55 (s, 3H), 1.36 – 1.24 (m, 12H).

**$^{13}C$  NMR (101 MHz,  $CDCl_3$ )**  $\delta$  173.3, 165.6, 151.2, 141.7, 138.1, 135.5, 134.5, 134.2, 129.3, 129.2, 127.9, 123.9, 123.6, 123.5, 122.9, 121.2, 119.9, 85.4, 82.9, 68.6, 61.3, 29.8, 28.1, 19.1, 14.3.

**HRMS (ESI)** Calcd. for  $C_{27}H_{30}N_2O_6Na^+$   $[M+Na]^+$ : 501.19961; found: 501.19980.

**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-7'-fluoro-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3i)**



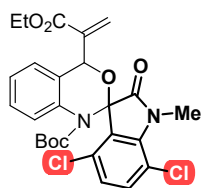
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (20.2 mg, 42% yield); m.p. 168.9-170.8 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.75 (d, *J* = 8.2 Hz, 1H), 7.39 – 7.30 (m, 1H), 7.11 – 7.01 (m, 2H), 6.96 – 6.82 (m, 3H), 6.57 (d, *J* = 1.2 Hz, 1H), 6.50 (s, 1H), 5.88 (d, *J* = 1.4 Hz, 1H), 4.37 – 4.13 (m, 2H), 3.44 (d, *J* = 2.7 Hz, 3H), 1.34 (s, 9H), 1.29 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.3, 165.5, 151.2, 147.9 (d, *J* = 243.9 Hz), 137.9, 135.2, 134.2, 131.3, 130.7, 129.4, 128.1, 124.0, 123.8, 123.6 (d, *J* = 6.2 Hz), 123.5, 119.0 (d, *J* = 2.9 Hz), 118.5 (d, *J* = 19.5 Hz), 85.6, 83.3, 68.8, 61.3, 29.0 (d, *J* = 5.6 Hz), 28.1, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>27</sub>FN<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 505.17454; found: 505.17484.

**tert-butyl 4',7'-dichloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3j)**



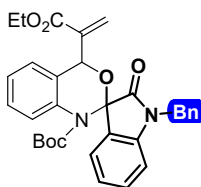
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (52.0 mg, 98% yield); m.p. 162.7-165.1 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.70 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.29 (m, 1H), 7.18 (d, *J* = 8.7 Hz, 1H), 7.09 – 6.98 (m, 1H), 6.86 (dd, *J* = 8.2, 2.0 Hz, 2H), 6.58 (d, *J* = 1.2 Hz, 1H), 6.55 (s, 1H), 5.89 (d, *J* = 1.1 Hz, 1H), 4.34 – 4.14 (m, 2H), 3.60 (s, 3H), 1.36 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.2, 165.5, 151.2, 141.6, 138.2, 136.0, 133.5, 132.4, 129.9, 129.0, 127.9, 127.4, 124.7, 124.1, 123.9, 123.5, 114.4, 86.1, 83.5, 68.7, 61.3, 29.8, 28.1, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>26</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 555.10601, 557.10306, 559.10011; found: 555.10651, 557.10364, 559.09967.

**tert-butyl 1'-benzyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3k)**



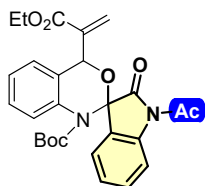
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford white solid (36.6 mg, 68% yield); m.p. 170.7-172.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.76 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.40 – 7.33 (m, 3H), 7.33 – 7.28 (m, 2H), 7.28 – 7.24 (m, 1H), 7.22 – 7.15 (m, 1H), 7.13 – 7.07 (m, 2H), 6.98 – 6.89 (m, 2H), 6.65 (d, *J* = 7.8 Hz, 1H), 6.59 (d, *J* = 1.1 Hz, 2H), 5.94 (s, 1H), 5.17 (d, *J* = 15.8 Hz, 1H), 4.69 (d, *J* = 15.8 Hz, 1H), 4.36 – 4.21 (m, 2H), 1.36 (s, 9H), 1.29 (t, *J* = 7.2 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.7, 165.7, 151.3, 143.3, 138.0, 135.7, 135.5, 134.3, 130.3, 129.2, 128.8, 128.5, 127.9, 127.6, 127.3, 123.9, 123.7, 123.6, 123.1, 122.9, 109.4, 86.1, 83.1, 68.7, 61.3, 43.7, 28.2, 14.3.

**HRMS (ESI)** Calcd. for C<sub>32</sub>H<sub>32</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 563.21526; found: 563.21558.

**tert-butyl 1'-acetyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3l)**



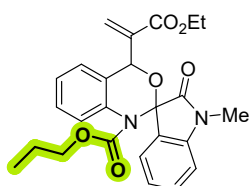
It was purified by flash chromatography (petroleum ether /EtOAc, 10:1) to afford white solid (35.1 mg, 71% yield); m.p. 127.5-130.3 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 8.28 (d, *J* = 8.2 Hz, 1H), 7.75 (d, *J* = 8.2 Hz, 1H), 7.42 – 7.33 (m, 2H), 7.18 – 7.07 (m, 3H), 6.95 – 6.88 (m, 1H), 6.59 (d, *J* = 1.1 Hz, 1H), 6.43 (s, 1H), 5.92 (s, 1H), 4.36 – 4.24 (m, 2H), 2.73 (s, 3H), 1.33 – 1.29 (m, 12H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.5, 170.9, 165.5, 151.2, 140.7, 137.6, 135.1, 134.1, 130.9, 129.5, 128.3, 127.7, 125.6, 124.1, 124.0, 123.5, 123.0, 116.9, 85.4, 84.0, 69.2, 61.4, 28.1, 26.8, 14.3.

**HRMS (ESI)** Calcd. for C<sub>27</sub>H<sub>28</sub>N<sub>2</sub>O<sub>7</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 515.17887; found: 515.17908.

**propyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3m)**



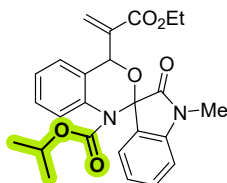
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford yellow solid (36.5 mg, 81% yield); m.p. 119.4-124.9 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.66 (d, *J* = 8.1 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.16 – 7.09 (m, 1H), 7.06 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.02 – 6.95 (m, 1H), 6.94 – 6.87 (m, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 6.62 – 6.53 (m, 2H), 5.91 (s, 1H), 4.37 – 4.18 (m, 2H), 4.15 – 3.92 (m, 2H), 3.25 (s, 3H), 1.54 (ddt, *J* = 14.0, 10.9, 7.0 Hz, 2H), 1.29 (t, *J* = 7.1 Hz, 3H), 0.81 (t, *J* = 7.4 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.4, 165.5, 152.7, 144.4, 137.8, 135.0, 134.7, 130.7, 129.3, 128.1, 127.7, 124.2, 124.0, 123.6, 123.3, 122.9, 108.5, 85.9, 68.9, 68.4, 61.3, 26.4, 22.0, 14.3, 10.4.

**HRMS (ESI)** Calcd. for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 473.16831; found: 473.16898.

**isopropyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3n)**



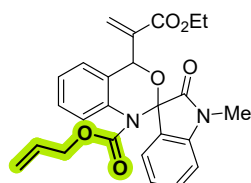
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford yellow solid (34.2 mg, 76% yield); m.p. 118.5-121.9 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.74 (d, *J* = 8.2 Hz, 1H), 7.34 (s, 2H), 7.14 – 7.08 (m, 1H), 7.06 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.93 – 6.87 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.63 – 6.51 (m, 2H), 5.91 (t, *J* = 1.3 Hz, 1H), 5.01 – 4.83 (m, 1H), 4.39 – 4.14 (m, 2H), 3.24 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.18 (d, *J* = 6.3 Hz, 3H), 0.98 (d, *J* = 6.2 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.5, 165.6, 151.9, 144.3, 137.9, 135.1, 134.4, 130.6, 129.3, 128.1, 124.0, 123.9, 123.4, 123.2, 122.9, 108.3, 85.9, 70.6, 68.8, 61.3, 26.3, 21.8, 14.3.

**HRMS (ESI)** Calcd. for C<sub>25</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 473.16831; found: 473.16855.

**allyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3o)**



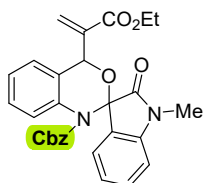
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (34.5 mg, 77% yield); m.p. 133.6-138.3 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.67 (dd, *J* = 8.2, 1.1 Hz, 1H), 7.40 – 7.30 (m, 2H), 7.16 – 7.10 (m, 1H), 7.06 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.03 – 6.95 (m, 1H), 6.95 – 6.89 (m, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 1.4 Hz, 2H), 5.92 (d, *J* = 1.3 Hz, 1H), 5.84 – 5.65 (m, 1H), 5.27 – 5.07 (m, 2H), 4.67 – 4.48 (m, 2H), 4.39 – 4.15 (m, 2H), 3.23 (s, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.4, 165.5, 152.3, 144.5, 137.8, 134.7, 134.8, 131.6, 130.8, 129.3, 128.2, 127.5, 124.3, 124.1, 123.6, 123.4, 123.0, 118.7, 108.6, 86.0, 69.0, 67.2, 61.3, 26.4, 14.3.

**HRMS (ESI)** Calcd. for C<sub>25</sub>H<sub>24</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 471.15266; found: 471.15292.

**benzyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3p)**



It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (42.4 mg, 85% yield); m.p. 141.5-142.8 °C.

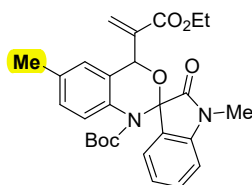
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.72 (d, *J* = 8.2 Hz, 1H), 7.37 – 7.23 (m, 5H), 7.14 – 7.01 (m, 4H), 7.01 – 6.94 (m, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.64 (d, *J* = 7.8 Hz, 1H), 6.59 – 6.51 (m, 2H), 5.88 (s, 1H), 5.13 – 4.89 (m, 2H), 4.38 – 4.12 (m, 2H), 2.82 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.2, 165.5, 152.3, 144.2, 137.7, 134.8, 134.7, 134.6, 130.6, 129.3, 128.6, 128.5, 128.4, 128.2, 127.6, 124.2, 124.0, 123.5, 123.2, 122.9, 108.7, 86.0, 68.8, 68.5, 61.2, 25.8, 14.2.

**HRMS (ESI)** Calcd. for C<sub>29</sub>H<sub>26</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 521.16831; found: 521.16840.

**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',6-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3q)**





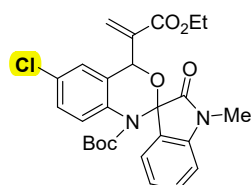
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (41.3 mg, 86% yield); m.p. 160.2-162.0 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.67 (d, *J* = 8.3 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.15 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.08 (dd, *J* = 7.4, 1.2 Hz, 1H), 7.01 – 6.95 (m, 1H), 6.80 (d, *J* = 7.7 Hz, 1H), 6.69 – 6.64 (m, 1H), 6.56 (d, *J* = 1.2 Hz, 1H), 6.50 (s, 1H), 5.88 (t, *J* = 1.3 Hz, 1H), 4.39 – 4.19 (m, 2H), 3.21 (s, 3H), 2.31 (s, 3H), 1.32 – 1.27 (m, 12H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.6, 165.7, 151.3, 144.1, 138.1, 134.3, 133.3, 132.9, 130.4, 129.2, 128.6, 128.5, 124.4, 123.3, 123.1, 122.9, 108.3, 85.8, 82.8, 68.6, 61.2, 28.1, 26.3, 21.1, 14.3.

**HRMS (ESI)** Calcd. for C<sub>27</sub>H<sub>30</sub>N<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 501.19961; found: 501.19980.

**tert-butyl 6-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3r)**



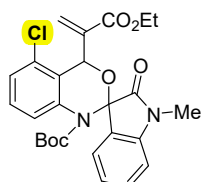
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (41.2 mg, 83% yield); m.p. 160.0-162.5 °C.

**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.76 (d, *J* = 8.8 Hz, 1H), 7.37 – 7.29 (m, 2H), 7.07 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.04 – 6.96 (m, 1H), 6.86 (dd, *J* = 2.4, 0.8 Hz, 1H), 6.81 (d, *J* = 7.8 Hz, 1H), 6.58 (d, *J* = 1.1 Hz, 1H), 6.49 (s, 1H), 5.90 (t, *J* = 1.3 Hz, 1H), 4.37 – 4.17 (m, 2H), 3.21 (s, 3H), 1.32 – 1.26 (m, 12H).

**<sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>)** δ 172.3, 165.3, 151.0, 144.1, 137.4, 135.9, 134.1, 130.6, 129.9, 129.1, 128.1, 128.0, 124.8, 124.2, 123.1, 123.0, 108.4, 86.0, 83.4, 68.2, 61.4, 28.0, 26.4, 14.3.

**HRMS (ESI)** Calcd. for C<sub>26</sub>H<sub>27</sub>ClN<sub>2</sub>O<sub>6</sub>Na<sup>+</sup> [M+Na]<sup>+</sup>: 521.14499, 523.14203; found: 521.14502, 523.14209.

**tert-butyl 5-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3s)**



It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (31.6 mg, 63% yield); m.p. 134.3-137.7 °C.

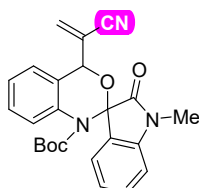
**<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)** δ 7.72 (d, *J* = 8.3 Hz, 1H), 7.36 – 7.31 (m, 1H), 7.31 – 7.26 (m, 1H), 7.22 (dd, *J* = 8.0, 1.0 Hz, 1H), 6.95 – 6.88 (m, 1H), 6.84 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.75 (d, *J* = 7.8 Hz, 1H),

6.40 (s, 1H), 6.14 (s, 1H), 5.44 (s, 1H), 4.42 – 4.17 (m, 2H), 3.15 (s, 3H), 1.32 (t,  $J = 7.1$  Hz, 3H), 1.27 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  171.2, 165.8, 151.0, 143.8, 137.6, 137.5, 131.1, 130.6, 129.1, 129.0, 128.1, 127.9, 124.9, 123.0, 122.8, 122.3, 108.3, 86.6, 83.5, 71.8, 61.0, 28.0, 26.4, 14.4.

HRMS (ESI) Calcd. for  $\text{C}_{26}\text{H}_{27}\text{ClN}_2\text{O}_6\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 521.14499, 523.14203; found: 521.14514, 523.14252.

### tert-butyl 4-(1-cyanovinyl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3t)



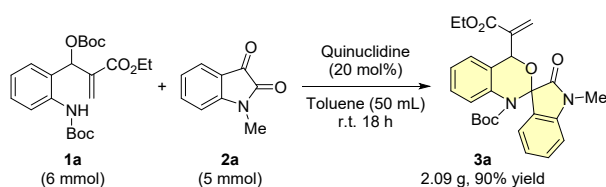
It was purified by flash chromatography (petroleum ether /EtOAc, 6:1) to afford White solid (37.6 mg, 90% yield); m.p. 184.3-186.5 °C.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.84 (d,  $J = 8.3$  Hz, 1H), 7.46 – 7.38 (m, 1H), 7.38 – 7.31 (m, 1H), 7.22 – 7.09 (m, 3H), 7.06 – 6.96 (m, 1H), 6.82 (d,  $J = 7.8$  Hz, 1H), 6.30 (s, 1H), 6.24 (s, 1H), 6.20 (s, 1H), 5.29 (s, 1H), 3.23 (s, 3H), 1.27 (s, 9H).

$^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  172.5, 151.0, 143.9, 135.8, 135.3, 130.8, 130.2, 129.0, 127.7, 124.0, 123.9, 123.5, 123.3, 123.1, 120.2, 116.3, 108.5, 86.1, 83.4, 71.3, 53.6, 28.0, 26.4.

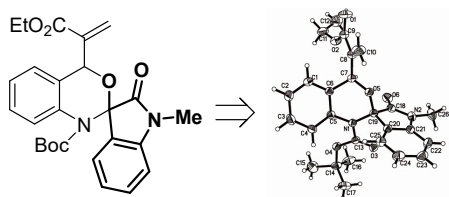
HRMS (ESI) Calcd. for  $\text{C}_{24}\text{H}_{23}\text{N}_3\text{O}_4\text{Na}^+$   $[\text{M}+\text{Na}]^+$ : 440.15808; found: 440.15823.

### 3. Scale-up experiment



In an ordinary vial charged with a magnetic stirring bar, **1a** (6.0 mmol, 1.2 equiv), **2a** (5.0 mmol, 1.0 equiv), quinuclidine (0.1 mmol, 0.2 equiv) and Toluene (50 mL) was added, and then the mixture was stirred at r.t. for 18 h. the products **3a** were isolated by flash chromatography on silica gel with yields of 90%.

#### 4. X-ray crystal data for compound 3a

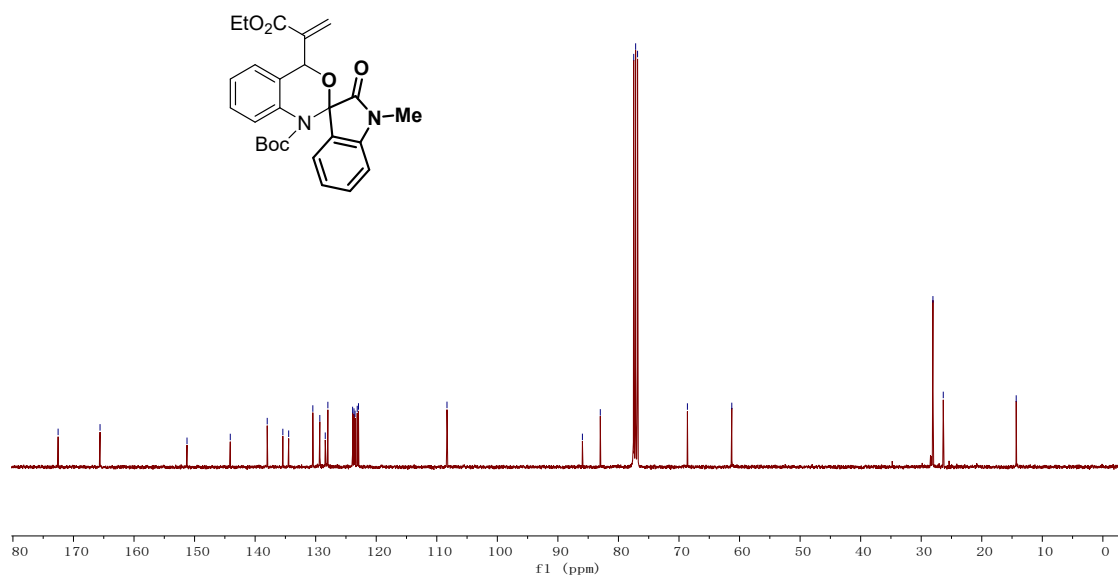
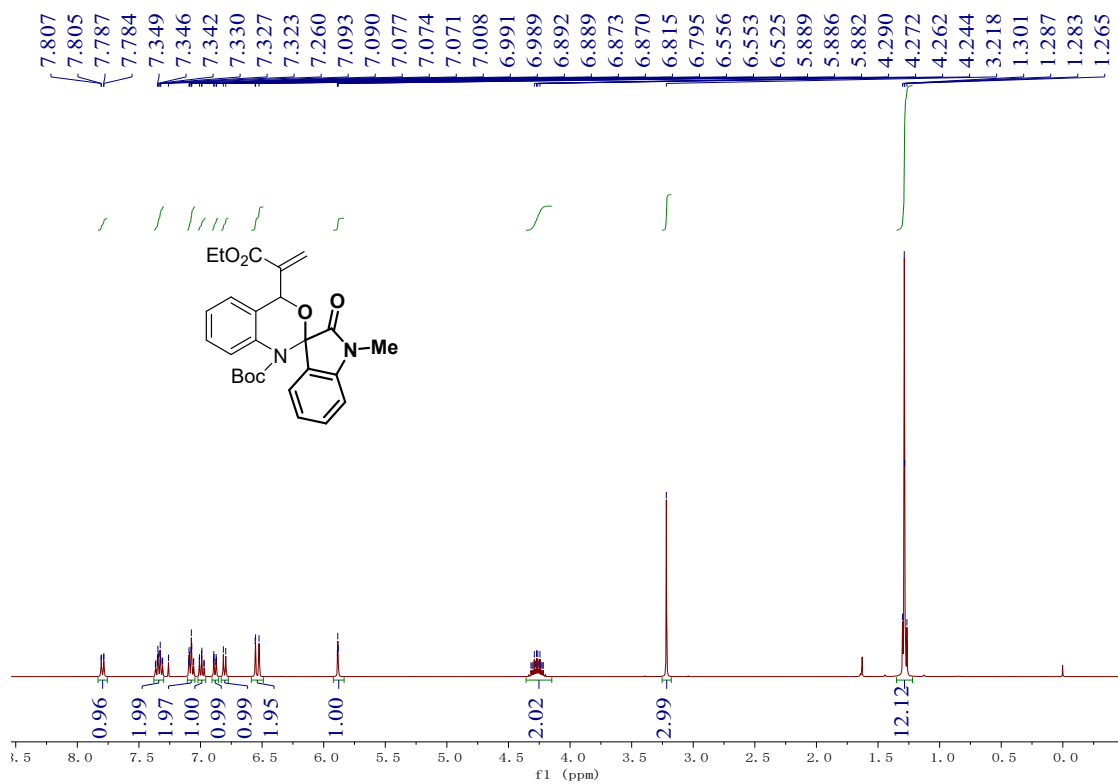


**3a**, CCDC (2360825)

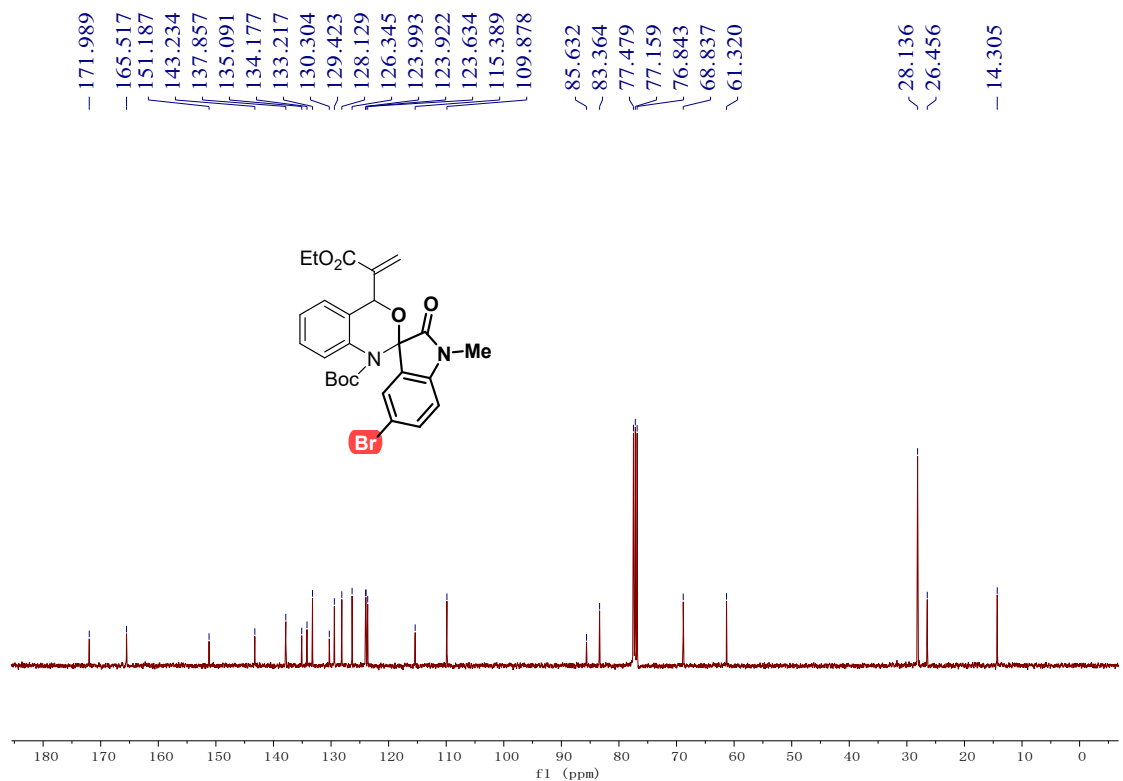
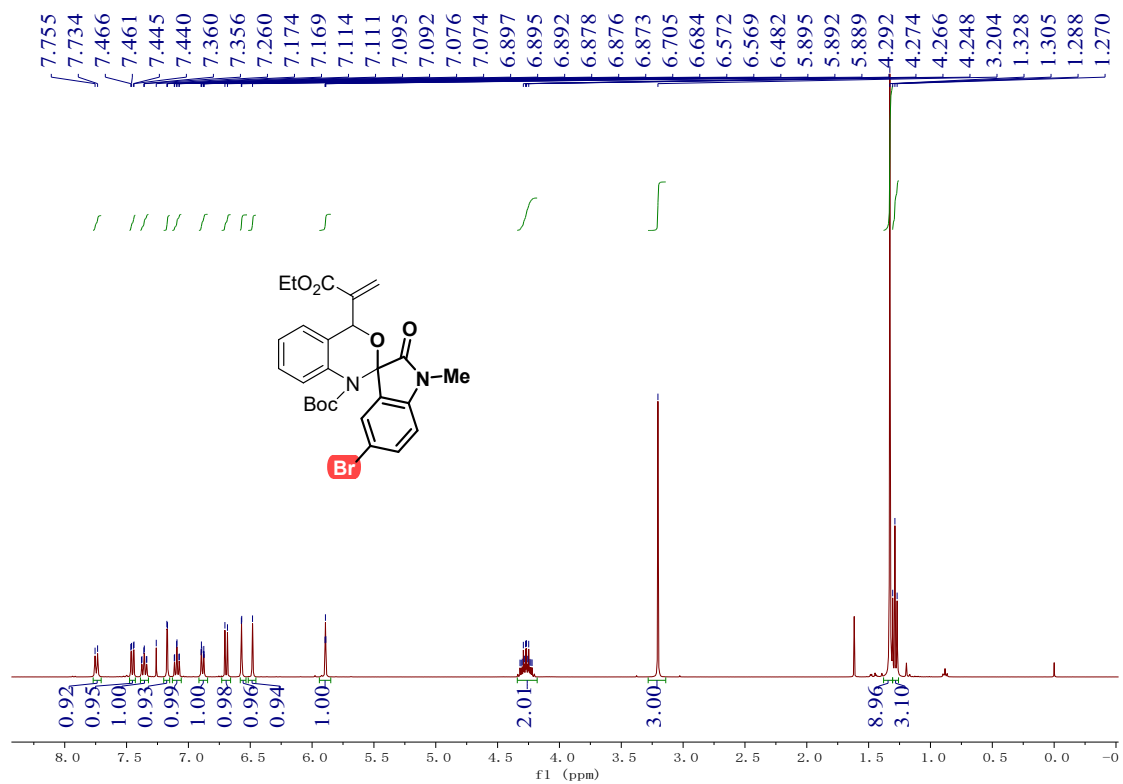
|   |   |
|---|---|
| Identification code                         | <b>3a</b>   |
| Empirical formula                           | <b>C<sub>26</sub>H<sub>28</sub>N<sub>2</sub>O<sub>6</sub></b> |
| Formula weight                              | <b>464.50</b>   |
| Temperature/K                               | <b>293(2)</b>   |
| Crystal system                              | <b>monoclinic</b>   |
| Space group                                 | <b>P21/c</b>  |
| a/Å   | <b>8.2639(3)</b>  |
| b/Å   | <b>23.4915(6)</b>   |
| c/Å   | <b>13.1699(4)</b>   |
| α /°  | <b>90</b>   |
| β /°  | <b>105.953(3)</b>   |
| γ /°  | <b>90</b>   |
| Volume/Å <sup>3</sup>                       | <b>2458.23(13)</b>  |
| Z   | <b>4</b>  |
| ρ calcd/cm <sup>3</sup>                     | <b>1.255</b>  |
| μ /mm <sup>-1</sup>                         | <b>0.736</b>  |
| F(000)                                      | <b>984.0</b>  |
| Crystal size/mm <sup>3</sup>                | <b>0.14 × 0.1 × 0.09</b>                                      |
| Radiation                                   | <b>CuK α (λ = 1.54184)</b>                                    |
| 2θ range for data collection/°              | <b>7.526 to 134.14</b>  |
| Index ranges                                | <b>-9 ≤ h ≤ 8, -25 ≤ k ≤ 28, -14 ≤ l ≤ 15</b>                 |
| Reflections collected                       | <b>9520</b>   |
| Independent reflections                     | <b>4370 [Rint = 0.0295, Rsigma = 0.0372]</b>                  |
| Data/restraints/parameters                  | <b>4370/17/320</b>  |
| Goodness-of-fit on F <sup>2</sup>           | <b>1.055</b>  |
| Final R indexes [I ≥ 2σ (I)]                | <b>R1 = 0.0585, wR2 = 0.1550</b>                              |
| Final R indexes [all data]                  | <b>R1 = 0.0716, wR2 = 0.1695</b>                              |
| Largest diff. peak/hole / e Å <sup>-3</sup> | <b>0.48/-0.27</b>   |

5. The copies of  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR for compounds 3a-3s

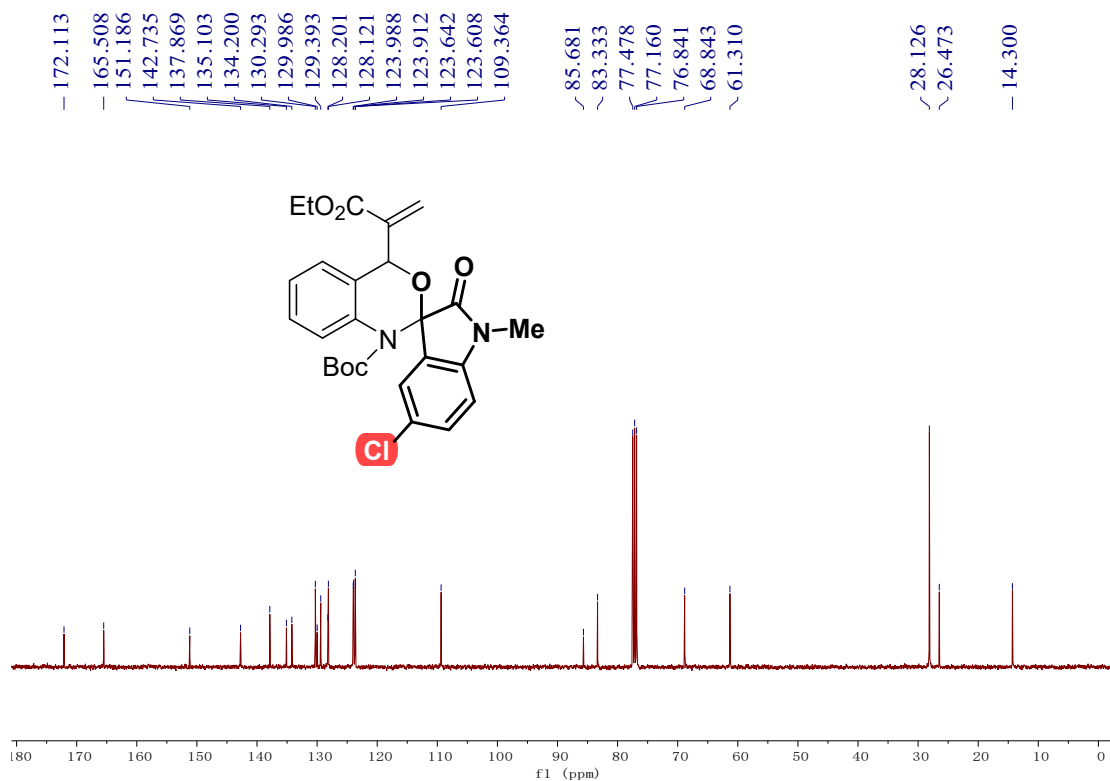
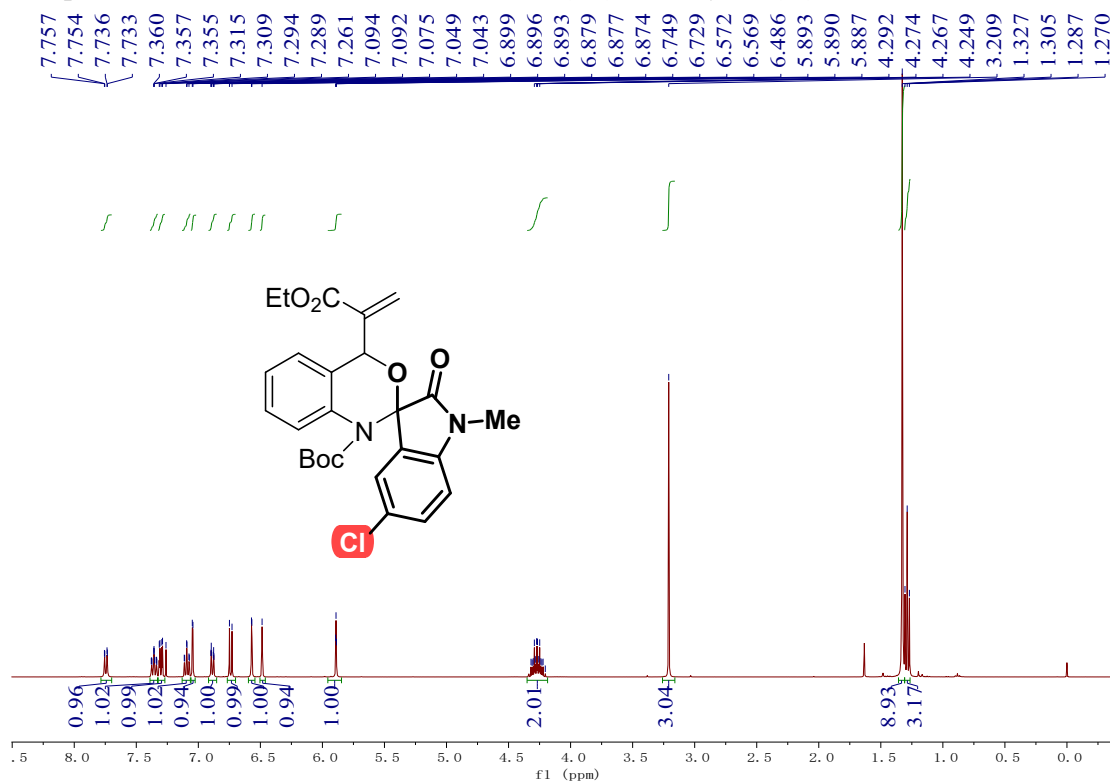
tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3a)



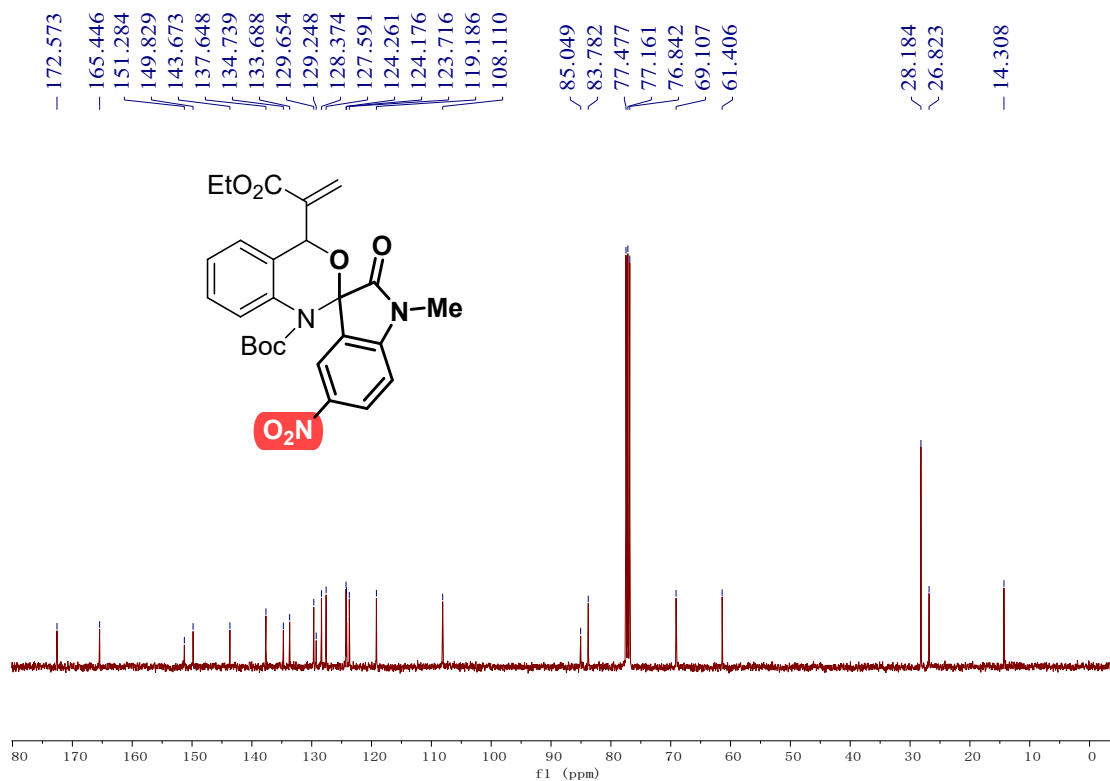
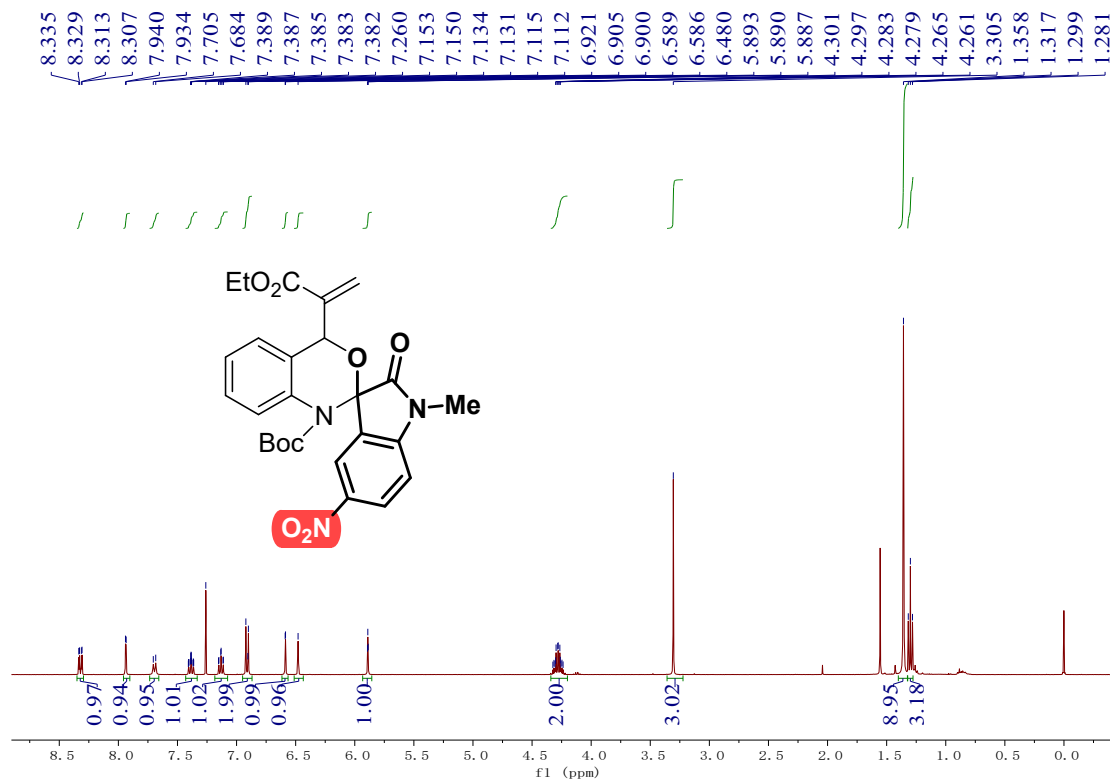
**tert-butyl 5'-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3b)**



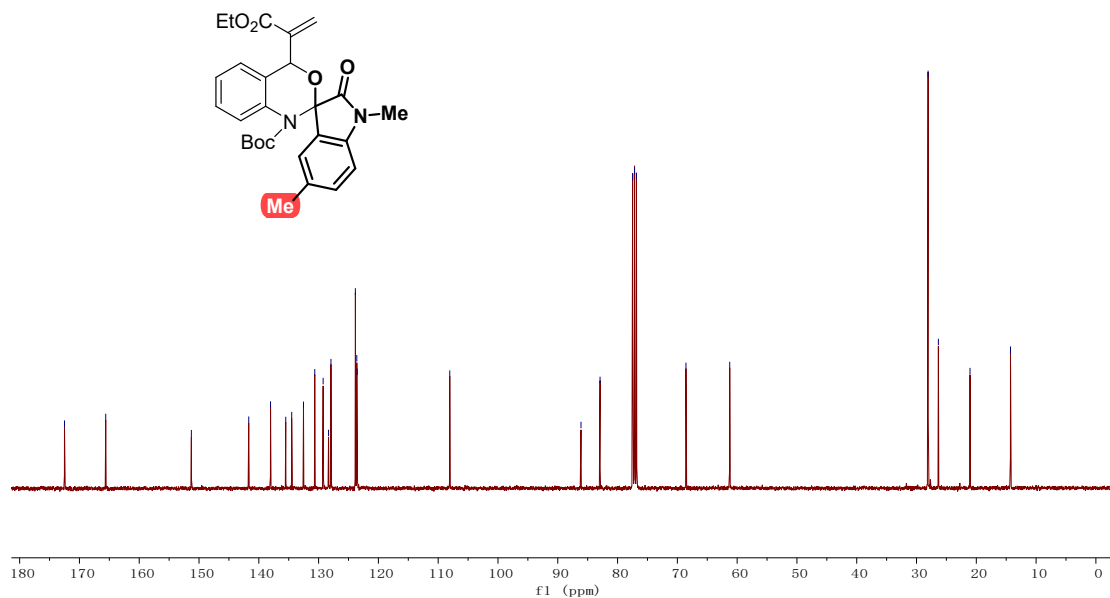
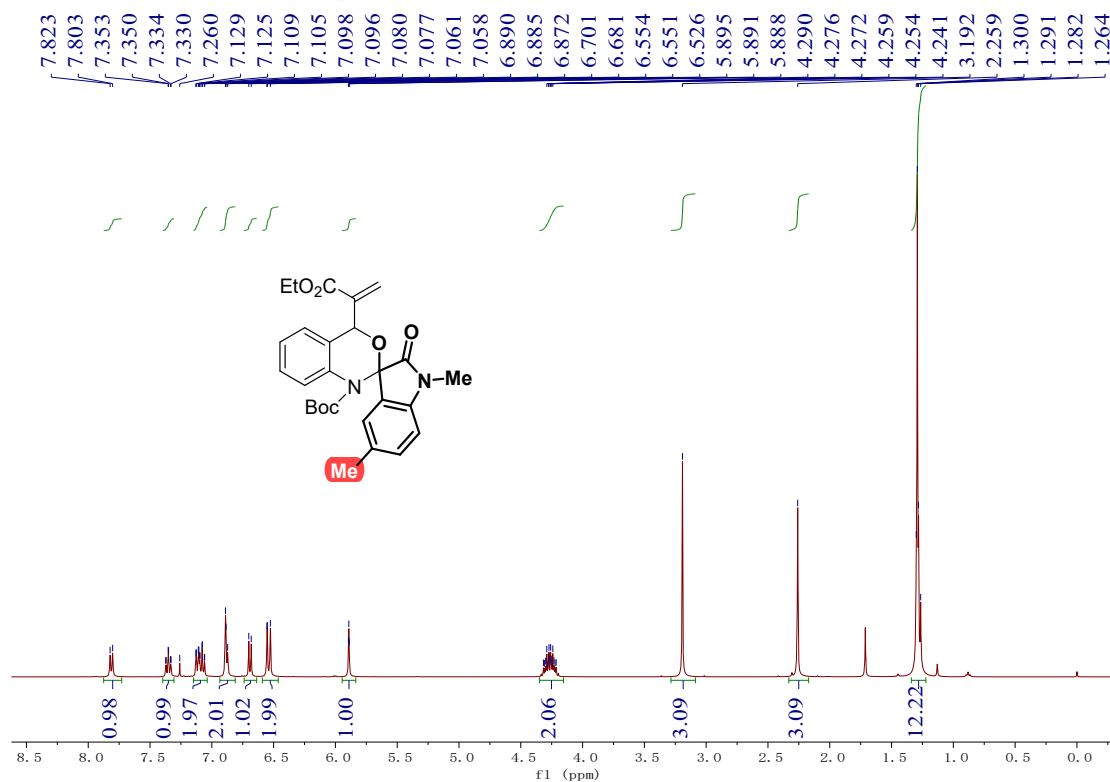
**tert-butyl 5'-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3c)**



**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-5'-nitro-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3d)**

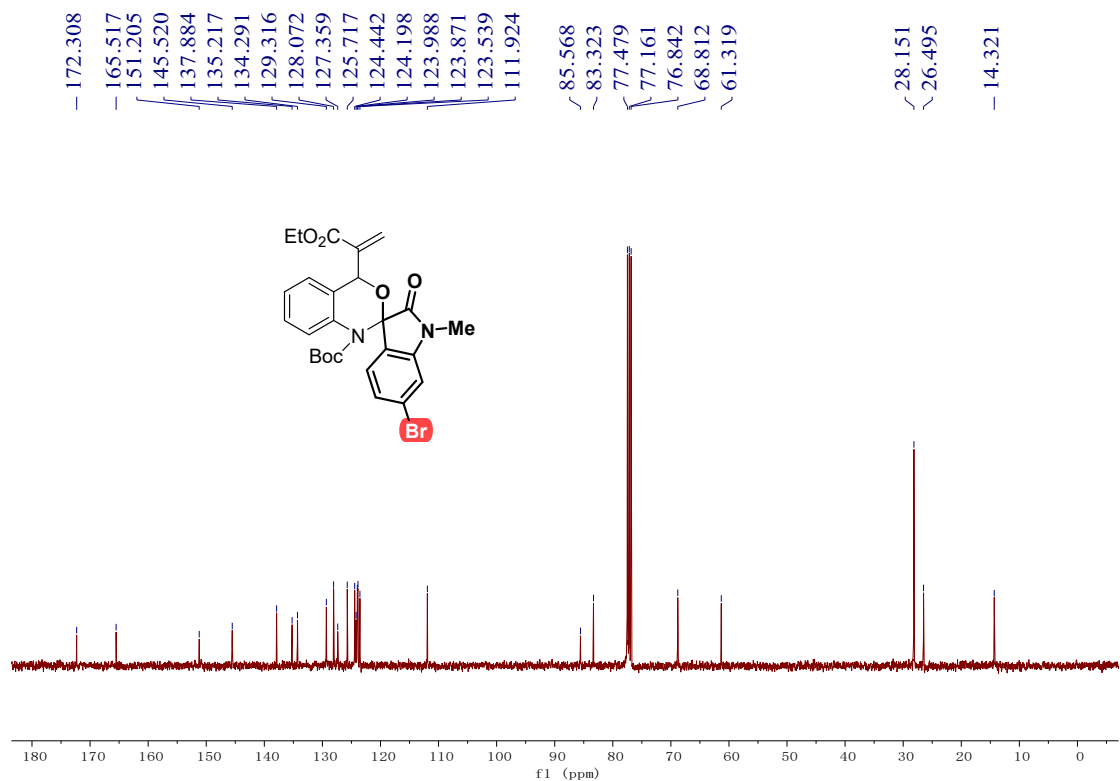
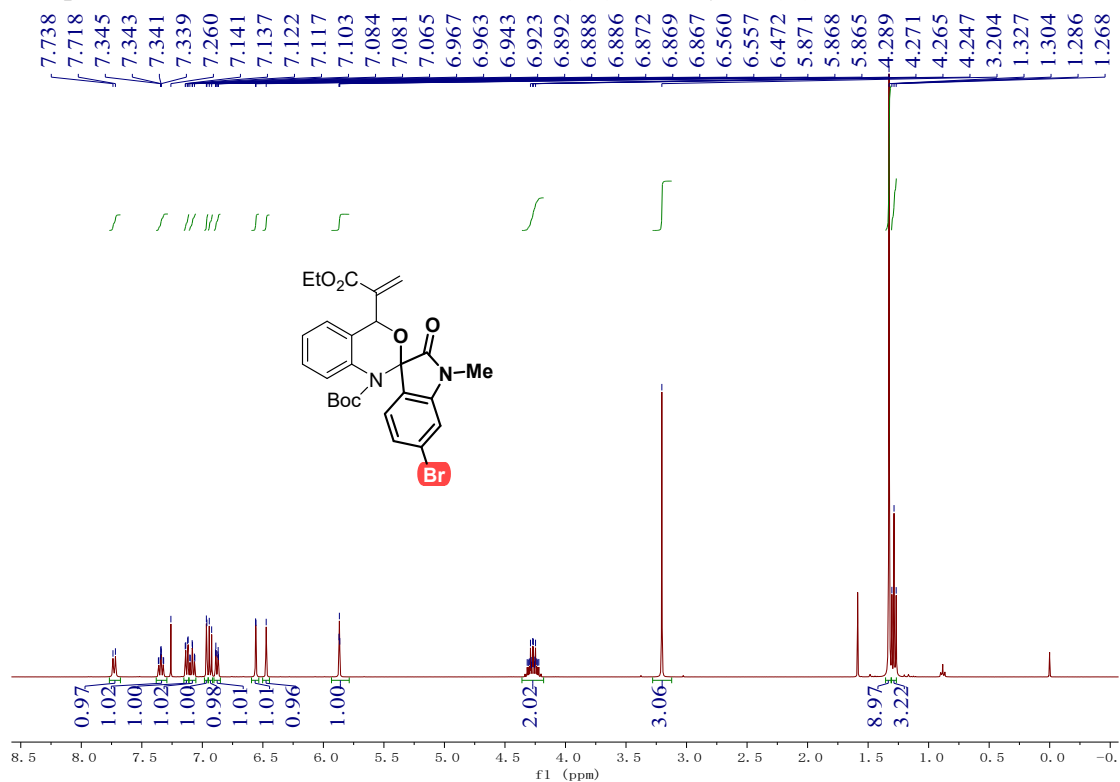


**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',5'-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3e)**

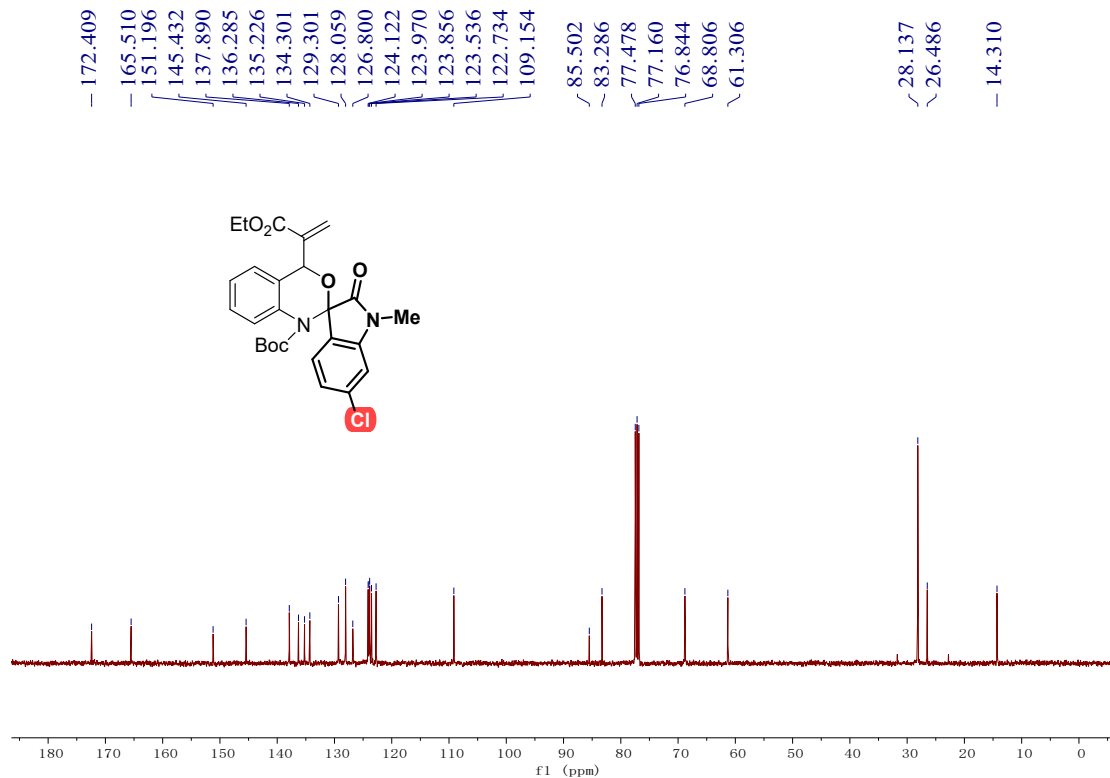
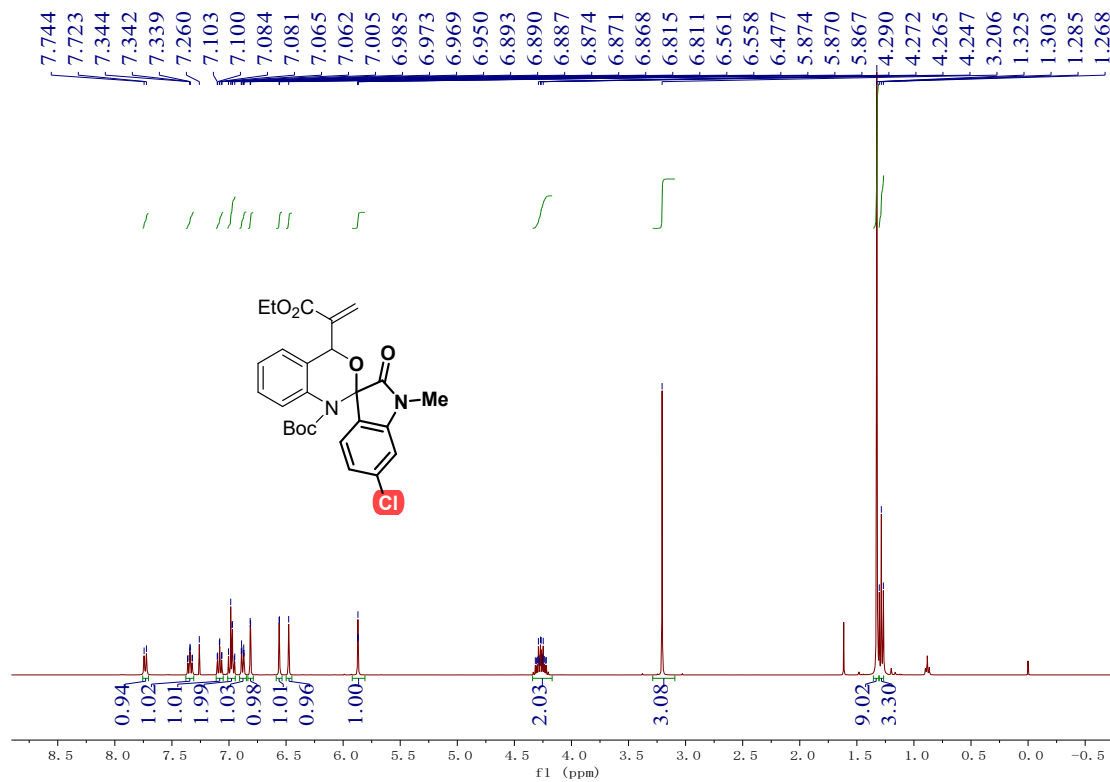




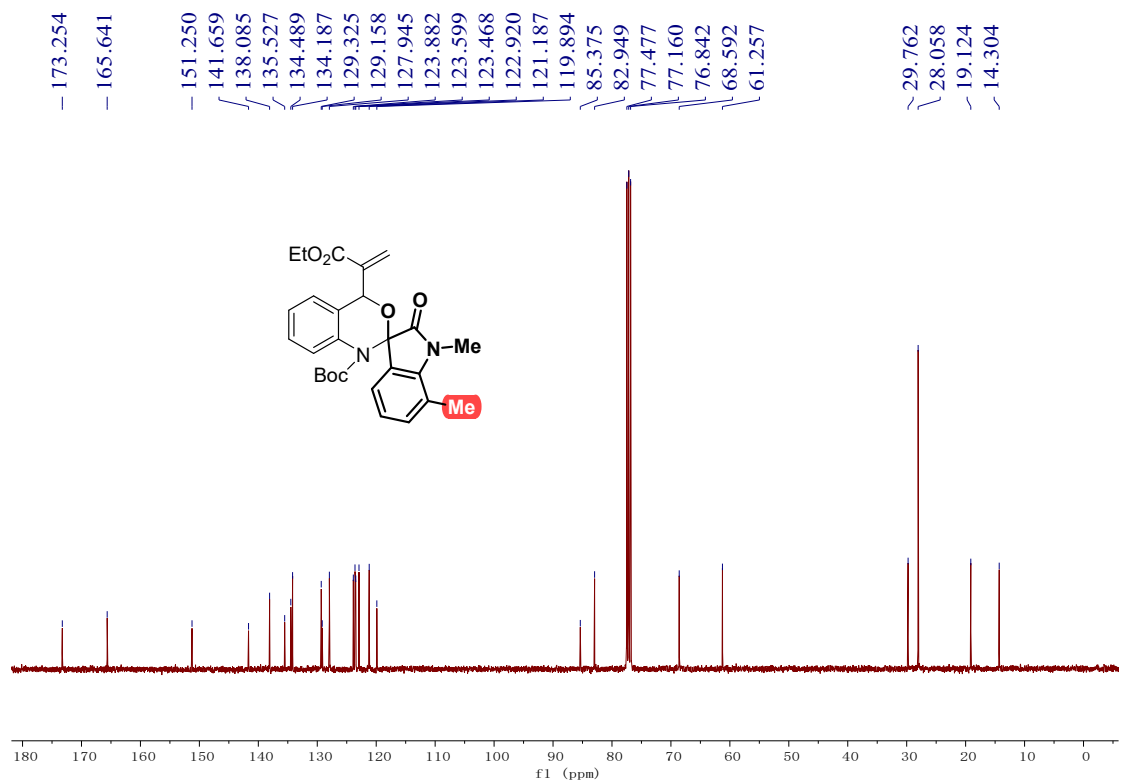
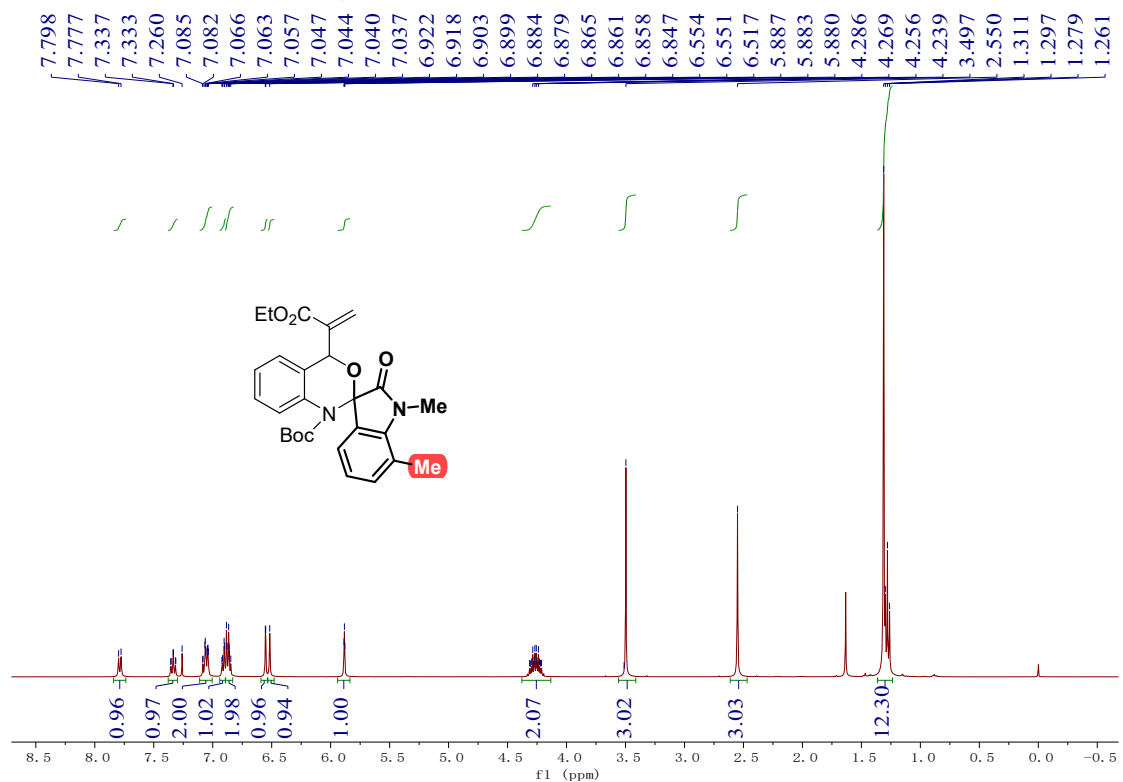
**tert-butyl 6'-bromo-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3f)**



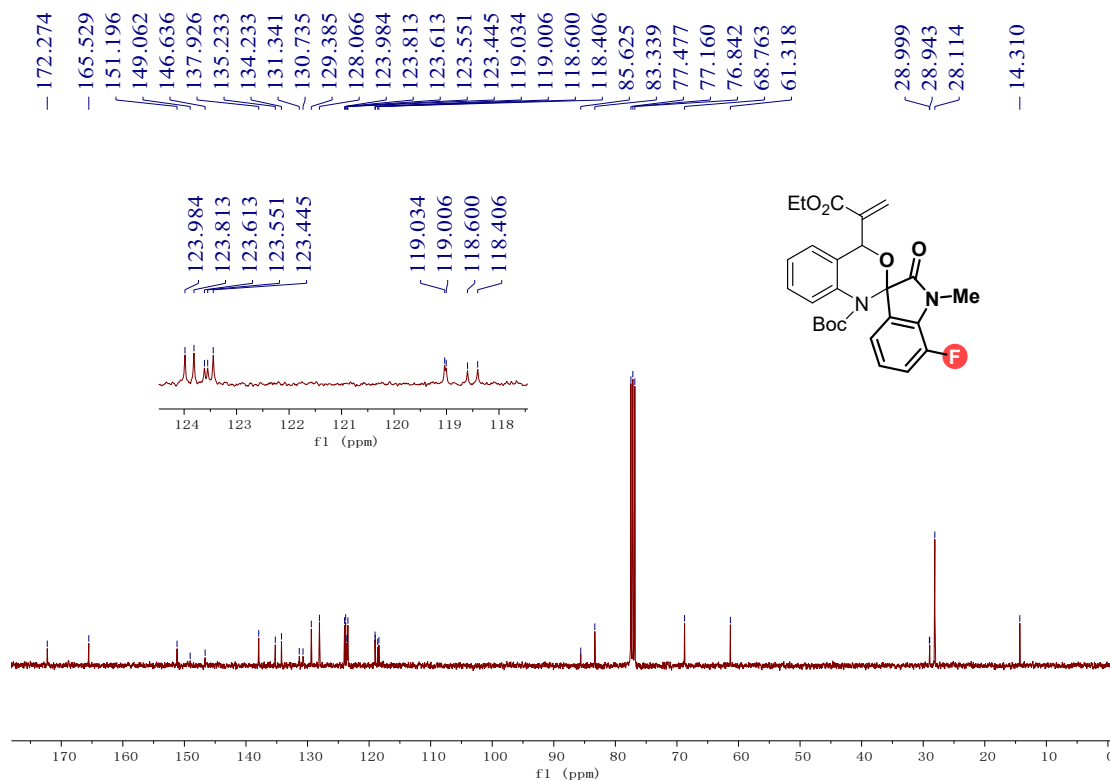
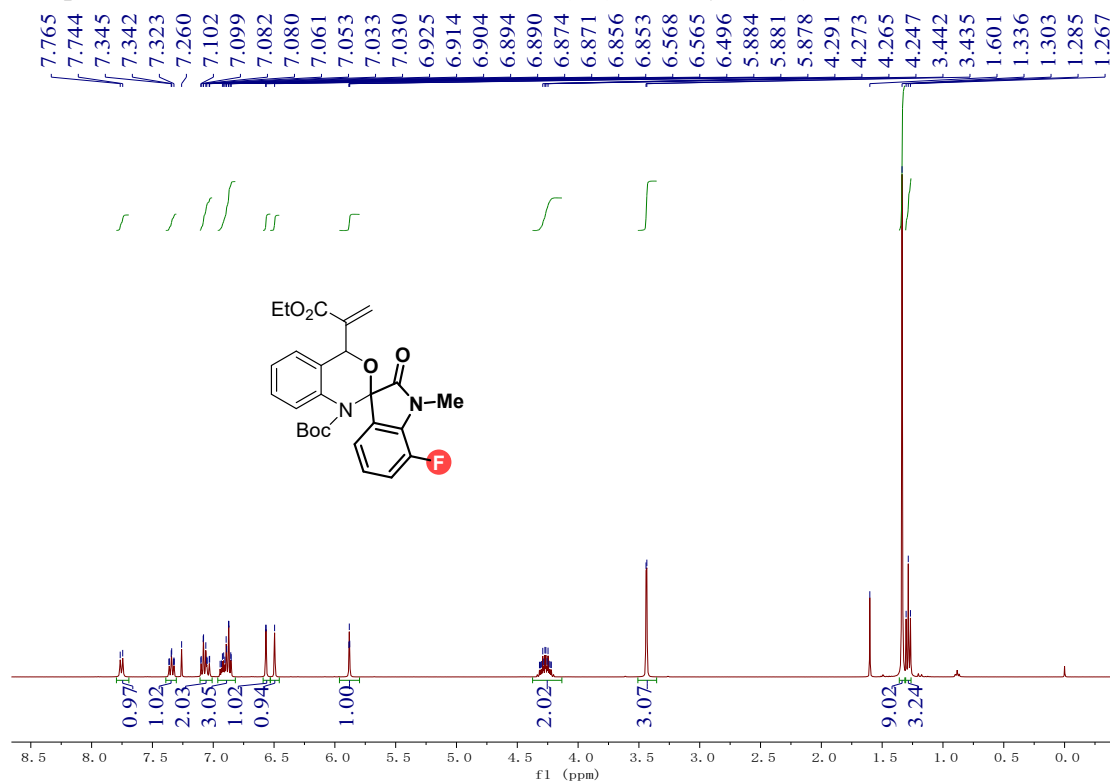
tert-butyl 6'-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3g)



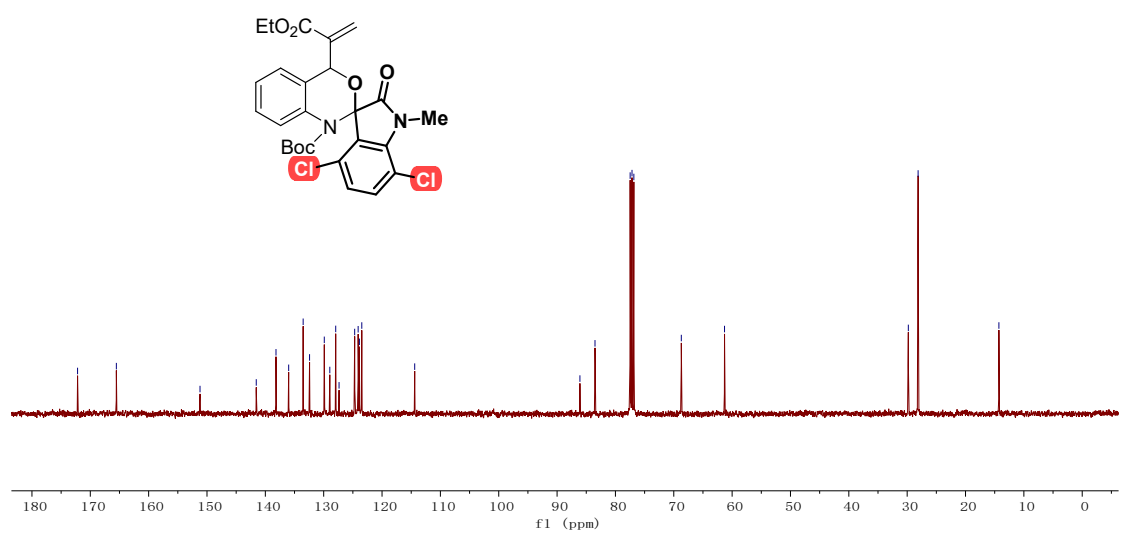
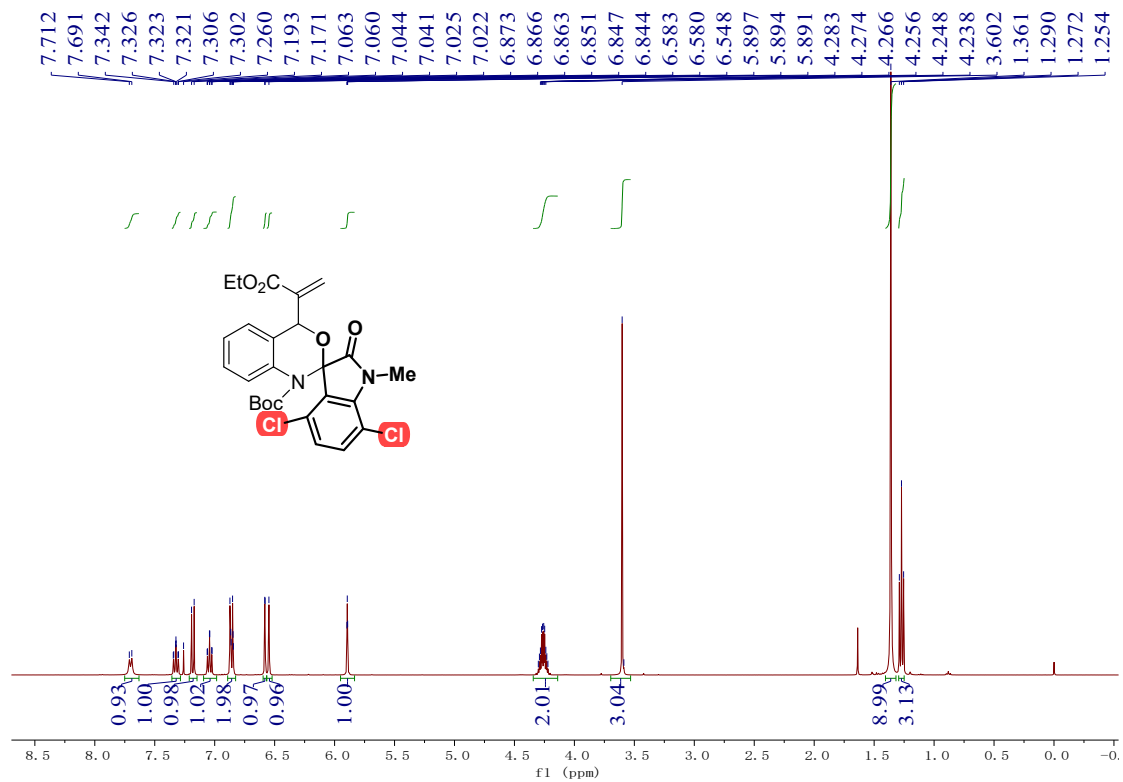
**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',7'-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3h)**



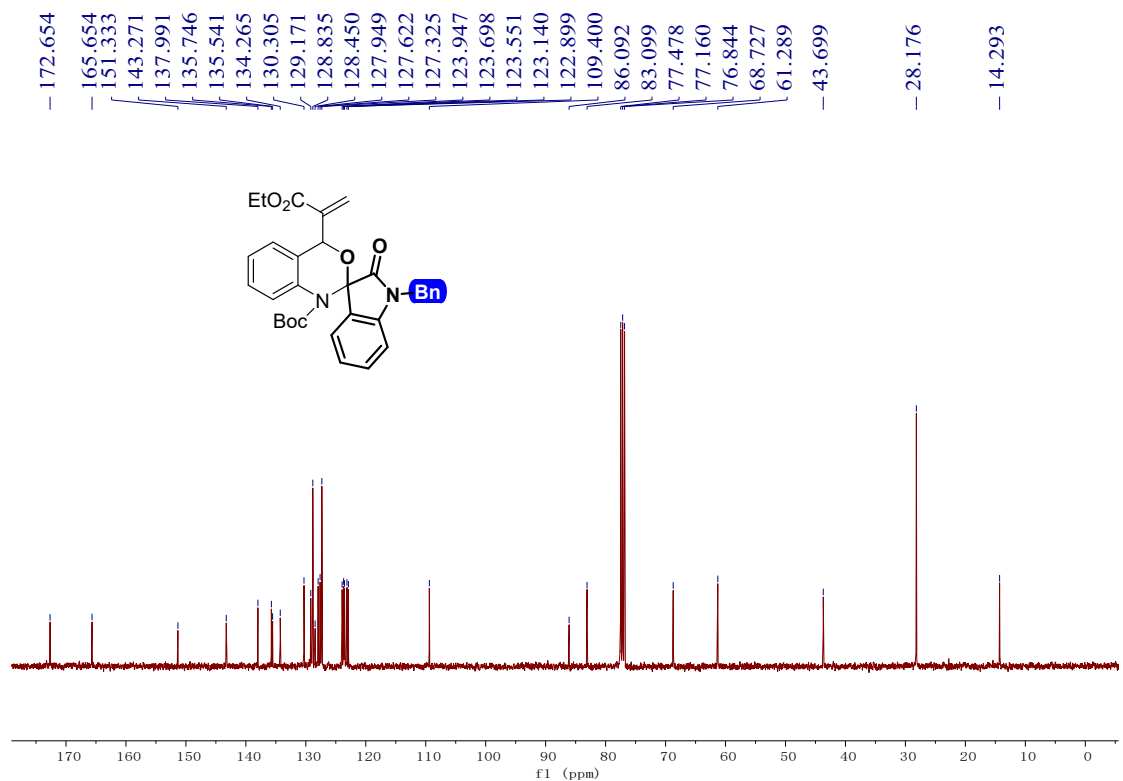
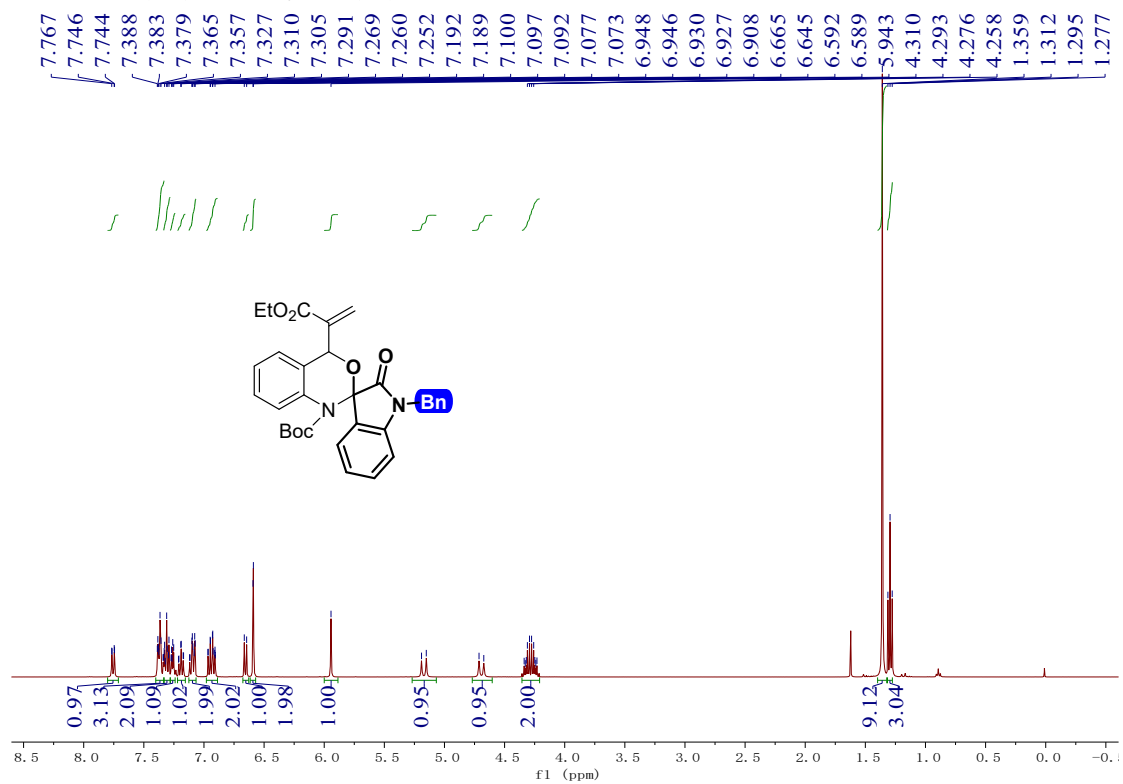
**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-7'-fluoro-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3i)**



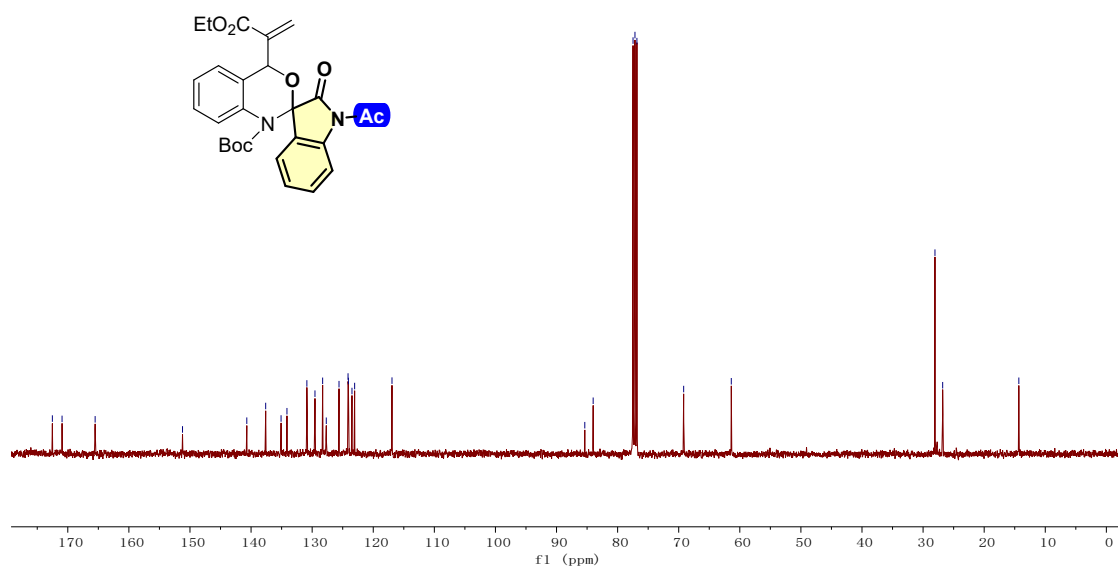
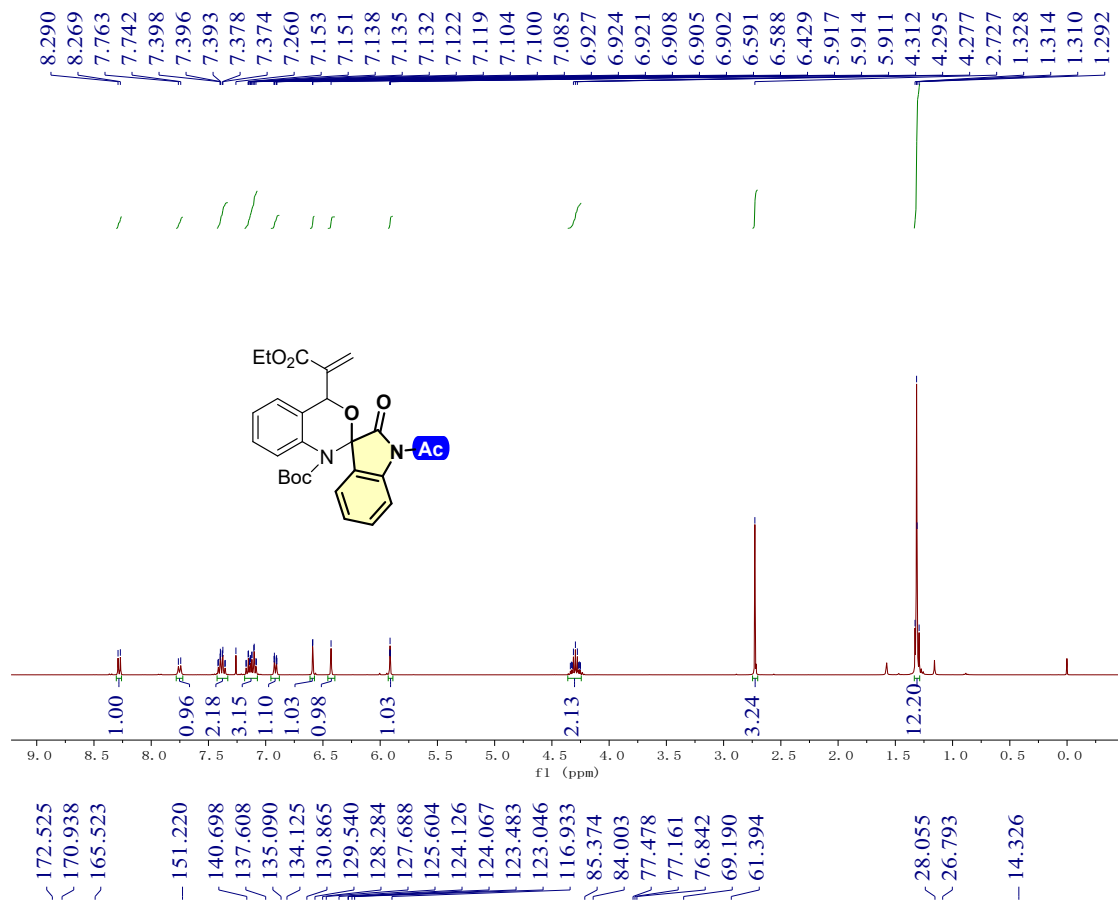
**tert-butyl 4',7'-dichloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3j)**



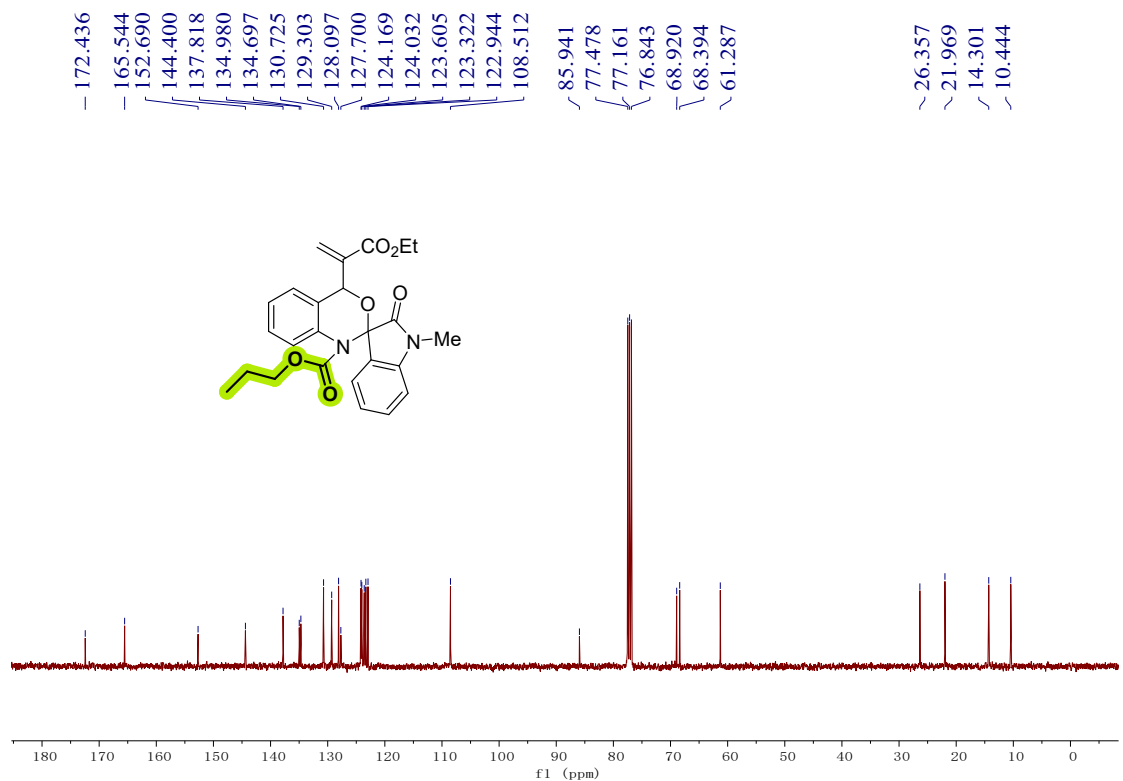
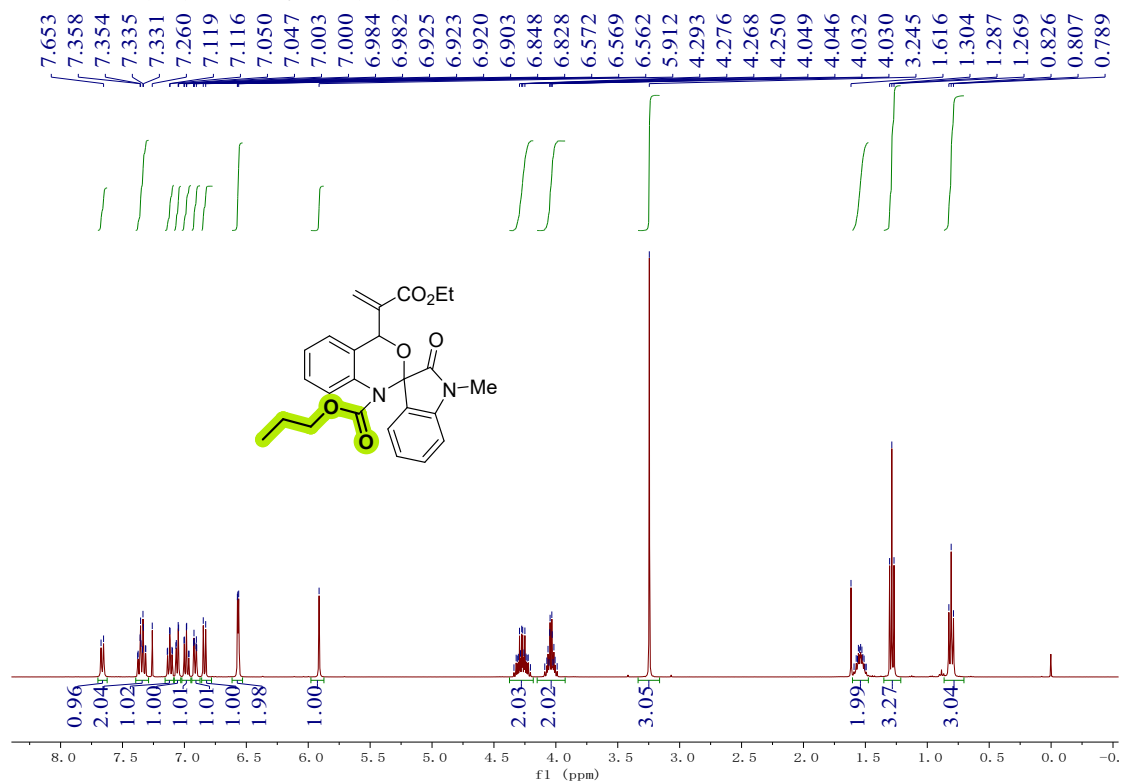
**tert-butyl 1'-benzyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3k)**



**tert-butyl 1'-acetyl-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3I)**

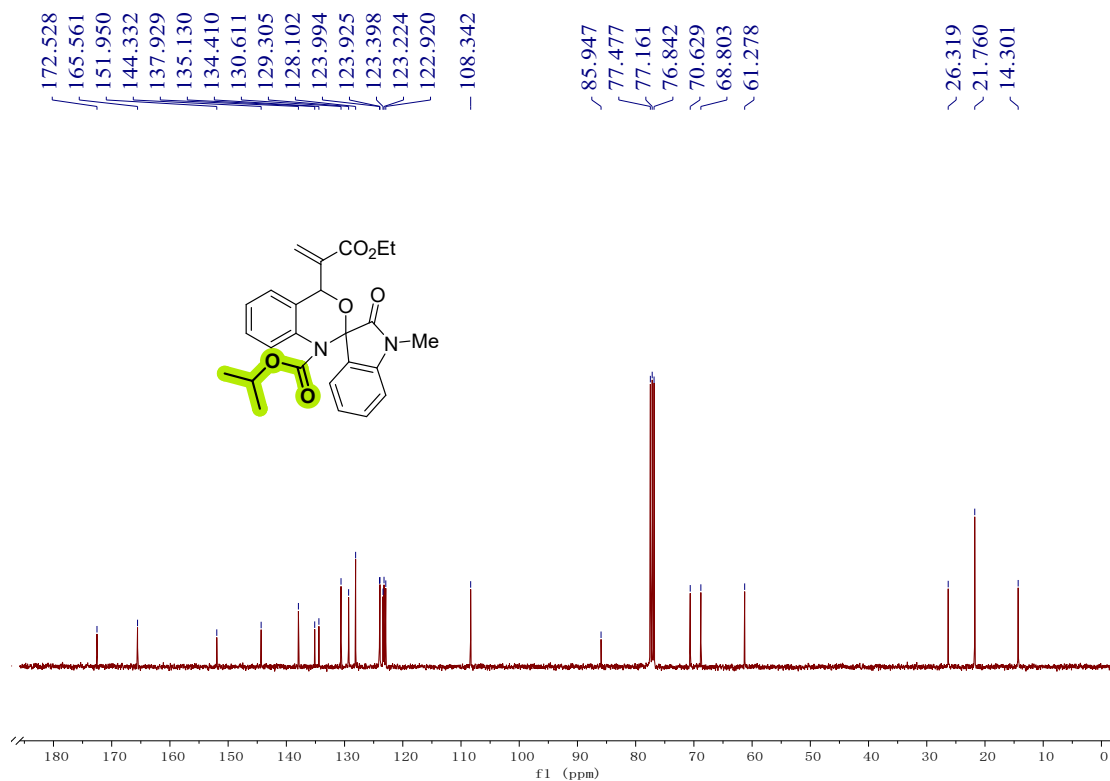
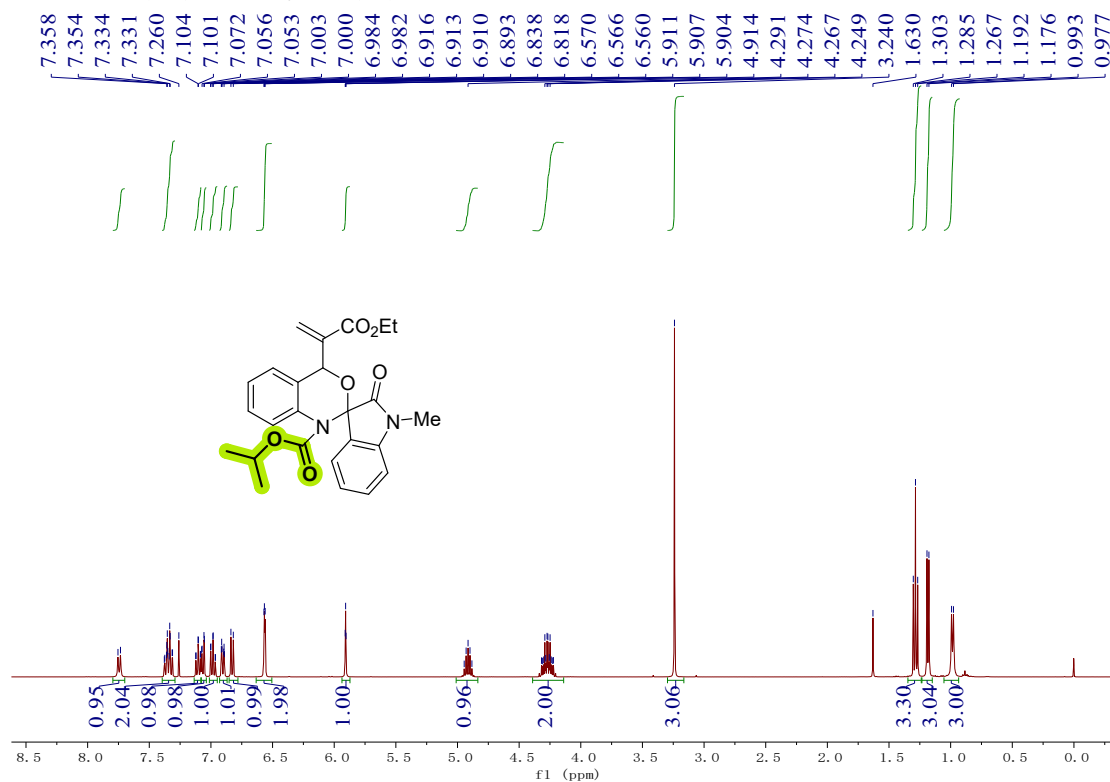


**propyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3m)**

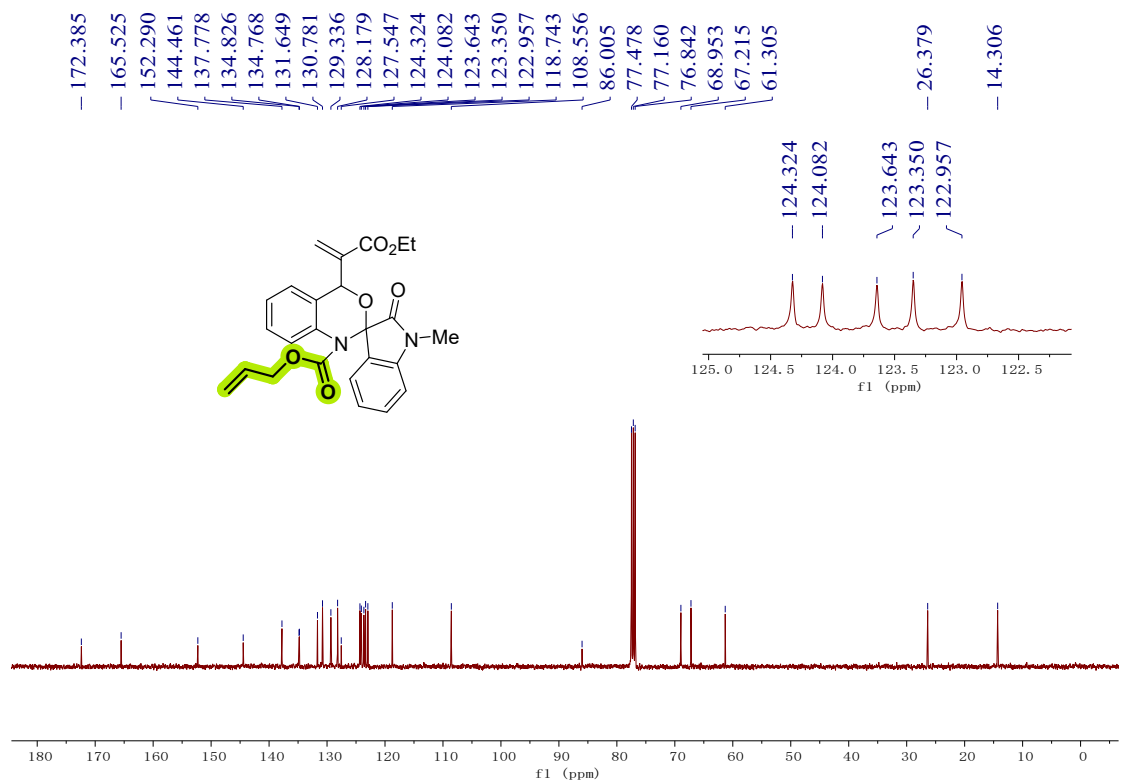
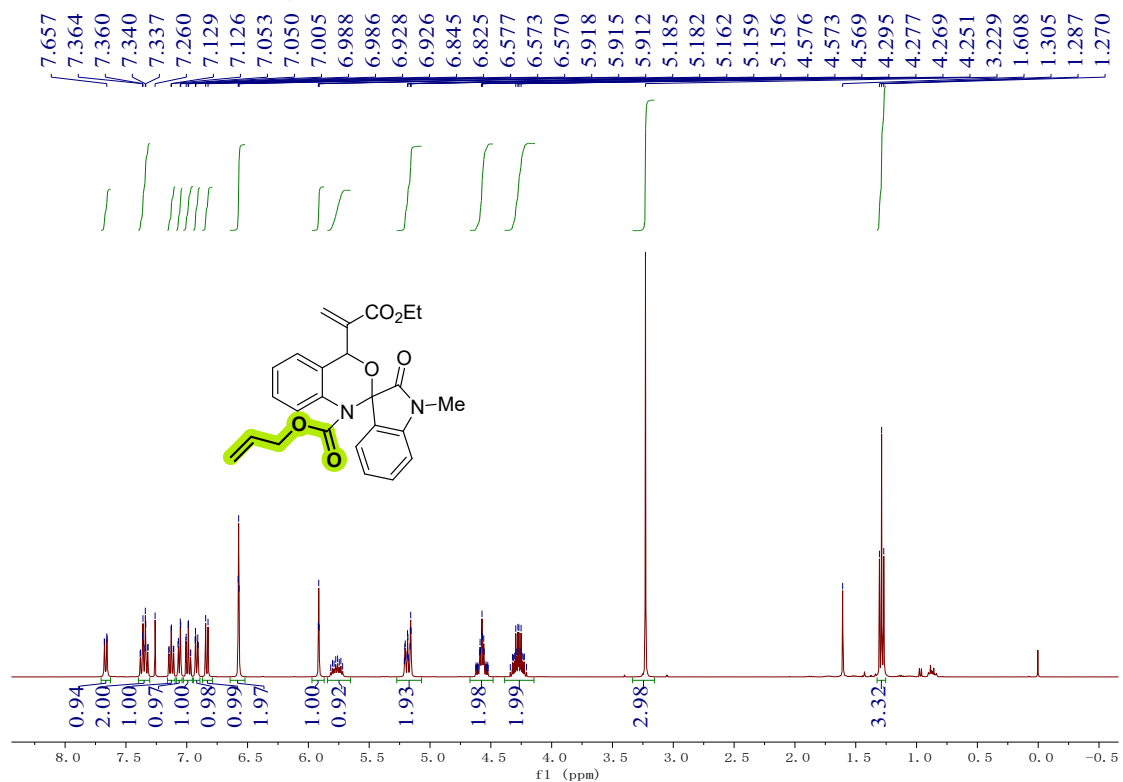




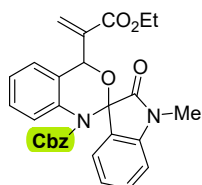
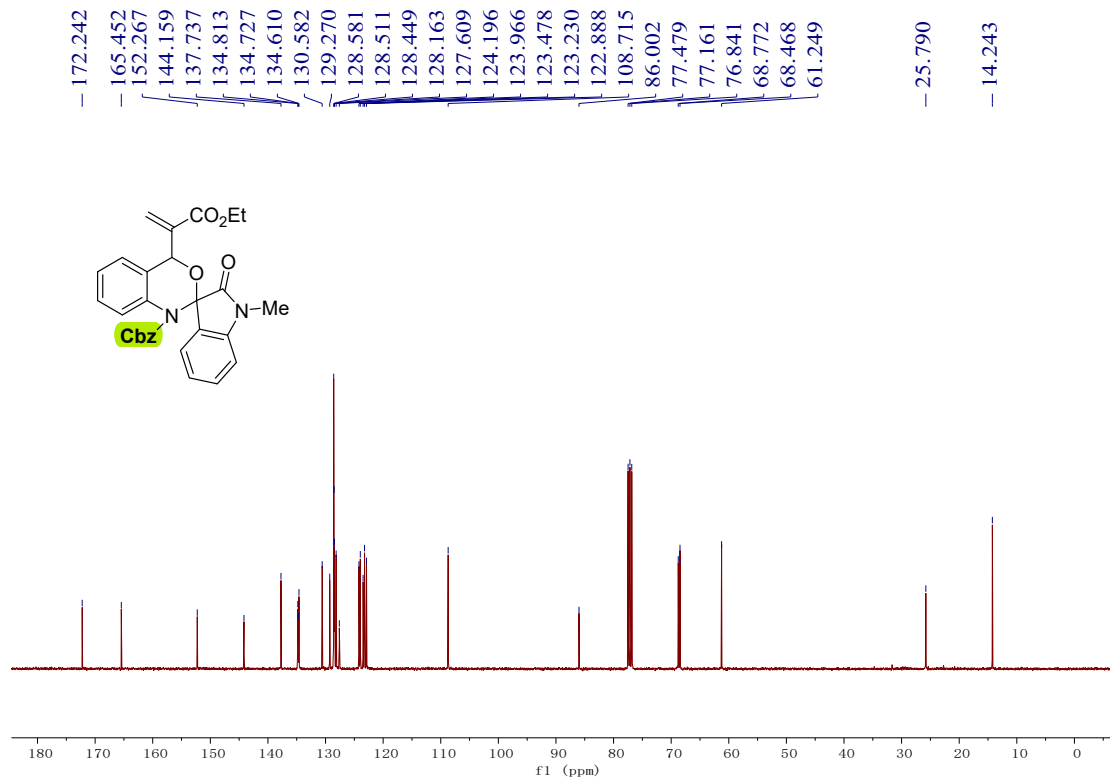
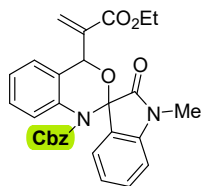
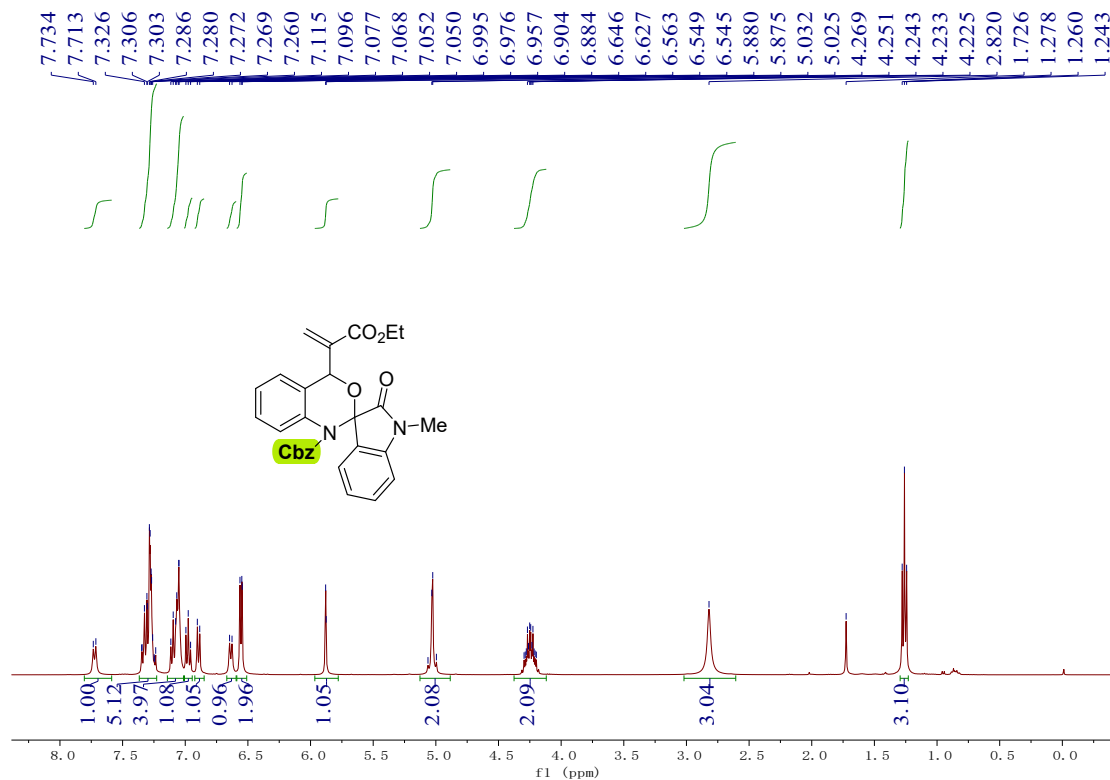
**isopropyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3n)**



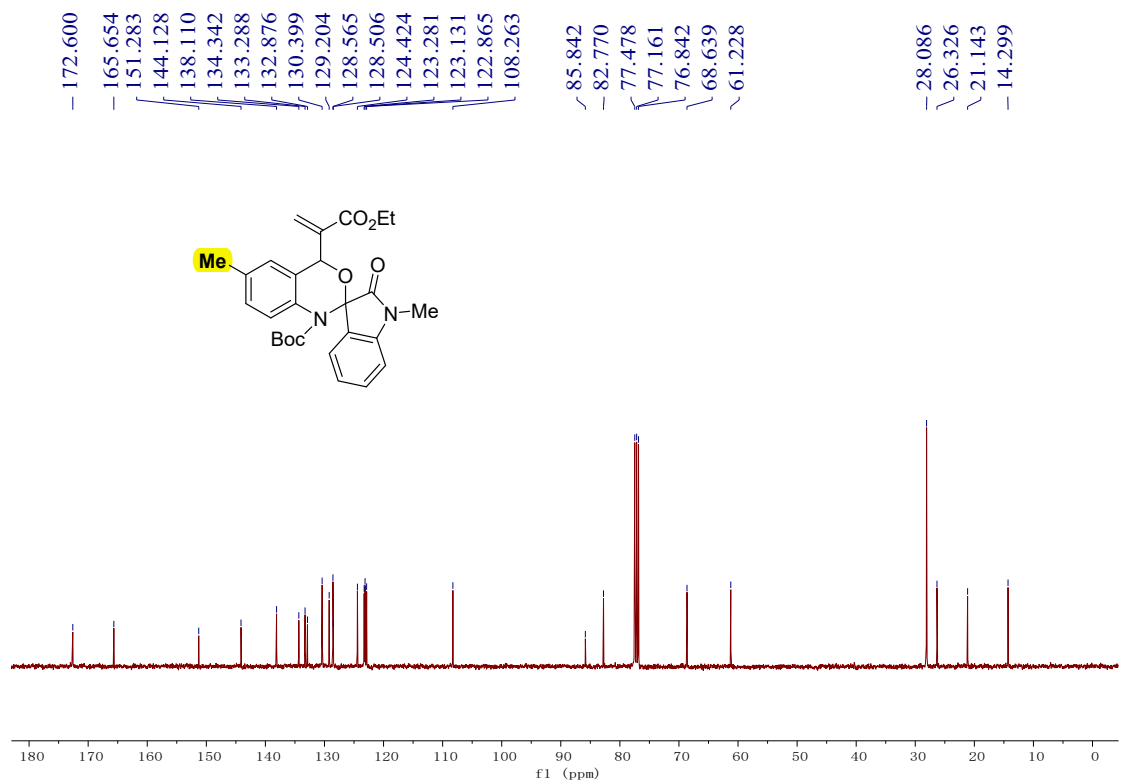
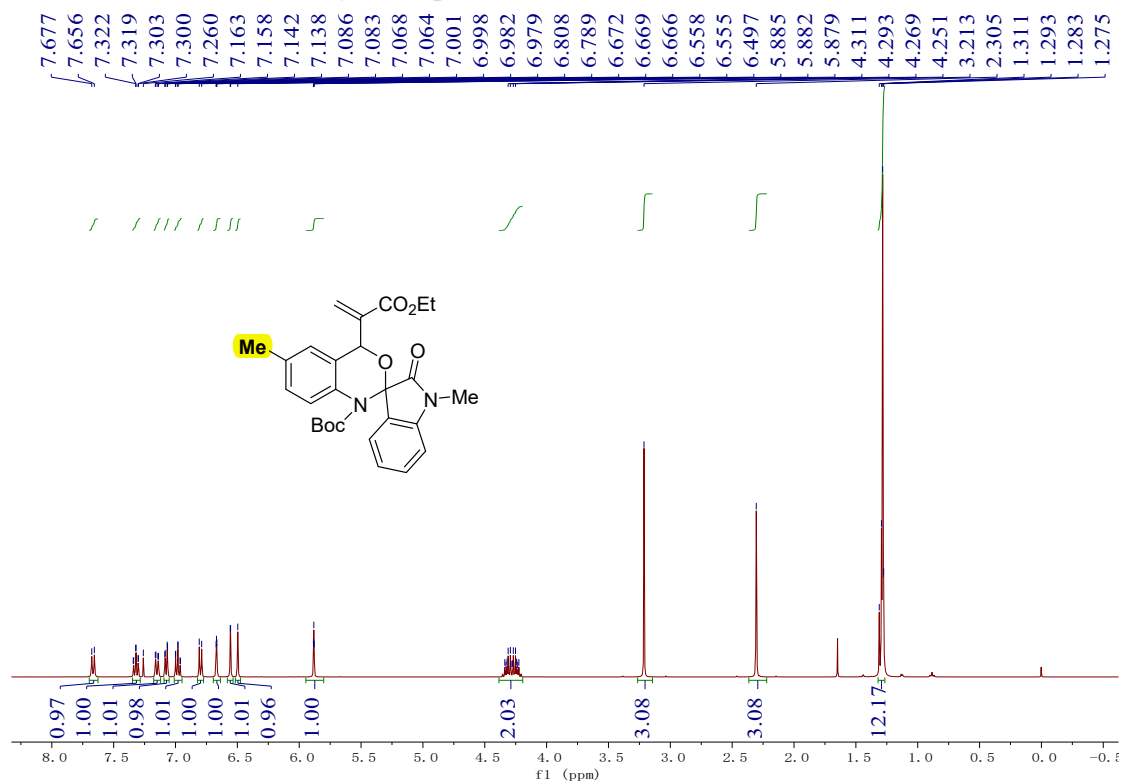
allyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3o)



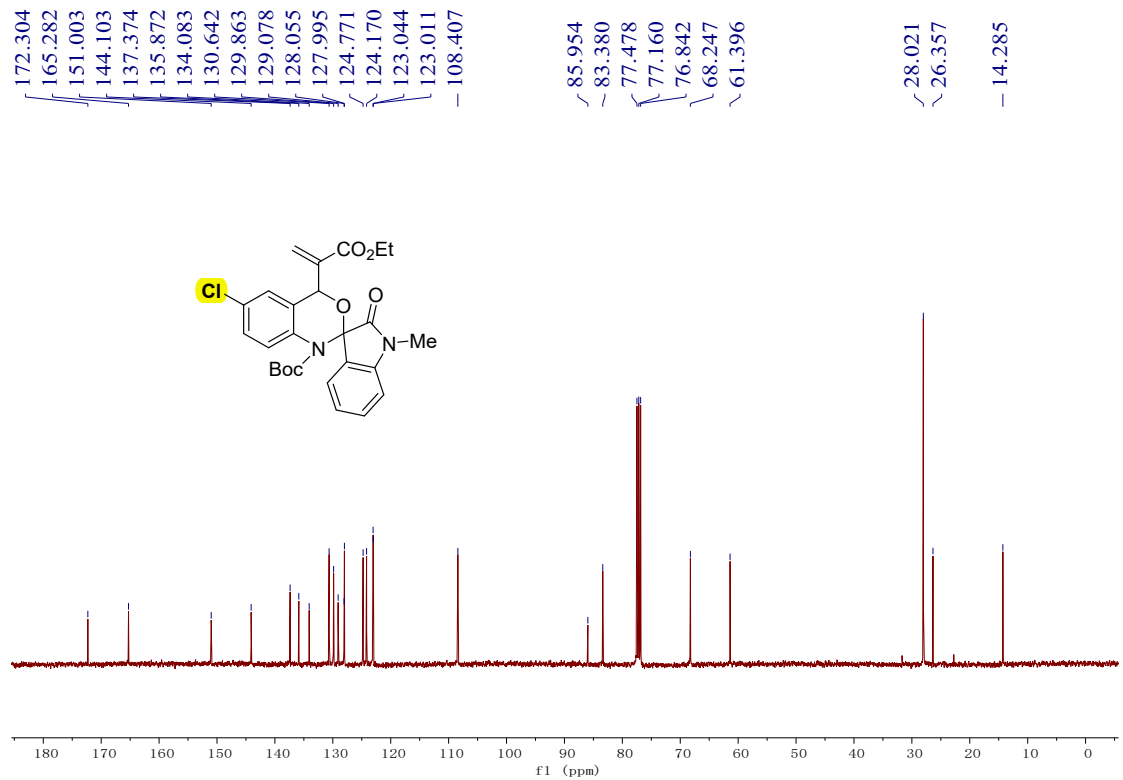
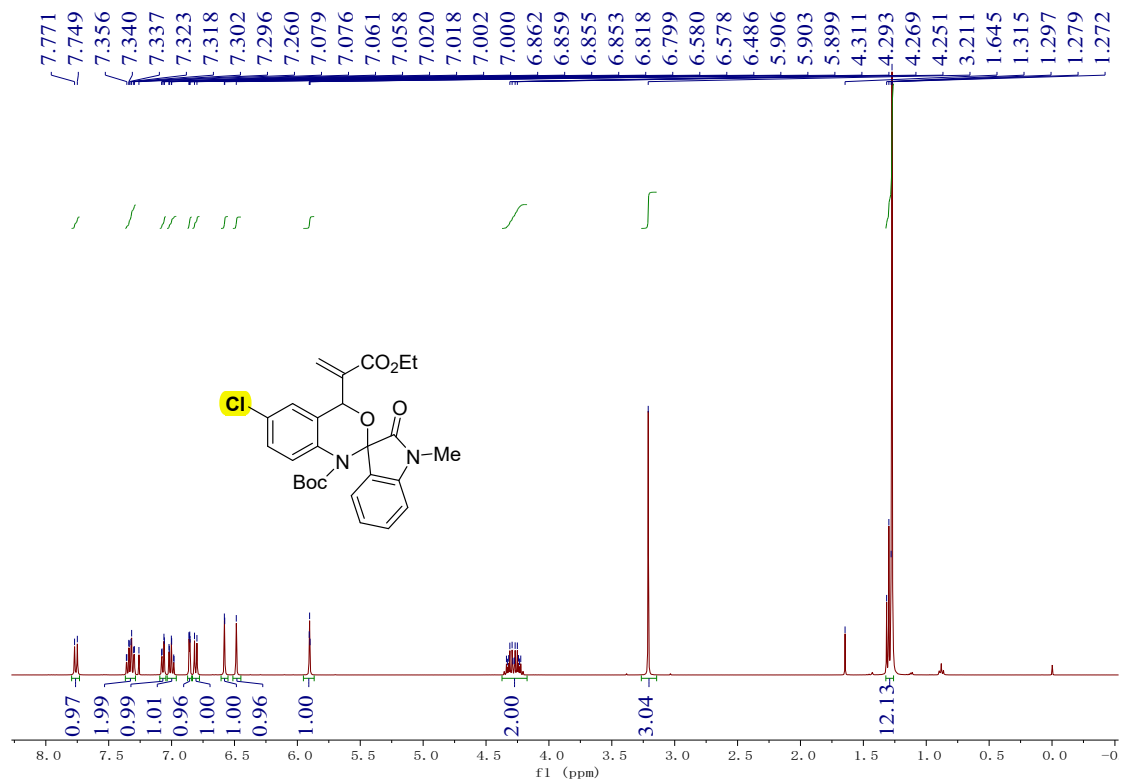
**benzyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3p)**



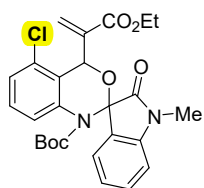
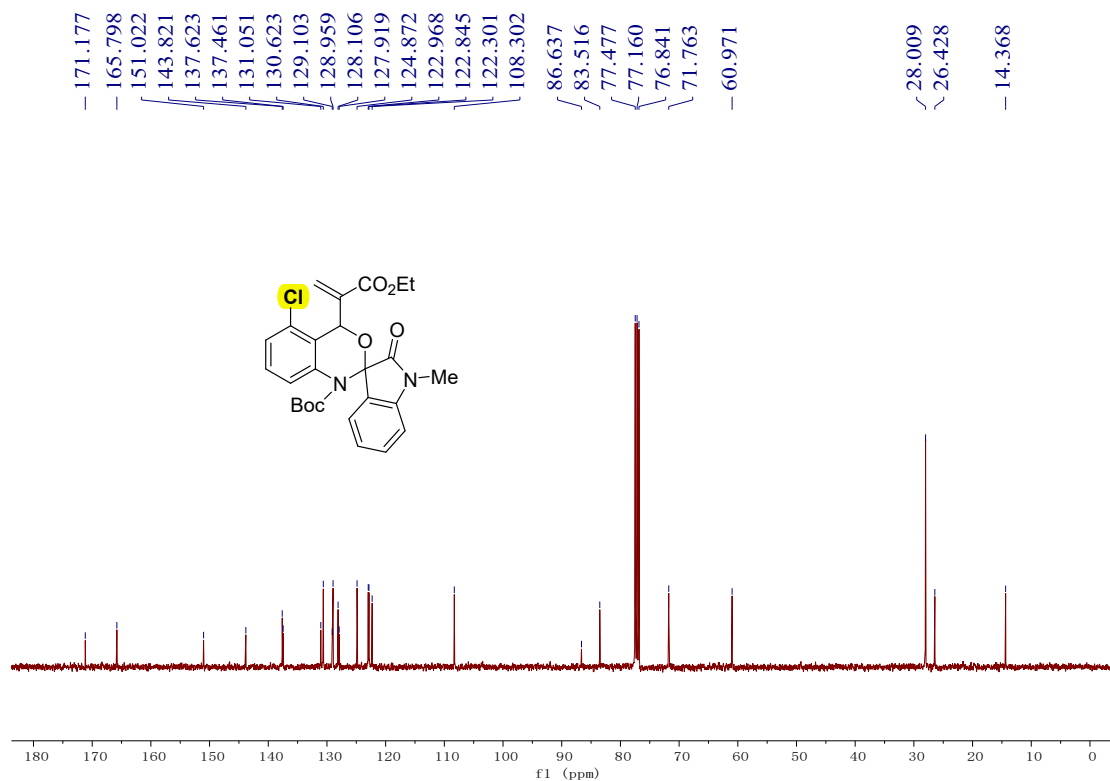
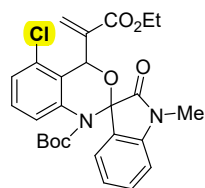
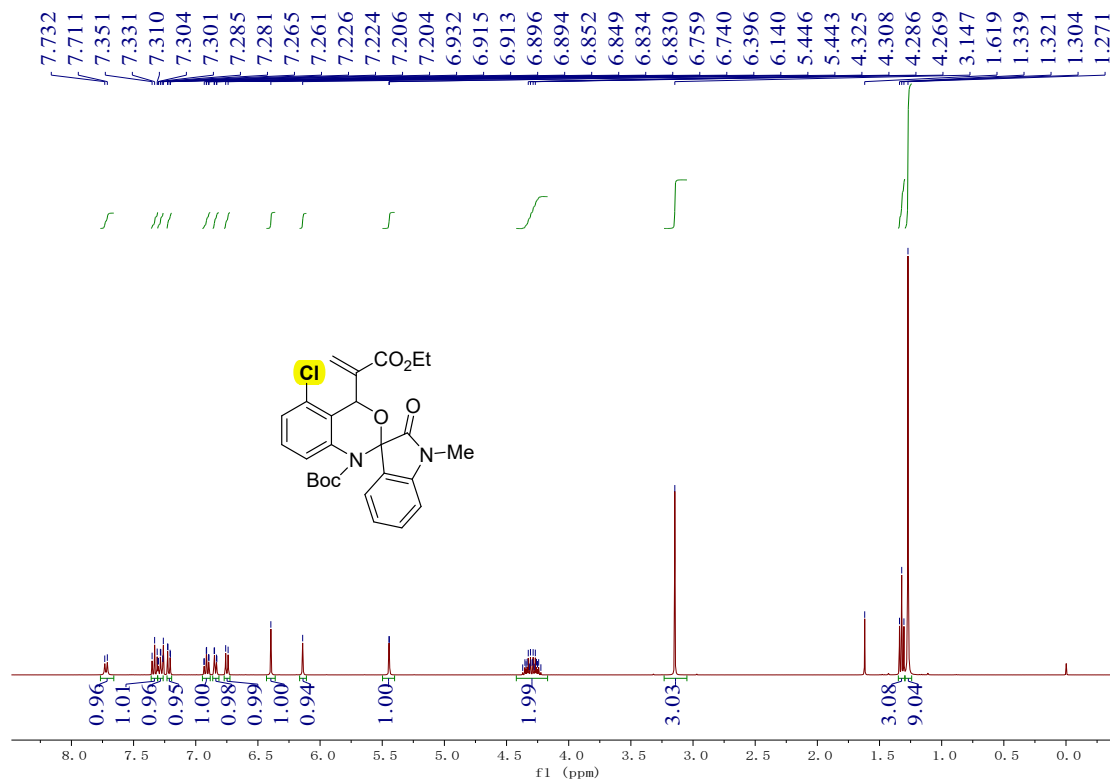
**tert-butyl 4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1',6-dimethyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3q)**



**tert-butyl 6-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3r)**



**tert-butyl 5-chloro-4-(3-ethoxy-3-oxoprop-1-en-2-yl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3s)**



**tert-butyl 4-(1-cyanovinyl)-1'-methyl-2'-oxospiro[benzo[d][1,3]oxazine-2,3'-indoline]-1(4H)-carboxylate (3t)**

