

## Supporting Information

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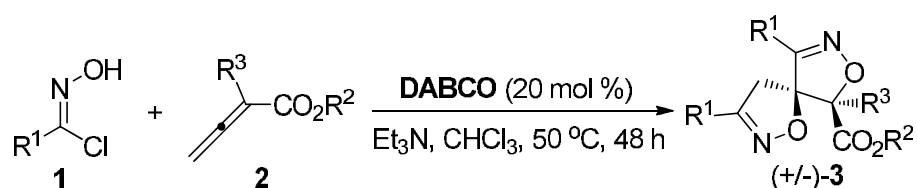
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## A: General Information and Starting Materials

**General Information.** Proton nuclear magnetic resonance ( $^1\text{H}$  NMR) spectra and carbon nuclear magnetic resonance ( $^{13}\text{C}$  NMR) spectra were recorded on a Bruker ACF300 spectrometer (500 MHz and 125 MHz). Chemical shifts for protons are reported in parts per million downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent ( $\text{CDCl}_3$ :  $\delta$  7.26). Chemical shifts for carbon are reported in parts per million downfield from tetramethylsilane and are referenced to the carbon resonances of the solvent ( $\text{CDCl}_3$ :  $\delta$  77.16). Data are represented as follows: chemical shift, integration, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants in Hertz (Hz). All high resolution mass spectra were obtained on a Finnigan/MAT 95XL-T mass spectrometer. For thin layer chromatography (TLC), Merck pre-coated TLC plates (Merck 60 F254) were used, and compounds were visualized with a UV light at 254 nm. Flash chromatography separations were performed on Merck 60 (0.040-0.063 mm) mesh silica gel.

**Starting Materials.** All solvents and inorganic reagents were from commercial sources and used without purification unless otherwise noted. The oxime halides and allenates were prepared following the literature procedures.<sup>1-2</sup>

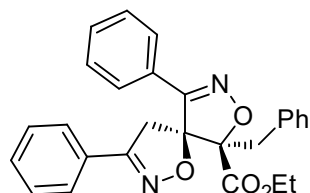
## B: General Procedure for Double 1,3-Dipolar Cycloadditions



To a solution of  $\text{CHCl}_3$  (0.15 mL) were added oxime halides **1** (0.25 mmol), allenates **2** (0.05 mmol),  $\text{Et}_3\text{N}$  (0.25 mmol) and DABCO (0.01 mmol). The reaction mixture was stirred at  $50^\circ\text{C}$  for 48 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to yield the desired product **3**.

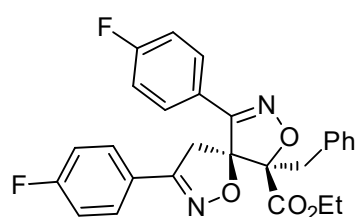
## C: Characterization Data

### Ethyl 6-benzyl-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3aa)



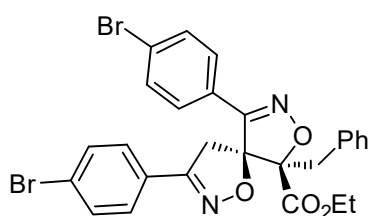
White solid, 73% yield. mp = 85-86°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.74-7.72 (m, 2H), 7.54-7.46 (m, 3H), 7.44-7.39 (m, 4H), 7.36-7.34 (m, 1H), 7.33-7.29 (m, 5H), 4.27-4.17 (m, 2H), 3.99 (d, *J* = 20.0 Hz, 1H), 3.65 (d, *J* = 20.0 Hz, 1H), 3.37 (d, *J* = 15.0 Hz, 1H), 2.99 (d, *J* = 15.0 Hz, 1H), 1.17 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.8, 157.1, 156.6, 133.5, 132.2, 130.9, 130.5, 130.5, 129.1, 129.0, 128.4, 128.0, 127.5, 127.0, 127.0, 99.7, 93.5, 62.1, 39.6, 38.3, 14.0. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>27</sub>H<sub>25</sub>N<sub>2</sub>O<sub>4</sub>) requires m/z 441.1814, found m/z 441.1817.

### Ethyl 6-benzyl-3,9-bis(4-fluorophenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ba)



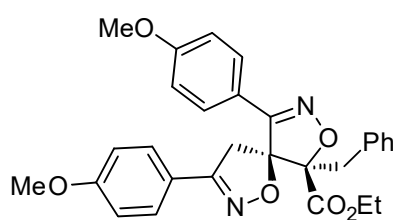
White solid, 87% yield. mp = 88-89°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.73-7.71 (m, 2H), 7.40-7.38 (m, 2H), 7.30-7.26 (m, 5H), 7.17-7.14 (m, 2H), 7.05-7.02 (m, 2H), 4.27-4.18 (m, 2H), 3.98 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 15.0 Hz, 1H), 3.37 (d, *J* = 15.0 Hz, 1H), 2.98 (d, *J* = 15.0 Hz, 1H), 1.17 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.8, 164.3 (*J* = 1005.0 Hz), 164.1 (*J* = 1005.0 Hz), 156.2, 155.6, 133.3, 130.5, 129.1 (*J* = 30.0 Hz), 129.0 (*J* = 30.0 Hz), 128.4, 127.5, 124.3 (*J* = 10.0 Hz), 123.1 (*J* = 10.0 Hz), 116.4 (*J* = 30.0 Hz), 116.2 (*J* = 30.0 Hz), 99.7, 93.5, 62.2, 39.7, 38.3, 14.0. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>27</sub>H<sub>23</sub>F<sub>2</sub>N<sub>2</sub>O<sub>4</sub>) requires m/z 477.1626, found m/z 477.1630.

### Ethyl 6-benzyl-3,9-bis(4-chlorophenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ca)



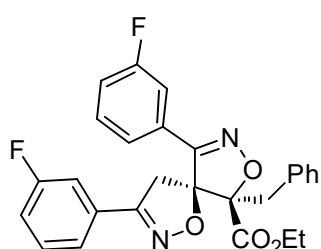
White solid, 58% yield. mp = 95-96°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.62-7.57 (m, 4H), 7.49-7.47 (m, 2H), 7.29-7.26 (m, 5H), 7.25-7.23 (m, 2H), 4.28-4.17 (m, 2H), 3.97 (d, *J* = 20.0 Hz, 1H), 3.54 (d, *J* = 20.0 Hz, 1H), 3.36 (d, *J* = 15.0 Hz, 1H), 2.98 (d, *J* = 15.0 Hz, 1H), 1.17 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.7, 156.2, 155.8, 133.2, 132.4, 132.3, 130.5, 128.5, 128.3, 128.2, 127.6, 126.9, 125.8, 125.5, 125.2, 99.7, 93.7, 62.3, 39.7, 38.0, 14.0. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>27</sub>H<sub>23</sub>Br<sub>2</sub>N<sub>2</sub>O<sub>4</sub>) requires m/z 597.0025, found m/z 597.0029.

### Ethyl 6-benzyl-3,9-bis(4-methoxyphenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3da)



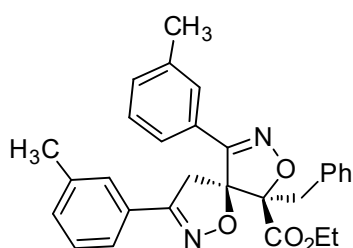
White solid, 76% yield. mp = 91-92°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.67 (d,  $J = 10.0$  Hz, 2H), 7.38 (d,  $J = 10.0$  Hz, 2H), 7.30-7.26 (m, 5H), 6.97 (d,  $J = 10.0$  Hz, 2H), 6.86 (d,  $J = 10.0$  Hz, 2H), 4.26-4.16 (m, 2H), 3.95 (d,  $J = 20.0$  Hz, 1H), 3.87 (s, 3H), 3.78 (s, 3H), 3.62 (d,  $J = 20.0$  Hz, 1H), 3.35 (d,  $J = 15.0$  Hz, 1H), 2.97 (d,  $J = 15.0$  Hz, 1H), 1.17 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 167.0, 161.7, 161.3, 156.8, 156.0, 133.7, 130.5, 128.6, 128.5, 128.3, 127.4, 120.7, 119.3, 114.5, 114.4, 99.6, 93.2, 62.0, 55.5, 55.3, 39.6, 38.6, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_6$ ) requires  $m/z$  501.2026, found  $m/z$  501.2029.

**Ethyl 6-benzyl-3,9-bis(3-fluorophenyl)-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ea)**



White solid, 56% yield. mp = 87-88°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.48-7.42 (m, 3H), 7.33-7.26 (m, 6H), 7.22-7.19 (m, 1H), 7.15-7.10 (m, 3H), 4.27-4.18 (m, 2H), 3.98 (d,  $J = 20.0$  Hz, 1H), 3.59 (d,  $J = 20.0$  Hz, 1H), 3.38 (d,  $J = 15.0$  Hz, 1H), 2.99 (d,  $J = 15.0$  Hz, 1H), 1.18 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.6, 162.8 ( $J = 1015.0$  Hz), 162.8 ( $J = 1015.0$  Hz), 156.0 ( $J = 15.0$  Hz), 155.8 ( $J = 10.0$  Hz), 133.2, 130.9, 130.8 ( $J = 20.0$  Hz), 130.7, 130.5, 130.5, 128.5, 127.6, 122.7 ( $J = 10.0$  Hz), 122.5 ( $J = 10.0$  Hz), 118.1 ( $J = 80.0$  Hz), 117.7 ( $J = 80.0$  Hz), 114.3 ( $J = 90.0$  Hz), 113.9 ( $J = 90.0$  Hz), 99.7, 93.8, 62.3, 39.6, 38.0, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{23}\text{F}_2\text{N}_2\text{O}_4$ ) requires  $m/z$  477.1626, found  $m/z$  477.1631.

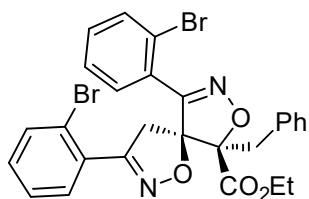
**Ethyl 6-benzyl-3,9-di-*m*-tolyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3fa)**



White solid, 67% yield. mp = 89-90°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.55 (s, 1H), 7.51-7.49 (m, 1H), 7.36-7.29 (m, 8H), 7.22-7.18 (m, 3H), 4.27-4.18 (m, 2H), 3.97 (d,  $J = 20.0$  Hz, 1H), 3.63 (d,  $J = 20.0$  Hz, 1H), 3.36 (d,  $J = 15.0$  Hz, 1H), 2.97 (d,  $J = 15.0$  Hz, 1H), 2.41 (s, 3H), 2.30 (s, 3H), 1.18 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.9, 157.3, 156.7, 138.9, 138.8, 133.6, 131.7, 131.3, 130.5, 128.9, 128.8, 128.4, 128.1, 128.0, 127.5, 127.4, 126.9, 124.1, 123.9, 99.7, 93.3, 62.1, 39.6, 38.4, 21.4, 21.3, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_4$ ) requires  $m/z$  469.2127, found  $m/z$  469.2133.

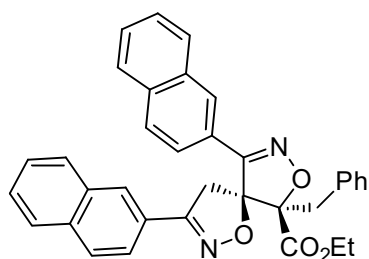
**Ethyl 6-benzyl-3,9-bis(2-bromophenyl)-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ga)**

White solid, 64% yield. mp = 97-98°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm)



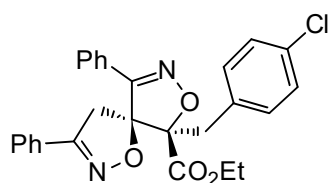
7.68-7.66 (m, 1H), 7.57-7.54 (m, 2H), 7.43-7.40 (m, 1H), 7.36-7.27 (m, 9H), 4.31-4.23 (m, 2H), 4.02 (d,  $J = 15.0$  Hz, 1H), 3.76 (d,  $J = 15.0$  Hz, 1H), 3.36 (d,  $J = 10.0$  Hz, 1H), 3.22 (d,  $J = 10.0$  Hz, 1H), 1.23 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.8, 157.4, 156.9, 133.6, 133.5, 132.9, 132.0, 131.8, 131.6, 131.0, 130.5, 129.8, 128.4, 128.2, 128.0, 127.6, 127.5, 123.7, 121.7, 101.4, 91.9, 62.2, 39.6, 39.5, 14.2. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{23}\text{Br}_2\text{N}_2\text{O}_4$ ) requires  $m/z$  597.0025, found  $m/z$  597.0029.

### Ethyl 6-benzyl-3,9-di(naphthalen-2-yl)-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ha)



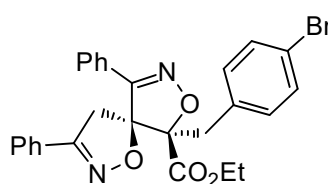
White solid, 90% yield. mp = 101-102°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 8.08-8.06 (m, 1H), 7.96-7.78 (m, 7H), 7.70-7.68 (m, 1H), 7.61-7.43 (m, 5H), 7.38-7.30 (m, 5H), 4.33-4.21 (m, 2H), 4.17 (d,  $J = 20.0$  Hz, 1H), 3.85 (d,  $J = 20.0$  Hz, 1H), 3.45 (d,  $J = 15.0$  Hz, 1H), 3.09 (d,  $J = 15.0$  Hz, 1H), 1.20 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.8, 157.4, 156.8, 134.4, 134.0, 133.6, 132.9, 130.6, 129.0, 128.6, 128.5, 128.4, 128.0, 127.7, 127.6, 127.5, 127.4, 127.3, 127.1, 127.0, 126.8, 125.7, 124.4, 123.9, 123.4, 99.9, 93.6, 62.2, 39.7, 38.4, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{35}\text{H}_{29}\text{N}_2\text{O}_4$ ) requires  $m/z$  541.2127, found  $m/z$  541.2132.

### Ethyl 6-(4-chlorobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ab)



White solid, 55% yield. mp = 93-94°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.72-7.71 (m, 2H), 7.50-7.41 (m, 6H), 7.38-7.35 (m, 2H), 7.32-7.24 (m, 4H), 4.26-4.18 (m, 2H), 3.95 (d,  $J = 20.0$  Hz, 1H), 3.66 (d,  $J = 20.0$  Hz, 1H), 3.33 (d,  $J = 15.0$  Hz, 1H), 2.93 (d,  $J = 15.0$  Hz, 1H), 1.18 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.7, 157.0, 156.5, 133.5, 132.1, 131.8, 131.0, 130.7, 129.1, 129.0, 128.6, 128.1, 127.5, 127.0, 126.9, 99.8, 93.1, 62.2, 38.9, 38.3, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{24}\text{ClN}_2\text{O}_4$ ) requires  $m/z$  475.1425, found  $m/z$  475.1430.

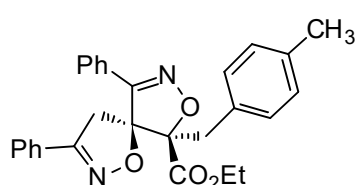
### Ethyl 6-(4-bromobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ac)



White solid, 61% yield. mp = 98-99°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.72 (d,  $J = 10.0$  Hz, 2H), 7.50-7.46 (m, 5H), 7.44-7.41 (m, 3H), 7.38-7.35 (m, 2H), 7.19 (d,  $J = 10.0$  Hz, 2H), 4.26-4.18 (m, 2H), 3.95 (d,  $J = 20.0$  Hz, 1H), 3.66 (d,  $J = 20.0$  Hz, 1H), 3.32 (d,  $J = 15.0$  Hz, 1H),

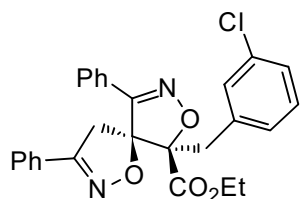
2.92 (d,  $J = 15.0$  Hz, 1H), 1.18 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.6, 157.1, 156.5, 132.6, 132.2, 131.5, 131.0, 130.7, 129.1, 129.0, 128.1, 127.0, 126.9, 126.8, 121.7, 99.8, 93.1, 62.3, 39.0, 38.3, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{24}\text{BrN}_2\text{O}_4$ ) requires  $m/z$  519.0919, found  $m/z$  519.0924.

**Ethyl 6-(4-methylbenzyl)-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ad)**



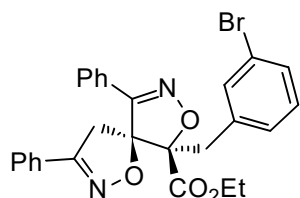
White solid, 55% yield. mp = 89-90°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.73-7.72 (m, 2H), 7.49-7.39 (m, 6H), 7.36-7.33 (m, 2H), 7.20 (d,  $J = 10.0$  Hz, 2H), 7.11 (d,  $J = 10.0$  Hz, 2H), 4.27-4.18 (m, 2H), 3.99 (d,  $J = 20.0$  Hz, 1H), 3.64 (d,  $J = 20.0$  Hz, 1H), 3.33 (d,  $J = 15.0$  Hz, 1H), 2.95 (d,  $J = 15.0$  Hz, 1H), 2.32 (s, 3H), 1.18 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.9, 157.0, 156.6, 137.1, 130.9, 130.5, 130.4, 130.3, 129.1, 129.0, 128.9, 128.2, 127.1, 127.0, 126.9, 99.7, 93.5, 62.1, 39.2, 38.2, 21.1, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{28}\text{H}_{27}\text{N}_2\text{O}_4$ ) requires  $m/z$  455.1971, found  $m/z$  455.1975.

**Ethyl 6-(3-chlorobenzyl)-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ae)**



White solid, 65% yield. mp = 91-92°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.73-7.71 (m, 2H), 7.50-7.41 (m, 6H), 7.38-7.35 (m, 2H), 7.31 (s, 1H), 7.25-7.20 (m, 3H), 4.28-4.19 (m, 2H), 3.94 (d,  $J = 20.0$  Hz, 1H), 3.67 (d,  $J = 20.0$  Hz, 1H), 3.34 (d,  $J = 15.0$  Hz, 1H), 2.93 (d,  $J = 15.0$  Hz, 1H), 1.19 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.6, 157.0, 156.5, 135.6, 134.1, 131.0, 130.7, 130.6, 129.6, 129.1, 129.0, 128.7, 128.1, 127.7, 127.0, 126.9, 126.8, 99.8, 93.0, 62.3, 39.2, 38.3, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{24}\text{ClN}_2\text{O}_4$ ) requires  $m/z$  475.1425, found  $m/z$  475.1428.

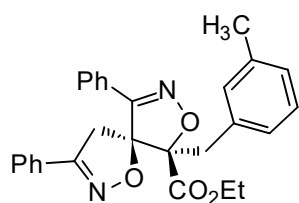
**Ethyl 6-(3-bromobenzyl)-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3af)**



White solid, 60% yield. mp = 97-98°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.73-7.71 (m, 2H), 7.50-7.45 (m, 6H), 7.43-7.36 (m, 4H), 7.26-7.25 (m, 1H), 7.19-7.16 (m, 1H), 4.28-4.19 (m, 2H), 3.94 (d,  $J = 20.0$  Hz, 1H), 3.67 (d,  $J = 20.0$  Hz, 1H), 3.33 (d,  $J = 15.0$  Hz, 1H), 2.92 (d,  $J = 15.0$  Hz, 1H), 1.19 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 166.6, 157.0, 156.5, 135.9, 133.4, 131.0, 130.7, 130.6, 129.9, 129.2, 129.1, 129.0, 128.1, 127.1, 127.0, 126.9, 122.3, 99.8, 93.0, 62.3, 39.2, 38.3, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{27}\text{H}_{24}\text{BrN}_2\text{O}_4$ ) requires  $m/z$  519.0919, found  $m/z$  519.0923.

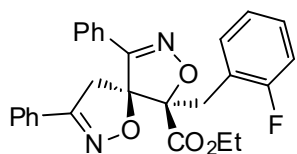
**Ethyl 6-(3-methylbenzyl)-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-**

### diene-6-carboxylate (3ag)



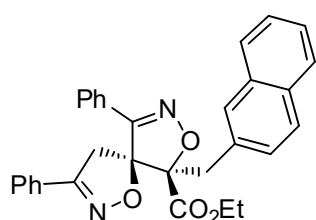
White solid, 63% yield. mp = 88-89°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.73-7.72 (m, 2H), 7.49-7.40 (m, 6H), 7.37-7.34 (m, 2H), 7.18-7.08 (m, 2H), 4.28-4.17 (m, 2H), 3.99 (d, *J* = 20.0 Hz, 1H), 3.65 (d, *J* = 20.0 Hz, 1H), 3.33 (d, *J* = 15.0 Hz, 1H), 2.94 (d, *J* = 15.0 Hz, 1H), 2.33 (s, 3H), 1.18 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.8, 157.1, 156.6, 137.9, 133.4, 131.3, 130.9, 130.5, 129.1, 129.0, 128.3, 128.2, 128.2, 127.4, 127.1, 127.1, 126.9, 99.8, 93.4, 62.1, 39.6, 38.3, 21.4, 14.0. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>28</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>) requires m/z 455.1971, found m/z 455.1976.

### Ethyl 6-(2-fluorobenzyl)-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ah)



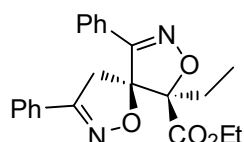
White solid, 76% yield. mp = 85-86°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.73-7.71 (m, 2H), 7.49-7.39 (m, 7H), 7.35-7.32 (m, 2H), 7.26-7.24 (m, 1H), 7.14-7.11 (m, 1H), 7.04-7.00 (m, 1H), 4.32-4.20 (m, 2H), 4.02 (d, *J* = 20.0 Hz, 1H), 3.64 (d, *J* = 20.0 Hz, 1H), 3.41 (d, *J* = 15.0 Hz, 1H), 3.14 (d, *J* = 15.0 Hz, 1H), 1.20 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.7, 162.0 (*J* = 975.0 Hz), 157.2, 156.7, 132.6 (*J* = 15.0 Hz), 130.9, 130.6, 129.3 (*J* = 35.0 Hz), 129.1, 129.0, 128.2, 127.0, 127.0, 126.9, 124.2 (*J* = 15.0 Hz), 120.6 (*J* = 60.0 Hz), 115.4 (*J* = 90.0 Hz), 99.7, 92.8, 62.3, 38.1, 31.9, 13.9. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>27</sub>H<sub>24</sub>FN<sub>2</sub>O<sub>4</sub>) requires m/z 459.1720, found m/z 459.1724.

### Ethyl 6-(naphthalen-2-ylmethyl)-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ai)



White solid, 60% yield. mp = 96-97°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.80-7.74 (m, 6H), 7.50-7.46 (m, 8H), 7.42-7.39 (m, 1H), 7.35-7.32 (m, 2H), 4.23-4.18 (m, 2H), 4.05 (d, *J* = 20.0 Hz, 1H), 3.69 (d, *J* = 20.0 Hz, 1H), 3.54 (d, *J* = 15.0 Hz, 1H), 3.14 (d, *J* = 15.0 Hz, 1H), 1.14 (t, *J* = 10.0 Hz, 3H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 166.9, 157.1, 156.6, 133.3, 132.7, 131.1, 131.0, 130.6, 129.5, 129.1, 129.0, 128.4, 128.2, 128.0, 127.8, 127.6, 127.1, 127.0, 126.0, 125.9, 99.9, 93.5, 62.2, 39.8, 38.3, 14.0. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>31</sub>H<sub>27</sub>N<sub>2</sub>O<sub>4</sub>) requires m/z 491.1971, found m/z 491.1975.

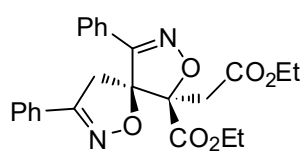
### Ethyl 6-ethyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3aj)



Yellow oil, 78% yield. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.69-7.67 (m, 2H), 7.53-7.51 (m, 2H), 7.47-7.40 (m, 4H), 7.38-7.35 (m, 2H), 4.36-4.23 (m, 2H), 3.78 (d, *J* = 15.0 Hz, 1H),

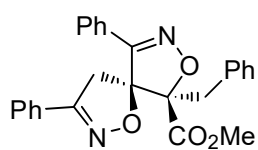
3.60 (d,  $J = 15.0$  Hz, 1H), 2.15-2.08 (m, 1H), 1.78-1.72 (m, 1H), 1.25 (t,  $J = 10.0$  Hz, 3H), 1.07 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 167.3, 156.6, 156.5, 130.9, 130.5, 129.1, 128.9, 128.2, 127.2, 127.0, 126.9, 99.4, 93.8, 62.1, 38.0, 27.6, 14.1, 8.4. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{22}\text{H}_{23}\text{N}_2\text{O}_4$ ) requires  $m/z$  379.1658, found  $m/z$  379.1662.

**Ethyl 6-(2-ethoxy-2-oxoethyl)-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ak)**



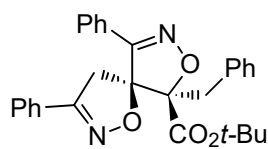
Yellow oil, 69% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.63-7.59 (m, 3H), 7.45-7.36 (m, 7H), 4.26 (q,  $J = 10.0$  Hz, 2H), 4.09-4.05 (m, 2H), 3.91 (d,  $J = 20.0$  Hz, 1H), 3.69 (d,  $J = 20.0$  Hz, 1H), 3.36 (s, 2H), 1.25 (t,  $J = 10.0$  Hz, 3H), 1.20 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 169.7, 168.1, 158.0, 157.6, 130.9, 130.6, 129.0, 128.9, 128.0, 127.3, 127.0, 126.9, 98.5, 90.7, 62.3, 61.1, 41.8, 35.7, 14.1, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{24}\text{H}_{25}\text{N}_4\text{O}_6$ ) requires  $m/z$  437.1713, found  $m/z$  437.1717.

**Methyl 6-benzyl-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-Carboxylate (3al)**



White solid, 80% yield. mp = 80-81°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.73-7.72 (m, 2H), 7.50-7.44 (m, 5H), 7.41-7.40 (m, 1H), 7.36-7.33 (m, 2H), 7.30-7.26 (m, 5H), 4.00 (d,  $J = 20.0$  Hz, 1H), 3.74 (s, 3H), 3.65 (d,  $J = 20.0$  Hz, 1H), 3.39 (d,  $J = 15.0$  Hz, 1H), 2.99 (d,  $J = 15.0$  Hz, 1H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 167.6, 157.0, 156.7, 133.5, 131.0, 130.6, 130.5, 129.1, 129.0, 128.4, 128.1, 127.5, 127.1, 127.0, 127.0, 99.7, 93.7, 52.8, 39.6, 38.3. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{26}\text{H}_{23}\text{N}_2\text{O}_4$ ) requires  $m/z$  427.1658, found  $m/z$  427.1662.

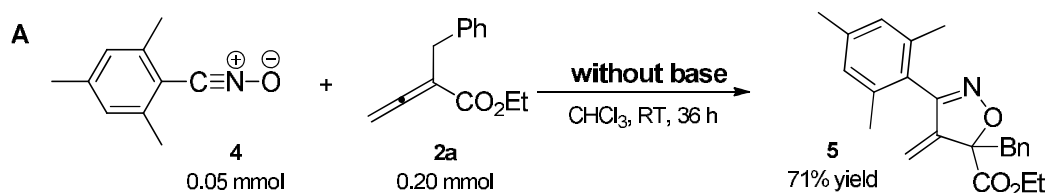
***tert*-Butyl 6-benzyl-3,9-diphenyl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3am)**



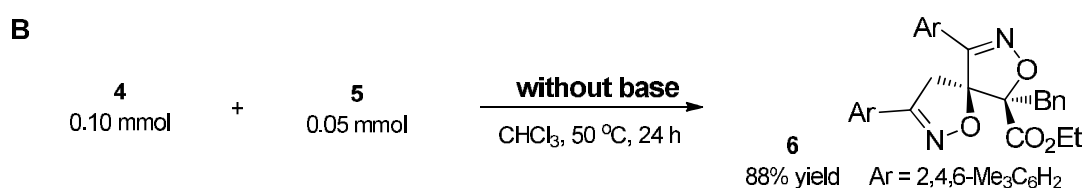
White solid, 56% yield. mp = 90-91°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.75-7.73 (m, 2H), 7.49-7.47 (m, 3H), 7.42-7.38 (m, 3H), 7.36-7.29 (m, 7H), 3.94 (d,  $J = 20.0$  Hz, 1H), 3.63 (d,  $J = 20.0$  Hz, 1H), 3.31 (d,  $J = 15.0$  Hz, 1H), 2.97 (d,  $J = 15.0$  Hz, 1H), 1.39 (s, 9H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 162.6, 154.4, 153.9, 131.2, 128.3, 128.0, 127.8, 126.4, 125.8, 125.7, 124.8, 124.7, 124.5, 124.4, 124.3, 97.1, 90.5, 80.9, 37.1, 35.7, 25.2. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{29}\text{H}_{29}\text{N}_2\text{O}_4$ ) requires  $m/z$  469.2127, found  $m/z$  469.2132.



## D: Control experiments.



To a solution of  $\text{CHCl}_3$  (0.30 mL) were added nitrile oxide **4** (0.05 mmol) and allenolate **2a** (0.20 mmol). The reaction mixture was stirred at room temperature for 36 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to afford the desired products **5** in 71% yield as a colourless oil.



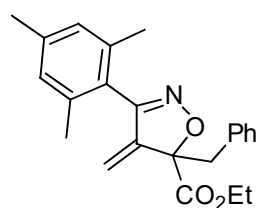
To a solution of  $\text{CHCl}_3$  (0.30 mL) were added nitrile oxides **4** (0.10 mmol) and **5** (0.05 mmol). The reaction mixture was stirred at 50°C for 24 h and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to afford the desired product **6** in 88% yield as a white solid.

**C**

<b>4</b> 0.25 mmol	+	<b>2a</b> 0.05 mmol	$\xrightarrow[\text{CHCl}_3, 50^\circ\text{C}]{\text{without base}}$		<b>5</b> X% yield	+	<b>6</b> Y% yield	
			Time (h)				Time (h)	
			X	Y		X	Y	
			3	34	34	12	<5	63
			6	16	54	24	<5	78

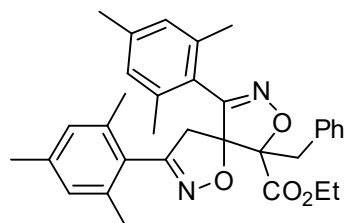
To a solution of  $\text{CHCl}_3$  (0.30 mL) were added nitrile oxide **4** (0.25 mmol) and allenolate **2a** (0.05 mmol). The reaction mixture was stirred at 50 °C for the time indicated and then the solvent was removed under vacuum. The residue was purified by silica gel chromatography to afford the desired products **5** and **6**.

### Ethyl 5-benzyl-3-mesityl-4-methylene-4,5-dihydroisoxazole-5-carboxylate (**5**)



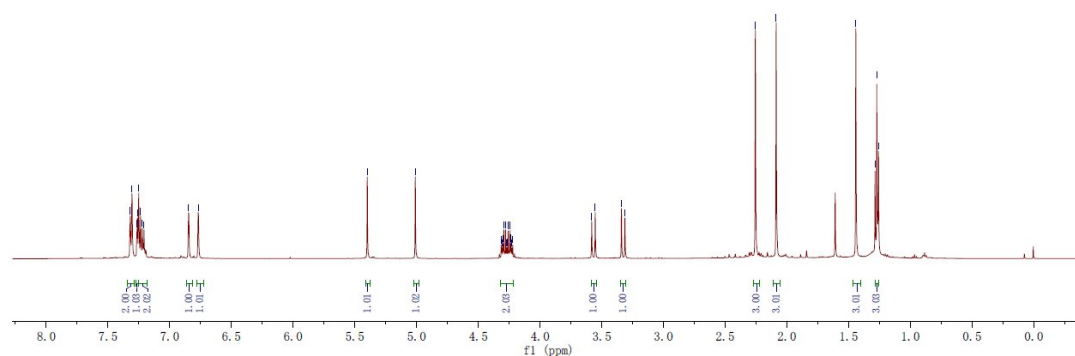
Colourless oil, 71% yield.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.32-7.31 (m, 2H), 7.26-7.25 (m, 1H), 7.24-7.21 (m, 2H), 6.85 (s, 1H), 6.77 (s, 1H), 5.40 (s, 1H), 5.01 (s, 1H), 4.31-4.22 (m, 2H), 3.57 (d,  $J = 15.0$  Hz, 1H), 3.33 (d,  $J = 15.0$  Hz, 1H), 2.26 (s, 3H), 2.09 (s, 3H), 1.44 (s, 3H), 1.27 (t,  $J = 15.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 167.0, 157.7, 148.1, 139.0, 137.7, 137.6, 134.2, 131.2, 128.1, 127.1, 123.1, 111.6, 89.3, 62.2, 42.3, 21.1, 19.2, 18.6, 14.0. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{23}\text{H}_{26}\text{NO}_3$ ) requires  $m/z$  364.1913, found  $m/z$  364.1917.

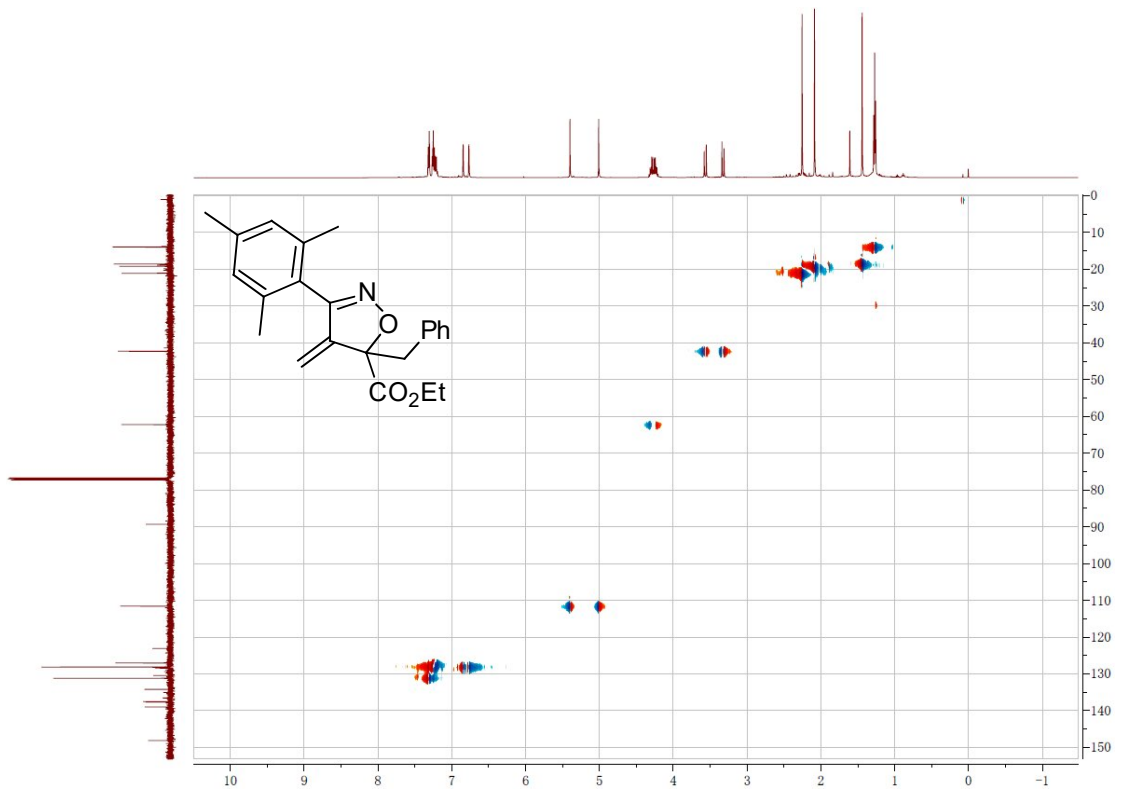
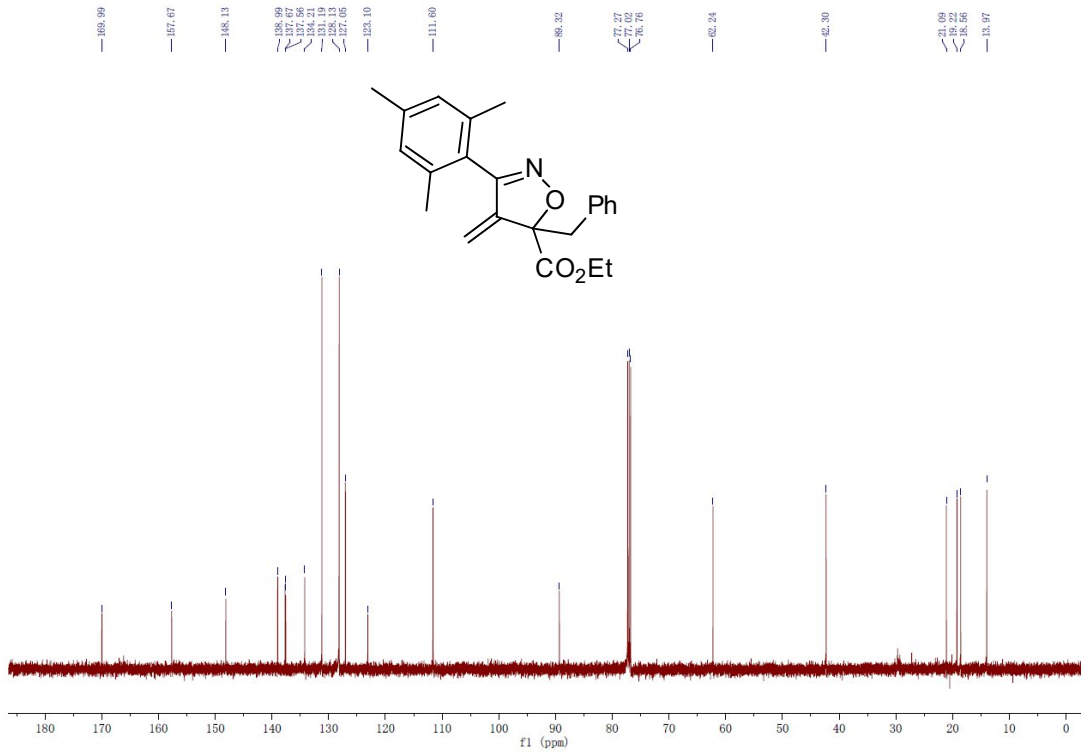
**Ethyl 6-benzyl-3,9-dimesityl-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (6)**



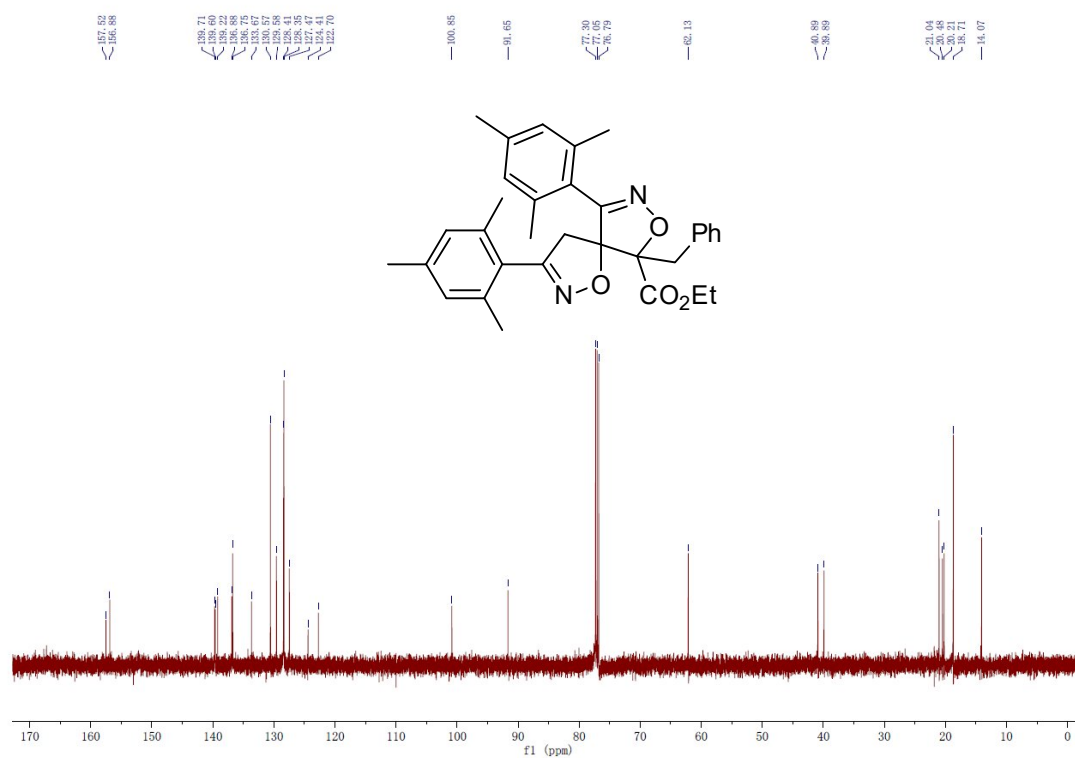
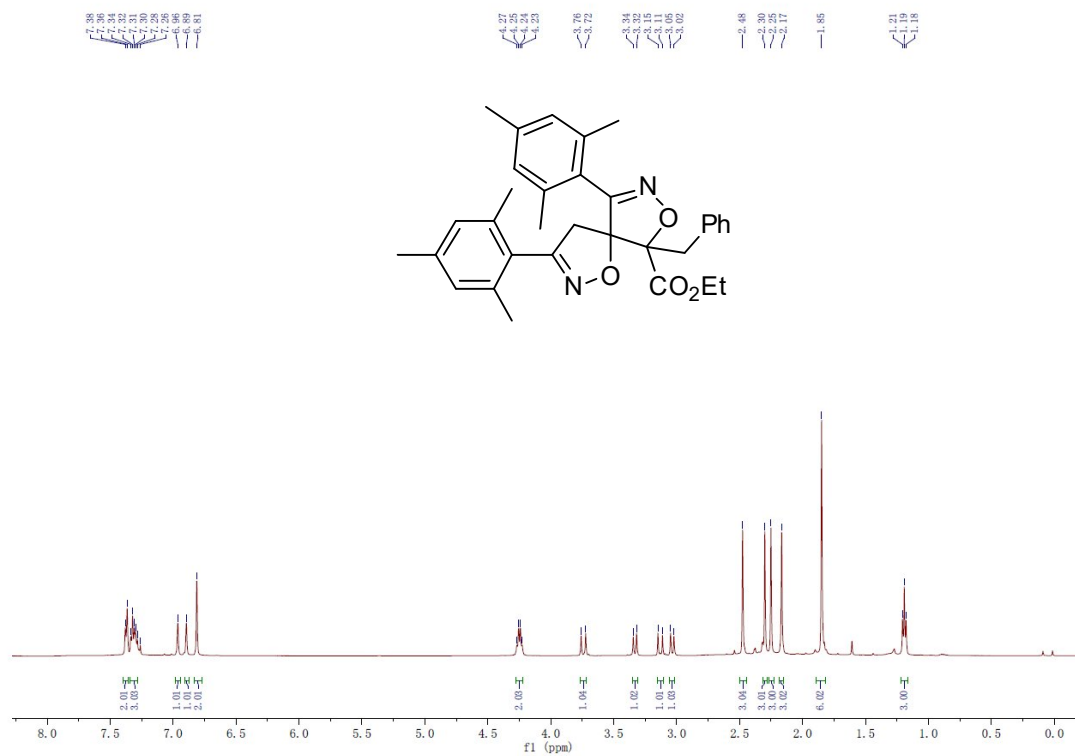
White solid, 88% yield. mp = 92-93°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ , 500 MHz):  $\delta$  (ppm) 7.38-7.36 (m, 2H), 7.34-7.28 (m, 3H), 6.96 (s, 1H), 6.89 (s, 1H), 6.81 (s, 2H), 4.27-4.23 (m, 2H), 3.74 (d,  $J = 20.0$  Hz, 1H), 3.33 (d,  $J = 20.0$  Hz, 1H), 3.13 (d,  $J = 15.0$  Hz, 1H), 3.04 (d,  $J = 15.0$  Hz, 1H), 2.48 (s, 3H), 2.30 (s, 3H), 2.25 (s, 3H), 2.17 (s, 3H), 1.85 (s, 6H), 1.19 (t,  $J = 10.0$  Hz, 3H).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ , 125 MHz):  $\delta$  (ppm) 157.5, 156.9, 139.7, 139.6, 139.2, 136.9, 136.8, 133.7, 130.6, 129.6, 128.4, 128.4, 127.5, 124.4, 122.7, 100.9, 71.7, 62.1, 40.9, 39.9, 21.0, 20.5, 20.2, 18.7, 14.1. HRMS (ESI): exact mass calculated for  $\text{M}^+$  ( $\text{C}_{33}\text{H}_{37}\text{N}_2\text{O}_4$ ) requires  $m/z$  525.2753, found  $m/z$  525.2758.

**Ethyl 5-benzyl-3-mesityl-4-methylene-4,5-dihydroisoxazole-5-carboxylate (5)**

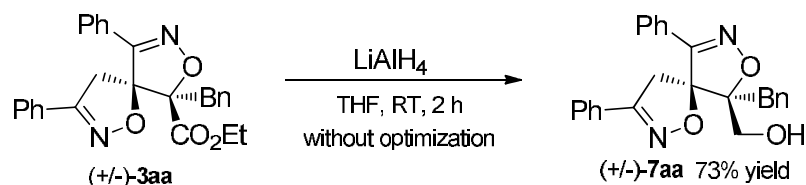




**Ethyl 6-benzyl-3,9-dimesityl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (6)**

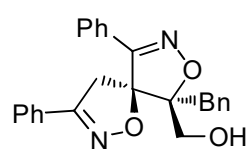


## E: Synthetic Transformations.



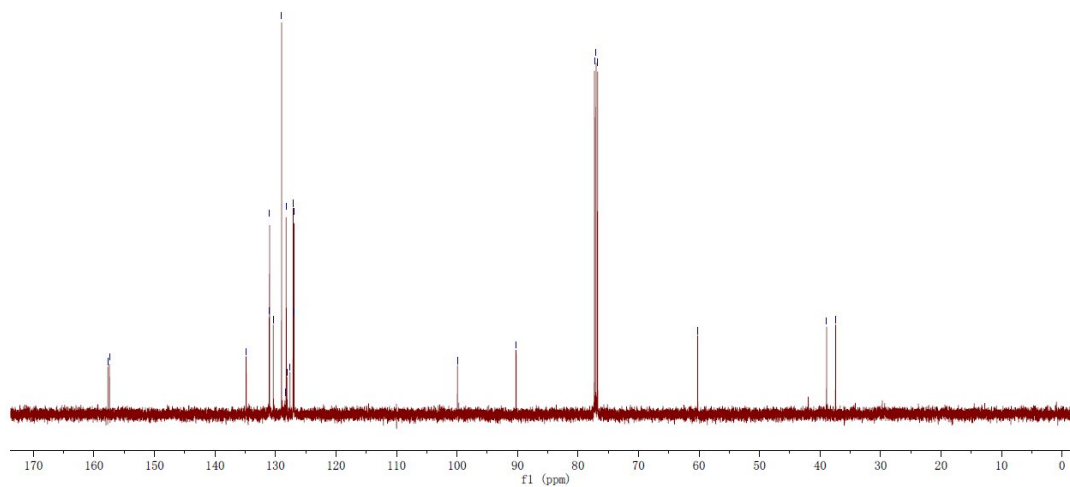
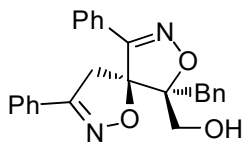
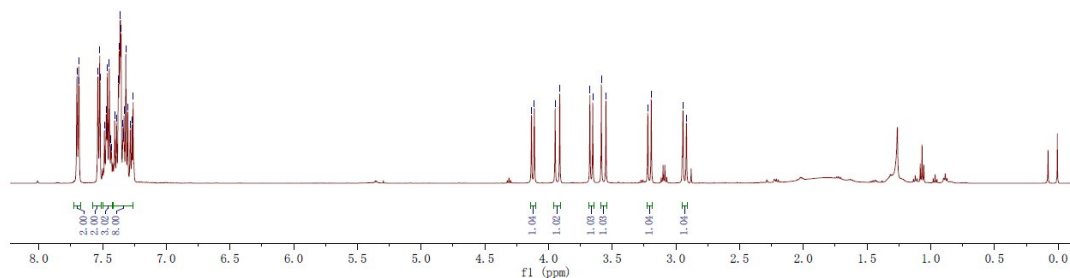
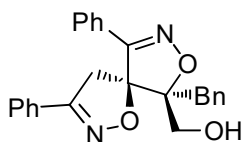
To a solution of **3aa** (0.1 mmol) in anhydrous THF (2.0 mL) was added LiAlH<sub>4</sub> (0.8 mmol) at 0°C. The resulting solution was stirred at room temperature for 2 h, then sat. NH<sub>4</sub>Cl (2.0 mL) was added to quench the reaction and the aqueous solution was extracted with DCM (3\*5 mL). The combined organic layers was dried with anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated to yield the crude product, which was purified by column chromatography to afford **7aa** in 73% yield as a white solid.

### (6-Benzyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-dien-6-yl)methanol



White solide, 73% yield. mp = 85-86°C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 7.70-7.68 (m, 2H), 7.54-7.52 (m, 2H), 7.49-7.43 (m, 3H), 7.39-7.27 (m, 8H), 4.12 (d, *J* = 10.0 Hz, 1H), 3.93 (d, *J* = 20.0 Hz, 1H), 3.67 (d, *J* = 15.0 Hz, 1H), 3.57 (d, *J* = 20.0 Hz, 1H), 3.21 (d, *J* = 15.0 Hz, 1H), 2.93 (d, *J* = 10.0 Hz, 1H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz): δ (ppm) 157.7, 157.4, 134.8, 131.0, 131.0, 130.4, 129.0, 128.3, 128.2, 128.1, 127.6, 127.1, 127.0, 126.9, 99.9, 90.2, 60.2, 38.9, 37.4. HRMS (ESI): exact mass calculated for M<sup>+</sup> (C<sub>25</sub>H<sub>23</sub>N<sub>2</sub>O<sub>3</sub>) requires m/z 399.1709, found m/z 399.1714.

# (6-Benzyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-dien-6-yl)methanol



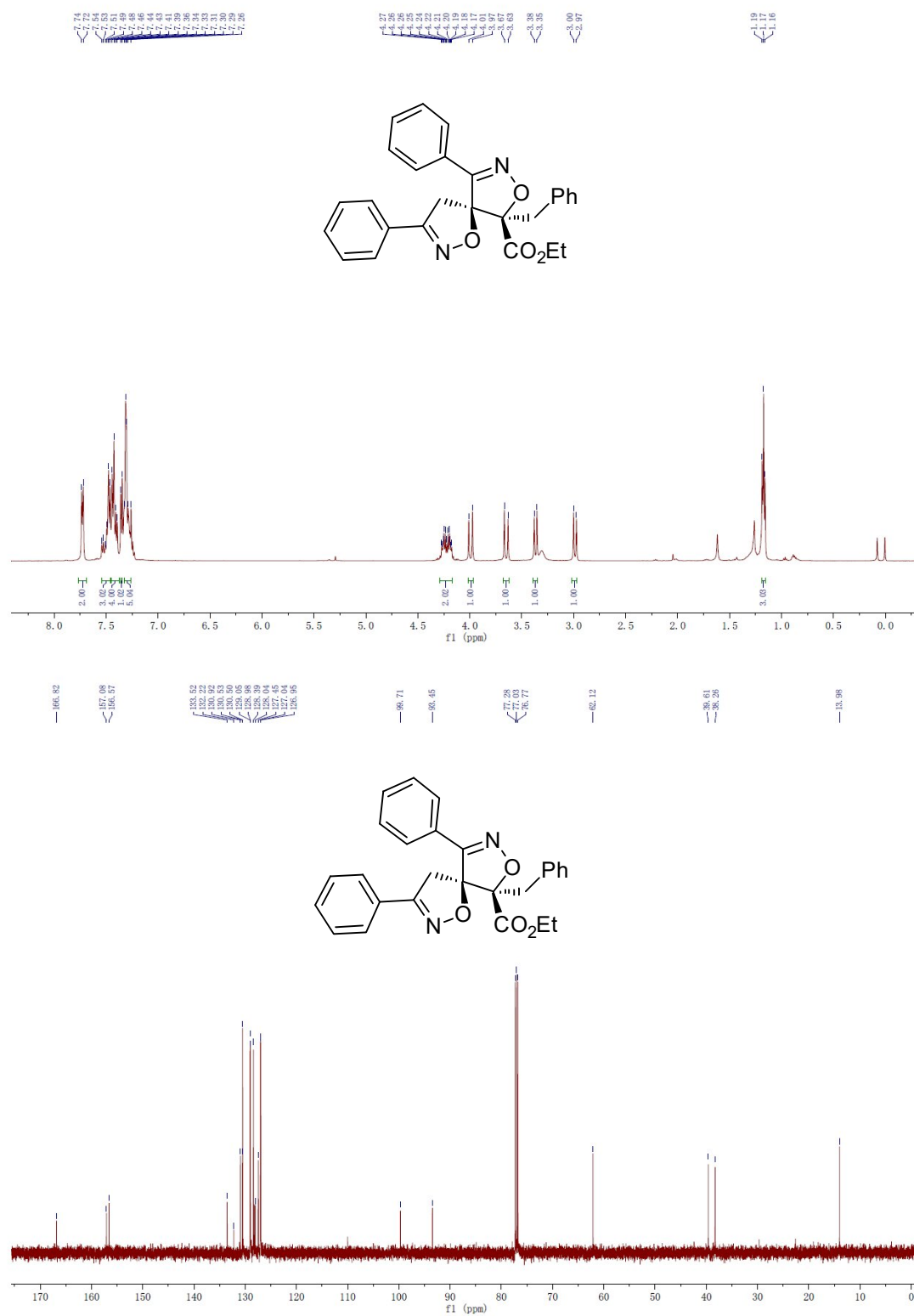
## F: Gram Scale Reaction



To a solution of  $\text{CHCl}_3$  (15.0 mL) were added oxime halide **1a** (3.10g, 20.0 mmol), allenolate **2a** (0.81g, 4.0 mmol),  $\text{Et}_3\text{N}$  (2.02g, 20.0 mmol,) and DABCO (0.09g, 0.8 mmol). The reaction mixture was stirred at  $50^\circ\text{C}$  for 48 h. The solvent is evaporated to give the crude product, which is directly purified by silica gel chromatography to provide the desired product **3aa** as a white solid (1.02g, 58% yield).

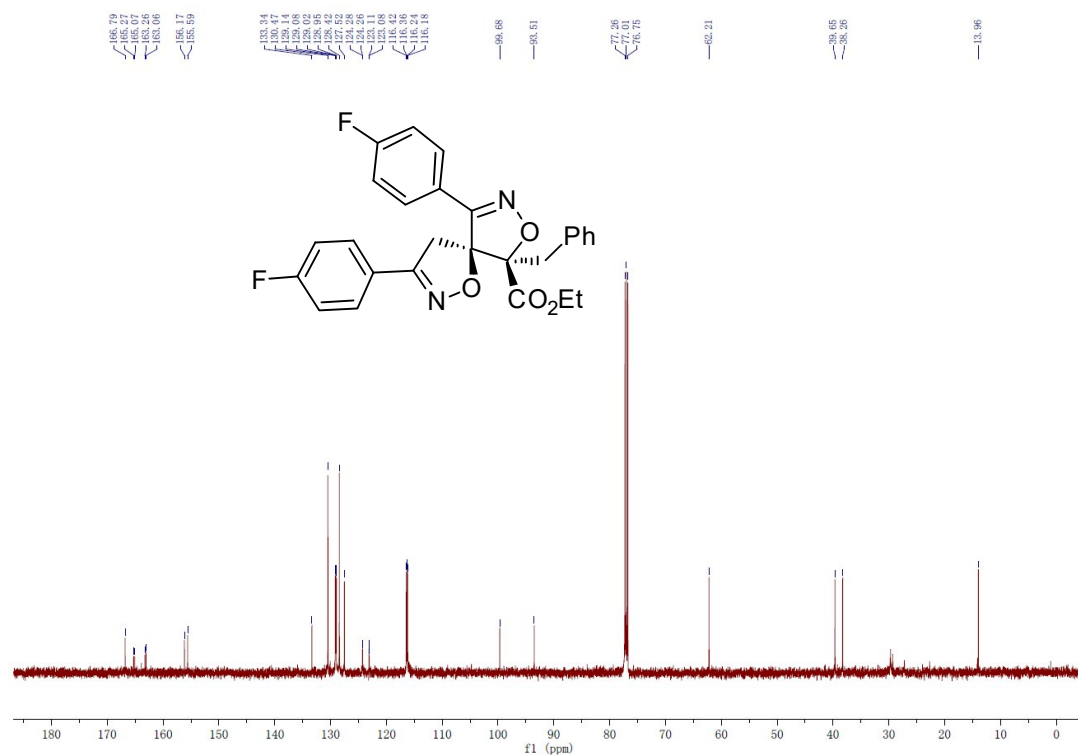
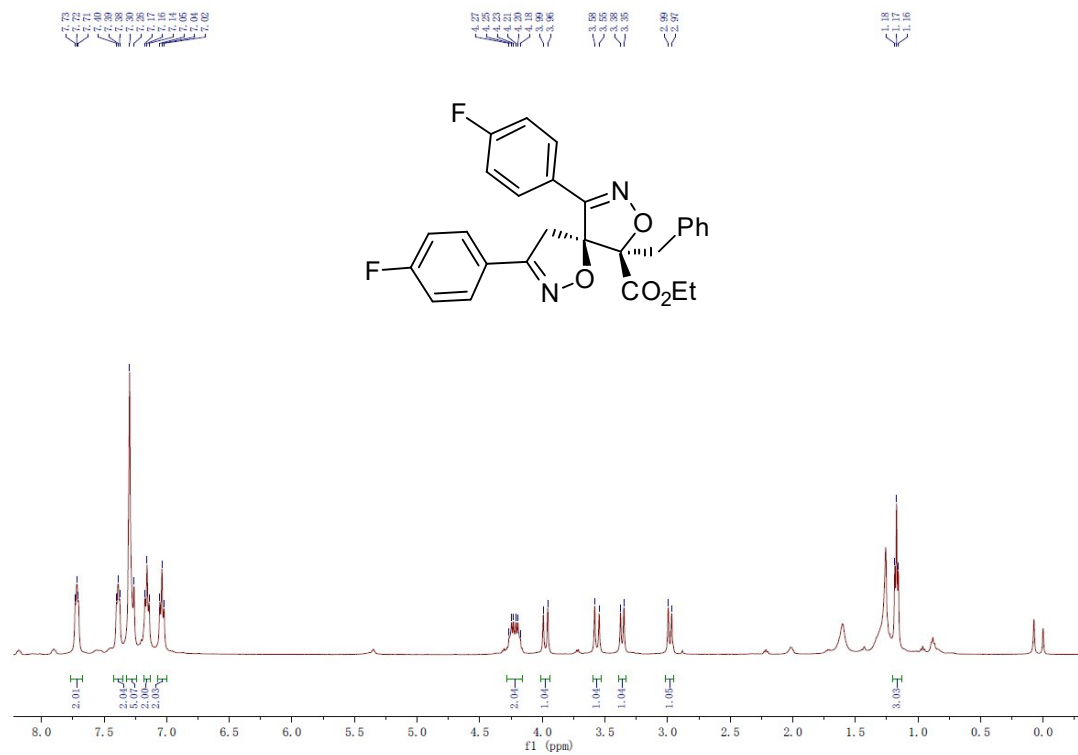
## G: NMR Analysis

### Ethyl 6-benzyl-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3aa)

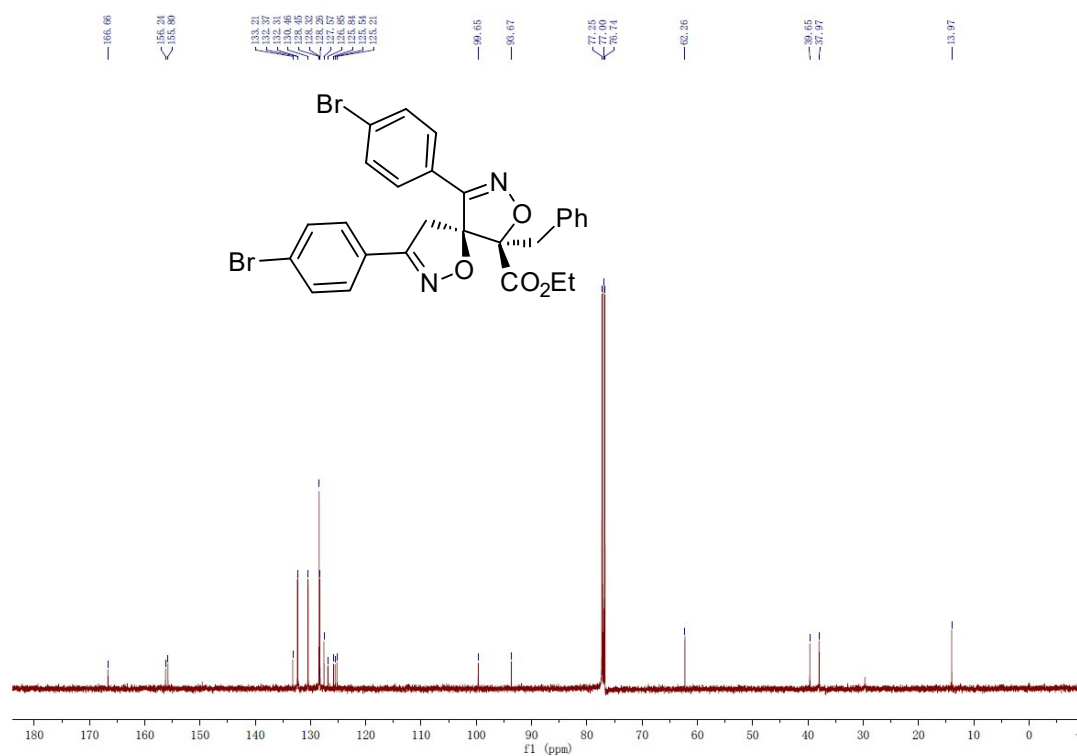
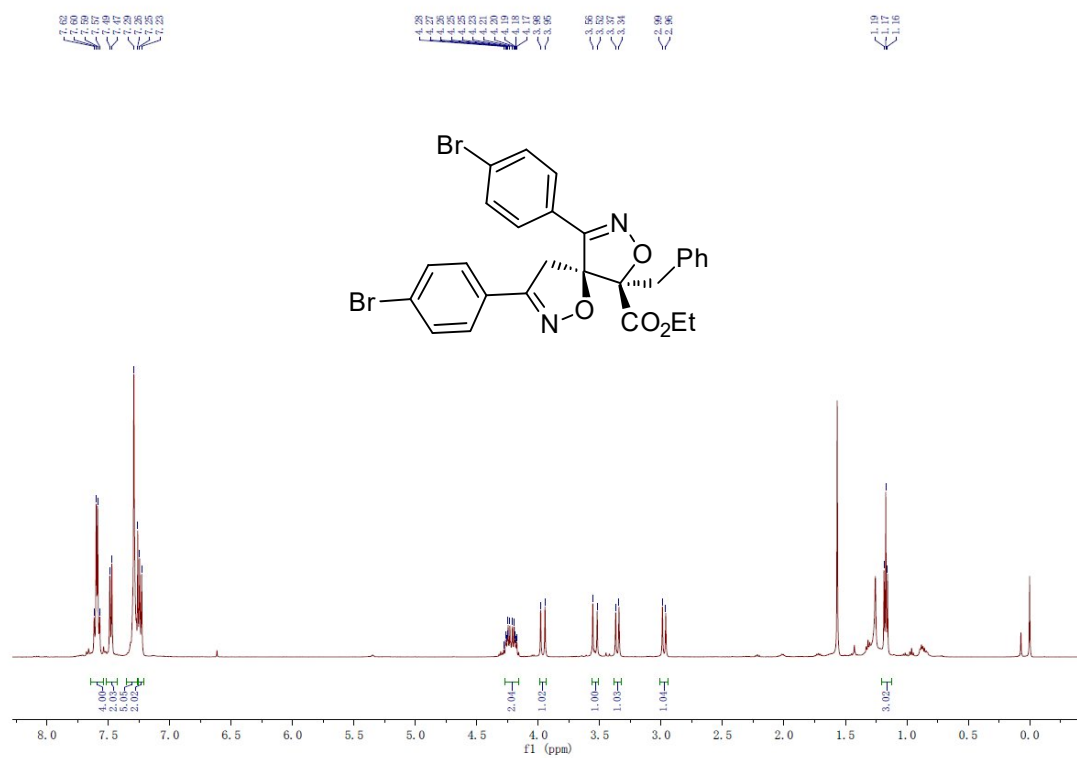




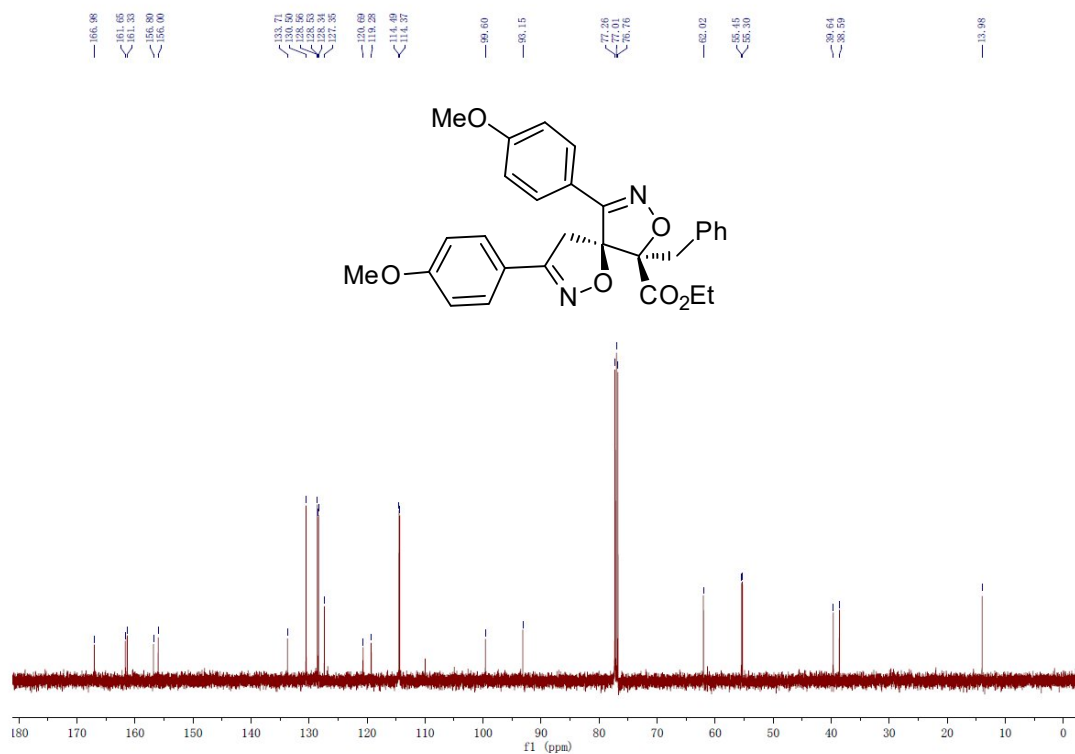
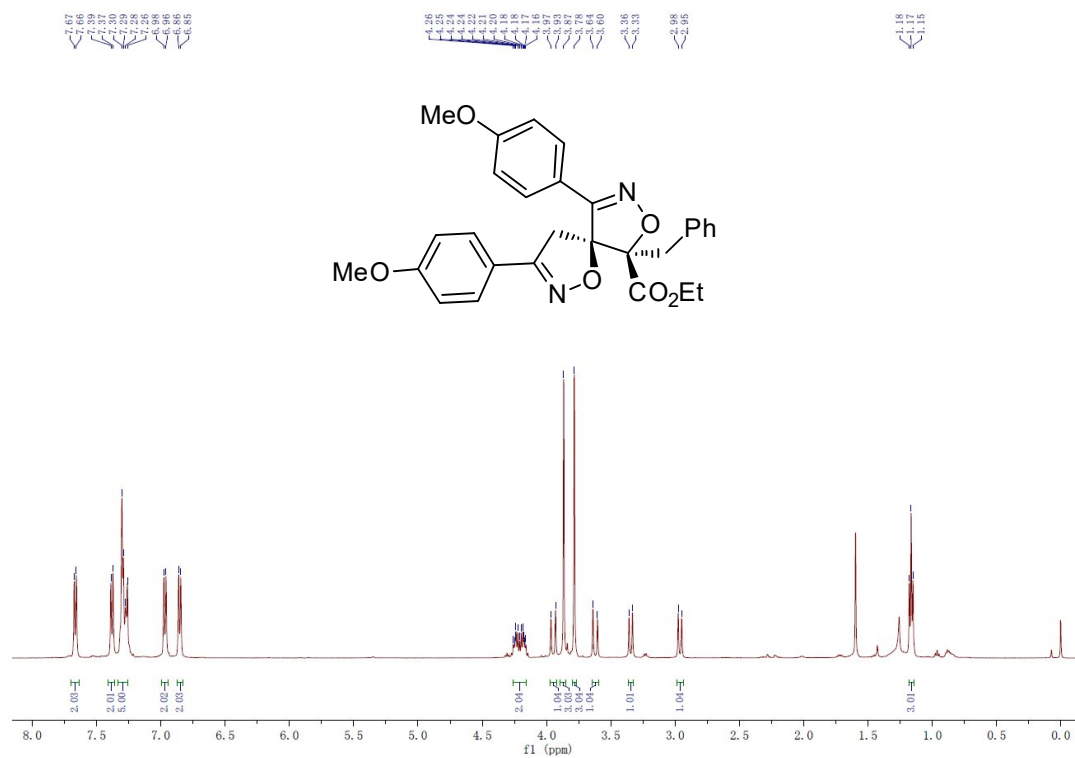
# Ethyl 6-benzyl-3,9-bis(4-fluorophenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ba)



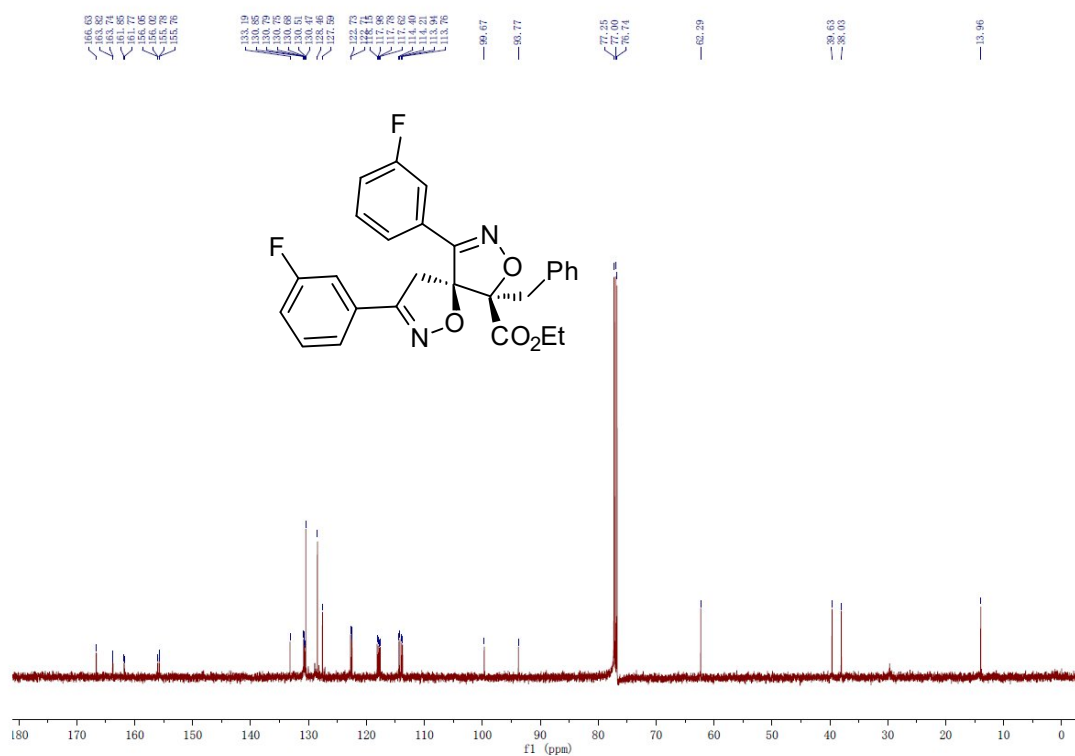
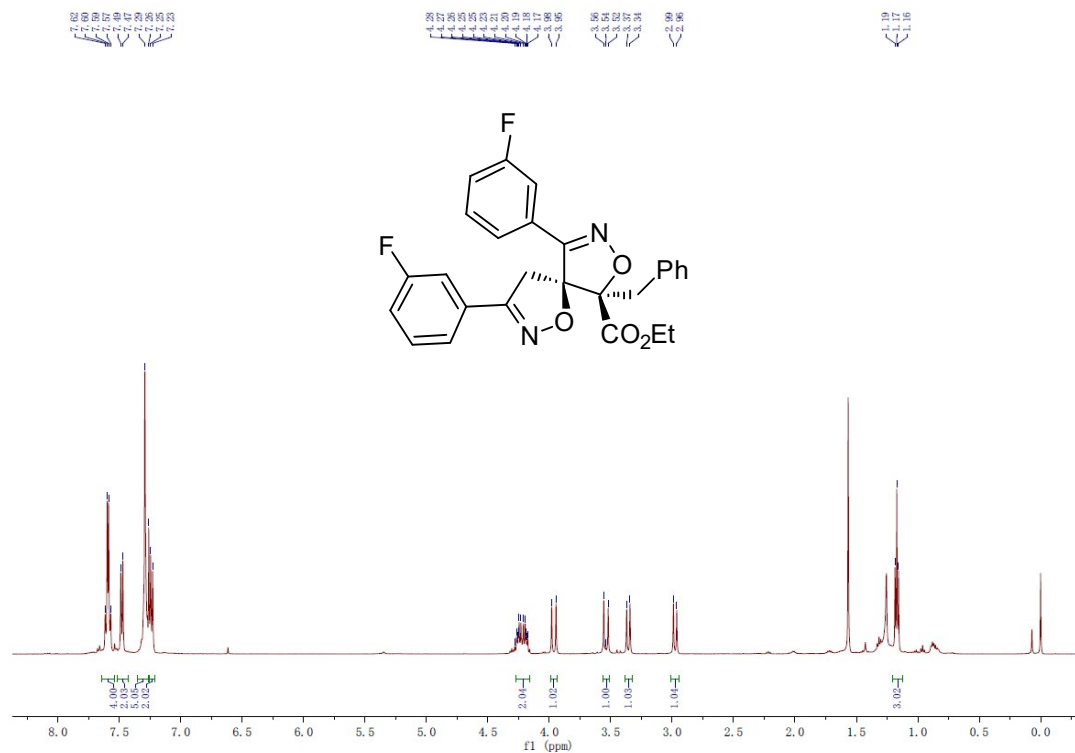
**Ethyl 6-benzyl-3,9-bis(4-bromophenyl)-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ca)**



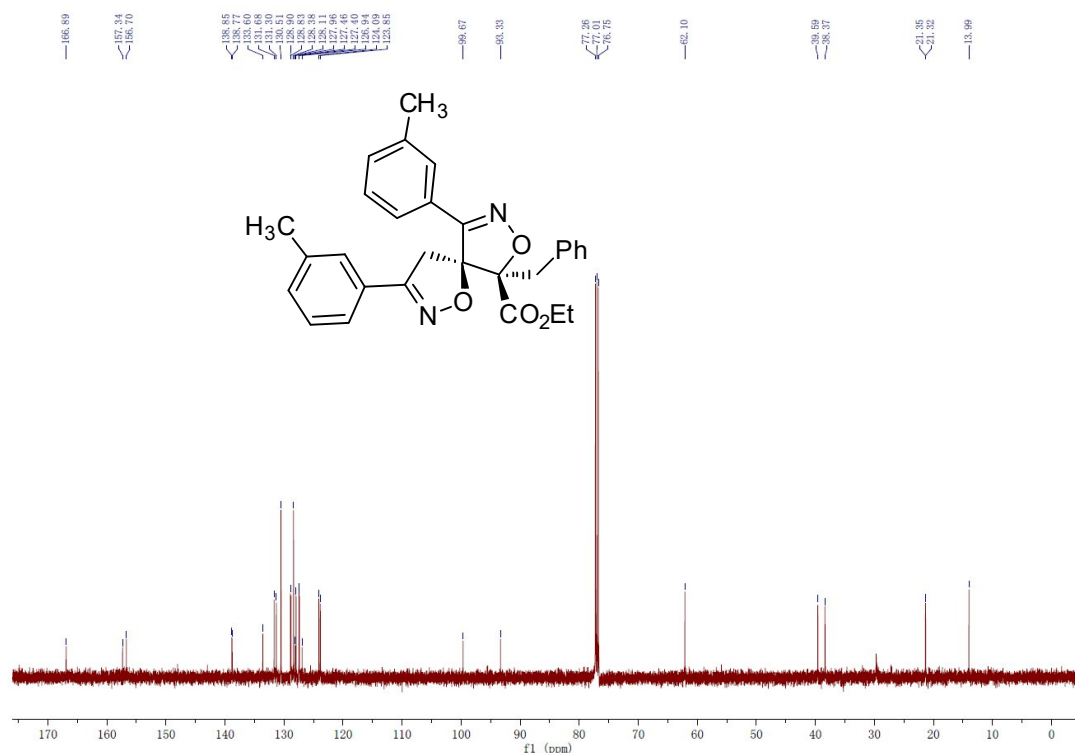
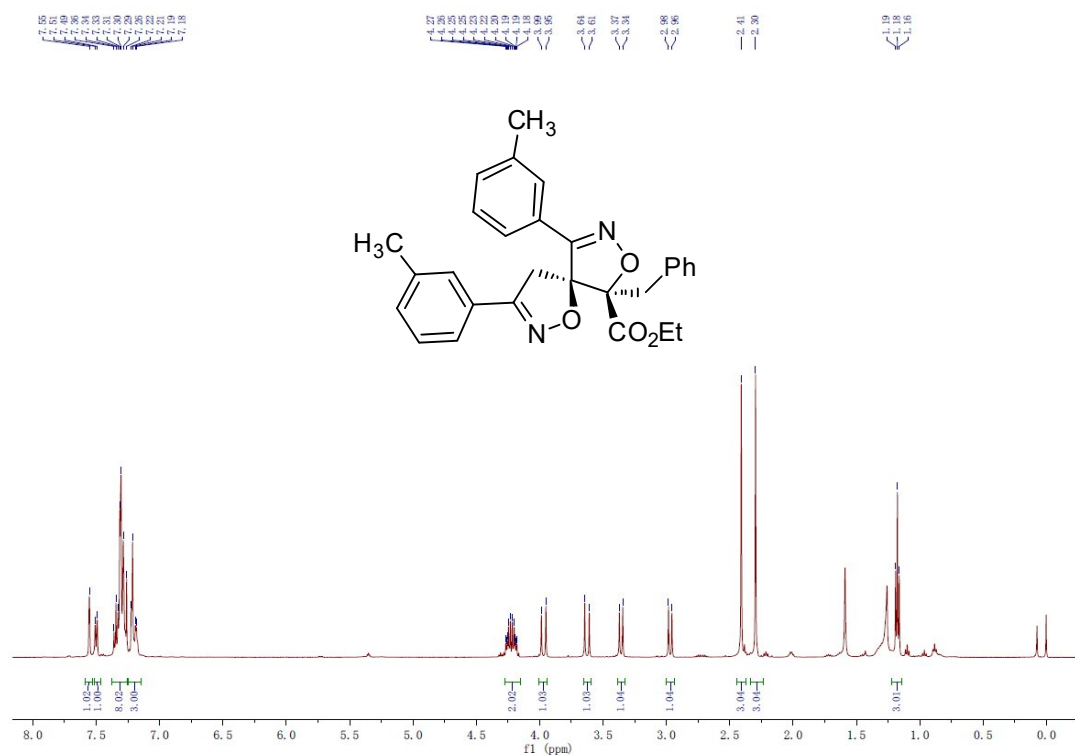
# Ethyl 6-benzyl-3,9-bis(4-methoxyphenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3da)



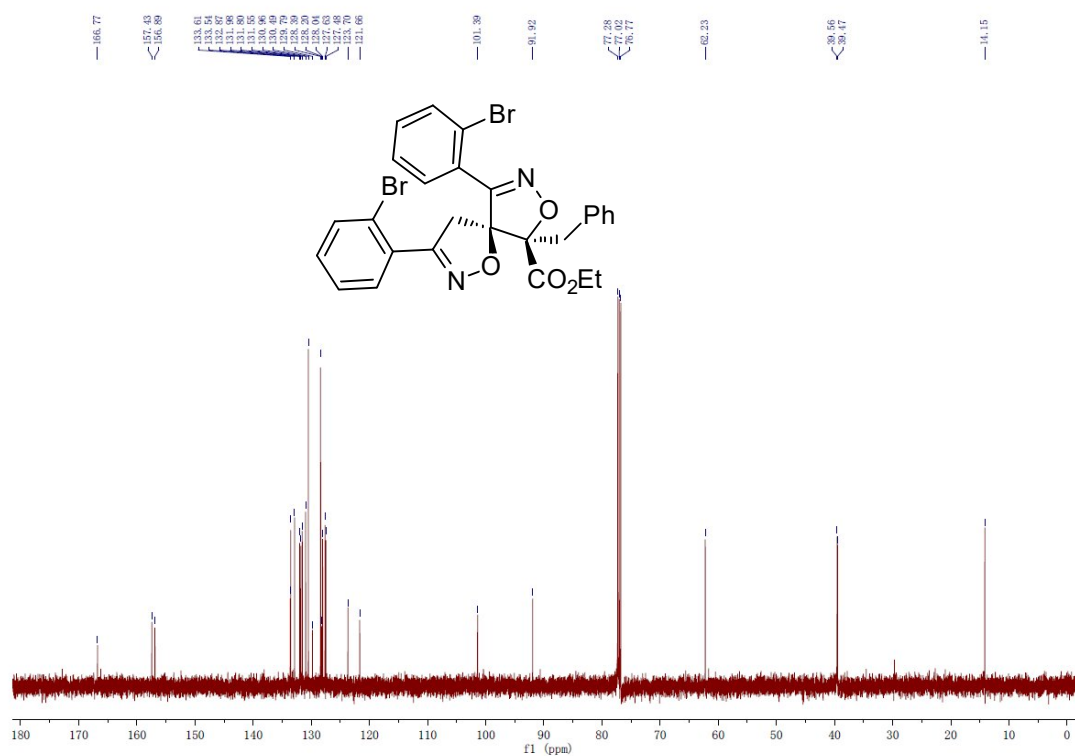
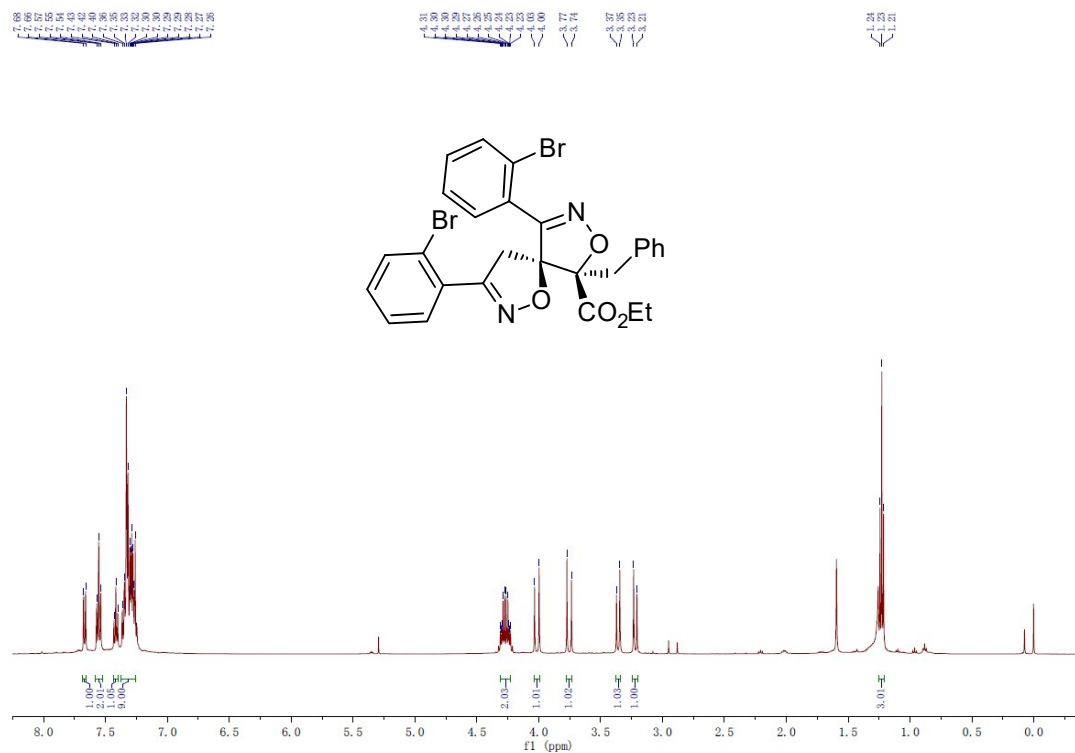
# Ethyl 6-benzyl-3,9-bis(3-fluorophenyl)-1,7-dioxo-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ea)



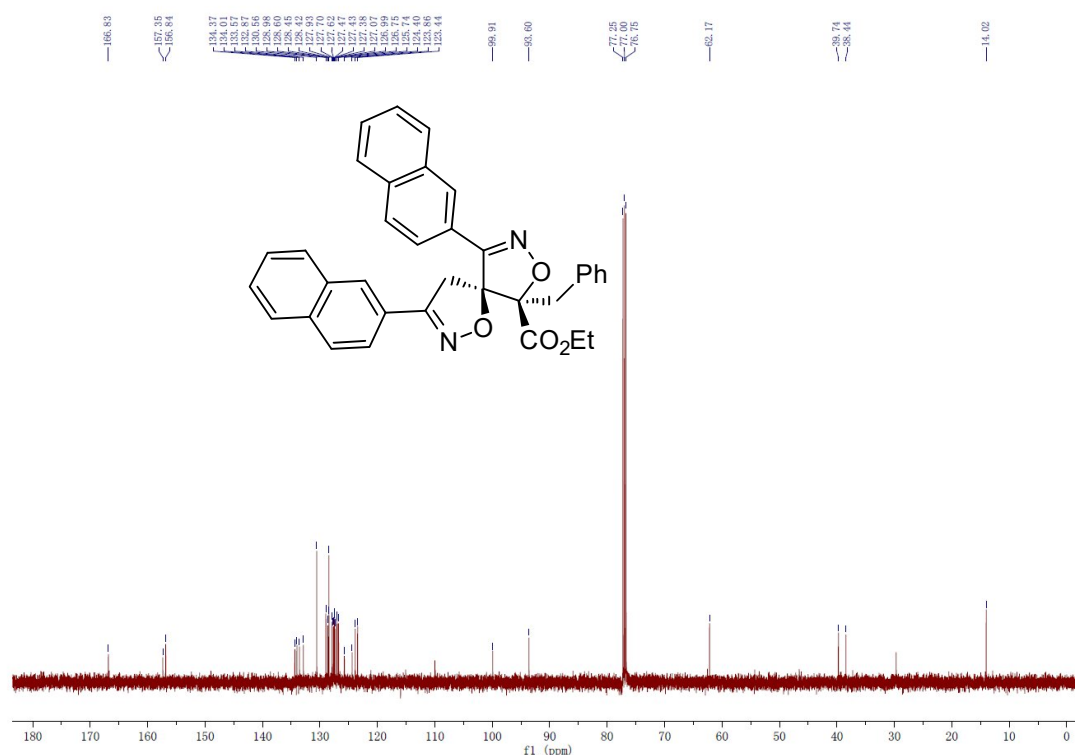
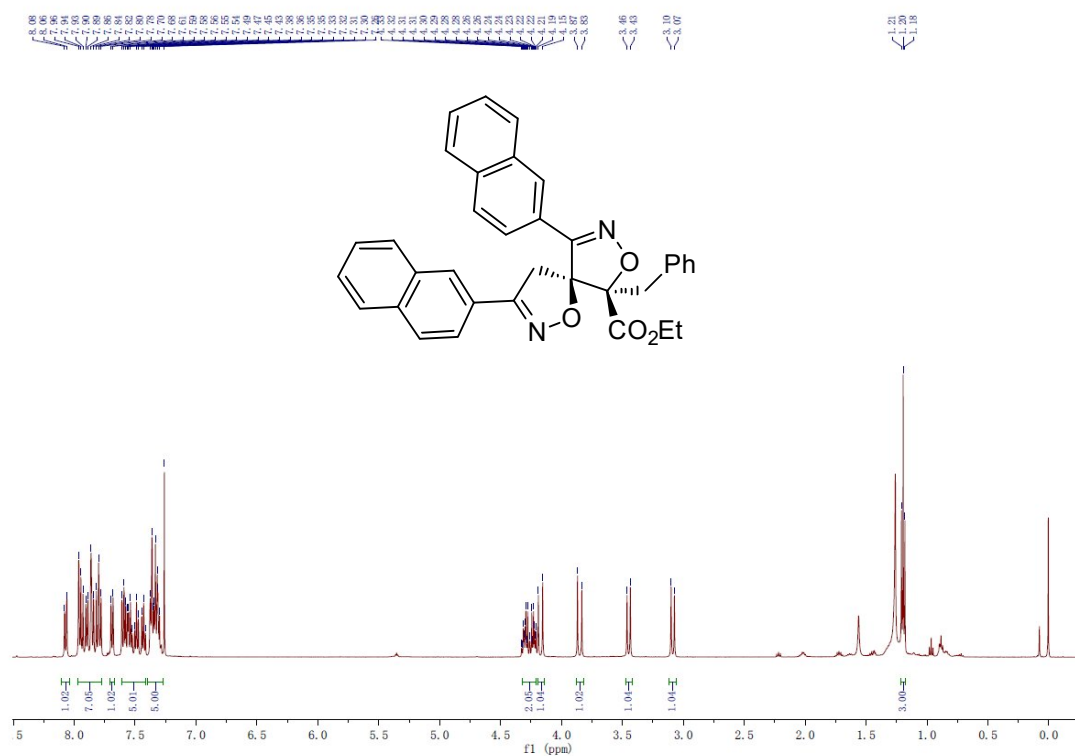
**Ethyl 6-benzyl-3,9-di-*m*-tolyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3fa)**



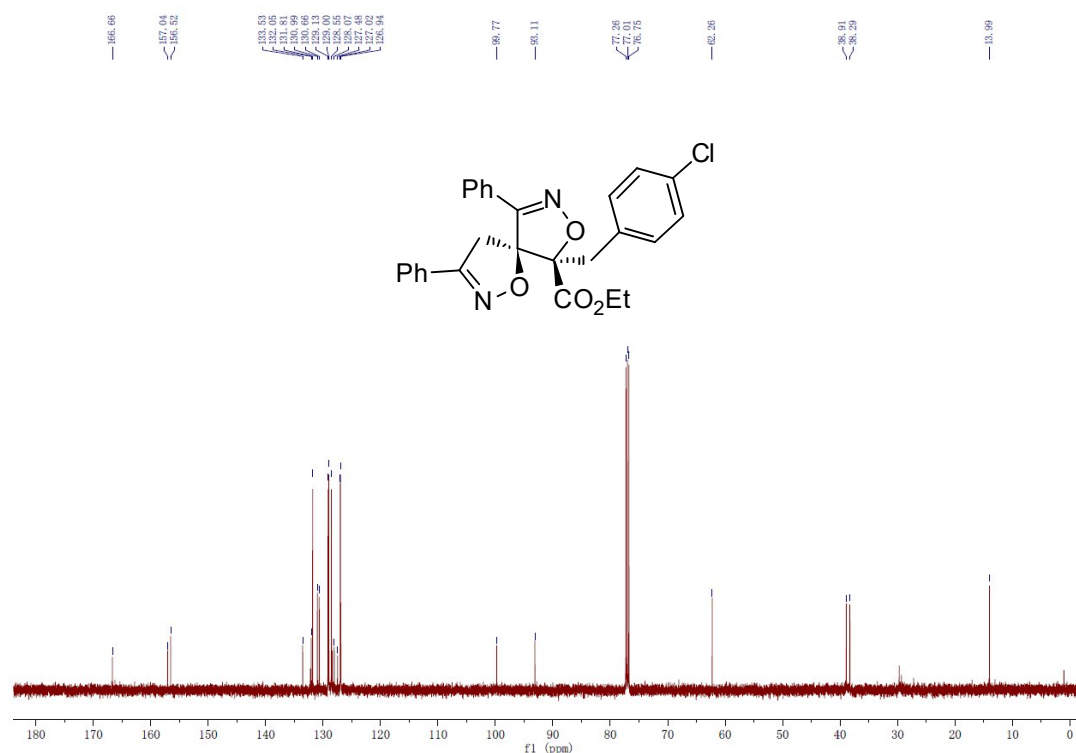
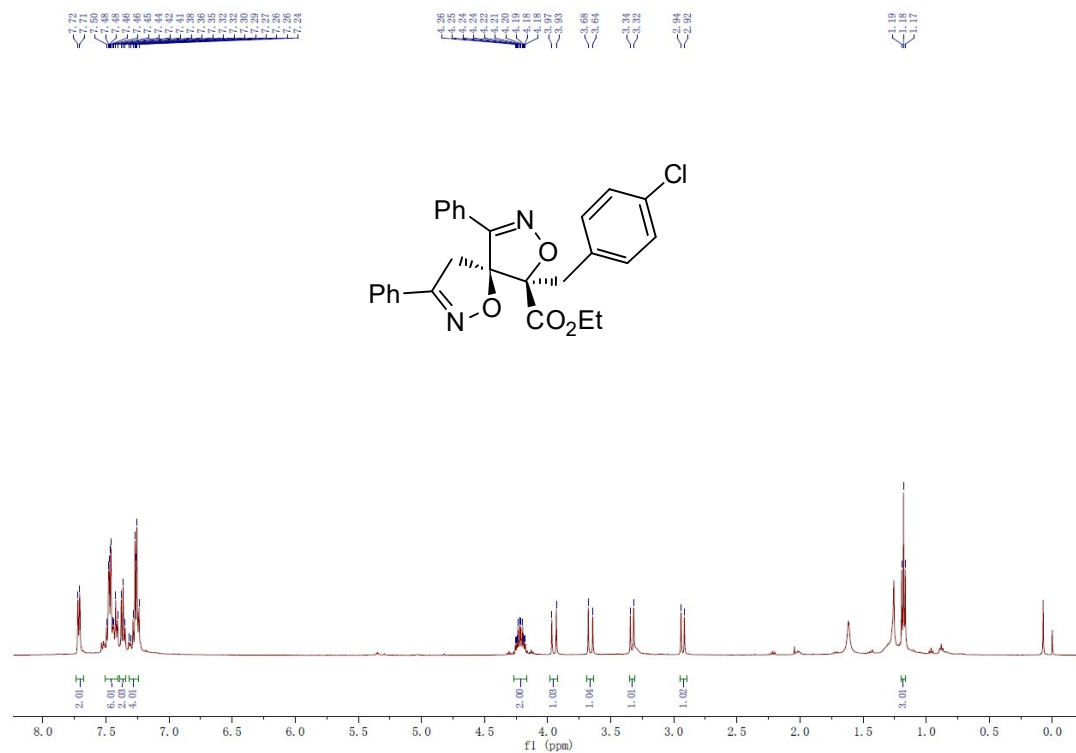
# Ethyl 6-benzyl-3,9-bis(2-bromophenyl)-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ga)



# Ethyl 6-benzyl-3,9-di(naphthalen-2-yl)-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ha)

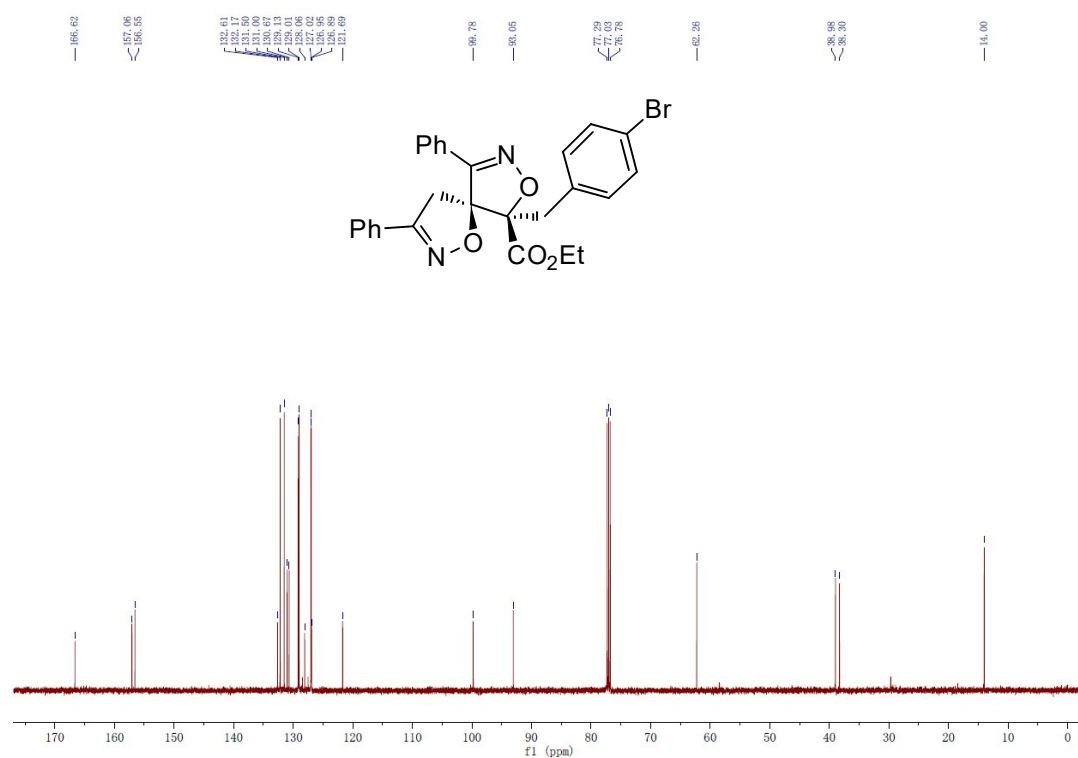
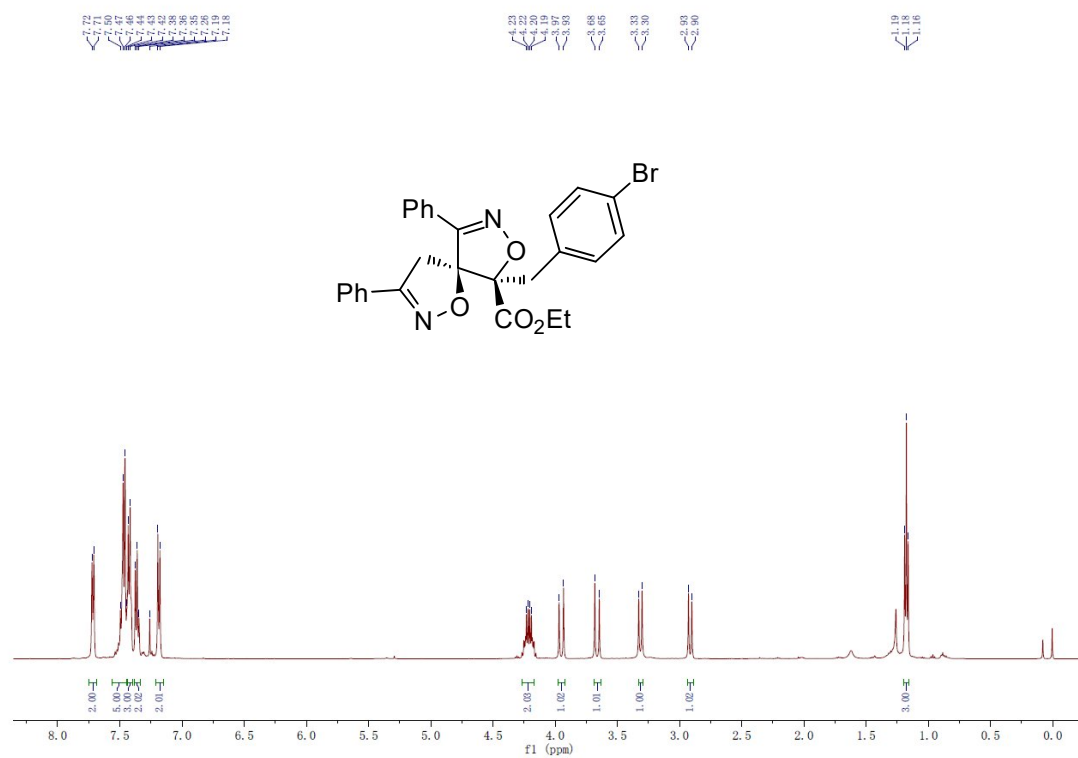


# Ethyl 6-(4-chlorobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ab)

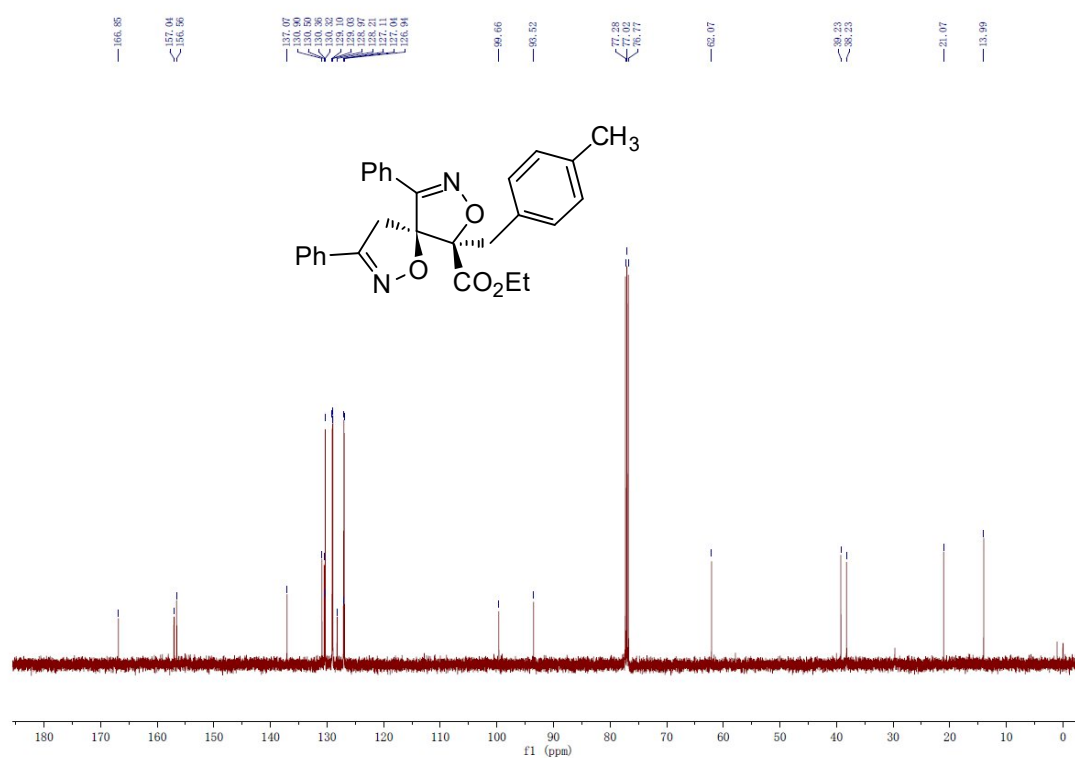
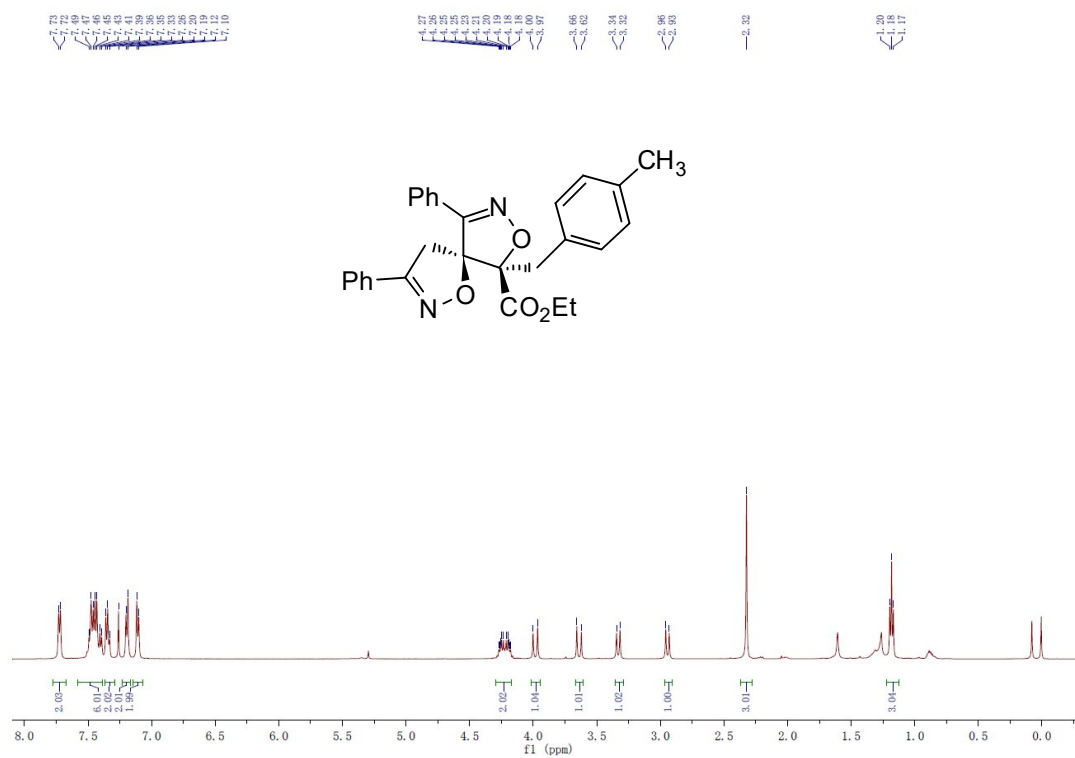




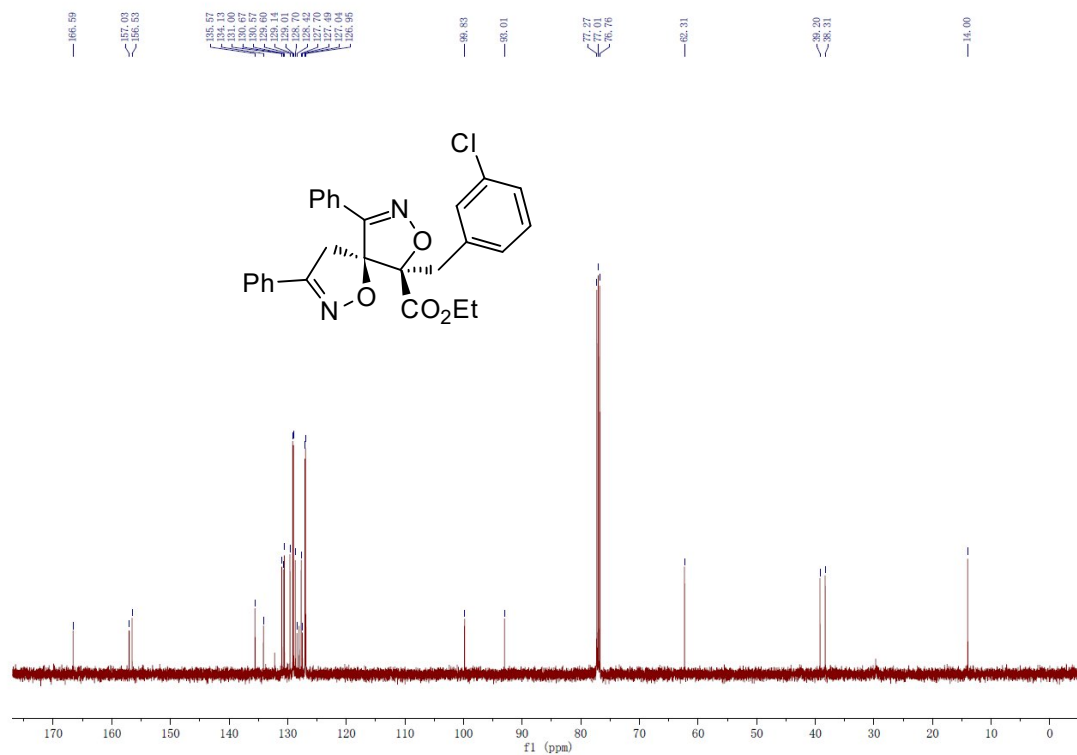
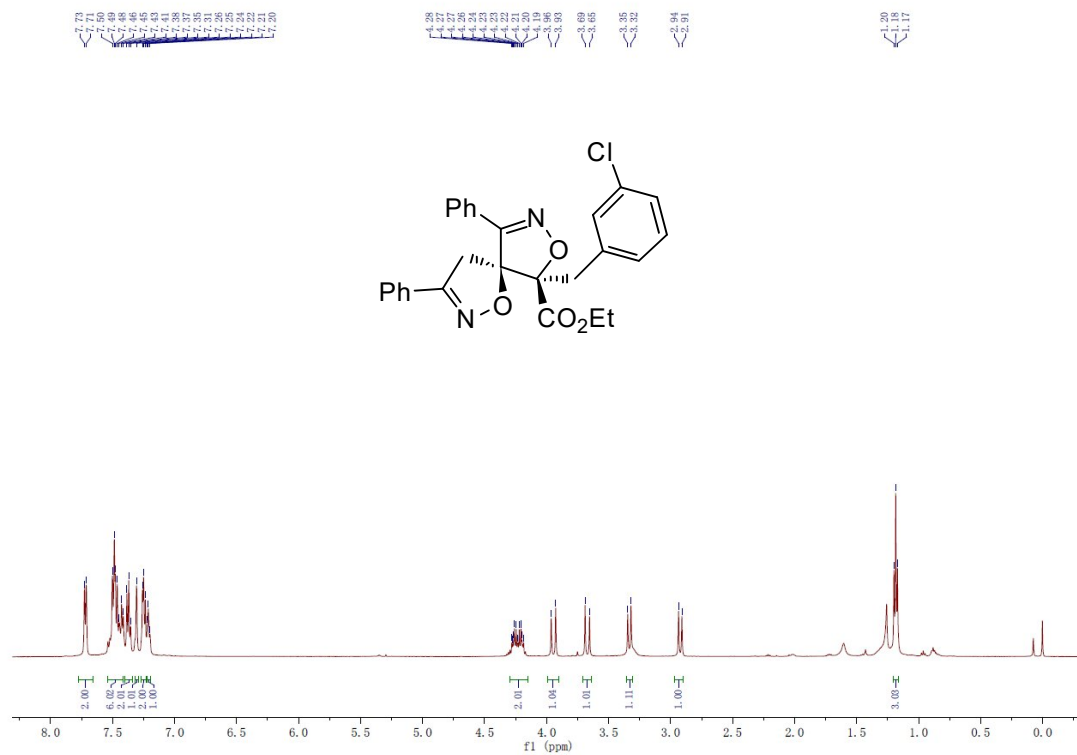
**Ethyl 6-(4-bromobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ac)**



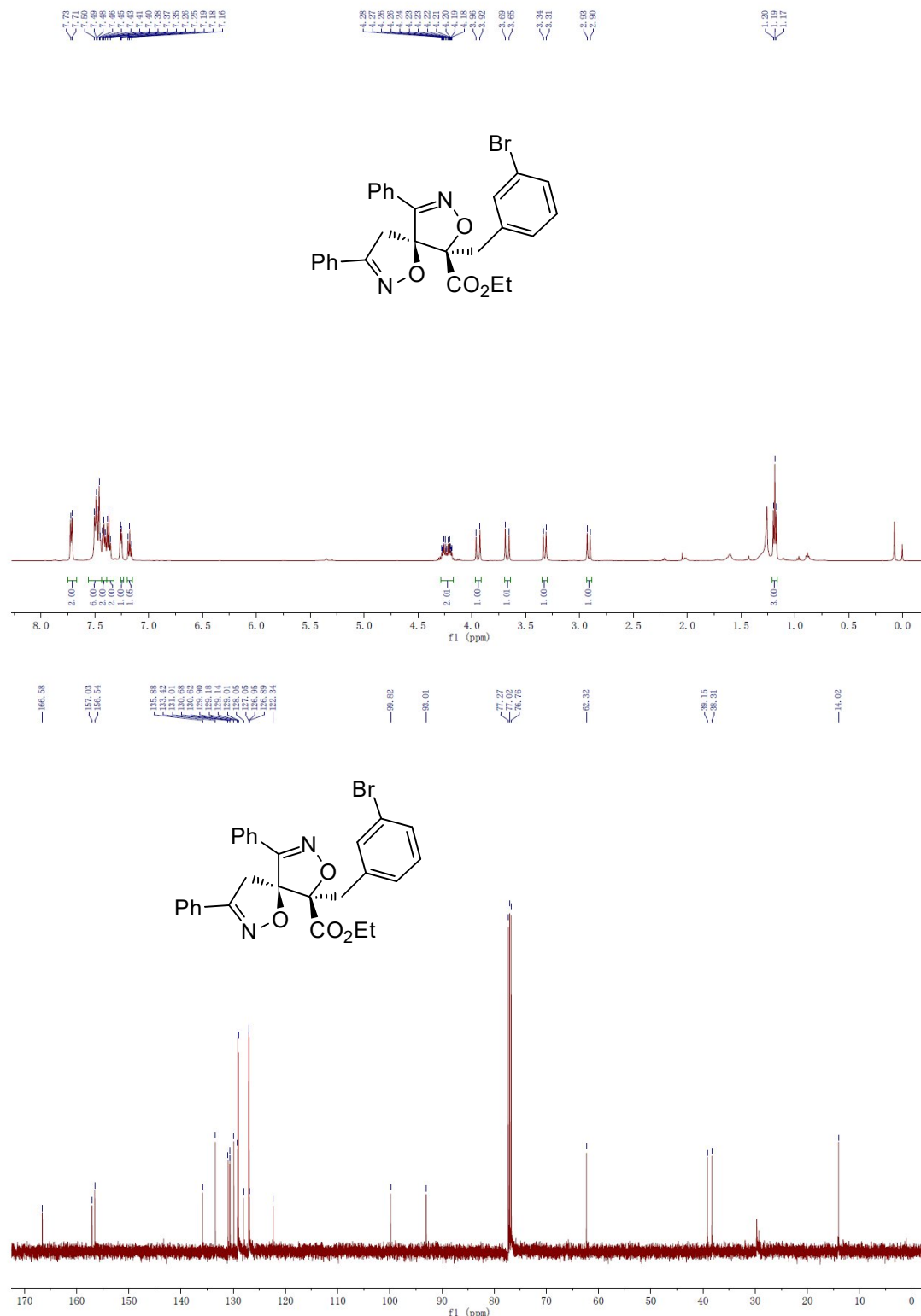
# Ethyl 6-(4-methylbenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ad)



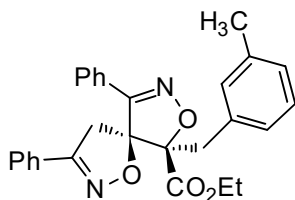
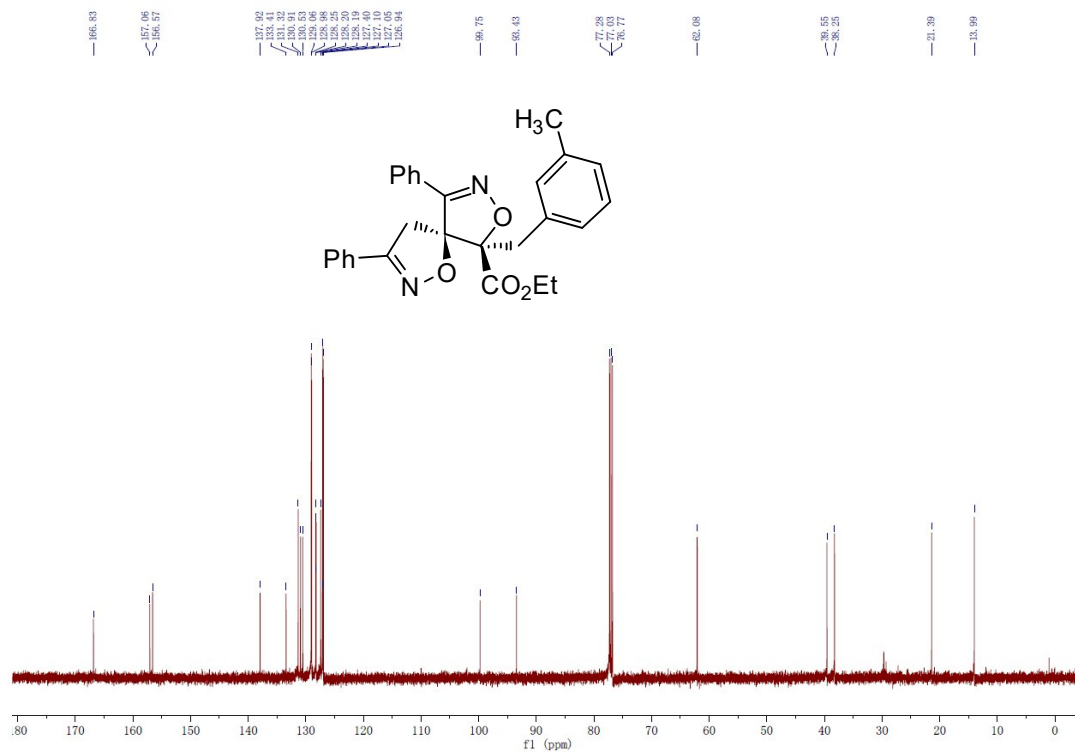
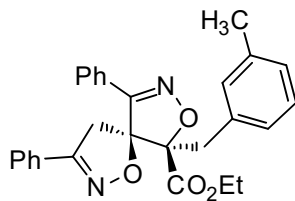
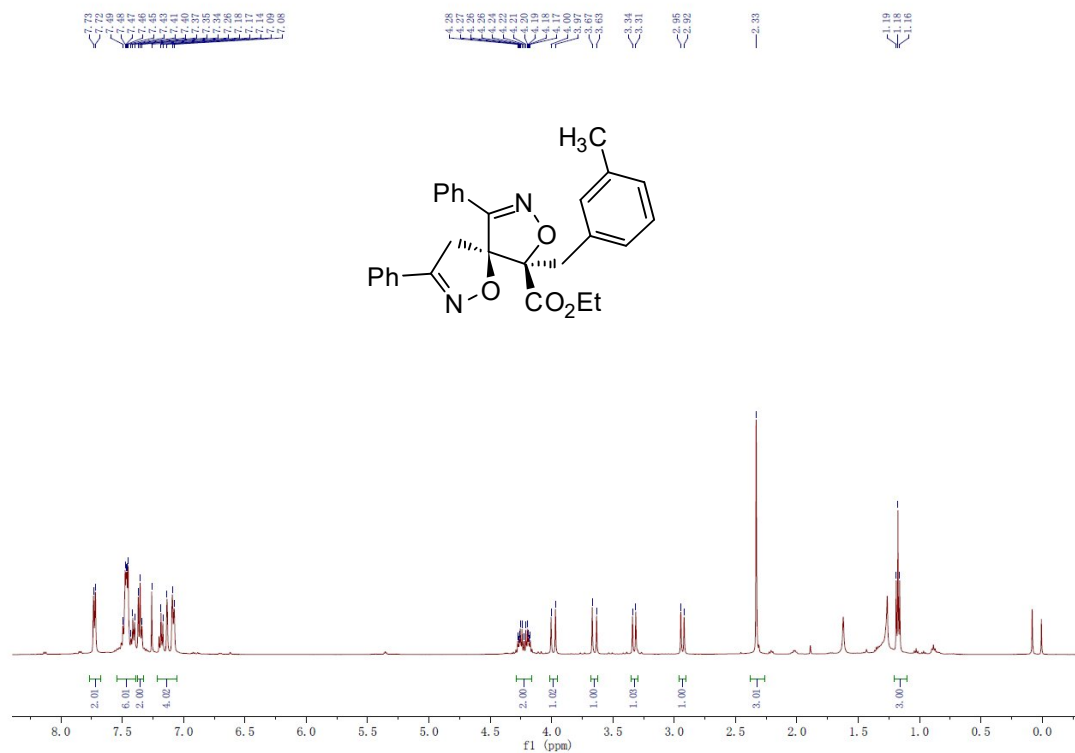
**Ethyl 6-(3-chlorobenzyl)-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3ae)**



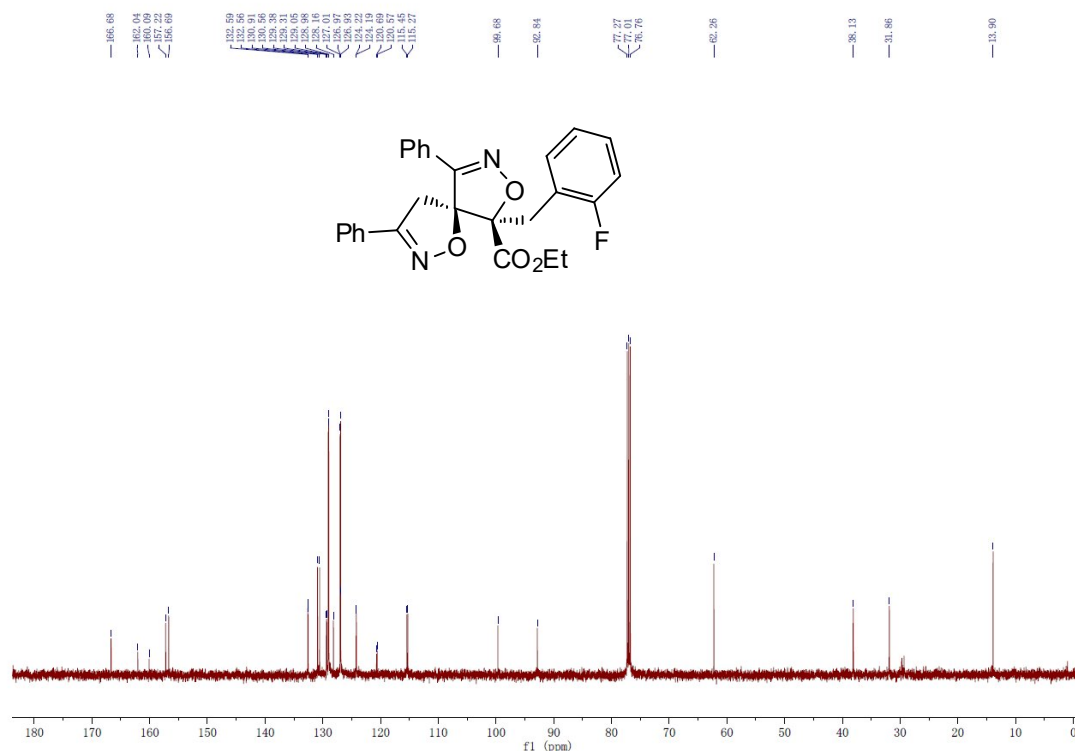
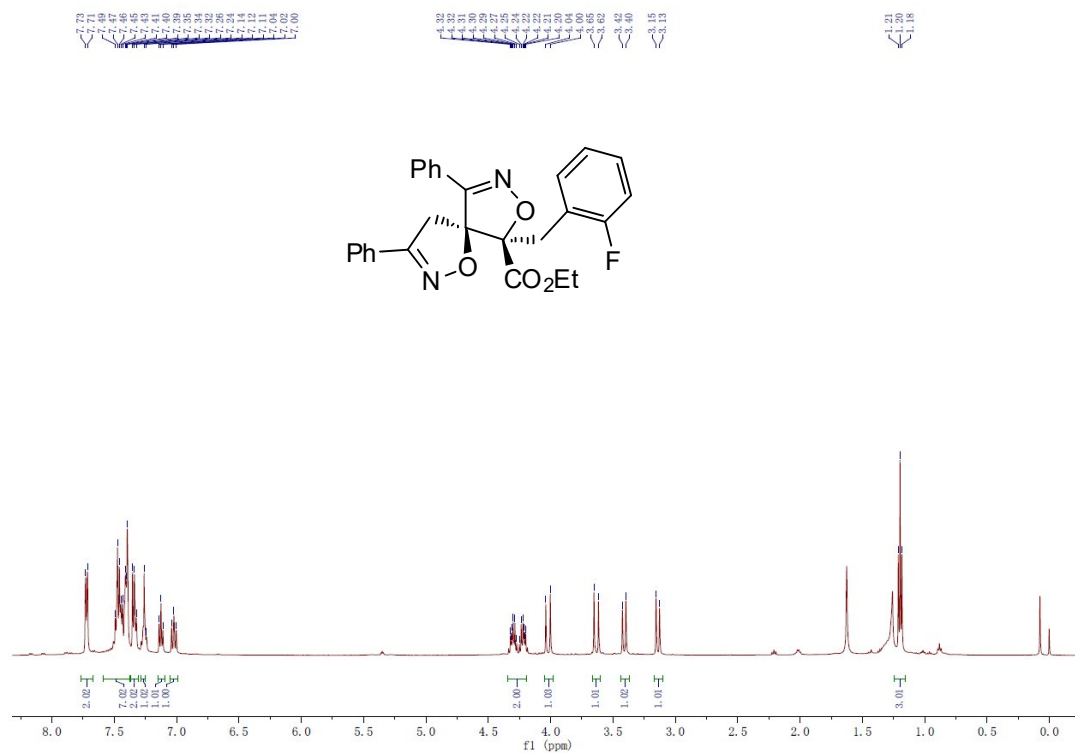
**Ethyl 6-(3-bromobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3af)**



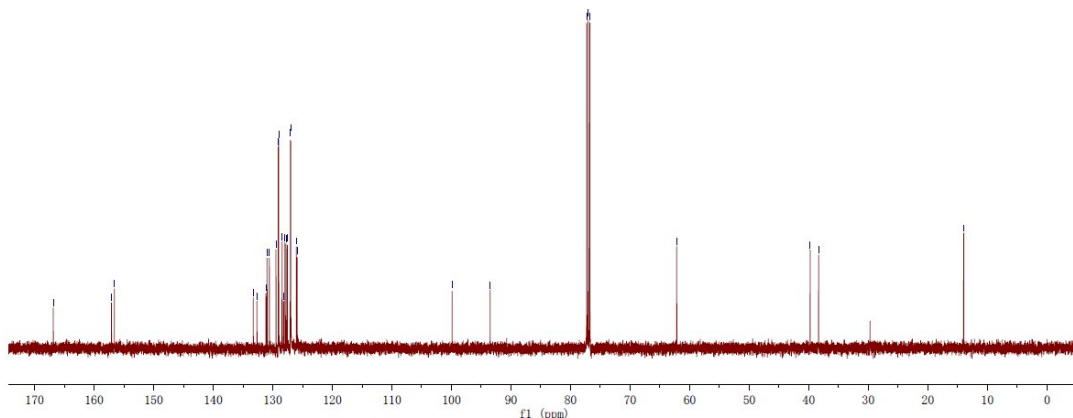
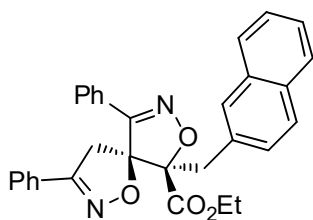
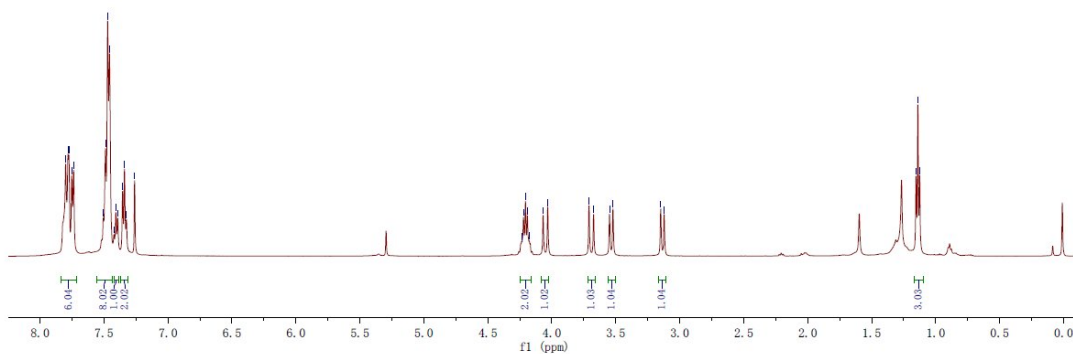
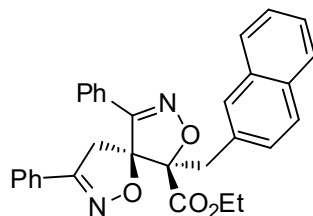
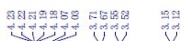
# Ethyl 6-(3-methylbenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ag)



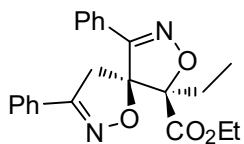
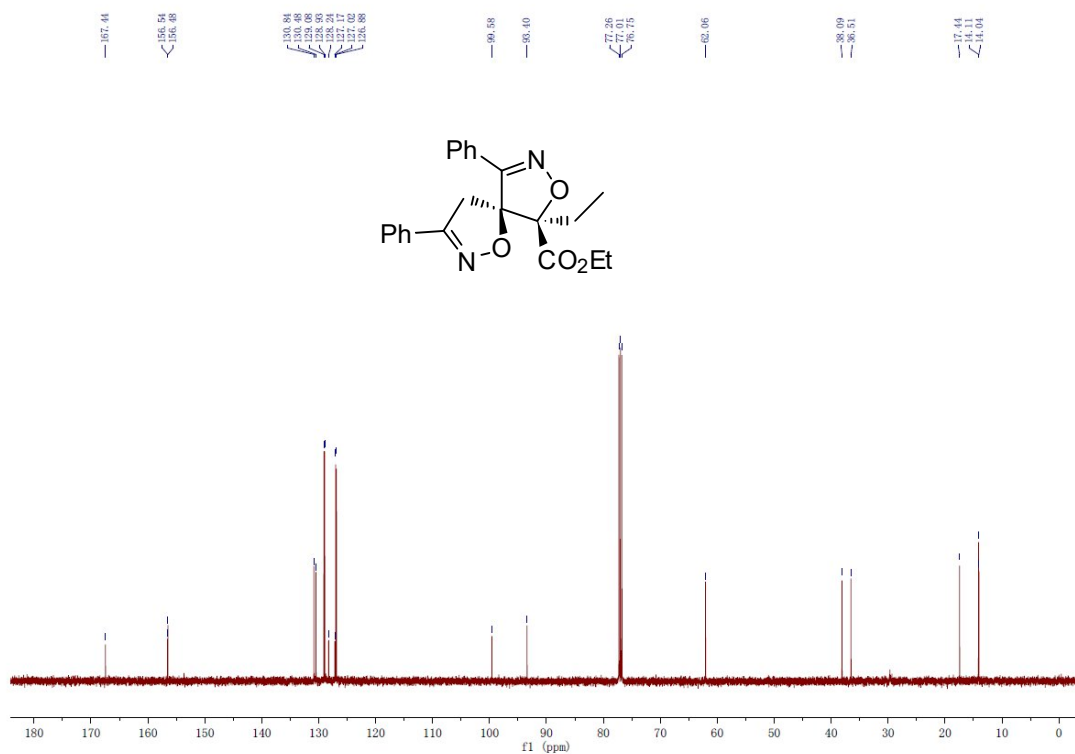
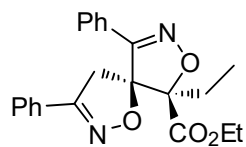
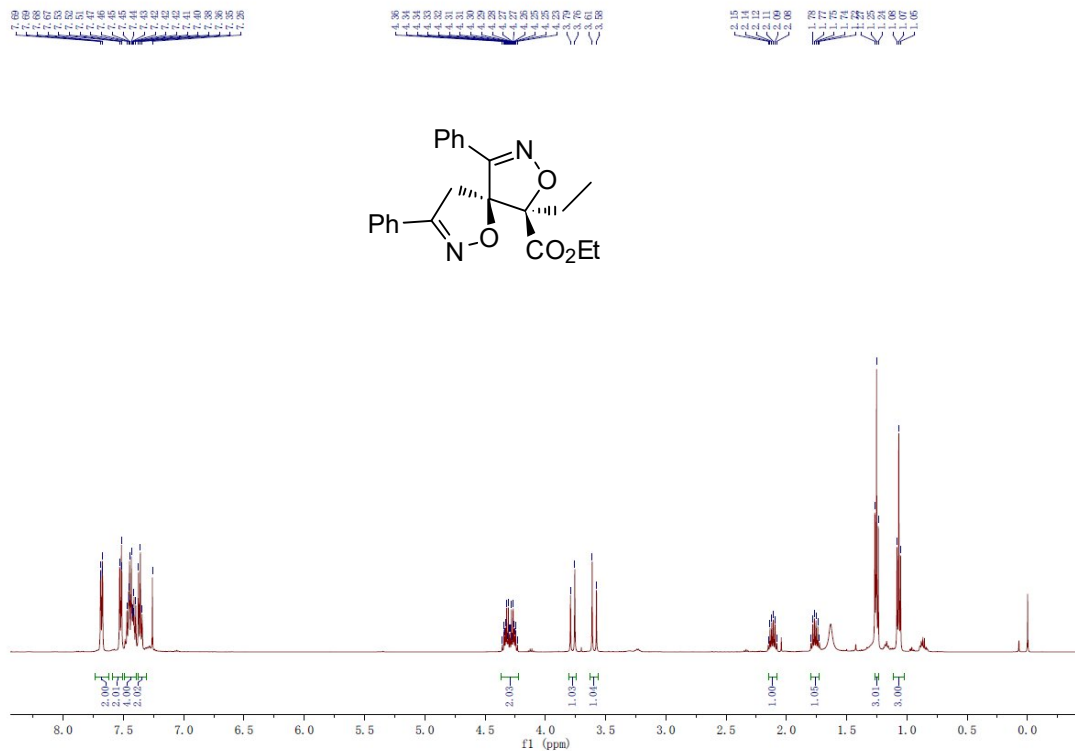
**Ethyl 6-(2-fluorobenzyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ah)**



# Ethyl 6-(naphthalen-2-ylmethyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate (3ai)

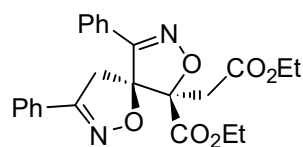
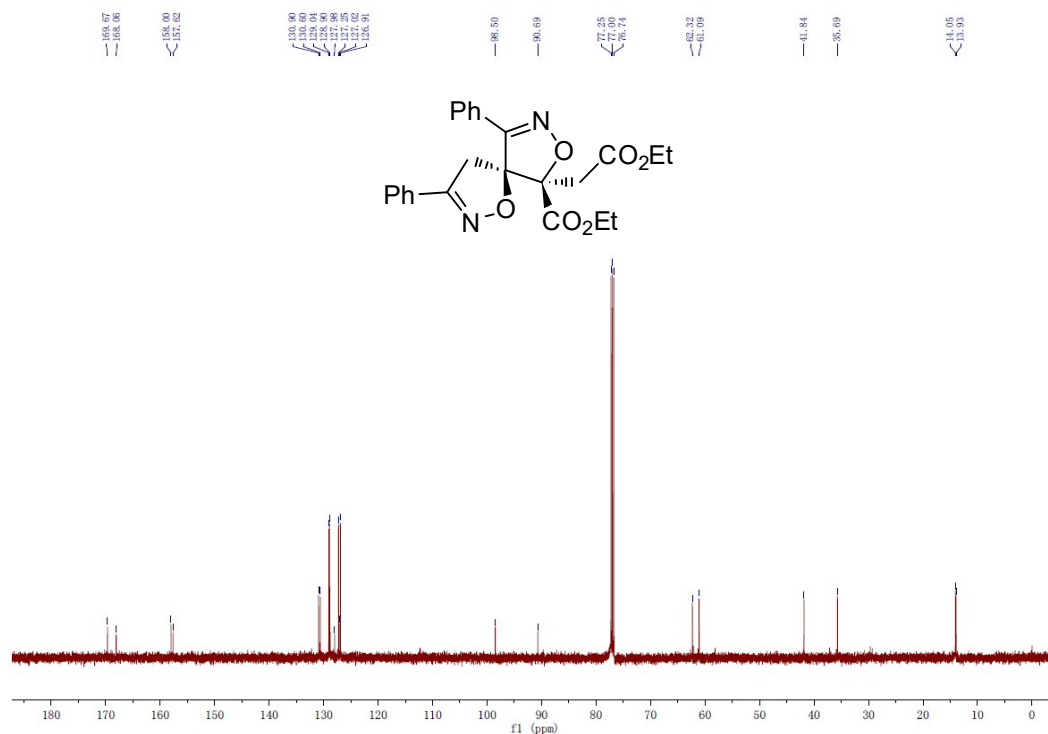
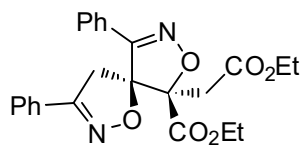
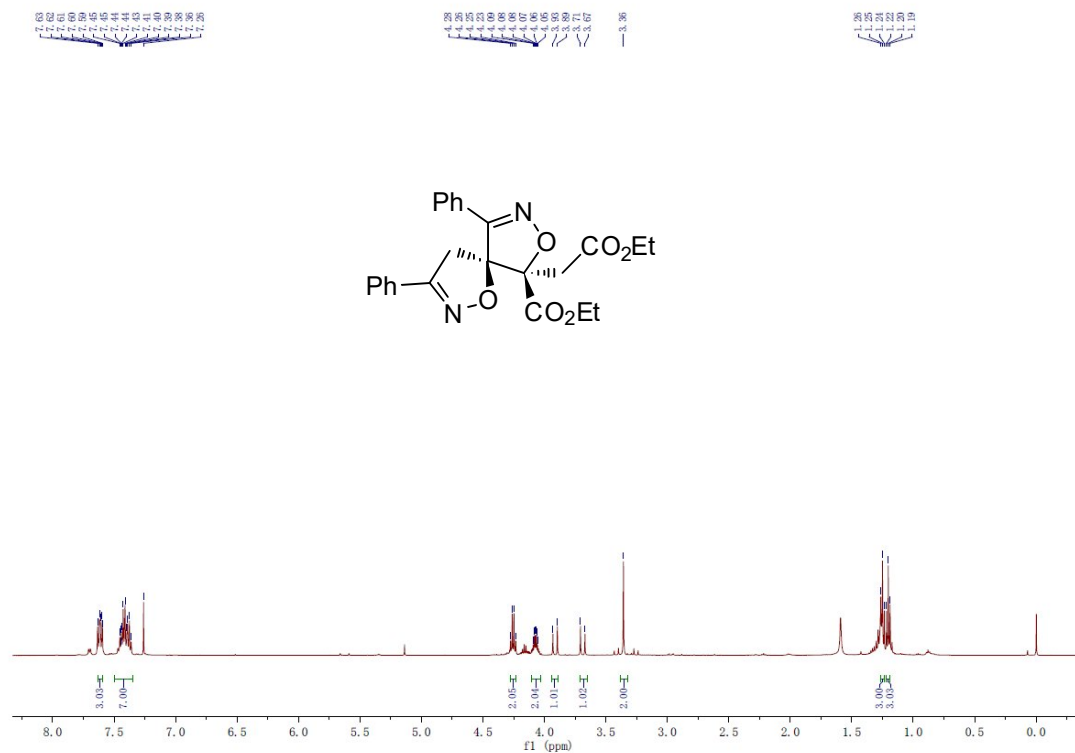


**Ethyl 6-ethyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3aj)**

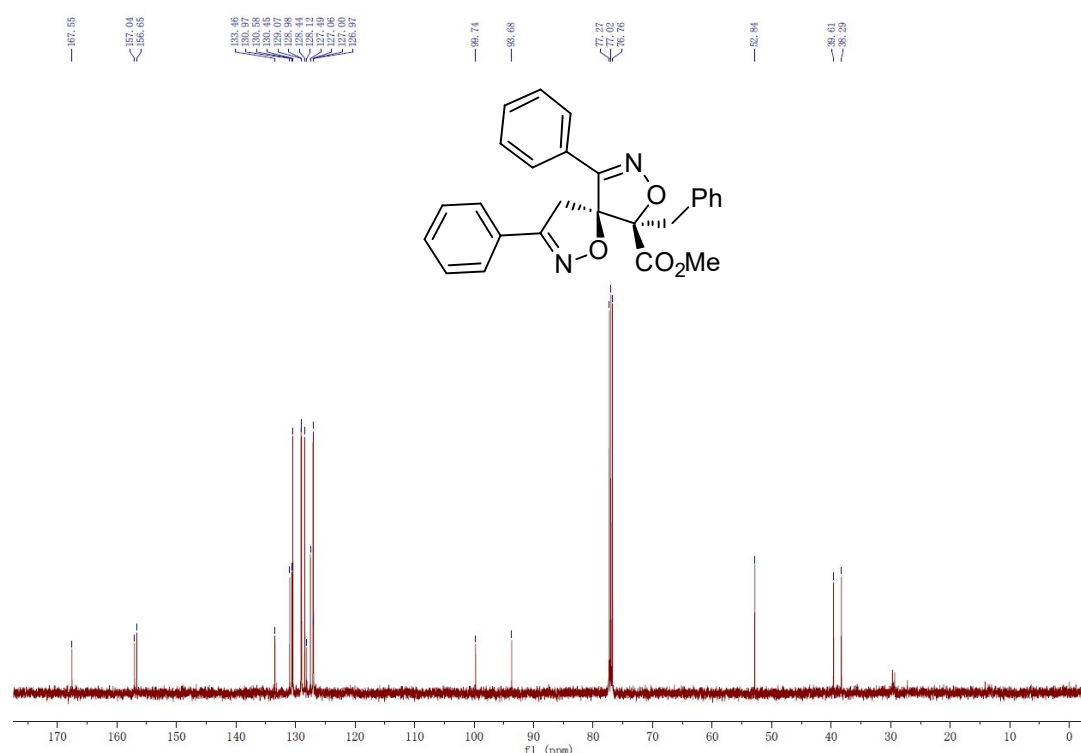
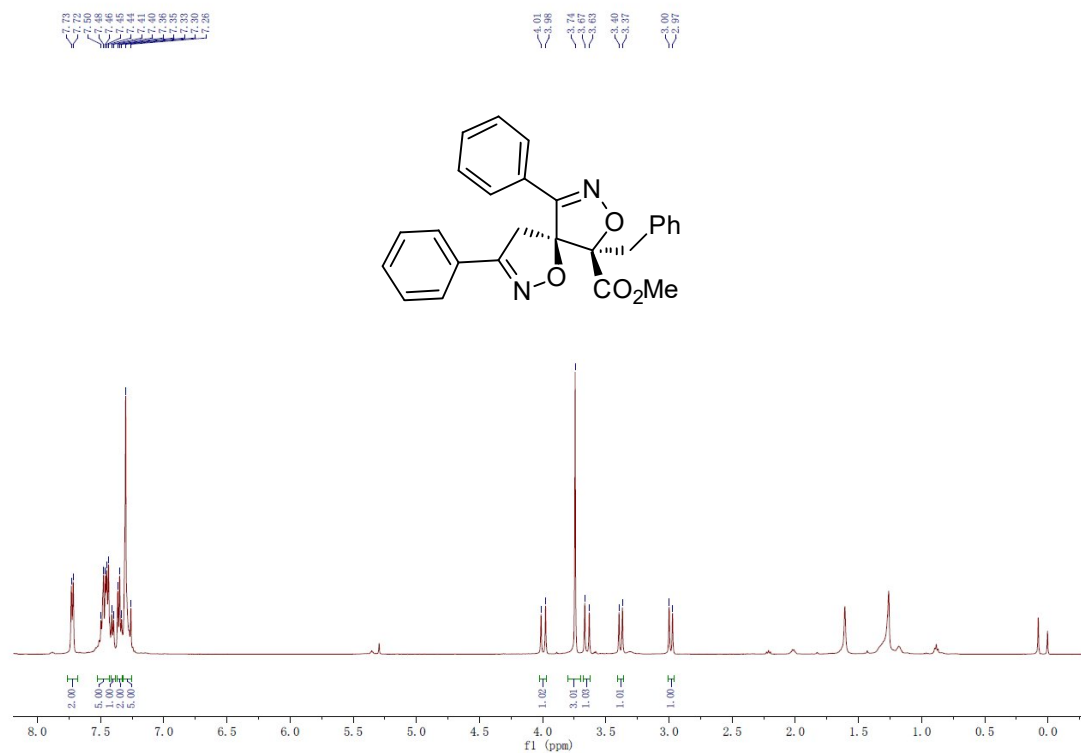




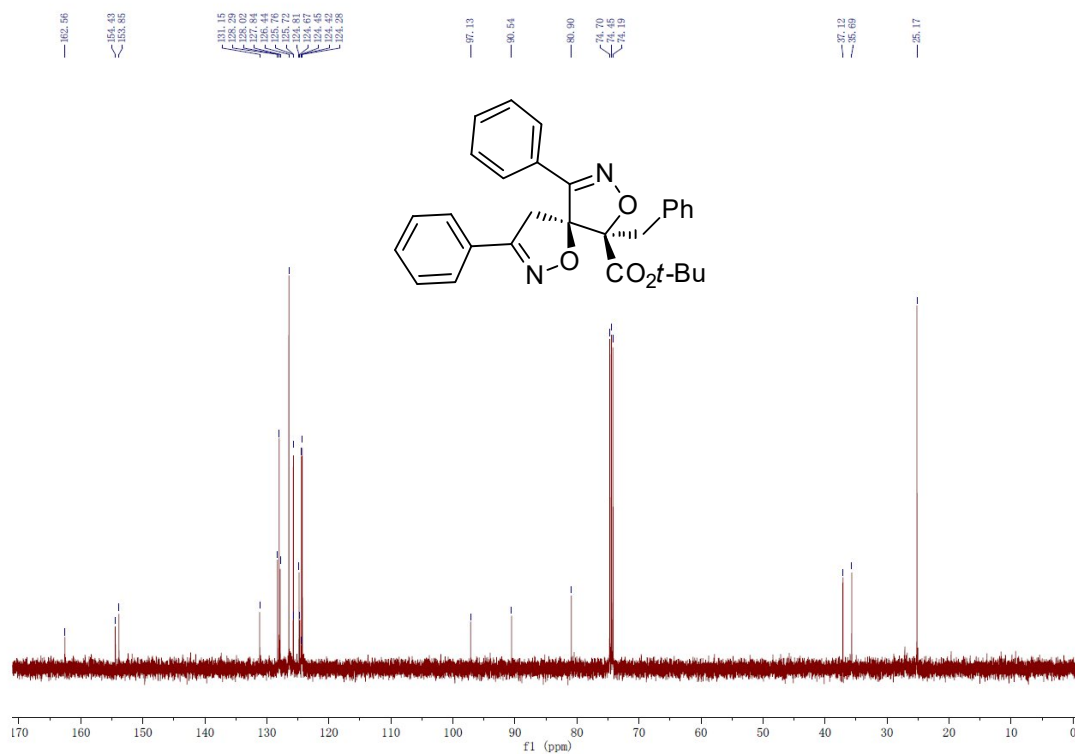
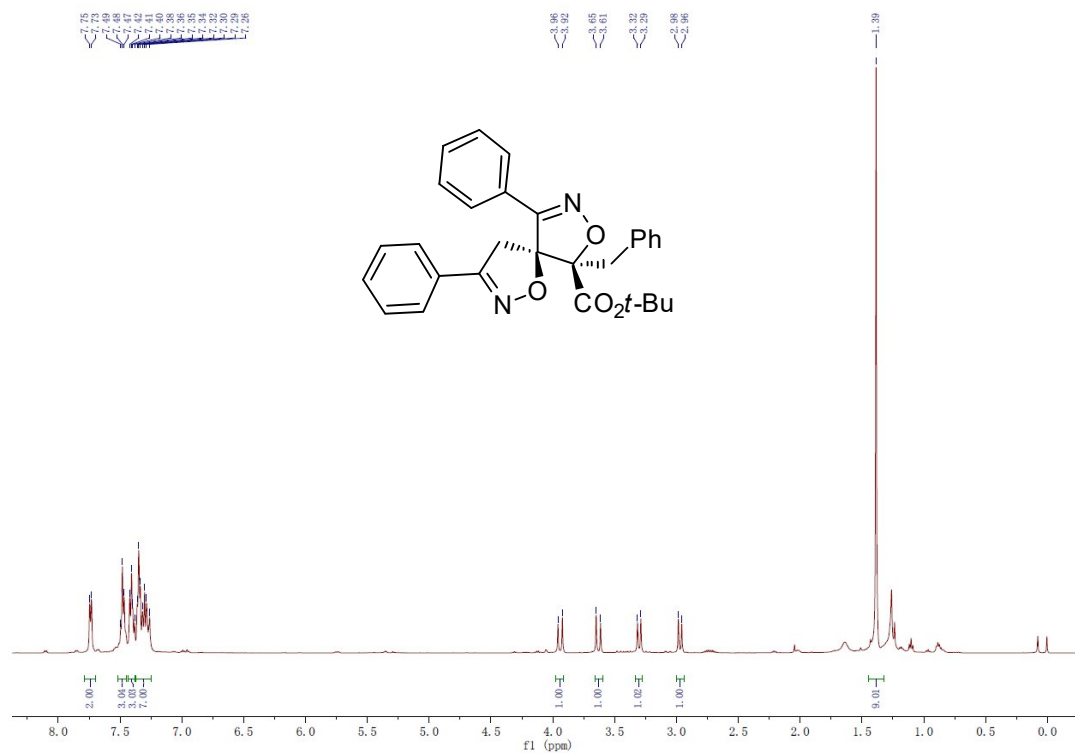
# Ethyl 6-(2-ethoxy-2-oxoethyl)-3,9-diphenyl-1,7-dioxaspiro[4.4]nona-2,8-diene-6-carboxylate(3ak)



**Methyl 6-benzyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3al)**

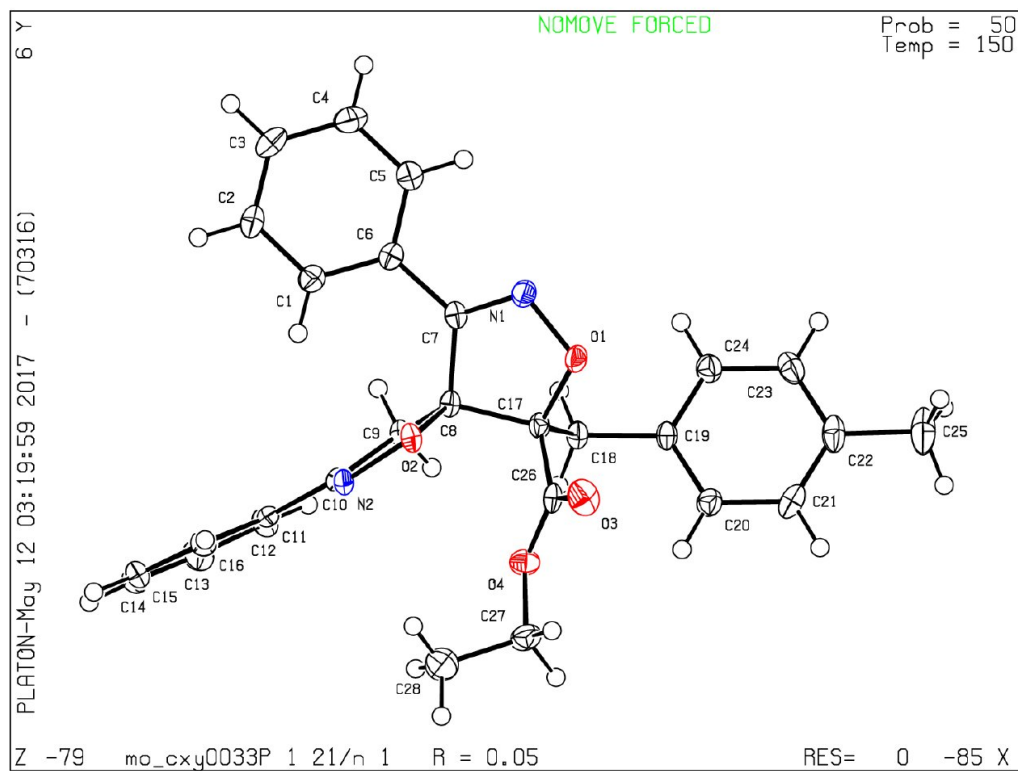


***tert*-Butyl 6-benzyl-3,9-diphenyl-1,7-dioxa-2,8-diazaspiro[4.4]nona-2,8-diene-6-carboxylate (3am)**



## H: Absolute Configuration and X-Ray Analysis Data

Datablock mo\_cxy0033\_0m - ellipsoid plot



### Crystal data and structure refinement for 3ad.

Identification code	<b>3ad</b>
Empirical formula	C <sub>28</sub> H <sub>26</sub> N <sub>2</sub> O <sub>4</sub>
Formula weight	454.51
Temperature/K	150
Crystal system	monoclinic
Space group	P2 <sub>1</sub> /n
a/Å	11.2591(7)
b/Å	10.2596(5)
c/Å	19.9617(11)
α/°	90
β/°	91.988(2)
γ/°	90
Volume/Å <sup>3</sup>	2304.5(2)
Z	4
ρ <sub>calc</sub> /g/cm <sup>3</sup>	1.310
μ/mm <sup>-1</sup>	0.088
F(000)	960.0
Crystal size/mm <sup>3</sup>	0.35 × 0.35 × 0.23
Radiation	MoKα (λ = 0.71073)
2θ range for data collection/°	5.374 to 55.008
Index ranges	-14 ≤ h ≤ 14, -12 ≤ k ≤ 13, -25 ≤ l ≤ 23
Reflections collected	28362
Independent reflections	5292 [R <sub>int</sub> = 0.0594, R <sub>sigma</sub> = 0.0514]
Data/restraints/parameters	5292/0/309
Goodness-of-fit on F <sup>2</sup>	1.031
Final R indexes [I >= 2σ (I)]	R <sub>1</sub> = 0.0488, wR <sub>2</sub> = 0.0981
Final R indexes [all data]	R <sub>1</sub> = 0.0860, wR <sub>2</sub> = 0.1116
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.27

## I: References

1. M. P. Bourbeau, J. T. Rider, *Org. Lett.* **2006**, *8*, 3679-3680.
2. R. Na, C. Jing, Q. Xu, H. Jiang, X. Wu, J. Shi, J. Zhong, M. Wang, D. Benitez, E. Tkatchouk, W. A. Goddard, III, H. Guo, O. Kwon, *J. Am. Chem. Soc.* **2011**, *133*, 13337-13348.