

## Supporting Information

### Copper-Catalyzed Intramolecular C–H Alkoxylation of Diaryltriazaoles: Synthesis of Tricyclic Triazole Benzoxazines

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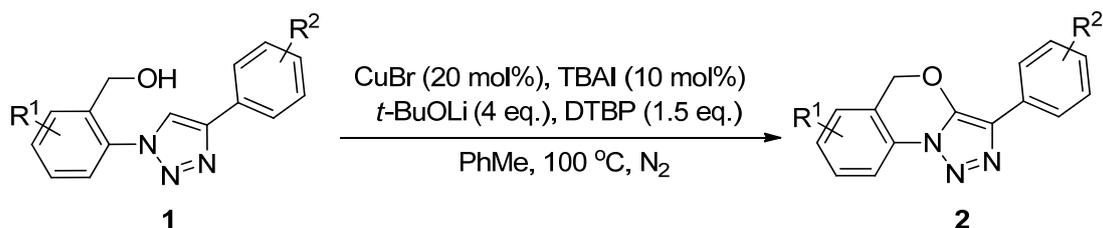
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## I. General Considerations:

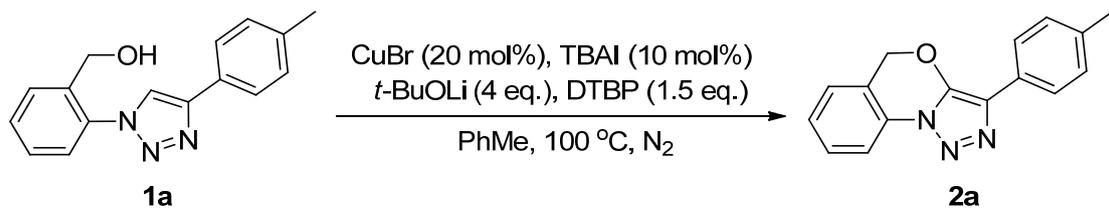
All solvents and reagents were purchased from the suppliers and used without further purification.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded in  $\text{CDCl}_3$  at room temperature on Bruker spectrometer (500 MHz or 600 MHz). The chemical-shifts scale is based on internal TMS. High-resolution mass spectra (HRMS) were equipped with an ESI source and a TOF detector. All reactions were monitored by TLC with HuanghaiGF 254 silica gel coated plates. Column chromatography was carried out using 300–400 mesh silica gel at medium pressure. Infrared spectra were taken on a Bruker Vertex Series FTIR (KBr) and are reported in reciprocal centimeters ( $\text{cm}^{-1}$ ). All reactions were carried out under dry nitrogen atmosphere.

## II. General Procedure for 1,2,3-Triazole Alkoxylation



(2-(4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)phenyl)methanol **1** (0.3 mmol), CuBr (8.6 mg, 0.06 mmol, 0.2 equiv), TBAI (11.1 mg, 0.03 mmol, 0.2 equiv), *t*-BuOLi (96.0 mg, 4.0 equiv), DTBP (65.8 mg, 1.5 equiv) and PhMe (2 mL) were sequentially added to a 15mL branch pipe. Then the tube was sealed and stirred at 100 °C (metal module heating) for 12 h. After consumption of the 1,4-disubstituted 1,2,3-triazoles monitored by TLC analysis,  $\text{H}_2\text{O}$  (15 mL) was added to the mixture and extracted with EtOAc in 3 times (3 x 15mL). The combined organic layers were washed with brine (3 x 5mL), dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with ethyl acetate / petroleum ether (mixture ratio from 1:9 to 1:6) afforded the desired product **2**.

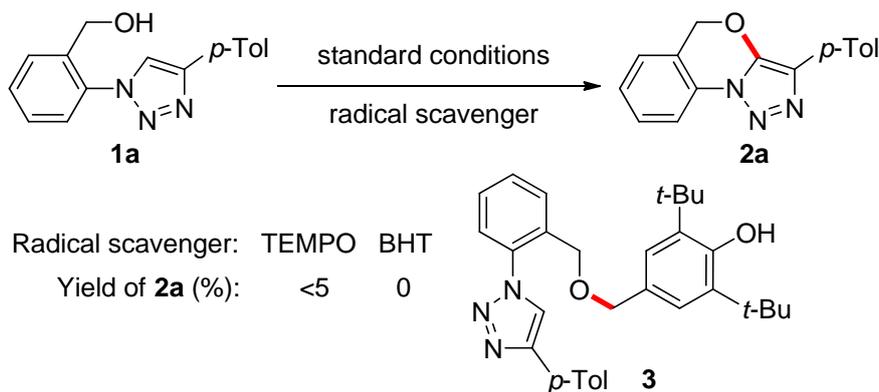
## III. Procedure for the synthesis of 2a on mmol scale



A mixture of (2-(4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)phenyl)methanol **1a** (265mg, 1 mmol), CuBr (29 mg, 0.2 mmol), TBAI (37 mg, 0.1 mmol), *t*-BuOLi (320 mg, 4.0 mmol), DTBP (218 mg, 1.5 mmol) and PhMe (7 mL) stirred at 100 °C (metal module heating) for 12 h. After consumption of the 1,4-disubstituted 1,2,3-triazole as monitored by TLC analysis, the reaction was cooled to room temperature, and  $\text{H}_2\text{O}$  (25 mL) was added. The mixture was extracted with EtOAc (3 x 25 mL), then the combined organic layers were washed with brine (3 x 5 mL), dried with  $\text{Na}_2\text{SO}_4$ , and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with ethyl acetate / petroleum ether (1:8) as eluent afforded product **2a** (205 mg, 0.78 mmol) in 78% yield.

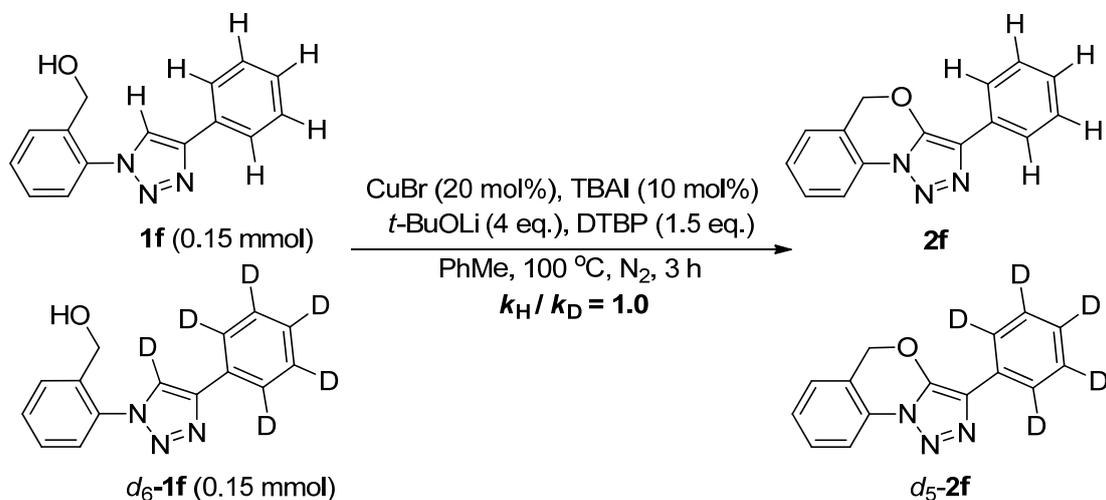
## IV. Mechanistic Studies

### (I) Inhibition of the C-H oxygenation with TEMPO and BHT



(2-(4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)phenyl)methanol **1a** (0.3 mmol), CuBr (8.6 mg, 0.06mmol), TBAI (11.1 mg, 0.03 mmol), *t*-BuOLi (96.0 mg, 4.0 equiv), DTBP (65.8 mg, 1.5 equiv), TEMPO (93.7 mg, 2.0 equiv) or BHT (132.2 mg, 2.0 equiv) in PhMe (2 mL) were sequentially added to a 15mL branch pipe. Then the tube was sealed and stirred at 100 °C for 12 h. Only a trace or no of desired product was detected by TLC. To the reaction involving BHT, H<sub>2</sub>O (15 mL) was added to the mixture and extracted with EtOAc in 3 times (3 x 15mL). The combined organic layers were washed with brine (3 x 5mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with ethyl acetate / petroleum ether (1:9) afforded the product of alkoxy radical trapping **3** (78.4 mg, 54% yield).

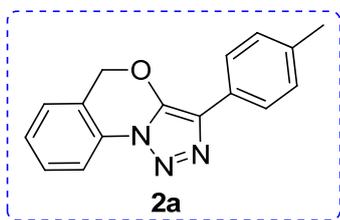
### (II) Kinetic isotope effect experiment



(2-(4-(*p*-Tolyl)-1*H*-1,2,3-triazol-1-yl)phenyl)methanol **1f** (0.15 mmol), *d*<sub>6</sub>-**1f** (0.15 mmol), CuBr (8.6 mg, 0.06 mmol), TBAI (11.1 mg, 0.03 mmol), *t*-BuOLi (96.0 mg, 4.0 equiv), DTBP (65.8 mg, 1.5 equiv) and PhMe (2 mL) were sequentially added to a 15 mL branch pipe. Then the tube was sealed and stirred at 100 °C for 3 h. After consumption of the 1,4-disubstitued 1,2,3-triazoles monitored by TLC analysis, H<sub>2</sub>O (15 mL) was added to the mixture and extracted with EtOAc in 3 times (3 x 15 mL). The combined organic layers were washed with brine (3 x 5mL), dried with Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure to afford the crude product. Purification by column chromatography on silica gel with EtOAc/Petroleum Ether (1:8) afforded the mixture product of **2f** and *d*<sub>5</sub>-**2f**. The ratio of which was determined by <sup>1</sup>H NMR as about 1.0.

## V. Characterization Data

### 3-(*p*-Tolyl)-5*H*-benzo[*d*][1,2,3]triazolo[5,1-*b*][1,3]oxazine (2a)



Orange crystals, 67.9 mg, 86% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 145-146 °C;

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 (d, *J* = 8.0 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 2H),

7.51 (t, *J* = 7.8 Hz, 1H), 7.37 (t, *J* = 7.6 Hz, 1H), 7.29 (d, *J* = 7.6 Hz, 1H), 7.25 (d,

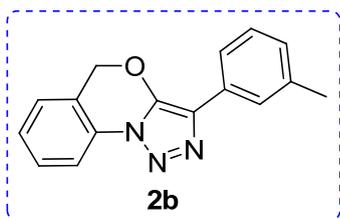
*J* = 7.2 Hz, 2H), 5.44 (s, 2H), 2.39 (s, 3H);

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 143.7, 137.1, 131.3, 129.9, 129.4, 128.2, 127.7, 127.1, 125.1, 125.0, 120.0, 115.5, 69.2, 21.3;

HRMS (ESI) *m/z*: calcd for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O [M + H]<sup>+</sup>: 264.1131, found: 264.1134;

IR (KBr) ν (cm<sup>-1</sup>): 3430, 2920, 1598, 1502, 1381, 1130, 1081, 977, 824, 755 cm<sup>-1</sup>.

### 3-(*m*-Tolyl)-5*H*-benzo[*d*][1,2,3]triazolo[5,1-*b*][1,3]oxazine (2b)



Yellow crystals, 57.6 mg, 73% yield: (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 123-126 °C;

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 8.0 Hz, 1H), 7.82 (s, 1H), 7.77 (d, *J* =

7.7 Hz, 1H), 7.52 (dd, *J* = 11.5, 4.0 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 1H), 7.33 (t, *J* =

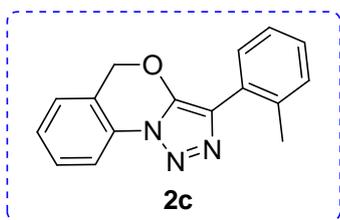
7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 5.45 (s, 2H), 2.42 (s, 3H);

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 144.0, 138.4, 131.3, 130.0, 129.8, 128.6, 128.2, 127.8, 125.8, 125.0, 122.3, 120.0, 115.5, 69.2, 21.6;

HRMS (ESI) *m/z*: calcd for C<sub>16</sub>H<sub>13</sub>N<sub>3</sub>O [M + H]<sup>+</sup>: 264.1131, found: 264.1134;

IR (KBr) ν (cm<sup>-1</sup>): 3429, 2920, 1608, 1500, 1450, 1359, 1206, 1129, 1086, 1058, 978, 753, 689 cm<sup>-1</sup>.

### 3-(*o*-Tolyl)-5*H*-benzo[*d*][1,2,3]triazolo[5,1-*b*][1,3]oxazine (2c)



Yellow crystals, 51.3 mg, 65% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 105-106 °C;

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.57-7.55 (m, 1H), 7.53

(t, *J* = 7.8 Hz, 1H), 7.38 (td, *J* = 7.6, 0.8 Hz, 1H), 7.30-7.27 (m, 4H), 5.39 (s, 2H),

2.50 (s, 3H);

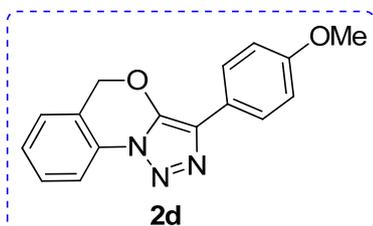
<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 144.2, 136.8, 131.4, 130.8, 130.0, 129.4, 128.9, 128.6, 128.2, 127.8, 125.8, 125.0,

120.1, 115.5, 69.1, 20.7;

HRMS (ESI)  $m/z$ : calcd for  $C_{16}H_{13}N_3O$   $[M + H]^+$ : 264.1131, found: 264.1133;

IR (KBr)  $\nu$  ( $cm^{-1}$ ): 3929, 2922, 2856, 1594, 1493, 1444, 1378, 1127, 1086, 978, 759  $cm^{-1}$ .

### 3-(4-Methoxyphenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2d)



Orange crystals, 62.8 mg, 75% yield: (eluent: ethyl acetate / petroleum ether = 1:7); m.p.: 128-129 °C;

$^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.02 (d,  $J$  = 8.0 Hz, 1H), 7.92-7.88 (m, 2H), 7.52 (t,  $J$  = 7.9 Hz, 1H), 7.37 (t,  $J$  = 7.5 Hz, 1H), 7.30 (d,  $J$  = 7.7 Hz, 1H),

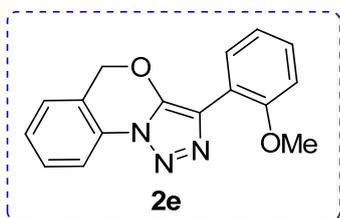
7.02-6.96 (m, 2H), 5.44 (s, 2H), 3.85 (s, 3H);

$^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  158.9, 143.3, 131.3, 130.0, 128.1, 127.7, 126.5, 125.0, 122.7, 120.0, 115.5, 114.1, 69.2, 55.3;

HRMS (ESI)  $m/z$ : calcd for  $C_{16}H_{13}N_3O_2$   $[M + H]^+$ : 280.1081, found: 280.1085;

IR (KBr)  $\nu$  ( $cm^{-1}$ ): 3443, 2943, 2797, 1605, 1540, 1318, 1212, 1095, 928, 784, 710  $cm^{-1}$ .

### 3-(2-Methoxyphenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2e)



Yellow oil, 51.9 mg, 62% yield (eluent: ethyl acetate / petroleum ether = 1:7);

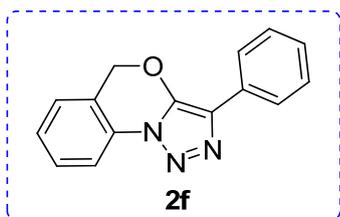
$^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.04 (d,  $J$  = 8.0 Hz, 1H), 7.67 (dd,  $J$  = 7.5, 1.4 Hz, 1H), 7.52 (t,  $J$  = 7.7 Hz, 1H), 7.37 (t,  $J$  = 7.6 Hz, 2H), 7.28 (d,  $J$  = 7.5 Hz, 1H), 7.06 (t,  $J$  = 7.5 Hz, 1H), 7.00 (d,  $J$  = 8.3 Hz, 1H), 5.37 (s, 2H), 3.88 (s, 3H);

$^{13}C$  NMR (150 MHz,  $CDCl_3$ )  $\delta$  156.7, 144.7, 131.5, 130.2, 129.9, 129.6, 128.7, 127.7, 125.0, 120.8, 120.4, 118.8, 115.6, 111.4, 69.0, 55.9;

HRMS (ESI)  $m/z$ : calcd for  $C_{16}H_{13}N_3O_2$   $[M + H]^+$ : 280.1081, found: 280.1083;

IR (KBr)  $\nu$  ( $cm^{-1}$ ): 3400, 2923, 2849, 1597, 1497, 1361, 1248, 1035, 756, 693  $cm^{-1}$ .

### 3-Phenyl-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2f)



Yellow crystals, 50.9 mg, 68% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 145-148 °C;

$^1H$  NMR (600 MHz,  $CDCl_3$ )  $\delta$  8.02 (d,  $J$  = 8.0 Hz, 1H), 7.98 (d,  $J$  = 7.7 Hz, 2H), 7.52 (t,  $J$  = 7.8 Hz, 1H), 7.45 (t,  $J$  = 7.6 Hz, 2H), 7.38 (t,  $J$  = 7.5 Hz, 1H), 7.31

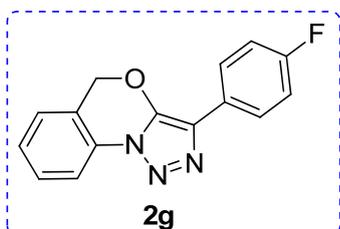
(dd,  $J$  = 11.6, 4.1 Hz, 2H), 5.46 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.0, 131.2, 130.0, 129.9, 128.7, 128.1, 127.8, 127.4, 125.2, 125.0, 119.9, 115.5, 69.3;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{11}\text{N}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 250.0975, found: 250.0974;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3430, 1600, 1502, 1360, 1130, 1079, 977, 765, 696  $\text{cm}^{-1}$ .

### 3-(4-Fluorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2g)



Yellow powder, 58.5 mg, 73% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 132-134  $^{\circ}\text{C}$ ;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.00 (d,  $J = 8.0$  Hz, 1H), 7.96-7.91 (m, 2H), 7.50 (d,  $J = 7.5$  Hz, 1H), 7.38 (td,  $J = 7.6, 0.9$  Hz, 1H), 7.30 (d,  $J = 7.4$  Hz, 1H),

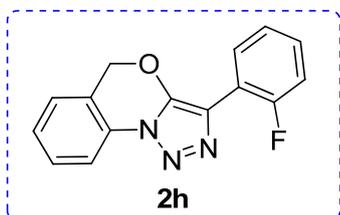
7.16-7.09 (m, 2H), 5.45 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0 ( $J = 245$  Hz), 143.7, 131.1, 130.0, 127.9, 127.3, 126.8 (d,  $J = 8.0$  Hz), 126.1 (d,  $J = 3.2$  Hz), 125.0, 119.8, 115.7, 115.5 (d,  $J = 18.9$  Hz), 69.3;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{10}\text{FN}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 268.0881, found: 268.0883;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3429, 2925, 1601, 1505, 1384, 1354, 1087, 1038, 961, 882, 789, 752, 685  $\text{cm}^{-1}$ .

### 3-(2-Fluorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2h)



Yellow powder, 56.9 mg, 71% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 136-137  $^{\circ}\text{C}$ ;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 8.0$  Hz, 1H), 7.87 (td,  $J = 7.5, 1.7$  Hz, 1H), 7.53 (t,  $J = 7.7$  Hz, 1H), 7.41-7.37 (m, 1H), 7.35 (dd,  $J = 8.1, 2.0$  Hz, 1H),

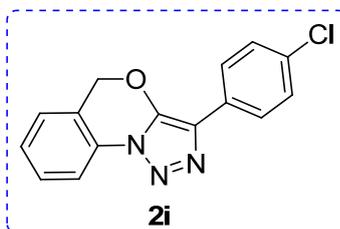
7.30 (d,  $J = 7.5$  Hz, 1H), 7.24 (dd,  $J = 7.5, 0.9$  Hz, 1H), 7.20-7.14 (m, 1H), 5.43 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  159.3 (d,  $J = 249$  Hz), 144.7, 131.3, 130.0, 129.6 (d,  $J = 7.5$  Hz), 129.5 (d,  $J = 3.6$  Hz), 127.9, 125.0, 124.3 (d,  $J = 3.5$  Hz), 124.1, 120.1, 117.7 (d,  $J = 14.5$  Hz), 116.0 (d,  $J = 21.4$  Hz), 115.6, 69.2;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{10}\text{FN}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 268.0881, found: 268.0878;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3401, 2971, 2923, 1594, 1496, 1447, 1383, 1090, 1051, 756  $\text{cm}^{-1}$ .

### 3-(4-Chlorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2i)



Yellow powder, 56.2mg, 66% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 176-180  $^{\circ}\text{C}$ ;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.0$  Hz, 1H), 7.92 (d,  $J = 8.4$  Hz, 2H), 7.53 (t,  $J = 7.7$  Hz, 1H), 7.41 (d,  $J = 8.4$  Hz, 2H), 7.39 (t,  $J = 7.2$  Hz, 1H), 7.31

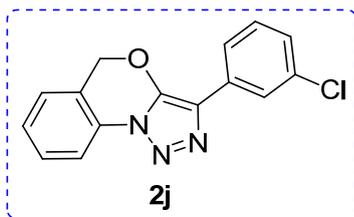
(d,  $J = 7.6$  Hz, 1H), 5.47 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.1, 133.0, 131.1, 130.1, 128.9, 128.5, 128.0, 127.2, 126.3, 125.0, 119.8, 115.5, 69.3;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{10}\text{ClN}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 284.0585, found: 284.0587

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3405, 2975, 1599, 1388, 1087, 1050, 882, 763  $\text{cm}^{-1}$ .

### 3-(3-Chlorophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2j)



White crystals, 64.7 mg, 76% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 163-164 °C;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (d,  $J = 8.0$  Hz, 1H), 7.95 (t,  $J = 1.7$  Hz, 1H), 7.87-7.85 (m, 1H), 7.51 (t,  $J = 7.7$  Hz, 1H), 7.39-7.34 (m, 2H), 7.30-7.25 (m,

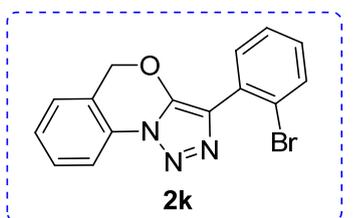
2H), 5.47 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 134.7, 131.7, 131.0, 130.1, 130.0, 128.0, 127.3, 126.9, 125.0, 125.0, 123.1, 119.7, 115.5, 69.4;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{10}\text{ClN}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 284.0585, found: 284.0589

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3425, 2924, 1589, 1504, 1452, 1382, 1210, 953, 838, 760, 598, 520  $\text{cm}^{-1}$ .

### 3-(2-Bromophenyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2k)



Yellow powder, 40.4 mg, 41% yield (eluent: ethyl acetate / petroleum ether = 1:8); m.p.: 120-122 °C;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 (d,  $J = 8.0$  Hz, 1H), 7.69 (d,  $J = 8.1$  Hz, 1H), 7.61 (dd,  $J = 7.7, 1.6$  Hz, 1H), 7.54 (t,  $J = 7.8$  Hz, 1H), 7.41 (td,  $J = 7.6, 1.0$  Hz,

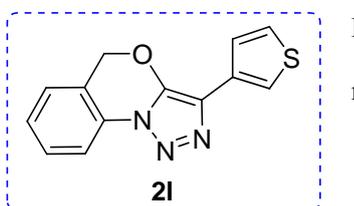
1H), 7.39 (t,  $J = 7.6$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 7.28-7.24 (m, 1H), 5.43 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  144.3, 133.2, 131.8, 131.3, 130.6, 130.0, 129.9, 128.4, 127.9, 127.4, 125.1, 122.9, 120.2, 115.6, 68.9;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{15}\text{H}_{10}\text{BrN}_3\text{O}$   $[\text{M} + \text{H}]^+$ : 328.0080, found: 328.0082;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3426, 2921, 2854, 1612, 1500, 1382, 1067, 982, 761  $\text{cm}^{-1}$ .

### 3-(Thiophen-3-yl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2l)



Brown crystals, 49.8 mg, 65% yield (eluent: ethyl acetate / petroleum ether = 1:6); m.p.: 124-125 °C;

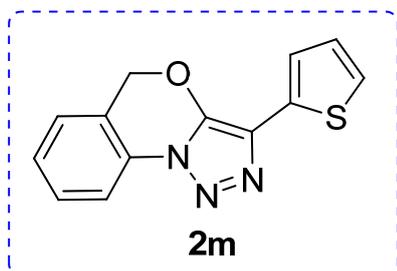
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.02 (d,  $J = 8.0$  Hz, 1H), 7.70 (dd,  $J = 3.0, 1.1$  Hz, 1H), 7.66 (dd,  $J = 5.0, 1.1$  Hz, 1H), 7.53-7.50 (m, 1H), 7.40 (dd,  $J = 5.0, 3.0$  Hz, 1H), 7.38 (td,  $J = 7.6, 0.9$  Hz, 1H), 7.30 (d,  $J = 7.6$  Hz, 1H), 5.45 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.3, 131.2, 130.5, 130.0, 127.8, 125.9, 125.6, 125.3, 125.0, 120.1, 119.9, 115.5, 69.3;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{13}\text{H}_9\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$ : 256.0539, found: 256.0541;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3428, 2923, 1607, 1503, 1367, 1079, 980, 773, 619  $\text{cm}^{-1}$ .

### 3-(Thiophen-2-yl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2m)



Brown crystals, 30.6 mg, 40% yield (eluent: ethyl acetate / petroleum ether = 1:6); 146-148  $^{\circ}\text{C}$ ;

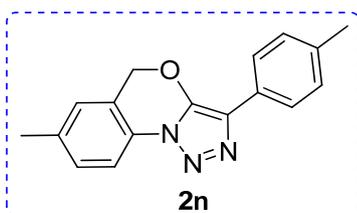
$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  8.01 (d,  $J = 8.0$  Hz, 1H), 7.51 (t,  $J = 7.8$  Hz, 1H), 7.43 (dd,  $J = 3.5, 1.1$  Hz, 1H), 7.38 (td,  $J = 7.6, 0.9$  Hz, 1H), 7.32-7.28 (m, 2H), 7.11 (dd,  $J = 5.0, 3.6$  Hz, 1H), 5.47 (s, 2H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  142.7, 131.6, 131.1, 130.0, 127.9, 127.5, 125.0, 124.8, 124.3, 123.5, 119.8, 115.5, 69.4;

HRMS (ESI)  $m/z$ : calcd for  $\text{C}_{13}\text{H}_9\text{N}_3\text{OS}$   $[\text{M} + \text{H}]^+$ : 256.0539, found: 256.0542;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3431, 2922, 2854, 1605, 1497, 1452, 1375, 1085, 976, 815, 760, 701  $\text{cm}^{-1}$ .

### 7-Methyl-3-(*p*-tolyl)-5H-benzo[d][1,2,3]triazolo[5,1-b][1,3]oxazine (2n)



Orange crystals, 53.2 mg, 64% yield (eluent: ethyl acetate / petroleum ether = 1:9); m.p.: 161-162  $^{\circ}\text{C}$ ;

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  7.89 (d,  $J = 8.1$  Hz, 1H), 7.86 (d,  $J = 8.1$  Hz, 2H), 7.30 (d,  $J = 8.1$  Hz, 1H), 7.27-7.23 (m, 2H), 7.09 (s, 1H), 5.39 (s, 2H),

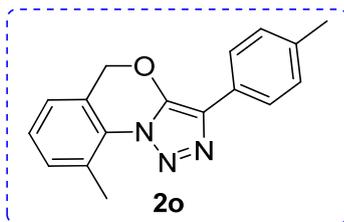
2.41 (s, 3H), 2.38 (s, 3H);

$^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  143.5, 137.9, 137.1, 130.4, 129.3, 129.0, 128.2, 127.2, 125.4, 125.0, 119.9, 115.3, 69.2, 21.3, 21.3;

HRMS (ESI)  $m/z$   $[\text{M} + \text{H}]^+$ : calcd for  $\text{C}_{17}\text{H}_{15}\text{N}_3\text{O}$ : 278.1288, found: 278.1285;

IR (KBr)  $\nu$  ( $\text{cm}^{-1}$ ): 3428, 2919, 1596, 1511, 1392, 1236, 986, 819, 516  $\text{cm}^{-1}$ .

### 9-Methyl-3-(*p*-tolyl)-5*H*-benzo[*d*][1,2,3]triazolo[5,1-*b*][1,3]oxazine (2o)



Yellow crystals, 54.9 mg, 66% yield (eluent: ethyl acetate / petroleum ether = 1:9); m.p.: 110-111 °C;

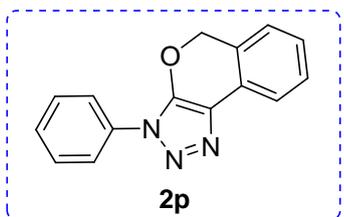
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.89 (d, *J* = 8.0 Hz, 2H), 7.35 (d, *J* = 7.7 Hz, 1H), 7.28-7.24 (m, 3H), 7.14 (d, *J* = 7.4 Hz, 1H), 5.34 (s, 2H), 2.84 (s, 3H), 2.39 (s, 3H);

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 144.7, 137.1, 133.3, 130.5, 129.4, 128.5, 127.2, 127.1, 125.1, 122.7, 121.8, 69.9, 21.3, 21.3;

HRMS (ESI) *m/z*: calcd for C<sub>17</sub>H<sub>15</sub>N<sub>3</sub>O [M + H]<sup>+</sup>: 278.1288, found: 278.1289;

IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3429, 3019, 2921, 2856, 1597, 1508, 1462, 1378, 1032, 979, 819, 767, 517 cm<sup>-1</sup>.

### 3-Phenyl-3,5-dihydroisochromeno[3,4-*d*][1,2,3]triazole (2p)



Yellow oil, 29.9 mg, 40% yield (eluent: ethyl acetate / petroleum ether = 1:8);

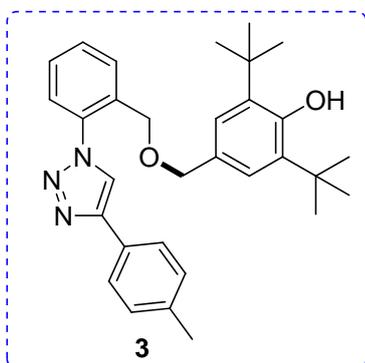
<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 7.87 (d, *J* = 7.6 Hz, 1H), 7.85-7.82 (m, 2H), 7.53 (t, *J* = 8.0 Hz, 2H), 7.42 (dt, *J* = 13.9, 4.1 Hz, 2H), 7.29-7.24 (m, 1H), 7.16 (d, *J* = 7.5 Hz, 1H), 5.55 (s, 2H);

<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 135.3, 129.7, 129.4, 129.3, 128.5, 128.3, 127.3, 126.8, 126.0, 124.5, 120.9, 120.5, 73.7;

HRMS (ESI) *m/z*: calcd for C<sub>15</sub>H<sub>11</sub>N<sub>3</sub>O [M + H]<sup>+</sup>: 250.0975, found: 250.0978;

IR (KBr)  $\nu$  (cm<sup>-1</sup>): 3432, 2929, 1670, 1581, 1464, 1387, 1210, 1135, 1049, 805, 722, 643 cm<sup>-1</sup>.

### 2,6-Di-*tert*-butyl-4-(((2-(4-(*p*-tolyl)-1*H*-1,2,3-triazol-1-yl)benzyl)oxy)methyl)phenol (3)



Yellow oil, 73.4 mg, 54% yield (eluent: ethyl acetate / petroleum ether = 1:9);

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.19 (s, 1H), 7.79 (d, *J* = 8.0 Hz, 2H), 7.68 – 7.67 (m, 1H), 7.54-7.51 (m, 2H), 7.49 – 7.47 (m, 1H), 7.26 (d, *J* = 7.9 Hz, 2H), 7.12 (s, 2H), 5.22 (s, 1H), 4.51 (s, 2H), 4.42 (s, 2H), 2.40 (s, 3H), 1.41 (s, 18H);

<sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 153.8, 147.9, 138.3, 136.3, 136.0, 133.2, 130.8, 129.9, 129.7, 129.0, 128.2, 127.6, 125.8, 125.3, 121.5, 73.7, 68.3, 34.4, 30.3,

21.5;

HRMS (ESI) *m/z*: calcd for C<sub>31</sub>H<sub>37</sub>N<sub>3</sub>O<sub>2</sub> [M + H]<sup>+</sup>: 484.2959, found: 484.2962.

## VI. Crystal data and structure of compound 2a

### Sample preparation and crystal measurement

Single crystal suitable for X-ray diffraction experiment was obtained by slow evaporation of CH<sub>2</sub>Cl<sub>2</sub> solution of **2a**. The data was collected at 293(2) K with an Xcalibur Eos Gemini diffractometer using graphite monochromatized enhanced X-ray source Mo-K $\alpha$  ( $\lambda=0.71073$  Å) radiation. CrysAlisPro was used for both data collection and processing. The intensities were corrected for absorption using empirical model implemented in SCALE3 ABSPACK scaling algorithm.

CCDC 1881658 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre.

### Crystal data:

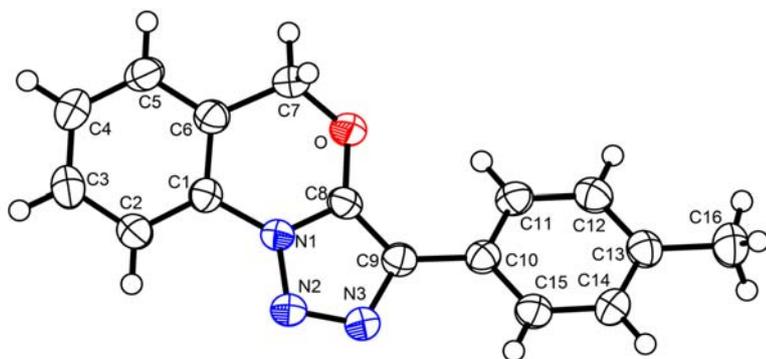
Bond precision: C-C = 0.0030 Å      Wavelength=0.71073

Cell: a = 12.837(2)    b = 7.3480(14)    c = 13.864(3)

Alpha = 90    beta = 105.977(5)    gamma = 90

Temperature: 293 K

	Calculated	Reported
Volume	1257.2(4)	1257.3(4)
Space group	P 21/n	P 21/n
Hall group	-P 2yn	-P 2yn
Sum formula	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O	C <sub>16</sub> H <sub>13</sub> N <sub>3</sub> O
Mr	263.29	265.31
D <sub>x</sub> ,g cm <sup>-3</sup>	1.391	1.402
Z	4	4
Mu (mm <sup>-1</sup> )	0.090	0.091
F000	552.0	560.0
F000'	552.21	
h,k,lmax	14,8,15	14,8,15
Nref	1831	1823
Data completeness = 0.996		Theta(max) = 23.351
R(reflections) = 0.0377( 1441)		wR2(reflections) = 0.0997( 1823)
S = 1.040    Npar = 182		

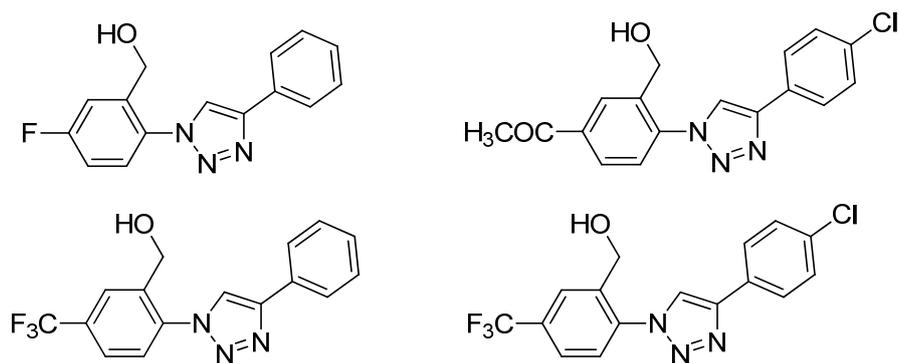


## VII. Determination of Minimum Inhibitory Concentrations (MIC)

Minimum inhibitory concentrations (MICs) of compounds were determined by microbroth dilution technique as described by a modified described method. The concentrations of conidial suspensions were adjusted to be  $1 \times 10^4$  spores/ mL for each fungus in a 1/4 liquid PDA growth medium. Each compound was dissolved in DMSO with the initial concentration of 6 mg/mL. A mixture formed from 4  $\mu$ L samples and 156  $\mu$ L conidial suspensions in the first row of a 96-cell microtiter plate, and then diluted two-fold with the same solution to adjust the concentration to 150–0.29  $\mu$ g/mL. Hymexazol, flutriafol, gronoverbeteraar and propamocarb were used as positive controls. The plates, securely sealed with a polyester sealing film (VWR) were incubated in a fungal incubator at 28 °C for 36 h, and the absorbance of each well was measured at 595 nm by an enzyme-labeled instrument. Each treatment was repeated five times and cultured in a microorganism incubator at 28 °C. The MIC was defined as the lowest concentration of the compound producing complete inhibition of visible growth.

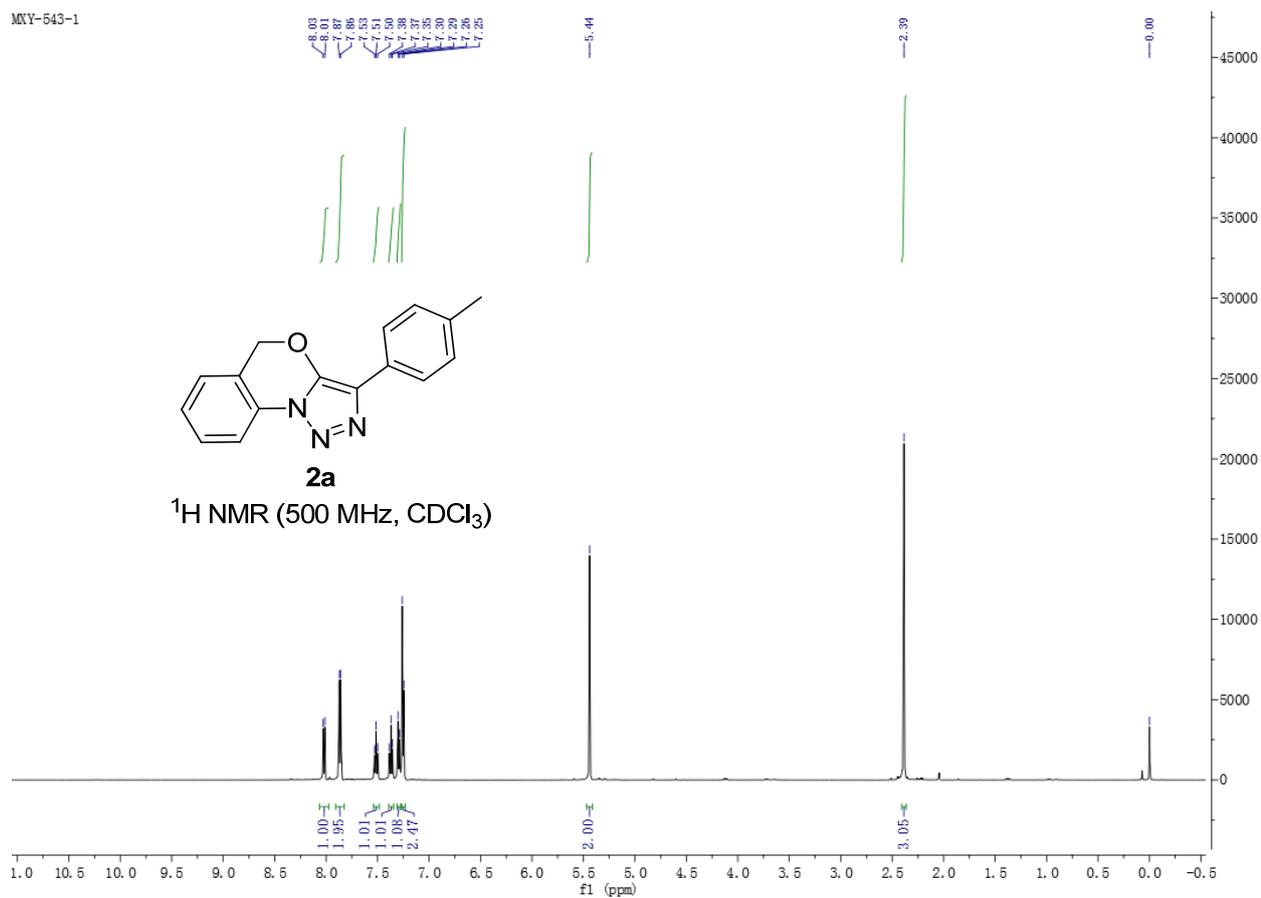
## VIII. Unsuccessful substrates

In the reactions of substrates shown below, only a trace of product was detected.

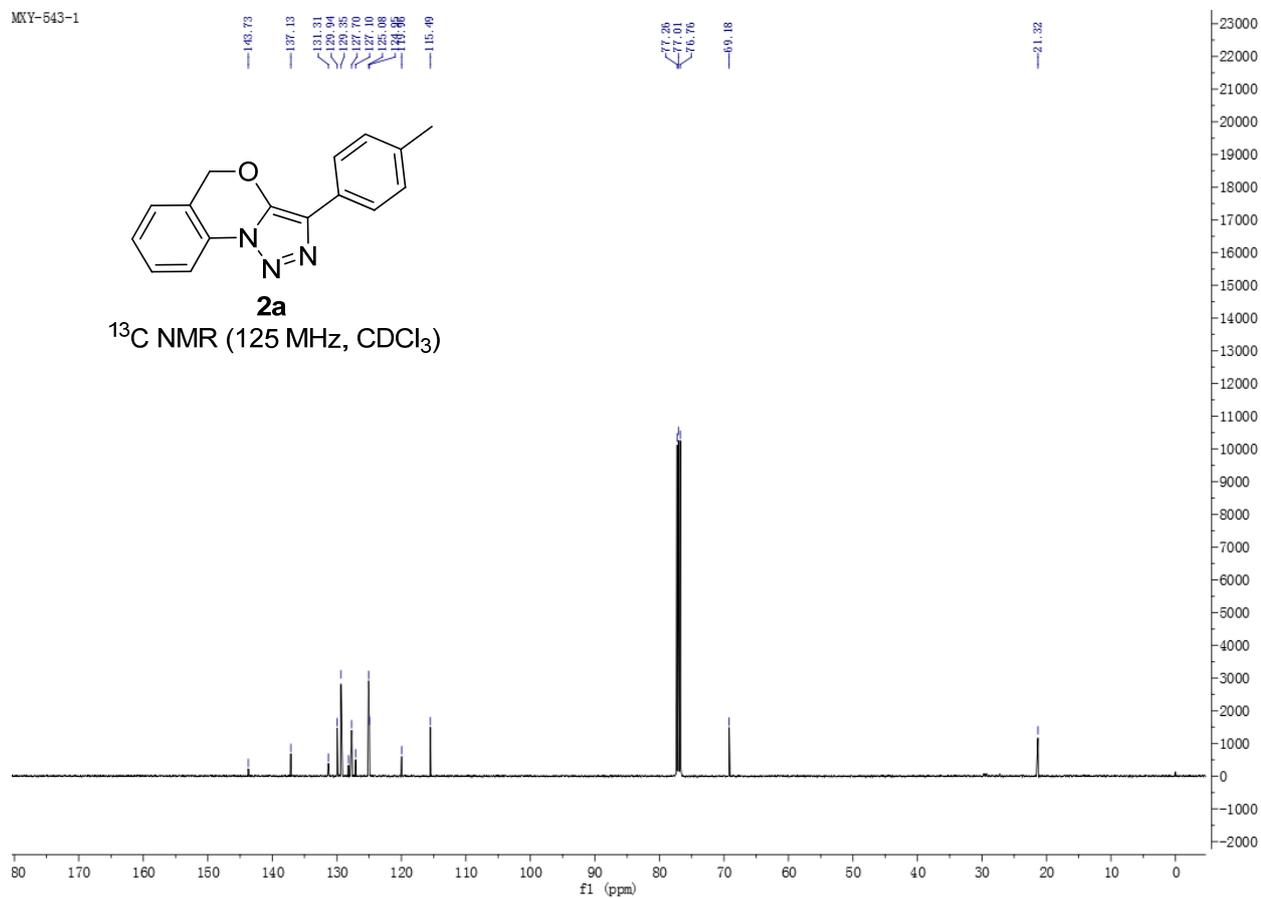


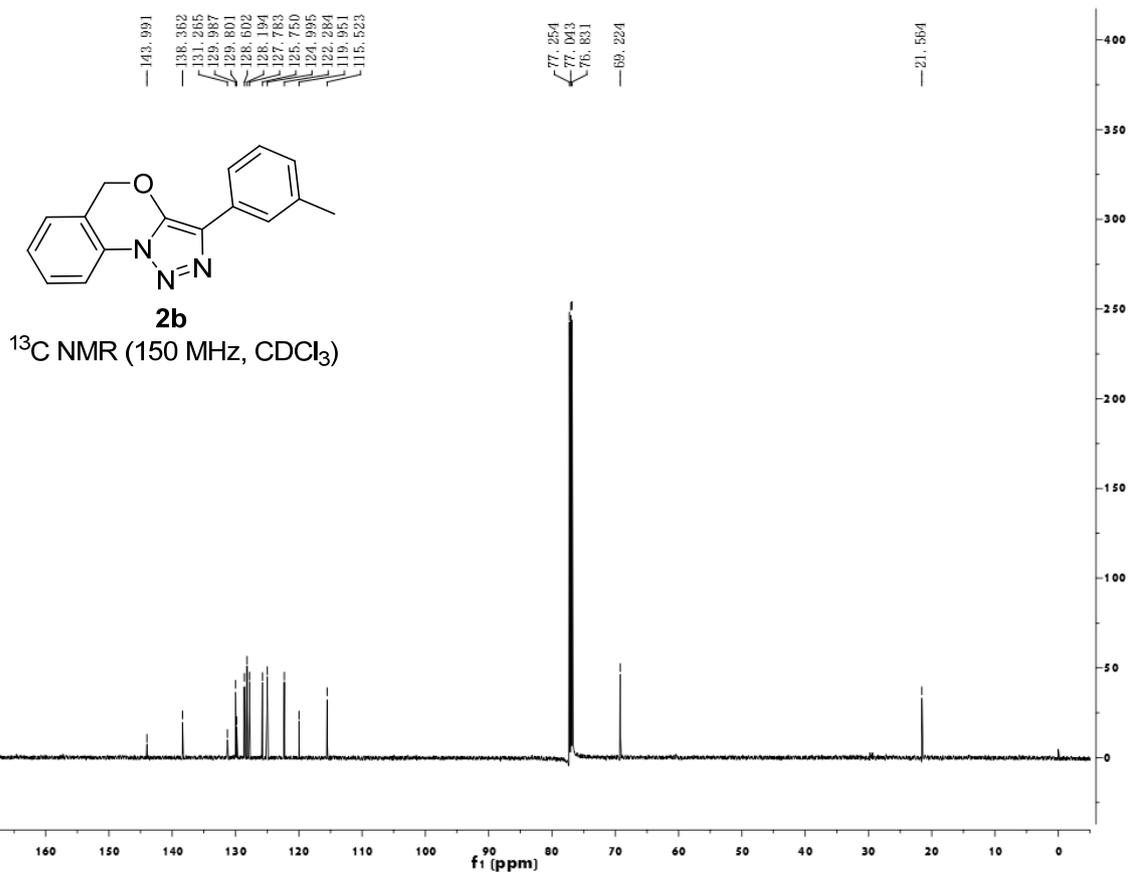
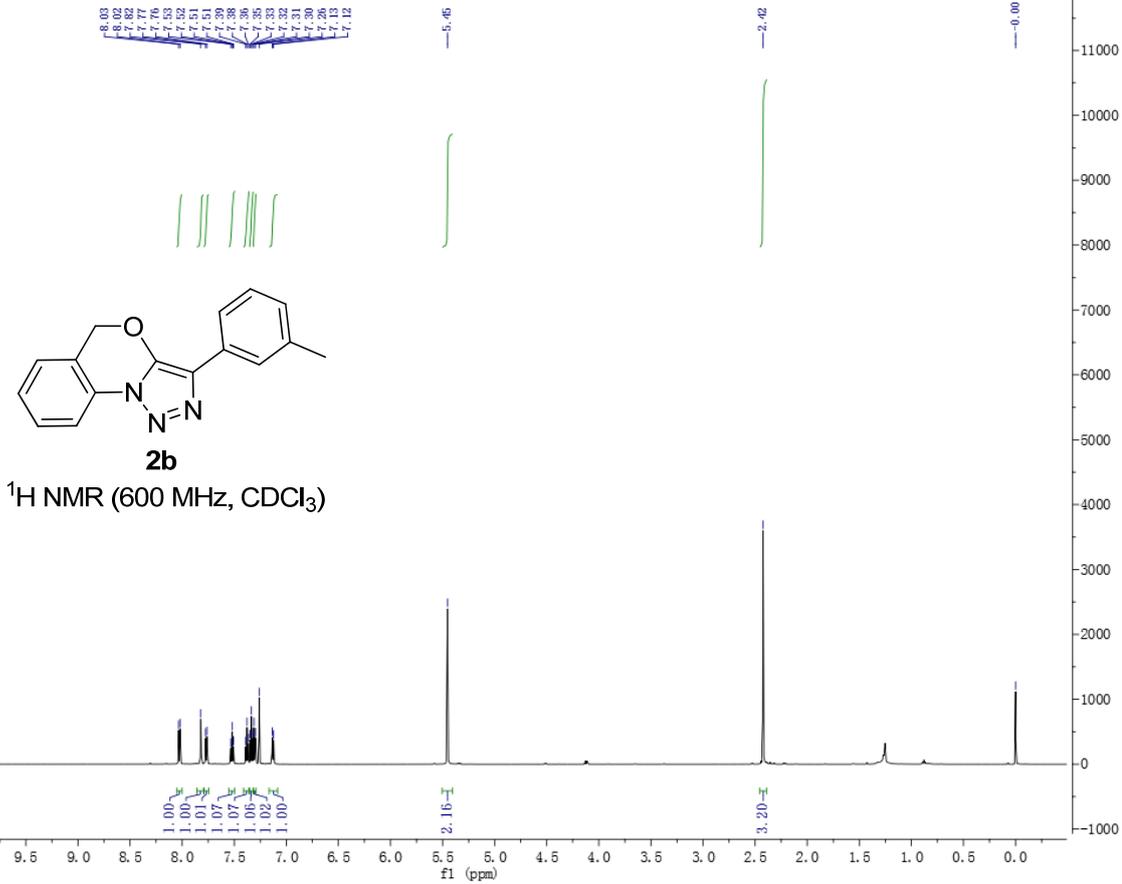
# IX. Copies of $^1\text{H}$ and $^{13}\text{C}$ NMR spectra

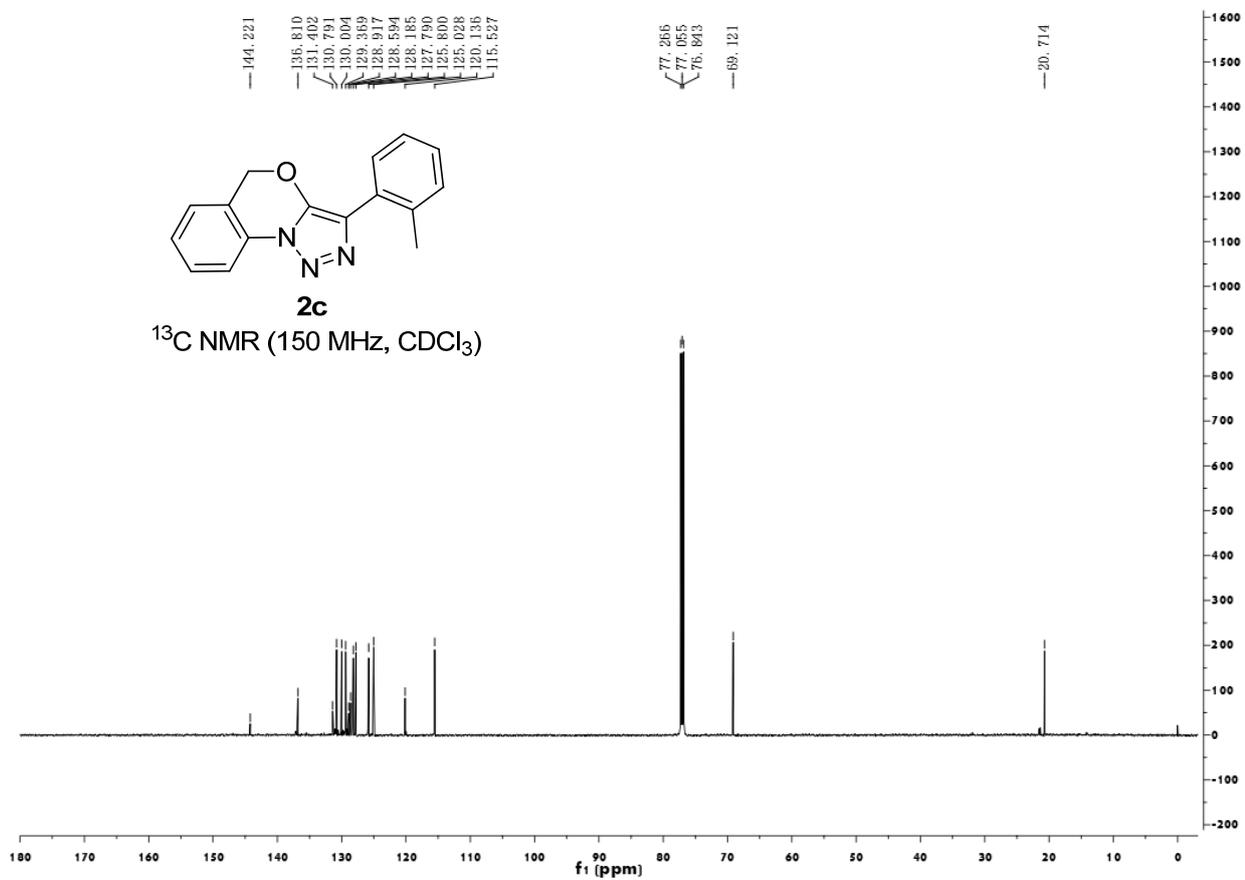
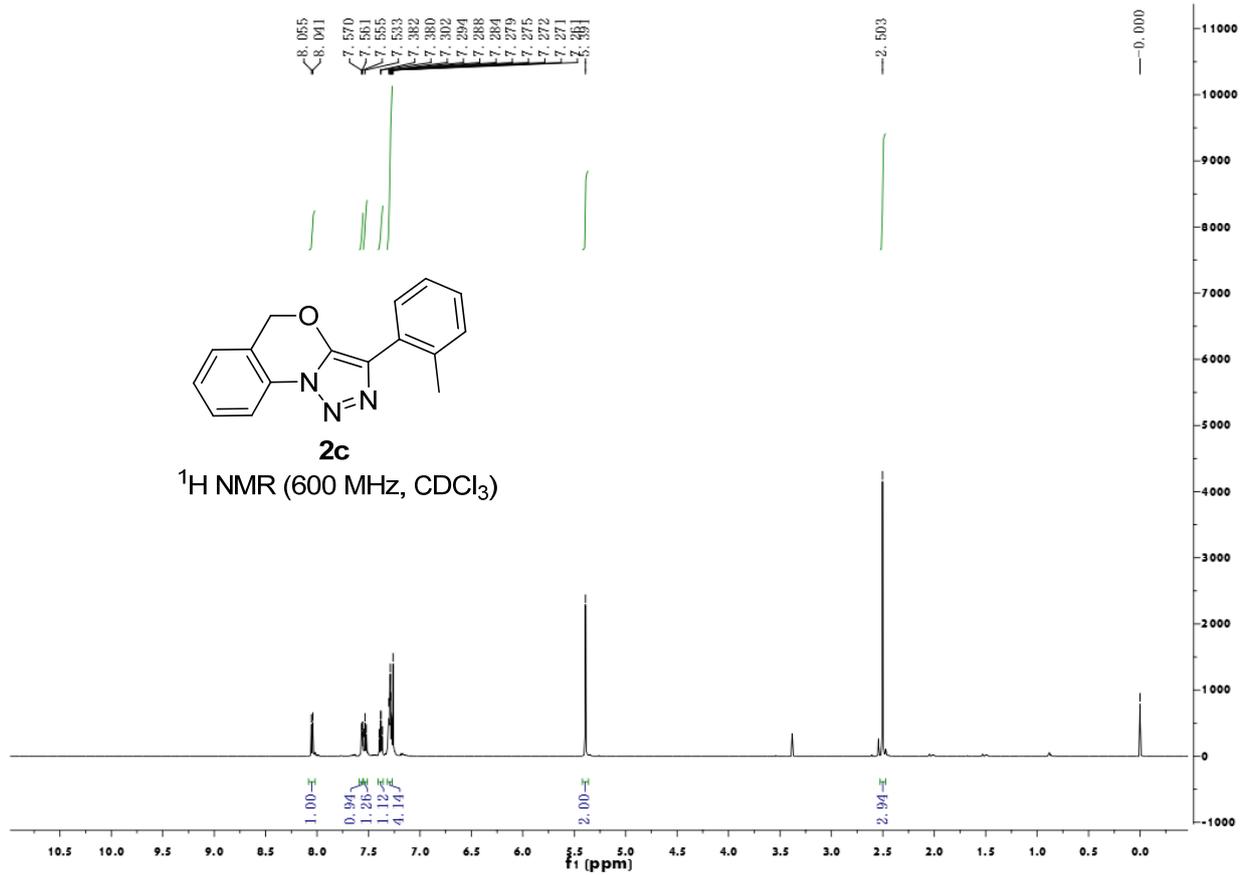
MY-543-1



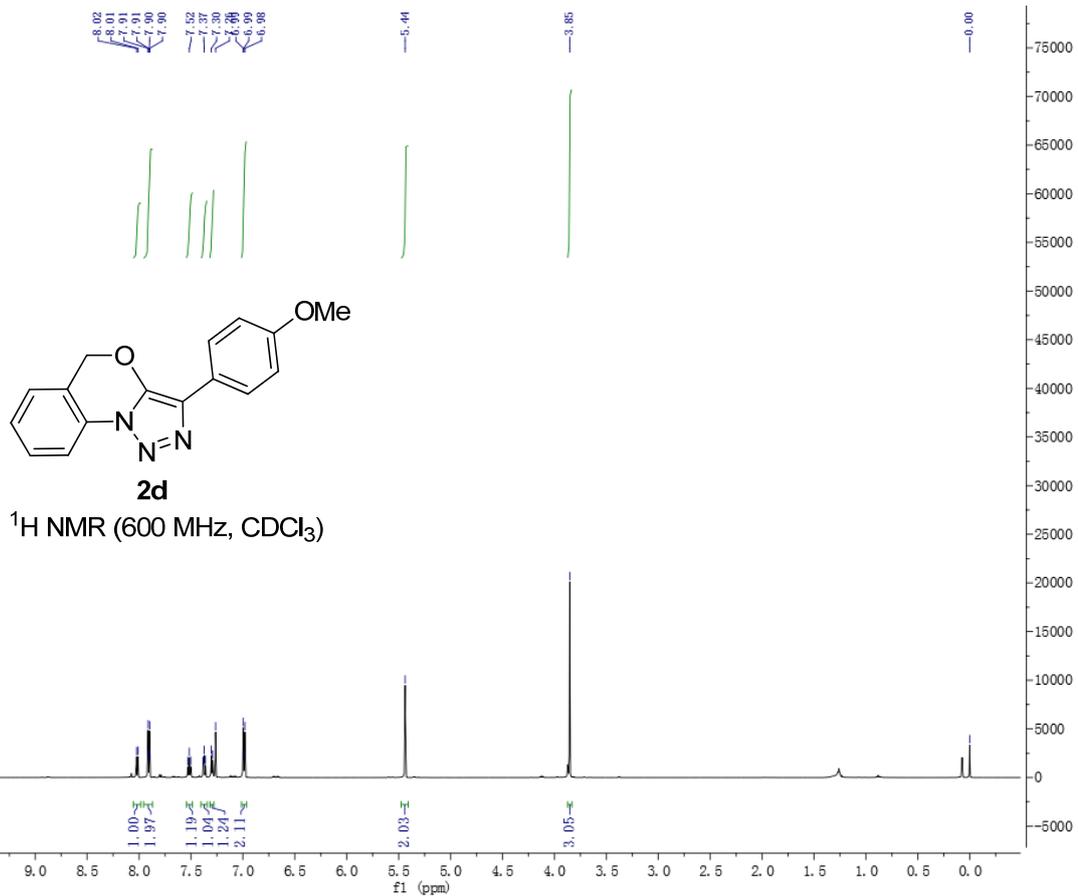
MY-543-1



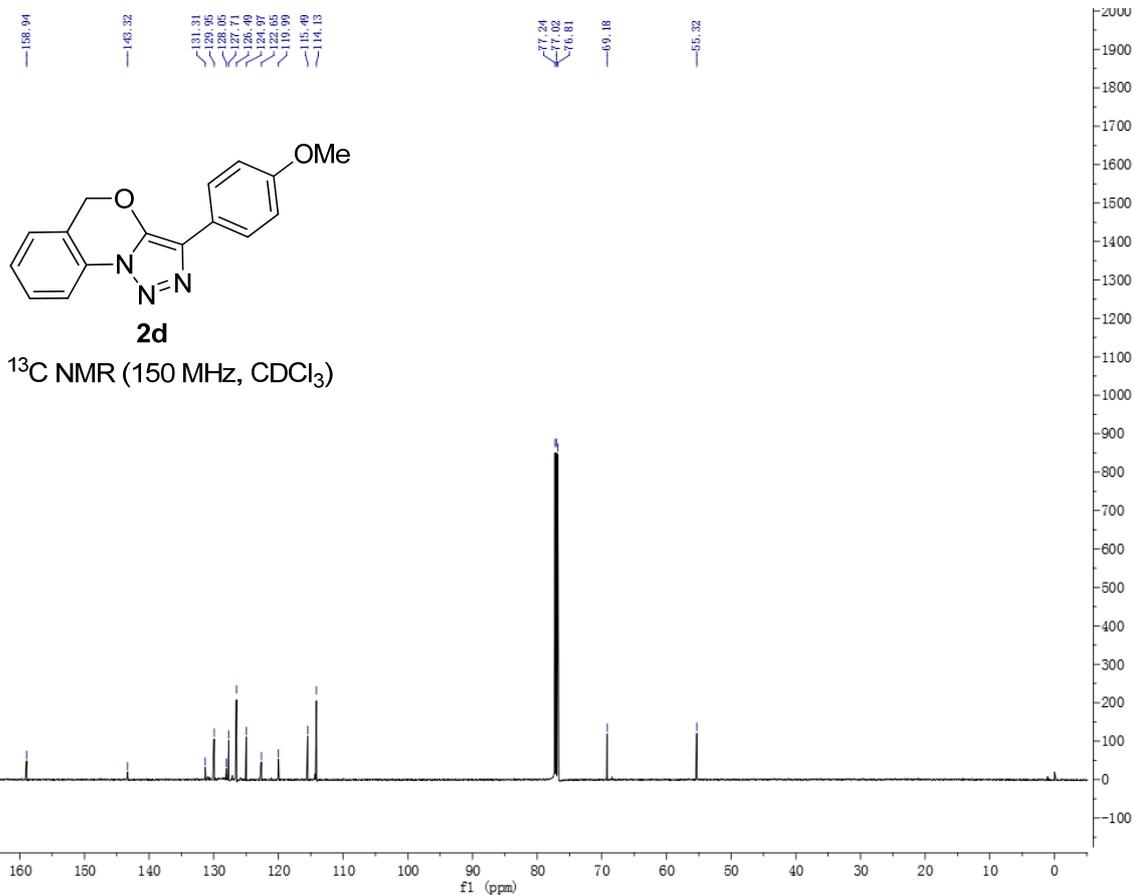


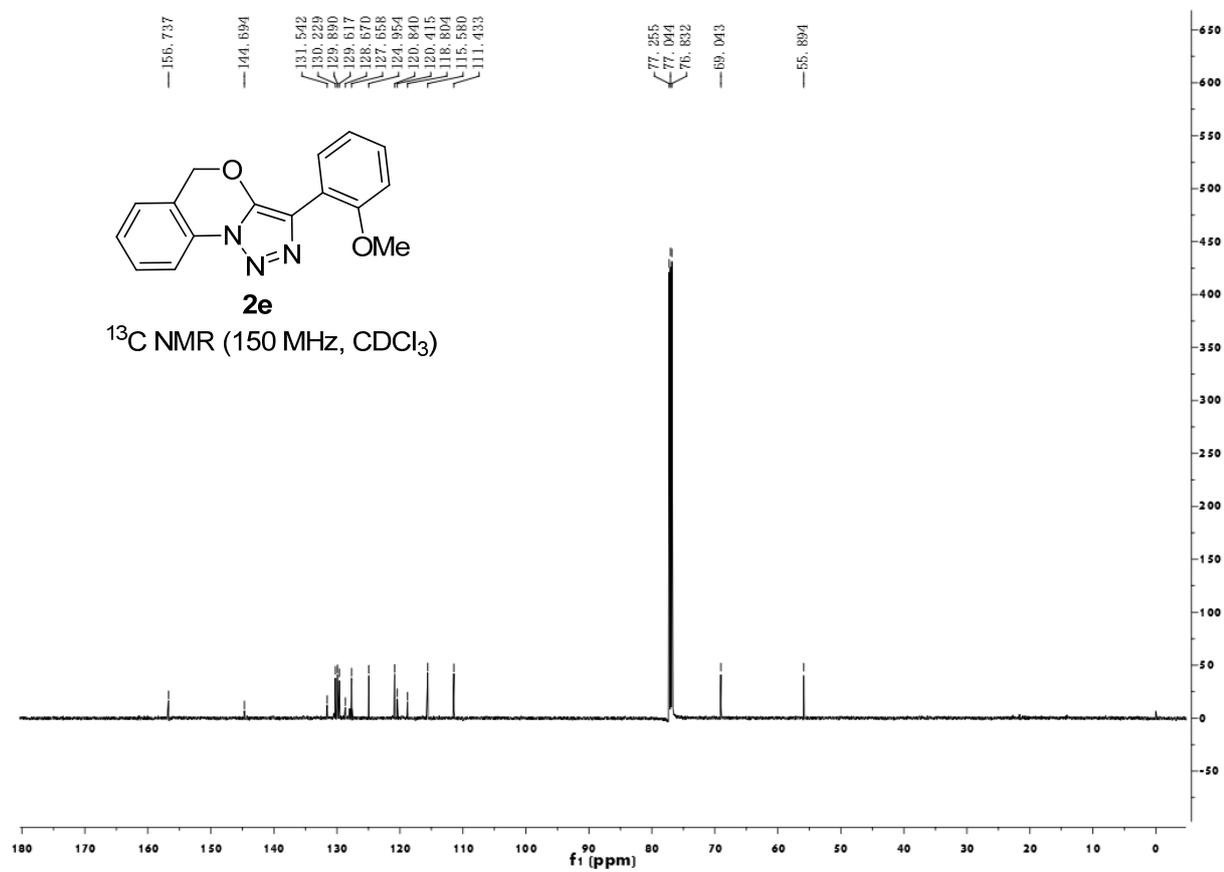
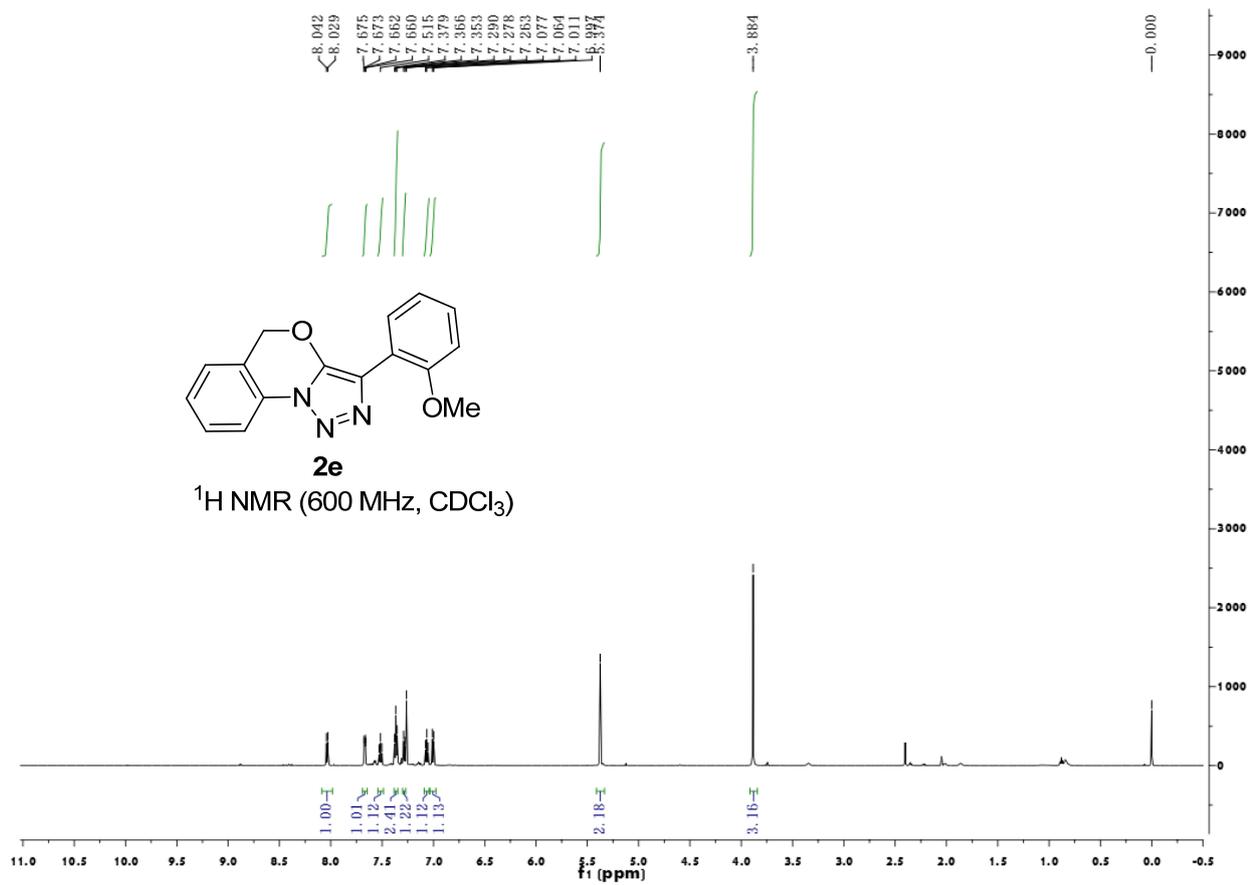


MY-589-2

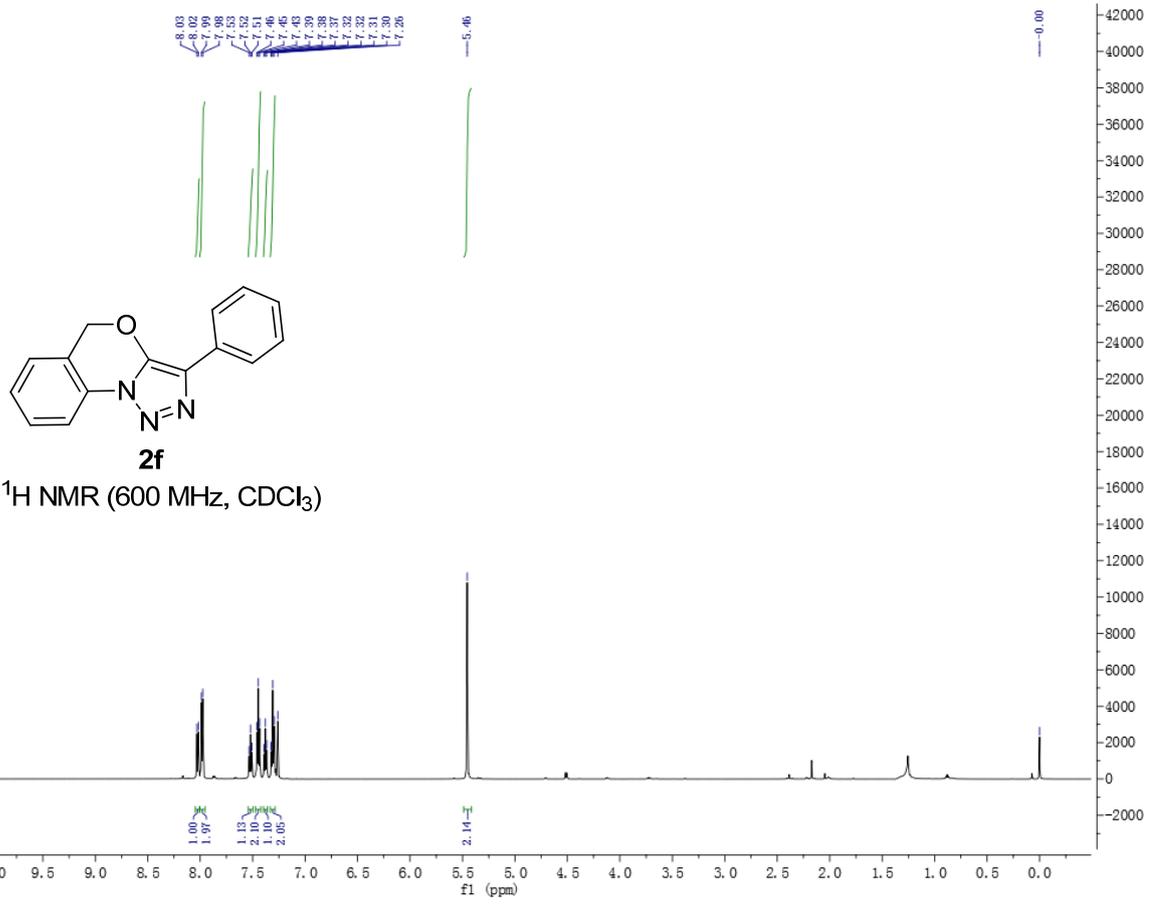


MY-589-2

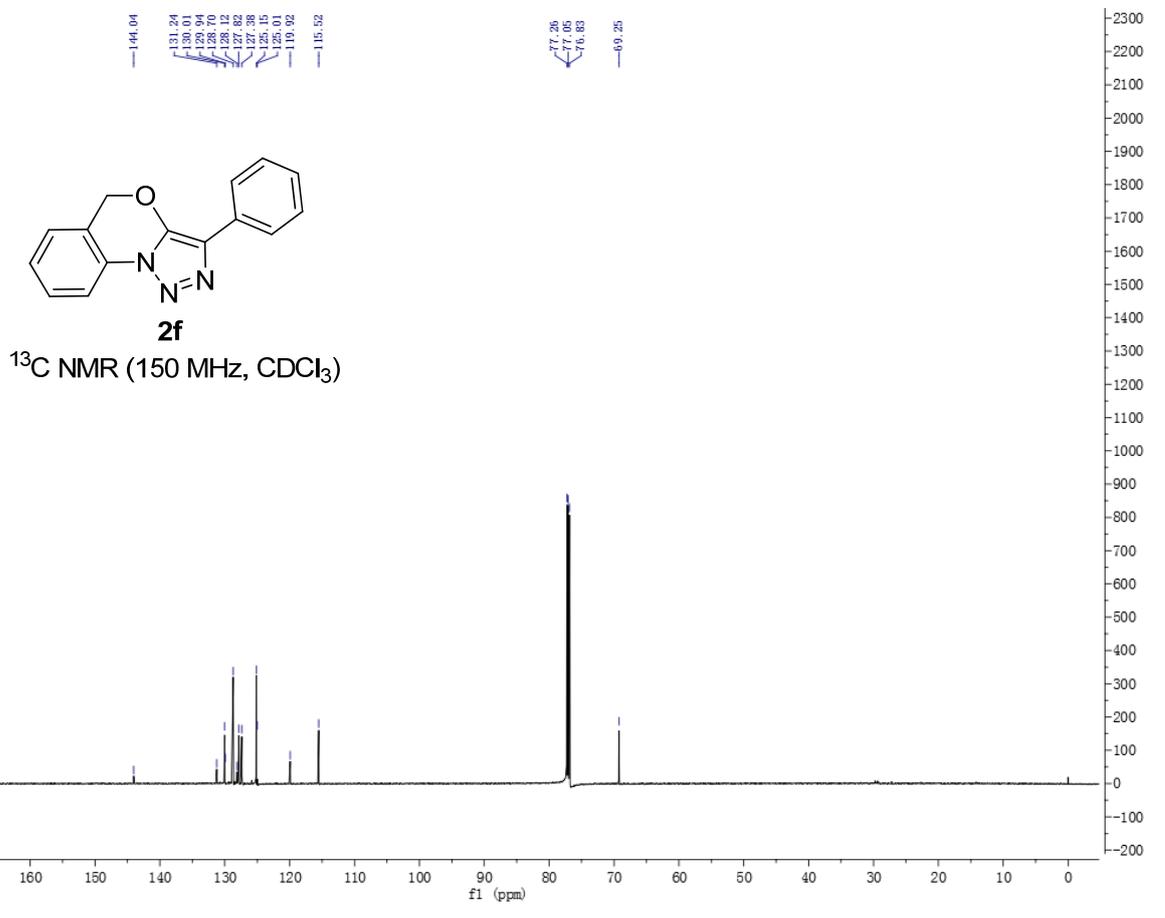


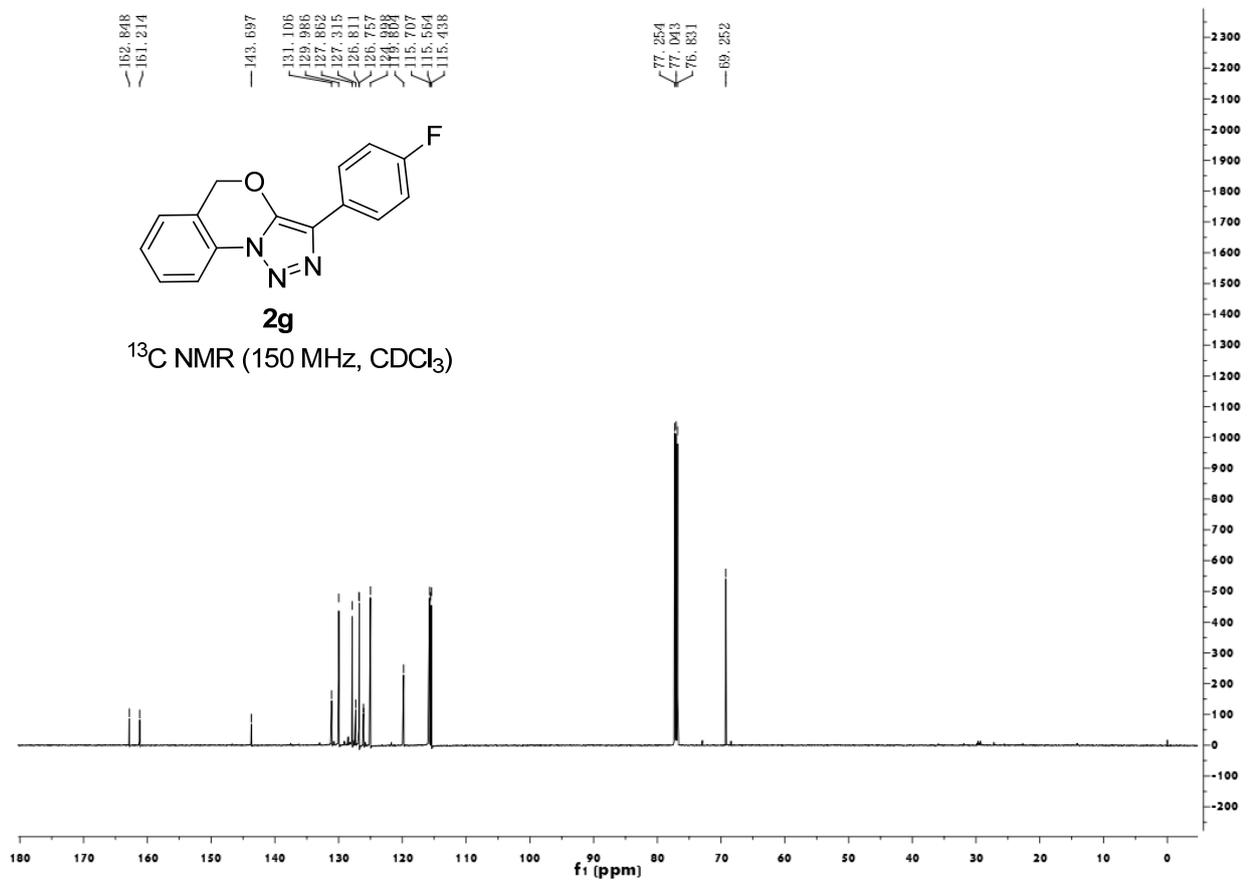
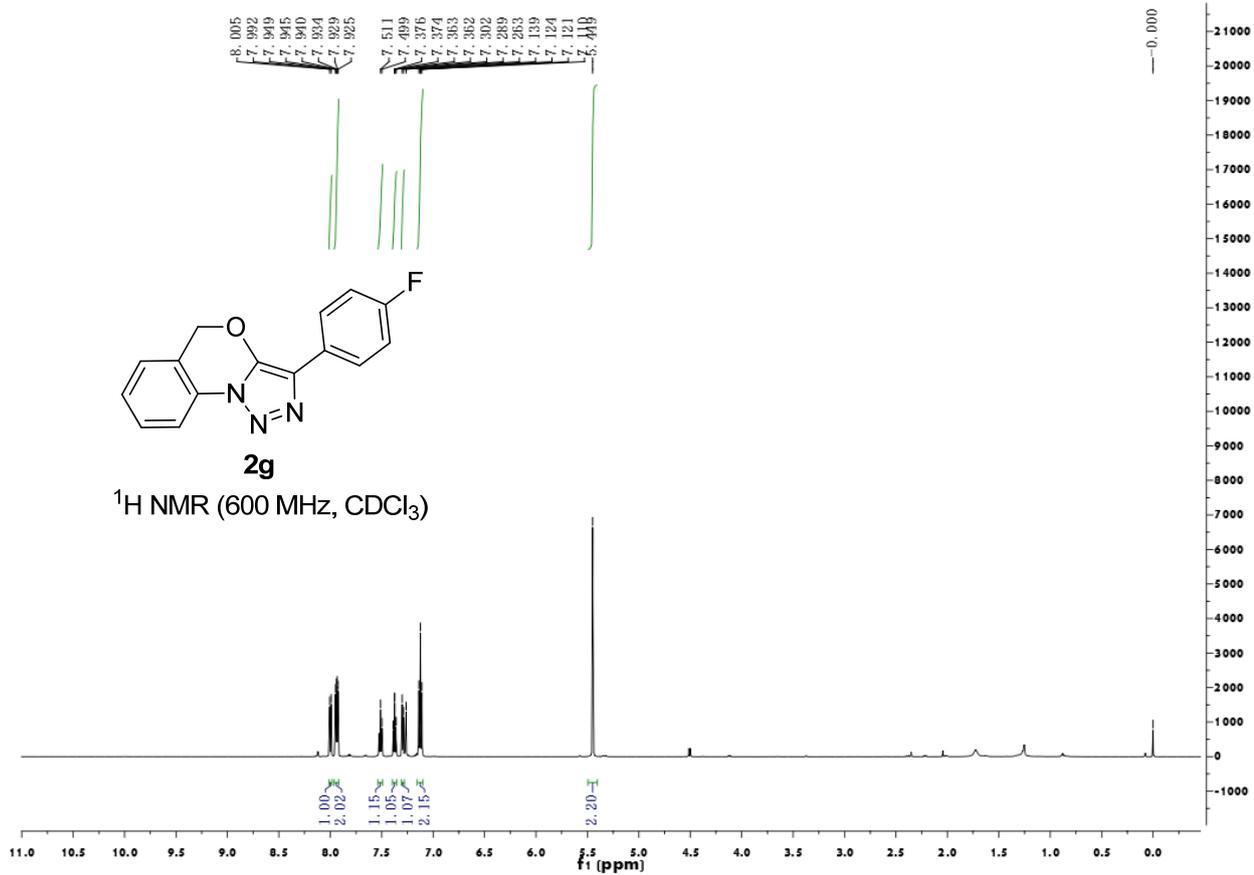


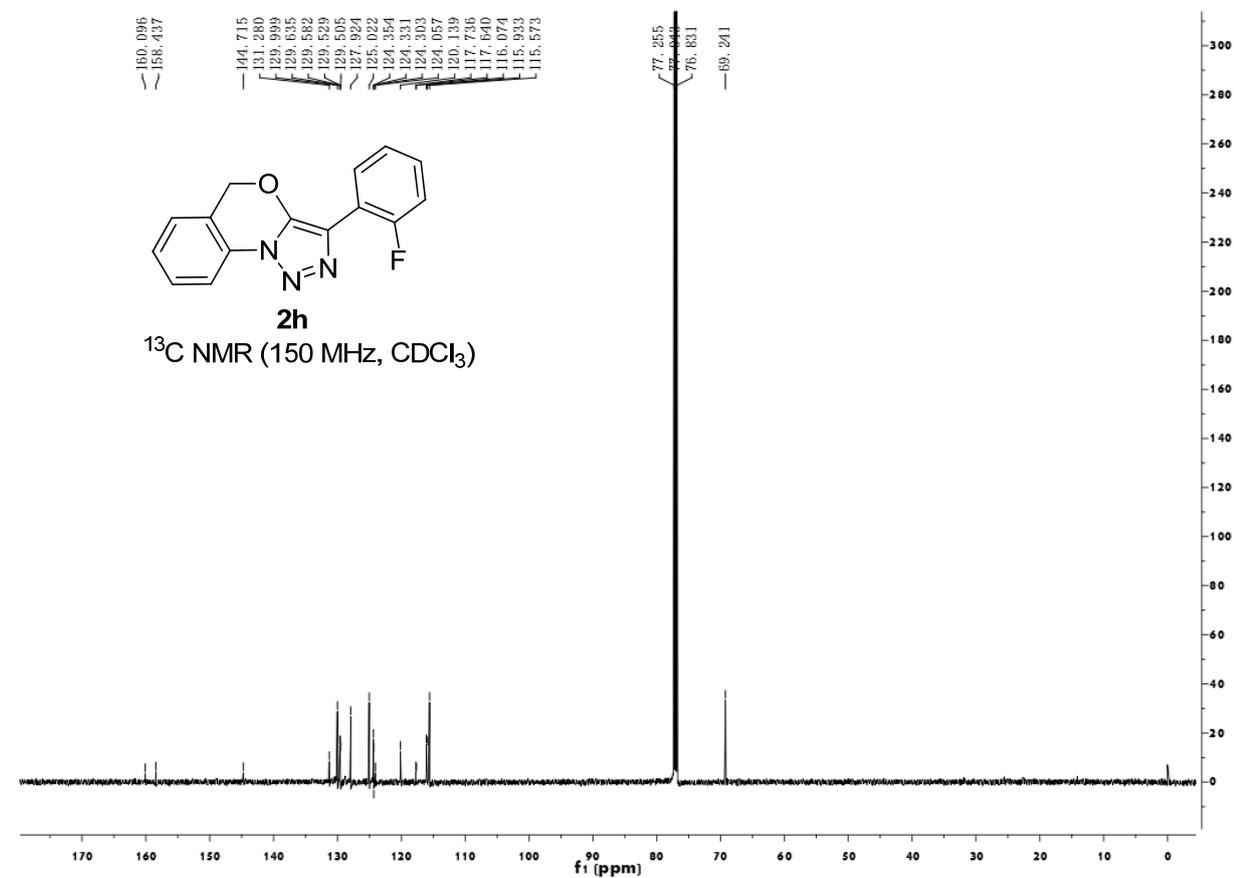
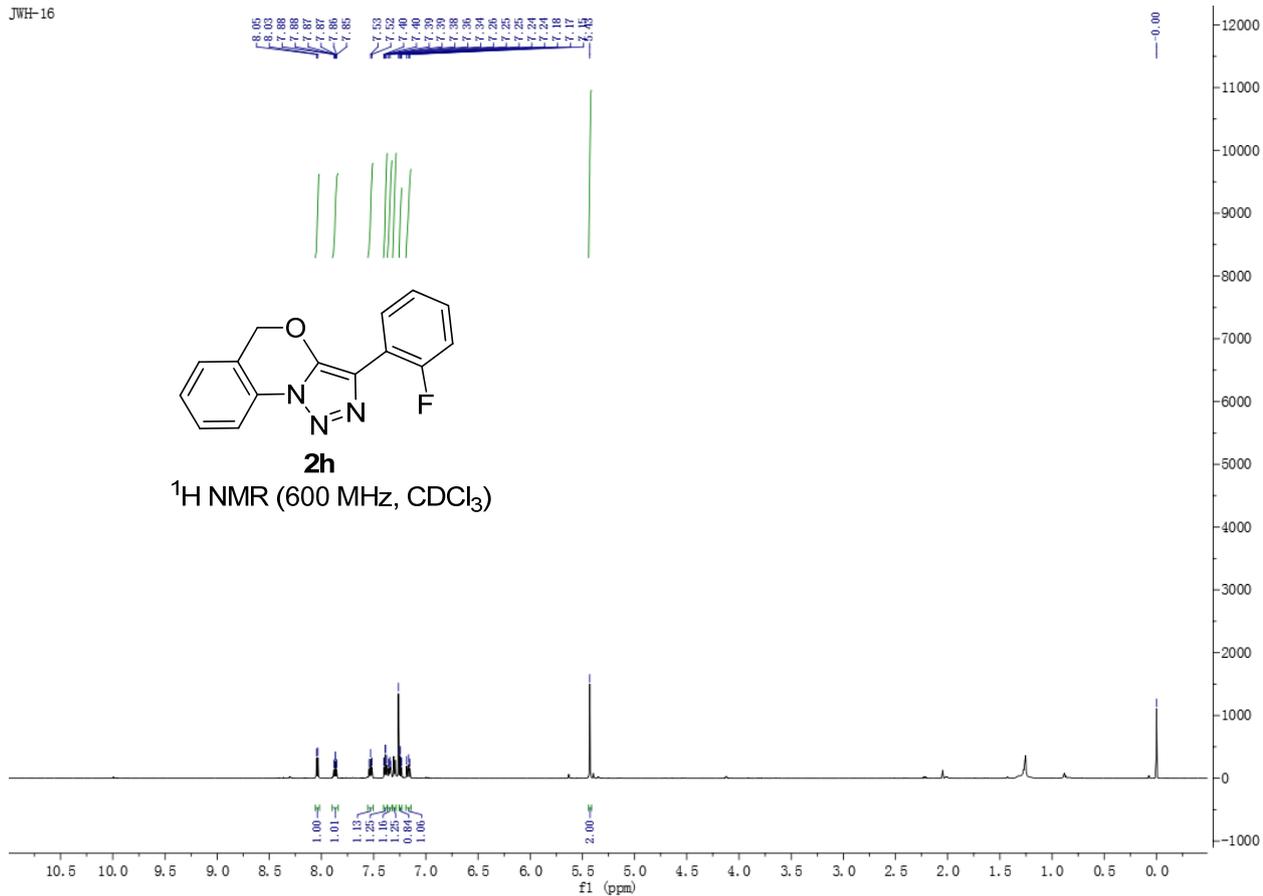
MY-591



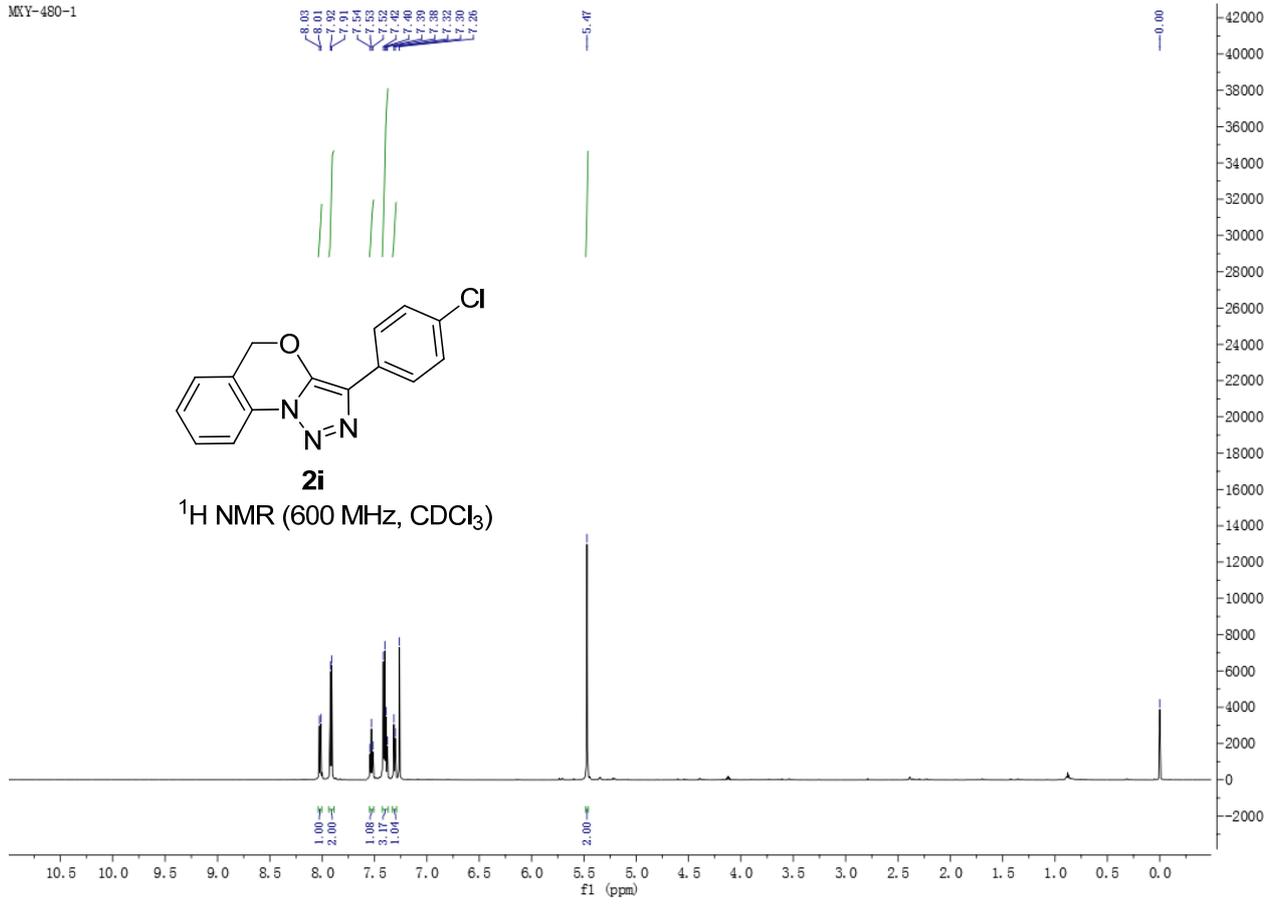
MY-591



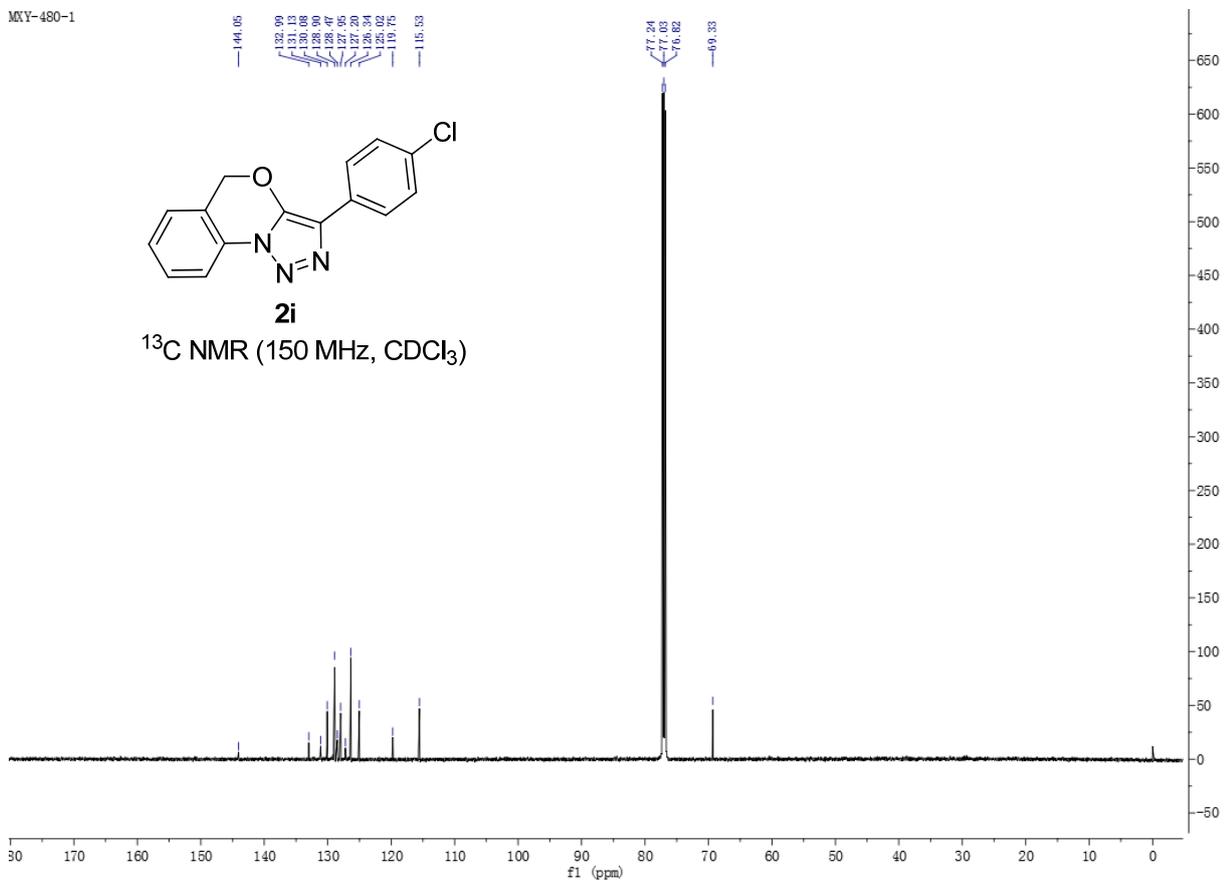


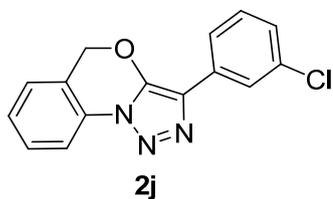


MY-480-1

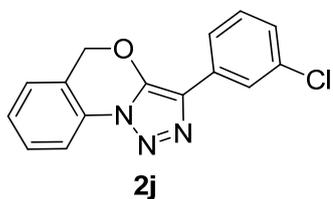
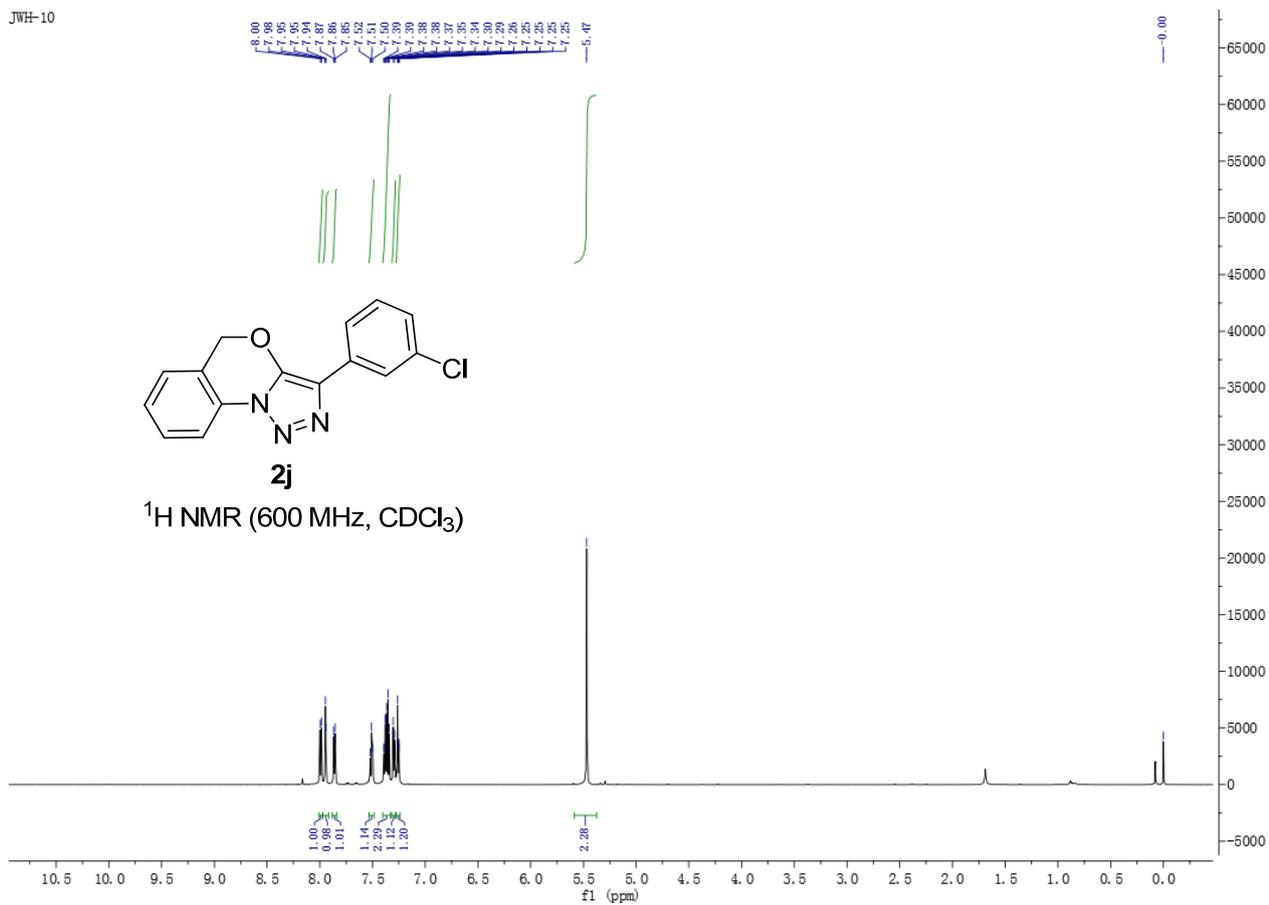


MY-480-1

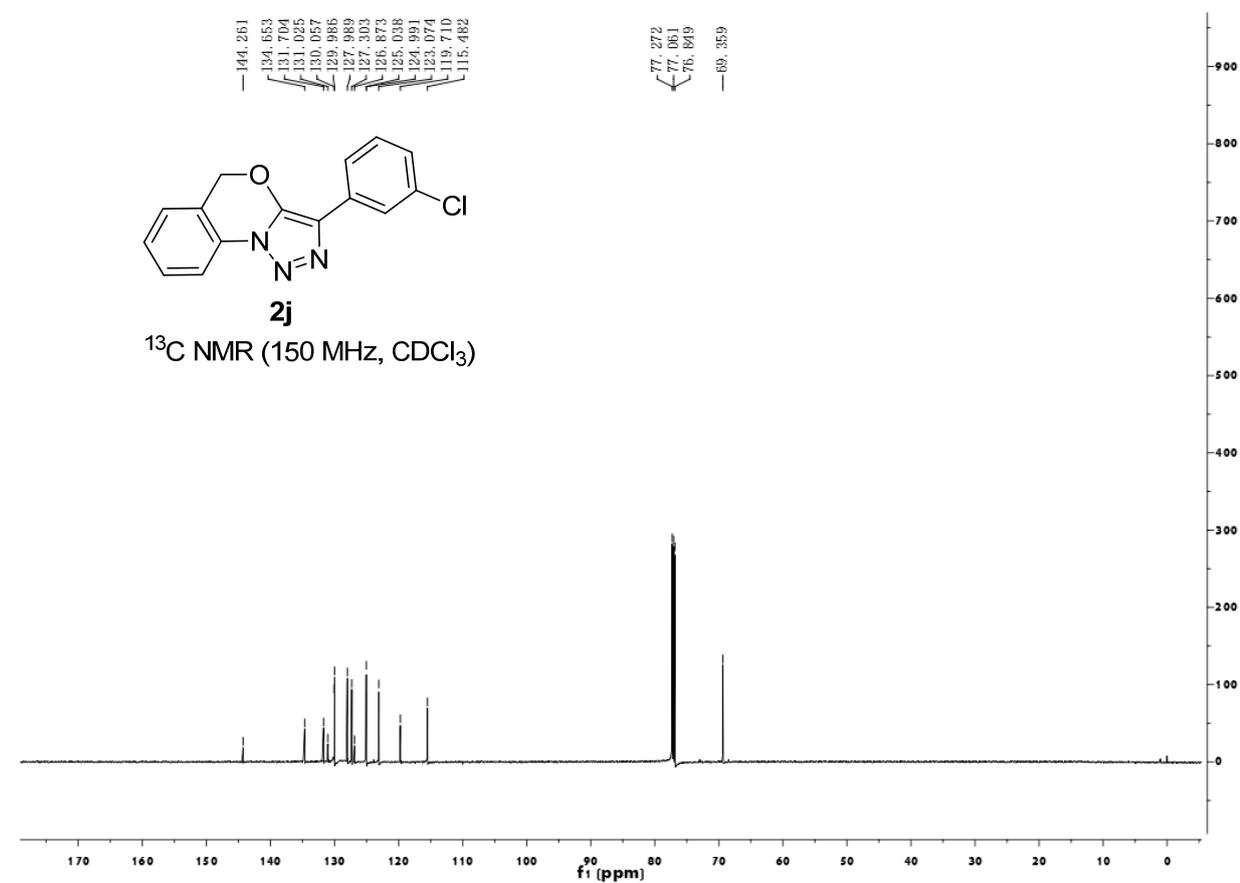


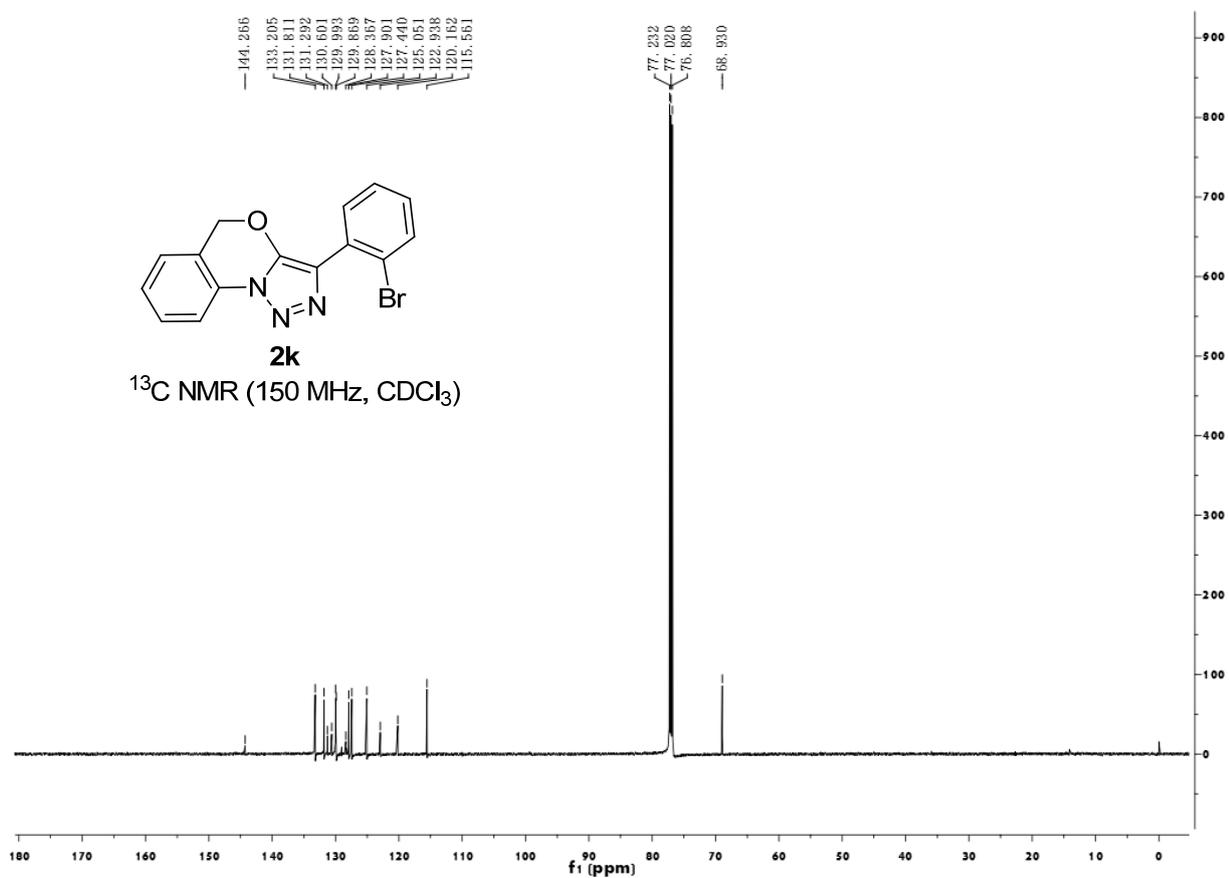
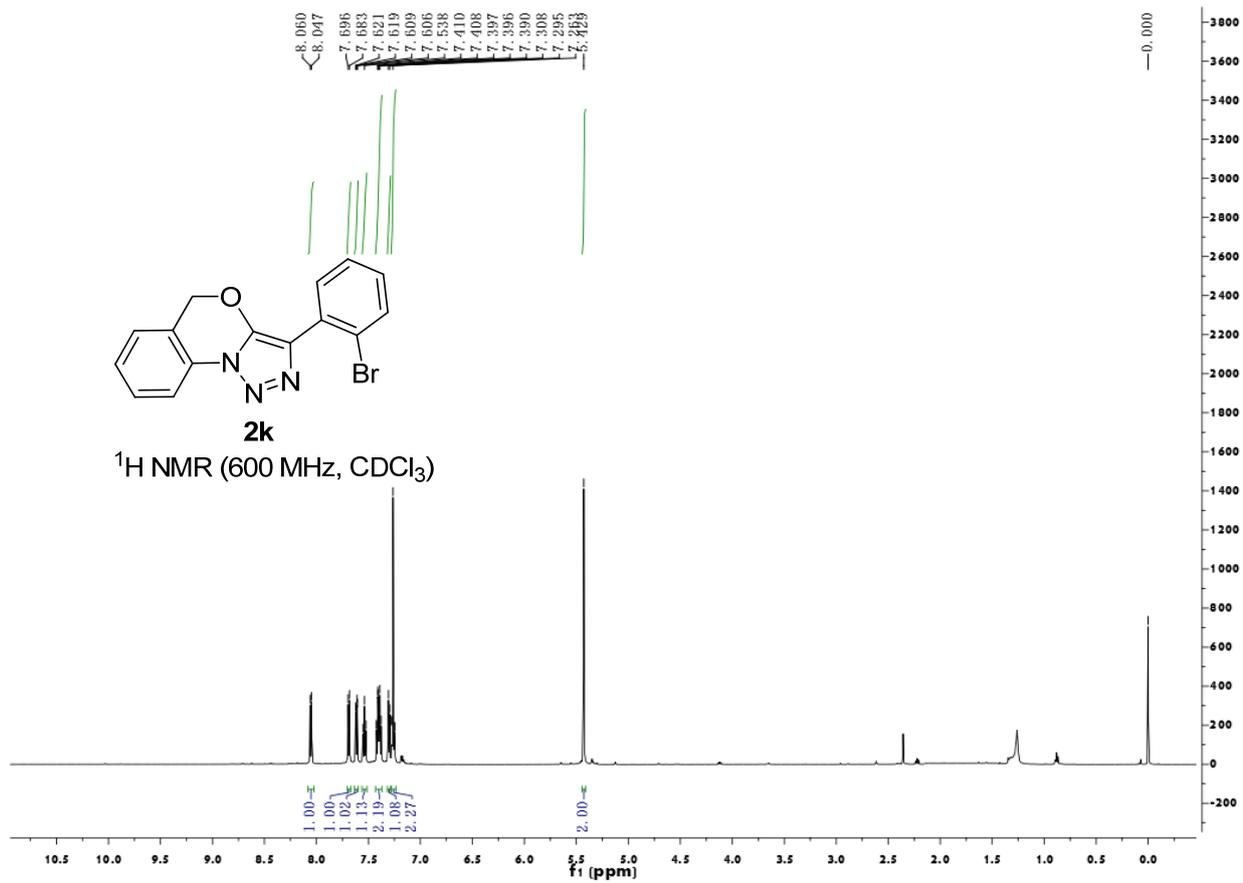


<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>)

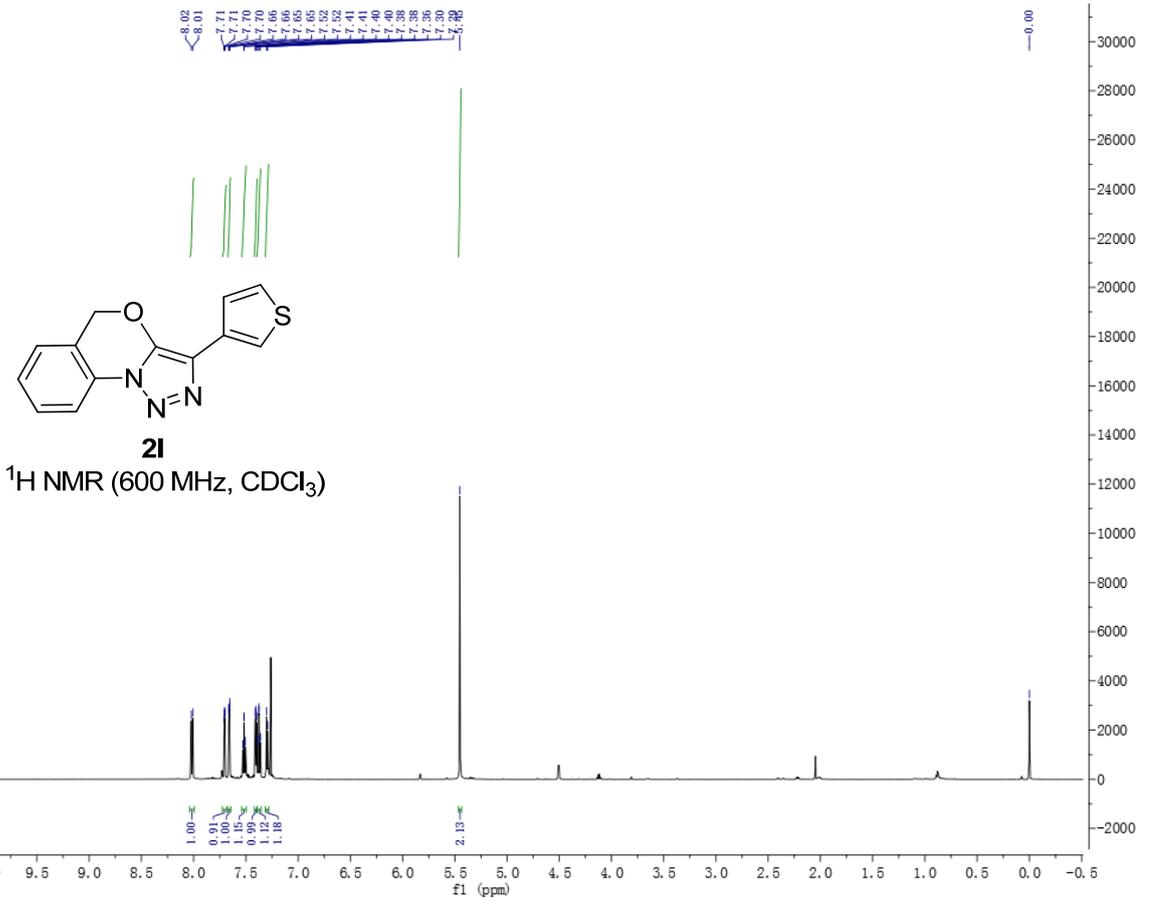


<sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>)





MY-620-1



MY-620-1

