

## Supporting Information

*for*

### **Metal-free three-component tandem cyclization for modular synthesis of 2,3-dihydrobenzothiazin-4-ones**

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## 1. General information

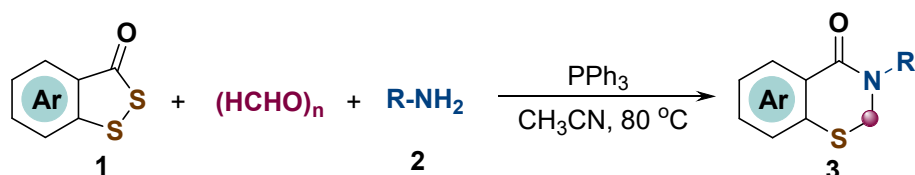
All reagents and solvents were obtained from commercial suppliers and used without further purification. The substituted amines were purchased from Bide Pharmatech Ltd and Energy chemical company. Unless otherwise stated, all experiments were conducted in a seal tube under air atmosphere. Reactions were monitored by TLC or GC-MS analysis. Flash column chromatography was performed over silica gel (200-300 mesh).

$^1\text{H}$ -NMR and  $^{13}\text{C}$ -NMR spectra were recorded in  $\text{CDCl}_3$  on a Bruker Avance 300 spectrometer (300 MHz  $^1\text{H}$ , 75 MHz  $^{13}\text{C}$ ) at room temperature. Chemical shifts were reported in ppm on the scale relative to  $\text{CDCl}_3$  ( $\delta = 7.26$  for  $^1\text{H}$ -NMR,  $\delta = 77.00$  for  $^{13}\text{C}$ -NMR) or  $\text{DMSO}-d_6$  ( $\delta = 2.50$  for  $^1\text{H}$ -NMR,  $\delta = 39.96$  for  $^{13}\text{C}$ -NMR) as an internal reference. High resolution mass spectra were recorded using Q-TOF time-of-flight mass spectrometer. Coupling constants ( $J$ ) were reported in Hertz (Hz).

## 2. General procedure for the synthesis of 1,2-benzodithiol-3-ones **1**

1,2-Benzodithiol-3-ones were prepared according to our previous work. AcOH (15 mL) was added to a mixture of benzo[d][1,2,3]triazin-4(3H)-one (3 mmol) and Na<sub>2</sub>S·9H<sub>2</sub>O or KSCN (12 mmol) in a 150 mL sealed tube. Then the reaction mixture was stirred at 120 °C in an oil bath for 8 h. Upon completion of the reaction, ethyl acetate was added to the mixture, and then washed with saturated brine with thrice. The combined water layers were extracted with ethyl acetate twice. The combined organic layers were dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. The solvents were removed via rotary evaporator and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 25:1, v/v) to give the desired product.

## 3. General procedure to synthesize 2,3-dihydrobenzothiazinones **3**

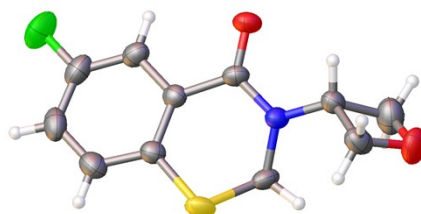


CH<sub>3</sub>CN (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1** (0.3 mmol), amines **2** (0.45 mmol), (HCHO)<sub>n</sub> (27 mg, 0.9 mmol) and PPh<sub>3</sub> (78.6 mg, 0.3 mmol) in a sealed tube. Then the reaction mixture was stirred at 80 °C for 16 h. Upon completion of the reaction, the solvents were removed via rotary evaporator and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc as the eluent) to give the desired product 2,3-dihydrobenzothiazinones **3**.

[Scale-up for larger synthesis of **3o**]: CH<sub>3</sub>CN (30 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1a** (0.84 g, 5 mmol), benzylamine **2o** (0.80 g, 7.5 mmol), (HCHO)<sub>n</sub> (0.45 g, 15 mmol) and PPh<sub>3</sub> (1.31 g, 5 mmol) in a 150 mL sealed tube. Then the reaction mixture was stirred at 80 °C under air for 18 h. Upon completion of the reaction, the solvents were removed via rotary evaporator and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the desired product 2,3-dihydrobenzothiazinones **3o** as white solid (0.98 g, 77%).

## 4. Crystal data of 3zc

Crystallographic data for compound **3zc** (CCDC-2292210) has already been deposited with the Cambridge Crystallographic Data Centre, Copies of the data can be obtained, free of charge, on application to CCDC (Email: deposit@ccdc.cam.ac.uk)

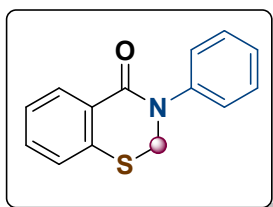


Displacement ellipsoids are drawn at 50% probability level

Bond precision:	C-C = 0.0039 Å	Wavelength=0.71073
Cell:	a=7.7589(11)    b=11.6408(17)    c=12.3519(15)	
	alpha=90    beta=107.201(15)    gamma=90	
Temperature:	293 K	
	Calculated	Reported
Volume	1065.7(3)	1065.7(3)
Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C11 H10 F N O2 S	C11 H10 F N O2 S
Sum formula	C11 H10 F N O2 S	C11 H10 F N O2 S
Mr	239.26	239.26
Dx, g cm <sup>-3</sup>	1.491	1.491
Z	4	4
Mu (mm <sup>-1</sup> )	0.301	0.301
F000	496.0	496.0
F000'	496.75	
h,k,lmax	10,15,16	9,15,15
Nref	2885	2417
Tmin,Tmax	0.947,0.956	0.481,1.000
Tmin'	0.947	
Correction method=	# Reported T Limits: Tmin=0.481 Tmax=1.000	
AbsCorr =	MULTI-SCAN	
Data completeness=	0.838	Theta(max)= 29.175
R(reflections)=	0.0579( 1520)	wR2(reflections)= 0.1138( 2417)
S =	1.043	Npar= 146

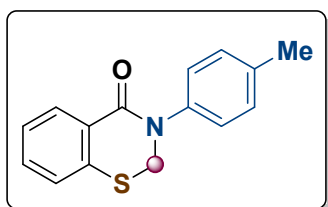
## 5. Characterization data for products

### 3-phenyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3a) (CAS Number: 2259305-57-0)



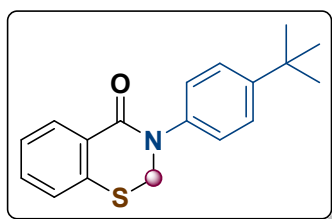
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a yellow oil (57.8 mg, 80%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J$  = 8.9 Hz, 1H), 7.47 – 7.34 (m, 6H), 7.33 – 7.29 (m, 2H), 4.98 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 142.2, 137.4, 135.7, 132.0, 131.2, 129.6, 127.3, 127.1, 126.3, 125.8, 51.7.

### 3-(p-tolyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3b) (CAS Number: 2259305-93-4)<sup>2</sup>



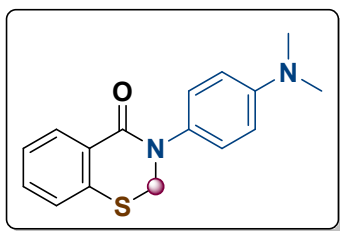
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (61.9 mg, 82%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (dd,  $J$  = 7.8, 1.4 Hz, 1H), 7.39 (dd,  $J$  = 7.0, 1.4 Hz, 1H), 7.33 (dd,  $J$  = 8.3, 6.8 Hz, 2H), 7.28 – 7.21 (m, 4H), 4.96 (s, 2H), 2.37 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 139.7, 137.3, 137.0, 135.7, 131.9, 131.1, 129.9, 127.3, 126.2, 125.6, 51.7, 21.1.

### 3-(4-(tert-butyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3c)



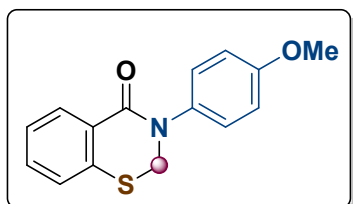
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (55.2 mg, 62%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (d,  $J$  = 6.7 Hz, 1H), 7.43 (t,  $J$  = 7.7 Hz, 3H), 7.38 – 7.34 (m, 1H), 7.30 (dt,  $J$  = 5.3, 3.0 Hz, 3H), 4.98 (s, 2H), 1.33 (s, 9H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.6, 150.0, 139.6, 137.3, 131.8, 131.2, 129.7, 128.4, 127.2, 126.2, 125.2, 51.7, 34.6, 31.3. HRMS (ESI, m/z) calcd for  $\text{C}_{18}\text{H}_{20}\text{NOS}$   $[\text{M}+\text{H}]^+$ : 298.1261; found: 298.1264.

### 3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3d)



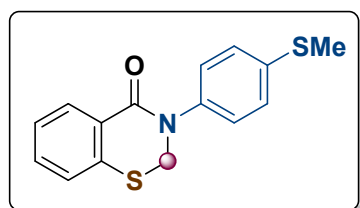
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow solid (60.5 mg, 71%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.22 (dd, *J* = 15.8, 8.2 Hz, 3H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.89 (s, 2H), 2.94 (s, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 149.5, 137.3, 131.6, 131.4, 131.0, 129.8, 127.1, 126.5, 126.0, 112.7, 51.8, 40.6. HRMS (ESI, m/z) calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 285.1057; found: 285.1058.

### 3-(4-methoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3e) (CAS Number: 2259305-59-2)<sup>2</sup>



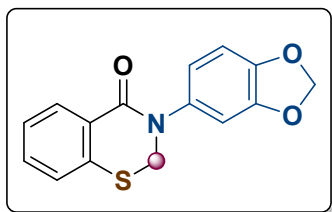
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 6:1, v/v) to give the product as a white solid (69.9 mg, 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.12 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.22 (dd, *J* = 8.8, 1.9 Hz, 3H), 6.88 (d, *J* = 8.9 Hz, 2H), 4.86 (s, 2H), 3.76 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 158.4, 137.3, 135.2, 131.8, 131.1, 129.7, 127.2, 127.1, 126.2, 114.5, 55.5, 51.8.

### 3-(4-(methylthio)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3f)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 6:1, v/v) to give the product as a white solid (70.6 mg, 83%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.18 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.33 – 7.27 (m, 5H), 4.96 (s, 2H), 2.50 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.5, 139.3, 137.5, 137.3, 132.0, 131.2, 129.5, 127.4, 127.3, 126.3, 126.2, 51.6, 16.1. HRMS (ESI, m/z) calcd for C<sub>15</sub>H<sub>14</sub>NOS<sub>2</sub> [M+H]<sup>+</sup>: 288.0512; found: 288.0512.

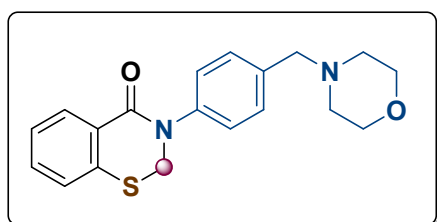
### 3-(benzo[d][1,3]dioxol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3g)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow oil (50.4 mg, 59%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (dd,  $J = 7.8, 1.1$  Hz, 1H), 7.44 – 7.37 (m, 1H), 7.32 (dd,  $J = 7.7, 6.4$  Hz, 2H), 6.88 (d,  $J = 1.5$  Hz, 1H), 6.86 – 6.76 (m, 2H), 6.00 (s, 2H), 4.91 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 148.0, 146.7, 137.3, 136.2, 131.9, 131.1, 129.5, 127.2, 126.3, 119.2, 108.4, 107.8, 101.6, 51.9. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{15}\text{H}_{12}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 286.0533; found: 286.0538.

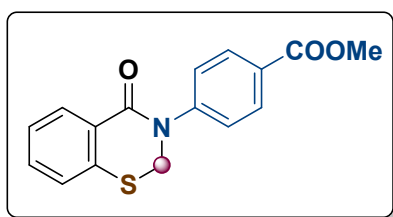
### 3-(4-(morpholinomethyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3h)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:4, v/v) to give the product as a colourless oil (78.5 mg, 77%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.18 (dd,  $J = 7.8, 1.1$  Hz, 1H), 7.41 (dd,  $J = 10.2, 4.8$  Hz, 3H), 7.32 (dt,  $J = 6.4, 3.0$  Hz, 4H), 4.97 (s, 2H), 3.75 – 3.68 (m, 4H), 3.51 (s, 2H), 2.51 – 2.40 (m, 4H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.5, 141.2, 137.3, 136.7, 131.9, 131.2, 129.9, 129.6, 127.3, 126.3, 125.6, 66.9, 62.8, 53.6, 51.6. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{19}\text{H}_{21}\text{N}_2\text{O}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 341.1319; found: 341.1320.

### methyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)benzoate (3i)

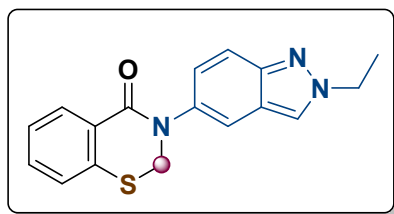


The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (58.9 mg, 66%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.19 (dd,  $J = 7.8, 1.1$  Hz, 1H), 8.10 (d,  $J = 8.6$  Hz, 2H), 7.47 (d,  $J = 8.7$  Hz, 2H), 7.42 (d,  $J = 8.4$  Hz, 1H), 7.38 – 7.29 (m, 2H), 5.03 (s, 2H), 3.93 (s, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 163.4, 146.0, 137.3, 132.2, 131.3, 130.6, 129.3, 128.3, 127.4, 126.4, 125.2, 52.2, 51.4. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{16}\text{H}_{14}\text{NO}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 300.0689; found: 300.0693.

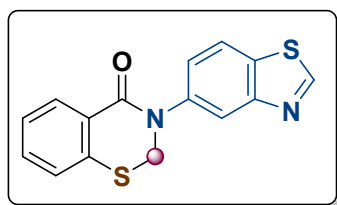


### 3-(2-ethyl-2H-indazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3j)



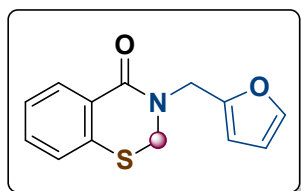
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a white solid (74.1 mg, 80%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.93 (s, 1H), 7.74 (d, *J* = 9.1 Hz, 1H), 7.62 (d, *J* = 1.2 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.36 – 7.31 (m, 1H), 7.27 (dt, *J* = 6.0, 3.6 Hz, 2H), 4.99 (s, 2H), 4.47 (q, *J* = 7.3 Hz, 2H), 1.62 (t, *J* = 7.3 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.8, 147.2, 137.8, 136.2, 131.8, 131.0, 129.6, 127.2, 126.2, 125.1, 122.6, 121.4, 118.5, 116.9, 51.9, 48.6, 15.8. HRMS (ESI, *m/z*) calcd for C<sub>17</sub>H<sub>16</sub>N<sub>3</sub>OS [M+H]<sup>+</sup>: 310.1009; found: 310.1012.

### 3-(benzo[d]thiazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3k)



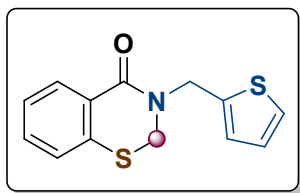
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (65.2 mg, 73%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 9.03 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *J* = 1.8 Hz, 1H), 7.97 (d, *J* = 8.6 Hz, 1H), 7.52 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.45 – 7.27 (m, 3H), 5.06 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 155.4, 153.9, 140.9, 137.4, 132.4, 132.1, 131.2, 129.4, 127.4, 126.4, 124.3, 122.2, 120.3, 51.9. HRMS (ESI, *m/z*) calcd for C<sub>15</sub>H<sub>11</sub>N<sub>2</sub>OS<sub>2</sub> [M+H]<sup>+</sup>: 299.0308; found: 299.0308.

### 3-(furan-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3l)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil solid (63.0 mg, 86%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.13 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 6.49 – 6.24 (m, 2H), 4.81 (s, 2H), 4.59 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.6, 150.0, 142.7, 137.1, 131.7, 130.9, 129.2, 127.1, 126.1, 110.5, 108.9, 47.9, 43.7. HRMS (ESI, *m/z*) calcd for C<sub>13</sub>H<sub>12</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 246.0584; found: 246.0589.

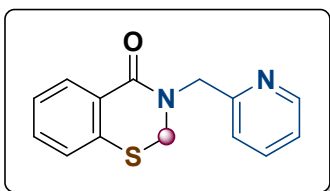
### 3-(thiophen-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3m)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (69.6 mg, 89%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.16 (d,  $J$  = 7.9 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.27 (dd,  $J$  = 8.4, 1.0 Hz, 2H), 7.25 – 7.22 (m, 1H), 7.07 (d,  $J$  = 2.7 Hz, 1H), 6.96 (dd,  $J$  = 5.0, 3.5 Hz, 1H), 4.99 (s, 2H), 4.55 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.7, 138.8, 137.0, 131.8, 130.9, 129.1, 127.2, 127.1, 126.9, 126.1, 125.9, 47.6, 45.8. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{13}\text{H}_{12}\text{NOS}_2$   $[\text{M}+\text{H}]^+$ : 262.0355; found: 262.0357.

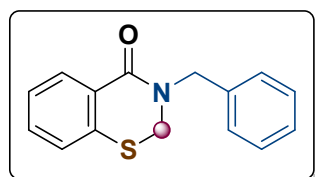
### 3-(pyridin-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3n)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (59.9 mg,

78%).  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.54 (d,  $J$  = 4.2 Hz, 1H), 8.14 (dd,  $J$  = 8.1, 1.4 Hz, 1H), 7.68 (td,  $J$  = 7.7, 1.8 Hz, 1H), 7.47 (d,  $J$  = 7.8 Hz, 1H), 7.40 – 7.30 (m, 1H), 7.30 – 7.27 (m, 1H), 7.26 – 7.19 (m, 2H), 4.96 (s, 2H), 4.71 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.9, 156.6, 149.2, 137.2, 137.1, 131.7, 130.8, 129.1, 127.1, 126.1, 122.7, 122.5, 53.2, 48.7. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{14}\text{H}_{13}\text{N}_2\text{OS}$   $[\text{M}+\text{H}]^+$ : 257.0744; found: 257.0748.

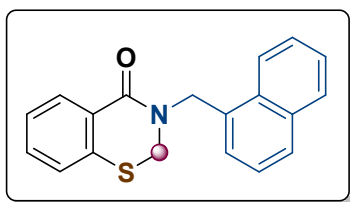
### 3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3o) (CAS Number: 2259305-43-4)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (65.7 mg, 86%).

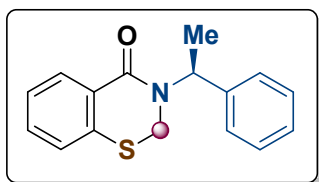
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.23 – 8.12 (m, 1H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 4.85 (s, 2H), 4.46 (s, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  163.8, 136.9, 136.2, 131.6, 130.7, 129.1, 128.6, 127.9, 127.6, 127.0, 126.0, 50.9, 47.6.

### 3-(naphthalen-1-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one(3p)



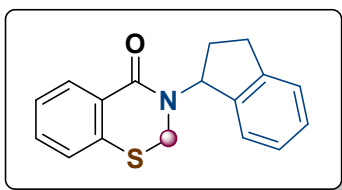
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (79.8 mg, 87%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.23 – 8.20 (m, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.89 – 7.77 (m, 2H), 7.56 – 7.45 (m, 3H), 7.45 – 7.39 (m, 1H), 7.36 – 7.24 (m, 2H), 7.20 (dd, *J* = 7.4, 1.2 Hz, 1H), 5.29 (s, 2H), 4.40 (s, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 137.0, 133.8, 131.6, 131.5, 131.4, 130.8, 129.4, 128.9, 128.6, 127.3, 127.1, 126.7, 126.1, 126.0, 125.1, 123.7, 48.6, 46.7. HRMS (ESI, *m/z*) calcd for C<sub>19</sub>H<sub>16</sub>NOS [M+H]<sup>+</sup>: 306.0948; found: 306.0950.

### (S)-3-(1-phenylethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3q)



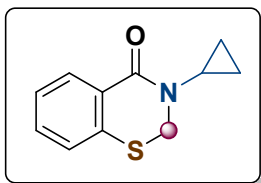
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (67.8 mg, 84%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 (dd, *J* = 7.7, 1.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 2H), 7.40 – 7.32 (m, 3H), 7.32 – 7.27 (m, 2H), 7.26 – 7.23 (m, 1H), 4.42 (d, *J* = 12.9 Hz, 1H), 4.17 (d, *J* = 12.9 Hz, 1H), 1.64 (d, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 139.7, 137.2, 131.6, 130.9, 129.6, 128.7, 127.7, 127.4, 127.1, 126.0, 51.9, 43.7, 16.4. HRMS (ESI, *m/z*) calcd for C<sub>16</sub>H<sub>16</sub>NOS [M+H]<sup>+</sup>: 270.0948; found: 270.0949.

### 3-(2,3-dihydro-1H-inden-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3r)



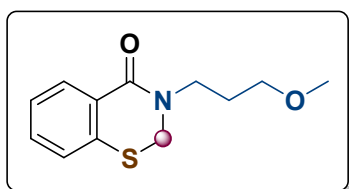
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (63.2 mg, 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 (dd, *J* = 10.1, 6.0 Hz, 5H), 6.40 (t, *J* = 8.2 Hz, 1H), 4.41 (d, *J* = 12.9 Hz, 1H), 4.21 (d, *J* = 12.9 Hz, 1H), 2.99 (qd, *J* = 16.0, 10.3 Hz, 2H), 2.67 – 2.51 (m, 1H), 1.96 (dq, *J* = 13.3, 8.9 Hz, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 164.2, 143.9, 140.4, 137.4, 131.6, 131.0, 129.5, 128.2, 127.1, 127.0, 126.0, 125.1, 124.4, 60.1, 44.2, 30.3, 30.2. HRMS (ESI, *m/z*) calcd for C<sub>17</sub>H<sub>16</sub>NOS [M+H]<sup>+</sup>: 282.0948; found: 282.0953.

### 3-cyclopropyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3s)



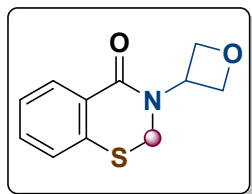
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (49.8 mg, 81%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.14 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.39 – 7.30 (m, 1H), 7.27 – 7.23 (m, 2H), 4.63 (s, 2H), 2.94 – 2.79 (m, 1H), 0.99 – 0.90 (m, 2H), 0.87 – 0.80 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 165.4, 137.1, 131.6, 130.6, 129.3, 127.0, 126.0, 49.5, 31.0, 8.1. HRMS (ESI, *m/z*) calcd for C<sub>11</sub>H<sub>12</sub>NOS [M+H]<sup>+</sup>: 206.0635; found: 206.0635.

### 3-(3-methoxypropyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3t)



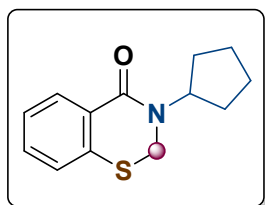
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (64.0 mg, 90%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 10.2, 4.5 Hz, 1H), 7.27 (dd, *J* = 4.1, 3.2 Hz, 2H), 4.61 (s, 2H), 3.71 (t, *J* = 6.8 Hz, 2H), 3.50 (t, *J* = 6.0 Hz, 2H), 3.35 (s, 3H), 1.98 – 1.90 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.8, 137.1, 131.4, 130.5, 129.6, 127.0, 126.0, 69.7, 58.6, 49.2, 46.1, 28.1. HRMS (ESI, *m/z*) calcd for C<sub>12</sub>H<sub>16</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 238.0897; found: 238.0899.

### 3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3u)



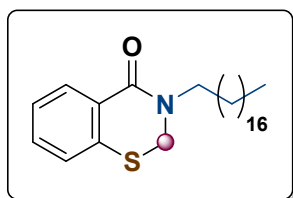
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (58.3 mg, 88%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.33 – 7.23 (m, 2H), 5.79 – 5.65 (m, 1H), 4.99 (t, *J* = 7.5 Hz, 2H), 4.86 (s, 2H), 4.74 (t, *J* = 6.7 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.6, 137.1, 131.9, 130.9, 128.9, 127.2, 126.2, 75.9, 49.4, 44.2. HRMS (ESI, *m/z*) calcd for C<sub>11</sub>H<sub>12</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 222.0584; found: 222.0590.

**3-cyclopentyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3v) (CAS Number: 2280826-56-2)**<sup>3</sup>



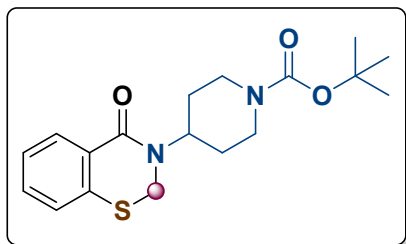
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (56.6 mg, 81%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.23 (dd, *J* = 11.2, 4.1 Hz, 2H), 5.21 – 5.03 (m, 1H), 4.47 (s, 2H), 1.98 (dd, *J* = 7.3, 4.1 Hz, 2H), 1.79 – 1.61 (m, 4H), 1.60 – 1.49 (m, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.7, 137.1, 131.3, 130.8, 129.9, 126.9, 125.9, 54.8, 43.8, 29.3, 24.3.

**3-octadecyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3w)**



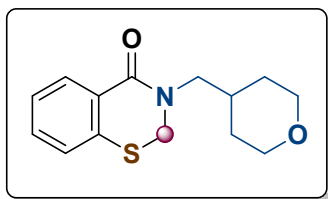
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (85.0 mg, 68%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.19 – 8.05 (m, 1H), 7.38 – 7.29 (m, 1H), 7.28 – 7.21 (m, 2H), 4.55 (s, 2H), 3.68 – 3.55 (m, 2H), 1.72 – 1.59 (m, 2H), 1.26 (s, 31H), 0.88 (t, *J* = 6.6 Hz, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.5, 137.0, 131.3, 130.6, 129.6, 127.0, 126.0, 48.5, 48.4, 31.9, 29.7, 29.7, 29.6, 29.6, 29.5, 29.4, 28.1, 27.0, 22.7, 14.1. HRMS (ESI, *m/z*) calcd for C<sub>26</sub>H<sub>44</sub>NOS [M+H]<sup>+</sup>: 418.3139; found: 418.3140.

**tert-butyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidine-1-carboxylate (3x)**



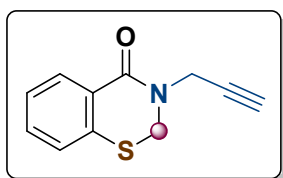
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the product as a colourless oil (96.0 mg, 92%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.11 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.30 – 7.22 (m, 2H), 4.80 (tt, *J* = 12.2, 3.9 Hz, 1H), 4.48 (s, 2H), 4.25 (d, *J* = 9.7 Hz, 2H), 2.84 (t, *J* = 12.3 Hz, 2H), 1.80 (d, *J* = 11.7 Hz, 2H), 1.65 (td, *J* = 12.3, 4.5 Hz, 2H), 1.47 (s, 9H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.3, 154.3, 136.9, 131.4, 130.7, 129.4, 126.9, 125.9, 79.5, 51.4, 43.3, 43.0, 29.2, 28.2. HRMS (ESI, *m/z*) calcd for C<sub>18</sub>H<sub>25</sub>N<sub>2</sub>O<sub>3</sub>S [M+H]<sup>+</sup>: 349.1581; found: 349.1586.

### 3-((tetrahydro-2H-pyran-4-yl)methyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3y)



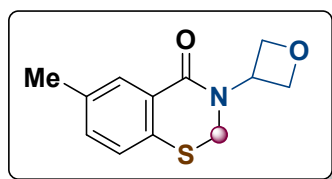
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (66.3 mg, 84%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.09 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.41 – 7.29 (m, 1H), 7.27 (d, *J* = 5.8 Hz, 2H), 4.57 (s, 2H), 3.97 (dd, *J* = 11.3, 3.3 Hz, 2H), 3.50 (d, *J* = 7.3 Hz, 2H), 3.36 (td, *J* = 11.8, 1.9 Hz, 2H), 2.00 (ddq, *J* = 15.0, 7.4, 3.7 Hz, 1H), 1.70 (dd, *J* = 12.9, 1.6 Hz, 2H), 1.39 (tt, *J* = 12.0, 6.0 Hz, 2H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 164.0, 137.0, 131.6, 130.7, 129.5, 127.1, 126.2, 67.6, 54.8, 49.8, 34.5, 30.8. HRMS (ESI, *m/z*) calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 264.1053; found: 264.1055.

### 3-(prop-2-yn-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3z)



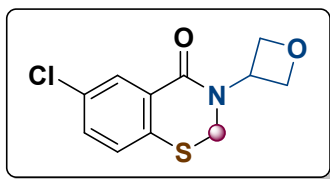
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (45.0 mg, 74%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.25 (dd, *J* = 11.7, 4.1 Hz, 2H), 4.71 (s, 2H), 4.48 (d, *J* = 2.5 Hz, 2H), 2.31 (s, 1H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.4, 137.0, 131.9, 130.8, 128.8, 127.1, 126.1, 77.7, 73.0, 47.2, 36.2. HRMS (ESI, *m/z*) calcd for C<sub>11</sub>H<sub>10</sub>NOS [M+H]<sup>+</sup>: 204.0478; found: 204.0474.

### 6-methyl-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3za)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (62.7 mg, 89%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 7.98 – 7.83 (m, 1H), 7.19 (d, *J* = 1.0 Hz, 2H), 5.83 – 5.64 (m, 1H), 4.99 (t, *J* = 7.5 Hz, 2H), 4.83 (s, 2H), 4.77 – 4.69 (m, 2H), 2.34 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.8, 136.2, 133.6, 132.9, 131.2, 128.6, 127.0, 75.9, 49.2, 44.2, 20.8. HRMS (ESI, *m/z*) calcd for C<sub>12</sub>H<sub>14</sub>NO<sub>2</sub>S [M+H]<sup>+</sup>: 236.0740; found: 236.0741.

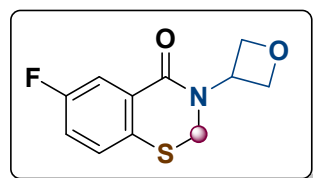
### 6-chloro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zb)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a yellow solid (55.8 mg, 73%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.04 (d,  $J = 2.2$  Hz, 1H), 7.33 (dd,  $J = 8.4, 2.3$  Hz, 1H), 7.24 (t,  $J = 5.6$  Hz, 1H), 5.78 – 5.64 (m, 1H), 5.00 (t,  $J = 7.5$  Hz, 2H), 4.86 (s, 2H), 4.75 – 4.68 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.5, 135.5, 132.3, 131.9, 130.7, 130.1, 128.4, 75.8, 49.4, 44.1. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{11}\text{H}_{11}\text{ClNO}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 256.0194; found: 256.0191.

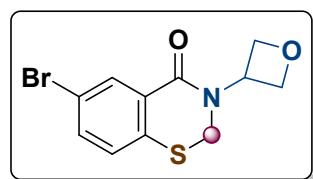
### 6-fluoro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zc)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (60.2 mg, 84%).

$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.74 (dd,  $J = 9.3, 2.7$  Hz, 1H), 7.24 (dd,  $J = 8.5, 5.1$  Hz, 1H), 7.07 (td,  $J = 8.3, 2.8$  Hz, 1H), 5.77 – 5.58 (m, 1H), 4.95 (t,  $J = 7.5$  Hz, 2H), 4.83 (s, 2H), 4.69 (t,  $J = 6.7$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.7 (d,  $J = 2.2$  Hz), 162.7 (d,  $J = 245.3$  Hz), 132.3 (d,  $J = 3.2$  Hz), 130.6 (d,  $J = 7.2$  Hz), 128.9 (d,  $J = 7.4$  Hz), 119.6 (d,  $J = 22.5$  Hz), 117.6 (d,  $J = 23.3$  Hz), 75.8, 49.5, 44.4. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{11}\text{H}_{11}\text{FNO}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 240.0490; found: 240.0492.

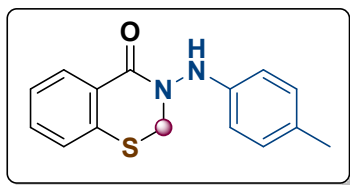
### 6-bromo-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zd)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (72.6 mg, 81%).

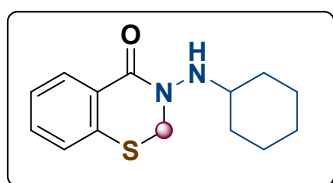
$^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  8.17 (d,  $J = 2.2$  Hz, 1H), 7.46 (dd,  $J = 8.3, 2.2$  Hz, 1H), 7.16 (d,  $J = 8.3$  Hz, 1H), 5.76 – 5.62 (m, 1H), 4.98 (t,  $J = 7.5$  Hz, 2H), 4.85 (s, 2H), 4.76 – 4.65 (m, 2H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  162.3, 136.1, 134.7, 133.5, 130.2, 128.6, 119.8, 75.7, 49.4, 44.1. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{11}\text{H}_{11}\text{BrNO}_2\text{S}$   $[\text{M}+\text{H}]^+$ : 299.9689; found: 299.9686.

### 3-(p-tolylamino)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4a)



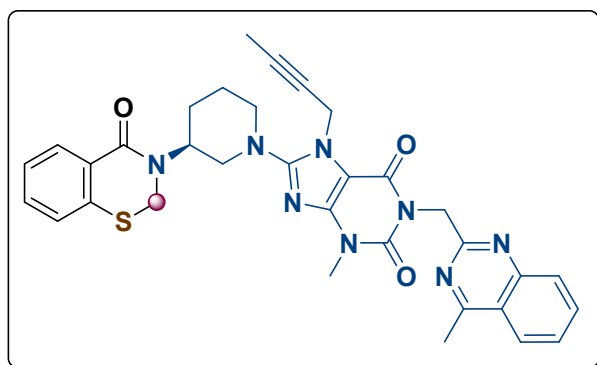
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1 v/v) to give the product as a brown oil (66.4 mg, 82%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.12 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.43 – 7.35 (m, 1H), 7.28 (ddd, *J* = 15.5, 8.3, 4.3 Hz, 2H), 7.05 (d, *J* = 8.2 Hz, 2H), 7.00 (s, 1H), 6.90 (d, *J* = 8.4 Hz, 2H), 4.81 (s, 2H), 2.25 (s, 3H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.6, 143.8, 136.7, 132.3, 131.3, 130.8, 129.9, 128.5, 127.3, 126.2, 114.4, 51.2, 20.6. HRMS (ESI, *m/z*) calcd for C<sub>15</sub>H<sub>15</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 271.0900; found: 271.0905.

### 3-(cyclohexylamino)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4b)



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 4:1 v/v) to give the product as a white solid (58.9 mg, 75%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.12 (dd, *J* = 7.1, 2.4 Hz, 1H), 7.44 – 7.32 (m, 1H), 7.31 – 7.24 (m, 2H), 5.39 (s, 1H), 4.70 (s, 2H), 2.98 (td, *J* = 10.0, 3.9 Hz, 1H), 1.97 (d, *J* = 10.1 Hz, 2H), 1.76 (d, *J* = 2.1 Hz, 2H), 1.34 – 1.14 (m, 6H). <sup>13</sup>C NMR (75 MHz, CDCl<sub>3</sub>) δ 163.8, 136.6, 131.8, 130.4, 128.6, 127.1, 126.0, 58.3, 51.8, 31.3, 25.9, 24.4. HRMS (ESI, *m/z*) calcd for C<sub>14</sub>H<sub>19</sub>N<sub>2</sub>OS [M+H]<sup>+</sup>: 263.1213; found: 263.1214.

### (S)-7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-8-(3-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidin-1-yl)-3,7-dihydro-1H-purine-2,6-dione (5)

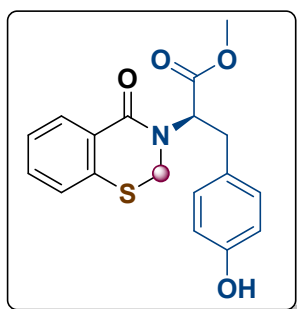


The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:2, v/v) to give the product as a white solid (128.3 mg, 69%). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.0 Hz, 1H), 8.00 (d, *J* = 8.2 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.74 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 1H), 7.42 – 7.33 (m, 1H), 7.31 – 7.25 (m, 2H), 5.58 (s, 2H), 4.93 – 4.85 (m, 2H), 4.69 – 4.57 (m, 2H), 4.11 (q, *J* = 7.1 Hz, 1H), 3.89 (d, *J* = 8.4 Hz, 1H), 3.79 (d, *J* =



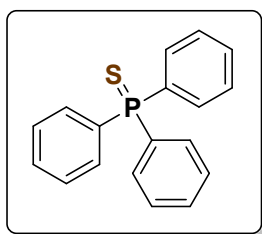
12.5 Hz, 1H), 3.56 (s, 3H), 3.15 (t,  $J = 11.4$  Hz, 1H), 2.88 (s, 3H), 2.03 (d,  $J = 7.5$  Hz, 2H), 1.73 (s, 3H), 1.25 (dd,  $J = 8.1, 6.2$  Hz, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  168.3, 163.6, 160.8, 155.3, 154.3, 151.6, 149.7, 147.6, 137.0, 133.1, 131.5, 130.8, 129.3, 128.6, 127.0, 126.5, 126.0, 124.6, 122.9, 104.5, 81.4, 72.8, 60.2, 52.4, 50.8, 46.1, 44.3, 35.4, 29.6, 27.7, 24.4, 21.6, 14.0. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{33}\text{H}_{33}\text{N}_8\text{O}_3\text{S}$   $[\text{M}+\text{H}]^+$ : 621.2391; found: 621.2391.

**Methyl (R)-3-(4-hydroxyphenyl)-2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)propanoate (6)**



The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (80.3 mg, 78%).  $^1\text{H}$  NMR (300 MHz, DMSO)  $\delta$  9.21 (s, 1H), 7.99 – 7.83 (m, 1H), 7.48 – 7.38 (m, 1H), 7.34 (d,  $J = 7.0$  Hz, 1H), 7.31 – 7.23 (m, 1H), 7.07 (d,  $J = 8.3$  Hz, 2H), 6.63 (d,  $J = 8.4$  Hz, 2H), 5.24 (dd,  $J = 10.5, 5.3$  Hz, 1H), 4.72 (d,  $J = 13.1$  Hz, 1H), 4.59 (d,  $J = 13.1$  Hz, 1H), 3.67 (s, 3H), 3.17 (qd,  $J = 14.4, 8.0$  Hz, 2H).  $^{13}\text{C}$  NMR (75 MHz, DMSO)  $\delta$  171.0, 163.5, 156.4, 137.9, 132.5, 130.7, 130.4, 128.8, 127.6, 126.3, 115.6, 60.5, 52.7, 46.7, 33.7. HRMS (ESI,  $m/z$ ) calcd for  $\text{C}_{18}\text{H}_{18}\text{NO}_4\text{S}$   $[\text{M}+\text{H}]^+$ : 344.0952; found: 344.0955.

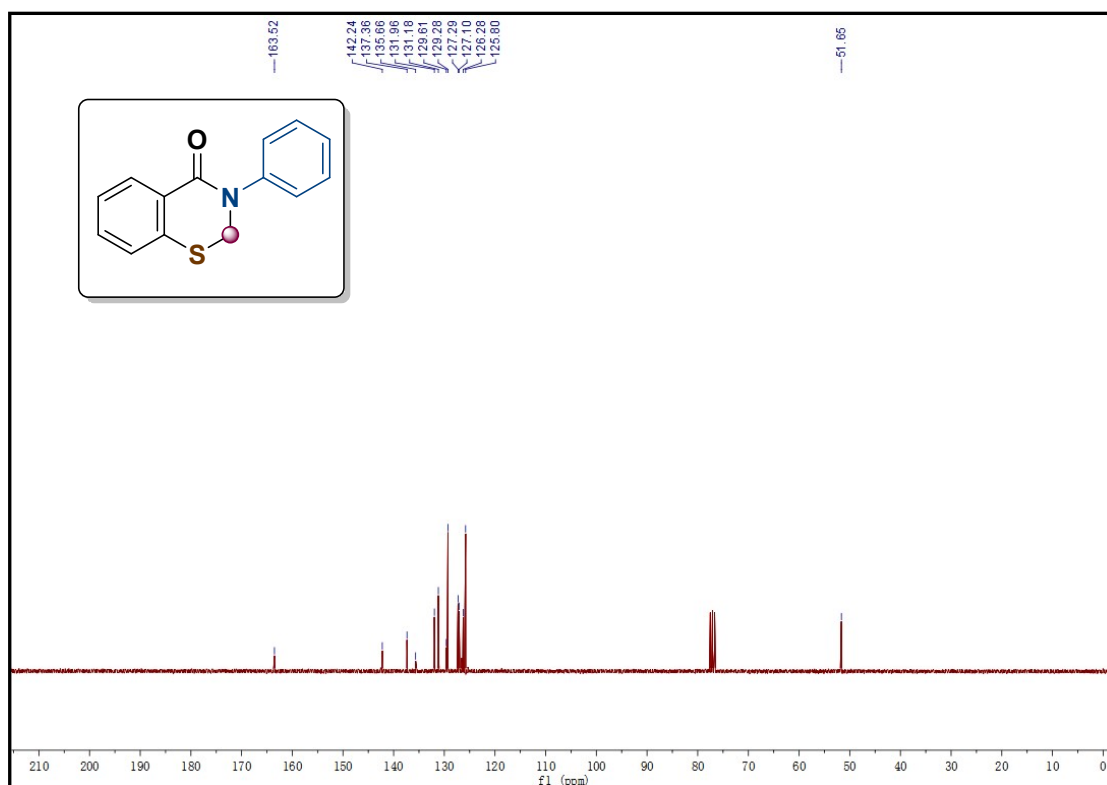
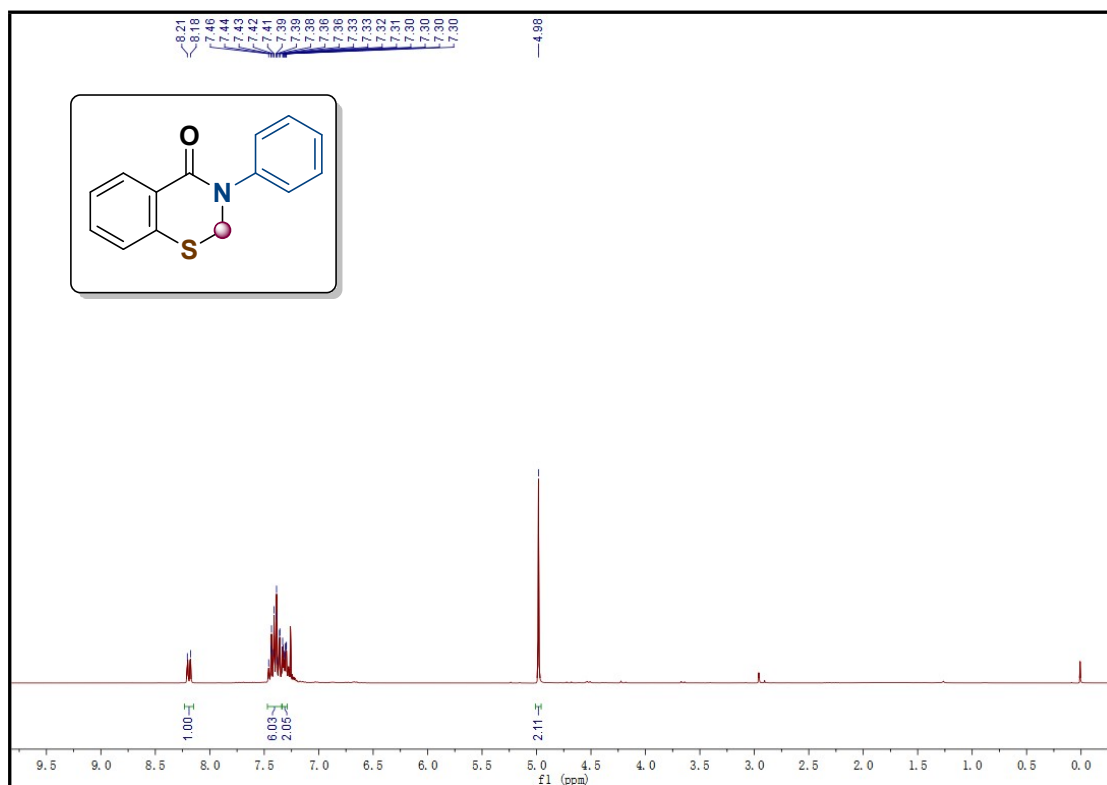
**Triphenylphosphine sulfide (CAS Number: 3878-45-3)**



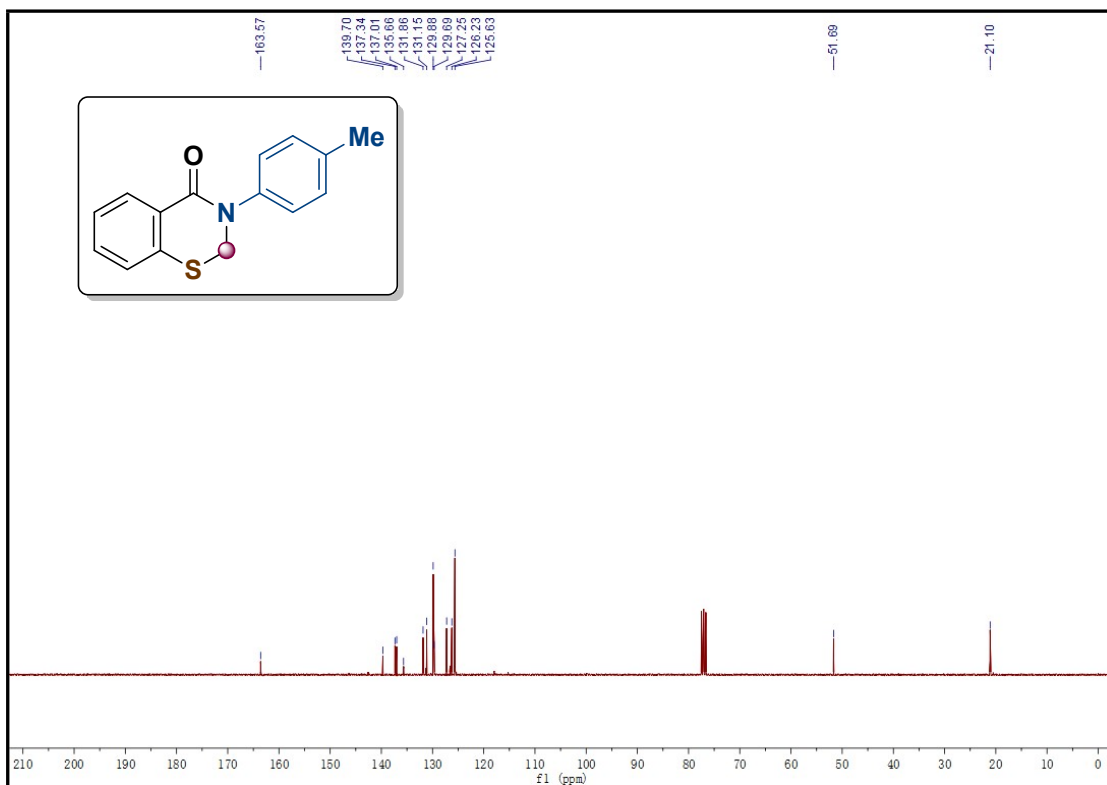
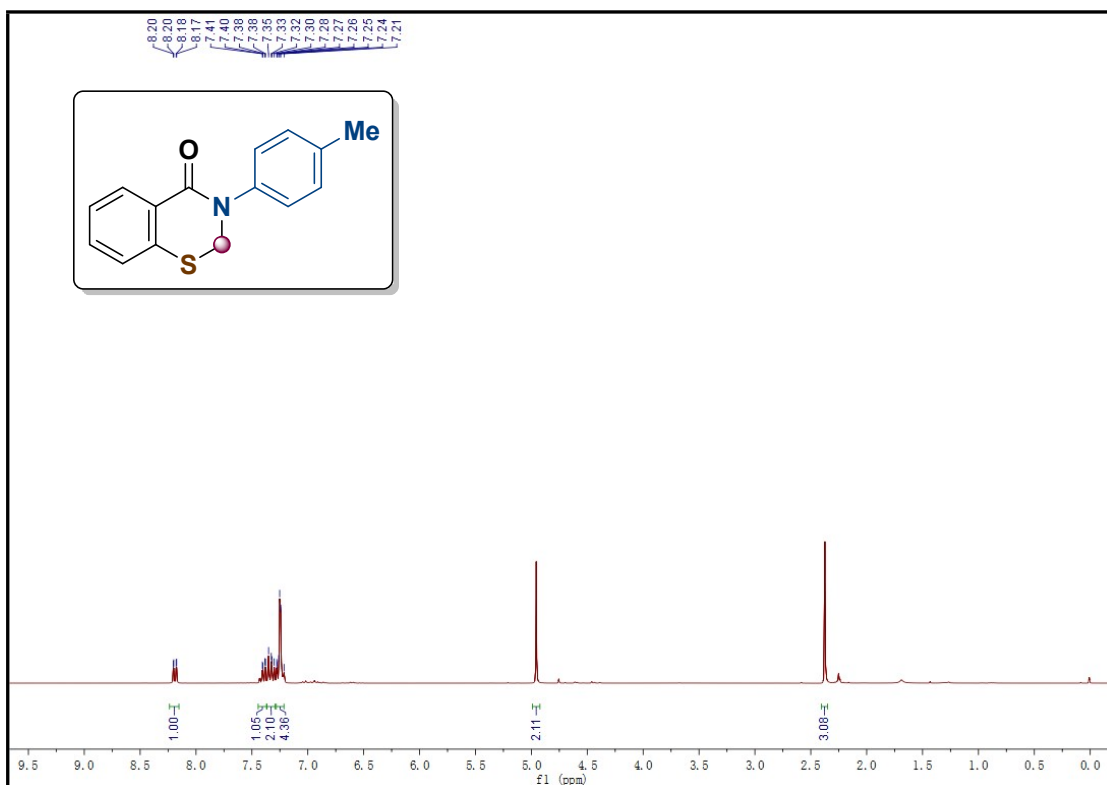
$\text{CH}_3\text{CN}$  (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1a** (50.4 mg, 0.3mmol) and  $\text{PPh}_3$  (78.6 mg, 0.3 mmol) in a sealed tube. Then the reaction mixture was stirred at 80 °C for 16 h. Then, the solvents were removed via rotary evaporator and the residue was purified by flash column chromatograph (silica gel, petroleum ether: EtOAc = 10:1, v/v) to give the product as the white solid.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  7.72 (dd,  $J = 13.3, 7.2$  Hz, 2H), 7.63 – 7.16 (m, 3H).  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  133.3, 132.1 (d,  $J = 10.7$  Hz), 131.5 (d,  $J = 3.0$  Hz), 128.4 (d,  $J = 12.5$  Hz).

## 6. NMR spectroscopic data

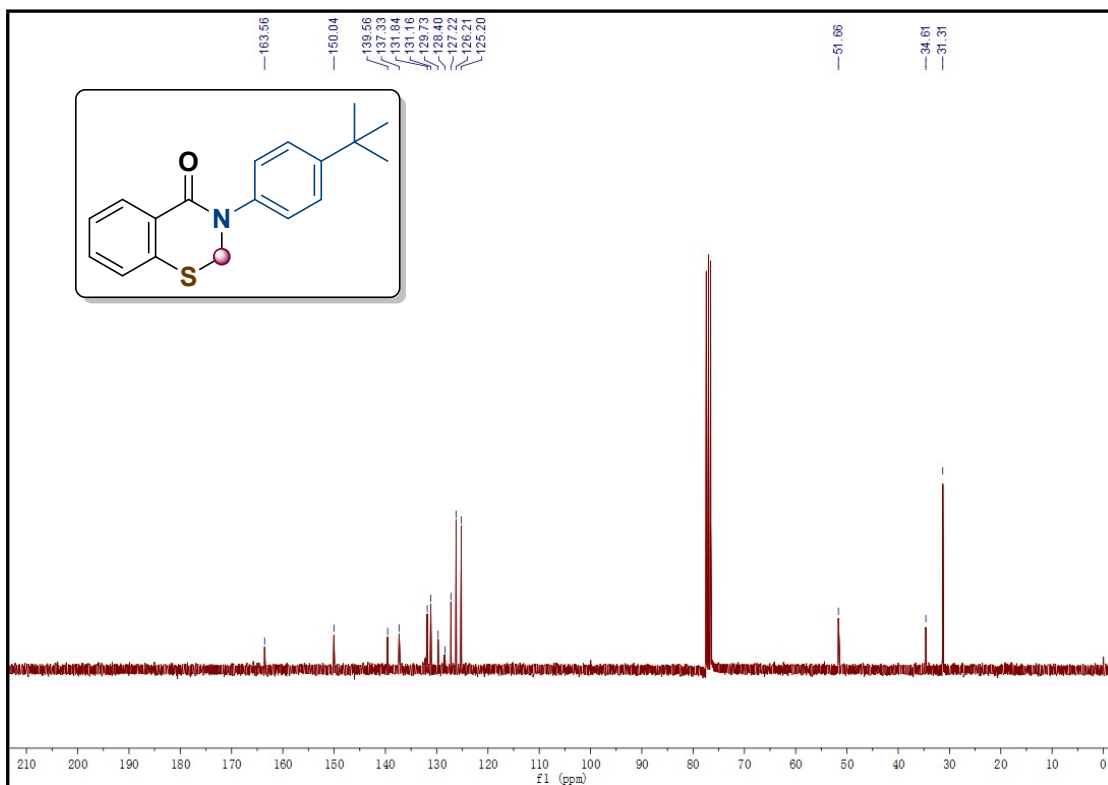
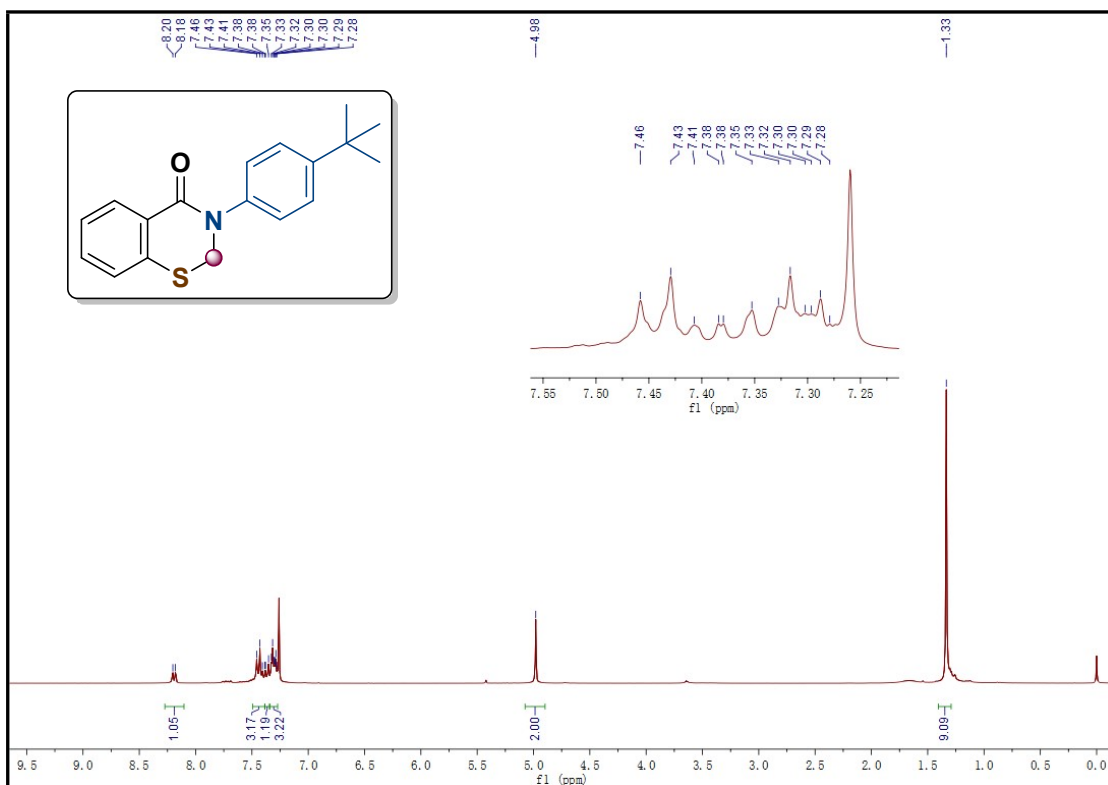
### 3-phenyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3a)



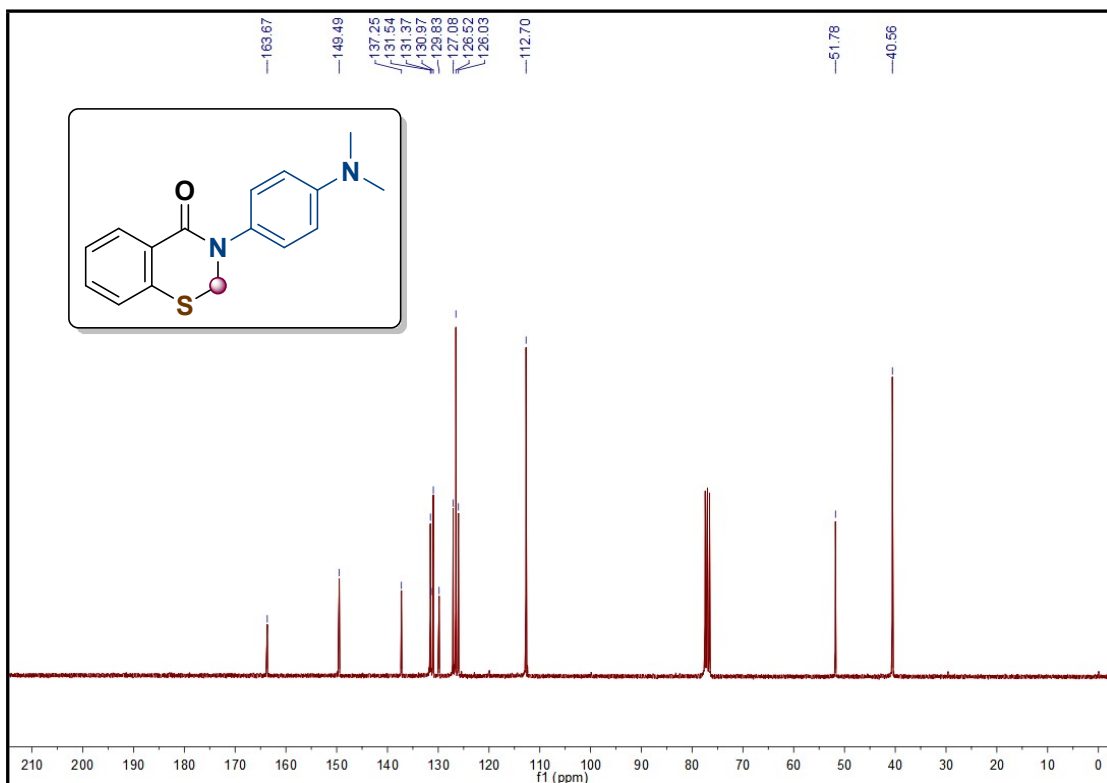
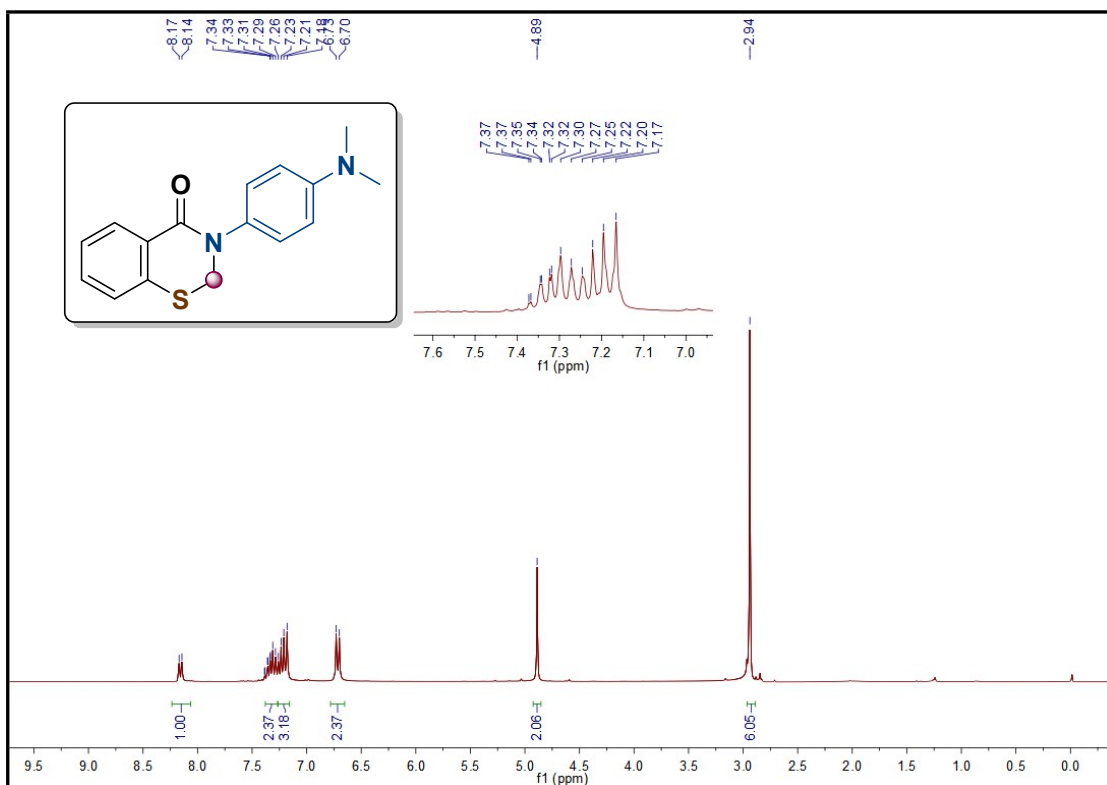
### 3-(p-tolyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3b)



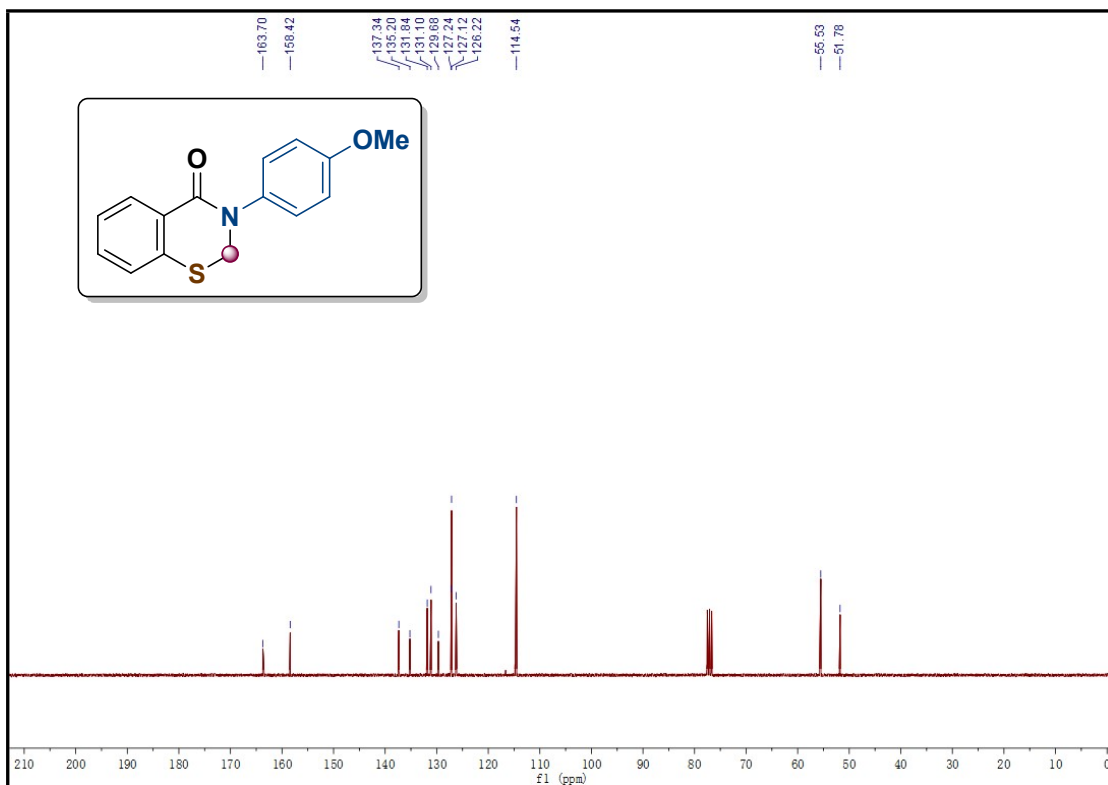
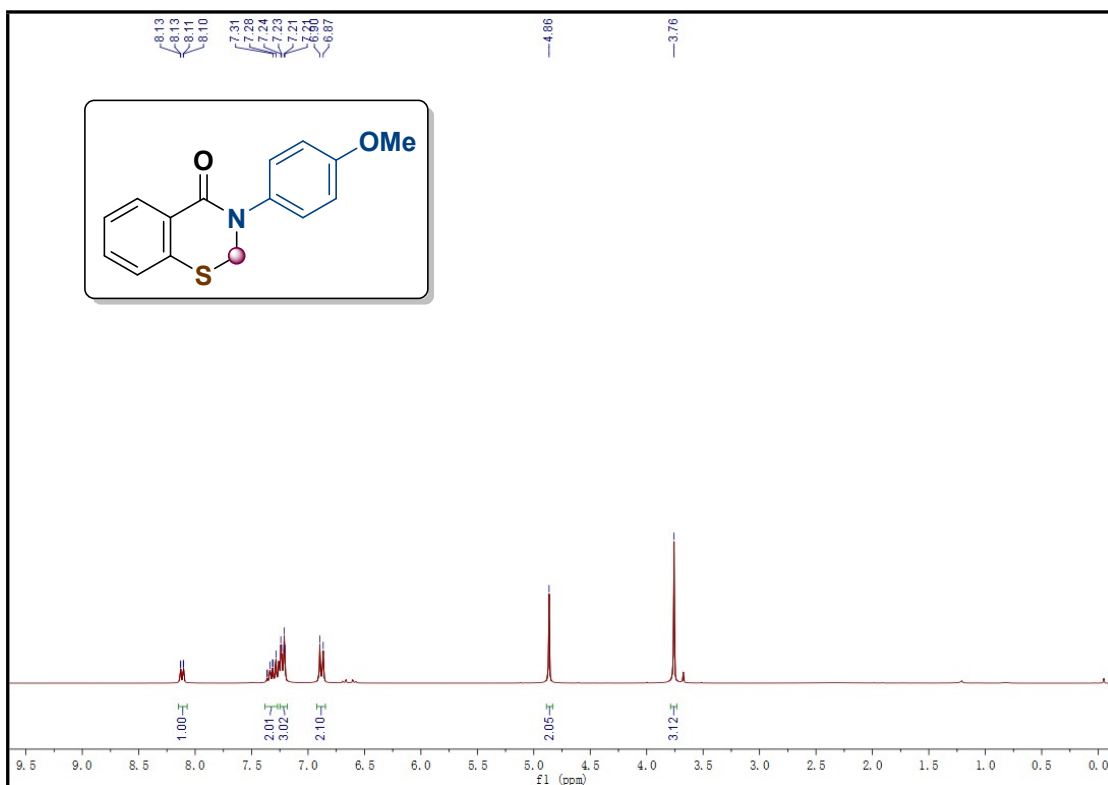
### 3-(4-(tert-butyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3c)



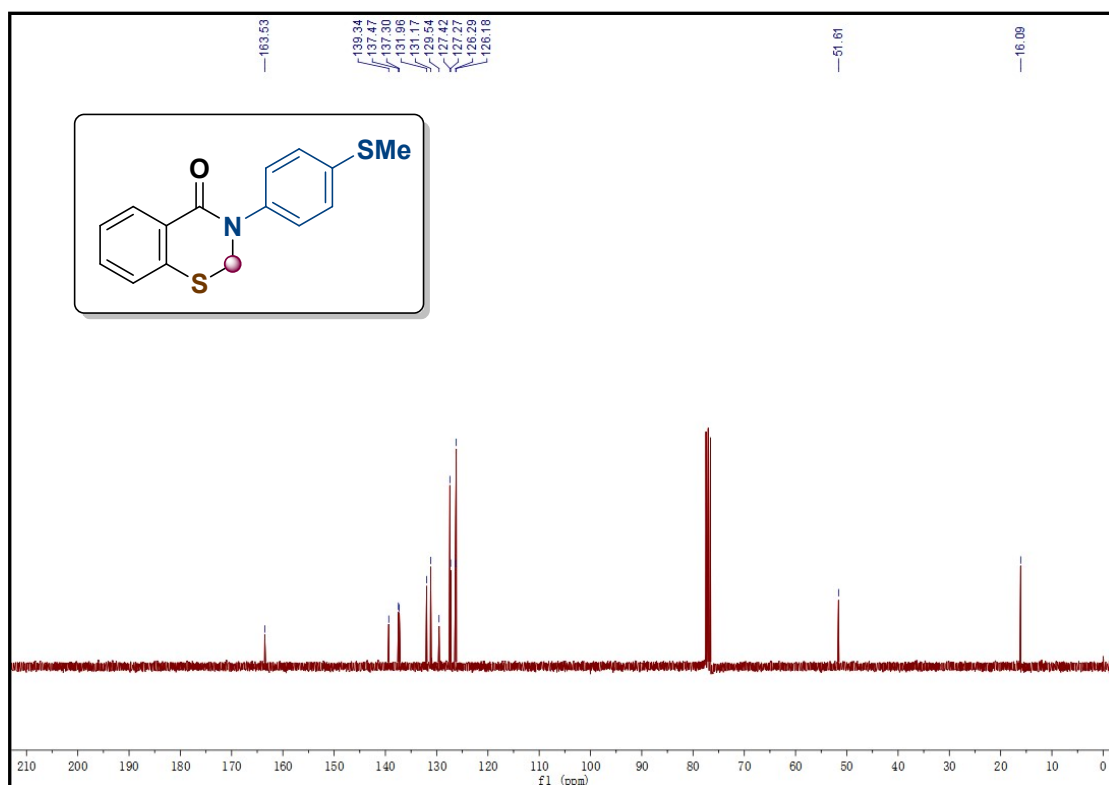
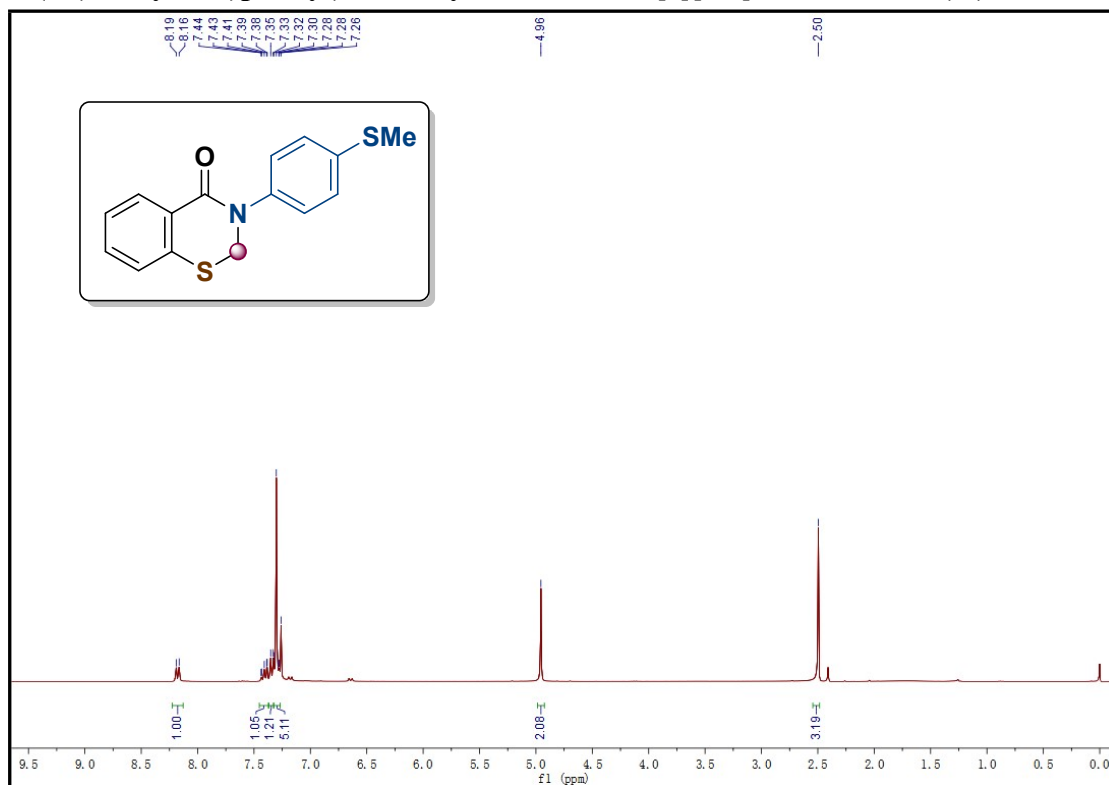
### 3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3d)



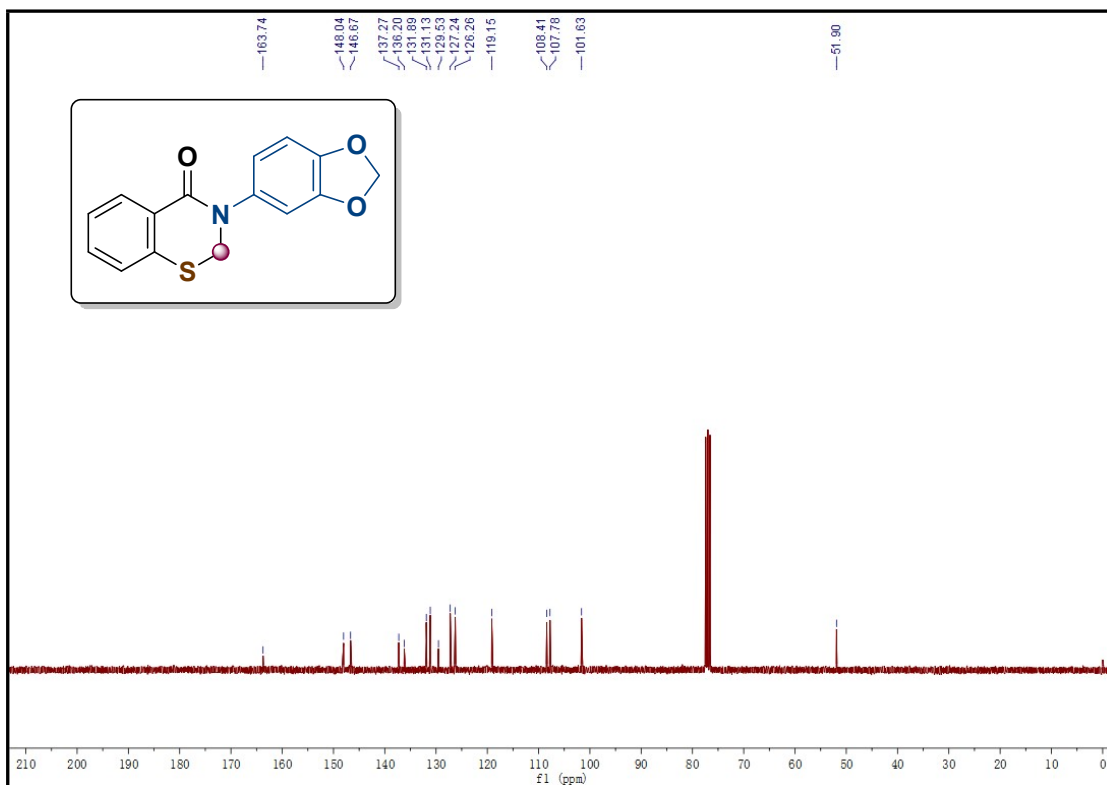
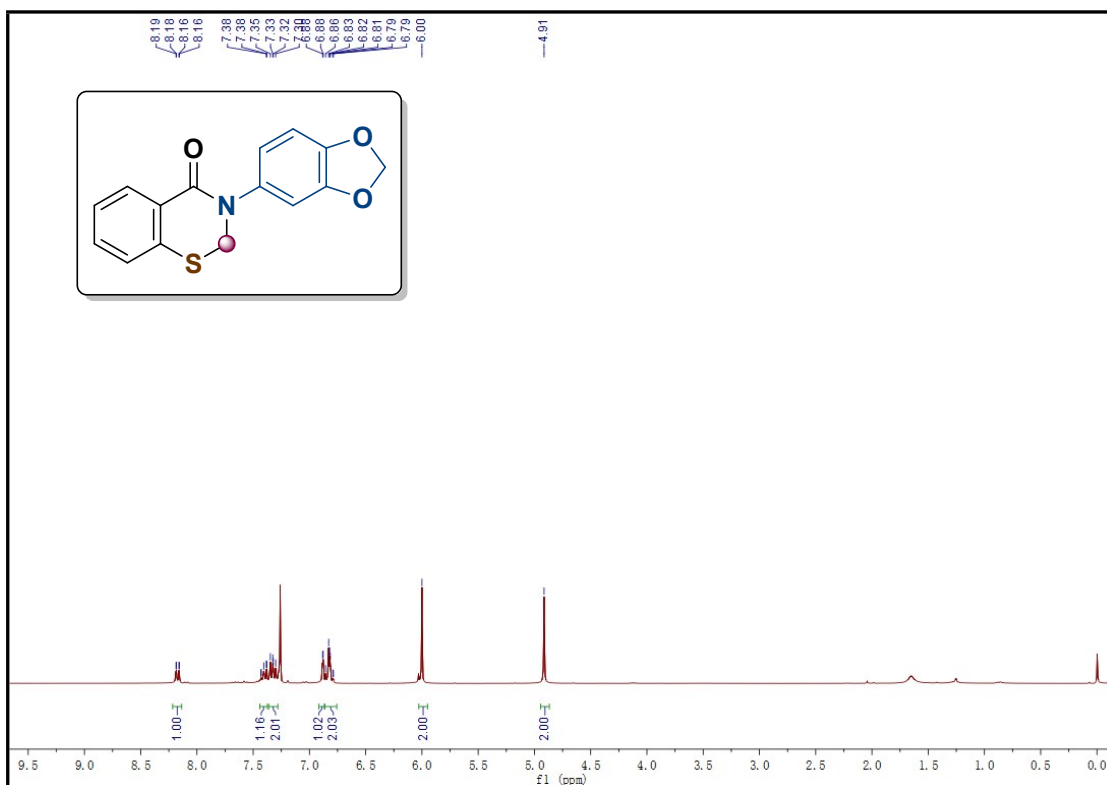
**3-(4-methoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3e)**



### 3-(4-(methylthio)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3f)

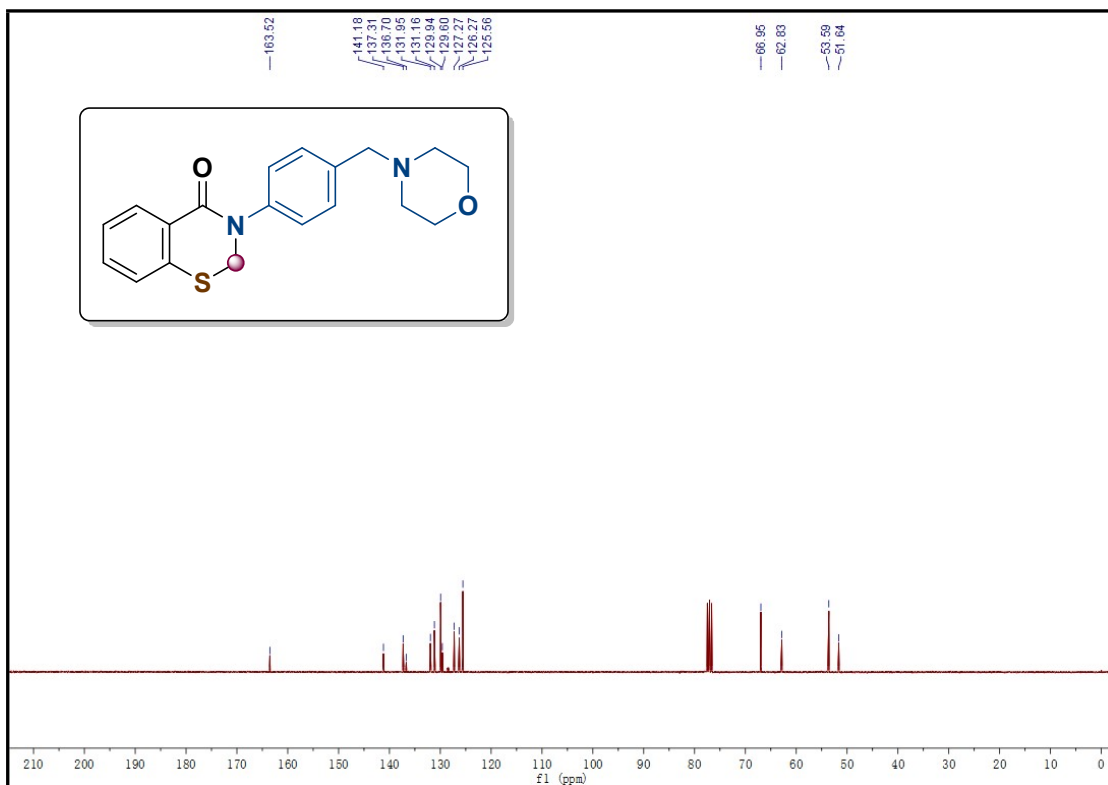
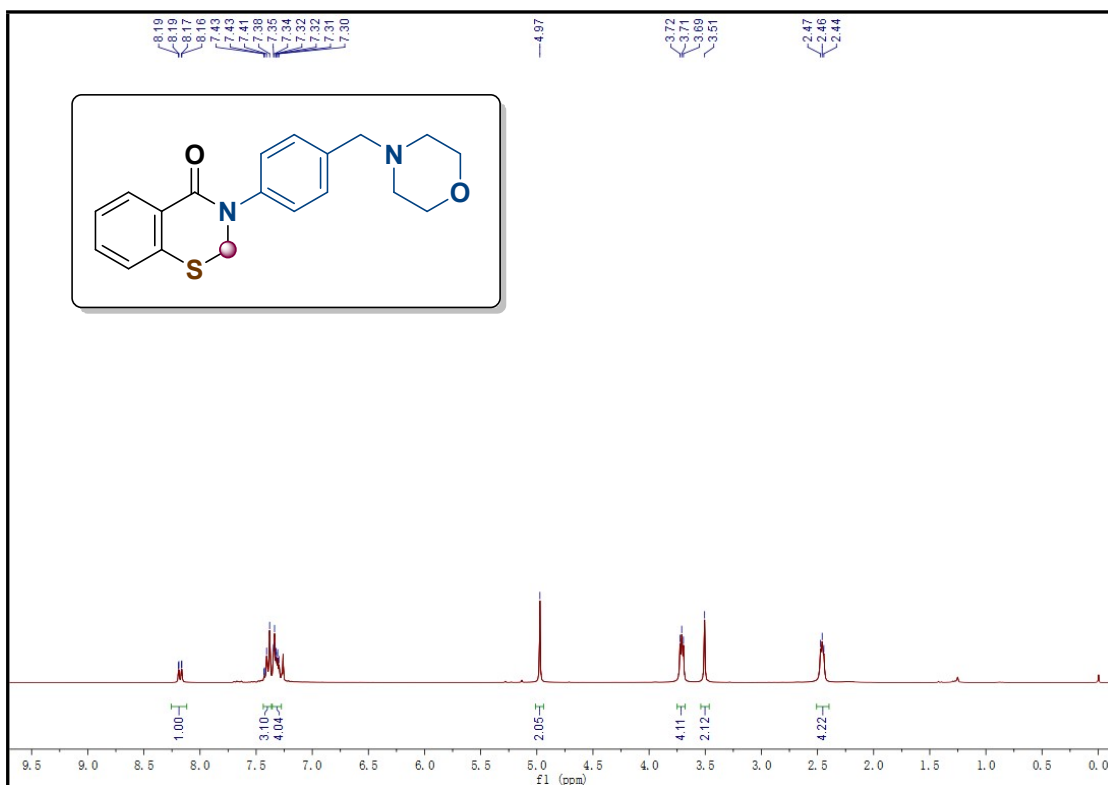


**3-(benzo[d][1,3]dioxol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3g)**

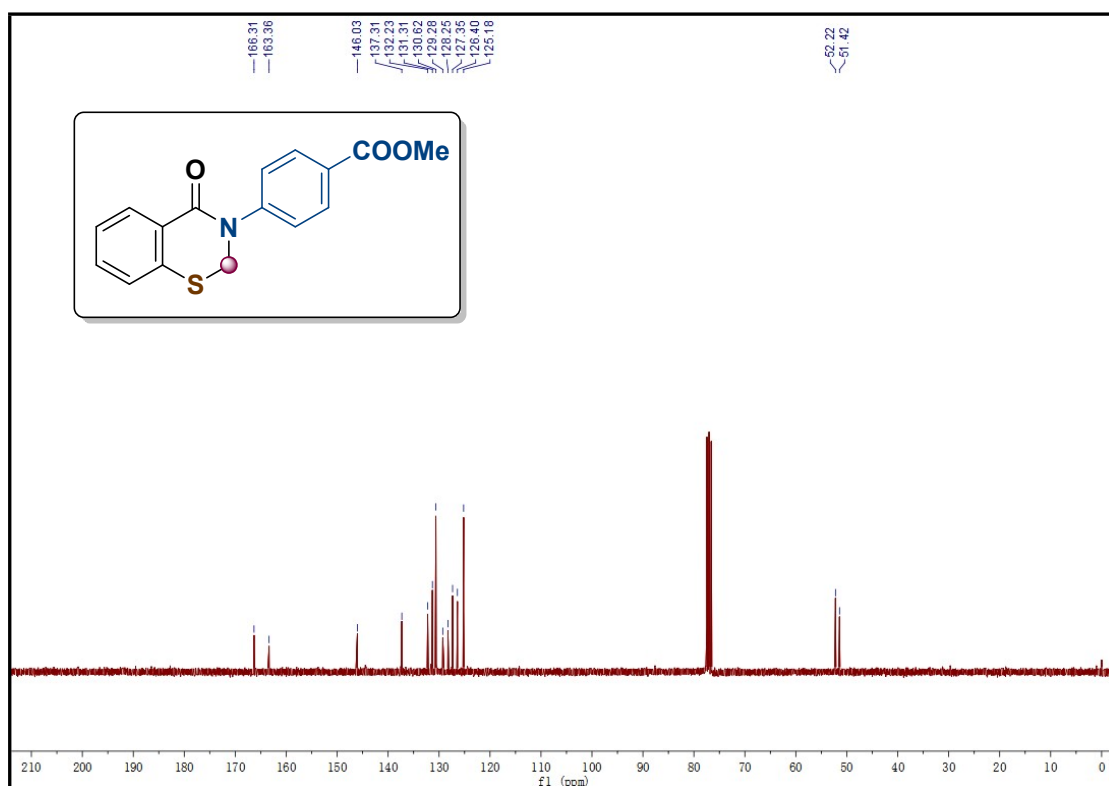
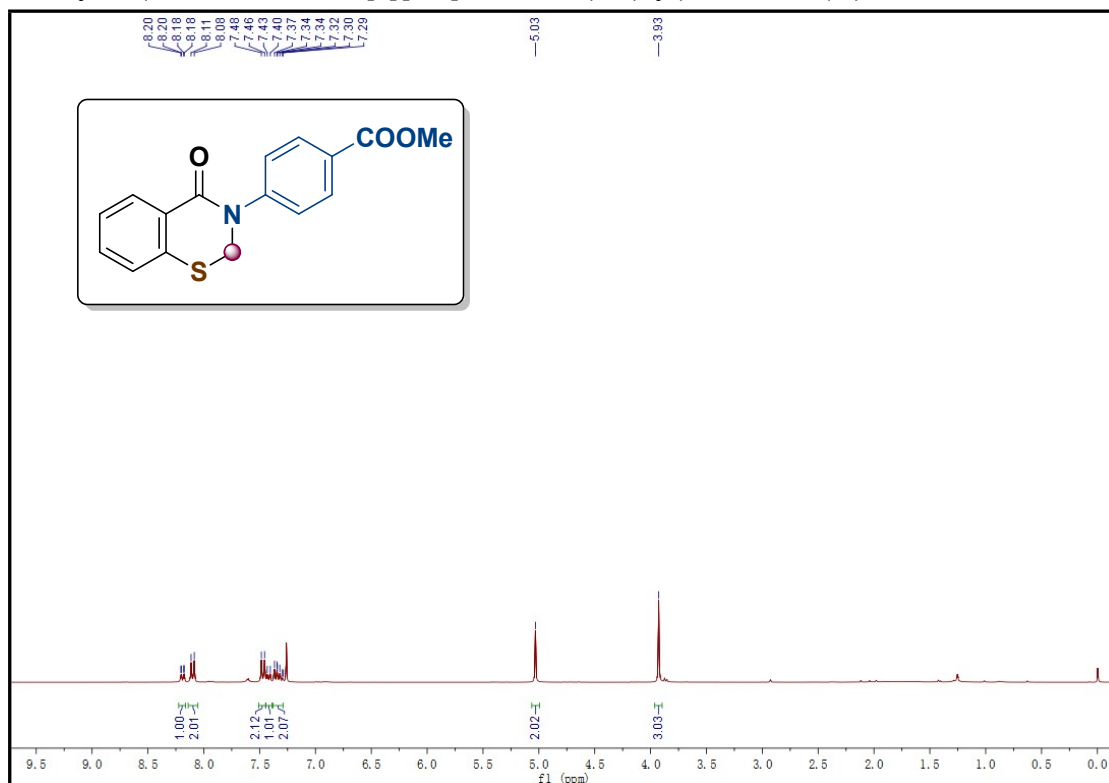




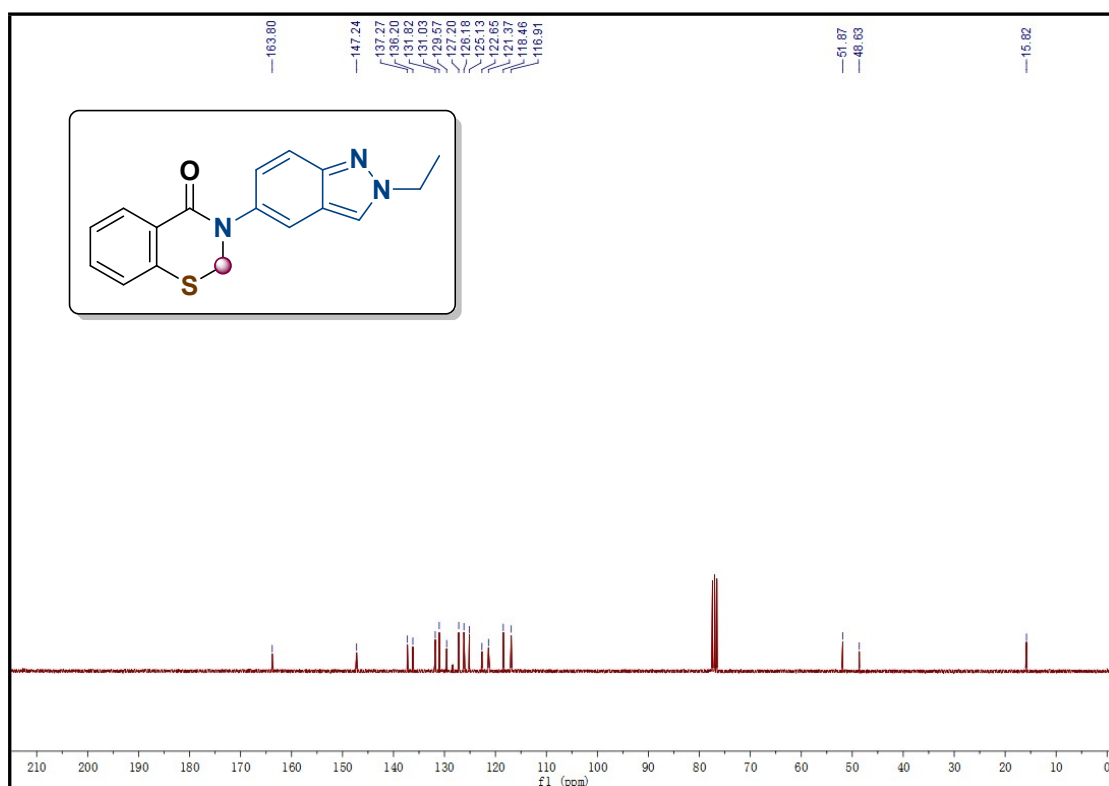
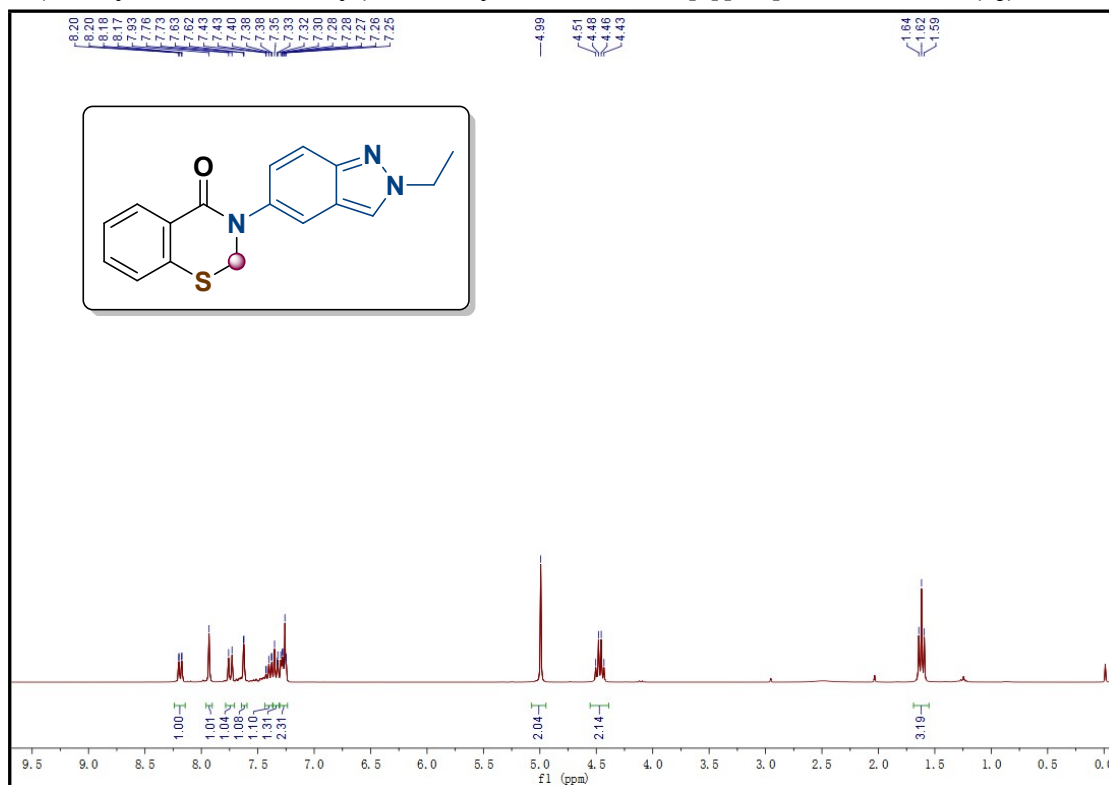
### 3-(4-(morpholinomethyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3h)



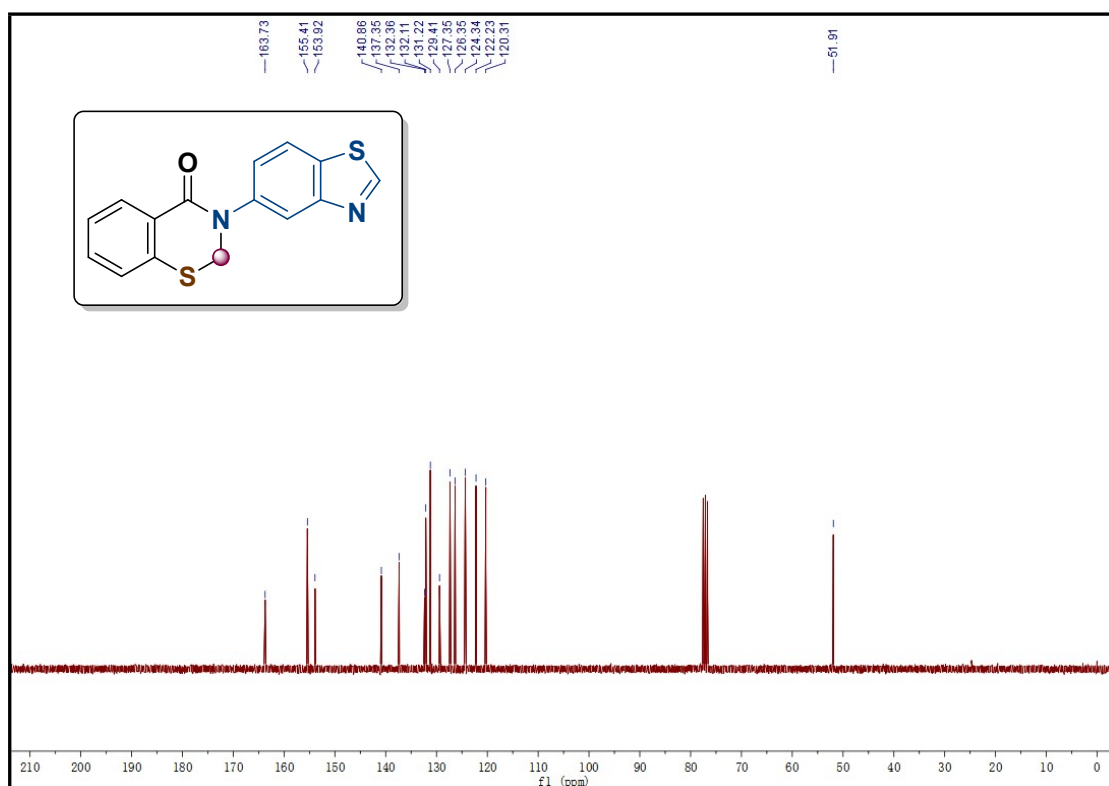
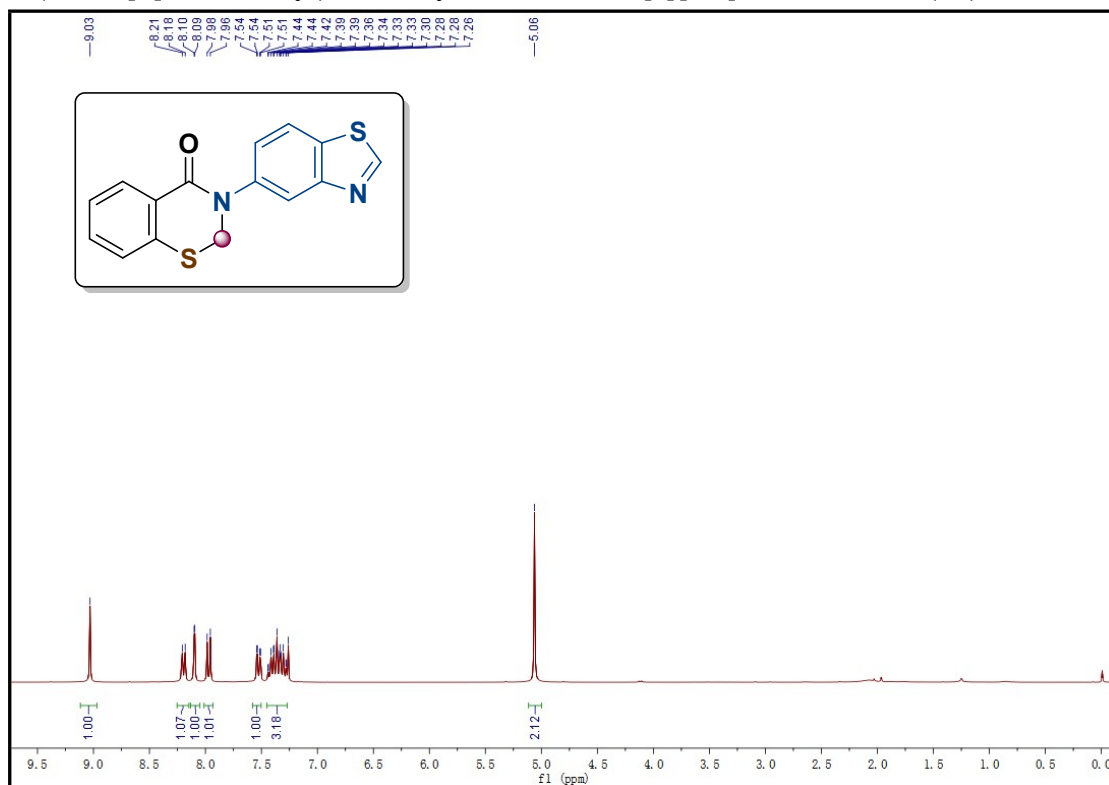
methyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)benzoate (3i)



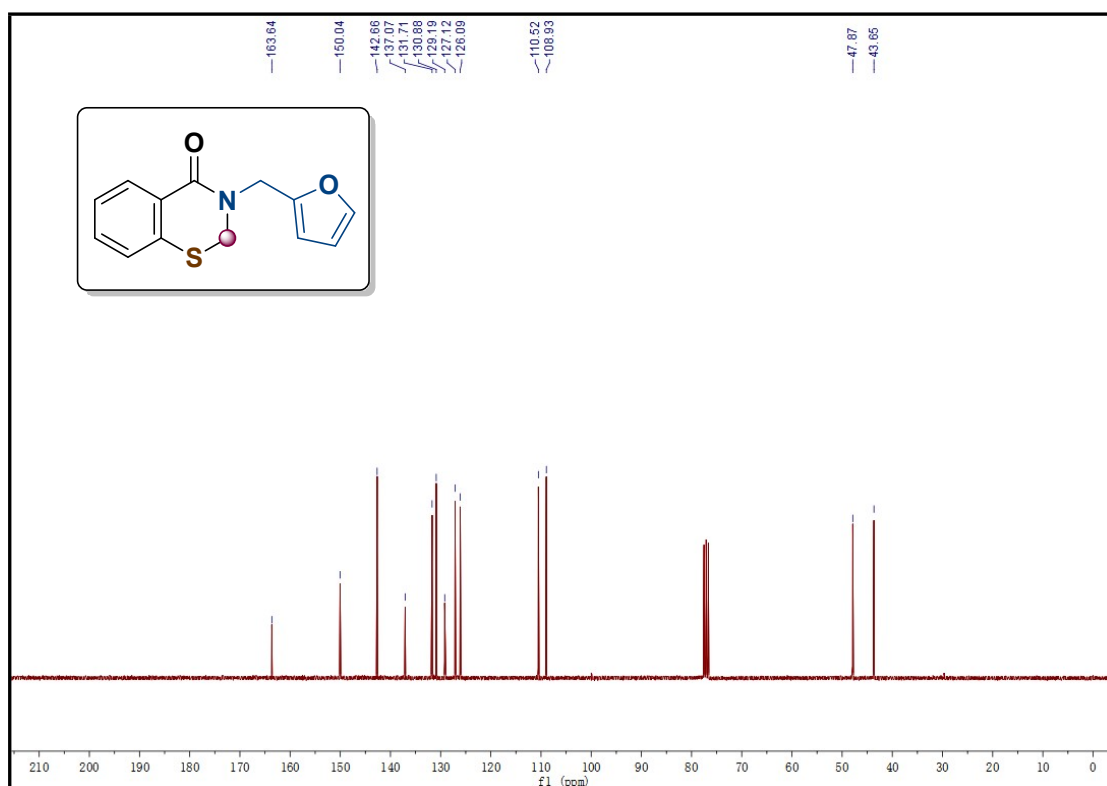
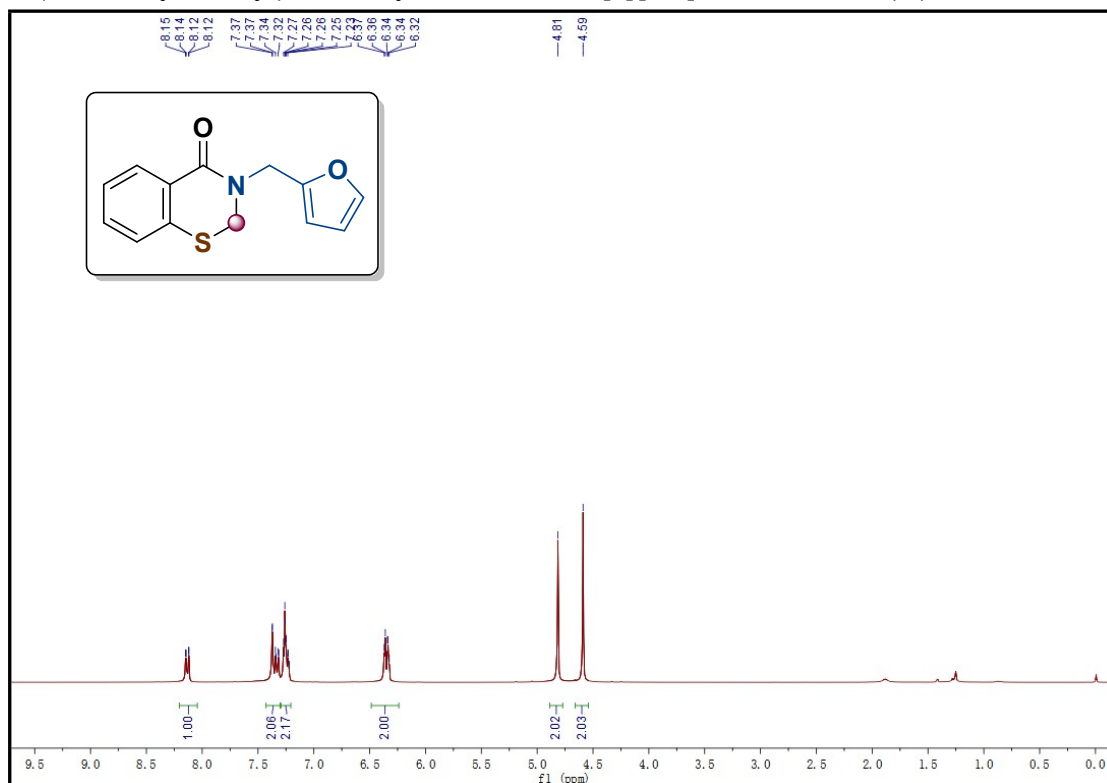
### 3-(2-ethyl-2H-indazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3j)



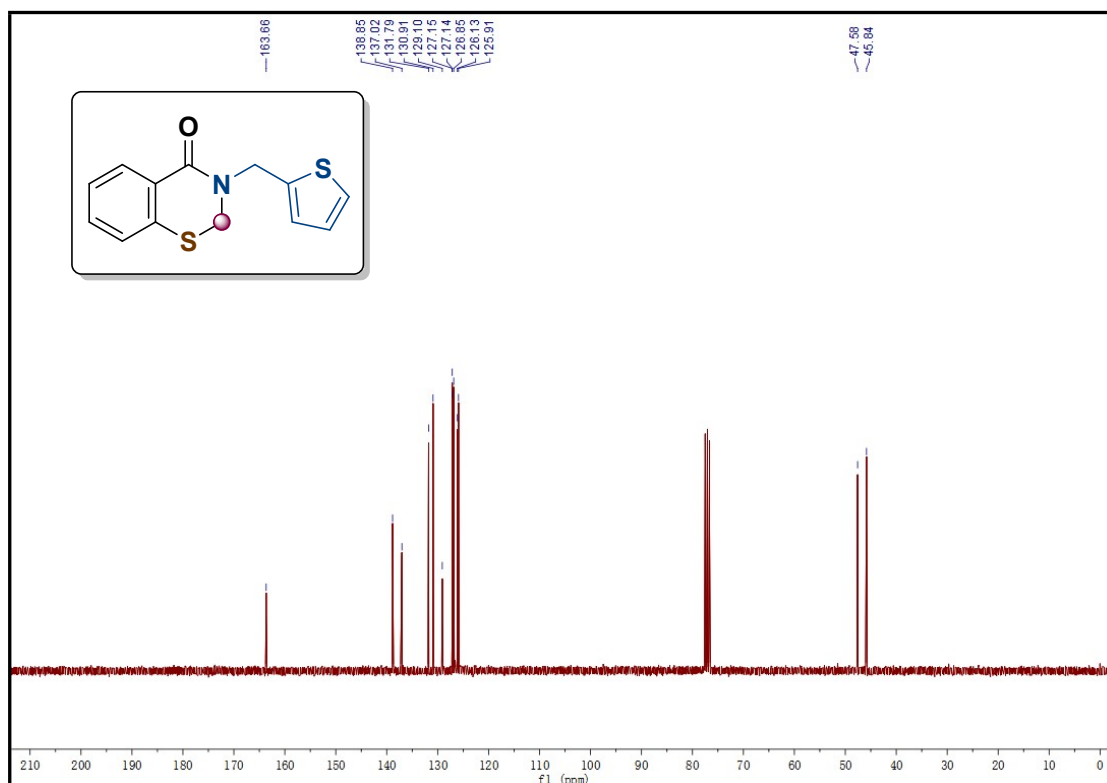
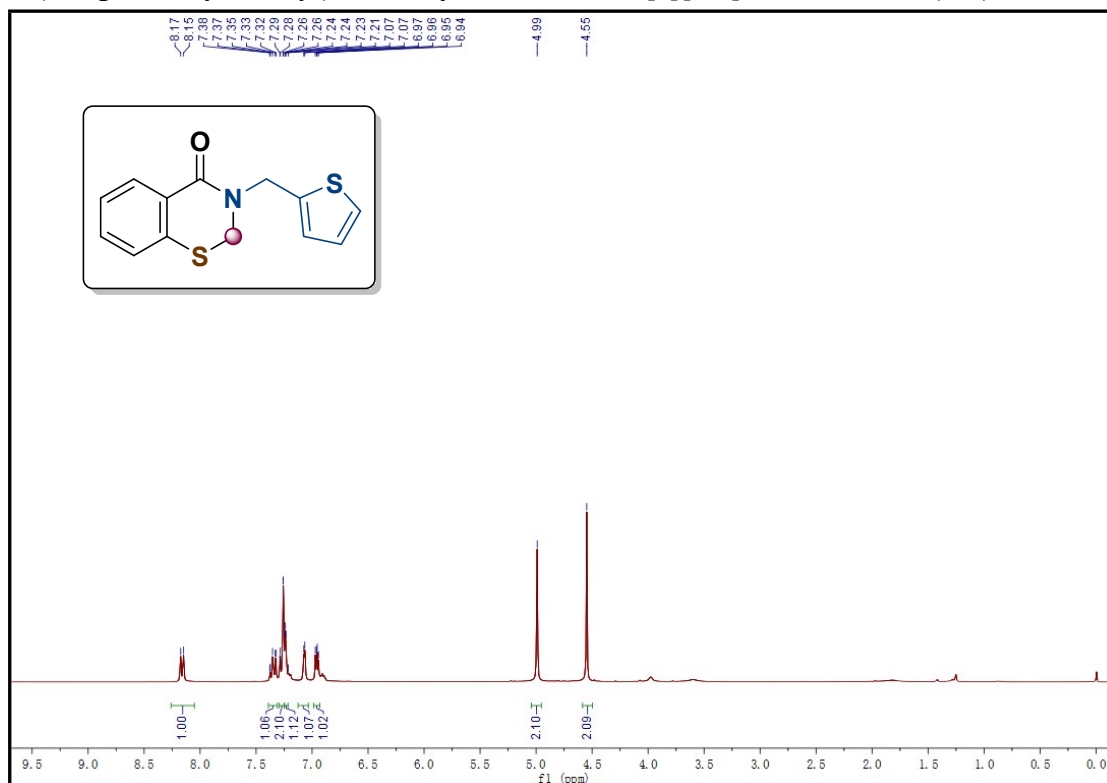
### 3-(benzo[d]thiazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3k)



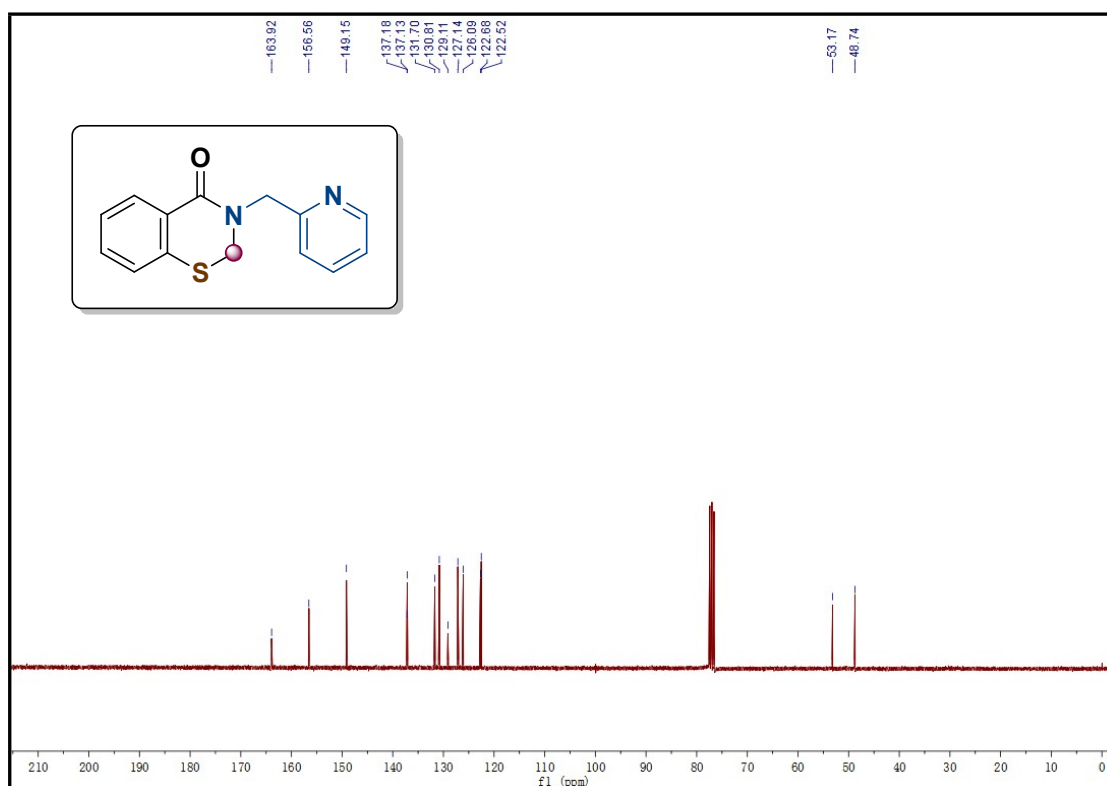
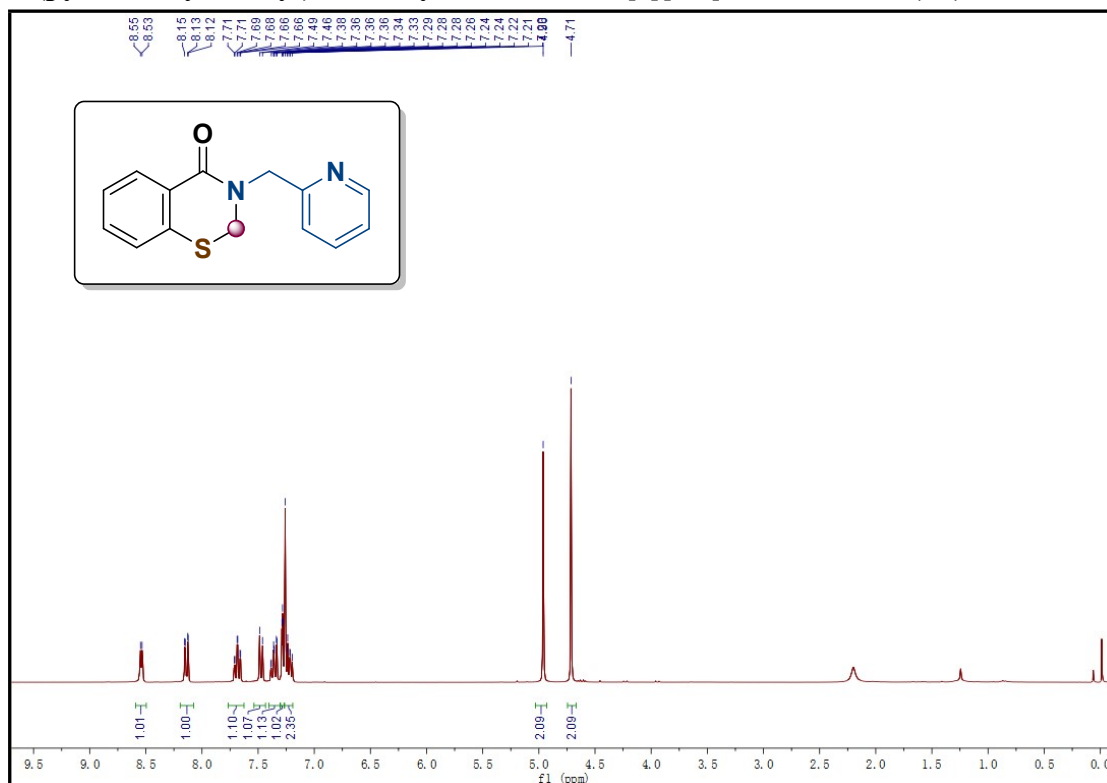
### 3-(furan-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3l)



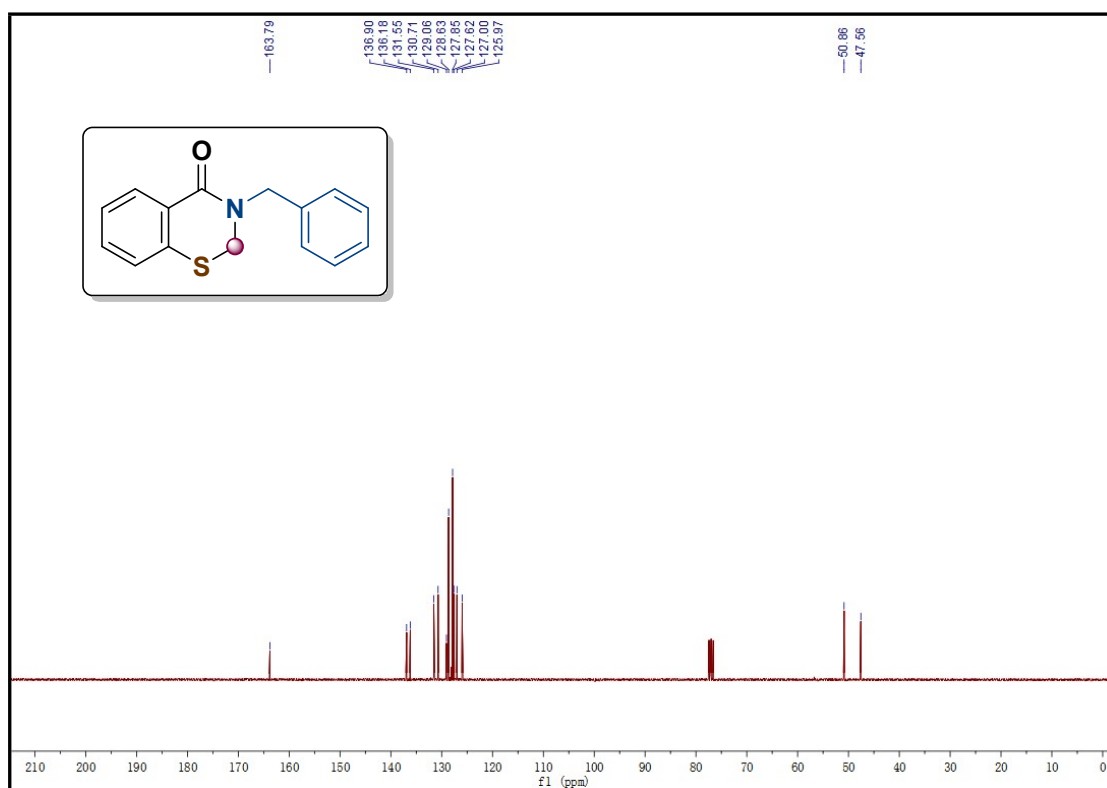
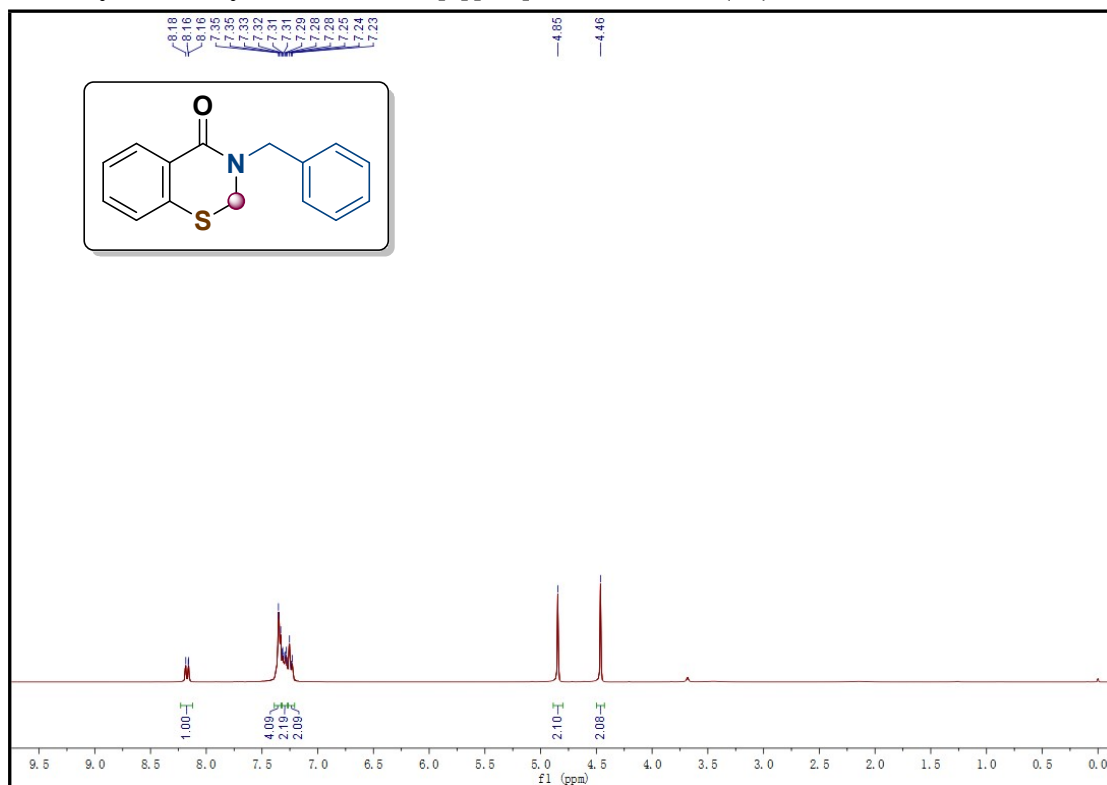
### 3-(thiophen-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3m)



### 3-(pyridin-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3n)

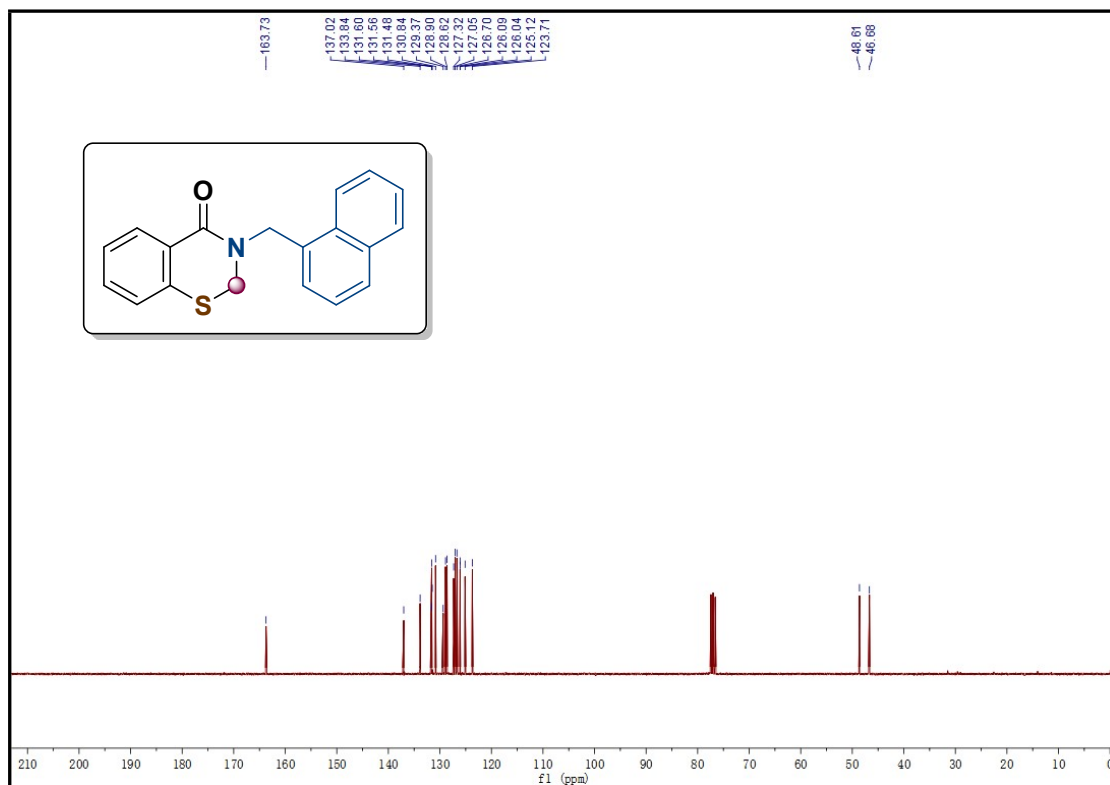
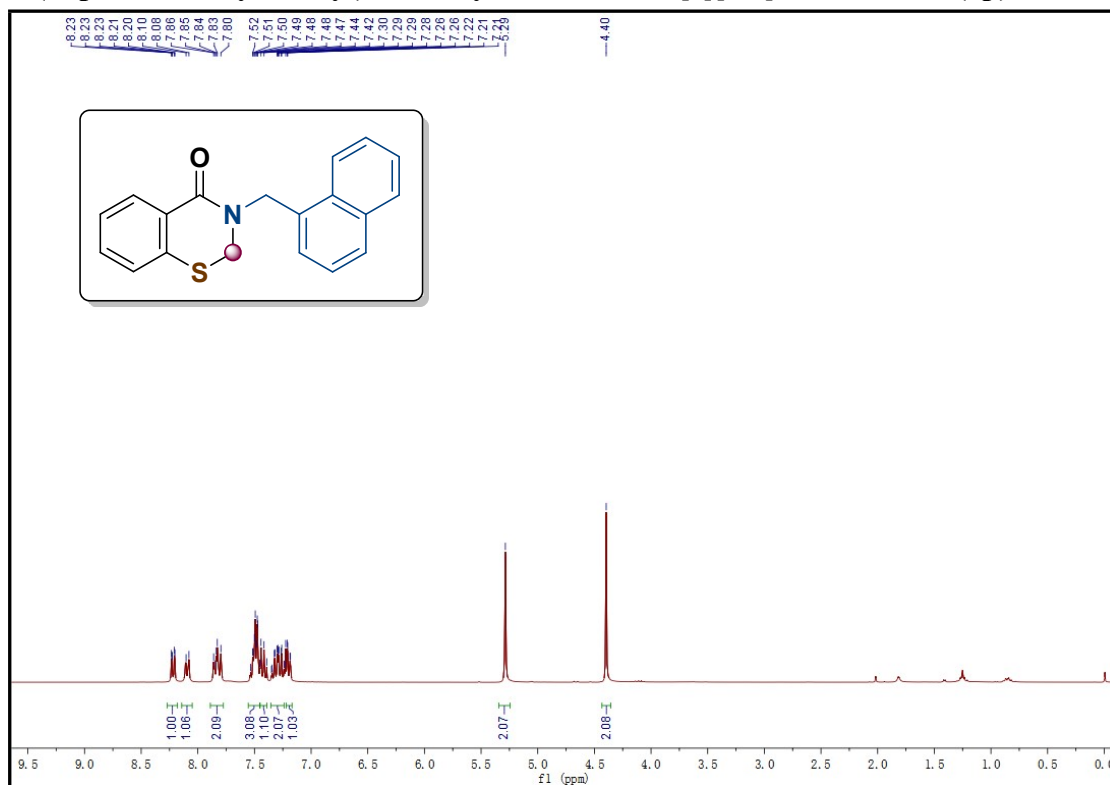


### 3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3o)

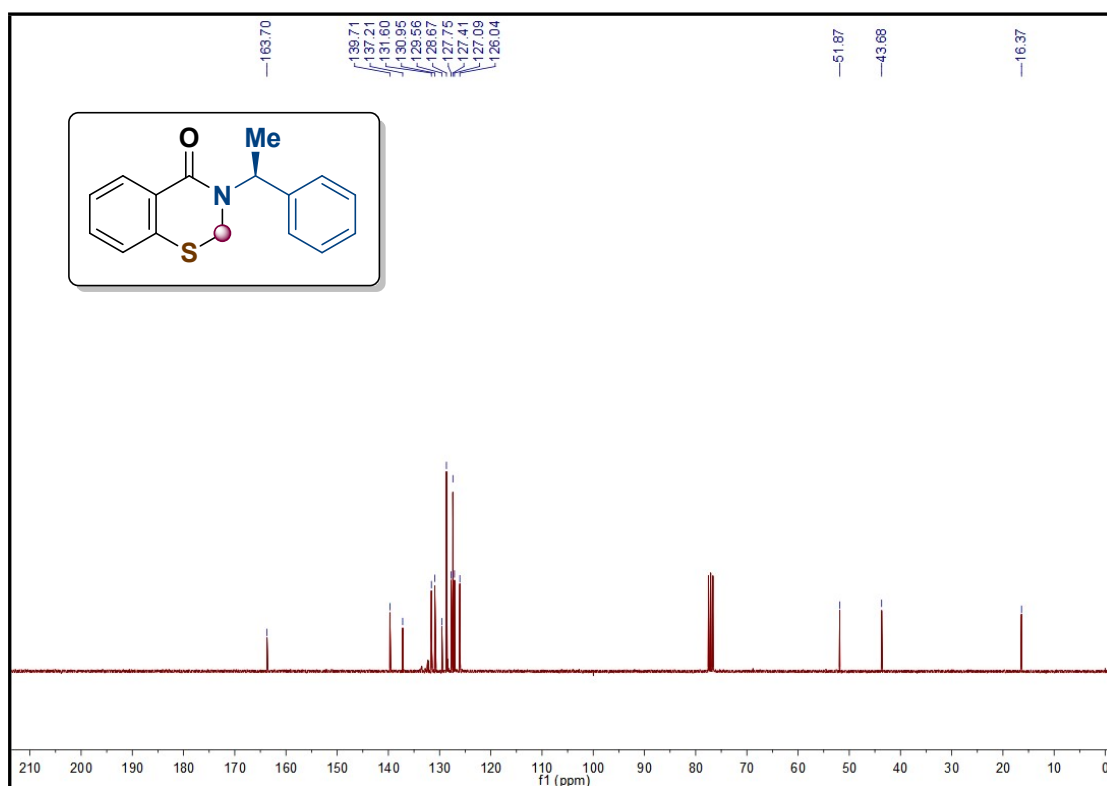
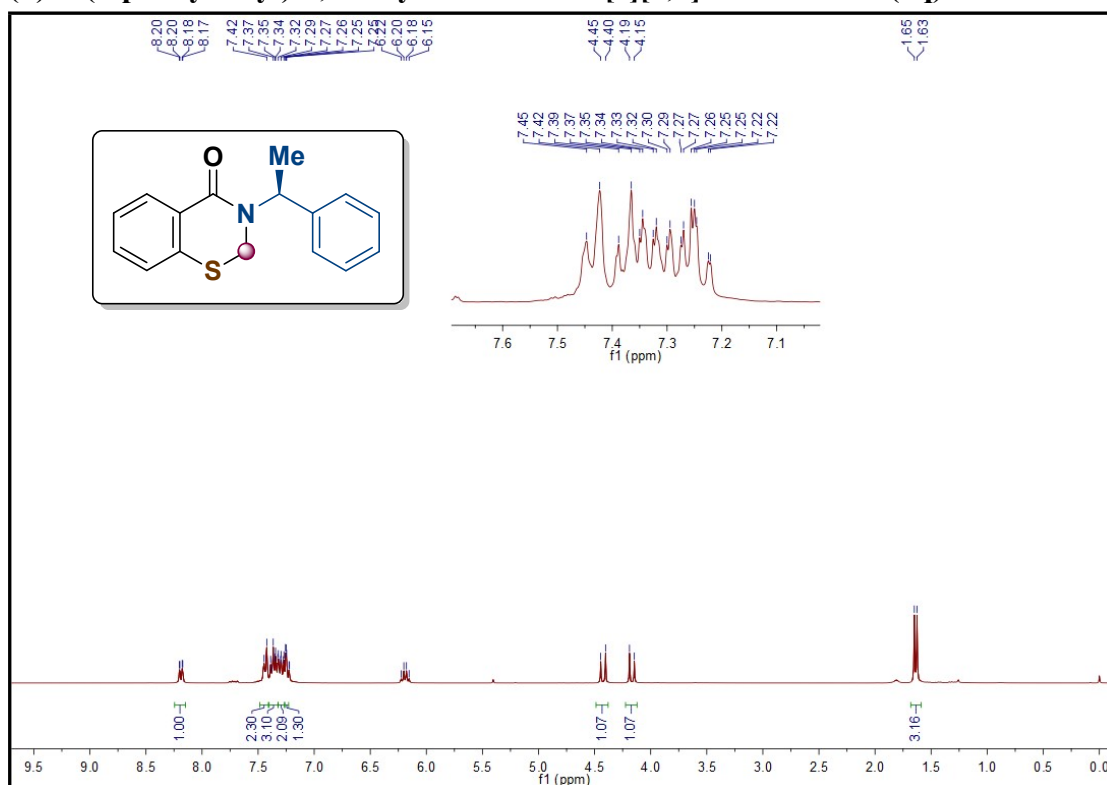




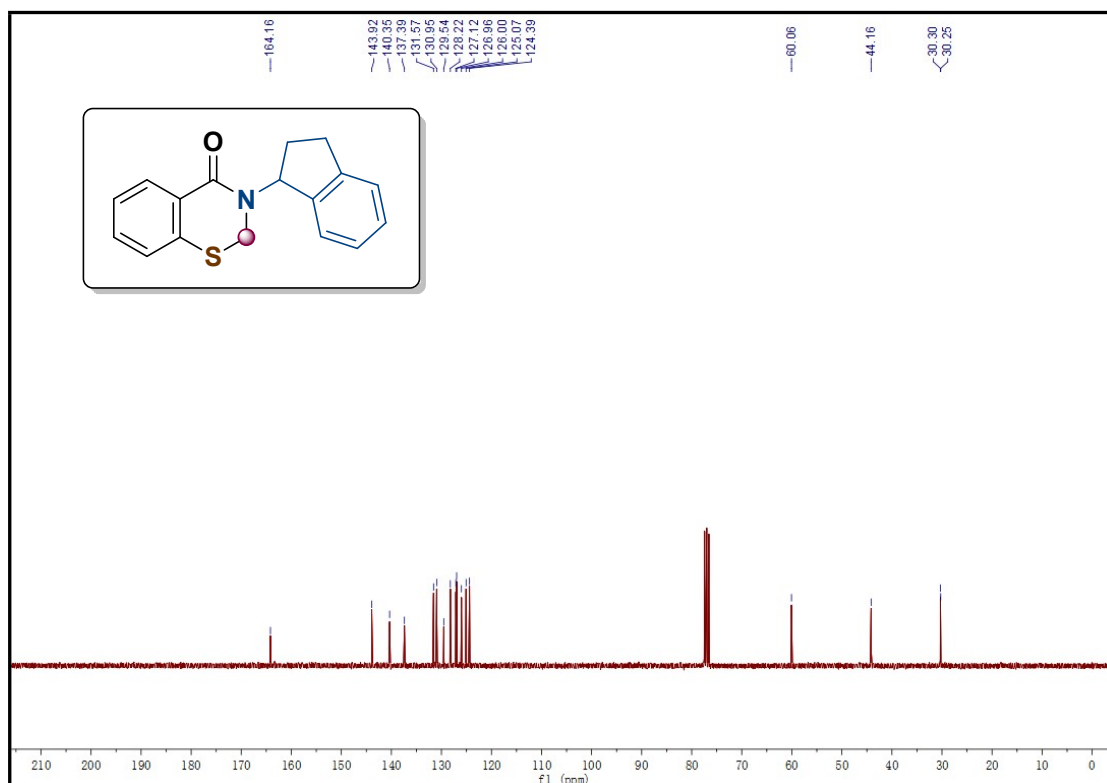
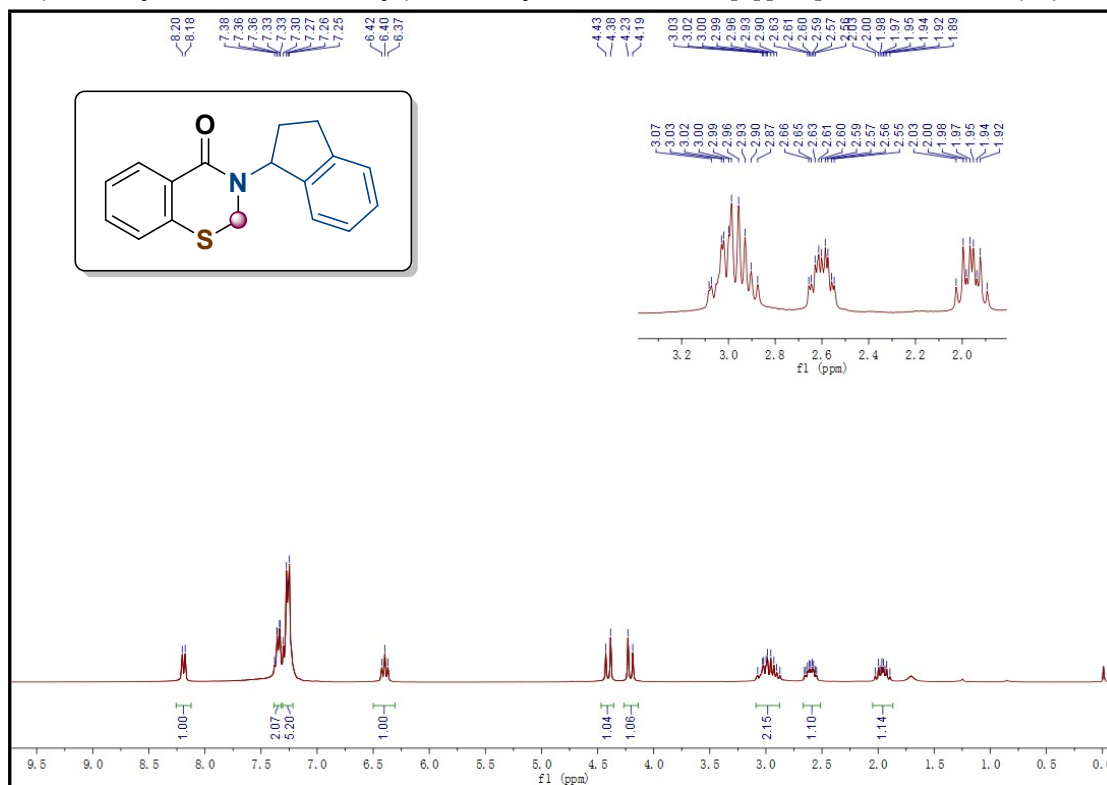
### 3-(naphthalen-1-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one(3p)



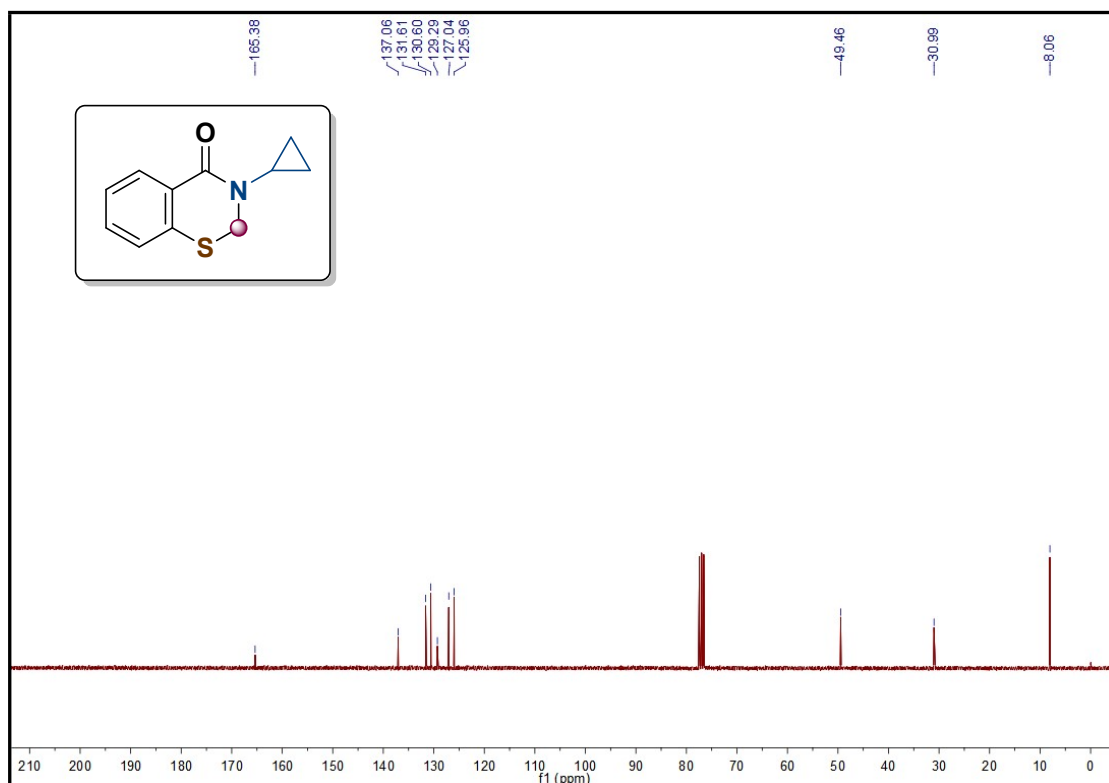
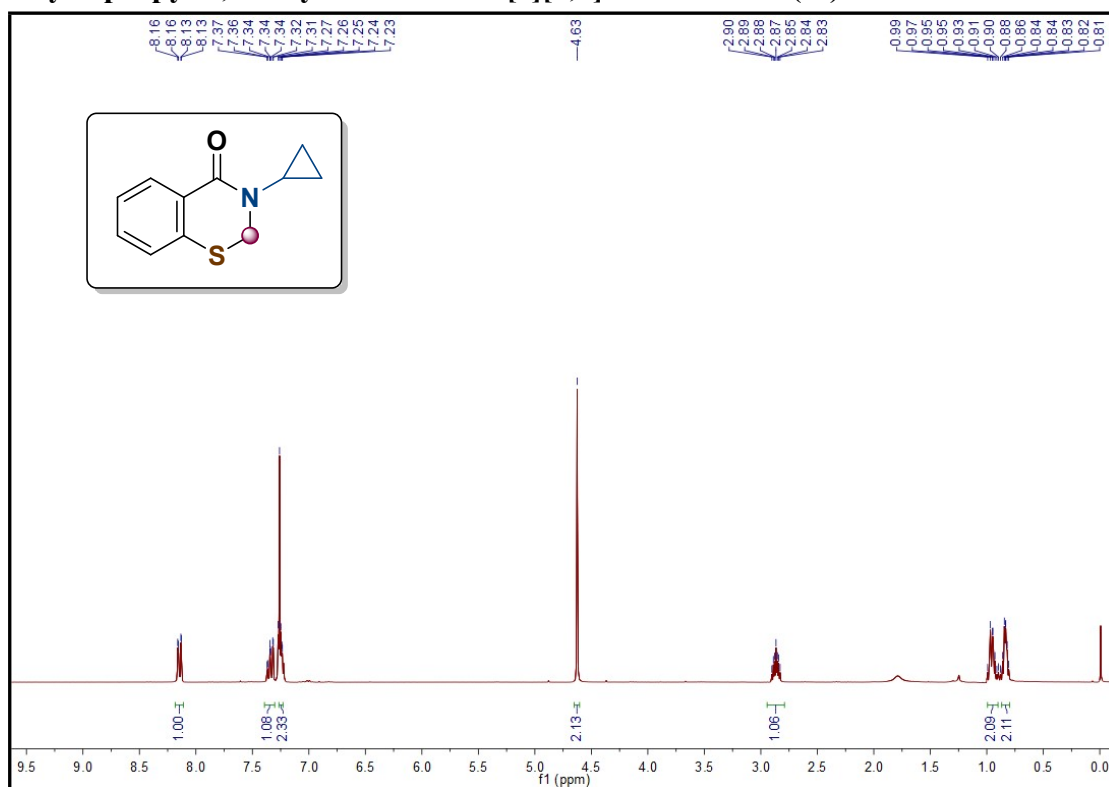
**(S)-3-(1-phenylethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3q)**



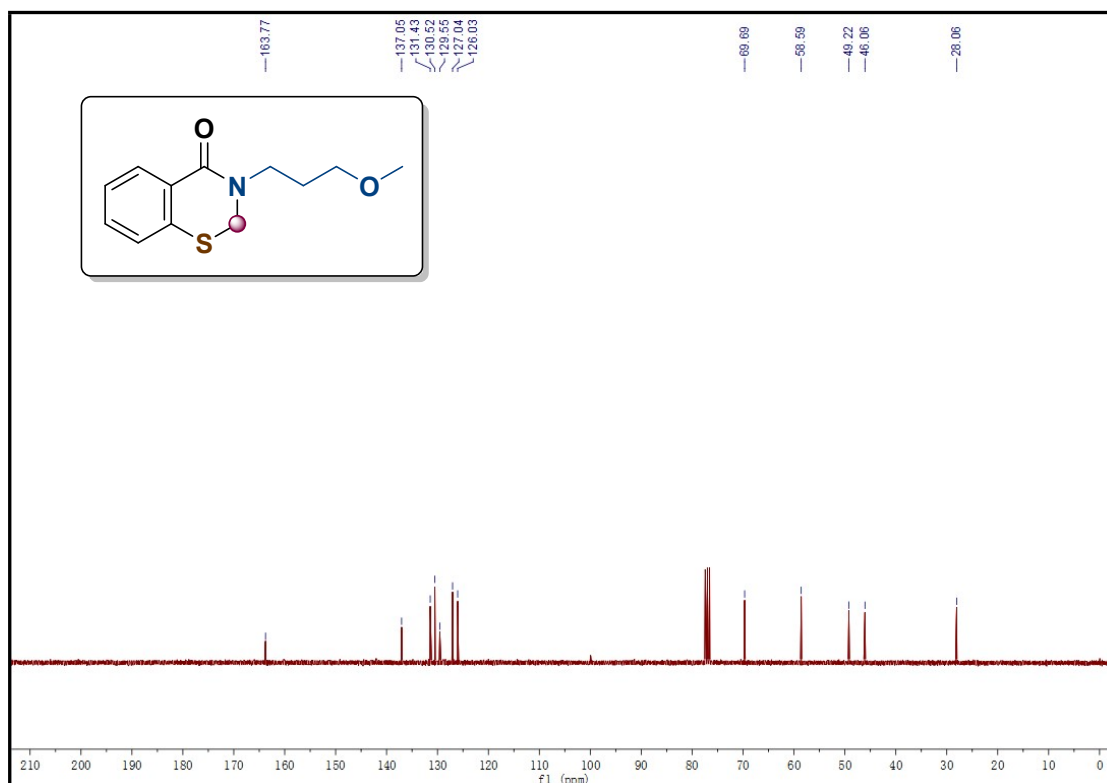
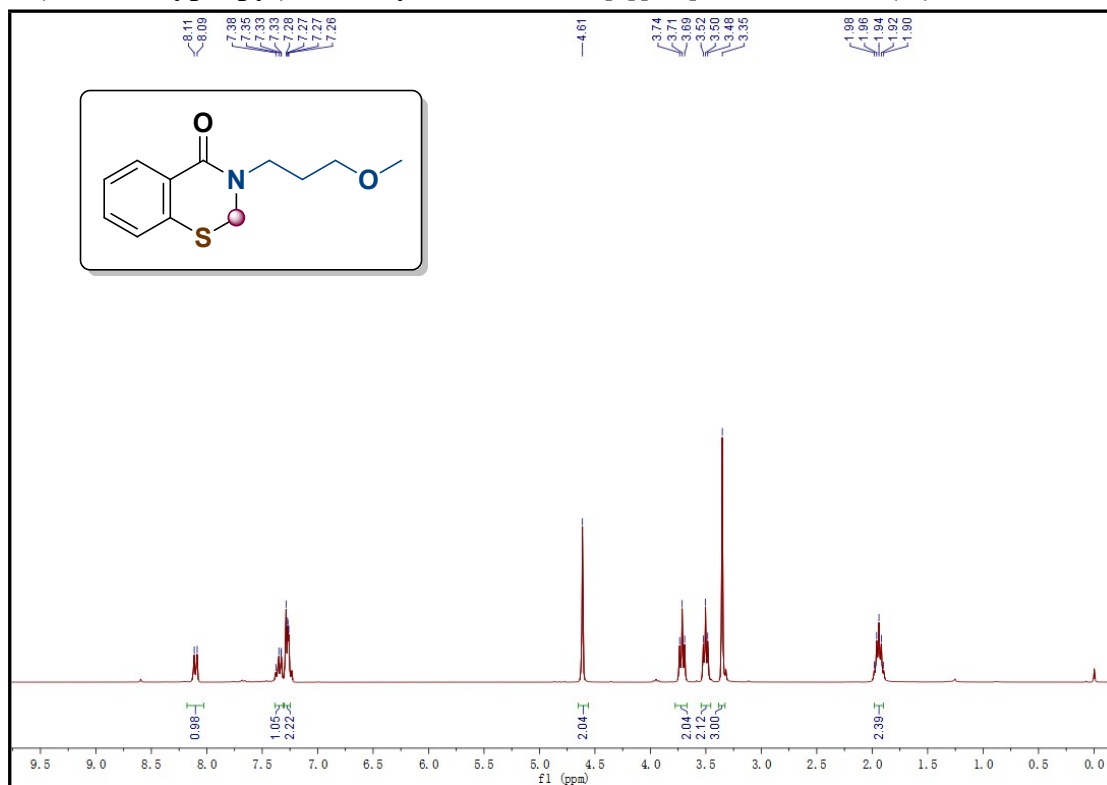
### 3-(2,3-dihydro-1H-inden-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3r)



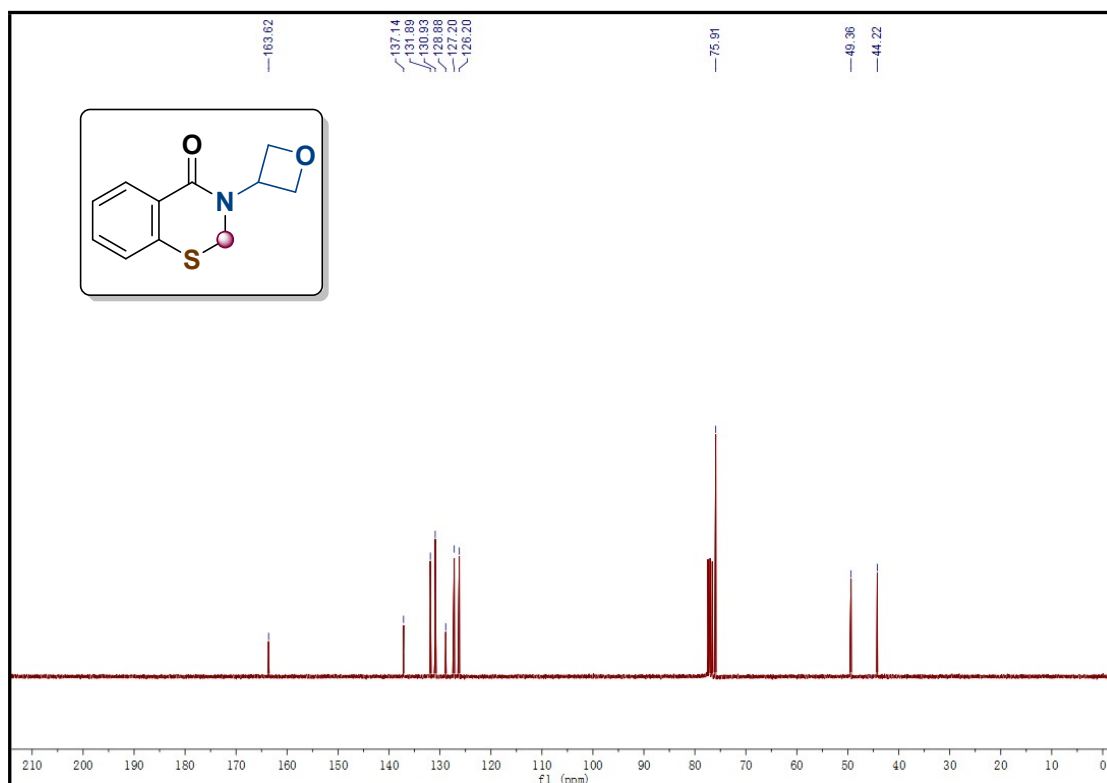
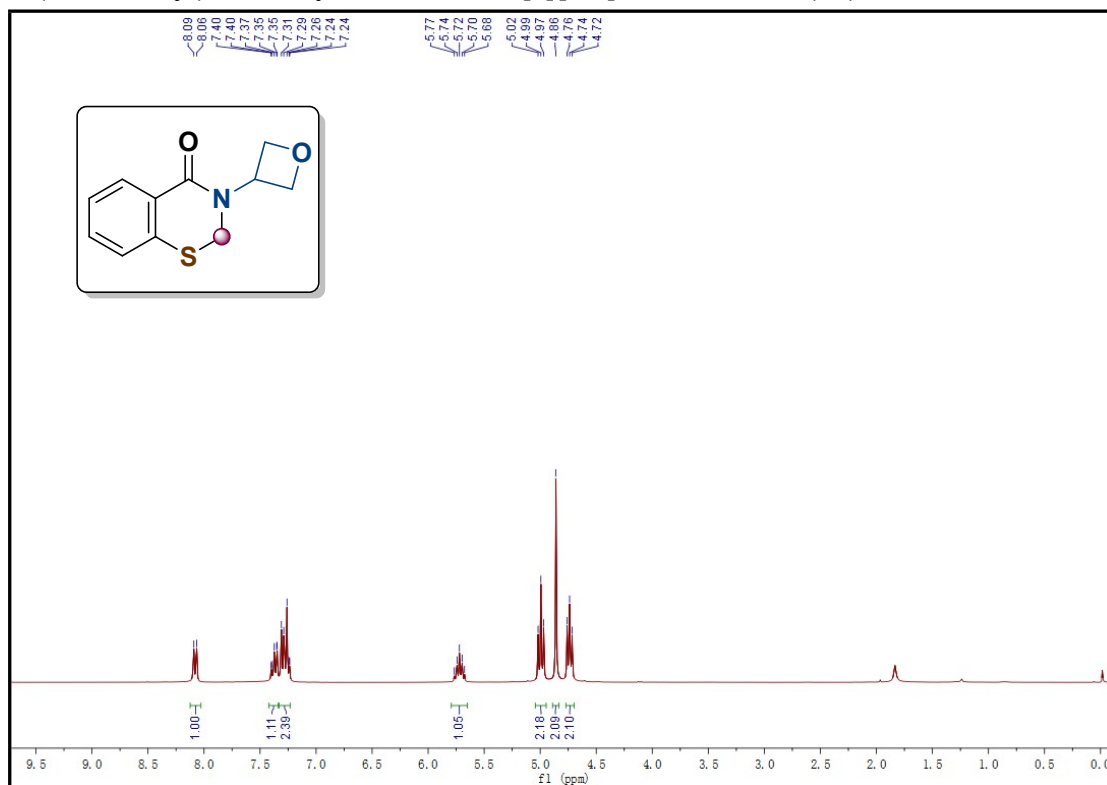
### 3-cyclopropyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3s)



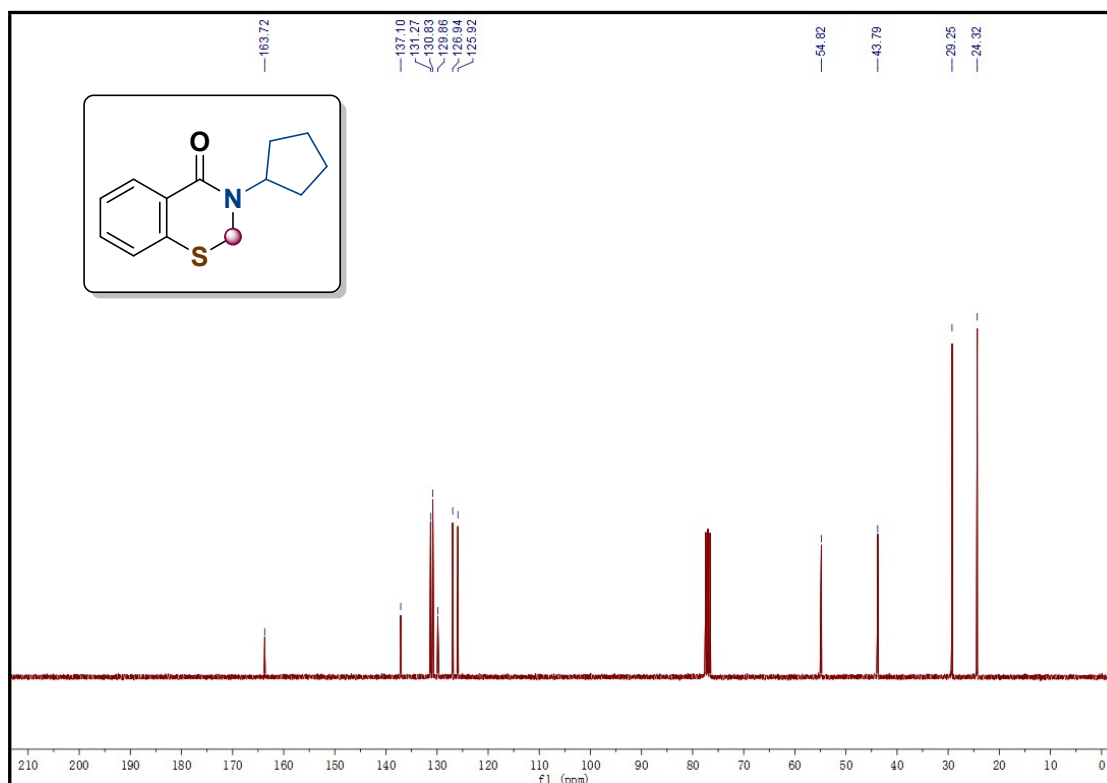
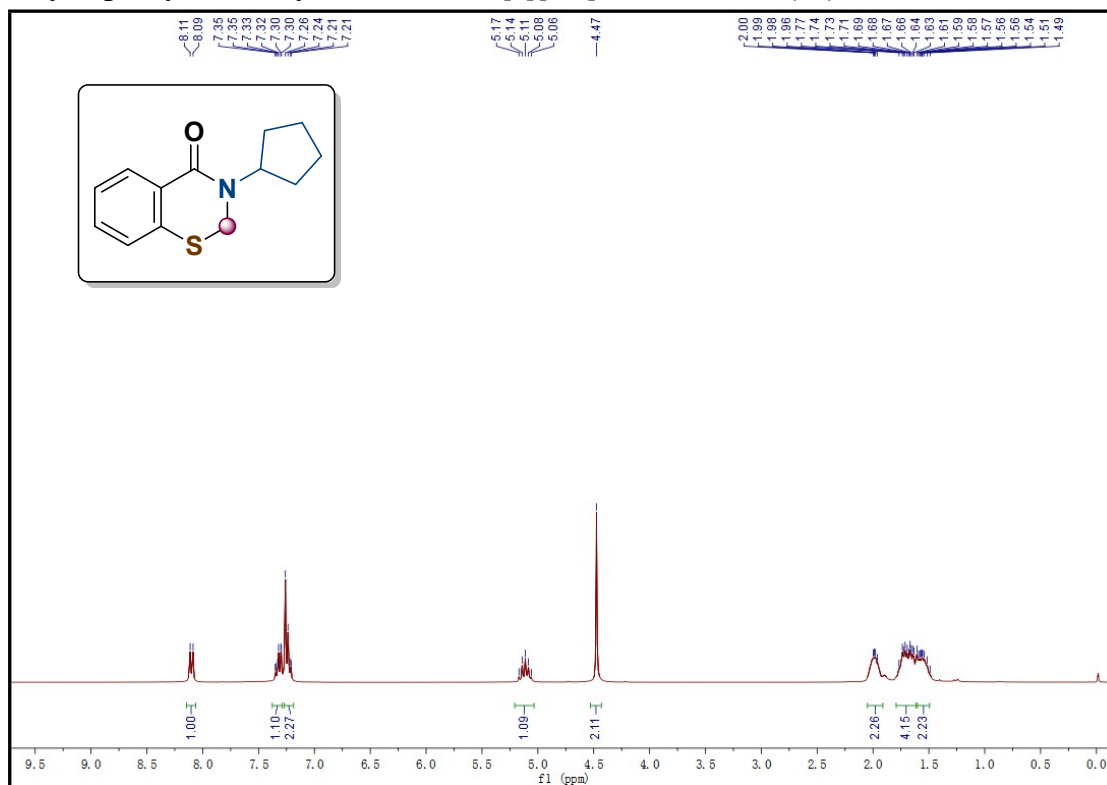
### 3-(3-methoxypropyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3t)



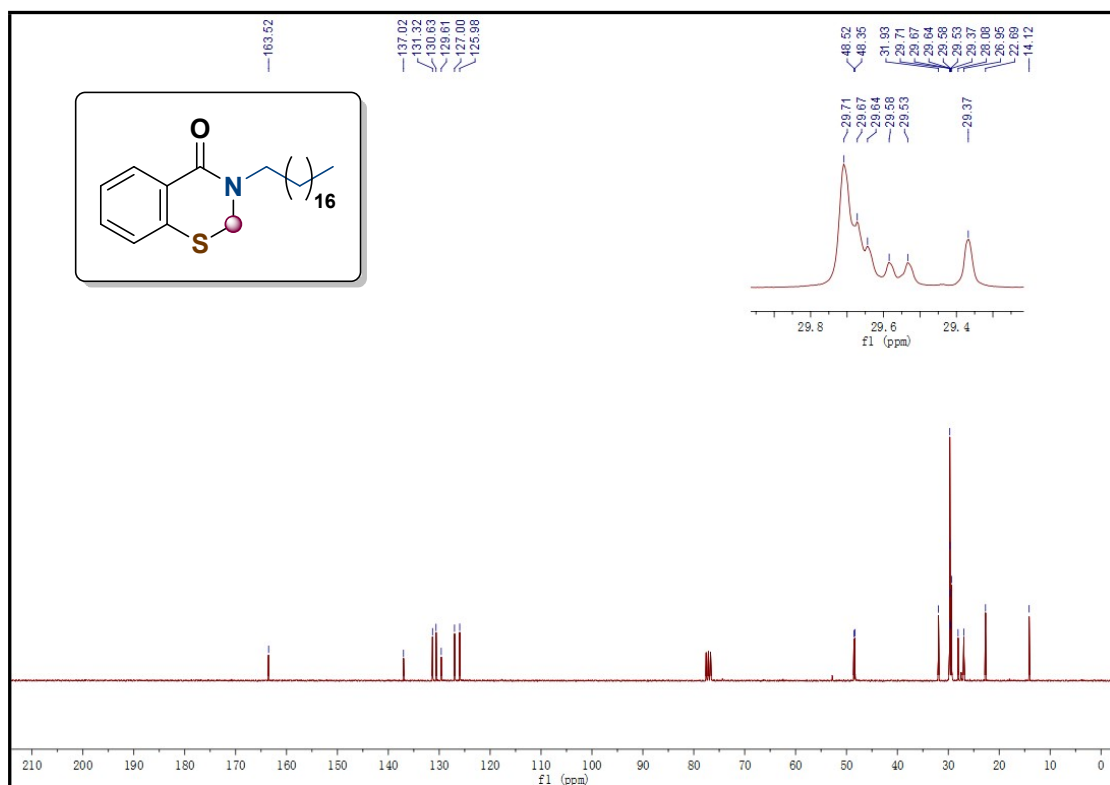
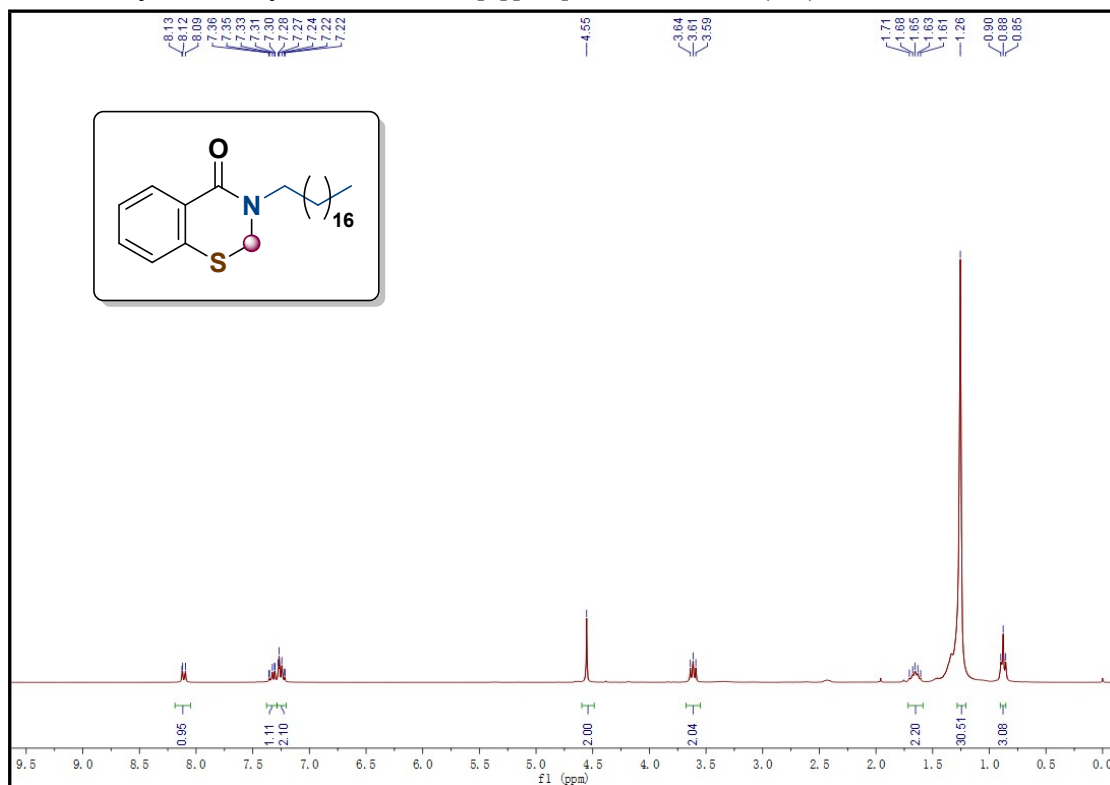
### 3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3u)



### 3-cyclopentyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3v)

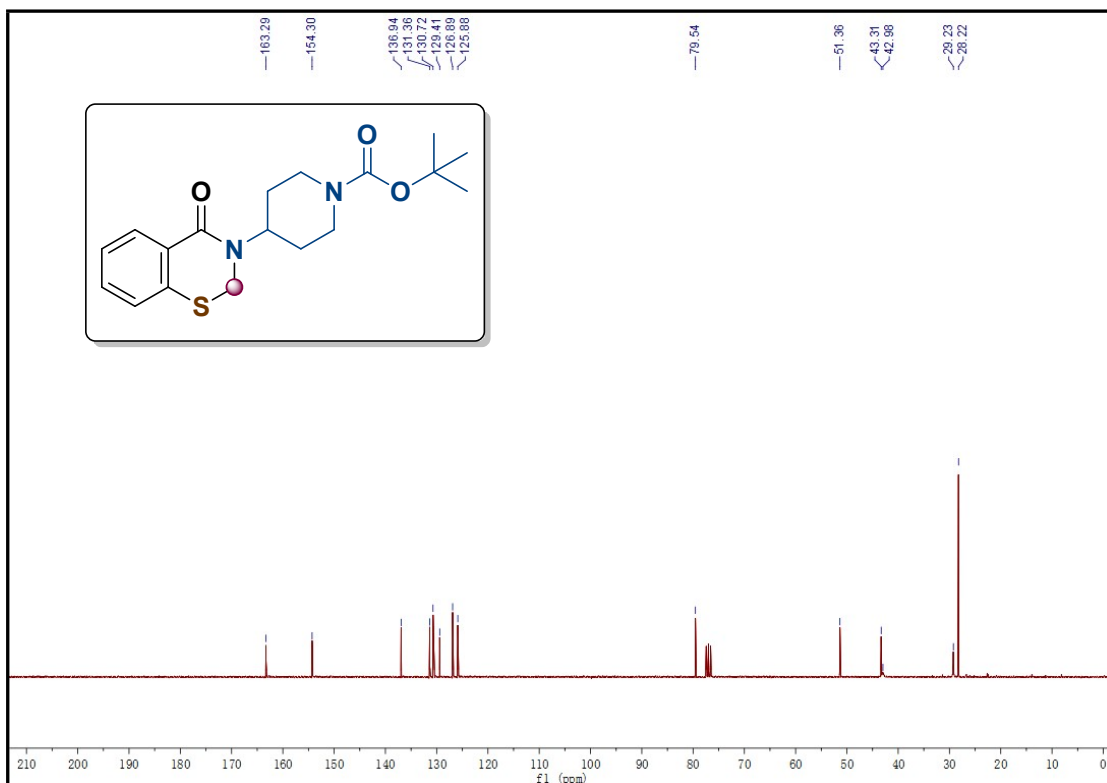
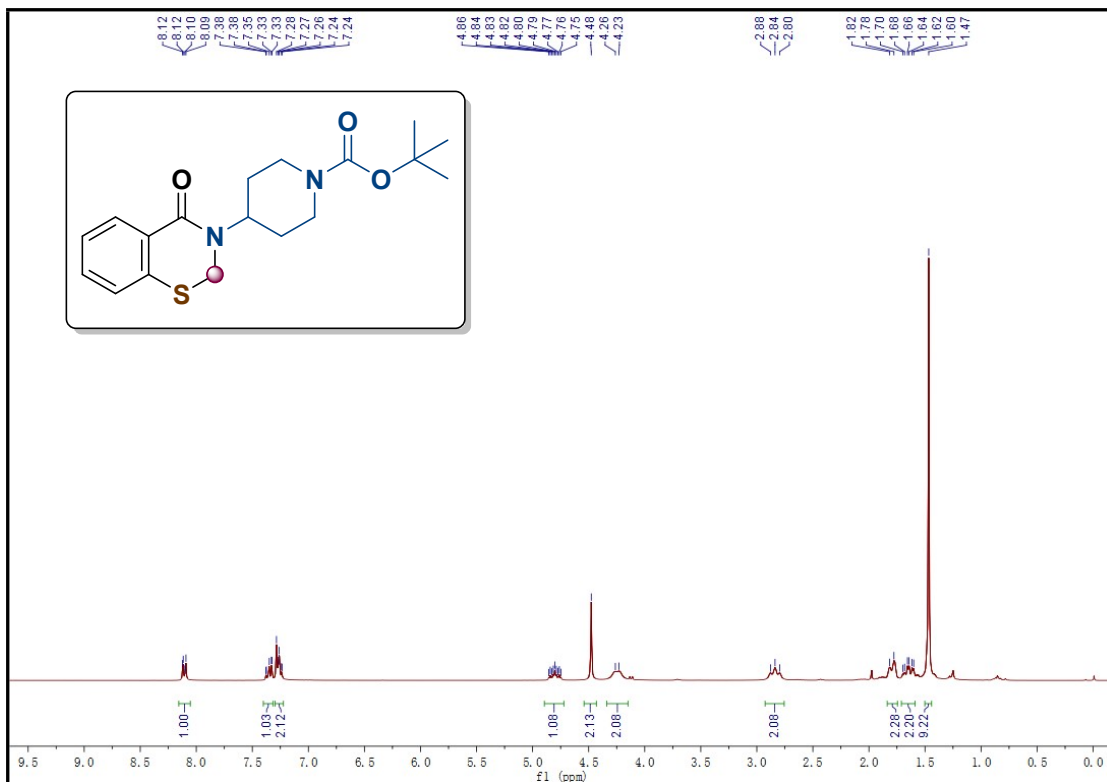


### 3-octadecyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3w)

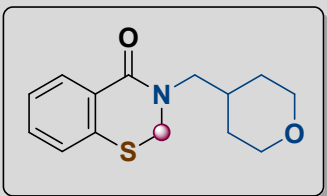
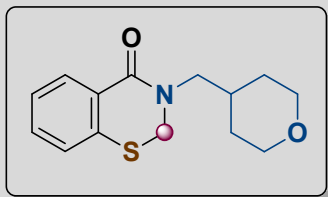




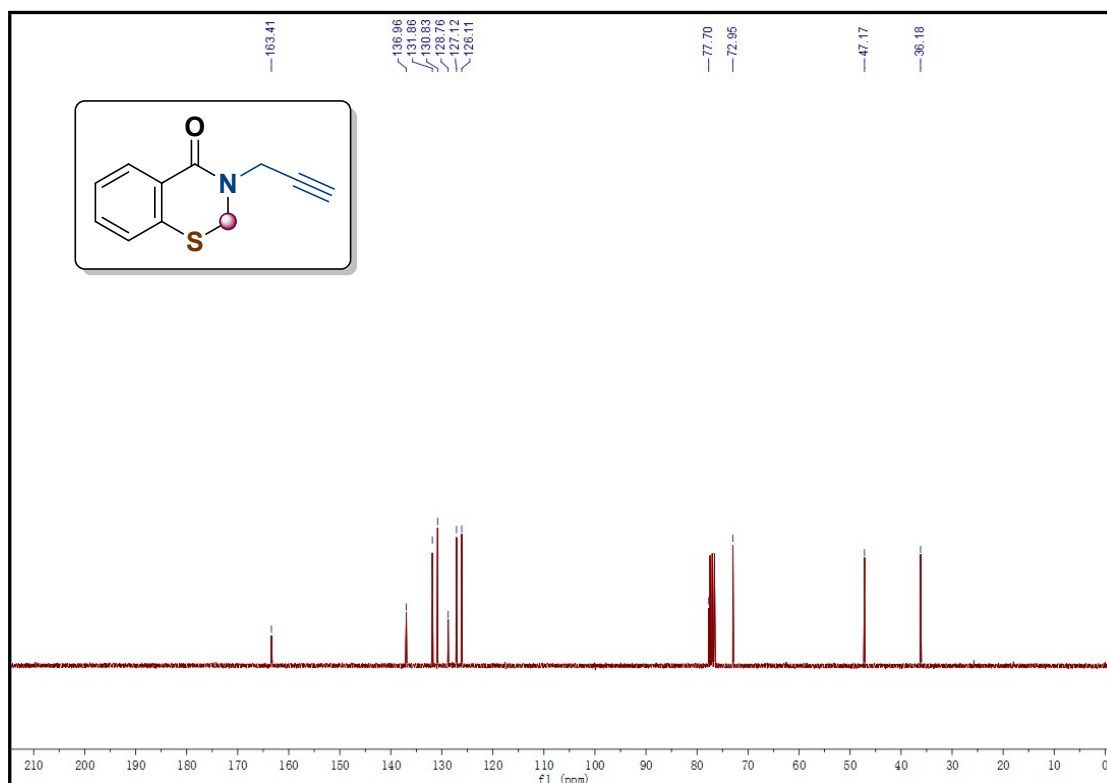
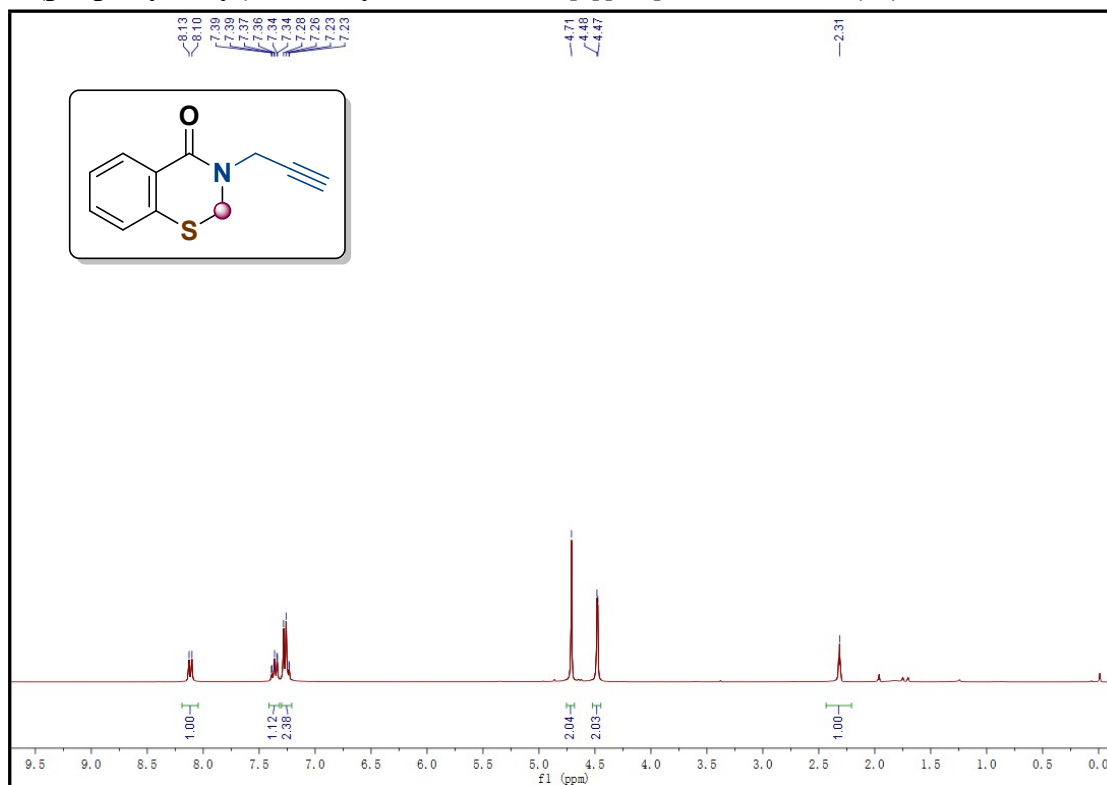
tert-butyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidine-1-carboxylate  
(3x)



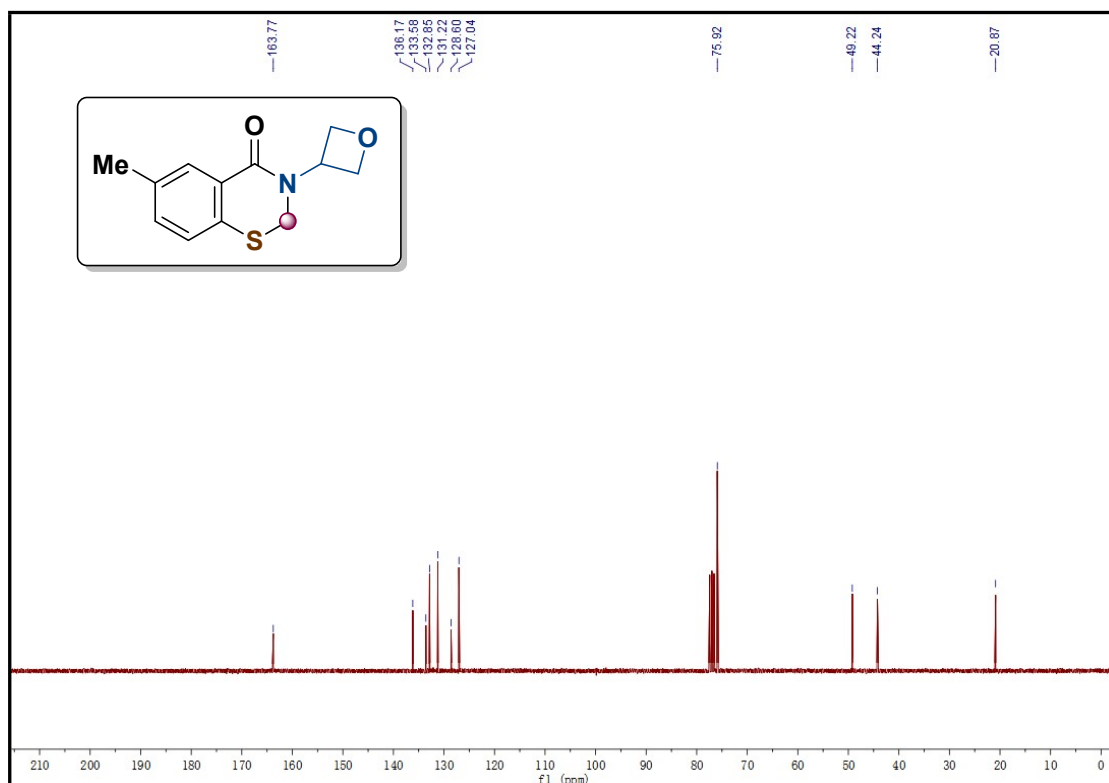
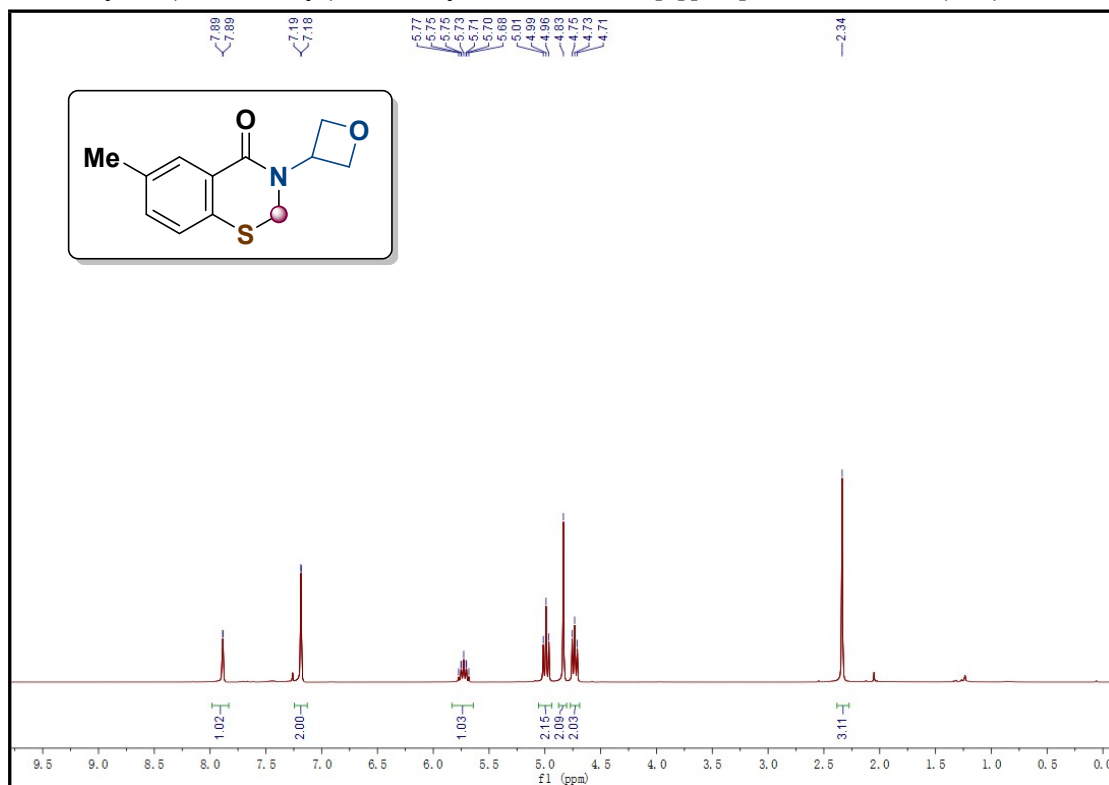
3-((tetrahydro-2H-pyran-4-yl)methyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one  
(3y)



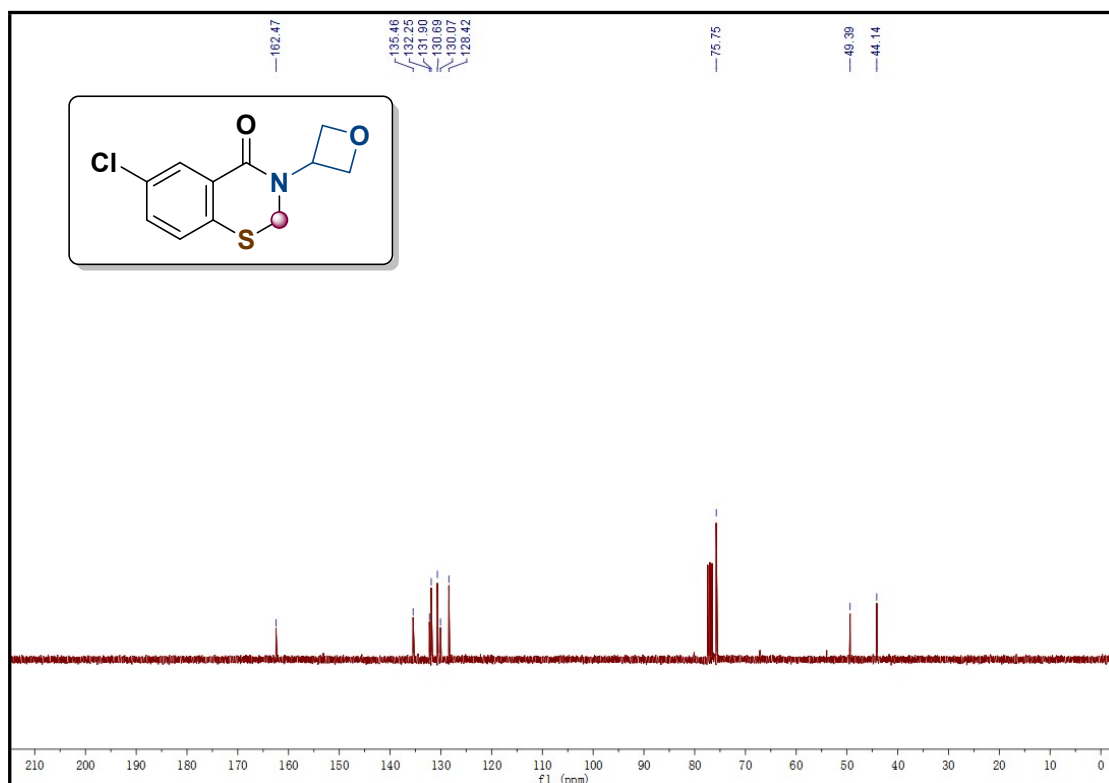
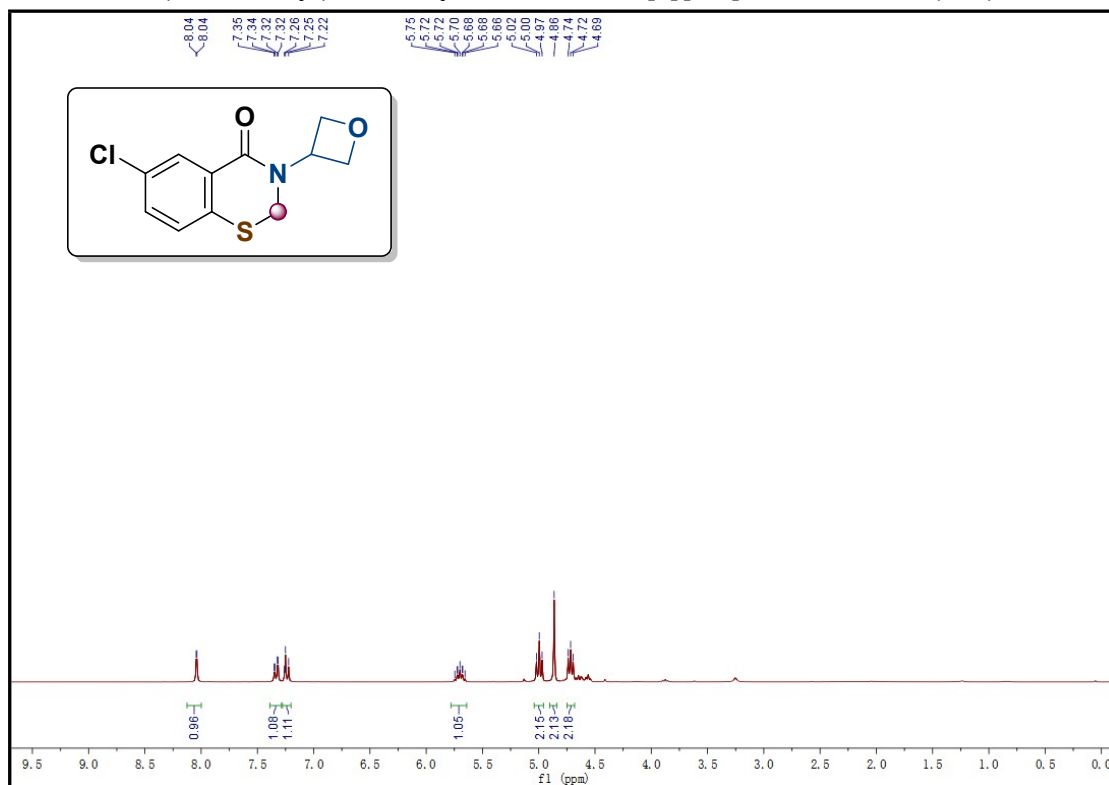
### 3-(prop-2-yn-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3z)



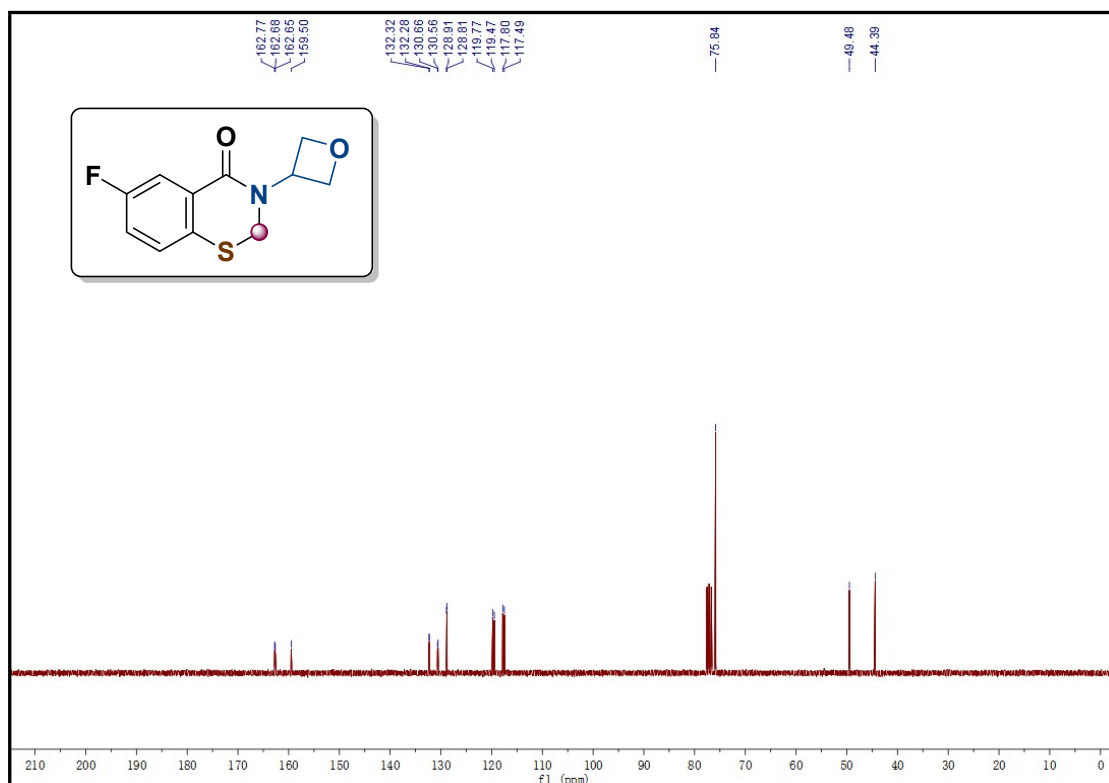
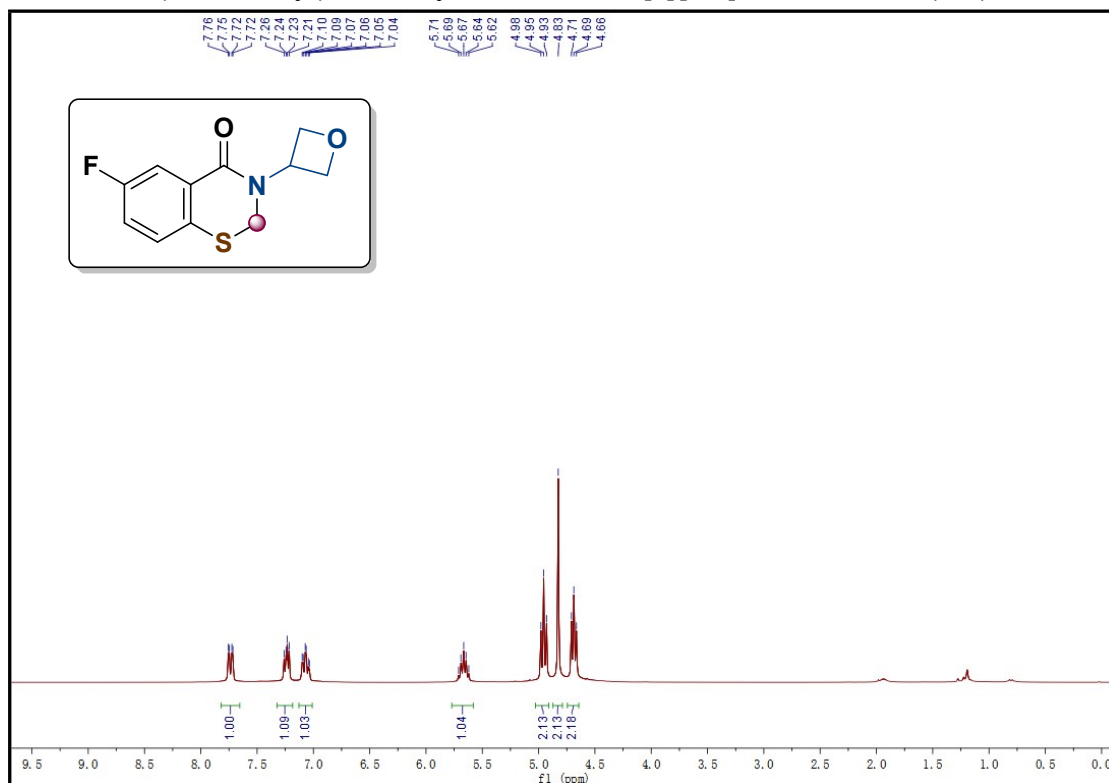
6-methyl-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3za)



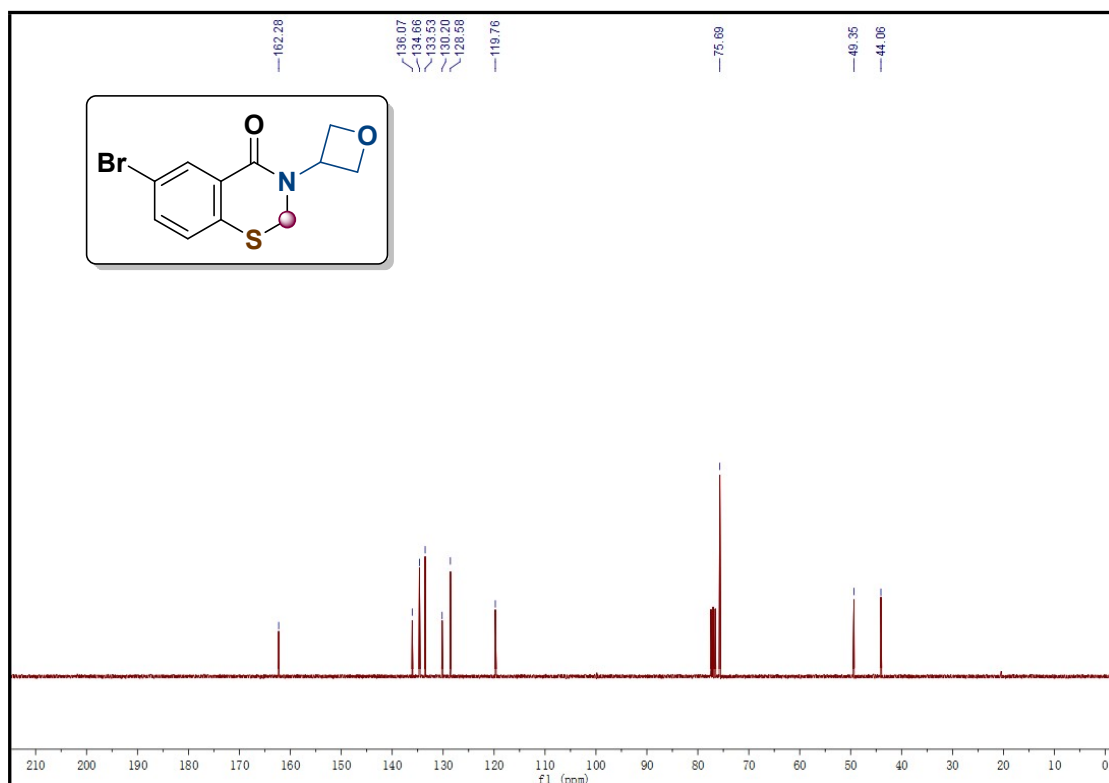
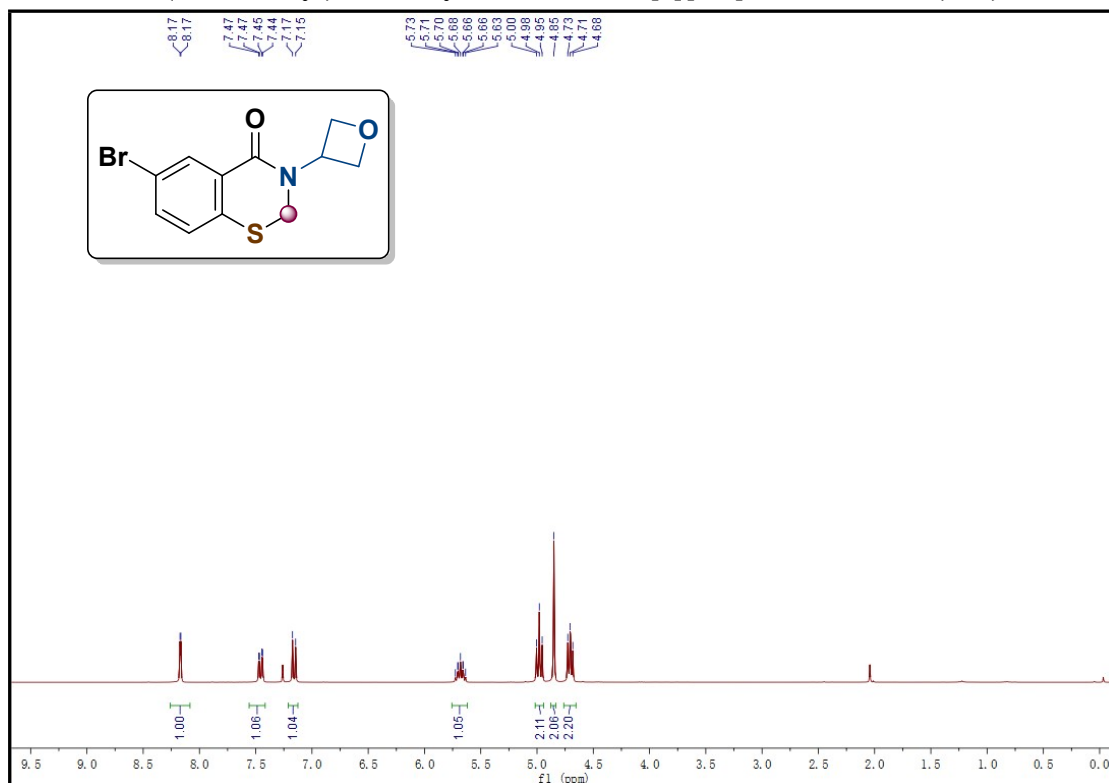
### 6-chloro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zb)



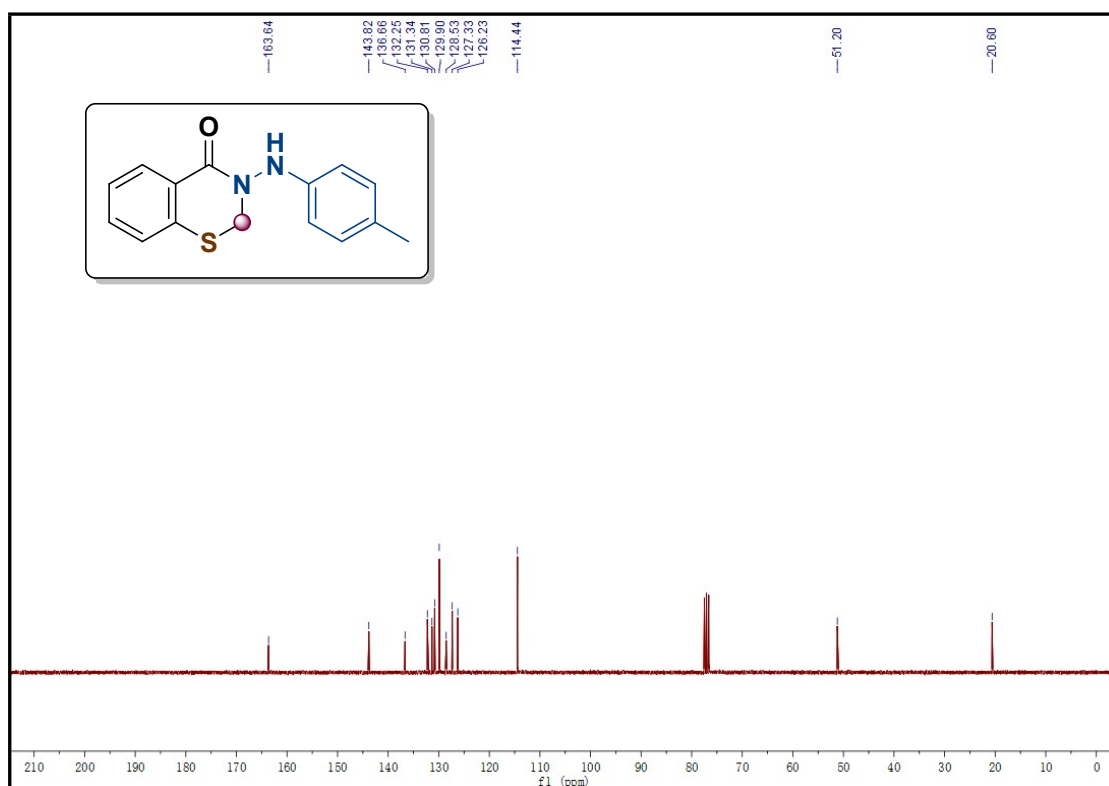
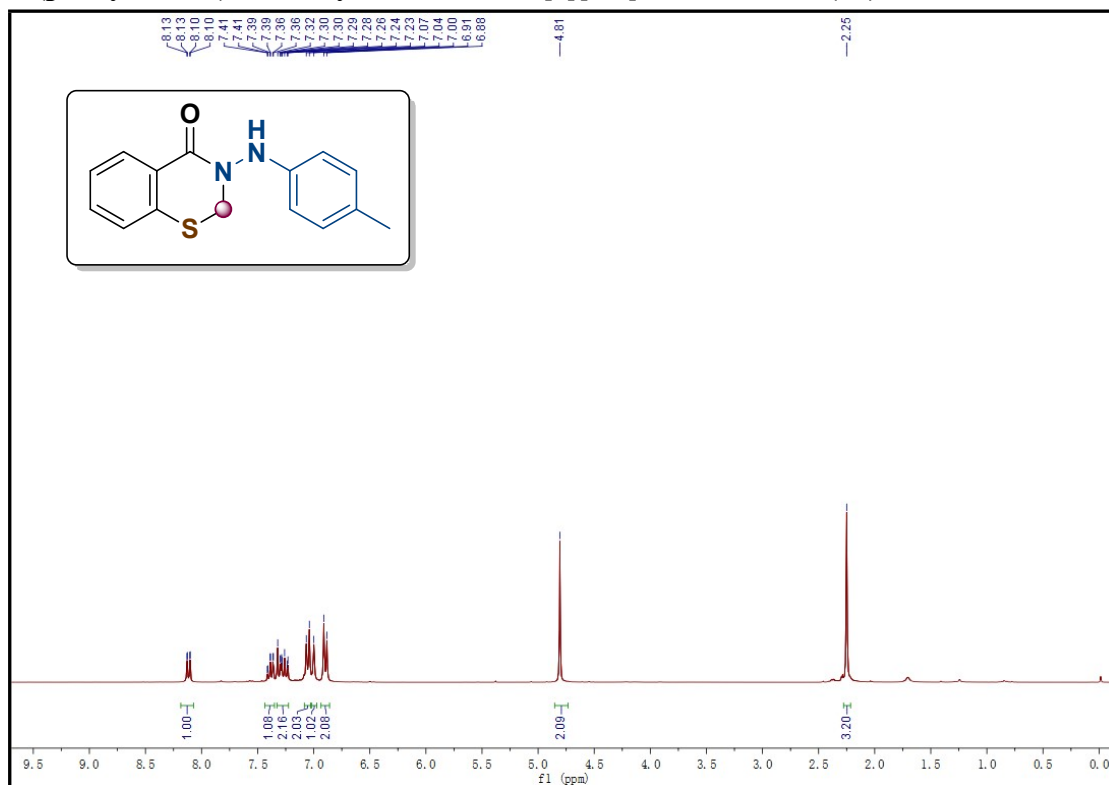
### 6-fluoro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zc)



### 6-bromo-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3zd)

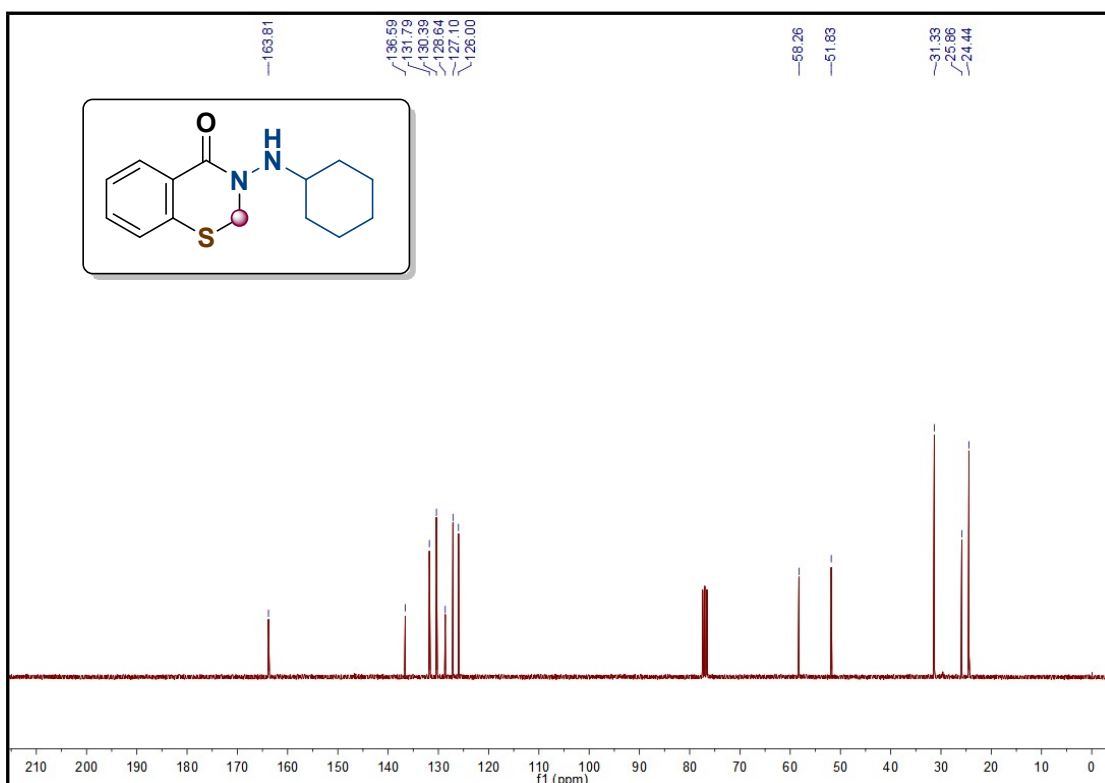
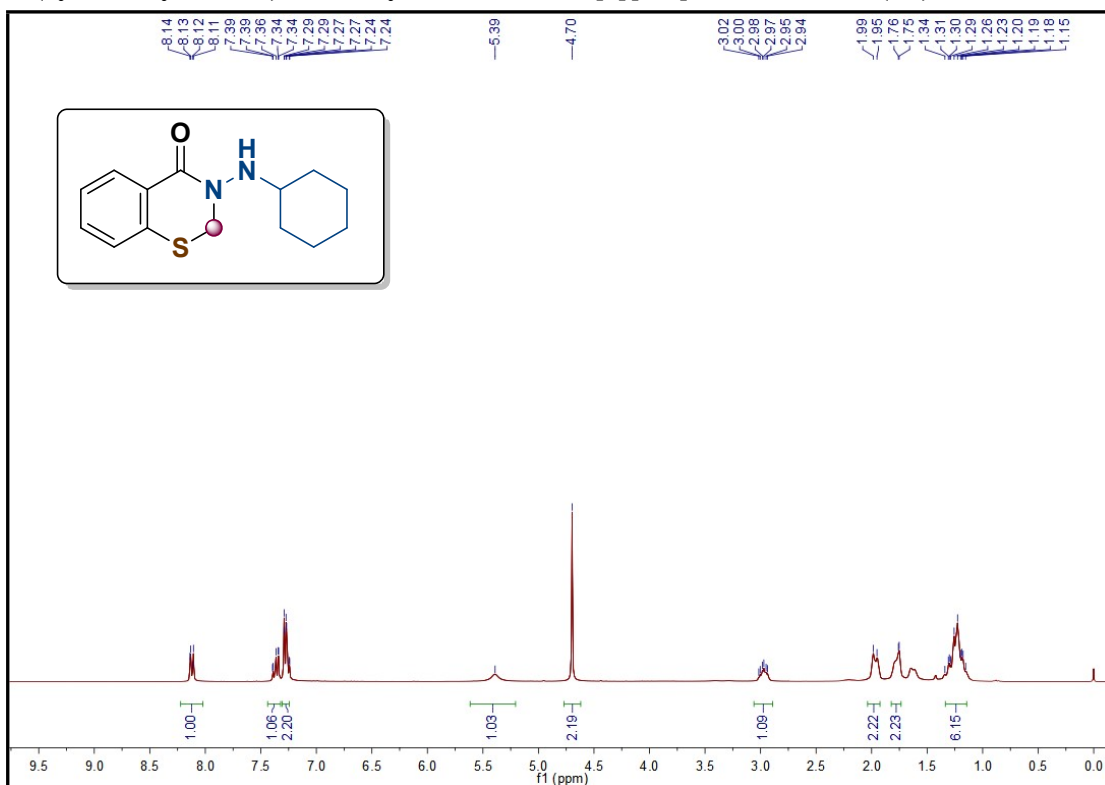


### 3-(p-tolylamino)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4a)

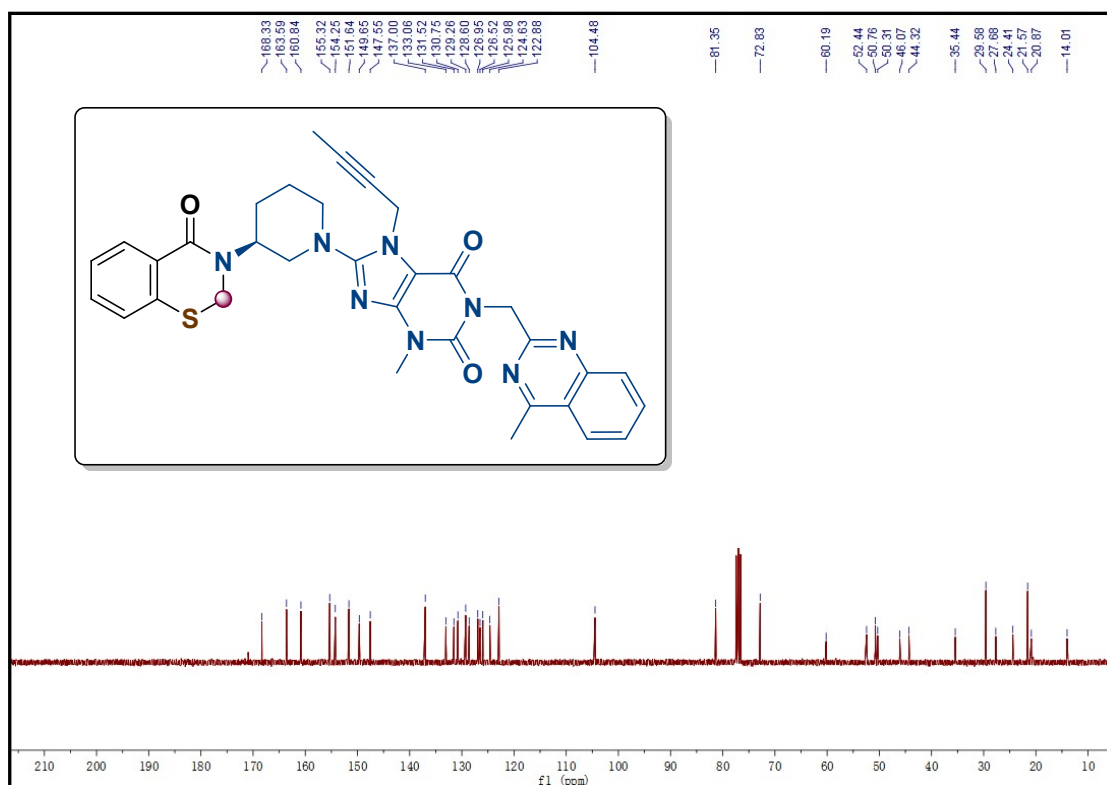
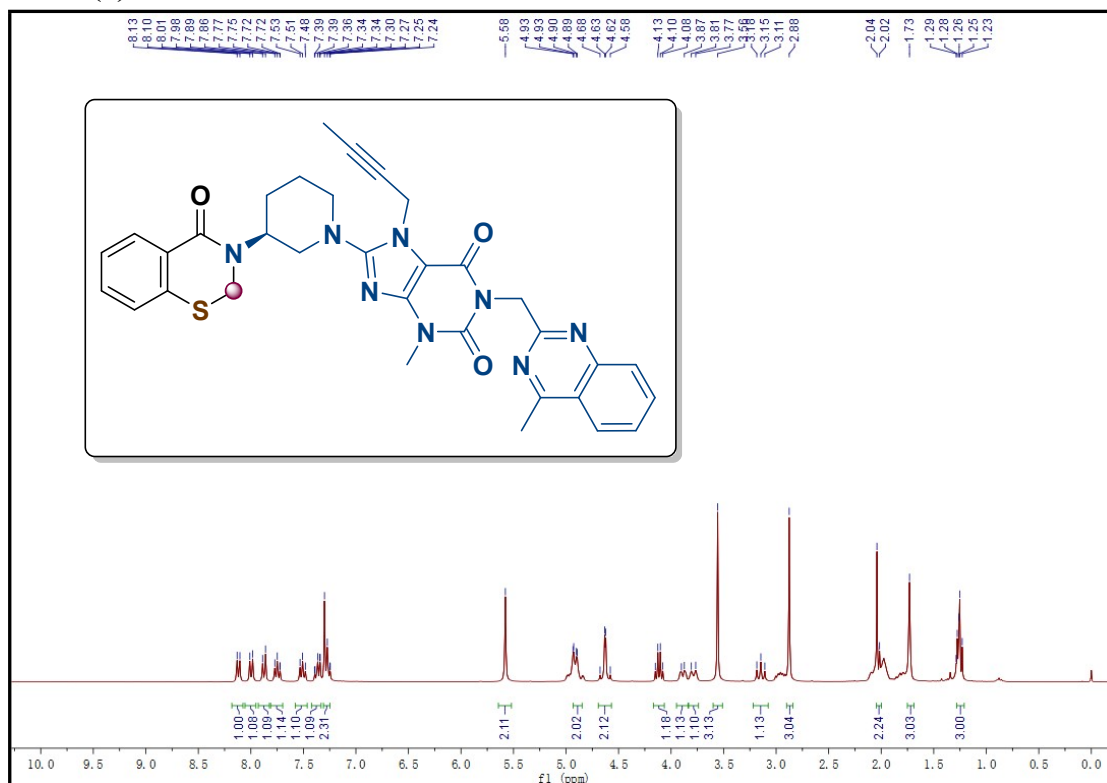




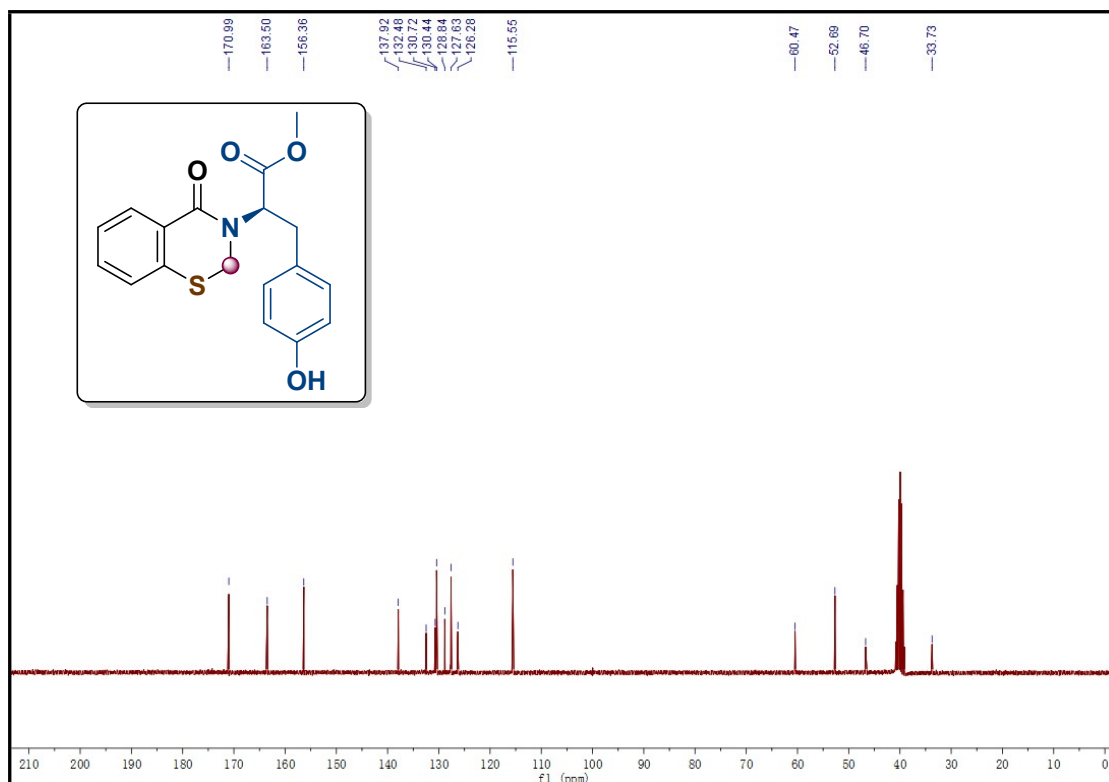
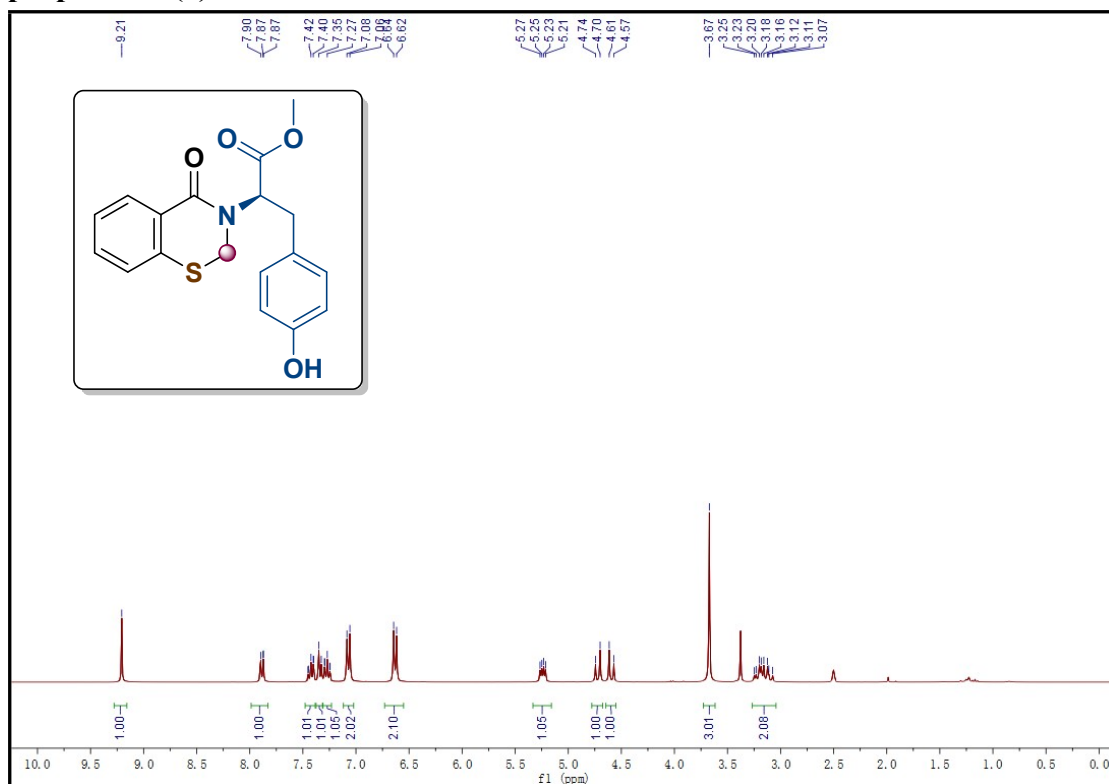
### 3-(cyclohexylamino)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4b)



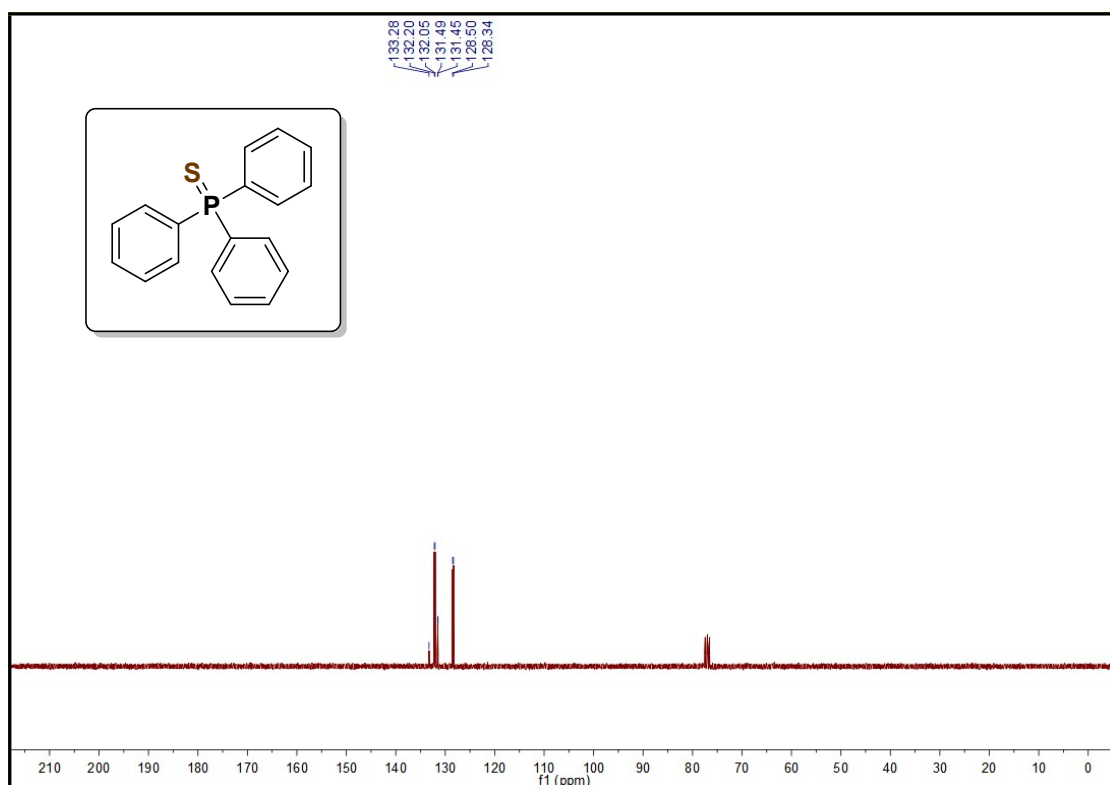
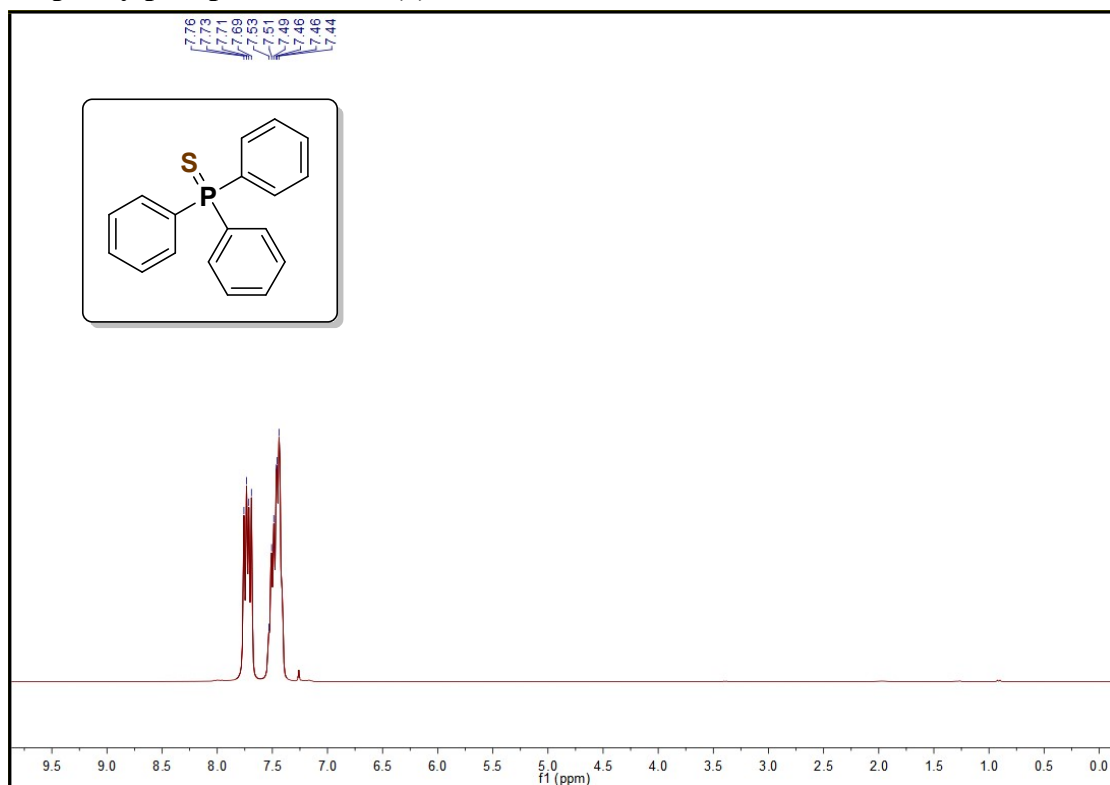
**(S)-7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-8-(3-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidin-1-yl)-3,7-dihydro-1H-purine-2,6-dione (5)**



**Methyl (R)-3-(4-hydroxyphenyl)-2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)propanoate (6)**



# Triphenylphosphine sulfide (8)



## 7. References

- 1 Y. Zhou, B. Zhang, J. Dong, J. Li, S. Yang, L. Ye, Assembly of Benzo[*c*][1,2]dithiol-3-ones via Acid-Promoted Denitrogenative Transannulation of Benzotriazinones. *Org. Lett.* 2022, **24**, 9012.
- 2 J. Xiong, G. Zhong, Y. Liu, Domino Reactions Initiated by Copper-Catalyzed Aryl-I Bond Thiolation For the Switchable Synthesis of 2,3-Dihydrobenzothiazinones and Benzoisothiazolones. *Adv. Synth. Catal.* 2019, **361**, 550.
- 3 K. Yang, B. Niu, Z. Ma, H. Wang, B. Lawrence, and H. Ge, Silver-Promoted Site-Selective Intramolecular Cyclization of 2-Methylthiobenzamide Through  $\alpha$ -C(sp<sup>3</sup>)-H Functionalization *J. Org. Chem.* 2019, **84**, 14045.