Supporting Information

for

Rongalite as the C1 Synthon to Assemble 2,3-Dihydrobenzothiazin-4-ones and Benzo[d][1,3]oxathiin-4-ones

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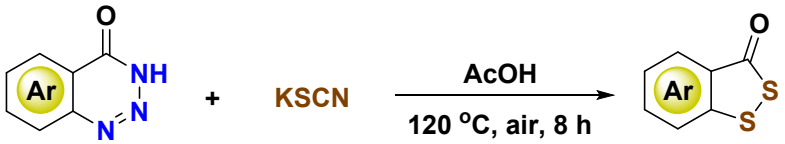
1. General information

All reagents and solvents were obtained from commercial suppliers and used without further purification. The 3*H*-benzo[c][1,2]dithiol-3-one (**1a**) was purchased from Bide Pharmatech Ltd and rongalite was purchased from Meryer Chemical Technology Co., Ltd.. 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).

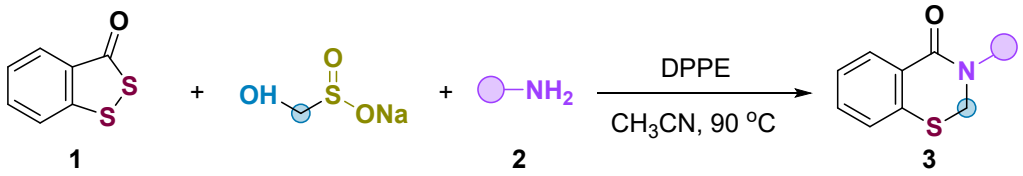
^{1}H-NMR and ^{13}C-NMR spectra were recorded in $CDCl_3$ on a Bruker Avance 300 spectrometer (300 MHz ^{1}H, 75 MHz ^{13}C) at room temperature. Chemical shifts were reported in ppm on the scale relative to $CDCl_3$ (δ = 7.26 for ^{1}H-NMR , δ = 77.00 for ^{13}C-NMR) or DMSO-d_6 (δ = 2.50 for ^{1}H-NMR, δ = 39.96 for ^{13}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 starting materials 1



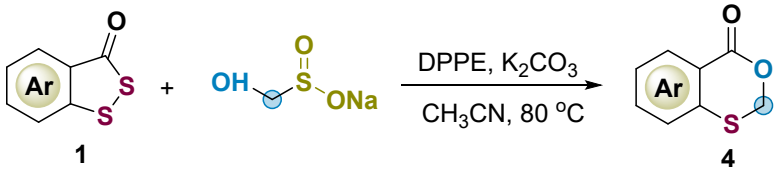
1,2-Benzodithiol-3-ones **1** were prepared according to our previous work which are known compounds. AcOH (15 mL) was added to a mixture of benzo[d][1,2,3]triazin-4(3H)-one (3 mmol) and KSCN (12 mmol) in a 150 mL sealed tube. Then the reaction mixture was stirred at 120 °C in an oil bath for 8 h. Upon 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_2SO_4. The solvents were removed via rotary evaporator and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 30:1, v/v) to give the desired product as yellow solid.

3. General procedure to synthesize products 3



CH_3CN (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1** (0.3 mmol), rongalite (0.9 mmol, 106 mg), amine **2** (0.4 mmol) and DPPE (0.2 mmol, 79.4 mg) in a sealed tube. Then the reaction mixture was stirred at 90 °C for 12 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 b2,3-dihydrobenzothiazinones **3**.

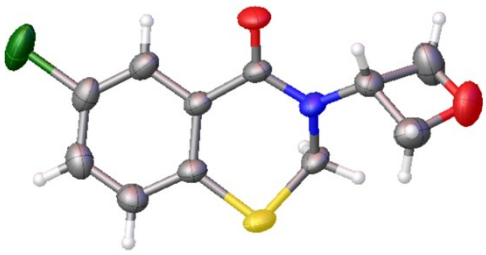
4. General procedure to synthesize products 4



CH_3CN (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1** (0.3 mmol), rongalite (0.9 mmol, 106 mg), K_2CO_3 (0.6 mmol, 82.8 mg) and DPPE (0.2 mmol, 79.4 mg) in a sealed tube. Then the reaction mixture was stirred at 80 °C for 12 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 benzo[d][1,3]oxathiin-4-ones **4**.

5. Crystal data of 3ca and 4i

Crystallographic data for compound **3ca** (CCDC-2523790) 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)



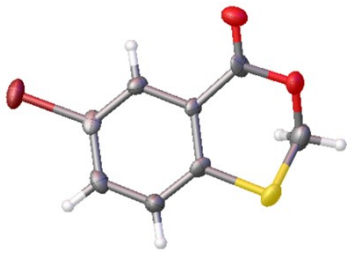
Displacement ellipsoids are drawn at 50% probability level

Bond precision: C-C = 0.0034 A Wavelength=0.71076
Cell: a=8.1568(5) b=11.8101(8) c=12.0950(8)
alpha=90 beta=106.848(2) gamma=90
Temperature: 302 K

	Calculated	Reported
Volume	1115.13(13)	1115.13(13)
Space group	P 21/n	P 1 21/n 1
Hall group	-P 2yn	-P 2yn
Moiety formula	$C_{11}H_{10}ClNO_2S$	$C_{11}H_{10}ClNO_2S$
Sum formula	$C_{11}H_{10}ClNO_2S$	$C_{11}H_{10}ClNO_2S$
Mr	255.71	255.71
Dx,g cm-3	1.523	1.523
Z	4	4
Mu (mm-1)	0.512	0.512
F000	528.0	528.0
F000'	529.29	
h,k,lmax	10,15,15	10,15,15
Nref	2574	2561
Tmin,Tmax	0.903,0.926	0.623,0.746
Tmin'	0.903	

Correction method= # Reported T Limits: Tmin=0.623
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.995 Theta(max)= 27.520
R(reflections)= 0.0478(2053) wR2(reflections)= 0.1303(2561)
S = 1.122 Npar= 145

Crystallographic data for compound **4i** (CCDC-2523791) 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

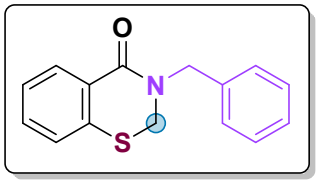
Bond precision: C-C = 0.0066 A Wavelength=0.71076
Cell: a=9.9100(13) b=22.220(3) c=7.4284(8)
alpha=90 beta=90 gamma=90
Temperature: 303 K

	Calculated	Reported
Volume	1635.7(4)	1635.7(4)
Space group	P c c n	P c c n
Hall group	-P 2ab 2ac	-P 2ab 2ac
Moiety formula	$C_8H_5BrO_2S$	$C_8H_5BrO_2S$
Sum formula	$C_8H_5BrO_2S$	$C_8H_5BrO_2S$
Mr	245.08	245.09
Dx,g cm-3	1.990	1.990
Z	8	8
Mu (mm-1)	5.229	5.229
F000	960.0	960.0
F000'	959.17	
h,k,lmax	12,28,9	12,28,9
Nref	1888	1881
Tmin,Tmax	0.539,0.593	0.177,0.746
Tmin'	0.529	

Correction method= # Reported T Limits: Tmin=0.177
Tmax=0.746 AbsCorr = MULTI-SCAN
Data completeness= 0.996 Theta(max)= 27.572
R(reflections)= 0.0566(1431) wR2(reflections)= 0.1311(1881)
S = 1.172 Npar= 110

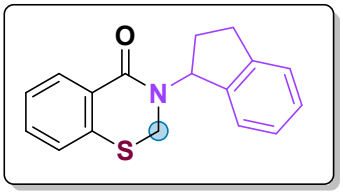
6. Characterization data for the products

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



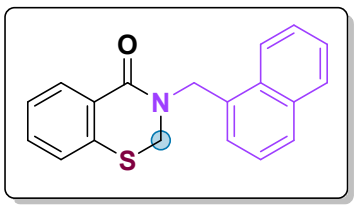
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (54.3 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.12 (m, 1H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 4.85 (s, 2H), 4.46 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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. HRMS (ESI, m/z) calcd for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791; found: 256.0793.

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



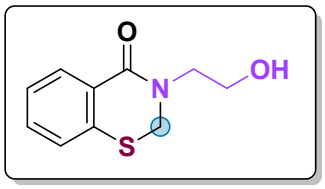
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (62.3 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 7.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 (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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{17}H_{16}NOS$ $[M+H]^+$: 282.0948; found: 282.0953.

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



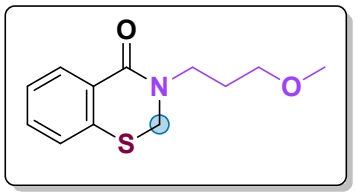
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (59.4 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.20 (m, 1H), 8.09 (d, J = 7.5 Hz, 1H), 7.89 – 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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{19}H_{16}NOS$ $[M+H]^+$: 306.0948; found: 306.0950.

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



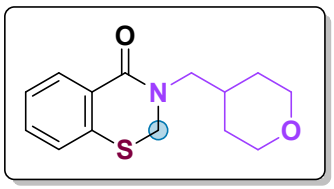
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a colourless oil (43.9 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.0 Hz, 1H), 7.42 – 7.16 (m, 3H), 4.66 (s, 2H), 3.79 (dd, *J* = 20.5, 4.6 Hz, 4H), 3.44 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.7, 137.3, 131.7, 130.5, 129.1, 127.2, 126.1, 61.1, 51.4, 50.1. HRMS (ESI, m/z) calcd for $C_{10}H_{12}NO_2S$ $[M+H]^+$: 210.0584; found: 210.0589.

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



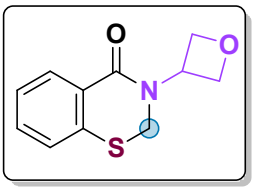
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (56.9 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 10.2, 4.5 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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{12}H_{16}NO_2S$ $[M+H]^+$: 238.0897; found: 238.0899.

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



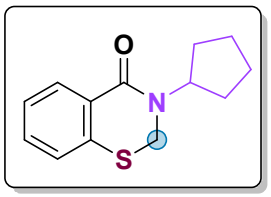
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (64.6 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.41 – 7.29 (m, 1H), 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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{14}H_{18}NO_2S$ $[M+H]^+$: 264.1053; found: 264.1055.

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



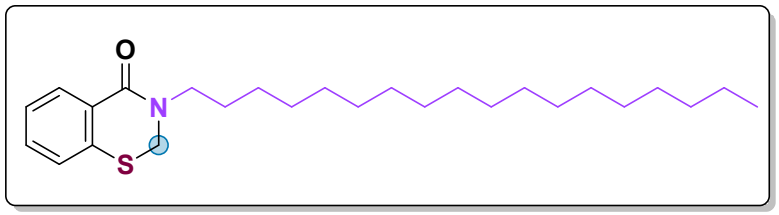
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (48.3 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.34 (m, 1H), 7.33 – 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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{11}H_{12}NO_2S$ $[M+H]^+$: 222.0584; found: 222.0590.

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



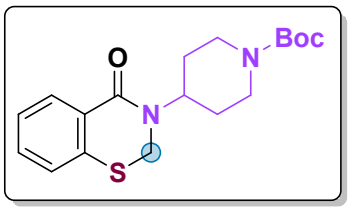
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a colourless oil (42.6 mg, 61%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.29 (m, 1H), 7.23 (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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.7, 137.1, 131.3, 130.8, 129.9, 126.9, 125.9, 54.8, 43.8, 29.3, 24.3. HRMS (ESI, m/z) calcd for $C_{13}H_{16}NOS$ $[M+H]^+$: 234.0947; found: 234.0947.

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



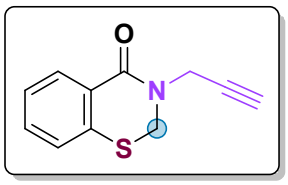
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (53.8 mg, 43%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.05 (m, 1H), 7.38 – 7.29 (m, 1H), 7.28 – 7.21 (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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{26}H_{44}NOS$ $[M+H]^+$: 418.3139; found: 418.3140.

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



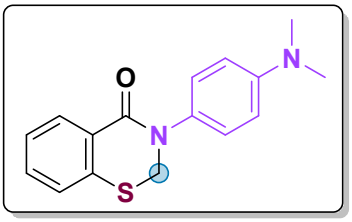
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the product as a colourless oil (77.2 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (dd, *J* = 6.9, 2.5 Hz, 1H), 7.40 – 7.31 (m, 1H), 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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{18}H_{25}N_2O_3S$ $[M+H]^+$: 349.1581; found: 349.1586.

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



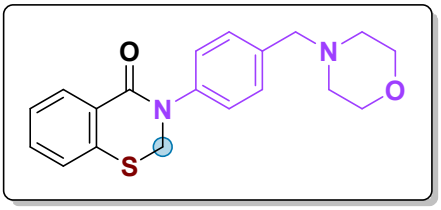
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (35.3 mg, 58%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.8 Hz, 1H), 7.41 – 7.32 (m, 1H), 7.25 (dd, *J* = 11.7, 4.1 Hz, 2H), 4.71 (s, 2H), 4.48 (d, *J* = 2.5 Hz, 2H), 2.31 (s, 1H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{11}H_{10}NOS$ $[M+H]^+$: 204.0478; found: 204.0474.

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



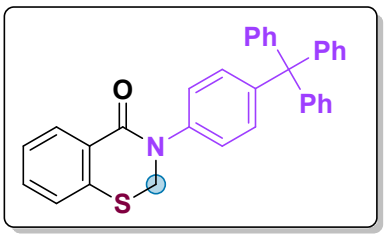
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow solid (56.2 mg, 66%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.22 (dd, *J* = 15.8, 8.2 Hz, 3H), 6.72 (d, *J* = 9.0 Hz, 2H), 4.89 (s, 2H), 2.94 (s, 6H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{16}H_{17}N_2OS$ $[M+H]^+$: 285.1057; found: 285.1058.

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



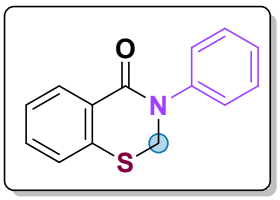
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:4, v/v) to give the product as a colourless oil (81.6 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.41 (dd, *J* = 10.2, 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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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 $C_{19}H_{21}N_2O_2S$ $[M+H]^+$: 341.1319; found: 341.1320.

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



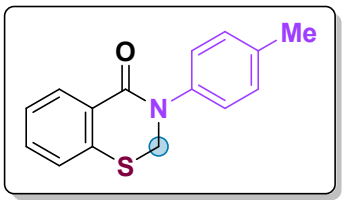
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (97.0 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.11 (d, *J* = 7.6 Hz, 1H), 7.31 (dd, *J* = 15.9, 8.8 Hz, 2H), 7.26 – 7.01 (m, 20H), 4.90 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.5, 146.5, 145.5, 139.8, 137.3, 131.9, 131.8, 131.2, 131.1, 129.7, 127.6, 127.3, 126.3, 126.0, 124.4, 64.8, 51.6. HRMS (ESI, m/z) calcd for $C_{33}H_{26}NOS$ $[M+H]^+$: 484.1730; found: 484.1730.

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



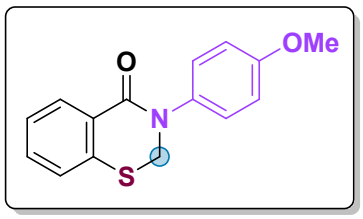
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a yellow oil (54.9 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.34 (m, 6H), 7.33 – 7.29 (m, 2H), 4.98 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.5, 142.2, 137.4, 135.7, 132.0, 131.2, 129.6, 127.3, 127.1, 126.3, 125.8, 51.7. HRMS (ESI, m/z) calcd for $C_{14}H_{12}NOS$ $[M+H]^+$: 242.0634; found: 242.0639.

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



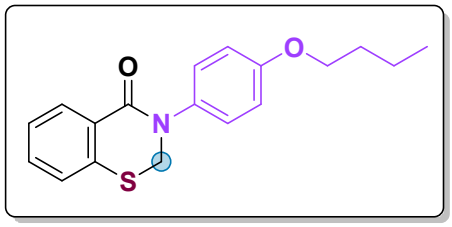
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (61.9 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.39 (dd, *J* = 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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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. HRMS (ESI, m/z) calcd for $C_{15}H_{14}NOS$ $[M+H]^+$: 256.0791; found: 256.0793.

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



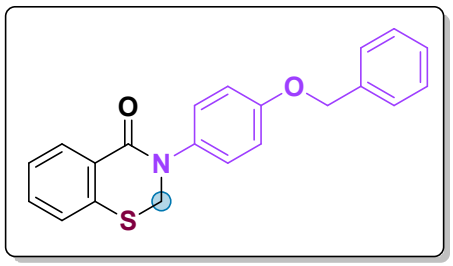
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 6:1, v/v) to give the product as a white solid (67.5 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.38 – 7.27 (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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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. HRMS (ESI, m/z) calcd for $C_{15}H_{14}NO_2S$ $[M+H]^+$: 272.0740; found: 272.0740.

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



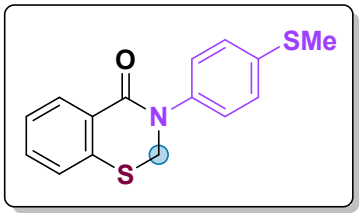
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 8:1, v/v) to give the product as a white solid (68.5 mg, 73%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.20 – 8.06 (m, 1H), 7.37 – 7.30 (m, 1H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.26 – 7.16 (m, 3H), 6.87 (d, *J* = 8.9 Hz, 2H), 4.87 (s, 2H), 3.91 (t, *J* = 6.5 Hz, 2H), 1.79 – 1.65 (m, 2H), 1.50 – 1.37 (m, 2H), 0.92 (t, *J* = 7.4 Hz, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.7, 158.0, 137.3, 134.9, 131.8, 131.1, 129.7, 127.2, 127.0, 126.2, 115.1, 68.0, 51.8, 31.2, 19.2, 13.8. HRMS (ESI, m/z) calcd for $C_{18}H_{20}NO_2S$ $[M+H]^+$: 314.1209; found: 314.1210.

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



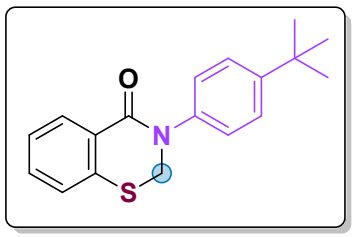
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 8:1, v/v) to give the product as a white solid (83.3 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (d, *J* = 7.7 Hz, 1H), 7.36 – 7.27 (m, 5H), 7.20 (dd, *J* = 14.7, 6.0 Hz, 4H), 6.93 (d, *J* = 8.9 Hz, 2H), 4.99 (s, 2H), 4.84 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.7, 157.6, 137.3, 136.7, 135.4, 131.8, 131.1, 129.7, 128.6, 128.1, 127.4, 127.2, 127.1, 126.3, 115.5, 70.3, 51.8. HRMS (ESI, m/z) calcd for $C_{21}H_{18}NO_2S$ [M+H]$^+$: 348.1053; found: 348.1058.

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



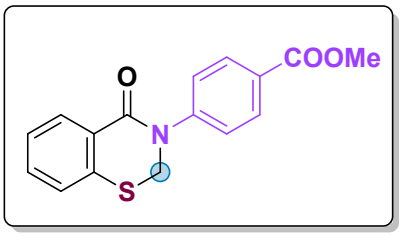
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 6:1, v/v) to give the product as a white solid (61.9 mg, 72%).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, *J* = 7.8 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.34 (d, *J* = 6.8 Hz, 1H), 7.33 – 7.27 (m, 5H), 4.96 (s, 2H), 2.50 (s, 3H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{15}H_{14}NOS_2$ [M+H]$^+$: 288.0512; found: 288.0512.

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



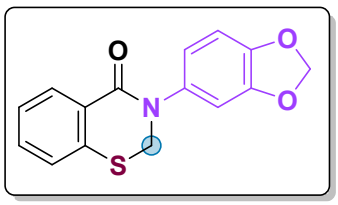
The reaction was performed following the general procedure by using DPPE as the additive. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (57.0 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 6.7 Hz, 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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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 $C_{18}H_{20}NOS$ [M+H]$^+$: 298.1261; found: 298.1264.

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



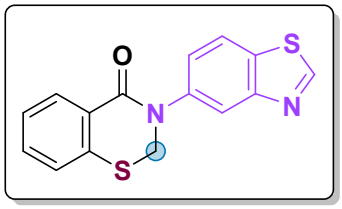
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (52.9 mg, 59%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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 $C_{16}H_{14}NO_3S$ $[M+H]^+$: 300.0689; found: 300.0693.

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



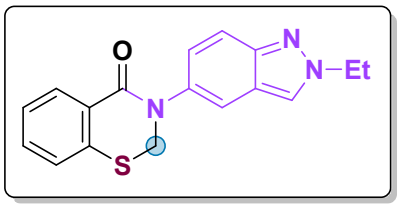
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow oil (51.3 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.44 – 7.37 (m, 1H), 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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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 $C_{15}H_{12}NO_3S$ $[M+H]^+$: 286.0533; found: 286.0538.

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



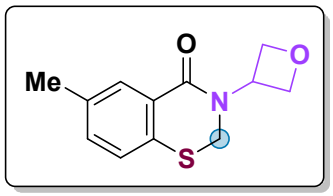
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (67.9 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{15}H_{11}N_2OS_2$ $[M+H]^+$: 299.0308; found: 299.0308.

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



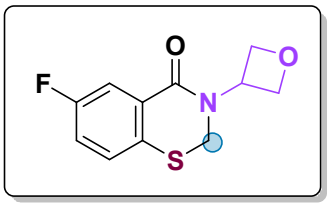
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a white solid (66.6 mg, 72%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.93 (s, 1H), 7.74 (d, *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). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) 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 $C_{17}H_{16}N_3OS$ $[M+H]^+$: 310.1009; found: 310.1012.

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



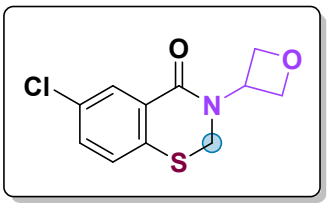
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (59.2 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.98 – 7.83 (m, 1H), 7.19 (d, *J* = 1.0 Hz, 2H), 5.83 – 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). ^{13}C NMR (75 MHz, $CDCl_3$) 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 $C_{12}H_{14}NO_2S$ $[M+H]^+$: 236.0740; found: 236.0741.

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



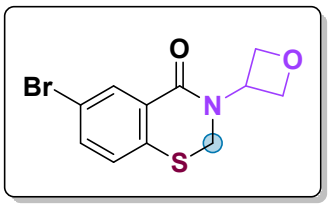
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (55.9 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 9.3, 2.7 Hz, 1H), 7.24 (dd, *J* = 8.5, 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}C NMR (75 MHz, $CDCl_3$) δ 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 $C_{11}H_{11}FNO_2S$ $[M+H]^+$: 240.0490; found: 240.0492.

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



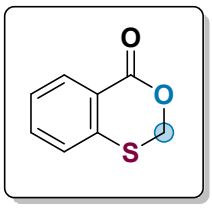
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a yellow solid (51.3 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, *J* = 2.2 Hz, 1H), 7.33 (dd, *J* = 8.4, 2.3 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}C NMR (75 MHz, $CDCl_3$) δ 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 $C_{11}H_{11}ClNO_2S$ $[M+H]^+$: 256.0194; found: 256.0191.

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



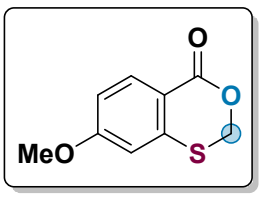
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (56.3 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (d, *J* = 2.2 Hz, 1H), 7.46 (dd, *J* = 8.3, 2.2 Hz, 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}C NMR (75 MHz, $CDCl_3$) δ 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 $C_{11}H_{11}BrNO_2S$ $[M+H]^+$: 299.9689; found: 299.9686.

4H-benzo[d][1,3]oxathiin-4-one (4a)



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 colourless oil (39.8 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.38 – 7.28 (m, 2H), 5.41 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.2, 138.7, 133.4, 132.7, 127.6, 126.8, 124.5, 68.8. HRMS (ESI, m/z) calcd for $C_8H_7O_2S$ $[M+H]^+$: 167.0161; found: 167.0166.

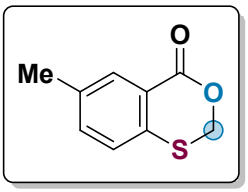
7-methoxy-4H-benzo[d][1,3]oxathiin-4-one (4b)



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 white solid (49.4 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.65

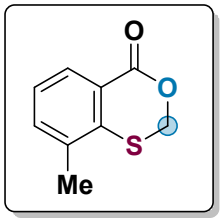
(d, J = 2.8 Hz, 1H), 7.25 (d, J = 8.6 Hz, 1H), 7.07 (dd, J = 8.6, 2.8 Hz, 1H), 5.39 (s, 2H), 3.84 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 163.3, 158.5, 129.6, 128.7, 125.3, 121.8, 115.6, 69.1, 55.7. HRMS (ESI, m/z) calcd for $C_9H_9O_3S$ $[M+H]^+$: 197.0267; found: 197.0270.

6-methyl-4H-benzo[d][1,3]oxathiin-4-one (4c)



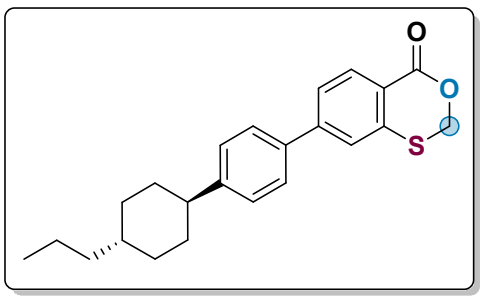
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a colourless oil (44.3 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.99 (s, 1H), 7.38 – 7.21 (m, 2H), 5.40 (s, 2H), 2.38 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 163.5, 137.0, 135.2, 134.5, 132.9, 127.4, 124.2, 68.8, 20.9. HRMS (ESI, m/z) calcd for $C_9H_9O_2S$ $[M+H]^+$: 181.0318; found: 181.0323.

8-methyl-4H-benzo[d][1,3]oxathiin-4-one (4d)



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 (37.8 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (d, J = 7.8 Hz, 1H), 7.37 (d, J = 7.4 Hz, 1H), 7.22 (d, J = 7.7 Hz, 1H), 5.39 (s, 2H), 2.35 (s, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 163.7, 138.6, 135.6, 134.5, 130.3, 126.0, 124.4, 68.0, 19.8. HRMS (ESI, m/z) calcd for $C_9H_9O_2S$ $[M+H]^+$: 181.0318; found: 181.0319.

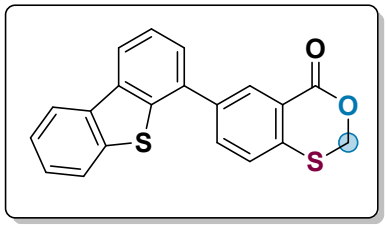
7-(4-((1s,4r)-4-propylcyclohexyl)phenyl)-4H-benzo[d][1,3]oxathiin-4-one (4e)



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 (94.4 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.41 (d, J = 2.0 Hz, 1H), 7.71 (dd, J = 8.2, 2.1 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 1H), 7.31 (d, J = 8.2 Hz, 2H), 5.45 (s, 2H), 2.51 (ddd, J = 12.2, 7.7, 3.0 Hz, 1H), 1.91 (t, J = 11.0 Hz, 4H), 1.59 – 1.43 (m, 2H), 1.42 – 1.28 (m, 3H), 1.28 – 1.18 (m, 2H), 1.15 – 0.99 (m, 2H), 0.91 (t, J = 7.1 Hz, 3H). $^{13}C\{^{1}H\}$ NMR (75 MHz, $CDCl_3$) δ 163.3, 148.0, 140.0, 136.9, 136.3, 131.8,

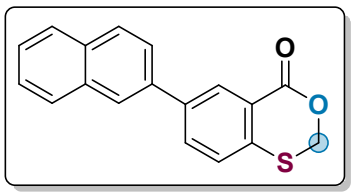
130.8, 128.3, 127.5, 126.7, 124.7, 68.8, 44.3, 39.7, 37.0, 34.2, 33.5, 20.0, 14.4. HRMS (ESI, m/z) calcd for $C_{23}H_{27}O_2S$ $[M+H]^+$: 367.1726; found: 367.1727.

6-(dibenzo[b,d]thiophen-4-yl)-4H-benzo[d][1,3]oxathiin-4-one (4f)



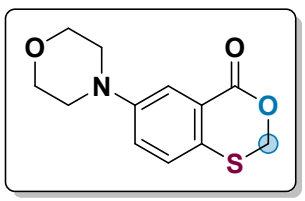
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a white solid (78.3 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.57 (d, *J* = 1.9 Hz, 1H), 8.20 (d, *J* = 6.7 Hz, 2H), 7.92 (dd, *J* = 8.1, 2.0 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.60 – 7.54 (m, 1H), 7.49 (dd, *J* = 6.0, 4.5 Hz, 4H), 7.33 (s, 1H), 5.52 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.1, 139.5, 139.2, 138.3, 136.5, 135.6, 134.6, 133.1, 132.4, 128.4, 128.1, 127.0, 126.8, 125.3, 124.9, 124.6, 122.7, 121.8, 121.2, 68.8. HRMS (ESI, m/z) calcd for $C_{20}H_{13}O_2S_2$[M+H]$^+$: 349.0351; found: 349.0354.

6-(naphthalen-2-yl)-4H-benzo[d][1,3]oxathiin-4-one (4g)



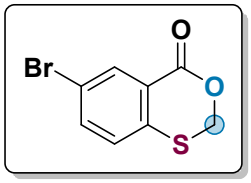
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (68.3 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.56 (d, *J* = 1.9 Hz, 1H), 8.06 (s, 1H), 7.93 (d, *J* = 8.6 Hz, 2H), 7.89 – 7.81 (m, 2H), 7.72 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.56 – 7.49 (m, 2H), 7.46 (d, *J* = 8.2 Hz, 1H), 5.47 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.4, 139.9, 137.4, 136.0, 133.5, 132.8 132.1, 131.2, 128.8, 128.2, 128.1, 127.6, 126.6, 126.4, 125.8, 124.8, 124.7, 68.8. HRMS (ESI, m/z) calcd for $C_{18}H_{13}O_2S$ $[M+H]^+$: 293.0631; found: 293.0631.

6-morpholino-4H-benzo[d][1,3]oxathiin-4-one (4h)



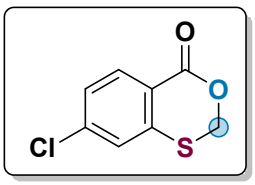
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the product as a yellow oil (65.5 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (d, *J* = 2.8 Hz, 1H), 7.30 – 7.25 (m, 1H), 7.10 (dd, *J* = 8.7, 2.8 Hz, 1H), 5.42 (s, 2H), 4.01 – 3.78 (m, 4H), 3.30 – 3.13 (m, 4H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 163.8, 150.1, 128.4, 127.8, 125.1, 121.3, 118.5, 69.1, 66.6, 48.7. HRMS (ESI, m/z) calcd for $C_{20}H_{13}O_2S_2$[M+H]$^+$: 252.0689; found: 252.0693.

6-bromo-4H-benzo[d][1,3]oxathiin-4-one (4i)



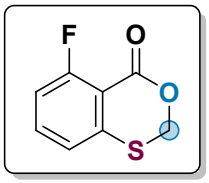
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (43.7 mg, 60%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.33 (d, *J* = 2.1 Hz, 1H), 7.63 (dd, *J* = 8.4, 2.2 Hz, 1H), 7.29 (d, *J* = 1.2 Hz, 1H), 5.45 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.0, 137.7, 136.4, 135.3, 129.0, 125.8, 120.3, 68.7. HRMS (ESI, m/z) calcd for $C_8H_6BrO_2S$ $[M+H]^+$: 244.9266; found: 244.9272.

7-chloro-4H-benzo[d][1,3]oxathiin-4-one (4j)



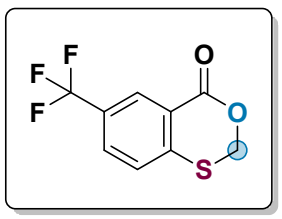
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (44.7 mg, 75%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.05 (d, *J* = 8.5 Hz, 1H), 7.31 (d, *J* = 1.5 Hz, 1H), 7.28 – 7.20 (m, 1H), 5.37 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.5, 140.4, 140.1, 134.0, 127.4, 127.3, 122.6, 68.6. HRMS (ESI, m/z) calcd for $C_8H_6ClO_2S$ $[M+H]^+$: 200.9772; found: 200.9777.

5-fluoro-4H-benzo[d][1,3]oxathiin-4-one (4k)



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 (38.6 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (td, *J* = 8.1, 5.1 Hz, 1H), 7.18 (d, *J* = 7.9 Hz, 1H), 7.11 – 6.98 (m, 1H), 5.38 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 164.1 (d, *J* = 265.5 Hz), 158.8 (d, *J* = 4.9 Hz), 141.3, 134.4 (d, *J* = 10.5 Hz), 123.6 (d, *J* = 4.1 Hz), 115.5 (d, *J* = 21.8 Hz), 113.7 (d, *J* = 8.7 Hz), 68.8. HRMS (ESI, m/z) calcd for $C_8H_6FO_2S$ $[M+H]^+$: 185.0067; found: 185.0069.

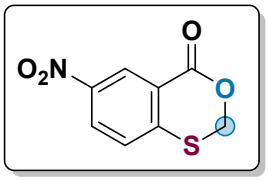
6-(trifluoromethyl)-4H-benzo[d][1,3]oxathiin-4-one (4l)



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 (54.7 mg, 78%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.31 (d, *J* = 8.2 Hz, 1H), 7.64 (s, 1H), 7.58 (d, *J* = 8.2 Hz, 1H), 5.47 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 162.0, 140.0, 134.9 (q, *J*

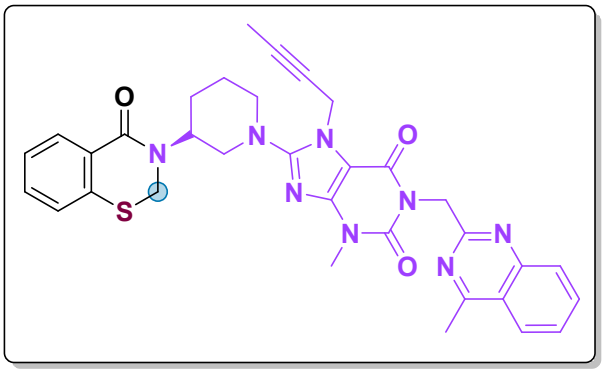
= 33.0 Hz), 129.8 (q, J = 273.4 Hz), 124.7 (q, J = 3.9 Hz), 123.4 (q, J = 3.6 Hz), 121.0, 68.8. HRMS (ESI, m/z) calcd for $C_9H_6F_3O_2S$ $[M+H]^+$: 235.0035; found: 235.0038.

6-nitro-4H-benzo[d][1,3]oxathiin-4-one (4m)



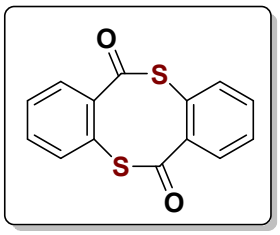
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the product as a yellow solid (35.4 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.38 (d, J = 8.6 Hz, 1H), 8.24 (d, J = 2.1 Hz, 1H), 8.13 (dd, J = 8.6, 2.1 Hz, 1H), 5.50 (s, 2H). ^{13}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 161.4, 141.0, 134.2, 131.1, 129.0, 122.7, 121.2, 68.9. HRMS (ESI, m/z) calcd for $C_8H_6NO_4S$ $[M+H]^+$: 212.0012; found: 212.0016.

(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)



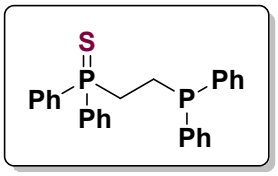
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:3, v/v) to give the product as a white solid (124.6 mg, 67%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, J = 8.0 Hz, 1H), 8.00 (d, J = 8.2 Hz, 1H), 7.87 (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}C{^{1}H} NMR (75 MHz, $CDCl_3$) δ 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 $C_{33}H_{33}N_8O_3S$ $[M+H]^+$: 621.2391; found: 621.2391.

6H,12H-dibenzo[b,f][1,5]dithiocine-6,12-dione (6)



CH_3CN (2 mL) was added to a mixture of benzo[c][1,2]dithiol-3-one **1a** (0.3 mmol, 50.4 mg), DPPE (0.2 mmol, 79.4 mg) in a sealed tube. Then, the mixture was stirred at 80 °C for about 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the desired **6** as white solid (28.5mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 – 7.31 (m, 4H), 7.29 – 7.22 (m, 4H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$) δ 197.4, 142.5, 135.6, 131.2, 131.0, 126.5, 125.2. HRMS (ESI, m/z) calcd for $C_{14}H_9O_2S_2$ $[M+H]^+$: 273.0038; found: 273.0039.

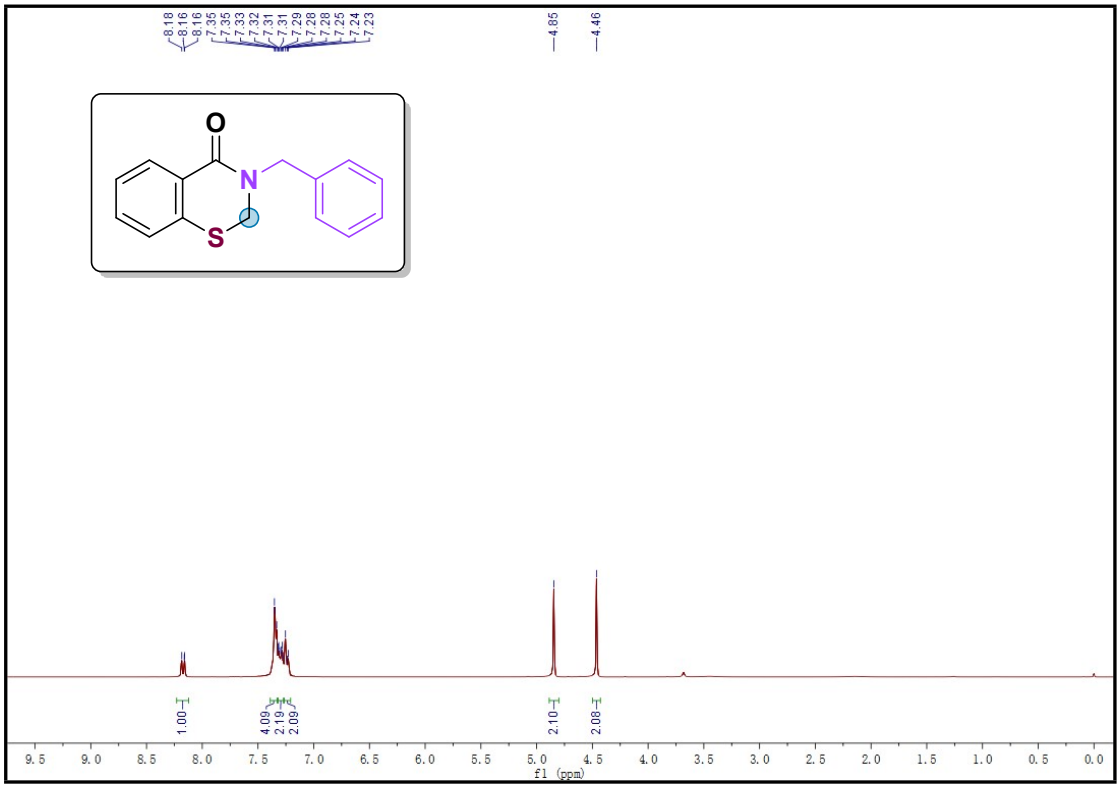
(2-(diphenylphosphaneyl)ethyl)diphenylphosphine sulfide (7)

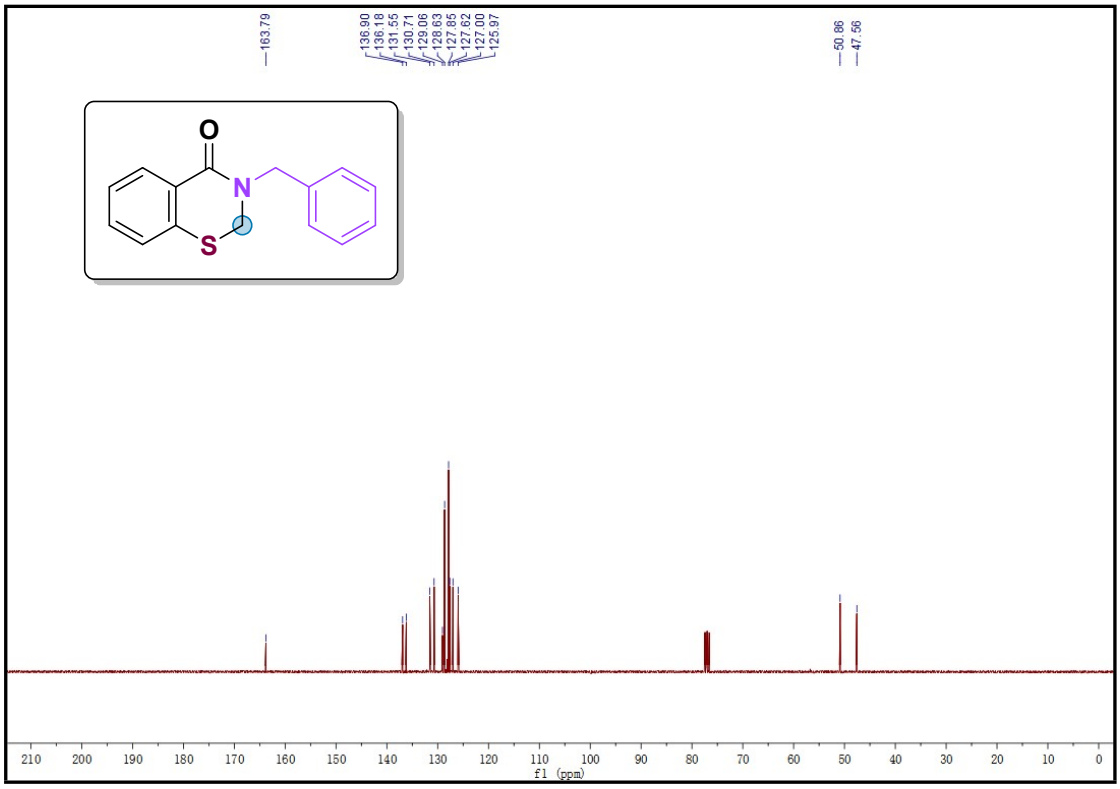


CH_3CN (2 mL) was added to a mixture of benzo[c][1,2]dithiol-3-one **1a** (0.3 mmol, 50.4 mg), DPPE (0.2 mmol, 79.4 mg) in a sealed tube. Then, the mixture was stirred at 80 °C for about 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 5:1, v/v) to give the desired **7** as white solid (41.3 mg, 48%). ^{1}H NMR (300 MHz, $CDCl_3$) ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.67 (m, 4H), 7.53 – 7.39 (m, 8H), 7.37 (dd, J = 8.2, 4.7 Hz, 8H), 2.558 – 2.47 (m, 2H), 2.40 – 2.25 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$). ^{13}C NMR (75 MHz, $CDCl_3$) δ 137.1 (d, J = 12.7 Hz), 132.9, 132.6, 131.7, 131.5 (d, J = 3.2 Hz), 131.0 (d, J = 10.1 Hz), 129.0, 128.7, 128.6, 128.5 (d, J = 2.8 Hz), 20.5 (d, J = 3.2 Hz), 19.9 (d, J = 3.2 Hz). HRMS (ESI, m/z) calcd for $C_{26}H_{25}P_2S$ $[M+H]^+$: 431.1147; found: 431.1150.

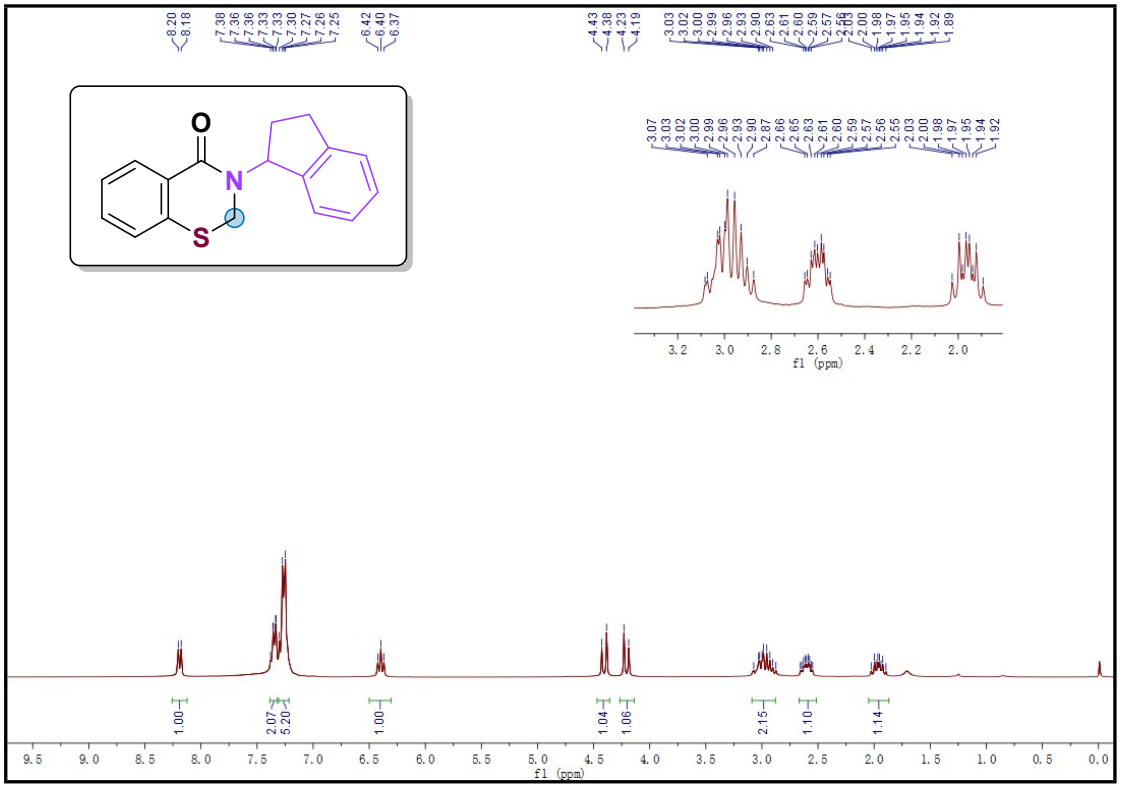
7. NMR spectroscopic data for the products

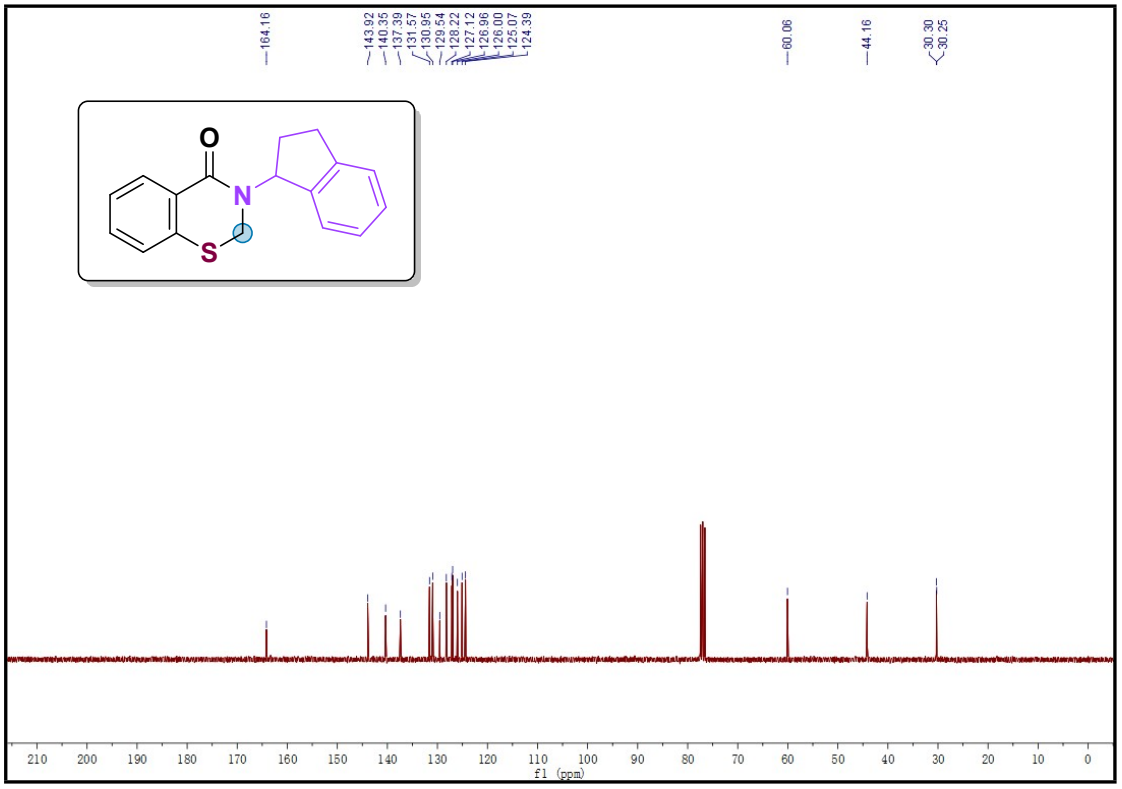
3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3a)



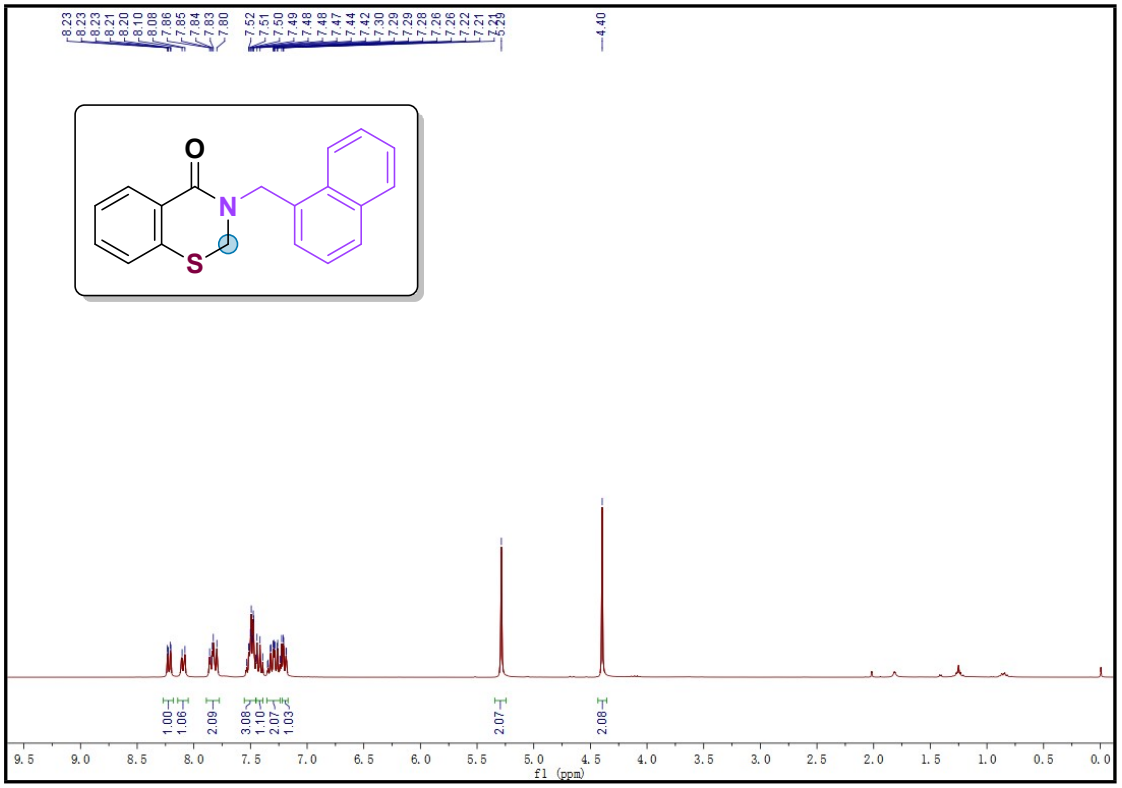


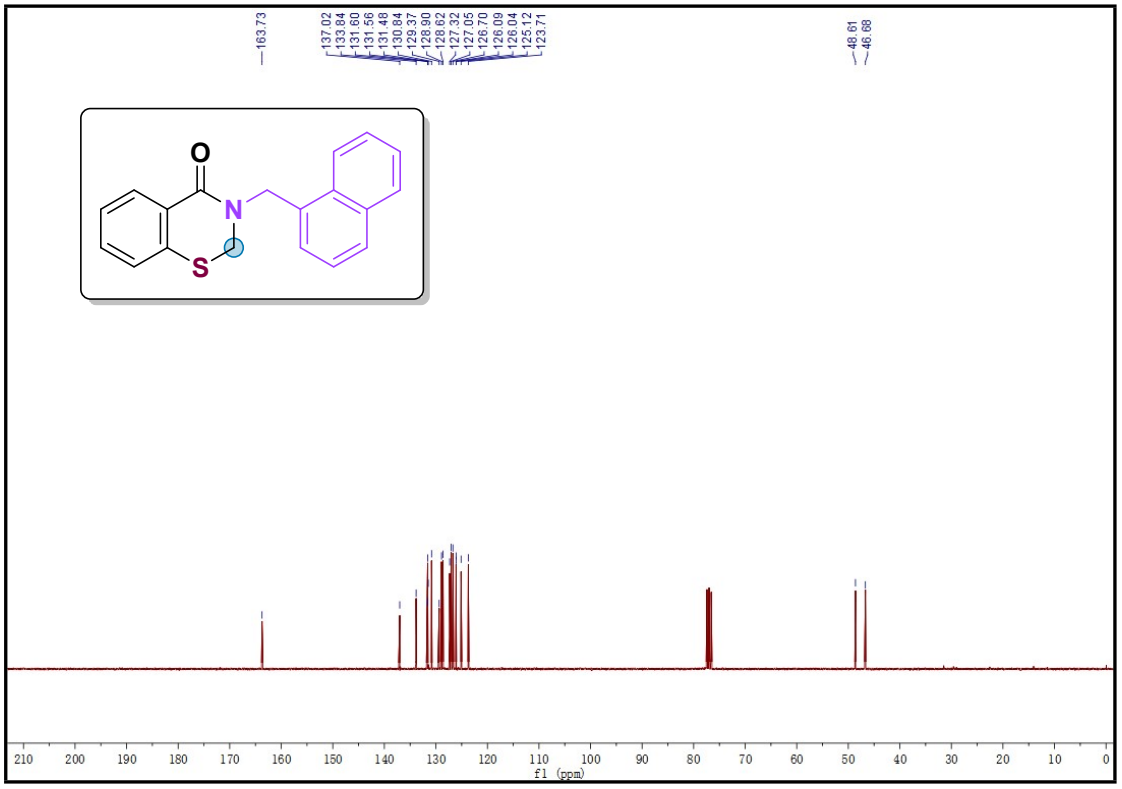
3-(2,3-dihydro-1H-inden-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3b)



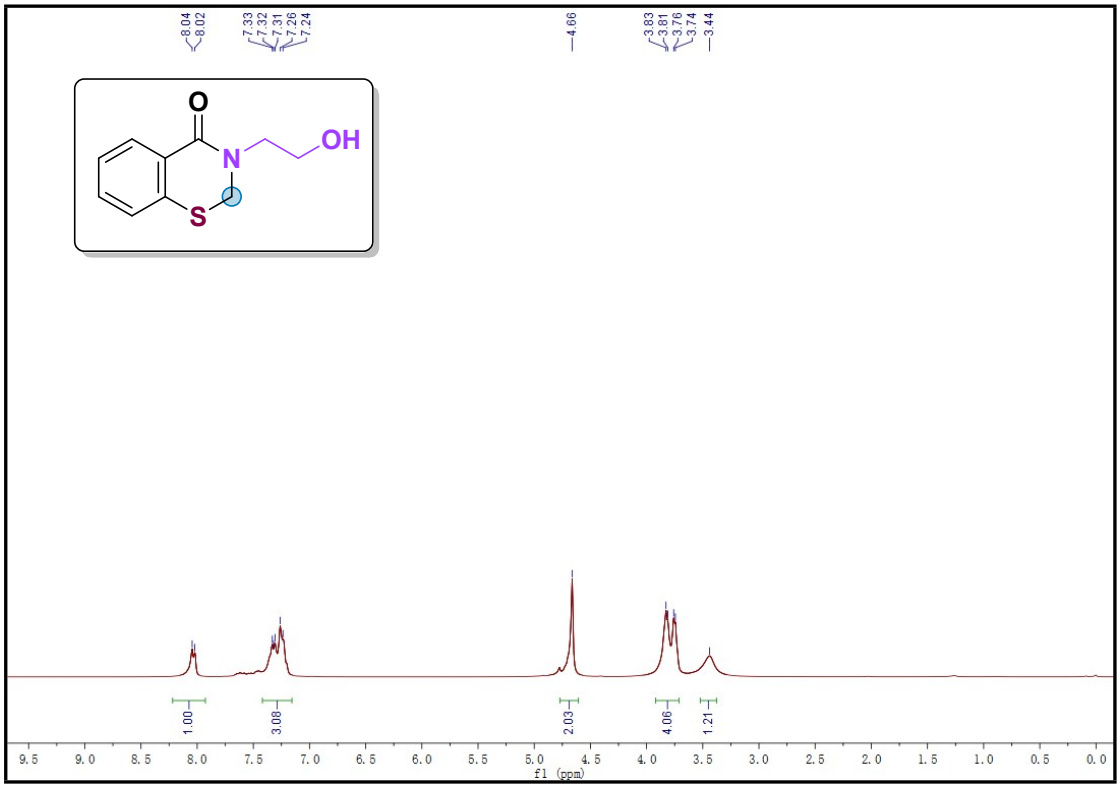


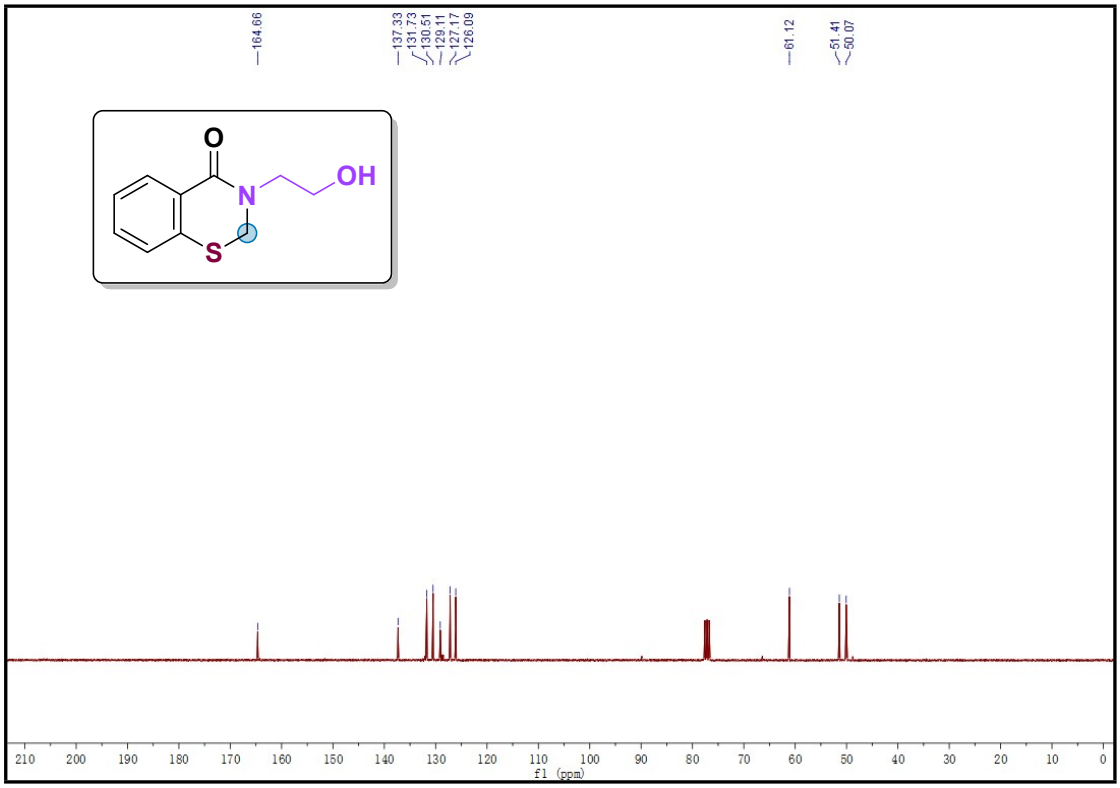
3-(naphthalen-1-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3c)



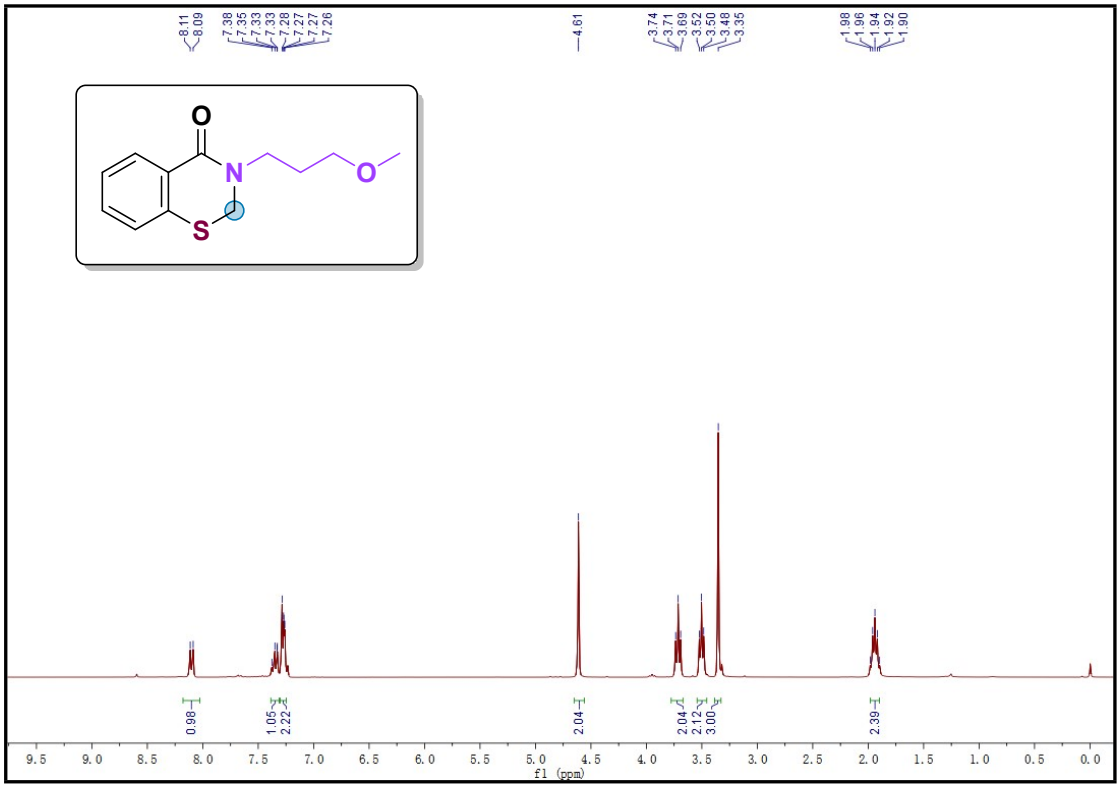


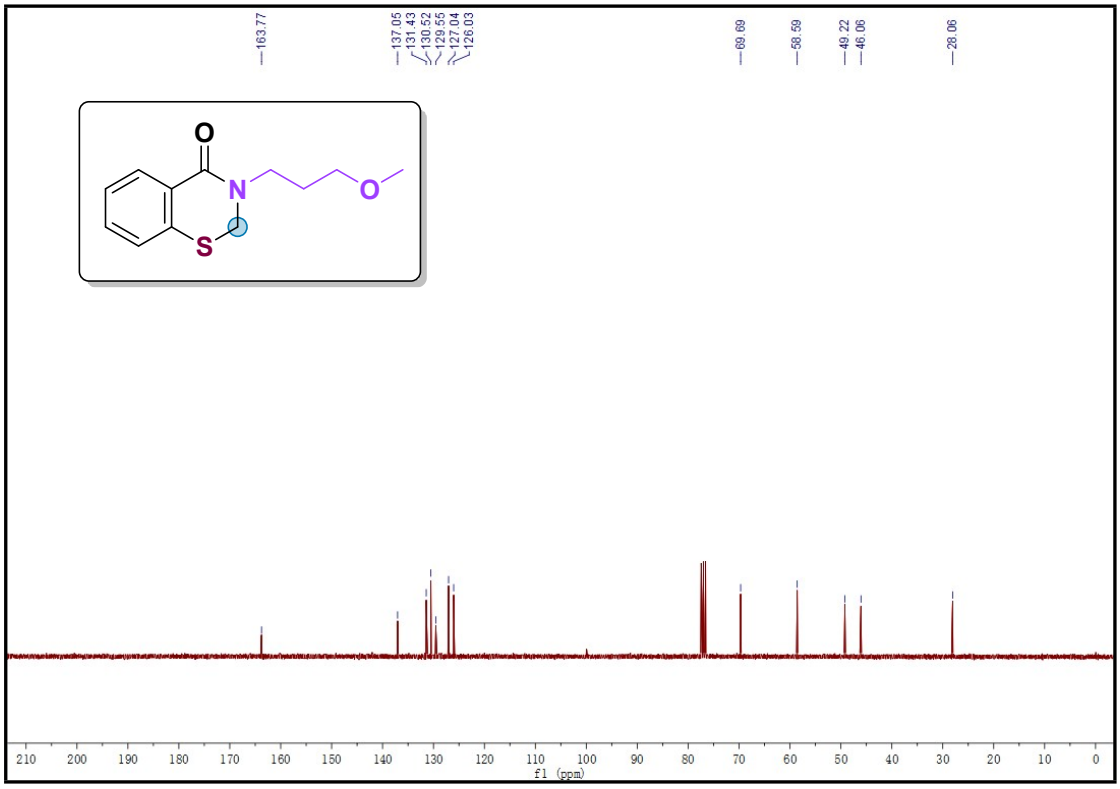
3-(2-hydroxyethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3d)



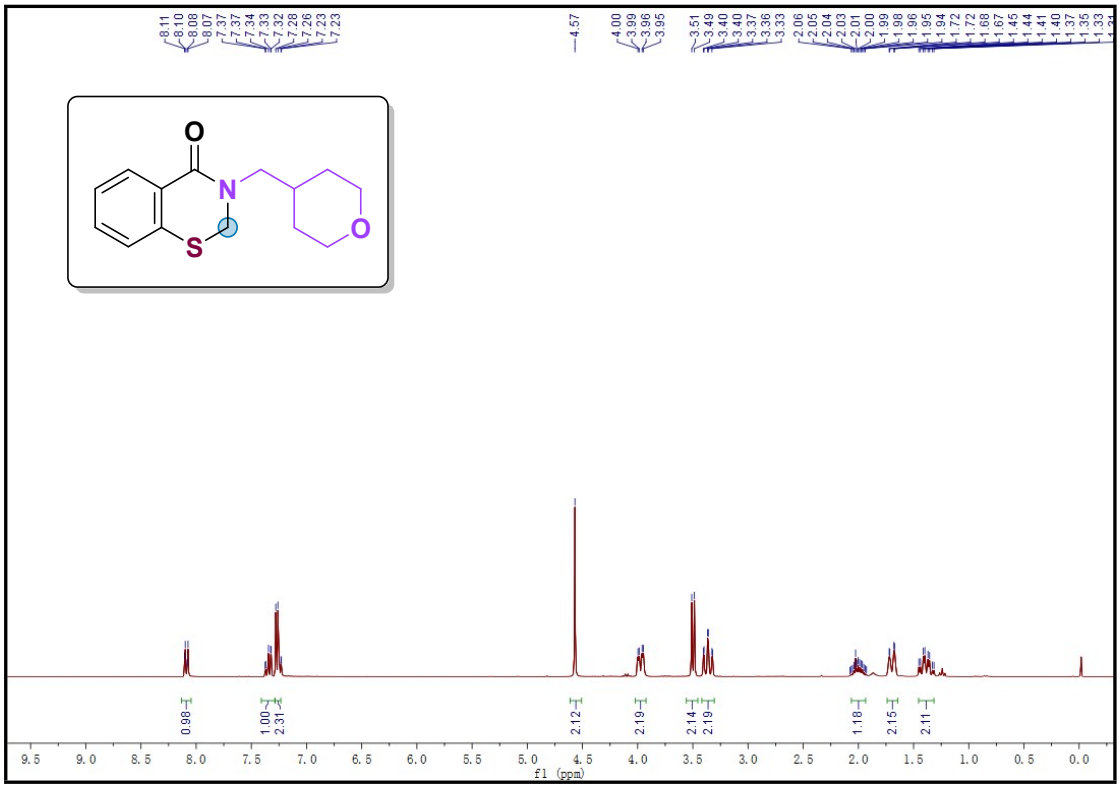


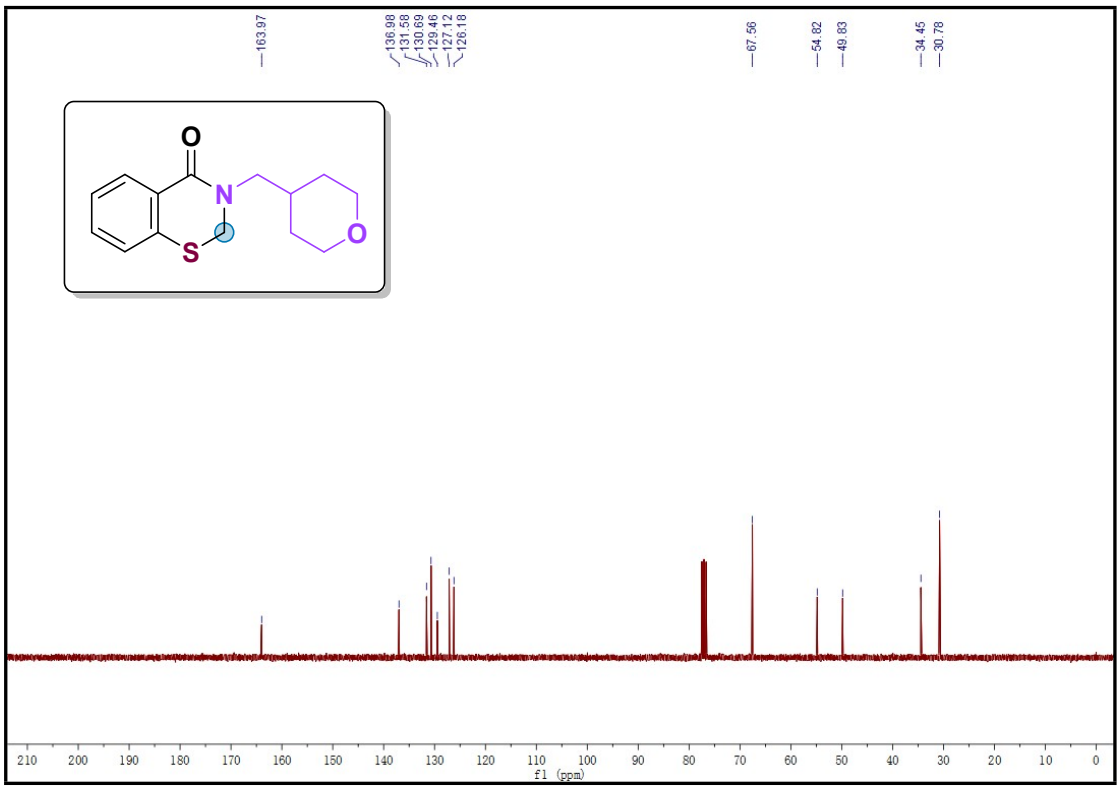
3-(3-methoxypropyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3e)



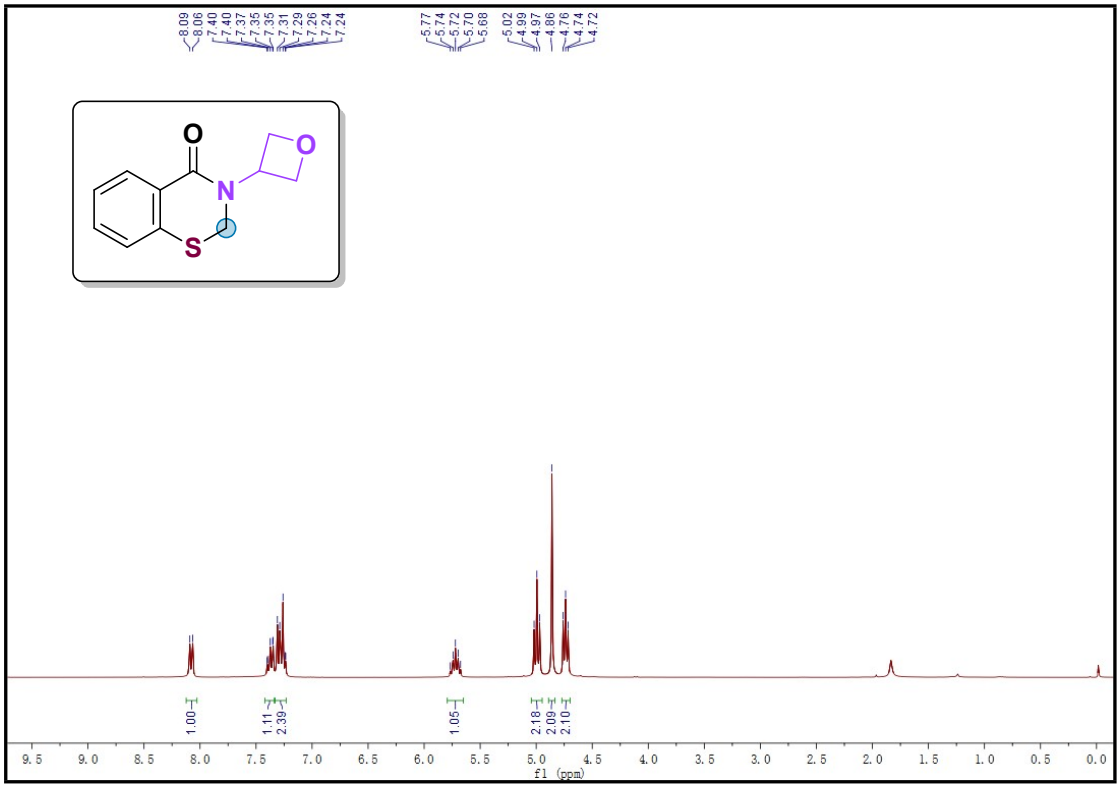


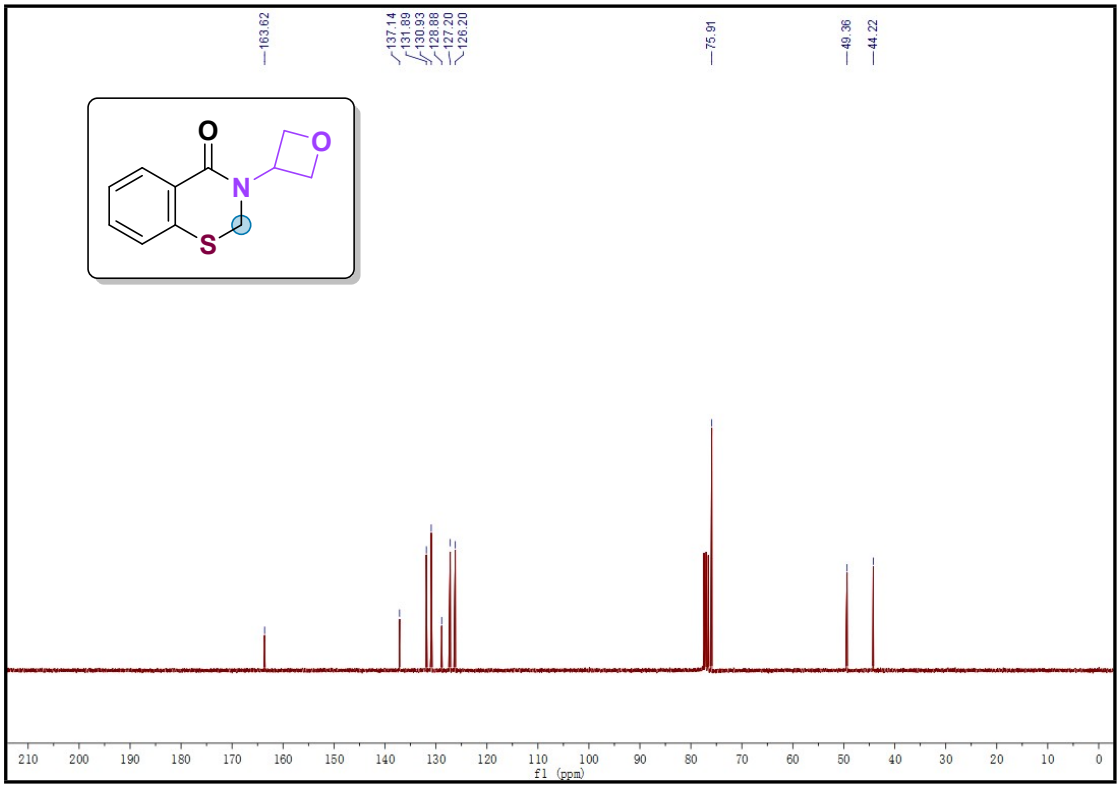
3-((tetrahydro-2H-pyran-4-yl)methyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3f)



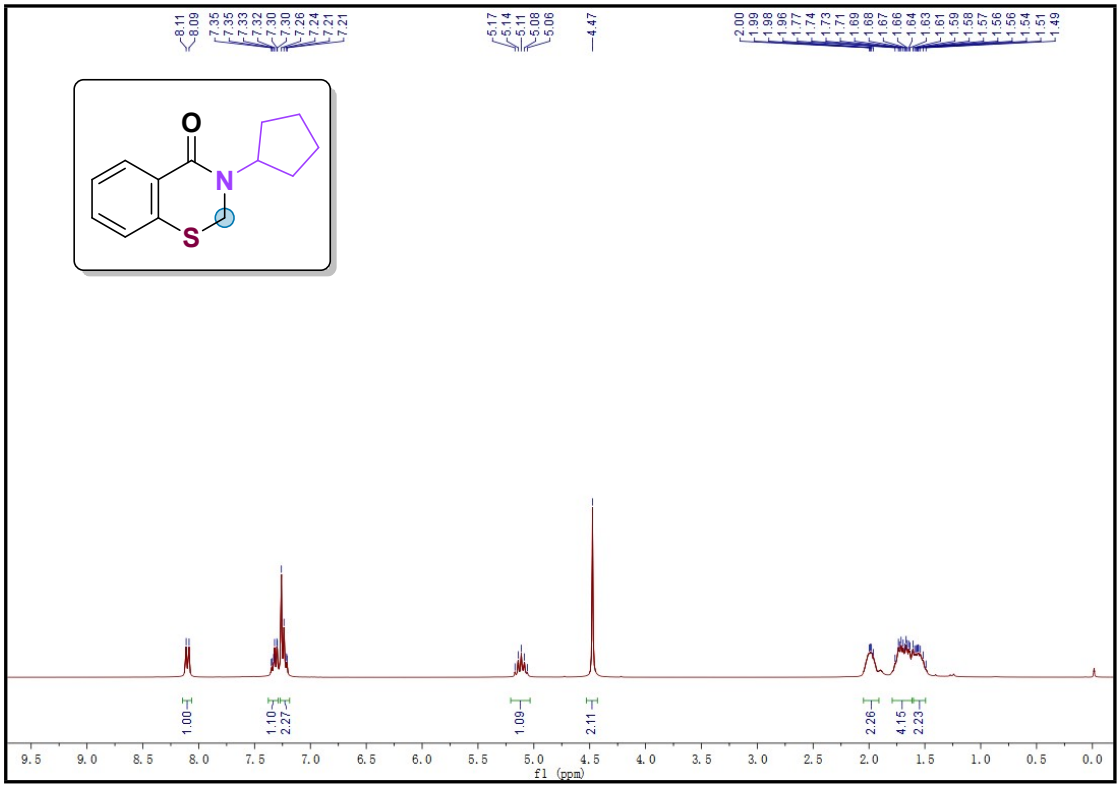


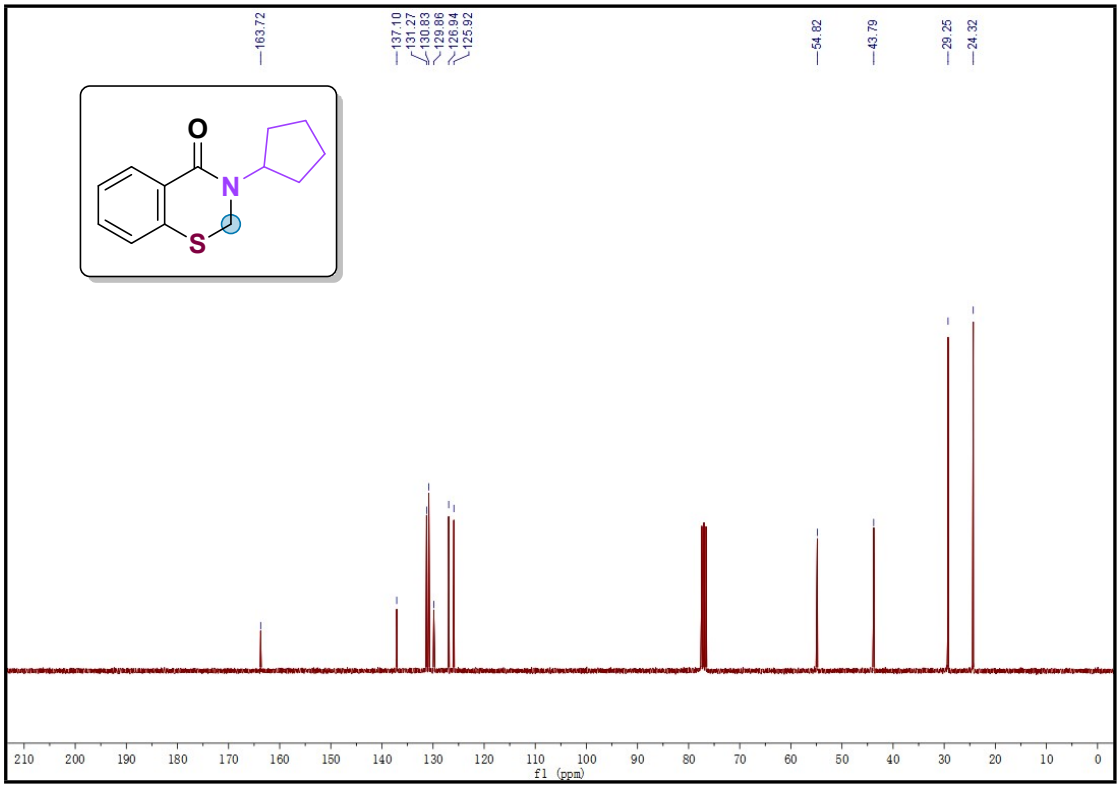
3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3g)



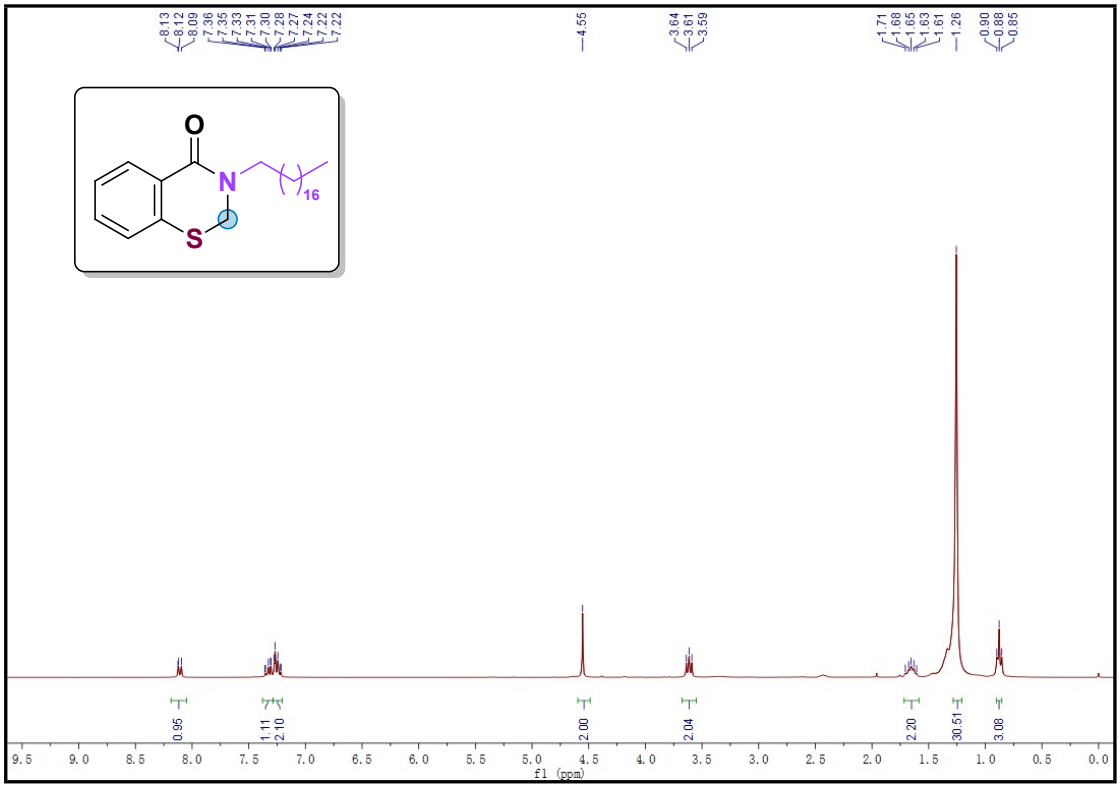


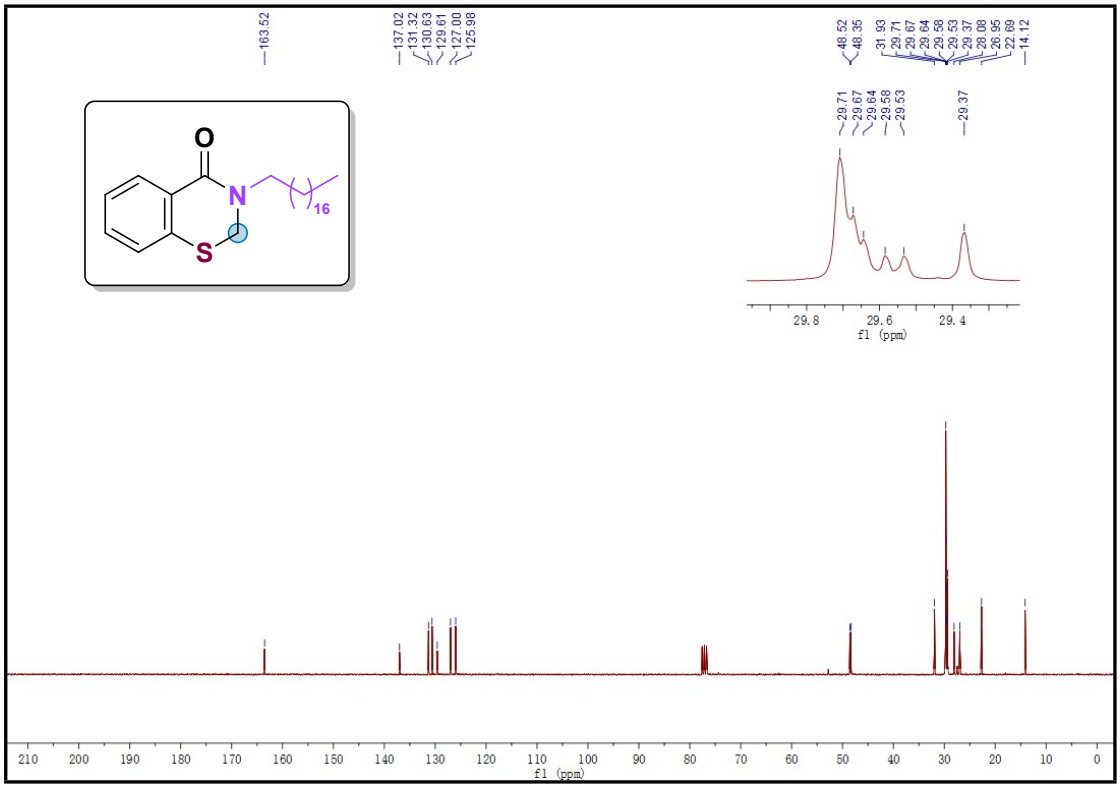
3-cyclopentyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3h)



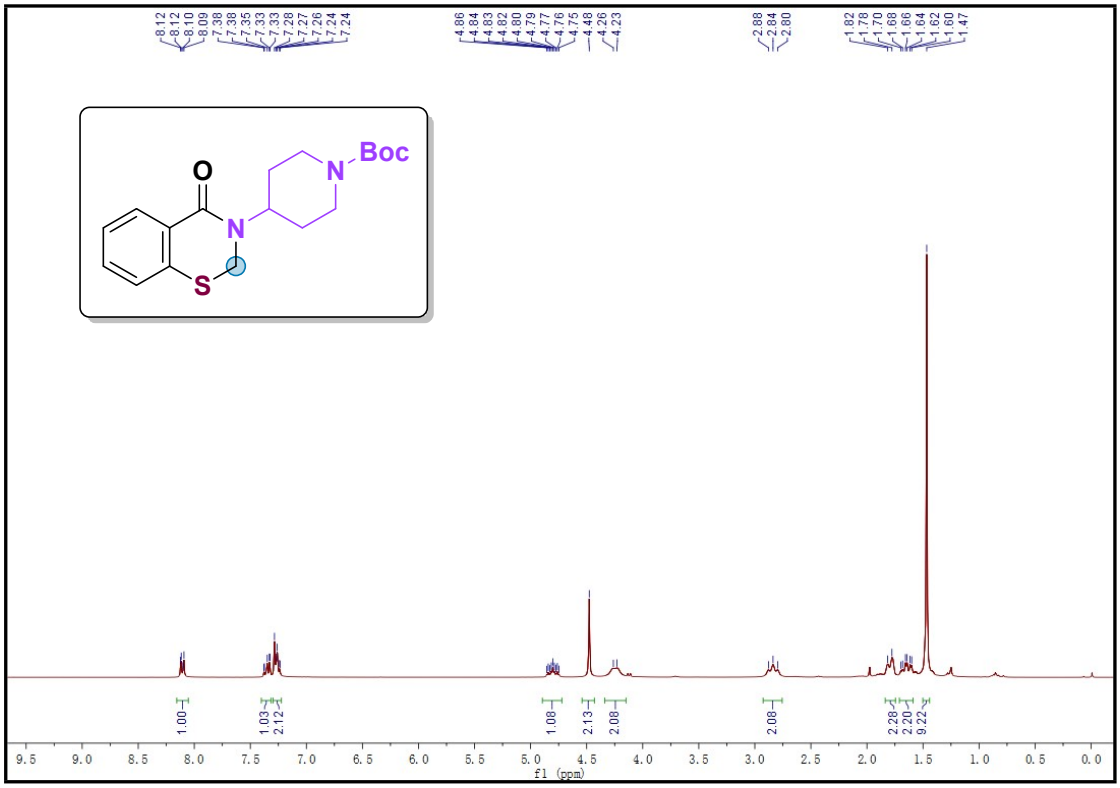


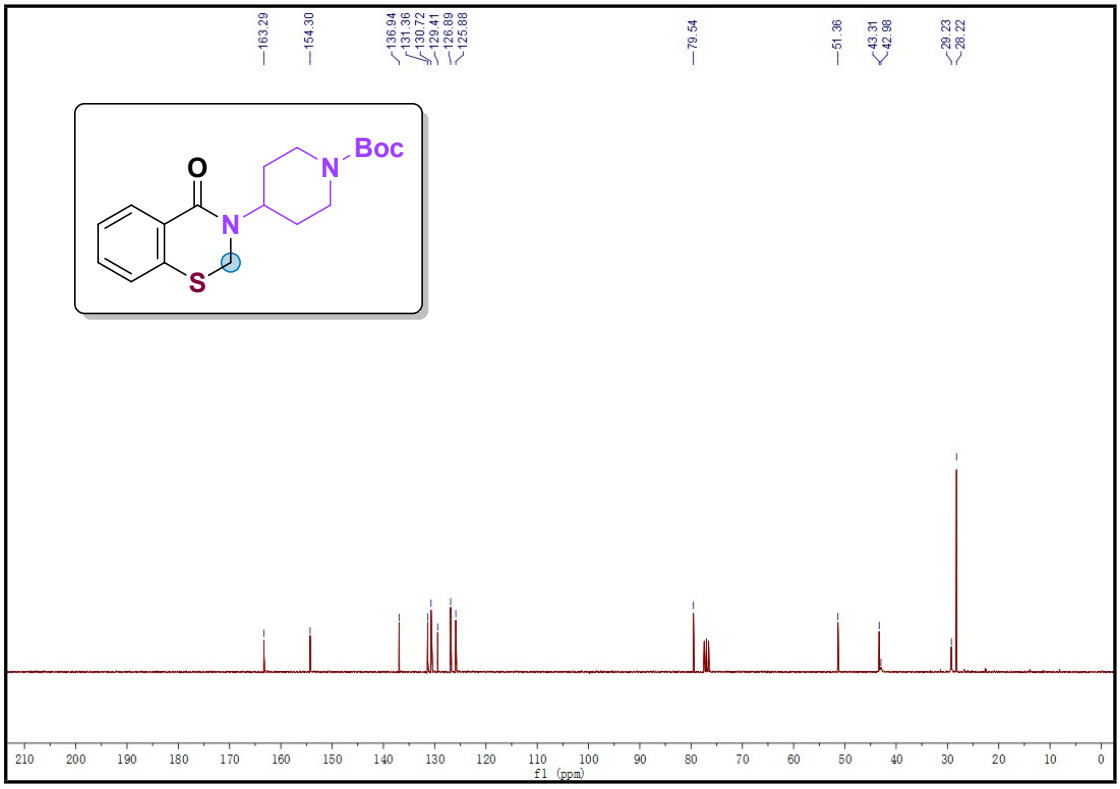
3-octadecyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3i)



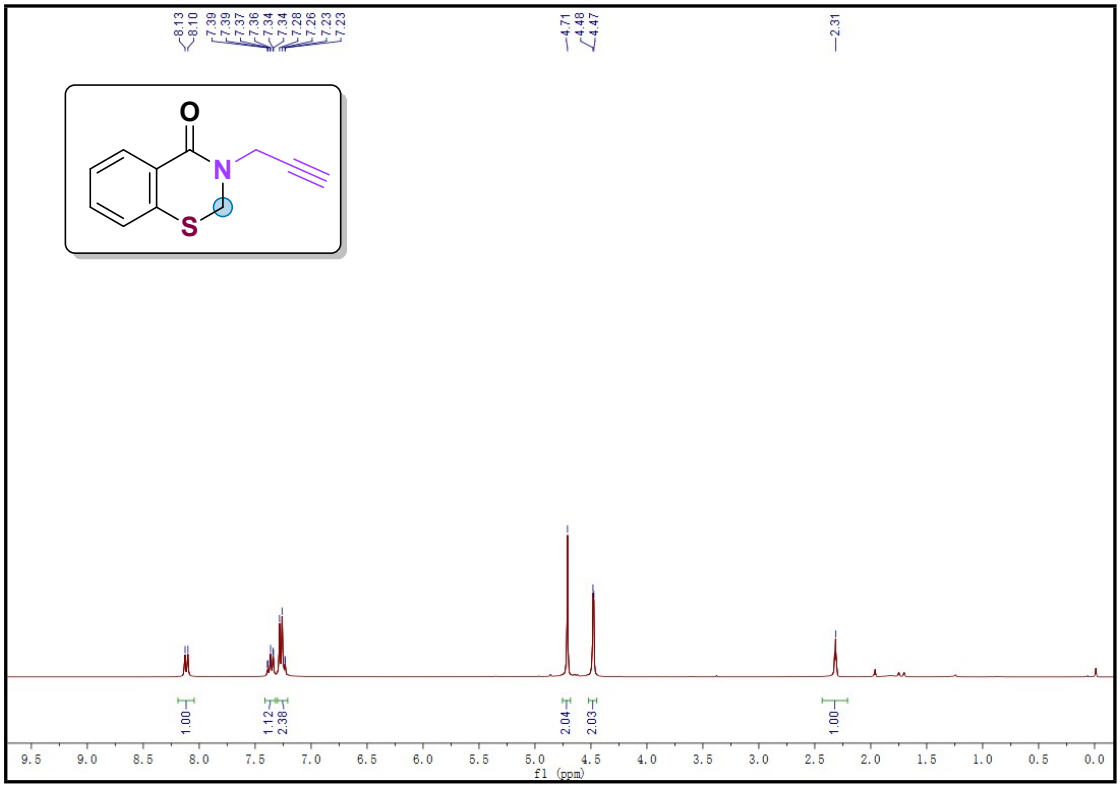


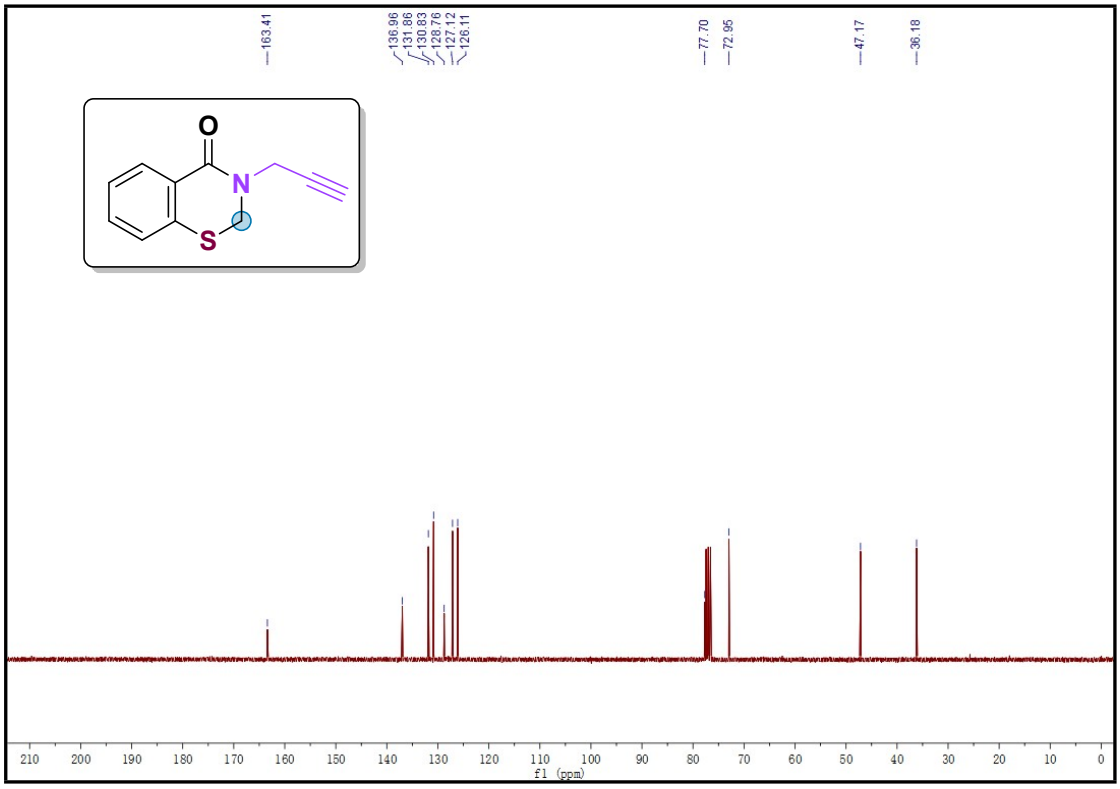
tert-butyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidine-1-carboxylate (3j)



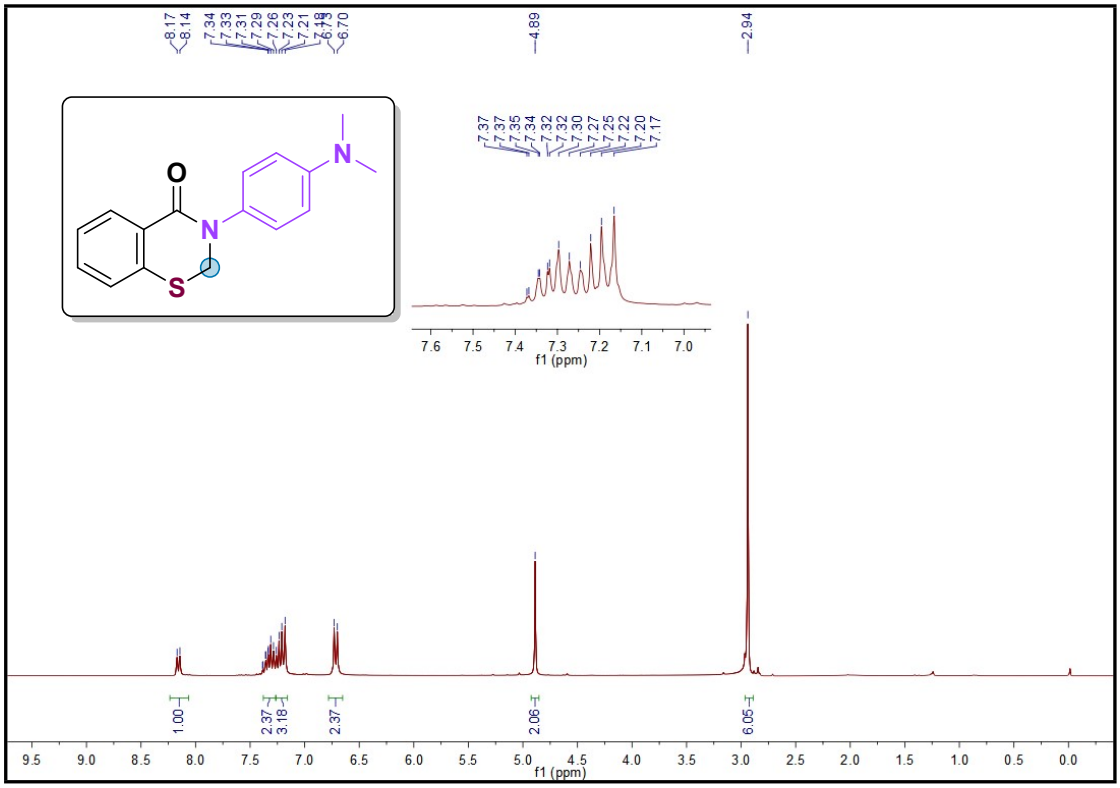


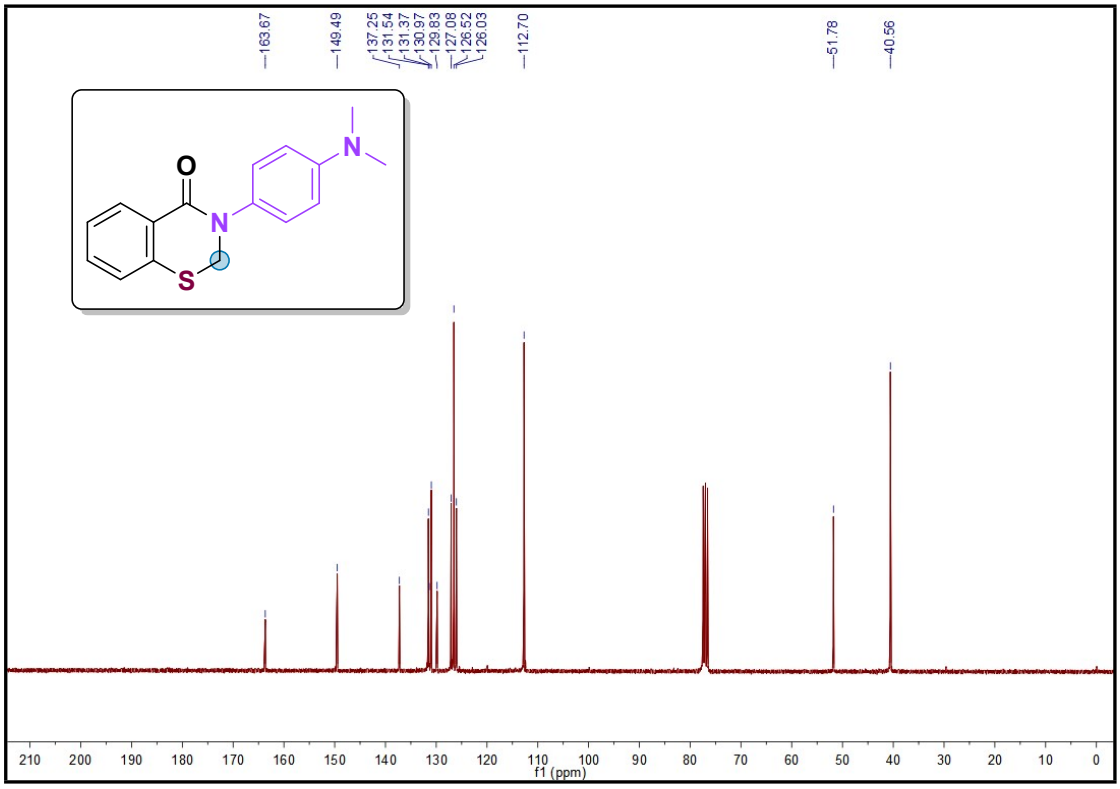
3-(prop-2-yn-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3k)



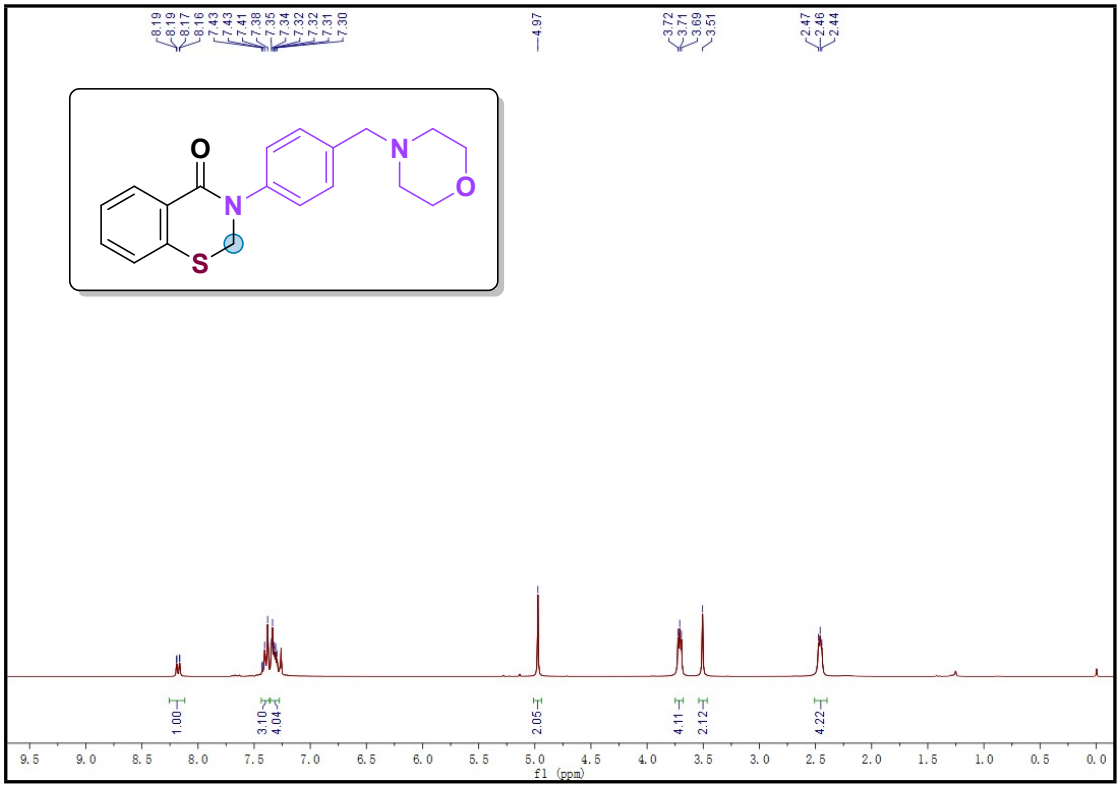


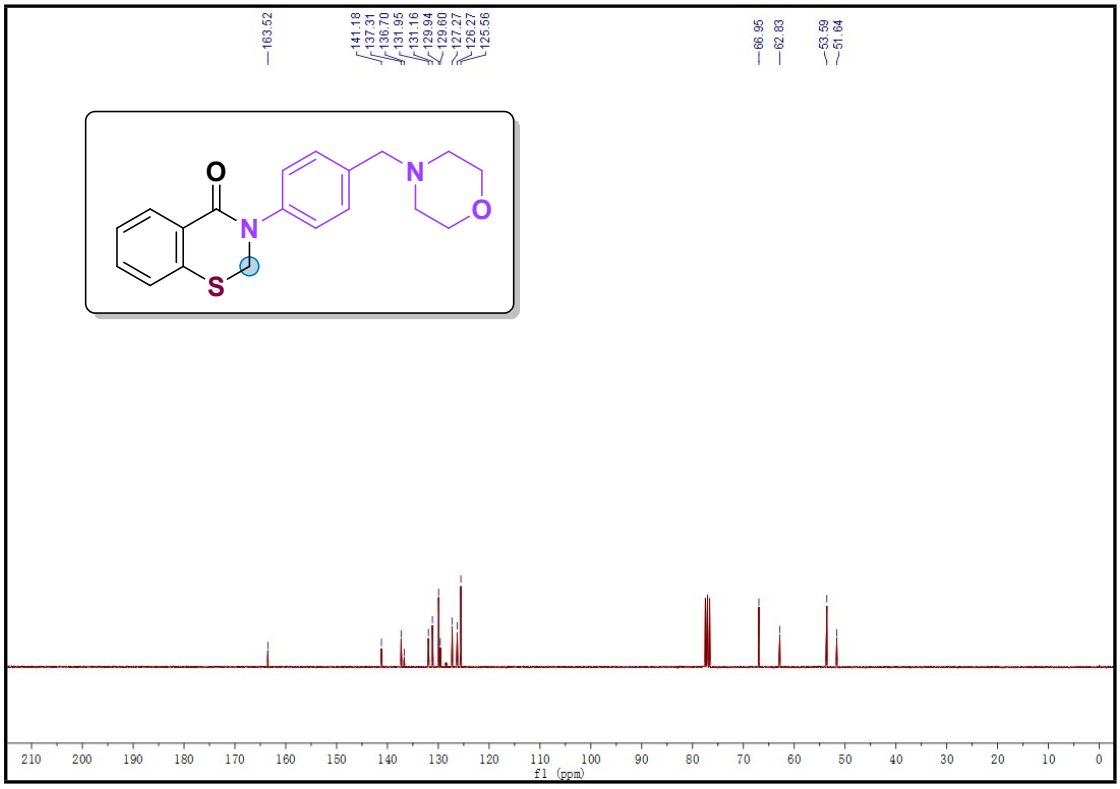
3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3l)



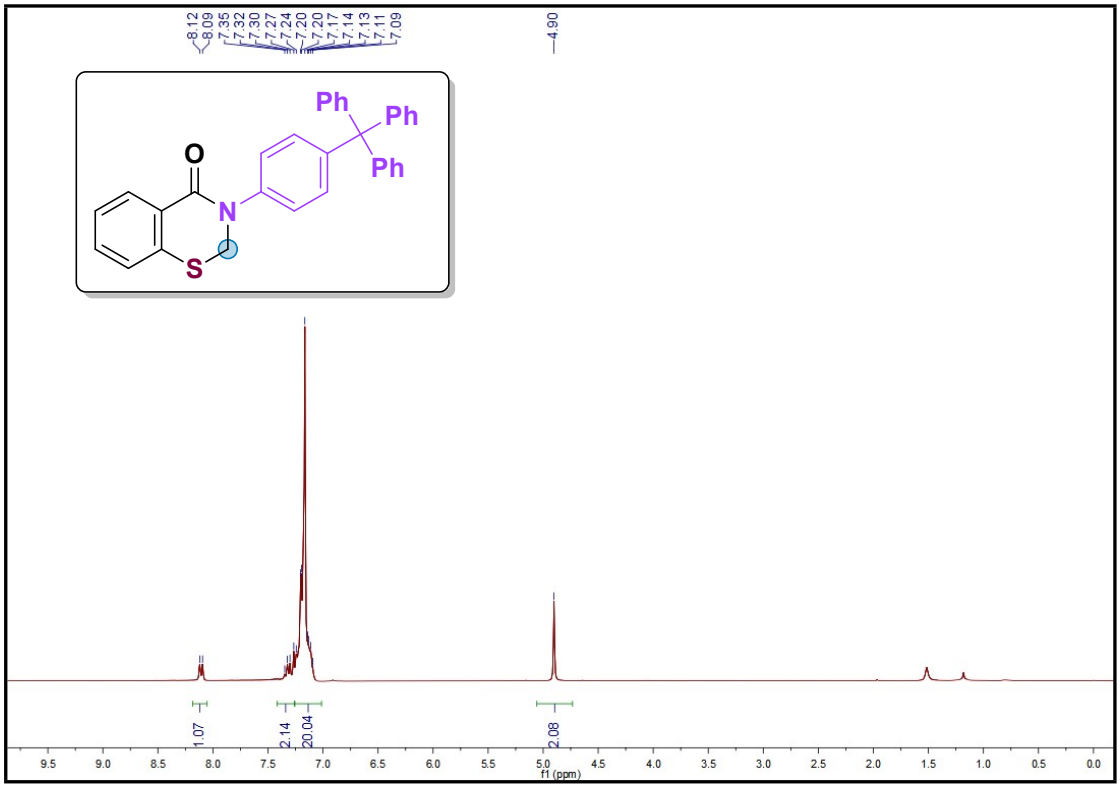


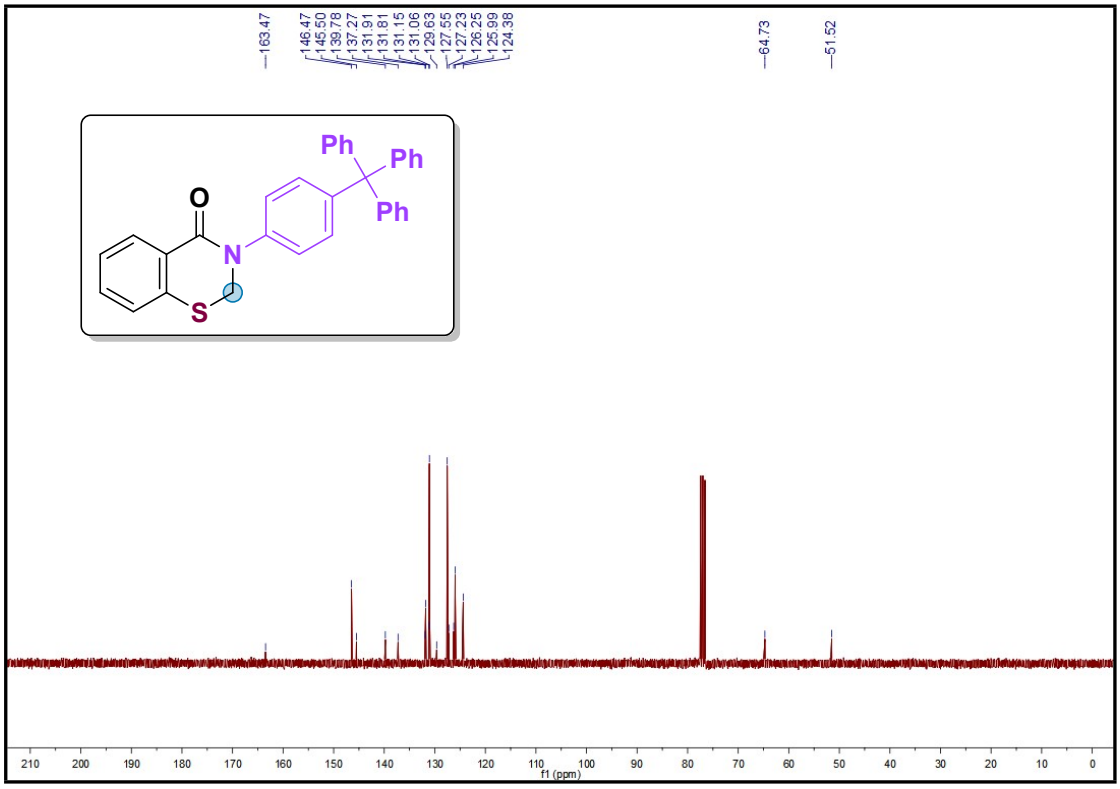
3-(4-(morpholinomethyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3m)



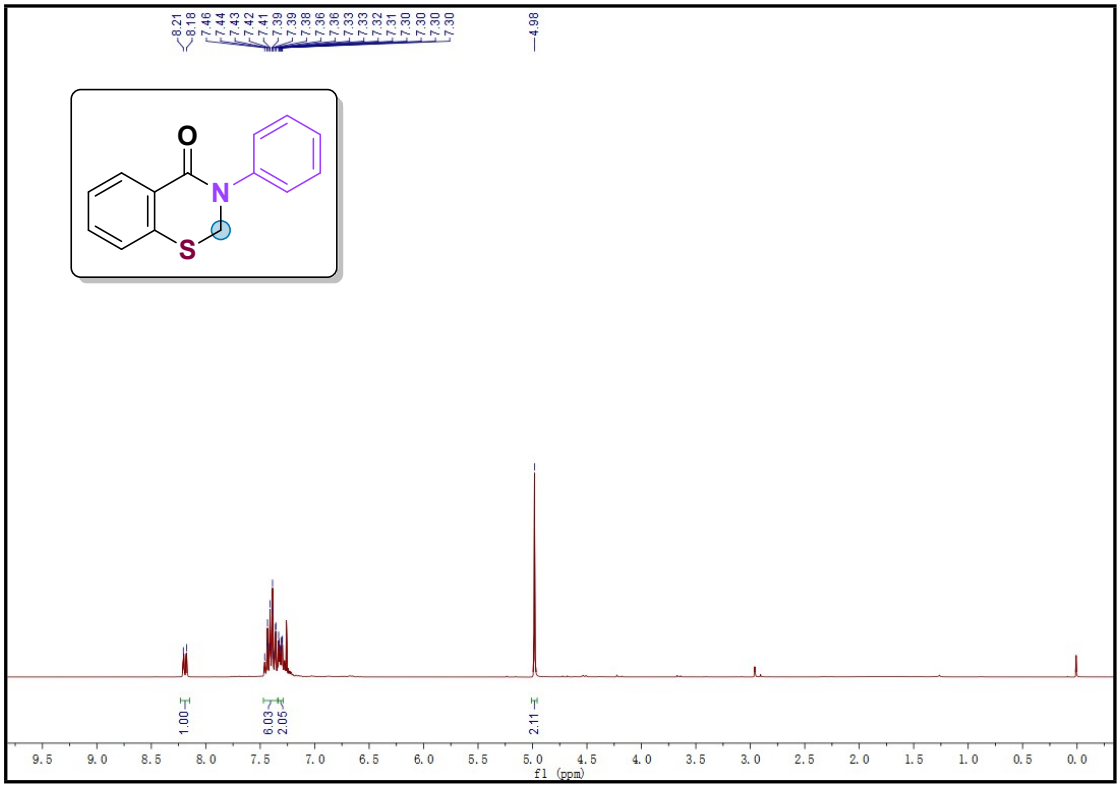


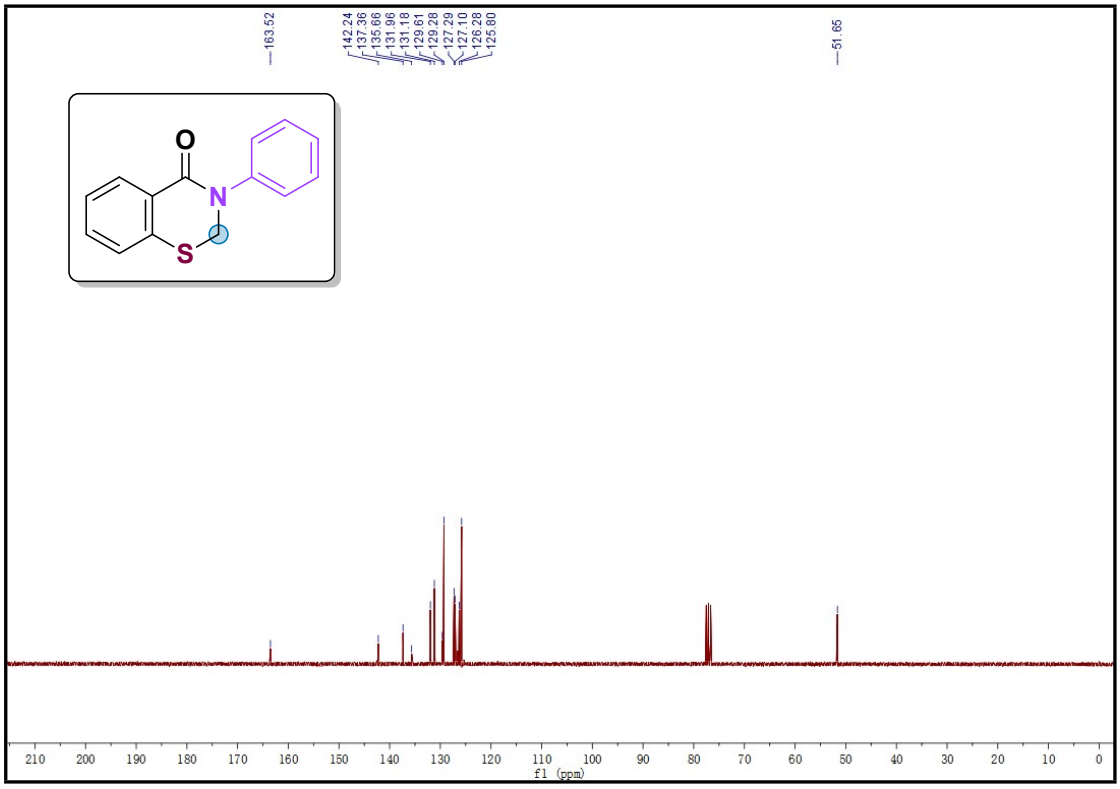
3-(4-tritylphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3n)



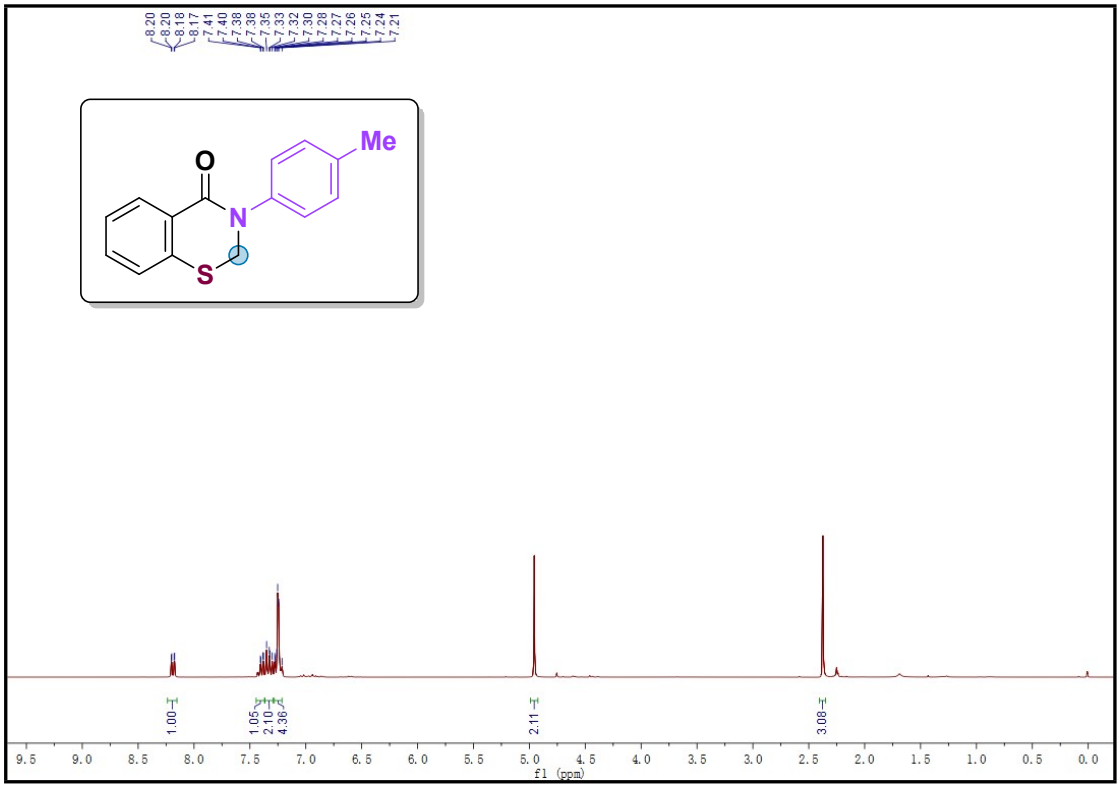


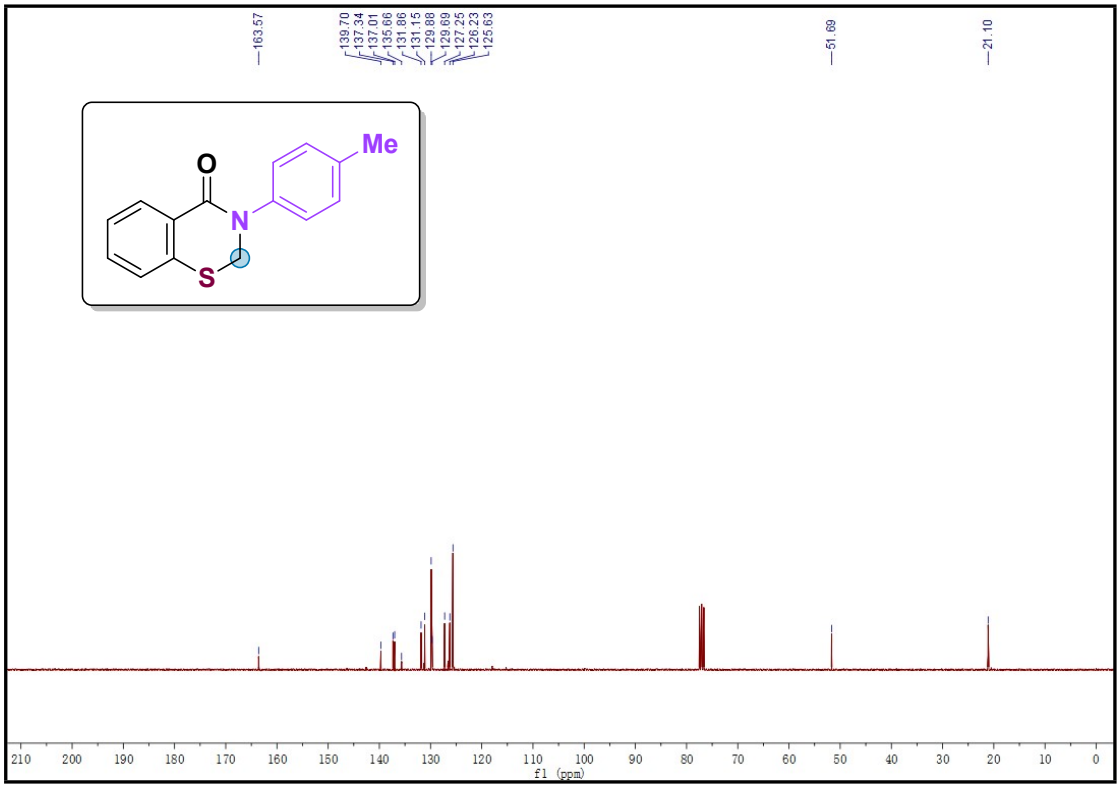
3-phenyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3o)



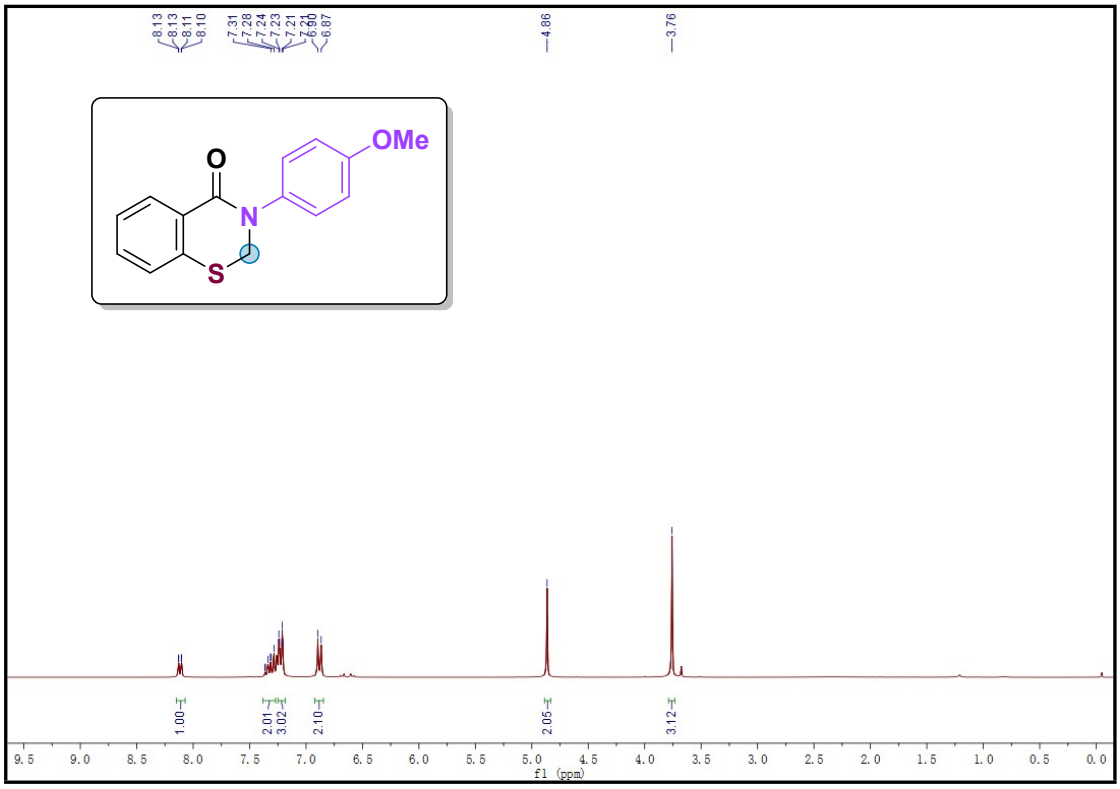


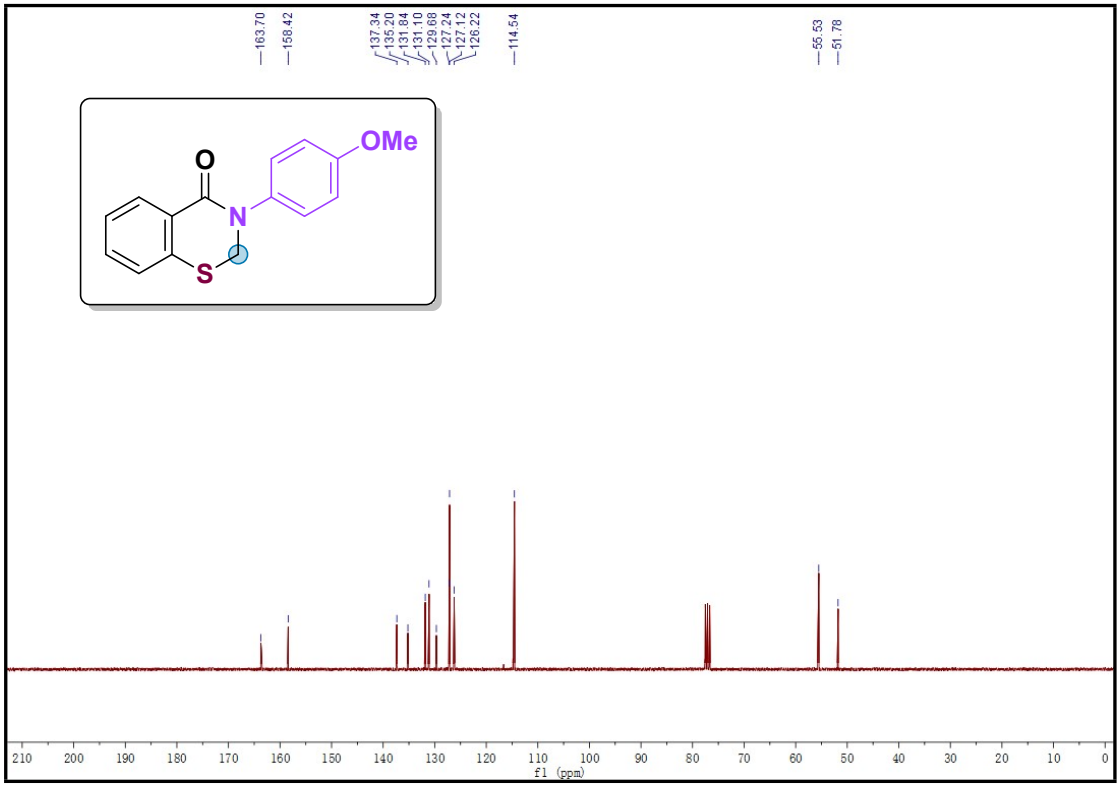
3-(p-tolyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3p)



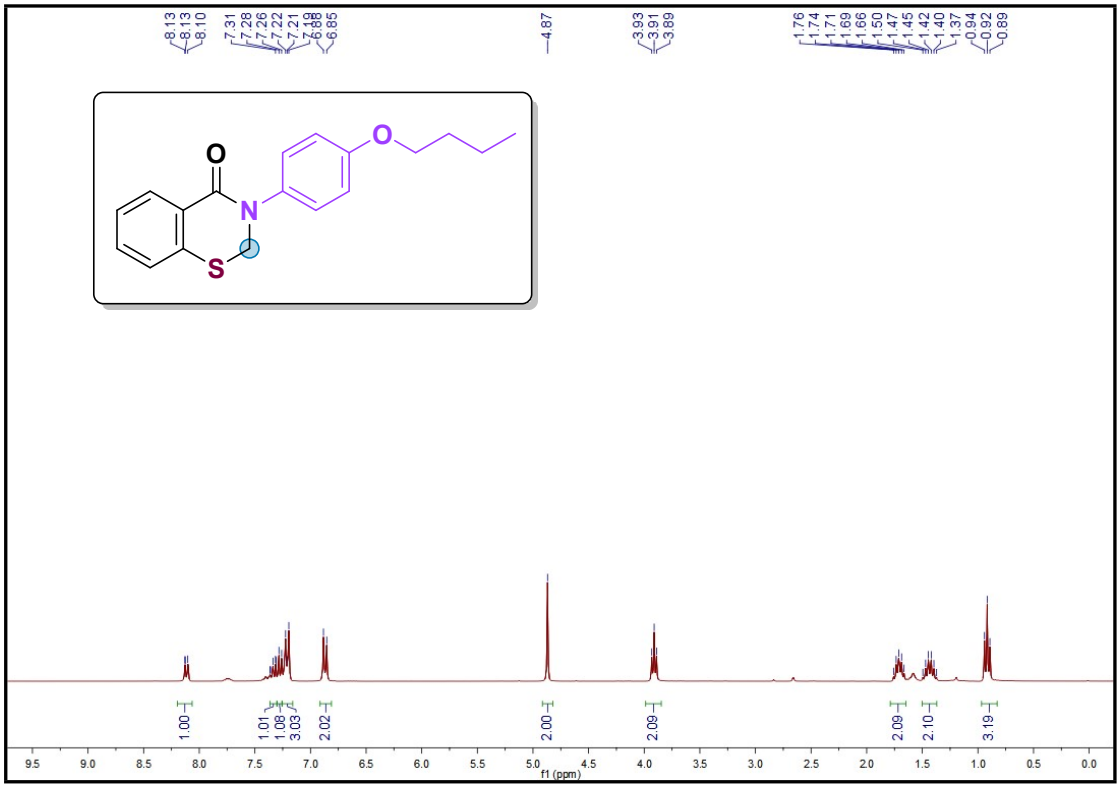


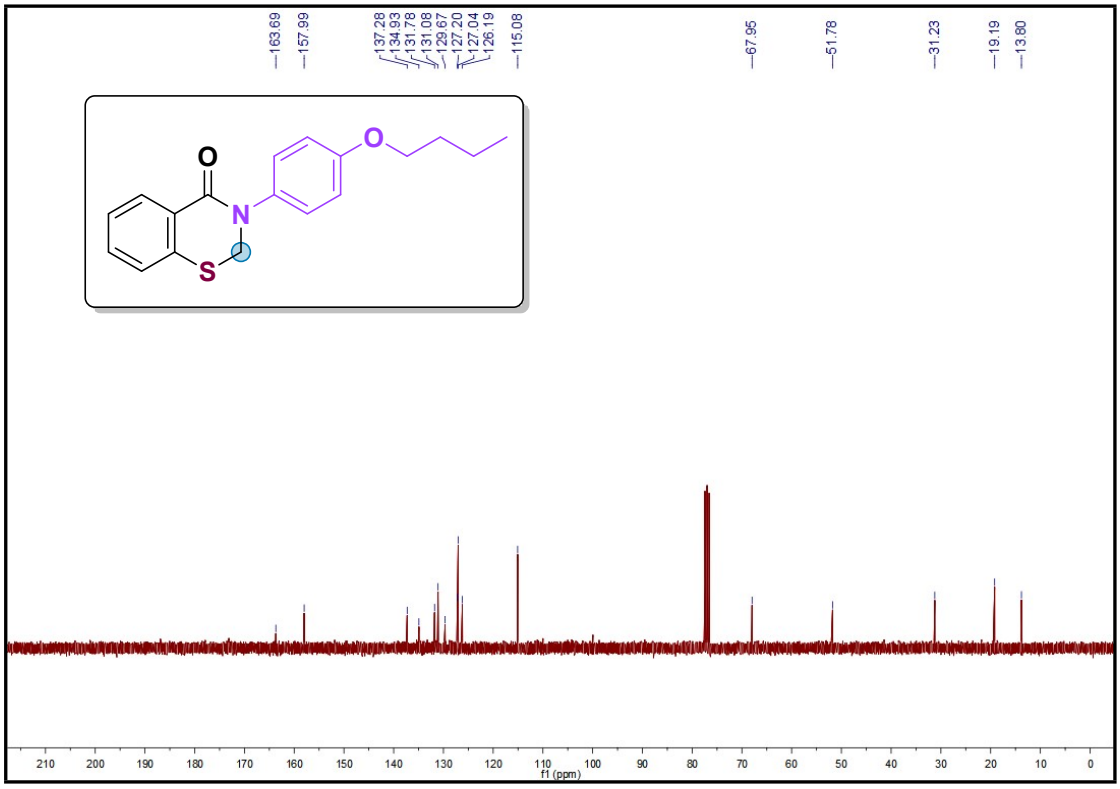
3-(4-methoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3q)



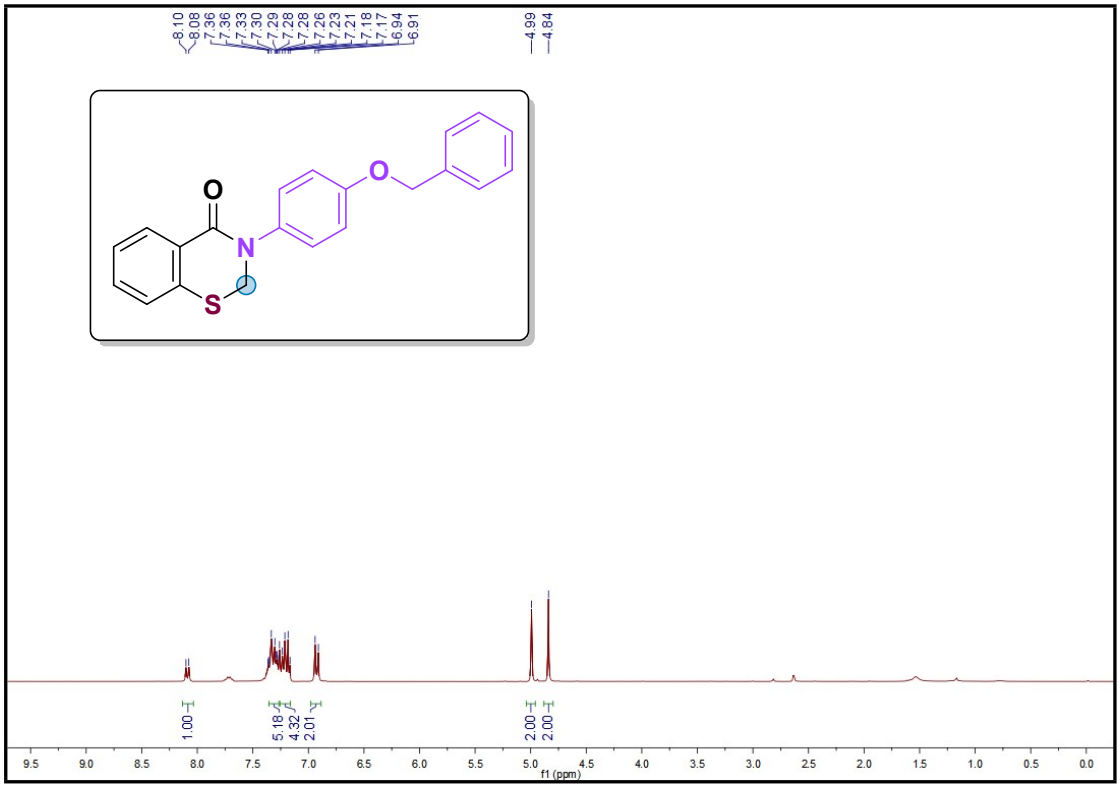


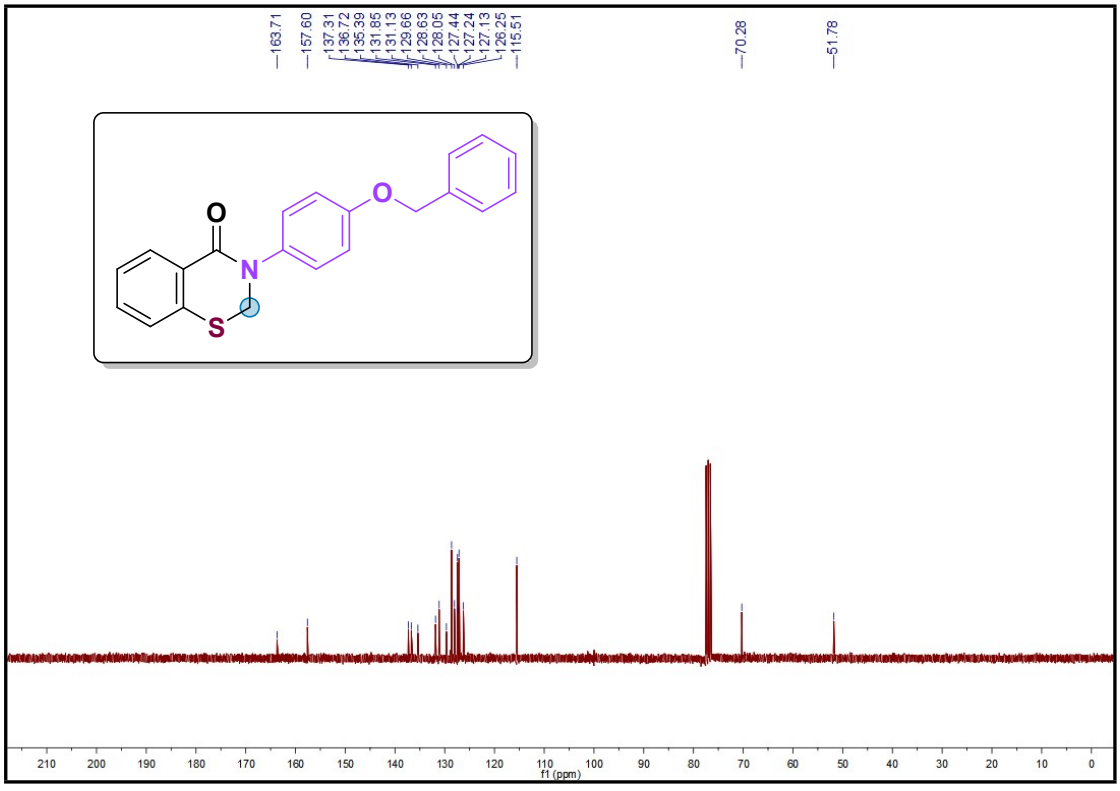
3-(4-butoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3r)



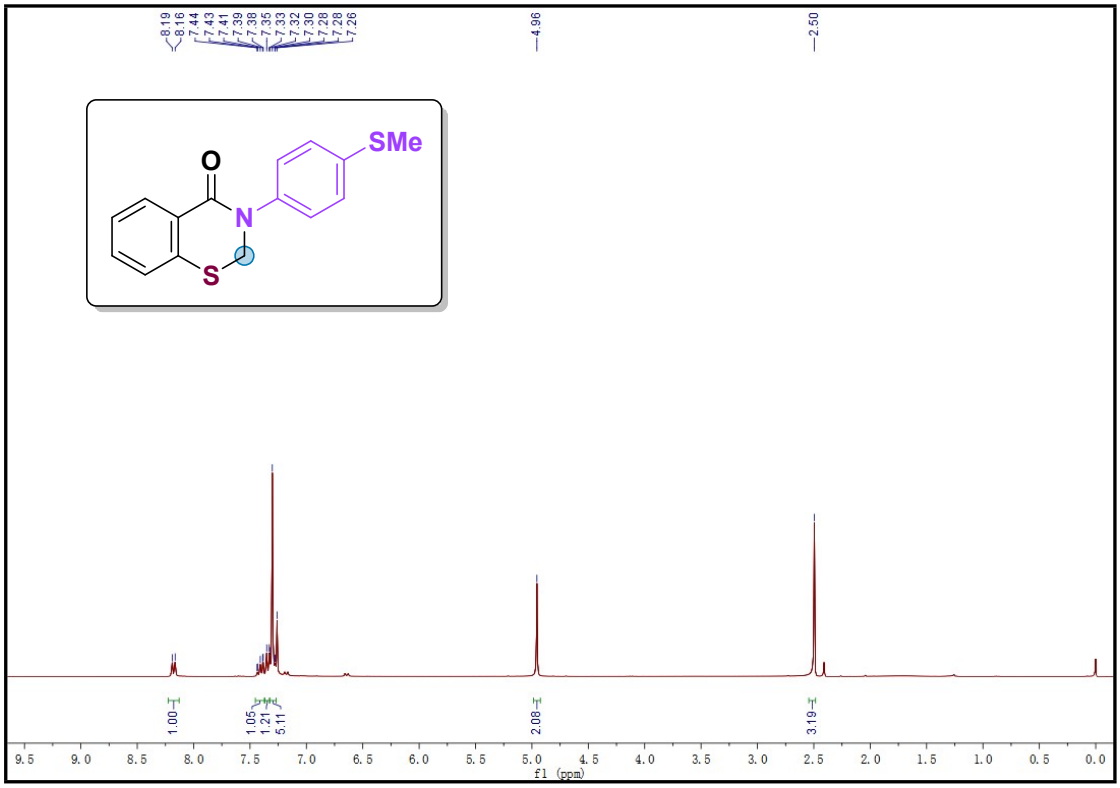


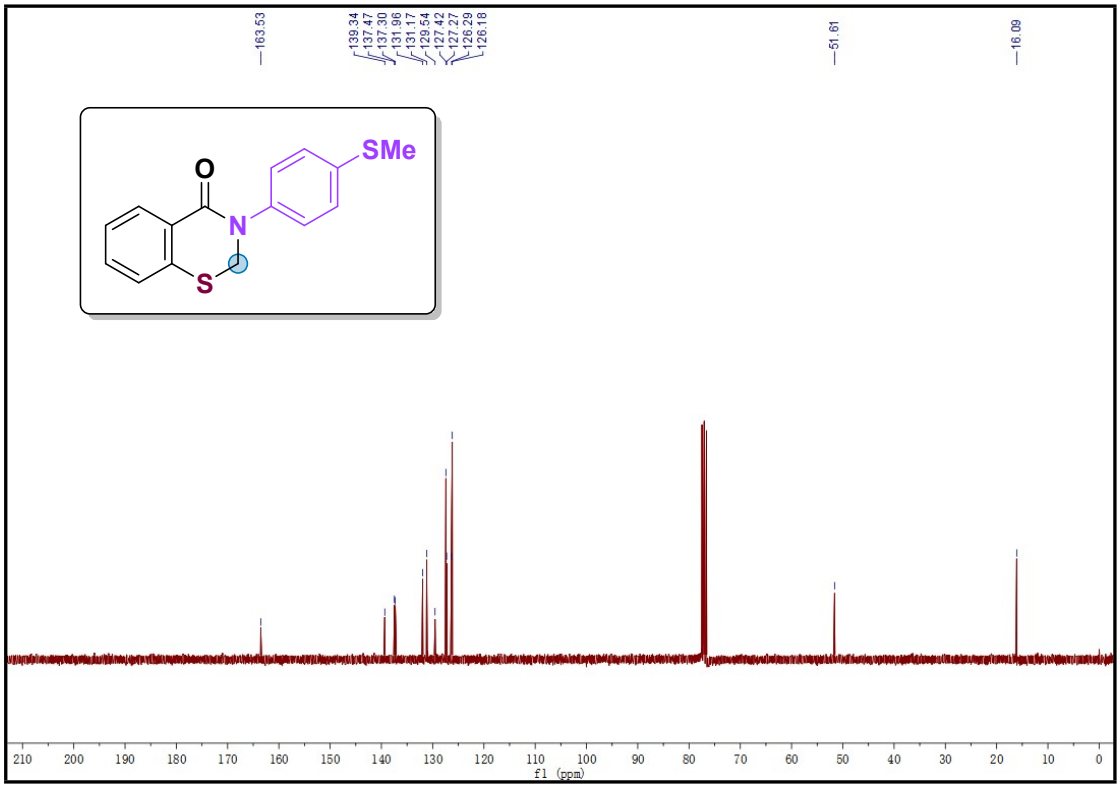
3-(4-(benzyloxy)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3s)



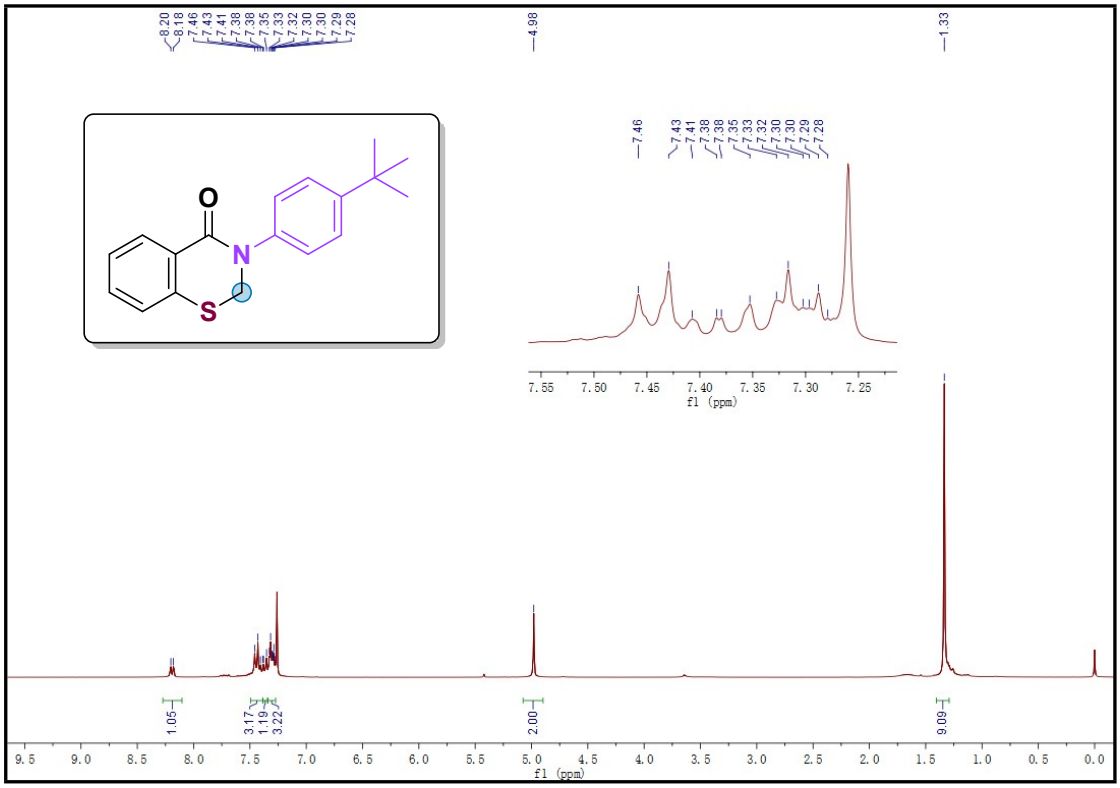


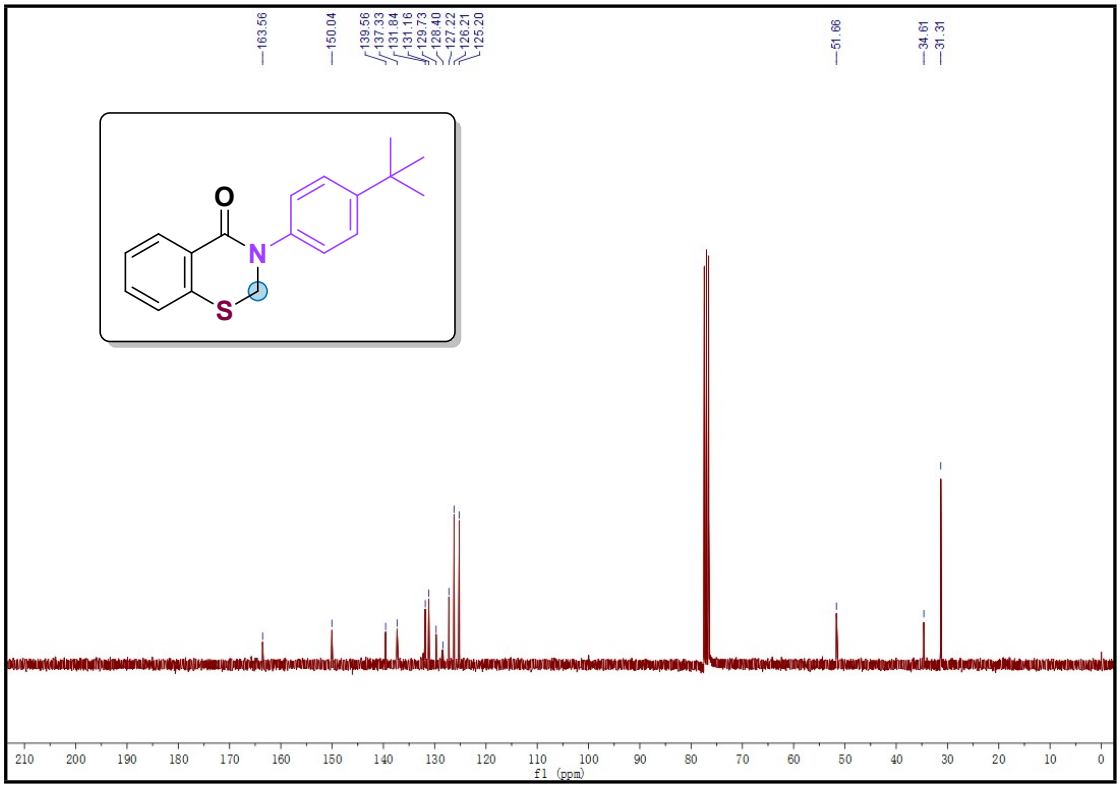
3-(4-(methylthio)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3t)



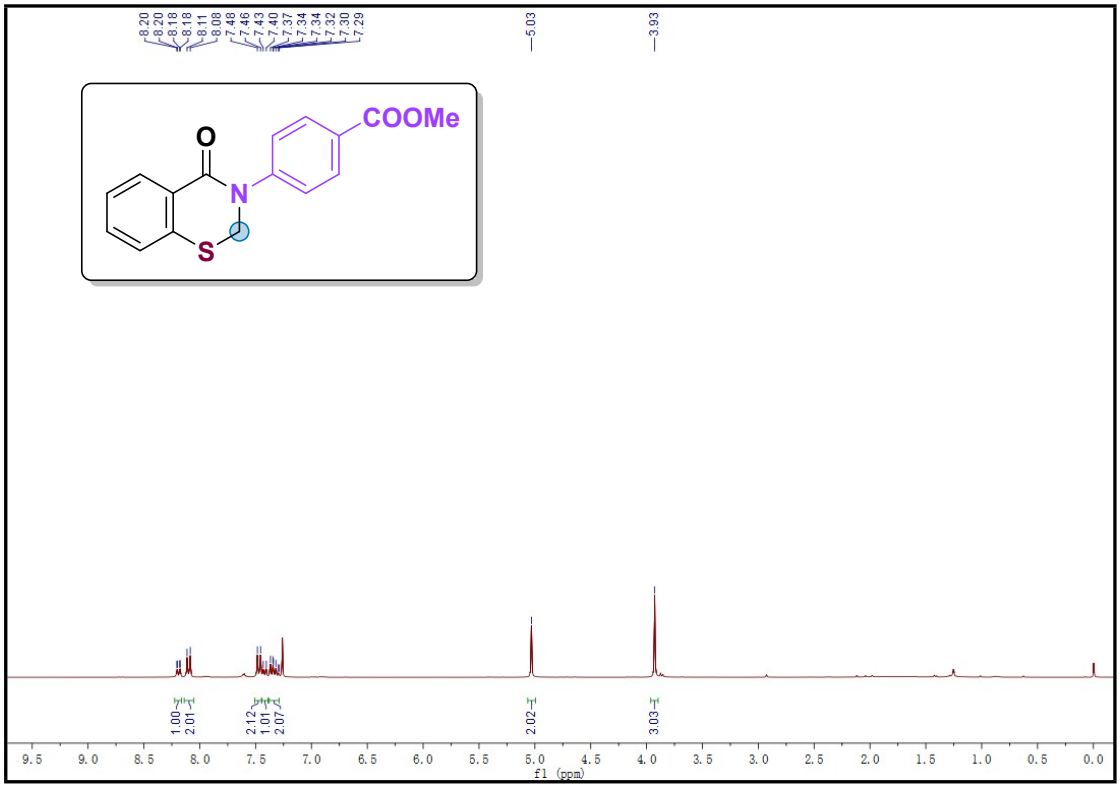


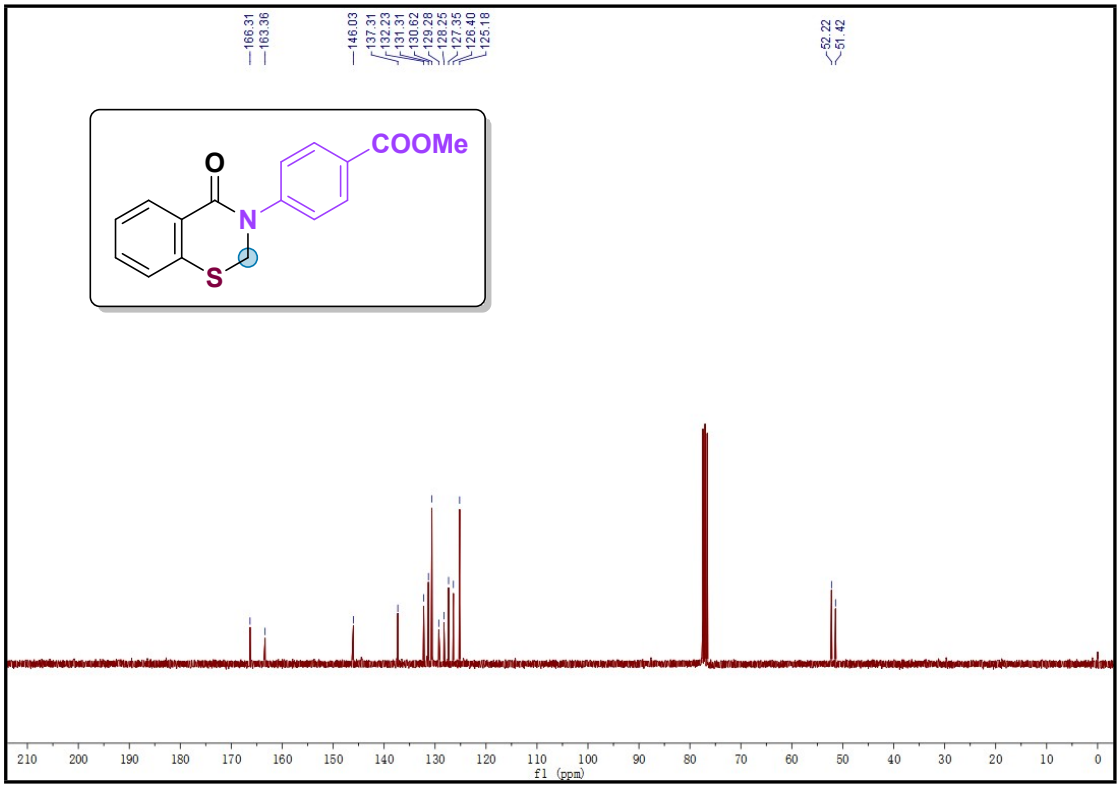
3-(4-(tert-butyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3u)



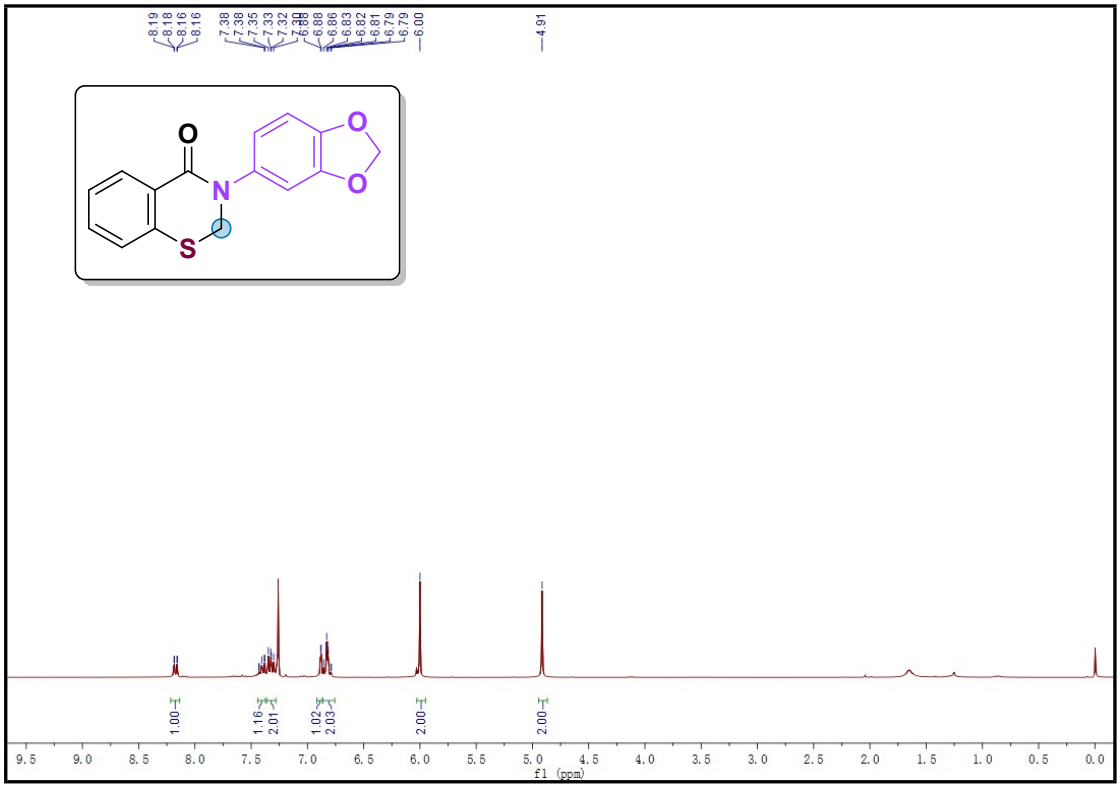


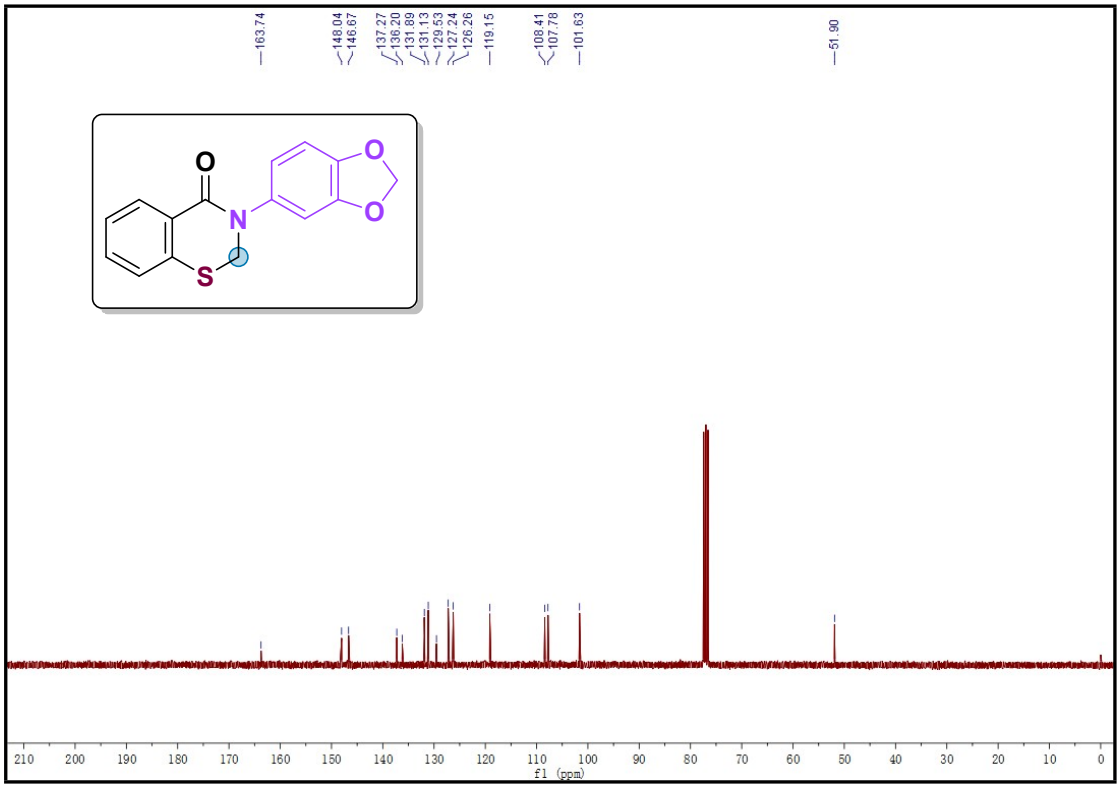
methyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)benzoate (3v)



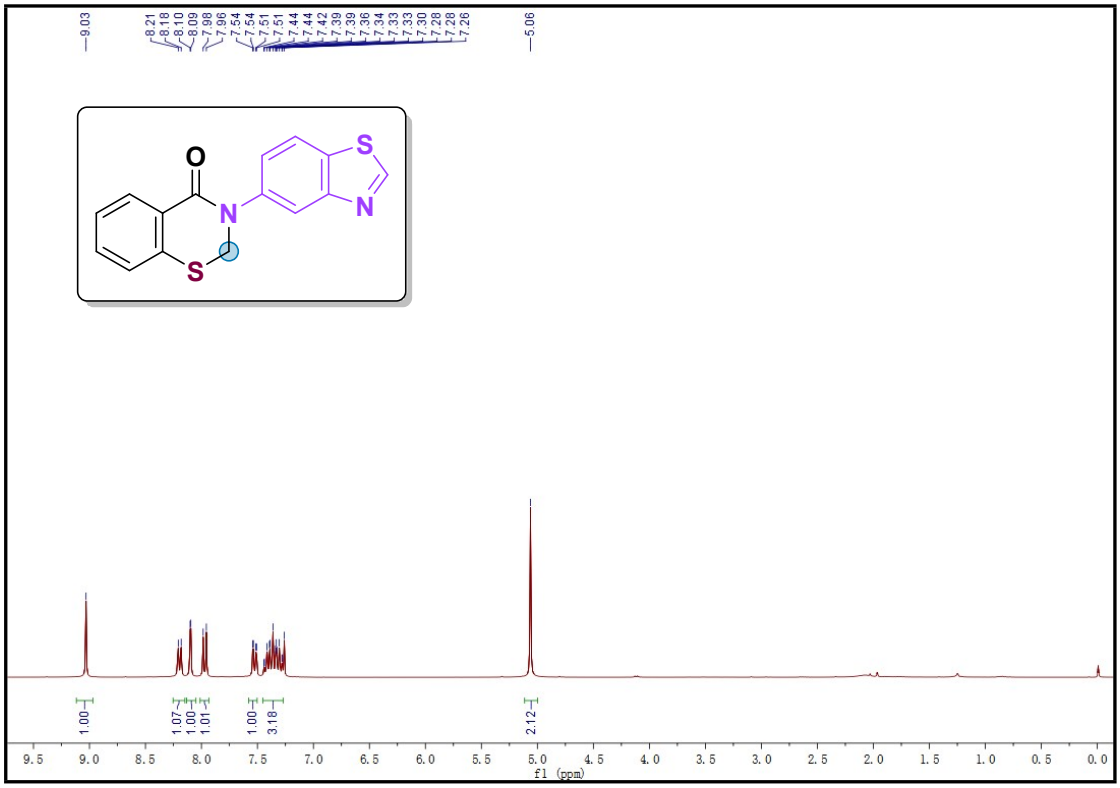


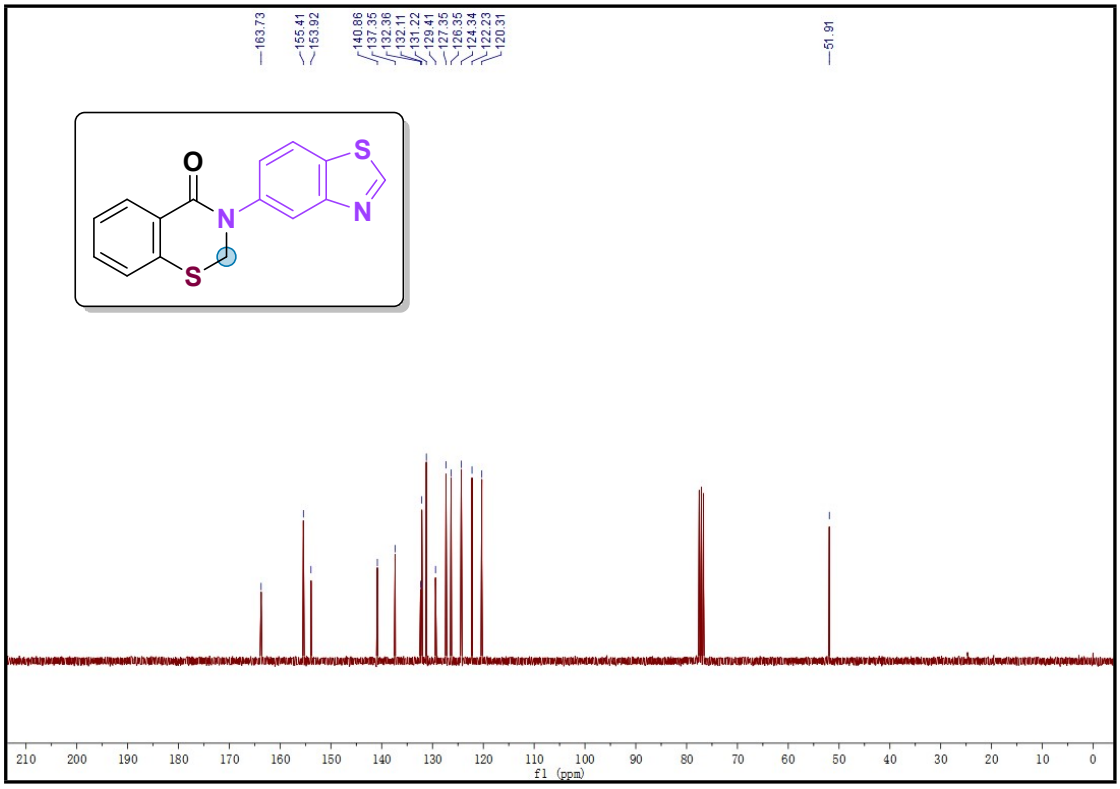
3-(benzo[d][1,3]dioxol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3w)



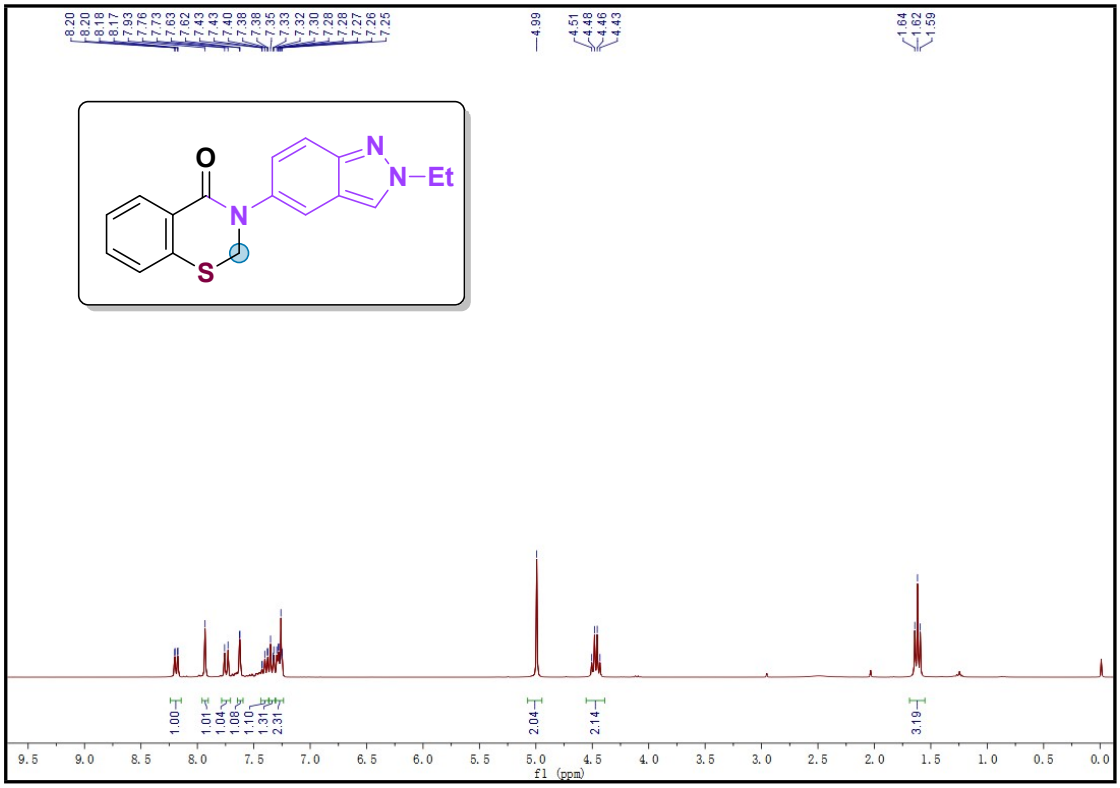


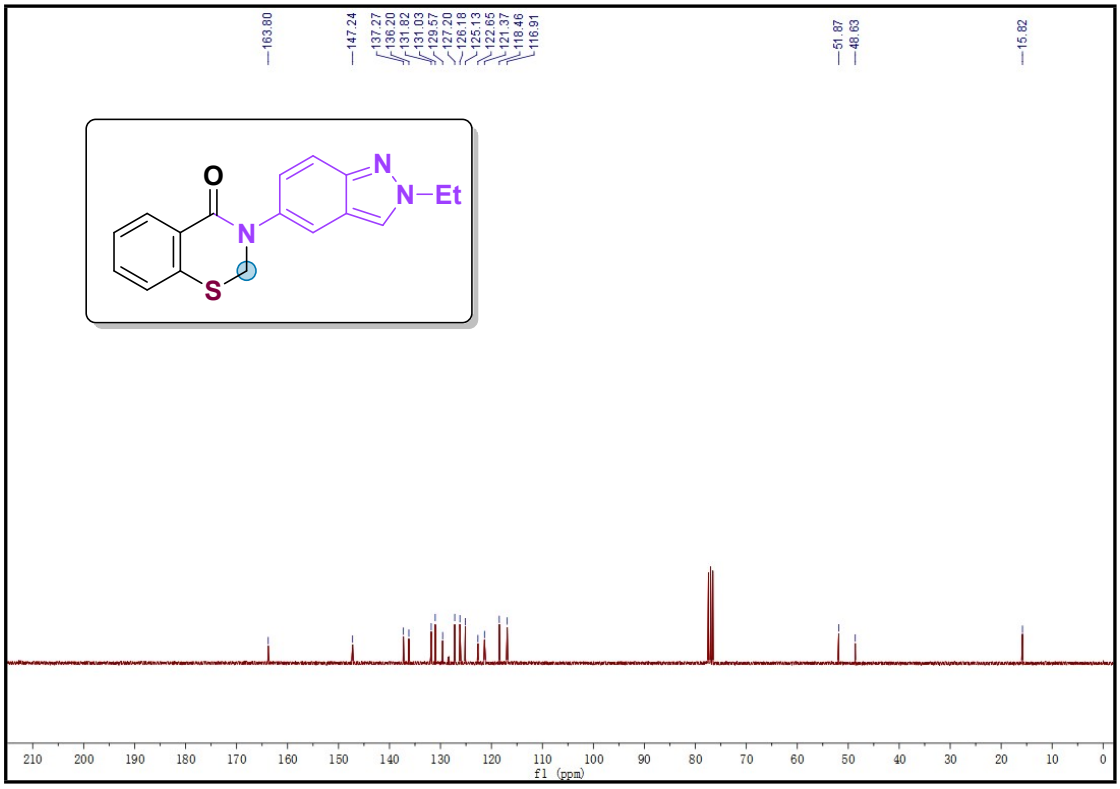
3-(benzo[d]thiazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3x)



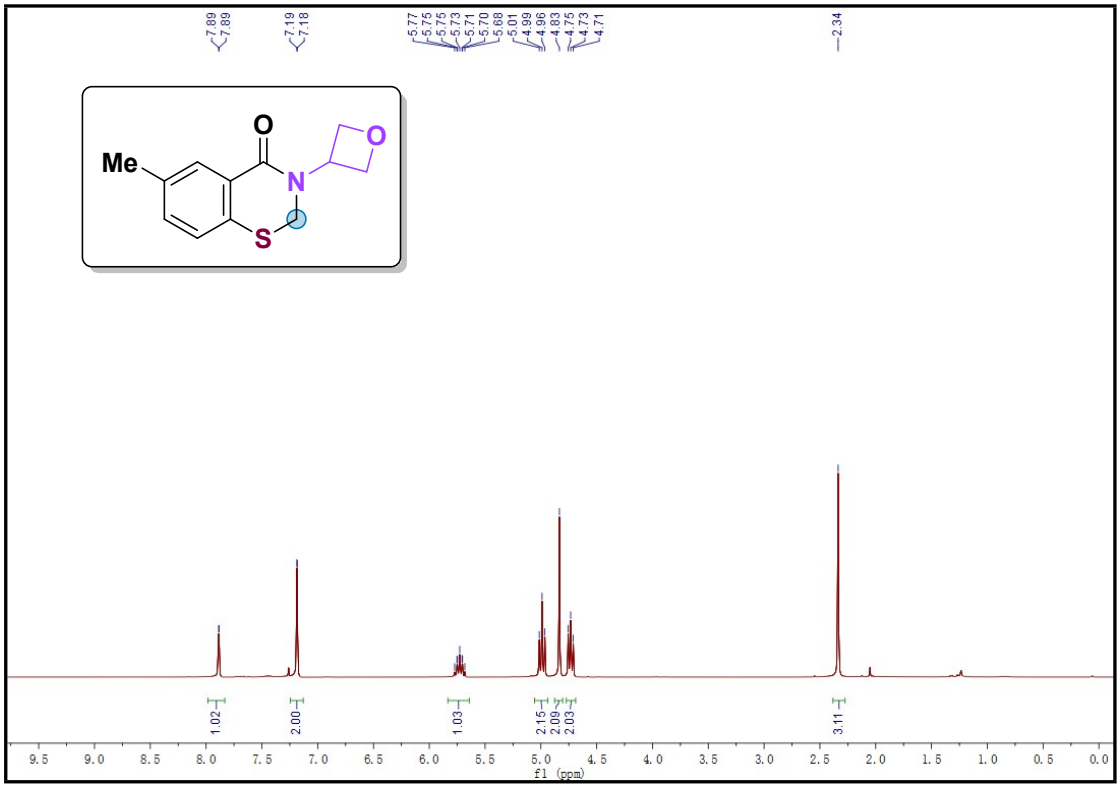


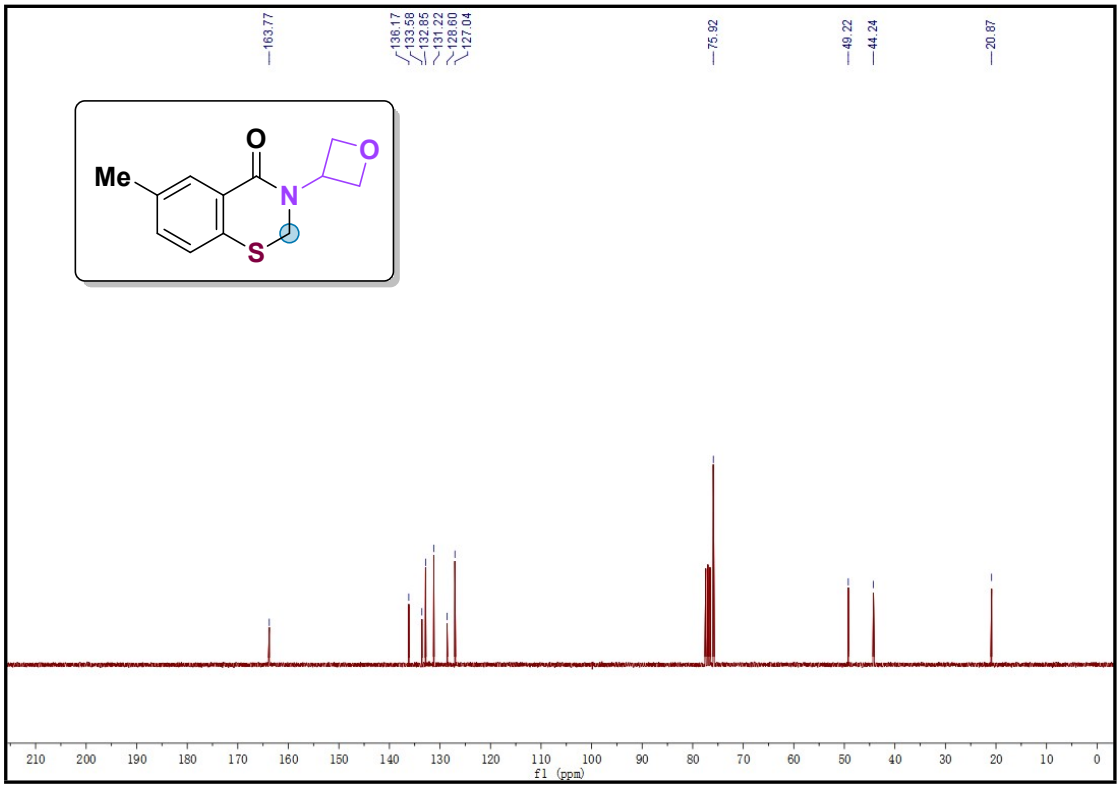
3-(2-ethyl-2H-indazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3y)



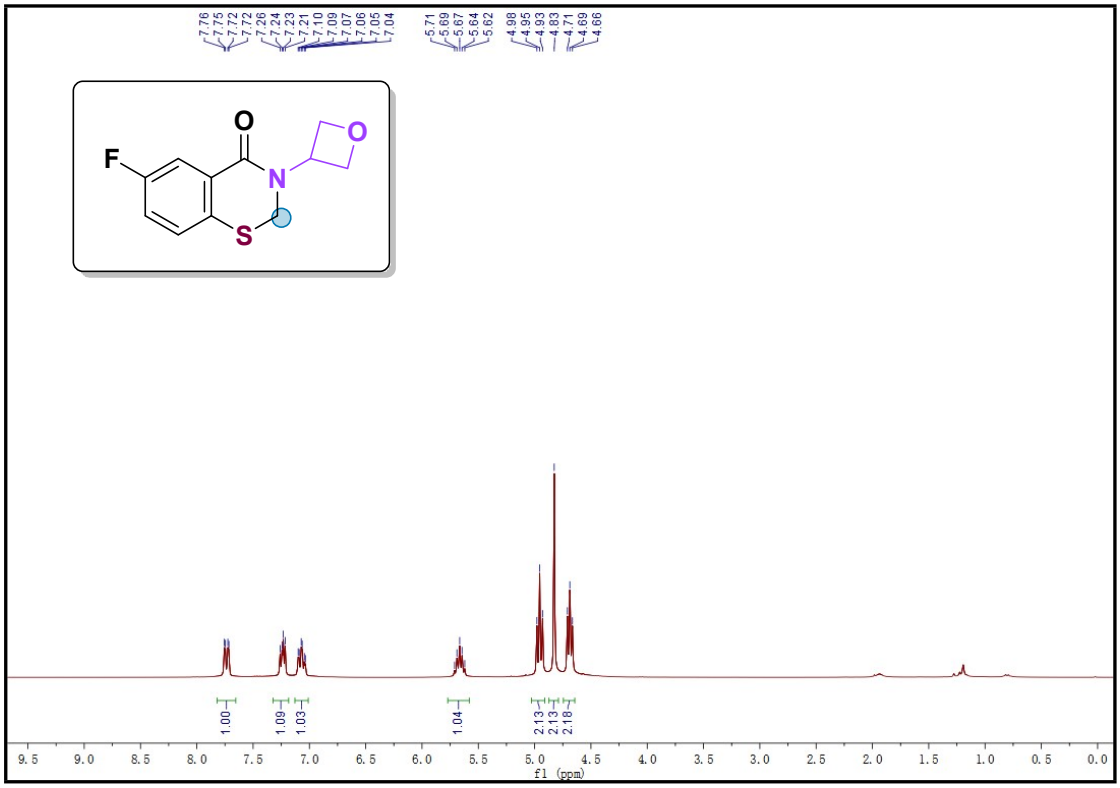


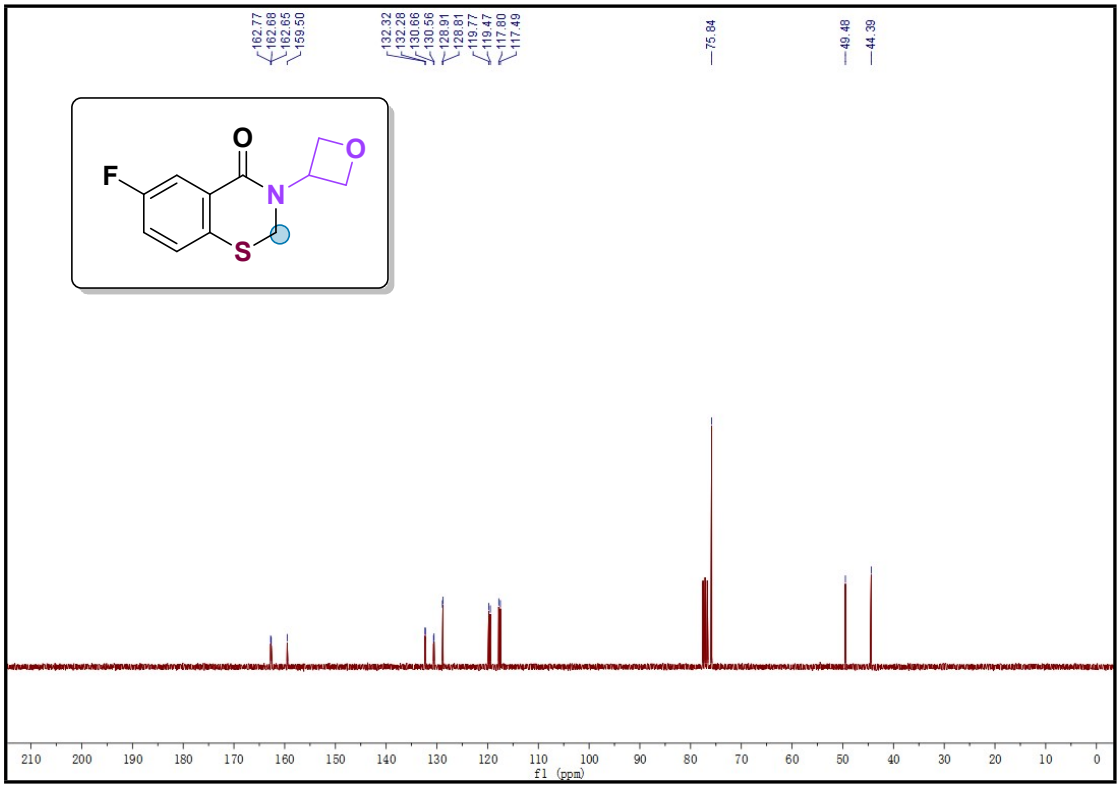
6-methyl-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3aa)



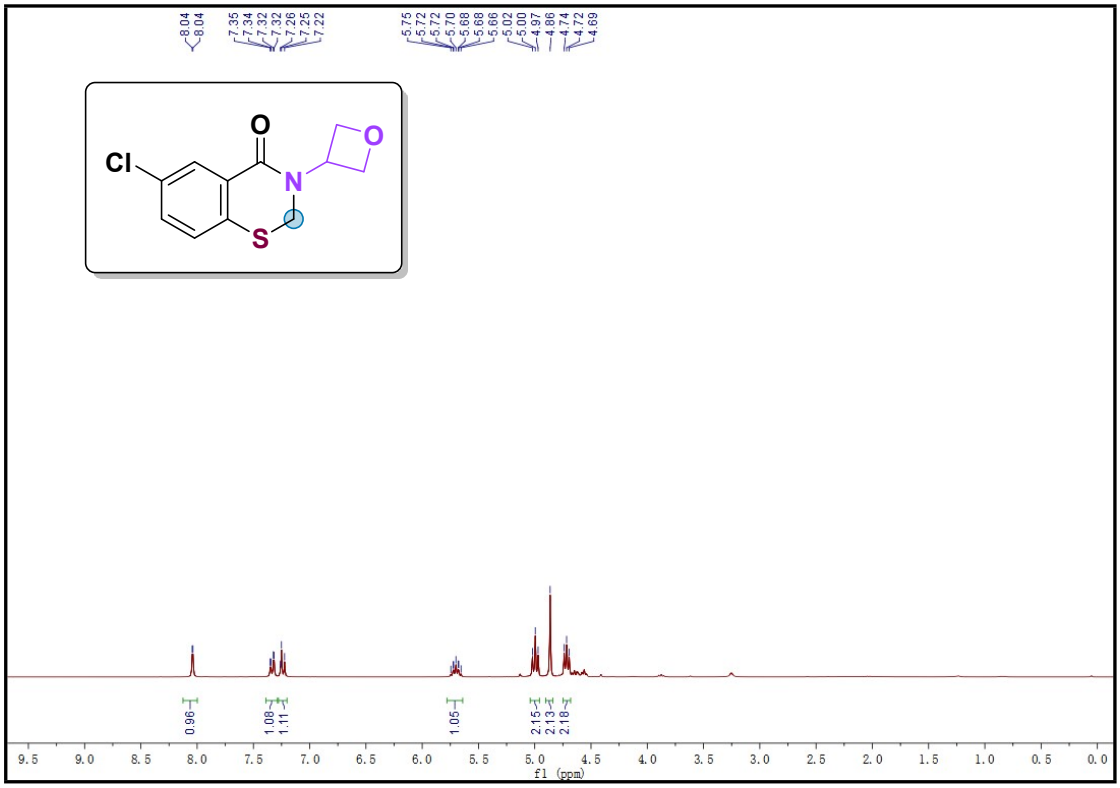


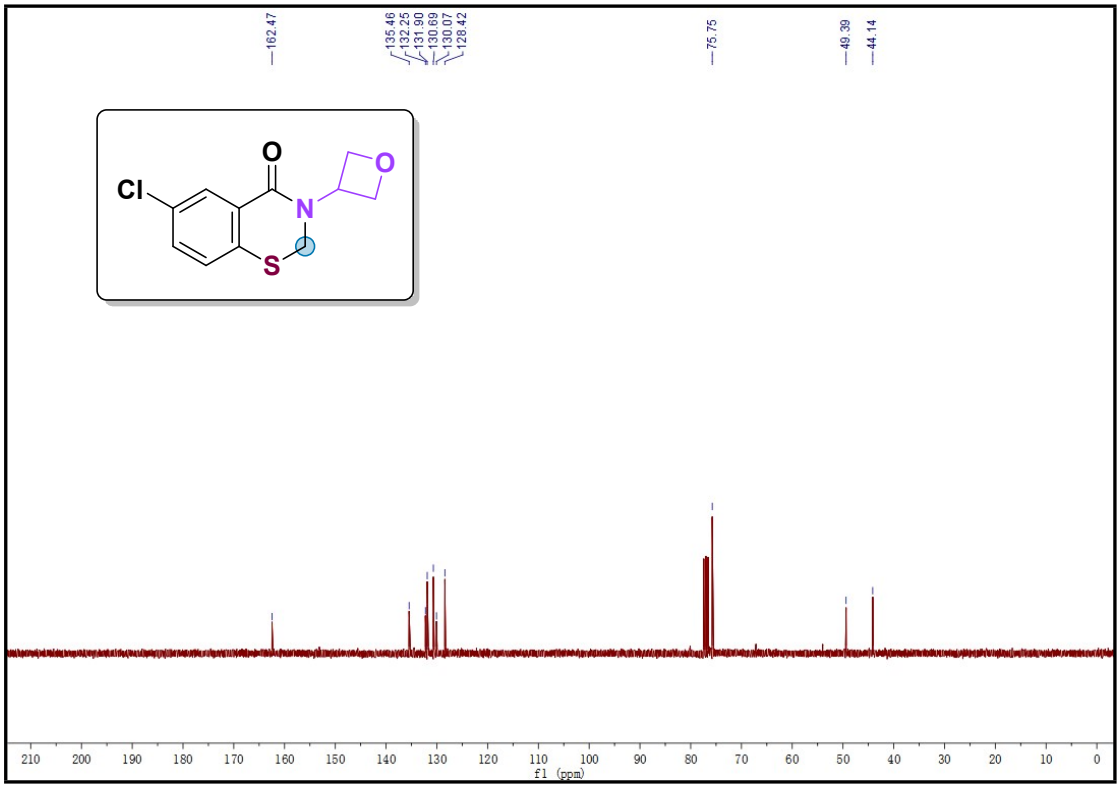
6-fluoro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3ba)



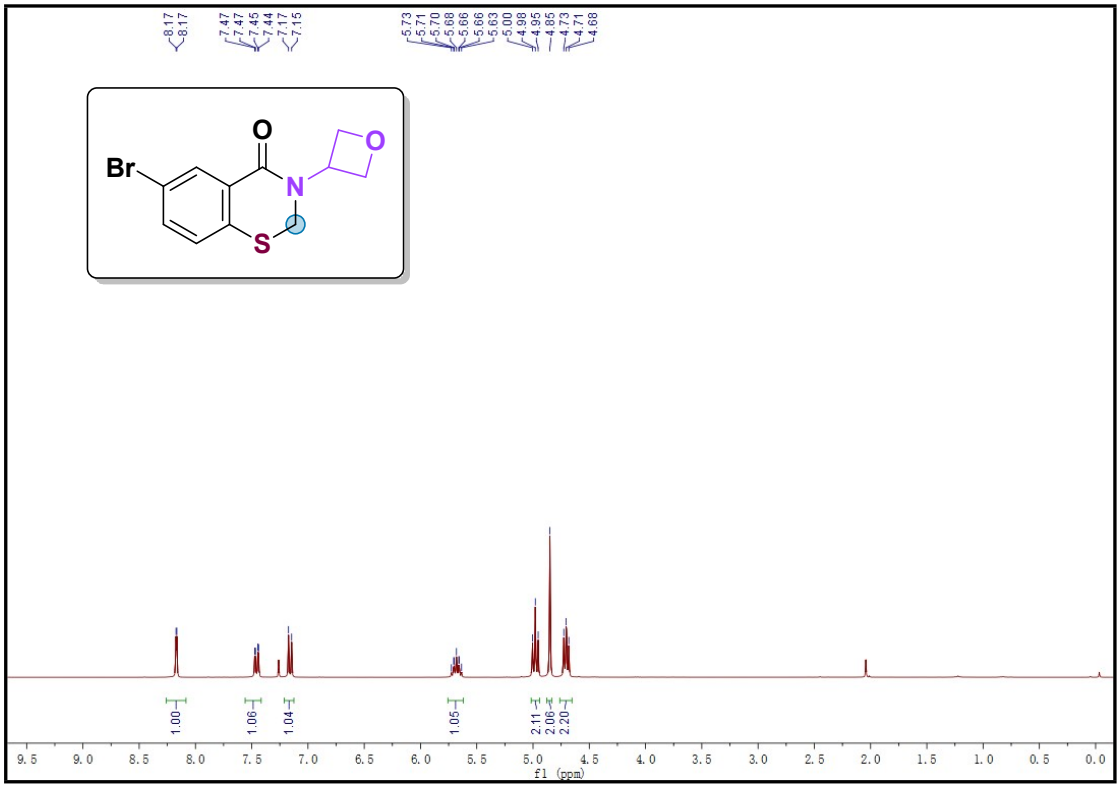


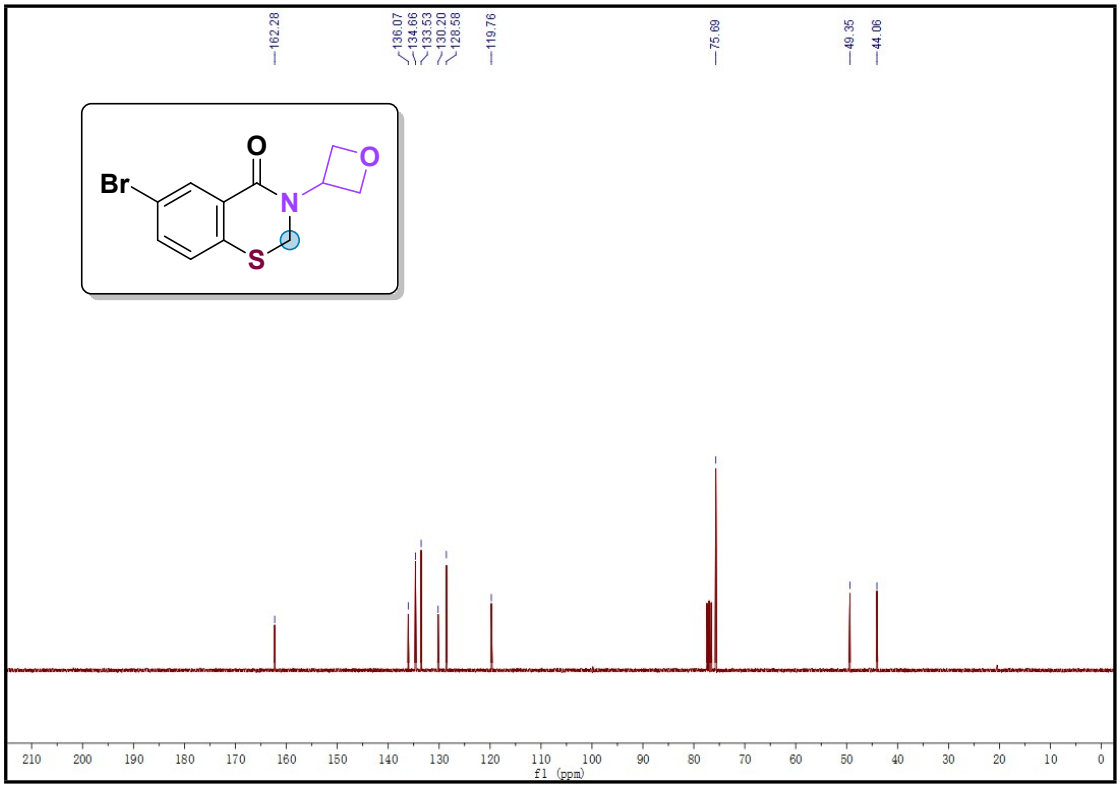
6-chloro-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3ca)



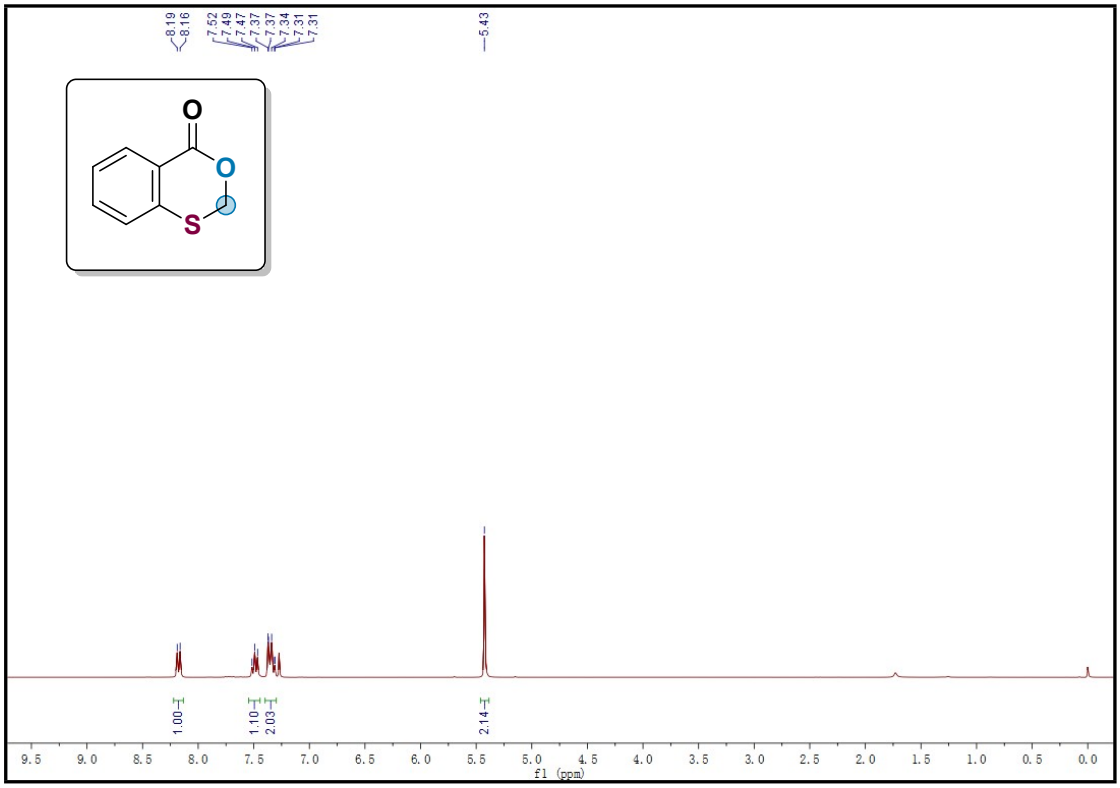


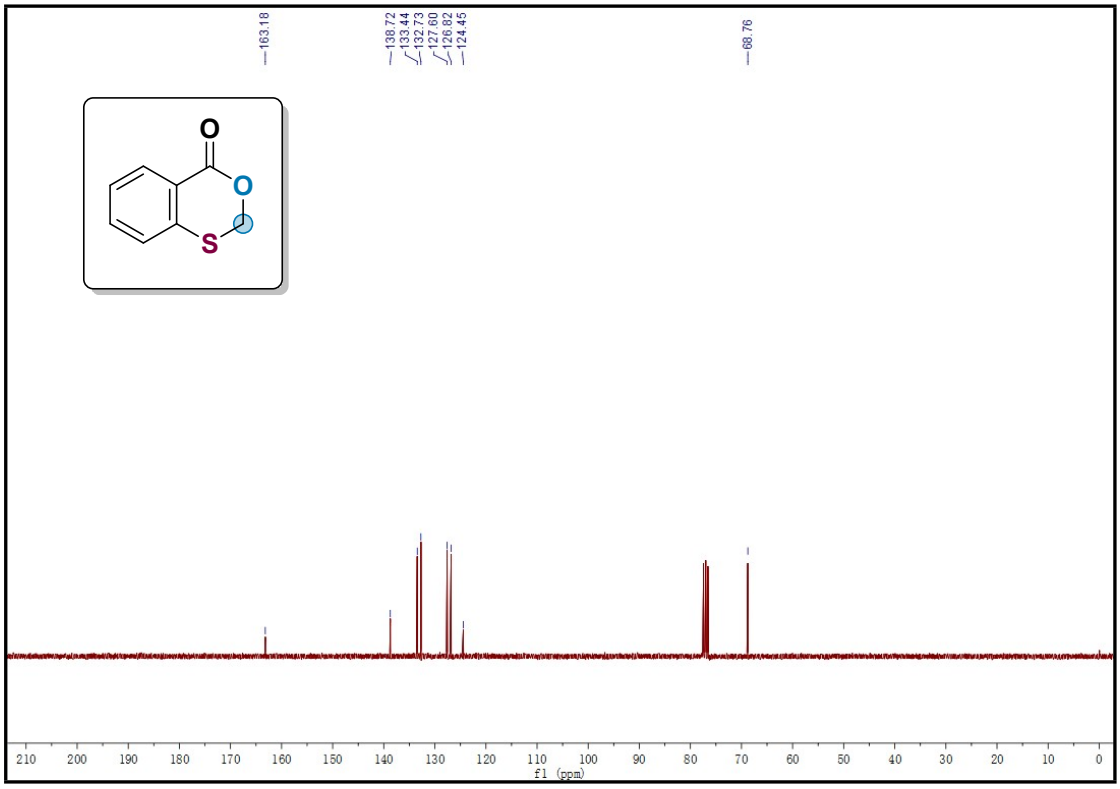
6-bromo-3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (3da)



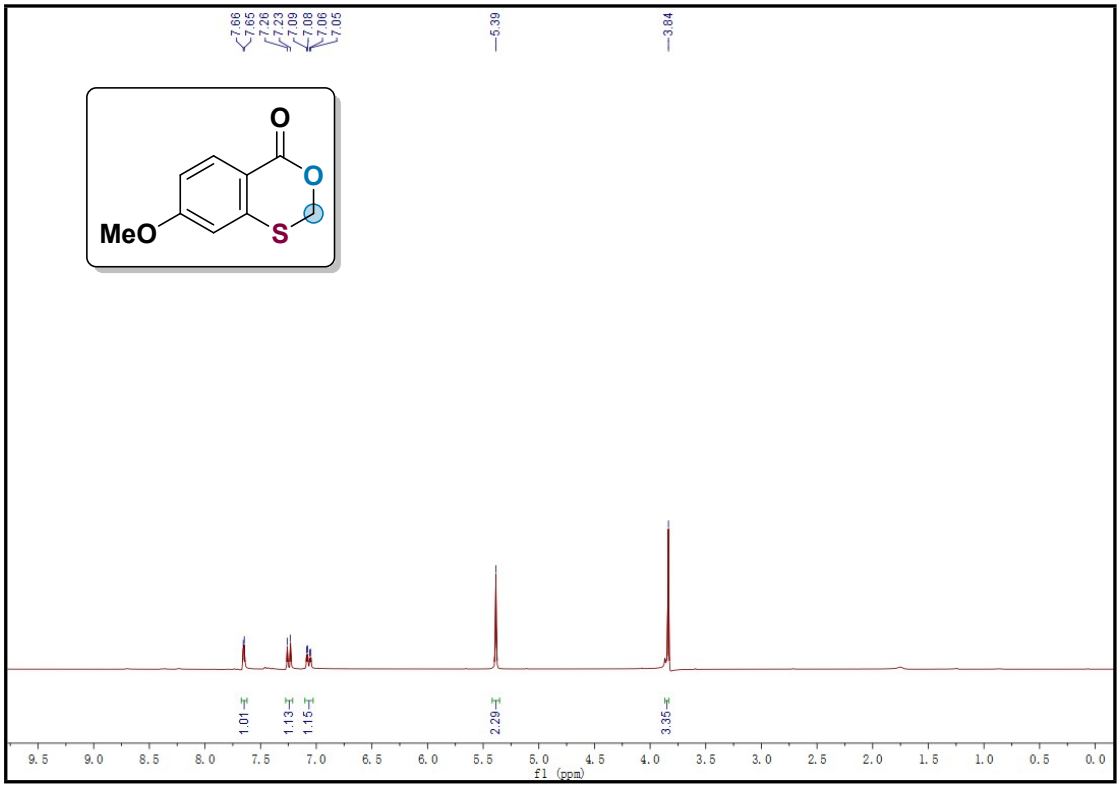


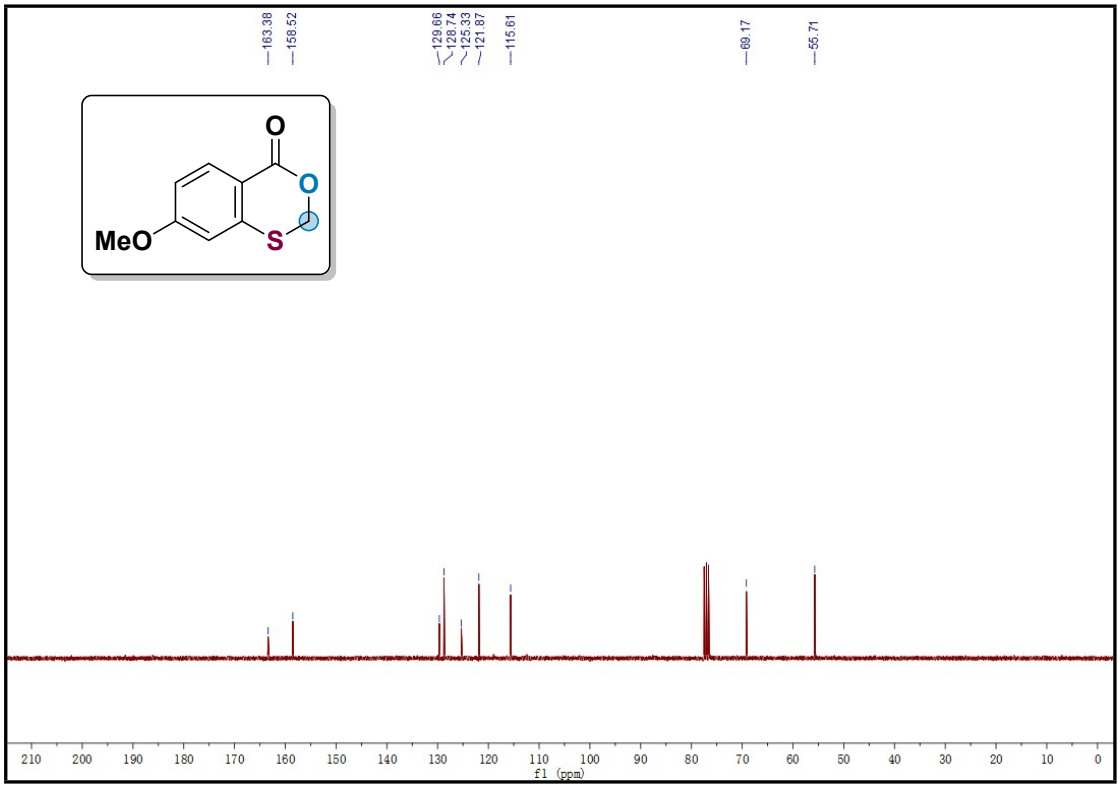
4H-benzo[d][1,3]oxathiin-4-one (4a)



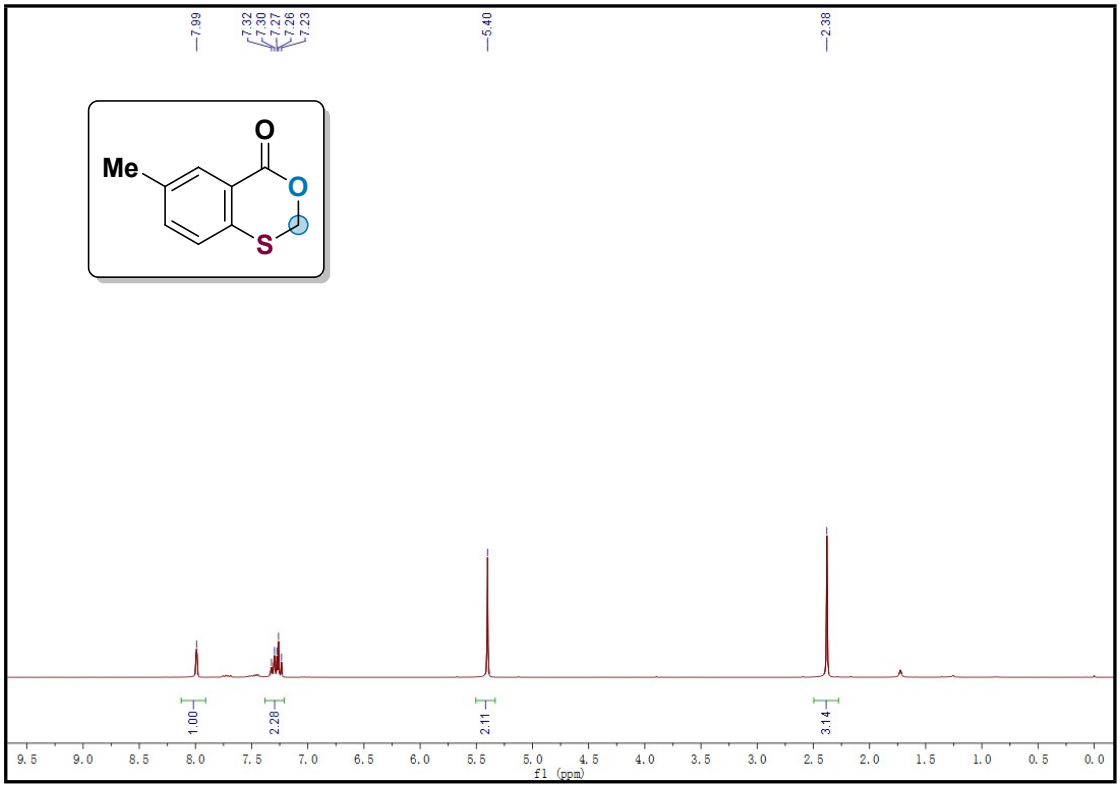


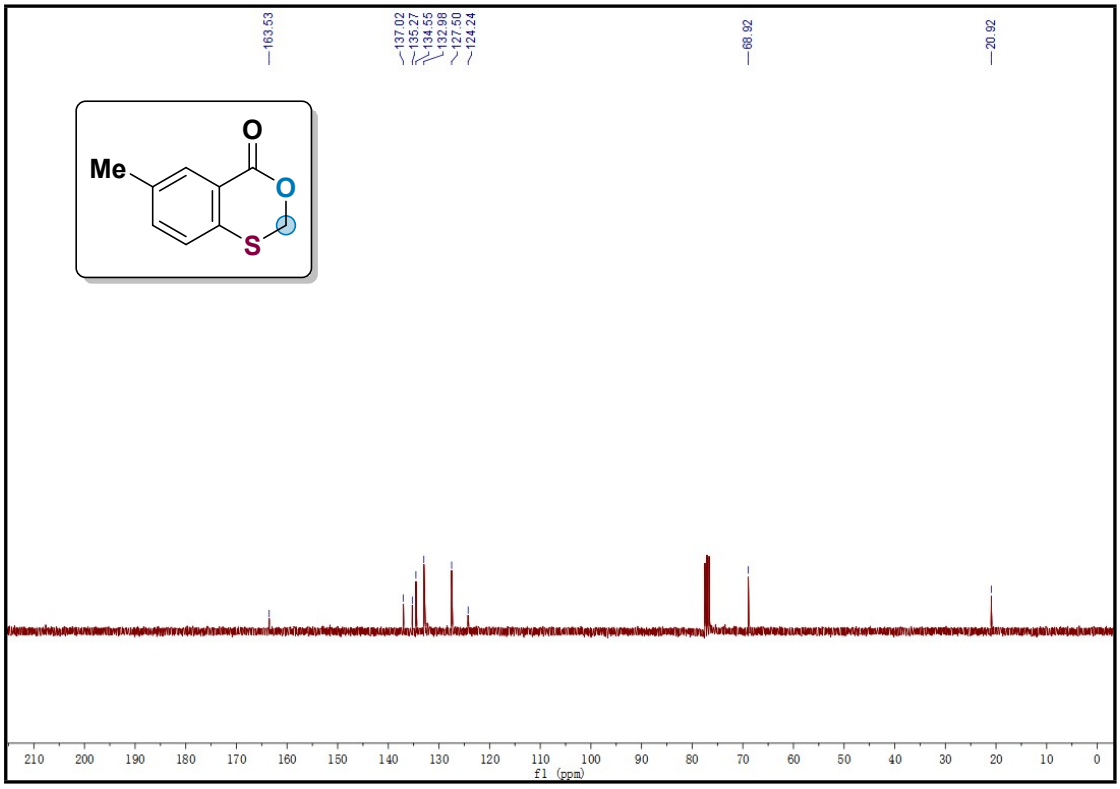
7-methoxy-4H-benzo[d][1,3]oxathiin-4-one (4b)



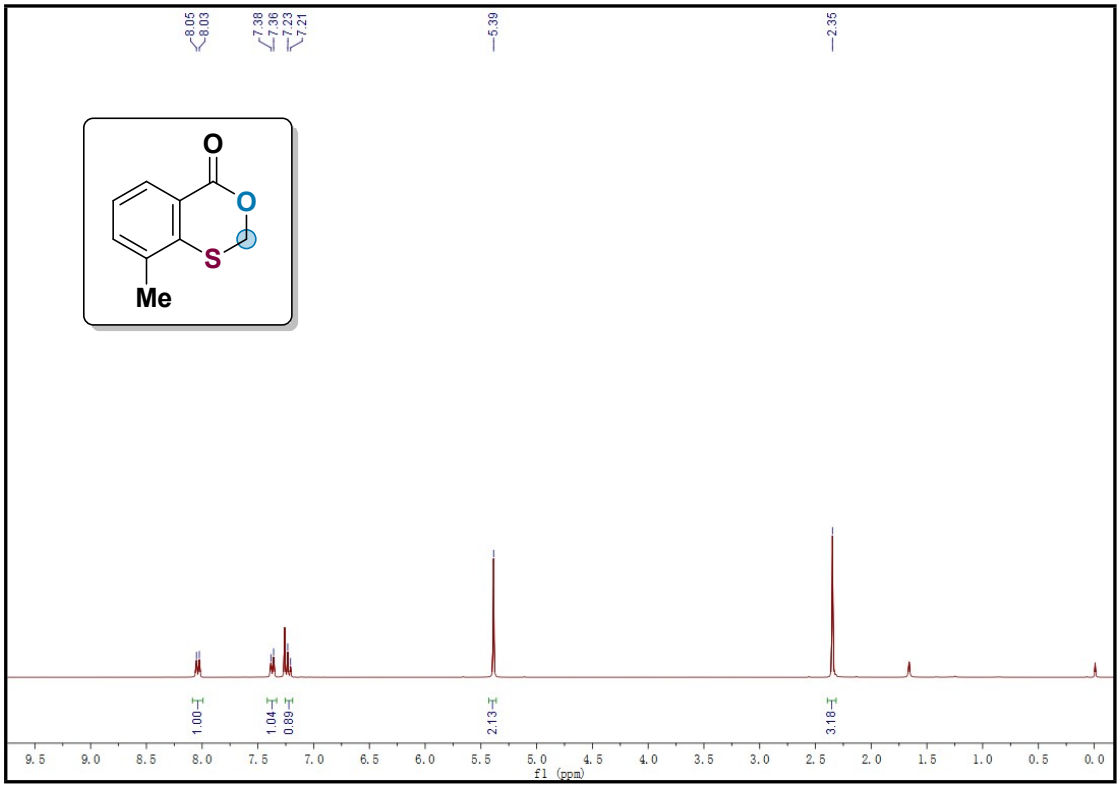


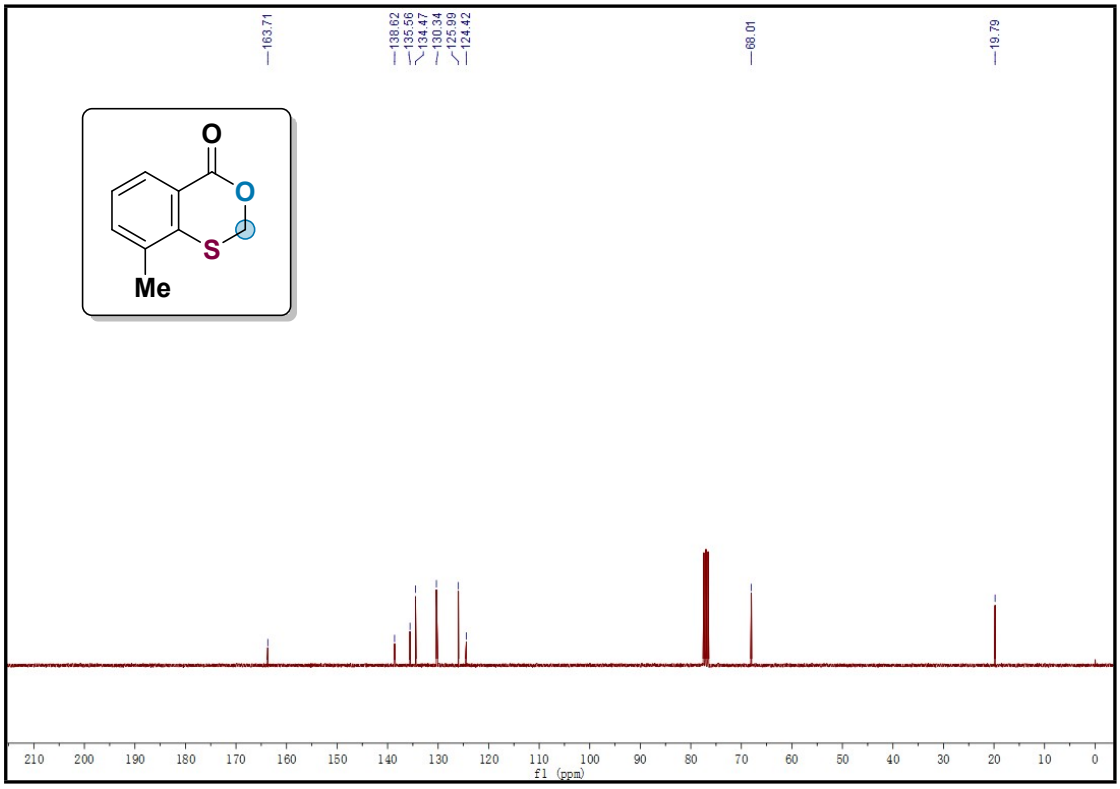
6-methyl-4H-benzo[d][1,3]oxathiin-4-one (4c)



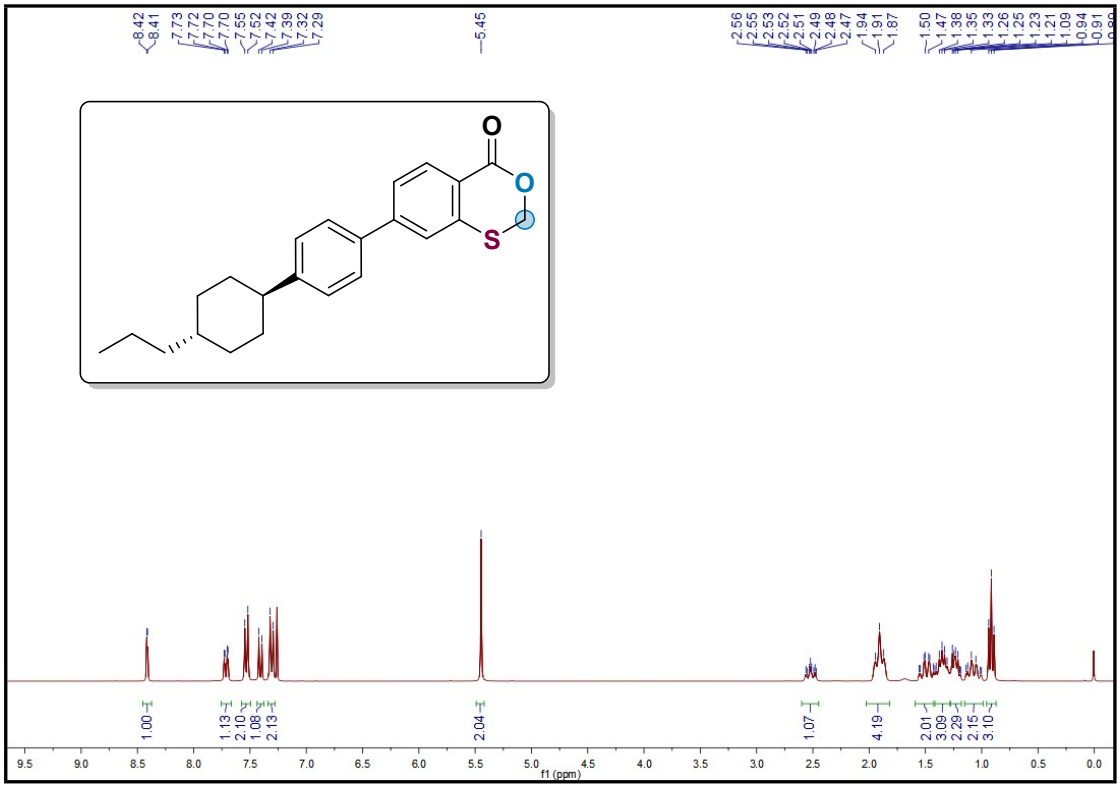


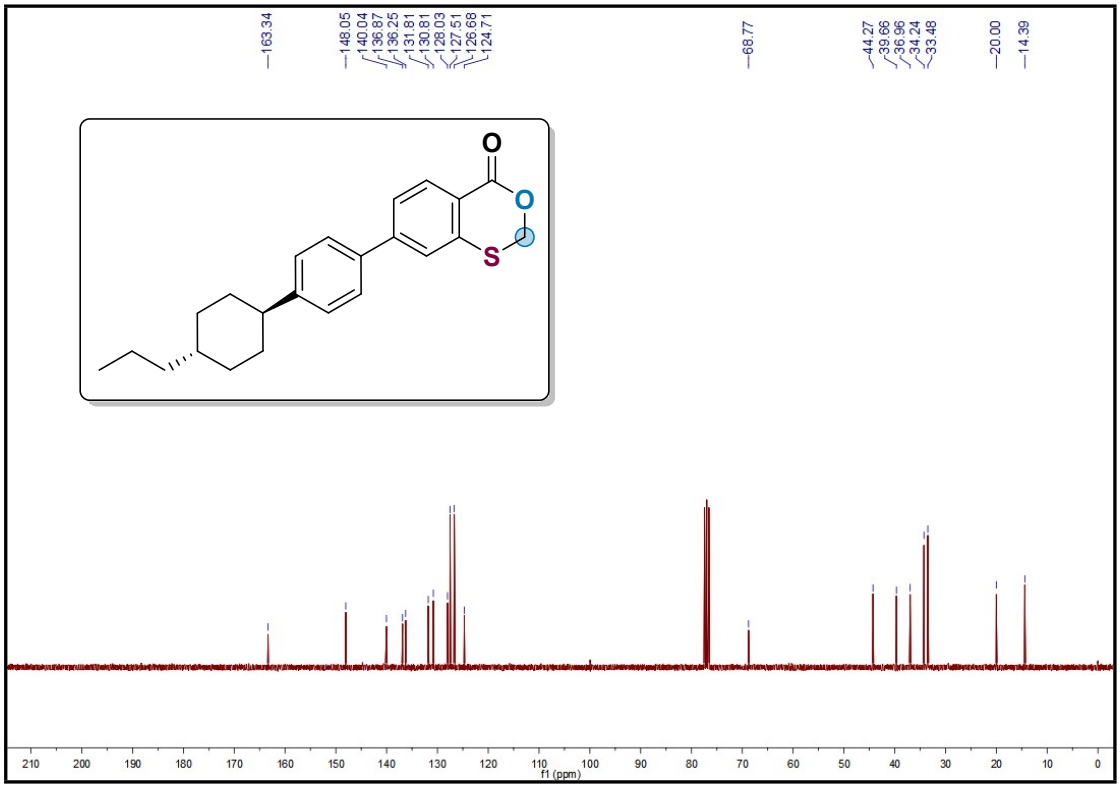
8-methyl-4H-benzo[d][1,3]oxathiin-4-one (4d)



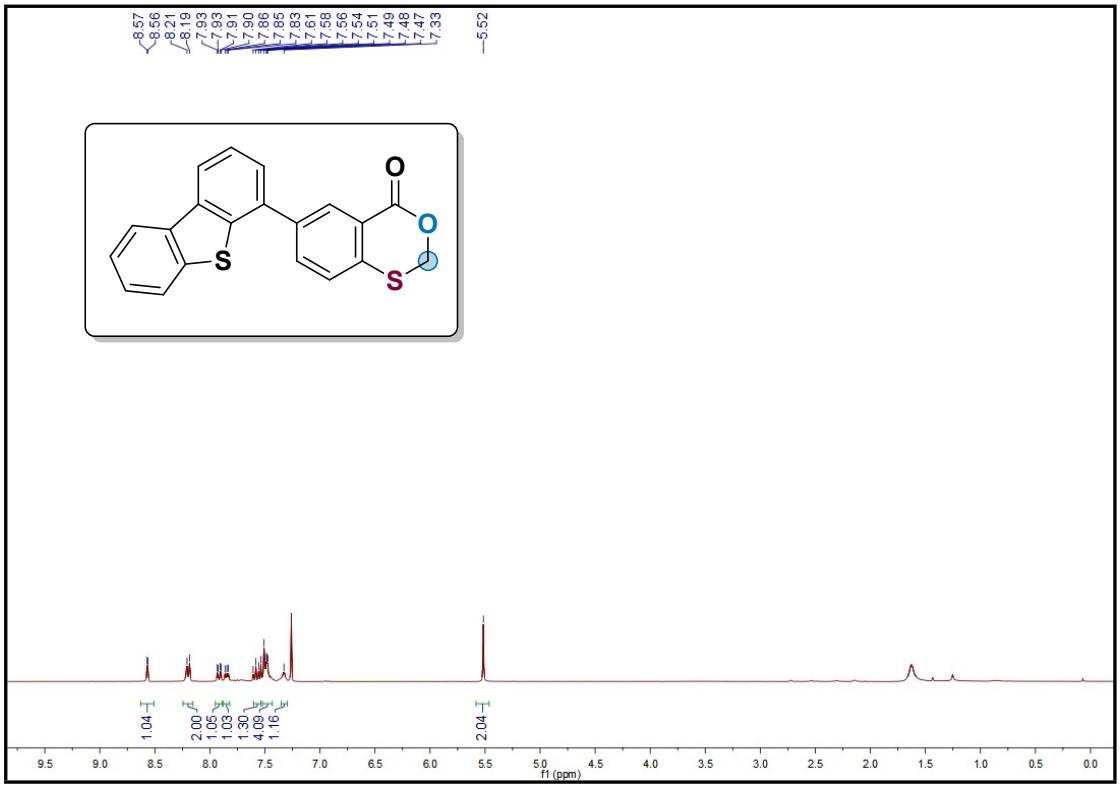


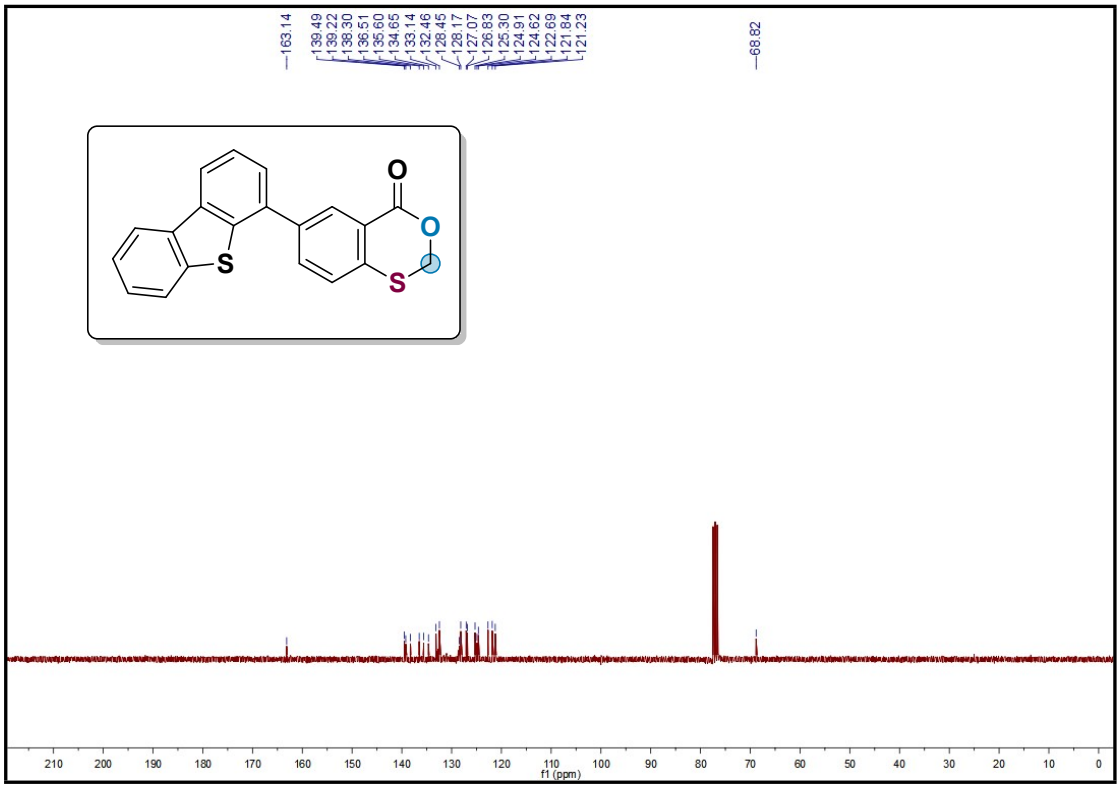
7-(4-((1s,4r)-4-propylcyclohexyl)phenyl)-4H-benzo[d][1,3]oxathiin-4-one (4e)



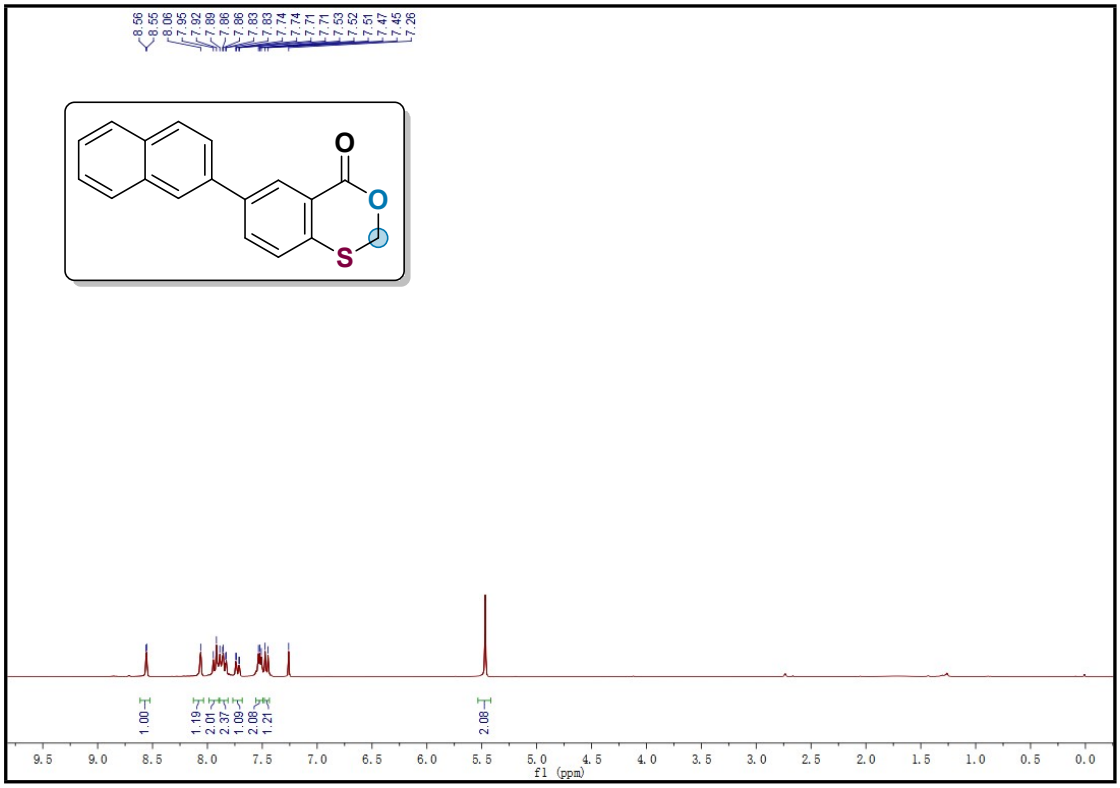


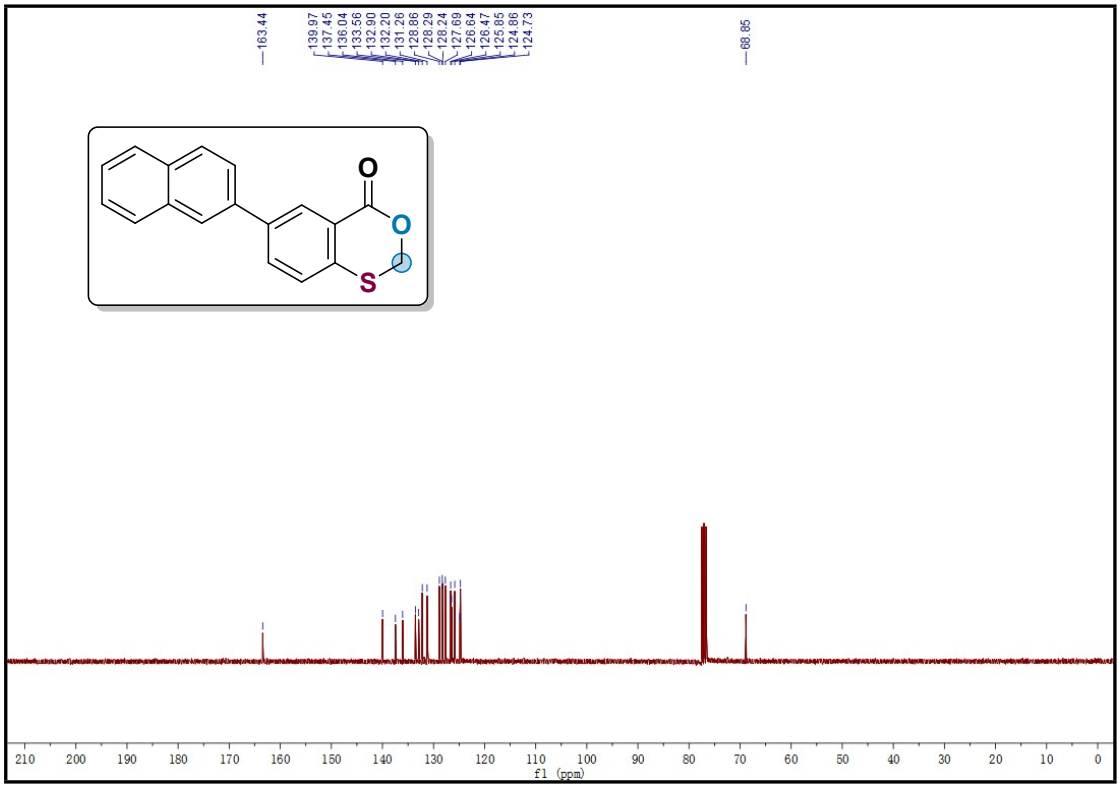
6-(dibenzo[b,d]thiophen-4-yl)-4H-benzo[d][1,3]oxathiin-4-one (4f)



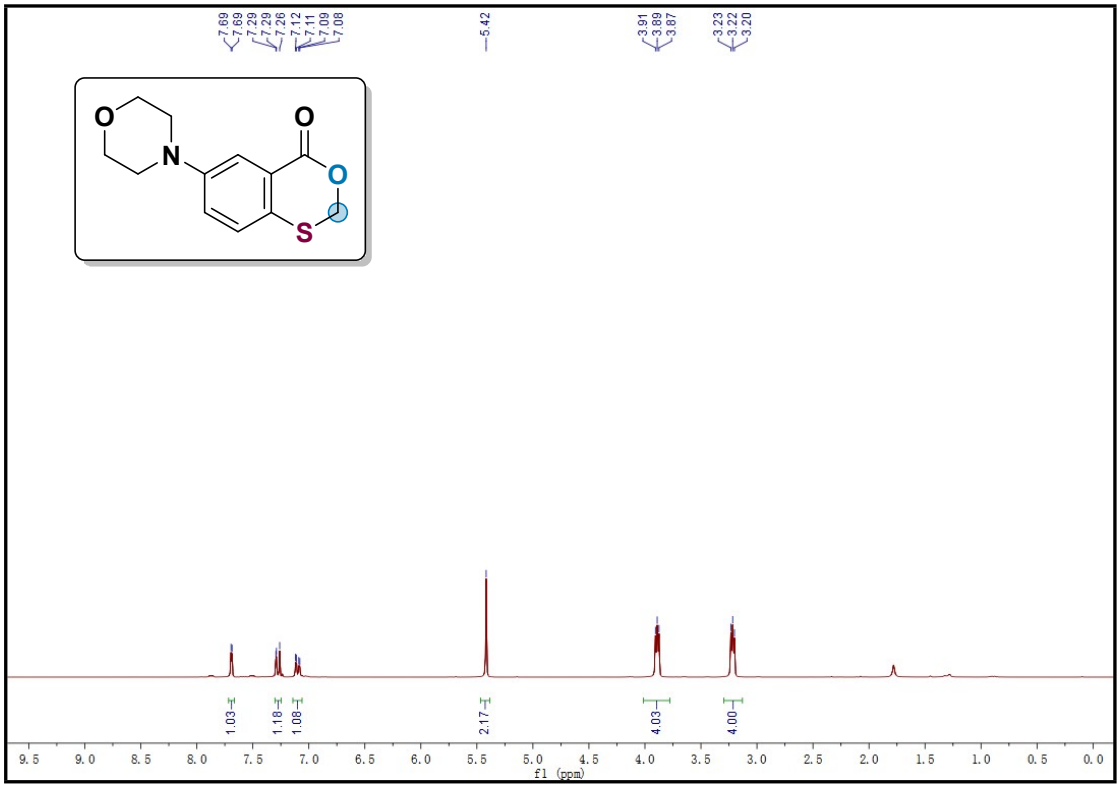


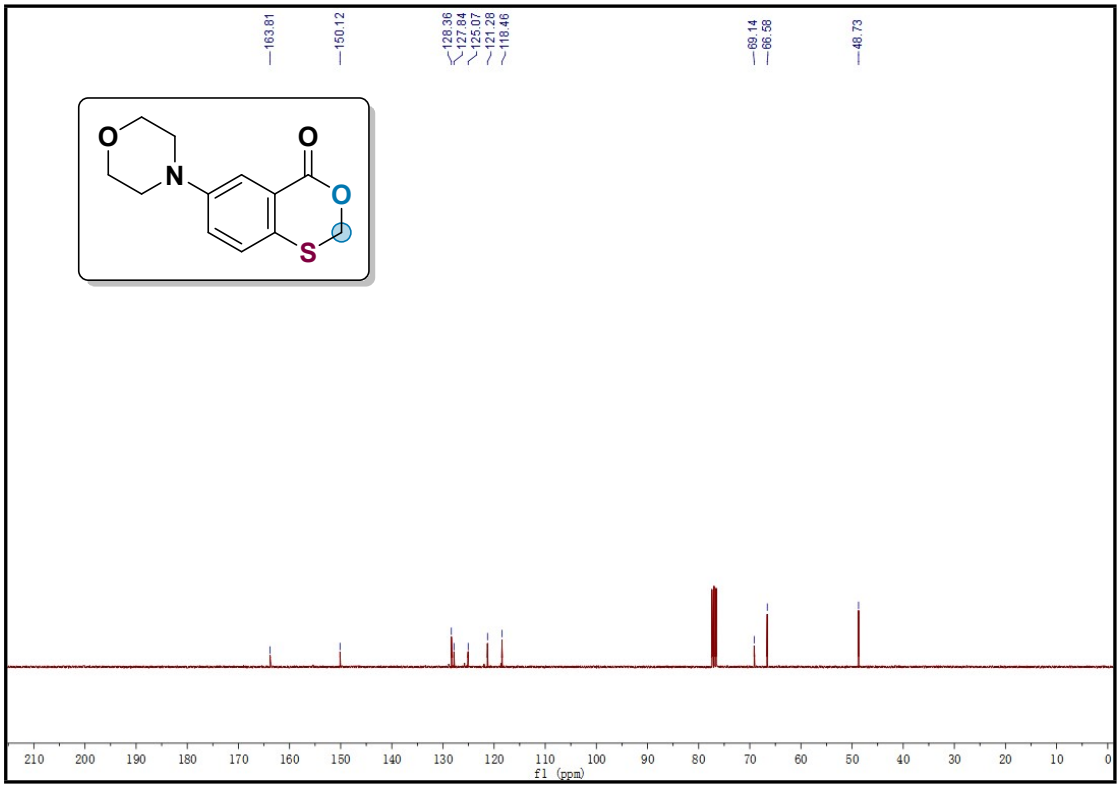
6-(naphthalen-2-yl)-4H-benzo[d][1,3]oxathiin-4-one (4g)



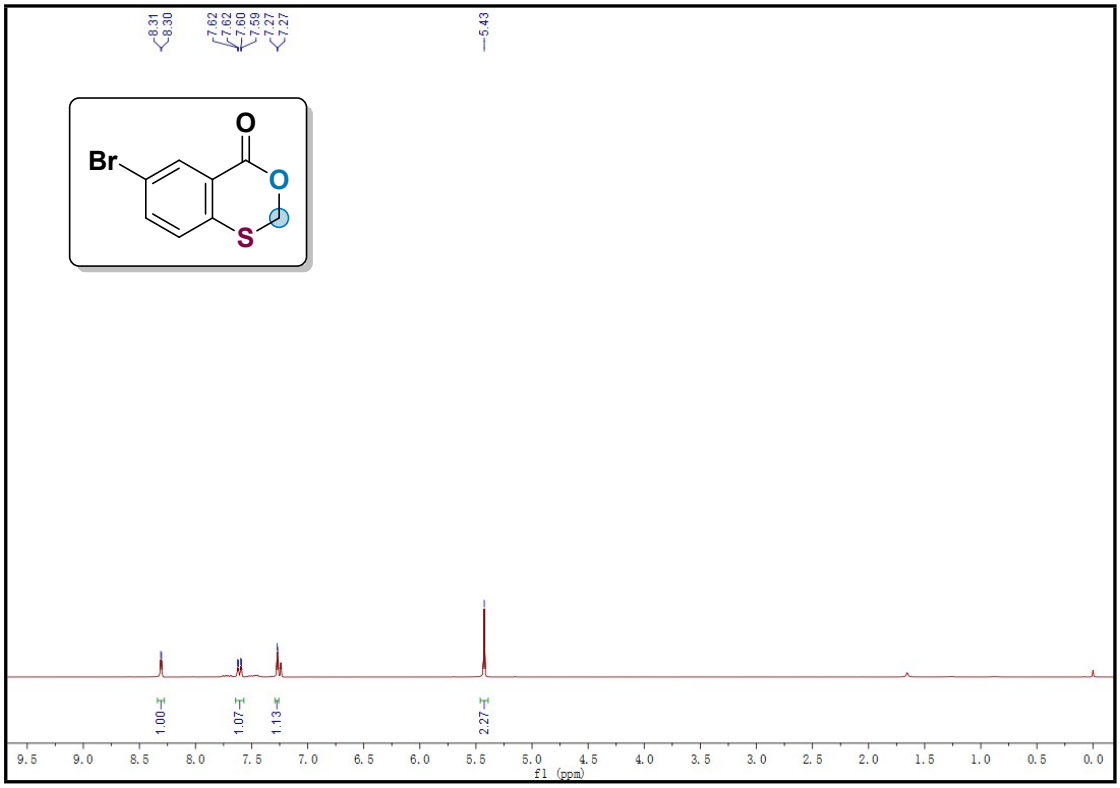


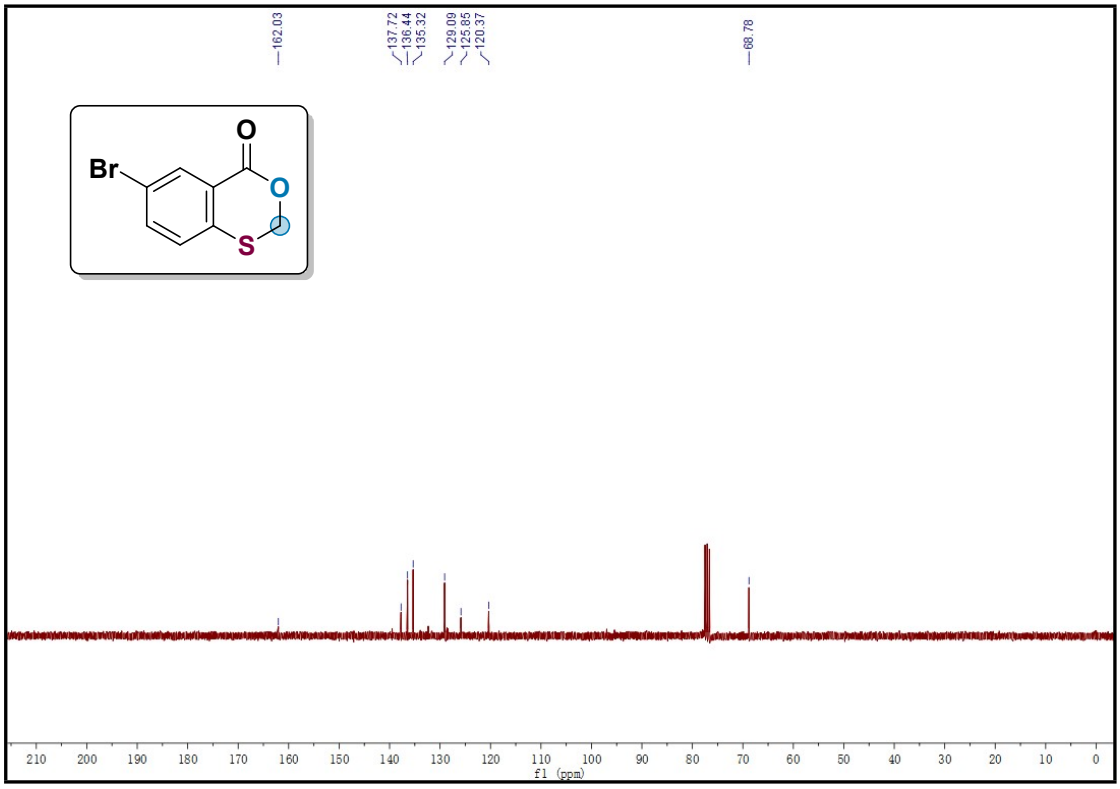
6-morpholino-4H-benzo[d][1,3]oxathiin-4-one (4h)



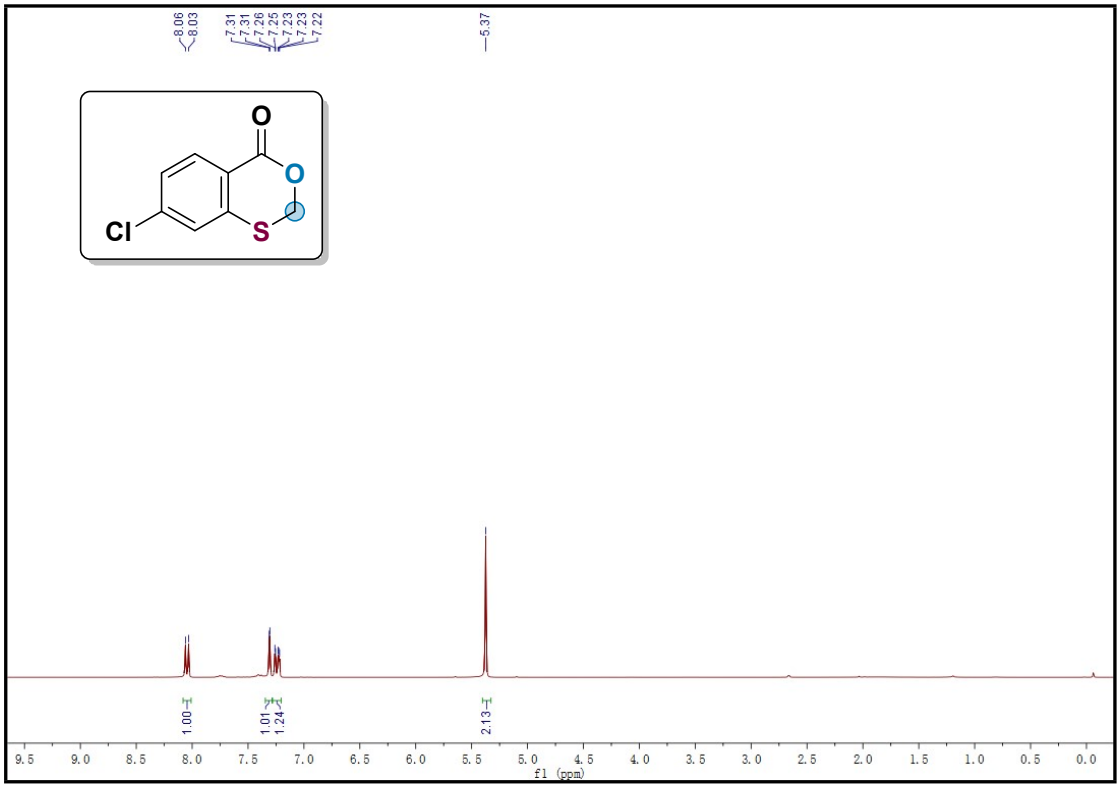


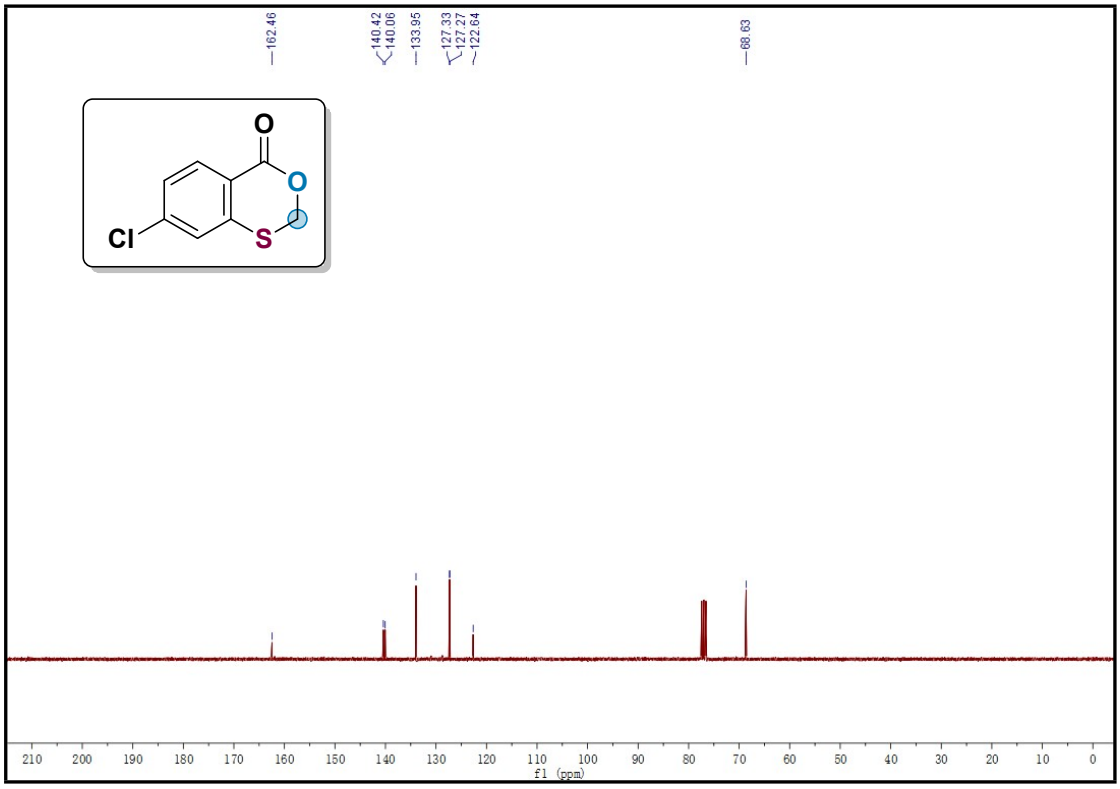
6-bromo-4H-benzo[d][1,3]oxathiin-4-one (4i)



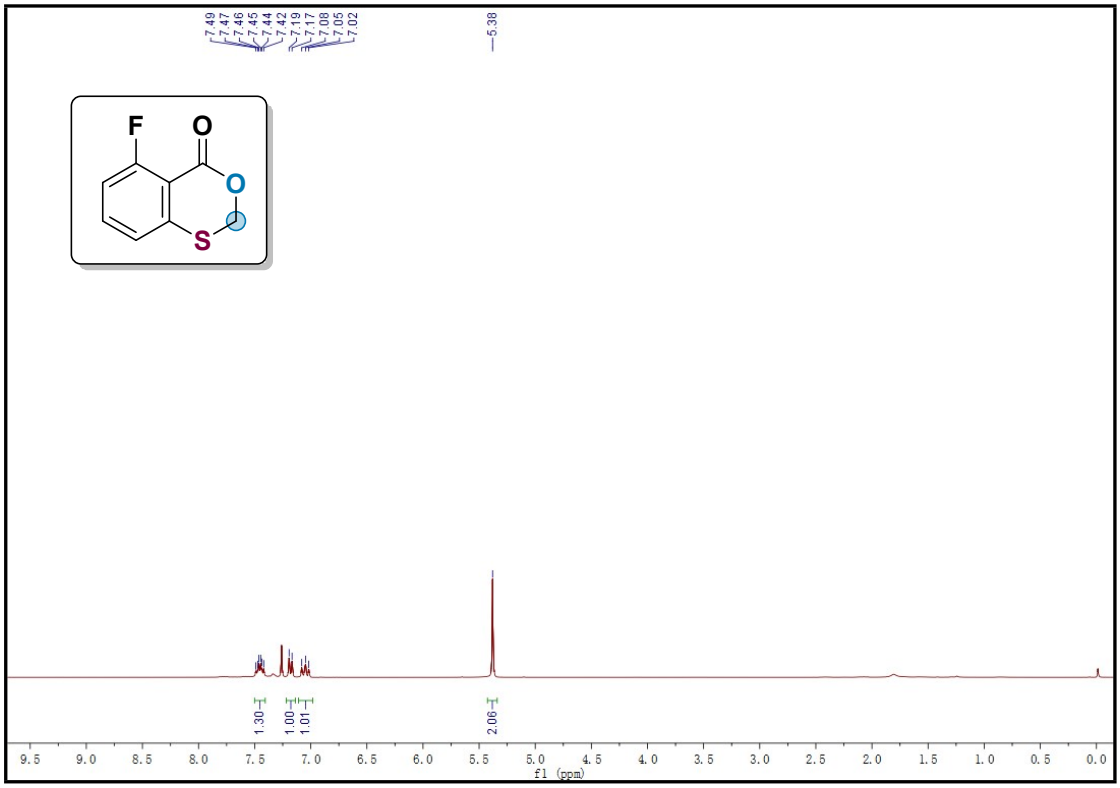


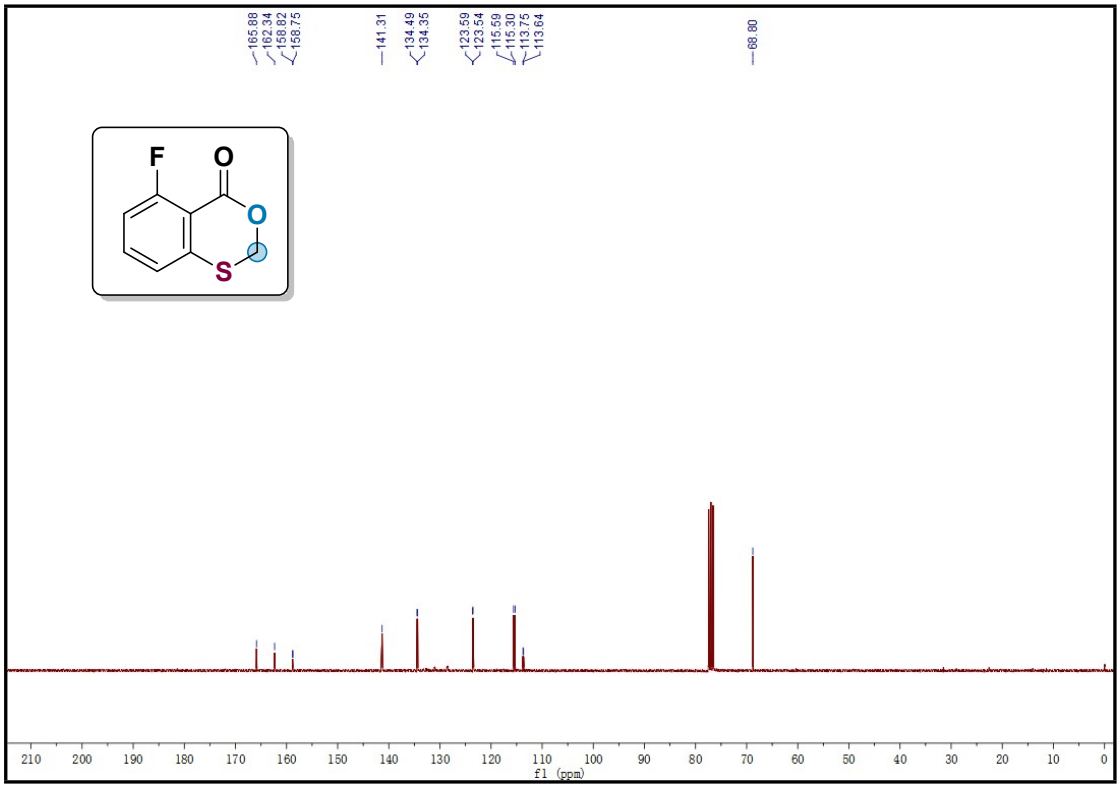
7-chloro-4H-benzo[d][1,3]oxathiin-4-one (4j)



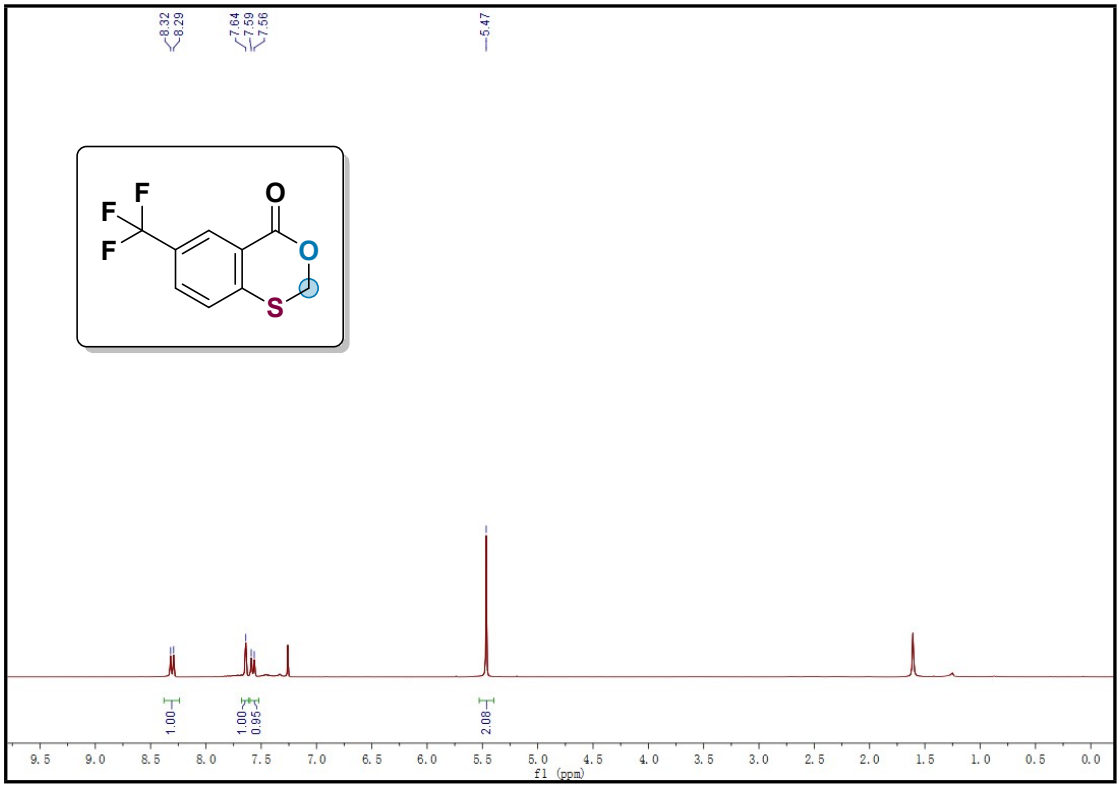


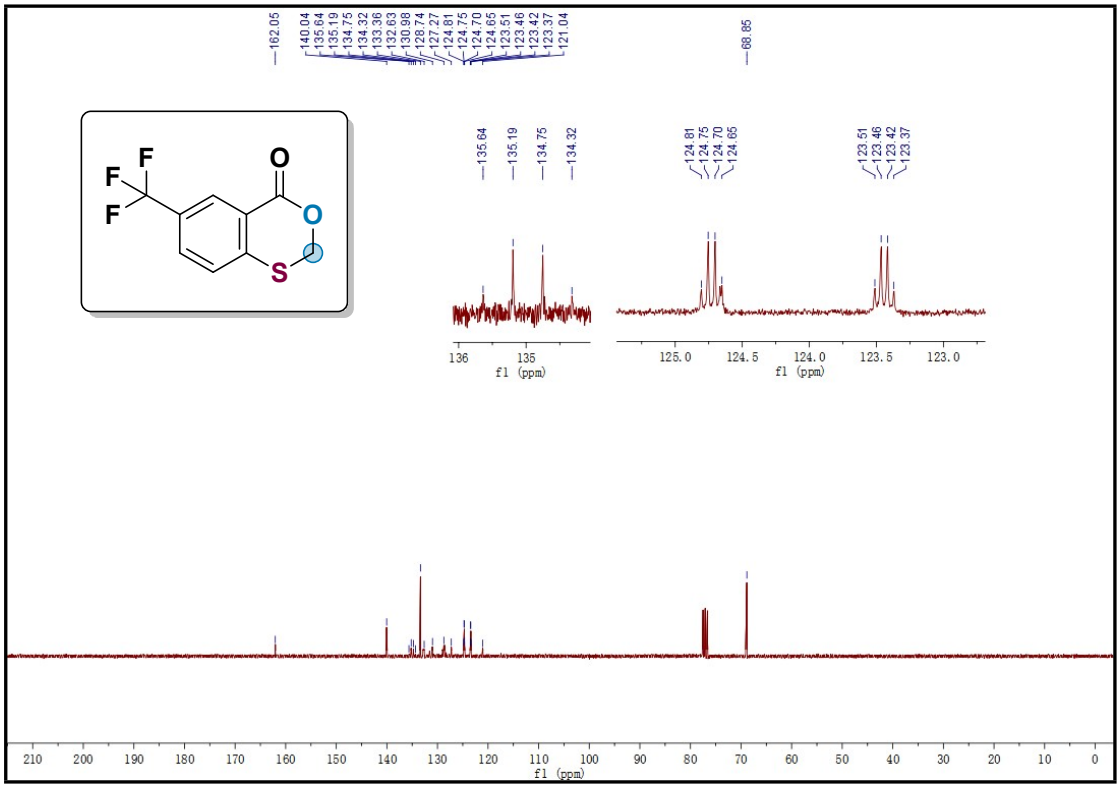
5-fluoro-4H-benzo[d][1,3]oxathiin-4-one (4k)



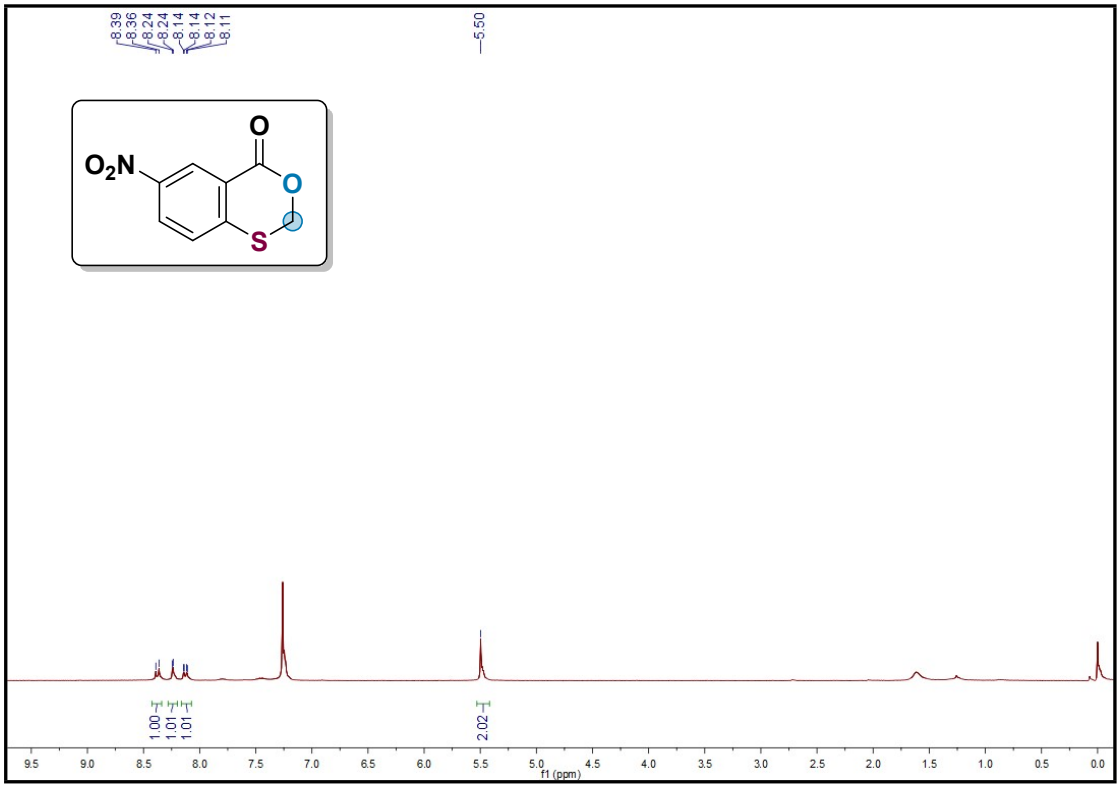


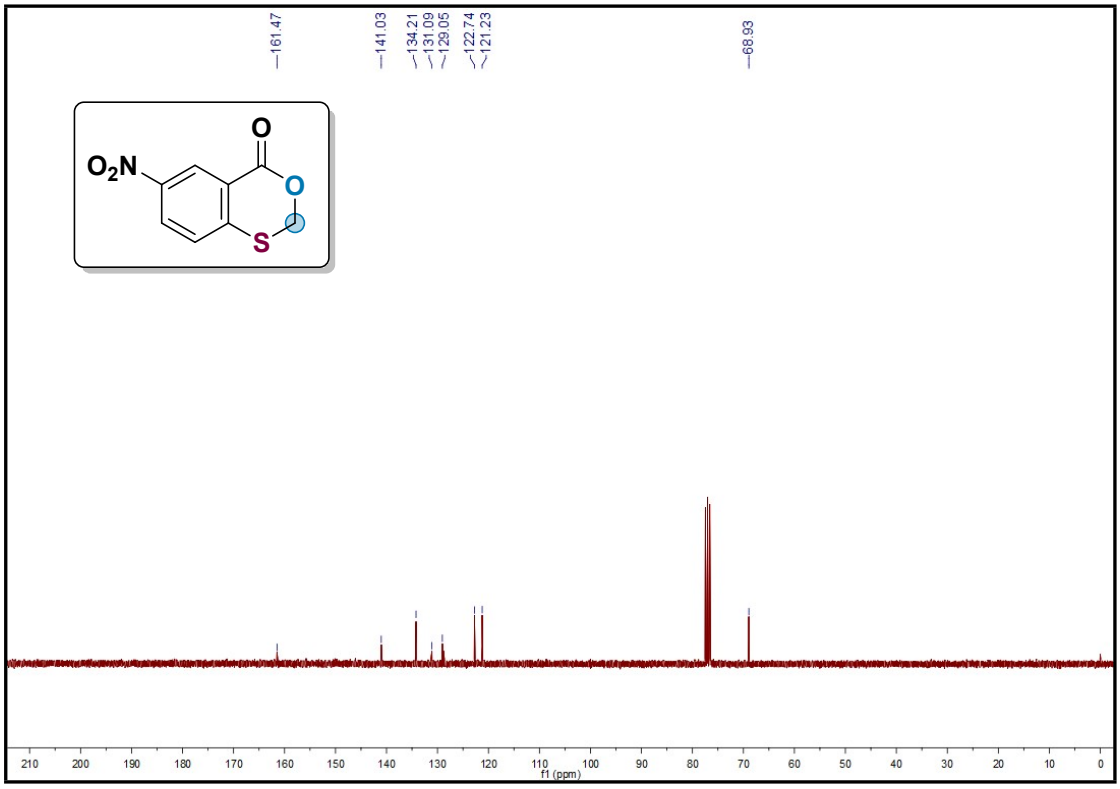
6-(trifluoromethyl)-4H-benzo[d][1,3]oxathiin-4-one (4l)



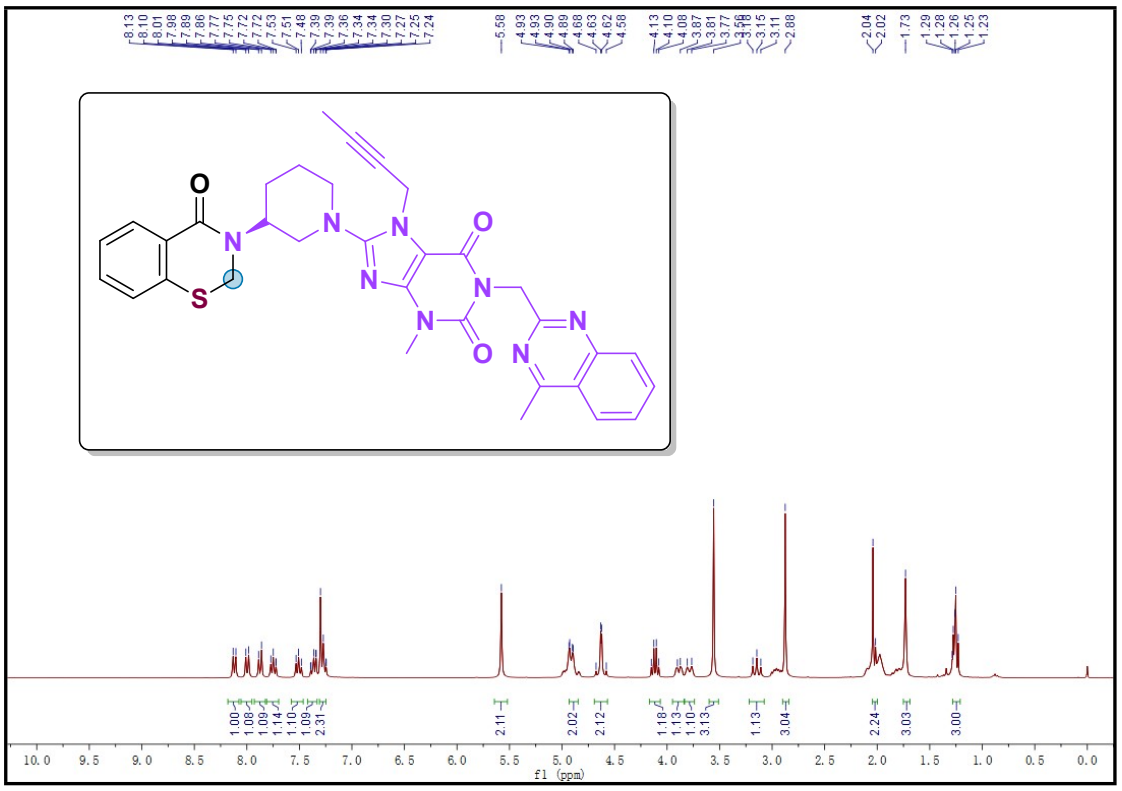


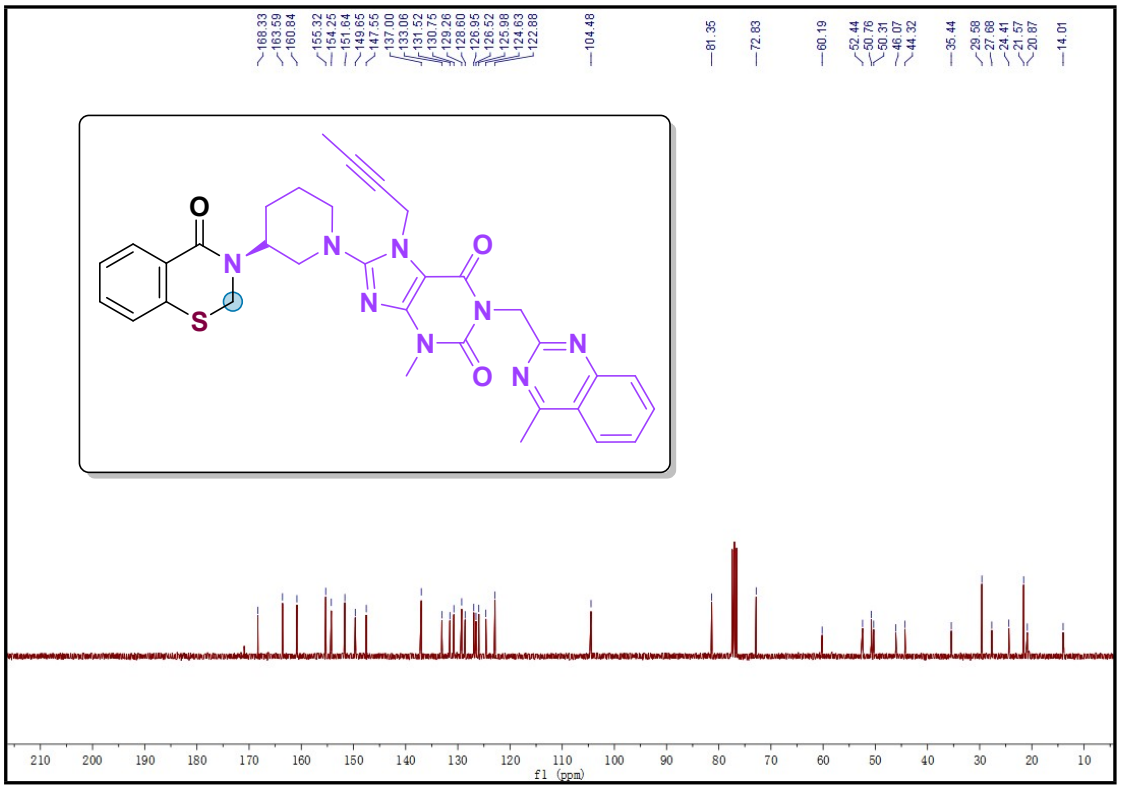
6-nitro-4H-benzo[d][1,3]oxathiin-4-one (4m)



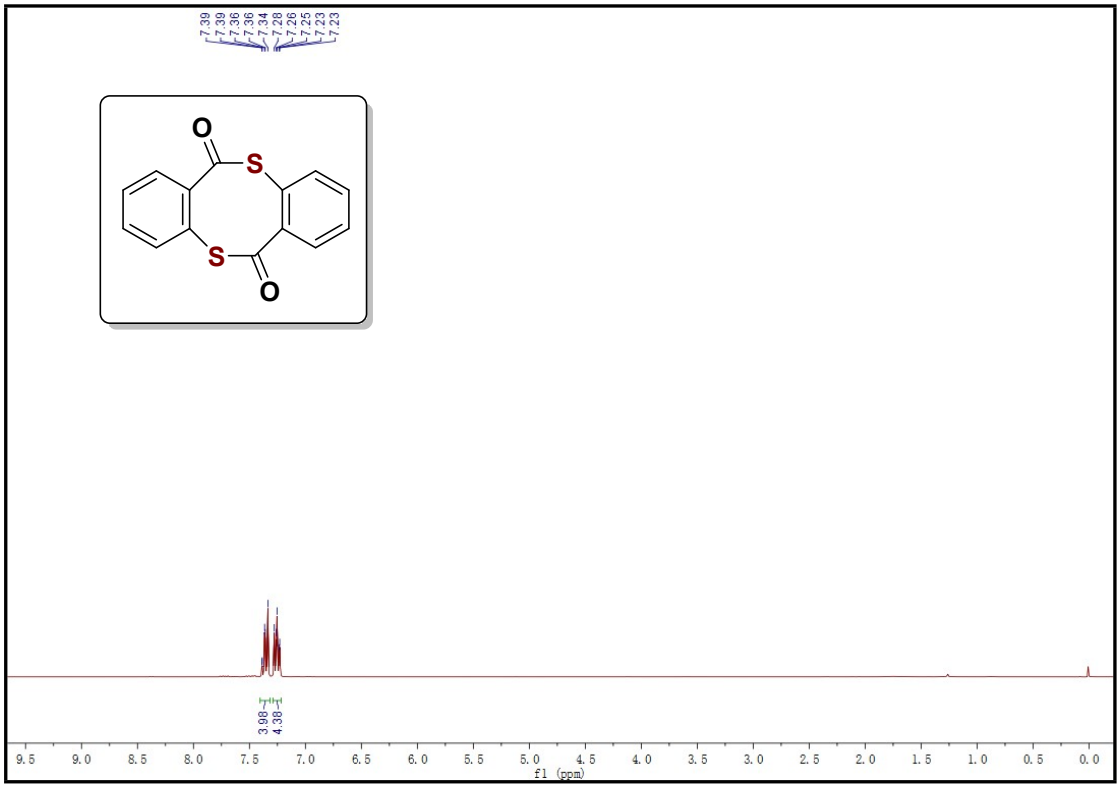


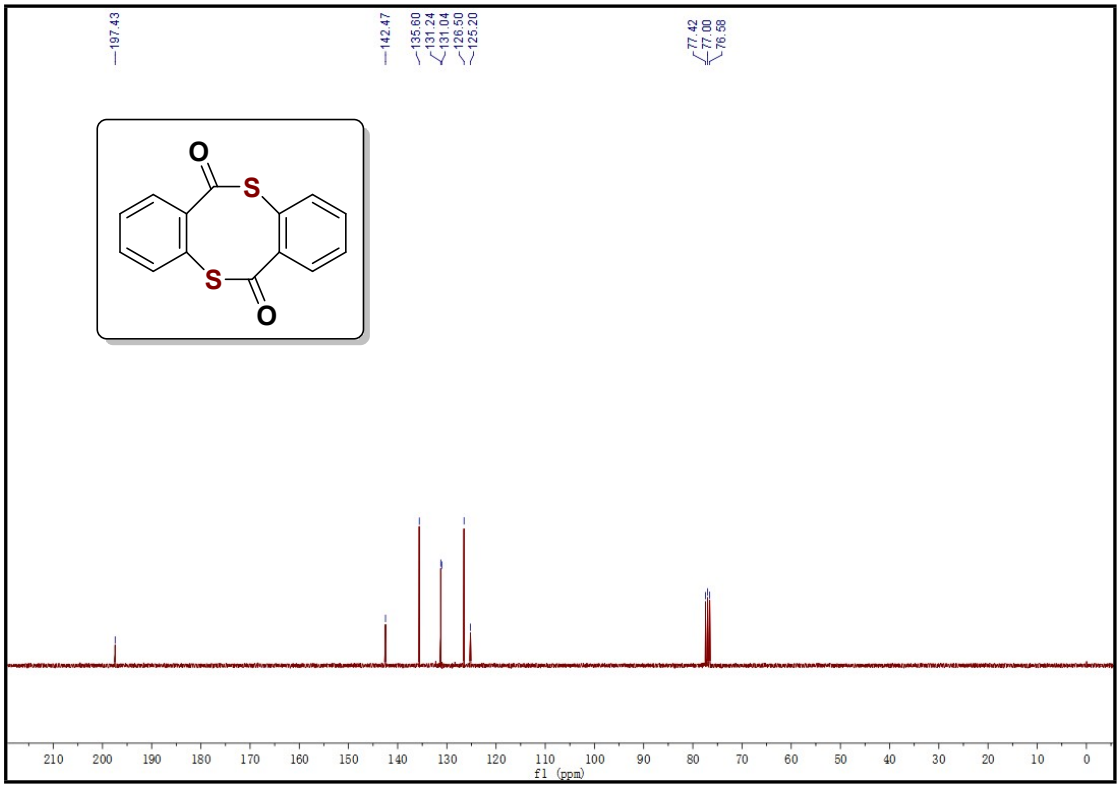
(S)-7-(but-2-yn-1-yl)-3-methyl-1-((4-methylquinazolin-2-yl)methyl)-8-(3-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)piperidin-1-yl)-3,7-dihydro-1H-purine-2,6-dione (5)





6H,12H-dibenzo[b,f][1,5]dithiocine-6,12-dione (6)





(2-(diphenylphosphaneyl)ethyl)diphenylphosphine sulfide (7)