Supporting Information

for

Substituents-Controlled Divergent Cyclization Reactions of Benzo[c][1,2]dithiol-3-ones and Hexahydro-1,3,5-triazines

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1. General information

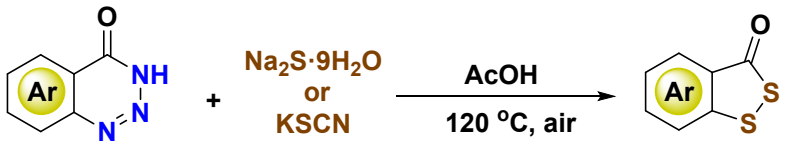
All reagents and solvents were obtained from commercial suppliers and used without further purification. The substituted amidines were purchased from Bide Pharmatech Ltd. Unless otherwise stated, all experiments were conducted in a seal tube under air atmosphere. Reactions were monitored by TLC or GC-MS 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). The 1,2-benzodithiol-3-ones **1** were prepared according to our previous work[1]. The 1,3,5-trimethyl-1,3,5-triazinane, 1,3,5-triphenyl-1,3,5-triazinane, 1,3,5-tribenzyl-1,3,5 -triazinane, 2,2'-(5-(3-hydroxypropyl)-1,3,5-triazinane-1,3-diyl)bis(ethan-1-ol) are commercially available. Other N-substituted hexahydro-1,3,5-triazines were prepared according the condensation of paraformaldehyde and substituted amines.[2]

[1] Zhou, Y.; Zhang, B.; Dong, J.; Li, J.; Yang, S.; Ye, L. *Org. Lett.* **2022**, *24*, 9012-9016.

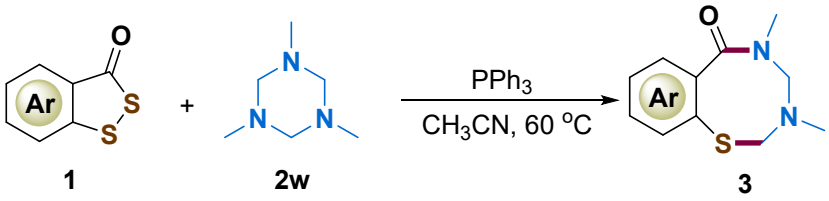
[2] (a) Guranova, N.; Dar'in, D.; Krasavin, M. *Synthesis* **2018**, *50*, 2001-2008. (b) Giumanini, A. G.; Verardo, G.; Zangrando, E.; Lassiani, L. *J. Prakt. Chem.* **1987**, *329*, 1087-1103. (c) Ruscoe, R. E.; Callingham, M.; Baker, J. A.; Korkis, S. E.; Lam, H. W. *Chem. Commun.* **2019**, *55*, 838-841.

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 $Na_2S·9H_2O$ 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_2SO_4. 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 the synthesis of 6*H*-benzo[g][1,3,5]thiadiazocin-6-ones 3

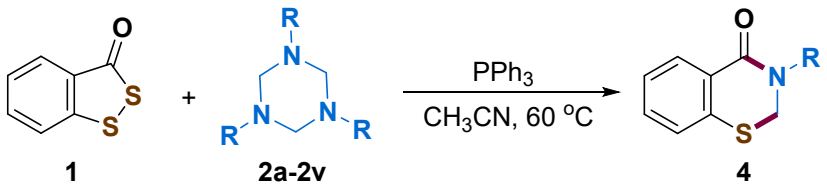


CH_3CN (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1** (0.3 mmol), 1,3,5-trimethyl-1,3,5-triazinane **2** (0.6 mmol) and PPh_3 (77.4 mg, 0.3 mmol) in a sealed tube. Then the reaction mixture was stirred at 60 °C in an oil bath under air for 12 h. Upon completion of the reaction, the solvents 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 6H-benzo[g][1,3,5]thiadiazocin-6-ones **3**.

[*Scale-up for larger synthesis of* ***3a***]: CH_3CN (30 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1a** (0.84 g, 5 mmol), 1,3,5-trimethyl-1,3,5-triazinane **2w** (1.29 g, 10 mmol) and PPh_3 (1.31 g, 5 mmol) in a 150 mL sealed tube. Then the reaction mixture was stirred at 60 °C in an oil bath 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 = 3:1, v/v) to give the desired product 6H-benzo[g][1,3,5]thiadiazocin-6-ones **3a** as white solid (0.87 g, 79%).

4. General procedure to synthesize 2,3-dihydrobenzothiazinones 4

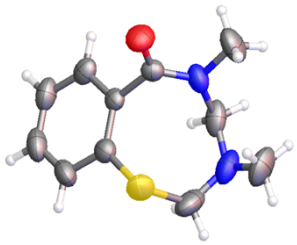


CH_3CN (2 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1** (0.3 mmol), 1,3,5-triazinane **2** (0.45 mmol) and PPh_3 (77.4 mg, 0.3 mmol) in a sealed tube. Then the reaction mixture was stirred at 60 °C in an oil bath under air for 12 h. Upon completion of the reaction, the solvents were removed 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 2,3-dihydrobenzothiazinones **4**.

[*Scale-up for larger synthesis of **4s***]: CH_3CN (25 mL) was added to a mixture of 1,2-benzodithiol-3-ones **1a** (0.84 g, 5 mmol), 1,3,5-triazinane **4s** (1.62 g, 7.5 mmol) and PPh_3 (1.31 g, 5 mmol) in a 150 mL sealed tube. Then the reaction mixture was stirred at 60 °C in an oil bath under air for 20 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 = 1:1, v/v) to give the desired product 2,3-dihydrobenzothiazinones **4s** as colourless oil (0.92 g, 88%).

5. Crystal data of 3a

Crystallographic data for compound **3a** (CCDC-2334598) 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 leve

Bond precision: C-C = 0.0046 A Wavelength=0.71073
Cell: a=6.5838(10) b=13.518(3) c=25.245(4)
alpha=90 beta=90.0100 gamma=90
Temperature: 298 K

	Calculated	Reported
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Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C11 H14 N2 O S	C11 H14 N2 O S
Sum formula	C11 H14 N2 O S	C11 H14 N2 O S
Mr	222.30	222.31
Dx,g cm-3	1.314	1.314
Z	8	8
Mu (mm-1)	0.263	0.263
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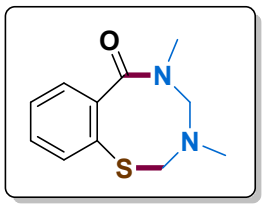
F000'	945.30	
h,k,lmax	7,16,30	7,16,30
Nref	3948	3940
Tmin,Tmax		0.531,1.000
Tmin'		

Correction method= # Reported T Limits: Tmin=0.531 Tmax=1.000
AbsCorr = MULTI-SCAN
Data completeness= 0.998 Theta(max)= 24.990
R(reflections)= 0.0513(2680) wR2(reflections)= 0.1747(3940)
S = 1.050 Npar= 282

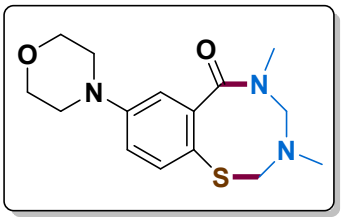
6. Characterization data for the products

3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3a)



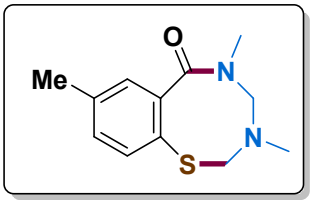
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (53.9 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.52 (dd, *J* = 6.5, 2.1 Hz, 1H), 7.39 (dd, *J* = 5.3, 3.6 Hz, 1H), 7.31 (dd, *J* = 8.4, 5.3 Hz, 2H), 4.32 (dd, *J* = 14.0, 8.6 Hz, 2H), 4.14 (d, *J* = 14.6 Hz, 1H), 3.95 (d, *J* = 13.6 Hz, 1H), 3.22 (s, 3H), 2.56 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 141.7, 135.2, 133.6, 130.3, 128.7, 128.2, 69.6, 65.2, 38.9, 37.5. HRMS (ESI, m/z) calcd for $C_{11}H_{15}N_2OS$ $[M+H]^+$: 223.0900; found: 223.0905.

3,5-dimethyl-8-morpholino-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3b)



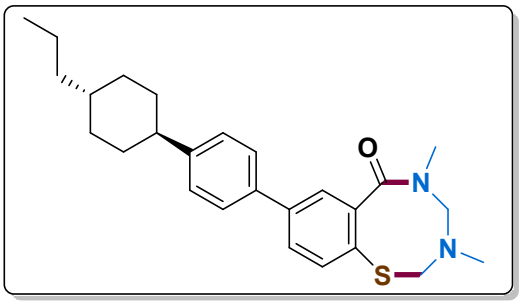
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a yellow oil (84.7 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 1H), 6.92 – 6.80 (m, 2H), 4.39 (d, *J* = 14.7 Hz, 1H), 4.18 (t, *J* = 13.9 Hz, 2H), 3.94 (d, *J* = 13.5 Hz, 1H), 3.84 – 3.77 (m, 4H), 3.23 (s, 3H), 3.20 – 3.13 (m, 4H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.5, 151.2, 142.7, 136.5, 122.6, 116.9, 113.7, 69.7, 66.6, 65.9, 48.2, 39.0, 37.6. HRMS (ESI, m/z) calcd for $C_{15}H_{22}N_3O_2S$ $[M+H]^+$: 308.1428; found: 308.1430.

3,5,8-trimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3c)



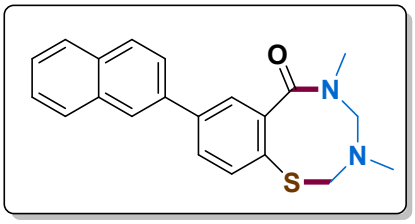
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (58.7 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 – 7.22 (m, 2H), 7.09 (d, *J* = 7.4 Hz, 1H), 4.28 (t, *J* = 12.9 Hz, 2H), 4.08 (d, *J* = 14.4 Hz, 1H), 3.91 (d, *J* = 13.6 Hz, 1H), 3.16 (s, 3H), 2.51 (s, 3H), 2.27 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.4, 140.4, 138.5, 135.5, 133.3, 129.5, 128.3, 69.7, 65.0, 38.9, 37.4, 21.0. HRMS (ESI, m/z) calcd for $C_{12}H_{17}N_2OS$ $[M+H]^+$: 237.1057; found: 237.1057.

3,5-dimethyl-8-(4-((1s,4r)-4-propylcyclohexyl)phenyl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3d)



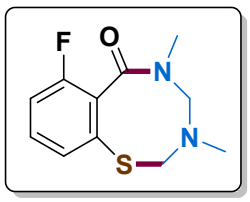
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (101.3 mg, 80%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.62 (d, *J* = 1.5 Hz, 1H), 7.55 (dd, *J* = 9.9, 4.9 Hz, 2H), 7.49 (d, *J* = 8.2 Hz, 2H), 7.25 (d, *J* = 8.3 Hz, 2H), 4.37 (dd, *J* = 27.8, 14.1 Hz, 2H), 4.16 (d, *J* = 14.6 Hz, 1H), 4.00 (d, *J* = 13.6 Hz, 1H), 3.24 (s, 3H), 2.58 (s, 3H), 2.53 – 2.41 (m, 1H), 1.87 (t, *J* = 11.1 Hz, 4H), 1.47 (td, *J* = 12.4, 2.7 Hz, 2H), 1.39 – 1.26 (m, 3H), 1.20 (dd, *J* = 9.4, 5.6 Hz, 2H), 1.10 – 0.97 (m, 2H), 0.88 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.3, 147.8, 141.7, 141.6, 136.9, 135.7, 132.1, 128.6, 127.4, 126.9, 126.6, 69.7, 65.4, 44.3, 39.7, 39.0, 37.6, 37.0, 34.3, 33.5, 20.0, 14.5. HRMS (ESI, m/z) calcd for $C_{26}H_{35}N_2OS$ $[M+H]^+$: 423.2465; found: 423.2468.

3,5-dimethyl-8-(naphthalen-2-yl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3e)



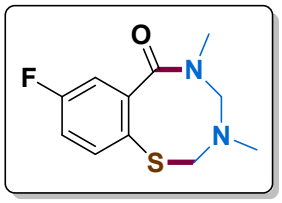
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (85.6 mg, 82%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.06 (s, 1H), 7.88 (dd, *J* = 22.7, 13.7 Hz, 4H), 7.77 – 7.63 (m, 3H), 7.54 – 7.45 (m, 2H), 4.44 (dd, *J* = 31.5, 14.1 Hz, 2H), 4.22 (d, *J* = 14.5 Hz, 1H), 4.06 (d, *J* = 13.6 Hz, 1H), 3.30 (s, 3H), 2.63 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2, 141.6, 136.7, 133.6, 132.8, 129.0, 128.7, 128.3, 127.6, 127.0, 126.5, 126.3, 126.0, 125.0, 70.0, 39.0, 37.6. HRMS (ESI, m/z) calcd for $C_{21}H_{21}N_2OS$ $[M+H]^+$: 349.1370; found: 349.1374.

7-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3f)



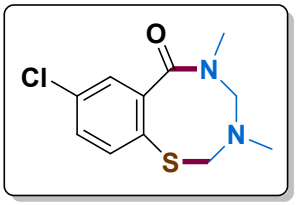
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (51.1 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (dd, *J* = 6.9, 6.0 Hz, 1H), 7.25 – 7.17 (m, 1H), 7.07 – 6.96 (m, 1H), 4.39 (d, *J* = 14.7 Hz, 1H), 4.28 (d, *J* = 13.6 Hz, 1H), 4.15 (d, *J* = 14.7 Hz, 1H), 3.88 (d, *J* = 13.6 Hz, 1H), 3.19 (s, 3H), 2.51 (s, 3H).^{13}C NMR (75 MHz, $CDCl_3$) δ 166.2, 159.0 (d, *J* = 255.8 Hz), 136.3 (d, *J* = 3.0 Hz), 130.9, 130.8, 116.4, 116.1, 69.5, 66.0, 38.9, 37.4. HRMS (ESI, m/z) calcd for $C_{11}H_{14}FN_2OS$ $[M+H]^+$: 241.0806; found: 241.0809.

8-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3g)



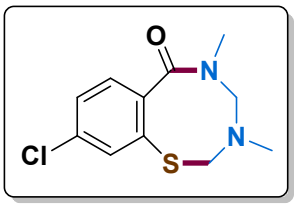
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (54.7 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 8.5, 5.4 Hz, 1H), 7.15 (dd, *J* = 8.6, 2.8 Hz, 1H), 7.06 (td, *J* = 8.4, 2.9 Hz, 1H), 4.35 (dd, *J* = 23.9, 14.2 Hz, 2H), 4.21 (d, *J* = 14.7 Hz, 1H), 3.98 (d, *J* = 13.6 Hz, 1H), 3.26 (s, 3H), 2.61 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 162.6 (d, *J* = 249.0 Hz), 143.7 (d, *J* = 8.0 Hz), 137.6 (d, *J* = 8.0 Hz), 129.0 (d, *J* = 3.6 Hz), 117.5 (d, *J* = 21.0 Hz), 115.2 (d, *J* = 23.3 Hz), 69.6, 65.7, 39.0, 37.6. HRMS (ESI, m/z) calcd for $C_{11}H_{14}FN_2OS$ $[M+H]^+$: 241.0806; found: 241.0807.

8-chloro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3h)



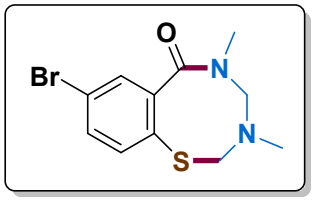
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (62.2 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, *J* = 8.3 Hz, 1H), 7.39 (d, *J* = 2.3 Hz, 1H), 7.28 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.33 (dd, *J* = 14.1, 10.8 Hz, 2H), 4.17 (d, *J* = 14.7 Hz, 1H), 3.95 (d, *J* = 13.6 Hz, 1H), 3.21 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 143.1, 136.6, 134.9, 132.2, 130.3, 128.3, 69.6, 65.5, 38.9, 37.6. HRMS (ESI, m/z) calcd for $C_{11}H_{14}ClN_2OS$ $[M+H]^+$: 257.0510; found: 257.0510.

9-chloro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3i)



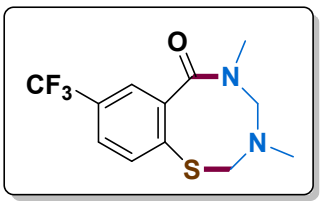
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (60.6 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 (d, *J* = 1.2 Hz, 1H), 7.38 – 7.27 (m, 2H), 4.32 (dd, *J* = 14.1, 9.0 Hz, 2H), 4.14 (d, *J* = 14.6 Hz, 1H), 3.97 (d, *J* = 13.6 Hz, 1H), 3.19 (s, 3H), 2.55 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.1, 139.7, 135.4, 135.3, 134.5, 129.6, 128.7, 69.5, 65.0, 38.7, 37.4. HRMS (ESI, m/z) calcd for $C_{11}H_{14}ClN_2OS$ $[M+H]^+$: 257.0510; found: 257.0515.

8-bromo-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3j)



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 (66.4 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 (d, *J* = 1.6 Hz, 1H), 7.50 – 7.36 (m, 2H), 4.34 (dd, *J* = 13.8, 11.1 Hz, 2H), 4.17 (d, *J* = 14.7 Hz, 1H), 3.95 (d, *J* = 13.6 Hz, 1H), 3.22 (s, 3H), 2.57 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.6, 143.2, 136.8, 133.3, 132.8, 131.2, 122.8, 69.6, 65.4, 38.9, 37.69. HRMS (ESI, m/z) calcd for $C_{11}H_{14}BrN_2OS$ $[M+H]^+$: 301.0005; found: 301.0007.

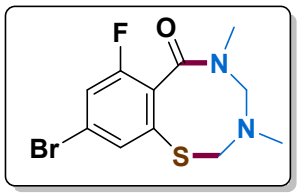
3,5-dimethyl-8-(trifluoromethyl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3k)



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 (50.6 mg, 57%). ^{1}H NMR (300 MHz, DMSO) δ 7.82 (s, 1H), 7.75 (d, *J* = 8.1 Hz, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 4.51 (d, *J* = 13.2 Hz, 1H), 4.34 – 4.20 (m, 2H), 4.09 (d, *J* = 13.2 Hz, 1H), 3.35 (s, 3H), 3.12 (s, 3H). ^{13}C NMR (75 MHz, DMSO) δ 169.4, 146.3, 134.8, 132.0 (q, *J* = 11.9 Hz), 130.6 (q, *J* = 32.3 Hz), 129.7 (q, *J* = 3.9 Hz), 129.3, 124.0 (q, *J* = 271.5

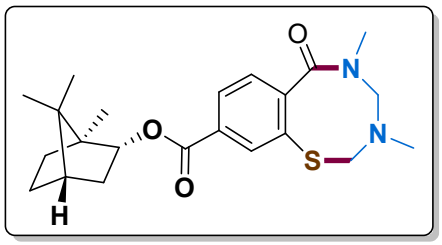
Hz), 68.9, 66.1, 38.4, 37.5. HRMS (ESI, m/z) calcd for $C_{12}H_{14}F_3N_2OS$ $[M+H]^+$: 297.0774; found: 297.0774.

9-bromo-7-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3l)



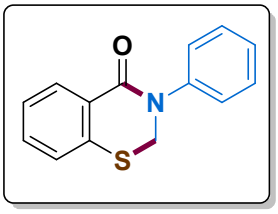
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (66.7 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.49 (d, *J* = 3.9 Hz, 1H), 7.20 (dd, *J* = 8.0, 6.3 Hz, 1H), 4.46 – 4.26 (m, 2H), 4.16 (dd, *J* = 14.7, 5.6 Hz, 1H), 3.92 (dd, *J* = 13.5, 5.9 Hz, 1H), 3.19 (d, *J* = 6.2 Hz, 3H), 2.52 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 165.5, 158.9 (d, *J* = 255.8 Hz), 138.0, 133.6, 123.1 (d, *J* = 10.4 Hz), 120.0, 119.7, 69.5, 66.1, 39.0, 37.5. HRMS (ESI, m/z) calcd for $C_{11}H_{13}BrFN_2OS$ $[M+H]^+$: 318.9911; found: 318.9913.

(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3,5-dimethyl-6-oxo-3,4,5,6-tetrahydro-2H-benzo[g][1,3,5]thiadiazocine-9-carboxylate (3m)



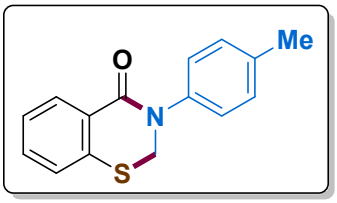
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a white solid (77.1 mg, 64%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.15 (s, 1H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 5.05 (d, *J* = 9.1 Hz, 1H), 4.40 – 4.25 (m, 2H), 4.13 (d, *J* = 14.6 Hz, 1H), 3.96 (dd, *J* = 13.7, 2.9 Hz, 1H), 3.20 (s, 3H), 2.55 (s, 3H), 2.47 – 2.36 (m, 1H), 2.08 – 1.98 (m, 1H), 1.72 (dd, *J* = 18.0, 4.0 Hz, 2H), 1.32 – 1.19 (m, 2H), 1.08 – 1.01 (m, 1H), 0.90 (s, 3H), 0.85 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 165.6, 133.1, 132.6, 128.5, 128.3, 124.4, 119.0, 81.2, 69.6, 49.2, 49.1, 47.9, 44.9, 39.0, 36.8, 28.1, 27.4, 19.7, 18.9, 13.6. HRMS (ESI, m/z) calcd for $C_{22}H_{31}N_2O_3S$ $[M+H]^+$: 403.2050; found: 403.2050.

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



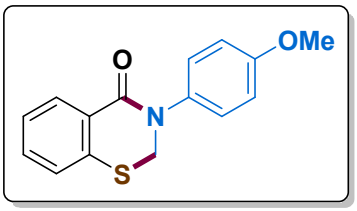
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a yellow oil (60.0 mg, 83%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 8.9 Hz, 1H), 7.47 – 7.34 (m, 6H), 7.33 – 7.29 (m, 2H), 4.98 (s, 2H). ^{13}C 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.

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



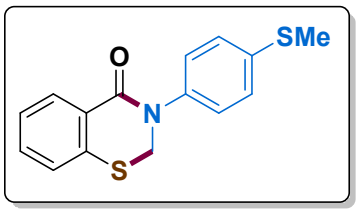
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (67.3 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.39 (dd, *J* = 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 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.

3-(4-methoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4c) (CAS Number: 2259305-59-2)



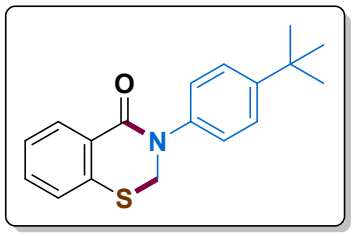
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 5:1, v/v) to give the product as a white solid (68.2 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (dd, *J* = 7.7, 1.0 Hz, 1H), 7.38 – 7.27 (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 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.

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



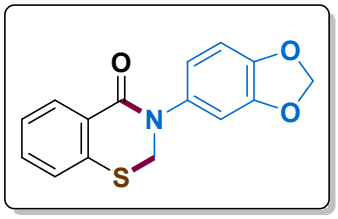
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1 to 5:1, v/v) to give the product as a white solid (68.0 mg, 79%).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (d, J = 7.8 Hz, 1H), 7.45 – 7.37 (m, 1H), 7.34 (d, J = 6.8 Hz, 1H), 7.33 – 7.27 (m, 5H), 4.96 (s, 2H), 2.50 (s, 3H). ^{13}C 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 (4e)



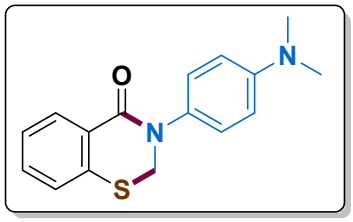
The reaction was performed following the general procedure by using DPPE as the additive. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 20:1, v/v) to give the product as a white solid (56.1 mg, 63%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, J = 6.7 Hz, 1H), 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 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.

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



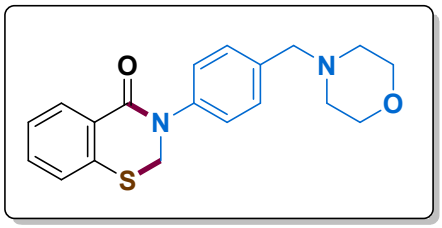
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow oil (53.0 mg, 62%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.17 (dd, J = 7.8, 1.1 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.32 (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 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-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4g)



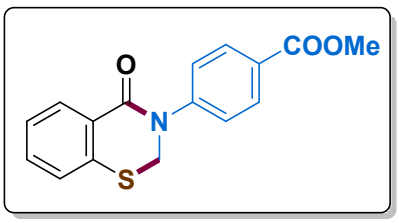
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a yellow solid (65.5 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.22 (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 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 (4h)



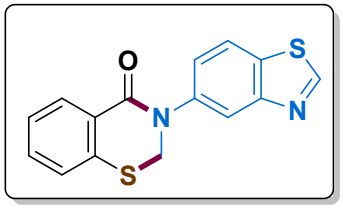
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:4, v/v) to give the product as a colourless oil (87.7 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.8, 1.1 Hz, 1H), 7.41 (dd, *J* = 10.2, 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 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.

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



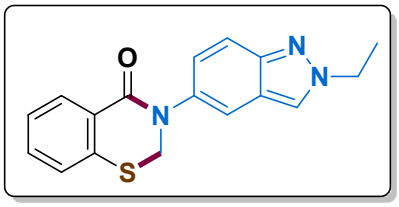
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a white solid (62.3 mg, 70%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.8, 1.1 Hz, 1H), 8.10 (d, *J* = 8.6 Hz, 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 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]thiazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4j)



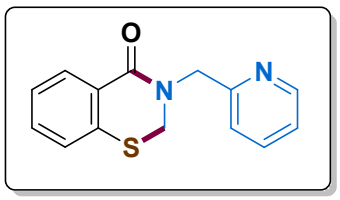
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (63.4 mg, 71%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 9.03 (s, 1H), 8.19 (d, *J* = 7.8 Hz, 1H), 8.10 (d, *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 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 (4k)



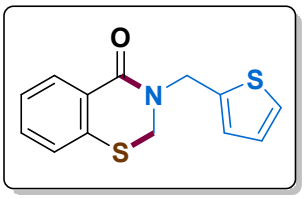
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a white solid (70.4 mg, 76%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (dd, *J* = 7.7, 0.9 Hz, 1H), 7.93 (s, 1H), 7.74 (d, *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 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.

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



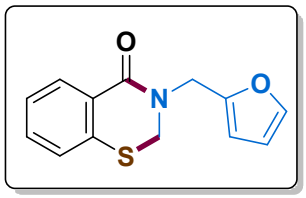
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (67.5 mg, 88%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.54 (d, *J* = 4.2 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.4 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}C NMR (75 MHz, $CDCl_3$) δ 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 $C_{14}H_{13}N_2OS$ $[M+H]^+$: 257.0744; found: 257.0748.

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



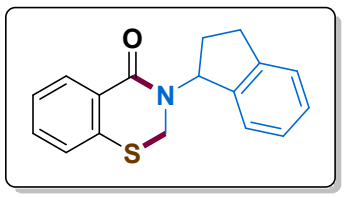
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (63.4 mg, 81%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.16 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.31 (m, 1H), 7.27 (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}C NMR (75 MHz, $CDCl_3$) δ 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 $C_{13}H_{12}NOS_2$ $[M+H]^+$: 262.0355; found: 262.0357.

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



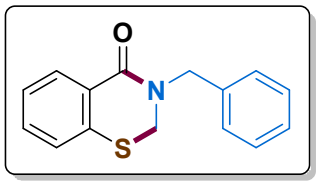
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil solid (63.2 mg, 86%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.13 (dd, *J* = 8.0, 1.4 Hz, 1H), 7.43 – 7.30 (m, 2H), 7.30 – 7.21 (m, 2H), 6.49 – 6.24 (m, 2H), 4.81 (s, 2H), 4.59 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) 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 $C_{13}H_{12}NO_2S$ $[M+H]^+$: 246.0584; found: 246.0589.

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



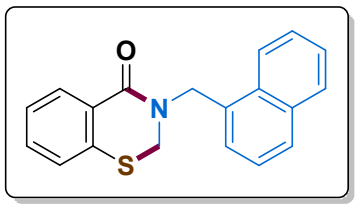
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (70.8 mg, 84%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 (d, *J* = 7.9 Hz, 1H), 7.39 – 7.32 (m, 2H), 7.27 (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 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-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4p) (CAS Number: 2259305-43-4)



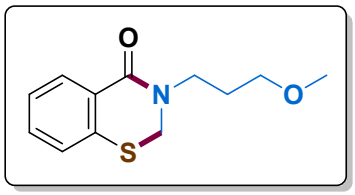
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (82.3 mg, 90%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.12 (m, 1H), 7.39 – 7.33 (m, 4H), 7.32 – 7.27 (m, 2H), 7.26 – 7.21 (m, 2H), 4.85 (s, 2H), 4.46 (s, 2H). ^{13}C 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.

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



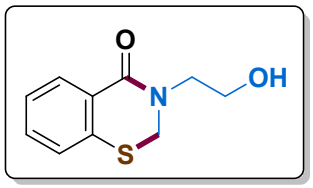
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (70.3 mg, 77%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.23 – 8.20 (m, 1H), 8.09 (d, *J* = 7.5 Hz, 1H), 7.89 – 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 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-(3-methoxypropyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4r)



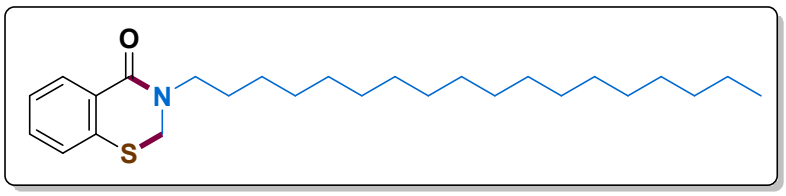
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 3:1, v/v) to give the product as a colourless oil (65.4 mg, 92%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.35 (dd, *J* = 10.2, 4.5 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 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-(2-hydroxyethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4s)



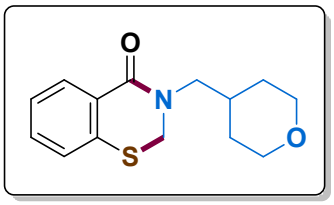
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the product as a colourless oil (59.6 mg, 95%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.0 Hz, 1H), 7.42 – 7.16 (m, 3H), 4.66 (s, 2H), 3.79 (dd, *J* = 20.5, 4.6 Hz, 4H), 3.44 (s, 1H). ^{13}C 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-octadecyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4t)



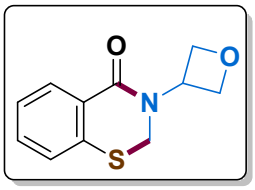
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the product as a colourless oil (70.0 mg, 56%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.19 – 8.05 (m, 1H), 7.38 – 7.29 (m, 1H), 7.28 – 7.21 (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 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.

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



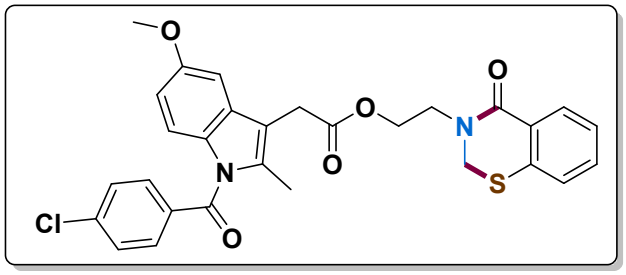
The reaction was performed following the general procedure. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (68.6 mg, 87%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.09 (dd, *J* = 7.3, 2.2 Hz, 1H), 7.41 – 7.29 (m, 1H), 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 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 (4v)



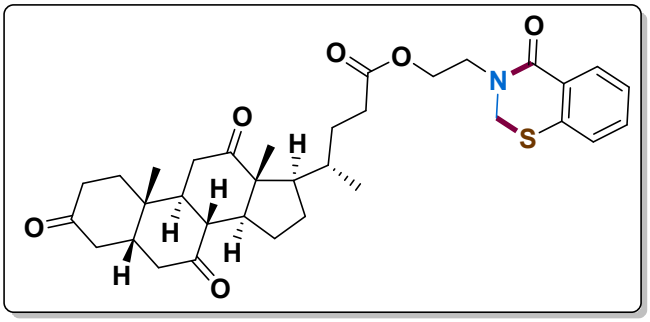
The reaction was performed following the general procedure under 80 °C. The residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 2:1, v/v) to give the product as a colourless oil (52.3 mg, 79%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.08 (d, *J* = 7.8 Hz, 1H), 7.42 – 7.34 (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 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.

2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)ethyl2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5)



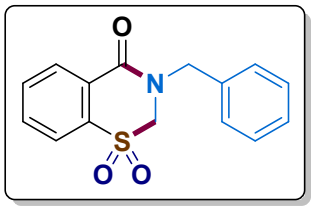
To a sealed tube, **4s** (40.2 mg, 0.2 mmol), Indometacin (85 mg, 0.24 mmol), DCC (82 mg, 0.4 mmol), 4-DMAP (12.2 mg, 0.1 mmol) CH_2Cl_2 (2 mL) were added. Then, the mixture was stirred at RT for about 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 1:1, v/v) to give the desired **5** as white solid (101.9 mg, 93%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.04 (dd, *J* = 7.7, 1.1 Hz, 1H), 7.65 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 7.34 (td, *J* = 7.5, 1.5 Hz, 1H), 7.26 – 7.17 (m, 2H), 6.94 (d, *J* = 2.4 Hz, 1H), 6.83 (d, *J* = 9.0 Hz, 1H), 6.62 (dd, *J* = 9.0, 2.4 Hz, 1H), 4.35 (t, *J* = 5.1 Hz, 2H), 4.28 (s, 2H), 3.82 (d, *J* = 5.2 Hz, 2H), 3.79 (s, 3H), 3.70 (s, 2H), 2.37 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 168.1, 163.8, 156.0, 139.2, 137.0 135.9, 133.8, 131.7, 131.1, 130.7, 130.6, 130.5, 129.7, 127.0, 127.0, 126.1, 115.0, 112.2, 111.6, 101.2, 63.4, 55.7, 49.5, 47.4, 30.3, 13.3. HRMS (ESI, m/z) calcd for $C_{29}H_{26}ClN_2O_5S$ $[M+H]^+$: 549.1246; found: 549.1248.

2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)ethyl(S)-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (6)



To a sealed tube, **4s** (40.2 mg, 0.2 mmol), Dehydrocholic acid (96.5 mg, 0.24 mmol), DCC (82 mg, 0.4 mmol), 4-DMAP (12.2 mg, 0.1 mmol) CH_2Cl_2 (2 mL) were added. Then, the mixture was stirred at RT 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 = 1:1, v/v) to give the desired **6** as white solid (104.4 mg, 88%).^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.0 Hz, 1H), 7.38 (dd, *J* = 10.5, 4.2 Hz, 1H), 7.33 – 7.27 (m, 2H), 4.68 (s, 2H), 4.33 (t, *J* = 5.3 Hz, 2H), 3.90 (t, *J* = 5.3 Hz, 2H), 2.99 – 2.80 (m, 3H), 2.37 (ddd, *J* = 16.5, 11.0, 4.8 Hz, 4H), 2.26 (d, *J* = 3.1 Hz, 2H), 2.21 – 2.18 (m, 1H), 2.12 (d, *J* = 5.4 Hz, 1H), 2.03 (d, *J* = 12.8 Hz, 3H), 1.93 (d, *J* = 14.9 Hz, 2H), 1.84 (dd, *J* = 14.4, 7.3 Hz, 2H), 1.75 – 1.55 (m, 3H), 1.41 (s, 3H), 1.33 – 1.24 (m, 3H), 1.07 (s, 3H), 0.85 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 211.8, 208.9, 208.6, 173.6, 163.8, 137.1, 131.6, 130.6, 129.1, 127.1, 126.1, 62.5, 56.8, 51.7, 49.8, 48.8, 47.4, 46.7, 45.5, 44.9, 42.7, 38.5, 36.4, 35.9, 35.3, 33.8, 31.3, 30.3, 27.5, 25.5, 24.8, 21.8, 18.6, 11.7. HRMS (ESI, m/z) calcd for $C_{34}H_{44}NO_6S$ $[M+H]^+$: 594.2884; found: 594.2887.

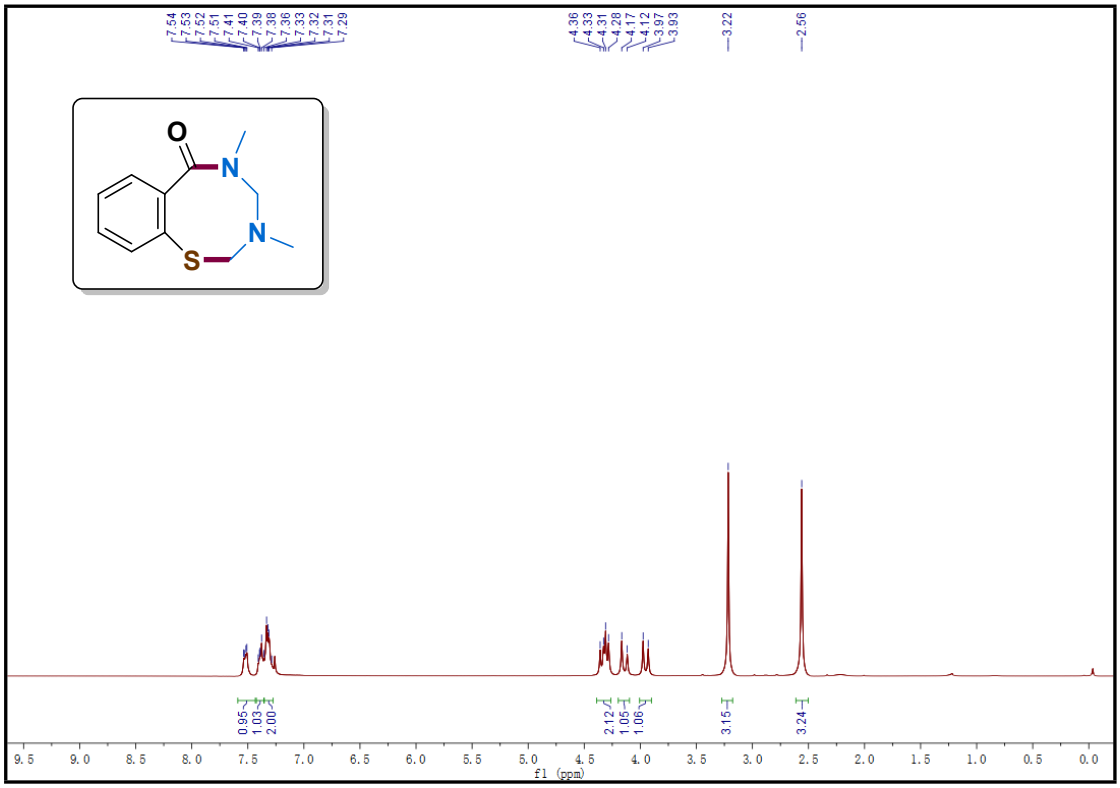
3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one 1,1-dioxide (7)

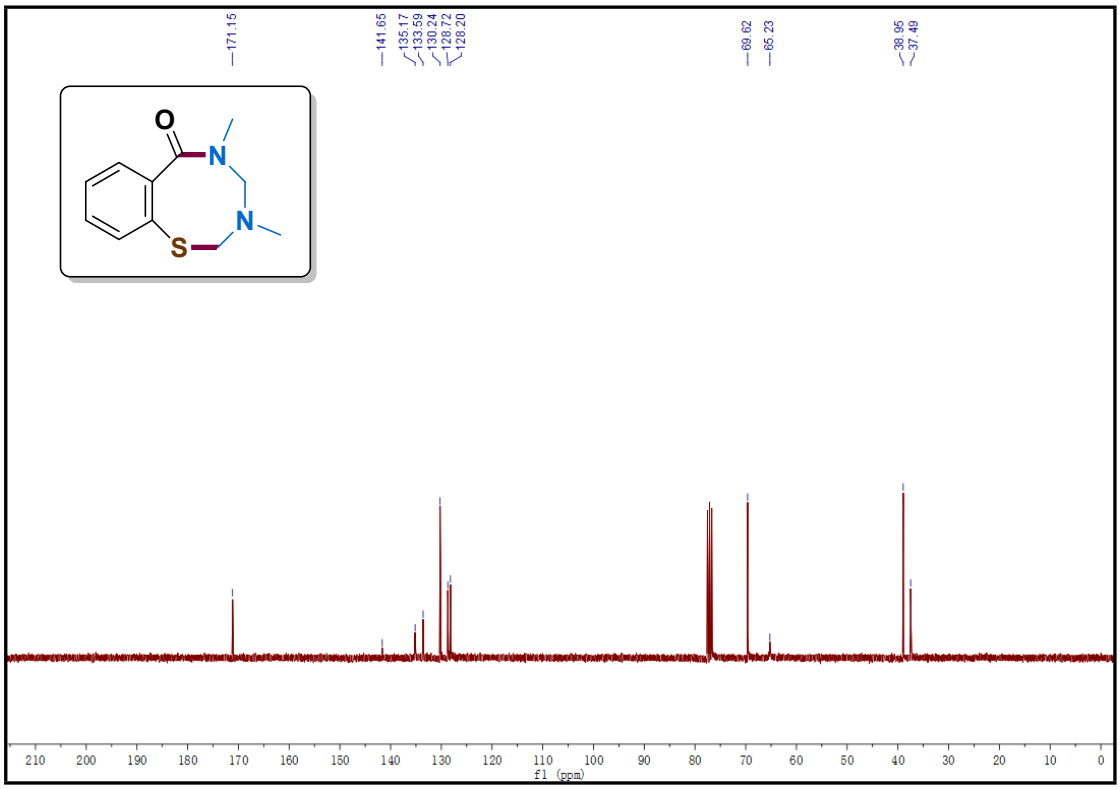


CH_2Cl_2 (2 mL) was added to a mixture of 3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one **4p** (51mg, 0.2 mmol), *m*-CPBA (104 mg, 0.6 mmol) in a sealed tube. Then, the mixture was stirred at RT for about 12 h. Upon completion of the reaction, the solvent was evaporated under reduced pressure and the residue was purified by flash column chromatograph (silica gel, petroleum ether:EtOAc = 10:1, v/v) to give the desired **7** as white solid (42.4 mg, 74%). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.18 (dd, *J* = 7.4, 1.5 Hz, 1H), 7.81 – 7.75 (m, 1H), 7.71 – 7.58 (m, 2H), 7.36 – 7.11 (m, 5H), 4.83 (s, 2H), 4.51 (s, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 161.2, 137.9, 134.5, 133.6, 133.0, 130.9, 128.9, 128.4, 128.2, 127.9, 122.1, 64.7, 52.0. HRMS (ESI, m/z) calcd for $C_{15}H_{14}NO_3S$ $[M+H]^+$: 288.0689; found: 288.0689.

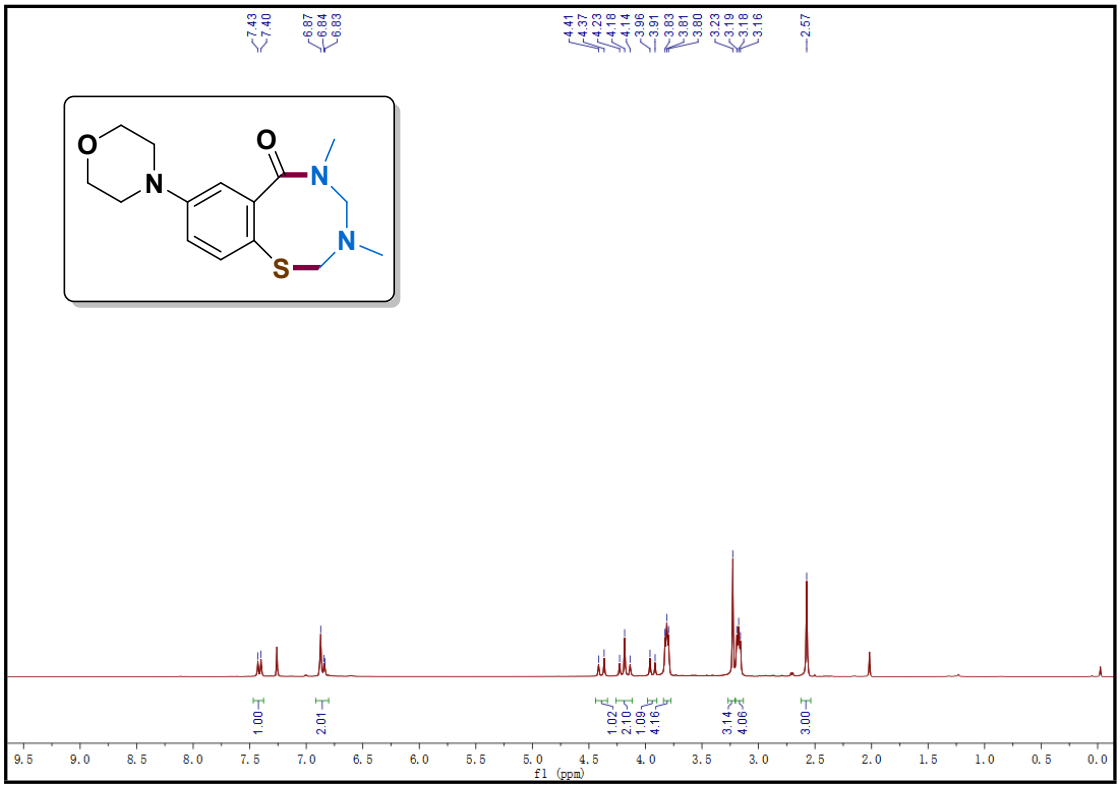
7. NMR spectroscopic data for the products

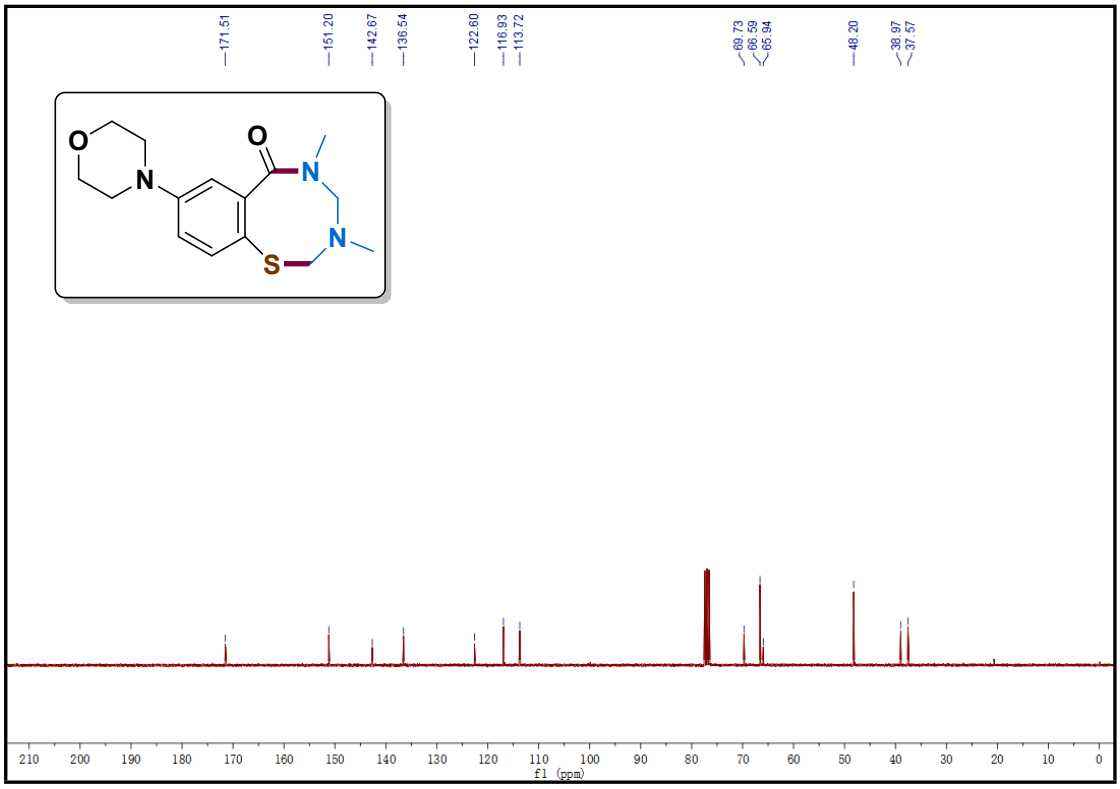
3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3a)



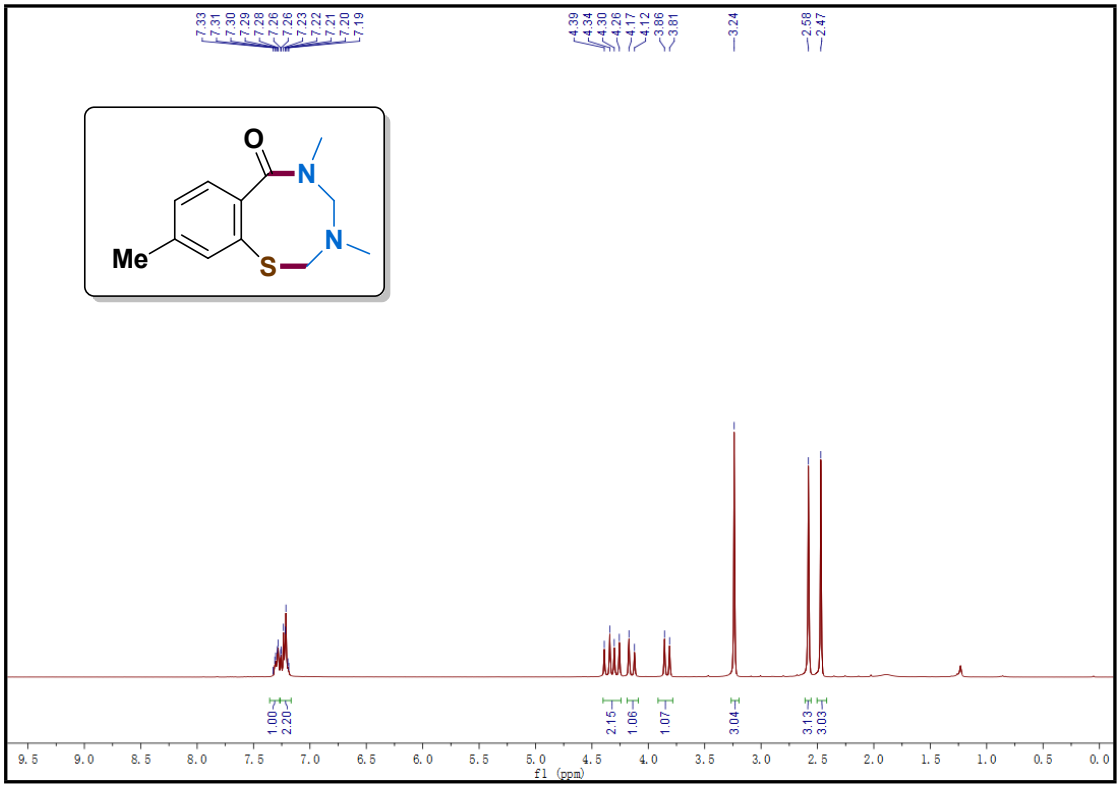


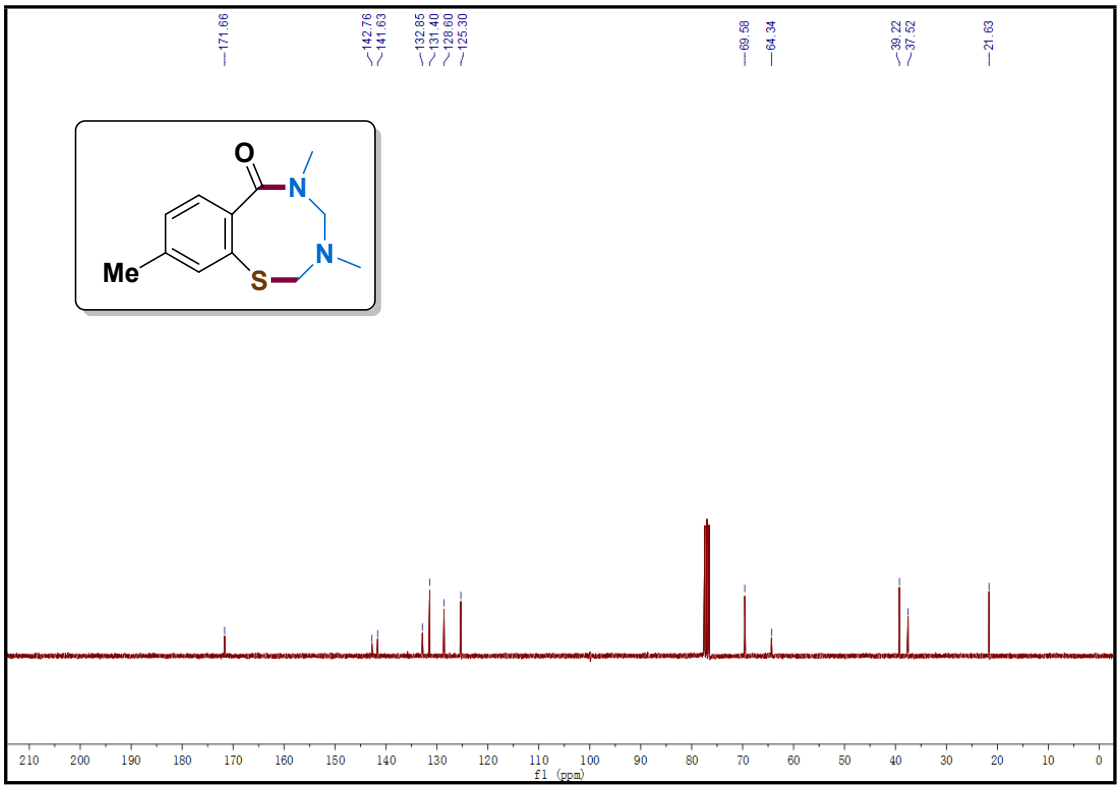
3,5-dimethyl-8-morpholino-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3b)



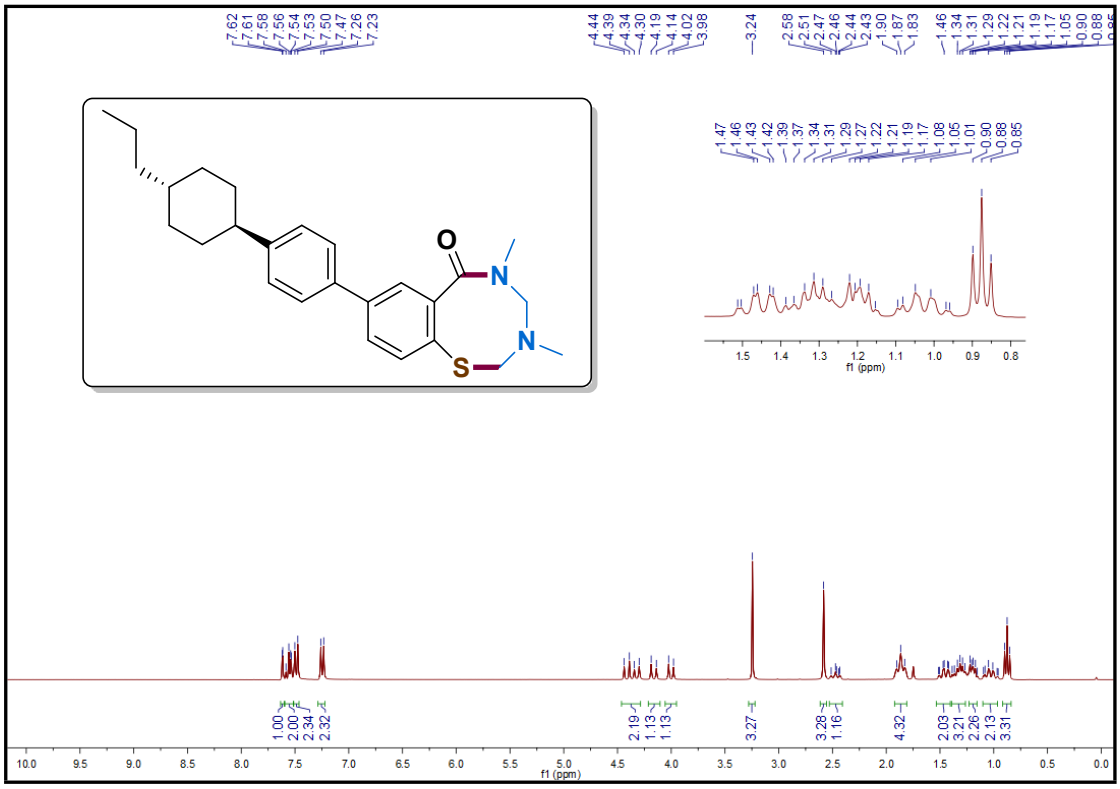


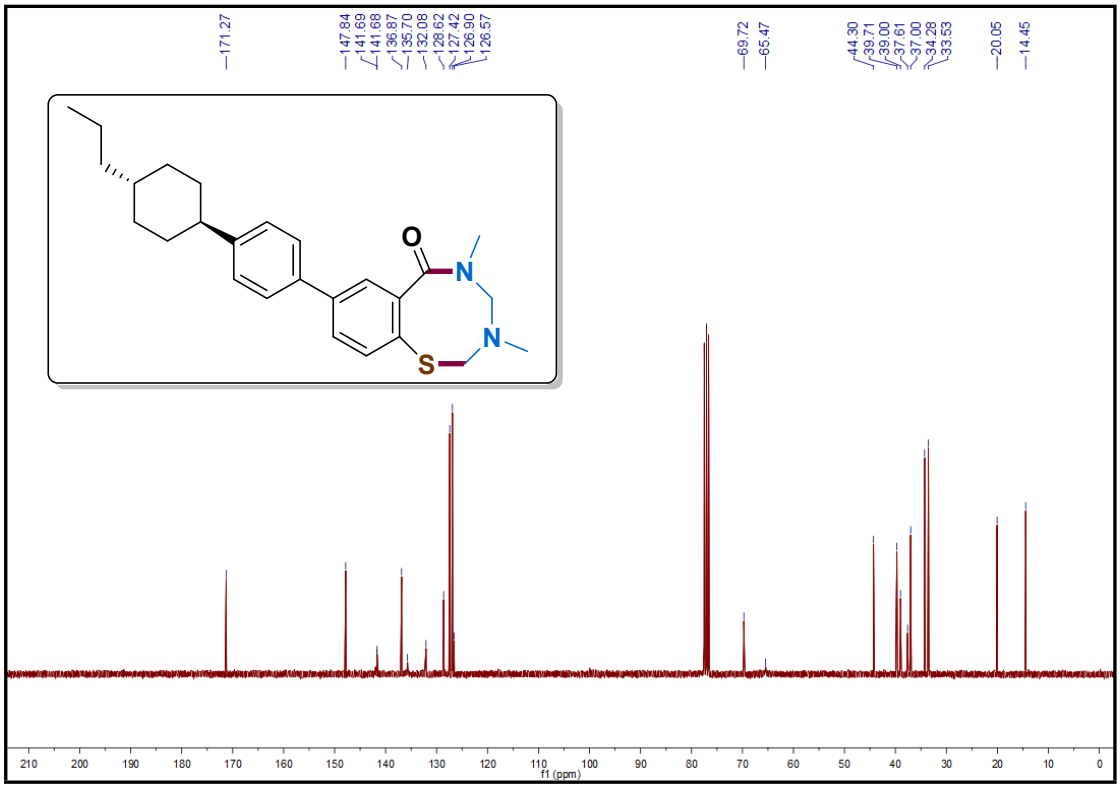
3,5,8-trimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3c)



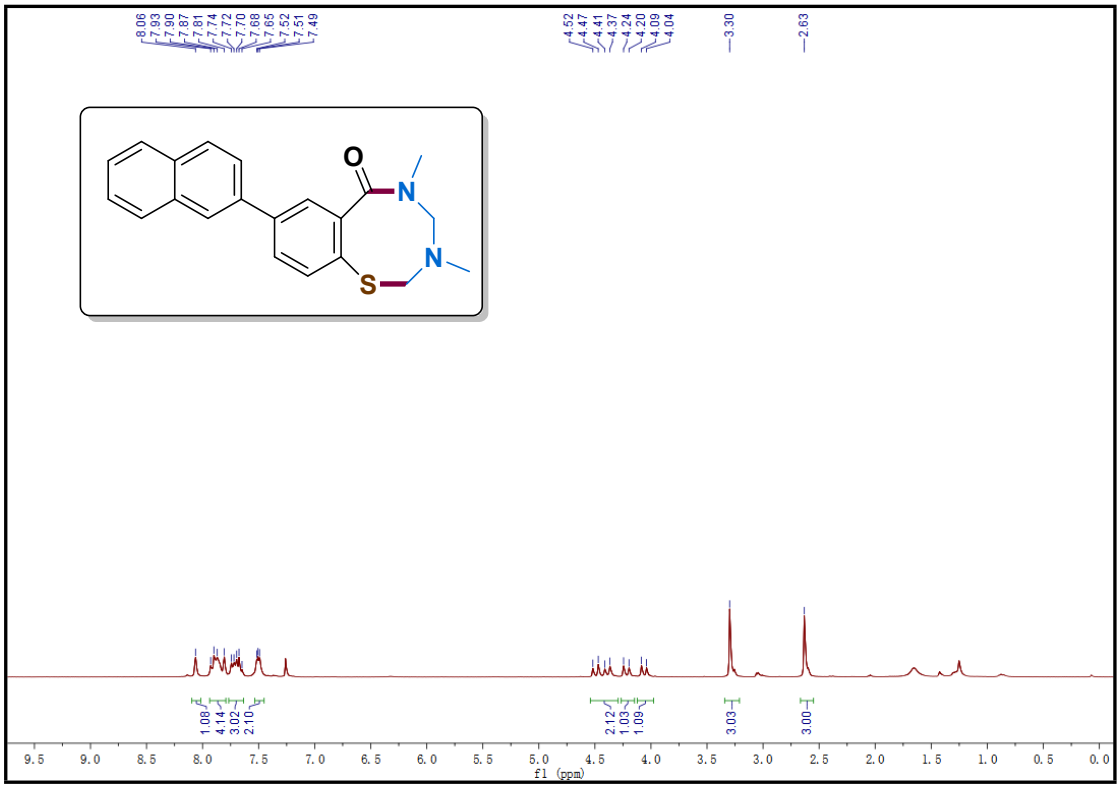


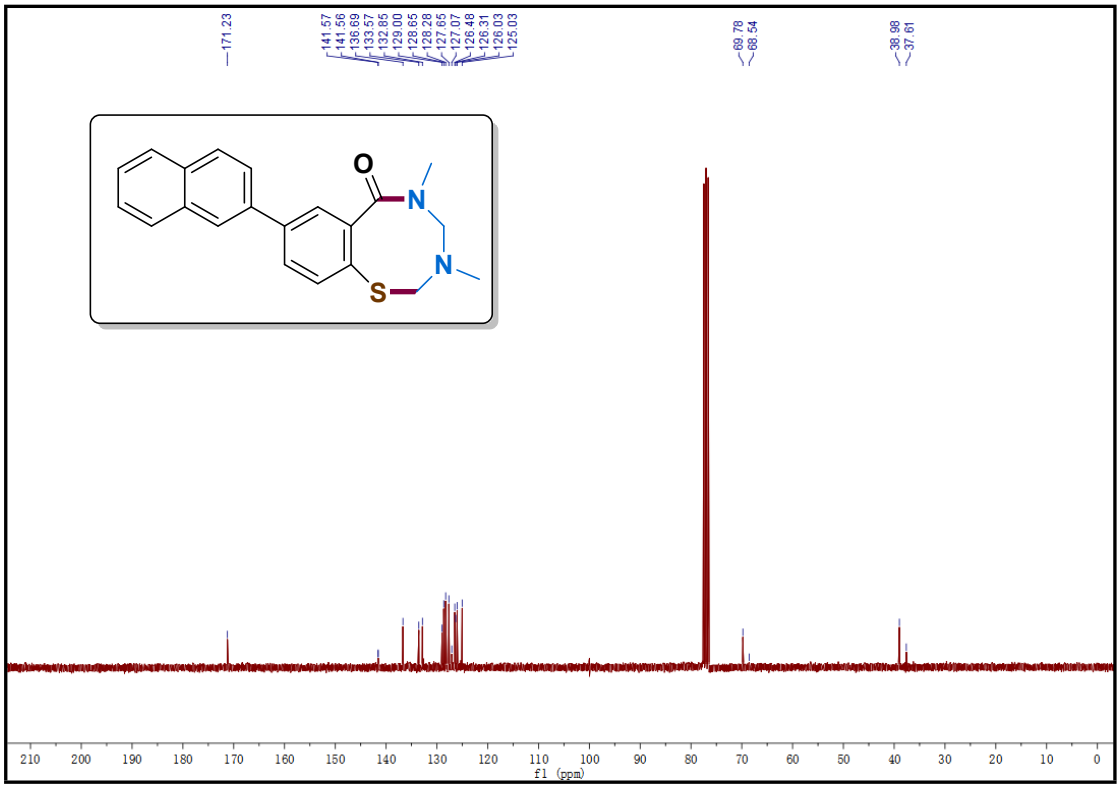
3,5-dimethyl-8-(4-((1s,4r)-4-propylcyclohexyl)phenyl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3d)



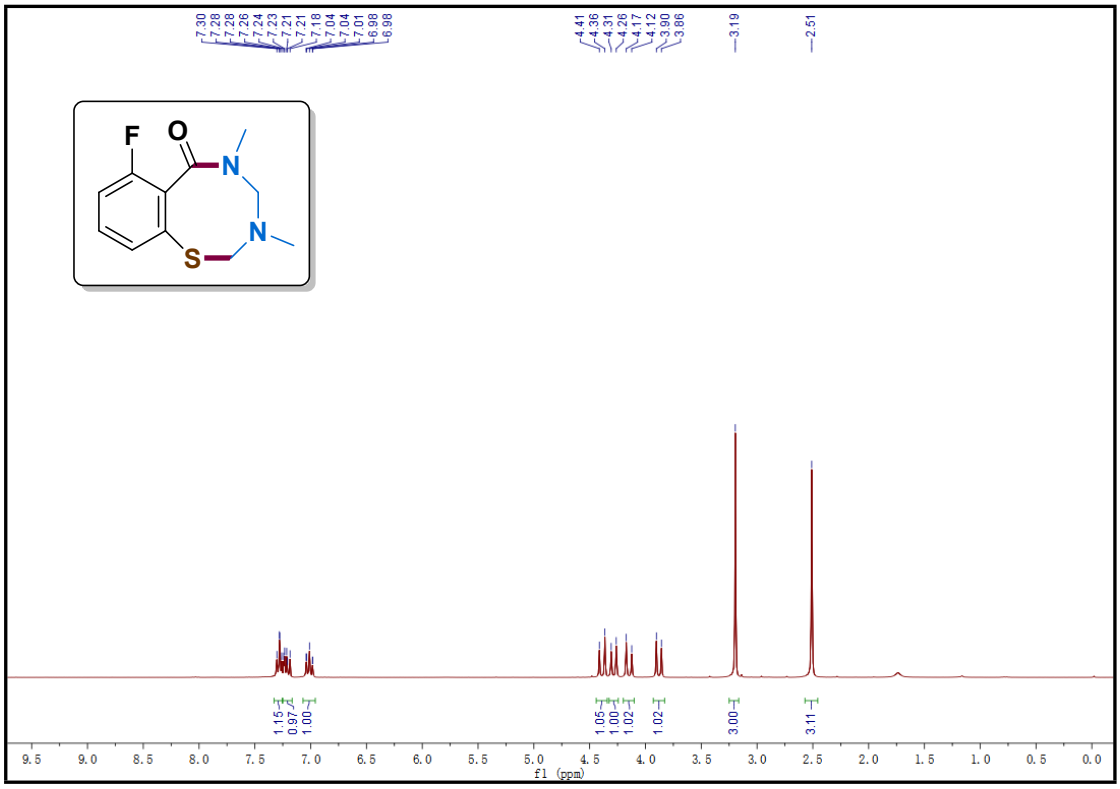


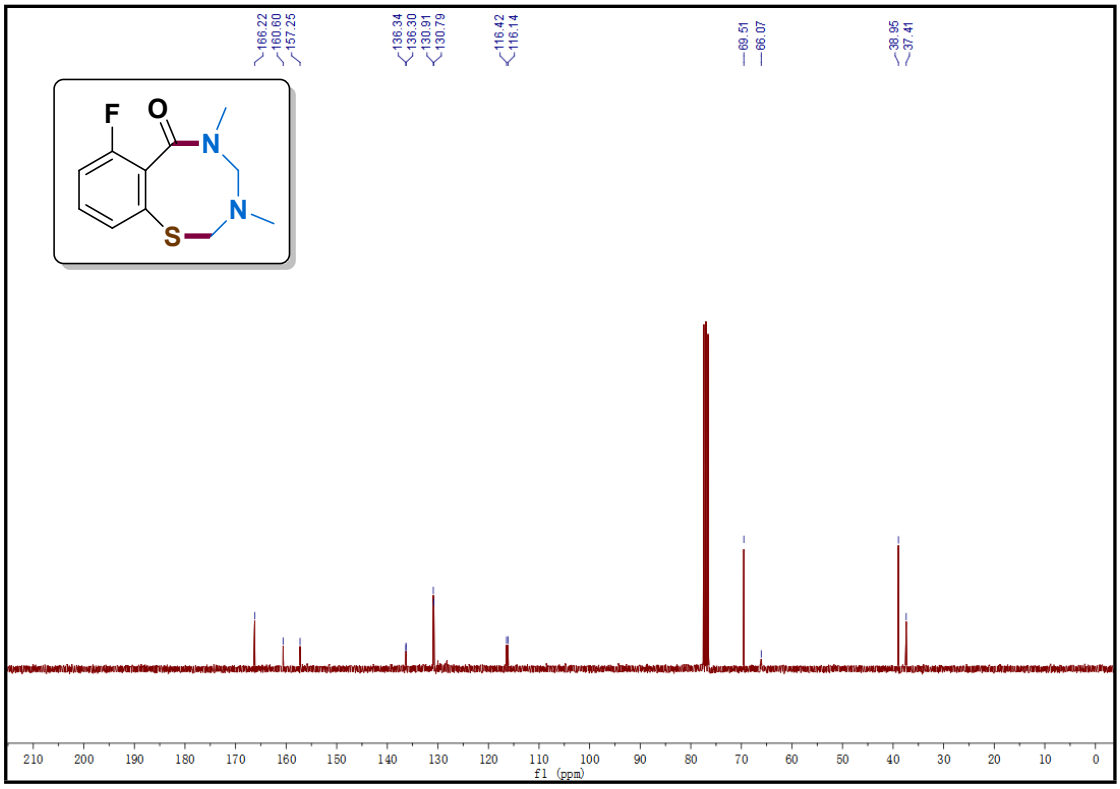
3,5-dimethyl-8-(naphthalen-2-yl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3e)



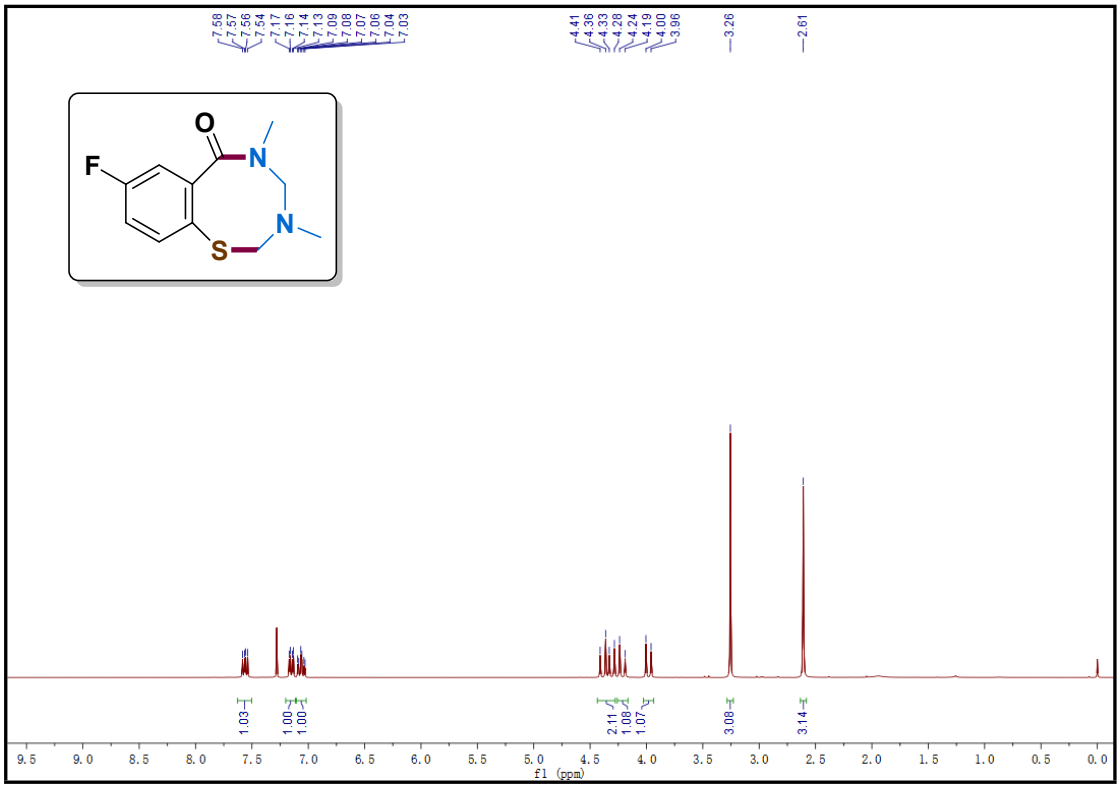


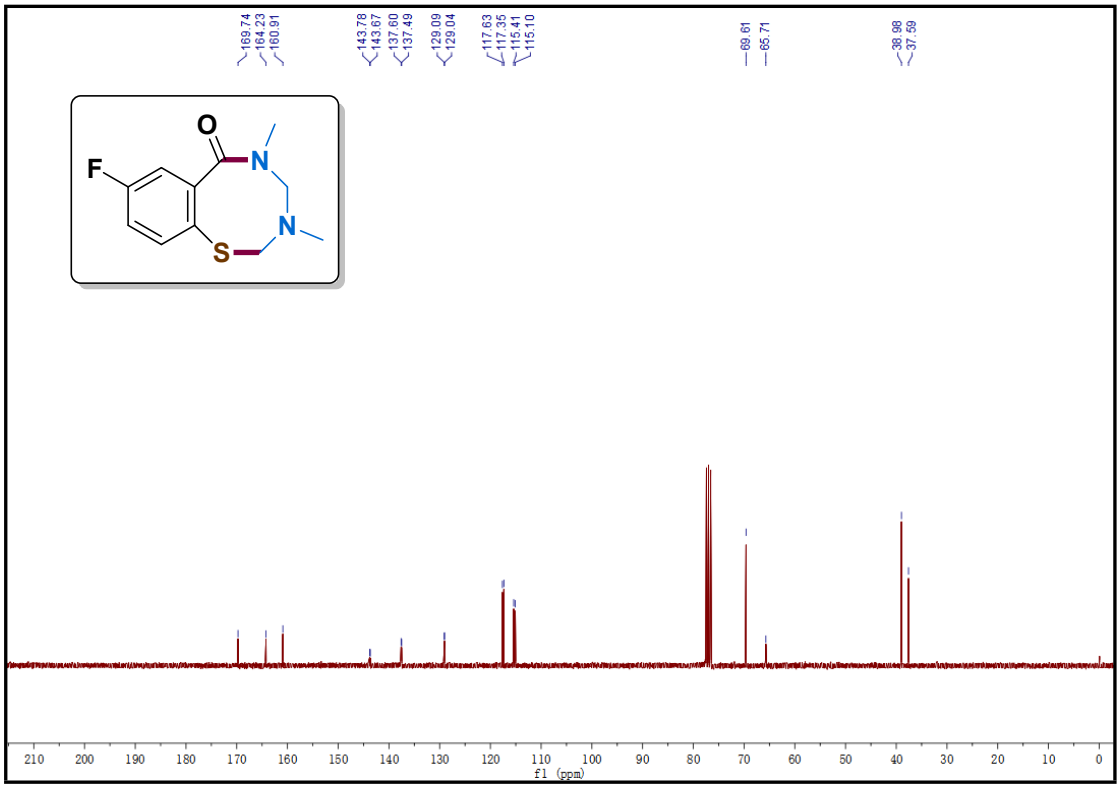
7-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3f)



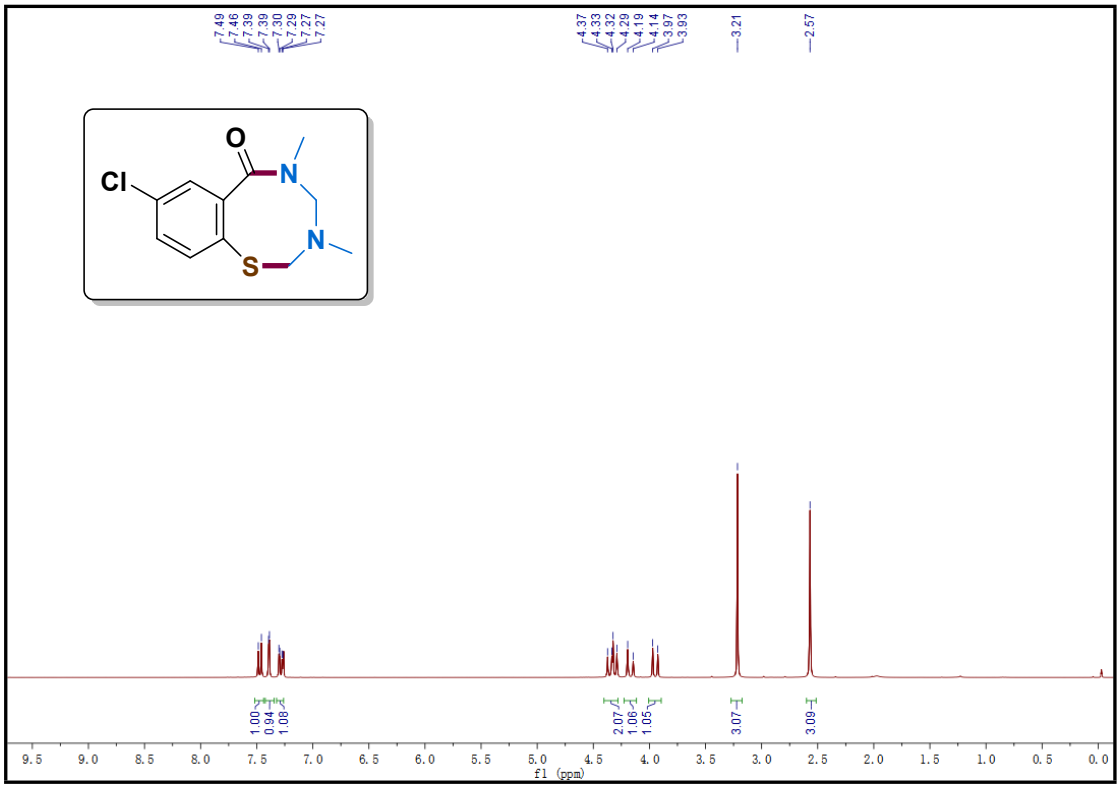


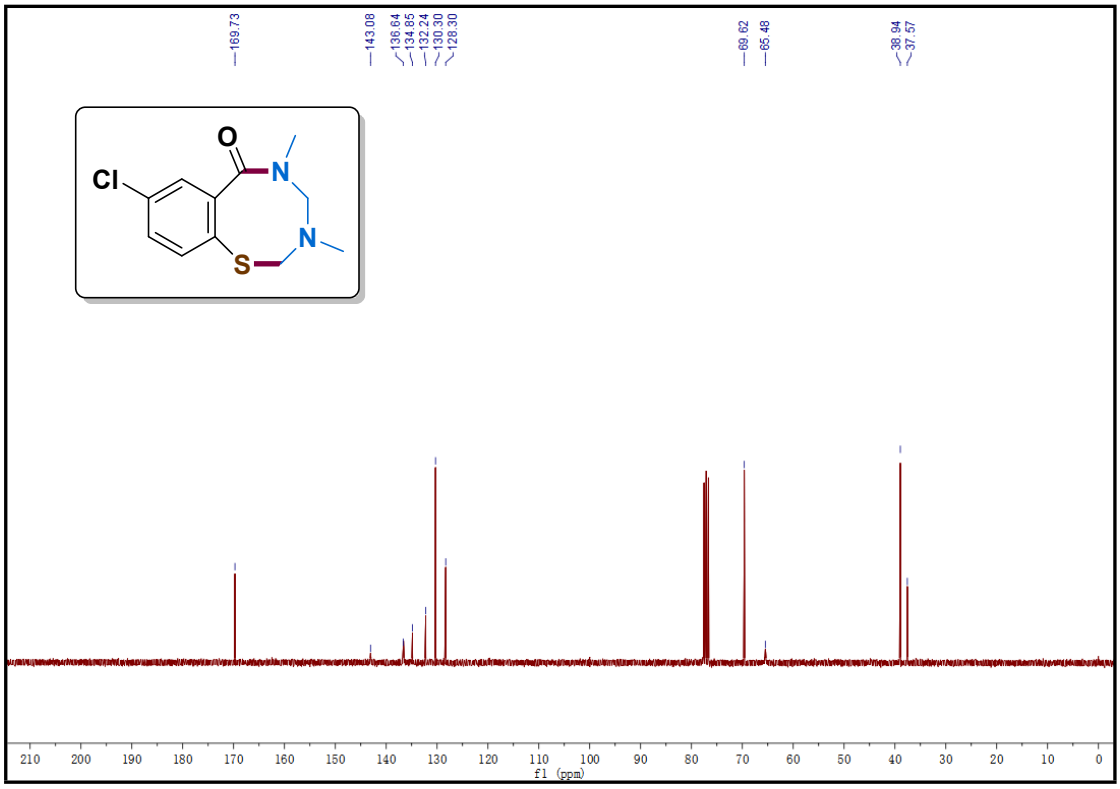
8-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3g)



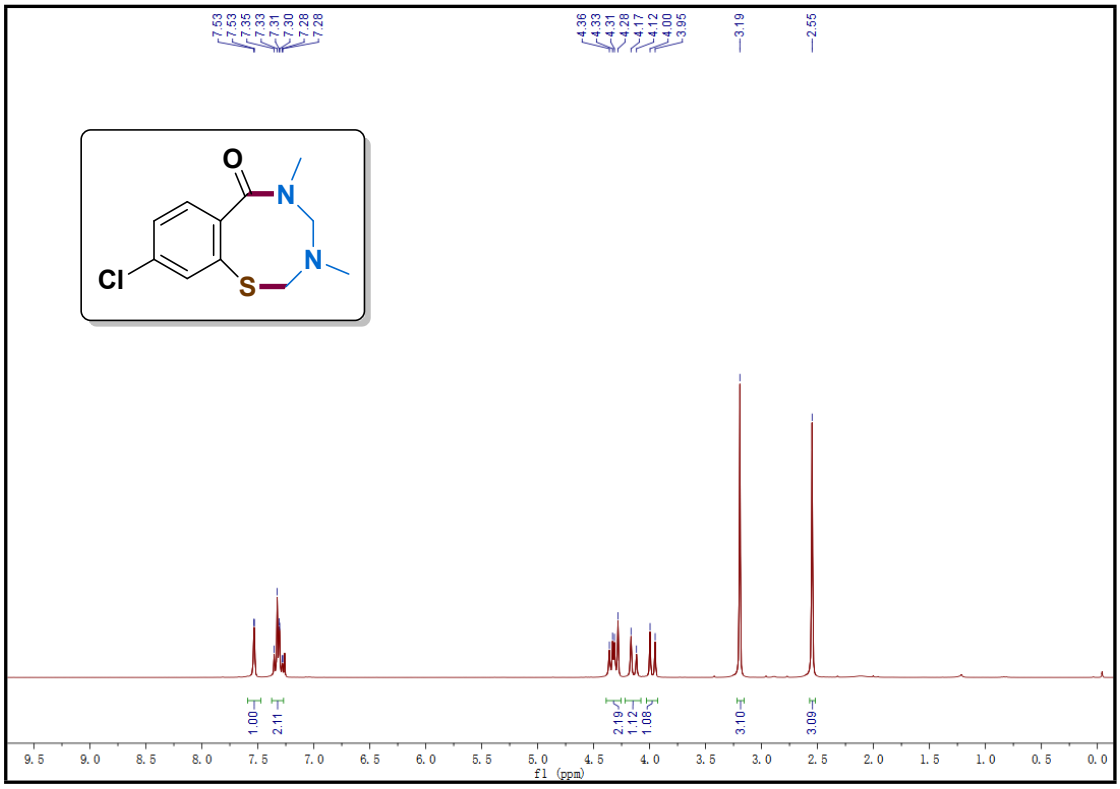


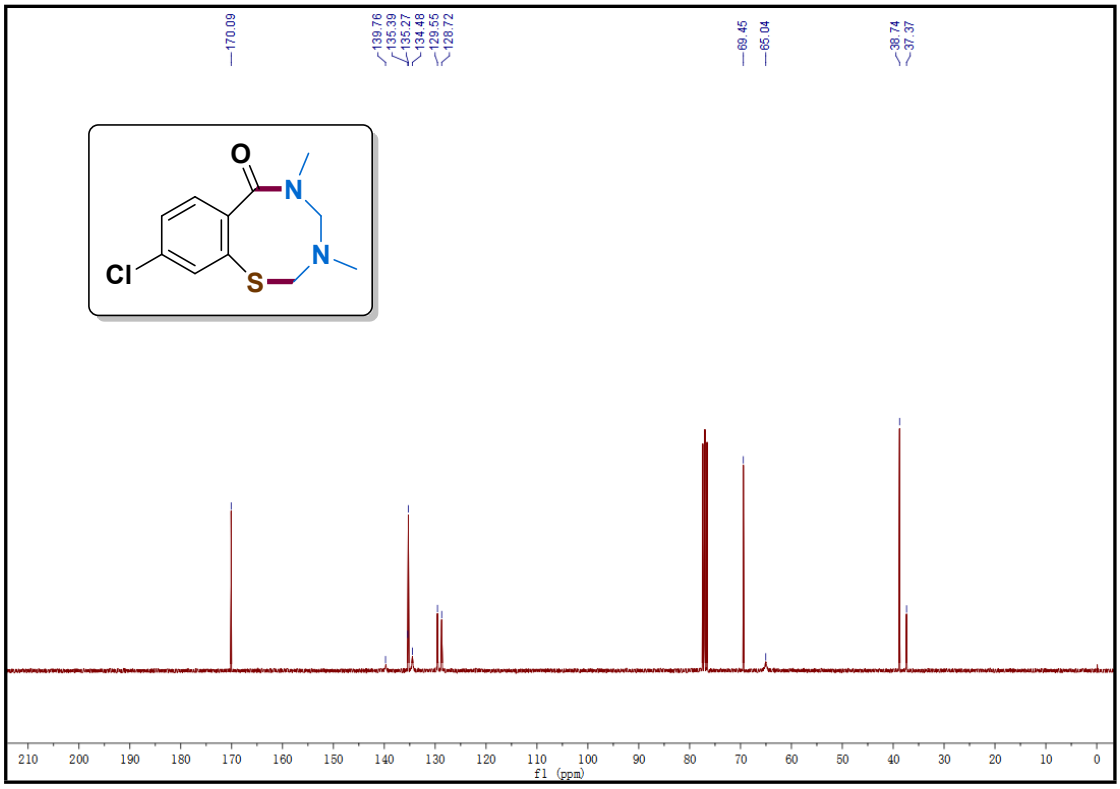
8-chloro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3h)



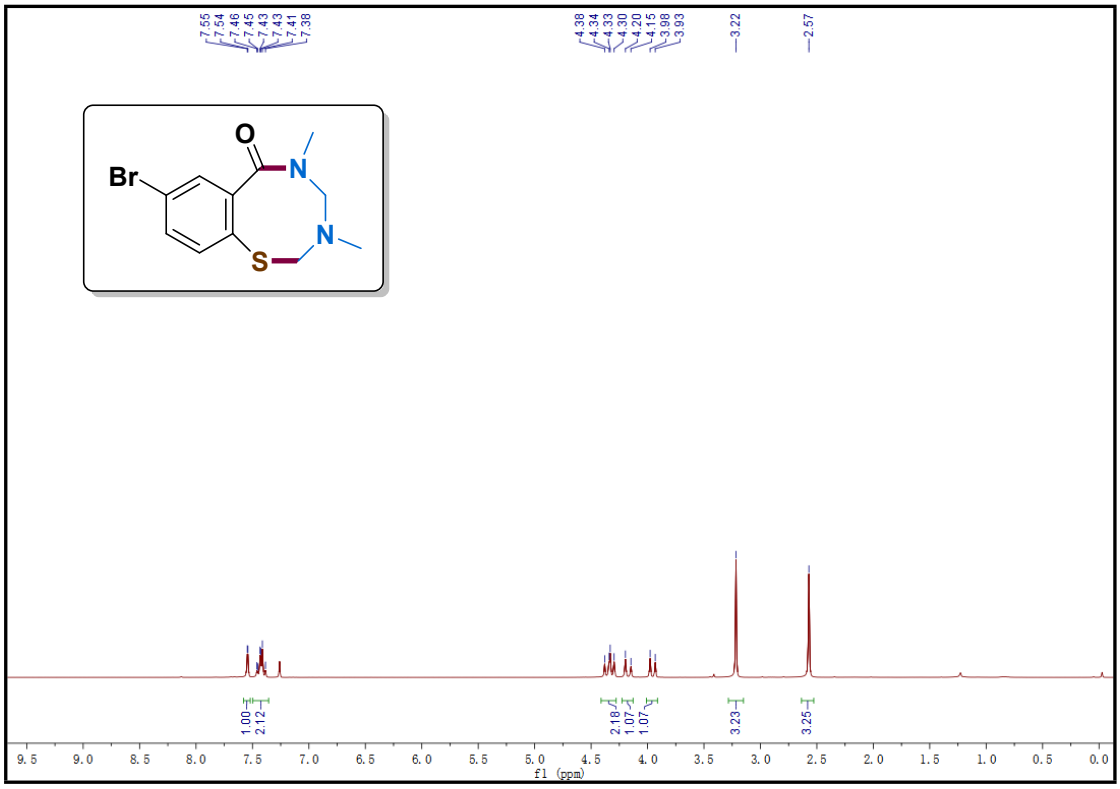


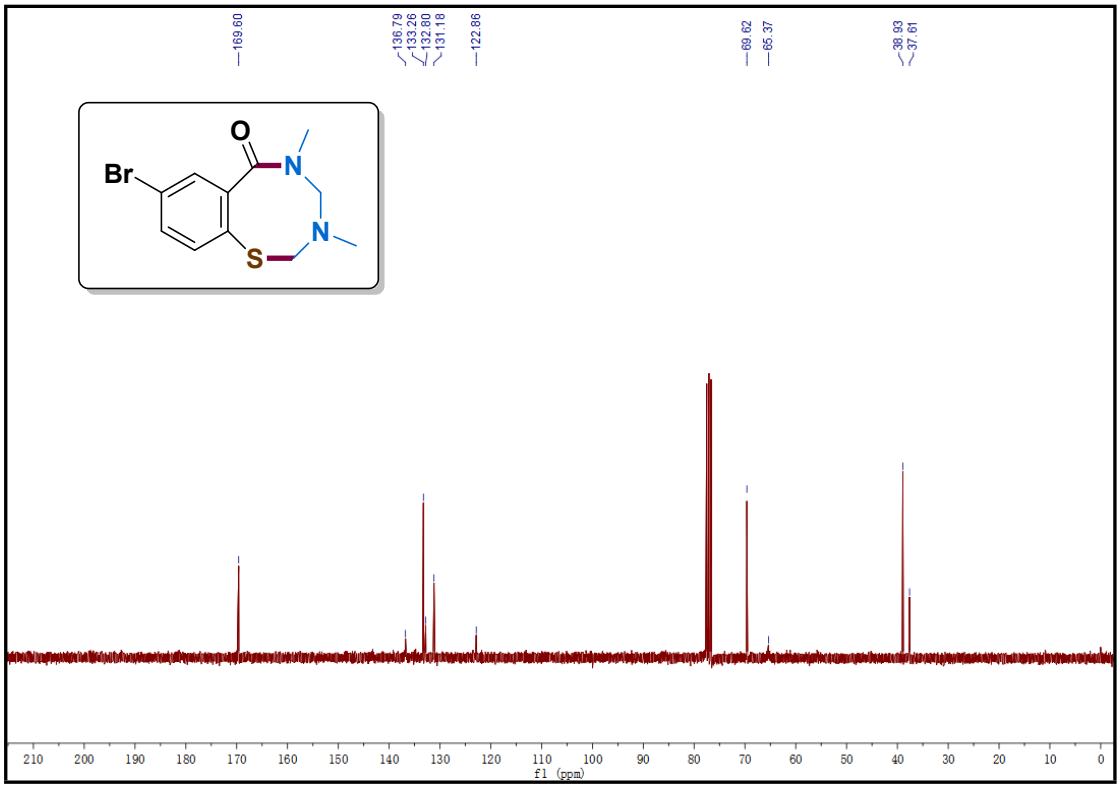
9-chloro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3i)



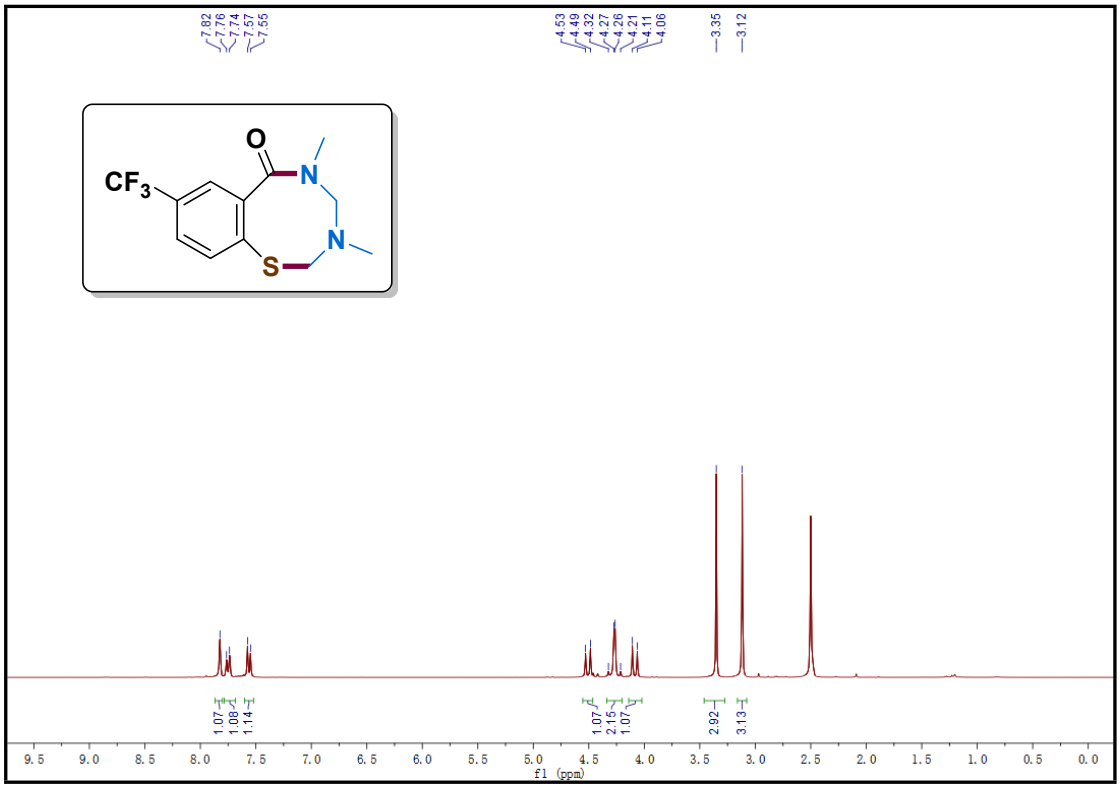


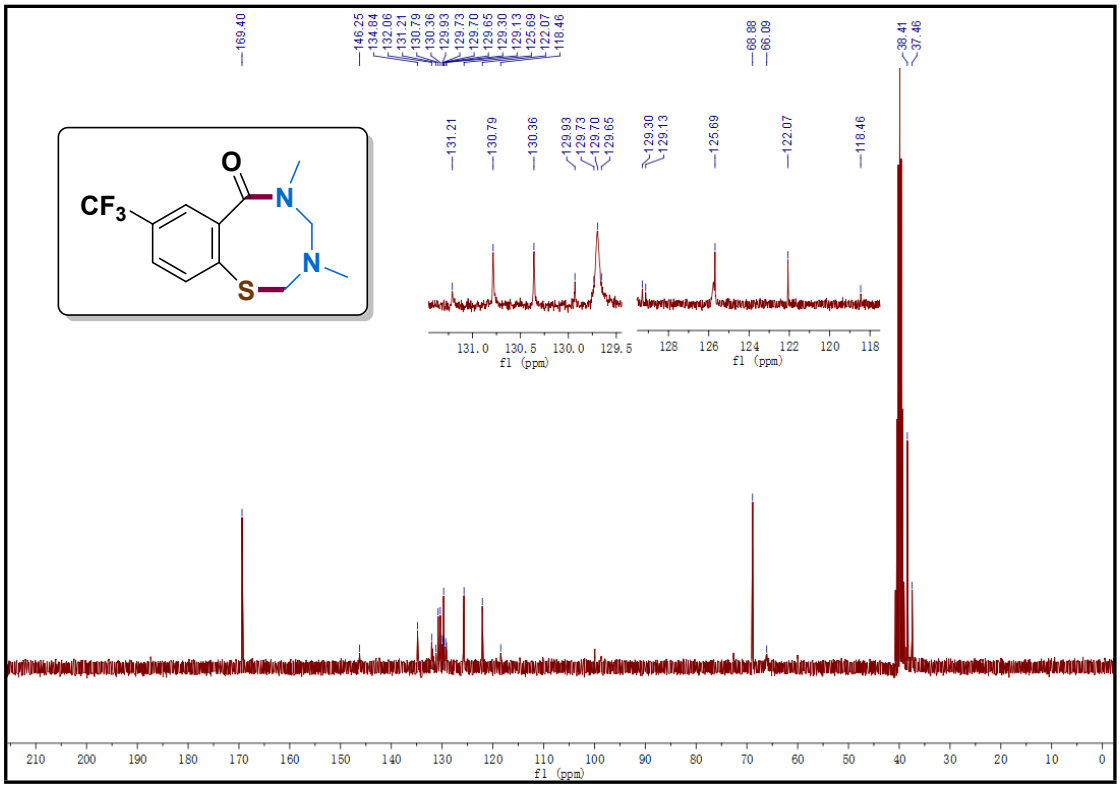
8-bromo-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3j)



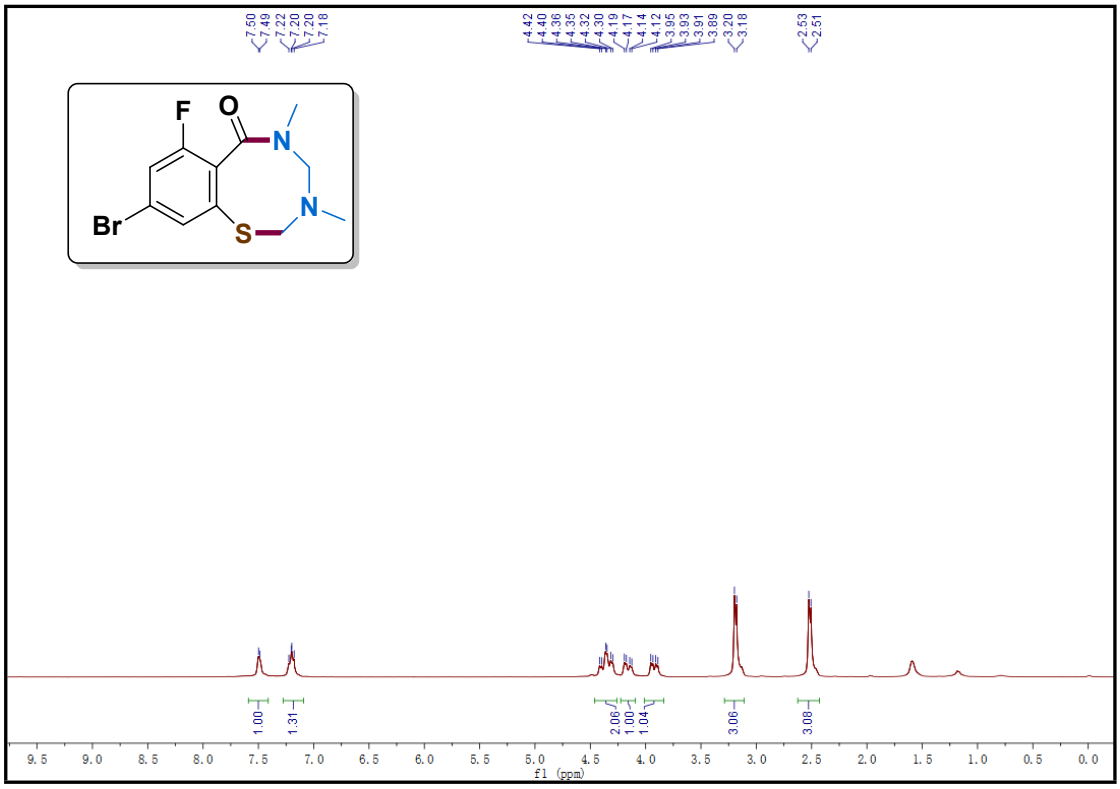


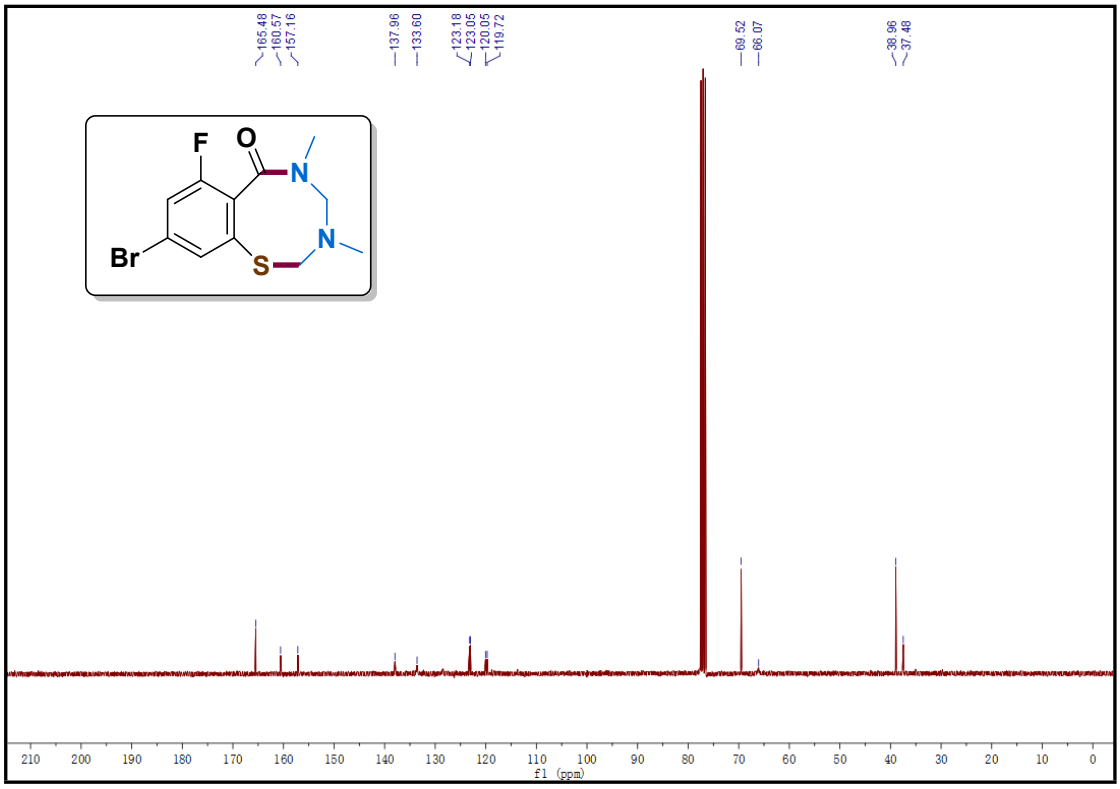
3,5-dimethyl-8-(trifluoromethyl)-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3k)



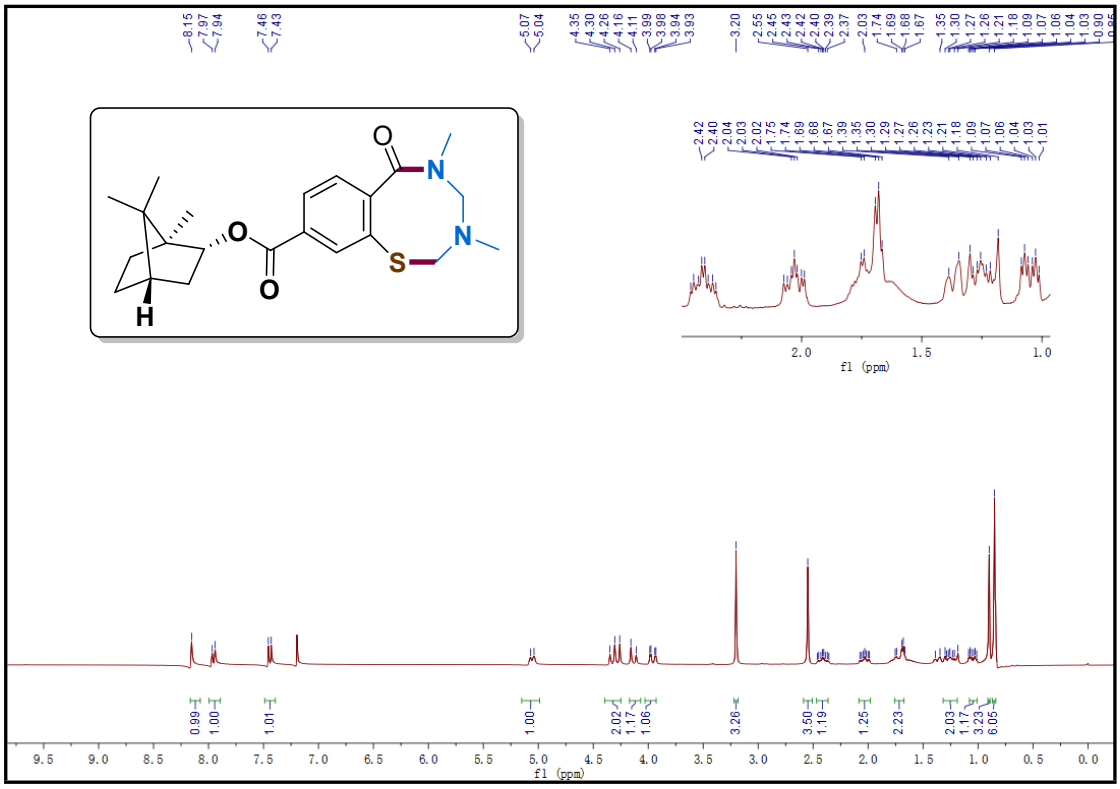


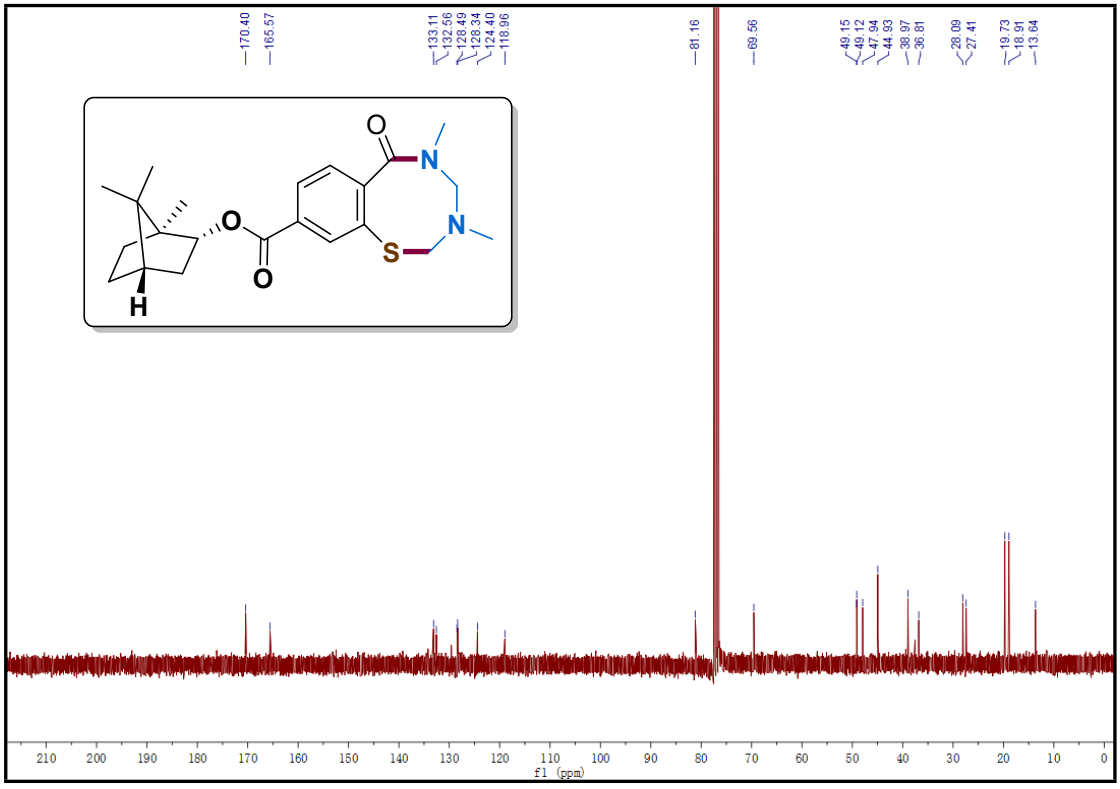
9-bromo-7-fluoro-3,5-dimethyl-2,3,4,5-tetrahydro-6H-benzo[g][1,3,5]thiadiazocin-6-one (3l)



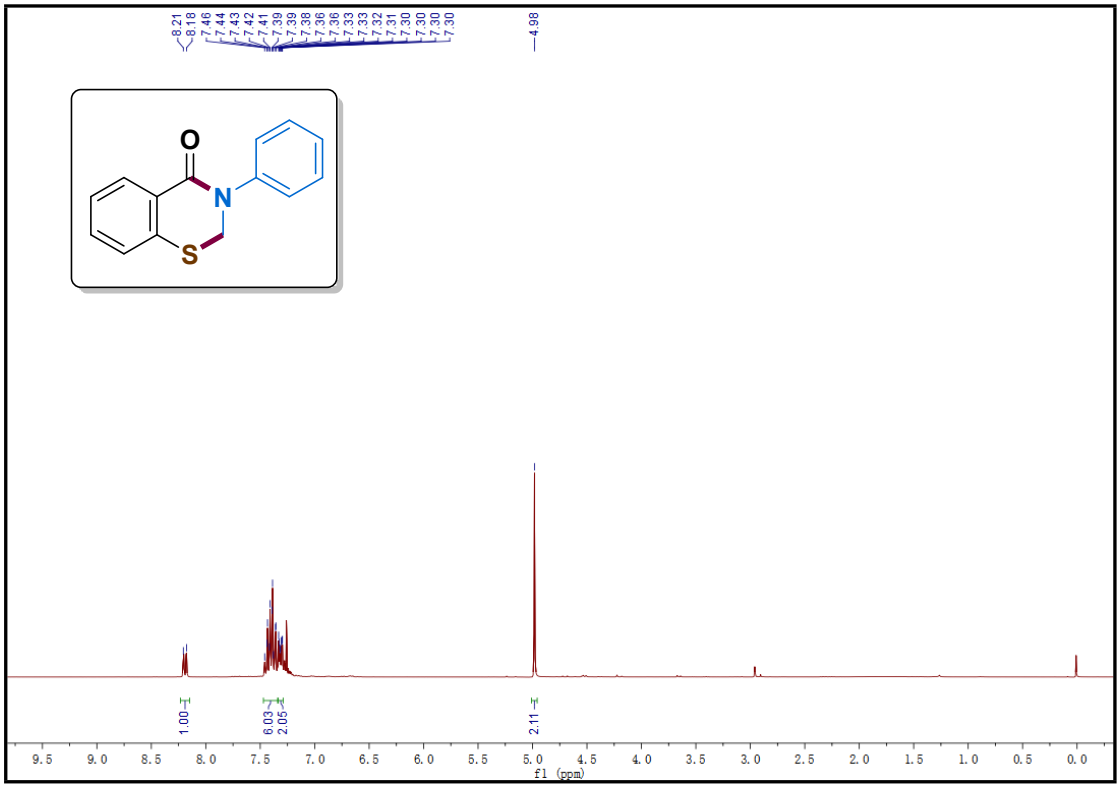


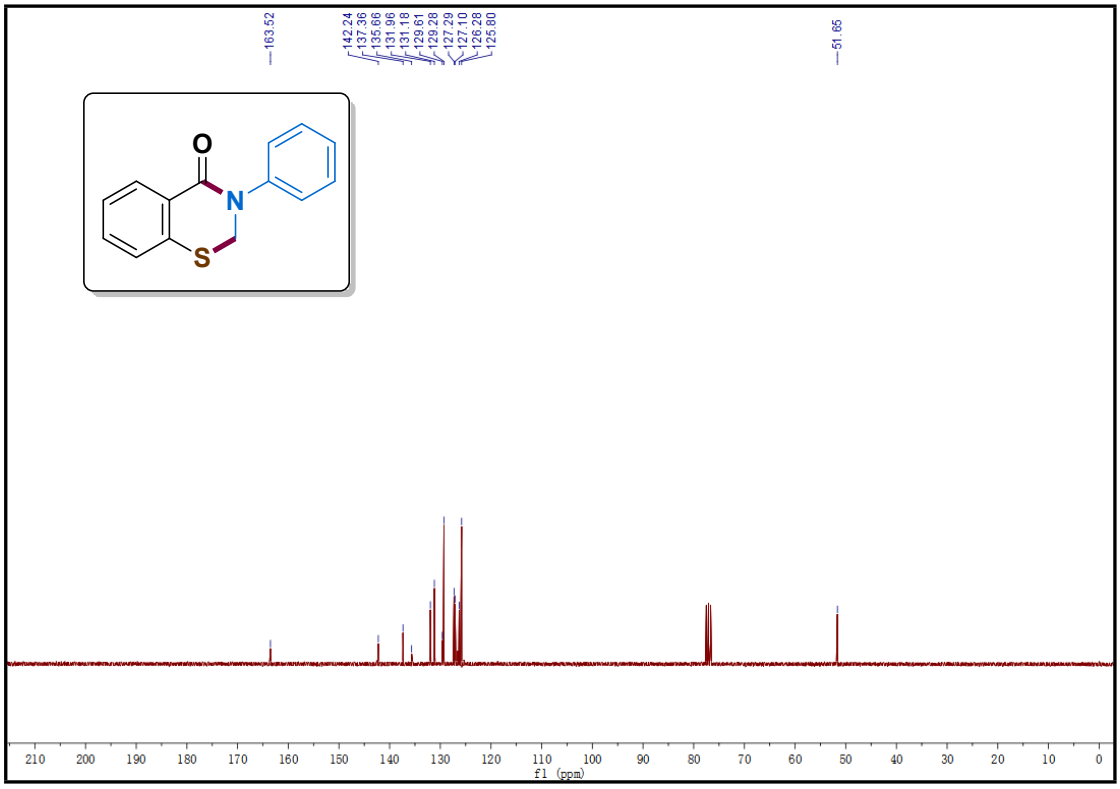
(1S,2R,4S)-1,7,7-trimethylbicyclo[2.2.1]heptan-2-yl 3,5-dimethyl-6-oxo-3,4,5,6-tetrahydro-2H-benzo[g][1,3,5]thiadiazocine-9-carboxylate (3m)



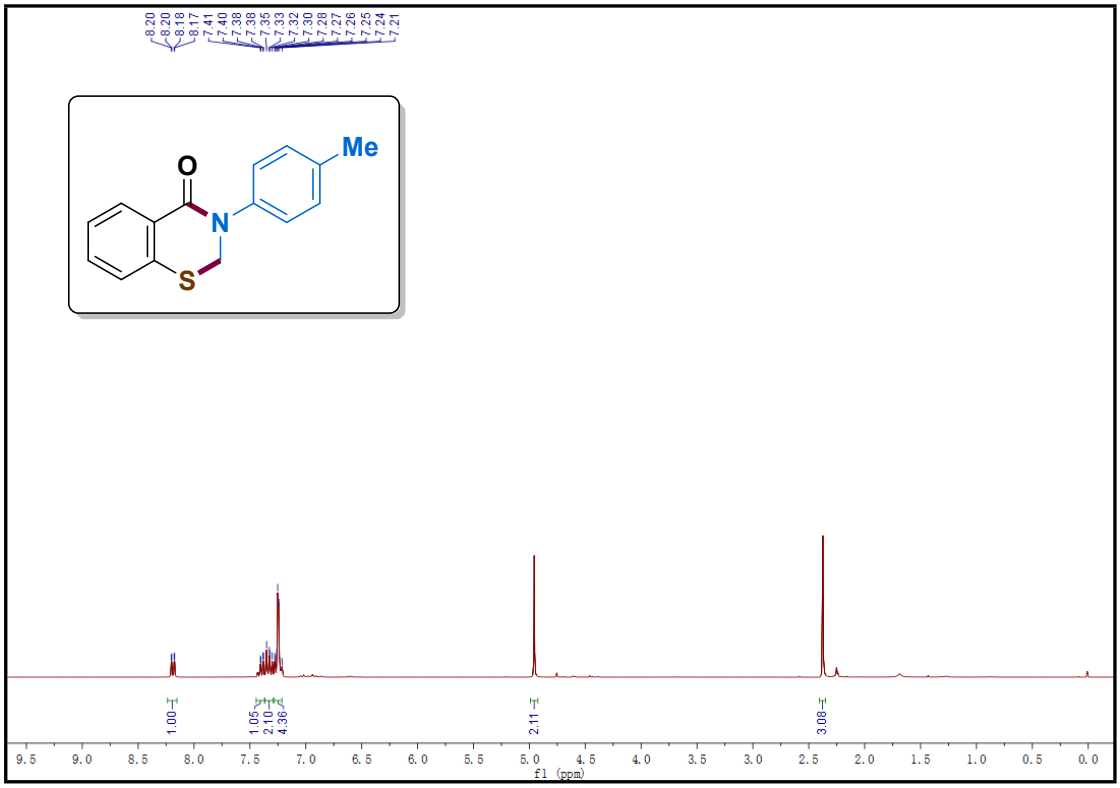


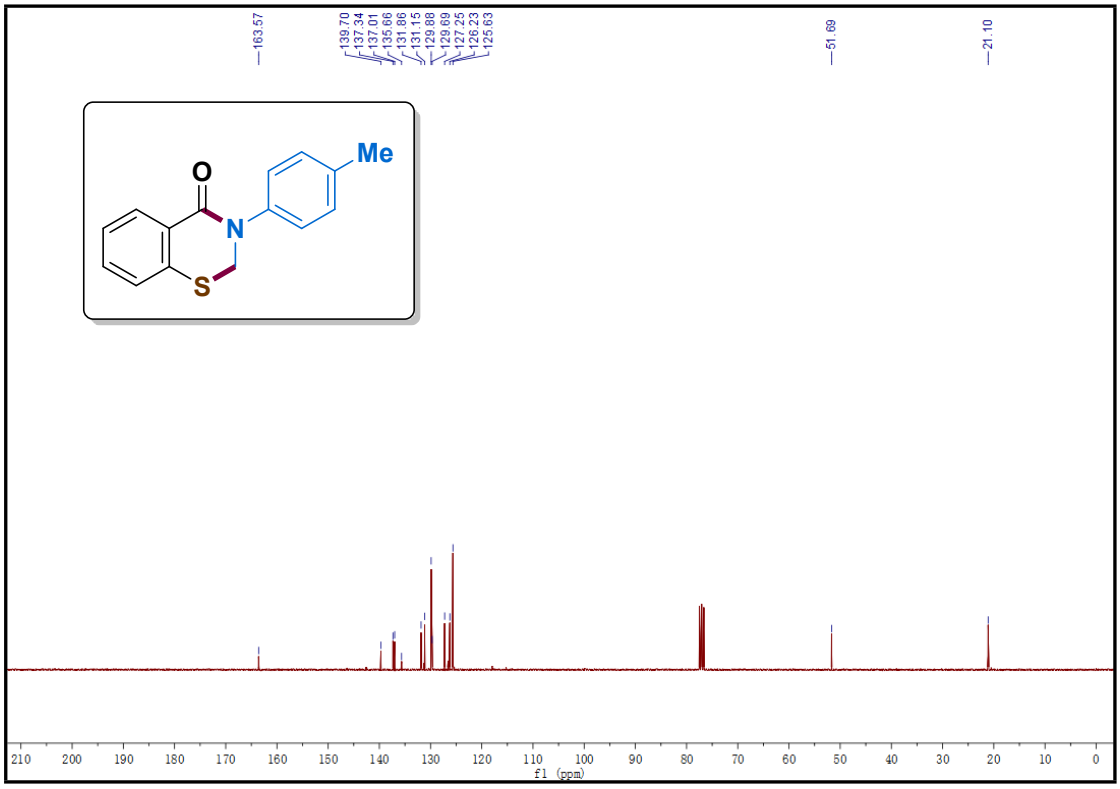
3-phenyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4a)



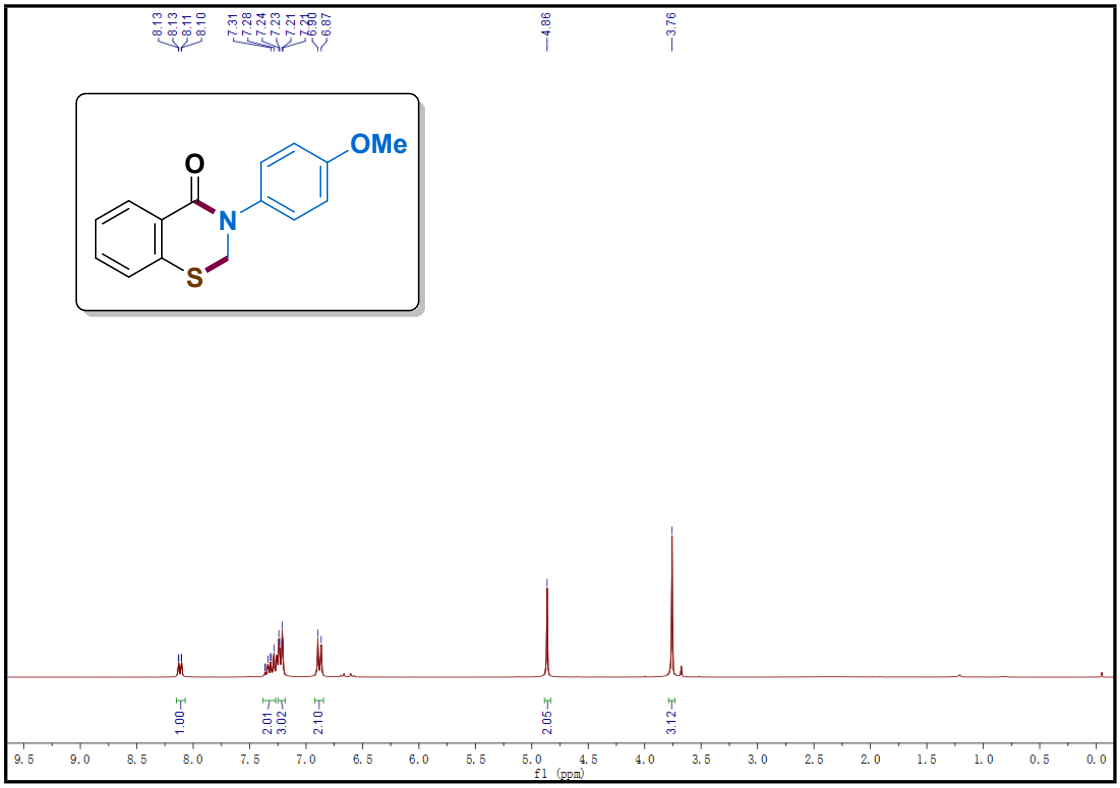


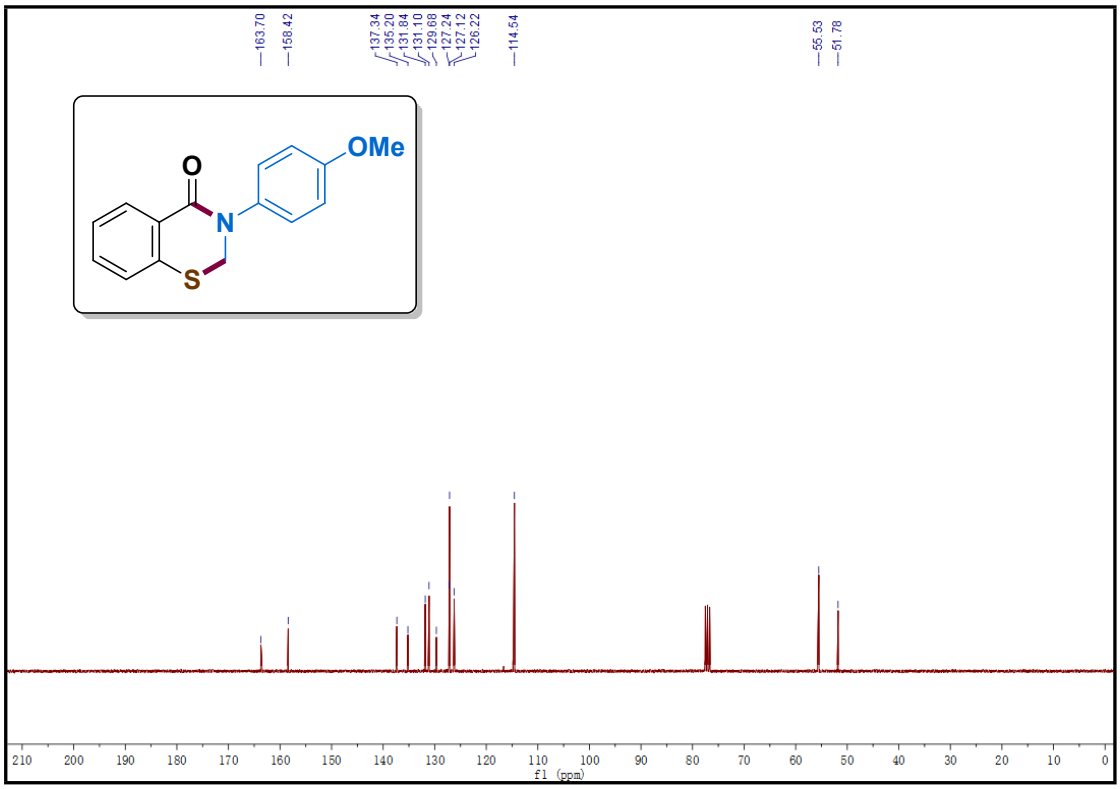
3-(p-tolyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4b)



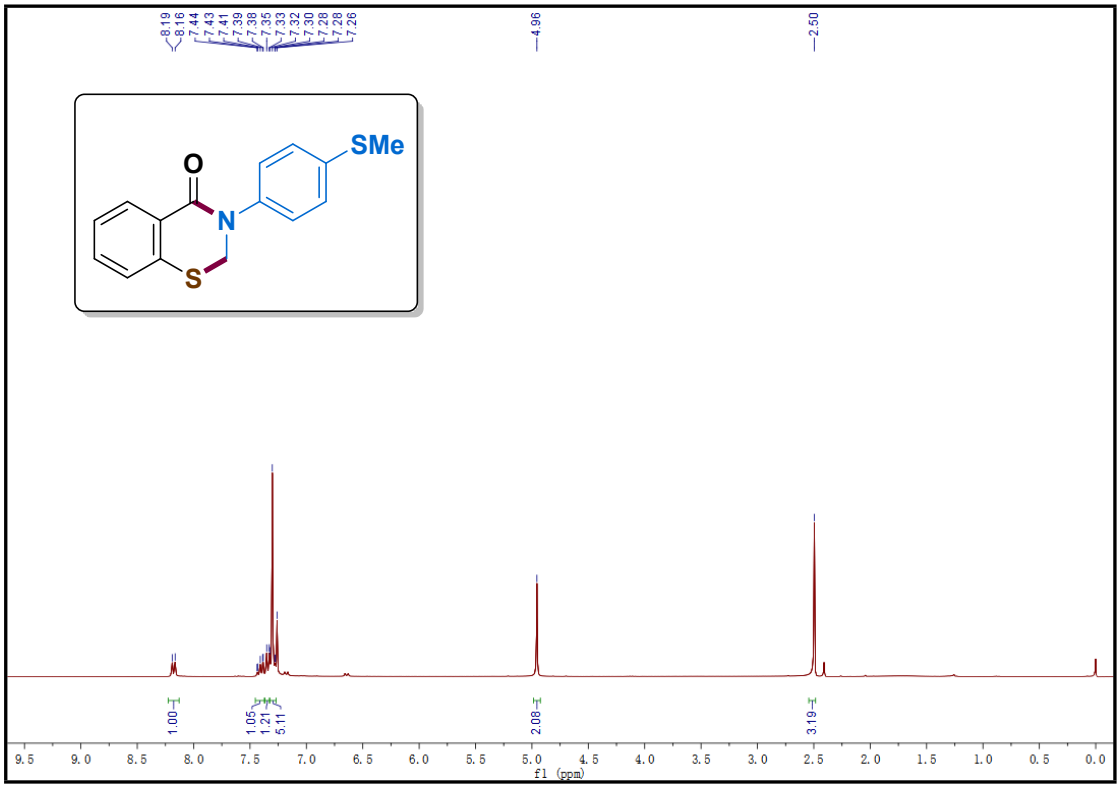


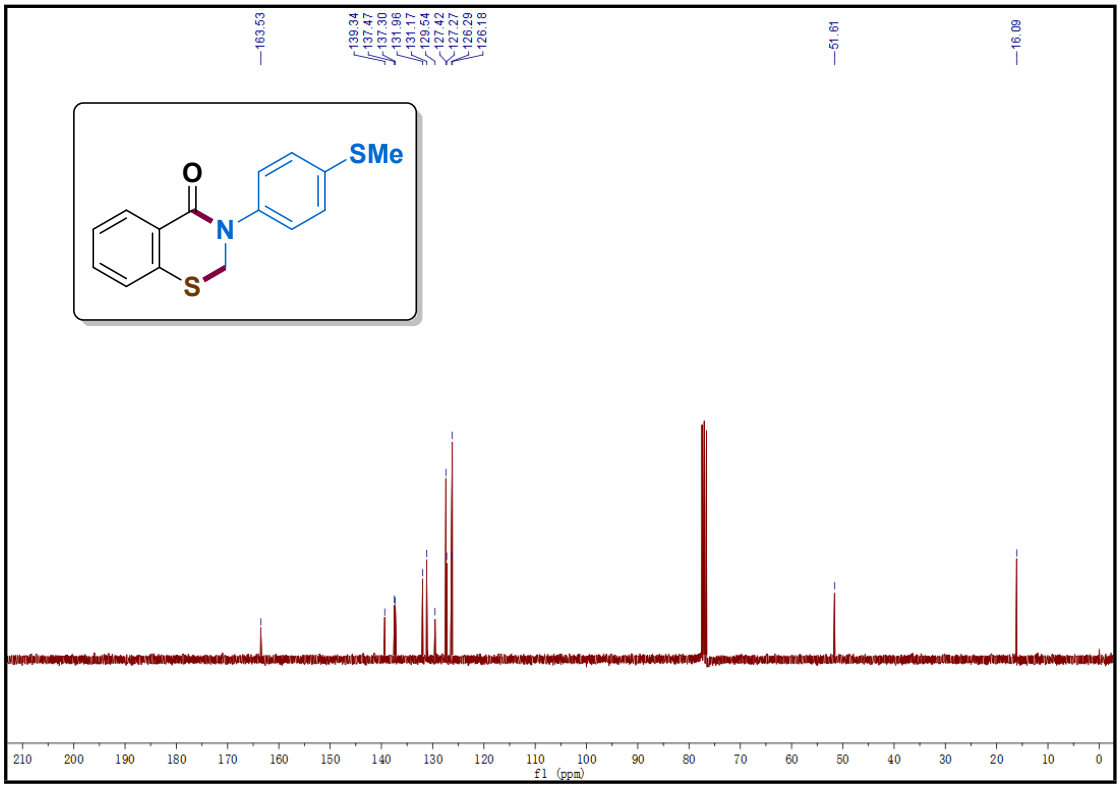
3-(4-methoxyphenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4c)



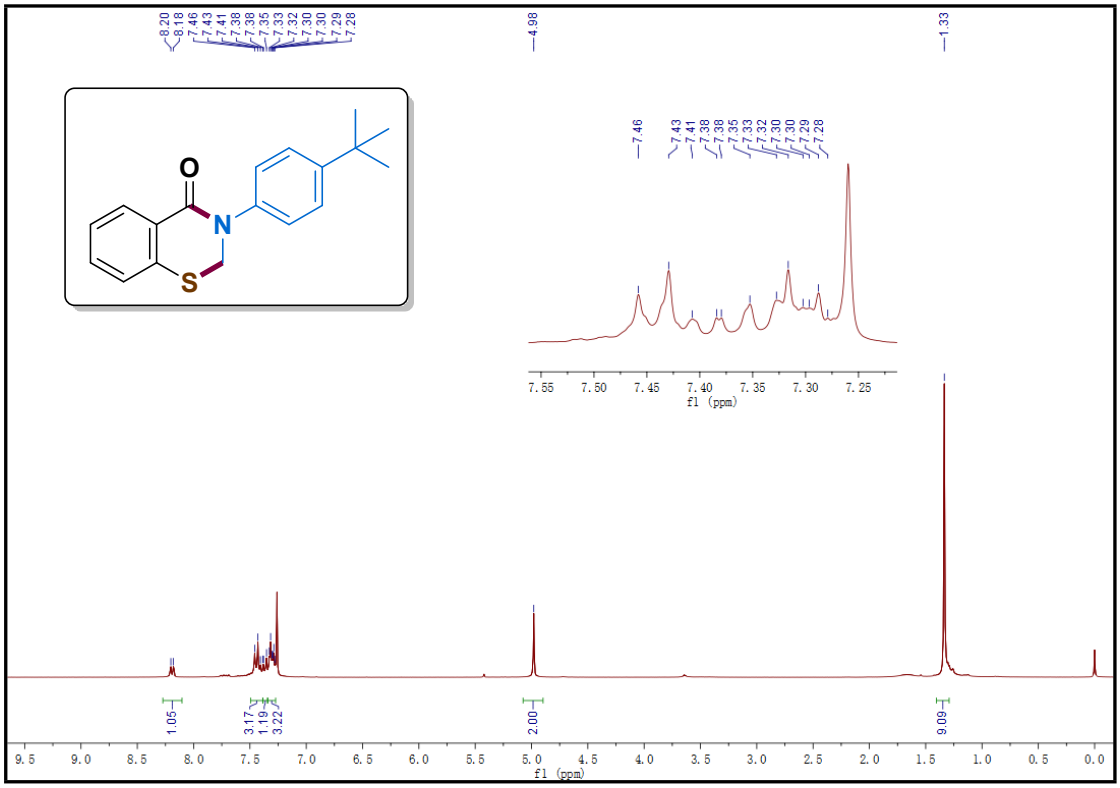


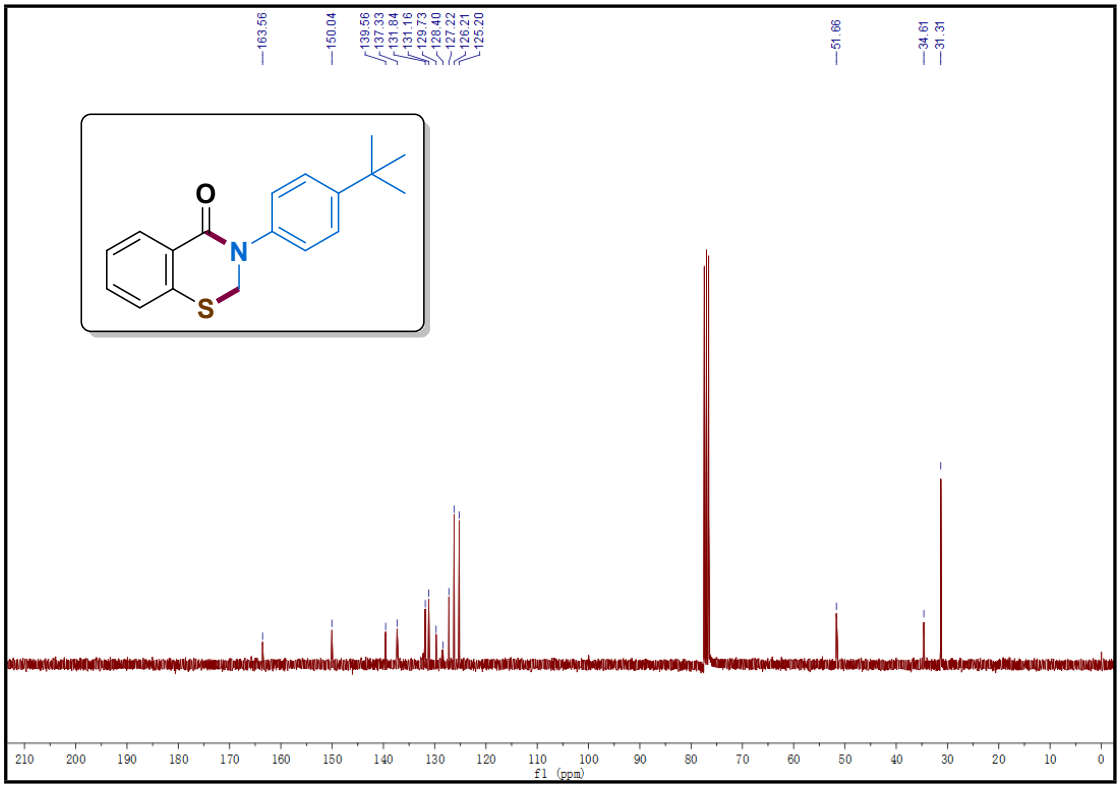
3-(4-(methylthio)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4d)



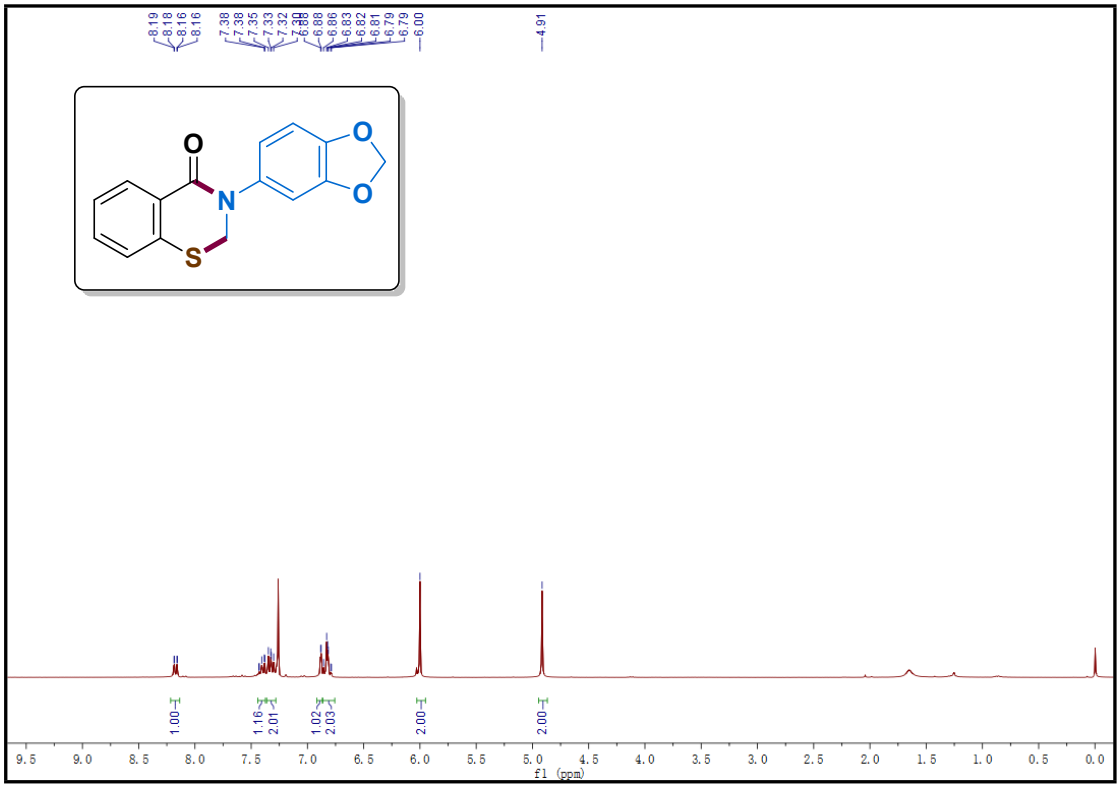


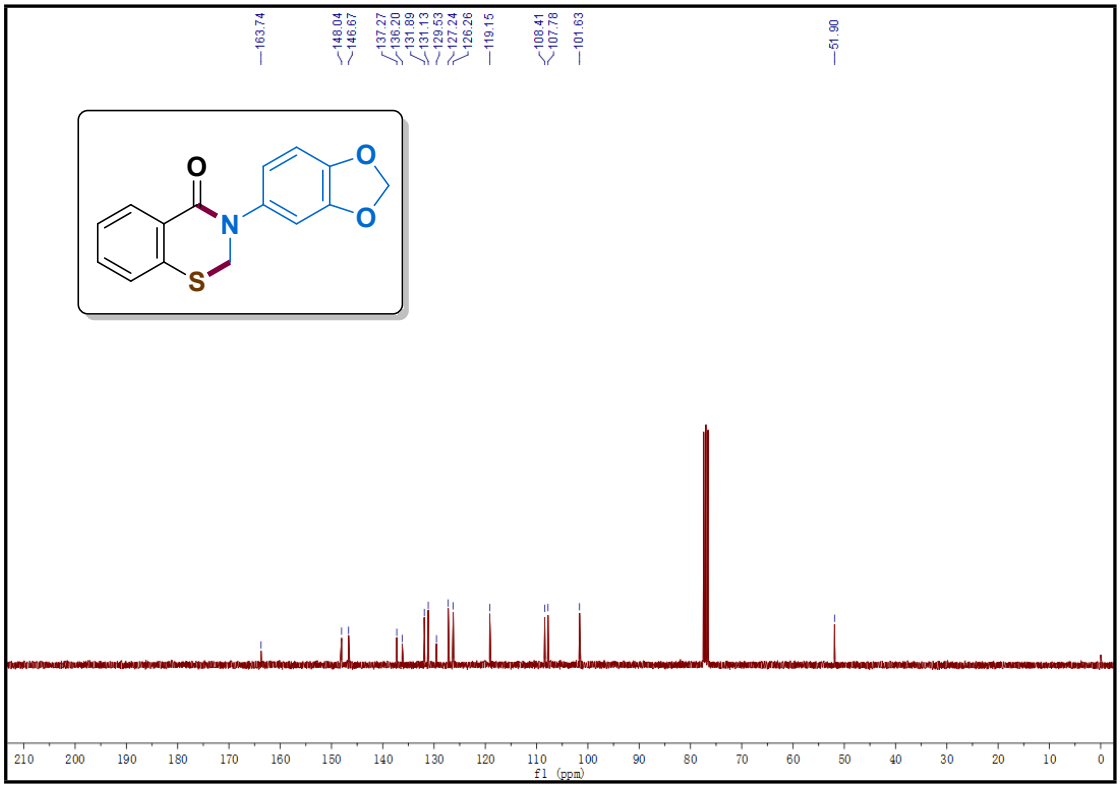
3-(4-(tert-butyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4e)



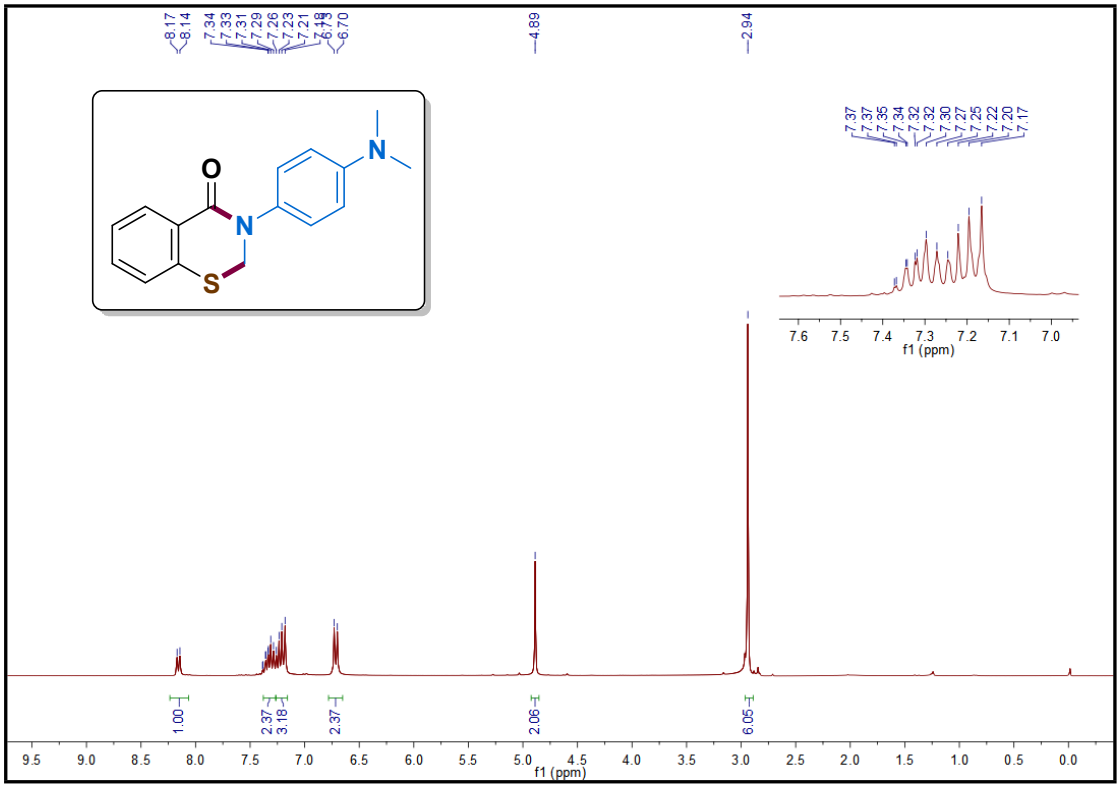


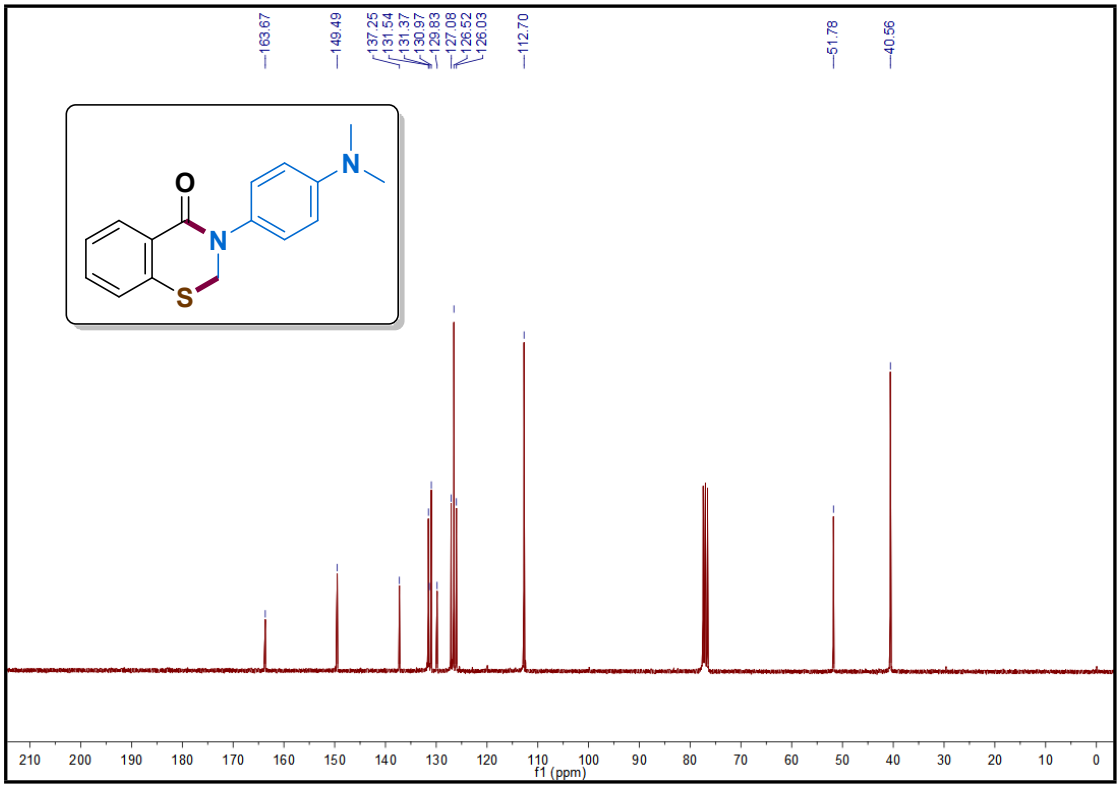
3-(benzo[d][1,3]dioxol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4f)



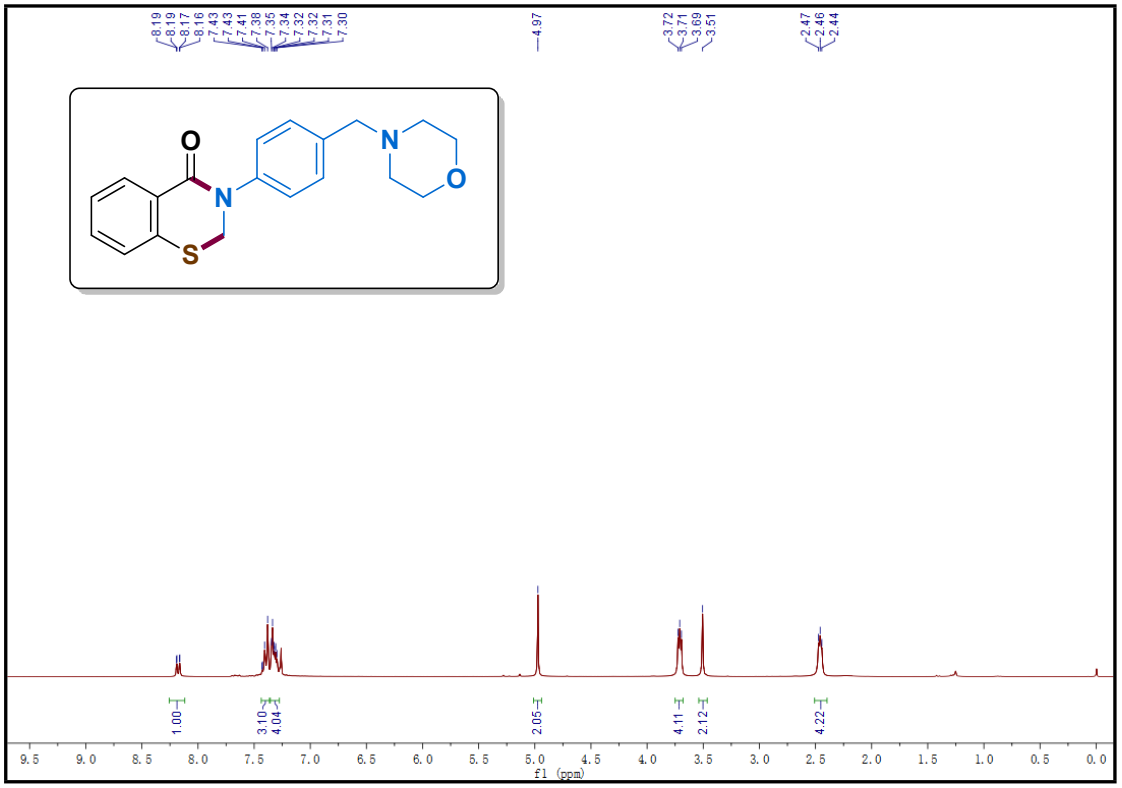


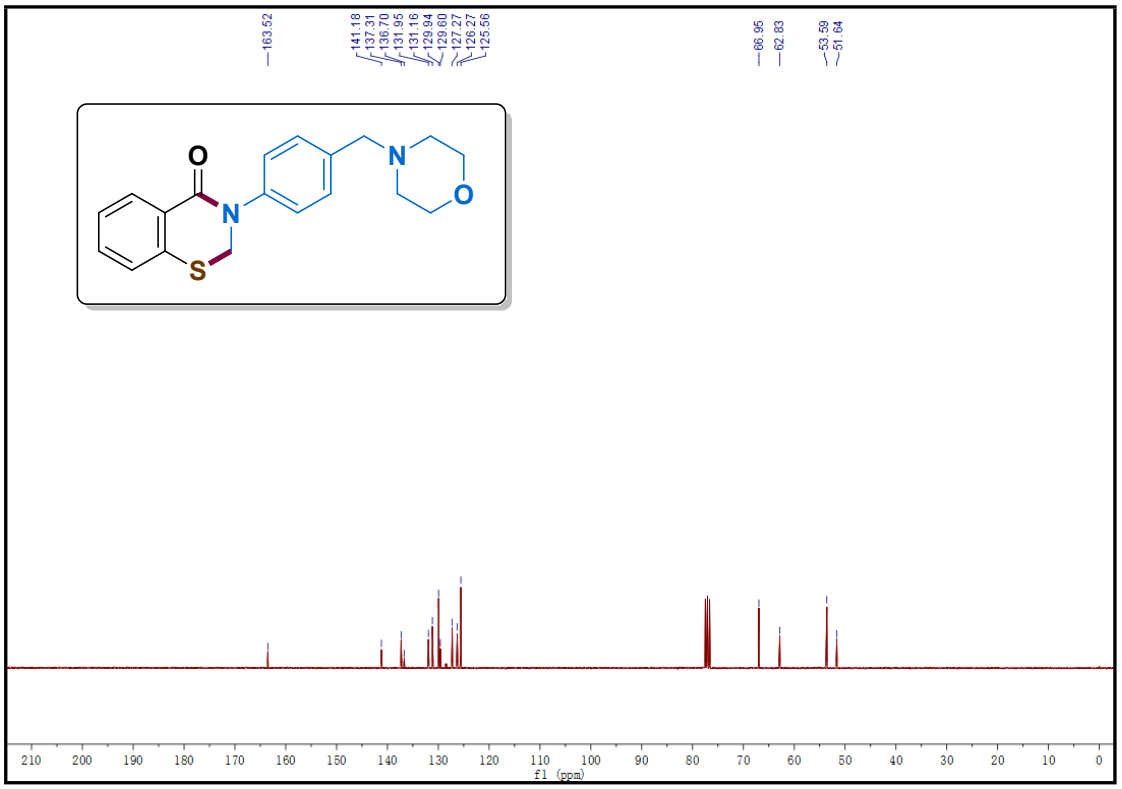
3-(4-(dimethylamino)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4g)



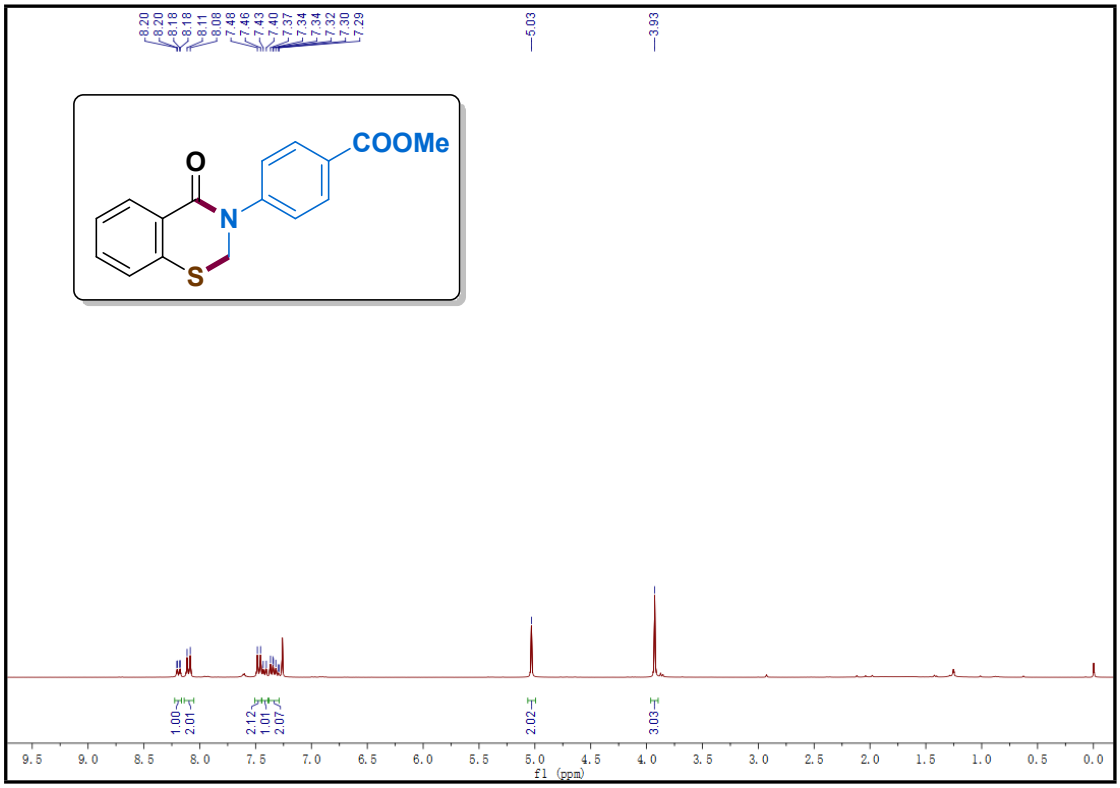


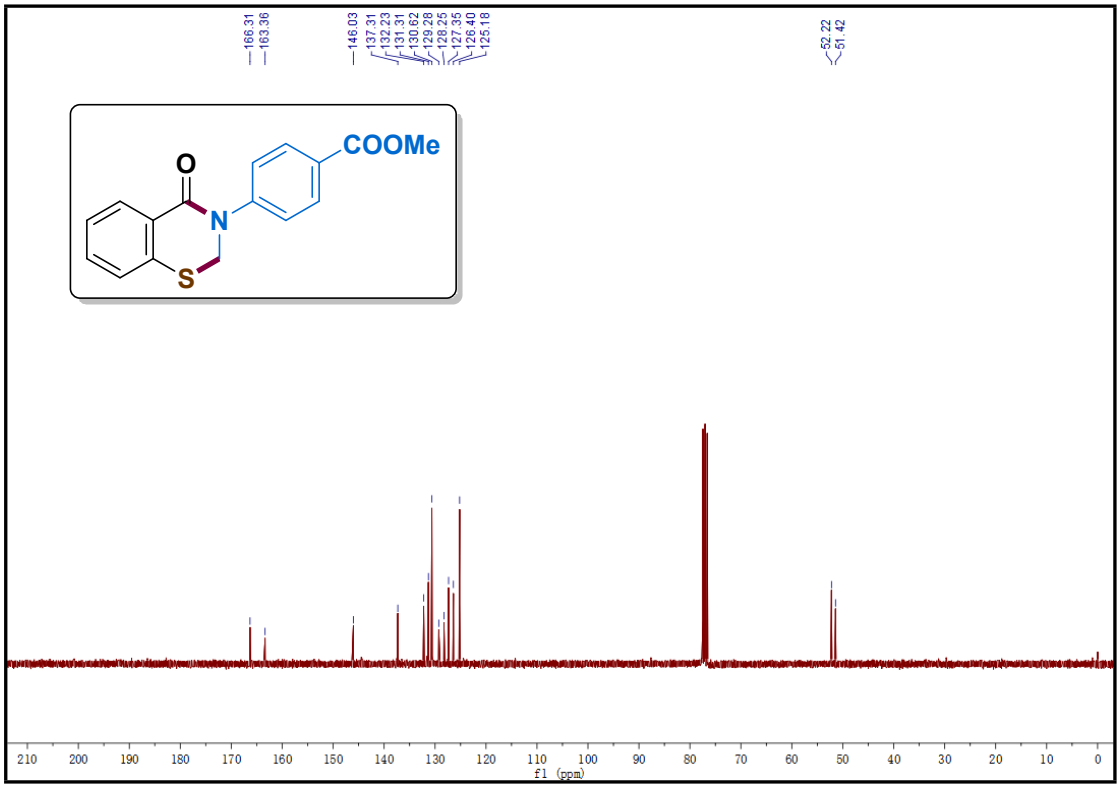
3-(4-(morpholinomethyl)phenyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4h)



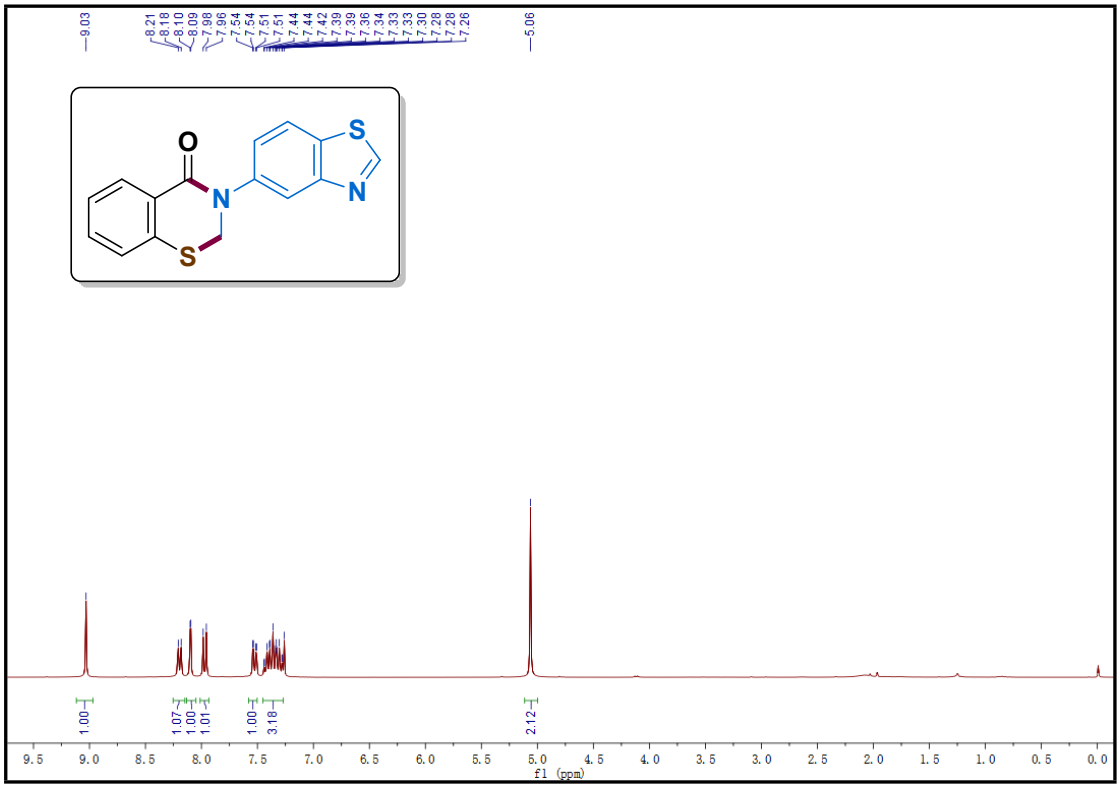


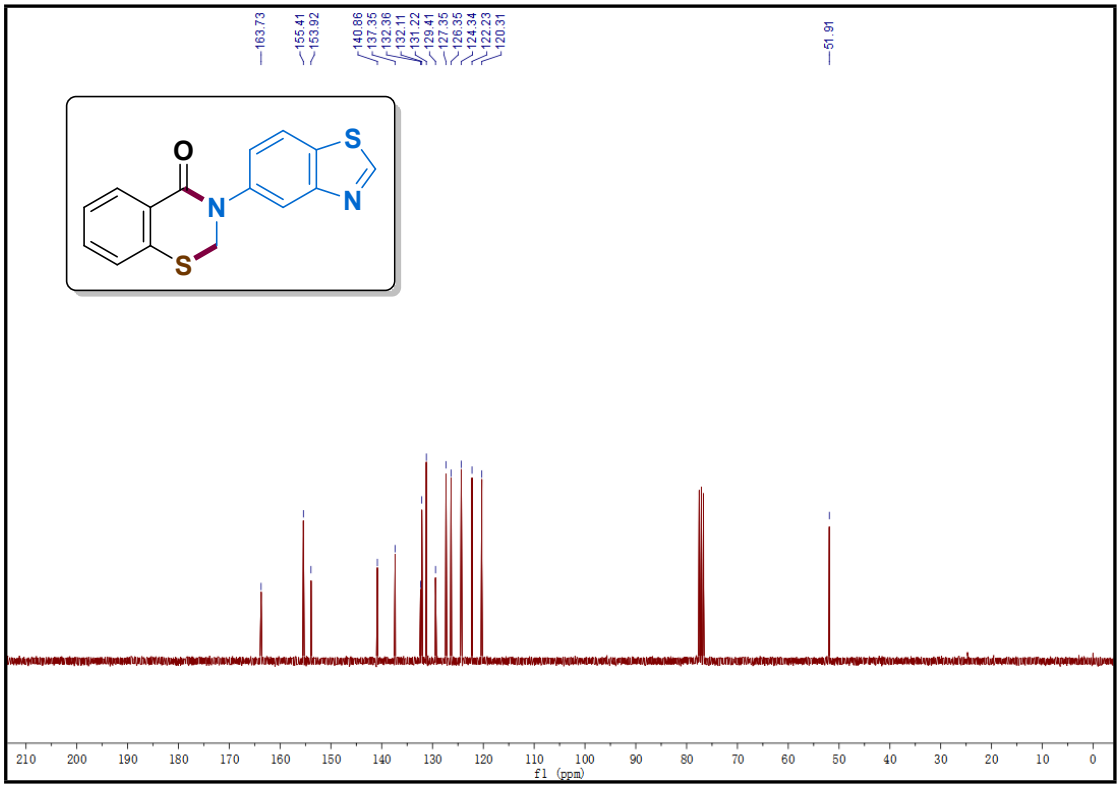
methyl 4-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)benzoate (4i)



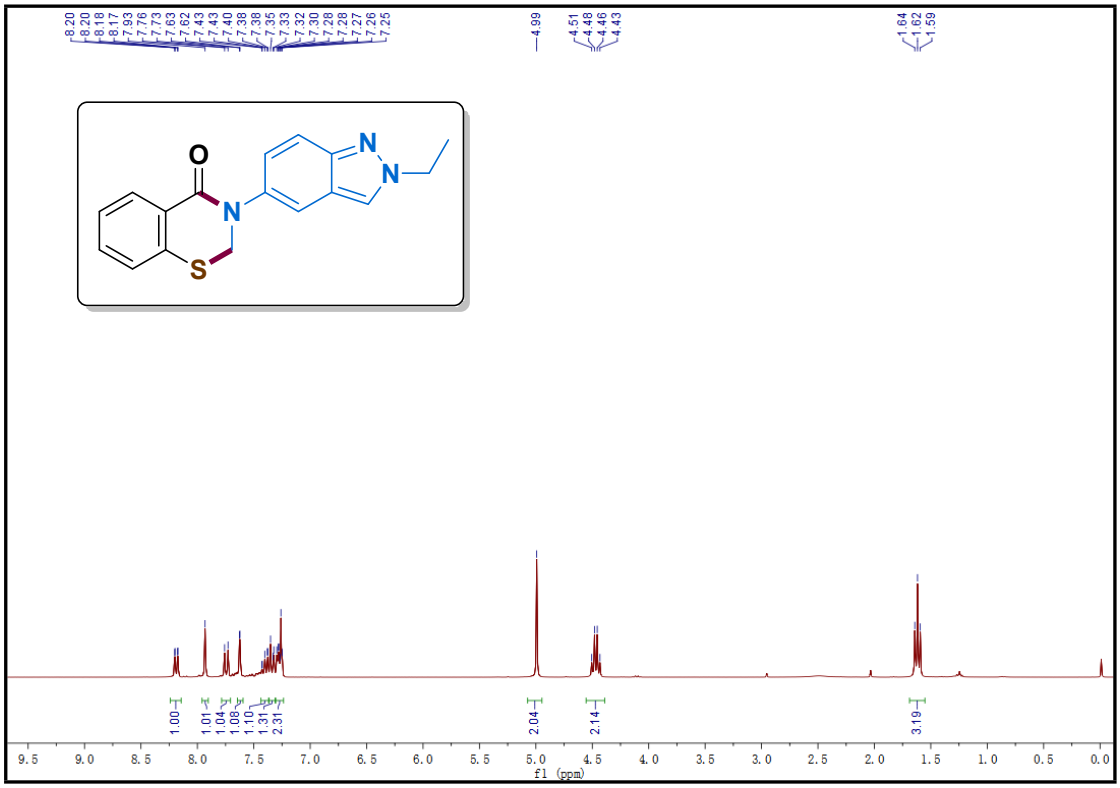


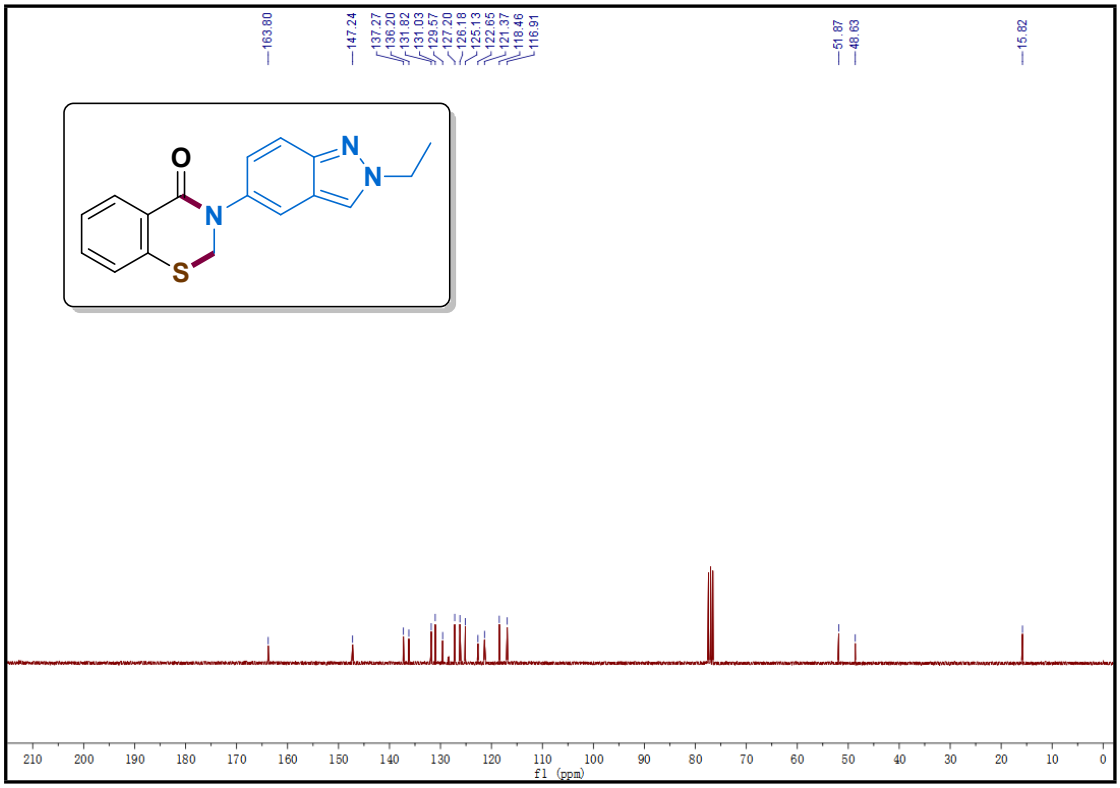
3-(benzo[d]thiazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4j)



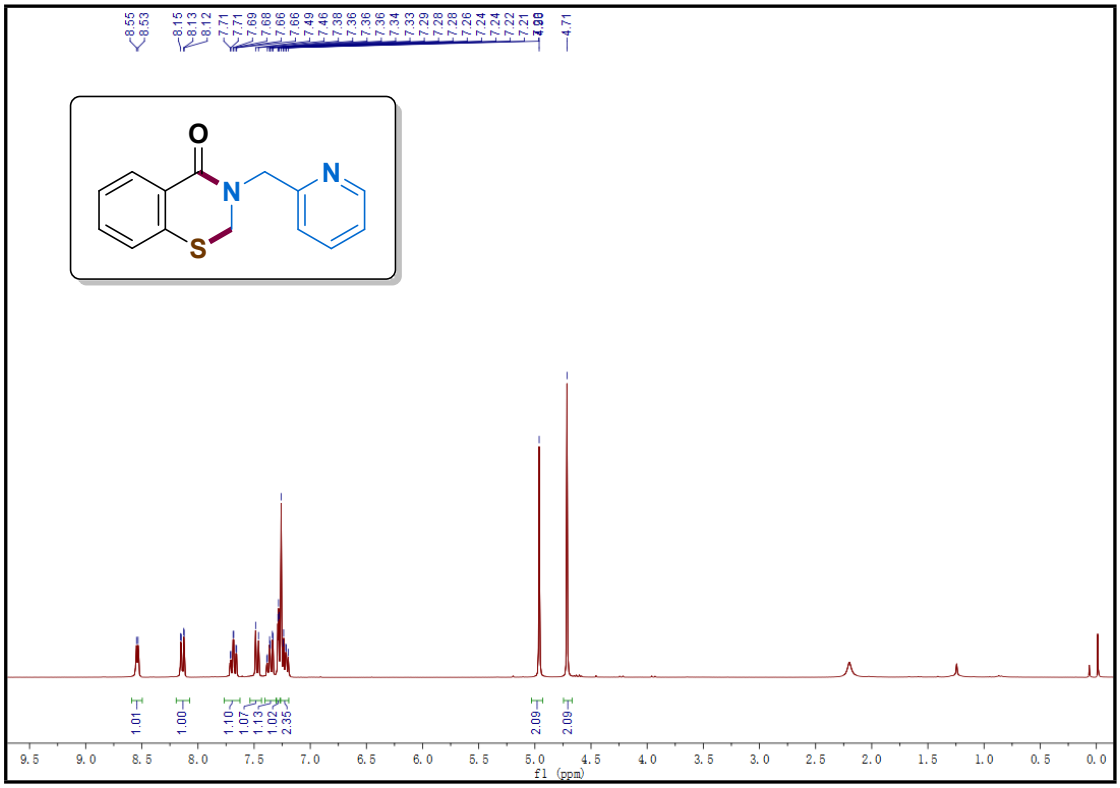


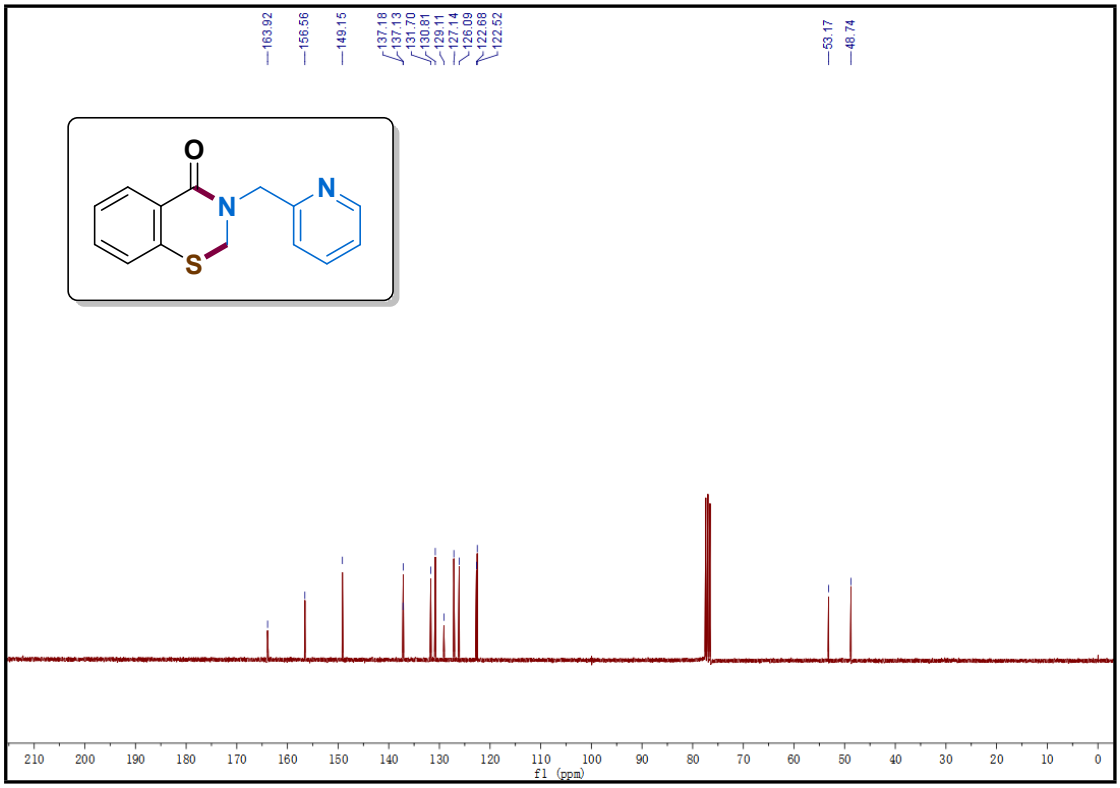
3-(2-ethyl-2H-indazol-5-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4k)



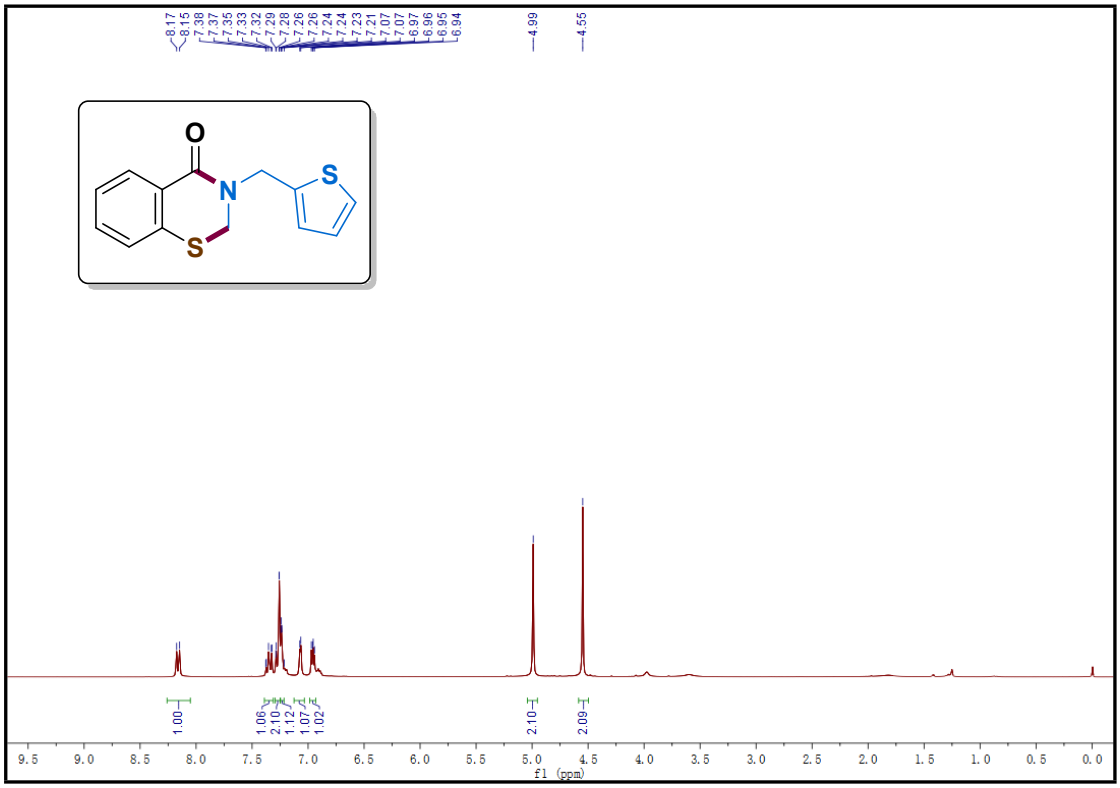


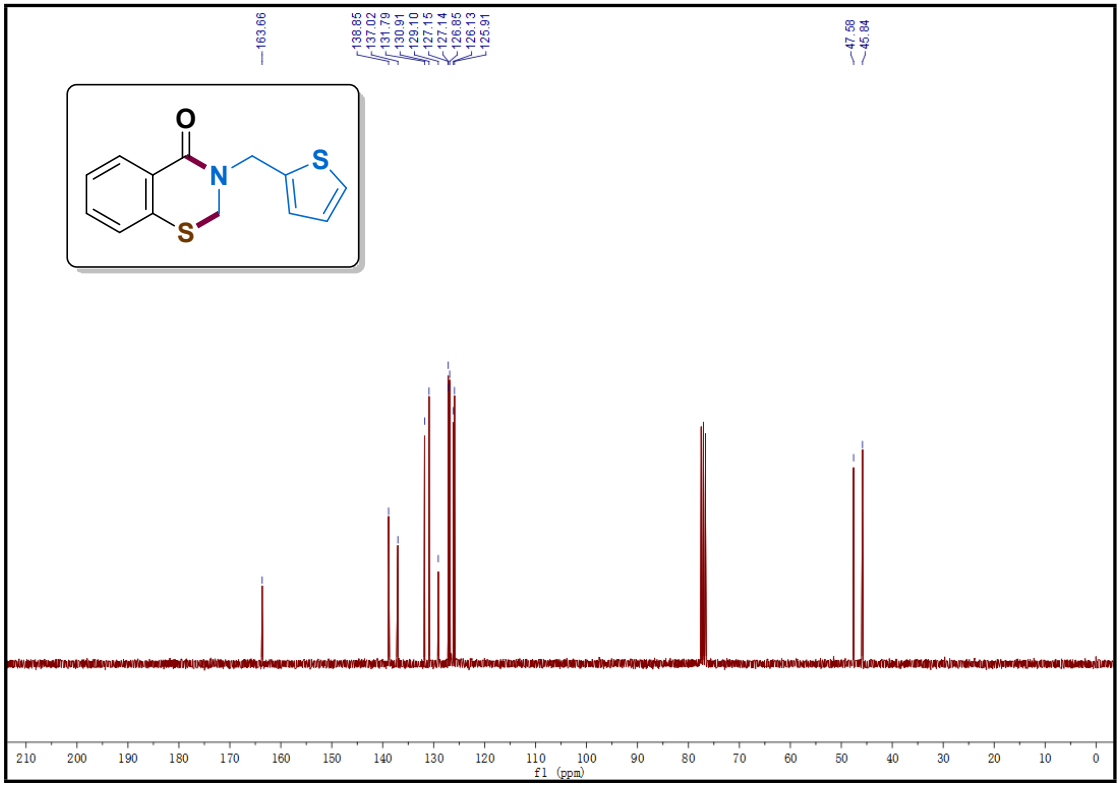
3-(pyridin-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4l)



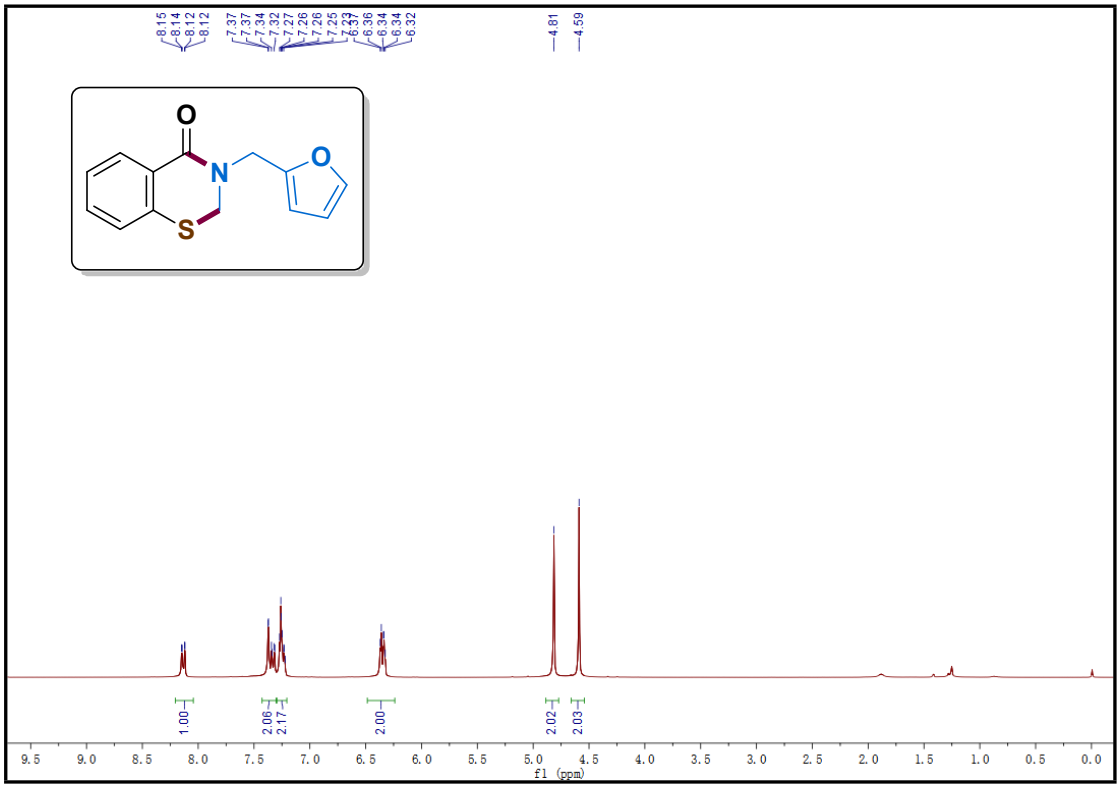


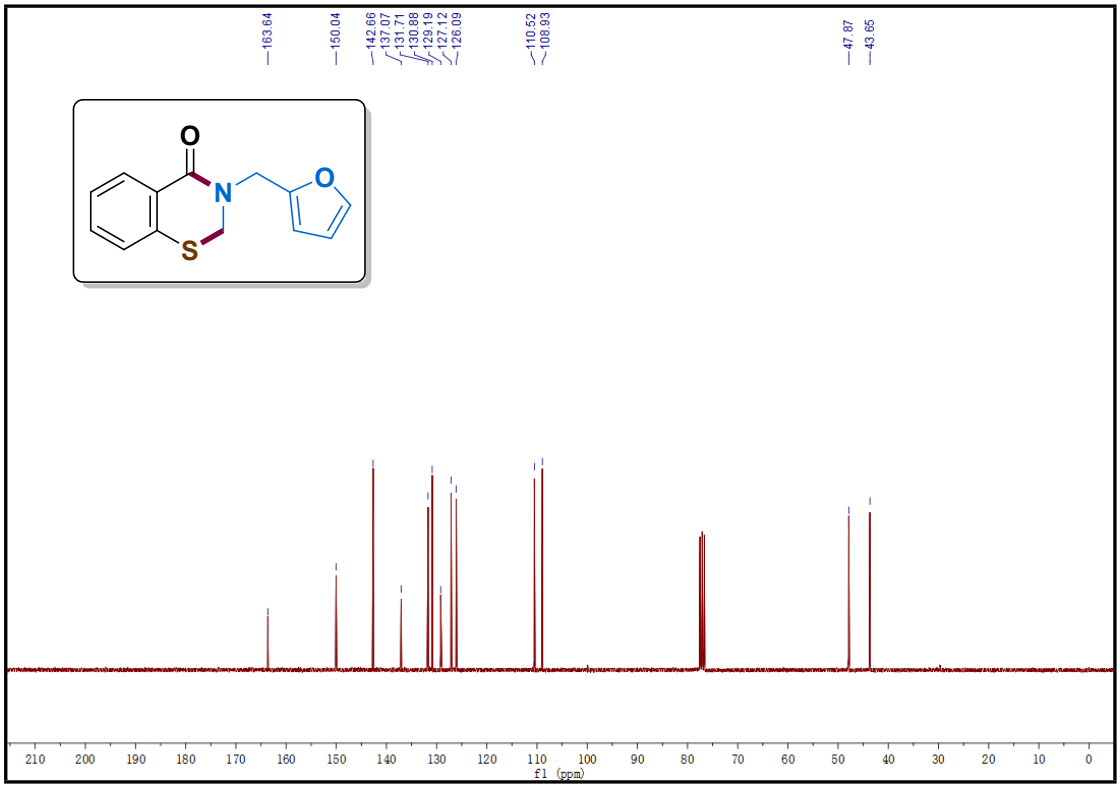
3-(thiophen-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4m)



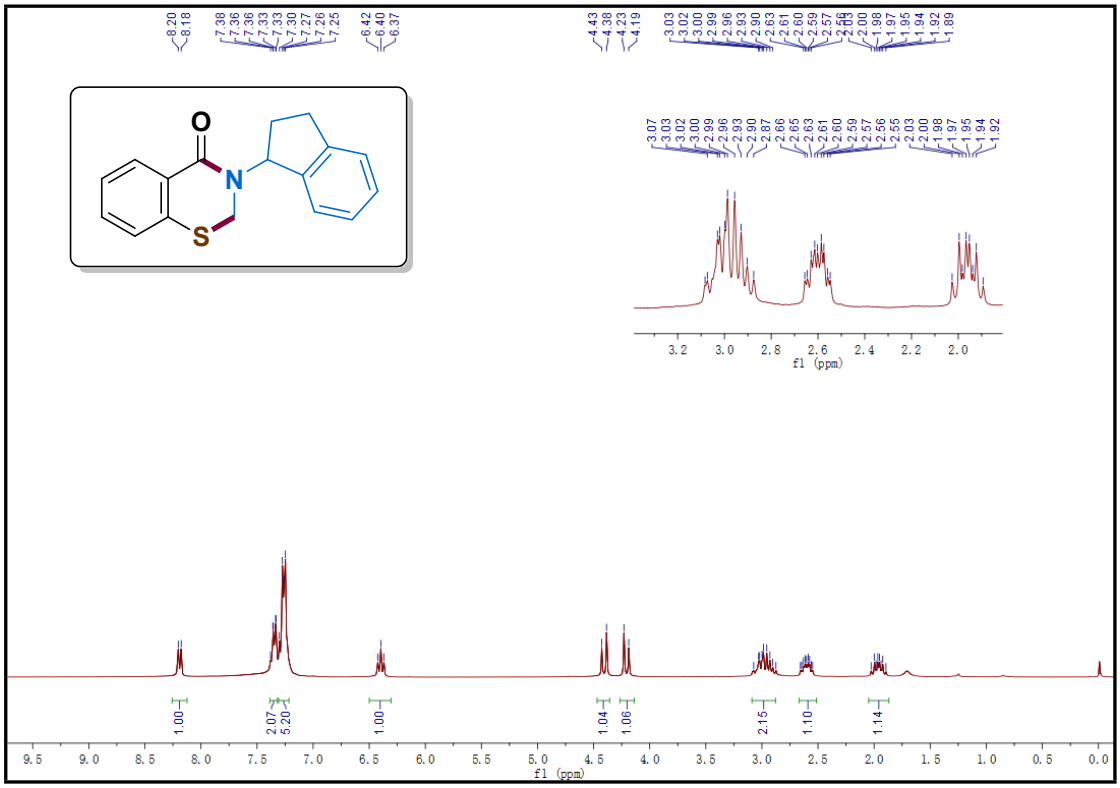


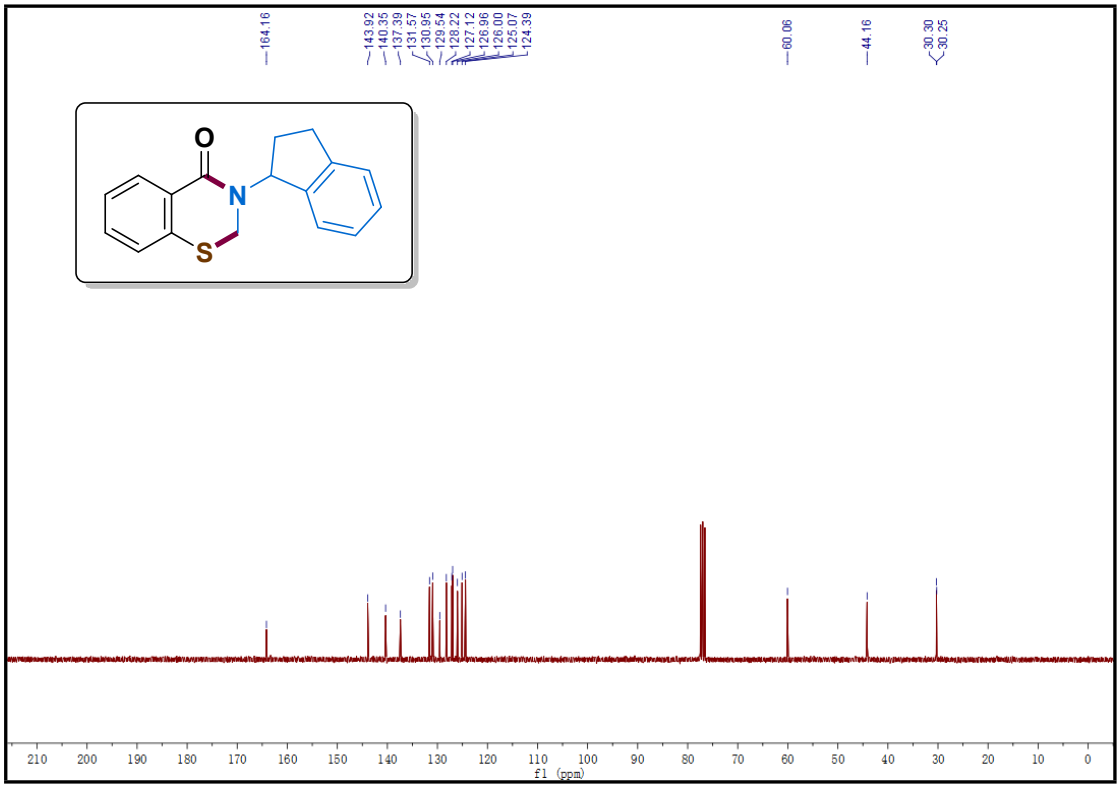
3-(furan-2-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4n)



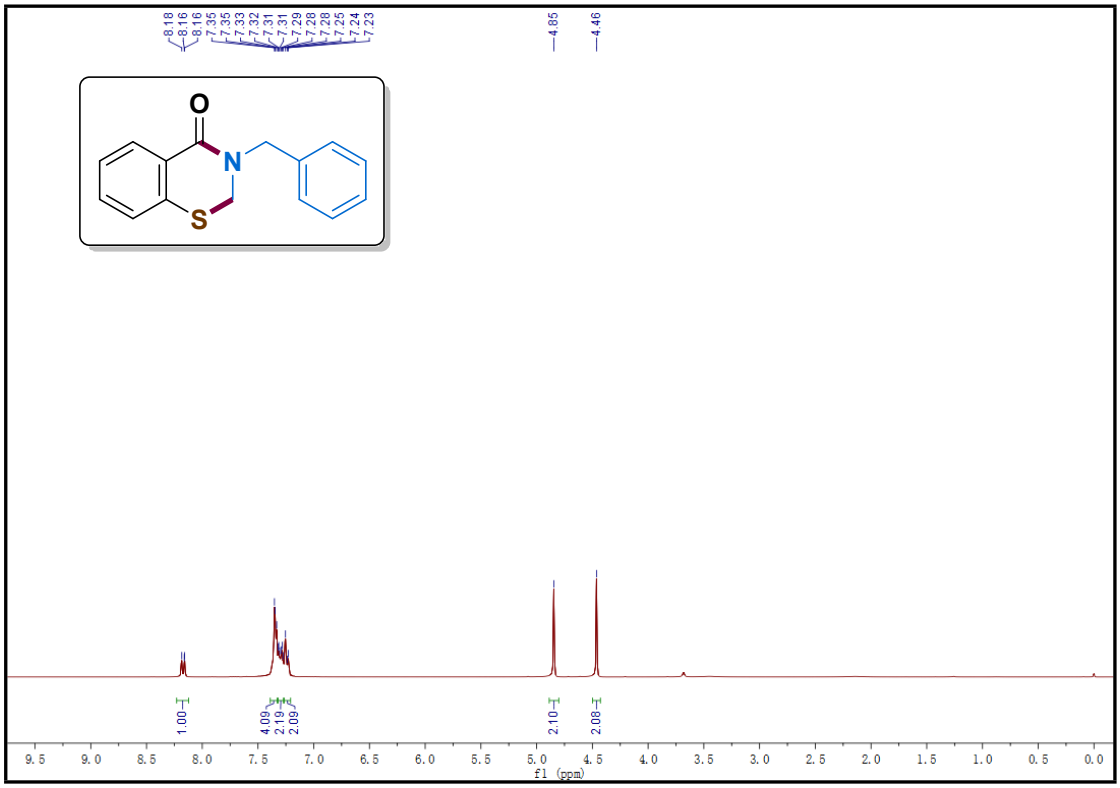


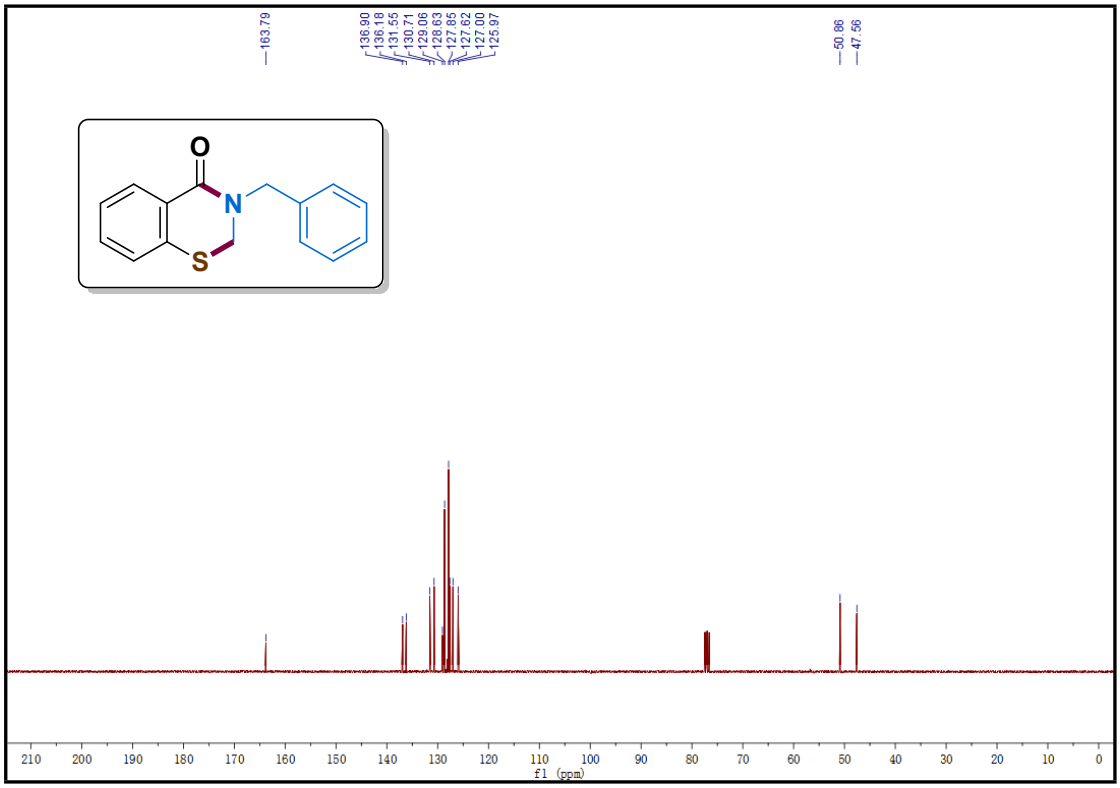
3-(2,3-dihydro-1H-inden-1-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4o)



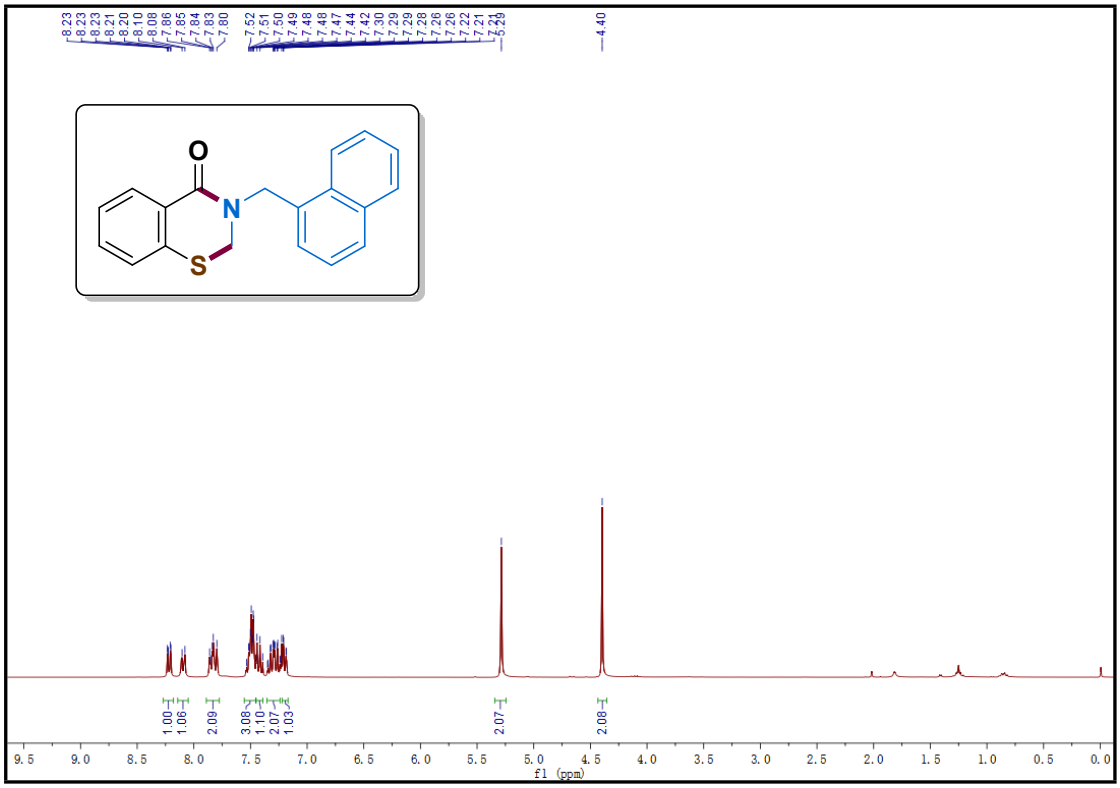


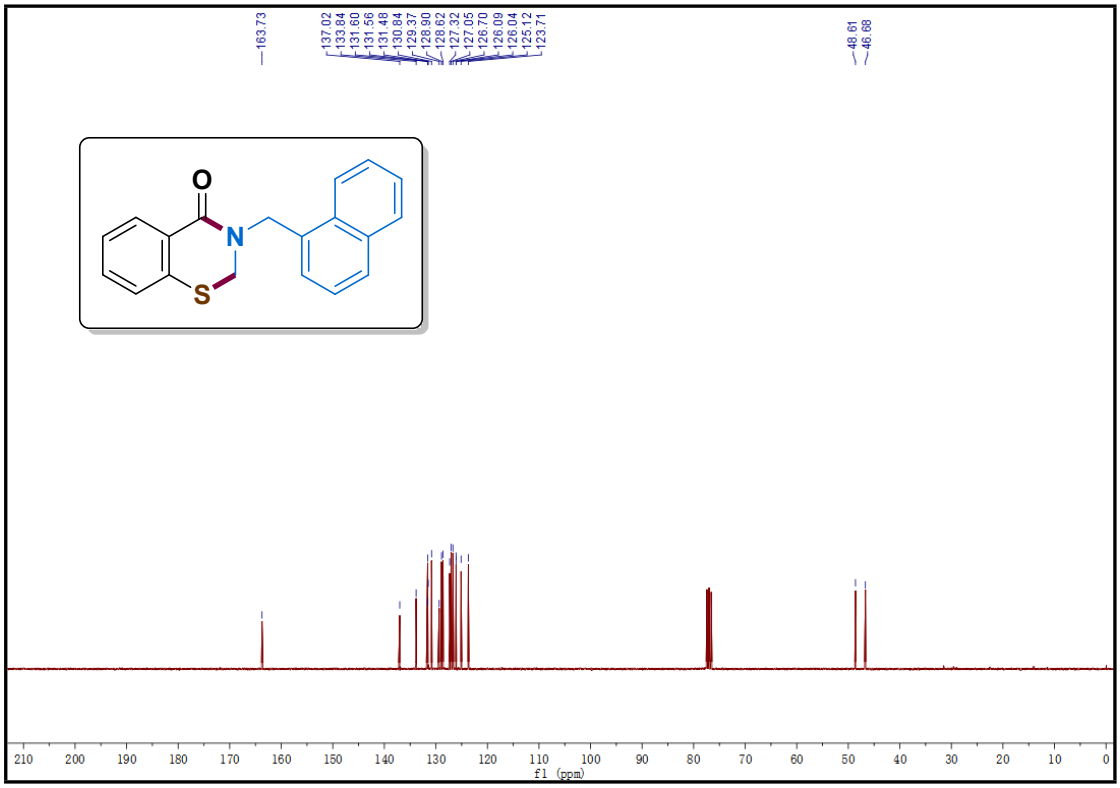
3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4p)



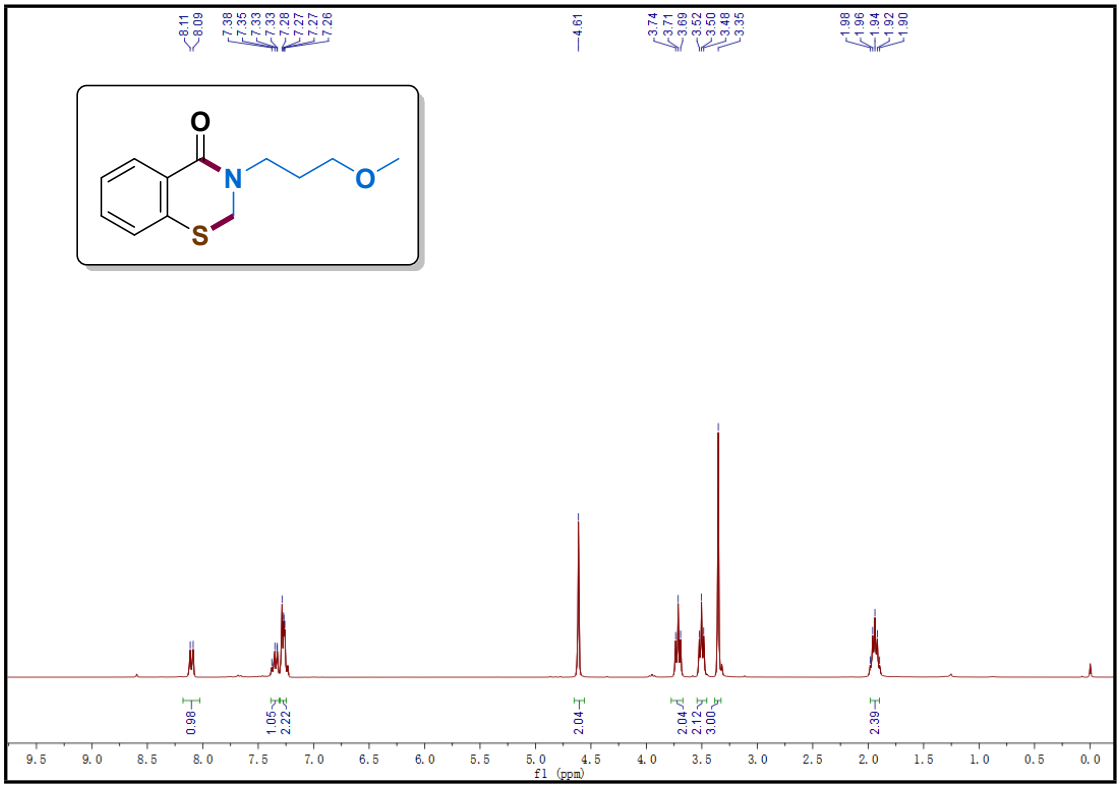


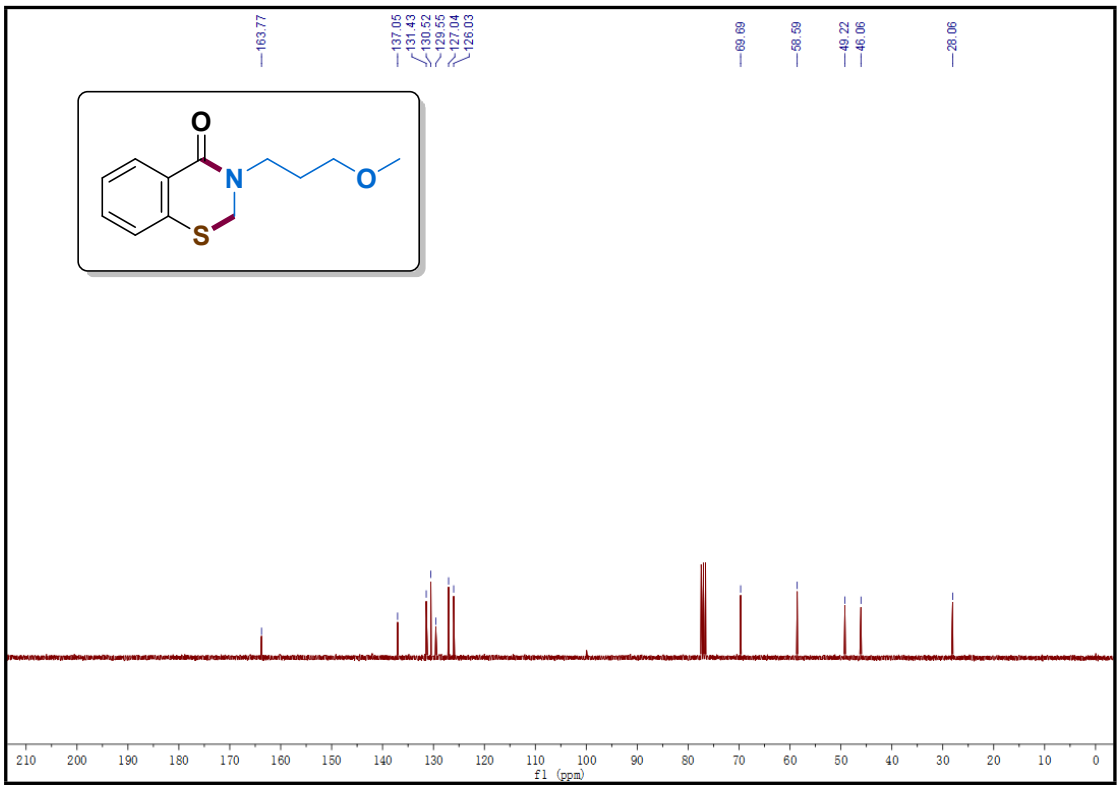
3-(naphthalen-1-ylmethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one(4q)



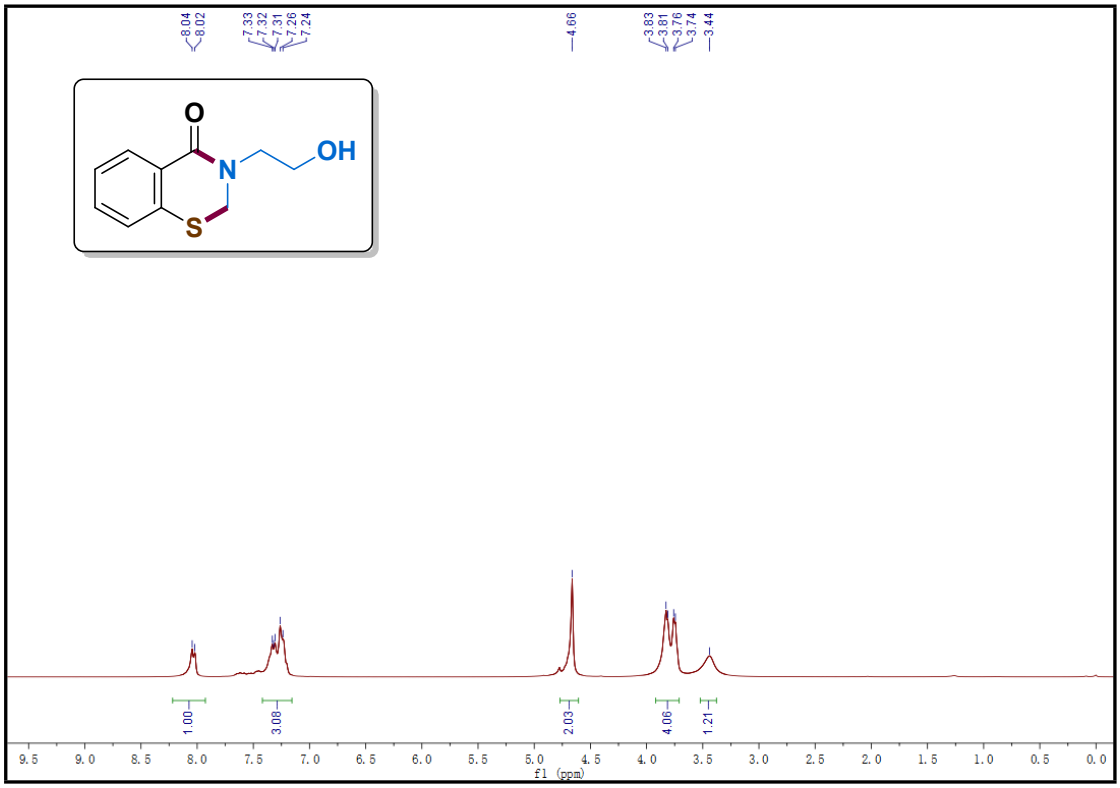


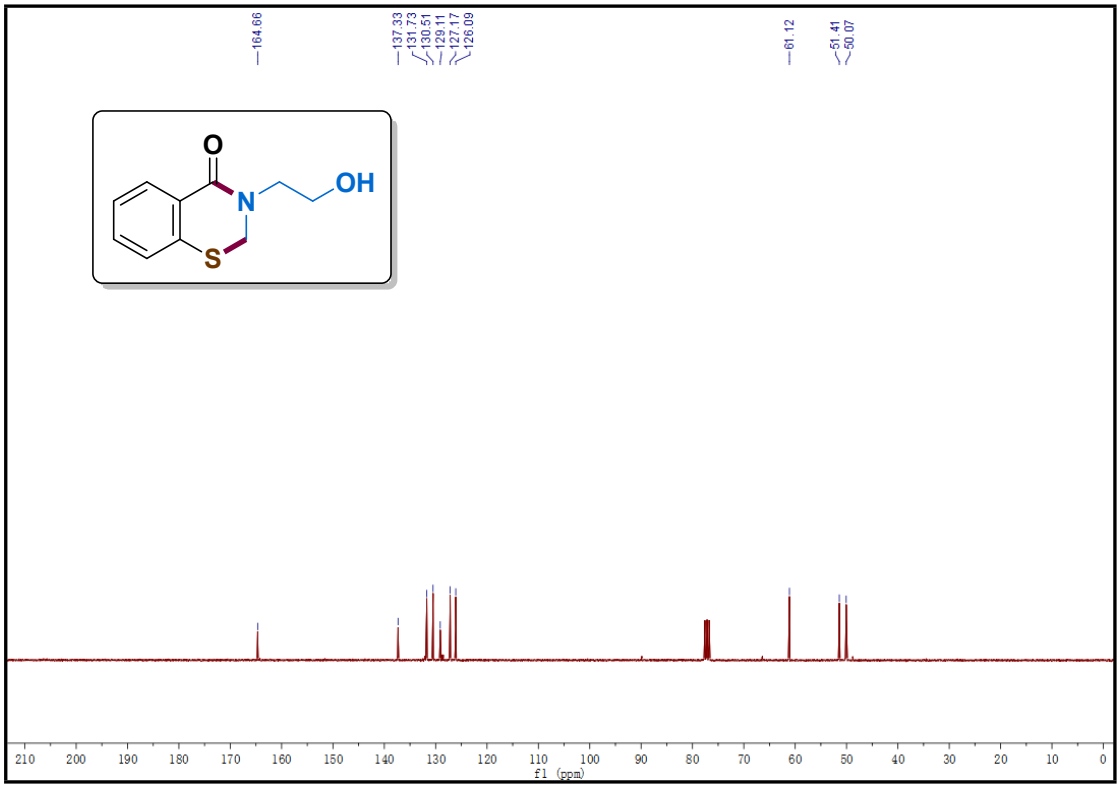
3-(3-methoxypropyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4r)



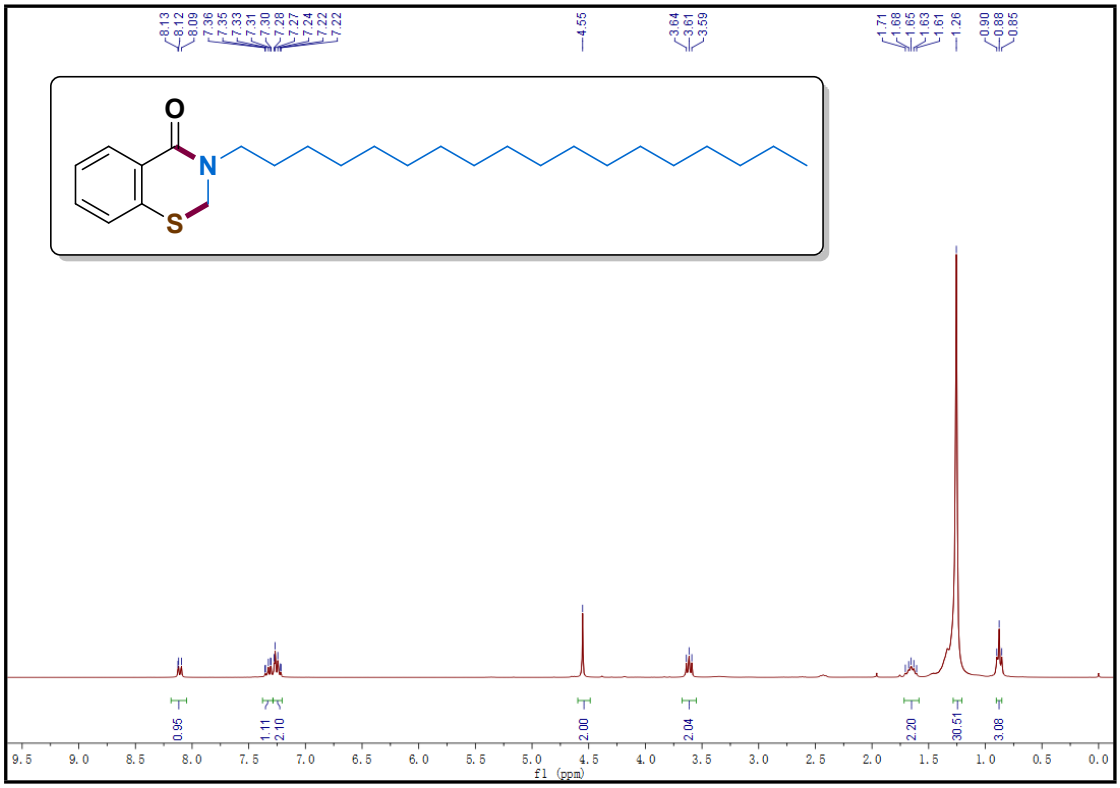


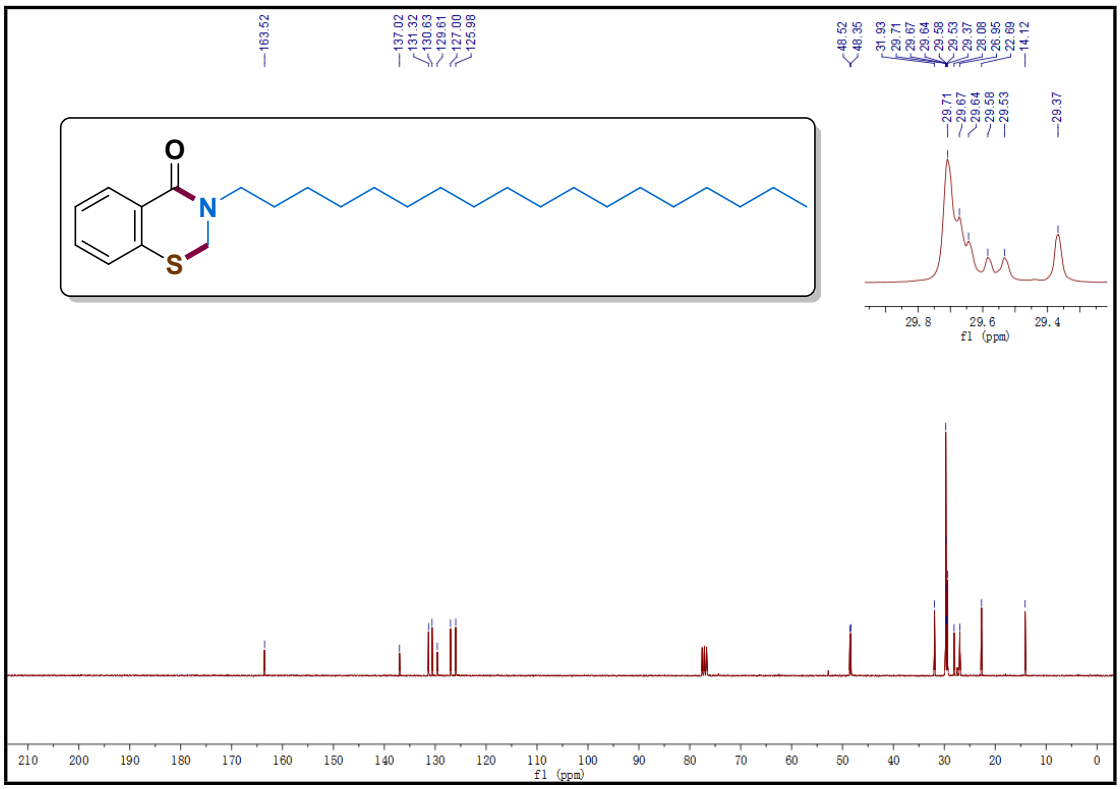
3-(2-hydroxyethyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4s)



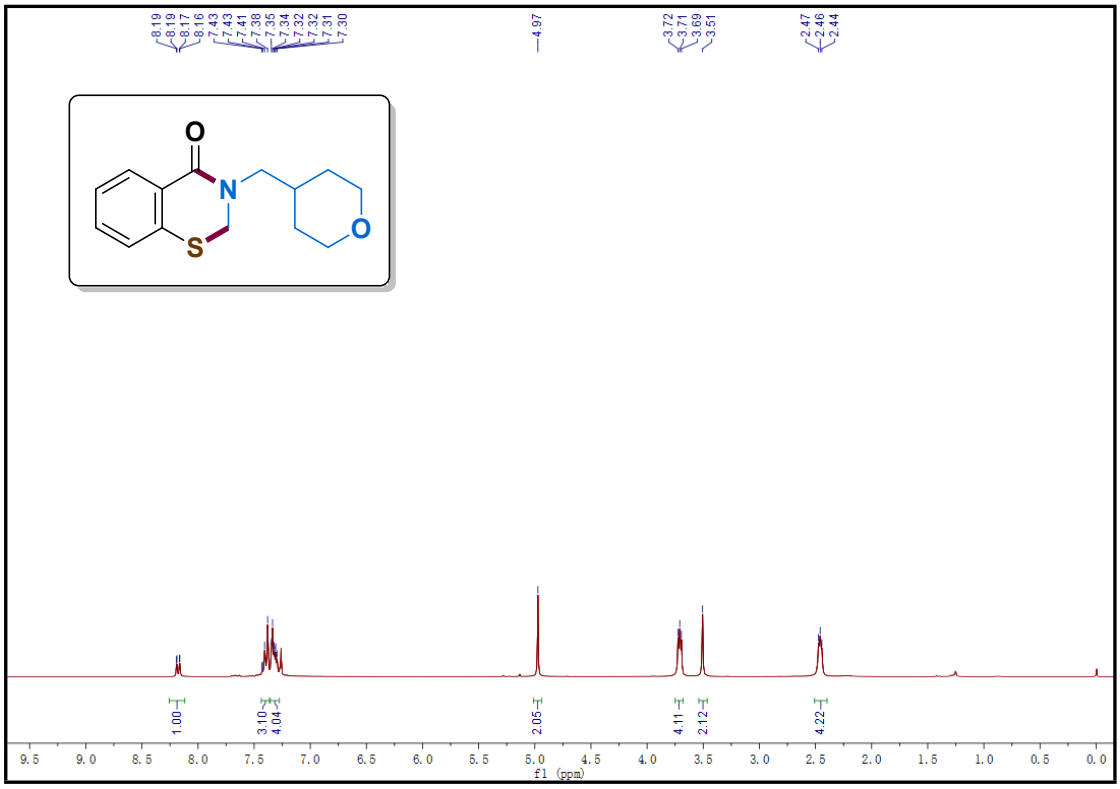


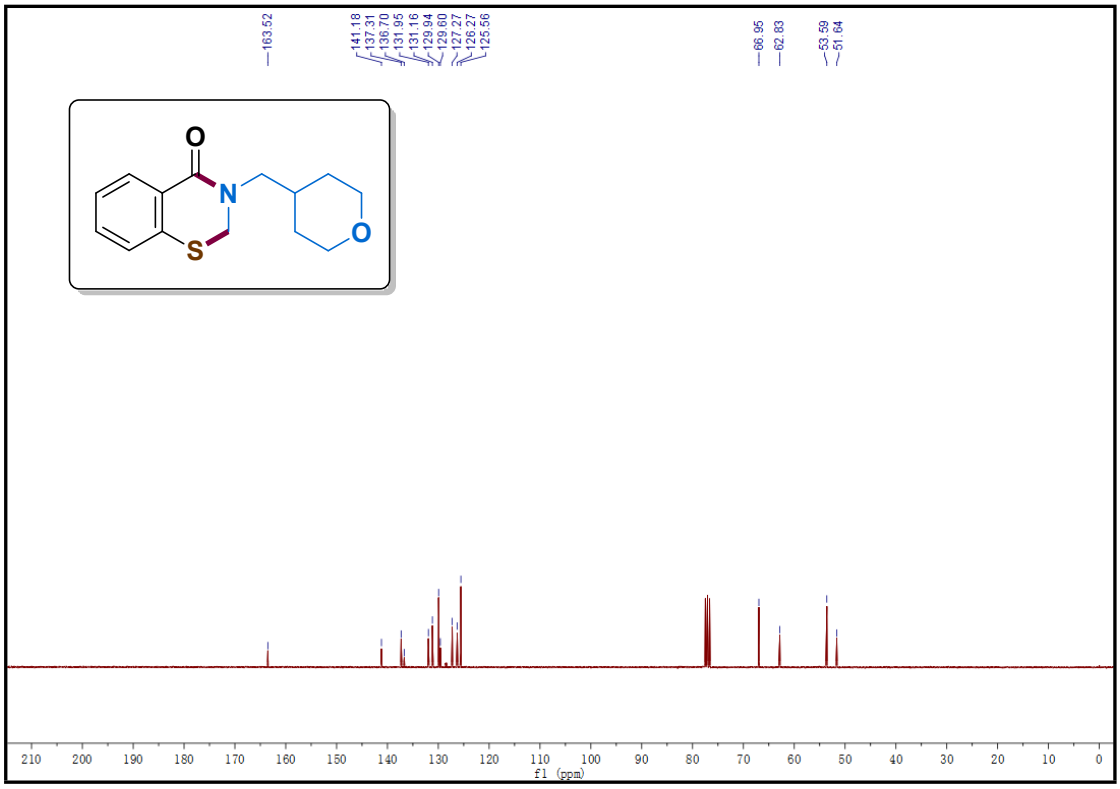
3-octadecyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4t)



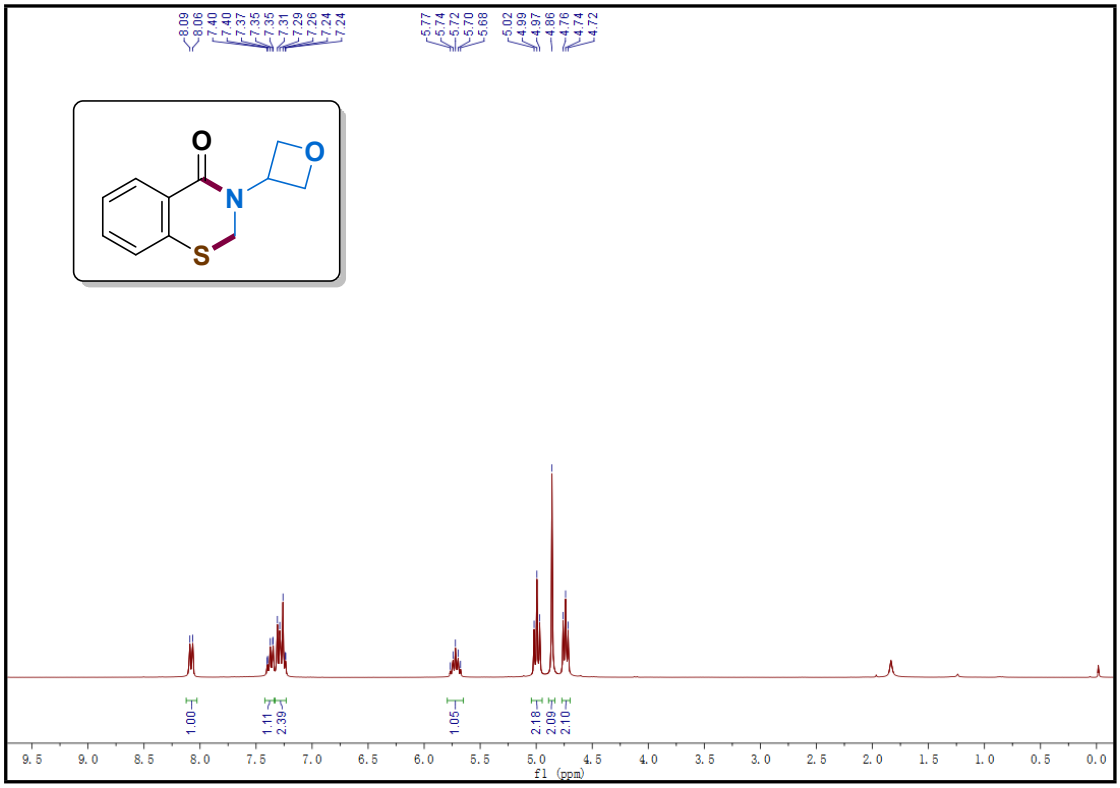


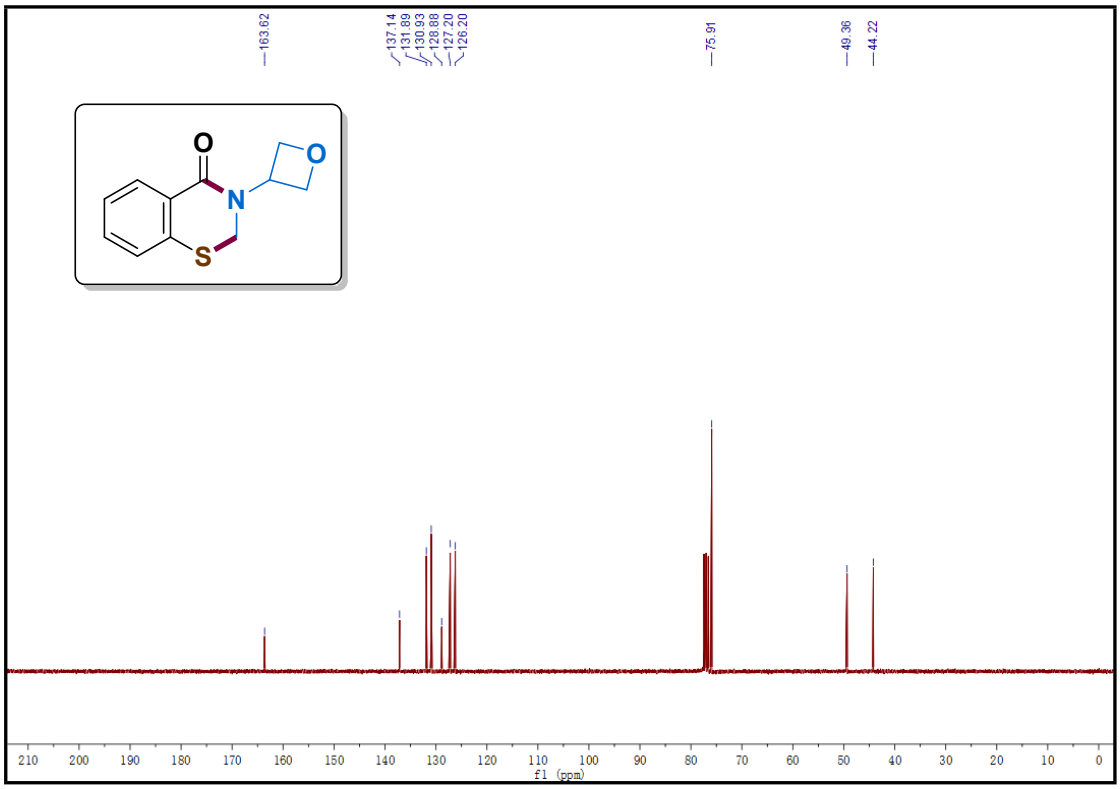
3-((tetrahydro-2H-pyran-4-yl)methyl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4u)



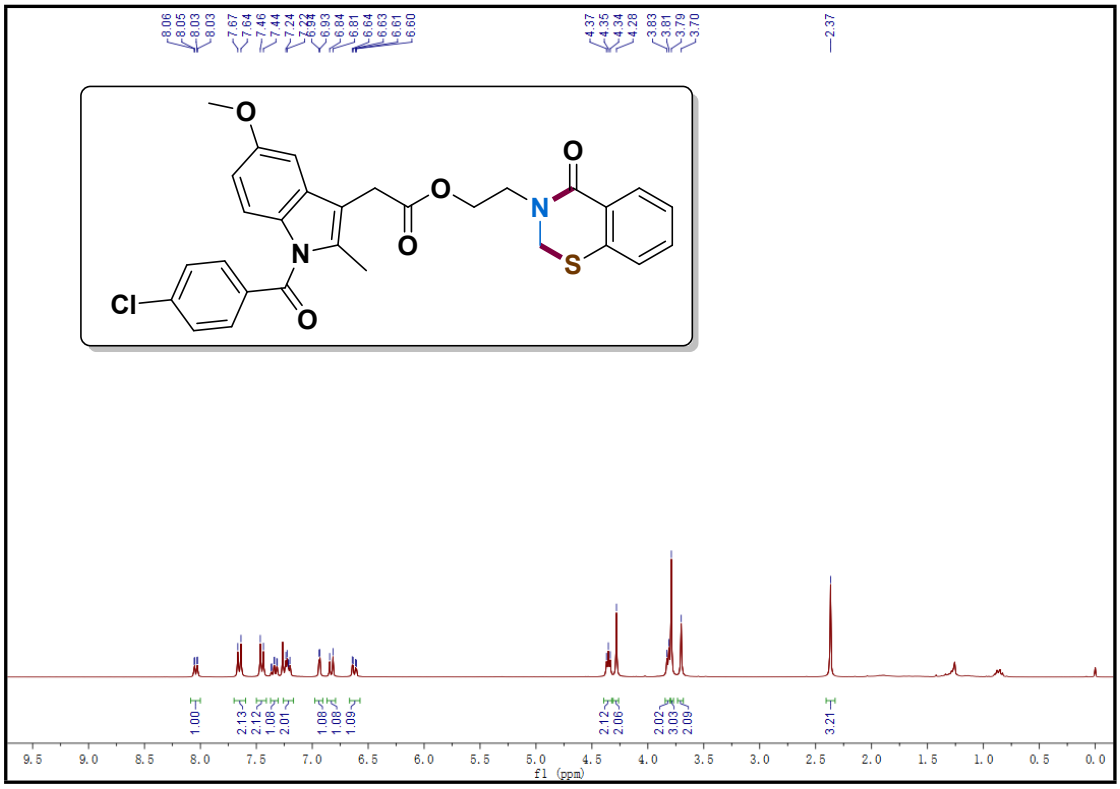


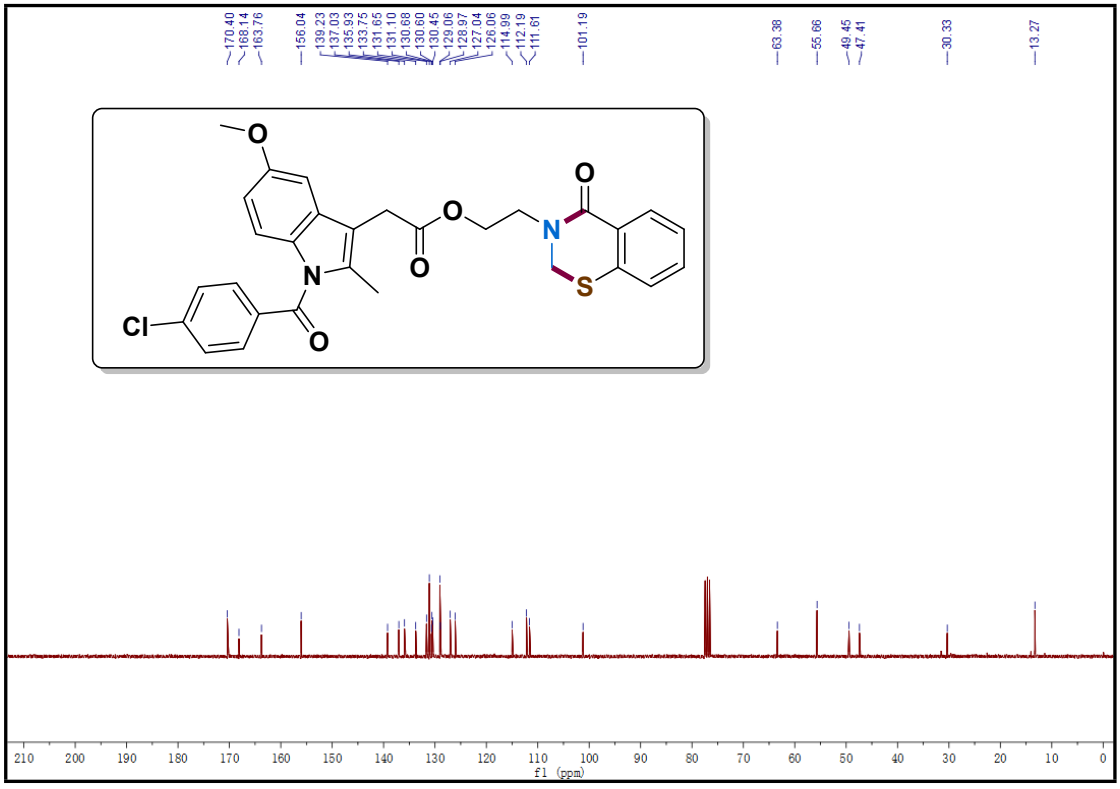
3-(oxetan-3-yl)-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one (4v)



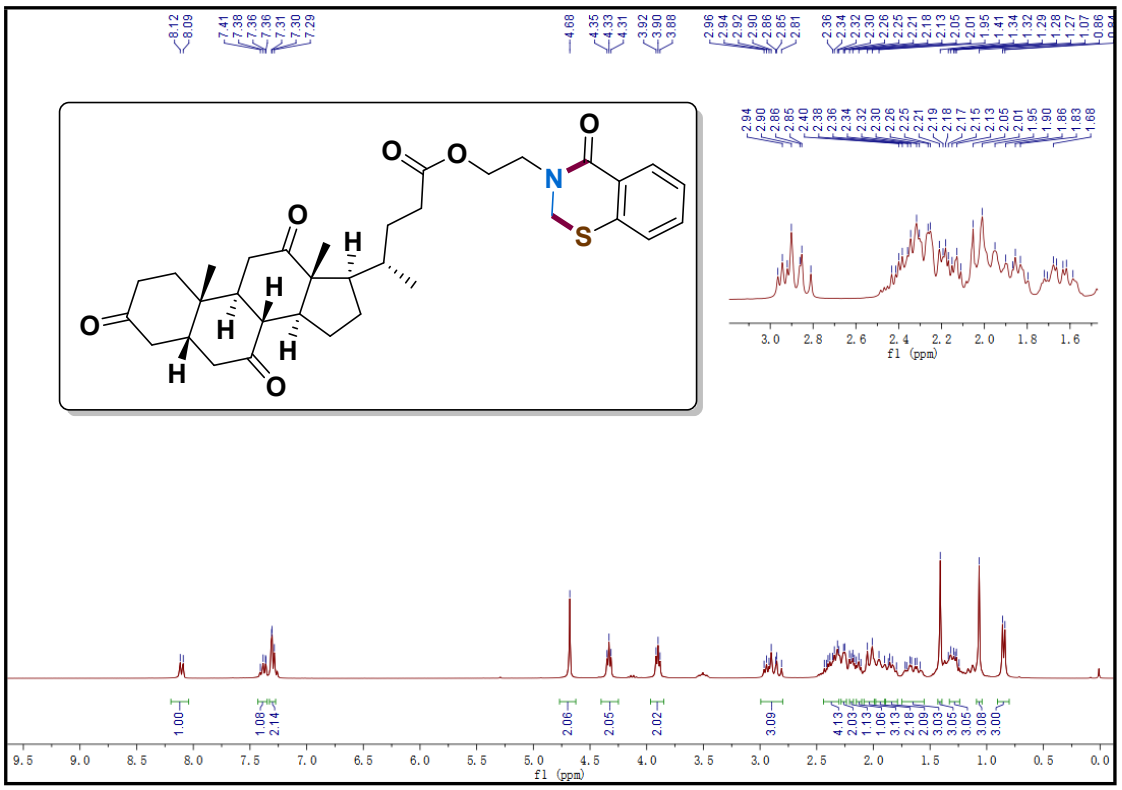


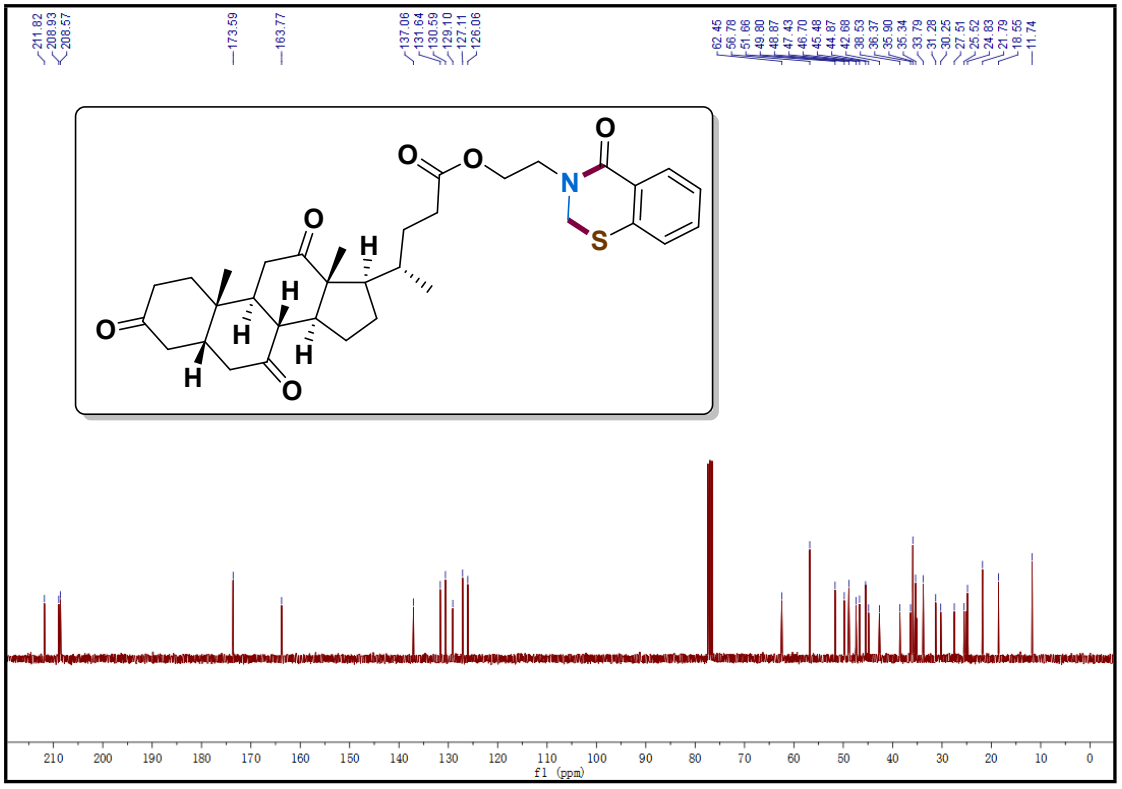
2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)ethyl2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1H-indol-3-yl)acetate (5)





2-(4-oxo-2H-benzo[e][1,3]thiazin-3(4H)-yl)ethyl(S)-4-((5S,8R,9S,10S,13R,14S,17R)-10,13-dimethyl-3,7,12-trioxohexadecahydro-1H-cyclopenta[a]phenanthren-17-yl)pentanoate (6)





3-benzyl-2,3-dihydro-4H-benzo[e][1,3]thiazin-4-one 1,1-dioxide (7)