

Supporting Information

Rhodium(III)-Catalyzed Intermolecular [3+3] Annulation of Benzoxazines with Quinone Compounds: Access to Spiro- Heterocyclic Scaffolds

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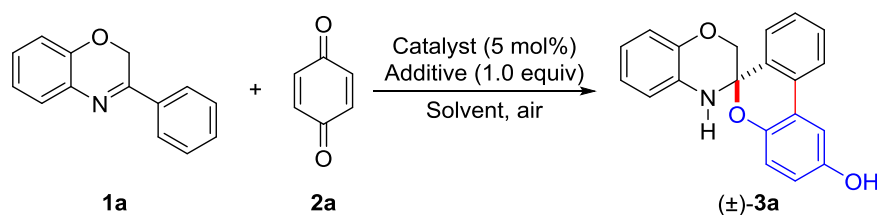
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(A) General Remarks.

Unless otherwise stated, all reactions were performed in sealed tube (capacity 15 mL). Commercially available reagents were used without further purification. NMR spectra were recorded on Bruker Avance NEO 500 or Bruker Avance III 600 instruments and calibrated using residual solvent peaks as internal reference. Chemical shifts (δ) were expressed in ppm with reference to the solvent signals. Coupling constants J are given in Hz. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) [quantitative time-of-flight (Q-TOF)] ionization sources on an Agilent 6200 Q-TOF MS. Infrared (IR) spectra were obtained with a Tenor 27 spectrophotometer using KBr pellets. Melting points were determined on a SGW X-4A melting point apparatus. Fluorescence spectra were recorded on an F-4600 fluorospectro photometer (HITACHI Company). UV-visible absorption spectra were acquired with a Lambda-35 UV-visible Spectrophotometer (PerkinElmer Company). X-ray diffraction was obtained by Bruker D8 QUEST. TLC analyses were performed on commercial glass plates bearing 0.25-mm layer of Merck Silica gel GF254. Silica gel (Huanghai 300 - 400 mesh) was used for flash column chromatography.

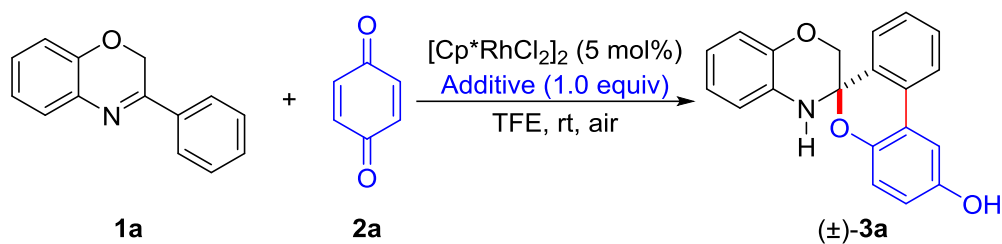
(B) Screening of reaction conditions for 3a.

Table S1. Optimization of Reaction Conditions.



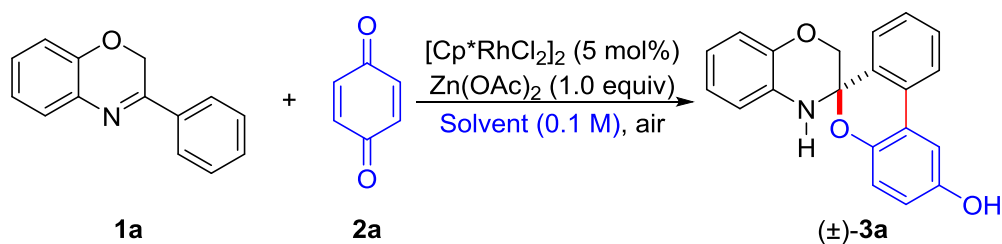
Entry ^a	Catalyst	Additive	Solvent	Temp. (°C)	Time (h)	Yield(%) ^b
1	[Cp*RhCl ₂] ₂	NaOAc	TFE	rt	4	28
2	[Cp*RhCl ₂] ₂	CsOAc	TFE	rt	10	22
3	[Cp*RhCl ₂] ₂	K ₃ PO ₄	TFE	rt	10	ND
4	[Cp*RhCl ₂] ₂	KHCO ₃	TFE	rt	10	trace
5	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	TFE	rt	10	76
6	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	MeOH	rt	10	22
7	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	HFIP	rt	10	13
8	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	DCM	rt	10	ND
9	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	THF	rt	10	ND
10	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	MeCN	rt	12	trace
11	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	PhCl	rt	12	NR
12	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	toluene	rt	12	NR
13	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	CPME	rt	12	NR
14	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	rt	48	92
15	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	94
16 ^c	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	94
17 ^d	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	95
18 ^{d,e}	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	79
19 ^{d,f}	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	81
20 ^{d,g}	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	88
21 ^{d,h}	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	50
22 ^{d,i}	[Cp*RhCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	68
23 ^d	[Cp*RhCl ₂] ₂	-	acetone	50	24	ND
24	-	Zn(OAc) ₂	acetone	50	24	ND
25 ^{d,j}	[Cp*IrCl ₂] ₂	Zn(OAc) ₂	acetone	50	24	NR
26 ^{d,j}	[Ru(<i>p</i> -Cymene)Cl ₂] ₂	Zn(OAc) ₂	acetone	50	24	NR
27 ^{d,j}	[Cp*Rh(CH ₃ CN) ₃][SbF ₆] ₂	Zn(OAc) ₂	acetone	50	24	45

^aReaction conditions: **1a** (0.1 mmol), **2a** (2.0 equiv), Catalyst (5 mol%), Solvent (0.1 M) under air. ^bIsolated Yields. ^cCatalyst (2.5 mol%). ^dCatalyst (1 mol%). ^e**2a** (1.0 equiv). ^f**2a** (1.2 equiv). ^g**2a** (1.5 equiv). ^hAdditive (0.2 equiv). ⁱAdditive (0.5 equiv). ^j**1a** (0.2 mmol). ND = Not Detected. NR = No Reaction.

Table S2. Optimization of the Additives.

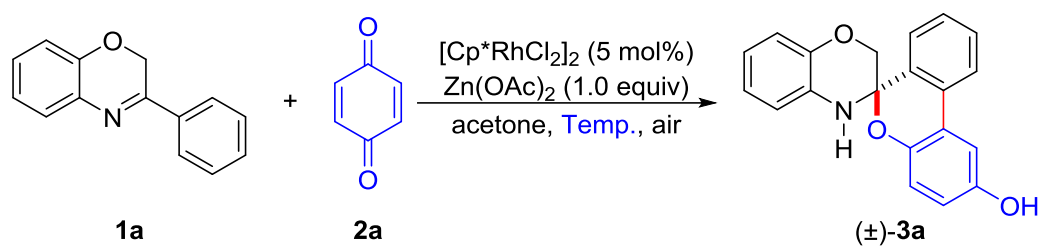
Entry ^a	Additive	T (h)	Yield(%) ^b
1	NaOAc	4	28
2	CsOAc	10	22
3	K ₃ PO ₄	10	ND
4	KHCO ₃	10	trace
5	Zn(OAc) ₂	10	76

^aReaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol% of [Cp*RhCl₂]₂, 0.1 mmol of Additive, 1.0 mL of TFE, room temperature under air. ^bIsolated yield refers to **1a**.

Table S3. Optimization of the Solvents.

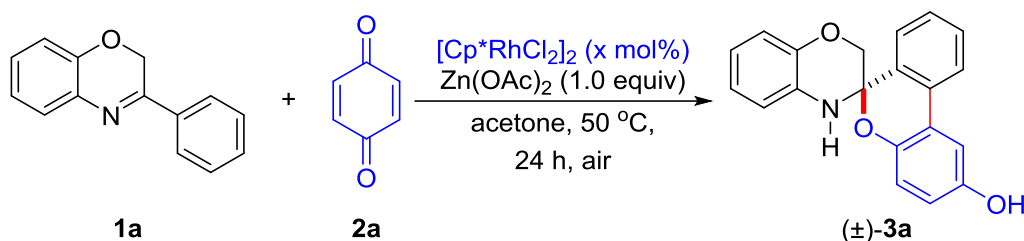
Entry ^a	Solvent	Temperature (°C)	Time (h)	Yield(%) ^b
1	TFE	rt	10	76
2	MeOH	rt	10	22
3	HFIP	rt	10	13
4	DCM	rt	10	ND
5	THF	rt	10	ND
6	MeCN	rt	12	trace
7	PhCl	rt	12	NR
8	toluene	rt	12	NR
9	CPME	rt	12	NR
10	acetone	rt	48	92

^aReaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol% of [Cp*RhCl₂]₂, 0.1 mmol of Zn(OAc)₂, 1.0 mL of Solvent, room temperature under air. ^bIsolated yield refers to **1a**.

Table S4. Optimization of Reaction Temperature.

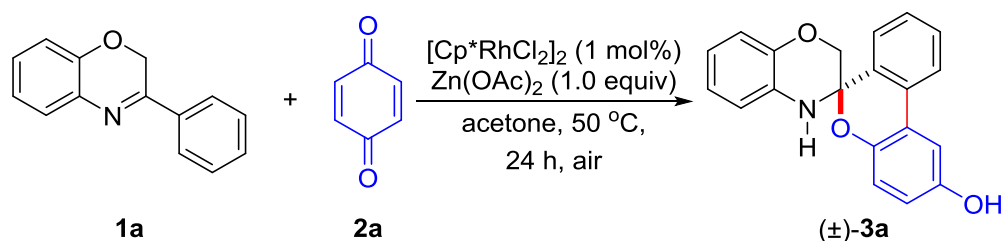
Entry ^a	Temp. (°C)	Time (h)	Yield(%) ^b
1	rt	48	92
2	50	24	94

^aReaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol% of $[\text{Cp}^*\text{RhCl}_2]_2$, 0.1 mmol of $\text{Zn}(\text{OAc})_2$, 1.0 mL of acetone, under air. ^bIsolated yield refers to **1a**.

Table S5. Optimization of the Catalyst Loading.

Entry ^a	Catalyst (x mol%)	Yield(%) ^b
1	5	94
2	2.5	94
3	1	95

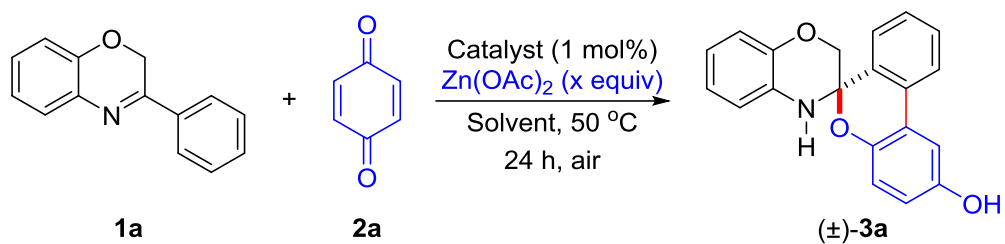
^aReaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 0.1 mmol of $\text{Zn}(\text{OAc})_2$, 1.0 mL of acetone, under air. ^bIsolated yield refers to **1a**.

Table S6. Optimization of the Equivalent of 2a.

Entry ^a	2a (x equiv)	Yield(%) ^b
1	2.0	95
2	1.0	79
3	1.2	81
4	1.5	88

^aReaction conditions: 0.1 mmol of **1a**, 1 mol% of $[\text{Cp}^*\text{RhCl}_2]_2$, 0.1 mmol of $\text{Zn}(\text{OAc})_2$, 1.0 mL of acetone, under air. ^bIsolated yield refers to **1a**.

Table S7. Optimization of the Equivalent of Additives.



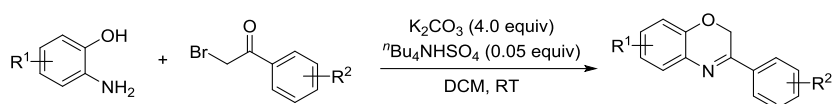
Entry ^a	Additive (x equiv)	Yield(%) ^b
1	1.0	95
2	0.2	50
3	0.5	68

^aReaction conditions: 0.1 mmol of **1a**, 0.2 mmol of **2a**, 1 mol% of $[\text{Cp}^*\text{RhCl}_2]_2$, 1.0 mL of acetone, 50 °C, under air. ^bIsolated yield refers to **1a**.

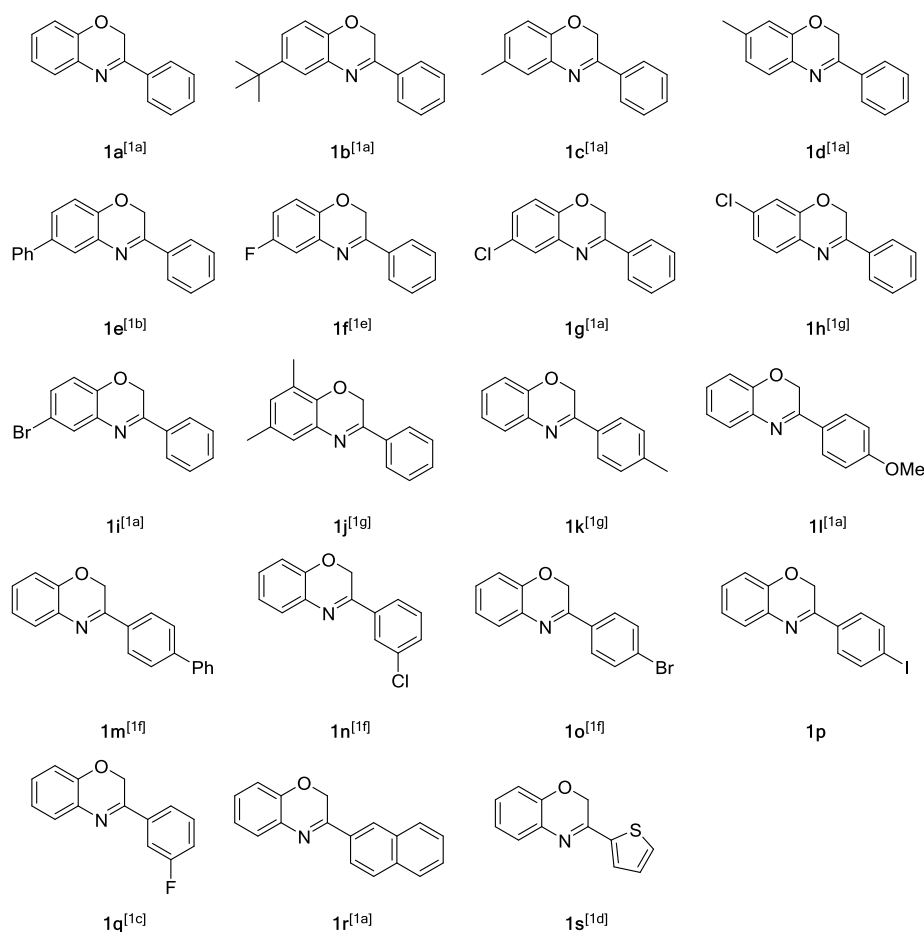
(C) General procedure for the Synthesis of Substrates 1 and 2.

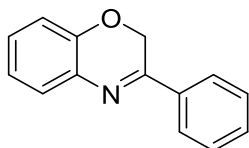
Substrates **1** were synthesized according to the previous literatures^[1].

2-Aminophenol (109 mg, 1.0 mmol) and CH₂Cl₂ (20 mL) were added into a round bottom bottle, and then aqueous K₂CO₃ (553 mg, 4.0 mmol) solution (20 mL) and ⁿBu₄NHSO₄ (17 mg, 0.05 mmol) were added. Next substituted 2-bromoacetophenone (199 mg, 1.0 mmol) dissolved in CH₂Cl₂ (5 mL) was added dropwise to the reaction mixture. The reaction mixture was stirred at room temperature and monitored by TLC until the consumption of the starting materials. After the reaction finished, the organic layer was extracted with dichloromethane, dried with anhydrous Na₂SO₄. The solvent was removed in vacuo. The crude mixture was purified by column chromatography with petroleum ether and EtOAc as eluent.



Scheme S1 List of starting material benzoxazines 1.

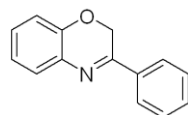




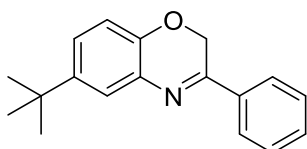
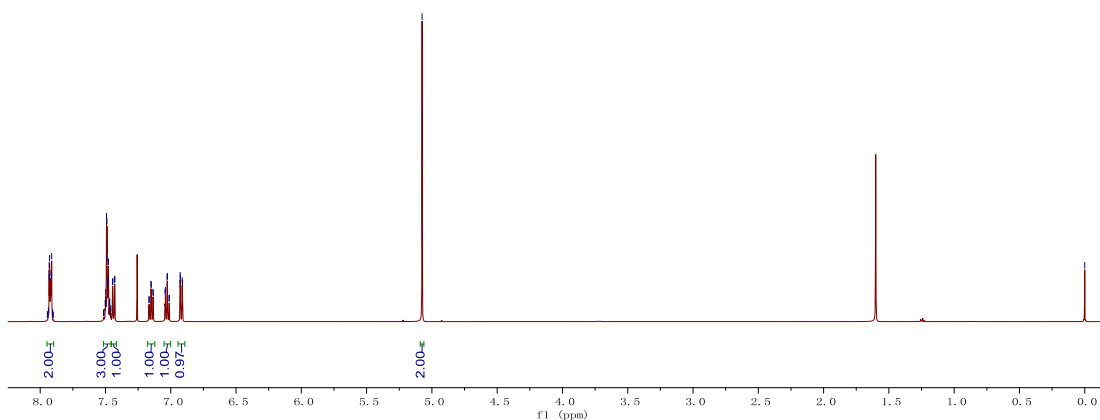
3-Phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1a**: A known compound^[1a]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.9$, 92% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.95-7.90 (m, 2H), 7.52-7.46 (m, 3H), 7.44 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.15 (td, $J = 7.5, 1.5$ Hz, 1H), 7.03 (td, $J = 7.5, 1.5$ Hz, 1H), 6.92 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.08 (s, 2H).



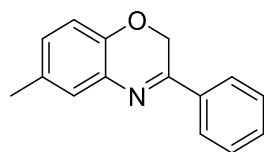
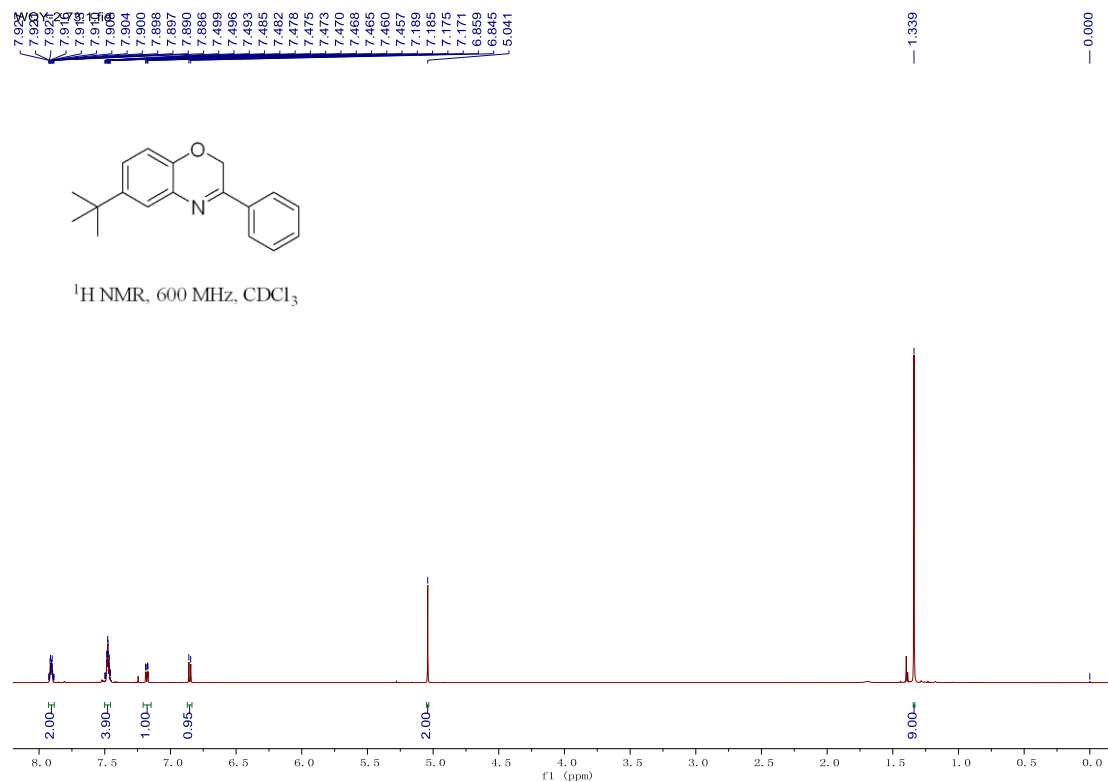
¹H NMR, 500 MHz, CDCl₃



6-(tert-Butyl)-3-phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1b**: A known compound^[1a]. Yellow oil. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.5$, 67% yield.

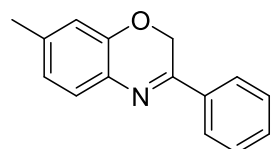
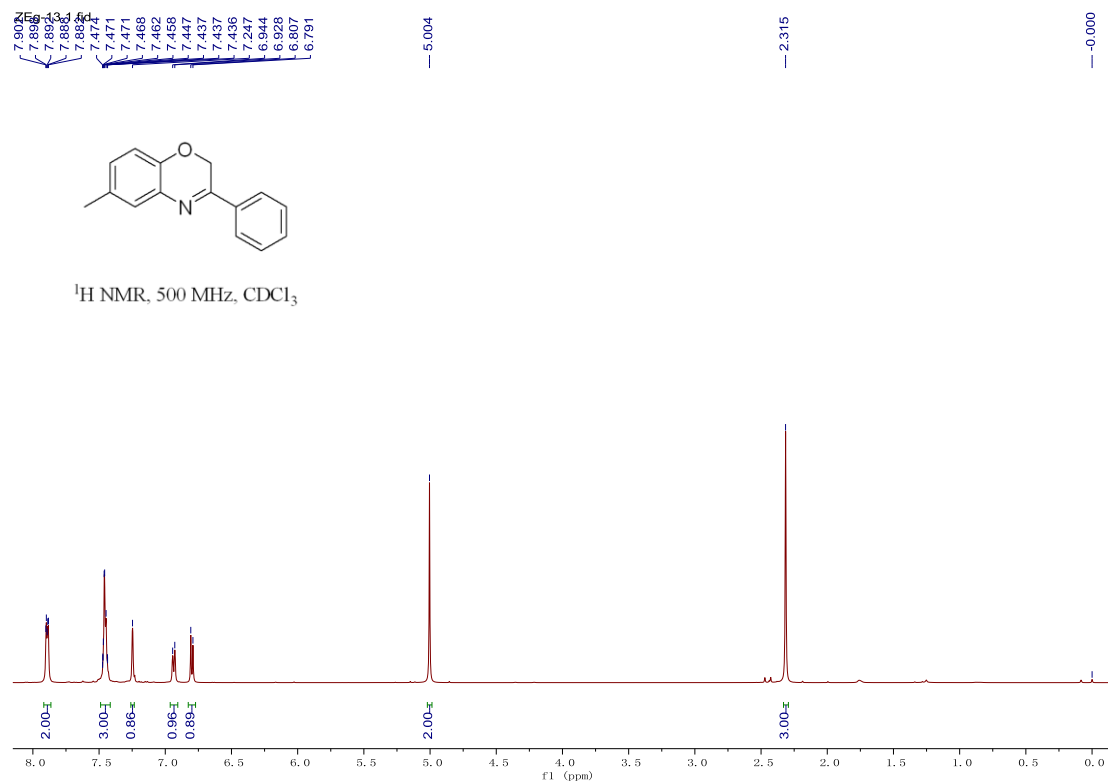
¹H NMR (600 MHz, CDCl₃, TMS) δ 7.93-7.89 (m, 2H), 7.50-7.46 (m, 4H), 7.18 (dd, $J = 8.4, 2.4$ Hz, 1H), 6.85 (d, $J = 8.4$ Hz, 1H), 5.04 (s, 2H), 1.34 (s, 9H).



6-Methyl-3-phenyl-2*H*-benzo[*b*][1,4]oxazine

Compound **1c**: A known compound^[1a]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, *R_f* = 0.5, 71% yield.

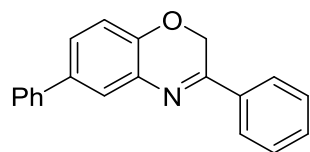
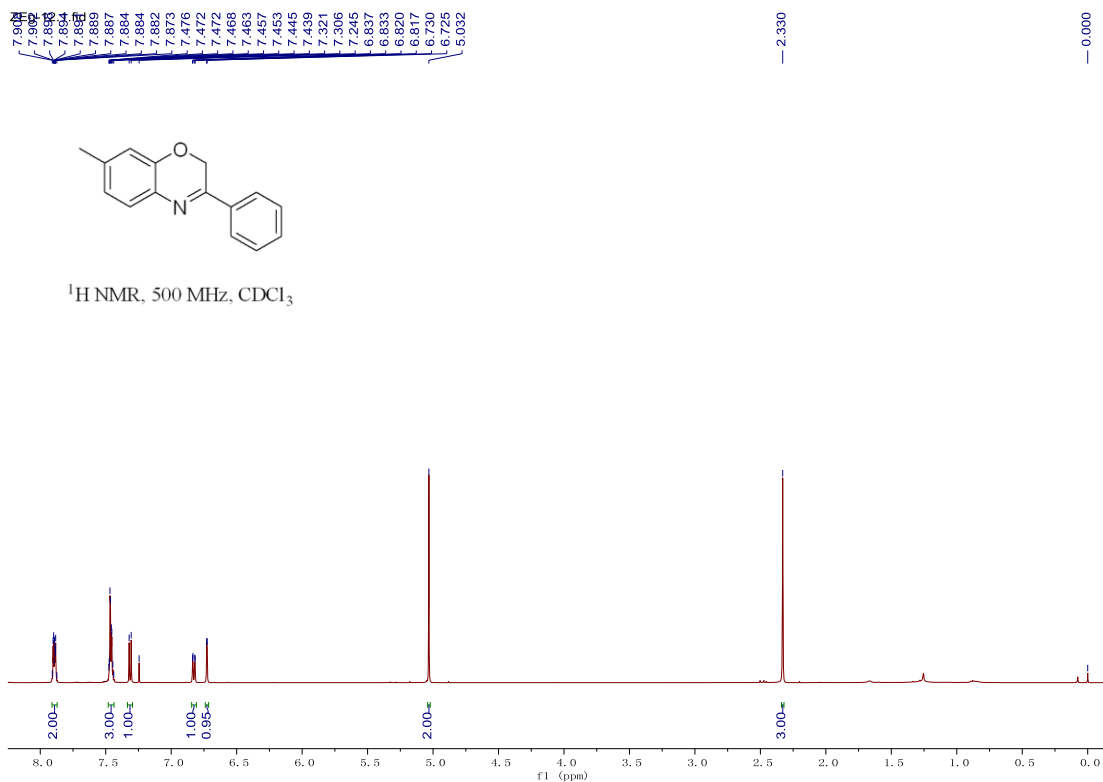
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.90-7.88 (m, 2H), 7.47-7.44 (m, 3H), 7.25 (s, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.80 (d, *J* = 8.0 Hz, 1H), 5.00 (s, 2H), 2.32 (s, 3H).



7-Methyl-3-phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1d**: A known compound^[1a]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 77% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.91-7.87 (m, 2H), 7.48-7.44 (m, 3H), 7.31 (d, J = 7.5 Hz, 1H), 6.83 (dd, J = 8.5, 2.0 Hz, 1H), 6.73 (d, J = 1.0 Hz, 1H), 5.03 (s, 2H), 2.33 (s, 3H).



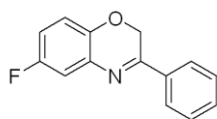
3,6-Diphenyl-2H-benzo[*b*][1,4]oxazine

Compound **1e**: A known compound^[1b]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 56% yield.

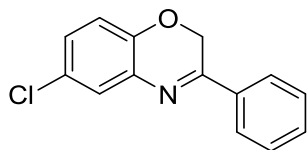
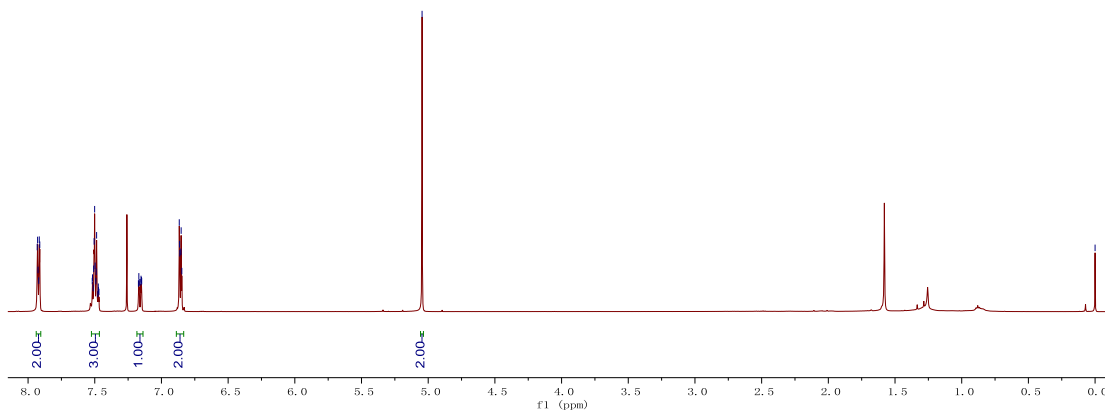
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.95-7.93 (m, 2H), 7.70 (d, J = 2.5 Hz, 1H), 7.62-7.60 (m, 2H), 7.51-7.47 (m, 3H), 7.45-7.42 (m, 2H), 7.40 (dd, J = 8.5, 2.5 Hz, 1H), 7.34-7.31 (m, 1H), 6.98 (d, J = 8.5 Hz, 1H), 5.11 (s, 2H).

7.932
7.926
7.924
7.920
7.916
7.912
7.519
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7.512
7.508
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7.490
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-0.000



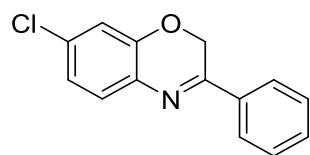
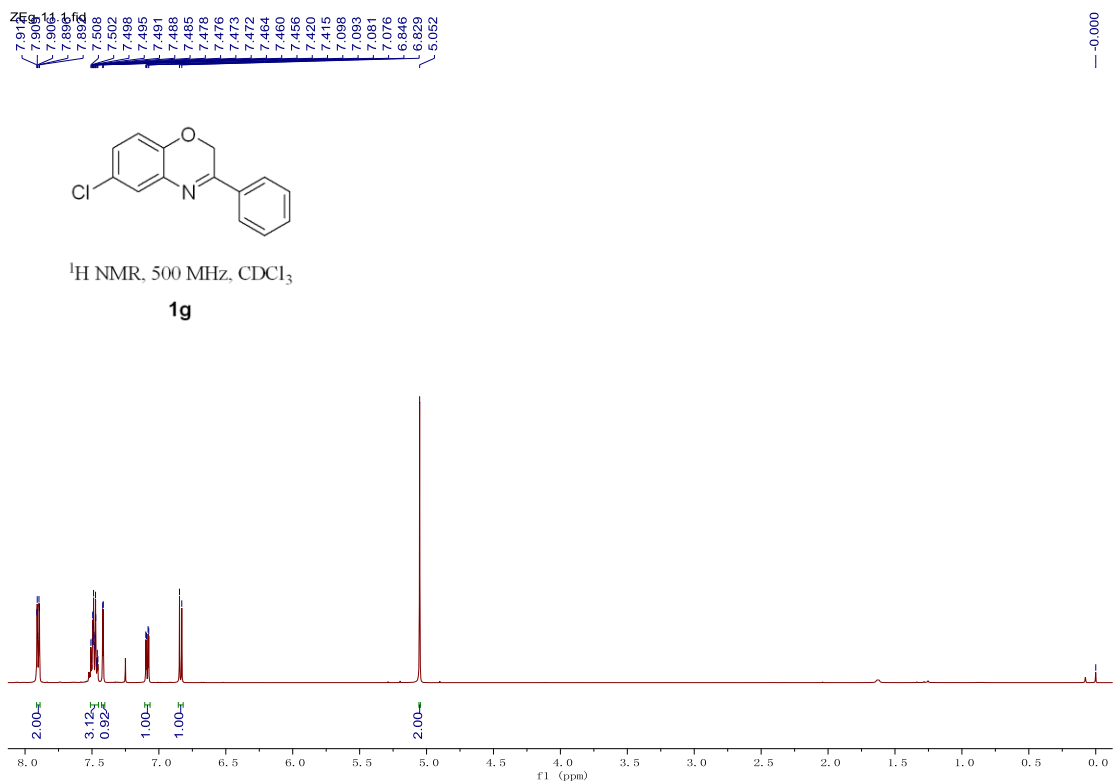
$^1\text{H NMR}$, 500 MHz, CDCl_3



6-Chloro-3-phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1g**: A known compound^[1a]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 80% yield.

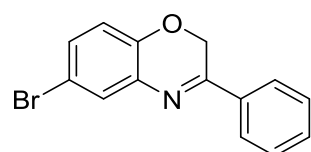
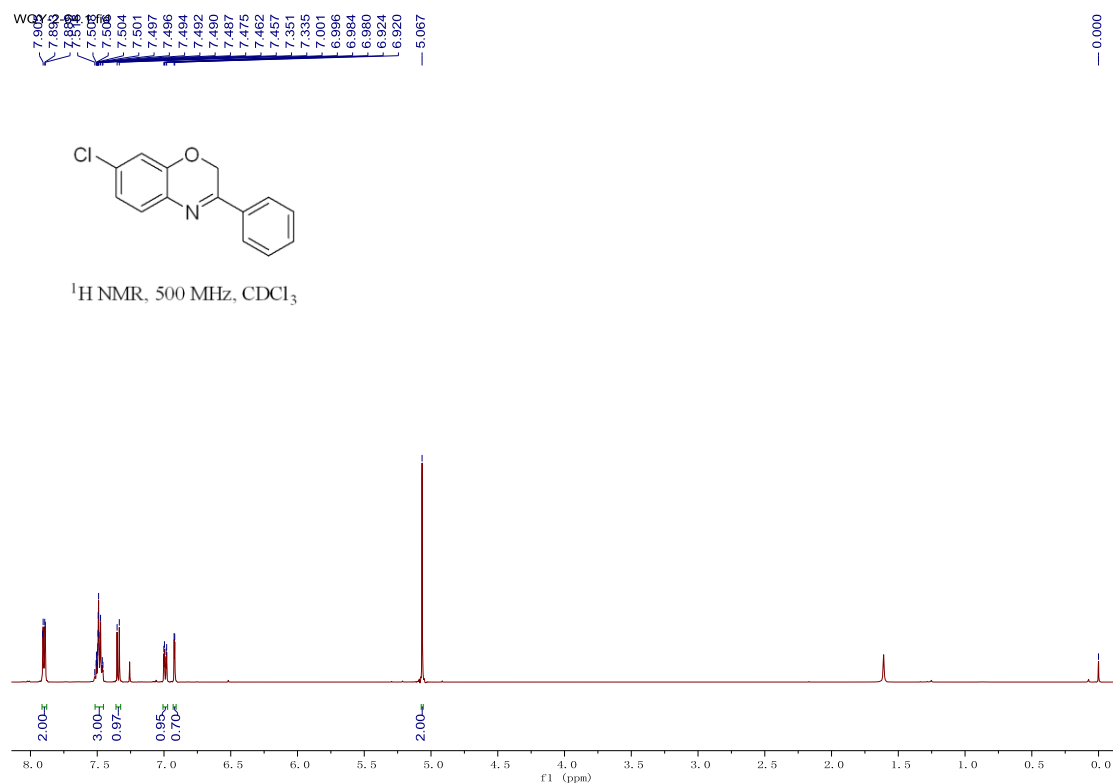
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.91-7.89 (m, 2H), 7.51-7.46 (m, 3H), 7.42 (d, J = 2.5 Hz, 1H), 7.09 (dd, J = 8.5, 2.5 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 5.05 (s, 2H).



7-Chloro-3-phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1h**: A known compound^[1g]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 80% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.91-7.89 (m, 2H), 7.51-7.46 (m, 3H), 7.34 (d, *J* = 8.0 Hz, 1H), 6.99 (dd, *J* = 8.5, 2.5 Hz, 1H), 6.92 (d, *J* = 2.0 Hz, 1H), 5.07 (s, 2H).



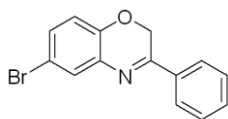
6-Bromo-3-phenyl-2H-benzo[b][1,4]oxazine

Compound **1i**: A known compound^[1a]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 82.5% yield.

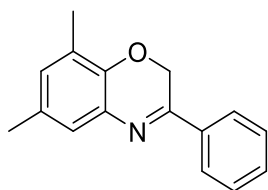
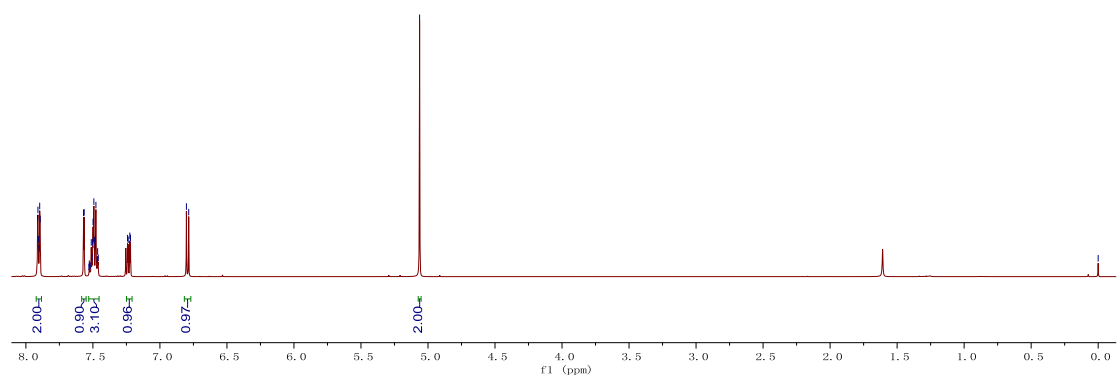
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.91-7.89 (m, 2H), 7.57 (d, *J* = 2.5 Hz, 1H), 7.53-7.46 (m, 3H), 7.23 (dd, *J* = 8.0, 2.5 Hz, 1H), 6.79 (d, *J* = 8.5 Hz, 1H), 5.06 (s, 2H).

7.915
7.907
7.900
7.893
7.884
7.875
7.570
7.565
7.530
7.527
7.524
7.520
7.512
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7.478
7.468
7.465
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7.220
6.802
6.785
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0.000



$^1\text{H NMR}$, 500 MHz, CDCl_3



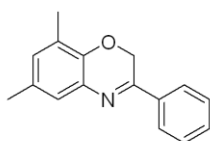
6,8-Dimethyl-3-phenyl-2H-benzo[*b*][1,4]oxazine

Compound **1j**: A known compound^[1g]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.5$, 67% yield.

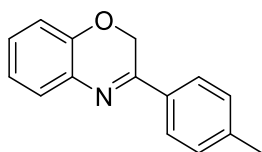
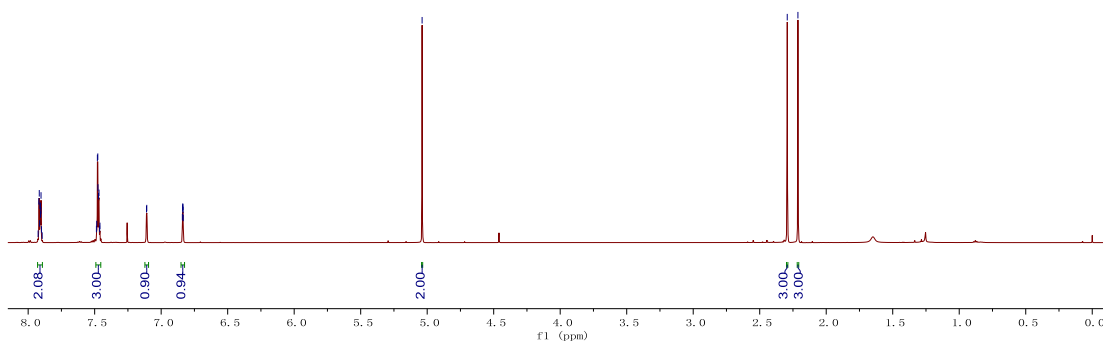
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.93-7.90 (m, 2H), 7.49-7.46 (m, 3H), 7.11 (d, $J = 1.0$ Hz, 1H), 6.84-6.83 (m, 1H), 5.04 (s, 2H), 2.29 (s, 3H), 2.21 (s, 3H).

7.925
7.916
7.914
7.911
7.909
7.905
7.903
7.900
7.895
7.487
7.484
7.480
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7.475
7.471
7.467
7.463
7.460
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6.837
6.835
6.834
5.038

2.293
2.213



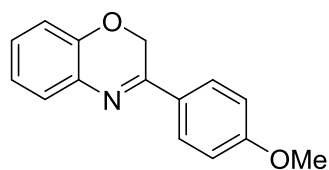
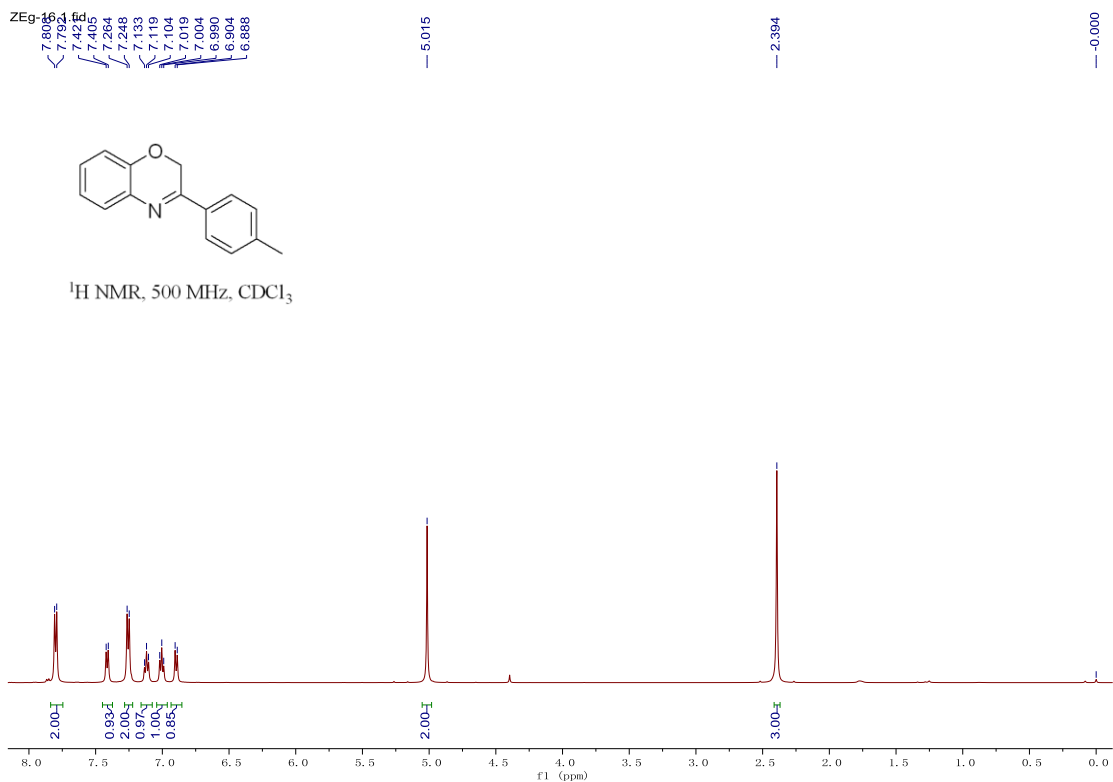
$^1\text{H NMR}$, 500 MHz, CDCl_3



3-(*p*-Tolyl)-2*H*-benzo[*b*][1,4]oxazine

Compound **1k**: A known compound^[1g]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.5, 79% yield.

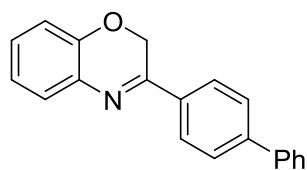
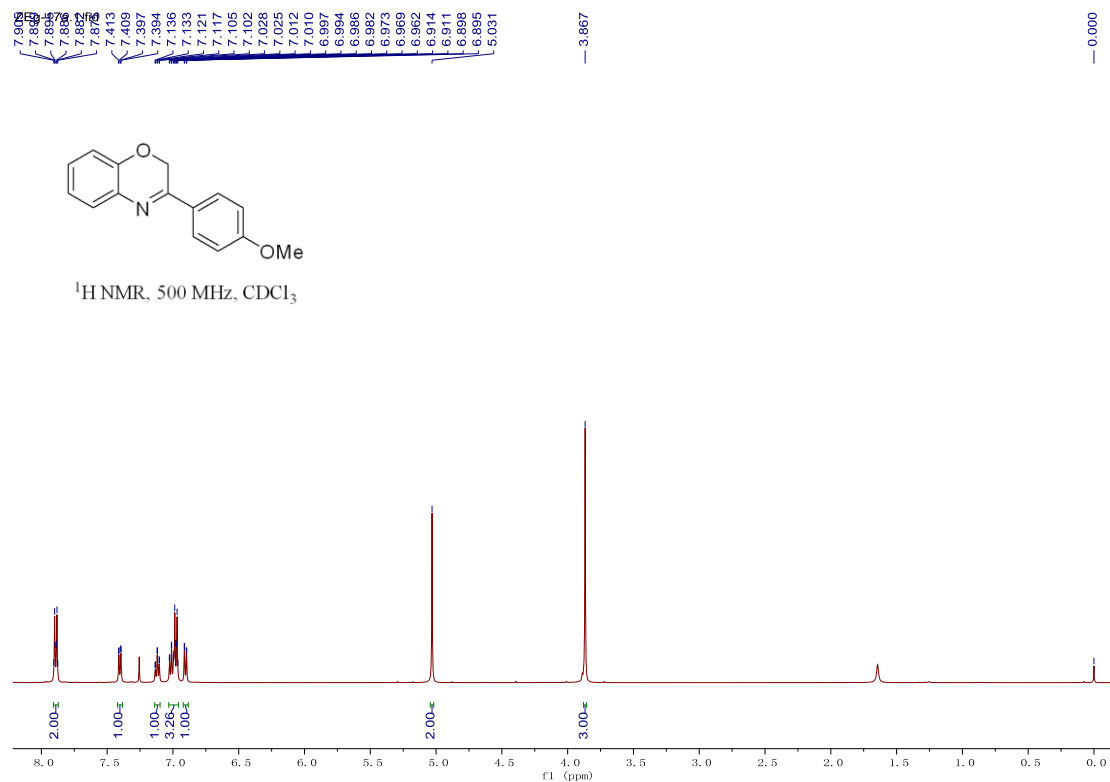
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.80 (d, J = 8.0 Hz, 2H), 7.41 (d, J = 8.0 Hz, 1H), 7.26 (d, J = 8.0 Hz, 2H), 7.12 (t, J = 7.5 Hz, 1H), 7.00 (t, J = 7.5 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.02 (s, 2H), 2.39 (s, 3H).



3-(4-Methoxyphenyl)-2H-benzo[*b*][1,4]oxazine

Compound **II**: A known compound^[1a]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.3$, 60% yield.

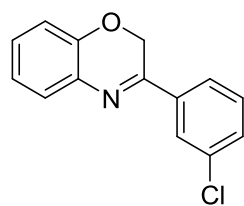
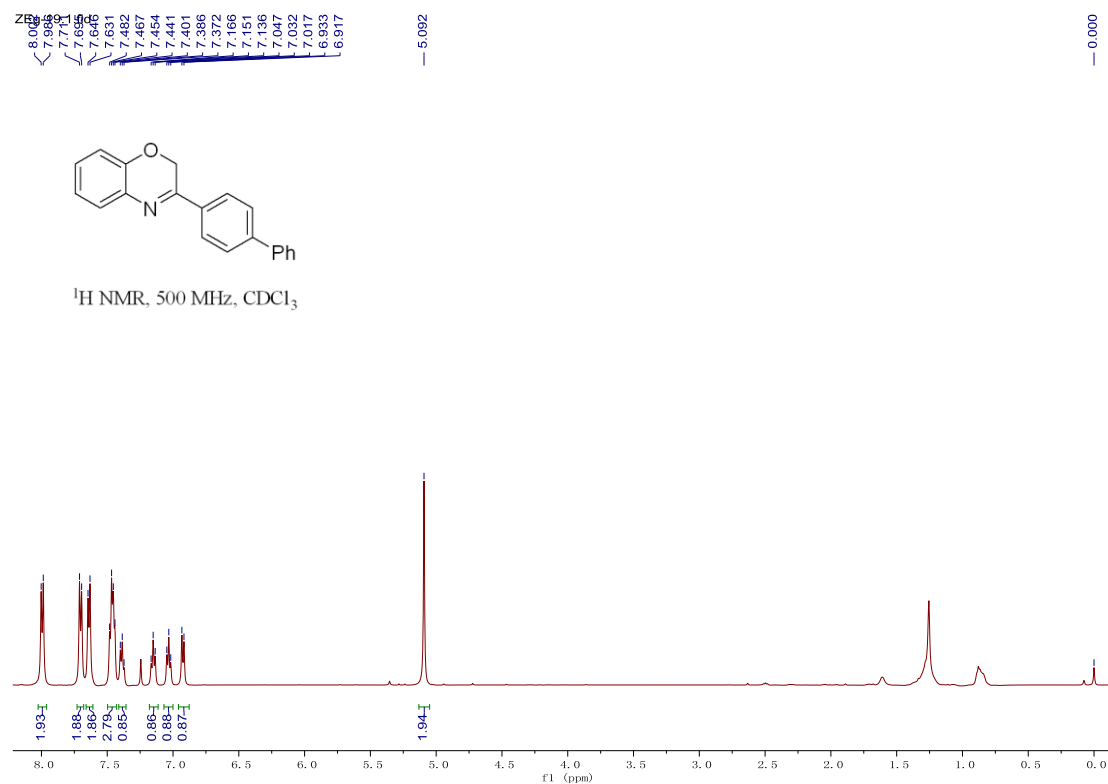
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.89 (dt, $J = 8.5, 2.0$ Hz, 2H), 7.40 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.12 (td, $J = 7.5, 1.5$ Hz, 1H), 7.03-6.96 (m, 3H), 6.90 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.03 (s, 2H), 3.87 (s, 3H).



3-([1,1'-Biphenyl]-4-yl)-2H-benzo[*b*][1,4]oxazine

Compound **1m**: A known compound^[1f]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.5$, 39% yield.

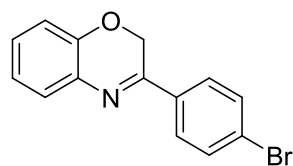
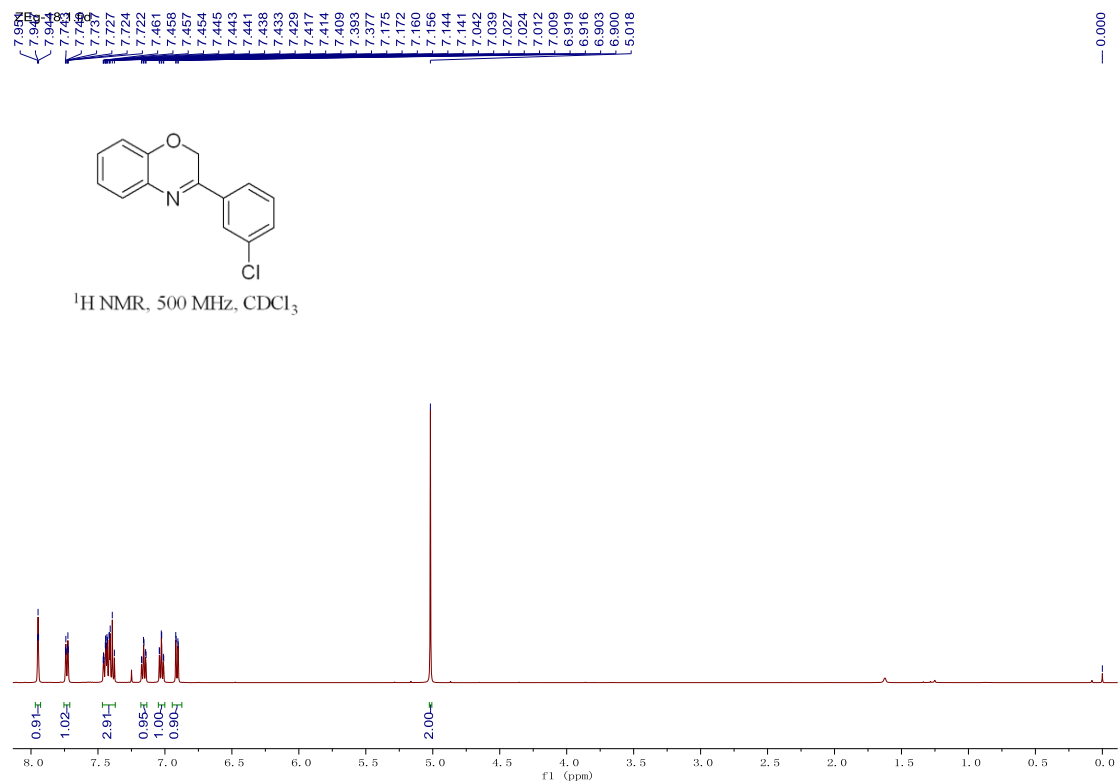
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.99 (d, $J = 8.0$ Hz, 2H), 7.70 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 7.5$ Hz, 2H), 7.48-7.44 (m, 3H), 7.37 (t, $J = 7.5$ Hz, 1H), 7.15 (t, $J = 7.5$ Hz, 1H), 7.03 (t, $J = 7.5$ Hz, 1H), 6.93 (d, $J = 8.0$ Hz, 1H), 5.09 (s, 2H).



3-(3-Chlorophenyl)-2H-benzo[*b*][1,4]oxazine

Compound **1n**: A known compound^[11]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.5$, 81% yield.

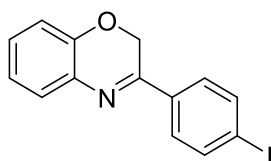
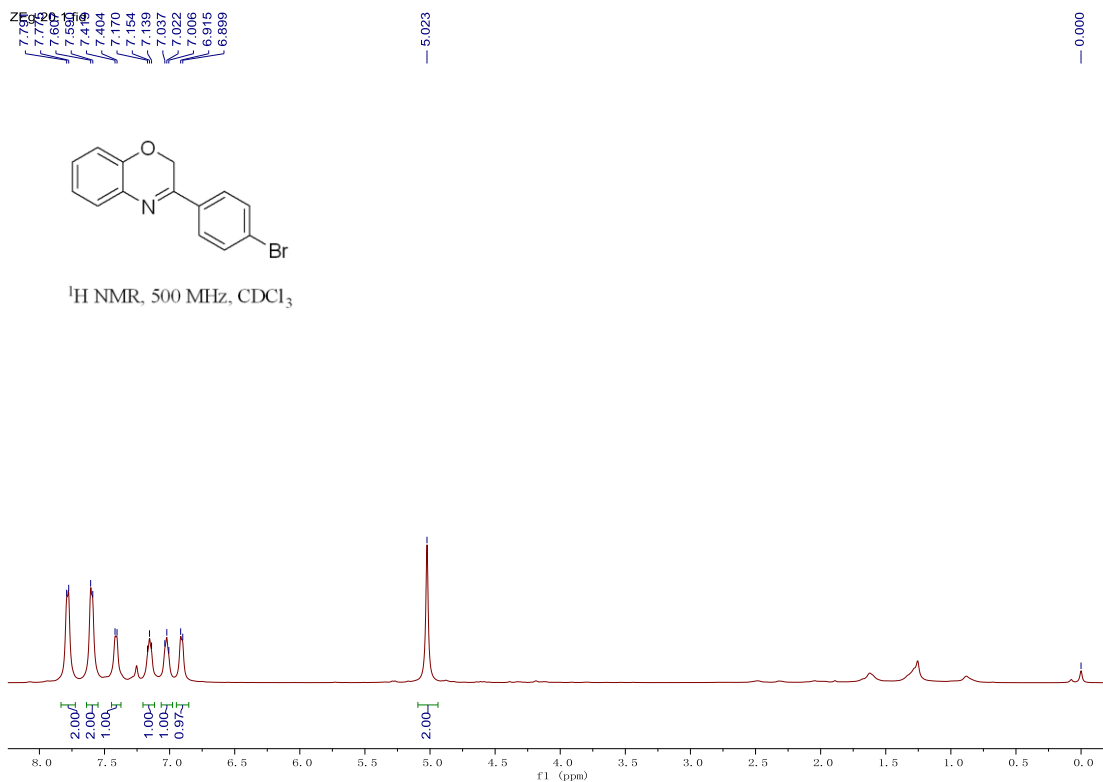
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.95 (t, $J = 1.5$ Hz, 1H), 7.73 (dt, $J = 8.0, 1.5$ Hz, 1H), 7.46-7.38 (m, 3H), 7.16 (td, $J = 7.5, 1.5$ Hz, 1H), 7.03 (td, $J = 7.5, 1.5$ Hz, 1H), 6.91 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.02 (s, 2H).



3-(4-Bromophenyl)-2*H*-benzo[*b*][1,4]oxazine

Compound **10**: A known compound^[1f]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, *R_f* = 0.5, 62% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.41 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 5.02 (s, 2H).



3-(4-Iodophenyl)-2*H*-benzo[*b*][1,4]oxazine

Compound **1p**: A white solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, *R_f* = 0.8, 89% yield. m.p. 148-150 °C.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.82 (d, *J* = 9.0 Hz, 2H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.42 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.16 (td, *J* = 7.5, 1.5 Hz, 1H), 7.02 (td, *J* = 7.5, 1.5 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.5 Hz, 1H), 5.02 (s, 2H).

¹³C NMR (125 MHz, CDCl₃) δ 157.7, 146.4, 138.1, 134.9, 133.7, 129.1, 128.05, 127.99, 122.6, 115.7, 98.2, 62.6.

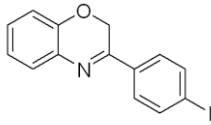
IR (KBr) ν (cm⁻¹): 3032, 1608, 1578, 1477, 1400, 1211, 1003, 975, 883, 756 cm⁻¹.

HRMS (ESI) calcd. for [C₁₄H₁₀INO+H]⁺ requires 335.98798, found 335.98779 [M+H]⁺.

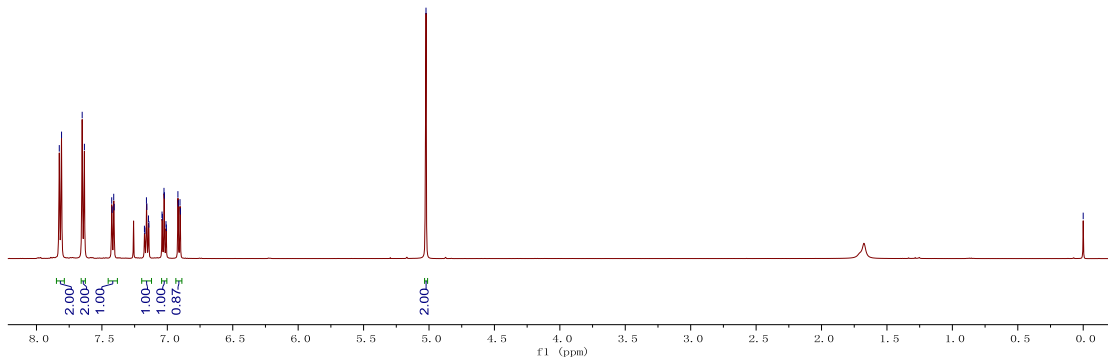
7.828
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7.422
7.410
7.406
7.175
7.172
7.160
7.156
7.144
7.141
7.090
7.086
7.026
7.023
7.010
7.007
6.919
6.916
6.903
6.900

5.023

0.000

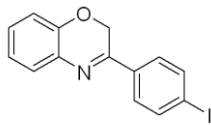


¹H NMR, 500 MHz, CDCl₃

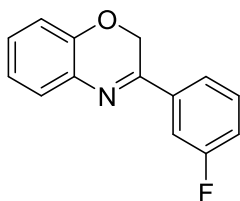
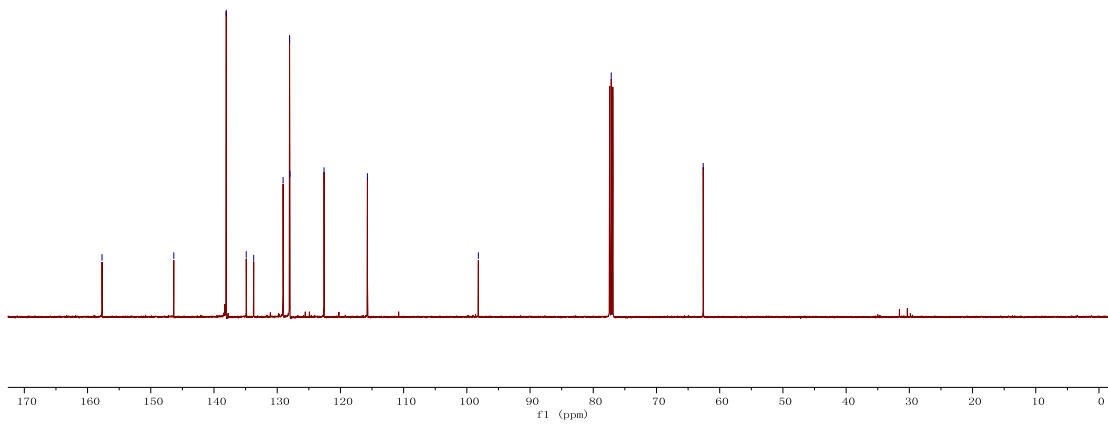


ZEH-190.1.fid

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127.988
122.591
115.729
98.182
77.160
62.611



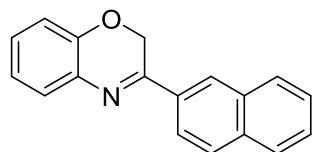
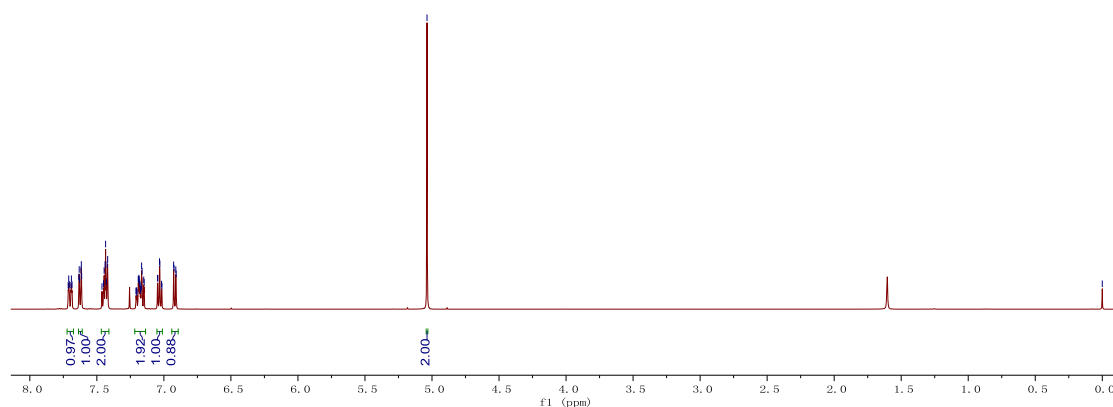
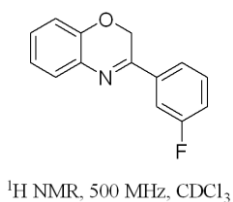
¹³C NMR, 125 MHz, CDCl₃



3-(3-Fluorophenyl)-2H-benzo[*b*][1,4]oxazine

Compound **1q**: A known compound^[1c]. White solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.8$, 89% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.70 (dt, $J = 10.0, 2.0$ Hz, 1H), 7.62 (dt, $J = 8.0, 1.5$ Hz, 1H), 7.46-7.42 (m, 2H), 7.21-7.15 (m, 2H), 7.03 (td, $J = 7.5, 1.5$ Hz, 1H), 6.92 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.04 (s, 2H).



3-(Naphthalen-2-yl)-2H-benzo[*b*][1,4]oxazine

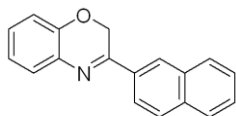
Compound **1r**: A known compound^[1a]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, $R_f = 0.8$, 60% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 8.24 (d, $J = 8.5$ Hz, 1H), 8.19 (s, 1H), 7.92 (d, $J = 8.5$ Hz, 2H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.57-7.52 (m, 2H), 7.48 (d, $J = 7.5$ Hz, 1H), 7.17 (t, $J = 7.5$ Hz, 1H), 7.05 (t, $J = 7.5$ Hz, 1H), 6.95 (d, $J = 8.0$ Hz, 1H), 5.20 (s, 2H).

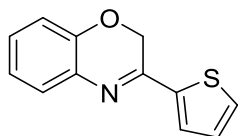
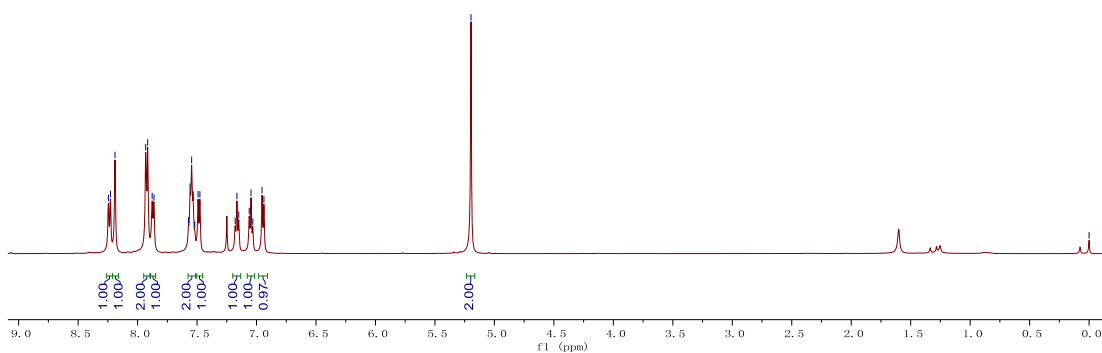
ZEq-72.11
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 8.190
 7.832
 7.816
 7.878
 7.862
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 7.559
 7.545
 7.532
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 7.061
 7.046
 7.031
 6.854
 6.838

— 5.197

— 0.000



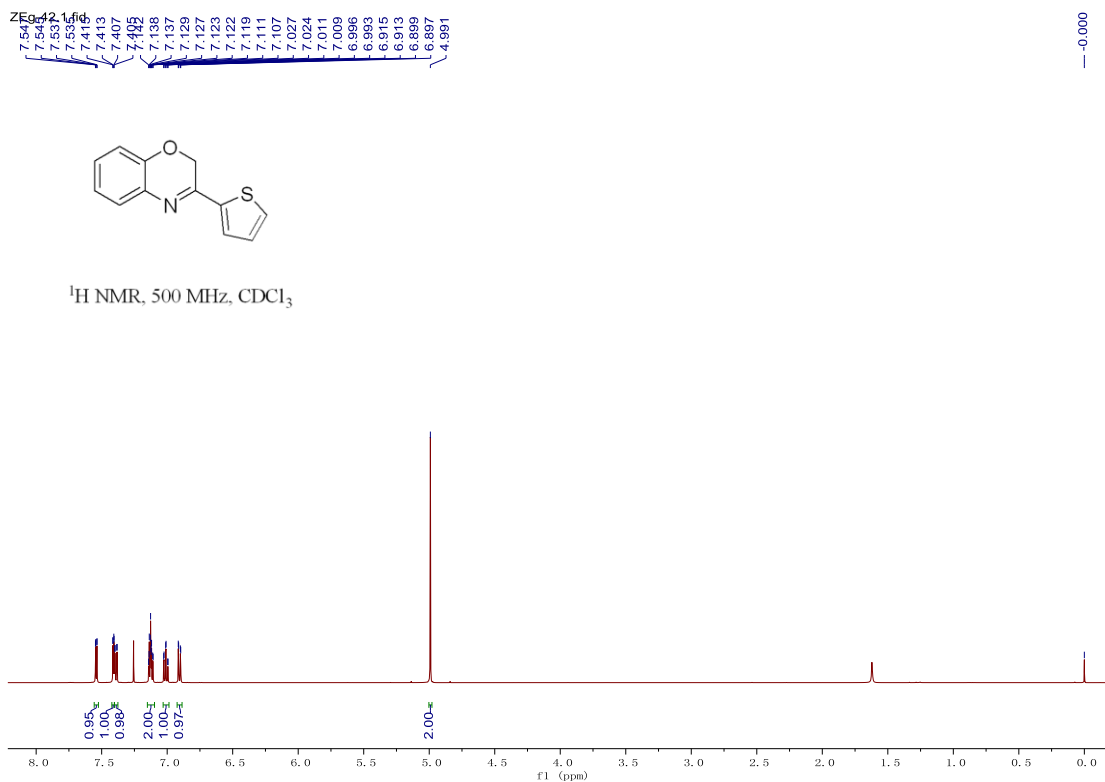
¹H NMR, 500 MHz, CDCl₃



3-(Thiophen-2-yl)-2H-benzo[*b*][1,4]oxazine

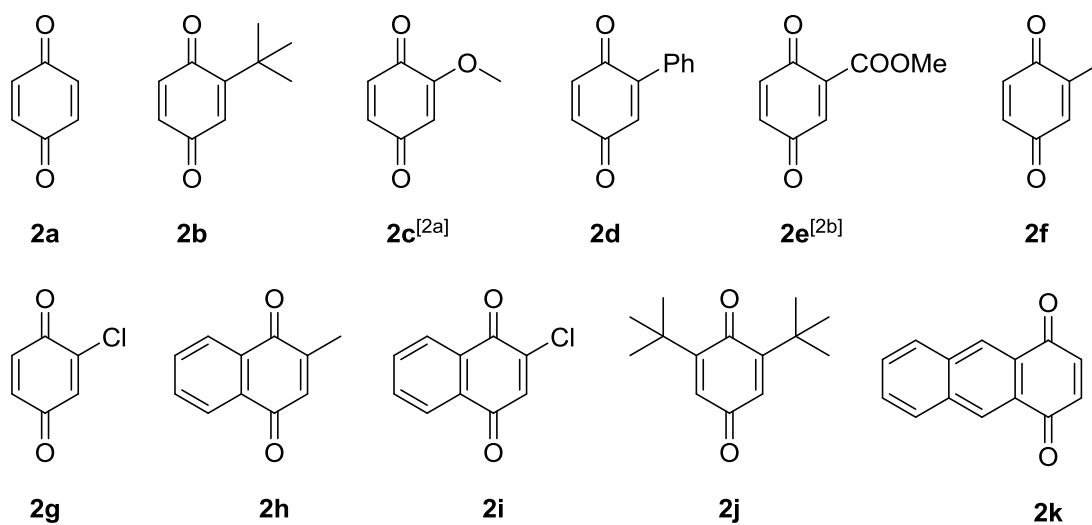
Compound **1s**: A known compound^[1d]. Yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 15/1, R_f = 0.6, 60% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.54 (dd, *J* = 5.0, 1.0 Hz, 1H), 7.41 (dd, *J* = 4.0, 1.0 Hz, 1H), 7.39 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.14-7.11 (m, 2H), 7.01 (td, *J* = 7.5, 1.5 Hz, 1H), 6.91 (dd, *J* = 8.0, 1.0 Hz, 1H), 4.99 (s, 2H).

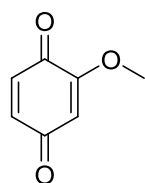
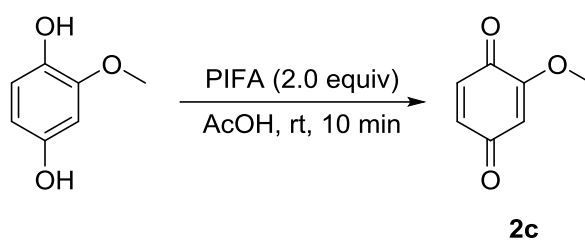


Most of the quinone compounds **2** employed in this work were commercially available, used as received from commercial sources, and are listed below. **2c** and **2e** were prepared following a reported procedure^[2].

Scheme S2 List of starting material quinone compounds **2.**



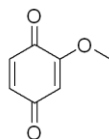
To a stirred solution of 2-methoxybenzene-1,4-diol (140 mg, 1.0 mmol) in acetic acid (7 mL), was added PIFA (860 mg, 2.0 mmol). The mixture was stirred at room temperature for a few minutes. Then the reaction was diluted with water and quenched with a saturated aqueous solution of NaHCO₃. Aqueous layer was extracted three times with DCM, the combined organic layers were dried over Na₂SO₄ and concentrated in vacuo. The crude product was rapidly filtered through a plug of silica with DCM as eluent to afford the desired product **2c** (125 mg, 90% yield).



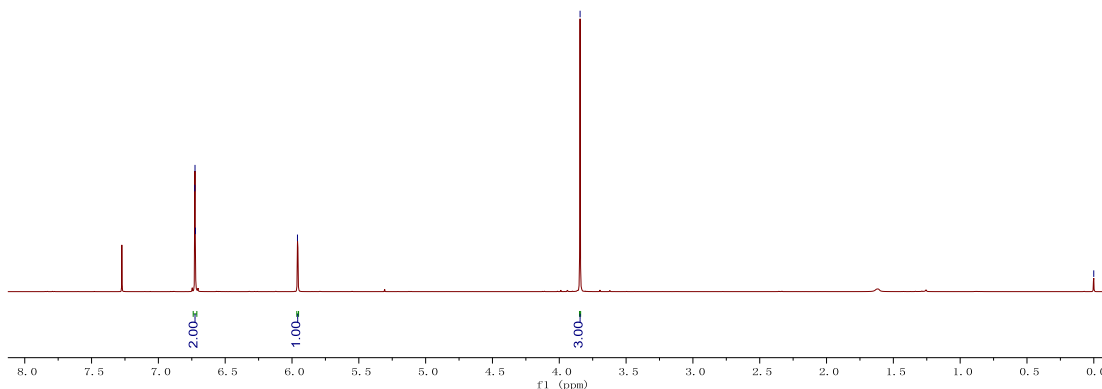
2-Methoxycyclohexa-2,5-diene-1,4-dione

Compound **2c**: A known compound^[2a]. Yellow solid. Column chromatography, eluent: CH₂Cl₂, R_f = 0.5, 90% yield.

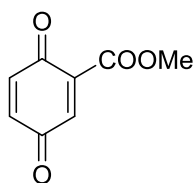
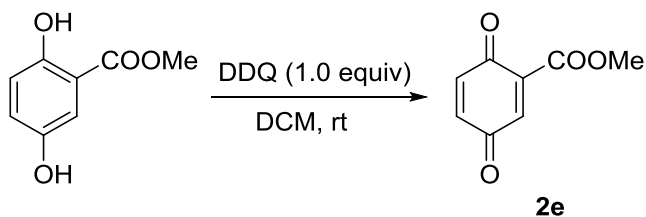
¹H NMR (500 MHz, CDCl₃, TMS) δ 6.73-6.72 (m, 2H), 5.96 (s, 1H), 3.84 (s, 3H).



¹H NMR, 500 MHz, CDCl₃



To a solution of methyl 2,5-dihydroxybenzoate (252 mg, 1.5 mmol) in DCM (3 mL) was added DDQ (341 mg, 1.5 mmol) portionwise at room temperature. After 2 h, the reaction mixture was diluted with DCM (15 mL), then washed with a mixture of water (10 mL) and saturated aqueous sodium bicarbonate (2 mL) five times. Combined organics were washed with brine (20 mL), dried over Na₂SO₄, and concentrated in vacuo to afford generally orange solids **2e** (166 mg, 67% yield).



Methyl 3,6-dioxocyclohexa-1,4-diene-1-carboxylate

Compound **2e**: A known compound^[2b]. Yellow solid. Recrystallize, 67% yield.

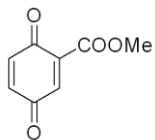
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.13 (d, $J = 1.5$ Hz, 1H), 6.84 (d, $J = 2.5$ Hz, 2H), 3.92 (s, 3H).

Zeg-59.1.fid

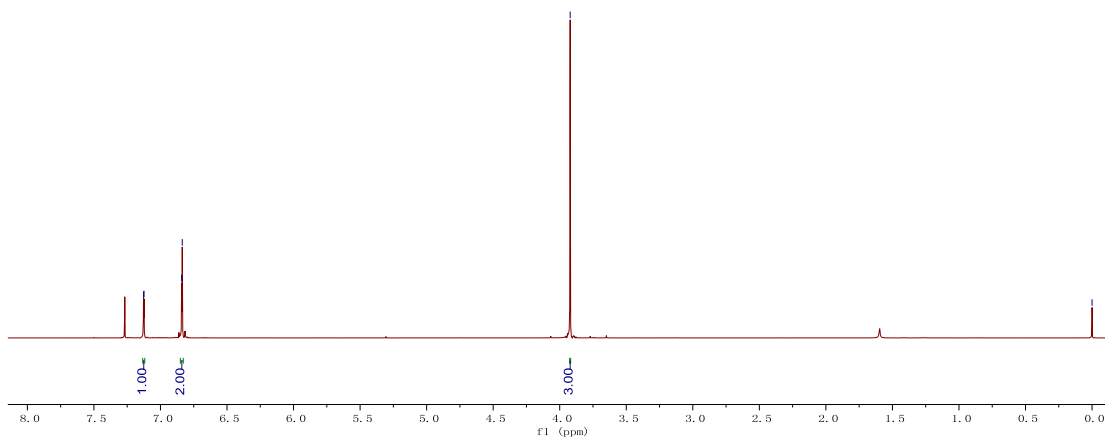
7.127
7.124
6.841
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3.921

0.000

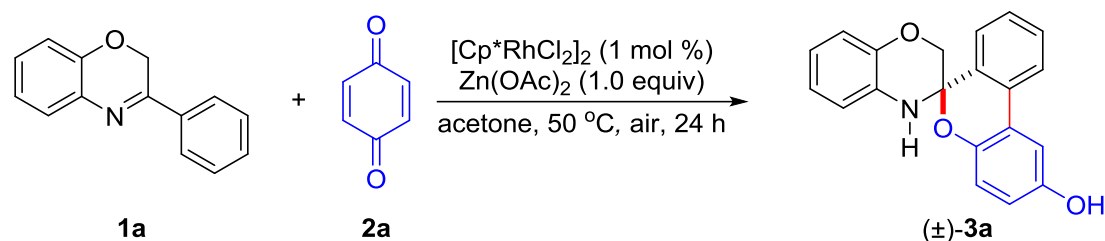


$^1\text{H NMR}$, 500 MHz, CDCl_3

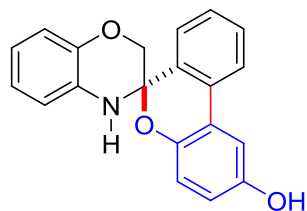


(D) General Procedure for Intermolecular Annulation and Analytical

Data of Products 3a-3z.



Under air atmosphere, acetone (0.1 M) was added to a mixture of **1a** (20.9 mg, 0.1 mmol), **2a** (21.7 mg, 0.2 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (0.6 mg, 1 mol%), $\text{Zn}(\text{OAc})_2$ (18.3 mg, 0.1 mmol). The reaction system was stirred for 24 h at 50 °C until **1a** was completely consumed by TLC monitoring. Then the solvent was removed under reduced pressure and the residue was purified by a silica gel flash column chromatography (eluent: petroleum ether/EtOAc, 4/1) to give the product **3a** (30.0 mg, 95% yield) as a white solid.



(±)-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

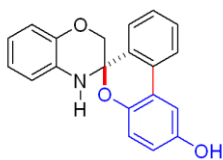
Compound **3a**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 30.0 mg, 95% yield. m.p. 118-124 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.23-8.16 (m, 1H), 7.83 (d, $J=8.0$ Hz, 1H), 7.58 (d, $J=7.5$ Hz, 1H), 7.53-7.49 (m, 1H), 7.45-7.40 (m, 1H), 7.34-7.33 (m, 1H), 6.90 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.84-6.77 (m, 4H), 6.73-6.69 (m, 1H), 6.48 (s, 1H), 4.35 (dd, $J = 11.0, 2.5$ Hz, 1H), 3.82 (d, $J = 11.0$ Hz, 1H).

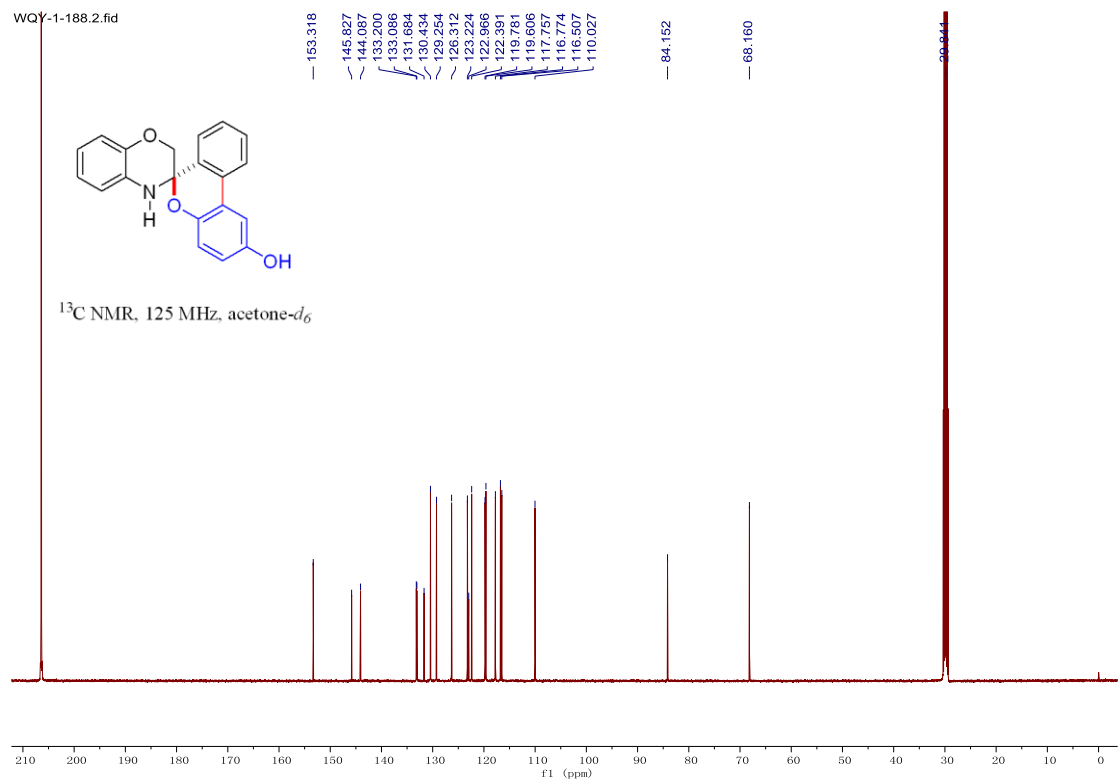
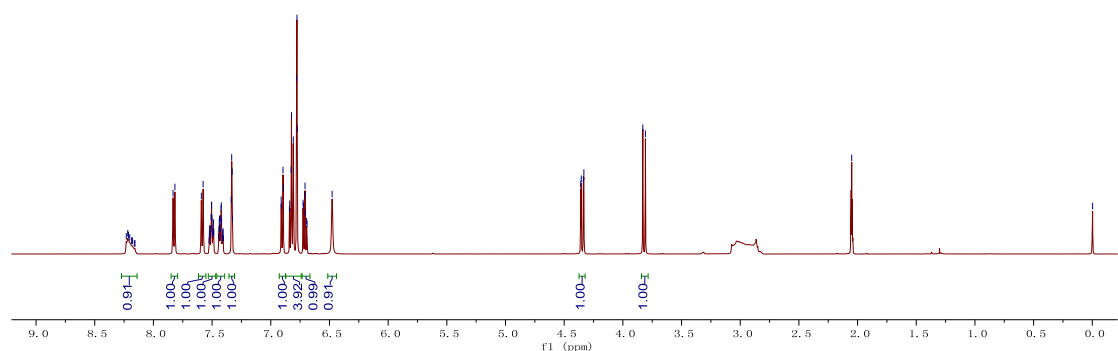
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.3, 145.8, 144.1, 133.2, 133.1, 131.7, 130.4, 129.3, 126.3, 123.2, 123.0, 122.4, 119.8, 119.6, 117.8, 116.8, 116.5, 110.0, 84.2, 68.2.

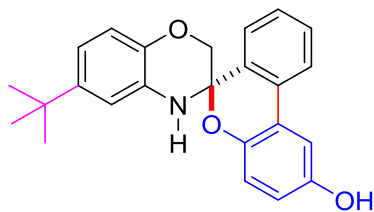
IR (KBr) $\nu(\text{cm}^{-1})$: 3358, 1691, 1611, 1496, 1311, 1208, 1039, 942, 854, 748 cm^{-1} .

HRMS (ESI) calcd. for $[C_{20}H_{15}NO_3+H]^+$ requires 318.11247, found 318.11252
[M+H]⁺.



¹H NMR, 500 MHz, acetone-*d*₆





(±)-6-(*tert*-Butyl)-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

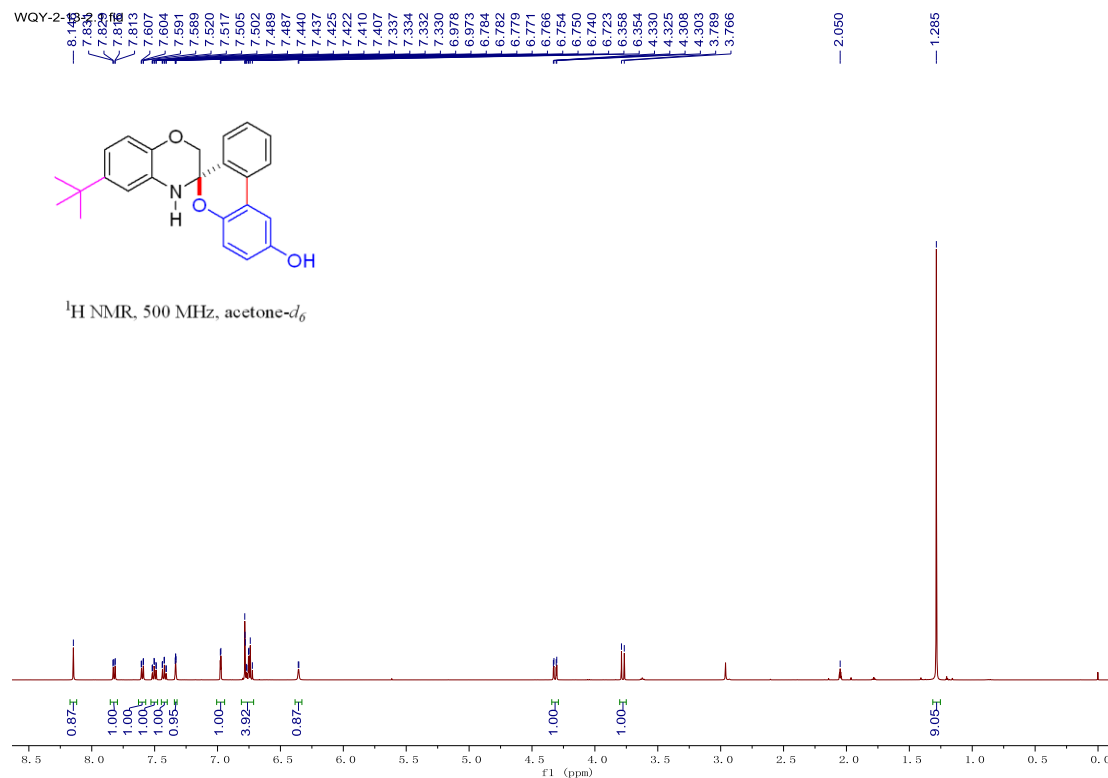
Compound **3b**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 34.7 mg, 93% yield. m.p. 147-151 °C.

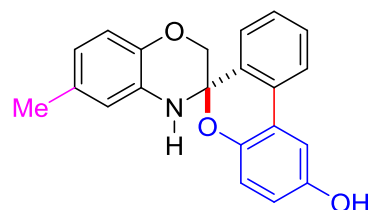
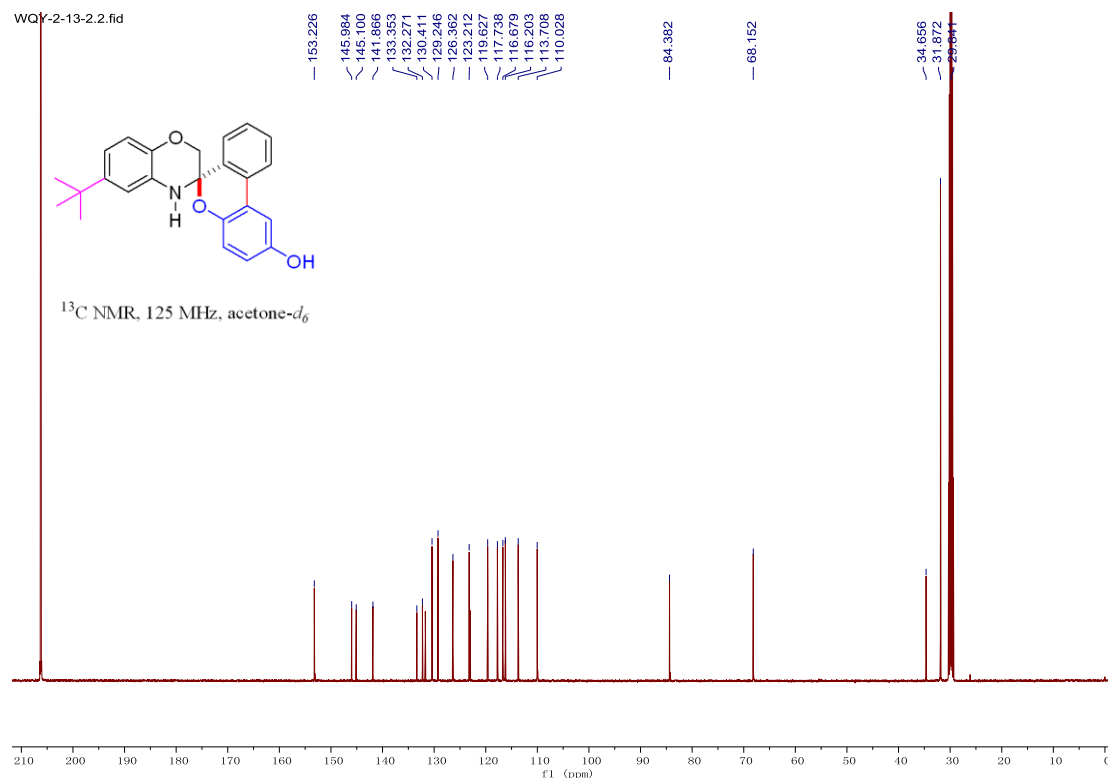
$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.15 (s, 1H), 7.82 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.60 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.50 (td, $J = 7.5, 1.5$ Hz, 1H), 7.42 (td, $J = 7.5, 1.5$ Hz, 1H), 7.34-7.33 (m, 1H), 6.98 (d, $J = 2.5$ Hz, 1H), 6.78-6.72 (m, 4H), 6.36 (d, $J = 2.0$ Hz, 1H), 4.32 (dd, $J = 11.0, 2.5$ Hz, 1H), 3.78 (d, $J = 11.5$ Hz, 1H), 1.29 (s, 9H).

$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.2, 146.0, 145.1, 141.9, 133.4, 132.3, 130.4, 129.2, 126.4, 123.2, 119.6, 117.7, 116.7, 116.2, 113.7, 110.0, 84.4, 68.2, 34.7, 31.9.

IR (KBr) $\nu(\text{cm}^{-1})$: 3360, 2961, 1493, 1313, 1296, 1200, 982, 813, 733, 642 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{24}\text{H}_{23}\text{NO}_3 + \text{H}]^+$ requires 374.17507, found 374.17490 $[\text{M} + \text{H}]^+$.





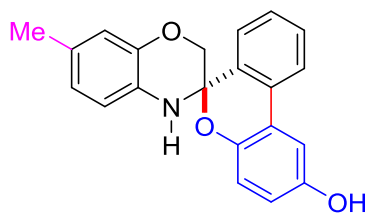
(±)-6-Methyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3c**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.2, 30.7 mg, 93% yield. m.p. 85-87 °C.

¹H NMR (500 MHz, DMSO-*d*₆) δ 9.19 (s, 1H), 7.81 (d, J = 7.5 Hz, 1H), 7.53-7.49 (m, 2H), 7.45-7.41 (m, 1H), 7.34 (d, J = 2.0 Hz, 1H), 7.26 (d, J = 2.0 Hz, 1H), 6.75 (d, J = 8.5 Hz, 1H), 6.69 (dd, J = 8.5, 3.0 Hz, 1H), 6.67 (d, J = 8.0 Hz, 1H), 6.61 (d, J = 2.5 Hz, 1H), 6.46-6.44 (m, 1H), 4.20 (dd, J = 11.0, 2.0 Hz, 1H), 3.71 (d, J = 11.5 Hz, 1H), 2.18 (s, 3H).

¹³C NMR (125 MHz, DMSO-*d*₆) δ 152.2, 144.2, 140.3, 131.94, 131.91, 130.4, 130.3, 129.7, 128.4, 125.6, 122.3, 121.6, 118.7, 118.6, 116.9, 115.7, 115.5, 109.2, 83.1, 67.0, 20.6.

IR (KBr) ν (cm⁻¹): 3250, 2921, 1617, 1492, 1311, 1217, 1051, 936, 855, 771 cm⁻¹.



(±)-7-Methyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

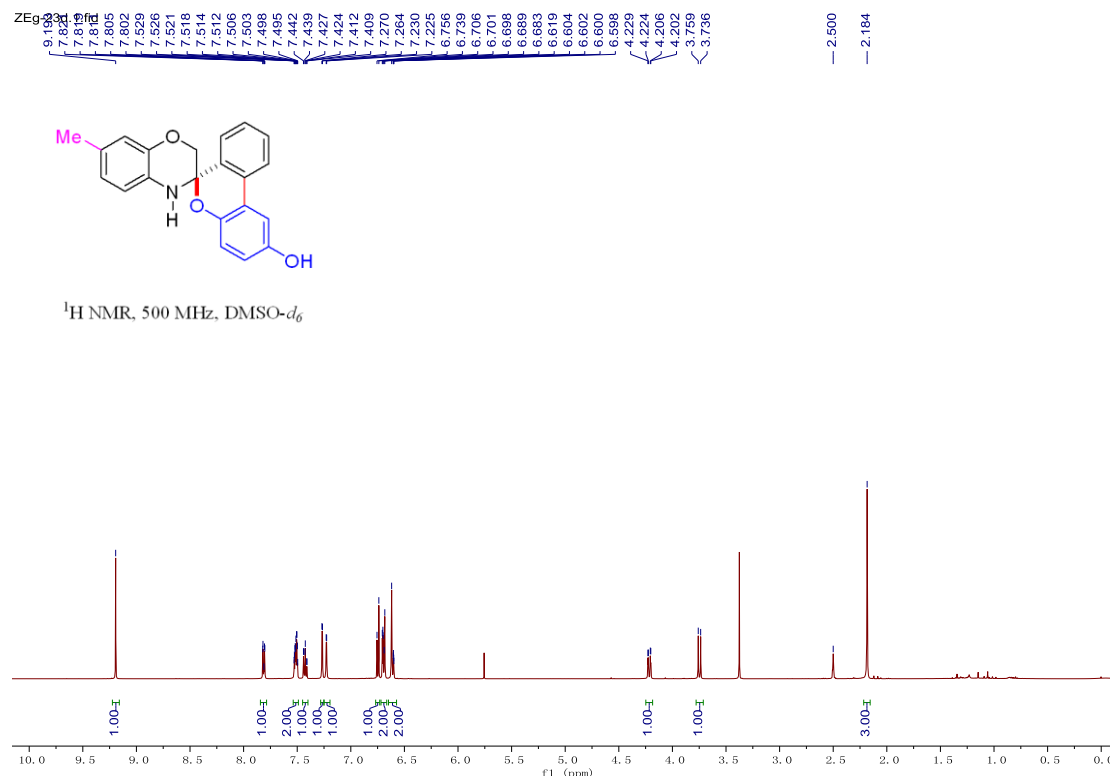
Compound **3d**: a yellow oil. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 27 mg, 82% yield.

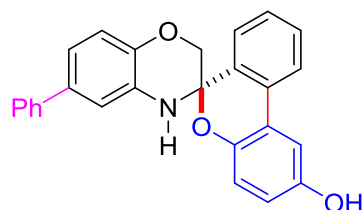
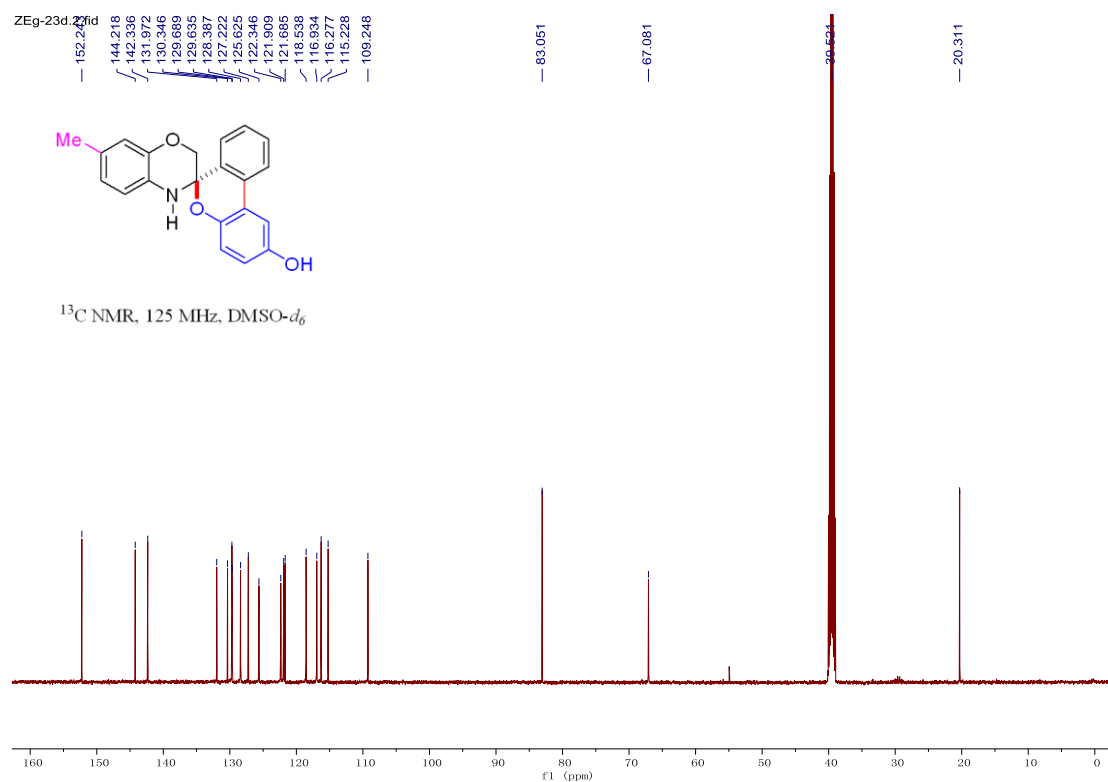
$^1\text{H NMR}$ (500 MHz, $\text{DMSO-}d_6$) δ 9.19 (s, 1H), 7.82-7.80 (m, 1H), 7.53-7.50 (m, 2H), 7.43 (td, $J = 7.5, 1.5$ Hz, 1H), 7.27 (d, $J = 2.5$ Hz, 1H), 7.23 (d, $J = 2.5$ Hz, 1H), 6.75 (d, $J = 8.5$ Hz, 1H), 6.71-6.68 (m, 2H), 6.62-6.60 (m, 2H), 4.22 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.75 (d, $J = 11.5$ Hz, 1H), 2.18 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 152.2, 144.2, 142.3, 132.0, 130.3, 129.7, 129.6, 128.4, 127.2, 125.6, 122.3, 121.9, 121.7, 118.5, 116.9, 116.3, 115.2, 109.2, 83.1, 67.1, 20.3.

IR (KBr) $\nu(\text{cm}^{-1})$: 3252, 2920, 1517, 1443, 1305, 1203, 1023, 945, 857, 770 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{21}\text{H}_{17}\text{NO}_3+\text{H}]^+$ requires 332.12812, found 332.12604 $[\text{M}+\text{H}]^+$.





(±)-6-Phenyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3e**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.2, 35 mg, 90% yield. m.p. 109-111 °C.

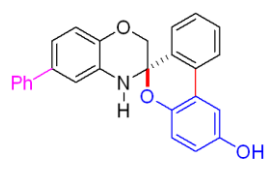
¹H NMR (600 MHz, CDCl₃, TMS) δ 7.68-7.66 (m, 1H), 7.52-7.51 (m, 3H), 7.47-7.43 (m, 1H), 7.41-7.36 (m, 3H), 7.31-7.28 (m, 1H), 7.20 (d, J = 1.2 Hz, 1H), 7.02 (dd, J = 8.4, 1.8 Hz, 1H), 6.98 (d, J = 7.8 Hz, 1H), 6.95-6.94 (m, 1H), 6.90 (d, J = 8.4 Hz, 1H), 6.72-6.69 (m, 1H), 4.98-4.90 (m, 2H), 4.41 (d, J = 11.4 Hz, 1H), 3.87 (d, J = 11.4 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 150.8, 145.6, 143.0, 141.1, 135.4, 132.0, 131.2, 130.6, 130.0, 128.9, 128.8, 127.0, 126.9, 125.3, 122.7, 122.3, 119.5, 119.2, 117.3, 117.0, 114.6, 109.6, 83.7, 67.9.

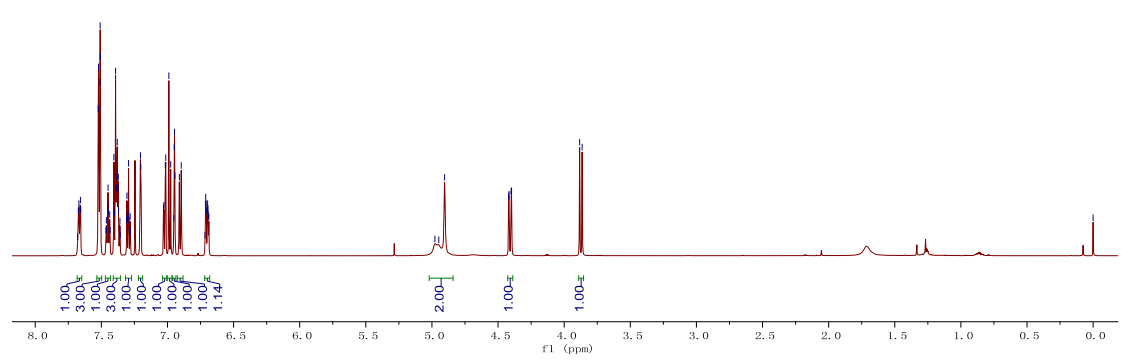
IR (KBr) ν (cm⁻¹): 3368, 1489, 1443, 1315, 1242, 1200, 1053, 945, 856, 763 cm⁻¹.

HRMS (ESI) calcd. for $[C_{26}H_{19}NO_3+H]^+$ requires 394.14377, found 394.14371
 $[M+H]^+$.

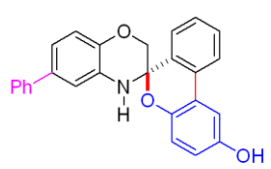
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6.698
6.696
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6.687
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4.401
4.398
3.883
3.864
0.000



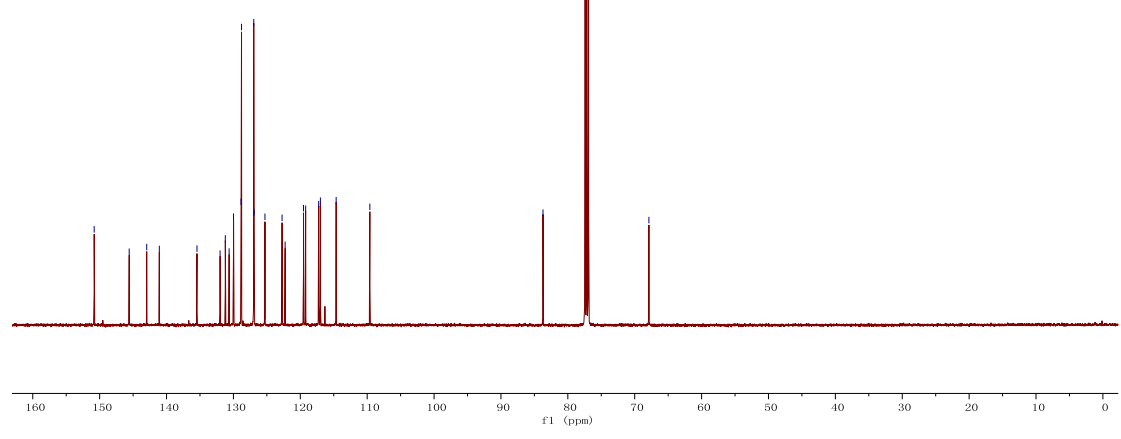
1H NMR, 600 MHz, $CDCl_3$

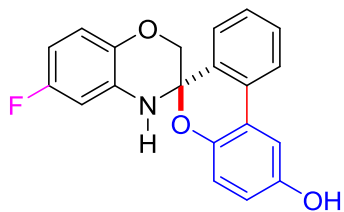


ZEH-60.2.fid
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 141.079
 135.447
 131.995
 131.212
 130.642
 129.883
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 128.856
 128.904
 128.904
 122.726
 122.266
 119.517
 119.200
 117.253
 116.993
 114.640
 109.600
 83.713
 77.160
 67.878



^{13}C NMR, 150 MHz, $CDCl_3$





(±)-6-Fluoro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3f**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 25.8 mg, 77% yield. m.p. 184-186 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.18 (s, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.57 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.51 (td, $J = 7.5, 1.5$ Hz, 1H), 7.43 (td, $J = 7.5, 1.5$ Hz, 1H), 7.34 (t, $J = 1.5$ Hz, 1H), 6.82-6.77 (m, 4H), 6.68 (dd, $J = 10.0, 3.0$ Hz, 1H), 6.45 (td, $J = 8.5, 3.0$ Hz, 1H), 4.35 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.82 (d, $J = 11.0$ Hz, 1H).

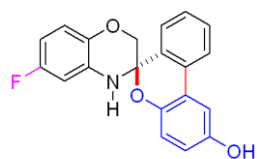
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 158.8 (d, $J = 233.5$ Hz), 153.4, 145.6, 140.2 (d, $J = 2.3$ Hz), 134.2 (d, $J = 11.1$ Hz), 132.8, 131.6, 130.6, 129.3, 126.2, 123.3, 122.9, 119.7, 117.8, 117.3 (d, $J = 9.6$ Hz), 110.1, 105.2 (d, $J = 23.4$ Hz), 102.8 (d, $J = 27.3$ Hz), 83.8, 68.2.

$^{19}\text{F NMR}$ (470 MHz, acetone- d_6) δ (-123.57)-(-123.62) (m).

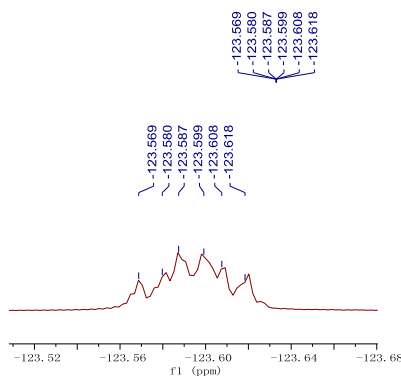
IR (KBr) ν (cm $^{-1}$): 3357, 1626, 1492, 1444, 1312, 1208, 1052, 986, 855, 770 cm $^{-1}$.

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{FNO}_3 + \text{H}]^+$ requires 336.10305, found 336.10114 $[\text{M} + \text{H}]^+$.

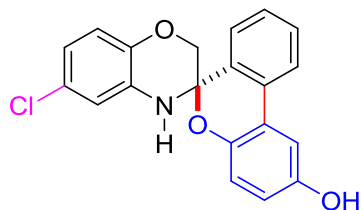
ZEh-47.1.fid



^{19}F NMR, 470 MHz, acetone- d_6



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2



(±)-6-Chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

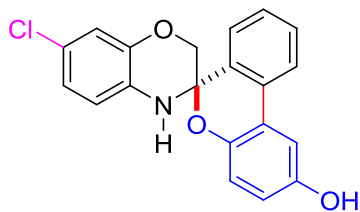
Compound **3g**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.3, 24.7 mg, 70% yield. m.p. 177-180 °C.

^1H NMR (500 MHz, acetone- d_6) δ 8.19-8.18 (m, 1H), 7.84 (d, J = 7.5 Hz, 1H), 7.57 (d, J = 8.0 Hz, 1H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 1H), 7.34-7.33 (m, 1H), 6.93 (d, J = 2.5 Hz, 1H), 6.82 (d, J = 9.0 Hz, 1H), 6.79-6.77 (m, 3H), 6.71 (dd, J = 8.5, 2.5 Hz, 1H), 4.37 (dd, J = 11.0, 2.0 Hz, 1H), 3.86 (d, J = 11.0 Hz, 1H).

^{13}C NMR (125 MHz, acetone- d_6) δ 153.4, 145.6, 142.9, 134.5, 132.7, 131.6, 130.6, 129.3, 126.6, 126.2, 123.3, 122.9, 119.6, 119.2, 118.0, 117.8, 115.8, 110.1, 83.7, 68.3.

IR (KBr) ν (cm^{-1}): 3355, 2923, 1609, 1496, 1306, 1206, 1051, 944, 855, 770 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{ClNO}_3+\text{H}]^+$ requires 352.07350, found 352.07132 $[\text{M}+\text{H}]^+$.



(±)-7-Chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

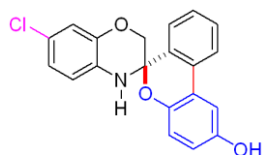
Compound **3h**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 26.4 mg, 75% yield. m.p. 186-188 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.24-8.22 (m, 1H), 7.83 (d, $J = 7.5$ Hz, 1H), 7.57 (d, $J = 8.0$ Hz, 1H), 7.53-7.49 (m, 1H), 7.44-7.40 (m, 1H), 7.33 (s, 1H), 6.91-6.83 (m, 3H), 6.79 (s, 2H), 6.67-6.66 (m, 1H), 4.37 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.88 (dd, $J = 11.5, 1.5$ Hz, 1H).

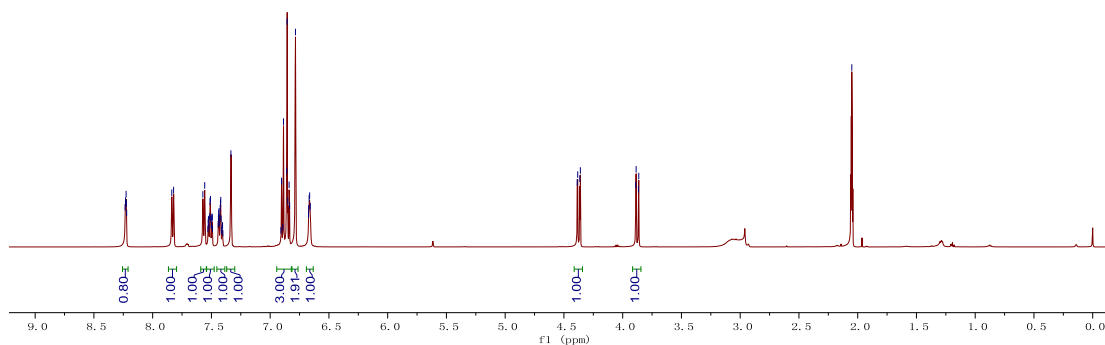
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.4, 145.6, 144.7, 132.7, 132.2, 131.6, 130.6, 129.3, 126.2, 123.6, 123.3, 122.9, 122.1, 119.6, 117.8, 117.3, 116.7, 110.1, 83.7, 68.3.

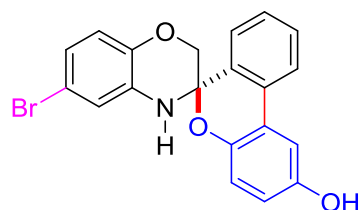
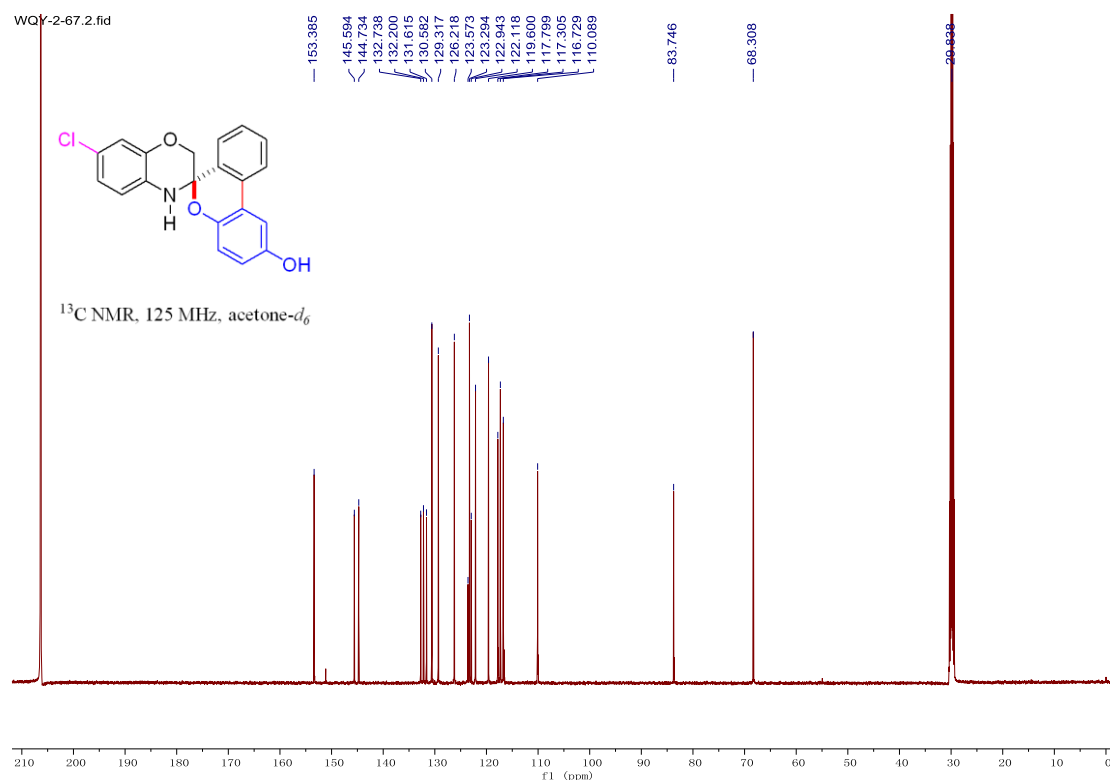
IR (KBr) $\nu(\text{cm}^{-1})$: 3362, 2923, 1593, 1495, 1303, 1198, 1052, 943, 855, 769 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{ClNO}_3+\text{H}]^+$ requires 352.07350, found 352.07205 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-6-Bromo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3i**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, R_f = 0.25, 36.3 mg, 92% yield. m.p. 200-206 °C.

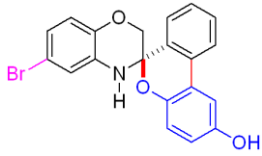
¹H NMR (500 MHz, acetone-*d*₆) δ 8.21-8.20 (m, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.54-7.50 (m, 1H), 7.45-7.41 (m, 1H), 7.33 (t, J = 1.5 Hz, 1H), 7.07 (d, J = 2.5 Hz, 1H), 6.85 (dd, J = 8.5, 2.5 Hz, 1H), 6.80-6.76 (m, 4H), 4.37 (dd, J = 11.0, 2.0 Hz, 1H), 3.86 (dd, J = 11.0, 1.0 Hz, 1H).

¹³C NMR (125 MHz, acetone-*d*₆) δ 153.4, 145.5, 143.4, 134.9, 132.6, 131.6, 130.6, 129.3, 126.2, 123.3, 122.9, 122.2, 119.6, 118.7, 118.4, 117.8, 113.9, 110.1, 83.6, 68.3.

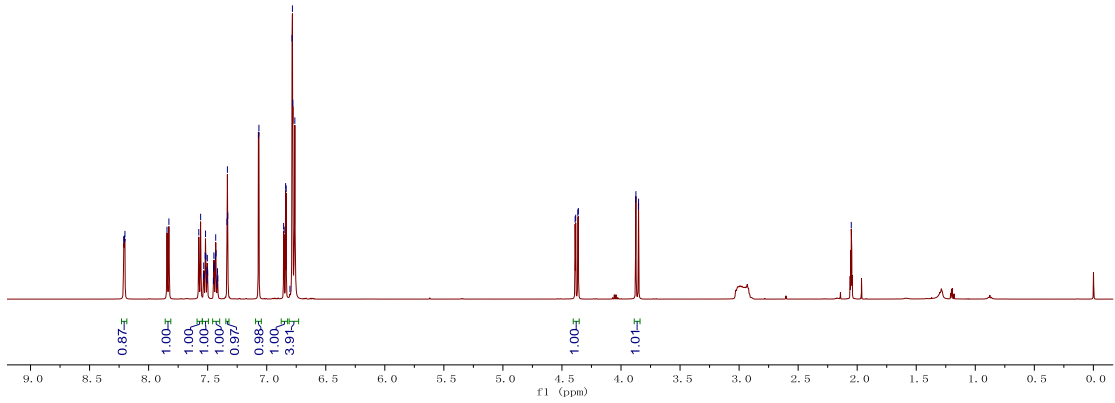
IR (KBr) ν (cm⁻¹): 3354, 2922, 1606, 1493, 1306, 1205, 1052, 944, 854, 751 cm⁻¹.

HRMS (ESI) calcd. for [C₂₀H₁₄BrNO₃+H]⁺ requires 396.02298, found 396.02310 [M+H]⁺.

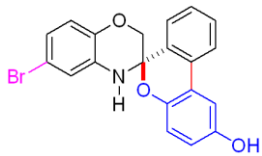
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 2.050



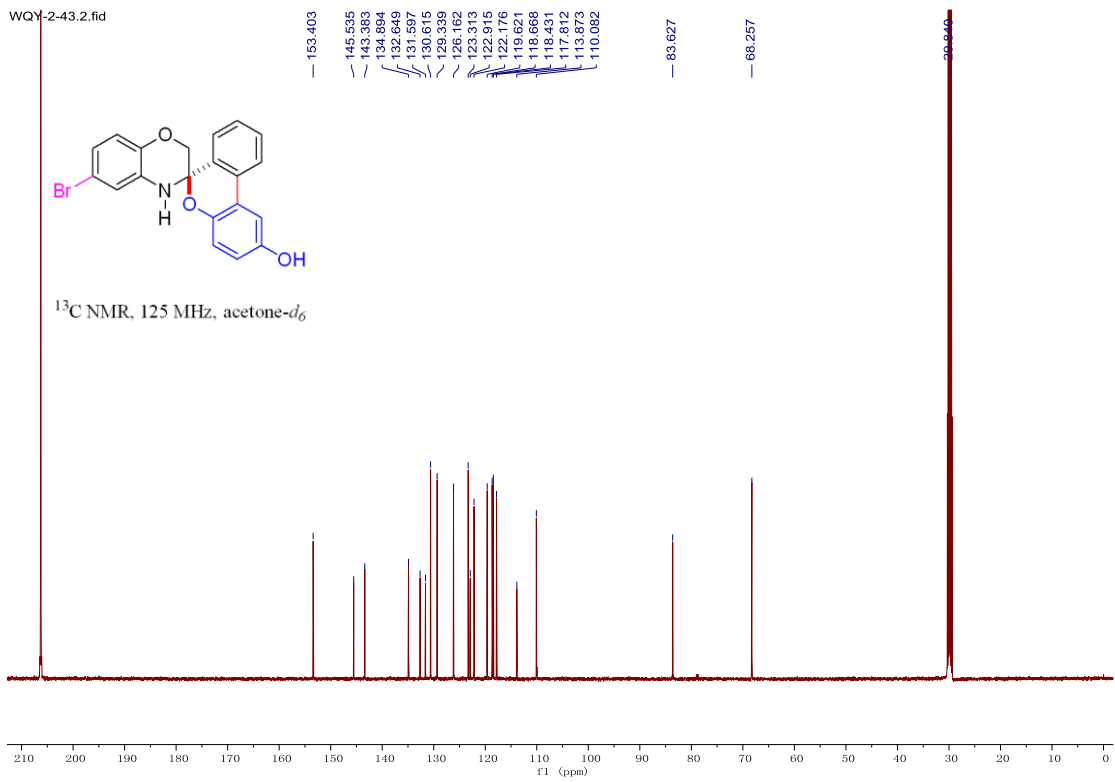
¹H NMR, 500 MHz, acetone-*d*₆

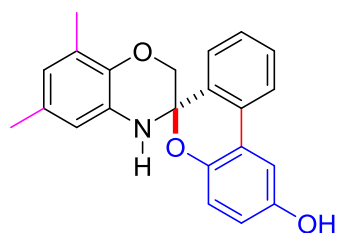


WQY-2-43.2.fid



¹³C NMR, 125 MHz, acetone-*d*₆





(±)-6,8-Dimethyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

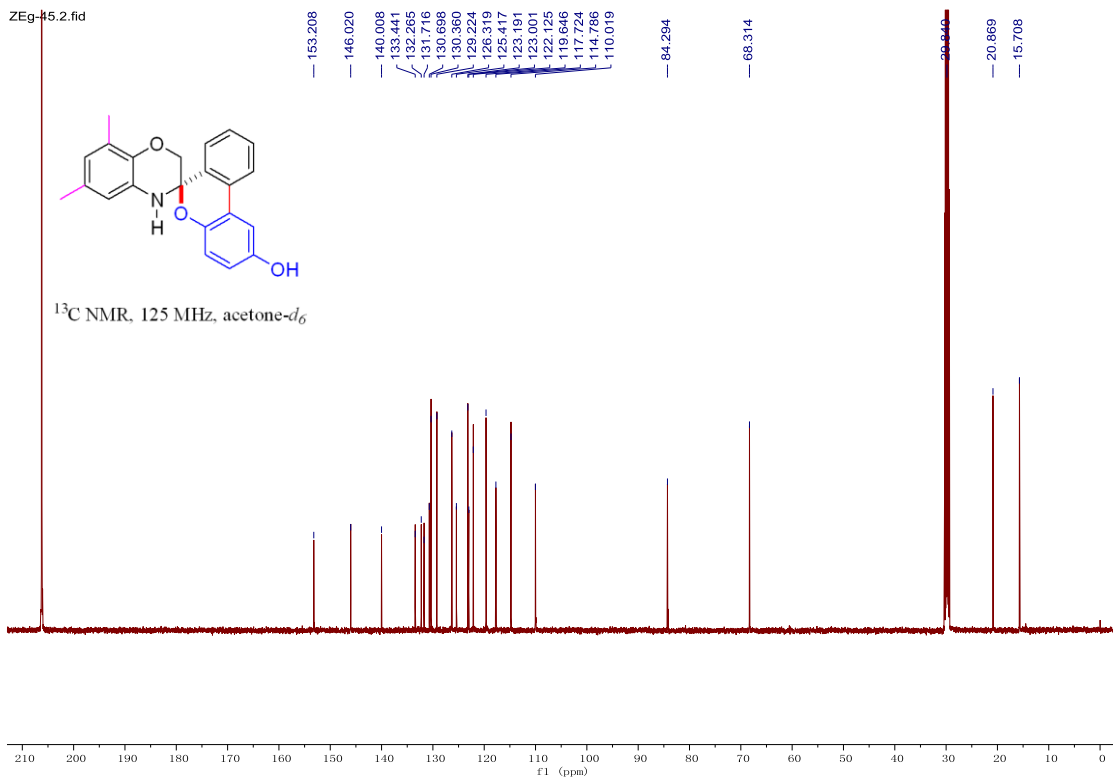
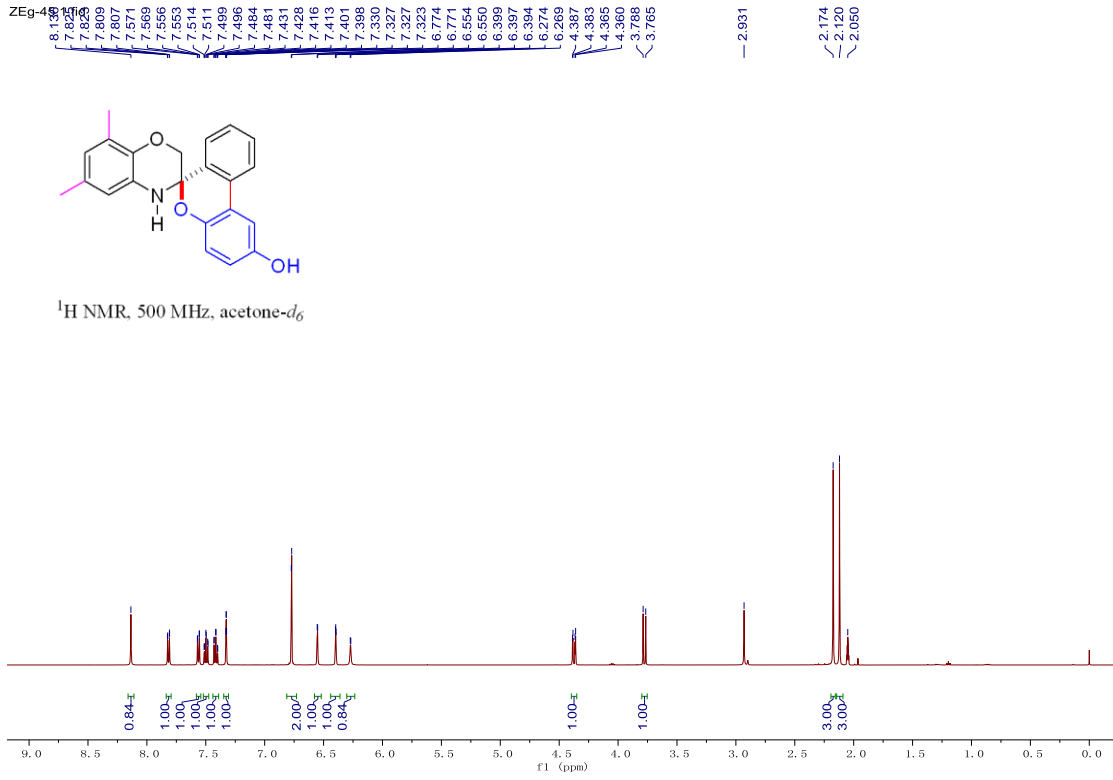
Compound **3j**: a yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.2$, 18.5 mg, 54% yield. m.p. 151-153 °C.

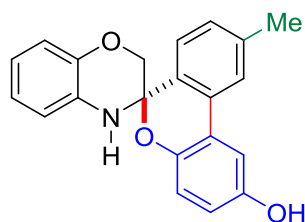
$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.14 (s, 1H), 7.82 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.56 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.50 (td, $J = 7.5, 1.5$ Hz, 1H), 7.41 (td, $J = 7.5, 1.5$ Hz, 1H), 7.33 (t, $J = 1.5$ Hz, 1H), 6.77 (d, $J = 1.5$ Hz, 2H), 6.55 (d, $J = 2.0$ Hz, 1H), 6.40-6.39 (m, 1H), 6.27 (d, $J = 2.5$ Hz, 1H), 4.37 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.78 (d, $J = 11.0$ Hz, 1H), 2.17 (s, 3H), 2.12 (s, 3H).

$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.2, 146.0, 140.0, 133.4, 132.3, 131.7, 130.7, 130.4, 129.2, 126.3, 125.4, 123.2, 123.0, 122.1, 119.6, 117.7, 114.8, 110.0, 84.3, 68.3, 20.9, 15.7.

IR (KBr) $\nu(\text{cm}^{-1})$: 3359, 2919, 1609, 1444, 1208, 1310, 1197, 940, 864, 749 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{22}\text{H}_{19}\text{NO}_3+\text{H}]^+$ requires 346.14377, found 346.14166 $[\text{M}+\text{H}]^+$.





(±)-9'-Methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

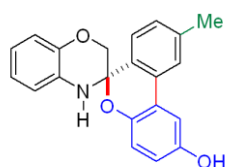
Compound **3k**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 29.8 mg, 90% yield. m.p. 173-175 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.10 (s, 1H), 7.65 (s, 1H), 7.45 (d, $J = 8.0$ Hz, 1H), 7.33 (t, $J = 1.5$ Hz, 1H), 7.25-7.23 (m, 1H), 6.89 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.83-6.80 (m, 2H), 6.76 (d, $J = 1.5$ Hz, 2H), 6.72-6.67 (m, 1H), 6.42 (s, 1H), 4.31 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.79 (d, $J = 11.0$ Hz, 1H), 2.42 (s, 3H).

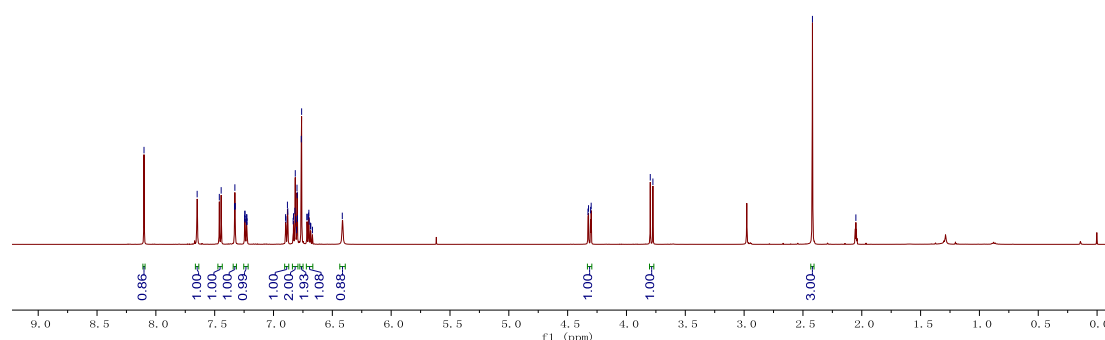
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.2, 146.0, 144.1, 140.2, 133.1, 131.5, 130.5, 129.9, 126.3, 123.7, 123.0, 122.3, 119.7, 119.5, 117.6, 116.8, 116.5, 110.0, 84.1, 68.3, 21.4.

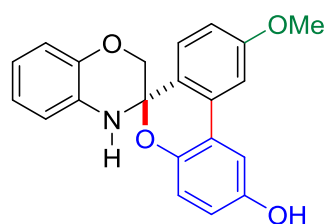
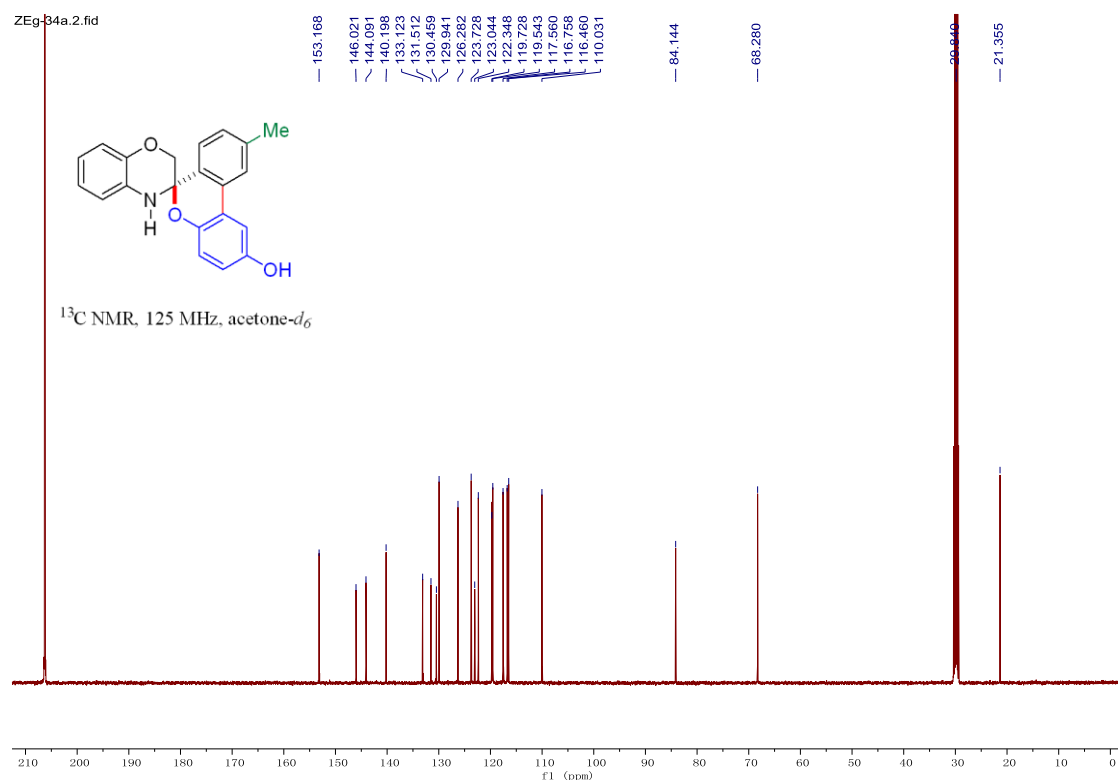
IR (KBr) $\nu(\text{cm}^{-1})$: 3363, 2922, 1612, 1501, 1312, 1209, 1040, 938, 838, 742 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{21}\text{H}_{17}\text{NO}_3+\text{H}]^+$ requires 332.12812, found 332.12625 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-9'-Methoxy-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3l**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 19.7 mg, 57% yield. m.p. 188-190 °C.

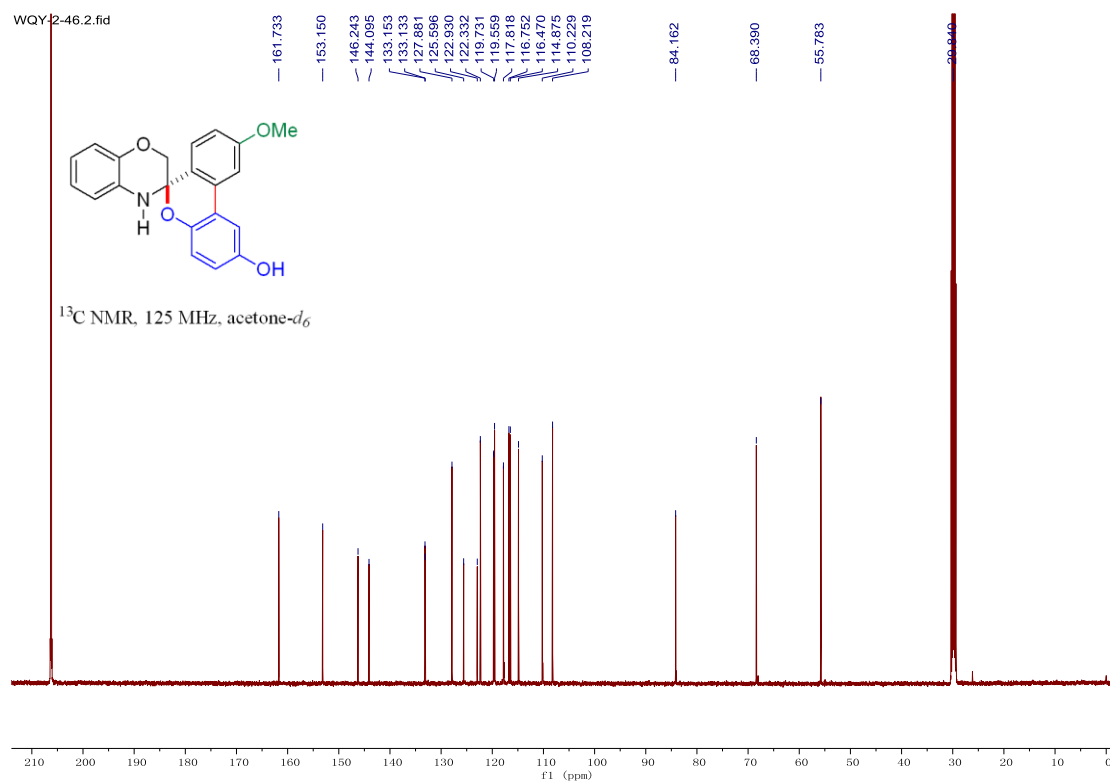
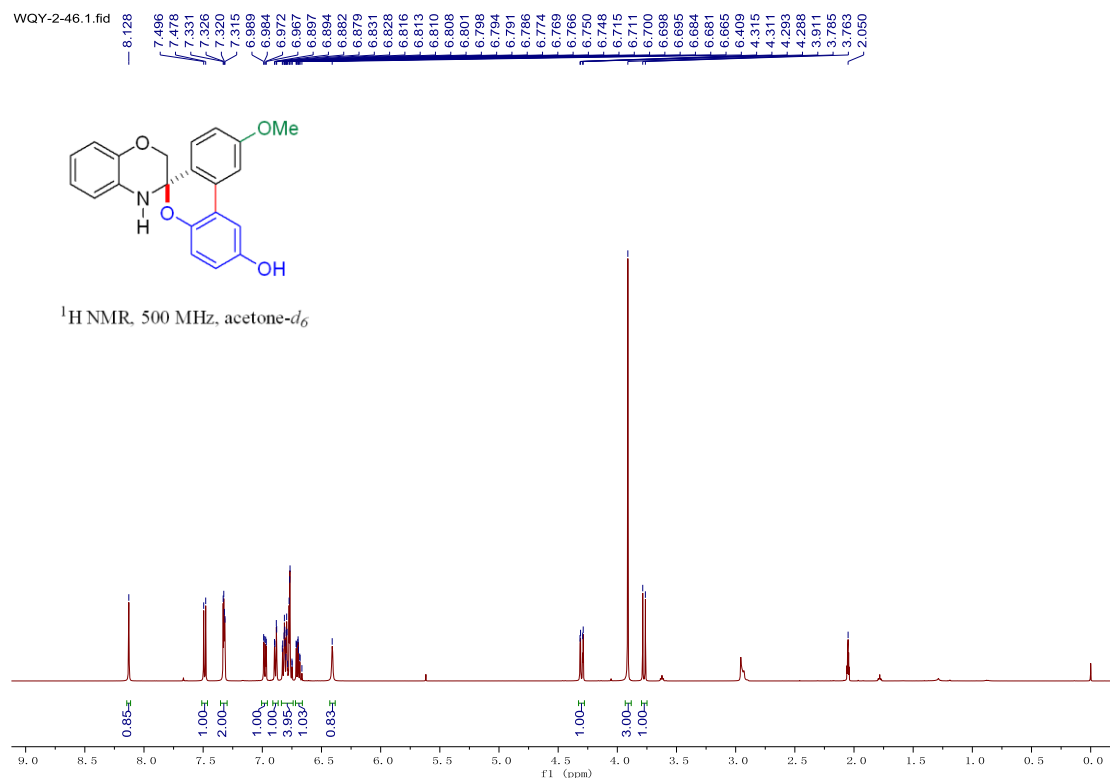
¹H NMR (500 MHz, acetone-*d*₆) δ 8.13 (s, 1H), 7.49 (d, $J = 9.0$ Hz, 1H), 7.33-7.32 (m, 2H), 6.98 (dd, $J = 8.5, 2.5$ Hz, 1H), 6.89 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.83-6.75 (m, 4H), 6.72-6.67 (m, 1H), 6.41 (s, 1H), 4.30 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.91 (s, 3H), 3.77 (d, $J = 11.0$ Hz, 1H).

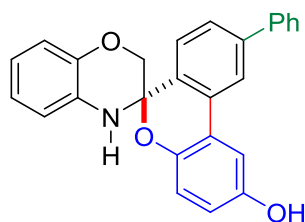
¹³C NMR (125 MHz, acetone-*d*₆) δ 161.7, 153.2, 146.2, 144.1, 133.2, 133.1, 127.9, 125.6, 122.9, 122.3, 119.7, 119.6, 117.8, 116.8, 116.5, 114.9, 110.2, 108.2, 84.2, 68.4, 55.8.

IR (KBr) ν (cm⁻¹): 3353, 2926, 1611, 1053, 1312, 1214, 1060, 938, 859, 746 cm⁻¹.

HRMS (ESI) calcd. for $[C_{21}H_{17}NO_4+H]^+$ requires 348.12303, found 348.12288

$[M+H]^+$.





(±)-9'-Phenyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

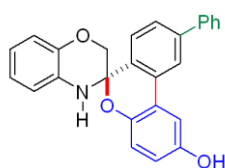
Compound **3m**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 23 mg, 60% yield. m.p. 85-87 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.14 (s, 1H), 8.08 (d, $J = 2.0$ Hz, 1H), 7.80-7.78 (m, 2H), 7.72-7.69 (m, 1H), 7.67-7.65 (m, 1H), 7.53-7.49 (m, 3H), 7.44-7.40 (m, 1H), 6.92 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.85-6.79 (m, 4H), 6.74-6.71 (m, 1H), 6.52 (s, 1H), 4.39 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.87 (d, $J = 11.0$ Hz, 1H).

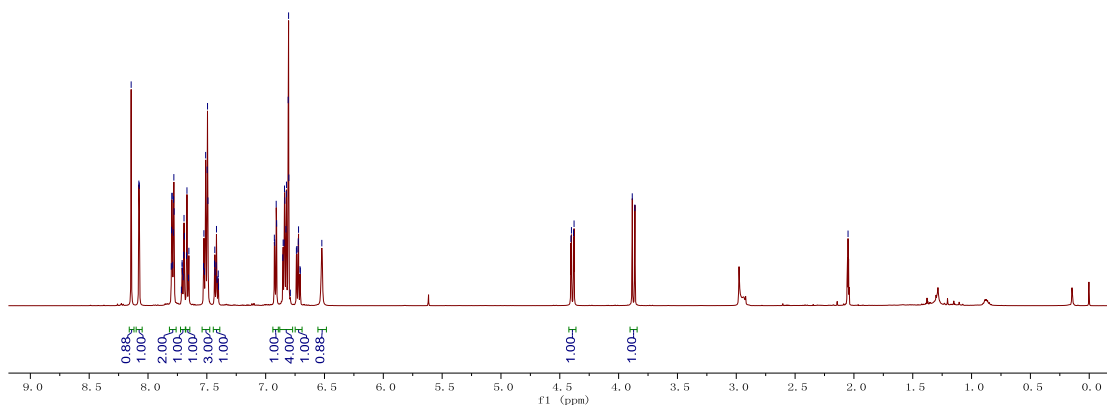
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.3, 146.1, 144.1, 143.1, 141.1, 133.0, 132.2, 129.8, 128.7, 127.9, 127.8, 127.0, 123.0, 122.4, 121.7, 119.8, 119.6, 117.9, 116.8, 116.5, 110.3, 84.2, 68.2.

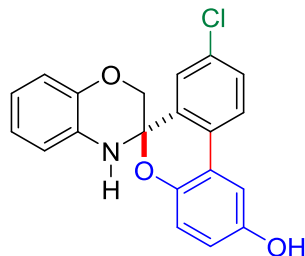
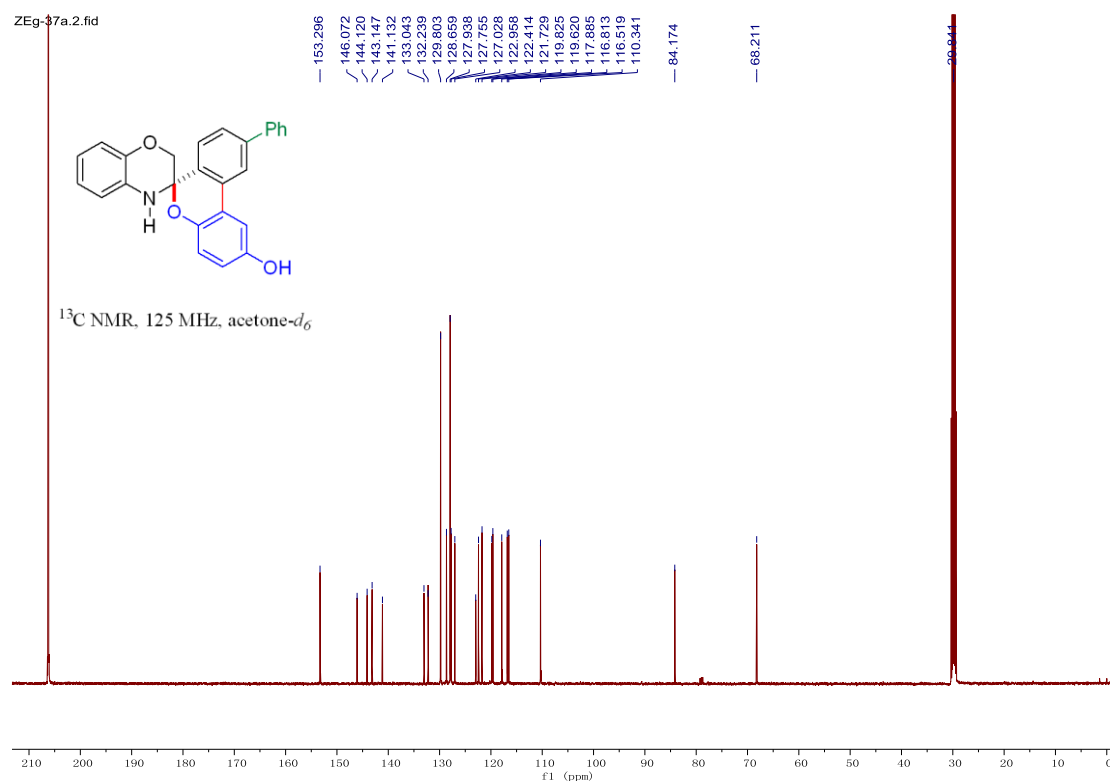
IR (KBr) $\nu(\text{cm}^{-1})$: 3358, 2923, 1611, 1500, 1311, 1212, 1061, 943, 857, 744 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{26}\text{H}_{19}\text{NO}_3+\text{H}]^+$ requires 394.14377, found 394.14139 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-9'-Chloro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3n**: a colorless oil. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 23 mg, 66% yield.

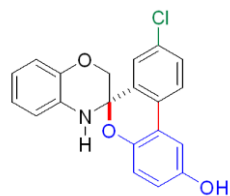
¹H NMR (500 MHz, DMSO-*d*₆) δ 9.26 (s, 1H), 7.86 (d, $J = 8.5$ Hz, 1H), 7.58 (dd, $J = 8.5, 2.5$ Hz, 1H), 7.53 (d, $J = 2.0$ Hz, 1H), 7.49 (d, $J = 2.5$ Hz, 1H), 7.26 (d, $J = 2.5$ Hz, 1H), 6.83-6.75 (m, 4H), 6.72 (dd, $J = 8.5, 3.0$ Hz, 1H), 6.68-6.64 (m, 1H), 4.23 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.82 (d, $J = 11.5$ Hz, 1H).

¹³C NMR (125 MHz, DMSO-*d*₆) δ 152.4, 144.0, 142.4, 133.7, 132.9, 132.0, 129.6, 129.4, 125.6, 124.5, 121.6, 120.8, 118.7, 118.5, 117.4, 115.8, 115.3, 109.4, 82.7, 66.6.

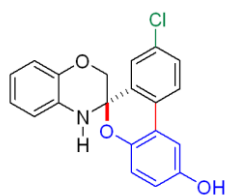
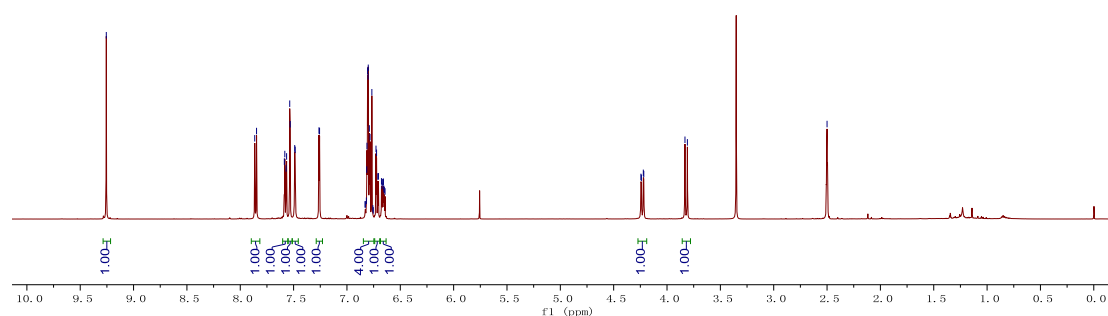
IR (KBr) ν (cm⁻¹): 3246, 2924, 1611, 1489, 1313, 1209, 1047, 947, 857, 785 cm⁻¹.

HRMS (ESI) calcd. for $[C_{20}H_{14}ClNO_3+H]^+$ requires 352.07350, found 352.07178

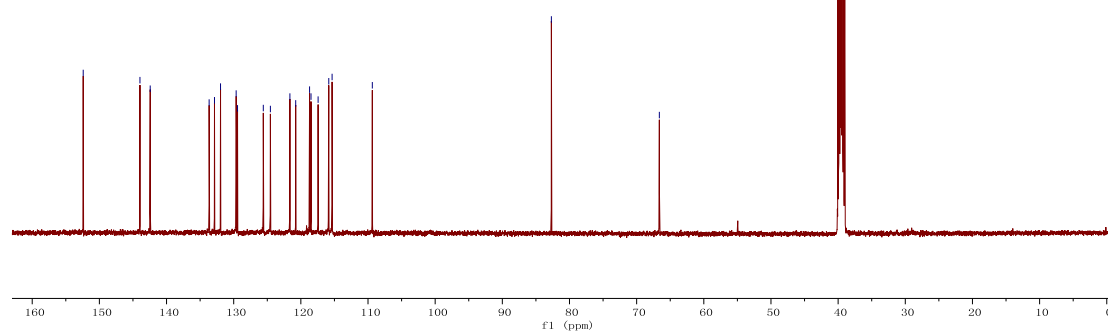
$[M+H]^+$

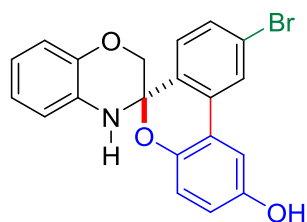


1H NMR, 500 MHz, $DMSO-d_6$



^{13}C NMR, 125 MHz, $DMSO-d_6$





(±)-9'-Bromo-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'--ol

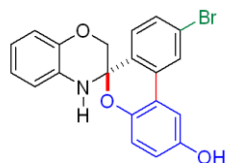
Compound **3o**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 17 mg, 43% yield. m.p. 199-202 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.31-8.29 (m, 1H), 7.98 (t, $J = 2.0$ Hz, 1H), 7.61-7.57 (m, 1H), 7.54-7.51 (m, 1H), 7.34 (d, $J = 3.0$ Hz, 1H), 6.89-6.87 (m, 1H), 6.84-6.78 (m, 4H), 6.73-6.70 (m, 1H), 6.54 (s, 1H), 4.36 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.82 (dd, $J = 11.5, 1.5$ Hz, 1H).

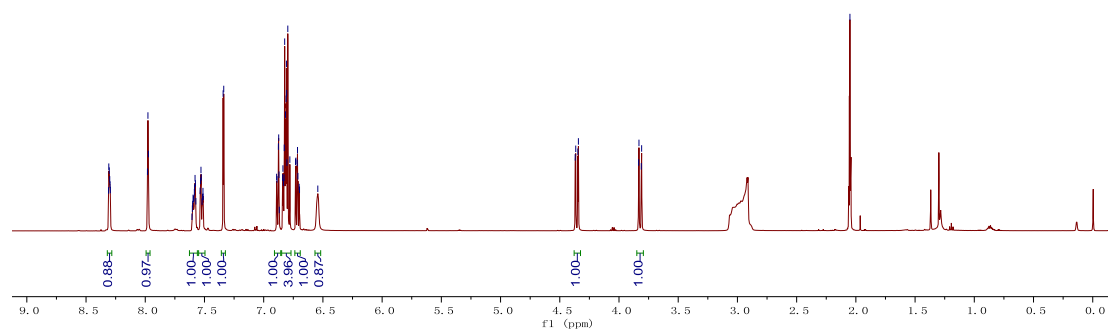
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.4, 146.1, 144.1, 134.1, 132.8, 132.3, 131.9, 128.7, 126.0, 124.4, 122.5, 121.7, 120.0, 119.8, 118.7, 116.8, 116.6, 110.2, 84.1, 67.9.

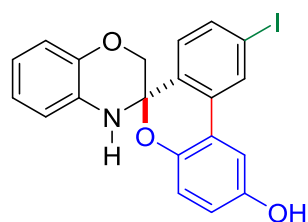
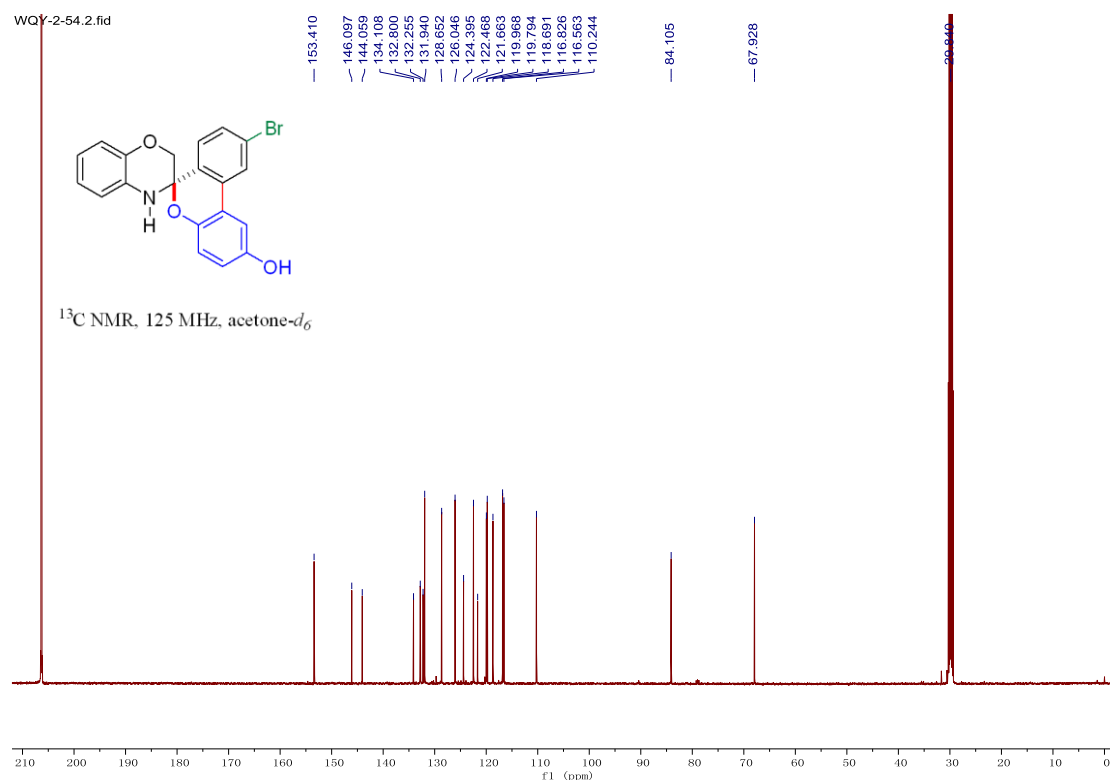
IR (KBr) $\nu(\text{cm}^{-1})$: 3350, 2922, 1611, 1433, 1311, 1209, 1045, 976, 857, 745 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{BrNO}_3+\text{H}]^+$ requires 396.02298, found 396.02295 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-9'-Iodo-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

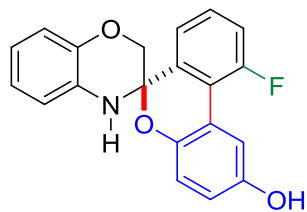
Compound **3p**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 8/1, R_f = 0.25, 41.2 mg, 93% yield. m.p. 135-137 °C.

¹H NMR (600 MHz, CDCl₃, TMS) δ 8.00-7.99 (m, 1H), 7.68-7.66 (m, 1H), 7.23-7.21 (m, 1H), 7.14-7.13 (m, 1H), 6.92 (dd, J = 7.8, 1.8 Hz, 1H), 6.90-6.86 (m, 2H), 6.81 (td, J = 7.8, 1.8 Hz, 1H), 6.75-6.72 (m, 2H), 4.84-4.81 (m, 2H), 4.34 (dd, J = 11.4, 2.4 Hz, 1H), 3.79 (d, J = 11.4 Hz, 1H).

¹³C NMR (150 MHz, CDCl₃) δ 150.9, 145.8, 143.3, 137.6, 132.8, 131.7, 131.6, 130.8, 127.2, 122.2, 120.8, 120.5, 119.7, 118.0, 116.8, 116.1, 109.6, 96.2, 83.7, 67.4.

IR (KBr) ν (cm⁻¹): 3360, 1612, 1585, 1497, 1431, 1311, 1207, 1045, 941, 744 cm⁻¹.

HRMS (ESI) calcd. for [C₂₀H₁₄INO₃+H]⁺ requires 444.00911, found 444.00729 [M+H]⁺.



(±)-10'-Fluoro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3q**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, 13.7 mg, 41% yield. R_f = 0.34, m.p. 157-159 °C.

$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.58 (d, J = 3.0 Hz, 1H), 7.37-7.31 (m, 2H), 7.21-7.16 (m, 1H), 6.94-6.91 (m, 2H), 6.88 (td, J = 7.5, 1.5 Hz, 1H), 6.81 (td, J = 7.5, 1.5 Hz, 1H), 6.76 (dd, J = 9.0, 3.0 Hz, 1H), 6.74 (dd, J = 8.0, 2.0 Hz, 1H), 4.91 (d, J = 15.0 Hz, 1H), 4.79 (s, 1H), 4.37 (dd, J = 11.5, 2.0 Hz, 1H), 3.84 (d, J = 11.0 Hz, 1H).

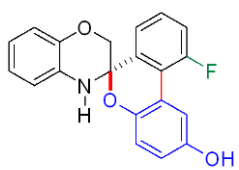
$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 159.7 (d, J = 251.1 Hz), 150.6, 145.5, 143.4, 135.3 (d, J = 3.5 Hz), 130.9, 129.7 (d, J = 9.3 Hz), 122.1, 120.9 (d, J = 3.3 Hz), 120.5, 119.4, 119.2 (d, J = 3.1 Hz), 119.1 (d, J = 11.0 Hz), 117.8 (d, J = 23.5 Hz), 117.5, 116.8, 116.1, 114.1 (d, J = 16.8 Hz), 83.3 (d, J = 2.8 Hz), 67.2.

$^{19}\text{F NMR}$ (470 MHz, CDCl_3) δ (-114.49)- (-114.53) (m).

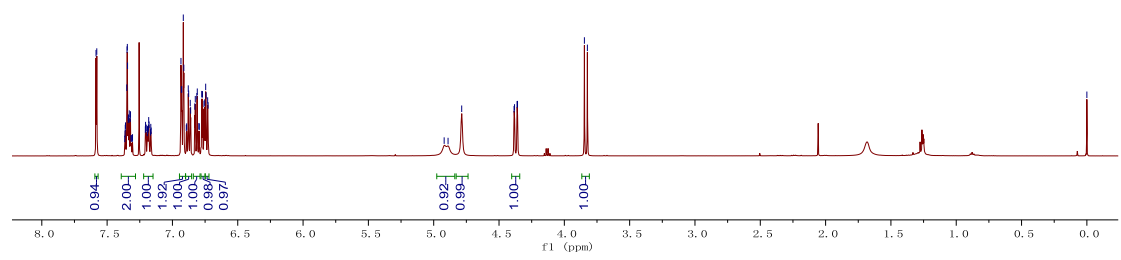
IR (KBr) ν (cm^{-1}): 3366, 2920, 1613, 1499, 1453, 1199, 1082, 949, 842, 740 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{FNO}_3+\text{H}]^+$ requires 336.10305, found 336.10291 $[\text{M}+\text{H}]^+$.

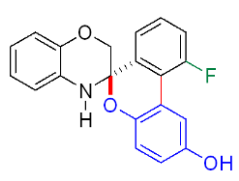
7.585
7.579
7.565
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7.547
7.545
7.544
7.539
7.536
7.532
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7.525
7.517
7.317
7.315
7.307
7.306
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7.193
7.191
7.188
7.187
7.184
7.182
7.179
7.168
7.166
7.163
6.935
6.931
6.929
6.917
6.913
6.894
6.891
6.879
6.876
6.861
6.861
6.828
6.825
6.813
6.810
6.798
6.795
6.776
6.770
6.758
6.753
6.746
6.742
6.730
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4.381
4.362
4.358
3.646
3.624
— 0.000



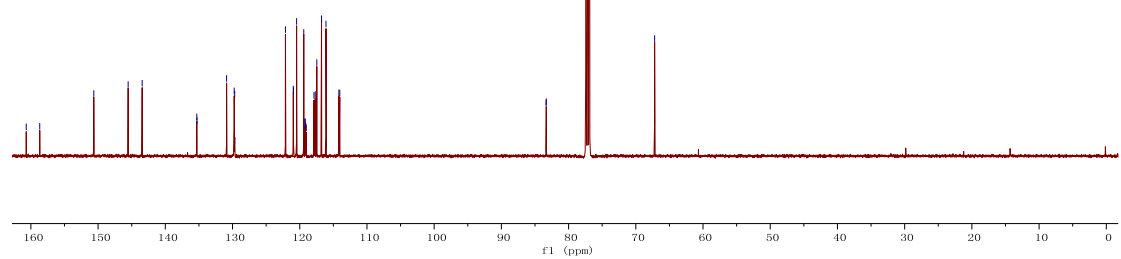
¹H NMR, 500 MHz, CDCl₃



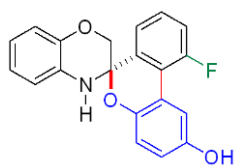
160.698
158.695
150.612
145.527
143.440
135.313
135.288
130.680
129.751
129.677
122.124
120.959
120.933
120.465
119.399
119.216
119.191
119.117
119.029
117.881
117.693
117.455
116.757
116.097
114.175
114.041
83.344
83.322
77.460
67.198



¹³C NMR, 125 MHz, CDCl₃

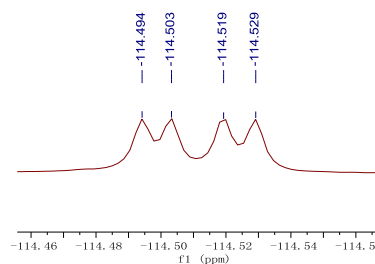


WQY-2-71A.4.fid

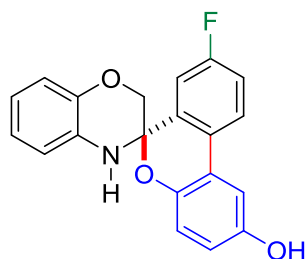


^{19}F NMR, 470 MHz, CDCl_3

-114.494
-114.503
-114.519
-114.529



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2



(±)-8'-Fluoro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Petroleum Compound **3q'**: a white solid. Column chromatography, eluent:EtOAc = 4/1, 19.4 mg, $R_f = 0.24$, 58% yield. m.p. 170-172 °C.

^1H NMR (600 MHz, acetone- d_6) δ 8.20 (d, $J = 1.2$ Hz, 1H), 7.90-7.87 (m, 1H), 7.37 (dd, $J = 9.6, 3.0$ Hz, 1H), 7.30-7.27 (m, 2H), 6.90 (dd, $J = 7.8, 1.2$ Hz, 1H), 6.85-6.76 (m, 4H), 6.74-6.71 (m, 1H), 6.54 (s, 1H), 4.35 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.85 (d, $J = 11.4$ Hz, 1H).

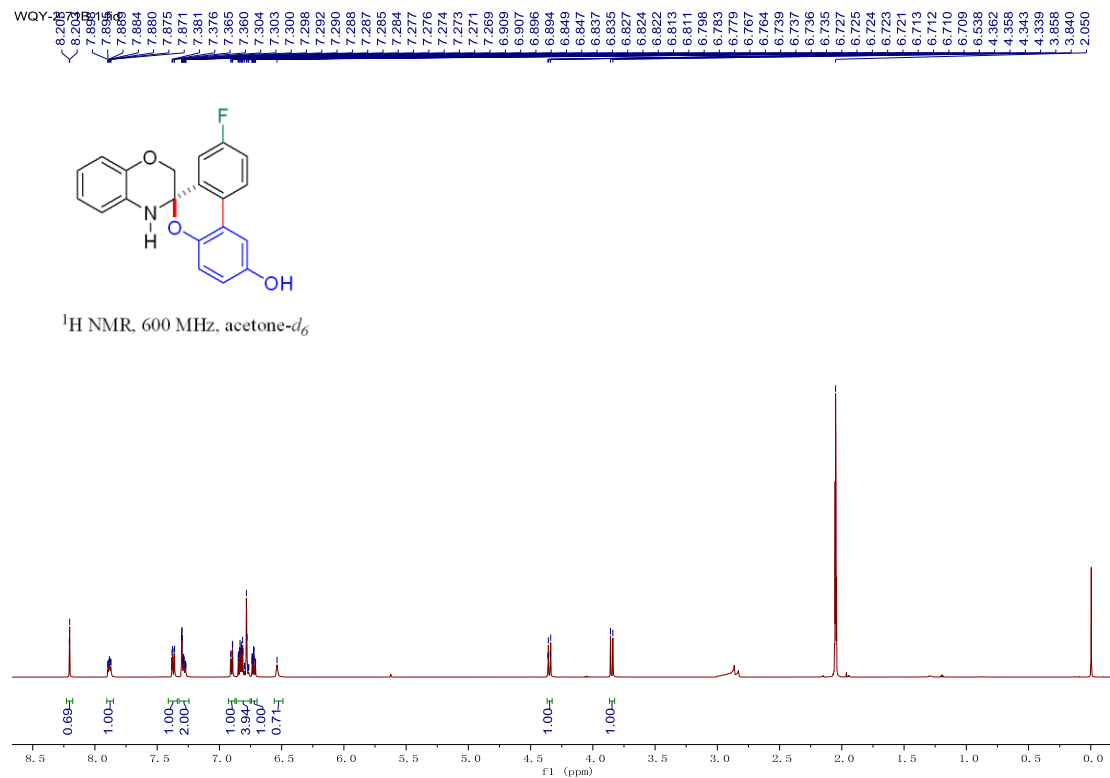
^{13}C NMR (150 MHz, acetone- d_6) δ 163.7 (d, $J = 203.5$ Hz), 153.4, 145.4, 144.1, 135.7 (d, $J = 5.6$ Hz), 132.8, 128.3 (d, $J = 2.8$ Hz), 125.7 (d, $J = 6.9$ Hz), 122.5, 122.4, 120.0, 119.7, 117.7, 117.3 (d, $J = 18.0$ Hz), 116.8, 116.7, 113.4 (d, $J = 19.8$ Hz), 110.0, 83.9 (d, $J = 1.6$ Hz), 67.8.

¹⁹F NMR (470 MHz, acetone-*d*₆) δ (-109.34)- (-109.39) (m).

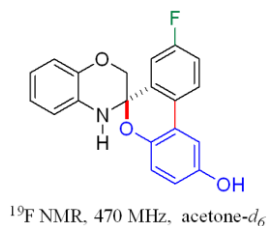
IR (KBr) ν(cm⁻¹): 3355, 2920, 1961, 1455, 1314, 1248, 1049, 950, 859, 748 cm⁻¹.

HRMS (ESI) calcd. for [C₂₀H₁₄FNO₃+Na]⁺ requires 358.08499, found 358.08359

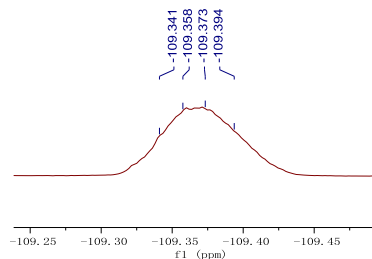
[M+Na]⁺.



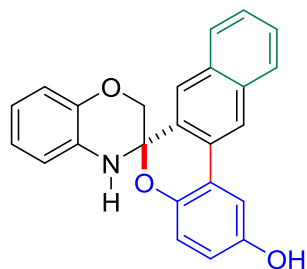
WQY-2-71B.2.fid



-109.341
-109.358
-109.373
-109.394



20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210 -2



(±)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-naphtho[2,3-*c*]chromen]-2'-ol

Compound **3r**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, R_f = 0.25, 29 mg, 80% yield. m.p. 140-145 °C.

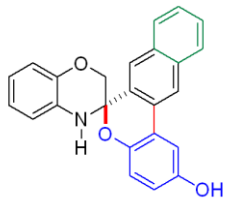
^1H NMR (500 MHz, acetone- d_6) δ 8.35 (d, J = 3.0 Hz, 1H), 8.23-8.22 (m, 1H), 8.14 (s, 1H), 8.03 (d, J = 8.0 Hz, 1H), 7.99-7.96 (m, 1H), 7.59-7.52 (m, 3H), 6.97 (dd, J = 8.0, 1.5 Hz, 1H), 6.88-6.82 (m, 4H), 6.76-6.72 (m, 1H), 6.61 (broad, 1H), 4.42 (dd, J = 11.5, 2.5 Hz, 1H), 3.85 (d, J = 11.5 Hz, 1H).

^{13}C NMR (125 MHz, acetone- d_6) δ 153.5, 146.3, 144.2, 134.8, 134.0, 133.2, 132.2, 129.4, 129.1, 128.9, 127.9, 127.3, 126.1, 123.2, 122.5, 122.2, 120.0, 119.9, 118.1, 116.8, 116.6, 110.4, 84.5, 68.5.

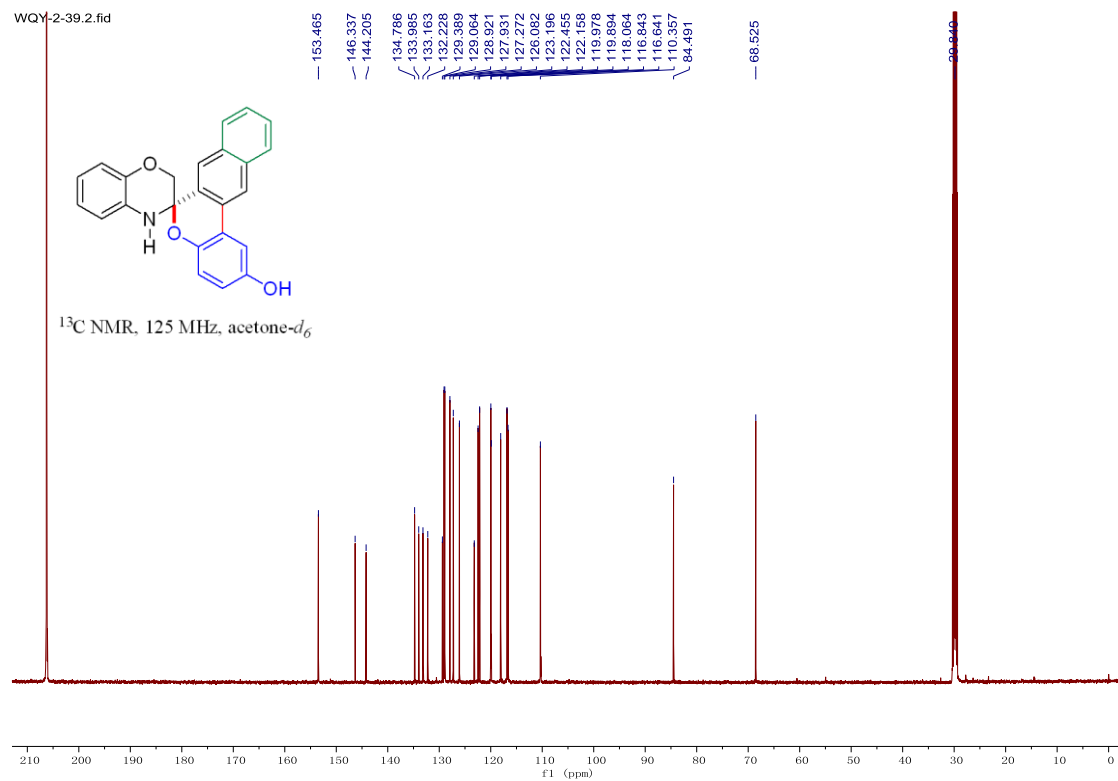
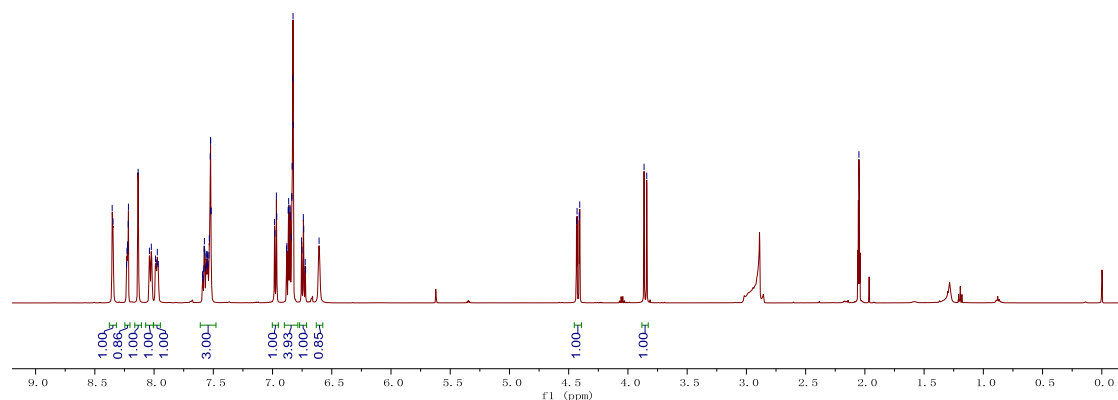
IR (KBr) ν (cm^{-1}): 3356, 2921, 1690, 1431, 1310, 1212, 1047, 946, 858, 749 cm^{-1} .

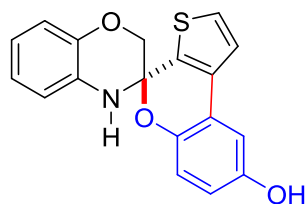
HRMS (ESI) calcd. for $[C_{24}H_{17}NO_3+H]^+$ requires 368.12812, found 368.12814

$[M+H]^+$.



1H NMR, 500 MHz, acetone- d_6





(±)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,4'-thieno[2,3-*c*]chromen]-8'-ol

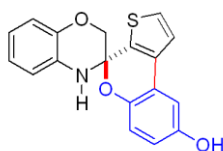
Compound **3s**: a yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.2$, 11 mg, 34% yield. m.p. 140-142 °C.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.18-8.15 (m, 1H), 7.63-7.61 (m, 1H), 7.47 (dt, $J = 5.0, 1.5$ Hz, 1H), 7.10 (d, $J = 2.5$ Hz, 1H), 6.85-6.80 (m, 3H), 6.78 (d, $J = 9.0$ Hz, 1H), 6.74-6.66 (m, 3H), 4.40 (dd, $J = 11.5, 2.0$ Hz, 1H), 3.99 (d, $J = 11.5$ Hz, 1H).

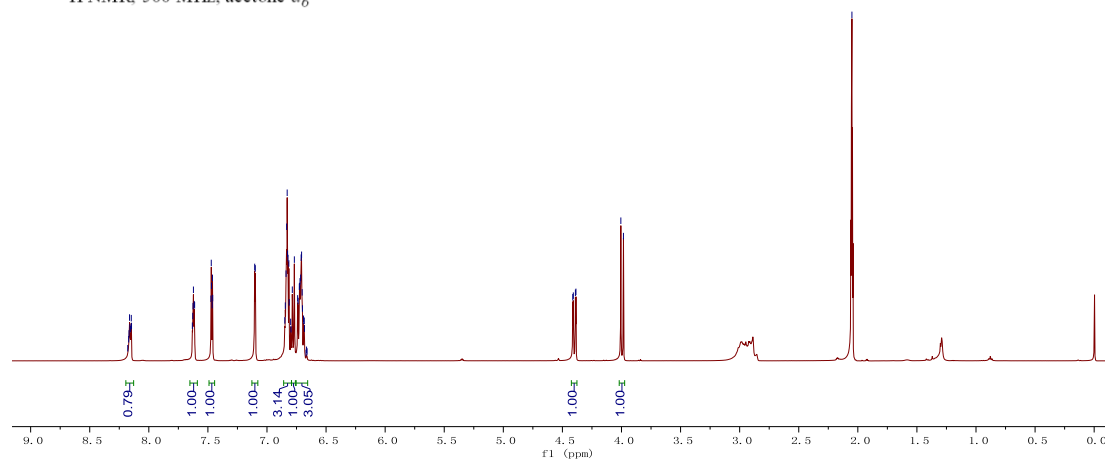
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.1, 145.2, 144.0, 135.7, 132.5, 132.2, 128.4, 123.7, 122.5, 121.4, 120.2, 119.0, 116.9, 116.41, 116.36, 110.6, 83.8, 69.2.

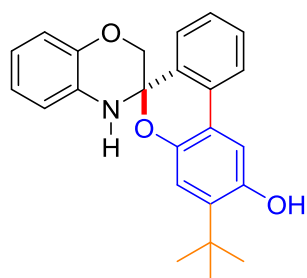
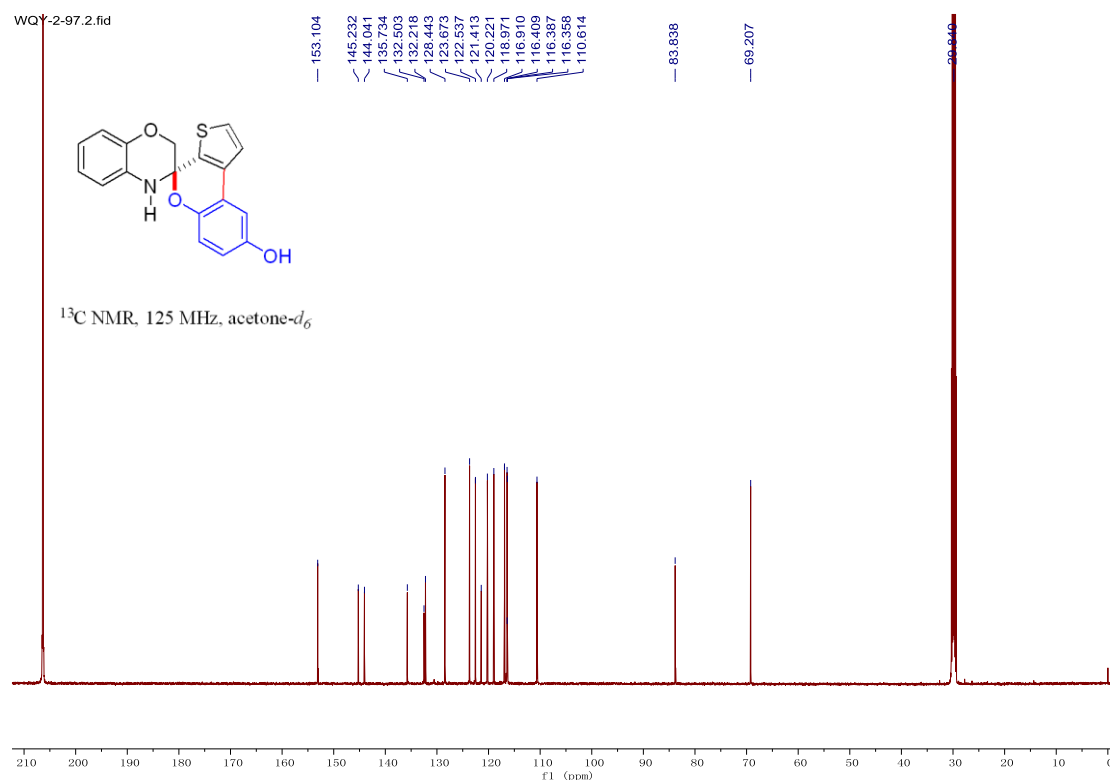
IR (KBr) $\nu(\text{cm}^{-1})$: 3361, 1612, 1449, 1311, 1312, 1283, 1208, 1037, 845, 747 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{18}\text{H}_{13}\text{NO}_3\text{S}+\text{H}]^+$ requires 324.06889, found 324.06714 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-3'-(*tert*-Butyl)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3t**: a colorless oil. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.3$, 30.5 mg, 82% yield.

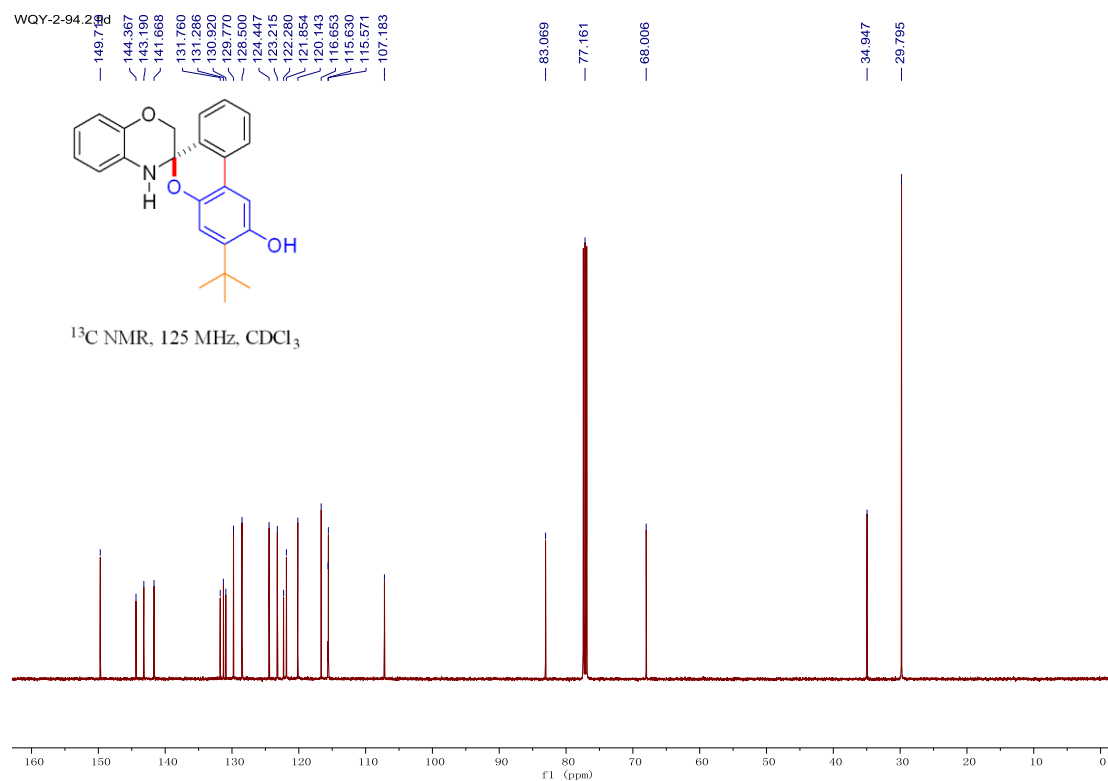
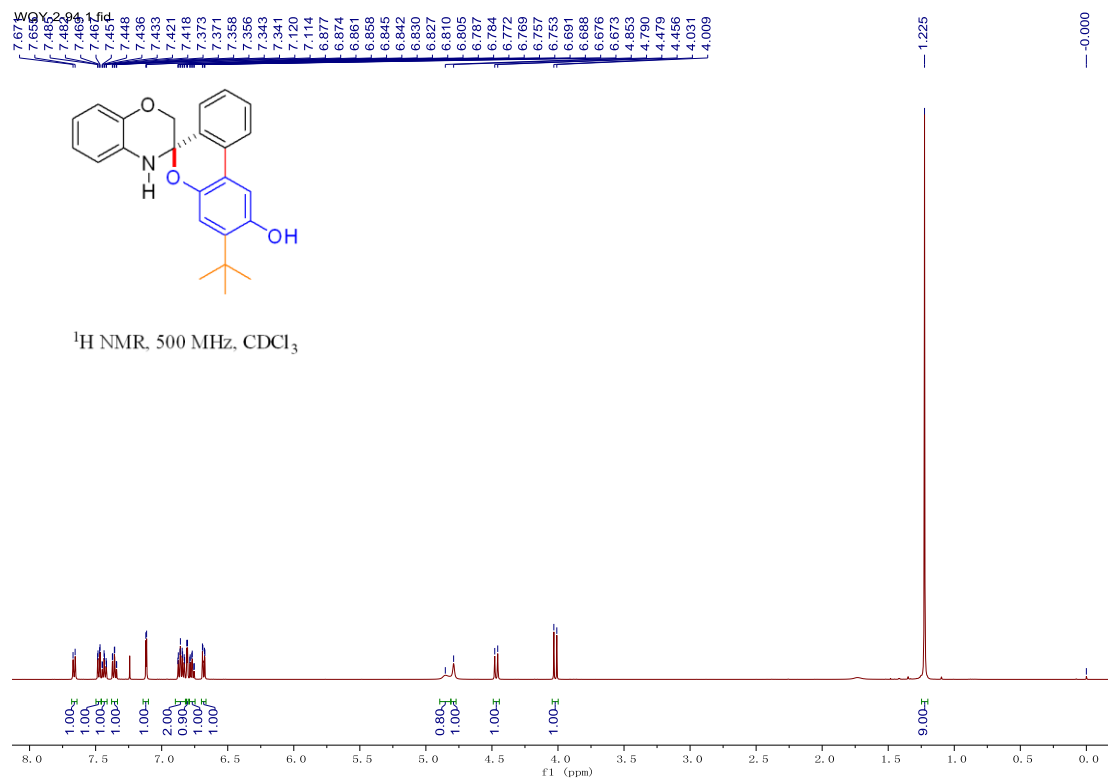
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.66 (d, $J = 8.0$ Hz, 1H), 7.48 (dd, $J = 7.5$, 1.5 Hz, 1H), 7.43 (td, $J = 7.5$, 1.5 Hz, 1H), 7.36 (td, $J = 7.5$, 1.0 Hz, 1H), 7.12 (d, $J = 3.0$ Hz, 1H), 6.88-6.83 (m, 2H), 6.81 (d, $J = 2.5$ Hz, 1H), 6.77 (td, $J = 7.5$, 1.5 Hz, 1H), 6.68 (dd, $J = 7.5$, 1.5 Hz, 1H), 4.85 (broad, 1H), 4.79 (broad, 1H), 4.47 (d, $J = 11.5$ Hz, 1H), 4.02 (d, $J = 11.5$ Hz, 1H), 1.23 (s, 9H).

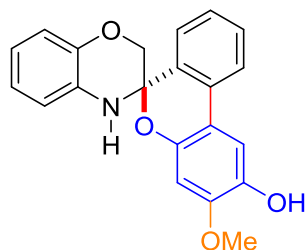
¹³C NMR (125 MHz, CDCl₃) δ 149.7, 144.4, 143.2, 141.7, 131.8, 131.3, 130.9, 129.8, 128.5, 124.4, 123.2, 122.3, 121.9, 120.1, 116.7, 115.63, 115.57, 107.2, 83.1, 68.0, 34.9, 29.8.

IR (KBr) $\nu(\text{cm}^{-1})$: 3394, 2955, 1501, 1420, 1312, 1281, 1211, 1196, 856, 748 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{24}\text{H}_{23}\text{NO}_3+\text{H}]^+$ requires 374.17507, found 374.17313

$[\text{M}+\text{H}]^+$.





(±)-3'-Methoxy-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3u**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 22.2 mg, 64% yield. m.p. 118-120 °C.

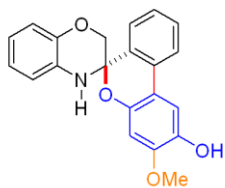
^1H NMR (600 MHz, acetone- d_6) δ 7.75 (d, $J = 8.4$ Hz, 1H), 7.53 (d, $J = 7.8$ Hz, 1H), 7.48-7.45 (m, 1H), 7.39 (s, 1H), 7.36-7.33 (m, 1H), 7.31 (s, 1H), 6.91 (dd, $J = 7.8, 1.8$ Hz, 1H), 6.85-6.82 (m, 2H), 6.73-6.70 (m, 1H), 6.53 (s, 1H), 6.49 (broad, 1H), 4.37 (dd, $J = 11.4, 2.4$ Hz, 1H), 3.84 (d, 1.2 Hz, 3H), 3.80 (d, $J = 11.4$ Hz, 1H).

^{13}C NMR (150 MHz, acetone- d_6) δ 150.0, 146.4, 144.1, 142.6, 133.1, 131.9, 131.8, 130.4, 128.1, 126.3, 122.5, 122.4, 119.7, 116.8, 116.5, 114.3, 109.7, 102.4, 84.5, 68.2, 56.3.

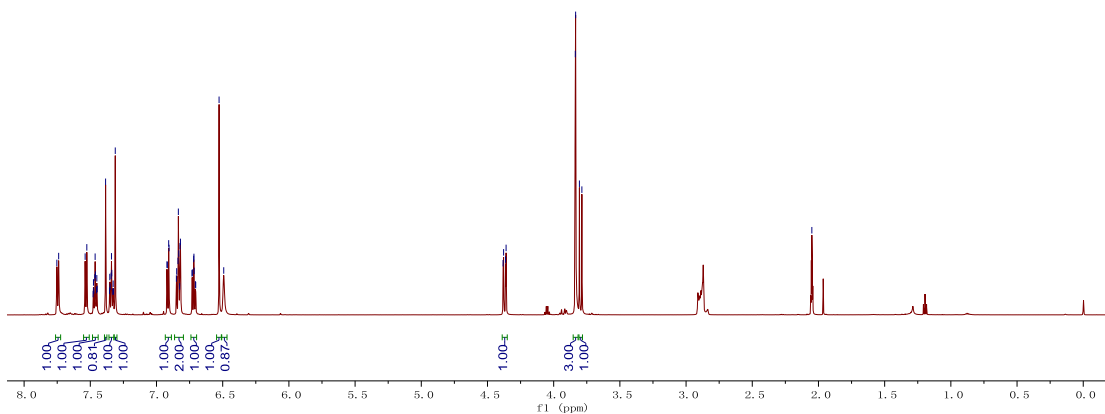
IR (KBr) $\nu(\text{cm}^{-1})$: 3362, 1697, 1605, 1491, 1439, 1310, 1197, 940, 864, 749 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{21}\text{H}_{17}\text{NO}_4+\text{H}]^+$ requires 348.12303, found 348.12283 $[\text{M}+\text{H}]^+$.

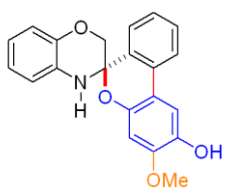
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6.716
6.706
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4.363
4.359
3.836
3.834
3.806
3.787
2.050



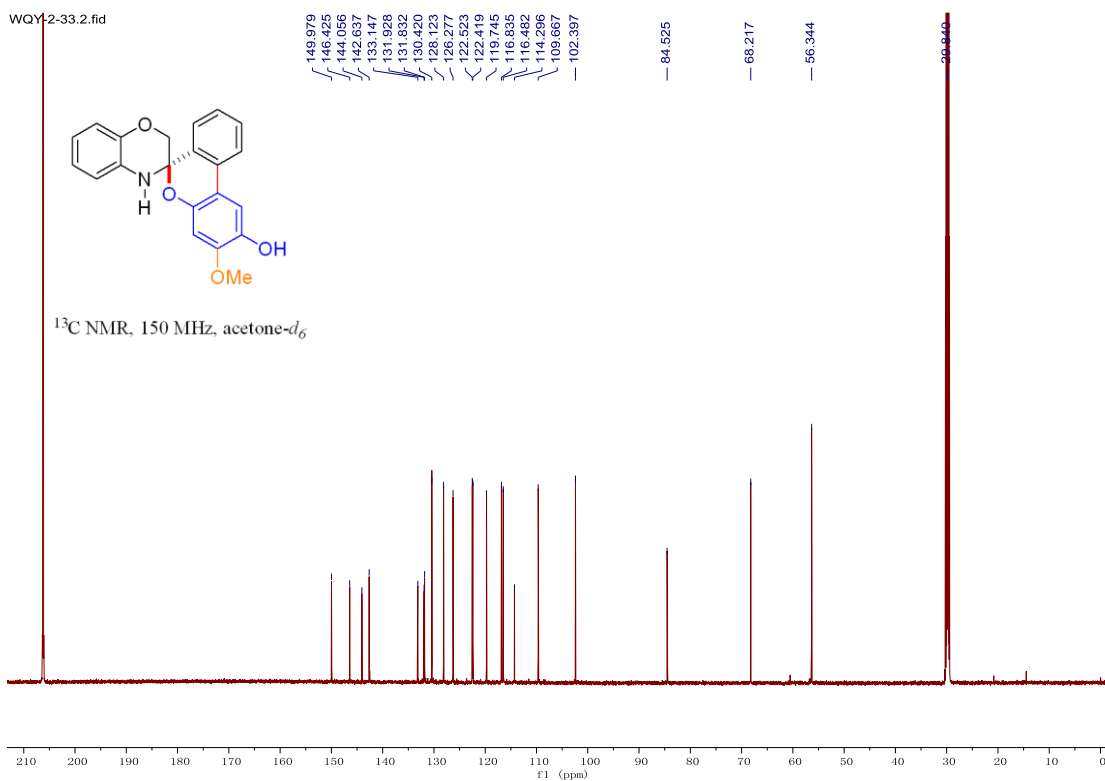
¹H NMR, 600 MHz, acetone-*d*₆

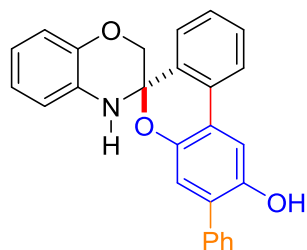


WQY-2-33.2.fid



¹³C NMR, 150 MHz, acetone-*d*₆





(±)-3'-Phenyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

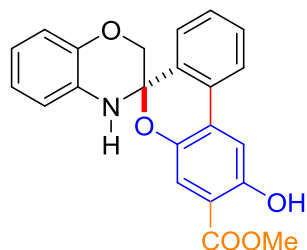
Compound **3v**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.3$, 21.1 mg, 54% yield. m.p. 185-188 °C.

$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.69-7.67 (m, 1H), 7.57-7.55 (m, 2H), 7.47-7.44 (m, 2H), 7.34 (td, $J = 7.5, 1.5$ Hz, 1H), 7.21 (d, $J = 2.5$ Hz, 1H), 7.18-7.11 (m, 3H), 6.96 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.85-6.81 (m, 2H), 6.78 (td, $J = 8.0, 1.5$ Hz, 1H), 6.48 (dd, $J = 7.5, 1.5$ Hz, 1H), 4.77 (s, 1H), 4.67 (s, 1H), 4.54 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.96 (d, $J = 11.5$ Hz, 1H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 150.3, 143.2, 142.4, 136.8, 132.9, 131.7, 130.9, 130.5, 129.6, 129.4, 128.7, 128.0, 127.2, 124.8, 123.0, 122.9, 121.7, 120.2, 118.1, 116.3, 116.2, 108.7, 83.5, 67.7.

IR (KBr) $\nu(\text{cm}^{-1})$: 3339, 2923, 1599, 1501, 1310, 1210, 1060, 938, 858, 745 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{26}\text{H}_{19}\text{NO}_3+\text{H}]^+$ requires 394.14377, found 394.14377 $[\text{M}+\text{H}]^+$.



(±)-Methyl 2'-hydroxy-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromene]-3'-carboxylate

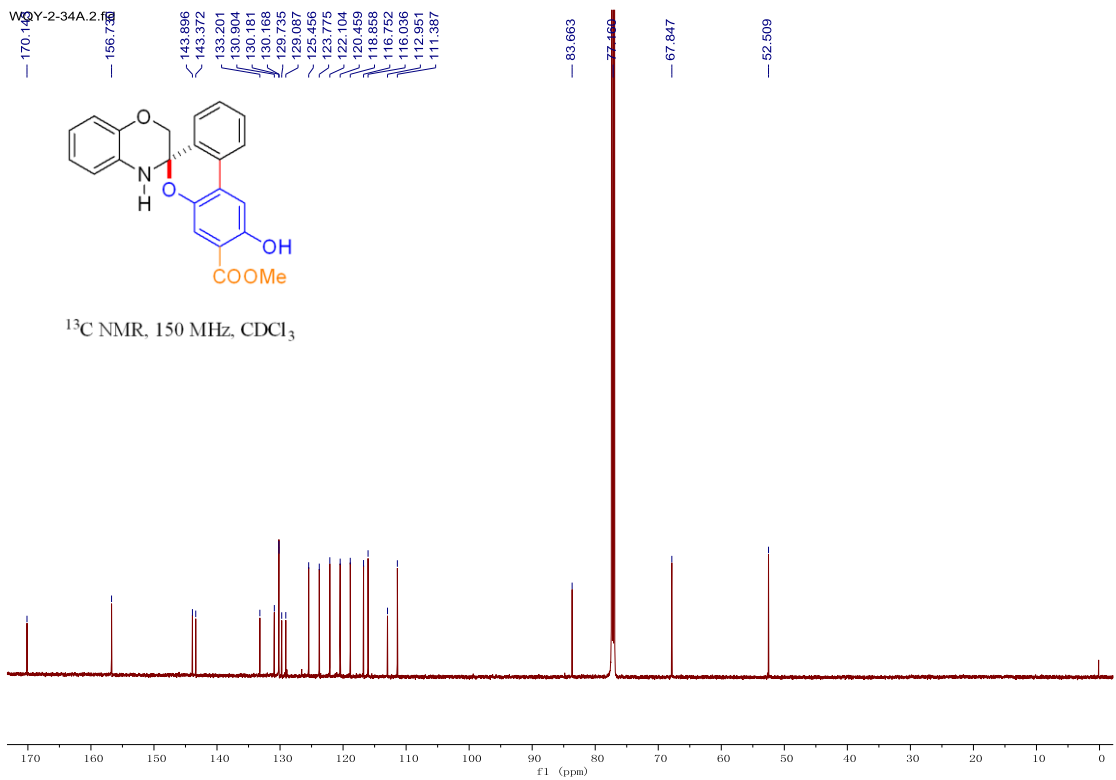
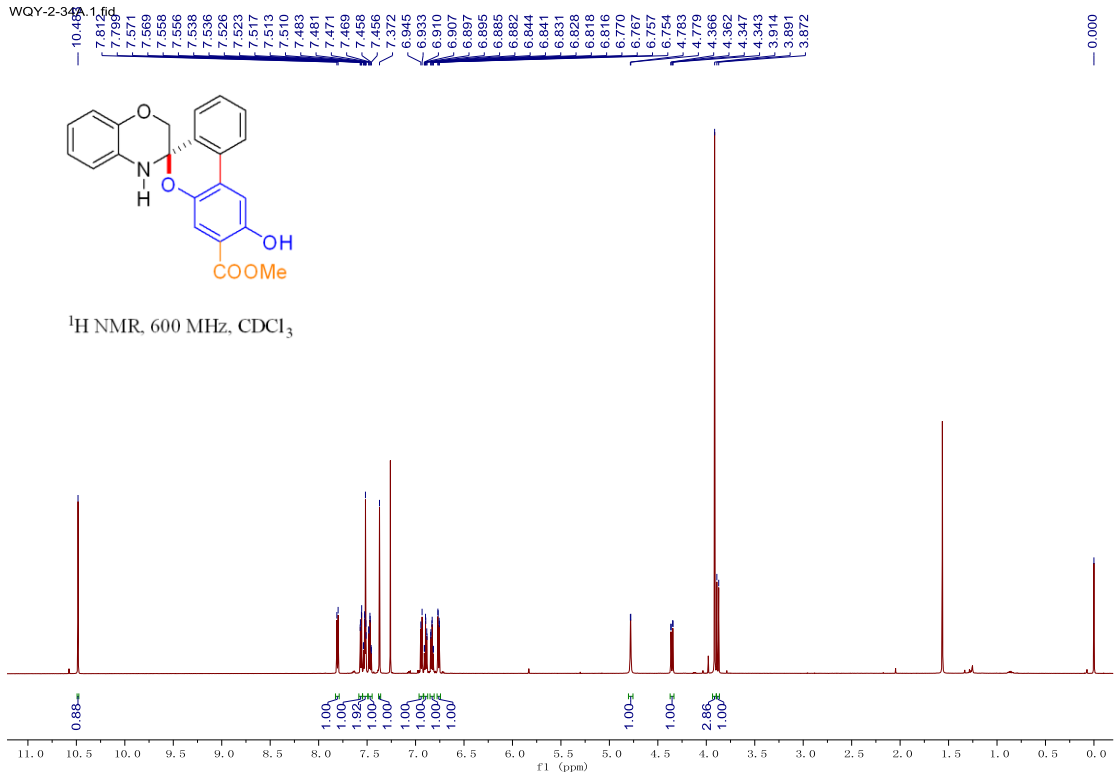
Compound **3w**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.67$, 5.5 mg, 15% yield. m.p. 202-205 °C.

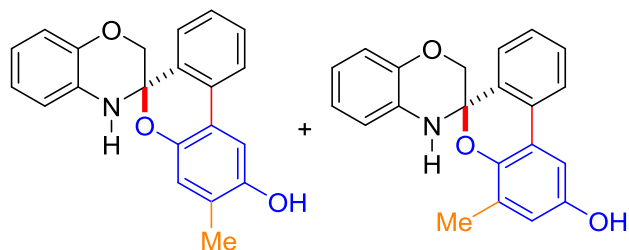
$^1\text{H NMR}$ (600 MHz, CDCl_3) δ 10.48 (s, 1H), 7.81 (d, $J = 7.8$ Hz, 1H), 7.56 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.54-7.51 (m, 2H), 7.47 (td, $J = 7.2$, 1.2 Hz, 1H), 7.37 (s, 1H), 6.94 (d, $J = 7.2$ Hz, 1H), 6.90 (td, $J = 7.8$, 1.8 Hz, 1H), 6.83 (td, $J = 7.8$, 1.8 Hz, 1H), 6.76 (dd, $J = 7.8$, 1.8 Hz, 1H), 4.78 (d, $J = 2.4$ Hz, 1H), 4.35 (dd, $J = 11.4$, 2.4 Hz, 1H), 3.91 (s, 3H), 3.88 (d, $J = 11.4$ Hz, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 170.1, 156.7, 143.9, 143.4, 133.2, 130.9, 130.18, 130.17, 129.7, 129.1, 125.5, 123.8, 122.1, 120.5, 118.9, 116.8, 116.0, 113.0, 111.4, 83.7, 67.8, 52.5.

IR (KBr) $\nu(\text{cm}^{-1})$: 3364, 2924, 1676, 1500, 1439, 1242, 1208, 730, 682, 589 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{22}\text{H}_{17}\text{NO}_5 + \text{H}]^+$ requires 376.11795, found 376.11621 $[\text{M} + \text{H}]^+$.





(±)-3'-Methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

(±)-4'-Methyl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3x** and **3x'** (mixture, 0.75:1 or 1:0.75): a white solid. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.25$, 18.1 mg, 55% yield. m.p. 85-88 °C.

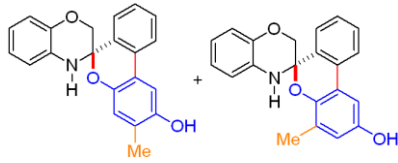
¹H NMR (500 MHz, acetone-*d*₆) δ 8.04 (broad, 1.34H), 7.80 (d, $J = 7.5$ Hz, 1H), 7.72 (d, $J = 8.0$ Hz, 0.75H), 7.57 (t, $J = 8.0$ Hz, 1.75H), 7.51-7.45 (m, 1.78H), 7.43-7.36 (m, 1.77H), 7.30 (d, $J = 2.0$ Hz, 0.73H), 7.15 (t, $J = 2.5$ Hz, 1H), 6.92-6.89 (m, 1.75H), 6.84-6.80 (m, 3.48H), 6.73-6.66 (m, 3.49H), 6.44 (broad, 1.50H), 4.34 (dd, $J = 11.0, 2.0$ Hz, 0.75H), 4.30 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.82 (d, $J = 8.0$ Hz, 1H), 3.79 (d, $J = 8.0$ Hz, 0.75H), 2.19 (s, 2.12H), 2.04 (s, 3H).

¹³C NMR (125 MHz, acetone-*d*₆) δ 152.8, 151.3, 145.7, 144.3, 144.1, 143.9, 133.5, 133.1, 132.9, 132.2, 131.9, 130.4, 129.5, 129.1, 128.7, 127.8, 126.3, 126.1, 123.4, 122.9, 122.7, 122.4, 122.3, 120.8, 120.3, 119.9, 119.8, 119.0, 116.8, 116.7, 116.6, 116.5, 109.3, 107.6, 84.1, 68.14, 68.11, 16.3, 15.8.

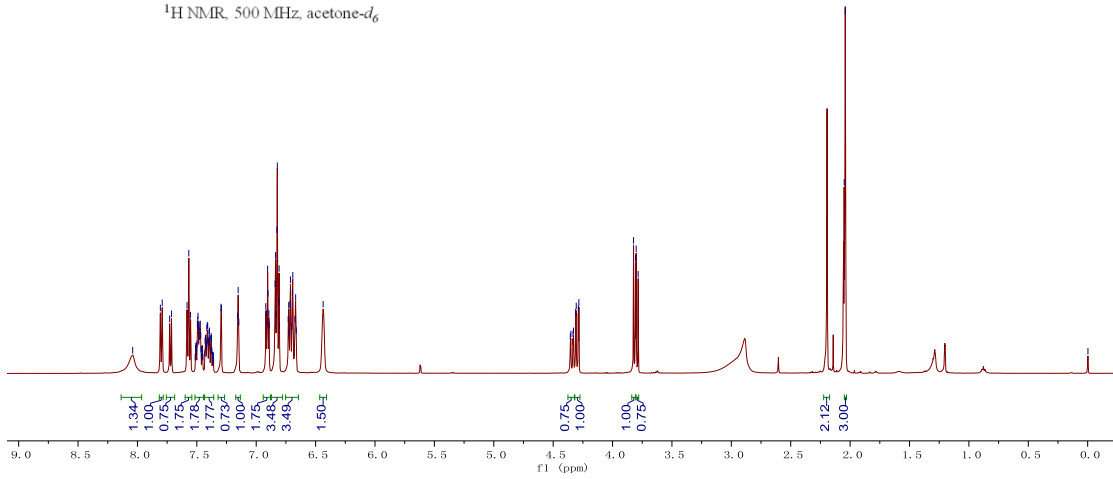
IR (KBr) ν (cm⁻¹): 3362, 1697, 1605, 1491, 1439, 1310, 1197, 940, 864, 749 cm⁻¹.

HRMS (ESI) calcd. for [C₂₁H₁₇NO₃+H]⁺ requires 332.12812, found 332.12796 [M+H]⁺.

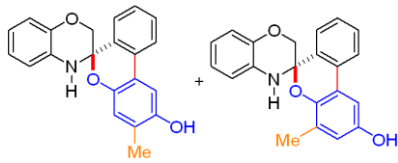
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6.730
6.726
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3.785
2.050
2.041



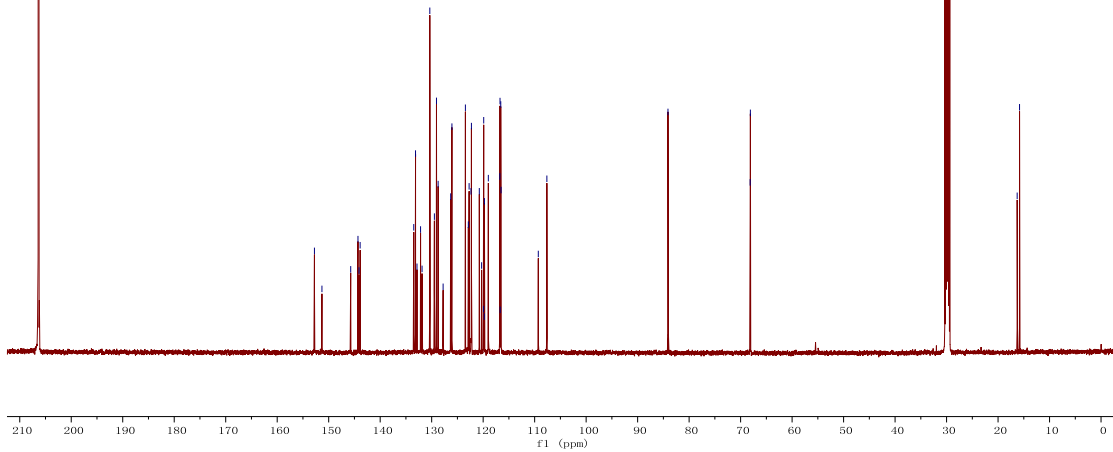
¹H NMR, 500 MHz, acetone-*d*₆

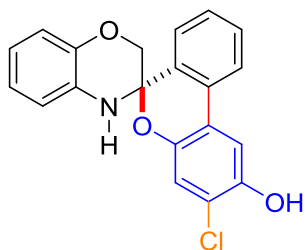


152.768
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133.135
132.852
132.158
131.865
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129.471
129.066
128.745
127.778
126.307
126.067
123.449
122.880
122.729
122.364
122.279
120.750
120.299
119.975
119.894
119.776
118.698
118.695
118.762
118.726
118.700
116.583
116.524
109.292
107.626
84.107
68.144
68.105
16.288
15.628



¹³C NMR, 125 MHz, acetone-*d*₆





(±)-3'-chloro-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **3y**: a white solid. Column chromatography, eluent: Petroleum/EtOAc/DCM = 15/1/8, $R_f = 0.36$, 14.6 mg, 42% yield. m.p. 166-170 °C.

^1H NMR (500 MHz, CDCl_3 , TMS) δ 7.70 (dd, $J = 8.0, 1.5$ Hz, 1H), 7.52 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.48 (td, $J = 7.5, 1.5$ Hz, 1H), 7.42-7.39 (m, 2H), 7.03 (s, 1H), 6.93 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.89 (td, $J = 7.5, 1.5$ Hz, 1H), 6.82 (td, $J = 7.5, 1.5$ Hz, 1H), 6.75 (dd, $J = 7.5, 1.5$ Hz, 1H), 5.35 (s, 1H), 4.79 (s, 1H), 4.37 (dd, $J = 11.5, 2.0$ Hz, 1H), 3.85 (d, $J = 11.5$ Hz, 1H).

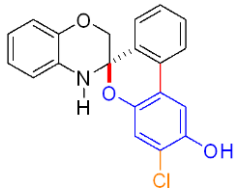
^{13}C NMR (125 MHz, CDCl_3) δ 146.8, 145.6, 143.3, 132.0, 130.9, 130.1, 130.0, 129.1, 125.4, 122.8, 122.1, 121.8, 120.7, 120.5, 118.8, 116.8, 116.0, 110.0, 84.1, 67.8.

IR (KBr) $\nu(\text{cm}^{-1})$: 3391, 2924, 1609, 1501, 1485, 1265, 1192, 941, 868, 748 cm^{-1} .

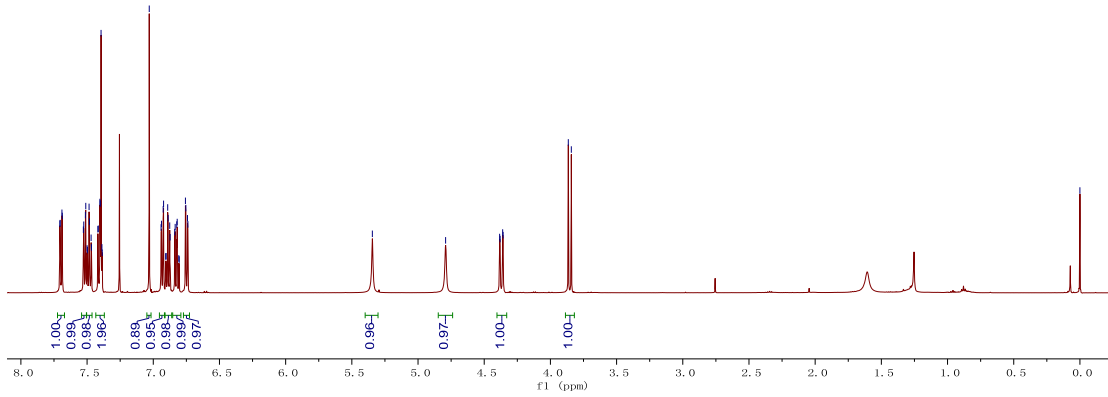
HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{ClNO}_3+\text{H}]^+$ requires 352.07350, found 352.07187 $[\text{M}+\text{H}]^+$.

7.706
7.700
7.690
7.687
7.683
7.525
7.510
7.500
7.497
7.485
7.482
7.470
7.467
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0.000

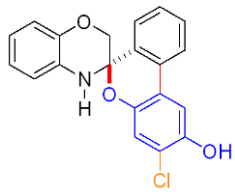


^1H NMR, 500 MHz, CDCl_3

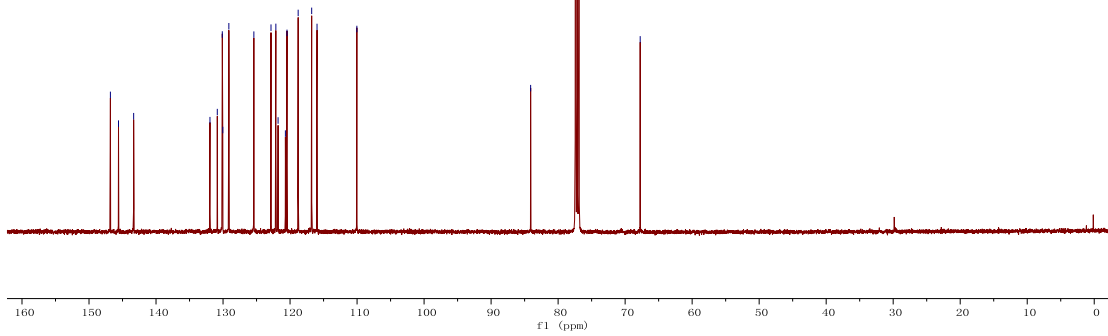


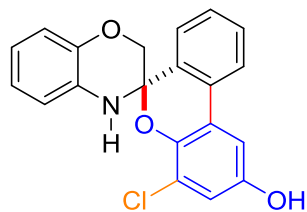
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122.170
121.787
120.656
120.455
118.791
118.773
115.975
110.032

84.101
77.469
67.752



^{13}C NMR, 125 MHz, CDCl_3





(±)-4'-chloro-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

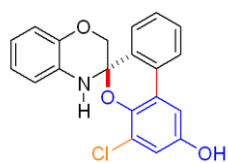
Compound **3y'**: a yellow oil. Column chromatography, eluent: Petroleum/EtOAc = 4/1, $R_f = 0.24$, 11 mg, 31% yield.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.55 (s, 1H), 7.86 (d, $J = 7.5$ Hz, 1H), 7.62 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.54 (td, $J = 7.5, 1.5$ Hz, 1H), 7.48 (td, $J = 7.5, 1.5$ Hz, 1H), 7.31 (d, $J = 3.0$ Hz, 1H), 6.91-6.89 (m, 1H), 6.88 (d, $J = 2.5$ Hz, 1H), 6.84-6.81 (m, 2H), 6.72 (td, $J = 7.5, 1.5$ Hz, 1H), 6.59 (broad, 1H), 4.34 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.85 (d, $J = 11.5$ Hz, 1H).

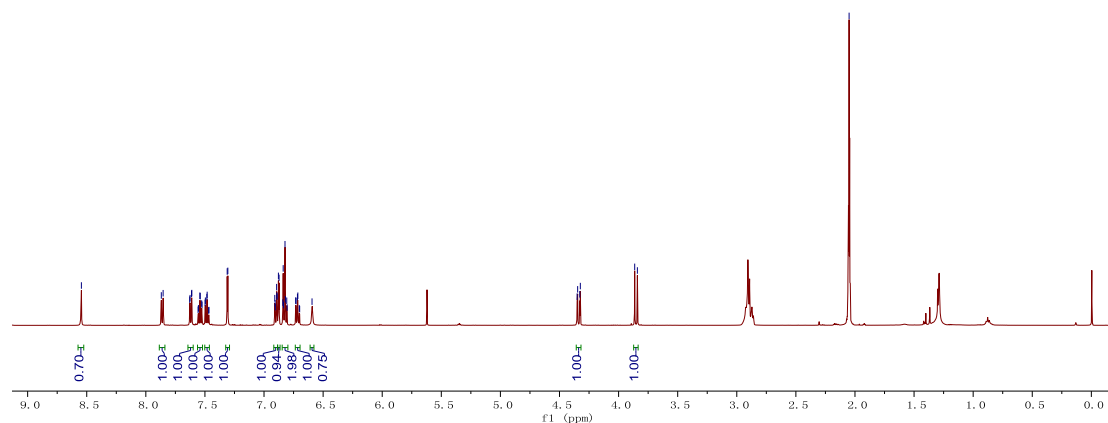
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.0, 144.3, 142.0, 133.3, 132.7, 131.1, 130.6, 129.9, 126.3, 124.7, 124.0, 123.8, 122.3, 120.0, 117.9, 116.8, 116.6, 109.4, 85.4, 68.1.

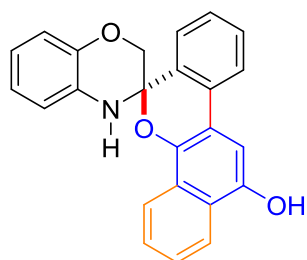
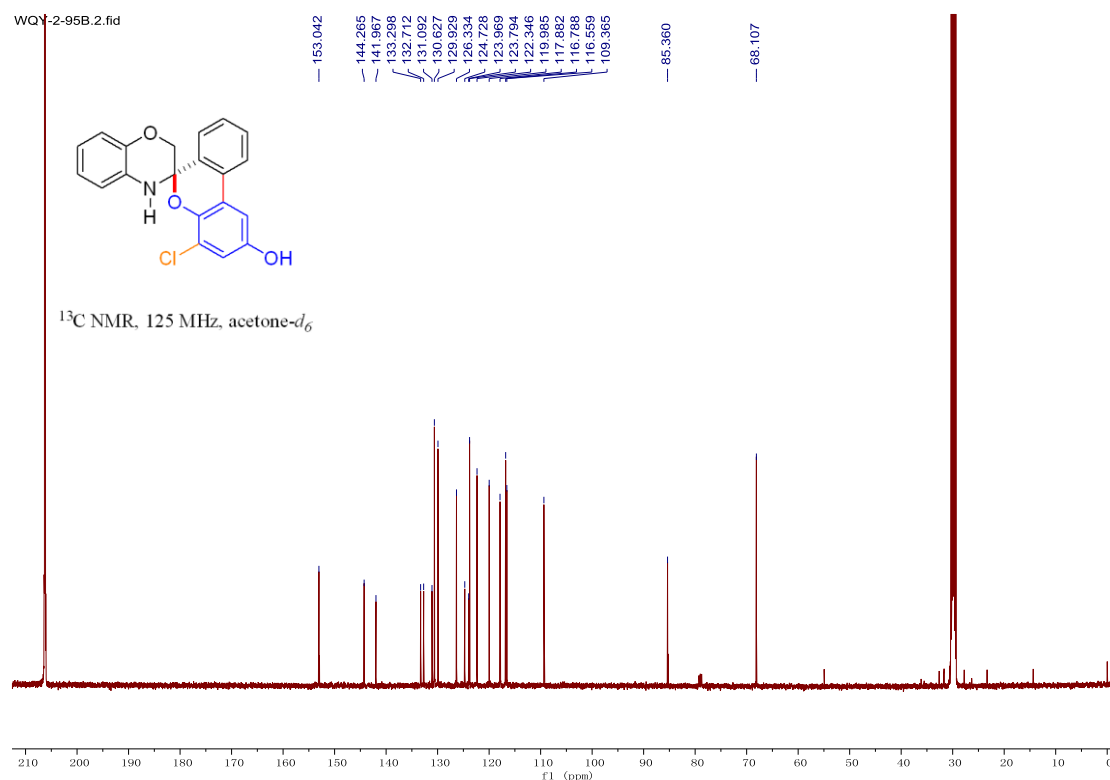
IR (KBr) $\nu(\text{cm}^{-1})$: 3361, 2922, 1690, 1500, 1432, 1310, 1211, 1060, 940, 857 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{20}\text{H}_{14}\text{ClNO}_3+\text{H}]^+$ requires 352.07350, found 352.07343 $[\text{M}+\text{H}]^+$.



$^1\text{H NMR}$, 500 MHz, acetone- d_6





(±)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-dibenzo[*c,h*]chromen]-12'-ol

Compound **3z**: a white solid. Column chromatography, eluent: Petroleum/CH₂Cl₂ = 1/1, R_f = 0.5, 29.5 mg, 80% yield. m.p. 114-120 °C.

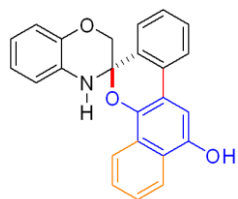
¹H NMR (500 MHz, CDCl₃, TMS) δ 8.11-8.07 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.57 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.52-7.47 (m, 2H), 7.45-7.38 (m, 2H), 7.19 (s, 1H), 6.96-6.90 (m, 2H), 6.85 (td, *J* = 7.5, 1.5 Hz, 1H), 6.81 (dd, *J* = 7.5, 1.5 Hz, 1H), 5.13-5.12 (m, 1H), 4.93 (broad, 1H), 4.48 (dd, *J* = 11.5, 2.0 Hz, 1H), 3.89 (d, *J* = 11.0 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 146.5, 143.7, 141.6, 131.7, 131.3, 131.2, 130.0, 128.4, 127.0, 126.9, 126.6, 125.7, 125.4, 122.8, 122.5, 121.9, 121.5, 120.3, 116.7, 116.1, 115.2, 102.9, 84.4, 67.7.

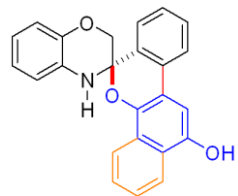
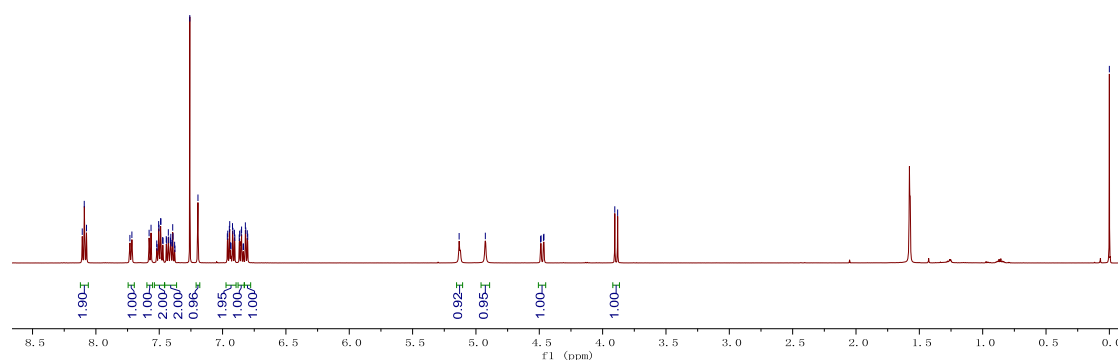
IR (KBr) ν (cm⁻¹): 3367, 1597, 1500, 1389, 1277, 1230, 1211, 1061, 1049, 760 cm⁻¹.

HRMS (ESI) calcd. for $[C_{24}H_{17}NO_3+H]^+$ requires 368.12812, found 368.12762

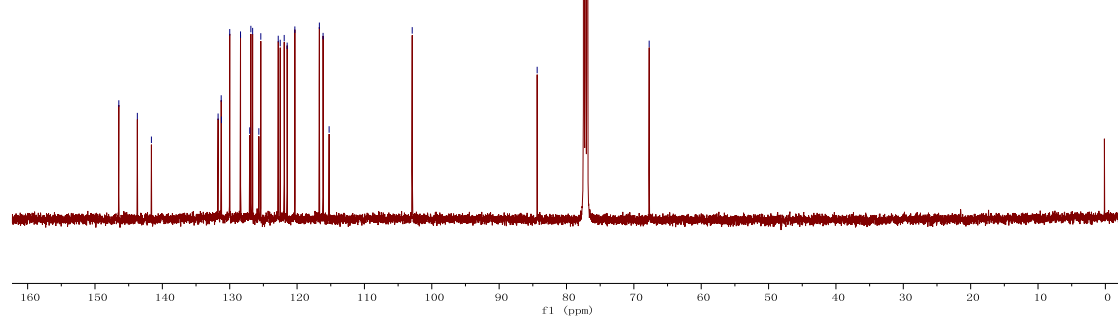
$[M+H]^+$.



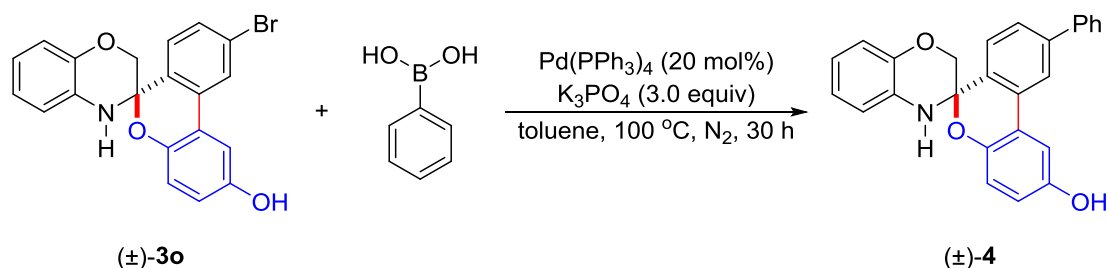
1H NMR, 500 MHz, $CDCl_3$



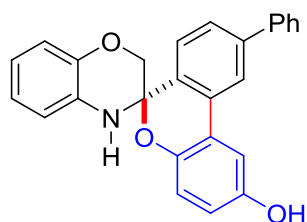
^{13}C NMR, 125 MHz, $CDCl_3$



(E) Derivatization of the Products.



An oven dried reaction tube, fitted with a magnetic stirrer, was charged with PhB(OH)_2 (61 mg, 0.5 mmol, 2.0 equiv), $\text{Pd(PPh}_3)_4$ (58 mg, 0.05 mmol, 20 mol%), K_3PO_4 (160 mg, 0.75 mmol, 3.0 equiv), substrate **(±)-3o** (99 mg, 0.25 mmol). The tube was fitted with a rubber septum and purged with nitrogen. The tube was evacuated and backfilled with nitrogen 3 times. Toluene (5.0 mL) was added by syringe under nitrogen atmosphere. The tube was sealed and the reaction was at 100 °C for 30 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford **(±)-4** (90.0 mg, 92%).



(±)-9'-Phenyl-2H,4H-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **4**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.3$, 90.0 mg, 92% yield. m.p. 85-87 °C.

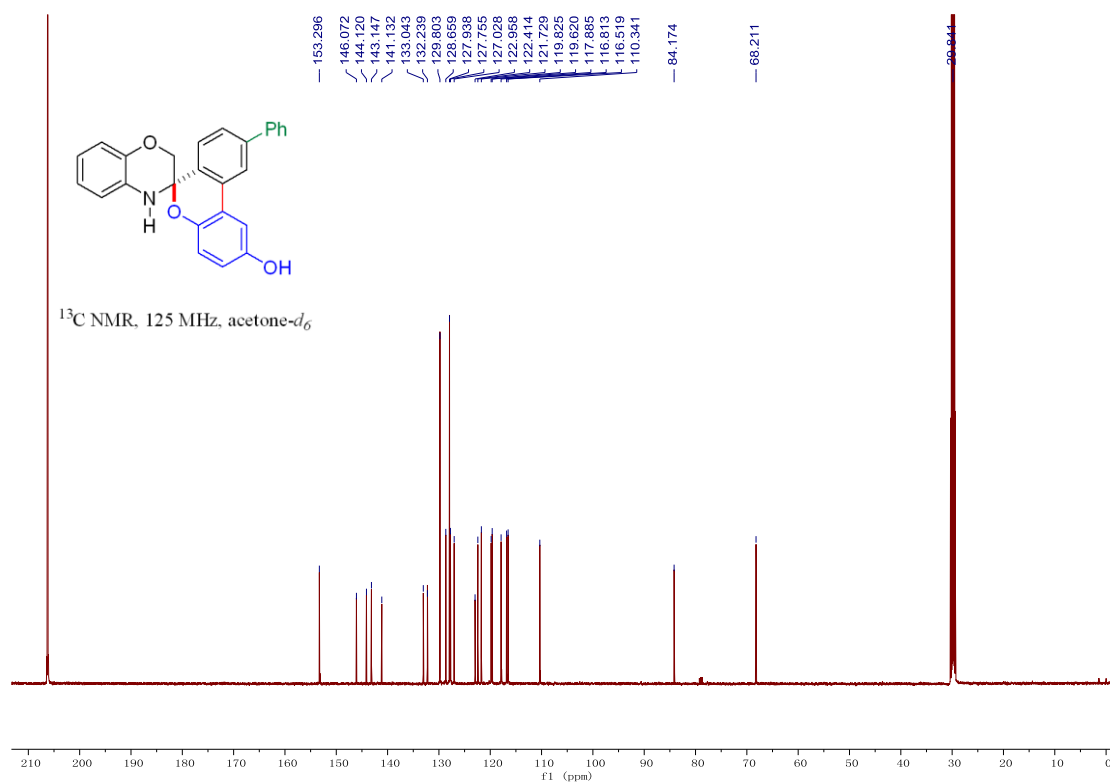
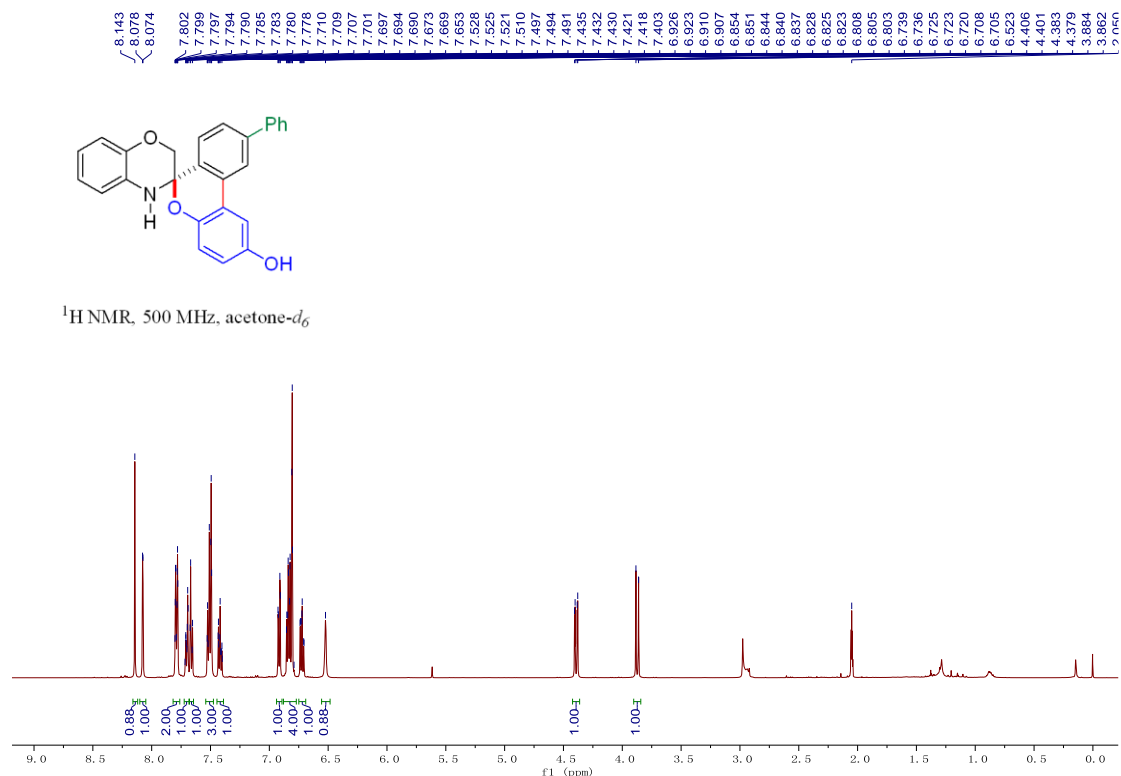
$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.14 (s, 1H), 8.08 (d, $J = 2.0$ Hz, 1H), 7.80-7.78 (m, 2H), 7.72-7.69 (m, 1H), 7.67-7.65 (m, 1H), 7.53-7.49 (m, 3H), 7.44-7.40 (m, 1H), 6.92 (dd, $J = 8.0, 1.5$ Hz, 1H), 6.85-6.79 (m, 4H), 6.74-6.71 (m, 1H), 6.52 (s, 1H), 4.39 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.87 (d, $J = 11.0$ Hz, 1H).

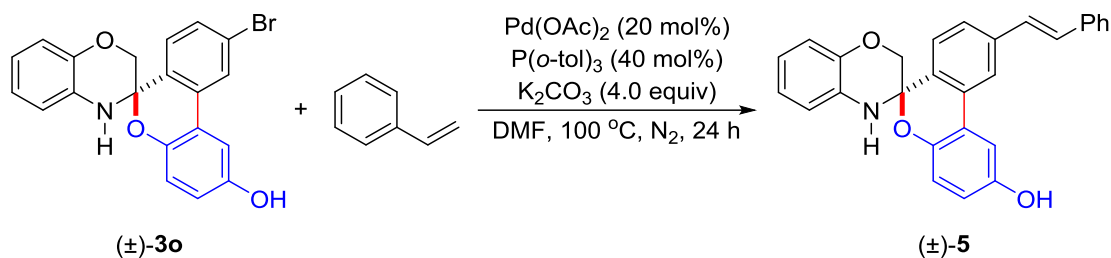
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.3, 146.1, 144.1, 143.1, 141.1, 133.0, 132.2, 129.8, 128.7, 127.9, 127.8, 127.0, 123.0, 122.4, 121.7, 119.8, 119.6, 117.9, 116.8, 116.5, 110.3, 84.2, 68.2.

IR (KBr) $\nu(\text{cm}^{-1})$: 3358, 2923, 1611, 1500, 1311, 1212, 1061, 943, 857, 744 cm^{-1} .

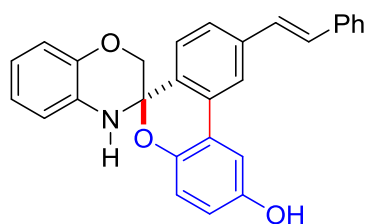
HRMS (ESI) calcd. for $[\text{C}_{26}\text{H}_{19}\text{NO}_3+\text{H}]^+$ requires 394.14377, found 394.14139

$[\text{M}+\text{H}]^+$.





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with $\text{P}(o\text{-tol})_3$ (30.0 mg, 0.1 mmol, 40 mol%), Pd(OAc)_2 (11.2 mg, 0.05 mmol, 20 mol%), K_2CO_3 (138 mg, 1.0 mmol, 4.0 equiv), substrate (±)-**3o** (99 mg, 0.25 mmol). The tube was fitted with a rubber septum and purged with nitrogen. The tube was evacuated and backfilled with nitrogen 3 times. DMF (5.0 mL) and PhCH=CH_2 (287 μL , 2.5 mmol, 10.0 equiv) was added by syringe under nitrogen atmosphere. The tube was sealed and the reaction was at 100 °C for 24 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 8/1) to afford (±)-**5** (36.4 mg, 35%).



(±)-(*E*)-9'-Styryl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

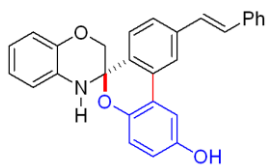
Compound **5**: a colorless solid. Column chromatography, eluent: Petroleum/EtOAc = 8/1, $R_f = 0.1$, 36.4 mg, 35% yield.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.24-8.22 (m, 1H), 8.08 (s, 1H), 7.67-7.65 (m, 3H), 7.58 (d, $J = 8.0$ Hz, 1H), 7.49-7.43 (m, 2H), 7.42-7.33 (m, 3H), 7.32-7.28 (m, 1H), 6.92-6.90 (m, 1H), 6.85-6.78 (m, 4H), 6.73-6.69 (m, 1H), 6.50 (broad, 1H), 4.36 (dd, $J = 11.0, 2.0$ Hz, 1H), 3.84 (d, $J = 11.0$ Hz, 1H).

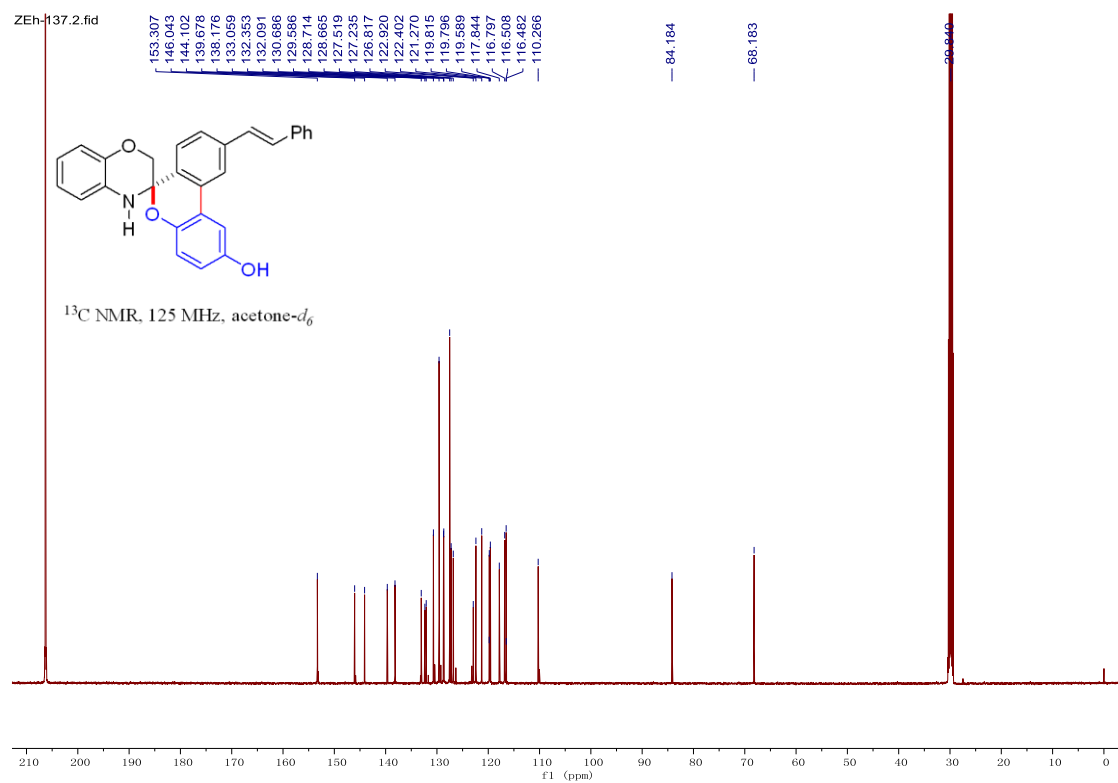
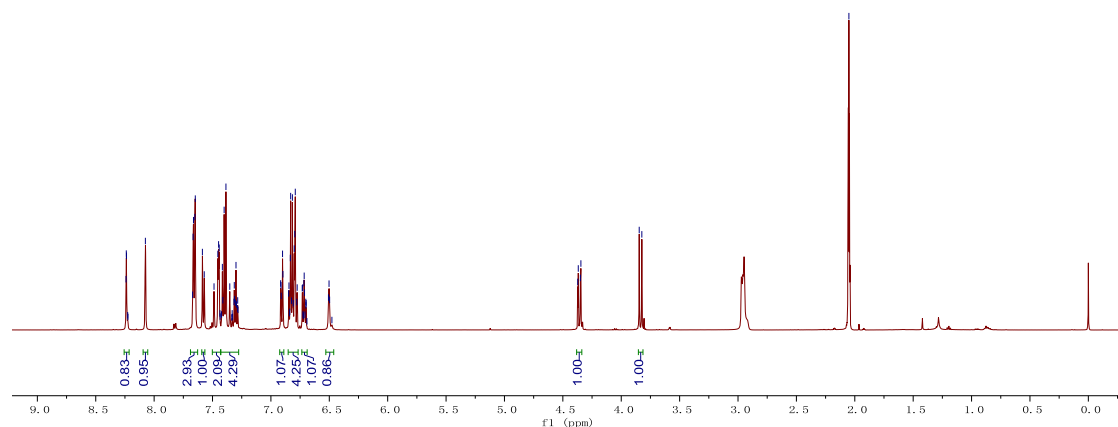
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.3, 146.0, 144.1, 139.7, 138.2, 133.1, 132.4, 132.1, 130.7, 129.6, 128.71, 128.67, 127.5, 127.2, 126.8, 122.9, 122.4, 121.3, 119.82, 119.80, 119.6, 117.8, 116.8, 116.51, 116.48, 110.3, 84.2, 68.2.

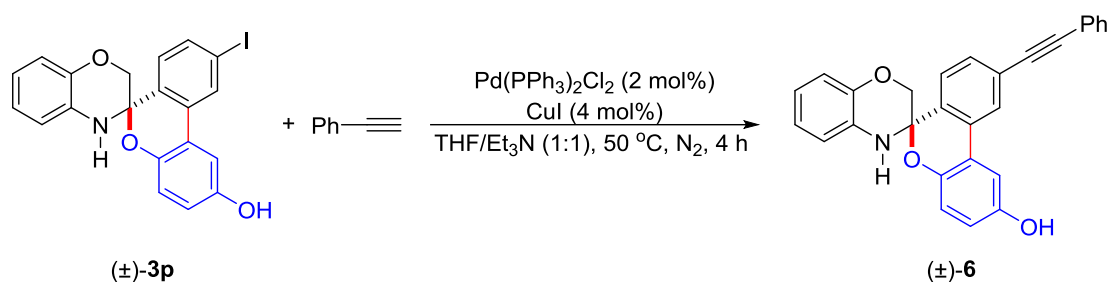
IR (KBr) $\nu(\text{cm}^{-1})$: 3352, 1690, 1609, 1501, 1431, 1312, 1277, 1254, 1211, 748 cm^{-1} .

HRMS (ESI) calcd. for $[C_{28}H_{21}NO_3+H]^+$ requires 420.15942, found 420.15933
 $[M+H]^+$.

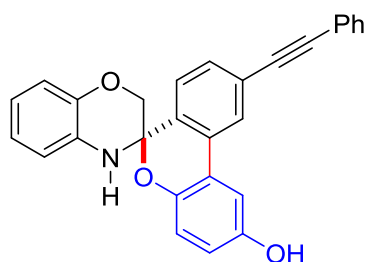


1H NMR, 500 MHz, acetone- d_6





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with Pd(PPh₃)₂Cl₂ (0.7 mg, 2 mol%), CuI (0.4 mg, 4 mol%), substrate (±)-**3p** (22.0 mg, 0.05 mmol). The tube was fitted with a rubber septum and purged with nitrogen. The tube was evacuated and backfilled with nitrogen 3 times. THF (0.5 mL), Et₃N (0.5 mL) and PhC≡CH (11 μL, 0.1 mmol, 2.0 equiv) was added by syringe under nitrogen atmosphere. The tube was sealed and the reaction was at 50 °C for 4 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford (±)-**6** (18.1 mg, 87%).



(±)-9'-(Phenylethynyl)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **6**: a yellow oil. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.1. 18.1 mg, 87% yield.

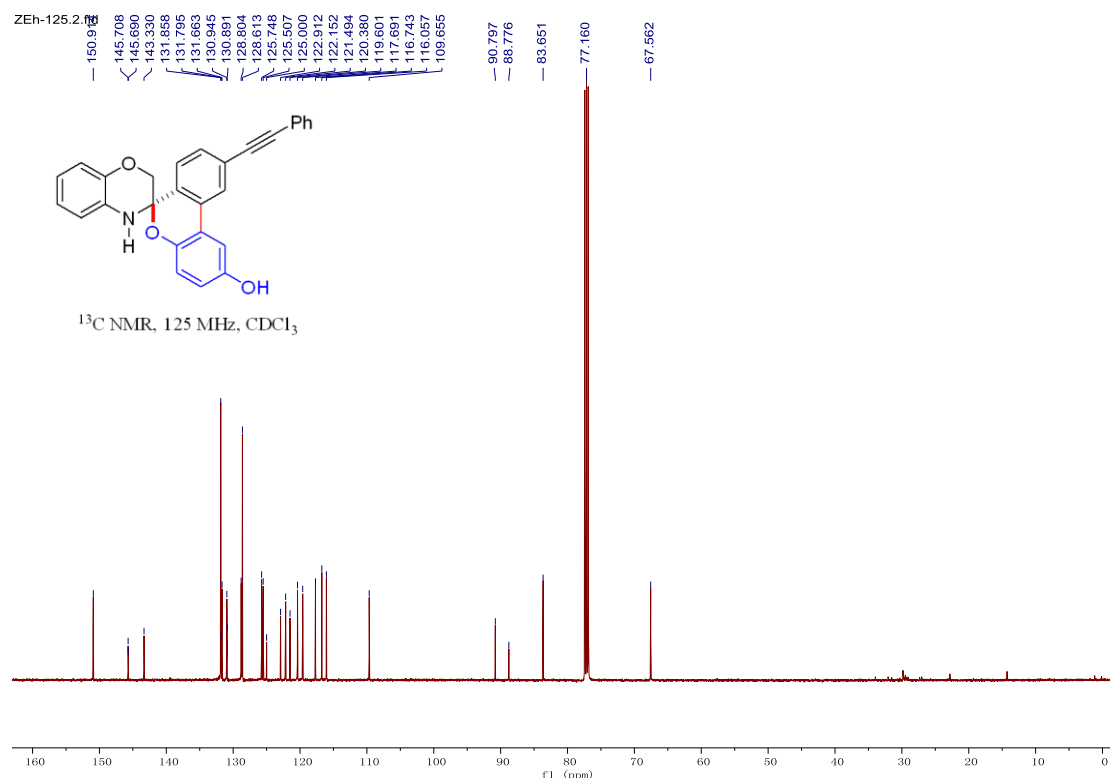
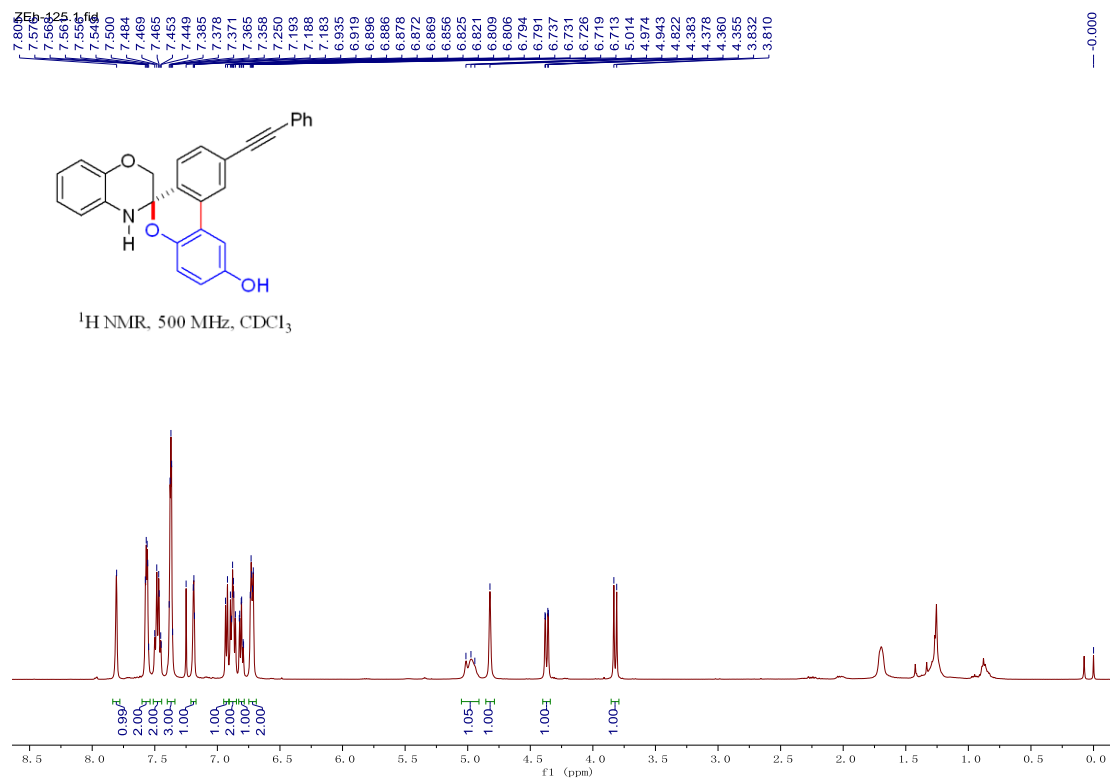
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.81 (s, 1H), 7.58-7.55 (m, 2H), 7.50-7.45 (m, 2H), 7.39-7.36 (m, 3H), 7.19-7.18 (m, 1H), 6.93 (d, *J* = 8.0 Hz, 1H), 6.90-6.86 (m, 2H), 6.81 (td, *J* = 8.0, 1.5 Hz, 1H), 6.74-6.71 (m, 2H), 5.01-4.94 (m, 1H), 4.82 (s, 1H), 4.37 (dd, *J* = 11.0, 2.5 Hz, 1H), 3.82 (d, *J* = 11.0 Hz, 1H).

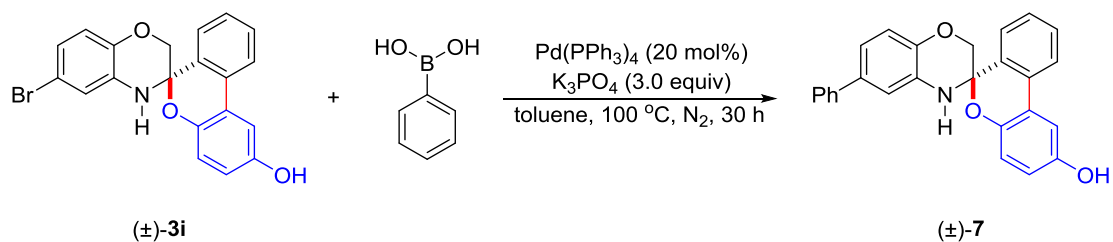
¹³C NMR (125 MHz, CDCl₃) δ 150.9, 145.71, 145.69, 143.3, 131.9, 131.7, 130.95, 130.89, 128.8, 128.6, 125.7, 125.5, 125.0, 122.9, 122.2, 121.5, 120.4, 119.6, 117.7, 116.7, 116.1, 109.7, 90.8, 88.8, 83.7, 67.6.

IR (KBr) $\nu(\text{cm}^{-1})$: 3341, 1609, 1501, 1435, 1285, 1207, 1049, 860, 756, 691 cm^{-1} .

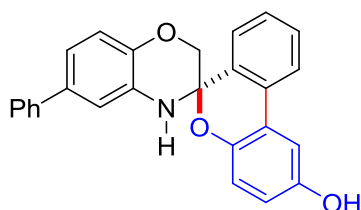
HRMS (ESI) calcd. for $[\text{C}_{28}\text{H}_{19}\text{NO}_3+\text{H}]^+$ requires 418.14377, found 418.14362

$[\text{M}+\text{H}]^+$.





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with PhB(OH)_2 (61 mg, 0.5 mmol, 2.0 equiv), $\text{Pd(PPh}_3)_4$ (58 mg, 0.05 mmol, 20 mol%), K_3PO_4 (160 mg, 0.75 mmol, 3.0 equiv), substrate $(\pm)\text{-3i}$ (99 mg, 0.25 mmol). The tube was fitted with a rubber septum and purged with nitrogen. The tube was evacuated and backfilled with nitrogen 3 times. Toluene (5.0 mL) was added by syringe under nitrogen atmosphere. The tube was sealed and the reaction was at 100 °C for 30 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford $(\pm)\text{-7}$ (32.0 mg, 33%).



$(\pm)\text{-6-Phenyl-2H,4H-spiro[benzo[}b\text{][1,4]oxazine-3,6'-benzo[}c\text{]chromen]-2'-ol}$

Compound **7**: a white solid. Column chromatography, eluent: Petroleum/EtOAc = 5/1, $R_f = 0.2$, 32.0 mg, 33% yield. m.p. 109-111 °C.

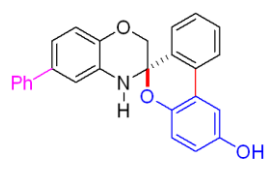
$^1\text{H NMR}$ (600 MHz, CDCl_3 , TMS) δ 7.68-7.66 (m, 1H), 7.52-7.51 (m, 3H), 7.47-7.43 (m, 1H), 7.41-7.36 (m, 3H), 7.31-7.28 (m, 1H), 7.20 (d, $J = 1.2$ Hz, 1H), 7.02 (dd, $J = 8.4, 1.8$ Hz, 1H), 6.98 (d, $J = 7.8$ Hz, 1H), 6.95-6.94 (m, 1H), 6.90 (d, $J = 8.4$ Hz, 1H), 6.72-6.69 (m, 1H), 4.98-4.90 (m, 2H), 4.41 (dd, $J = 11.4, 1.8$ Hz, 1H), 3.87 (d, $J = 11.4$ Hz, 1H).

$^{13}\text{C NMR}$ (150 MHz, CDCl_3) δ 150.8, 145.6, 143.0, 141.1, 135.4, 132.0, 131.2, 130.6, 130.0, 128.9, 128.8, 127.0, 126.9, 125.3, 122.7, 122.3, 119.5, 119.2, 117.3, 117.0, 114.6, 109.6, 83.7, 67.9.

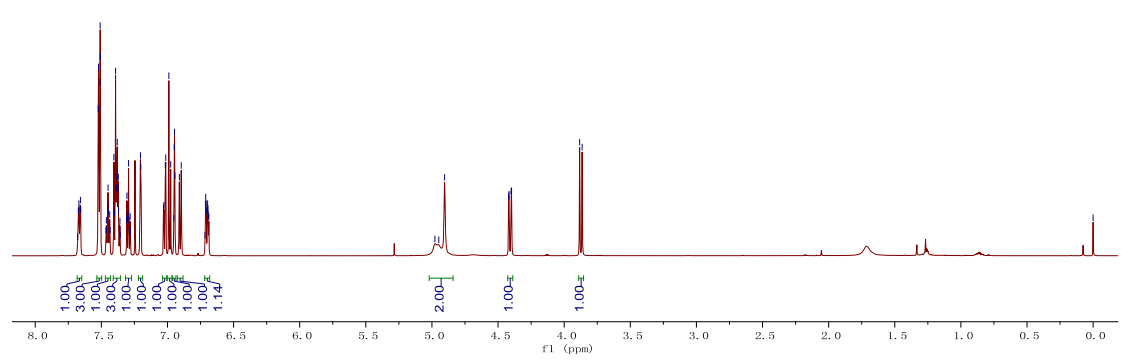
IR (KBr) $\nu(\text{cm}^{-1})$: 3368, 1489, 1443, 1315, 1242, 1200, 1053, 945, 856, 763 cm^{-1} .

HRMS (ESI) calcd. for $[C_{26}H_{19}NO_3+H]^+$ requires 394.14377, found 394.14371
 $[M+H]^+$.

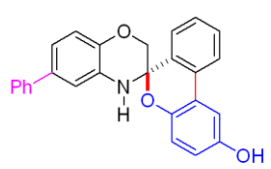
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0.000



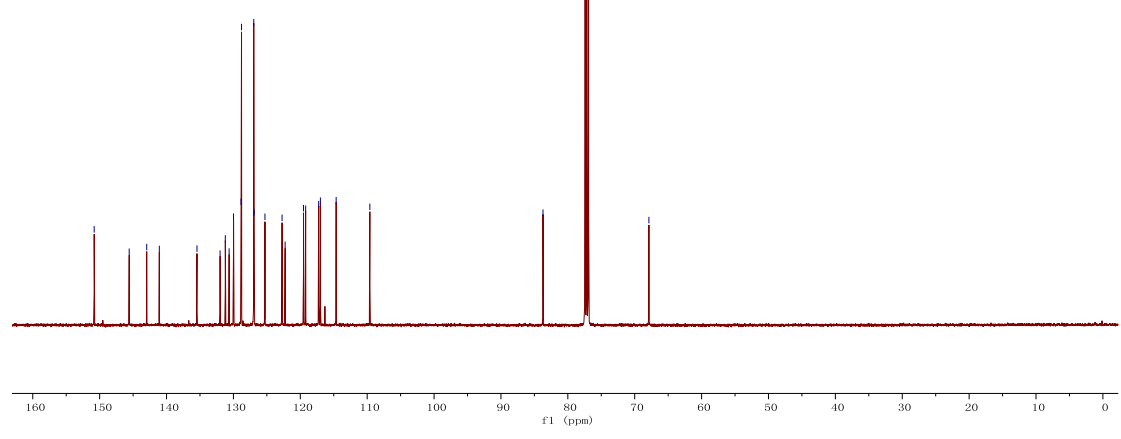
1H NMR, 600 MHz, $CDCl_3$

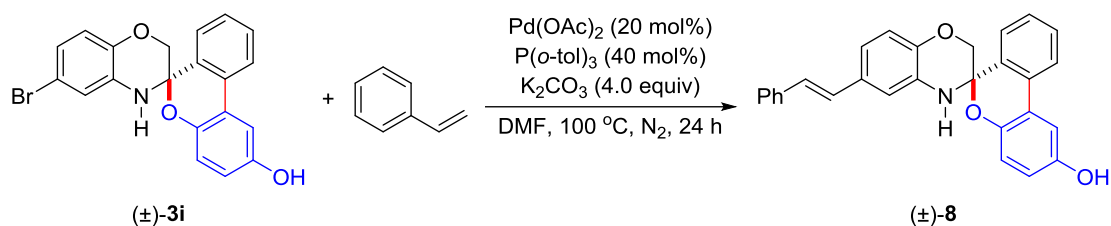


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 131.995
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 130.642
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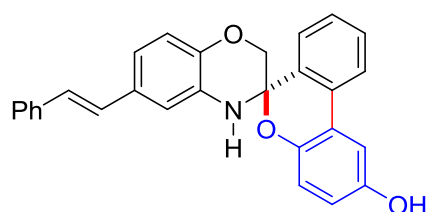


^{13}C NMR, 150 MHz, $CDCl_3$





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with $\text{P}(o\text{-tol})_3$ (30.0 mg, 0.1 mmol, 40 mol%), Pd(OAc)_2 (11.2 mg, 0.05 mmol, 20 mol%), K_2CO_3 (138 mg, 1.0 mmol, 4.0 equiv), substrate (\pm)-**3i** (99 mg, 0.25 mmol). The tube was fitted with a rubber septum and purged with nitrogen. The tube was evacuated and backfilled with nitrogen 3 times. DMF (5.0 mL) and $\text{PhCH}=\text{CH}_2$ (287 μL , 2.5 mmol, 10.0 equiv) was added by syringe under nitrogen atmosphere. The tube was sealed and the reaction was at 100 °C for 24 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford (\pm)-**8** (70.0 mg, 66%).



(*E*)-6-Styryl-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromen]-2'-ol

Compound **8**: a blue oil. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.3, 70.0 mg, 66% yield.

$^1\text{H NMR}$ (500 MHz, acetone- d_6) δ 8.22 (s, 1H), 7.84 (d, J = 8.0 Hz, 1H), 7.61 (d, J = 7.5 Hz, 1H), 7.56-7.50 (m, 3H), 7.44 (t, J = 7.5 Hz, 1H), 7.36-7.33 (m, 3H), 7.24-7.21 (m, 1H), 7.17-7.14 (m, 2H), 7.04 (d, J = 16.5 Hz, 1H), 6.99 (dd, J = 8.5, 2.0 Hz, 1H), 6.84 (d, J = 8.5 Hz, 1H), 6.81-6.78 (m, 2H), 6.54 (s, 1H), 4.38 (dd, J = 11.5, 2.0 Hz, 1H), 3.87 (d, J = 11.5 Hz, 1H).

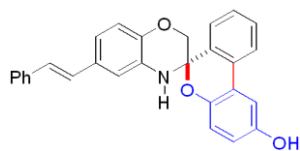
$^{13}\text{C NMR}$ (125 MHz, acetone- d_6) δ 153.3, 145.8, 144.2, 138.7, 133.2, 133.1, 132.1, 131.7, 130.5, 129.54, 129.46, 129.3, 127.9, 127.1, 127.0, 126.3, 123.3, 123.0, 119.6, 118.9, 117.8, 117.0, 114.2, 110.1, 84.1, 68.4.

IR (KBr) $\nu(\text{cm}^{-1})$: 3364, 1593, 1493, 1443, 1296, 1250, 1211, 1053, 961, 856 cm^{-1} .

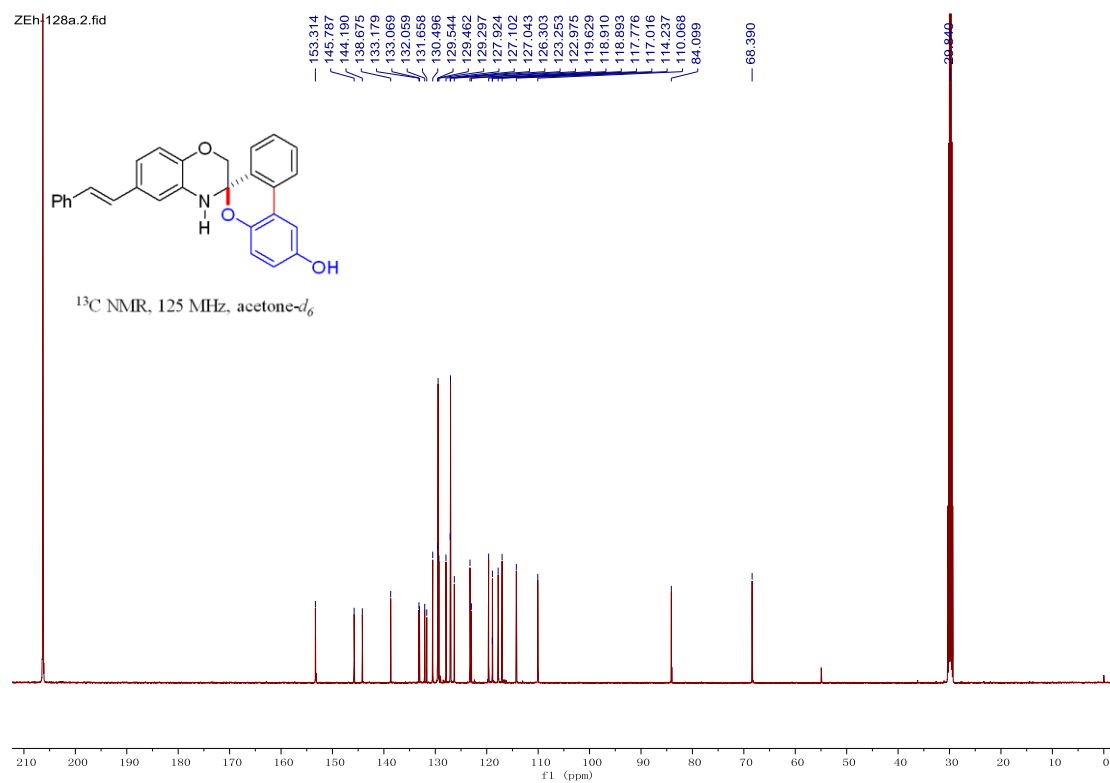
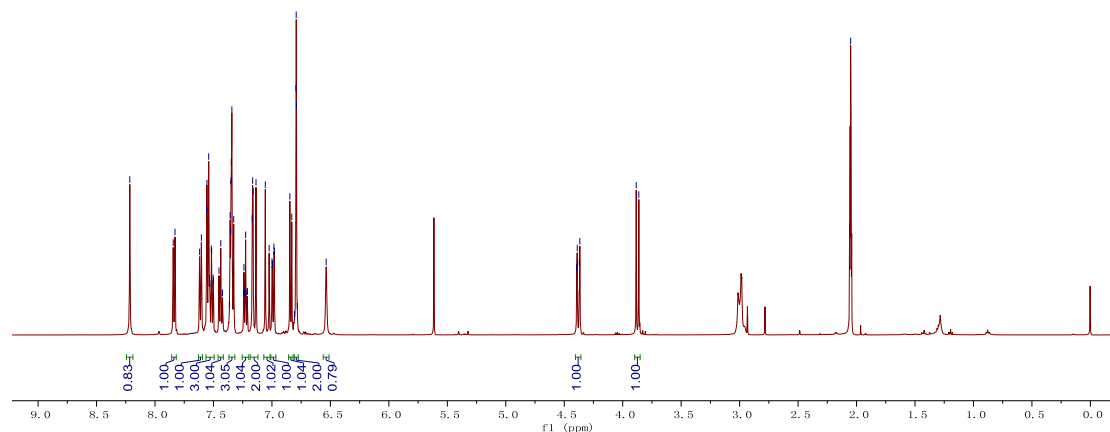
HRMS (ESI) calcd. for $[C_{28}H_{21}NO_3+H]^+$ requires 420.15942, found 420.15924

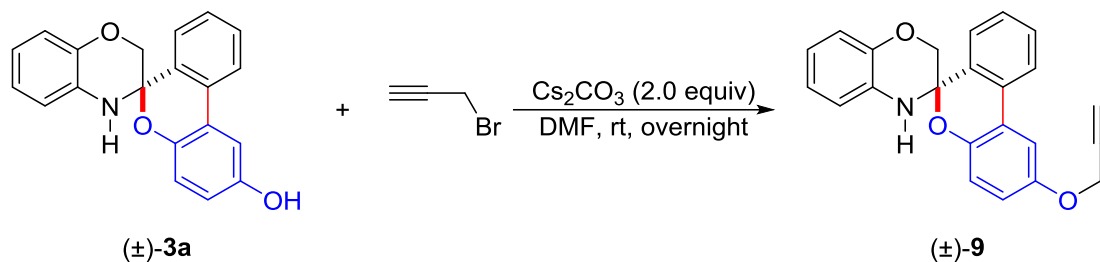
$[M+H]^+$.

ZEh-128a.2.fid
8.216
7.845
7.829
7.618
7.603
7.558
7.541
7.534
7.531
7.519
7.516
7.503
7.499
7.453
7.438
7.423
7.364
7.358
7.353
7.350
7.347
7.343
7.330
7.327
7.242
7.240
7.237
7.229
7.225
7.222
7.213
7.210
7.210
7.169
7.165
7.161
7.136
7.057
7.024
7.024
6.996
6.983
6.979
6.847
6.830
6.807
6.795
6.792
6.790
6.783
6.536
4.393
4.389
4.371
4.367
3.885
3.862
2.050

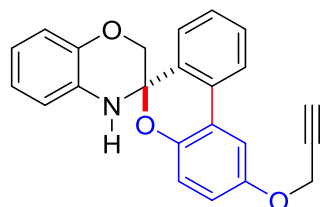


1H NMR, 500 MHz, acetone- d_6





(±)-**3a** (381 mg, 1.2 mmol), Cs₂CO₃ (782 mg, 2.4 mmol), and DMF (10 mL) were added to a 50 mL round bottom flask. 3-Bromopropyne (207 μL, 2.4 mmol) was added slowly to the reaction mixture. The reaction mixture was stirred at room temperature overnight. The mixture was concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford (±)-**9** (313 mg, 73%).



(±)-2'-(Prop-2-yn-1-yloxy)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromene]

Compound **9**: a yellow oil. Column chromatography, eluent: Petroleum/EtOAc = 5/1, R_f = 0.6. 313 mg, 73% yield.

¹H NMR (600 MHz, CDCl₃, TMS) δ 7.73 (d, *J* = 7.8 Hz, 1H), 7.51 (d, *J* = 7.8 Hz, 1H), 7.48 (td, *J* = 7.2, 1.2 Hz, 1H), 7.40-7.37 (m, 2H), 6.97 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.90-6.86 (m, 2H), 6.81 (td, *J* = 7.8, 1.8 Hz, 1H), 6.75-6.73 (m, 1H), 4.80 (s, 1H), 4.71 (d, *J* = 2.4 Hz, 2H), 4.38 (dd, *J* = 11.4, 2.4 Hz, 1H), 3.85 (d, *J* = 11.4 Hz, 1H), 2.55 (t, *J* = 2.4 Hz, 1H).

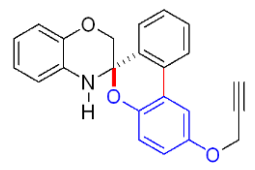
¹³C NMR (125 MHz, CDCl₃) δ 152.9, 146.4, 143.4, 132.1, 131.1, 130.7, 130.0, 128.8, 125.3, 122.7, 122.1, 122.0, 120.3, 119.4, 116.8, 116.7, 116.0, 109.9, 83.7, 78.8, 75.8, 67.8, 56.7.

IR (KBr) ν(cm⁻¹): 3356, 3283, 2916, 1069, 1493, 1192, 1038, 941, 841, 748 cm⁻¹.

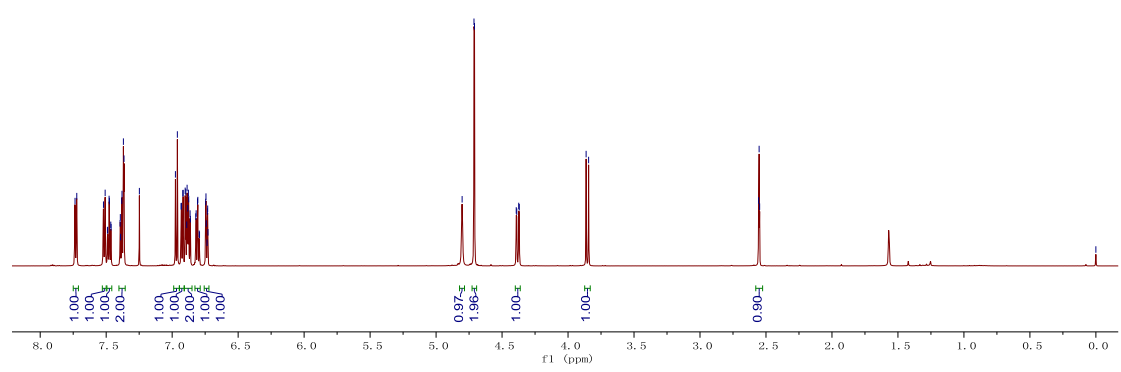
HRMS (ESI) calcd. for [C₂₃H₁₇NO₃+H]⁺ requires 356.12812, found 356.12799 [M+H]⁺.

7.738
7.729
7.724
7.709
7.690
7.490
7.488
7.478
7.476
7.465
7.463
7.395
7.393
7.391
7.382
7.370
7.365
7.248
6.975
6.961
6.932
6.930
6.919
6.917
6.901
6.897
6.889
6.887
6.882
6.877
6.874
6.864
6.862
6.821
6.818
6.808
6.805
6.795
6.793
6.746
6.744
6.742
6.736
6.735
6.731
6.729
4.803
4.713
4.709
4.393
4.389
4.374
4.370
3.863
3.844
2.556
2.548

0.000

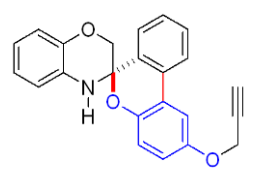


¹H NMR, 600 MHz, CDCl₃

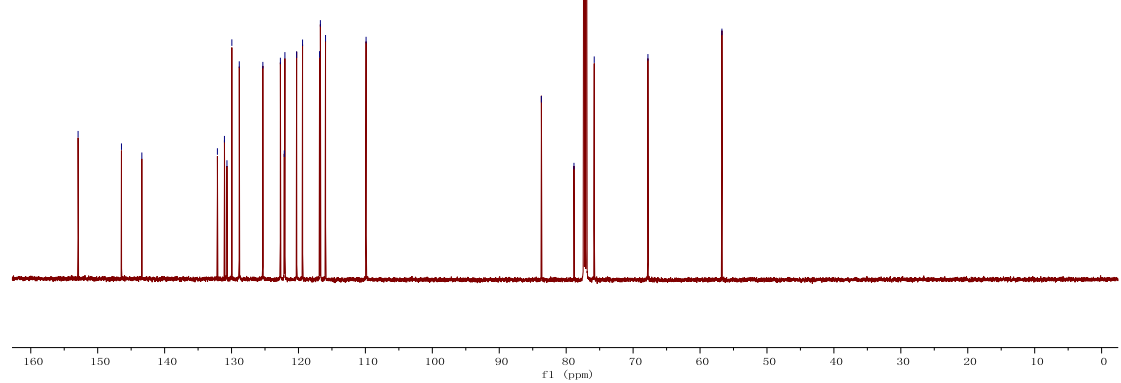


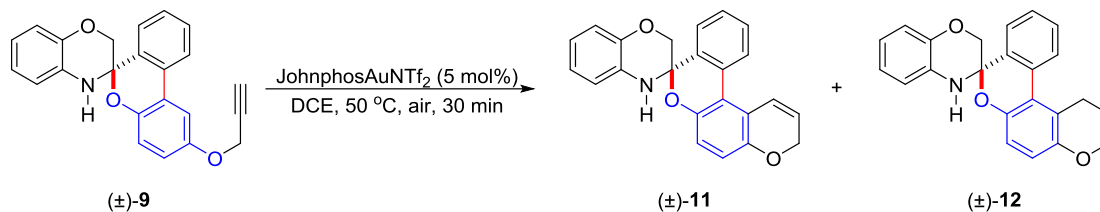
ZEH-129 id
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146.448
143.403
132.111
131.060
129.663
128.845
128.323
122.703
122.121
120.028
120.275
119.390
116.848
116.727
115.958
109.898

83.706
78.838
77.460
75.810
67.786
56.731

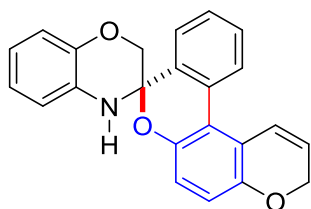


¹³C NMR, 150 MHz, CDCl₃





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with JohnPhosAuNTf₂ (3.9 mg, 5 mol%), substrate (±)-**9** (35.5 mg, 0.1 mmol). DCE (1 mL) was added by syringe. The tube was sealed and the reaction was at 50 °C for 30 min. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/THF, 150/1) to afford (±)-**11** (18 mg, 51%) and (±)-**12** (8 mg, 23%).



(±)-2*H*,3'*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,8'-benzo[*c*]pyrano[3,2-*f*]chromene]

Compound **11**: a yellow oil. Column chromatography, eluent: Petroleum/THF = 150/1, R_f = 0.1, 18 mg, 51% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.65 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.59 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.48 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (td, *J* = 7.5, 1.0 Hz, 1H), 6.95-6.91 (m, 2H), 6.90-6.86 (m, 2H), 6.82-6.79 (m, 2H), 6.74 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.01-5.97 (m, 1H), 4.76-4.73 (m, 2H), 4.66-4.62 (m, 1H), 4.45 (dd, *J* = 11.5, 2.5 Hz, 1H), 3.95 (d, *J* = 11.5 Hz, 1H).

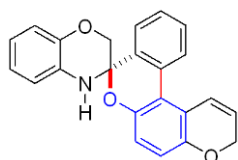
¹³C NMR (125 MHz, CDCl₃) δ 150.5, 146.6, 143.6, 134.1, 131.0, 130.1, 129.2, 128.4, 127.8, 124.61, 124.59, 122.0, 121.2, 120.3, 119.6, 119.1, 119.0, 117.4, 116.7, 116.0, 83.4, 66.7, 64.0.

¹³C NMR (DEPT135°, 125 MHz, CDCl₃) δ 129.1 (CH), 128.3 (CH), 127.7 (CH), 124.51 (CH), 124.49 (CH), 121.9 (CH), 121.1 (CH), 120.2 (CH), 118.9 (CH), 117.3 (CH), 116.6 (CH), 115.9 (CH), 66.6 (CH₂), 63.9 (CH₂).

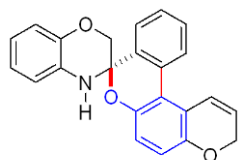
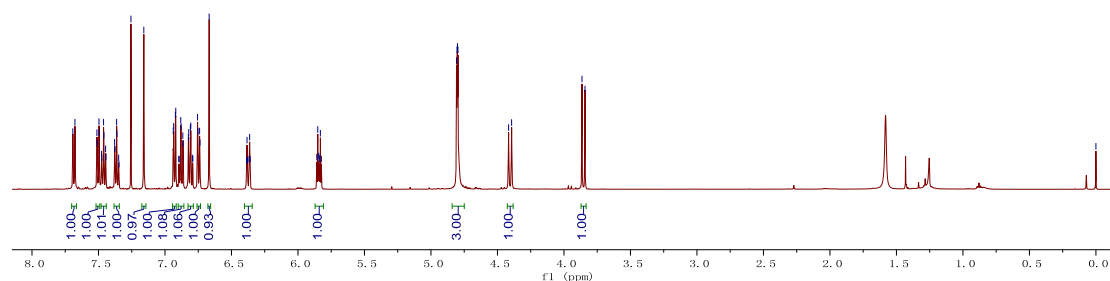
IR (KBr) ν(cm⁻¹): 3352, 1501, 1435, 1312, 1211, 1057, 991, 826, 748, 706 cm⁻¹.

HRMS (ESI) calcd. for $[C_{23}H_{17}NO_3+H]^+$ requires 356.12812, found 356.12796

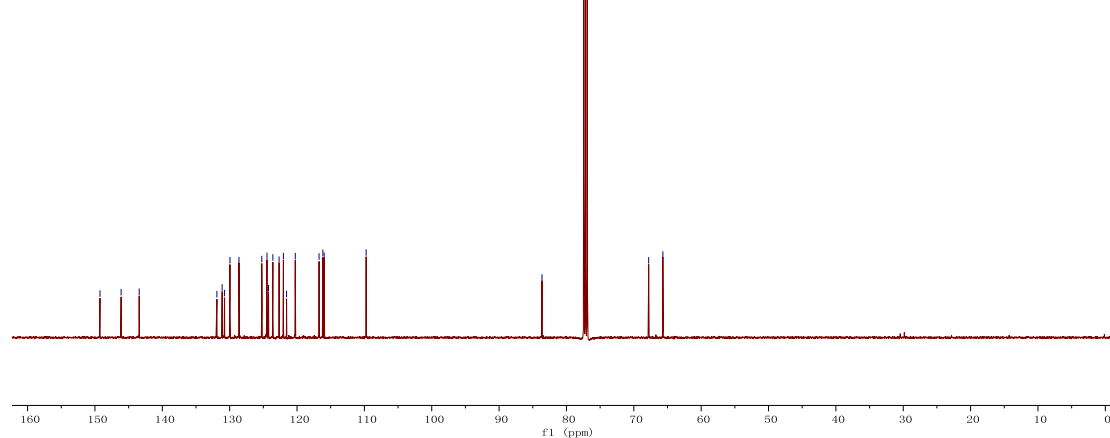
$[M+H]^+$



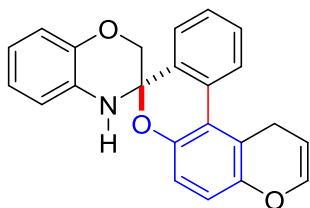
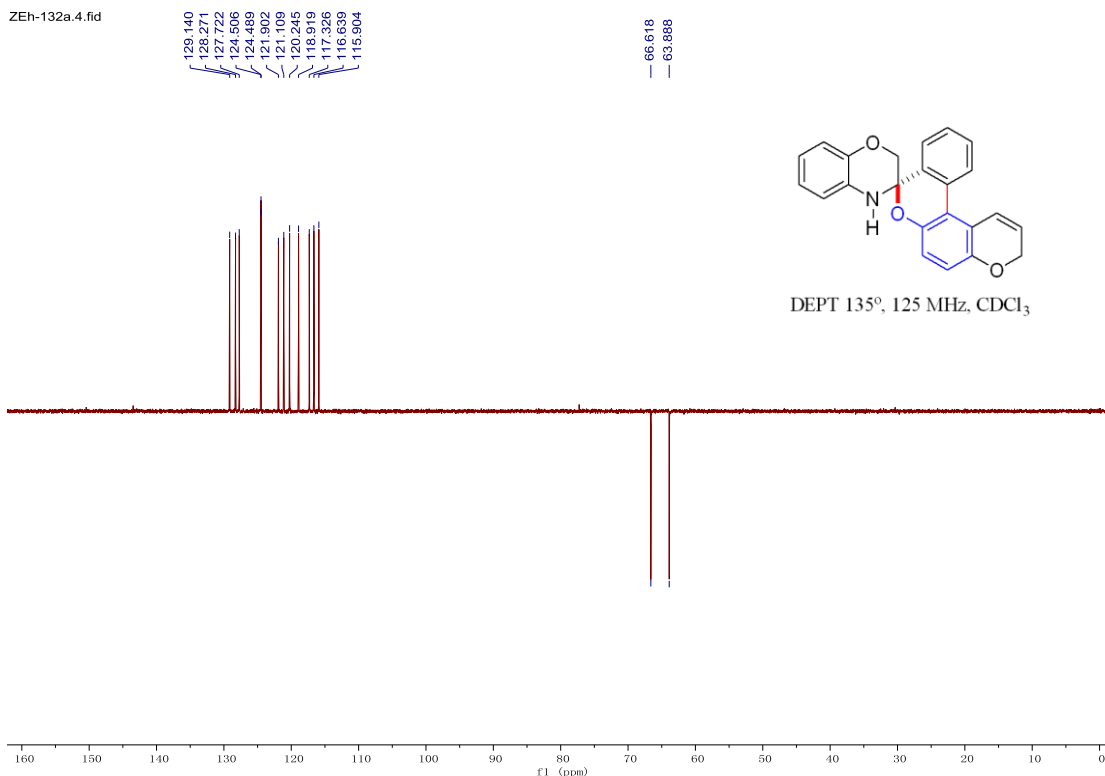
1H NMR, 500 MHz, $CDCl_3$



^{13}C NMR, 125 MHz, $CDCl_3$



ZEH-132a.4.fid



(±)-1'*H*,2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,8'-benzo[*c*]pyrano[3,2-*f*]chromene]

Compound **12**: a yellow oil. Column chromatography, eluent: Petroleum/THF = 150/1, R_f = 0.1, 8 mg, 23% yield.

¹H NMR (500 MHz, CDCl₃, TMS) δ 7.69 (d, J = 8.0 Hz, 1H), 7.50 (dd, J = 7.5, 1.5 Hz, 1H), 7.46 (td, J = 7.5, 1.5 Hz, 1H), 7.36 (td, J = 7.5, 1.5 Hz, 1H), 7.16 (s, 1H), 6.93 (dd, J = 8.0, 1.5 Hz, 1H), 6.88 (td, J = 7.5, 1.5 Hz, 1H), 6.81 (td, J = 7.5, 1.5 Hz, 1H), 6.75 (dd, J = 7.5, 1.5 Hz, 1H), 6.67 (s, 1H), 6.37 (dt, J = 10.0, 2.0 Hz, 1H), 5.84 (dt, J = 9.5, 3.5 Hz, 1H), 4.81-4.80 (m, 3H), 4.40 (d, J = 11.0 Hz, 1H), 3.85 (d, J = 11.0 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 149.3, 146.1, 143.4, 131.9, 131.1, 130.8, 130.0, 128.6, 125.2, 124.5, 124.2, 123.6, 122.7, 122.0, 121.6, 120.3, 116.7, 116.2, 116.0, 109.7, 83.6, 67.8, 65.7.

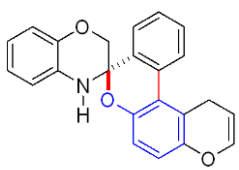
¹³C NMR (DEPT135°, 125 MHz, CDCl₃) δ 129.8 (CH), 128.5 (CH), 125.1 (CH), 124.3 (CH), 123.5 (CH), 122.5 (CH), 121.9 (CH), 120.1 (CH), 116.6 (CH), 116.0 (CH), 115.9 (CH), 109.6 (CH), 67.7 (CH₂), 65.6 (CH₂).

IR (KBr) ν(cm⁻¹): 3356, 2920, 1501, 1423, 1269, 1184, 1053, 979, 941, 748 cm⁻¹.

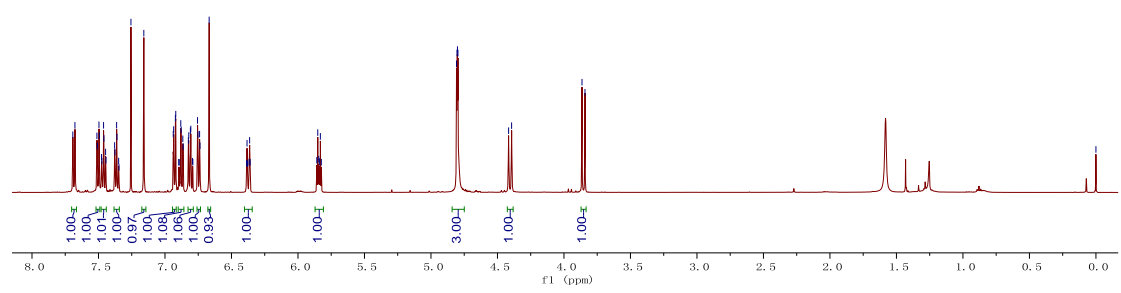
HRMS (ESI) calcd. for [C₂₃H₁₇NO₃+H]⁺ requires 356.12812, found 356.12747 [M+H]⁺.

7.659
7.677
7.512
7.502
7.495
7.492
7.477
7.474
7.462
7.459
7.447
7.444
7.379
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7.348
7.346
7.256
7.159
6.938
6.935
6.922
6.919
6.896
6.893
6.881
6.878
6.866
6.863
6.824
6.821
6.809
6.806
6.794
6.790
6.752
6.752
6.740
6.737
6.686
6.587
6.585
6.575
6.567
6.567
6.564
6.564
6.560
5.858
5.851
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4.797
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4.394
3.842

0.000

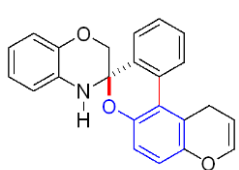


¹H NMR, 500 MHz, CDCl₃

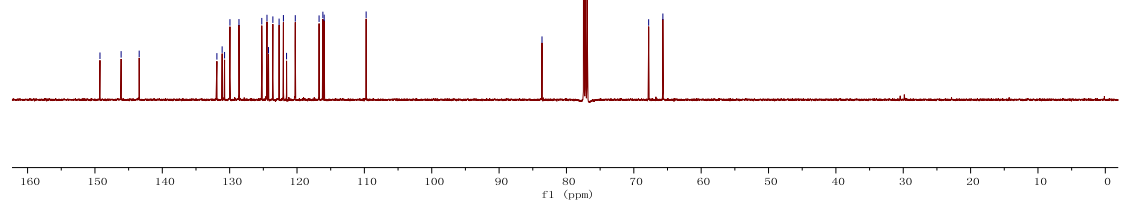


Zeh-132
148.212
148.172
148.066
131.895
131.117
130.755
129.957
128.618
125.229
124.459
124.232
123.584
122.661
122.021
121.553
120.260
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116.159
115.970
109.739

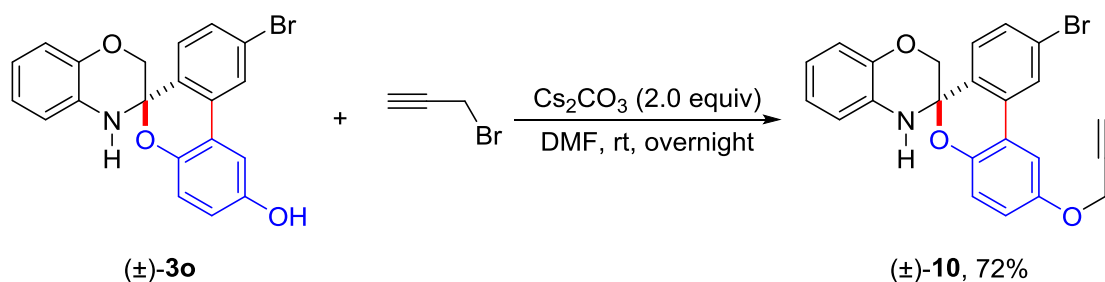
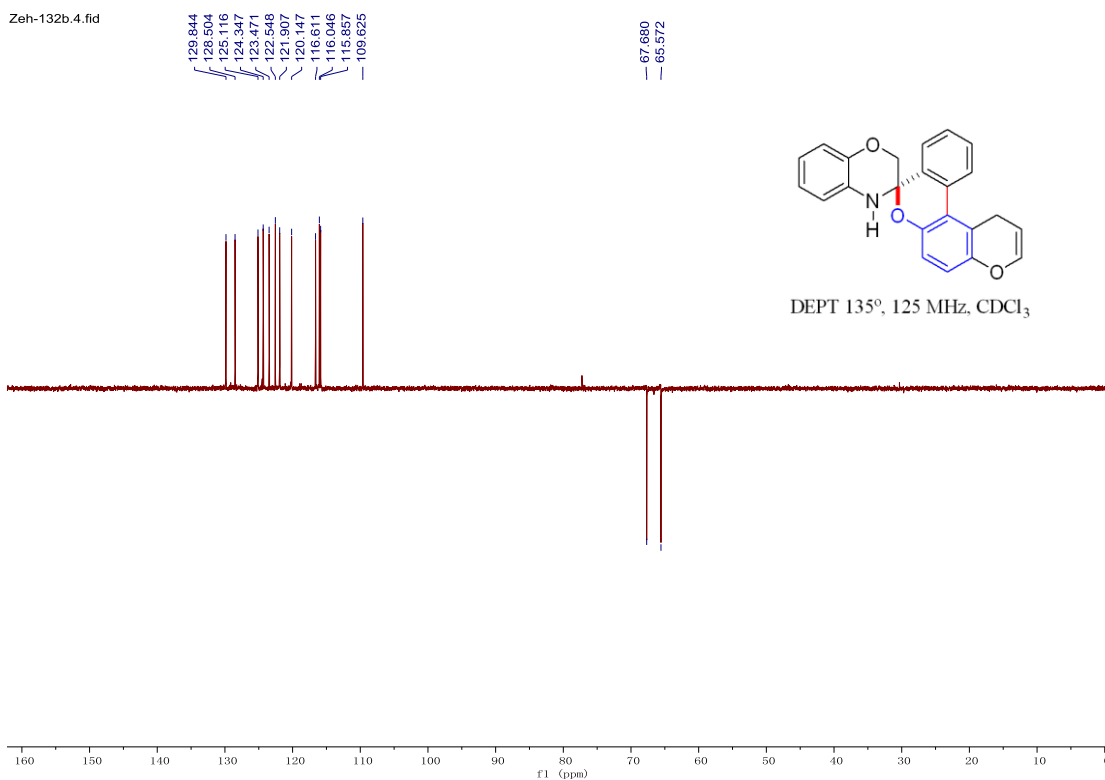
83.629
77.160
67.794
65.686



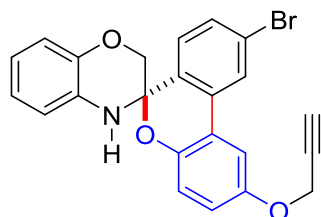
¹³C NMR, 125 MHz, CDCl₃



Zeh-132b.4.fid



(±)-**3o** (395 mg, 1.0 mmol), Cs₂CO₃ (652 mg, 2.0 mmol), and DMF (15 mL) were added to a 50 mL round bottom flask. 3-Bromopropyne (172 μL, 2.0 mmol) was added slowly to the reaction mixture. The reaction mixture was stirred at room temperature overnight. The mixture was concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford (±)-**10** (310 mg, 72%).



(±)-9'-bromo-2'-(prop-2-yn-1-yloxy)-2*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,6'-benzo[*c*]chromene]

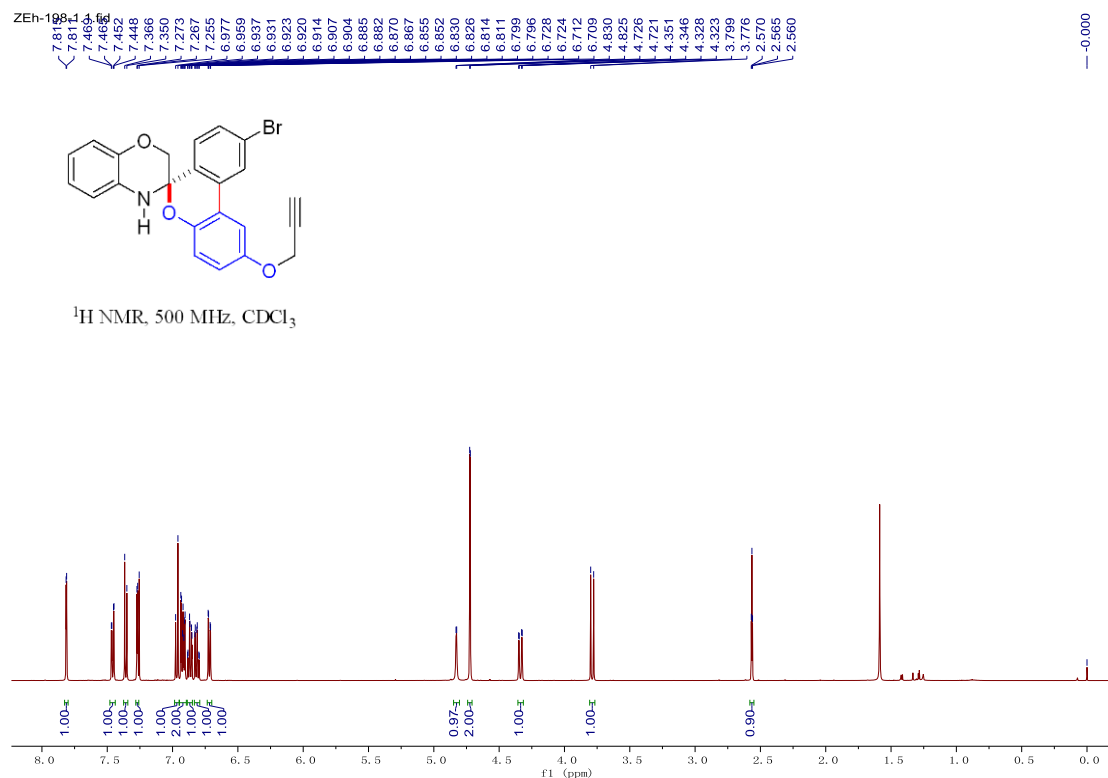
Compound **10**: A yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 8/1, $R_f = 0.6$, 72% yield. m.p. 58-60 °C.

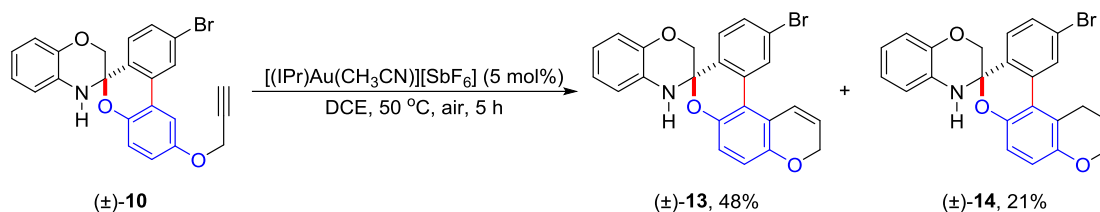
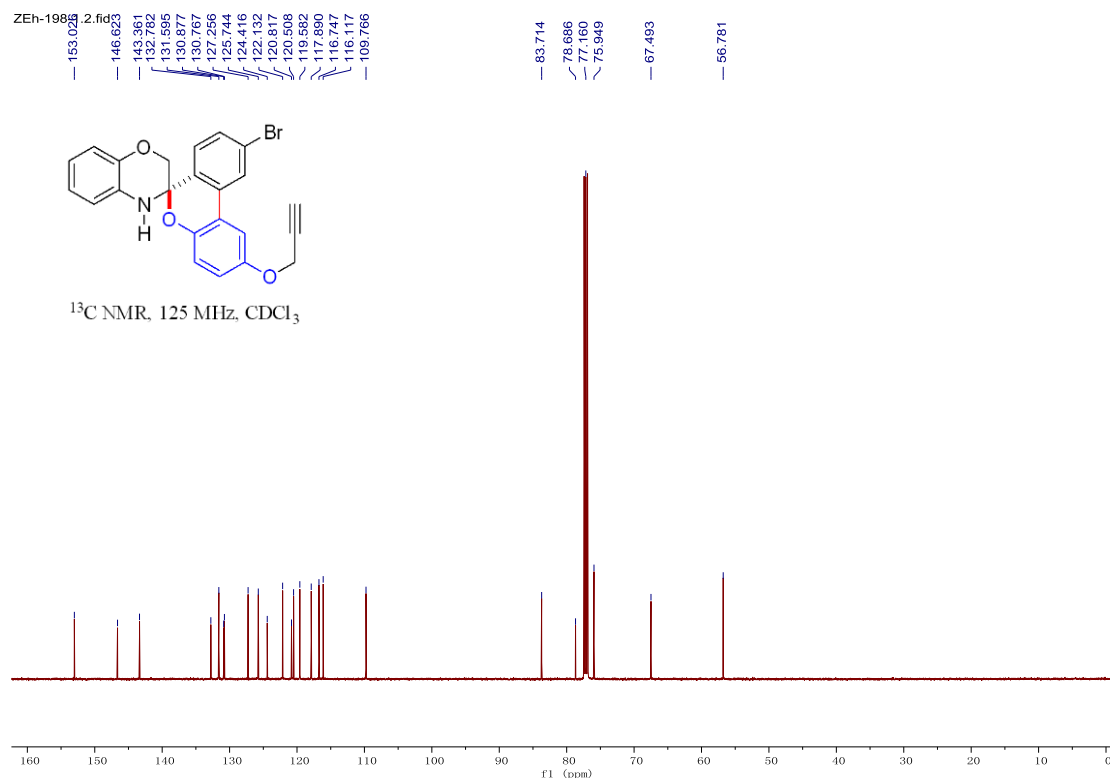
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.81 (d, $J = 2.0$ Hz, 1H), 7.46 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.36 (d, $J = 8.0$ Hz, 1H), 7.27 (d, $J = 3.0$ Hz, 1H), 6.97 (d, $J = 9.0$ Hz, 1H), 6.94-6.90 (m, 2H), 6.87 (td, $J = 7.5, 1.5$ Hz, 1H), 6.81 (td, $J = 7.5, 1.5$ Hz, 1H), 6.72 (dd, $J = 7.5, 1.5$ Hz, 1H), 4.83 (d, $J = 2.5$ Hz, 1H), 4.72 (d, $J = 2.5$ Hz, 2H), 4.34 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.79 (d, $J = 11.5$ Hz, 1H), 2.57 (t, $J = 2.5$ Hz, 1H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 153.0, 146.6, 143.4, 132.8, 131.6, 130.9, 130.8, 127.3, 125.7, 124.4, 122.1, 120.8, 120.5, 119.6, 117.9, 116.7, 116.1, 109.8, 83.7, 78.7, 75.9, 67.5, 56.8.

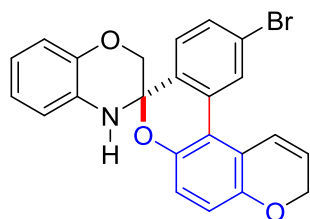
IR (KBr) $\nu(\text{cm}^{-1})$: 3366, 2920, 1613, 1499, 1453, 1199, 1082, 949, 842, 740 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{23}\text{H}_{16}\text{BrNO}_3+\text{H}]^+$ requires 434.03863, found 434.03833 $[\text{M}+\text{H}]^+$.





An oven dried reaction tube, fitted with a magnetic stirrer, was charged with $[(\text{IPr})\text{Au}(\text{CH}_3\text{CN})][\text{SbF}_6]$ (4.3 mg, 5 mol%), substrate (\pm) -**10** (43.3 mg, 0.1 mmol). DCE (1 mL) was added by syringe. The tube was sealed and the reaction was at 50°C for 5 h. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/THF, 150/1) to afford (\pm) -**13** (20.6 mg, 48%) and (\pm) -**14** (9.1 mg, 21%).



(±)-11'-bromo-2*H*,3'*H*,4*H*-spiro[benzo[*b*][1,4]oxazine-3,8'-benzo[*c*]pyrano[3,2-*f*]chromene]

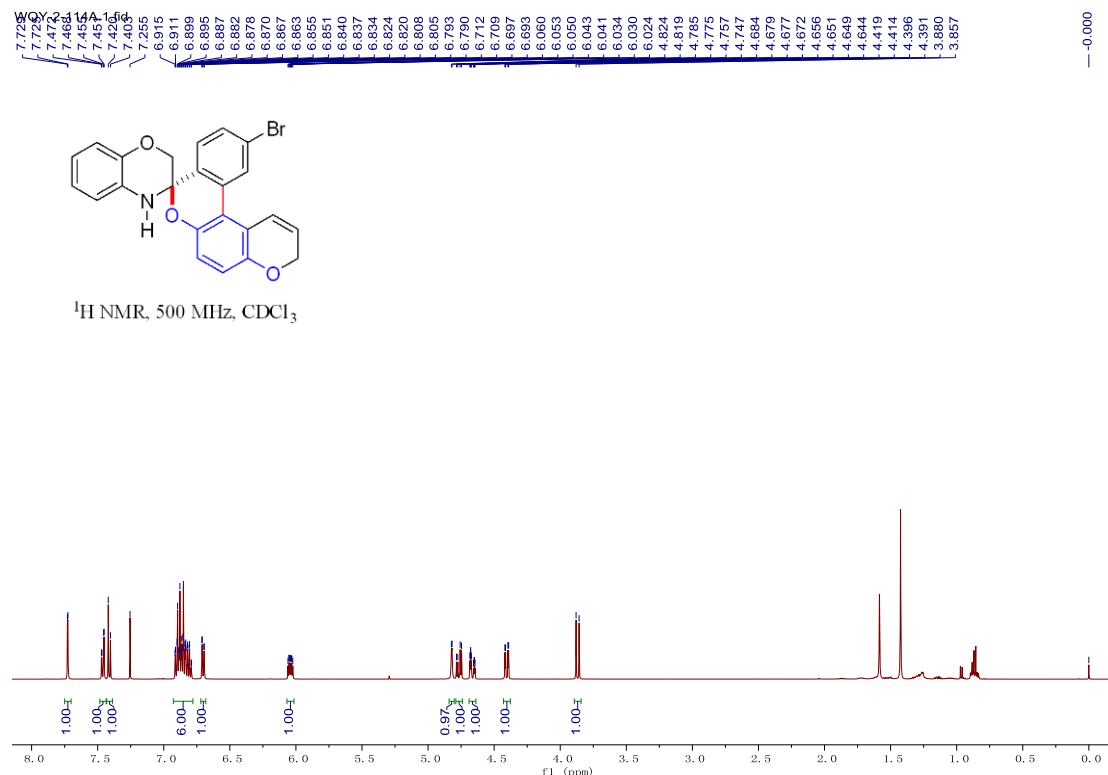
Compound **13**: A white solid. Column chromatography, eluent: Petroleum/THF = 150/1, $R_f = 0.1$, 48% yield. m.p. 123-125 °C.

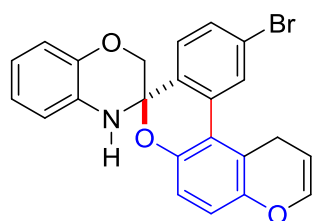
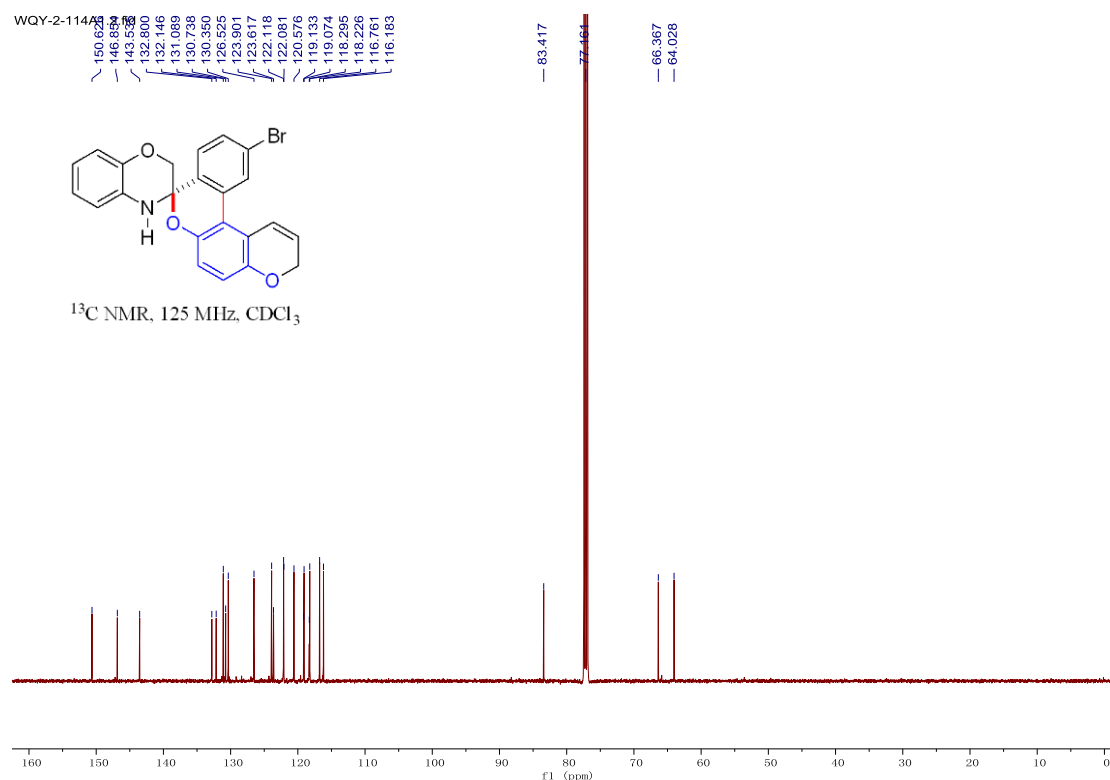
$^1\text{H NMR}$ (500 MHz, CDCl_3 , TMS) δ 7.73 (d, $J = 2.0$ Hz, 1H), 7.46 (dd, $J = 8.5, 2.0$ Hz, 1H), 7.41 (d, $J = 8.5$ Hz, 1H), 6.92-6.79 (m, 6H), 6.70 (dd, $J = 7.5, 1.5$ Hz, 1H), 6.06-6.02 (m, 1H), 4.82 (d, $J = 2.5$ Hz, 1H), 4.77 (dd, $J = 14.0, 5.0$ Hz, 1H), 4.68-4.64 (m, 1H), 4.40 (dd, $J = 11.5, 2.5$ Hz, 1H), 3.87 (d, $J = 11.5$ Hz, 1H).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3) δ 150.6, 146.9, 143.5, 132.8, 132.1, 131.1, 130.7, 130.4, 126.5, 123.9, 123.6, 122.12, 122.08, 120.6, 119.13, 119.07, 118.3, 118.2, 116.8, 116.2, 83.4, 66.4, 64.0.

IR (KBr) $\nu(\text{cm}^{-1})$: 2917, 1660, 1461, 1397, 1311, 1214, 1043, 997, 829, 736 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{23}\text{H}_{16}\text{BrNO}_3+\text{H}]^+$ requires 434.03863, found 434.03833 $[\text{M}+\text{H}]^+$.





(±)-11'-bromo-1'H,2H,4H-spiro[benzo[*b*][1,4]oxazine-3,8'-benzo[*c*]pyrano[3,2-*f*]chromene]

Compound **14**: A white solid. Column chromatography, eluent: Petroleum/THF = 150/1, R_f = 0.1, 21% yield. m.p. 120-122 °C.

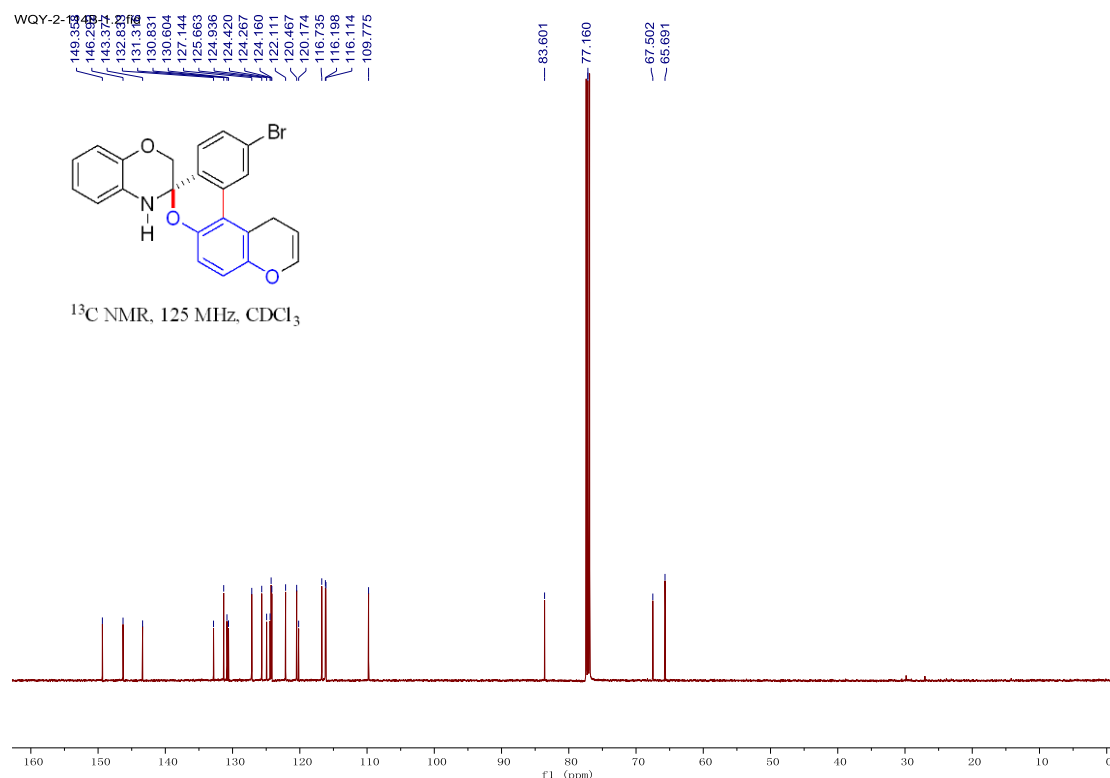
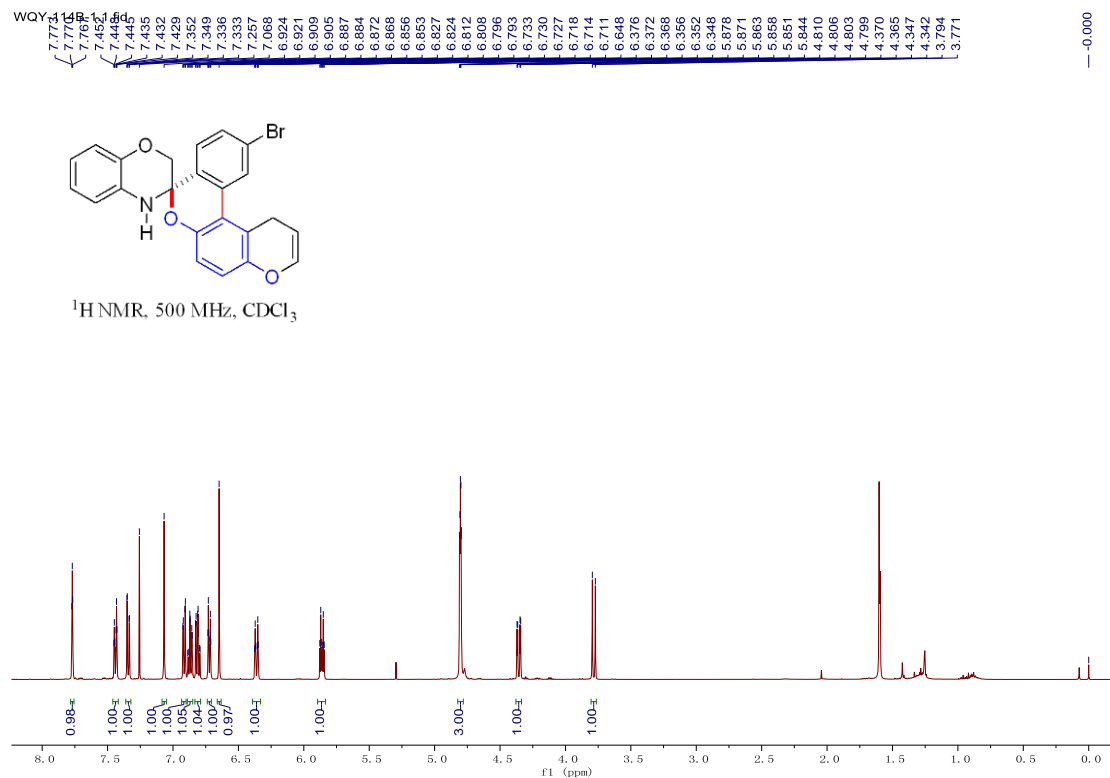
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.77 (t, J = 1.5 Hz, 1H), 7.44 (dt, J = 8.5, 1.5 Hz, 1H), 7.34 (dd, J = 8.0, 1.5 Hz, 1H), 7.07 (s, 1H), 6.91 (dd, J = 7.5, 1.5 Hz, 1H), 6.87 (td, J = 7.5, 1.5 Hz, 1H), 6.81 (td, J = 7.5, 1.5 Hz, 1H), 6.72 (dt, J = 7.5, 1.5 Hz, 1H), 6.65 (s, 1H), 6.36 (dt, J = 10.0, 2.0 Hz, 1H), 5.86 (dt, J = 10.0, 3.5 Hz, 1H), 4.81-4.80 (m, 3H), 4.36 (dd, J = 11.5, 2.5 Hz, 1H), 3.78 (d, J = 11.5 Hz, 1H).

¹³C NMR (125 MHz, CDCl₃) δ 149.4, 146.3, 143.4, 132.8, 131.3, 130.8, 130.6, 127.1, 125.7, 124.9, 124.4, 124.3, 124.2, 122.1, 120.5, 120.2, 116.7, 116.2, 116.1, 109.8, 83.6, 67.5, 65.7.

IR (KBr) ν (cm⁻¹): 2920, 1610, 1501, 1426, 1404, 1310, 1210, 1045, 940, 744 cm⁻¹.

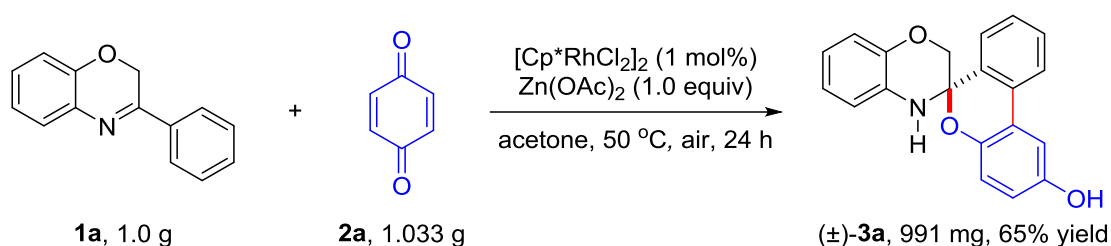
HRMS (ESI) calcd. for [C₂₃H₁₆BrNO₃+H]⁺ requires 434.03863, found 434.03671

[M+H]⁺.



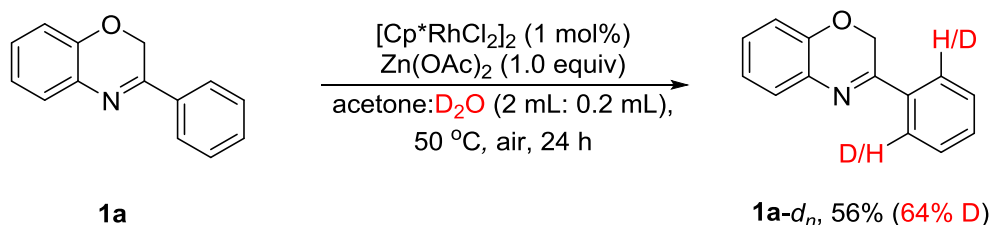
(F) Gram Scale Experiments

An oven dried reaction tube, fitted with a magnetic stirrer, was charged with $\text{Zn}(\text{OAc})_2$ (0.875 g, 4.8 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (29.6 mg, 1 mol %), substrate **1a** (1.0 g, 4.8 mmol), **2a** (1.033 g, 9.57 mmol). The tube was fitted with a rubber septum and acetone (47 mL) was added by syringe. Then the tube was sealed and the reaction was at 50 °C for 24 h under air. Afterwards, the mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 4/1) to afford (\pm)-**3a** (991 mg, 65% yield).

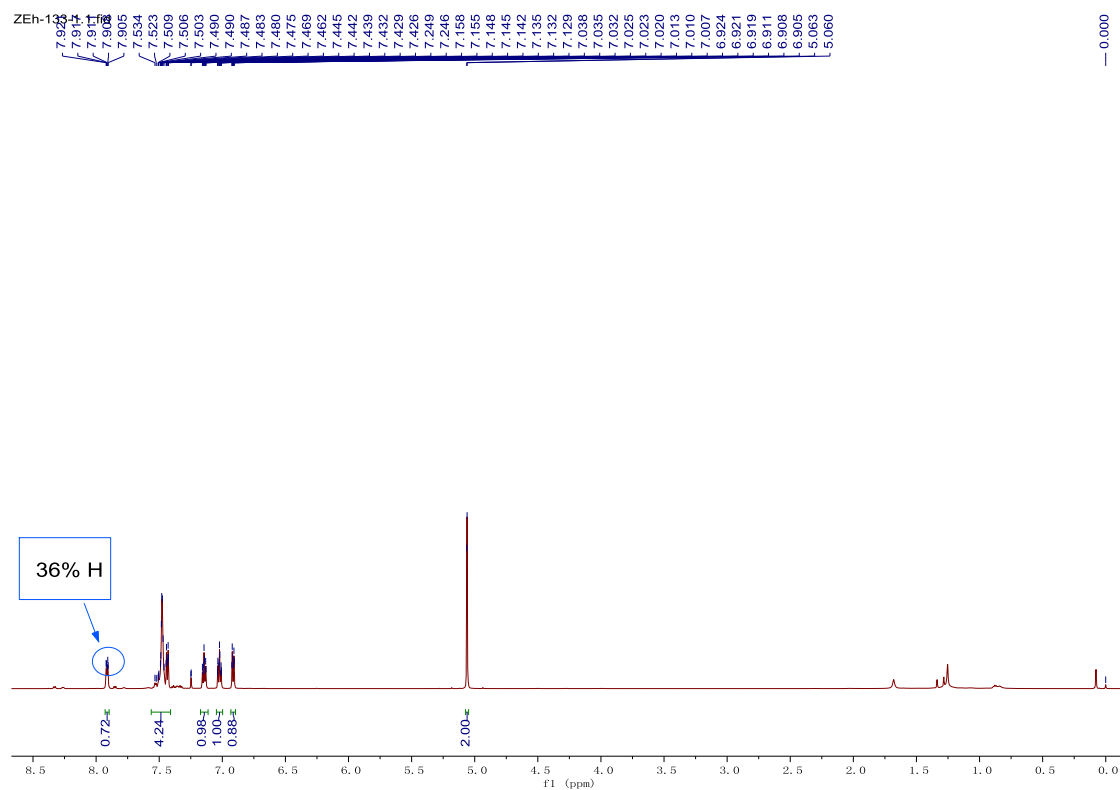


(G) Mechanistic Experiments

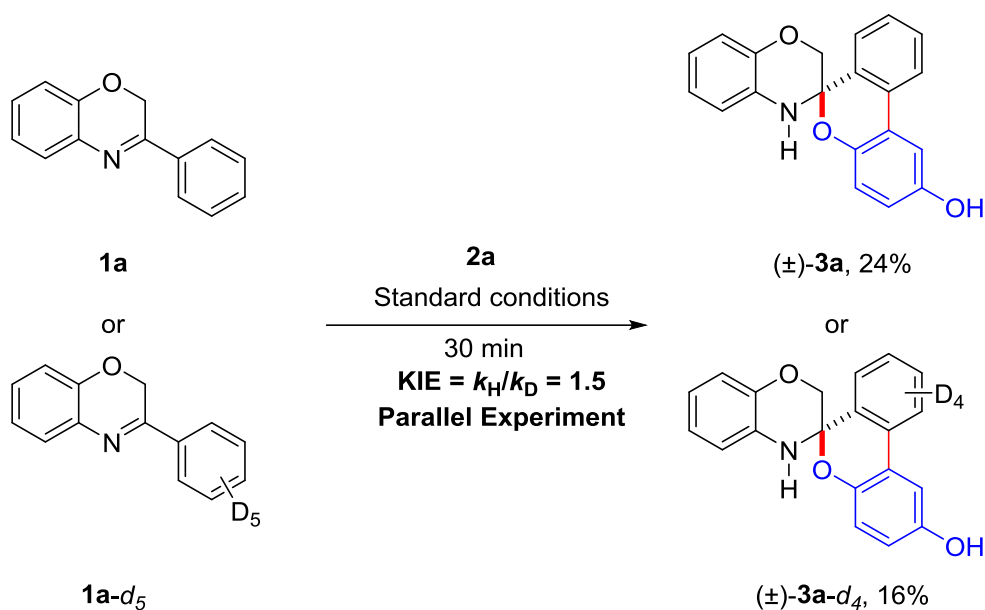
a) H/D exchange



An oven dried 15 mL schlenk tube was charged with **1a** (41.8 mg, 0.2 mmol), $\text{Zn}(\text{OAc})_2$ (36.6 mg, 0.2 mmol), and catalyst $[\text{Cp}^*\text{RhCl}_2]_2$ (1.2 mg, 1 mol %). The tube was added acetone (2.0 mL) and D_2O (0.2 mL) at 50 °C for 24 h under air. Afterwards, the reaction mixture was filtered through a short pad of celite, the solvent was removed under reduced pressure and the crude reaction mixture was directly purified through column chromatography on silica gel using petroleum ether/ ethylacetate (8:1) as eluent to recover the starting material (56%). The deuterium incorporation (64%) was determined by ^1H NMR spectroscopy.

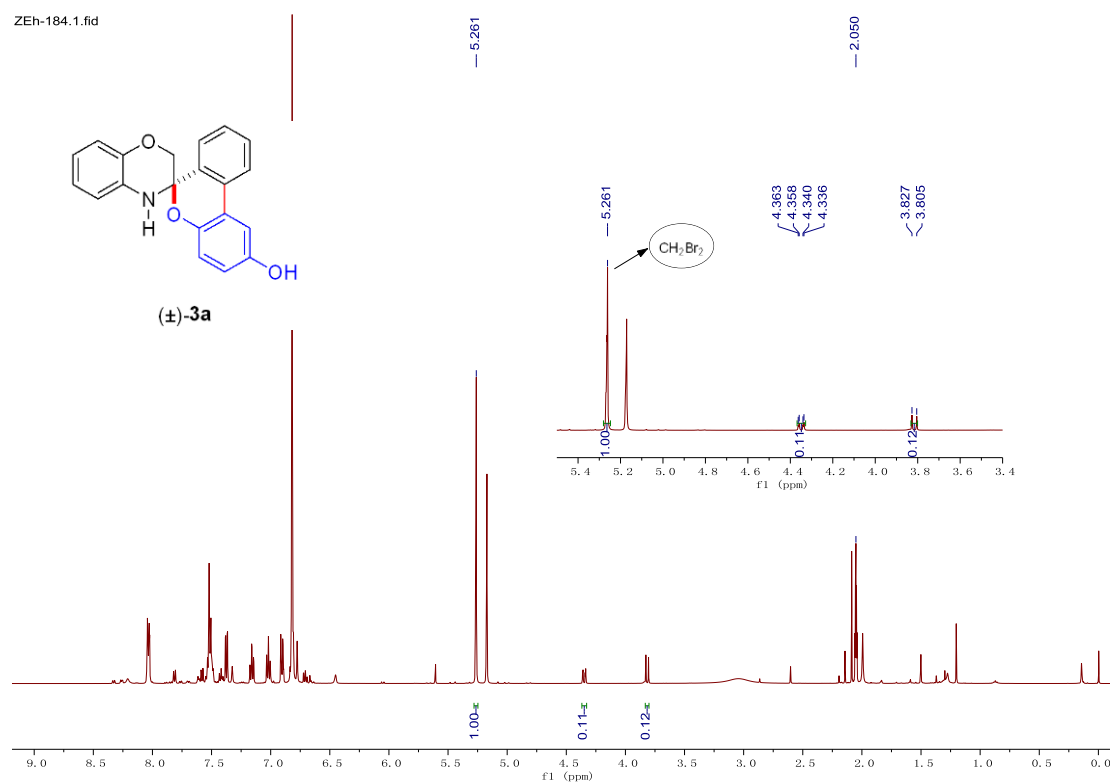


b) KIE Experiments

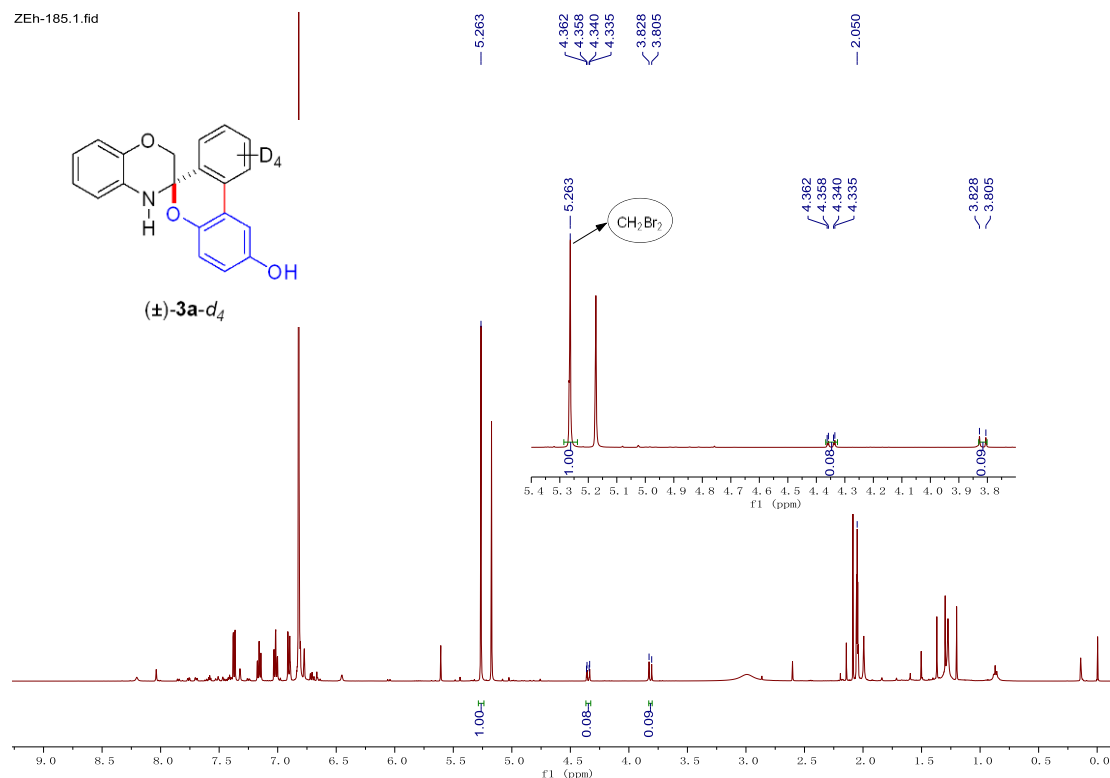


To an oven dried reaction flask were added imines **1a** (20.9 mg, 0.1 mmol), **2a** (21.7 mg, 0.2 mmol), $[Cp^*RhCl_2]_2$ (0.6 mg, 1 mol%), $Zn(OAc)_2$ (18.3 mg, 0.1 mmol) with a stir bar. Acetone (1.0 mL) was added and the mixture was stirred at 50 °C for 30 min under air. Afterwards, it was evaporated under reduced pressure and the in-situ yield (24%, 30 min) of product **3a** was determined by 1H NMR analysis by using CH_2Br_2 as

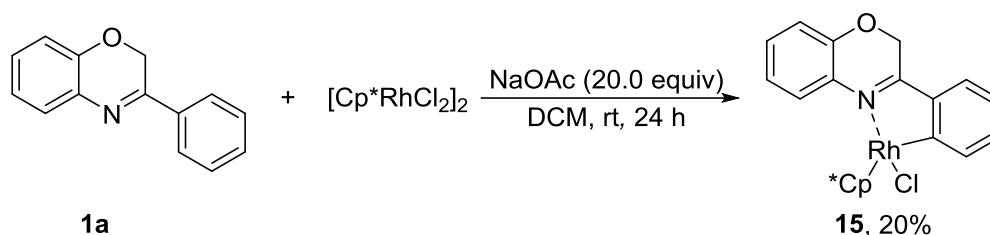
an internal standard.



To an oven dried reaction flask were added imines **1a-d₅** (21.4 mg, 0.1 mmol), **2a** (21.7 mg, 0.2 mmol), [Cp**Rh*Cl₂]₂ (0.6 mg, 1 mol%), Zn(OAc)₂ (18.3 mg, 0.1 mmol) with a stir bar. Acetone (1.0 mL) was added and the mixture was stirred at 50 °C for 30 min under air. Afterwards, it was evaporated under reduced pressure and the in-situ yield (16%, 30 min) of product **3a-d₄** was determined by ¹H NMR analysis by using CH₂Br₂ as an internal standard.



c) Preparation of the rhodacyclic complex **15**^[3]



Benzoxazines **1a** (21.9 mg, 0.105 mmol), $[\text{Cp}^*\text{RhCl}_2]_2$ (30.9 mg, 0.05 mmol) and NaOAc (82.03 mg, 1.0 mmol) were weighted into a Schlenk tube equipped with a stir bar. DCM (2.5 mL) was added, and the mixture was stirred at room temperature for 24 h under air. Afterwards, followed by filtration of any precipitate. The solvent was then removed and the brown product was purified by recrystallization using dichloromethane and diethyl ether to give product complex **15** (4.8 mg, 20% yield).

Compound **15**^[3]: a yellow solid. Column chromatography, eluent: Petroleum/EtOAc = 1/1, $R_f = 0.6$, 4.8 mg, 20% yield.

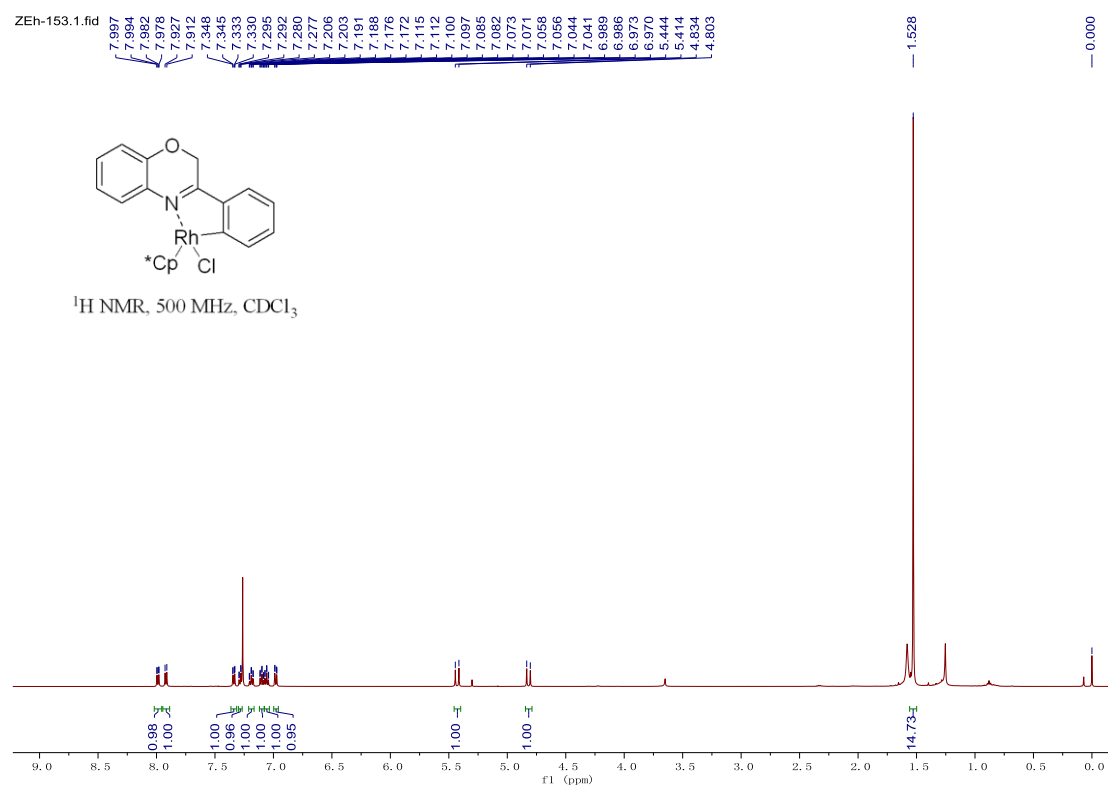
¹H NMR (500 MHz, CDCl₃, TMS) δ 7.99 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.92 (d, $J = 7.5$ Hz, 1H), 7.34 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.29 (dd, $J = 7.5, 1.5$ Hz, 1H), 7.19 (td, $J = 7.5, 1.5$

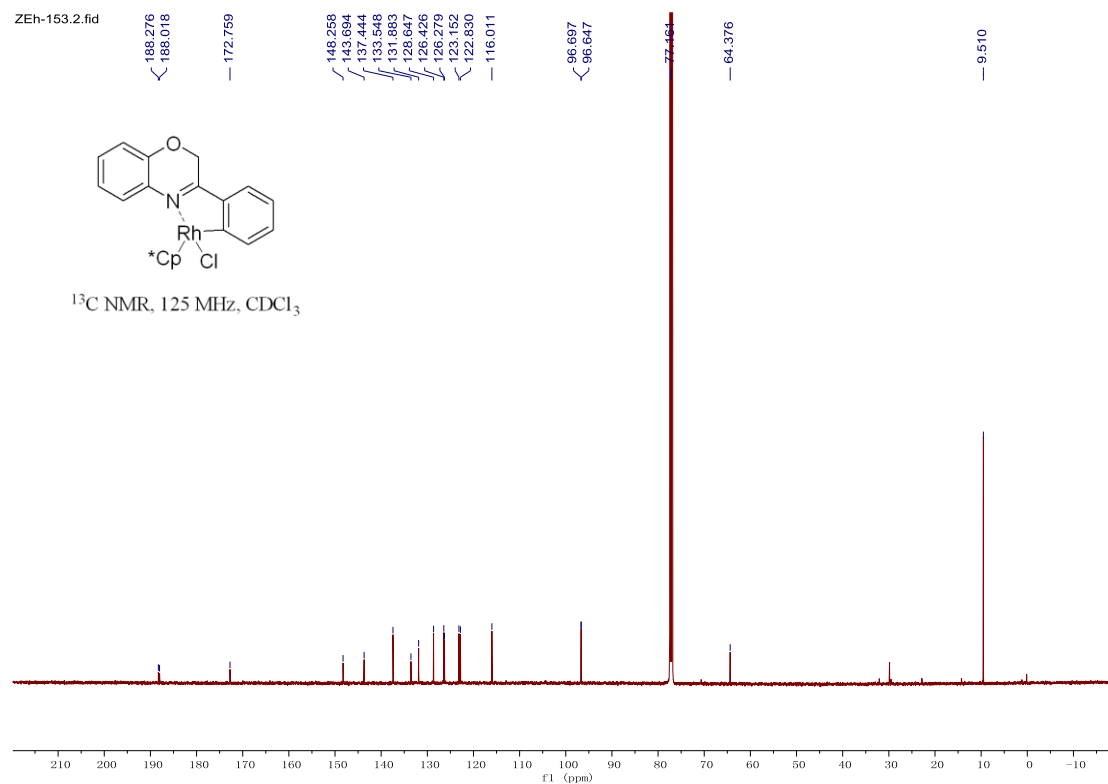
Hz, 1H), 7.10 (td, $J = 7.5, 1.5$ Hz, 1H), 7.06 (td, $J = 7.5, 1.5$ Hz, 1H), 6.98 (dd, $J = 8.0, 1.5$ Hz, 1H), 5.43 (d, $J = 15.0$ Hz, 1H), 4.82 (d, $J = 15.5$ Hz, 1H), 1.53 (s, 15H).

^{13}C NMR (125 MHz, CDCl_3) δ 188.1 (d, $J = 32.3$ Hz), 172.8, 148.3, 143.7, 137.4, 133.5, 131.9, 128.6, 126.4, 126.3, 123.2, 122.8, 116.0, 96.7 (d, $J = 6.3$ Hz), 64.4, 9.5.

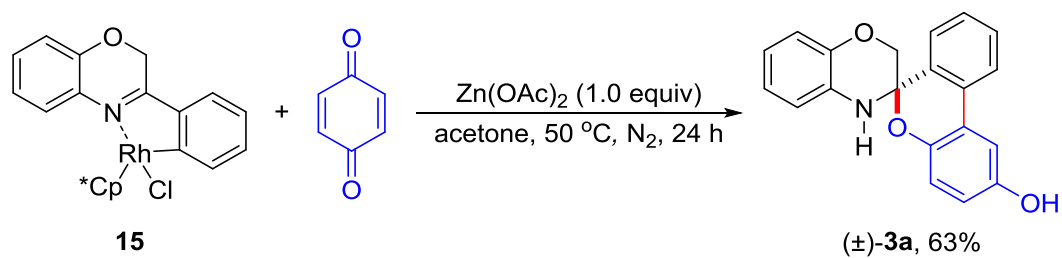
IR (KBr) $\nu(\text{cm}^{-1})$: 3366, 2920, 1613, 1499, 1453, 1199, 1082, 949, 842 740 cm^{-1} .

HRMS (ESI) calcd. for $[\text{C}_{24}\text{H}_{25}\text{NORhCl}+\text{Na}]^+$ requires 504.05719, found 504.05753 $[\text{M}+\text{Na}]^+$.



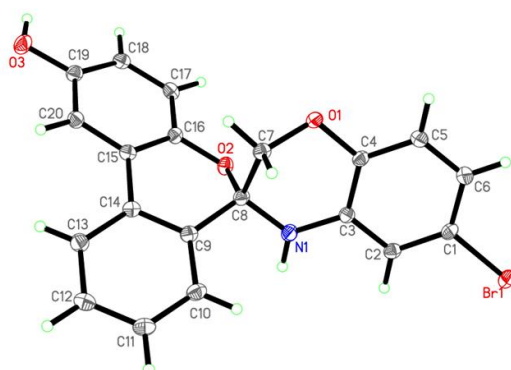
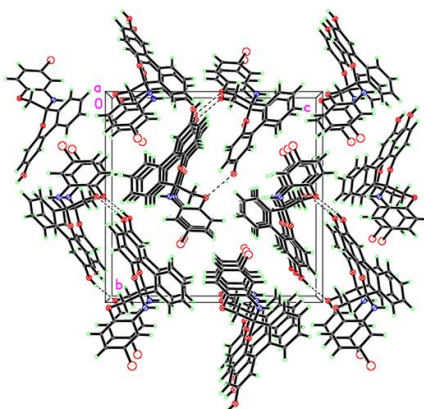


d) Stoichiometric reaction between complex **15** and **2a**



Complex **15** (7 mg, 0.015 mmol), **2a** (3 mg, 0.03 mmol), Zn(OAc)₂ (3 mg, 0.015 mmol) were weighted into a Schlenk tube equipped with a stir bar. Acetone (1.0 mL) was added, and the mixture was stirred at 50 °C for 24 h under N₂. The mixture was cooled to room temperature and concentrated in vacuum. The residue was purified by flash column chromatography (petroleum ether/EtOAc, 5/1) to afford **3a** (3.0 mg, 63%).

(H) X-ray Crystal Data of Compound **3i**.



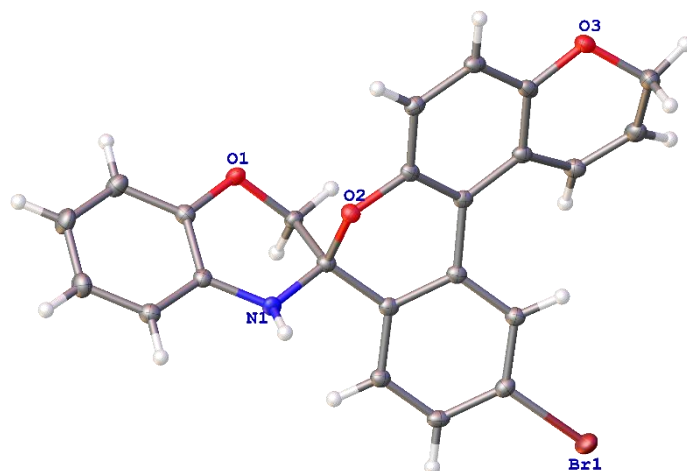
The crystal data of **3i** have been deposited in CCDC with number 2261847.

Table S8. Crystal data and structure refinement for 221220e_0m.

Identification code	221220e_0m	
Empirical formula	$C_{20}H_{14}BrNO_3$	
Formula weight	396.23	
Temperature	100.0 K	
Wavelength	1.34139 Å	
Crystal system	Orthorhombic	
Space group	P212121	
Unit cell dimensions	$a = 6.1673(15)$ Å	$a = 90^\circ$
	$b = 15.976(4)$ Å	$b = 90^\circ$

	$c = 16.479(4) \text{ \AA}$	$g = 90^\circ$
Volume	$1623.6(7) \text{ \AA}^3$	
Z	4	
Density (calculated)	1.621 Mg/m^3	
Absorption coefficient	2.385 mm^{-1}	
F(000)	800	
Crystal size	$0.12 \times 0.1 \times 0.1 \text{ mm}^3$	
Theta range for data collection	$3.352 \text{ to } 70.461^\circ$	
Index ranges	$-8 \leq h \leq 8, -22 \leq k \leq 21, -23 \leq l \leq 22$	
Reflections collected	24321	
Independent reflections	4582 [R(int) = 0.0675]	
Completeness to theta = 53.594°	98.5 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7534 and 0.5418	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	4582 / 0 / 227	
Goodness-of-fit on F^2	1.090	
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0403, wR2 = 0.0978$	
R indices (all data)	$R1 = 0.0416, wR2 = 0.0988$	
Absolute structure parameter	-0.013(11)	
Extinction coefficient	n/a	
Largest diff. peak and hole	$0.543 \text{ and } -0.879 \text{ e.\AA}^{-3}$	

(I) X-ray Crystal Data of Compound 13.



The crystal data of **13** have been deposited in CCDC with number 2283919.

Table S9. Crystal data and structure refinement for 124311.

Identification code	124311
Empirical formula	C ₂₃ H ₁₆ BrNO ₃
Formula weight	434.28
Temperature/K	99.97(14)
Crystal system	monoclinic
Space group	P2 ₁ /c
a/Å	14.11122(19)
b/Å	11.90270(16)
c/Å	26.9246(4)
α /°	90
β /°	105.0778(14)
γ /°	90
Volume/Å ³	4366.61(10)
Z	8
ρ_{calc} /cm ³	1.321
μ /mm ⁻¹	2.741
F(000)	1760.0
Crystal size/mm ³	0.14 × 0.12 × 0.08
Radiation	Cu K α (λ = 1.54184)

2 Θ range for data collection/ $^{\circ}$	6.488 to 133.202
Index ranges	$-16 \leq h \leq 15$, $-7 \leq k \leq 14$, $-31 \leq l \leq 32$
Reflections collected	22661
Independent reflections	7498 [$R_{\text{int}} = 0.0284$, $R_{\text{sigma}} = 0.0326$]
Data/restraints/parameters	7498/0/509
Goodness-of-fit on F^2	1.050
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0364$, $wR_2 = 0.0900$
Final R indexes [all data]	$R_1 = 0.0420$, $wR_2 = 0.0922$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.94/-0.82

(J) References.

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