

## Supporting Information

### **Palladium-catalyzed dearomative 1,4-arylmethylenation of naphthalenes**

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### Contents

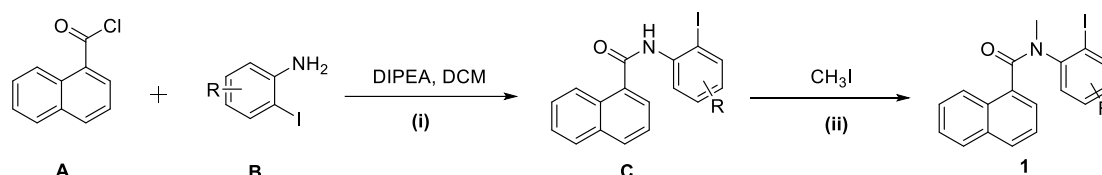
I. General information.....	2
II. Procedures for the synthesis of substrates.....	2
III. Optimization of the reaction conditions.....	5
IV. General procedure for product synthesis.....	6
V. Initial trial of asymmetric catalysis.....	6
VI. Characterization data.....	8
VII. References.....	22
VIII. NMR spectra.....	23
IX. Single crystal X-ray structure analysis.....	56

## I. General information

Unless stated otherwise, all reactions were carried out in flame-dried glassware under a dry argon atmosphere. All solvents were purified and dried according to standard methods prior to use. NMR data were obtained for  $^1\text{H}$  at 500 MHz or 400MHz, and for  $^{13}\text{C}$  at 125 MHz or 100 MHz, and for  $^{19}\text{F}$  at 470 MHz. Chemical shifts of  $^1\text{H}$  NMR are recorded in parts per million (ppm,  $\delta$ ) relative to tetramethylsilane ( $\delta = 0.00$  ppm) with the solvent resonance as the internal standard ( $\text{CDCl}_3$ :  $\delta = 7.26$  ppm). Data are reported as follows: chemical shift in ppm ( $\delta$ ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constant (Hz) and integration. Chemical shifts of  $^{13}\text{C}$  NMR are reported in ppm as the internal standard ( $\text{CDCl}_3$ :  $\delta = 77.0$  ppm). High resolution mass measurement were performed on Agilent QTOF 6520 mass spectrometer with electron spray ionization (ESI). Melting point (mp) were measured on a microscopic melting point apparatus. Flash column chromatography was carried out using commercially available 200-300 mesh silica gel under pressure unless stated otherwise. Gradient flash chromatography was conducted with PE/EA. Their volume/volume ratios are provided in the parenthesis.

## II. Procedures for the synthesis of substrates

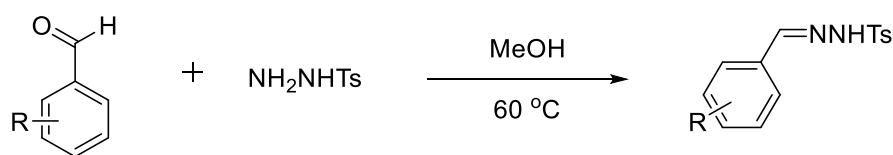
### Synthesis of substrate **1**<sup>1</sup>



(i) 1-Naphthoyl chloride **A** (1.0 equiv) was dissolved in DCM (0.2 M), then DIPEA (1.3 equiv) and substituted 2-iodoaniline **B** (1.2 equiv) were added at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and extracted with DCM (50 mL  $\times$  3). The combined organic layers were dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtrated. The solvent was removed / evaporated under reduced pressure, and crude product **C** was used in the following transformations without purification.

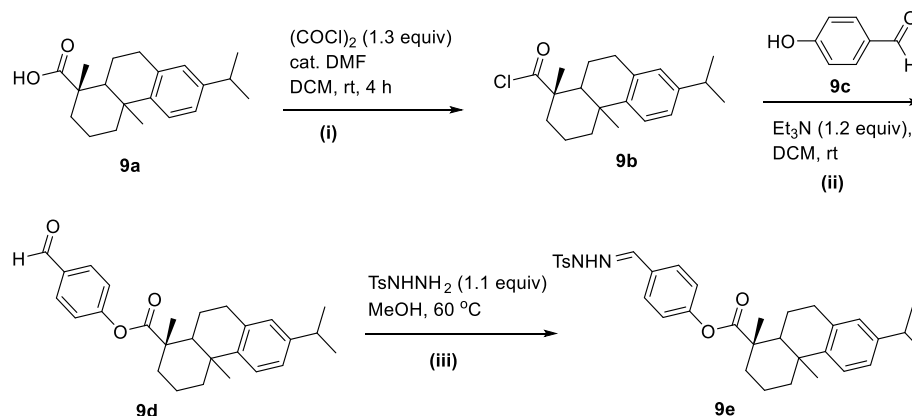
(ii) To a solution of crude product **C** in THF (0.2 M), potassium tert-butoxide (1.2 equiv) was added carefully at room temperature. After 20 min, iodomethane (1.2 equiv) was added dropwise. Then the reaction mixture was stirred at room temperature. After completion (monitored by TLC), the reaction mixture was quenched with saturated aqueous  $\text{NaHCO}_3$  and extracted with EA (50 mL  $\times$  3). The combined ethyl acetate extract was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and filtered. After the solvent was removed under reduced pressure, the crude product was purified by silica gel column chromatography (PE/EA = 20:1) to afford the desired product.

## Synthesis of *N*-tosylhydrazones



*N*-Tosylhydrazones was prepared according to literature procedure.<sup>2</sup> A solution of pure 4-methylbenzenesulfonylhydrazide (5 mmol) in methanol (5 mL) was stirred and heated to  $60\text{ }^\circ\text{C}$  until the 4-methylbenzenesulfonylhydrazide was completely dissolved. Then the aldehydes were slowly added to the mixture. After approximately 5-30 min the crude products was obtained as precipitates. The precipitates were washed with petroleum ether and dried in vacuo to afford the pure products. The reaction provides the *N*-tosylhydrazones in 75-99% yields.

## Synthesis of **9e**

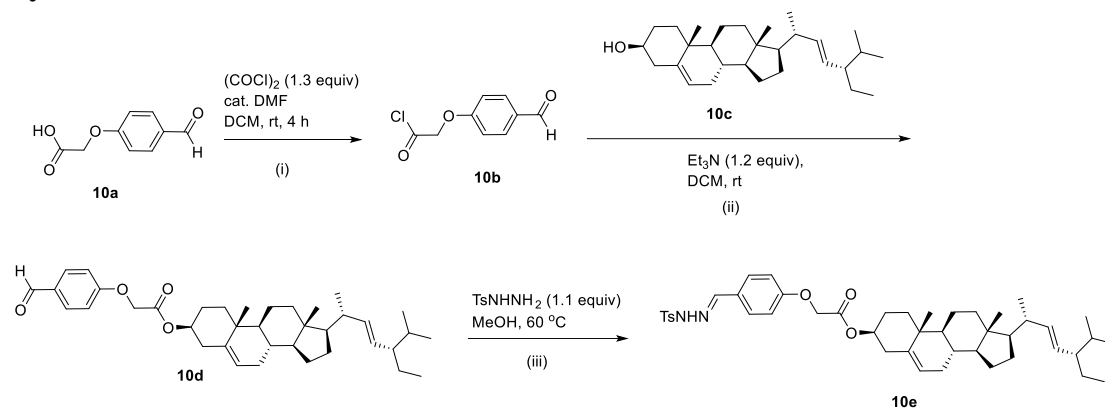


(i): A 100 mL round-bottom flask was charged with **9a** (3000 mg, 10 mmol), dry DCM (50 mL) and catalytic amount of DMF (3 drop). The reaction mixture was cooled to  $0\text{ }^\circ\text{C}$  and stirred for 5 minutes. Then,  $(\text{COCl})_2$  (1.12 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride in quantitative yield which was used in the next step without further purification.<sup>[3]</sup>

(ii): A 100 mL round-bottom flask was charged with **9c** (1220 mg, 10 mmol), raw material **9b** from the previous step dry DCM (50 mL). The reaction mixture was stirred at room temperature overnight. The resulting mixture was concentrated under reduced pressure and immediately used in the next step.<sup>[4]</sup>

(iii): Typical procedure. A suspension of pure 4-methylbenzenesulfonyl hydrazide (11 mmol) in methanol (40 mL) was stirred and heated to  $60\text{ }^\circ\text{C}$  until it was completely dissolved. Then **9d** was slowly added to the reaction mixture. After approximately 5-30 min the crude products was obtained by filtration. The precipitates are washed with petroleum ether and dried in vacuo to afford spectroscopically pure products. The reaction provides **9e** in about 75% yields.<sup>[2]</sup>

## Synthesis of 10e



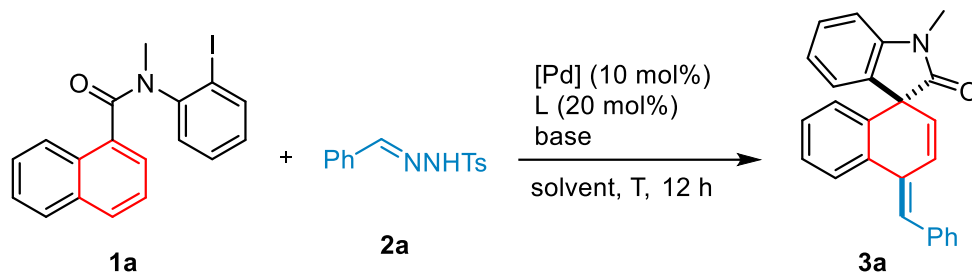
**(i):** A 100 mL round-bottom flask was charged with **10a** (3000 mg, 10 mmol), dry DCM (50 mL) and catalytic amount of DMF (3 drop). The reaction mixture was cooled to 0 °C and stirred for 5 minutes. Then,  $(\text{COCl})_2$  (1.12 mL, 1.3 equiv.) was added dropwise to the reaction mixture and stirred at room temperature for 4 h. The resulting mixture was concentrated under reduced pressure to afford acid chloride in quantitative yield which was used in the next step without further purification. <sup>[3]</sup>

**(ii):** A 100 mL round-bottom flask was charged with **10c** (1220 mg, 10 mmol), raw material **10b** from the previous step dry DCM (50 mL). The reaction mixture was stirred at room temperature overnight. The resulting mixture was concentrated under reduced pressure and immediately used in the next step. <sup>[4]</sup>

**(iii):** Typical procedure. A suspension of pure 4-methylbenzenesulfonyl hydrazide (11 mmol) in methanol (40 mL) was stirred and heated to 60 °C until it was completely dissolved. Then **10d** was slowly added to the reaction mixture. After approximately 5-30 min the crude products was obtained by filtration. The precipitates are washed with petroleum ether and dried in vacuo to afford spectroscopically pure products. The reaction provides **10e** in about 75% yields. <sup>[2]</sup>

### III. Optimization of the reaction conditions

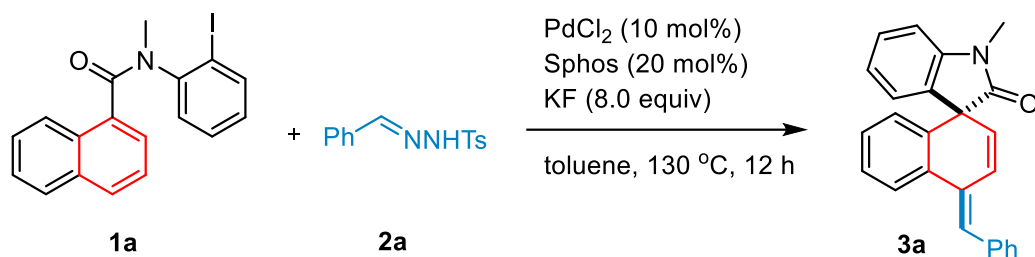
Table S1:



Entry	Catalyst	Ligand	Base	Solvent	Yield (%)
1	PdCl <sub>2</sub>	SPhos	KF	<i>N,N</i> -Dimethylacetamide	trace
2	PdCl <sub>2</sub>	SPhos	KF	<i>N,N</i> -Dimethylformamide	trace
3	PdCl <sub>2</sub>	SPhos	KF	1,2-Dimethoxyethane	trace
4	PdCl <sub>2</sub>	SPhos	KF	1,4-Dioxane	trace
5	PdCl <sub>2</sub>	SPhos	KF	Dichloroethane	trace
6	PdCl <sub>2</sub>	SPhos	KF	Tetrahydrofuran	trace
7	PdCl <sub>2</sub>	SPhos	KF	Toluene	45
8 <sup>b</sup>	PdCl <sub>2</sub>	SPhos	KF	Toluene	52
9 <sup>c</sup>	PdCl <sub>2</sub>	SPhos	KF	Toluene	58
10 <sup>d</sup>	PdCl <sub>2</sub>	SPhos	KF	Toluene	73
11	PdCl <sub>2</sub>	PPh <sub>3</sub>	KF	Toluene	NR
12	PdCl <sub>2</sub>	PCy <sub>3</sub>	KF	Toluene	NR
13	PdCl <sub>2</sub>	XPhos	KF	Toluene	NR
14	PdCl <sub>2</sub>	TFP	KF	Toluene	NR
15	[Pd(allyl)Cl] <sub>2</sub>	SPhos	KF	Toluene	18
16	Pd(acac) <sub>2</sub>	SPhos	KF	Toluene	25
17	Pd(TFA) <sub>2</sub>	SPhos	KF	Toluene	trace
18	Pd(OAc) <sub>2</sub>	SPhos	KF	Toluene	12
19	Pd(acac) <sub>2</sub>	SPhos	KF	<i>N,N</i> -Dimethylacetamide	trace
20	Pd(acac) <sub>2</sub>	SPhos	KF	1,2-Dimethoxyethane	trace
21	Pd(acac) <sub>2</sub>	SPhos	KF	1,4-Dioxane	trace
22	Pd(acac) <sub>2</sub>	SPhos	KF	Dichloroethane	trace
23	Pd(acac) <sub>2</sub>	PCy <sub>3</sub>	KF	Toluene	8
24	Pd(acac) <sub>2</sub>	TFP	KF	Toluene	NR
25	Pd(acac) <sub>2</sub>	XPhos	KF	Toluene	15
26	Pd(dba) <sub>2</sub>	SPhos	KF	Toluene	20
27	PdCl <sub>2</sub>	SPhos	Cs <sub>2</sub> CO <sub>3</sub>	Toluene	NR
28	PdCl <sub>2</sub>	SPhos	K <sub>2</sub> CO <sub>3</sub>	Toluene	NR
29	PdCl <sub>2</sub>	SPhos	K <sub>3</sub> PO <sub>4</sub>	Toluene	NR
30	PdCl <sub>2</sub>	SPhos	Ag <sub>3</sub> PO <sub>4</sub>	toluene	NR
31	PdCl <sub>2</sub>	SPhos	Na <sub>2</sub> CO <sub>3</sub>	Toluene	NR
32	PdCl <sub>2</sub>	SPhos	CsF	Toluene	NR
33	PdCl <sub>2</sub>	SPhos	Et <sub>3</sub> N	Toluene	NR

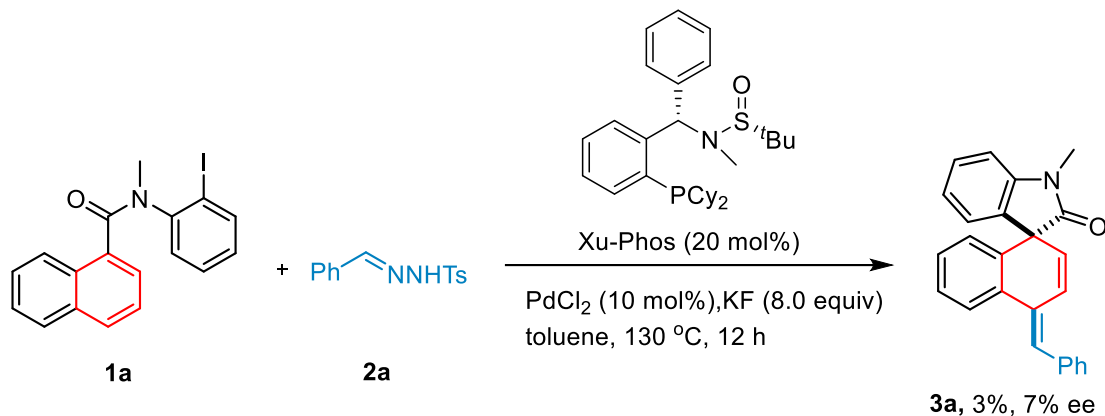
Reaction conditions: **1a** (0.1 mmol), **2a** (0.3 mmol), catalyst (0.01 mmol), ligand (0.02 mmol), base (0.25 mmol), 120 °C, 12 h, solvent (1.0 mL). <sup>b</sup>base (0.5 mmol). <sup>c</sup>base (0.8 mmol). <sup>d</sup>base (0.8 mmol), 130 °C.

#### IV. General procedure for product synthesis

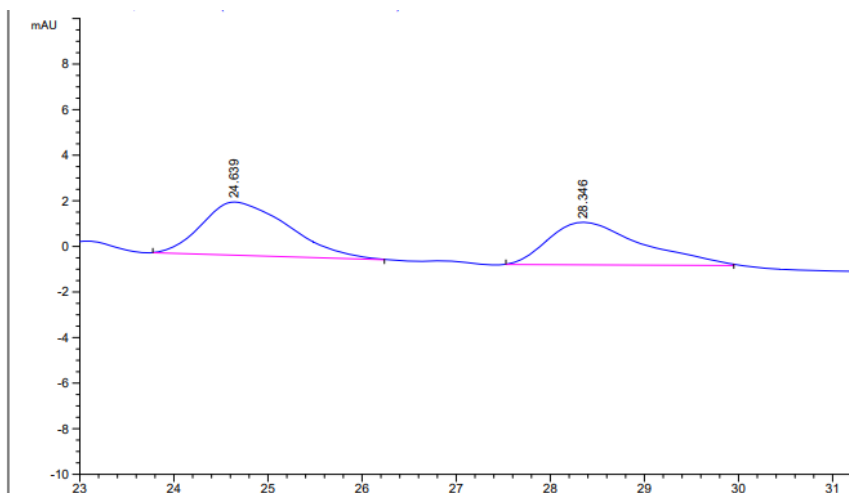


*N*-(2-iodophenyl)-*N*-methyl-1-naphthamide **1a** (38.7 mg, 0.1 mmol), (*Z*)-*N'*-benzylidene-4-methylbenzenesulfonylhydrazide **2a** (78.6 mg, 0.3 mmol), PdCl<sub>2</sub> (1.8 mg, 10 mol %), Sphos (8.2 mg, 20 mol %) and KF (46.4 mg, 8.0 equiv) were stirred in toluene (1.0 mL) under Ar atmosphere at 130 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **3a** as a white solid (25.5 mg, 73%).

#### V. Initial trial of asymmetric catalysis



*N*-(2-iodophenyl)-*N*-methyl-1-naphthamide **1a** (38.7 mg, 0.1 mmol), (*Z*)-*N'*-benzylidene-4-methylbenzenesulfonylhydrazide **2a** (78.6 mg, 0.3 mmol), PdCl<sub>2</sub> (1.8 mg, 10 mol %), Xu-Phos (9.9 mg, 20 mol %) and KF (46.4 mg, 8.0 equiv) were stirred in toluene (1.0 mL) under Ar atmosphere at 130 °C for 12 h. After completion, the reaction mixture was purified by flash chromatography eluting with ethyl acetate and petroleum ether (1:20) to give the product **3a** as a white solid.

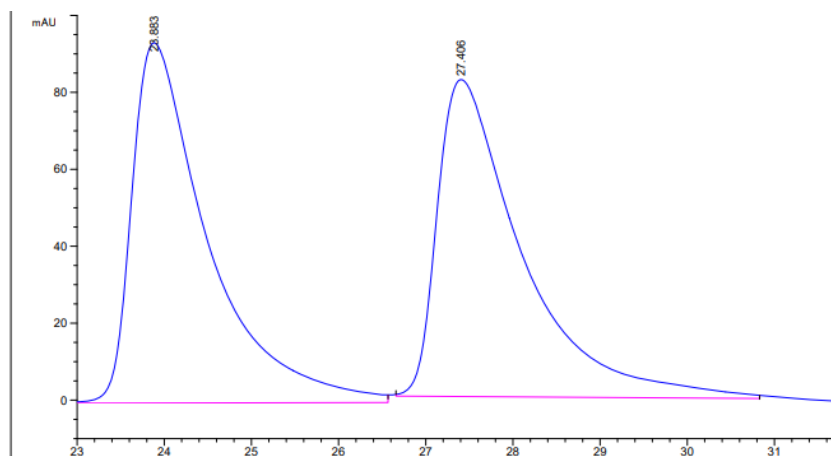


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 面积百分比报告  
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排序 : 信号  
 乘积因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	24.639	BB	0.7991	149.76675	2.33087	53.6657
2	28.346	BB	0.8251	129.30696	1.86458	46.3343
总量 :				279.07372	4.19545	



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 面积百分比报告  
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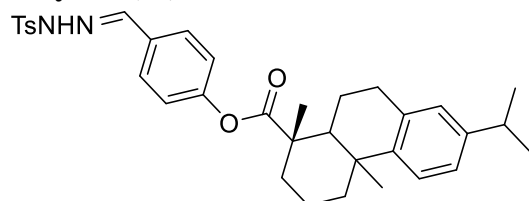
排序 : 信号  
 乘积因子 : 1.0000  
 稀释因子 : 1.0000  
 内标使用乘积因子和稀释因子

信号 1: VWD1 A, 波长=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 mAU *s	峰高 [mAU]	峰面积 %
1	23.883	BB	0.8803	5673.80664	93.62251	50.5013
2	27.406	MM	1.1251	5561.17480	82.38062	49.4987
总量 :				1.12350e4	176.00314	

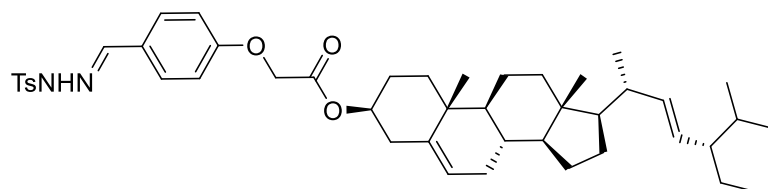
## VI. Characterization data

### 4-((Z)-(2-tosylhydrazono)methyl)phenyl (1S)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (9e)



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1); m.p. 129-130 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.25 – 7.99 (m, 1H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.63 (q, *J* = 2.8, 2.4 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.31 (d, *J* = 8.1 Hz, 2H), 7.20 (d, *J* = 8.2 Hz, 1H), 7.03 (d, *J* = 8.1 Hz, 1H), 6.96 (d, *J* = 8.7 Hz, 2H), 6.91 (s, 1H), 2.96 (dd, *J* = 11.1, 5.4 Hz, 2H), 2.83 (p, *J* = 6.9 Hz, 1H), 2.41 (s, 3H), 2.36 (d, *J* = 13.0 Hz, 1H), 2.03 – 1.92 (m, 2H), 1.89 – 1.74 (m, 3H), 1.72 – 1.52 (m, 2H), 1.39 (s, 3H), 1.26 (s, 3H), 1.23 (s, 3H), 1.22 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.3, 152.6, 146.6, 145.9, 144.3, 135.1, 134.5, 130.7, 129.7, 128.5, 127.9, 126.9, 124.2, 124.1, 121.8, 48.0, 44.8, 37.9, 36.93, 36.4, 33.4, 30.1, 25.1, 23.9, 21.9, 21.6, 18.5, 16.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>34</sub>H<sub>41</sub>N<sub>2</sub>O<sub>4</sub>S<sup>+</sup> 573.2782; found 573.2787.

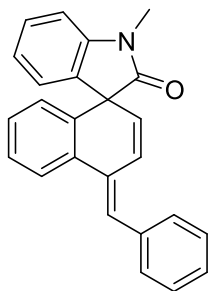
### (3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4-((Z)-(2-tosylhydrazono)methyl)phenoxy)acetate (10e)



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 3/1); m.p. 175-176 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.92 (s, 1H), 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (s, 1H), 7.51 (d, *J* = 8.8 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.8 Hz, 2H), 5.43 – 5.32 (m, 1H), 5.15 (dd, *J* = 15.1, 8.6 Hz, 1H), 5.01 (dd, *J* = 15.1, 8.6 Hz, 1H), 4.72 (ddd, *J* = 15.0, 9.4, 5.3 Hz, 1H), 4.61 (s, 2H), 2.40 (s, 3H), 2.34 (d, *J* = 8.2 Hz, 2H), 2.15 – 1.93 (m, 3H), 1.93 – 1.81 (m, 2H), 1.69 (ddd, *J* = 17.6, 9.0, 4.2 Hz, 2H), 1.64 – 1.46 (m, 7H), 1.46 – 1.35 (m, 2H), 1.33 – 1.24 (m, 1H), 1.24 – 1.10 (m, 4H), 1.01 (s, 3H), 0.87 – 0.82 (m, 4H), 0.79 (d, *J* = 6.9 Hz, 5H), 0.69 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 167.9, 159.6, 147.8, 144.2, 139.1, 138.3, 135.3, 129.7, 129.3, 129.0, 127.9, 126.8, 123.1, 114.8, 75.4, 65.4, 56.7, 55.9, 51.2, 50.0, 42.2, 40.5, 39.6, 37.9, 36.8, 36.5, 31.9, 31.8, 28.9, 27.6, 25.4, 24.3, 21.6, 21.2, 21.1, 21.0, 19.3, 19.0, 12.2, 12.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>63</sub>N<sub>2</sub>O<sub>5</sub>S<sup>+</sup> 743.4452; found 743.4468.

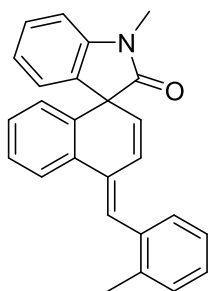
### (E)-4'-benzylidene-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3a)





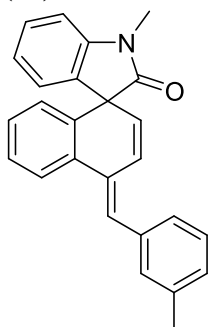
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 25.5 mg, yield: 73%. m.p. 249-250 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.99 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.55 – 7.45 (m, 2H), 7.44 – 7.35 (m, 3H), 7.37 – 7.27 (m, 3H), 7.20 (dd, *J* = 9.9, 0.9 Hz, 1H), 7.17 – 7.10 (m, 1H), 7.09 – 7.00 (m, 2H), 6.99 – 6.90 (m, 1H), 6.66 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.70 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.31 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.0, 143.5, 137.2, 134.7, 134.5, 133.2, 130.1, 129.6, 128.6, 128.2, 127.9, 127.7, 127.3, 127.1, 126.6, 125.3, 124.8, 123.4, 123.1, 108.3, 56.1, 26.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>20</sub>NO<sup>+</sup> 350.1539; found 350.1544.

**(E)-1-methyl-4'-(2-methylbenzylidene)-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3b)**



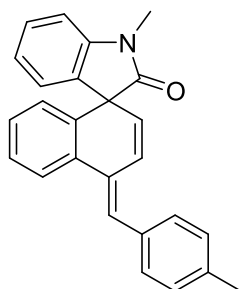
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 21.6 mg, yield: 60%. m.p. 356-357 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 7.5 Hz, 1H), 7.41 (d, *J* = 8.3 Hz, 3H), 7.39 – 7.18 (m, 5H), 7.20 – 7.05 (m, 3H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.68 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.72 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.35 (s, 3H), 2.42 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.5, 143.7, 137.3, 135.2, 134.8, 134.6, 133.6, 129.8, 129.3, 128.9, 128.2, 128.0, 127.6, 127.1, 127.0, 125.8, 125.1, 123.7, 123.4, 108.6, 56.5, 27.1, 21.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO<sup>+</sup> 364.1696; found 364.1689.

**(E)-1-methyl-4'-(3-methylbenzylidene)-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3c)**



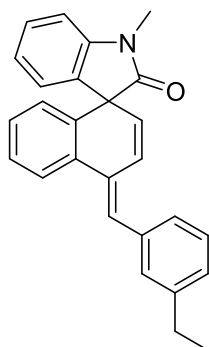
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 30.2 mg, yield: 83%. m.p. 285-286 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 – 7.92 (m, 1H), 7.39 (s, 1H), 7.36 – 7.27 (m, 5H), 7.20 (d, *J* = 10.1 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.08 – 7.01 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.65 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.68 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.31 (s, 2H), 2.39 (s, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.1, 143.5, 137.8, 137.1, 134.8, 134.4, 130.2, 128.5, 128.1, 127.9, 127.6, 127.3, 126.8, 126.7, 125.5, 124.8, 123.4, 123.1, 108.2, 56.1, 26.8, 21.4. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO<sup>+</sup> 364.1696; found 364.1690.

**(E)-1-methyl-4'-(4-methylbenzylidene)-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3d)**



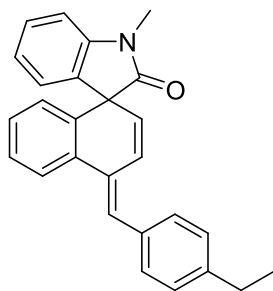
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 29.8 mg, yield: 82%. m.p. 233-234 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.91 (d, *J* = 8.0 Hz, 1H), 7.42 – 7.28 (m, 5H), 7.24 – 7.12 (m, 3H), 7.11 – 7.09 (m, 1H), 7.08 – 6.99 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.64 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.68 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.31 (s, 3H), 2.38 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.1, 143.5, 137.0, 134.9, 134.4, 134.3, 133.4, 129.5, 129.0, 128.5, 127.8, 127.6, 127.3, 126.8, 126.7, 125.4, 124.8, 123.4, 123.0, 108.2, 56.1, 26.8, 21.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO<sup>+</sup> 364.1696; found 364.1693.

**(E)-4'-(3-ethylbenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3e)**



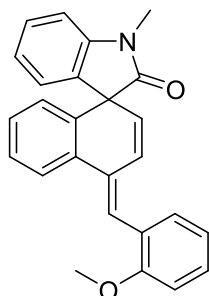
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 29.6 mg, yield: 62%. m.p. 294-295 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.99 (d, *J* = 7.6 Hz, 1H), 7.42 (d, *J* = 7.8 Hz, 3H), 7.38 – 7.29 (m, 2H), 7.27 – 7.21 (m, 3H), 7.21 – 7.01 (m, 3H), 6.96 (d, *J* = 7.8 Hz, 1H), 6.66 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.70 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.33 (s, 3H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.29 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.4, 143.6, 143.5, 135.1, 134.8, 134.5, 133.6, 133.0, 129.7, 128.8, 128.1, 127.9, 127.5, 127.0, 125.6, 125.1, 123.5, 123.3, 108.7, 56.4, 28.9, 27.1, 15.6. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>24</sub>NO<sup>+</sup> 378.1852; found 378.1855.

**(E)-4'-(4-ethylbenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3f)**



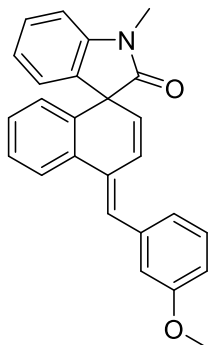
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 26.8 mg, yield: 71%. m.p. 302-302 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.92 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 3H), 7.35 – 7.28 (m, 2H), 7.25 – 7.21 (m, 3H), 7.14 – 7.10 (m, 1H), 7.07 – 7.00 (m, 2H), 6.95 (dd, *J* = 7.8, 0.9 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.68 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.31 (s, 3H), 2.68 (q, *J* = 7.7 Hz, 2H), 1.27 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.2, 143.2, 143.1, 134.9, 134.5, 129.6, 128.5, 127.7, 127.3, 126.7, 125.5, 124.8, 123.4, 123.1, 108.2, 56.0, 28.6, 26.7, 15.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>24</sub>NO<sup>+</sup> 378.1852; found 378.1855.

**(E)-4'-(2-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3g)**



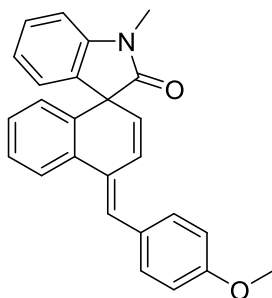
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 21.3 mg, yield: 56%. m.p. 249-250 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 8.5 Hz, 2H), 7.42 – 7.29 (m, 3H), 7.22 (d, *J* = 9.6 Hz, 1H), 7.18 – 7.01 (m, 3H), 6.96 (dd, *J* = 8.2, 3.7 Hz, 3H), 6.66 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.69 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.87 (s, 3H), 3.33 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 176.9, 158.5, 143.2, 134.6, 133.9, 133.1, 130.1, 129.3, 128.6, 128.2, 127.5, 127.3, 126.9, 126.6, 126.2, 124.9, 124.5, 123.0, 122.7, 113.2, 107.8, 55.9, 55.0, 26.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO<sub>2</sub><sup>+</sup> 380.1645; found 380.1641.

**(E)-4'-(3-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3h)**



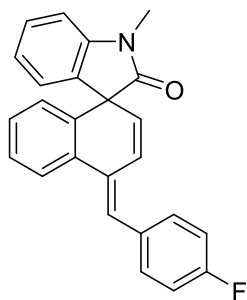
A White solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 29.6 mg, yield: 78%. m.p. 189-190 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.97 (d,  $J = 7.8$  Hz, 1H), 7.38 (s, 1H), 7.36 – 7.29 (m, 3H), 7.22 (dd,  $J = 9.9, 0.8$  Hz, 1H), 7.13 (td,  $J = 7.5, 1.2$  Hz, 1H), 7.07 (d,  $J = 7.9$  Hz, 1H), 7.05 – 6.98 (m, 3H), 6.95 (d,  $J = 8.0$  Hz, 1H), 6.91 – 6.82 (m, 1H), 6.65 (dd,  $J = 7.9, 1.4$  Hz, 1H), 5.69 (dd,  $J = 10.0, 1.7$  Hz, 1H), 3.84 (s, 3H), 3.31 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.0, 159.5, 143.4, 138.6, 134.7, 134.5, 133.1, 130.2, 129.2, 128.6, 128.0, 127.7, 127.3, 127.1, 126.6, 125.2, 124.8, 123.4, 123.1, 122.1, 114.9, 112.8, 108.2, 56.1, 55.3, 26.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{22}\text{NO}_2^+$  380.1645; found 380.1640.

**(E)-4'-(4-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3i)**



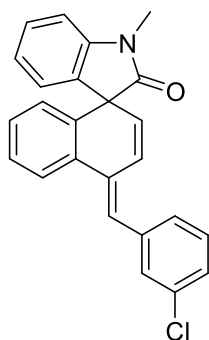
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 30.4 mg, yield: 80%. m.p. 298-299 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.96 (dd,  $J = 8.1, 1.2$  Hz, 1H), 7.47 – 7.38 (m, 2H), 7.36 (s, 1H), 7.35 – 7.28 (m, 2H), 7.20 (dd,  $J = 9.9, 0.8$  Hz, 1H), 7.16 – 7.09 (m, 1H), 7.09 – 6.99 (m, 2H), 6.98 – 6.87 (m, 3H), 6.64 (dd,  $J = 7.8, 1.3$  Hz, 1H), 5.68 (dd,  $J = 9.9, 1.7$  Hz, 1H), 3.85 (s, 3H), 3.31 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2, 158.8, 143.4, 134.9, 134.3, 133.5, 130.9, 129.7, 129.0, 128.5, 127.7, 127.2, 126.8, 126.5, 125.1, 124.8, 123.4, 122.9, 113.7, 108.2, 56.1, 55.3, 26.8. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{26}\text{H}_{22}\text{NO}_2^+$  380.1645; found 380.1654.

**(E)-4'-(4-fluorobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3j)**



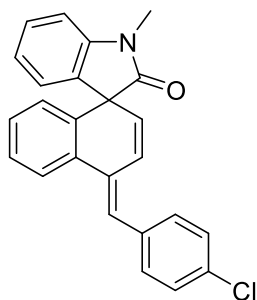
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 21.3 mg, yield: 58%. m.p. 235-236 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.05 – 7.80 (m, 1H), 7.49 – 7.40 (m, 2H), 7.38 – 7.28 (m, 3H), 7.14 (dd,  $J = 7.7, 1.1$  Hz, 1H), 7.12 – 7.10 (m, 1H), 7.10 – 7.06 (m, 2H), 7.06 – 7.01 (m, 2H), 6.95 (d,  $J = 7.9$  Hz, 1H), 6.64 (dd,  $J = 7.8, 1.3$  Hz, 1H), 5.71 (dd,  $J = 10.0, 1.7$  Hz, 1H), 3.31 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 161.9 (d,  $J = 245.9$  Hz), 143.6, 134.6, 134.5, 133.2 (d,  $J = 3.0$  Hz), 133.10, 131.2 (d,  $J = 7.8$  Hz), 130.2, 128.7, 128.1, 127.8, 127.4, 127.3, 126.4, 124.8, 124.2, 123.4, 123.1, 115.3 (d,  $J = 21.6$  Hz), 108.3, 56.2, 26.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{FNO}^+$  368.1445; found 368.1444.

**(E)-4'-(3-chlorobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3k)**



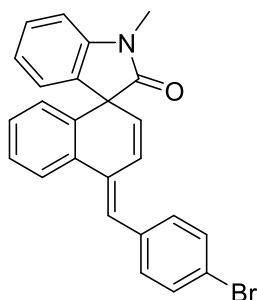
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 22.3 mg, yield: 58%. m.p. 258-259 °C.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (dd,  $J = 8.2, 1.3$  Hz, 1H), 7.46 (d,  $J = 7.2$  Hz, 2H), 7.43 – 7.37 (m, 3H), 7.36 – 7.28 (m, 2H), 7.20 (dd,  $J = 10.0, 0.9$  Hz, 1H), 7.14 (td,  $J = 7.5, 1.3$  Hz, 1H), 7.02 (dd,  $J = 7.8, 1.9$  Hz, 1H), 6.98 – 6.86 (m, 2H), 6.63 (dd,  $J = 7.8, 1.4$  Hz, 1H), 5.64 (dd,  $J = 10.0, 1.7$  Hz, 1H), 3.29 (s, 3H).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 144.6, 137.0, 134.4, 133.9, 133.1, 133.0, 129.8, 129.5, 128.3, 128.0, 127.9, 127.2, 127.1, 127.0, 126.4, 125.7, 123.2, 123.2, 109.0, 55.7, 26.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{ClNO}^+$  384.1150; found 384.1157.

**(E)-4'-(4-chlorobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3l)**



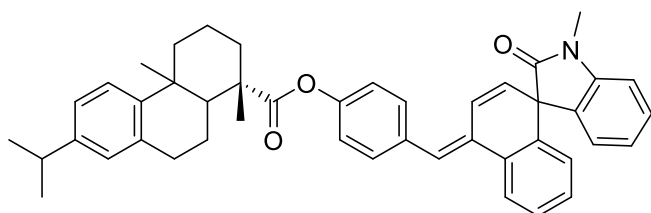
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 28.8 mg, yield: 75%. m.p. 400-401 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.40 (d, *J* = 8.6 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.20 – 7.09 (m, 2H), 7.10 – 7.02 (m, 2H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.72 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.30 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.8, 143.5, 135.7, 134.5, 133.0, 132.9, 130.8, 130.7, 128.7, 128.5, 128.1, 127.7, 127.3, 126.3, 124.8, 123.9, 123.4, 123.1, 108.3, 56.2, 26.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>ClNO<sup>+</sup> 384.1150; found 384.1141.

**(E)-4'-((4-bromobenzylidene)-1-methyl-4'-H-spiro[indoline-3,1'-naphthalen]-2-one (3m)**



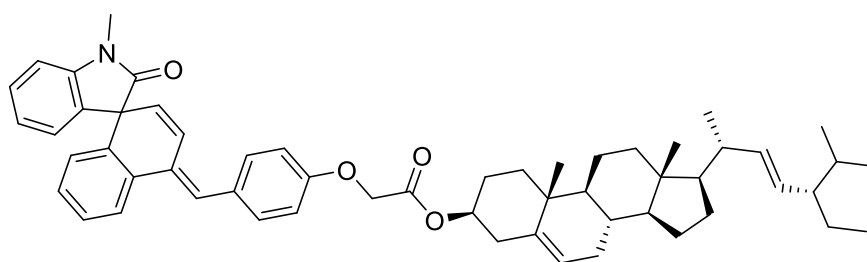
A White solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 33.8 mg, yield: 79%. m.p. 225-226 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.52 (d, *J* = 8.4 Hz, 2H), 7.41 – 7.29 (m, 5H), 7.21 – 7.08 (m, 2H), 7.09 – 6.99 (m, 2H), 6.95 (dt, *J* = 7.8, 0.8 Hz, 1H), 6.64 (dd, *J* = 8.1, 1.3 Hz, 1H), 5.73 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.30 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.8, 143.5, 136.1, 134.5, 133.0, 131.4, 131.1, 130.7, 128.7, 128.1, 127.8, 127.7, 127.3, 126.3, 124.8, 123.9, 123.4, 123.1, 121.0, 108.3, 56.2, 26.8. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>BrNO<sup>+</sup> 428.0645; found 428.0641.

**4-((E)-(1-methyl-2-oxo-4'-H-spiro[indoline-3,1'-naphthalen]-4'-ylidene)methyl)phenyl (1S)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (3n)**



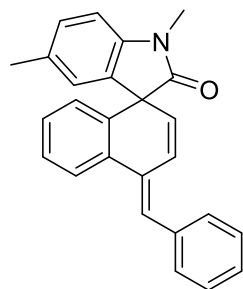
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 45.3 mg, yield: 70%. m.p. 340-341 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.02 – 7.90 (m, 1H), 7.82 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.51 (m, 1H), 7.47 (d, *J* = 8.5 Hz, 1H), 7.42 – 7.28 (m, 2H), 7.24 – 7.15 (m, 2H), 7.15 – 7.10 (m, 1H), 7.05 (d, *J* = 8.4 Hz, 2H), 7.04 – 7.01 (m, 2H), 6.98 (dd, *J* = 8.6, 3.9 Hz, 1H), 6.97 – 6.94 (m, 1H), 6.94 – 6.88 (m, 1H), 6.65 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.70 (dd, *J* = 10.0, 1.7 Hz, 1H), 3.31 (s, 3H), 3.11 – 2.88 (m, 2H), 2.90 – 2.68 (m, 2H), 2.65 – 2.37 (m, 2H), 2.35 (s, 2H), 1.97 (dd, *J* = 20.3, 12.2 Hz, 3H), 1.39 (d, *J* = 15.7 Hz, 3H), 1.27 (d, *J* = 8.1 Hz, 3H), 1.24 (s, 3H), 1.22 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.2, 176.9, 150.2, 146.7, 145.8, 143.5, 134.6, 134.5, 133.1, 131.8, 130.5, 130.3, 129.5, 129.0, 128.6, 128.2, 128.0, 127.7, 127.3, 126.9, 126.5, 124.8, 124.3, 124.2, 124.0, 123.4, 123.0, 121.9, 121.7, 121.3, 108.2, 56.1, 47.9, 44.8, 37.9, 37.0, 36.4, 33.4, 26.3, 25.1, 23.9, 21.8, 18.5, 16.6, 11.4. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>45</sub>H<sub>46</sub>NO<sub>3</sub><sup>+</sup> 648.3472; found 648.3491.

**(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4-((E)-(1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalen]-4'-ylidene)methyl)phenoxy)acetate (3o)**



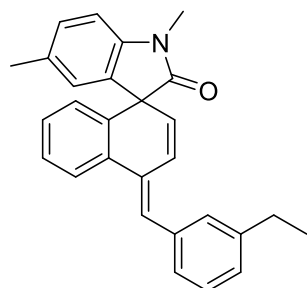
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), 40.9 mg, yield: 50%. m.p. 337-338 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.82 (d, *J* = 8.8 Hz, 1H), 7.45 (dd, *J* = 8.7, 4.1 Hz, 1H), 7.26 (d, *J* = 9.3 Hz, 1H), 7.15 (t, *J* = 7.3 Hz, 1H), 7.06 (d, *J* = 8.1 Hz, 2H), 7.04 – 6.93 (m, 2H), 6.96 – 6.72 (m, 2H), 6.46 (dd, *J* = 7.9, 1.4 Hz, 1H), 6.37 (dd, *J* = 10.2, 3.4 Hz, 1H), 5.96 – 5.80 (m, 1H), 5.49 – 5.36 (m, 2H), 5.18 (dd, *J* = 15.2, 8.6 Hz, 1H), 5.13 – 4.99 (m, 1H), 4.78 (d, *J* = 6.7 Hz, 1H), 4.70 – 4.64 (m, 1H), 4.62 (s, 2H), 3.28 (s, 3H), 2.38 (d, *J* = 9.2 Hz, 5H), 2.03 (ddd, *J* = 23.7, 16.4, 9.8 Hz, 3H), 1.91 (d, *J* = 12.1 Hz, 3H), 1.80 – 1.60 (m, 3H), 1.56 – 1.39 (m, 5H), 1.33 – 1.26 (m, 1H), 1.23 – 1.15 (m, 5H), 1.05 (s, 3H), 0.88 (d, *J* = 6.3 Hz, 3H), 0.87 – 0.78 (m, 6H), 0.73 (s, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 178.4, 168.4, 156.3, 139.2, 138.2, 136.4, 136.2, 135.5, 134.0, 130.9, 130.1, 129.6, 129.2, 128.6, 128.1, 126.9, 126.8, 125.0, 124.9, 123.1, 122.9, 114.9, 114.4, 107.8, 65.6, 56.7, 55.9, 54.6, 51.2, 49.9, 42.1, 40.4, 39.5, 37.9, 36.8, 36.5, 31.8, 28.9, 27.6, 26.6, 25.4, 24.3, 21.2, 21.0, 20.9, 19.2, 18.9, 12.2, 12.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>56</sub>H<sub>68</sub>NO<sub>4</sub><sup>+</sup> 818.5143; found 818.5145.

**(E)-4'-benzylidene-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4a)**



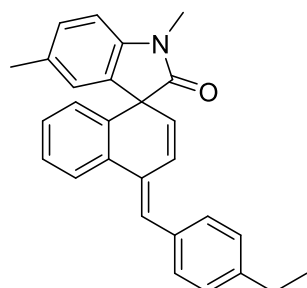
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 26.6 mg, yield: 73%. m.p. 244-245 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (d, *J* = 8.1 Hz, 1H), 7.47 (d, *J* = 7.7 Hz, 2H), 7.43 – 7.36 (m, 3H), 7.36 – 7.28 (m, 2H), 7.23 – 7.18 (m, 1H), 7.17 – 7.08 (m, 2H), 6.99 – 6.80 (m, 2H), 6.66 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.68 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.29 (s, 3H), 2.26 (s, 3H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) δ 177.0, 137.2, 134.8, 133.0, 130.1, 129.6, 128.8, 128.2, 128.0, 127.6, 127.4, 127.2, 127.1, 126.5, 125.5, 125.2, 123.0, 108.0, 56.2, 26.8, 21.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>22</sub>NO<sup>+</sup> 364.1696; found 364.1701.

**(E)-4'-(3-ethylbenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4b)**



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 23.5 mg, yield: 60%. m.p. 225-226 °C. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.01 (d, *J* = 8.1 Hz, 1H), 7.44 (d, *J* = 8.1 Hz, 3H), 7.42 – 7.31 (m, 1H), 7.26 (dd, *J* = 9.0, 5.2 Hz, 3H), 7.22 – 7.02 (m, 2H), 7.04 – 6.79 (m, 2H), 6.70 (dd, *J* = 7.8, 1.4 Hz, 1H), 5.71 (dd, *J* = 9.9, 1.6 Hz, 1H), 3.33 (s, 3H), 2.72 (q, *J* = 7.7 Hz, 2H), 2.30 (s, 3H), 1.31 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 177.5, 143.7, 141.4, 135.3, 134.9, 133.7, 133.4, 129.9, 129.2, 128.2, 127.8, 127.2, 127.0, 125.8, 123.4, 108.4, 56.5, 29.0, 27.1, 21.4, 15.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>26</sub>NO<sup>+</sup> 392.2009; found 392.2002.

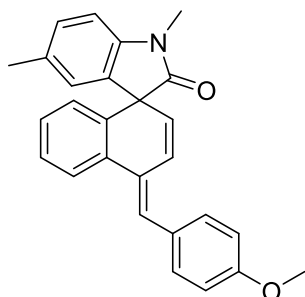
**(E)-4'-(4-ethylbenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4c)**





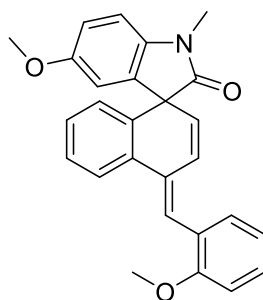
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 32.1 mg, yield: 82%. m.p. 284-285 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.97 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.46 – 7.37 (m, 3H), 7.31 (ddd, *J* = 8.2, 7.2, 1.4 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.18 – 7.04 (m, 2H), 6.91 – 6.76 (m, 2H), 6.65 (dd, *J* = 7.8, 1.3 Hz, 1H), 5.67 (dd, *J* = 10.0, 1.6 Hz, 1H), 3.29 (s, 3H), 2.68 (q, *J* = 7.6 Hz, 2H), 2.26 (s, 4H), 1.27 (t, *J* = 7.6 Hz, 3H). <sup>13</sup>C NMR (125MHz, CDCl<sub>3</sub>) δ 177.1, 143.2, 141.0, 134.7, 133.2, 133.1, 129.6, 128.8, 127.9, 127.5, 126.9, 126.6, 125.4 123.0, 107.8, 56.0, 28.6, 26.7, 20.9, 15.3. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>28</sub>H<sub>26</sub>NO<sup>+</sup> 392.2009; found 392.2012.

**(E)-4'-(4-methoxybenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4d)**



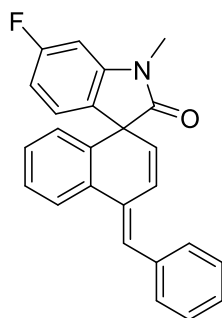
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 27.9 mg, yield: 71%. m.p. 271-272 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.96 (d, *J* = 8.2 Hz, 1H), 7.42 (d, *J* = 8.5 Hz, 2H), 7.36 (s, 1H), 7.31 (d, *J* = 7.0 Hz, 1H), 7.23 – 7.15 (m, 1H), 7.16 – 7.05 (m, 2H), 6.94 (d, *J* = 8.8 Hz, 2H), 6.83 (d, *J* = 7.9 Hz, 2H), 6.71 – 6.51 (m, 1H), 5.66 (dd, *J* = 9.9, 1.7 Hz, 1H), 3.85 (s, 3H), 3.29 (s, 3H), 2.26 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.5, 159.2, 141.4, 135.3, 134.8, 133.8, 133.4, 131.3, 130.1, 129.3, 129.2, 128.1, 128.0, 127.8, 127.1, 127.0, 125.9, 125.4, 123.3, 114.1, 108.3, 56.6, 55.7, 27.2, 21.4. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>24</sub>NO<sub>2</sub><sup>+</sup> 394.1802; found 394.1797.

**(E)-5-methoxy-4'-(2-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4e)**



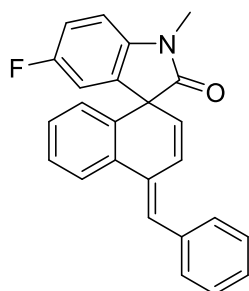
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 28.7 mg, yield: 70%. m.p. 233-234 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.04 (d, *J* = 8.1 Hz, 1H), 7.52 (s, 1H), 7.47 (dd, *J* = 7.5, 1.8 Hz, 1H), 7.38 – 7.27 (m, 2H), 7.20 – 7.05 (m, 3H), 7.04 – 6.89 (m, 3H), 6.68 – 6.53 (m, 2H), 5.65 (dd, *J* = 9.9, 1.8 Hz, 1H), 3.89 (s, 3H), 3.70 (s, 3H), 3.29 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.9, 157.7, 156.5, 136.8, 136.1, 134.2, 133.3, 131.2, 129.4, 129.0, 128.8, 128.7, 127.8, 127.6, 127.3, 127.0, 126.3, 126.0, 123.3, 121.5, 120.1, 113.3, 111.5, 110.3, 108.6, 56.5, 55.7, 55.4, 26.9. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>27</sub>H<sub>24</sub>NO<sub>3</sub><sup>+</sup> 410.1751; found 410.1744.

**(E)-4'-benzylidene-6-fluoro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(4f)**



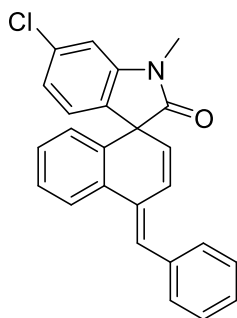
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 29.4 mg, yield: 80%. m.p. 279-280 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.98 (dt, *J* = 8.1, 0.8 Hz, 1H), 7.50 – 7.45 (m, 2H), 7.43 – 7.35 (m, 3H), 7.36 – 7.27 (m, 2H), 7.20 (dd, *J* = 10.0, 0.9 Hz, 1H), 7.16 – 7.13 (m, 1H), 6.97 (dd, *J* = 8.1, 5.3 Hz, 1H), 6.76 – 6.67 (m, 2H), 6.63 (dd, *J* = 7.9, 1.0 Hz, 1H), 5.66 (dd, *J* = 9.9, 1.6 Hz, 1H), 3.29 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 177.3, 163.3 (d, *J* = 244.3 Hz), 145.0 (d, *J* = 11.4 Hz), 137.1, 134.2, 133.3, 130.0 (d, *J* = 3.1 Hz), 129.9, 129.6, 128.3, 128.0, 127.8, 127.2, 126.9, 126.8, 126.0, 125.9, 125.7, 123.2, 109.5 (d, *J* = 22.3 Hz), 97.1 (d, *J* = 27.9 Hz), 55.7, 27.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>FNO<sup>+</sup> 368.1445; found 368.1451.

**(E)-4'-benzylidene-5-fluoro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(4g)**



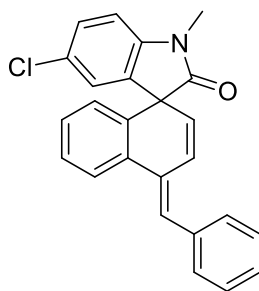
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 20.9 mg, yield: 57%. m.p. 217-218 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 – 7.85 (m, 1H), 7.47 (d, *J* = 7.6 Hz, 2H), 7.43 (d, *J* = 8.0 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.37 – 7.29 (m, 1H), 7.24 – 7.19 (m, 1H), 7.15 (td, *J* = 7.5, 1.3 Hz, 1H), 7.06 – 6.99 (m, 2H), 6.87 (dt, *J* = 8.2, 3.2 Hz, 2H), 6.78 (dd, *J* = 7.7, 2.6 Hz, 1H), 6.64 (dd, *J* = 7.9, 1.4 Hz, 1H), 5.67 (dd, *J* = 10.0, 1.8 Hz, 1H), 3.30 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.8, 158.7 (d, *J* = 240.8 Hz), 139.4, 137.1, 133.5 (d, *J* = 82.9 Hz), 130.4 (d, *J* = 12.3 Hz), 129.6, 128.4, 128.3, 128.1, 127.9, 127.2, 127.1, 126.3, 125.8, 123.2, 114.9 (d, *J* = 23.5 Hz), 112.9, 112.8, 108.8 (d, *J* = 7.5 Hz), 108.2, 56.4, 27.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>25</sub>H<sub>19</sub>FNO<sup>+</sup> 368.1445; found 368.1440.

**(E)-4'-benzylidene-6-chloro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(4h)**



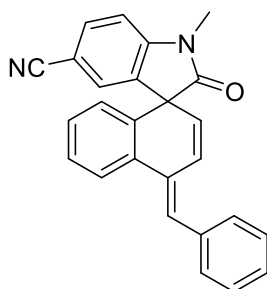
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 29.9 mg, yield: 78%. m.p. 266-267 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.98 (d,  $J = 7.8$  Hz, 1H), 7.55 – 7.44 (m, 2H), 7.44 – 7.37 (m, 3H), 7.38 – 7.28 (m, 2H), 7.20 (dd,  $J = 9.9, 0.9$  Hz, 1H), 7.18 – 7.11 (m, 1H), 7.02 (dd,  $J = 7.9, 1.9$  Hz, 1H), 6.99 – 6.87 (m, 2H), 6.63 (dd,  $J = 7.9, 1.3$  Hz, 1H), 5.64 (dd,  $J = 10.0, 1.7$  Hz, 1H), 3.29 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.9, 144.7, 137.1, 134.4, 133.9, 133.2, 133.0, 129.8, 129.6, 128.3, 128.0, 127.9, 127.2, 127.1, 127.0, 126.4, 125.7, 123.2, 123.3, 109.0, 77.0, 26.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{ClNO}^+$  384.1150; found 384.1143.

**(E)-4'-benzylidene-5-chloro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4i)**



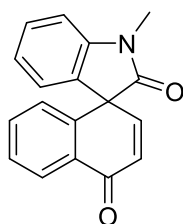
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 24.2 mg, yield: 63%. m.p. 240-241 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.99 (dd,  $J = 8.3, 1.3$  Hz, 1H), 7.50 – 7.43 (m, 3H), 7.40 (t,  $J = 7.7$  Hz, 2H), 7.33 (dd,  $J = 8.2, 1.3$  Hz, 1H), 7.32 – 7.27 (m, 2H), 7.21 (dd,  $J = 10.0, 0.9$  Hz, 1H), 7.16 (t,  $J = 7.5$  Hz, 1H), 7.00 (d,  $J = 2.2$  Hz, 1H), 6.87 (d,  $J = 8.3$  Hz, 1H), 6.64 (dd,  $J = 7.8, 1.4$  Hz, 1H), 5.65 (dd,  $J = 9.9, 1.7$  Hz, 1H), 3.30 (s, 3H).  $^{13}\text{C}$  NMR (125MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 142.0, 137.0, 136.2, 133.6, 133.1, 129.6, 128.6, 128.3, 128.1, 127.9, 127.2, 127.0, 126.1, 125.9, 125.2, 123.2, 109.2, 56.1, 26.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{19}\text{ClNO}^+$  384.1150; found 384.1155.

**(E)-4'-benzylidene-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-5-carbonitrile (4j)**



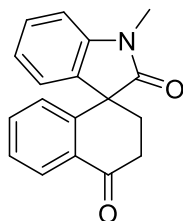
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 25.1 mg, yield: 67%. m.p. 250-251 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.00 (dd, *J* = 8.2, 1.2 Hz, 1H), 7.66 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.46 (dt, *J* = 6.0, 1.3 Hz, 3H), 7.41 (dd, *J* = 8.4, 6.7 Hz, 2H), 7.36 (ddd, *J* = 8.3, 7.2, 1.4 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.28 (d, *J* = 1.6 Hz, 1H), 7.23 (dd, *J* = 9.9, 0.8 Hz, 1H), 7.16 (ddd, *J* = 8.3, 7.2, 1.2 Hz, 1H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.58 (dd, *J* = 7.9, 1.3 Hz, 1H), 5.61 (dd, *J* = 9.9, 1.6 Hz, 1H), 3.34 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 176.7, 147.2, 136.8, 135.7, 133.8, 133.2, 132.9, 129.6, 129.4, 128.3, 128.2, 127.7, 127.4, 126.9, 126.5, 125.1, 123.4, 118.8, 108.7, 106.6, 55.6, 29.6, 27.0. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>26</sub>H<sub>19</sub>N<sub>2</sub>O<sup>+</sup> 375.1492; found 375.1501.

### 1-methyl-4'H-spiro[indoline-3,1'-naphthalene]-2,4'-dione (5)



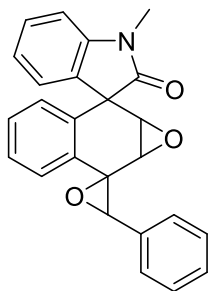
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), 21.5 mg, yield: 78%. m.p. 259-260 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.26 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.55 – 7.34 (m, 3H), 7.07 (td, *J* = 7.6, 1.1 Hz, 1H), 7.03 (d, *J* = 7.8 Hz, 1H), 6.92 (dd, *J* = 7.4, 1.2 Hz, 1H), 6.75 (dd, *J* = 7.6, 1.4 Hz, 1H), 6.71 (d, *J* = 9.9 Hz, 1H), 6.66 (d, *J* = 10.0 Hz, 1H), 3.36 (s, 3H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 184.4, 173.7, 143.5, 140.3, 133.0, 130.7, 129.6, 128.4, 127.0, 126.8, 124.8, 124.7, 123.8, 108.9, 108.8, 56.2, 27.2. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>14</sub>NO<sub>2</sub><sup>+</sup> 276.1019; found 276.1020.

### 1-methyl-2',3'-dihydro-4'H-spiro[indoline-3,1'-naphthalene]-2,4'-dione (6)



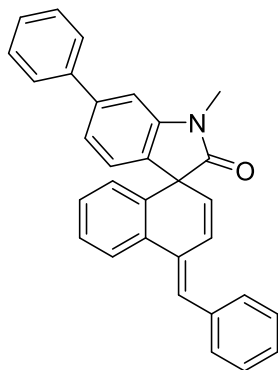
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 10/1), 25.2 mg, yield: 91%. m.p. 328-329 °C. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.27 – 7.99 (m, 1H), 7.38 (td, *J* = 6.4, 3.3 Hz, 3H), 7.20 – 7.05 (m, 2H), 6.98 (d, *J* = 7.8 Hz, 1H), 6.77 – 6.54 (m, 1H), 3.44 (ddd, *J* = 17.7, 10.7, 5.9 Hz, 1H), 3.29 (s, 3H), 2.81 (ddd, *J* = 17.7, 5.9, 5.0 Hz, 1H), 2.59 – 2.32 (m, 2H). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 196.9, 177.5, 143.4, 142.2, 133.8, 133.5, 133.0, 128.7, 128.1, 127.8, 127.2, 124.0, 123.1, 108.5, 51.6, 33.4, 32.6, 26.5. HRMS (ESI) *m/z*: [M+H]<sup>+</sup> calcd for C<sub>18</sub>H<sub>16</sub>NO<sub>2</sub><sup>+</sup> 278.1176; found 278.1174.

### 1-methyl-3''-phenyl-1a',7a'-dihydrodispiro[indoline-3,2'-naphtho[2,3-b]oxirene-7',2''-oxiran]-2-one (7)



A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 15/1), 17.2 mg, yield: 45%. m.p. 290-291 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.88 (dd,  $J = 7.7, 1.5$  Hz, 1H), 7.63 – 7.58 (m, 2H), 7.59 – 7.54 (m, 1H), 7.50 (dt,  $J = 7.7, 1.4$  Hz, 1H), 7.45 (dt,  $J = 8.0, 1.5$  Hz, 1H), 7.42 – 7.33 (m, 3H), 7.35 – 7.30 (m, 1H), 7.07 (t,  $J = 7.6$  Hz, 1H), 7.03 – 6.95 (m, 2H), 5.61 (s, 1H), 5.43 (d,  $J = 1.8$  Hz, 1H), 3.40 (d,  $J = 1.8$  Hz, 1H), 3.30 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  176.6, 163.3, 143.1, 138.3, 137.1, 134.4, 133.2, 132.3, 131.0, 130.2, 129.9, 129.8, 129.6, 129.5, 129.2, 128.9, 128.7, 128.5, 127.8, 127.6, 124.4, 123.3, 108.2, 75.5, 74.2, 60.2, 57.7, 56.8, 26.7. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{25}\text{H}_{20}\text{NO}_3^+$  382.1438; found 382.1437.

**(E)-4'-benzylidene-1-methyl-6-phenyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (8)**



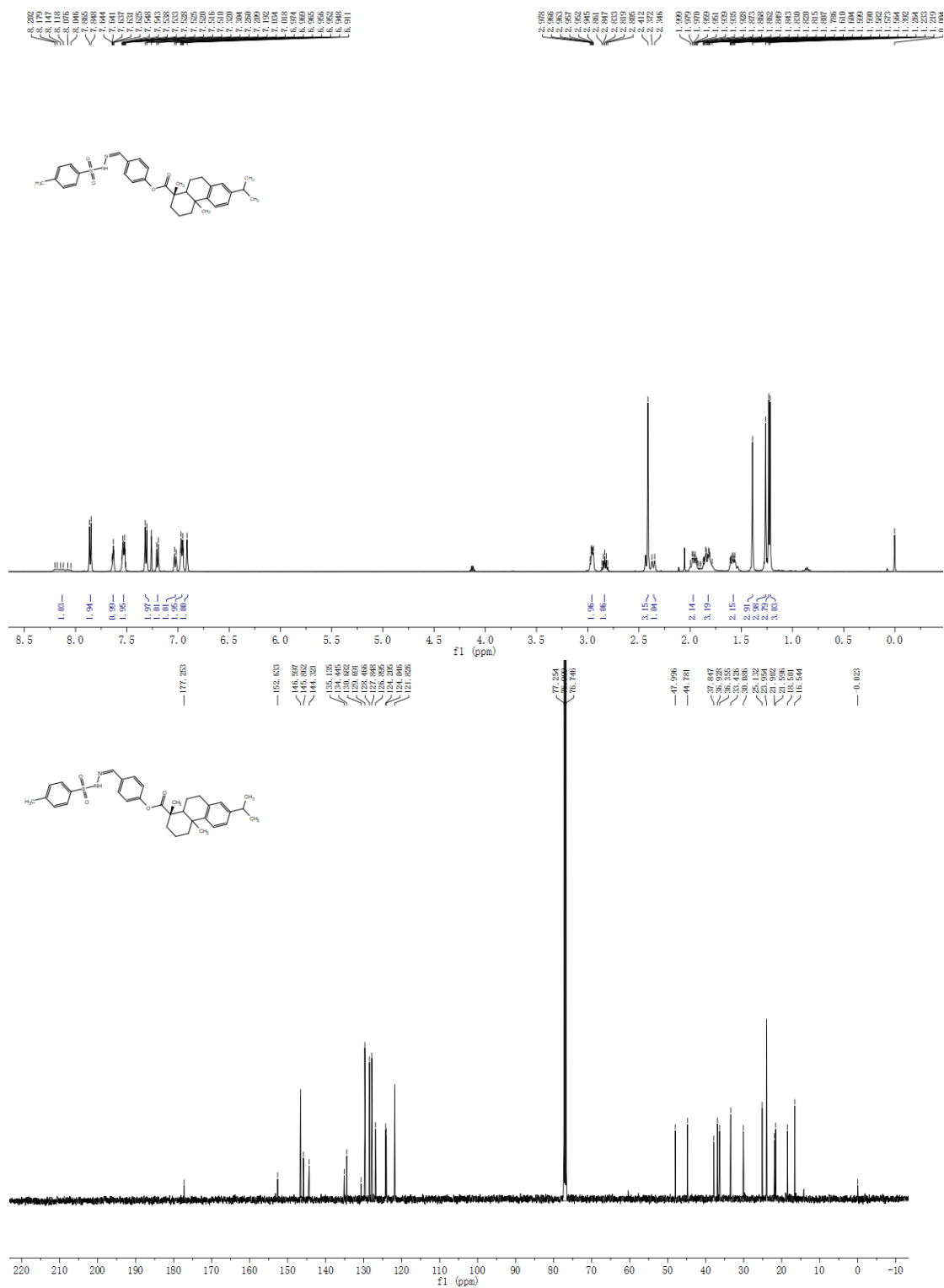
A white solid after purification by flash column chromatography (petroleum ether/ethyl acetate = 20/1), 38.7 mg, yield: 91%. m.p. 255-256 °C.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.06 – 7.92 (m, 1H), 7.68 – 7.57 (m, 2H), 7.54 – 7.45 (m, 4H), 7.46 – 7.37 (m, 4H), 7.36 – 7.27 (m, 3H), 7.26 – 7.20 (m, 1H), 7.20 – 7.12 (m, 2H), 7.09 (d,  $J = 7.7$  Hz, 1H), 6.73 (dd,  $J = 7.9, 1.4$  Hz, 1H), 5.73 (dd,  $J = 10.0, 1.7$  Hz, 1H), 3.37 (s, 3H).  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  177.2, 144.0, 142.2, 140.9, 137.2, 134.4, 133.7, 133.2, 130.1, 129.6, 128.8, 128.3, 128.0, 127.7, 127.6, 127.3, 127.2, 127.1, 127.0, 126.7, 125.4, 124.9, 123.1, 122.4, 107.2, 56.0, 26.9. HRMS (ESI)  $m/z$ :  $[\text{M}+\text{H}]^+$  calcd for  $\text{C}_{31}\text{H}_{24}\text{NO}^+$  426.1852; found 426.1845.

## VII. References

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## VIII. NMR spectra

### 4-((Z)-(2-tosylhydrazono)methyl)phenyl (1S)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthrene-1-carboxylate (9e)

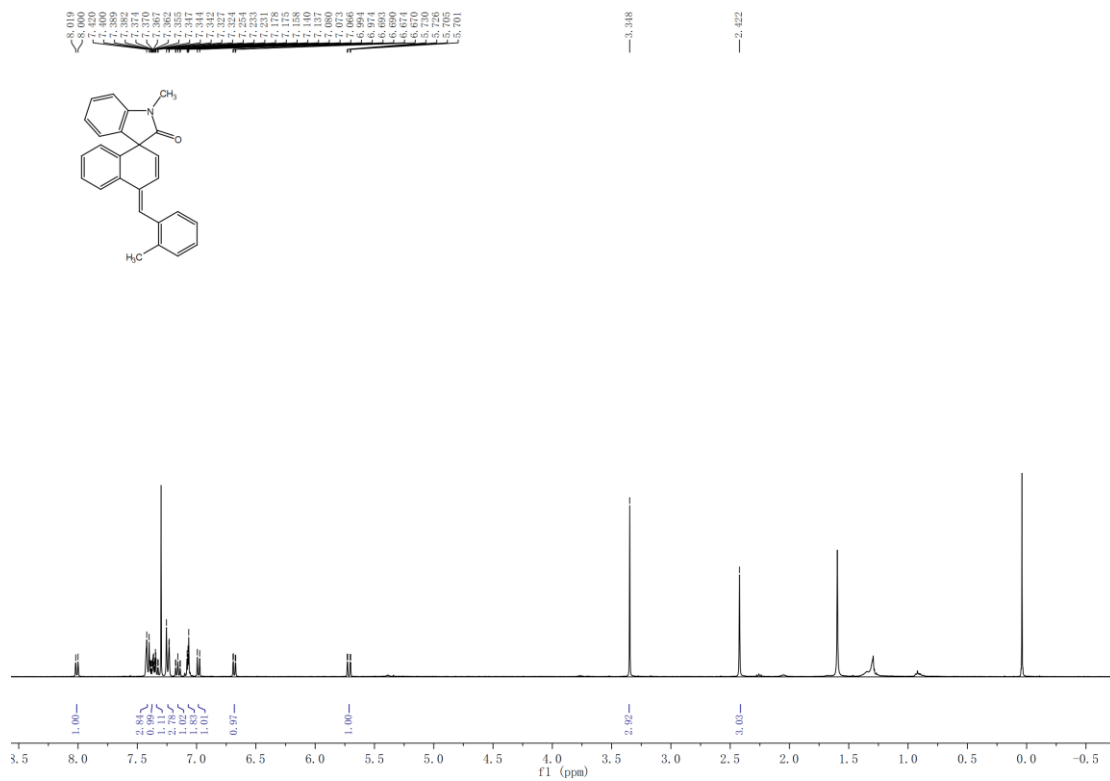








**(E)-1-methyl-4'-(2-methylbenzylidene)-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3b)**





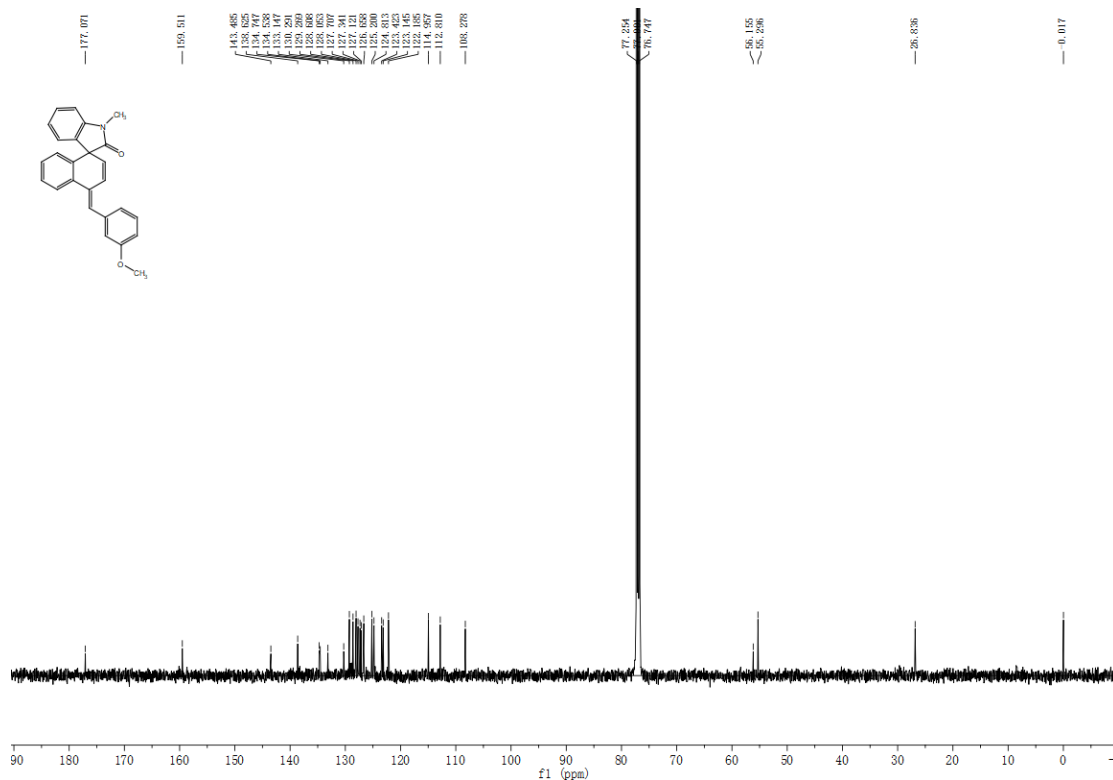
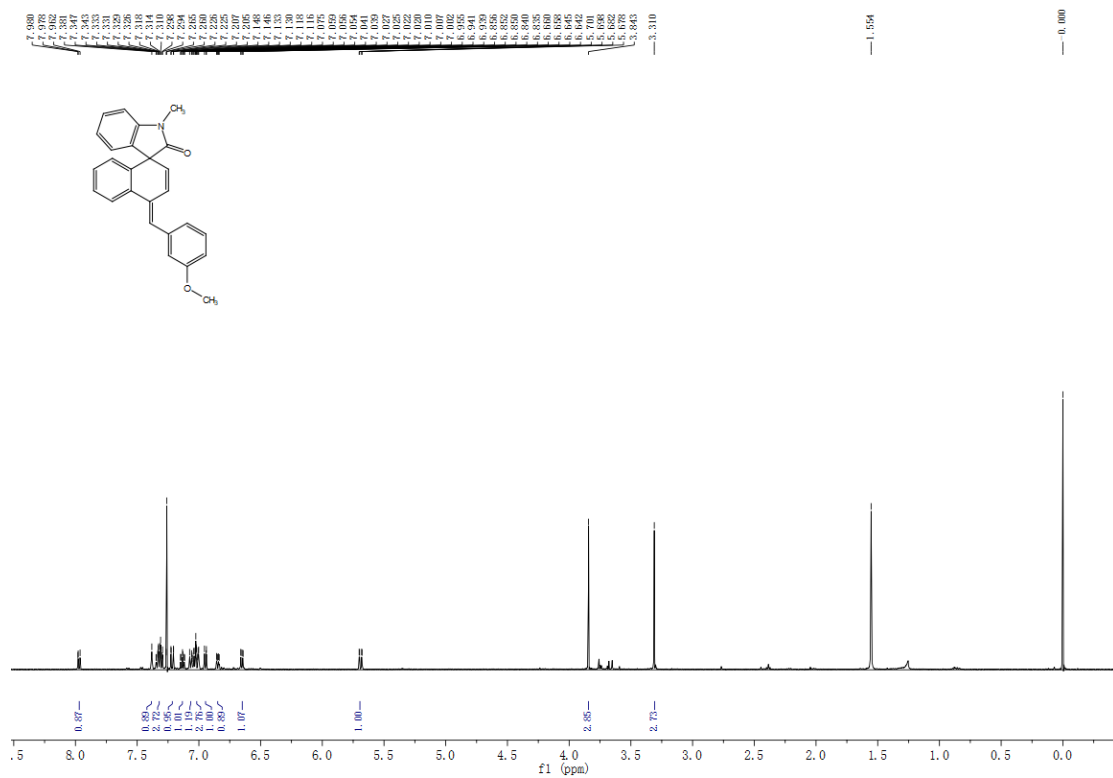






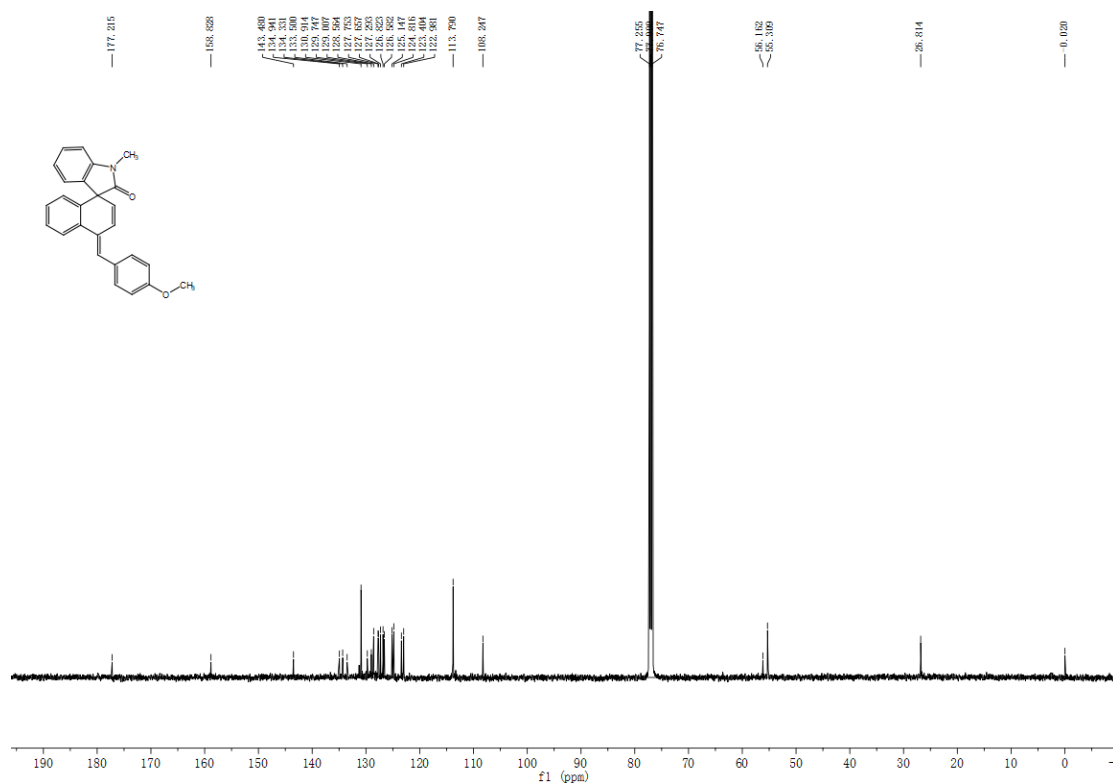
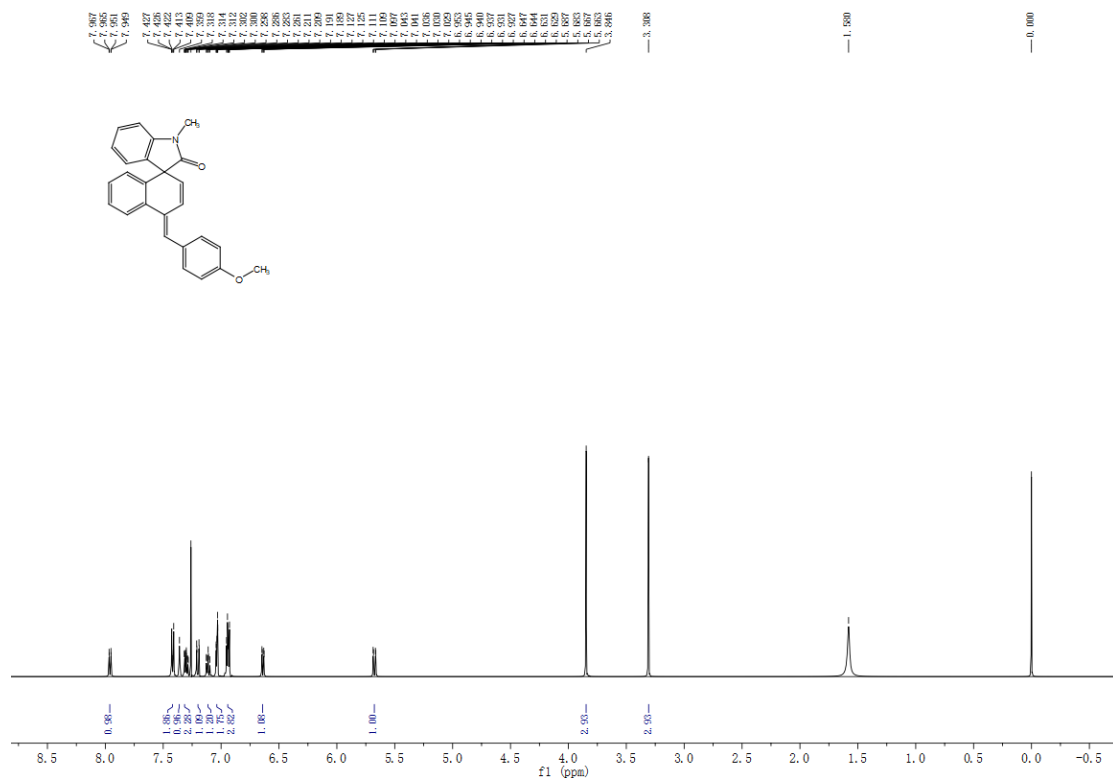


**(E)-4'-(3-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3h)**

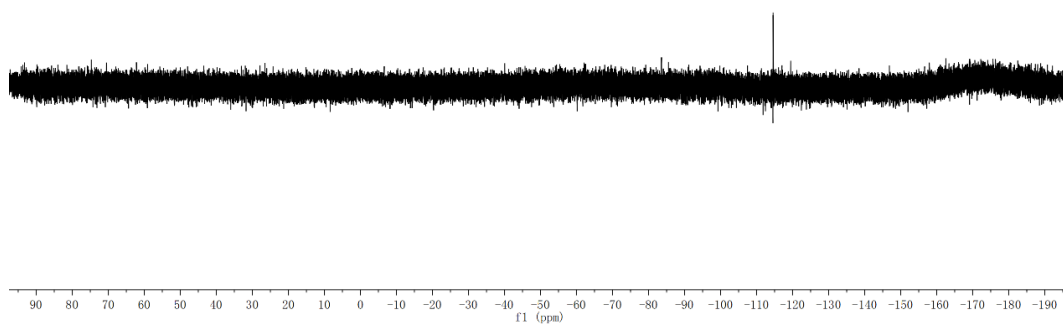
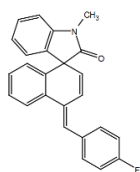




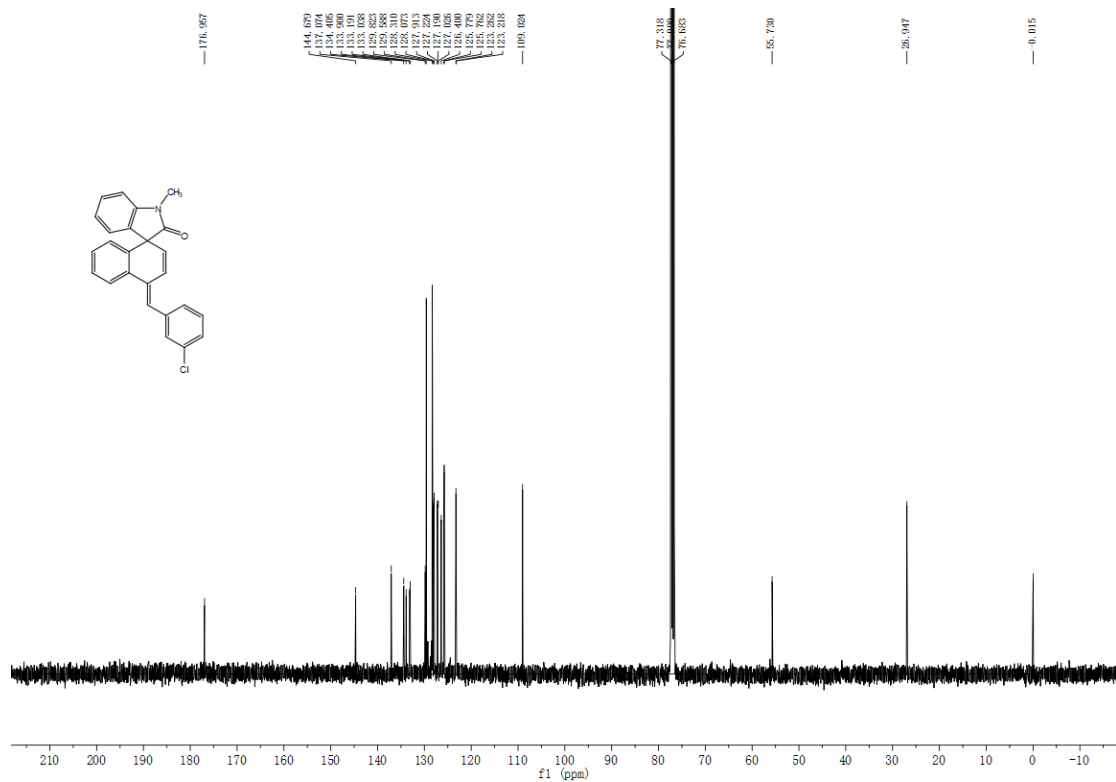
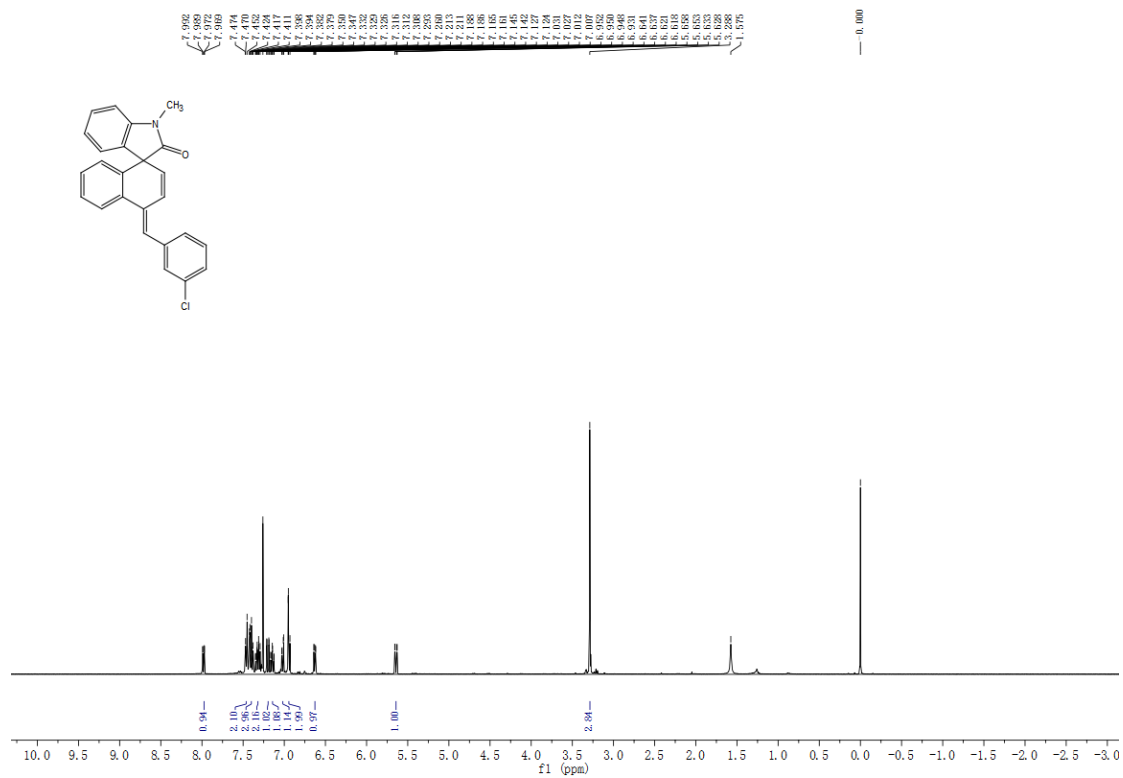
**(E)-4'-(4-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3i)**



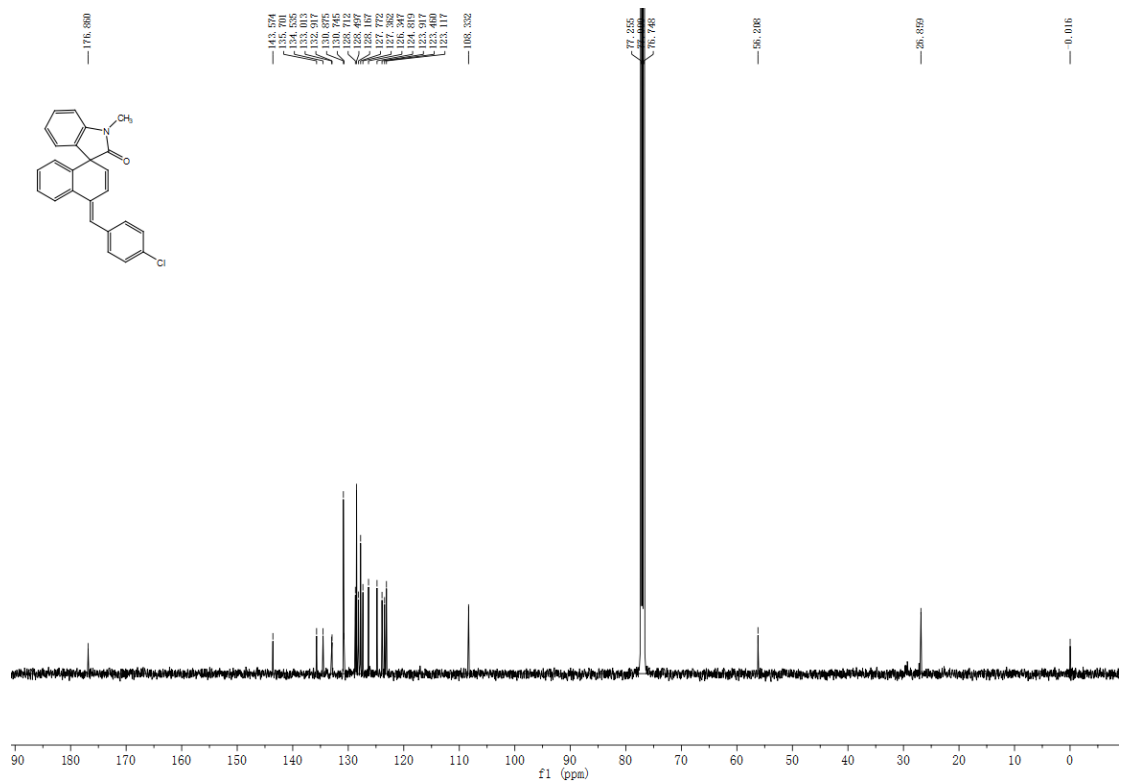
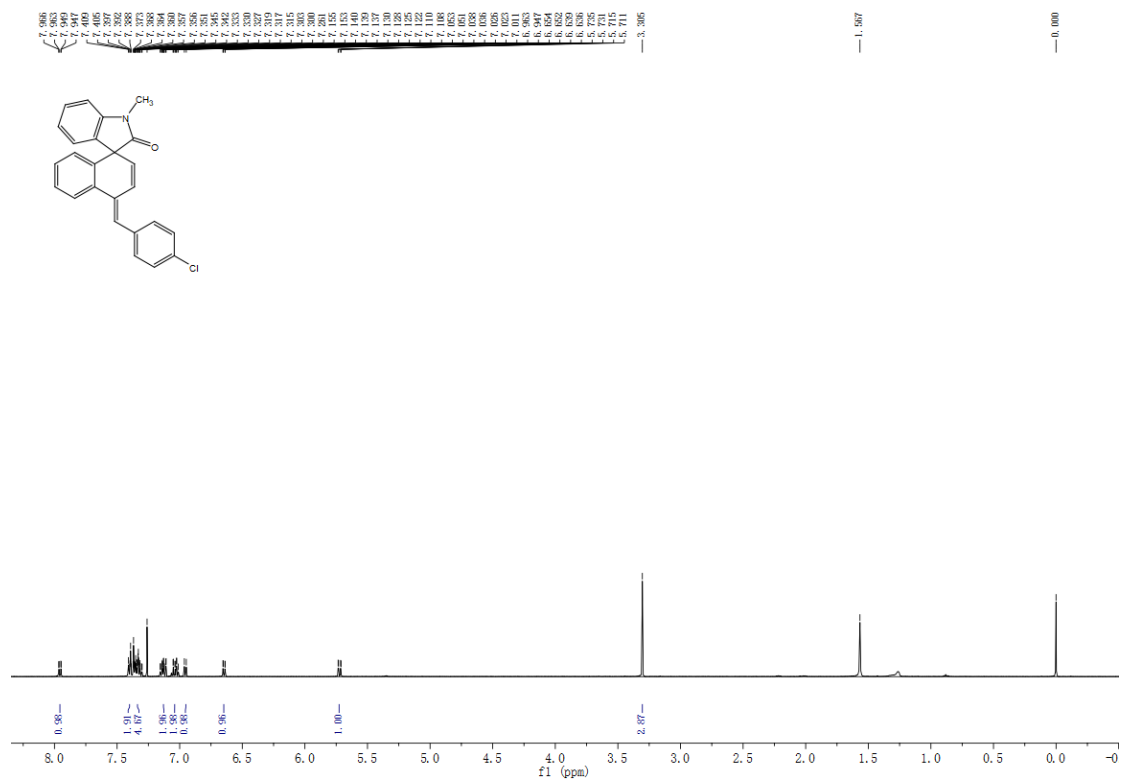




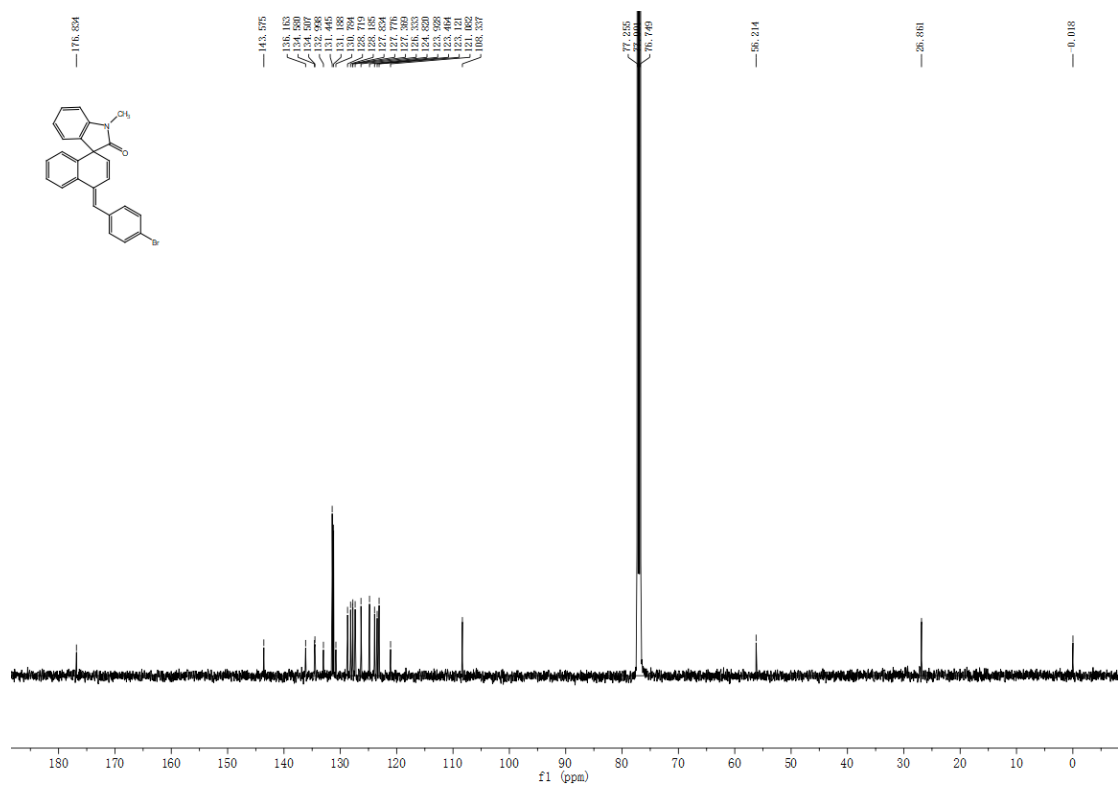
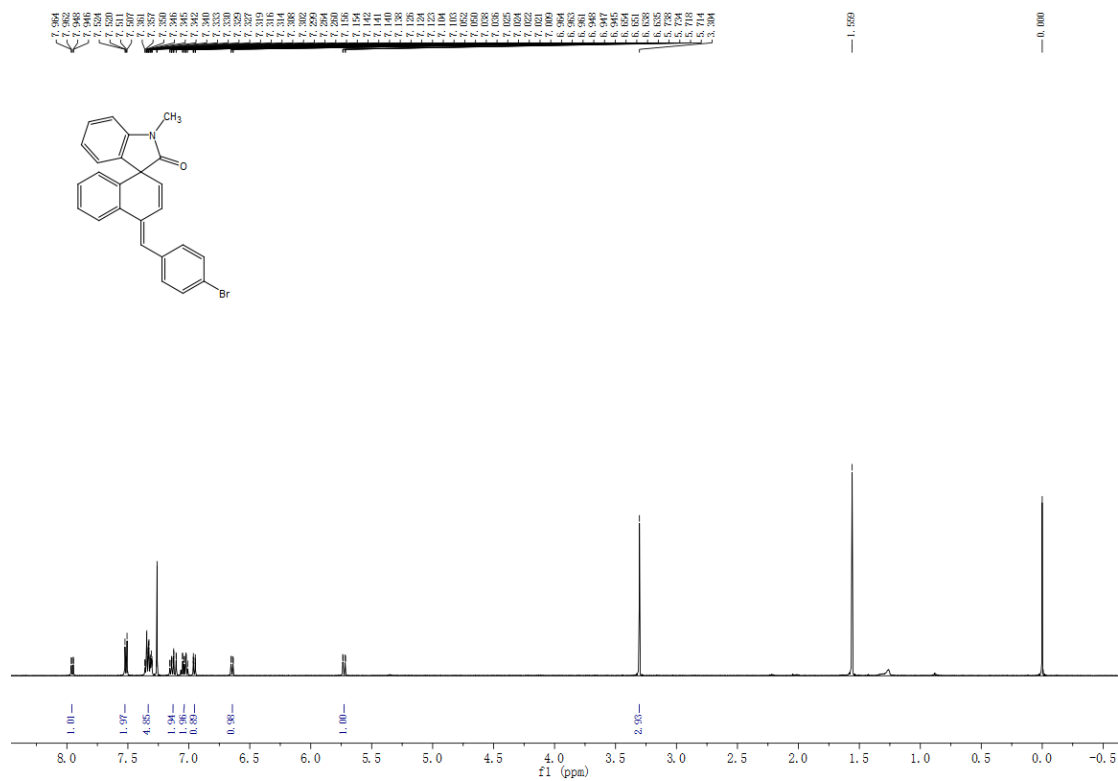
**(E)-4'-(3-chlorobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(3k)**



**(E)-4'-(4-chlorobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (31)**

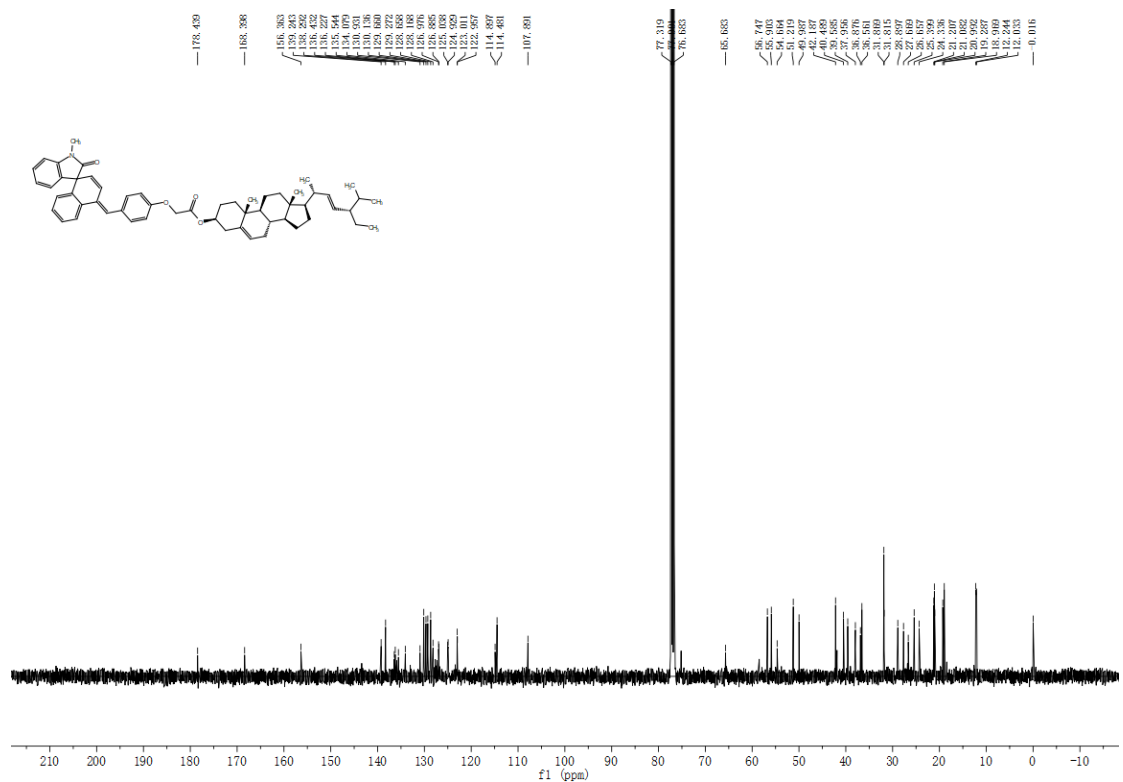
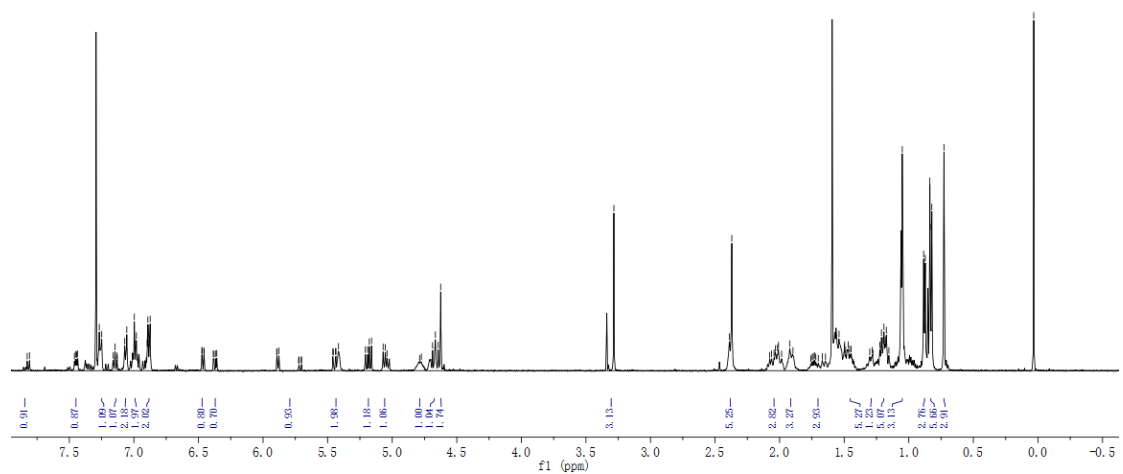
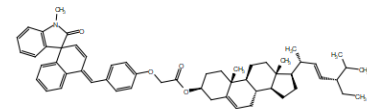
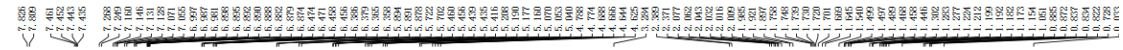


(E)-4'-(4-bromobenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (3m)



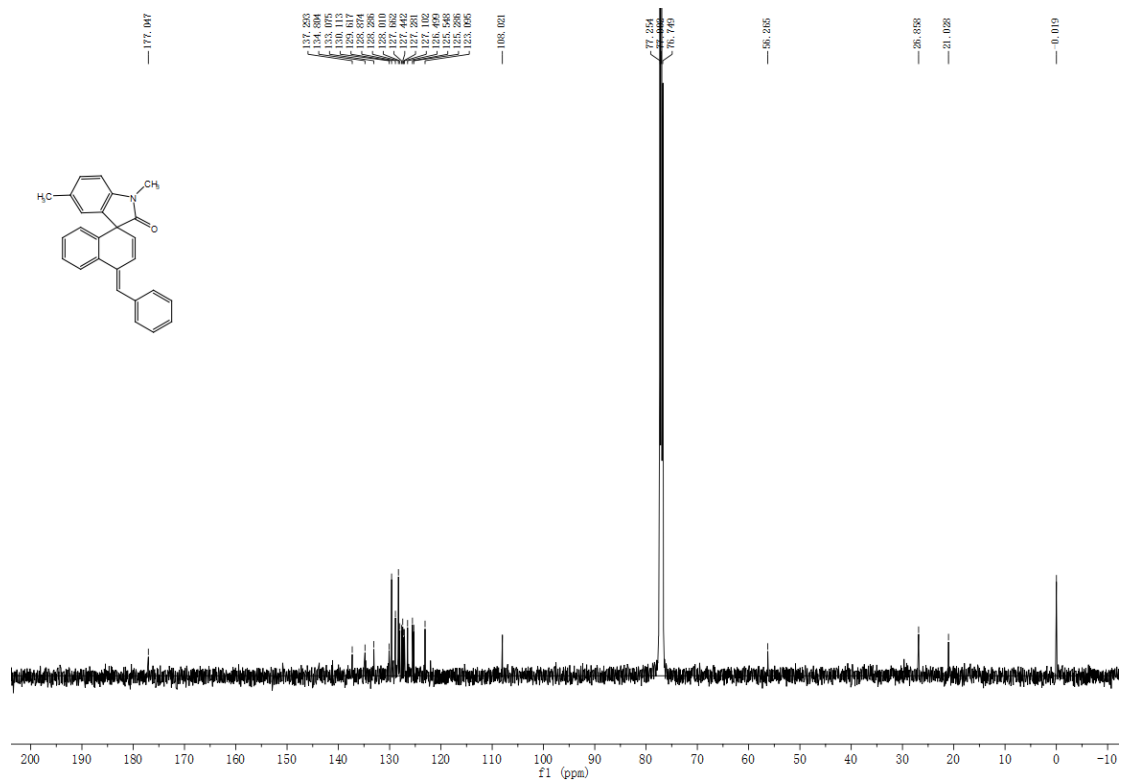
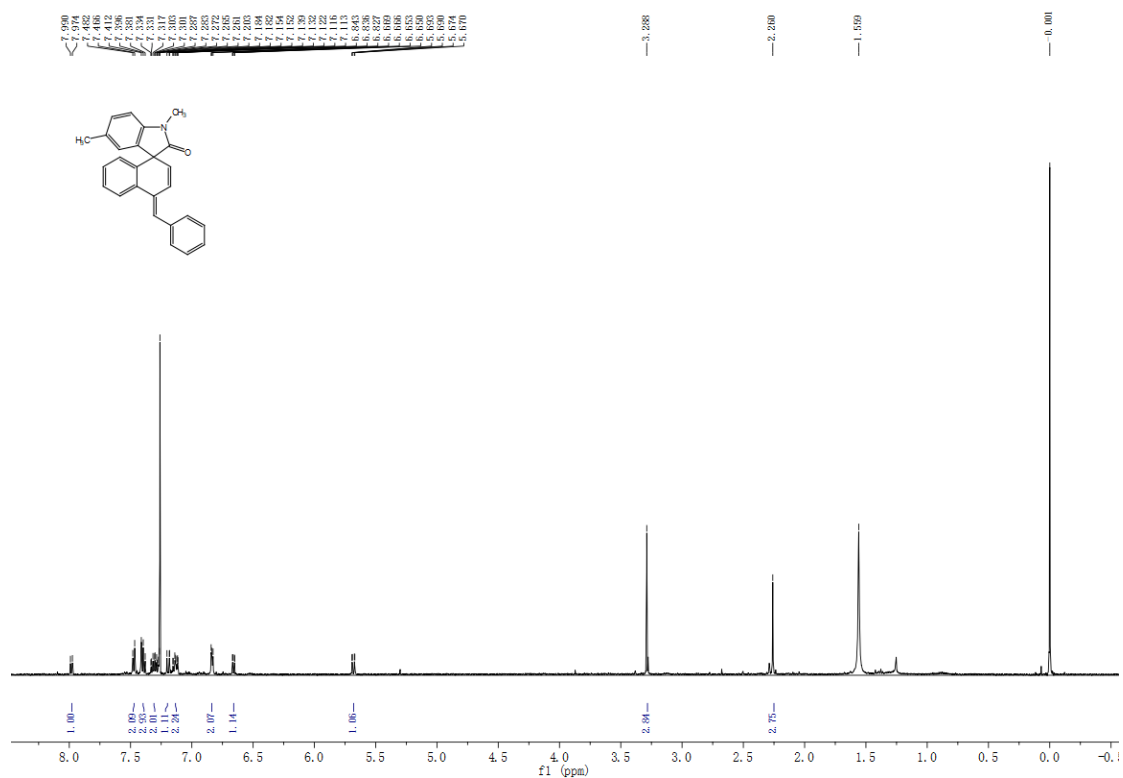


**(3S,8S,9S,10R,13R,14S,17R)-17-((2R,5S,E)-5-ethyl-6-methylhept-3-en-2-yl)-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 2-(4-((E)-(1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalen]-4'-ylidene)methyl)phenoxy)acetate (3o)**

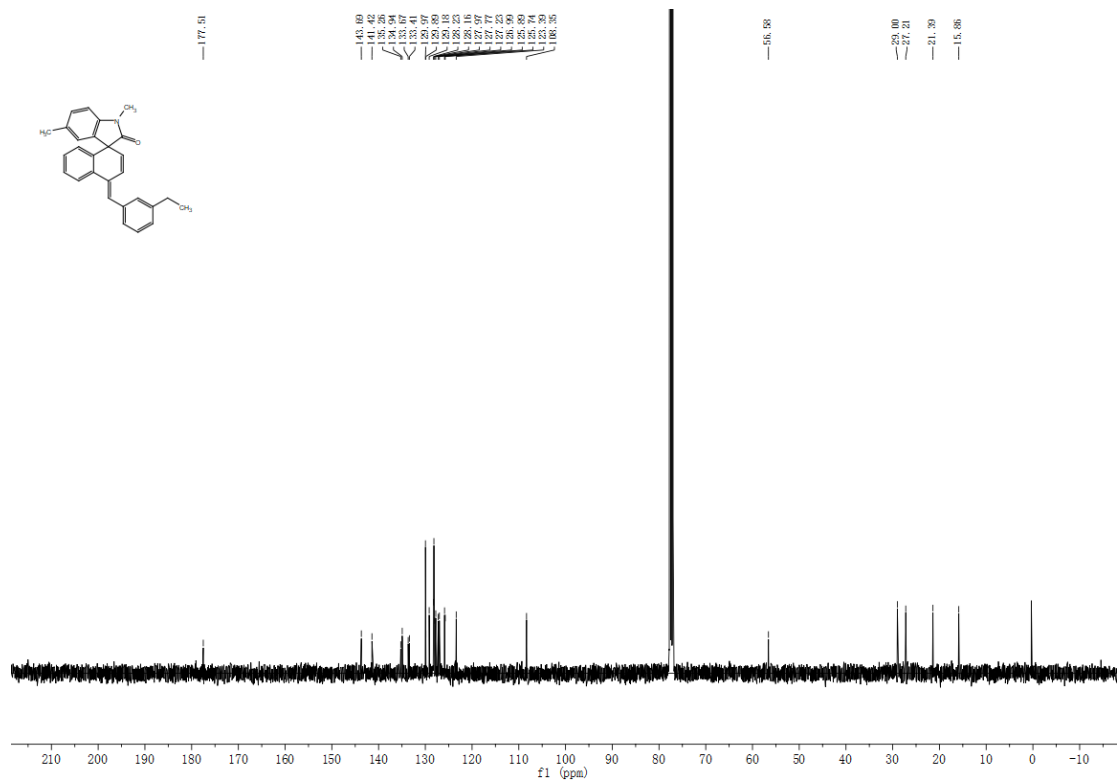
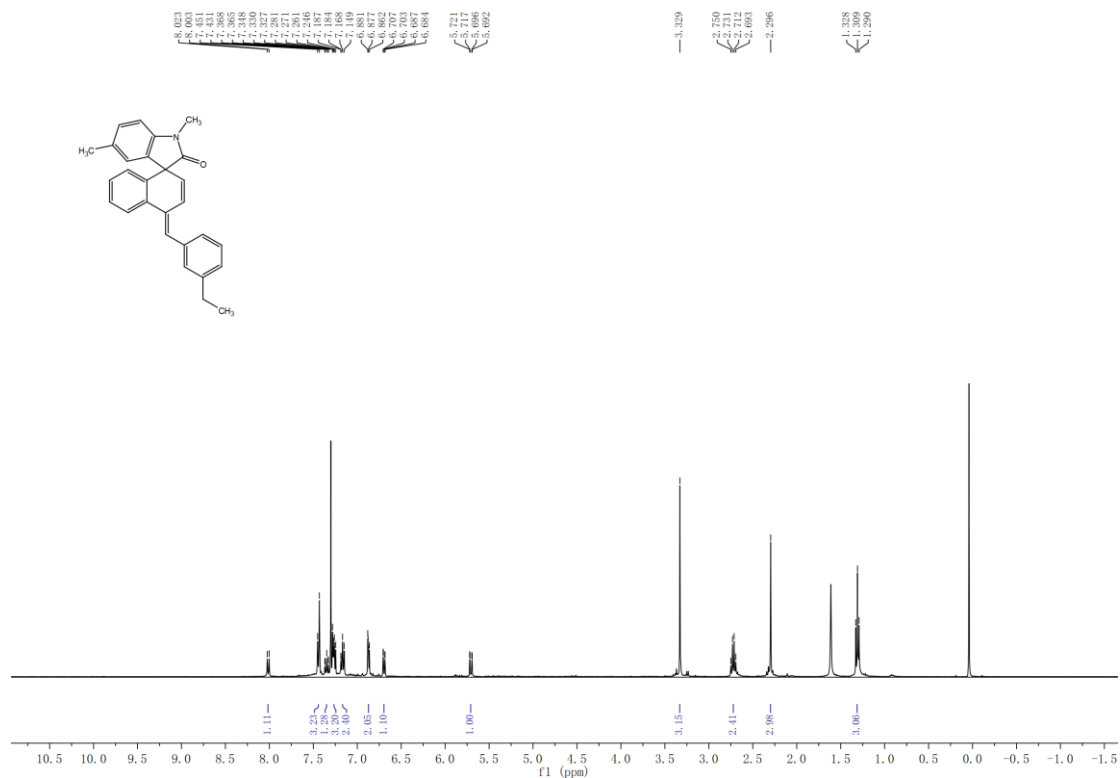




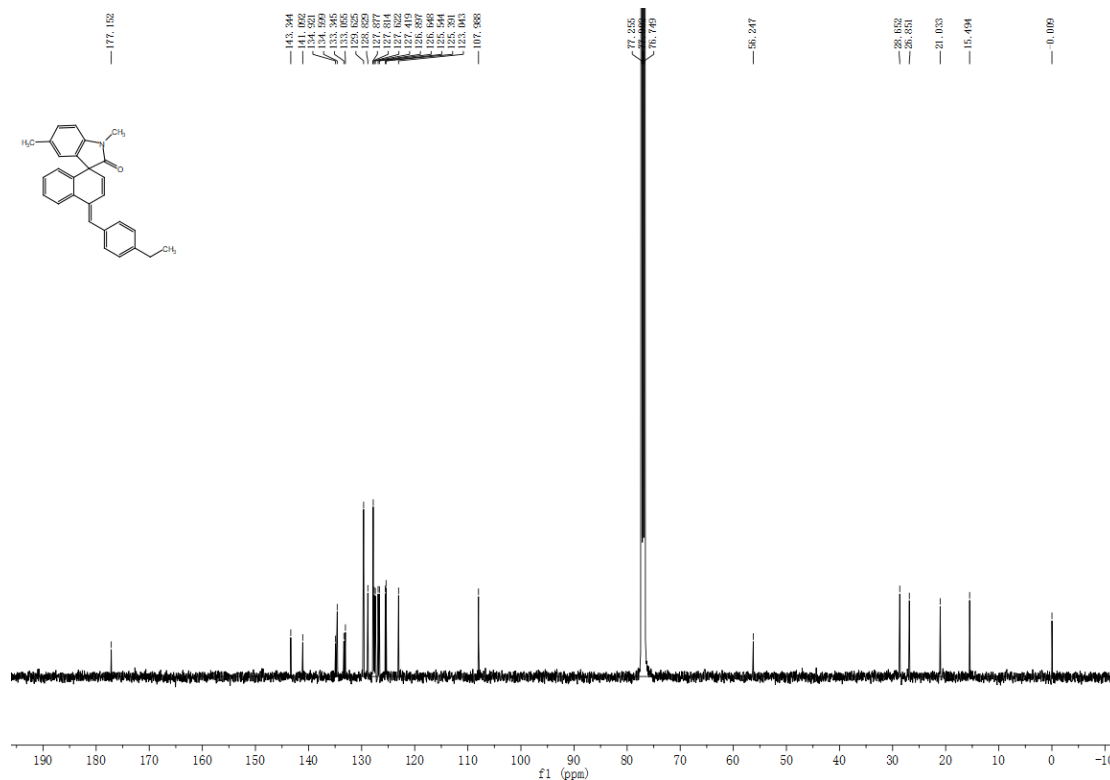
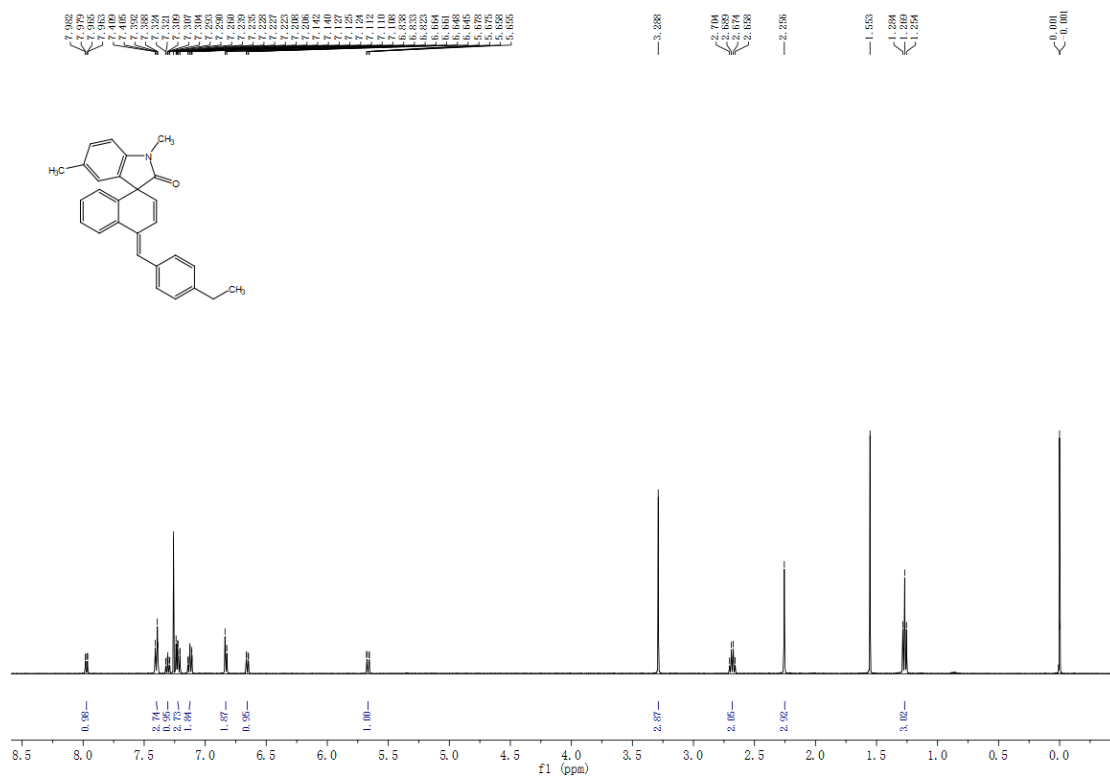
**(E)-4'-benzylidene-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4a)**



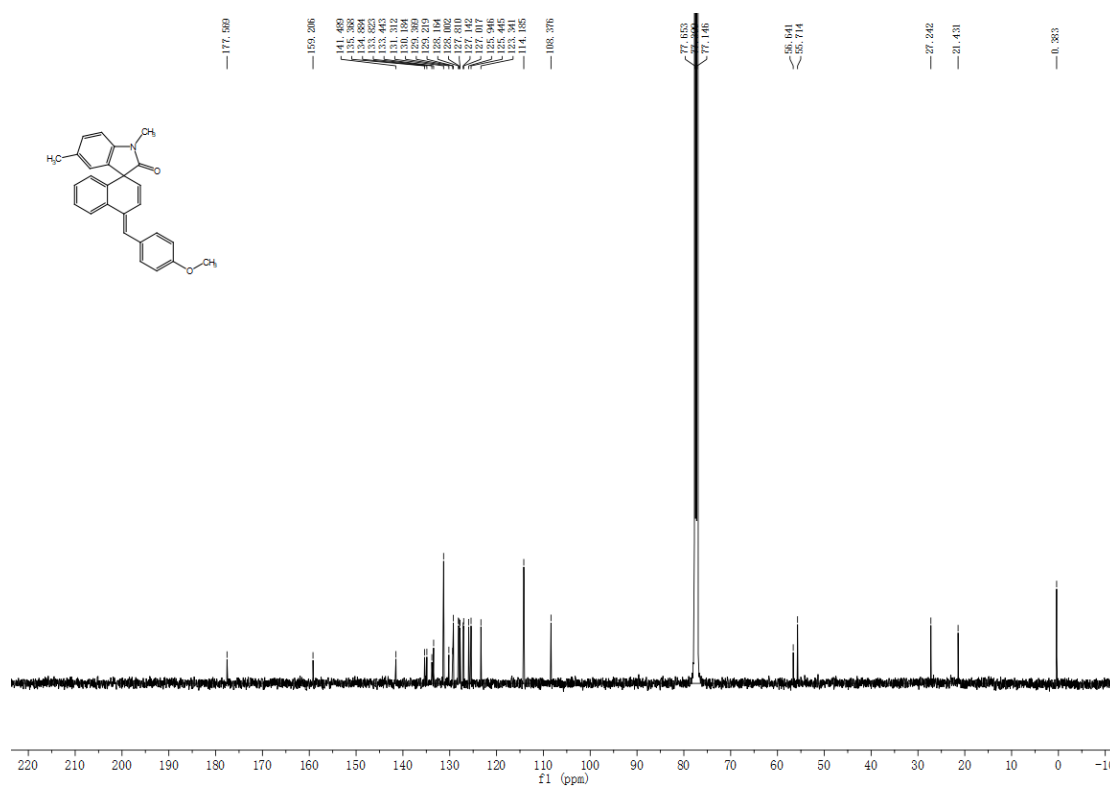
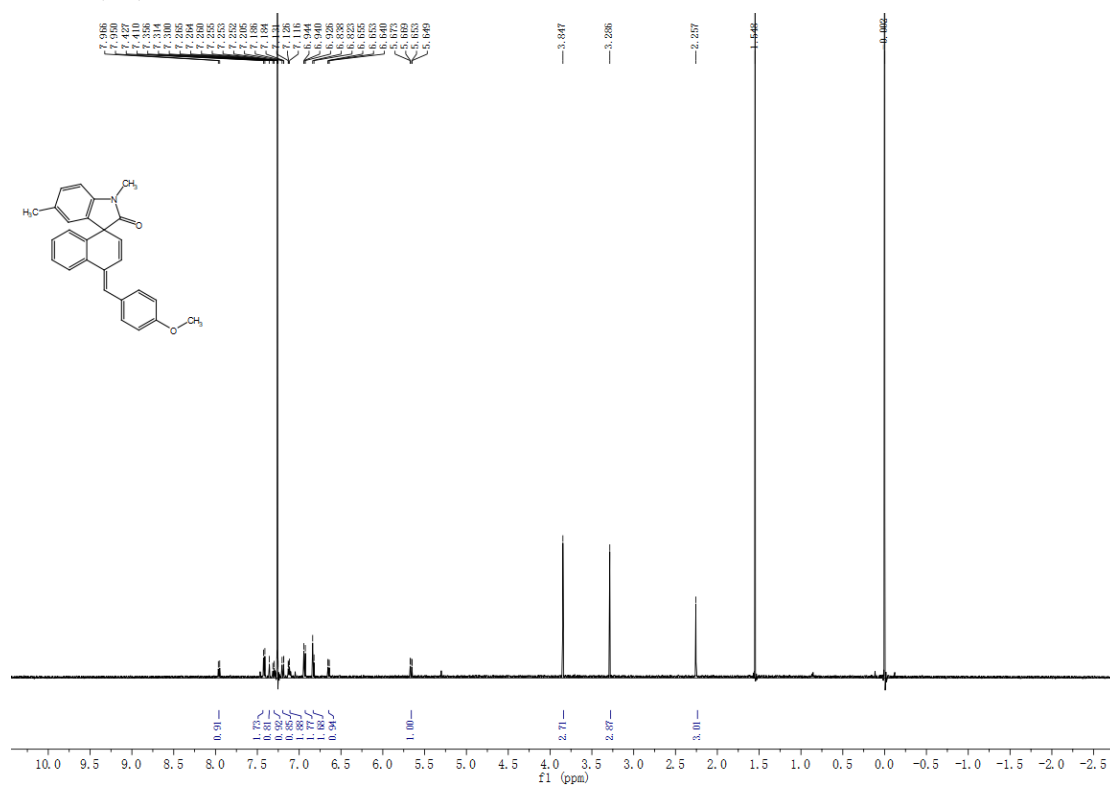
**(E)-4'-(3-ethylbenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4b)**



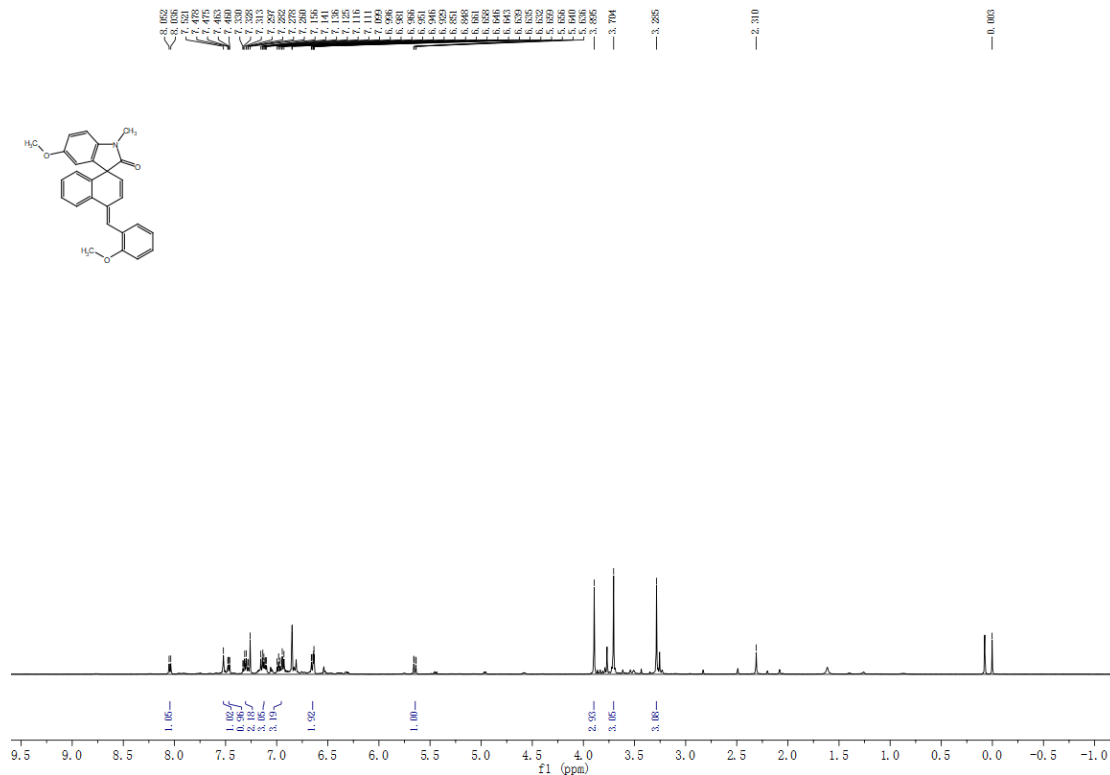
**(E)-4'-(4-ethylbenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4c)**



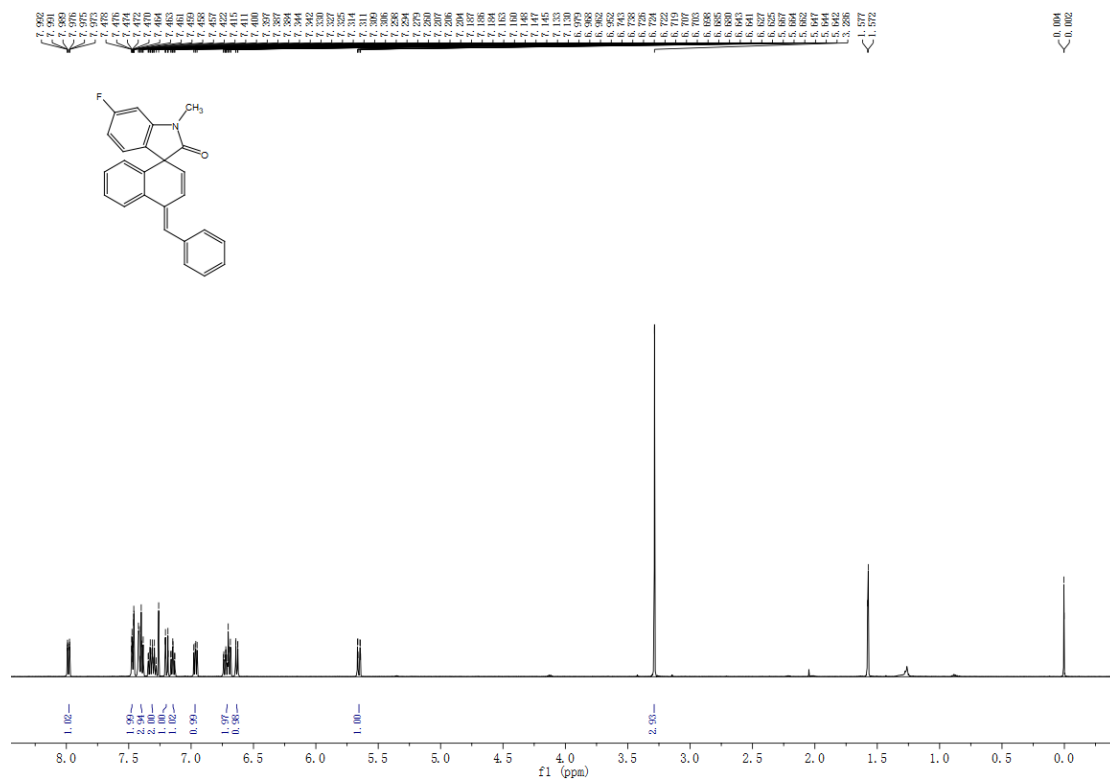
**(E)-4'-(4-methoxybenzylidene)-1,5-dimethyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4d)**

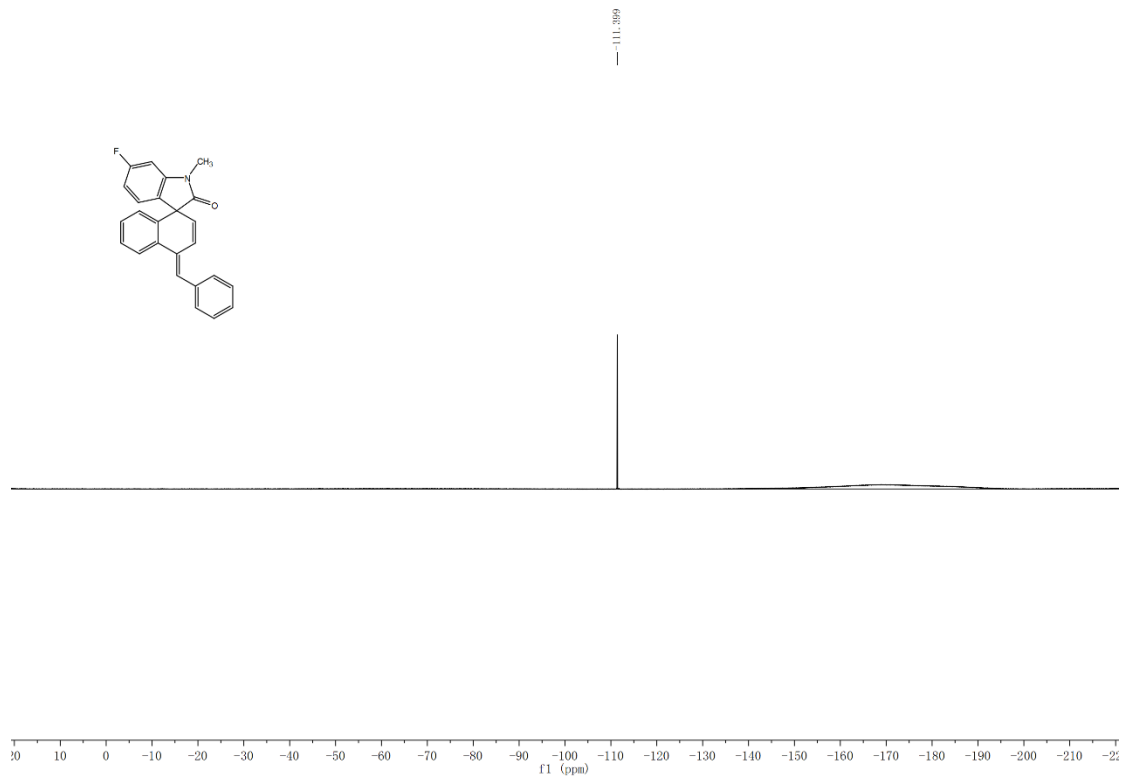


**(E)-5-methoxy-4'-(2-methoxybenzylidene)-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4e)**

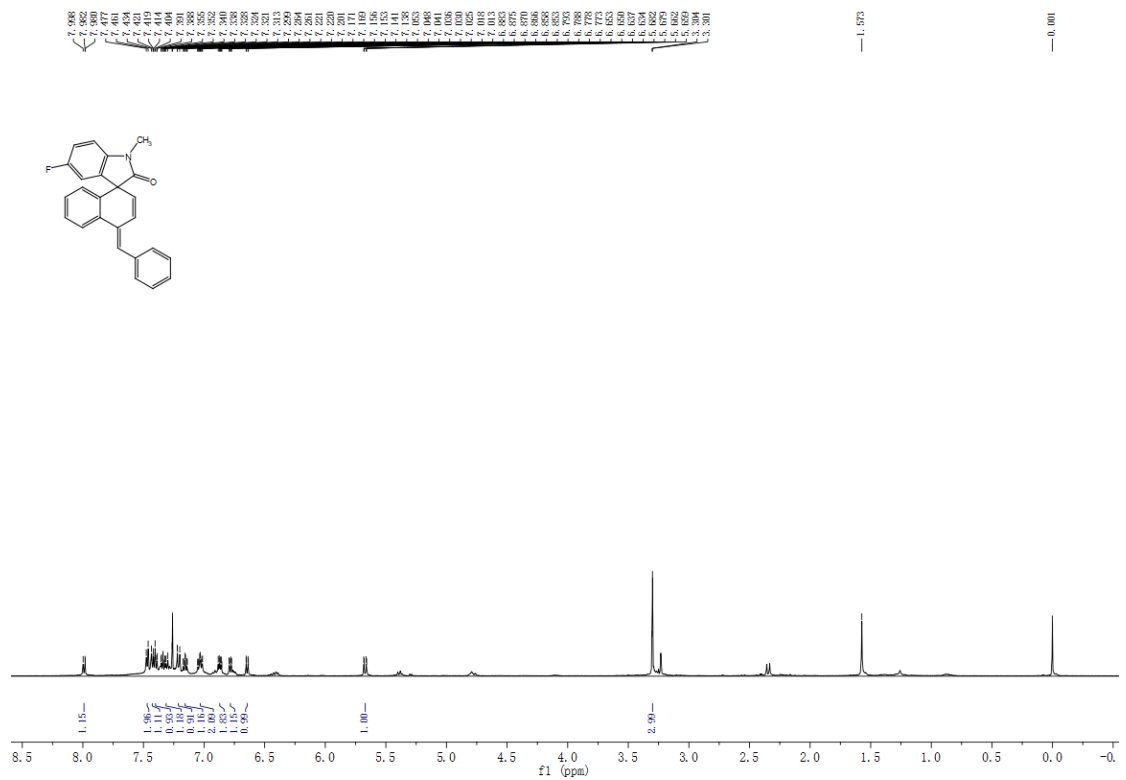


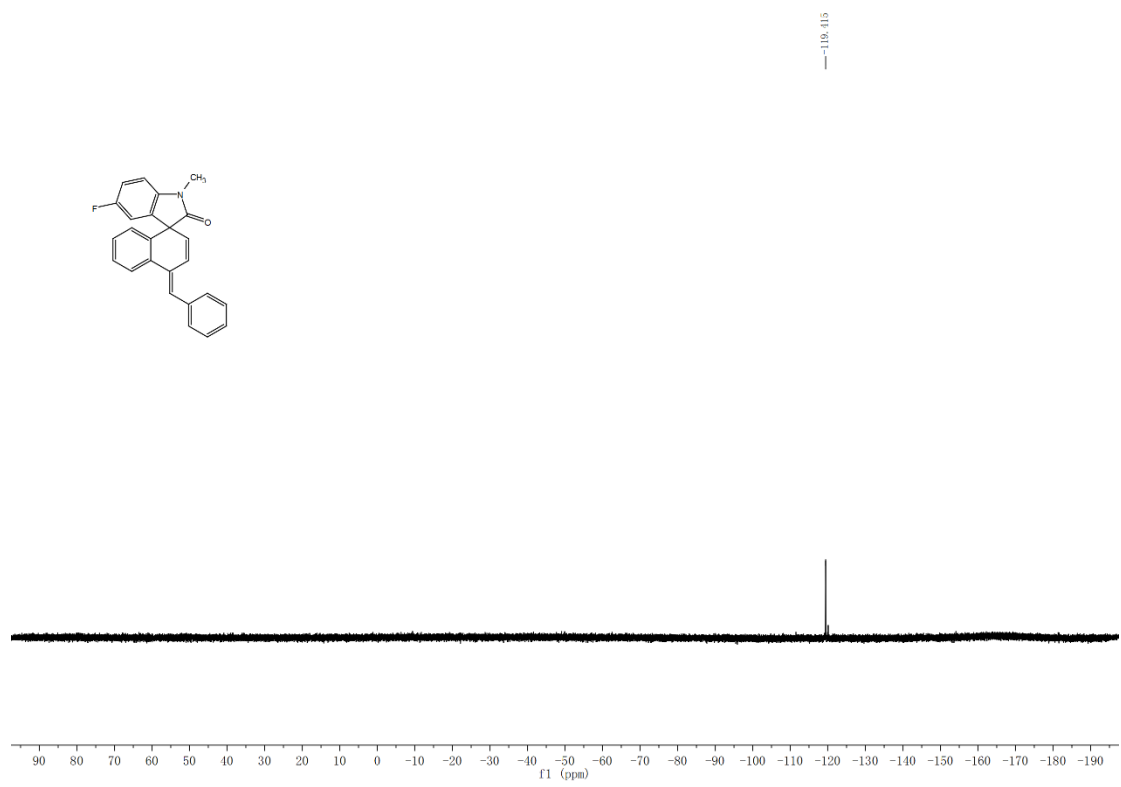
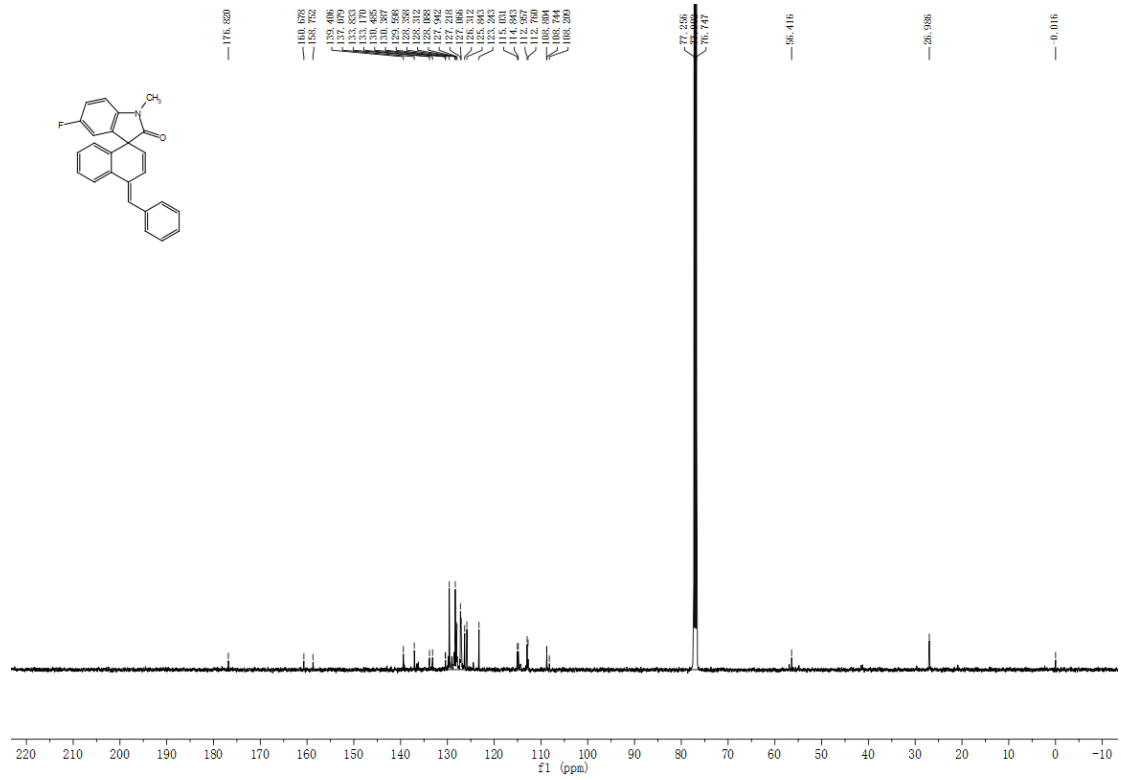
**(E)-4'-benzylidene-6-fluoro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(4f)**





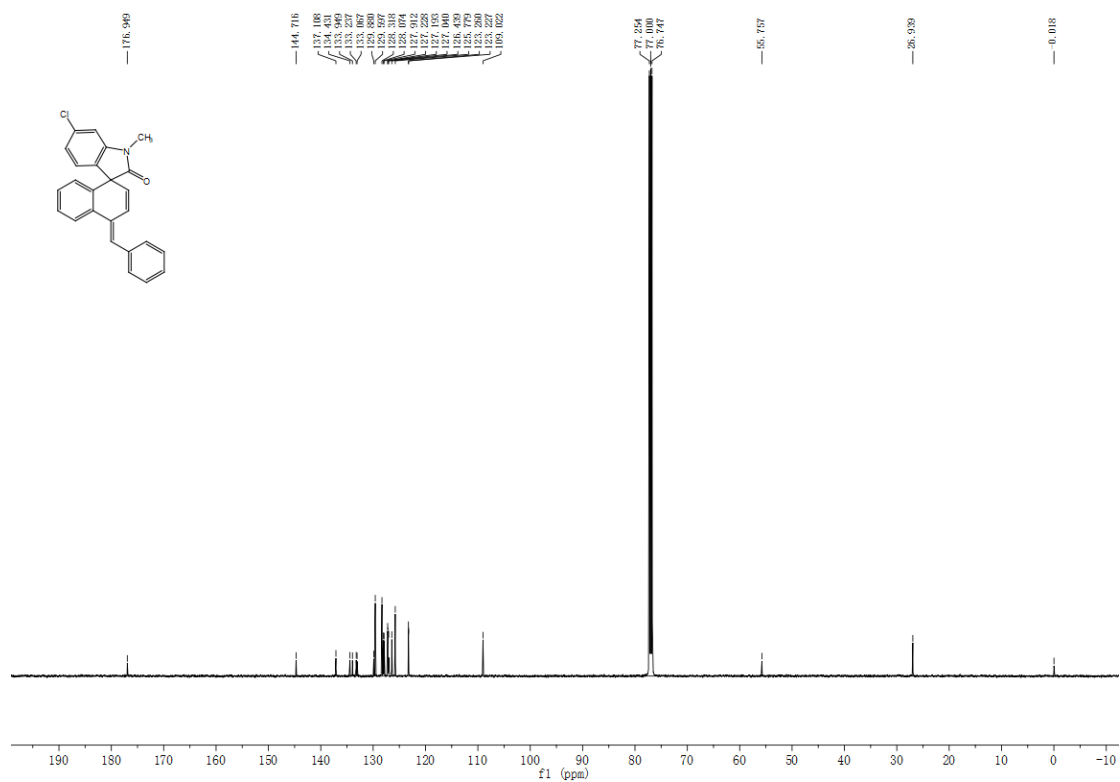
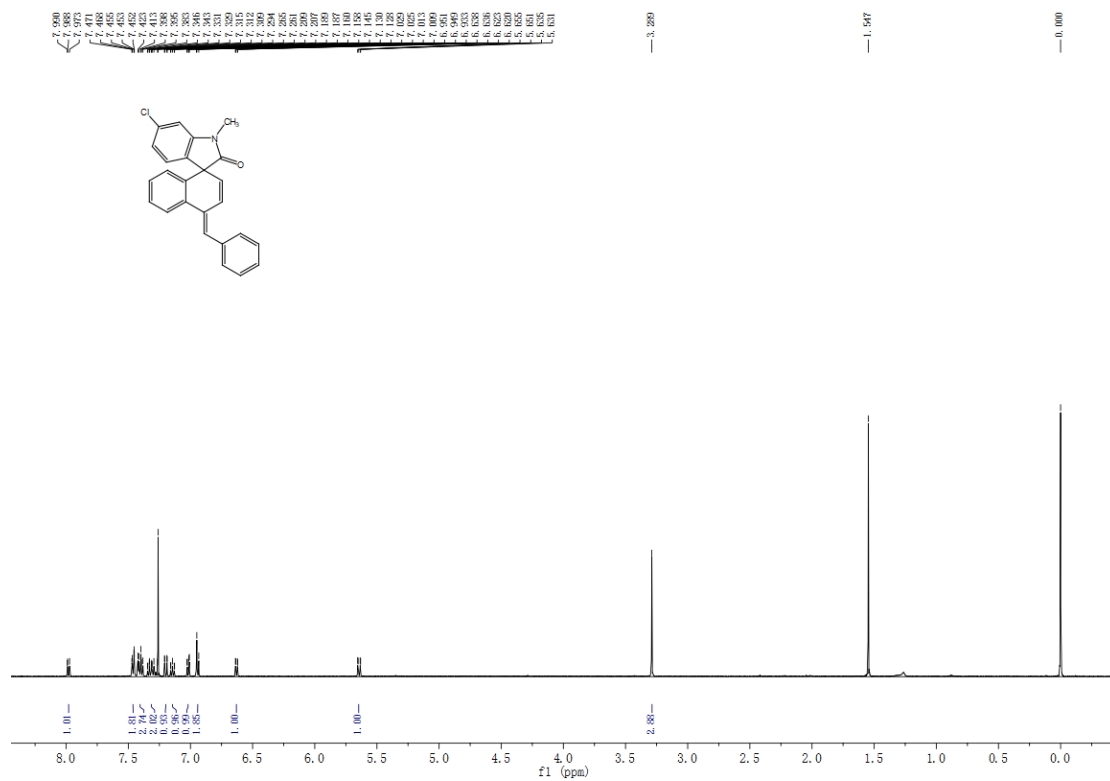
**(E)-4'-benzylidene-5-fluoro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one (4g)**



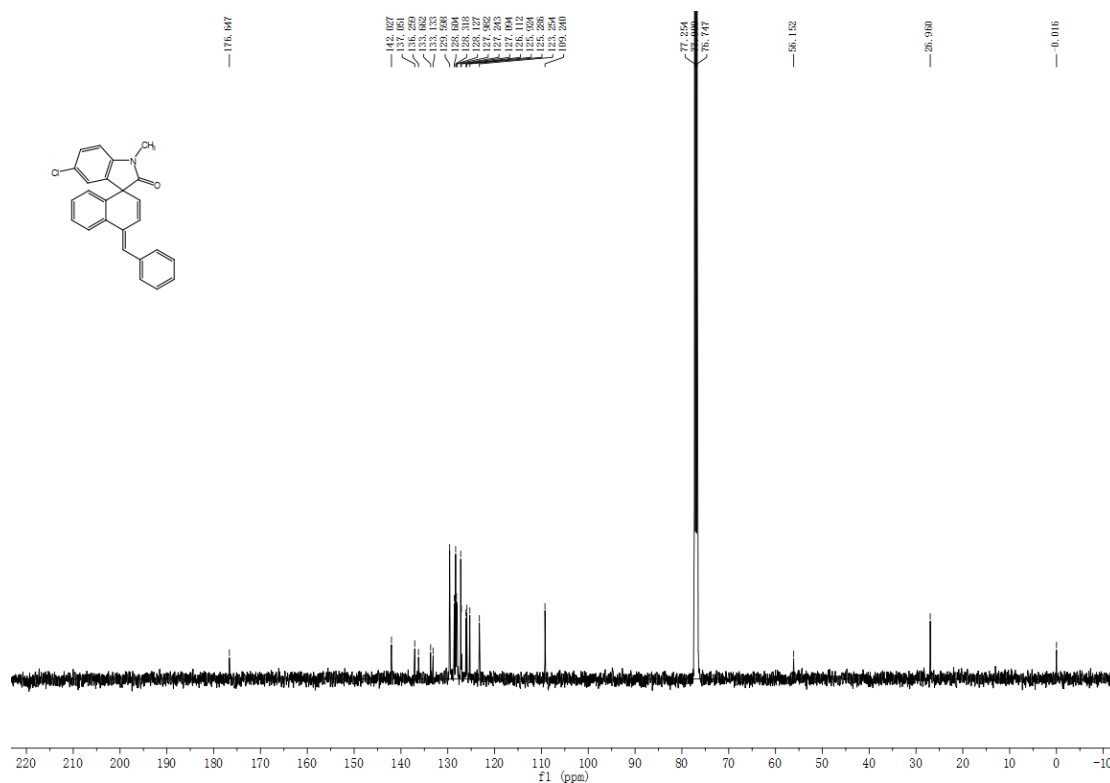
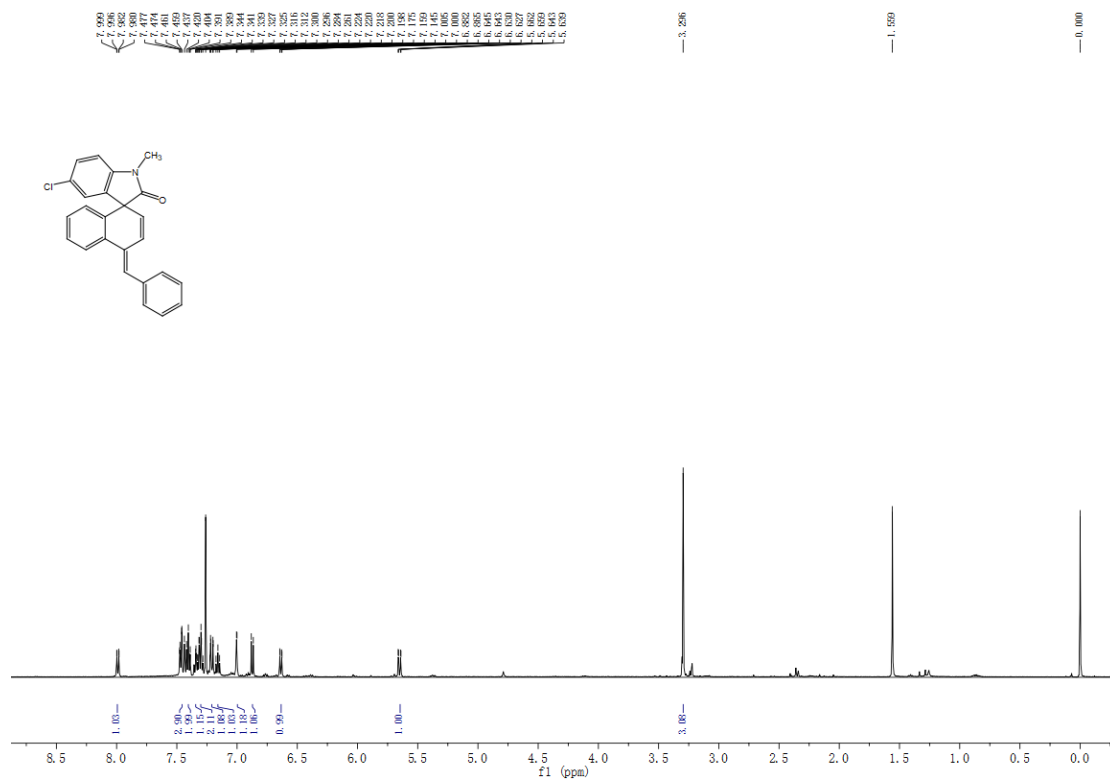




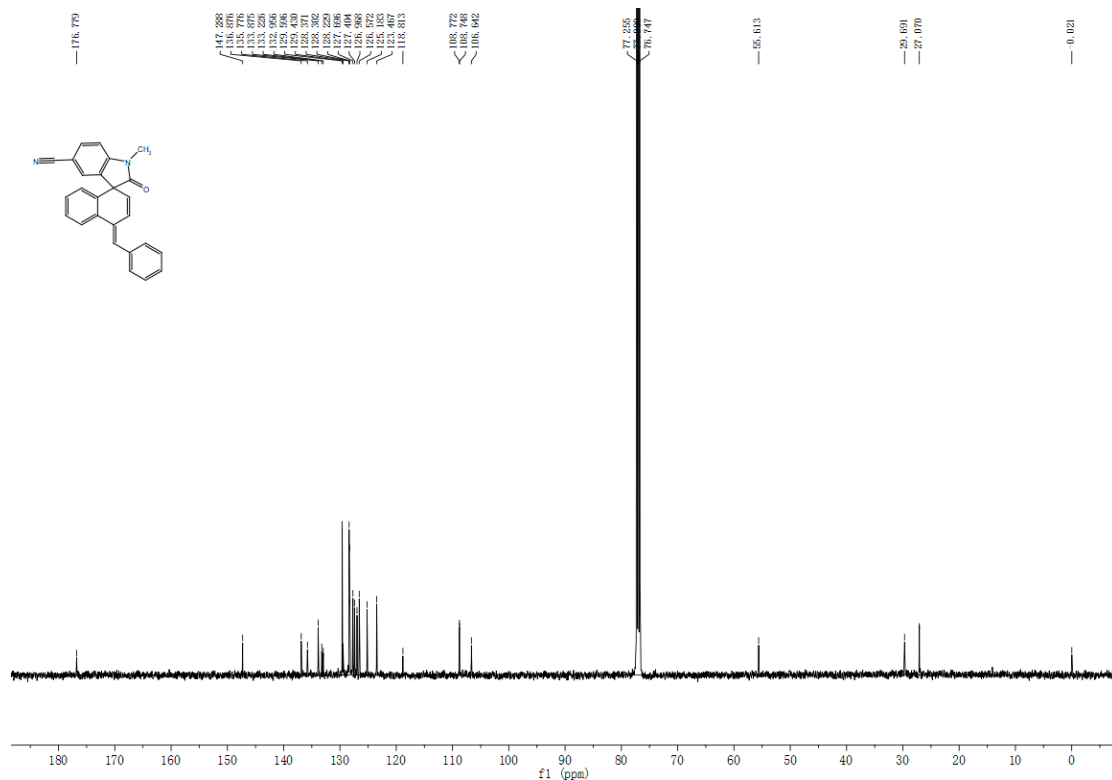
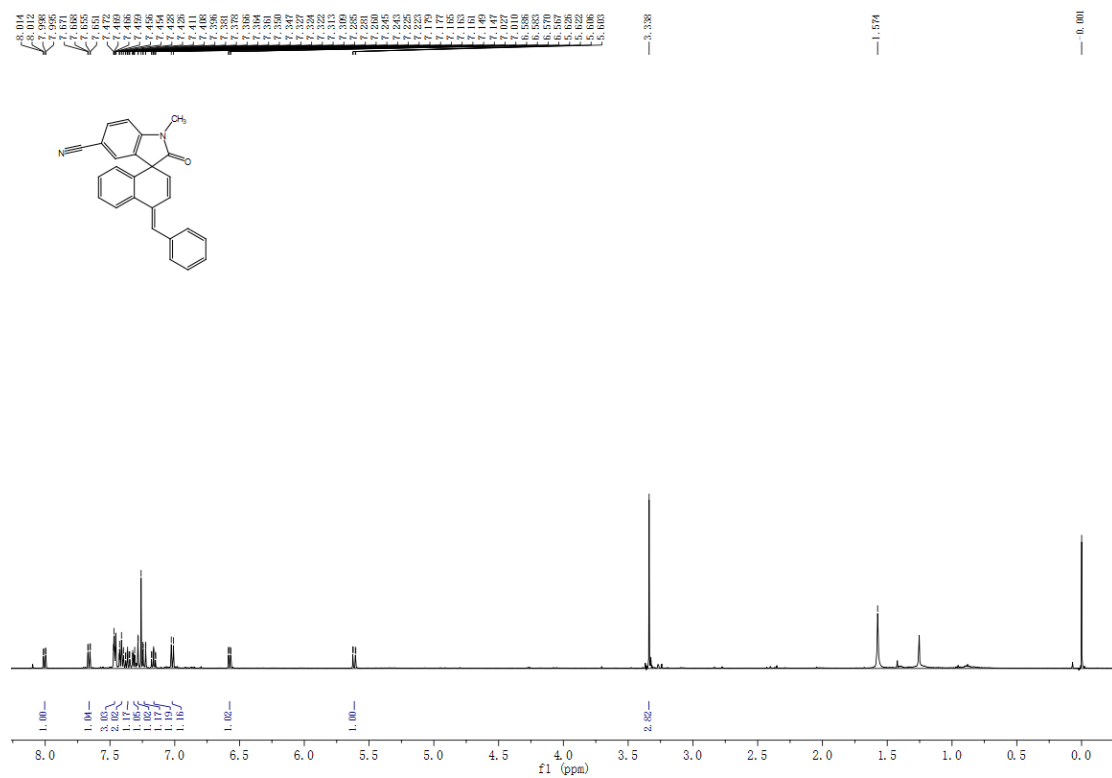
**(E)-4'-benzylidene-6-chloro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one  
(4h)**



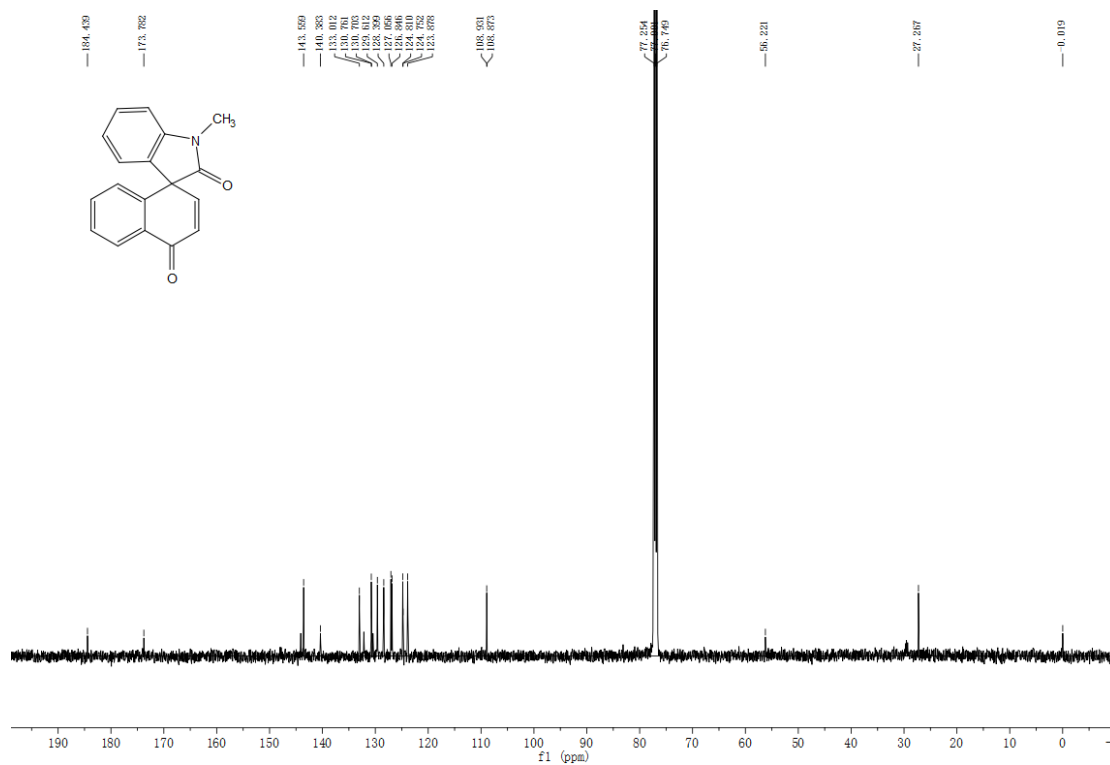
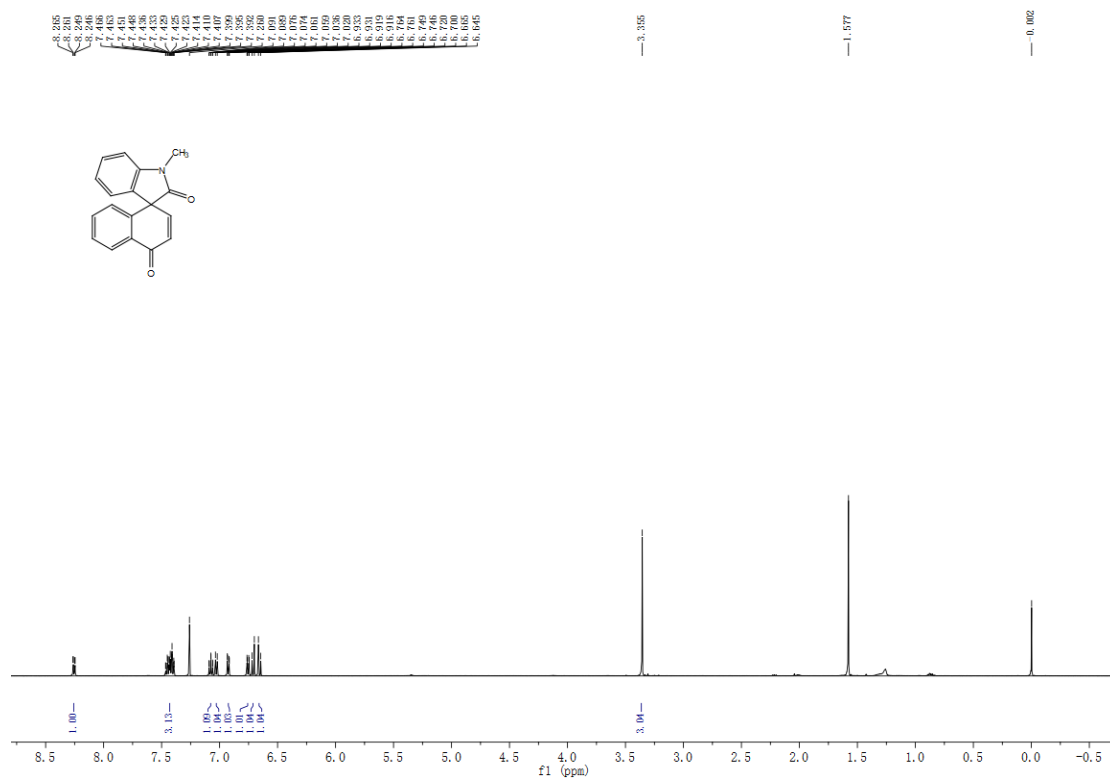
**(E)-4'-benzylidene-5-chloro-1-methyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(4i)**



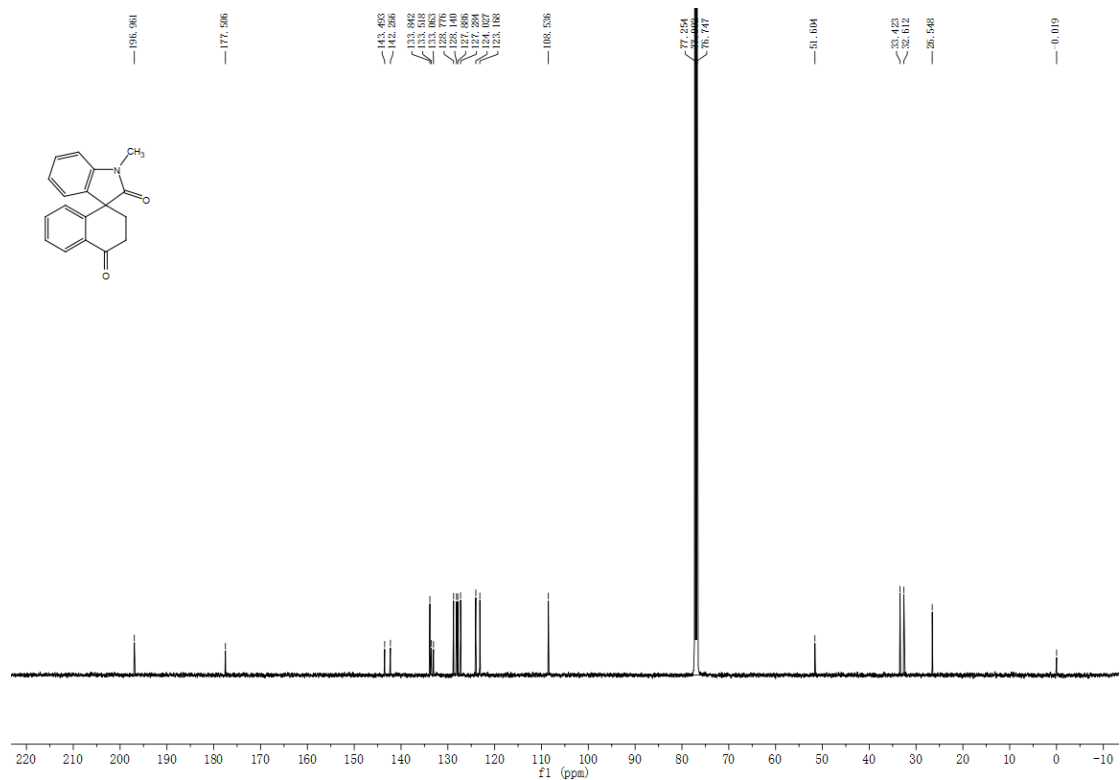
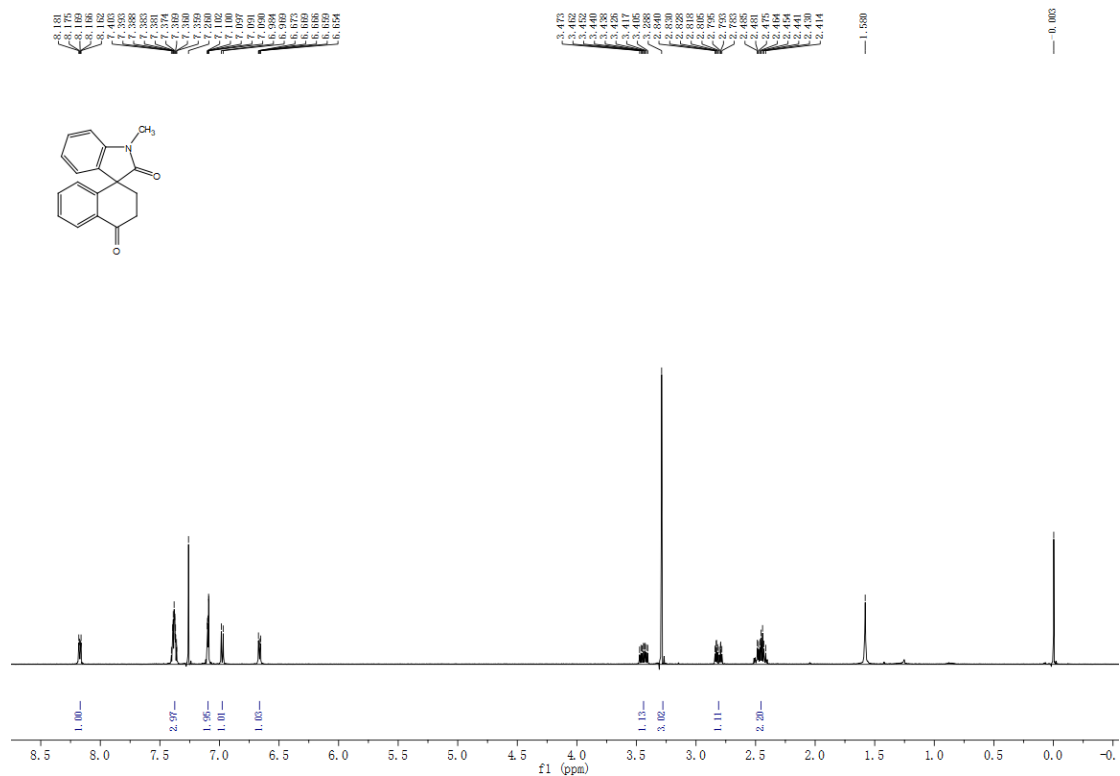
**(E)-4'-benzylidene-1-methyl-2-oxo-4'H-spiro[indoline-3,1'-naphthalene]-5-carbonitrile (4j)**



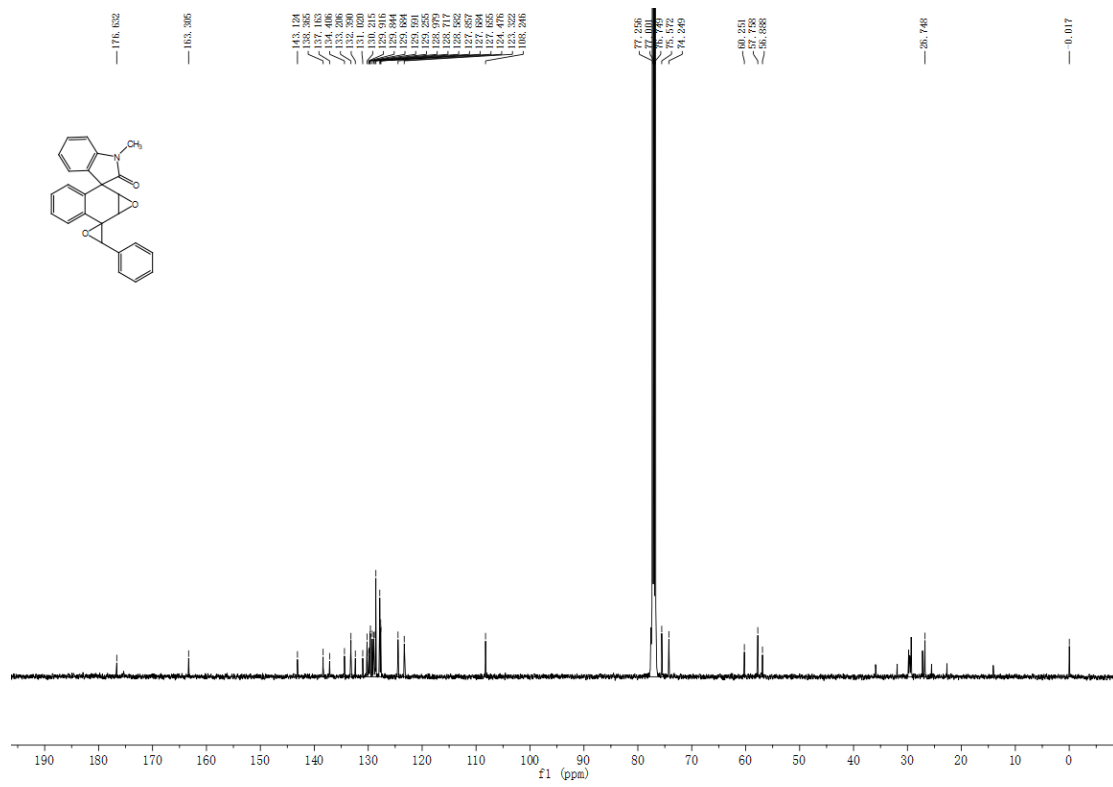
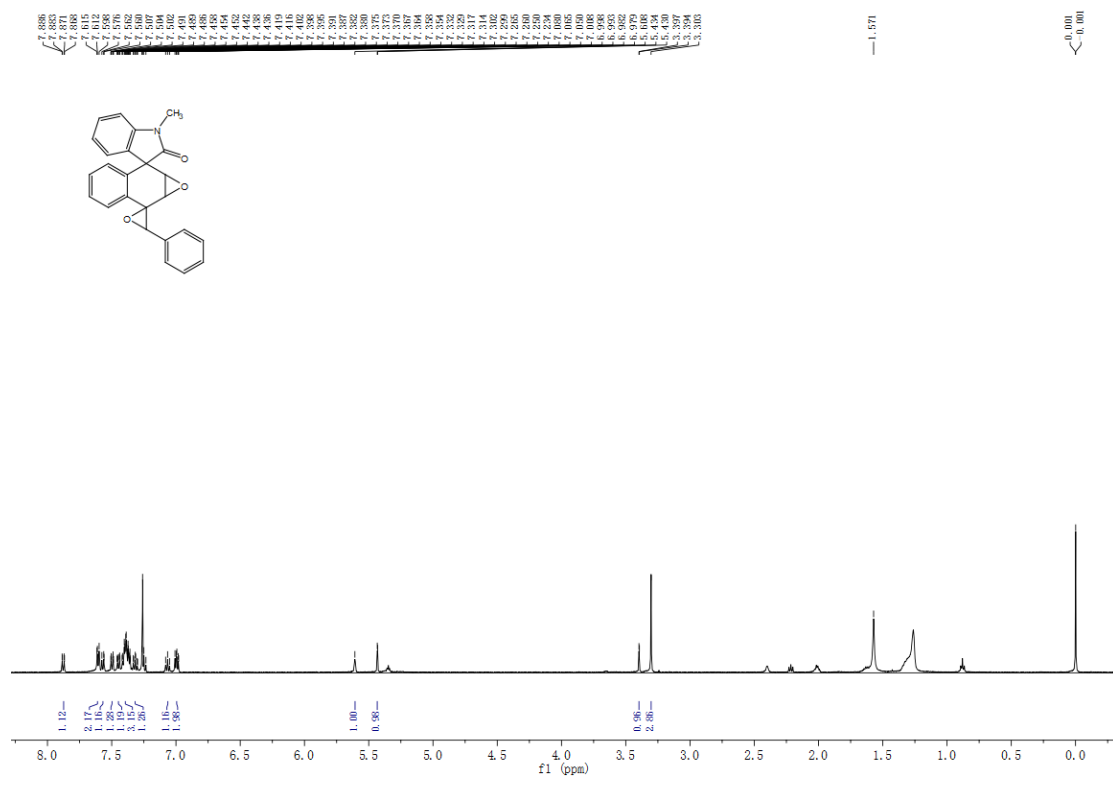
# 1-methyl-4'H-spiro[indoline-3,1'-naphthalene]-2,4'-dione (5)



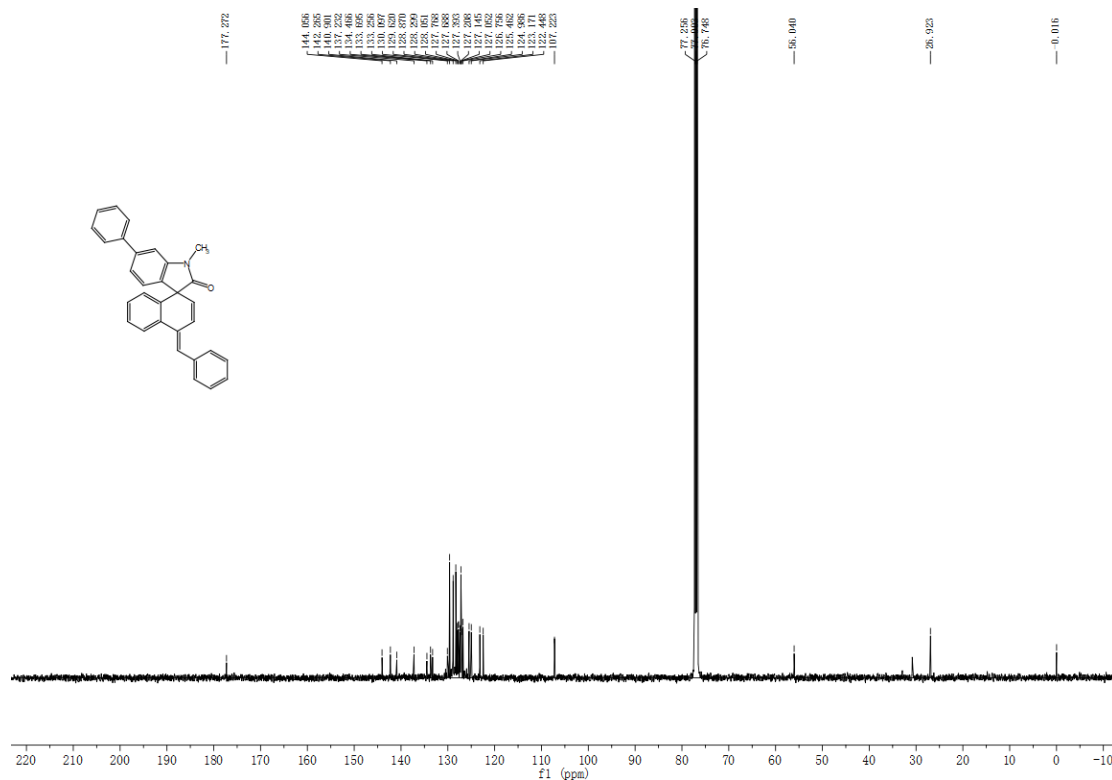
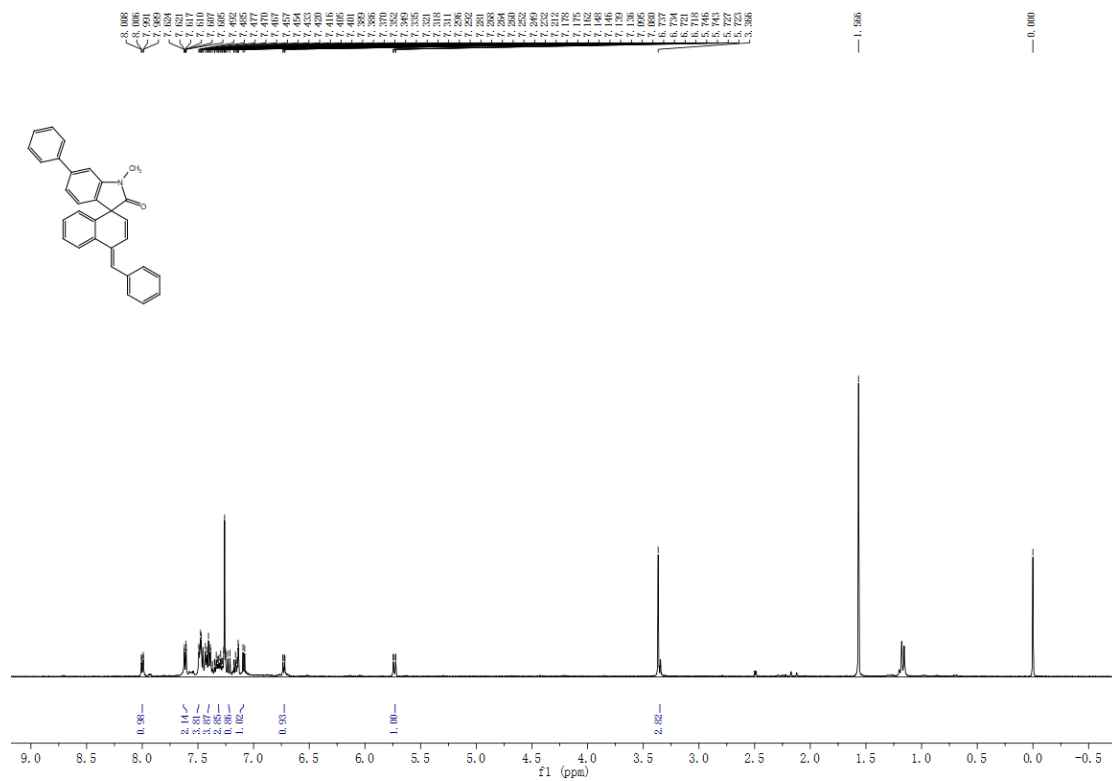
# 1-methyl-2',3'-dihydro-4'H-spiro[indoline-3,1'-naphthalene]-2,4'-dione (6)



**1-methyl-3''-phenyl-1a',7a'-dihydrodispiro[indoline-3,2'-naphtho[2,3-b]oxirene-7',2''-oxiran]-2-one (7)**

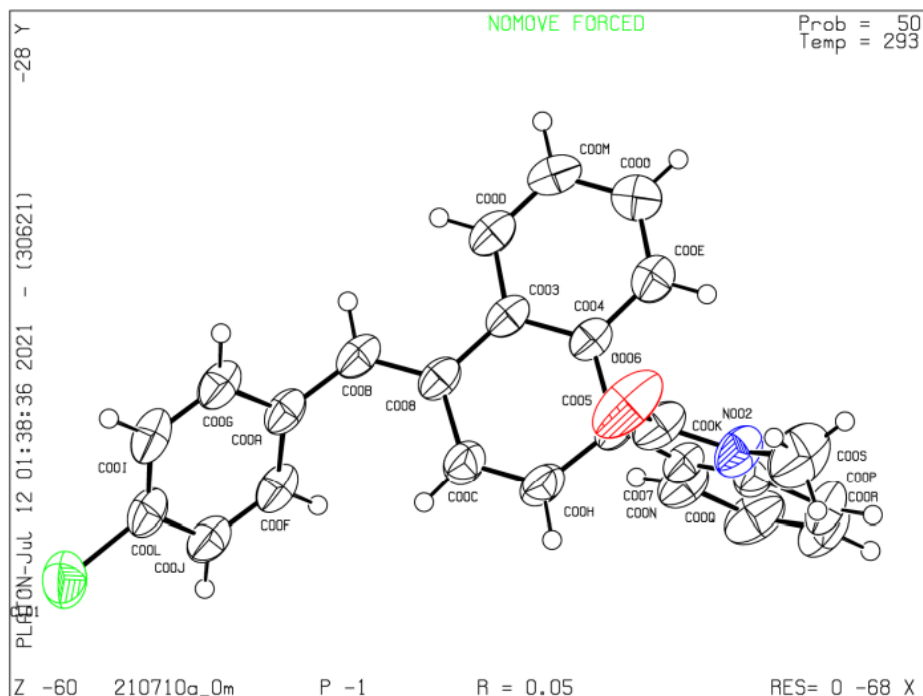


**(E)-4'-benzylidene-1-methyl-6-phenyl-4'H-spiro[indoline-3,1'-naphthalen]-2-one**  
**(8)**



## IX. Single crystal X-ray structure analysis

Datablock 210710a\_0m - ellipsoid plot



**Table 1 Summary of X-ray crystallographic data for 3L.**

CCDC Number	2132508
Empirical formula	C <sub>25</sub> H <sub>18</sub> ClNO
Formula weight	383.85
Temperature/K	293.15
Crystal system	triclinic
Space group	P-1
a/Å	8.006(19)
b/Å	9.36(2)
c/Å	14.18(3)
α/°	90.17(3)
β/°	93.99(3)
γ/°	104.70(3)
Volume/Å <sup>3</sup>	1025(4)
Z	2
ρ <sub>calc</sub> /cm <sup>3</sup>	1.244
μ/mm <sup>-1</sup>	0.201
F(000)	400.0



Crystal size/mm <sup>3</sup>	0.22 × 0.21 × 0.2
Radiation	MoK $\alpha$ ( $\lambda = 0.71073$ )
2 $\Theta$ range for data collection/°	2.88 to 49.99
Index ranges	-9 ≤ h ≤ 9, -11 ≤ k ≤ 11, -16 ≤ l ≤ 16
Reflections collected	10075
Independent reflections	3607 [R <sub>int</sub> = 0.1840, R <sub>sigma</sub> = 0.1155]
Data/restraints/parameters	3607/0/254
Goodness-of-fit on F <sup>2</sup>	1.044
Final R indexes [I ≥ 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0526, wR <sub>2</sub> = 0.1272
Final R indexes [all data]	R <sub>1</sub> = 0.0703, wR <sub>2</sub> = 0.1403
Largest diff. peak/hole / e Å <sup>-3</sup>	0.29/-0.48