Supporting Information

Construction of Spirocarbocyclic Scaffolds through Dearomatization Using Calcium Carbide as an Alkyne Source

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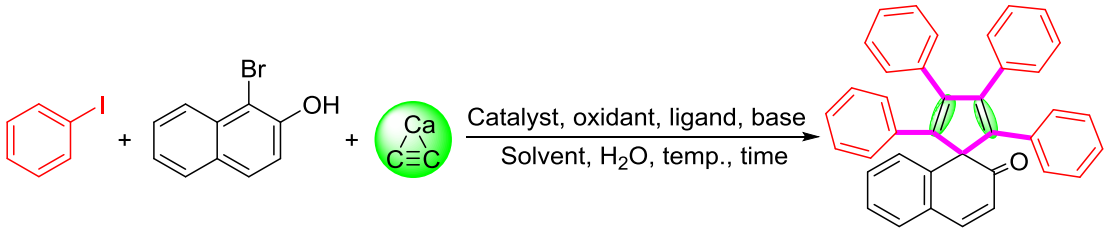
1. Experimental Section

1.1 General Information

^{1}H NMR and ^{13}C NMR spectra were recorded on a Mercury-600 MB or 400 MB instrument using $CDCl_3$ and DMSO-d_6 as solvent and Me_4Si as internal standard. High-resolution mass spectra (HRMS) (ESI) were obtained with a Bruker Daltronics APEX II 47e and Orbitrap Elite mass spectrometer. IR spectra were measured by FT-3000 Fourier Transform Infrared spectrometer. Melting points were observed in an electrothermal melting point apparatus (X-5, Beijing Tech Instrument Co. Ltd, China). Calcium carbide was purchased from Macklin Chemical Company (China, purity: 98%), and ground into powder (*ca.* 50−100 mesh) in a ceramic mortar prior to use. The solvents were all deoxygenated with nitrogen gas for 5 min and dehydrated with molecular sieve for over 12 h prior to use. Unless otherwise noted, the reagents were reagent grade and used without any further purification. Column chromatography was carried out on a flash chromatographic system using silica gel (200-300 mesh) and petroleum ether (60–90 °C) and ethyl acetate as eluent. For thin layer chromatography (TLC), silica gel plates precoated with GF-254 were used. Various 1-arylnaphthalen-2-ols were synthesized by reactions of the corresponding 1-bromonaphthalen-2-ols with arylboronic acids according to literature procedure. [1]

1.2 Condition optimization for synthesis of 5a[a]



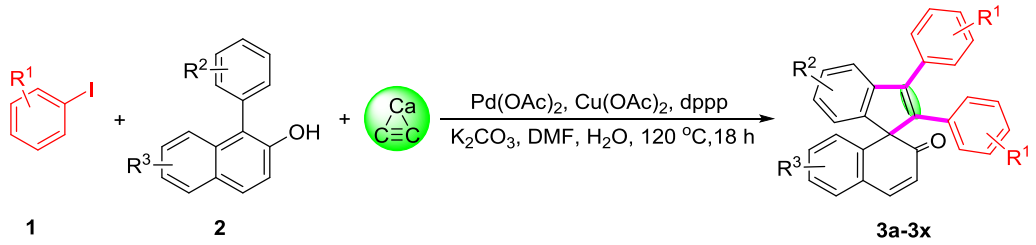
1a **4a** **5a**

Entry	Catalyst	Cu salt	Ligand	Base	Solvent	Yield (%)[b]
1	$Pd(OAc)_2$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	37
2	$Pd_2(dba)_3$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	0
3	$Pd(PPh_3)_4$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	7
4	$PdCl_2$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	31
5	$Pd(PPh_3)_2Cl_2$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	24

6	$Pd(dppf)Cl_2$	$Cu(OAc)_2$	dppp	K_2CO_3	DMF	23
7	$Pd(OAc)_2$	$CuBr_2$	dppp	K_2CO_3	DMF	48
8	**$Pd(OAc)_2$**	**CuI**	**dppp**	**K_2CO_3**	**DMF**	**78**
9	$Pd(OAc)_2$	AgOAc	dppp	K_2CO_3	DMF	0
10	$Pd(OAc)_2$	$AgNO_3$	dppp	K_2CO_3	DMF	Trace
11	$Pd(OAc)_2$	CuI	dppp	DMAP	DMF	15
12	$Pd(OAc)_2$	CuI	dppp	^tBuOK	DMF	11
13	$Pd(OAc)_2$	CuI	dppp	Cs_2CO_3	DMF	52
14	$Pd(OAc)_2$	CuI	dppp	NaOH	DMF	21
15	$Pd(OAc)_2$	CuI	Xantphos	K_2CO_3	DMF	46
16	$Pd(OAc)_2$	CuI	dppb	K_2CO_3	DMF	74
17	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMSO	43
18	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	NMP	26
19	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	PhMe	12
20[c]	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMF	67
21[d]	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMF	78
22[e]	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMF	74
23[f]	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMF	33
24[g]	$Pd(OAc)_2$	CuI	dppp	K_2CO_3	DMF	74

[a]Reaction conditions: **1a** (0.8 mmol), **2a** (0.2 mmol), CaC_2 (1.2 mmol), catalyst (0.02 mmol), Cu salt (0.04 mmol), ligand (0.03 mmol), base (0.4 mmol), and H_2O (2.4 mmol) in solvent (4 mL) were stirred in an oil bath at 120 °C for 18 h; [b]The isolated yield; [c]At 100 °C; [d]At 140 °C; [e]Time 15 h; [f]With 0.8 mmol of CaC_2; [g]With 1.5 mmol of CaC_2.

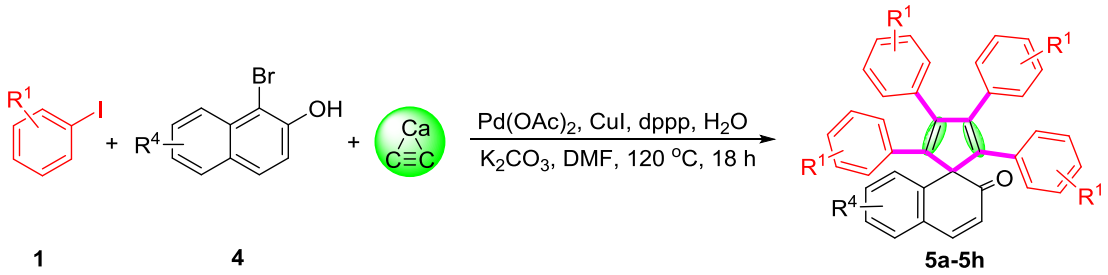
1.3 The general procedure for the synthesis of products 3a−3x.



Iodoarene **1** (0.4 mmol), 1-arylnaphthalen-2-ol **2** (0.2 mmol), calcium carbide (0.6 mmol, 38.4 mg), potassium carbonate (0.4 mmol, 55.3 mg), copper acetate (0.42 mmol, 76.3 mg), palladium(II) acetate (0.02 mmol, 4.5 mg),

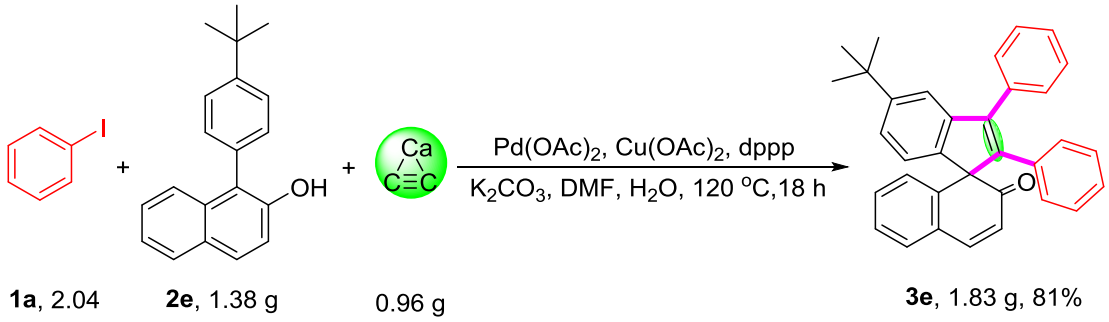
1,3-bis(diphenylphosphino) propane (0.03 mmol, 12.4 mg) and water (1.2 mmol, 21.6 mg) in *N*,*N*-dimethylformamide (4 mL) under open air condition were heated in an oil bath at 120 °C for 18 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ethyl acetate (EA)/petroleum ether (PE) (1:10−1:20) as eluent to give the pure product **3a**−**3x**.

1.4 The general procedure for the synthesis of products 5a−5h.



Iodoarene **1** (0.8 mmol), 1-bromonaphthalen-2-ol **4** (0.2 mmol), calcium carbide (1.2 mmol, 76.8 mg), potassium carbonate (0.4 mmol, 55.3 mg), cuprous iodide (0.04 mmol, 7.7 mg), palladium (II) acetate (0.02 mmol, 4.5 mg), 1,3-bis(diphenylphosphino) propane (0.03 mmol, 12.4 mg) and water (2.4 mmol, 43.2 mg) in *N*,*N*-dimethylformamide (4 mL) were heated in an oil bath at 120 °C for 18 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×10 mL), and washed with saturated brine (3×10 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ethyl acetate (EA)/petroleum ether (PE) (1:10−1:20) as eluent to give the pure product **5a**−**5h**.

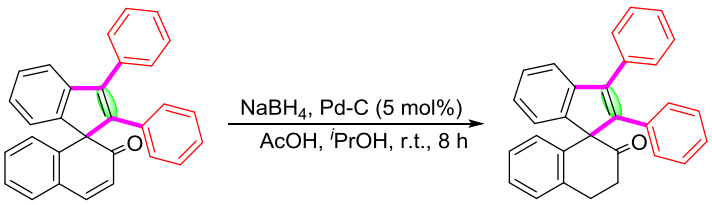
1.5 Gram-scale synthesis of 5-(*tert*-butyl)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (3e)



1a, 2.04 **2e**, 1.38 g 0.96 g **3e**, 1.83 g, 81%

Iodobenzene **1a** (10 mmol, 2.04 g), 5-(*tert*-butyl)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one **2e** (5 mmol, 1.38 g), calcium carbide (15 mmol, 0.96 g), potassium carbonate (10 mmol, 1.38 g), copper acetate (10.5 mmol, 1.91 g), palladium (II) acetate (0.5 mmol, 0.11 g), 1,3-bis(diphenylphosphino) propane (0.75 mmol, 0.31 g) and water (30 mmol, 0.54 g) in *N*,*N*-dimethylformamide (50 mL) under open air condition were heated in an oil bath at 120 °C for 18 h . After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×50 mL), and washed with saturated brine (3×50 mL). The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ethyl acetate (EA)/petroleum ether (PE) (1:20) as eluent to give the pure product **3e** (1.83 g, 81%).

1.6 The Synthesis of 2,3-diphenyl-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (6)



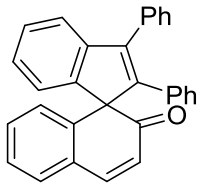
3a **6**, 76%

2,3-Diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3a**) (0.2 mmol, 0.08 g), $NaBH_4$ (0.8 mmol, 0.03 g), Pd-C (0.01 mmol, 0.001 g) and AcOH (1.6 mmol, 0.10 g) in ^{i}PrOH (3 mL) were stirred at room temperature for 8 h. After the completion of the reaction, the resulting mixture was filtered to remove the solid, and the liquor was extracted with ethyl acetate (3×50 mL), and washed with saturated brine (3×50 mL).

The resulting organic phase was dried with anhydrous sodium sulfate, and concentrated under reduced pressure. The residue was isolated by column chromatography using petroleum ethyl acetate (EA)/petroleum ether (PE) (1:20) as eluent to give the pure product **6** (60.5 mg, 76%).

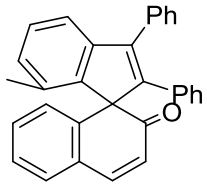
2. Analytical data for compounds 3a−3x

2.1 *2,3-Diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3a**)[2]



Yellow solid (58.6 mg, 74% yield). M.p. 175 – 176 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). IR (KBr): 3058, 2939, 2841, 1658, 1617, 1596, 1567, 1480, 1030, 741 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.9 Hz, 1H), 7.54 (d, *J* = 7.4 Hz, 2H), 7.47 – 7.39 (m, 4H), 7.29 (t, *J* = 7.2 Hz, 2H), 7.23 (d, *J* = 7.8 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.08 – 6.96 (m, 6H), 6.86 (d, *J* = 7.0 Hz, 2H), 6.41 (d, *J* = 9.9 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.7, 147.7, 146.2, 145.4, 145.1, 144.7, 141.1, 135.2, 134.3, 130.7, 129.9, 129.7, 129.5, 129.1, 128.8, 127.9, 127.8, 127.7, 127.6, 127.0, 126.9, 126.6, 126.3, 121.9, 121.7, 71.7 ppm.

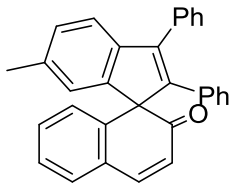
2.2 *7-Methyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3b**)



Yellow solid (55.8 mg, 68% yield). M.p. 196 – 197 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 9.9 Hz, 1H), 7.36 (d, *J* = 6.5 Hz, 2H), 7.31 – 7.24 (m, 8H), 7.04 – 6.88 (m, 5H), 6.61 (d, *J* = 6.9 Hz, 2H), 6.31 (d, *J* = 9.9 Hz, 1H), 1.82 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 197.2, 149.0, 148.9, 146.7, 145.6, 143.2, 139.2, 134.6, 134.4, 132.8, 131.0, 130.4, 129.5, 129.3, 129.0, 128.5, 128.3, 128.0, 127.7, 127.6,

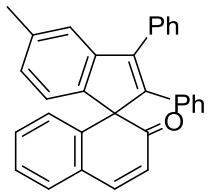
127.5, 127.4, 127.2, 127.1, 118.9, 71.3, 18.1 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{31}H_{23}O^+$: 411.1743; Found: 411.1741.

2.3 *6-Methyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3c**) [2]



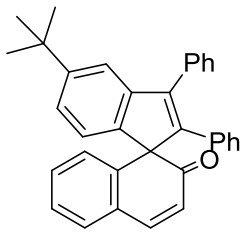
Yellow solid (64.0 mg, 78% yield). M.p. 210 – 211 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 9.9 Hz, 1H), 7.58 (d, *J* = 7.4 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.30 – 7.17 (m, 3H), 7.08 (d, *J* = 7.8 Hz, 1H), 7.01 (t, *J* = 5.8 Hz, 4H), 6.90 – 6.86 (m, 3H), 6.44 (d, *J* = 9.9 Hz, 1H), 2.27 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.9, 148.0, 146.2, 144.6, 144.2, 142.8, 141.4, 136.3, 135.4, 134.5, 130.7, 129.9, 129.7, 129.5, 129.1, 128.8, 128.6, 127.9, 127.8, 127.5, 127.0, 126.9, 126.6, 122.5, 121.6, 71.5, 21.5 ppm.

2.4 *5-Methyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3d**) [2]



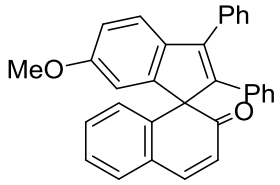
Yellow solid (66.4 mg, 81% yield). M.p. 186 – 187 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.55 (d, *J* = 6.9 Hz, 2H), 7.49 – 7.39 (m, 4H), 7.27 (t, *J* = 7.5 Hz, 1H), 7.17 (t, *J* = 7.6 Hz, 1H), 7.10 (s, 1H), 7.00 – 6.96 (m, 4H), 6.92 – 6.84 (m, 4H), 6.41 (d, *J* = 9.9 Hz, 1H), 2.31 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.8, 146.1, 145.6, 145.3, 144.9, 144.7, 141.3, 137.6, 135.3, 134.4, 130.6, 129.8, 129.6, 129.5, 129.1, 128.8, 127.9, 127.8, 127.5, 127.1, 126.9, 126.8, 126.5, 122.5, 121.3, 71.4, 21.5 ppm.

2.5 *5-(tert-Butyl)-2,3-Diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3e**)



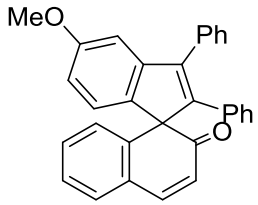
Yellow solid (78.7 mg, 87% yield). M.p. 171 – 172 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.54 (d, *J* = 6.8 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.29 – 7.24 (m, 3H), 7.16 (t, *J* = 6.8 Hz, 1H), 7.09 (dd, *J* = 8.0, 1.8 Hz, 1H), 6.98 (d, *J* = 6.2 Hz, 3H), 6.93 (d, *J* = 7.9 Hz, 1H), 6.84 – 6.82 (m, 2H), 6.39 (d, *J* = 9.9 Hz, 1H), 1.25 (s, 9H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.0, 150.9, 146.1, 145.1, 145.0, 144.9, 144.7, 141.4, 135.3, 134.5, 130.6, 129.8, 129.7, 129.6, 129.1, 128.8, 127.9, 127.8, 127.4, 127.0, 126.8, 126.5, 123.5, 121.0, 118.9, 71.4, 34.8, 31.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{34}H_{29}O^+$: 453.2213; Found: 453.2215.

2.6 *6-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3f**) [2]



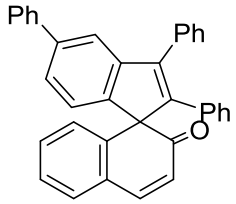
Yellow solid (65.6 mg, 77% yield). M.p. 237 – 238 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.56 (d, *J* = 7.4 Hz, 2H), 7.48 – 7.40 (m, 4H), 7.29 – 7.17 (m, 3H), 7.00 (t, *J* = 8.4 Hz, 4H), 6.86 (s, 2H), 6.80 (d, *J* = 8.3 Hz, 1H), 6.62 (s, 1H), 6.41 (d, *J* = 9.9 Hz, 1H), 3.70 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.7, 158.7, 149.3, 146.2, 144.3, 143.2, 141.3, 138.3, 135.4, 134.6, 130.7, 130.0, 129.6, 129.5, 128.9, 128.8, 127.9, 127.8, 127.6, 127.0, 126.7, 126.5, 122.4, 112.5, 108.8, 71.4, 55.5 ppm.

2.7 *5-Methoxy-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3g**) [2]



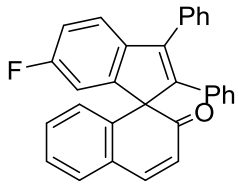
Yellow solid (70.7 mg, 83% yield). M.p. 107 – 108 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). IR (KBr): 3052, 2936, 2833, 1656, 1616, 1593, 1560, 1476, 1033, 745 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 10.0 Hz, 1H), 7.54 – 7.52 (m, 2H), 7.47 – 7.39 (m, 4H), 7.25 (d, *J* = 6.4 Hz, 1H), 7.17 (t, *J* = 7.2, 1H), 7.01 – 6.96 (m, 4H), 6.91 (d, *J* = 8.3 Hz, 1H), 6.84 – 6.82 (m, 3H), 6.61 (dd, *J* = 8.2, 2.5 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.73 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.9, 159.8, 147.0, 146.3, 146.0, 144.5, 141.4, 139.9, 135.1, 134.3, 130.6, 129.8, 129.6, 129.5, 129.1, 128.8, 127.9, 127.8, 127.5, 127.0, 126.9, 126.5, 122.3, 111.9, 107.7, 71.0, 55.5 ppm.

2.8 *2,3,5-Triphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3h**)



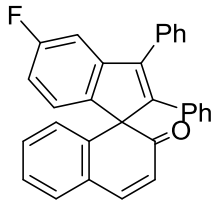
Yellow solid (71.8 mg, 76% yield). M.p. 223 – 224 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 10.0 Hz, 1H), 7.63 (d, *J* = 6.9 Hz, 2H), 7.55 – 7.40 (m, 9H), 7.36 – 7.29 (m, 3H), 7.22 (t, *J* = 6.9 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 1H), 7.08 – 7.04 (m, 4H), 6.94 – 6.92 (m, 2H), 6.48 (d, *J* = 10.0 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.7, 146.7, 146.3, 146.1, 145.8, 144.7, 141.4, 141.3, 141.0, 135.1, 134.3, 130.8, 130.0, 129.7, 129.6, 129.2, 129.0, 128.7, 128.0, 127.9, 127.7, 127.4, 127.3, 127.2, 127.1, 126.6, 125.6, 121.9, 120.8, 71.6 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{36}H_{25}O^+$: 473.1900; Found: 473.1905.

2.9 *6-Fluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3i**) [2]



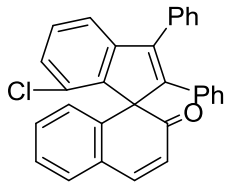
Yellow solid (53.0 mg, 64% yield). M.p. 231 – 232 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). IR (KBr): 3061, 2920, 2851, 1660, 1615, 1595, 1561, 1473, 746, 699 cm^{-1}. 3058, 2939, 2841, 1658, 1617, 1596, 1567, 1480, 1036, 752 ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.52 – 7.49 (m, 2H), 7.46 – 7.36 (m, 4H), 7.29 (t, *J* = 7.4 Hz, 1H), 7.23 – 7.16 (m, 2H), 7.02 – 6.90 (m, 5H), 6.81 (dd, *J* = 7.8, 1.5 Hz, 2H), 6.72 (dd, *J* = 8.3, 2.4 Hz, 1H), 6.39 (d, *J* = 10.0 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.0, 161.7 (d, *J* = 244.9 Hz), 149.3 (d, *J* = 8.1 Hz), 146.3, 144.9 (d, *J* = 4.0 Hz), 143.8, 141.4 (d, *J* = 2.3 Hz), 140.4, 134.9, 134.1, 130.8, 130.1, 129.6, 129.4, 129.0, 128.9, 128.0, 127.9, 127.8, 127.0 (d, *J* = 23.1 Hz), 126.4, 122.7, 122.6, 114.6 (d, *J* = 22.5 Hz), 109.7 (d, *J* = 24.2 Hz), 71.4 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -115.1 ppm.

2.10 *5-Fluoro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3j**) [2]



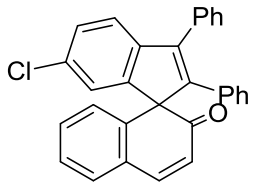
Yellow solid (65.4 mg, 79% yield). M.p. 103 – 104 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 9.9 Hz, 1H), 7.53 – 7.39 (m, 6H), 7.31 – 7.26 (m, 1H), 7.19 (t, *J* = 7.6 Hz, 1H), 7.06 – 6.93 (m, 6H), 6.85 (d, *J* = 7.7 Hz, 2H), 6.76 (t, *J* = 7.4 Hz, 1H), 6.40 (d, *J* = 9.9 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.3, 163.0 (d, *J* = 243.2 Hz), 147.8 (d, *J* = 8.9 Hz), 147.1, 146.2, 143. 9 (d, *J* = 2.9 Hz), 143.1 (d, *J* = 2.5 Hz), 140.7, 134.6, 134.0, 130.8, 130.0, 129.6, 129.4, 129.0 (d, *J* = 17.8 Hz), 128.1, 128.0, 127.8, 127.3, 126.9, 126.4, 122.7 (d, *J* = 9.2 Hz), 113.0, 112.9 (d, *J* = 23.5 Hz), 109.1 (d, *J* = 24.2 Hz), 71.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -114.3 ppm.

2.11 *7-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3k**) [2]



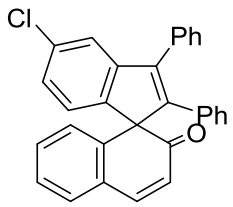
Yellow solid (58.5 mg, 68% yield). M.p. 183 – 184 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 9.9 Hz, 1H), 7.37 – 7.25 (m, 10H), 7.17 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.06 (t, *J* = 7.4 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.89 (d, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.2 Hz, 2H), 6.33 (d, *J* = 9.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 195.8, 150.0, 148.8, 147.6, 145.7, 142.5, 137.7, 134.0, 133.8, 131.4, 130.2, 129.5, 129.4, 129.3, 129.0, 128.4, 127.8, 127.7, 127.6, 127.5, 127.1, 126.7, 119.5, 71.2 ppm.

2.12 *6-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3l**) [2]



Yellow solid (61.9 mg, 72% yield). M.p. 251 – 252 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ7.69 (d, *J* = 9.9 Hz, 1H), 7.55 – 7.39 (m, 6H), 7.32 – 7.18 (m, 4H), 7.04 – 6.98 (m, 5H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.43 (d, *J* = 9.8 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 195.9, 149.1, 146.5, 145.6, 144.1, 143.9, 140.2, 134.7, 134.0, 131.9, 130.9, 130.2, 129.6, 129.4, 129.1, 129.0, 128.2, 128.1, 128.0, 127.9, 127.3, 126.9, 126.4, 122.7, 122.3, 71.4 ppm.

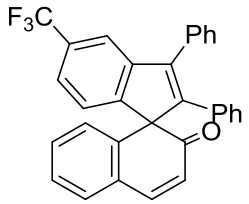
2.13 *5-Chloro-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3m**) [2]



Yellow solid (64.5 mg, 75% yield). M.p. 148 – 149 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (d, *J* = 9.8 Hz, 1H), 7.53 – 7.39 (m, 6H), 7.31 – 7.26 (m, 2H), 7.19 (t, *J* = 7.5 Hz,

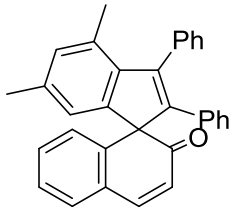
1H), 7.05 – 6.91 (m, 6H), 6.84 (dd, *J* = 8.0, 1.4 Hz, 2H), 6.40 (d, *J* = 10.0 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.0, 147.4, 146.8, 146.3, 145.9, 143.7, 140.3, 134.5, 133.9, 133.8, 130.8, 130.1, 129.6, 129.4, 129.1, 129.0, 128.1, 128.0, 127.8, 127.4, 126.9, 126.4, 126.2, 122.7, 122.0, 71.2 ppm.

2.14 *2,3-Diphenyl-5-(trifluoromethyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3n**)[2]



Yellow solid (78.0 mg, 84% yield). M.p. 192 – 193 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 9.9 Hz, 1H), 7.55 – 7.42 (m, 7H), 7.36 – 7.30 (m, 2H), 7.23 – 7.19 (m, 1H), 7.11 (d, *J* = 7.8 Hz, 1H), 7.07 – 6.99 (m, 3H), 6.95 (d, *J* = 7.3 Hz, 1H), 6.87 – 6.84 (m, 2H), 6.42 (d, *J* = 10.0 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 195.6, 151.0, 147.0, 146.4, 146.3, 143.6, 139.7, 134.2, 133.7, 130.8, 130.3 (q, *J* = 31.8), 130.2, 129.6, 129.3, 129.1, 128.2, 128.0, 127.5, 126.8, 126.4, 124.2 (q, *J* = 270.8), 123.3 (q, *J* = 3.9), 122.0, 118.4 (q, *J* = 3.8), 71.6 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.1 ppm.

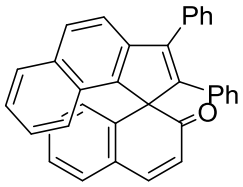
2.15 *4,6-Dimethyl-2,3-diphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3o**) [2]



Yellow solid (61.9 mg, 73% yield). M.p. 249 – 250 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (d, *J* = 10.0 Hz, 1H), 7.58 (d, *J* = 7.3 Hz, 1H), 7.53 (d, *J* = 7.5 Hz, 1H), 7.49 – 7.38 (m, 4H), 7.28 (t, *J* = 6.8 Hz, 1H), 7.21 (t, *J* = 7.6 Hz, 1H), 7.08 (d, *J* = 7.6 Hz, 1H), 6.97 – 6.93 (m, 3H), 6.83 – 6.80 (d, *J* = 4.4 Hz, 3H), 6.71 (s, 1H), 6.44 (d, *J* = 9.9 Hz, 1H), 2.22 (s, 3H), 1.92 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.9, 148.2, 146.5, 146.1, 144.6, 141.7, 140.1, 138.3, 136.1, 134.5, 132.9, 132.0,

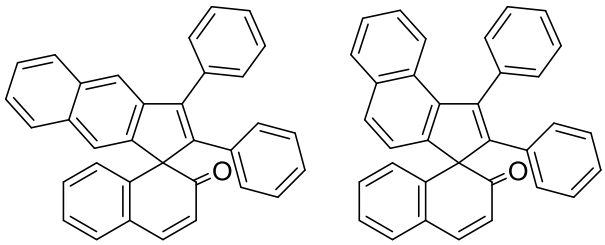
130.7, 130.0, 129.9, 129.6, 128.9, 128.8, 128.5, 127.8, 127.6, 127.5, 127.0, 126.6, 120.3, 71.1, 21.2, 20.1 ppm.

2.16 *2,3-Diphenyl-2'H-spiro[cyclopenta[a]naphthalene-1,1'-naphthalen]-2'-one* (**3p**)[2]



Yellow solid (71.4 mg, 80% yield). M.p. 228 – 229 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.5 Hz, 1H), 7.83 (d, *J* = 8.1 Hz, 1H), 7.62 (d, *J* = 8.5 Hz, 1H), 7.55 (d, *J* = 10.0 Hz, 1H), 7.43 (d, *J* = 6.8 Hz, 2H), 7.38 – 7.26 (m, 5H), 7.24 – 7.20 (m, 2H), 7.11 (t, *J* = 7.1 Hz, 2H), 7.03 (t, *J* = 7.4 Hz, 1H), 6.96 (t, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 7.8 Hz, 1H), 6.68 (d, *J* = 7.2 Hz, 2H), 6.36 (d, *J* = 9.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.7, 150.2, 145.9, 145.8, 144.6, 143.5, 140.0, 134.5, 134.4, 133.2, 130.6, 130.4, 129.8, 129.7, 129.2, 129.1, 129.0, 128.5, 128.2, 127.8, 127.7, 127.6, 127.4, 127.3, 127.2, 127.0, 125.0, 123.4, 119.9, 71.5 ppm.

2.17 *2,3-Diphenyl-2'H-spiro[cyclopenta[b]naphthalene-1,1'-naphthalen]-2'-one and 1,2-diphenyl-2'H-spiro[cyclopenta[a]naphthalene-3,1'-naphthalen]-2'-one* (**3q**)

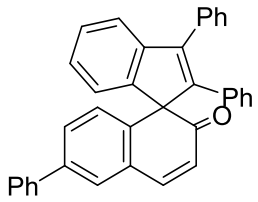


60:40

Yellow solid (73.2 mg, 82% yield). M.p. 143 – 144 ºC. Purified by column chromatography (EA/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79 – 7.74 (m, 1.2H), 7.70 (d, *J* = 9.9 Hz, 0.8H), 7.65 (s, 1H), 7.59 (d, *J* = 8.8 Hz, 1.6H), 7.55 – 7.48 (m, 3.4H), 7.46 – 7.39 (m, 2.4H), 7.35 (t, *J* = 7.5 Hz, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.18 – 7.12 (m, 2.6H), 7.02 – 6.94 (m, 4H), 6.90 – 6.78 (m, 2H), 6.45 (d, *J* =

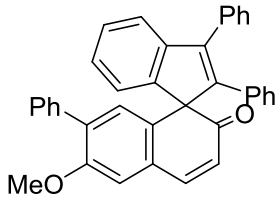
9.9 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.9, 196.2, 146.8, 146.6, 146.3, 146.2, 146.1, 145.9, 145.2, 144.6, 143.9, 142.0, 140.4, 140.2, 138.0, 135.2, 134.3, 134.2, 134.1, 133.5, 132.5, 130.7, 130.6, 130.1, 130.0, 129.9, 129.8, 129.7, 129.6, 129.5, 129.2, 129.1, 129.0, 128.9, 128.8, 128.7, 128.2, 128.0, 127.9, 127.8, 127.7, 127.6, 127.5, 127.2, 127.1, 126.9, 126.8, 126.7, 126.4, 125.9, 125.6, 125.5, 125.2, 124.3, 120.5, 120.3, 119.8, 71.9, 70.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{34}H_{23}O^+$: 447.1743; Found: 447.1745.

2.18 *2,3,6'-Triphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3r**) [3]



Yellow solid (67.1 mg, 71% yield). M.p. 145 – 146 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 9.9 Hz, 1H), 7.65 (s, 1H), 7.5 (t, *J* = 6.4 Hz, 4H), 7.48 – 7.27 (m, 9H), 7.10 – 6.99 (m, 6H), 6.90 (t, *J* = 5.1 Hz, 2H), 6.46 (d, *J* = 9.9 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.6, 147.7, 146.1, 145.5, 145.0, 144.8, 140.5, 139.9, 139.7, 135.2, 134.4, 130.1, 129.6, 129.3, 129.1, 128.9, 128.8, 128.5, 128.0, 127.9, 127.8, 127.7, 127.4, 127.1, 127.0, 126.9, 126.4, 121.9, 121.7, 71.6 ppm.

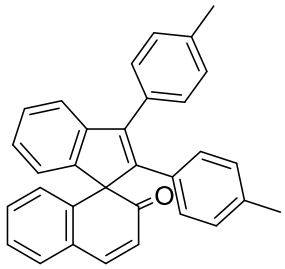
2.19 *7'-Methoxy-2,3,6'-triphenyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3s**)



Yellow solid (65.3 mg, 65% yield). M.p. 203 – 204 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). IR (KBr): 3058, 2932, 2837, 1665, 1600, 1594, 1470, 1439, 1263, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.42 (m, 10H), 7.36 – 7.28 (m, 3H), 7.15 – 7.05 (m, 5H), 6.99 – 6.93 (m, 3H), 6.82 (d, *J* = 8.7 Hz, 1H), 6.28 (d, *J* = 10.3 Hz, 1H), 3.67 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.9, 156.0, 148.1, 145.5, 145.4, 144.3, 143.7, 135.2, 135.1, 134.5, 132.7, 131.2, 131.0, 130.9, 129.6, 129.3, 128.9, 128.8, 128.2, 128.0, 127.8, 127.7,

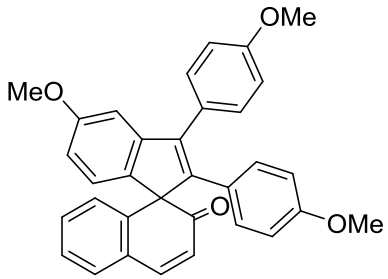
127.6, 127.1, 127.0, 126.6, 126.4, 121.8, 121.7, 113.1, 71.6, 55.8 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{37}H_{27}O_2^+$: 503.2006; Found: 503.2010.

2.20 *2,3-Di-p-tolyl-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3t**) [2]



Yellow solid (69.6 mg, 82% yield). M.p. 113–114 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.99 (d, *J* = 10.0 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.35 – 7.28 (m, 5H), 7.25 – 7.12 (m, 3H), 7.04 (t, *J* = 7.4 Hz, 1H), 6.92 (d, *J* = 7.5 Hz, 1H), 6.85 – 6.80 (m, 3H), 6.66 (d, *J* = 8.2 Hz, 2H), 6.40 (d, *J* = 10.0 Hz, 1H), 2.37 (s, 3H), 2.08 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, DMSO-d_6) δ 196.3, 147.7, 147.5, 145.5, 144.7, 143.9, 141.0, 137.7, 137.0, 132.3, 132.1, 131.6, 131.2, 130.9, 130.2, 129.9, 129.4, 129.2, 129.1, 128.8, 128.2, 128.1, 126.7, 126.2, 121.7, 71.5, 21.4, 21.0 ppm.

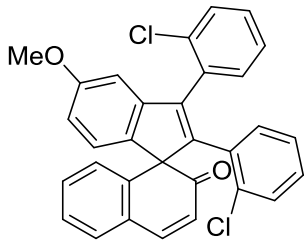
2.21 *5-Methoxy-2,3-bis(4-methoxyphenyl)-4a',8a'-dihydro-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3u**)



Yellow solid (84.0 mg, 86% yield). M.p.= 207 – 208 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.9 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.41 (d, *J* = 7.6 Hz, 1H), 7.27 – 7.23 (m, 1H), 7.16 (t, *J* = 7.6 Hz, 1H), 7.00 – 6.95 (m, 3H), 6.88 (d, *J* = 8.2 Hz, 1H), 6.82 – 6.77 (m, 3H), 6.58 – 6.52 (m, 3H), 6.38 (d, *J* = 9.9 Hz, 1H), 3.87 (s, 3H), 3.73 (s, 3H), 3.65 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 197.2, 159.8, 159.1, 158.3, 147.4, 146.0, 145.3, 142.7, 141.9, 139.6, 130.7, 130.6, 130.3, 129.8, 129.5, 127.5,

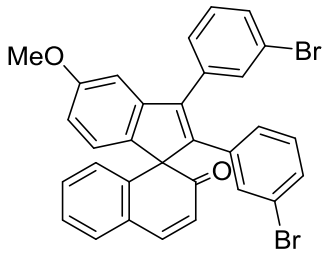
127.4, 127.0, 126.9, 126.5, 122.1, 114.3, 113.4, 111.4, 107.5, 70.8, 55.4, 55.2, 55.0. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{33}H_{27}O_4^+$: 487.1904; Found: 487.1907.

2.22 *2,3-Bis(2-chlorophenyl)-5-methoxy-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3v**)



Yellow solid (44.5 mg, 45% yield). M.p. 197–198 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.35 (m, 2H), 7.27 – 7.24 (m, 2H), 7.23 (s, 1H), 7.21 – 7.16 (m, 2H), 7.15 – 7.11 (m, 1H), 7.09 (dd, *J* = 8.0, 1.2 Hz, 1H), 7.03 – 6.90 (m, 3H), 6.85 – 6.75 (m, 2H), 6.71 – 7.68 (m, 1H), 6.52 (d, *J* = 6.2 Hz, 1H), 6.24 (d, *J* = 9.9 Hz, 1H), 3.79 (s, 3H). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 198.2, 159.8, 146.6, 146.3, 145.3, 143.4, 139.6, 139.2, 134.2, 133.4, 133.1, 133.0, 131.6, 130.8, 130.6, 130.0, 129.5, 129.3, 129.2, 129.1, 128.9, 128.3, 127.8, 127.0, 126.6, 125.4, 124.1, 113.0, 107.7, 72.8, 55.5. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{31}H_{21}Cl_2O_2^+$: 495.0913; Found: 495.0918.

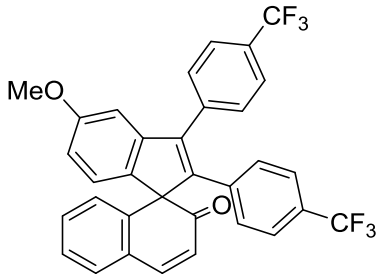
2.23 *2,3-Bis(3-bromophenyl)-5-methoxy-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3w**)



Yellow solid (98.9 mg, 85% yield). M.p. 193–194 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.6 Hz, 2H), 7.55 (d, *J* = 8.2 Hz, 1H), 7.42 (t, *J* = 9.4 Hz, 2H), 7.34 –7.27 (m, 2H), 7.18 (q, *J* = 7.8 Hz, 2H), 6.93 – 6.85 (m, 4H), 6.80 (d, *J* = 2.4 Hz, 1H), 6.72 (d, *J* = 8.0 Hz, 1H), 6.64 (dd, *J* = 8.2, 2.4 Hz, 1H), 6.38 (d, *J* = 9.9 Hz, 1H), 3.75 (s, 3H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 196.3, 159.9, 146.2, 146.0, 145.5,

144.1, 140.4, 139.9, 136.6, 136.0, 132.1, 131.7, 131.3, 130.8, 130.6, 130.3, 130.0, 129.6, 129.5, 128.2, 127.8, 127.7, 126.9, 126.4, 122.9, 122.5, 122.1, 112.4, 107.8, 71.0, 55.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{31}H_{21}Br_2O_2^+$: 582.9903; Found: 582.9907.

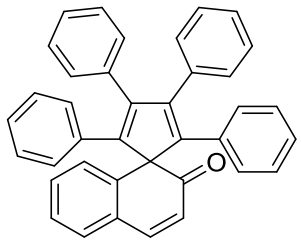
2.24 *5-Methoxy-2,3-bis(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one* (**3x**)[2]



Yellow solid (100.1 mg, 89% yield). M.p. 243–244 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). IR (KBr): 3058, 2917, 2847, 1661, 1616, 1596, 1562, 1479, 1324, 840 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.75 – 7.64 (m, 5H), 7.45 (d, *J* = 7.6 Hz, 1H), 7.32 – 7.27 (m, 3H), 7.21 (t, *J* = 6.9 Hz, 1H), 6.96 – 6.91 (m, 4H), 6.79 (d, *J* = 2.3 Hz, 1H), 6.68 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 1H), 3.75 (s, 3H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 196.1, 160.0, 146.3, 145.8, 145.7, 145.0, 140.3, 139.9, 138.3, 137.5, 130.8, 130.4 (q, *J* = 32.4 Hz), 130.2, 129.8, 129.6, 129.2, 129.1 (q, *J* = 32.1 Hz), 127.9, 126.8, 126.3, 126.0 (q, *J* = 3.8 Hz), 125.6 (q, *J* = 270.6 Hz), 125.1 (q, *J* = 3.7 Hz), 124.0 (q, *J* = 270.7 Hz), 122.6, 112.7, 107.8, 71.2, 55.5 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.8, -62.5 ppm.

3. Analytical data for compounds 5a−5h

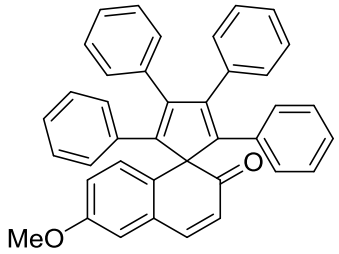
3.1 2,3,4,5-Tetraphenyl-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5a**)[4]



Yellow solid (77.7 mg, 78% yield). M.p. 207 – 208 °C. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^1H NMR (400 MHz, DMSO-d_6)

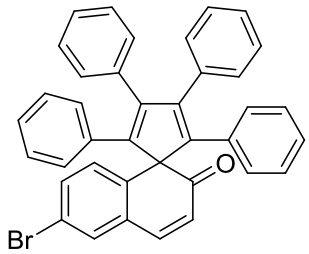
δ 7.61 (d, *J* = 9.9 Hz, 1H), 7.47 – 7.31 (m, 4H), 7.13 (s, 6H), 7.00 – 6.93 (m, 10H), 6.54 (d, *J* = 7.2 Hz, 4H), 6.20 (d, *J* = 9.9 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) δ 195.2, 148.2, 147.2, 146.8, 138.1, 135.4, 134.6, 131.3, 130.7, 130.5, 130.0, 128.8, 128.4, 128.3, 128.2, 127.6, 127.5, 127.2, 127.0, 75.7 ppm.

3.2 6'-Methoxy-2,3,4,5-tetraphenyl-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5b**)



Yellow solid (80.3 mg, 76% yield). M.p. 182 – 183 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). IR (KBr): 3057, 2944, 2833, 1660, 1602, 1564, 1495, 1273, 764, 700 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.22 (t, *J* = 10.0 Hz, 2H), 7.15 – 7.08 (m, 6H), 7.02 – 6.90 (m, 11H), 6.76 (d, *J* = 2.7 Hz, 1H), 6.68 – 6.65 (m, 4H), 6.19 (d, *J* = 9.9 Hz, 1H), 3.81 (s, 3H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.1, 158.7, 147.9, 146.8, 145.5, 135.2, 134.6, 131.5, 130.1, 129.9, 129.1, 128.2, 127.8, 127.7, 127.6, 126.9, 126.8, 116.9, 113.9, 75.5, 55.3 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{39}H_{29}O_2^+$: 529.2162; Found: 529.2166.

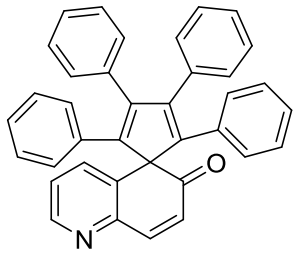
3.3 6'-Bromo-2,3,4,5-tetraphenyl-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5c**)



Yellow solid (93.3 mg, 81% yield). M.p. 247 – 248 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.44 (dd, *J* = 8.3, 2.1 Hz, 1H), 7.39 (d, *J* = 2.1 Hz, 1H), 7.25 – 7.19 (m, 2H), 7.15 – 7.09 (m, 6H), 7.03 – 6.95 (m, 10H), 6.65 – 6.63 (m, 4H), 6.21 (d, *J* = 10.0 Hz, 1H)

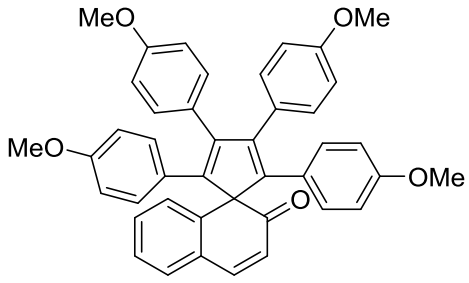
ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 195.1, 147.5, 147.4, 143.9, 137.4, 134.9, 134.3, 133.2, 132.4, 132.0, 130.0, 129.0, 128.7, 128.5, 127.8, 127.7, 127.1, 127.0, 121.1, 75.6 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{38}H_{26}OBr^+$: 577.1162; Found: 577.1161.

3.3 2,3,4,5-Tetraphenyl-6'H-spiro[cyclopentane-1,5'-quinoline]-2,4-dien-6'-one (**5d**)[4]



Yellow solid (72.9 mg, 73% yield). M.p. 219 – 220 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:10). IR (KBr): 3052, 2922, 2850, 1666, 1594, 1560, 1488, 1442, 767, 701 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.55 (dd, *J* = 4.6, 1.7 Hz, 1H), 7.60 (d, *J* = 6.2 Hz, 1H), 7.49 (d, *J* = 10.1 Hz, 1H), 7.23 (dd, *J* = 7.9, 4.7 Hz, 1H), 7.16 – 7.08 (m, 6H), 7.03 – 6.94 (m, 10H), 6.62 (d, *J* = 7.0 Hz, 4H), 6.41 (d, *J* = 10.1 Hz, 1H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 194.8, 149.3, 149.1, 147.8, 147.0, 146.5, 134.8, 134.7, 134.4, 134.0, 131.3, 130.0, 128.9, 127.9, 127.8, 127.2, 124.2, 75.2 ppm.

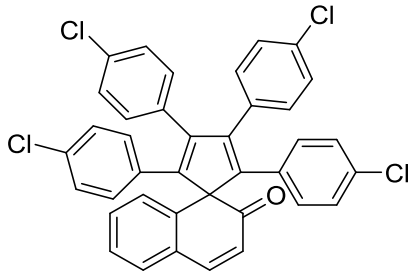
3.4 2,3,4,5-Tetrakis(4-methoxyphenyl)-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5e**)[4]



Yellow solid (82.8 mg, 67% yield). M.p. 201 – 202 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:15). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.32 – 7.29 (m, 3H), 7.25 (d, *J* = 6.3 Hz, 2H), 6.91 (d, *J* = 8.8 Hz, 4H), 6.65 (d, *J* = 8.8 Hz, 4H), 6.56 (d, *J* = 8.9 Hz, 4H), 6.47 (d, *J* = 8.9 Hz, 4H), 6.17 (d, *J* = 9.9 Hz, 1H), 3.72 (s, 6H), 3.62 (s, 6H) ppm. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) δ 196.7,

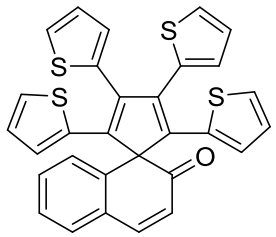
158.3, 158.1, 146.6, 145.9, 145.7, 139.3, 131.4, 130.5, 130.4, 130.2, 129.5, 127.9, 127.4, 127.3, 127.2, 127.0, 113.2, 113.1, 75.7, 55.0, 54.9 ppm.

3.5 2,3,4,5-Tetrakis(4-chlorophenyl)-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5f**)[4]



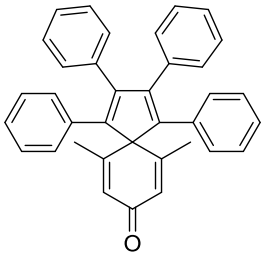
Yellow solid (93.8 mg, 74% yield). M.p. 208 – 209 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.22 (m, 4H), 7.23 (d, *J* = 6.6 Hz, 1H), 7.12 (d, *J* = 8.4 Hz, 4H), 6.94 (d, *J* = 8.5 Hz, 4H), 6.89 (d, *J* = 8.4 Hz, 4H), 6.53 (d, *J* = 8.5 Hz, 4H), 6.18 (d, *J* = 9.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 194.6, 147.6, 145.9, 137.2, 133.5, 133.3, 132.9, 132.4, 131.2, 130.7, 130.5, 130.2, 130.0, 128.4, 128.2, 128.1, 127.1, 126.8, 76.1 ppm.

3.6 2,3,4,5-Tetra(thiophen-2-yl)-2'H-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5g**)[4]



Yellow solid (63.7 mg, 61% yield). M.p. 148 – 149 ºC. Purified by column chromatography (ethyl acetate/petroleum ether, 1:20). IR (KBr): 3067, 2919, 2851, 1655, 1615, 1594, 1560, 1232, 769, 702 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 9.9 Hz, 1H), 7.38 – 7.33 (m, 5H), 7.26 (t, *J* = 3.9 Hz, 1H), 7.04 (d, *J* = 5.1 Hz, 2H), 6.99 – 6.95 (m, 4H), 6.70 (t, *J* = 4.4 Hz, 2H), 6.42 (d, *J* = 3.7 Hz, 2H), 6.29 (d, *J* = 9.9 Hz, 1H) ppm. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) δ 194.3, 145.8, 143.5, 139.1, 138.7, 135.5, 135.2, 131.1, 130.4, 129.9, 129.1, 128.2, 127.5, 127.2, 127.1, 127.0, 126.8, 126.5, 74.3 ppm.

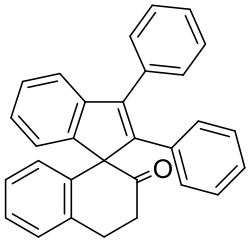
3.7 *6,10-dimethyl-1,2,3,4-tetraphenylspiro[4.5]deca-1,3,6,9-tetraen-8-one* (**5h**)[5]



Yellow solid (55.2 mg, 58% yield). M.p. 224 – 225 °C. Purified by column chromatography (EA/petroleum ether, 1:20). IR (KBr): 3050, 2910, 2849, 1661, 1625, 1487, 1441, 1376, 892, 695 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 – 7.06 (m, 12H), 6.97 – 6.95 (m, 4H), 6.92 – 6.90 (m, 4H), 6.32 (s, 2H), 1.94 (s, 6H). ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 186.6, 156.6, 149.2, 143.2, 134.9, 133.8, 130.8, 129.7, 128.6, 128.1, 128.0, 127.5, 127.3, 71.2, 18.4 ppm.

4. Analytical data for compound 6

2,3-Diphenyl-3',4'-dihydro-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**6**)



Yellow solid (60.5 mg, 76% yield). M.p. 117 – 118 °C. Purified by column chromatography (EA/petroleum ether, 1:20). ^1H NMR (400 MHz, $CDCl_3$) δ 7.43 – 7.39 (m, 3H), 7.36 – 7.27 (m, 4H), 7.23 – 7.21 (m, 2H), 7.18 – 7.15 (m, 1H), 7.12 – 6.99 (m, 5H), 6.82 (d, *J* = 7.5 Hz, 1H), 6.76 – 6.73 (m, 2H), 3.24 – 3.19 (m, 1H), 3.04 – 2.90 (m, 2H), 2.70 – 2.65 (m, 1H) ppm. $^{13}C\{^1H\}$ NMR (150 MHz, $CDCl_3$) δ 207.7, 150.7, 148.4, 145.2, 143.1, 136.8, 136.5, 135.4, 134.5, 129.6, 129.4, 128.4, 128.4, 128.1, 127.8, 127.6, 127.5, 127.2, 127.1, 127.0, 126.4, 122.9, 121.4, 72.7, 40.1, 28.5 ppm. HRMS (ESI): *m/z* $(M+H)^+$ calcd for $C_{30}H_{23}O^+$: 399.1743; Found: 399.1740.

5. ^{1}H, $^{13}C\{^{1}H\}$ NMR and ^{19}F NMR spectra for products 3a−3x

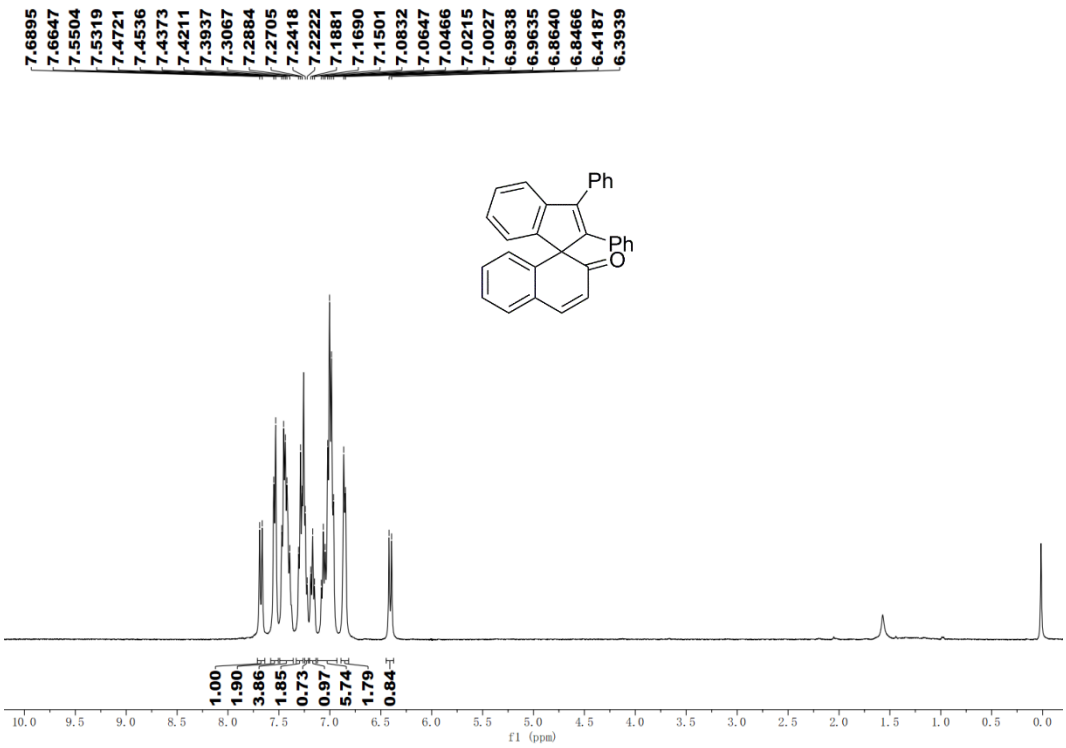


Fig S1. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3a**)

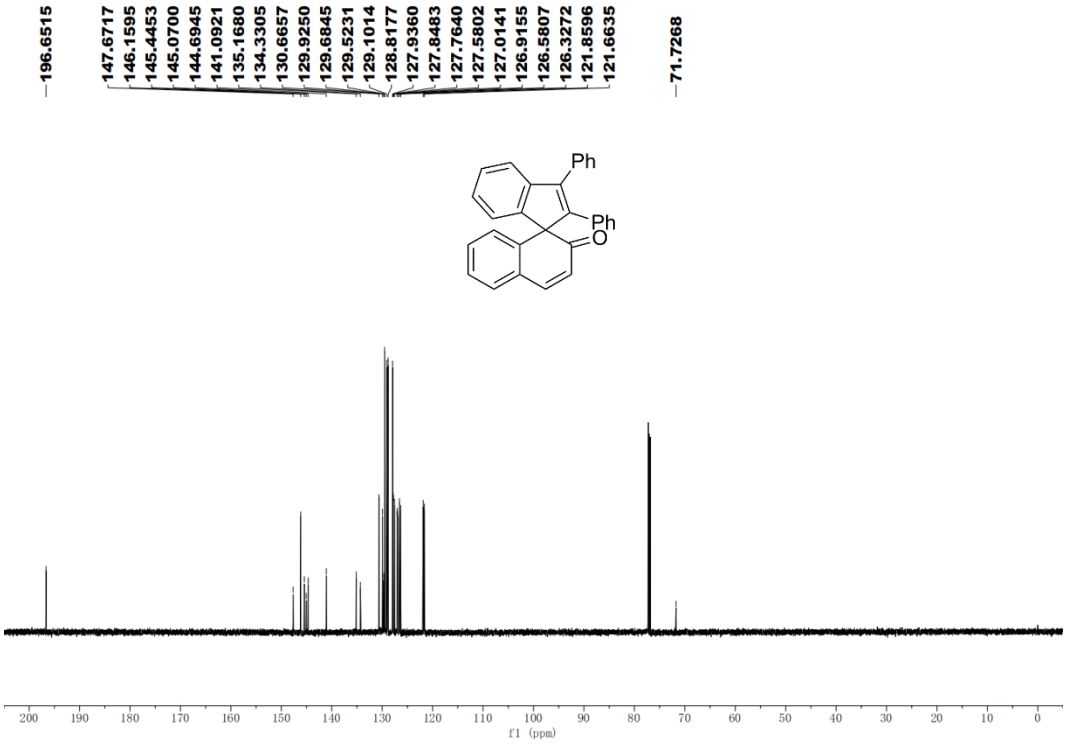


Fig S2. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3a**)

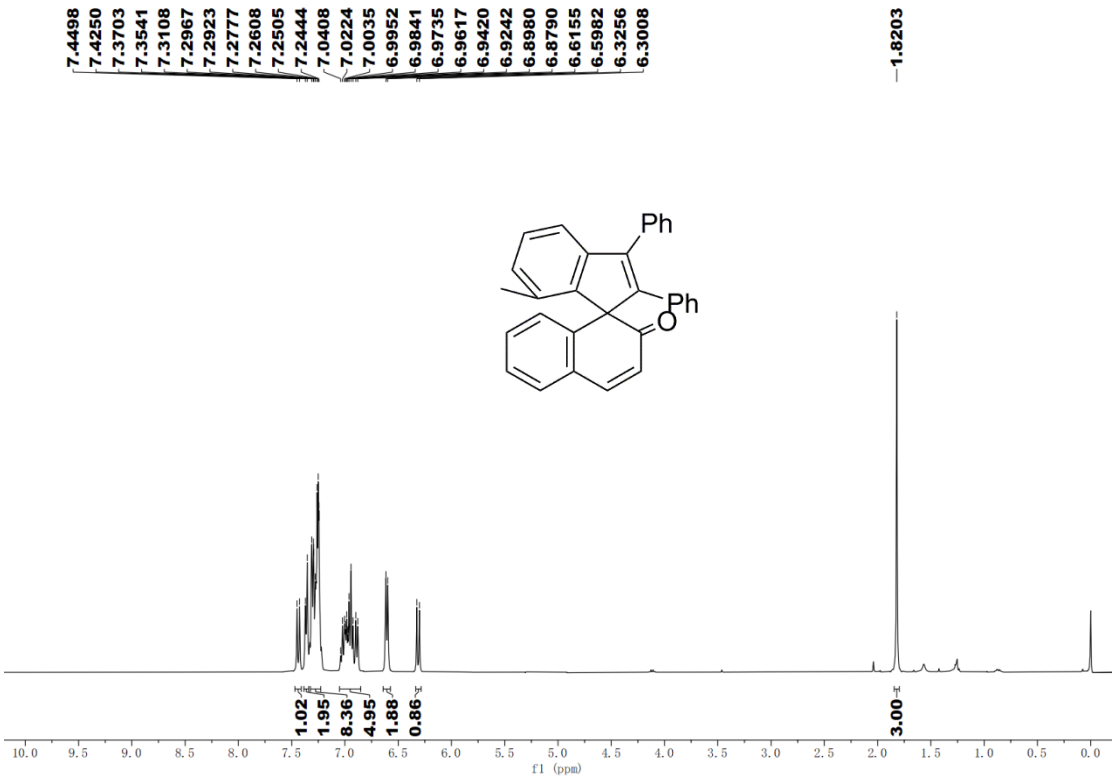


Fig S3. ^{1}H NMR (400 MHz, $CDCl_3$) of 7-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3b**)

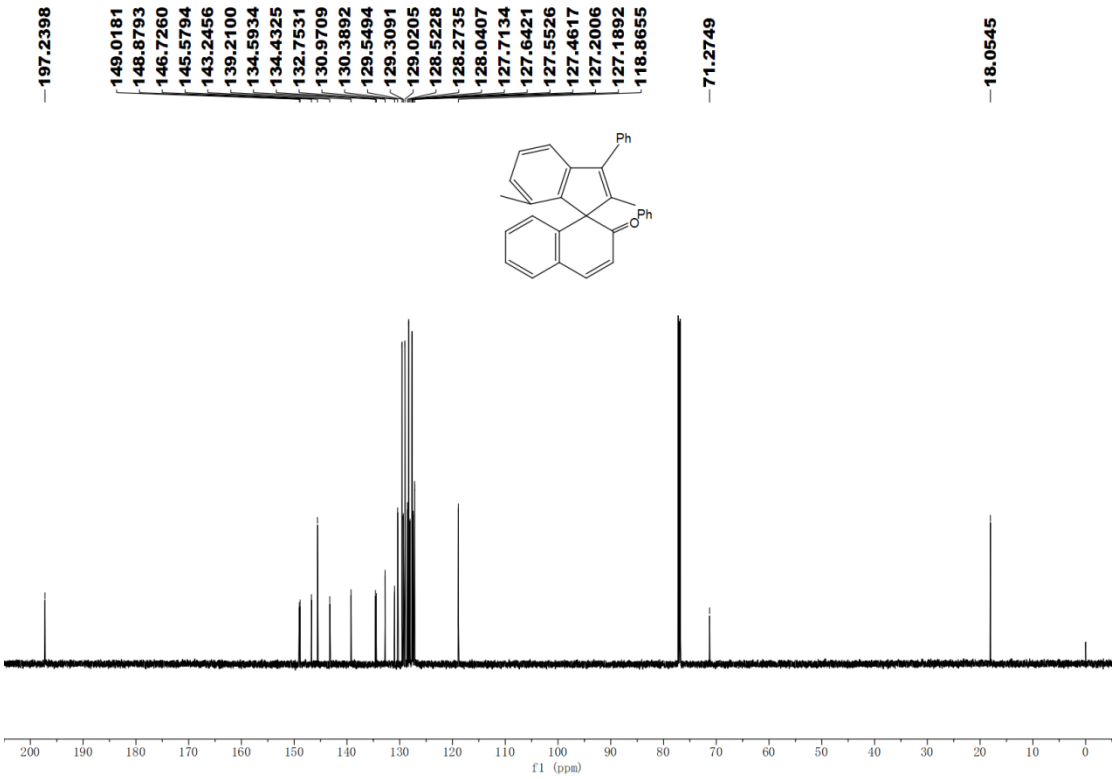


Fig S4. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 7-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3b**)

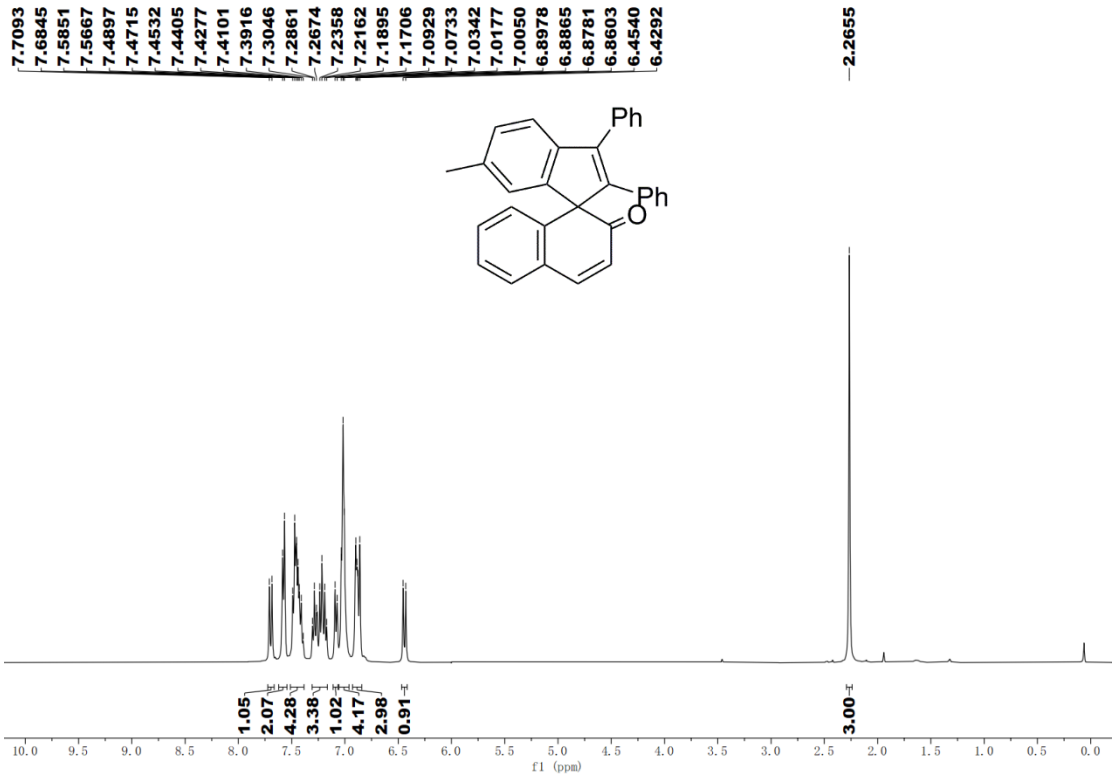


Fig S5. ^{1}H NMR (400 MHz, $CDCl_3$) of 6-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3c**)

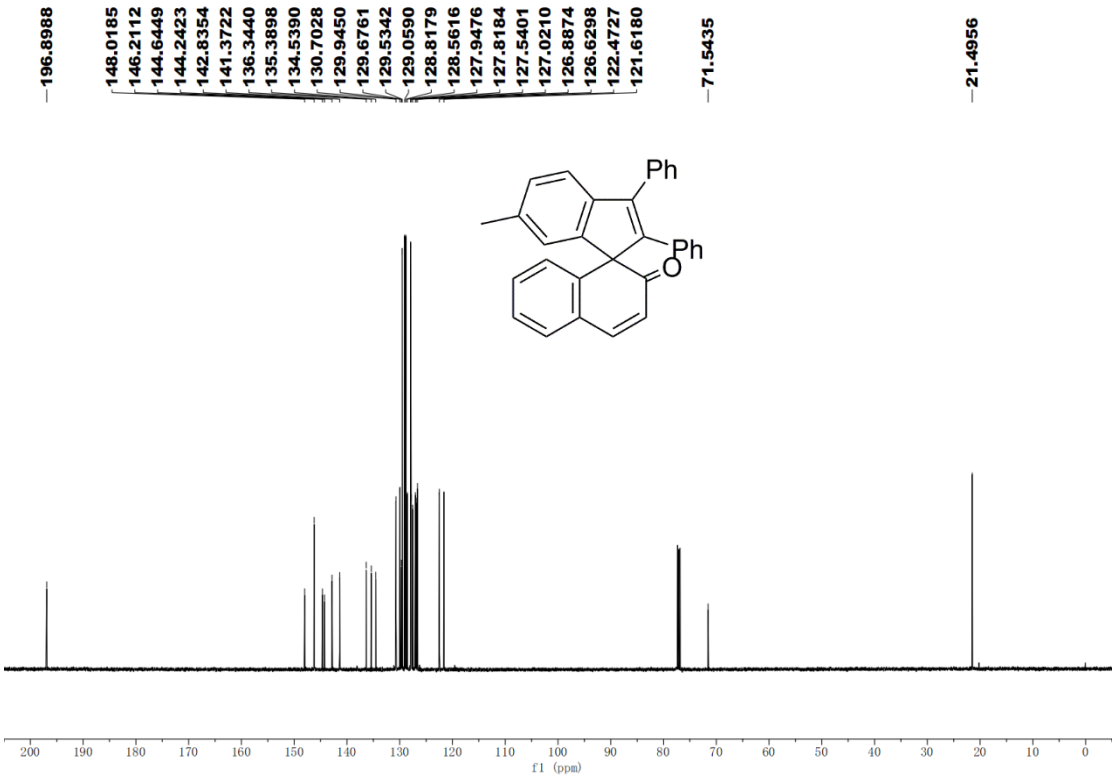


Fig S6. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3c**)

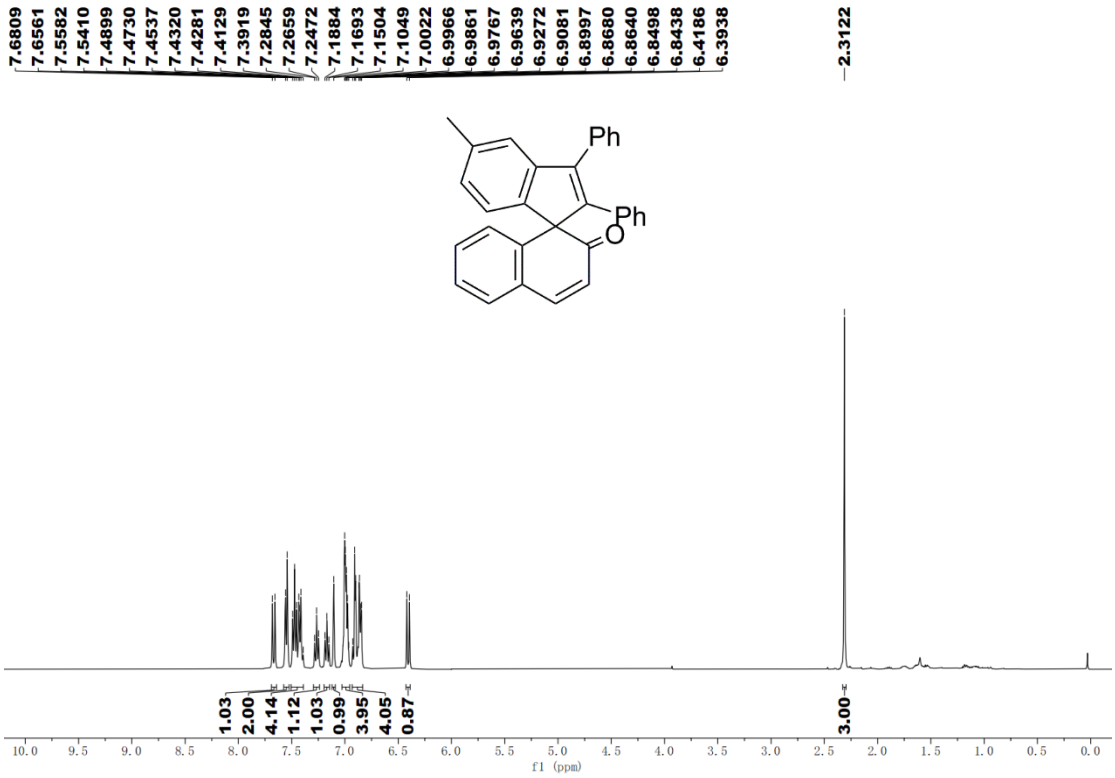


Fig S7. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3d**)

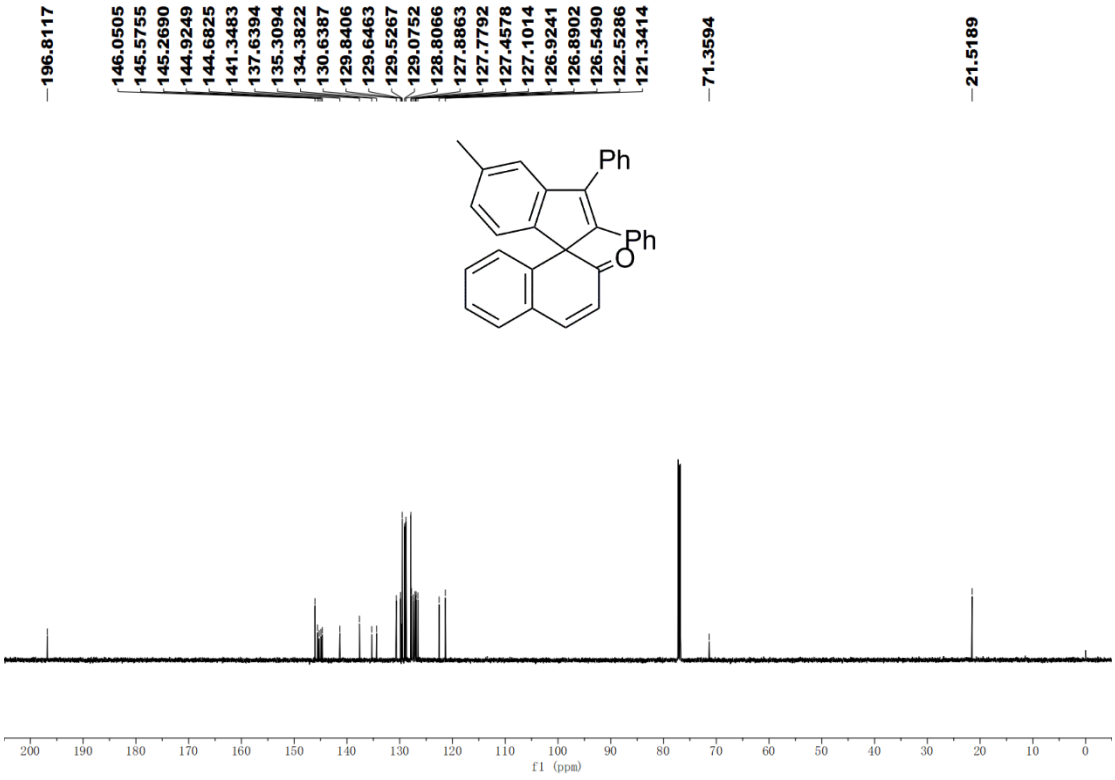


Fig S8. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-methyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3d**)

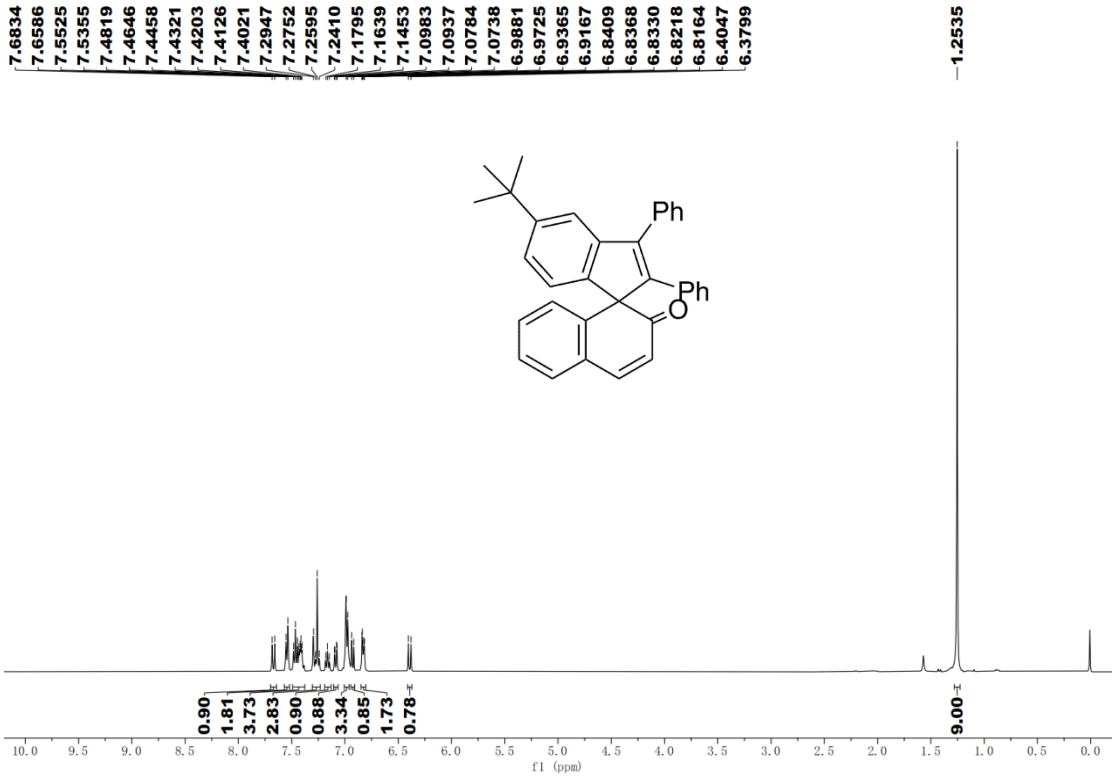


Fig S9. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-(*tert*-butyl)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3e**)

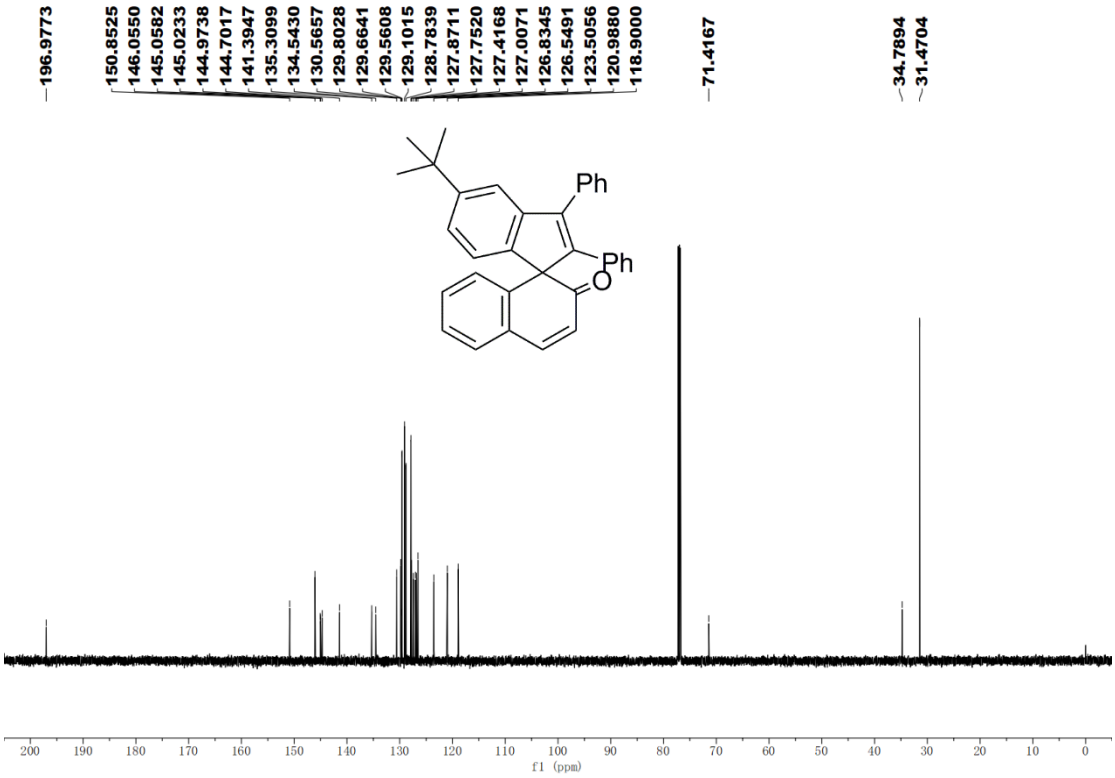


Fig S10. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-(*tert*-butyl)-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3e**)

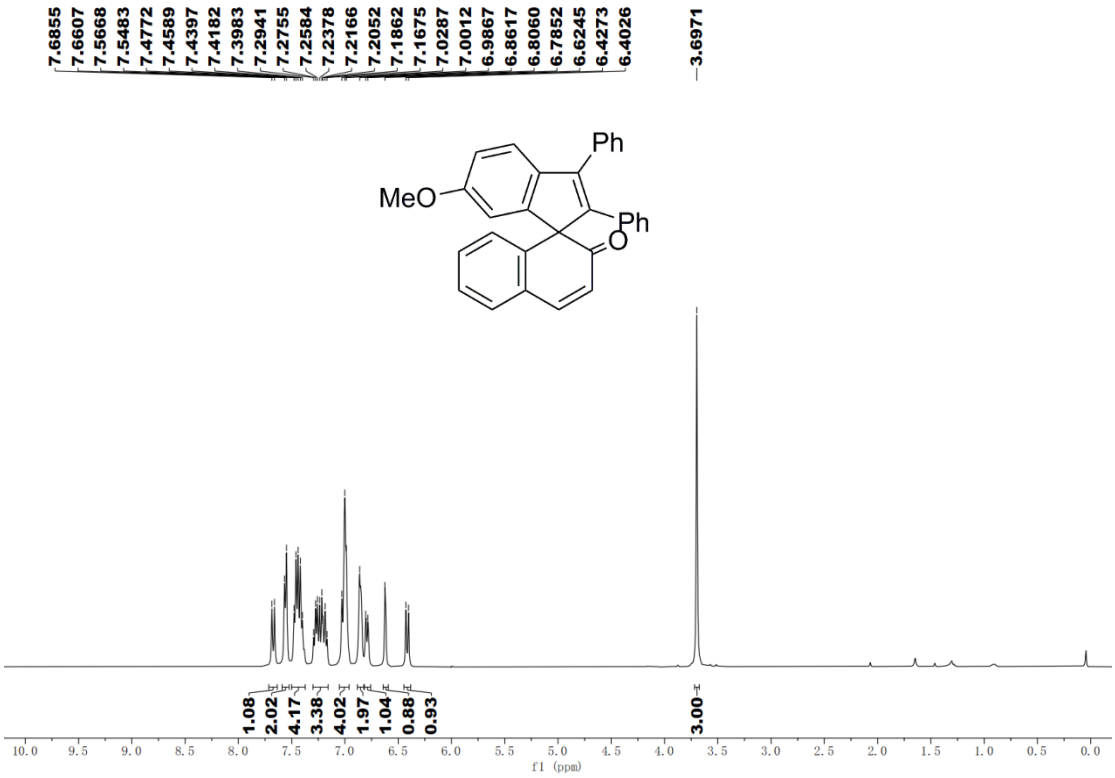


Fig S11. ^{1}H NMR (400 MHz, $CDCl_3$) of 6-methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3f**)

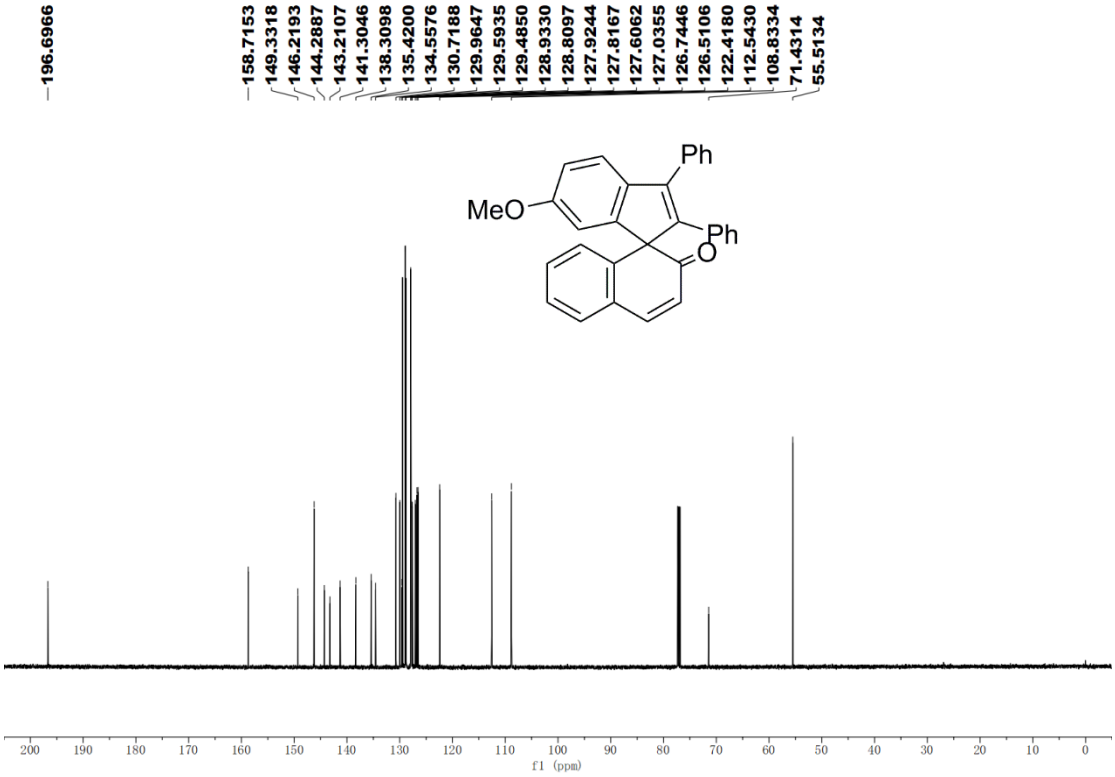


Fig S12. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6-methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3f**)

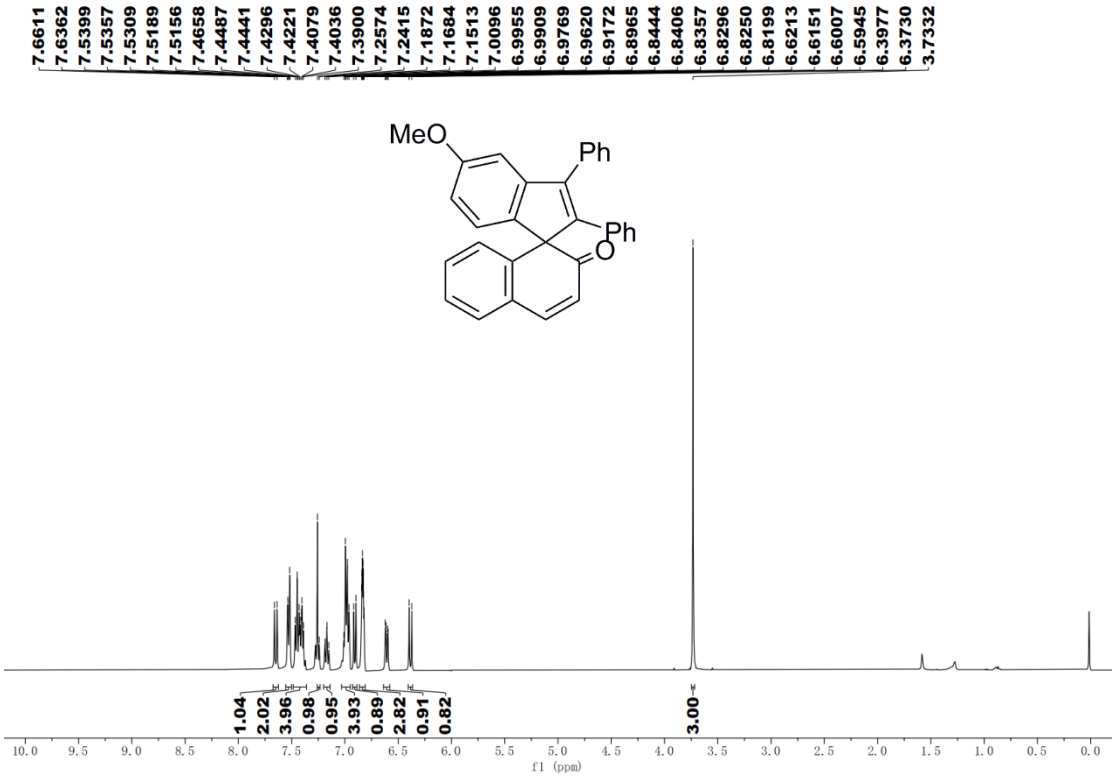


Fig S13. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3g)**

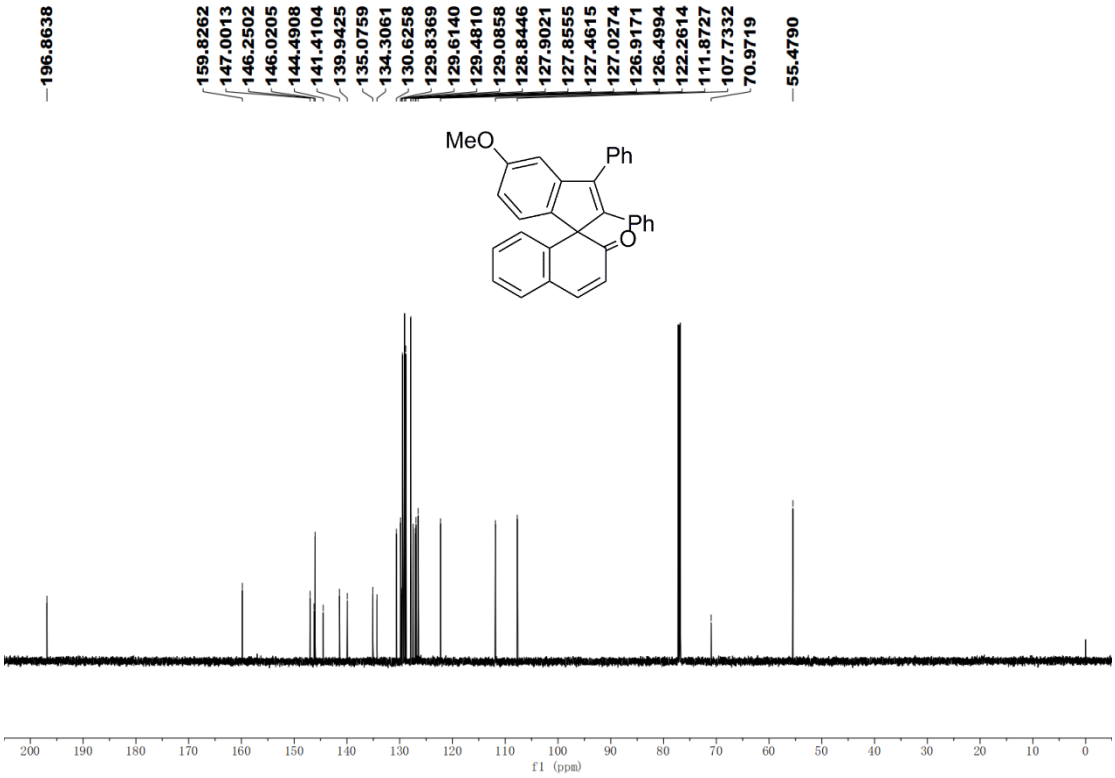


Fig S14. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-methoxy-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3g)**

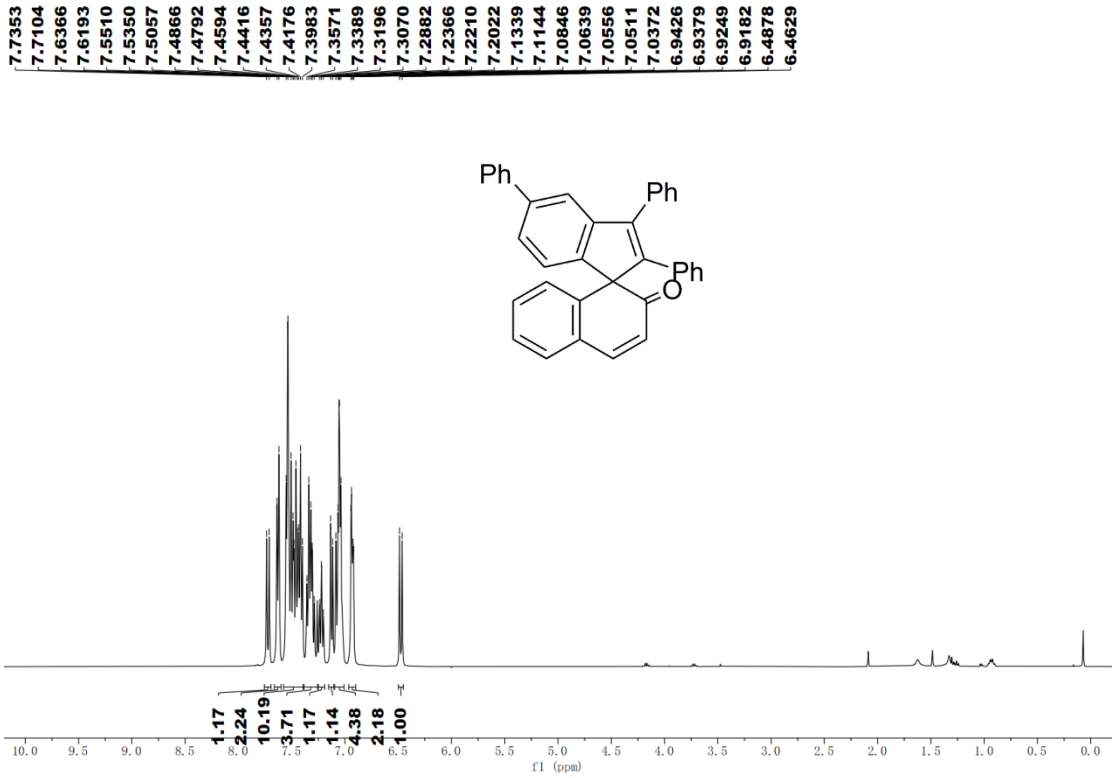


Fig S15. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,5-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3h**)

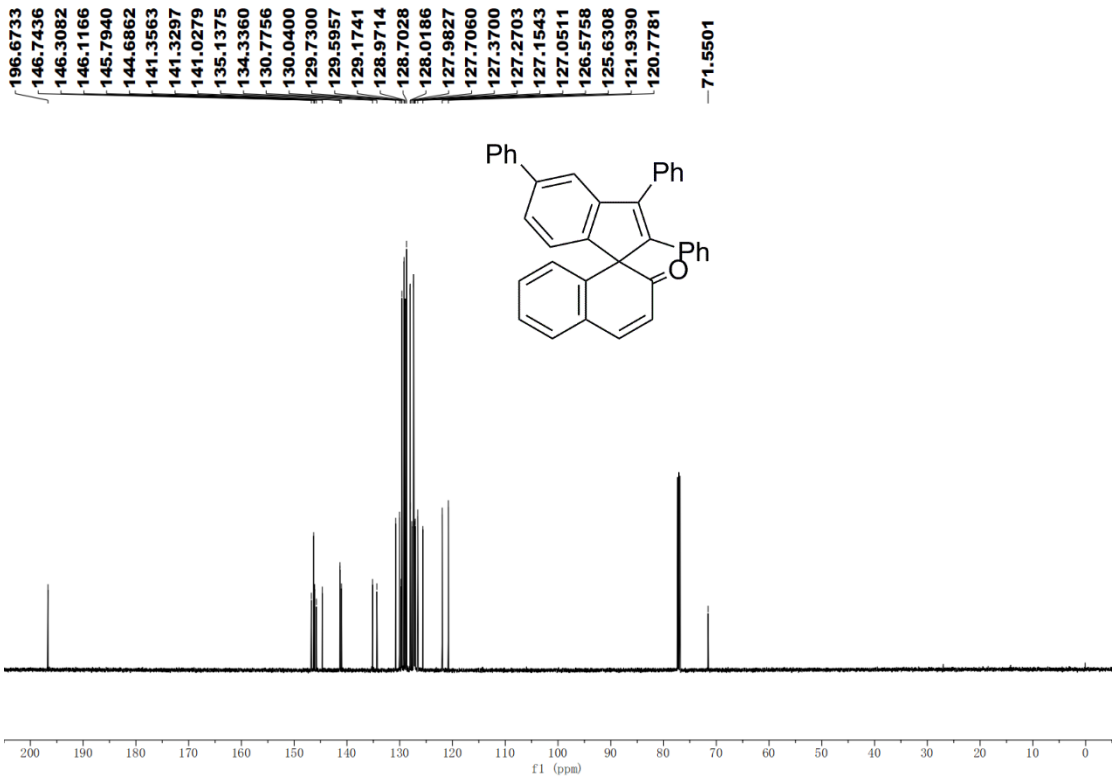


Fig S16. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,5-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3h**)

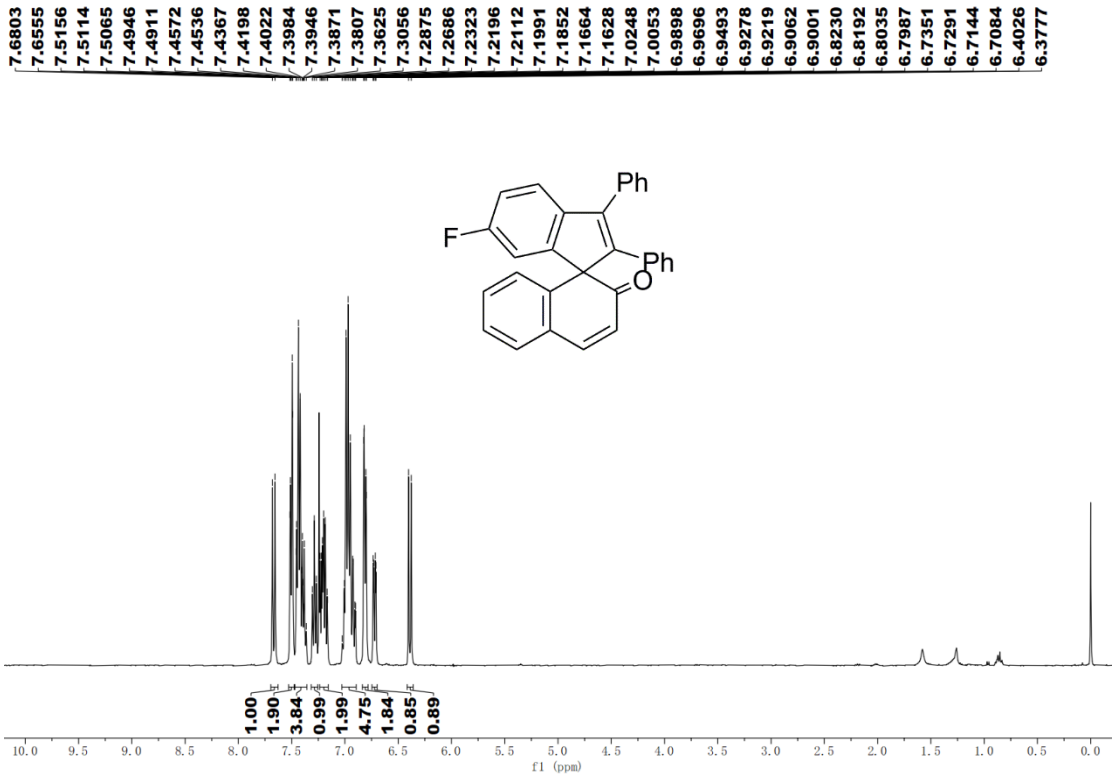


Fig S17. ^{1}H NMR (400 MHz, $CDCl_3$) of 6-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3i**)

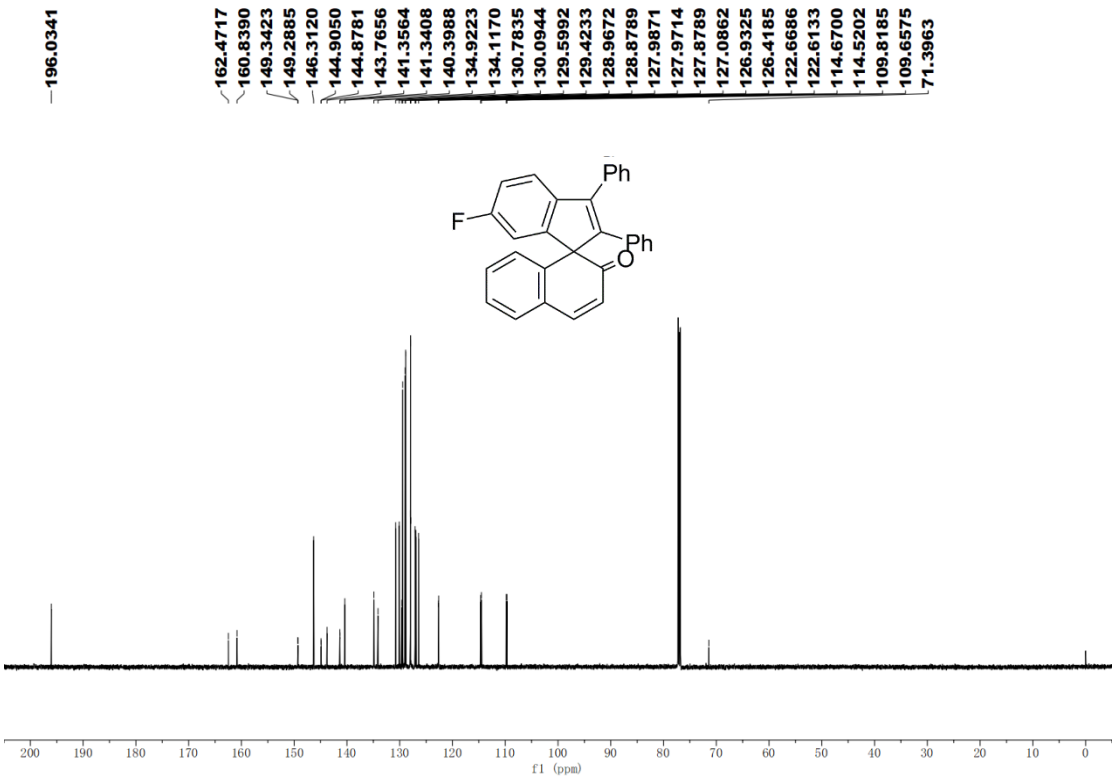


Fig S18. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3i**)

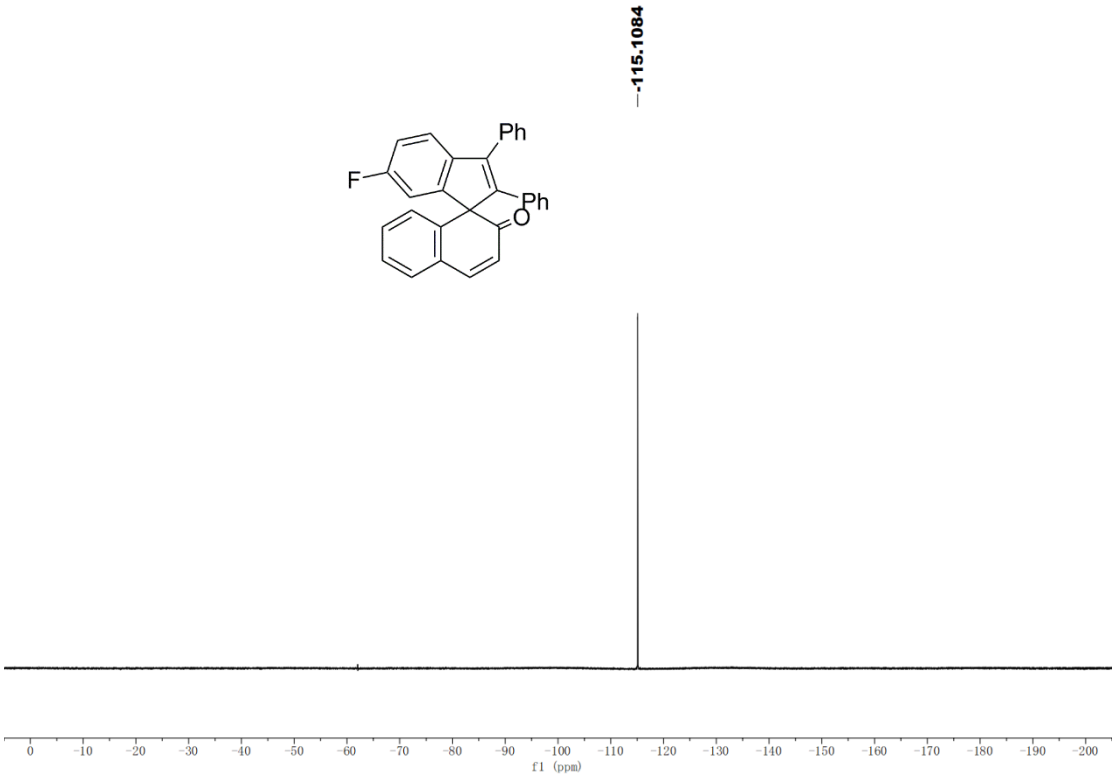


Fig S19. ^{19}F NMR (376 MHz, $CDCl_3$) of 6-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3i**)

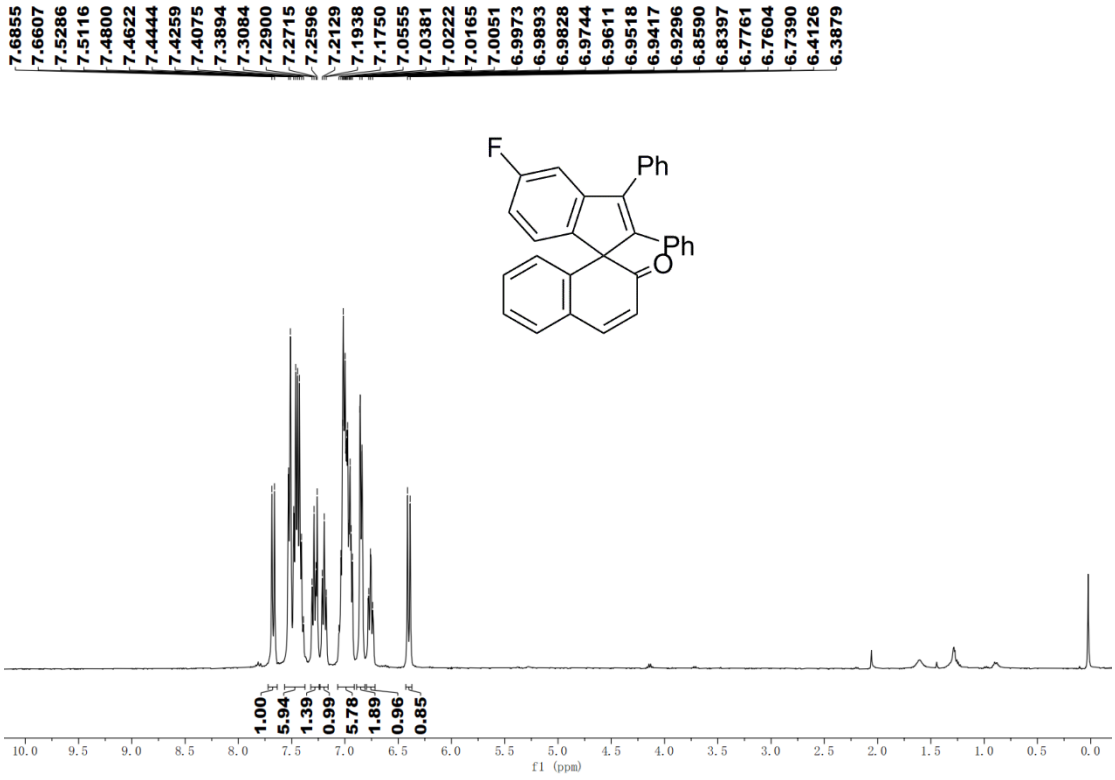


Fig S20. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3j**)

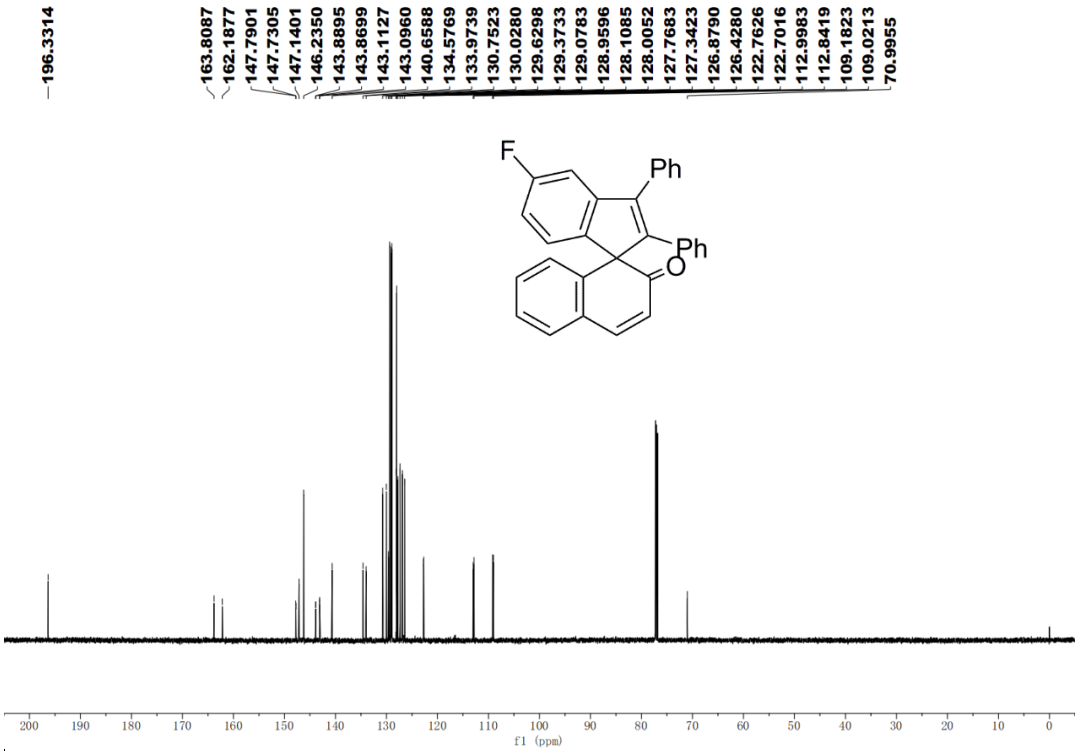


Fig S21. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3j**)

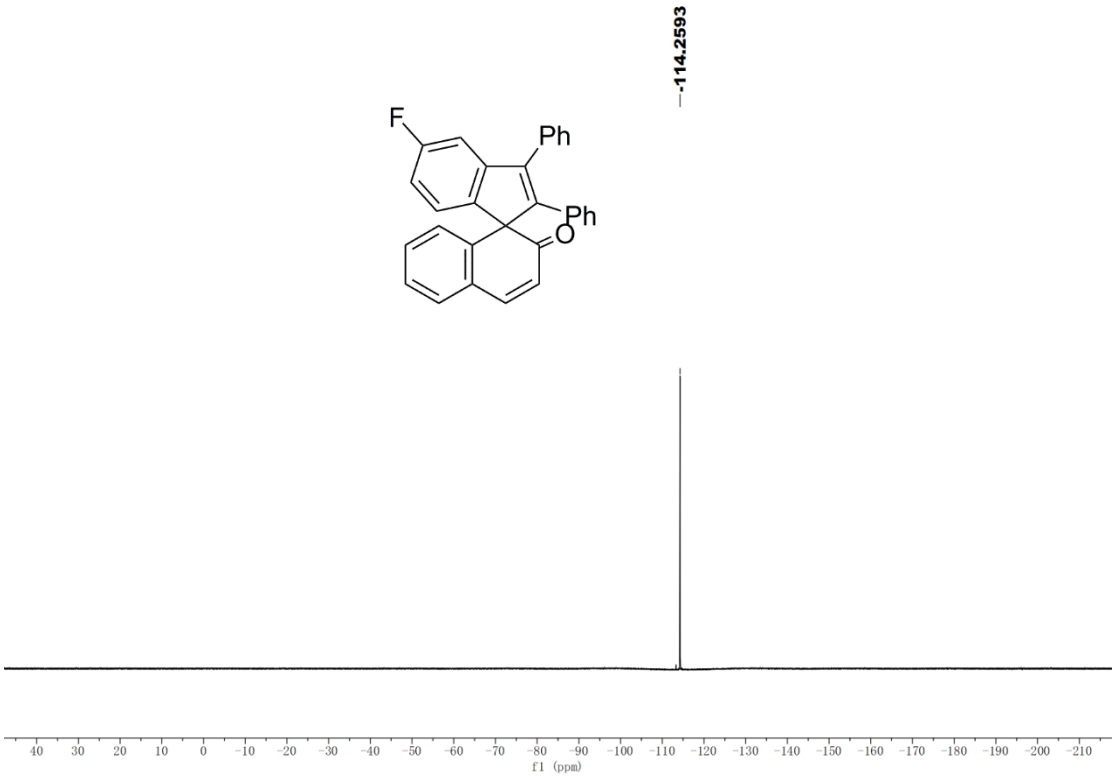


Fig S22. ^{19}F NMR (376 MHz, $CDCl_3$) of 5-fluoro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3j**)

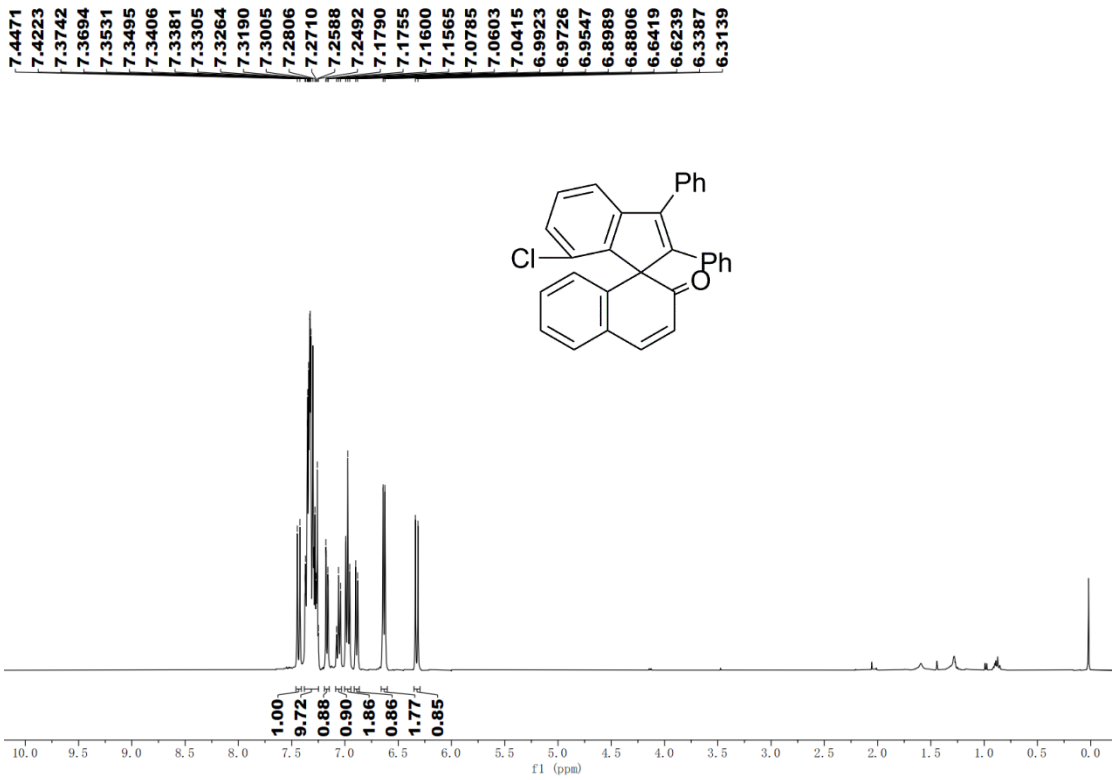


Fig S23. ^{1}H NMR (400 MHz, $CDCl_3$) of 7-chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3k**)

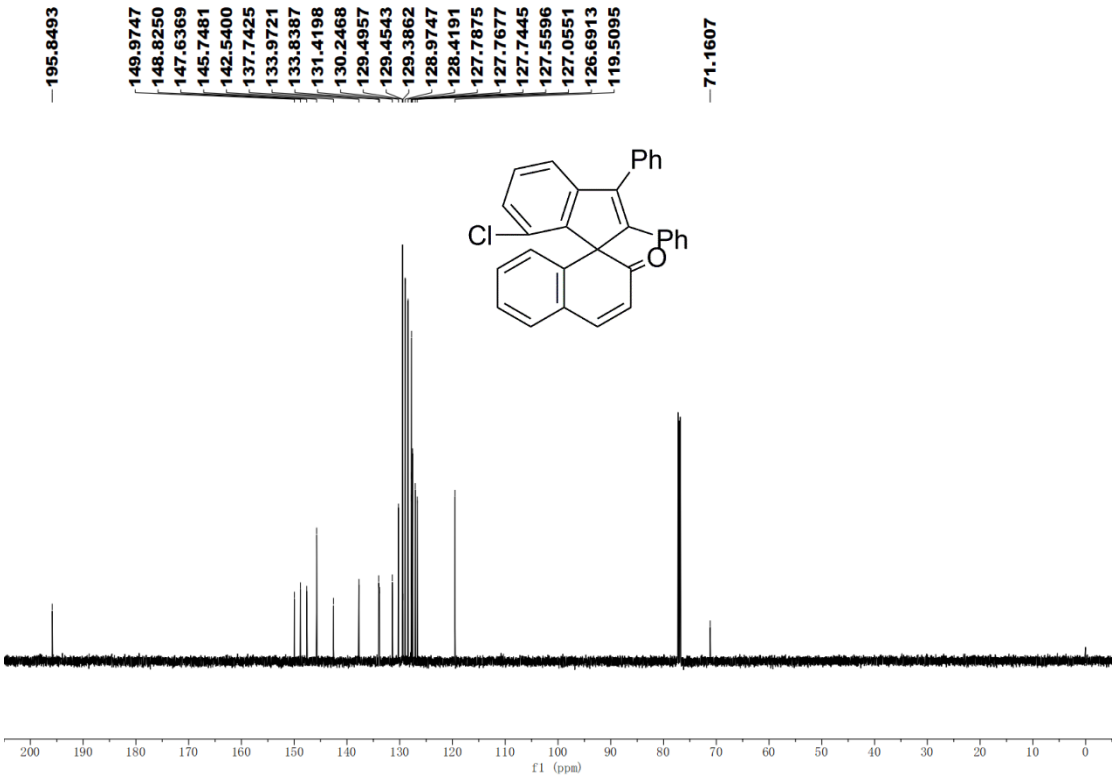


Fig S24. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 7-chloro-2,3-diphenyl-2'*H*-spiro [indene-1,1'-naphthalen]-2'-one (**3k**)

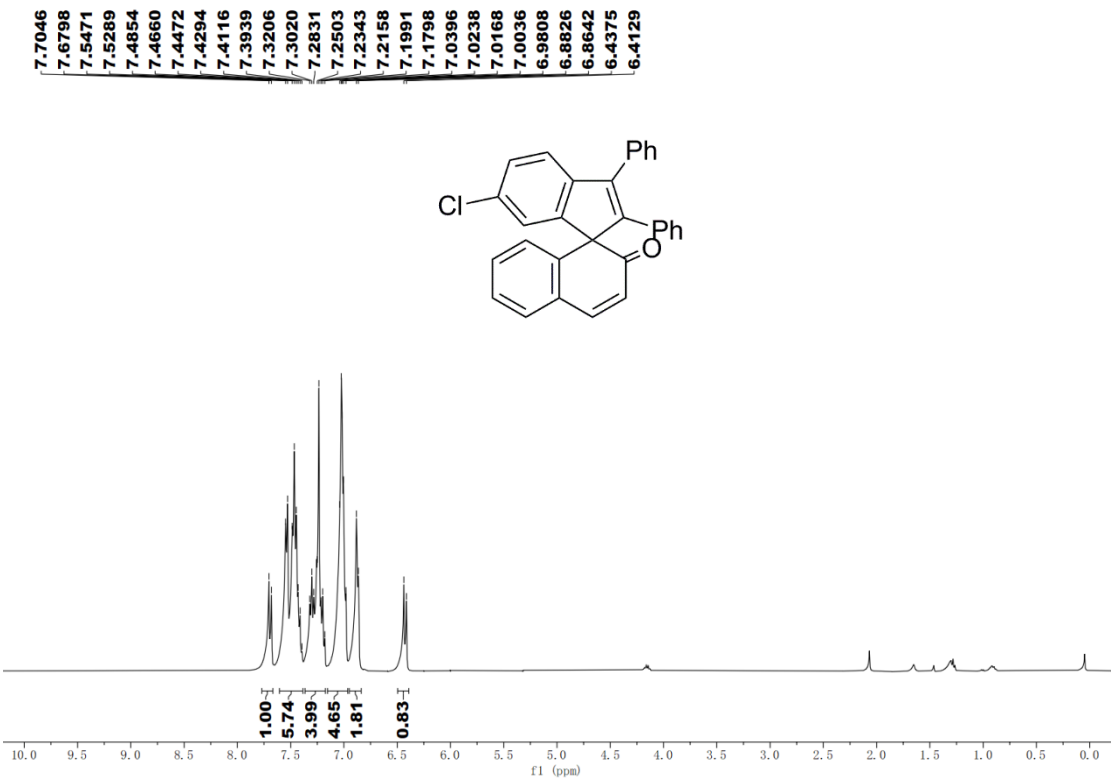


Fig S25. ^{1}H NMR (400 MHz, $CDCl_3$) of 6-chloro-2,3-diphenyl-2'*H*-spiro[indene -1,1'-naphthalen]-2'-one (**3l**)

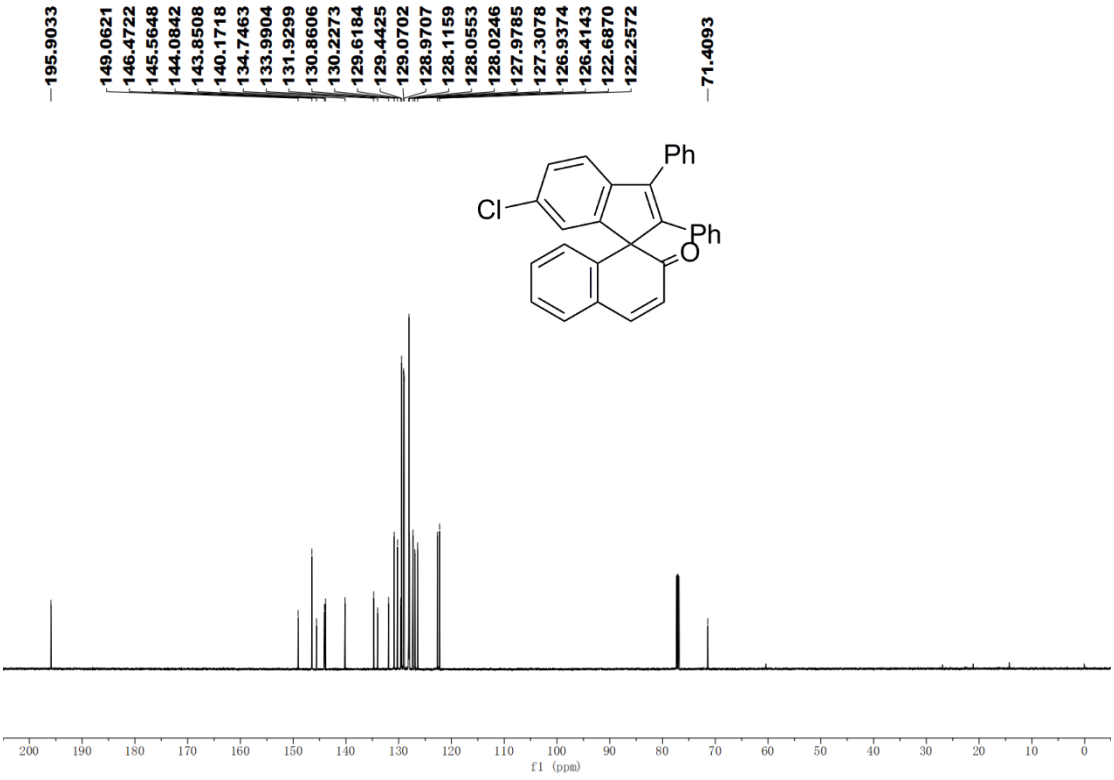


Fig S26. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6-chloro-2,3-diphenyl-2'*H*-spiro [indene-1,1'-naphthalen]-2'-one (**3l**)

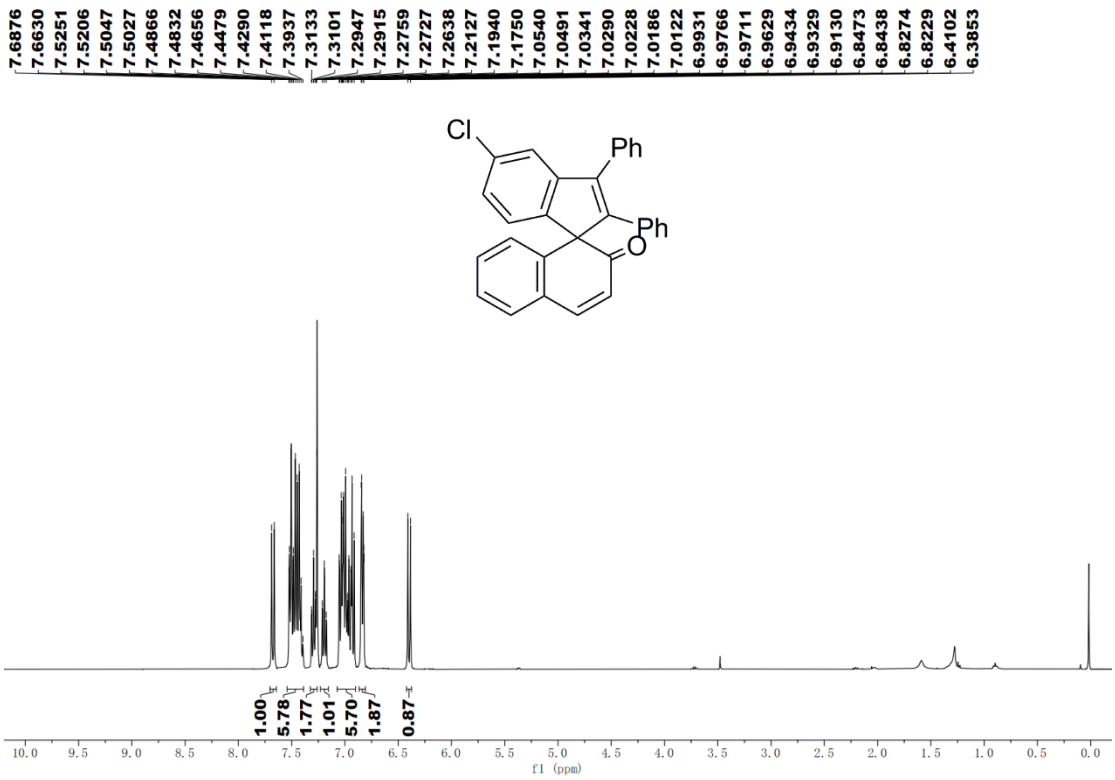


Fig S27. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3m**)

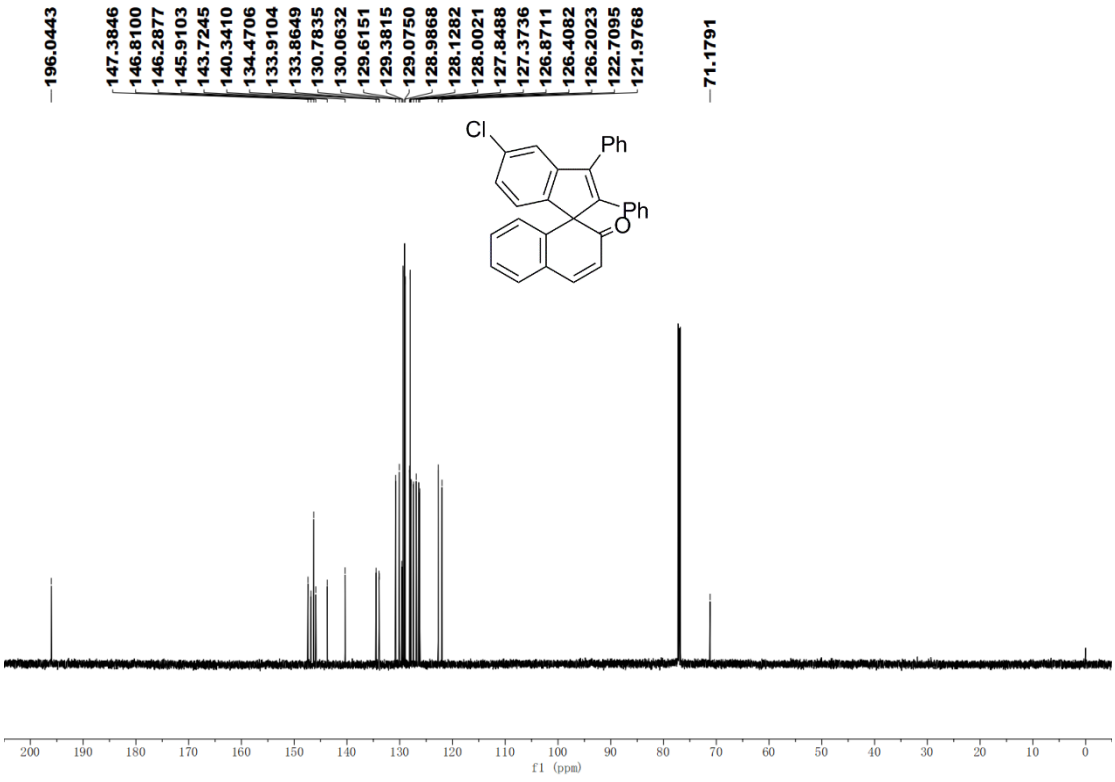


Fig S28. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-chloro-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3m**)

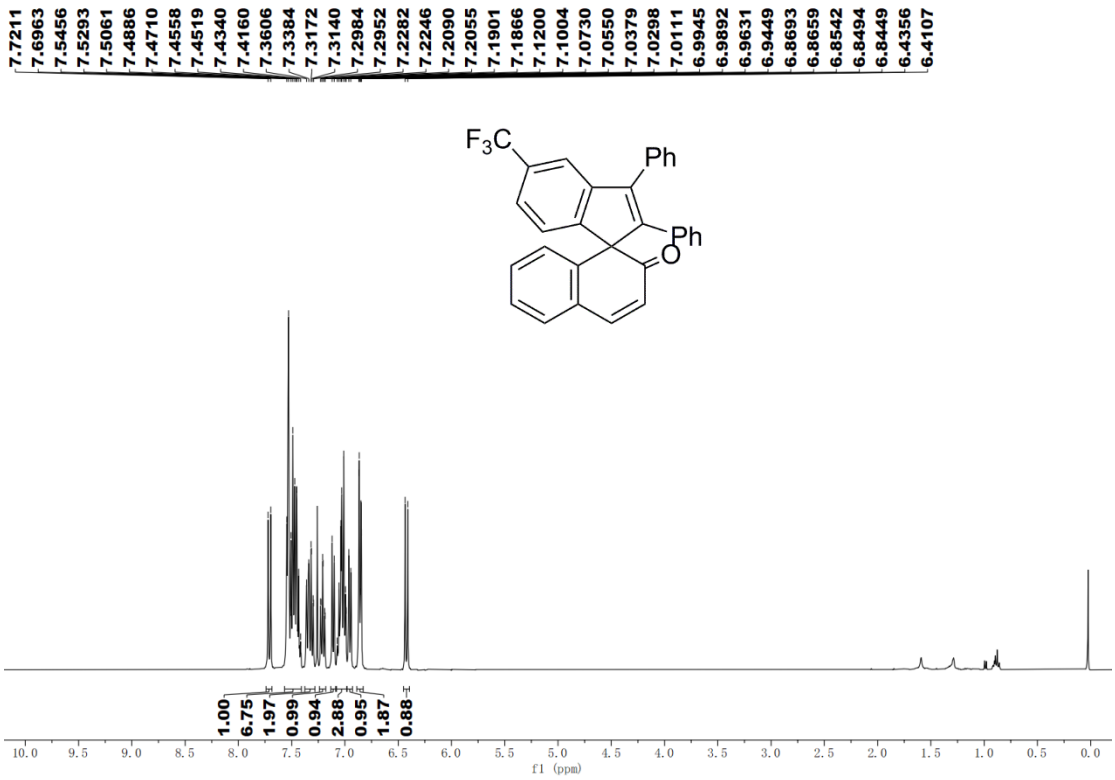


Fig S29. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-diphenyl-5-(trifluoromethyl)-2′*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3n**)

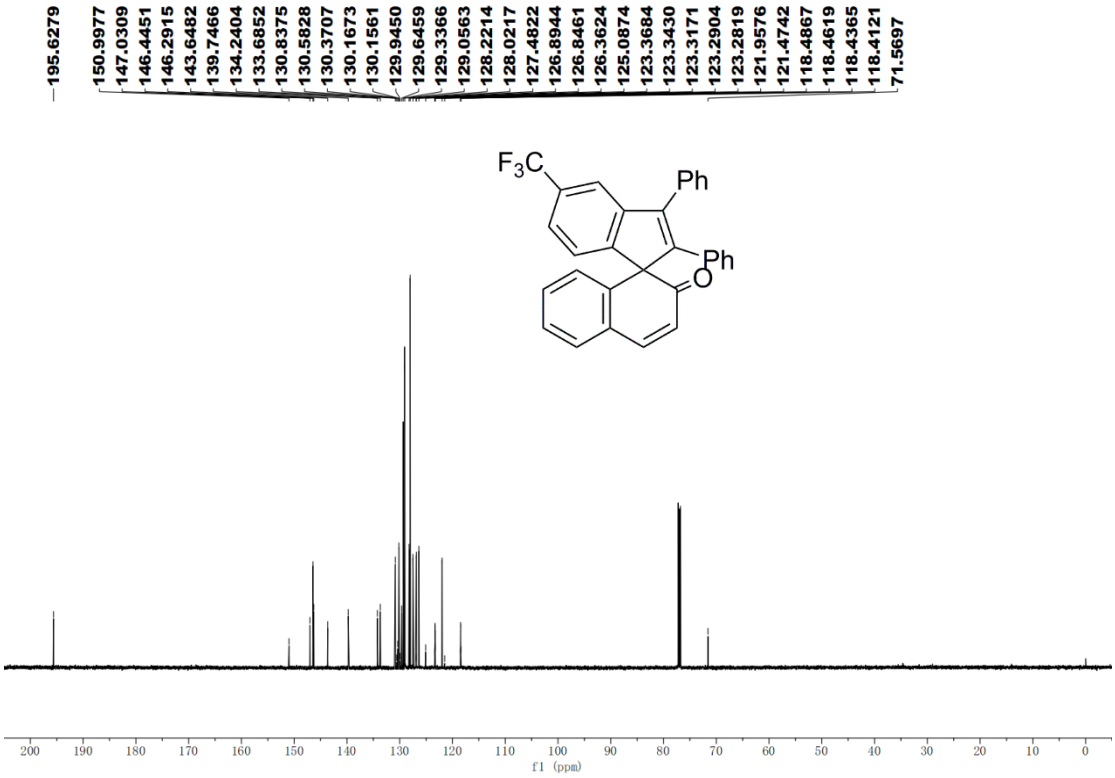


Fig S30. ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$) of 2,3-diphenyl-5-(trifluoromethyl)-2′*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3n**)

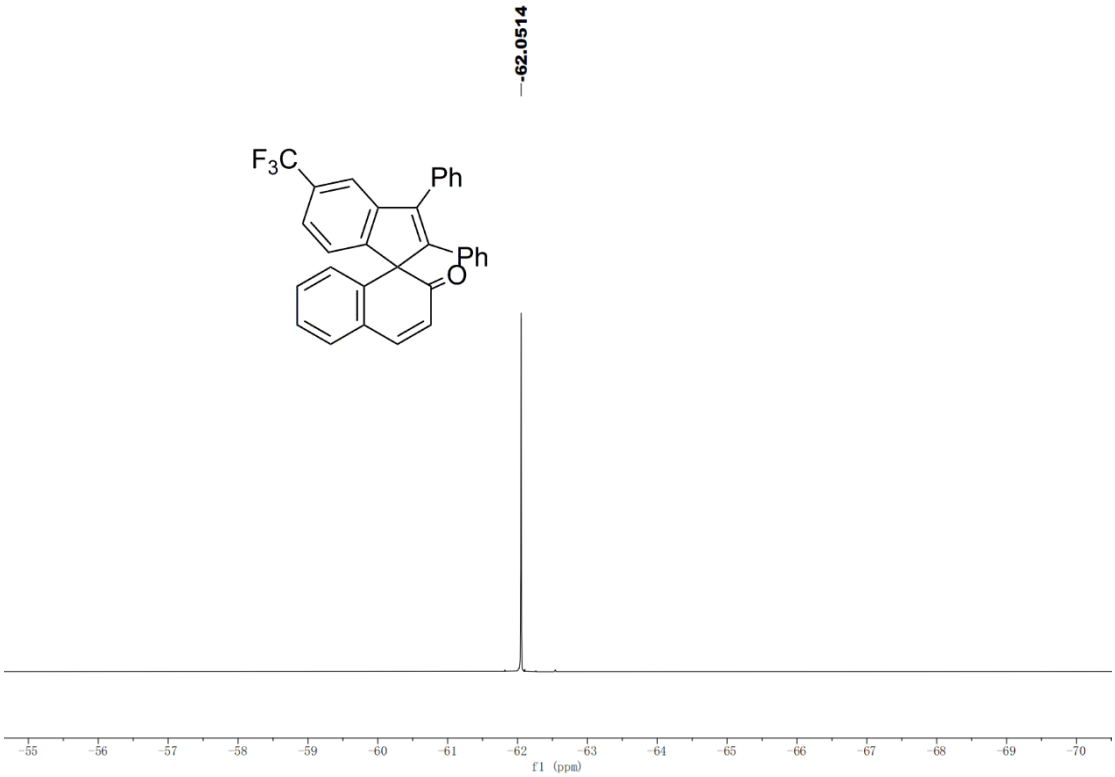


Fig S31. ^{19}F NMR (376 MHz, $CDCl_3$) of 2,3-diphenyl-5-(trifluoromethyl)-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3n**)

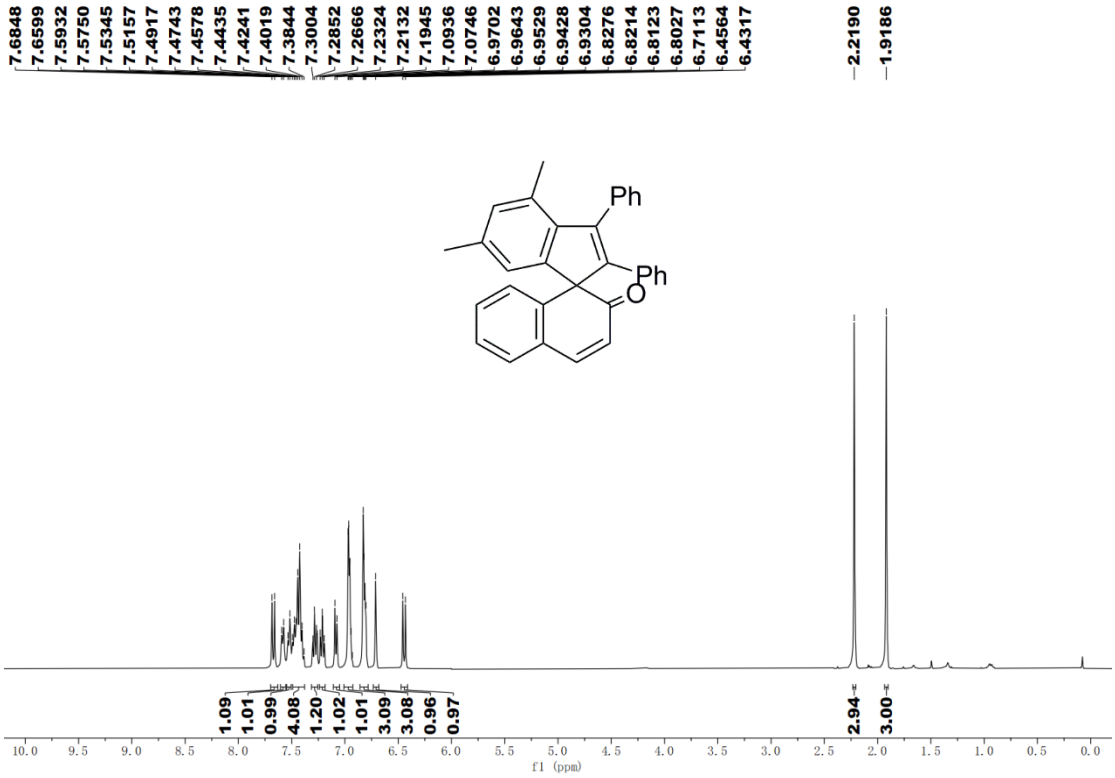


Fig S32. ^{1}H NMR (400 MHz, $CDCl_3$) of 4,6-dimethyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3o**)

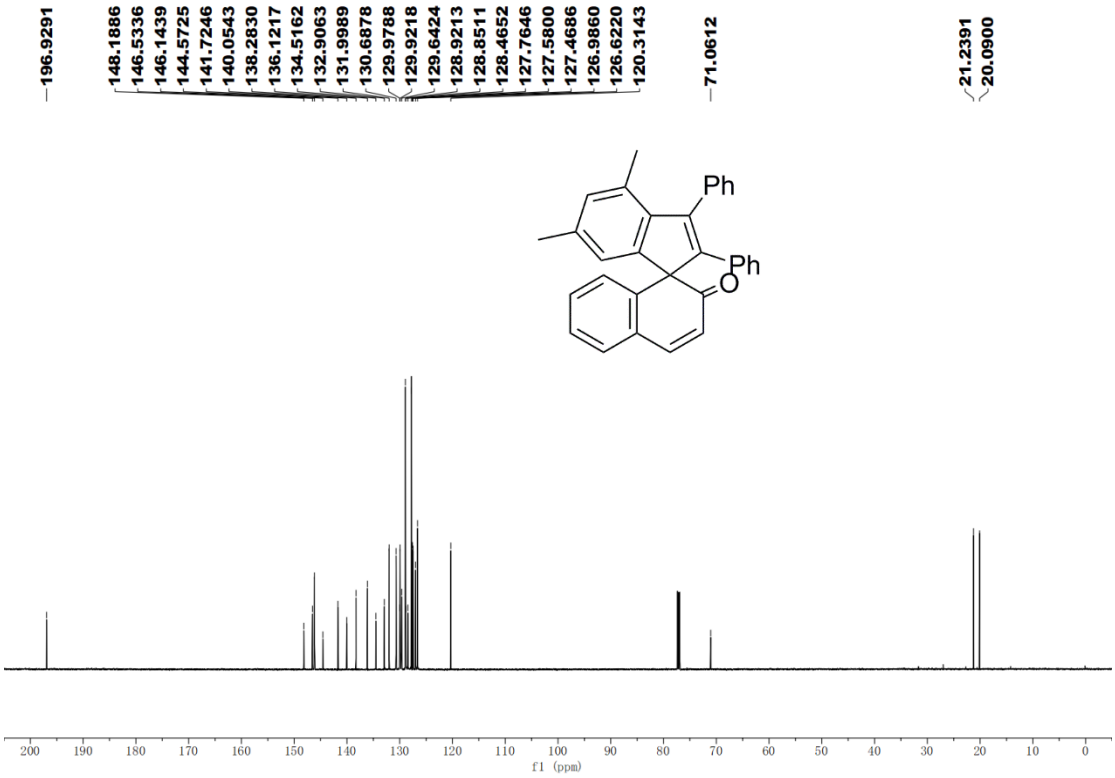


Fig S33. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 4,6-dimethyl-2,3-diphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3o**)

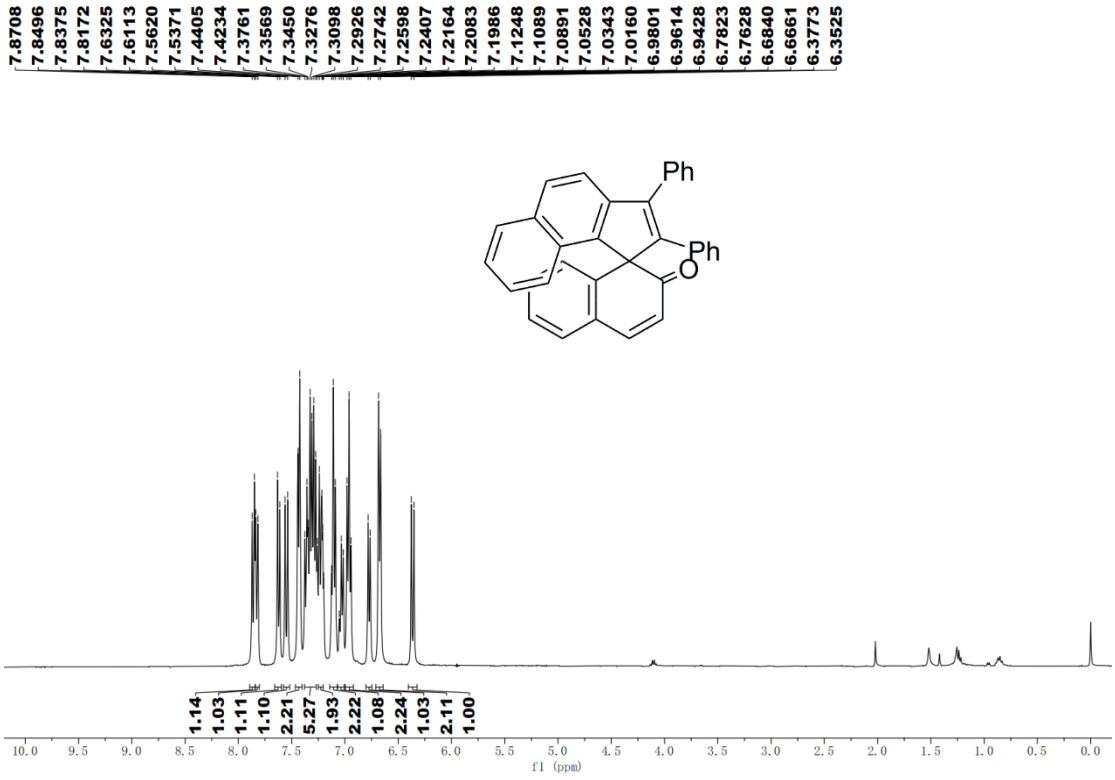


Fig S34. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[cyclopenta[a]naphthalene-1,1'-naphthalen]-2'-one (**3p**)

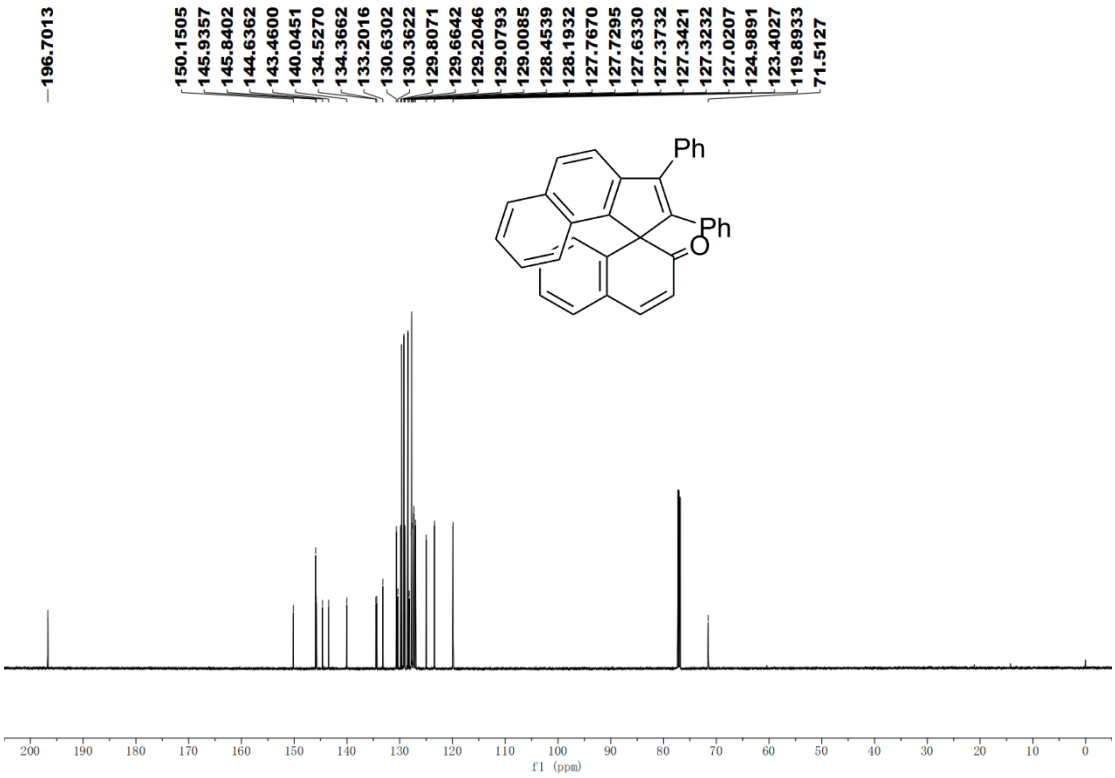


Fig S35. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[cyclopenta[a]naphthalene-1,1'-naphthalen]-2'-one (**3p**)

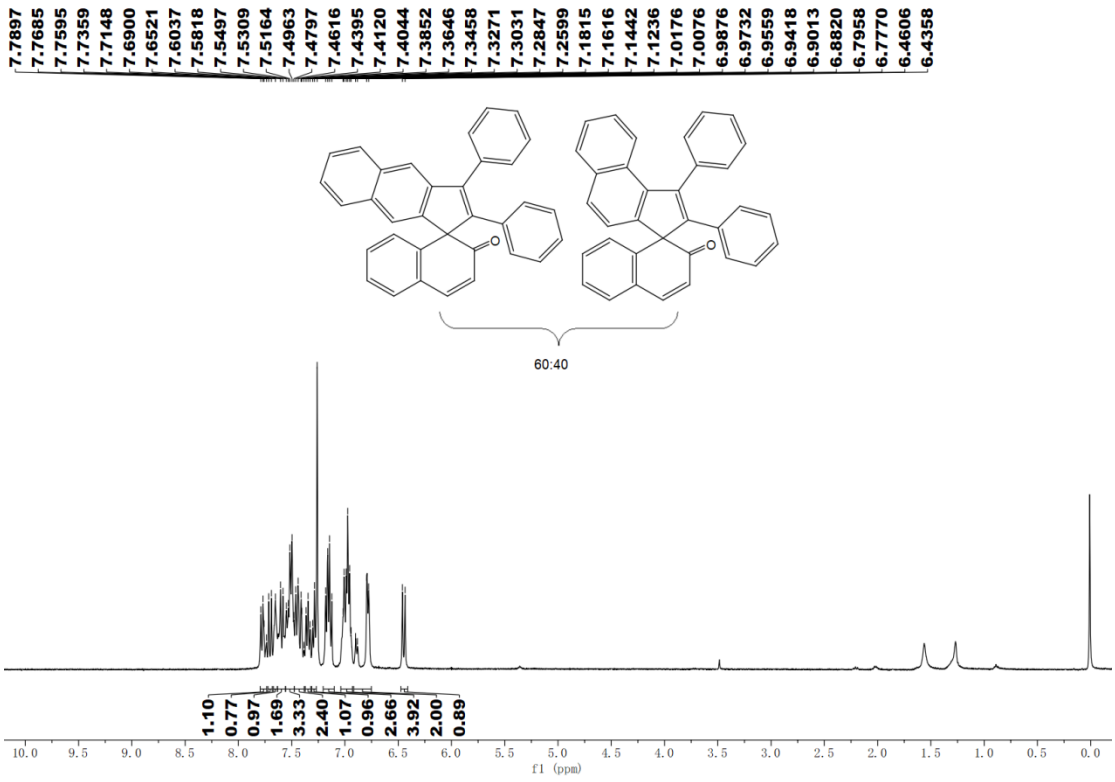


Fig S36. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[cyclopenta[*b*]naphthalene-1,1'-naphthalen]-2'-one and 1,2-diphenyl-2'*H*-spiro[cyclopenta[*a*]naphthalene-3,1'-naphthalen]-2'-one (**3q**)

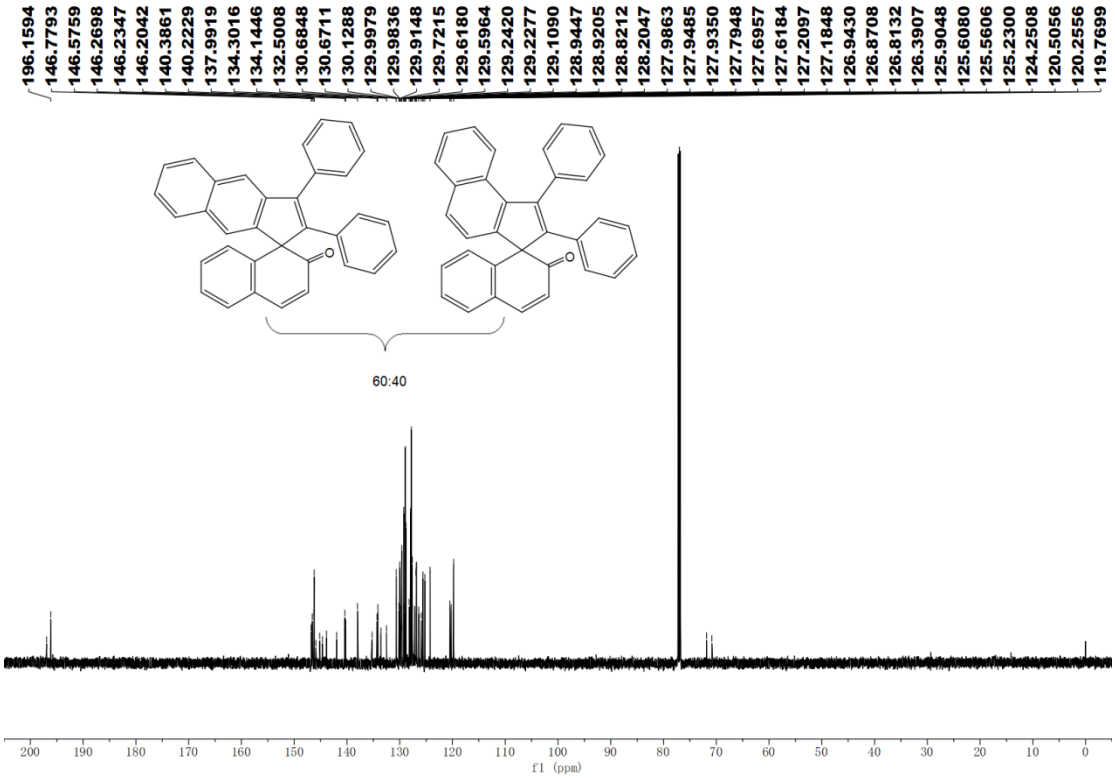


Fig S37. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-diphenyl-2'*H*-spiro[cyclopenta[*b*]naphthalene-1,1'-naphthalen]-2'-one and 1,2-diphenyl-2'*H*-spiro[cyclopenta[*a*]naphthalene-3,1'-naphthalen]-2'-one (**3q**)

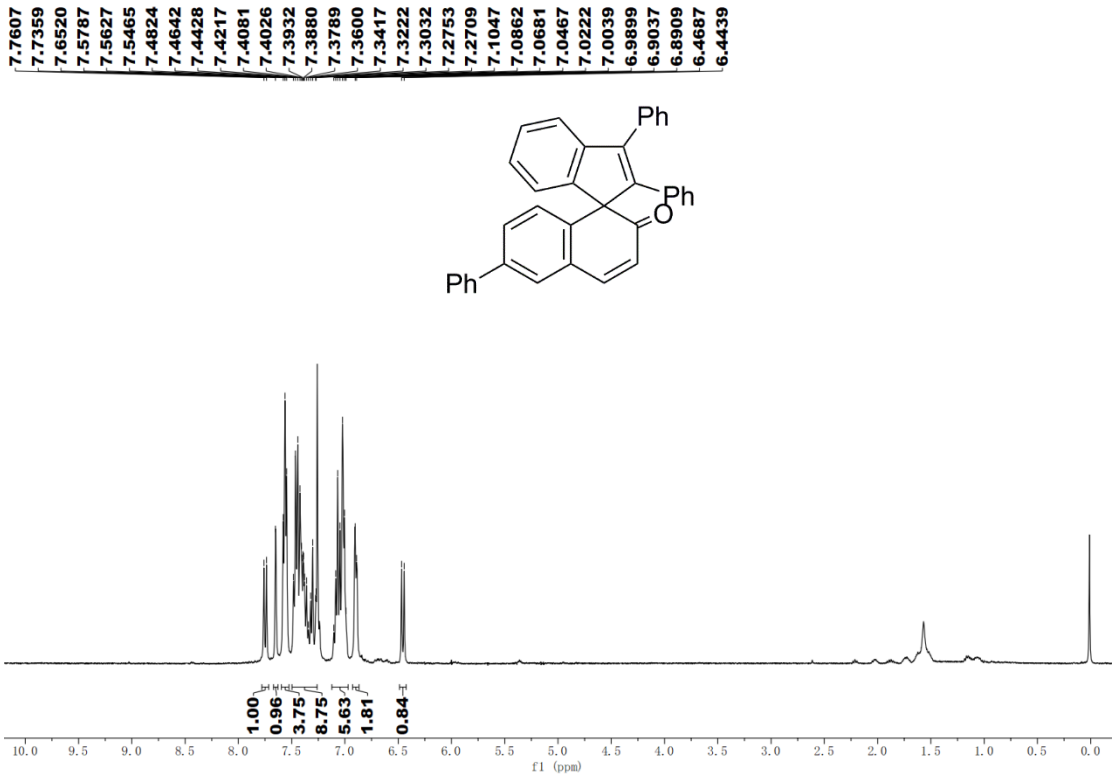


Fig S38. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,6'-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3r**)

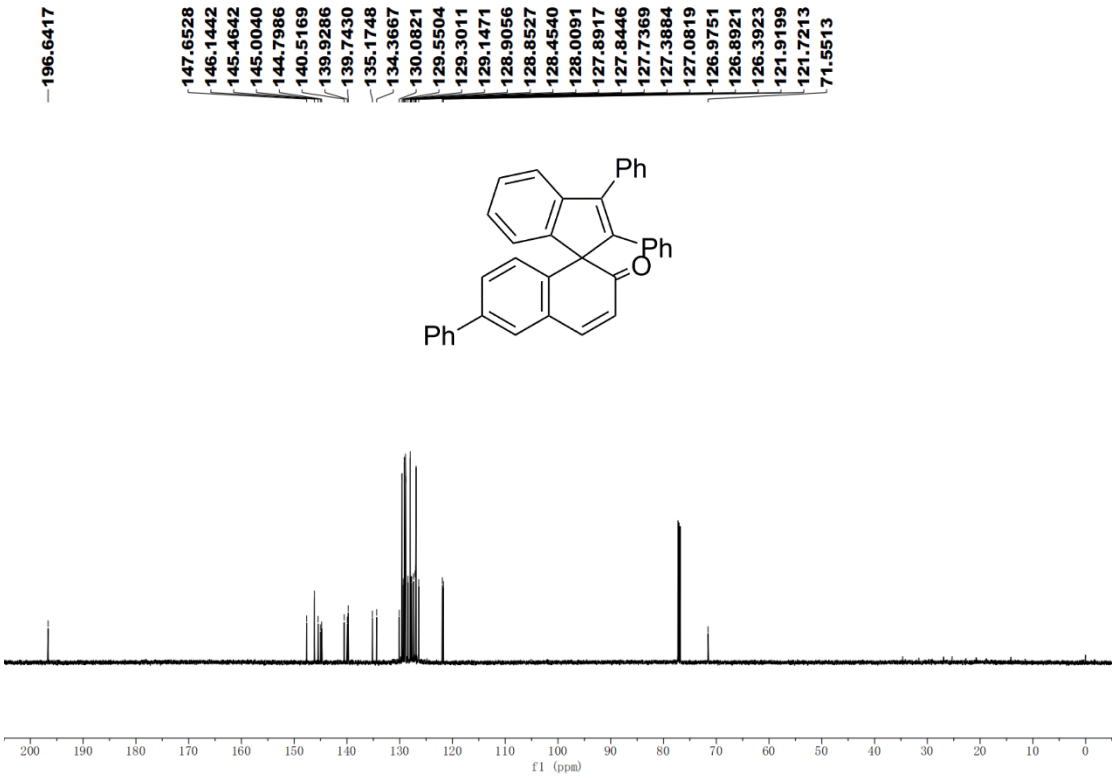


Fig S39. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,6'-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3r**)

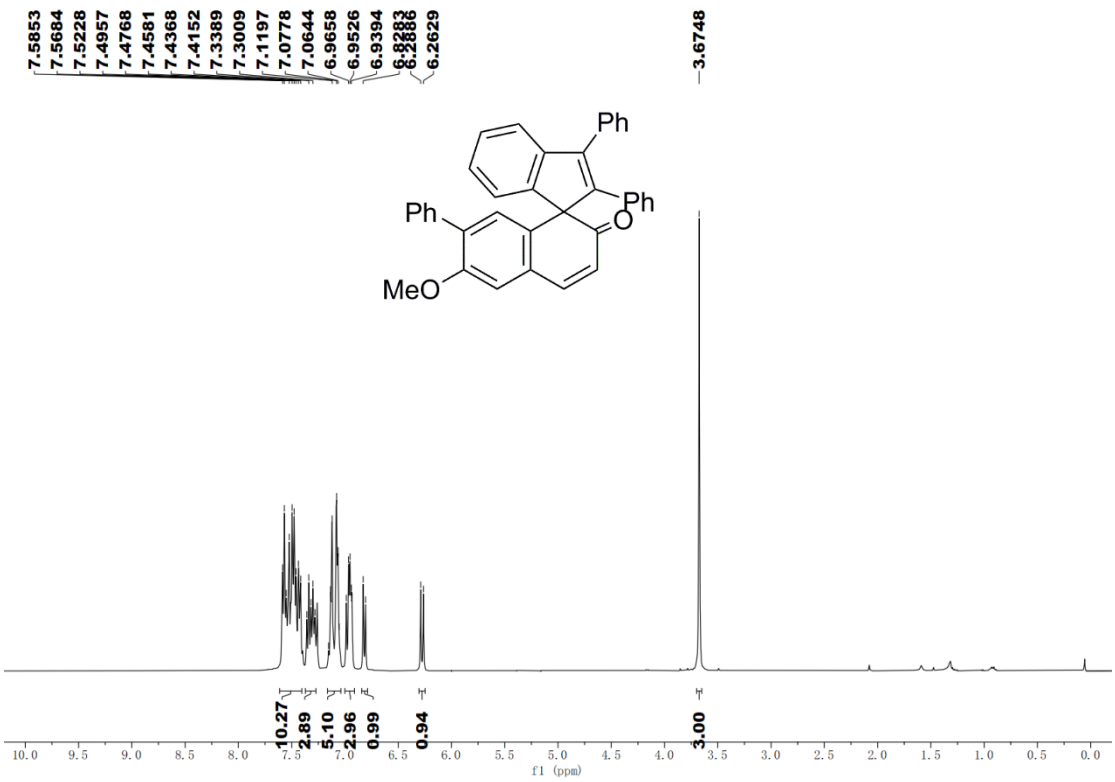


Fig S40. ^{1}H NMR (400 MHz, $CDCl_3$) of 7'-methoxy-2,3,6'-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3s**)

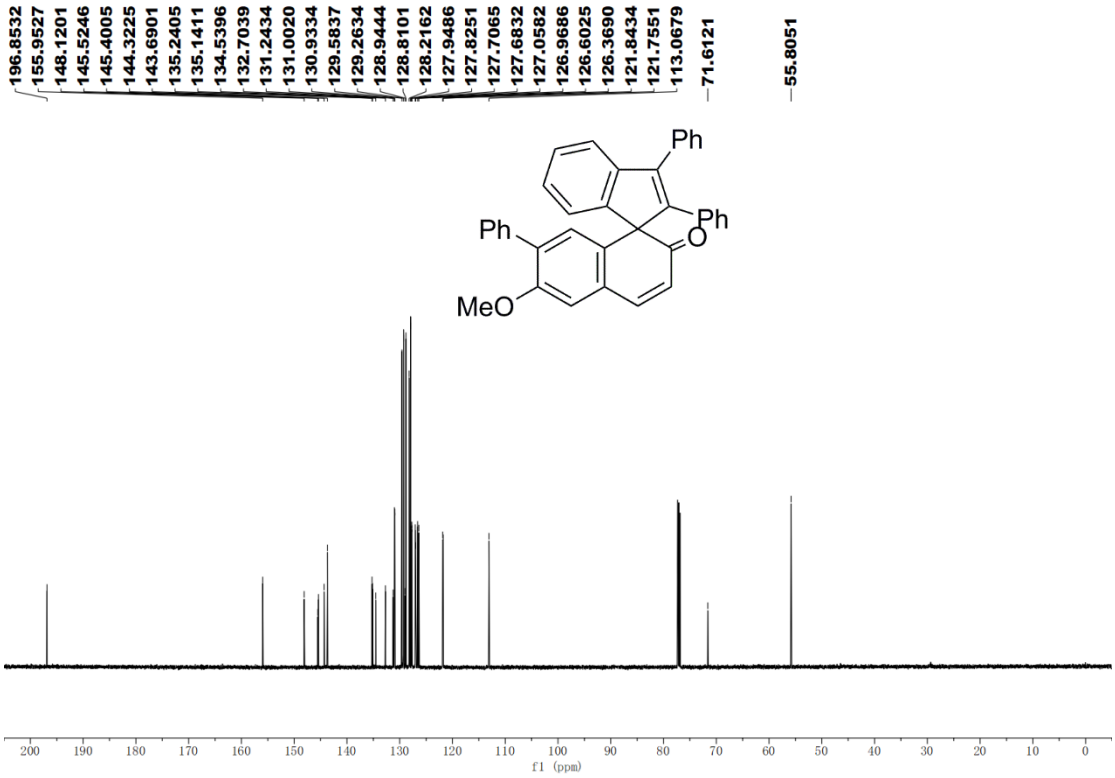


Fig S41. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 7'-methoxy-2,3,6'-triphenyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3s**)

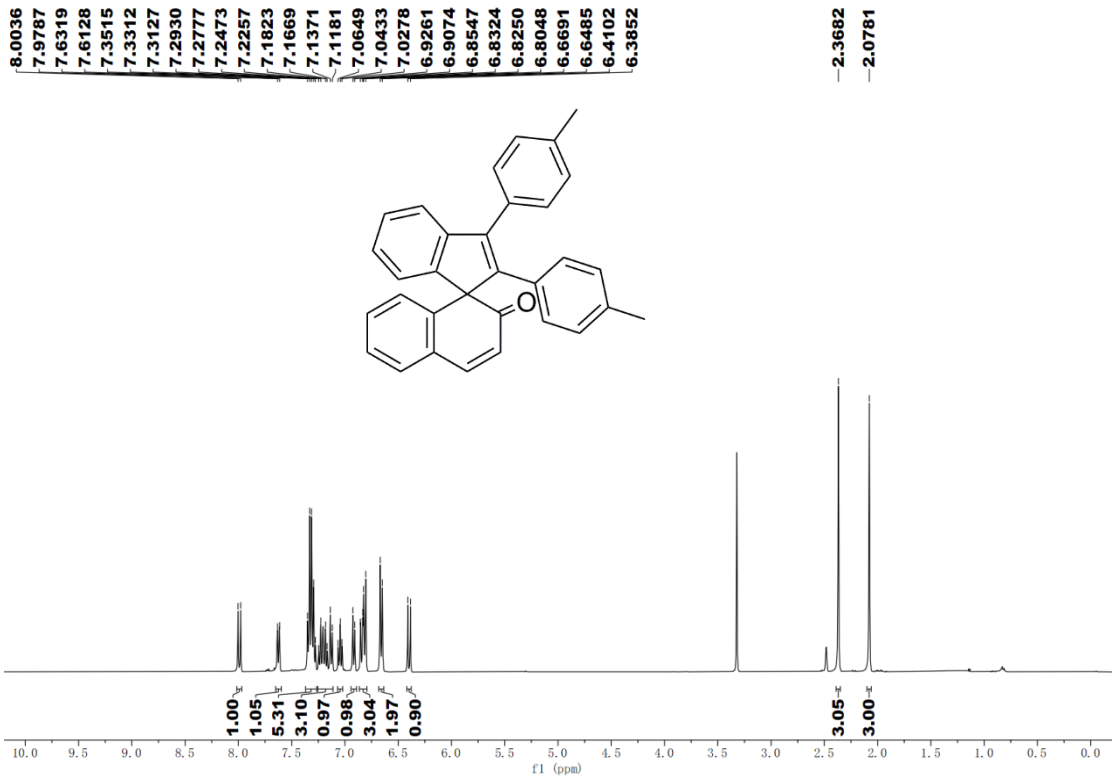


Fig S42. ^{1}H NMR (400 MHz, DMSO-d_6) of 2,3-di-p-tolyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3t**)

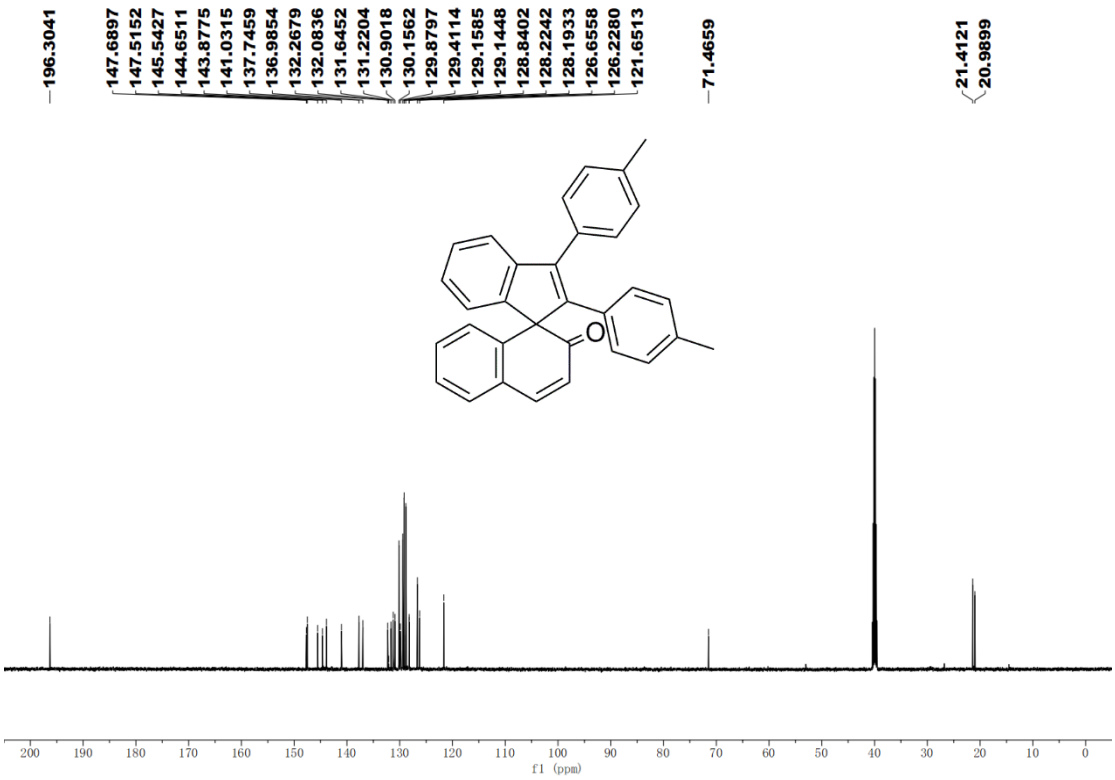


Fig S43. $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) of 2,3-di-p-tolyl-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3t**)

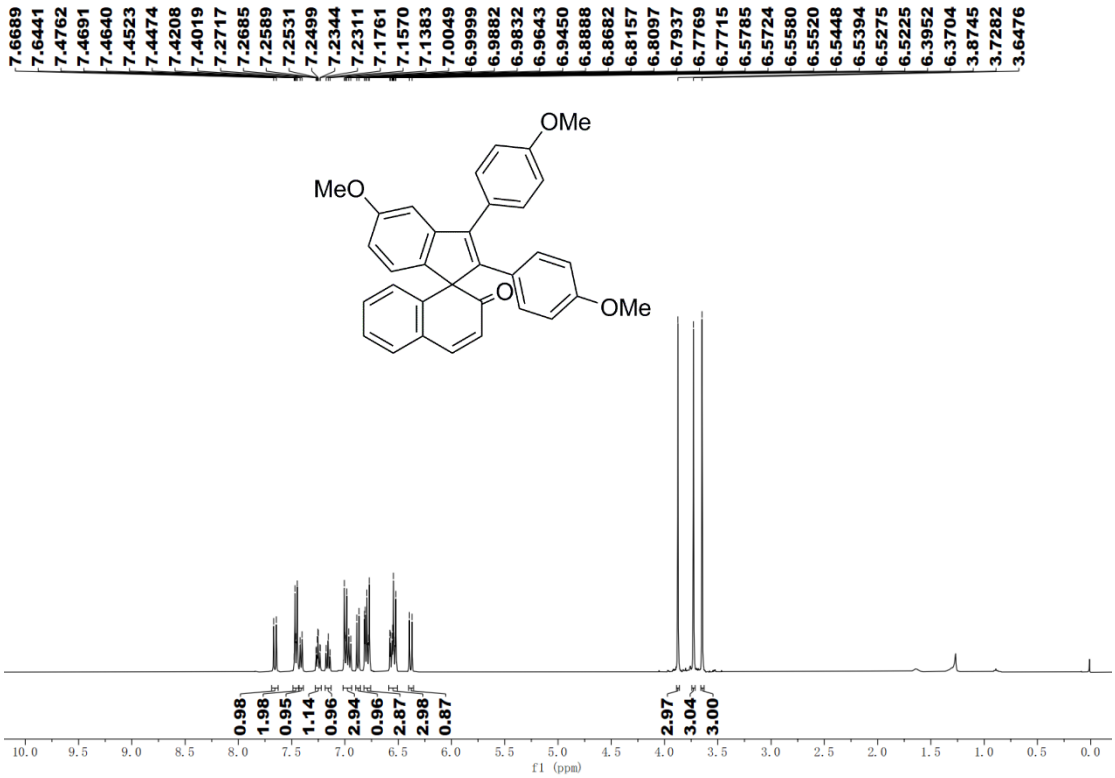


Fig S44. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxy-2,3-bis(4-methoxyphenyl)-4a',8a'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3u**)

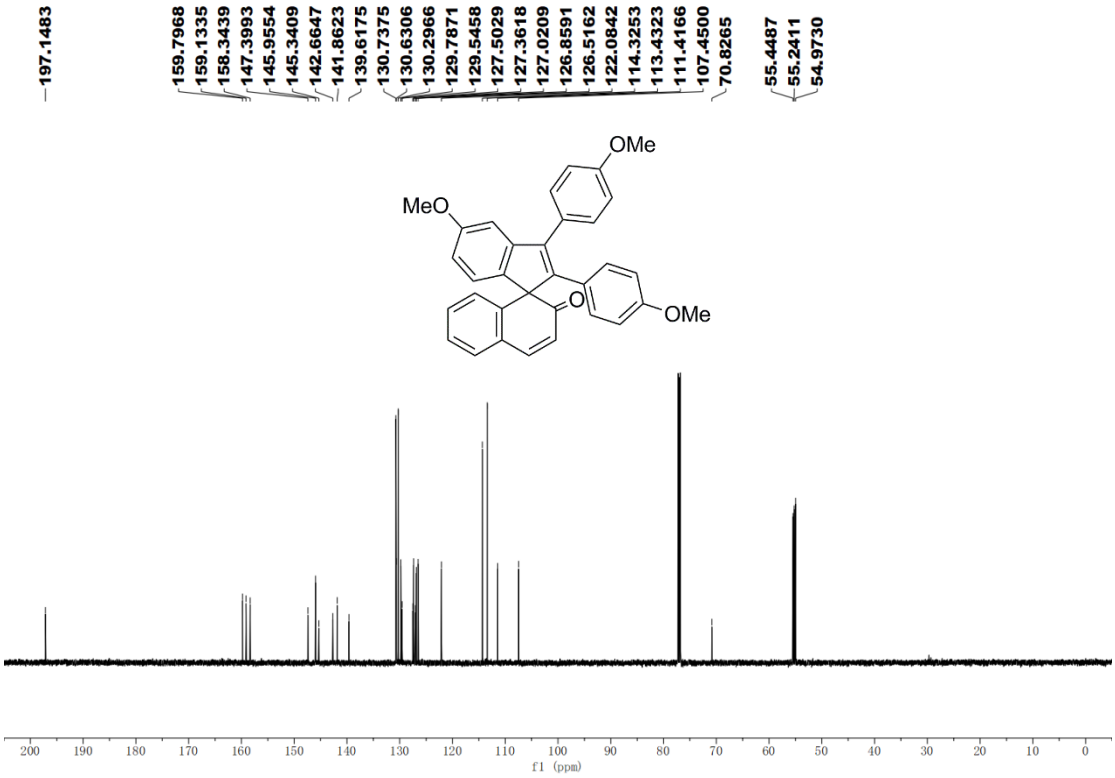


Fig S45. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-methoxy-2,3-bis(4-methoxyphenyl)-4a',8a'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3u**)

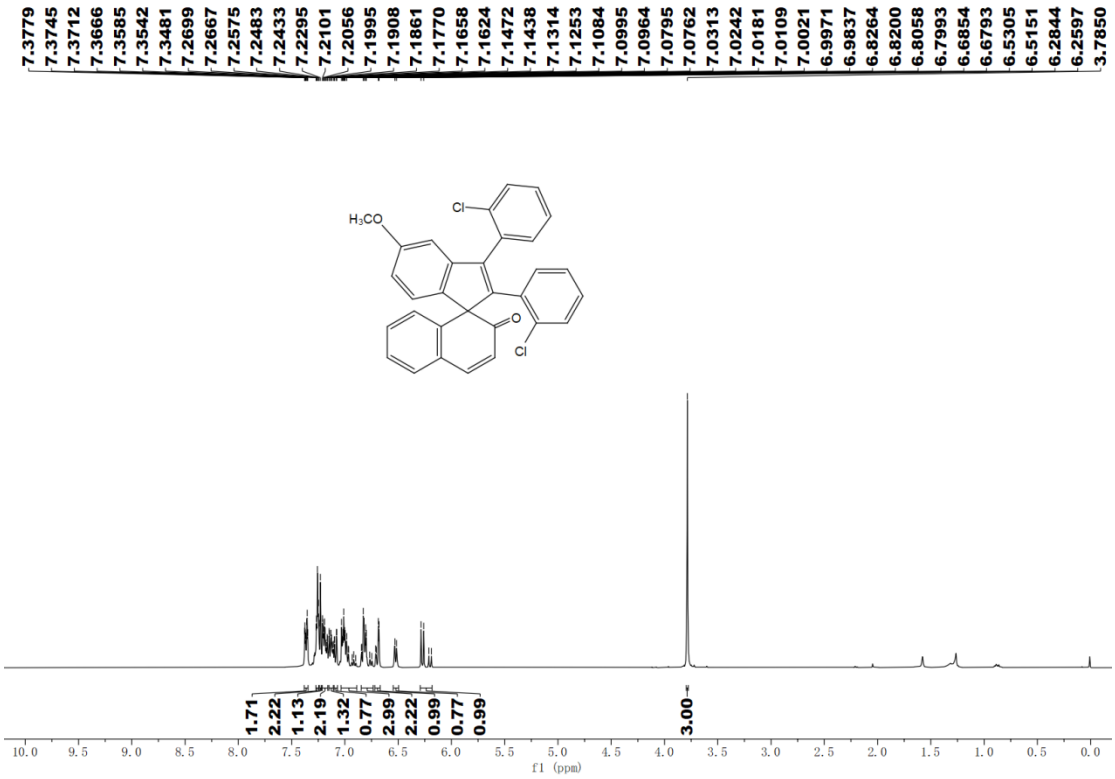


Fig S46. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-bis(2-chlorophenyl)-5-methoxy-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3v**)

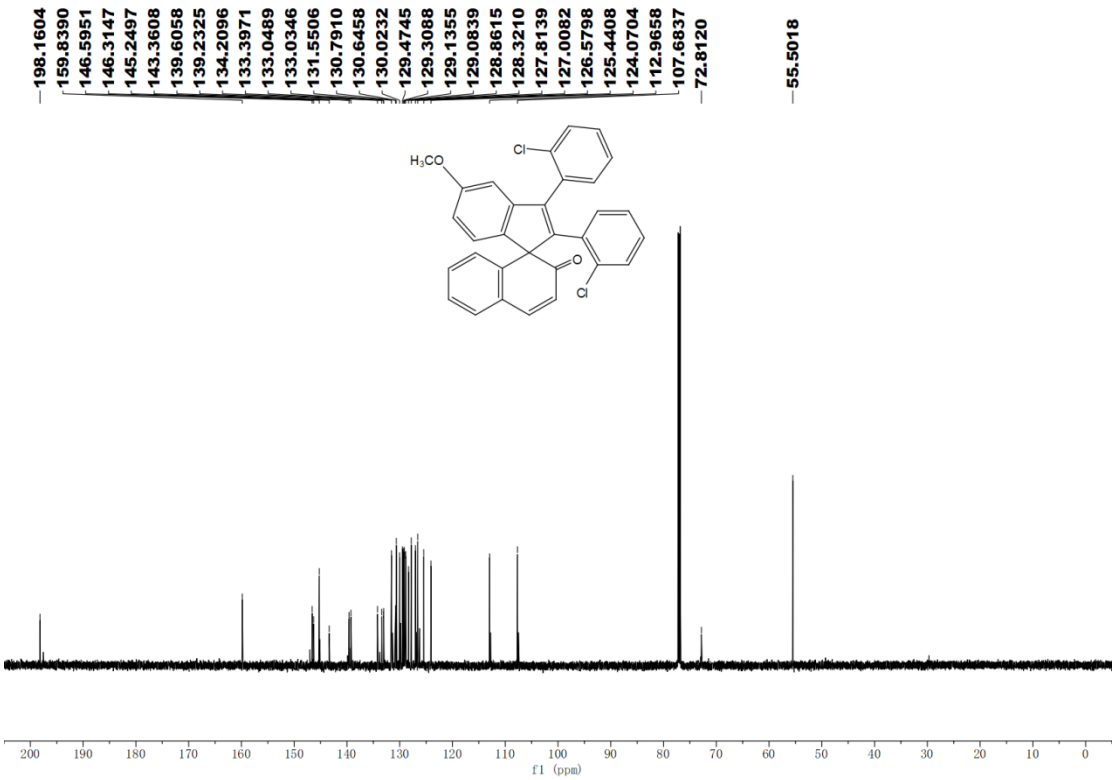


Fig S47. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-bis(2-chlorophenyl)-5-methox y-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3v**)

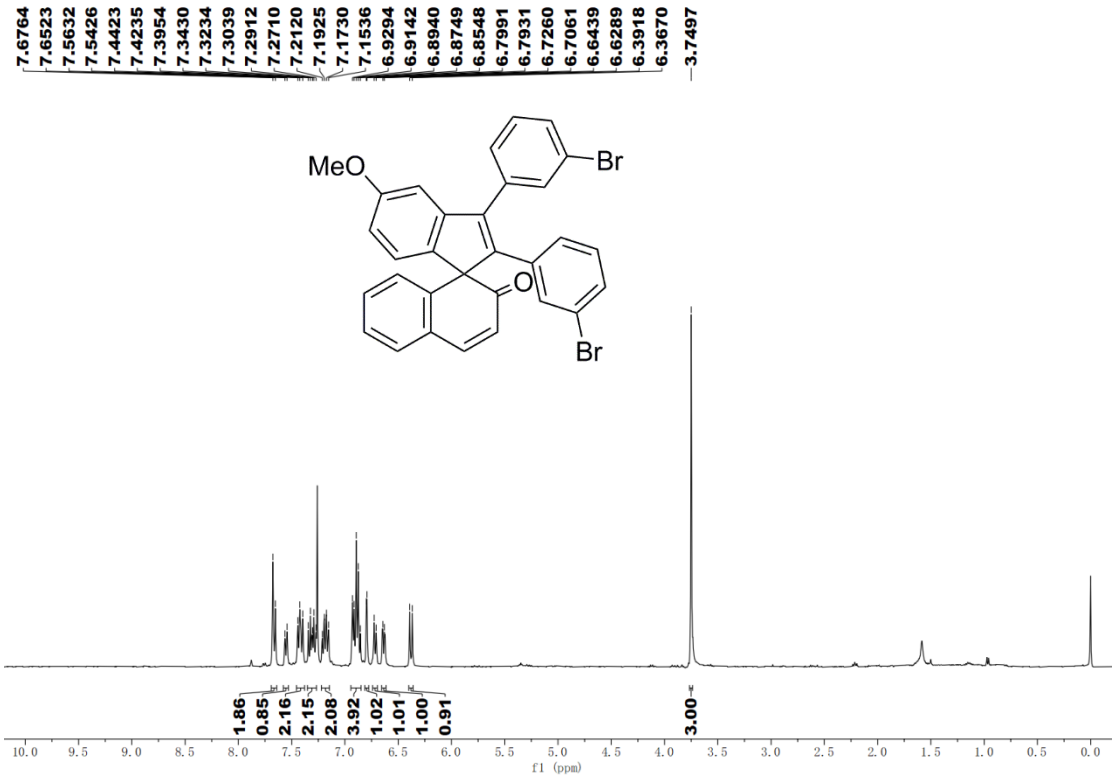


Fig S48. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-bis(3-bromophenyl)-5-methoxy-2'*H* -spiro[indene-1,1'-naphthalen]-2'-one (**3w**)

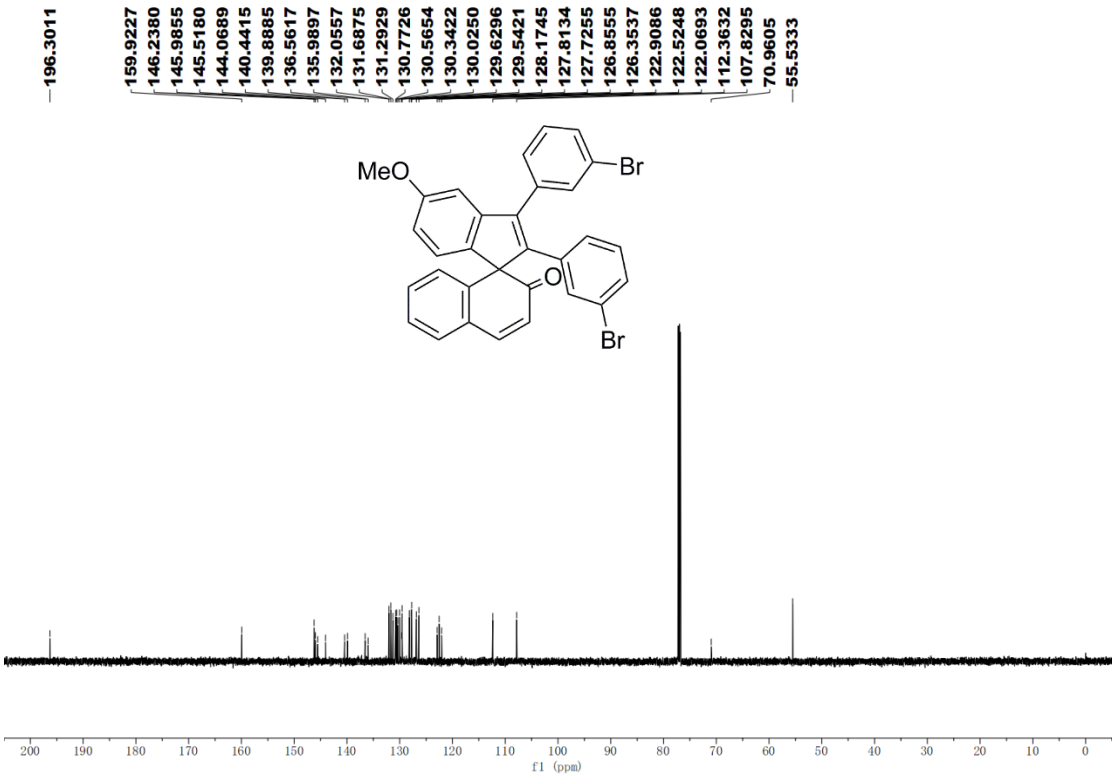


Fig S49. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-bis(3-bromophenyl)-5-methoxy-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**3w**)

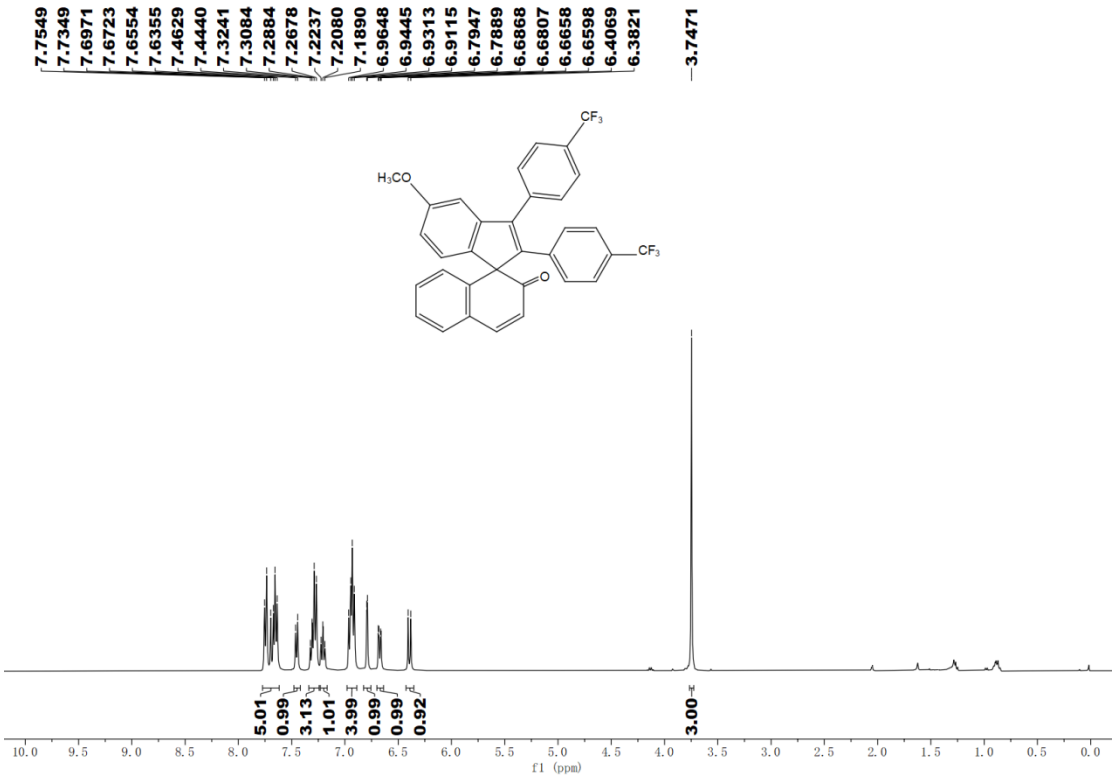


Fig S50. ^{1}H NMR (400 MHz, $CDCl_3$) of 5-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3x**)

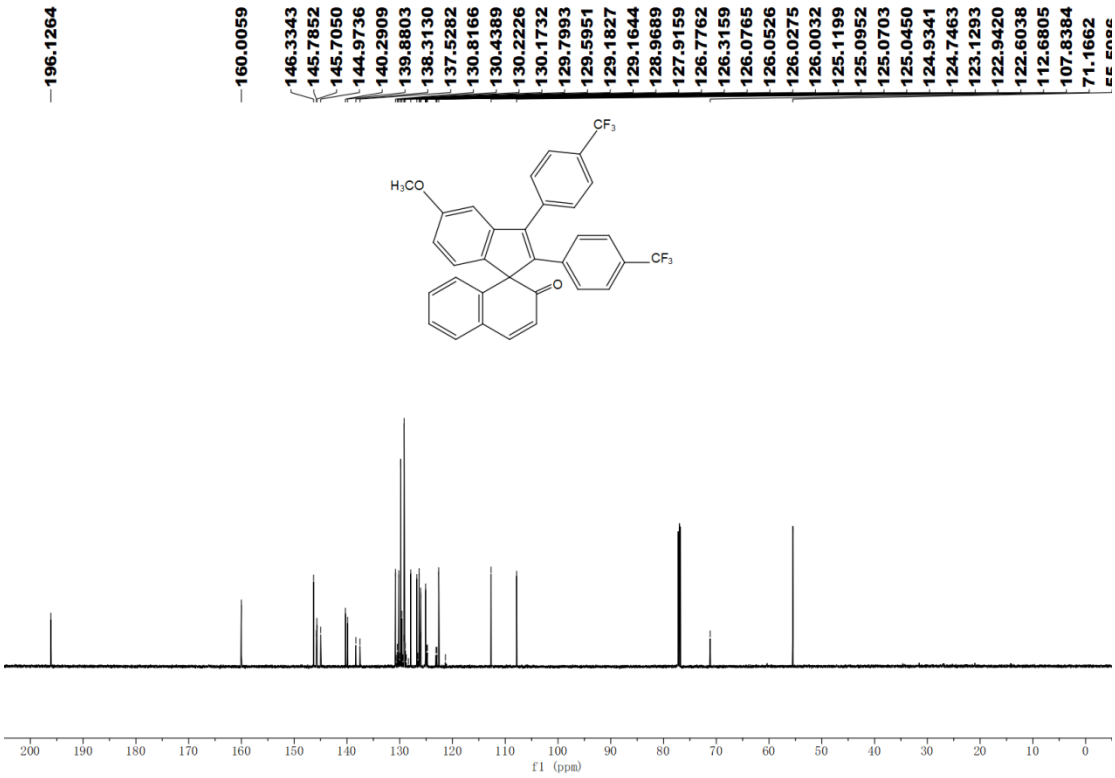


Fig S51. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 5-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3x**)

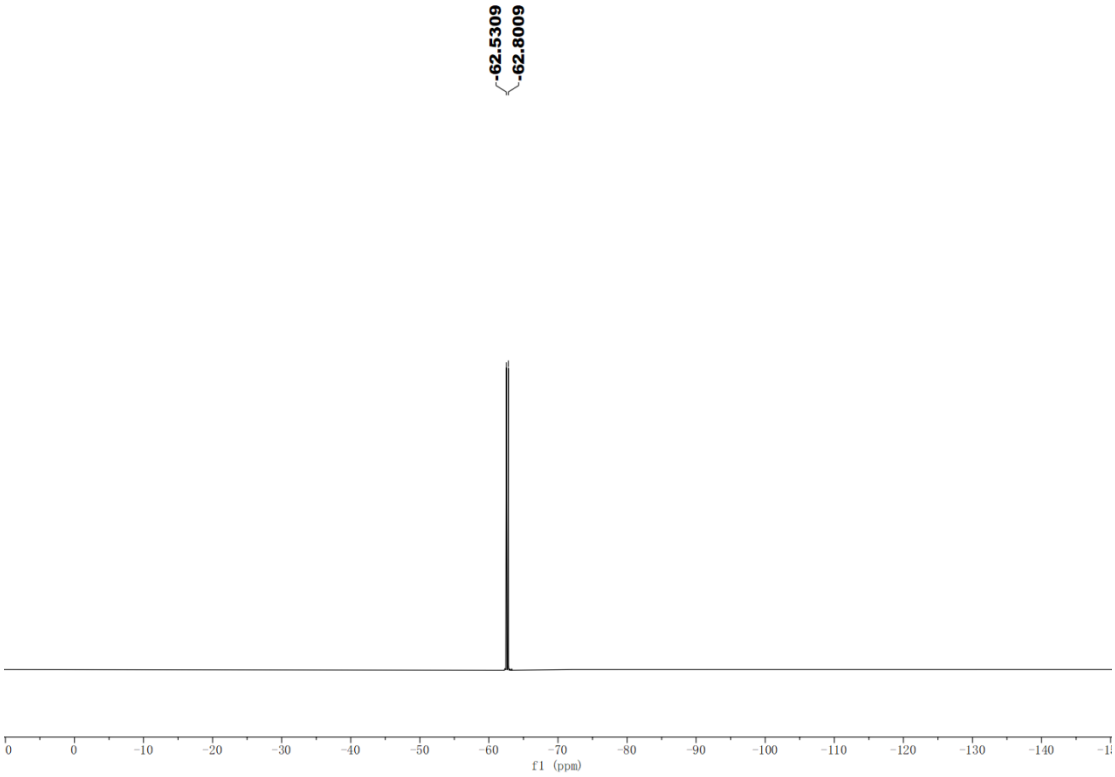


Fig S52.^{19}F NMR (376 MHz, $CDCl_3$) of 5-methoxy-2,3-bis(4-(trifluoromethyl)phenyl)-2'H-spiro[indene-1,1'-naphthalen]-2'-one (**3x**)

5. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for products 5a−5h

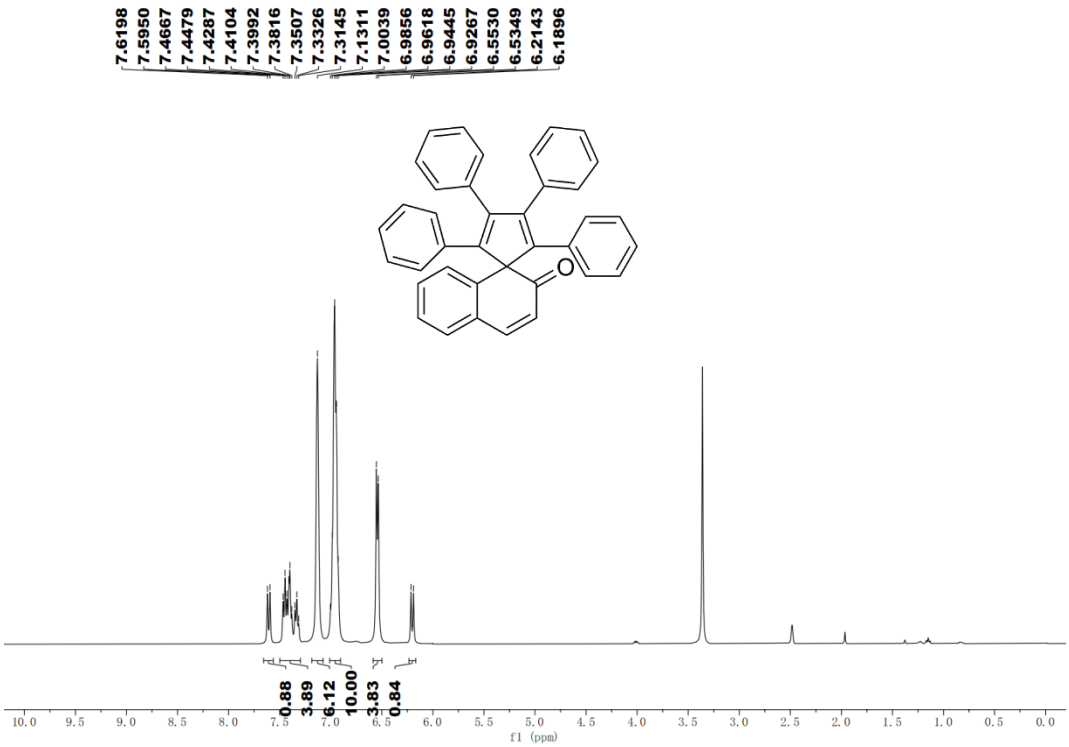


Fig S53. ^{1}H NMR (400 MHz, DMSO-d_6) of 2,3,4,5-tetraphenyl-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5a**)

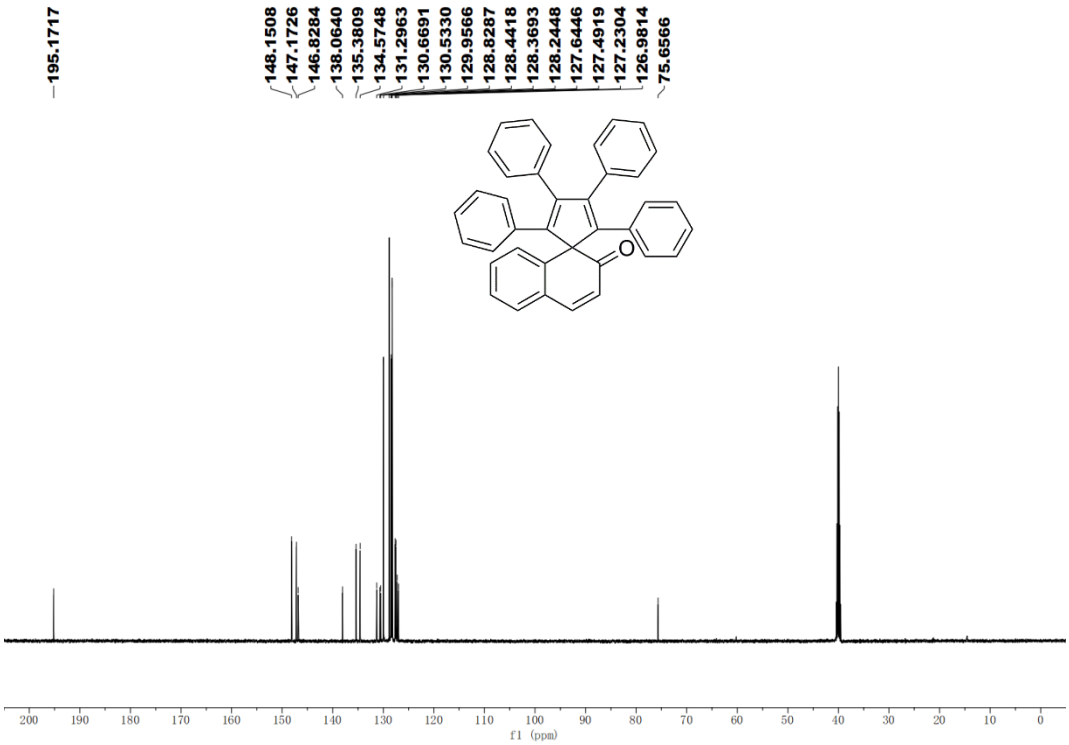


Fig S54. $^{13}C\{^{1}H\}$ NMR (150 MHz, DMSO-d_6) of 2,3,4,5-tetraphenyl-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5a**)

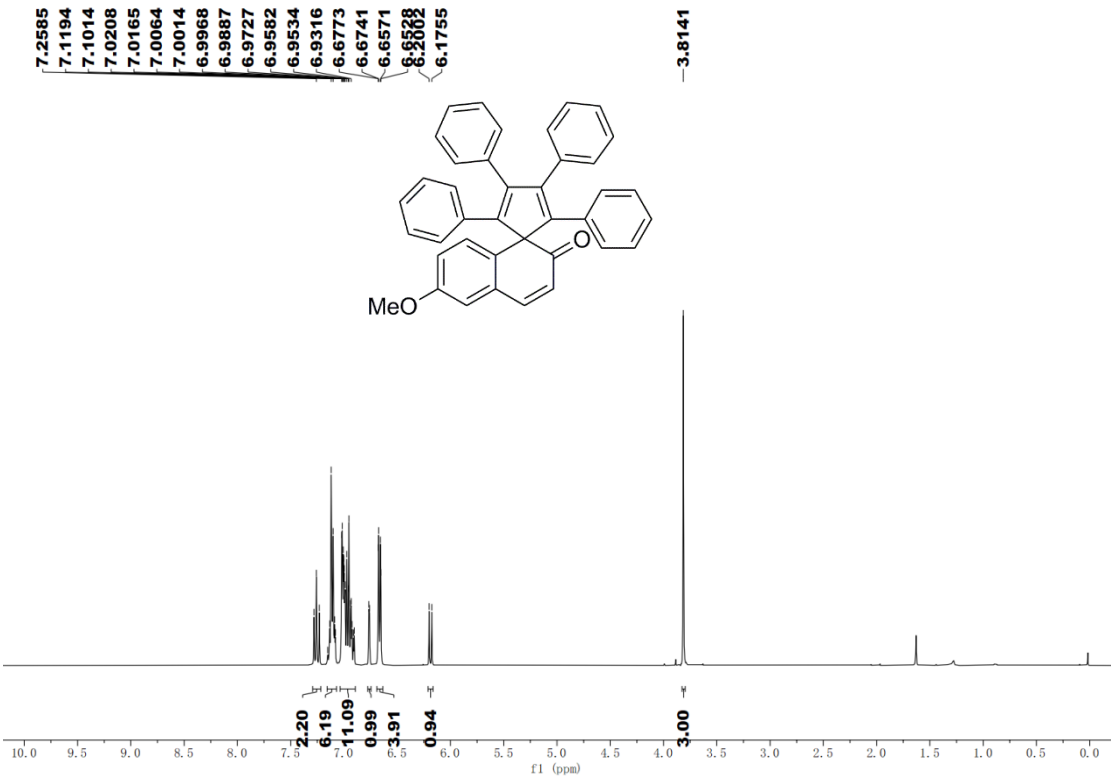


Fig S55. ^{1}H NMR (400 MHz, $CDCl_3$) of 6'-methoxy-2,3,4,5-tetraphenyl-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5b**)

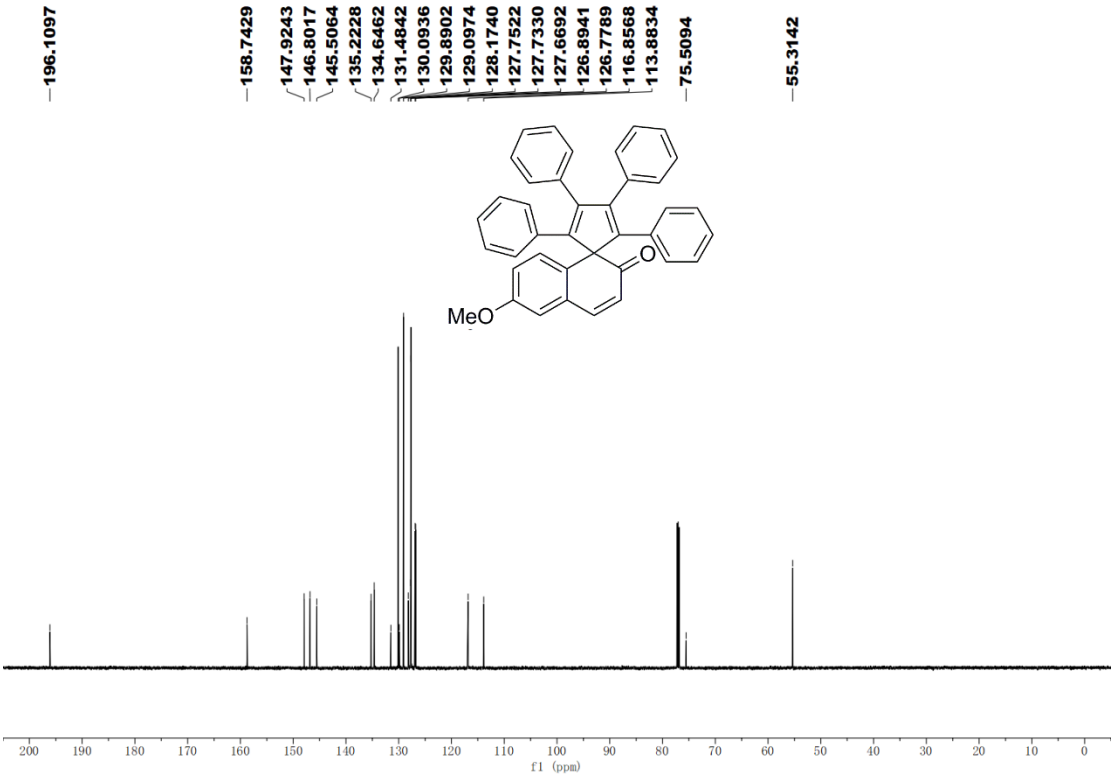


Fig S56. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6'-methoxy-2,3,4,5-tetraphenyl-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5b**)

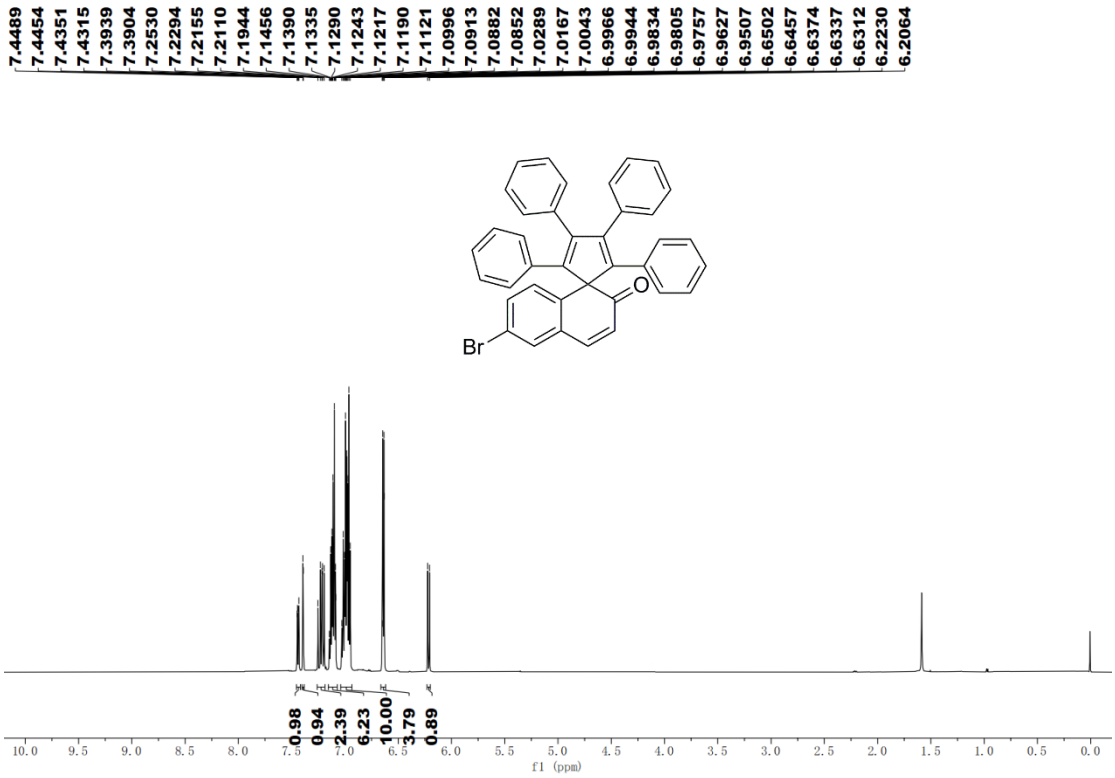


Fig S57. ^{1}H NMR (400 MHz, $CDCl_3$) of 6'-bromo-2,3,4,5-tetraphenyl-2'*H*-spiro [cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5c**)

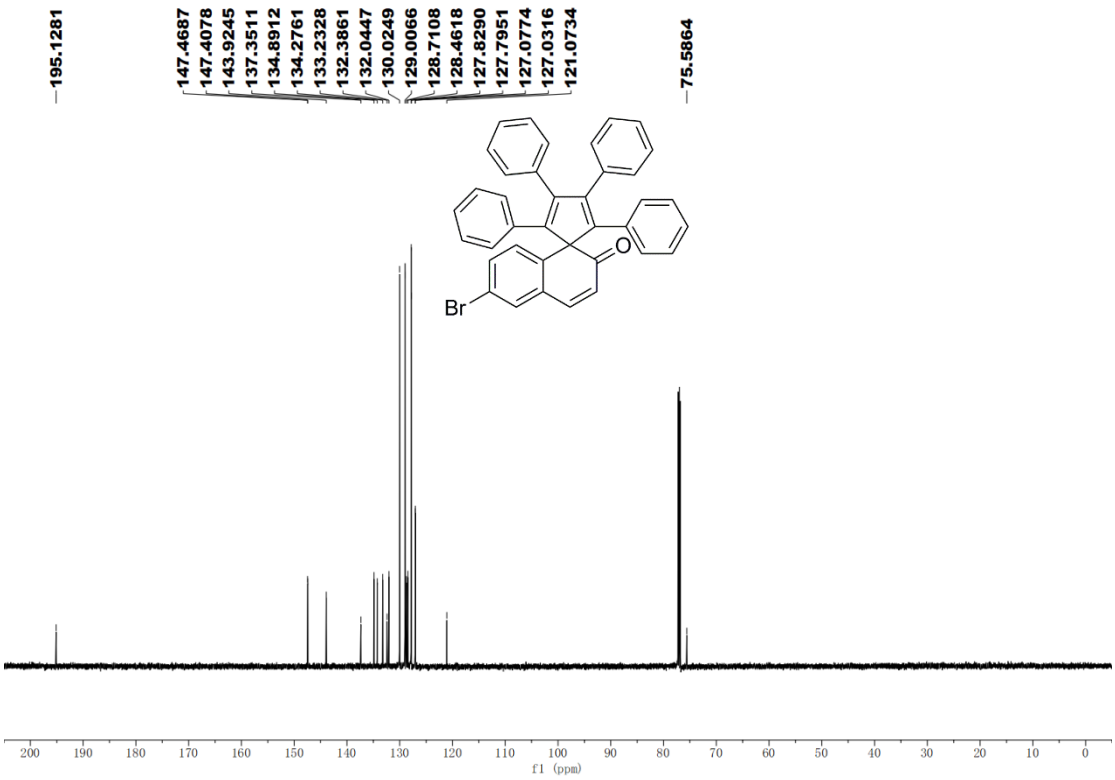


Fig S58. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6'-bromo-2,3,4,5-tetraphenyl-2'*H* -spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5c**)

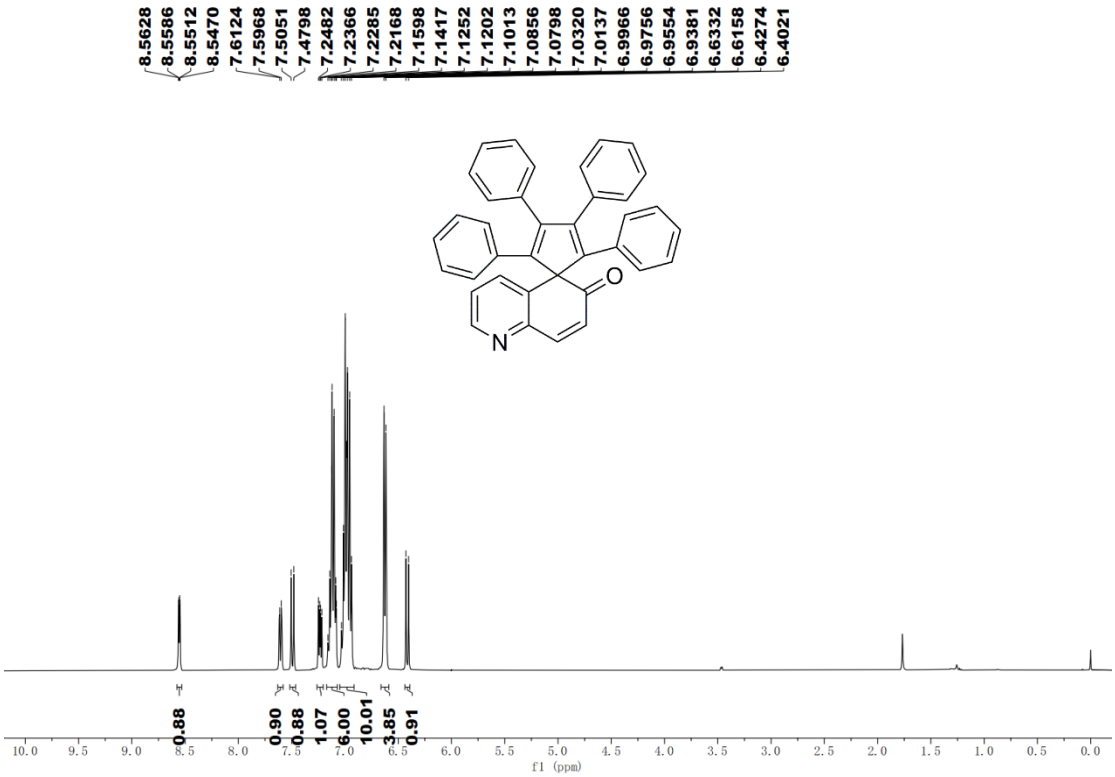


Fig S59. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,4,5-tetraphenyl-6'*H*-spiro[cyclopentane-1,5'-quinoline]-2,4-dien-6'-one (**5d**)

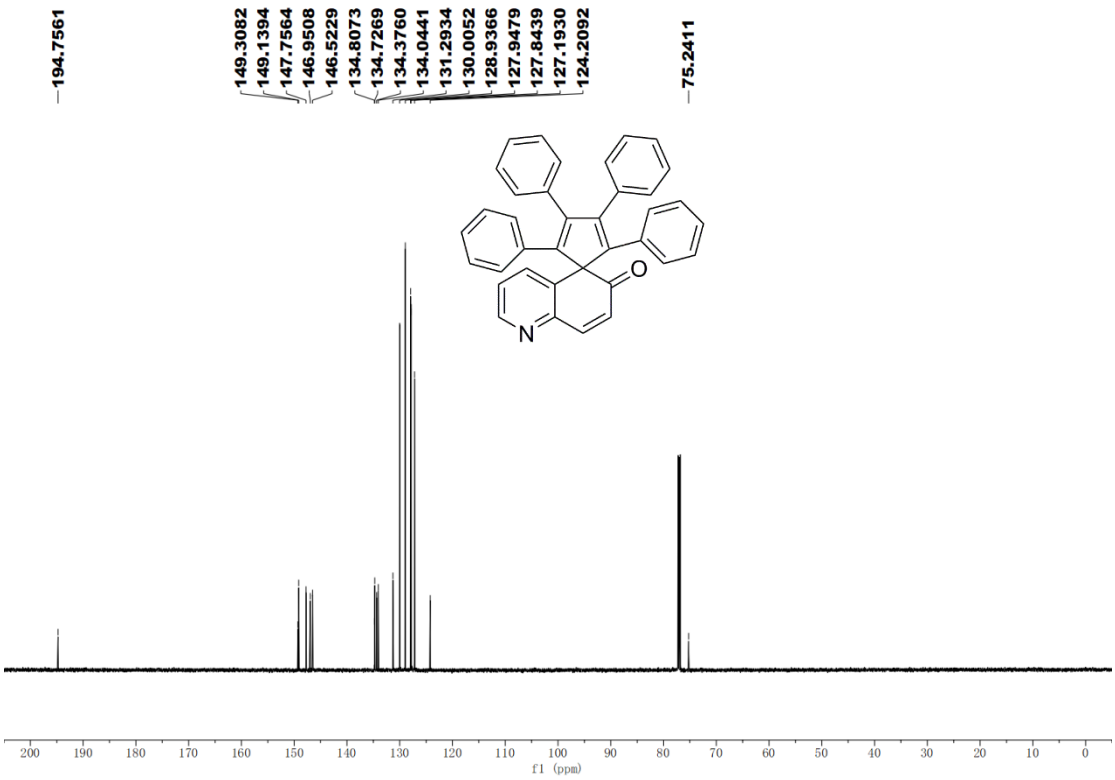


Fig S60. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,4,5-tetraphenyl-6'*H*-spiro[cyclopentane-1,5'-quinoline]-2,4-dien-6'-one (**5d**)

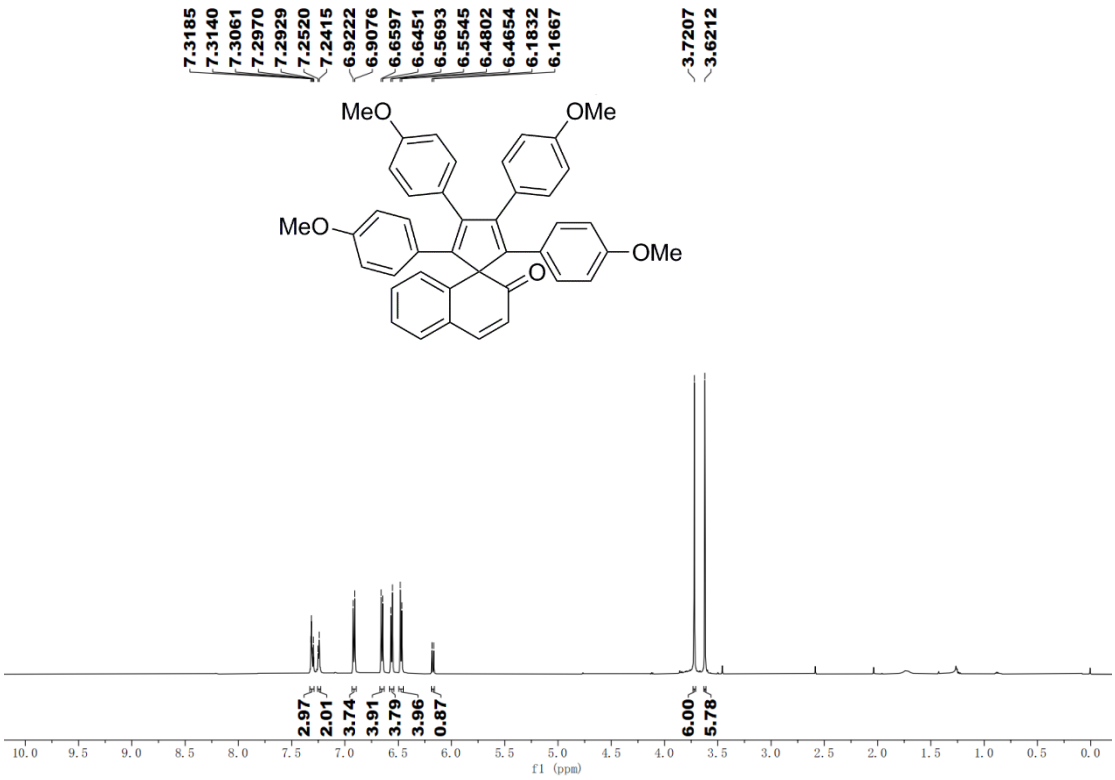


Fig S61. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,4,5-tetrakis(4-methoxyphenyl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5e**)

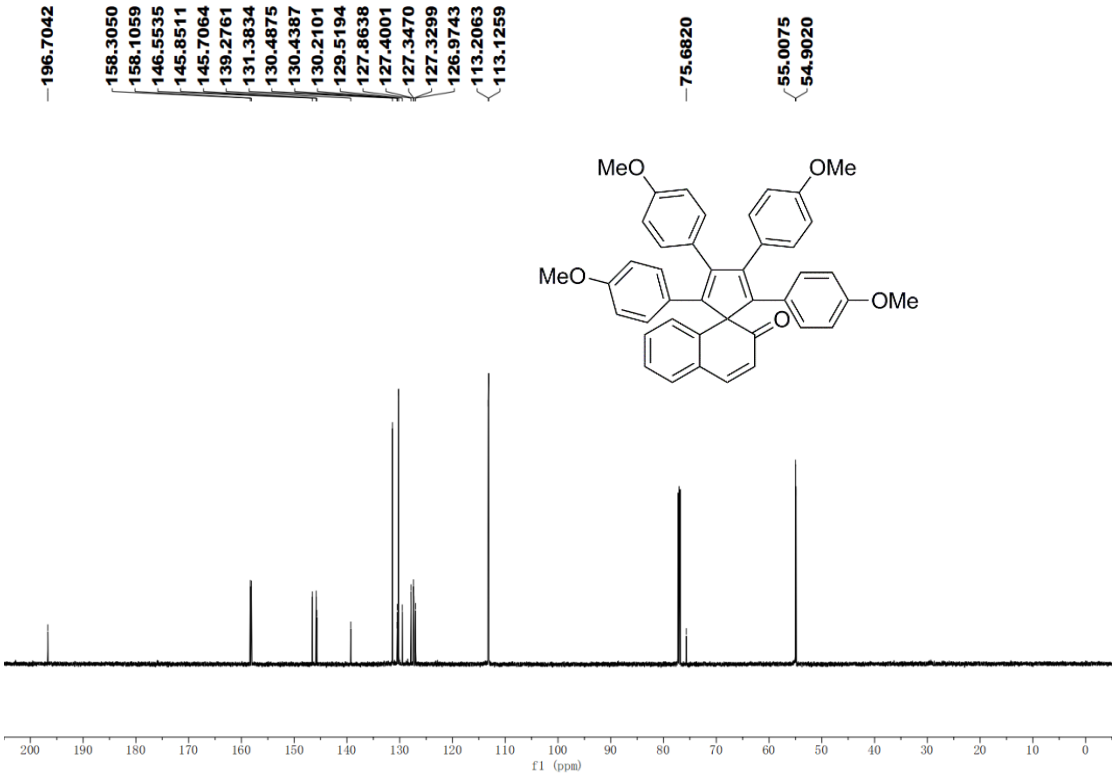


Fig S62. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,4,5-tetrakis(4-methoxyphenyl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5e**)

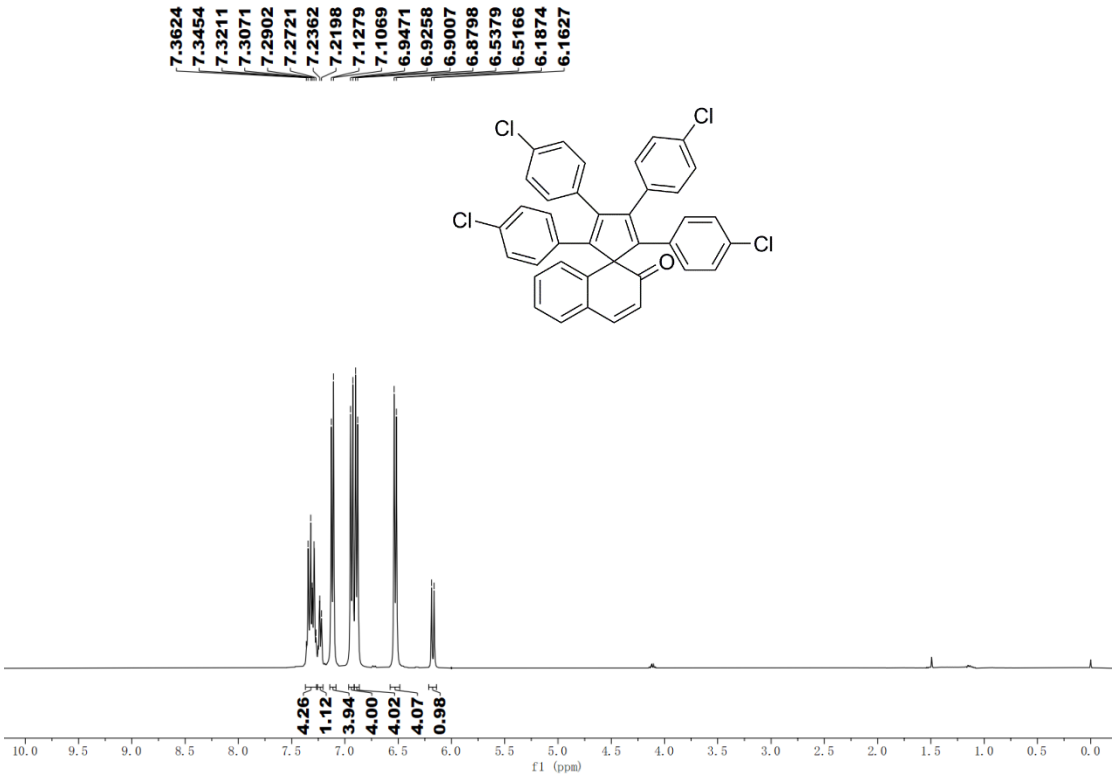


Fig S63. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,4,5-tetrakis(4-chlorophenyl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5f**)

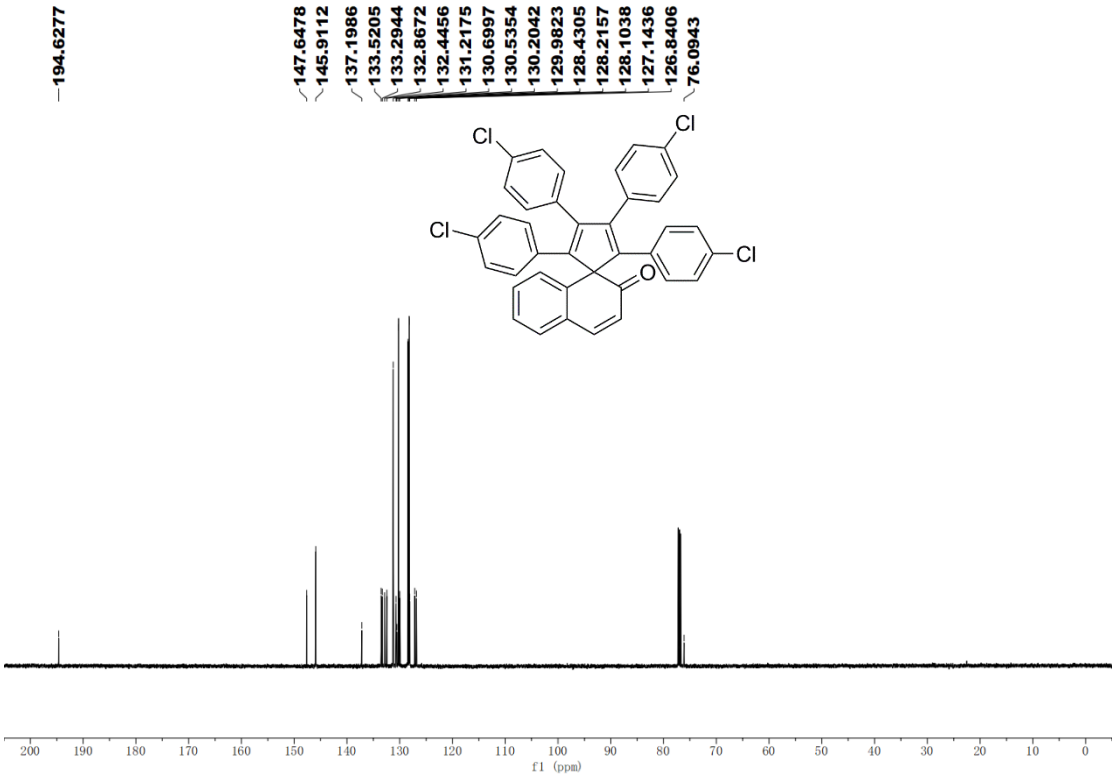


Fig S64. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,4,5-tetrakis(4-chlorophenyl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5f**)

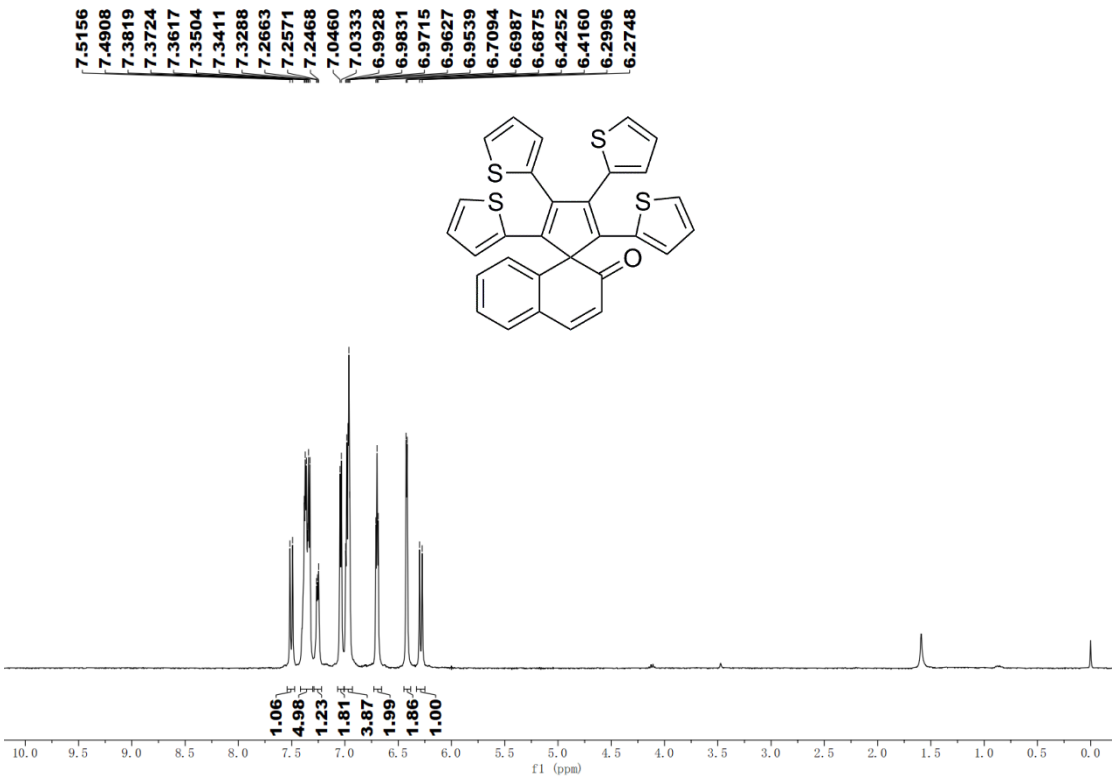


Fig S65. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3,4,5-tetra(thiophen-2-yl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5g**)

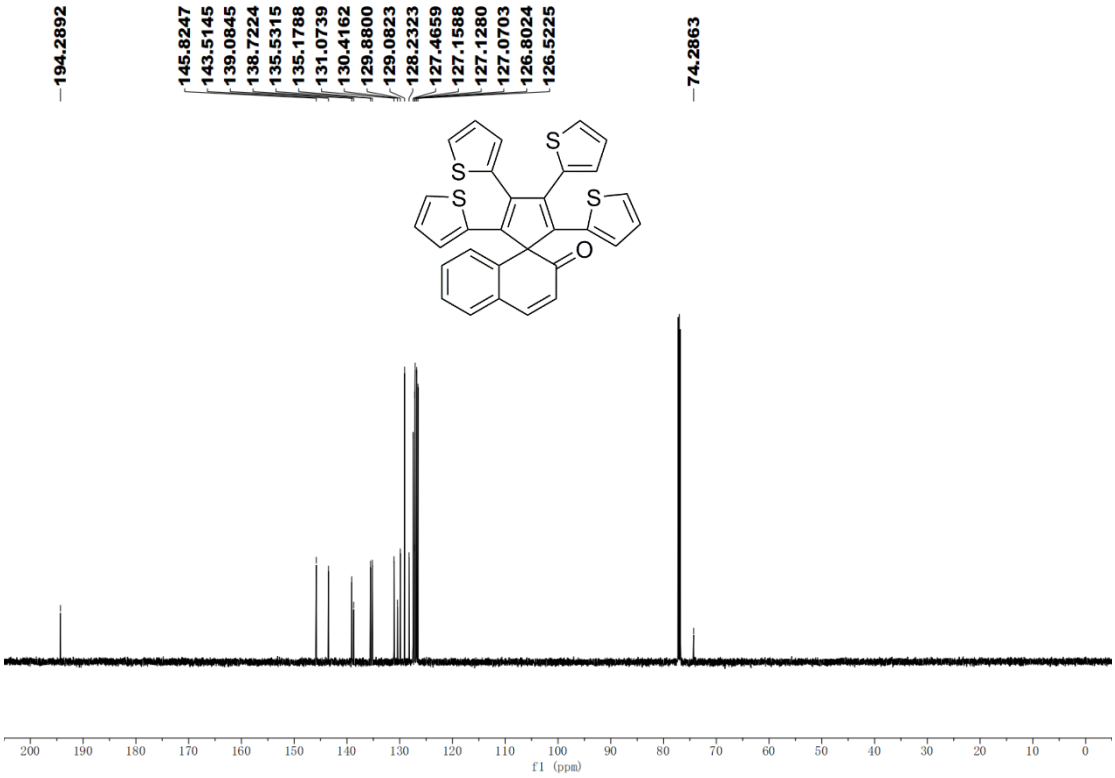


Fig S66. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3,4,5-tetra(thiophen-2-yl)-2'*H*-spiro[cyclopentane-1,1'-naphthalene]-2,4-dien-2'-one (**5g**)

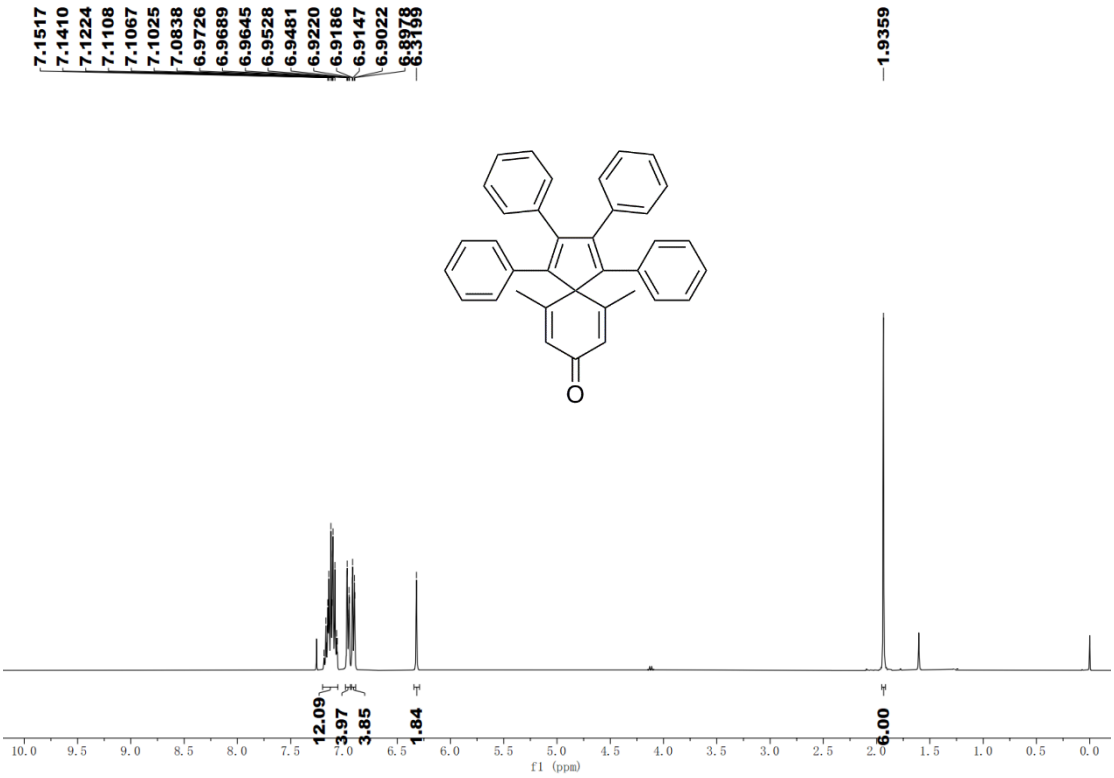


Fig S67. ^{1}H NMR (400 MHz, $CDCl_3$) of 6,10-dimethyl-1,2,3,4-tetraphenylspiro [4.5]deca-1,3,6,9-tetraen-8-one (**5h**)

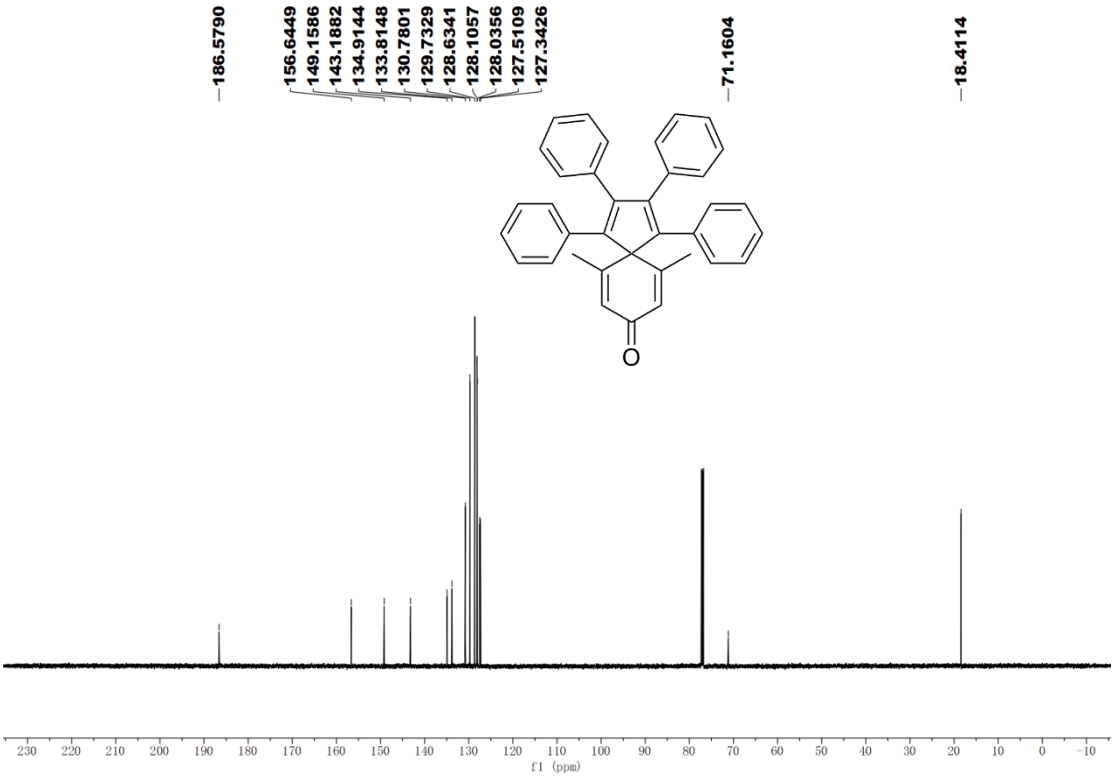


Fig S68. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 6,10-dimethyl-1,2,3,4-tetrapheny lspiro[4.5]deca-1,3,6,9-tetraen-8-one (**5h**)

7. ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra for compound 6

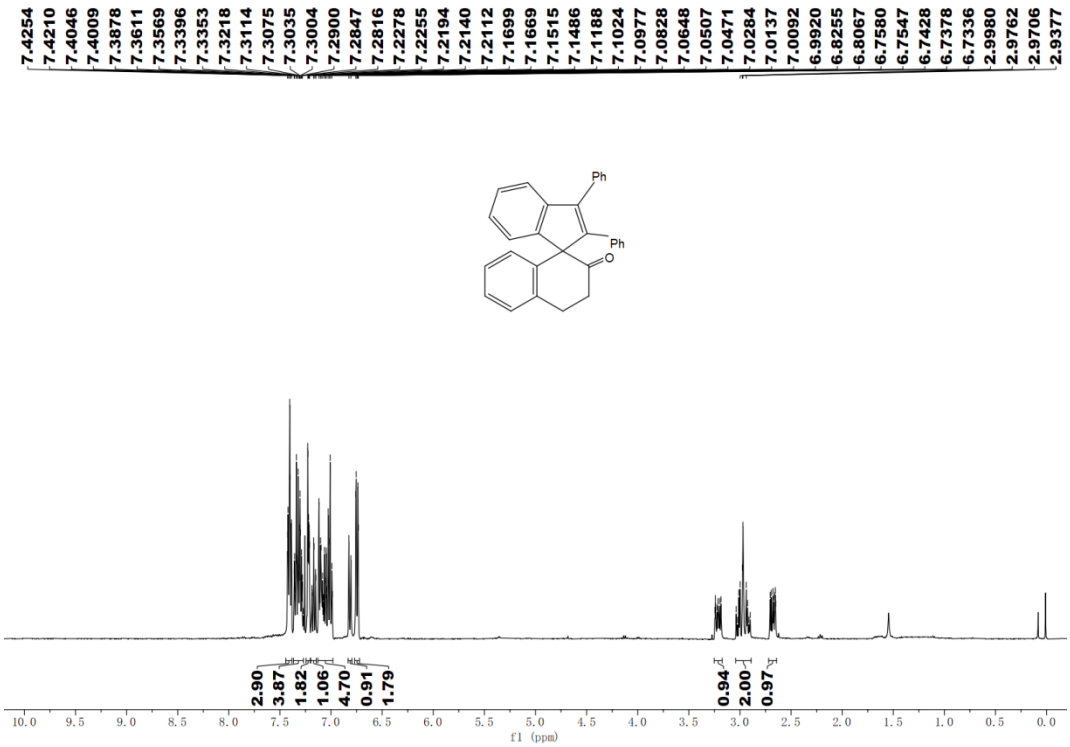


Fig S69. ^{1}H NMR (400 MHz, $CDCl_3$) of 2,3-diphenyl-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**6**)

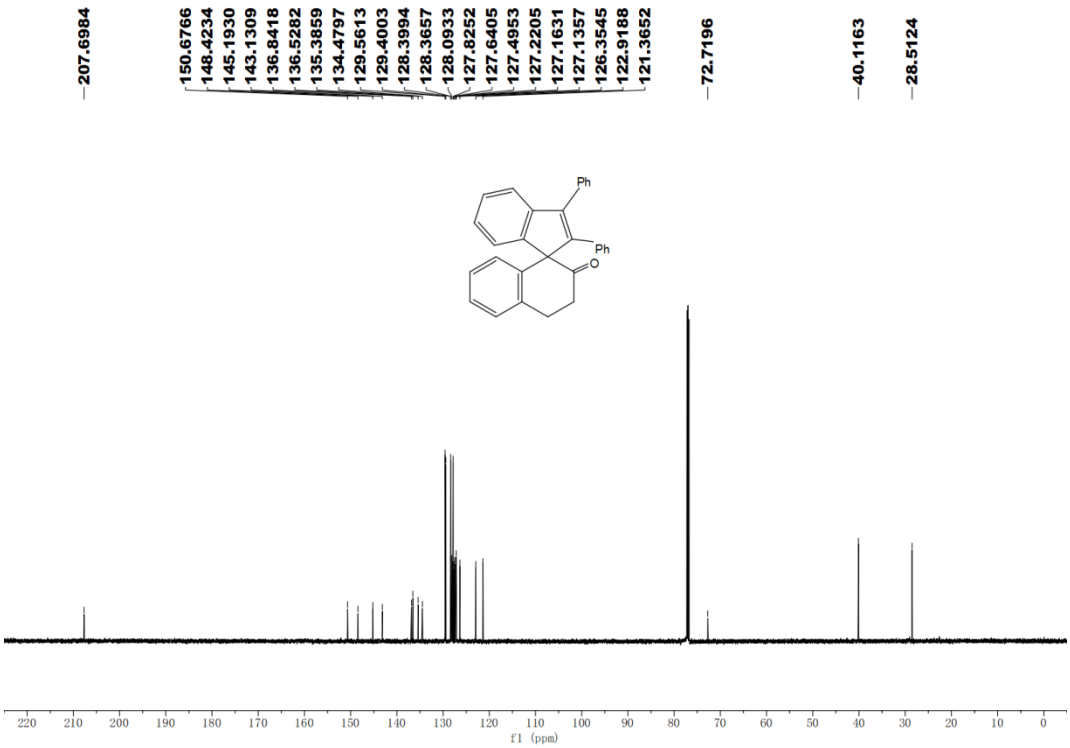


Fig S70. $^{13}C\{^{1}H\}$ NMR (150 MHz, $CDCl_3$) of 2,3-diphenyl-3',4'-dihydro-2'*H*-spiro[indene-1,1'-naphthalen]-2'-one (**6**)

8. X-ray crystallographic data of compound 3l

Thermal ellipsoids are set at a 50% probability level. Crystal data have been deposited to CCDC, number 2376960.

Crystallization Details:

The obtained compound **3l** (48 mg) was dissolved in $CDCl_3$ (0.5 mL) in a NMR tube at room temperature. Then petroleum ether (2 mL) was added to the solution slowly along the tube wall, resulting in a two-phase mixture. The yellow crystal of **3l** was formed after the two-phase mixture has diffused.

Experimental

Single crystals of $C_{30}H_{19}ClO$ were obtained from the solution of **3l** in $CDCl_3$ and measured on a XtaLAB Synergy R, DW system, HyPix diffractometer. The crystal was kept at 279.5(3) K during data collection. Using Olex2, the structure was solved with the SHELXT structure solution program using Intrinsic Phasing and refined with the SHELXL refinement package using Least Squares minimisation.

Crystal structure determination

Crystal Data for $C_{30}H_{19}ClO$ (M = 430.90 g/mol): monoclinic, space group $P2_1/n$ (no. 14), a = 8.96420(10) Å, b = 17.4048(2) Å, c = 14.3991(2) Å, β = 95.5460(10), V = 2236.03(5) $Å^3$, Z = 4, T = 279.5(3) K, μ(Cu Kα) = 1.655 mm^{-1}, Dcalc = 1.280 g/cm^3, 15282 reflections measured ($7.992 \leq 2\Theta \leq 152.706$), 4459 unique ($R_{int}$ = 0.0235, R_{sigma} = 0.0201) which were used in all calculations. The final R_1 was 0.0414 ($I > 2\sigma(I)$) and wR_2 was 0.1176 (all data).

Refinement model description

Number of restraints - 0, number of constraints - unknown.

Details:

1. Fixed Uiso

At 1.2 times of:

All C(H) groups

2. a Aromatic/amide H refined with riding coordinates:

C2(H2), C3(H3), C5(H5), C7(H7), C9(H9), C11(H11), C13(H13), C15(H15), C17(H17), C20(H20), C21(H21), C22(H22), C23(H23), C24(H24), C25(H25), C26(H26), C27(H27), C29(H29), C30(H30)

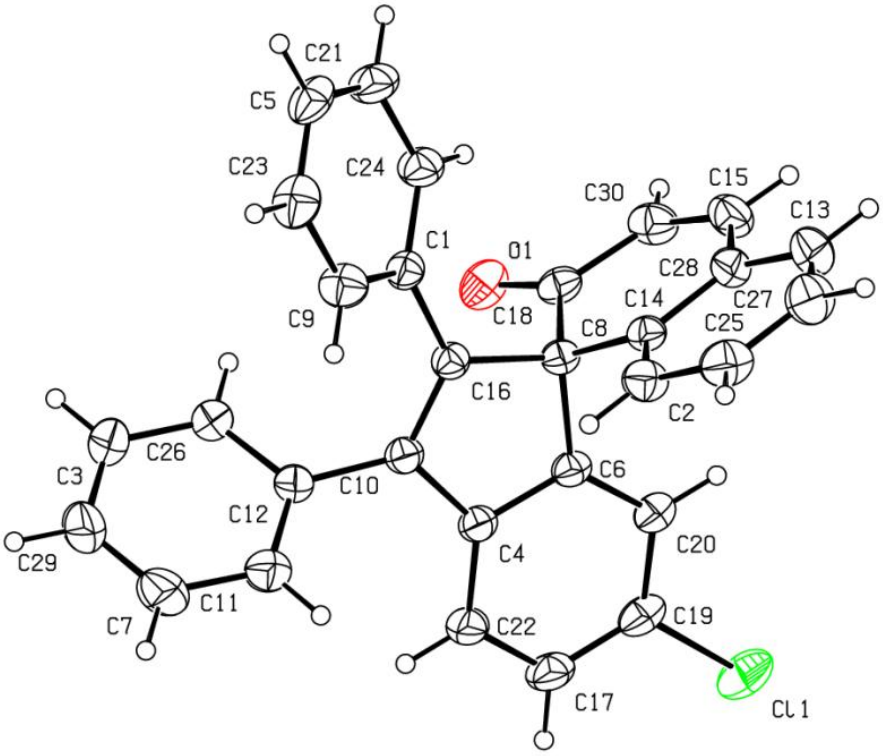


Table S1 Crystallographic Data of Compound 3l.

Empirical formula	$C_{30}H_{19}ClO$
Formula weight	430.90
Temperature/K	279.5(3)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	8.96420(10)
b/Å	17.4048(2)
c/Å	14.3991(2)
α/°	90
β/°	95.5460(10)
γ/°	90
Volume/Å^3	2236.03(5)
Z	4
ρcalcg/cm^3	1.280
μ/mm^{-1}	1.655
F(000)	896.0
Crystal size/mm^3	0.18 × 0.15 × 0.12
Radiation	Cu Kα (λ = 1.54184)
2Θ range for data collection/°	7.992 to 152.706
Index ranges	$-11 \le h \le 11$, $-21 \le k \le 21$, $-17 \le l \le 15$
Reflections collected	15282
Independent reflections	4459 [R_{int} = 0.0235, R_{sigma} = 0.0201]
Data/restraints/parameters	4459/0/289
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0414, wR_2 = 0.1136
Final R indexes [all data]	R_1 = 0.0462, wR_2 = 0.1176
Largest diff. peak/hole / e Å^{-3}	0.19/-0.33

Table S2 Fractional Atomic Coordinates ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($Å^2 \times 10^3$) for Compound 3l. U_{eq} is defined as 1/3 of the trace of the orthogonalised U_{IJ} tensor.

Atom	x	y	z	U(eq)
Cl1	11059.3(5)	3953.3(3)	5102.6(3)	79.57(18)
O1	8030.1(12)	3631.4(7)	8601.0(7)	60.3(3)
C1	4182.0(15)	3783.9(7)	7990.6(9)	41.9(3)
C2	4896.1(18)	5100.9(9)	6277.0(10)	53.9(4)
C3	3684(2)	1269.2(10)	7641.4(14)	70.1(5)
C4	6876.7(15)	3159.6(7)	6312.0(9)	41.7(3)
C5	1910.5(19)	3956.5(10)	9175.3(12)	61.3(4)
C6	7517.8(14)	3869.3(7)	6560.9(9)	40.6(3)
C7	3094(3)	1368.9(13)	6003.6(15)	83.5(6)
C8	6626.8(14)	4243.0(7)	7296.8(8)	39.4(3)
C9	2714.7(16)	3554.9(10)	7713.4(12)	56.3(4)
C10	5560.8(15)	3040.6(7)	6826.9(9)	41.3(3)
C11	3951(2)	2033.6(10)	5982.3(11)	63.0(4)
C12	4665.1(16)	2325.3(8)	6801.0(9)	45.7(3)
C13	6248(2)	6413.0(10)	7038.4(14)	69.4(5)
C14	6051.5(15)	5031.2(7)	6981.5(9)	42.0(3)
C15	7925.6(18)	5619.0(10)	8129.4(12)	60.0(4)
C16	5381.6(14)	3658.7(7)	7376.1(9)	39.6(3)
C17	8827.5(19)	2945.5(9)	5314.3(11)	59.2(4)
C18	7723.0(15)	4232.6(9)	8199.3(9)	45.2(3)
C19	9434.7(17)	3651.0(10)	5572.8(10)	54.7(4)
C20	8796.8(16)	4128.3(9)	6202.8(10)	47.8(3)
C21	3340(2)	4199.1(10)	9450.9(12)	62.4(4)
C22	7539.2(18)	2695.3(8)	5682.2(10)	53.2(3)
C23	1600.2(18)	3635.4(10)	8304.0(14)	64.8(4)
C24	4462.5(17)	4118.9(9)	8864.9(11)	54.1(4)
C25	4424(2)	5820.0(11)	5957.9(12)	66.5(4)
C26	4533.1(18)	1925.7(9)	7628.0(11)	54.5(4)
C27	5104(3)	6473.7(10)	6337.2(14)	75.9(5)
C28	6732.0(17)	5695.6(8)	7373.8(10)	50.7(3)
C29	2959(3)	993.0(12)	6831.2(17)	83.4(6)
C30	8383.8(17)	4956.0(10)	8509.0(11)	56.3(4)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for 3l. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Cl1	61.5(3)	110.8(4)	71.9(3)	5.5(2)	34.7(2)	-1.5(2)
O1	52.7(6)	72.3(7)	55.5(6)	15.8(5)	3.7(5)	7.7(5)
C1	42.0(7)	39.4(6)	45.7(7)	2.9(5)	11.1(5)	4.8(5)
C2	60.1(9)	52.0(8)	49.0(8)	-0.9(6)	2.2(6)	7.5(7)
C3	86.3(13)	57.2(9)	71.3(11)	1.7(8)	30.6(9)	-13.3(8)
C4	48.1(7)	40.2(6)	37.9(6)	2.6(5)	9.9(5)	5.8(5)
C5	56.7(9)	63.7(9)	68.7(10)	17.4(8)	32.4(8)	18.1(7)
C6	42.6(7)	43.4(7)	36.7(6)	1.4(5)	8.6(5)	6.0(5)
C7	91.6(14)	85.3(13)	73.4(12)	-27.4(10)	6.4(10)	-31.8(11)
C8	39.4(6)	41.4(6)	38.3(6)	-2.4(5)	8.6(5)	1.5(5)
C9	41.5(7)	65.9(9)	61.8(9)	-5.4(7)	7.6(6)	7.0(7)
C10	45.0(7)	41.1(6)	38.4(6)	0.4(5)	7.3(5)	2.7(5)
C11	72.7(10)	67.3(10)	49.5(8)	-6.9(7)	8.0(7)	-10.9(8)
C12	49.1(7)	42.4(7)	46.9(7)	-3.6(5)	11.5(6)	-0.6(6)
C13	87.2(13)	43.5(8)	79.1(12)	-3.6(8)	16.8(10)	-0.2(8)
C14	45.3(7)	42.2(7)	40.1(6)	-1.9(5)	11.6(5)	2.7(5)
C15	57.4(9)	58.2(9)	64.9(9)	-18.2(7)	8.0(7)	-13.7(7)
C16	38.7(6)	40.8(6)	39.9(6)	0.4(5)	6.4(5)	2.5(5)
C17	70.5(10)	60.3(9)	50.7(8)	-0.2(7)	26.4(7)	15.6(8)
C18	37.1(6)	58.7(8)	41.1(7)	-1.5(6)	10.7(5)	3.5(6)
C19	50.3(8)	70.1(10)	46.2(7)	7.7(7)	18.3(6)	8.7(7)
C20	46.3(7)	54.1(8)	44.2(7)	3.1(6)	11.2(6)	0.8(6)
C21	67.3(10)	69.2(10)	54.4(9)	-3.6(7)	24.9(8)	10.0(8)
C22	70.0(9)	43.7(7)	48.6(8)	-2.3(6)	19.5(7)	7.0(7)
C23	39.8(8)	70.7(10)	85.9(12)	8.3(9)	16.0(7)	8.0(7)
C24	49.1(8)	60.7(9)	54.7(8)	-9.3(7)	15.9(6)	-0.2(6)
C25	74.8(11)	69.1(11)	55.3(9)	8.5(8)	4.1(8)	22.4(9)
C26	64.7(9)	50.1(8)	50.4(8)	-1.5(6)	14.9(7)	-4.1(7)
C27	102.0(15)	50.3(9)	77.1(12)	11.5(8)	17.6(11)	21.1(9)
C28	56.4(8)	43.1(7)	54.4(8)	-5.4(6)	14.5(6)	-2.3(6)
C29	91.7(14)	67.4(11)	95.3(15)	-16.9(10)	31.2(12)	-32.8(10)
C30	46.2(8)	70.6(10)	51.0(8)	-11.2(7)	-0.3(6)	-1.9(7)

Table S4 Bond Lengths for Compound 3l.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl1	C19	1.7455(15)	C8	C16	1.5224(18)
O1	C18	1.2143(18)	C8	C18	1.5517(18)
C1	C9	1.395(2)	C9	C23	1.380(2)
C1	C16	1.4734(18)	C10	C12	1.4800(19)
C1	C24	1.388(2)	C10	C16	1.3538(18)
C2	C14	1.383(2)	C11	C12	1.382(2)
C2	C25	1.385(2)	C12	C26	1.394(2)
C3	C26	1.374(2)	C13	C27	1.372(3)
C3	C29	1.367(3)	C13	C28	1.393(2)
C4	C6	1.3946(19)	C14	C28	1.4006(19)
C4	C10	1.4673(18)	C15	C28	1.456(2)
C4	C22	1.3900(18)	C15	C30	1.325(2)
C5	C21	1.371(3)	C17	C19	1.380(2)
C5	C23	1.377(3)	C17	C22	1.386(2)
C6	C8	1.5320(17)	C18	C30	1.444(2)
C6	C20	1.3776(19)	C19	C20	1.393(2)
C7	C11	1.390(3)	C21	C24	1.381(2)
C7	C29	1.375(3)	C25	C27	1.378(3)
C8	C14	1.5196(18)			

Table S5 Bond Angles for Compound 3l.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C9	C1	C16	120.57(12)	C2	C14	C8	120.44(12)
C24	C1	C9	117.55(13)	C2	C14	C28	119.30(13)
C24	C1	C16	121.87(12)	C28	C14	C8	120.19(12)
C14	C2	C25	120.36(15)	C30	C15	C28	124.33(14)
C29	C3	C26	119.92(17)	C1	C16	C8	121.96(11)
C6	C4	C10	109.06(11)	C10	C16	C1	127.08(12)
C22	C4	C6	119.42(13)	C10	C16	C8	110.96(11)
C22	C4	C10	131.50(13)	C19	C17	C22	119.86(13)
C21	C5	C23	119.31(14)	O1	C18	C8	120.34(13)
C4	C6	C8	108.92(11)	O1	C18	C30	122.49(13)
C20	C6	C4	122.06(12)	C30	C18	C8	117.14(12)
C20	C6	C8	128.93(12)	C17	C19	Cl1	119.07(12)
C29	C7	C11	120.66(17)	C17	C19	C20	122.03(14)
C6	C8	C18	104.13(10)	C20	C19	Cl1	118.89(13)
C14	C8	C6	111.17(10)	C6	C20	C19	117.22(14)
C14	C8	C16	113.29(10)	C5	C21	C24	120.52(16)
C14	C8	C18	115.46(11)	C17	C22	C4	119.40(14)
C16	C8	C6	101.73(10)	C5	C23	C9	120.53(16)
C16	C8	C18	109.81(10)	C21	C24	C1	121.17(15)
C23	C9	C1	120.88(15)	C27	C25	C2	120.35(17)
C4	C10	C12	124.51(11)	C3	C26	C12	121.32(15)
C16	C10	C4	109.24(11)	C13	C27	C25	119.90(16)
C16	C10	C12	126.05(12)	C13	C28	C14	119.44(15)
C12	C11	C7	119.87(16)	C13	C28	C15	121.51(15)
C11	C12	C10	122.41(13)	C14	C28	C15	119.05(13)
C11	C12	C26	118.33(14)	C3	C29	C7	119.87(17)
C26	C12	C10	119.26(13)	C15	C30	C18	122.05(14)
C27	C13	C28	120.64(16)				

Table S6 Hydrogen Atom Coordinates (Å×10^4) and Isotropic Displacement Parameters (Å^2×10^3) for Compound 3l.

Atom	x	y	z	U(eq)
H2	4433.48	4662.63	6016.09	65
H3	3603.36	1013.13	8201.15	84
H5	1158.12	4008.31	9572.6	74
H7	2607.89	1176.67	5452.49	100
H9	2484.51	3345.22	7122.86	68
H11	4043.32	2281.36	5418.54	76
H13	6705.63	6855.22	7292.24	83
H15	8397.31	6064.91	8360.8	72
H17	9281.47	2638.32	4894.13	71
H20	9216.92	4602.08	6374.58	57
H21	3555.61	4419.3	10036.93	75
H22	7121.99	2221.17	5509.21	64
H23	631.9	3471.43	8112.02	78
H24	5423.24	4292.4	9059.59	65
H25	3644.74	5861.89	5485.32	80
H26	5029.57	2107.06	8181.72	65
H27	4787.98	6955.21	6118.05	91
H29	2375.92	551.73	6839.59	100
H30	9155.08	4956.77	8989.82	68

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