Organocatalytic Enantioselective (4+3) Cyclization for the Synthesis of Spiro-Fused Heterocyclic Compounds Containing Isoindolinone, Oxepine and Indole Moieties

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1. General information

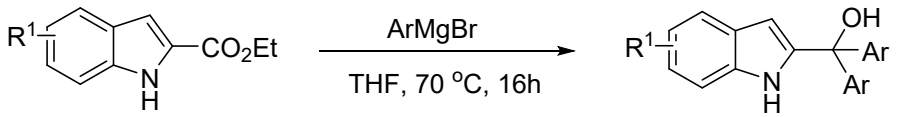
All solvents and reagents were purchased at the highest commercial quality and used without further purification, unless otherwise stated. Analytical thin layer chromatography (TLC) was performed on precoated silica gel 50 GF254 plates. Flash column chromatography was performed using silica gel (100-200 mesh). Visualization on TLC

was achieved by use of UV light (254, 365nm). Chemicals were purchased from commercial suppliers and used without further purification unless otherwise stated. 1H, 13C, 19F NMR spectra were collected on a Bruker AV 400 MHz NMR spectrometer using residue solvent peaks as an internal standard (1H NMR: $CDCl_3$ at 7.26 ppm; CD_2Cl_2 at 5.32 ppm; acetone-D6 at 2.05 ppm;13C NMR: $CDCl_3$ at 77.16 ppm; CD_2Cl_2 at 53.84 ppm; acetone-D6 at 29.84 ppm). Multiplicities were given as s (singlet), d (doublet), t (triplet), dd (doublets of doublet), or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants were reported as a J value in hertz. A high resolution mass spectrum (HRMS) was determined by 1290II-6230 TOF using ESI ionization. Infrared spectra were recorded on an ATR-FTIR spectrometer (NICOLET iS10). Optical rotations were reported as follows: [α]D20 (c: g/100 mL, in DCM). Enantiomeric excess was determined by chiral high-performance liquid chromatography (chiral HPLC) using DAICEL CHIRALPAK columns such as IA, AD-H, IE-3, IC-3, and IB-3. The melting point of each compound was determined by melting point meter SGW X-4A. Fluorescence measurements were performed on an Agilent Cary Eclipse Fluorescence Spectrophotometer. The racemic products employed to determine enantiomeric ratios were prepared by using diphenylphosphate as a catalyst. Optical rotation values were measured with instruments operating at λ = 589 nm, corresponding to the sodium D line at the temperatures indicated. The racemic products employed to determine enantiomeric ratios were synthesized by using 1,1′- binaphthyl-2,2′-diyl hydrogen phosphate as a catalyst. The all of chiral phosphoric acid catalysis were purchased from Daicel Chiral Technologies (CHINA) CO. LTD.

2. Methods of synthesizing substrates

2.1 Methods of synthesizing substrates 2-indolylmethanols 1

2-Indolylmethanols **1** are known compounds and were synthesized according to the literature procedures. [1-5]

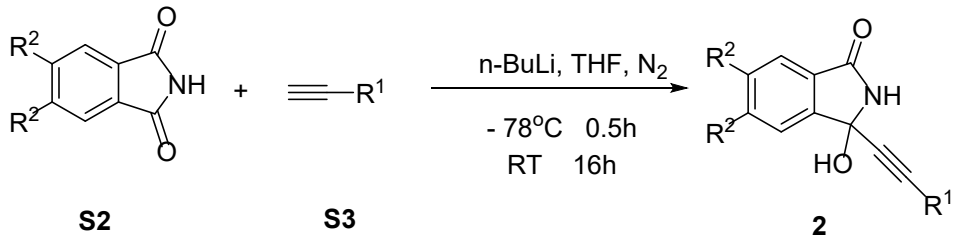


S1 **1**

Under argon atmosphere, arylmagnesium bromide (20 mmol, 4 equiv.) was added to a Schlenk bottle. Then, the solution of ethyl 1*H*-indole-2-carboxylate **S1** (5 mmol, 1 equiv.) in anhydrous THF was added dropwise to the Schlenk bottle at RT. Subsequently, the reaction mixture was stirred at 70 °C in an oil bath overnight. After the completion of the reaction indicated by TLC, the reaction mixture was quenched by saturated ammonium chloride solution and extracted by ethyl acetate for three times. The combined organic layers were dried and concentrated under reduced pressure to give a residue. Finally, the residue was purified by flash column chromatography on silica gel to afford pure 2-indolylmethanols **1**.

Compounds **1** were similar with the previously reported work. [1-5]

2.2 Methods of synthesizing substrates α-(3-isoindolinonyl)propargylic alcohol 2



S2 **S3** **2**

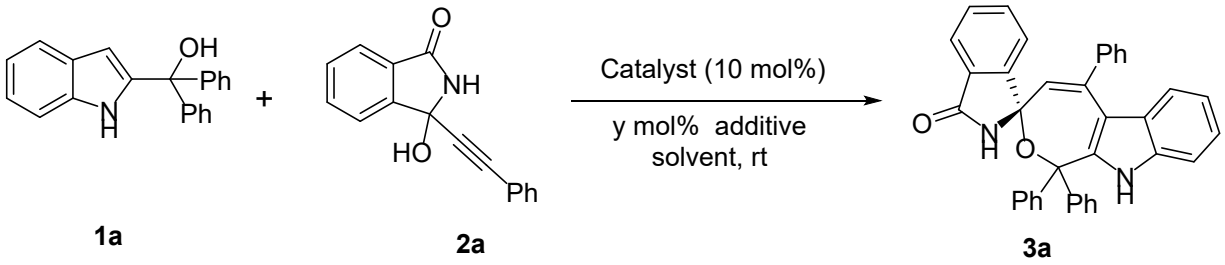
All α-(3-isoindolinonyl)propargylic alcohol **2** substrates were synthesized according to the reported literature.[6-11] At -78 °C, under N_2, a flame-dried flask charged with a solution of the terminal alkyne **S3** (6 mmol, 3.0 equiv) in dry THF (15 mL), was added n-BuLi (6 mmol, 3.0 equiv) dropwise. The reaction was stirred for 0.5 h at -78 °C. Then a solution of **S2** (2 mmol, 1.0 equiv) in THF (5 mL) was added via syringe at -78 °C. The reaction mixture was then slowly warmed up to room temperature and stirred for 16 h. Upon completion, the reaction mixture was cooled to 0 °C and a saturated aqueous NH_4Cl solution (10 mL) was added dropwise. The organic layer was separated. The aqueous layer was extracted with ethyl acetate (3×10 mL). The combined organic layers were washed with brine (30 mL), dried over anhydrous Na_2SO_4, filtered, and concentrated. The crude product was purified directly by flash column chromatography on silica gel (petroleum

ether/ ethyl acetate = 10:1~5:1) to give the desired α-(3-isoindolinonyl)propargylic alcohol **2**.

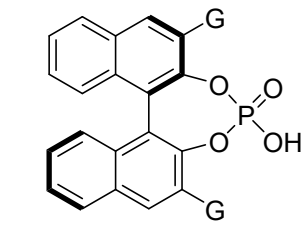
Compounds **2** were similar with the previously reported work. [6-11]

3. Optimization of reaction conditions of 3a

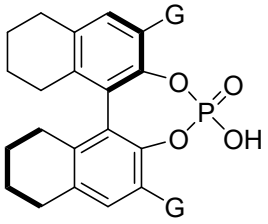
Table S1. Optimization of the reaction conditions of **3a**



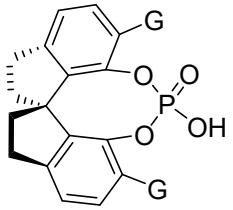
1a **2a** **3a**



(*R*)-**A1**: G = 9-anthracenyl
(*R*)-**A2**: G = 3,5-$(CF_3)_2C_6H_3$
(*R*)-**A3**: G = 9-phenanthrenyl
(*R*)-**A4**: G = 4-Ph-C_6H_4
(*R*)-**A5**: G = 4-NO_2-C_6H_4
(*R*)-**A6**: G = 2,4,6-$(Me)_3$Ph



(*R*)-**B1**: G = 9-anthracenyl



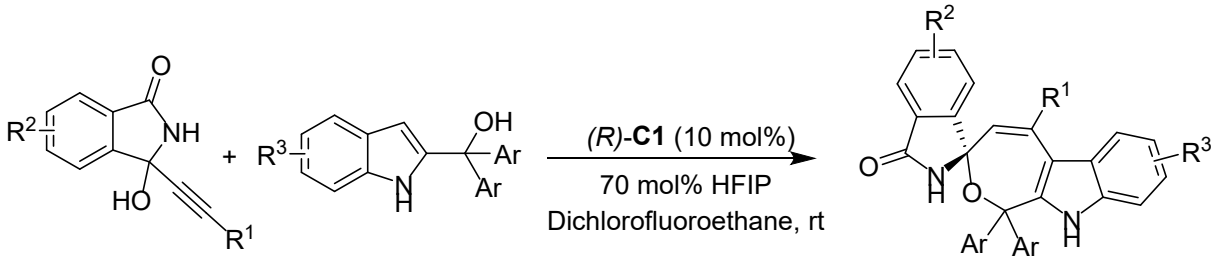
(*R*)-**C1**: G = 9-anthracenyl
(*S*)-**C2**: G = 2,4,6-$(Me)_3$Ph
(*S*)-**C3**: G = 9-phenanthrenyl

[a]Entry	Catalyst (10 mol%)	Solvent (5 mL)	y mol%	additive	Yield (%)[b]	ee (%)[c]
1	(*R*)-**A1**	DCM	0	-	60	74
2	(*R*)-**A2**	DCM	0	-	72	8
3	(*R*)-**A3**	DCM	0	-	27	2
4	(*R*)-**A4**	DCM	0	-	54	5
5	(*R*)-**A5**	DCM	0	-	91	0
6	(*R*)-**A6**	DCM	0	-	27	48

7	(*R*)-**B1**	DCM	0	-	73	66
8	(*R*)-**C1**	DCM	0	-	41	89
9	(*S*)-**C2**	DCM	0	-	77	79
10	(*S*)-**C3**	DCM	0	-	46	60
11	(*R*)-**C1**	DCM	50	4-F-$C_6H_4B(OH)_2$	-	-
12	(*R*)-**C1**	DCM	50	2,2,2-Trifluoroethanol	33	79
13	(*R*)-**C1**	DCM	50	HFIP	77	84
14	(*R*)-**C1**	DCM	60	HFIP	82	85
15	(*R*)-**C1**	DCM	70	HFIP	91	88
16	(*R*)-**C1**	DCM	80	HFIP	92	83
17	(*R*)-**C1**	PhMe	70	HFIP	-	-
18	(*R*)-**C1**	PhCl	70	HFIP	81	79
19	(*R*)-**C1**	PhF	70	HFIP	34	75
20	(*R*)-**C1**	Hexafluorobenzene	70	HFIP	54	22
21	(*R*)-**C1**	THF	70	HFIP	-	-
22	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	91	92
23 [d]	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	78	89
24 [e]	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	-	-
25 [f]	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	62	90
26 [g]	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	92	81
27	(*R*)-**C1**	CH_3CFCl_2	0	HFIP	44	92
28 [h]	(*R*)-**C1**	CH_3CFCl_2	70	HFIP	62	92

[a]Unless noted, the reaction was carried out with **1a** (0.11 mmol), **2a** (0.1 mmol), and catalyst (10 mol %) in 5.0 mL of solvent at room temperature for 48 h. [b]Isolated yield. [c]The ee was determined by HPLC analysis on a chiral stationary phase. [d]Additive Na_2SO_4 (30 mg). [e]Additive 4Å (30 mg). [f] Temperature at 0 [o]C. [g]Temperature at 40 [o]C. [h](*R*)-**C1** (5 mol %) was used.

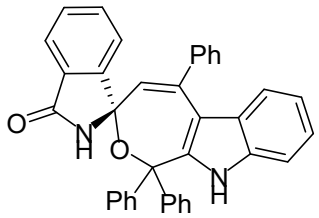
4. General procedure to synthesize target compound 3



2 **1** **3**

2-indolymethanols **1** (0.11 mmol, 1.1 eq), α-(3-isoindolinonyl) propargylic alcohols **2** (0.1 mmol, 1.0 eq), chiral phosphoric acid *(R)*-**C1** (7.8 mg, 10 mol%, 0.01 mmol) and HFIP (12 mg, 70 mol%, 0.07 mmol) were added to a dried tube under an air atmosphere. Then, dichlorofluoroethane (5 mL) was added to the reaction mixture, which was stirred at rt for 48 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified by column chromatography using pure DCM as eluent to afford products **3**.

5. Characterization data of target products 3



(S)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3a)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3a** as a white solid in 91% yield (48 mg) with 92% ee.

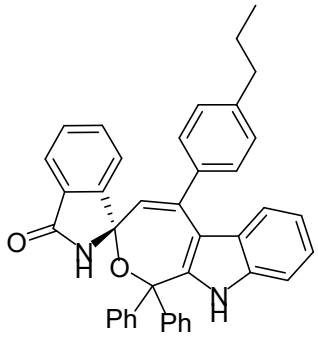
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.88 (s, 1H), 7.72 – 7.64 (m, 2H), 7.61 (t, *J*=7.5, 1H), 7.48 (t, *J*=7.4, 1H), 7.37 – 7.30 (m, 2H), 7.29 – 7.14 (m, 12H), 7.14 – 7.08 (m, 3H), 6.92 – 6.83 (m, 1H), 6.71 (d, *J*=8.0, 1H), 6.60 (s, 1H), 6.18 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 150.1, 145.6, 143.6, 143.5, 143.1, 138.9, 135.7, 133.6, 131.0, 130.1, 129.2, 129.0, 129.0, 128.7, 128.4, 128.3, 128.2, 128.0, 126.8, 126.3, 123.9, 123.6, 123.7, 121.7, 121.4, 114.6, 112.5, 89.0, 83.7 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{27}N_2O_2$ 531.2067; Found: 531.2069.

IR (KBr, cm^{-1}) 3401, 3227, 3038, 1709, 1533, 1492, 1434, 1409, 1233, 1007, 966.

M.P. 293-295 ºC. **$[\alpha]^{20}_D$** = +55 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm) tR = 9.865 min (minor), 14.954 min (major).



(S)-1',1'-diphenyl-5'-(4-propylphenyl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3b)

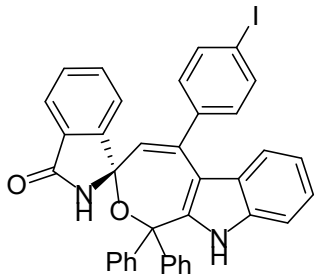
The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3b** as a white solid in 81% yield (46 mg) with 94% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.97 (s, 1H), 7.81 – 7.72 (m, 2H), 7.72 – 7.66 (m, 1H), 7.60 – 7.52 (m, 1H), 7.42 (d, J=7.0, 2H), 7.38 – 7.24 (m, 9H), 7.22 – 7.17 (m, 1H), 7.15 – 7.05 (m, 4H), 6.98 (t, J=7.3, 1H), 6.83 (d, J=8.1, 1H), 6.68 (s, 1H), 6.24 (s, 1H), 2.66 – 2.46 (m, 2H), 1.69 – 1.56 (m, 2H), 0.94 (t, J=7.3, 3H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.2, 145.8, 144.2, 143.8, 143.5, 143.1, 136.4, 135.8, 133.6, 131.1, 130.1, 129.1, 129.0, 128.9, 128.3, 128.2, 128.1, 126.9, 125.6, 124.0, 123.9, 123.8, 121.9, 121.4, 114.9, 112.5, 89.1, 83.7, 38.3, 25.1, 14.2 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{40}H_{33}N_2O_2$ 573.2537; Found: 573.2540.

IR (KBr, cm^{-1}) 3378, 3217, 3002, 1716, 1522, 1487, 1411, 1253, 958.

M.P. 298-300 ºC. **$[\alpha]^{20}_{D}$** = +37 º (c = 1.2, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 8.896 min (minor), 12.755 min (major).



(S)-5'-(4-iodophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3c)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3c** as a white solid in 87% yield (57 mg) with 90% ee.

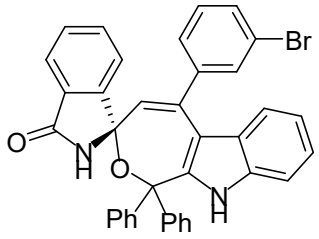
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (s, 1H), 7.81 – 7.67 (m, 3H), 7.64 – 7.54 (m, 3H), 7.51 – 7.12 (m, 12H), 7.04 – 6.92 (m, 3H), 6.84 (d, J=7.9, 1H), 6.68 (s, 1H), 6.27 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.3, 149.8, 145.4, 143.7, 143.3, 142.0, 138.3, 137.9, 135.6, 133.6, 130.9, 130.2, 130.1, 129.1, 129.0, 128.9, 128.3, 128.2, 127.6, 126.7, 126.5, 123.9, 123.7, 121.6, 121.5, 113.9, 112.6, 95.0, 88.8, 83.6 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}IN_2O_2$ 657.1033; Found: 657.1036.

IR (KBr, cm^{-1}) 3586, 3428, 1704, 1444, 1370, 1275, 1005, 750, 700.

M.P. 314-316 ºC. **$[\alpha]^{20}_{D}$** = +68 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 11.170 min (minor), 20.114 min (major).



(S)-5'-(3-bromophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3d)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3d** as a white solid in 83% yield (50 mg) with 91% ee.

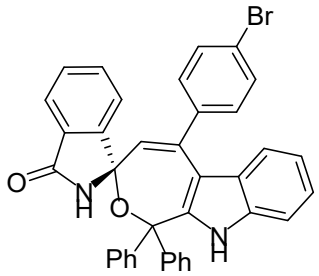
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (s, 1H), 7.81 – 7.66 (m, 3H), 7.57 (t, J=7.3, 1H), 7.48 – 7.26 (m, 13H), 7.23 (t, J=7.7, 1H), 7.17 – 7.11 (m, 2H), 7.01 (t, J=7.6, 1H), 6.84 (d, J=8.1, 1H), 6.68 (s, 1H), 6.27 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 149.8, 145.4, 143.8, 143.3, 141.6, 141.0, 135.7, 133.7, 132.0, 131.1, 130.9, 130.3, 130.2, 129.1, 129.1, 129.0, 128.3, 128.2, 127.9, 127.5, 127.2, 126.5, 123.99, 123.97, 123.7, 122.8, 121.6, 121.5, 113.9, 112.6, 88.8, 83.7 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}BrN_2O_2$ 611.1152; Found: 611.1161

IR (KBr, cm^{-1}) 3436, 3303, 3052, 2917, 1712, 1599, 1468, 1367, 1264, 1001, 699.

M.P. 295-297 ºC. **$[\alpha]^{20}_D$** = +26 º (c = 1.1, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 7.343 min (major), 9.531 min (minor).



(S)-5'-(4-bromophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3e)

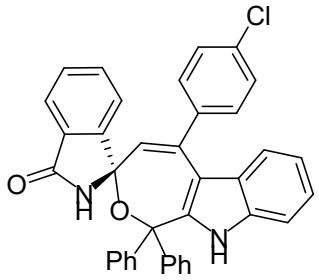
The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3e** as a white solid in 91% yield (55 mg) with 88% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (s, 1H), 7.81 – 7.73 (m, 2H), 7.70 (t, J=7.4, 1H), 7.57 (t, J=7.3, 1H), 7.46 – 7.24 (m, 13H), 7.21 (t, J=7.7, 1H), 7.10 (d, J=7.4, 2H), 7.01 (t, J=7.6, 1H), 6.84 (d, J=8.1, 1H), 6.69 (s, 1H), 6.27 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 149.9, 145.5, 143.8, 143.4, 141.9, 137.8, 135.7, 133.7, 131.9, 131.0, 130.2, 130.0, 129.1, 129.04, 128.96, 128.3, 128.2, 127.9, 126.8, 126.5, 123.97, 123.69, 123.3, 121.6, 121.6, 114.0, 112.6, 88.9, 83.7 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}BrN_2O_2$ 611.1152; Found: 611.1159.

IR (KBr, cm^{-1}) 3434, 3063, 2914, 1704, 1487, 1443, 1369, 1007, 750.

M.P. 291-293 ºC. **$[\alpha]^{20}_D$** = +54 º (c = 1.2, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 10.439 min (minor), 17.509 min (major).



(S)-5'-(4-chlorophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3f)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3f** as a white solid in 85% yield (48 mg) with 92% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87 (s, 1H), 7.70 – 7.57 (m, 3H), 7.53 – 7.45 (m, 1H), 7.35 – 7.10 (m, 14H), 7.09 – 7.03 (m, 2H), 6.96 – 6.88 (m, 1H), 6.75 (d, J=8.0, 1H), 6.60 (s, 1H), 6.18 (s, 1H) ppm.

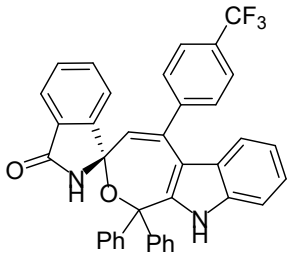
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 149.9, 145.5, 143.7, 143.4, 141.9, 137.4, 135.7, 135.0, 133.7, 131.0, 130.2, 129.7, 129.1, 129.1, 129.0, 128.9, 128.3, 128.2, 127.9, 126.8, 126.6, 124.0, 123.7, 121.6, 114.1, 112.6, 88.9, 83.7 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}ClN_2O_2$ 565.1677; Found: 565.1677.

IR (KBr, cm^{-1}) 3583, 3424, 2920, 2845, 1697, 1444, 1369, 1006, 749.

M.P. 293-295 ºC. **$[\alpha]^{20}_D$** = +59 º (c = 1.2, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 9.176 min (minor), 15.132 min (major).



(S)-1',1'-diphenyl-5'-(4-(trifluoromethyl)phenyl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3g)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3g** as a white solid in 84% yield (50 mg) with 87% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (s, 1H), 7.80 – 7.68 (m, 3H), 7.63 – 7.51 (m, 3H), 7.45 – 7.19 (m, 14H), 7.00 (t, J=7.6, 1H), 6.79 (d, J=8.1, 1H), 6.72 (s, 1H), 6.35 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 149.8, 145.5, 143.9, 143.3, 142.5, 141.8, 135.7, 133.7, 131.0, 130.3, 129.1, 129.04, 128.96, 128.7, 128.4, 128.3, 128.1, 127.9, 125.7 (q, J

= 3.8 Hz), 124.8 (q, J = 272.0 Hz), 124.0, 123.7, 121.7, 121.4, 113.8, 112.7, 88.9, 83.8 ppm.

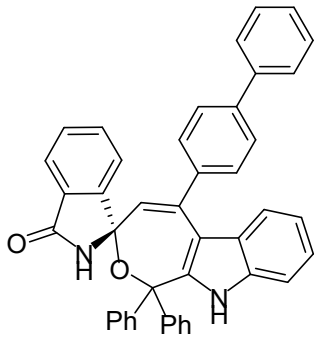
^{19}F NMR (376 MHz, CD_2Cl_2) δ -62.82 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{26}F_3N_2O_2$ 599.1941; Found: 599.1945.

IR (KBr, cm^{-1}) 3433, 3247, 1708, 1614, 1534, 1469, 1322, 1163, 1015, 700.

M.P. 321-323 ºC. **$[\alpha]^{20}_D$** = +29 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 6.809 min (minor), 11.521 min (major).



(S)-5'-([1,1'-biphenyl]-4-yl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3h)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3h** as a white solid in 78% yield (47 mg) with 94% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.14 (s, 1H), 7.79 (t, J=7.5, 2H), 7.75 – 7.69 (m, 1H), 7.65 – 7.58 (m, 3H), 7.59 – 7.52 (m, 2H), 7.49 – 7.42 (m, 4H), 7.40 – 7.26 (m, 12H), 7.24 – 7.18 (m, 1H), 7.01 (t, J=7.2, 1H), 6.95 (d, J=8.0, 1H), 6.72 (s, 1H), 6.35 (s, 1H) ppm.

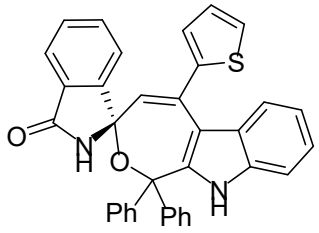
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.2, 145.8, 143.7, 142.7, 142.0, 141.0, 138.0, 135.9, 133.7, 131.1, 130.2, 129.4, 129.08, 129.05, 129.03, 128.9, 128.32, 128.28, 128.11 , 128.06, 127.5, 127.4, 126.9, 126.3, 124.03, 123.95, 123.8, 121.9, 121.6, 114.6, 112.7, 89.1, 83.8 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{43}H_{31}N_2O_2$ 607.2380; Found: 607.2385.

IR (KBr, cm^{-1}) 3432, 3059, 3024, 2922, 1706, 1599, 1486, 1476, 1006.

M.P. 322-324ºC. $[\alpha]^{20}_D$ = +82 º (c = 1.3, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 14. 566 min (minor), 22.262 min (major).



(S)-1',1'-diphenyl-5'-(thiophen-2-yl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3i)

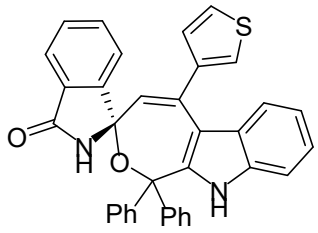
The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3i** as a white solid in 92% yield (49 mg) with 90% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.86 (s, 1H), 7.70 – 7.57 (m, 3H), 7.50 – 7.42 (m, 1H), 7.35 – 7.08 (m, 14H), 6.98 – 6.92 (m, 2H), 6.85 – 6.80 (m, 1H), 6.54 (s, 1H), 6.19 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.3, 150.0, 145.7, 143.6, 143.0, 140.6, 137.9, 135.7 133.6, 131.0, 130.1, 129.0, 128.9, 128.22, 128.19, 127.9, 127.6), 126.7, 126.1, 125.2, 124.5, 123.9, 123.7, 121.7, 121.5, 114.7, 112.5, 89.0, 83.6 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}N_2O_2S$ 537.1631; Found: 537.1636.
IR (KBr, cm^{-1}) 3428, 3254, 1696, 1610, 1535, 1433, 1016, 699.

M.P. 273-275 ºC. $[\alpha]^{20}_D$ = +48 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 11.517 min (minor), 18.430 min (major).



(S)-1',1'-diphenyl-5'-(thiophen-3-yl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3j)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3j** as a white solid in 83% yield (45 mg) with 95% ee.

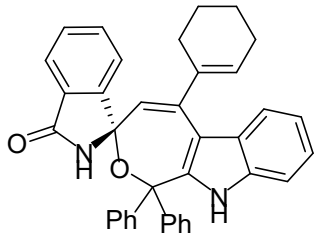
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.87 (s, 1H), 7.71 – 7.57 (m, 3H), 7.47 (t, J=7.2, 1H), 7.37 – 7.11 (m, 13H), 7.05 (d, J=8.0, 1H), 6.97 (t, J=7.5, 1H), 6.91 – 6.85 (m, 2H), 6.48 (s, 1H), 6.21 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.3, 149.8, 145.5, 143.5, 143.0, 141.9, 136.7, 135.7, 133.6, 131.0, 130.2, 129.0, 128.9, 128.3, 128.2, 127.92, 127.88, 127.4, 126.8, 126.5, 125.4, 124.0, 123.9, 123.7, 121.9, 121.5, 114.2, 112.6, 88.8, 83.5 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{35}H_{25}N_2O_2S$ 537.1631; Found: 537.1634.

IR (KBr, cm^{-1}) 3428, 3256, 1687, 1618, 1531, 1322, 1005, 719.

M.P. 270-272 ºC. **$[\alpha]^{20}_D$** = +65 º (c = 1.3, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 8.738 min (minor), 13.767 min (major).



(S)-5'-(cyclohex-1-en-1-yl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3k)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3k** as a yellow solid in 76% yield (41 mg) with 83% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.84 (s, 1H), 7.74 (d, J=7.8, 1H), 7.71 (d, J=7.5, 1H), 7.60 (t, J=7.6, 1H), 7.51 – 7.37 (m, 7H), 7.37 – 7.31 (m, 3H), 7.24 (t, J=7.5, 2H), 7.20 – 7.13 (m, 2H), 6.99 (t, J=7.6, 1H), 6.86 (s, 1H), 6.39 (s, 1H), 4.54 (s, 1H), 2.72 – 2.52 (m, 1H), 2.24 – 2.14 (m, 1H), 2.07 – 1.97 (m, 1H), 1.89 – 1.79 (m, 3H), 1.31 – 1.23 (m, 2H) ppm.

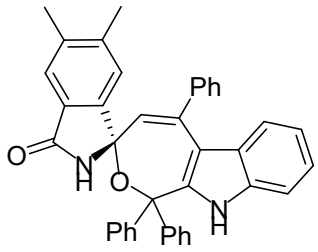
^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 147.7, 144.6, 143.1, 142.0, 138.4, 135.1, 133.9, 132.4, 129.4, 129.2, 129.0, 128.7, 128.5, 128.3, 127.9, 127.2, 123.6, 123.3, 121.4, 120.8, 120.3, 113.9, 112.3, 103.2, 83.1, 72.8, 30.7, 26.8, 23.9, 20.5 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{31}N_2O_2$ 535.2380; Found: 535.2382.

IR (KBr, cm^{-1}) 3438, 2948, 1694, 1647, 1521, 1443, 1312, 1037, 758.

M.P. 291-293 ºC. $[\alpha]^{20}_D$ = +94 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 90/10, flow rate = 1 mL/min, λ = 254 nm), tR = 15.418 min (minor), 17.001 min (major).



(S)-5,6-dimethyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3l)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3l** as a white solid.in 83% yield (46 mg) with 94% ee.

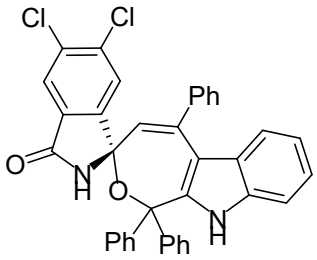
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.99 (s, 1H), 7.60 – 7.15 (m, 18H), 6.96 (t, J = 7.5 Hz, 1H), 6.79 (d, J = 8.0 Hz, 1H), 6.58 (s, 1H), 6.26 (s, 1H), 2.41 (s, 4H), 2.38 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.9, 148.0, 145.7, 143.7, 143.4, 142.7, 139.3, 139.0 , 135.7, 129.1, 129.0, 128.7, 128.4, 128.1, 128.0, 126.8, 126.7, 124.7, 124.5, 124.5, 123.8, 121.7, 121.4, 114.6, 112.5, 88.8, 83.6, 21.0, 20.3 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{31}N_2O_2$ 559.2380; Found: 559.2387.

IR (KBr, cm^{-1}) 3395, 3052, 1434, 1367, 1232, 975, 744, 699.

M.P. 327-329 ºC. **$[\alpha]^{20}_D$** = -38 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 1 mL/min, λ = 254 nm), tR = 9.129 min (minor), 14.977 min (major).



(S)-5,6-dichloro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3m)

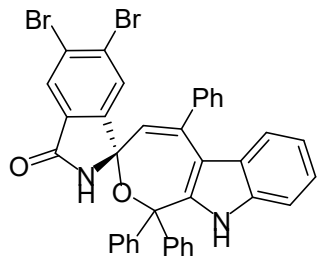
The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3m** as a white solid in 81% yield (48 mg) with 95% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.92 (s, 1H), 7.86 (s, 1H), 7.78 (s, 1H), 7.42 – 7.19 (m, 17H), 6.98 (t, J=7.4, 1H), 6.83 – 6.70 (m, 2H), 6.18 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.2, 149.1, 145.2, 143.6, 143.3, 138.6, 137.8, 135.7, 134.8, 131.0, 129.4, 129.2, 129.1, 129.0, 128.8, 128.4, 128.3, 127.9, 126.7, 126.0, 125.9, 125.1, 124.0, 121.7, 121.6, 114.5, 112.6, 88.6, 84.0 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{25}Cl_2N_2O_2$ 599.1288; Found: 599.1283.

IR (KBr, cm^{-1}) 3386, 2925, 1719, 1601, 1450, 1270, 1165, 1110, 697.

M.P. 154-156 ºC. **$[\alpha]^{20}_D$** = +36 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 8.095 min (minor), 15.111 min (major).



(S)-5,6-dibromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3n)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3n** as a white solid in 88% yield (60 mg) with 95% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.01 (s, 1H), 7.86 (s, 1H), 7.75 – 7.61 (m, 2H), 7.46 – 7.16 (m, 16H), 6.98 (t, J=7.6, 1H), 6.81 (d, J=8.1, 1H), 6.70 (s, 1H), 6.22 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 168.4, 151.6, 145.4, 143.4, 138.7, 135.7, 133.5, 130.0, 129.3, 129.1, 129.03, 128.97, 128.8, 128.4, 128.33, 128.29, 128.0, 127.9, 127.2, 126.7, 125.53, 125.49, 123.9, 121.7, 121.5, 114.5, 112.6, 88.7, 83.9 ppm.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{24}Br_2N_2NaO_2$ 711.0076; Found: 711.0066.

IR (KBr, cm^{-1}) 3579, 3061, 2920, 2853, 1709, 1446, 1276, 1010.

M.P. 332-334 ºC. **$[\alpha]^{20}_D$** = -10 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 7.712 min (minor), 11.678 min (major).

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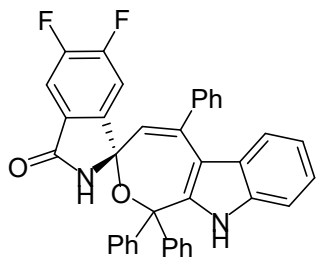


(S)-5,6-difluoro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3o)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3o** as an white solid in 79% yield (45 mg) with 92% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.94 (s, 1H), 7.58 (t, J=7.8, 1H), 7.54 – 7.47 (m, 1H), 7.43 – 7.17 (m, 17H), 6.97 (t, J=7.6, 1H), 6.82 – 6.74 (m, 2H), 6.17 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 154.5 (d, J = 255.3 Hz), 154.3 (d, J = 254.8 Hz), 145.3, 143.6, 143.3, 138.7, 135.7, 129.4, 129.2, 129.1, 129.0, 128.8, 128.4, 128.3, 127.9 126.7, 125.2, 124.0, 121.7, 121.5, 114.5, 113.1 (d, J = 15.2 Hz), 112.9 (d, J = 14.1 Hz), 112.6, 88.5, 83.9 ppm.

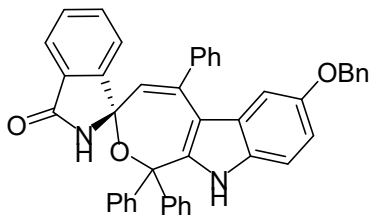
^{19}F NMR (376 MHz, CD_2Cl_2) δ -129.57 (d, J = 18.9 Hz), -135.43 (d, J = 18.9 Hz) ppm.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{24}F_2N_2NaO_2$ 589.1698; Found: 589.1704.

IR (KBr, cm^{-1}) 3589, 3051, 2920, 1695, 1444, 1371, 1009, 697.

M.P. 298-300 ºC. **$[\alpha]^{20}_D$** = +20 º (c = 1.1, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 4.858 min (minor), 8.040 min (major).



(S)-7'-(benzyloxy)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3p)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3p** as a white solid in 90% yield (57 mg) with 90% ee.

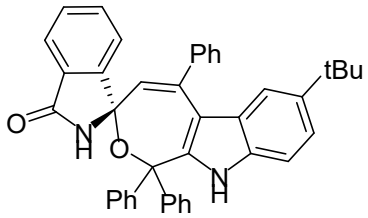
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (s, 1H), 7.81 – 7.73 (m, 2H), 7.73 – 7.66 (m, 1H), 7.61 – 7.54 (m, 1H), 7.45 – 7.39 (m, 2H), 7.37 – 7.15 (m, 19H), 6.95 – 6.86 (m, 1H), 6.71 (s, 1H), 6.28 (d, J=2.3, 1H), 6.24 (s, 1H), 4.75 (s, 2H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 154.4, 150.2, 145.8, 144.1, 143.7, 143.2, 138.7, 138.0, 133.7, 131.1, 131.0, 130.2, 129.3, 129.05, 129.00, 128.99, 128.8, 128.5, 128.29, 128.26, 128.2, 128.1, 128.0, 127.4, 125.9, 124.0, 123.8, 115.1, 114.4, 113.4, 104.6, 89.1, 83.8, 71.0 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{44}H_{33}N_2O_3$ 637.2486; Found: 637.2485.

IR (KBr, cm-1) 3413, 1701, 1444, 1369, 1275, 1183, 1012, 729.

M.P. 280-282 ºC. **$[\alpha]^{20}_D$** = +33 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 90/10, flow rate = 1 mL/min, λ = 254 nm), tR = 11. 925 min (minor), 16.210 min (major).



(S)-7'-(tert-butyl)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3q)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3q** as a white solid in 83% yield (49 mg) with 91% ee.

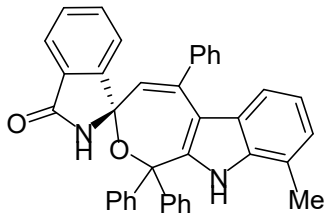
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.88 (s, 1H), 7.81 – 7.75 (m, 2H), 7.70 (t, J=7.5, 1H), 7.57 (t, J=7.4, 1H), 7.45 – 7.19 (m, 17H), 6.75 (s, 1H), 6.72 (s, 1H), 6.26 (s, 1H), 1.13 (s, 9H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.2, 145.8, 144.4, 143.7, 143.6, 143.3, 139.0, 133.9, 133.6, 131.1, 130.1, 129.1, 129.03, 129.00, 128.6, 128.24, 128.18, 128.1, 126.6, 125.7, 124.0, 123.8, 122.2, 117.8, 114.8, 111.9, 89.1, 83.8, 34.9, 31.8 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{41}H_{35}N_2O_2$ 587.2693; Found: 587.2696.

IR (KBr, cm^{-1}) 3436, 2958, 2922, 2844, 1702, 1446, 1365, 1276, 1014.

M.P. 267-269 ºC. $[\alpha]^{20}_D$ = -57 º (c = 1.2, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 7.587 min (minor), 11.761 min (major).



(S)-9'-methyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3r)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3r** as a white solid in 88% yield (48 mg) with 92% ee.

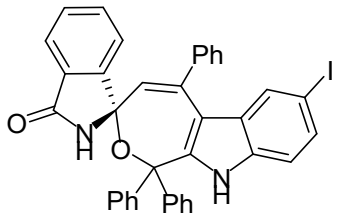
^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.83 – 7.76 (m, 2H), 7.74 – 7.66 (m, 2H), 7.58 (t, J=7.5, 1H), 7.52 – 7.46 (m, 2H), 7.43 – 7.21 (m, 13H), 7.04 (d, J=7.1, 1H), 6.92 (t, J=7.6, 1H), 6.74 (s, 1H), 6.68 (d, J=8.1, 1H), 6.31 (s, 1H), 2.36 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 150.2, 145.7, 143.5, 143.3, 143.1, 139.0, 135.3, 133.6, 131.1, 130.2, 129.18, 129.16, 129.04, 128.99, 128.7, 128.5, 128.30, 128.25, 128.1, 126.5, 126.4, 124.4, 124.0, 123.8, 121.79, 121.75, 119.4, 115.3, 89.1, 83.8, 16.6 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{29}N_2O_2$ 545.2224; Found: 545.2226.

IR (KBr, cm^{-1}) 3419, 3057, 1697, 1614, 1467, 1445, 1368, 981.

M.P. 261-263 ºC. $[\alpha]^{20}_D$ = +45 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 11.883 min (minor), 15.785 min (major).



(S)-7'-iodo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3s)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3s** as a white solid in 86% yield (56 mg) using with 91% ee.

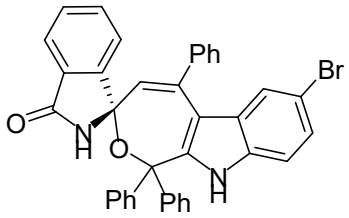
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.22 (s, 1H), 7.80 – 7.67 (m, 3H), 7.61 – 7.55 (m, 1H), 7.48 – 7.24 (m, 14H), 7.22 – 7.11 (m, 4H), 6.64 (s, 1H), 6.29 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 149.9, 145.3, 144.4, 143.2, 142.4, 138.4, 134.8, 133.7, 132.3, 130.9, 130.4, 130.2, 129.4, 129.2, 129.1, 129.0, 128.9, 128.8, 128.4, 128.29, 128.26, 127.8, 126.7, 123.9, 123.7, 114.6, 113.8, 89.0, 85.1, 83.5 ppm.
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}IN_2O_2$ 657.1033; Found: 657.1033.

IR (KBr, cm^{-1}) 3432, 3278, 3057, 1704, 1448, 1377, 1011, 755, 638.

M.P. 297-299 ºC. **$[\alpha]^{20}_D$** = +43 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 7.893 min (minor), 14. 552 min (major).



(S)-7'-bromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3t)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3t** as a white solid in 91% yield (55 mg) with 86% ee.

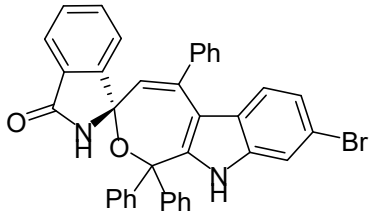
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.00 (s, 1H), 7.69 (d, J=7.5, 1H), 7.66 – 7.57 (m, 2H), 7.52 – 7.44 (m, 1H), 7.34 – 7.15 (m, 15H), 7.13 – 7.07 (m, 2H), 6.83 (d, J=1.7, 1H), 6.55 (s, 1H), 6.19 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.0, 145.3, 144.8, 143.3, 142.4, 138.5, 134.4, 133.7, 131.0, 130.2, 129.5, 129.2, 129.1, 129.0, 128.9, 128.4, 128.38, 128.35, 128.0, 127.0, 126.9, 124.1, 124.0, 123.7, 114.8, 114.2, 89.1, 83.7 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}BrN_2O_2$ 611.1152; Found: 611.1151.

IR (KBr, cm^{-1}) 3058, 1701, 1657, 1596, 1446, 1277, 759, 700.

M.P. 281-283 ºC. **$[\alpha]^{20}_D$** = +32º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 6.357 min (minor), 10.500 min (major).



(S)-8'-bromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3u)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3u** as a white solid in 83% yield (50 mg) with 91% ee.

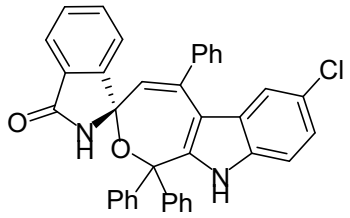
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.54 (s, 1H), 7.79 – 7.68 (m, 3H), 7.59 (t, J=7.3, 1H), 7.50 (s, 1H), 7.44 – 7.37 (m, 2H), 7.36 – 7.24 (m, 11H), 7.23 – 7.15 (m, 2H), 7.04 (d, J=8.6, 1H), 6.70 – 6.62 (m, 2H), 6.29 (s, 1H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 150.0, 145.4, 144.3, 143.3, 142.6, 138.7, 136.4, 133.8, 130.9, 130.2, 129.3, 129.2, 129.0, 128.9, 128.8, 128.4, 128.3, 128.2, 127.9, 126.6, 125.5, 124.8, 124.0, 123.7, 122.9, 117.2, 115.3, 114.7, 89.1, 83.6 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}BrN_2O_2$ 611.1152; Found: 611.1158.

IR (KBr, cm^{-1}) 3428, 3268, 3058, 1702, 1654, 1491, 1376, 1013, 700.

M.P. 279-281 ºC. **$[\alpha]^{20}_D$** = +43 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 9.293 min (minor), 10.766 min (major).



(S)-7'-chloro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3v)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3v** as a white solid in 84% yield (47 mg) with 83% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.03 (s, 1H), 7.71 – 7.57 (m, 3H), 7.51 – 7.45 (m, 1H), 7.36 – 7.16 (m, 14H), 7.14 – 7.02 (m, 3H), 6.67 (d, J=2.0, 1H), 6.55 (s, 1H), 6.18 (s, 1H) ppm.

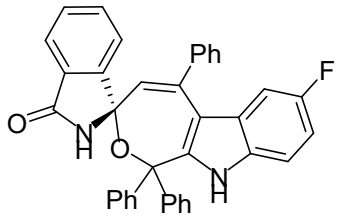
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.1, 145.4, 145.0, 143.4, 142.5, 138.6, 134.2, 133.7, 131.0, 130.2, 129.5, 129.2, 129.1, 129.0, 128.9, 128.4, 128.4, 128.3, 128.0, 127.8, 127.2, 126.9, 124.3, 124.0, 123.8, 121.0, 114.4, 113.9, 89.1, 83.7 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}ClN_2O_2$ 565.1677; Found: 565.1679.

IR (KBr, cm^{-1}) 3434, 3292, 3060, 2926, 1705, 1613, 1466, 1377, 1013, 699.

M.P. 286-288 ºC. **$[\alpha]^{20}_D$** = +152 º (c = 1.1, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 75/25, flow rate = 0.8 mL/min, λ = 254 nm), tR = 5.540 min (minor), 8.316 min (major).



(S)-7'-fluoro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3w)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3w** as a white solid in 82% yield (45 mg) with 95% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.32 (d, J=13.3, 1H), 7.81 – 7.67 (m, 3H), 7.58 (t, J=7.3, 1H), 7.45 – 7.18 (m, 16H), 6.93 (t, J=9.0, 1H), 6.67 (s, 1H), 6.50 – 6.37 (m, 1H), 6.27 (s, 1H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 158.7 (d, J = 236.5 Hz), 150.1, 145.5, 145.4, 143.5, 142.8, 138.5, 133.8, 132.4, 131.0, 130.2, 129.4, 129.2, 129.04, 129.00, 128.9, 128.42, 128.38, 128.3, 128.0, 127.2 (d, J = 10.4 Hz), 126.4, 124.1, 123.8, 114.8 (d, J = 4.7 Hz), 113.6 (d, J = 9.8 Hz), 112.6, 112.4, 106.5, 106.3, 89.2, 83.8 ppm.

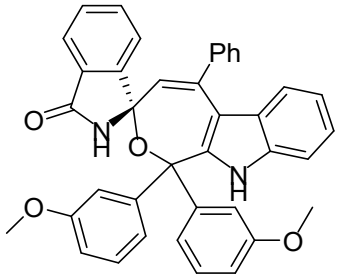
^{19}F NMR (376 MHz, CD_2Cl_2) δ -122.40 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{26}FN_2O_2$ 549.1973; Found: 549.1974.

IR (KBr, cm^{-1}) 3430, 3261, 3059, 2925, 1705, 1598, 1484, 1313, 1175, 1014.

M.P. 290-292 ºC. **$[\alpha]^{20}_D$** = +33º (c = 1.2, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 10.527 min (minor), 13.249 min (major).



(S)-1',1'-bis(3-methoxyphenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3x)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3x** as a white solid in 83% yield (42 mg) with 85% ee.

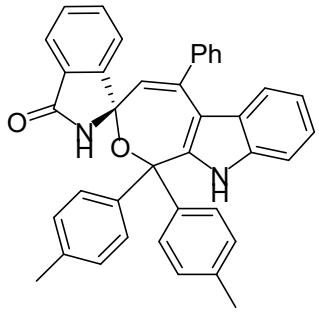
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.09 (s, 1H), 7.82 – 7.66 (m, 3H), 7.57 (t, J=7.3, 1H), 7.40 – 7.15 (m, 9H), 7.05 (s, 1H), 6.99 – 6.79 (m, 7H), 6.70 (s, 1H), 6.29 (s, 1H), 3.76 (s, 3H), 3.70 (s, 3H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.4, 160.2, 159.9, 150.0, 147.3, 145.0, 143.2, 143.1, 139.0, 135.7, 133.6, 131.0, 130.1, 130.0, 129.2, 129.0, 128.7, 128.5, 126.7, 126.2, 124.0, 123.8, 123.6, 121.7, 121.4, 121.1, 120.4, 115.3, 114.6, 114.6, 113.7, 113.2, 112.6, 89.0, 83.5, 55.7 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{31}N_2O_4$ 591.2278; found: 591.2282.

IR (KBr, cm^{-1}) 3427, 3059, 2948, 1696, 1527, 1425, 1216, 992, 688.

M.P. 250-252 ºC. **$[\alpha]^{20}_D$** = +32 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 1 mL/min, λ = 254 nm), tR = 15.352 min (minor), 21.935 min (major).



(S)-5'-phenyl-1',1'-di-p-tolyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3y)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3y** as a white solid in 92% yield (51 mg) with 89% ee.

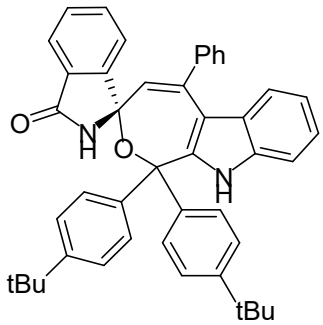
^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.11 (s, 1H), 7.78 (d, J=7.5, 1H), 7.76 – 7.67 (m, 2H), 7.61 – 7.54 (m, 1H), 7.38 – 7.22 (m, 8H), 7.21 – 7.06 (m, 7H), 6.97 (t, J=7.6, 1H), 6.80 (d, J=8.1, 1H), 6.71 (s, 1H), 6.27 (s, 1H), 2.33 (s, 6H) ppm.
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 150.3, 143.8, 143.1, 142.8, 141.0, 139.3, 139.0, 138.1, 135.7, 133.6, 131.1, 130.1, 129.6, 129.2, 128.9, 128.9, 128.8, 128.5, 127.9, 126.9, 126.3, 123.9, 123.8, 121.7, 121.4, 114.4, 112.5, 89.1, 83.7, 21.4, 21.3 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{39}H_{31}N_2O_2$ 559.2380; Found: 559.2382.

IR (KBr, cm^{-1}) 3581, 3422, 3059, 2924, 2851, 1712, 1472, 1216, 750.

M.P. 307-309 ºC. **$[\alpha]^{20}_D$** = +66º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 9.745 min (minor), 14. 606 min (major).



(S)-1',1'-bis(4-(tert-butyl)phenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3z)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3z** as a white solid in 85% yield (55 mg) with 96% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.51 (s, 1H), 7.81 (d, J=7.5, 1H), 7.77 (d, J=7.6, 1H), 7.70 (t, J=7.3, 1H), 7.58 (t, J=7.4, 1H), 7.36 – 7.21 (m, 8H), 7.20 – 7.03 (m, 7H), 6.94 (t, J=7.5, 1H), 6.79 (d, J=8.1, 1H), 6.72 (s, 1H), 6.24 (s, 1H), 1.26 (s, 9H), 1.22 (s, 9H) ppm.

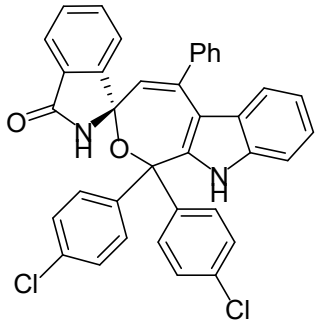
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.7, 152.1, 151.1, 150.3, 144.3, 143.2, 142.6, 140.8, 139.5, 135.7, 133.7, 130.9, 130.4, 130.1, 129.0, 128.6, 128.5, 127.6, 126.9, 126.1, 125.81, 125.75, 124.9, 123.9, 123.8, 123.6, 121.6, 121.3, 114.5, 112.6, 89.0, 83.6, 35.0, 34.9, 31.6, 31.5 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{45}H_{43}N_2O_2$ 643.3319; Found: 643.3328.

IR (KBr, cm^{-1}) 3585, 3420, 2928, 1698, 1361, 1005, 987, 737.

M.P. 337-339 ºC. **$[\alpha]^{20}_D$** = +103º (c = 1.4, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 90/10, flow rate = 1 mL/min, λ = 254 nm), tR = 12.561 min (minor), 16.016 min (major).



(S)-1',1'-bis(4-chlorophenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3aa)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3aa** as a white solid in 88% yield (53 mg) with 90% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.00 (s, 1H), 7.69 (d, J=7.5, 1H), 7.65 – 7.56 (m, 2H), 7.53 – 7.45 (m, 1H), 7.32 – 7.15 (m, 10H), 7.15 – 7.03 (m, 5H), 6.94 – 6.85 (m, 1H), 6.71 (d, J=8.1, 1H), 6.56 (s, 1H), 6.21 (s, 1H) ppm.

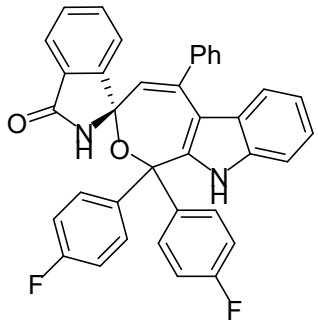
^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.6, 149.8 144.1, 143.2, 142.3, 141.9, 138.6, 135.9, 135.2, 134.3, 133.8, 130.9, 130.4, 130.3, 129.9, 129.4, 129.3, 129.2, 128.8, 128.5, 128.4, 126.6, 126.0, 124.2, 124.1, 123.6, 121.8, 121.7, 117.2, 114.8, 112.6, 89.0, 82.9 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{37}H_{25}Cl_2N_2O_2$ 599.1288; Found: 599.1288.

IR (KBr, cm^{-1}) 3429, 3251, 3059, 1703, 1589, 1489, 1006, 831, 695.

M.P. 291-293 ºC. **$[\alpha]^{20}_D$** = +49º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 85/15, flow rate = 1 mL/min, λ = 254 nm), tR = 8.073 min (minor), 10.711 min (major).



(S)-1',1'-bis(4-fluorophenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3ab)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **3ab** as a white solid in 80% yield (45 mg) with 91% ee.

^{1}H NMR (400 MHz, Acetone) δ 8.06 (s, 1H), 7.78 (d, J=7.5, 1H), 7.74 – 7.68 (m, 2H), 7.61 – 7.55 (m, 1H), 7.45 – 7.16 (m, 11H), 7.06 – 6.92 (m, 5H), 6.81 (d, J=8.0, 1H), 6.67 (s, 1H), 6.30 (s, 1H) ppm.

^{13}C NMR (101 MHz, Acetone) δ 169.5, 163.3 (d, J = 247.9 Hz), 163.0 (d, J = 246.4 Hz), 150.0, 143.2, 143.0, 141.5, 139.5, 138.8, 135.8, 133.8, 131.0 (d, J = 8.2 Hz), 130.3, 129.7 (d, J = 8.1 Hz), 129.3, 128.8, 128.4, 126.8, 126.2, 124.2, 124.1, 123.6, 121.8, 121.7, 115.9 (d, J = 21.7 Hz), 115.2 (d, J = 21.7 Hz), 112.6, 89.1, 83.0 ppm.

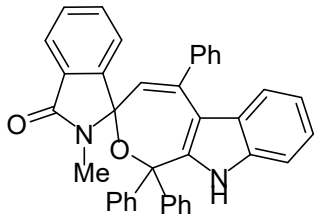
^{19}F NMR (376 MHz, Acetone) δ -114.06 (s), -115.07 (s) ppm.

HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{37}H_{24}F_2N_2NaO_2$ 589.1698; Found: 589.1698.

IR (KBr, cm^{-1}) 3434, 3259, 3153, 1694, 1598, 1501, 1223, 832, 702.

M.P. 301-303 ºC. **$[\alpha]^{20}_D$** = +131 º (c = 1.0, CH_2Cl_2).

HPLC (IE-3, hexane/isopropyl alcohol = 80/20, flow rate = 0.8 mL/min, λ = 254 nm), tR = 7.659 min (minor), 10.645 min (major).



2-methyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (5)

The resultant residue was purified by flash silicagel column chromatography (eluent: petroleum ether/DCM = 1:2, v/v) to afford **7** as a white solid in 52% yield (28 mg).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.85 (s, 1H), 7.71 (d, J=7.4, 1H), 7.47 – 7.29 (m, 15H), 7.24 – 7.16 (m, 3H), 7.13 (t, J=7.6, 1H), 6.96 (t, J=7.6, 1H), 6.72 (d, J=8.1, 1H), 6.27 (d, J=7.8, 1H), 5.95 (s, 1H), 2.95 (s, 3H) ppm.

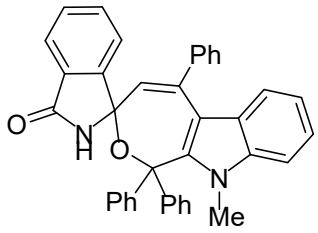
^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 149.4, 145.4, 144.8, 143.9, 142.9, 140.0, 135.3, 132.9, 131.5, 129.4, 129.2, 129.0, 128.9, 128.9, 128.8, 128.7, 128.5, 128.5, 127.1, 125.2, 123.8, 123.3, 123.1, 121.9, 121.3, 115.4, 112.5, 94.9, 83.5, 26.2 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{29}N_2O_2$ 545.2224; Found: 545.2227.

IR (KBr, cm^{-1}) 3405, 3199, 3033, 1689, 1507, 1451, 1241, 1012.

M.P. 314-316 ºC.

HPLC (IE-3, hexane/isopropyl alcohol = 93/07, flow rate = 1 mL/min, λ = 254 nm), tR = 39.902 min (major), 42.809 min (minor).



10'-methyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (7)

The resultant residue was purified by flash silicagel column chromatography (eluent: petroleum ether/EA = 3:1, v/v) to afford **9** as a white solid in 22% yield (12 mg).

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.34 (s, 1H), 7.72 – 7.63 (m, 2H), 7.58 (d, J=7.6, 1H), 7.50 (d, J=4.0, 3H), 7.44 (d, J=7.2, 1H), 7.41 – 7.36 (m, 1H), 7.33 – 7.20 (m, 15H), 6.12 (s, 1H), 3.48 (s, 3H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 167.5, 145.7, 143.7, 143.3, 142.6, 142.5, 138.5, 132.2, 131.9, 129.4, 129.0, 128.9, 128.8, 128.7, 128.5, 128.3, 127.6, 123.4, 122.5, 121.1, 120.3, 119.3, 111.0, 109.1, 90.7, 89.6, 31.4 ppm.

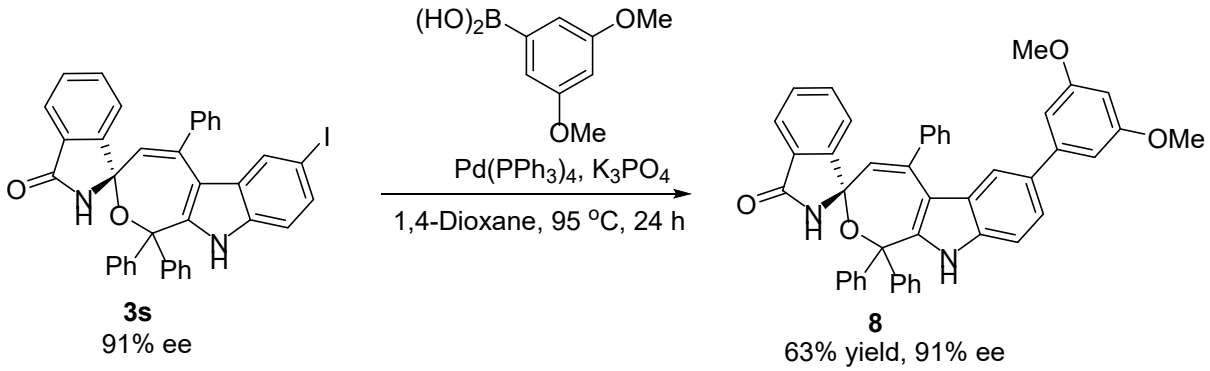
HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{38}H_{29}N_2O_2$ 545.2224; Found: 545.2229.

IR (KBr, cm^{-1}) 3401, 3209, 3012, 1705, 1512, 1438, 1153, 891.

M.P. 319-321 ºC.

6. Experimental Procedures for the Transformation of 3s to 8

To the solution of **3s** (65.6 mg, 0.1 mmol) in 1,4-dioxane (3 mL) was added $Pd(PPh_3)_4$ (11.6 mg, 0.01 mmol), (4-methoxyphenyl)boronic acid (20 mg, 0.11 mmol) and K_3PO_4(42.5 mg, 0.2 mmol). Then, the reaction mixture was stirred at 95 °C for 24 hours under N_2 atmosphere. After the completion of the reaction which was indicated by TLC, water (5 mL) was added to the mixture and the aqueous layer was extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Finally,the residue was purified by preparative thin layer chromatography (petroleum ether/ethyl acetate =2:1) on silica gel to afford pure product **8**.



(S)-7'-(3,5-dimethoxyphenyl)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (8)

The resultant residue was purified by flash silicagel column chromatography (eluent: pure DCM) to afford **8** as a white solid in 63% yield (42 mg) with 91% ee.

^{1}H NMR (400 MHz, CD_2Cl_2) δ 8.09 (s, 1H), 7.78 (t, J=7.3, 2H), 7.71 (t, J=7.5, 1H), 7.58 (t, J=7.6, 1H), 7.47 – 7.41 (m, 4H), 7.38 – 7.23 (m, 13H), 6.95 (s, 1H), 6.82 (s, 1H), 6.48 (d, J=2.2, 2H), 6.35 (t, J=2.1, 1H), 6.29 (s, 1H), 3.74 (s, 6H) ppm.

^{13}C NMR (101 MHz, CD_2Cl_2) δ 169.5, 161.5, 150.0, 145.5, 144.4, 144.3, 143.4, 142.9, 138.9, 135.3, 134.7, 133.7, 130.9, 130.2, 129.2, 129.1, 129.00, 128.97, 128.7, 128.6, 128.3,

128.2, 128.0, 127.2, 126.1, 123.9, 123.7, 123.5, 120.1, 115.0, 112.7, 105.5, 99.4, 89.1, 83.7, 55.8 ppm.

HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{45}H_{35}N_2O_4$ 667.2591; Found: 667.2594.

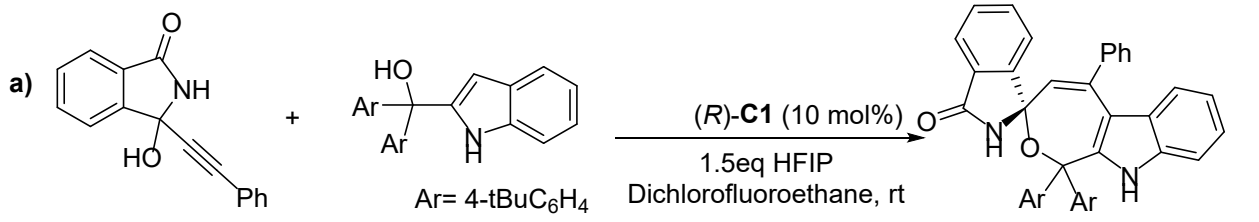
IR (KBr, cm^{-1}) 3403, 3045, 2943, 2821, 1627, 1401, 1341, 1201, 812.

M.P. 332-334 ºC. **$[\alpha]^{20}_D$** = +87 º (c =1.0, CH_2Cl_2)

HPLC (OD-H, hexane/isopropyl alcohol = 70/30, flow rate = 1 mL/min, λ = 254 nm), tR = 4.246 min (minor), 5.748 min (major).

8. Scale-up experiment

2-indolymethanols **1l** (1.5 mmol), α-(3-isoindolinonyl) propargylic alcohol **2a** (1.0 mmol), chiral phosphoric acid **(R)-C1** (10 mol%) and HFIP (1.5 eq) were added to a dried tube under an air atmosphere. Then, dichlorofluoroethane (10 mL) was added to the reaction mixture, which was stirred at rt for 72 h. After the completion of the reaction which was indicated by TLC, the reaction mixture was directly purified by column chromatography using PE:EA=3:1 as eluent to afford pure products **(S)-3z**.

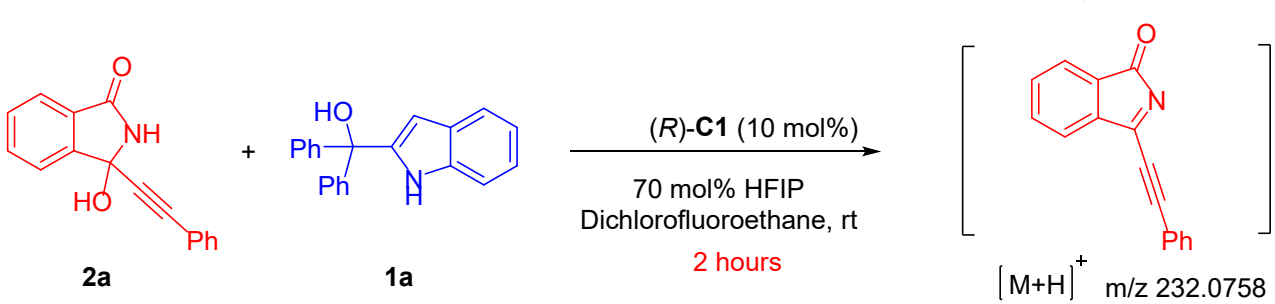


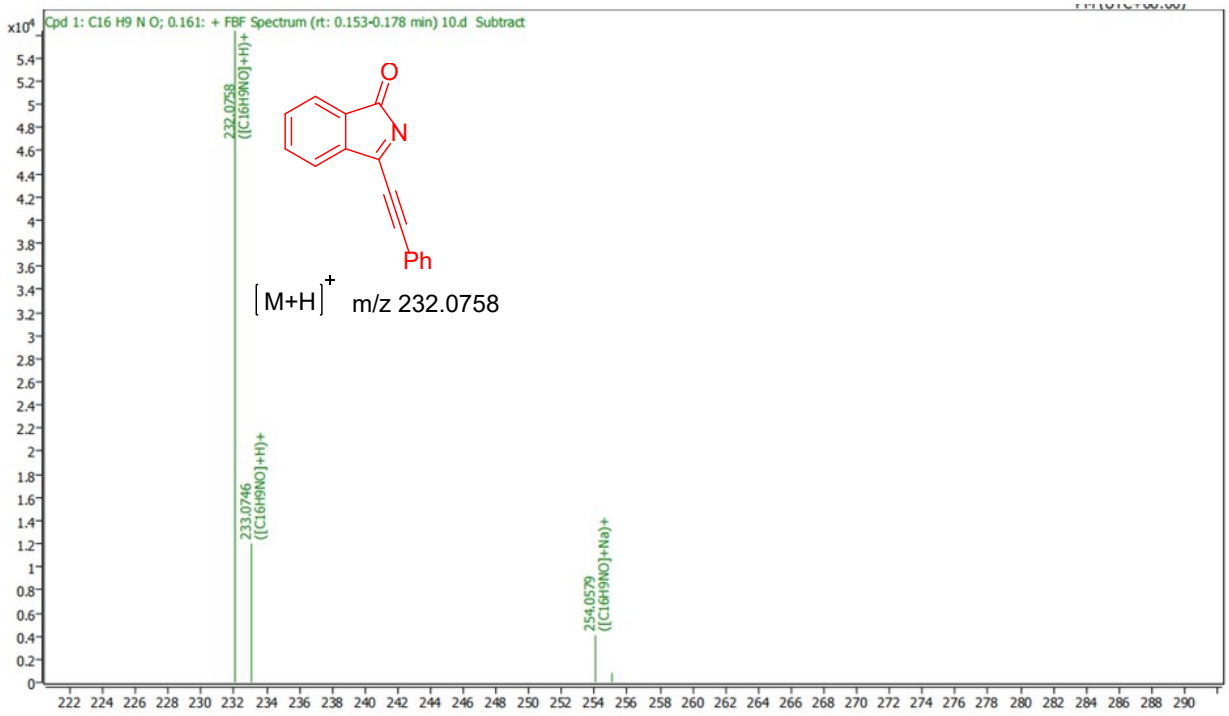
2a (1 mmol) **1l** (1.5 mmol) **3z** 78% yield (501mg), 92% ee

9. HR MS copies of intermediates

To get a mechanistic insight into reaction mechanism, we performed the following control experiment. To gain insight into the mechanism of mono-cyclization reaction and bis-cyclization reaction, we monitored the reaction of 2-indolylmethanol with propargylic

alcohols and tried to isolated some intermediate products. Disappointingly, we failed to obtain intermediate product. Therefore, we tried to detect the signals of some possible intermediates via HRMS. After stirring the reaction for 2 hours, we detect a useful signals via HRMS . The signal at [M+H]+ m/z 232.0758 was possibly due to propargylic *N*-acyl imines intermediate.

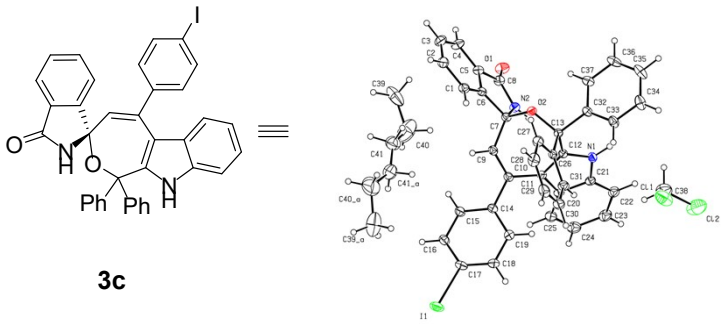




10. X-Ray Structure and Crystal Data of 3c

Single crystal of **3c** was obtained from the mixed solution of dichloromethane and petroleum ether (1:1) maintained at rt for a week. The absolute structure of product **3c** was

determined by X-ray diffraction analysis of a single crystal (Bruker APEX-II CCD' diffractometer). The X-ray data have been deposited at the Cambridge Crystallographic Data Center (CCDC 2314995). The stereochemistry of other products was assumed by analogy.



3c

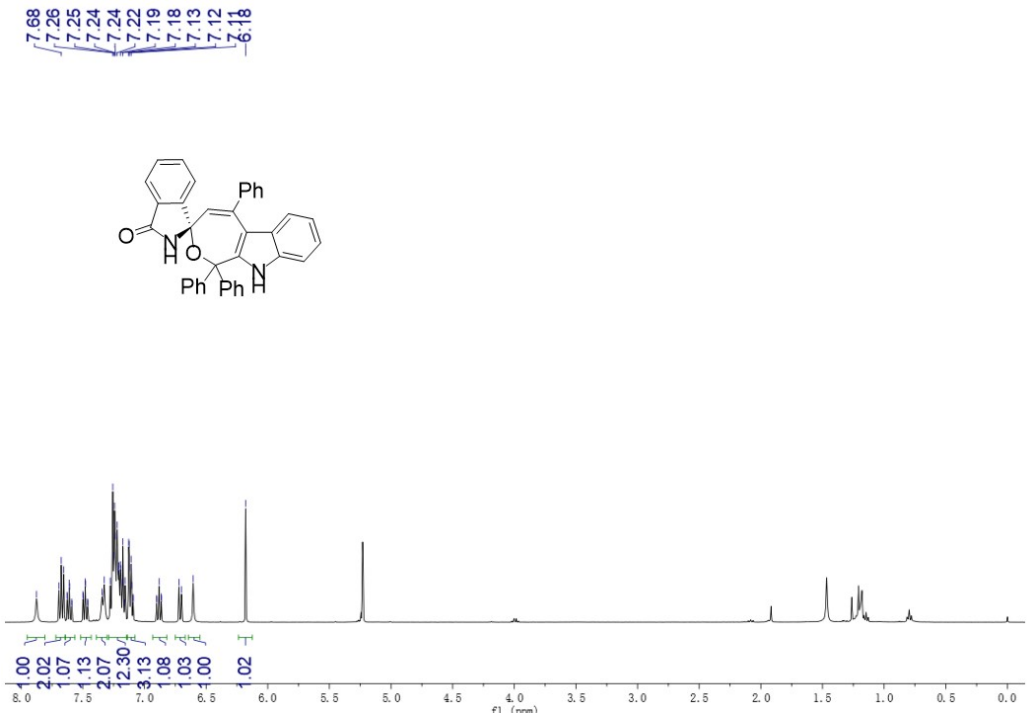
Table 1 Crystal data and structure refinement for 3c.

Identification code	mo_231204_RKH012_0m
Empirical formula	$C_{41}H_{34}Cl_2IN_2O_2$
Formula weight	784.50
Temperature/K	170.00
Crystal system	monoclinic
Space group	C2
a/Å	26.7116(11)
b/Å	10.1135(4)
c/Å	16.0912(6)
α/°	90
β/°	122.7760(10)
γ/°	90

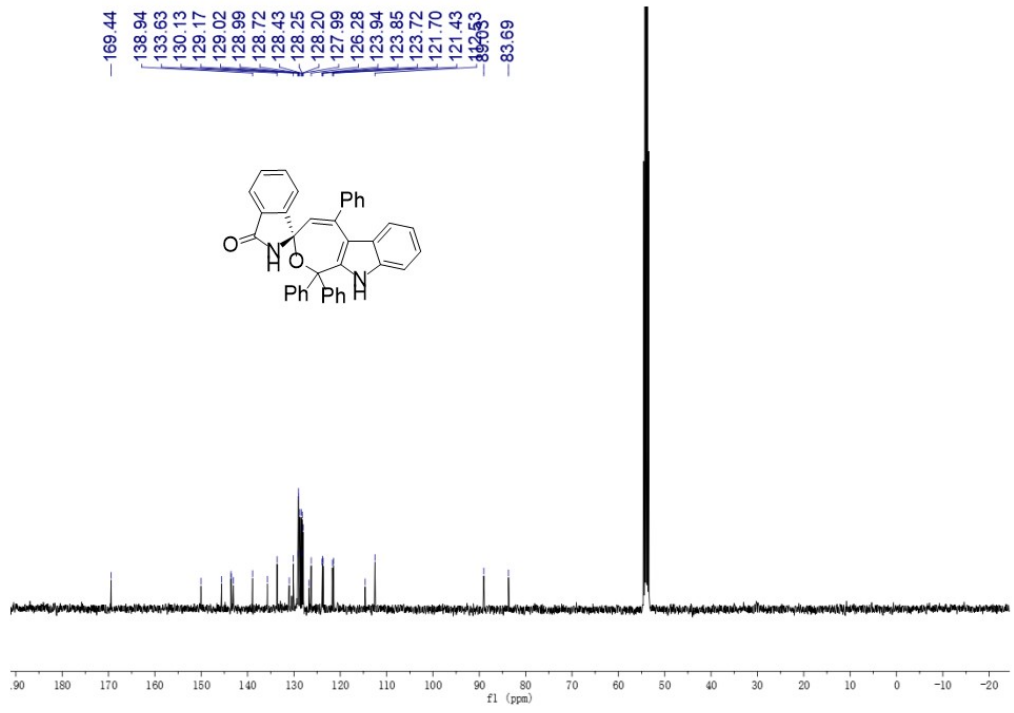
Volume/Å^3	3654.9(3)
Z	4
ρ_{calc}g/cm^3	1.426
μ/mm^{-1}	1.060
F(000)	1588.0
Crystal size/mm^3	0.42 × 0.17 × 0.1
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.416 to 55.032
Index ranges	-34 ≤ h ≤ 34, -13 ≤ k ≤ 13, -20 ≤ l ≤ 20
Reflections collected	57727
Independent reflections	8380 [R_{int} = 0.0412, R_{sigma} = 0.0285]
Data/restraints/parameters	8380/4/434
Goodness-of-fit on F^2	1.096
Final R indexes [I>=2σ (I)]	R_1 = 0.0366, wR_2 = 0.0812
Final R indexes [all data]	R_1 = 0.0438, wR_2 = 0.0852
Largest diff. peak/hole / e Å^{-3}	0.38/-0.52
Flack parameter	0.009(5)

11. Copies of NMR spectra

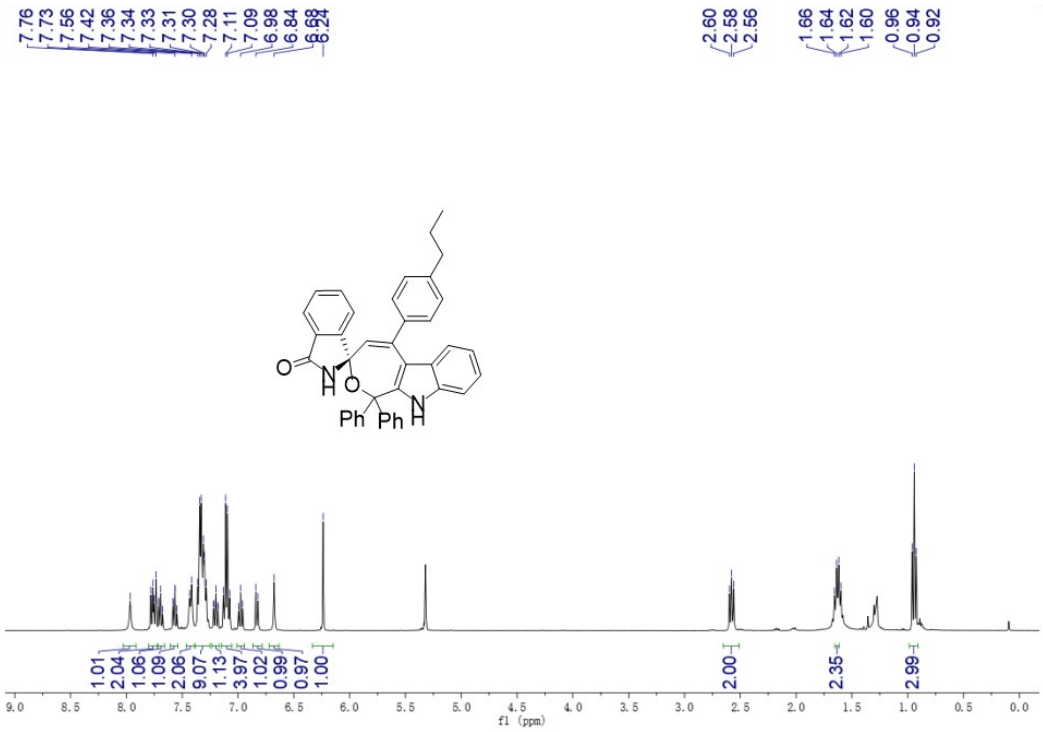
^{1}H NMR (400 MHz, CD_2Cl_2) of **3a**



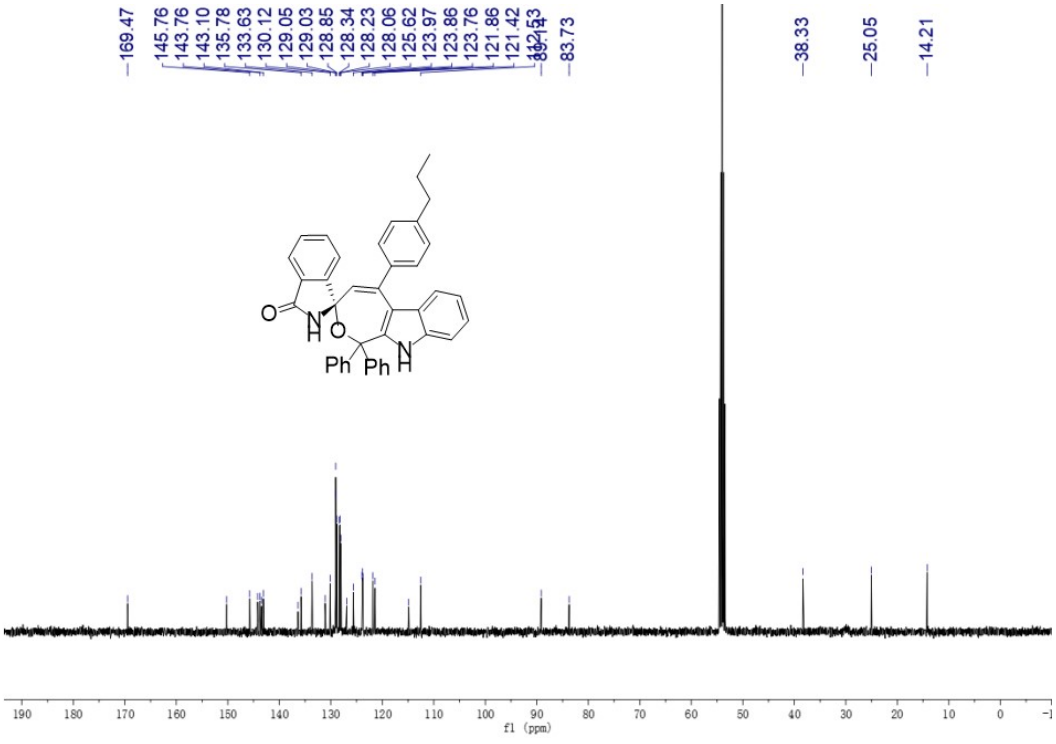
^{13}C NMR (101 MHz, CD_2Cl_2) of **3a**



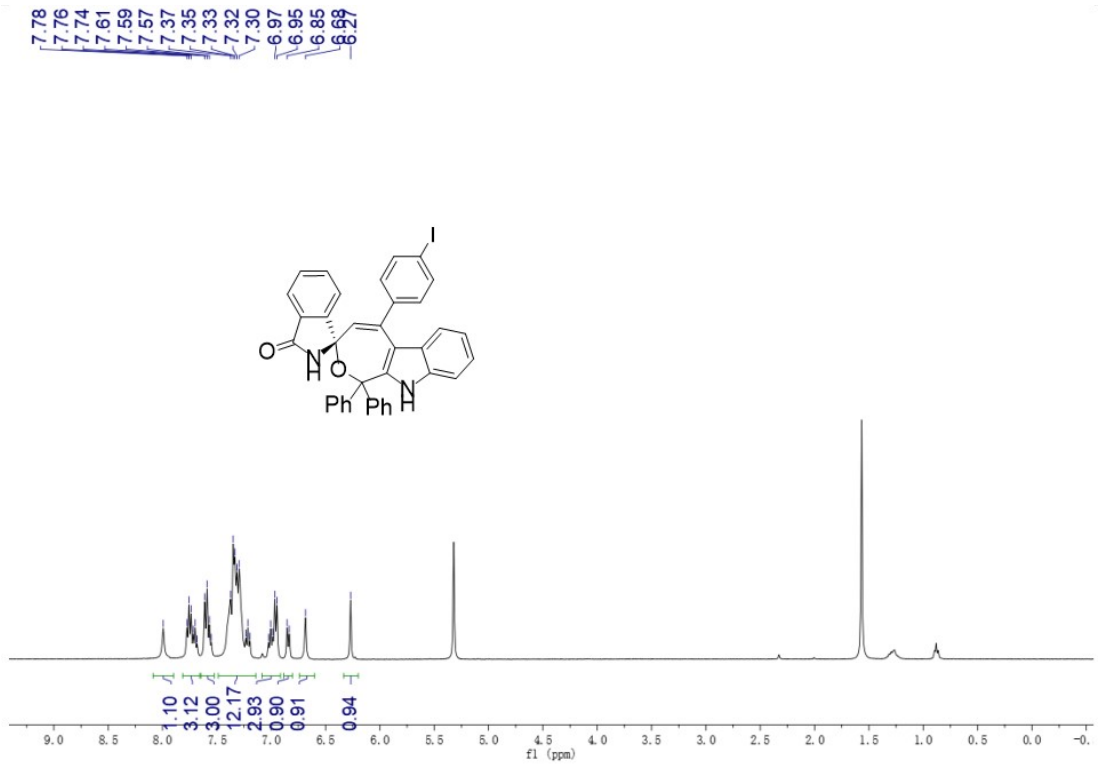
^{1}H NMR (400 MHz, CD_2Cl_2) of **3b**



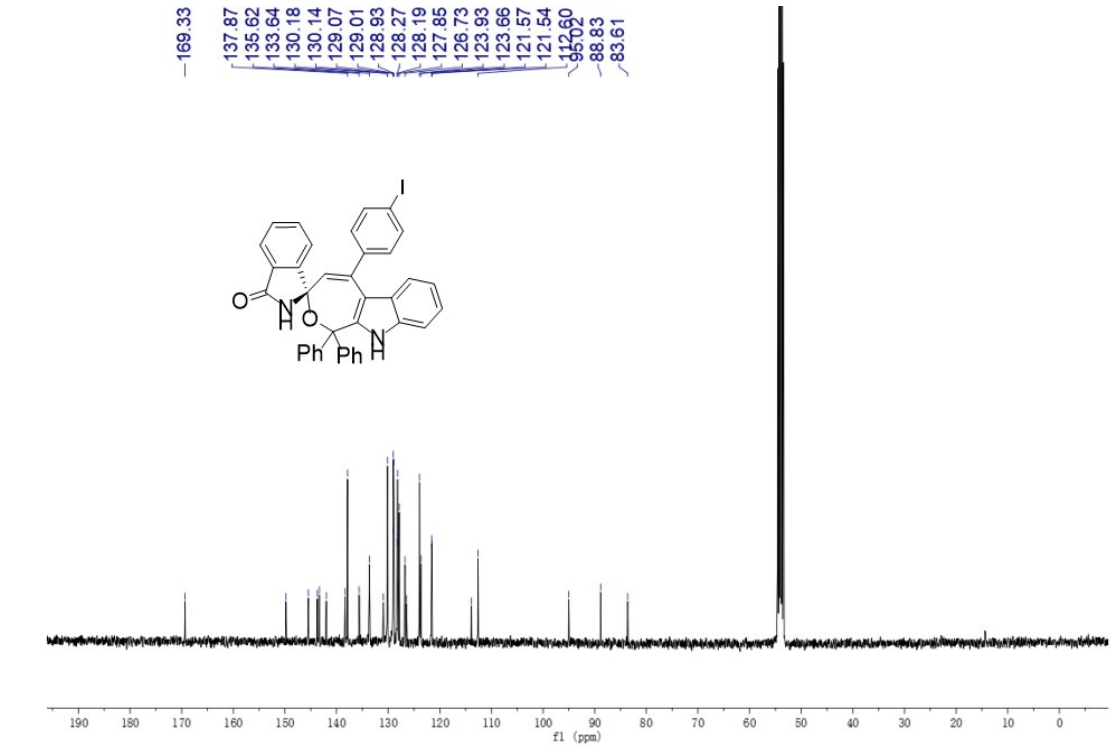
^{13}C NMR (101 MHz, CD_2Cl_2) of **3b**



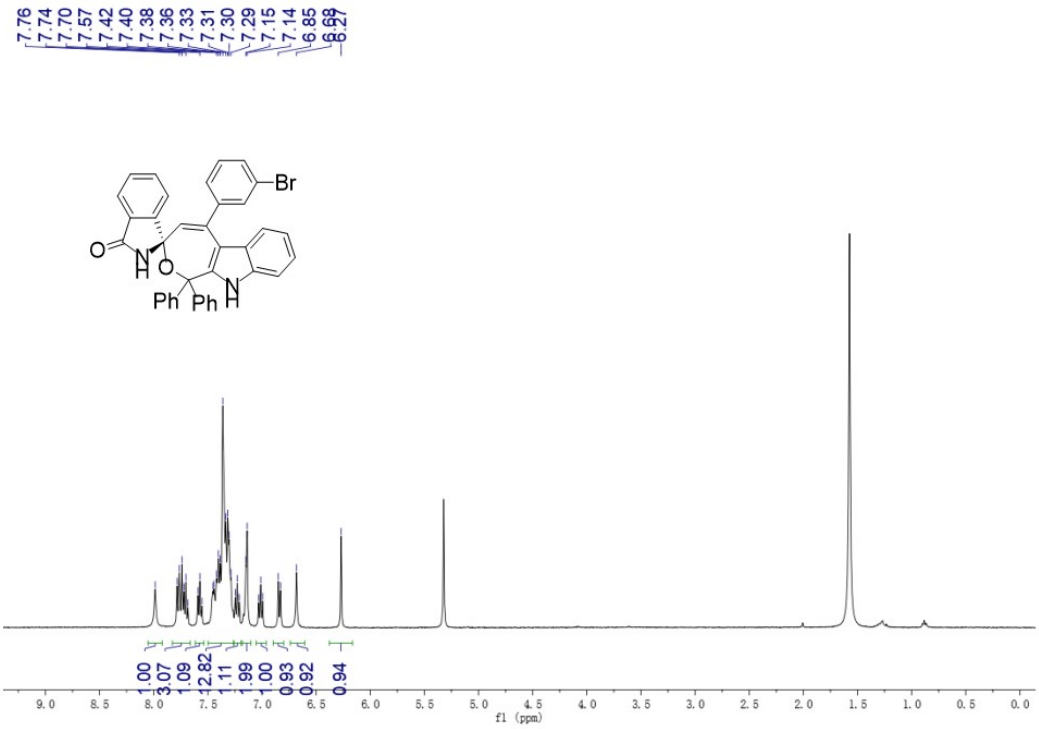
^{1}H NMR (400 MHz, CD_2Cl_2) of **3c**



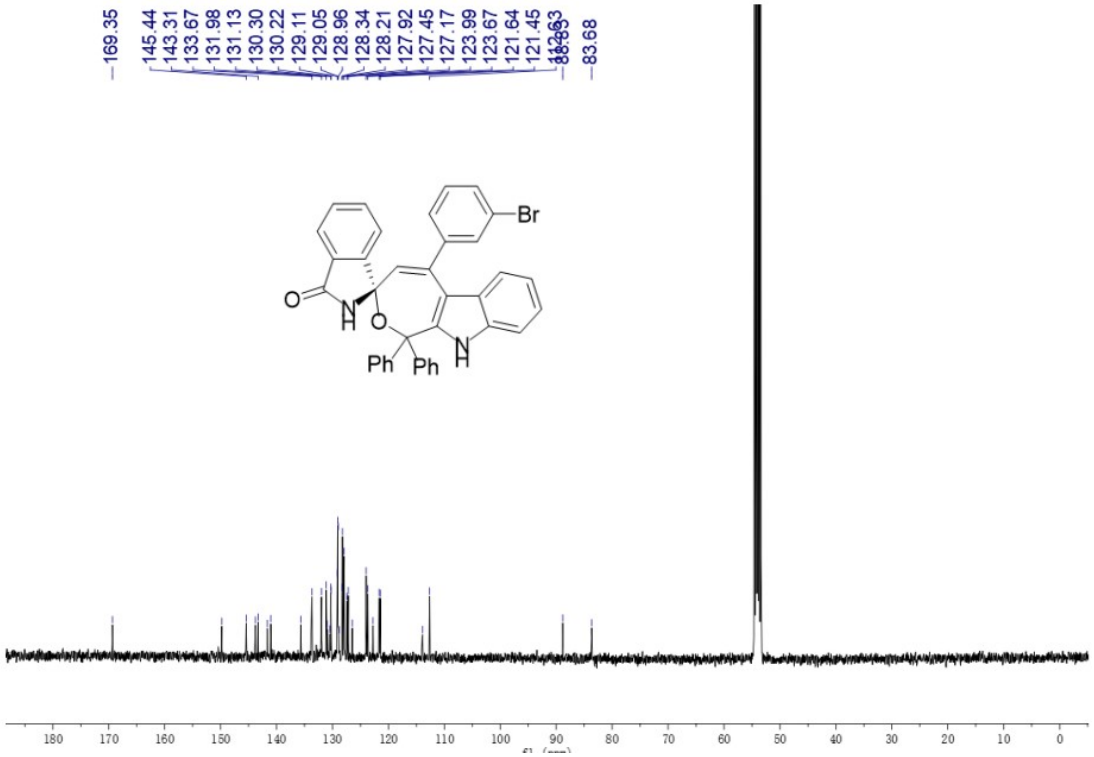
^{13}C NMR (101 MHz, CD_2Cl_2) of **3c**



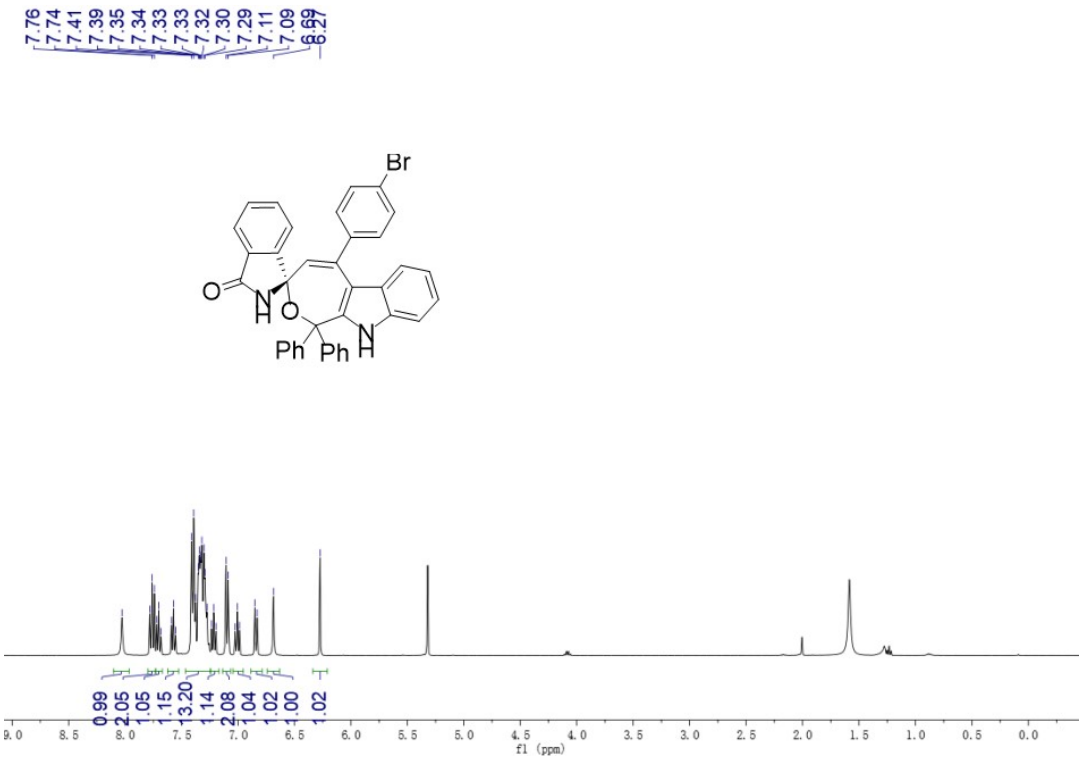
^{1}H NMR (400 MHz, CD_2Cl_2) of **3d**



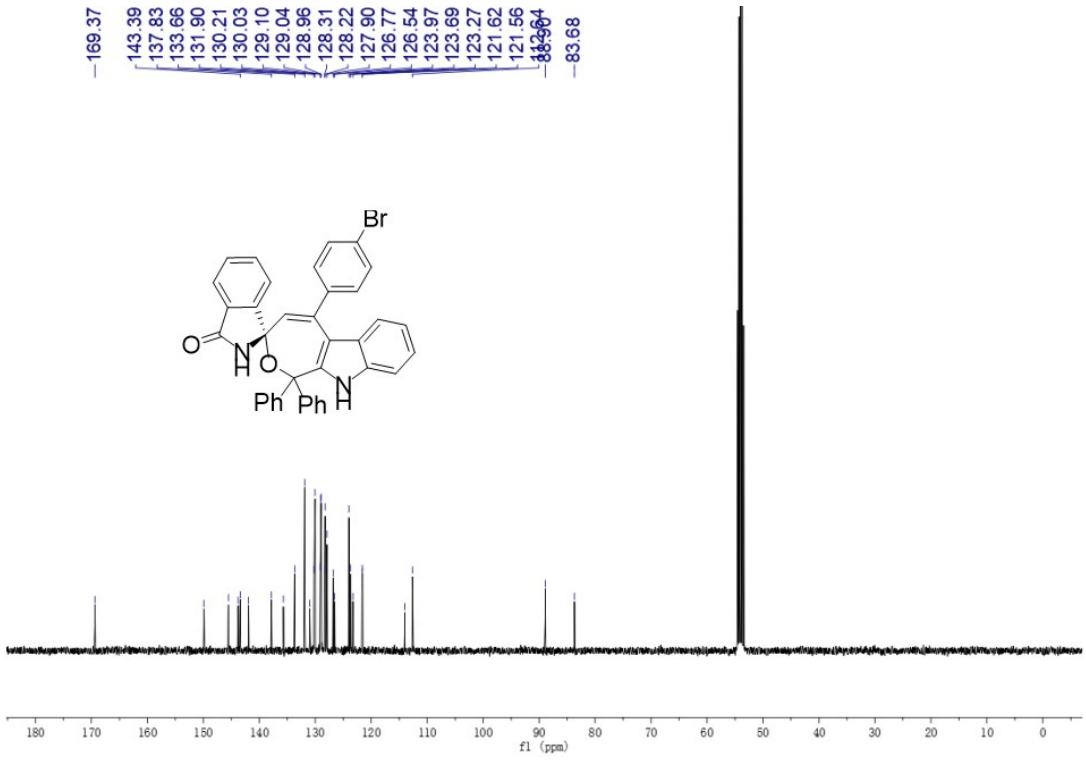
^{13}C NMR (101 MHz, CD_2Cl_2) of **3d**



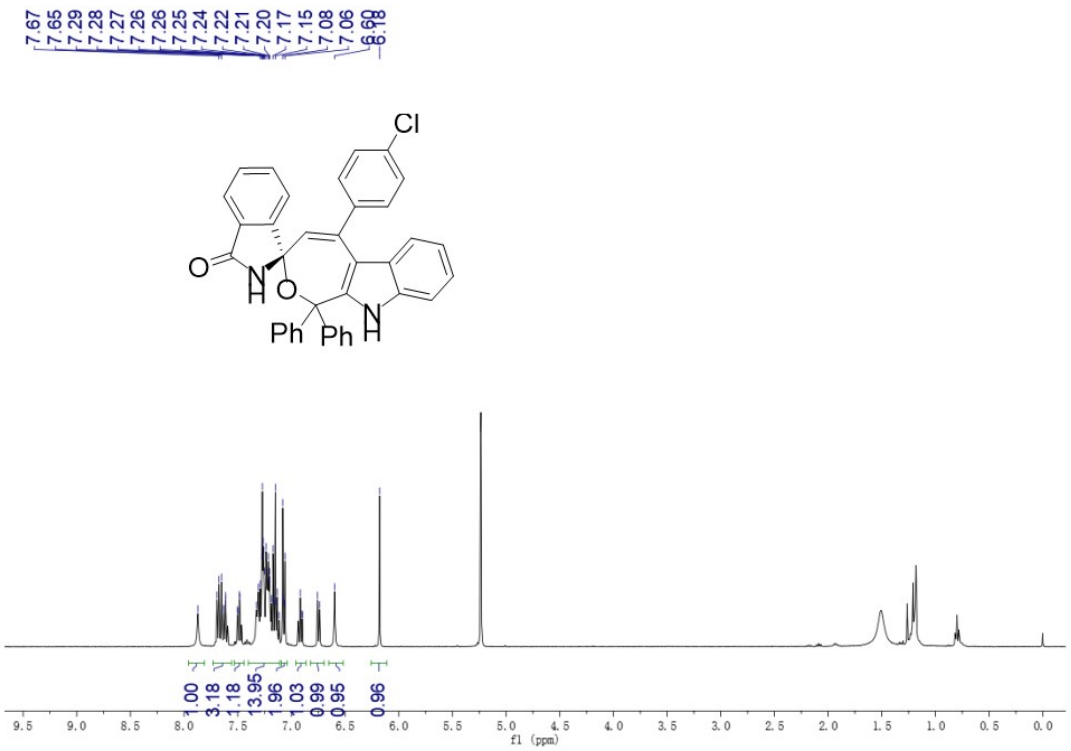
^{1}H NMR (400 MHz, CD_2Cl_2) of **3e**



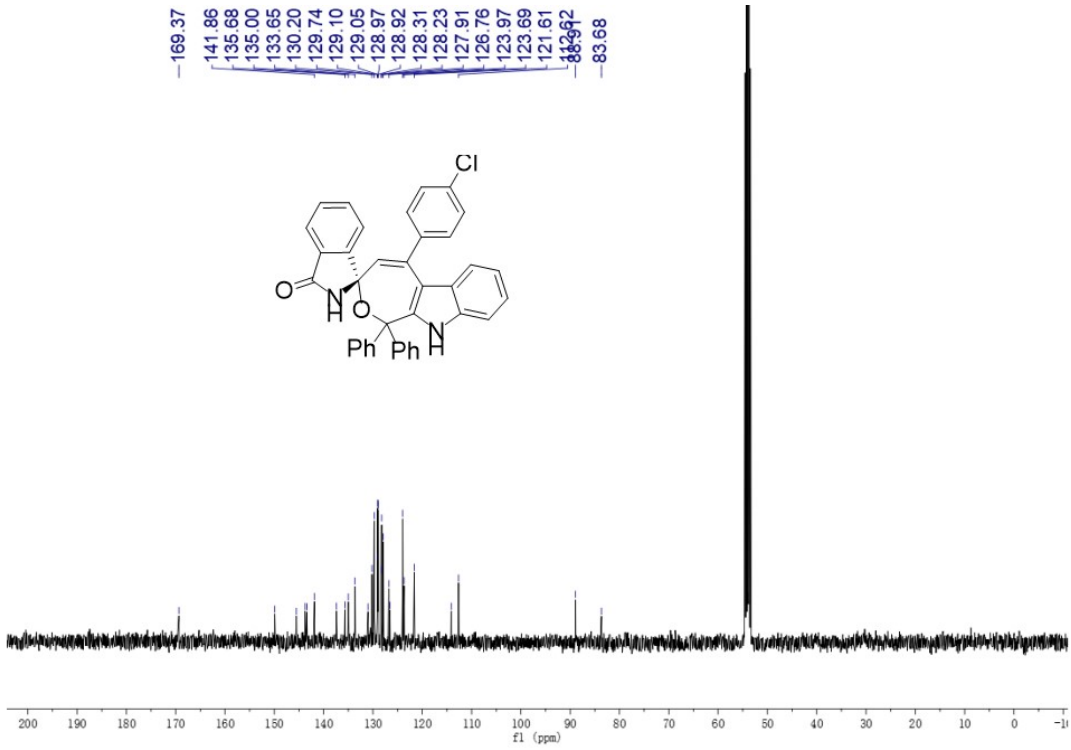
^{13}C NMR (101 MHz, CD_2Cl_2) of **3e**



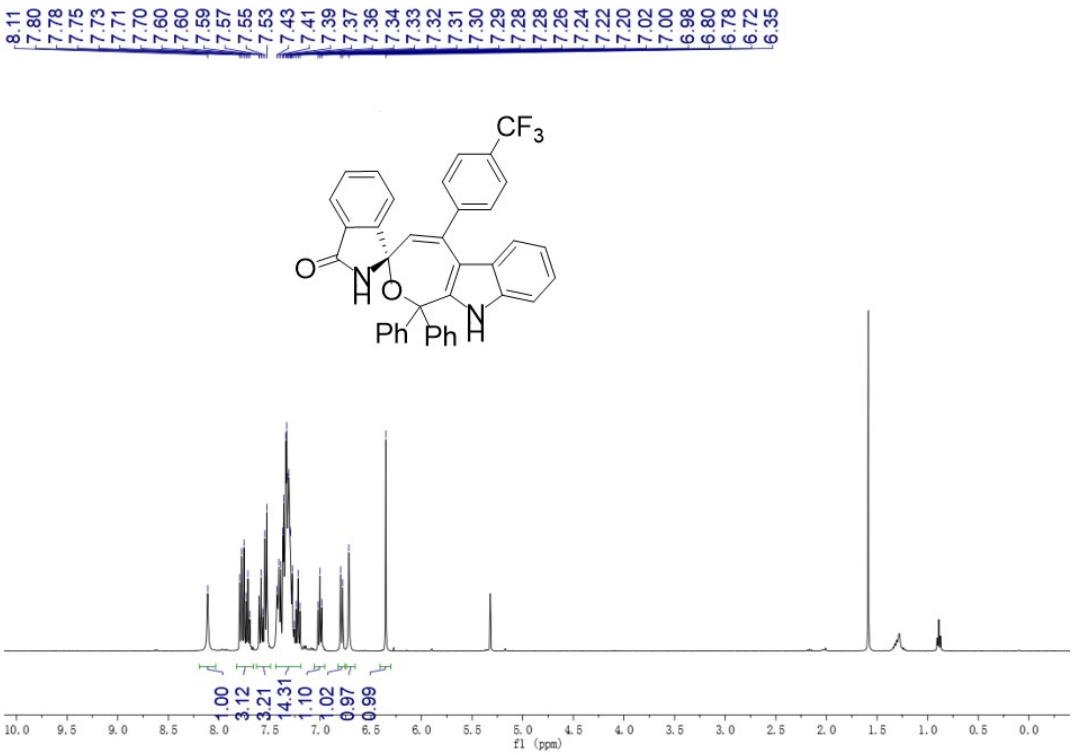
^{1}H NMR (400 MHz, CD_2Cl_2) of **3f**



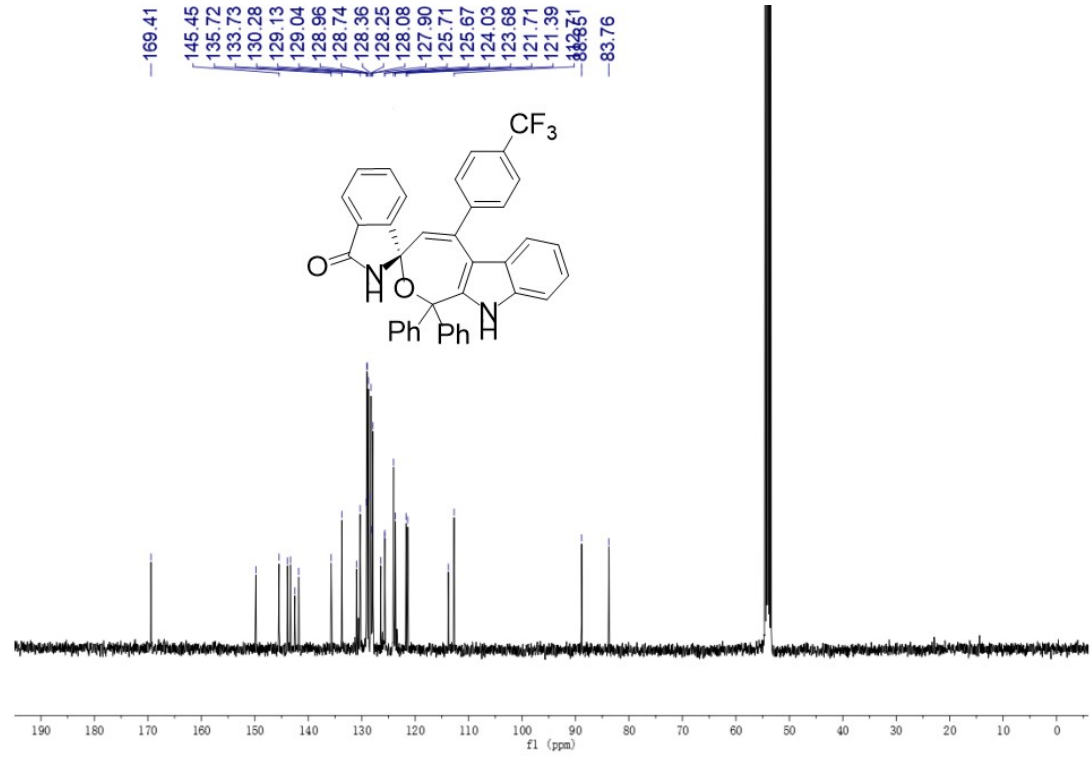
^{13}C NMR (101 MHz, CD_2Cl_2) of **3f**



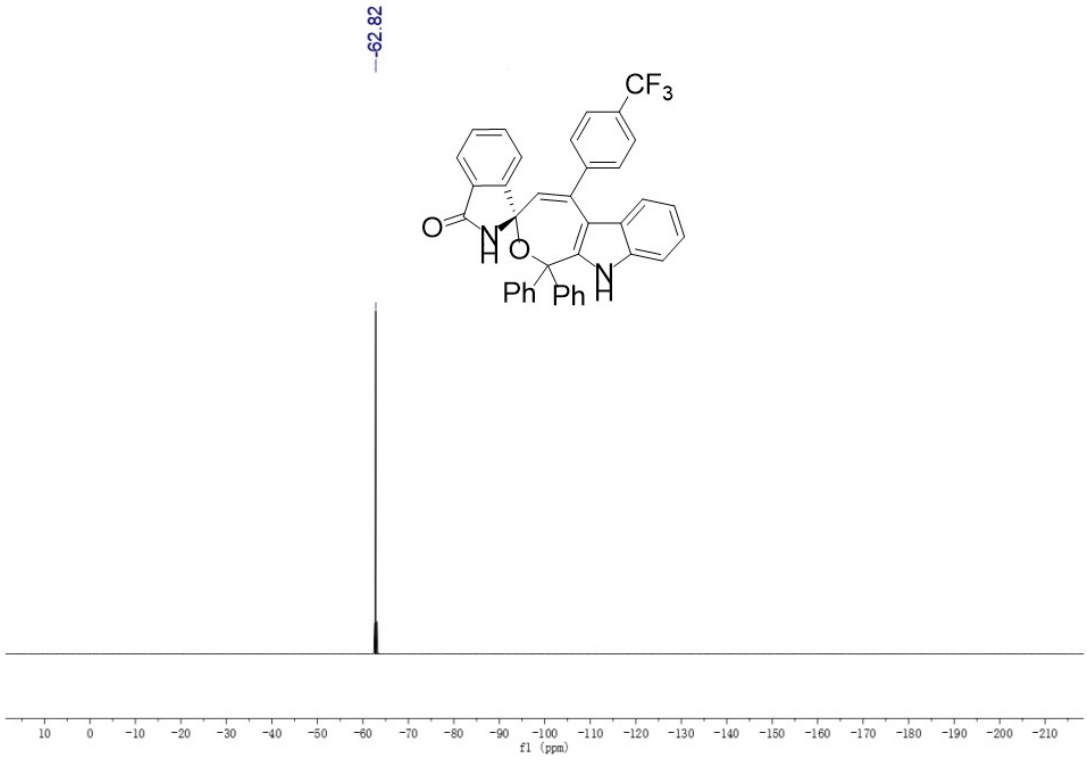
^{1}H NMR (400 MHz, CD_2Cl_2) of **3g**



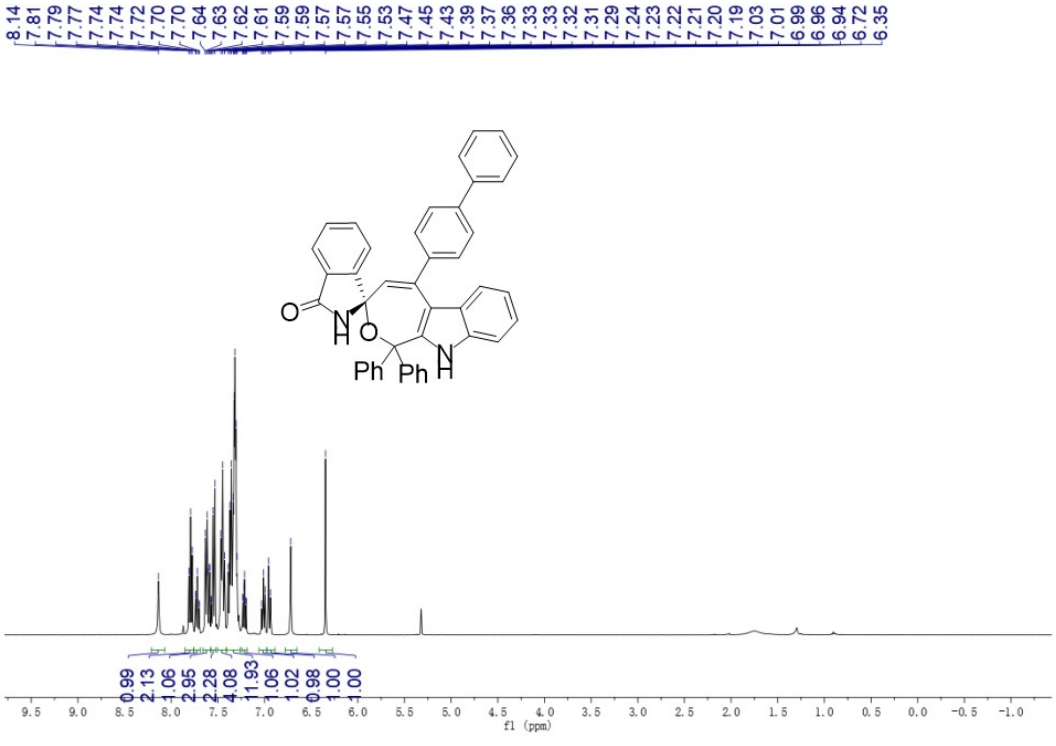
^{13}C NMR (101 MHz, CD_2Cl_2) of **3g**



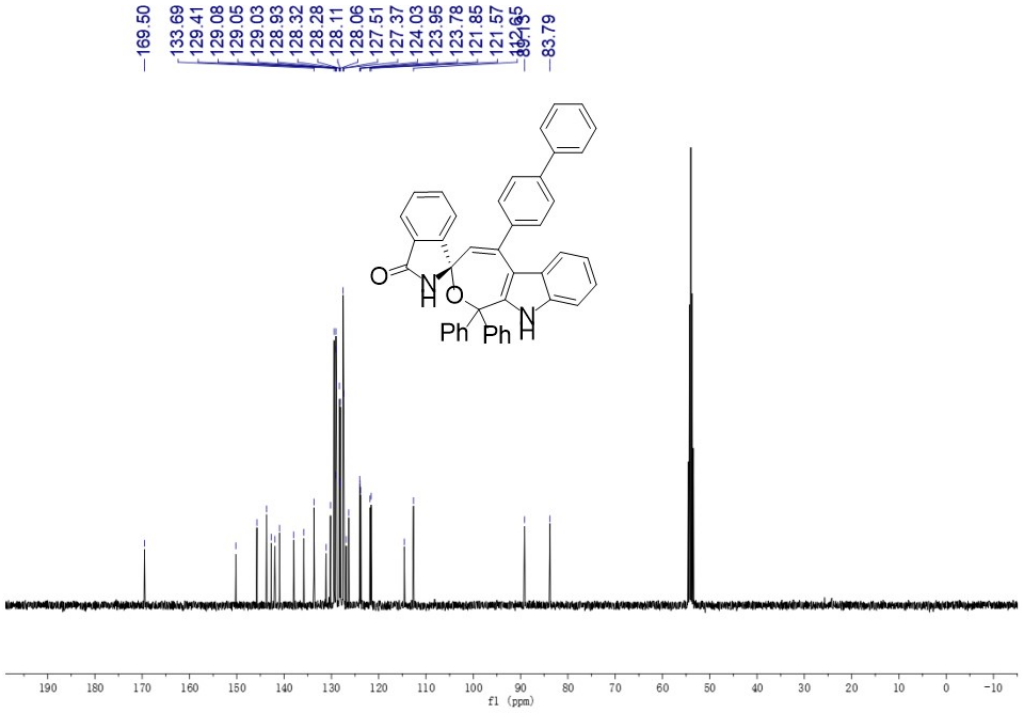
^{19}F NMR (376MHz, CD_2Cl_2) of **3g**



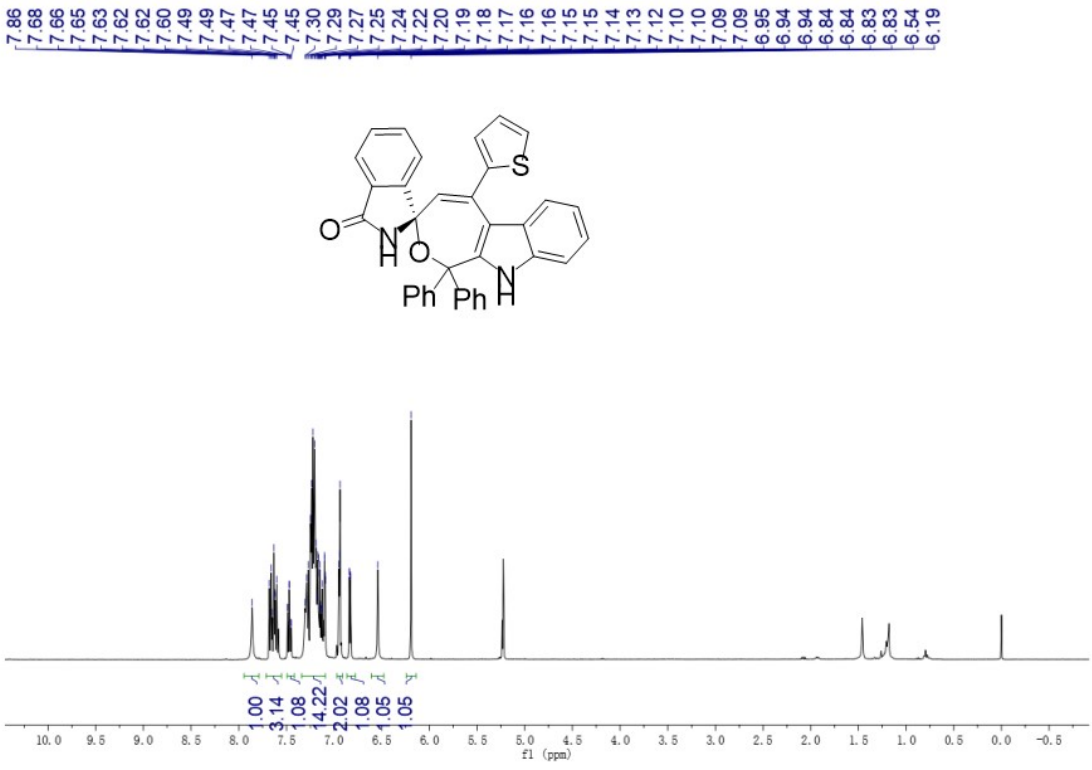
^{1}H NMR (400 MHz, CD_2Cl_2) of **3h**



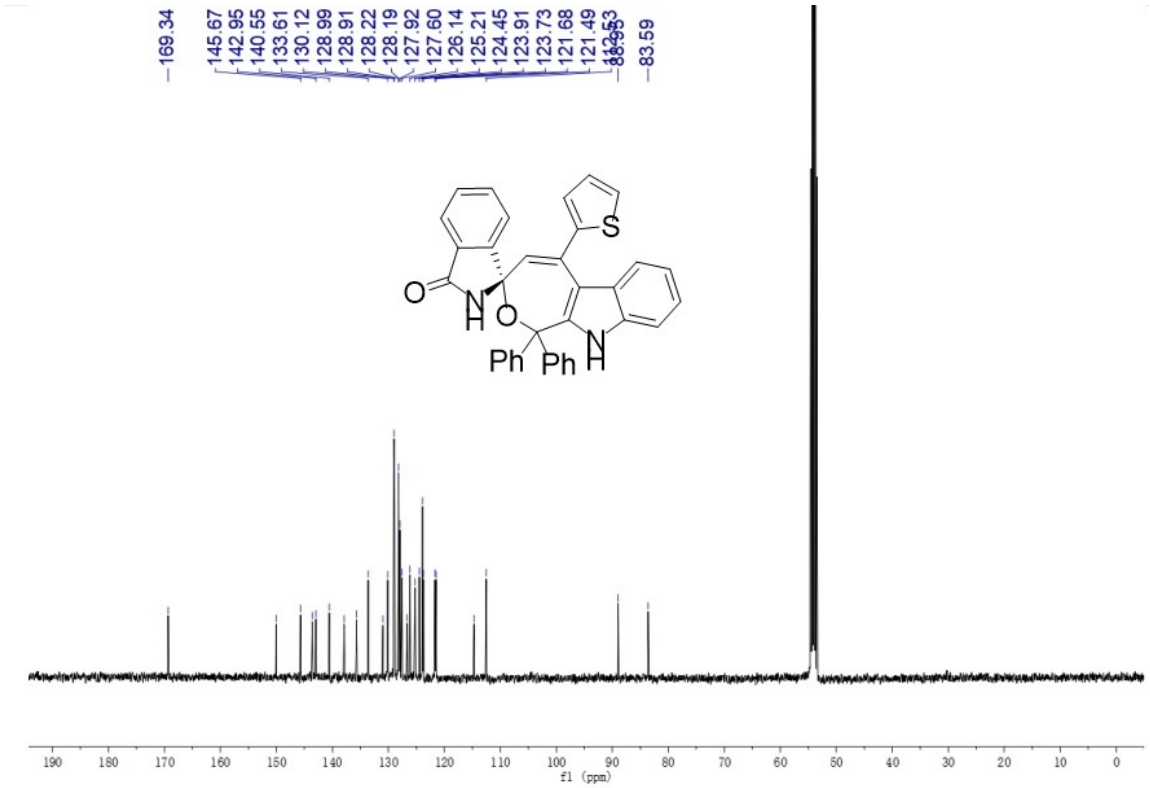
^{13}C NMR (101 MHz, CD_2Cl_2) of **3h**



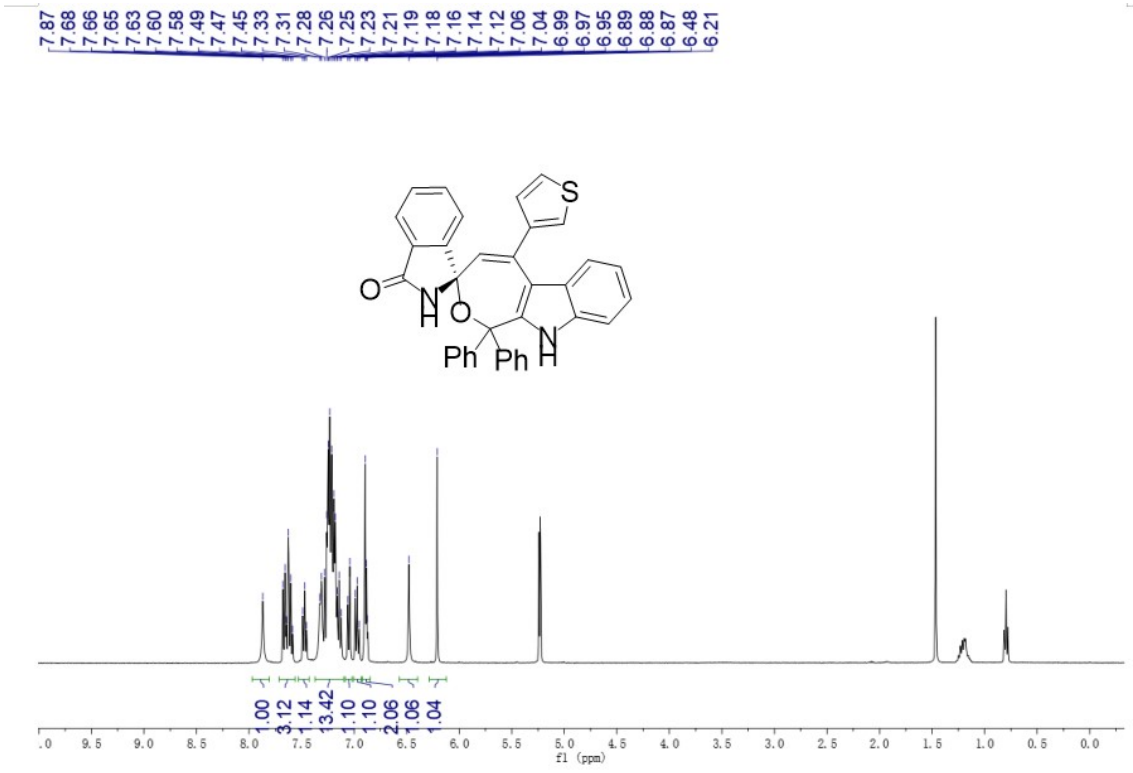
^{1}H NMR (400 MHz, CD_2Cl_2) of **3i**



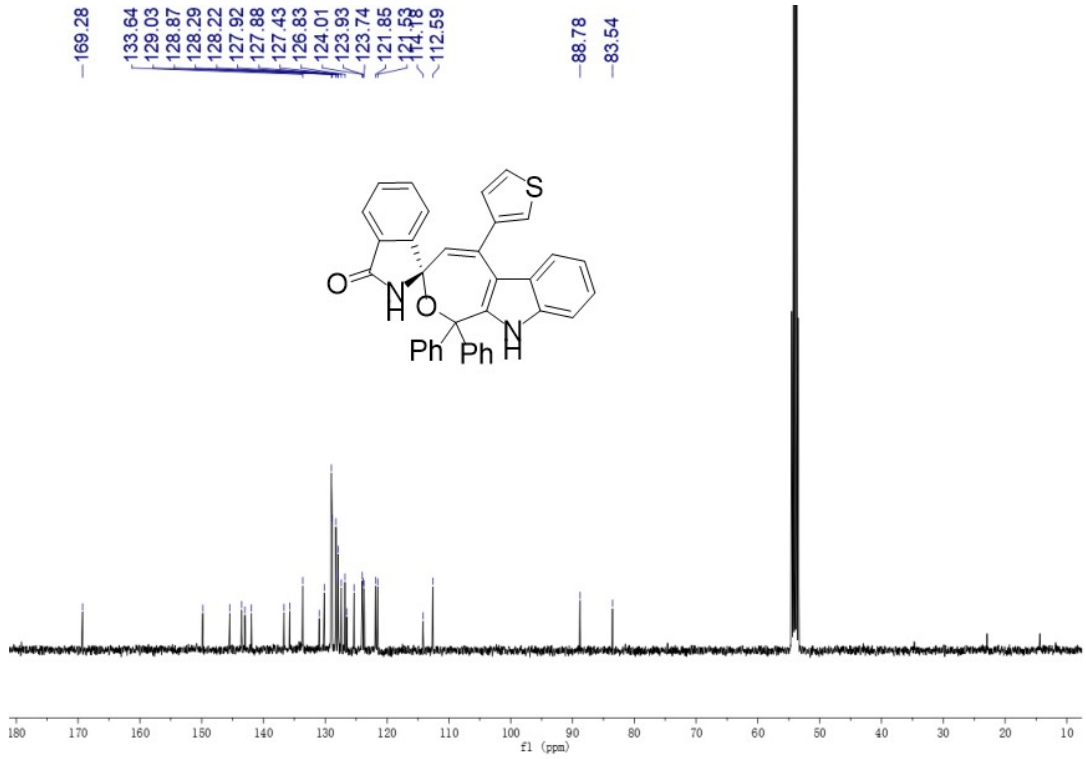
^{13}C NMR (101 MHz, CD_2Cl_2) of **3i**



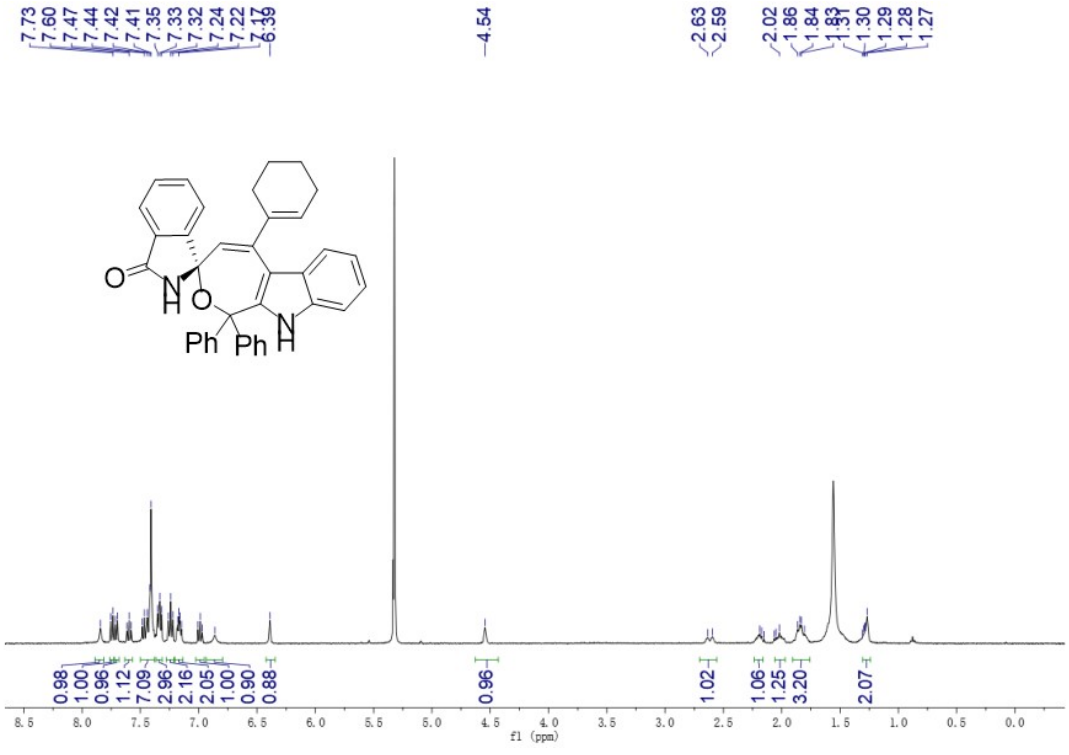
^{1}H NMR (400 MHz, CD_2Cl_2) of **3j**



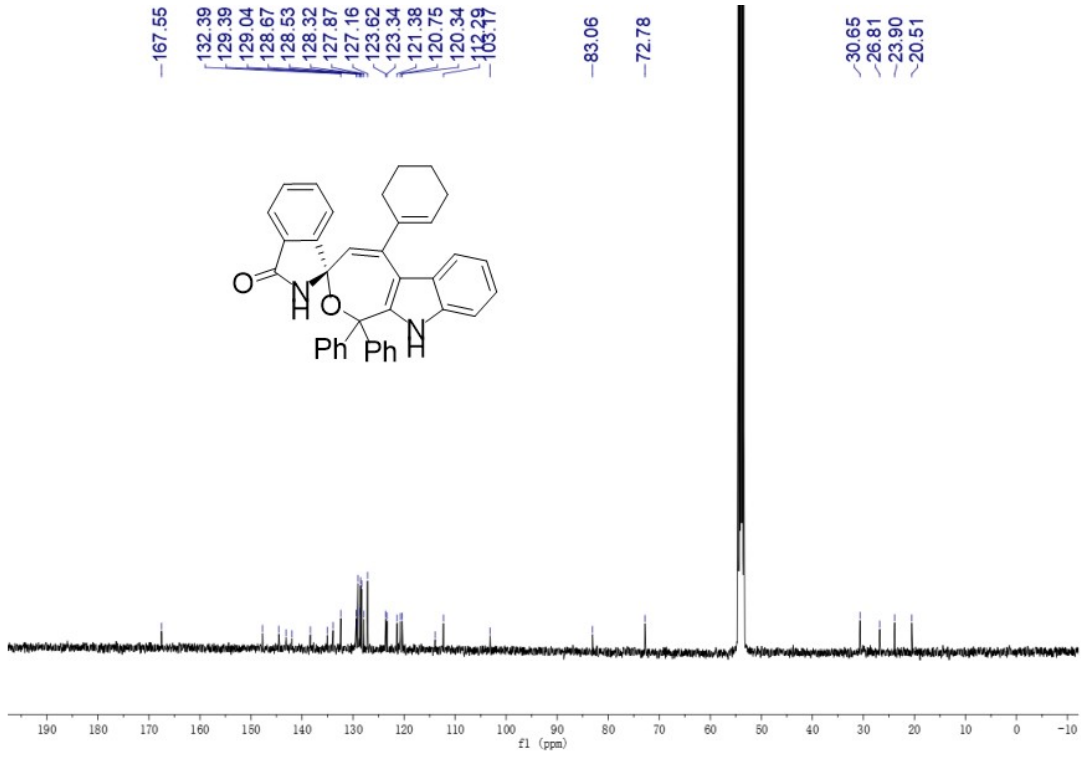
^{13}C NMR (101 MHz, CD_2Cl_2) of **3j**



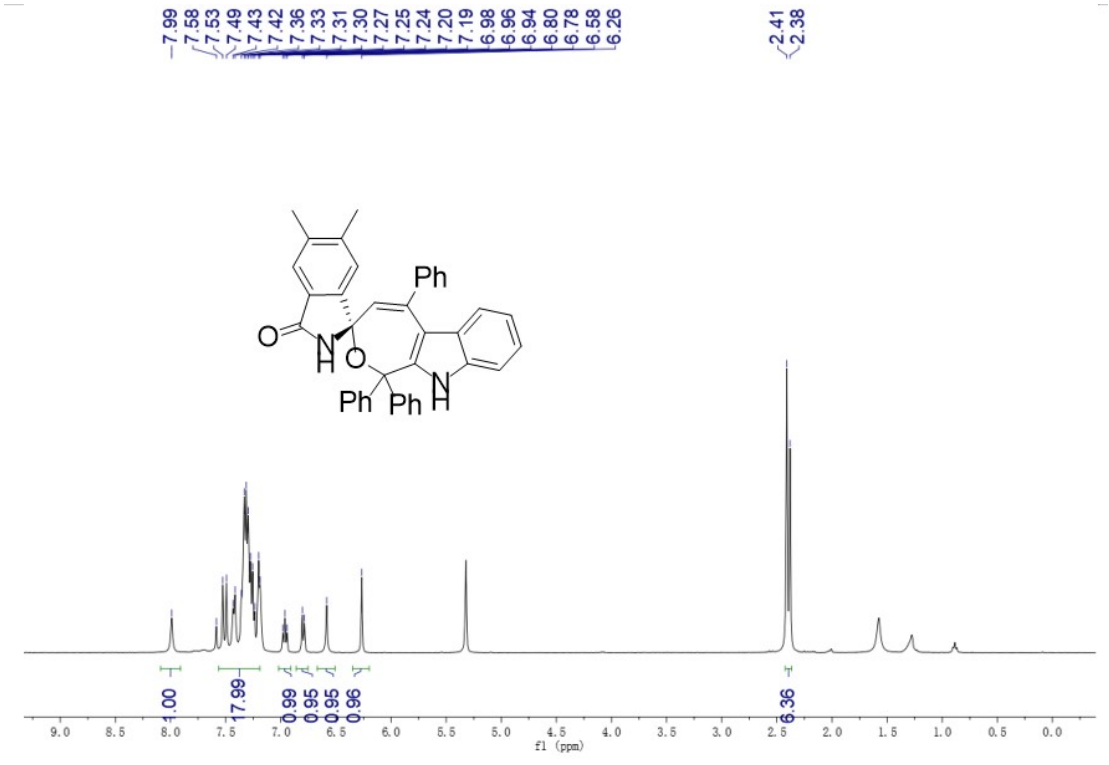
^{1}H NMR (400 MHz, CD_2Cl_2) of **3k**



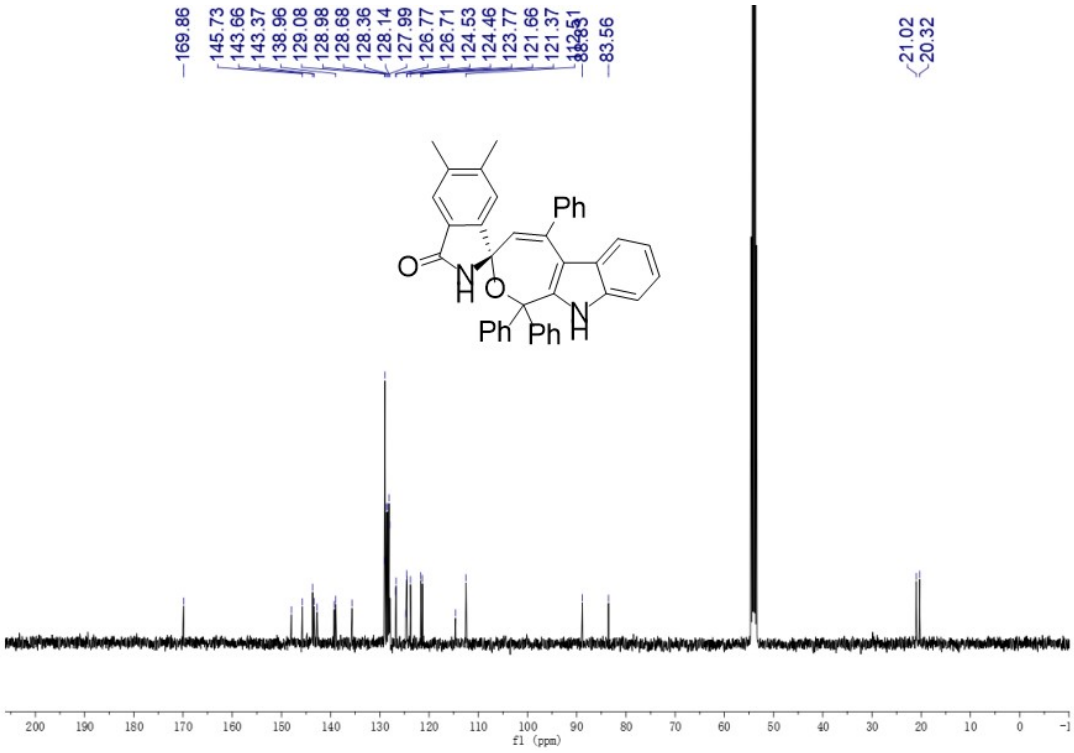
^{13}C NMR (101 MHz, CD_2Cl_2) of **3k**



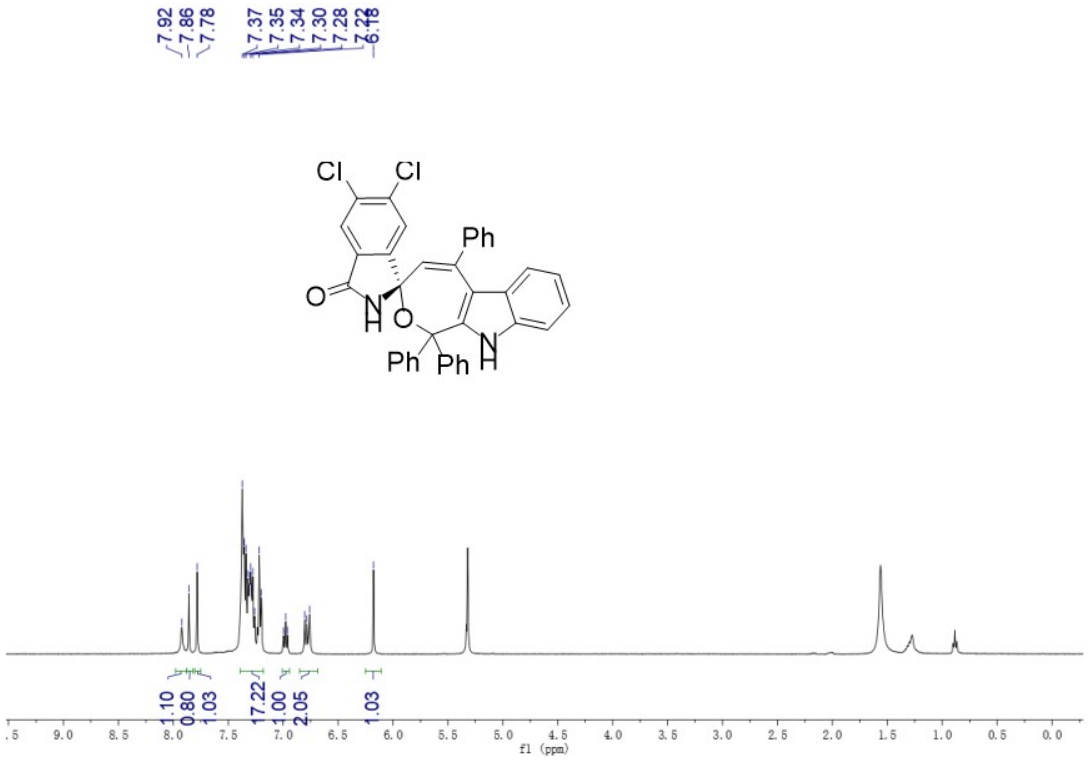
^{1}H NMR (400 MHz, CD_2Cl_2) of **3l**



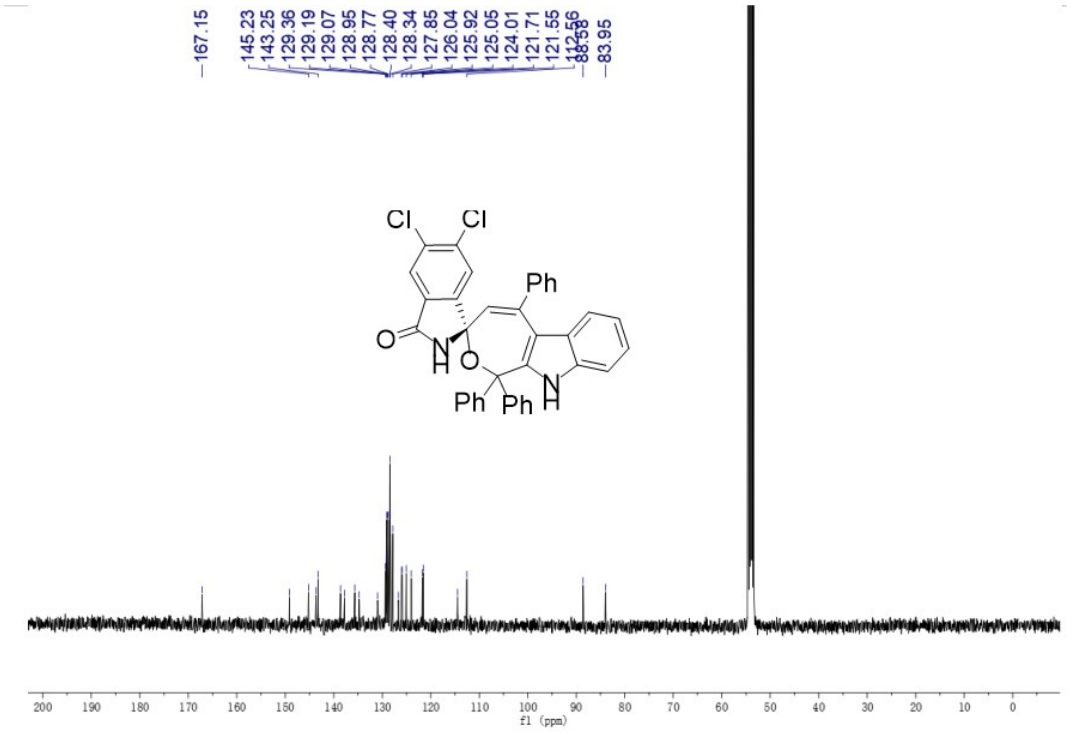
^{13}C NMR (101 MHz, CD_2Cl_2) of **3l**



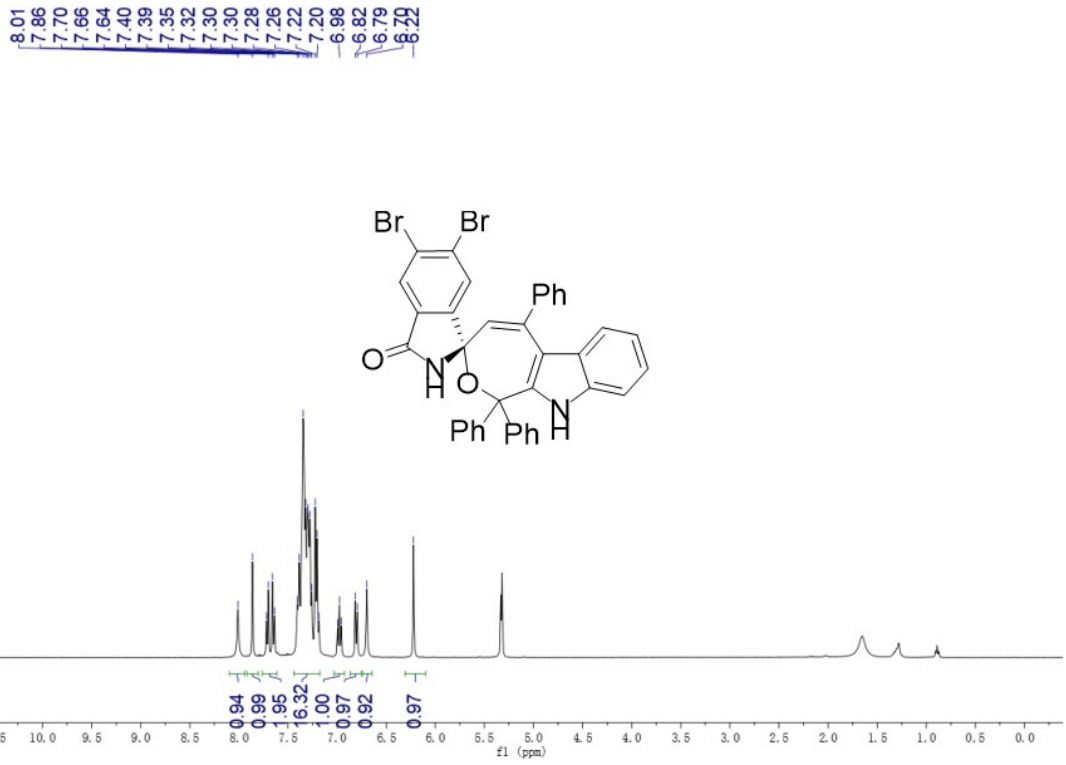
^{1}H NMR (400 MHz, CD_2Cl_2) of **3m**



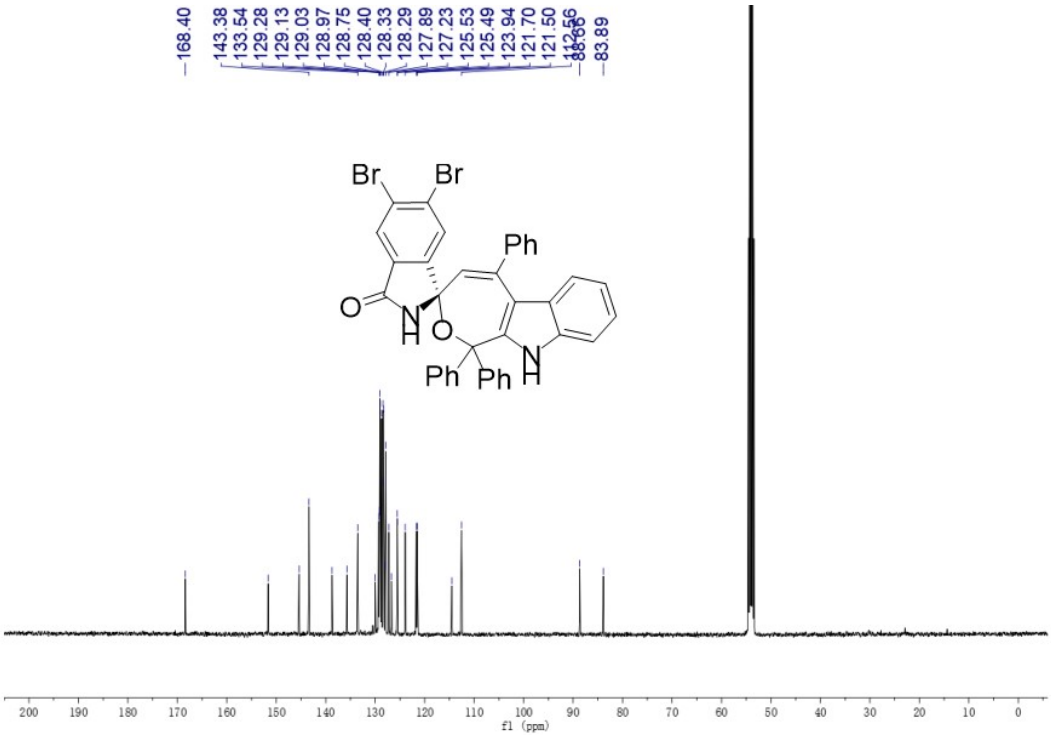
^{13}C NMR (101 MHz, CD_2Cl_2) of **3m**



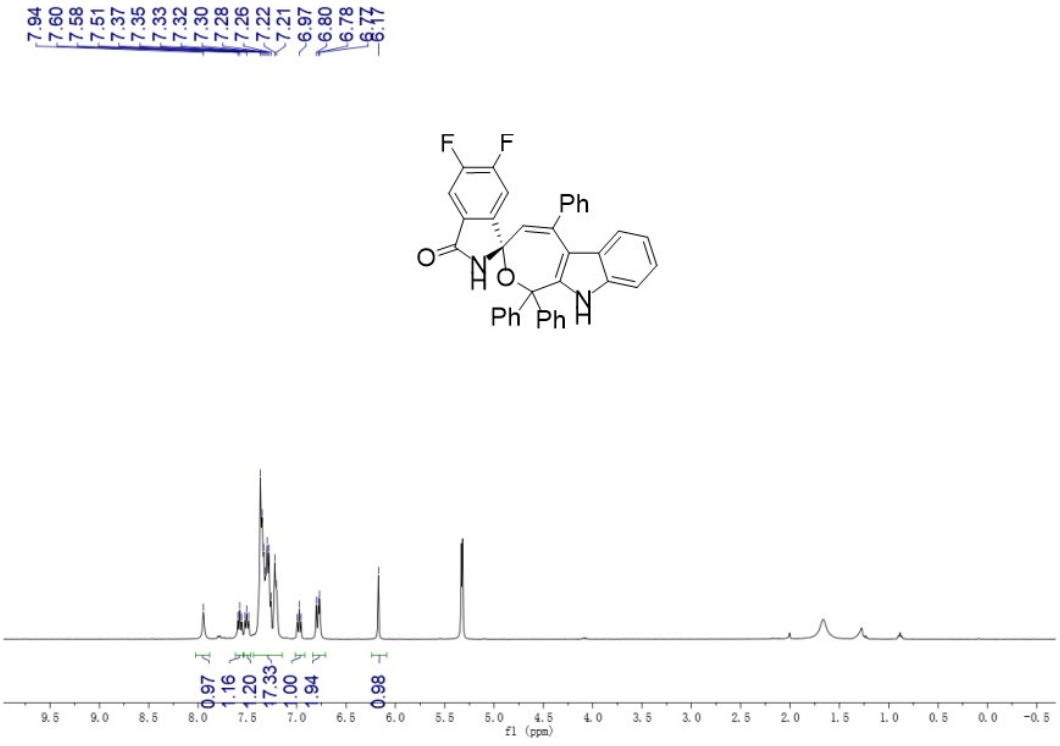
^{1}H NMR (400 MHz, CD_2Cl_2) of **3n**



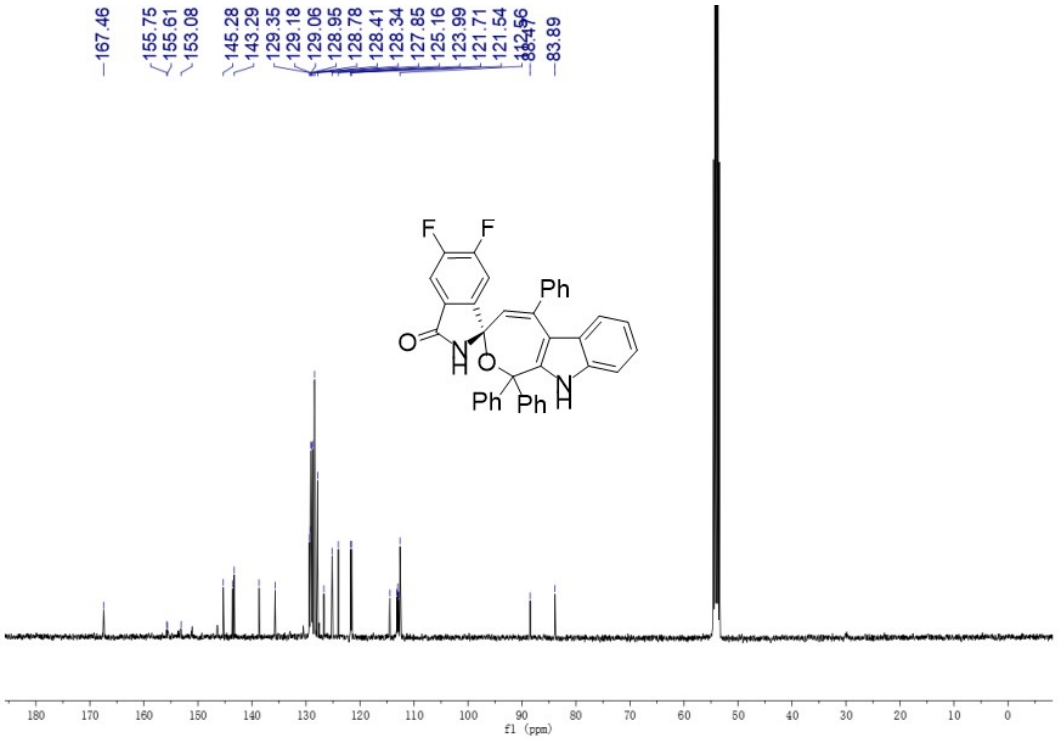
^{13}C NMR (101 MHz, CD_2Cl_2) of **3n**



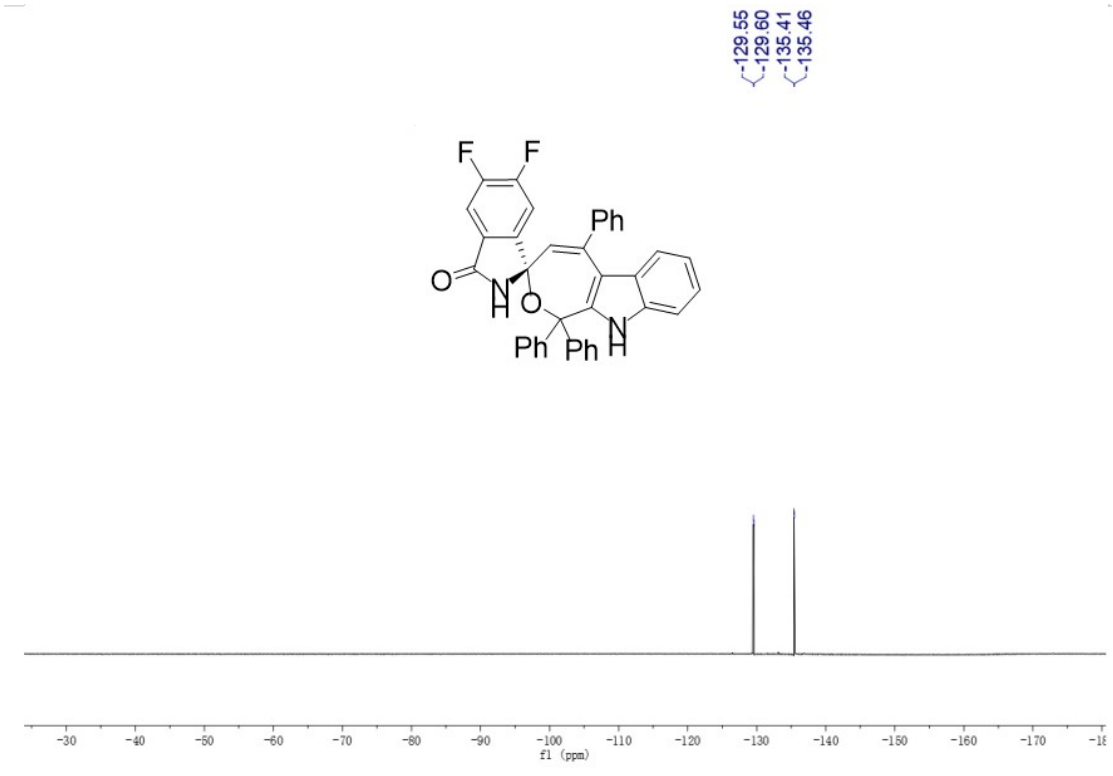
^{1}H NMR (400 MHz, CD_2Cl_2) of **3o**



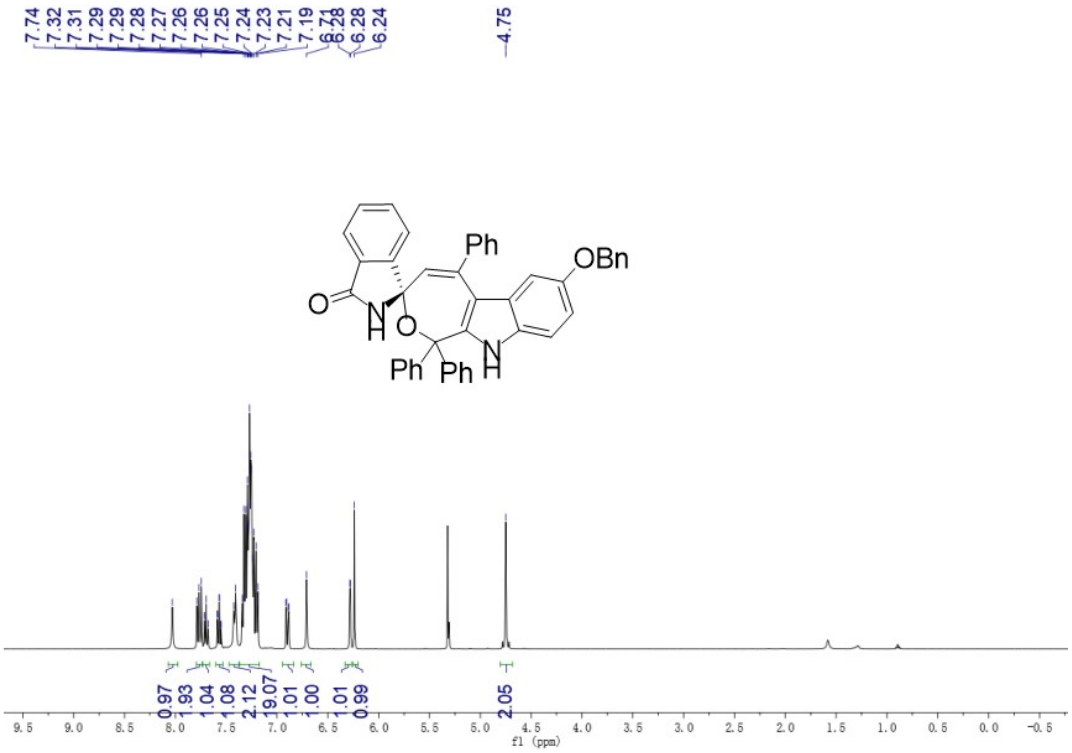
^{13}C NMR (101 MHz, CD_2Cl_2) of **3o**



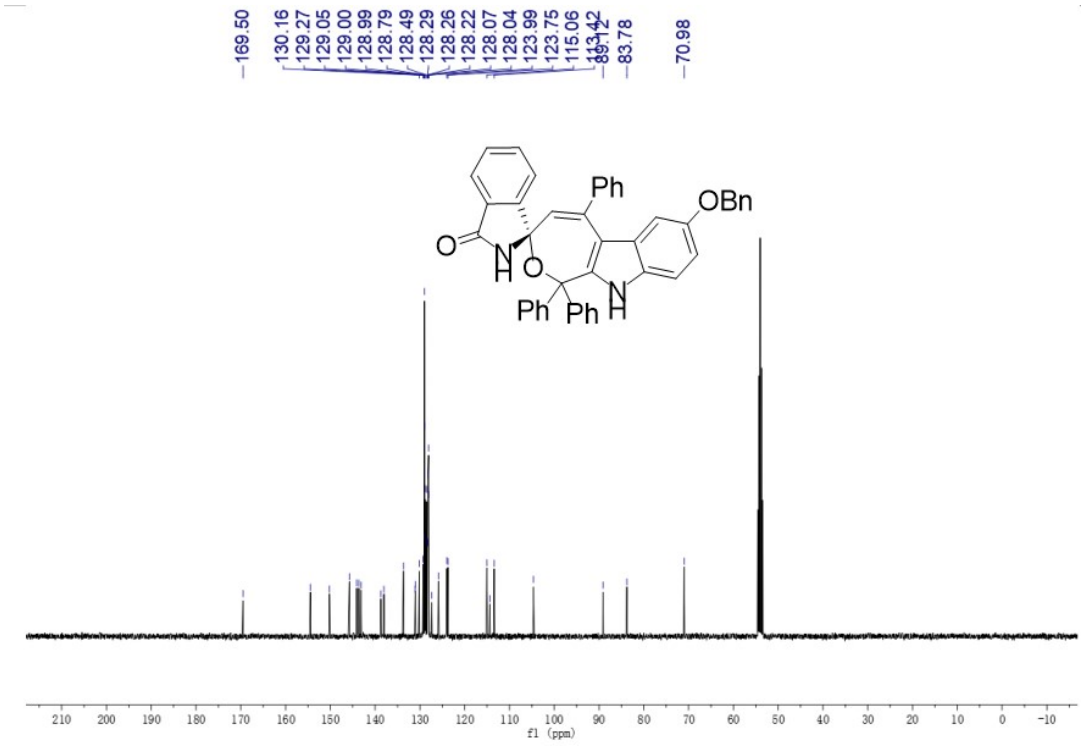
^{19}F NMR (376MHz, CD_2Cl_2) of **3o**



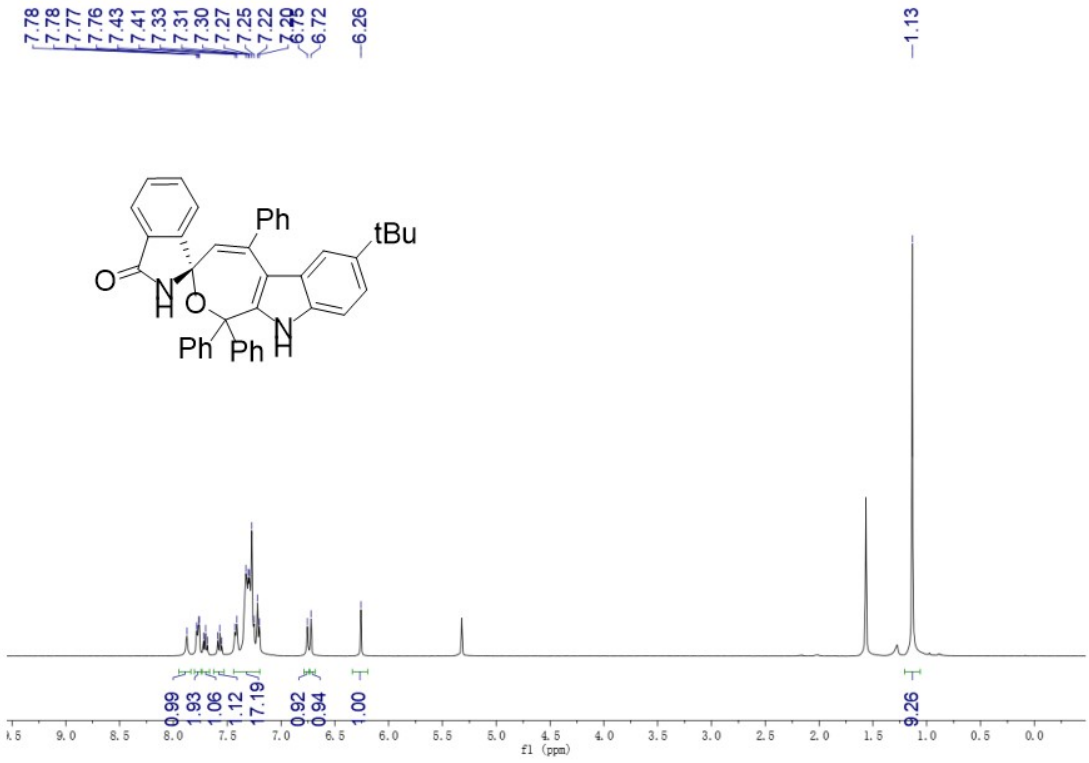
^{1}H NMR (400 MHz, CD_2Cl_2) of **3p**



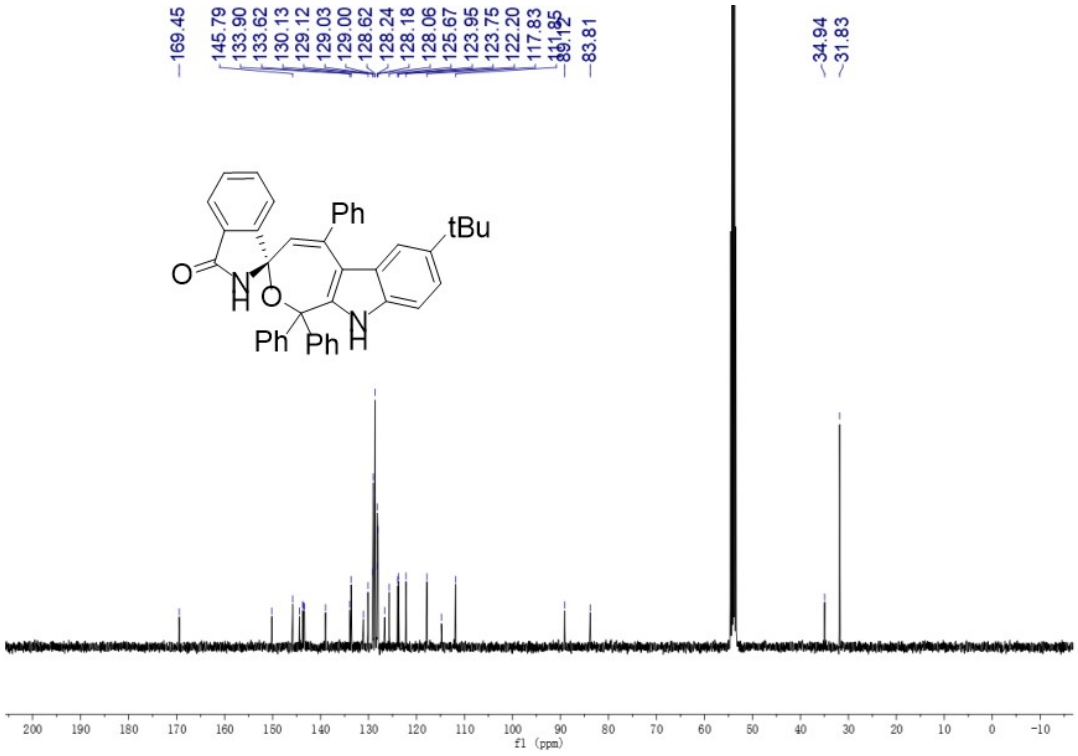
^{13}C NMR (101 MHz, CD_2Cl_2) of **3p**



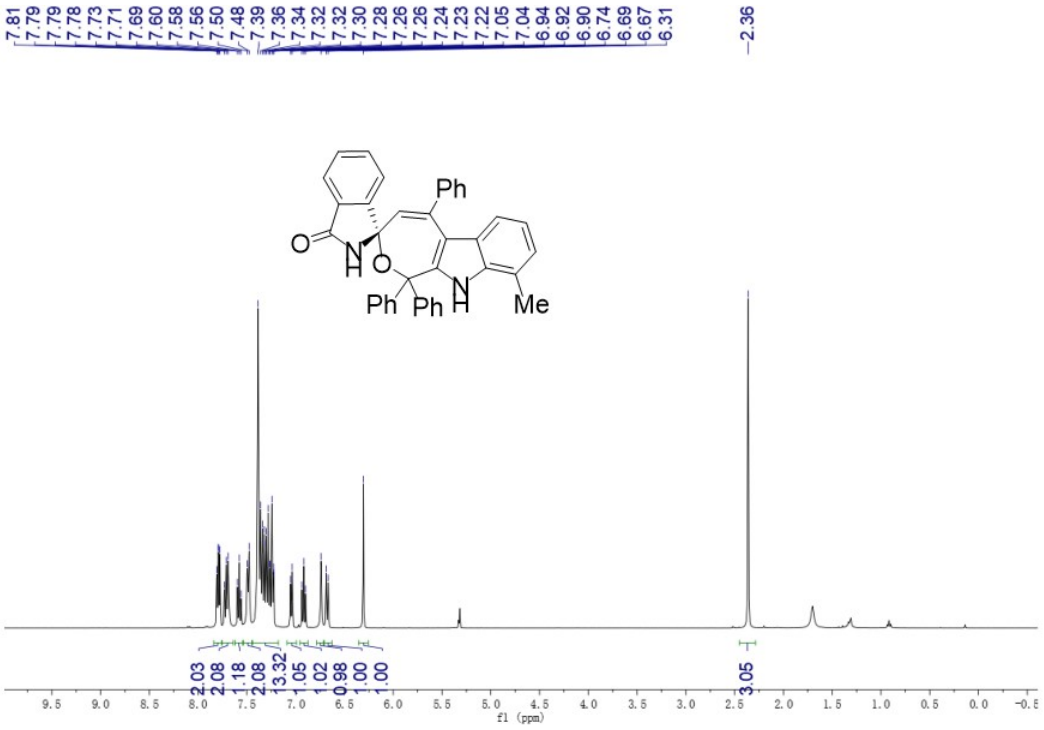
^{1}H NMR (400 MHz, CD_2Cl_2) of **3q**



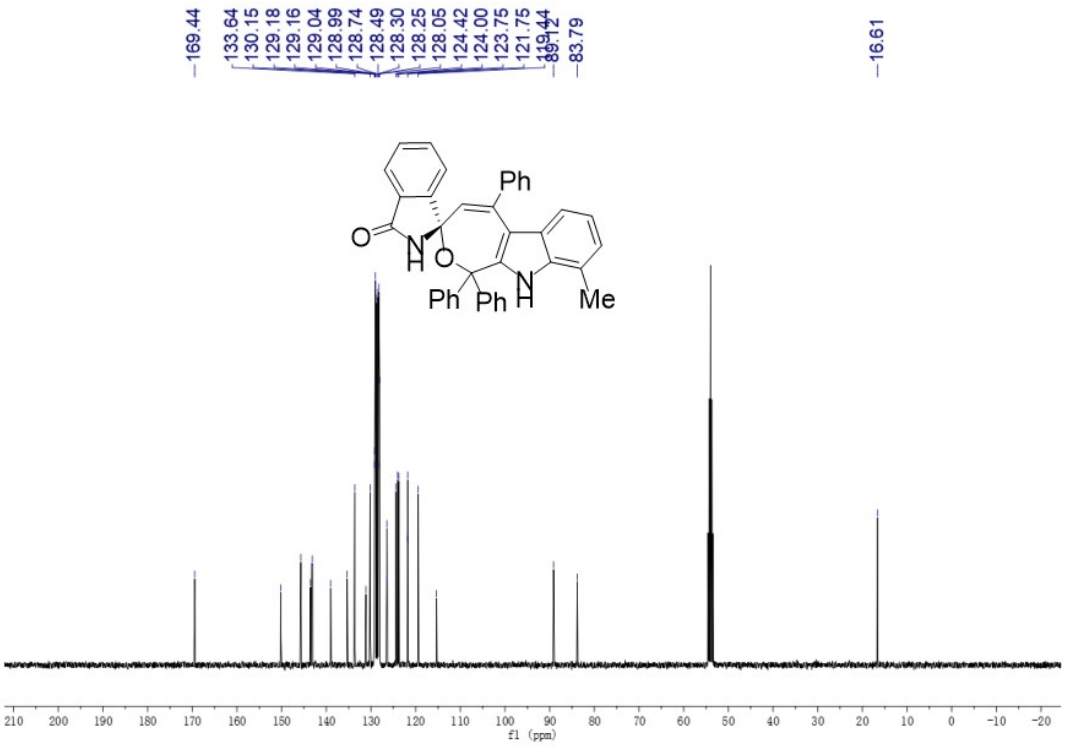
^{13}C NMR (101 MHz, CD_2Cl_2) of **3q**



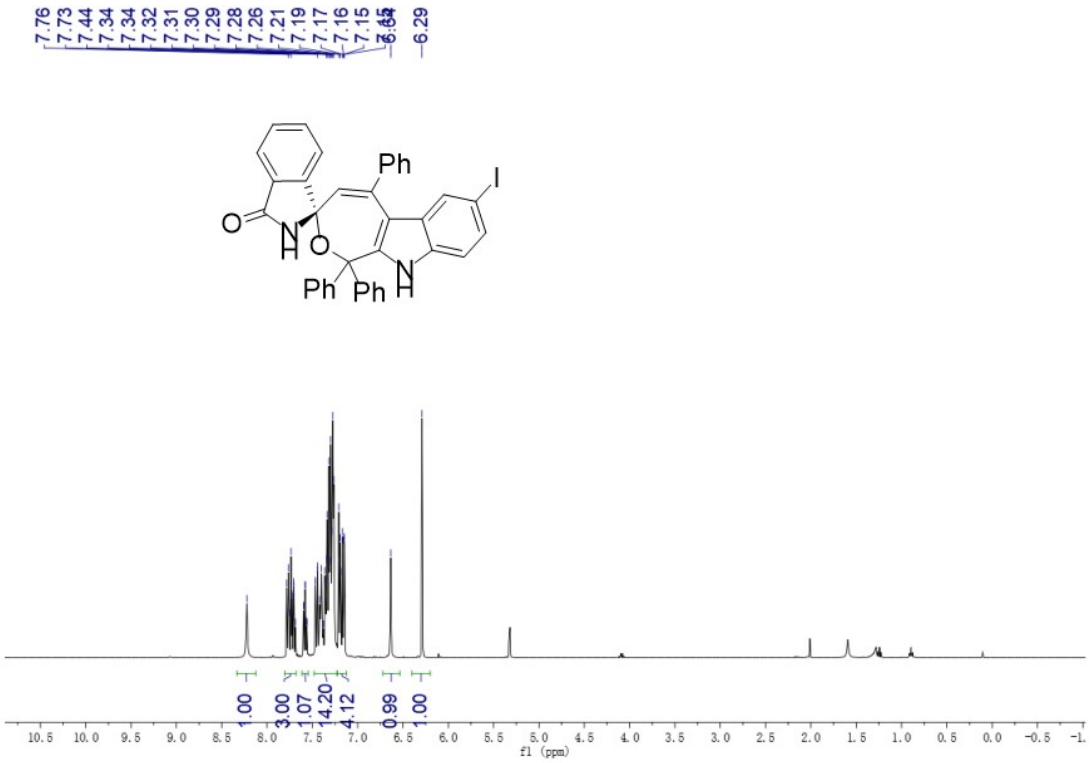
^{1}H NMR (400 MHz, CD_2Cl_2) of **3r**



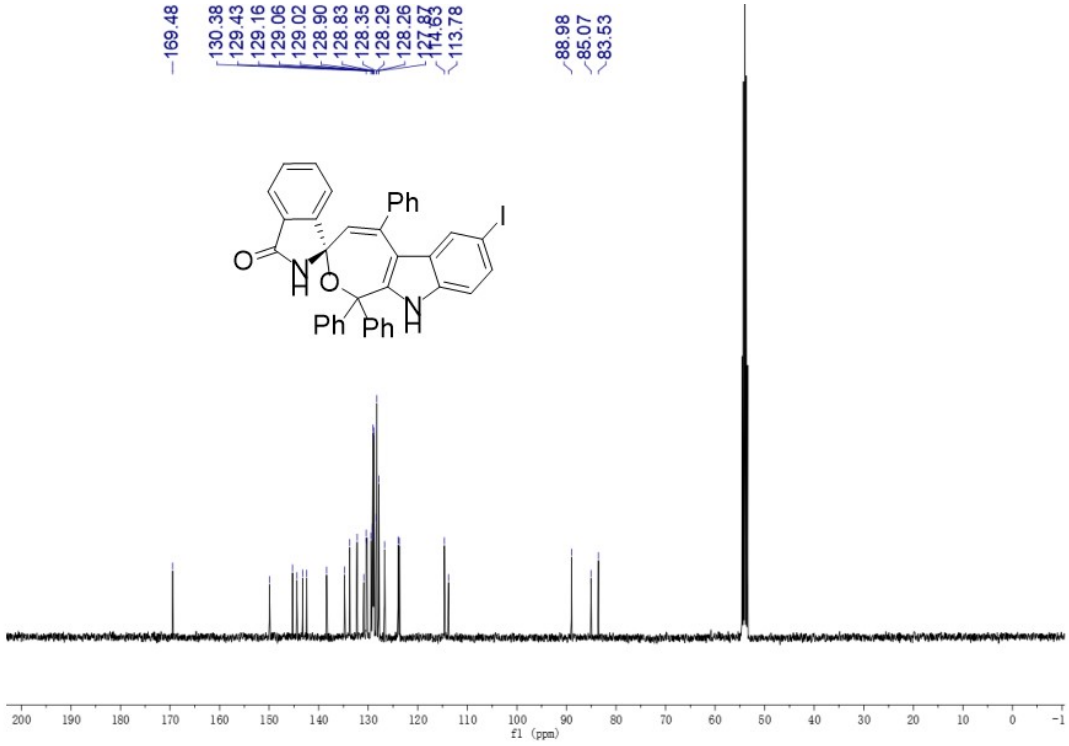
^{13}C NMR (101 MHz, CD_2Cl_2) of **3r**



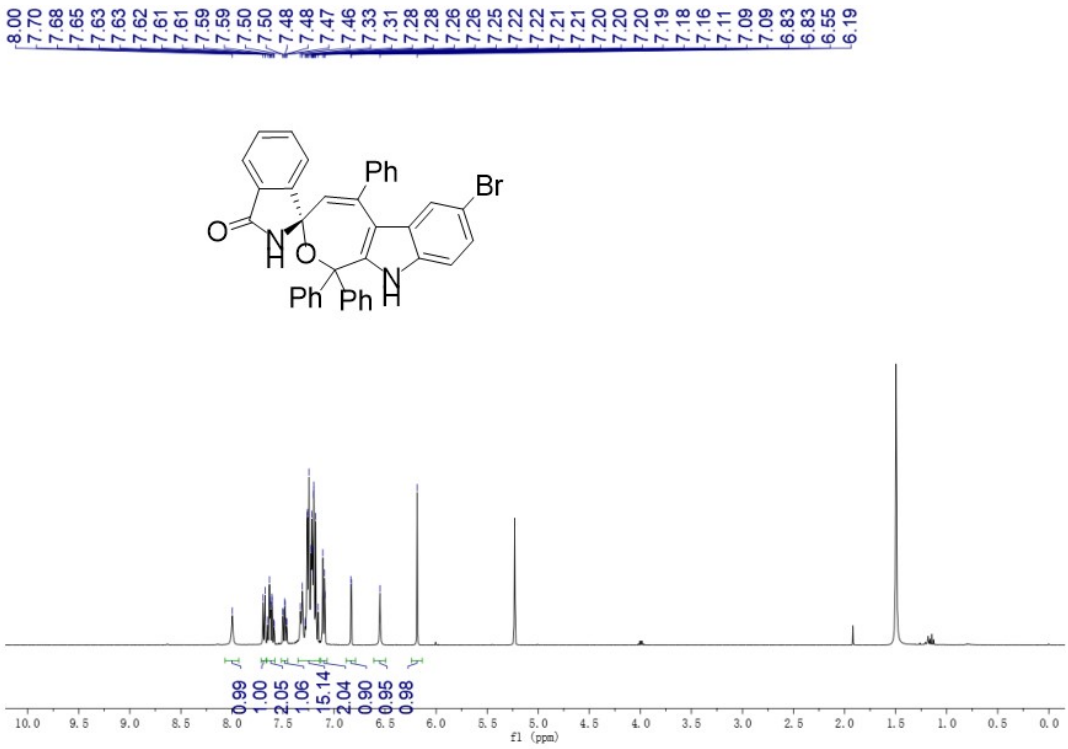
^{1}H NMR (400 MHz, CD_2Cl_2) of **3s**



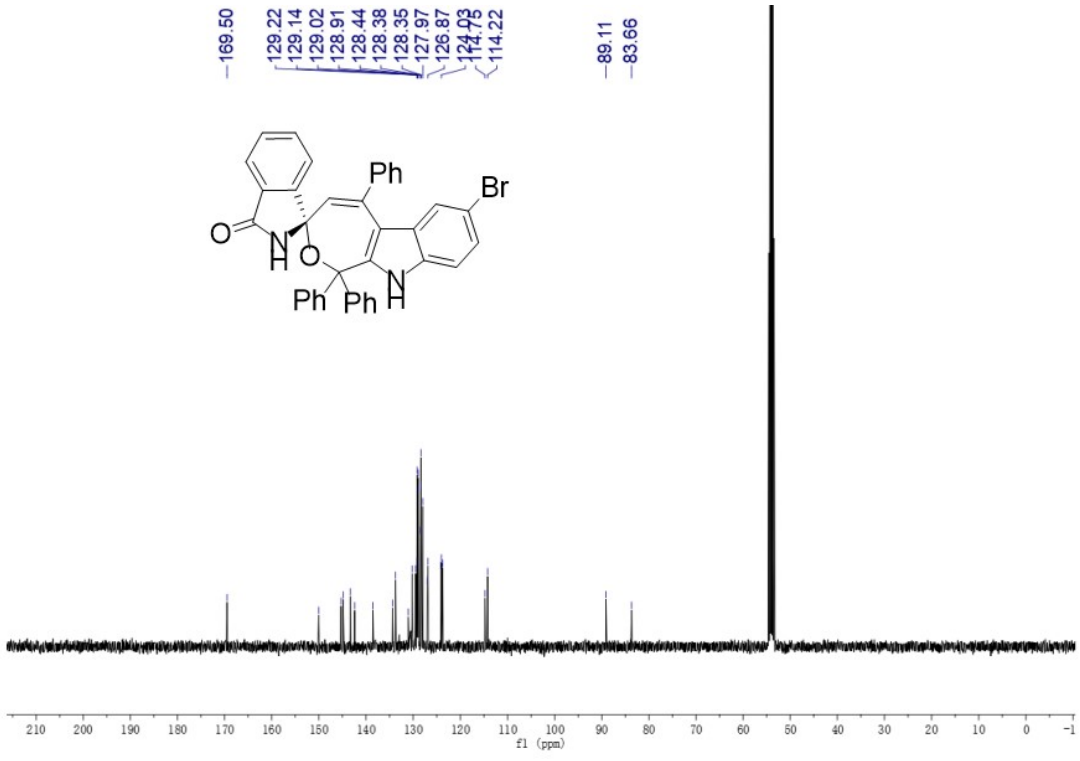
^{13}C NMR (101 MHz, CD_2Cl_2) of **3s**



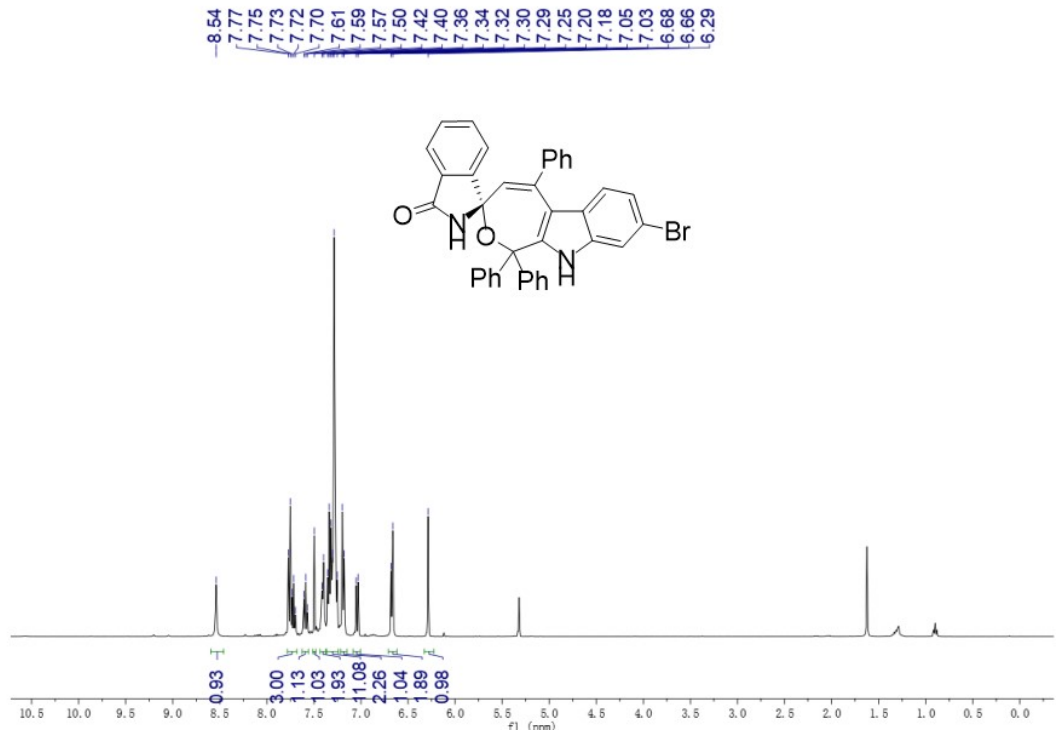
^{1}H NMR (400 MHz, CD_2Cl_2) of **3t**



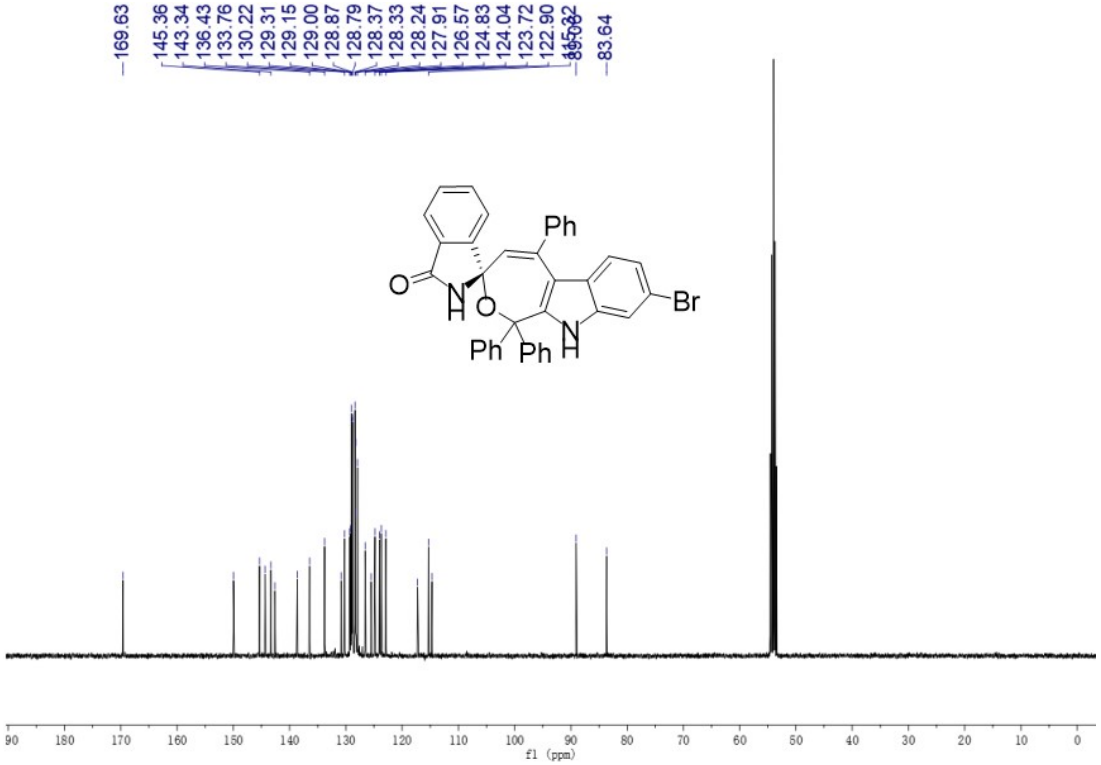
^{13}C NMR (101 MHz, CD_2Cl_2) of **3t**



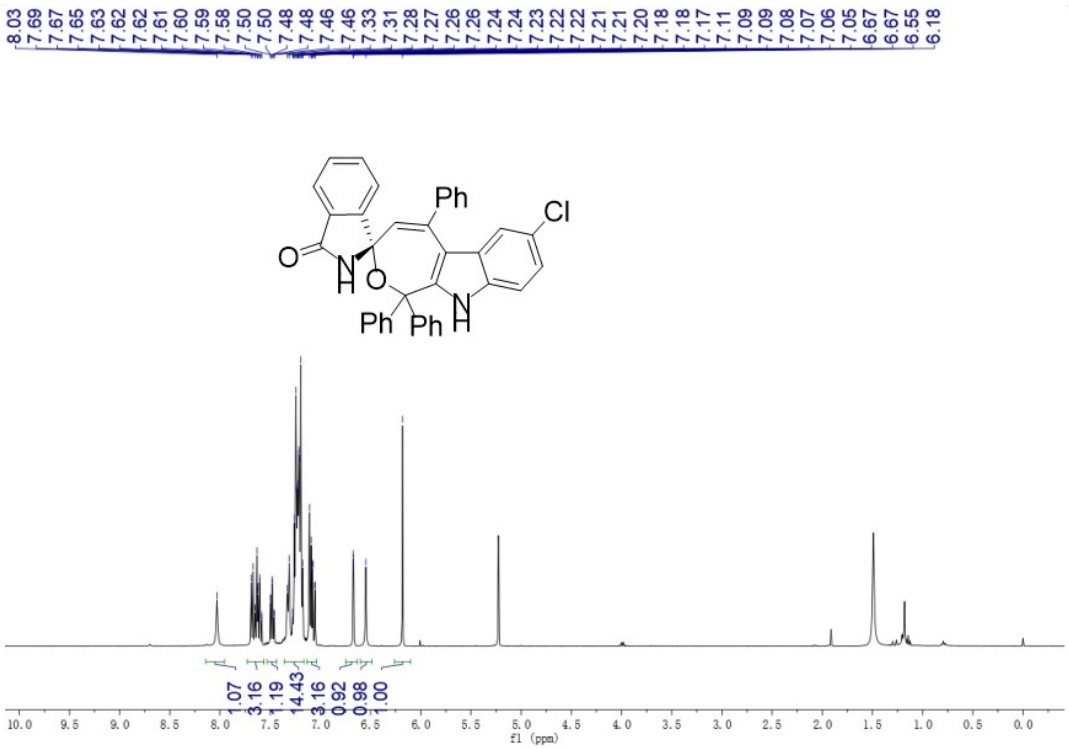
^{1}H NMR (400 MHz, CD_2Cl_2) of **3u**



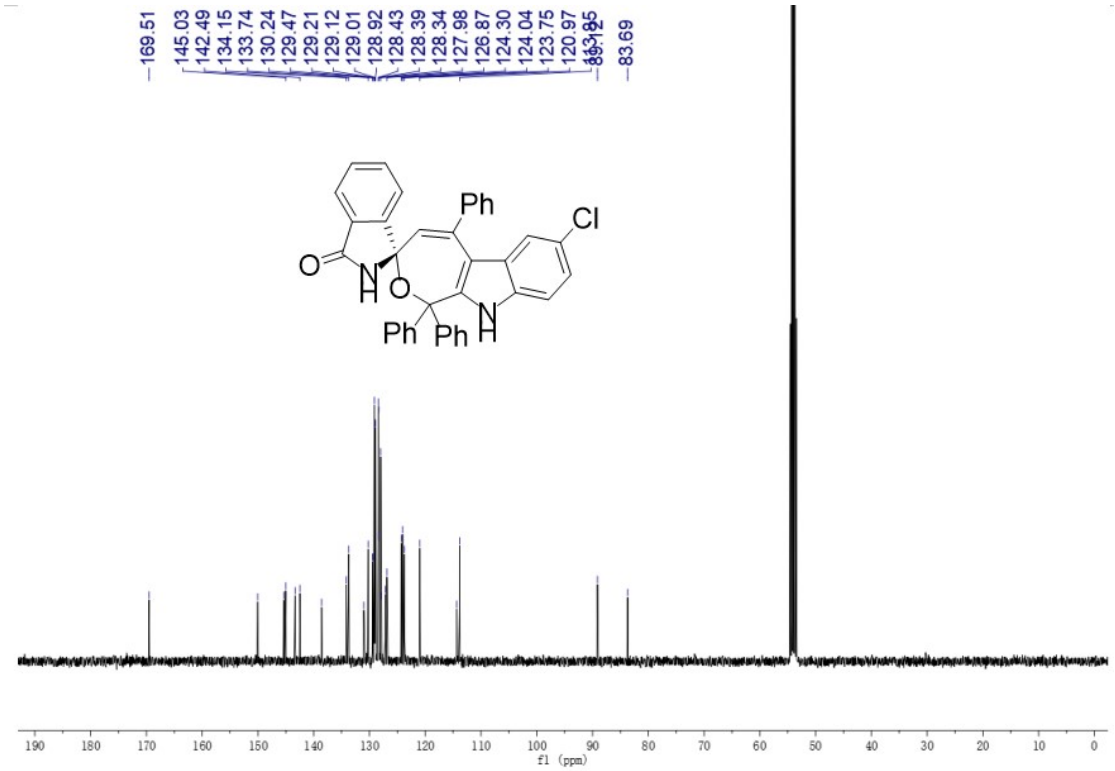
^{13}C NMR (101 MHz, CD_2Cl_2) of **3u**



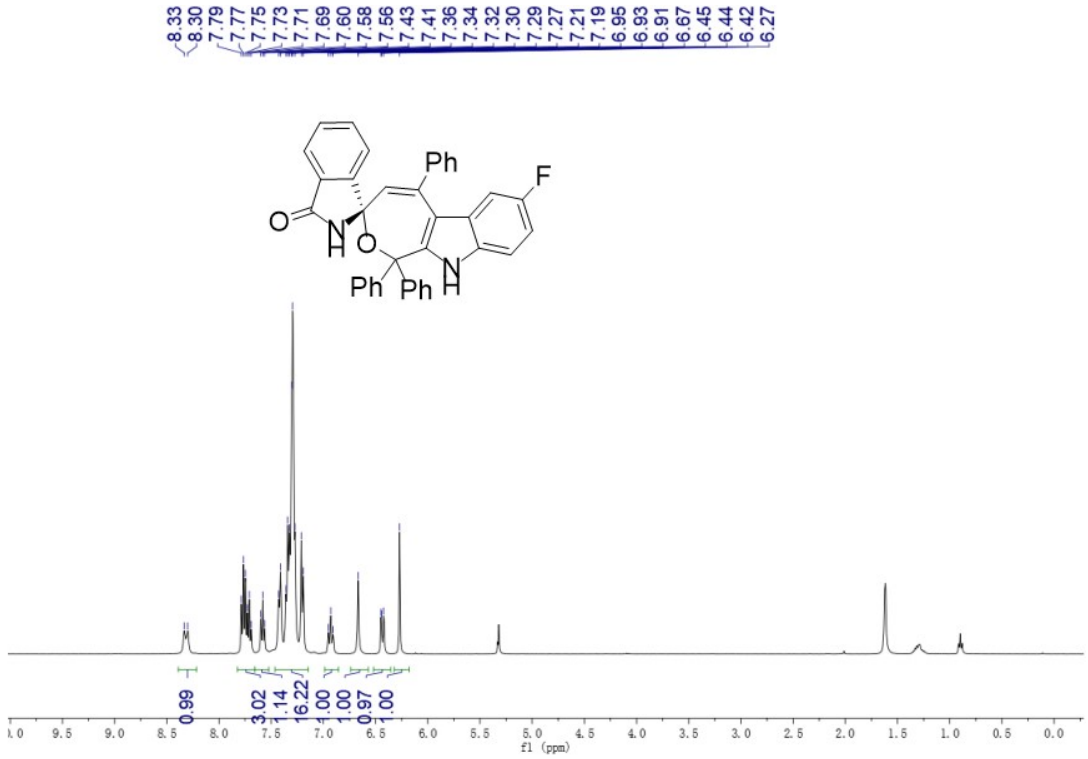
^{1}H NMR (400 MHz, CD_2Cl_2) of **3v**



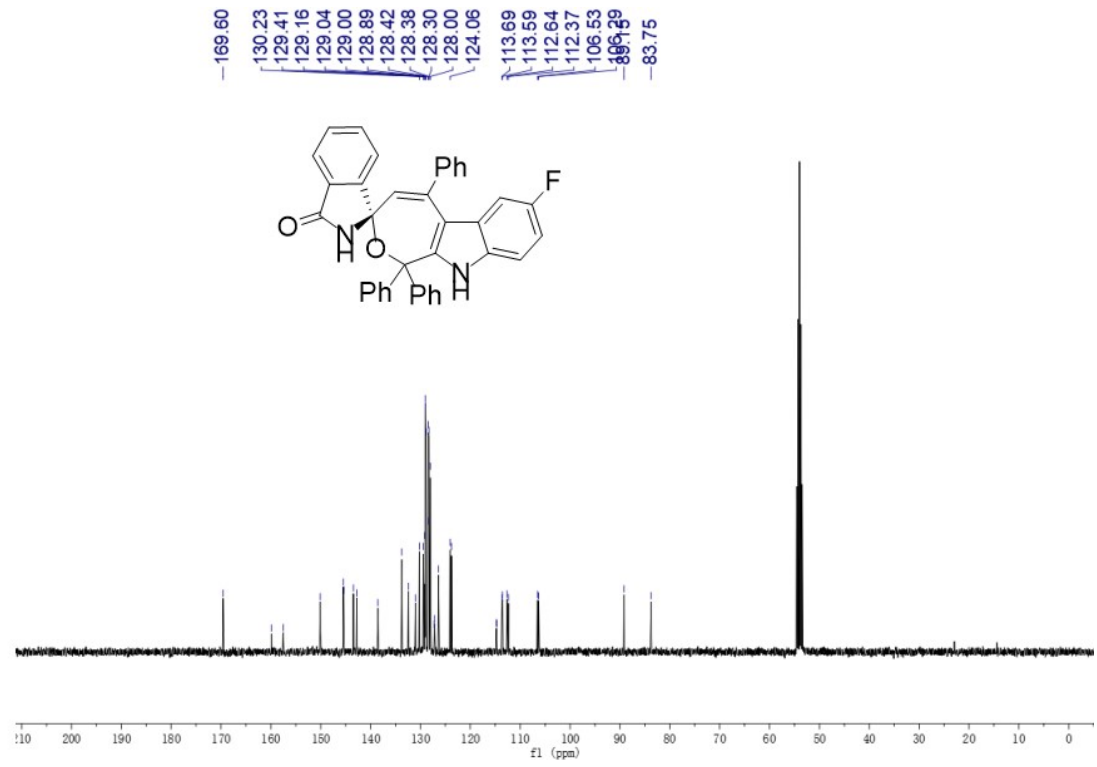
^{13}C NMR (101 MHz, CD_2Cl_2) of **3v**



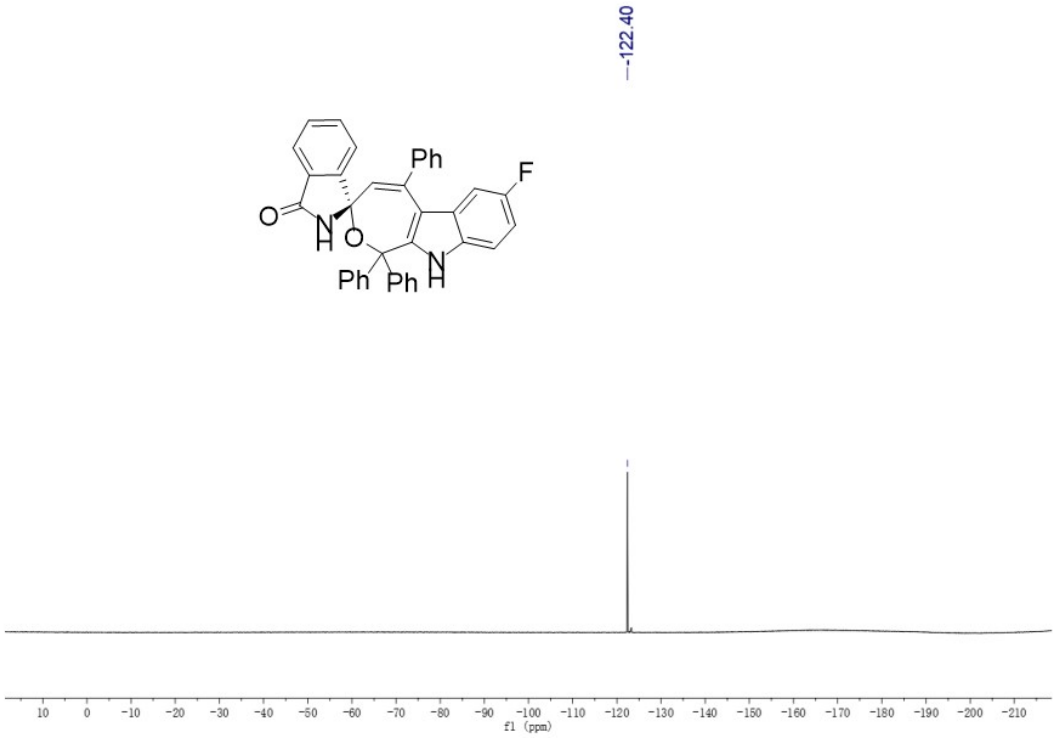
^{1}H NMR (400 MHz, CD_2Cl_2) of **3w**



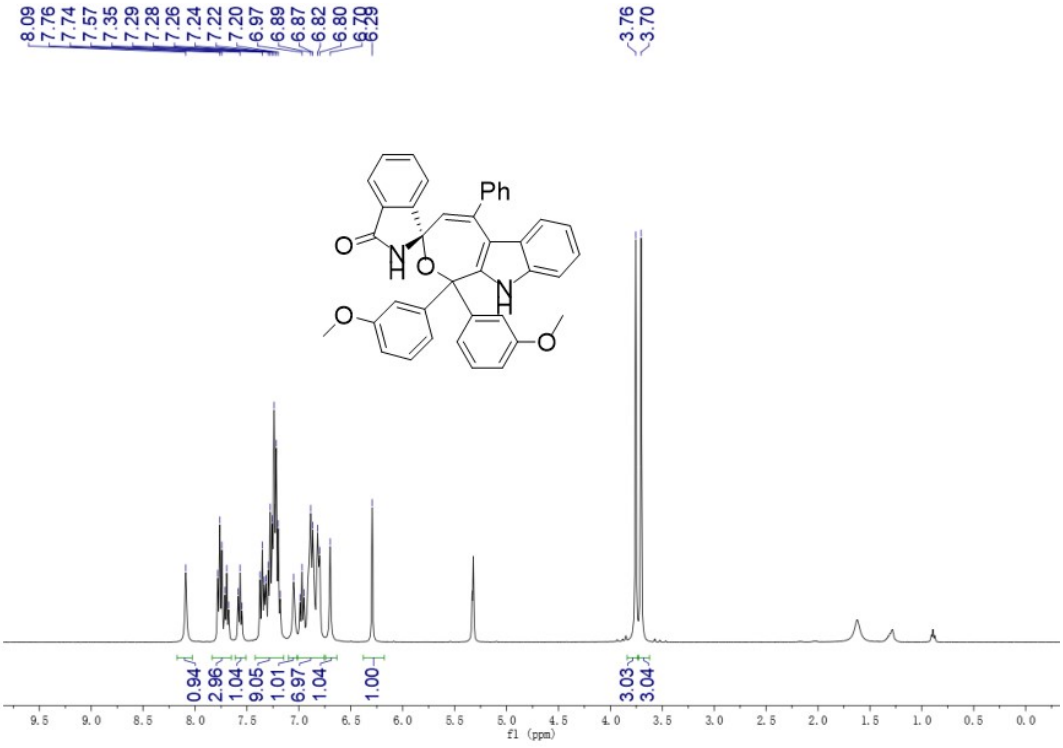
^{13}C NMR (101 MHz, CD_2Cl_2) of **3w**



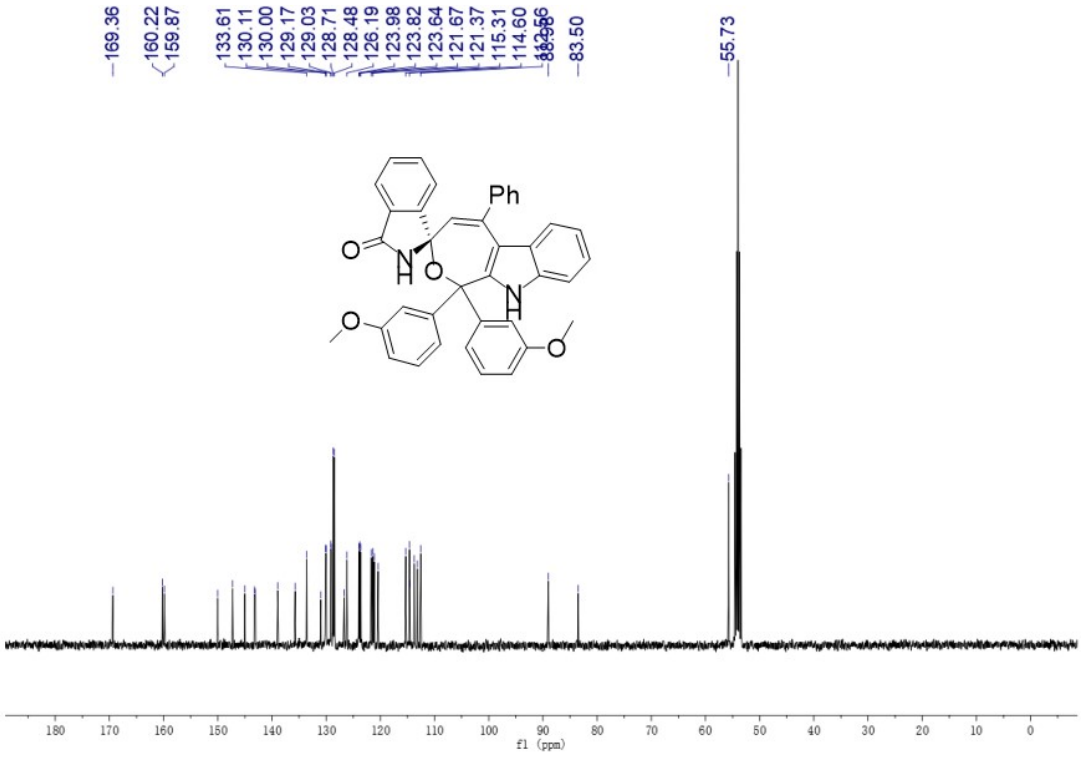
^{19}F NMR (376MHz, CD_2Cl_2) of **3w**



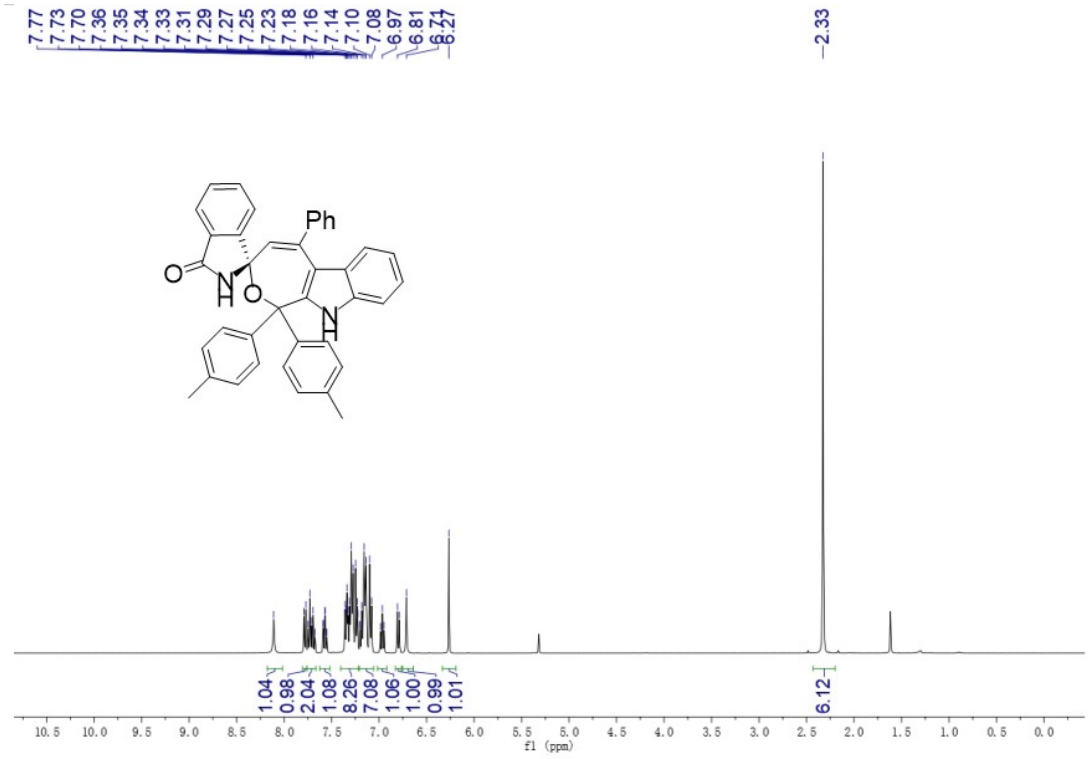
^{1}H NMR (400 MHz, CD_2Cl_2) of **3x**



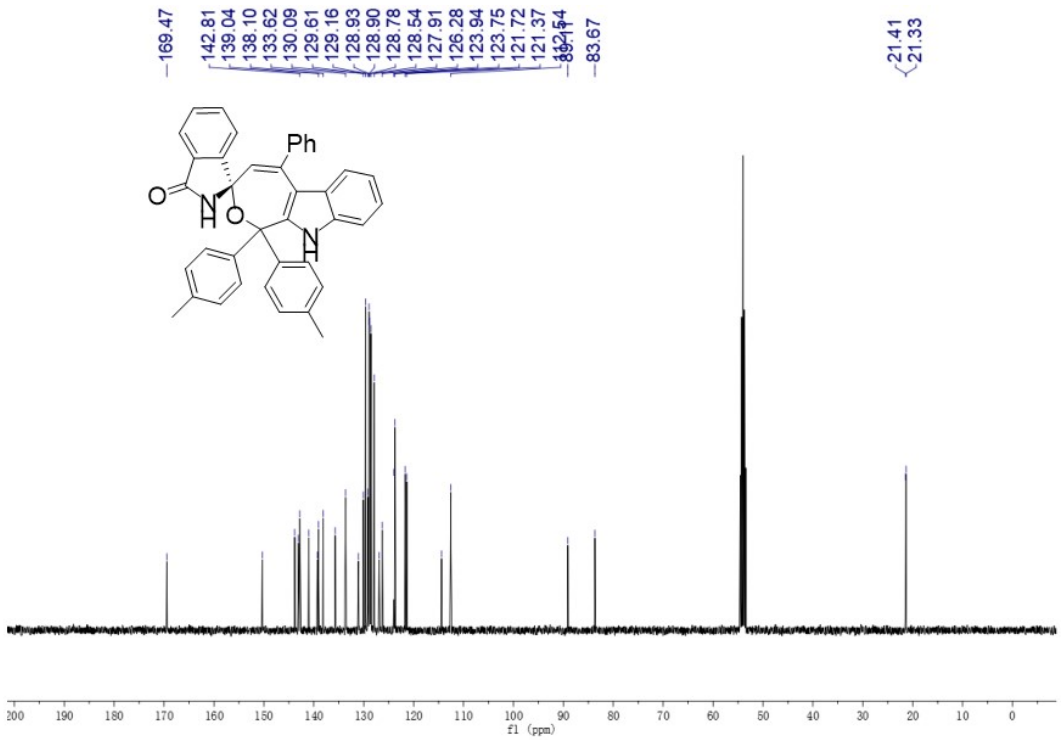
^{13}C NMR (101 MHz, CD_2Cl_2) of **3x**



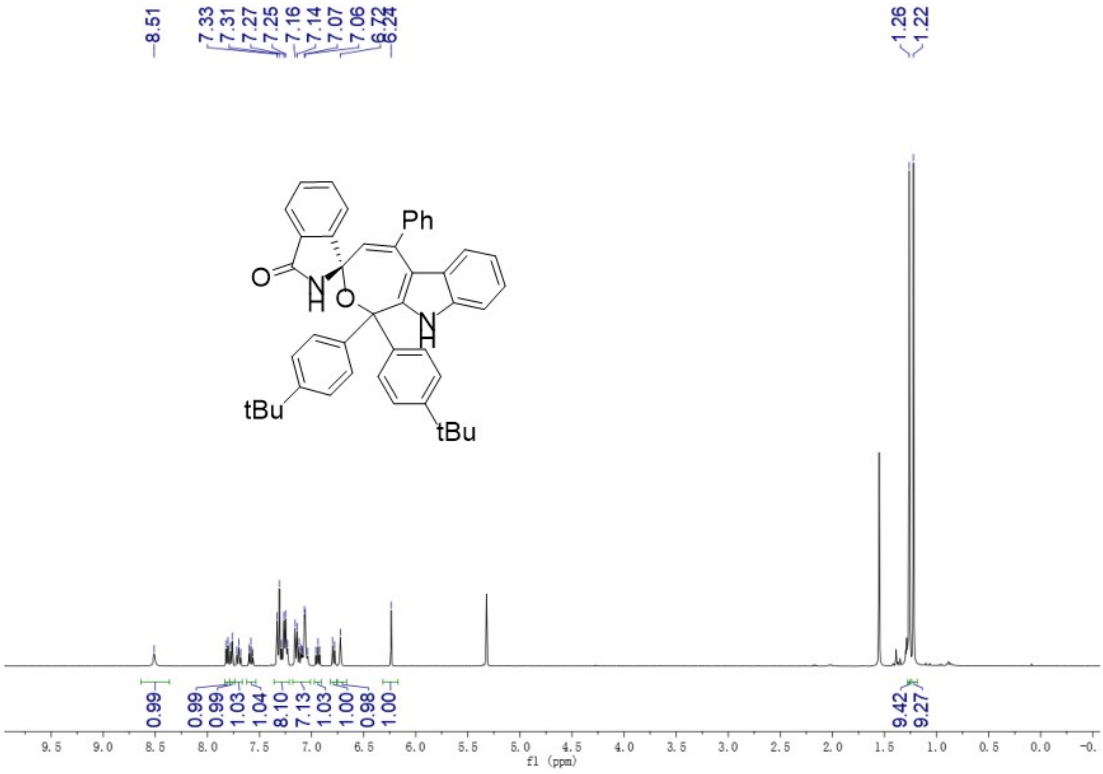
^{1}H NMR (400 MHz, CD_2Cl_2) of **3y**



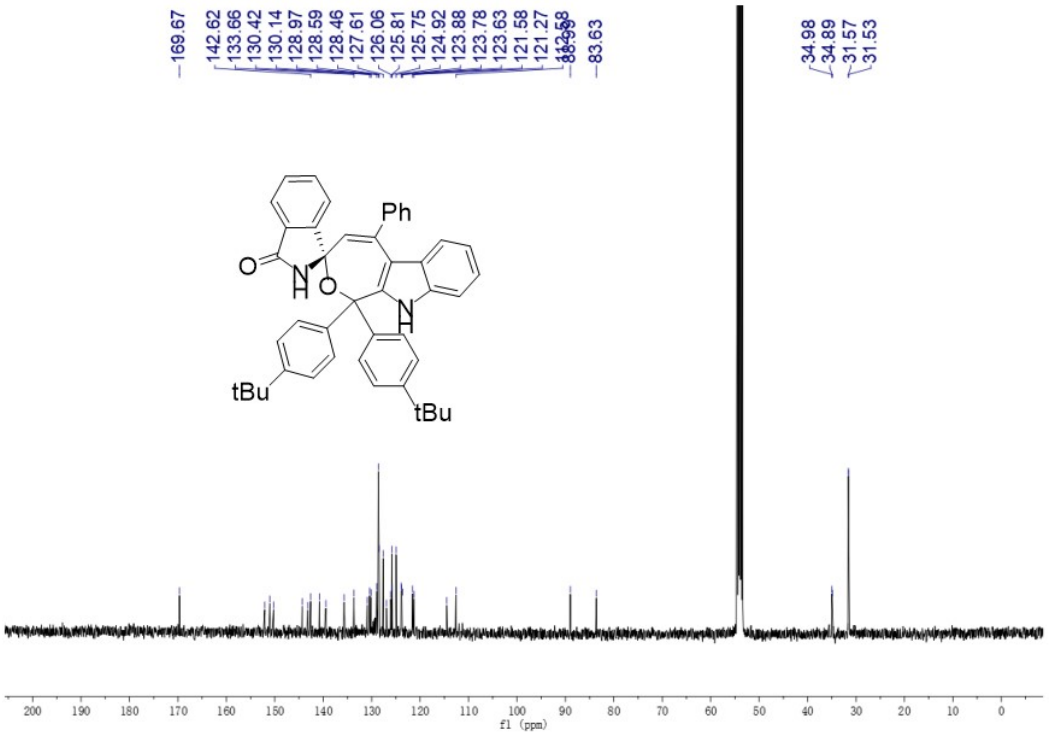
^{13}C NMR (101 MHz, CD_2Cl_2) of **3y**



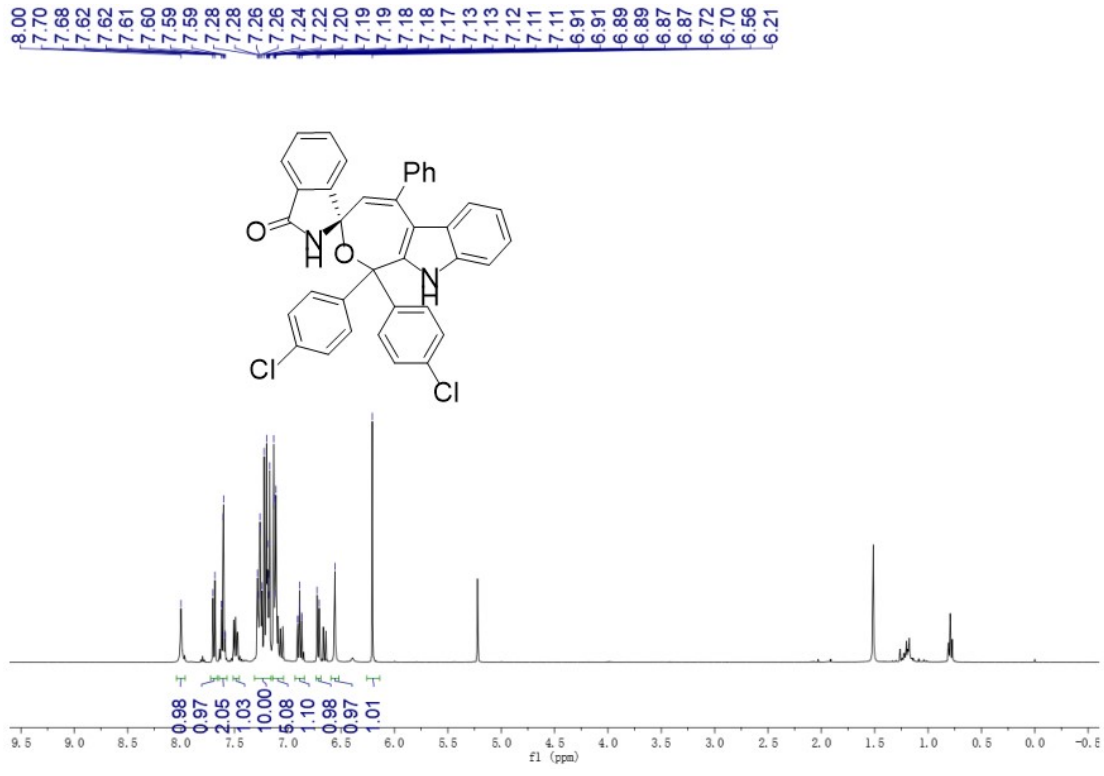
^{1}H NMR (400 MHz, CD_2Cl_2) of **3z**



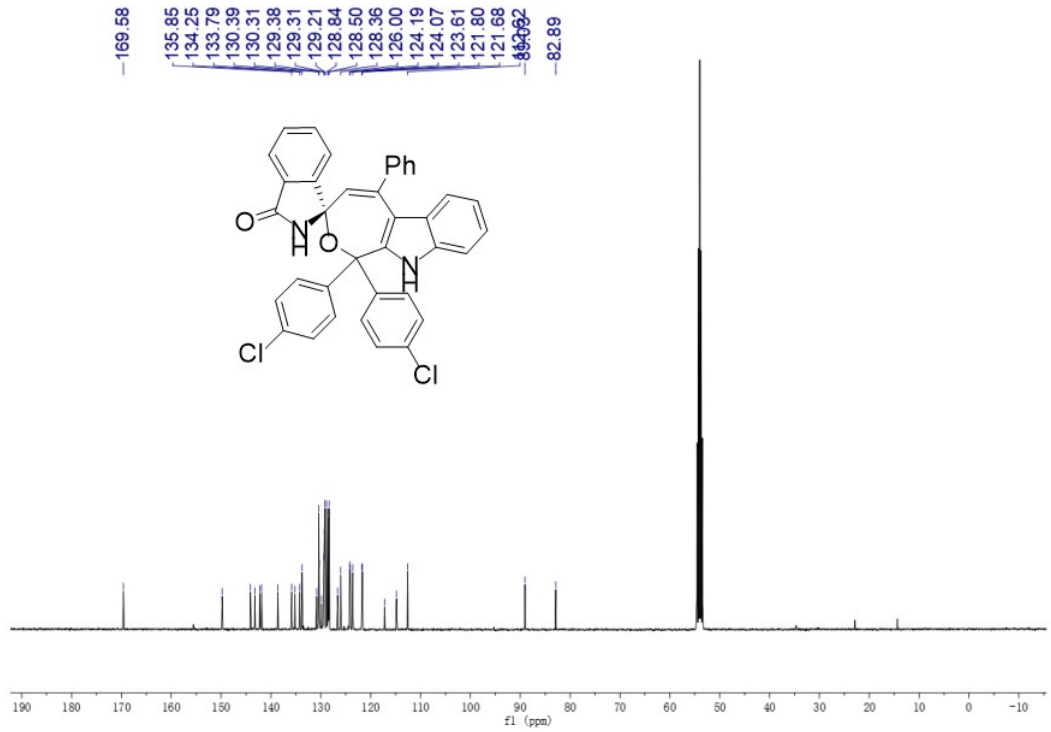
^{13}C NMR (101 MHz, CD_2Cl_2) of **3z**



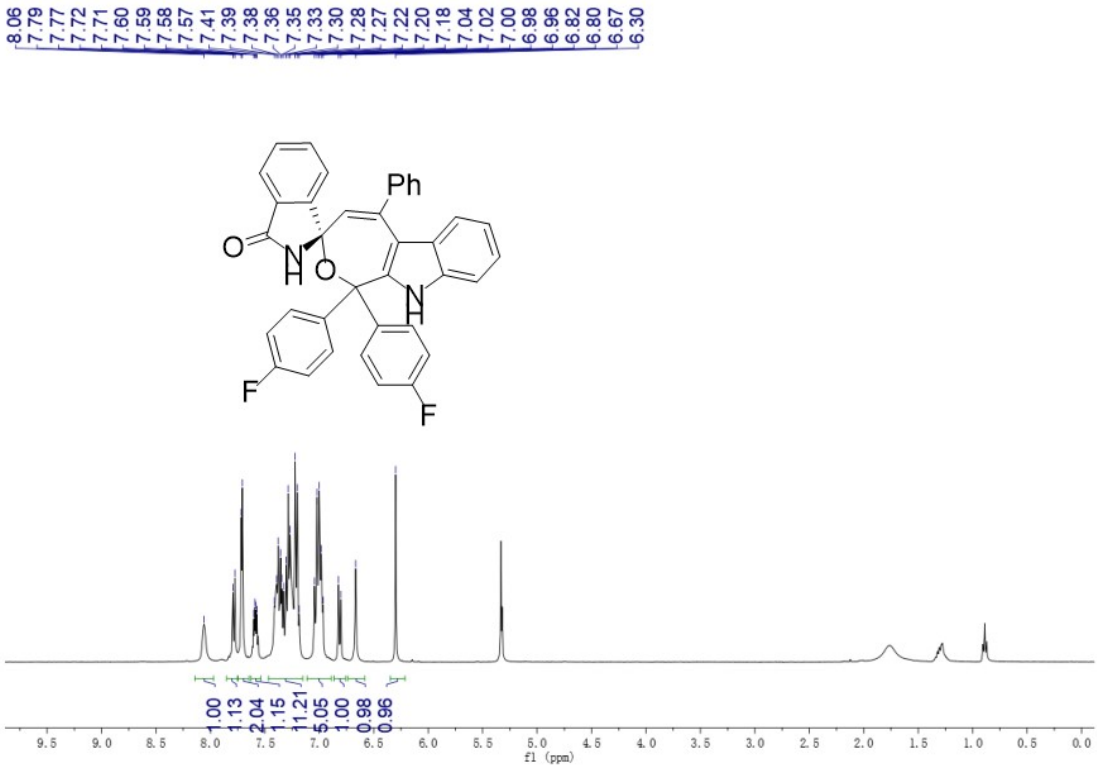
^{1}H NMR (400 MHz, CD_2Cl_2) of **3aa**



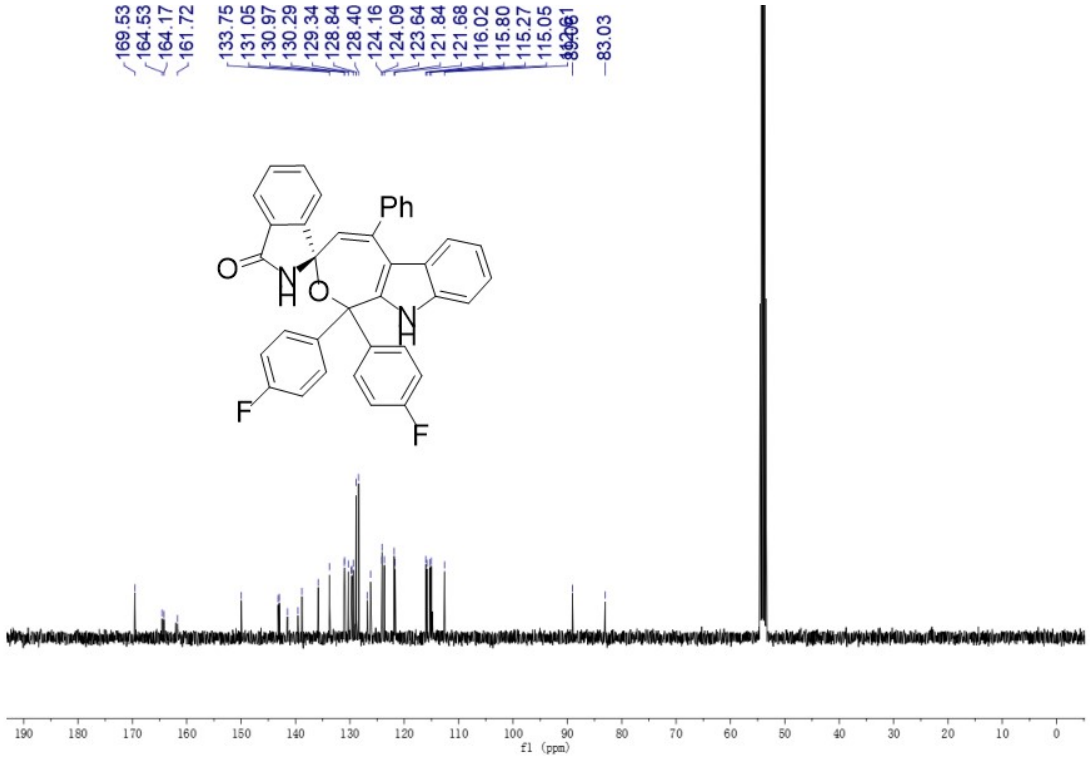
^{13}C NMR (101 MHz, CD_2Cl_2) of **3aa**



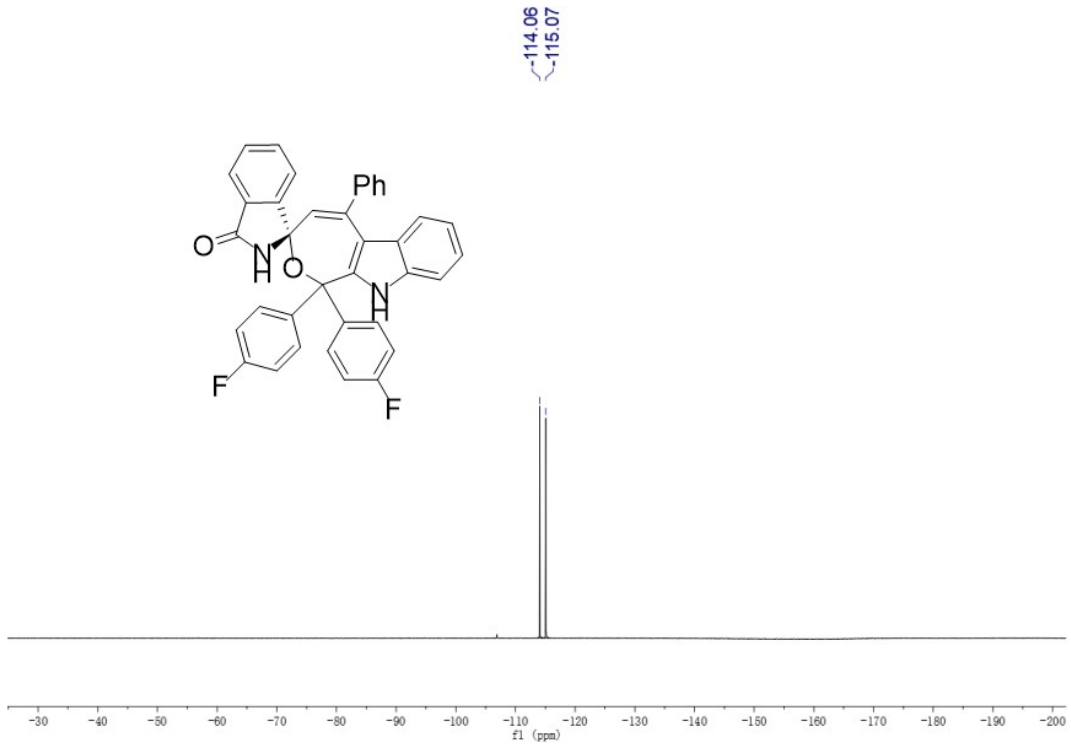
^{1}H NMR (400 MHz, CD_2Cl_2) of **3ab**



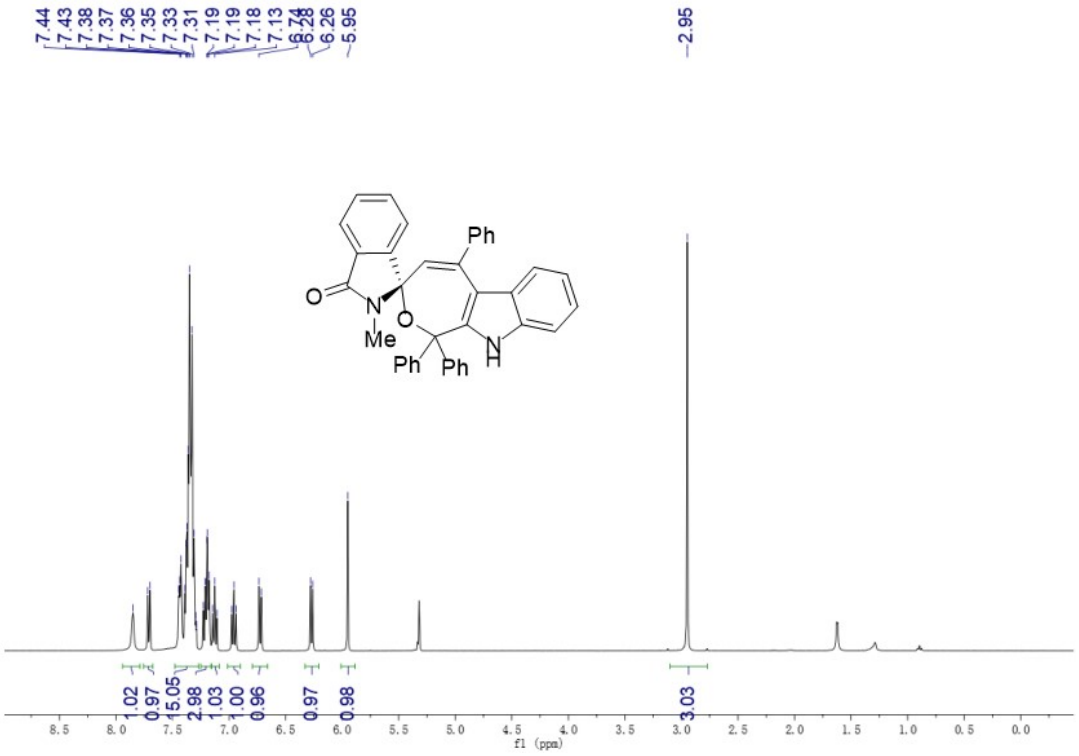
^{13}C NMR (101 MHz, CD_2Cl_2) of **3ab**



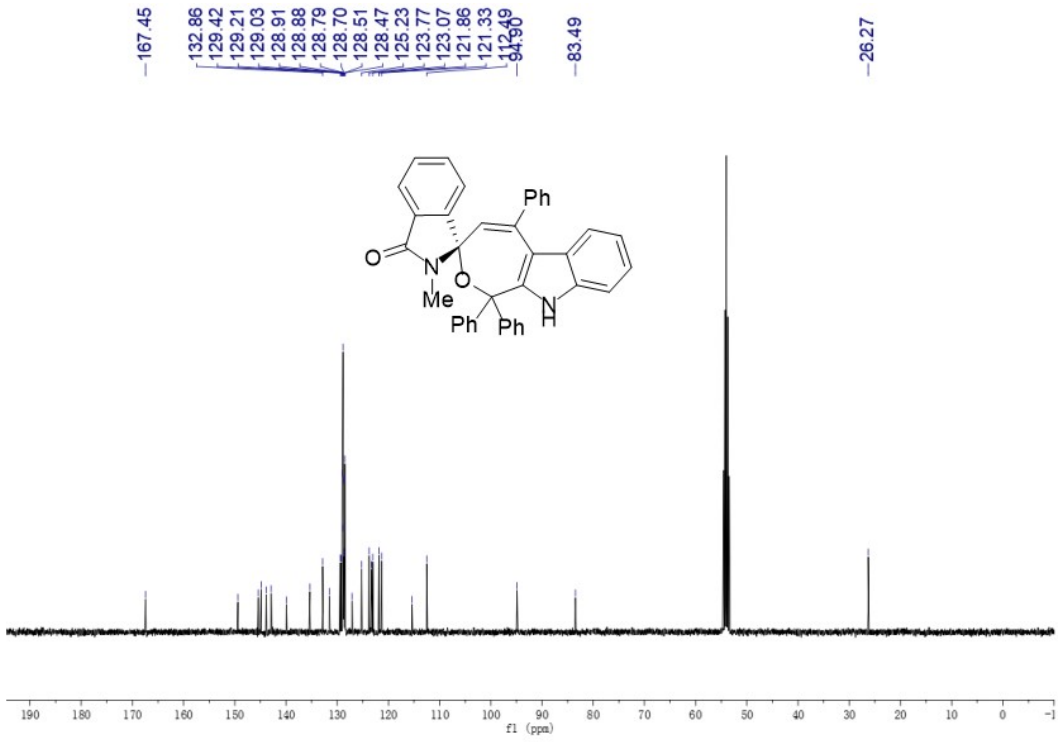
^{19}F NMR (376MHz, CD_2Cl_2) of **3ab**



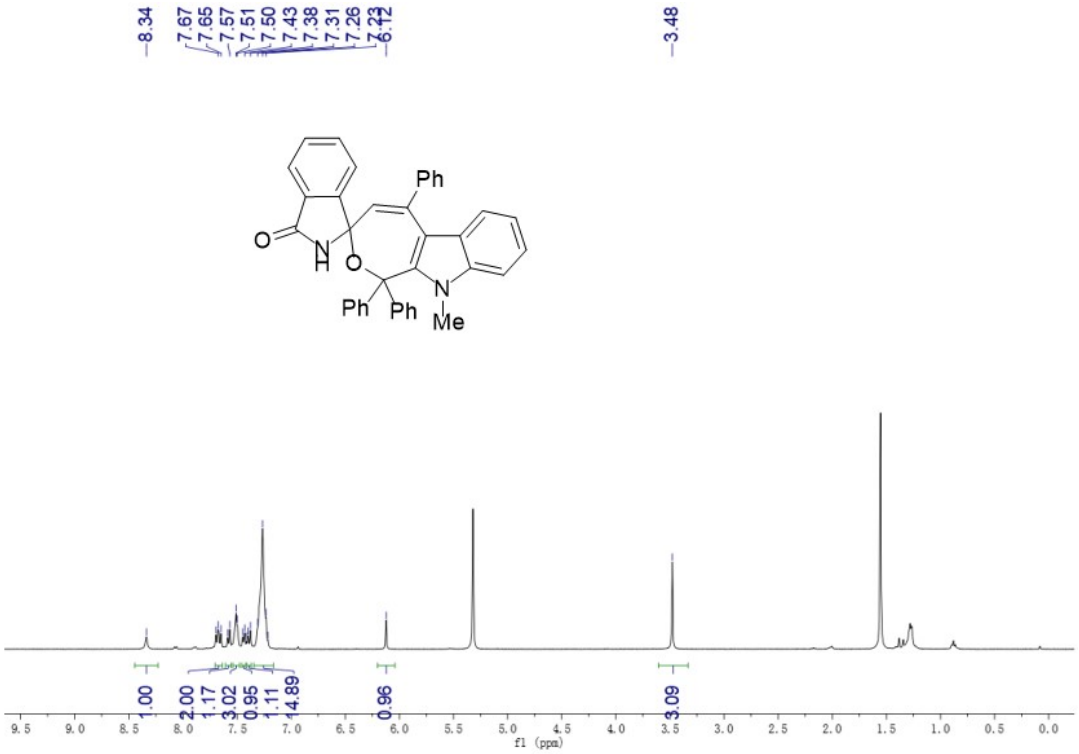
^{1}H NMR (400 MHz, CD_2Cl_2) of **5**



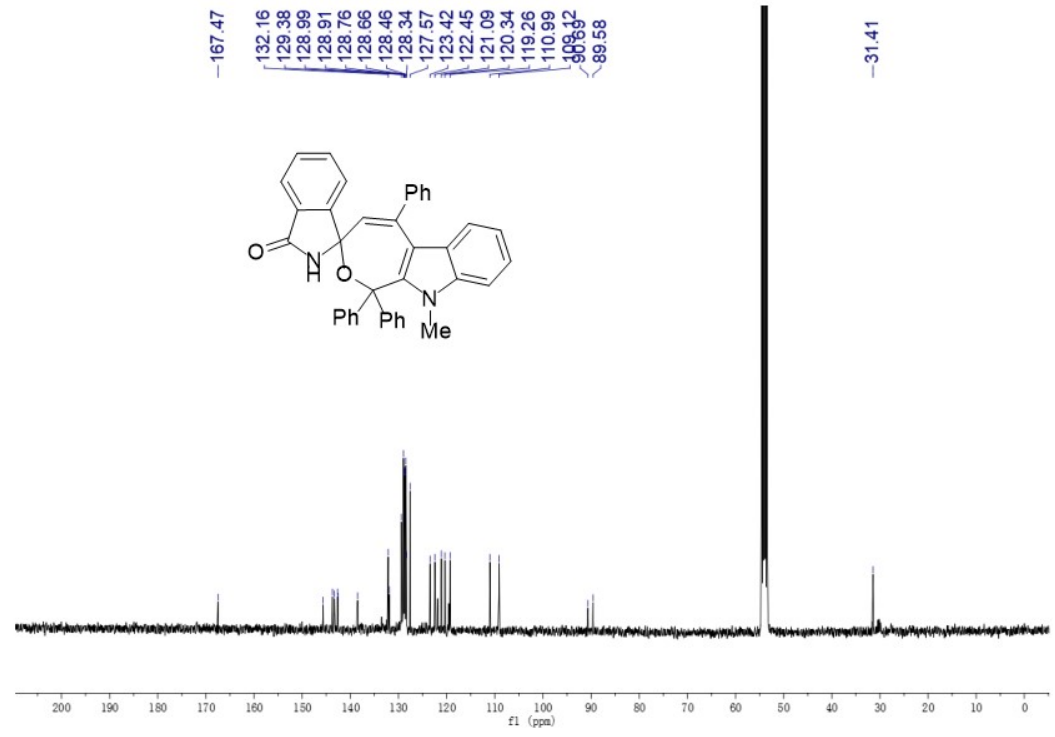
^{13}C NMR (400 MHz, CD_2Cl_2) of **5**



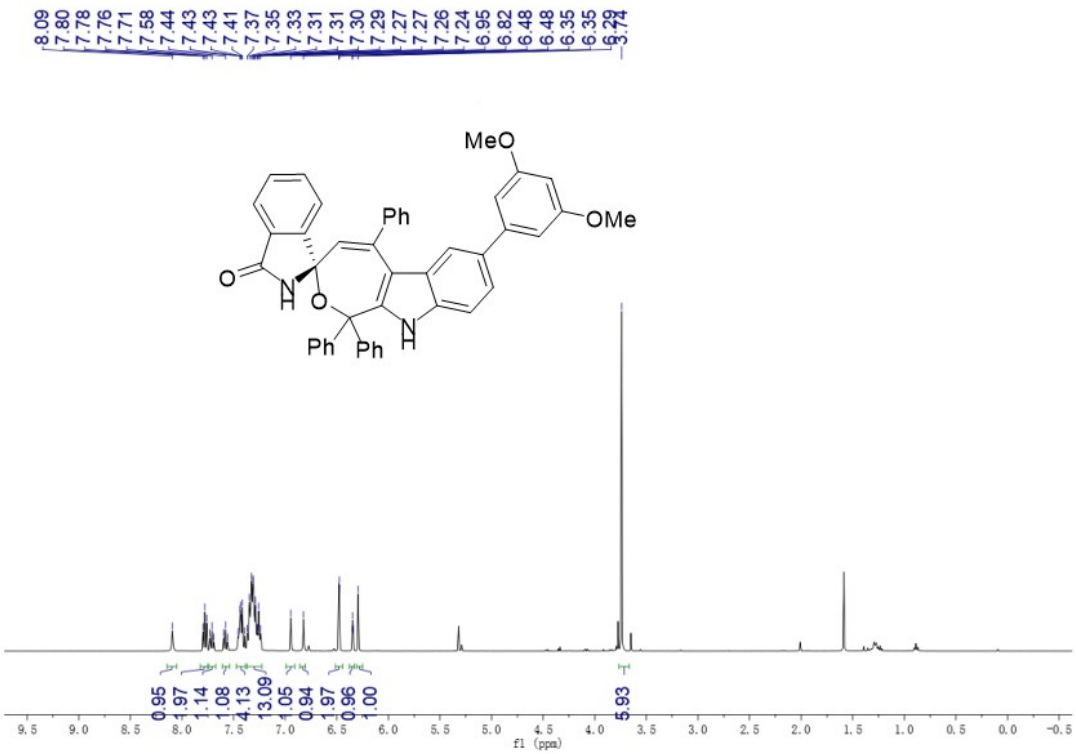
^{1}H NMR (400 MHz, CD_2Cl_2) of **7**



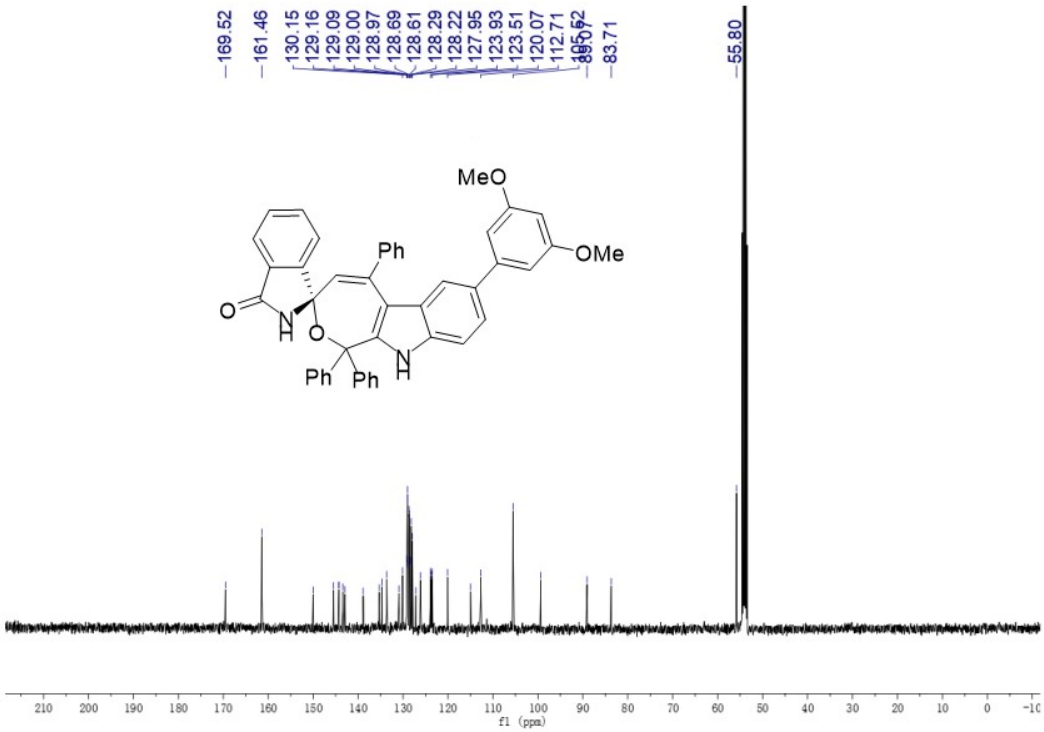
^{13}C NMR (400 MHz, CD_2Cl_2) of **7**



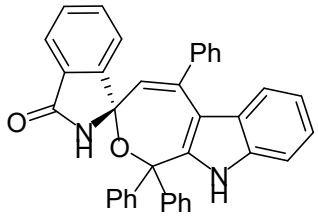
^{1}H NMR (400 MHz, CD_2Cl_2) of **8**



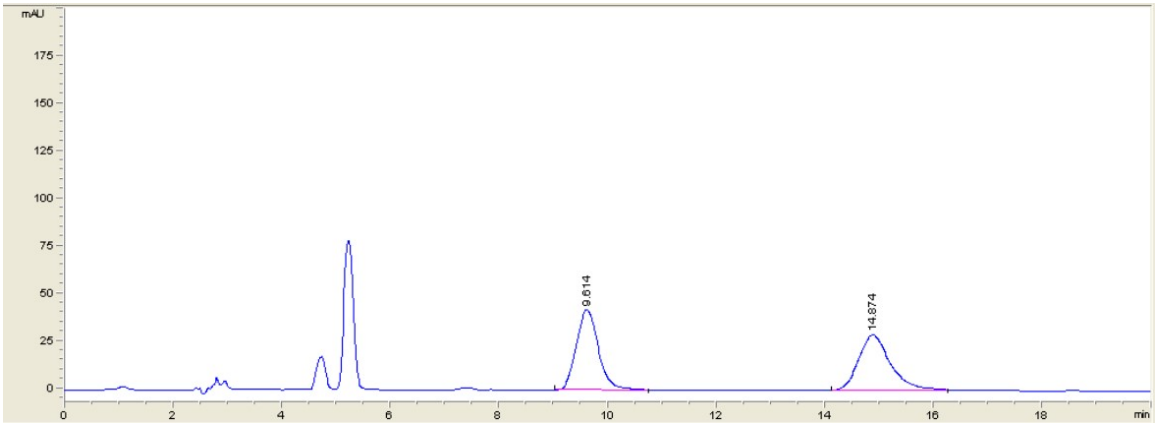
^{13}C NMR (400 MHz, CD_2Cl_2) of **8**



12. HPLC data



(S)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3a)



#	Time	Area	Height	Width	Area%
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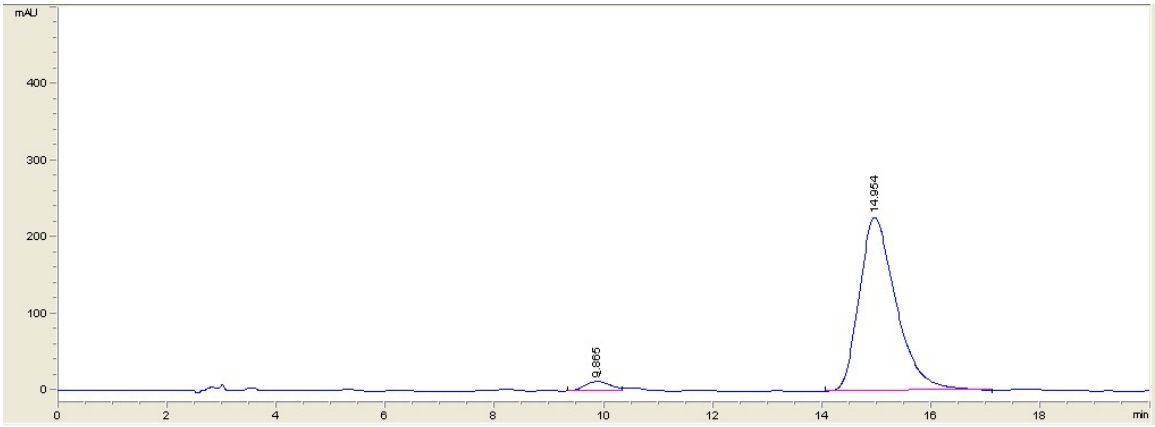
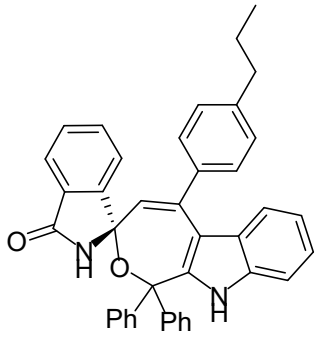
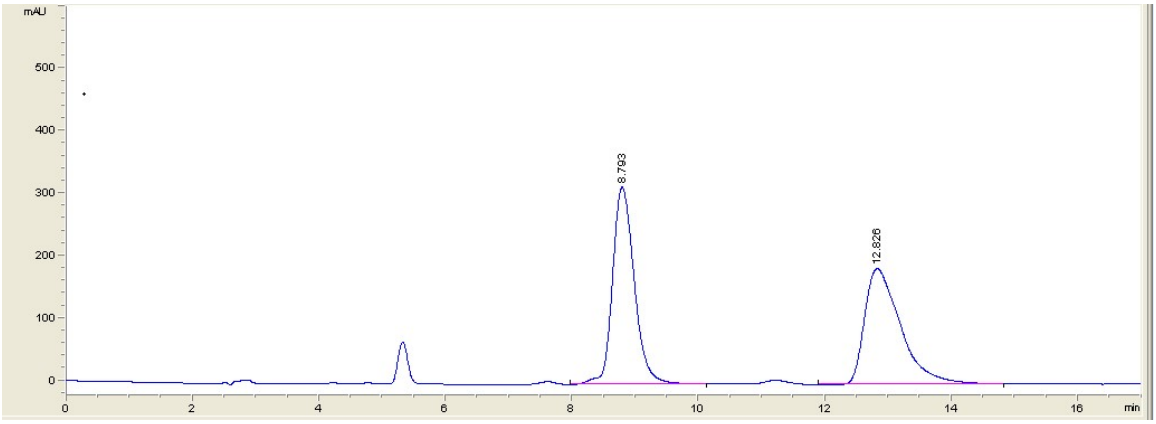
2	14.874	1190.1	29.2	0.616	49.670



#	Time	Area	Height	Width	Area%
1	9.865	431.5	12.7	0.5663	3.930
2	14.954	10548	225.8	0.7051	96.070



(S)-1',1'-diphenyl-5'-(4-propylphenyl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3b)



#	Time	Area	Height	Width	Area%
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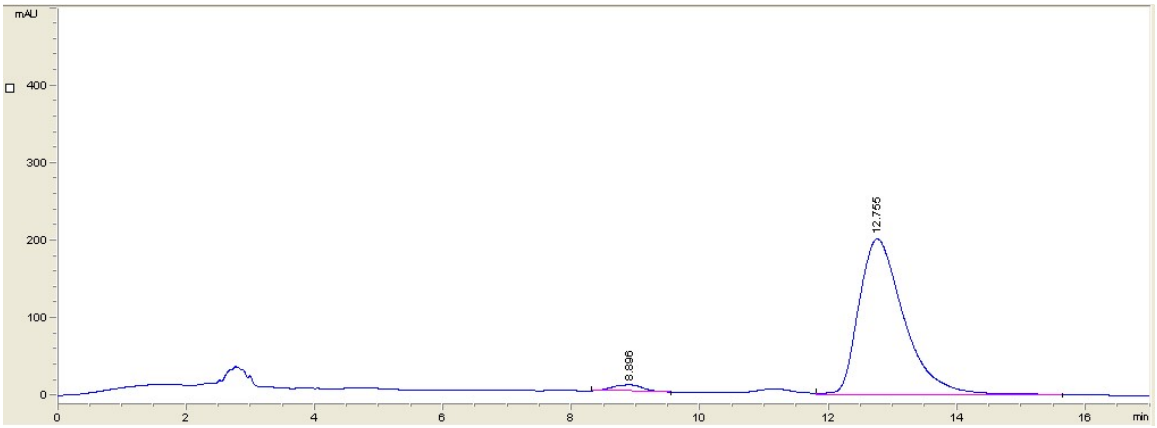
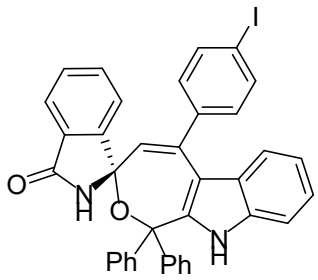
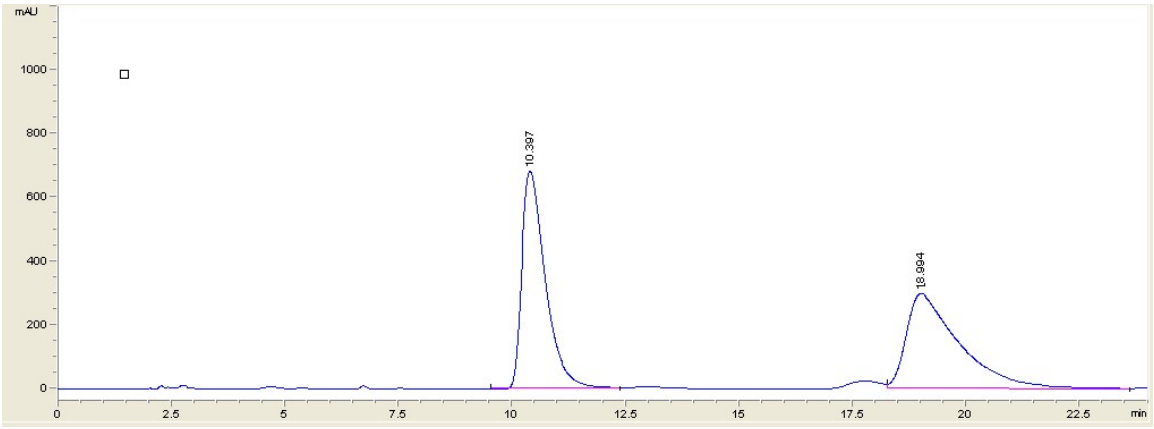
2	12.826	7388.4	185.6	0.5808	49.116



#	Time	Area	Height	Width	Area%
1	8.896	315.9	8.9	0.59	3.111
2	12.755	9837.8	201.1	0.8152	96.889



(S)-5'-(4-iodophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3c)



#	Time	Area	Height	Width	Area%
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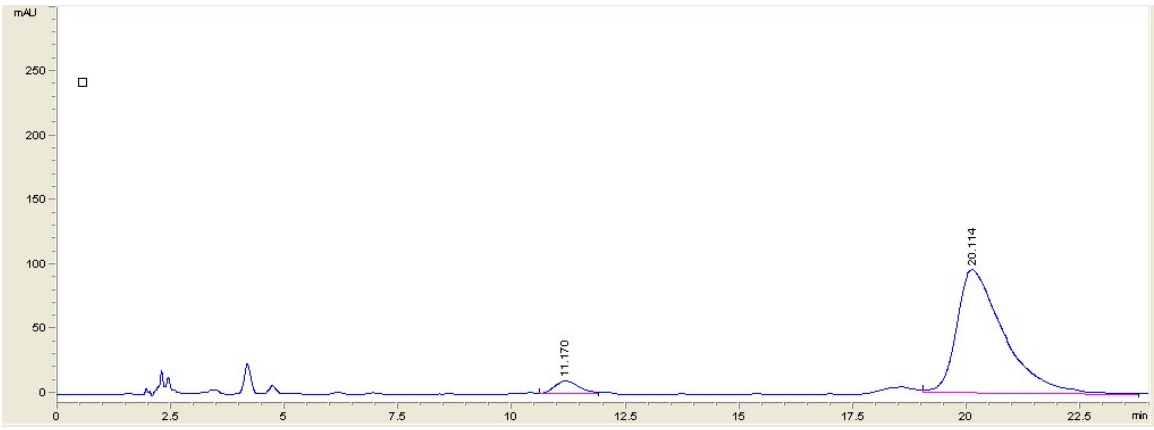
2	18.994	24380.8	296.8	1.3689	49.524



#	Time	Area	Height	Width	Area%
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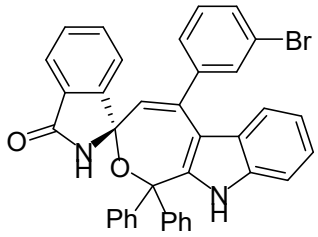
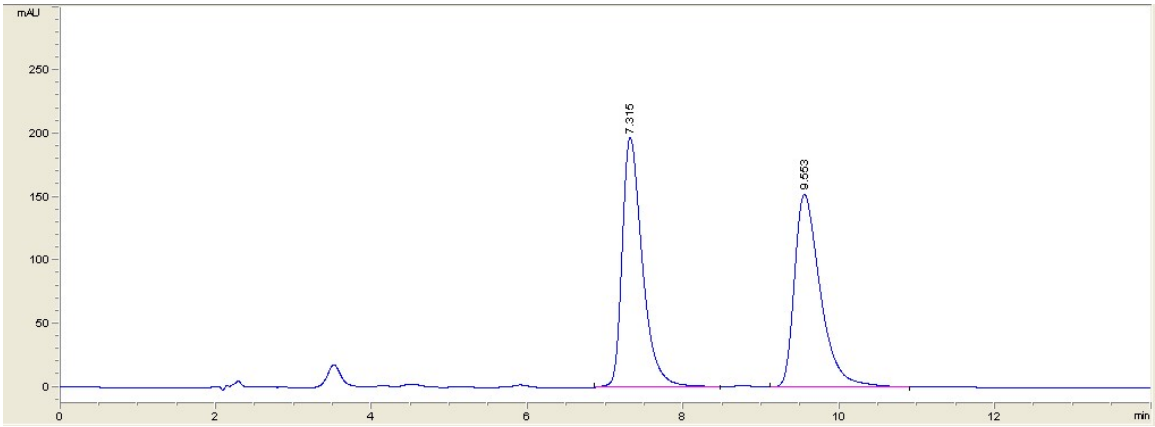


(S)-5'-(3-bromophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3d)



#	Time	Area	Height	Width	Area%
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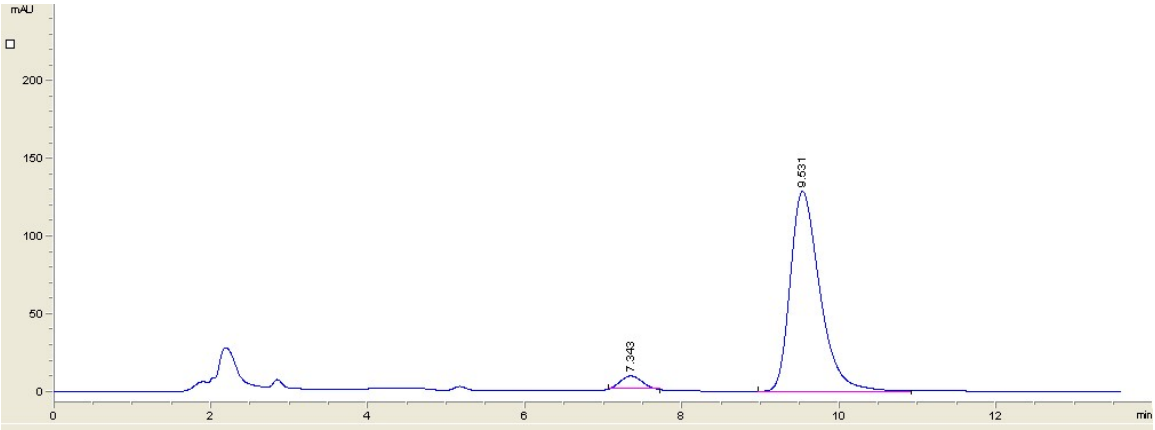
2	9.553	3504.3	152	0.3534	49.496



#	Time	Area	Height	Width	Area%
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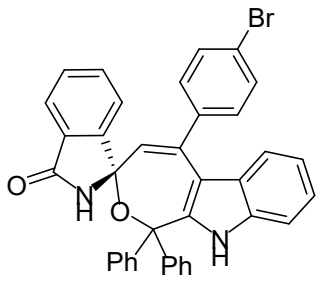
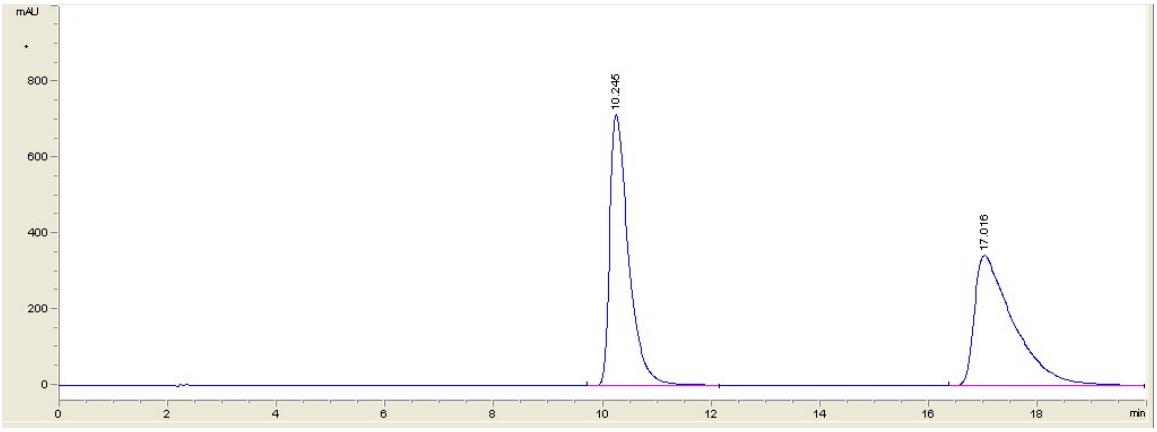
2	9.531	3410.5	129	0.4407	95.410



(S)-5'-(4-bromophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3e)



#	Time	Area	Height	Width	Area%
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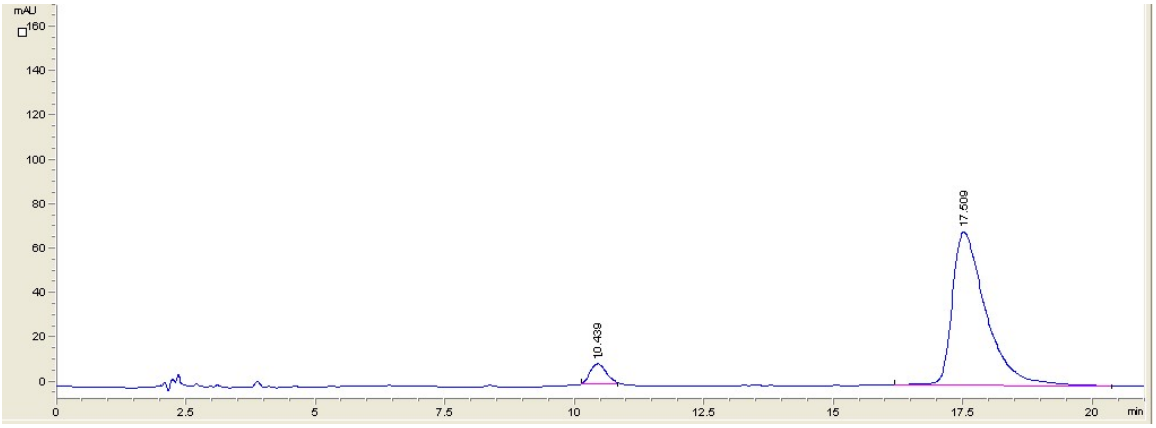
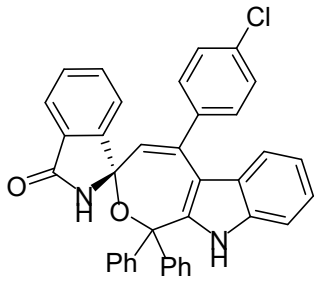
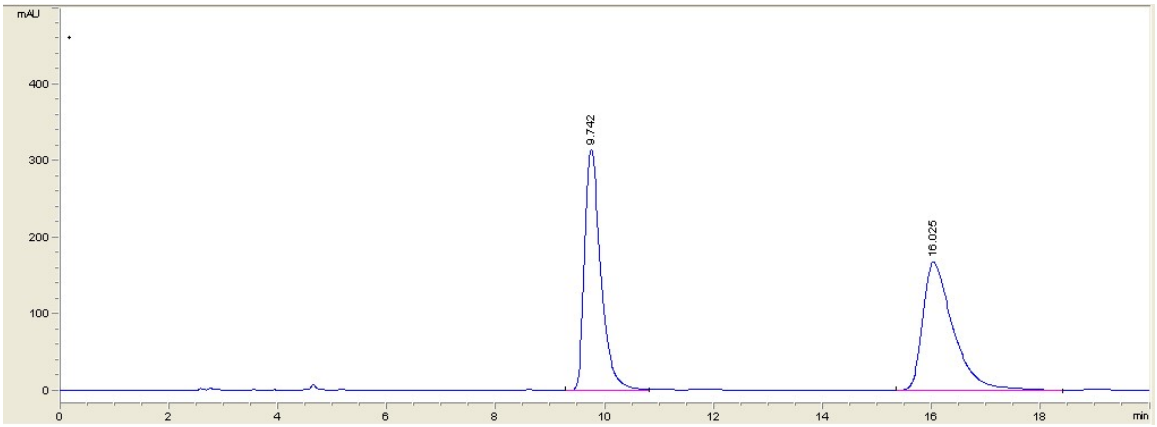


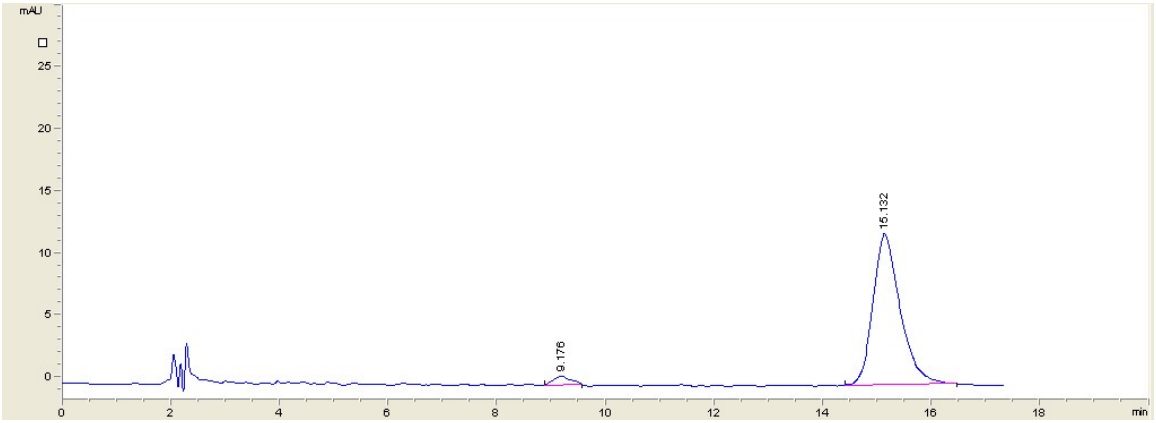
#	Time	Area	Height	Width	Area%
1	10.439	196.4	9.1	0.3598	5.871
2	17.509	3149.3	69.2	0.7585	94.129



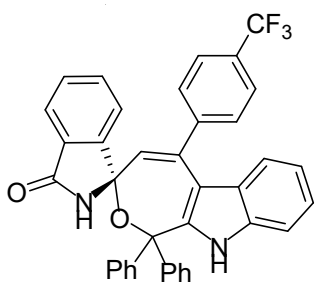
(S)-5'-(4-chlorophenyl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3f)



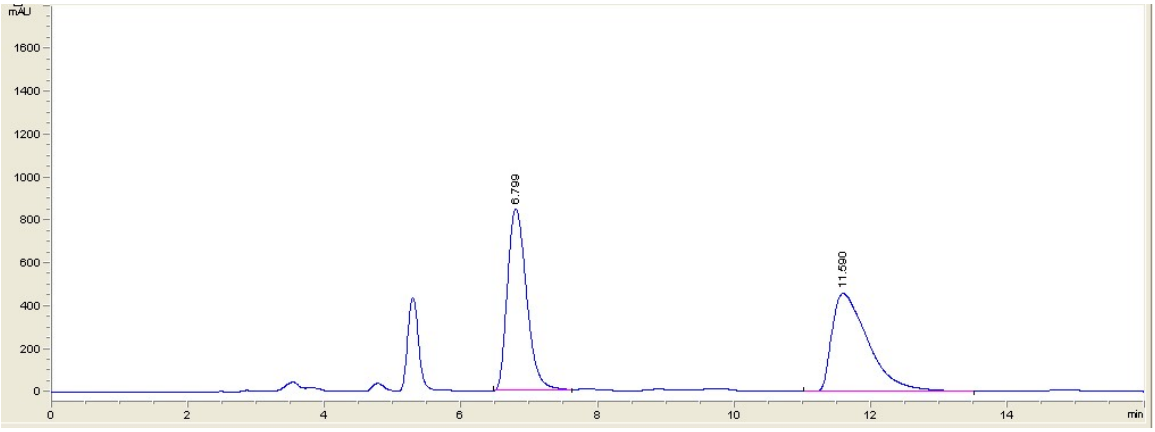
#	Time	Area	Height	Width	Area%
1	9.742	6509.9	314.7	0.3141	50.001
2	16.025	6509.7	167.7	0.5751	49.999



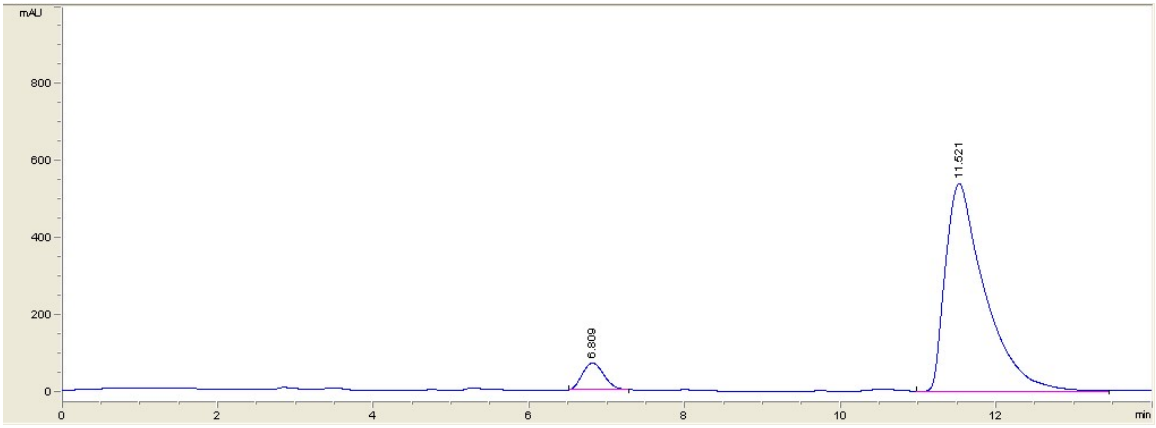
#	Time	Area	Height	Width	Area%
1	9.176	17.2	7.4E-1	0.3847	3.895
2	15.132	423.4	12.2	0.5787	96.105



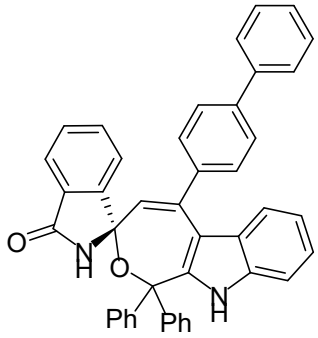
(S)-1',1'-diphenyl-5'-(4-(trifluoromethyl)phenyl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3g)



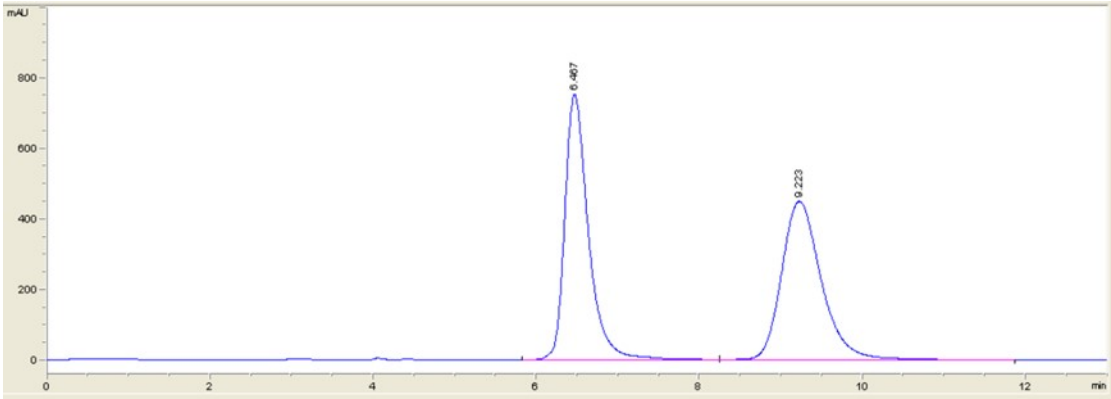
#	Time	Area	Height	Width	Area%
1	6.799	16659.8	847.5	0.3276	49.955
2	11.59	16689.9	457.6	0.5828	50.045



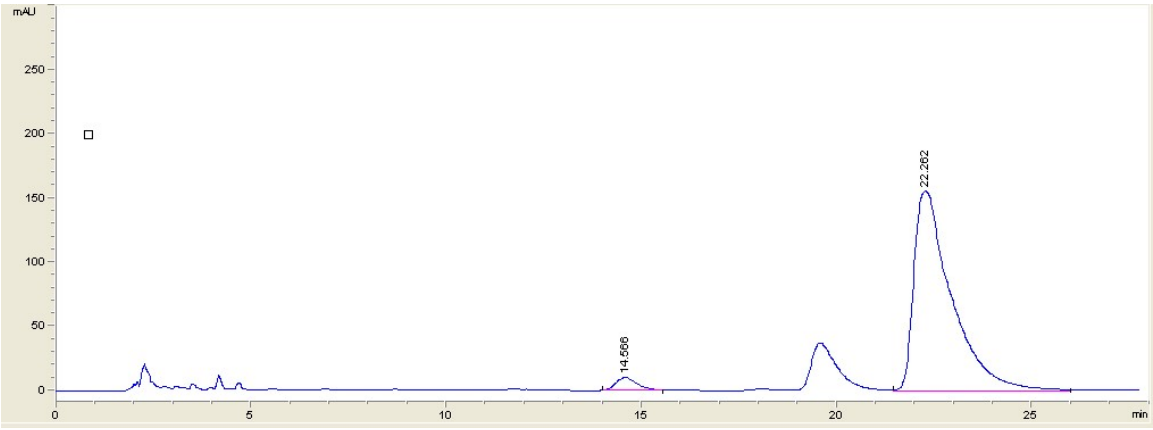
#	Time	Area	Height	Width	Area%
1	6.809	1350.6	69.8	0.3226	6.503
2	11.521	19417.6	541.1	0.5981	93.497



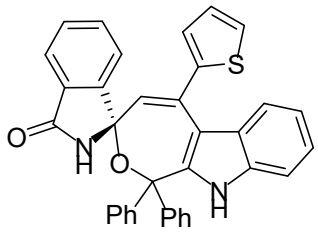
(S)-5'-([1,1'-biphenyl]-4-yl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3h)



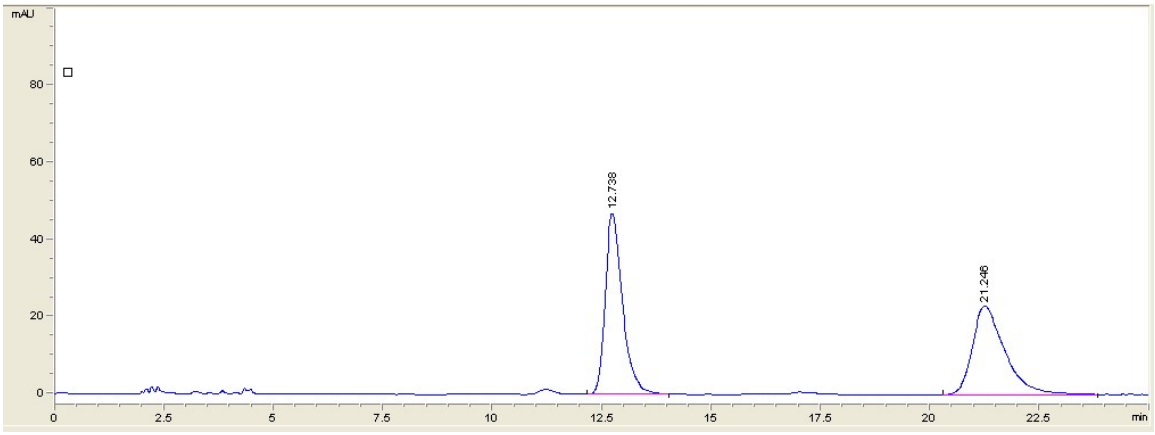
#	Time	Area	Height	Width	Area%
1	6.467	15325.3	753.6	0.3071	49.790
2	9.223	15454.6	450	0.5244	50.210



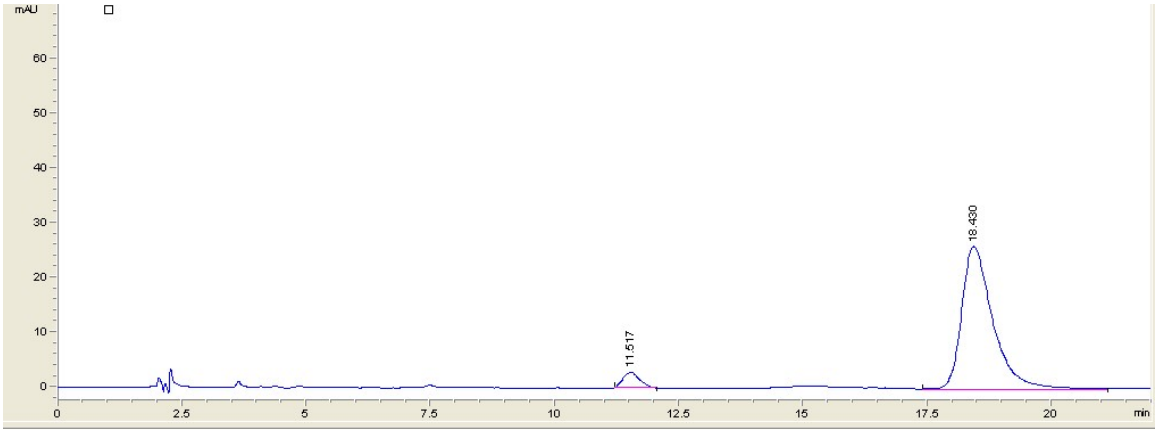
#	Time	Area	Height	Width	Area%
1	14.566	353.3	9.7	0.609	3.229
2	22.262	10589.1	156.2	1.1295	96.771



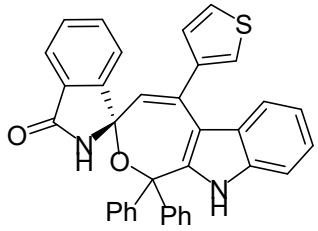
(S)-1',1'-diphenyl-5'-(thiophen-2-yl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3i)



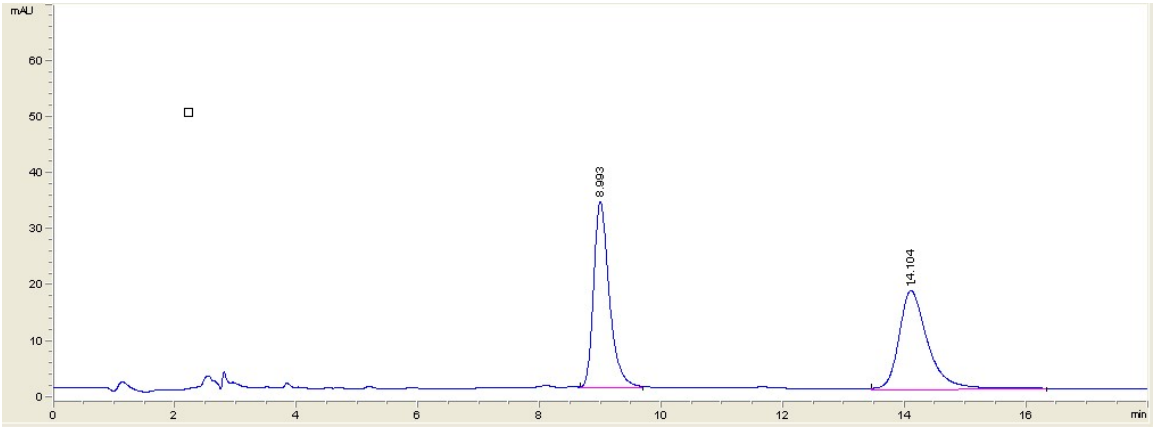
#	Time	Area	Height	Width	Area%
1	12.738	1285.8	46.9	0.4131	51.483
2	21.246	1211.7	23	0.877	48.517



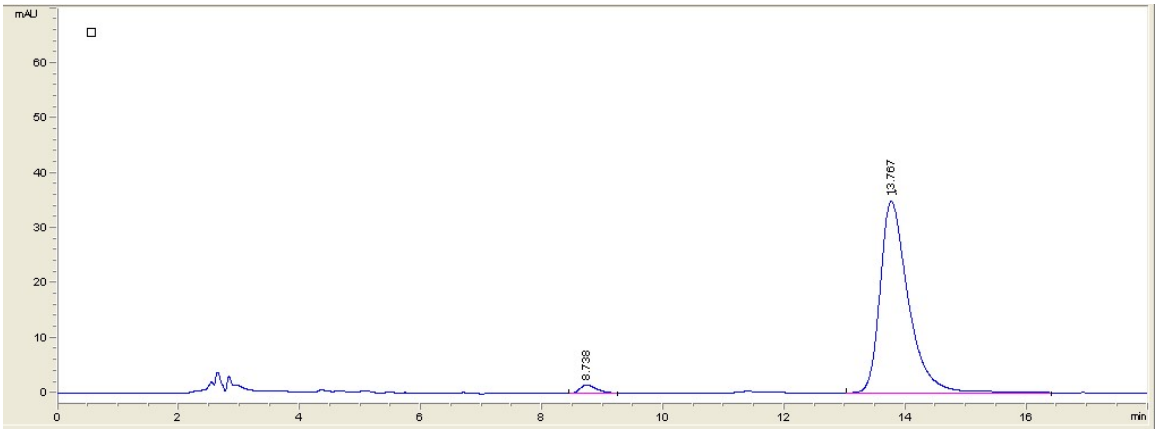
#	Time	Area	Height	Width	Area%
1	11.517	64.5	2.8	0.3812	5.209
2	18.43	1173.2	26.3	0.7439	94.791



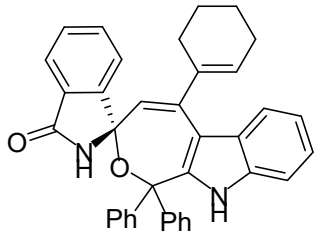
(S)-1',1'-diphenyl-5'-(thiophen-3-yl)-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3j)



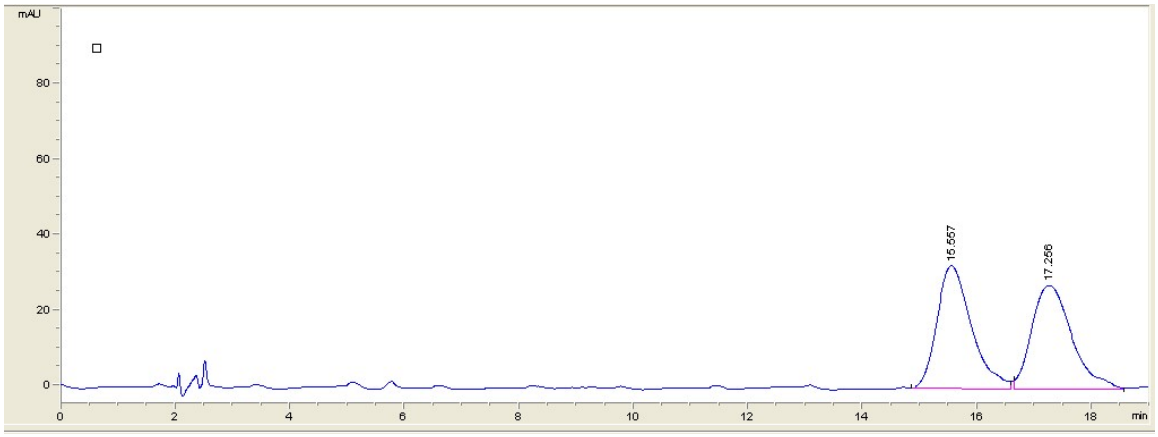
#	Time	Area	Height	Width	Area%
1	8.993	596.4	33.2	0.2706	49.654
2	14.104	604.7	17.7	0.5697	50.346



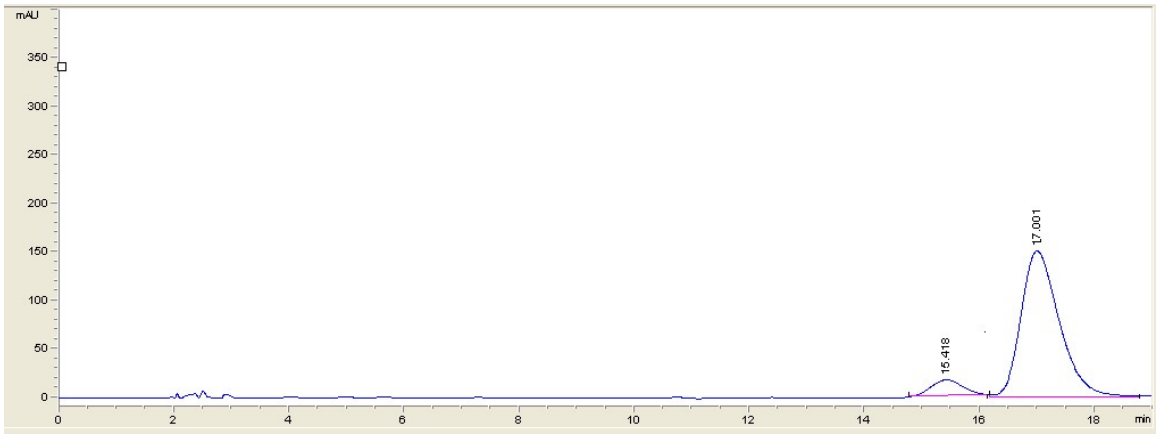
#	Time	Area	Height	Width	Area%
1	8.738	30.9	1.6	0.2915	2.584
2	13.767	1164.3	35	0.554	97.416



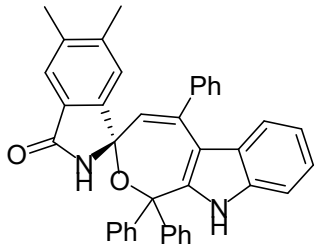
(S)-5'-(cyclohex-1-en-1-yl)-1',1'-diphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3k)



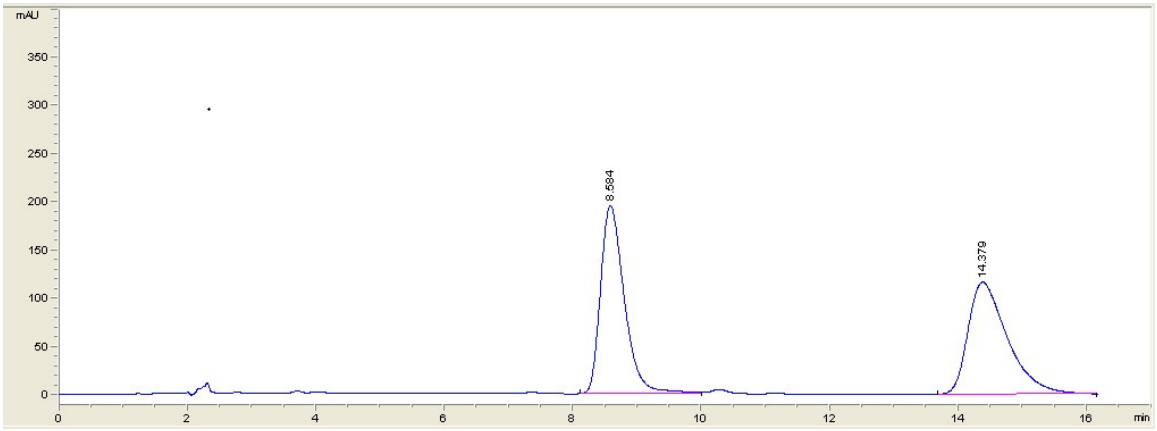
#	Time	Area	Height	Width	Area%
1	15.557	1377.2	32.6	0.7032	50.939
2	17.256	1326.4	27.5	0.8031	49.061



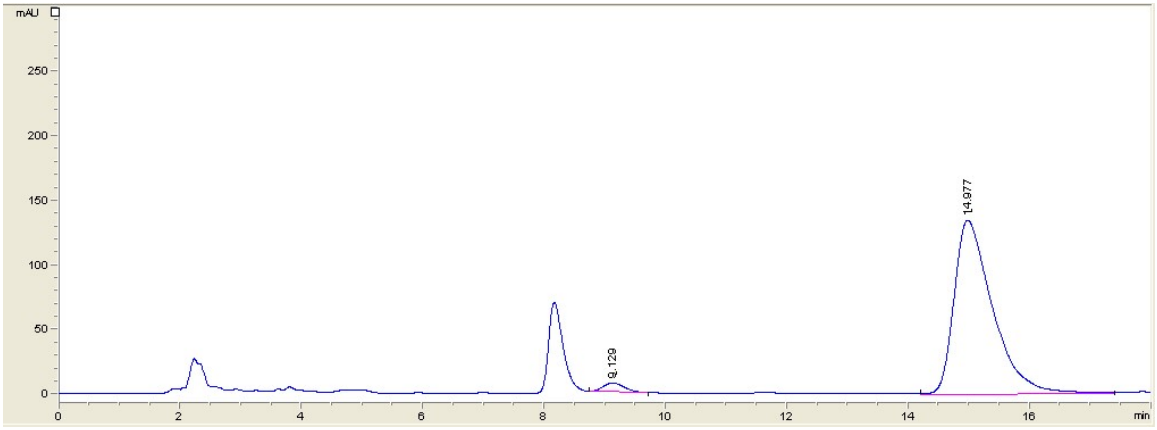
#	Time	Area	Height	Width	Area%
1	15.418	656.6	16.8	0.6513	8.644
2	17.001	6939.7	150.8	0.7667	91.356



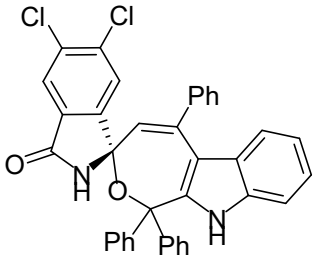
(S)-5,6-dimethyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3l)



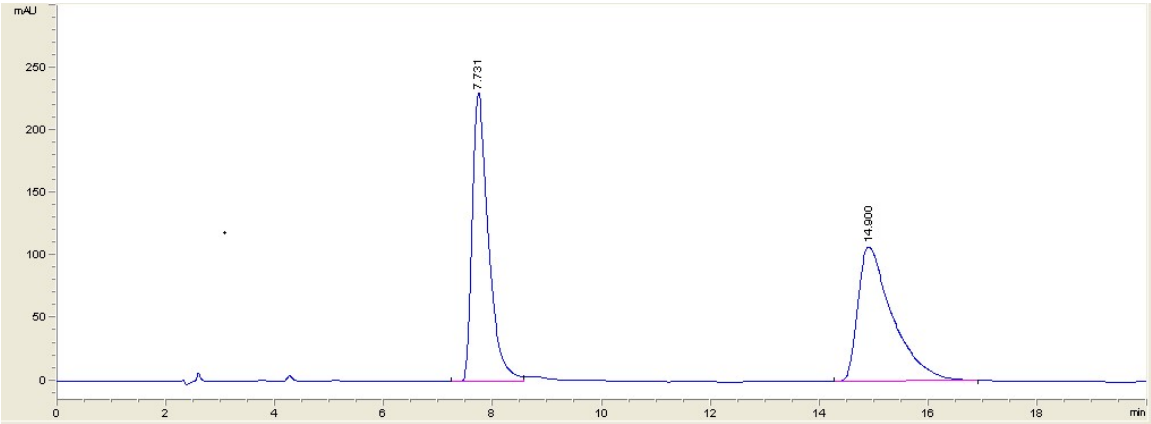
#	Time	Area	Height	Width	Area%
1	8.584	5046.7	194.9	0.3981	50.447
2	14.379	4957.2	116.2	0.6404	49.553



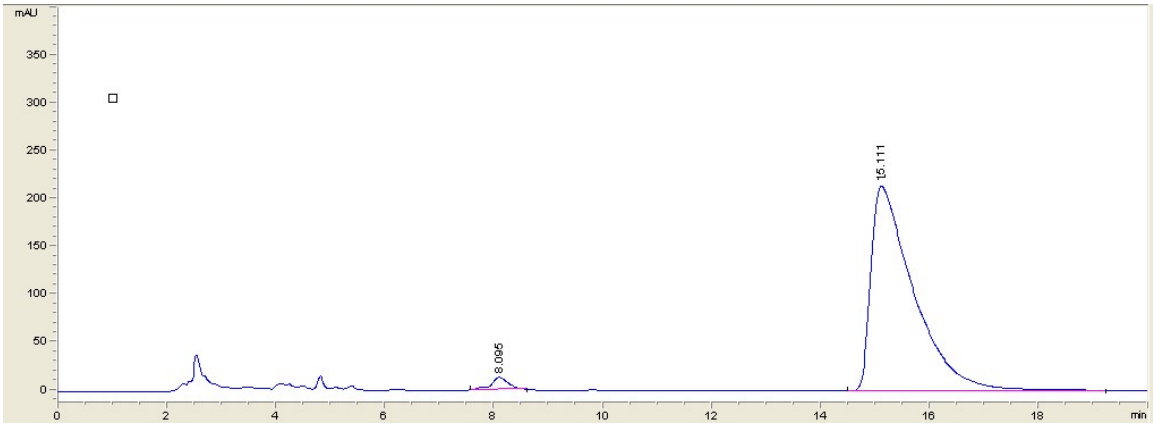
#	Time	Area	Height	Width	Area%
1	9.129	192	7.3	0.4408	3.103
2	14.977	5997	135	0.7403	96.897



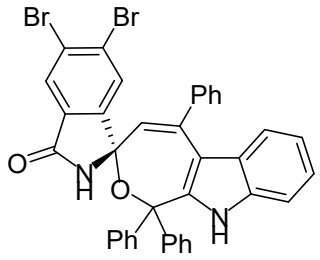
(S)-5,6-dichloro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3m)



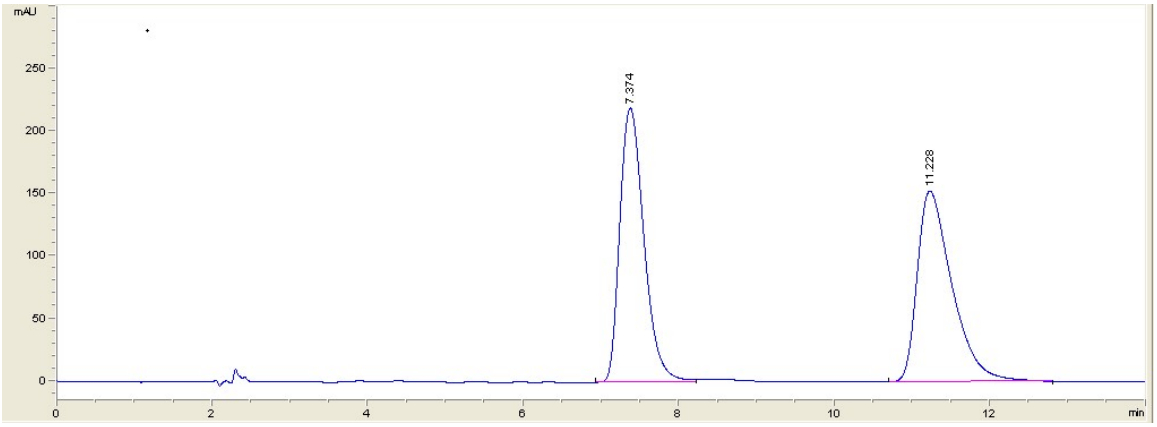
#	Time	Area	Height	Width	Area%
1	7.731	4763.6	230.1	0.3144	49.973
2	14.9	4768.7	107.4	0.6375	50.027



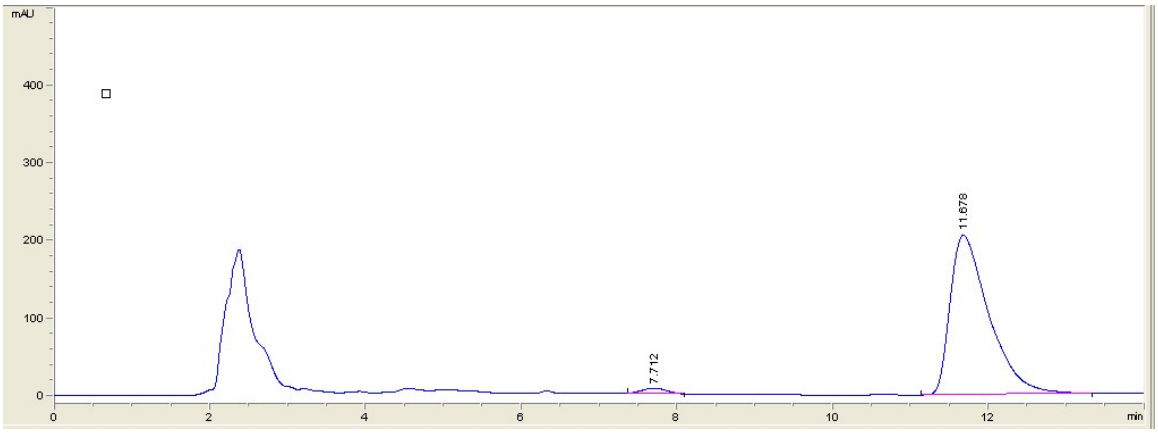
#	Time	Area	Height	Width	Area%
1	8.095	290.8	12.8	0.378	2.426
2	15.111	11697.4	214.8	0.9077	97.574



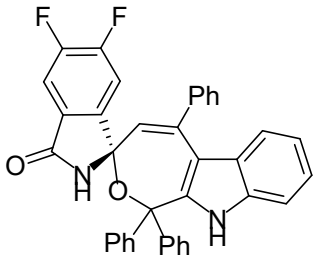
(S)-5,6-dibromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3n)



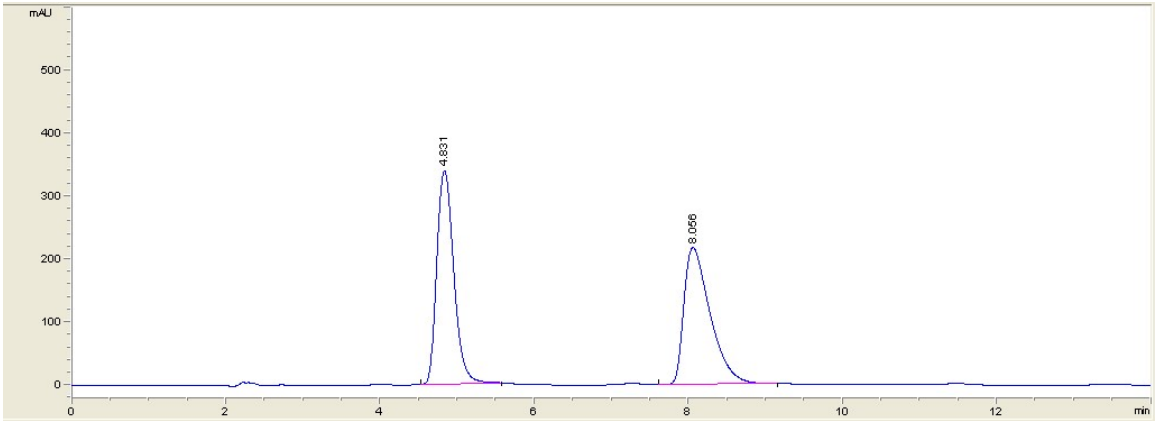
#	Time	Area	Height	Width	Area%
1	7.374	4758	219.3	0.3405	50.083
2	11.228	4742.2	152.5	0.4706	49.917



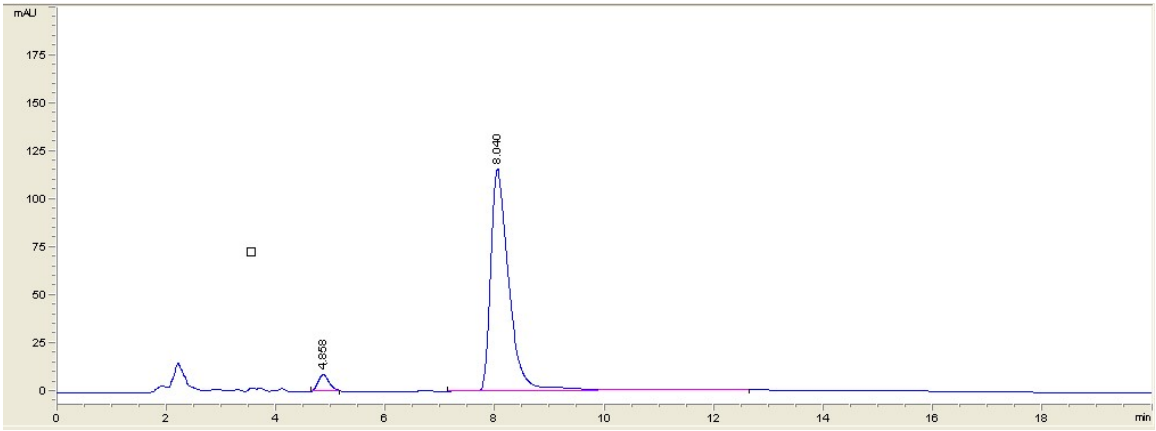
#	Time	Area	Height	Width	Area%
1	7.712	173.6	7.6	0.3799	2.376
2	11.678	7131.3	205.4	0.5302	97.624



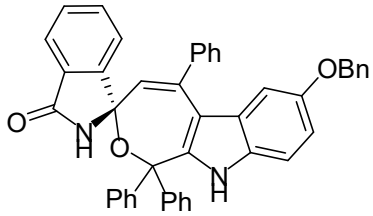
(S)-5,6-difluoro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3o)



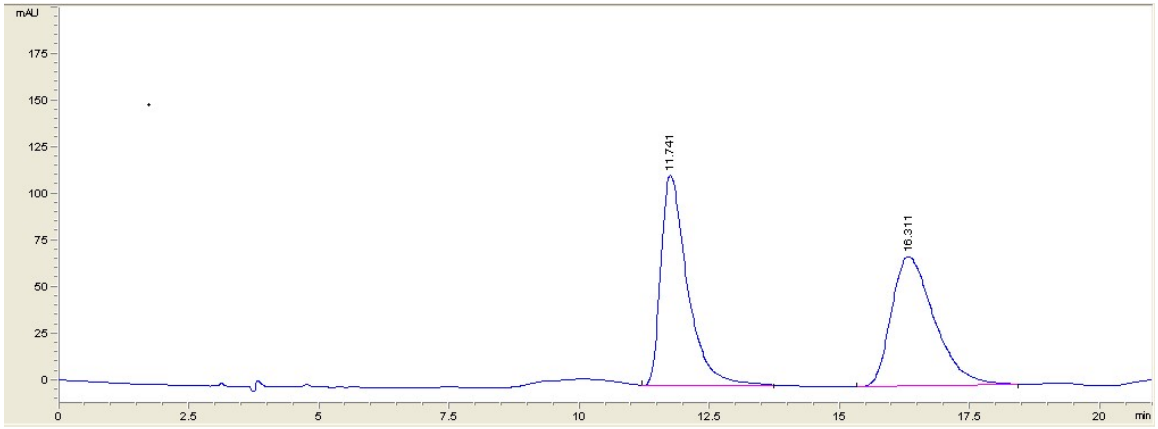
#	Time	Area	Height	Width	Area%
1	4.831	5249.4	339.6	0.2576	50.400
2	8.056	5166.2	217.4	0.3588	49.600



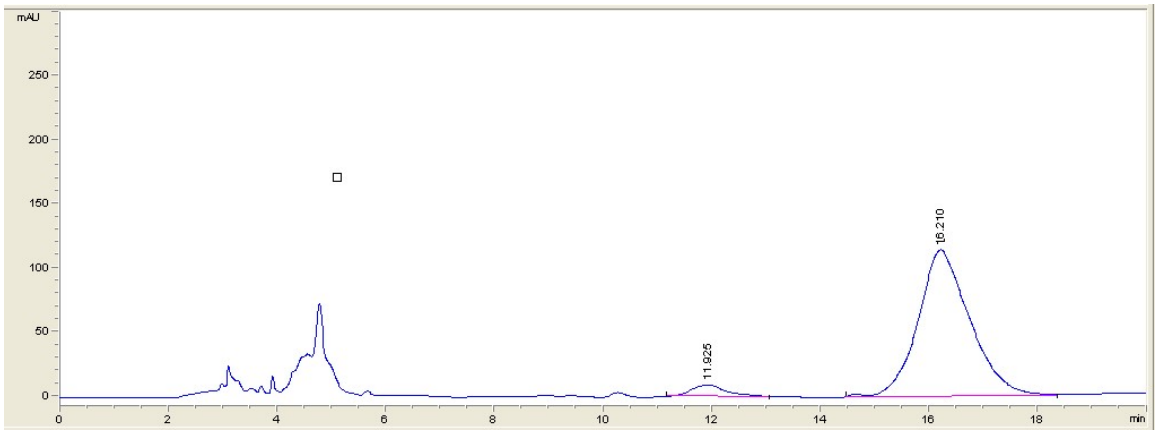
#	Time	Area	Height	Width	Area%
1	4.858	121.2	8.8	0.2296	4.164
2	8.04	2789.4	115.9	0.4013	95.836



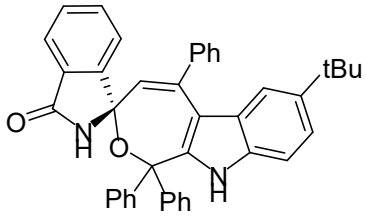
(S)-7'-(benzyloxy)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3p)



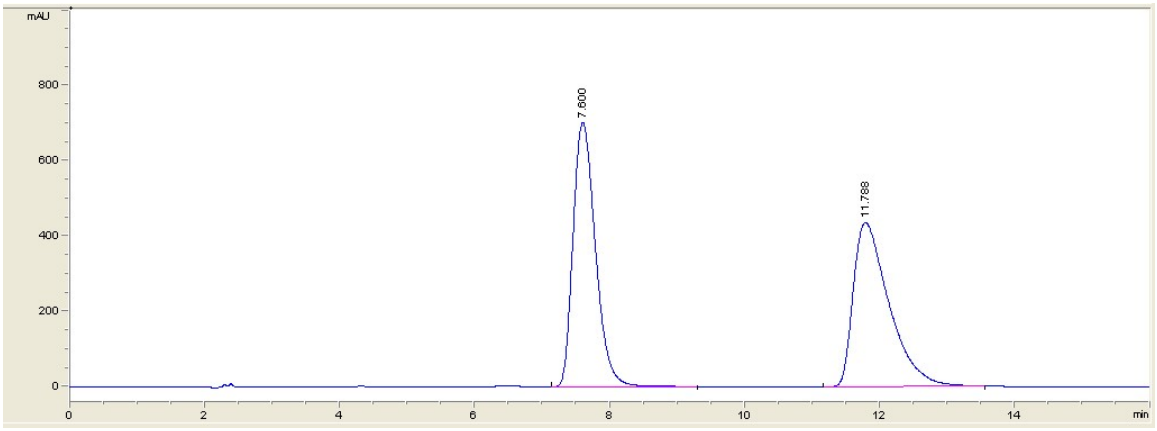
#	Time	Area	Height	Width	Area%
1	11.741	4046.3	112.9	0.5417	50.467
2	16.311	3971.5	69.2	0.8847	49.533



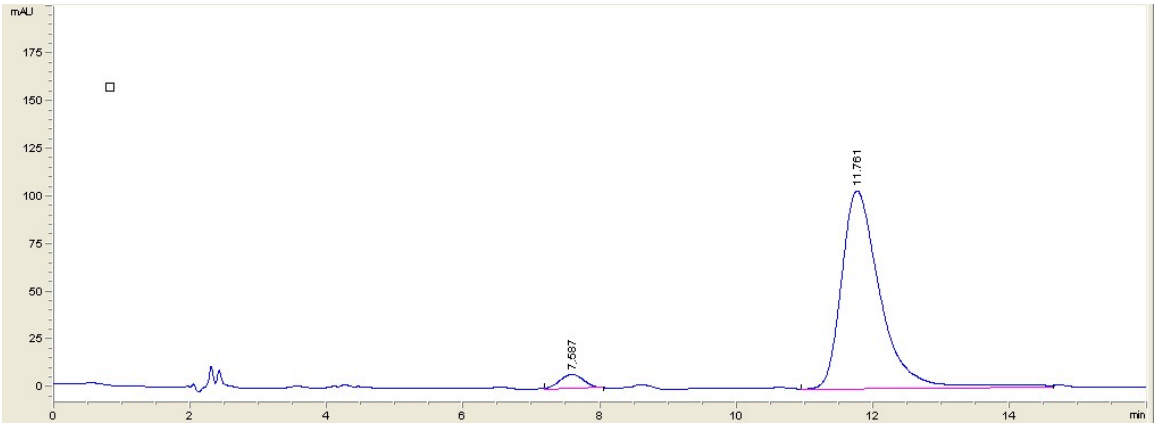
#	Time	Area	Height	Width	Area%
1	11.925	404.7	9	0.7455	5.029
2	16.21	7642.9	114.5	1.1123	94.971



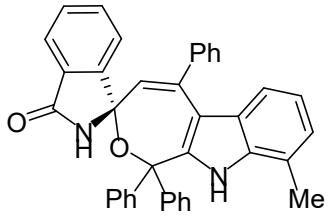
(S)-7'-(tert-butyl)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3q)



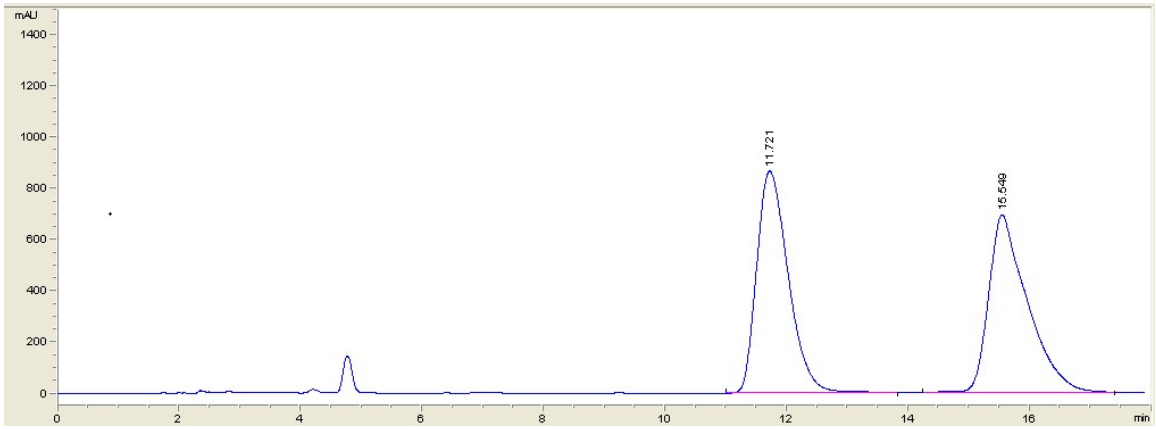
#	Time	Area	Height	Width	Area%
1	7.6	16320.8	703.3	0.3639	50.150
2	11.788	16223.3	436.7	0.5645	49.850



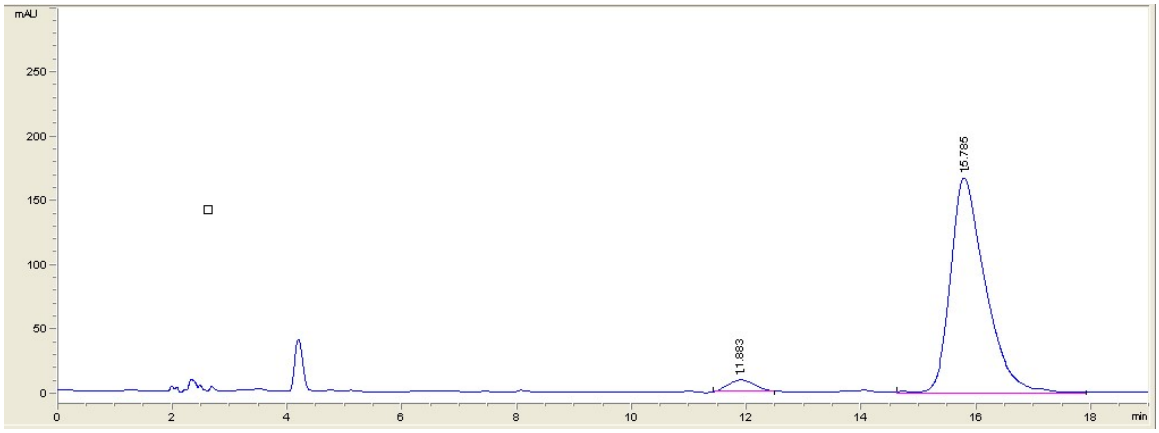
#	Time	Area	Height	Width	Area%
1	7.587	191.9	7.6	0.4209	4.385
2	11.761	4184.4	104.3	0.6686	95.615



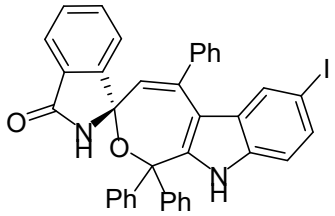
(S)-9'-methyl-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3r)



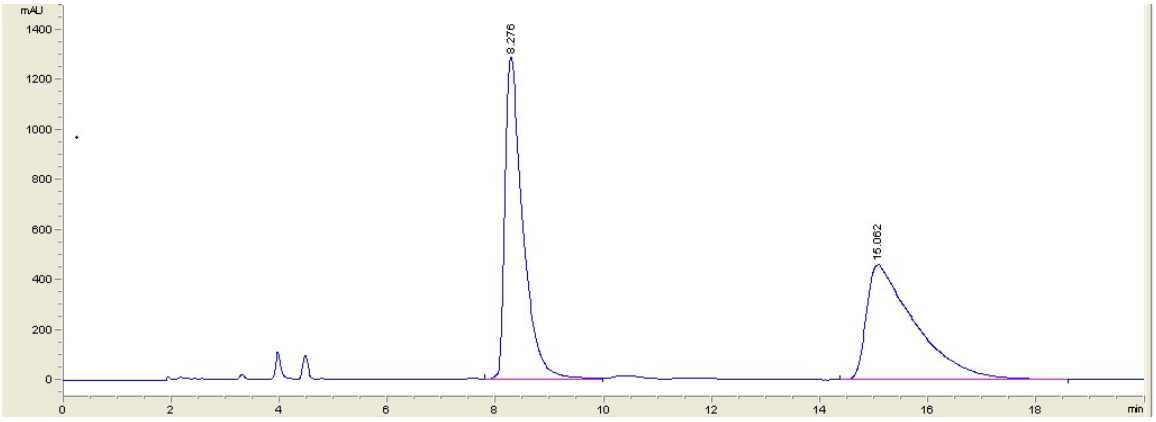
#	Time	Area	Height	Width	Area%
1	11.721	31319.6	866.3	0.5674	50.320
2	15.549	30920.7	695.6	0.6206	49.680



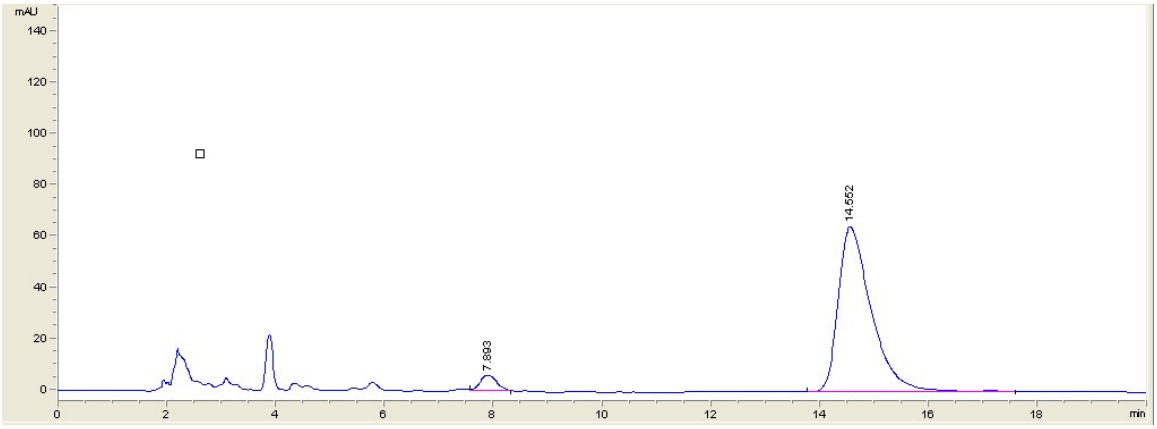
#	Time	Area	Height	Width	Area%
1	11.883	314.8	9.3	0.5612	4.237
2	15.785	7115.8	167.5	0.708	95.763



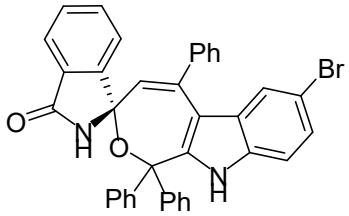
(S)-7'-iodo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3s)



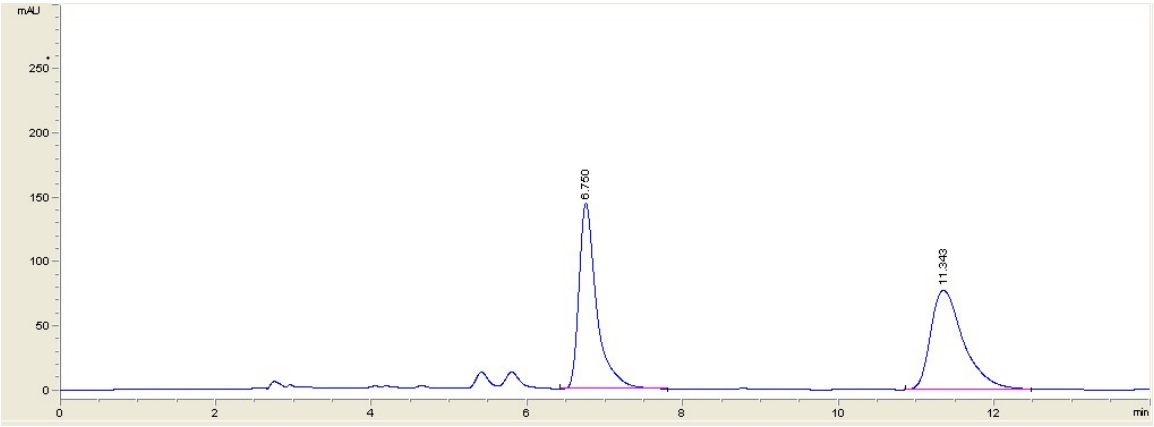
#	Time	Area	Height	Width	Area%
1	8.276	29724.2	1288.5	0.339	50.852
2	15.062	28728.1	460.7	0.8701	49.148



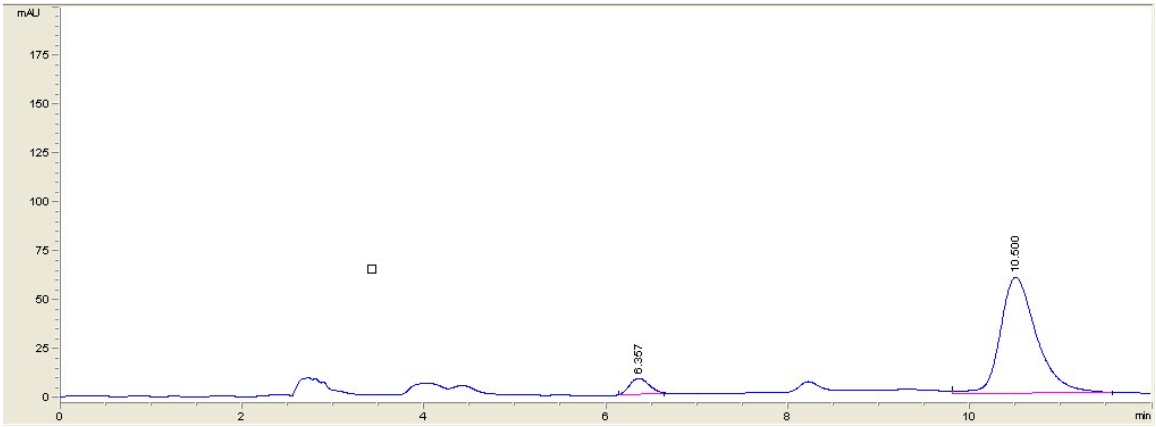
#	Time	Area	Height	Width	Area%
1	7.893	133.8	6.2	0.3614	4.572
2	14.552	2792.1	64.8	0.7179	95.428



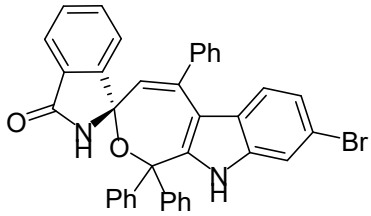
(S)-7'-bromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3t)



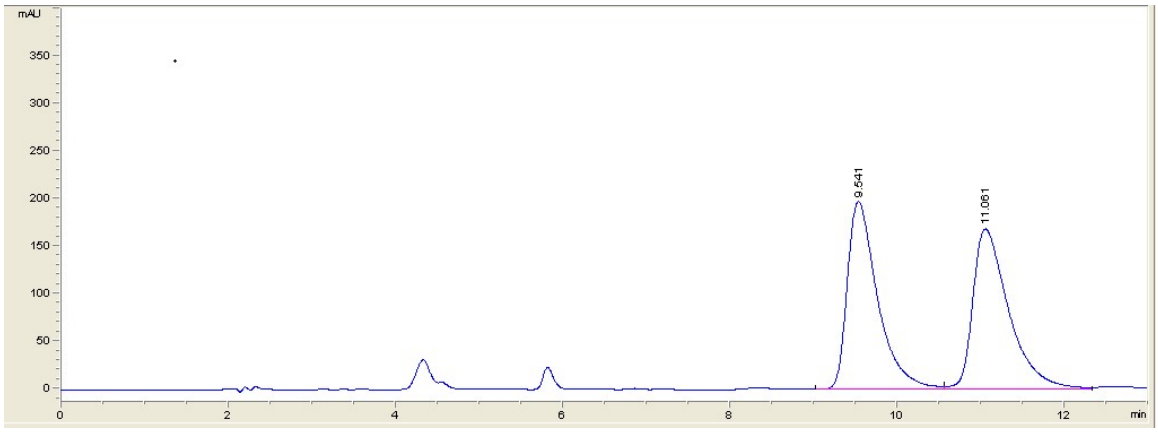
#*	Time	Area	Height	Width	Area%
1	6.75	2288	144.4	0.2343	50.277
2	11.343	2262.8	77	0.4446	49.723



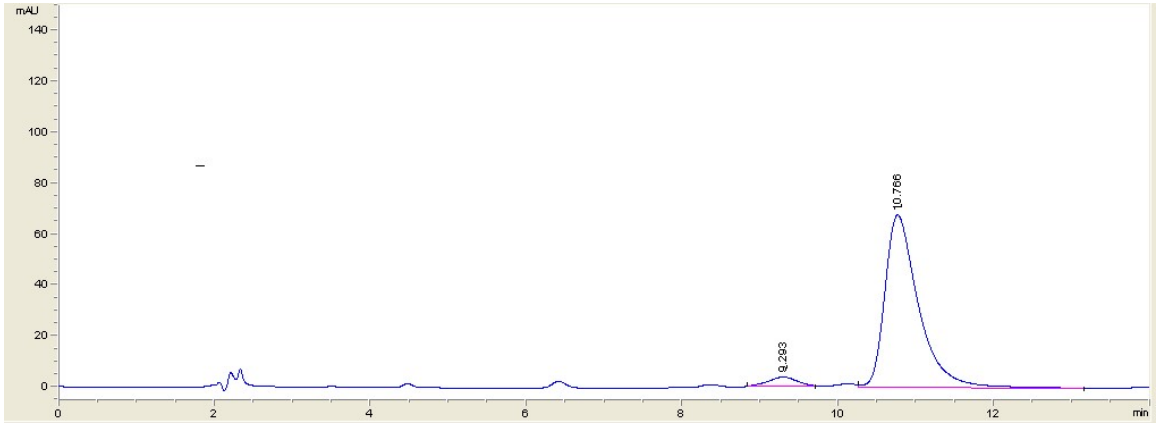
#	Time	Area	Height	Width	Area%
1	6.357	121.2	8.2	0.2473	6.816
2	10.5	1657.5	59.4	0.4215	93.184



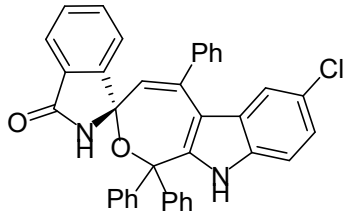
(S)-8'-bromo-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3u)



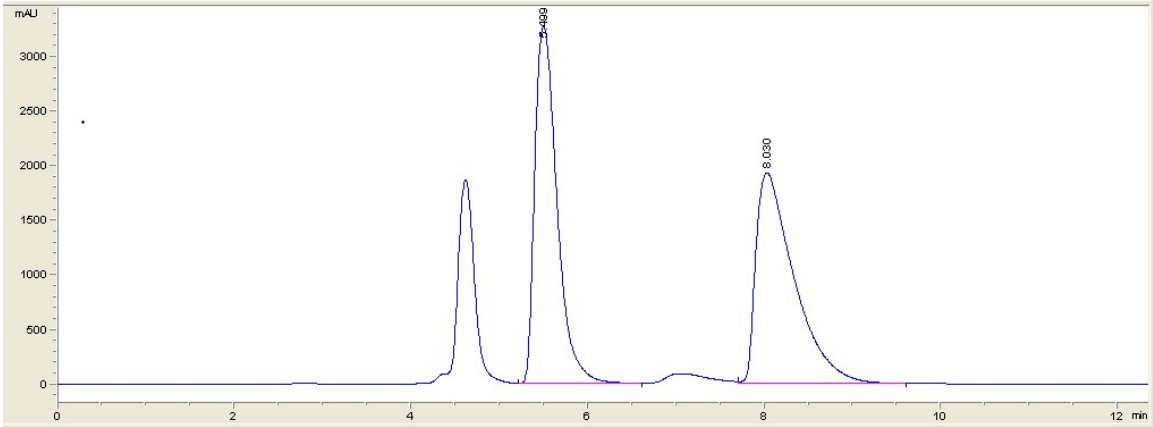
#	Time	Area	Height	Width	Area%
1	9.541	5016.9	197.6	0.3806	49.648
2	11.061	5088	168.9	0.4535	50.352



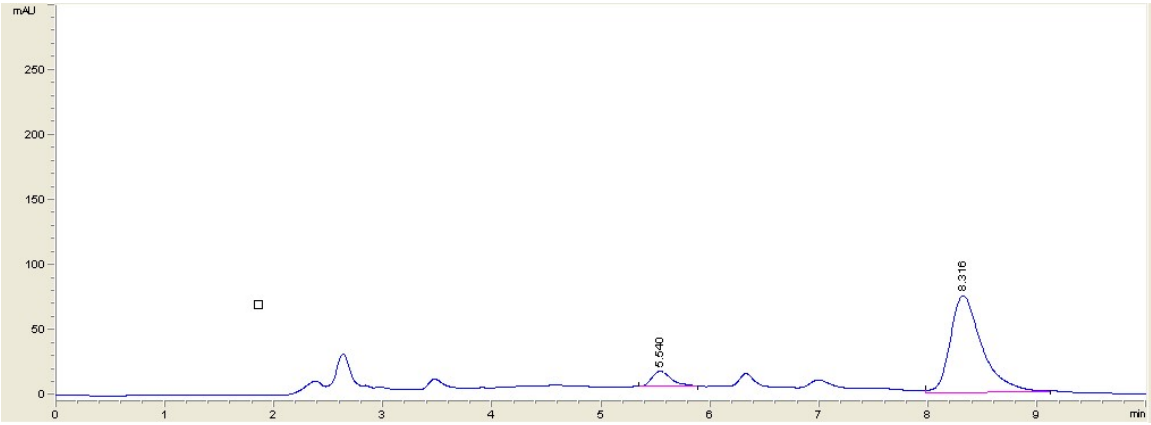
#	Time	Area	Height	Width	Area%
1	9.293	101.7	3.8	0.4457	4.719
2	10.766	2052.7	67.8	0.5047	95.281



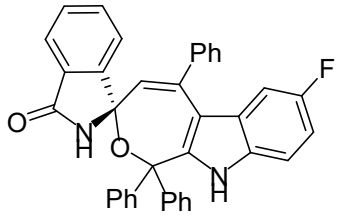
(S)-7'-chloro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3v)



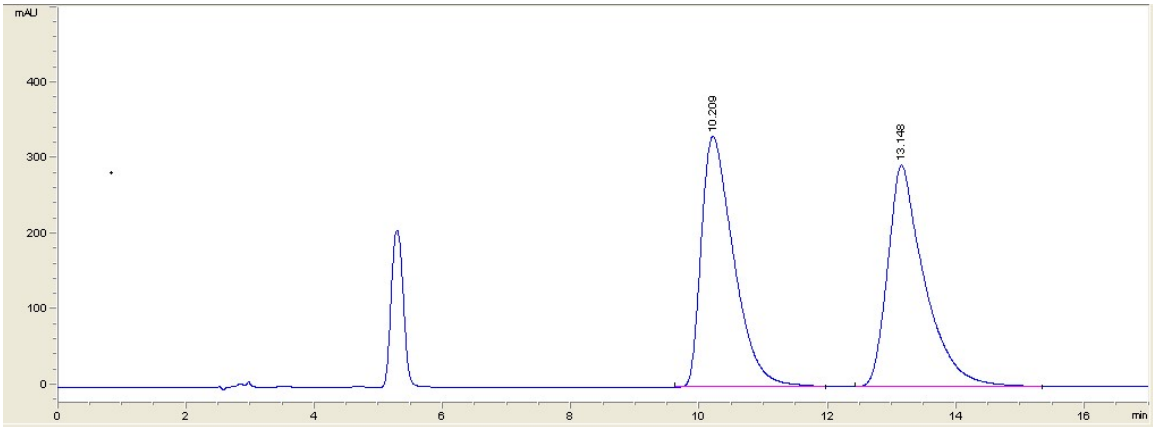
#	Time	Area	Height	Width	Area%
1	5.499	57909.4	3286.4	0.2755	49.653
2	8.03	58718.9	1936.2	0.4441	50.347



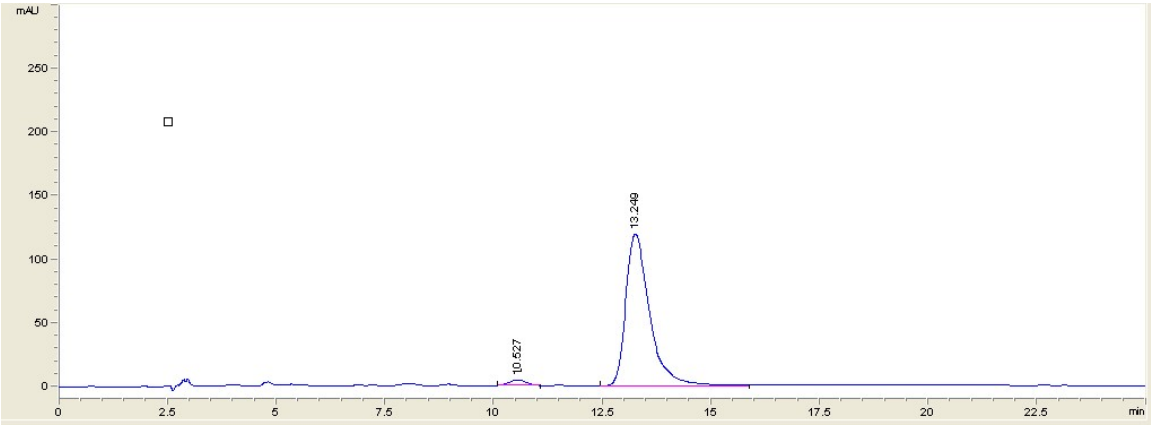
#	Time	Area	Height	Width	Area%
1	5.54	141.2	11.4	0.2066	8.411
2	8.316	1537.9	74.8	0.3099	91.589



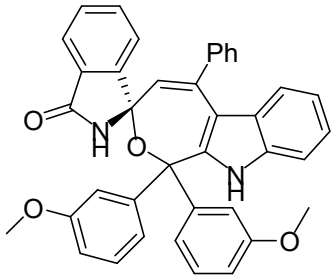
(S)-7'-fluoro-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3w)



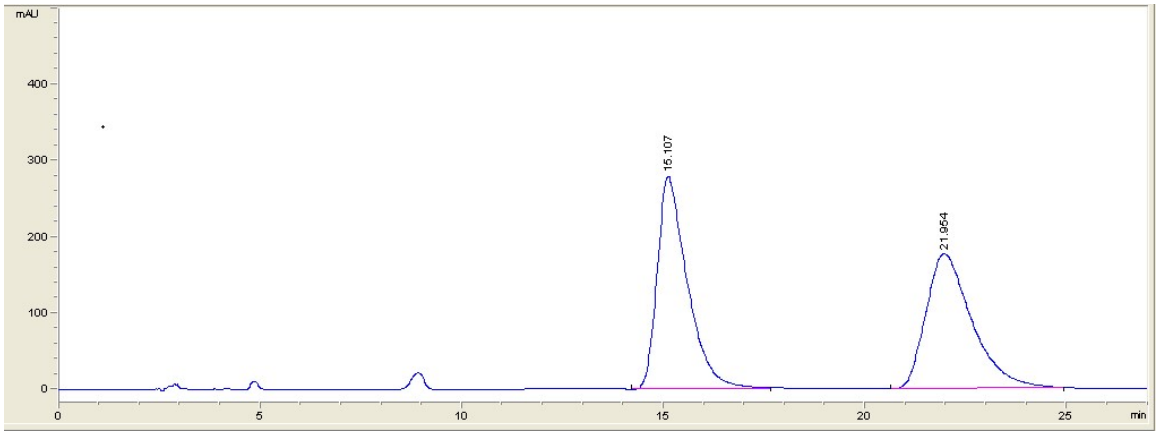
#	Time	Area	Height	Width	Area%
1	10.209	11662.1	331.8	0.5324	50.028
2	13.148	11649	293.2	0.5625	49.972



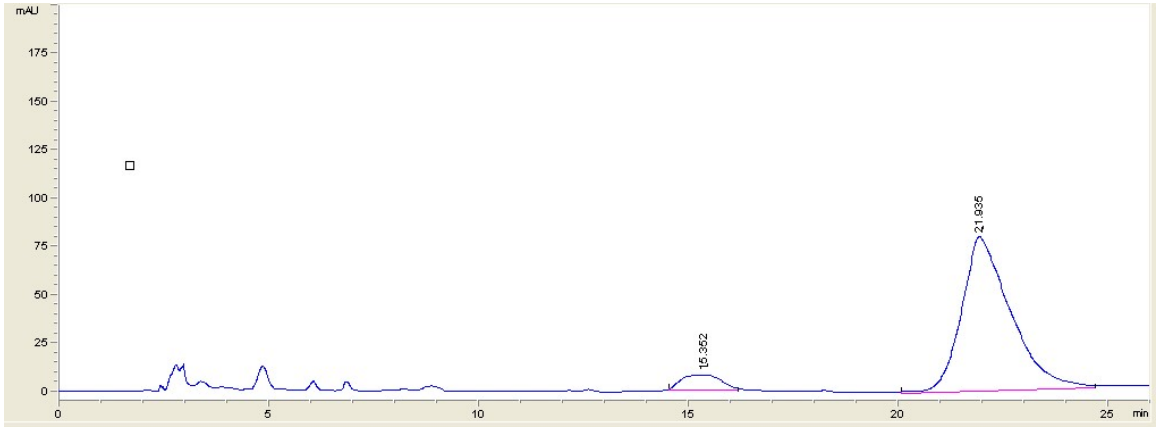
#	Time	Area	Height	Width	Area%
1	10.527	123	4.4	0.4647	2.584
2	13.249	4637.4	119.8	0.6453	97.416



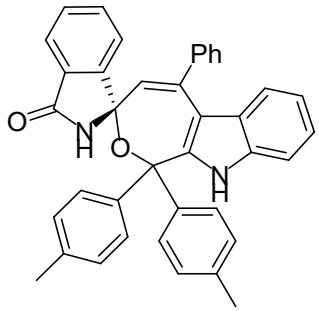
(S)-1',1'-bis(3-methoxyphenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3x)



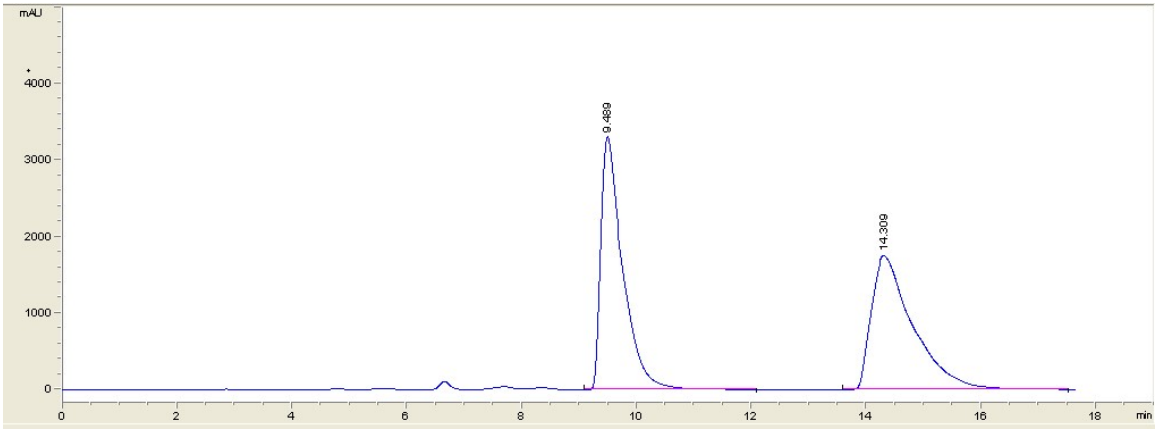
#	Time	Area	Height	Width	Area%
1	15.107	14503.3	278.9	0.7523	50.816
2	21.954	14037.6	176.7	1.1889	49.184



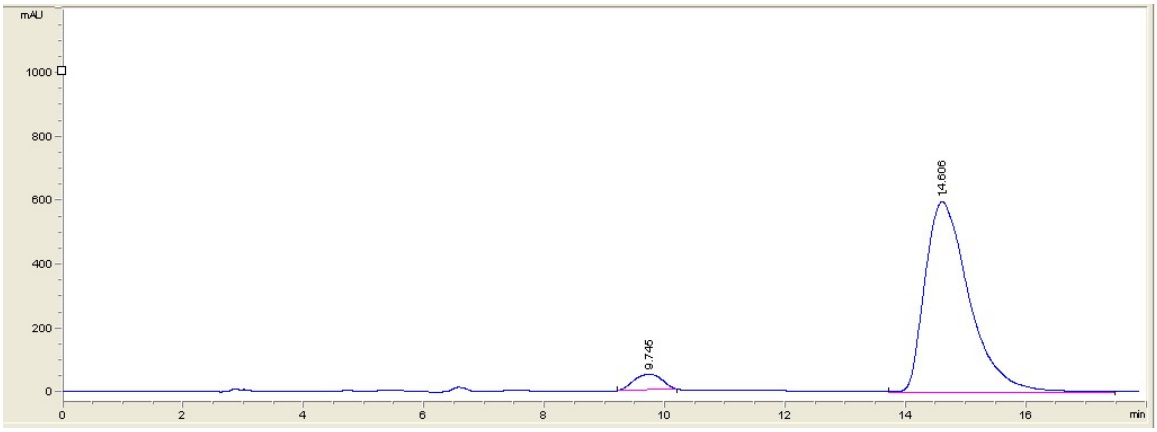
#	Time	Area	Height	Width	Area%
1	15.352	509.4	7.8	1.0861	7.254
2	21.935	6513.5	80	1.3569	92.746



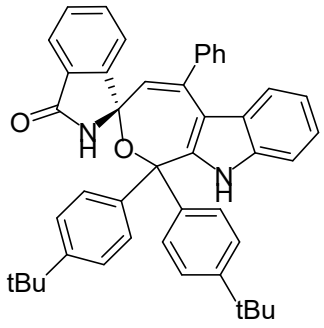
(S)-5'-phenyl-1',1'-di-p-tolyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3y)



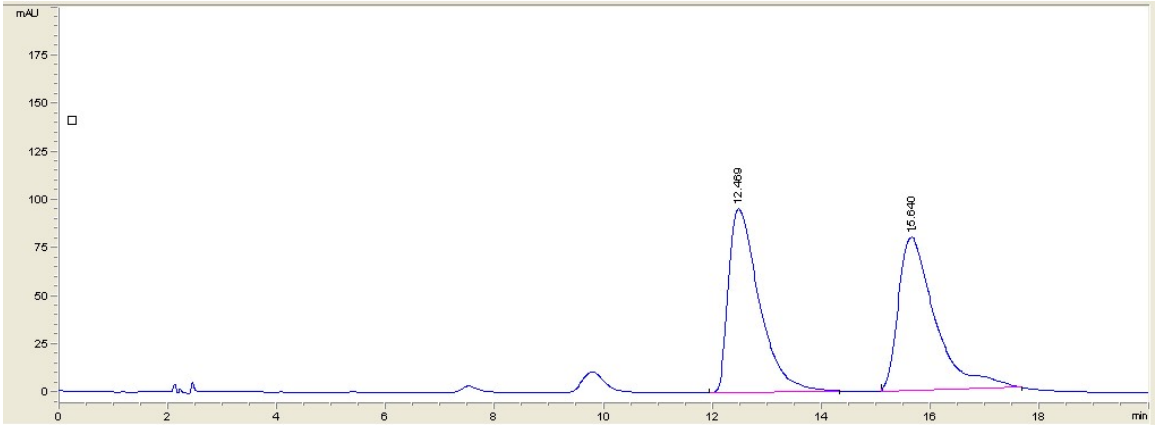
#	Time	Area	Height	Width	Area%
1	9.489	87976.5	3299.2	0.3868	50.064
2	14.309	87750.1	1747.3	0.7548	49.936



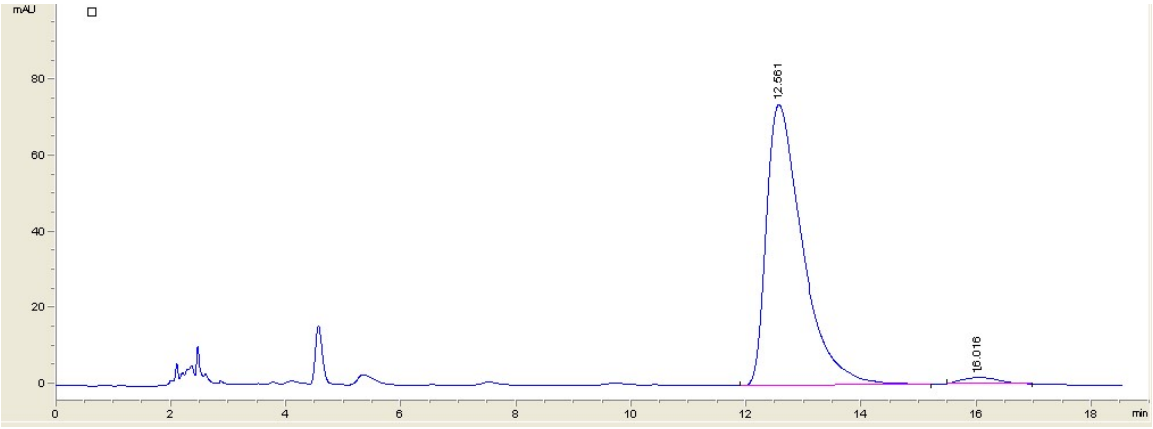
#	Time	Area	Height	Width	Area%
1	9.745	1756.1	51.5	0.568	5.360
2	14.606	31005.9	598.6	0.8632	94.640



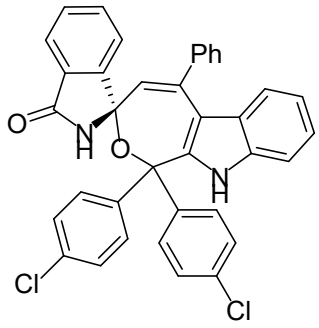
(S)-1',1'-bis(4-(tert-butyl)phenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3z)



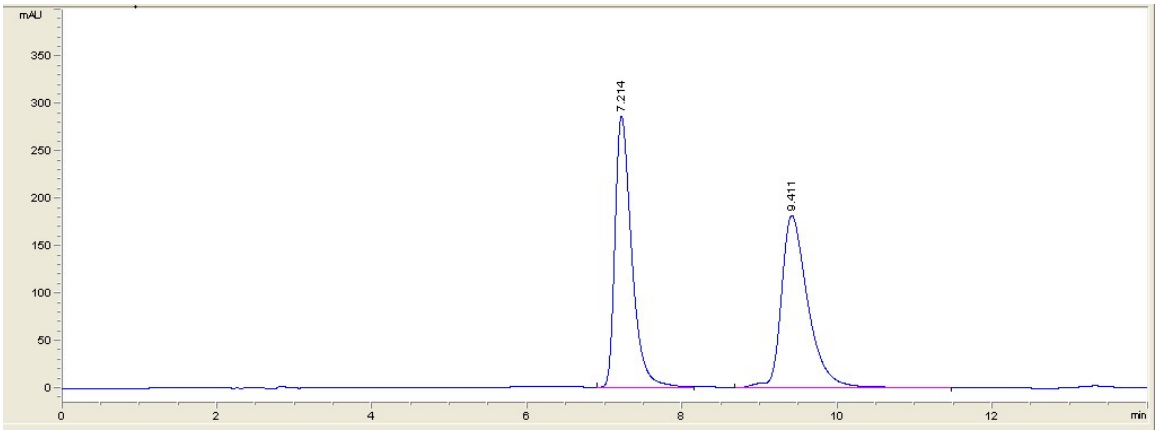
#	Time	Area	Height	Width	Area%
1	12.469	3740.8	95.5	0.5849	49.834
2	15.64	3765.7	79.8	0.7861	50.166



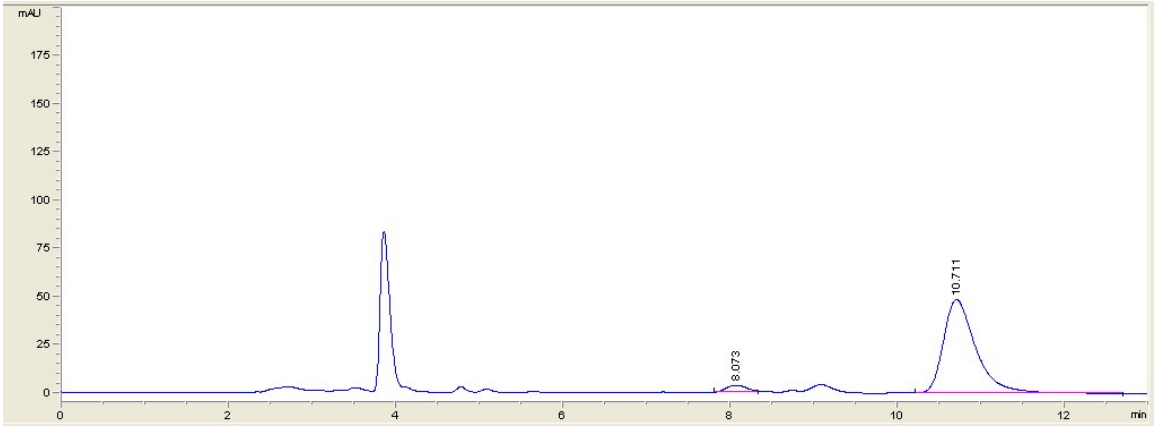
#	Time	Area	Height	Width	Area%
1	12.561	3218.4	73.8	0.7265	97.779
2	16.016	73.1	1.7	0.7344	2.221



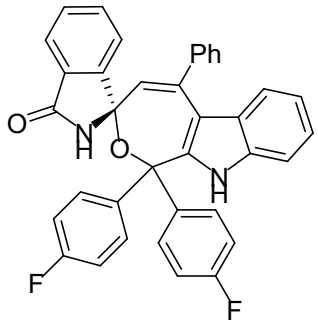
(S)-1',1'-bis(4-chlorophenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3aa)



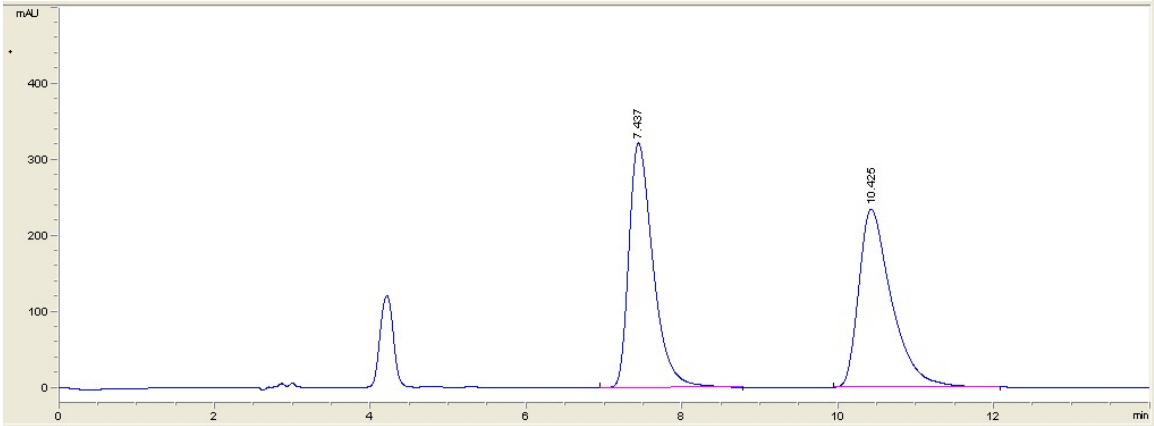
#	Time	Area	Height	Width	Area%
1	7.214	4376.9	287.3	0.2302	49.587
2	9.411	4449.9	182.3	0.3662	50.413



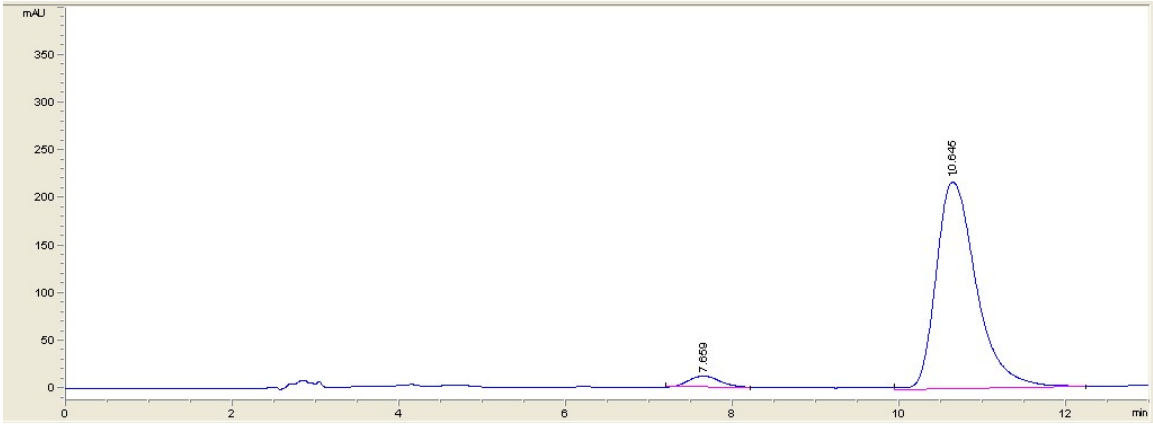
#	Time	Area	Height	Width	Area%
1	8.073	66.3	3.7	0.2962	4.791
2	10.711	1316.7	48.5	0.4097	95.209



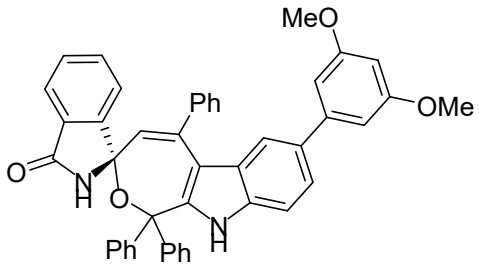
(S)-1',1'-bis(4-fluorophenyl)-5'-phenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (3ab)



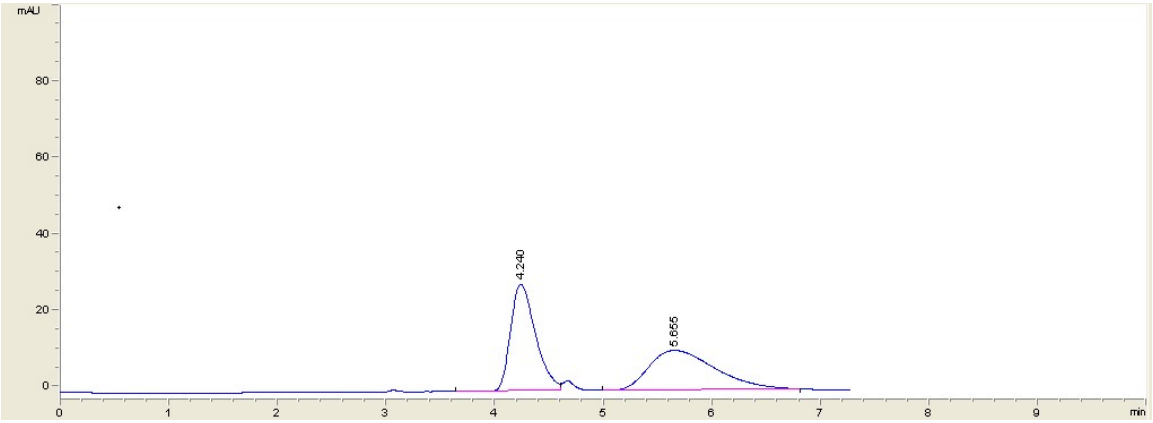
#	Time	Area	Height	Width	Area%
1	7.437	6948	321.5	0.3308	50.189
2	10.425	6895.6	234.2	0.4366	49.811



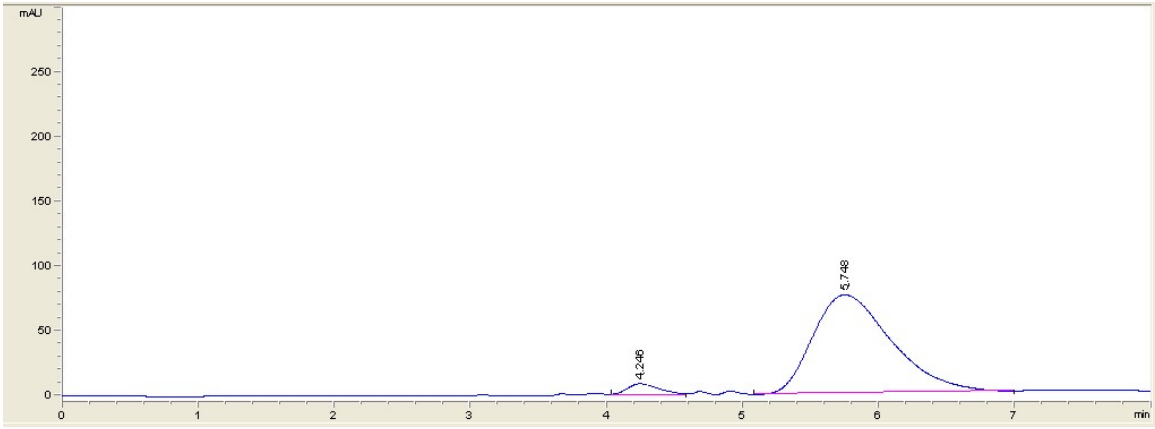
#	Time	Area	Height	Width	Area%
1	7.659	340.2	12.1	0.4691	4.410
2	10.645	7374.3	217.4	0.5652	95.590



(S)-7'-(3,5-dimethoxyphenyl)-1',1',5'-triphenyl-1',10'-dihydrospiro[isoindoline-1,3'-oxepino[3,4-b]indol]-3-one (8)



#	Time	Area	Height	Width	Area%
1	4.24	452.5	28.1	0.2477	49.947
2	5.655	453.4	10.5	0.6573	50.053



#	Time	Area	Height	Width	Area%
1	4.246	138.9	8.5	0.2732	4.337
2	5.748	3062.8	76.1	0.6707	95.663

13. References

[1] Y.-Y. He, X.-X. Sun, G.-H. Li, G.-J. Mei, F. Shi, *J. Org. Chem.,* 2017, **82**, 2462−2471.

[2] X.-X. Sun, H.-H. Zhang, G.-H. Li, Y.-Y. He, F. Shi, *Chem. Eur. J.,* 2016, **22**, 17526-17532.

[3] J. Mao, H. Zhang, X.-F. Ding, X. Luo, W.-P. Deng, *J. Org. Chem.,* 2019, **84**, 11186−11194.

[4] M. Sun, C. Ma, S.-J. Zhou, S.-F. Lou, J. Xiao, Y. Jiao, F. Shi, *Angew. Chem. Int. Ed.,* 2019, **58**, 8703–8708.

[5] Z. W. Qiu, B. Q. Li, H. F. Liu, Z. Q. Zhu, H. P. Pan, N. Feng, A. J. Ma, J. B. Peng, X. Z. Zhang, *J. Org. Chem.,* 2021, **86**, 7490-7499.

[6] C. Qian, T. Huang, J. Sun, P. Li, *Org. Lett.,* 2022, **24**, 6472-6476.

[7] R. A. Unhale, M. M. Sadhu, V. K. Singh, *Org. Lett.,* 2022, **24**, 3319-3324.

[8] C. Qian, M. Liu, J. Sun, P. Li, *Org. Chem. Front.,* 2022, **9**, 1234-1240.

[9] H.-Q. Wang, S.-F. Wu, J.-R. Yang, Y.-C. Zhang, F. Shi, *J. Org. Chem.,* 2022, **88**, 7684-7702.

[10] Y. Xia, M. Liu, C. Qian, P. Li, M. Dong, W. Li, *Org. Chem. Front.,* 2023, **10**, 30-34.

[11] C. Khajuria, M. M. Sadhu, R. A. Unhale, V. K. Singh, *Tetrahedron Letters.,* 2022, **112**.