Supporting Information

Diverting the Mannich Reaction to Access 2,2-Disubstituted Indolin-3-ones by Merging 1,2-Aryl Migration and Copper-Catalyzed Aerobic Oxidation

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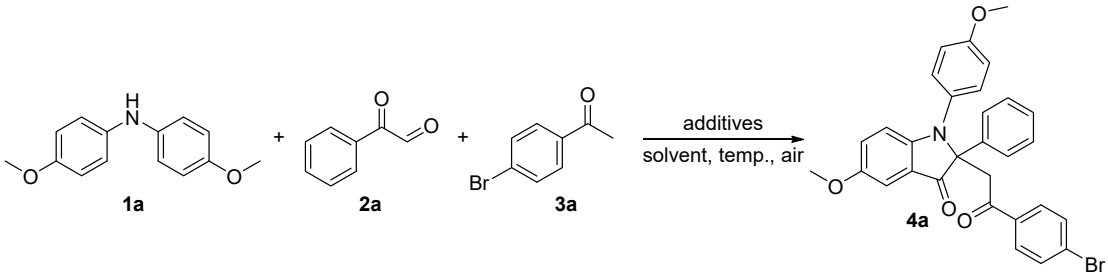
1. General Information

NMR spectra were recorded on Bruker AVANCE III HD 600MHz. Chemical shifts (δ) were reported in parts per million (ppm) relative to residual solvent peaks rounded to the nearest 0.01 for proton and 0.1 for carbon (*ref: $CDCl_3$ [^1H: 7.26, ^{13}C: 77.16], DMSO-d_6 [^1H: 2.5,3.3, ^{13}C:39.52]*). Coupling constants (*J*) were reported in Hz to the nearest 0.1 Hz. Multiplicities are abbreviated as follows: singlet (s), doublet (d), triplet (t), quartet (q), doublet-doublet (dd), quintet (quint), sextet (sext), septet (sept), multiplet (m), and broad (b). High-resolution mass spectrometry (HRMS) data was obtained on Thermo Scientific Q Exactive instrument (ESI Source, mass analyzer type is orbitrap).

Materials and Methods: Unless otherwise stated, starting materials were purchased from commercial sources. Solvents were purchased in HPLC quality. Reactions were monitored by thin layer chromatography (TLC). Compounds were visualized by UV-light at 254 nm and by dipping the plates in a phosphomolybdic acid ethanol solution followed by heating. Flash column chromatography was performed over silica gel (300-400 mesh). The $CDCl_3$ used in the NMR experiments was stored over anhydrous K_2CO_3 before use.

2. Optimization of the reaction conditions

2.1 Screening condition optimization for Scheme 2[a]

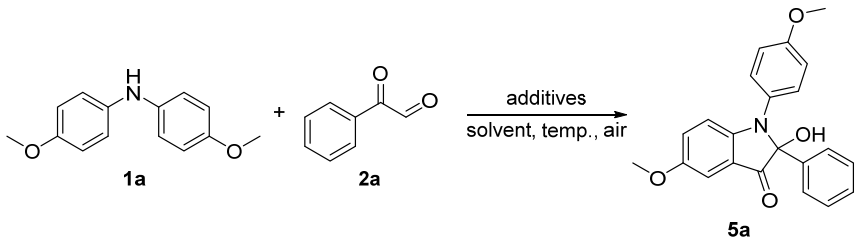


Entry	Additives (equiv)	Solvent	T (℃)	Yield% (**4a**)[b]
1	-	DCE	80	Trace
2	benzoic acid (0.5)	DCE	80	Trace
3	L-proline (0.3)	DCE	80	Trace
4	TFA (0.2)	DCE	80	52
5	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	DCE	80	85
6	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	DCE	60	23
7	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	xylene	80	55
8	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	DMA	80	Trace
9	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	*i*-PrOH	80	Trace
10	$Cu(TFA)_2 \cdot xH_2O$ (0.05)	DCE	80	29
11[c]	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	DCE	80	20
12	TBHP (1.0)	DCE	80	Trace
13	PIDA (1.0)	DCE	80	Trace

[a] **1a** (0.2 mmol), **2a** (0.3 mmol), **3a** (0.4 mmol), additive and solvent (2.0 mL, *c* 0.1 M) were added to a pressure vessel under air atmosphere and stirred at a certain temperature. [b] Isolated yields. [c] Reaction was conducted in O_2 (1 atm) atmosphere.

2.2 Screening condition optimization for Scheme 3[a]

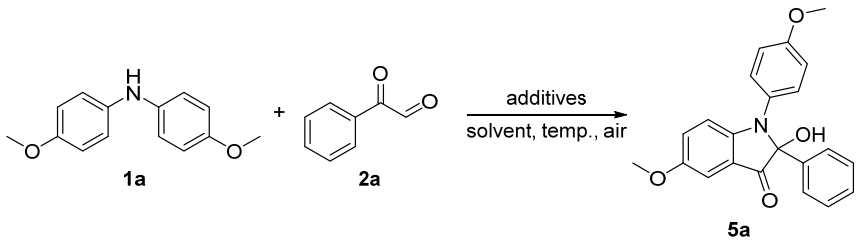
2.1.1 Screening the solvents



Entry	Additives (equiv)	Solvent	T (°C)	Yield% (**5a**)[b]
1	TFA (0.1)	DMA	80	Not detected
2	TFA (0.1)	1,4-dioxane	80	Trace
3	TFA (0.1)	Hexone	80	40
4	TFA (0.1)	n-Butanol	80	Not detected
5	TFA (0.1)	Cyclohexanol	80	Not detected
6	TFA (0.1)	DCE	80	60
7	TFA (0.1)	DMF	80	Not detected

[a] **1a** (0.2 mmol), **2a** (0.4 mmol), TFA (0.02 mmol) and solvent (2.0 mL, *c* 0.1 M) were added to a pressure vessel under air atmosphere and stirred at 80℃ for 4 h. [b] Isolated yields.

2.1.2 Screening the acids

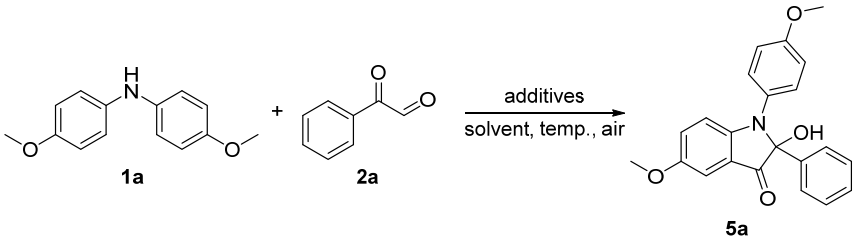


Entry	Additives (equiv)	Solvent	T (°C)	Yield% (**5a**)[b]
1	TFAA (0.5)	DCE	80	60
2	HI (0.5)	DCE	80	25
3	HBr (0.5)	DCE	80	40
4	TsOH (0.5)	DCE	80	Not detected
5	$FeCl_3$ (0.1)	DCE	80	30
6	$Sc(CF_3SO_3)_3$ (0.1)	DCE	80	40
7	$In(CF_3SO_3)_3$ (0.1)	DCE	80	45

8	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	80	71
9	$ZrCl_4$ (0.1)	DCE	80	20
10	CF_3SO_3H (0.1)	DCE	80	20
11	$H_2NCH_2SO_3H$ (0.1)	DCE	80	Trace
12	$Na_2WO_4 \cdot 2H_2O$ (0.1)	DCE	80	Trace

[a] **1a** (0.2 mmol), **2a** (0.4 mmol), additive and DCE (2.0 mL, *c* 0.1 M) were added to a pressure vessel under air atmosphere and stirred at 80℃ for 2.5 h. [b] Isolated yield.

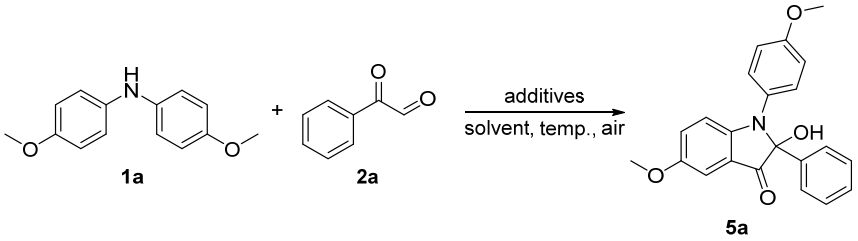
2.1.3 Screening the Temperature



Entry	Additives (equiv)	Solvent	T (℃)	Yield% (**5a**)[b]
1	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	R.T.	Not detected
2	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	40	87
3	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	90
4	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	80	70
5	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	90	50
6	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	100	Trace

[a] **1a** (0.2 mmol), **2a** (0.4 mmol), $Cu(TFA)_2 \cdot 2H_2O$ (0.02 mmol) and DCE (2.0 mL, *c* 0.1 M) were sealed in a pressure bottle and heated by magnetic stirring at a certain temperature for 2.5 h. [b] Isolated yield.

2.1.4 Screening the ratio of raw materials

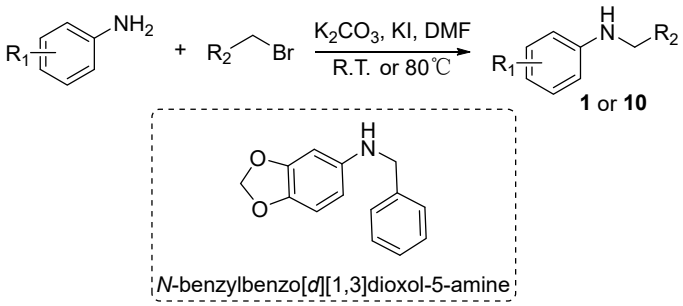


Entry	**1a:2a**	Additives (equiv)	Solvent	T (°C)	Yield% (**5a**)[b]
1	1:1	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	66
2	1:1.2	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	78
3	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	78
4	1:1.7	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	82
5	1:2.5	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	94
6	1:6	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	100
7	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.05)	DCE	60	80
8	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.1)	DCE	60	85
9	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.15)	DCE	60	87
10	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.2)	DCE	60	85
11	1:1.5	$Cu(TFA)_2 \cdot xH_2O$ (0.3)	DCE	60	85

[a] **1a**:**2a**:$Cu(TFA)_2 \cdot xH_2O$ at a certain ratio and DCE (2.0 mL, *c* 0.1 M) were sealed in a pressure bottle and heated by magnetic stirring at 60℃ for 2.5 h. [b] Isolated yield.

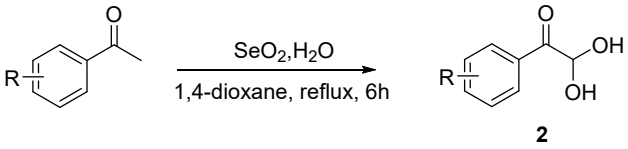
3. General procedure

3.1 General procedure for the synthesis of 1 and 10



As exemplified for *N*-benzylbenzo[*d*][1,3]dioxol-5-amine: K_2CO_3 (1.39 g, 10 mmol) and KI (1.66 g, 10 mmol) were added to a stirred solution of benzo[*d*][1,3]dioxol-5-amine (1.37 g, 10 mmol) in DMF (10 mL) and stirred at 25℃ for 5 minutes. Then benzyl bromide (1070 μL, 9 mmol) was slowly dropped to the solution and the reaction was maintained at 25℃ for 15 minutes. After the reaction was complete, as monitored by TLC, the reaction was quenched by slow addition of water and ethyl acetate. The mixture was then poured into a separating funnel. After the phases were separated, and the aqueous phase was extracted three times with EA. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product can be separated by preparative TLC or silica gel column chromatography to obtain the target product.

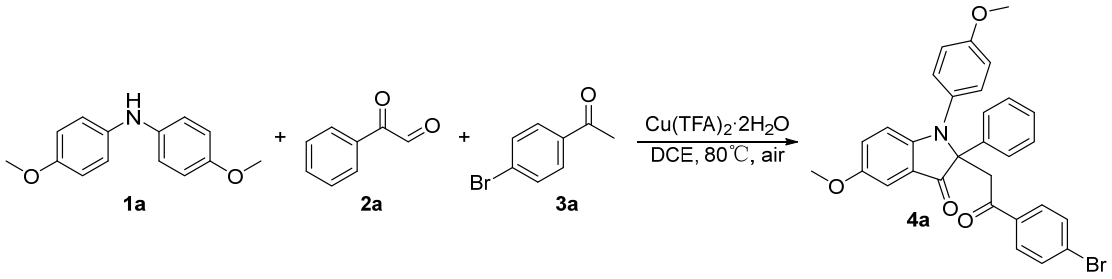
3.2 General procedure for the synthesis of 2



To a 100 mL two-neck round bottom flask SeO_2, (5.00 g, 45.0 mmol), H_2O (0.77 g, 42.5 mmol) and 1,4-dioxane (25.0 mL) were added and fitted with a condenser. The mixture was heated to reflux with stirring until the solid dissolved. Then, substituted aryl ketones (50.0 mmol) was added into the solution. The reaction mixture was allowed to reflux for 6 h. After the reaction was completed, the reaction mixture was cooled to room temperature and filtered through a Celite pad. The Celite pad was washed several

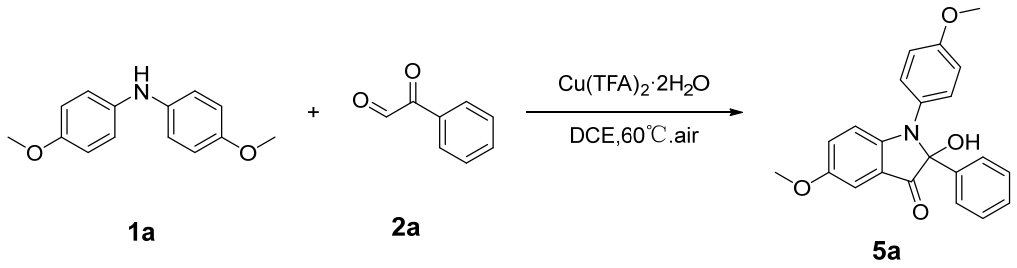
times with ethyl acetate. The combined filtrate was evaporated on a rotary evaporator to afford the crude product. Recrystallization of the crude product with hot water gave pure substituted arylglyoxals monohydrate **2** as white solid.

3.3 General procedure for the synthesis of 4a – 4aa



Take the synthesis of **4a** as an example, to a solution of **1a** (0.2 mmol) in DCE (2 mL, *c* 0.1 M) was added **2a** (0.3 mmol), **3a** (0.4 mmol) and $Cu(TFA)_2 \cdot xH_2O$ (0.04 mmol). After stirring at 80°C for 5-12 h, the resulting mixture was extracted by CH_2Cl_2. Organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography with PE:EA = 3:1 as an eluent to afford the target product **4a**.

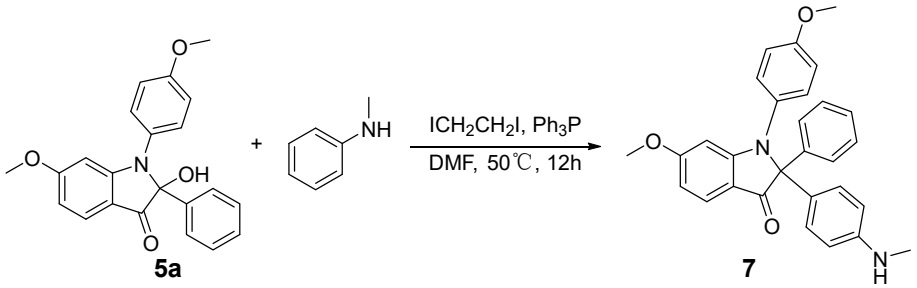
3.4 General procedure for the synthesis of 5a – 5z



Take the synthesis of **5a** as an example, to a flame-dried pressure sealed tube charged with 40.2 mg (0.3 mmol) 2,2-dihydroxy-1-phenylethan-1-one (**2a**) and 45.9 mg (0.2 mmol) of bis(4-methoxyphenyl)amine (**1a**) was added DCE (2 mL, *c* 0.1 M) and $Cu(TFA)_2 \cdot xH_2O$ (9.3mg, 0.03mmol). Then the pressure tube was quickly closed. The reaction mixture was heated up to 60°C using an oil bath and stirred at the same temperature for 2.5 h, and the reaction were monitored by TLC. When the reaction is completed, the reaction was quenched by slow addition of water and ethyl acetate. The

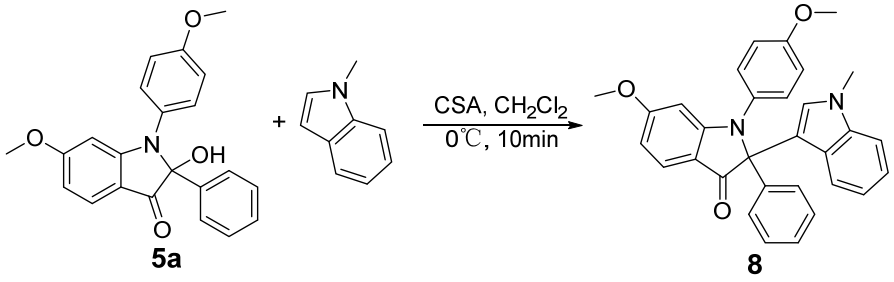
mixture was then poured into a separating funnel. After the phases were separated, and the aqueous phase was extracted three times with EA. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product can be separated by preparative TLC or silica gel column chromatography to obtain the target product **5a**.

3.5 General procedure for the synthesis of 7



To a flame-dried pressure sealed tube charged with alcohol **5a** (1.0 eq., 0.5 mmol, 180.6 mg), triphenylphosphine (1.2 eq., 0.6 mmol, 157.4 mg) and anhydrous DMF (5.0 mL) under N_2 atmosphere. 1,2-Diiodoethane (1.2 eq., 0.6 mmol, 169.1 mg) was then added and the resulting mixture was stirred for around 1 min until the 1,2-diiodoethane was completely dissolved. *N*-methylaniline (4.0 eq., 2.0 mmol, 217 μL) was added subsequently and the mixture was stirred at 50°C for 12 h. Dichloromethane (20 mL) was added and the resulting solution was washed with water. The organic layer was dried over Na_2SO_4. After filtration, the solvent was removed by concentration under reduced pressure. The residue was subjected to flash column chromatography to afford the pure product **7**.

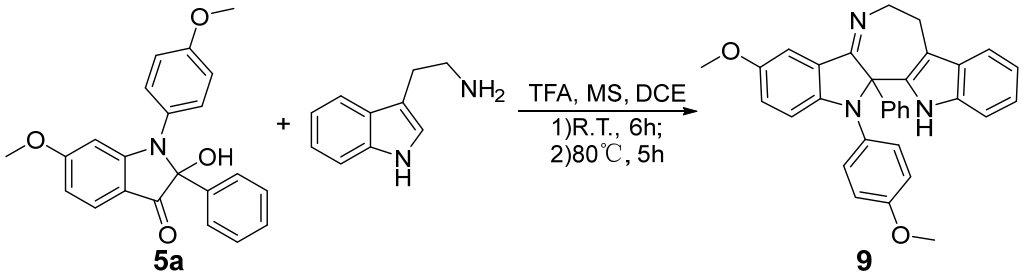
3.6 General procedure for the synthesis of 8



To a solution of **5a** (0.26 mmol) in CH_2Cl_2 (*c* 0.1 M) was added 1-methyl-1*H*-indole

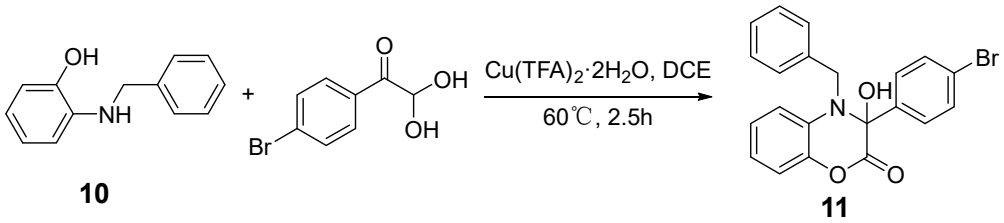
(0.28 mmol) and CSA (0.28 mmol). After stirring at 0℃ for 10 minutes, the resulting mixture was neutralized with satd aqueous $NaHCO_3$ at 0℃, then extracted by CH_2Cl_2. Organic layer was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by column chromatography with PE-EA as an eluent to afford the target product **8**.

3.7 General procedure for the synthesis of 9



To a flame-dried pressure sealed tube charged with 108.6 mg (0.3 mmol) 2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**5a**) and 72.3 mg (0.45 mmol) of 2-(1*H*-indol-3-yl)ethan-1-amine was added 3 mL (*c* 0.1 M) of 1,2-dichloroethane and TFA (4.5 μL, 0.06 mmol). Then 200 mg molecular sieve was added to the system and the pressure tube was quickly closed. The reaction mixture was firstly stirred at room temperature for 6 h, then heated up to 80℃ using an oil bath and stirring for five more hours. When the reaction is completed, the reaction was quenched by slow addition of water and ethyl acetate. The mixture was then poured into a separating funnel. After the phases were separated, and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product can be separated by preparative TLC or silica gel column chromatography to obtain the target product **9**.

3.8 General procedure for the synthesis of 11

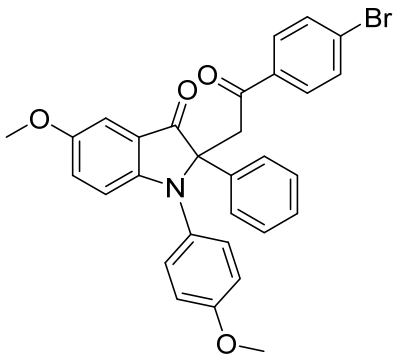


10 **11**

To a flame-dried pressure sealed tube charged with **10 (**39.8 mg, 0.2 mmol)、1-(4-bromophenyl)-2,2-dihydroxyethan-1-one (69 mg, 0.3 mmol) and $Cu(TFA)_2 \cdot xH_2O$ (9.3 mg, 0.03mmol) was added 2 mL (*c* 0.1 M) of 1,2-dichloroethane. Then the pressure tube was quickly closed. The reaction mixture was heated up to 60℃ using an oil bath and stirred at the same temperature for 2.5 h, and the reaction were monitored by TLC. When the reaction is completed, the reaction was quenched by slow addition of water and ethyl acetate. The mixture was then poured into a separating funnel. After the phases were separated, and the aqueous phase was extracted three times with ethyl acetate. The combined organic layers were washed with brine, dried over Na_2SO_4, and concentrated by rotary evaporation. The crude product can be separated by preparative TLC or silica gel column chromatography to obtain the target product **11**.

4. Synthesis and characterization data of compounds 4-5, 7-9 and 11

2-(2-(4-bromophenyl)-2-oxoethyl)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4a**)



Compound **4a** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(4-bromophenyl)ethan-1-one. **4a** was obtained in 81% yield (87.6 mg) as orange solid.

mp: 173.1-174.4°C

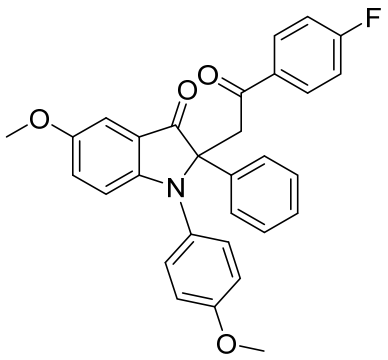
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (d, J = 7.8 Hz, 2H), 7.40 (dt, J = 12.1, 8.1 Hz, 6H), 7.33 (t, J = 7.2 Hz, 1H), 7.17 – 7.13 (m, 2H), 7.10 (d, J = 9.8 Hz, 1H), 6.94 (d, J = 8.8 Hz, 2H), 6.61 (d, J = 8.8 Hz, 2H), 4.07 (d, J = 17.3 Hz, 1H), 3.87 (d, J = 17.3 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.7, 195.0, 156.7, 154.9, 153.4, 138.6, 135.1, 132.6, 131.6, 129.2, 129.1, 128.2, 126.6, 126.0, 124.7, 121.4, 114.4, 112.3, 105.5, 75.4, 55.7, 55.4, 43.4.

IR (KBr, cm^{-1}): 3425, 3060, 2962, 2836, 1702, 1677, 1583, 1511, 1248, 1147, 1030, 1004, 823.

HRMS (ESI): m/z calcd for $C_{30}H_{25}BrNO_4^+$ $(M+H)^+$ 542.0961, found 542.0966.

2-(2-(4-fluorophenyl)-2-oxoethyl)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4b**)



Compound **4b** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(4-fluorophenyl)ethan-1-one **4b** was obtained in 54% yield (52.0 mg) as yellow solid.

mp: 175.2-176.1°C

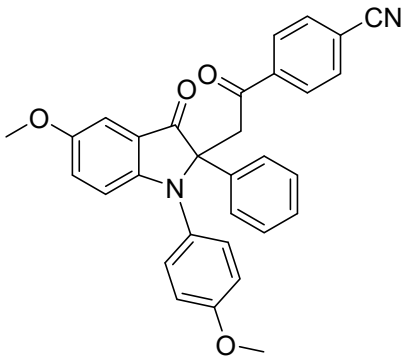
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.61 – 7.55 (m, 4H), 7.37 (dd, J = 8.4, 6.7 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.18 – 7.13 (m, 2H), 7.11 (d, J = 8.7 Hz, 1H), 6.99 – 6.91 (m, 4H), 6.62 (d, J = 8.9 Hz, 2H), 4.11 (d, J = 17.3 Hz, 1H), 3.90 (d, J = 17.3 Hz, 1H), 3.79 (s, 3H), 3.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.8, 194.4, 166.5, 164.8, 156.8, 155.0, 153.4, 138.8, 132.9, 132.9, 132.7, 130.4, 130.4, 129.2, 128.2, 126.6, 126.1, 124.8, 121.5, 115.5, 115.4, 114.5, 112.4, 105.6, 75.5, 55.8, 55.4, 43.5.

IR (KBr, cm^{-1}): 3436, 1708, 1677, 1631, 1594, 1512, 1335, 1247, 1144, 1032, 820.

HRMS (ESI): m/z calcd for $C_{30}H_{25}FNO_4^+$ $(M+H)^+$ 482.1762, found 482.1764.

4-(2-(5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindolin-2-yl)acetyl)benzonitrile (**4c**)



Compound **4c** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 4-acetylbenzonitrile **4c** was

obtained in 52% yield (50.8 mg) as orange solid.

mp: 172.6-174.9°C

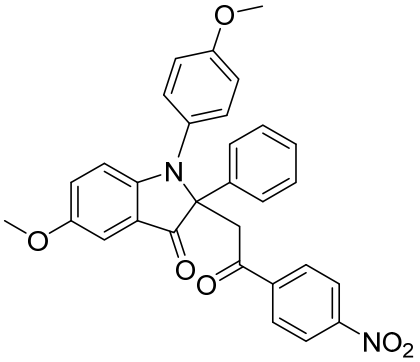
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.57 (d, J = 7.5 Hz, 2H), 7.48 (d, J = 8.3 Hz, 2H), 7.37 (t, J = 7.5 Hz, 2H), 7.32 (t, J = 7.4 Hz, 1H), 7.25 (d, J = 8.4 Hz, 2H), 7.15 (d, J = 7.5 Hz, 2H), 7.13 – 7.08 (m, 1H), 6.95 (d, J = 8.7 Hz, 2H), 6.61 (d, J = 8.7 Hz, 2H), 4.09 (d, J = 17.3 Hz, 1H), 3.89 (d, J = 17.2 Hz, 1H), 3.79 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.5, 195.0, 156.8, 154.9, 153.6, 139.3, 138.4, 132.6, 132.2, 129.2, 128.4, 128.1, 126.9, 126.0, 124.6, 121.4, 117.8, 116.2, 114.5, 112.5, 105.6, 75.6, 55.8, 55.4, 43.6.

IR (KBr, cm^{-1}): 3442, 1698, 1683, 1632, 1604, 1509, 1490, 1439, 1336, 1280, 1248, 1146, 1030, 826.

HRMS (ESI): m/z calcd for $C_{31}H_{25}N_2O_4^+$ $(M+H)^+$ 489.1809, found 489.1810.

5-methoxy-1-(4-methoxyphenyl)-2-(2-(4-nitrophenyl)-2-oxoethyl)-2-phenylindolin-3-one (**4d**)



Compound **4d** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(4-nitrophenyl)ethan-1-one. **4d** was obtained in 36% yield (36.6 mg) as orange solid.

mp: 201.5-203.9°C

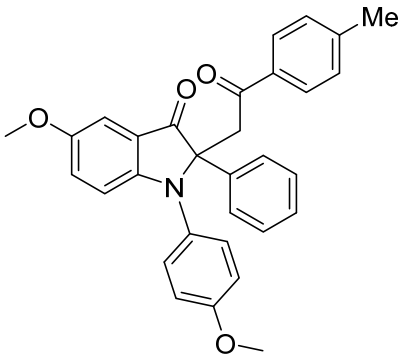
^{1}H NMR (600 MHz, $CDCl_3$): δ 8.12 (d, J = 8.9 Hz, 2H), 7.65 (d, J = 8.8 Hz, 2H), 7.59 – 7.55 (m, 2H), 7.41 – 7.33 (m, 3H), 7.19 – 7.10 (m, 3H), 6.95 (d, J = 9.0 Hz, 2H), 6.61 (d, J = 9.0 Hz, 2H), 4.14 (d, J = 17.4 Hz, 1H), 3.92 (d, J = 17.4 Hz, 1H), 3.81 (s, 3H), 3.63 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.4, 194.9, 156.8, 154.9, 153.6, 150.2, 140.8, 138.4, 132.6, 129.2, 128.7, 128.4, 126.9, 126.0, 124.6, 123.6, 121.4, 114.6, 112.5, 105.6, 75.6, 55.8, 55.4, 43.9.

IR (KBr, cm^{-1}): 3427, 1698, 1631, 1601, 1531, 1509, 1492, 1347, 1283, 1248, 1031, 826.

HRMS (ESI): m/z calcd for $C_{30}H_{25}N_2O_6^+$ $(M+H)^+$ 509.1707, found 509.1872.

5-methoxy-1-(4-methoxyphenyl)-2-(2-oxo-2-(*p*-tolyl)ethyl)-2-phenylindolin-3-one (**4e**)



Compound **4e** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(*p*-tolyl)ethan-1-one. **4e** was obtained in 48% yield (45.8 mg) as yellow solid.

mp: 211.8-213.0℃

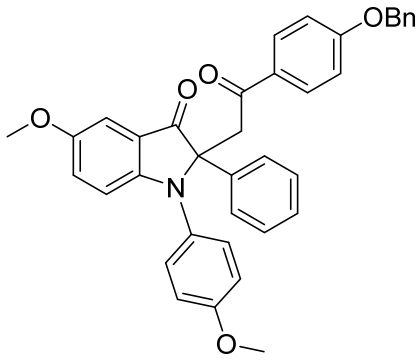
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.75 (d, J = 7.7 Hz, 2H), 7.50 (t, J = 7.4 Hz, 1H), 7.40 (d, J = 7.9 Hz, 2H), 7.36 (t, J = 7.7 Hz, 2H), 7.27 - 7.22 (m, 4H), 7.16 (d, J = 2.2 Hz, 1H), 6.95 (d, J = 8.8 Hz, 1H), 6.90 (d, J = 8.8 Hz, 2H), 6.81 (dd, J = 8.8, 2.3 Hz, 1H), 4.30 (s, 2H), 3.82 (s, 3H), 3.79 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.7, 159.2, 154.8, 136.4, 135.9, 133.8, 133.1, 132.1, 131.4, 130.2, 129.7, 129.4, 129.2, 128.5, 128.1, 127.3, 117.2, 114.6, 112.3, 111.1, 100.9, 56.0, 55.4, 36.5, 21.2.

IR (KBr, cm^{-1}): 3437, 1693, 1631, 1604, 1576, 1511, 1493, 1350, 1282, 1247, 1182, 1148, 1031, 825.

HRMS (ESI): m/z calcd for $C_{31}H_{28}NO_4^+$ $(M+H)^+$ 478.2012, found 478.2014.

2-(2-(4-(benzyloxy)phenyl)-2-oxoethyl)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4f**)



Compound **4f** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(4-(benzyloxy)phenyl)ethan-1-one. **4f** was obtained in 40% yield (45.5 mg) as orange solid.

mp: 75.8-77.6℃

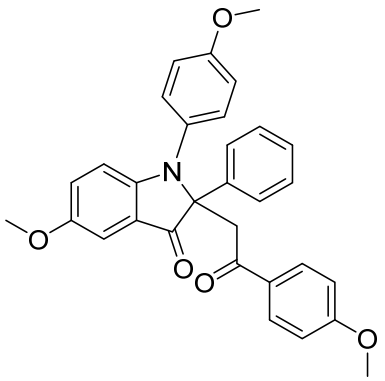
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 – 7.55 (m, 4H), 7.41 – 7.36 (m, 6H), 7.36 – 7.31 (m, 2H), 7.20 – 7.08 (m, 3H), 6.98 (d, J = 9.0 Hz, 2H), 6.84 (d, J = 8.9 Hz, 2H), 6.63 (d, J = 9.0 Hz, 2H), 5.05 (s, 2H), 4.11 (d, J = 17.3 Hz, 1H), 3.90 (d, J = 17.3 Hz, 1H), 3.80 (s, 3H), 3.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 201.1, 194.3, 162.6, 156.7, 155.1, 153.3, 139.0, 136.1, 132.8, 130.1, 130.1, 129.7, 129.6, 129.1, 128.7, 128.5, 128.3, 128.1, 127.5, 126.5, 126.2, 124.9, 121.6, 114.7, 114.5, 114.4, 112.3, 105.6, 75.5, 70.1, 55.8, 55.4, 43.4.

IR (KBr, cm^{-1}): 3433, 1678, 1631, 1600, 1540, 1511, 1488, 1446, 1351, 1281, 1247, 1172, 1031, 833.

HRMS (ESI): m/z calcd for $C_{37}H_{32}NO_5^+$ $(M+H)^+$ 570.2275, found 570.2278.

5-methoxy-1-(4-methoxyphenyl)-2-(2-(4-methoxyphenyl)-2-oxoethyl)-2-phenylindolin-3-one (**4g**)



Compound **4g** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-(4-methoxyphenyl)ethan-1-one. **4g** was obtained in 57.3% yield (56.5 mg) as orange solid.

mp: 175.6-177.7°C

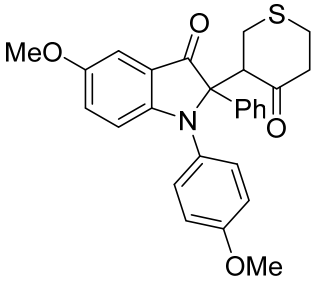
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.56 (ddd, J = 10.9, 8.0, 1.8 Hz, 4H), 7.37 (t, J = 7.6 Hz, 2H), 7.35 – 7.29 (m, 1H), 7.16 (d, J = 2.7 Hz, 1H), 7.14 (dd, J = 8.9, 2.7 Hz, 1H), 7.09 (d, J = 8.9 Hz, 1H), 6.99 – 6.94 (m, 2H), 6.77 – 6.73 (m, 2H), 6.64 – 6.59 (m, 2H), 4.08 (d, J = 17.2 Hz, 1H), 3.89 (d, J = 17.2 Hz, 1H), 3.79 (dd, J = 3.2, 1.2 Hz, 6H), 3.64 (d, J = 1.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 201.1, 194.3, 163.4, 156.7, 155.1, 153.3, 139.0, 132.8, 130.1, 129.5, 129.1, 128.1, 126.5, 126.1, 124.9, 121.6, 114.4, 113.5, 112.3, 105.6, 75.44, 55.8, 55.4, 55.4, 43.3.

IR (KBr, cm^{-1}): 3433, 1697, 1631, 1598, 1511, 1492, 1384, 1350, 1246.

HRMS (ESI): m/z calcd for $C_{31}H_{28}NO_5^+$ $(M+H)^+$ 494.1962, found 494.2111.

5-methoxy-1-(4-methoxyphenyl)-2-(4-oxotetrahydro-2*H*-thiopyran-3-yl)-2-phenylindolin-3-one (**4h**)



Compound **4h** was synthesized according to general procedure **3.3** starting from bis(4-

methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and tetrahydro-4*H*-thiopyran-4-one. **4h** was obtained in 59% yield (54.2 mg) as yellow solid, dr ~ 20:1.

mp:182.6-185.1℃

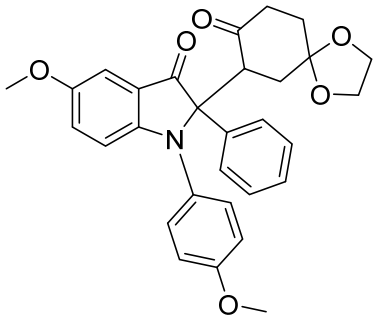
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 – 7.24 (m, 4H), 7.05 (ddd, J = 8.9, 5.4, 1.9 Hz, 3H), 6.85 – 6.80 (m, 2H), 6.63 (d, J = 8.2 Hz, 2H), 6.39 (d, J = 8.9 Hz, 1H), 3.95 (dd, J = 12.1, 3.8 Hz, 1H), 3.85 (d, J = 16.5 Hz, 6H), 3.61 (dd, J = 14.1, 12.0 Hz, 1H), 3.07 (dt, J = 13.6, 8.1 Hz, 1H), 2.97 – 2.91 (m, 1H), 2.85 (dt, J = 14.1, 3.5 Hz, 1H), 2.77 – 2.72 (m, 2H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 206.8, 203.2, 158.7, 155.8, 153.0, 136.9, 131.3, 130.8, 128.7, 128.4, 127.5, 127.1, 122.1, 114.7, 112.1, 103.9, 75.7, 59.9, 55.9, 55.5, 45.7, 32.6, 32.0.

IR (KBr, cm^{-1}): 3427, 1691, 1680, 1631, 1603, 1577, 1510, 1493, 1434, 1337, 1247, 1138, 1029, 842, 601.

HRMS (ESI): m/z calcd for $C_{27}H_{26}NO_4S^+$ $(M+H)^+$ 460.1577, found 460.1579.

5-methoxy-1-(4-methoxyphenyl)-2-(8-oxo-1,4-dioxaspiro[4.5]decan-7-yl)-2-phenylindolin-3-one (**4i**)



Compound **4i** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1,4-dioxaspiro[4.5]decan-8-one. **4i** was obtained in 68% yield (67.9 mg) as yellow solid.

mp: 211.4-212.6℃

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.15 (m, 4H), 7.01 (dd, J = 8.8, 2.7 Hz, 3H), 6.80 – 6.77 (m, 2H), 6.52 (d, J = 155.3 Hz, 3H), 3.99 (ddd, J = 6.2, 4.5, 1.2 Hz, 2H), 3.92 (qd, J = 5.9, 2.8 Hz, 2H), 3.87 – 3.84 (m, 1H), 3.81 (s, 3H), 3.79 (s, 3H), 2.63 (td, J = 13.2, 8.0 Hz, 2H), 2.04 – 1.90 (m, 3H).

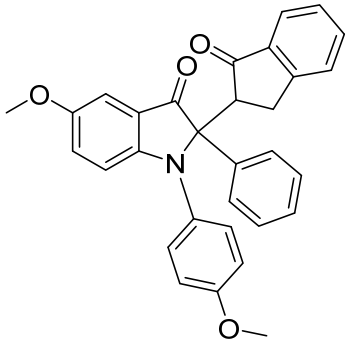
^{13}C NMR (151 MHz, $CDCl_3$): δ 207.7, 158.5, 156.2, 152.8, 137.3, 131.4, 130.8, 128.5, 128.0, 127.4, 127.2, 114.6, 111.9, 107.7, 104.0, 64.7, 64.6, 55.8, 55.4, 51.7, 38.7, 35.8,

35.3.

IR (KBr, cm^{-1}): 3425, 1722, 1690, 1631, 1606, 1577, 1511, 1493, 1434, 1340, 1286, 1248, 1146, 1031.

HRMS (ESI): m/z calcd for $C_{30}H_{30}NO_6^+$ $(M+H)^+$ 500.2068, found 500.2070.

5-methoxy-1-(4-methoxyphenyl)-2-(1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2-phenylindolin-3-one (**4j-syn**)



Compound **4j-syn** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 2,3-dihydro-1*H*-inden-1-one. **4j-syn** was obtained in 46% yield (43.0 mg) as yellow solid.

mp: 220.2-221.3°C

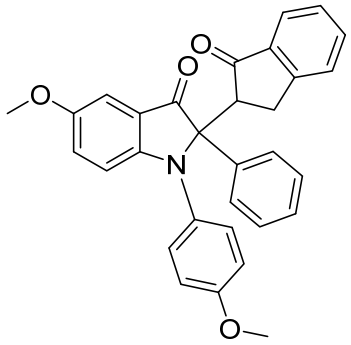
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.58 (d, J = 7.5 Hz, 2H), 7.52 (d, J = 7.6 Hz, 1H), 7.40 (t, J = 7.6 Hz, 2H), 7.36 – 7.31 (m, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.14 (d, J = 2.7 Hz, 1H), 7.08 (dd, J = 8.9, 2.7 Hz, 1H), 6.96 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 8.4 Hz, 2H), 6.77 (d, J = 8.9 Hz, 1H), 6.35 (d, J = 7.6 Hz, 2H), 4.39 - 4.29 (m, 1H), 3.79 (s, 3H), 3.55 (s, 3H), 3.32 (dd, J = 17.8, 8.9 Hz, 1H), 2.71 (dd, J = 17.8, 4.4 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 203.5, 200.2, 157.5, 156.7, 153.2, 152.8, 138.1, 137.2, 134.0, 131.8, 129.0, 128.0, 127.9, 127.2, 127.1, 127.0, 125.9, 123.4, 119.7, 113.7, 111.2, 105.4, 79.0, 55.8, 55.3, 30.6.

IR (KBr, cm^{-1}): 3431, 1707, 1693, 1631, 1606, 1510, 1489, 1335, 1292, 1276, 1245, 1025.

HRMS (ESI): m/z calcd for $C_{31}H_{26}NO_4^+$ $(M+H)^+$ 476.1856, found 476.1860.

5-methoxy-1-(4-methoxyphenyl)-2-(1-oxo-2,3-dihydro-1*H*-inden-2-yl)-2-phenylindolin-3-one (**4j-anti**)



Compound **4j-anti** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 2,3-dihydro-1*H*-inden-1-one. **4j-anti** was obtained in 26% yield (25.0 mg) as yellow solid.

mp: 218.5-220.8℃

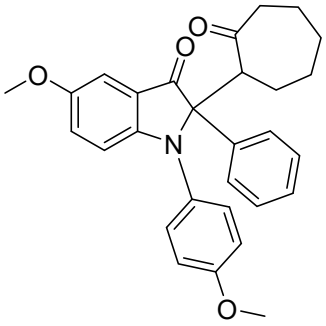
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.45 (t, J = 7.2 Hz, 1H), 7.41 – 7.32 (m, 3H), 7.12 (dd, J = 9.0, 2.8 Hz, 1H), 7.01 (d, J = 2.7 Hz, 1H), 6.91 (d, J = 8.2 Hz, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.22 (dd, J = 17.1, 8.2 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 203.69, 137.23, 134.49, 130.78, 128.43, 128.17, 127.58, 126.80, 125.78, 123.42, 114.02, 111.65, 55.80, 55.37, 47.35, 31.45, 30.20, 29.71.

IR (KBr, cm^{-1}): 3431, 1707, 1693, 1631, 1606, 1510, 1489, 1335, 1292, 1276, 1245, 1025.

HRMS (ESI): m/z calcd for $C_{31}H_{26}NO_4^+$ $(M+H)^+$ 476.1856, found 476.1859.

5-methoxy-1-(4-methoxyphenyl)-2-(2-oxocycloheptyl)-2-phenylindolin-3-one (**4k**)



Compound **4k** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and cycloheptanone. **4k** was obtained in 52% yield (47.5 mg) as brown solid, dr ~ 10:1.

mp: 75.9-77.8℃

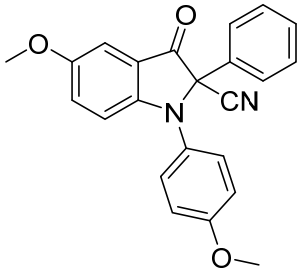
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.25 – 7.20 (m, 4H), 7.09 – 7.05 (m, 2H), 7.00 (dd, J = 8.9, 2.7 Hz, 1H), 6.78 – 6.74 (m, 2H), 6.67 (d, J = 8.4 Hz, 2H), 6.46 (d, J = 8.9 Hz, 1H), 3.85 (dd, J = 10.9, 2.4 Hz, 1H), 3.82 (s, 3H), 3.78 (s, 3H), 2.36 – 2.30 (m, 2H), 2.09 – 2.04 (m, 1H), 1.92 – 1.80 (m, 4H), 1.63 – 1.56 (m, 1H), 1.40 – 1.34 (m, 1H), 1.23 – 1.17 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 211.4, 203.2, 158.5, 156.0, 153.3, 138.7, 132.3, 130.0, 128.9, 128.4, 127.6, 127.1, 122.6, 114.9, 112.2, 104.5, 56.8, 56.2, 55.7, 43.7, 29.5, 29.0, 26.7, 24.3.

IR (KBr, cm^{-1}): 3438, 2930, 1711, 1693, 1631, 1511, 1493, 1450, 1329, 1292, 1275, 1245, 1029.

HRMS (ESI): m/z calcd for $C_{29}H_{30}NO_4^+$ $(M+H)^+$ 456.2170, found 456.2171.

5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindoline-2-carbonitrile (**4l**)



Compound **4l** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and TMSCN. **4l** was obtained in 72% yield (53.3 mg) as brown solid.

mp: 99.9-101.6℃

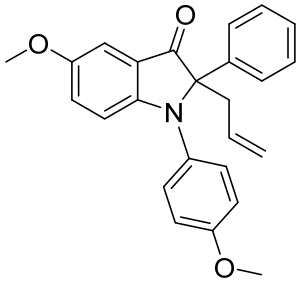
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 (dd, J = 6.6, 2.9 Hz, 2H), 7.42 – 7.38 (m, 3H), 7.23 (dd, J = 9.0, 2.7 Hz, 1H), 7.13 (d, J = 8.9 Hz, 2H), 7.11 (d, J = 2.6 Hz, 1H), 6.90 (d, J = 9.0 Hz, 1H), 6.85 (d, J = 8.9 Hz, 2H), 3.81 (s, 3H), 3.77 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 191.1, 158.7, 156.5, 154.4, 132.8, 131.1, 129.6, 129.3, 129.2, 127.5, 126.4, 117.5, 115.1, 115.0, 113.0, 105.6, 73.4, 55.9, 55.4.

IR (KBr, cm^{-1}): 3414, 2996, 2959, 2929, 1717, 1509, 1489, 1439, 1337, 1294, 1282, 1246, 1031, 1019, 824.

HRMS (ESI): m/z calcd for $C_{23}H_{19}N_2O_3^+$ $(M+H)^+$ 371.1390, found 371.1390.

2-allyl-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4m**)



Compound **4m** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and allyltrimethylsilane. **4m** was obtained in 90% yield (69.3 mg) as orange solid.

mp: 154.8-155.8℃

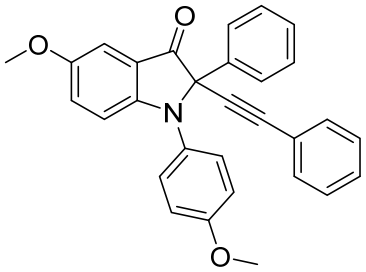
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.36 – 7.27 (m, 5H), 7.16 (dd, J = 9.0, 2.7 Hz, 1H), 7.11 (d, J = 9.0 Hz, 1H), 7.06 (d, J = 2.6 Hz, 1H), 7.02 – 6.96 (m, 2H), 6.81 – 6.74 (m, 2H), 5.48 (ddt, J = 17.1, 10.2, 6.9 Hz, 1H), 4.98 – 4.89 (m, 2H), 3.78 (s, 3H), 3.77 (s, 3H), 3.31 (dd, J = 14.0, 6.9 Hz, 1H), 2.83 (dd, J = 14.0, 7.0 Hz, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 201.2, 156.7, 155.7, 153.0, 138.9, 132.3, 131.1, 128.9, 127.9, 127.9, 126.2, 125.1, 120.1, 119.7, 114.3, 111.9, 105.0, 77.1, 55.8, 55.4, 37.4.

IR (KBr, cm^{-1}): 3436, 1703, 1631, 1603, 1540, 1511, 1489, 1441, 1349, 1283, 1245, 1027, 824.

HRMS (ESI): m/z calcd for $C_{25}H_{24}NO_3^+$ $(M+H)^+$ 386.1750, found 386.1751.

5-methoxy-1-(4-methoxyphenyl)-2-phenyl-2-(phenylethynyl)indolin-3-one (**4n**)



Compound **4m** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and trimethyl(phenylethynyl)silane. **4n** was obtained in 87% yield (77.5 mg) as orange solid.

mp: 60.8-61.5℃

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.60 (d, J = 7.4 Hz, 2H), 7.37 – 7.31 (m, 5H), 7.25

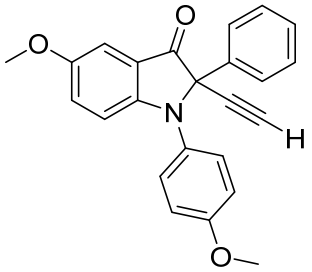
(qd, J = 6.8, 2.0 Hz, 3H), 7.18 (dd, J = 8.9, 2.7 Hz, 1H), 7.14 (d, J = 8.7 Hz, 3H), 6.92 (d, J = 9.0 Hz, 1H), 6.81 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H), 3.75 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.3, 157.9, 156.3, 153.6, 137.0, 132.9, 131.8, 128.7, 128.6, 128.5, 128.3, 128.1, 127.5, 126.9, 122.0, 118.3, 114.3, 112.9, 105.6, 87.2, 84.5, 74.7, 55.8, 55.3.

IR (KBr, cm^{-1}): 3434, 2929, 1712, 1631, 1511, 1489, 1442, 1335, 1277, 1246, 1029, 824, 756, 690.

HRMS (ESI): m/z calcd for $C_{30}H_{24}NO_3^+$ $(M+H)^+$ 446.1751, found 446.1752.

2-ethynyl-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4o**)



Compound **4o** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and ethynyltrimethylsilane. **4o** was obtained in 43% yield (31.7 mg) as yellow solid.

mp: 167.8-169.2℃

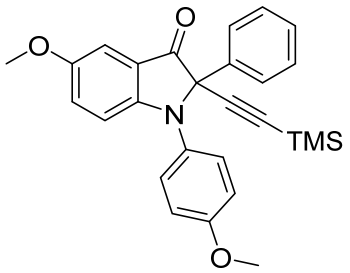
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.54 (d, J = 7.0 Hz, 2H), 7.35 (dt, J = 15.8, 5.0 Hz, 3H), 7.18 (dd, J = 8.9, 2.6 Hz, 1H), 7.11 (d, J = 2.6 Hz, 1H), 7.09 (d, J = 8.9 Hz, 2H), 6.93 (d, J = 9.0 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 2.53 (s, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 195.9, 157.8, 156.2, 153.7, 136.3, 132.6, 128.8, 128.6, 128.5, 127.2, 126.8, 118.1, 114.4, 112.8, 105.6, 79.0, 75.7, 73.8, 55.8, 55.3.

IR (KBr, cm^{-1}): 3433, 3261, 1743, 1697, 1631, 1604, 1509, 1486, 1375, 1351, 1247, 1049.

HRMS (ESI): m/z calcd for $C_{24}H_{20}NO_3^+$ $(M+H)^+$ 370.1438, found 370.1438

5-methoxy-1-(4-methoxyphenyl)-2-phenyl-2-((trimethylsilyl)ethynyl)indolin-3-one (**4o'**)



Compound **4o'** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1,2-bis(trimethylsilyl)ethyne. **4o'** was obtained in 18% yield (15.9 mg) as brown solid.

mp: 171.2-172.5℃

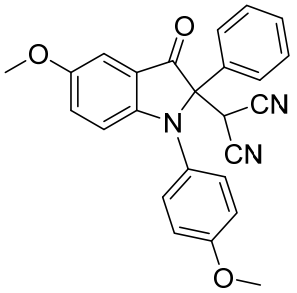
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.52 (d, J = 7.5 Hz, 2H), 7.38 – 7.28 (m, 3H), 7.17 (dd, J = 8.9, 2.2 Hz, 1H), 7.11 (d, J = 2.4 Hz, 1H), 7.08 (d, J = 8.6 Hz, 2H), 6.89 (d, J = 8.9 Hz, 1H), 6.79 (d, J = 8.6 Hz, 2H), 3.80 (s, 3H), 3.77 (s, 3H), 0.08 (s, 9H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 196.2, 157.9, 156.5, 153.6, 136.9, 132.9, 128.7, 128.4, 128.3, 127.7, 126.9, 118.3, 114.2, 113.0, 105.6, 99.9, 92.9, 74.9, 55.9, 55.4.

IR (KBr, cm^{-1}): 3426, 2957, 1711, 1631, 1608, 1512, 1487, 1339, 1278, 1248, 1030, 846.

HRMS (ESI): m/z calcd for $C_{27}H_{28}NO_3Si^+$ $(M+H)^+$ 442.1833, found 442.1835.

2-(5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindolin-2-yl)malononitrile (**4p**)



Compound **4p** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 2-(trimethylsilyl)malononitrile. **4p** was obtained in 62% yield (50.7 mg) as brown solid.

mp: 176.5-178.2℃

^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 – 7.40 (m, 3H), 7.35 (dd, J = 6.5, 2.7 Hz, 2H), 7.23 (dd, J = 14.6, 5.7 Hz, 3H), 7.08 (d, J = 2.6 Hz, 1H), 6.93 (d, J = 9.0 Hz, 1H), 6.88

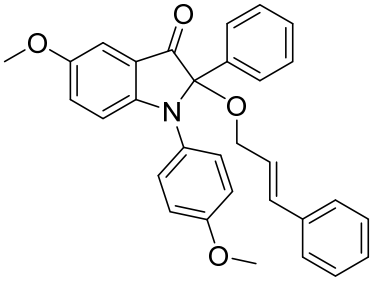
(d, J = 8.9 Hz, 2H), 4.93 (s, 1H), 3.80 (s, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 195.4, 159.2, 157.3, 154.2, 132.8, 130.0, 129.7, 129.6, 129.0, 128.8, 126.2, 117.6, 115.1, 112.2, 109.9, 109.8, 105.2, 75.7, 55.8, 55.4, 27.8.

IR (KBr, cm^{-1}): 3438, 1691, 1631, 1603, 1512, 1493, 1344, 1294, 1280, 1242, 1030.

HRMS (ESI): m/z calcd for $C_{25}H_{20}N_3O_3^+$ $(M+H)^+$ 410.1499, found 410.1499.

2-(cinnamyloxy)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4q**)



Compound **4q** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and (*E*)-3-phenylprop-2-en-1-ol. **4q** was obtained in 80% yield (76.4 mg) as orange solid.

mp: 71.8-73.1℃

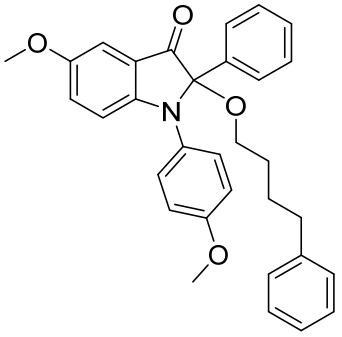
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.45 - 7.42 (m, 2H), 7.38 - 7.30 (m, 6H), 7.26 (dd, J = 10.7, 7.2 Hz, 4H), 7.23 - 7.21 (m, 2H), 7.13 (d, J = 9.0 Hz, 1H), 7.07 (d, J = 2.8 Hz, 1H), 6.88 - 6.83 (m, 2H), 6.64 (d, J = 16.1 Hz, 1H), 6.39 (dt, J = 16.0, 5.7 Hz, 1H), 4.34 (ddd, J = 12.2, 5.7, 1.6 Hz, 1H), 4.08 (ddd, J = 12.1, 6.2, 1.6 Hz, 1H), 3.76 (s, 3H), 3.67 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 198.3, 157.0, 155.1, 153.6, 136.7, 136.6, 132.4, 131.5, 129.1, 128.9, 128.7, 128.3, 126.9, 126.6, 125.6, 125.4, 119.0, 115.0, 112.4, 106.0, 95.8, 64.5, 56.2, 55.6.

IR (KBr, cm^{-1}): 3425, 1710, 1631, 1576, 1513, 1487, 1448, 1281, 1249, 1144, 1026, 824, 739.

HRMS (ESI): m/z calcd for $C_{31}H_{28}NO_4^+$ $(M+H)^+$ 478.2013, found 478.2017.

5-methoxy-1-(4-methoxyphenyl)-2-phenyl-2-(4-phenylbutoxy)indolin-3-one (**4r**)



Compound **4r** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 4-phenylbutan-1-ol. **4r** was obtained in 49% yield (48.3 mg) as orange viscous oily liquid.

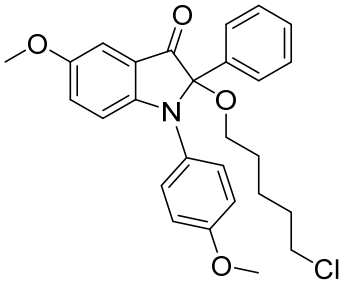
^{1}H NMR (600 MHz, $CHCl_3$): δ 7.50 – 7.47 (m, 2H), 7.32 –7.26 (m, 5H), 7.24 – 7.16 (m, 7H), 7.13 (d, J = 2.8 Hz, 1H), 6.79 (d, J = 9.0 Hz, 2H), 3.83 (s, 3H), 3.75 (s, 3H), 3.68 (dd, J = 7.6, 5.3 Hz, 1H), 3.54 (q, J = 4.6, 3.3 Hz, 1H), 2.68 – 2.61 (m, 2H), 1.73 (d, J = 6.4 Hz, 4H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 198.5, 156.8, 155.0, 153.5, 142.5, 136.8, 131.6, 128.9, 128.9, 128.7, 128.7, 128.6, 126.4, 126.1, 124.9, 119.0, 115.0, 114.9, 112.4, 106.0, 96.0, 63.4, 56.1, 55.7, 55.6, 55.4, 35.2, 29.8, 27.9.

IR (KBr, cm^{-1}): 3452, 1631, 1595, 1539, 1510, 1489, 1384, 1350, 1244, 1109, 728.

HRMS (ESI): m/z calcd for $C_{32}H_{32}NO_4^+$ $(M+H)^+$ 494.2326, found 494.2325.

2-((5-chloropentyl)oxy)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4s**)



Compound **4s** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 5-chloropentan-1-ol. **4s** was obtained in 55% yield (51.2 mg) as orange viscous oily liquid.

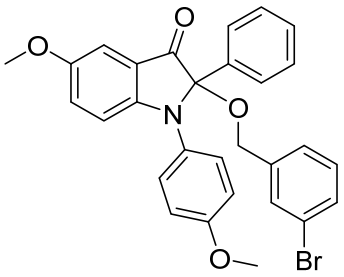
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.35 (dt, J = 6.2, 1.6 Hz, 2H), 7.31 – 7.22 (m, 4H), 7.20 – 7.16 (m, 2H), 7.14 (d, J = 9.0 Hz, 1H), 7.08 (d, J = 2.8 Hz, 1H), 6.87 – 6.82 (m, 2H), 3.76 (s, 3H), 3.67 (s, 3H), 3.64 – 3.58 (m, 3H), 3.33 (dt, J = 8.7, 6.3 Hz, 1H), 1.73 – 1.66 (m, 2H), 1.64 – 1.57 (m, 2H), 1.48 – 1.42 (m, 2H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 198.4, 156.8, 155.0, 153.5, 136.8, 131.6, 128.9, 128.6, 126.5, 124.9, 119.0, 114.9, 112.4, 106.0, 96.0, 63.3, 56.1, 55.5, 45.7, 32.2, 28.7, 23.5.

IR (KBr, cm^{-1}): 3448, 1631, 1596, 1509, 1383, 1350, 1215, 758.

HRMS (ESI): m/z calcd for $C_{27}H_{29}ClNO_4^+$ $(M+H)^+$ 466.1780, found 466.1780.

2-((3-bromobenzyl)oxy)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4t**)



Compound **4t** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and (3-bromophenyl)methanol. **4t** was obtained in 83% yield (87.8 mg) as orange viscous oily liquid.

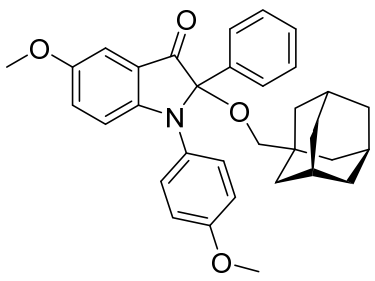
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.49 – 7.46 (m, 1H), 7.41 – 7.35 (m, 4H), 7.34 (dd, J = 9.0, 2.8 Hz, 1H), 7.32 – 7.25 (m, 4H), 7.19 – 7.14 (m, 3H), 7.12 (d, J = 2.8 Hz, 1H), 6.86 – 6.81 (m, 2H), 4.70 (d, J = 11.6 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 3.78 (s, 3H), 3.67 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 198.0, 157.0, 155.2, 153.7, 140.3, 136.5, 131.4, 131.0, 130.9, 130.5, 129.1, 129.1, 128.8, 126.9, 126.5, 125.1, 122.1, 119.1, 115.0, 112.7, 106.1, 96.1, 79.7, 65.0, 56.2, 55.6.

IR (KBr, cm^{-1}): 3448, 2163, 1631, 1596, 1509, 1383, 1350, 1215, 758.

HRMS (ESI): m/z calcd for $C_{29}H_{25}BrNO_4^+$ $(M+H)^+$ 530.0961, found 530.0966.

2-(((3*r*,5*r*,7*r*)-adamantan-1-yl)methoxy)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4u**)



Compound **4u** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and ((3*r*,5*r*,7*r*)-adamantan-1-yl)methanol. **4u** was obtained in 83% yield (84.5 mg) as yellow solid.

mp: 155.9-156.6°C

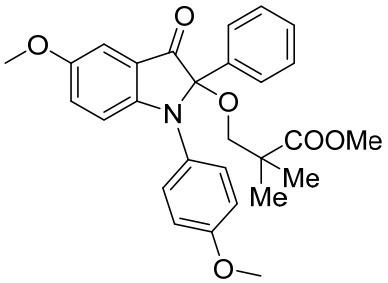
^{1}H NMR (600 MHz, $CHCl_3$): δ 7.45 – 7.40 (m, 2H), 7.21 (dd, J = 10.4, 7.1 Hz, 3H), 7.16 (dd, J = 9.0, 7.4 Hz, 4H), 7.08 (d, J = 2.7 Hz, 1H), 6.75 (d, J = 8.8 Hz, 2H), 3.79 (s, 3H), 3.72 (s, 3H), 3.23 (d, J = 8.2 Hz, 1H), 2.99 (d, J = 8.2 Hz, 1H), 1.98 – 1.94 (m, 3H), 1.71 (d, J = 12.0 Hz, 3H), 1.65 (d, J = 12.3 Hz, 3H), 1.58 (d, J = 2.9 Hz, 6H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.4, 156.5, 154.9, 153.2, 137.0, 132.0, 128.5, 128.4, 128.4, 128.1, 127.0, 126.3, 126.2, 124.1, 119.6, 114.3, 112.1, 105.5, 96.0, 73.8, 55.9, 55.8, 55.4, 55.3, 39.7, 39.1, 37.2, 37.1, 33.9, 28.2, 28.2.

IR (KBr, cm^{-1}): 3437, 2906, 2846, 1712, 1631, 1608, 1511, 1492, 1439, 1348, 1244, 1067, 1032, 817.

HRMS (ESI): m/z calcd for $C_{33}H_{36}NO_4^+$ $(M+H)^+$ 510.2639, found 510.2637.

methyl 3-((5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindolin-2-yl)oxy)-2,2-dimethylpropanoate (**4v**)



Compound **4v** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and methyl 3-hydroxy-2,2-dimethylpropanoate. **4v** was obtained in 64% yield (60.8 mg) as orange solid.

mp: 55.6-57.4°C

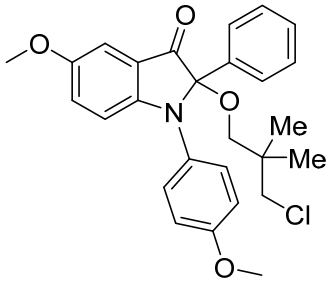
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.31 (dd, J = 9.0, 2.8 Hz, 1H), 7.27 – 7.21 (m, 5H), 7.17 (dd, J = 9.0, 4.1 Hz, 3H), 7.08 (d, J = 2.8 Hz, 1H), 6.86 – 6.81 (m, 2H), 3.77 (s, 3H), 3.75 (d, J = 8.1 Hz, 1H), 3.67 (s, 3H), 3.63 (s, 3H), 3.36 (s, 3H), 3.26 (d, J = 8.1 Hz, 1H), 1.19 (s, 3H), 1.11 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 197.9, 176.1, 156.7, 154.9, 153.6, 136.6, 131.7, 128.9, 128.7, 126.4, 124.7, 119.2, 114.8, 112.8, 106.0, 95.5, 79.6, 70.3, 56.1, 55.6, 52.3, 43.2, 22.7, 22.5.

IR (KBr, cm^{-1}): 3435, 2934, 2835, 1737, 1722, 1631, 1513, 1492, 1440, 1333, 1280, 1247, 1154, 1079, 1029, 824.

HRMS (ESI): m/z calcd for $C_{28}H_{30}NO_6^+$ $(M+H)^+$ 476.2068, found 476.2063.

2-(3-chloro-2,2-dimethylpropoxy)-5-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4w**)



Compound **4w** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 3-chloro-2,2-dimethylpropan-1-ol. **4w** was obtained in 89% yield (82.8 mg) as orange viscous oily liquid.

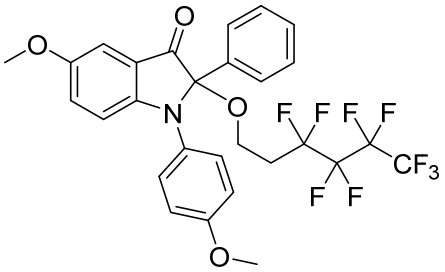
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.35 – 7.25 (m, 6H), 7.18 (dd, J = 10.2, 9.0 Hz, 3H), 7.08 (d, J = 2.8 Hz, 1H), 6.85 – 6.81 (m, 2H), 3.77 (s, 3H), 3.67 (s, 3H), 3.57 (s, 2H), 3.50 (d, J = 8.4 Hz, 1H), 3.13 (d, J = 8.4 Hz, 1H), 0.97 (s, 3H), 0.94 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 198.1, 156.7, 154.9, 153.6, 136.9, 131.7, 129.0, 128.9, 128.7, 126.4, 124.6, 119.2, 114.8, 112.8, 106.0, 95.6, 68.9, 56.1, 55.6, 53.0, 36.9, 22.8, 22.7.

IR (KBr, cm^{-1}): 3452, 1631, 1604, 1555, 1544, 1510, 1489, 1350, 1077, 1031, 738.

HRMS (ESI): m/z calcd for $C_{27}H_{29}ClNO_4^+$ $(M+H)^+$ 466.1780, found 466.1780.

5-methoxy-1-(4-methoxyphenyl)-2-((3,3,4,4,5,5,6,6,6-nonafluorohexyl)oxy)-2-phenylindolin-3-one (**4x**)



Compound **4x** was synthesized according to general procedure **3.3** starting from bis(4-

methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 3,3,4,4,5,5,6,6,6-nonafluorohexan-1-ol. **4x** was obtained in 44% yield (53.4 mg) as brown viscous oily liquid.

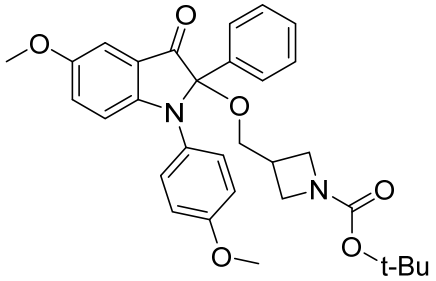
^{1}H NMR (600 MHz, $CHCl_3$): δ 7.46 – 7.37 (m, 2H), 7.28 – 7.18 (m, 4H), 7.16 – 7.01 (m, 4H), 6.82 – 6.70 (m, 2H), 3.96 (ddt, J = 10.0, 6.6, 4.9 Hz, 1H), 3.80 (s, 3H), 3.78 (s, 1H), 3.73 (s, 3H), 2.56 – 2.35 (m, 2H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 198.4, 156.8, 155.0, 153.5, 136.8, 131.6, 128.9, 128.6, 126.5, 124.9, 119.0, 114.9, 112.4, 106.0, 96.0, 79.7, 63.3, 56.1, 55.5, 45.7, 32.2, 28.7, 23.5.

IR (KBr, cm^{-1}): 3456, 1772, 1734, 1717, 1631, 1544, 1510, 1489, 1350, 1078.

HRMS (ESI): m/z calcd for $C_{28}H_{23}F_9NO_4^+$ $(M+H)^+$ 608.1478, found 608.1475.

tert-butyl 3-(((5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindolin-2-yl)oxy)methyl)azetidine-1-carboxylate (**4y**)



Compound **4y** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and *tert*-butyl 3-(hydroxymethyl)azetidine-1-carboxylate. **4y** was obtained in 56% yield (59.4 mg) as brown solid.

mp: 65.5-66.7℃

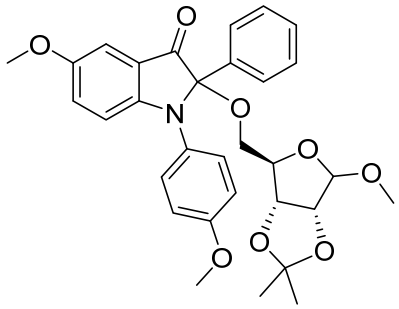
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.32 (dq, J = 5.8, 3.3, 2.7 Hz, 3H), 7.27 (dd, J = 5.1, 2.0 Hz, 3H), 7.15 (dd, J = 9.1, 3.7 Hz, 3H), 7.07 (d, J = 2.8 Hz, 1H), 6.87 - 6.83 (m, 2H), 5.75 (s, 1H), 3.90 - 3.81 (m, 2H), 3.77 (s, 3H), 3.74 (d, J = 5.5 Hz, 1H), 3.68 (s, 3H), 3.59 (dd, J = 8.5, 5.4 Hz, 1H), 3.55 (d, J = 8.3 Hz, 1H), 3.40 (dd, J = 9.3, 6.3 Hz, 1H), 2.81 - 2.74 (m, 1H), 1.37 (s, 9H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 198.3, 156.8, 156.1, 155.1, 153.6, 136.6, 131.5, 129.0, 129.0, 128.8, 126.4, 124.8, 119.0, 114.9, 112.6, 106.0, 95.8, 78.8, 65.2, 56.2, 55.6, 55.4, 28.5.

IR (KBr, cm^{-1}): 3434, 2930, 1710, 1692, 1631, 1513, 1487, 1448, 1389, 1245, 1133, 1028, 827.

HRMS (ESI): m/z calcd for $C_{31}H_{35}N_2O_6^+$ $(M+H)^+$ 531.2490, found 531.2483.

5-methoxy-2-(((3a*R*,4*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methoxy)-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**4z**)



Compound **4z** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and ((3a*R*,4*R*,6a*R*)-6-methoxy-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)methanol. **4z** was obtained in 46% yield (50.3 mg) as orange viscous oily liquid, dr = 1.35:1.

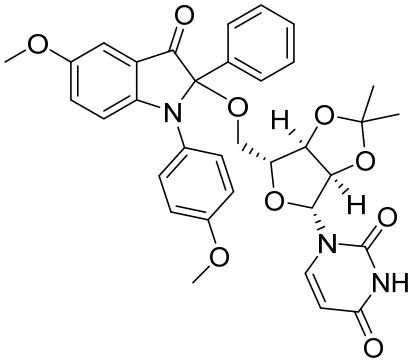
^{1}H NMR (major + minor) (600 MHz, DMSO-d$_6$): δ 7.41 - 7.38 (m, 2H), 7.36 - 7.25 (m, 10H), 7.23 - 7.11 (m, 7H), 7.08 (dd, J = 5.7, 2.8 Hz, 2H), 6.91 - 6.88 (m, 2H), 6.88 - 6.84 (m, 2H), 4.92 (s, 1H), 4.89 (s, 1H), 4.71 (d, J = 6.0 Hz, 1H), 4.53 (d, J = 5.9 Hz, 1H), 4.37 (d, J = 5.9 Hz, 1H), 4.23 (dt, J = 14.1, 6.8 Hz, 2H), 4.17 (d, J = 6.0 Hz, 1H), 3.77 (d, J = 2.4 Hz, 6H), 3.68 (d, J = 1.2 Hz, 6H), 3.61 (dd, J = 9.3, 5.9 Hz, 1H), 3.51 (dd, J = 9.2, 7.1 Hz, 1H), 3.21 (s, 3H), 3.11 (s, 2H), 1.39 (s, 3H), 1.35 (s, 3H), 1.26 (s, 3H), 1.14 (s, 3H).

^{13}C NMR (major + minor) (151 MHz, DMSO-d$_6$): δ 198.0, 197.6, 156.9, 156.8, 155.1, 154.8, 153.7, 136.6, 136.3, 131.5, 131.4, 129.1, 129.1, 129.0, 129.0, 128.8, 126.5, 126.4, 125.0, 124.5, 119.0, 115.0, 114.9, 112.6, 112.6, 112.1, 111.9, 109.2, 106.1, 106.1, 96.0, 95.9, 85.0, 84.8, 84.5, 81.9, 81.4, 65.2, 64.7, 56.2, 55.6, 54.9, 54.8, 26.8, 26.6, 25.2, 24.7.

IR (KBr, cm^{-1}): 3452, 1772, 1734, 1631, 1555, 1544, 1510, 1489, 1350, 1107, 761.

HRMS (ESI): m/z calcd for $C_{31}H_{34}NO_8^+$ $(M+H)^+$ 548.2279, found 548.2280.

1-((3a*R*,4*R*,6*R*,6a*R*)-6-(((5-methoxy-1-(4-methoxyphenyl)-3-oxo-2-phenylindolin-2-yl)oxy)methyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)pyrimidine-2,4(1*H*,3*H*)-dione (**4aa**)



Compound **4aa** was synthesized according to general procedure **3.3** starting from bis(4-methoxyphenyl)amine, 2-oxo-2-phenylacetaldehyde and 1-((3a*R*,4*R*,6*R*,6a*R*)-6-(hydroxymethyl)-2,2-dimethyltetrahydrofuro[3,4-*d*][1,3]dioxol-4-yl)pyrimidine-2,4(1*H*,3*H*)-dione. **4aa** was obtained in 36% yield (45.2 mg) as brown solid, dr = 1:1.

mp: 105.2-107.5°C

4aa-diastereoisomer A: ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 11.44 (d, J = 2.2 Hz, 1H), 7.68 (d, J = 8.0 Hz, 1H), 7.36 – 7.22 (m, 7H), 7.20 – 7.17 (m, 2H), 7.12 – 7.07 (m, 2H), 6.79 – 6.75 (m, 2H), 5.86 (d, J = 2.1 Hz, 1H), 5.42 (dd, J = 8.0, 2.2 Hz, 1H), 5.03 (dd, J = 6.3, 2.2 Hz, 1H), 4.86 (dd, J = 6.4, 4.5 Hz, 1H), 4.18 (q, J = 4.4 Hz, 1H), 3.88 (dd, J = 10.3, 3.8 Hz, 1H), 3.77 (s, 3H), 3.65 (s, 3H), 3.50 (dd, J = 10.3, 4.8 Hz, 1H), 1.49 (s, 3H), 1.29 (s, 3H), 1.17 (t, J = 7.1 Hz, 1H).

4aa-diastereoisomer A: ^{13}C NMR (151 MHz, DMSO-d$_6$): δ 197.40, 163.15, 156.54, 154.86, 153.23, 150.24, 142.32, 135.70, 130.85, 128.61, 128.52, 128.43, 126.06, 125.01, 118.38, 114.29, 113.39, 112.08, 105.62, 101.78, 95.50, 91.20, 84.44, 83.56, 79.87, 62.96, 55.73, 55.06, 27.04, 25.23.

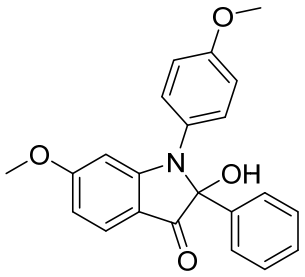
4aa-diastereoisomer B: ^{1}H NMR (600 MHz, DMSO-d$_6$): δ 11.35 (d, J = 2.2 Hz, 1H), 7.79 (d, J = 8.0 Hz, 1H), 7.35 – 7.22 (m, 7H), 7.20 (d, J = 8.8 Hz, 2H), 7.10 – 7.06 (m, 2H), 6.69 (d, J = 8.8 Hz, 2H), 5.82 (d, J = 2.0 Hz, 1H), 5.58 (dd, J = 8.0, 2.2 Hz, 1H), 5.02 (dd, J = 6.3, 2.0 Hz, 1H), 4.65 (dd, J = 6.4, 4.2 Hz, 1H), 4.31 (dt, J = 7.8, 3.7 Hz, 1H), 3.92 – 3.88 (m, 1H), 3.77 (s, 3H), 3.63 (s, 3H), 3.55 (dd, J = 9.7, 3.2 Hz, 1H), 1.50 (s, 3H), 1.26 (s, 3H), 1.17 (t, J = 7.1 Hz, 1H).

4aa-diastereoisomer B: ^{13}C NMR (151 MHz, DMSO-d$_6$): δ 197.63, 163.37, 156.60, 155.07, 153.26, 150.40, 143.53, 135.91, 130.88, 128.55, 128.34, 126.54, 126.11, 125.31, 118.40, 114.25, 113.35, 112.15, 105.71, 101.81, 95.49, 93.32, 91.26, 85.61, 83.66, 80.99, 80.62, 64.23, 61.41, 55.87, 55.08, 27.15, 25.33.

IR (KBr, cm^{-1}): 3437, 2924, 1710, 1692, 1678, 1631, 1577, 1513, 1489, 1450, 1247, 1081, 1029, 825.

HRMS (ESI): m/z calcd for $C_{34}H_{34}N_3O_9^+$ $(M+H)^+$ 628.2290, found 628.2282.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-phenylindolin-3-one (**5a**)



Compound **5a** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2-oxo-2-phenylacetaldehyde. **5a** was obtained in 87.0% yield (62.8 mg) as red solid.

mp: 110.3-112.2℃

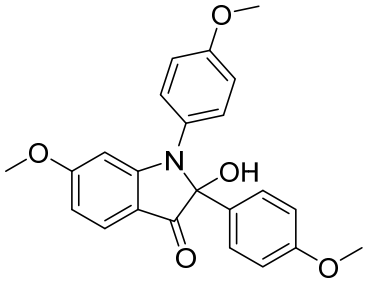
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.42 (dd, J = 7.6, 2.2 Hz, 2H), 7.27 (dd, J = 5.9, 4.1 Hz, 3H), 7.15 (dd, J = 9.0, 3.4 Hz, 3H), 7.08 (d, J = 2.8 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.80 – 6.75 (m, 2H), 3.79 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.0, 157.6, 156.0, 153.5, 137.1, 131.2, 128.7, 128.6, 128.5, 127.0, 126.1, 117.7, 114.5, 112.1, 106.0, 92.0, 56.0, 55.4.

IR (KBr, cm^{-1}): 3435, 1690, 1624, 1576, 1570, 1557, 1542, 1513, 1493, 1330, 1248, 1168, 1027, 825.

HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_4^+$ $(M+H)^+$ 362.1387, found 362.1381.

2-hydroxy-6-methoxy-1,2-bis(4-methoxyphenyl)indolin-3-one (**5b**)



Compound **5b** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-methoxyphenyl)ethan-1-one. **5b** was

obtained in 62.5% yield (48.9 mg) as orange solid.

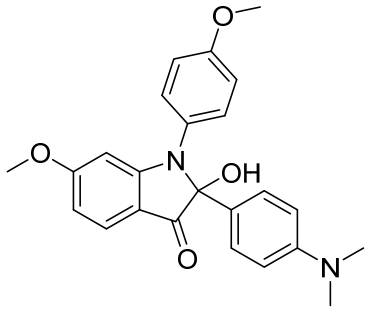
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.34 (d, J = 8.5 Hz, 2H), 7.14 (dd, J = 15.4, 8.9 Hz, 3H), 7.04 (s, 1H), 6.86 (d, J = 8.9 Hz, 1H), 6.81 – 6.74 (m, 4H), 3.76 (s, 3H), 3.74 (s, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 200.2, 159.5, 157.1, 154.9, 153.1, 132.0, 130.0, 128.0, 127.8, 126.8, 117.9, 114.7, 114.0, 111.7, 106.5, 92.2, 56.2, 55.6, 55.4.

IR (KBr, cm^{-1}): 3444, 1632, 1509, 1489, 1384, 1247, 1042, 593.

HRMS (ESI): m/z calcd for $C_{23}H_{22}NO_5^+$ $(M+H)^+$ 392.1492, found 392.1492.

2-(4-(dimethylamino)phenyl)-2-hydroxy-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5c**)



Compound **5c** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 1-(4-(dimethylamino)phenyl)-2,2-dihydroxyethan-1-one. **5c** was obtained in 46.1% yield (37.3 mg) as orange solid.

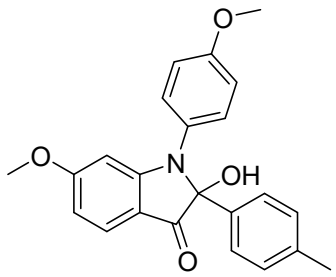
^{1}H NMR (600 MHz, $CDCl_3$): δ 10.05 (s, 1H), 7.86 (d, J = 8.6 Hz, 2H), 7.21 (d, J = 8.4 Hz, 2H), 7.06 – 6.90 (m, 5H), 6.67 (d, J = 8.6 Hz, 2H), 3.82 (s, 3H), 3.63 (s, 3H), 3.09 (s, 6H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 200.4, 156.9, 154.6, 152.9, 150.5, 132.3, 127.6, 127.4, 126.6, 124.9, 118.0, 114.7, 112.3, 111.5, 106.6, 92.6, 56.2, 55.6.

IR (KBr, cm^{-1}): 3445, 2926, 1589, 1509, 1488, 1438, 1375, 1244, 1159, 1034, 609.

HRMS (ESI): m/z calcd for $C_{24}H_{25}N_2O_4^+$ $(M+H)^+$ 405.1809, found 405.1803.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(p-tolyl)indolin-3-one (**5d**)



Compound **5d** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(p-tolyl)ethan-1-one. **5d** was obtained in 72.3% yield (54.2 mg) as brown viscous oily liquid.

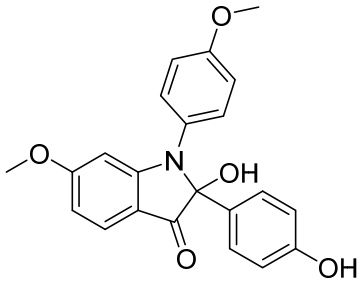
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.31 (d, J = 8.2 Hz, 2H), 7.18 – 7.15 (m, 2H), 7.13 (dd, J = 8.9, 2.8 Hz, 1H), 7.07 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 2.8 Hz, 1H), 6.87 (d, J = 8.9 Hz, 1H), 6.79 – 6.75 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H), 2.28 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 200.2, 157.5, 155.9, 153.4, 138.5, 134.1, 131.3, 129.3, 128.5, 126.9, 126.0, 117.7, 114.5, 112.0, 106.0, 92.1, 55.9, 55.4, 21.2.

IR (KBr, cm^{-1}): 3429, 1709, 1629 1510, 1489, 1439, 1279, 1245, 1178, 1033, 822.

HRMS (ESI): m/z calcd for $C_{23}H_{22}NO_4^+$ $(M+H)^+$376.1543, found 376.1541.

2-hydroxy-2-(4-hydroxyphenyl)-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5e**)



Compound **5e** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-hydroxyphenyl)ethan-1-one. **5e** was obtained in 59.1% yield (44.6 mg) as orange solid.

mp: 155-159℃

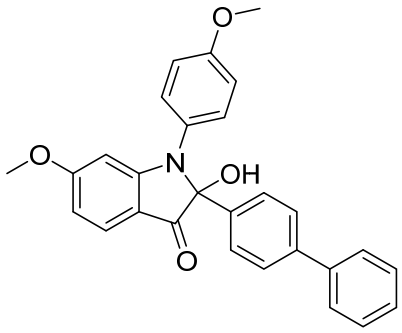
^{1}H NMR (600 MHz, DMSO-d_6): δ 9.42 (s, 1H), 7.25 – 7.19 (m, 3H), 7.18 – 7.12 (m, 3H), 7.03 (d, J = 2.8 Hz, 1H), 6.90 – 6.81 (m, 3H), 6.66 – 6.60 (m, 2H), 3.75 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 200.3, 157.6, 157.0, 154.8, 153.0, 132.1, 128.2, 127.9, 127.7, 126.8, 117.9, 115.4, 114.7, 111.6, 106.5, 92.2, 56.2, 55.6.

IR (KBr, cm^{-1}): 3364, 1673, 1512, 1459, 1340, 1237, 1169, 1133, 1100, 1026, 824.

HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_5^+$ $(M+H)^+$ 378.1336, found 378.1334.

2-([1,1'-biphenyl]-4-yl)-2-hydroxy-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5f**)



Compound **5f** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 1-([1,1'-biphenyl]-4-yl)-2,2-dihydroxyethan-1-one. **5f** was obtained in 73.0% yield (63.8 mg) as orange solid.

mp: 144-146°C

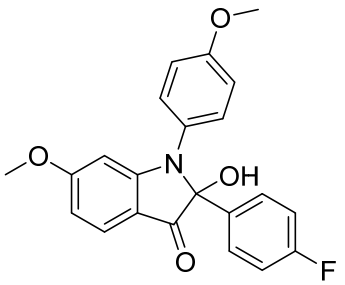
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.61 (d, J = 7.8 Hz, 2H), 7.59 – 7.56 (m, 2H), 7.46 (d, J = 8.6 Hz, 2H), 7.43 (q, J = 5.7, 3.9 Hz, 3H), 7.34 (d, J = 7.7 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.09 – 7.06 (m, 1H), 6.93 (d, J = 8.9 Hz, 1H), 6.89 – 6.84 (m, 2H), 3.76 (s, 3H), 3.68 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 199.9, 157.1, 155.1, 153.2, 140.3, 140.0, 137.4, 131.9, 129.4, 128.0, 127.3, 127.1, 127.0, 126.8, 117.9, 114.8, 111.7, 106.6, 92.3, 56.2, 55.6.

IR (KBr, cm^{-1}): 3422, 2929, 1676, 1513, 1491, 1447, 1334, 1293, 1249, 1026, 825, 759.

HRMS (ESI): m/z calcd for $C_{28}H_{24}NO_4^+$ $(M+H)^+$ 438.1670, found 438.1695.

2-(4-fluorophenyl)-2-hydroxy-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5g**)



Compound **5g** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 1-(4-fluorophenyl)-2,2-dihydroxyethan-1-one. **5g** was obtained in 91.4% yield (69.3 mg) as orange solid.

mp: 140-142℃

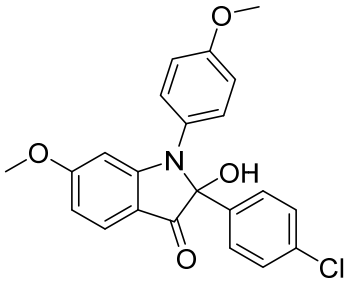
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.45 (s, 1H), 7.39 (dd, J = 8.6, 5.5 Hz, 2H), 7.23 (dd, J = 11.6, 7.6 Hz, 3H), 7.11 – 7.05 (m, 3H), 6.89 (d, J = 8.9 Hz, 1H), 6.86 (d, J = 8.8 Hz, 2H), 3.76 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 199.9, 163.1, 161.5, 157.3, 155.1, 153.2, 134.4, 131.7, 128.8, 128.1, 127.0, 117.7, 115.6, 115.5, 114.8, 111.8, 106.5, 91.8, 56.2, 55.6.

IR (KBr, cm^{-1}): 3446, 1686, 1627, 1604, 1509, 1492, 1334, 1283, 1244, 1168, 1032, 832, 572.

HRMS (ESI): m/z calcd for $C_{22}H_{19}FNO_4^+$ $(M+H)^+$ 380.1293, found 380.1291.

2-(4-chlorophenyl)-2-hydroxy-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5h**)



Compound **5h** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 1-(4-chlorophenyl)-2,2-dihydroxyethan-1-one. **5h** was obtained in 93.0% yield (73.5 mg) as orange solid.

mp: 130-133℃

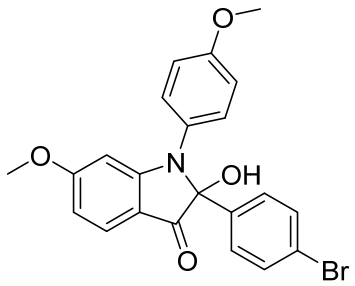
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.49 (s, 1H), 7.39 – 7.35 (m, 2H), 7.35 – 7.31 (m, 2H), 7.26 – 7.20 (m, 3H), 7.07 (d, J = 2.8 Hz, 1H), 6.89 (d, J = 8.9 Hz, 1H), 6.88 – 6.84 (m, 2H), 3.76 (s, 3H), 3.69 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 199.7, 157.3, 155.2, 153.3, 137.3, 133.2, 131.7, 128.7, 128.6, 128.1, 127. 0, 117.7, 114.9, 111.8, 106.5, 91.8, 56.2, 55.6.

IR (KBr, cm^{-1}): 3448, 1686, 1513, 1492, 1438, 1331, 1284, 1249, 1168, 1089, 1031, 831, 573.

HRMS (ESI): m/z calcd for $C_{22}H_{19}ClNO_4^+$ $(M+H)^+$ 396.0997, found 396.0993.

2-(4-bromophenyl)-2-hydroxy-6-methoxy-1-(4-methoxyphenyl)indolin-3-one (**5i**)



Compound **5i** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5i** was obtained in 90.8% yield (79.7 mg) as orange solid.

mp: 138-142℃

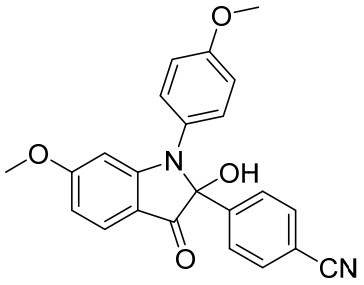
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.38 (d, J = 7.3 Hz, 2H), 7.29 (d, J = 8.6 Hz, 2H), 7.16 – 7.11 (m, 3H), 7.02 (q, J = 2.8 Hz, 1H), 6.86 (dd, J = 8.9, 1.7 Hz, 1H), 6.78 (d, J = 8.7 Hz, 2H), 3.77 (d, J = 2.1 Hz, 3H), 3.75 – 3.74 (m, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 199.6, 157.3, 155.2, 153.3, 137.7, 131.7, 131.6, 128.9, 128.2, 127.0, 121.9, 117.7, 114.9, 111.8, 106.5, 91.8, 56.2, 55.6.

IR (KBr, cm^{-1}): 3445, 1687, 1632, 1513, 1493, 1248, 1167, 1095, 1009, 824.

HRMS (ESI): m/z calcd for $C_{22}H_{19}BrNO_4^+$ $(M+H)^+$ 440.0492, found 440.0493.

4-(2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-3-oxoindolin-2-yl)benzonitrile (**5j**)



Compound **5j** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 4-(2,2-dihydroxyacetyl)benzonitrile. **5j** was obtained in 95.4% yield (73.7 mg) as red solid.

mp: 141-143℃

^{1}H NMR (600 MHz, DMSO-d_6): δ 7.71 (dd, J = 8.4, 1.6 Hz, 2H), 7.64 (d, J = 1.8 Hz, 1H), 7.51 (dd, J = 8.4, 1.6 Hz, 2H), 7.22 (dt, J = 9.0, 2.1 Hz, 1H), 7.20 – 7.16 (m, 2H),

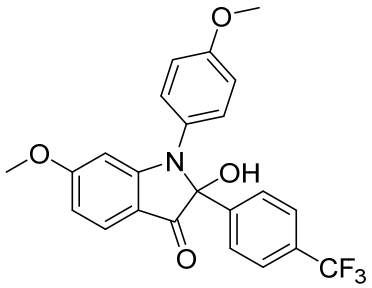
7.03 (t, J = 2.1 Hz, 1H), 6.86 (s, 1H), 6.84 – 6.80 (m, 2H), 3.72 (d, J = 1.5 Hz, 3H), 3.65 (d, J = 1.5 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d_6) δ 199.2, 157.4, 155.4, 153.4, 143.8, 132.8, 131.4, 128.4, 127.7, 127.1, 119.0, 117.6, 114.9, 112.0, 111.4, 106.5, 91.8, 56.3, 55.6.

IR (KBr, cm^{-1}): 3337, 2227, 1684, 1514, 1492, 1439, 1332, 1249, 1171, 1100, 1021, 829, 791, 576.

HRMS (ESI) m/z calcd for $C_{23}H_{19}N_2O_4^+$ $(M+H)^+$ 387.1339, found 387.1335.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(4-(trifluoromethyl)phenyl)indolin-3-one (**5k**)



Compound **5k** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-(trifluoromethyl)phenyl)ethan-1-one. **5k** was obtained in 96.1% yield (82.5 mg) as orange solid.

mp: 151-154℃

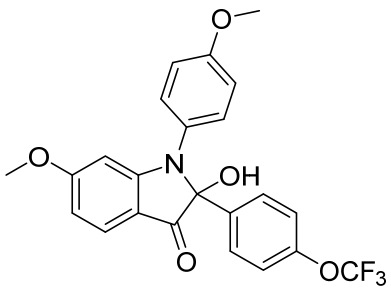
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.55 (d, J = 8.4 Hz, 2H), 7.52 (d, J = 8.3 Hz, 2H), 7.19 – 7.11 (m, 3H), 7.02 (d, J = 2.7 Hz, 1H), 6.88 (d, J = 8.9 Hz, 1H), 6.81 – 6.77 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 199.4, 157.4, 155.4, 153.4, 143.0, 131.5, 128.3, 127.6, 127.1, 125.7, 125.5, 123.7, 117.6, 114.9, 111.9, 106.5, 91.8, 56.2, 55.6.

IR (KBr, cm^{-1}): 3423, 1686, 1514, 1493, 1325, 1249, 1236, 1169, 1115, 1098, 1018, 824.

HRMS (ESI): m/z calcd for $C_{23}H_{19}F_3NO_4^+$ $(M+H)^+$ 430.1261, found 430.1261.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(4-(trifluoromethoxy)phenyl)indolin-3-one (**5l**)



Compound **5l** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-(trifluoromethoxy)phenyl)ethan-1-one. **5l** was obtained in 86.7% yield (77.2 mg) as orange solid.

mp: 140-141℃

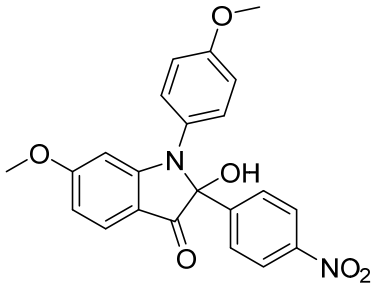
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.47 – 7.43 (m, 2H), 7.14 (dd, J = 9.0, 6.7 Hz, 3H), 7.11 – 7.07 (m, 2H), 7.02 (d, J = 2.7 Hz, 1H), 6.85 (d, J = 8.9 Hz, 1H), 6.80 – 6.76 (m, 2H), 3.77 (s, 3H), 3.74 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.6, 157.8, 156.0, 153.7, 149.5, 135.9, 130.9, 128.9, 127.9, 127.1, 121.2, 120.8, 119.5, 117.5, 114.7, 112.2, 106.0, 91.5, 55.9, 55.4.

IR (KBr, cm^{-1}): 3448, 1686, 1637, 1513, 1492, 1466, 1334, 1270, 1248, 1168, 1033, 1015, 823.

HRMS (ESI): m/z calcd for $C_{23}H_{19}F_3NO_5^+$ $(M+H)^+$ 446.1210, found 446.1206 .

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(4-nitrophenyl)indolin-3-one (**5m**)



Compound **5m** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-nitrophenyl)ethan-1-one. **5m** was obtained in 86.2% yield (70.0 mg) as yellow solid.

mp: 120-121℃

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10 – 8.06 (m, 2H), 7.58 (d, J = 9.0 Hz, 2H), 7.17 –

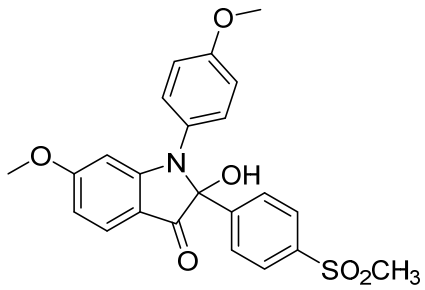
7.11 (m, 3H), 6.99 (d, J = 2.8 Hz, 1H), 6.86 (d, J = 8.9 Hz, 1H), 6.78 – 6.74 (m, 2H), 3.76 (s, 3H), 3.73 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 199.1, 157.5, 155.4, 153.5, 147.8, 145.8, 131.4, 128.5, 128.1, 127.2, 124.0, 117.6, 114.9, 112.0, 106.5, 91.7, 56.3, 55.6.

IR (KBr, cm^{-1}): 3452, 1678, 1641 1631, 1576, 1558, 1541, 1513, 1493, 1348, 1249.

HRMS (ESI): m/z calcd for $C_{22}H_{19}N_2O_6^+$ $(M+H)^+$ 407.1238, found 407.1234.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(4-(methylsulfonyl)phenyl)indolin-3-one (**5n**)



Compound **5n** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(4-(methylsulfonyl)phenyl)ethan-1-one. **5n** was obtained in 58.5% yield (51.4 mg) as orange solid.

mp: 149-152℃

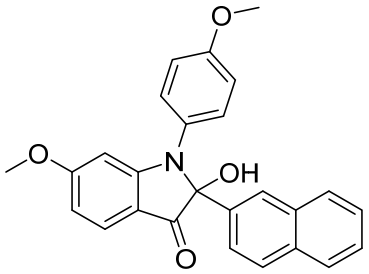
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.15 (dd, J = 9.0, 2.8 Hz, 1H), 7.14 – 7.10 (m, 2H), 6.99 (d, J = 2.7 Hz, 1H), 6.86 (d, J = 8.9 Hz, 1H), 6.78 – 6.74 (m, 2H), 3.75 (s, 3H), 3.73 (s, 3H), 2.97 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.2, 157.9, 156.1, 153.7, 143.6, 140.4, 130.6, 129.1, 127.6, 127.4, 127.0, 117.3, 114.7, 112.2, 106.0, 91.5, 55.9, 55.5, 55.4, 44.4.

IR (KBr, cm^{-1}): 3448, 1682, 1514, 1492, 1335, 1315, 1291, 1251, 1016, 833, 759, 574.

HRMS (ESI): m/z calcd for $C_{23}H_{22}NO_6S^+$ $(M+H)^+$ 440.1162, found 440.1161.

2-hydroxy-6-methoxy-1-(4-methoxyphenyl)-2-(naphthalen-2-yl)indolin-3-one (**5o**)



Compound **5o** was synthesized according to general procedure **3.4** starting from bis(4-methoxyphenyl)amine and 2,2-dihydroxy-1-(naphthalen-2-yl)ethan-1-one. **5o** was obtained in 88.4% yield (72.7 mg) as red solid.

mp: 163-167℃

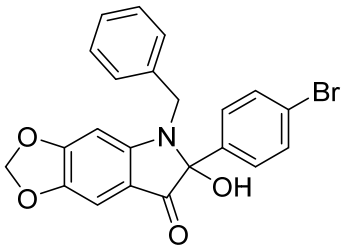
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.03 (s, 1H), 7.92 (dt, J = 6.2, 3.5 Hz, 1H), 7.84 (dt, J = 7.0, 3.5 Hz, 1H), 7.78 (d, J = 8.6 Hz, 1H), 7.52 (d, J = 1.7 Hz, 1H), 7.48 (dd, J = 6.2, 3.2 Hz, 2H), 7.33 (dt, J = 8.7, 1.7 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.09 (d, J = 1.3 Hz, 1H), 6.94 (d, J = 9.0 Hz, 1H), 6.81 (d, J = 9.0 Hz, 2H), 3.78 (s, 3H), 3.64 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 200.0, 157.2, 155.3, 153.2, 135.8, 133.2, 133.1, 131.9, 128.5, 128.3, 128.1, 127.9, 126.9, 126.8, 126.7, 126.2, 124.1, 117.9, 114.8, 111.8, 106.5, 79.7, 56.2, 55.5.

IR (KBr, cm^{-1}): 3321, 1678, 1635 1512, 1491, 1338, 1293, 1281, 1163, 1132, 1032, 832, 792.

HRMS (ESI): m/z calcd for $C_{26}H_{22}NO_4^+$ $(M+H)^+$ 412.1543, found 412.1541.

5-benzyl-6-(4-bromophenyl)-6-hydroxy-5,6-dihydro-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-one (**5p**)



Compound **5p** was synthesized according to general procedure **3.4** starting from *N*-benzylbenzo[*d*][1,3]dioxol-5-amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5p** was obtained in 57.4% yield (50.2 mg) as yellow solid.

mp: 156-158℃

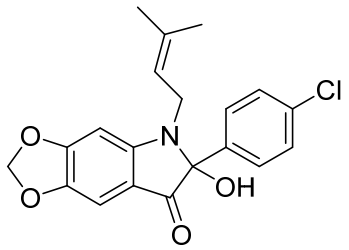
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.54 (s, 2H), 7.35 (d, J = 7.7 Hz, 2H), 7.32 – 7.26 (m, 5H), 7.21 (t, J = 7.4 Hz, 1H), 6.92 (d, J = 3.3 Hz, 1H), 6.15 (s, 1H), 6.03 (d, J = 7.8 Hz, 2H), 4.42 (d, J = 16.5 Hz, 1H), 4.26 – 4.19 (m, 1H), 3.38 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 196.3, 160.0, 157.5, 141.6, 138.5, 137.9, 131.9, 128.9, 128.8, 127.8, 127.4, 122.0, 109.3, 102.7, 92.2, 90.6, 46.5.

IR (KBr, cm^{-1}): 3435, 1665, 1642, 1596, 1495, 1469, 1399, 1338, 1245, 1034.

HRMS (ESI): m/z calcd for $C_{22}H_{17}BrNO_4^+$ $(M+H)^+$ 438.0335, found 438.0338.

6-(4-chlorophenyl)-6-hydroxy-5-(3-methylbut-2-en-1-yl)-5,6-dihydro-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-one (**5q**)



Compound **5q** was synthesized according to general procedure **3.4** starting from *N*-(3-methylbut-2-en-1-yl)benzo[*d*][1,3]dioxol-5-amine and 1-(4-chlorophenyl)-2,2-dihydroxyethan-1-one. **5q** was obtained in 62.3% yield (46.2 mg) as yellow solid.

mp: 154-158℃

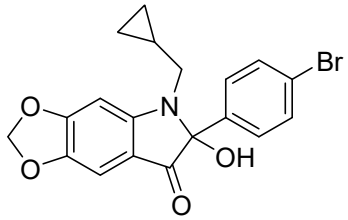
^{1}H NMR (600 MHz, DMSO-d_6): δ 7.38 (d, J = 8.6 Hz, 2H), 7.32 (d, J = 8.6 Hz, 2H), 7.03 (s, 1H), 6.86 (s, 1H), 6.38 (s, 1H), 6.07 (d, J = 5.8 Hz, 2H), 5.09 (d, J = 2.0 Hz, 1H), 3.90 (dd, J = 16.2, 7.6 Hz, 1H), 3.58 (dd, J = 16.2, 5.7 Hz, 1H), 1.58 (d, J = 1.5 Hz, 3H), 1.55 (d, J = 1.4 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 196.8, 160.3, 157.6, 141.2, 137.7, 134.2, 133.2, 128.6, 128.5, 121.7, 109.0, 102.6, 102.6, 91.4, 90.3, 25.8, 18.0.

IR (KBr, cm^{-1}): 3438, 2912, 1655, 1626, 1593, 1492, 1474, 1439, 1400, 1342, 1311, 1243, 1090, 1031, 937, 809, 649.

HRMS (ESI): m/z calcd for $C_{20}H_{19}ClNO_4^+$ $(M+H)^+$ 372.0997, found 372.0996.

6-(4-bromophenyl)-5-(cyclopropylmethyl)-6-hydroxy-5,6-dihydro-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-one (**5r**)



Compound **5r** was synthesized according to general procedure **3.4** starting from *N*-(cyclopropylmethyl)benzo[*d*][1,3]dioxol-5-amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5r** was obtained in 34.4% yield (27.6 mg) as yellow solid.

mp: 145-148℃

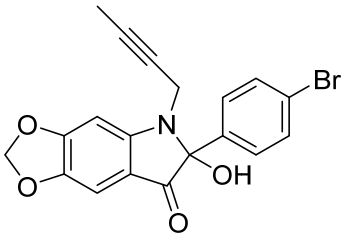
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.52 (d, J = 8.6 Hz, 2H), 7.29 – 7.22 (m, 2H), 7.03 (s, 1H), 6.85 (d, J = 1.5 Hz, 1H), 6.69 (s, 1H), 6.08 (d, J = 8.6 Hz, 2H), 3.17 (dd, J = 15.0, 7.0 Hz, 1H), 2.95 - 2.90 (m, 1H), 0.90 (t, J = 6.8 Hz, 1H), 0.31 (qd, J = 6.5, 3.7 Hz, 2H), 0.17 – 0.10 (m, 1H), 0.07 – 0.02 (m, 1H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 196.7, 160.8, 157.8, 141.2, 138.4, 131.6, 128.8, 121.7, 108.7, 102.5, 102.4, 91.4, 90.7, 46.8, 11.0, 5.5, 4.2.

IR (KBr, cm^{-1}): 3448, 1661, 1629, 1597, 1508, 1472, 1393, 1350, 1302, 1244, 1031, 809.

HRMS (ESI): m/z calcd for $C_{19}H_{17}BrNO_4^+$ $(M+H)^+$ 402.0335, found 402.0334.

6-(4-bromophenyl)-5-(but-2-yn-1-yl)-6-hydroxy-5,6-dihydro-7*H*-[1,3]dioxolo[4,5-*f*]indol-7-one (**5s**)



Compound **5s** was synthesized according to general procedure **3.4** starting from *N*-(but-2-yn-1-yl)benzo[*d*][1,3]dioxol-5-amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5s** was obtained in 19.9% yield (15.9 mg) as yellow solid.

mp: 159-161℃

^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.53 (d, J = 8.6 Hz, 2H), 7.29 (d, J = 8.3 Hz, 2H), 7.14 (s, 1H), 6.91 (s, 1H), 6.67 (s, 1H), 6.10 (d, J = 11.6 Hz, 2H), 3.98 (dd, J = 18.2, 2.7

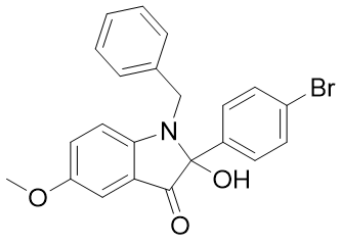
Hz, 1H), 3.87 (dd, J = 18.2, 2.6 Hz, 1H), 1.69 (d, J = 2.5 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 196.3, 159.4, 157.5, 141.8, 137.5, 131.5, 129.1, 122.1, 109.4, 102.7, 102.6, 91.4, 91.1, 79.7, 75.5, 31.5, 3.5.

IR (KBr, cm^{-1}): 3448, 2918, 1665, 1624, 1503, 1474, 1399, 1329, 1243, 1032.

HRMS (ESI): m/z calcd for $C_{19}H_{15}BrNO_4^+$ $(M+H)^+$ 400.0179, found 400.0179.

1-benzyl-2-(4-bromophenyl)-2-hydroxy-6-methoxyindolin-3-one (**5t**)



Compound **5t** was synthesized according to general procedure **3.4** starting from *N*-benzyl-4-methoxyaniline and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5t** was obtained in 44.4% yield (37.6 mg) as yellow solid.

mp: 141-143℃

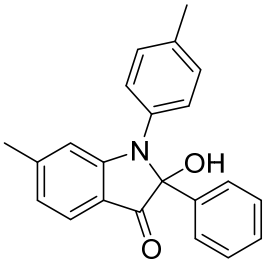
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.54 (d, J = 8.6 Hz, 2H), 7.35 (d, J = 7.2 Hz, 2H), 7.31 – 7.26 (m, 5H), 7.21 (dd, J = 8.5, 6.4 Hz, 1H), 7.16 (dd, J = 8.8, 2.8 Hz, 1H), 7.00 (d, J = 2.7 Hz, 1H), 6.50 (d, J = 8.9 Hz, 1H), 4.38 (d, J = 16.5 Hz, 1H), 4.21 (d, J = 16.6 Hz, 1H), 3.70 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 199.3, 156.2, 152.7, 138.8, 137.7, 131.9, 128.9, 128.8, 128.0, 127.6, 127.3, 122.1, 117.6, 110.8, 106.9, 91.8, 56.2, 46.7.

IR (KBr, cm^{-1}): 3437, 1688, 1679, 1659, 1642, 1631, 1500, 1436, 1334, 1285, 1232, 1009, 828, 762.

HRMS (ESI): m/z calcd for $C_{22}H_{19}BrNO_3^+$ $(M+H)^+$424.0543, found 424.0543.

2-hydroxy-6-methyl-2-phenyl-1-(p-tolyl)indolin-3-one (**5u**)



Compound **5u** was synthesized according to general procedure **3.4** starting from di-p-tolylamine and 2-oxo-2-phenylacetaldehyde. **5u** was obtained in 84.5% yield (55.7 mg) as orange solid.

mp: 121-124℃

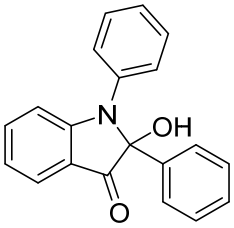
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.51 – 7.48 (m, 3H), 7.38 (dd, J = 8.5, 1.9 Hz, 1H), 7.32 (d, J = 7.0 Hz, 3H), 7.23 – 7.20 (m, 2H), 7.11 (d, J = 8.2 Hz, 2H), 7.02 (d, J = 8.4 Hz, 1H), 3.66 – 3.45 (m, 1H), 2.36 (s, 3H), 2.33 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 199.6, 157.9, 139.5, 137.0, 135.7, 135.3, 129.8, 129.1, 128.5, 128.5, 126.0, 125.4, 124.6, 117.9, 110.7, 91.7, 20.9, 20.4.

IR (KBr, cm^{-1}): 3572, 3435, 1672, 1666, 1625, 1514, 1494, 1355, 1288, 1119, 743.

HRMS (ESI): m/z calcd for $C_{22}H_{20}NO_2^+$ $(M+H)^+$ 330.1489, found 330.1489.

2-hydroxy-1,2-diphenylindolin-3-one (**5v**)



Compound **5v** was synthesized according to general procedure **3.4** starting from diphenylamine and 2-oxo-2-phenylacetaldehyde. **5v** was obtained in 16.8% yield (10.1 mg) as yellow solid.

mp: 94-97℃

^{1}H NMR (600 MHz, $CDCl_3$): δ 8.00 – 7.95 (m, 2H), 7.82 (d, J = 8.4 Hz, 2H), 7.63 (t, J = 7.5 Hz, 1H), 7.48 (t, J = 7.7 Hz, 2H), 7.34 (t, J = 7.6 Hz, 2H), 7.18 (d, J = 7.9 Hz, 2H), 7.12 (t, J = 7.4 Hz, 1H), 6.96 (d, J = 8.6 Hz, 2H), 6.52 (dd, J = 18.1, 10.3 Hz, 1H).

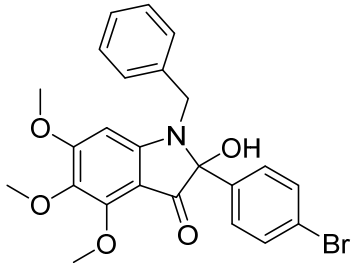
^{13}C NMR (151 MHz, $CDCl_3$): δ 195.5, 192.7, 150.5, 139.7, 134.7, 133.4, 132.5, 129.9,

129.6, 129.0, 124.3, 124.2, 121.7, 114.3.

IR (KBr, cm^{-1}): 3572, 3452, 3352, 1640, 1631, 1617, 1585, 1573, 1528, 1495, 1167.

HRMS (ESI): m/z calcd for $C_{20}H_{16}NO_2^+$ $(M+H)^+$ 302.1175, found 302.1175.

1-benzyl-2-(4-bromophenyl)-2-hydroxy-4,5,6-trimethoxyindolin-3-one (**5w**)



Compound **5w** was synthesized according to general procedure **3.4** starting from *N*-benzyl-3,4,5-trimethoxyaniline and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5w** was obtained in 63.0% yield (61.1 mg) as yellow solid.

mp: 144-146℃

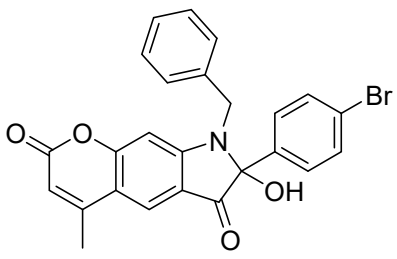
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.53 (d, J = 8.3 Hz, 2H), 7.35 (dd, J = 7.5, 2.9 Hz, 2H), 7.32 – 7.25 (m, 4H), 7.23 – 7.18 (m, 2H), 5.91 (d, J = 2.1 Hz, 1H), 4.48 – 4.43 (m, 1H), 4.25 (dd, J = 16.4, 3.7 Hz, 1H), 3.90 (d, J = 3.1 Hz, 3H), 3.69 (d, J = 1.3 Hz, 3H), 3.59 (d, J = 2.0 Hz, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 194.3, 163.0, 158.6, 152.3, 138.6, 138.2, 133.1, 131.8, 128.9, 128.7, 127.9, 127.3, 122.0, 102.4, 91.6, 87.5, 61.7, 61.5, 56.6, 46.4.

IR (KBr, cm^{-1}): 3469, 2936, 1609, 1489, 1451, 1423, 1395, 1304, 1242, 1203, 1144, 1011, 995, 768, 731.

HRMS (ESI): m/z calcd for $C_{24}H_{23}BrNO_5^+$ $(M+H)^+$ 484.0754, found 484.0757.

8-benzyl-7-(4-bromophenyl)-7-hydroxy-4-methyl-7,8-dihydropyrano[3,2-*f*]indole-2,6-dione (**5x**)



Compound **5x** was synthesized according to general procedure **3.4** starting from 7-(benzylamino)-4-methyl-2*H*-chromen-2-one and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5x** was obtained in 70.7% yield (67.2 mg) as yellow solid.

mp: 186-187℃

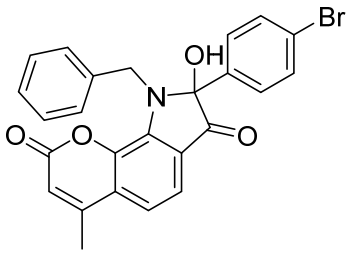
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.89 (s, 1H), 7.61 (s, 1H), 7.56 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 7.6 Hz, 2H), 7.31 (dd, J = 17.3, 8.1 Hz, 4H), 7.24 (t, J = 7.3 Hz, 1H), 6.40 (s, 1H), 6.12 (d, J = 1.4 Hz, 1H), 4.56 (d, J = 16.4 Hz, 1H), 4.35 (d, J = 16.4 Hz, 1H), 2.37 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 197.4, 161.2, 160.7, 159.7, 154.5, 137.4, 136.8, 132.1, 128.9, 128.0, 127.6, 123.9, 122.6, 115.3, 112.3, 110.3, 95.5, 91.9, 46.3, 18.7.

IR (KBr, cm^{-1}): 3448, 1701, 1627, 1501, 1439, 1410, 1350, 1178, 1067, 1027, 827, 701.

HRMS (ESI): m/z calcd for $C_{25}H_{19}BrNO_4^+$ $(M+H)^+$ 476.0492, found 476.0494.

9-benzyl-8-(4-bromophenyl)-8-hydroxy-4-methyl-8,9-dihydropyrano[3,2-*g*]indole-2,7-dione (**5x'**)



Compound **5x** was synthesized according to general procedure **3.4** starting from 7-(benzylamino)-4-methyl-2*H*-chromen-2-one and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5x** was obtained in 5.3% yield (5.0 mg) as yellow solid.

mp: 190-194℃

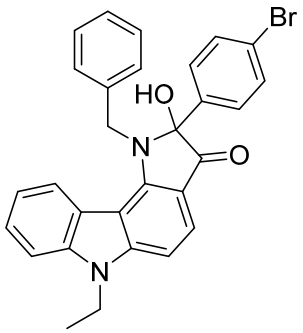
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.85 (d, J = 8.8 Hz, 1H), 7.62 (s, 1H), 7.59 – 7.55 (m, 2H), 7.37 – 7.33 (m, 4H), 7.29 (t, J = 7.6 Hz, 2H), 7.25 – 7.21 (m, 1H), 6.55 (d, J = 8.8 Hz, 1H), 6.12 (d, J = 1.4 Hz, 1H), 4.61 (d, J = 16.7 Hz, 1H), 4.37 (d, J = 16.7 Hz, 1H), 2.34 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 194.9, 162.0, 159.7, 154.4, 152.3, 137.6, 136.7, 136.4, 132.1, 128.9, 128.9, 127.7, 127.5, 122.6, 110.9, 109.7, 106.0, 104.0, 92.0, 46.2, 19.0.

IR (KBr, cm^{-1}): 3438, 1722, 1620, 1604, 1556, 1402, 1343, 1158, 1027, 827, 752.

HRMS (ESI): m/z calcd for $C_{25}H_{19}BrNO_4^+$ $(M+H)^+$ 476.0492, found 476.0494.

1-benzyl-2-(4-bromophenyl)-6-ethyl-2-hydroxy-1,6-dihydropyrrolo[3,2-*c*]carbazol-3(2*H*)-one (**5y**)



Compound **5y** was synthesized according to general procedure **3.4** starting from *N*-benzyl-9-ethyl-9*H*-carbazol-2-amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5y** was obtained in 42.3% yield (43.1 mg) as red solid.

mp: 149-151℃

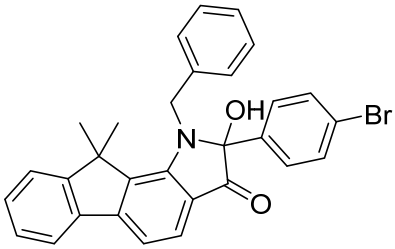
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.74 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.8 Hz, 1H), 7.55 (dd, J = 16.0, 8.4 Hz, 3H), 7.47 – 7.39 (m, 5H), 7.34 (s, 1H), 7.30 (t, J = 7.6 Hz, 2H), 7.22 (t, J = 7.4 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.67 (d, J = 8.8 Hz, 1H), 4.51 (d, J = 16.8 Hz, 1H), 4.40 (s, 2H), 4.32 (d, J = 16.7 Hz, 1H), 1.26 (t, J = 7.1 Hz, 3H), 1.21 (s, 2H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 198.9, 157.9, 140.9, 139.1, 138.2, 133.5, 131.9, 129.1, 128.8, 127.6, 127.4, 127.3, 125.0, 122.0, 121.3, 121.2, 118.8, 118.7, 110.1, 109.9, 107.6, 91.5, 47.1, 37.6, 14.6.

IR (KBr, cm^{-1}): 3423, 2974, 1672, 1625, 1604, 1583, 1474, 1437, 1396, 1354, 1325, 1307, 1229, 1152, 1077,1035, 1012, 798, 749.

HRMS (ESI): m/z calcd for $C_{29}H_{24}BrN_2O_2^+$ $(M+H)^+$ 511.1016, found 511.1010.

1-benzyl-2-(4-bromophenyl)-2-hydroxy-10,10-dimethyl-1,10-dihydroindeno[1,2-



g]indol-3(2*H*)-one (**5z**)

Compound **5z** was synthesized according to general procedure **3.4** starting from *N*-benzyl-9,9-dimethyl-9*H*-fluoren-2-amine and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **5z** was obtained in 90.3% yield (91.9 mg) as orange solid.

mp: 110-113℃

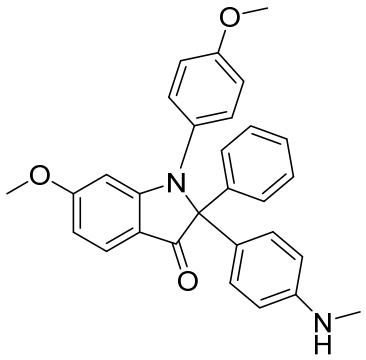
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.96 (d, J = 4.3 Hz, 1H), 7.81 - 7.77 (m, 1H), 7.55 - 7.51 (m, 2H), 7.44 (d, J = 7.5 Hz, 1H), 7.41 - 7.37 (m, 2H), 7.36 - 7.32 (m, 3H), 7.28 (dtd, J = 7.4, 6.0, 1.6 Hz, 3H), 7.24 - 7.18 (m, 2H), 6.81 (d, J = 2.1 Hz, 1H), 4.56 (dd, J = 16.5, 2.1 Hz, 1H), 4.36 (dd, J = 16.5, 3.2 Hz, 1H), 1.40 (s, 3H), 1.27 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d$_6$): δ 198.7, 165.9, 161.1, 152.2, 138.3, 138.2, 137.6, 131.9, 130.3, 129.0, 128.7, 128.0, 127.7, 127.3, 126.9, 123.0, 122.1, 120.0, 117.0, 103.9, 91.8, 47.2, 46.4, 27.7, 27.3.

IR (KBr, cm^{-1}): 3448, 2960, 1683, 1624, 1504, 1474, 1341, 1302, 1209, 1071, 1010, 754, 734.

HRMS (ESI): m/z calcd for $C_{30}H_{25}BrNO_2^+$ $(M+H)^+$ 510.1063, found 510.1063.

6-methoxy-1-(4-methoxyphenyl)-2-(4-(methylamino)phenyl)-2-phenylindolin-3-one (**7**)



Compound **7** was synthesized according to general procedure **3.5** starting from **5a** and N-methylaniline. **7** was obtained in 92.9% yield (209 mg) as orange solid.

mp: 137.8-140.8℃

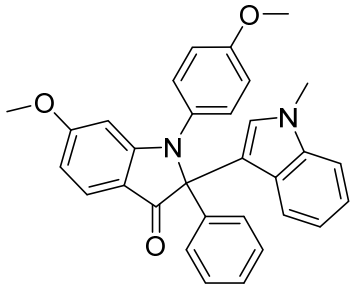
^{1}H NMR (600 MHz, DMSO-d$_6$): δ 7.30 – 7.21 (m, 6H), 7.01 (d, J = 2.8 Hz, 1H), 6.94 (d, J = 9.0 Hz, 1H), 6.91 – 6.84 (m, 4H), 6.72 (d, J = 9.1 Hz, 2H), 6.41 (d, J = 8.7 Hz, 2H), 3.75 (s, 3H), 3.63 (s, 3H), 2.61 (s, 3H).

^{13}C NMR (151 MHz, DMSO-d_6): δ 201.4, 157.0, 155.6, 153.4, 149.8, 139.2, 133.3, 130.0, 129.1, 128.6, 128.2, 127.0, 124.6, 119.4, 114.6, 113.4, 111.6, 105.4, 82.9, 79.7, 56.1, 55.5, 30.0.

IR (KBr, cm^{-1}): 3375, 2933, 2829, 1671, 1631, 1612, 1527, 1510, 1488, 1436, 1337, 1278, 1244, 1193, 1156, 1055, 1031, 815.

HRMS (ESI): m/z calcd for $C_{29}H_{27}N_2O_3^+$ $(M+H)^+$ 451.2016, found 451.2016.

6-methoxy-1-(4-methoxyphenyl)-2-(1-methyl-1*H*-indol-3-yl)-2-phenylindolin-3-one (**8**)



Compound **8** was synthesized according to general procedure **3.6** starting from **5a** and 1-methyl-1*H*-indole. **8** was obtained in 99.0% yield (145.6 mg) as orange solid.

mp: 178.0-180.5°C

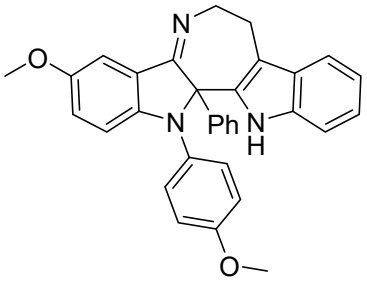
^{1}H NMR (600 MHz, $CHCl_3$): δ 7.58 – 7.53 (m, 2H), 7.31 – 7.27 (m, 3H), 7.19 (s, 1H), 7.19 – 7.15 (m, 2H), 7.10 (ddd, J = 8.2, 6.9, 1.2 Hz, 1H), 6.97 – 6.91 (m, 5H), 6.83 (ddd, J = 8.1, 7.0, 1.1 Hz, 1H), 6.56 (d, J = 9.0 Hz, 2H), 3.81 (s, 3H), 3.67 (s, 3H), 3.65 (s, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 201.3, 157.2, 155.9, 153.2, 138.3, 137.3, 133.4, 130.8, 128.5, 128.3, 128.1, 128.0, 127.6, 126.6, 121.6, 121.2, 119.3, 119.3, 113.9, 113.0, 112.0, 109.3, 105.2, 79.5, 55.9, 55.3, 32.9.

IR (KBr, cm^{-1}): 3436, 1703, 1693, 1671, 1631, 1609, 1576, 1541, 1511, 1486, 1440, 1335, 1245, 1230, 742.

HRMS (ESI): m/z calcd for $C_{31}H_{27}N_2O_3^+$ $(M+H)^+$ 475.2016, found 475.2020.

3-methoxy-13-(4-methoxyphenyl)-12*b*-phenyl-7,12,12b,13-tetrahydro-6*H*-azepino[3,2-*b*:4,5-*b'*]diindole (**9**)



Compound **9** was synthesized according to general procedure **3.7** starting from **5a** and 2-(1*H*-indol-3-yl)ethan-1-amine. **9** was obtained in 78.1% yield (113.5 mg) as brown solid.

mp: 182.0-184.4°C

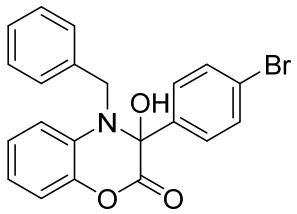
^{1}H NMR (600 MHz, $CHCl_3$): δ 8.09 (d, J = 5.9 Hz, 1H), 7.50 – 7.43 (m, 3H), 7.29 – 7.27 (m, 2H), 7.25 – 7.21 (m, 3H), 7.22 – 7.19 (m, 1H), 7.10 (ddd, J = 8.2, 7.0, 1.2 Hz, 1H), 7.03 (ddd, J = 8.0, 7.0, 1.0 Hz, 1H), 6.99 – 6.93 (m, 3H), 6.84 (d, J = 2.3 Hz, 1H), 6.71 – 6.65 (m, 2H), 3.79 (s, 3H), 3.67 (s, 3H), 2.95 (t, J = 6.9 Hz, 2H), 2.91 – 2.85 (m, 1H), 2.75 – 2.69 (m, 1H).

^{13}C NMR (151 MHz, $CDCl_3$): δ 178.5, 159.1, 156.6, 140.9, 137.3, 136.3, 132.1, 128.7, 128.0, 127.9, 127.6, 127.2, 126.1, 122.0, 121.9, 119.2, 118.9, 114.9, 113.8, 113.5, 111.8, 111.2, 110.3, 70.2, 55.8, 55.6, 44.3, 26.2.

IR (KBr, cm^{-1}): 3419, 1716, 1603, 1513, 1489, 1456, 1445, 1430, 1356, 1243, 1203, 1172, 1021, 818, 744, 695.

HRMS (ESI): m/z calcd for $C_{32}H_{28}N_3O_2^+$ $(M+H)^+$ 486.2176, found 486.2173.

4-benzyl-3-(4-bromophenyl)-3-hydroxy-3,4-dihydro-2H-benzo[*b*][1,4]oxazin-2-one (**11**)



Compound **11** was synthesized according to general procedure **3.8** starting from 2-(benzylamino)phenol and 1-(4-bromophenyl)-2,2-dihydroxyethan-1-one. **11** was obtained in 68.0% yield (55.8 mg) as brown solid.

mp: 172-173℃

^{1}H NMR (600 MHz, DMSO-d$_6$): δ 8.37 (s, 1H), 7.68 – 7.63 (m, 2H), 7.61 – 7.55 (m, 2H), 7.33 (t, J = 7.6 Hz, 2H), 7.30 – 7.22 (m, 3H), 7.12 (dd, J = 7.6, 1.7 Hz, 1H), 7.08 (dd, J = 7.6, 1.9 Hz, 1H), 7.06 – 6.98 (m, 2H), 5.28 (d, J = 16.3 Hz, 1H), 5.08 (d, J = 16.3 Hz, 1H).

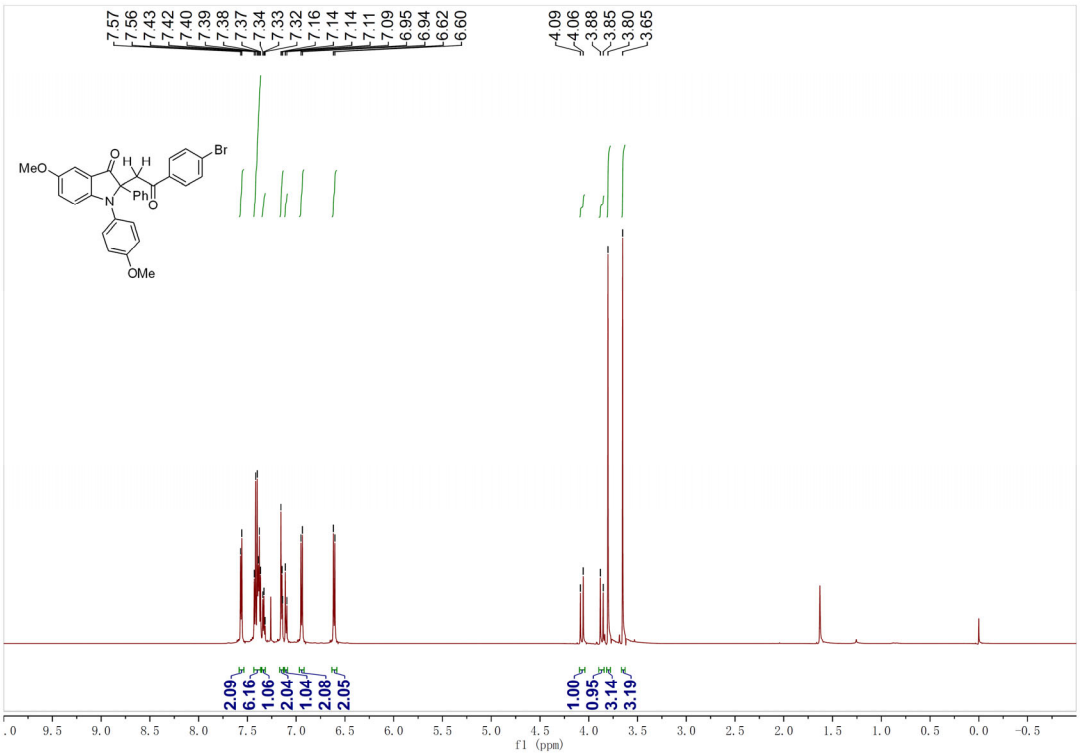
^{13}C NMR (151 MHz, DMSO-d$_6$): δ 163.7, 142.5, 139.0, 136.8, 131.2, 129.8, 129.1, 128.8, 127.7, 127.0, 124.2, 123.3, 122.8, 118.4, 115.9, 97.0, 44.8.

IR (KBr, cm^{-1}): 3448, 1665, 1498, 1401, 1220, 1170, 1042, 828, 755, 700.

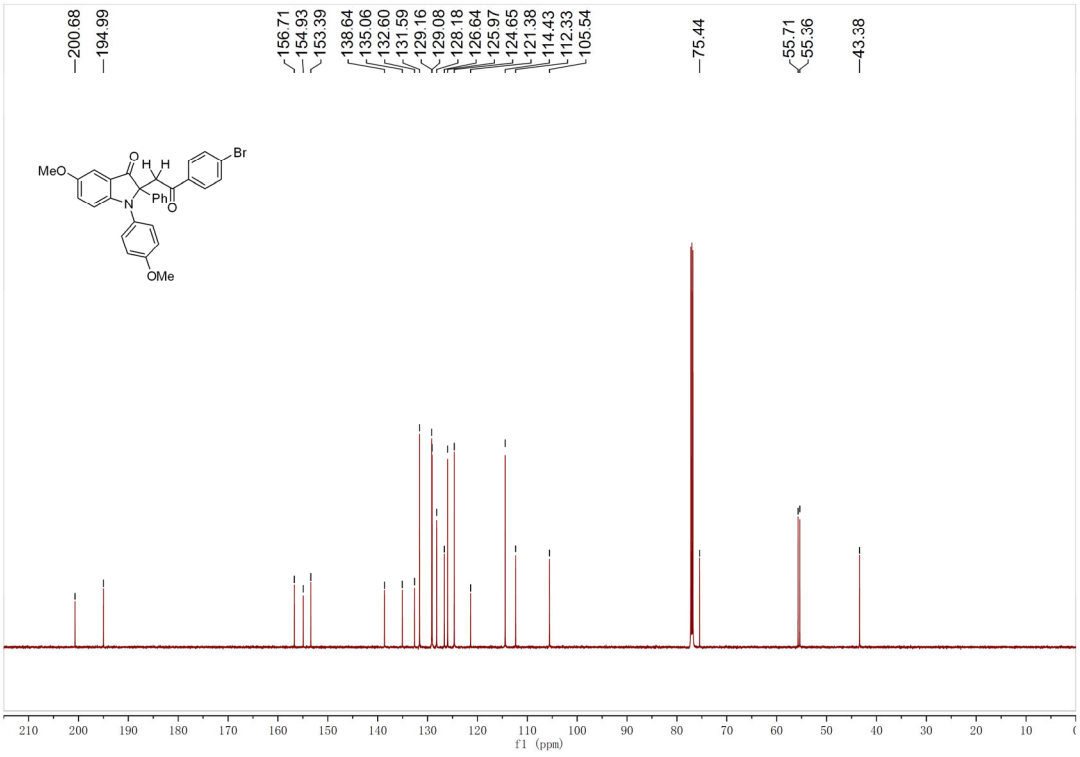
HRMS (ESI): m/z calcd for $C_{21}H_{17}BrNO_3^+$ $(M+H)^+$ 410.0386, found 410.0389.

5. Copies of the ^{1}H、^{13}C spectra

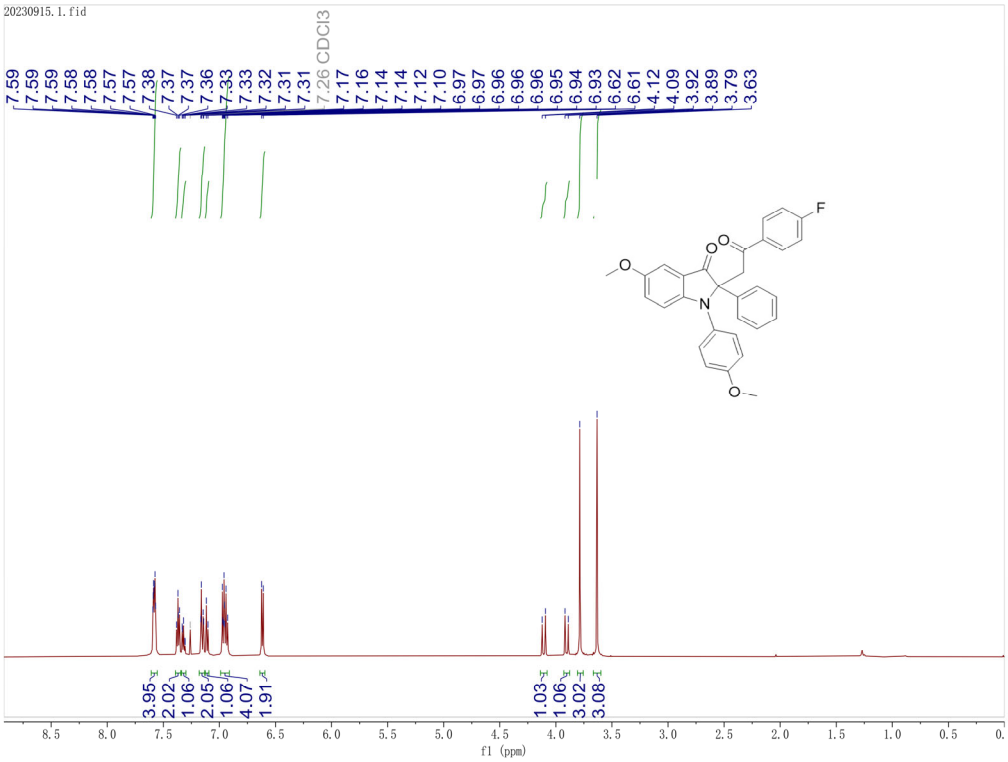
^{1}H NMR of compound **4a** (in $CDCl_3$)



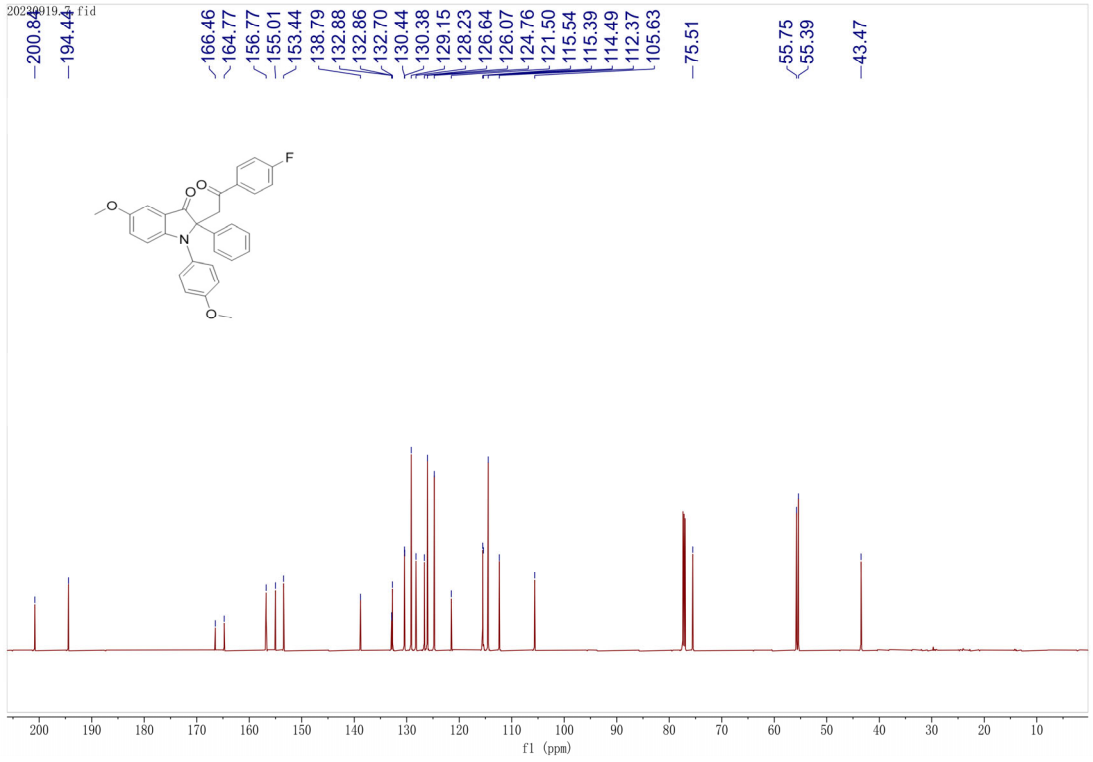
^{13}C NMR of compound **4a** (in $CDCl_3$)



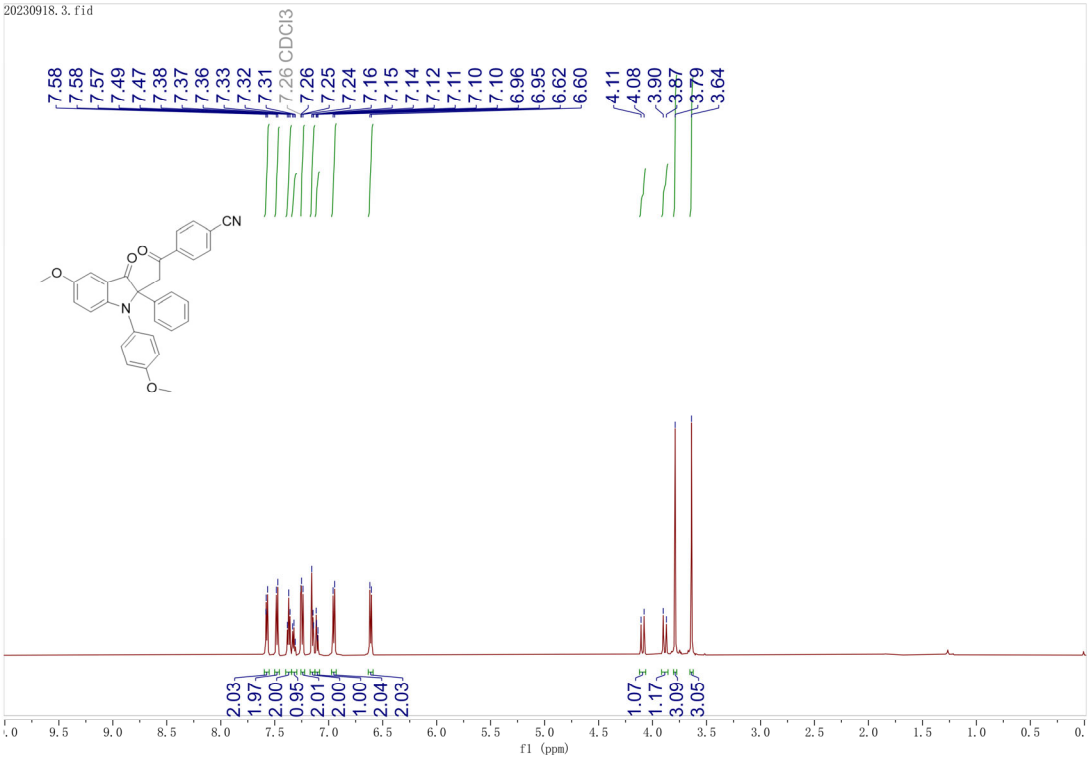
^{1}H NMR of compound **4b** (in $CDCl_3$)



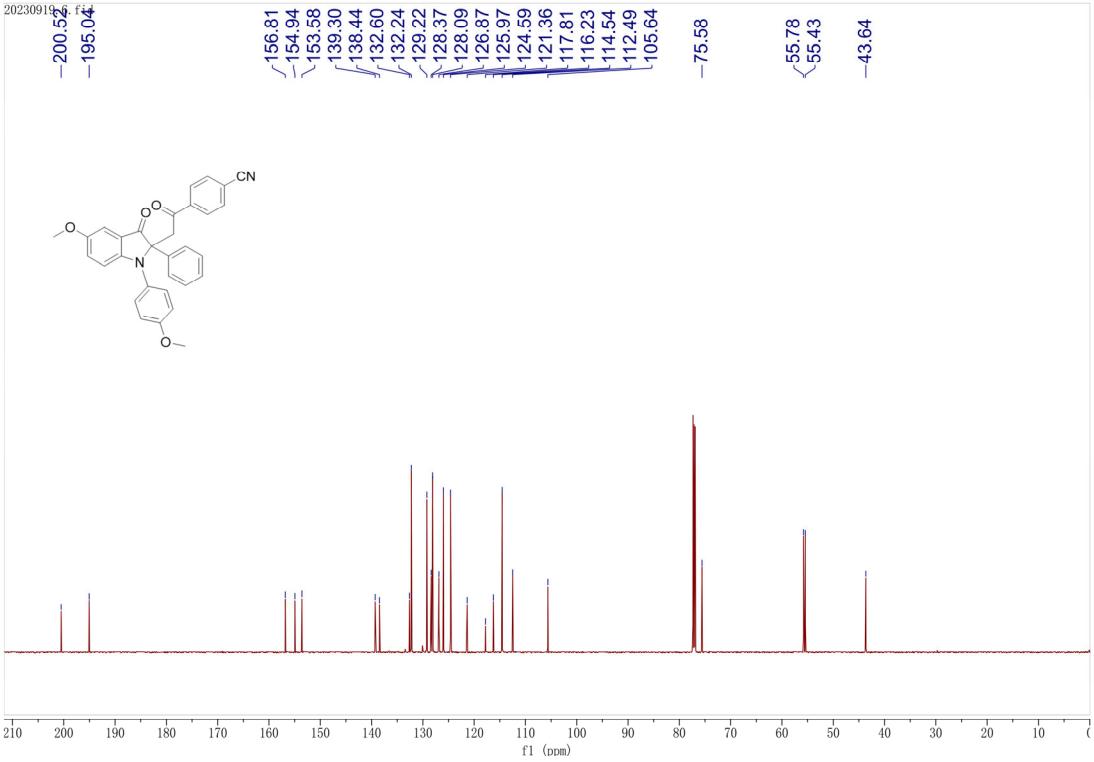
^{13}C NMR of compound **4b** (in $CDCl_3$)



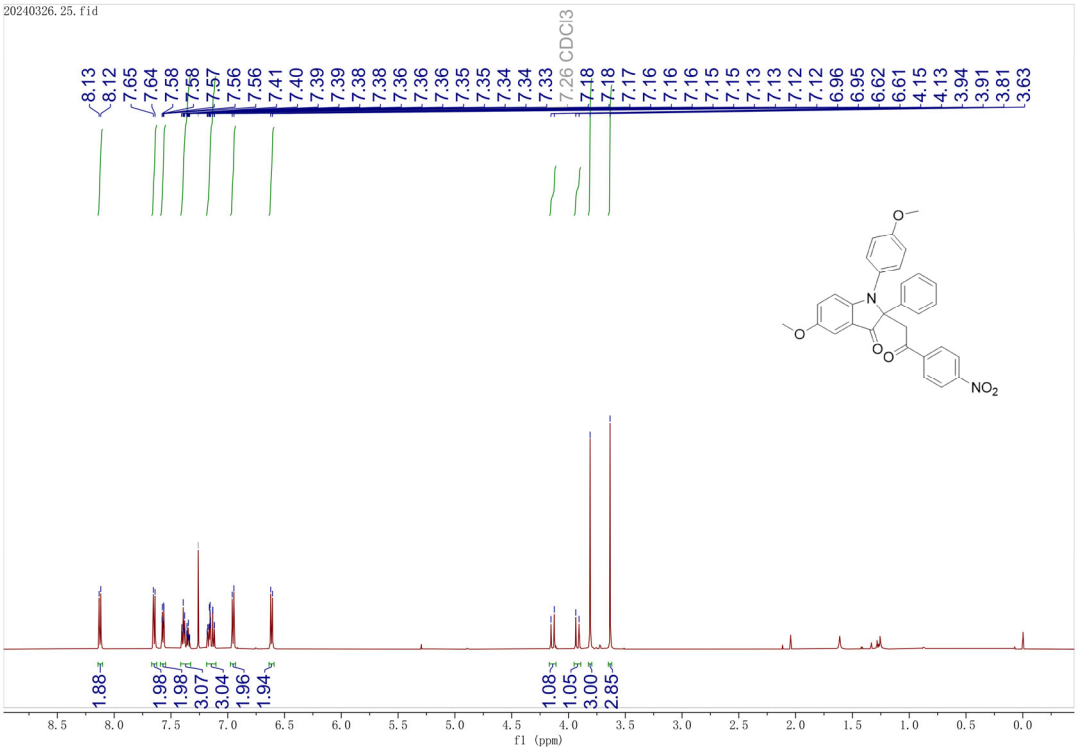
^{1}H NMR of compound **4c** (in $CDCl_3$)



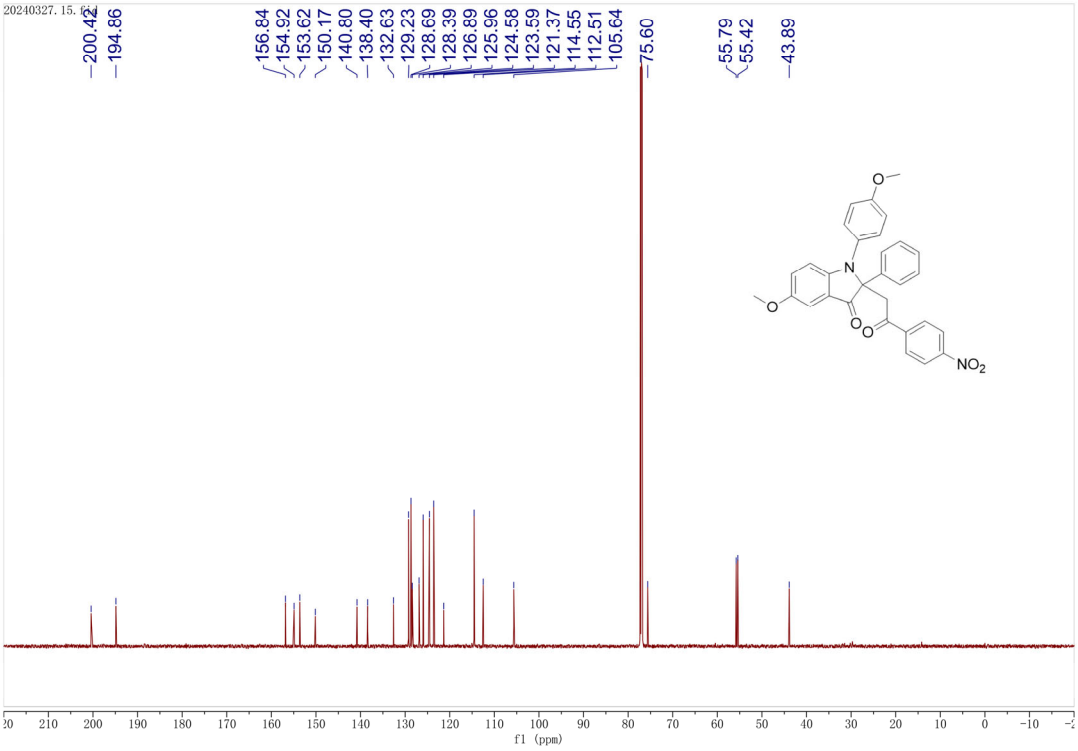
^{13}C NMR of compound **4c** (in $CDCl_3$)



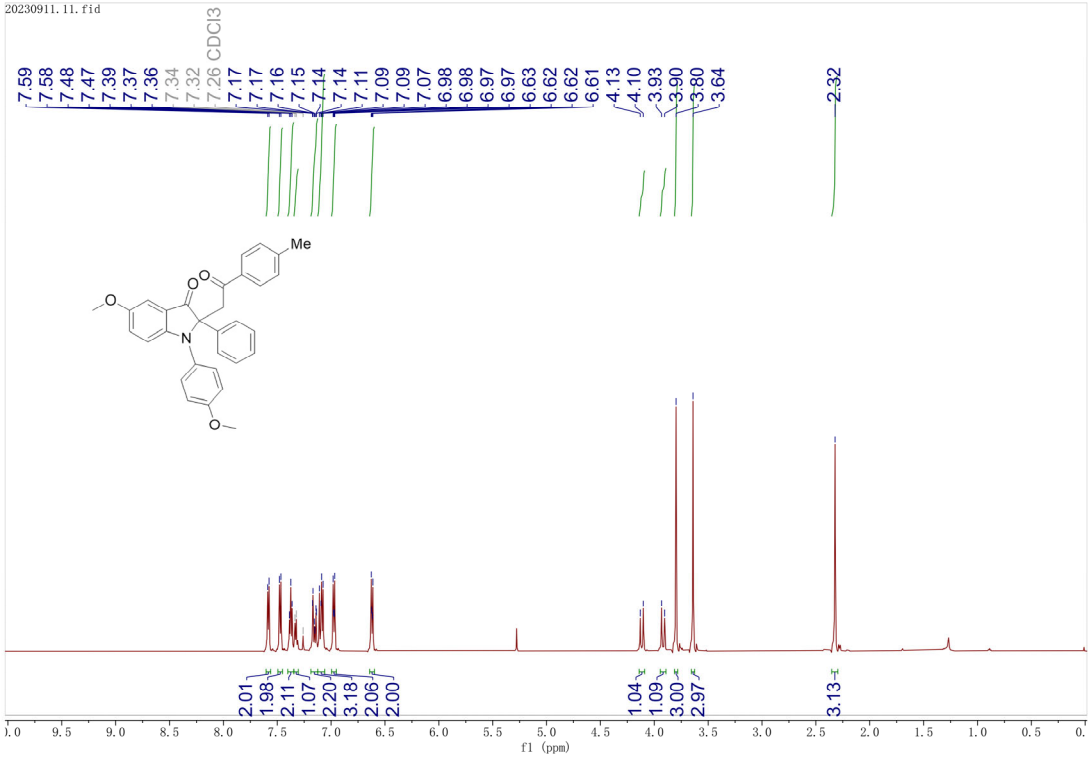
^{1}H NMR of compound **4d** (in $CDCl_3$)



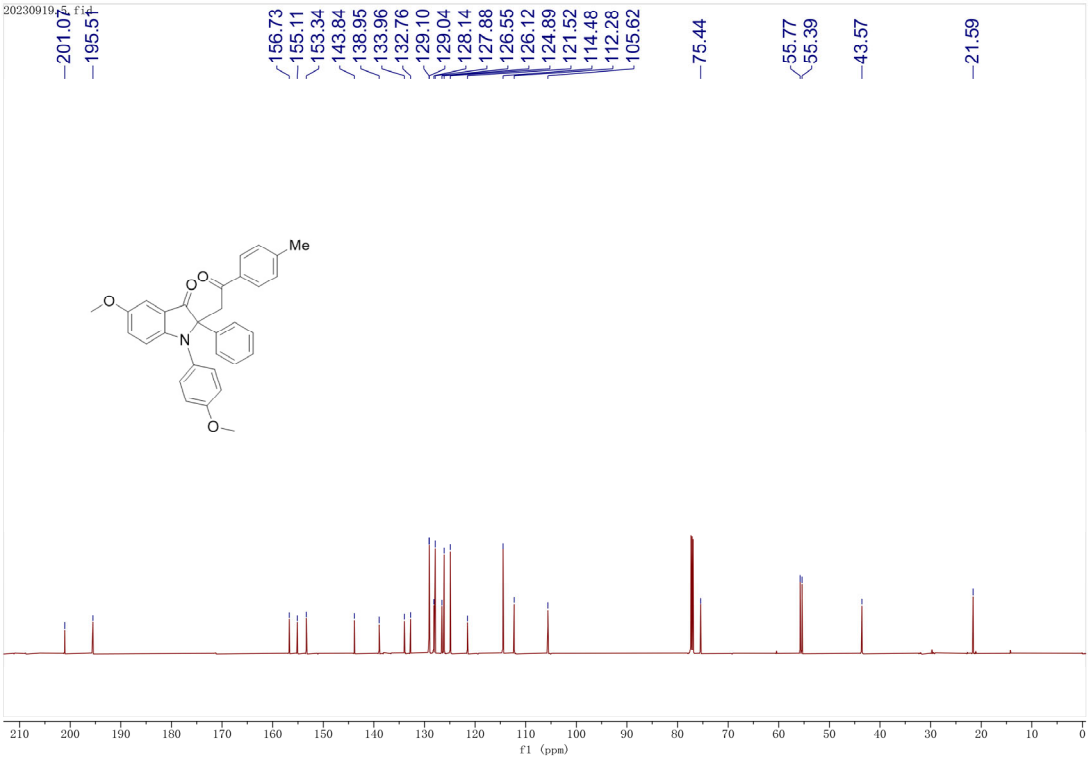
^{13}C NMR of compound **4d** (in $CDCl_3$)



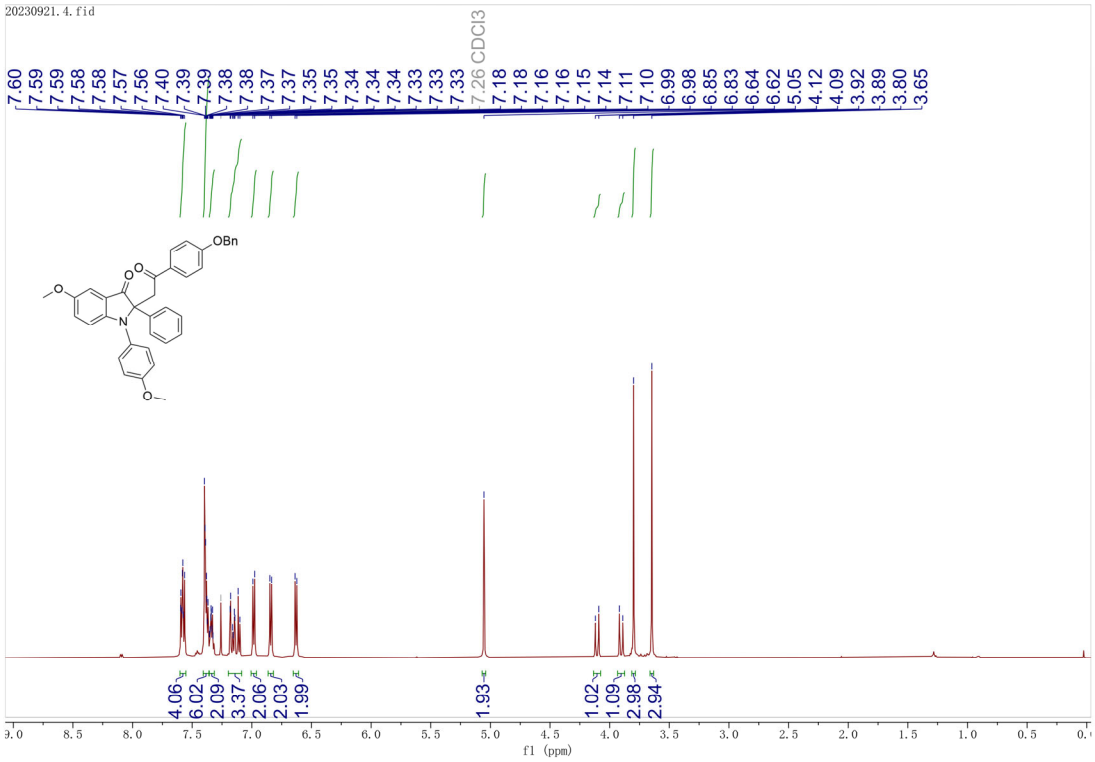
^{1}H NMR of compound **4e** (in $CDCl_3$)



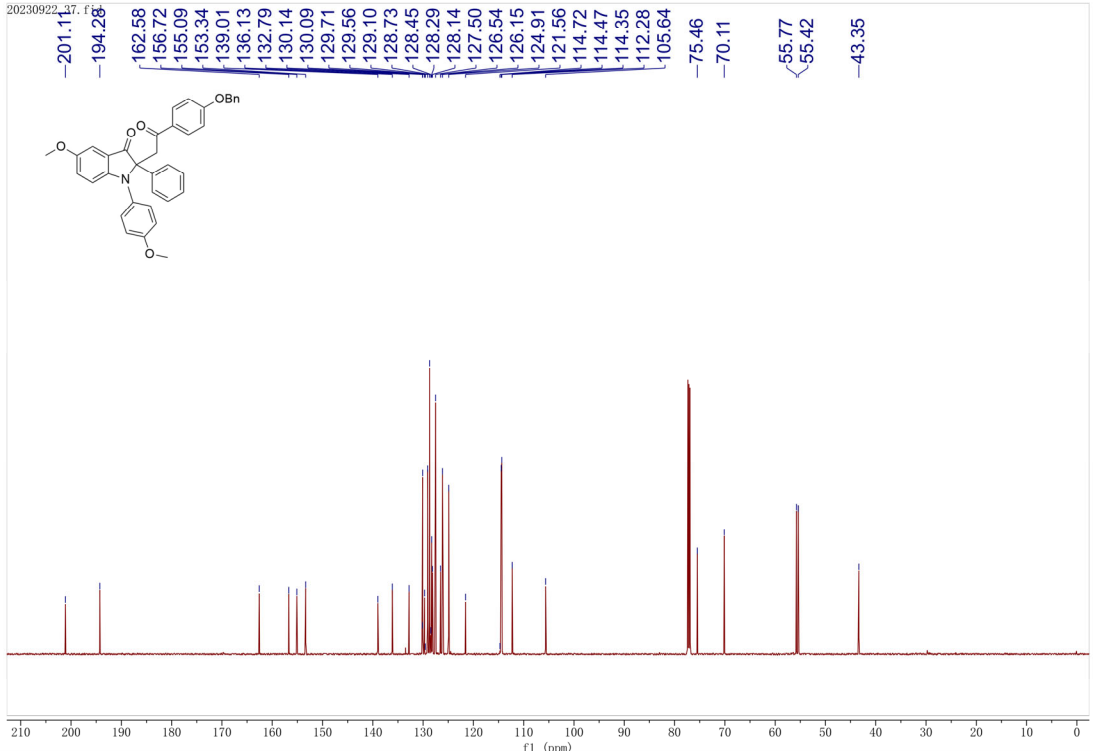
^{13}C NMR of compound **4e** (in $CDCl_3$)



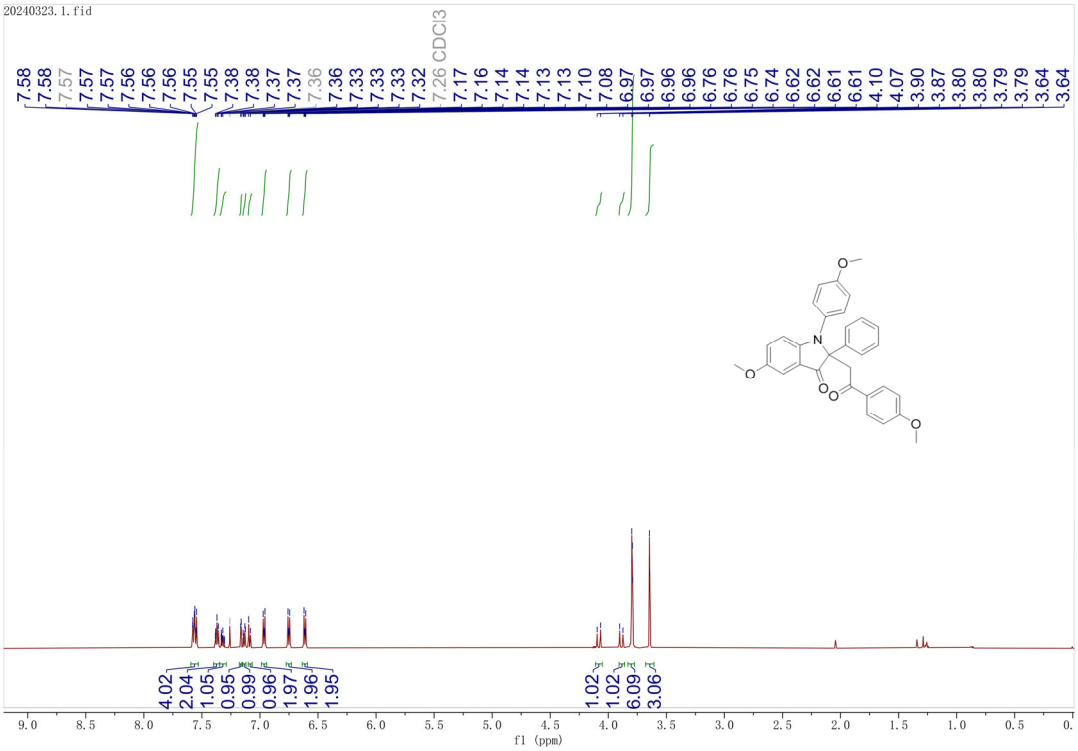
^{1}H NMR of compound **4f** (in $CDCl_3$)



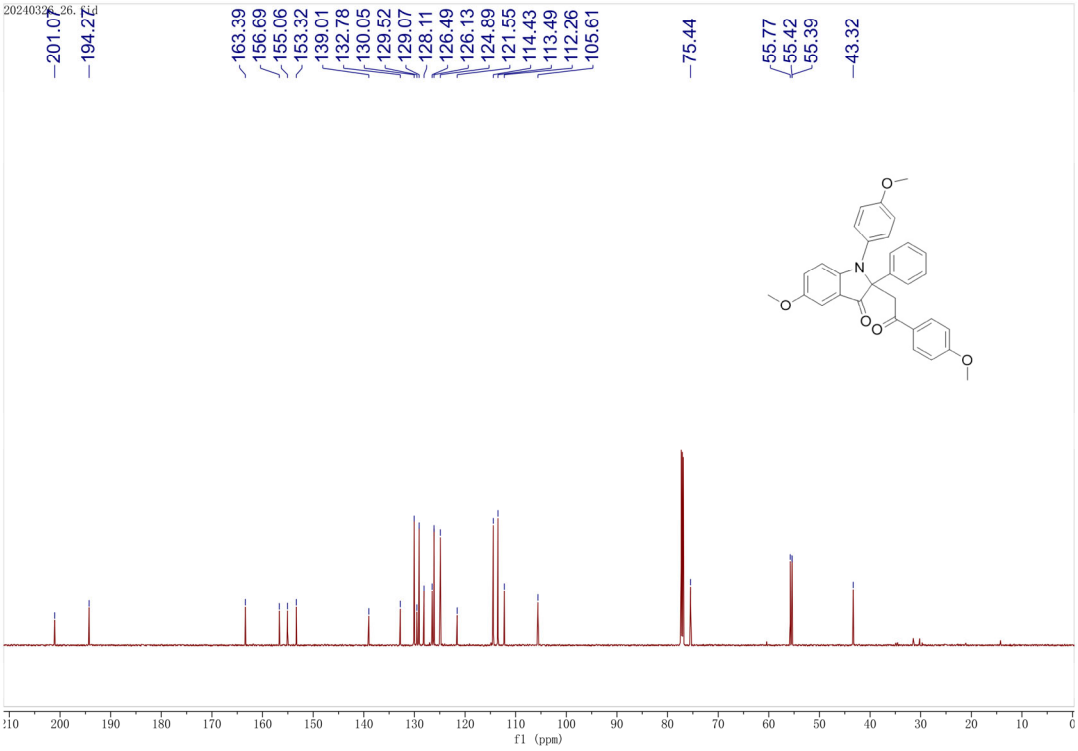
^{13}C NMR of compound **4f** (in $CDCl_3$)



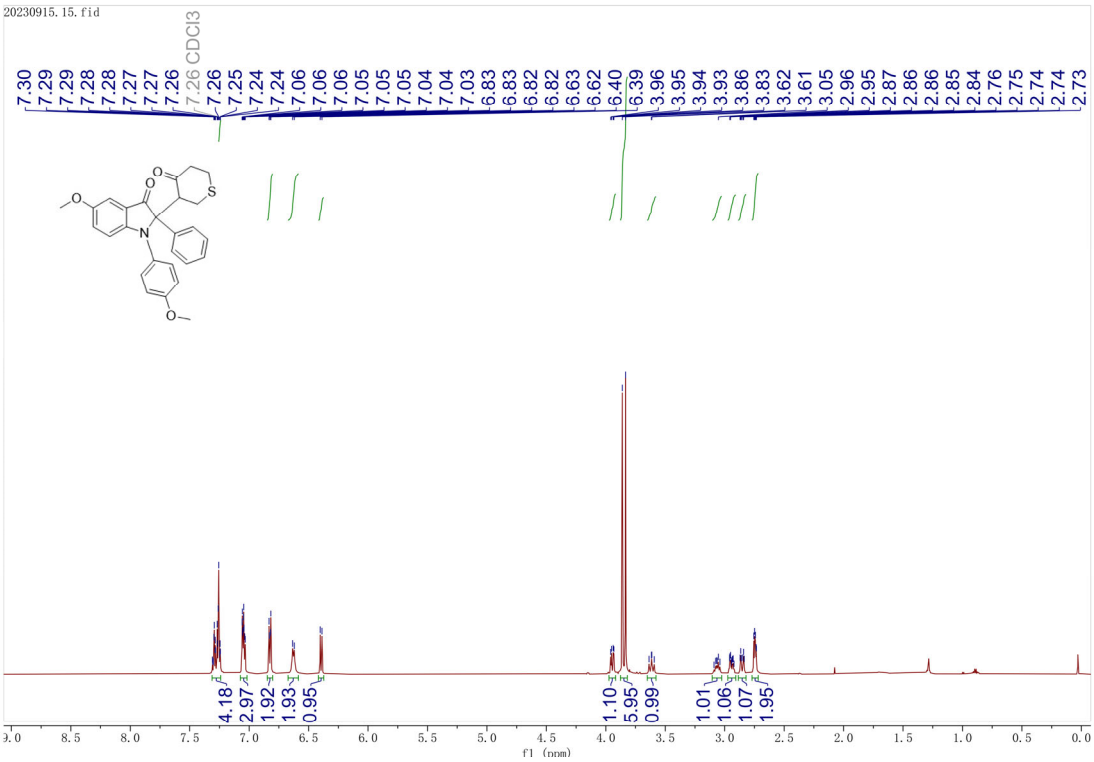
^{1}H NMR of compound **4g** (in $CDCl_3$)



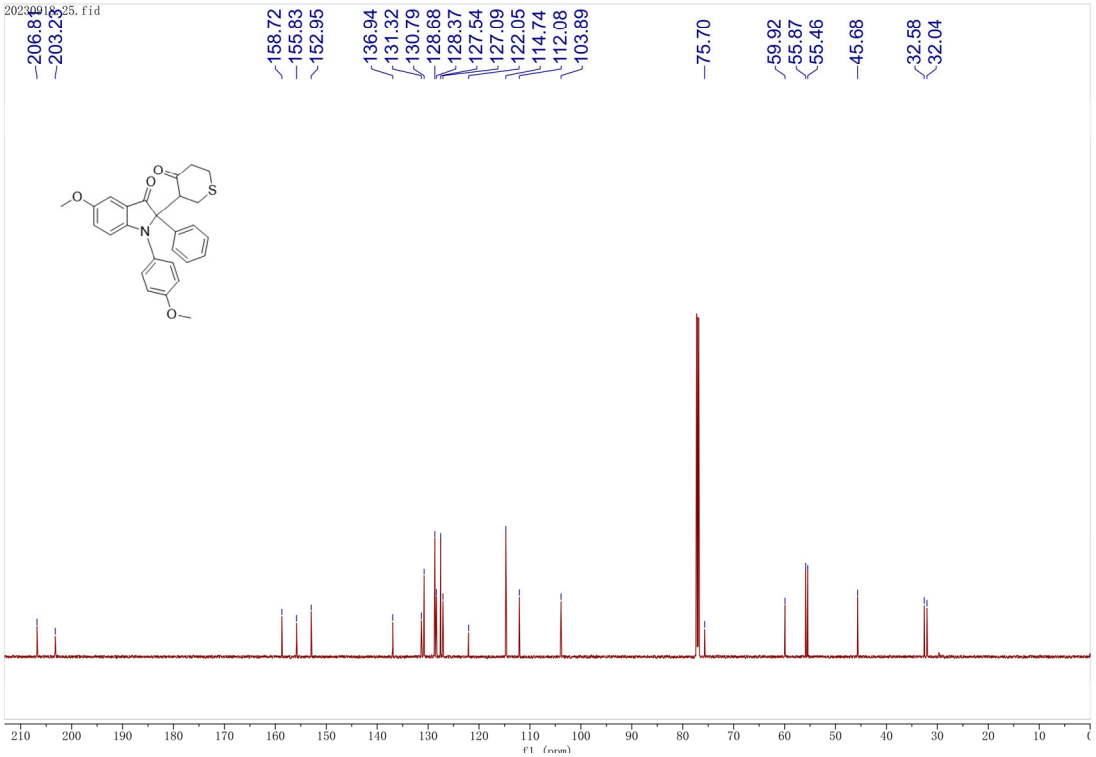
^{13}C NMR of compound **4g** (in $CDCl_3$)



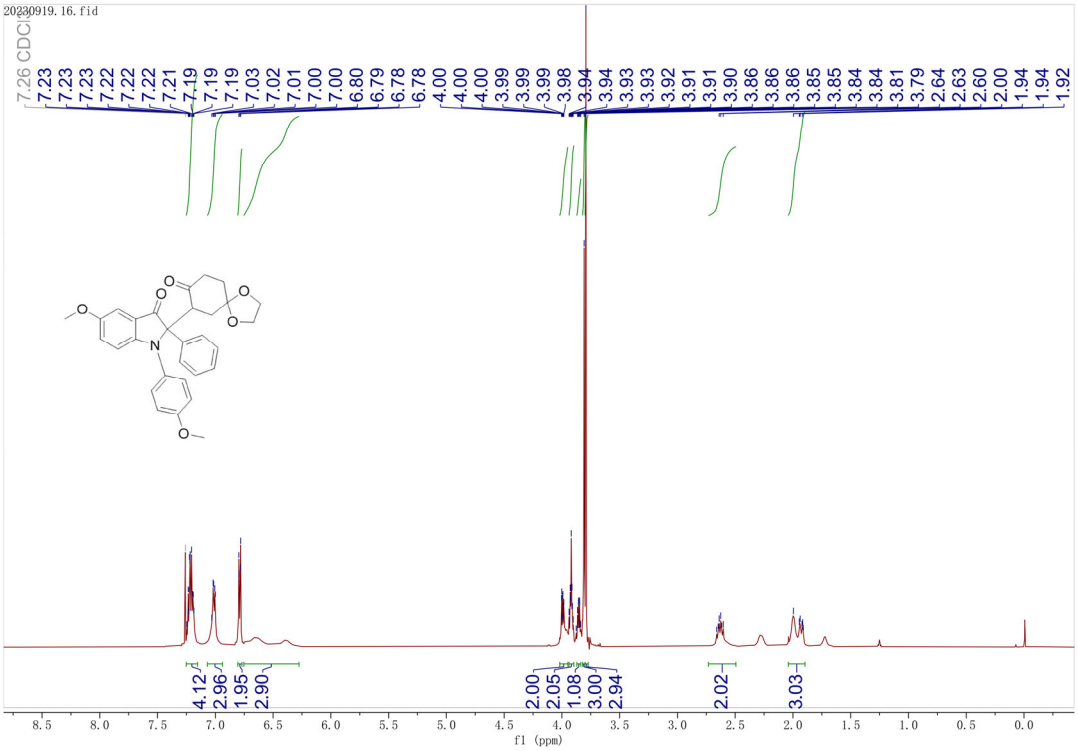
^{1}H NMR of compound **4h** (in $CDCl_3$)



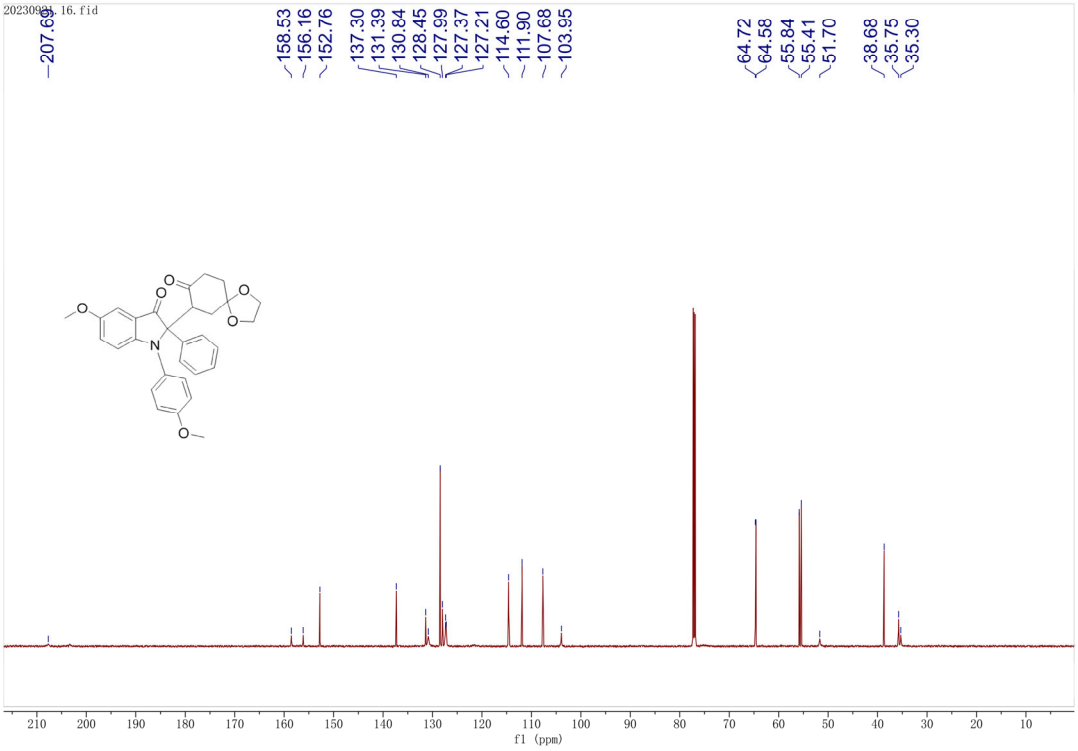
^{13}C NMR of compound **4h** (in $CDCl_3$)



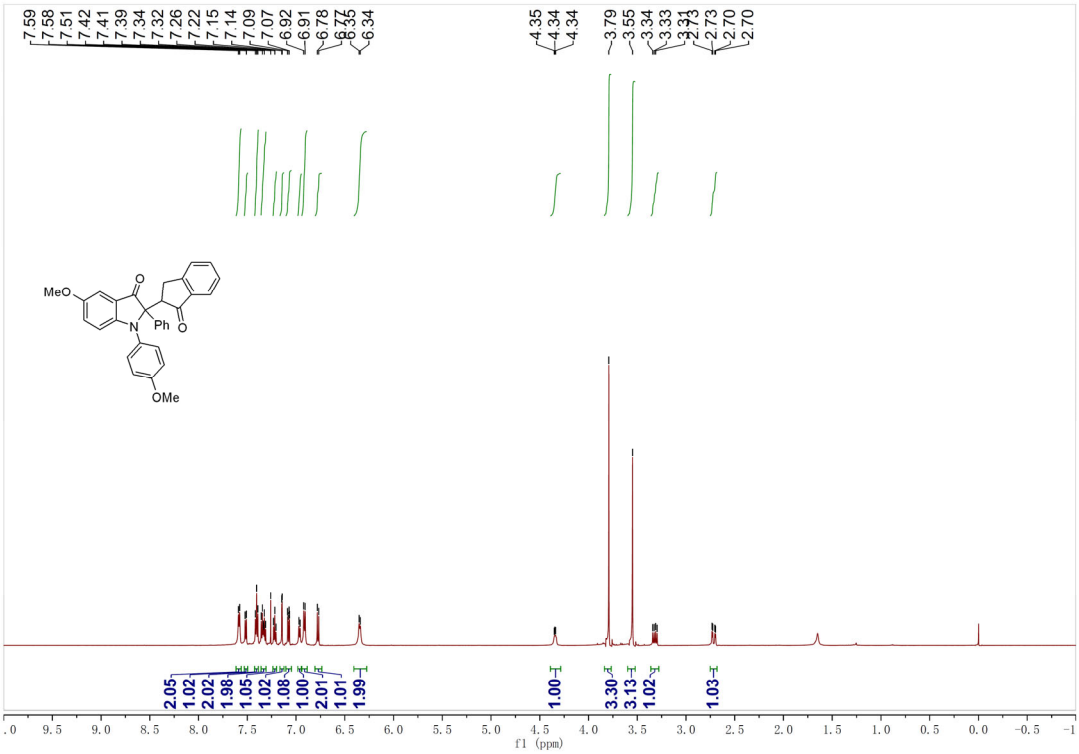
^{1}H NMR of compound **4i** (in $CDCl_3$)



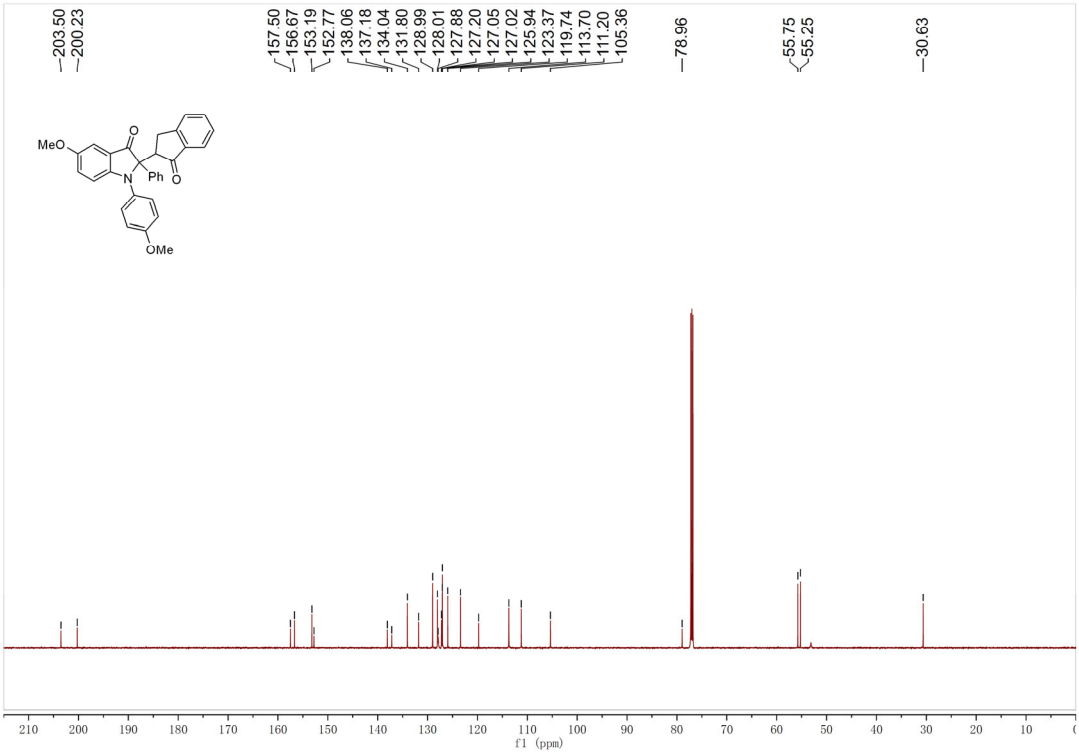
^{13}C NMR of compound **4i** (in $CDCl_3$)



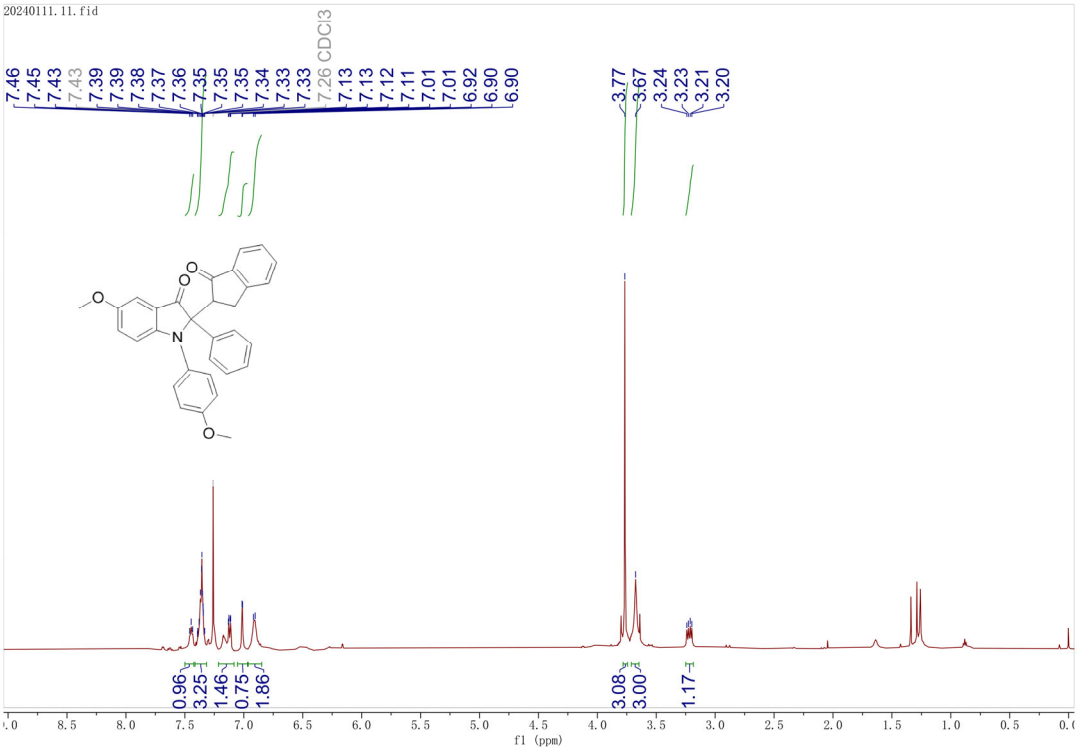
^{1}H NMR of compound **4j-syn** (in $CDCl_3$)



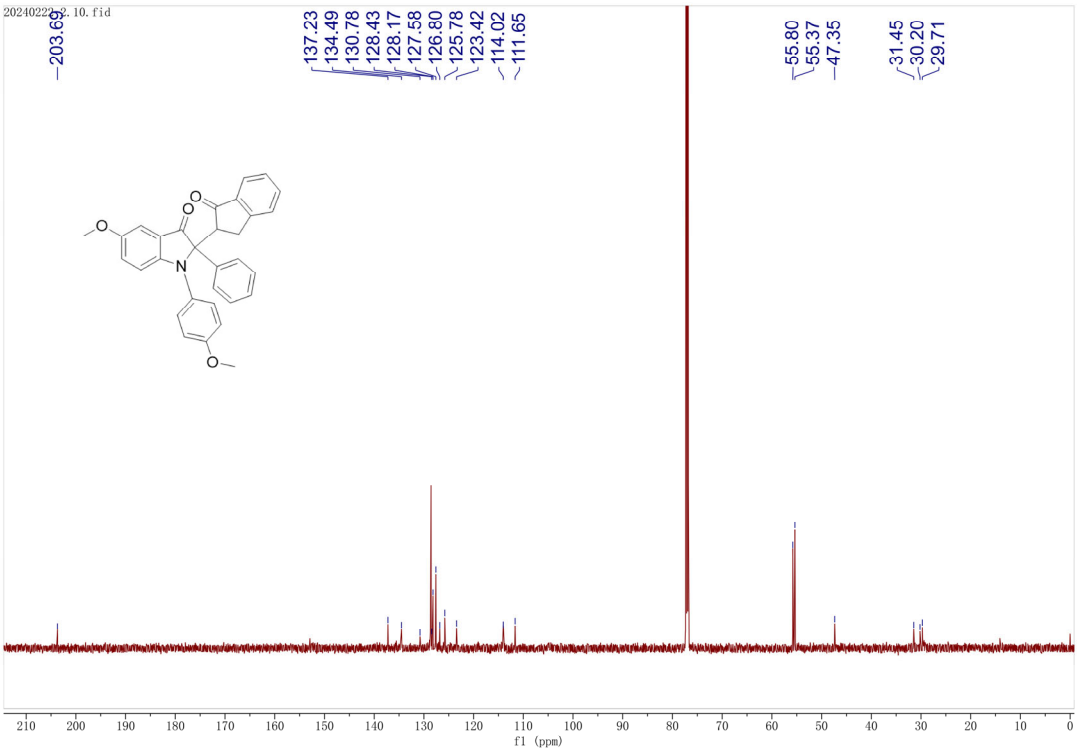
^{13}C NMR of compound **4j-syn** (in $CDCl_3$)



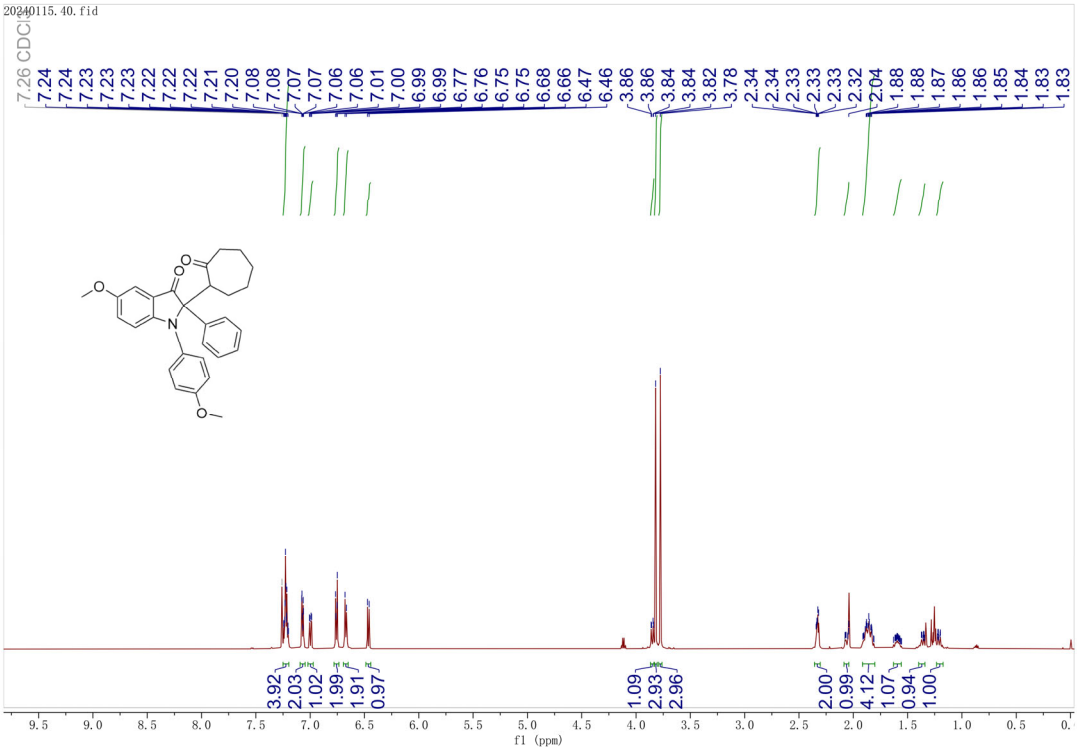
^{1}H NMR of compound **4j-anti** (in $CDCl_3$)



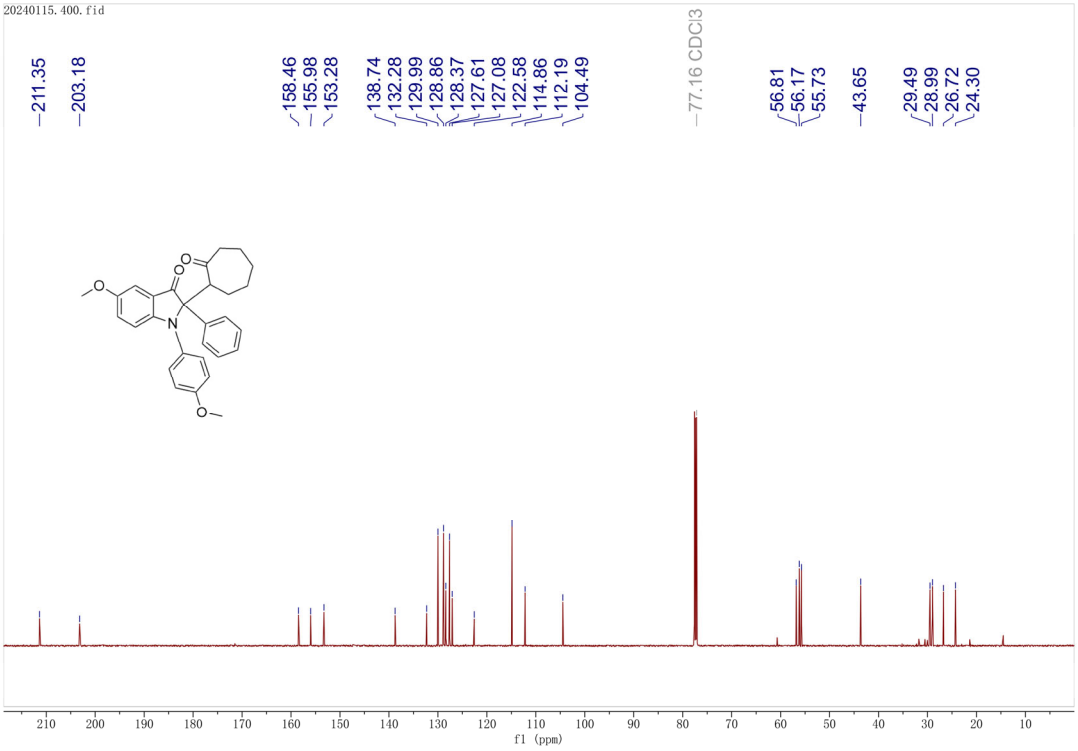
^{13}C NMR of compound **4j-anti** (in $CDCl_3$)



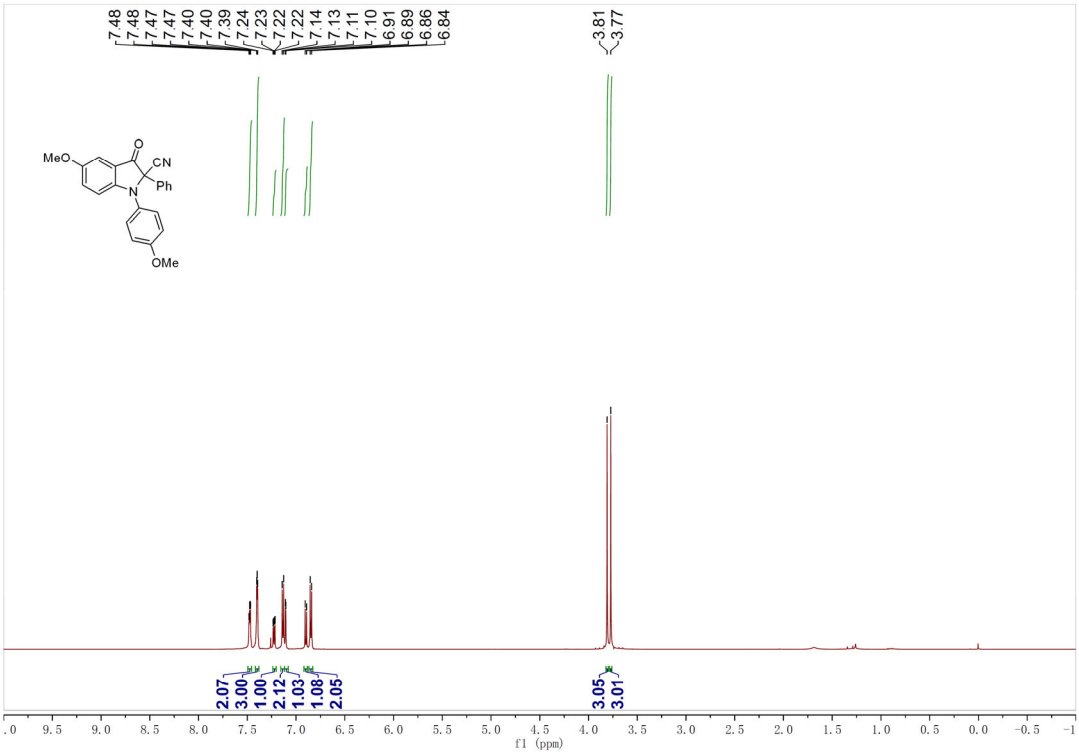
^{1}H NMR of compound **4k** (in $CDCl_3$)



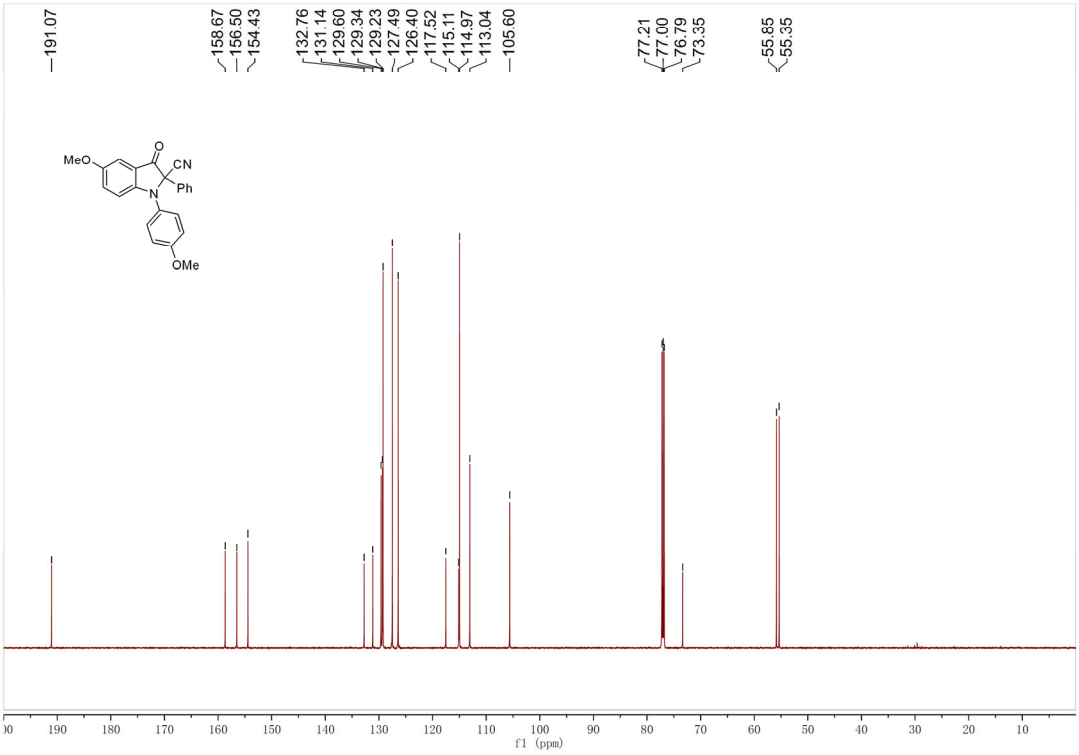
^{13}C NMR of compound **4k** (in $CDCl_3$)



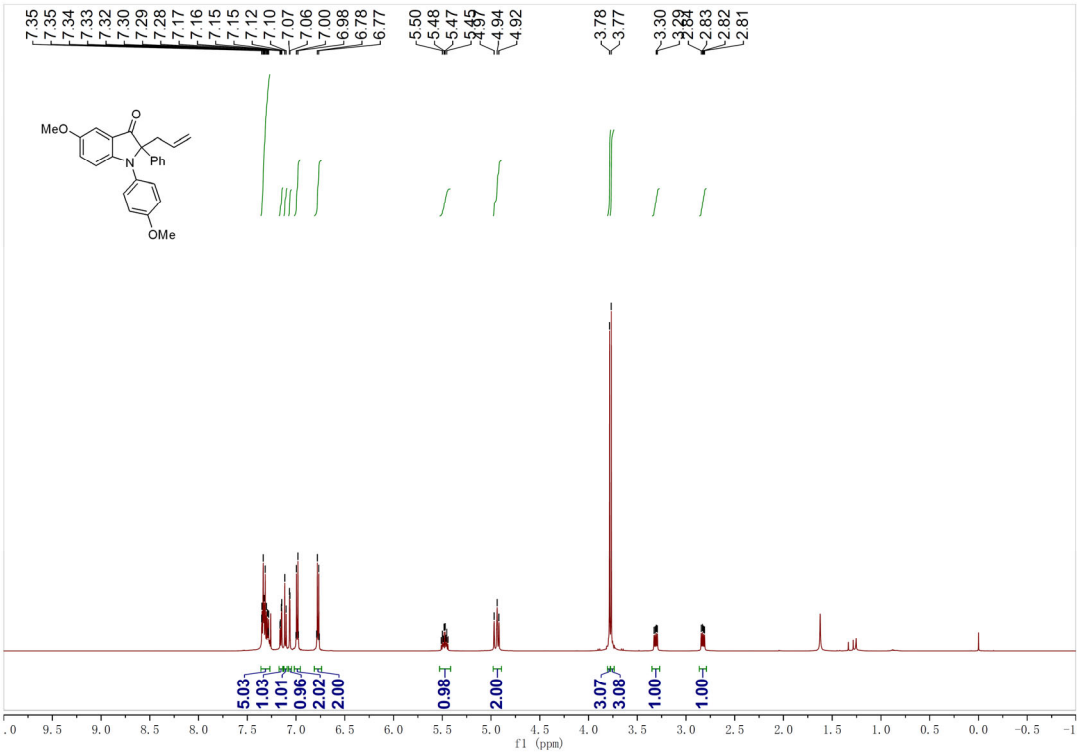
^{1}H NMR of compound **4l** (in $CDCl_3$)



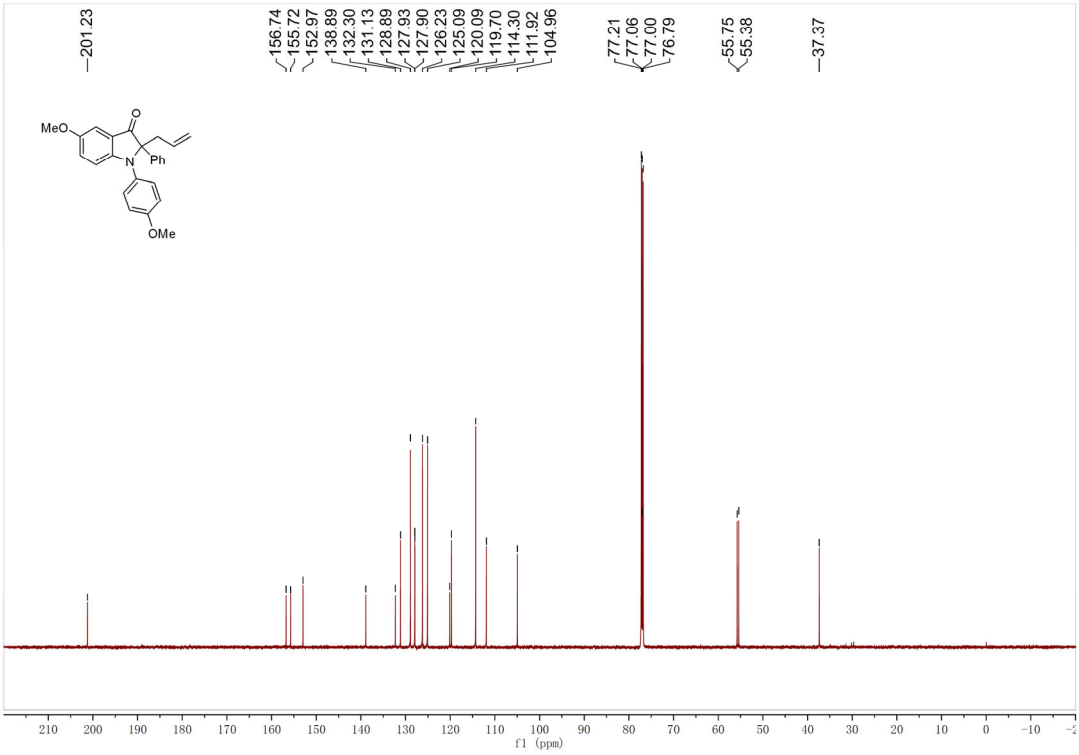
^{13}C NMR of compound **4l** (in $CDCl_3$)



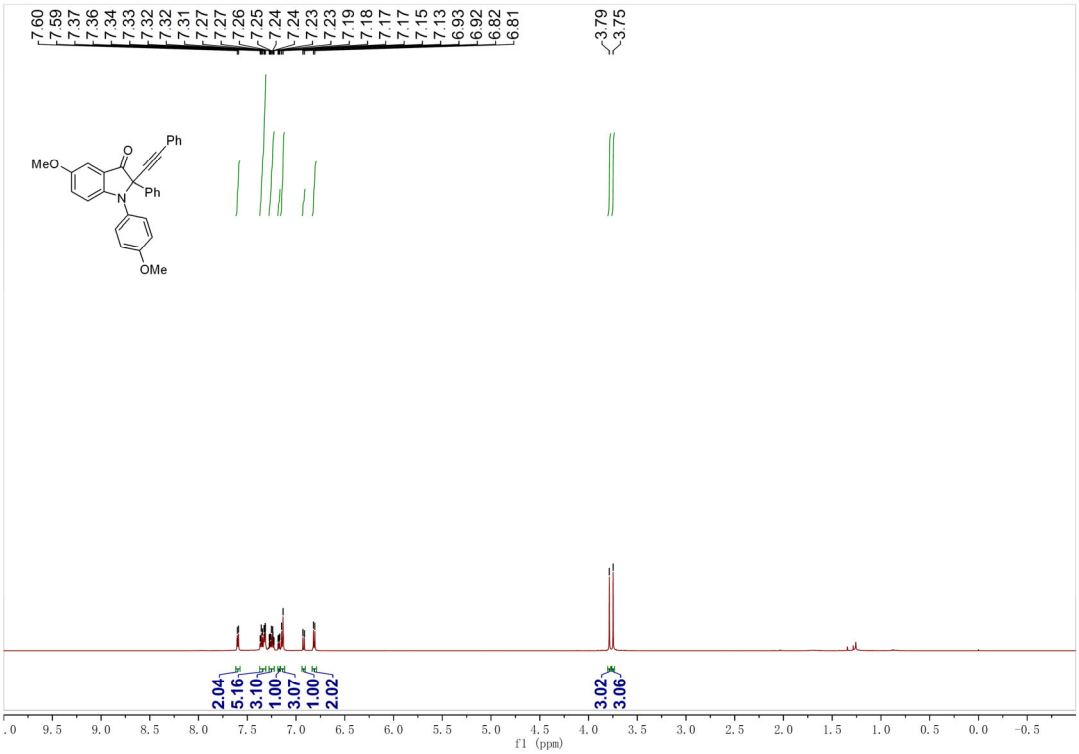
^{1}H NMR of compound **4m** (in $CDCl_3$)



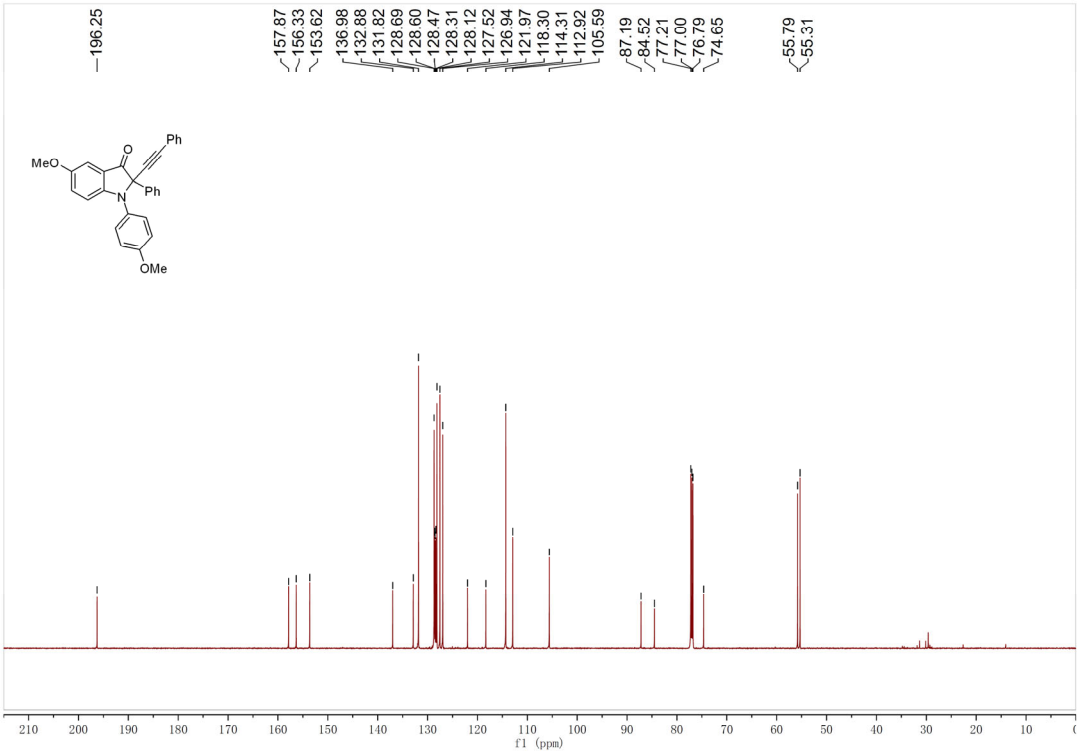
^{13}C NMR of compound **4m** (in $CDCl_3$)



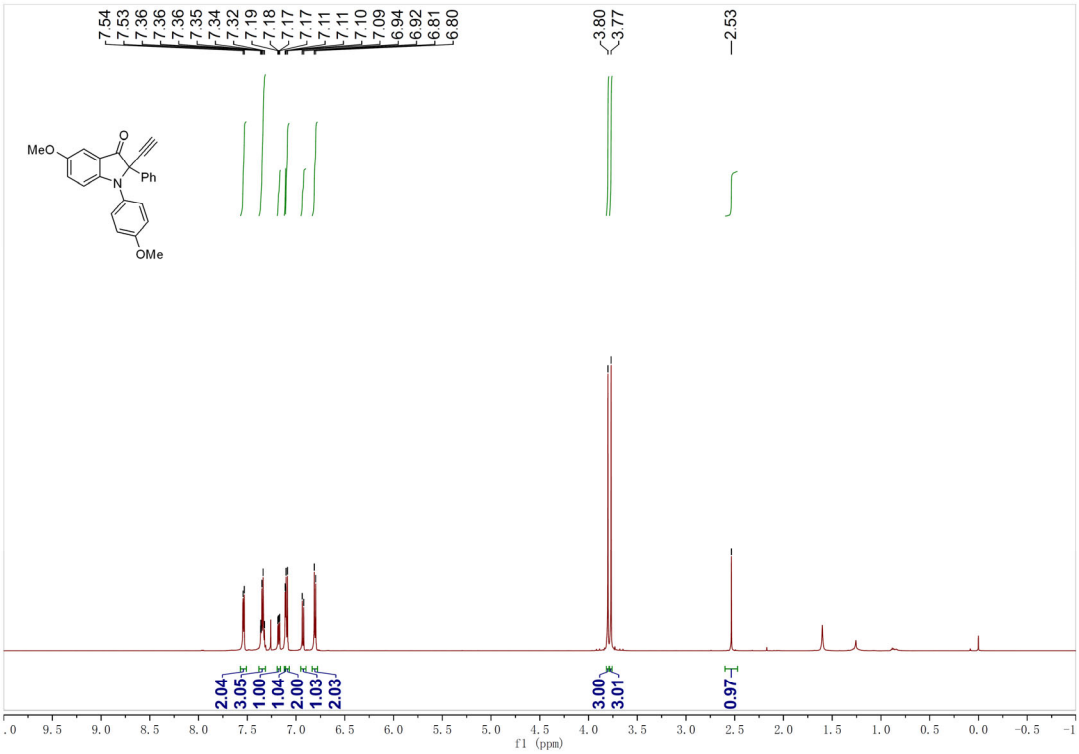
^{1}H NMR of compound **4n** (in $CDCl_3$)



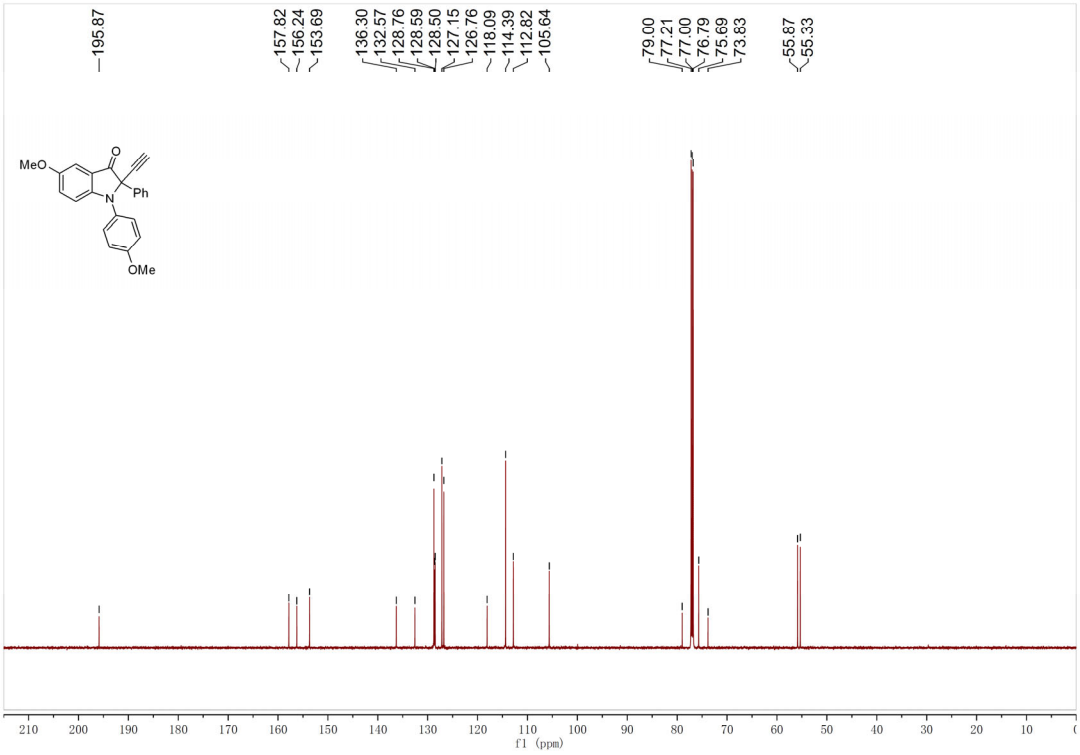
^{13}C NMR of compound **4n** (in $CDCl_3$)



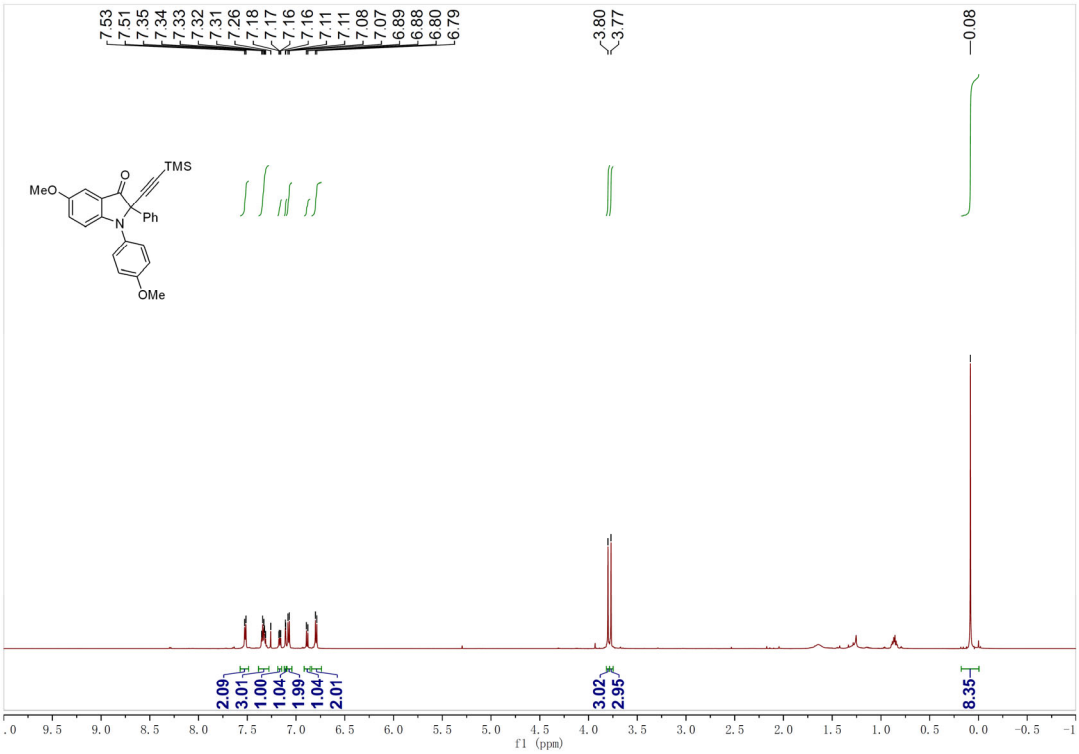
^{1}H NMR of compound **4o** (in $CDCl_3$)



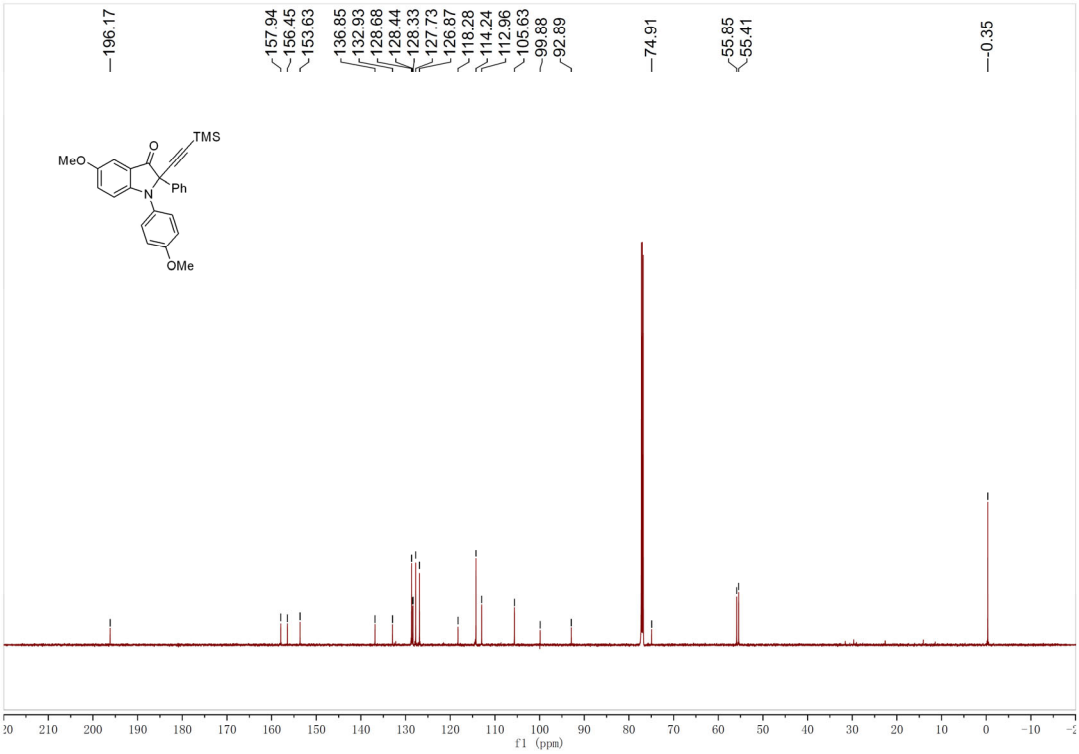
^{13}C NMR of compound **4o** (in $CDCl_3$)



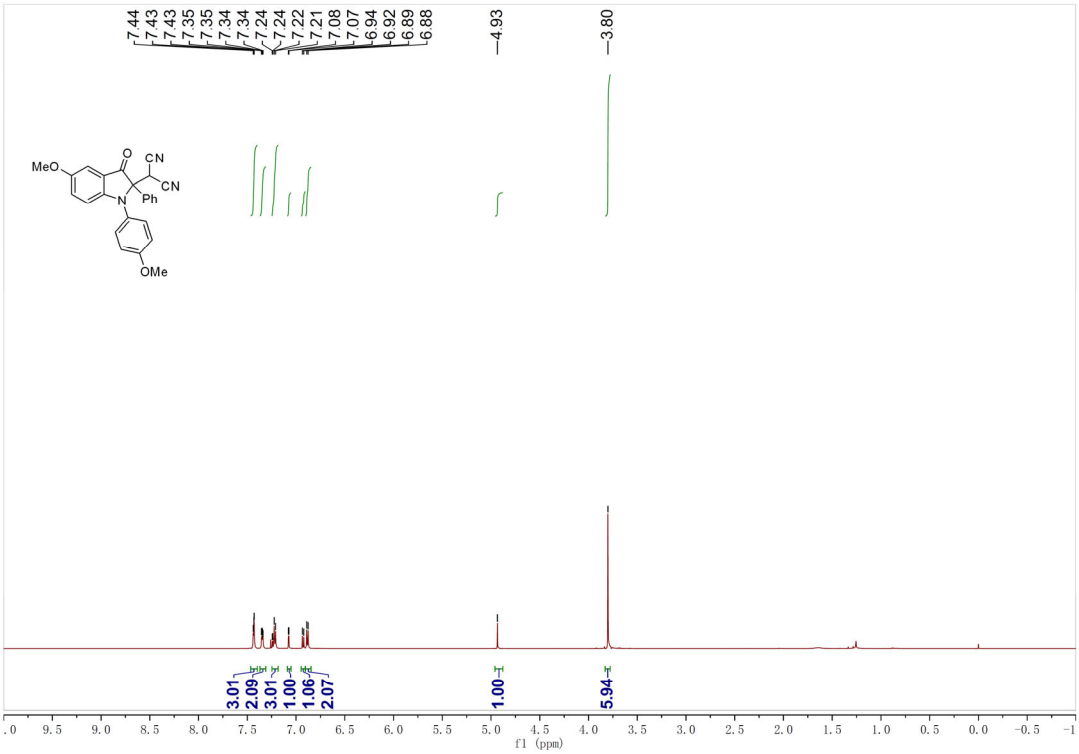
^{1}H NMR of compound **4o'** (in $CDCl_3$)



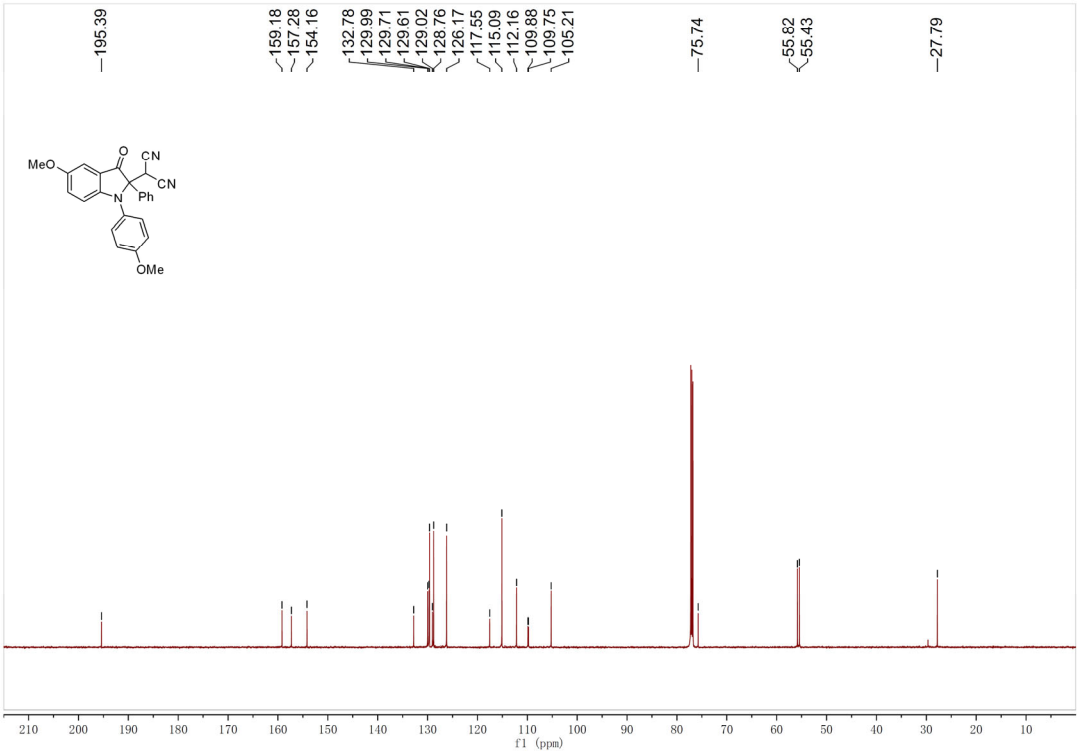
^{13}C NMR of compound **4o'** (in $CDCl_3$)



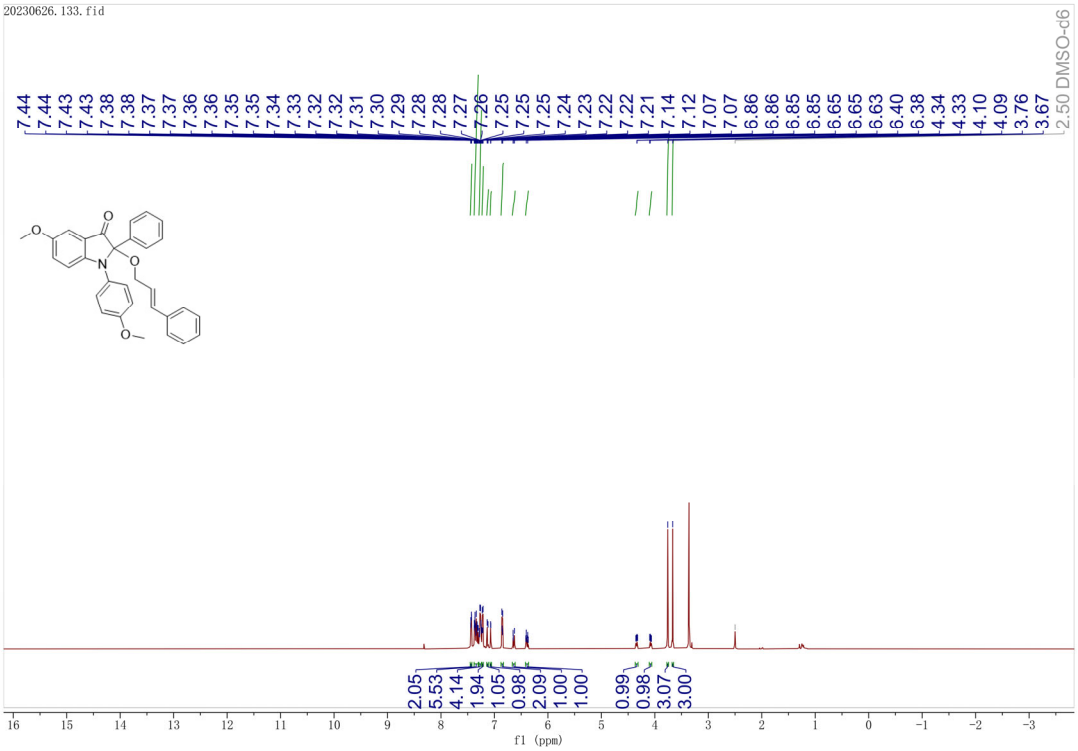
^{1}H NMR of compound **4p** (in $CDCl_3$)



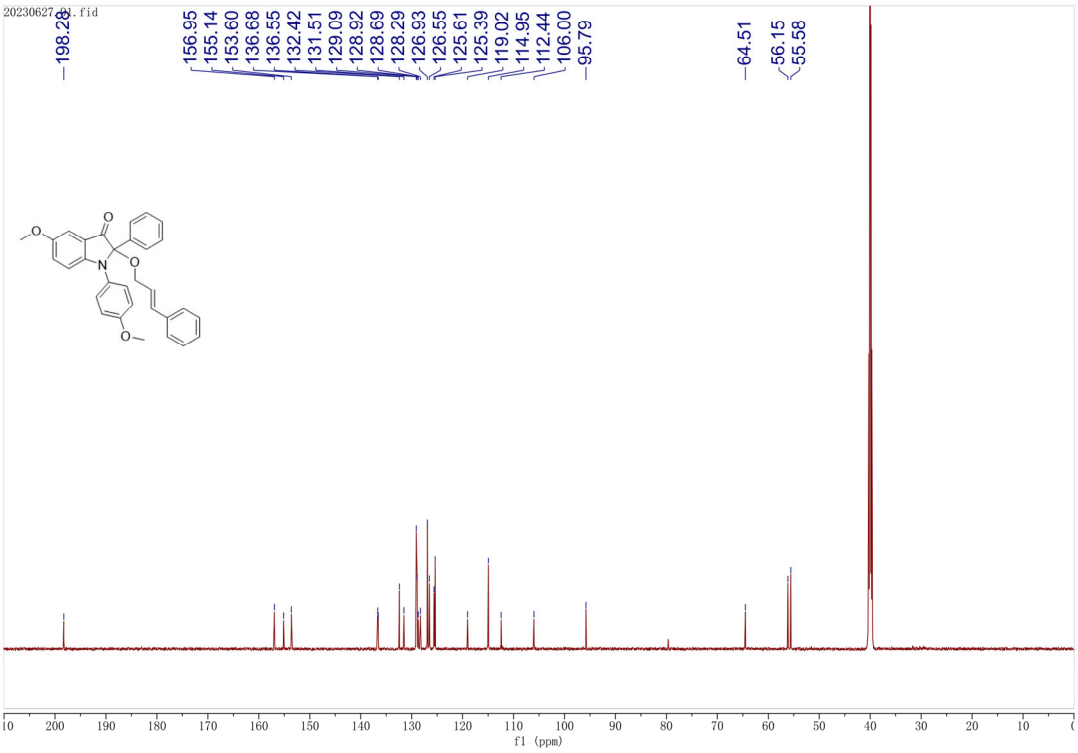
^{13}C NMR of compound **4p** (in $CDCl_3$)



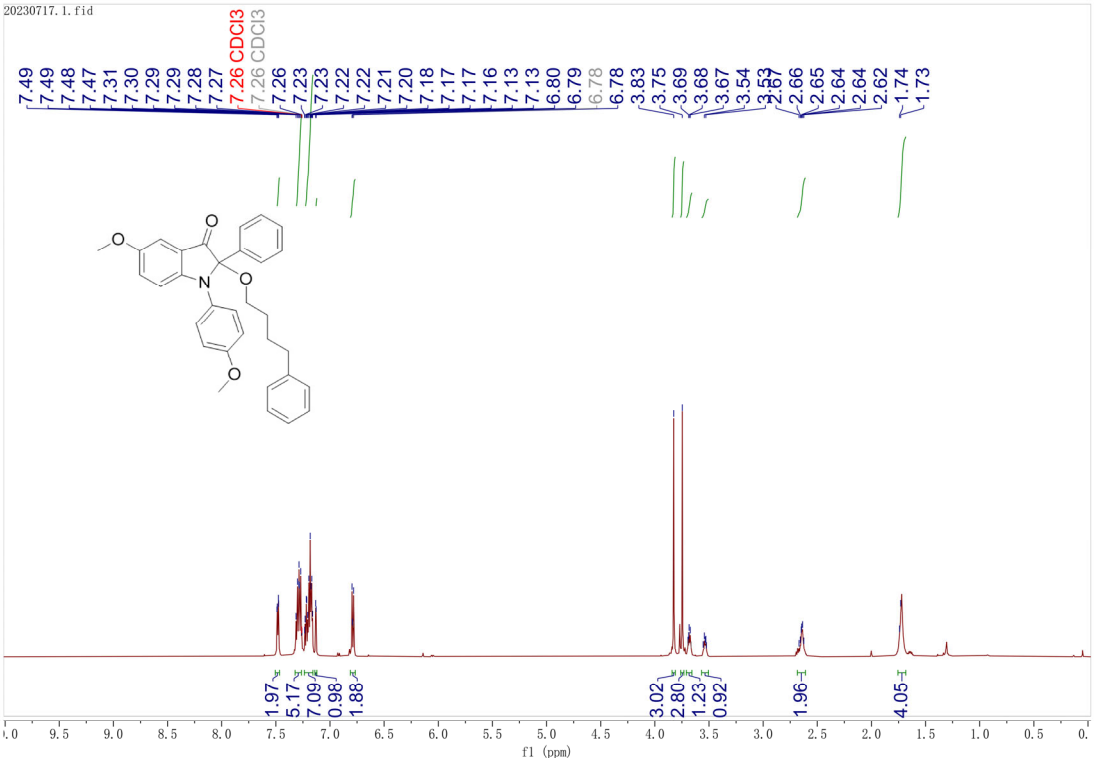
^{1}H NMR of compound **4q** (in DMSO-d$_6$)



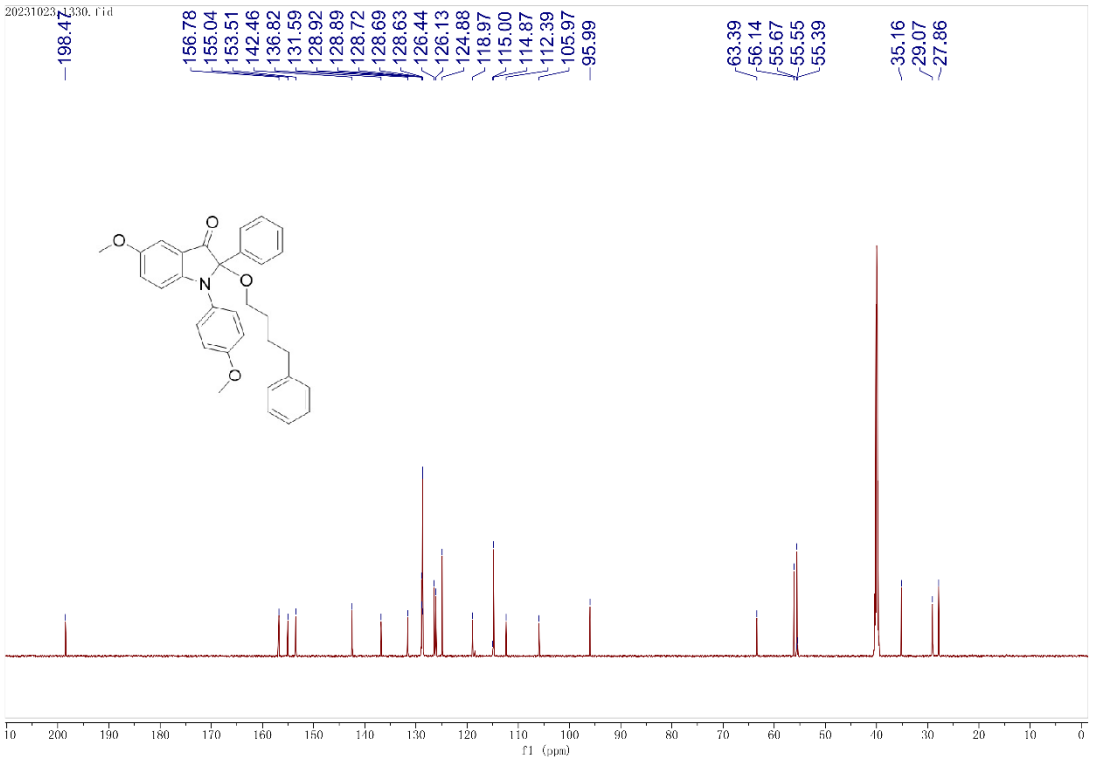
^{13}C NMR of compound **4q** (in DMSO-d$_6$)



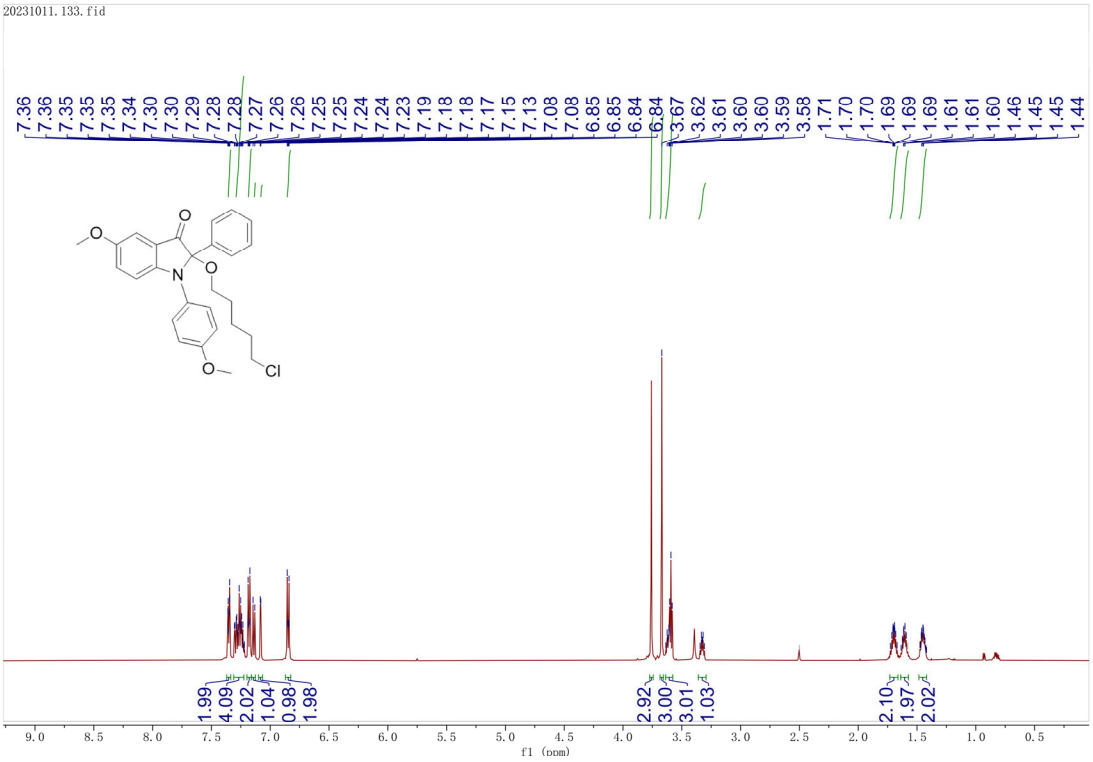
^{1}H NMR of compound **4r** (in $CHCl_3$)



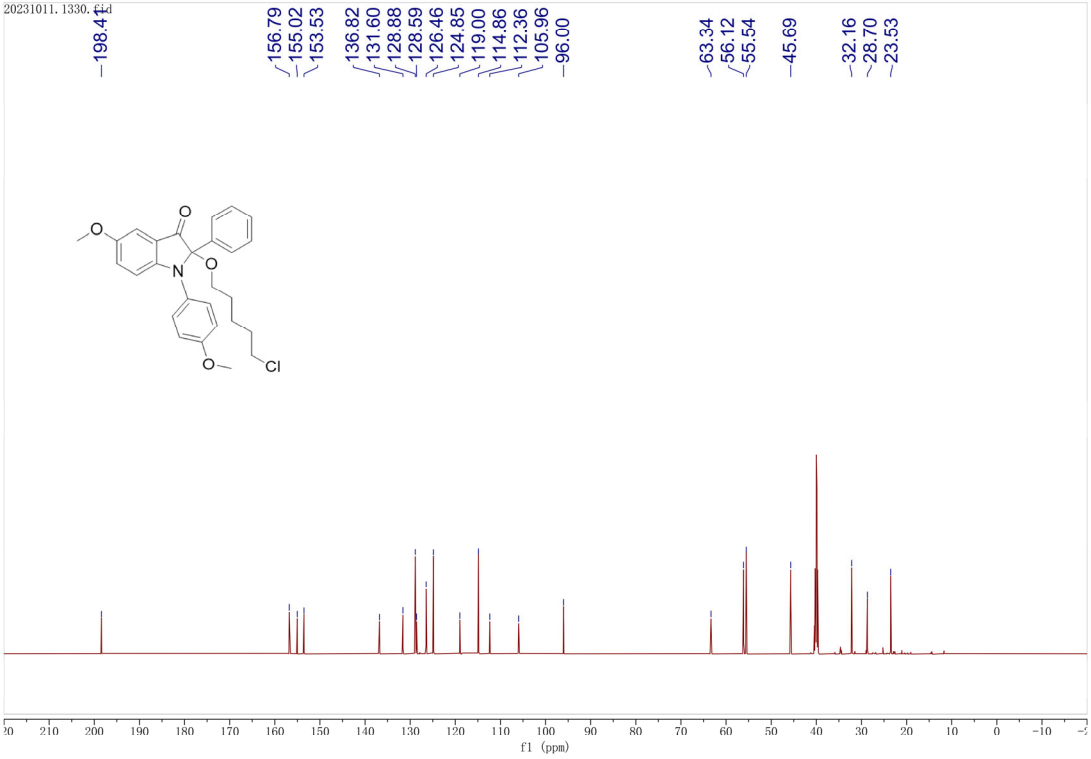
^{13}C NMR of compound **4r** (in DMSO-d_6)



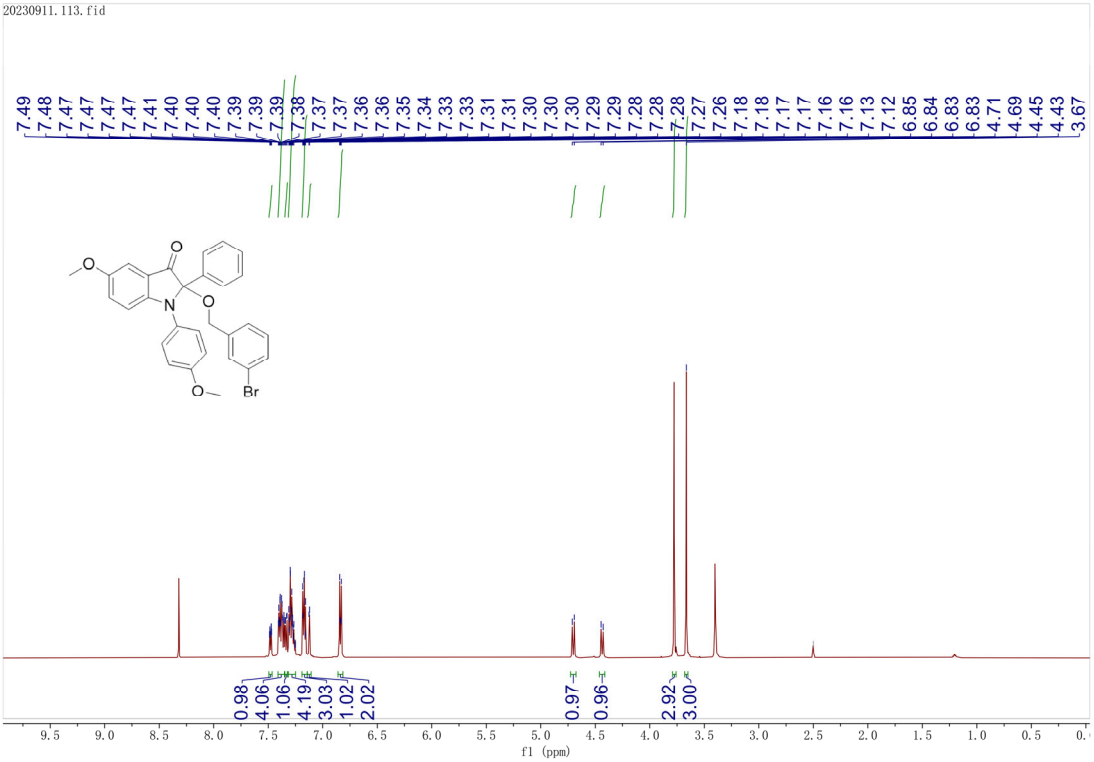
^{1}H NMR of compound **4s** (in DMSO-d_6)



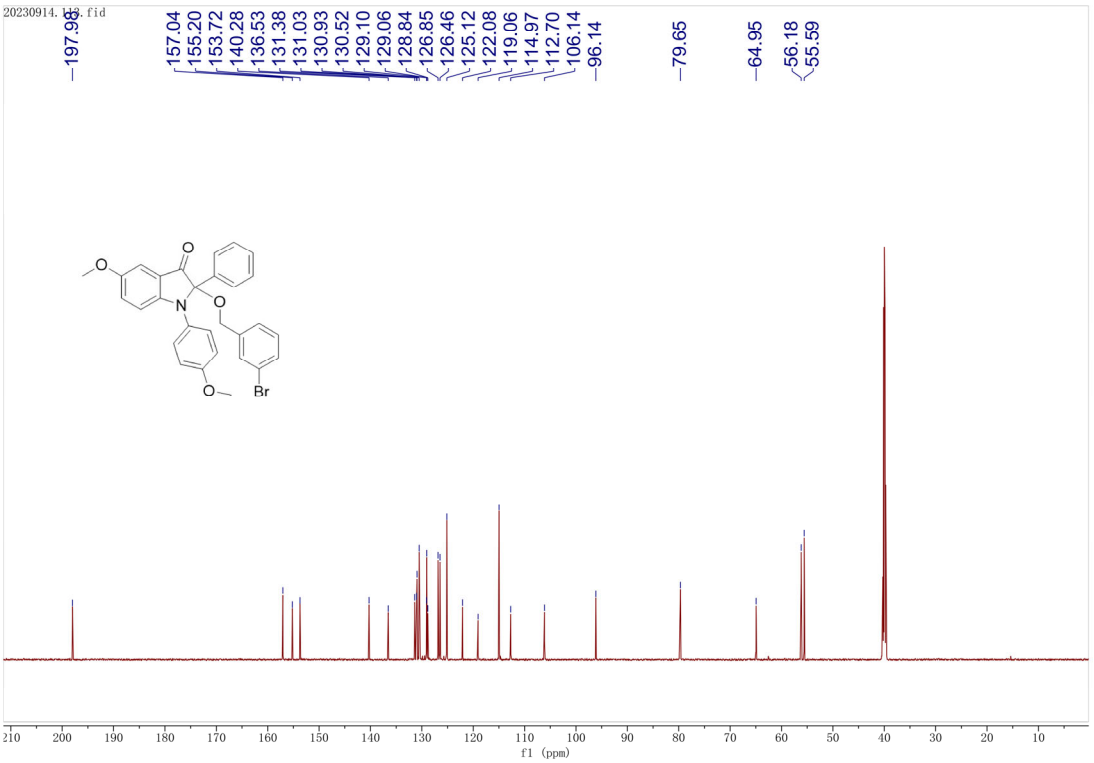
^{13}C NMR of compound **4s** (in DMSO-d_6)



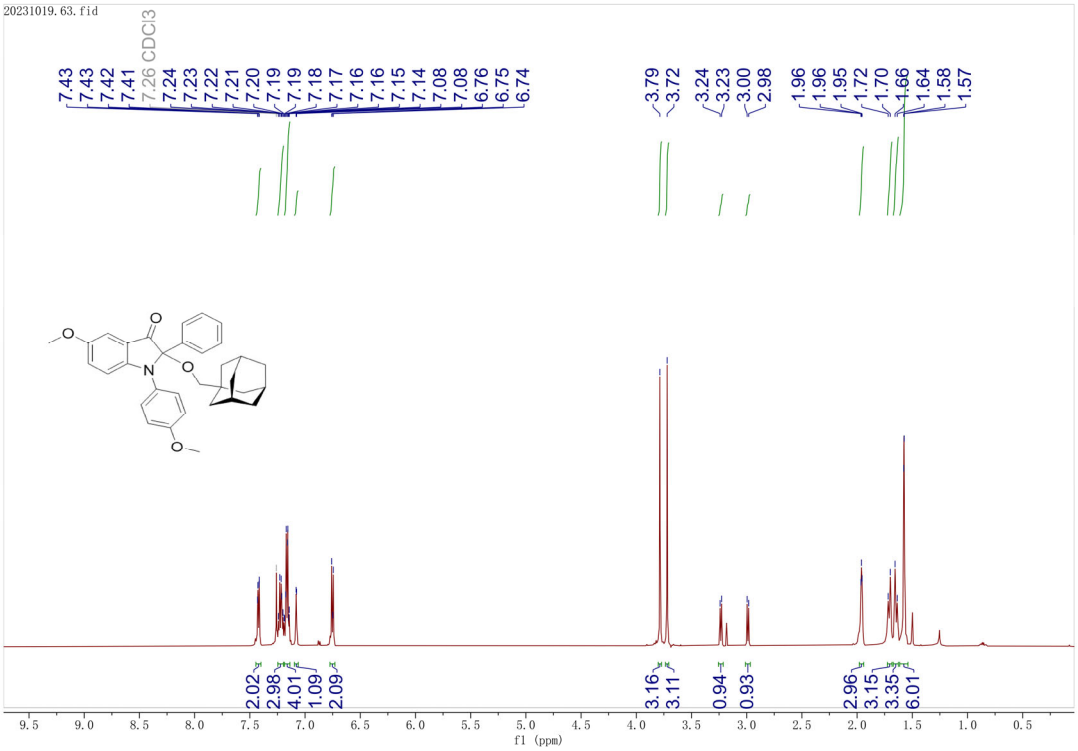
^{1}H NMR of compound **4t** (in DMSO-d$_6$)



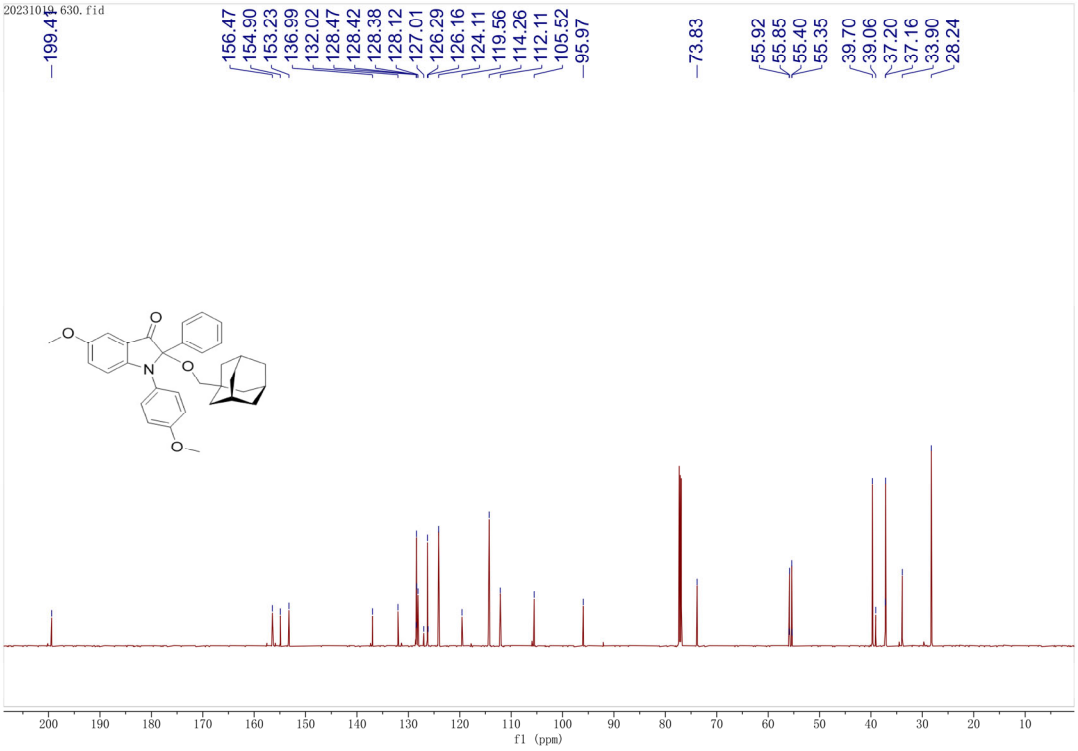
^{13}C NMR of compound **4t** (in DMSO-d$_6$)



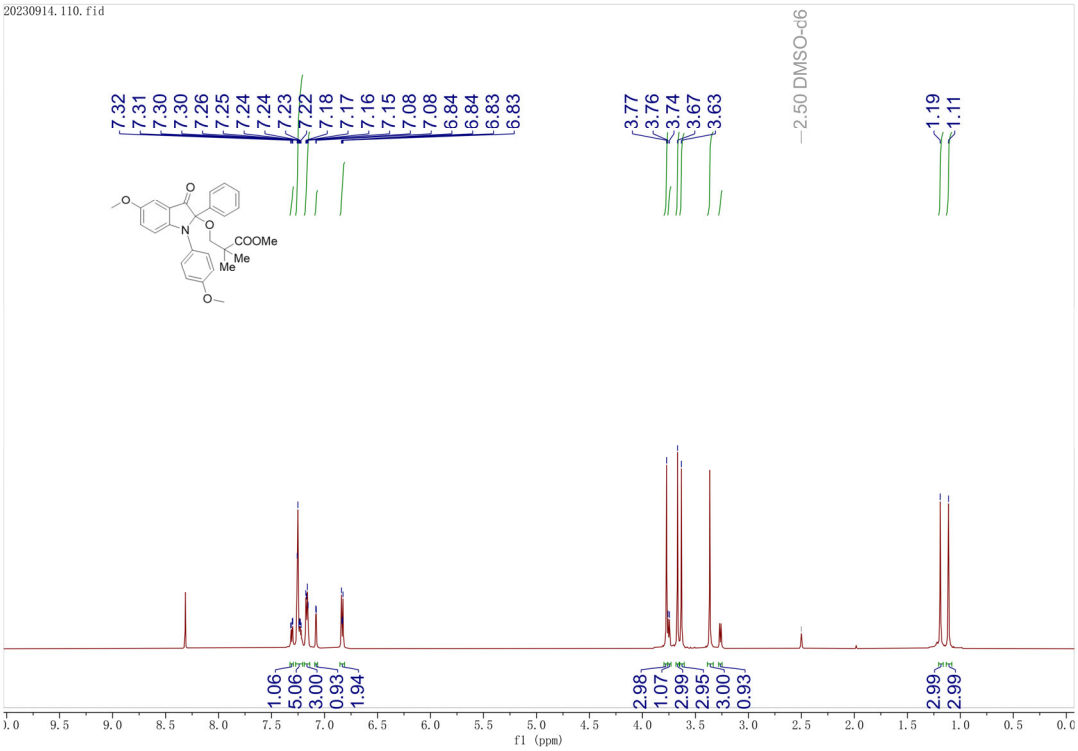
^{1}H NMR of compound **4u** (in $CHCl_3$)



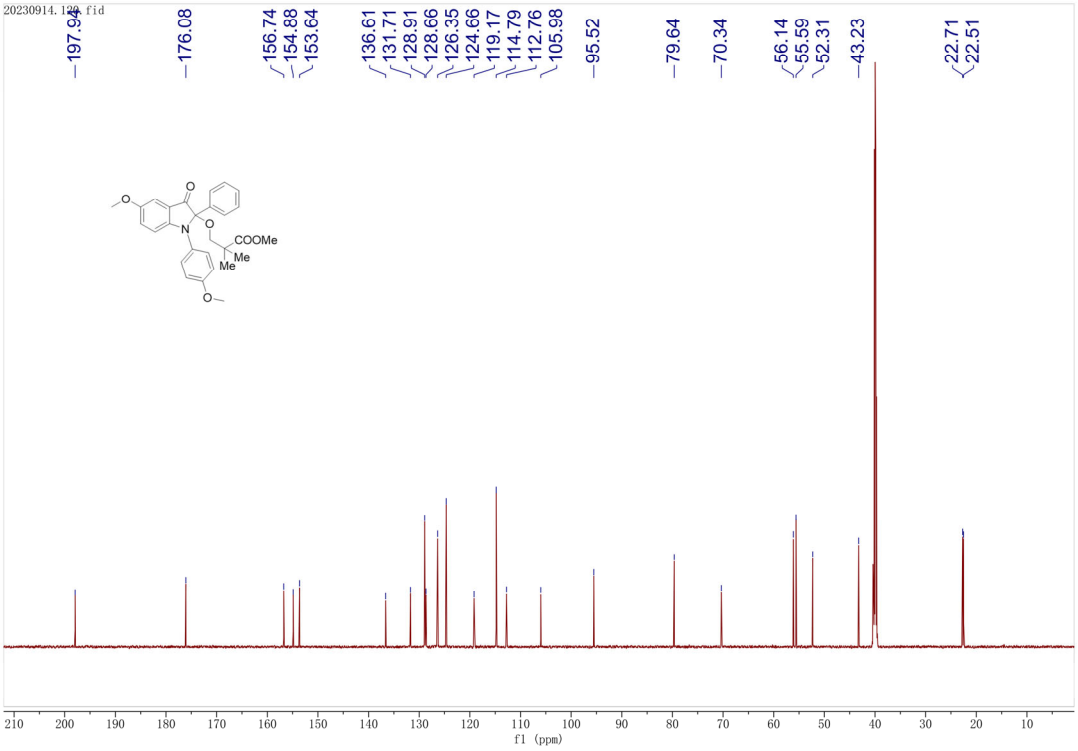
^{13}C NMR of compound **4u** (in $CHCl_3$)



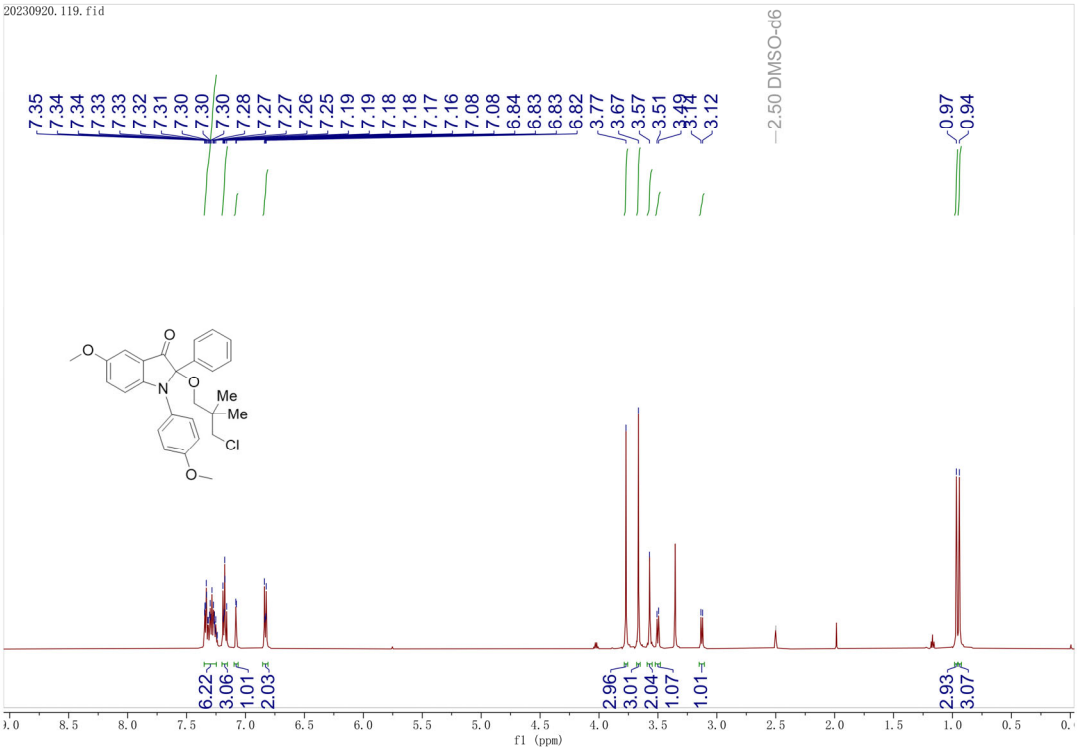
^{1}H NMR of compound **4v** (in DMSO-d$_6$)



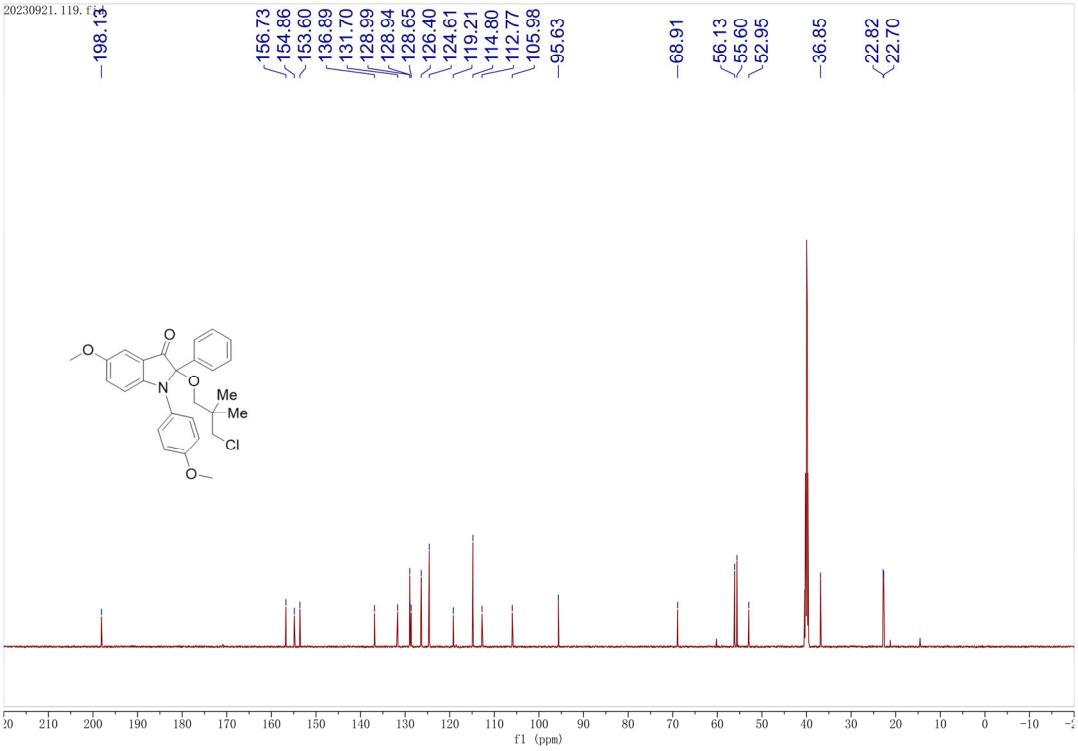
^{13}C NMR of compound **4v** (in DMSO-d$_6$)



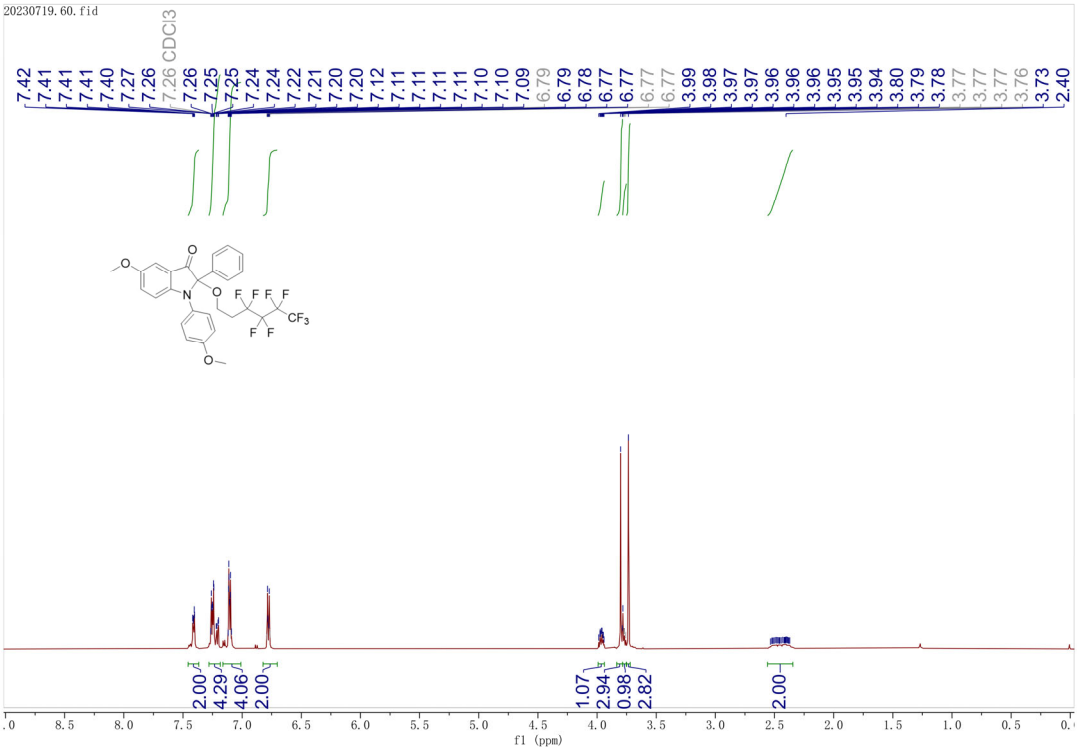
^{1}H NMR of compound **4w** (in DMSO-d_6)



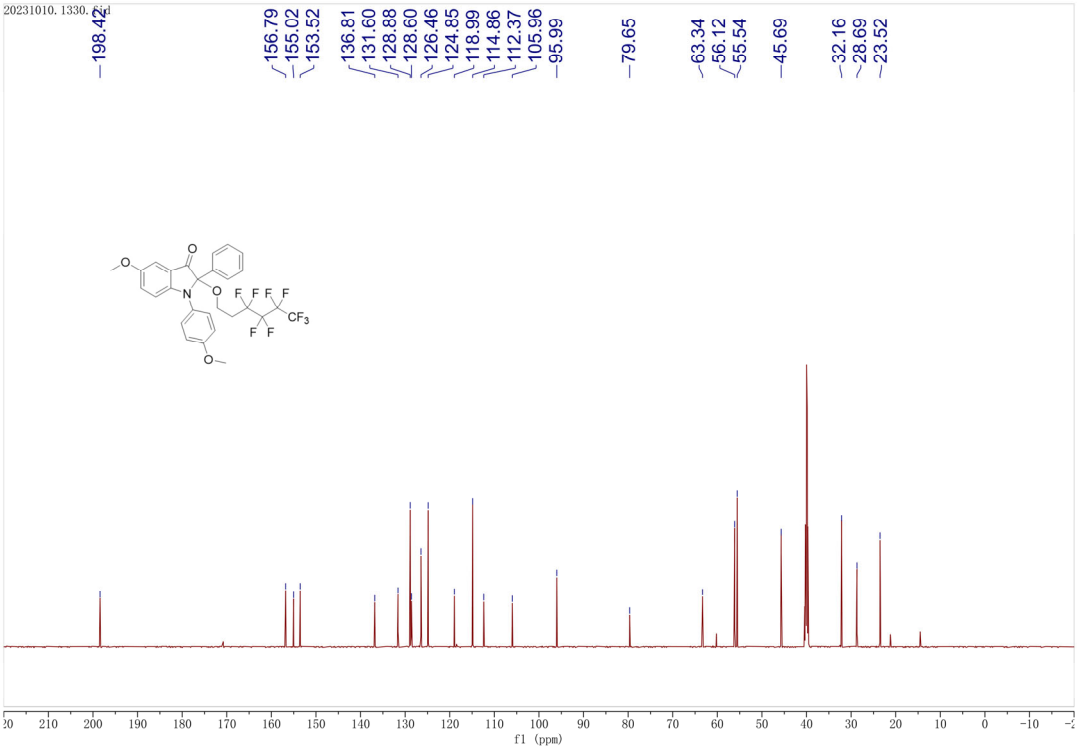
^{13}C NMR of compound **4w** (in DMSO-d_6)



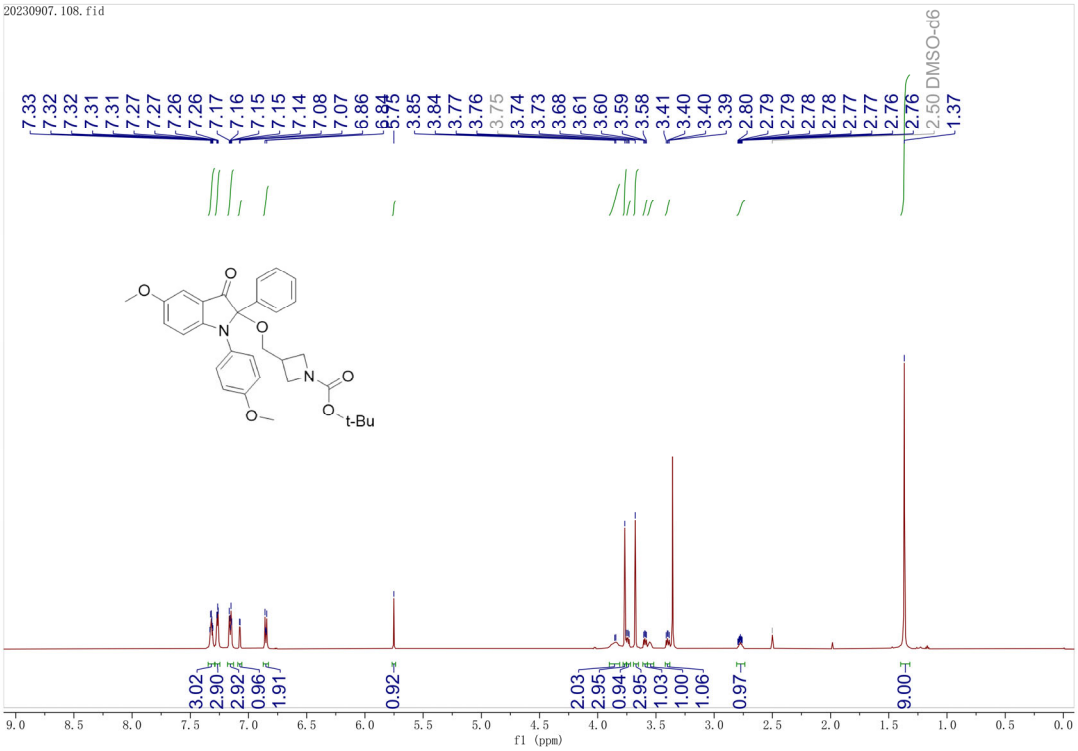
^{1}H NMR of compound **4x** (in $CDCl_3$)



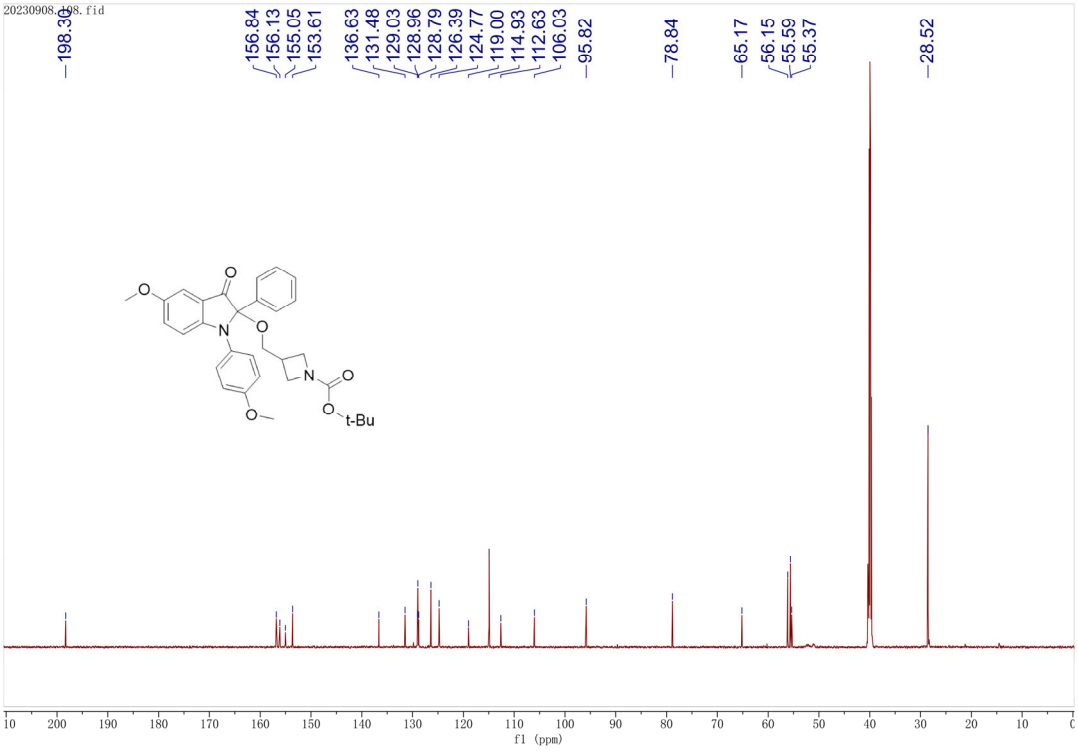
^{13}C NMR of compound **4x** (in DMSO-d_6)



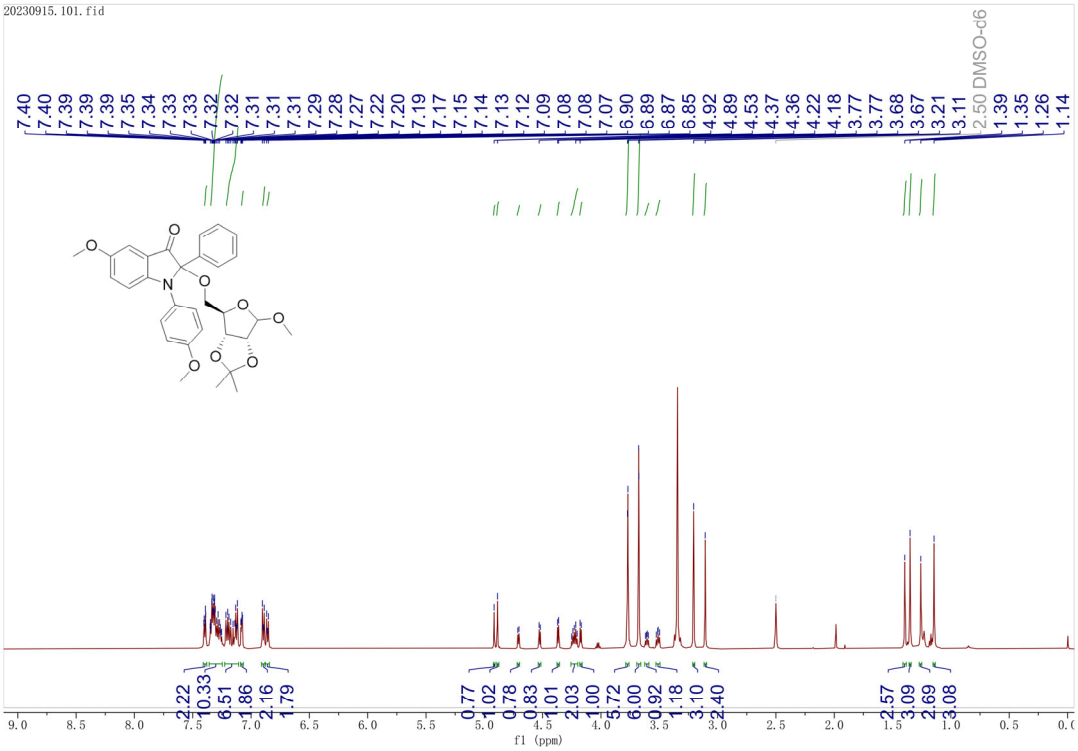
^{1}H NMR of compound **4y** (in DMSO-d$_6$)



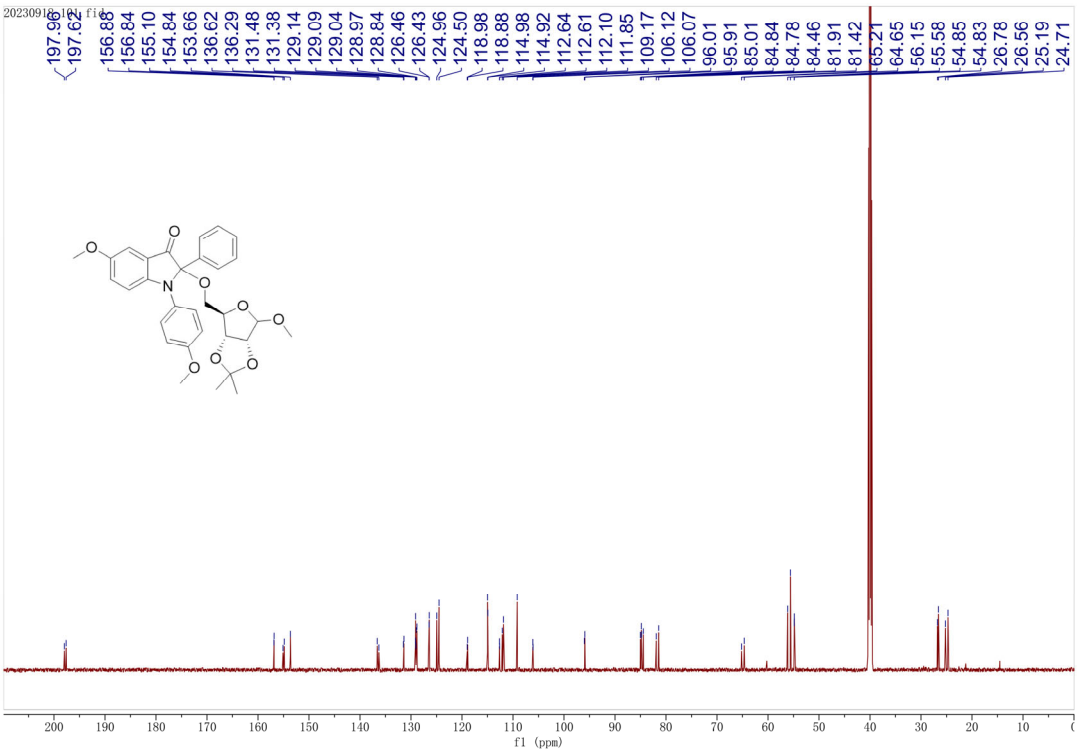
^{13}C NMR of compound **4y** (in DMSO-d$_6$)



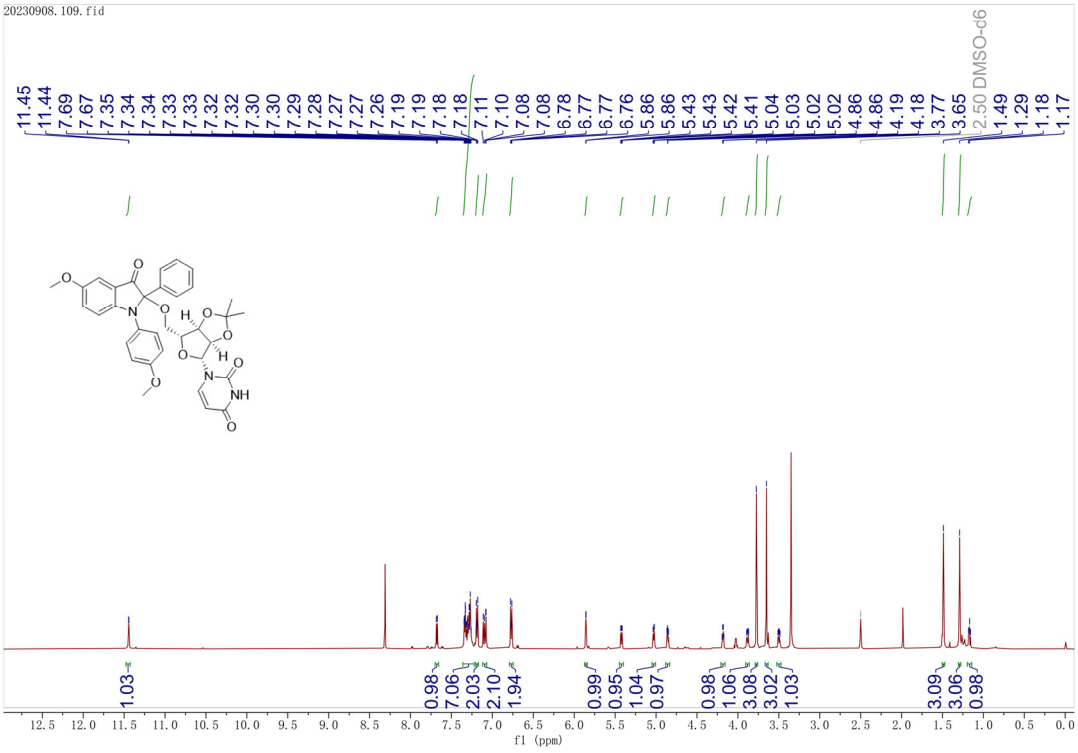
^{1}H NMR of compound **4z (major + minor)** (in DMSO-d_6)



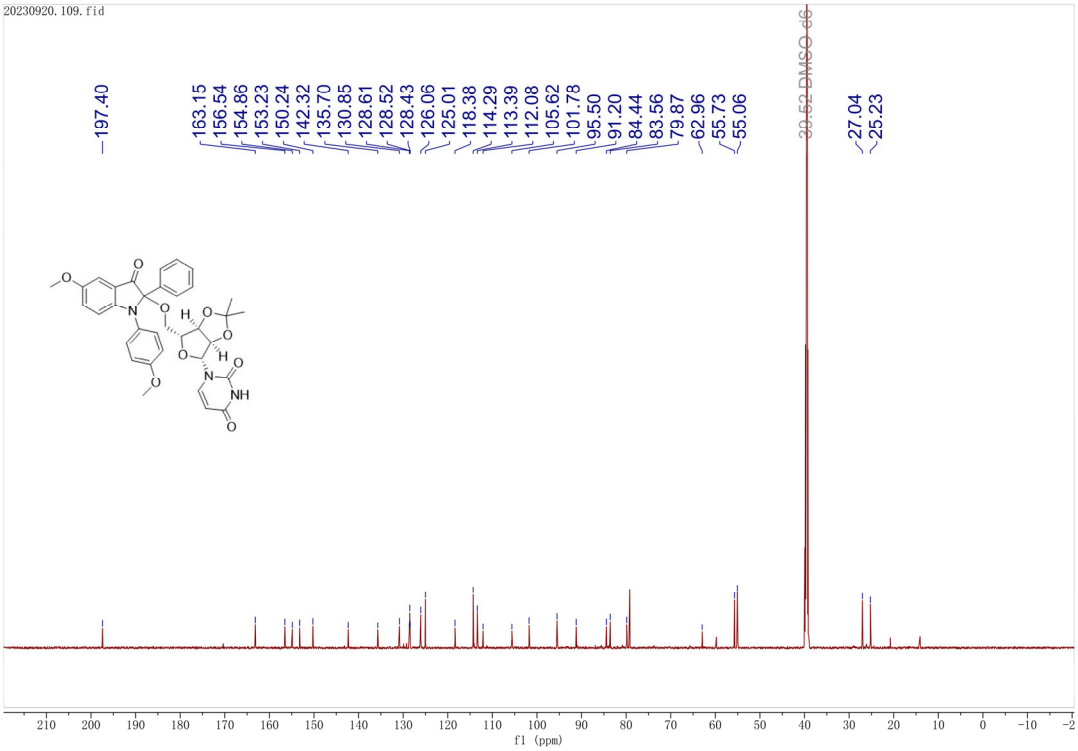
^{13}C NMR of compound **4z (major + minor)** (in DMSO-d_6)



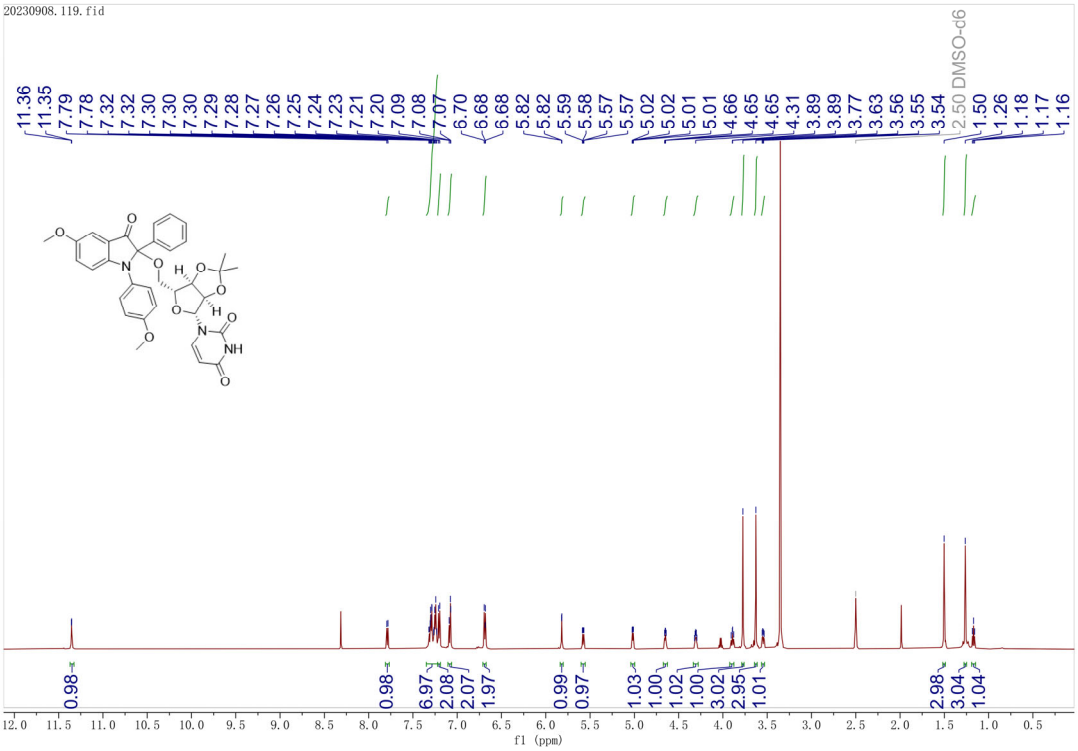
^{1}H NMR of compound **4aa-diastereoisomer A** (in DMSO-d_6)



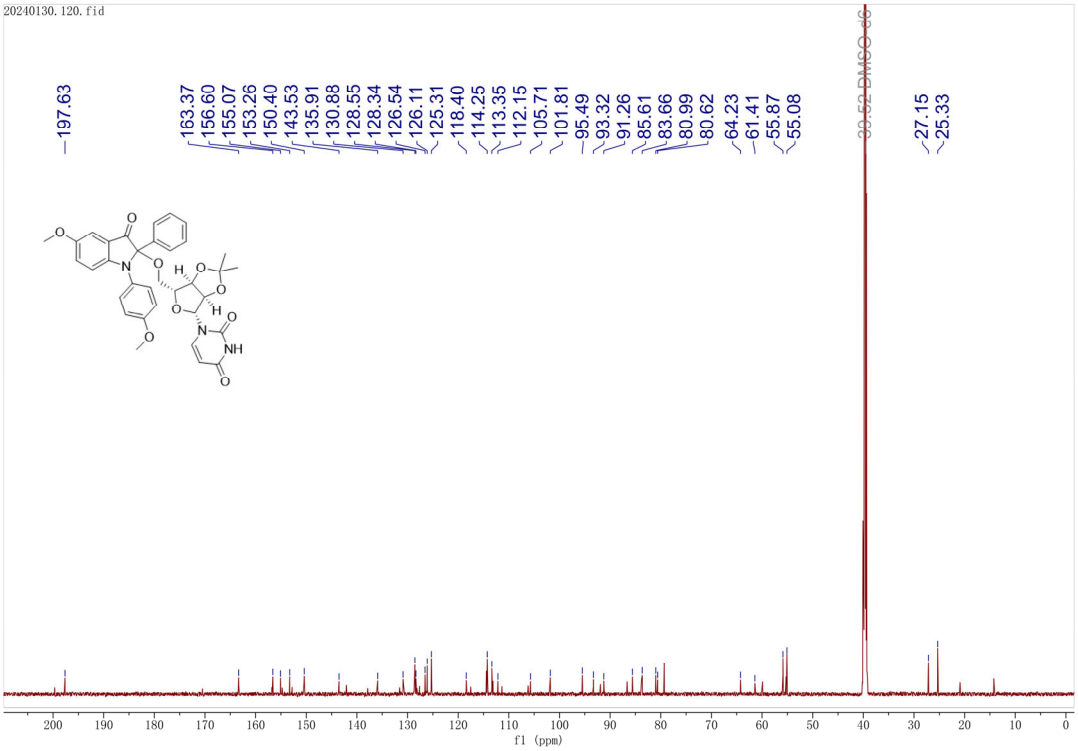
^{13}C NMR of compound **4aa-diastereoisomer A** (in DMSO-d_6)



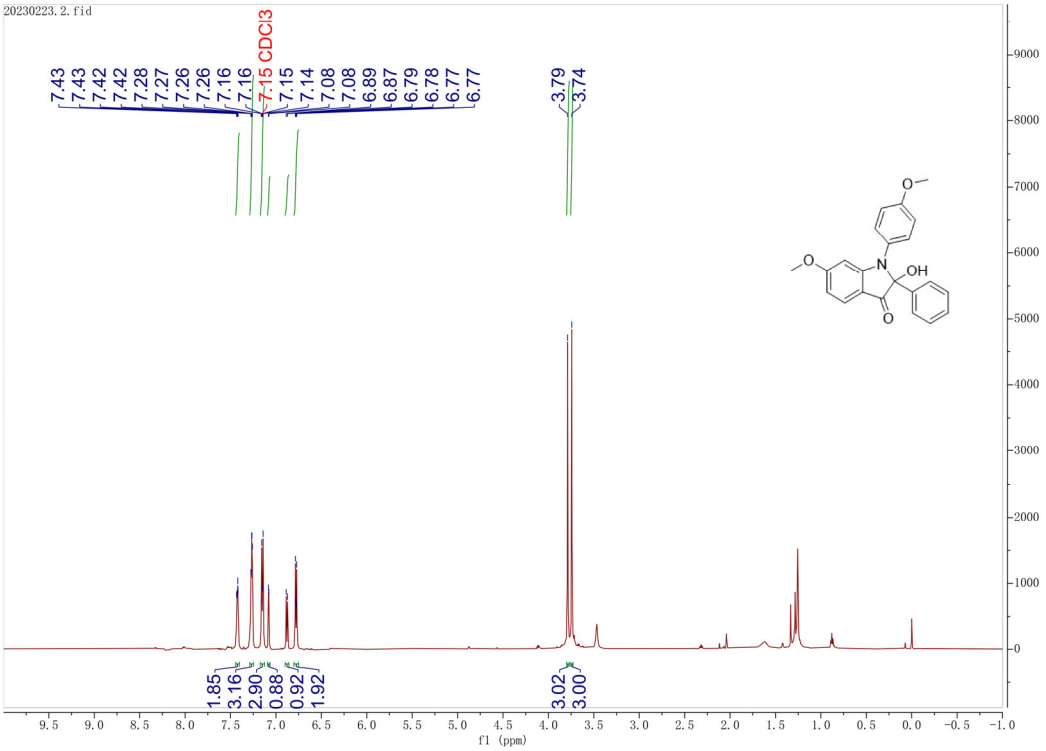
^{1}H NMR of compound **4aa-diastereoisomer B** (in DMSO-d_6)



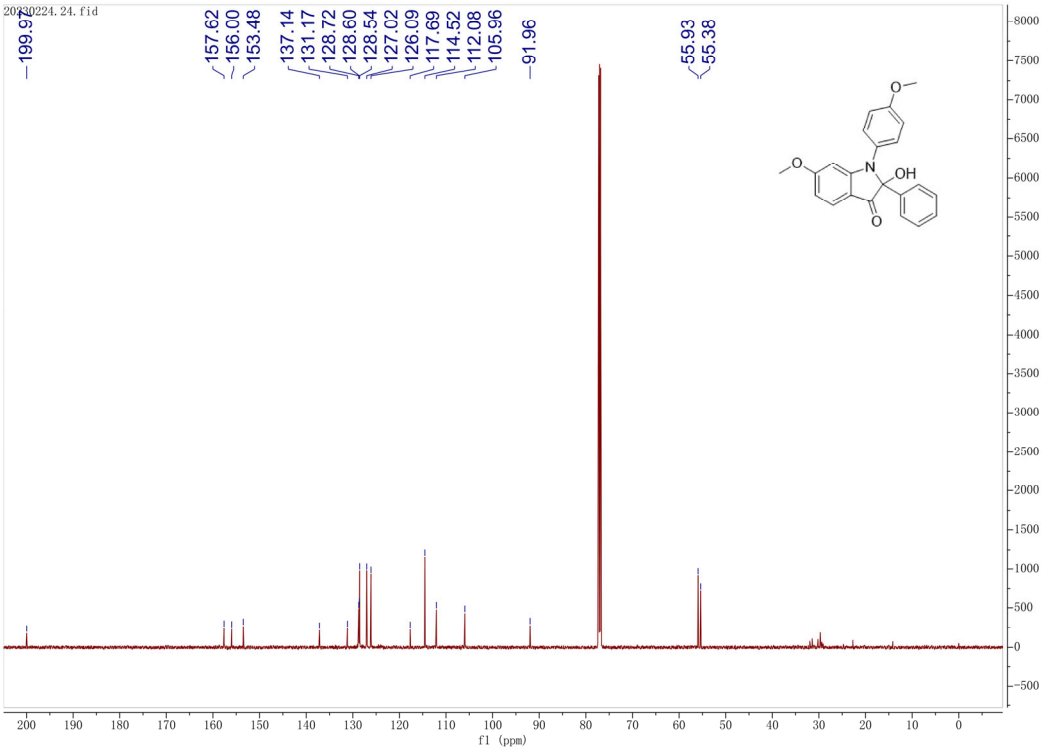
^{13}C NMR of compound **4aa-diastereoisomer B** (in DMSO-d_6)



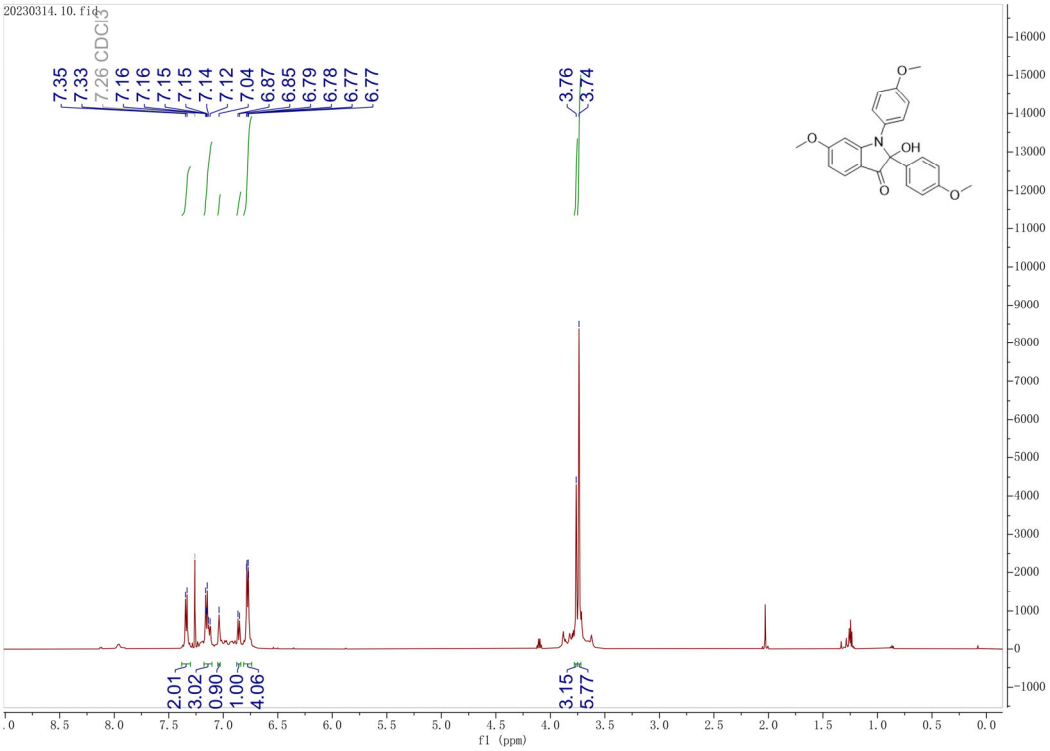
^{1}H NMR of compound **5a** (in $CHCl_3$)



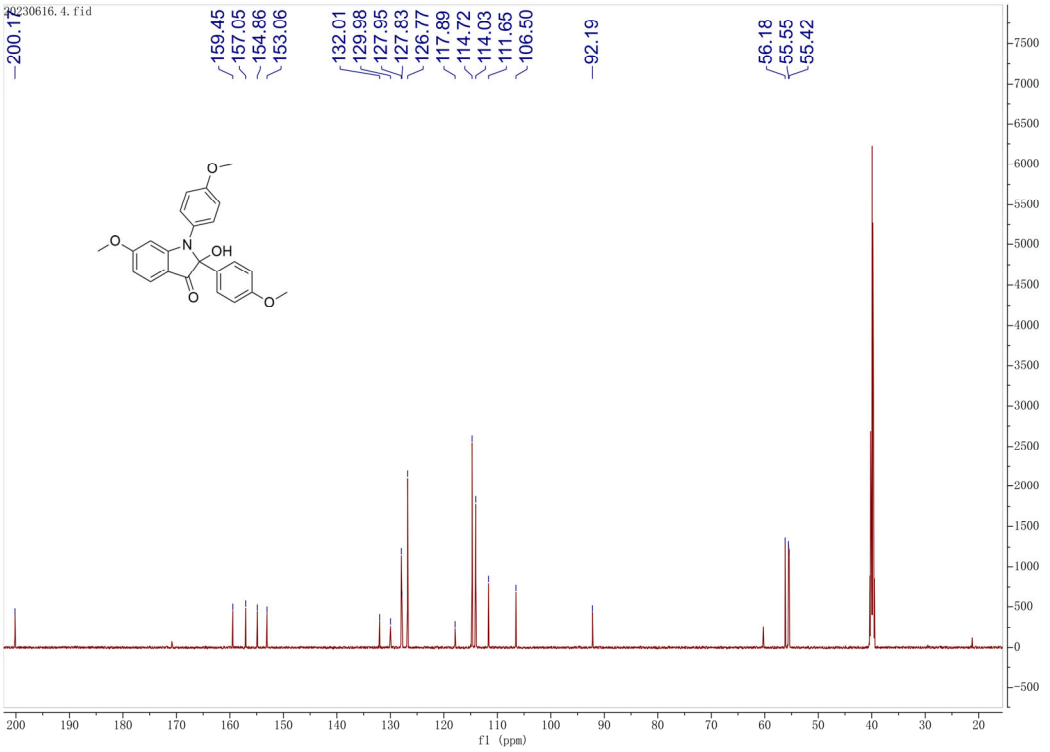
^{13}C NMR of compound **5a** (in $CHCl_3$)



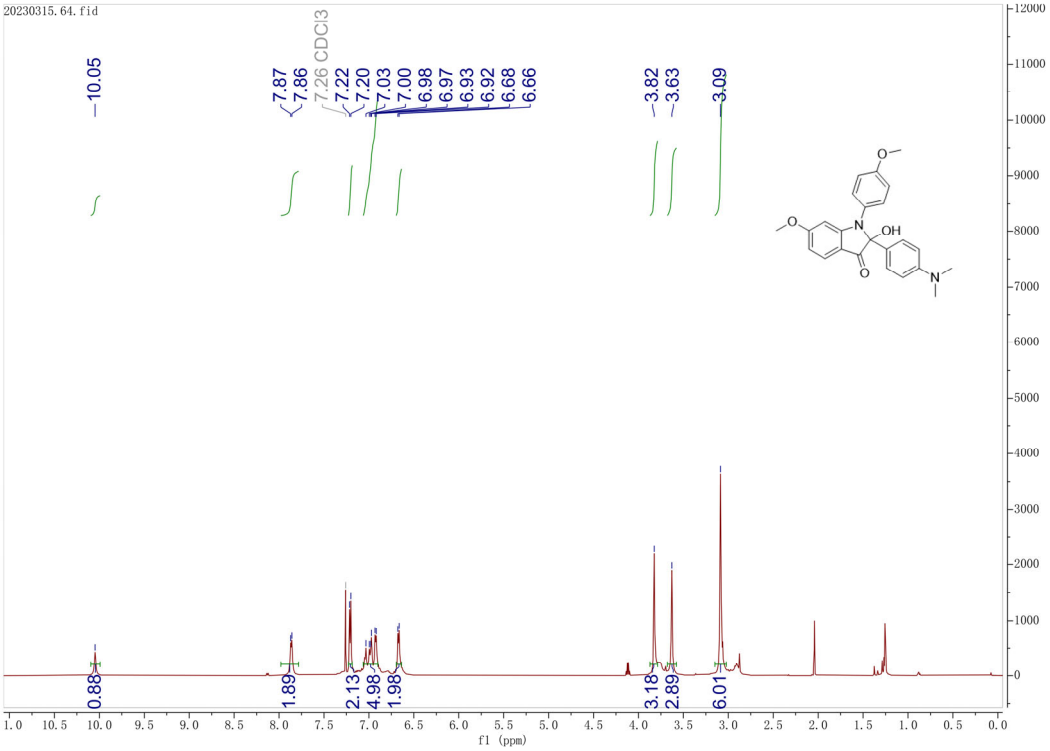
^{1}H NMR of compound **5b** (in $CHCl_3$)



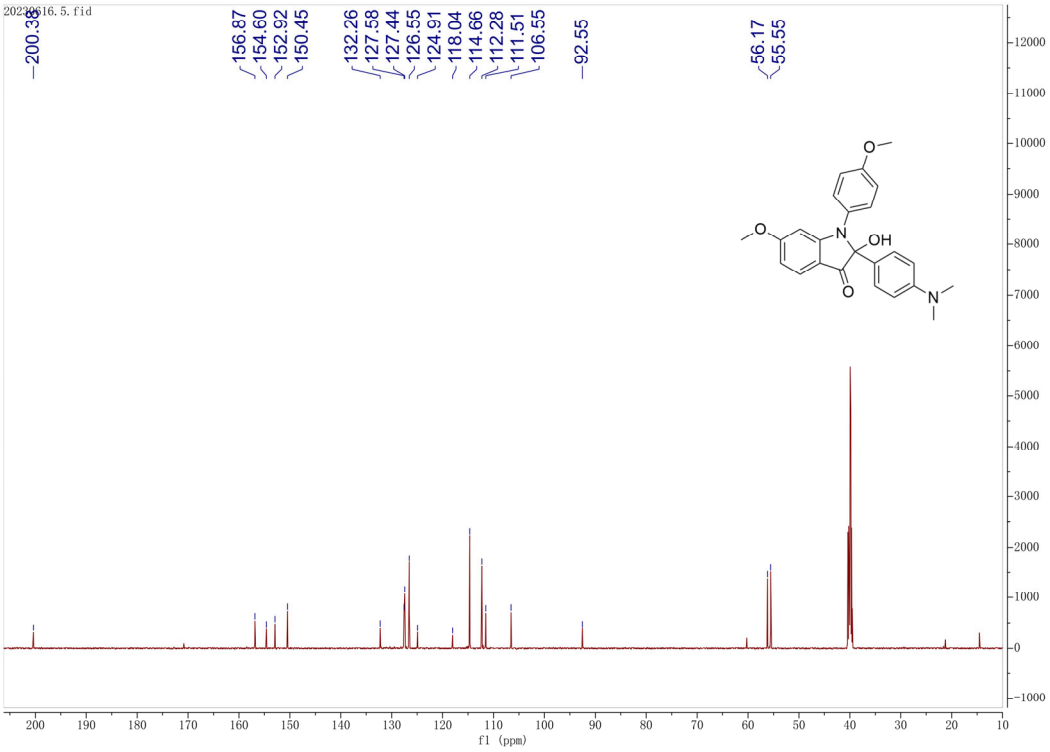
^{13}C NMR of compound **5b** (in DMSO-d_6)



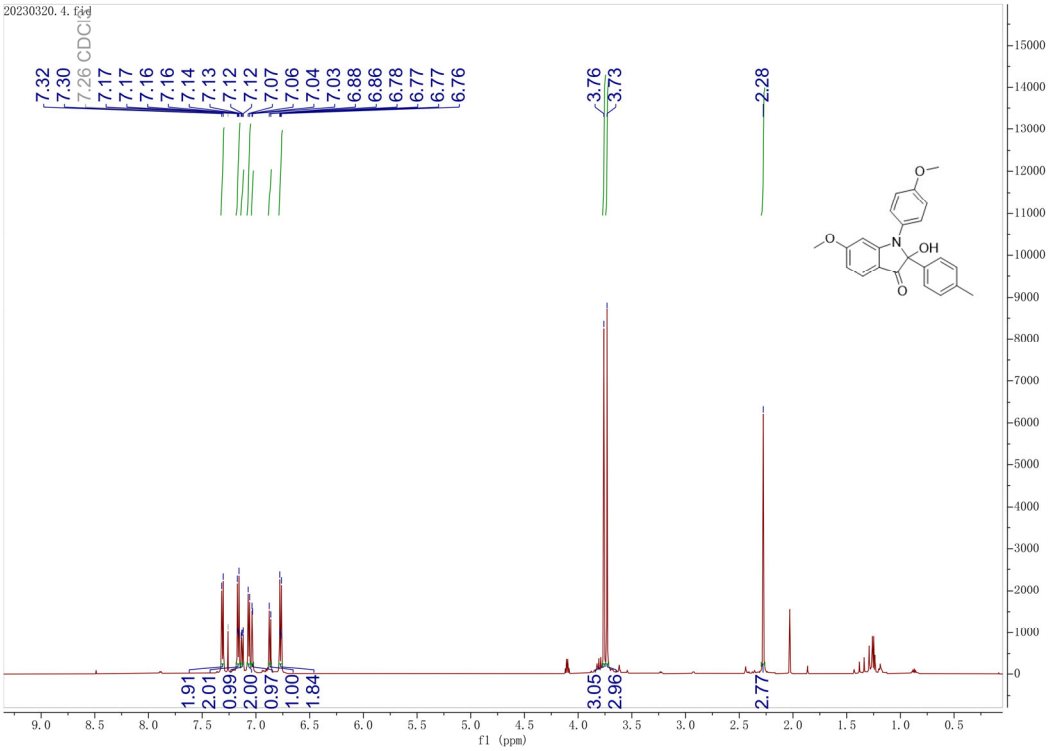
^{1}H NMR of compound **5c** (in $CHCl_3$)



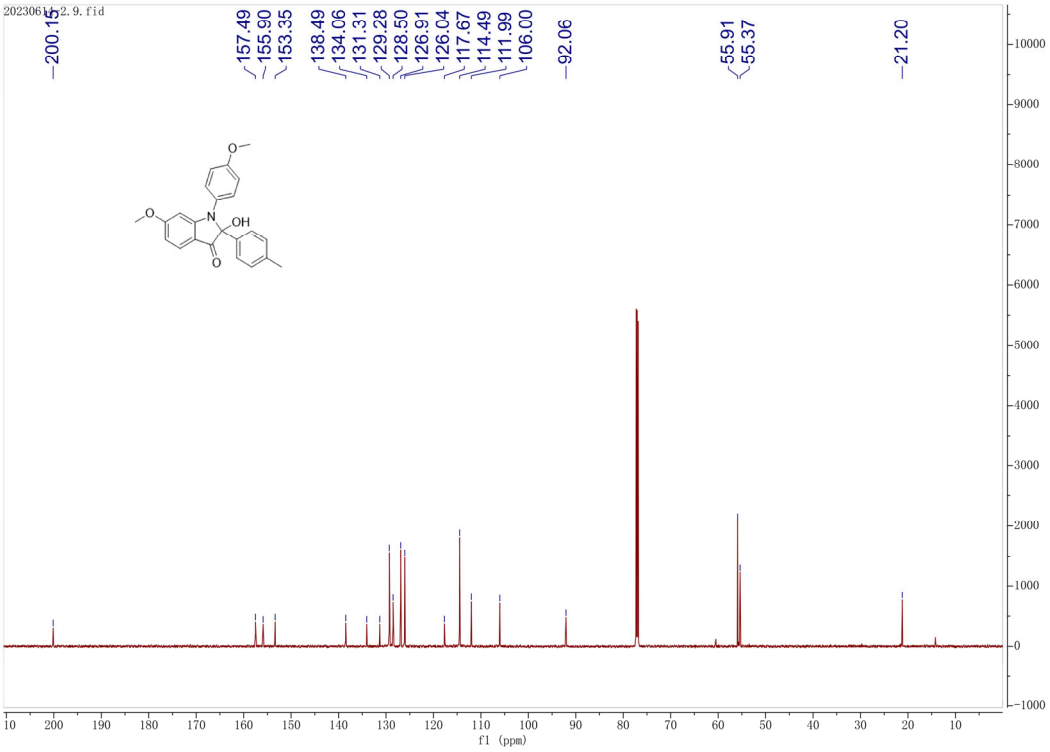
^{13}C NMR of compound **5c** (in DMSO-d_6)



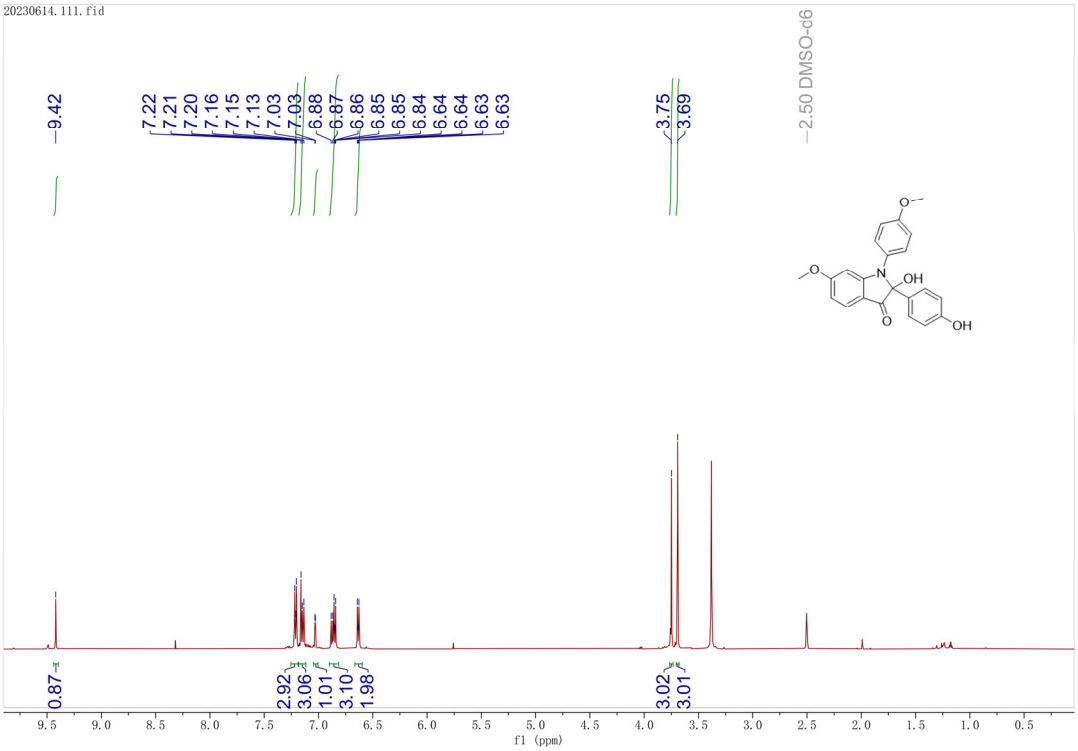
^{1}H NMR of compound **5d** (in $CHCl_3$)



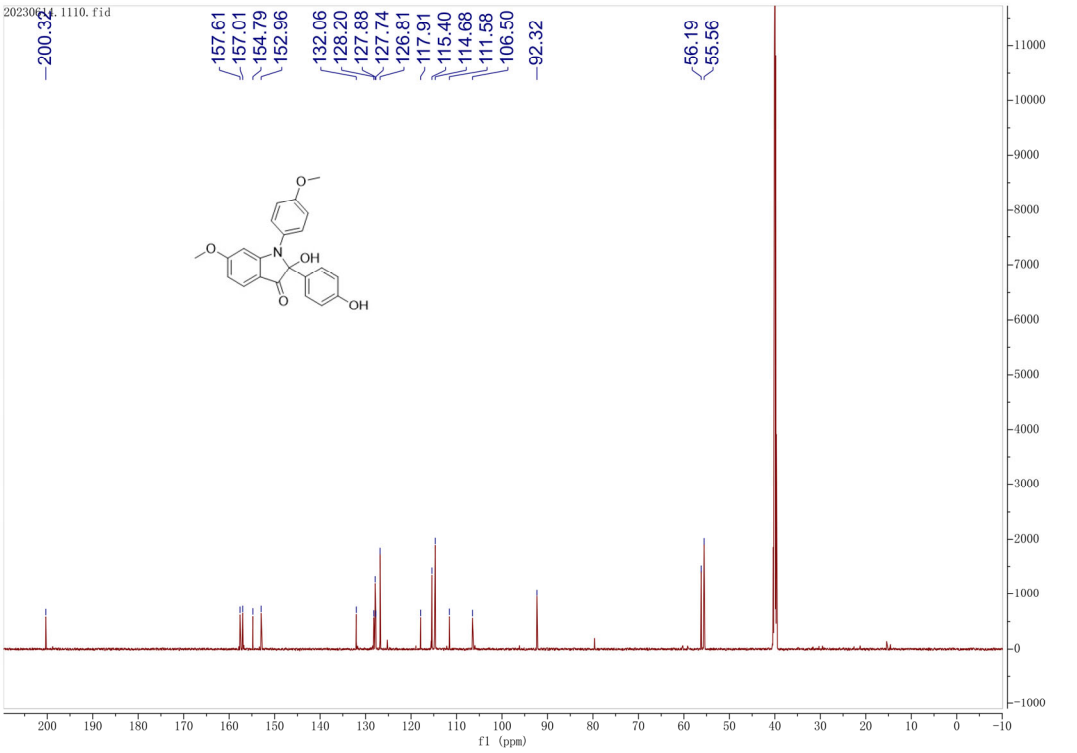
^{13}C NMR of compound **5d** (in $CHCl_3$)



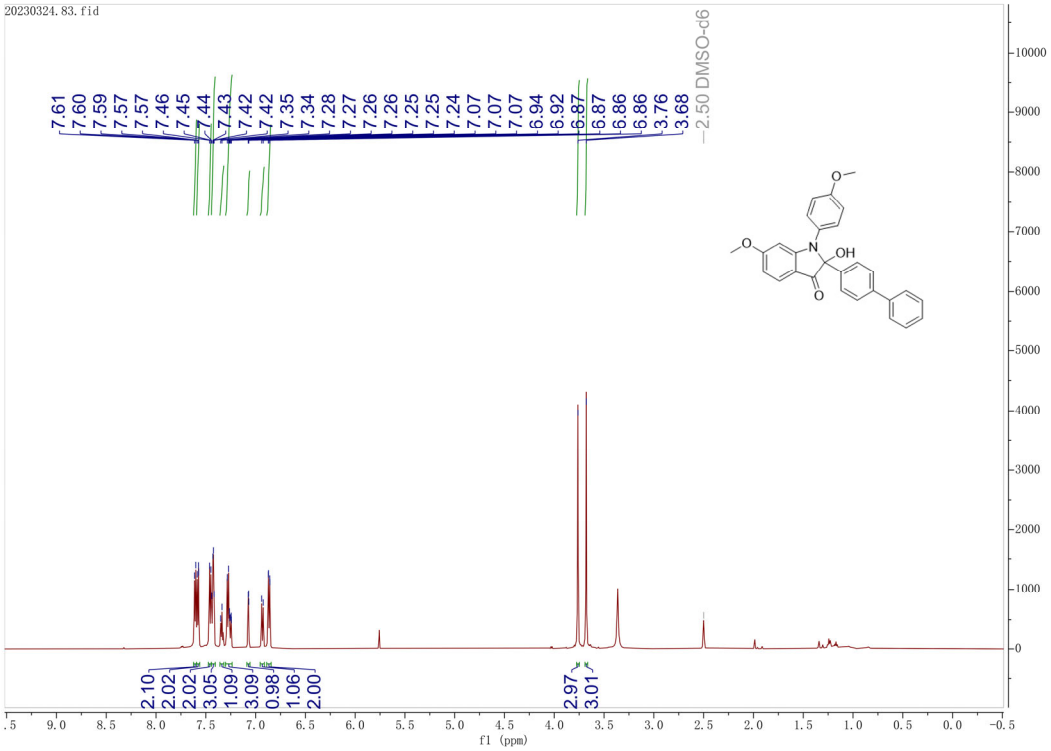
^{1}H NMR of compound **5e** (in DMSO-d_6)



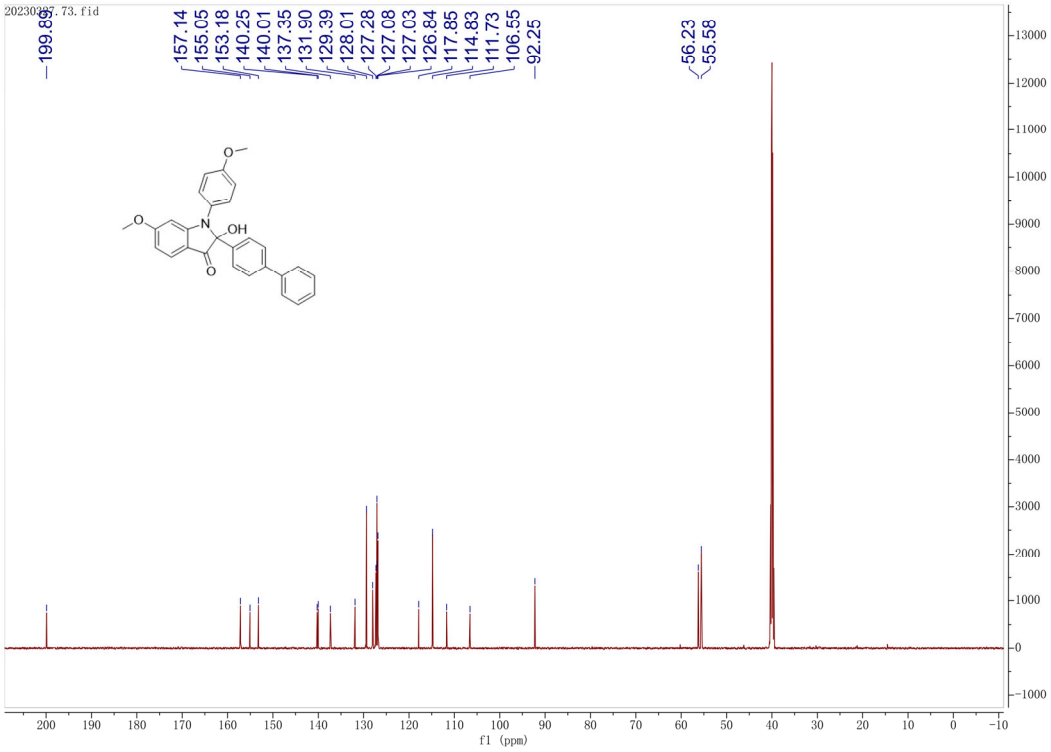
^{13}C NMR of compound **5e** (in DMSO-d_6)



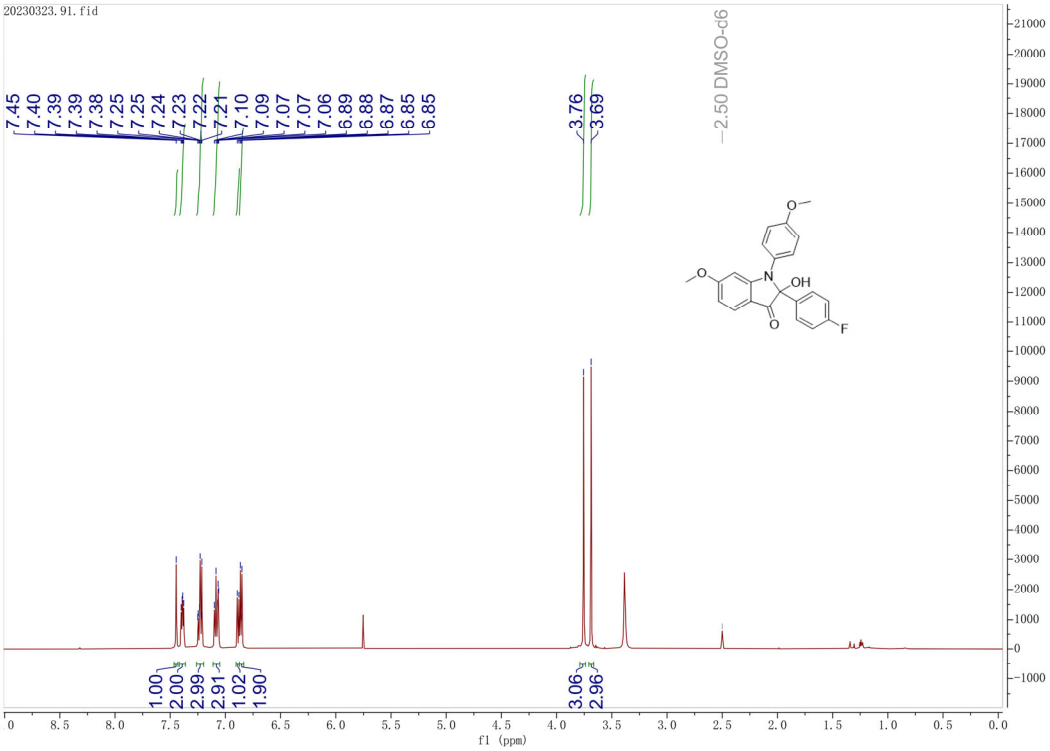
^{1}H NMR of compound **5f** (in DMSO-d$_6$)



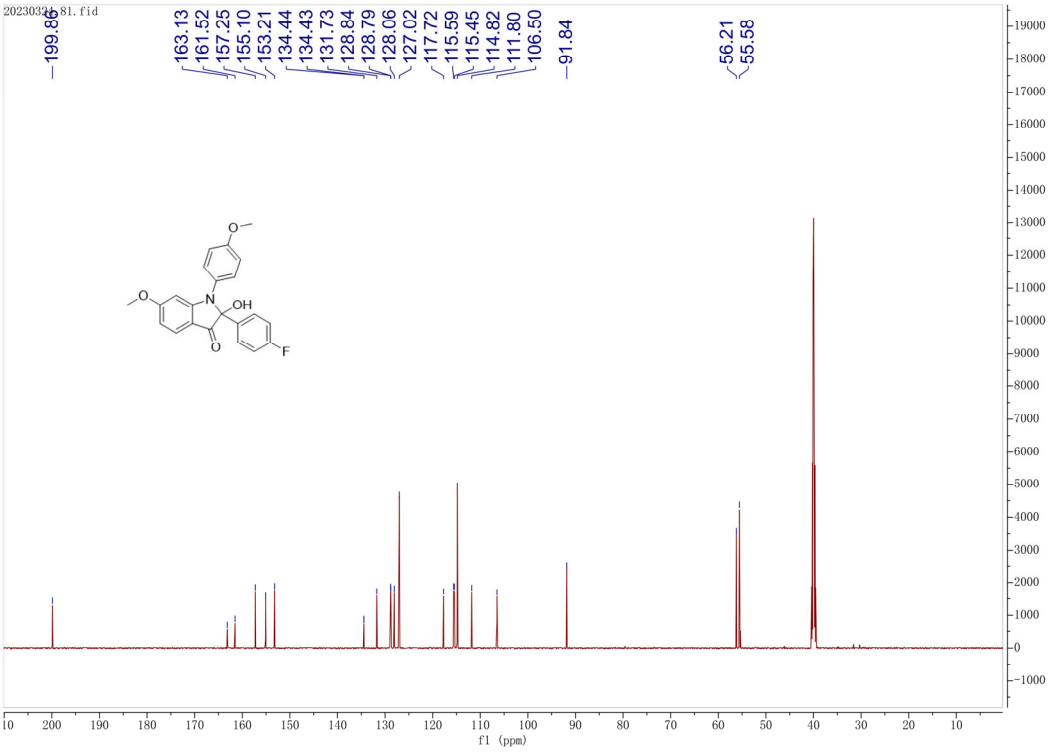
^{13}C NMR of compound **5f** (in DMSO-d$_6$)



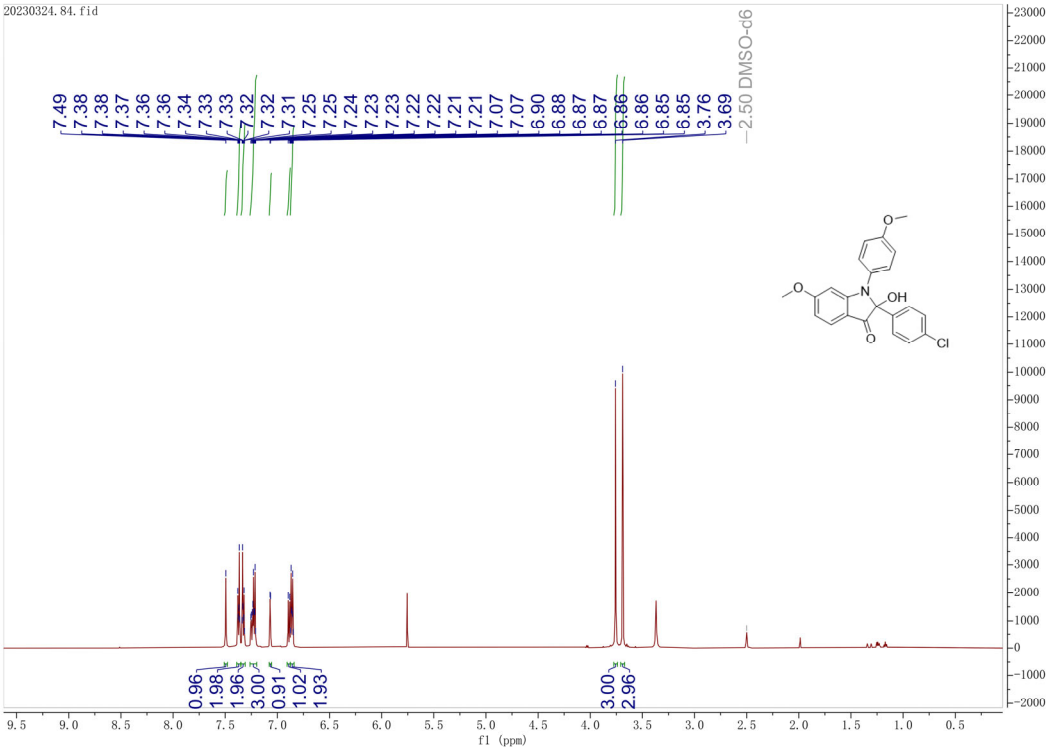
^{1}H NMR of compound **5g** (in DMSO-d$_6$)



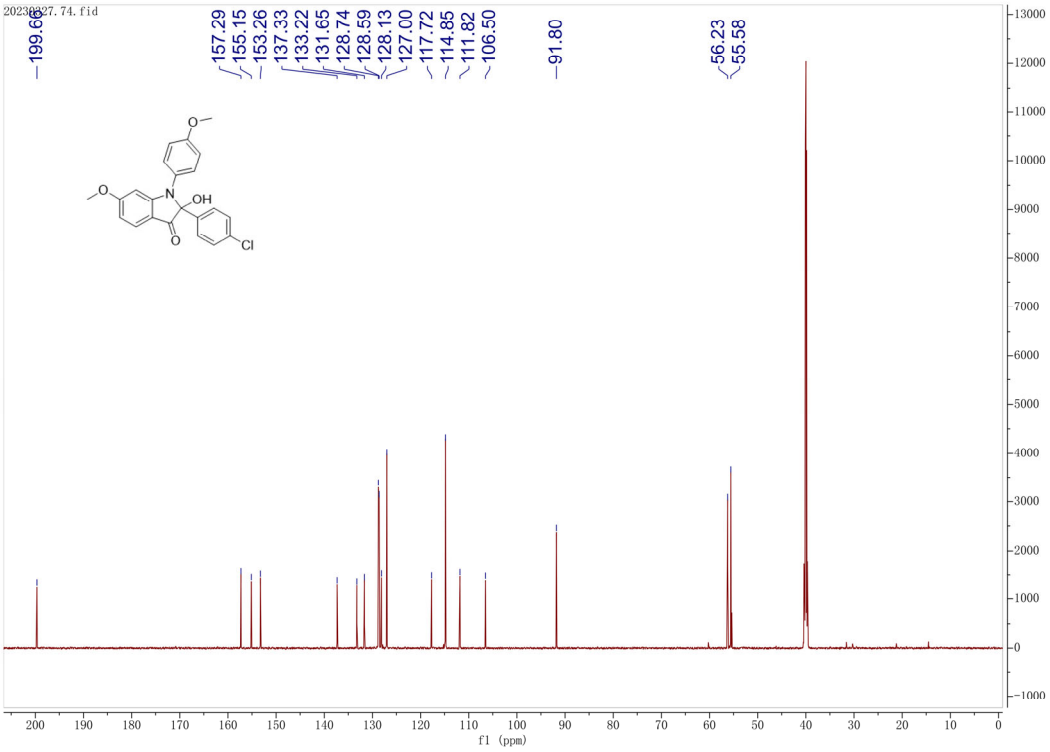
^{13}C NMR of compound **5g** (in DMSO-d$_6$)



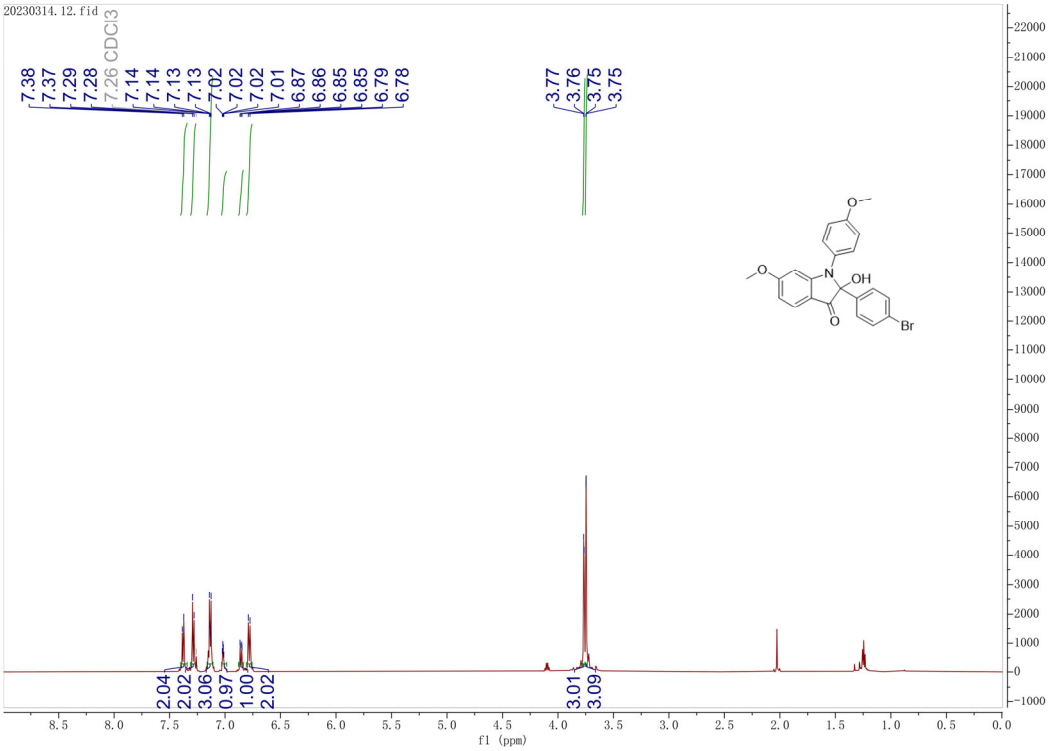
^{1}H NMR of compound **5h** (in DMSO-d$_6$)



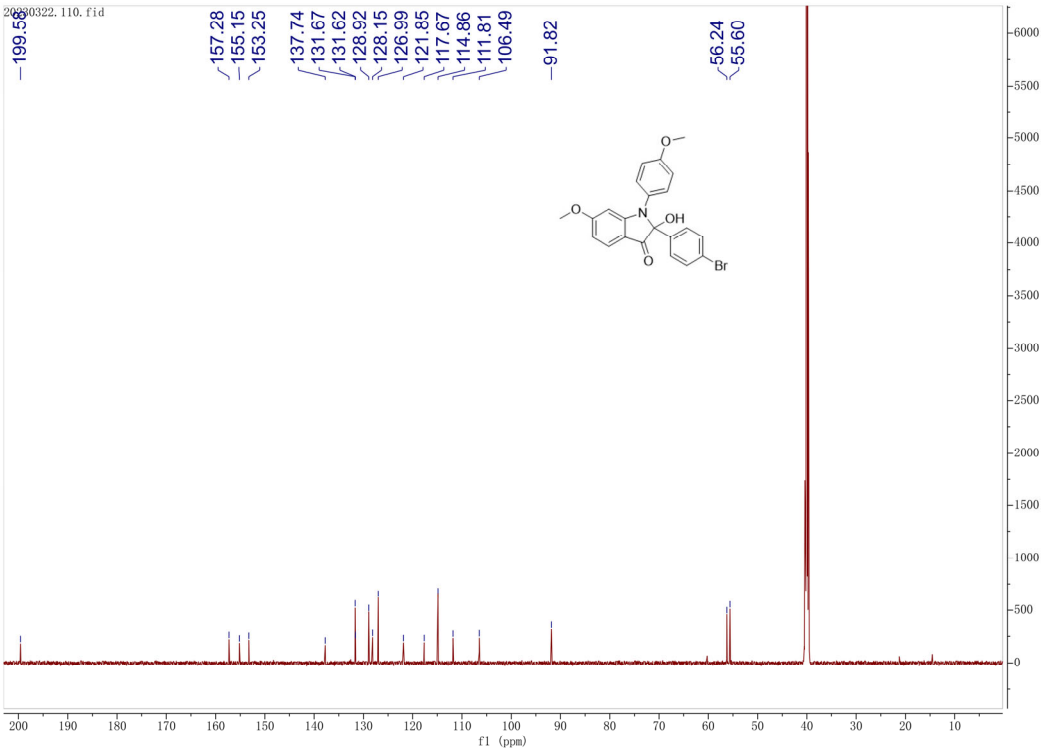
^{13}C NMR of compound **5h** (in DMSO-d$_6$)



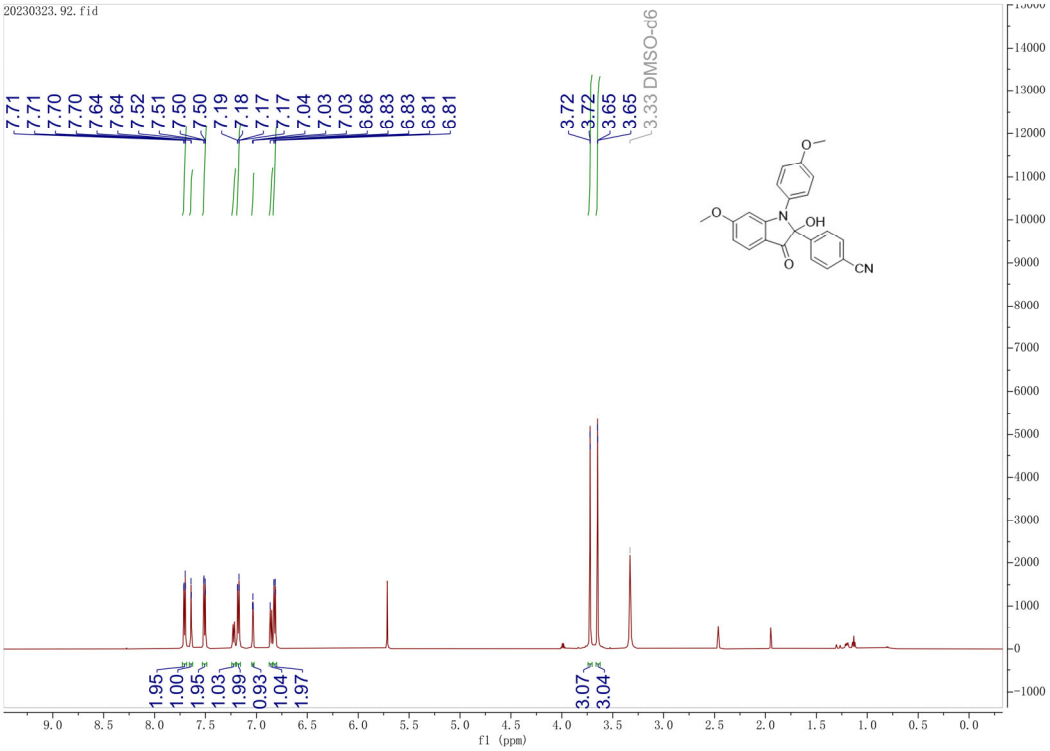
^{1}H NMR of compound **5i** (in $CDCl_3$)



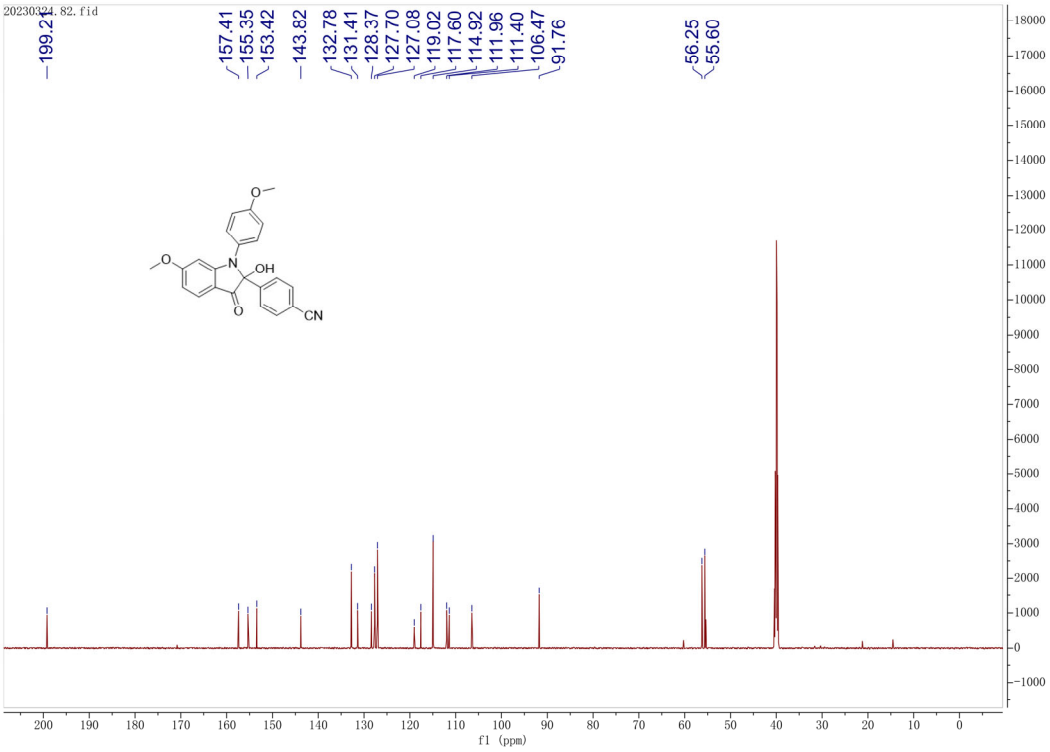
^{13}C NMR of compound **5i** (in DMSO-d_6)



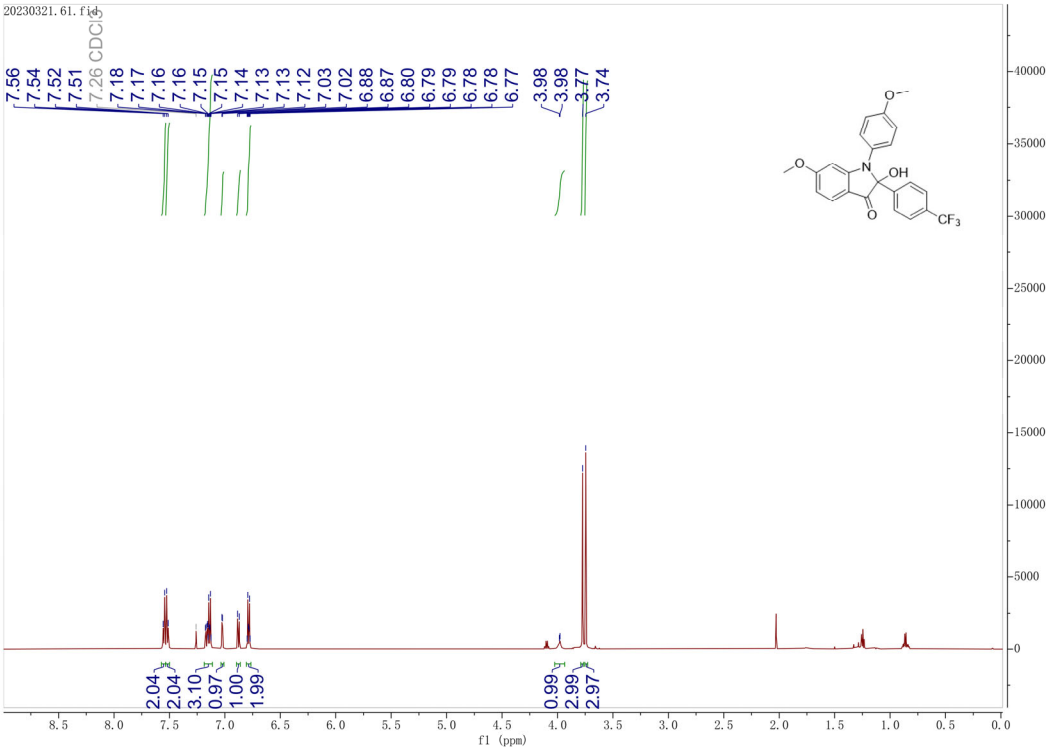
^{1}H NMR of compound **5j** (in DMSO-d$_6$)



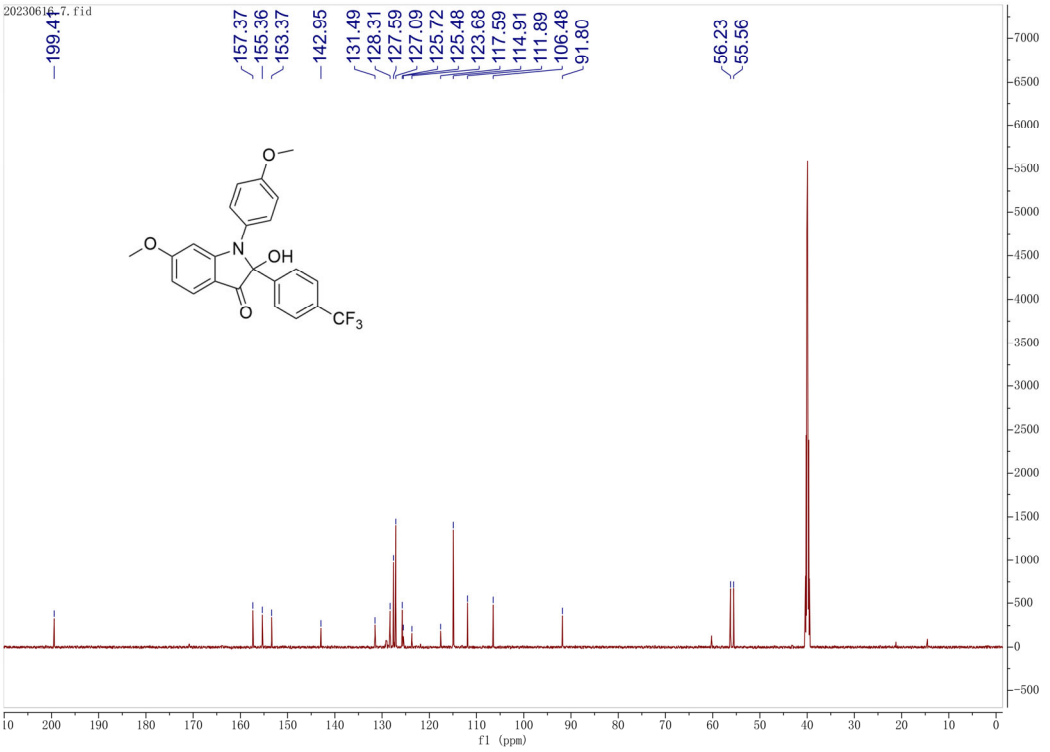
^{13}C NMR of compound **5j** (in DMSO-d$_6$)



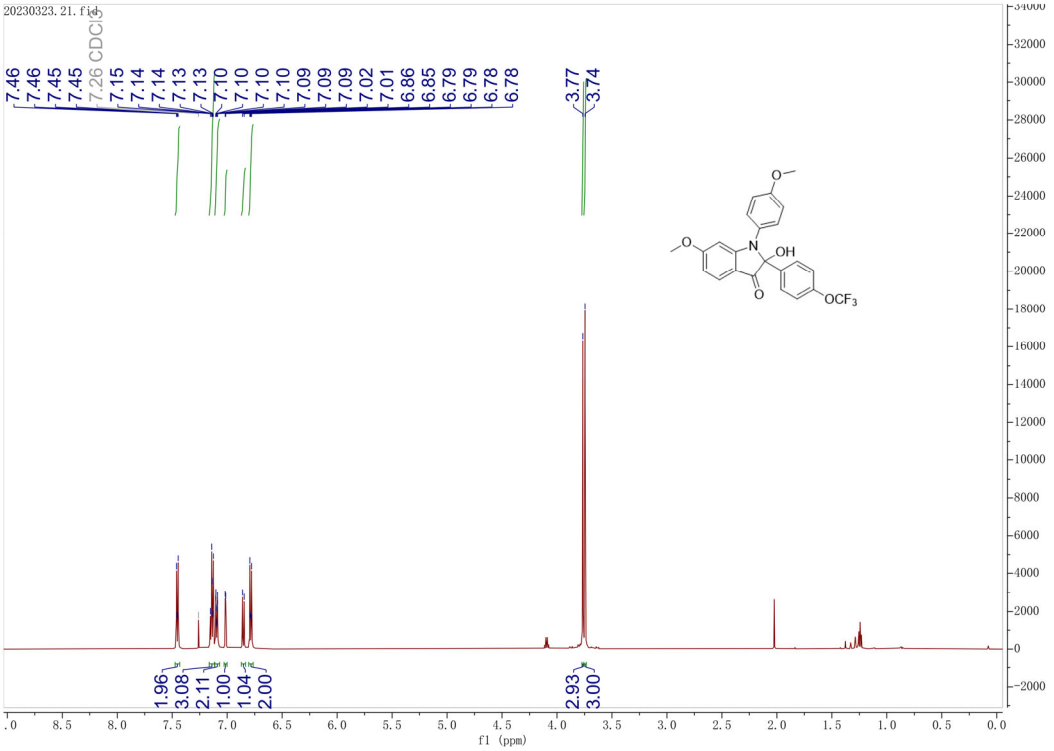
^{1}H NMR of compound **5k** (in $CDCl_3$)



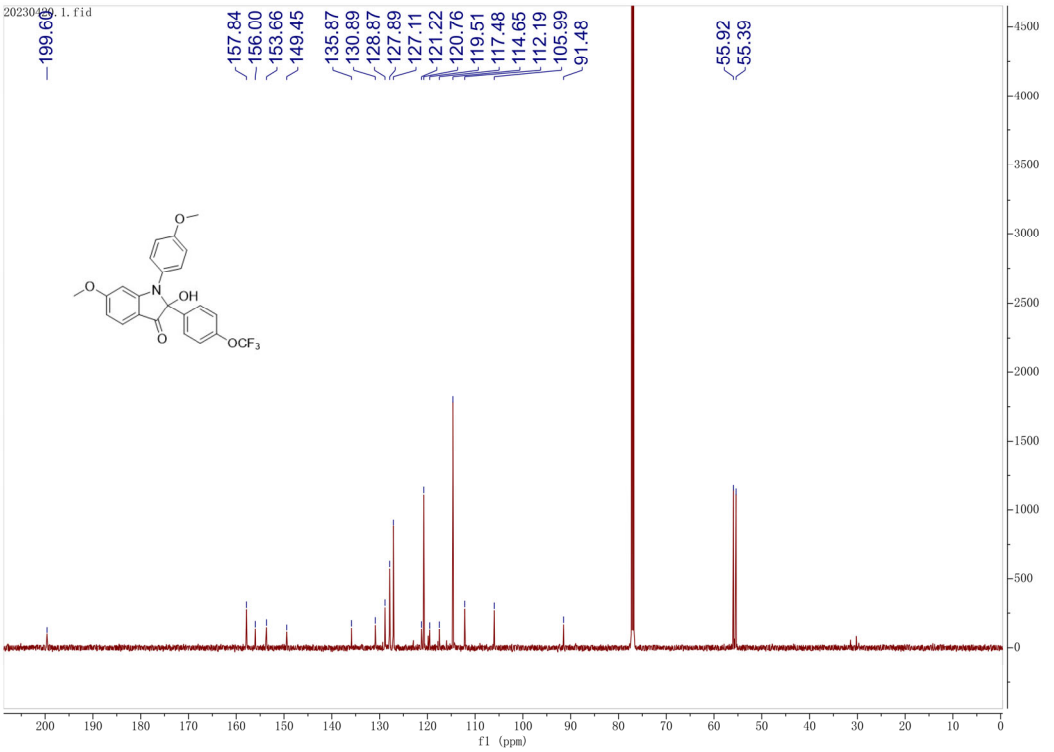
^{13}C NMR of compound **5k** (in DMSO-d_6)



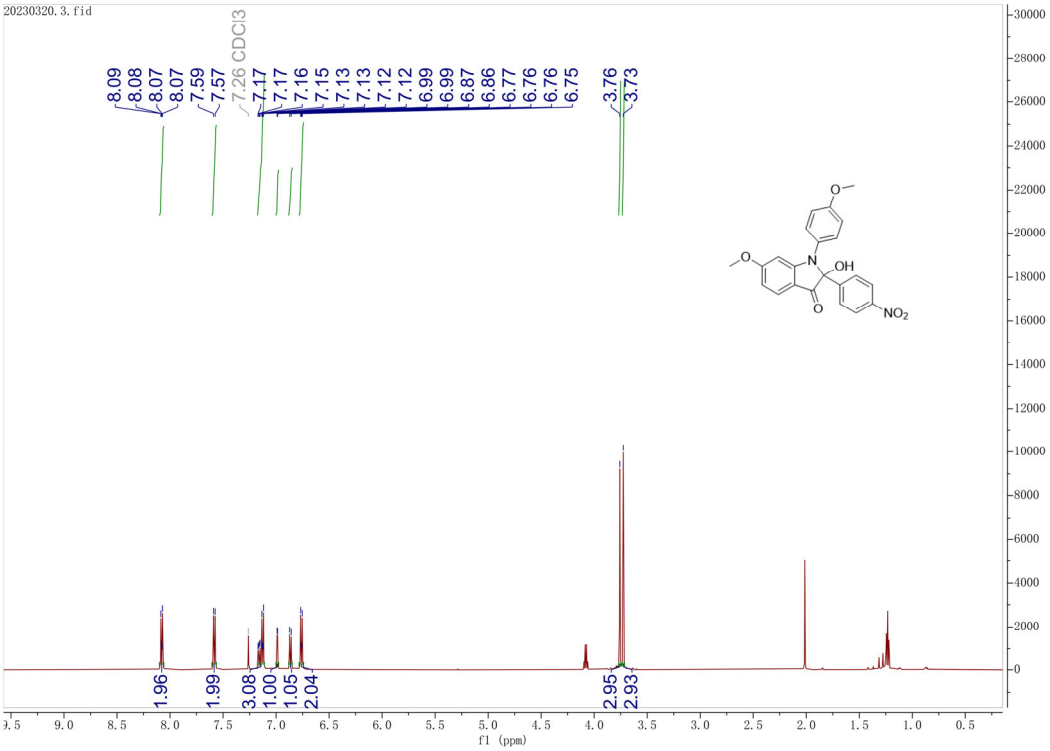
^{1}H NMR of compound **5l** (in $CDCl_3$)



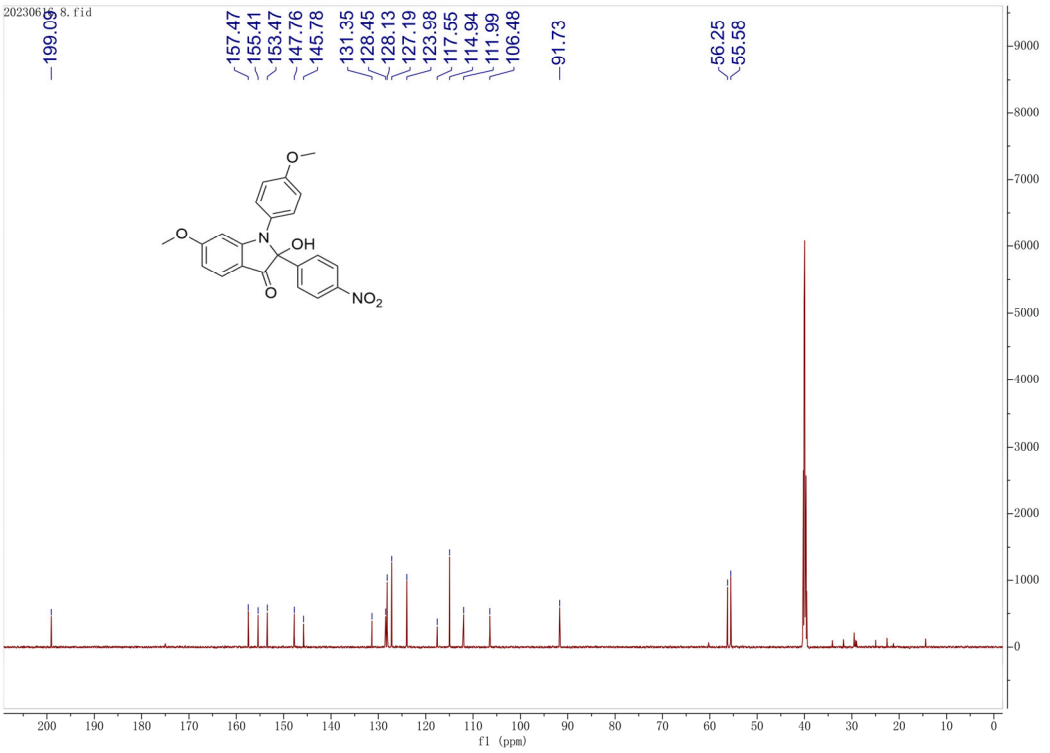
^{13}C NMR of compound **5l** (in $CDCl_3$)



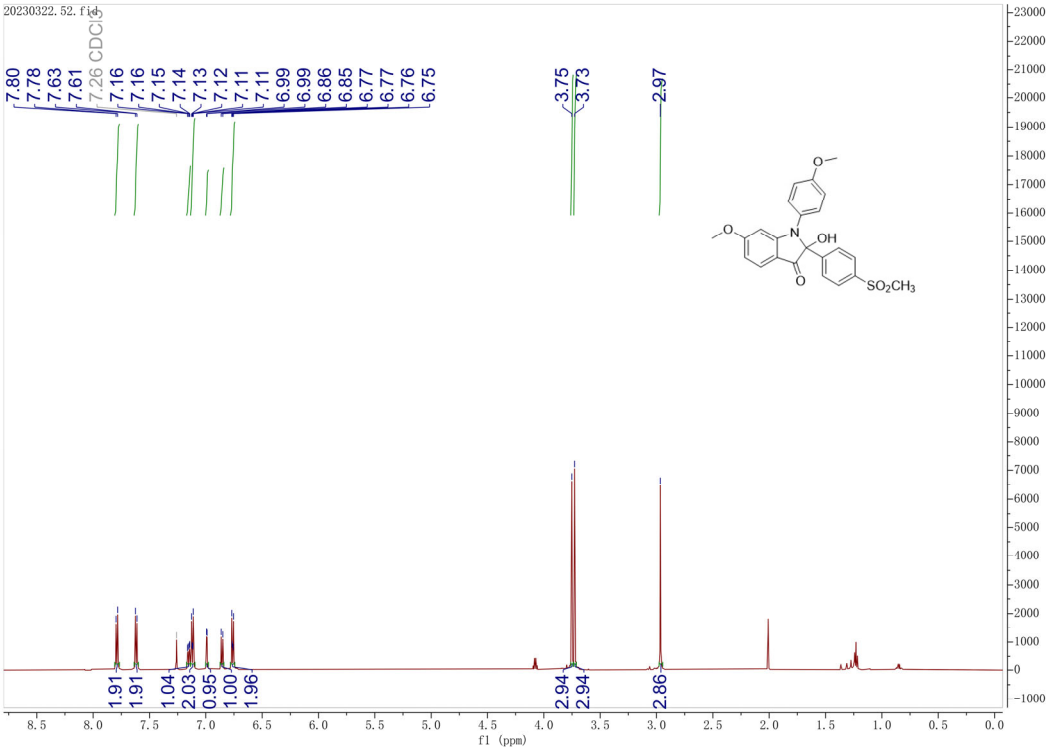
^{1}H NMR of compound **5m** (in $CDCl_3$)



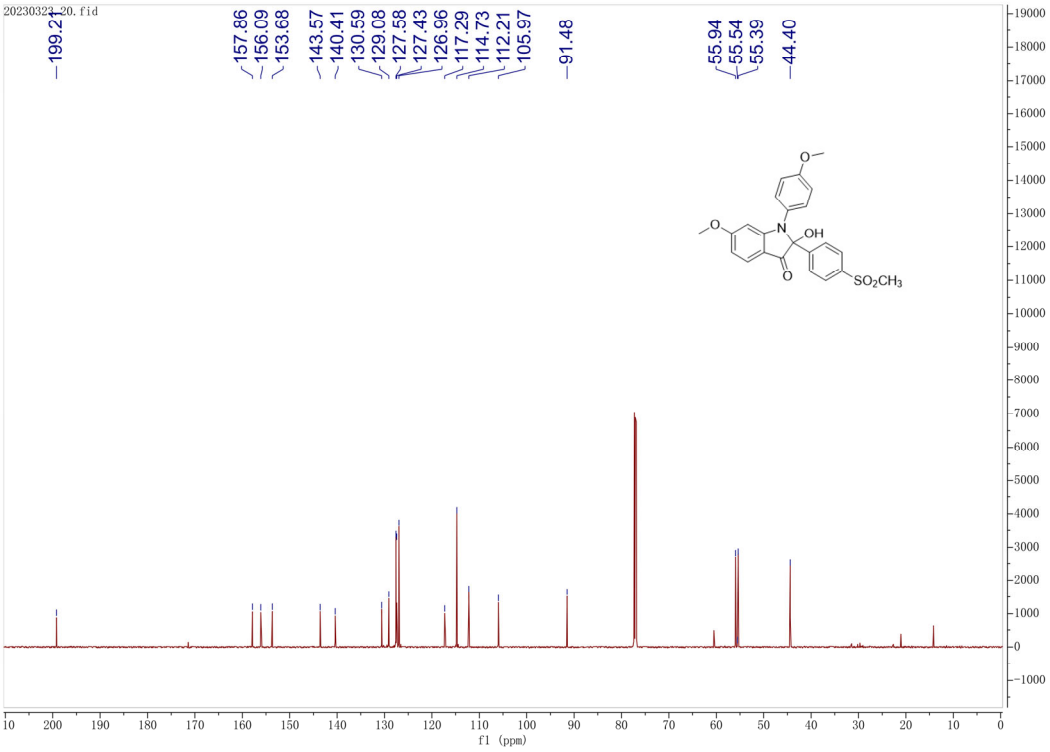
^{13}C NMR of compound **5m** (in DMSO-d_6)



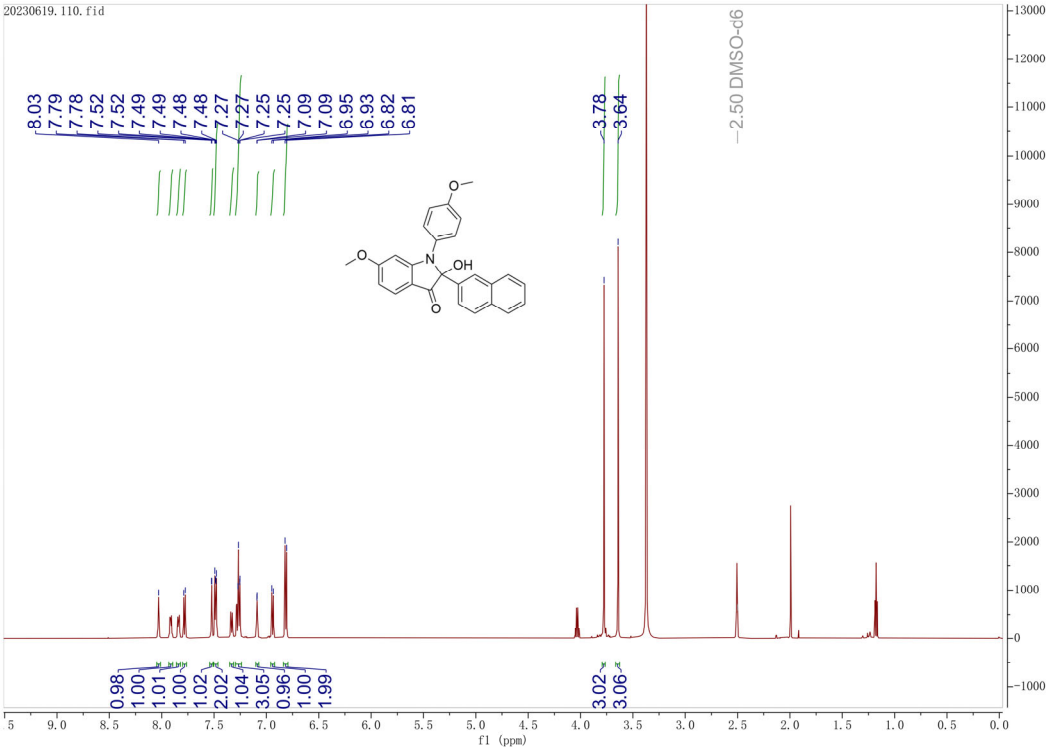
^{1}H NMR of compound **5n** (in $CDCl_3$)



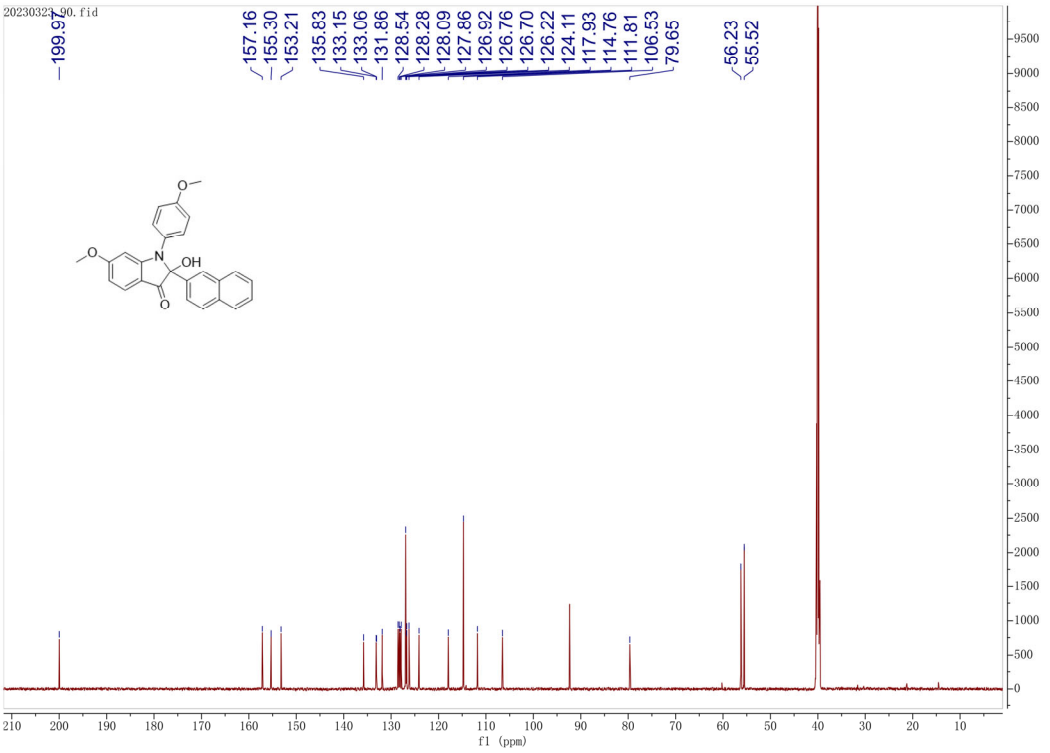
^{13}C NMR of compound **5n** (in $CDCl_3$)



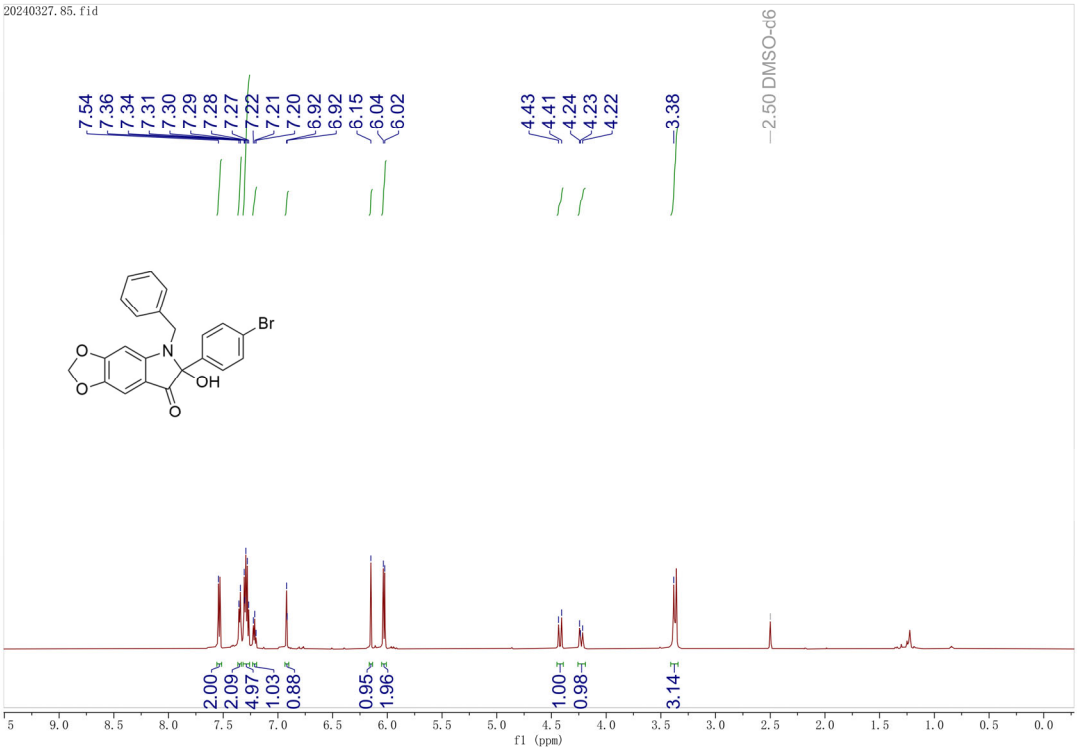
^{1}H NMR of compound **5o** (in DMSO-d$_6$)



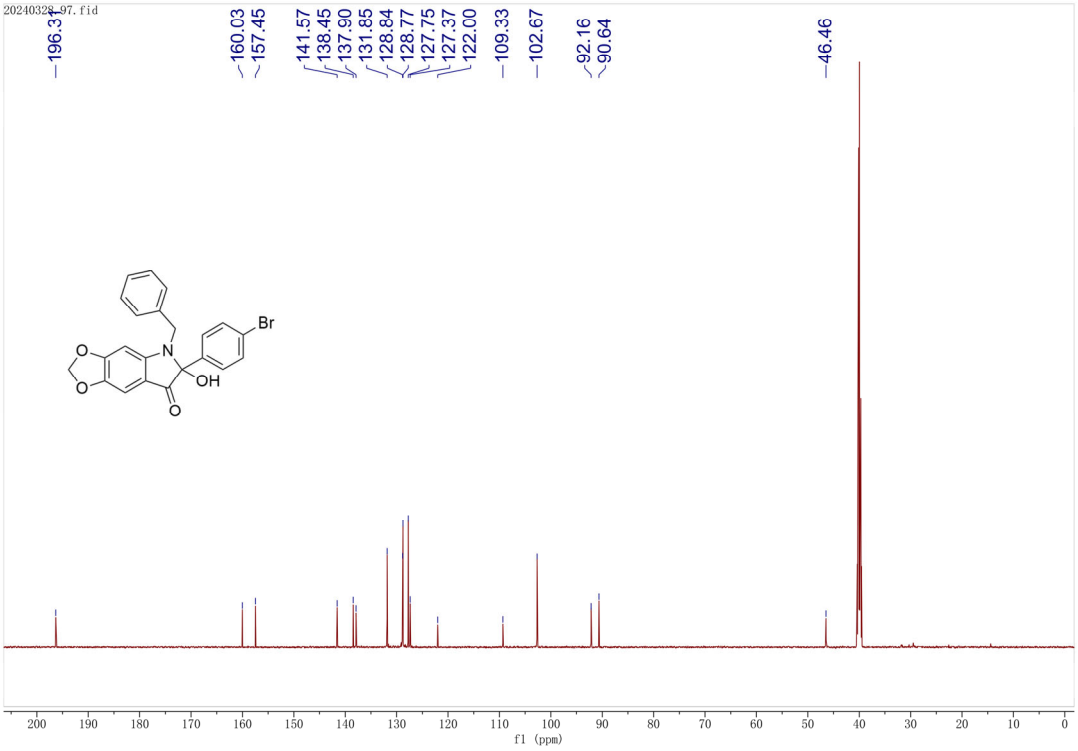
^{13}C NMR of compound **5o** (in DMSO-d$_6$)



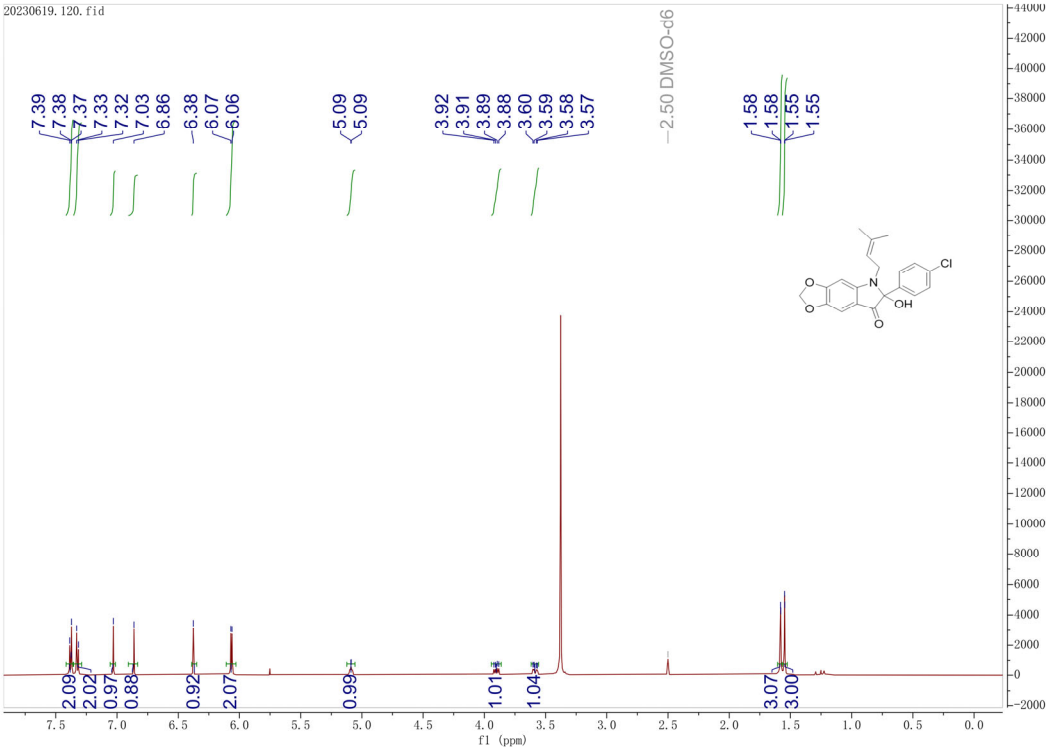
^{1}H NMR of compound **5p** (in DMSO-d$_6$)



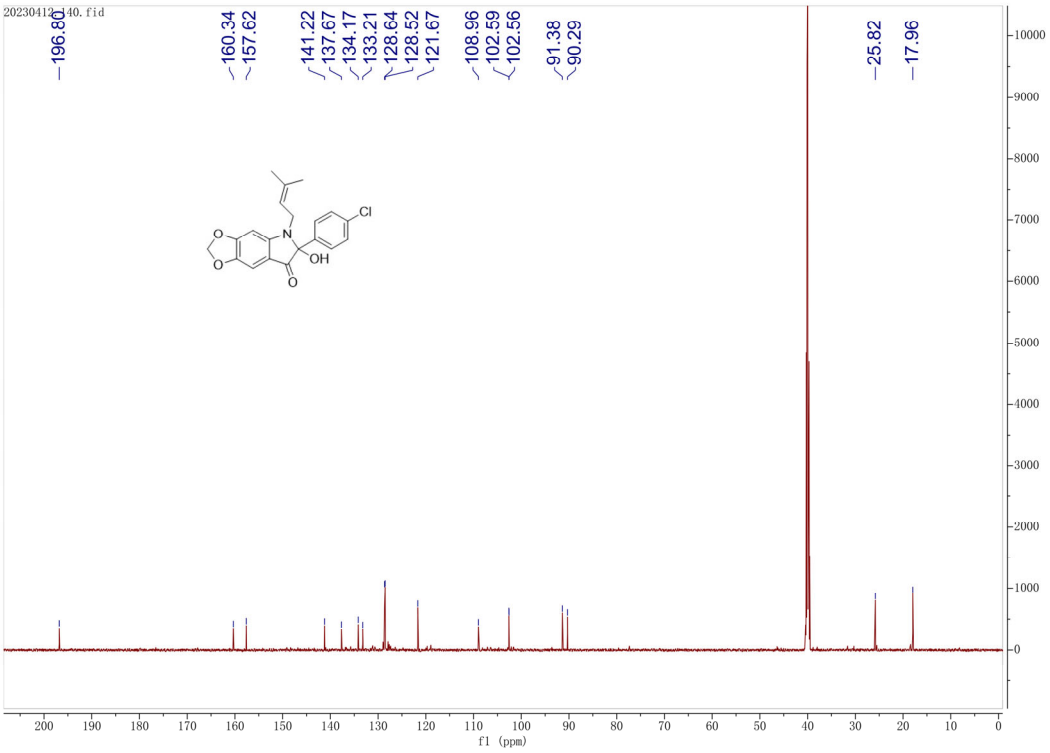
^{13}C NMR of compound **5p** (in DMSO-d$_6$)



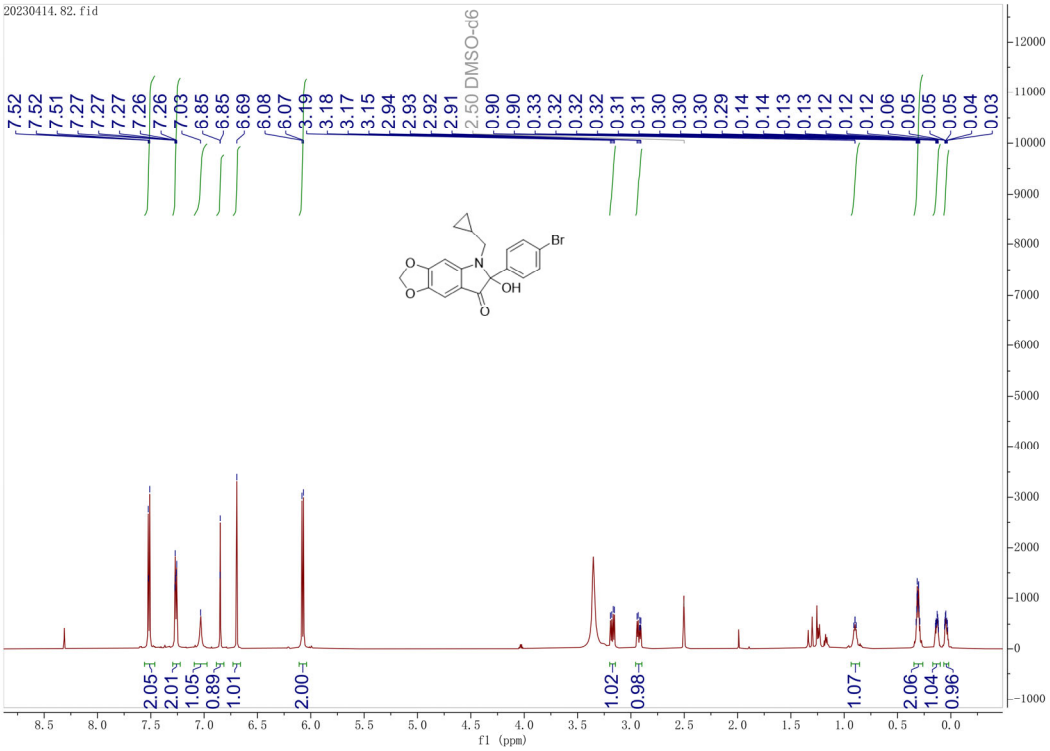
^{1}H NMR of compound **5q** (in DMSO-d$_6$)



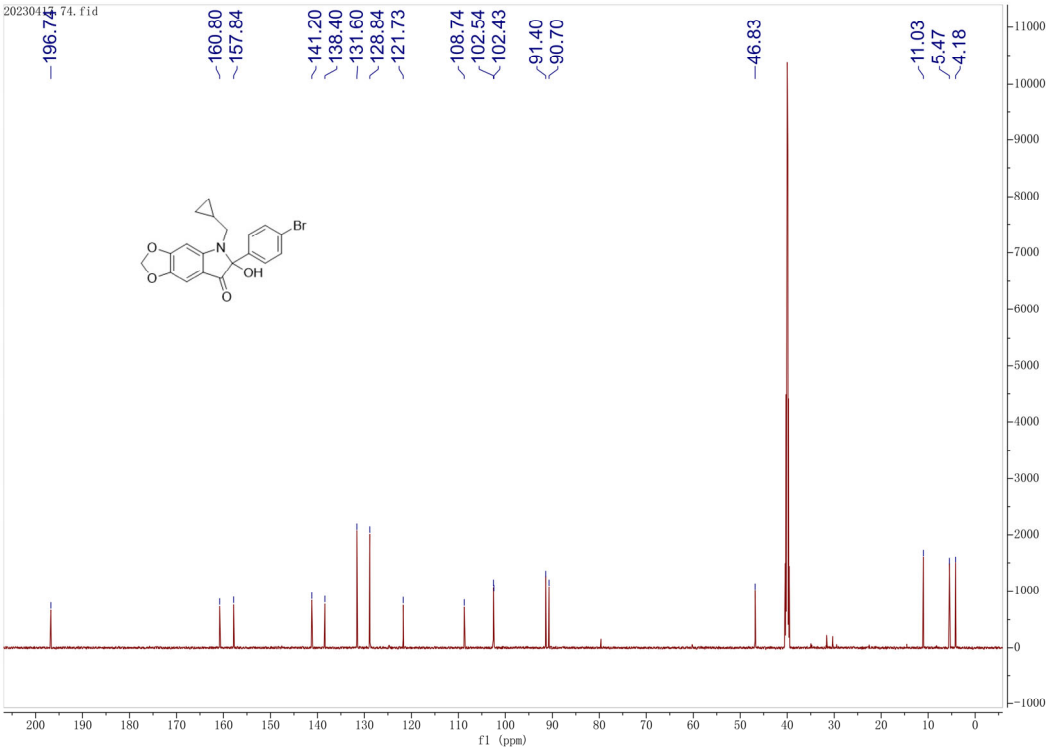
^{13}C NMR of compound **5q** (in DMSO-d$_6$)



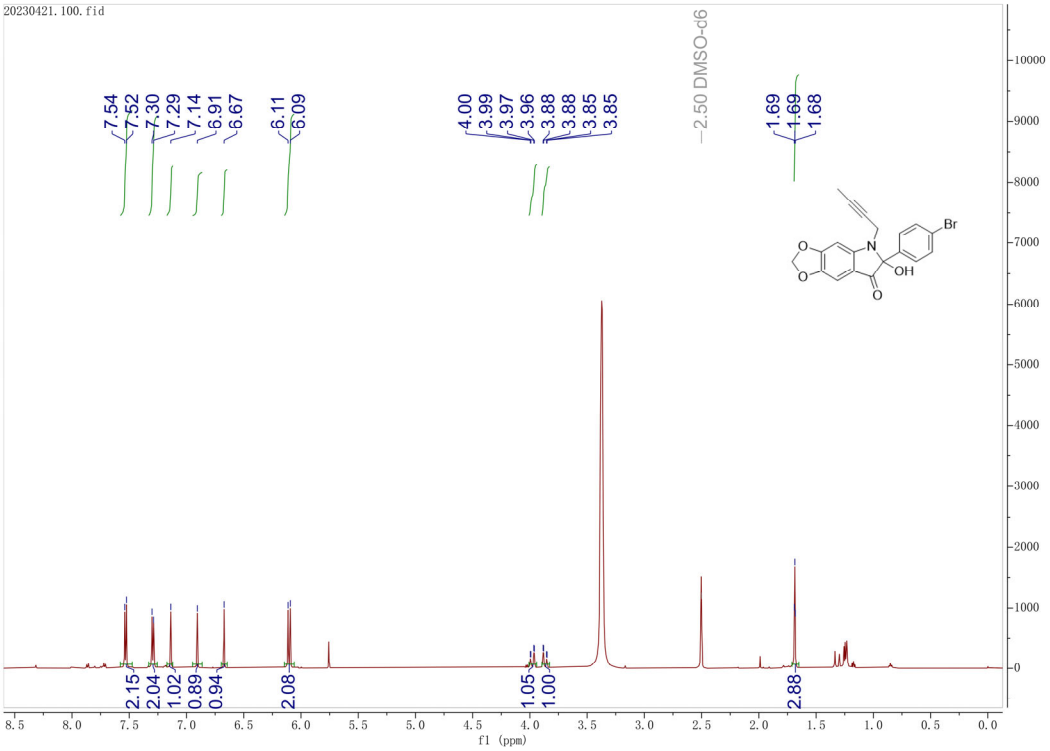
^{1}H NMR of compound **5r** (in DMSO-d_6)



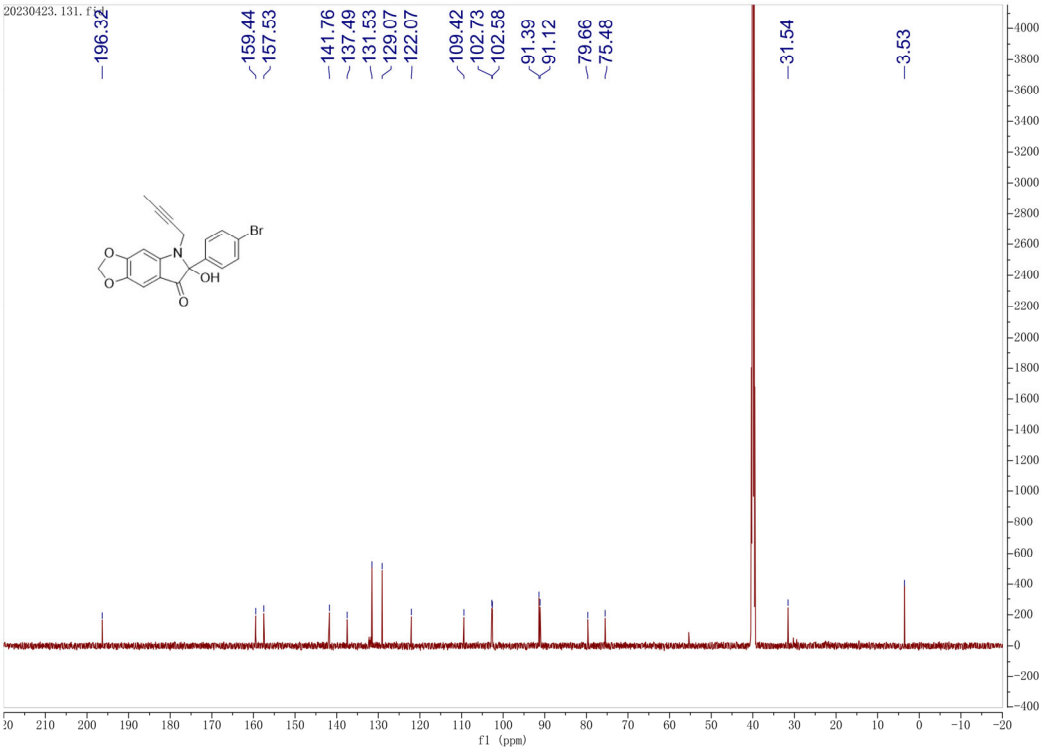
^{13}C NMR of compound **5r** (in DMSO-d_6)



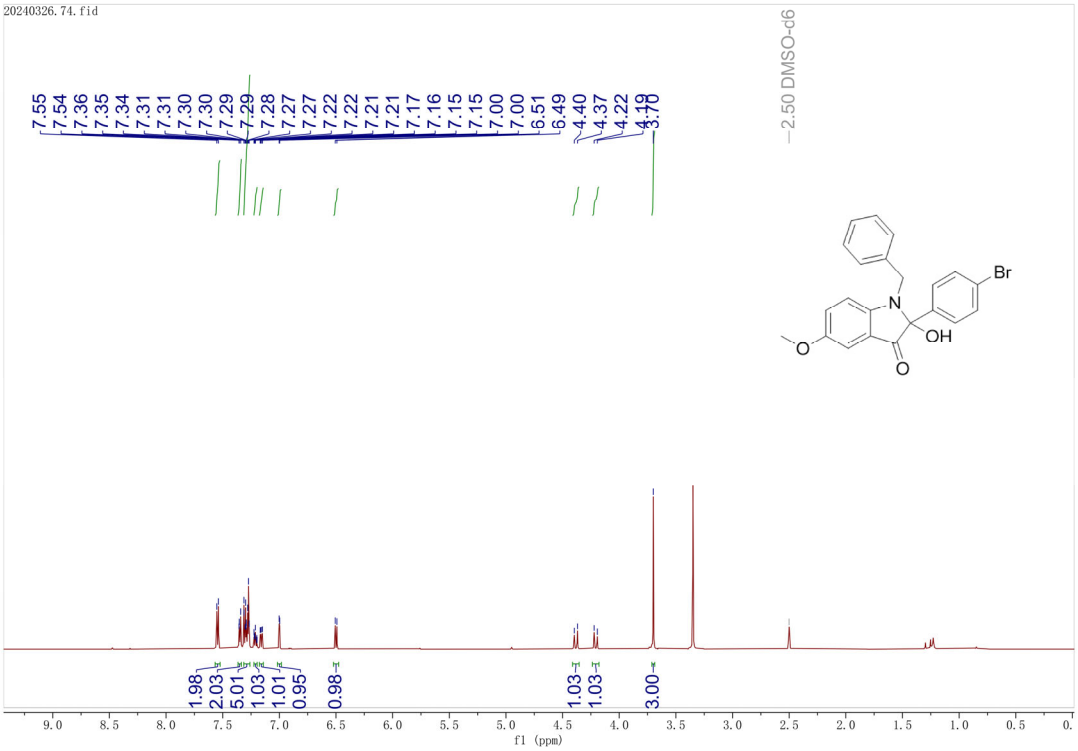
^{1}H NMR of compound **5s** (in DMSO-d$_6$)



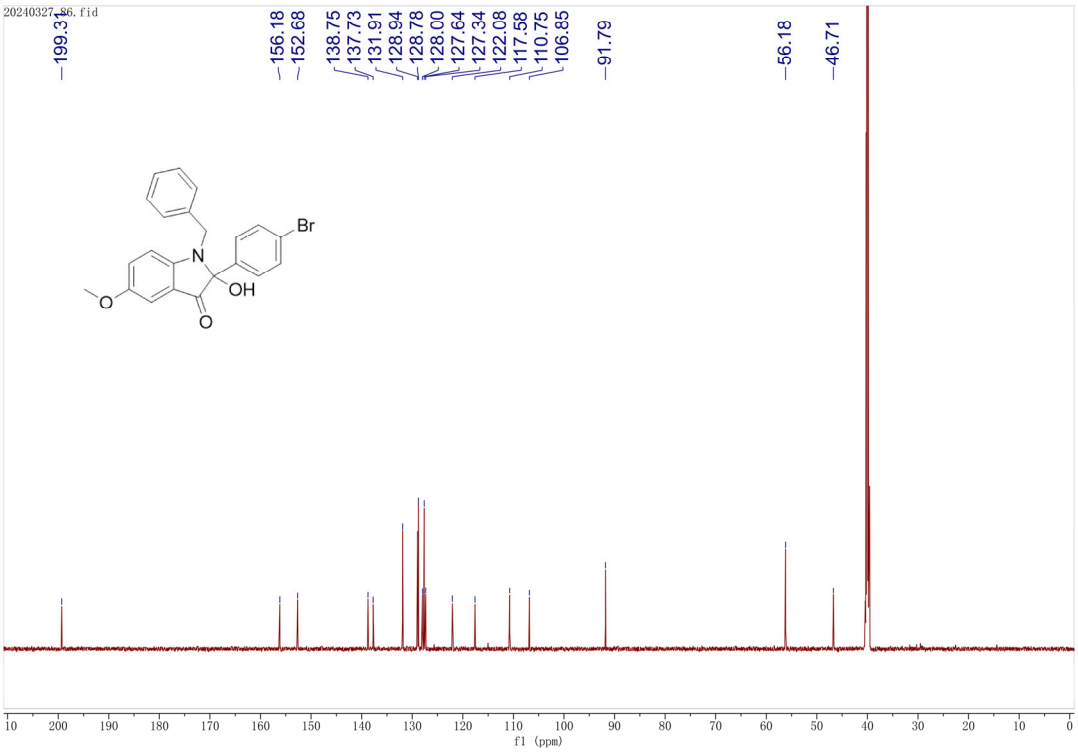
^{13}C NMR of compound **5s** (in DMSO-d$_6$)



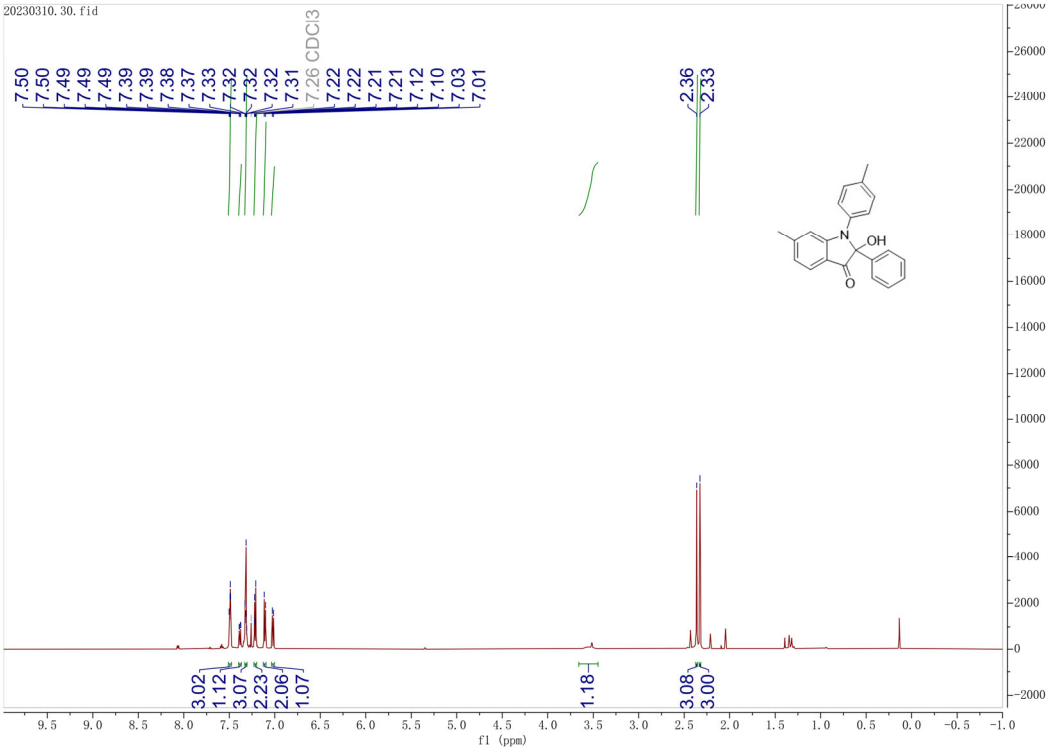
^{1}H NMR of compound **5t** (in DMSO-d$_6$)



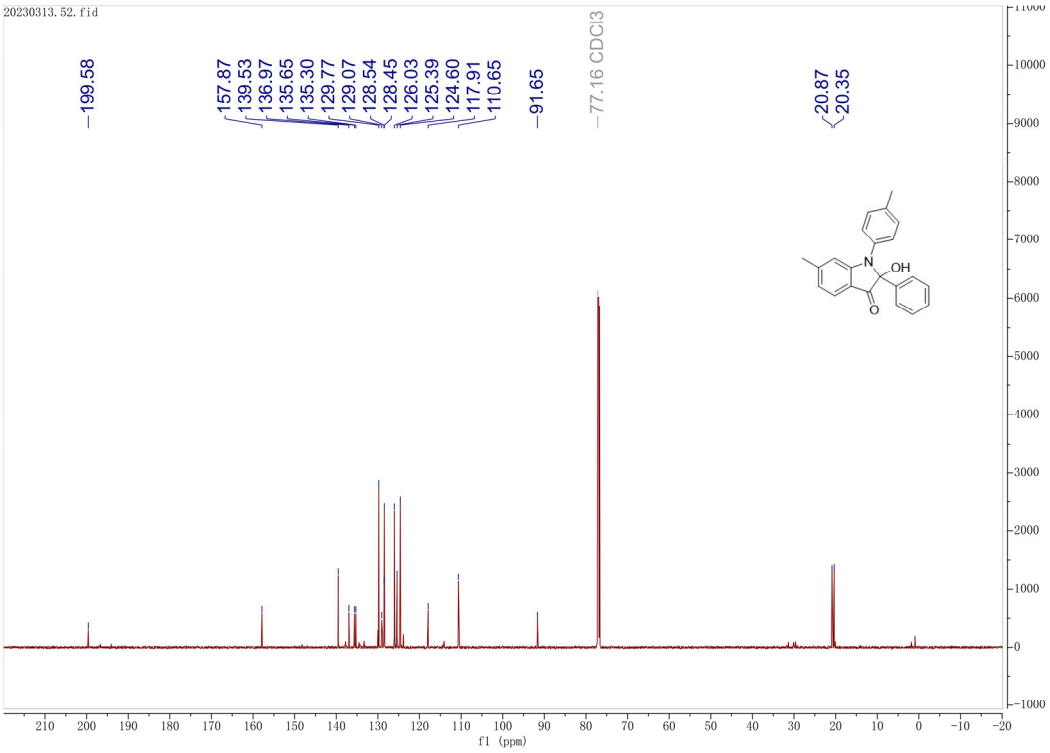
^{13}C NMR of compound **5t** (in DMSO-d$_6$)



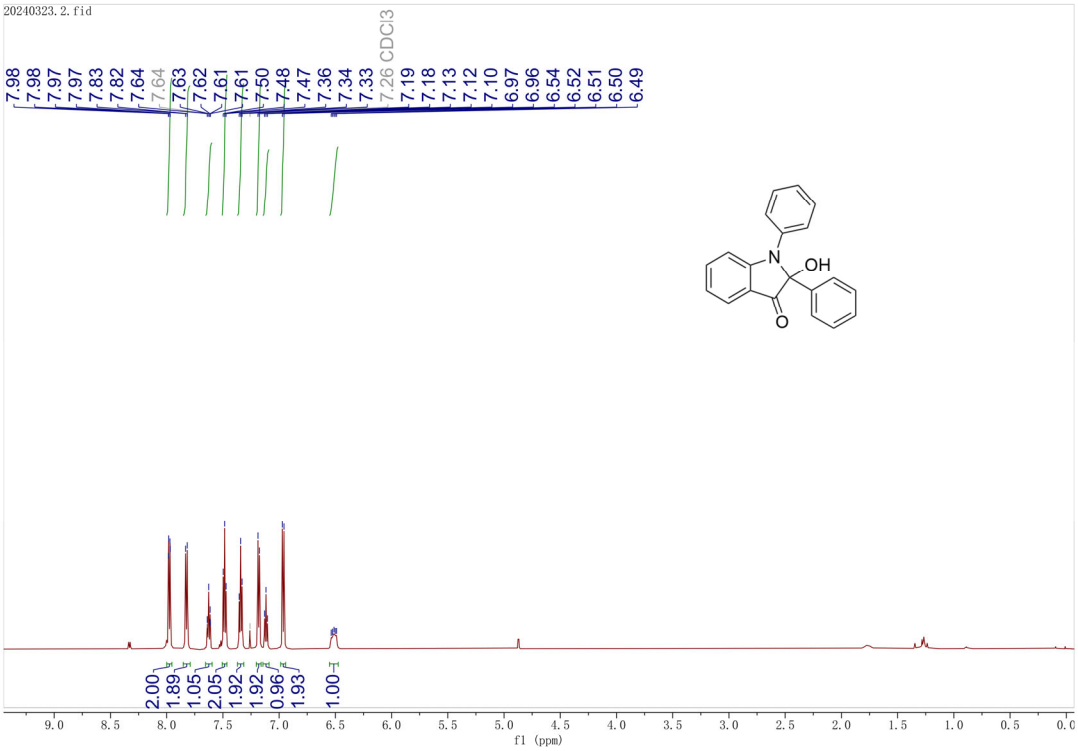
^{1}H NMR of compound **5u** (in $CDCl_3$)



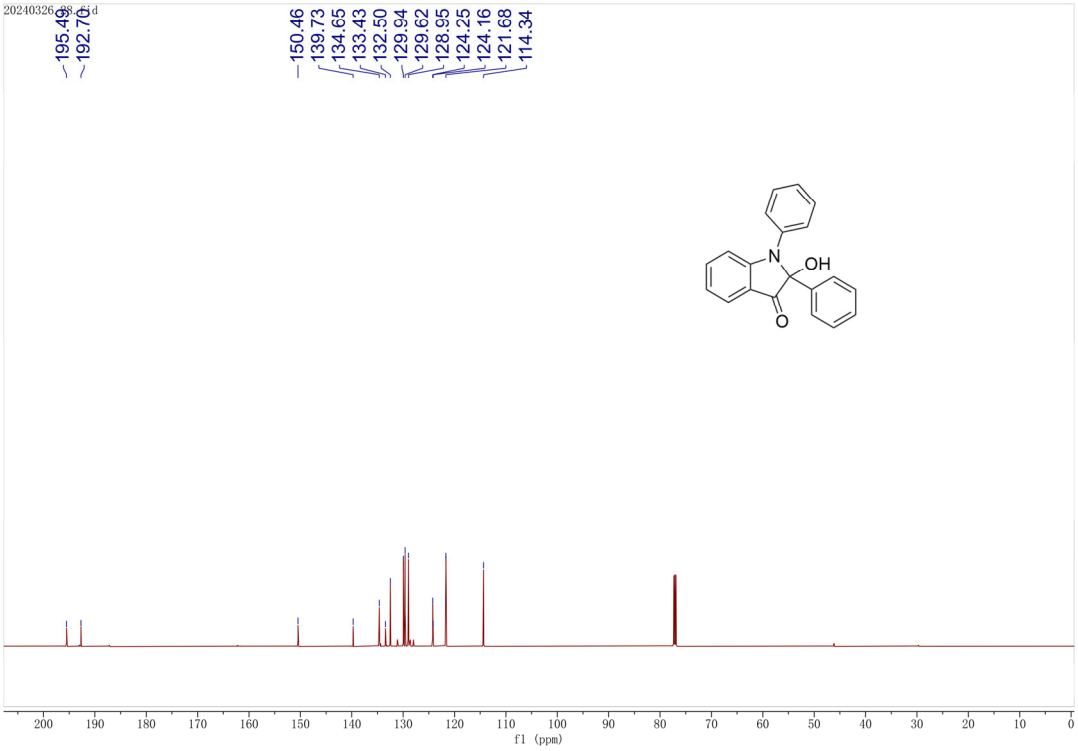
^{13}C NMR of compound **5u** (in $CDCl_3$)



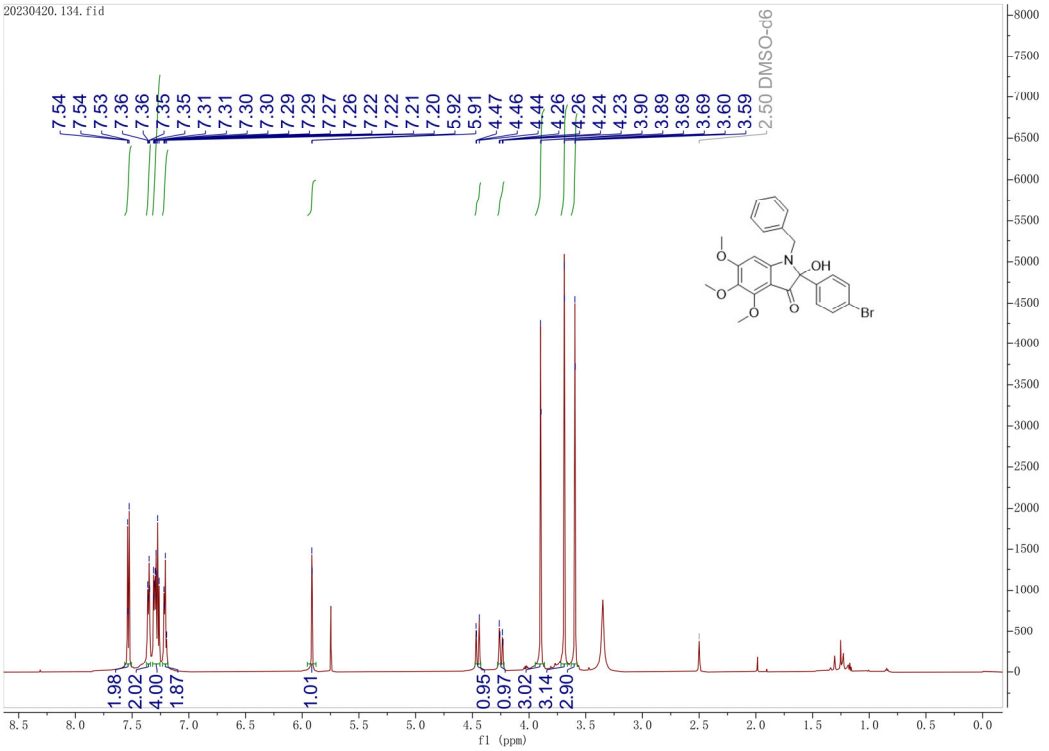
^{1}H NMR of compound **5v** (in $CDCl_3$)



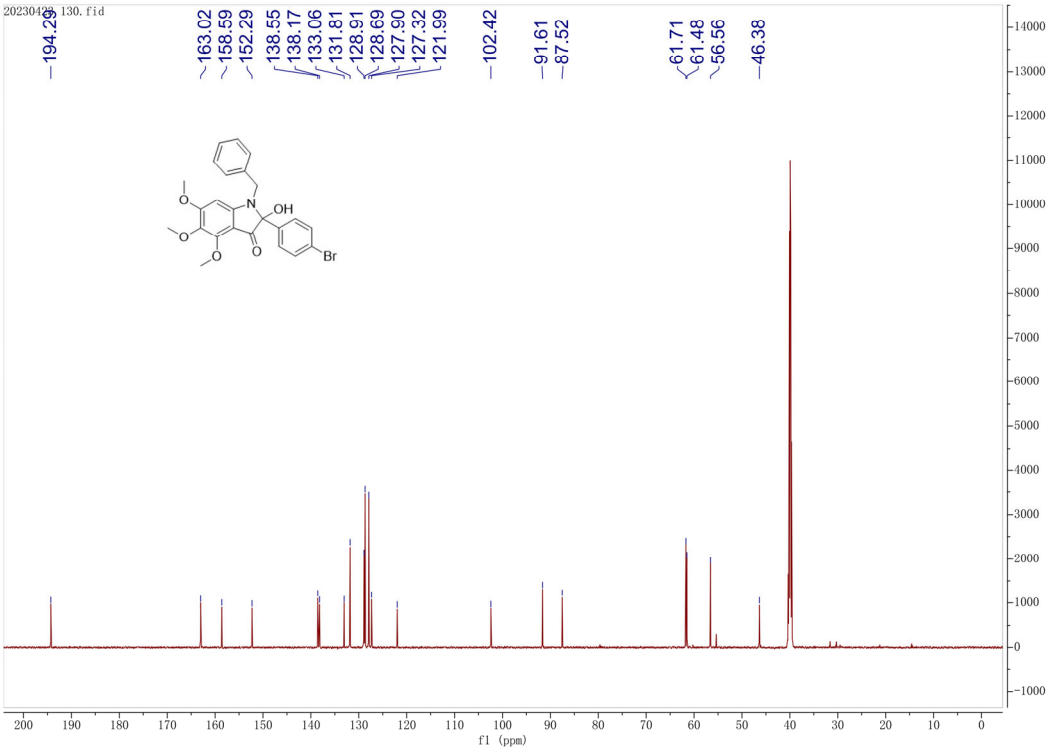
^{13}C NMR of compound **5v** (in $CDCl_3$)



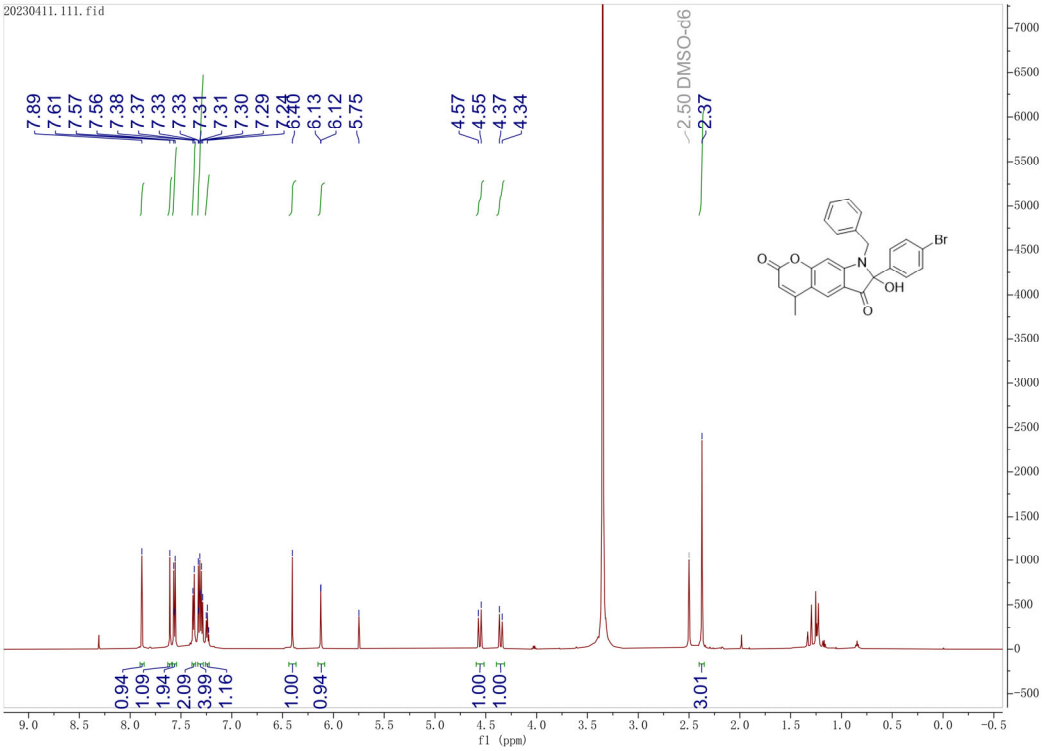
^{1}H NMR of compound **5w** (in DMSO-d$_6$)



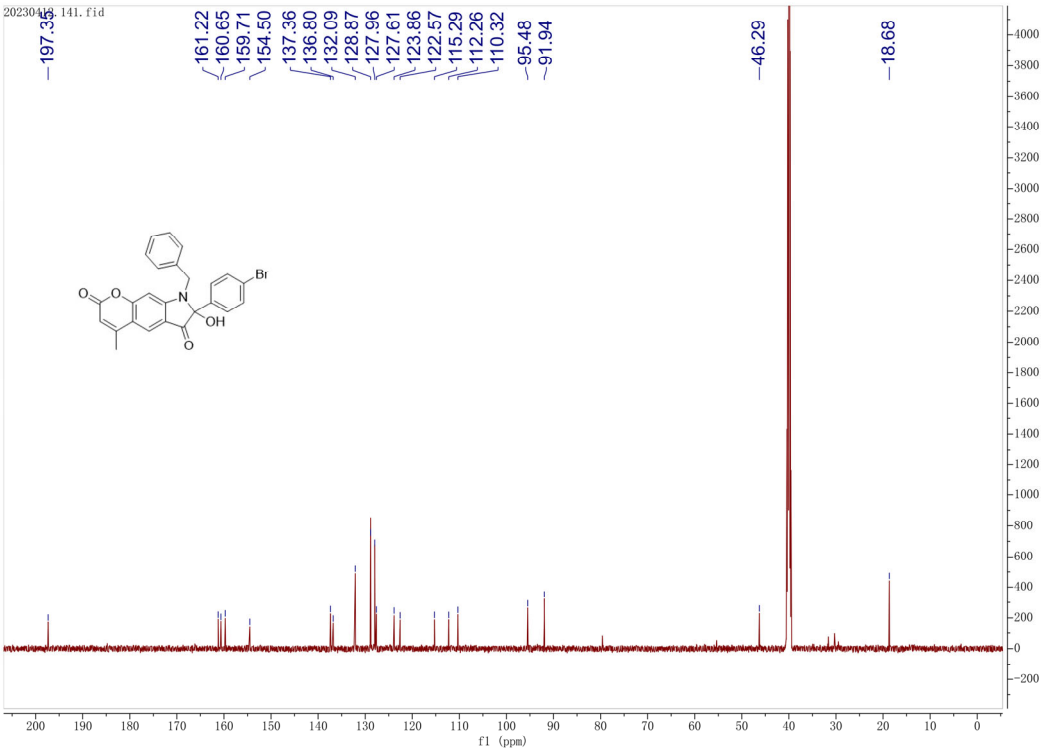
^{13}C NMR of compound **5w** (in DMSO-d$_6$)



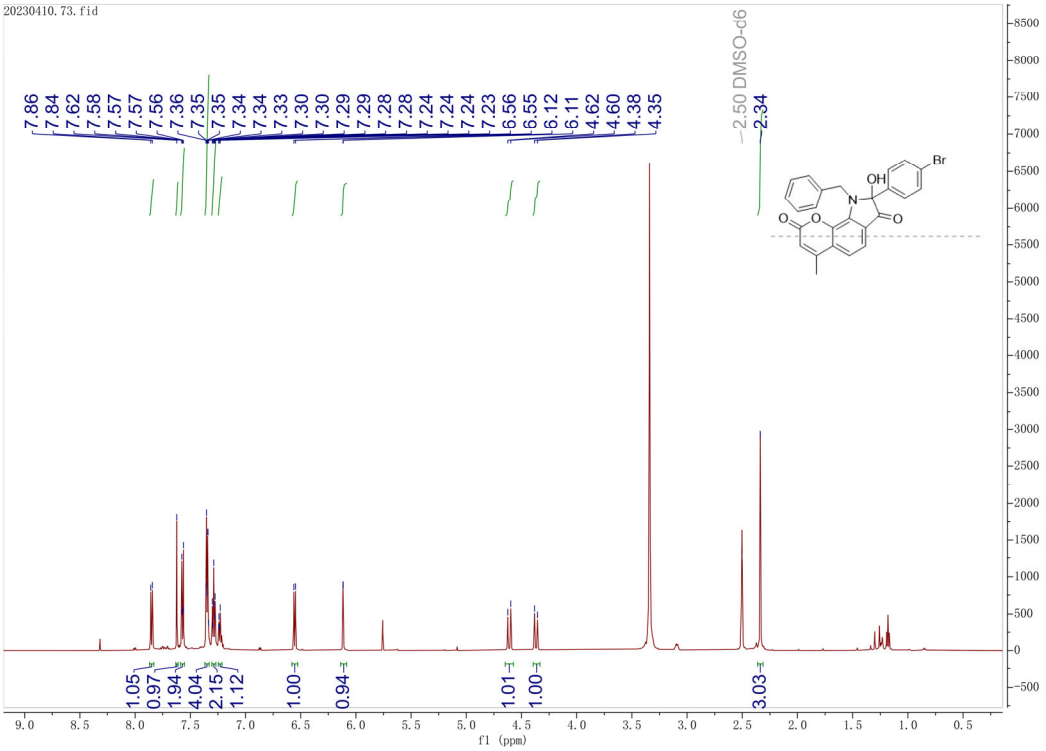
^{1}H NMR of compound **5x** (in DMSO-d_6)



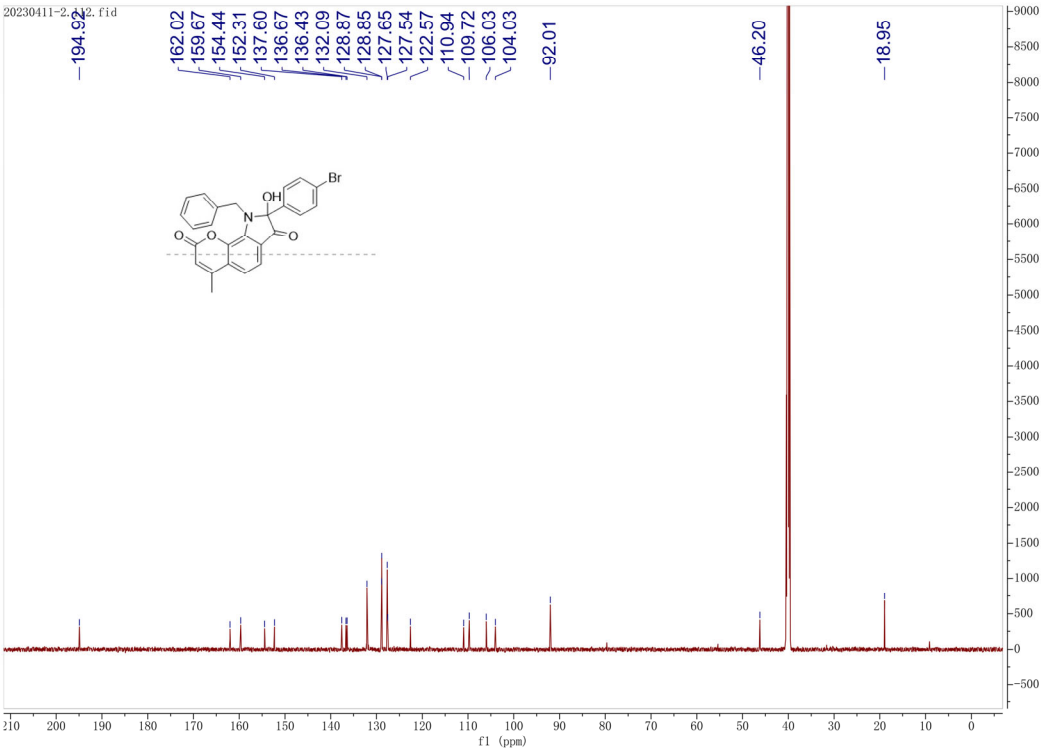
^{13}C NMR of compound **5x** (in DMSO-d_6)



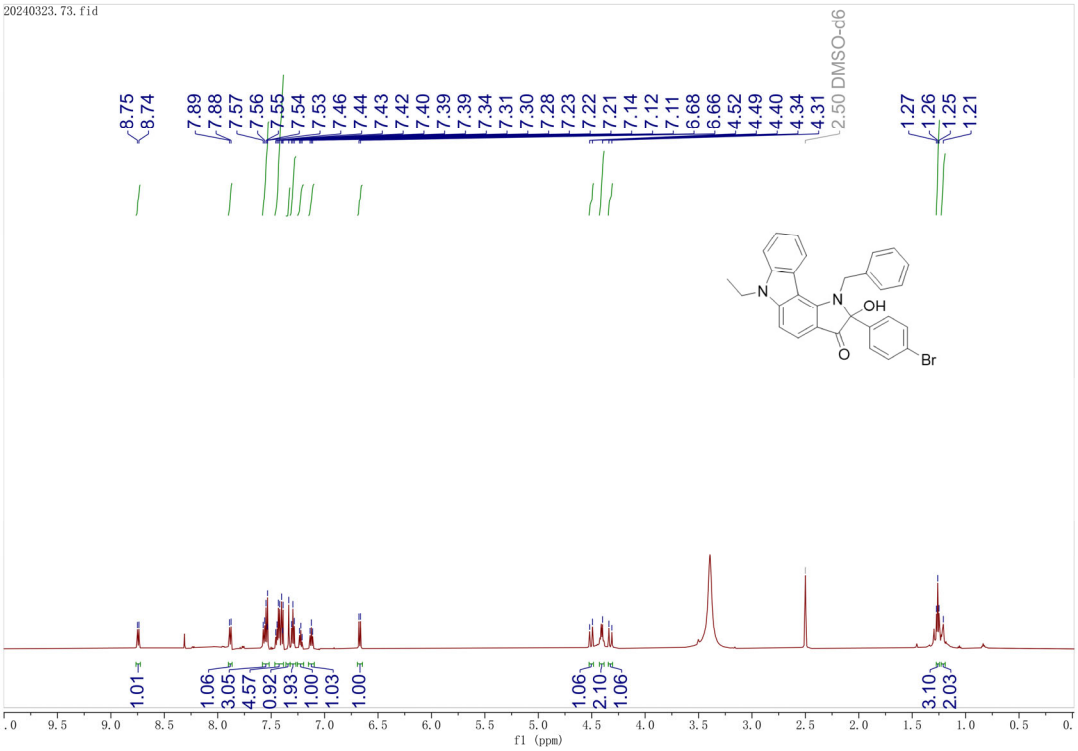
^{1}H NMR of compound **5x'** (in DMSO-d_6)



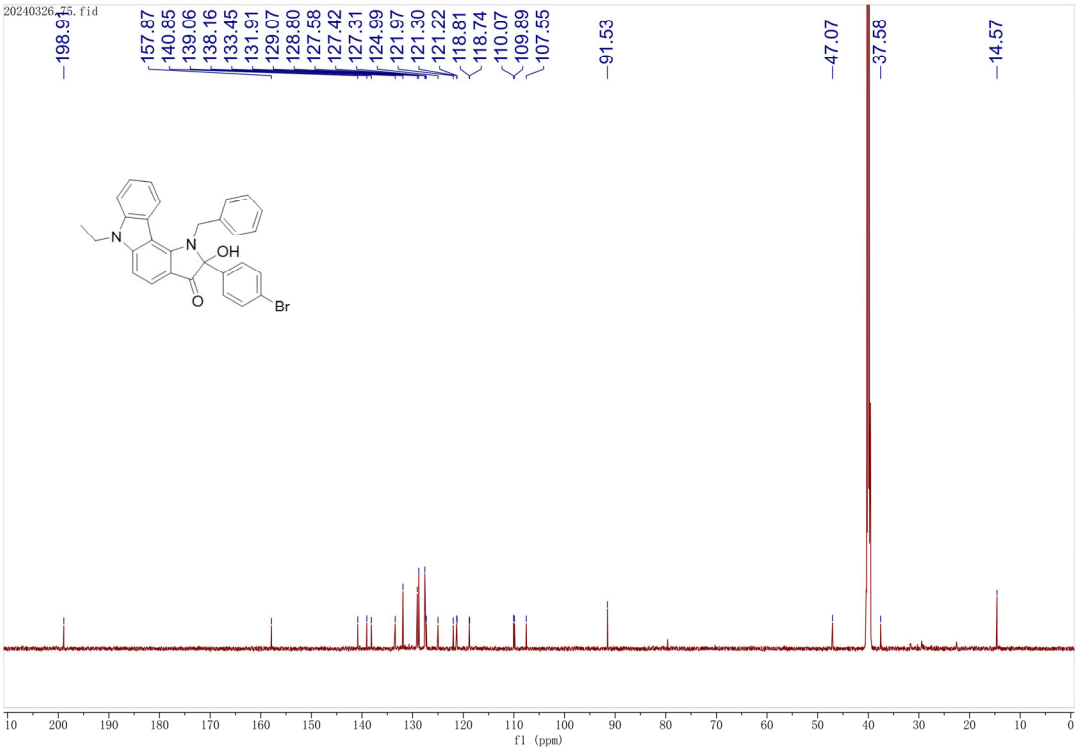
^{13}C NMR of compound **5x'** (in DMSO-d_6)



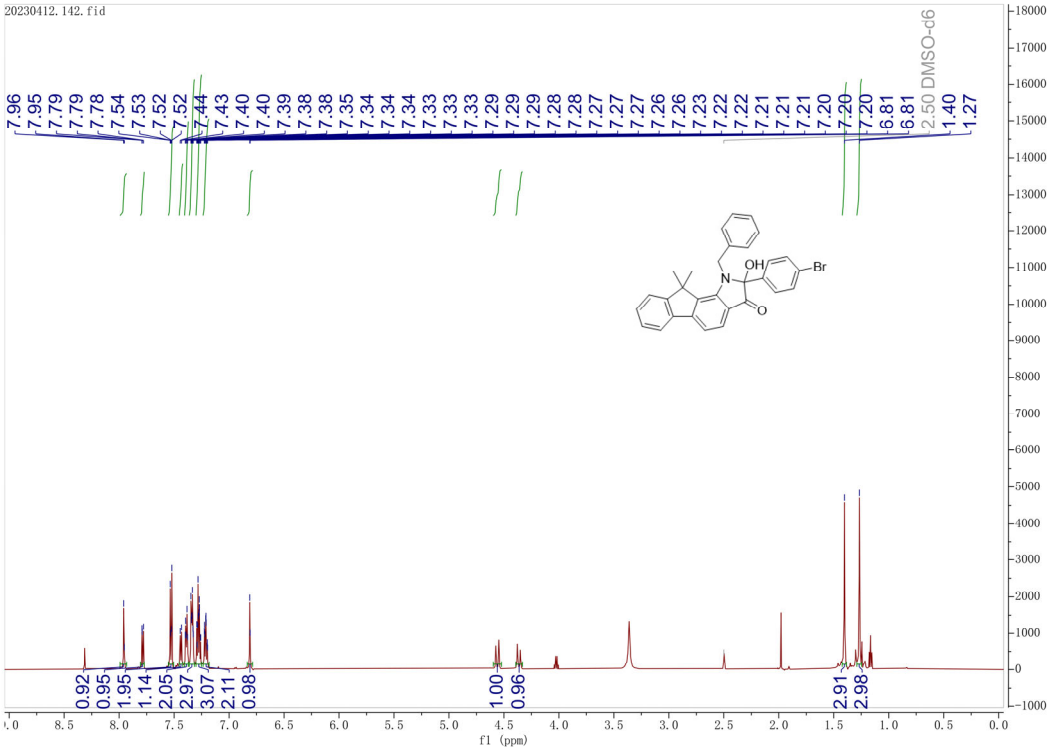
^{1}H NMR of compound **5y** (in DMSO-d$_6$)



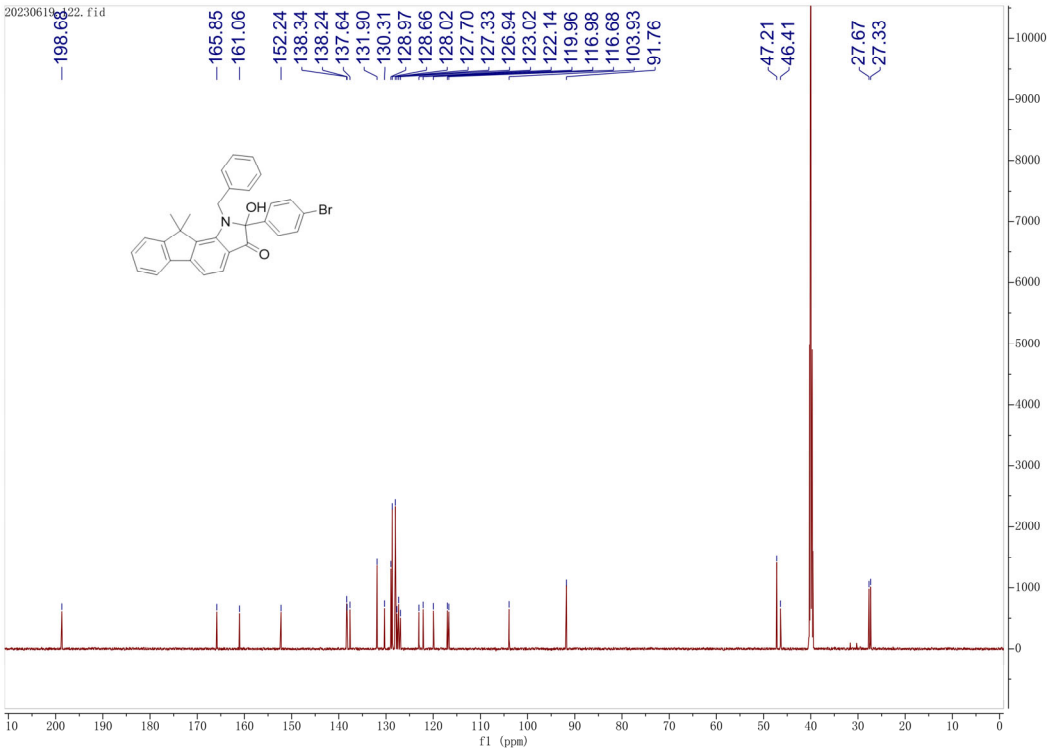
^{13}C NMR of compound **5y** (in DMSO-d$_6$)



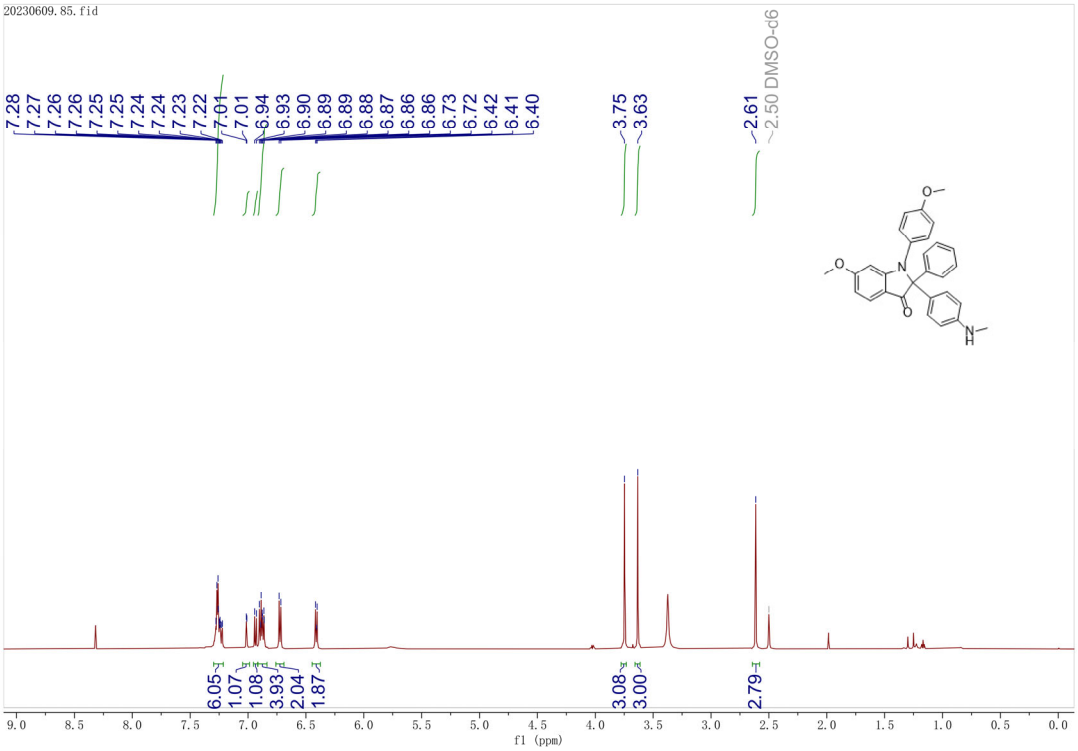
^{1}H NMR of compound **5z** (in DMSO-d_6)



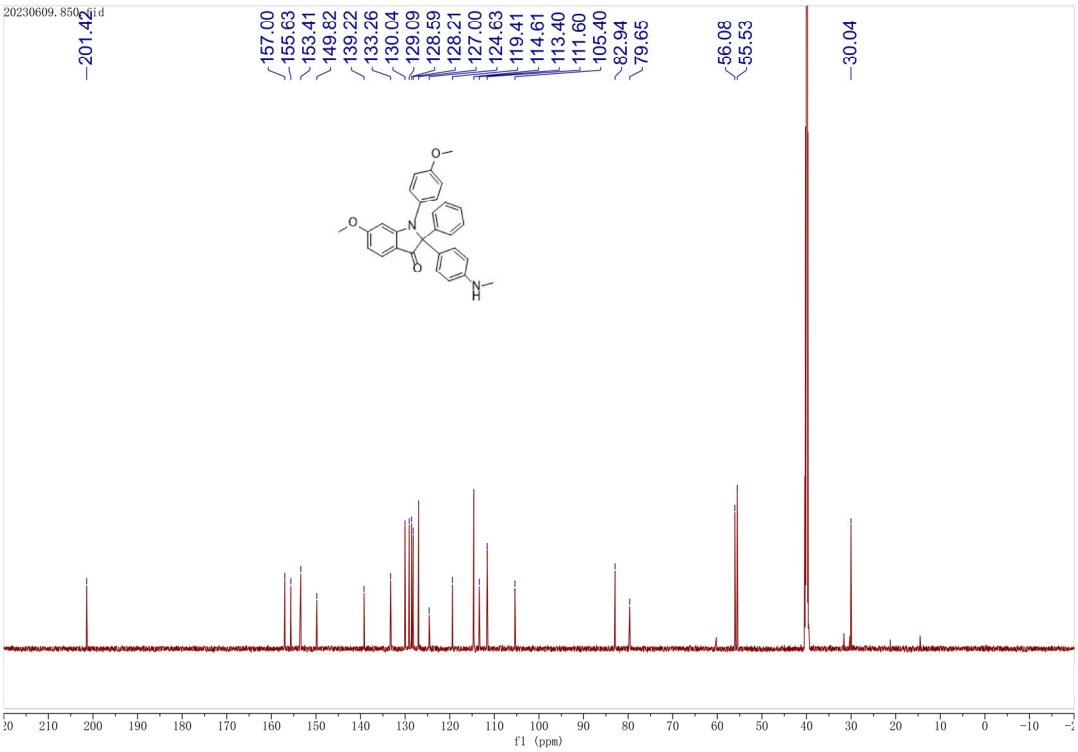
^{13}C NMR of compound **5z** (in DMSO-d_6)



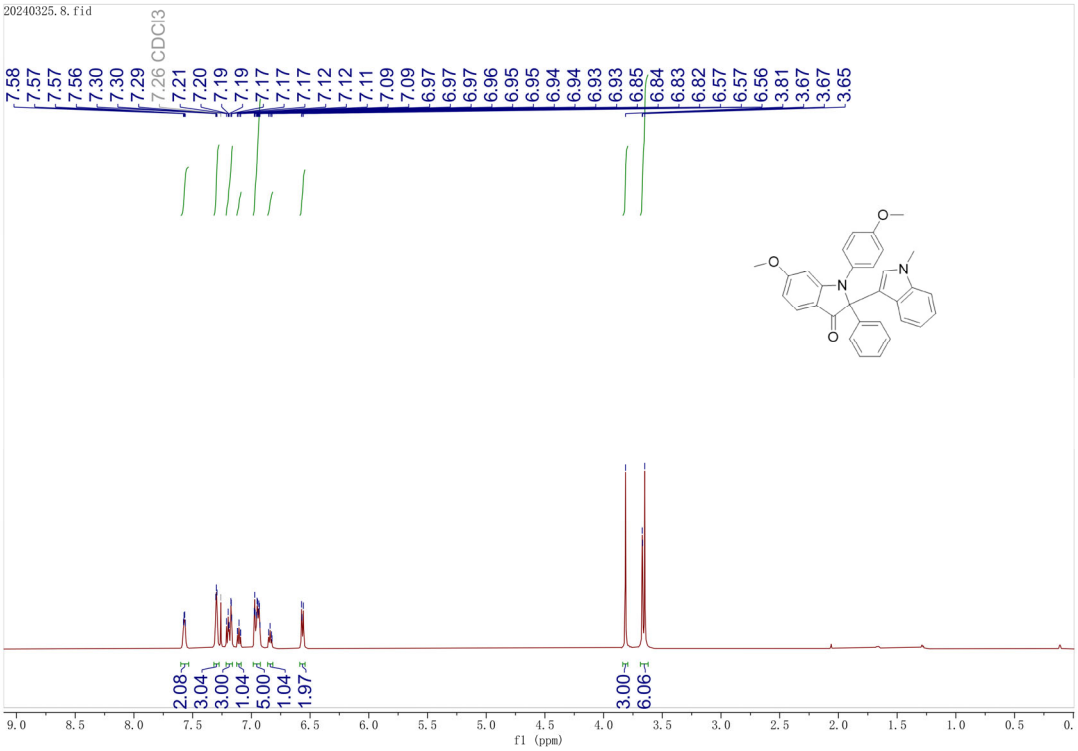
^{1}H NMR of compound **7** (in DMSO-d_6)



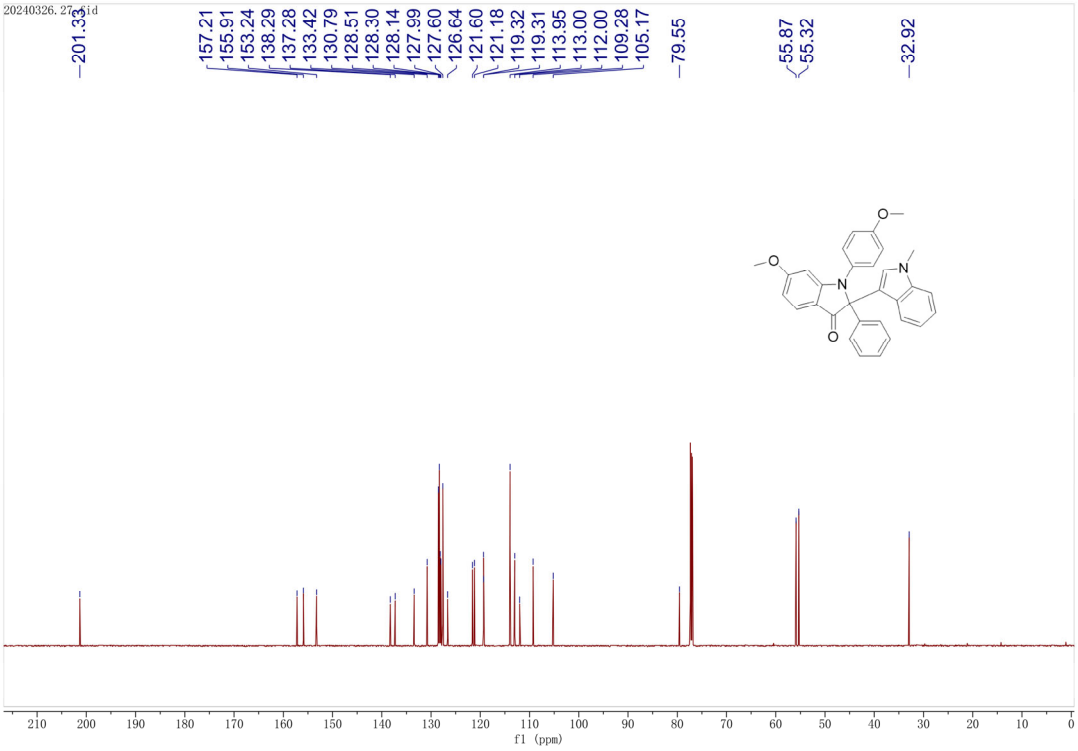
^{13}C NMR of compound **7** (in DMSO-d_6)



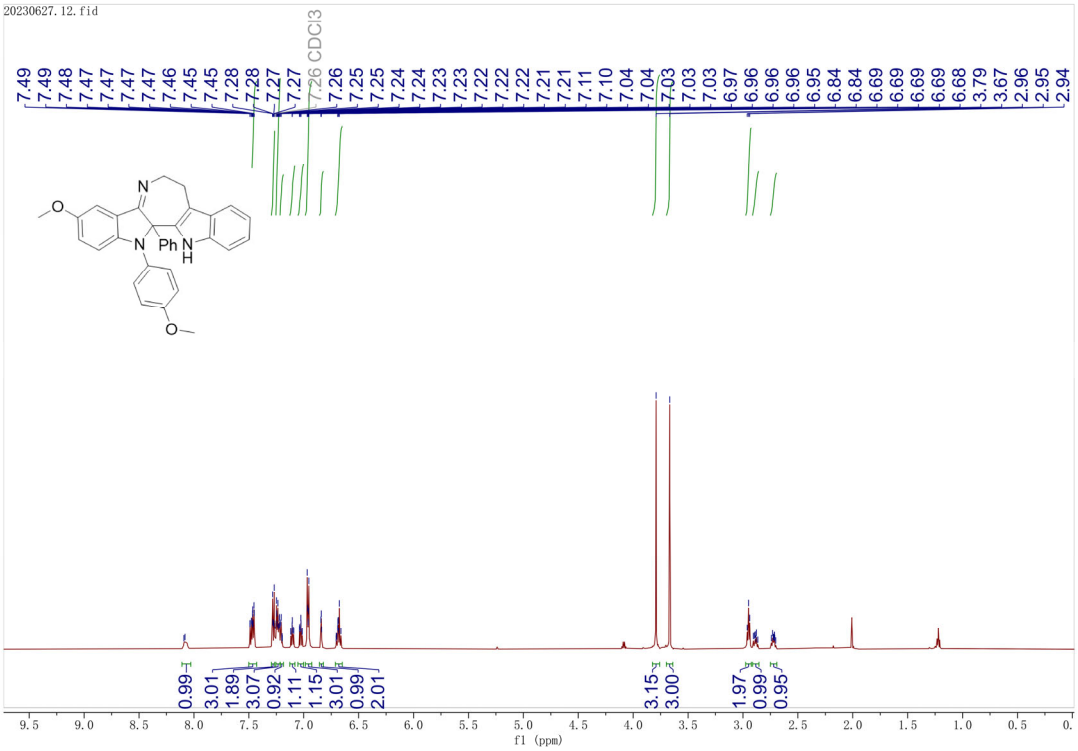
^{1}H NMR of compound **8** (in $CDCl_3$)



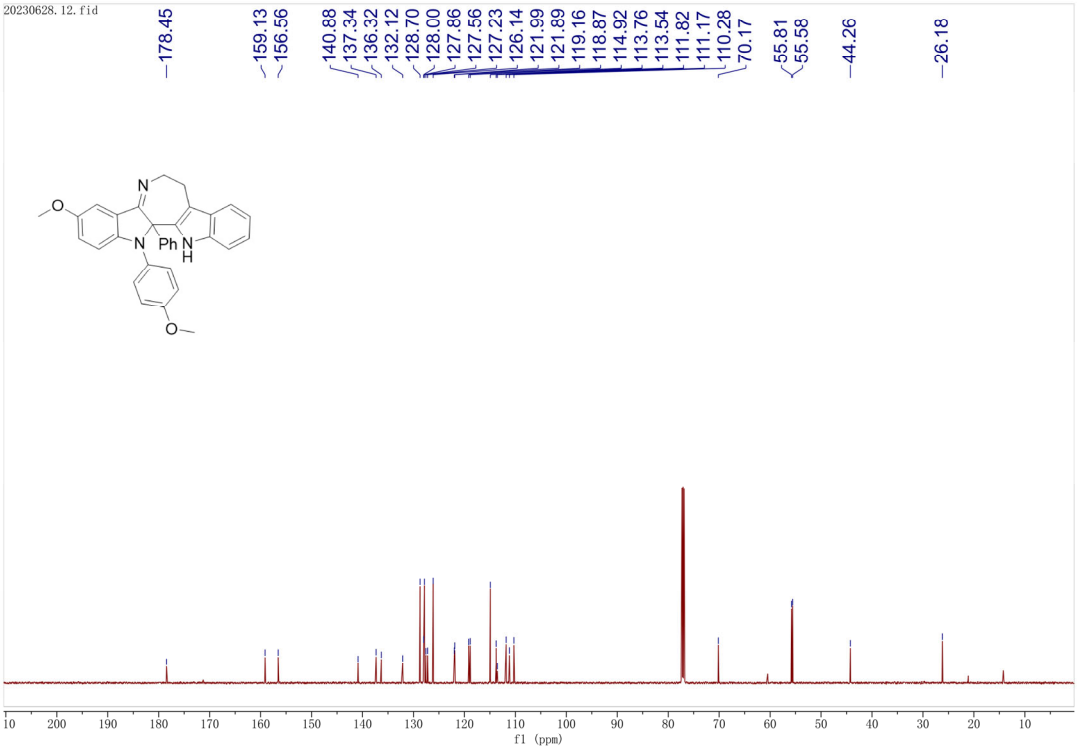
^{13}C NMR of compound **8** (in $CDCl_3$)



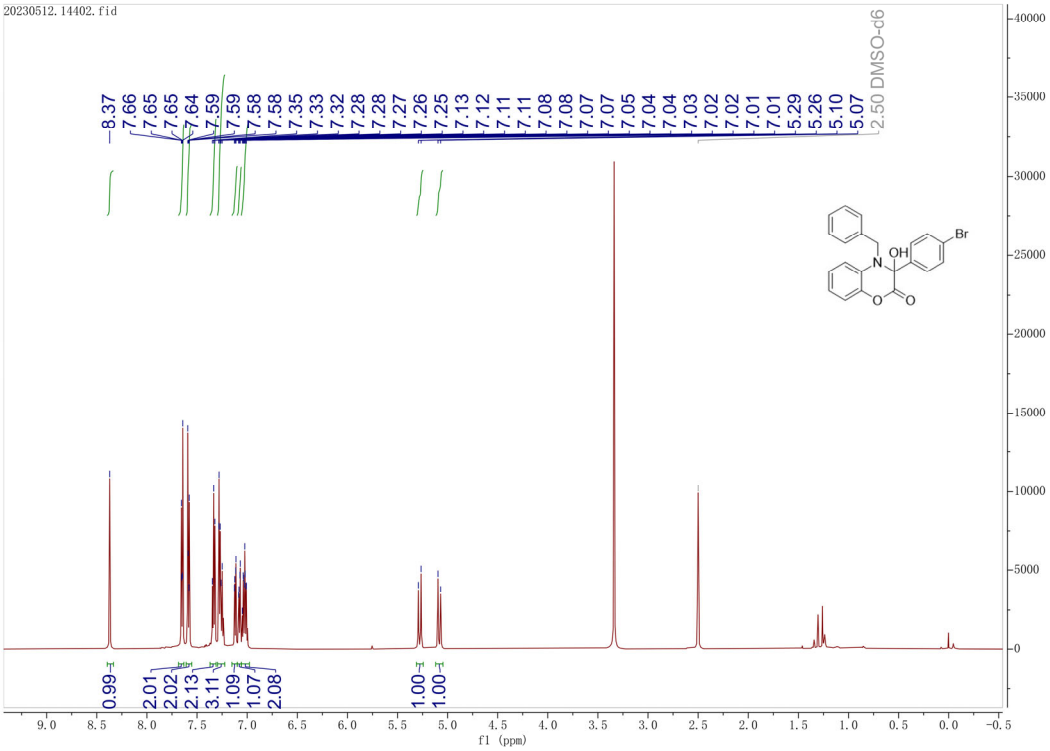
^{1}H NMR of compound **9** (in $CDCl_3$)



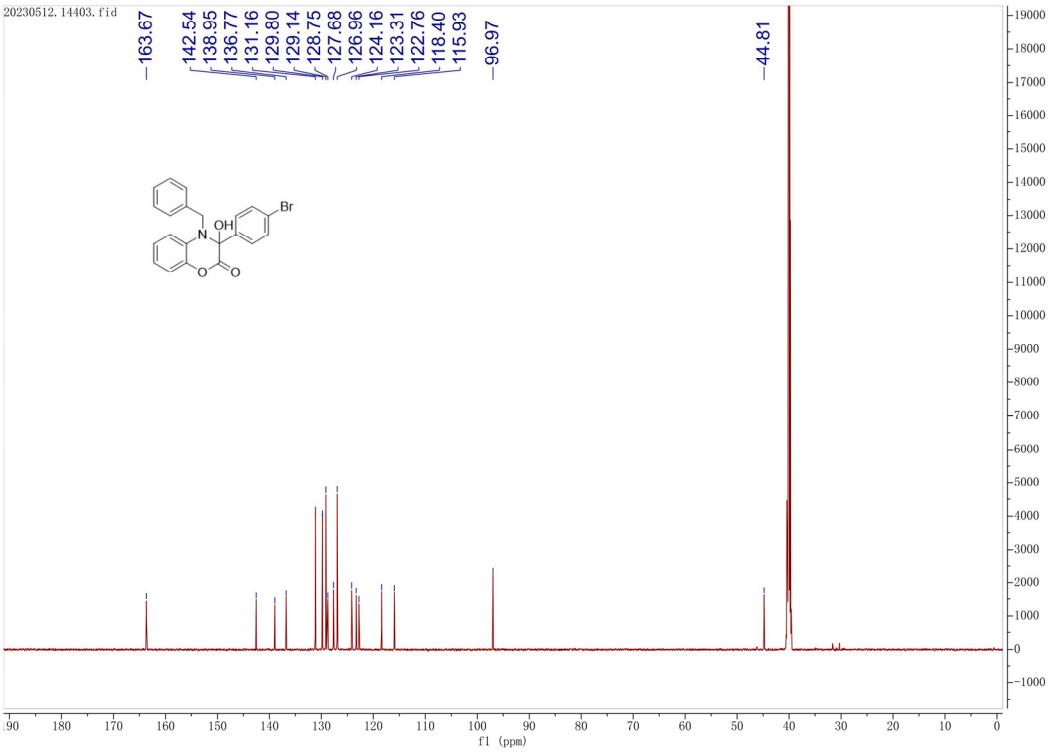
^{13}C NMR of compound **9** (in $CDCl_3$)



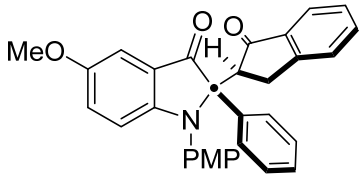
^{1}H NMR of compound **11** (in DMSO-d_6)



^{13}C NMR of compound **11** (in DMSO-d_6)



6. Crystallographic data and molecular structure of 4j-syn, 4j-anti and 5o



4j-syn

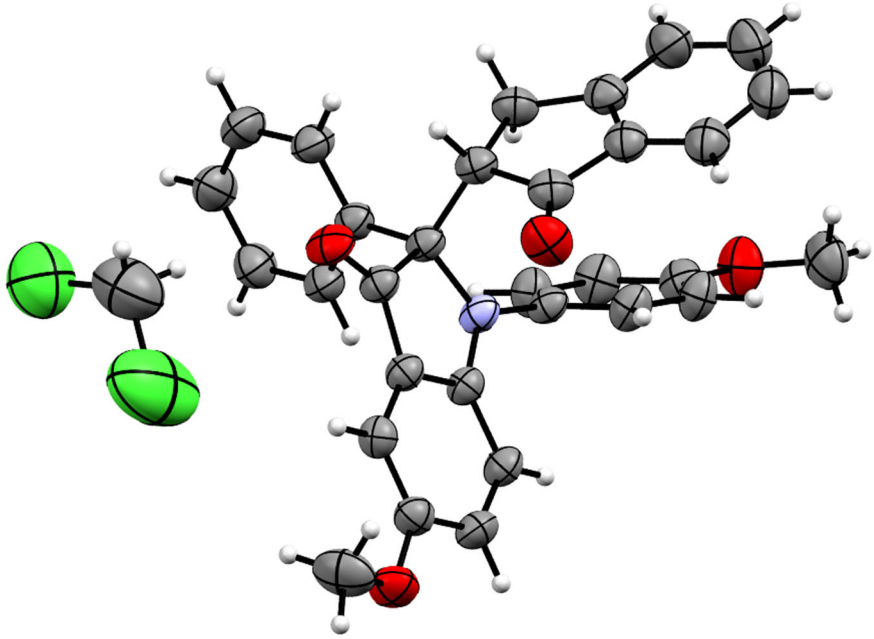


Figure 6.1.1 Molecular structure of **4j-syn** with 50% probability ellipsoids

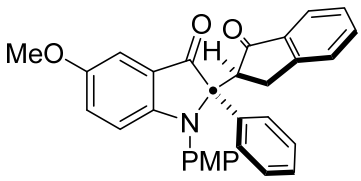
Crystal Data for Compound **4j-syn**: CCDC 2335401 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 5 mg of pure **4j-syn** was completely dissolved in the mixed solvent of 3 mL CH_2Cl_2; and then 2 mL of n-hexane was added slowly. After a week of solvent evaporation, some yellow transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature.

Datablock: 1_a

```
Bond precision:   C-C = 0.0049 A          Wavelength=1.54178

Cell:          a=11.1016(1)      b=11.6870(1)      c=12.0350(1)
               alpha=99.312(1)   beta=108.167(1)   gamma=104.303(1)
Temperature:   273 K

                Calculated                Reported
Volume          1388.43(3)                1388.43(2)
Space group     P -1                      P -1
Hall group      -P 1                      -P 1
Moiety formula  C31 H25 N O4, C H2 Cl2    C31 H25 N O4, C H2 Cl2
Sum formula     C32 H27 Cl2 N O4          C32 H26 Cl2 N O4
Mr              560.45                    559.44
Dx,g cm-3       1.341                     1.338
Z               2                         2
Mu (mm-1)       2.415                     2.415
F000            584.0                     582.0
F000'           587.01
h,k,lmax        13,13,14                  13,13,14
Nref            4908                      4822
Tmin,Tmax       0.617,0.647               0.396,0.753
Tmin'           0.560

Correction method= # Reported T Limits: Tmin=0.396 Tmax=0.753
AbsCorr = NONE

Data completeness= 0.982           Theta(max)= 66.599

R(reflections)= 0.0917( 4265)                wR2(reflections)=
                                             0.2689( 4822)
S = 1.026                  Npar= 354
```

Figure 6.1.2 Crystal Data for Compound **4j-syn**



4j-anti

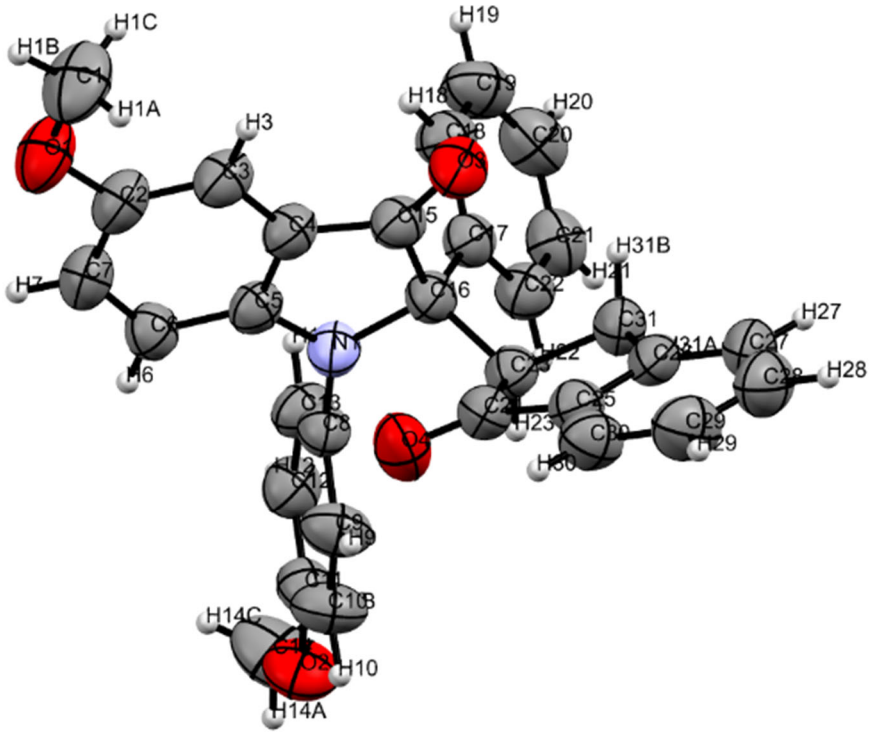


Figure 6.2.1 Molecular structure of **4j-anti** with 50% probability ellipsoids

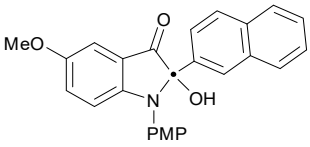
Crystal Data for Compound **4j-anti**: CCDC 2335400 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 5 mg of pure **4j-anti** was completely dissolved in the mixed solvent of 3 mL Acetone; and then 2 mL of PE was added slowly. After a week of solvent evaporation, some yellow transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature.

Datablock: 1_a

```
Bond precision:   C-C = 0.0032 A          Wavelength=1.54178

Cell:           a=9.9116(9)        b=10.4753(9)      c=12.7392(11)
                alpha=113.711(3)   beta=93.324(4)    gamma=92.899(4)
Temperature:    273 K

                 Calculated                Reported
Volume           1205.03(19)               1205.03(18)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C31 H25 N O4              C31 H25 N O4
Sum formula      C31 H25 N O4              C31 H25 N O4
Mr               475.52                    475.52
Dx,g cm-3        1.311                     1.311
Z                2                         2
Mu (mm-1)        0.696                     0.696
F000             500.0                     500.0
F000'            501.51
h,k,lmax         11,12,15                  11,12,15
Nref             4279                      4216
Tmin,Tmax        0.858,0.882               0.349,0.753
Tmin'            0.858

Correction method= # Reported T Limits: Tmin=0.349 Tmax=0.753
AbsCorr = NONE

Data completeness= 0.985          Theta(max)= 66.770

R(reflections)= 0.0773( 3400)                wR2(reflections)=
                                             0.2271( 4216)
S = 1.143                 Npar= 327
```

Figure 6.2.2 Crystal Data for Compound **4j-anti**



5o

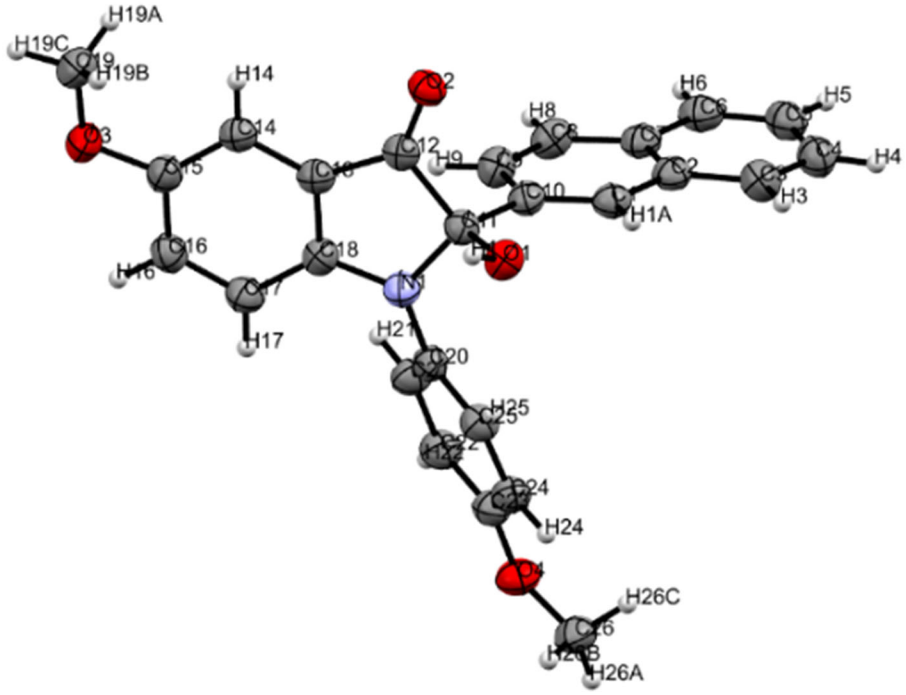


Figure 6.3.1 Molecular structure of **5o** with 50% probability ellipsoids

Crystal Data for Compound **5o**: CCDC 2262414 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic.

Sample preparation: In a 10 mL glass bottle, 5 mg of pure **5o** was completely dissolved in the mixed solvent of 3 mL CH_2Cl_2; and then 2 mL of MeOH was added slowly. After a week of solvent evaporation, some yellow transparent crystals were obtained. The crystals were mounted on a glass fiber for diffraction experiments. Intensity data were collected on a Bruker SMART APEX CCD diffractometer with Mo Kα radiation (0.71073 Å) at room temperature.

Datablock: mo_0428_3_0m

```
Bond precision:   C-C = 0.0032 A          Wavelength=0.71073

Cell:           a=10.8438(5)      b=10.9757(4)      c=11.4845(5)
                alpha=61.863(2)   beta=63.537(2)    gamma=60.929(1)
Temperature:    150 K

                 Calculated                Reported
Volume           1011.07(8)                1011.07(8)
Space group      P -1                      P -1
Hall group       -P 1                      -P 1
Moiety formula   C26 H21 N O4              C26 H21 N O4
Sum formula      C26 H21 N O4              C26 H21 N O4
Mr               411.44                    411.44
Dx,g cm-3        1.352                     1.351
Z                2                         2
Mu (mm-1)        0.091                     0.091
F000             432.0                     432.0
F000'            432.21
h,k,lmax         12,13,13                  12,13,13
Nref             3556                      3529
Tmin,Tmax        0.991,0.994               0.011,0.028
Tmin'            0.991

Correction method= # Reported T Limits: Tmin=0.011 Tmax=0.028
AbsCorr = NONE

Data completeness= 0.992           Theta(max)= 25.000

R(reflections)= 0.0443( 2957)                wR2(reflections)=
                                             0.1154( 3529)
S = 1.096                  Npar= 283
```

Figure 6.3.2 Crystal Data for Compound **5o**