Supporting Information

Highly Enantioselective Electrosynthesis of C2-Quaternary Indolin-3-ones

Fo-Yun Lu‡, Yu-Jue Chen‡, Yuan Chen, Xuan Ding, Zhi Guan* and Yan-Hong He*

Key Laboratory of Luminescent and Real-Time Analytical Chemistry, Ministry of Education, School of Chemistry and Chemical Engineering, Southwest University, Chongqing 400715, China

Emails: guanzhi@swu.edu.cn (for Z. Guan); heyh@swu.edu.cn (for Y.-H. He)

(‡ These authors contributed equally to this work)

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1. General experimental details

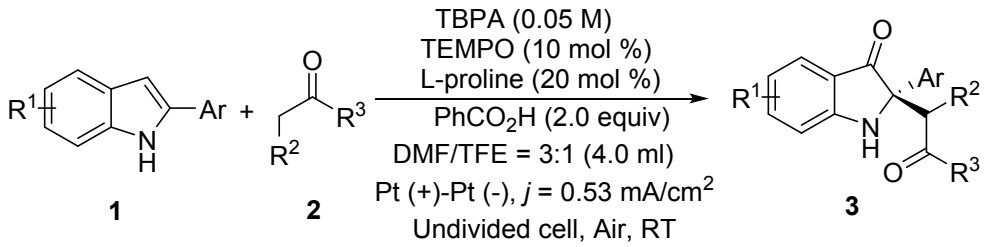
The electrolysis instrument used is a dual display potentiostat (DJS-292B) (Shanghai Leici Chuang Yi Instrument Co., Ltd.) The anode electrode and cathode electrode used were all platinum electrodes (1.5 cm × 1.0 cm × 0.2 mm) (Gaoss Union). Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin-layer chromatography (TLC) with GF 254 silica gel plates using UV light and vanillic aldehyde as visualizing agents. Flash column chromatography was performed using 200-300 mesh silica gel at increased pressure. ^{1}H NMR spectra and ^{13}C NMR spectra were respectively recorded on 600 MHz and 150 MHz NMR spectrometers. Chemical shifts (δ) were expressed in ppm with TMS as the internal standard, and coupling constants (*J*) were reported in Hz. High-resolution mass spectra were obtained by using ESI ionization sources (Varian 7.0 T FTICR-MS). Melting points were taken on a melting-point apparatus and were uncorrected. The enantiomeric excess (e.e.) and diastereomeric ratio (d.r.) of products were determined by chiral HPLC analysis performed using Chiralpak AD-H, and Chiralpak IA (Daicel Chiral Technologies CO., LTD.)

Abbreviations

DMF = N,N-dimethylformamide, TFE = 2,2,2-trifluoroethanol, TBPA = tetrabutylammonium perchlorate, TEMPO = (2,2,6,6-Tetramethylpiperidin-1-yl)oxyl, MeCN = acetonitrile, ACT = 4-acetamido-TEMPO, HFIP = 1,1,1,3,3,3-hexafluoro-2-propanol, NMP = 1-methyl-2-pyrrolidinone, DMA = N,N-dimethylacetamide, TFA = 2,2,2-trifluoroacetic acid，CP_2Fe = ferrocene.

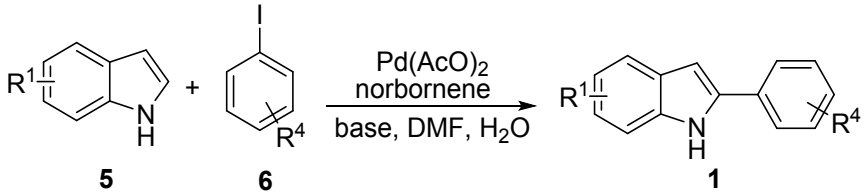
2. Experimental procedures

2.1. General procedure for the synthesis of products 3



To an oven-dried, undivided electrochemical cell equipped with a magnetic stirring bar, a platinum net anode (1.0 cm × 1.5 cm × 0.2 mm) and a platinum net cathode (1.0 cm × 1.5 cm × 0.2 mm) were added 2-arylindole **1** (0.2 mmol, 1.0 equiv), TEMPO (0.02 mmol, 10 mol%, 0.1 equiv), L-proline (0.04 mmol, 20 mol%, 0.2 equiv), $PhCO_2H$ (0.4 mmol, 2.0 equiv), Tetrabutylammonium perchlorate (TBPA) (0.05 M), DMF (3.0 mL), 2,2,2-trifluoroethanol (1.0 mL) and ketone **2** (1.0 mmol, 5.0 equiv). The resultant mixture was initiated at a constant current of 0.8 mA ($j \approx 0.53$ mA cm^{-2}, the distance between the cathode and the anode is about 1.0 cm) under the air atmosphere at RT. The reaction was monitored by TLC. After completion of the reaction, 20 mL of ethyl acetate was added, and washed with brine. The organic phase was dried over anhydrous Na_2SO_4, and filtered. The organic solvent was removed under reduced pressure. The residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate: v/v, 20/1 - 5/1 as eluant) to give the product **3**.

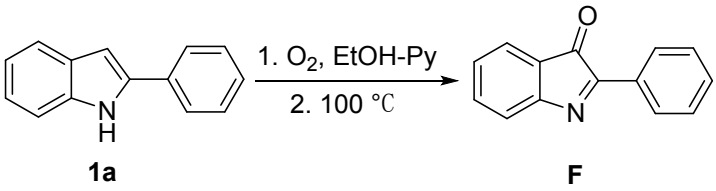
2.2. General procedure for the synthesis of 2-arylindoles



Following the literature,[1] some modifications were made. A high pressure tube equipped with a magnetic stirring bar was charged with indole substrate **5** (15.0 mmol, 1.0 equiv.), norbornene (30.0 mmol, 2.0 equiv.), the base [30.0 mmol, 2 equiv. K_2CO_3 (**1b**, **1d**, **1f-o**) or 2 equiv. $KHCO_3$ (**1c**, **1e**)] and $Pd(AcO)_2$ (0.75 mmol, 5 mol %). A solution of water (0.5 M) in DMF (15.0 mL) was added via syringe, and then the aryl iodide **6** (30.0 mmol, 2.0 equiv.) was added via syringe. The reaction mixture was then placed in a preheated oil bath at 70 °C (**1b**, **1d**, **1f-o**) or 90 °C (**1c**, **1e**). Vigorous stirring was applied. The reaction was monitored by

TLC. Upon completion, the reaction mixture was cooled to room temperature, diluted with EtOAc, and filtered. The filtrate was washed with H_2O (3 times) and brine, the organic phase was concentrated in vacuum to remove the solvent. The residue was directly submitted to flash column chromatography to afford the 2-arylindole product (**1b-o**). Substrate **1p** was synthesized according to the literature method.[2]

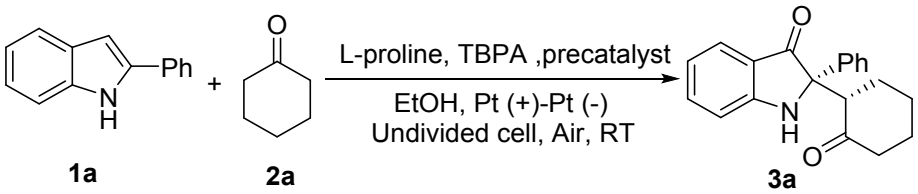
2.3. The synthesis of intermediate F.



Following the literature,[3] some modifications were made. A round-bottom flask was charged with methylene blue (MB, 82 mg, 0.25 mmol, 0.1 equiv.) and 2-phenylindole (**1a**, 483.1 mg, 2.5 mmol, 1.0 equiv.) in methanol solution (50 mL) and pyridine (2.0 mL), The resultant mixture was stirred at r.t. under irradiation of 2 × 32 W CFLs (Philips) under oxygen bubbling and monitored by TLC. After completion of the reaction, the reaction mixture was concentrated in *vacuo,* diluted with ether and washed with water. The ether layer was dried over Na_2S0_4, evaporated to dryness and heated at 100℃ under reduced pressure for 5-10 min to afford a solid which was chromatographed over silica gel column, elution with petroleum ether - ethyl acetate gave the 2-phenyl-3*H*-indol-3-one (**F**). **^{1}H NMR** (600 MHz, $CDCl_3$): δ 8.33 (d, *J* = 7.4 Hz, 2H), 7.51 – 7.38 (m, 5H), 7.34 (d, *J* = 7.2 Hz, 1H), 7.18 (t, *J* = 7.1 Hz, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 193.4, 161.1, 159.8, 136.7, 132.1, 130.1, 129.3, 128.8, 128.3, 124.6, 123.2, 121.9. **HRMS** (EI): m/z: calcd for $C_{14}H_9NO$ $(M+H)^+$: 208.0757, found: 208.0759.

3. Optimization of reaction conditions.

Table S1. Mediator screening [a]

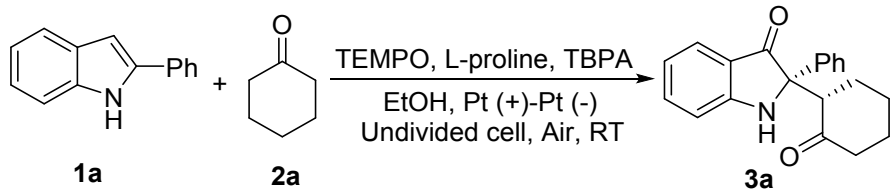


1a **2a** **3a**

Entry	Mediator	Yield (%)	ee (%)
1	**TEMPO**	**16**	**97**
2	CP_2Fe	trace	--
3	KI	trace	--
4	$(4\text{-}BrPh)_3N$	trace	--
5	ACT	14	98
6	--	3	98

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), mediator (0.04 mmol, 0.2 equiv) and TBPA (0.1 mmol, 0.5 equiv) in EtOH (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S2. Effect of TEMPO loading on the reaction [a]

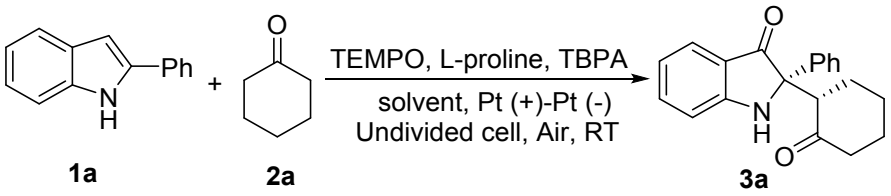


1a **2a** **3a**

Entry	TEMPO (mol %)	Yield (%)	ee (%)
1	5	13	98
2	**10**	**23**	**97**
3	20	16	97
4	50	16	96
5	100	14	97

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO and TBPA (0.1 mmol, 0.5 equiv) in EtOH (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S3. Effect of solvent on the reaction [a]

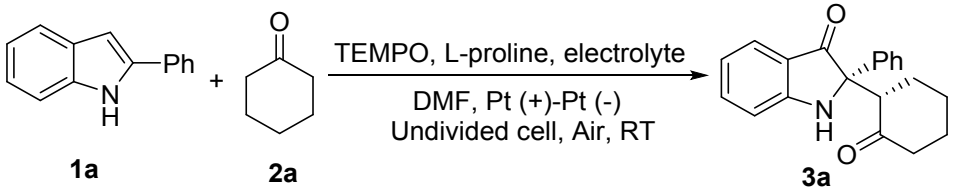


1a 2a 3a

Entry	Solvent	Yield (%)	ee (%)
1	MeCN	14	92
2	THF	11	98
3	DCE	17	93
4	EtOH	23	97
5	**DMF**	**41**	**97**
6	DCM	4	98

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and TBPA (0.1 mmol, 0.5 equiv) in solvents (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S4. Effect of electrolyte on the reaction [a]

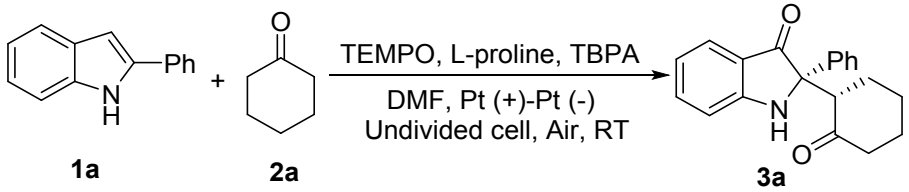


1a 2a 3a

Entry	Electrolyte	Yield (%)	ee (%)
1	n-Bu_4NBF_4	23	--
2	n-Bu_4NPF_6	37	--
3	**n-Bu_4NClO_4**	**41**	**97**
4	Et_4NOTs	29	--
5	$LiClO_4$	34	--
6	--	NR	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and electrolytes (0.1 mmol, 0.5 equiv) in DMF (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

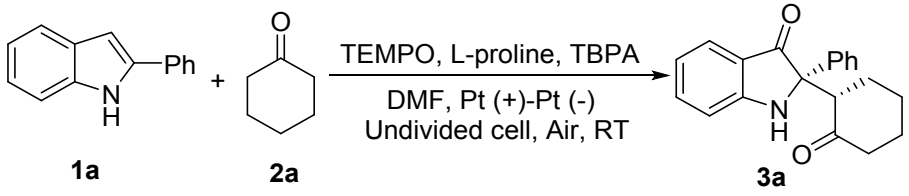
Table S5. Effect of electrolyte loading on the reaction [a]



Entry	TBPA (mmol)	Yield (%)	ee (%)
1	0.1	41	97
2	**0.2**	**46**	**97**
3	0.4	43	95
4	0.6	40	--
6	--	NR	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and TBPA in DMF (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

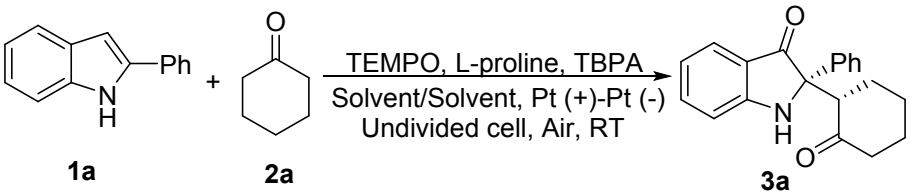
Table S6. Effect of molar ratio of substrates on the reaction [a]



Entry	Molar ratio (**1a**:**2a**)	Yield (%)	ee (%)
1	0.2:0.4	29	--
2	0.2:0.6	35	--
3	**0.2:1.0**	**46**	**97**
4	0.2:1.6	26	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a**, L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and TBPA (0.2 mmol, 1.0 equiv) in DMF (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S7. Effect of mixed solvent on the reaction [a]

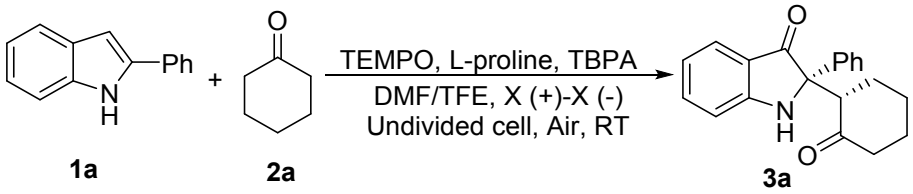


Entry	Solvent	Yield (%)	ee (%)
1	3:1 DMF/THF	25	--

2	**3:1 DMF/TFE**	**54**	**98**
3	3:1 DMF/H_2O	18	--
4	3:1 DMA/TFE	21	--
5	3:1 NMP/TFE	33	--
6	2:2 DMF/HFIP	44	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and TBPA (0.2 mmol, 1.0 equiv) in mixture of solvent (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S8. Effect of electrode material on reaction [a]

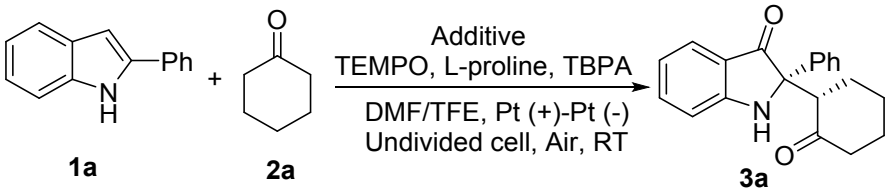


1a **2a** **3a**

Entry	Anode	Cathode	Yield (%)	ee (%)
1	**Pt**	**Pt**	**54**	**98**
2	C	Pt	messy	--
3	RVC	Pt	40	97
4	Ti	Pt	31	--
5	Pt net	Pt	32	--
6	Pt	C	messy	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv) and TBPA (0.2 mmol, 1.0 equiv) in DMF/TFE = 3:1 (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S9. Effect of additives on the reaction [a]



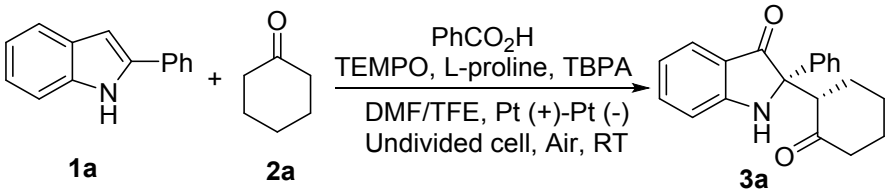
1a **2a** **3a**

Entry	Additive	Yield (%)	ee (%)
1	2,6-lutidine	59	93
2	$NaCO_3$	messy	--
3	H_2O	46	92
4	TFA	trace	--

5	CH_3CO_2H	61	98
6	p-$CH_3C_6H_4CO_2H$	49	97
7	**$C_6H_5CO_2H$**	**67**	**98**
8	m-$NO_2C_6H_4CO_2H$	29	--

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv), TBPA (0.2 mmol, 1.0 equiv) and additives (0.4 mmol, 2.0 equiv) in DMF/TFE = 3:1 (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1.

Table S10. Effect of $PhCO_2H$ loading on the reaction [a]



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

Entry	$PhCO_2H$ (x mol %)	Yield (%)	ee (%)
1	20	48 (47)[b]	98 (97)[b]
2	100	42	98
3	150	62	98
4	**200**	**67** (53)[c]	**97** (98)[c]
5	300	40	98

[a] Reaction conditions: 2-phenylindole **1a** (0.2 mmol, 1.0 equiv), cyclohexanone **2a** (1.0 mmol, 5.0 equiv), L-proline (0.04 mmol, 0.2 equiv), TEMPO (0.02 mmol, 0.1 equiv), TBPA (0.2 mmol, 1.0 equiv) and benzoic acid in DMF/TFE = 3:1 (4.0 mL) under a constant current of 0.53 mA cm^{-2} in an undivided cell at RT in air for 24 h. Yield refers to the isolated product after chromatography on silica gel. ee and d.r. were determined by HPLC analysis using a chiral column (IA). Diastereomeric ratio (d.r.) of 3a: > 20:1. [b] j = 0.47 mA cm^{-2}, t = 32 h. [c] The proportion of L-proline was 10 mol % .

4. Mechanistic study and proposed mechanism for the reaction without TEMPO

4.1. Cyclic voltammetry

The electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Cyclic voltammetry was performed in a three-electrode cell [volume 12 mL; DMF (9 mL) and TFE (3 mL as solvent, $n$$Bu_4N^+ClO_4^-$ 0.05 M as the supporting electrolyte], 1 mM concentration of TEMPO, 2 mM concentration of **1a**, **3a** and L-

proline, glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl) as the reference electrode. The scan speed was 1 $mV \cdot s^{-1}$. The potential ranges investigated for oxidations were +0.4 to +1.6 V vs Ag/AgCl (saturated aqueous KCl) for **1a,** TEMPO**, 3a** and L-proline. As shown **Figure S1**, the oxidation potentials of **1a**, TEMPO**, 3a,** and L-proline were determined as: **1a** [E_{ox} = +1.02 V vs Ag/AgCl (saturated aqueous KCl)], TEMPO [E_{ox} = +0.78 V vs Ag/AgCl (saturated aqueous KCl)], **3a** [E_{ox} = +1.24 V vs Ag/AgCl (saturated aqueous KCl)] and L-proline had an irreversible broad peak at +1.14 V vs Ag/AgCl (saturated aqueous KCl), which could be a result of slow electrode kinetics and/or decomposition of the resultant amine radical cation.

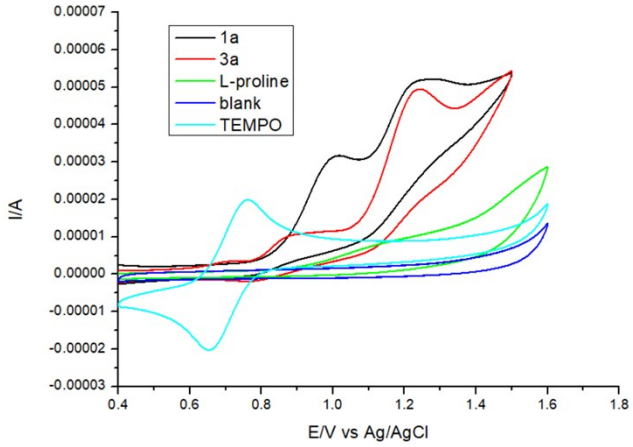


Figure S1. Cyclic voltammograms recorded in DMF/TFE (9:3) with 0.05 M $n$$Bu_4N^+ClO_4^-$ as the supporting electrolyte. **1a** (2 mM). TEMPO (1 mM). 3a (2 mM). L-proline (2 mM).

In order to determine the redox potential of **2a** and the enamine intermediate, the electrochemical measurements were carried out by a computer-controlled electrochemical analyzer. Cyclic voltammetry was performed in a three-electrode cell [volume 12 mL; DMF (9 mL) and TFE (3mL) as solvent, $n$$Bu_4N^+ClO_4^-$ 0.05 M as the supporting electrolyte], 0.02 M concentration of **2a**, **2a** (0.02 M) + L-proline (0.02 M) and **2a** (0.02 M) + L-proline (0.02 M) + benzoic acid (0.02 M) with glassy carbon (diameter 3 mm) as the working electrode, Pt wire as the auxiliary electrode, and Ag/AgCl (saturated aqueous KCl) as the reference electrode. The scan speed was 1 $mV \cdot s^{-1}$. The potential ranges investigated for oxidations were 0 to +2.0 V vs Ag/AgCl (saturated aqueous KCl) for **2a**, **2a**+L-proline, **2a**+L-proline+benzoic acid. As shown in **Figure S2**, the oxidation potentials of **2a**, **2a**+L-proline, **2a**+L-

proline+benzoic acid were determined as: neither **2a**, **2a**+L-proline, **2a**+L-proline+benzoic acid have obvious oxidation peaks. These results ruled out the possibility that radicals generated by oxidation of **2a** or enamine may be intermediates of the reaction.

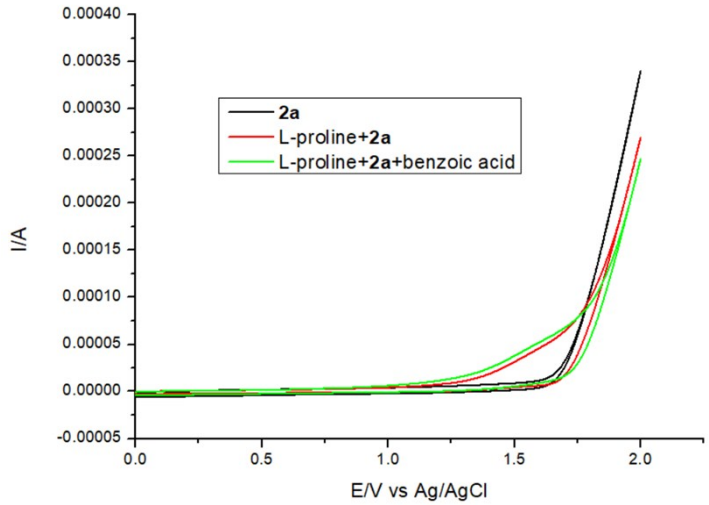
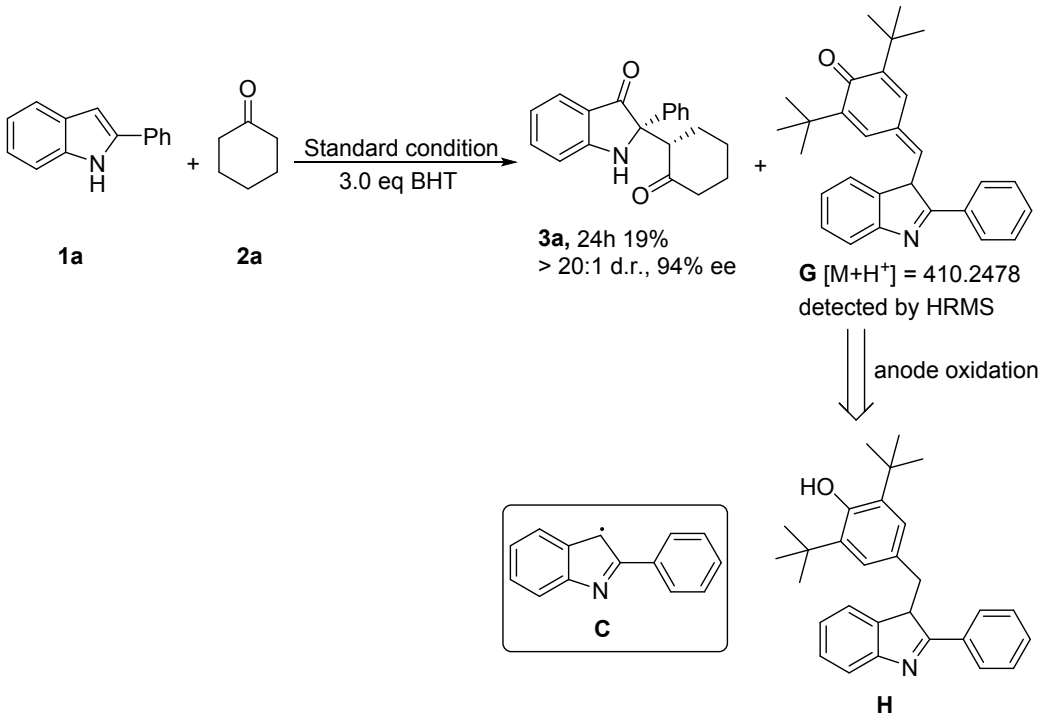
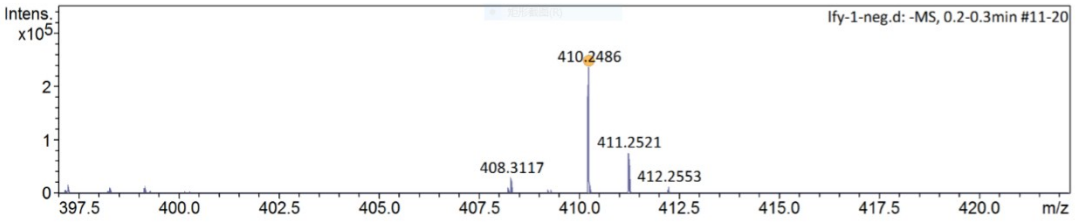


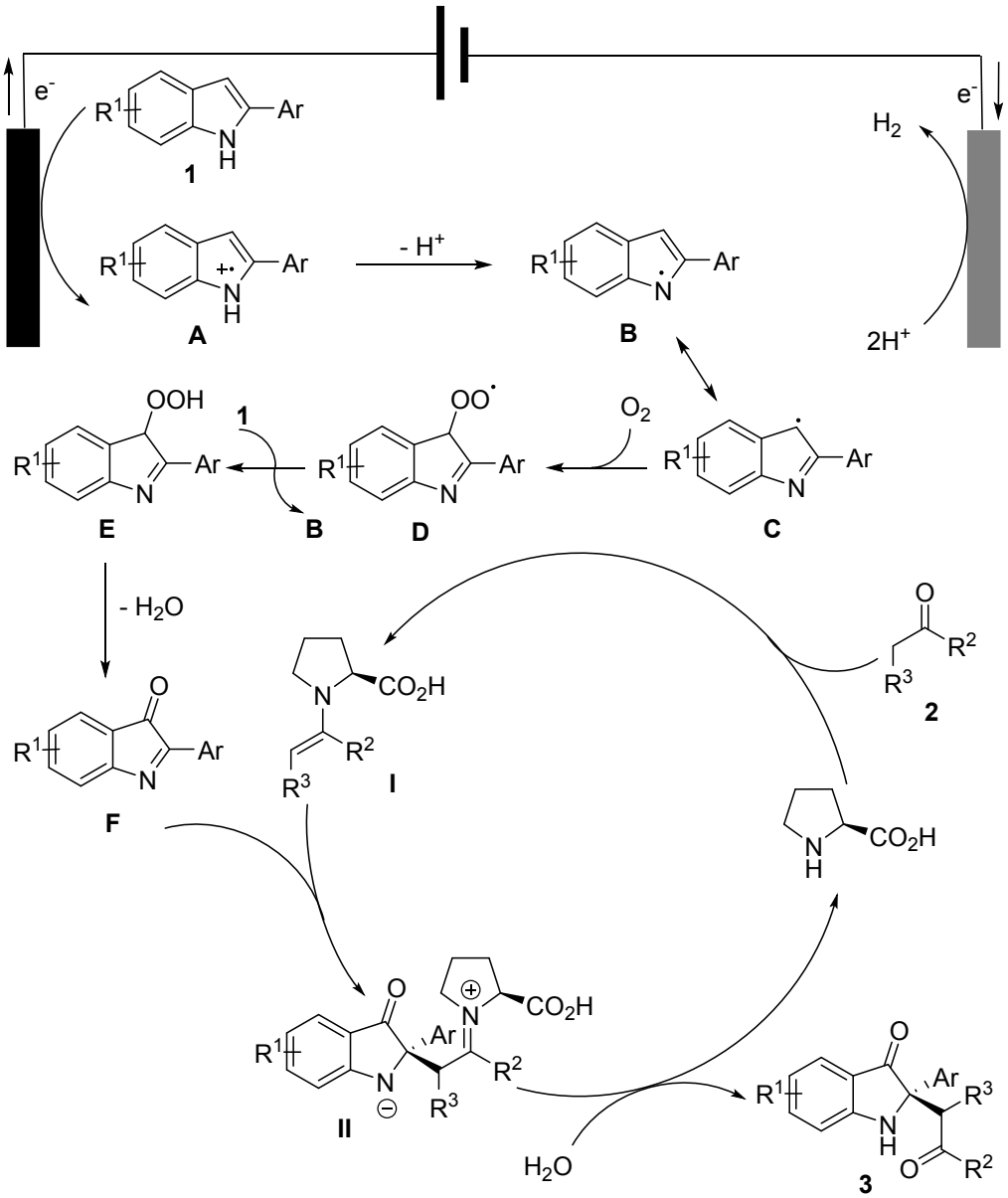
Figure S2. Cyclic voltammograms recorded in DMF/TFE (9:3) with 0.05 M nBu$_4$N$^+$ClO$_4^-$ as the supporting electrolyte. **2a** (0.02 M), **2a**+L-proline (0.02 M), **2a**+L-proline+benzoic acid (0.02 M).

4.2. The radical-trapping experiments





Meas. m/z	#	Ion Formula	m/z	err [ppm]	mSigma	# mSigma	Score	rdb	e⁻ Conf	N-Rule
410.2486	1	C29H32NO	410.2489	0.7	0.1	1	100.00	14.0	even	ok



Scheme S1. Possible mechanism for the reaction without TEMPO.

A plausible mechanism without TEMPO is shown in **Scheme S1**. The 2-arylindole **1** is

oxidized directly to the radical cation **A** at the anode (Cyclic voltammetry experiments indicate: **1a** [Eox = +1.02 V vs Ag/AgCl], **3a** [Eox = +1.24 V vs Ag/AgCl], and L-proline has an irreversible broad peak at +1.14 V vs Ag/AgCl, **Figure S1**). The radical cation **A** deprotonates to produce radical **B**, and its resonance is **C**[4]. The addition of the radical **C** to O_2 produces the radical **D**. Hydrogen transfer between radical **D** and **1** to form intermediate **E**, which loses one molecule of water to produce the key intermediate **F**[5]. In the organic catalytic cycle, the electron-rich enamine (**I**)[6], achieved by condensation of ketone **2** and L-proline, undergoes a nucleophilic addition to electrophile **F** to afford intermediate **II**. The hydrolysis of **II** regenerates L-proline and forms product **3**.

5. Crystallographic data

X-ray crystal structure analysis of 3a.

Crystallographic data (excluding structure factors) for the structures reported in this work have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC 1916014**. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

3a

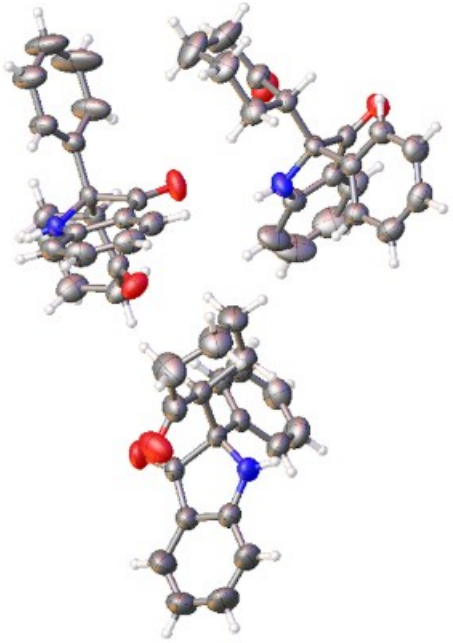


Table 1 Crystal data and structure refinement for ov_gz0325.

Identification code	ov_gz0325
Empirical formula	$C_{60}H_{57}N_3O_6$
Formula weight	916.08
Temperature/K	293(2)
Crystal system	orthorhombic
Space group	$P2_12_12_1$
a/Å	9.94998(9)
b/Å	15.87830(14)
c/Å	31.7019(3)
α/°	90
β/°	90
γ/°	90
Volume/Å^3	5008.55(7)
Z	4
ρ_{calc}g/cm^3	1.215
μ/mm^{-1}	0.621
F(000)	1944.0
Crystal size/mm^3	0.2 × 0.2 × 0.2

Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	7.882 to 143.646
Index ranges	-12 ≤ h ≤ 10, -18 ≤ k ≤ 19, -33 ≤ l ≤ 38
Reflections collected	21015
Independent reflections	9026 [R_{int} = 0.0209, R_{sigma} = 0.0219]
Data/restraints/parameters	9026/0/622
Goodness-of-fit on F^2	1.052
Final R indexes [I>=2σ (I)]	R_1 = 0.0380, wR_2 = 0.0969
Final R indexes [all data]	R_1 = 0.0410, wR_2 = 0.0996
Largest diff. peak/hole / e $Å^{-3}$	0.30/-0.23
Flack parameter	0.06(7)

Table 2 Fractional Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters ($Å^2$×10^3) for ov_gz0325. U_{eq} is defined as 1/3 of of the trace of the orthogonalised U_{IJ}tensor.

Atom	*x*	*y*	*z*	U(eq)
O1	-696(2)	-5450.8(12)	-397.3(5)	63.4(5)
O2	-3703(3)	-4573.4(19)	-302.6(7)	91.8(8)
N1	-2178(2)	-3917.6(12)	-1052.5(6)	52.9(5)
C1	-1551(3)	-3443.3(16)	-751.4(8)	56.6(6)
C2	-1570(4)	-2567.8(18)	-701.3(10)	77.7(9)
C3	-811(6)	-2228(2)	-382.2(13)	106.5(15)
C4	-31(5)	-2716(2)	-111.2(12)	107.1(15)
C5	-30(4)	-3575(2)	-152.1(10)	85.1(10)
C6	-811(3)	-3936.7(17)	-472.8(8)	59.6(7)
C7	-1083(3)	-4809.1(15)	-571.9(7)	50.5(5)
C8	-1936(3)	-4815.0(14)	-982.3(7)	45.9(5)
C9	-1006(3)	-5190.0(15)	-1313.6(7)	47.4(5)
C10	-184(3)	-4689.8(18)	-1561.4(8)	59.5(6)
C11	728(3)	-5047(2)	-1840.4(10)	74.4(8)
C12	839(3)	-5906(2)	-1875.4(10)	71.8(8)
C13	42(3)	-6409.4(19)	-1628.0(9)	65.0(7)
C14	-866(3)	-6060.9(16)	-1350.0(8)	57.1(6)
C15	-3271(3)	-5308.7(16)	-942.2(7)	51.6(6)
C16	-4156(3)	-4986(2)	-589.6(8)	65.5(7)
C17	-5609(4)	-5259(3)	-597.5(12)	96.0(12)
C18	-6229(4)	-5212(3)	-1028.8(12)	90.1(11)

C19	-5416(3)	-5720(2)	-1338.3(11)	77.3(9)
C20	-4006(3)	-5361.9(18)	-1369.7(8)	60.2(6)
O3	-3280.4(18)	-7687.8(10)	-905.1(6)	56.4(4)
O4	-5384.1(19)	-8510.2(13)	-1504.5(5)	58.9(5)
N2	-5150.6(17)	-8790.8(10)	-405.4(5)	34.5(3)
C21	-6186(2)	-8222.6(12)	-443.2(6)	37.1(4)
C22	-6940(2)	-7865.2(15)	-119.8(8)	49.5(5)
C23	-7931(3)	-7292.7(17)	-231.6(9)	60.6(7)
C24	-8175(3)	-7069.1(16)	-647.1(10)	59.6(6)
C25	-7434(2)	-7424.4(15)	-967.7(8)	51.5(5)
C26	-6451(2)	-8013.2(13)	-863.1(7)	39.7(4)
C27	-5556(2)	-8517.4(14)	-1123.5(6)	39.5(4)
C28	-4859(2)	-9146.0(12)	-821.5(6)	35.6(4)
C29	-5589(2)	-9991.2(14)	-883.2(6)	42.6(5)
C30	-6679(3)	-10204.2(16)	-633.5(8)	56.0(6)
C31	-7366(4)	-10955(2)	-686.3(11)	79.4(9)
C32	-6972(5)	-11497(2)	-995.6(15)	104.0(14)
C33	-5907(5)	-11297(3)	-1246.4(16)	120.5(19)
C34	-5230(4)	-10543(2)	-1199.8(11)	81.3(10)
C35	-3336(2)	-9202.9(13)	-902.8(6)	39.2(4)
C36	-2609(2)	-9781.1(15)	-587.8(8)	50.6(5)
C37	-1095(3)	-9814.7(16)	-666.6(10)	58.9(6)
C38	-475(3)	-8953.3(18)	-651.5(11)	67.9(7)
C39	-1152(3)	-8364.0(18)	-966.6(10)	65.4(7)
C40	-2664(2)	-8343.9(14)	-918.7(7)	43.8(5)
O5	-5578.7(17)	-8289.0(11)	-3414.7(5)	49.0(4)
O6	-5304.8(18)	-9558.0(12)	-2640.1(6)	61.8(5)
N3	-5258.6(18)	-7734.6(13)	-2340.4(6)	46.3(4)
C41	-3959(2)	-7756.2(15)	-2477.5(7)	47.0(5)
C42	-2797(3)	-7595(2)	-2245.3(11)	71.8(8)
C43	-1592(3)	-7613(3)	-2459.0(15)	96.0(13)
C44	-1504(3)	-7798(2)	-2885.5(15)	89.3(12)
C45	-2639(3)	-7963.7(18)	-3113.4(11)	62.5(7)
C46	-3869(2)	-7934.8(14)	-2908.1(7)	44.9(5)
C47	-5217(2)	-8097.1(13)	-3060.4(6)	38.0(4)
C48	-6181.6(19)	-7896.9(13)	-2688.6(6)	37.0(4)
C50	-7934(2)	-7107.2(16)	-3123.3(8)	48.1(5)
C51	-8542(3)	-6371.5(17)	-3259.1(9)	57.8(6)
C52	-8137(3)	-5607.8(17)	-3106.6(9)	56.3(6)
C53	-7101(3)	-5569.1(16)	-2820.8(9)	56.8(6)

C54	-6494(2)	-6297.9(15)	-2678.1(7)	47.6(5)
C55	-6906(2)	-7080.7(14)	-2824.8(6)	38.3(4)
C56	-7162(2)	-8617.6(14)	-2590.0(7)	41.9(5)
C57	-8066(2)	-8418.0(18)	-2210.1(8)	55.4(6)
C58	-8987(3)	-9153(2)	-2102.0(11)	72.4(8)
C59	-8174(4)	-9933(2)	-2007.0(13)	90.7(11)
C60	-7322(4)	-10176.4(19)	-2390.9(14)	84.8(10)
C61	-6455(2)	-9459.8(16)	-2542.4(8)	50.2(5)

Table 3 Anisotropic Displacement Parameters ($Å^2 \times 10^3$) for ov_gz0325. The Anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U_{11}+2hka^*b^*U_{12}+\cdots]$.

Atom	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
O1	90.2(14)	55.3(10)	44.8(8)	14.4(8)	-15.6(9)	3.8(10)
O2	86.8(16)	125(2)	64.1(12)	-24.5(13)	9.0(12)	-19.0(15)
N1	68.0(13)	41.1(10)	49.7(10)	8.7(8)	-17.8(10)	0.1(10)
C1	71.6(16)	46.6(12)	51.6(12)	6.9(10)	-7.7(12)	-6.9(12)
C2	117(3)	45.6(14)	70.6(17)	6.6(12)	-13.9(18)	-6.2(16)
C3	175(5)	48.7(17)	96(2)	-1.2(17)	-27(3)	-27(2)
C4	161(4)	75(2)	85(2)	0.7(18)	-47(3)	-43(3)
C5	112(3)	74(2)	69.6(18)	9.3(15)	-39.7(19)	-26(2)
C6	74.9(18)	53.2(14)	50.5(13)	7.7(11)	-17.2(13)	-12.7(13)
C7	61.8(14)	49.8(12)	39.9(10)	10.5(9)	-8.7(10)	-4.1(12)
C8	56.5(13)	41.2(11)	40(1)	8.4(9)	-8.7(10)	-3.8(10)
C9	54.1(13)	49.6(12)	38.4(10)	7.9(9)	-10.2(10)	-4.8(11)
C10	66.3(16)	53.8(14)	58.5(14)	13.0(11)	-1.9(13)	-8.8(13)
C11	70.2(19)	85(2)	68.3(17)	14.5(16)	14.9(15)	-10.8(16)
C12	68.5(18)	84(2)	62.6(16)	-1.8(15)	6.1(14)	8.5(16)
C13	74.1(18)	61.0(16)	59.9(14)	-1.2(12)	-2.0(14)	6.7(15)
C14	68.2(16)	50.0(13)	53.1(13)	8.6(11)	-1.8(12)	-2.2(12)
C15	59.5(14)	47.0(12)	48.4(12)	9.1(10)	-4.8(11)	-8.3(11)
C16	69.5(17)	77.8(18)	49.2(13)	6.1(13)	0.7(13)	-10.4(15)
C17	72(2)	137(3)	80(2)	-1(2)	13.7(17)	-22(2)
C18	61.4(18)	113(3)	96(2)	7(2)	-2.4(18)	-14(2)
C19	69.0(19)	86(2)	77.0(19)	4.2(17)	-15.2(16)	-25.2(17)
C20	65.8(16)	62.1(15)	52.7(13)	4.0(11)	-11.2(12)	-14.1(14)
O3	51.5(9)	41.7(8)	76.1(11)	10.9(8)	4.3(9)	0.9(8)
O4	62.2(10)	83.5(12)	31.0(7)	7.9(8)	0.7(7)	6.8(10)
N2	39.9(9)	37.1(8)	26.4(7)	-1.7(6)	-0.4(6)	-0.5(7)
C21	36.4(10)	35.3(9)	39.7(9)	-4.2(8)	2.0(8)	-5.4(8)
C22	53.3(13)	48.9(12)	46.4(11)	-12.4(10)	6.4(10)	-0.4(11)

C23	51.2(14)	56.2(14)	74.6(17)	-21.1(13)	8.2(13)	5.9(12)
C24	41.9(12)	46.8(12)	90.2(19)	-6.2(13)	-4.7(13)	6.3(11)
C25	42.5(12)	48.2(12)	63.6(14)	5.5(11)	-7.5(11)	-0.9(10)
C26	35.1(10)	41.5(11)	42.5(10)	0.8(8)	-2.0(8)	-2.3(8)
C27	37.5(10)	49.0(11)	31.9(9)	1.9(8)	-1.0(8)	-4.1(9)
C28	39.9(10)	38(1)	28.9(8)	-1.4(7)	1.8(8)	-0.1(8)
C29	45.8(11)	42.3(11)	39.8(10)	-6.7(9)	0.0(9)	-3.7(9)
C30	59.3(14)	52.7(13)	56.0(13)	-12.2(11)	10.3(11)	-15.3(12)
C31	82(2)	70.8(18)	85(2)	-18.1(16)	17.6(18)	-32.8(17)
C32	108(3)	68(2)	136(3)	-44(2)	28(3)	-42(2)
C33	110(3)	92(3)	160(4)	-87(3)	45(3)	-34(3)
C34	75(2)	79(2)	90(2)	-47.7(18)	29.6(17)	-24.3(17)
C35	39.5(10)	41.5(10)	36.5(9)	-2.1(8)	4.4(8)	0.3(9)
C36	46.5(12)	43.1(11)	62.3(13)	8.8(10)	0.1(11)	2.7(10)
C37	45.7(13)	53.0(14)	78.0(17)	3.8(13)	-0.2(12)	11.1(11)
C38	40.8(13)	64.7(16)	98(2)	7.1(16)	-7.7(14)	1.2(12)
C39	43.4(13)	57.9(15)	95(2)	17.1(14)	7.8(14)	-3.9(12)
C40	43.6(11)	45.7(12)	42.1(10)	8.7(9)	3.5(9)	-1.6(9)
O5	52.1(9)	55.4(9)	39.4(7)	-0.5(7)	-2.5(7)	0.0(7)
O6	50.1(10)	58.9(11)	76.4(12)	15.6(9)	7.4(9)	8.0(8)
N3	39.5(9)	64.0(12)	35.3(8)	2.8(8)	-6.6(7)	-4.2(9)
C41	38.4(11)	48.4(12)	54.3(12)	6.4(10)	-12.1(10)	0.3(10)
C42	50.8(15)	77.5(19)	87(2)	-9.9(16)	-31.2(15)	4.4(14)
C43	36.4(14)	98(3)	154(4)	-30(3)	-31.7(19)	6.9(15)
C44	31.5(13)	88(2)	149(4)	-9(2)	9.1(17)	1.7(14)
C45	39.0(12)	61.6(15)	87.1(19)	7.3(14)	12.5(12)	3.6(11)
C46	34.7(10)	45.9(11)	54.0(12)	9.1(10)	-1.7(9)	0.5(9)
C47	37.2(10)	37.5(10)	39.4(10)	7.7(8)	-1.3(8)	1.1(8)
C48	31.2(9)	44.7(10)	35.1(9)	3.2(8)	-4.1(8)	-3.3(8)
C50	39.8(11)	49.7(12)	54.9(12)	0.1(10)	-6.9(10)	1.7(10)
C51	46.4(13)	60.4(15)	66.5(15)	8.8(12)	-9.8(11)	9.2(12)
C52	49.7(13)	51.5(13)	67.7(15)	12.1(12)	11.4(12)	13.4(11)
C53	58.3(15)	45.5(12)	66.5(15)	-1.3(11)	11.0(12)	-3.6(11)
C54	41.8(11)	50.1(12)	50.9(12)	-3(1)	-0.6(10)	-3.7(10)
C55	30.7(9)	45.3(10)	38.8(9)	1.4(8)	2.7(8)	-1.5(9)
C56	33.3(10)	47.7(11)	44.6(10)	5.8(9)	-2.0(8)	-3.2(9)
C57	40.4(12)	67.3(15)	58.6(13)	5.7(12)	8.9(10)	-6.7(12)
C58	50.4(15)	82(2)	84(2)	14.0(16)	21.1(14)	-12.7(15)
C59	70(2)	86(2)	116(3)	45(2)	23(2)	-8.6(18)
C60	71.0(19)	52.6(16)	131(3)	26.1(18)	19(2)	-3.9(15)

C61	46.8(13)	49.1(12)	54.7(13)	8.6(10)	2.1(10)	-2.9(10)

Table 4 Bond Lengths for ov_gz0325.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
O1	C7	1.222(3)	C28	C35	1.539(3)
O2	C16	1.208(4)	C29	C30	1.385(3)
N1	C1	1.367(3)	C29	C34	1.379(3)
N1	C8	1.462(3)	C30	C31	1.385(4)
C1	C2	1.399(4)	C31	C32	1.361(5)
C1	C6	1.391(4)	C32	C33	1.362(6)
C2	C3	1.373(5)	C33	C34	1.381(5)
C3	C4	1.392(6)	C35	C36	1.538(3)
C4	C5	1.371(5)	C35	C40	1.520(3)
C5	C6	1.402(4)	C36	C37	1.528(3)
C6	C7	1.446(3)	C37	C38	1.501(4)
C7	C8	1.554(3)	C38	C39	1.525(4)
C8	C9	1.521(4)	C39	C40	1.513(3)
C8	C15	1.547(3)	O5	C47	1.218(3)
C9	C10	1.385(4)	O6	C61	1.196(3)
C9	C14	1.395(3)	N3	C41	1.365(3)
C10	C11	1.388(4)	N3	C48	1.459(3)
C11	C12	1.373(5)	C41	C42	1.394(3)
C12	C13	1.373(5)	C41	C46	1.397(3)
C13	C14	1.378(4)	C42	C43	1.377(5)
C15	C16	1.512(4)	C43	C44	1.386(6)
C15	C20	1.543(3)	C44	C45	1.367(5)
C16	C17	1.510(5)	C45	C46	1.387(3)
C17	C18	1.502(5)	C46	C47	1.449(3)
C18	C19	1.506(5)	C47	C48	1.553(3)
C19	C20	1.517(4)	C48	C55	1.544(3)
O3	C40	1.210(3)	C48	C56	1.536(3)
O4	C27	1.220(2)	C50	C51	1.384(3)
N2	C21	1.375(3)	C50	C55	1.394(3)
N2	C28	1.464(2)	C51	C52	1.366(4)
C21	C22	1.391(3)	C52	C53	1.373(4)
C21	C26	1.397(3)	C53	C54	1.382(4)
C22	C23	1.387(4)	C54	C55	1.389(3)
C23	C24	1.386(4)	C56	C57	1.536(3)
C24	C25	1.377(4)	C56	C61	1.519(3)

C25	C26	1.393(3)	C57	C58	1.523(4)
C26	C27	1.454(3)	C58	C59	1.510(5)
C27	C28	1.547(3)	C59	C60	1.533(5)
C28	C29	1.539(3)	C60	C61	1.507(4)

Table 5 Bond Angles for ov_gz0325.

Atom	Atom	Atom	Angle/°	Atom	Atom	Atom	Angle/°
C1	N1	C8	110.84(19)	C35	C28	C27	112.05(16)
N1	C1	C2	128.4(3)	C30	C29	C28	120.67(19)
N1	C1	C6	112.0(2)	C34	C29	C28	121.6(2)
C6	C1	C2	119.6(3)	C34	C29	C30	117.6(2)
C3	C2	C1	117.8(3)	C31	C30	C29	121.8(2)
C2	C3	C4	122.9(3)	C32	C31	C30	119.3(3)
C5	C4	C3	119.7(3)	C31	C32	C33	119.8(3)
C4	C5	C6	118.4(3)	C32	C33	C34	121.2(3)
C1	C6	C5	121.5(3)	C29	C34	C33	120.1(3)
C1	C6	C7	107.6(2)	C36	C35	C28	112.93(17)
C5	C6	C7	130.8(3)	C40	C35	C28	112.71(18)
O1	C7	C6	129.9(2)	C40	C35	C36	110.49(18)
O1	C7	C8	123.1(2)	C37	C36	C35	112.3(2)
C6	C7	C8	106.87(19)	C38	C37	C36	111.6(2)
N1	C8	C7	102.20(17)	C37	C38	C39	110.9(2)
N1	C8	C9	112.10(19)	C40	C39	C38	112.7(2)
N1	C8	C15	111.4(2)	O3	C40	C35	123.3(2)
C9	C8	C7	104.4(2)	O3	C40	C39	121.7(2)
C9	C8	C15	112.37(19)	C39	C40	C35	115.0(2)
C15	C8	C7	113.79(18)	C41	N3	C48	110.57(17)
C10	C9	C8	121.8(2)	N3	C41	C42	127.8(2)
C10	C9	C14	117.5(3)	N3	C41	C46	112.13(19)
C14	C9	C8	120.4(2)	C42	C41	C46	120.0(2)
C9	C10	C11	120.9(3)	C43	C42	C41	117.3(3)
C12	C11	C10	120.7(3)	C42	C43	C44	122.7(3)
C13	C12	C11	119.1(3)	C45	C44	C43	120.2(3)
C12	C13	C14	120.7(3)	C44	C45	C46	118.4(3)
C13	C14	C9	121.1(3)	C41	C46	C47	107.61(19)
C16	C15	C8	112.9(2)	C45	C46	C41	121.5(2)
C16	C15	C20	113.1(2)	C45	C46	C47	130.9(2)
C20	C15	C8	111.25(19)	O5	C47	C46	128.7(2)
O2	C16	C15	121.6(3)	O5	C47	C48	124.65(19)

O2	C16	C17	121.7(3)	C46	C47	C48	106.42(17)
C17	C16	C15	116.6(3)	N3	C48	C47	102.79(16)
C18	C17	C16	113.2(3)	N3	C48	C55	110.91(18)
C17	C18	C19	110.2(3)	N3	C48	C56	112.19(17)
C18	C19	C20	109.8(3)	C55	C48	C47	104.34(15)
C19	C20	C15	113.7(2)	C56	C48	C47	113.24(17)
C21	N2	C28	108.85(15)	C56	C48	C55	112.69(16)
N2	C21	C22	127.4(2)	C51	C50	C55	120.4(2)
N2	C21	C26	112.35(17)	C52	C51	C50	120.6(2)
C22	C21	C26	120.2(2)	C51	C52	C53	119.6(2)
C23	C22	C21	117.5(2)	C52	C53	C54	120.4(2)
C24	C23	C22	122.3(2)	C53	C54	C55	120.7(2)
C25	C24	C23	120.2(2)	C50	C55	C48	120.45(19)
C24	C25	C26	118.4(2)	C54	C55	C48	121.32(18)
C21	C26	C27	107.13(18)	C54	C55	C50	118.1(2)
C25	C26	C21	121.2(2)	C57	C56	C48	112.17(19)
C25	C26	C27	131.6(2)	C61	C56	C48	112.44(17)
O4	C27	C26	130.0(2)	C61	C56	C57	112.02(19)
O4	C27	C28	123.8(2)	C58	C57	C56	111.7(2)
C26	C27	C28	106.16(16)	C59	C58	C57	110.6(2)
N2	C28	C27	102.72(16)	C58	C59	C60	110.2(3)
N2	C28	C29	110.92(16)	C61	C60	C59	112.3(3)
N2	C28	C35	111.64(17)	O6	C61	C56	122.2(2)
C29	C28	C27	105.79(17)	O6	C61	C60	122.1(2)
C29	C28	C35	113.09(17)	C60	C61	C56	115.6(2)

Table 6 Hydrogen Atom Coordinates (Å×10⁴) and Isotropic Displacement Parameters (Å²×10³) for ov_gz0325.

Atom	*x*	*y*	*z*	U(eq)
H1	-2650.6	-3715.53	-1255.79	63
H2	-2079.68	-2227.21	-878.38	93
H3	-818.2	-1647.1	-345.34	128
H4	486.15	-2459.19	96.57	128
H5	476.21	-3910.52	28.54	102
H10	-243.59	-4106.71	-1540.65	71
H11	1269.08	-4700.69	-2005.22	89
H12	1446.43	-6143.13	-2064.09	86
H13	114.7	-6991.86	-1648.32	78
H14	-1393.01	-6412.39	-1183.66	69
H15	-3025.85	-5887.1	-866.51	62

H17A	-5669.57	-5833.49	-495.5	115
H17B	-6119.16	-4904.51	-406.6	115
H18A	-6265.71	-4629.79	-1120.48	108
H18B	-7140.21	-5427.77	-1018.29	108
H19A	-5842.91	-5705.28	-1613.2	93
H19B	-5373.77	-6301.98	-1246.19	93
H20A	-4055.23	-4802.07	-1491.24	72
H20B	-3482.9	-5710.83	-1559.81	72
H2A	-4741.24	-8916.92	-175.02	41
H22	-6785.62	-8004.92	160.88	59
H23	-8451.02	-7050.42	-20.13	73
H24	-8840.95	-6677.67	-709.61	72
H25	-7585.69	-7275.01	-1247.33	62
H30	-6957.66	-9832.34	-424.35	67
H31	-8087.67	-11088.47	-512.47	95
H32	-7429.13	-12001.24	-1035.47	125
H33	-5630.8	-11674.84	-1452.98	145
H34	-4531.18	-10407.17	-1382.25	98
H35	-3223.57	-9456.39	-1182.43	47
H36A	-2771.33	-9579.75	-303.47	61
H36B	-2976.36	-10345.28	-609.32	61
H37A	-676.26	-10169.61	-455.08	71
H37B	-927.23	-10064.53	-940.87	71
H38A	476	-8994.09	-716.09	82
H38B	-564.67	-8724.22	-369.23	82
H39A	-800.45	-7799.26	-928.41	78
H39B	-929.27	-8543.97	-1250.52	78
H3A	-5500.02	-7638.67	-2084.43	56
H42	-2833.98	-7479.68	-1957.93	86
H43	-806.34	-7497.63	-2311.17	115
H44	-668.46	-7808.42	-3017.08	107
H45	-2588.43	-8092.92	-3399.09	75
H50	-8212.31	-7622.49	-3231.87	58
H51	-9233.57	-6397.38	-3456.07	69
H52	-8559.8	-5116.86	-3195.84	68
H53	-6806.89	-5048.89	-2722.72	68
H54	-5801.84	-6263.94	-2481.71	57
H56	-7757.68	-8669.3	-2834.94	50
H57A	-7507.4	-8287.73	-1967.81	67
H57B	-8606.14	-7925.3	-2272.83	67

H58A -9532	-9008.56	-1858.81	87
H58B -9585.45	-9262.6	-2337.26	87
H59A -8773.54	-10393.53	-1935.49	109
H59B -7593.18	-9829.12	-1766.98	109
H60A -6752.83	-10650.13	-2317.44	102
H60B -7911.26	-10353.08	-2618.02	102

Experimental

Single crystals of $C_{60}H_{57}N_3O_6$ **[ov_gz0325]** were **[]**. A suitable crystal was selected and **[]** on a diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2 [1], the structure was solved with the SIR2004 [2] structure solution program using Direct Methods and refined with the ShelXL [3] refinement package using Least Squares minimisation.

1. Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
2. Burla, M.C., Caliandro, R., Camalli, M., Carrozzini, B., Cascarano, G.L., De Caro, L., Giacovazzo, C., Polidori, G., Siliqi, D., Spagna, R. (2007). J. Appl. Cryst. 40, 609-613.
3. Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.

Crystal structure determination of [ov_gz0325]

Crystal Data for $C_{60}H_{57}N_3O_6$ (M =916.08 g/mol): orthorhombic, space group $P2_12_12_1$ (no. 19), a = 9.94998(9) Å, b = 15.87830(14) Å, c = 31.7019(3) Å, V = 5008.55(7) Å^3, Z = 4, T = 293(2) K, μ (CuK α) = 0.621 mm^{-1}, *Dcalc* = 1.215 g/cm^3, 21015 reflections measured (7.882° ≤ 2Θ ≤ 143.646°), 9026 unique (R_{int} = 0.0209, R_{sigma} = 0.0219) which were used in all calculations. The final R_1 was 0.0380 (I > 2 σ (I)) and wR_2 was 0.0996 (all data).

Refinement model description

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

Details:

1. Fixed Uiso

 At 1.2 times of:

 All C(H) groups, All C(H,H) groups, All N(H) groups

2.a Ternary CH refined with riding coordinates:

 C15(H15), C35(H35), C56(H56)

2.b Secondary CH2 refined with riding coordinates:

 C17(H17A,H17B), C18(H18A,H18B), C19(H19A,H19B), C20(H20A,H20B), C36(H36A, H36B), C37(H37A,H37B), C38(H38A,H38B), C39(H39A,H39B), C57(H57A,H57B), C58(H58A,H58B), C59(H59A,H59B), C60(H60A,H60B)

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

 N1(H1), C2(H2), C3(H3), C4(H4), C5(H5), C10(H10), C11(H11), C12(H12), C13(H13), C14(H14), N2(H2A), C22(H22), C23(H23), C24(H24), C25(H25), C30(H30), C31(H31), C32(H32), C33(H33), C34(H34), N3(H3A), C42(H42), C43(H43), C44(H44), C45(H45), C50(H50), C51(H51), C52(H52), C53(H53), C54(H54)

X-ray crystal structure analysis of 4e

Crystallographic data (excluding structure factors) for the structures reported in this work

have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. **CCDC 1921830**. Copy of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge DB21EZ, UK (fax:+ 44 (1223) 336033; e-mail: deposit@ccdc.cam.ac.uk).

4e

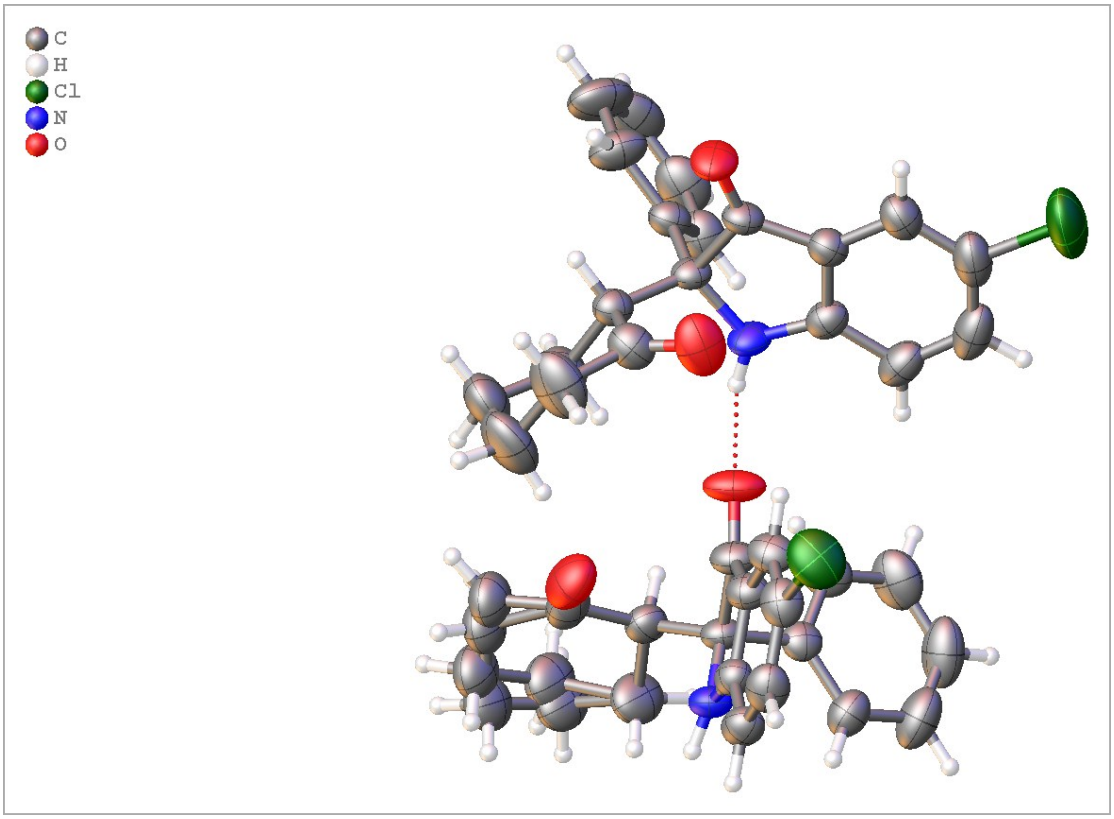


Table 1 Crystal data and structure refinement for gz190604_lfy.

Identification code	gz190604_lfy
Empirical formula	C20H17.27ClNO2
Formula weight	339.07
Temperature/K	278(30)
Crystal system	orthorhombic
Space group	P212121
a/Å	10.00050(10)
b/Å	15.08900(10)
c/Å	23.6172(2)
α /°	90
β /°	90
γ /°	90
Volume/Å3	3563.78(5)
Z	8
ρ calcg/cm3	1.264
μ /mm-1	1.982

F(000) 1418.0
Crystal size/mm3 0.2 × 0.05 × 0.05
Radiation CuKα (λ = 1.54184)
2Θ range for data collection/° 6.952 to 143.762
Index ranges -12 ⩽ h ⩽ 11, -18 ⩽ k ⩽ 18, -18 ⩽ l ⩽ 28
Reflections collected 40048
Independent reflections 6958 [Rint = 0.0395, Rsigma = 0.0218]
Data/restraints/parameters 6958/66/467
Goodness-of-fit on F2 1.050
Final R indexes [I>=2σ (I)] R1 = 0.0376, wR2 = 0.1011
Final R indexes [all data] R1 = 0.0395, wR2 = 0.1034
Largest diff. peak/hole / e Å-3 0.21/-0.25
Flack parameter 0.005(5)

Table 2 Fractional Atomic Coordinates (×104) and Equivalent Isotropic Displacement Parameters (Å2×103) for gz190604_lfy. Ueq is defined as 1/3 of of the trace of the orthogonalised UIJ tensor.

Atom	x	y	z	U(eq)
Cl2	11276.4(8)	5647.3(7)	6639.3(4)	81.7(3)
Cl1	8207.9(13)	8351.4(6)	8659.6(6)	107.9(4)
O1	7221(2)	4607.9(13)	8922.7(7)	59.5(5)
O4	5576.1(19)	5103.7(17)	6382.7(7)	63.3(6)
N2	6982(2)	4872.5(14)	5028.7(7)	43.4(4)
N1	6304(2)	5141.4(14)	7533.0(7)	47.5(5)
O3	6274(3)	3360.4(16)	5771.8(11)	79.3(7)
O2	8983(2)	4437.7(17)	7843.6(12)	78.6(7)
C21	8084(2)	5032.4(15)	5356.7(9)	41.2(5)
C29	5122(2)	5939.5(16)	5224.3(10)	42.2(5)
C8	6227(2)	4486.1(15)	7981.2(8)	38.9(5)
C26	7750(3)	5159.3(17)	5926.0(9)	45.0(5)
C1	6709(2)	5934.4(17)	7736.1(10)	45.8(5)
C7	6931(2)	4966.3(16)	8477.8(9)	42.7(5)
C27	6297(3)	5089.3(19)	5967.1(9)	46.3(5)
C28	5765(2)	5036.3(17)	5352.5(8)	40.2(5)
C9	4777(2)	4321.0(18)	8172.5(9)	45.5(5)
C22	9425(3)	5073.4(18)	5187.4(11)	50.7(6)
C6	7097(3)	5880.4(16)	8303.6(10)	45.9(5)
C25	8721(3)	5330.4(19)	6332.8(11)	52.1(6)
C15	6941(3)	3617.9(16)	7823.2(10)	44.2(5)
C2	6806(3)	6747.4(19)	7446.1(13)	59.1(7)
C10	3707(3)	4745(2)	7916.7(14)	59.8(7)
C35	4737(3)	4286.1(17)	5275.1(11)	48.8(6)
C16	8434(3)	3742(2)	7748.1(12)	57.5(6)

C30	5497(3)	6455.5(19)	4768.4(13)	55.6(6)
C24	10023(3)	5385.5(18)	6154.7(13)	55.0(6)
C20	6357(3)	3167(2)	7296.0(12)	60.1(7)
C40	5298(3)	3402(2)	5469.9(15)	63.9(7)
C23	10374(3)	5254.9(19)	5592.4(13)	55.9(6)
C4	7645(3)	7399(2)	8311.8(16)	67.6(8)
C5	7578(3)	6614.5(19)	8596.5(13)	57.8(6)
C3	7263(3)	7467(2)	7745.0(17)	69.8(9)
C34	4082(3)	6243(2)	5568.0(13)	59.9(7)
C33	3454(3)	7039(2)	5454.3(18)	76.7(9)
C14	4515(3)	3748(3)	8621.7(13)	70.2(8)
C32	3840(4)	7541(2)	4996(2)	84.5(11)
C36	4177(4)	4267(3)	4667.4(16)	77.7(9)
C11	2404(3)	4601(3)	8102.0(18)	79(1)
C31	4858(4)	7250(2)	4659.4(18)	78.3(10)
C12	2165(4)	4046(3)	8545.0(18)	87.3(12)
C13	3207(4)	3617(3)	8803.1(16)	92.3(13)
C17	9179(4)	2932(3)	7563(2)	98.1(14)
C39	4474(13)	2575(8)	5200(6)	76(2)
C19	7074(4)	2309(2)	7158.0(17)	81.5(10)
C38	4014(11)	2682(7)	4588(5)	81.2(18)
C37	3287(15)	3522(8)	4502(5)	83.1(18)
C18	8543(5)	2480(3)	7056(2)	105.1(15)
C0AA	3276(18)	3379(10)	4661(6)	81.2(17)
C1AA	4114(13)	2530(7)	4827(7)	78.2(19)
C0	4631(15)	2611(10)	5412(6)	74(2)

Table 3 Anisotropic Displacement Parameters (Å2×103) for gz190604_lfy. The Anisotropic displacement factor exponent takes the form: -2π2[h2a*2U11+2hka*b*U12+…].

Atom	U11	U22	U33	U23	U13	U12
Cl2	56.5(4)	98.8(6)	89.9(6)	-13.5(5)	-24.6(4)	-0.5(4)
Cl1	115.2(8)	54.8(4)	153.7(10)	-32.6(5)	20.2(7)	-20.3(5)
O1	80.7(13)	65.2(11)	32.6(8)	2.3(7)	-18.0(8)	-5.5(10)
O4	49.7(10)	111.0(17)	29.2(7)	4.6(9)	3.0(7)	8.6(11)
N2	45.5(11)	55.1(11)	29.6(8)	1.3(7)	4.5(8)	1.4(9)
N1	58.3(12)	56.3(12)	27.9(8)	6.5(8)	-7.6(8)	-7(1)
O3	81.0(16)	67.5(14)	89.4(16)	25.0(12)	3.3(14)	11.7(13)
O2	44.9(11)	77.4(15)	113.6(19)	-17.3(14)	-1.6(11)	-5.5(11)
C21	42.6(12)	39.6(11)	41.5(11)	4.2(9)	2.4(9)	3.4(9)
C29	37.9(11)	48.5(12)	40.2(11)	-2.1(9)	-8.0(9)	-2.8(9)
C8	42.3(11)	47.7(12)	26.7(9)	1.4(8)	-3.3(8)	-3(1)
C26	45.3(12)	52.0(13)	37.8(11)	4.1(9)	-1.1(9)	5.4(10)
C1	40.6(12)	50.6(13)	46.1(12)	6.7(10)	3.6(10)	3(1)

C7	46.3(12)	52.2(12)	29.5(10)	-3.3(9)	-2.0(9)	-1.9(10)
C27	45.6(12)	62.9(15)	30.3(10)	5.1(9)	-0.3(9)	5.8(12)
C28	39.8(11)	51.6(13)	29(1)	3.3(9)	1.3(8)	-0.1(10)
C9	45.0(13)	53.9(13)	37.6(11)	-6(1)	2.2(9)	-2.8(11)
C22	47.9(14)	53.2(14)	51.2(13)	3.1(11)	9.7(11)	4.1(11)
C6	46.8(13)	48.5(13)	42.5(12)	-3.7(10)	1.6(10)	-0.3(10)
C25	50.8(13)	63.2(15)	42.3(12)	0.9(11)	-6.9(10)	9.7(12)
C15	45.2(12)	48.1(12)	39.2(11)	-0.8(9)	0.0(9)	-2.8(11)
C2	54.9(16)	57.7(15)	64.6(16)	18.7(13)	7.7(13)	5.5(13)
C10	47.2(14)	59.4(16)	72.8(17)	-4.4(13)	-2.8(13)	3.8(13)
C35	48.0(13)	51.6(14)	46.9(12)	3.1(10)	7.3(11)	-5.4(11)
C16	48.1(15)	64.4(16)	60.0(15)	-7.6(13)	-2.2(12)	2.4(13)
C30	50.9(14)	52.7(15)	63.1(15)	11.3(12)	-2.8(12)	-4.3(12)
C24	47.0(14)	52.4(14)	65.4(16)	0.3(12)	-11.0(12)	5.5(11)
C20	62.0(17)	62.2(16)	56.3(15)	-16.7(13)	-3.2(13)	-7.0(14)
C40	60.7(18)	55.1(16)	76.0(19)	7.8(14)	19.0(16)	-5.3(14)
C23	39.2(12)	54.9(15)	73.7(17)	0.9(13)	5.5(12)	2.6(11)
C4	60.7(17)	45.0(14)	97(2)	-11.8(15)	12.0(17)	-3.0(12)
C5	56.5(16)	53.1(14)	63.6(16)	-12.3(12)	2.8(13)	-1.8(12)
C3	59.3(18)	46.2(14)	104(2)	16.3(15)	15.1(18)	3.1(13)
C34	48.6(14)	71.3(18)	59.7(15)	-2.4(14)	0.1(12)	9.7(13)
C33	54.6(18)	72(2)	103(3)	-12.6(19)	-3.8(17)	17.7(16)
C14	60.9(18)	96(2)	53.3(15)	13.5(16)	7.8(13)	-10.7(17)
C32	62(2)	50.2(16)	141(3)	4.2(19)	-17(2)	6.7(15)
C36	83(2)	85(2)	65.7(18)	-8.4(17)	-17.2(16)	-30.6(19)
C11	46.9(16)	88(2)	102(3)	-20(2)	6.0(17)	5.8(16)
C31	70(2)	57.9(18)	106(3)	28.0(18)	-8(2)	-4.6(15)
C12	54.0(19)	115(3)	93(3)	-27(2)	22.6(19)	-14(2)
C13	84(3)	126(3)	66(2)	7(2)	25.1(19)	-34(3)
C17	64(2)	93(3)	137(4)	-34(3)	7(2)	20(2)
C39	84(3)	59(2)	85(5)	-9(4)	-7(4)	-20(3)
C19	95(3)	65.4(19)	84(2)	-27.4(17)	5(2)	-3.0(19)
C38	87(3)	73(3)	83(4)	-13(3)	-9(4)	-27(2)
C37	87(3)	85(3)	77(4)	-6(3)	-17(3)	-32(3)
C18	95(3)	95(3)	125(3)	-50(3)	23(3)	13(2)
C0AA	86(3)	78(3)	79(4)	-6(3)	-14(3)	-30(3)
C1AA	87(3)	64(3)	83(5)	-6(4)	-11(4)	-21(3)
C0	83(4)	56(3)	83(6)	-5(4)	-7(5)	-19(3)

Table 4 Bond Lengths for gz190604_lfy.

Atom	Atom	Length/Å	Atom	Atom	Length/Å
Cl2	C24	1.743(3)	C25	C24	1.370(4)
Cl1	C4	1.748(3)	C15	C16	1.514(4)

O1	C7	1.217(3)	C15	C20	1.535(3)
O4	C27	1.218(3)	C2	C3	1.373(5)
N2	C21	1.368(3)	C10	C11	1.392(5)
N2	C28	1.458(3)	C35	C40	1.518(4)
N1	C8	1.451(3)	C35	C36	1.541(4)
N1	C1	1.351(3)	C16	C17	1.496(5)
O3	C40	1.210(4)	C30	C31	1.383(4)
O2	C16	1.207(4)	C24	C23	1.388(4)
C21	C26	1.398(3)	C20	C19	1.515(5)
C21	C22	1.401(3)	C40	C39	1.626(12)
C29	C28	1.537(3)	C40	C0	1.375(14)
C29	C30	1.381(4)	C4	C5	1.363(5)
C29	C34	1.396(4)	C4	C3	1.396(5)
C8	C7	1.548(3)	C34	C33	1.381(5)
C8	C9	1.539(3)	C33	C32	1.376(6)
C8	C15	1.538(3)	C14	C13	1.390(5)
C26	C27	1.460(4)	C32	C31	1.365(6)
C26	C25	1.391(4)	C36	C37	1.486(12)
C1	C6	1.398(3)	C36	C0AA	1.614(15)
C1	C2	1.408(4)	C11	C12	1.361(6)
C7	C6	1.449(3)	C12	C13	1.370(6)
C27	C28	1.548(3)	C17	C18	1.518(6)
C28	C35	1.541(3)	C39	C38	1.526(11)
C9	C10	1.385(4)	C19	C18	1.512(6)
C9	C14	1.394(4)	C38	C37	1.474(15)
C22	C23	1.375(4)	C0AA	C1AA	1.581(18)
C6	C5	1.392(4)	C1AA	C0	1.482(13)

Table 5 Bond Angles for gz190604_lfy.

Atom	Atom	Atom	Angle/˚	Atom	Atom	Atom	Angle/˚
C21	N2	C28	110.18(17)	C3	C2	C1	117.5(3)
C1	N1	C8	111.15(18)	C9	C10	C11	120.9(3)
N2	C21	C26	112.1(2)	C28	C35	C36	111.5(2)
N2	C21	C22	128.1(2)	C40	C35	C28	111.2(2)
C26	C21	C22	119.8(2)	C40	C35	C36	113.6(3)
C30	C29	C28	122.7(2)	O2	C16	C15	122.3(3)
C30	C29	C34	118.1(3)	O2	C16	C17	122.6(3)
C34	C29	C28	119.2(2)	C17	C16	C15	115.1(3)
N1	C8	C7	102.08(18)	C29	C30	C31	120.6(3)
N1	C8	C9	112.0(2)	C25	C24	Cl2	119.7(2)
N1	C8	C15	112.25(18)	C25	C24	C23	121.7(2)
C9	C8	C7	106.39(18)	C23	C24	Cl2	118.6(2)
C15	C8	C7	111.77(19)	C19	C20	C15	111.9(3)

C15	C8	C9	111.8(2)	O3	C40	C35	121.5(3)
C21	C26	C27	107.0(2)	O3	C40	C39	126.9(6)
C25	C26	C21	121.5(2)	O3	C40	C0	113.9(7)
C25	C26	C27	131.5(2)	C35	C40	C39	111.6(5)
N1	C1	C6	111.8(2)	C0	C40	C35	123.6(7)
N1	C1	C2	128.3(2)	C22	C23	C24	121.3(2)
C6	C1	C2	119.8(3)	C5	C4	Cl1	119.8(3)
O1	C7	C8	123.7(2)	C5	C4	C3	121.6(3)
O1	C7	C6	129.9(2)	C3	C4	Cl1	118.6(3)
C6	C7	C8	106.42(18)		C4	C5	C6 117.6(3)
O4	C27	C26	129.9(2)	C2	C3	C4	121.7(3)
O4	C27	C28	123.6(2)	C33	C34	C29	120.7(3)
C26	C27	C28	106.44(19)		C32	C33	C34 120.3(3)
N2	C28	C29	113.35(18)		C13	C14	C9 120.0(3)
N2	C28	C27	102.37(18)		C31	C32	C33 119.4(3)
N2	C28	C35	111.7(2)	C35	C36	C0AA	103.2(6)
C29	C28	C27	106.42(19)		C37	C36	C35 118.5(5)
C29	C28	C35	110.38(19)		C12	C11	C10 120.2(4)
C35	C28	C27	112.24(19)		C32	C31	C30 121.0(3)
C10	C9	C8	121.7(2)	C11	C12	C13	119.9(3)
C10	C9	C14	118.2(3)	C12	C13	C14	120.7(4)
C14	C9	C8	120.1(2)	C16	C17	C18	112.9(4)
C23	C22	C21	118.1(2)	C38	C39	C40	116.3(8)
C1	C6	C7	107.2(2)	C18	C19	C20	110.4(3)
C5	C6	C1	121.7(2)	C37	C38	C39	111.7(8)
C5	C6	C7	131.0(2)	C38	C37	C36	108.6(9)
C24	C25	C26	117.6(2)	C19	C18	C17	110.9(3)
C16	C15	C8	112.4(2)	C1AA	C0AA	C36	112.0(10)
C16	C15	C20	109.6(2)	C0	C1AA	C0AA	110.4(10)
C20	C15	C8	113.4(2)	C40	C0	C1AA	109.5(10)

Table 6 Hydrogen Atom Coordinates (Å×104) and Isotropic Displacement Parameters (Å2×103) for gz190604_lfy.

Atom	x	y	z	U(eq)
H2	7004.13	4700.27	4681.71	52
H1	6117.63	5038.59	7183.67	57
H22	9666.61	4980.39	4811.78	61
H25	8496.1	5404.84	6711.88	63
H15	6816.71	3208.09	8140.73	53
H2A	6570.75	6795.01	7066.43	71
H10	3861.98	5130.97	7616.89	72
H35	3983.22	4423.08	5525.59	59
H30	6185.72	6267.08	4532.7	67

H20A	5416.39	3044.75	7358.8	72
H20B	6427.29	3566.58	6975.69	72
H23	11268.92	5290.95	5487.48	67
H5	7845.36	6571.32	8972.65	69
H3	7318.61	8014.31	7565.06	84
H34	3809.11	5905.32	5876.61	72
H33	2767.84	7235.56	5688.3	92
H14	5214.24	3453	8800.08	84
H32	3411.14	8073.76	4917.46	101
H36	3720(80)	4890(60)	4620(30)	93
H36A	4920(100)	4210(70)	4410(40)	93
H11	1695.34	4883.92	7922.71	95
H31	5125.71	7591.38	4351.71	94
H12	1295.18	3958.66	8672.52	105
H13	3037.96	3232.94	9102.84	111
H17A	9216.8	2516.11	7875.5	118
H17B	10088.82	3097.3	7467.81	118
H39A	5031.65	2050.56	5223.18	91
H39B	3691.4	2469.58	5433.66	91
H19A	6969.49	1896.07	7469.69	98
H19B	6679.31	2044.36	6823.02	98
H38A	4786.04	2666.8	4339.85	97
H38B	3435.98	2190.39	4487.66	97
H37A	2482.09	3528.97	4731.34	100
H37B	3029.63	3580.69	4107.81	100
H18A	8648.32	2850.92	6723.45	126
H18B	8994.93	1921.82	6984.16	126
H0AA	2539.88	3447.7	4924.69	97
H0AB	2901.07	3298.35	4285.45	97
H1AA	3553.25	2007.23	4797.72	94
H1AB	4856.22	2461.02	4565.85	94
H0	4521.08	2191.32	5697.03	89

Table 7 Atomic Occupancy for gz190604_lfy.

Atom	Occupancy	Atom	Occupancy	Atom	Occupancy
H36	0.547(16)	H36A	0.453(16)	C39	0.547(16)
H39A	0.547(16)	H39B	0.547(16)	C38	0.547(16)
H38A	0.547(16)	H38B	0.547(16)	C37	0.547(16)
H37A	0.547(16)	H37B	0.547(16)	C0AA	0.453(16)
H0AA	0.453(16)	H0AB	0.453(16)	C1AA	0.453(16)
H1AA	0.453(16)	H1AB	0.453(16)	C0	0.453(16)
H0	0.453(16)				

Experimental

Single crystals of C20H17.27ClNO2 [gz190604_lfy] were []. A suitable crystal was selected and [] on a SuperNova, Dual, Cu at home/near, EosS2 diffractometer. The crystal was kept at 278(30) K during data collection. Using Olex2 [1], the structure was solved with the ShelXT [2] structure solution program using Intrinsic Phasing and refined with the ShelXL [3] refinement package using Least Squares minimisation.

Dolomanov, O.V., Bourhis, L.J., Gildea, R.J, Howard, J.A.K. & Puschmann, H. (2009), J. Appl. Cryst. 42, 339-341.
Sheldrick, G.M. (2015). Acta Cryst. A71, 3-8.
Sheldrick, G.M. (2015). Acta Cryst. C71, 3-8.
Crystal structure determination of [gz190604_lfy]

Crystal Data for C20H17.27375ClNO2 (M =339.07 g/mol): orthorhombic, space group P212121 (no. 19), a = 10.00050(10) Å, b = 15.08900(10) Å, c = 23.6172(2) Å, V = 3563.78(5) Å3, Z = 8, T = 278(30) K, μ(CuKα) = 1.982 mm-1, Dcalc = 1.264 g/cm3, 40048 reflections measured ($6.952^\circ \leqslant 2\Theta \leqslant 143.762^\circ$), 6958 unique (Rint = 0.0395, Rsigma = 0.0218) which were used in all calculations. The final R1 was 0.0376 ($I > 2\sigma(I)$) and wR2 was 0.1034 (all data).

Refinement model description

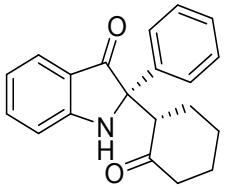
Number of restraints - 66, number of constraints - unknown.

Details:

1. Fixed Uiso
 At 1.2 times of:
  All C(H) groups, All C(H,H) groups, All N(H) groups
2. Uiso/Uaniso restraints and constraints
C37 ≈ C0AA ≈ C38 ≈ C1AA ≈ C39 ≈ C0 ≈ C36: within 1.7A
with sigma of 0.004 and sigma for terminal atoms of 0.008
3. Others
 Sof(H36A)=Sof(C0AA)=Sof(H0AA)=Sof(H0AB)=Sof(C1AA)=Sof(H1AA)=Sof(H1AB)=Sof(C0)=
 Sof(H0)=1-FVAR(1)
 Sof(H36)=Sof(C39)=Sof(H39A)=Sof(H39B)=Sof(C38)=Sof(H38A)=Sof(H38B)=Sof(C37)=
 Sof(H37A)=Sof(H37B)=FVAR(1)
4.a Ternary CH refined with riding coordinates:
 C15(H15), C35(H35)
4.b Secondary CH2 refined with riding coordinates:
 C20(H20A,H20B), C17(H17A,H17B), C39(H39A,H39B), C19(H19A,H19B), C38(H38A,
 H38B), C37(H37A,H37B), C18(H18A,H18B), C0AA(H0AA,H0AB), C1AA(H1AA,H1AB)
4.c Aromatic/amide H refined with riding coordinates:
 N2(H2), N1(H1), C22(H22), C25(H25), C2(H2A), C10(H10), C30(H30), C23(H23),
 C5(H5), C3(H3), C34(H34), C33(H33), C14(H14), C32(H32), C11(H11), C31(H31),

C12(H12), C13(H13), C0(H0)

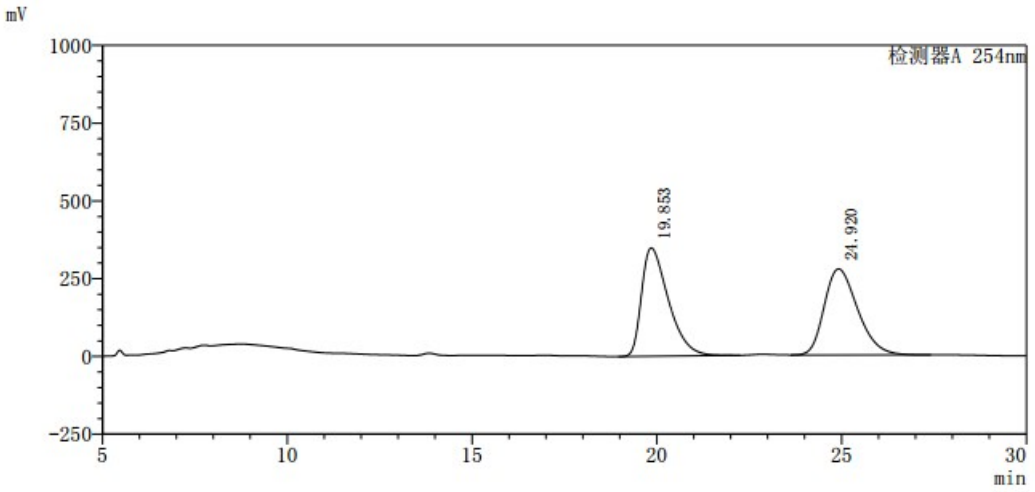
6. Characterization of products



(S)-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3a)[5]

Yellow solid. 67 % yield. m.p. 206-207 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 3H), 7.43 (t, J = 7.6 Hz, 1H), 7.31 (t, J = 7.6 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.95 (d, J = 8.2 Hz, 1H), 6.83 (t, J = 7.4 Hz, 1H), 5.18 (s, 1H), 3.50 (dd, J = 13.3, 5.3 Hz, 1H), 2.38 – 2.26 (m, 2H), 2.05 – 1.85 (m, 3H), 1.64 – 1.58 (m, 2H), 1.53 – 1.46 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.7, 159.5, 137.5, 136.2, 128.8, 127.8, 125.6, 124.9, 121.4, 119.3, 111.8, 71.4, 58.6, 42.1, 28.4, 26.7, 25.2. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak IA, hexane/isopropanol = 91:9, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 19.701 min, tRminor = 25.190 min.

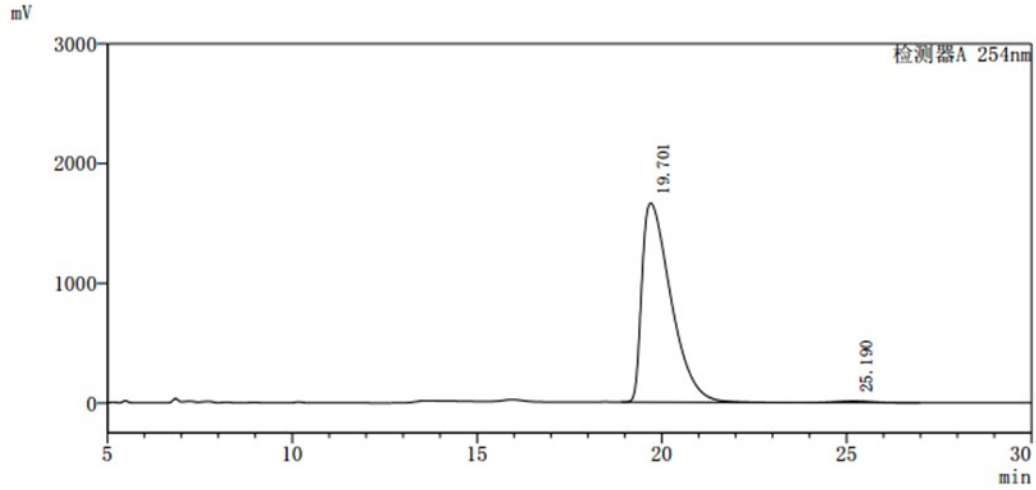
HPLC of 3a (racemic)



检测器A 254nm

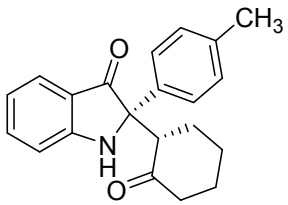
No.	Retention Time	Area	Height	Concentration
1	19.853	17628975	348671	50.308
2	24.920	17413252	276737	49.692
总计		35042227	625408	

HPLC of 3a (chiral)



检测器A 254nm

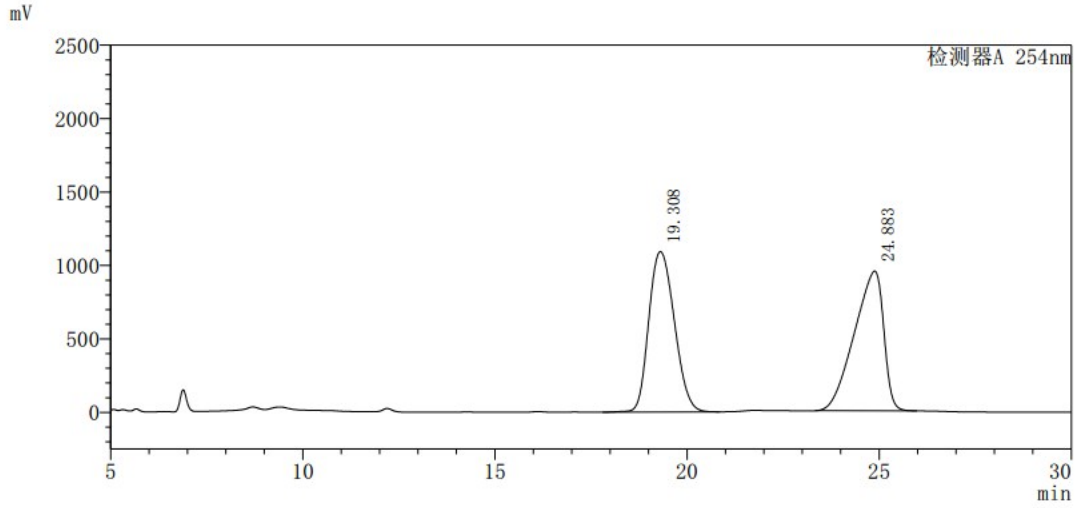
No.	Retention Time	Area	Height	Concentration
1	19.701	90978379	1663003	98.951
2	25.190	964212	13451	1.049
总计		91942592	1676454	



(S)-2-((S)-2-oxocyclohexyl)-2-(p-tolyl)indolin-3-one (3b)

Yellow solid. 62% yield. m.p. 91-92 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.47 – 7.41 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.81 (t, *J* = 7.4 Hz, 1H), 5.24 (s, 1H), 3.48 (dd, *J* = 13.3, 5.3 Hz, 1H), 2.40 – 2.23 (m, 5H), 2.04 – 1.85 (m, 3H), 1.66 – 1.44 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 200.9, 159.5, 137.5, 136.2, 134.4, 129.5, 125.5, 125.0, 121.4, 119.2, 111.8, 71.3, 58.5, 42.1, 28.4, 26.7, 25.2, 20.9. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 18.916 min, tRminor = 23.823 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_2$ $(M+Na)^+$: 342.1465; found: 342.1472.

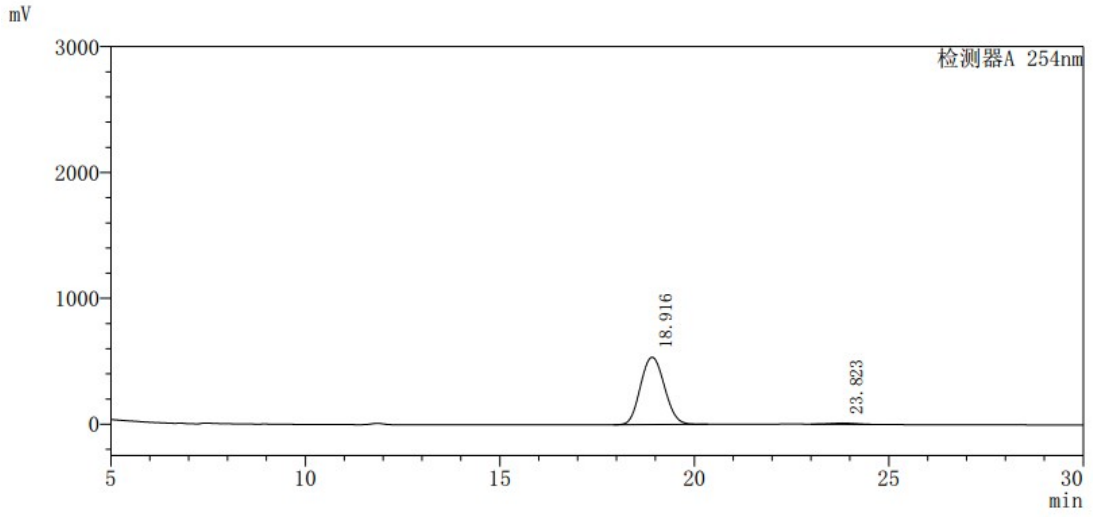
HPLC of 3b (racemic)



检测器A 254nm

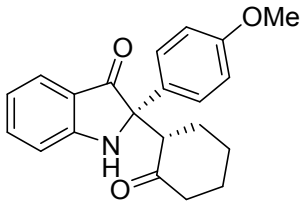
No.	Retention Time	Area	Height	Concentration
1	19.308	50605560	1092289	49.980
2	24.883	50646261	951515	50.020
总计		101251822	2043804	

HPLC of 3b (chiral)



检测器A 254nm

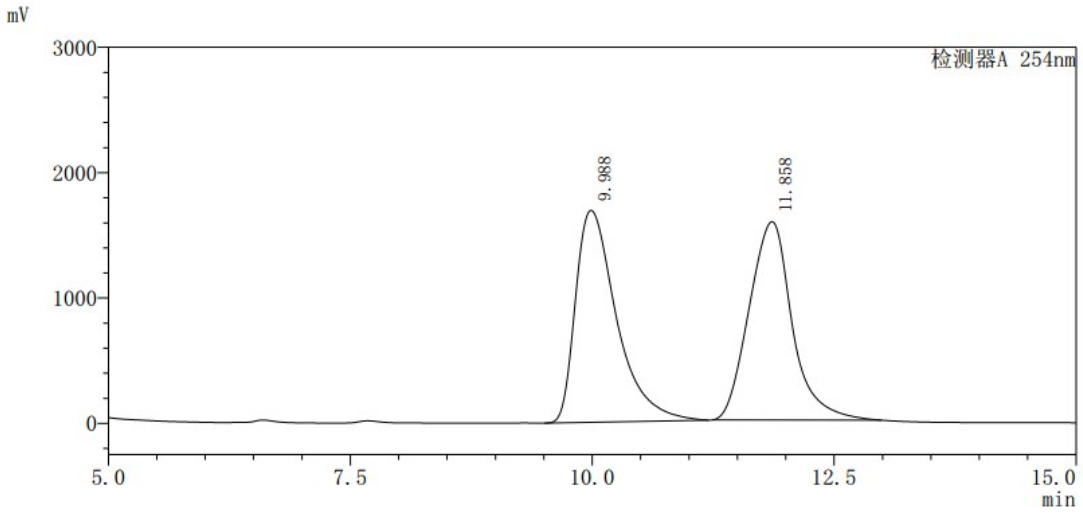
No.	Retention Time	Area	Height	Concentration
1	18.916	22895232	534793	98.151
2	23.823	431289	9272	1.849
总计		23326522	544065	



(S)-2-(4-fluorophenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3c)

Yellow solid. 62% yield. m.p. 90-93 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.46 (d, *J* = 8.9 Hz, 2H), 7.42 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.84 – 6.80 (m, 3H), 5.20 (s, 1H), 3.75 (s, 3H), 3.44 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.37 – 2.27 (m, 2H), 2.04 – 1.96 (m, 2H), 1.89 – 1.87 (m, 1H), 1.65 – 1.42 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.2, 201.1, 159.5, 159.3, 136.2, 129.2, 126.8, 125.0, 121.4, 119.2, 114.2, 111.8, 70.9, 58.4, 55.3, 42.1, 28.3, 26.7, 25.2. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 9.986 min, tRminor = 11.727 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_3$ $(M+Na)^+$: 358.1414; found: 358.1419.

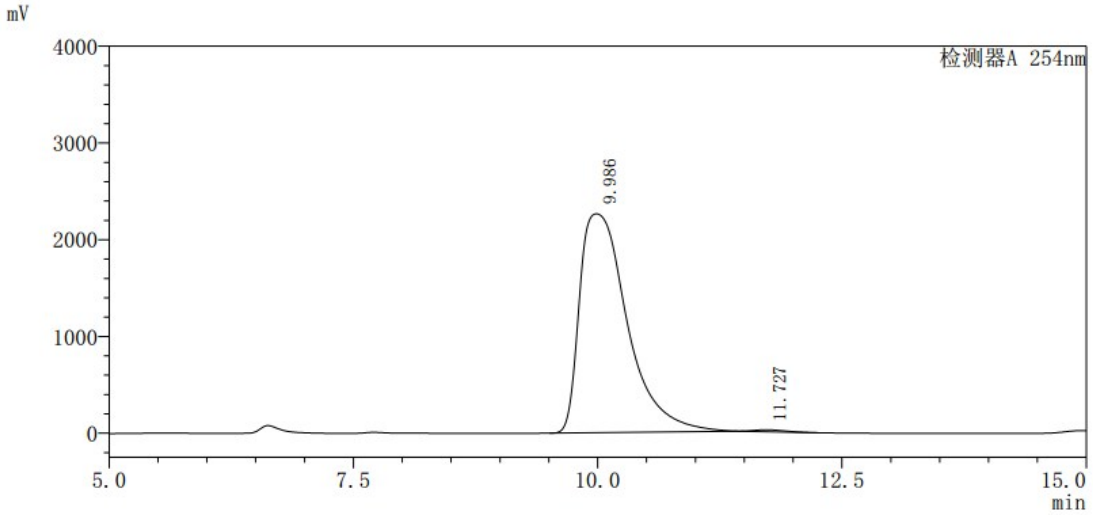
HPLC of 3c (racemic)



检测器A 254nm

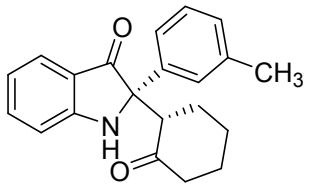
No.	Retention Time	Area	Height	Concentration
1	9.988	49802624	1690243	50.361
2	11.858	49088252	1583160	49.639
总计		98890876	3273404	

HPLC of 3c (chiral)



检测器A 254nm

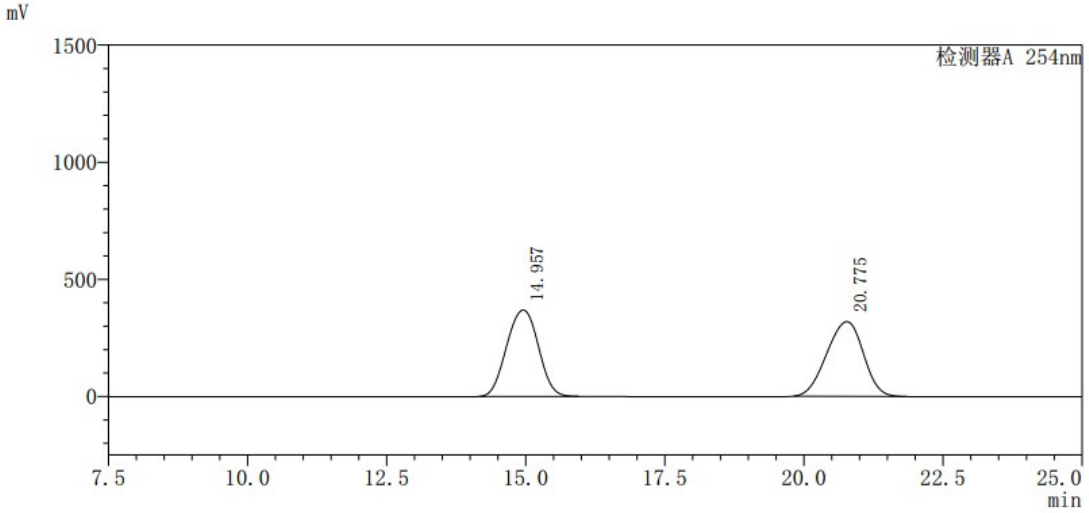
No.	Retention Time	Area	Height	Concentration
1	9.986	77002485	2262463	99.444
2	11.727	430889	19350	0.556
总计		77433374	2281813	



(S)-2-((S)-2-oxocyclohexyl)-2-(m-tolyl)indolin-3-one (3d)

Yellow solid. 71% yield. m.p. 200-201 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J*=7.7 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.4 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.08 (s, 1H), 3.49 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.39 – 2.22 (m, 5H), 2.07 – 1.86 (m, 3H), 1.67 – 1.57 (m, 2H), 1.53 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.8, 159.4, 138.4, 137.4, 136.2, 128.6, 128.6, 126.1, 125.0, 122.6, 121.5, 119.3, 111.8, 71.3, 58.7, 42.1, 28.4, 26.7, 25.2, 21.7. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 14.670 min, tRminor = 20.655 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_2$ $(M+Na)^+$: 342.1465; found: 342.1467.

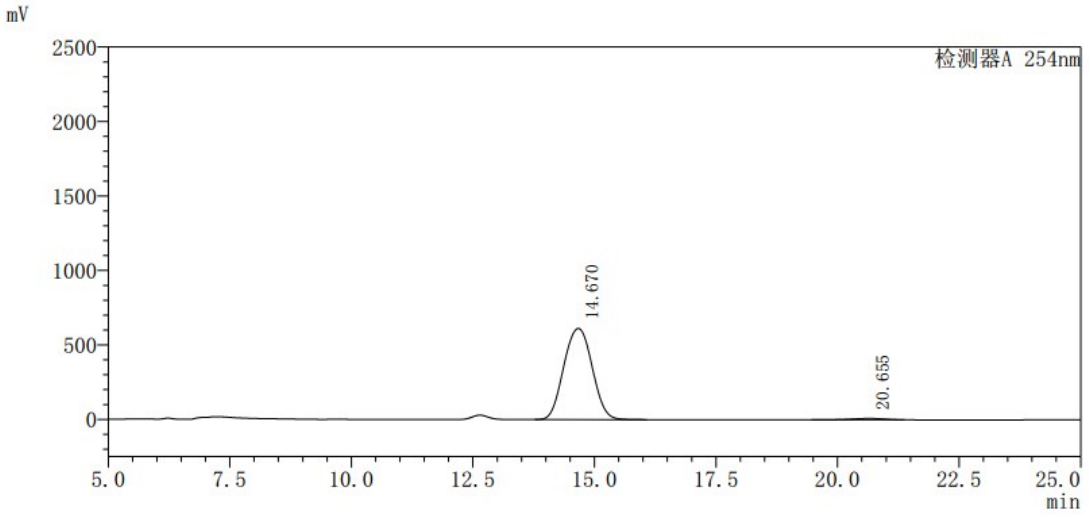
HPLC of 3d (racemic)



检测器A 254nm

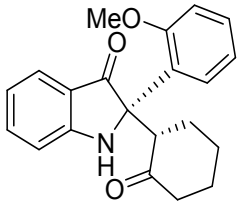
No.	Retention Time	Area	Height	Concentration
1	14.957	14647816	368772	50.070
2	20.775	14606898	318912	49.930
总计		29254714	687684	

HPLC of 3d (chiral)



检测器A 254nm

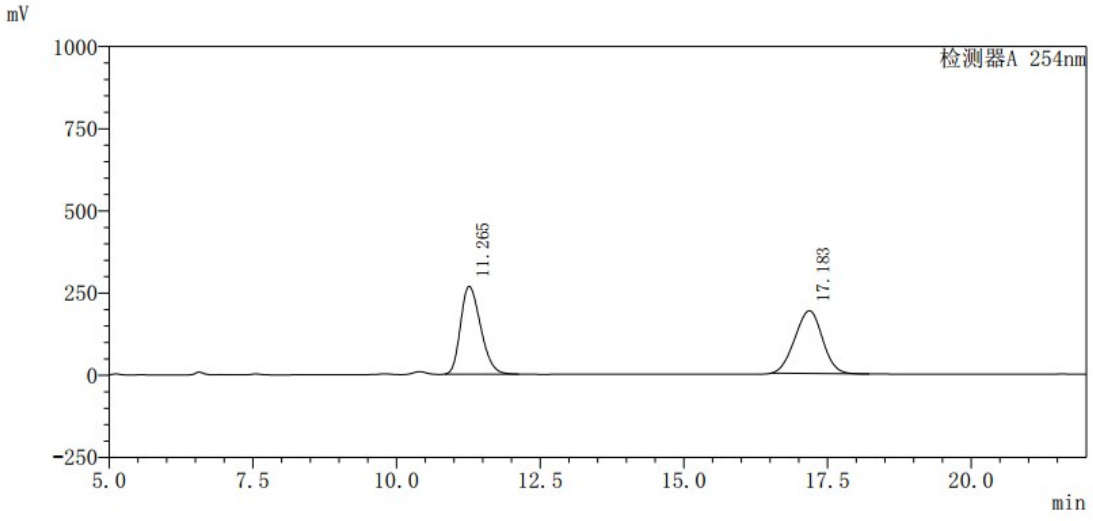
No.	Retention Time	Area	Height	Concentration
1	14.670	24850103	611838	98.279
2	20.655	435172	9063	1.721
总计		25285275	620901	



(S)-2-(2-methoxyphenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3e)

Yellow solid. 58% yield. m.p. 190-191 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.59 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J = 7.6* Hz, 1H), 7.29 – 7.25 (m, 1H), 7.17 – 7.16 (m, 2H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 6.82 – 6.80 (m, 1H), 5.16 (s, 1H), 3.81 (s, 3H), 3.51 (dd, *J* = 13.3, 5.3 Hz, 1H), 2.41 – 2.27 (m, 2H), 2.07 – 2.05 (m, 1H), 1.99 – 1.88(m, 2H), 1.68 – 1.59 (m, 2H), 1.56 – 1.45 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 207.9, 200.6, 159.9, 159.4, 139.3, 136.2, 129.7, 124.9, 121.4, 119.3, 117.9, 112.6, 112.1, 111.8, 71.3, 58.7, 55.3, 42.0, 28.4, 26.7, 25.2. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 11.144 min, tRminor = 16.963 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_3$ $(M+Na)^+$: 358.1414; found: 358.1418.

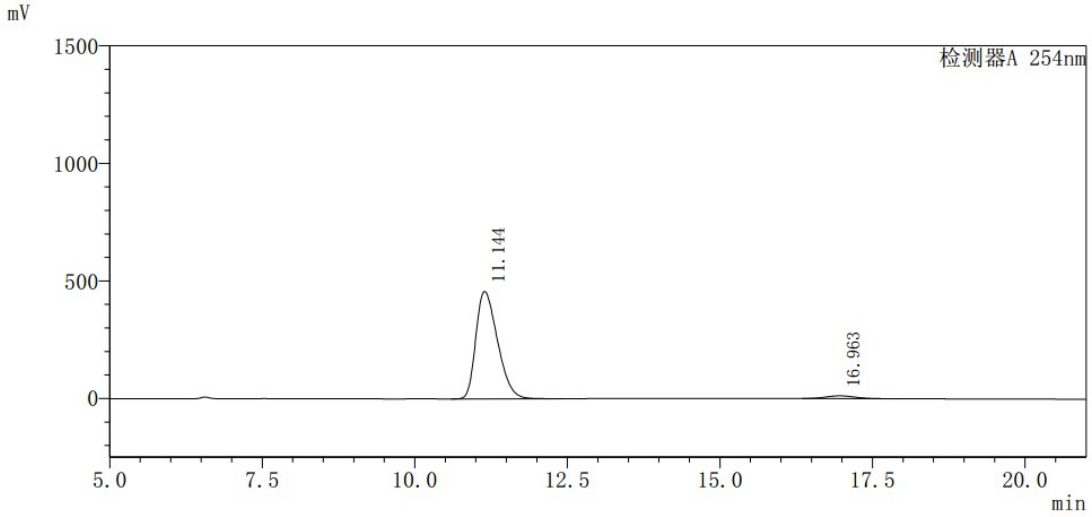
HPLC of 3e (racemic)



检测器A 254nm

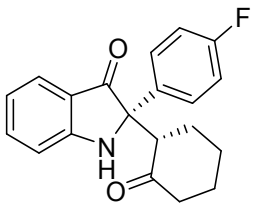
No.	Retention Time	Area	Height	Concentration
1	11.265	6477872	267086	50.275
2	17.183	6407105	191184	49.725
总计		12884977	458270	

HPLC of 3e (chiral)



检测器A 254nm

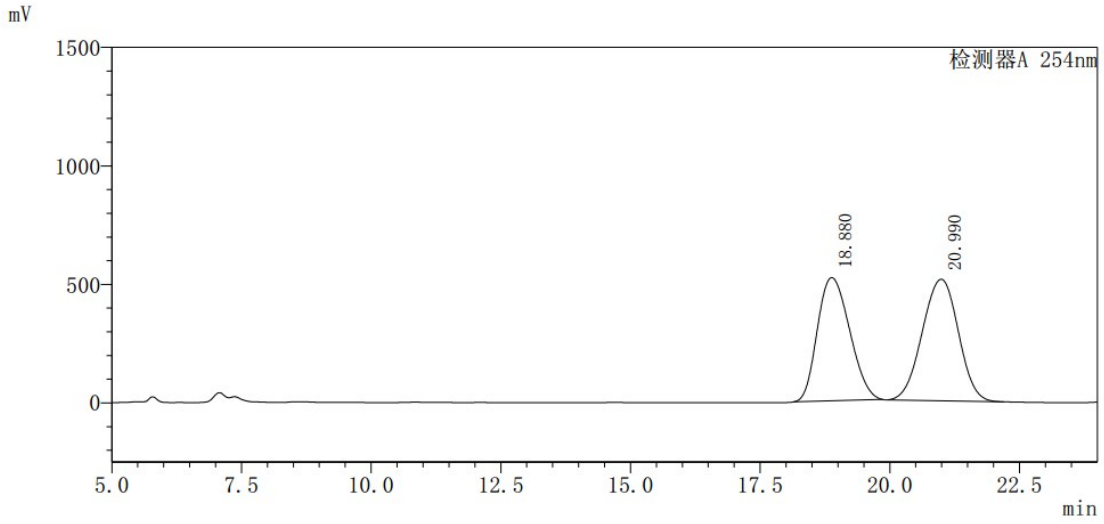
No.	Retention Time	Area	Height	Concentration
1	11.144	11294469	456918	96.685
2	16.963	387259	11796	3.315
总计		11681728	468714	



(S)-2-(4-fluorophenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3f)

Yellow solid. 58% yield. m.p. 66-67 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 – 7.55 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 6.99 (t, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.26 (s, 1H), 3.41 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.38 – 2.28 (m, 2H), 2.04 – 1.89 (m, 3H), 1.65 – 1.55 (m, 2H), 1.51 – 1.43 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ208.1, 200.9, 163.3, 161.6, 159.4, 136.5, 133.3, 133.2, 130.1, 128.5, 127.6, 127.5, 125.0, 121.2, 119.4, 115.6, 115.5, 111.9, 70.8, 58.5, 42.1, 28.3, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 18.671 min, tRminor = 20.985 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}FNO_2(M+Na)^+$: 346.1214; found: 346.1215.

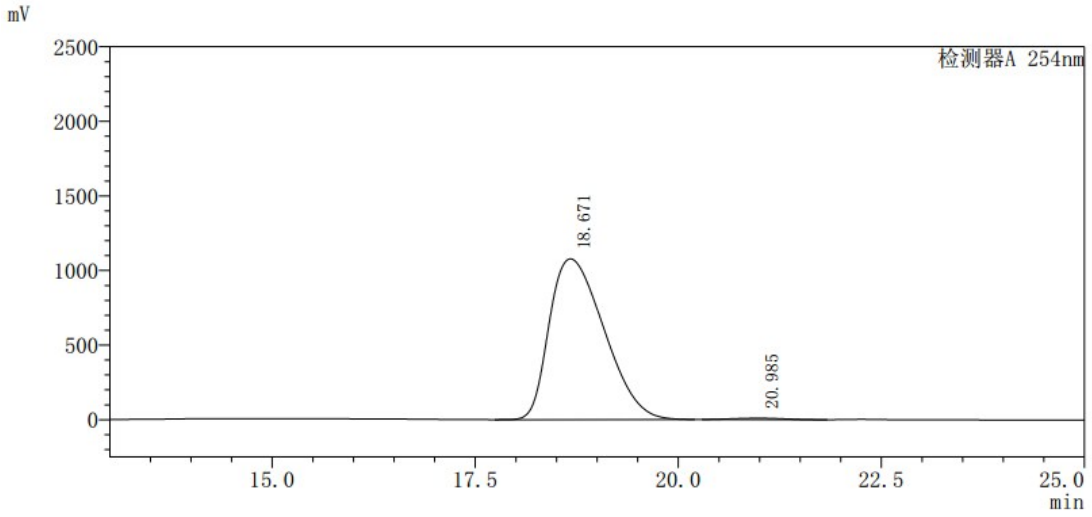
HPLC of 3f (racemic)



检测器A 254nm

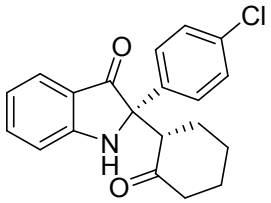
No.	Retention Time	Area	Height	Concentration
1	18.880	22516465	520454	47.576
2	20.990	24810747	512944	52.424
总计		47327211	1033398	

HPLC of 3f (chiral)



检测器A 254nm

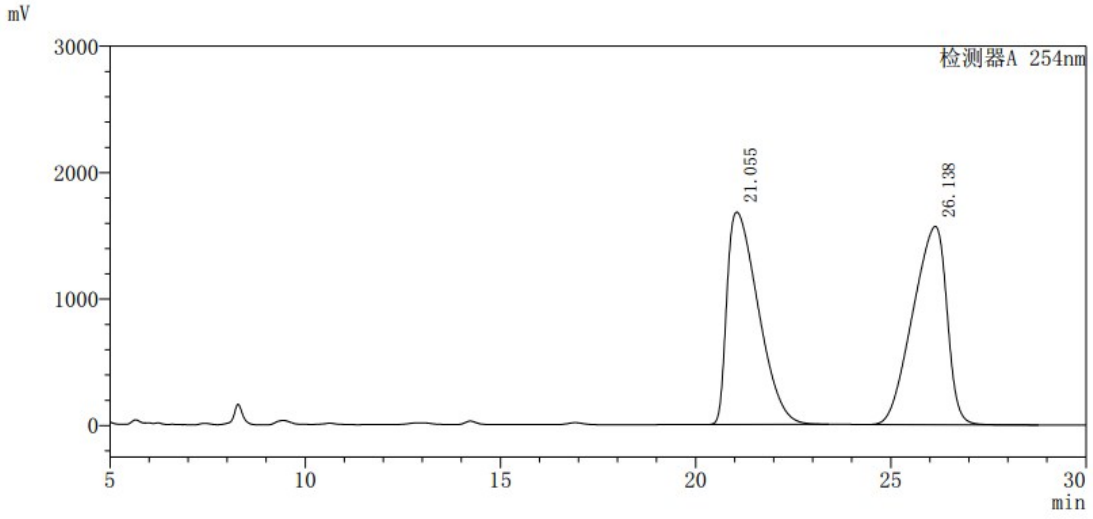
No.	Retention Time	Area	Height	Concentration
1	18.671	50511515	1077363	99.223
2	20.985	395515	9165	0.777
总计		50907029	1086528	



(S)-2-(4-chlorophenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3g)

Yellow solid. 50% yield. m.p. 99-100 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 – 7.53 (m, 3H), 7.44 (t, *J*=7.6 Hz, 1H), 7.28 (d, *J*=8.6 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 5.23 (s, 1H), 3.41 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.38 – 2.25 (m, 2H), 2.07 – 1.89 (m, 3H), 1.65 – 1.55 (m, 2H), 1.50 – 1.43 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 200.6, 159.4, 136.5, 136.2, 133.9, 130.2, 128.8, 128.5, 127.3, 125.0, 121.2, 119.5, 111.9, 70.8, 58.4, 42.1, 28.3, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 21.317 min, tRminor = 25.576 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}ClNO_2(M+Na)^+$: 362.0918; found: 362.0920.

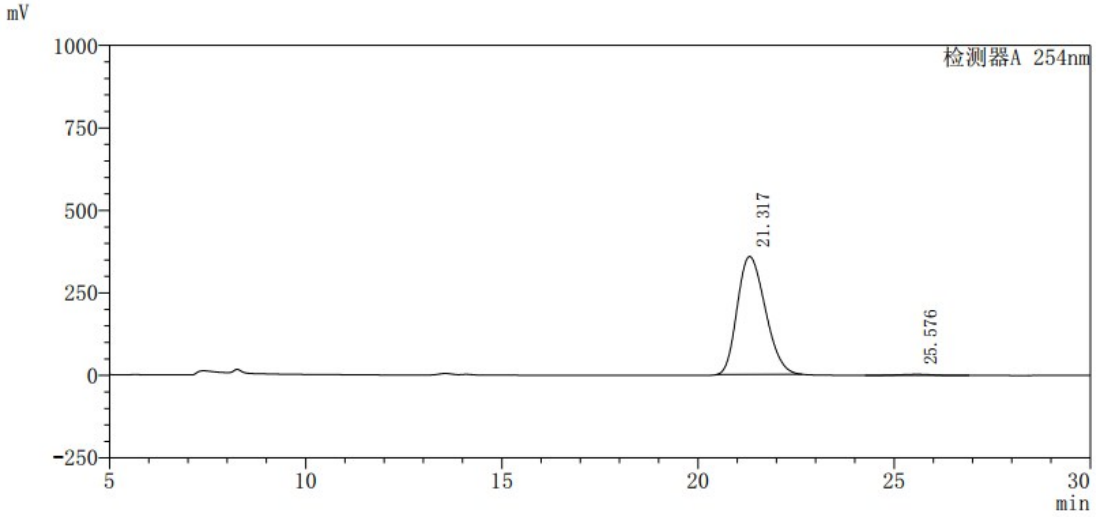
HPLC of 3g (racemic)



检测器A 254nm

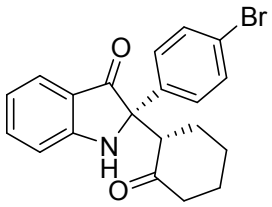
No.	Retention Time	Area	Height	Concentration
1	21.055	93710632	1679689	49.554
2	26.138	95396973	1568777	50.446
总计		189107605	3248466	

HPLC of 3g (chiral)



检测器A 254nm

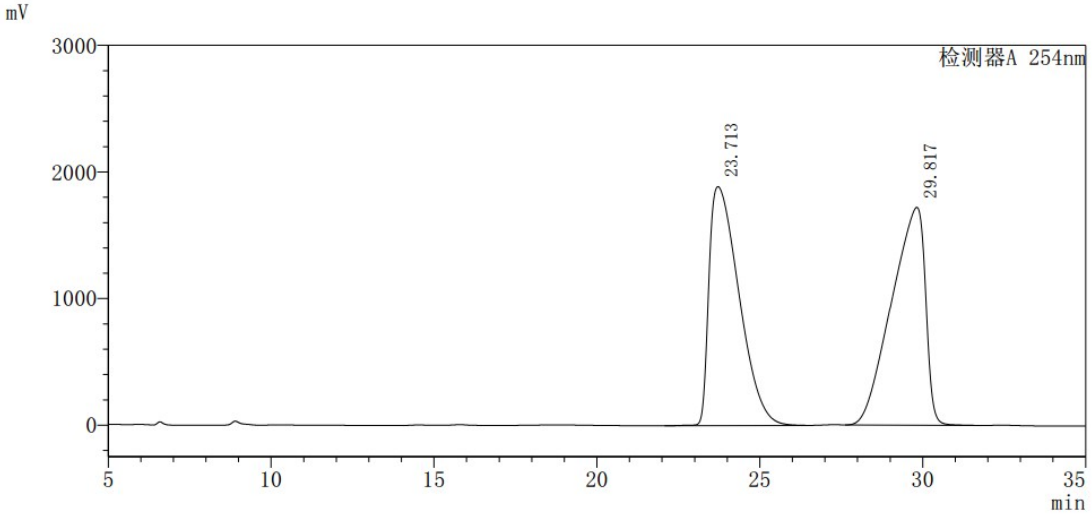
No.	Retention Time	Area	Height	Concentration
1	21.317	17773537	357518	98.894
2	25.576	198816	3274	1.106
总计		17972353	360792	



(S)-2-(4-bromophenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3h)

Yellow solid. 48% yield. m.p. 109-111 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.42 (m, 5H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 3.40 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.39 – 2.25 (m, 2H), 2.05 – 1.89 (m, 3H), 1.65 – 1.56 (m, 2H), 1.50 – 1.43 (m, 1H); **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.4, 159.3, 136.8, 136.5, 131.8, 127.7, 125.0, 122.0, 121.2, 119.5, 111.9, 70.8, 58.4, 42.1, 28.3, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 91:9, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 23.455 min, tRminor = 28.512 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}BrNO_2(M+Na)^+$: 406.0413; found: 406.0413.

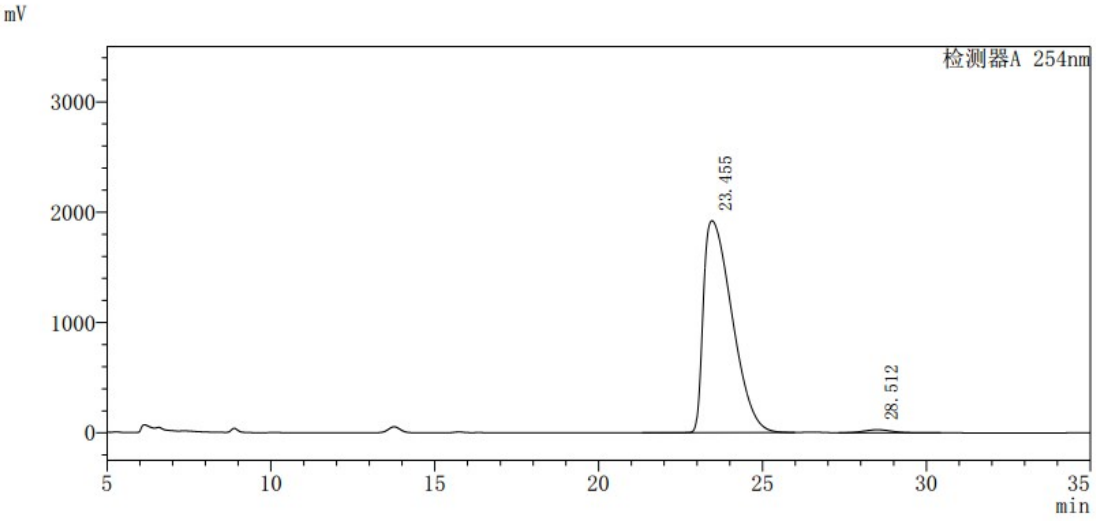
HPLC of 3h (racemic)



检测器A 254nm

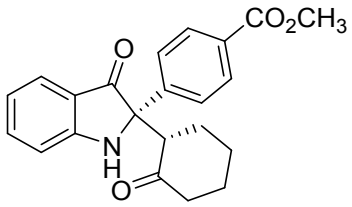
No.	Retention Time	Area	Height	Concentration
1	23.713	121089393	1888011	49.341
2	29.817	124323904	1720793	50.659
总计		245413297	3608804	

HPLC of 3h (chiral)



检测器A 254nm

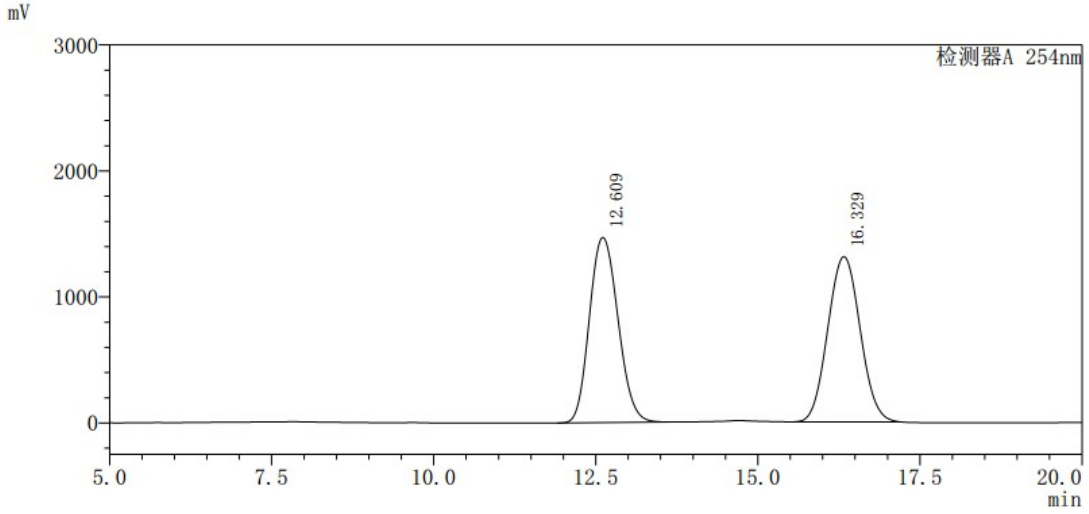
No.	Retention Time	Area	Height	Concentration
1	23.455	116983113	1921076	98.645
2	28.512	1606713	27560	1.355
总计		118589827	1948636	



methyl 4-((S)-3-oxo-2-((S)-2-oxocyclohexyl)indolin-2-yl)benzoate (3i)

Yellow solid. 43% yield. m.p. 88-90 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.97 (d, *J* = 8.5 Hz, 2H), 7.68 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 7.6 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.29 (s, 1H), 3.89 (s, 3H), 3.49 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.39 – 2.29 (m, 2H), 2.07 – 2.03 (m, 1H), 1.92-1.88 (m, 2H), 1.66 – 1.56 (m, 2H), 1.53 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 207.8, 200.1, 166.7, 159.4, 142.9, 136.6, 129.9, 129.7, 125.9, 125.0, 121.2, 119.6, 111.9, 71.4, 58.6, 52.1, 42.1, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 12.475 min, tRminor = 16.209 min. **HRMS** (EI): m/z: calcd for $C_{22}H_{21}NO_4$ $(M+Na)^+$: 386.1363; found: 386.1362.

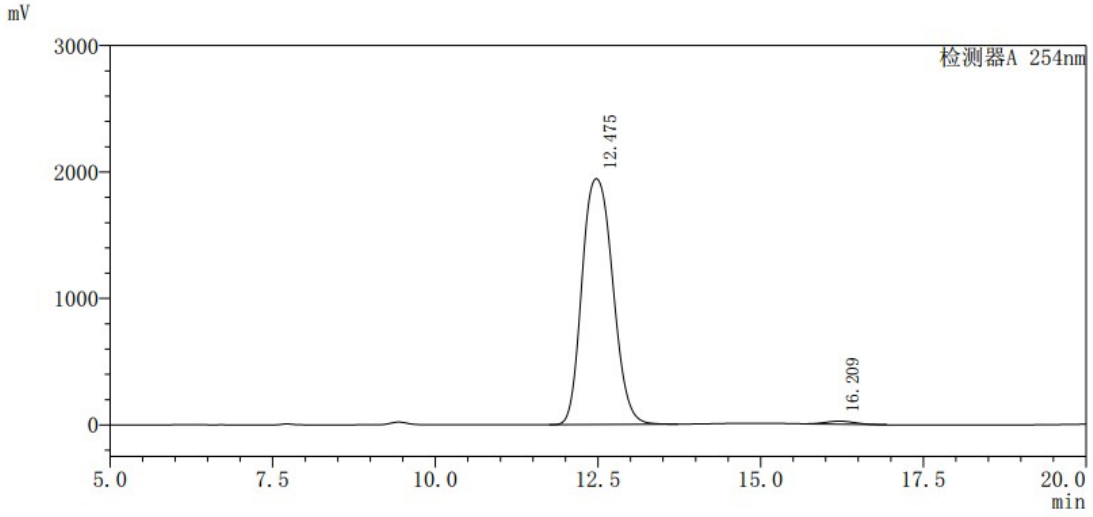
HPLC of 3i (racemic)



检测器A 254nm

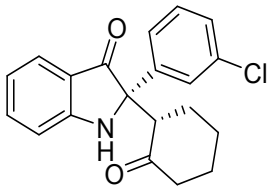
No.	Retention Time	Area	Height	Concentration
1	12.609	45208220	1469623	49.771
2	16.329	45625100	1311661	50.229
总计		90833320	2781284	

HPLC of 3i (chiral)



检测器A 254nm

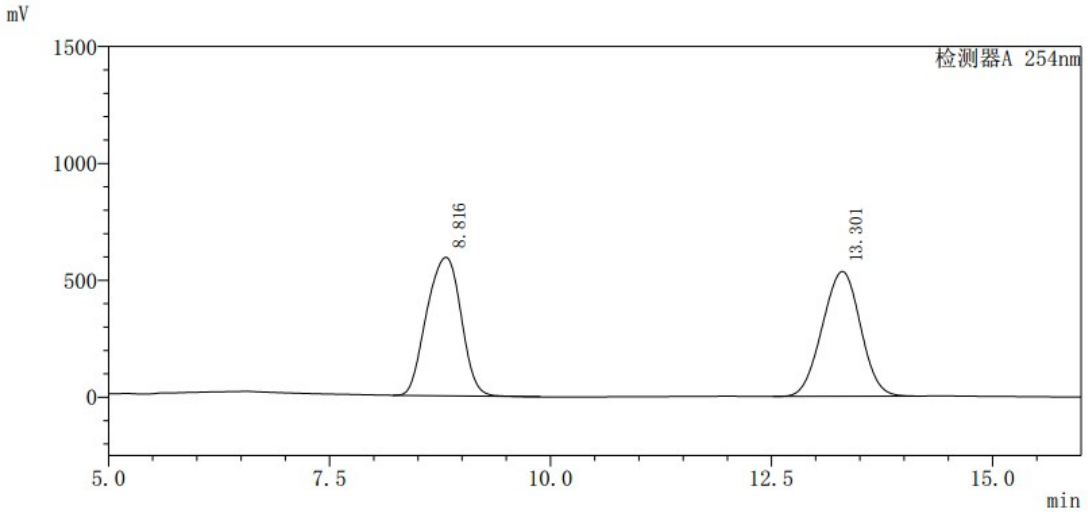
No.	Retention Time	Area	Height	Concentration
1	12.475	64138596	1944652	98.842
2	16.209	751568	24164	1.158
总计		64890164	1968816	



(S)-2-(3-chlorophenyl)-2-((S)-2-oxocyclohexyl)indolin-3-one (3j)

Yellow solid. 50% yield. m.p. 215-217 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.58 – 7.56 (m, 2H), 7.51 (d, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.23 (m, 2H), 6.95 (d, *J* = 8.2 Hz, 1H), 6.85 (t, *J* = 7.4 Hz, 1H), 5.20 (s, 1H), 3.42 (dd, *J* = 13.4, 5.1 Hz, 1H), 2.39 – 2.23 (m, 2H), 2.06 – 1.89 (m, 3H), 1.67 – 1.57(m, 2H), 1.51 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 207.9, 200.3, 159.3, 140.0, 136.5, 134.7, 129.9, 128.0, 126.0, 125.0, 124.1, 121.2, 119.6, 112.0, 70.9, 58.6, 42.1, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 8.763 min, tRminor = 13.293 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}ClNO_2$ $(M+Na)^+$: 362.0918; found: 362.0920.

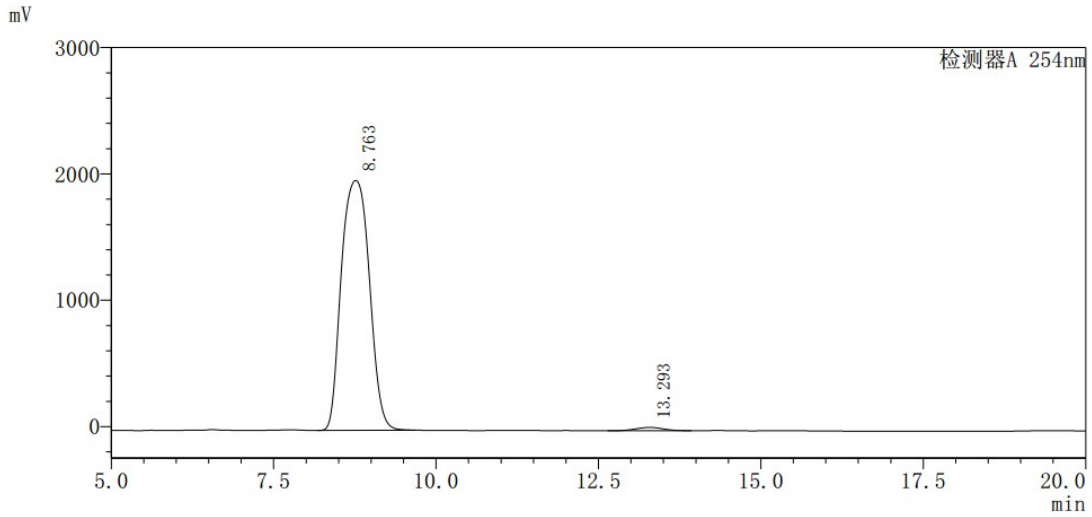
HPLC of 3j (racemic)



检测器A 254nm

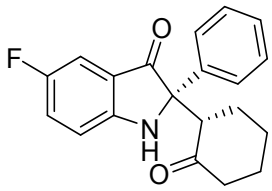
No.	Retention Time	Area	Height	Concentration
1	8.816	16078893	592460	50.044
2	13.301	16050330	533987	49.956
总计		32129223	1126446	

HPLC of 3j (chiral)



检测器A 254nm

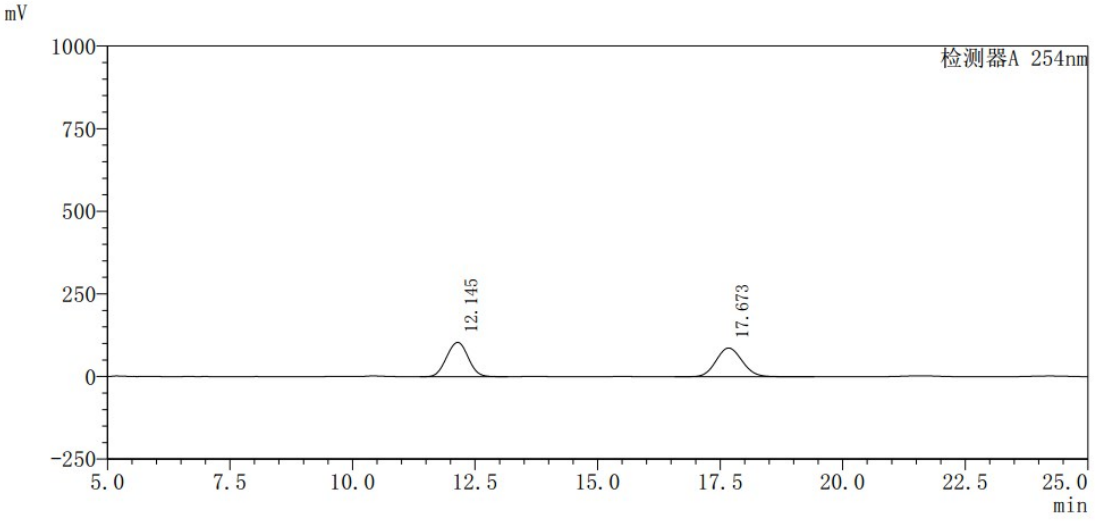
No.	Retention Time	Area	Height	Concentration
1	8.763	59578717	1978120	98.748
2	13.293	755257	25716	1.252
总计		60333974	2003836	



(S)-5-fluoro-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3k)

Yellow solid. 50% yield. m.p. 86-87 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.53 (d, *J* = 7.6 Hz, 2H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.2 Hz, 1H), 7.24 – 7.17 (m, 2H), 6.92 (dd, *J* = 8.7, 3.7 Hz, 1H), 5.10 (s, 1H), 3.52 (dd, *J* = 13.2, 5.1 Hz, 1H), 2.40 – 2.19 (m, 2H), 2.06 – 2.03 (m, 1H), 1.92 – 1.82 (m, 2H), 1.67 – 1.56 (m, 2H), 1.53 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.4, 200.4, 157.7, 156.1, 155.9, 137.2, 128.9, 127.9, 125.4, 123.9, 123.7, 122.2, 122.2, 112.9, 112.9, 110.2, 110.0, 72.5, 59.0, 42.0, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 12.051 min, tRminor = 17.650 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}FNO_2$ $(M+Na)^+$: 346.1214; found: 346.1212.

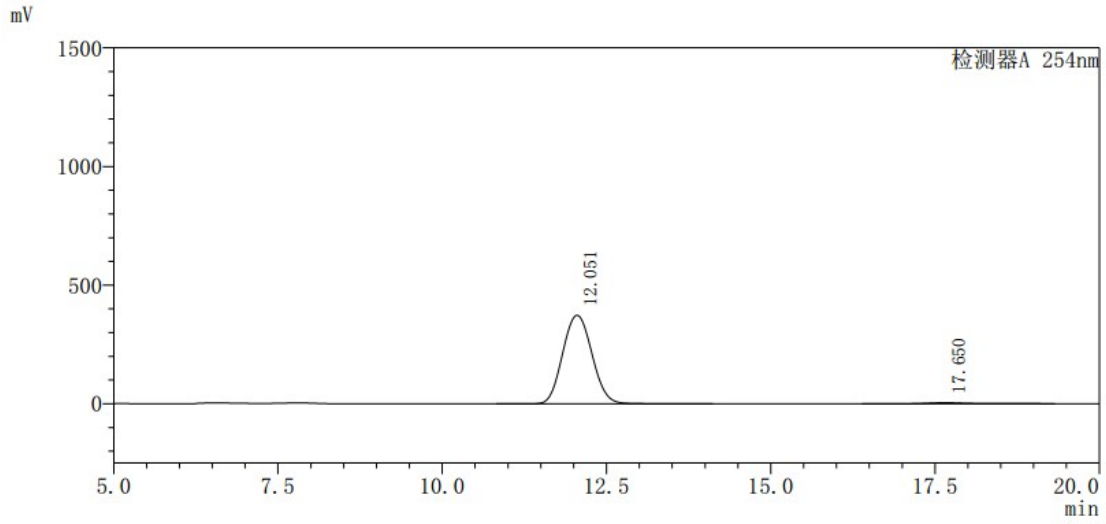
HPLC of 3k (racemic)



检测器A 254nm

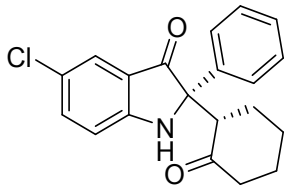
No.	Retention Time	Area	Height	Concentration
1	12.145	3178509	103623	49.699
2	17.673	3217017	86908	50.301
总计		6395526	190531	

HPLC of 3k (chiral)



检测器A 254nm

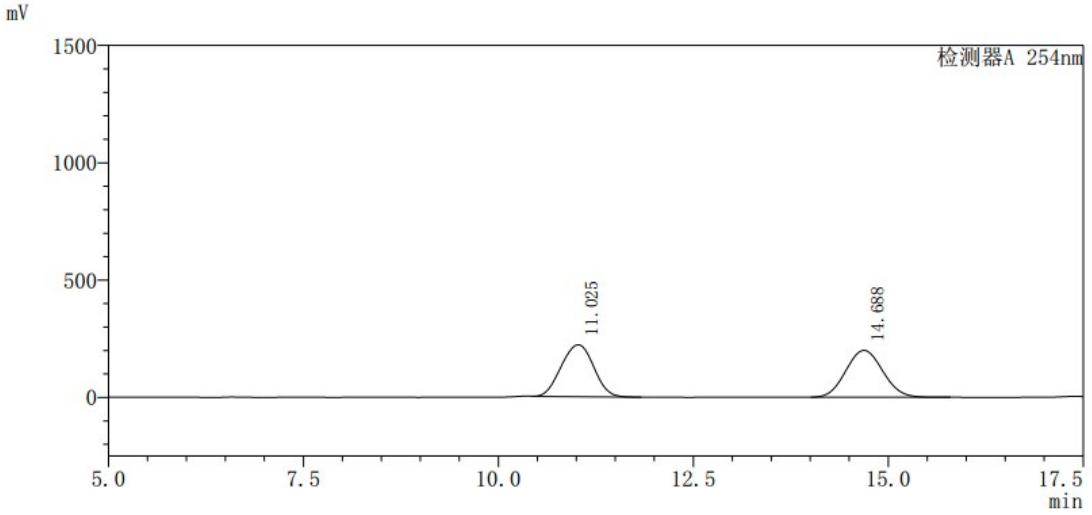
No.	Retention Time	Area	Height	Concentration
1	12.051	11595138	373184	98.303
2	17.650	200215	4425	1.697
总计		11795353	377608	



(S)-5-chloro-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3l)

Yellow solid. 46% yield. m.p. 224-226 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.52 – 7.46 (m, 3H), 7.37 (dd, *J* = 8.6 Hz, 2.1 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 5.21 (s, 1H), 3.51 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.40 – 2.29 (m, 2H), 2.06 – 1.88 (m, 3H), 1.64 – 1.58 (m, 2H), 1.51 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 207.9, 199.5, 157.7, 136.9, 136.0, 128.9, 128.0, 125.4, 124.6, 124.4, 122.6, 113.0, 72.2, 58.9, 42.0, 28.4, 26.6, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 10.939 min, tRminor = 14.670 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}ClNO_2$ $(M+Na)^+$: 362.0918; found: 362.0917.

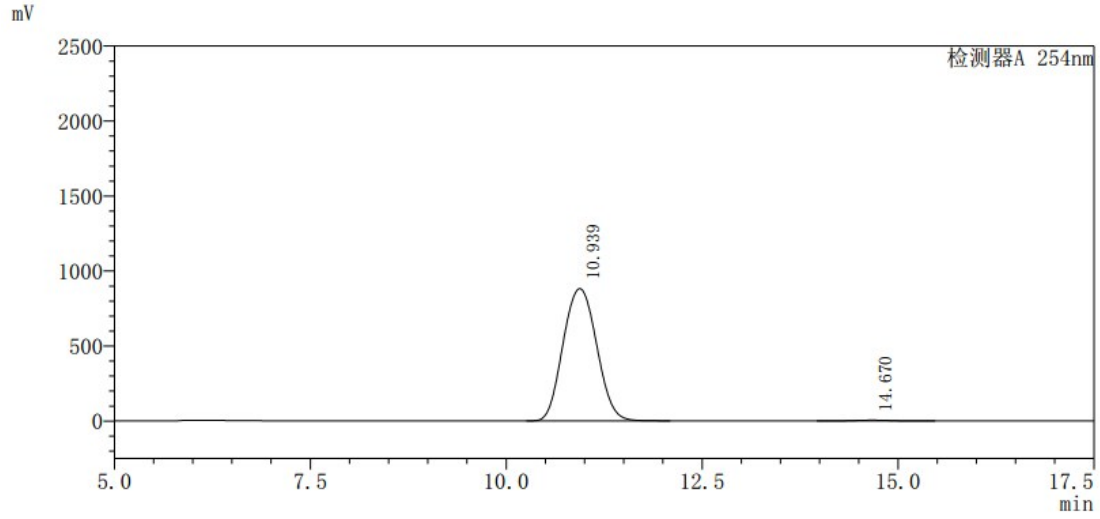
HPLC of 3l (racemic)



检测器A 254nm

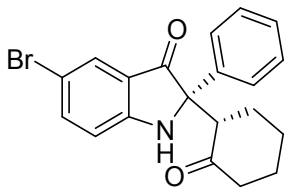
No.	Retention Time	Area	Height	Concentration
1	11.025	6416894	220876	49.335
2	14.688	6590003	199849	50.665
总计		13006897	420725	

HPLC of 3l (chiral)



检测器A 254nm

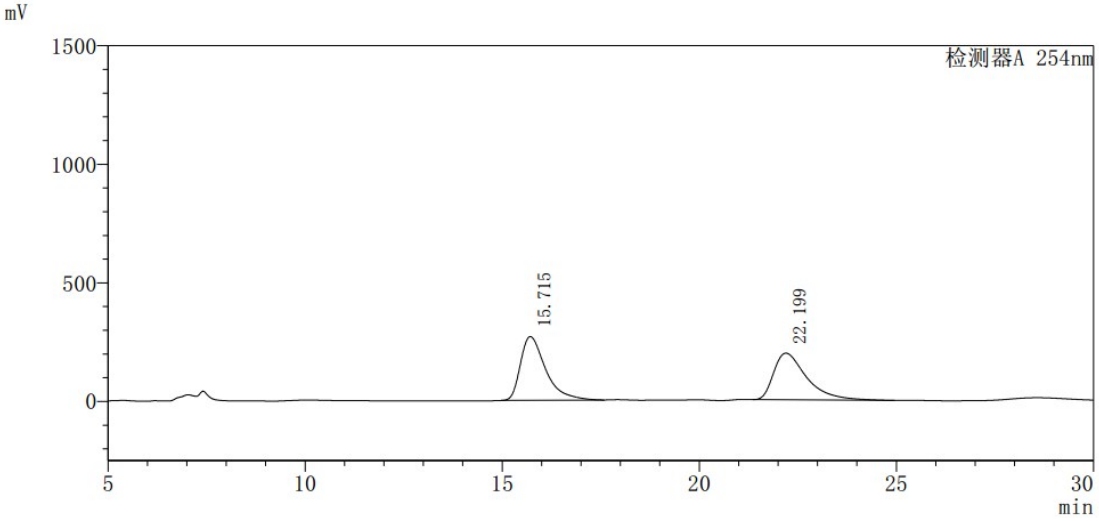
No.	Retention Time	Area	Height	Concentration
1	10.939	26389203	882108	99.314
2	14.670	182386	5583	0.686
总计		26571589	887690	



(S)-5-bromo-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3m)[5]

Yellow solid. 41% yield. m.p. 174-175 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.66 (d, *J* = 1.8 Hz, 1H), 7.52 – 7.49 (m, 3H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.28 – 7.26 (m, 1H), 6.85 (d, *J* = 8.6 Hz, 1H), 5.17 (s, 1H), 3.50 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.39 – 2.29 (m, 2H), 2.05 – 1.88 (m, 3H), 1.66 – 1.56 (m, 2H), 1.50 – 1.44 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 207.9, 199.3, 158.0, 138.6, 136.9, 128.9, 128.0, 127.5, 125.4, 123.1, 113.4, 111.4, 72.0, 58.9, 42.0, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 15.497 min, tRminor = 22.319 min.

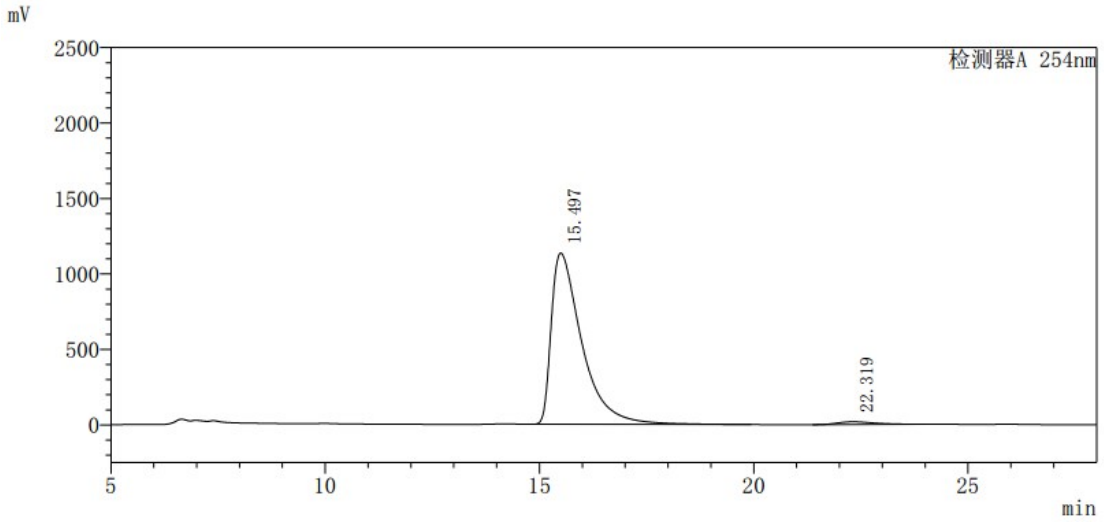
HPLC of 3m (racemic)



检测器A 254nm

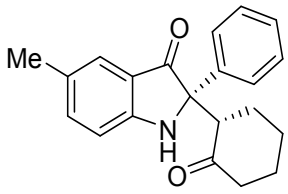
No.	Retention Time	Area	Height	Concentration
1	15.715	11945862	269157	50.947
2	22.199	11501646	196958	49.053
总计		23447508	466115	

HPLC of 3m (chiral)



检测器A 254nm

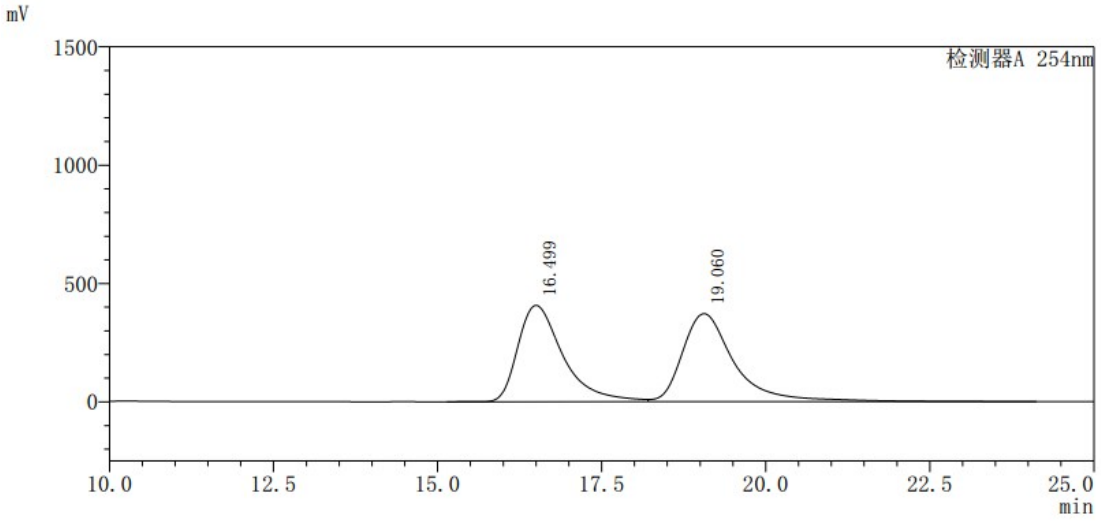
No.	Retention Time	Area	Height	Concentration
1	15.497	56381390	1135305	98.130
2	22.319	1074341	18112	1.870
总计		57455731	1153418	



(S)-5-methyl-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3n)

Yellow solid. 47% yield. m.p. 187-188 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.5 Hz, 2H), 7.37 (s, 1H), 7.30 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.23 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.99 (s, 1H), 3.51 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.39 – 2.29 (m, 2H), 2.27 (s, 3H), 2.05 – 2.02 (m, 1H), 1.94 – 1.85 (m, 2H), 1.66 – 1.57 (m, 2H), 1.54 – 1.47 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.9, 157.9, 137.7, 137.5, 128.9, 128.8, 127.7, 125.5, 124.5, 121.6, 111.8, 71.8, 58.6, 42.1, 28.4, 26.7, 25.2, 20.6. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 16.390 min, tRminor = 18.930 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_2$ $(M+Na)^+$: 342.1465; found: 342.1468.

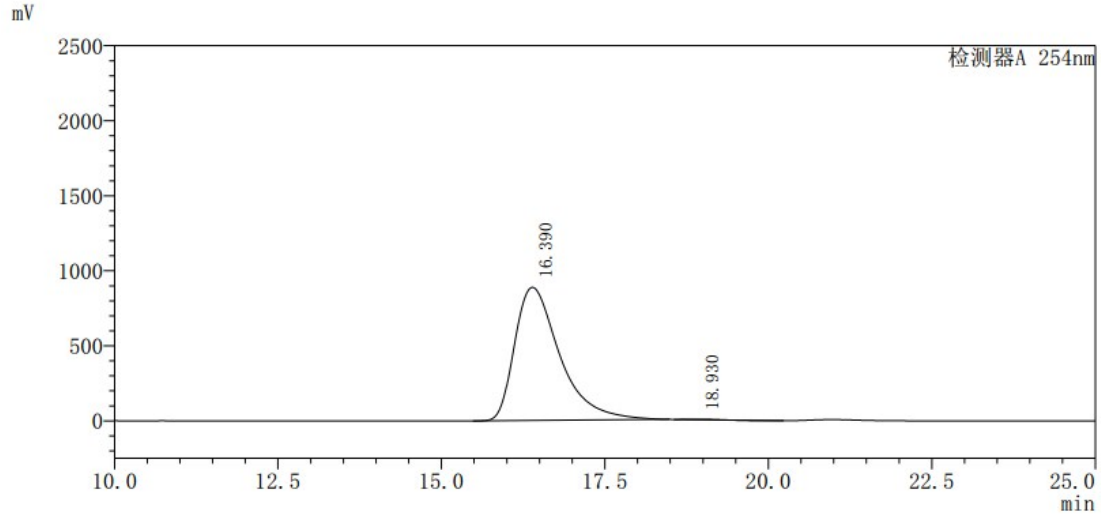
HPLC of 3n (racemic)



检测器A 254nm

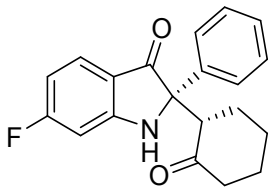
No.	Retention Time	Area	Height	Concentration
1	16.499	19523208	407016	48.875
2	19.060	20422361	371970	51.125
总计		39945569	778986	

HPLC of 3n (chiral)



检测器A 254nm

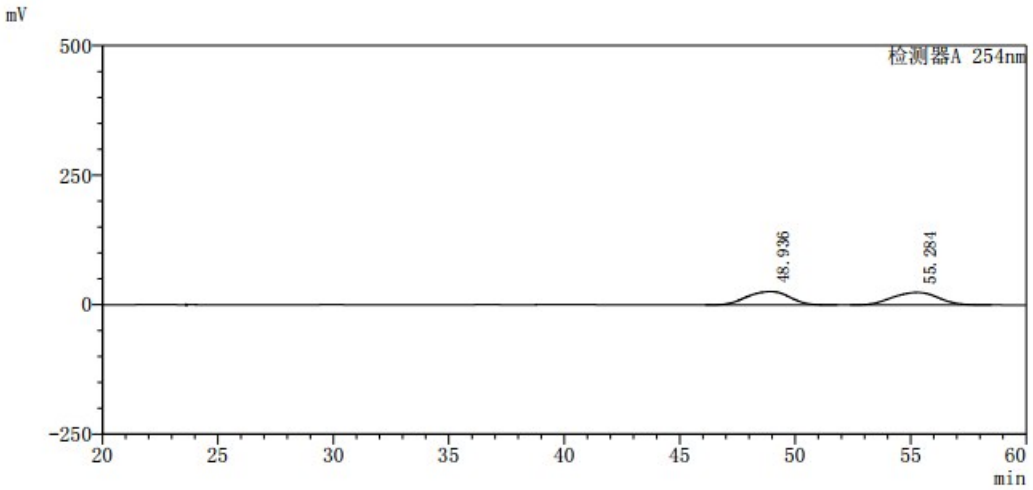
No.	Retention Time	Area	Height	Concentration
1	16.390	42592503	886776	99.855
2	18.930	62023	3358	0.145
总计		42654527	890134	



(S)-6-fluoro-2-((S)-2-oxocyclohexyl)-2-phenylindolin-3-one (3o)

White solid. 43% yield. m.p. 130-133 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 – 7.53 (m, 3H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 6.61 – 6.59 (m, 1H), 6.54 – 6.51 (m, 1H), 5.29 (s, 1H), 3.48 (dd, *J* = 13.4, 5.2 Hz, 1H), 2.40 – 2.22 (m, 2H), 2.07 – 1.88 (m, 3H), 1.67 – 1.57 (m, 2H), 1.50 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 198.8, 169.7, 168.0, 160.9 (d, *J* = 13.7 Hz), 137.2, 133.6, 130.2, 128.8, 128.5, 127.9, 127.1 (d, *J* = 12.2 Hz), 125.5, 117.8, 107.6 (d, *J* = 24.3 Hz), 98.4 (d, *J* = 26.0 Hz), 72.0, 58.5, 42.1, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 48.089 min, tRminor = 54.705 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{18}FNO_2$ $(M+Na)^+$: 346.1214; found: 346.1217.

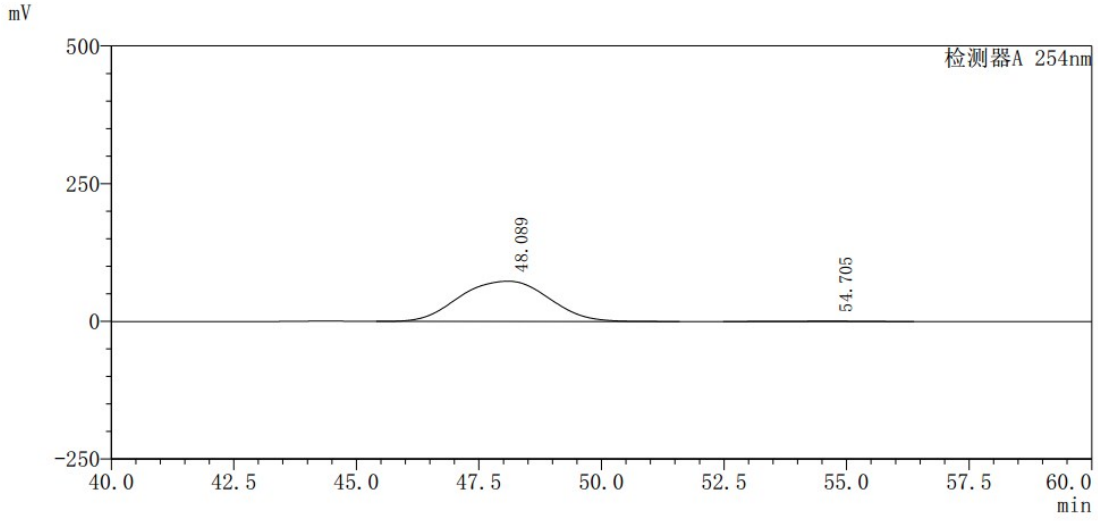
HPLC of 3o (racemic)



检测器A 254nm

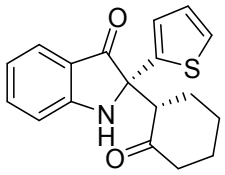
No.	Retention Time	Area	Height	Concentration
1	48.936	3354951	25879	49.894
2	55.284	3369240	24222	50.106
总计		6724192	50101	

HPLC of 3o (chiral)



检测器A 254nm

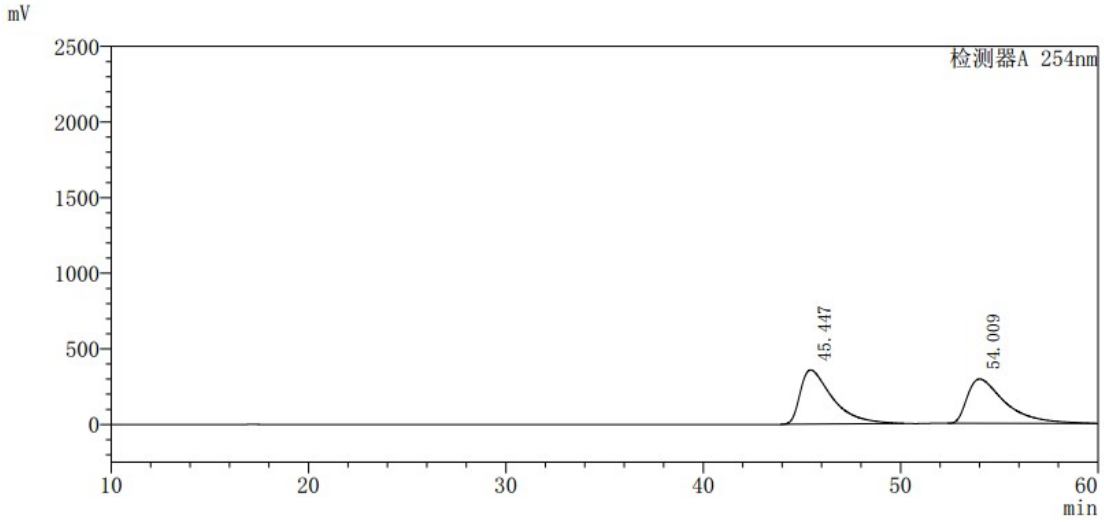
No.	Retention Time	Area	Height	Concentration
1	48.089	9242242	73141	98.957
2	54.705	97431	799	1.043
总计		9339674	73940	



(R)-2-((S)-2-oxocyclohexyl)-2-(thiophen-2-yl)indolin-3-one (3p)

Gray solid. 37% yield. m.p. 161-163 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.45 (t, *J* = 7.6 Hz, 1H), 7.18 (d, *J* = 5.0, 1H), 7.11 – 7.10 (m, 1H), 6.95 – 6.92 (m, 2H), 6.87 (t, *J* = 7.4 Hz, 1H), 5.19 (s, 1H), 3.35 (dd, *J* = 12.9, 5.1 Hz, 1H), 2.39 – 2.19 (m, 3H), 2.07 – 1.93 (m, 2H), 1.70 – 1.55 (m, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 199.5, 159.3, 142.6, 136.5, 127.3, 125.2, 124.9, 124.2, 120.7, 119.7, 112.1, 70.1, 59.0, 42.1, 28.4, 26.9, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 95:5, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 45.098 min, tRminor = 54.322 min. **HRMS** (EI): m/z: calcd for $C_{18}H_{17}NO_2S$ $(M+Na)^+$: 334.0872; found: 334.0876.

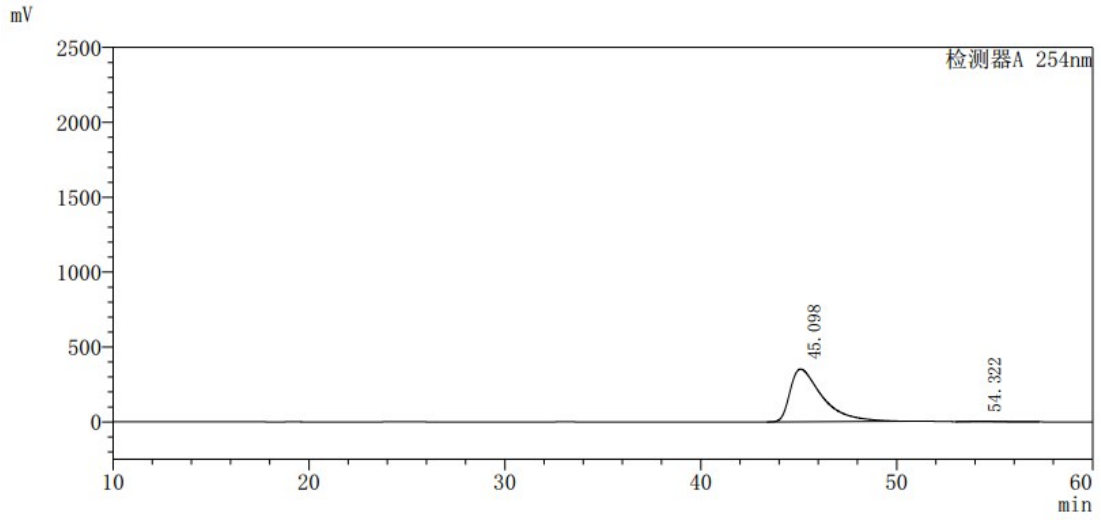
HPLC of 3p (racemic)



检测器A 254nm

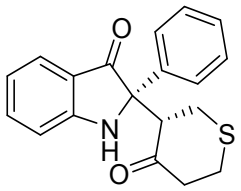
No.	Retention Time	Area	Height	Concentration
1	45.447	40658749	358833	50.906
2	54.009	39211092	292996	49.094
总计		79869841	651829	

HPLC of 3p (chiral)



检测器A 254nm

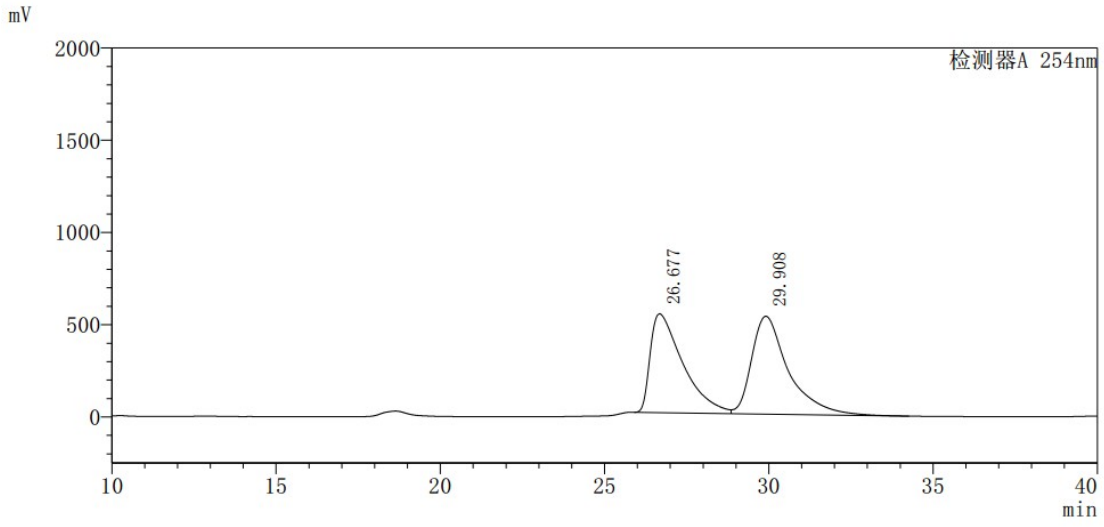
No.	Retention Time	Area	Height	Concentration
1	45.098	40117380	351500	99.101
2	54.322	364009	3505	0.899
总计		40481389	355005	



(S)-2-((S)-4-oxotetrahydro-2H-thiopyran-3-yl)-2-phenylindolin-3-one (3q)

Yellow solid. 67% yield. m.p. 103-105 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.59 – 7.55 (m, 3H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.34 (t, *J* = 7.4 Hz, 2H), 7.29 – 7.27 (m, 1H), 6.98 (d, *J* = 8.1 Hz, 1H), 6.86 (t, *J* = 7.4 Hz, 1H), 5.25 (s, 1H), 3.83 (t, *J* = 7.9 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.83 (d, *J* = 8.1 Hz, 2H), 2.77 – 2.70 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$) : δ 205.3, 199.5, 159.3, 136.5, 129.1, 128.2, 125.6, 125.2, 121.0, 119.8, 111.9, 71.5, 60.3, 44.3, 30.5, 29.4. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 26.790 min, tRminor = 29.713 min. **HRMS** (EI): m/z: calcd for $C_{19}H_{17}NO_2S$ $(M+Na)^+$: 346.0872; found: 346.0876.

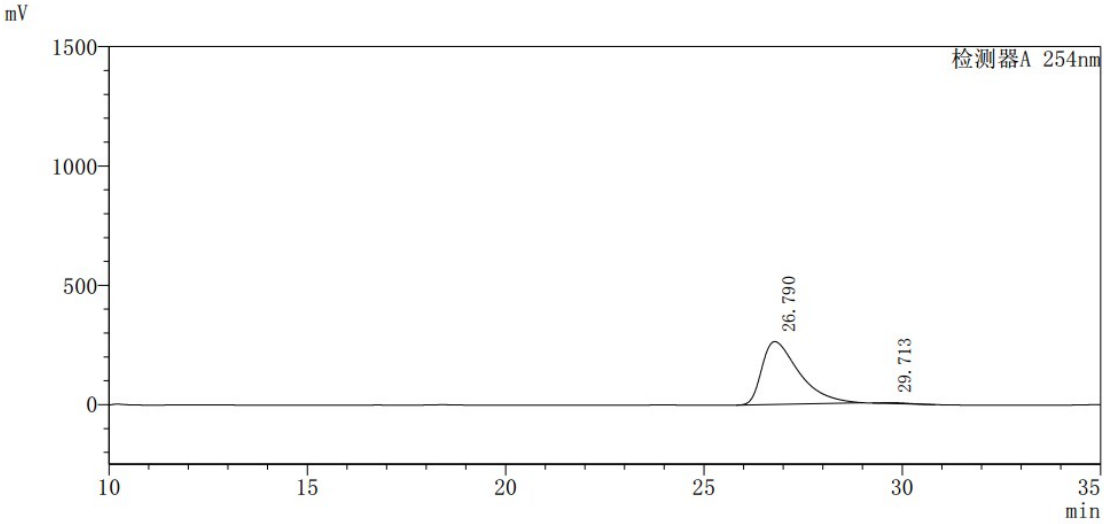
HPLC of 3q (racemic)



检测器A 254nm

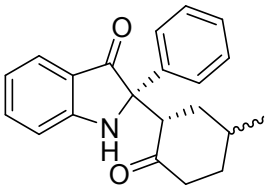
No.	Retention Time	Area	Height	Concentration
1	26.677	36918831	535484	47.177
2	29.908	41337303	530488	52.823
总计		78256134	1065972	

HPLC of 3q (chiral)



检测器A 254nm

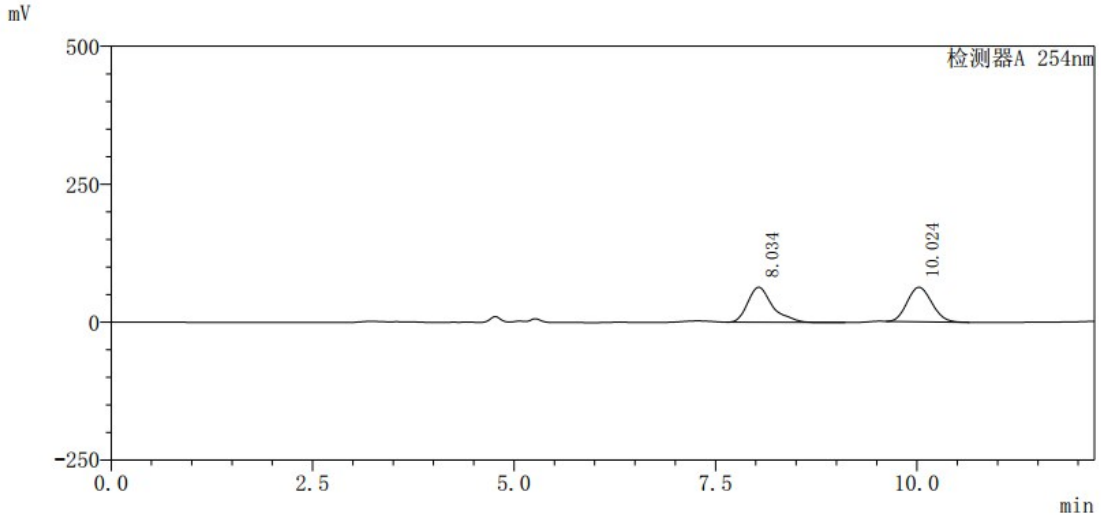
No.	Retention Time	Area	Height	Concentration
1	26.790	17192867	263260	99.045
2	29.713	165850	3465	0.955
总计		17358717	266725	



(2S)-2-((1S)-5-methyl-2-oxocyclohexyl)-2-phenylindolin-3-one (3r)

Yellow solid. 60% yield. m.p. 190-192 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 – 7.51 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.14 (s, 1H), 3.72 (dd, *J* = 13.2, 5.5 Hz, 1H), 2.51 – 2.45 (m, 1H), 2.25 – 2.13 (m, 2H), 1.90 – 1.74 (m, 3H), 1.68 – 1.65 (m, 1H), 1.15 (d, *J* = 7.1 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.5, 200.7, 159.6, 137.4, 136.3, 128.9, 127.8, 125.4, 125.0, 121.4, 119.4, 111.8, 71.5, 53.3, 37.5, 33.5, 31.6, 26.8, 17.5. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 8.290 min, tRminor = 10.052 min. **HRMS** (EI): m/z: calcd for $C_{21}H_{21}NO_2$ $(M+Na)^+$: 342.1465; found: 342.1465.

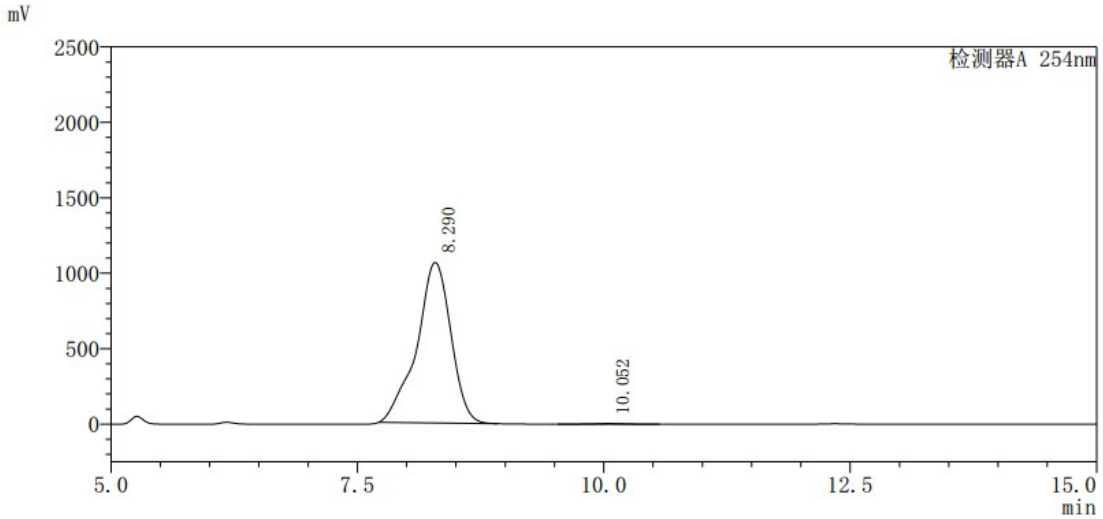
HPLC of 3r (racemic)



检测器A 254nm

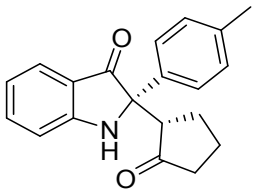
No.	Retention Time	Area	Height	Concentration
1	8.034	1359993	63437	50.721
2	10.024	1321315	62361	49.279
总计		2681307	125798	

HPLC of 3r (chiral)



检测器A 254nm

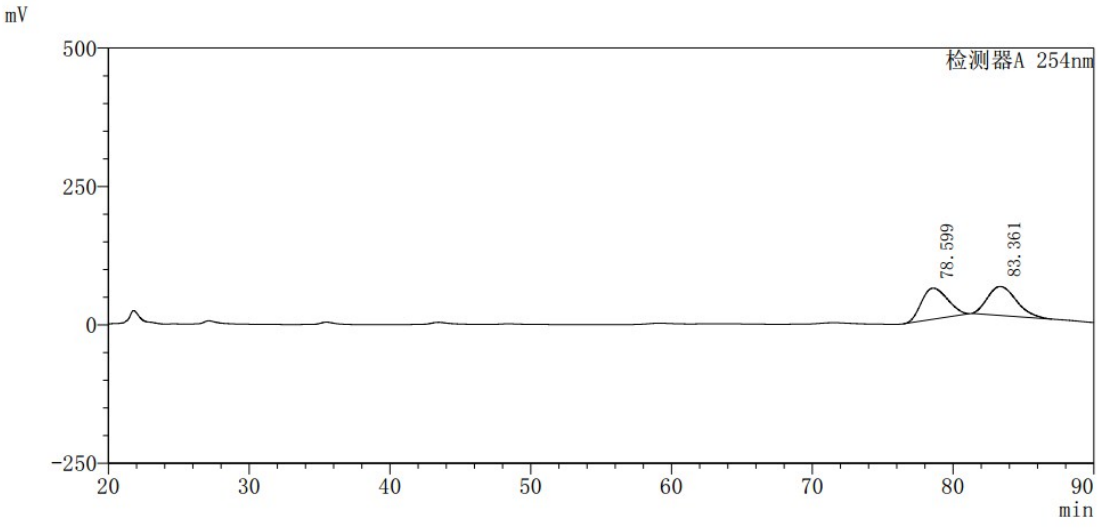
No.	Retention Time	Area	Height	Concentration
1	8.290	25800373	1064084	99.563
2	10.052	113355	4939	0.437
总计		25913728	1069023	



(S)-2-((S)-2-oxocyclopentyl)-2-(p-tolyl)indolin-3-one (3s)

Yellow solid. 50% yield. m.p. 79-80 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.61 (d, *J* = 7.5 Hz, 1H), 7.45 – 7.40 (m, 3H), 7.12 (d, *J* = 8.0 Hz, 2H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.77 (s, 1H), 3.13 – 3.10 (m, 1H), 2.29 – 2.19 (m, 5H), 2.05 – 1.92 (m, 2H), 1.83 – 1.70 (m, 2H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 215.9, 199.5, 158.8, 136.6, 135.8, 133.0, 128.3, 125.1, 124.2, 119.8, 118.4, 111.1, 99.0, 69.8, 55.0, 37.8, 24.9, 19.9, 19.7. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 97:3, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 78.841 min, tRminor = 83.310 min. **HRMS** (EI): m/z: calcd for $C_{20}H_{19}NO_2$ $(M+Na)^+$: 328.1308; found: 328.1310.

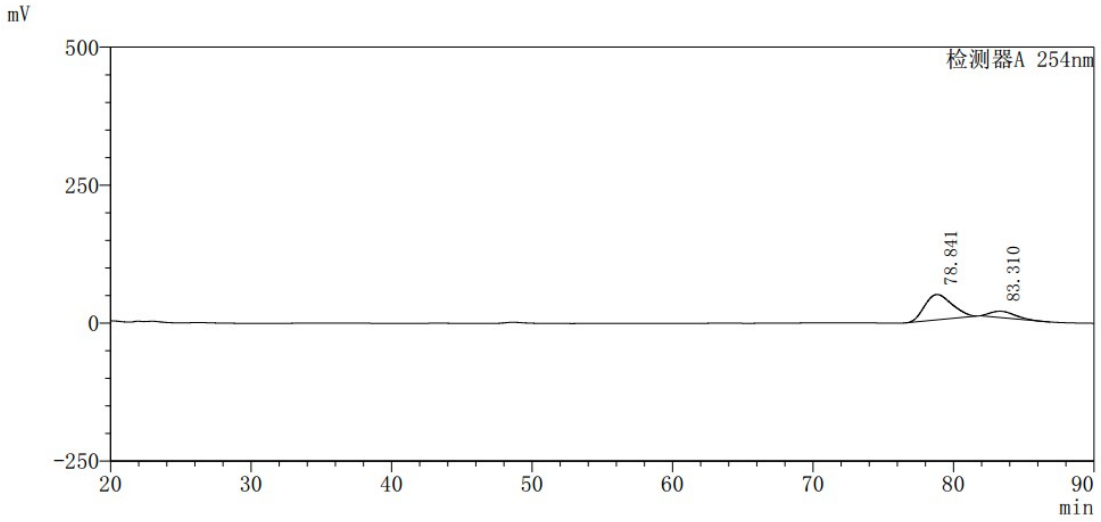
HPLC of 3s (racemic)



检测器A 254nm

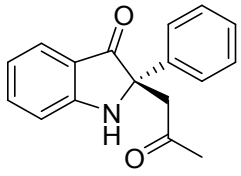
No.	Retention Time	Area	Height	Concentration
1	78.599	7270004	56250	49.401
2	83.361	7446248	52218	50.599
总计		14716252	108467	

HPLC of 3s (chiral)



检测器A 254nm

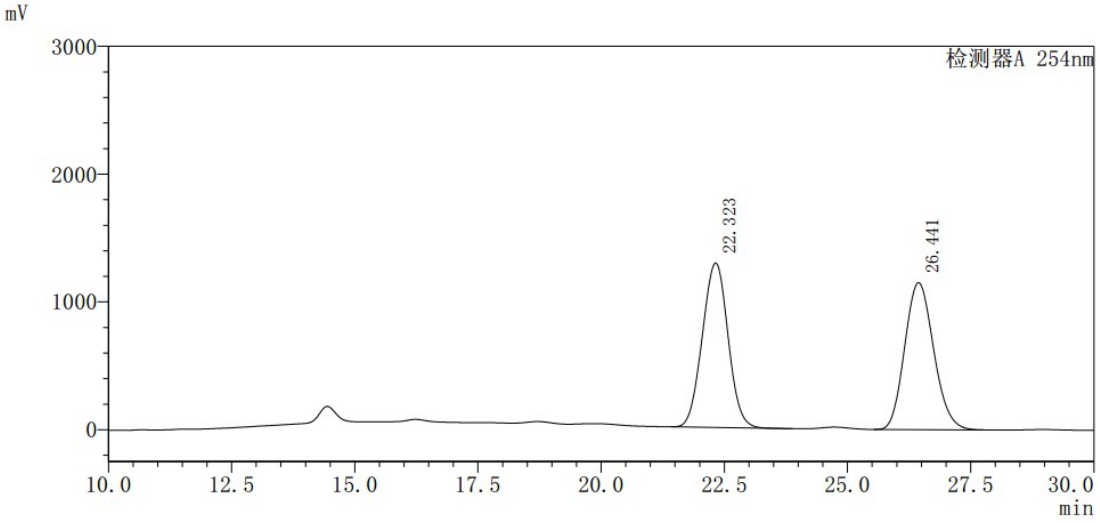
No.	Retention Time	Area	Height	Concentration
1	78.841	6227537	45845	81.686
2	83.310	1396237	11381	18.314
总计		7623774	57226	



(S)-2-(2-oxopropyl)-2-phenylindolin-3-one (3t)[5]

Yellow solid. 49% yield. m.p. 103-104 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.55 – 7.53 (m, 3H), 7.48 (t, *J* = 7.7 Hz, 1H), 7.31 (t, *J* = 7.7 Hz, 2H), 7.26 – 7.23 (m, 1H), 6.95 (d, *J* = 8.3 Hz, 1H), 6.80 (t, *J* = 7.4 Hz, 1H), 6.10 (s, 1H), 3.72 (d, *J* = 17.4 Hz, 1H), 2.72 (d, *J* = 17.4 Hz, 1H), 2.10 (s, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 206.7, 200.3, 160.1, 137.9, 137.7, 128.7, 127.7, 125.6, 125.4, 119.0, 118.3, 112.0, 69.0, 49.5, 31.4. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 25.577 min, tRminor = 21.759 min

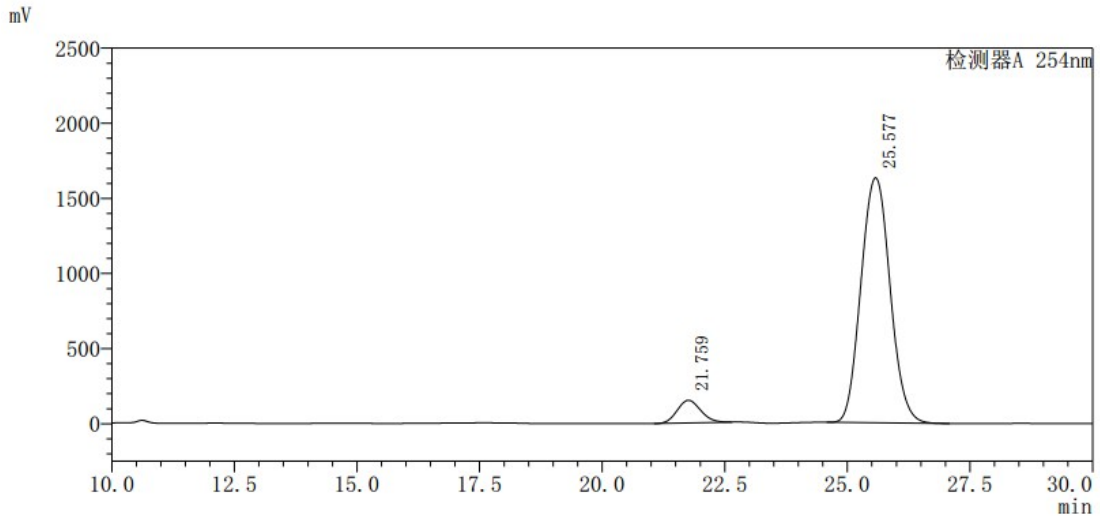
HPLC of 3t (racemic)



检测器A 254nm

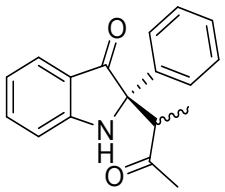
No.	Retention Time	Area	Height	Concentration
1	22.323	46844303	1288015	49.828
2	26.441	47167532	1151008	50.172
总计		94011835	2439023	

HPLC of 3t (chiral)



检测器A 254nm

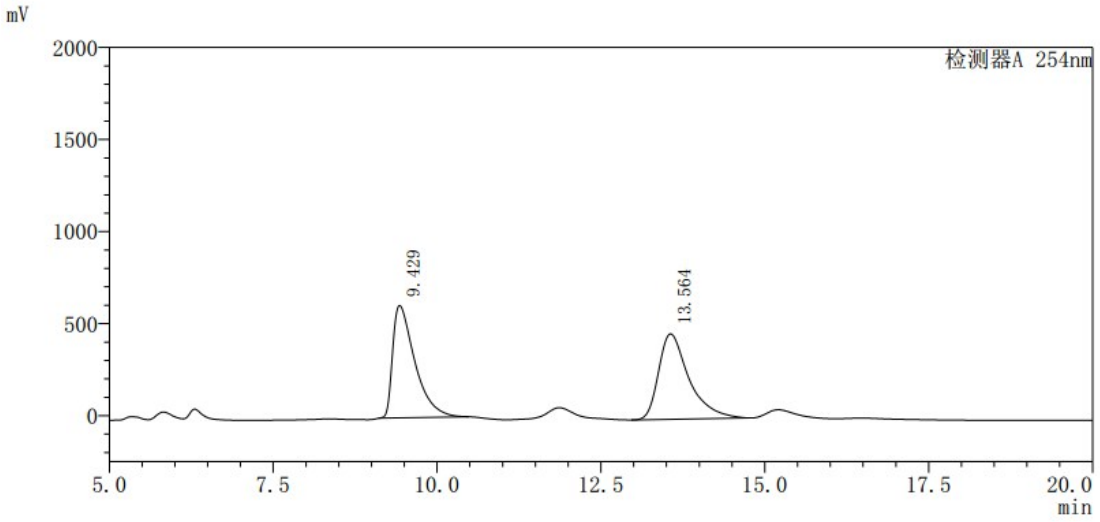
No.	Retention Time	Area	Height	Concentration
1	21.759	5012228	150776	6.907
2	25.577	67559714	1631292	93.093
总计		72571941	1782067	



(S)-2-(3-oxobutan-2-yl)-2-phenylindolin-3-one (3u)[5]

Yellow solid. 64% yield. m.p. 127-129 °C. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.65 (d, *J* = 7.4 Hz, 2H), 7.53 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 1H), 7.33 (t, *J* = 7.6 Hz, 2H), 7.28 – 7.26 (m, 1H), 6.97 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 5.35 (s, 1H), 3.73 (q, *J* = 7.2 Hz, 1H), 2.10 (s, 3H), 1.05 (d, *J* = 7.2 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.7, 201.1, 160.5, 137.7, 137.3, 128.7, 127.9, 125.9, 125.1, 120.7, 119.7, 112.7, 72.68, 53.2, 30.5, 12.2. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 9.293 min, tRminor = 13.654 min.

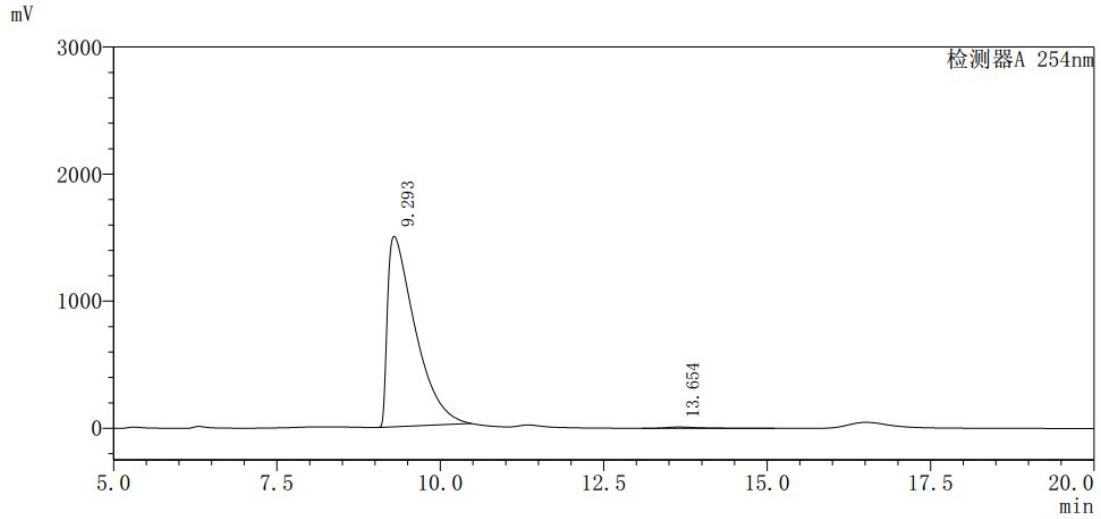
HPLC of 3u (racemic)



检测器A 254nm

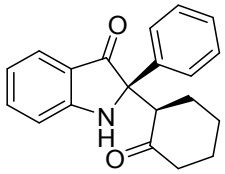
No.	Retention Time	Area	Height	Concentration
1	9.429	14429562	610751	49.135
2	13.564	14937790	464114	50.865
总计		29367352	1074865	

HPLC of 3u (chiral)



检测器A 254nm

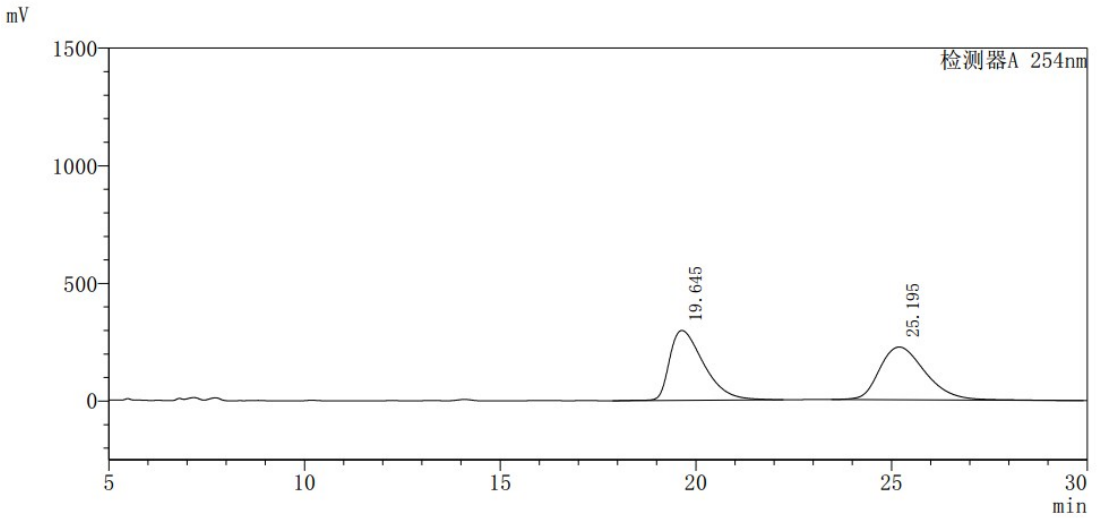
No.	Retention Time	Area	Height	Concentration
1	9.293	44224869	1498729	99.150
2	13.654	379076	10557	0.850
总计		44603944	1509287	



(R)-2-((R)-2-oxocyclohexyl)-2-phenylindolin-3-one (4a)

Yellow solid. 56% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ7.59 –7.55 (m, 3H), 7.44 (t, *J* = 7.6 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26 – 7.24 (m, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.84 (t, *J* = 7.3 Hz, 1H), 5.08 (s, 1H), 3.50 (dd, *J* = 13.3, 5.0 Hz, 1H), 2.39 – 2.30 (m, 2H), 2.05 – 2.03 (m, 1H), 1.97 – 1.87 (m, 2H), 1.67 – 1.57 (m, 2H), 1.53 – 1.47 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$) δ 208.0, 200.7, 159.4, 137.5, 136.2, 128.78, 127.8, 125.6, 125.0, 121.4, 119.4, 111.8, 71.3, 58.6, 42.1, 28.4, 26.7, 25.2. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak IA, hexane/isopropanol = 91:9, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 25.153 min, tRminor = 20.213 min.

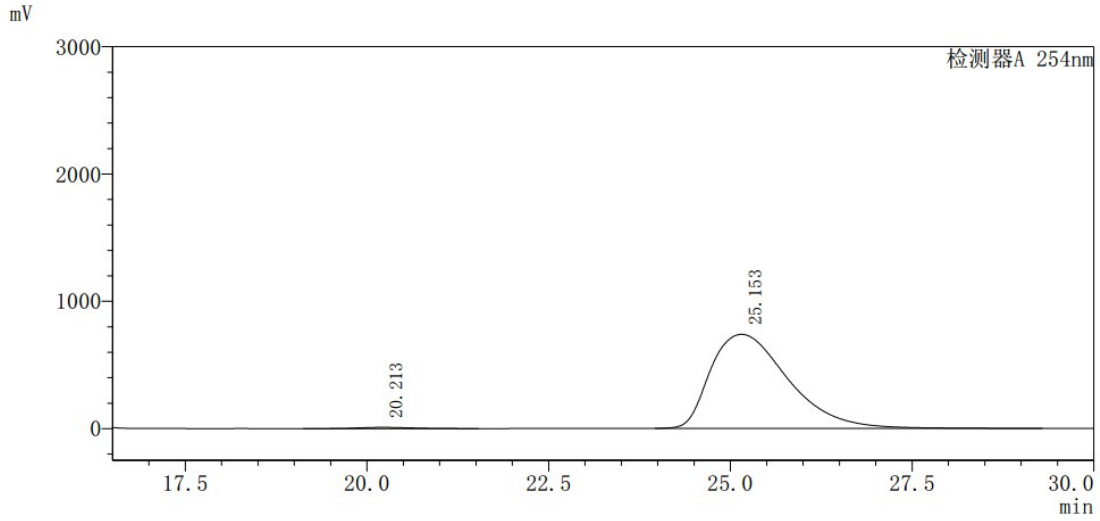
HPLC of 4a (racemic)



检测器A 254nm

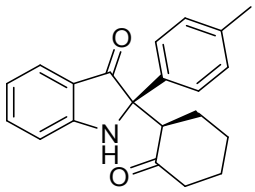
No.	Retention Time	Area	Height	Concentration
1	19.645	18044003	296994	49.611
2	25.195	18326675	224361	50.389
总计		36370678	521355	

HPLC of 4a (chiral)



检测器A 254nm

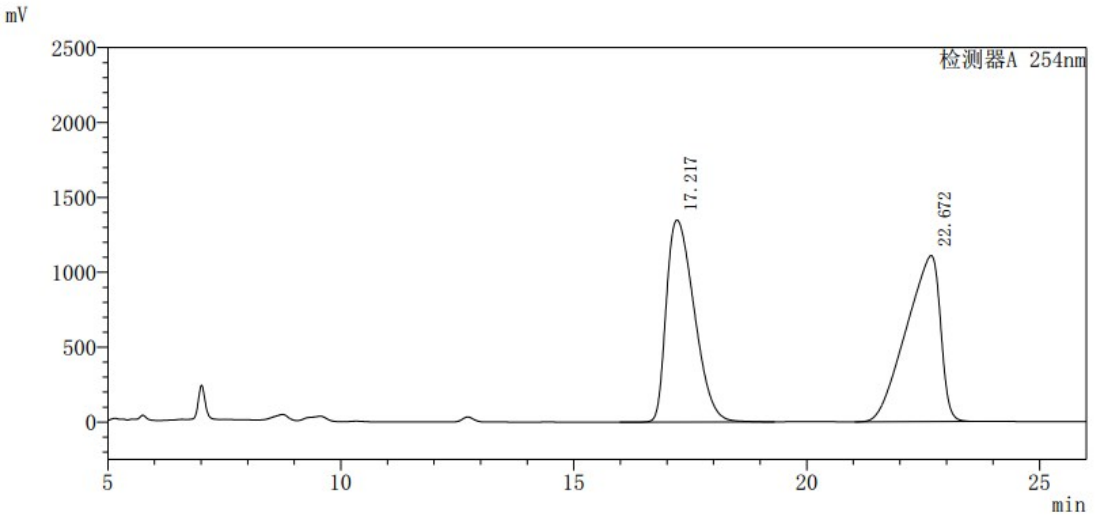
No.	Retention Time	Area	Height	Concentration
1	20.213	482659	9555	0.870
2	25.153	55024282	738793	99.130
总计		55506941	748349	



(R)-2-((R)-2-oxocyclohexyl)-2-(p-tolyl)indolin-3-one (4b)

Yellow solid. 62% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.41 (m, 3H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.94 (d, *J* = 8.2 Hz, 1H), 6.82 (t, *J* = 7.4 Hz, 1H), 5.00 (s, 1H), 3.47 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.38 – 2.29 (m, 5H), 2.04 – 1.87 (m, 3H), 1.66 – 1.46 (m, 3H). **^{13}C NMR** (150 MHz, CDCl3): δ 208.1, 200.8, 159.5, 137.6, 136.2, 134.4, 129.5, 125.5, 125.0, 121.5, 119.3, 111.8, 71.2, 58.5, 42.1, 28.4, 26.7, 25.2, 20.9. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 22.910 min, tRminor = 17.401 min.

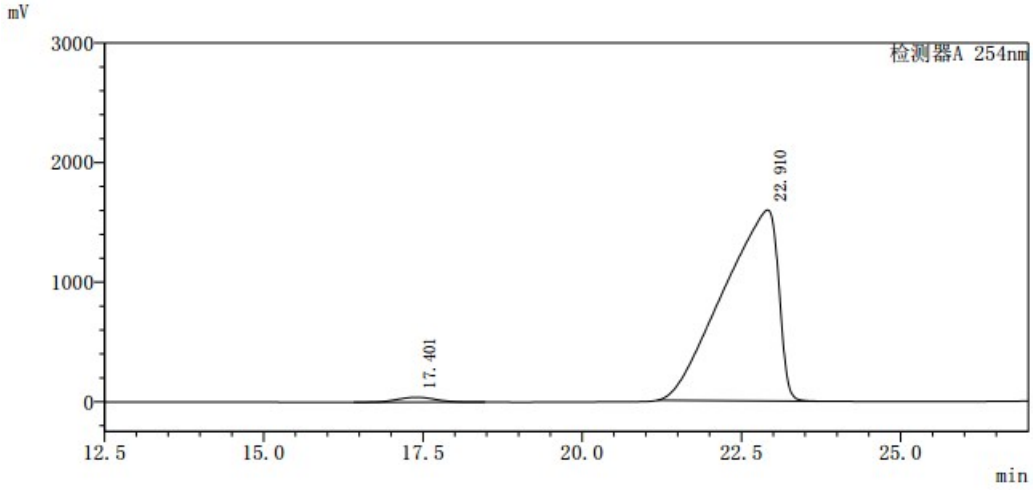
HPLC of 4b (racemic)



检测器A 254nm

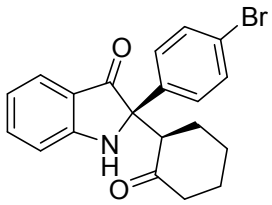
No.	Retention Time	Area	Height	Concentration
1	17.217	56322635	1349526	49.894
2	22.672	56562464	1107999	50.106
总计		112885099	2457525	

HPLC of 4b (chiral)



检测器A 254nm

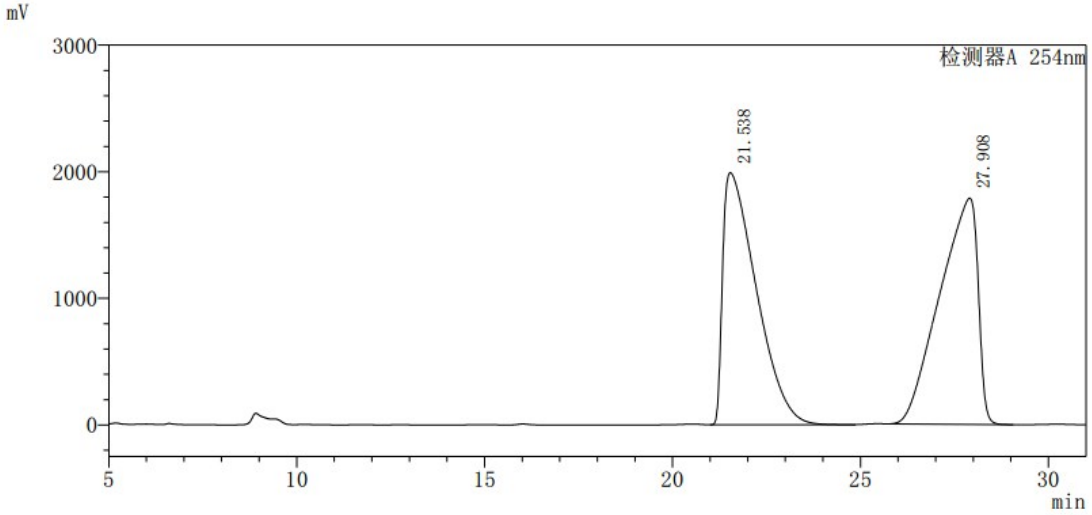
No.	Retention Time	Area	Height	Concentration
1	17.401	1700564	40869	1.734
2	22.910	96377881	1597237	98.266
总计		98078446	1638107	



(R)-2-(4-bromophenyl)-2-((R)-2-oxocyclohexyl)indolin-3-one (4c)

Yellow solid. 54% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.56 (d, *J* = 7.6 Hz, 1H), 7.48 – 7.42 (m, 5H), 6.93 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.3 Hz, 1H), 5.24 (s, 1H), 3.39 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.38 – 2.24 (m, 2H), 2.09 – 1.88 (m, 3H), 1.65 – 1.55 (m, 2H), 1.50 – 1.43 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 200.5, 159.4, 136.8, 136.5, 131.8, 127.6, 125.0, 122.0, 121.2, 119.5, 111.9, 70.9, 58.4, 42.1, 28.3, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 91:9, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 27.287 min, tRminor = 22.542 min.

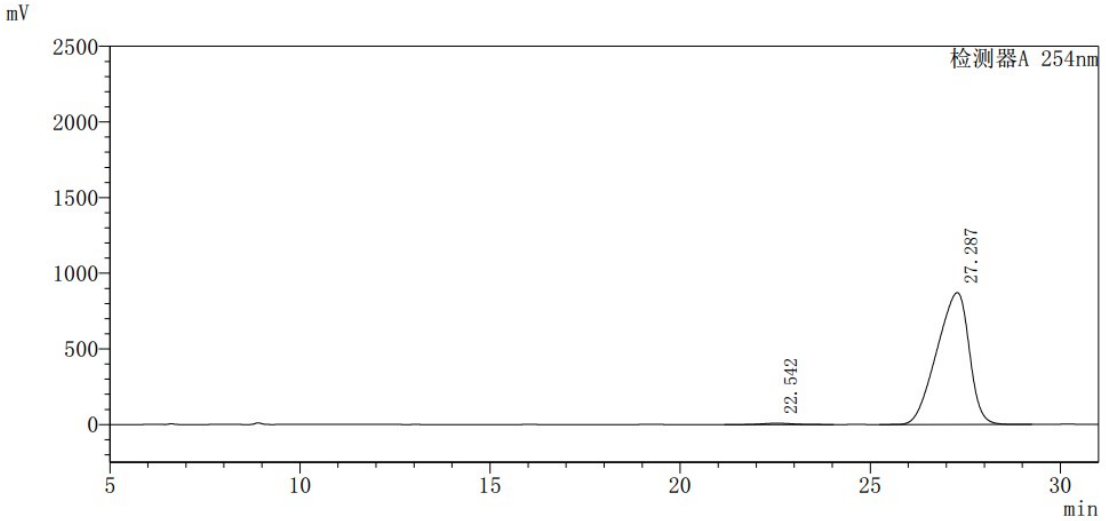
HPLC of 4c (racemic)



检测器A 254nm

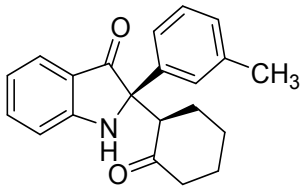
No.	Retention Time	Area	Height	Concentration
1	21.538	123665438	1990971	49.394
2	27.908	126699888	1788153	50.606
总计		250365326	3779125	

HPLC of 4c (chiral)



检测器A 254nm

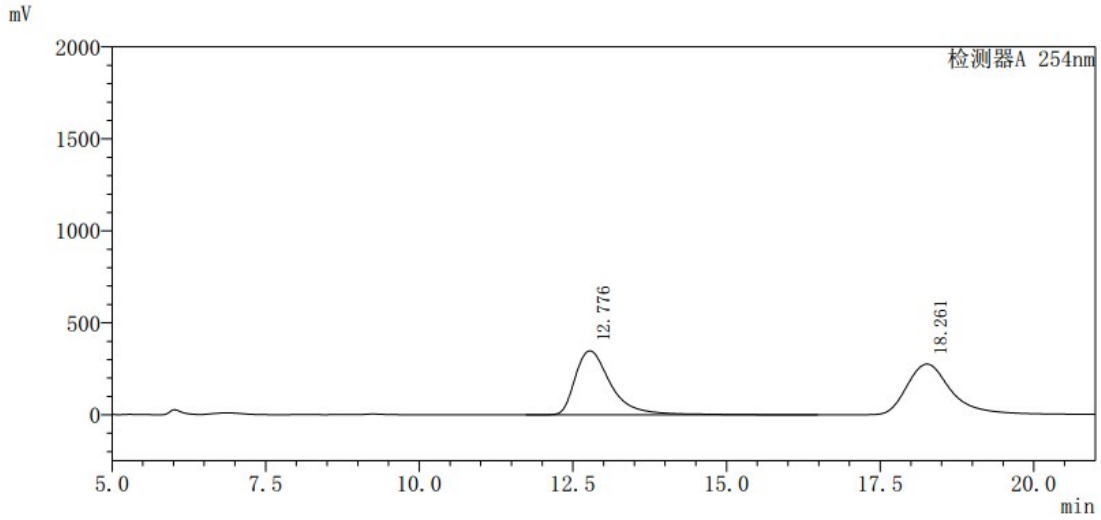
No.	Retention Time	Area	Height	Concentration
1	22.542	459773	8497	0.882
2	27.287	51691224	872039	99.118
总计		52150997	880536	



(R)-2-((R)-2-oxocyclohexyl)-2-(m-tolyl)indolin-3-one (4d)

Yellow solid. 61% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 (d, *J* = 7.6 Hz, 1H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.36 – 7.33 (m, 2H), 7.19 (t, *J* = 7.7 Hz, 1H), 7.06 (d, *J* = 7.3 Hz, 1H), 6.96 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.08 (s, 1H), 3.50 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.39 – 2.29 (m, 5H), 2.04 – 2.02 (m, 1H), 1.94 – 1.88 (m, 2H), 1.66 – 1.57 (m, 2H), 1.53 – 1.46 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 200.9, 159.5, 138.5, 137.4, 136.2, 128.6, 128.6, 126.1, 125.0, 122.6, 121.5, 119.3, 111.8, 71.4, 58.8, 42.1, 28.4, 26.7, 25.2, 21.7. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 18.433 min, tRminor = 12.861 min.

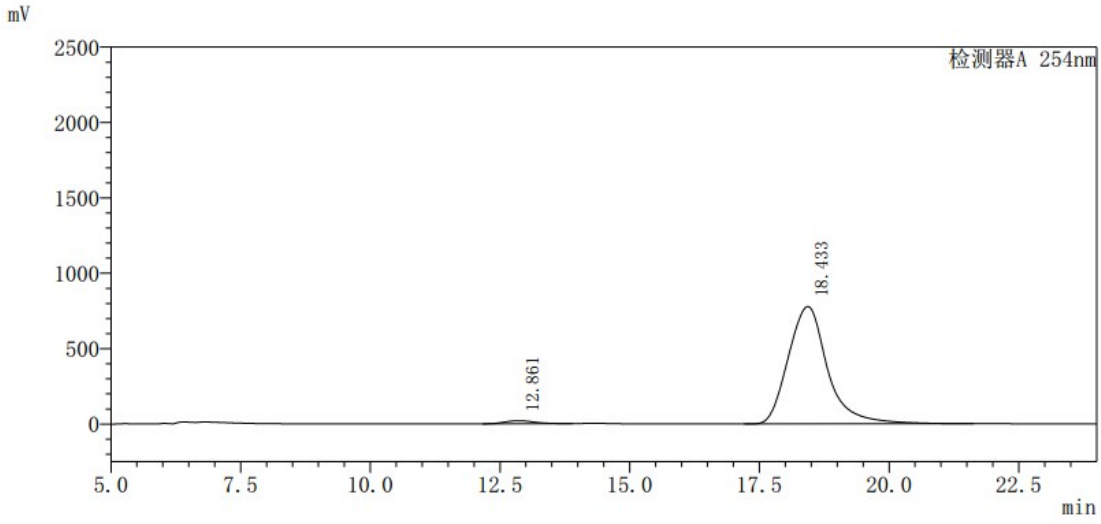
HPLC of 4d (racemic)



检测器A 254nm

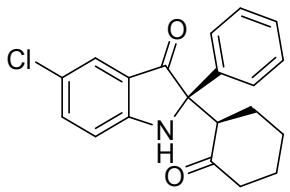
No.	Retention Time	Area	Height	Concentration
1	12.776	14059500	347515	49.855
2	18.261	14141008	275257	50.145
总计		28200507	622772	

HPLC of 4d (chiral)



检测器A 254nm

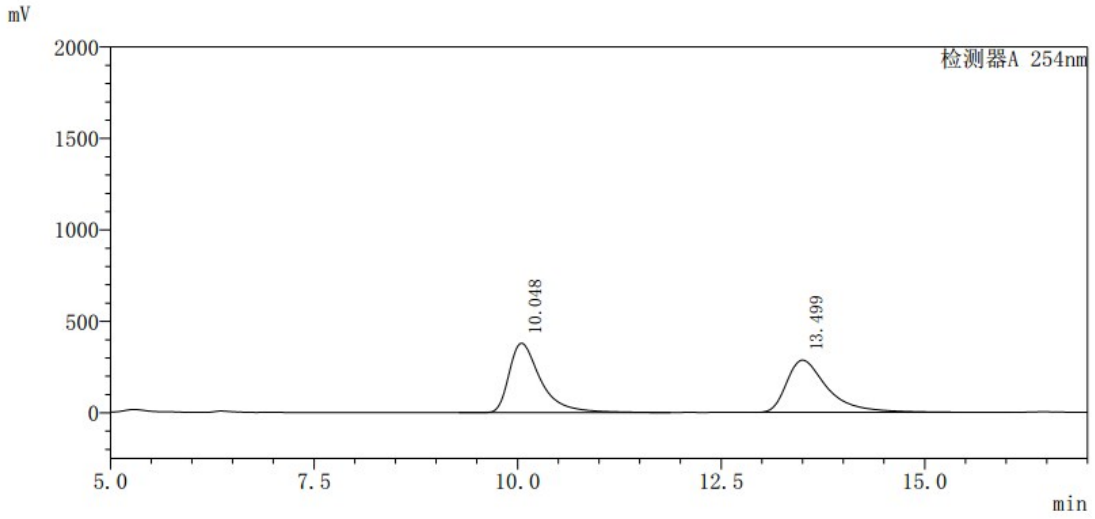
No.	Retention Time	Area	Height	Concentration
1	12.861	784491	19771	1.872
2	18.433	41124616	778284	98.128
总计		41909107	798054	



(R)-5-chloro-2-((R)-2-oxocyclohexyl)-2-phenylindolin-3-one (4e)

Yellow solid. 45% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.52 – 7.51 (m, 3H), 7.37 (dd, *J* = 8.6 Hz, 2.0 Hz, 1H), 7.32 (t, *J* = 7.6 Hz, 2H), 7.27 (d, *J* = 7.3 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 1H), 5.18 (s, 1H), 3.52 (dd, *J* = 13.3, 5.1 Hz, 1H), 2.39 – 2.29 (m, 2H), 2.05 – 2.03 (m, 1H), 1.91 – 1.88 (m, 2H), 1.66 – 1.57 (m, 2H), 1.51 – 1.44 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.0, 199.6, 157.7, 136.9, 136.0, 128.9, 128.0, 125.4, 124.6, 124.4, 122.6, 113.0, 72.2, 58.9, 42.0, 28.4, 26.7, 25.1. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 85:15, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 13.368 min, tRminor = 9.987 min

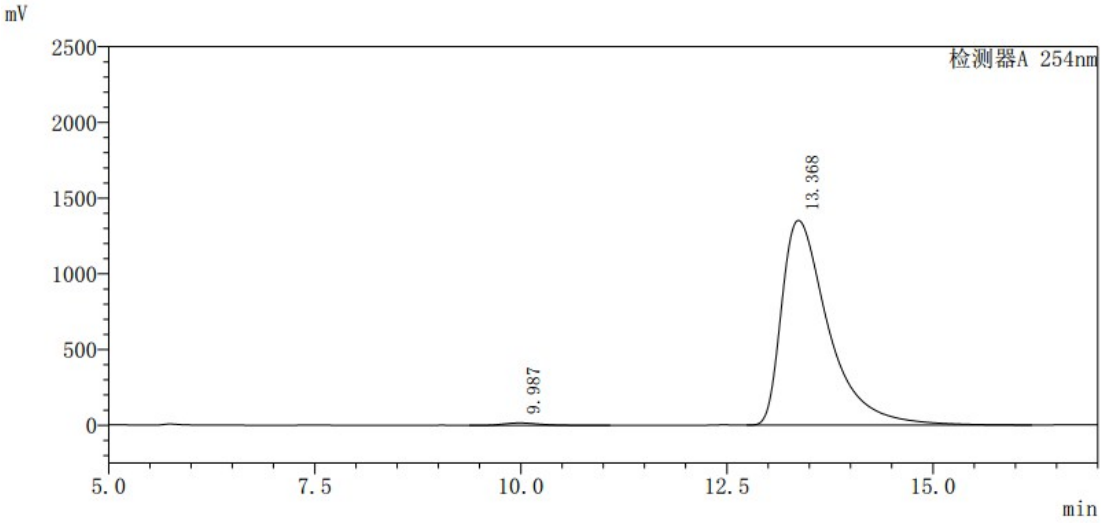
HPLC of 4e (racemic)



检测器A 254nm

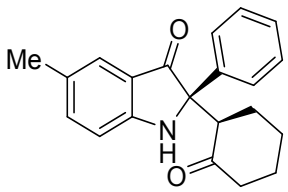
No.	Retention Time	Area	Height	Concentration
1	10.048	10306695	379298	50.736
2	13.499	10007725	285536	49.264
总计		20314420	664833	

HPLC of 4e (chiral)



检测器A 254nm

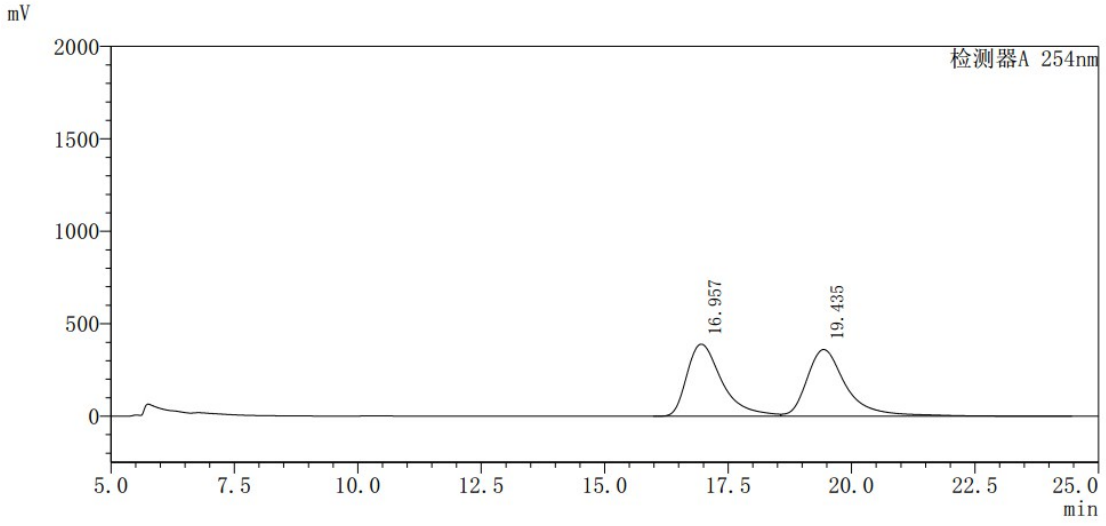
No.	Retention Time	Area	Height	Concentration
1	9.987	480681	16013	0.891
2	13.368	53481587	1352850	99.109
总计		53962268	1368862	



(R)-5-methyl-2-((R)-2-oxocyclohexyl)-2-phenylindolin-3-one (4f)

Yellow solid. 50% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.54 (d, *J* = 7.7 Hz, 2H), 7.37 (s, 1H), 7.30 (t, *J* = 7.7 Hz, 2H), 7.28 – 7.23 (m, 2H), 6.89 (d, *J* = 8.2 Hz, 1H), 4.93 (s, 1H), 3.51 (dd, *J* = 13.3, 5.2 Hz, 1H), 2.38 – 2.88 (m, 2H), 2.27 (s, 3H), 2.04 – 2.02 (m, 1H), 1.94 – 1.87 (m, 2H), 1.66 – 1.56 (m, 2H), 1.54 – 1.47 (m, 1H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.1, 201.0, 157.9, 137.7, 137.6, 128.9, 128.8, 127.7, 125.5, 124.5, 121.6, 111.8, 71.8, 58.6, 42.1, 28.4, 26.7, 25.2, 20.6. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 90:10, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 19.490 min, tRminor = 17.006 min.

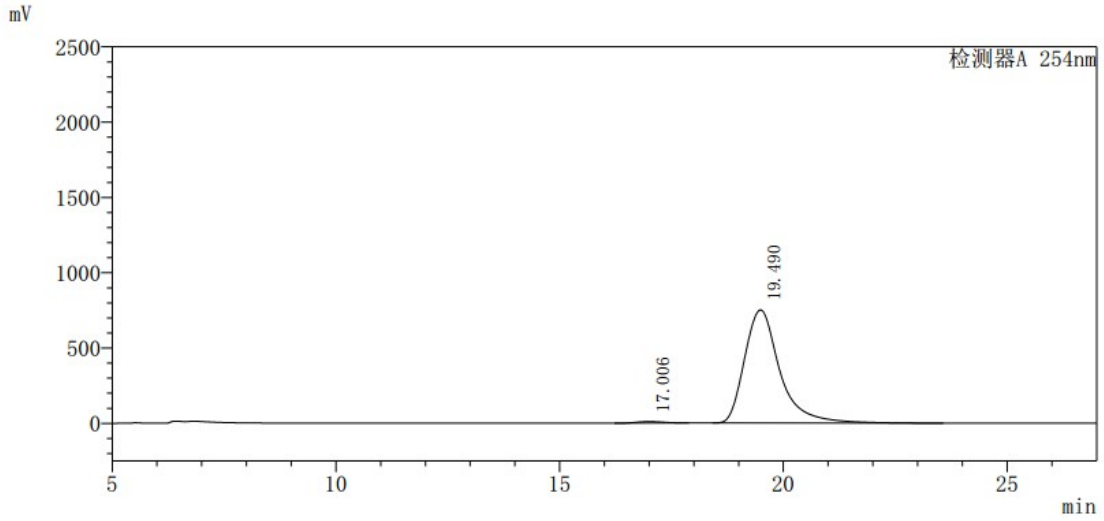
HPLC of 4f (racemic)



检测器A 254nm

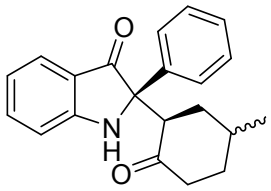
No.	Retention Time	Area	Height	Concentration
1	16.957	19260171	389722	49.019
2	19.435	20030925	360928	50.981
总计		39291095	750650	

HPLC of 4f (chiral)



检测器A 254nm

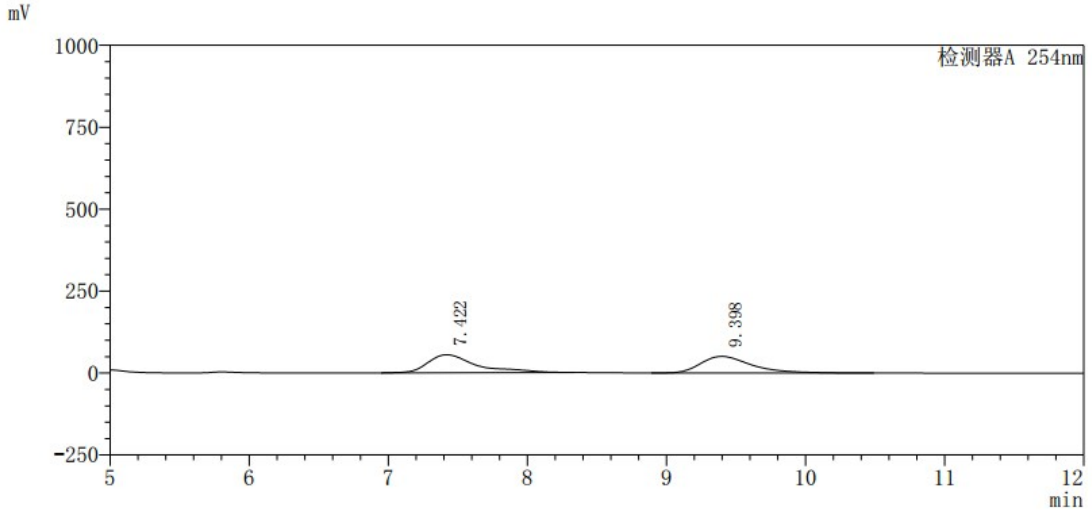
No.	Retention Time	Area	Height	Concentration
1	17.006	439967	10421	1.055
2	19.490	41282620	750946	98.945
总计		41722588	761368	



(2R)-2-((1R)-5-methyl-2-oxocyclohexyl)-2-phenylindolin-3-one (4g)

Yellow solid. 62% yield. **^{1}H NMR** (600 MHz, $CDCl_3$): δ 7.57 – 7.51 (m, 3H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.27 – 7.24 (m, 1H), 6.96 (d, *J* = 8.1 Hz, 1H), 6.83 (t, *J* = 7.4 Hz, 1H), 5.18 (s, 1H), 3.73 (dd, *J* = 13.2, 5.5 Hz, 1H), 2.51 – 2.45 (m, 1H), 2.24 – 2.12 (m, 2H), 1.90 – 1.64 (m, 4H), 1.15 (d, *J* = 7.0 Hz, 3H). **^{13}C NMR** (150 MHz, $CDCl_3$): δ 208.6, 200.8, 159.6, 137.4, 136.3, 128.9, 127.8, 125.4, 125.1, 121.3, 119.4, 111.8, 71.5, 53.4, 37.5, 33.5, 31.6, 26.8, 17.5. The Enantiomeric excess (ee) was determined by HPLC (Daicel Chiralpak AD-H, hexane/isopropanol = 80:20, flow rate 1.0 mL/min, λ = 254 nm), tRmajor = 9.301 min, tRminor = 7.382 min.

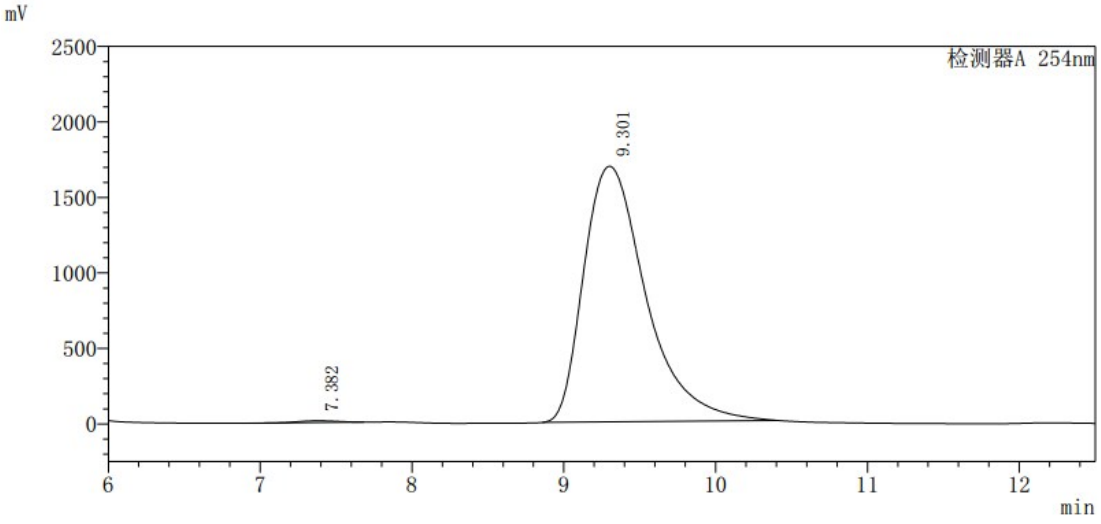
HPLC of 4g (racemic)



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.422	1329384	54699	50.738
2	9.398	1290694	50746	49.262
总计		2620078	105445	

HPLC of 4g (chiral)



检测器A 254nm

No.	Retention Time	Area	Height	Concentration
1	7.382	234800	12368	0.485
2	9.301	48217904	1693016	99.515
总计		48452703	1705384	

7. References

(1) Gao, Y.-D.; Zhu, W.-Y.; Yin, L.; Dong, B.; Fu, J.-J.; Ye, Z.-W.; Xue, F.-T.; Jiang, C. Palladium-catalyzed direct C2-arylation of free (N-H) indoles via norbornene-mediated regioselective CH activation. *Tetrahedron Lett*. **2017**, *58*, 2213 - 2216.

(2) Cheng, Y.-N.; Xie, G.-Y.; Sun, S.-J.; You, X.-F. A Practical Synthesis of 3-{[4-(2,6-Dichlorophenyl)piperidin-1-yl]-methyl}-2-(thiophen-2-yl)-1H-indole as a New Ligand for Opioid Receptor Like 1 Receptor. *Chinese Journal of Organic Chemistry*. **2013**, *33*, 630 - 633.

(3) Ling, K.-Q. Facile Synthesis of 2-Aryl-3H-indol-3-ones via Singlet Oxygenation of 2-Arylindoles. *Synth. Commun*. **1995**, *25*, 3831 - 3835.

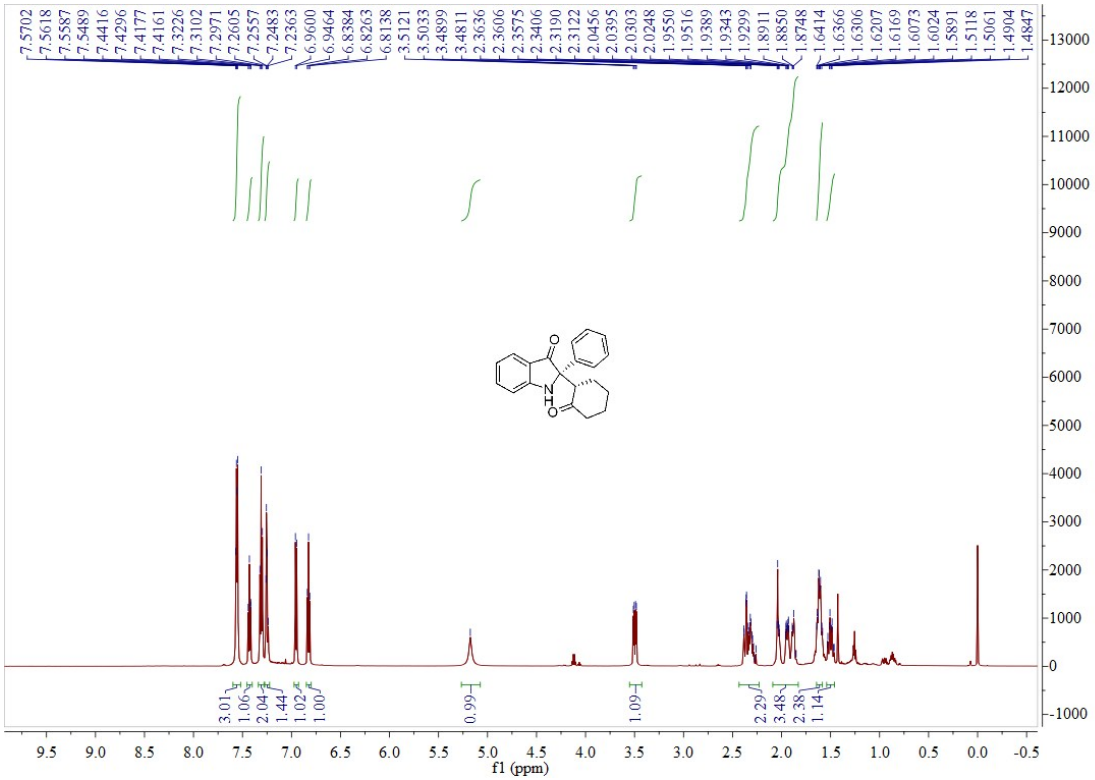
(4) Huang, H.; Cai, J.; Ji, X.; Xiao, F.; Chen, Y.; Deng, G.-J. Internal Oxidant-Triggered Aerobic Oxygenation and Cyclization of Indoles under Copper Catalysis. *Angew. Chem., Int. Ed*. **2016**, *55*, 307 – 311.

(5) Ding, X.; Dong, C.-L.; Guan, Z.; He, Y.-H. Concurrent Asymmetric Reactions Combining Photocatalysis and Enzyme Catalysis: Direct Enantioselective Synthesis of 2,2-Disubstituted Indol-3-ones from 2-Arylindoles. *Angew. Chem. Int. Ed.* **2019**, *58*, 118 - 124.

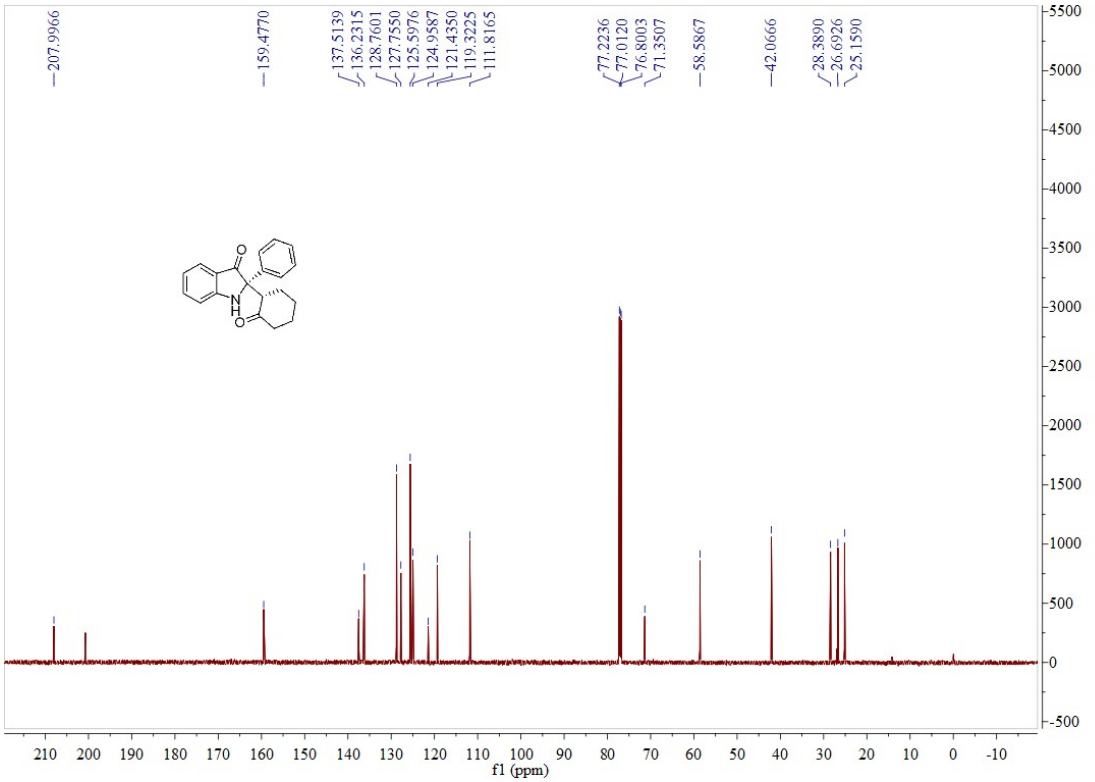
(6) (a) List, B.; Lerner, R. A.; Barbas III, C. F. Proline-Catalyzed Direct Asymmetric Aldol Reactions. *J. Am. Chem. Soc*. **2000**, *122*, 2395 - 2396. (b) List, B. Enamine Catalysis Is a Powerful Strategy for the Catalytic Generation and Use of Carbanion Equivalents. *Acc. Chem. Res*. **2004**, *37*, 548 - 557.

8. ^{1}H NMR and ^{13}C NMR spectra of the products

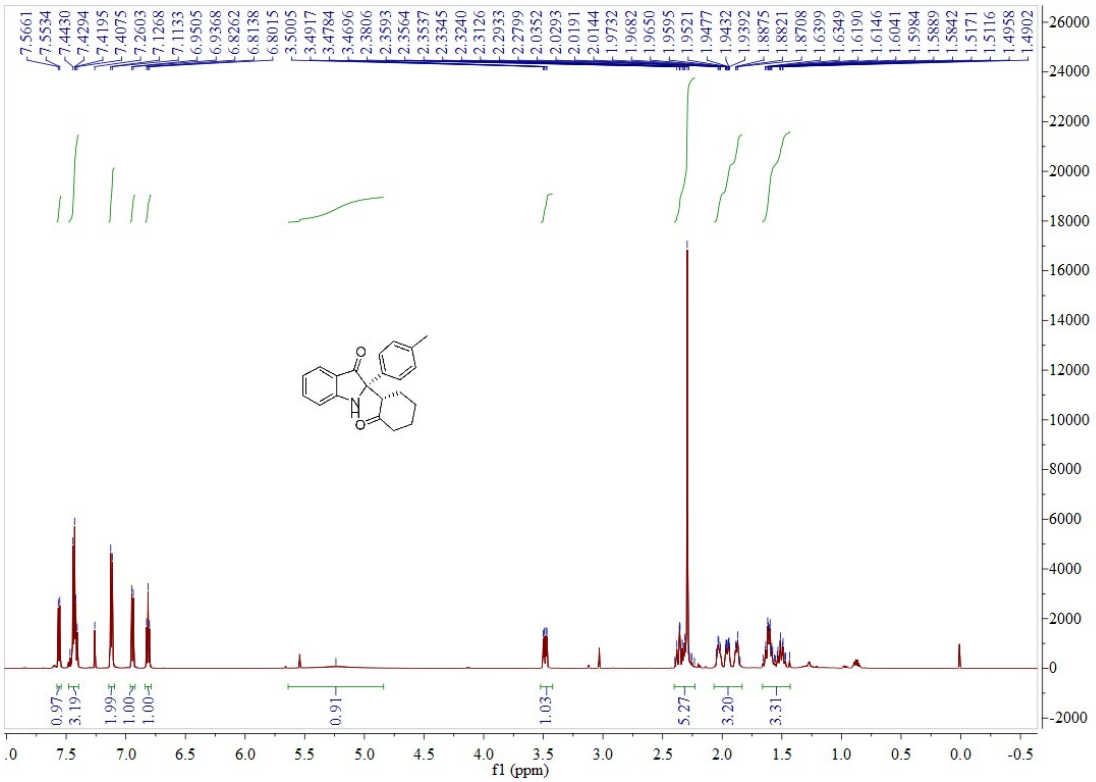
^{1}H NMR Spectrum ($CDCl_3$) of 3a



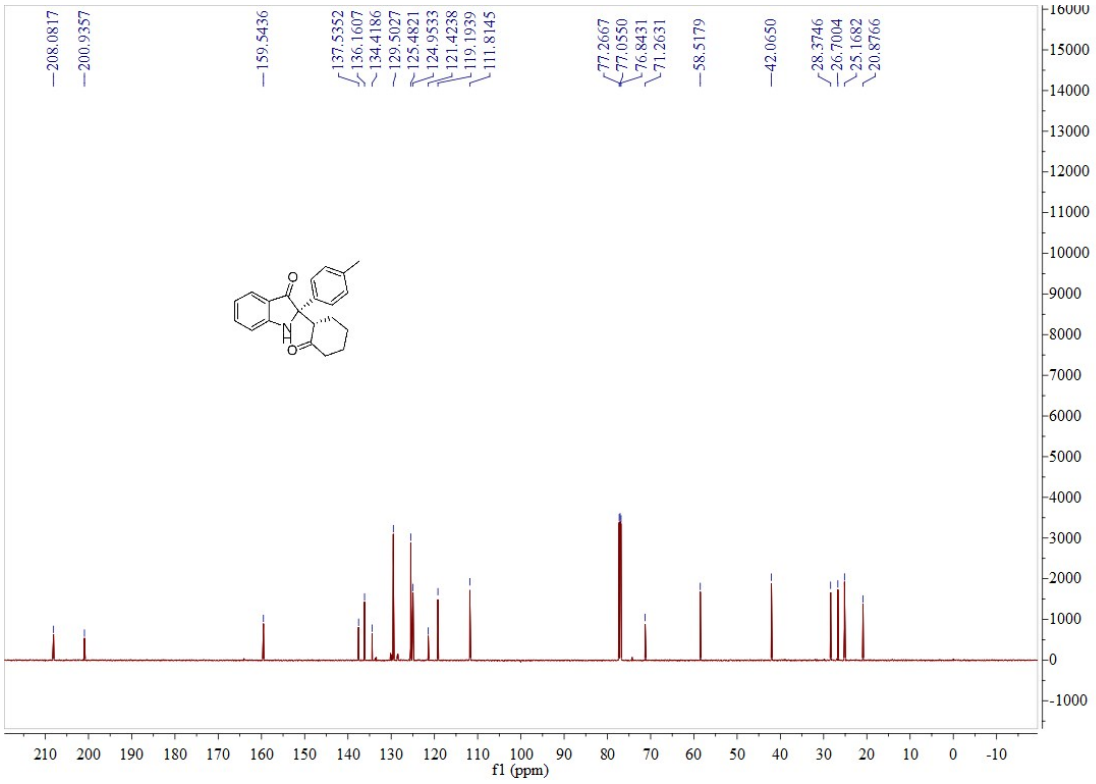
^{13}C NMR Spectrum ($CDCl_3$) of 3a



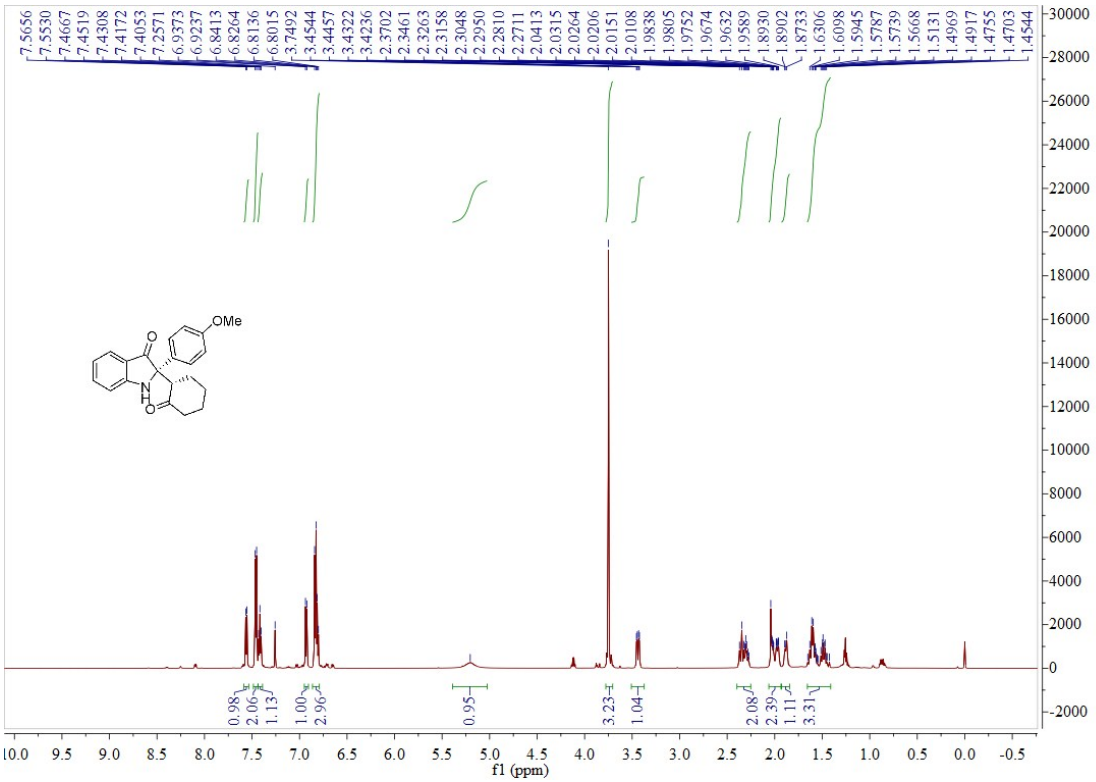
^{1}H NMR Spectrum ($CDCl_3$) of 3b



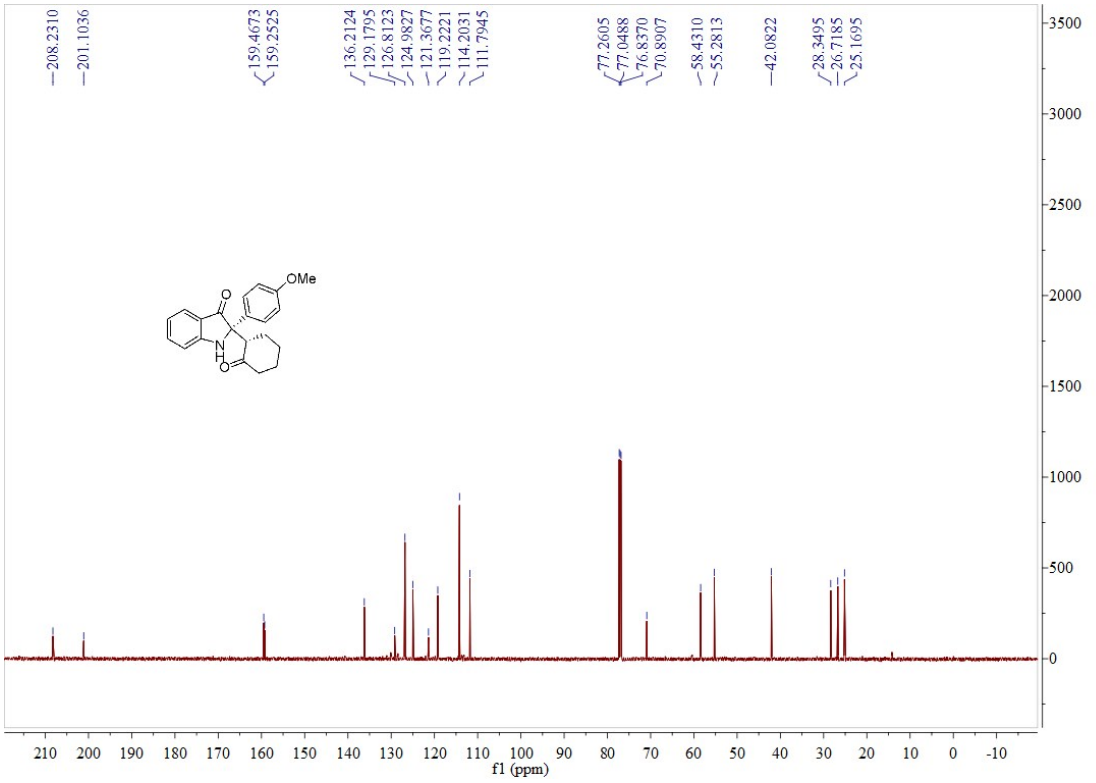
^{13}C NMR Spectrum ($CDCl_3$) of 3b



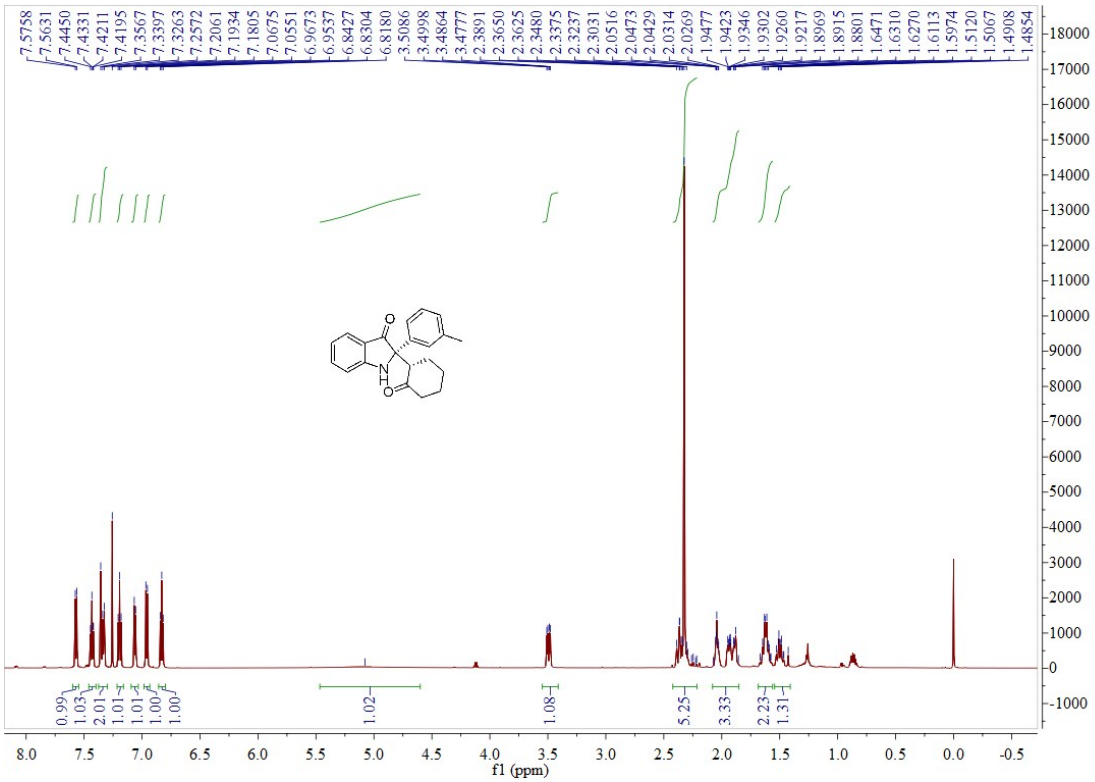
^{1}H NMR Spectrum ($CDCl_3$) of 3c



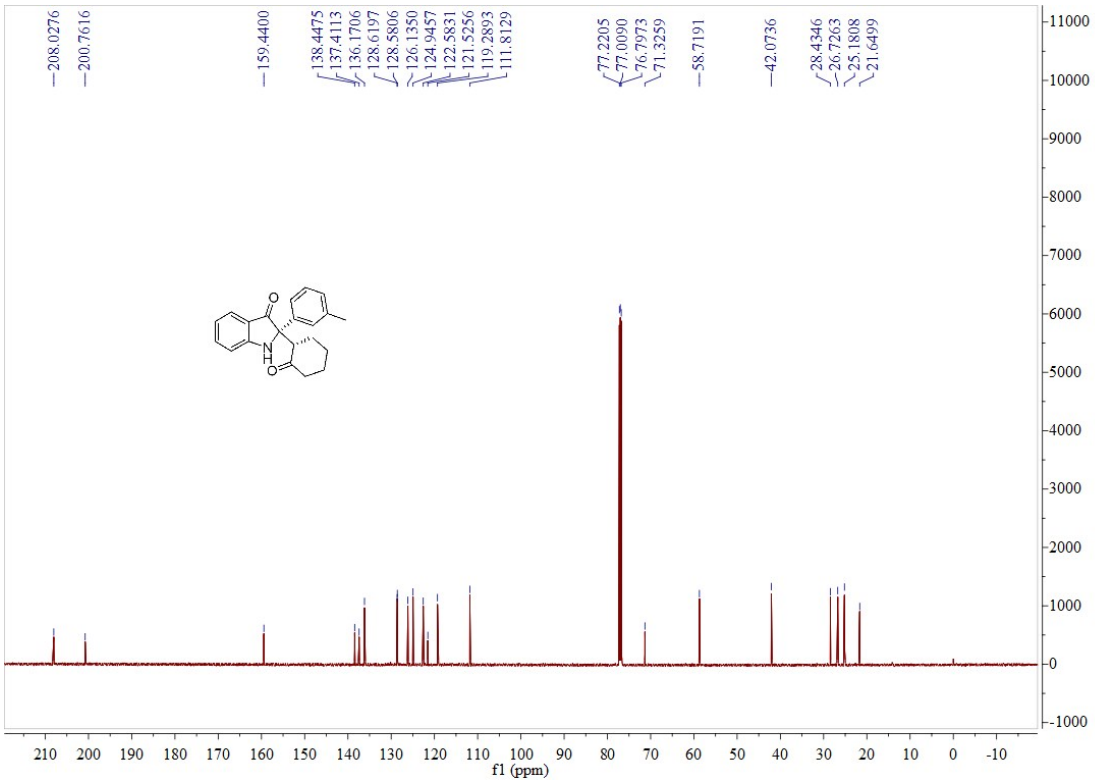
^{13}C NMR Spectrum ($CDCl_3$) of 3c



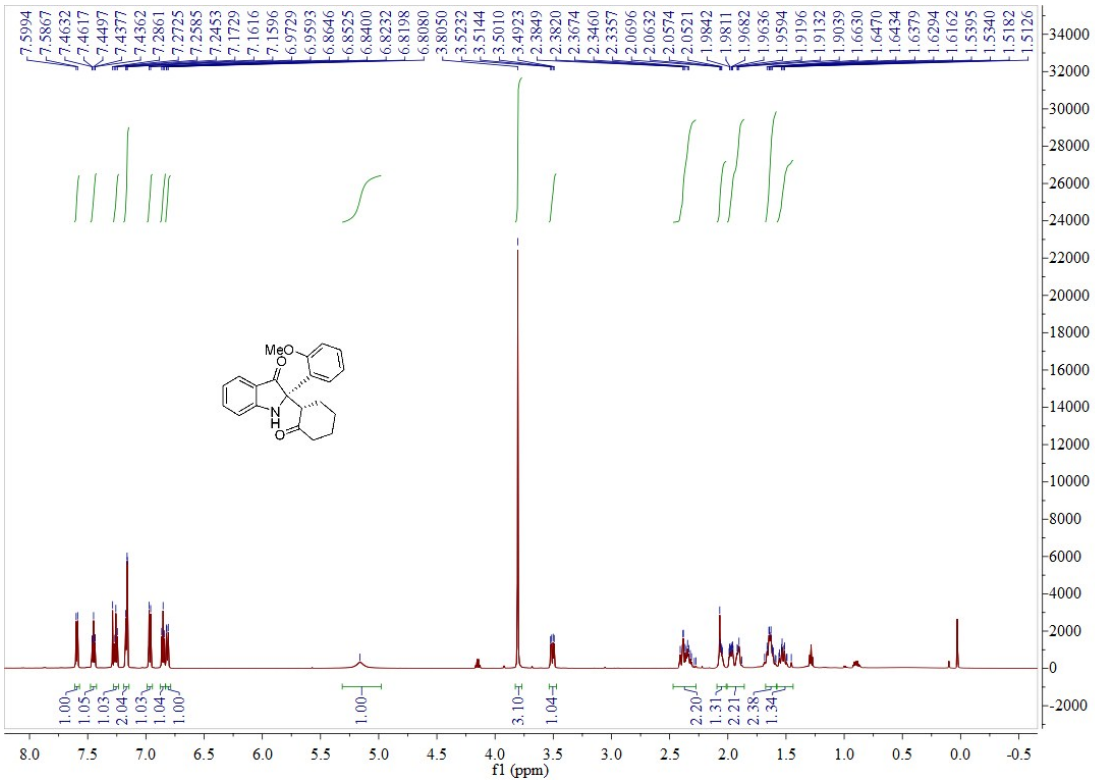
^{1}H NMR Spectrum ($CDCl_3$) of 3d



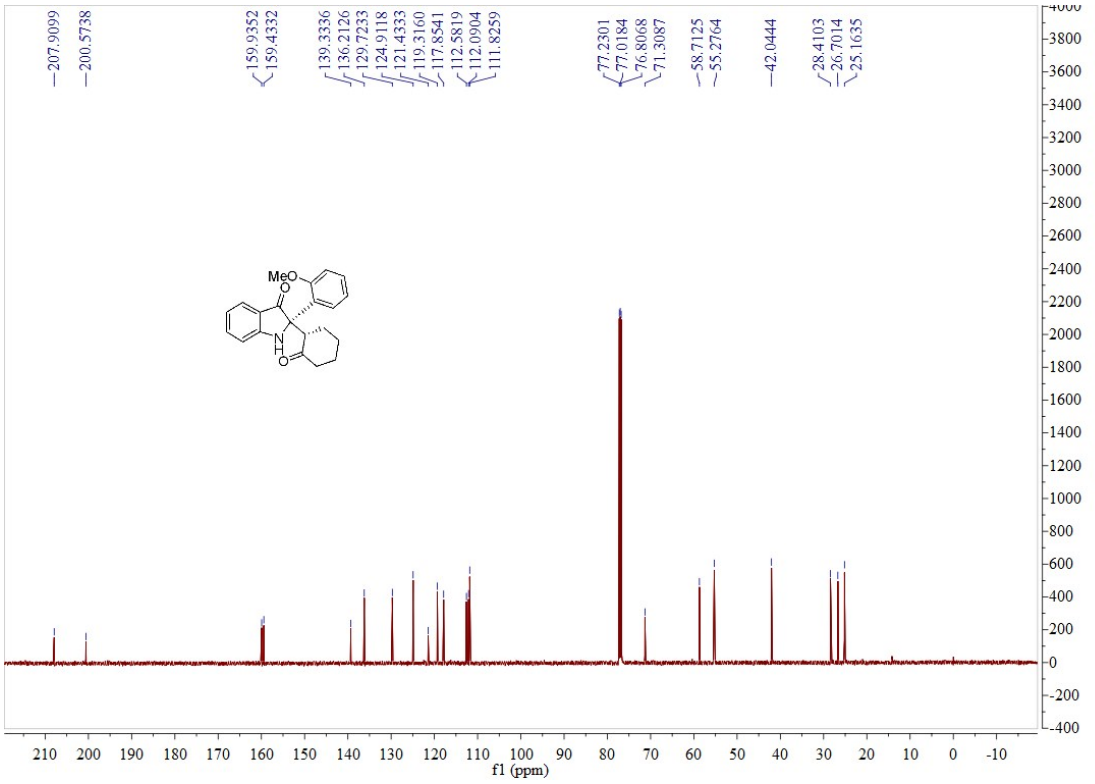
^{13}C NMR Spectrum ($CDCl_3$) of 3d



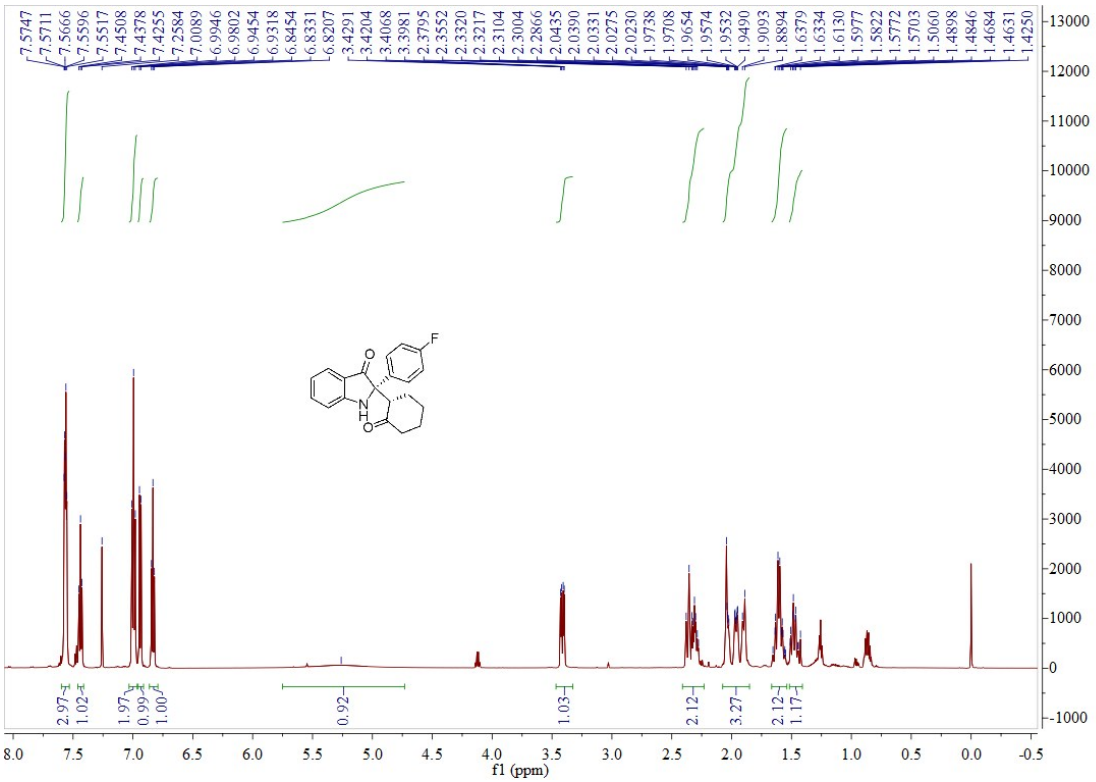
^{1}H NMR Spectrum ($CDCl_3$) of 3e



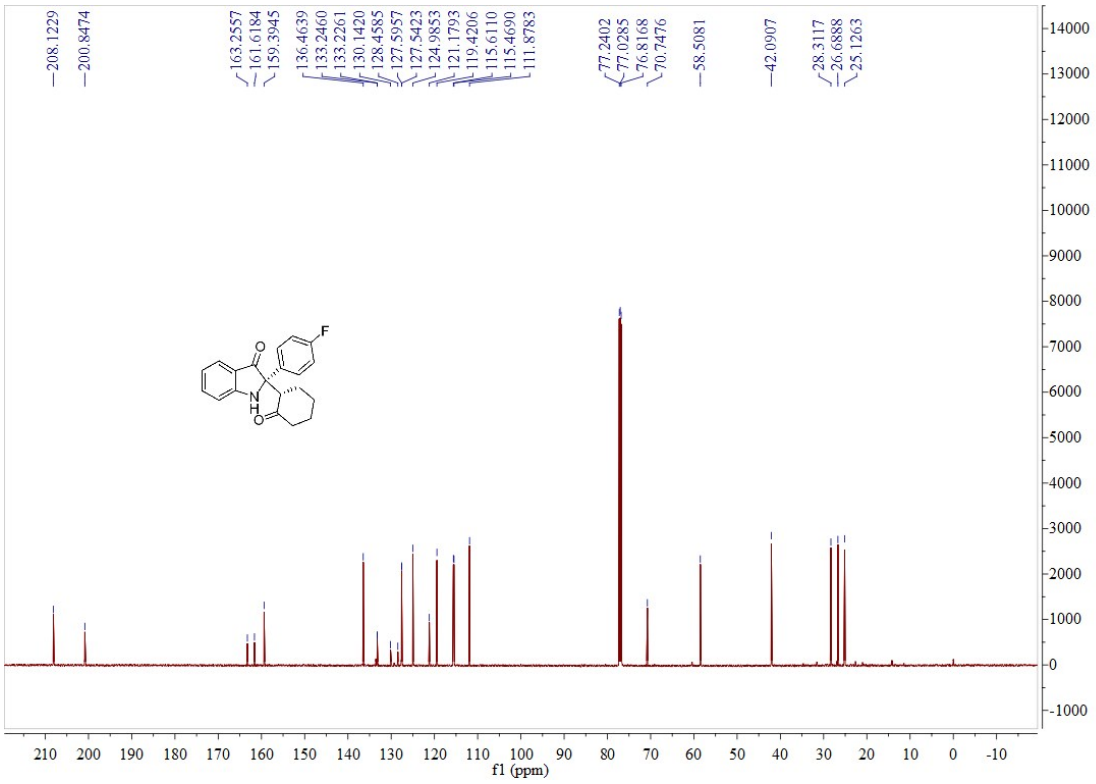
^{13}C NMR Spectrum ($CDCl_3$) of 3e



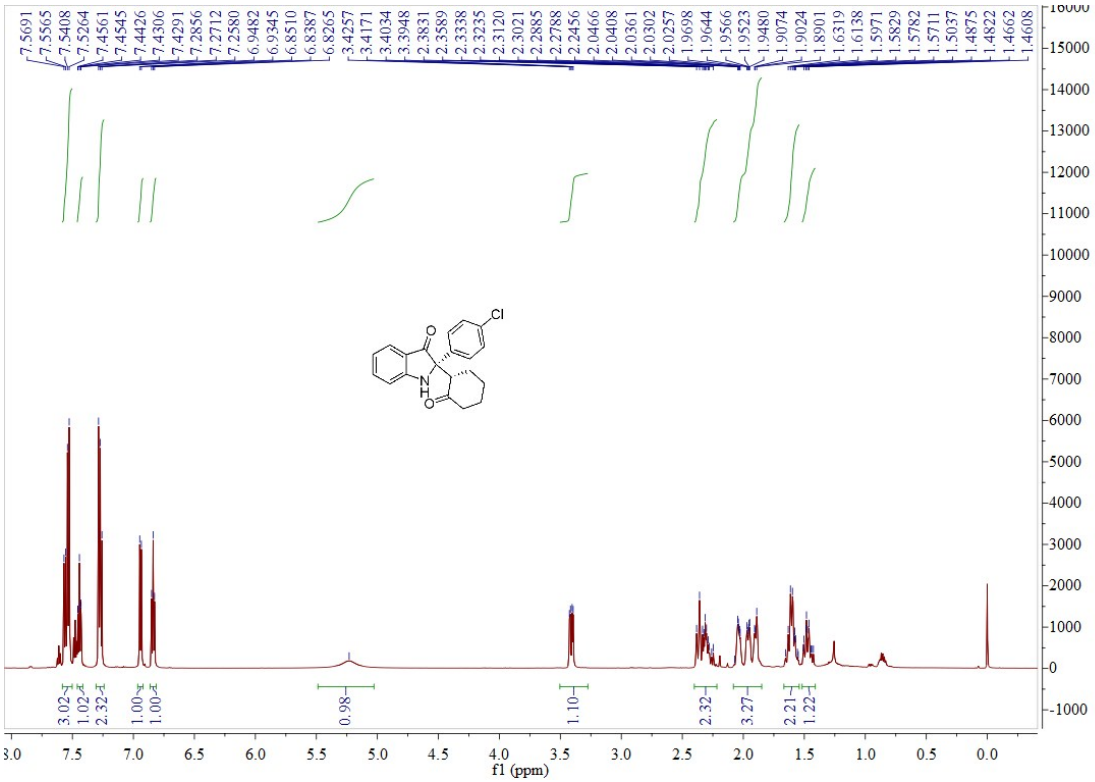
^{1}H NMR Spectrum ($CDCl_3$) of 3f



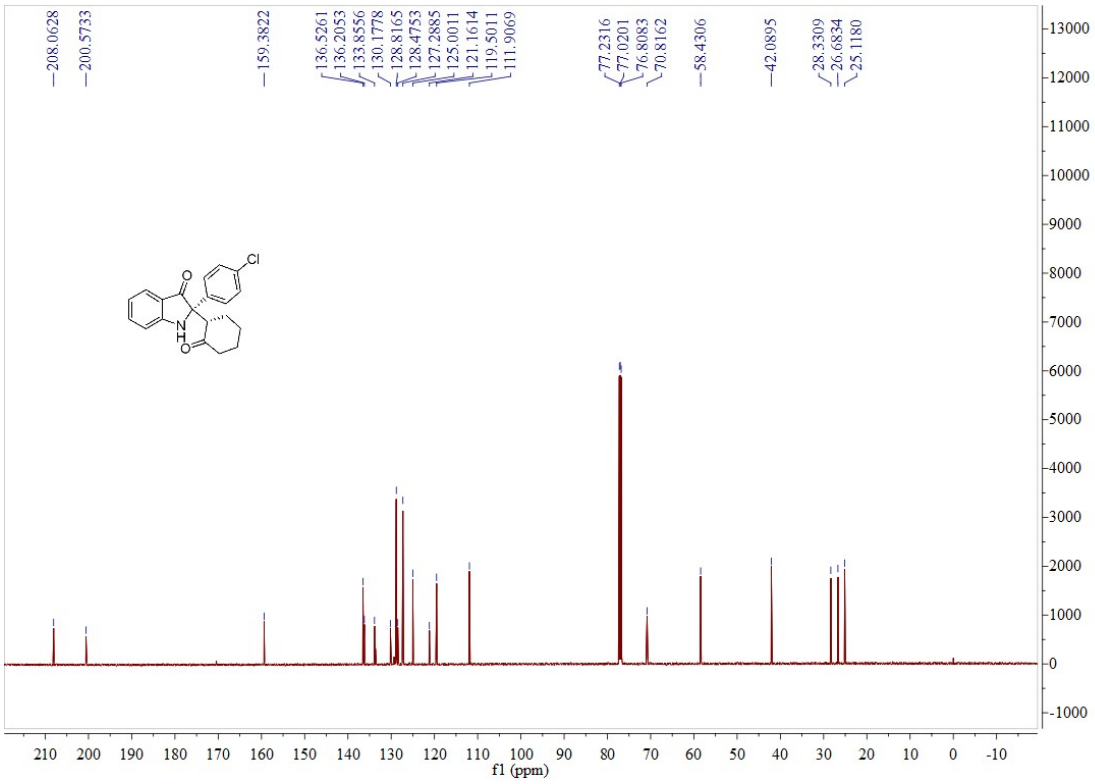
^{13}C NMR Spectrum ($CDCl_3$) of 3f



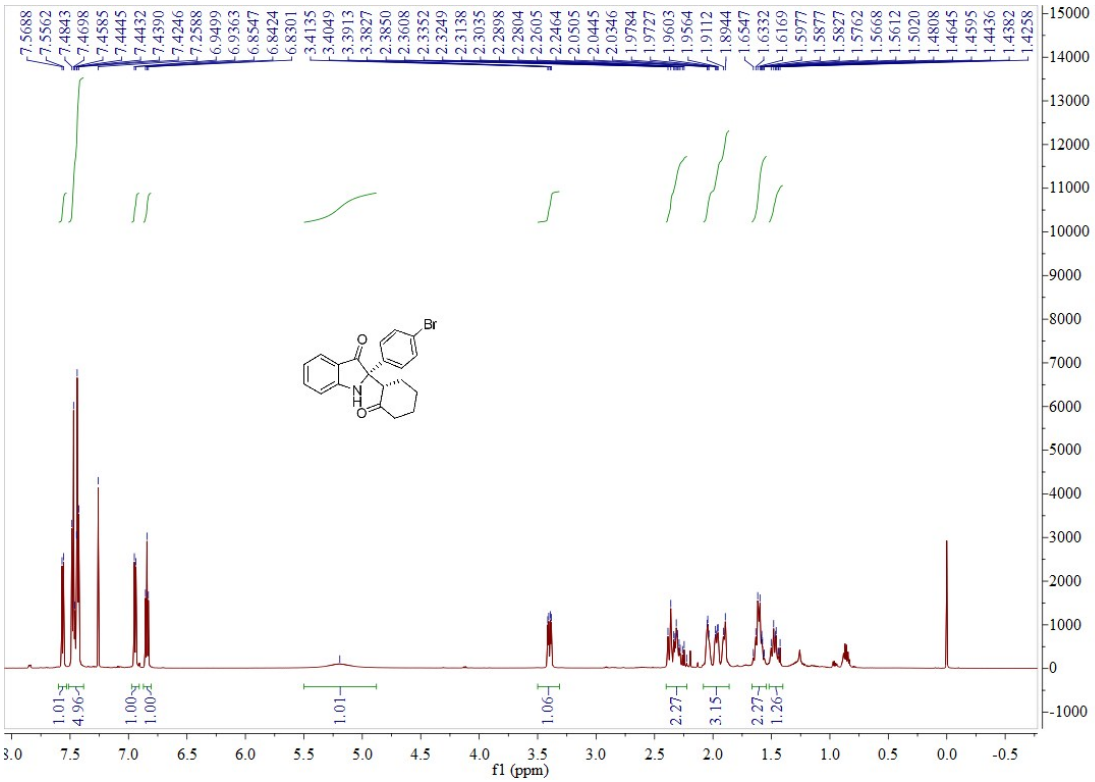
^{1}H NMR Spectrum ($CDCl_3$) of 3g



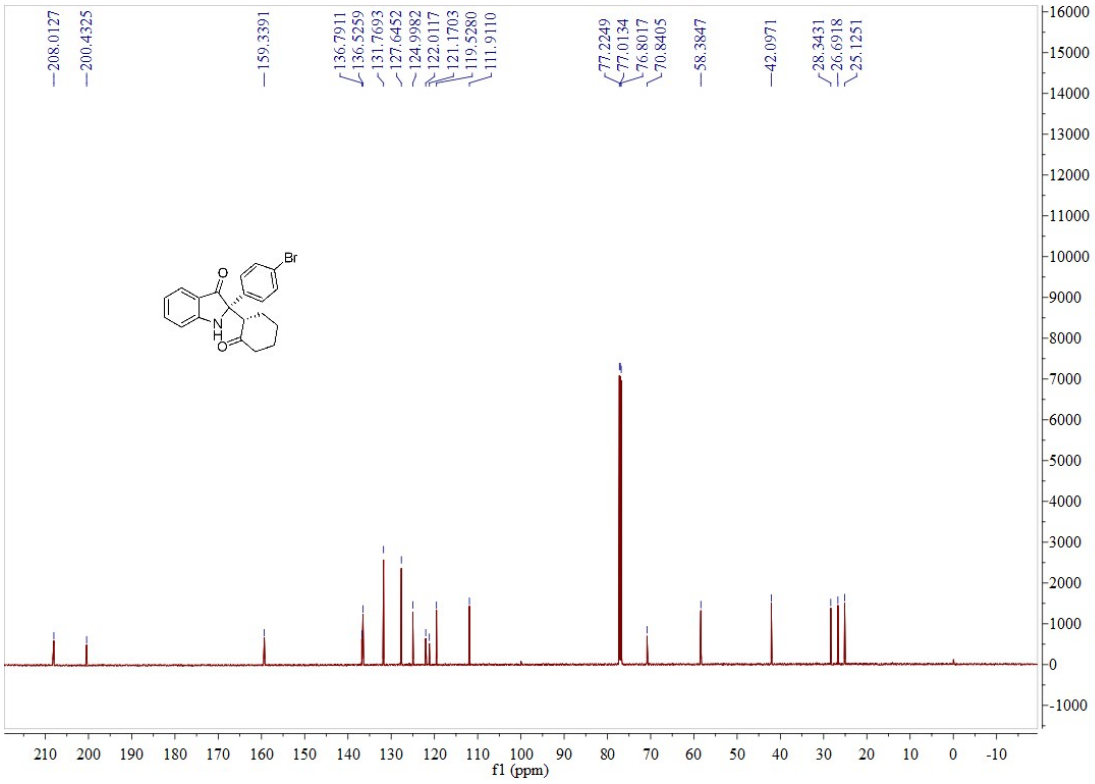
^{13}C NMR Spectrum ($CDCl_3$) of 3g



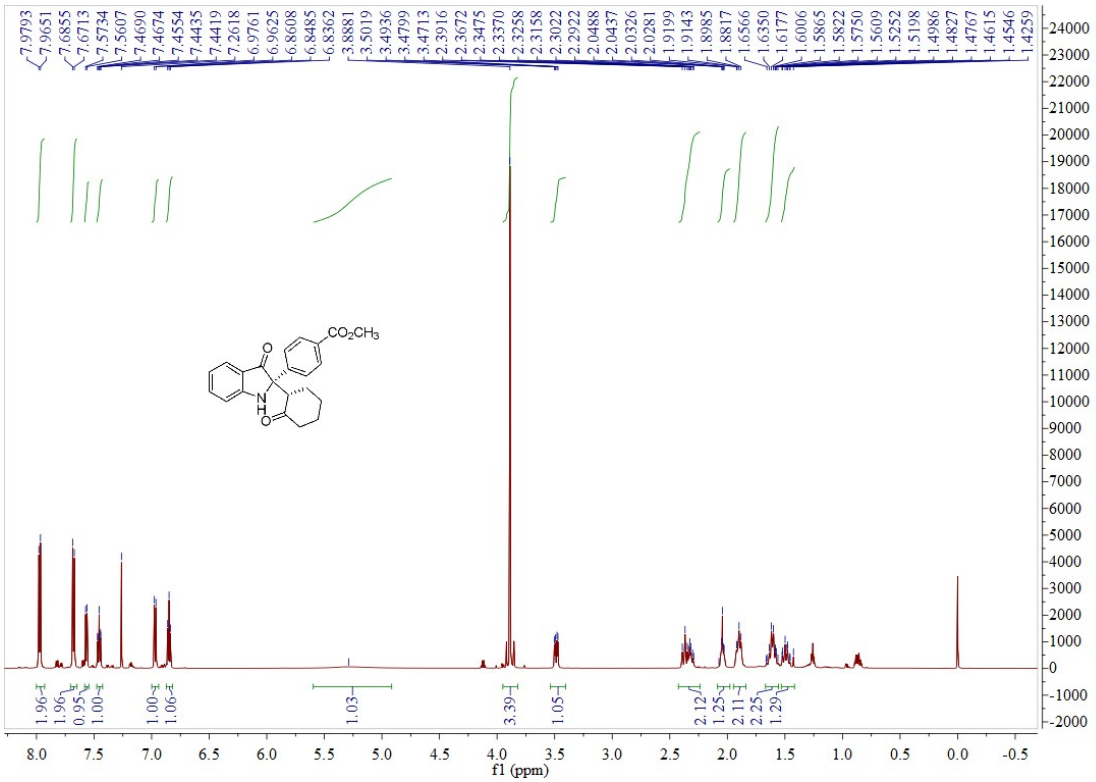
^{1}H NMR Spectrum ($CDCl_3$) of 3h



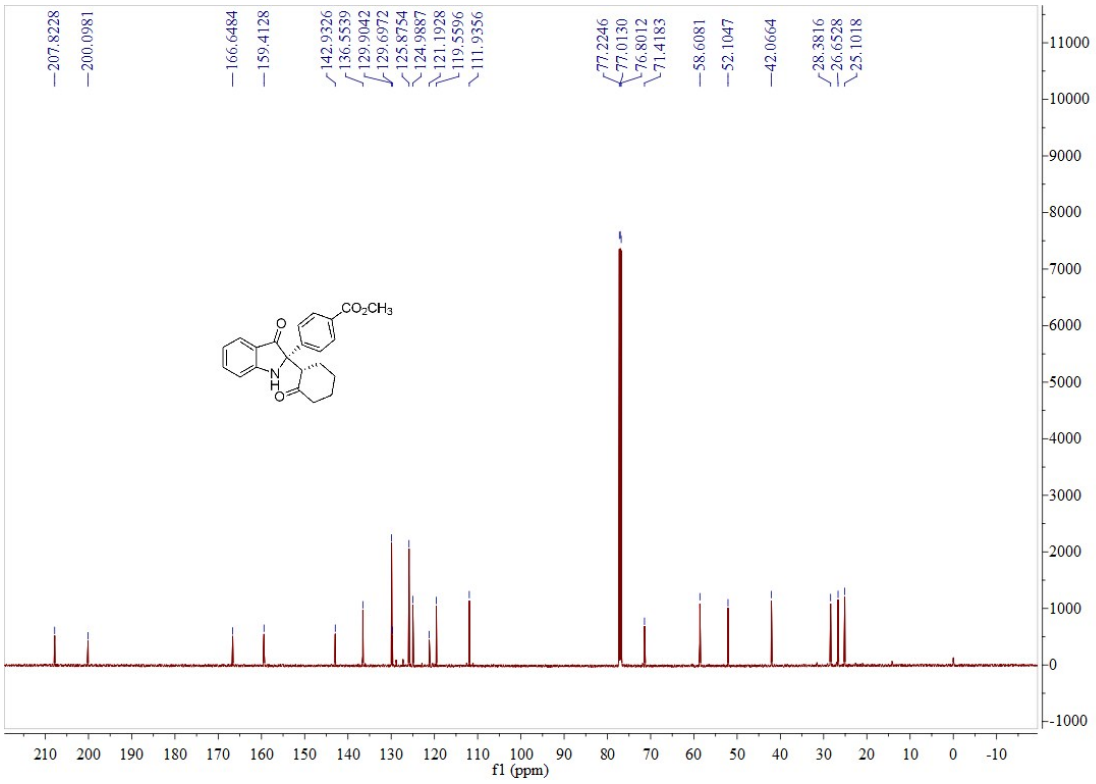
^{13}C NMR Spectrum ($CDCl_3$) of 3h



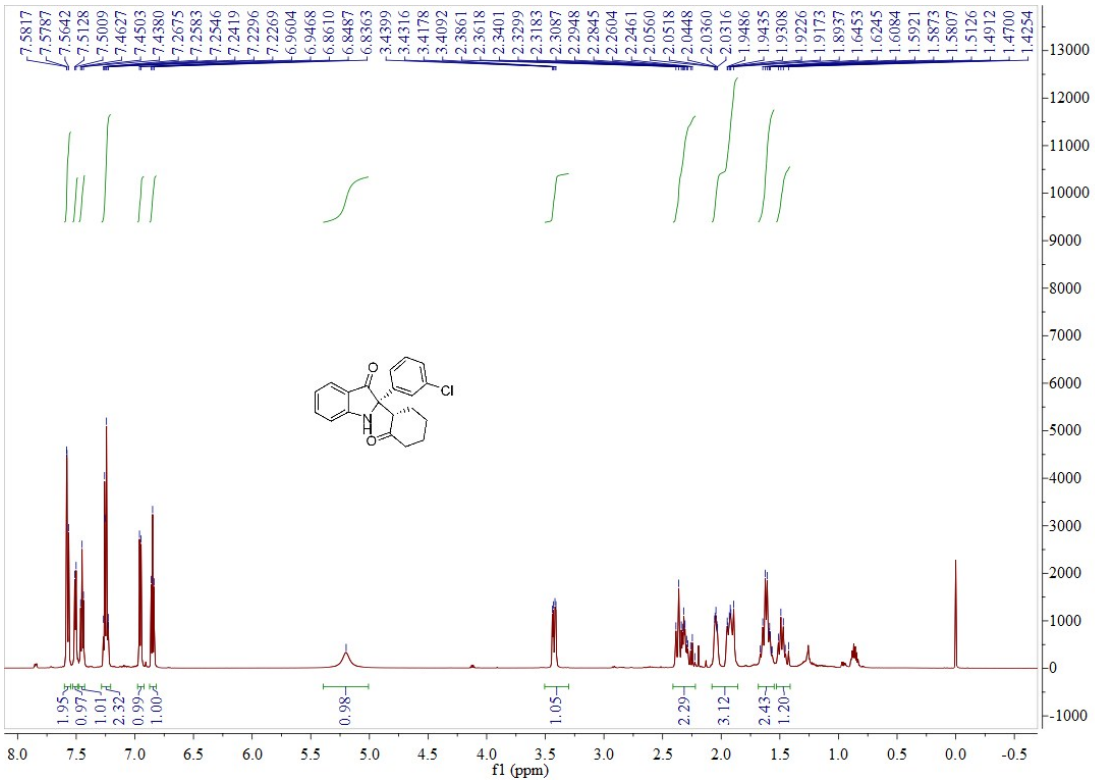
^{1}H NMR Spectrum ($CDCl_3$) of 3i



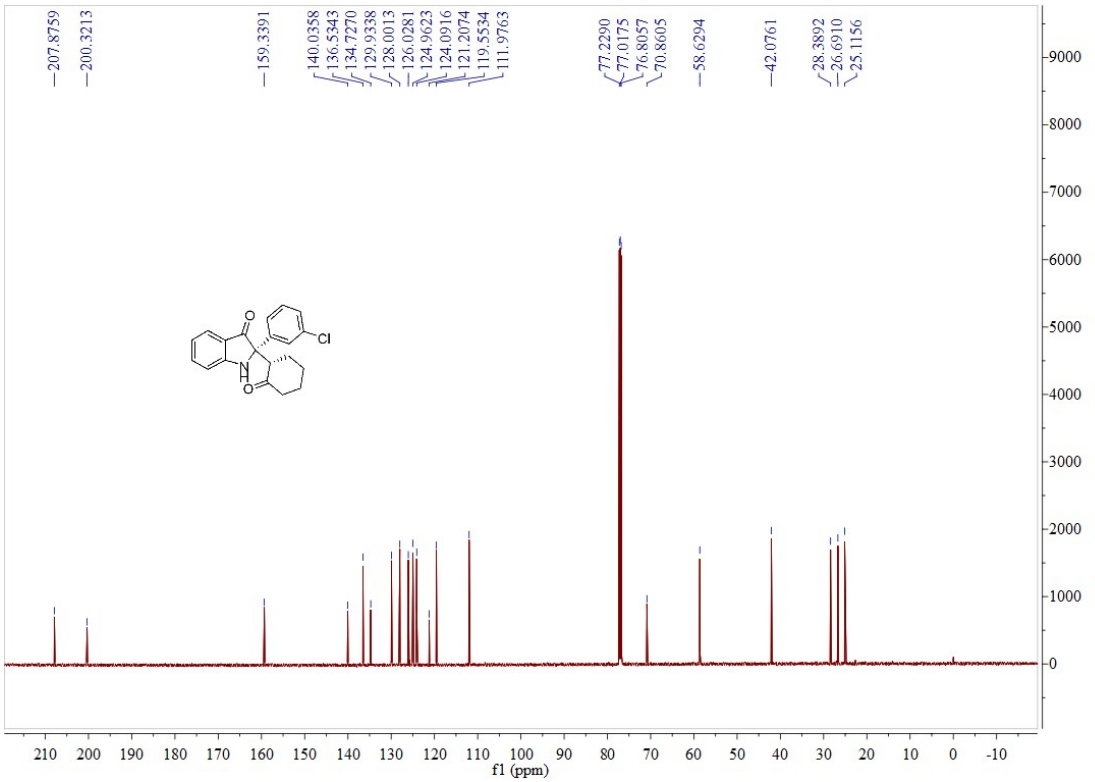
^{13}C NMR Spectrum ($CDCl_3$) of 3i



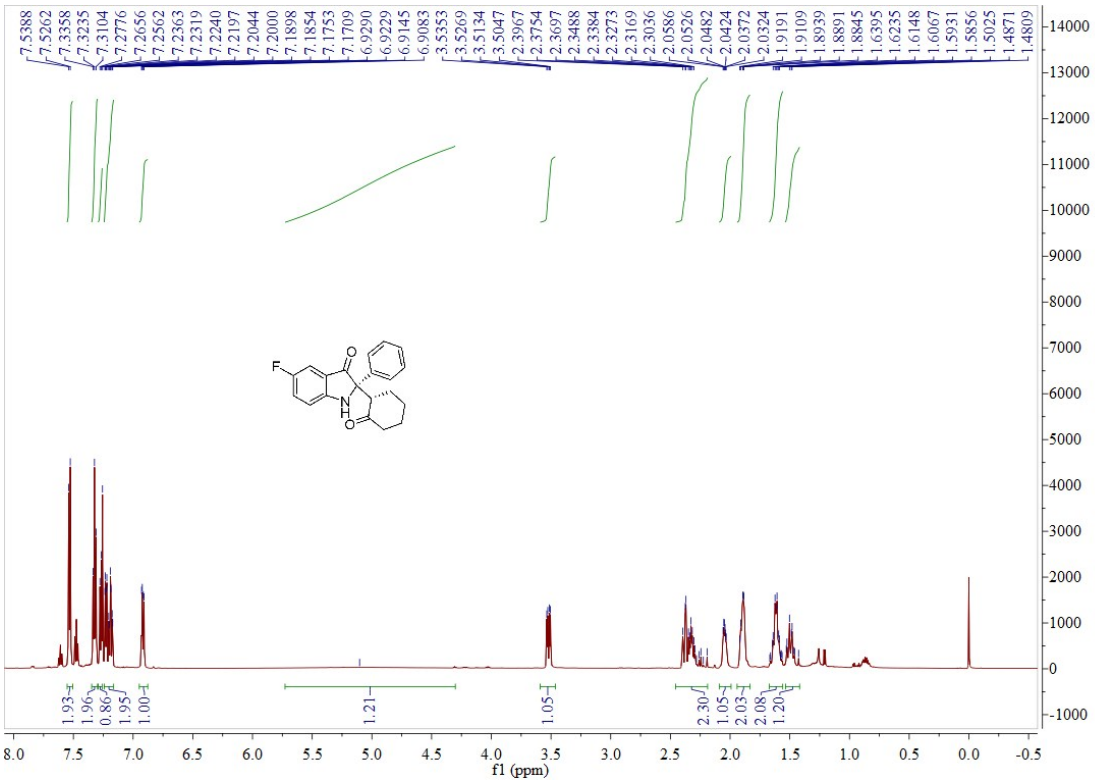
^{1}H NMR Spectrum ($CDCl_3$) of 3j



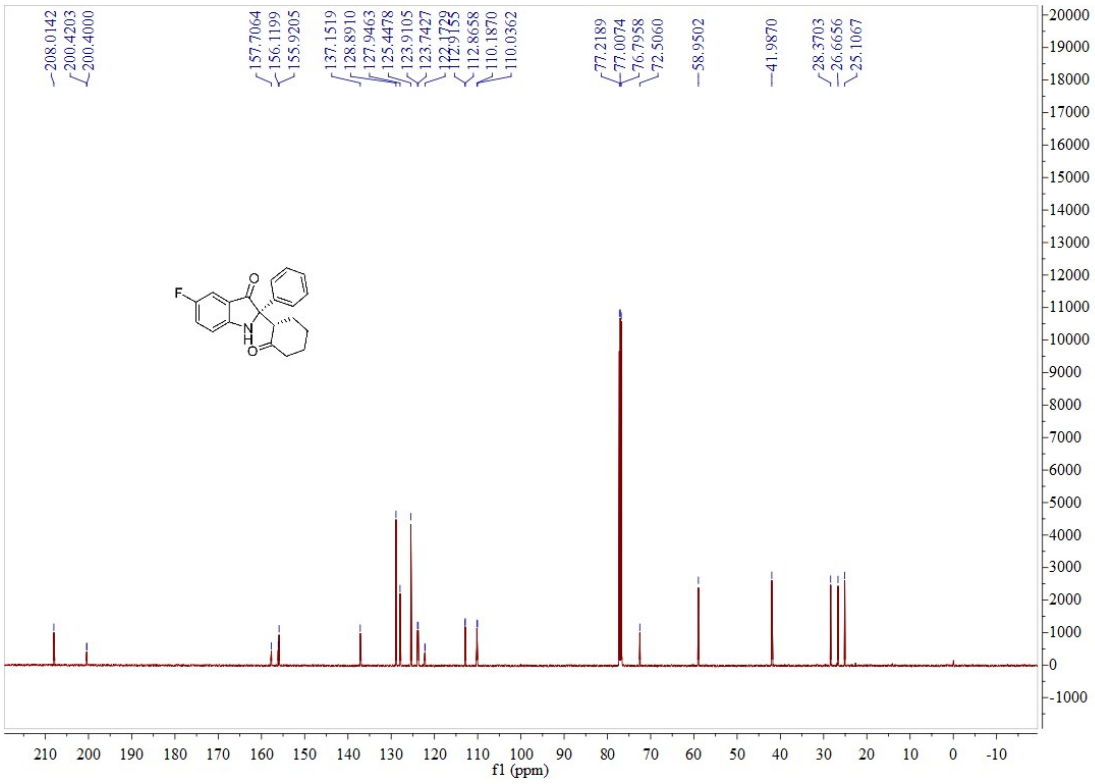
^{13}C NMR Spectrum ($CDCl_3$) of 3j



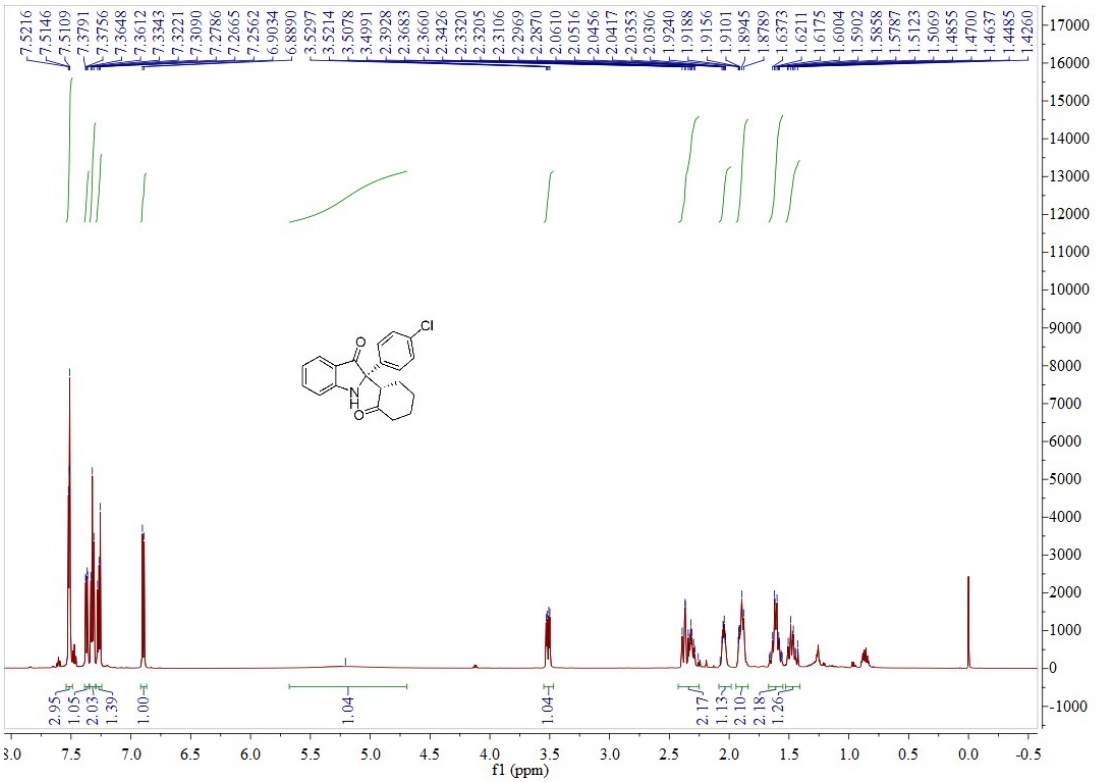
^{1}H NMR Spectrum ($CDCl_3$) of 3k



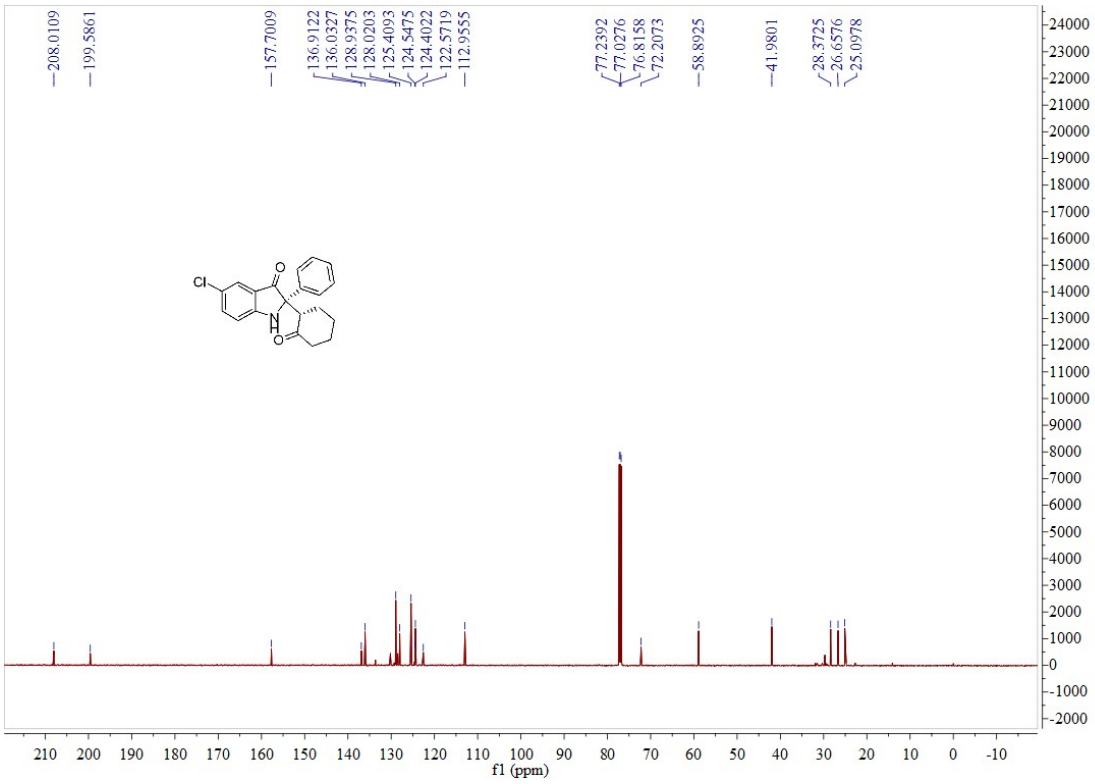
^{13}C NMR Spectrum ($CDCl_3$) of 3k



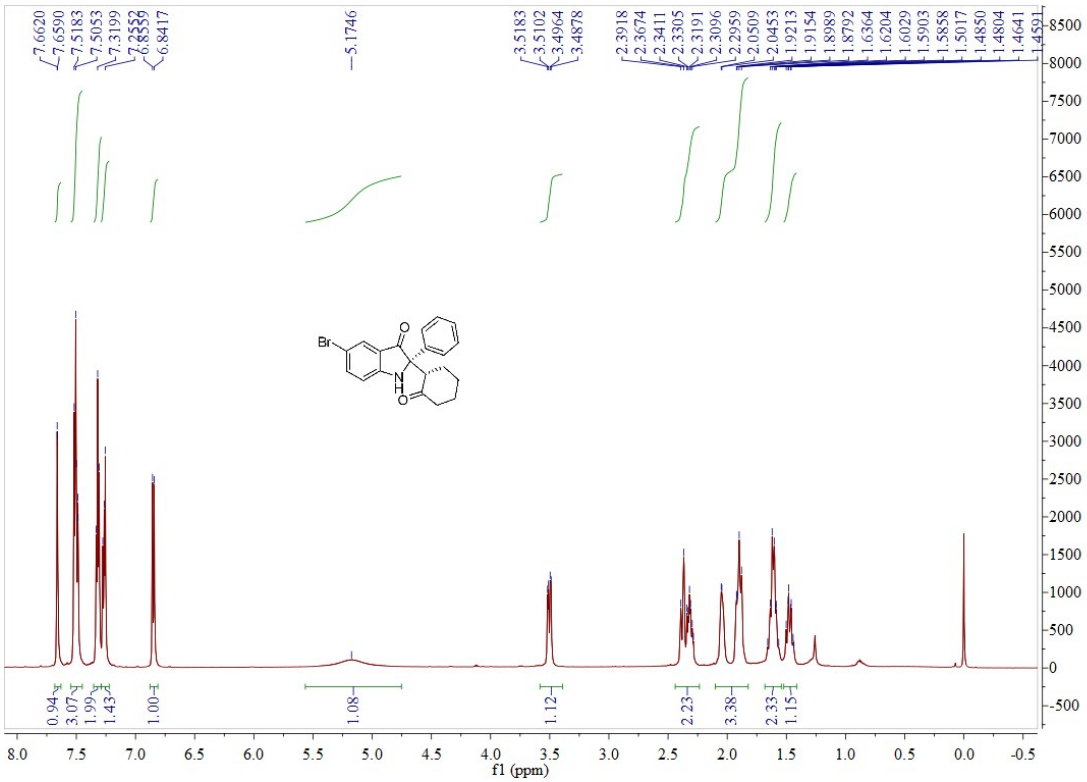
^{1}H NMR Spectrum ($CDCl_3$) of 3l



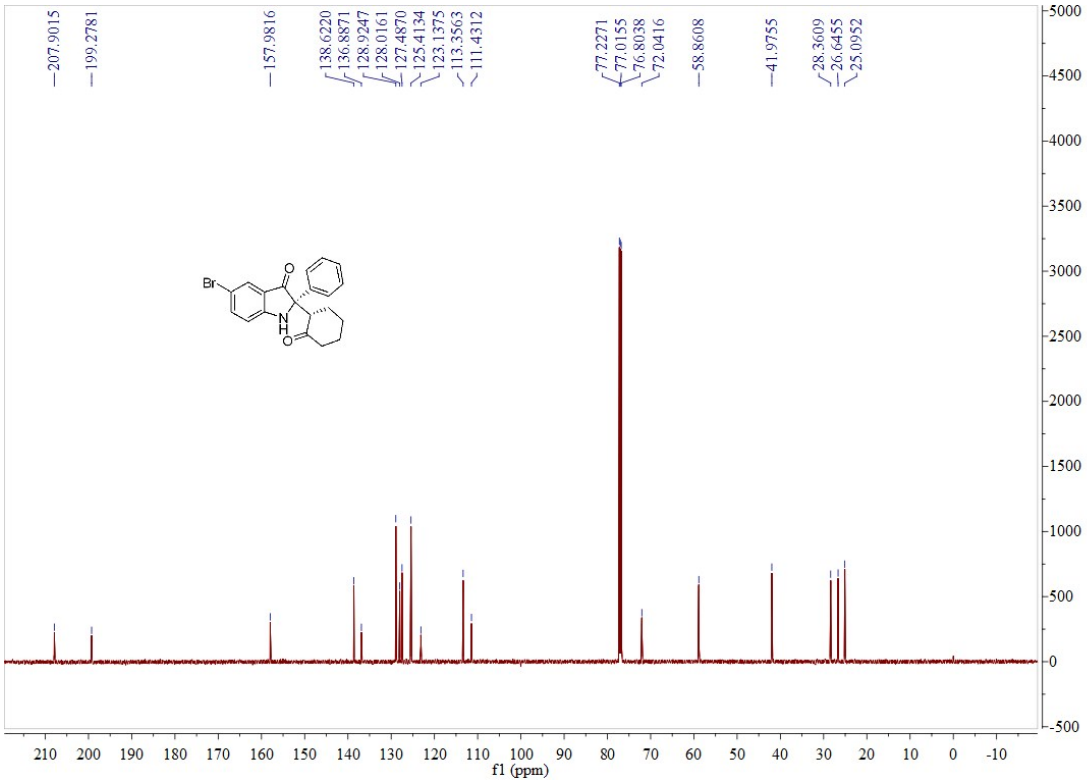
^{13}C NMR Spectrum ($CDCl_3$) of 3l



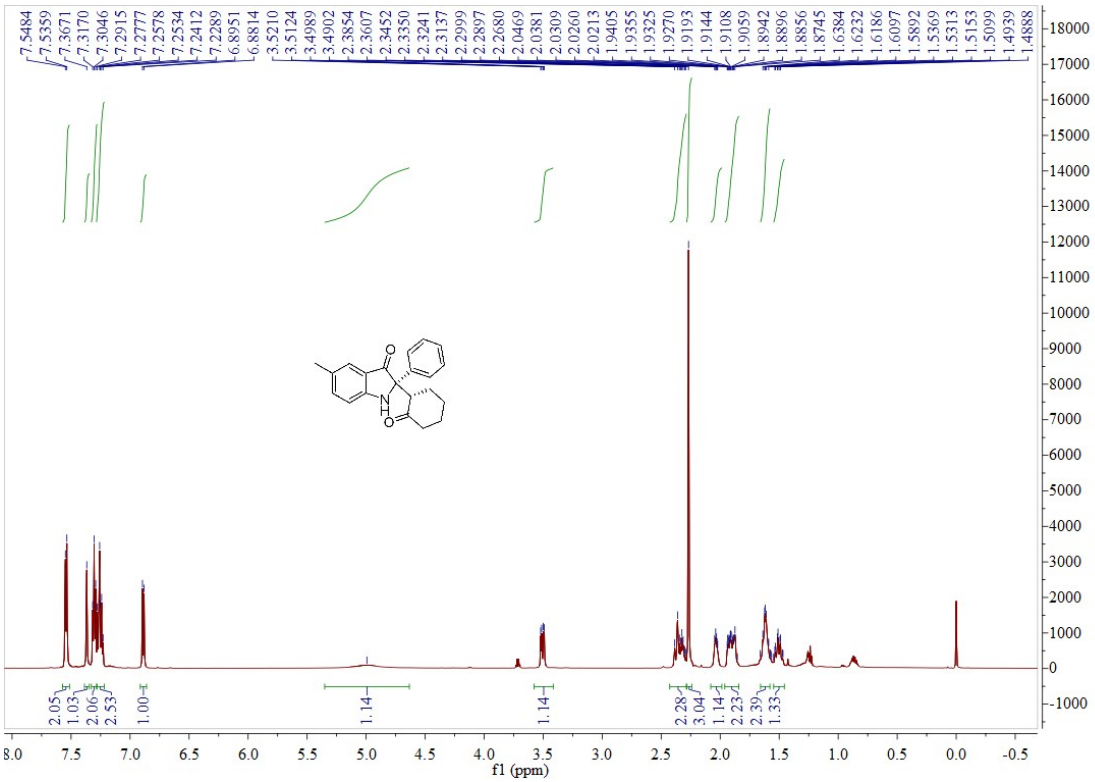
^{1}H NMR Spectrum ($CDCl_3$) of 3m



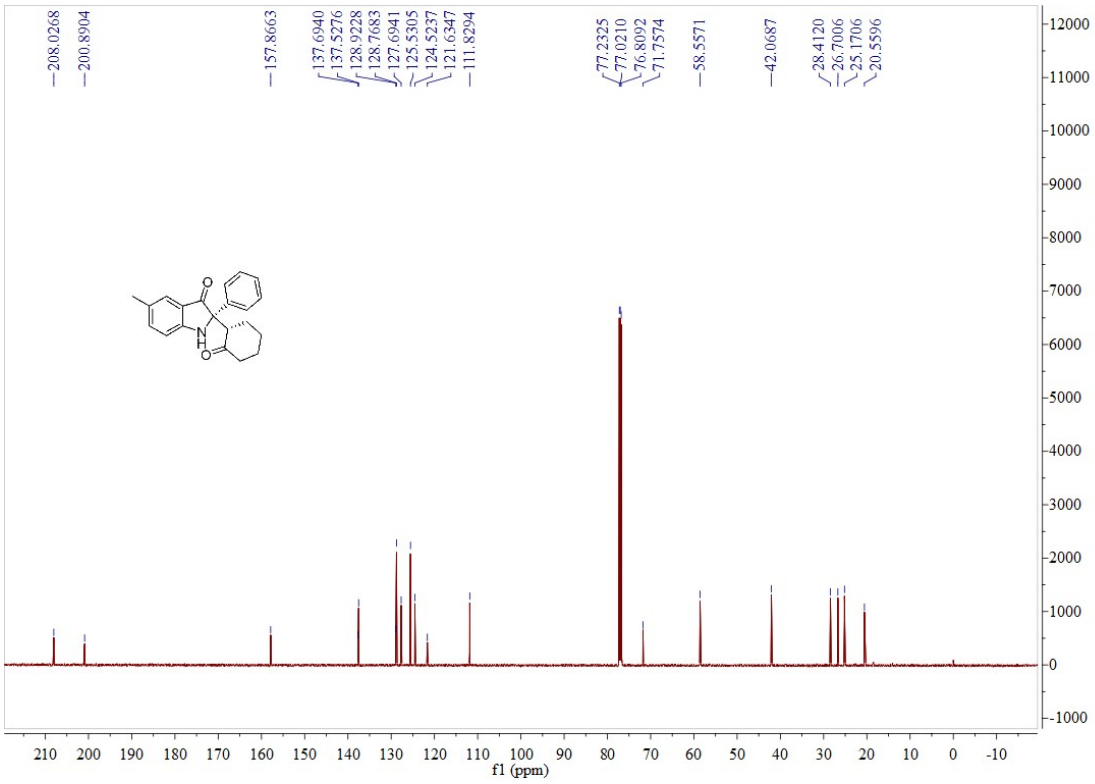
^{13}C NMR Spectrum ($CDCl_3$) of 3m



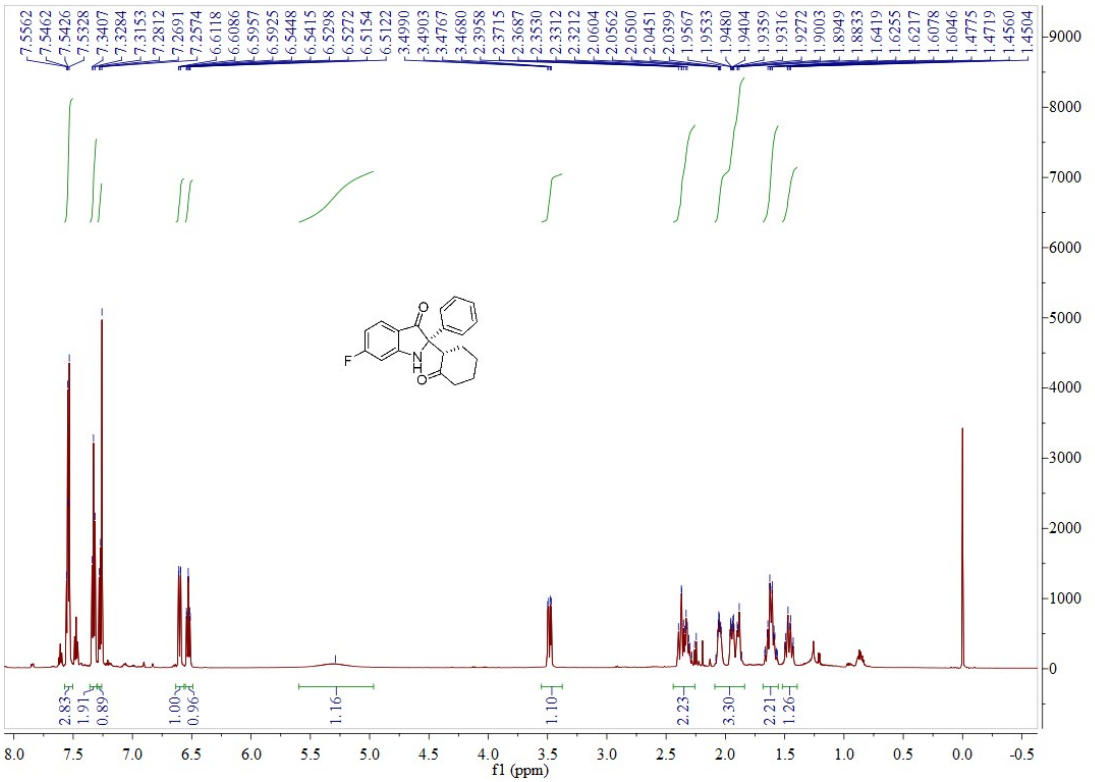
^{1}H NMR Spectrum ($CDCl_3$) of 3n



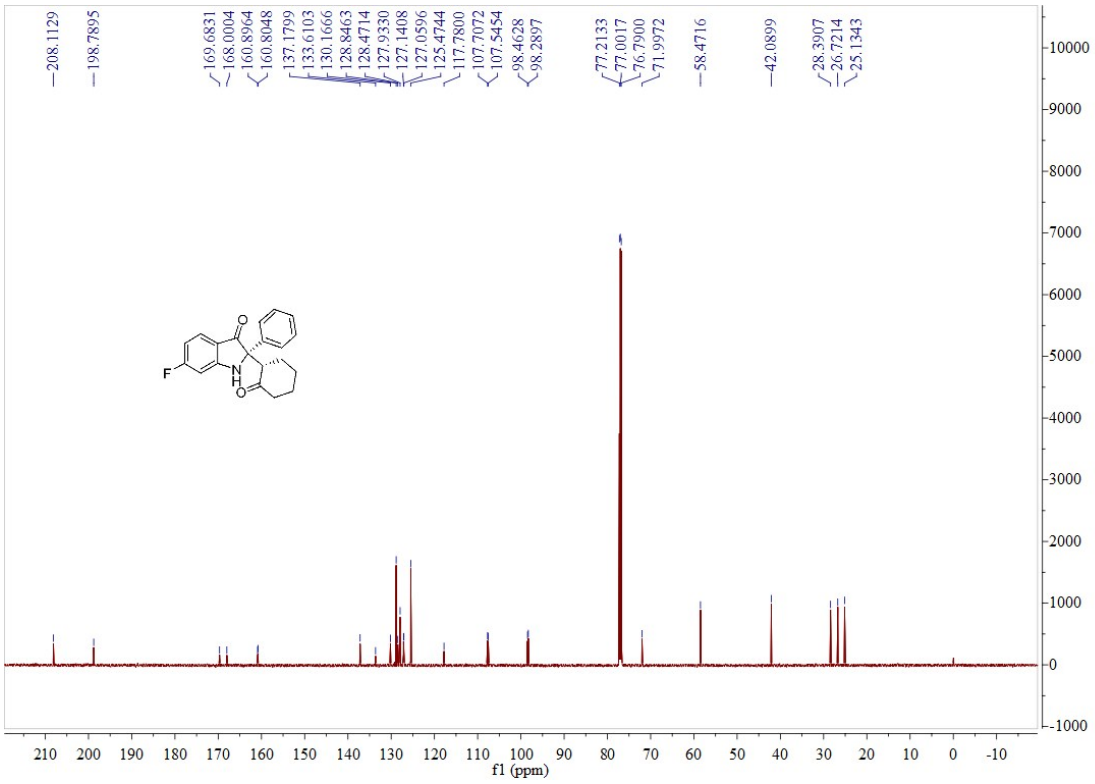
^{13}C NMR Spectrum ($CDCl_3$) of 3n



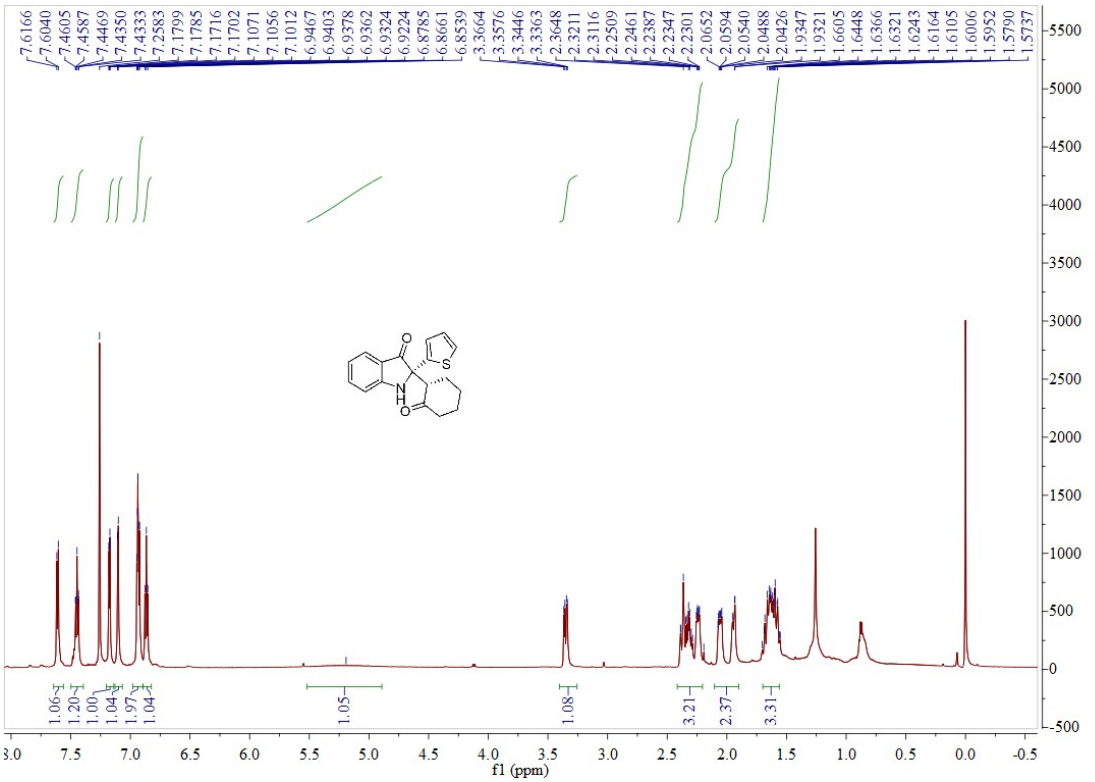
^{1}H NMR Spectrum ($CDCl_3$) of 3o



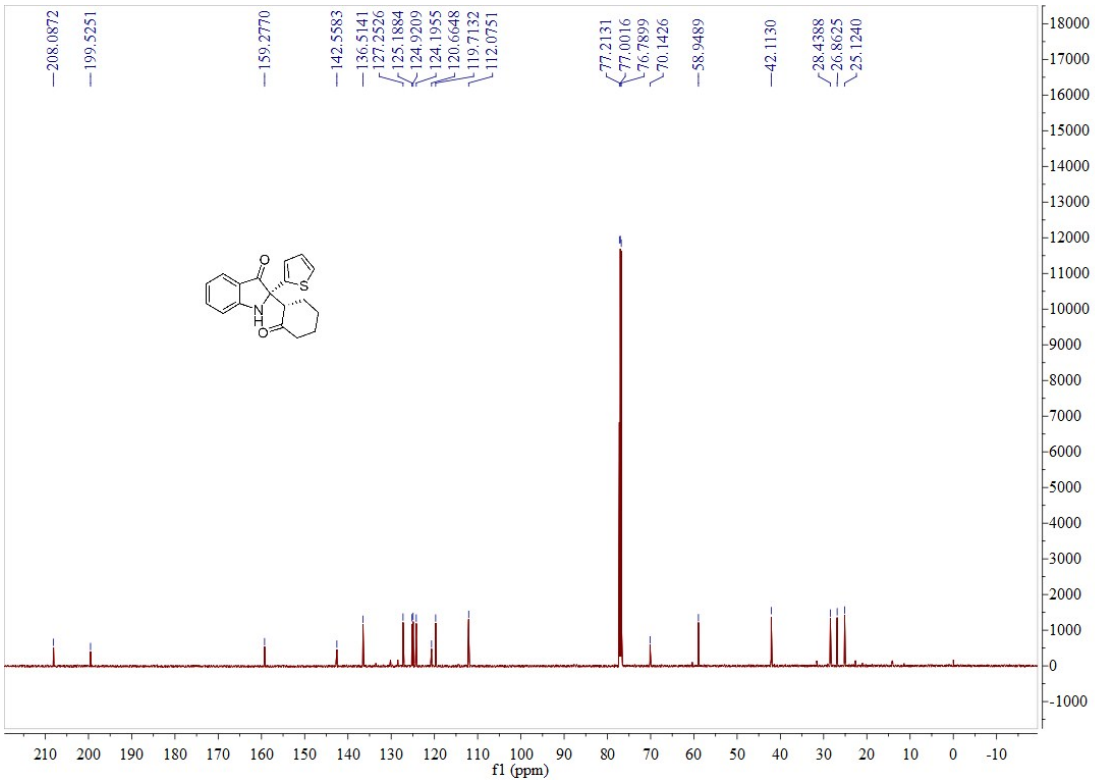
^{13}C NMR Spectrum ($CDCl_3$) of 3o



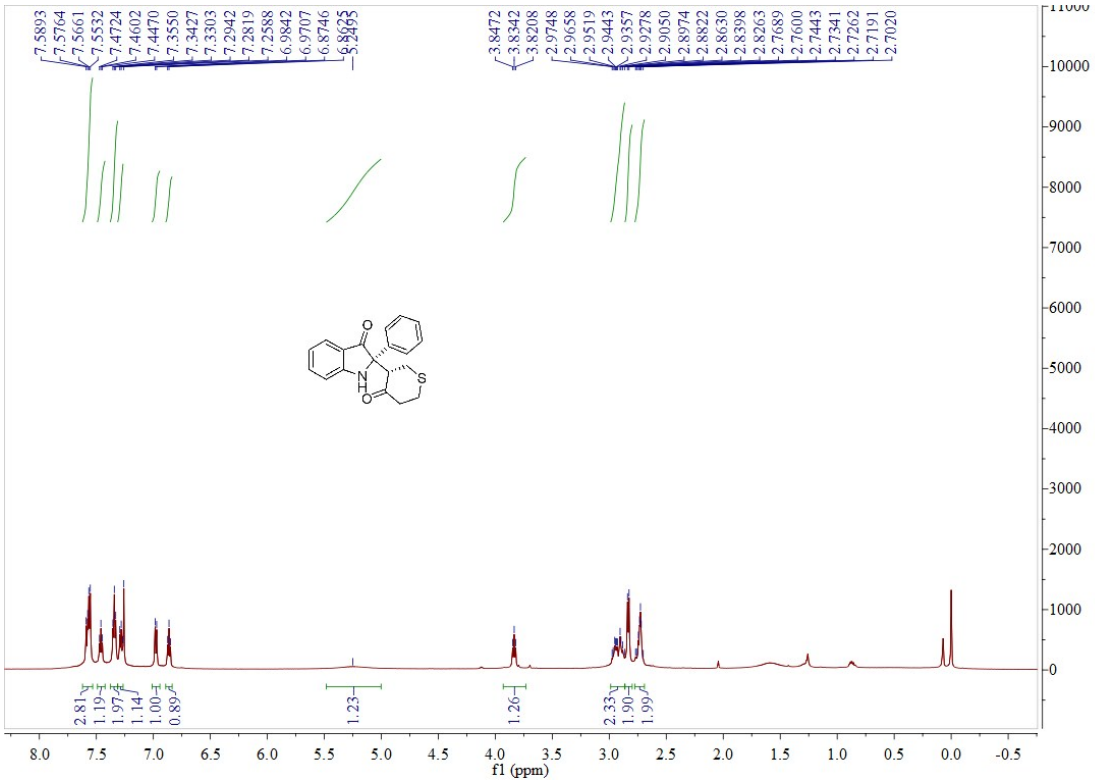
^{1}H NMR Spectrum ($CDCl_3$) of 3p



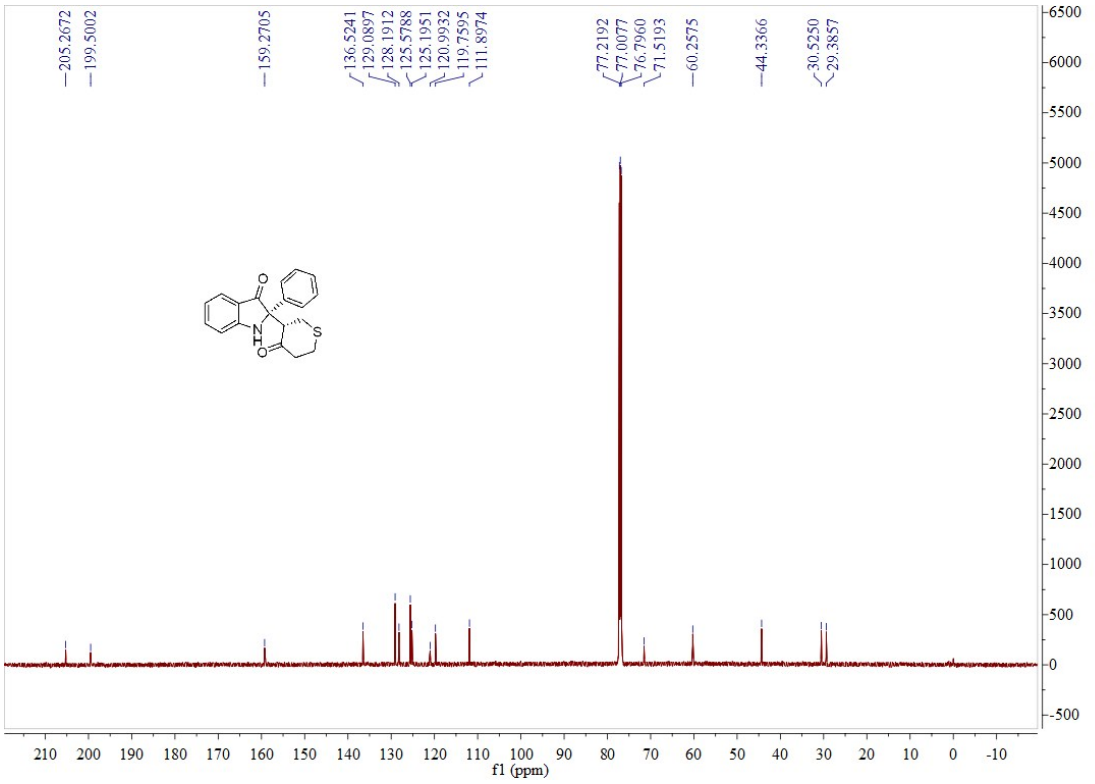
^{13}C NMR Spectrum ($CDCl_3$) of 3p



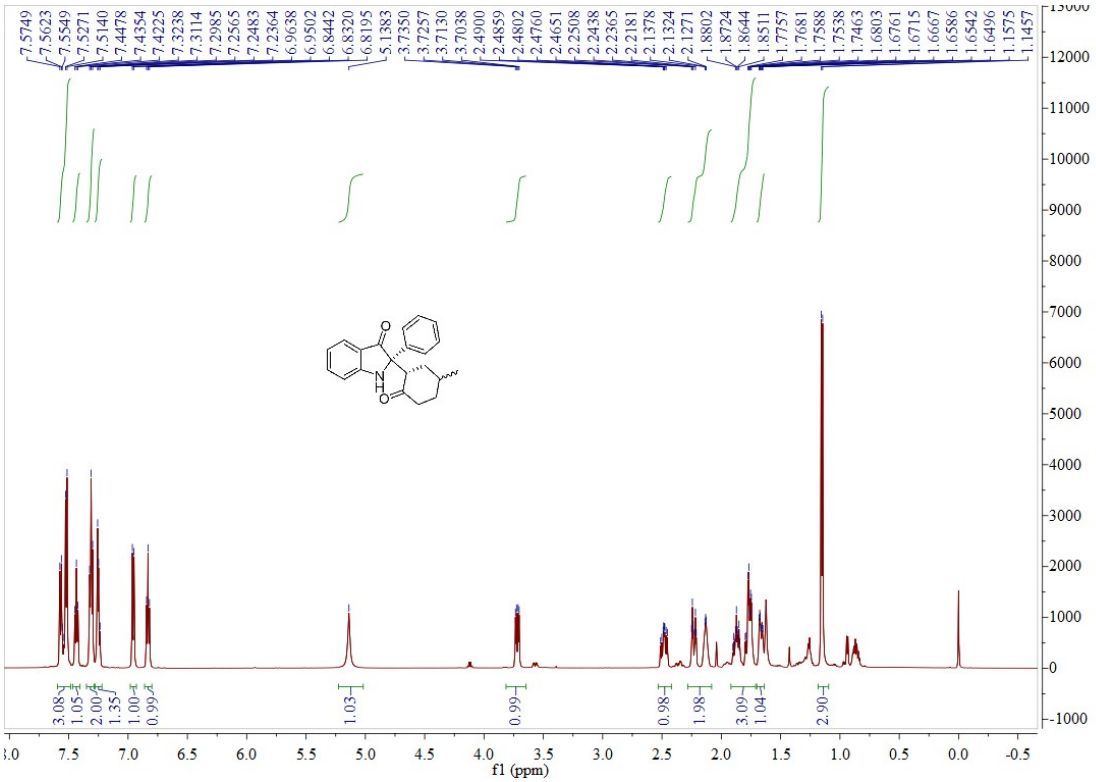
^{1}H NMR Spectrum ($CDCl_3$) of 3q



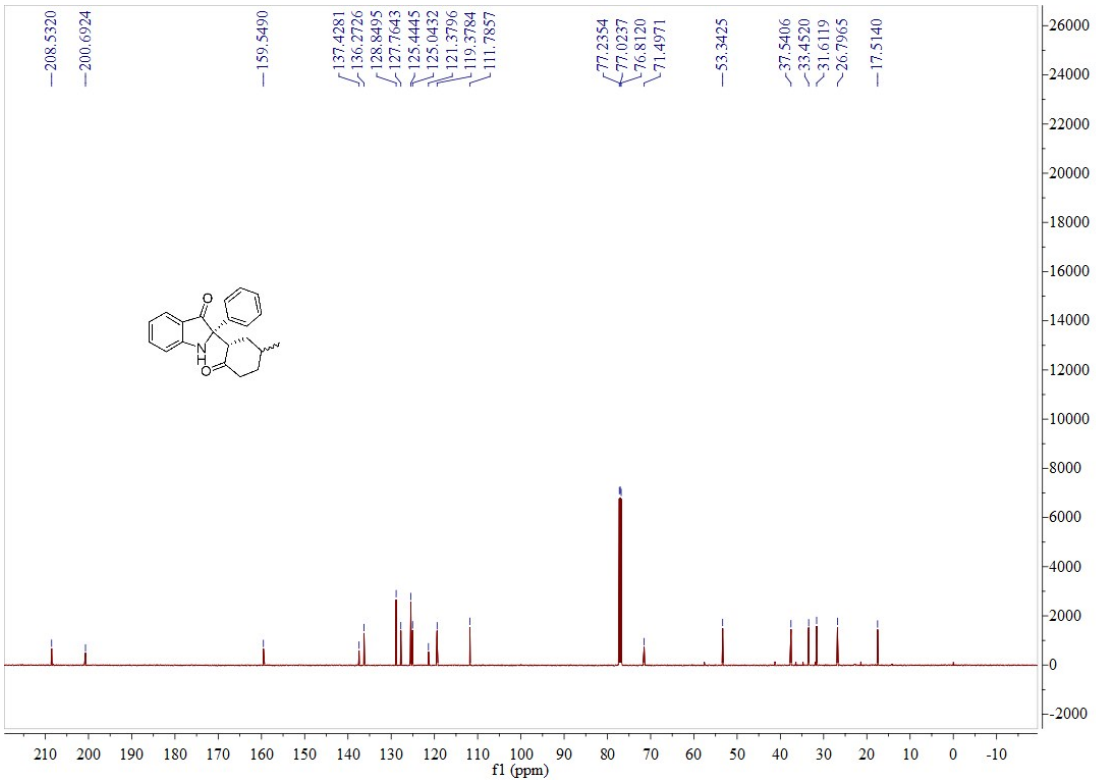
^{13}C NMR Spectrum ($CDCl_3$) of 3q



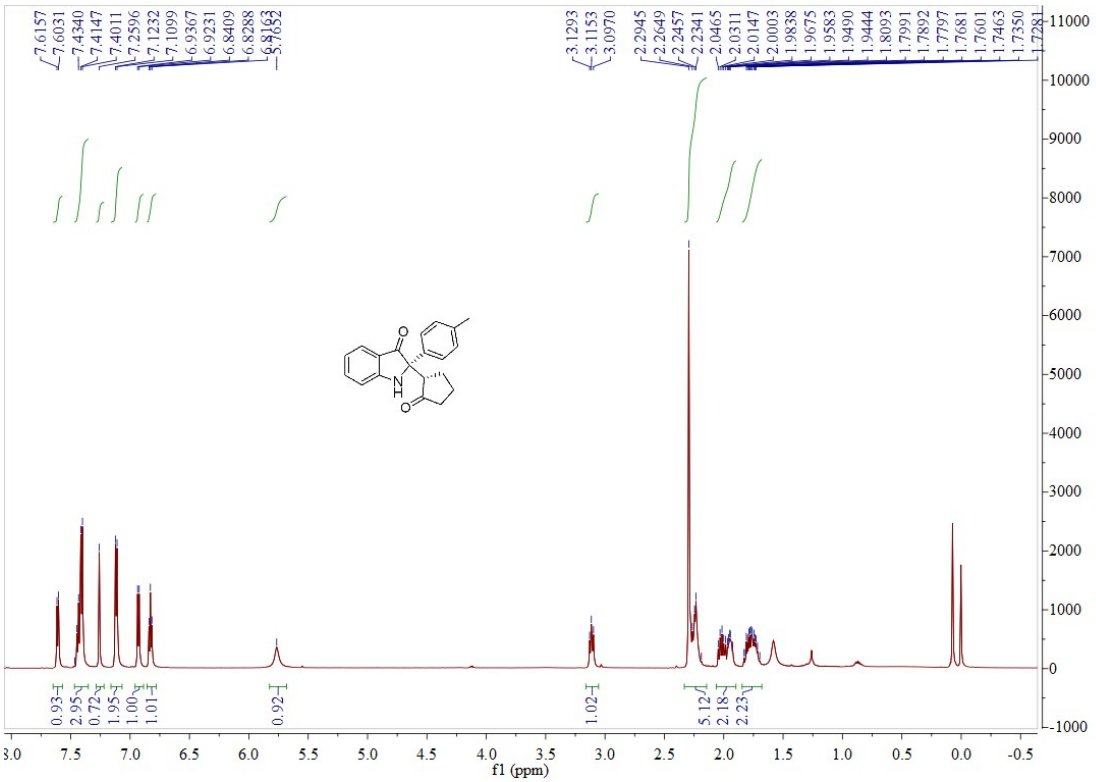
^{1}H NMR Spectrum ($CDCl_3$) of 3r



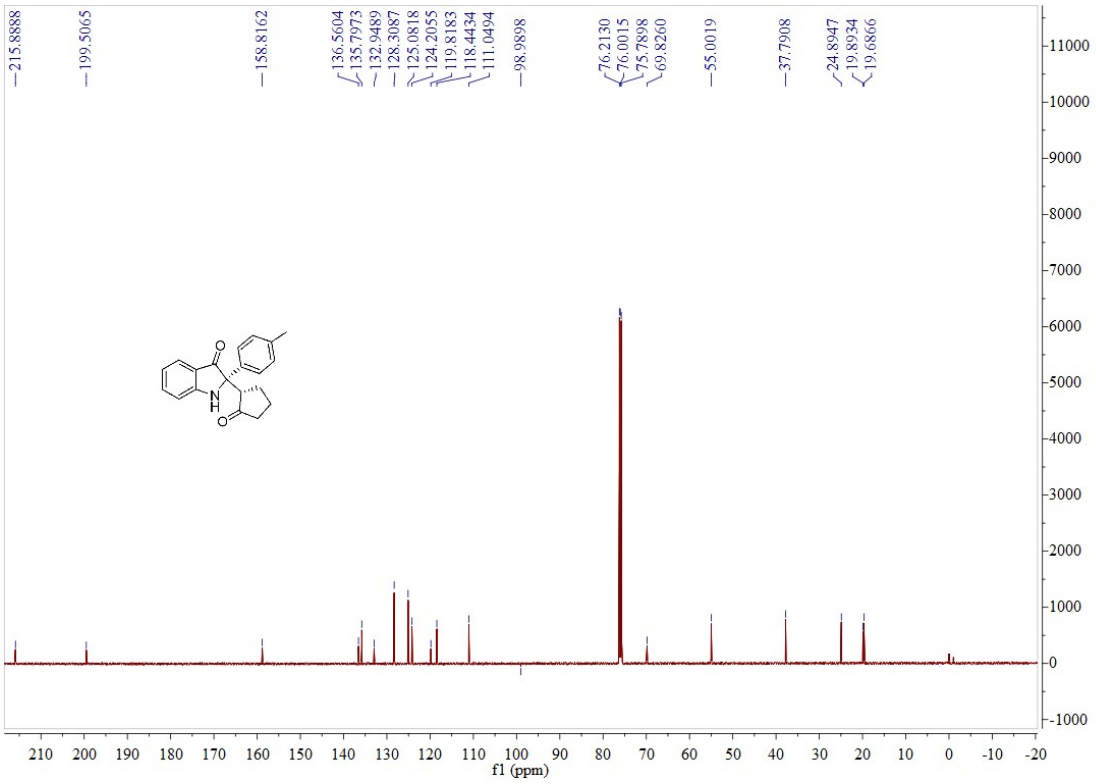
^{13}C NMR Spectrum ($CDCl_3$) of 3r



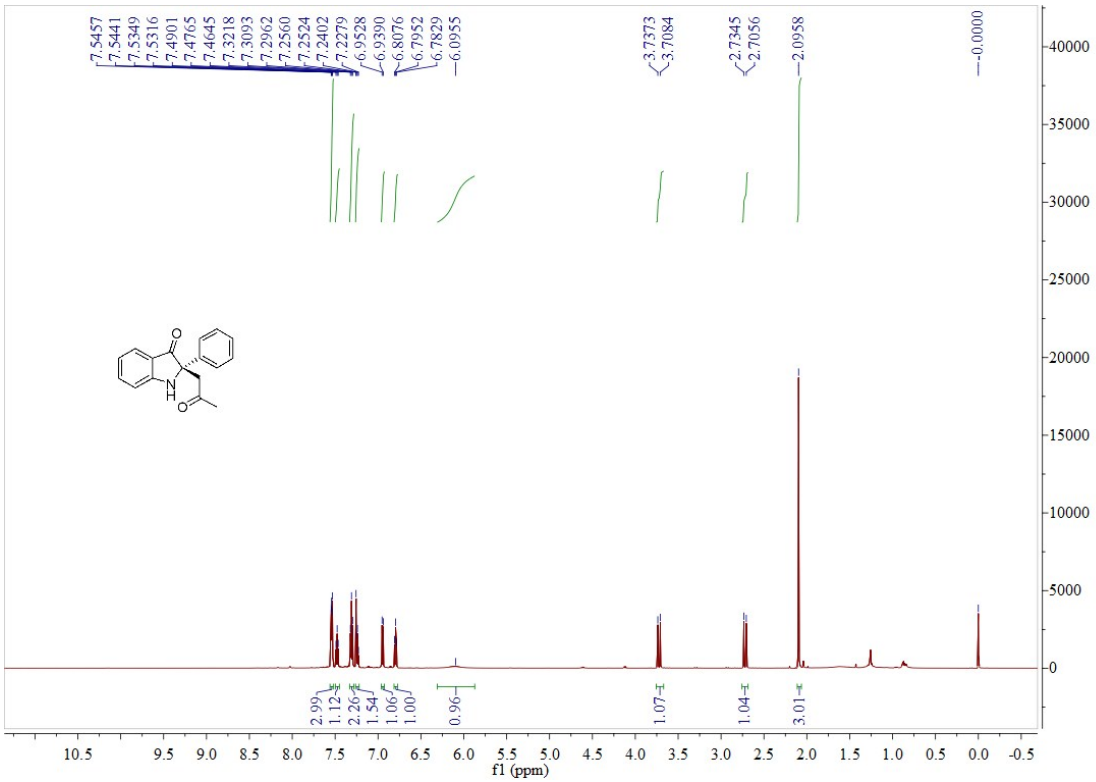
^{1}H NMR Spectrum ($CDCl_3$) of 3s



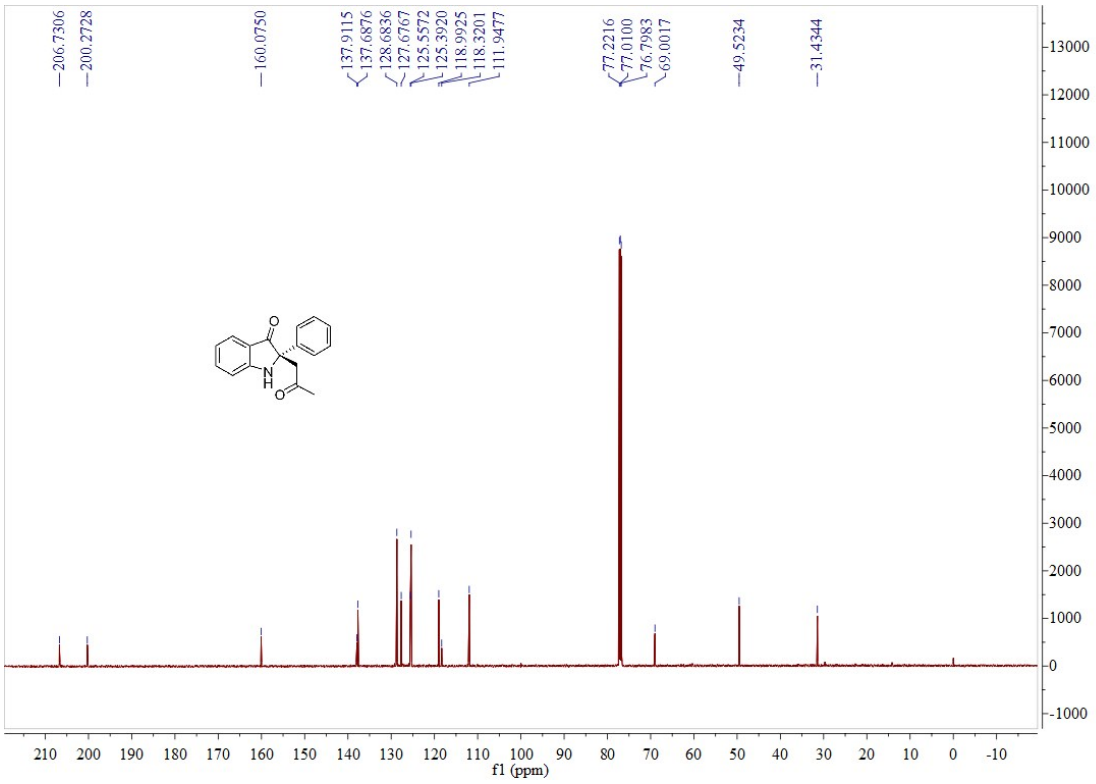
^{13}C NMR Spectrum ($CDCl_3$) of 3s



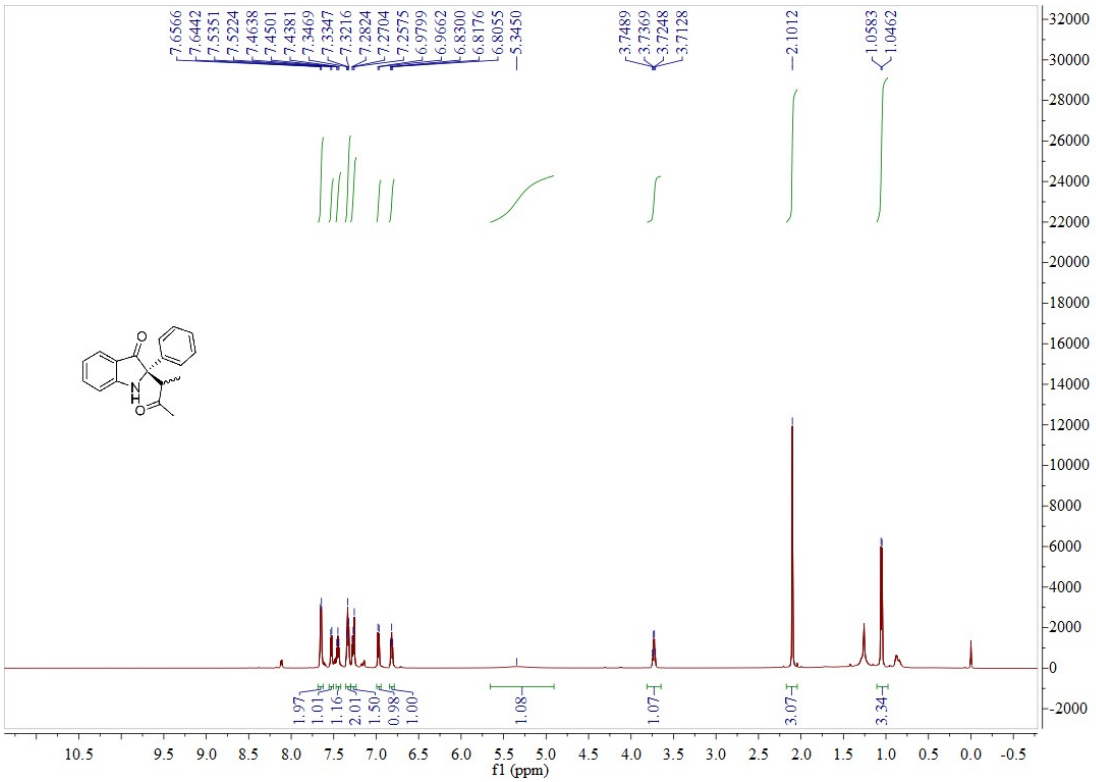
^{1}H NMR Spectrum ($CDCl_3$) of 3t



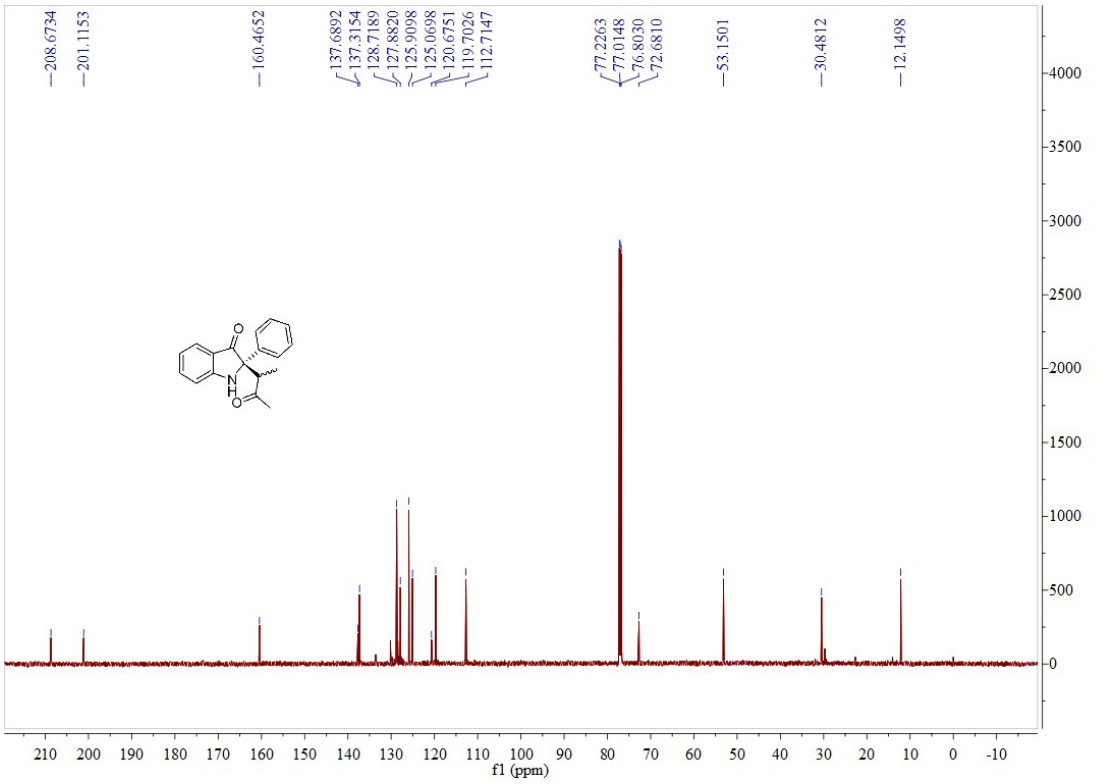
^{13}C NMR Spectrum ($CDCl_3$) of 3t



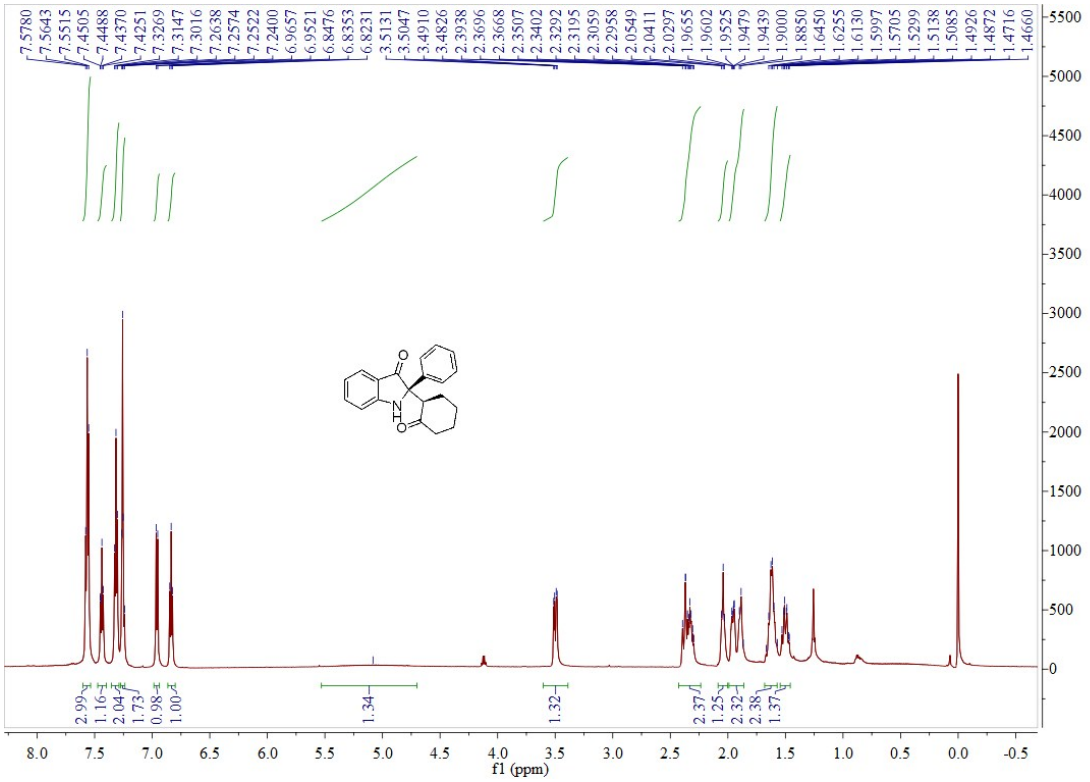
^{1}H NMR Spectrum ($CDCl_3$) of 3u



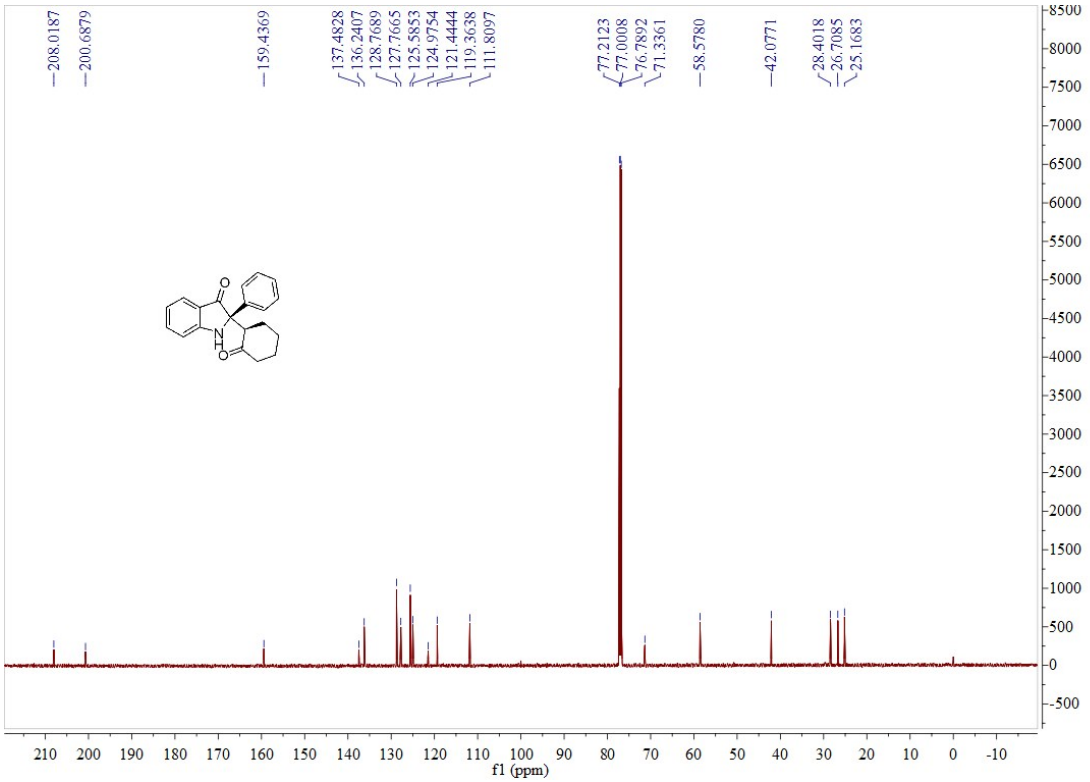
^{13}C NMR Spectrum ($CDCl_3$) of 3u



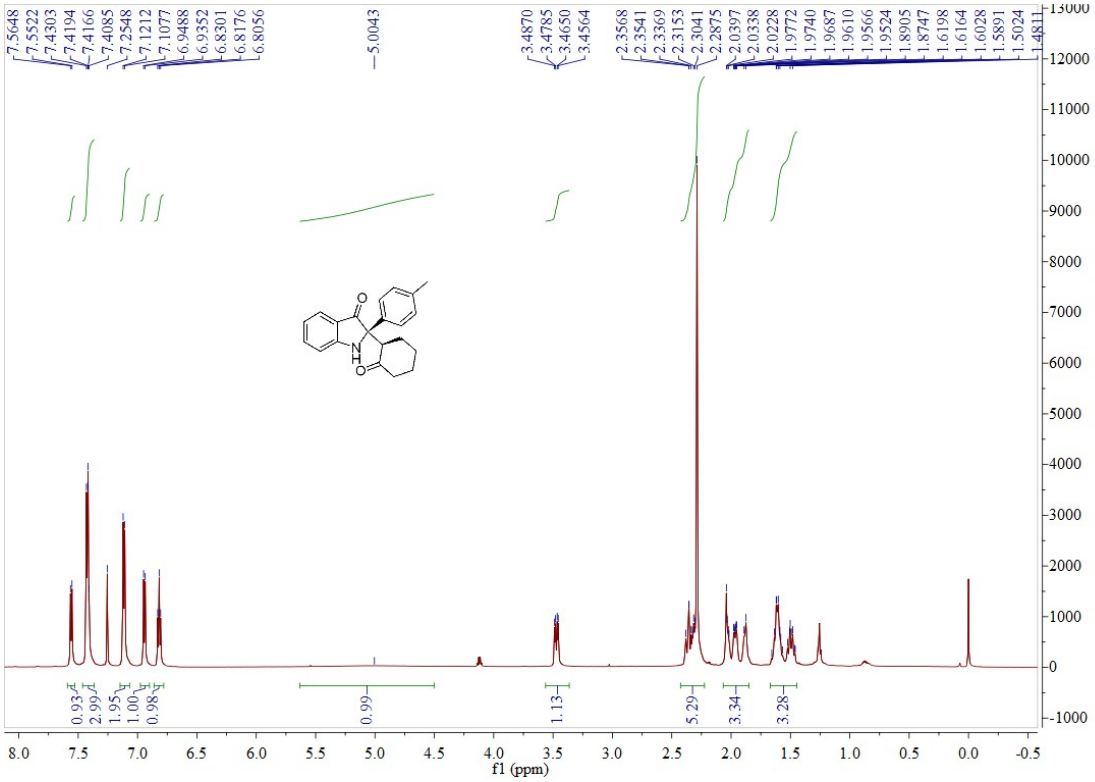
^{1}H NMR Spectrum ($CDCl_3$) of 4a



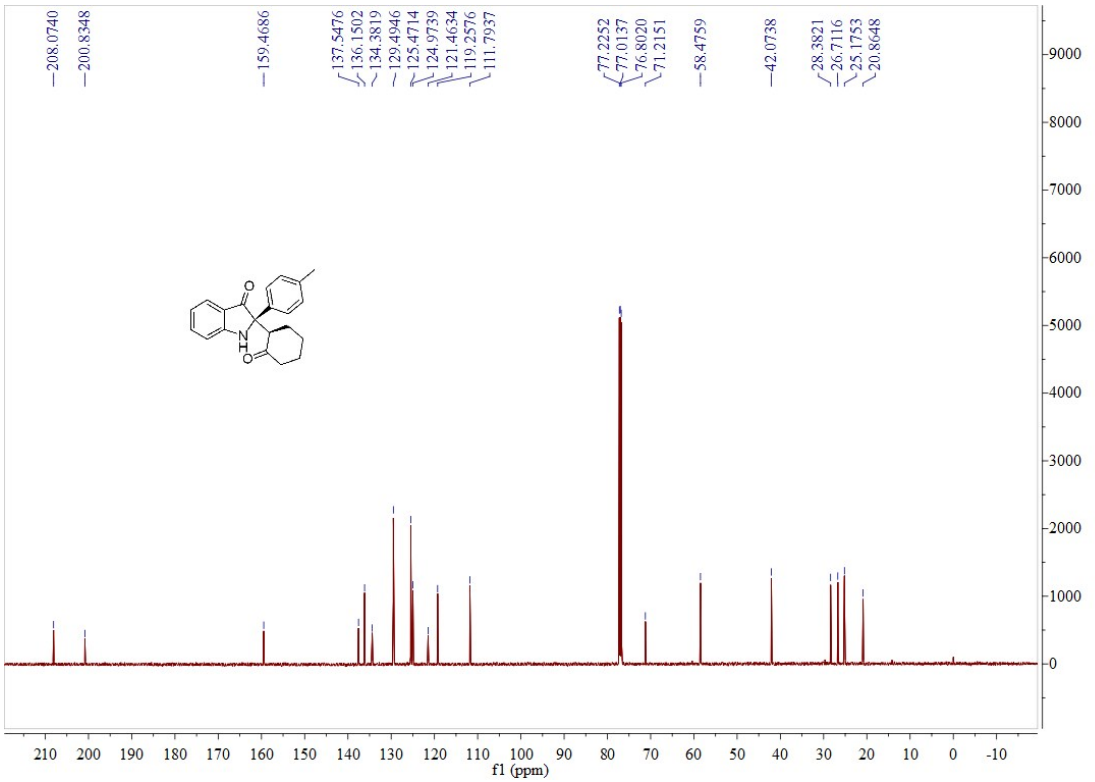
^{13}C NMR Spectrum ($CDCl_3$) of 4a



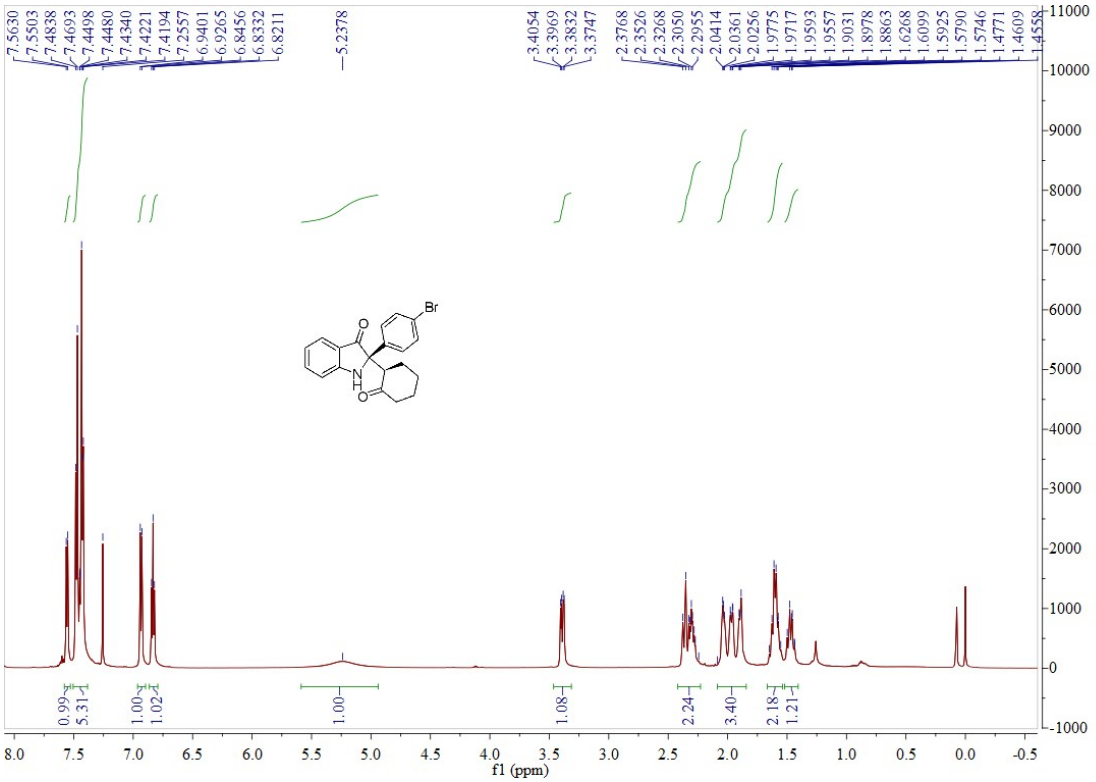
^{1}H NMR Spectrum ($CDCl_3$) of 4b



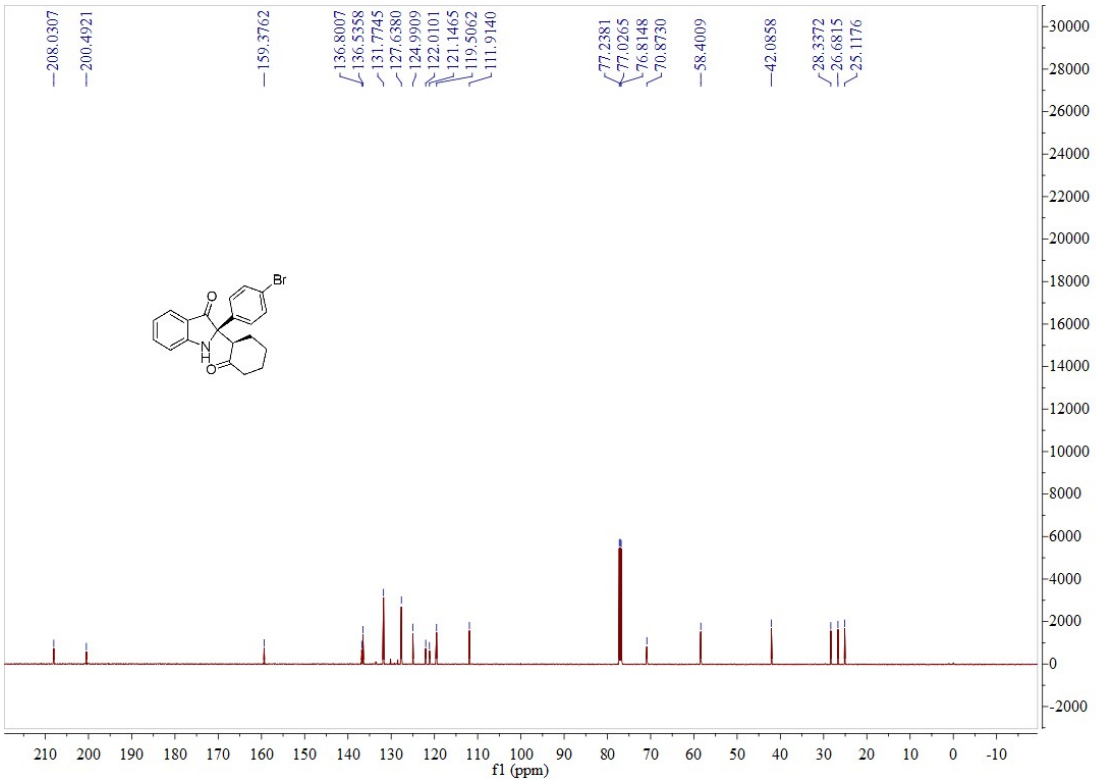
^{13}C NMR Spectrum ($CDCl_3$) of 4b



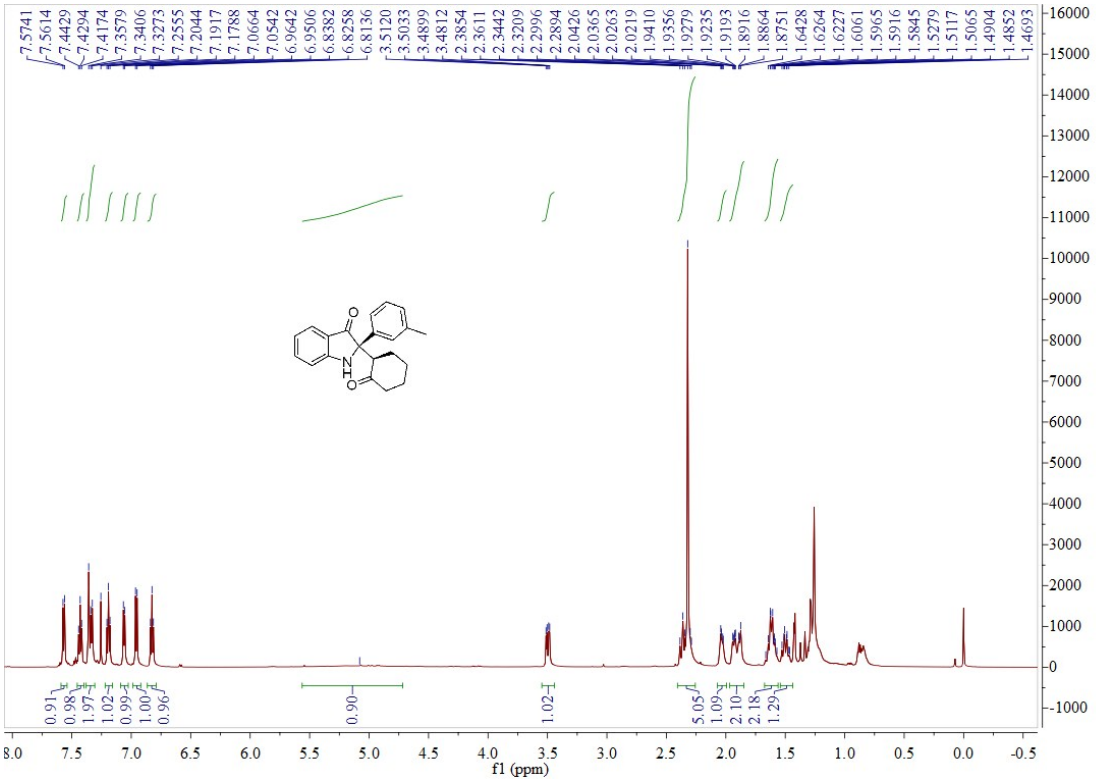
^{1}H NMR Spectrum ($CDCl_3$) of 4c



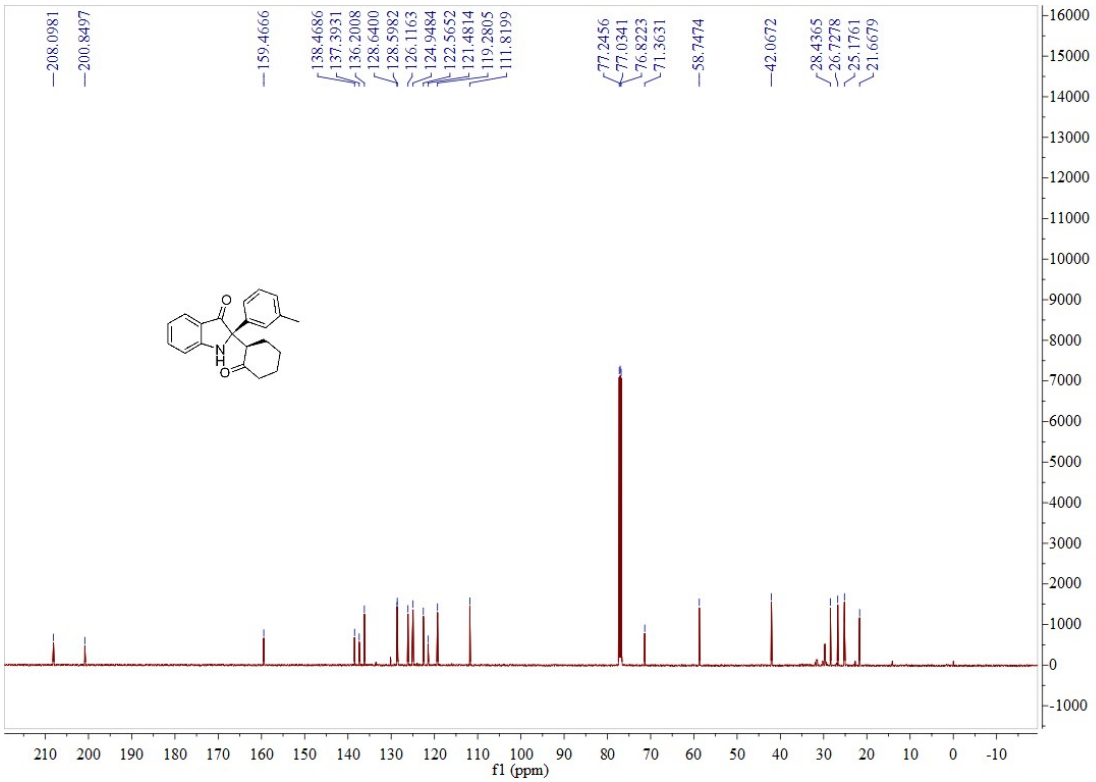
^{13}C NMR Spectrum ($CDCl_3$) of 4c



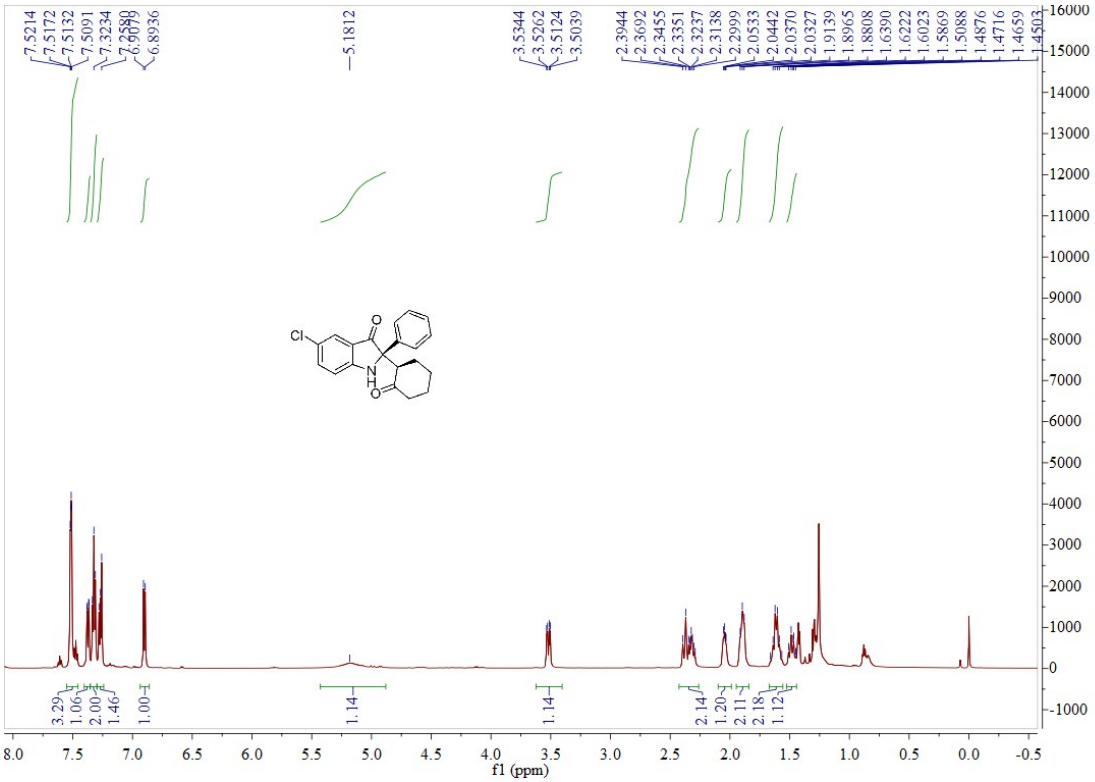
^{1}H NMR Spectrum ($CDCl_3$) of 4d



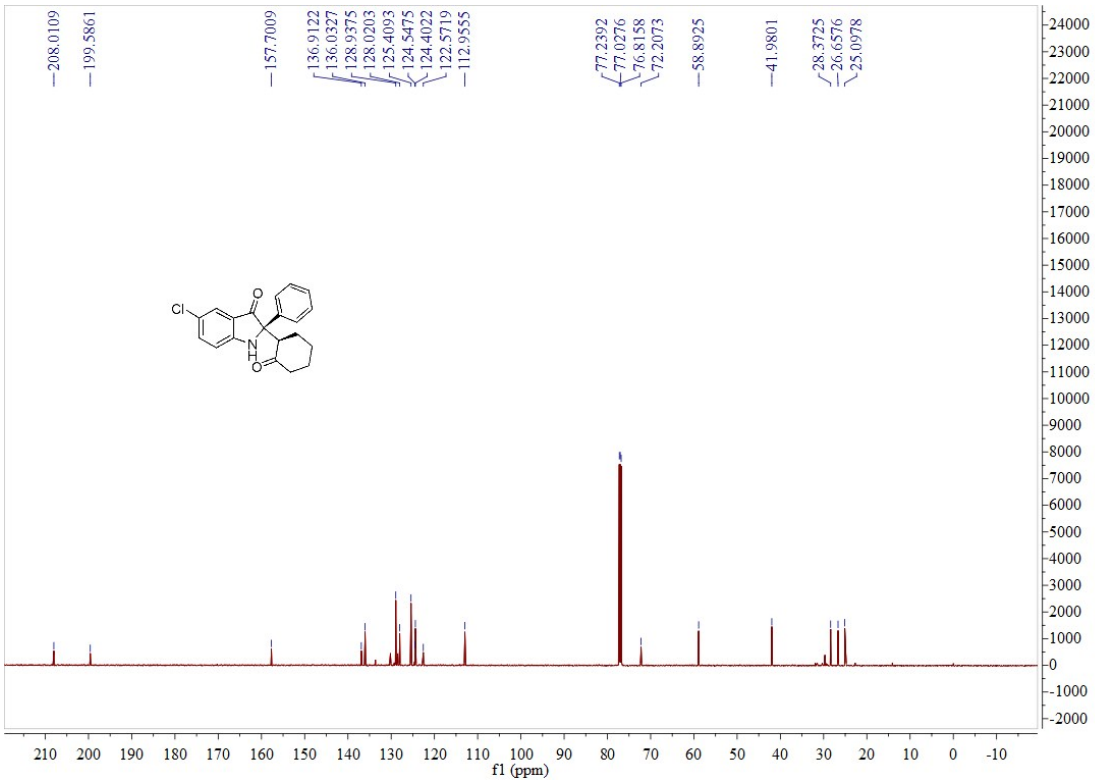
^{13}C NMR Spectrum ($CDCl_3$) of 4d



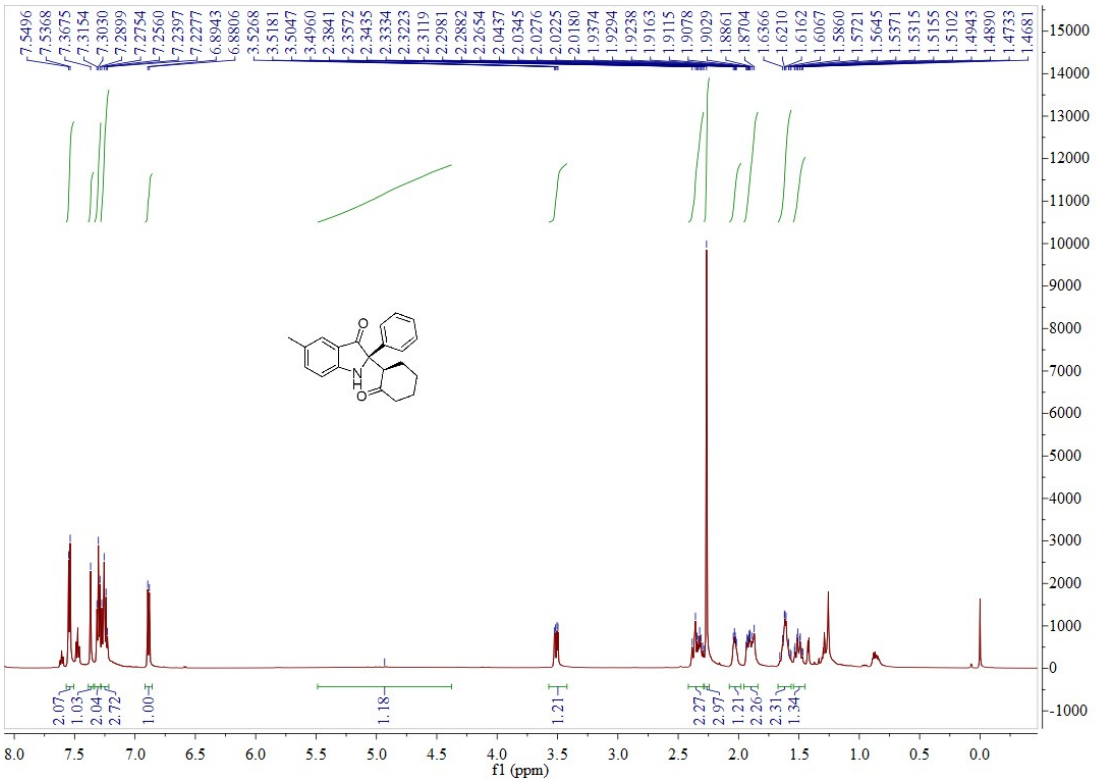
^{1}H NMR Spectrum ($CDCl_3$) of 4e



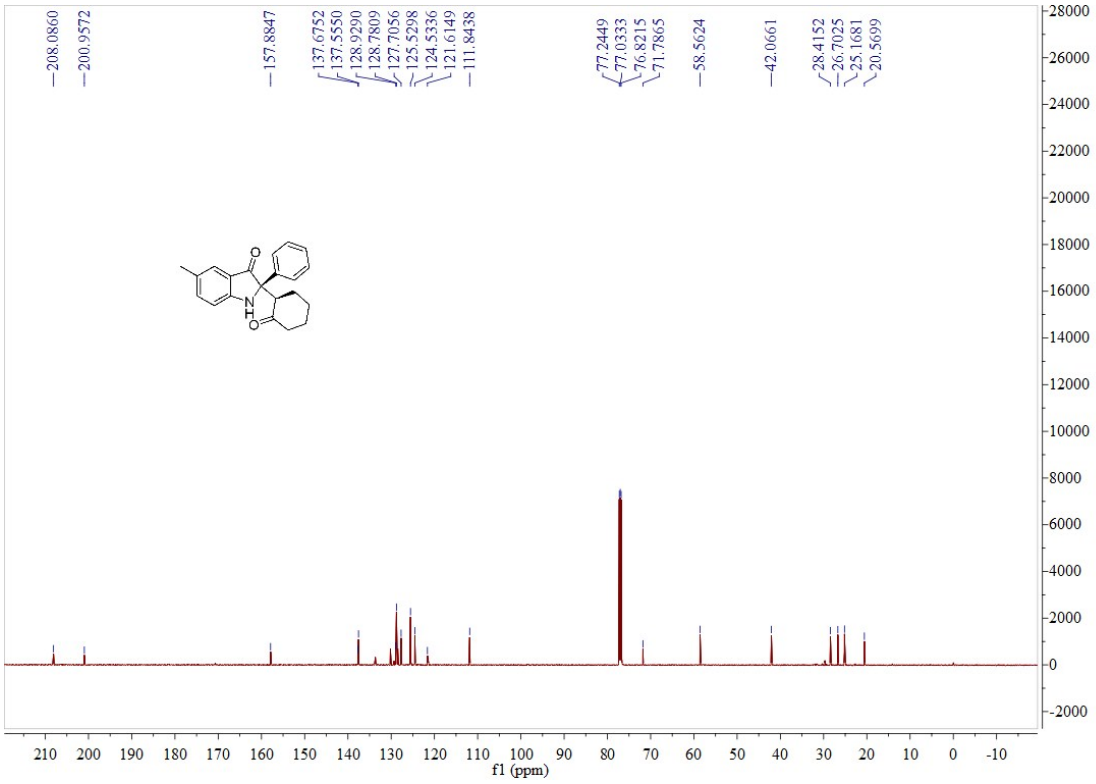
^{13}C NMR Spectrum ($CDCl_3$) of 4e



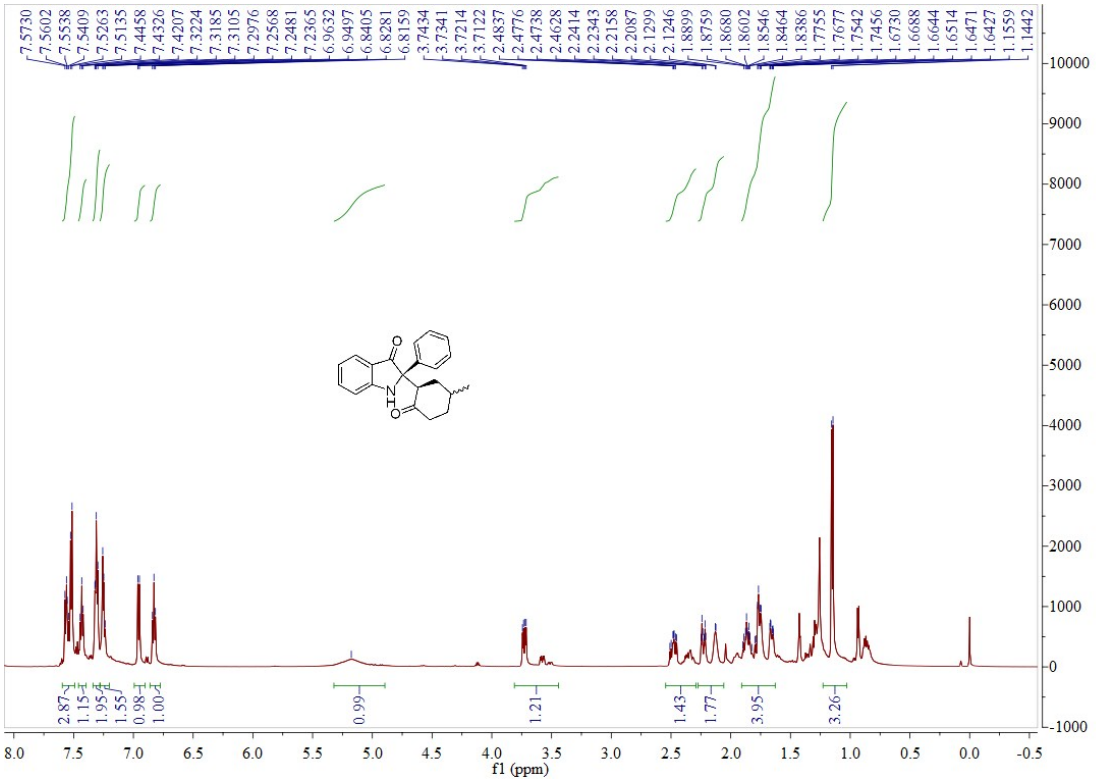
^{1}H NMR Spectrum ($CDCl_3$) of 4f



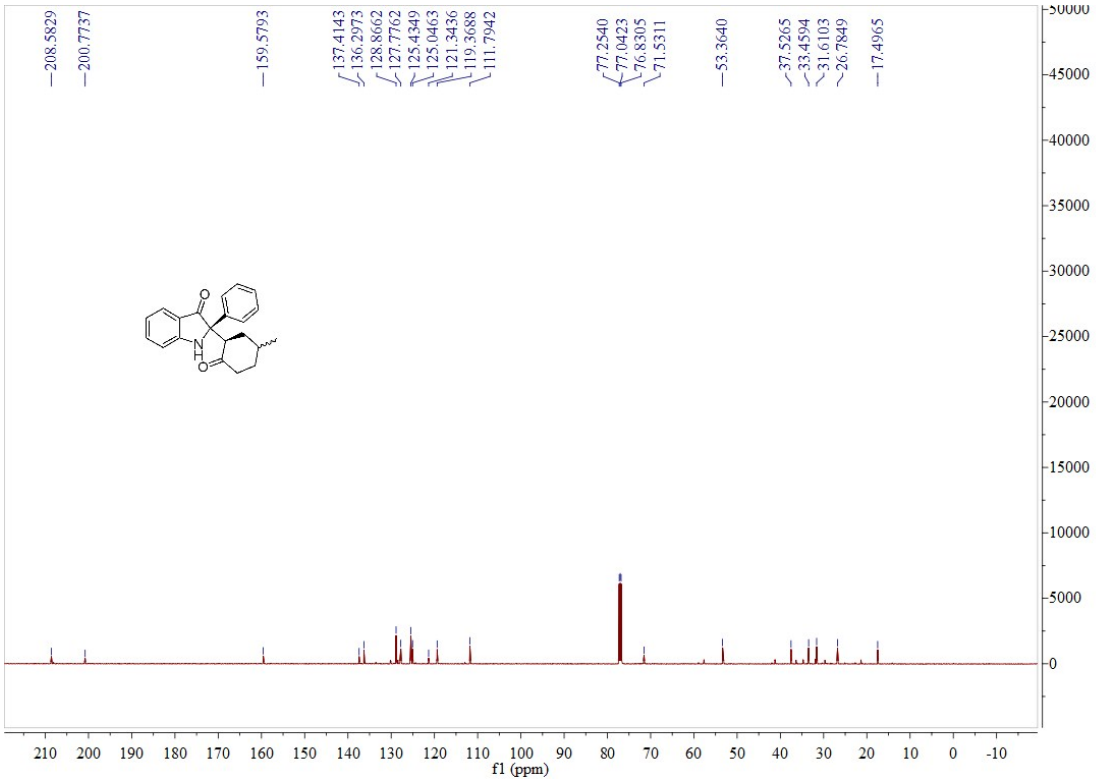
^{13}C NMR Spectrum ($CDCl_3$) of 4f



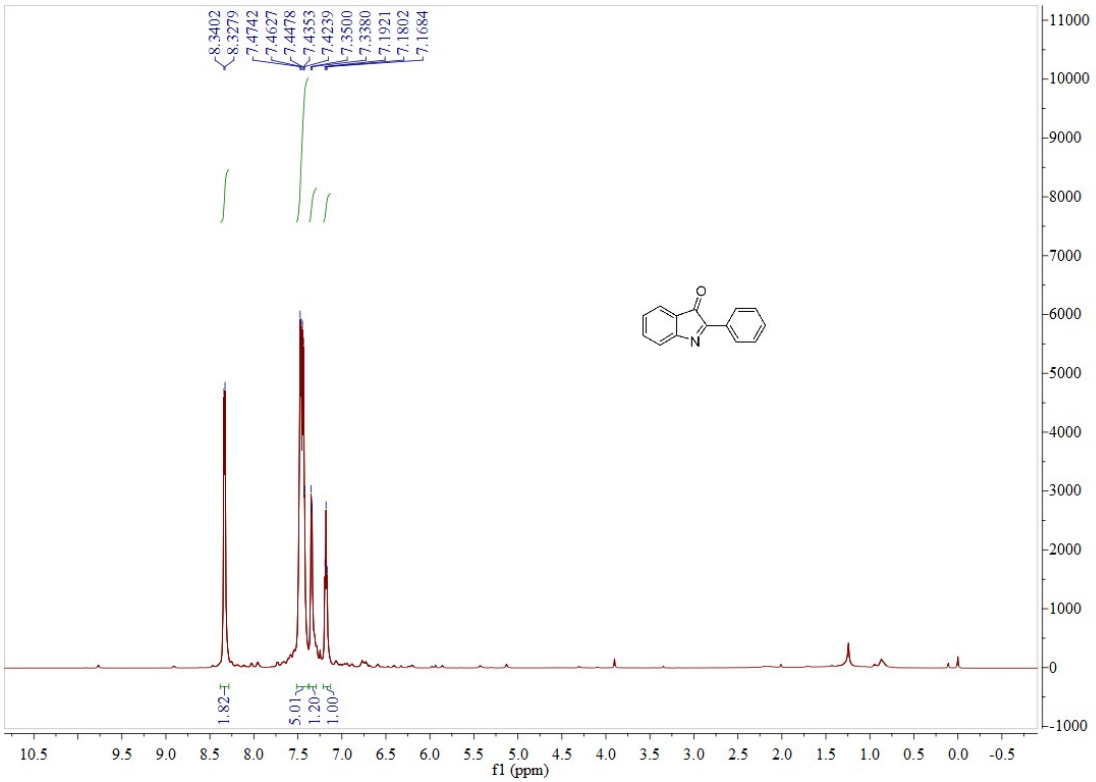
^{1}H NMR Spectrum ($CDCl_3$) of 4g



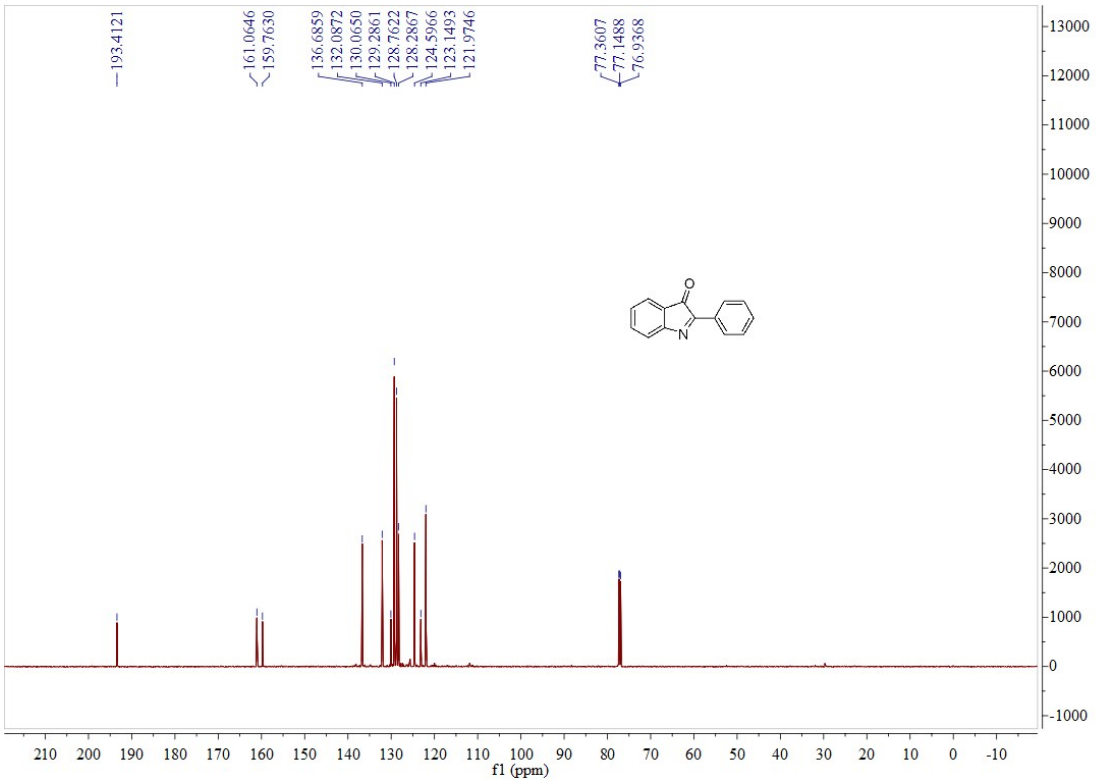
^{13}C NMR Spectrum ($CDCl_3$) of 4g



^{1}H NMR Spectrum ($CDCl_3$) of 2-phenyl-3H-indol-3-one

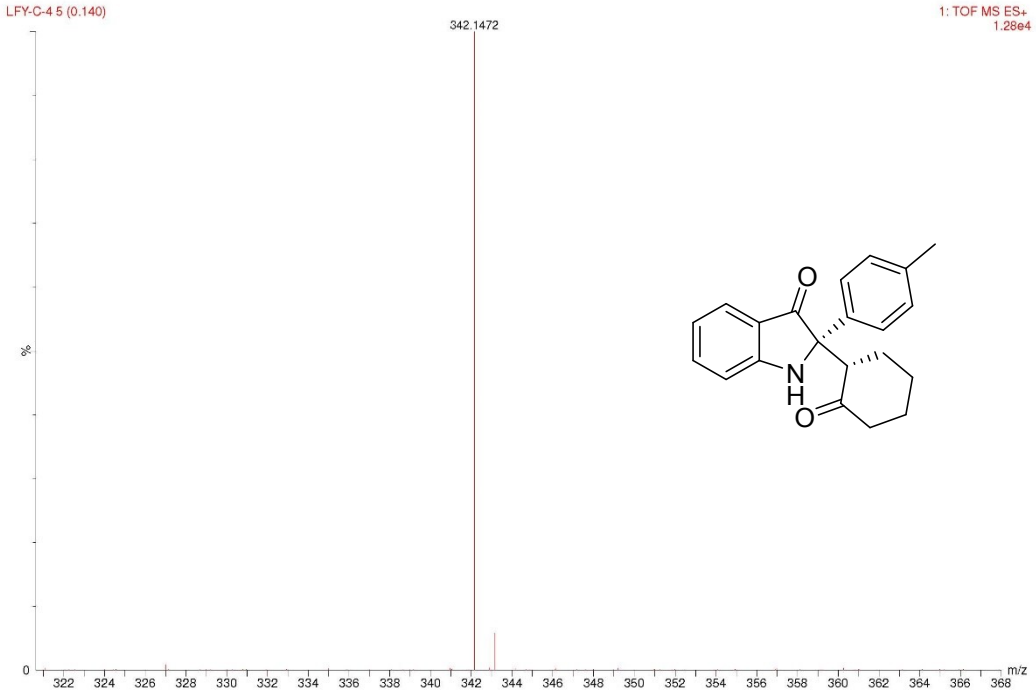


^{13}C NMR Spectrum ($CDCl_3$) of 2-phenyl-3H-indol-3-one

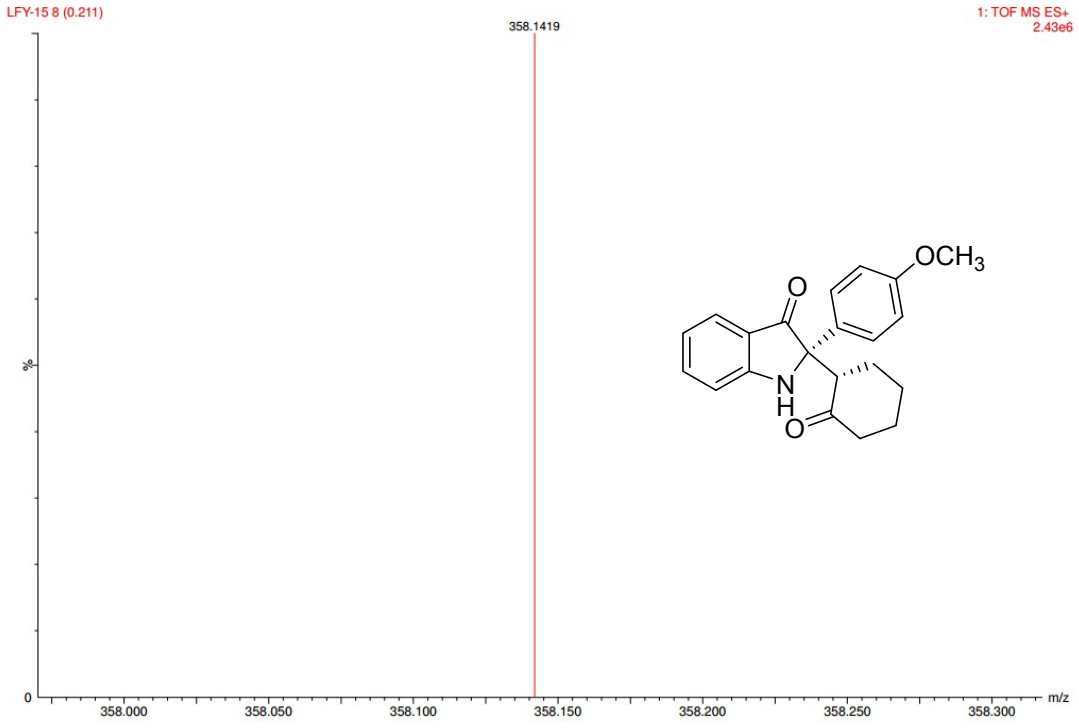


9. HRMS of the products

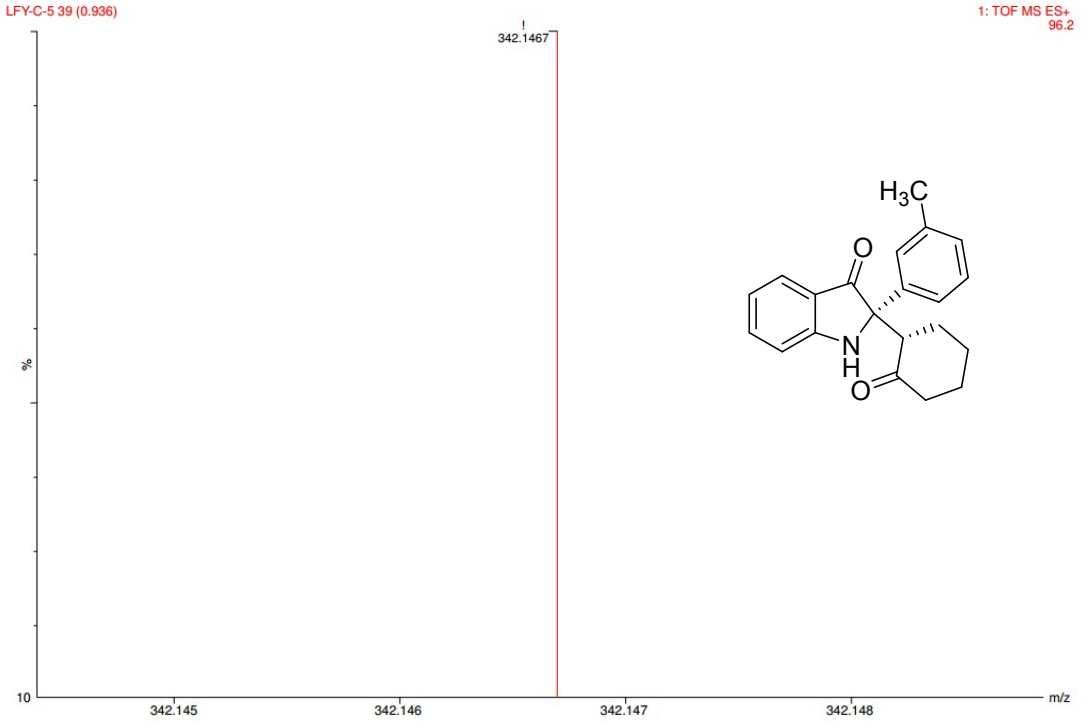
HRMS-3b



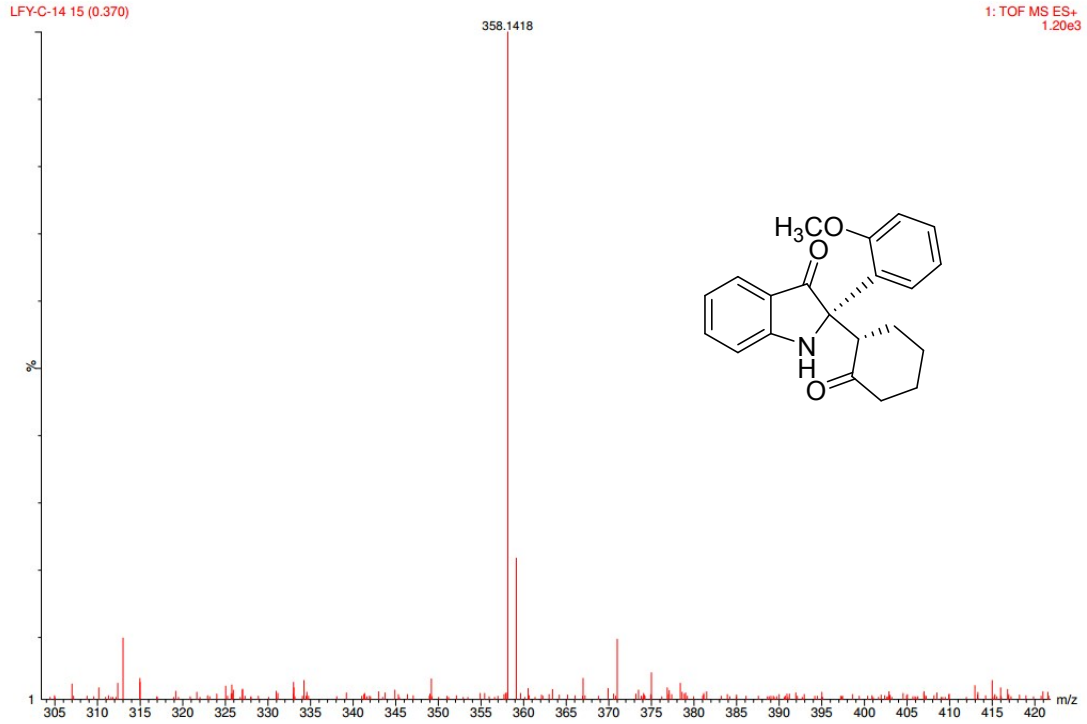
HRMS-3c



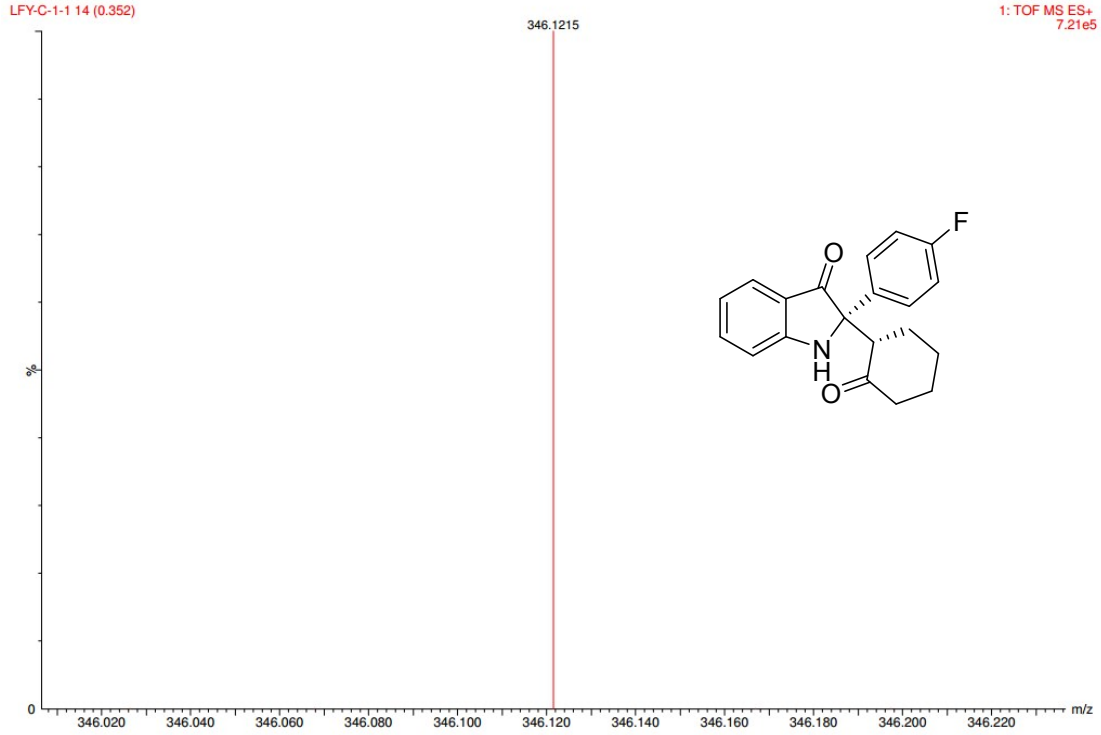
HRMS-3d



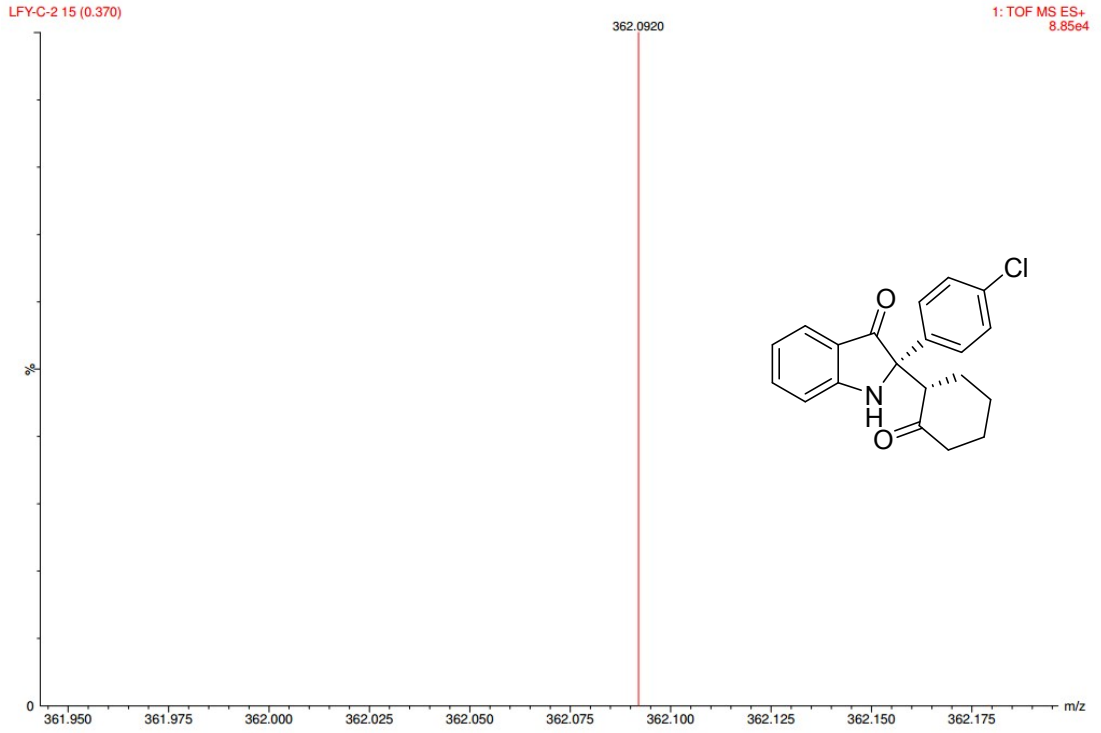
HRMS-3e



HRMS-3f

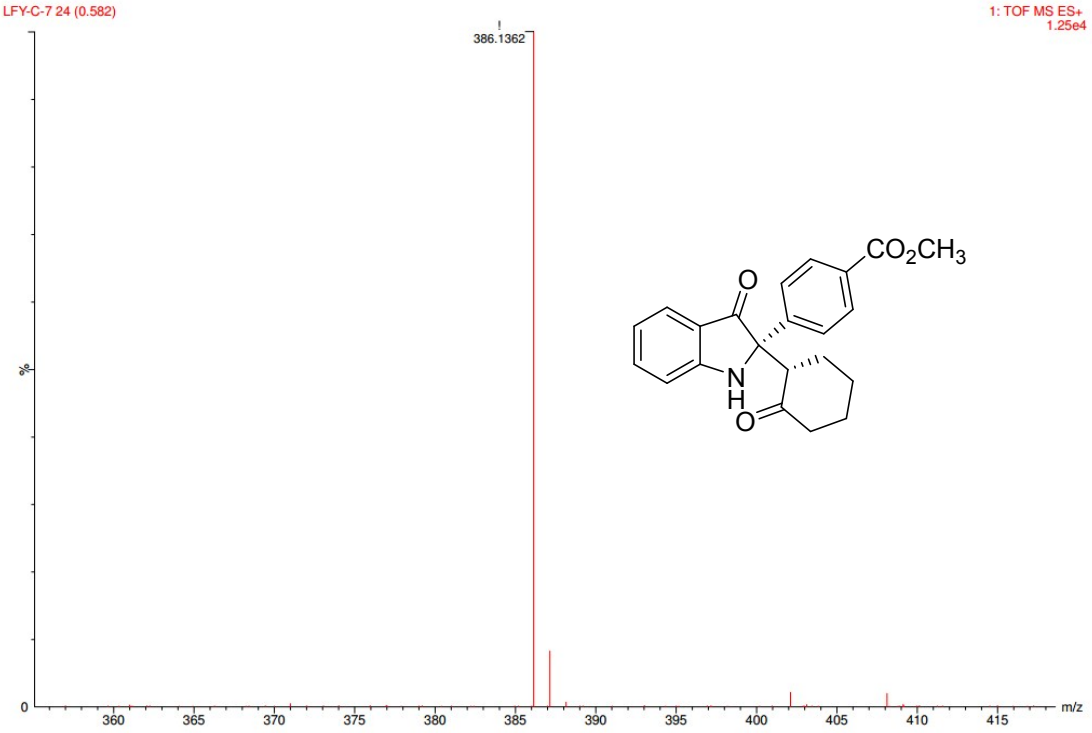


HRMS-3g



HRMS-3h

HRMS-3i



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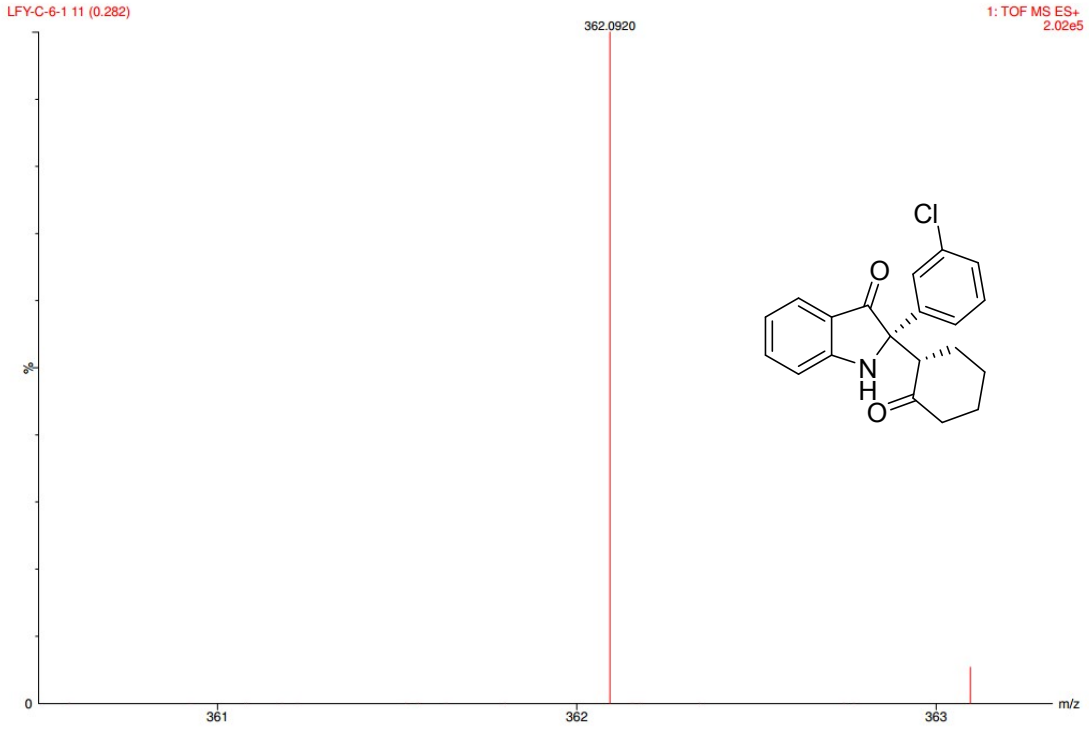
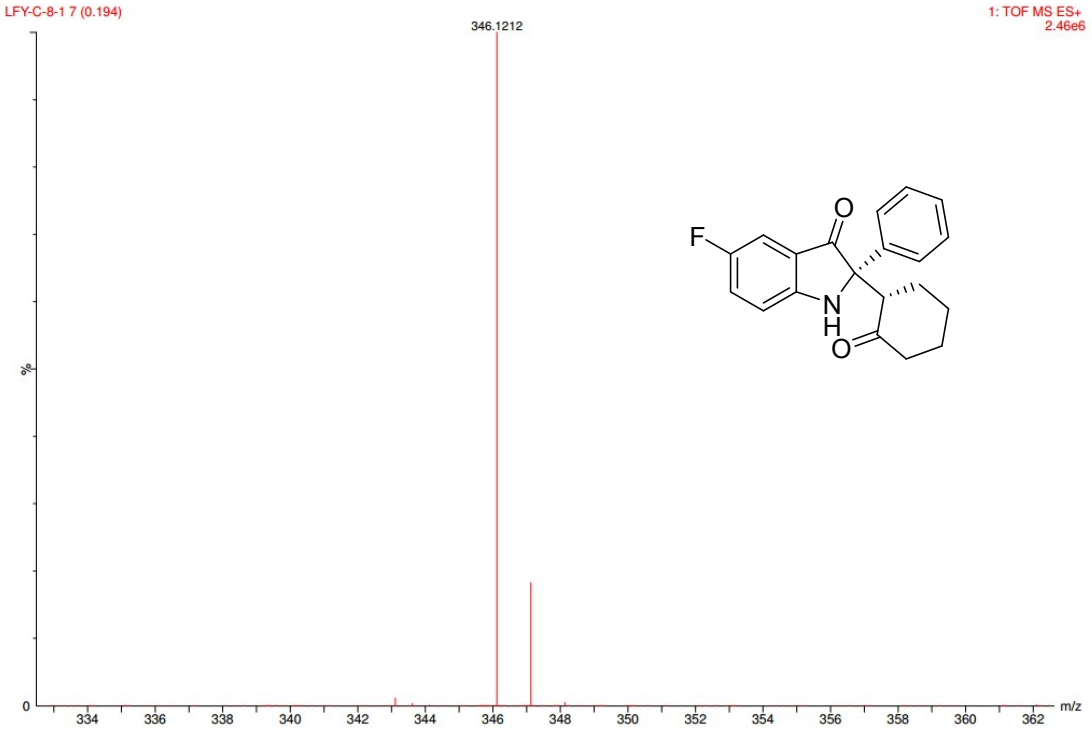
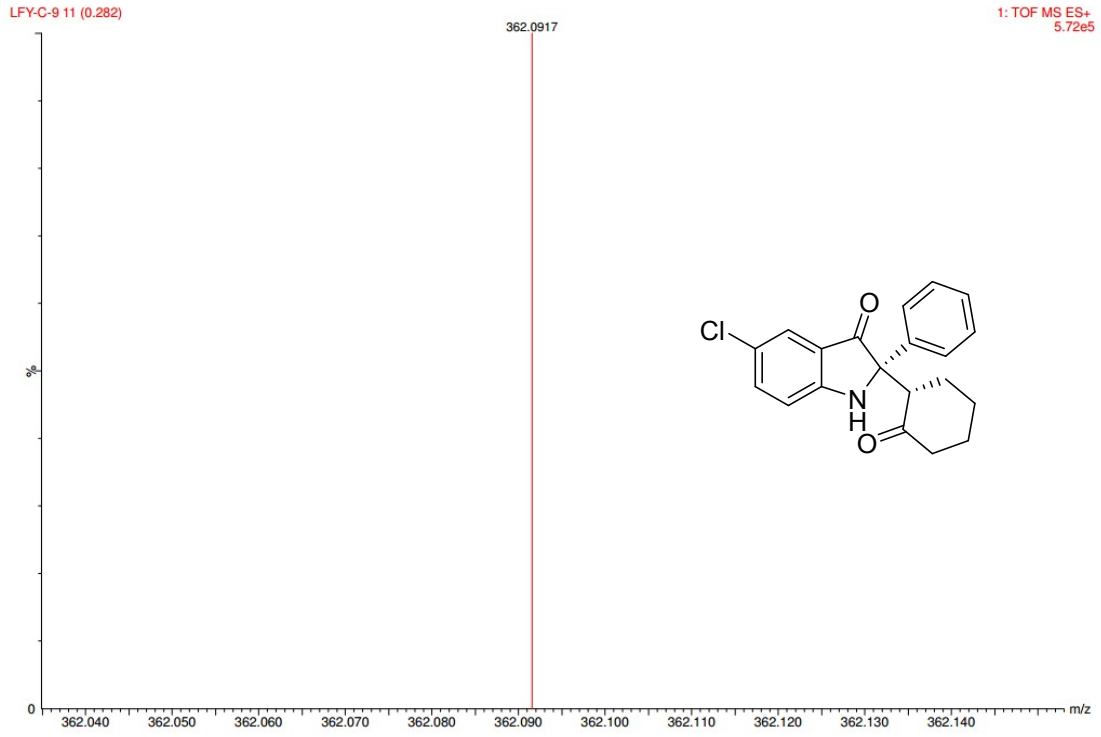


HRMS-3k



HRMS-3l



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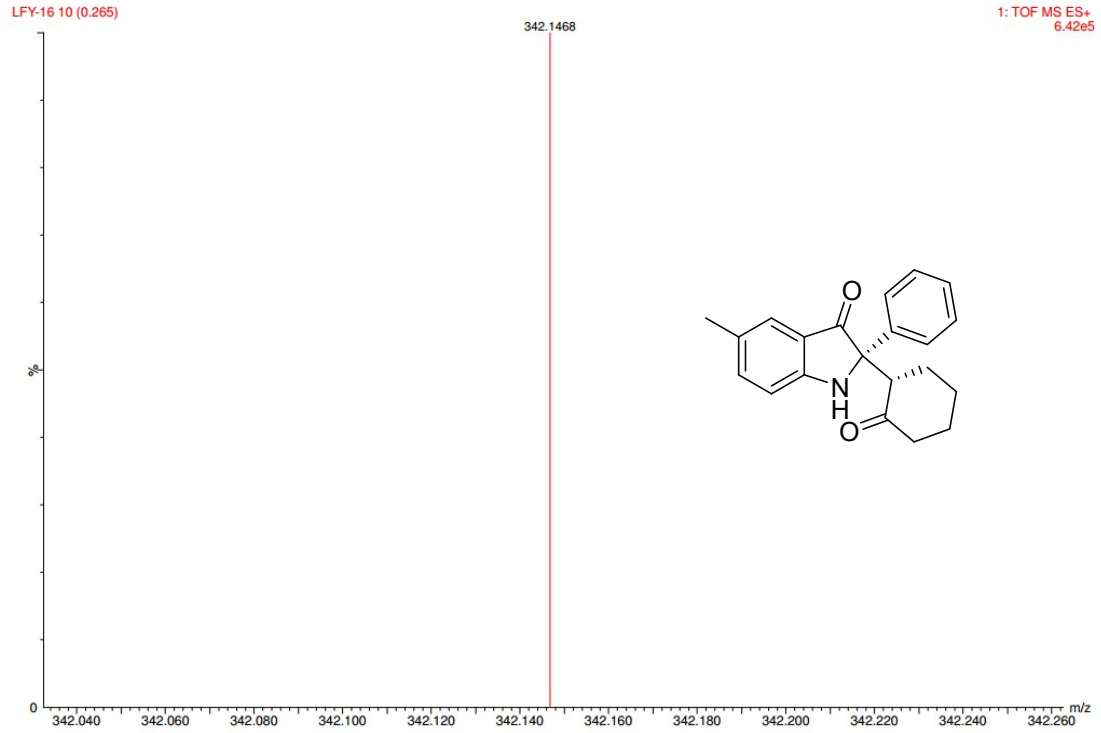
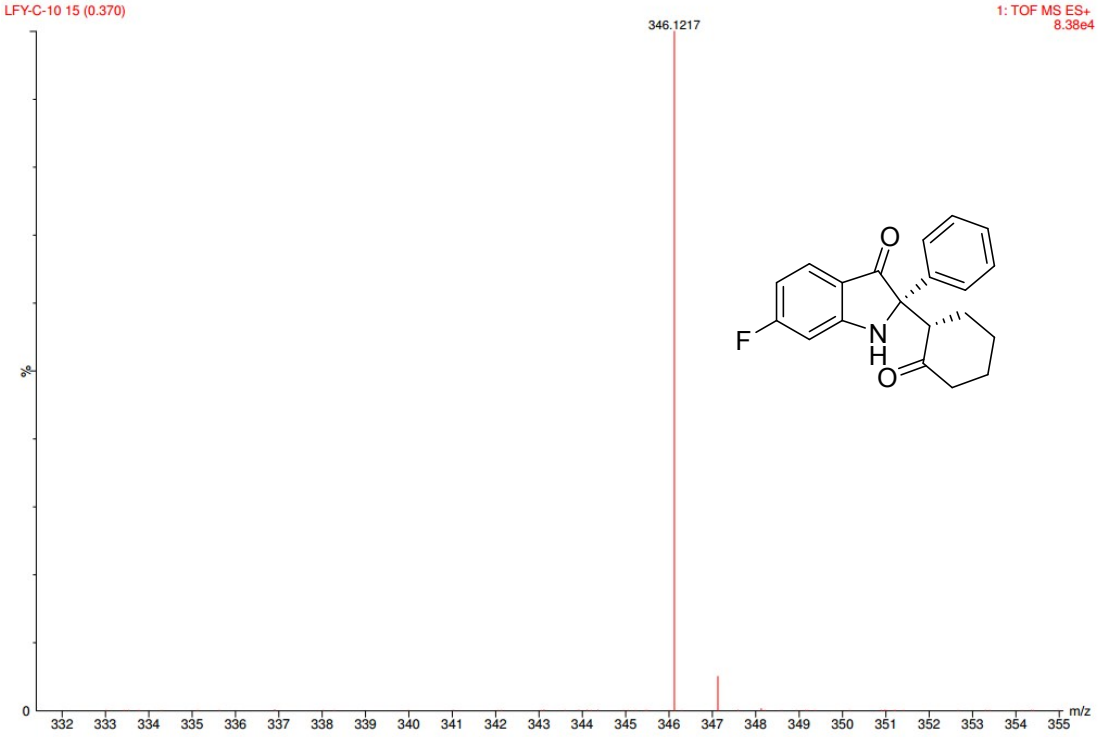
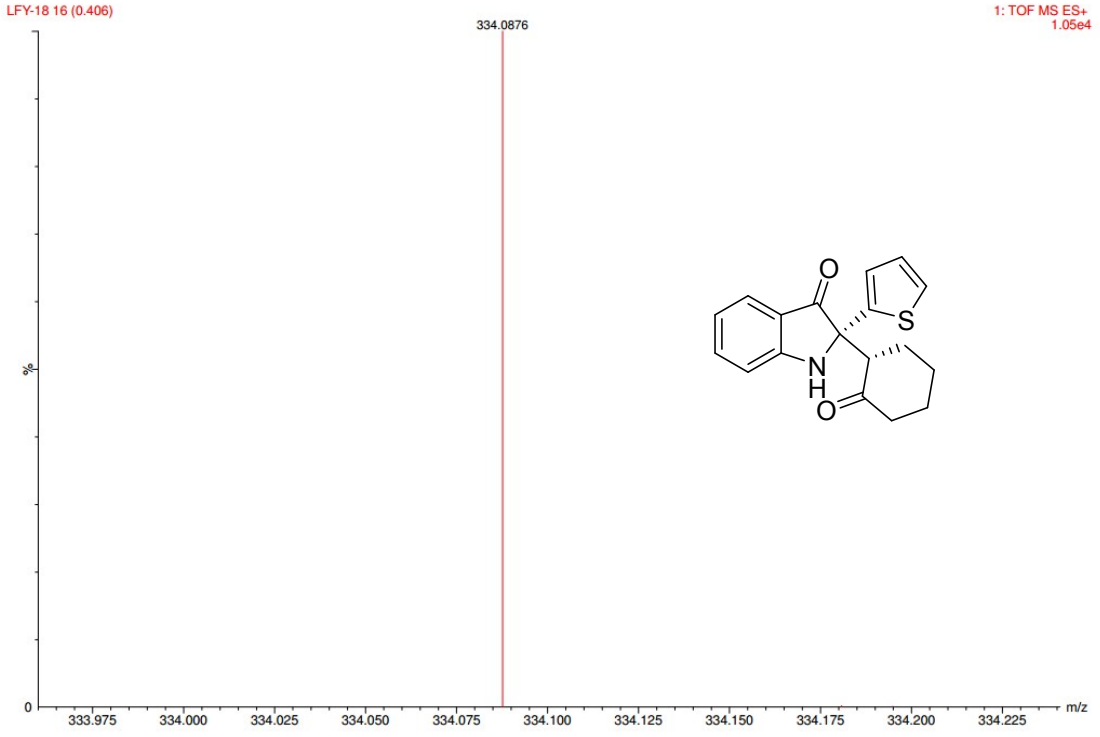


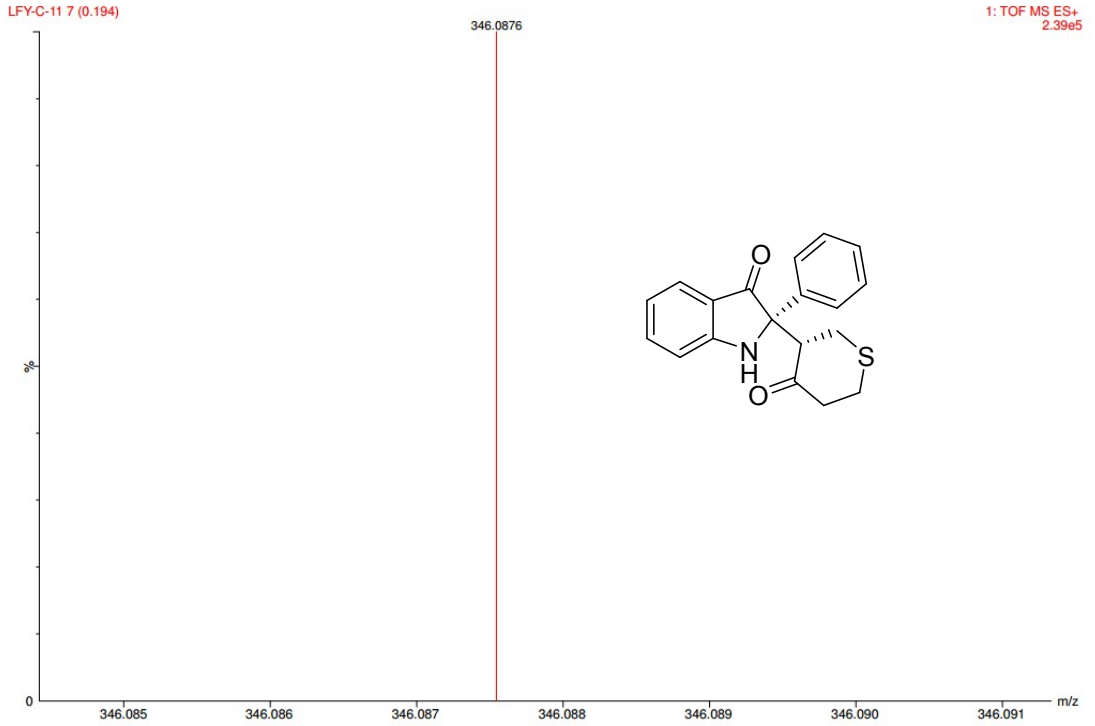
HRMS-3o



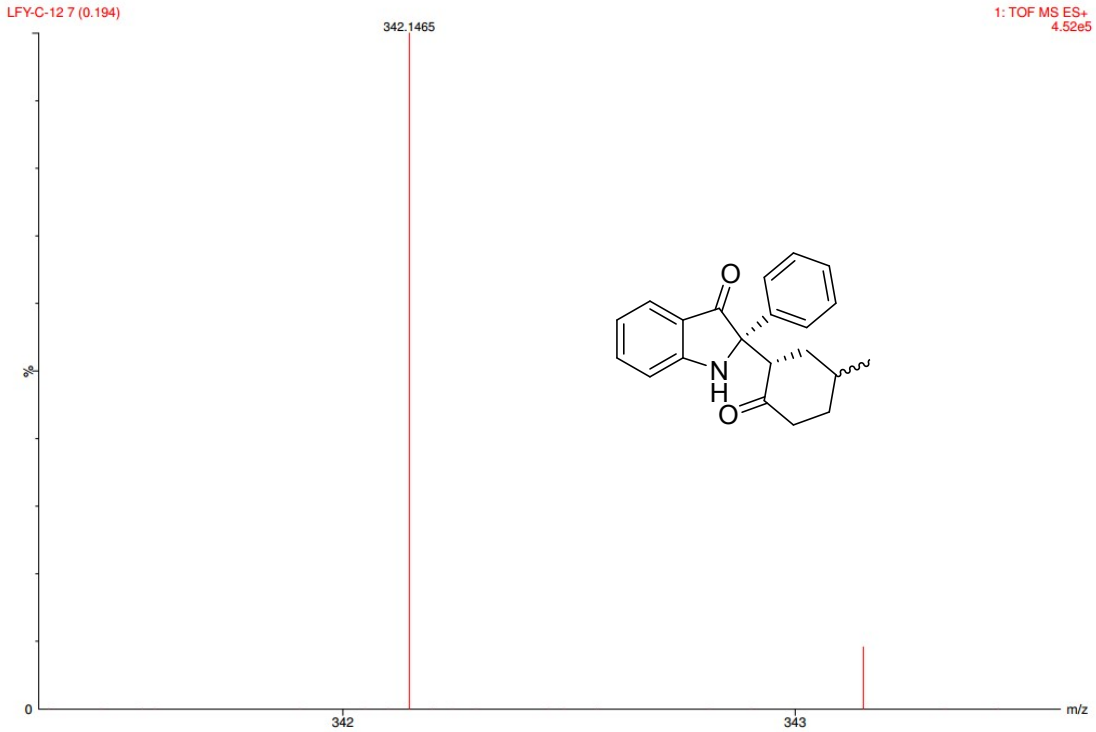
HRMS-3p



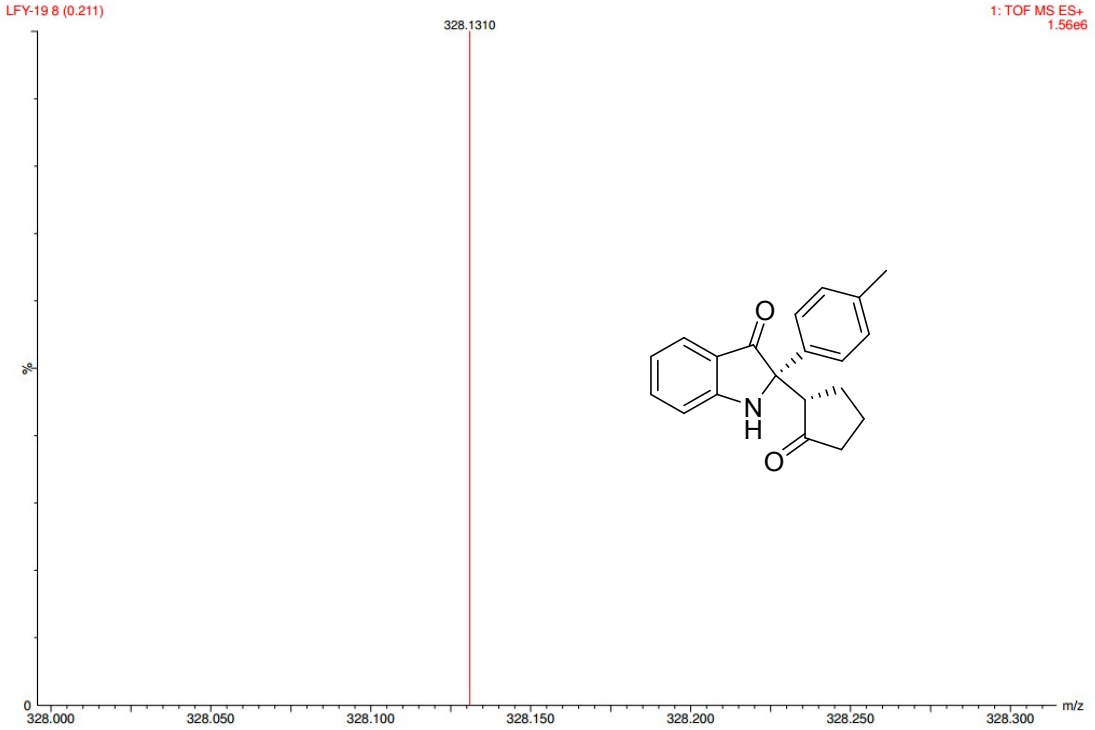
HRMS-3q



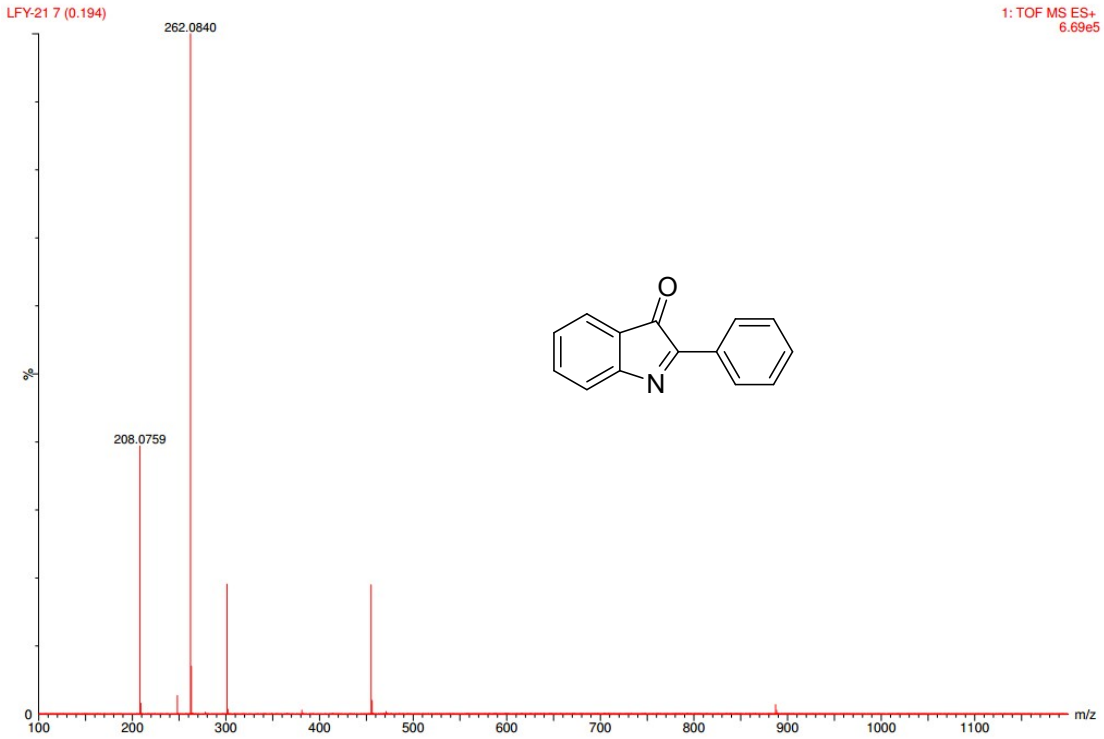
HRMS-3r



HRMS-3s



HRMS-2-phenyl-3H-indol-3-one



HRMS-G

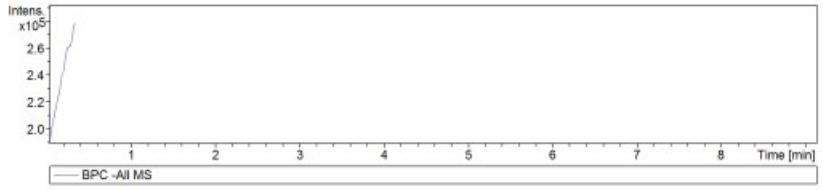
Compound Spectrum SmartFormula Report

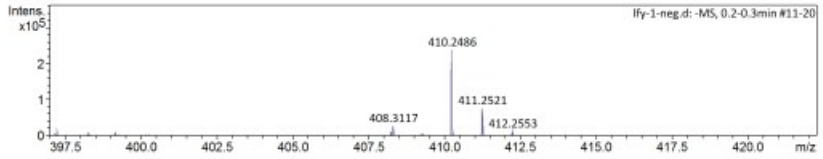
Analysis Info

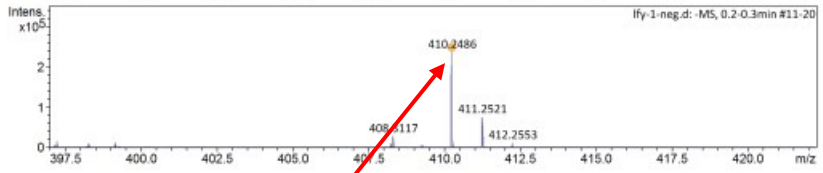
Analysis Name	D:\Data\wzf\lfy-1-neg.d	Acquisition Date	4/25/2019 10:27:40 AM
Method	DirectInfusion - MS - positive.m	Operator	Demo User
Sample Name	1	Instrument	impact II 1825265.10221
Comment			

Acquisition Parameter

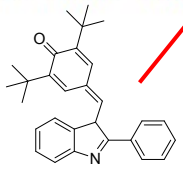
Source Type	ESI	Ion Polarity	Negative	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	3000 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1300 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C







Meas. m/z	#	Ion Formula	m/z	e⁻ Conf	N-Rule
410.2486	1	C29H32NO	410.2489	even	ok



G [M+H$^+$] = 410.2478

lfy-1-neg.d
Bruker Compass DataAnalysis 4.4 printed: 4/25/2019 4:43:50 PM by: demo Page 1 of 1

HRMS-^{18}O-3a ($H_2{}^{18}O$):

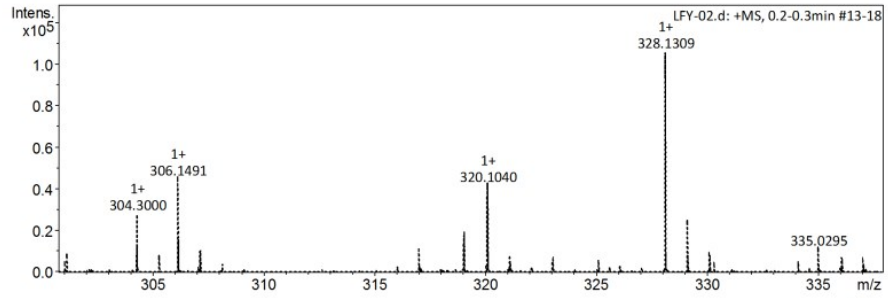
Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\2019\guanzhi\LFY-02.d	Acquisition Date	7/8/2019 10:12:10 AM
Method	DirectInfusion - MS - positive.m		
Sample Name		Operator	Demo User
Comment		Instrument	impact II 1825265.10221

Acquisition Parameter

Source Type	ESI	Ion Polarity	Positive	Set Nebulizer	0.4 Bar
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	5.0 l/min
Scan End	1300 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	Score	rdb	N-Rule	e⁻ Conf
306.1491	1	C20H20NO2	C20H19NO2	306.1489	M+H	-0.7	1+	33.2	100.00	12.0	ok	even
328.1309	1	C20H19NNaO2		328.1308	M+Na	-0.3	1+	27.9	100.00	12.0	ok	even

HRMS-^{18}O-3a ($^{18}O_2$)

Mass Spectrum SmartFormula Report

Analysis Info

Analysis Name	D:\Data\2019\guanzhi\LYF-01.d	Acquisition Date	6/27/2019 11:57:47 AM
Method	DirectInfusion - MS - positive.m		
Sample Name		Operator	Demo User
Comment		Instrument	impact II 1825265.10221

Acquisition Parameter

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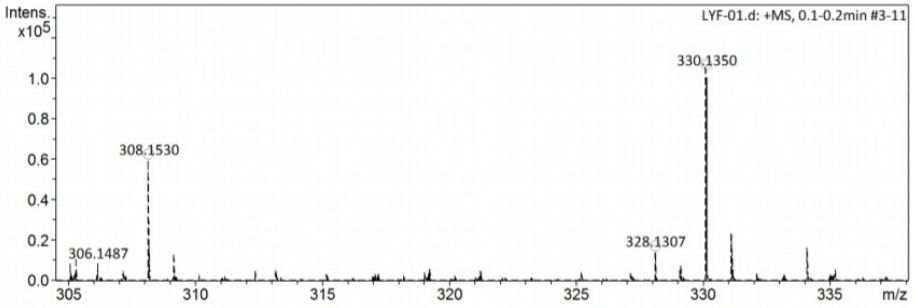
Focus	Not active	Set Capillary	4500 V	Set Dry Heater	180 °C
Scan Begin	50 m/z	Set End Plate Offset	-500 V	Set Dry Gas	4.0 l/min
Scan End	1300 m/z	Set Charging Voltage	2000 V	Set Divert Valve	Source
		Set Corona	0 nA	Set APCI Heater	0 °C



Meas. m/z	#	Ion Formula	Sum Formula	m/z	Adduct	err [ppm]	z	mSigma	I
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308.1530	1	C20H20NO^18O	C20H19NO^18O	308.1531	M+H	0.3	1+	n.a.	59887
328.1307	1	C20H19NNaO2	C20H19NO2	328.1308	M+Na	0.3	1+	760.6	14509
330.1350	1	C20H19NNaO^18O	C20H19NO^18O	330.1350	M+Na	0.0	1+	n.a.	104146