Supporting Information

Palladium-catalyzed asymmetric carbamoyl-carbonylation of alkenes

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1. General Information

^{1}H, ^{13}C and ^{19}F NMR spectra were collected on a 300 or 400 MHz spectrometer using $CDCl_3$ and DMSO-d_6 as solvent. Chemical shifts of ^{1}H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm). Data are reported as follows: chemical shift in ppm (δ), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, sext = sextet, hept = heptet, m = multiplet), coupling constant (Hz), and integration. High Resolution Mass measurement was performed with Electron Spray Ionization (ESI) method on a Q-TOF mass spectrometer operating in positive-ion mode. Melting point (m.p.) was measured on a microscopic melting point apparatus. Optical rotations were measured on an automatic polarimeter with $[\alpha]_D^{20}$ values reported in degrees. PE refers to petroleum ether (b.p. 60–90 °C) and EA refers to ethyl acetate. Flash column chromatography was carried out using commercially available 200–300 mesh under pressure unless otherwise indicated. Gradient flash chromatography was conducted eluting with PE/EA. All other starting materials and solvents were commercially available and were used without further purification unless otherwise stated.

2. Procedures for the Synthesis of Substrates 1 and Substrates 6

Carbamoyl chlorides **1a-1s** were synthesized according to the reported methods.[1-2]

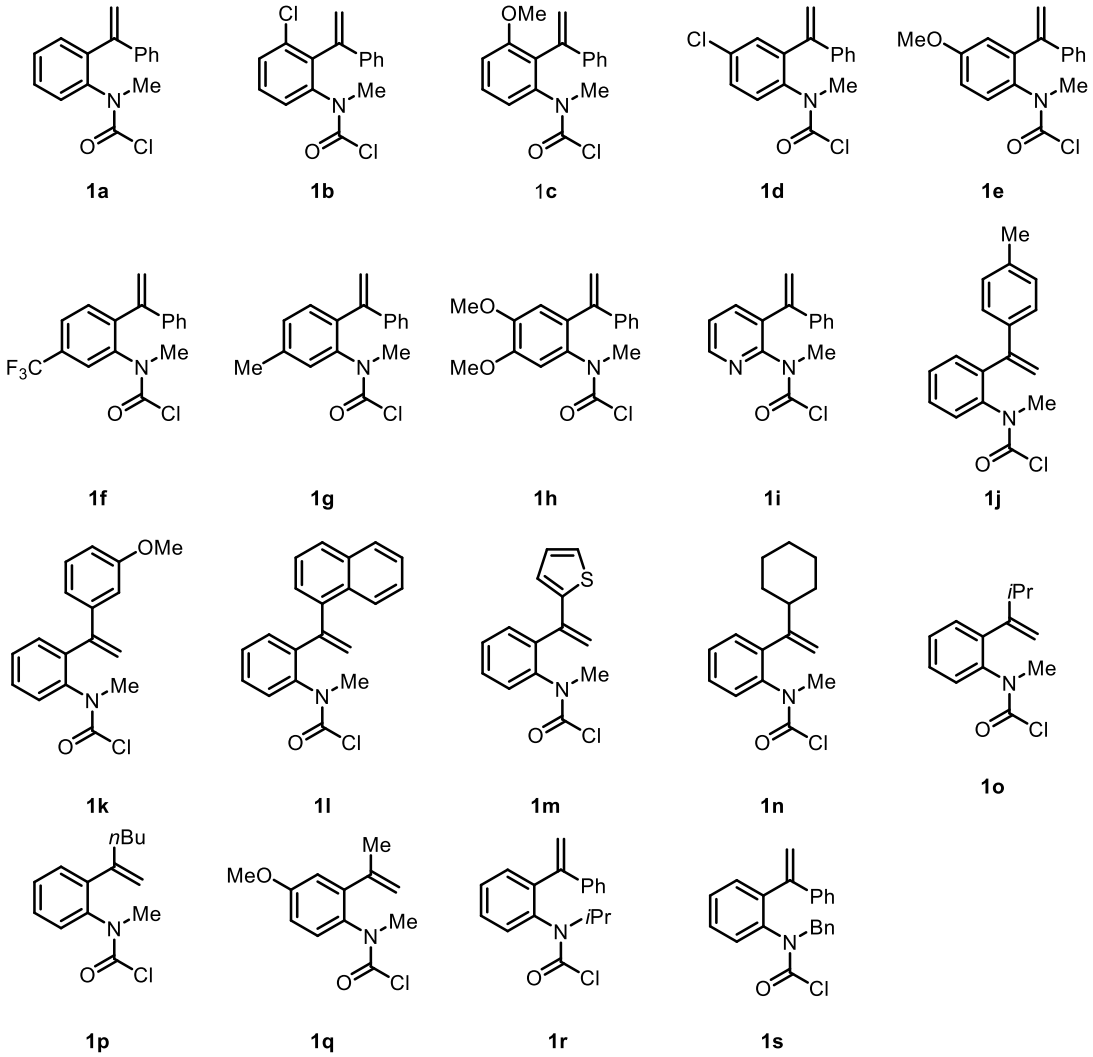
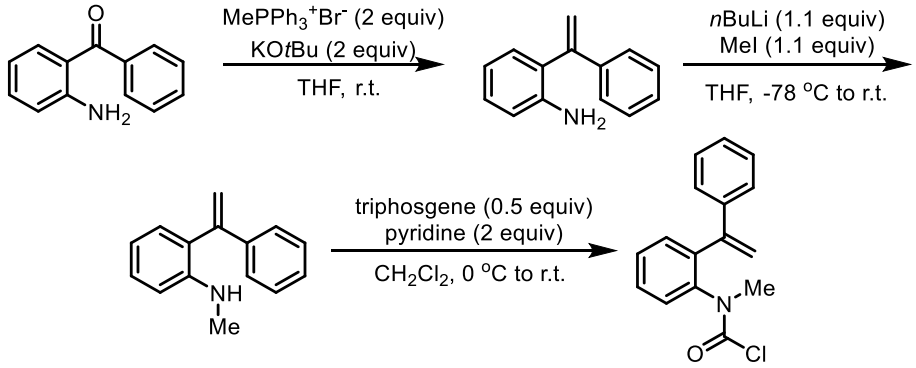


Figure S1. Structures of Substrates 1

Preparation of Substrates 1

General Procedure 1

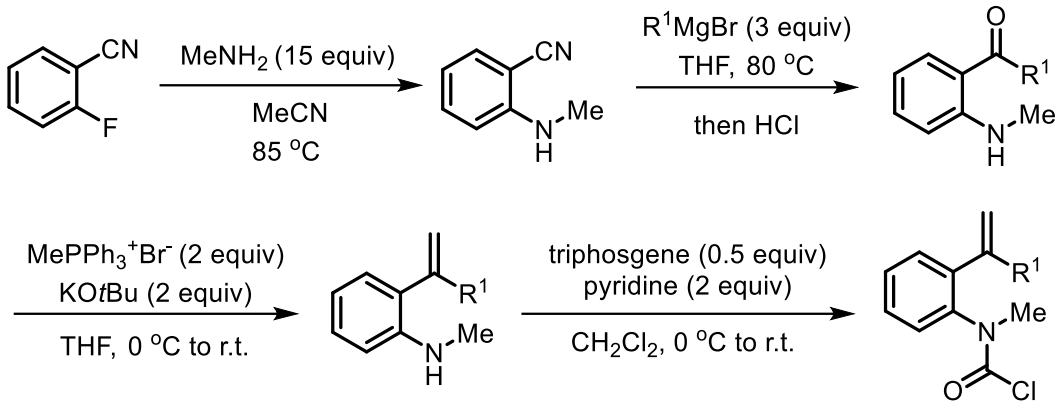


To a solution of methyl triphenylphosphonium bromide (2 equiv) in THF (0.3 M), was added slowly potassium *tert*-butoxide (2 equiv) at 0 °C. The suspension turned yellow upon addition of the base. The suspension was warmed to room temperature and stirred for 30 min. The 2-aminobenzophenone (10 mmol) was added in THF (10 mL). The reaction was stirred until the consumption of starting material monitored by TLC (2 h). The completion the reaction was diluted with 200 mL PE and filtered over a silica plug eluting with mixtures of EA and PE. The crude styrene was concentrated under reduced pressure and used with no further purification assuming full conversion.

The 2-aminostyrene was dissolved in THF (0.3 M) and cooled to -78 °C. Then *n*-butyl lithium (1.1 equiv, 2.5 M in hexane) was added dropwise. The reaction was warmed slowly to -45 °C and stirred for 30 min. Then the reaction was cooled to -78 °C. The iodomethane (1.1 equiv) was added and the reaction was warmed to room temperature and stirred overnight. The reaction was quenched with H_2O then diluted with ethyl acetate. The organic layer was separated, dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the methylated amine. The methylated amine was purified with flash column chromatography.

The methylated amine was dissolved in CH_2Cl_2 (0.3 M) and cooled to 0 °C. Then pyridine (2 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until the completion indicated by TLC. The reaction was quenched with 1 N HCl and extracted twice with CH_2Cl_2. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography.

General Procedure 2



2-Fluorobenzonitrile (10 mmol) was dissolved in MeCN (0.3 M) equipped with a magnetic stir bar, and then methylamine (15 equiv, 40% wt. in H_2O) was added. The reaction was stirred at 85 ºC (oil bath temperature) for 12 h. After cooling to room temperature, the reaction was diluted with EA and washed twice with water. The organic layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

The *N*-methyl aniline was dissolved in THF (0.3 M). Then Grignard reagent (3 equiv) was added slowly. The reaction was stirred at 80 ºC (oil bath temperature) for 6 h. After cooling to 0 ºC, the reaction was quenched slowly with 1M aq. HCl. The imine hydrolysis was stirred at room temperature for 1 h. In some cases the imine hydrolysis required refluxing 4M HCl in EtOH overnight to convert to the corresponding ketone. The reaction was quenched with $NaHCO_3$, and then diluted with EA. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography.

The aniline was carried forward following **General Procedure 1** to obtain the carbmoyl chlorides.

Carbamoyl chlorides **6a-6f** were synthesized according to the reported methods.[3-4]

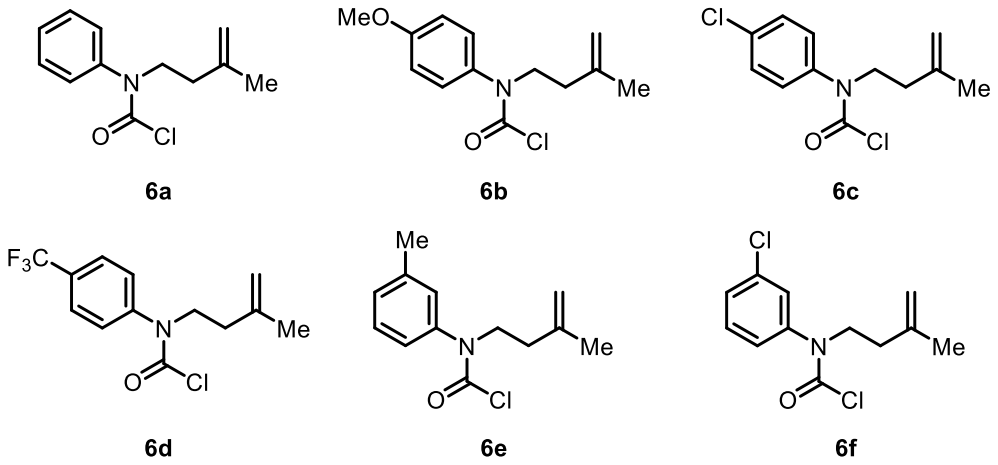
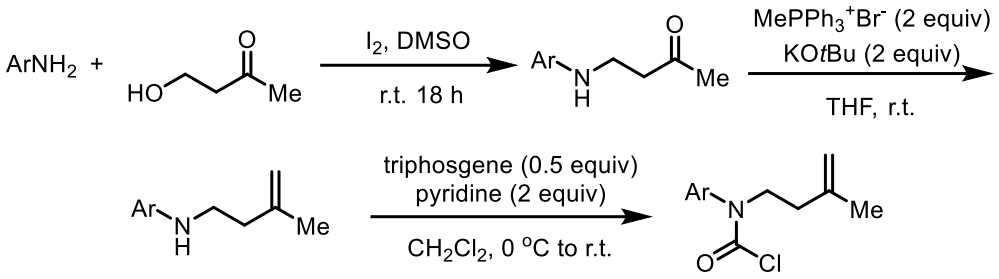


Figure S2. Structures of Substrate 6

Preparation of Substrates 6

General Procedure

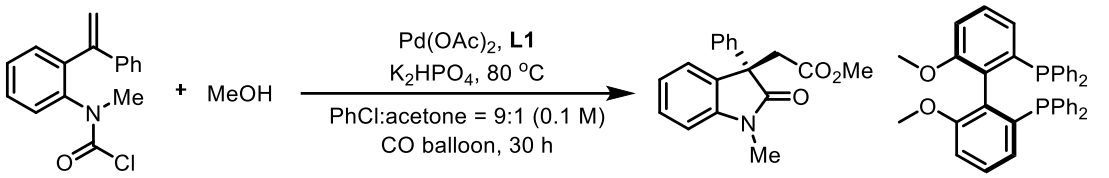


A 100 mL bottle was subsequently charged with 10 mmol aromatic amines, 10 mmol 4-hydroxybutan-2-one, 10 mol % I_2 (254 mg), 20 mL DMSO. The resulting mixture was performed at room temperature until complete consumption of the starting material as monitored by TLC. After reaction was complete, the resulting mixture was poured into water (200 mL). If the desired products were isolated as solids from aqueous solutions, which were treated through vacuum filtering, washing with water and vacuum drying. If no solid precipitated, the aqueous solutions were extracted with EA (100 mL×3). The combined organic extracts were washed with brine (50 mL×3), then dried over Na_2SO_4 and concentrated in vacuum. The resulting residue was purified by silica gel column chromatography (EA/PE = 1/20-1/4) to afford the desired products.

To a solution of methyl triphenylphosphonium bromide (2 equiv) in THF (0.3 M), was added slowly potassium *tert*-butoxide (2 equiv) at 0 °C. The suspension turned yellow upon addition of the base. The suspension was warmed to room temperature and stirred for 30 min. The *β*-aminoketones (10 mmol) was added in THF (10 mL). The reaction was stirred until the consumption of the starting material observed by TLC (2 h). The completion of the reaction was diluted with 200 mL of PE and filtered over a silica plug eluting with mixtures of EA and PE. The crude styrene was concentrated under reduced pressure and used with no further purification assuming full conversion.

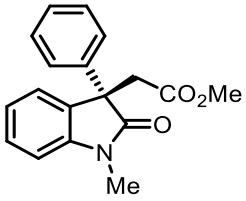
The styrene was dissolved in CH_2Cl_2 (0.3 M) and cooled to 0 °C. Then pyridine (2 equiv) was added followed by triphosgene (0.5 equiv). The reaction was warmed to room temperature and stirred until completion indicated by TLC. The reaction was quenched with 1 N HCl and extracted twice with CH_2Cl_2. The organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The crude starting materials were purified by flash column chromatography to obtain **6**.

3. General Procedure for the Palladium-Catalyzed Asymmetric Carbamoyl-Carbonylation of Activated Alkenes



1a **2a** **3a** (*S*)-OMe-BIPHEP, **L1**

An oven-dried 10 mL Schlenk tube was charged with substrate **1a** (27.2 mg, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol %), **L1** (5.8 mg, 10 mol %), and K_2HPO_4 (52.3 mg, 0.3 mmol). The vial was thoroughly flushed with CO, and MeOH (12 μL, 0.3 mmol), as well as PhCl/acetone (9/1, 1.0 mL) was added under balloon pressure of CO. Then the reaction mixture was stirred at room temperature for 5 min, and then raised to 80 °C (oil bath temperature) for 30 h with stirring. After the reaction vessel was cooled to room temperature, the reaction mixture was diluted with EA (10 mL) and filtered through a plug of celite. When some alcohols with high boiling point were used, the reaction mixture required Dess-Martin periodinane (254.5 mg, 0.6 mmol) in DCM (2 mL) at room temperature for 2 h. The reaction was filtered, and concentrated under reduced pressure. The solution was purified by flash column chromatography on silica gel (PE/EA = 5/1) to afford the desired product **3a** in 95% yield (28.2 mg).



methyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3a)

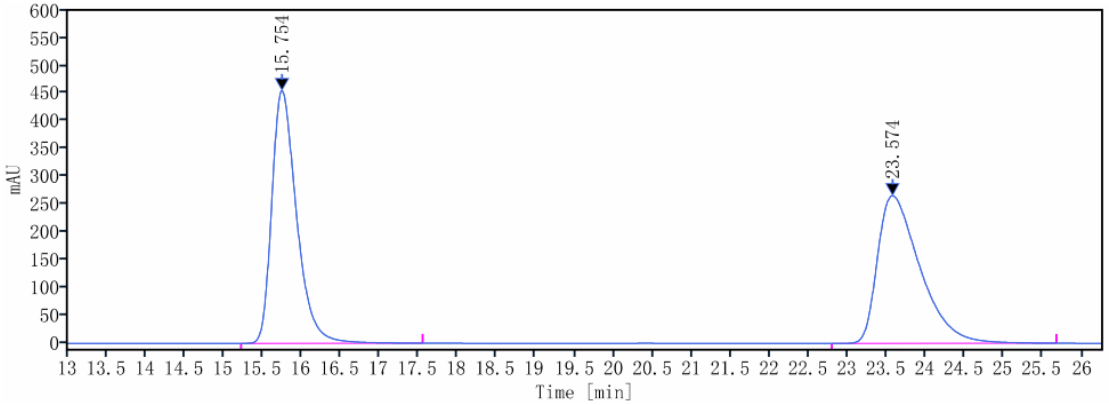
95% yield (28.2 mg); 96.5:3.5 er; White solid; m.p. 63 – 65 °C; R_f = 0.5 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -97 (*c* = 0.2, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 – 7.21 (m, 7H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.55 (d, *J* = 16.3 Hz, 1H), 3.43 (s, 3H), 3.27 (d, *J* = 16.3 Hz, 1H), 3.23 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 170.1, 144.6, 139.1, 131.1, 128.7, 127.7, 126.6, 124.5, 122.5, 108.5, 53.2, 51.7, 41.8, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{17}NO_3+H]^+$ 296.1287, found 296.1281.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 15.7 min (major), t_{R2} = 23.7 min (minor).



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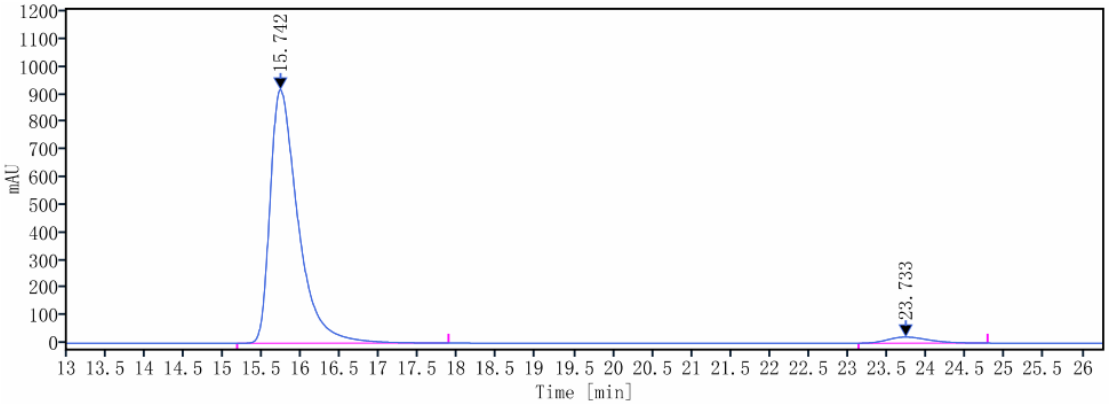

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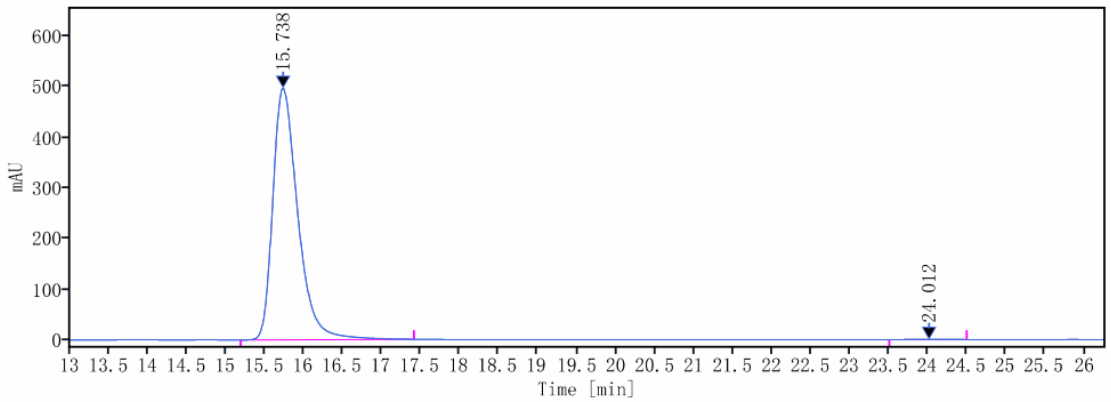
15.742	BM m	0.3737	22799.0974	918.1440	96.5855
23.733	MM m	0.5564	805.9912	22.2074	3.4145

After recrystallization



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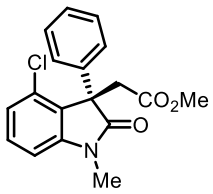


methyl (S)-2-(4-chloro-1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3b)

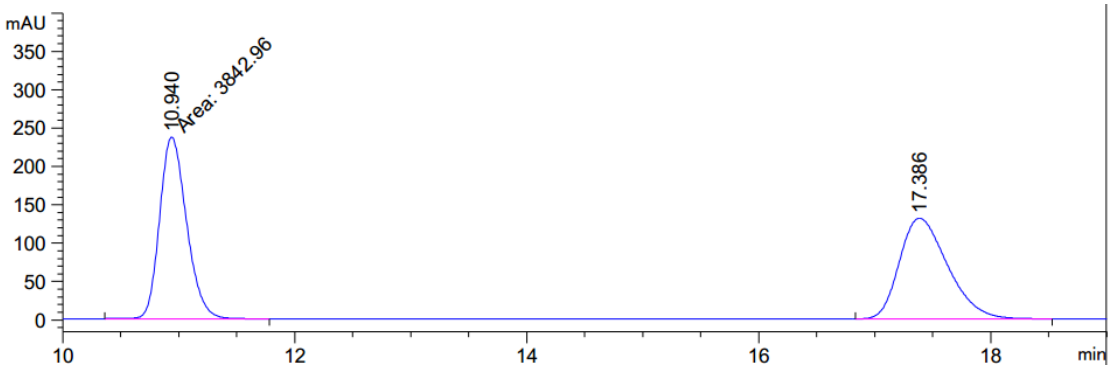
90% yield (29.8 mg); 95:5 er; White solid; m.p. 115 – 117 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -136 (c = 0.24, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.20 (m, 6H), 7.03 (d, *J* = 8.2 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.76 (dd, *J* = 25.2 Hz, 16.4 Hz, 2H), 3.48 (s, 3H), 3.23 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.5, 170.4, 146.7, 136.7, 131.0, 130.1, 128.8, 128.2, 127.9, 126.4, 123.6, 106.9, 54.3, 51.8, 38.8, 27.0 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{16}ClNO_3+H]^+$ 330.0897, found 330.0894.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.1 min (major), t_{R2} = 18.2 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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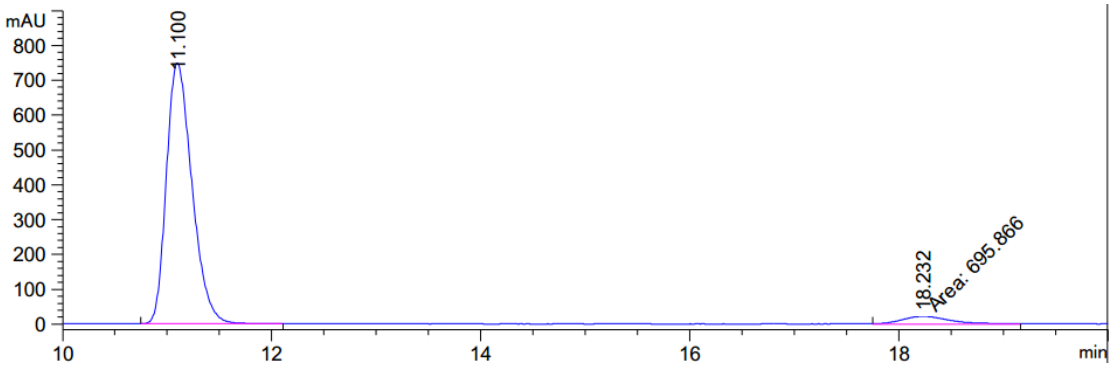

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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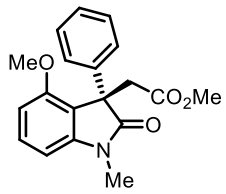


methyl (S)-2-(4-methoxy-1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3c)

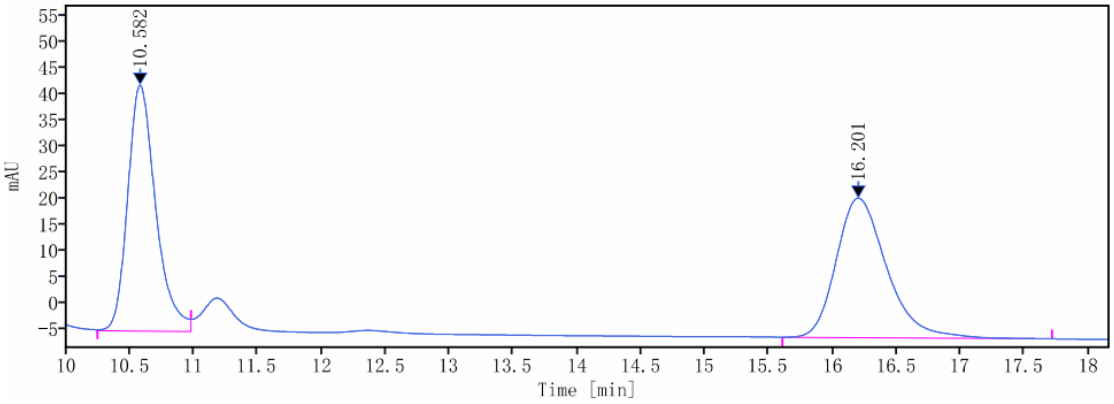
92% yield (29.9 mg); 96:4 er; White solid; m.p. 167 – 169 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -168 (*c* = 0.18, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 6H), 6.66 (d, *J* = 8.5 Hz, 1H), 6.57 (d, *J* = 7.8 Hz, 1H), 3.75 (s, 3H), 3.64 – 3.53 (dd, *J* = 17.3 Hz, 16.3 Hz, 2H), 3.44 (s, 3H), 3.20 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 178.5, 170.8, 156.0, 145.9, 138.3, 130.2, 128.5, 127.6, 126.6, 116.6, 106.1, 101.8, 55.5, 53.4, 51.6, 39.9, 26.9 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_4+H]^+$ 326.1392, found 326.1387.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 10.6 min (major), t_{R2} = 16.2 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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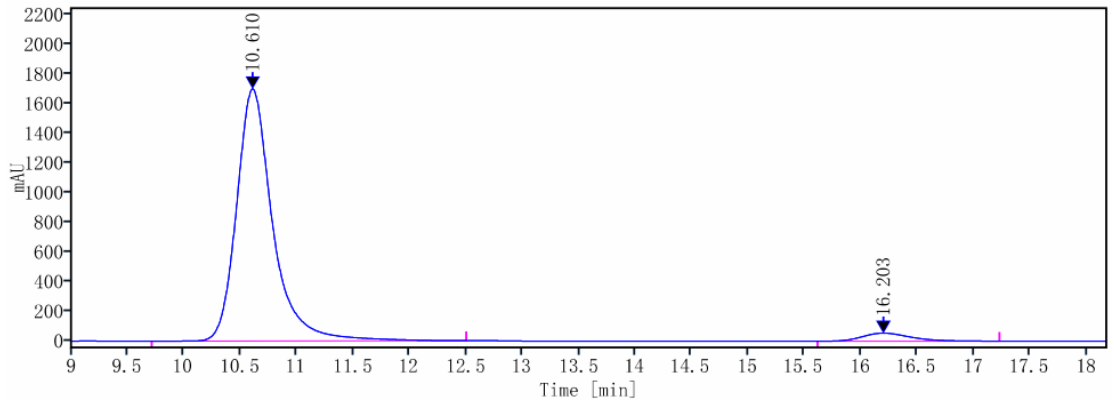
16.201	BM m	0.4195	731.5059	26.7108	50.4994



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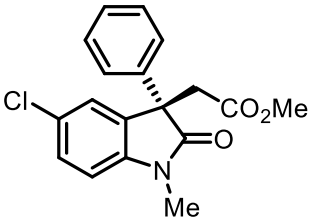
16.203	MM m	0.4515	1599.5467	54.3246	4.0558



methyl (S)-2-(5-chloro-1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3d)

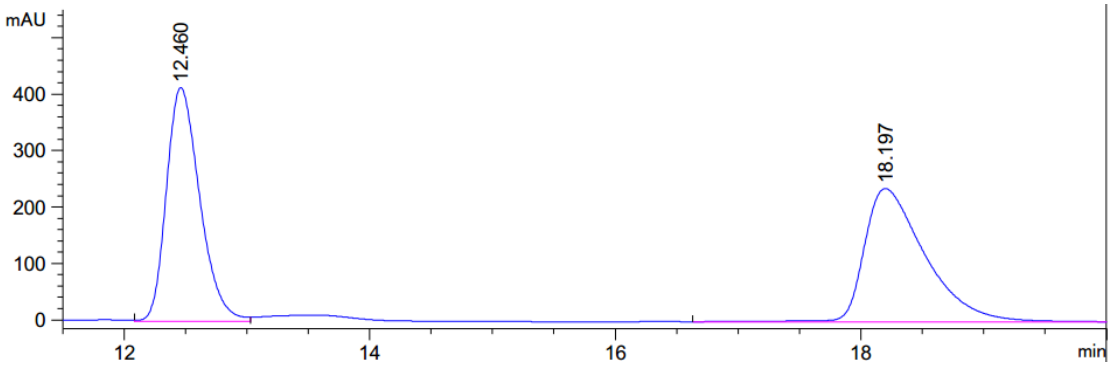
98% yield (32.2 mg); 95.5:4.5 er; White solid; m.p. 88 – 90 °C; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -127 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 7H), 6.84 (d, *J* = 8.3 Hz, 1H), 3.58 – 3.50 (m, 4H), 3.29 – 3.24 (m, 4H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 170.0, 143.3, 138.3, 133.0, 128.9, 128.7, 127.9, 127.8, 126.5, 124.8, 109.4, 53.4, 51.9, 41.5, 26.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{16}ClNO_3+H]^+$ 330.0897, found 330.0895.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 12.4 min (major), t_{R2} = 18.5 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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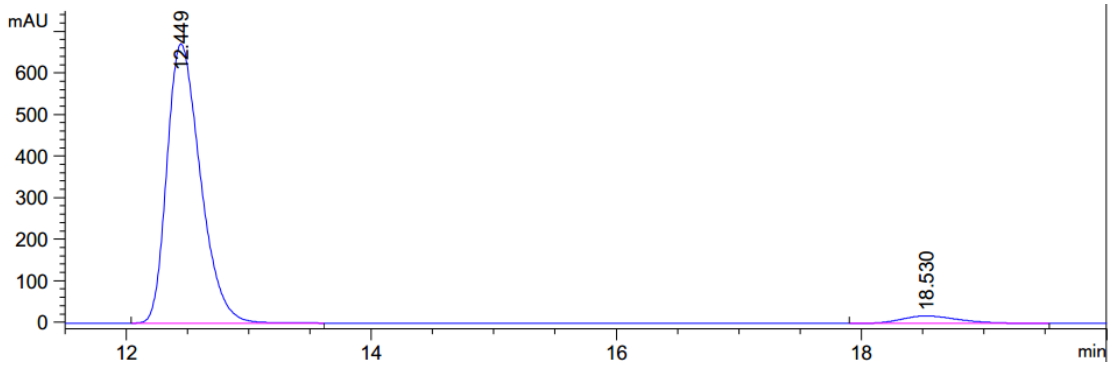
2	18.197	VB	0.5182	8092.97217	235.94826	50.8697



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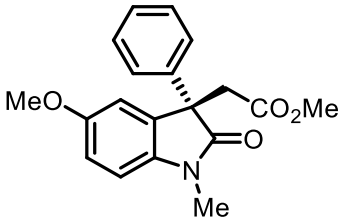


methyl (S)-2-(5-methoxy-1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3e)

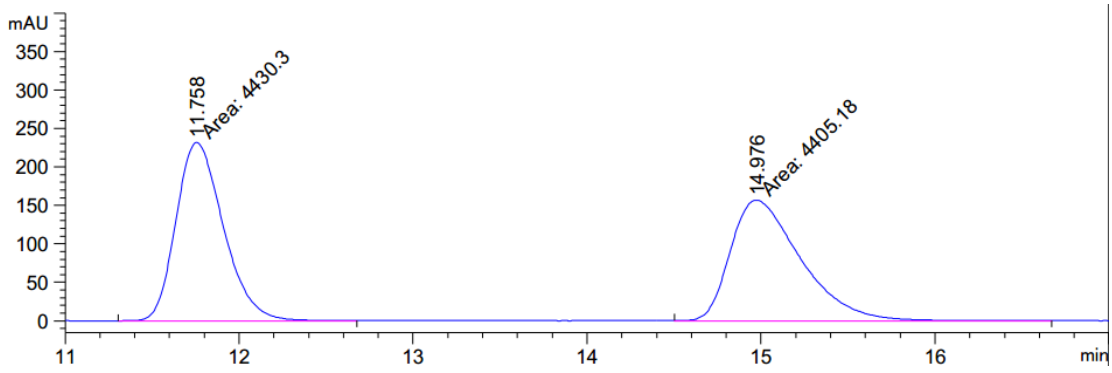
97% yield (31.4 mg); 96:4 er; White solid; m.p. 118 – 120 °C; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -129 (c = 0.16, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.22 (m, 5H), 6.91 – 6.81 (m, 3H), 3.79 (s, 3H), 3.54 (d, *J* = 16 Hz, 1H), 3.46 (s, 3H), 3.25 (d, *J* = 16 Hz, 1H), 3.22 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 170.1, 155.9, 139.0, 138.2, 132.5, 128.7, 127.7, 126.6, 112.6, 112.2, 108.7, 55.8, 53.6, 51.8, 41.6, 26.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_4+H]^+$ 326.1392, found 326.1389.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 11.7 min (major), t_{R2} = 15.3 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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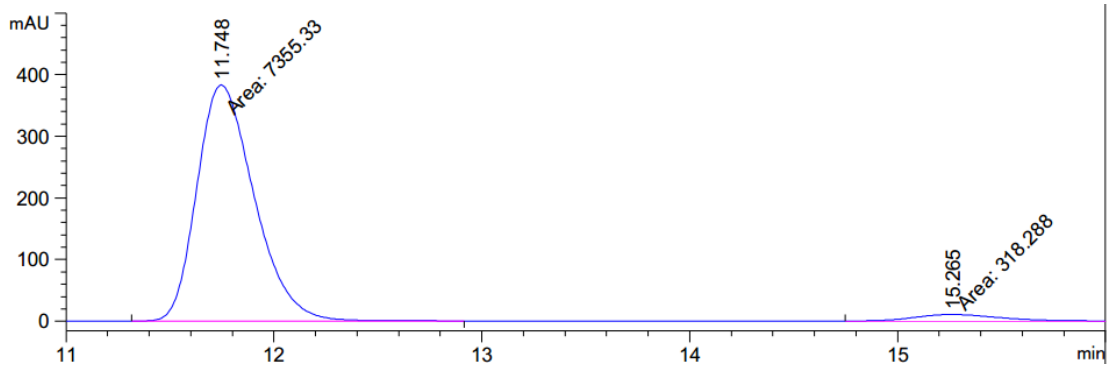

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
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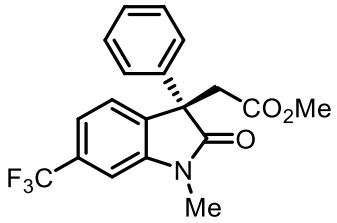
2	15.265	MM	0.4912	318.28830	10.80036	4.1478



methyl (S)-2-(1-methyl-2-oxo-3-phenyl-6-(trifluoromethyl)indolin-3-yl)acetate (3f)

91% yield (33.2 mg); 95:5 er; White solid; m.p. 102 – 105 °C; R_f = 0.5 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -68 (c = 0.24, EA).

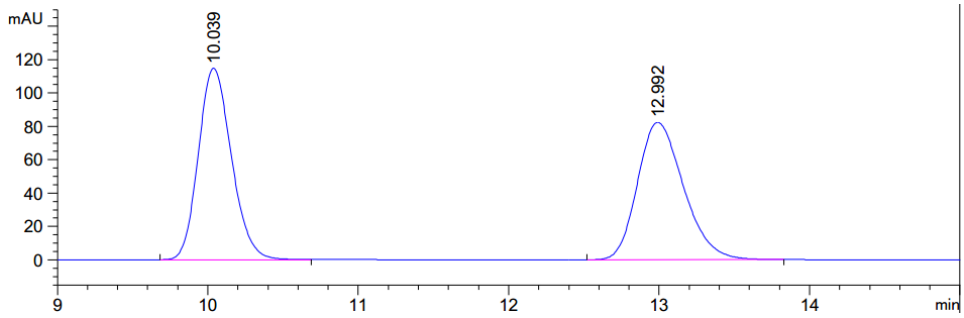
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (s, 2H), 7.29 – 7.26 (m, 5H), 7.13 (s, 1H), 3.59 (d, *J* = 16.7 Hz, 1H), 3.48 (s, 3H), 3.32 (d, *J* = 16.7 Hz, 1H), 3.28 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 177.8, 170.0, 145.3, 138.1, 135.2, 131.1 (q, *J* = 32.6 Hz), 128.9, 128.0, 126.4, 124.5, 122.7 (q, *J* = 278.9 Hz), 119.5 (q, *J* = 4.1 Hz), 105.19 (q, *J* = 3.8 Hz), 53.2, 51.9, 41.6, 26.8 ppm.

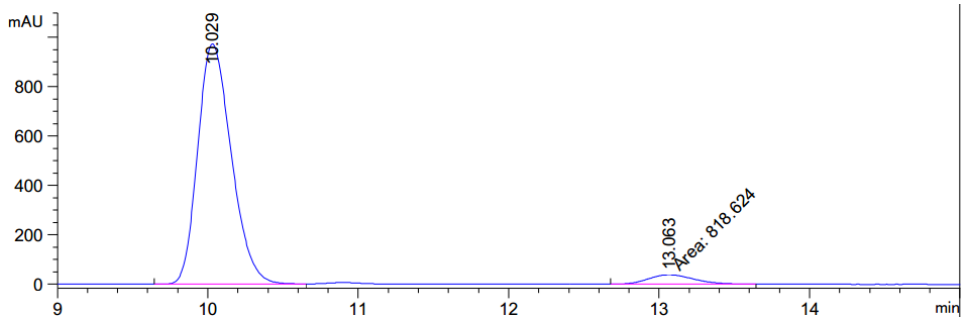
^{19}F NMR (282 MHz, $CDCl_3$) δ -62.40 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{16}F_3NO_3+H]^+$ 364.1161, found 364.1157.

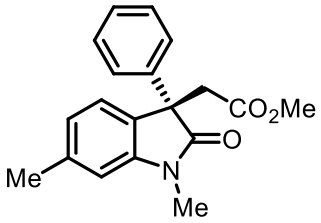
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.0 min (major), t_{R2} = 13.1 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.039	BB	0.2361	1755.32483	114.95640	50.0498
2	12.992	BB	0.3301	1751.83386	82.36510	49.9502



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.029	BV	0.2433	1.51378e4	973.86273	94.8696
2	13.063	MM	0.3556	818.62378	38.37143	5.1304



methyl (S)-2-(1,6-dimethyl-2-oxo-3-phenylindolin-3-yl)acetate (3g)

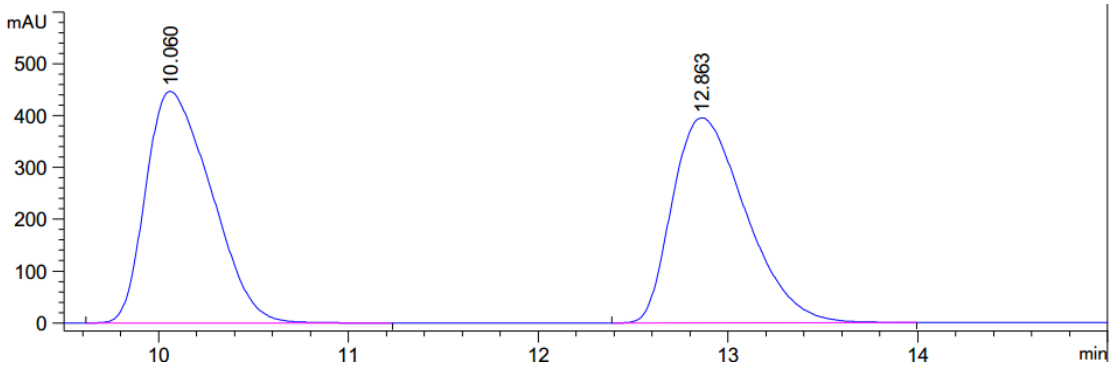
99% yield (30.6 mg); 95.5:4.5 er; White solid; m.p. 128 – 130 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -86 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.35 – 7.15 (m, 6H), 6.91 (dd, *J* = 7.5, 0.8 Hz, 1H), 6.74 (s, 1H), 3.53 (d, *J* = 16.3 Hz, 1H), 3.45 (s, 3H), 3.27 – 3.22 (m, 4H), 2.41 (s,3H) ppm.

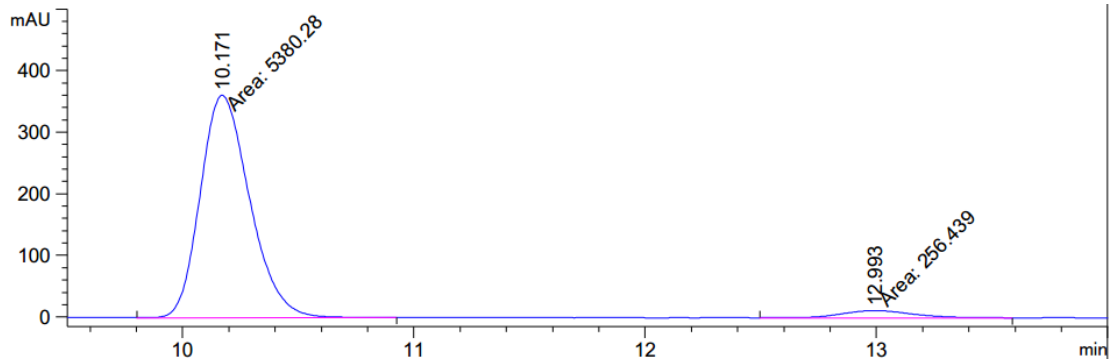
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 170.2, 144.6, 139.3, 138.8, 128.7, 128.0, 127.6, 126.6, 124.2, 123.0, 109.4, 53.0, 51.7, 41.8, 26.7, 21.9 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_3+H]^+$ 310.1443, found 310.1439.

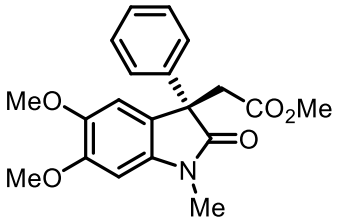
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.2 min (major), t_{R2} = 13.0 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.060	VB	0.3967	1.06674e4	446.62823	49.9967
2	12.863	VB	0.4246	1.06689e4	395.63437	50.0033



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.171	MM	0.2482	5380.28467	361.33466	95.4506
2	12.993	MM	0.3606	256.43921	11.85376	4.5494



methyl (S)-2-(5,6-dimethoxy-1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3h)

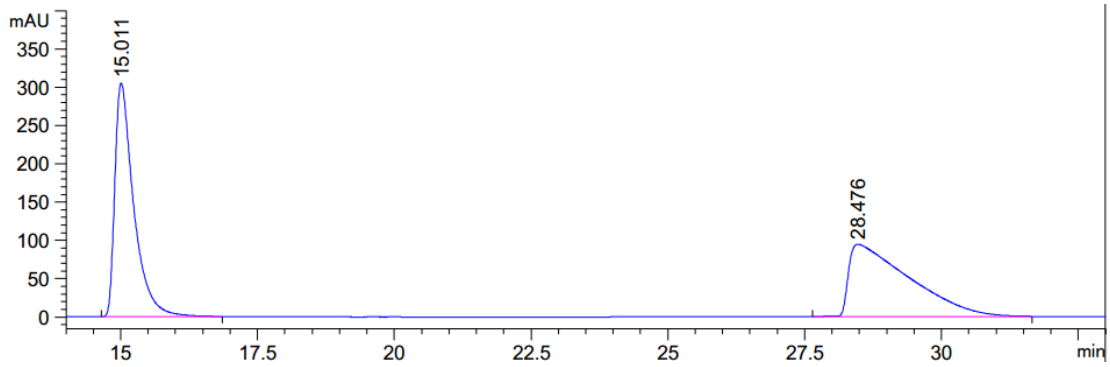
97% yield (34.5 mg); 94:6 er; White solid; m.p. 142 – 144 °C; R_f = 0.3 (PE/EA = 1/1); $[\alpha]_D^{20}$ = -95 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.24 (m, 5H), 6.92 (s, 1H), 6.56 (s, 1H), 3.96 (s, 3H), 3.85 (s, 3H), 3.52 (d, *J* = 16.2 Hz, 1H), 3.48 (s, 1H), 3.28 – 3.23 (m, 4H) ppm.

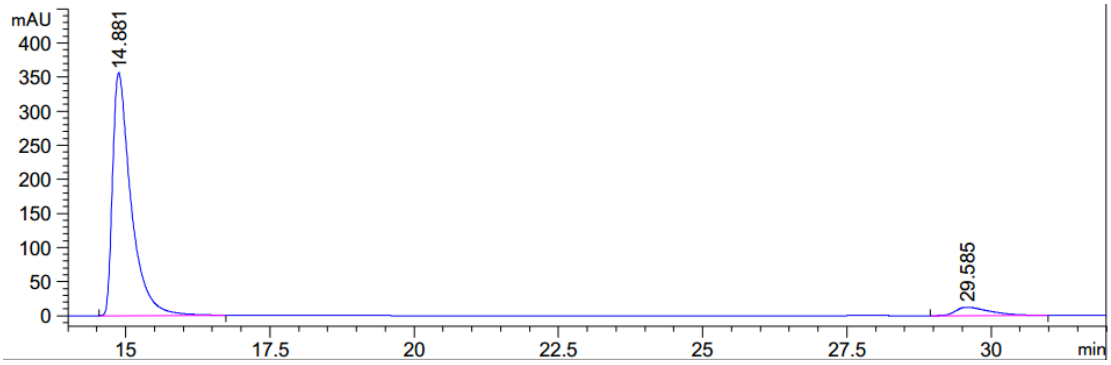
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.3, 170.3, 149.9, 145.0, 139.4, 138.5, 128.7, 127.6, 126.6, 121.5, 109.7, 94.3, 56.9, 56.3, 53.5, 51.8, 41.6, 26.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{20}H_{21}NO_5+H]^+$ 356.1498, found 356.1491.

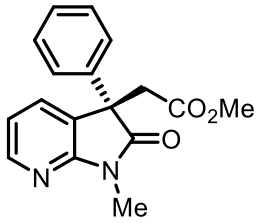
HPLC: Daicel Chiralcel OD-H, n-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 14.9 min (major), t_{R2} = 29.6 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.011	VB	0.3567	7345.07715	305.27200	50.3035
2	28.476	BB	1.0306	7256.43799	94.42481	49.6965



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	14.881	BB	0.3293	7913.80713	356.02631	93.8650
2	29.585	BB	0.5943	517.24414	12.40981	6.1350



methyl (S)-2-(1-methyl-2-oxo-3-phenyl-2,3-dihydro-1H-pyrrolo[2,3-b]pyridin-3-yl)acetate (3i)

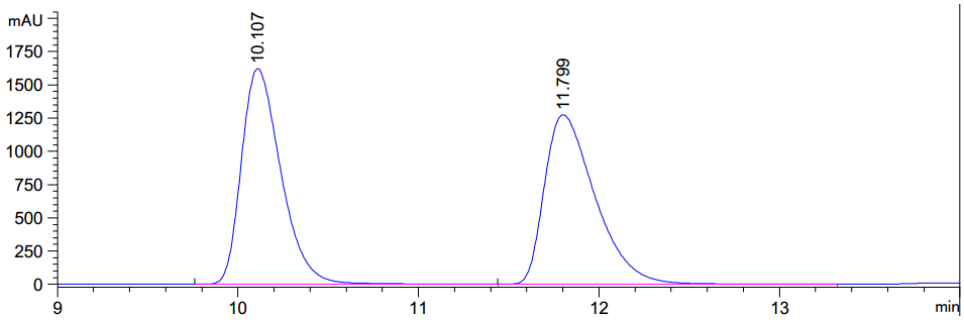
91% yield (26.9 mg); 91.5:8.5 er; White solid; m.p. 108 – 110 °C; R_f = 0.5 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -85 (c = 0.12, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.26 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.60 (dd, *J* = 7.3, 1.6 Hz, 1H), 7.35 – 7.27 (m, 5H), 7.02 (dd, *J* = 7.3, 5.3 Hz, 1H), 3.54 – 3.49 (m, 4H), 3.33 – 3.28 (m, 4H) ppm.

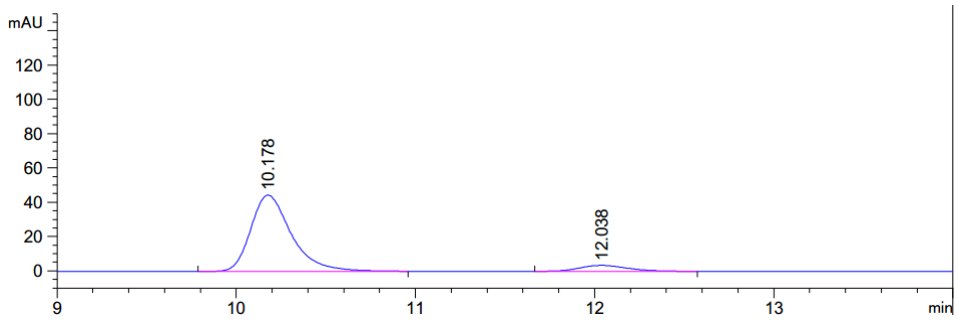
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.6, 169.9, 157.9, 147.5, 137.8, 132.0, 128.9, 128.0, 126.5, 125.8, 118.0, 52.9, 51.9, 41.6, 25.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{17}H_{16}N_2O_3+H]^+$ 297.1239, found 297.1233.

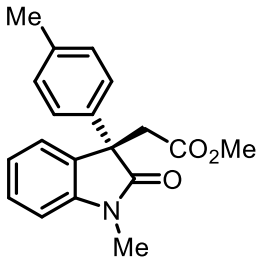
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.2 min (major), t_{R2} = 12.0 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.107	VV	0.2358	2.46920e4	1620.06934	49.8638
2	11.799	VB	0.2972	2.48269e4	1274.80005	50.1362



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.178	BB	0.2396	699.45471	44.45330	91.4154
2	12.038	BB	0.2860	65.68451	3.48373	8.5846



methyl (S)-2-(1-methyl-2-oxo-3-(p-tolyl)indolin-3-yl)acetate (3j)

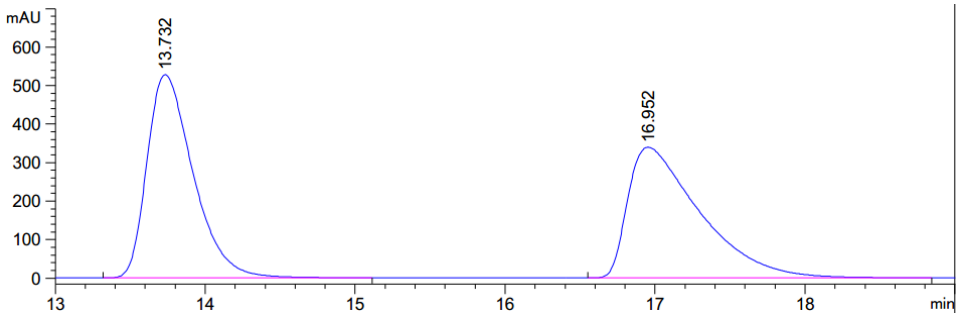
96% yield (29.7 mg); 96.5:3.5 er; Colorless oil; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -126 (c = 0.11, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (td, *J* = 7.7, 1.3 Hz, 1H), 7.26 (t, 1H), 7.21 – 7.19 (m, 2H), 7.11 – 7.07 (m, 3H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.53 (d, *J* = 16.3 Hz, 1H), 3.43 (s, 3H), 3.27 – 3.22 (m, 4H), 2.28 (s, 3H) ppm.

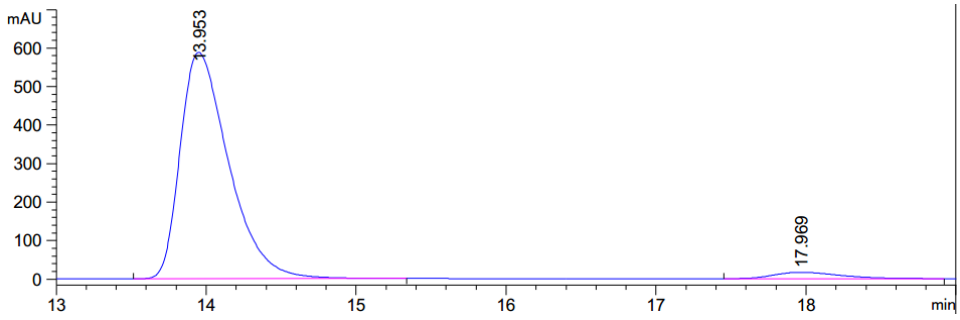
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.2, 170.2, 144.6, 137.4, 136.1, 131.3, 129.4, 128.6, 126.5, 124.4, 122.5, 108.4, 53.0, 51.7, 41.8, 26.7, 21.0 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_3+H]^+$ 310.1443, found 310.1439.

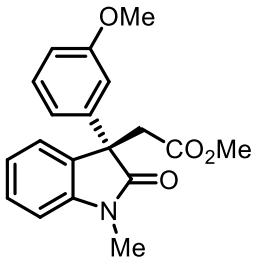
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 14.0 min (major), t_{R2} = 18.0 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.732	BB	0.3277	1.13074e4	528.37756	49.9815
2	16.952	BB	0.4927	1.13157e4	339.60721	50.0185



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.953	BB	0.3419	1.32022e4	588.06952	96.2698
2	17.969	BB	0.4651	511.54993	16.71052	3.7302



methyl (S)-2-(3-(3-methoxyphenyl)-1-methyl-2-oxoindolin-3-yl)acetate (3k)

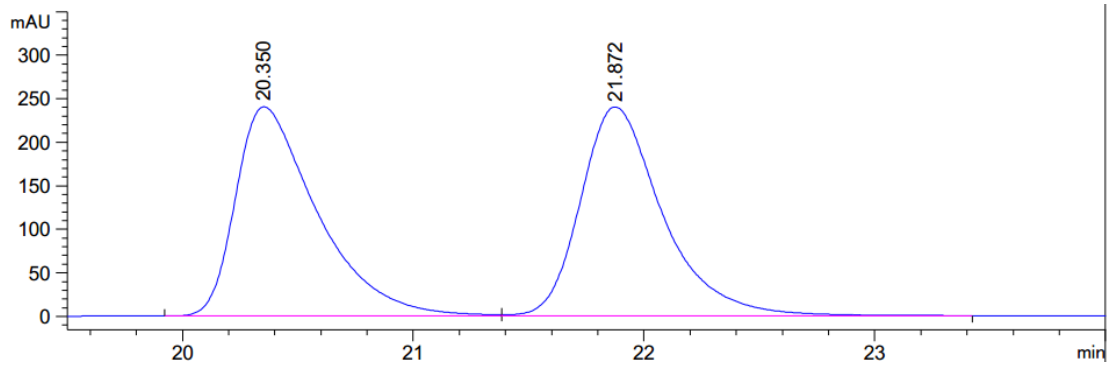
97% yield (31.7 mg); 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -78 (c = 0.2, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.25 (m, 2H), 7.20 (td, *J* = 8.0, 1.6 Hz, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.93 – 6.89 (m, 3H), 6.78 (d, *J* = 8.3 Hz, 1H), 3.74 (s, 3H), 3.53 (d, *J* = 16.4 Hz, 1H), 3.43 (s, 3H), 3.28 – 3.23 (m, 4H) ppm.

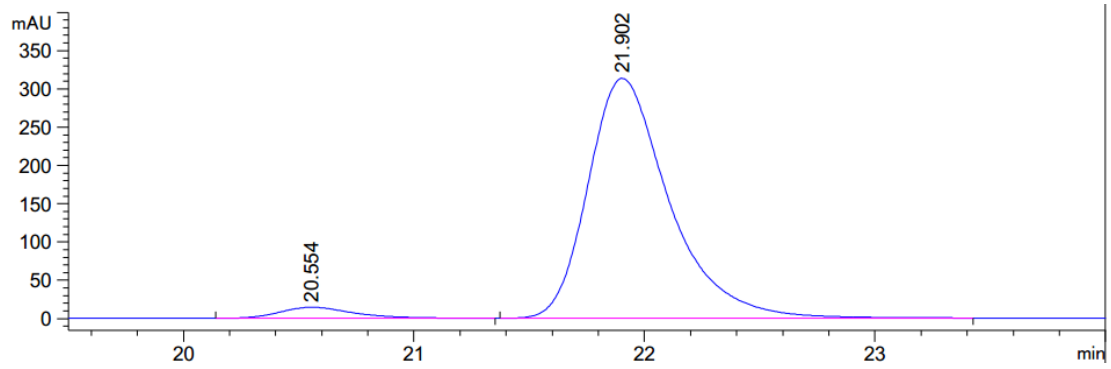
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 170.1, 159.7, 144.6, 140.6, 131.0, 129.6, 128.7, 124.5, 122.5, 119.0, 113.2, 112.5, 108.4, 55.2, 53.2, 51.7, 41.8, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_4+H]^+$ 326.1392, found 326.1389.

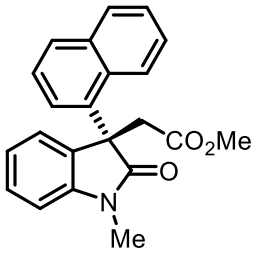
HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 20.6 min (minor), t_{R2} = 21.9 min (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.350	BV	0.3651	5912.62744	240.30495	49.8651
2	21.872	VB	0.3750	5944.61523	239.98563	50.1349



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.554	BB	0.3324	322.19321	14.43458	4.0230
2	21.902	BB	0.3702	7686.66846	313.30194	95.9770



methyl (S)-2-(1-methyl-3-(naphthalen-1-yl)-2-oxoindolin-3-yl)acetate (3l)

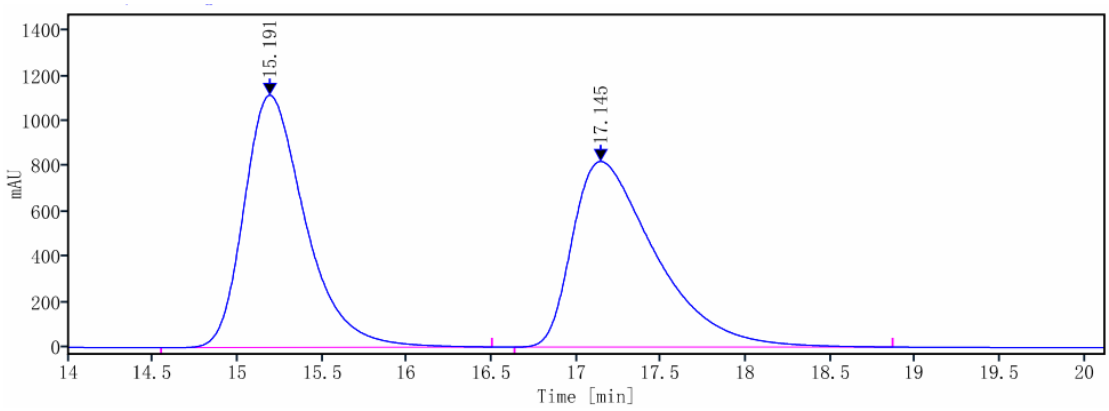
94% yield (32.5 mg); 96:4 er; White solid; m.p. 99 – 101 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -60 (c = 0.22, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78 – 7.69 (m, 4H), 7.51 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.45 – 7.32 (m, 4H), 7.13 (t, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.7 Hz, 1H), 3.68 (d, *J* = 16.3 Hz, 1H), 3.46 (s, 3H), 3.37 (d, *J* = 16.4 Hz, 1H), 3.26 (s, 3H) ppm.

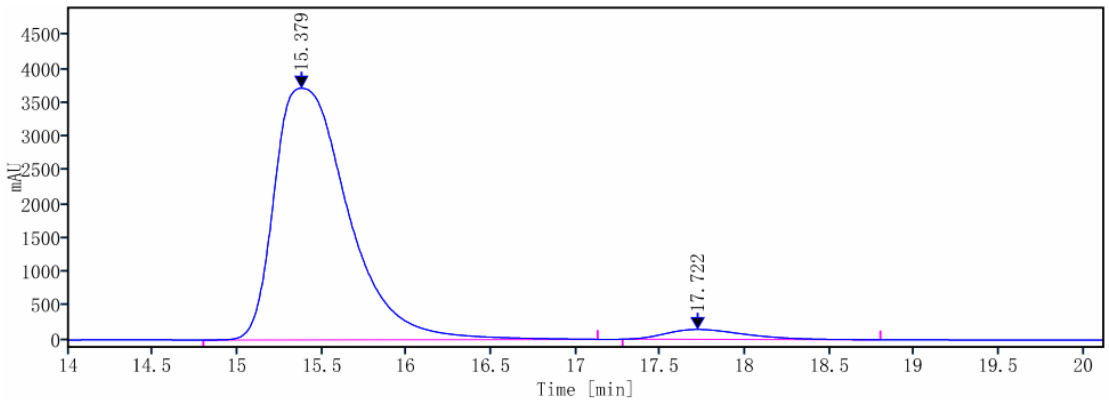
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 170.1, 144.5, 136.3, 133.0, 132.5, 131.0, 128.7, 128.5, 128.1, 127.4, 126.2, 126.2, 125.5, 124.4, 122.5, 108.5, 53.3, 51.7, 41.6, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{22}H_{19}NO_3+H]^+$ 346.1443, found 346.1439.

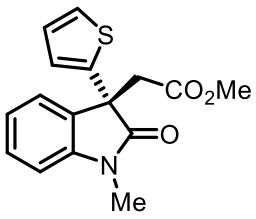
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 15.4 min (major), t_{R2} = 17.7 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.191	BM m	0.3844	28017.4812	1114.1534	50.0588
17.145	MM m	0.5157	27951.6498	820.0159	49.9412



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.379	BM m	0.4642	112602.0786	3719.4451	95.9374
17.722	MM m	0.5001	4768.2412	147.1348	4.0626



methyl (S)-2-(1-methyl-2-oxo-3-(thiophen-2-yl)indolin-3-yl)acetate (3m)

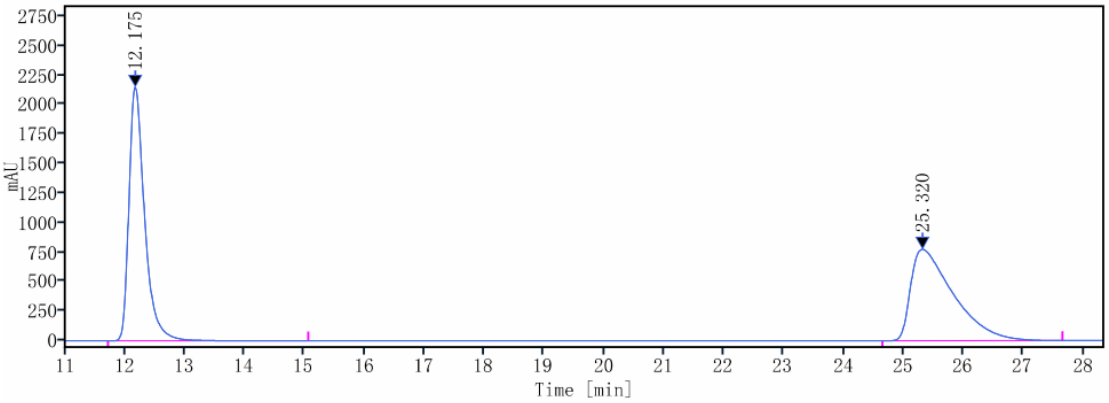
98% yield (29.6 mg); 96.5:3.5 er; White solid; m.p. 55 – 57 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -127 (c = 0.29, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.39 – 7.34 (m, 2H), 7.20 (d, *J* = 4.7 Hz, 1H), 7.11 (t, *J* = 7.5 Hz, 1H), 6.92 – 6.90 (m, 3H), 3.55(d, *J* = 16.6 Hz, 1H), 3.46 (s, 3H), 3.32 – 3.25 (m, 4H) ppm.

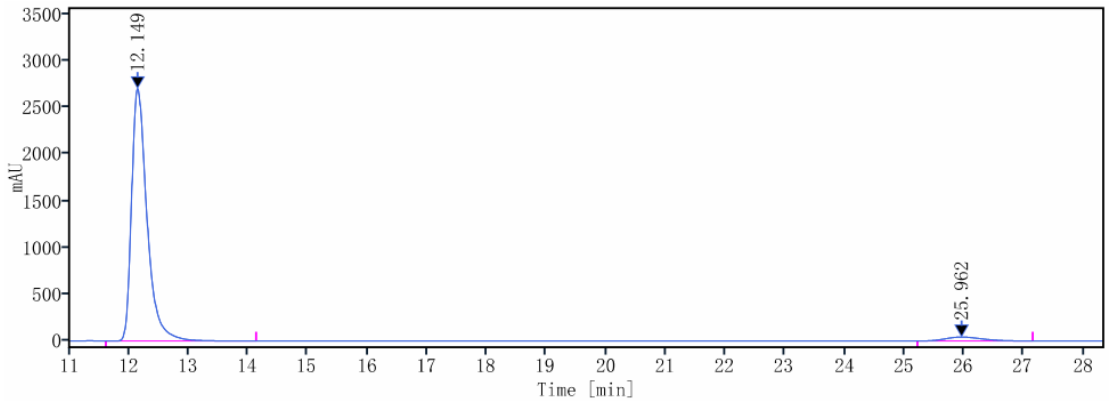
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.9, 169.6, 144.3, 142.8, 130.9, 129.2, 126.9, 125.4, 125.2, 124.0, 122.6, 108.6, 51.8, 51.1, 43.0, 26.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{16}H_{15}NO_3S+H]^+$ 302.0851, found 302.0842.

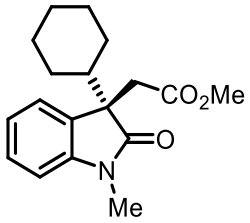
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 12.1 min (major), t_{R2} = 26.0 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.175	BB	3.3433	39096.5375	2150.9074	50.4959
25.320	BB	3.0077	38328.6032	776.2129	49.5041



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
12.149	MB m	0.2738	48772.5247	2699.8661	96.4052
25.962	MM m	0.6594	1818.6694	42.4877	3.5948



methyl (S)-2-(3-cyclohexyl-1-methyl-2-oxoindolin-3-yl)acetate (3n)

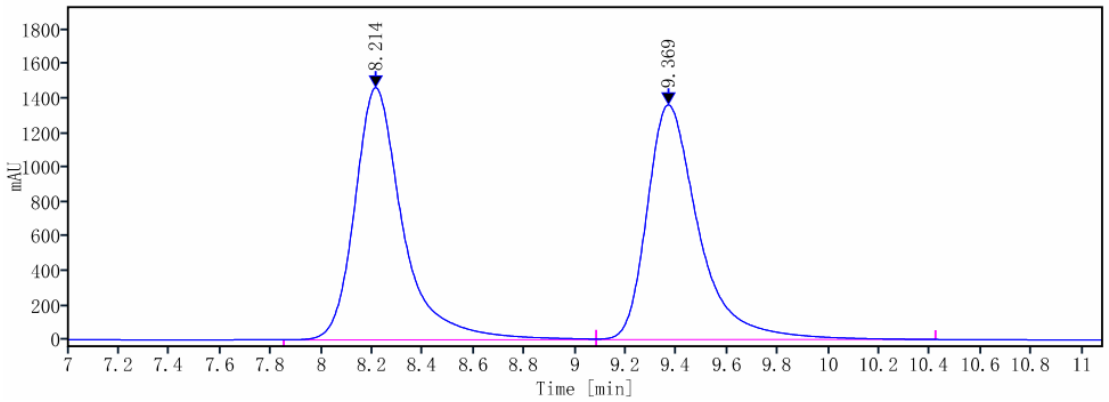
95% yield (28.6 mg); 95:5 er; White solid; m.p. 76 – 78 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -52 (c = 0.19, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.24 (m, 1H), 7.14 (d, *J* = 7.1 Hz, 1H), 7.01 (t, *J* = 7.4 Hz, 1H), 6.83 (d, *J* = 7.8 Hz, 1H), 3.39 (s, 3H), 3.23 (s, 3H), 3.01 (s, 2H), 1.83 – 1.50 (m, 6H), 1.20 – 0.97 (m, 4H), 0.80 (qd, *J* = 12.4, 3.5 Hz, 1H) ppm.

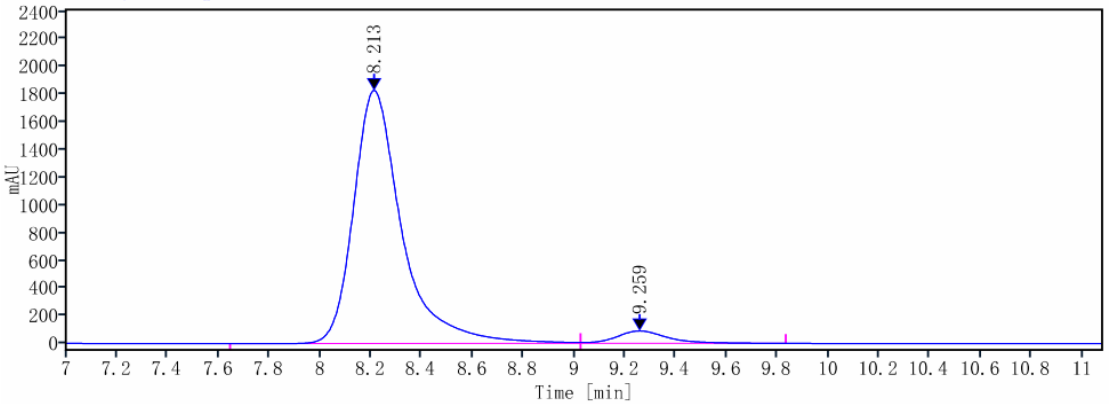
^{13}C NMR (75 MHz, $CDCl_3$) δ 179.5, 170.8, 144.9, 130.6, 128.1, 123.2, 121.9, 107.7, 53.7, 53.1, 51.5, 45.4, 38.9, 27.1, 26.7, 26.6, 26.3, 26.1 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{23}NO_3+H]^+$ 302.1756, found 302.1747.

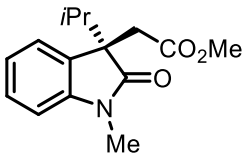
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 8.2 min (major), t_{R2} = 9.3 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.214	VM m	0.1973	19356.6641	1463.8103	50.0405
9.369	MM m	0.2134	19325.3011	1363.3368	49.9595



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.213	BM m	0.1984	24208.3359	1828.9191	95.0284
9.259	MM m	0.2107	1266.4989	90.2888	4.9716



methyl (S)-2-(3-isopropyl-1-methyl-2-oxoindolin-3-yl)acetate (3o)

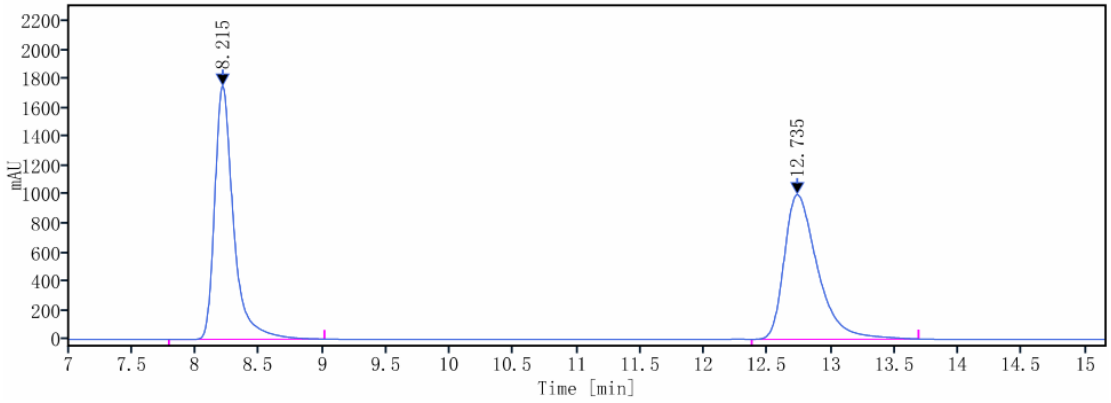
96% yield (25.1 mg); 95.5:4.5 er; Colorless oil; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = +22 (c = 0.25, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 – 7.25 (m, 1H), 7.14 (d, *J* = 7.3 Hz, 1H), 7.02 (t, *J* = 7.5 Hz, 1H), 6.84 (d, *J* = 7.8 Hz, 1H), 3.40 (s, 3H), 3.24 (s, 3H), 3.02 (dd, *J* = 20.4 Hz, *J* = 16.2 Hz, 2H), 2.12 (hept, *J* = 6.8 Hz, 1H), 0.94 (d, *J* = 6.9 Hz, 3H), 0.72 (d, *J* = 6.7 Hz, 3H).

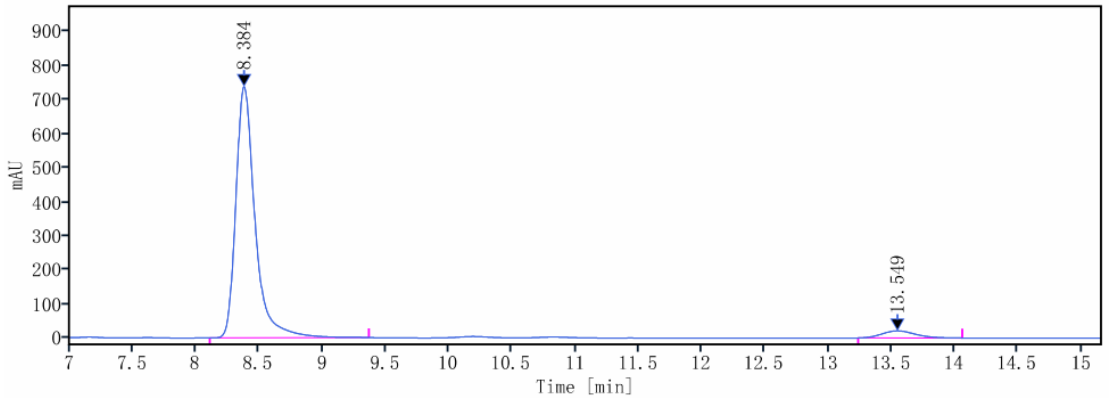
^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 170.6, 144.8, 129.9, 128.1, 123.2, 122.0, 107.8, 52.9, 51.6, 39.4, 35.4, 26.1, 17.2, 16.9 ppm.

HRMS (ESI-TOF) calcd for $[C_{15}H_{19}NO_3+H]^+$ 262.1443, found 262.1436.

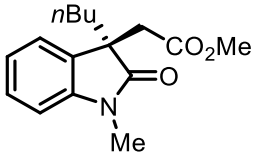
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 1 mL/min, uv-vis λ = 250 nm, t_{R1} = 8.4 min (major), t_{R2} = 13.5 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.215	BM m	0.1551	17991.3243	1748.3955	49.6769
12.735	VM m	0.2767	18225.3798	999.5485	50.3231



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.384	MM m	0.1594	7810.9961	738.1860	95.3144
13.549	MM m	0.2826	383.9807	20.9737	4.6856



methyl (R)-2-(3-butyl-1-methyl-2-oxoindolin-3-yl)acetate (3p)

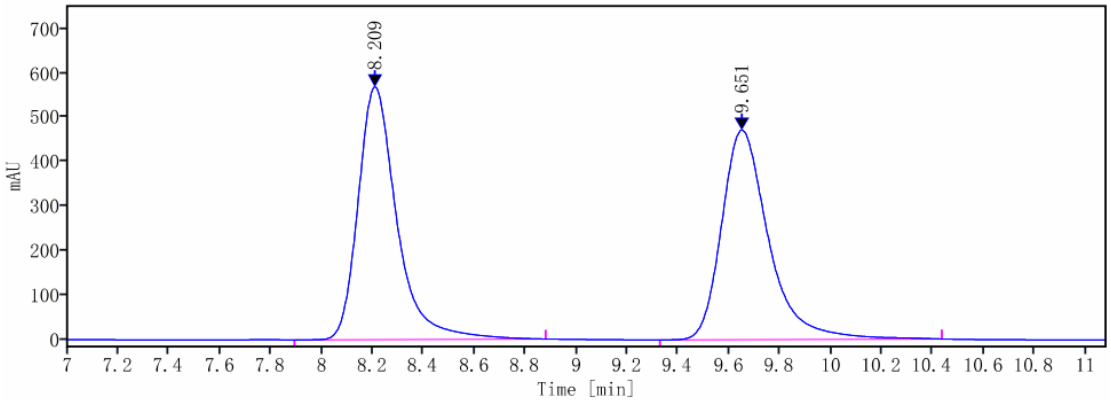
92% yield (25.3 mg); 95.5:4.5 er; White solid; m.p. 58 – 60 °C; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -5 (c = 0.16, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.28 (td, *J* = 7.7, 1.4 Hz, 1H), 7.17 – 7.14 (m, 1H), 7.04 (td, *J* = 7.5, 1.0 Hz, 1H), 6.85 (d, *J* = 7.7 Hz, 1H), 3.42 (s, 3H), 3.25 (s, 3H), 2.93 (dd, *J* = 45.2, 16.2 Hz, 2H), 1.89 – 1.69 (m, 2H), 1.26 – 1.11 (m, 2H), 1.07 – 0.92 (m, 1H), 0.86 – 0.71 (m, 4H) ppm.

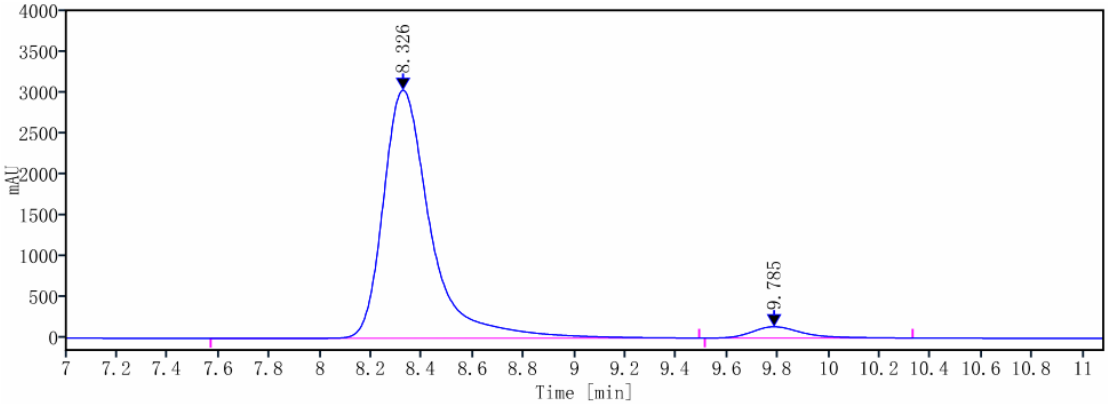
^{13}C NMR (75 MHz, $CDCl_3$) δ 179.4, 170.3, 144.4, 131.3, 128.1, 122.4, 122.3, 107.9, 51.5, 49.7, 41.2, 37.9, 26.3, 25.6, 22.7, 13.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{16}H_{21}NO_3+H]^+$ 276.1600, found 276.1597.

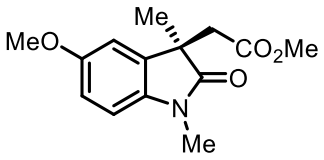
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 8.3 min (major), t_{R2} = 9.8 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.209	VM m	0.1605	6025.3820	569.2274	49.9080
9.651	MM m	0.1945	6047.5937	471.8786	50.0920



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.326	BM m	0.1943	39052.4571	3030.8250	95.3961
9.785	MM m	0.2083	1884.7272	138.0624	4.6039



methyl (R)-2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate (3q)

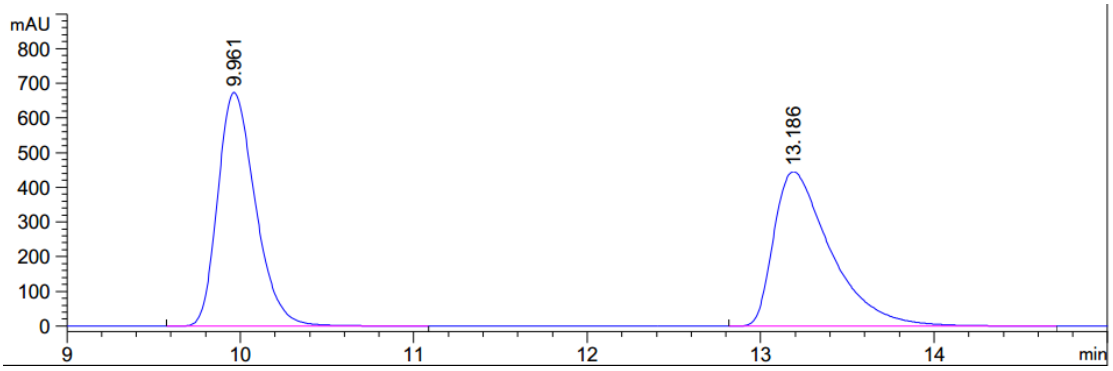
93% yield (24.5 mg); 95.5:4.5 er; White solid; m.p. 78 – 80 °C; R_f = 0.1 (PE/EA = 4/1); $[\alpha]_D^{20}$ = +17 (c = 0.14, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 6.83 – 6.75 (m, 3H), 3.79 (s, 3H), 3.48 (s, 3H), 3.23 (s, 3H), 2.91 (dd, *J* = 66. Hz, 16.5 Hz, 2H), 1.37 (s, 3H) ppm.

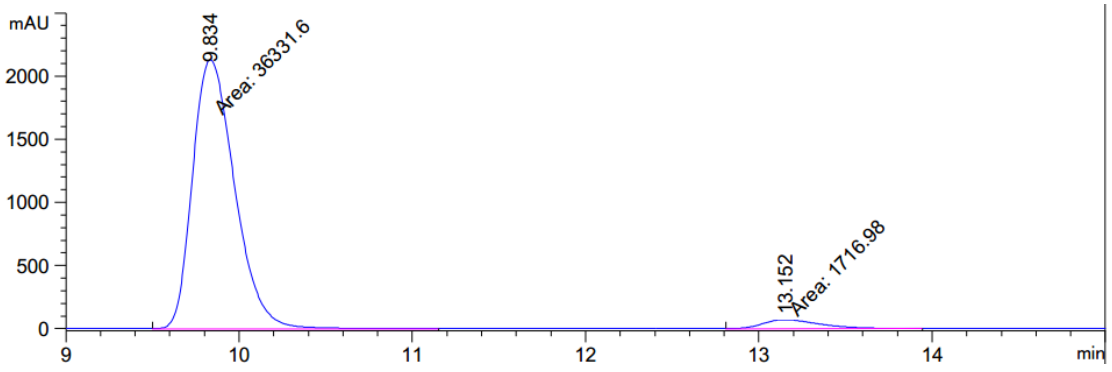
^{13}C NMR (101 MHz, $CDCl_3$) δ 179.5, 170.3, 155.9, 137.1, 134.4, 111.9, 110.2, 108.3, 55.8, 51.6, 45.9, 41.3, 26.5, 24.3 ppm.

HRMS (ESI-TOF) calcd for $[C_{14}H_{17}NO_4+H]^+$ 264.1236, found 264.1233.

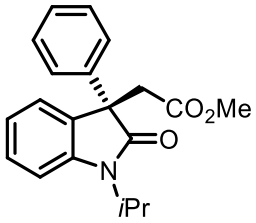
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 9.8 min (major), t_{R2} = 13.2 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.961	VB	0.2317	1.01562e4	674.32428	49.9545
2	13.186	BB	0.3425	1.01747e4	445.39276	50.0455



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.834	MM	0.2839	3.63316e4	2133.14111	95.4874
2	13.152	MM	0.3932	1716.98376	72.78358	4.5126



methyl (S)-2-(1-isopropyl-2-oxo-3-phenylindolin-3-yl)acetate (3r)

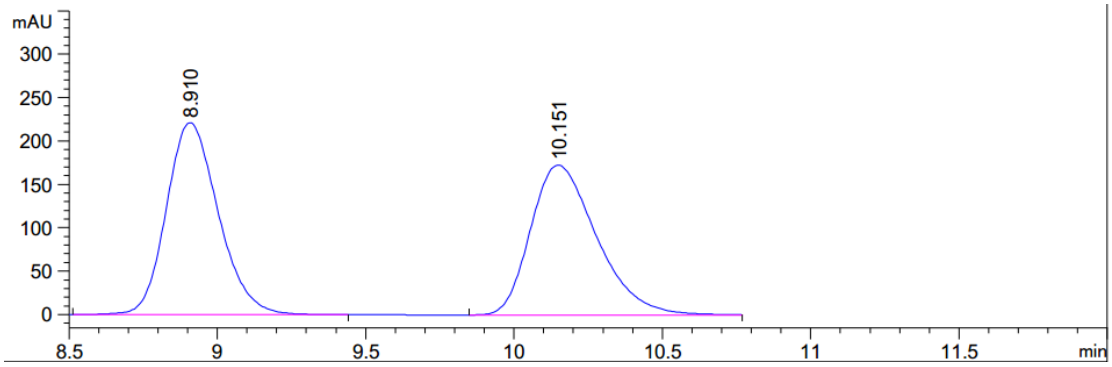
62% yield (20.0 mg); 93.5:6.5 er; White solid; m.p. 65 – 67 °C; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -35 (c = 0.16, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32 – 7.23 (m, 7H), 7.09 – 7.04 (m, 2H), 4.64 (hept, *J* = 7.0 Hz, 1H), 3.58 (d, *J* = 16.1 Hz, 1H), 3.43 (s, 3H), 3.24 (d, *J* = 16.1 Hz, 1H), 1.50 (t, *J* = 7.3 Hz, 6H) ppm.

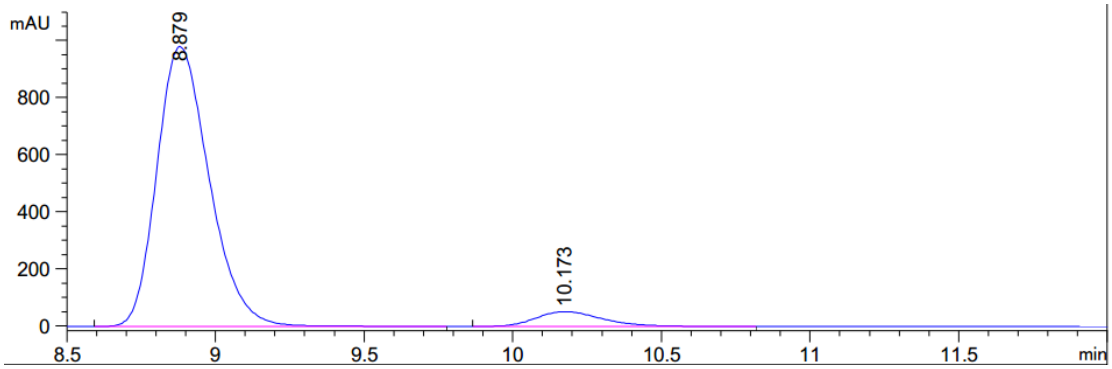
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.7, 170.0, 143.2, 139.6, 131.8, 128.7, 128.3, 127.6, 126.4, 124.6, 122.0, 110.0, 53.0, 51.6, 44.1, 41.6, 19.4, 19.0 ppm.

HRMS (ESI-TOF) calcd for $[C_{20}H_{21}NO_3+H]^+$ 324.1600, found 324.1592.

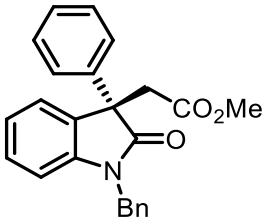
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 8.9 min (major), t_{R2} = 10.2 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.910	VB	0.1881	2696.84009	221.33765	50.2123
2	10.151	BBA	0.2408	2674.03052	172.58652	49.7877



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.879	BB	0.1886	1.19860e4	980.34070	93.7418
2	10.173	BB	0.2383	800.18542	51.78182	6.2582



methyl (S)-2-(1-benzyl-2-oxo-3-phenylindolin-3-yl)acetate (3s)

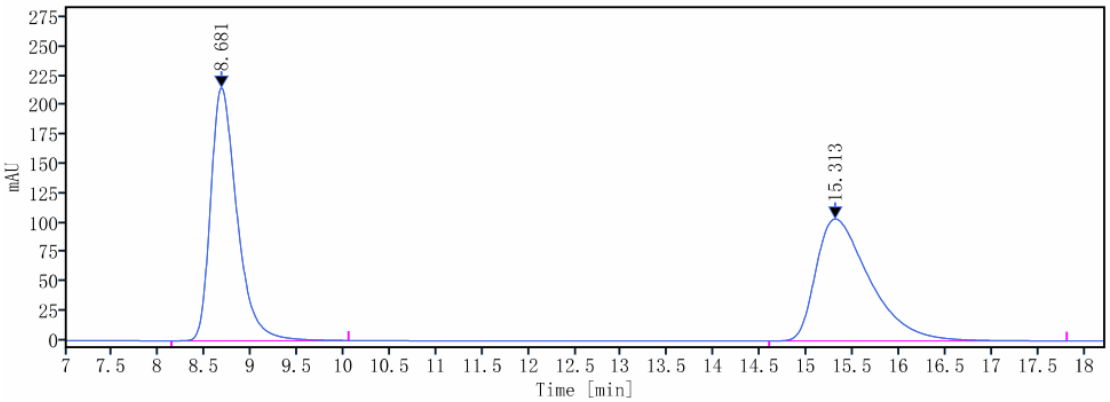
51% yield (18.9 mg); 93.5:6.5 er; White solid; m.p. 101 – 103 °C; R_f = 0.6 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -56 (c = 0.23, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.18 (m, 12H), 7.05 (t, *J* = 7.5 Hz, 1H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.93 (dd, *J* = 43.2Hz, 15.8 Hz, 2H), 3.64 (d, *J* = 16.2 Hz, 1H), 3.38 (s, 3H), 3.31 (d, *J* = 16.2 Hz, 1H) ppm.

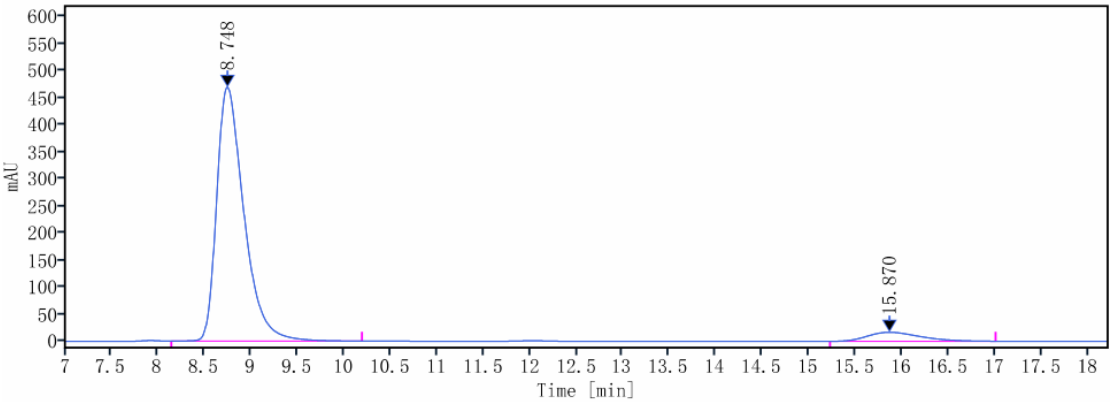
^{13}C NMR (101 MHz, $CDCl_3$) δ 178.1, 170.1, 143.7, 139.4, 136.0, 131.2, 128.8, 128.7, 128.6, 127.8, 127.6, 127.5, 126.6, 124.5, 122.6, 109.5, 53.4, 51.7, 44.3, 41.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{24}H_{21}NO_3+H]^+$ 372.1600, found 372.1595.

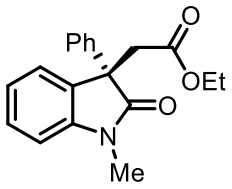
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 1 mL/min, uv-vis λ = 250 nm, t_{R1} = 8.7 min (major), t_{R2} = 15.9 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.681	BM m	0.3005	4248.1985	214.9976	50.3417
15.313	MM m	0.6131	4190.5323	103.7770	49.6583



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
8.748	BM m	0.3090	9519.2893	468.5274	93.5146
15.870	MM m	0.6054	660.1756	16.7293	6.4854



ethyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3t)

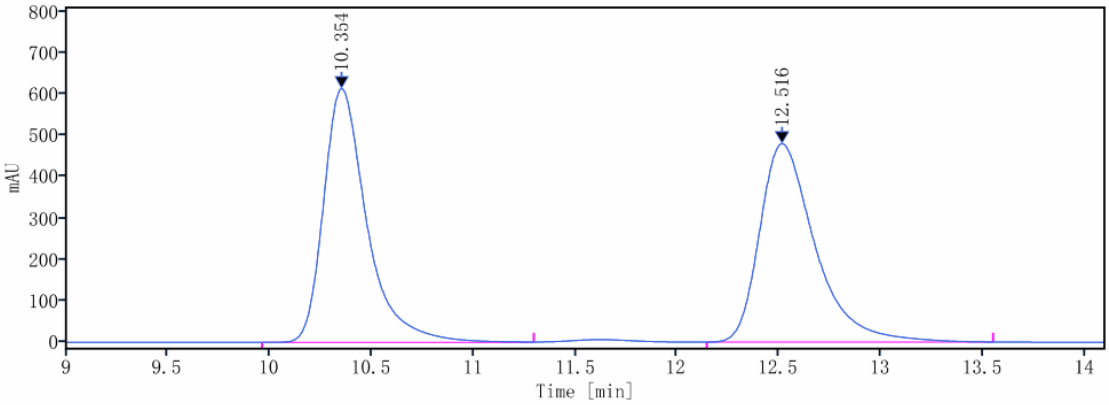
96% yield (29.6 mg); 96.5:3.5 er; White solid; m.p. 81 – 83 °C; R_f = 0.5 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -83 (c = 0.12, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 7H), 7.10 (td, *J* = 7.5, 1.0 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.87 (qq, *J* = 10.8, 7.1 Hz, 2H), 3.58 (d, *J* = 16.0 Hz, 1H), 3.26 – 3.21 (m, 4H), 0.97 (t, *J* = 7.1 Hz, 3H) ppm.

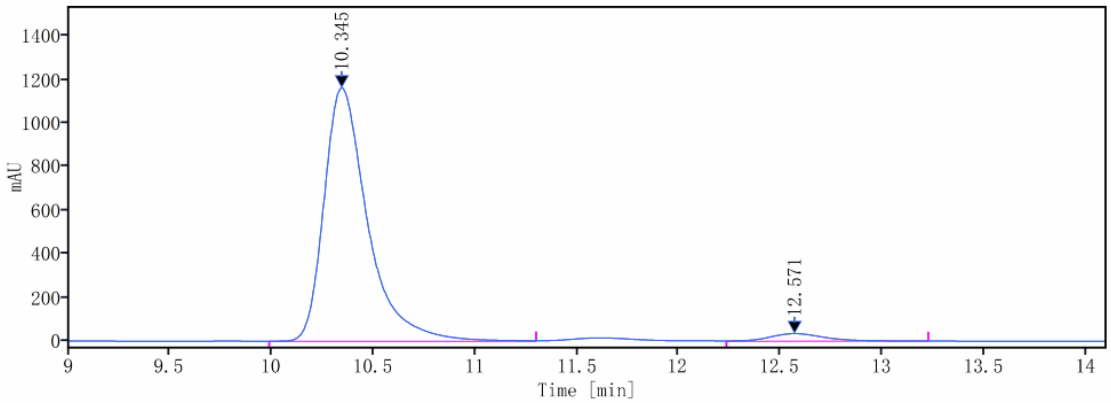
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.1, 169.6, 144.6, 139.2, 131.1, 128.7, 127.7, 126.6, 124.6, 122.5, 108.4, 60.6, 53.3, 42.2, 26.7, 13.9 ppm.

HRMS (ESI-TOF) calcd for $[C_{19}H_{19}NO_3+H]^+$ 310.1443, found 310.1439.

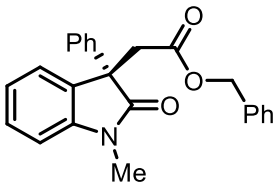
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 10.3 min (major), t_{R2} = 12.6 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.354	BV	1.3334	9067.3813	614.0225	49.9216
12.516	MM m	0.2871	9095.8599	480.0050	50.0784



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.345	BV	1.3124	17304.7846	1162.2105	96.3875
12.571	VM m	0.2831	648.5681	34.8571	3.6125



benzyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3u)

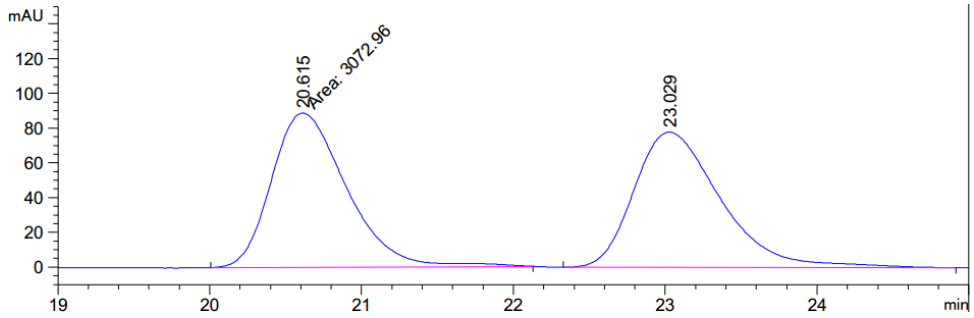
85% yield (31.6 mg); 95:5 er; Colorless oil; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -85 (c = 0.15, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.20 (m, 10H), 7.10 – 7.03 (m, 3H), 6.77 (d, *J* = 7.8 Hz, 1H), 4.87 – 4.78 (m, 2H), 3.46 (dd, *J* = 137.1, 16.0 Hz, 2H), 2.99 (s, 3H) ppm.

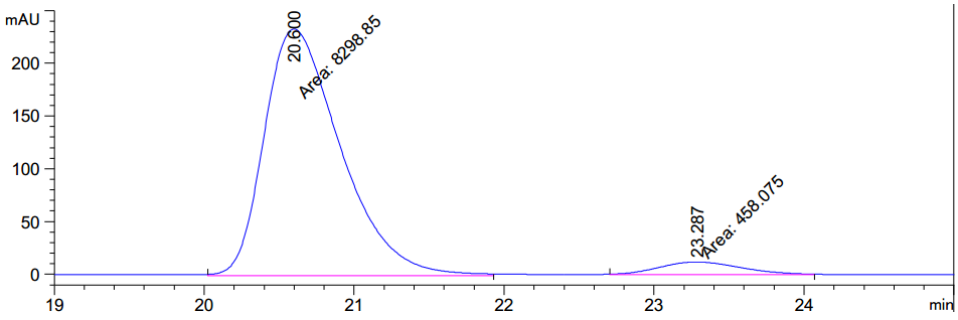
^{13}C NMR (101 MHz, $CDCl_3$) δ 177.9, 169.5, 144.5, 139.2, 135.2, 130.9, 128.7, 128.7, 128.5, 128.4, 128.3, 127.7, 126.6, 124.6, 122.5, 108.6, 66.6, 53.3, 42.2, 26.4 ppm.

HRMS (ESI-TOF) calcd for $[C_{24}H_{21}NO_3+H]^+$ 372.1600, found 372.1592.

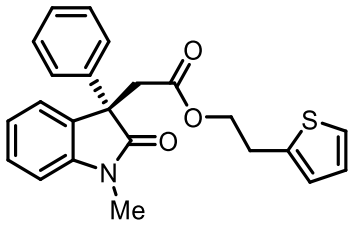
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 20.6 min (major), t_{R2} = 23.3 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.615	MM	0.5762	3072.95557	88.88560	49.8554
2	23.029	BB	0.6071	3090.77612	77.86682	50.1446



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	20.600	MM	0.5914	8298.85156	233.86845	94.7690
2	23.287	MM	0.6360	458.07535	12.00408	5.2310



2-(thiophen-2-yl)ethyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3v)

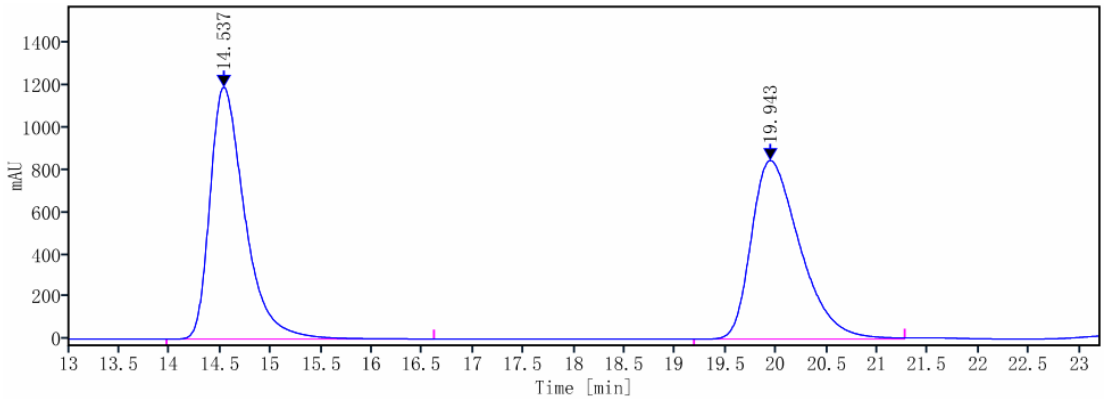
93% yield (36.4 mg); 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -84 (c = 0.27, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.20 (m, 7H), 7.13 – 7.06 (m, 2H), 6.91 – 6.88 (m, 2H), 6.73 (d, *J* = 2.8 Hz, 1H), 4.05 (t, *J* = 6.8 Hz, 2H), 3.43 (dd, *J* = 86.4 Hz, 16.3 Hz, 2H), 3.21 (s, 3H), 2.88 (t, *J* = 6.9 Hz, 2H) ppm.

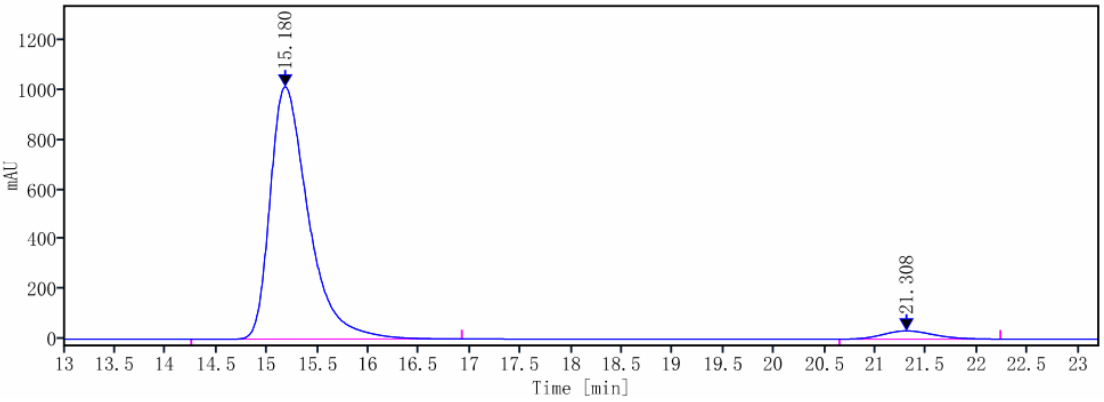
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 169.6, 144.6, 139.5, 139.1, 131.0, 128.8, 128.7, 127.7, 126.9, 126.6, 125.5, 124.6, 124.0, 122.6, 108.5, 64.7, 53.2, 42.0, 29.0, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{23}H_{21}NO_3S+H]^+$ 392.1320, found 392.1314.

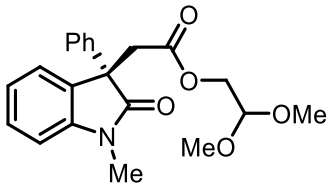
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 15.2 min (major), t_{R2} = 21.3 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.537	BB	2.6450	28513.9027	1193.1076	50.1261
19.943	BV	2.0853	28370.4868	845.8696	49.8739



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
15.180	MM m	0.3975	26529.8934	1012.9843	95.8154
21.308	MM m	0.5402	1158.6642	33.2781	4.1846



2,2-dimethoxyethyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3w)

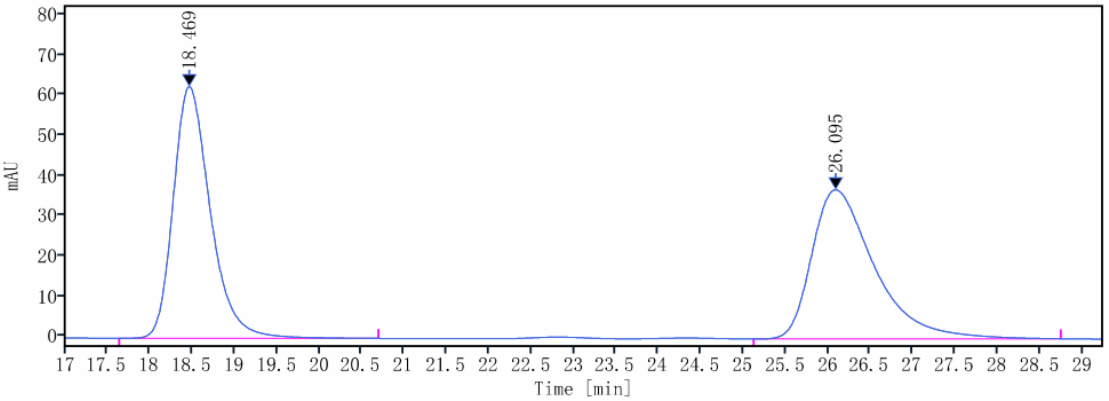
93% yield (34.2 mg); 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -71 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.21 (m, 7H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.30 (t, *J* = 5.3 Hz, 1H), 3.93 – 3.82 (m, 2H), 3.59 (d, *J* = 16.4 Hz, 1H), 3.35 – 3.24 (m, 10H) ppm.

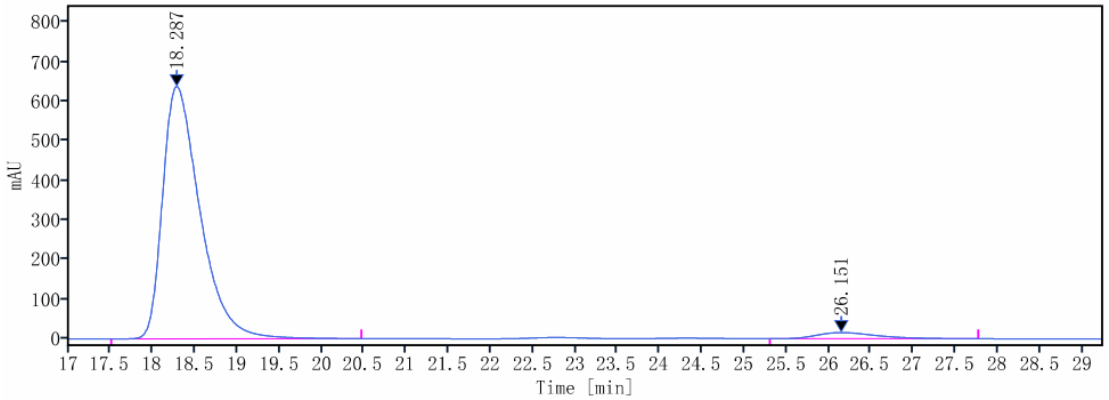
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.9, 169.3, 144.6, 139.0, 131.0, 128.7, 127.7, 126.6, 124.5, 122.5, 108.5, 100.8, 62.9, 53.7, 53.7, 53.2, 41.7, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{21}H_{23}NO_5+H]^+$ 370.1654, found 370.1651.

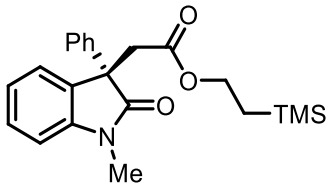
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 18.3 min (major), t_{R2} = 26.2 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
18.469	BM m	0.4639	1907.2907	62.7055	50.0772
26.095	BM m	0.7720	1901.4099	37.1552	49.9228



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
18.287	BM m	0.4685	19597.1687	637.6668	96.2057
26.151	BM m	0.7506	772.8990	15.6106	3.7943



2-(trimethylsilyl)ethyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3x)

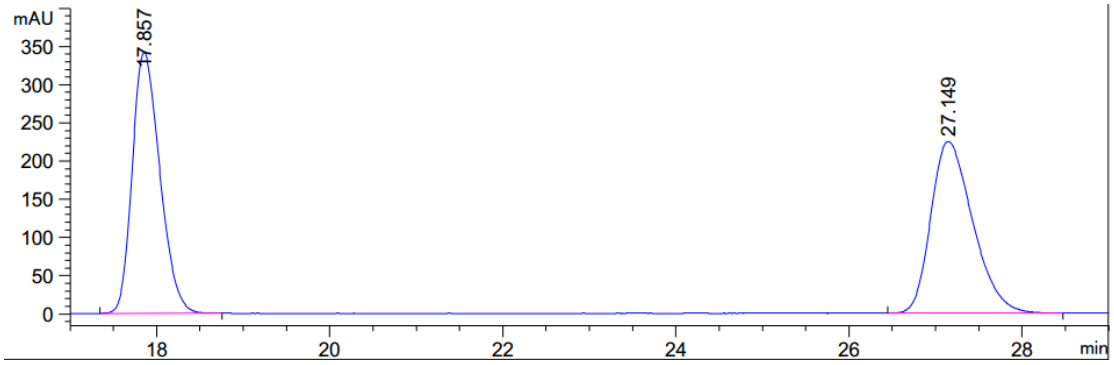
97% yield (37.2 mg); 96:4 er; Colorless oil; R_f = 0.7 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -71 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.61 – 7.45 (m, 7H), 7.34 (t, *J* = 7.4 Hz, 1H), 7.14 (d, *J* = 7.7 Hz, 1H), 4.24 – 4.06 (m, 2H), 3.79 (d, *J* = 16.2 Hz, 1H), 3.50 – 3.45 (m, 4H), 1.04 – 0.89 (m, 2H), 0.20 (s, 9H) ppm.

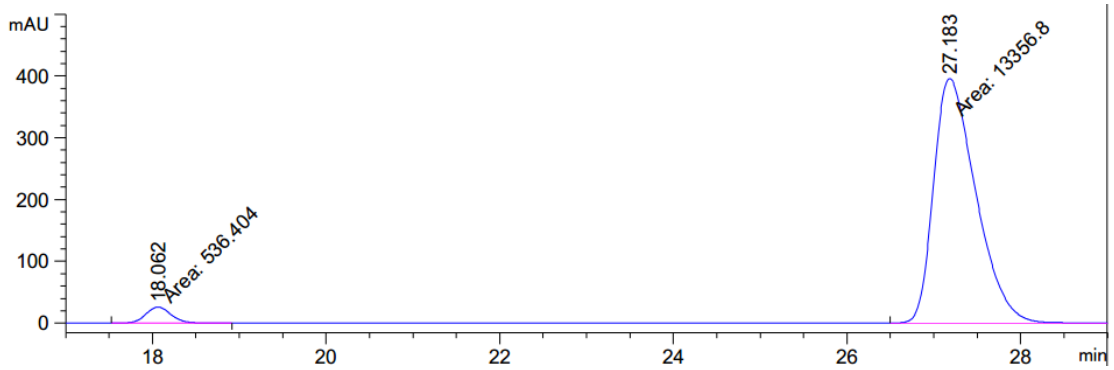
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 173.0, 141.1, 130.3, 126.0, 121.3, 64.3, 46.7, 45.3, 43.4, 31.9, 31.2, 24.7, 18.9, 0.0 ppm.

HRMS (ESI-TOF) calcd for $[C_{22}H_{27}NO_3Si+H]^+$ 382.1838, found 382.1838.

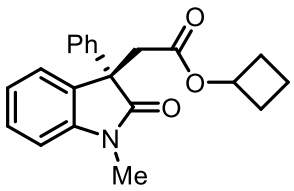
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 18.1 min (minor), t_{R2} = 27.2 min (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	17.857	BB	0.3447	7566.13428	341.18427	50.0010
2	27.149	BB	0.5207	7565.82275	224.79837	49.9990



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	18.062	MM	0.3417	536.40399	26.16271	3.8609
2	27.183	MM	0.5630	1.33568e4	395.43063	96.1391



cyclobutyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3y)

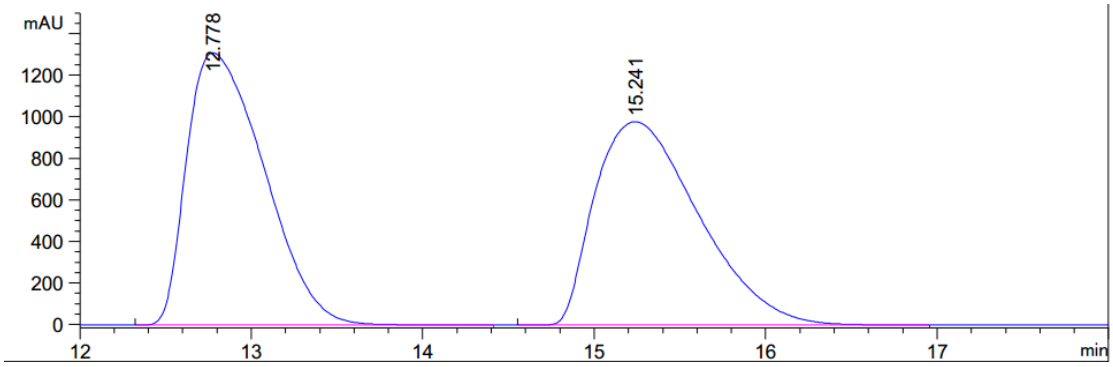
98% yield (32.8 mg); 96:4 er; White solid; m.p. 52 – 54 °C; R_f = 0.5 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -68 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.23 (m, 7H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.67 (p, *J* = 7.4 Hz, 1H), 3.57 (d, *J* = 15.8 Hz, 1H), 3.23 – 3.17 (m, 4H), 2.16 – 2.08 (m, 2H), 1.76 – 1.41 (m, 4H) ppm.

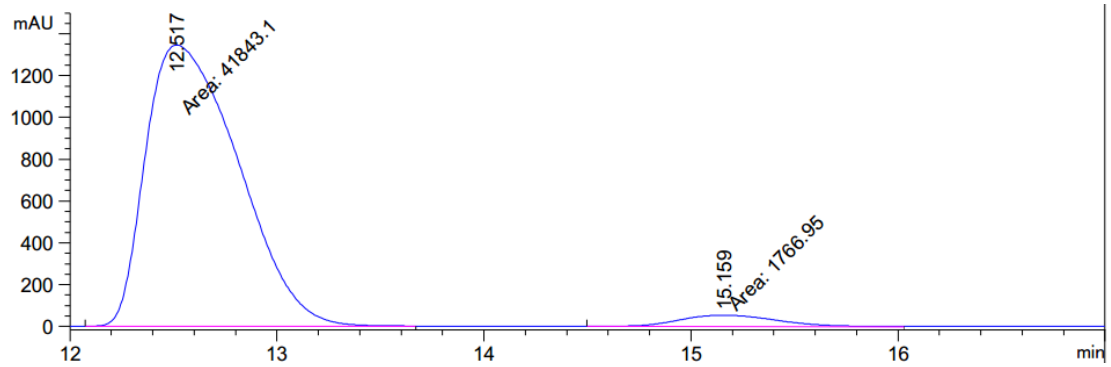
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 168.8, 144.6, 139.2, 131.0, 128.7, 127.7, 126.6, 124.7, 122.5, 108.3, 69.0, 53.3, 42.3, 30.0, 29.7, 26.7, 13.5 ppm.

HRMS (ESI-TOF) calcd for $[C_{21}H_{21}NO_3+H]^+$ 336.1600, found 336.1598.

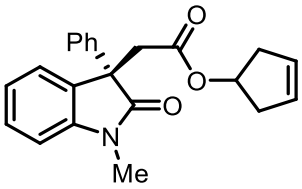
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 12.5 min (major), t_{R2} = 15.2 min (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.778	BB	0.5164	4.11617e4	1310.64941	49.9044
2	15.241	BB	0.6725	4.13194e4	978.75604	50.0956



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.517	MM	0.5184	4.18431e4	1345.37708	95.9483
2	15.159	MM	0.5482	1766.95251	53.72072	4.0517



cyclopent-3-en-1-yl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3z)

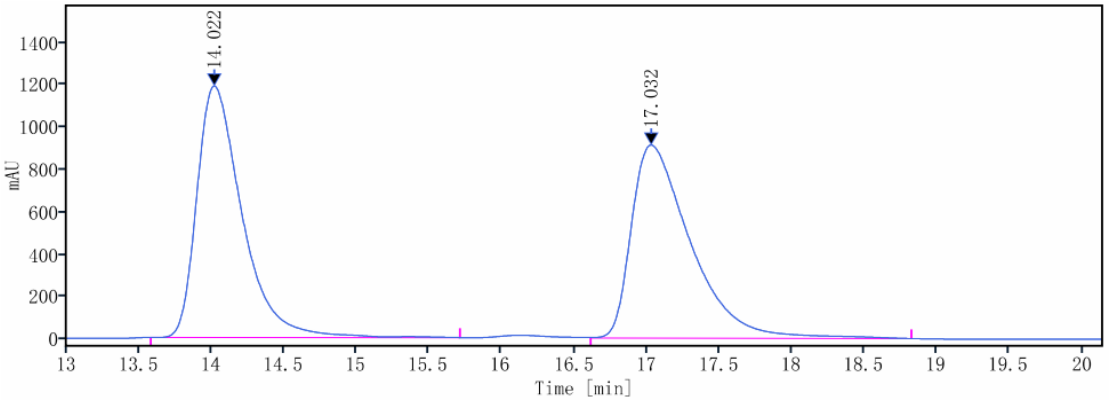
81% yield (28.1 mg); 96:4 er; Colorless oil; R_f = 0.7 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -68 (c = 0.14, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 – 7.20 (m, 7H), 7.10 (t, *J* = 7.5 Hz, 1H), 6.87 (d, *J* = 7.8 Hz,1H), 5.60 – 5.49 (m, 2H), 5.10 (tt, *J* = 6.8, 2.0 Hz, 1H), 3.60 (d, *J* = 15.6 Hz, 1H), 3.20 – 3.15 (m, 4H), 2.57 – 2.37 (m, 2H), 2.09 (d, *J* = 17.8 Hz, 1H), 1.58 (d, *J* = 18.0 Hz, 1H) ppm.

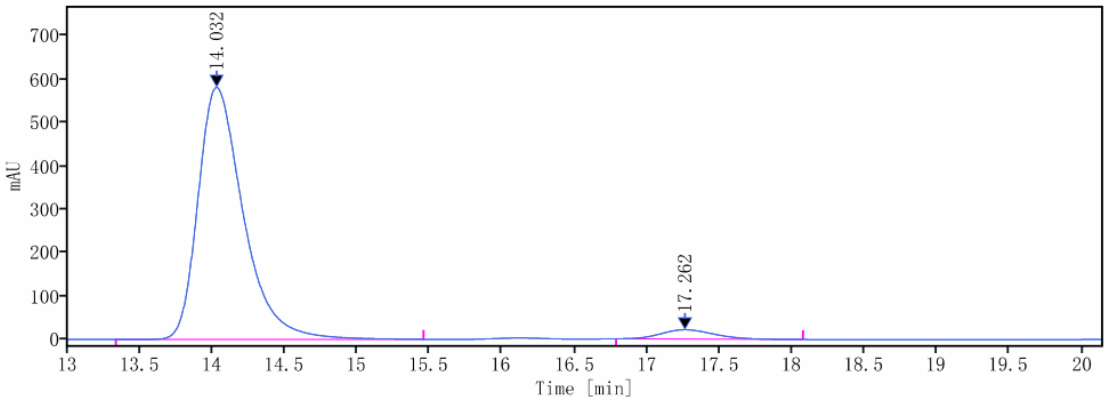
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.0, 169.4, 144.6, 139.3, 130.8, 128.7, 128.6, 128.4, 127.8, 127.6, 126.6, 124.6, 122.4, 108.5, 74.3, 53.3, 42.5, 39.5, 39.2, 26.6 ppm.

HRMS (ESI-TOF) calcd for $[C_{22}H_{21}NO_3+H]^+$ 348.1600, found 348.1602.

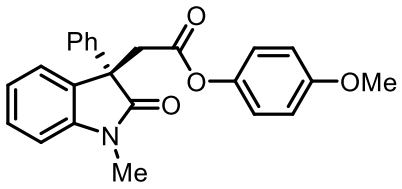
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 14.0 min (major), t_{R2} = 17.3 min (minor).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.022	MM m	0.3287	25682.3686	1185.4952	49.8157
17.032	VM m	0.4255	25872.4074	910.6530	50.1843



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.032	BM m	0.3304	12632.0578	581.6400	95.8307
17.262	MM m	0.3934	549.5756	21.5563	4.1693



4-methoxyphenyl (S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetate (3aa)

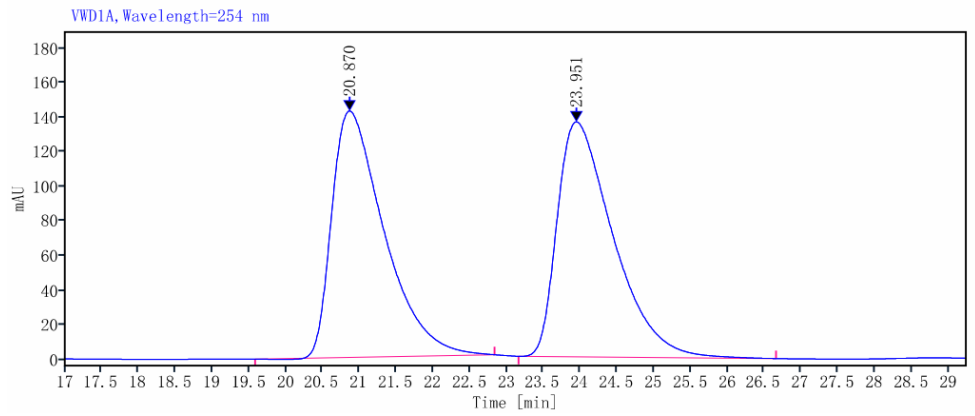
73% yield (30.2 mg， with 10 mol % Pd $(OAc)_2$, 20 mol% **L1**); 96:4 er; White solid; m.p. 98 – 100 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -47 (c = 0.12, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.28 (m, 7H), 7.224 – 7.17 (m, 1H), 6.95 (d, *J* = 7.8 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.60 – 6.54 (m, 2H), 3.85 (d, *J* = 15.7 Hz, 1H), 3.75 (s, 3H), 3.49 (d, *J* = 15.8 Hz, 1H), 3.22 (s, 3H) ppm.

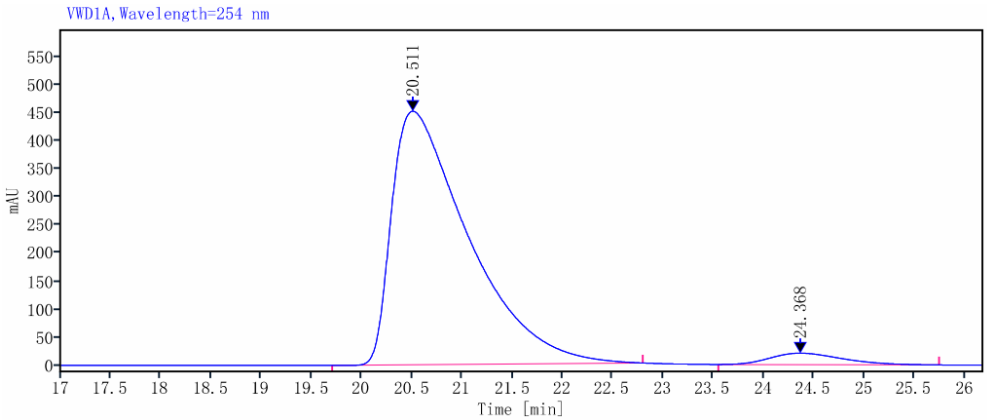
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.8, 168.7, 157.3, 144.8, 143.7, 139.0, 130.7, 128.9, 128.8, 127.8, 126.7, 124.9, 122.6, 122.0, 114.4, 108.7, 55.5, 53.4, 42.3, 26.7 ppm.

HRMS (ESI-TOF) calcd for $[C_{22}H_{23}NO_4+H]^+$ 388.1543, found 388.1545.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 20.5 min (major), t_{R2} = 24.4 min (minor).

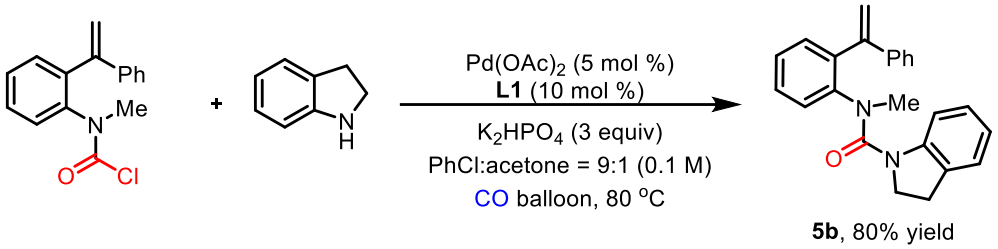


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.870	MM m	0.7456	7020.6421	142.3047	49.4599
23.951	MM m	0.8039	7173.9636	135.6636	50.5401

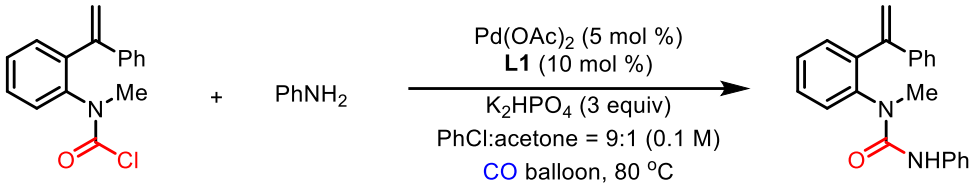


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.511	MM m	0.7860	24037.5726	452.3437	95.9469
24.368	MM m	0.7577	1015.4276	20.4712	4.0531

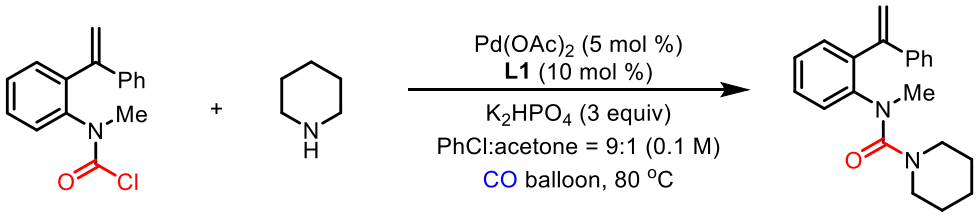
In addition, we also investigated the reaction with some nitrogen nucleophiles such as indoline, aniline and piperidine under the standard condition. Unfortunately, no desired product was detected, and only amidation products **5b-5d** were isolated. Controlled experiments showed that the competitive side reaction can occur directly even without base.



5b, 80% yield

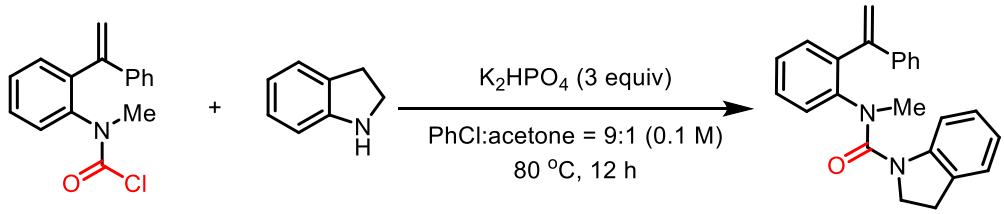


5c, 90 % yield

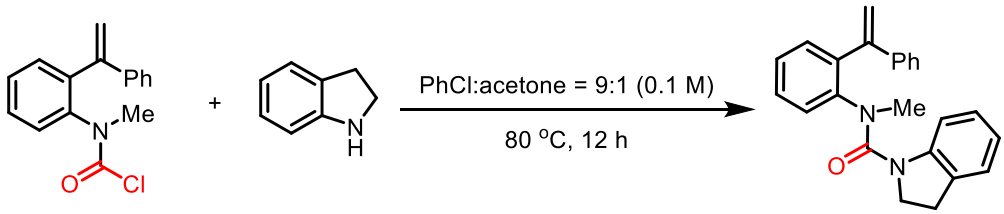


5d, 92% yield

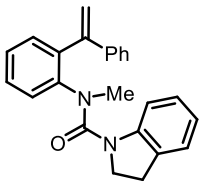
Controlling experiment



3a **5b**, 78% yield



3a **5b**, 73% yield



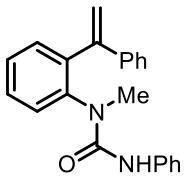
N-methyl-N-(2-(1-phenylvinyl)phenyl)indoline-1-carboxamide (5b)

80% yield (28.4mg); colorless oil; Rf = 0.3 (PE/EA = 4/1);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.0 Hz, 1H), 7.47 – 7.41 (m, 1H), 7.39 – 7.24 (m, 9H), 7.18 – 7.12 (m, 2H), 7.06 (dd, *J* = 7.3, 1.4 Hz, 1H), 6.89 (td, *J* = 7.4, 1.1 Hz, 1H), 5.60 (d, *J* = 1.1 Hz, 1H), 5.15 (d, *J* = 1.1 Hz, 1H), 3.13 (t, *J* = 8.5 Hz, 2H), 2.93 (s, 3H), 2.83 (t, *J* = 8.4 Hz, 2H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 157.5, 147.2, 144.4, 143.0, 140.6, 139.6, 131.9, 130.5, 129.1, 128.1, 128.1, 127.9, 127.0, 126.4, 124.1, 121.8, 116.4, 116.1, 49.6, 39.1, 28.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{24}H_{23}N_2O+H]^+$ 355.1805, found 355.1808.



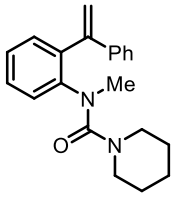
1-methyl-3-phenyl-1-(2-(1-phenylvinyl)phenyl)urea (5c)

90% yield (28.3 mg); colorless oil; Rf = 0.3 (PE/EA = 6/1);

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.54 – 7.47 (m, 3H), 7.33 – 7.14 (m, 10H), 7.01 – 6.95 (m, 1H), 5.98 (s, 1H), 5.62 (d, *J* = 1.2 Hz, 1H), 5.35 (d, *J* = 1.1 Hz, 1H), 2.83 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 148.1, 140.7, 140.6, 138.9, 132.1, 129.9, 129.1, 128.7, 128.6, 128.3, 128.0, 126.5, 122.6, 119.1, 117.1, 36.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{21}H_{24}N_2O+H]^+$ 329.1648, found 329.1649.



N-methyl-N-(2-(1-phenylvinyl)phenyl)piperidine-1-carboxamide (5d)

92% yield (29.4 mg); colorless oil; Rf = 0.3 (PE/EA = 4/1);

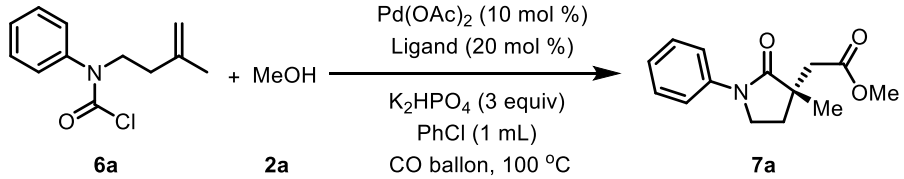
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 6.68 (m, 9H), 5.66 (d, *J* = 1.3 Hz, 1H), 5.33 (d, *J* = 1.3 Hz, 1H), 2.92 (d, *J* = 3.0 Hz, 7H), 1.41 (td, *J* = 6.3, 3.7 Hz, 2H), 1.27 (ddt, *J* = 7.6, 4.6, 2.5 Hz, 4H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.7, 148.1, 140.7, 140.6, 138.9, 132.1, 129.9, 129.1, 128.7, 128.6, 128.3, 128.0, 126.5, 122.6, 119.1, 117.1, 36.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{21}H_{24}N_2O+H]^+$ 321.1961, found 321.1961.

4. Optimization of Reaction Parameters for the Palladium-Catalyzed Asymmetric Carbamoyl-Carbonylation of Unactivated Alkenes

Table S1 Ligand Screening



6a **2a** **7a**

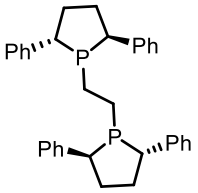
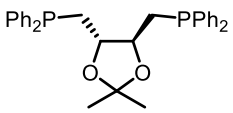
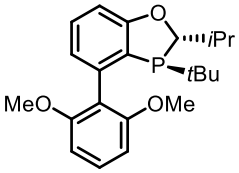
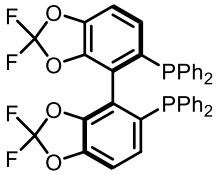
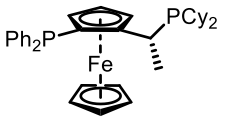
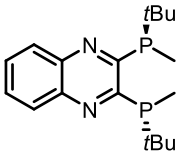
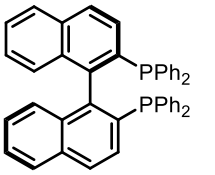
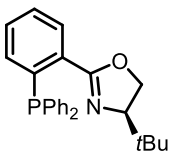
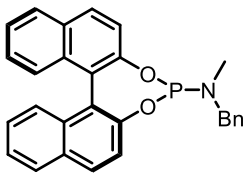
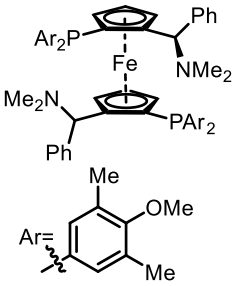
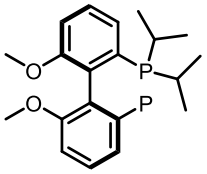
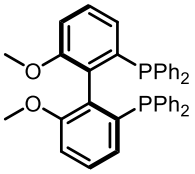
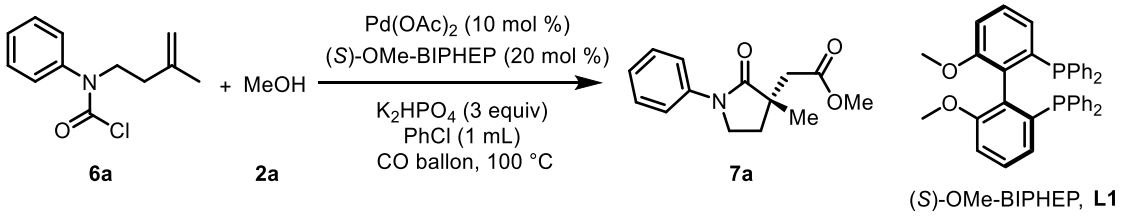
			
15% yield, 5% ee	15% yield, 9% ee	12% yield, 16% ee	17% yield, 22% ee
			
22% yield, 29% ee	17% yield, 30% ee	8% yield, 11% ee	trace, 29% ee
			
trace, 40% ee	19% yield, 29% ee	54% yield, 2% ee	28% yield, 35% ee

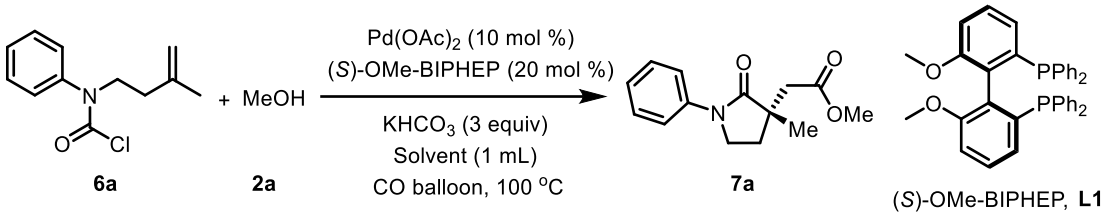
Table S2. Base Screening



Entry	[Pd]	Base	Solvent	Yield%	er
1	$Pd(OAc)_2$	K_2CO_3	PhCl	15	92:8
2	$Pd(OAc)_2$	Na_2CO_3	PhCl	40	78:22
3	$Pd(OAc)_2$	K_3PO_4	PhCl	20	70.5:29.5
4	$Pd(OAc)_2$	KH_2PO_4	PhCl	trace	-
5	$Pd(OAc)_2$	$KHCO_3$	PhCl	55	83.5:16.5
6	$Pd(OAc)_2$	Li_2CO_3	PhCl	nd	-
7	$Pd(OAc)_2$	Et_3N	PhCl	nd	-
8	$Pd(OAc)_2$	Ag_2CO_3	PhCl	nd	-

[a] Reaction conditions: **6a** (0.1 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (10 mol %), (*S*)-OMe-BIPHEP (20 mol %), Base (0.3 mmol) in 1 mL solvent, 100 °C (oil bath temperature), 24 h, CO (balloon). [b] Isolated yields. [c] The er values were determined by HPLC analysis on a chiral stationary phase.

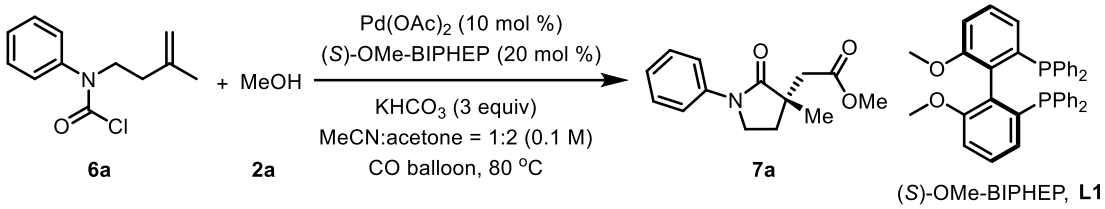
Table S3. Solvent Screening



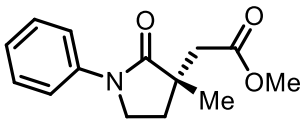
Entry	[Pd]	Base	Solvent	Yield%	ee%
1	$Pd(OAc)_2$	$KHCO_3$	THF	nd	-
2	$Pd(OAc)_2$	$KHCO_3$	DCM	nd	-
3	$Pd(OAc)_2$	$KHCO_3$	Et_2O	nd	-
4	$Pd(OAc)_2$	$KHCO_3$	1,4-Dioxane	nd	-
5	$Pd(OAc)_2$	$KHCO_3$	Tol	20	58
6	$Pd(OAc)_2$	$KHCO_3$	Benzene	55	0
7	$Pd(OAc)_2$	$KHCO_3$	Benzotrifluoride	65	86
8	$Pd(OAc)_2$	$KHCO_3$	Mesitylene	trace	55
9	$Pd(OAc)_2$	$KHCO_3$	o-Xylene	40	44
10	$Pd(OAc)_2$	$KHCO_3$	PhF	47	30
11	$Pd(OAc)_2$	$KHCO_3$	C_6F_6	50	87
12	$Pd(OAc)_2$	$KHCO_3$	Acetone	82	87
13	$Pd(OAc)_2$	$KHCO_3$	MeCN	68	90
14	$Pd(OAc)_2$	$KHCO_3$	MeCN:Acetone (1:4)	80	89
15	$Pd(OAc)_2$	$KHCO_3$	MeCN:Acetone (1:2)	88	90

[a] Reaction conditions: **6a** (0.1 mmol), **2a** (1 mmol), $Pd(OAc)_2$ (10 mol %), (*S*)-OMe-BIPHEP (20 mol %), $KHCO_3$ (0.3 mmol) in 1 mL solvent, 100 °C (oil bath temperature), 24 h, CO (balloon). [b] Isolated yields. [c] The er values were determined by HPLC analysis on a chiral stationary phase.

5. General Procedure for the Palladium-Catalyzed Asymmetric Carbamoyl-Carbonylation of Unactivated Alkenes



An oven-dried 10 mL Schlenk tube was charged with the substrate **6a** (27.2 mg, 0.1 mmol), $Pd(OAc)_2$ (2.2 mg, 10 mol %), **L1** (11.6 mg, 20 mol %), and $KHCO_3$ (30 mg, 0.3 mmol). The vial is thoroughly flushed with CO, and MeOH (45 μL, 1 mmol), as well as MeCN/acetone (1/2, 1.0 mL) was added under balloon pressure of CO. Then the reaction mixture was stirred at room temperature for 5 min, and then raised to 80 ^{o}C (oil bath temperature) for 48 h with stirring. After the reaction vessel was cooled to room temperature, the reaction mixture was filtered through a plug of celite and concentrated under reduced pressure. The solution was purified by flash column chromatography on silica gel (PE/EA = 10/1) to afford the desired product **7a** in 83% yield (20.6 mg).



methyl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7a)

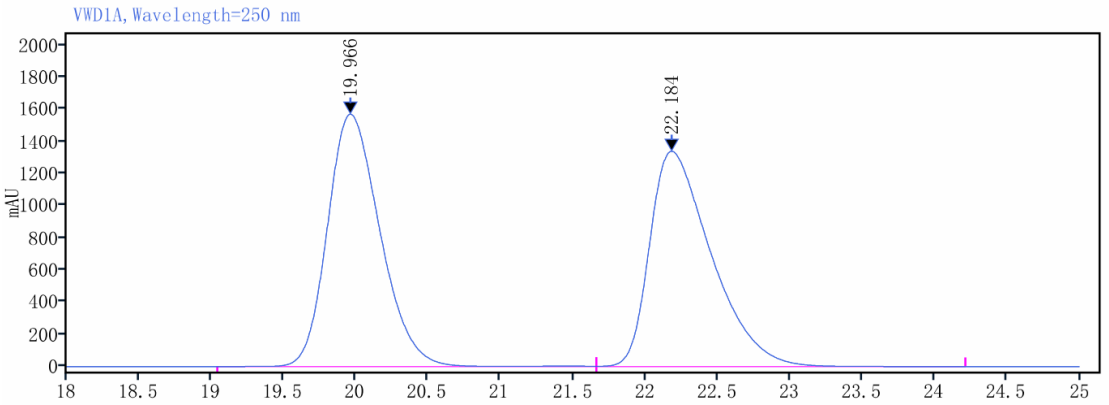
83% yield (20.6 mg); 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -17 (c = 0.13, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.60 (m, 2H), 7.53 – 7.35 (m, 2H), 7.24 – 7.09 (m, 1H), 3.96 – 3.79 (m, 2H), 3.72 (s, 3H), 2.78 (d, *J* = 16.0 Hz, 1H), 2.69 (s, 1H), 2.42 – 2.30 (m, 1H), 2.09 (ddd, *J* = 12.8, 7.4, 3.9 Hz, 1H), 1.34 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 171.8, 139.6, 128.9, 124.6, 119.9, 51.6, 45.2, 43.8, 41.6, 30.4, 23.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{14}H_{17}NO_3+H]^+$ 248.1281, found 248.1283.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 20. 0 min (minor), t_{R2} = 22.1 min (major).



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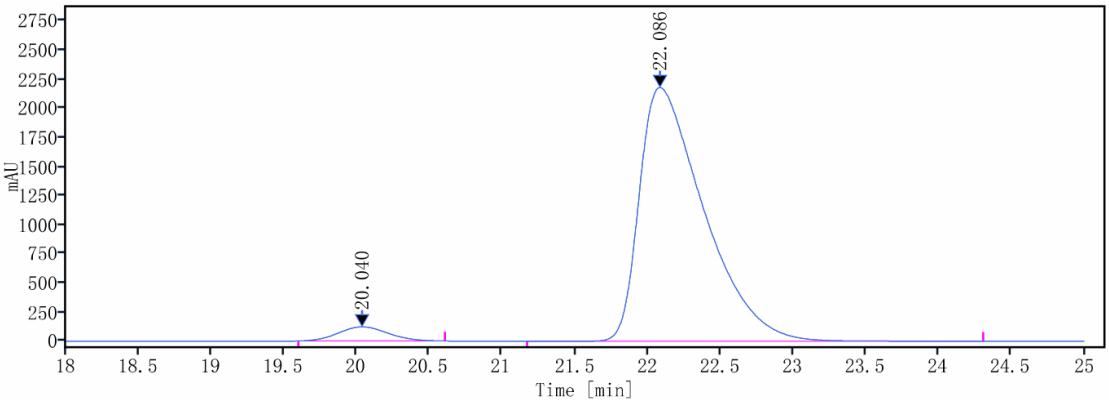
22.184	VB	2.5493	39523.2689	1337.2866	49.9910



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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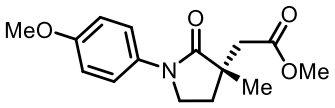
22.086	MM m	0.4644	67142.6969	2179.7126	95.8697



methyl (S)-2-(1-(4-methoxyphenyl)-3-methyl-2-oxopyrrolidin-3-yl)acetate (7b)

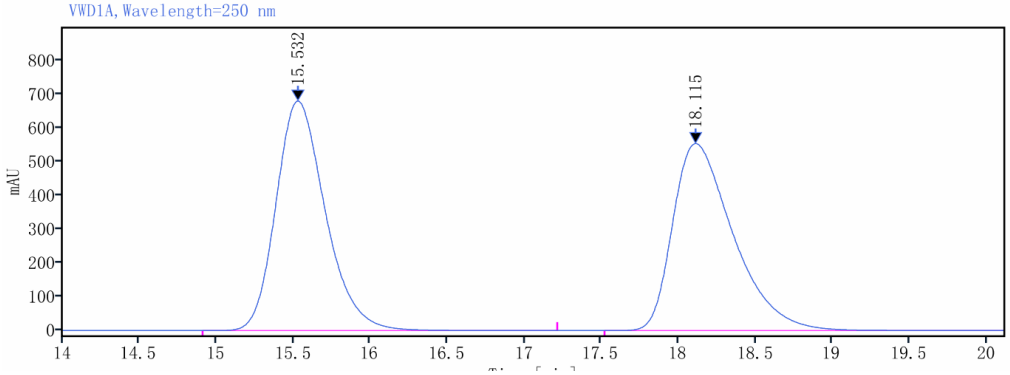
85% yield (23.5 mg), 96:4 er; 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 6/1); $[\alpha]_D^{20}$ = -13 (c = 0.064, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.57 (d, *J* = 9.1 Hz, 2H), 6.94 (d, *J* = 9.1 Hz, 2H), 3.84 – 3.76 (m, 5H), 3.72 (s, 3H), 2.76 (d, *J* = 16.0 Hz, 1H), 2.65 (d, *J* = 16.0 Hz, 1H), 2.43 – 2.23 (m, 1H), 2.15 – 1.87 (m, 1H), 1.33 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 176.7, 171.8, 156.6, 132.9, 121.8, 114.1, 55.5, 51.6, 45.7, 43.5, 41.6, 30.5, 23.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{15}H_{19}NO_3+H]^+$ 278.1387, found 278.1389.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 80/20, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 15. 5 min (minor), t_{R2} = 17.9 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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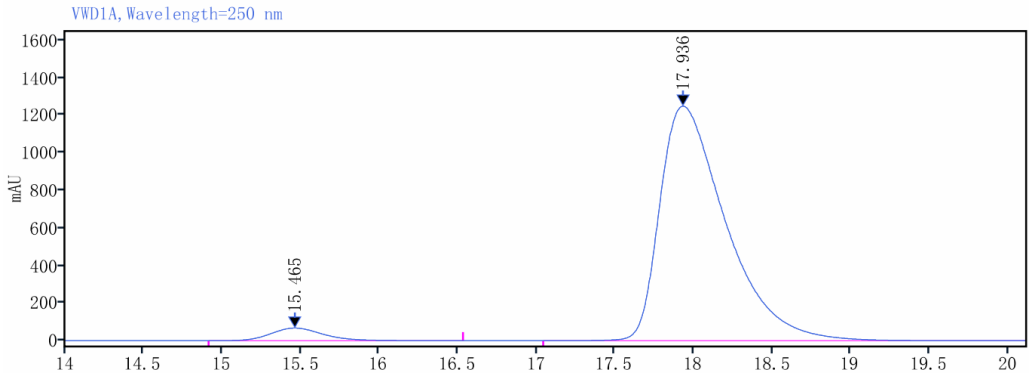
18.115	BB	2.8083	15167.9082	554.6957	49.9976



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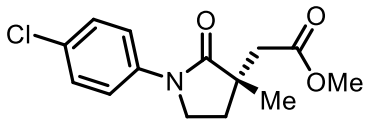


methyl (S)-2-(1-(4-chlorophenyl)-3-methyl-2-oxopyrrolidin-3-yl)acetate (7c)

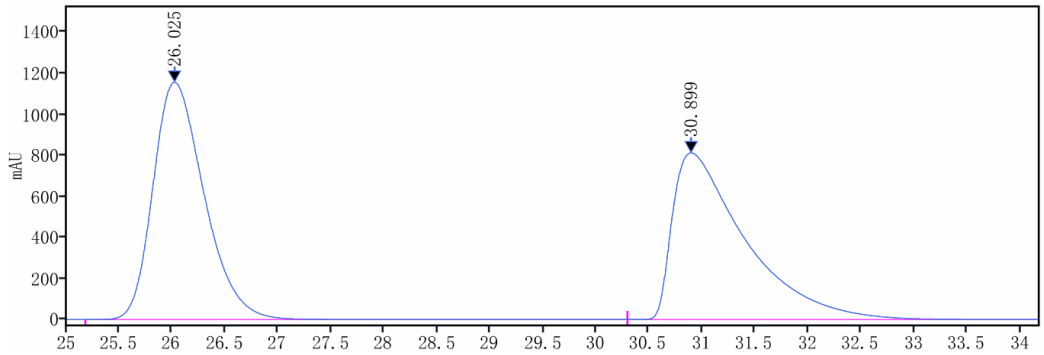
78% yield (21.9 mg), 95:5 er; White solid; m.p. 60 – 62 °C; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -48 (c = 0.044, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (d, *J* = 9.0 Hz, 2H), 7.36 (d, *J* = 9.0 Hz, 1H), 3.88 – 3.77 (m, 2H), 3.71 (s, 3H), 2.79 (d, *J* = 16.2 Hz, 1H), 2.64 (d, *J* = 16.2 Hz, 1H), 2.49 – 2.30 (m, 1H), 2.15 – 2.04 (m, 1H), 1.33 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.2, 171.7, 138.2, 129.6, 128.8, 120.9, 51.7, 45.2, 43.7, 41.5, 30.2, 23.3 ppm.

HRMS (ESI-TOF) calcd for $[C_{14}H_{16}ClNO_3+H]^+$ 281.0891, found 281.0896.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 25. 2 min (minor), t_{R2} = 30.4 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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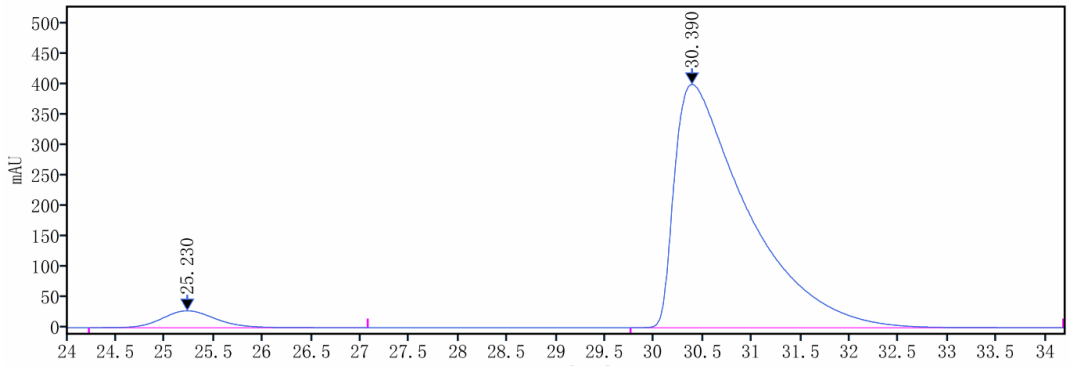
30.899	BB	4.8717	38747.2218	812.4906	49.9678



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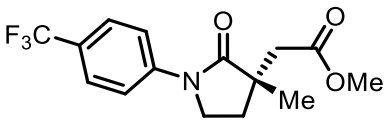


methyl (S)-2-(3-methyl-2-oxo-1-(4-(trifluoromethyl)phenyl)pyrrolidin-3-yl)acetate (7d)

65% yield (21.2 mg), 95.5:4.5 er; White solid; m.p. 81 – 83 °C; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -16 (c = 0.044, EA).

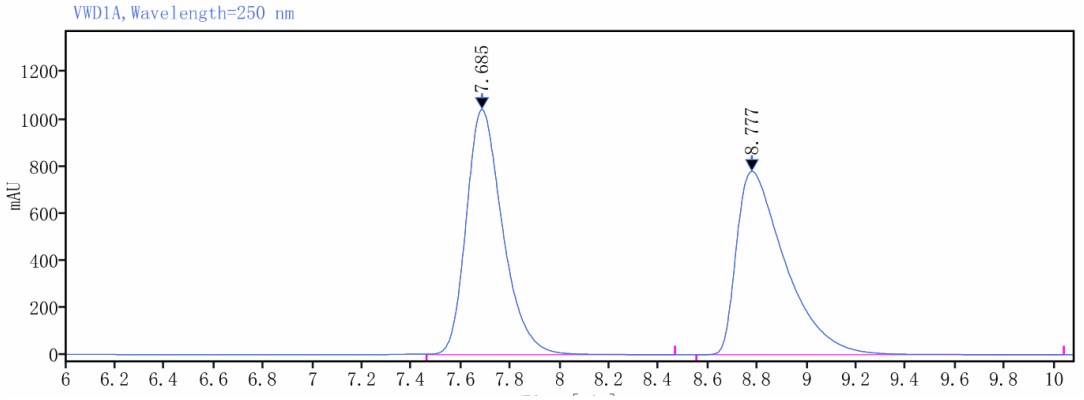
^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.75 (m, 2H), 7.74 – 7.60 (m, 2H), 3.96 – 3.75 (m, 2H), 3.70 (s, 3H), 2.80 (d, *J* = 16.3 Hz, 1H), 2.64 (d, *J* = 16.3 Hz, 1H), 2.40 (dt, *J* = 12.8, 8.5 Hz, 1H), 2.08 (ddd, *J* = 12.8, 7.1, 4.2 Hz, 1H), 1.32 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 177.7, 171.6, 142.5, 126.0, 126.0, 119.2, 51.7, 45.0, 43.8, 41.5, 30.1, 23.4 ppm.

^{19}F NMR (282 MHz, $CDCl_3$) δ -62.14 ppm.

HRMS (ESI-TOF) calcd for $[C_{15}H_{16}F_3NO_3+H]^+$ 316.1155, found 316.1162.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 80/20, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 7.5 min (minor), t_{R2} = 8.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
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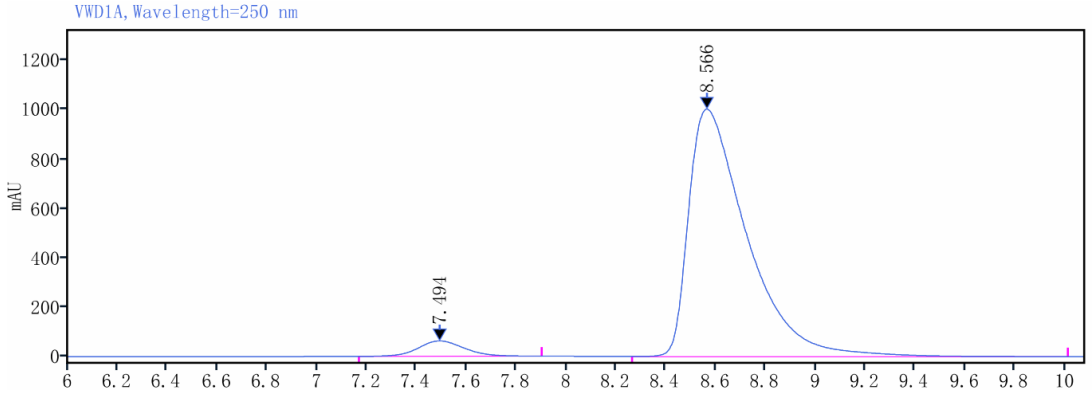
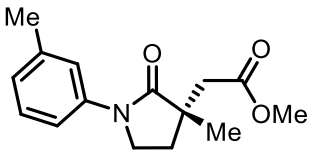


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
7.494	MM m	0.1967	801.7390	62.4825	4.6910
8.566	MM m	0.2426	16289.1349	1002.5571	95.3090



methyl (S)-2-(3-methyl-2-oxo-1-(m-tolyl)pyrrolidin-3-yl)acetate (7e)

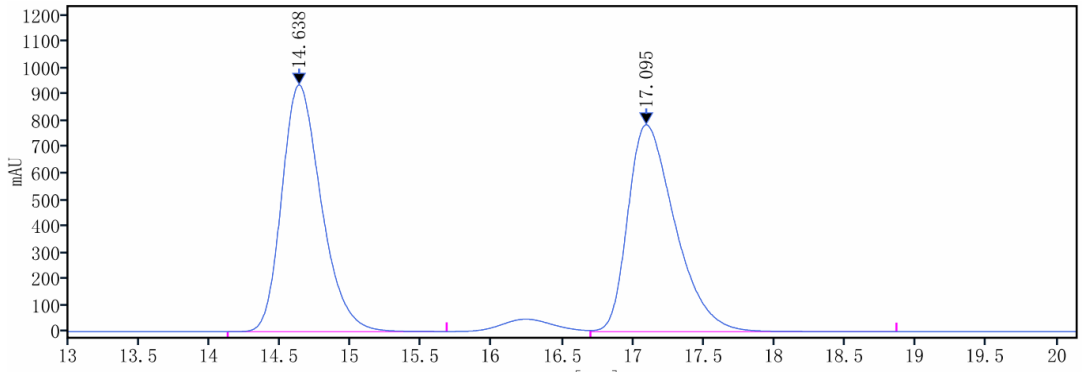
70% yield (18.3 mg), 95.5:4.5 er; Colorless oil; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -14 (c = 0.056, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.93 – 7.75 (m, 2H), 7.74 – 7.60 (m, 2H), 3.96 – 3.75 (m, 2H), 3.70 (s, 3H), 2.80 (d, *J* = 16.3 Hz, 1H), 2.64 (d, *J* = 16.3 Hz, 1H), 2.40 (dt, *J* = 12.8, 8.5 Hz, 1H), 2.08 (ddd, *J* = 12.8, 7.1, 4.2 Hz, 1H), 1.32 (s, 3H) ppm.

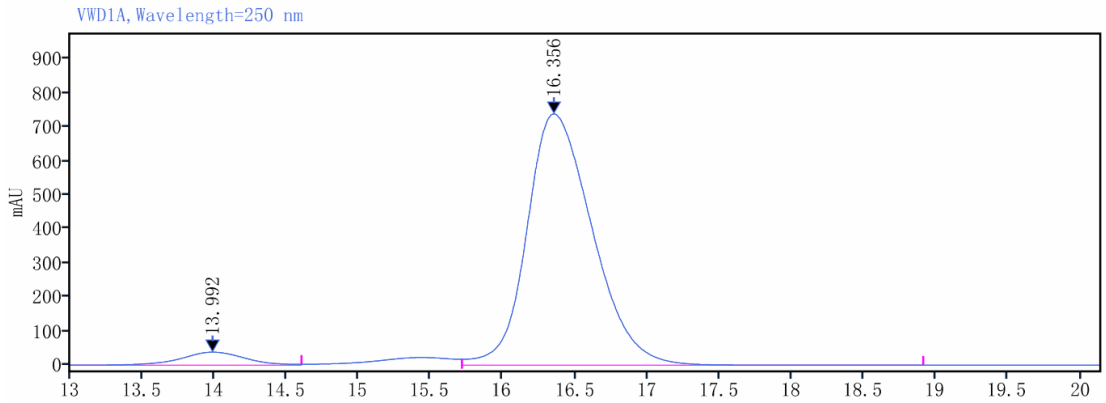
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 171.7, 139.5, 138.7, 128.6, 125.4, 120.8, 116.9, 51.6, 45.3, 43.8, 41.5, 30.4, 23.1, 21.6 ppm.

HRMS (ESI-TOF) calcd for $[C_{15}H_{19}NO_3+H]^+$ 262.1438, found 262.1442.

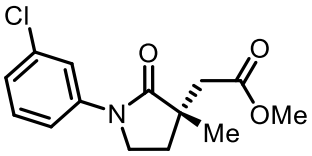
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 14.0 min (minor), t_{R2} = 16.4 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
14.638	BB	1.5488	18168.9912	936.1692	49.9661
17.095	VB	2.1651	18193.6475	785.1142	50.0339



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
13.992	BV	1.7848	1185.0596	38.2215	4.8438
16.356	VB	3.1947	23280.3086	738.2542	95.1562



methyl (S)-2-(1-(3-chlorophenyl)-3-methyl-2-oxopyrrolidin-3-yl)acetate (7f)

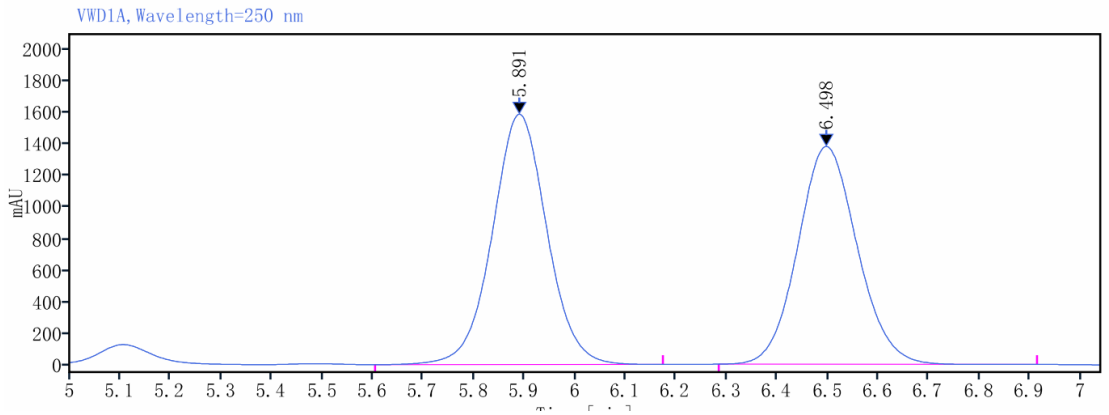
75% yield (21.1 mg), 95.5:4.5 er; Colorless oil; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -21 (c = 0.048, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.76 (t, *J* = 2.1 Hz, 1H), 7.66 – 7.51 (m, 1H), 7.34 – 7.26 (m, 1H), 7.13 (m, 1H), 3.88 – 3.77 (m, 2H), 3.69 (s, 3H), 2.77 (d, *J* = 16.2 Hz, 1H), 2.62 (d, *J* = 16.2 Hz, 1H), 2.37 (dt, *J* = 12.9, 8.5 Hz, 1H), 2.05 (ddd, *J* = 12.8, 7.2, 4.1 Hz, 1H), 1.30 (s, 3H) ppm.

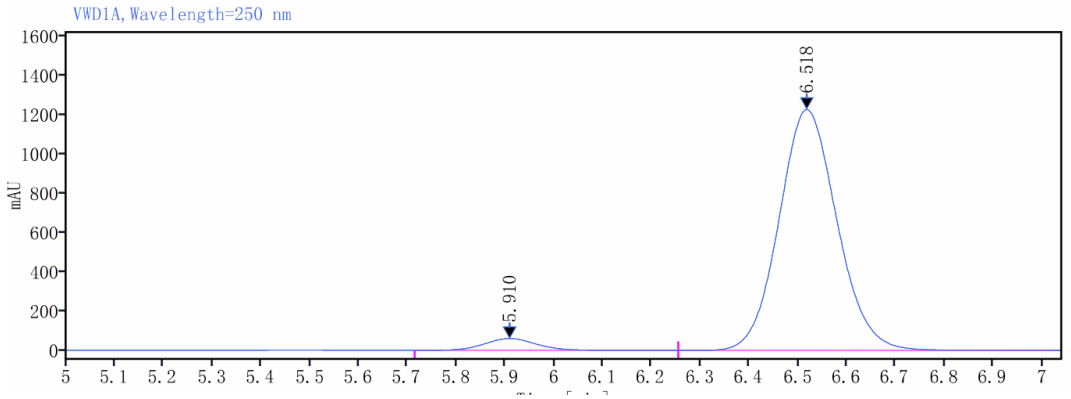
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.3, 171.6, 140.7, 134.6, 129.8, 124.4, 119.8, 117.6, 51.7, 45.1, 43.8, 41.5, 30.1, 23.3 ppm.

HRMS (ESI-TOF) calcd for $[C_{14}H_{16}ClNO_3+H]^+$ 282.0891, found 282.0897.

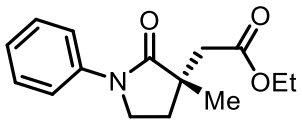
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 80/20, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 5.9 min(minor), t_{R2} = 6.5 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
5.891	BB	0.5695	11863.2664	1579.3950	51.3913
6.498	MM m	0.1262	11220.9316	1374.8252	48.6087



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
5.910	VB	0.5400	449.9957	60.4945	4.2439
6.518	MM m	0.1275	10153.2364	1227.3201	95.7561



ethyl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7g)

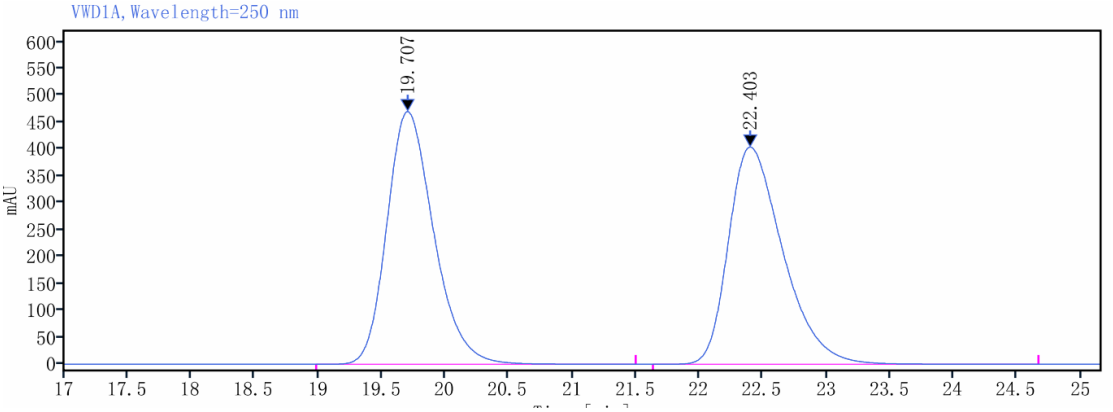
78% yield (20.3 mg), 96:4 er; Colorless oil; R_f = 0.3 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -11 (c = 0.044, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.69 (dd, *J* = 8.8, 1.1 Hz, 1H), 7.40 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.21 – 7.15 (m, 1H), 4.17 (q, *J* = 7.1 Hz, 2H), 3.92 – 3.80 (m, 2H), 2.77 (d, *J* = 15.9 Hz, 1H), 2.63 (d, *J* = 16.0 Hz, 1H), 2.51 – 2.30 (m, 1H), 2.07 (ddd, *J* = 12.8, 7.5, 3.7 Hz, 1H), 1.33 (s, 3H), 1.27 (t, *J* = 7.1 Hz, 3H) ppm.

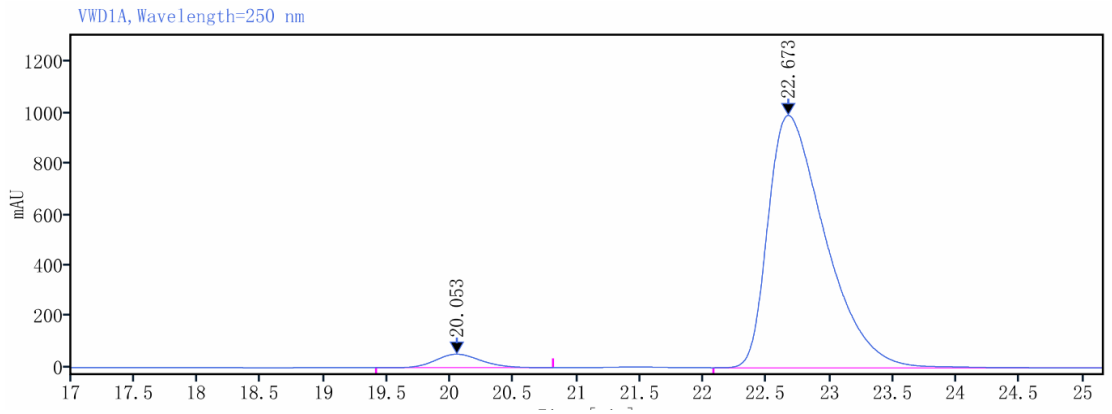
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 171.3, 139.6, 128.9, 124.5, 119.9, 60.5, 45.2, 43.8, 41.9, 30.3, 23.2, 14.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{15}H_{19}NO_3+H]^+$ 262.1438, found 262.1443.

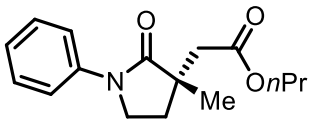
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 20.0 min (minor), t_{R2} = 22.7 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
19.707	BB	2.5150	12034.1704	470.1118	49.9887
22.403	BB	3.0333	12039.6325	403.9433	50.0113



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
20.053	MM m	0.3842	1314.3136	52.8454	4.0458
22.673	BB	3.3400	31171.4171	991.6588	95.9542



propyl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7h)

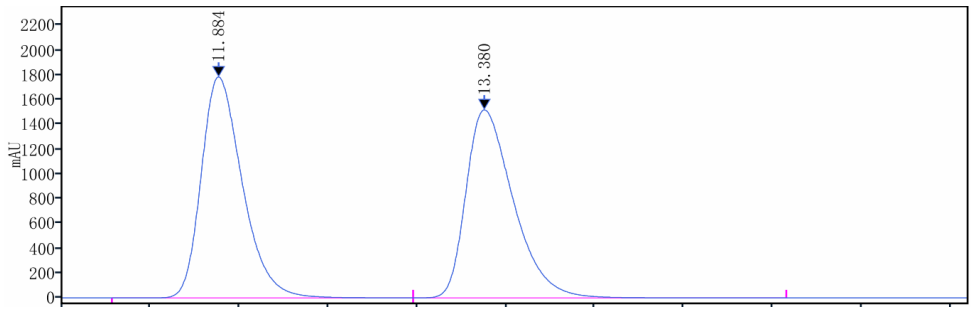
74% yield (20.3 mg), 95.5:4.5 er; Colorless oil; R_f = 0.4 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -5 (c = 0.124, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 – 7.68 (m, 2H), 7.41 (dd, *J* = 8.7, 7.3 Hz, 2H), 7.17 – 7.15 (m, 1H), 4.08 (t, *J* = 6.7 Hz, 2H), 3.90 – 3.82 (m, 2H), 2.79 (d, *J* = 15.9 Hz, 1H), 2.65 (d, *J* = 16.0 Hz, 1H), 2.45 – 2.35 (m 1H), 2.11 – 2.03 (m, 1H), 1.67 (q, *J* = 7.1 Hz, 2H), 1.34 (s, 3H), 0.96 (t, *J* = 7.4 Hz, 3H) ppm.

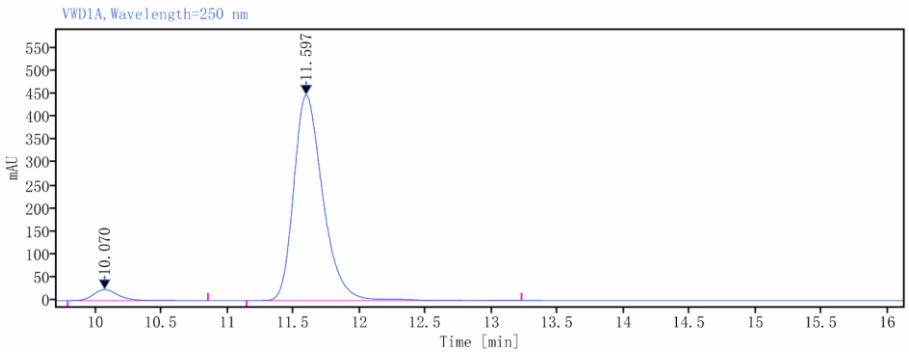
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.1, 171.4, 139.6, 128.8, 124.5, 119.8, 66.2, 45.2, 43.8, 41.8, 30.4, 23.2, 22.0, 10.4 ppm.

HRMS (ESI-TOF) calcd for $[C_{16}H_{21}O_3H]^+$ 276.1594, found 276.1596.

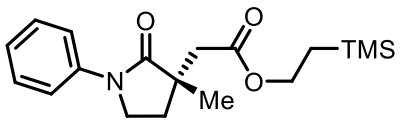
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} =10.1 min (minor), t_{R2} = 11.6 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
11.884	BB	1.6957	28721.7668	1784.7345	50.5047
13.380	BB	2.1010	28147.7207	1519.1508	49.4953



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.070	MM m	0.1980	310.0876	23.9581	4.3470
11.597	MM m	0.2342	6823.2785	446.6558	95.6530



2-(trimethylsilyl)ethyl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7i)

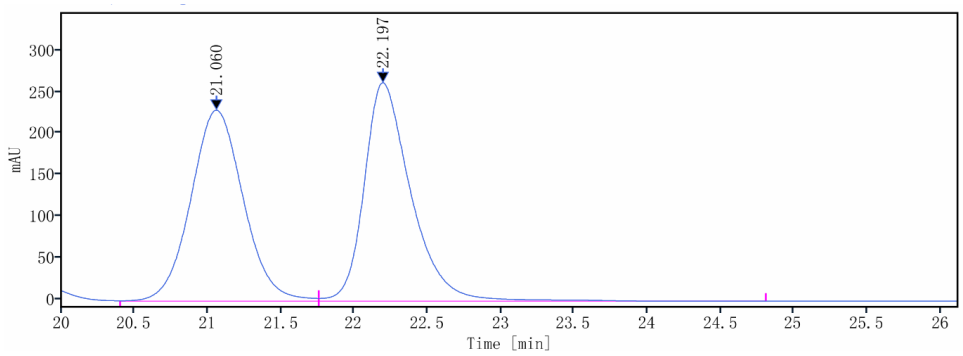
68% yield (22.6 mg), 95.5:4.5 er; Colorless oil; R_f = 0.6 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -48 (c = 0.044, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (dt, *J* = 8.0, 1.1 Hz, 2H), 7.47 – 7.35 (m, 2H), 7.24 – 7.12 (m, 1H), 4.23 – 4.17 (m, 2H), 3.90 – 3.79 (m, 2H), 2.73 (s, 1H), 2.62 (d, *J* = 16.0 Hz, 1H), 2.45 – 2.40 (m, 1H), 2.08 (ddd, *J* = 12.8, 7.4, 3.9 Hz, 1H), 1.34 (s, 3H), 1.11 – 0.89 (m, 2H), 0.07 (s, 9H) ppm.

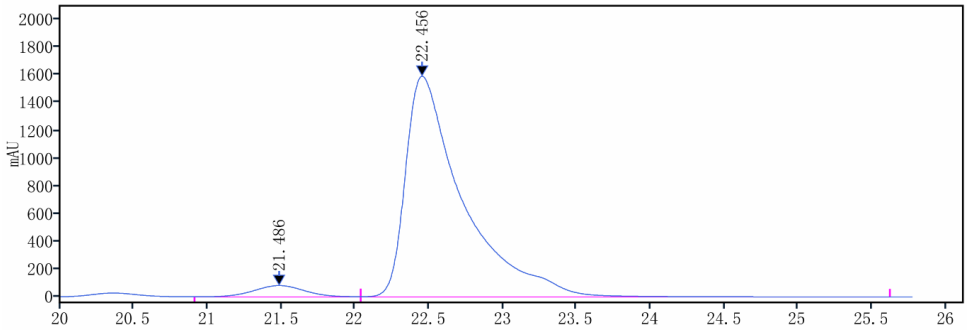
^{13}C NMR (75 MHz, $CDCl_3$) δ 178.6, 173.0, 141.1, 130.3, 126.0, 121.3, 64.3, 46.7, 45.3, 43.4, 31.9, 24.7, 18.9, 0.0 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{27}NO_3Si+H]^+$ 334.1833, found 334.1837.

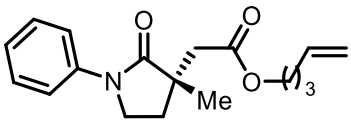
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 21.5 min (minor), t_{R2} = 22.5 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.060	VV	1.3551	5721.1528	229.7883	49.4737
22.197	VB	3.0520	5842.8646	262.8411	50.5263



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
21.486	VV	1.1267	1977.6051	81.7599	4.3957
22.456	VBA	3.5843	43011.5751	1590.9596	95.6043



pent-4-en-1-yl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7j)

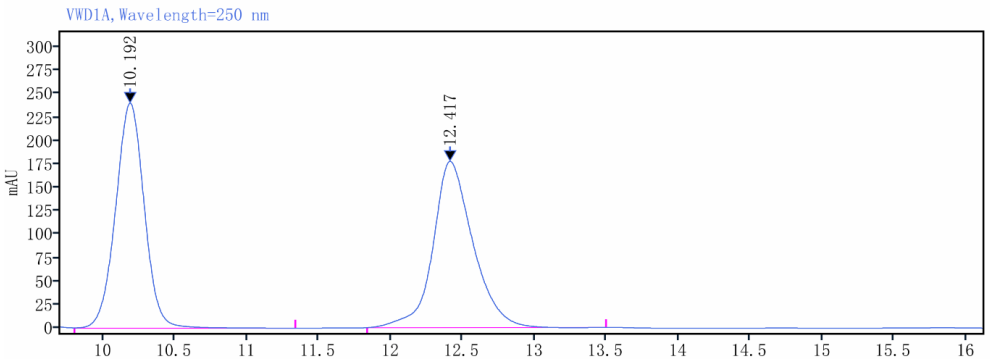
74% yield (20.3 mg), 96:4 er; Colorless oil; R_f = 0.4 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -45 (c = 0.04, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.72 – 7.68 (m, 2H), 7.44 – 7.38 (m, 2H), 7.31 – 7.19 (m, 1H), 5.81 (ddt, *J* = 16.9, 10.2, 6.6 Hz, 1H), 5.17 – 4.97 (m, 1H), 4.13 (t, *J* = 6.6 Hz, 2H), 3.99 – 3.74 (m, 2H), 2.79 (d, *J* = 15.9 Hz, 1H), 2.66 (d, *J* = 15.9 Hz, 1H), 2.41 (dt, *J* = 12.9, 8.4 Hz, 1H), 2.23 – 2.00 (m, 2H), 1.76 (t, *J* = 7.4 Hz, 2H), 1.34 (s, 3H) ppm.

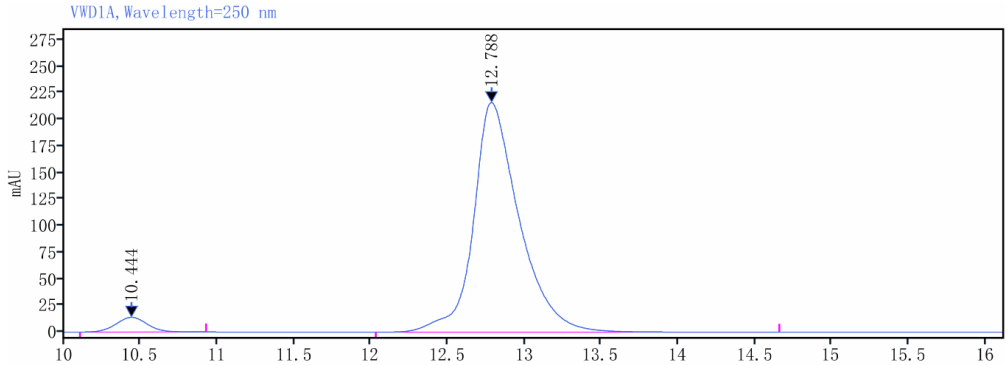
^{13}C NMR (75 MHz, $CDCl_3$) δ 177.0, 171.3, 139.6, 137.4, 128.8, 124.5, 119.8, 115.4, 64.0, 54.4, 45.2, 43.8, 41.8, 30.4, 27.7, 23.2 ppm.

HRMS (ESI-TOF) calcd for $[C_{18}H_{23}NO_3+H]^+$ 302.1751, found 302.1750.

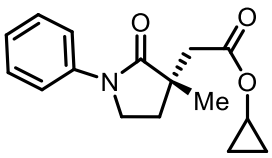
HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 90/10, flow rate = 1.0 mL/min, uv-vis λ = 250 nm, t_{R1} = 10.4 min (minor), t_{R2} = 12.8 min (major).



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.192	VB	1.5362	3327.0615	240.0845	49.2649
12.417	MM m	0.2843	3426.3470	177.4396	50.7351



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
10.444	MM m	0.2176	195.4469	13.8571	4.1790
12.788	BB	2.6283	4481.4858	216.1413	95.8210



cyclopropyl (S)-2-(3-methyl-2-oxo-1-phenylpyrrolidin-3-yl)acetate (7k)

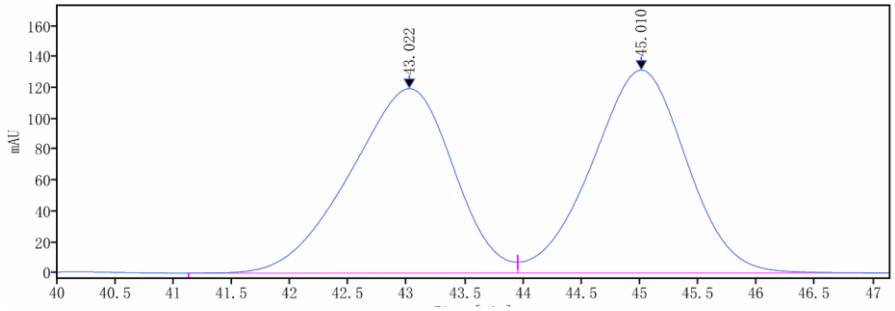
75% yield (20.5 mg), 95.5:4.5 er; Colorless oil; R_f = 0.6 (PE/EA = 10/1); $[\alpha]_D^{20}$ = -23 (c = 0.048, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 – 7.61 (m, 2H), 7.37 – 7.32 (m, 2H), 7.15 – 7.10 (m, 1H), 4.11 (dt, J = 6.4, 2.5 Hz, 1H), 3.87 – 3.70 (m, 2H), 2.68 (dd, J = 16.0, 1.3 Hz, 1H), 2.55 (dd, J = 16.0, 1.2 Hz, 1H), 2.33 (dt, J = 12.7, 8.4 Hz, 1H), 2.02 (m, 1H), 1.27 (s, 3H). 0.66 (dt, *J* = 5.3, 3.3 Hz, 4H) ppm.

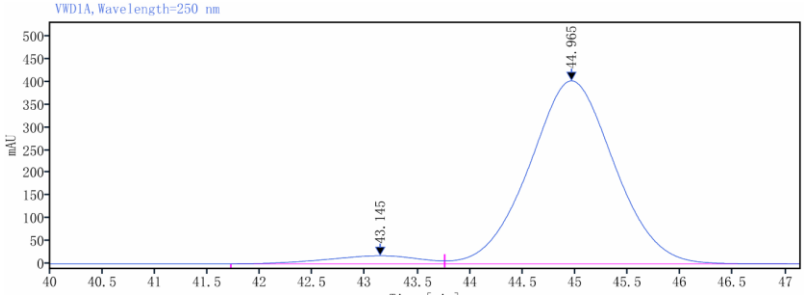
^{13}C NMR (75 MHz, $CDCl_3$) δ 176.8, 172.1, 139.5, 128.8, 124.5, 119.8, 48.9, 45.1, 43.7, 41.7, 30.3, 23.1, 5.0, 4.9 ppm.

HRMS (ESI-TOF) calcd for $[C_{16}H_{19}NO_3+H]^+$ 274.1438, found 274.1438.

HPLC: Daicel Chiralcel AD-H, *n*-hexane/isopropanol 95/5, flow rate = 0.5mL/min, uv-vis λ = 250 nm, t_{R1} = 43.1 min (minor), t_{R2} = 45.0 min (major).



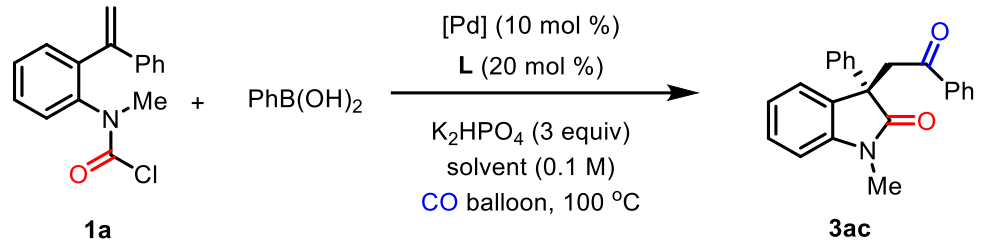
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
43.022	BV	2.8209	7367.7695	119.4999	49.8014
45.010	VB	3.3424	7426.5260	131.4646	50.1986



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
43.145	MM m	0.9056	1082.4778	17.9247	4.5669
44.965	VB	4.3768	22620.0560	401.8514	95.4331

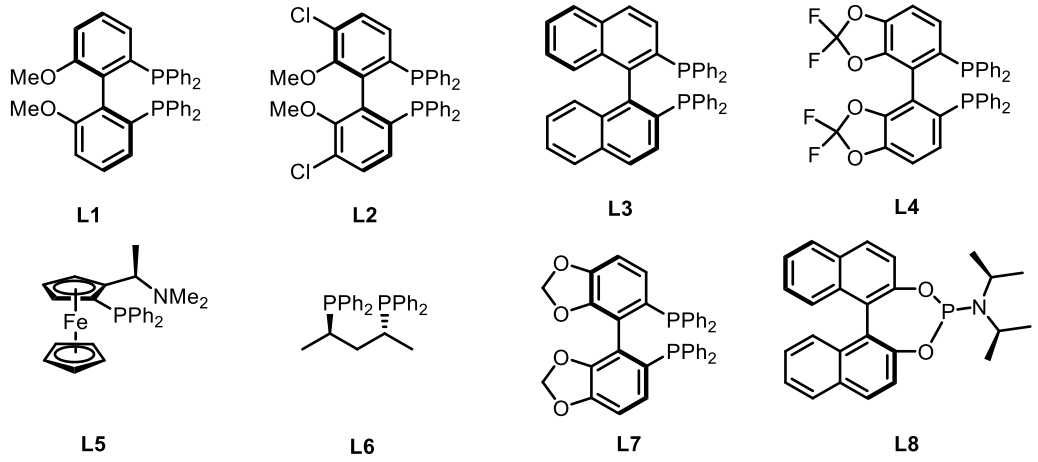
6. Further Study of the Reaction

Table S4 Condition Screening for phenylboronic acid

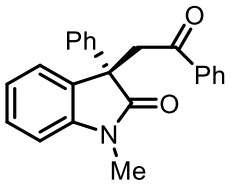


1a **3ac**

Entry	[Pd]	Ligand	Solvent	Yield of **3ac** %	er of **3ac**
1	$Pd(OAc)_2$	**L1**	PhCl	trace	-
2	$Pd(OAc)_2$	**L2**	PhCl	n.d.	-
3	$Pd(OAc)_2$	**L3**	PhCl	n.d.	-
4	$Pd(OAc)_2$	**L4**	PhCl	n.d.	-
5	$Pd(OAc)_2$	**L5**	PhCl	42%	67.5:32.5
6	$Pd(OAc)_2$	**L6**	PhCl	trace	-
7	$Pd(OAc)_2$	**L7**	PhCl	38	70.5:29.5
8	$Pd(OAc)_2$	**L8**	PhCl	65	79:21
9	**$Pd(OAc)_2$**	**L5**	**THF**	**55**	**91:9**
10	$Pd(OAc)_2$	**L5**	EA	7	70:30
11	$Pd(OAc)_2$	**L5**	PhMe	trace	76.5:23.5
12	$Pd(OAc)_2$	**L5**	MeCN	52	75:25
13	$Pd(OAc)_2$	**L5**	Acetone	43	86.5:13.5
14	$Pd(dba)_2$	**L5**	THF	56	67.5:32.5
15	$Pd_2(dba)_3$	**L5**	THF	49	66.5:33.5
16	$Pd(dba)_2$	**L5**	THF	52	70:40



a) Reaction conditions: **1a** (0.1 mmol), $PhB(OH)_2$ (0.3 mmol), [Pd] (10 mol %), **L** (20 mol %), K_2HPO_4 (0.3 mmol) in 1.0 mL solvent, 80 °C (oil bath temperature), 30 h, CO balloon. b) Isolated yields are given. c) Determined by HPLC analysis. n.d. = Not determined.



(S)-1-methyl-3-(2-oxo-2-phenylethyl)-3-phenylindolin-2-one (3ab)

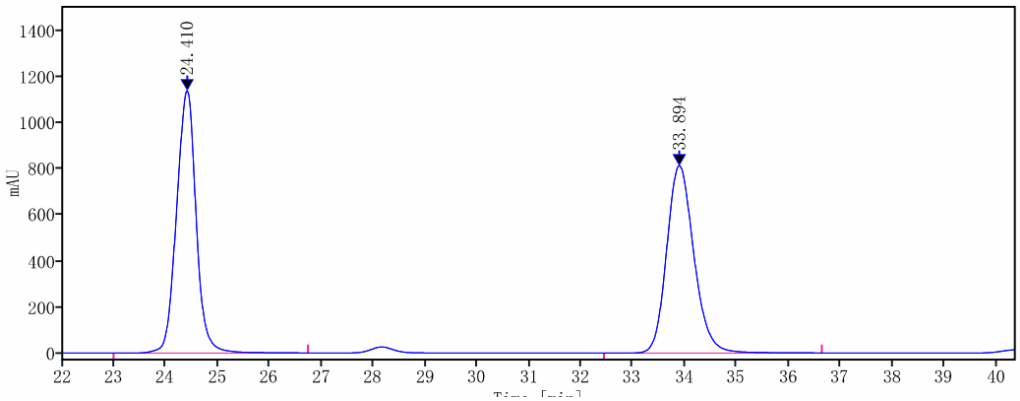
55% yield (18.8 mg); 91:9 er; White solid; m.p. 102 – 104 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -53 (c = 0.1, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.90 – 7.82 (m, 2H), 7.55 – 7.27 (m, 10H), 7.07 (td, *J* = 7.5, 1.0 Hz, 1H), 6.97 (dd, *J* = 7.7, 1.0 Hz, 1H), 4.29 – 3.94 (m, 2H), 3.32 (s, 3H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 195.8, 178.6, 144.8, 139.6, 136.4, 133.3, 131.6, 128.7, 128.6, 128.4, 128.0, 127.6, 126.8, 124.1, 122.2, 108.5, 53.1, 47.0, 26.8 ppm.

HRMS (ESI-TOF) calcd for $[C_{23}H_{19}NO_2+H]^+$ 342.1489, found 342.1492.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 70/30, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 25.1 min (major), t_{R2} = 35.4 min (minor).



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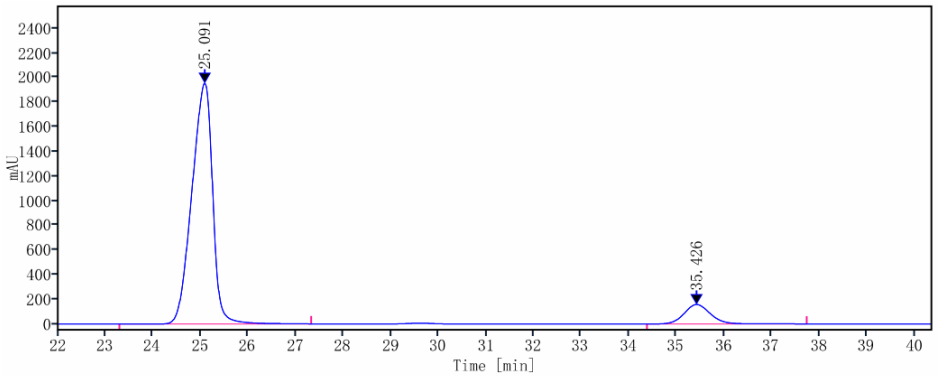

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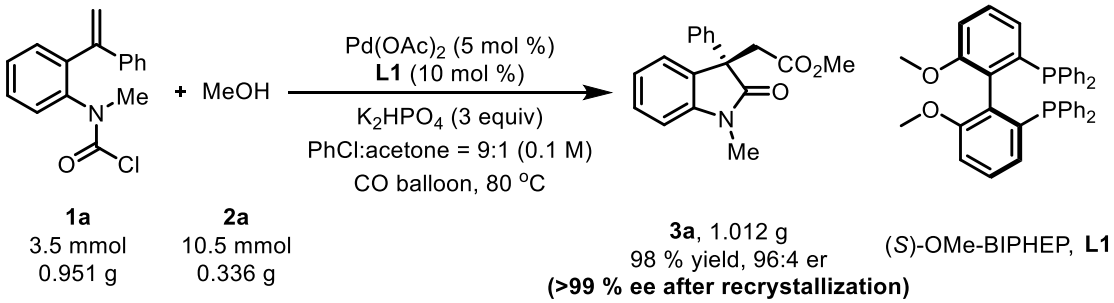
35.426	MM m	0.5896	6089.2304	158.0127	9.3486



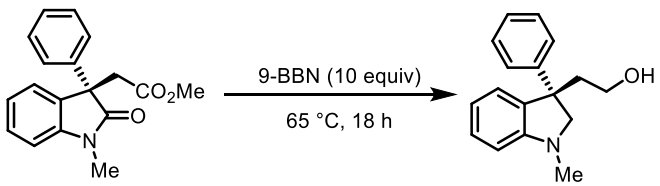
1a
3.5 mmol
0.951 g

2a
10.5 mmol
0.336 g

3a, 1.012 g
98 % yield, 96:4 er
(>99 % ee after recrystallization)

(*S*)-OMe-BIPHEP, **L1**

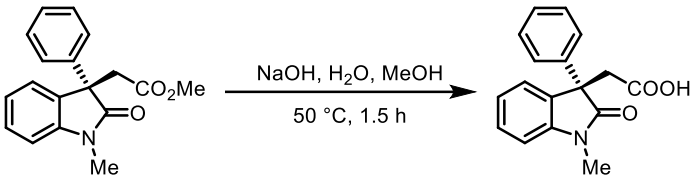
An oven-dried 350 mL Schlenk tube was charged with the substrate **1a** (0.951 g, 3.5 mmol), $Pd(OAc)_2$ (39.3 mg, 5 mol %), **L1** (203.9 mg, 10 mol %), and K_2HPO_4 (1.829 g, 10.5 mmol). The vial is thoroughly flushed with CO, and MeOH (424 μL, 10.5 mmol), as well as PhCl/acetone (9/1, 35 mL) was added under balloon pressure of CO. Then the reaction mixture was stirred at room temperature for 30 seconds, then raise to 80 °C (oil bath temperature) for 36 h with stirring. After the reaction vessel was cooled to room temperature, the reaction mixture was diluted with EA (50 mL) and filtered through a plug of celite. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 5/1) to afford the desired product **3a** in 98% yield (1.012 g).



3a **8**

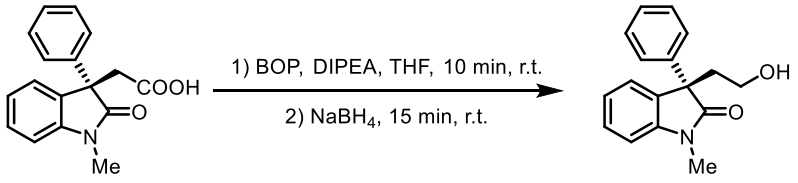
An oven-dried 10 mL Schlenk tube equipped with a magnetic stirring bar was charged with **3a** (59.1 mg, 0.2 mmol) and 9-BBN (4 mL, 0.5 M in THF, 2 mmol). The tube was evacuated and back-filled with argon three times. The tube sealed tightly with a stopper,

and the reaction mixture was heated at 65 ºC (oil bath temperature) for 18 h with stirring. After cooling the tube, the mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the desired product **8** in 95% yield (48.1 mg).



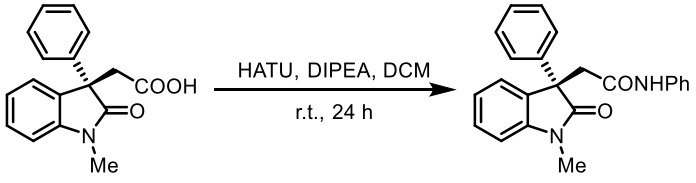
3a **9**

To a solution of **3a** (59.1 mg, 0.2 mmol) in 0.75 mL of MeOH, was added a solution of NaOH (40 mg, 1 mmol) in water (0.25 mL). The mixture was stirred at 50 ºC (oil bath temperature) for 1.5 h. After cooling to 0 ºC, the mixture was treated with an aqueous solution of 1 N HCl to pH = 1 and extracted with EA (3×10 mL). The combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, filtrated, and evaporated to dryness under reduced pressure. The resultant crude product **9** was purified by flash column chromatography on silica gel using PE/EA 1:2, delivering product in 98% yield (54.9 mg).



9 **10**

To a solution of **9** (56.3 mg, 0.2 mmol) and DIPEA (42 μL, 0.24 mmol) in THF (1 mL), was added the Castros reagent (BOP) (106.2 mg, 0.24 mmol). The solution was stirred at r.t. for 10 min. Then $NaBH_4$ (3×7.6 mg, 3×0.2 mmol) was added every 5 min, the TLC method to detect the response process. Then the reaction solution was neutralized with 1 N HCl, and water was added to the reaction solution followed by extraction with chloroform. The obtained chloroform layer was dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The resultant crude product was purified by flash column chromatography on silica gel using PE/EA = 2:1 to give **10** in 85% yield (45.2 mg).



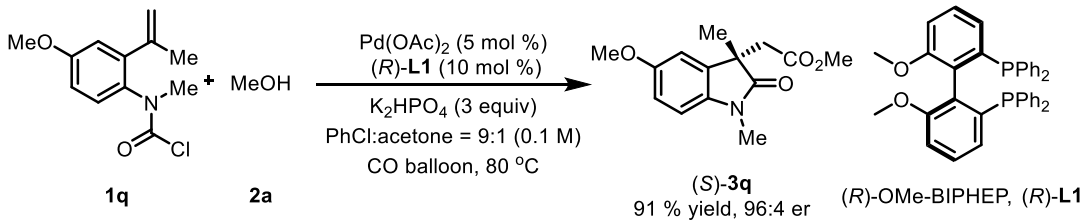
9 **11**

To a solution of **9** (56.3 mg, 0.2 mmol) and DIPEA (70 μL, 0.4 mmol) in CH_2Cl_2 (2 mL), was added HATU (91.3 mg, 0.24 mmol) at room temperature. The resulting

solution was stirred for 30 min. Then aniline (20 μL, 0.22 mmol) was added and the reaction mixture was stirred for another 24 h. The mixture was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 5/1) to afford the desired product **11** in 82% yield (58.2 mg).

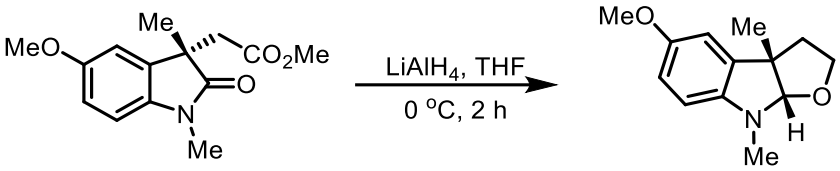
9 **12**

To a solution of **9** (56.3 mg, 0.2 mmol) and $SOCl_2$ (0.1 mL, 1.38 mmol) in CH_2Cl_2 (2 mL), was added DMF (1 drop) at room temperature. Then the reaction mixture was allowed to 45 °C (oil bath temperature) for 1 h. The solvent was removed under reduced pressure; The another dichloromethane (8 mL) and aluminum chloride ($AlCl_3$; 266.7 mg, 2 mmol) were added to the resulting mixture at 0 °C, followed by refluxing under heating for 6 h. After the completion of the reaction, the mixture was treated with ice water and then extracted twice with 10 mL of CH_2Cl_2. The combined organic phase was washed with water (10 mL) and saturated brine (10 mL), dried with Na_2SO_4 and concentrated under reduced pressure to give a crude product. The crude product was purified by flash column chromatography on silica gel (PE/EA = 6/1) to give **12** in 90% yield (47.6 mg).



1q **2a** (*S*)-**3q** 91 % yield, 96:4 er (*R*)-OMe-BIPHEP, (*R*)-**L1**

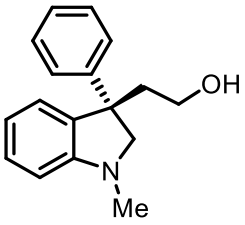
An oven-dried 10 mL Schlenk tube was charged with the substrate **1q** (0.024 g, 0.1 mmol), $Pd(OAc)_2$ (1.1 mg, 5 mol %), (*R*)-**L1** (5.8 mg, 10 mol %), and K_2HPO_4 (52.3 mg, 0.3 mmol). The vial is thoroughly flushed with CO, and MeOH (12 μL, 0.3 mmol), as well as PhCl/acetone (9/1, 1 mL) was added under balloon pressure of CO. Then the reaction mixture was stirred at room temperature for 30 seconds, then raise to 80 °C (oil bath temperature) for 30 h with stirring. After the reaction vessel was cooled to room temperature, the reaction mixture was diluted with EA (10 mL) and filtered through a plug of celite. The solution was concentrated under reduced pressure and purified by flash column chromatography on silica gel (PE/EA = 4/1) to afford the desired product (*S*)-**3q** in 91% yield (24.0 mg).



(*S*)-**3q**, 96:4 er

13, 90% yield, 96:4 er

To a solution of (*S*)-**3q** (26.3 mg, 0.1 mmol) in THF (2 mL), was added $LiAlH_4$ (11.4 mg, 0.3 mmol) at 0 °C. The resulting solution was stirred for 2 h at 0 °C. Then the reaction solution was neutralized with H_2O, and then extracted twice with 10 mL of EA. The combined organic phase was washed with saturated brine (10 mL), dried over Na_2SO_4 and concentrated to give a crude product. The crude product was purified by flash column chromatography on silica gel (PE/EA = 10/1) to give **13** in 90% yield (40.1 mg).



(S)-2-(1-methyl-3-phenylindolin-3-yl)ethan-1-ol (8)

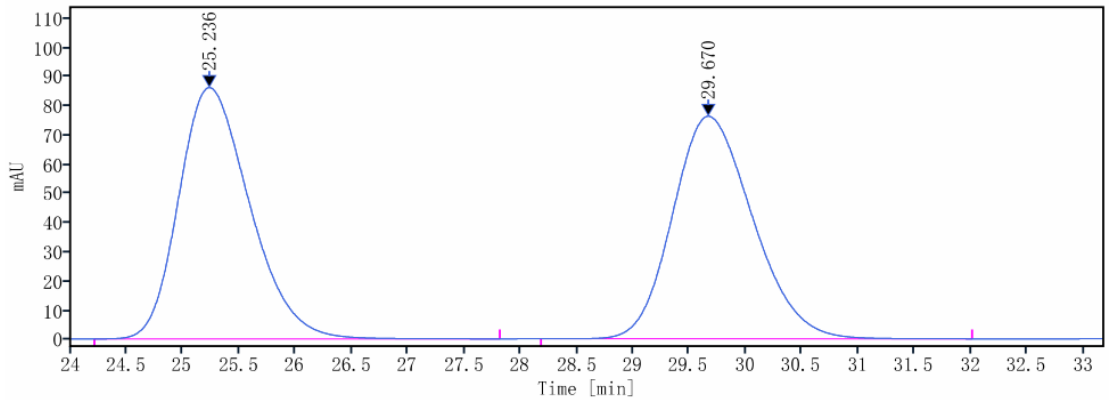
95% yield (48.1mg); > 99% ee; Colorless oil; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -12 (c = 0.23, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.40 (m, 2H), 7.31 (t, *J* = 7.5 Hz, 2H), 7.24 – 7.17 (m, 2H), 6.98 (d, *J* = 7.3 Hz, 1H), 6.85 – 6.80 (m, 1H), 6.67 (d, *J* = 7.9 Hz, 1H), 3.63 – 3.56 (m, 2H), 3.35 – 3.27 (m, 2H), 3.11 (br, 1H), 2.78 (s, 3H), 2.64 – 2.54 (m, 1H), 2.15 (dt, *J* = 13.9, 4.8 Hz, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 153.0, 146.3, 134.9, 128.4, 128.2, 126.9, 126.5, 124.8, 119.5, 109.1, 70.8, 60.3, 51.5, 42.4, 36.5 ppm.

HRMS (ESI-TOF) calcd for $[C_{17}H_{19}NO+H]^+$ 254.1545, found 254.1543.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 95/5, flow rate = 1 mL/min, uv-vis λ = 250 nm, t_{R1} = 25.3 min (major), t_{R2} =29.7 min (minor).



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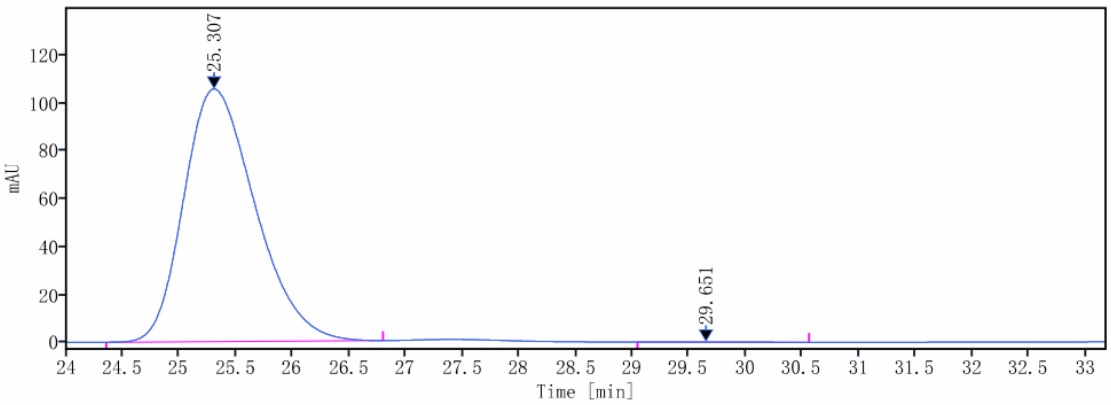

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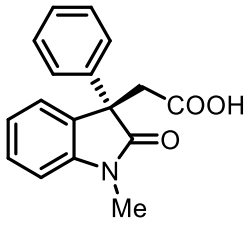
29.651	MM m	0.4886	3.6193	0.0873	0.0781

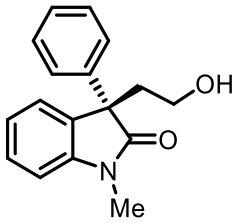


(S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)acetic acid (9)

98% yield (54.9 mg); White solid; m.p. 164 – 166 °C; R_f = 0.5 (EA); $[\alpha]_D^{20}$ = -117 (c = 0.22, EA).

^{1}H NMR (300 MHz, DMSO-d_6) δ 12.18 (s, 1H), 7.40 – 7.20 (m, 7H), 7.08 – 7.03 (m, 2H), 3.36 (s, 2H), 3.14 (s, 3H) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ 178.0, 171.3, 144.8, 140.5, 132.4, 129.0, 128.7, 127.7, 126.8, 124.5, 122.5, 109.0, 53.4, 41.4, 26.9 ppm.



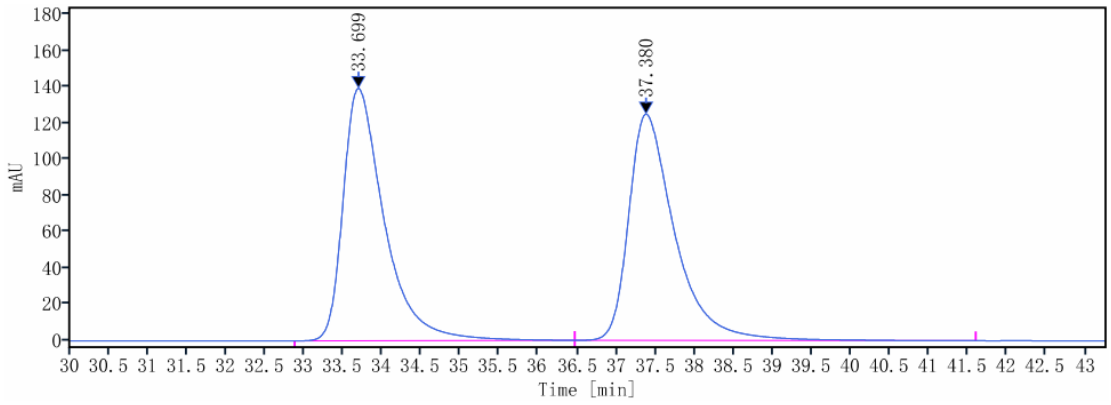
(S)-3-(2-hydroxyethyl)-1-methyl-3-phenylindolin-2-one (10)

85% yield (45.2 mg); > 99% ee; White solid; m.p. 80 – 82 °C; R_f = 0.1 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -42 (c = 0.18, EA).

^{1}H NMR (300 MHz, DMSO-d_6) δ 7.36 – 7.21 (m, 7H), 7.09 (t, J = 6.9 Hz, 2H), 4.48 (t, J = 5.2 Hz, 1H), 3.15 – 3.01 (m, 5H), 2.53 – 2.35 (m, 2H) ppm.

^{13}C NMR (75 MHz, DMSO-d_6) δ 178.0, 144.0, 141.2, 132.2, 128.9, 128.6, 127.5, 126.9, 124.8, 122.8, 109.2, 57.7, 54.6, 39.8, 26.6 ppm.

HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 90/10, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 33.2 min (major), t_{R2} =37.6 min (minor).



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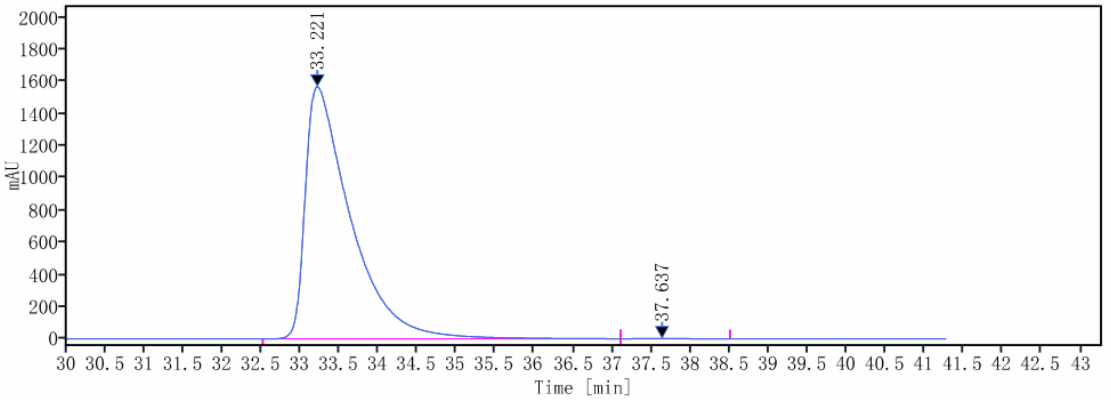

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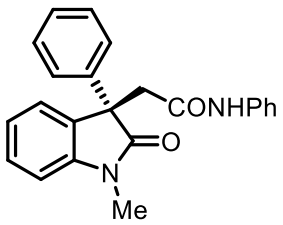


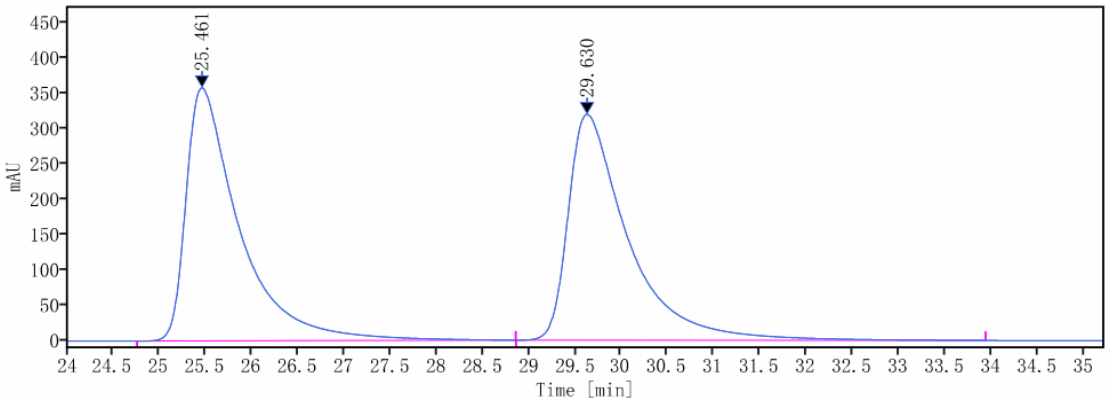
(S)-2-(1-methyl-2-oxo-3-phenylindolin-3-yl)-N-phenylacetamide (11)

82% yield (58.2 mg); > 99% ee; White solid; m.p. 176 – 178 °C; R_f = 0.3 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -48 (c = 0.26, EA).

^{1}H NMR (300 MHz, $CDCl_3$) δ 8.62 (s, 1H), 7.37 – 7.35 (m, 2H), 7.31 – 7.24 (m, 7H), 7.17 (t, *J* = 7.7 Hz, 2H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.99 (t, *J* = 7.3 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 3.45 (d, *J* = 15.3 Hz, 1H), 3.24 (s, 3H), δ 3.19 (d, J = 15.3 Hz, 1H) ppm.

^{13}C NMR (75 MHz, $CDCl_3$) δ 179.1, 167.1, 143.2, 139.1, 137.8, 131.8, 128.9, 128.8, 128.7, 127.8, 126.5, 124.6, 124.2, 123.2, 120.1, 108.8, 54.3, 45.0, 26.8 ppm.

HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 25.3 min (major), t_{R2} =30.0 min (minor).



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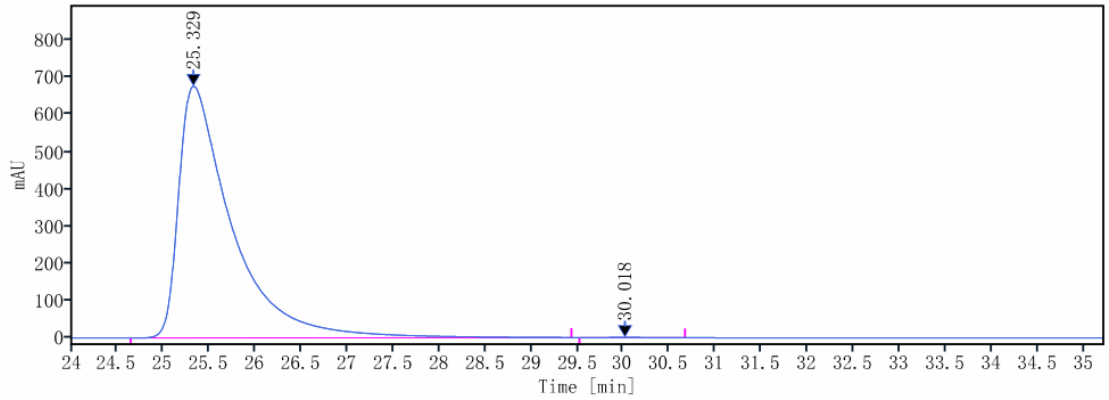
29.630	BM m	0.6542	14419.2541	319.6730	49.9990



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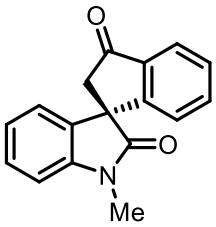
30.018	MM m	0.4474	14.6049	0.3913	0.0536



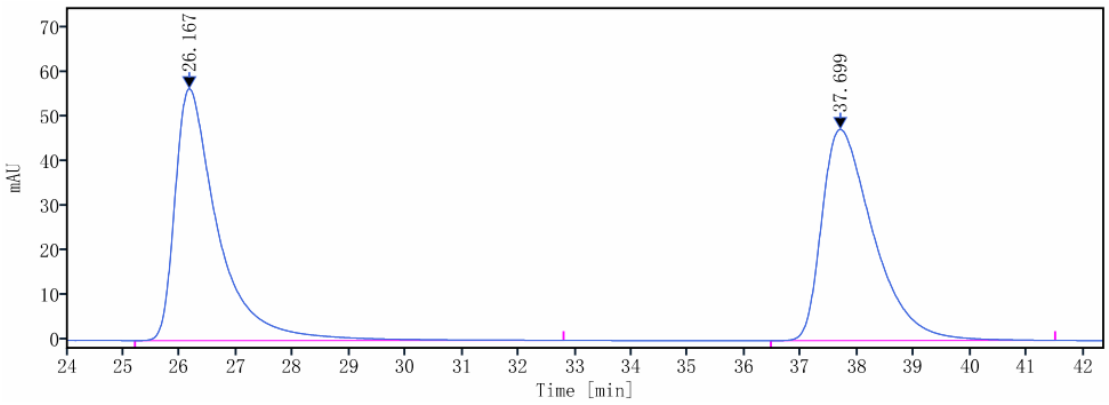
(S)-1'-methylspiro[indene-1,3'-indolin]-3(2H)-one (12)

90% yield (47.6 mg); >99% ee; White solid; m.p. 190 – 192 °C; R_f = 0.4 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -50 (c = 0.22, EA).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 7.4 Hz, 1H), 7.54 – 7.44 (m, 2H), 7.36 (t, *J* = 7.6 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 7.00 – 6.95 (m, 3H), 3.33 (s, 3H), 3.08 (dd, *J* = 131.5, 18.6 Hz, 2H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 203.5, 177.7, 154.5, 143.8, 136.5, 135.6, 132.6, 129.1, 129.0, 124.5, 124.1, 123.5, 123.3, 108.6, 54.2, 47.5, 26.9 ppm.

HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 80/20, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 25.9 min (major), t_{R2} =38.7 min (minor).



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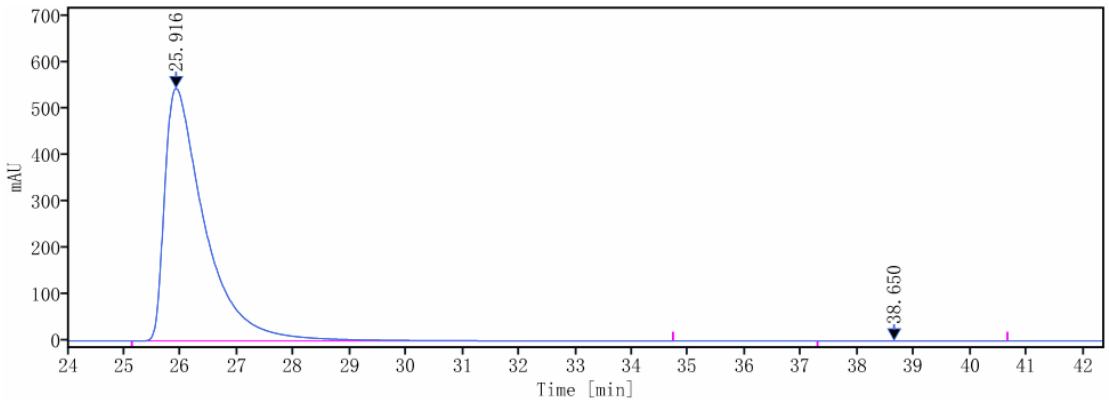
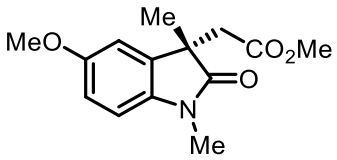
37.699	BM m	0.9556	3008.5141	47.4571	50.1379



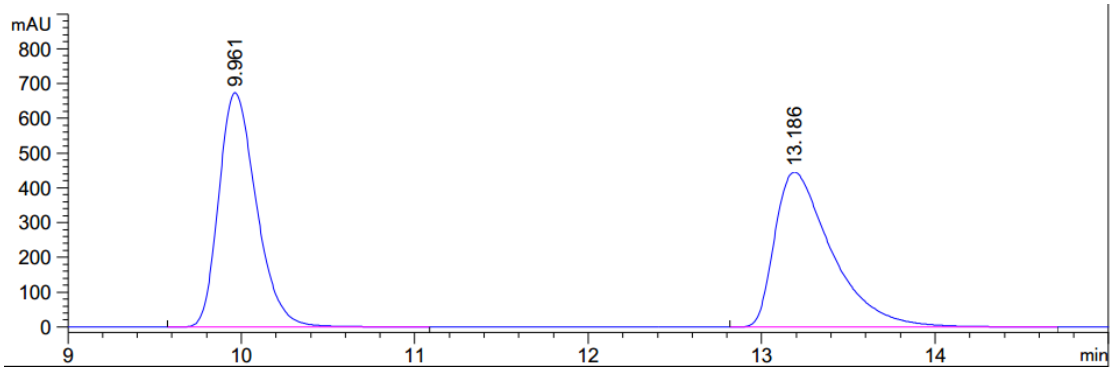
RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
25.916	BB	9.5983	27004.3693	545.5355	99.9703
38.650	MM m	0.7549	8.0223	0.1248	0.0297



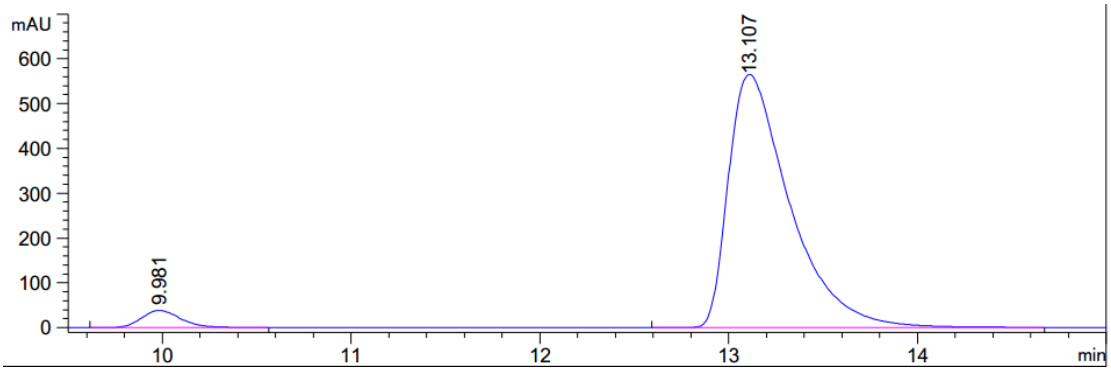
methyl (S)-2-(5-methoxy-1,3-dimethyl-2-oxoindolin-3-yl)acetate ((S)-3q)

91% yield (24.0 mg); 96:4 er; R_f = 0.1 (PE/EA = 4/1); $[\alpha]_D^{20}$ = -15 (c = 0.15, EA);

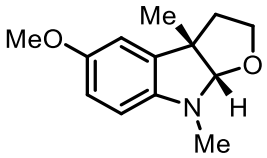
HPLC: Daicel Chiralcel OD-H, *n*-hexane/isopropanol 60/40, flow rate = 0.5 mL/min, uv-vis λ = 254 nm, t_{R1} = 10.0 min (minor), t_{R2} = 13.1 min (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.961	VB	0.2317	1.01562e4	674.32428	49.9545
2	13.186	BB	0.3425	1.01747e4	445.39276	50.0455



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.981	BB	0.2242	550.03180	38.14199	4.1340
2	13.107	BB	0.3393	1.27549e4	565.08789	95.8660



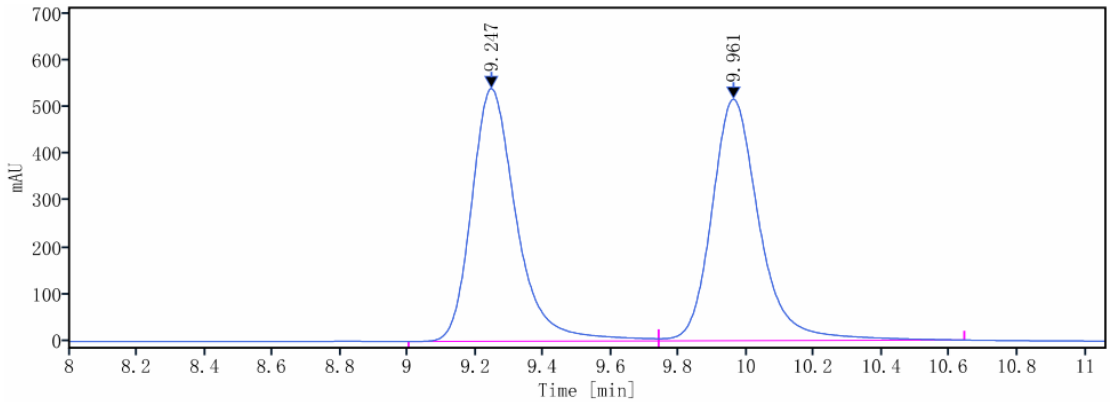
(3aS,8aS)-5-methoxy-3a,8-dimethyl-3,3a,8,8a-tetrahydro-2H-furo[2,3-b]indole (13)

91% yield (40.1 mg); 96:4 er; yellow oil; R_f = 0.8 (PE/EA = 4/1).

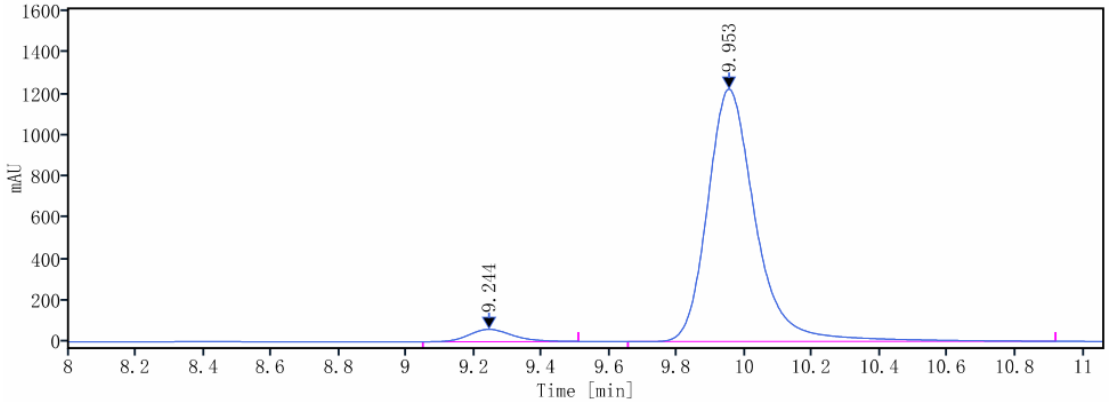
^{1}H NMR (400 MHz, $CDCl_3$) δ 6.70 – 6.64 (m, 2H), 6.29 (d, *J* = 8.2 Hz, 1H), 5.04 (s, 1H), 3.95 (ddd, *J* = 8.8, 7.1, 1.9 Hz, 1H), 3.75 (s, 3H), 3.47 (ddd, *J* = 10.8, 8.6, 5.5 Hz, 1H), 2.88 (s, 3H), 2.16 – 1.99 (m, 2H), 1.45 (s, 3H) ppm.

^{13}C NMR (101 MHz, $CDCl_3$) δ 152.7, 145.0, 136.0, 112.1, 110.5, 105.6, 105.3, 67.4, 56.1, 52.5, 41.5, 31.7, 24.5 ppm.

HPLC: Daicel Chiralcel IA-3, *n*-hexane/isopropanol 95/5, flow rate = 0.5 mL/min, uv-vis λ = 250 nm, t_{R1} = 9.2 min (minor), t_{R2} =10.0 min (major).

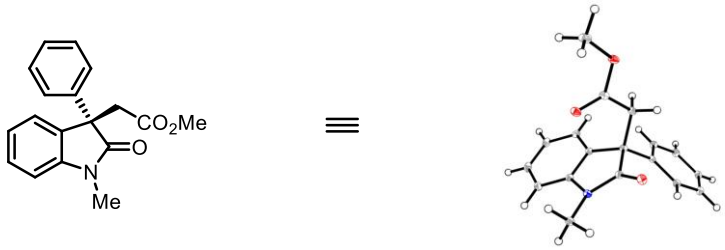


RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.247	VM m	0.1395	4967.2094	538.9905	49.7442
9.961	MM m	0.1486	5018.2917	515.1522	50.2558



RetTime[min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
9.244	MM m	0.1360	527.5895	59.7672	4.1955
9.953	MM m	0.1500	12047.5810	1222.3993	95.8045

7. Crystal Structure of 3a and 7d



3a CCDC 1999951

ORTEP plot of the crystal structure of 3a (50% ellipsoid probability)

X-ray crystallographic data of **3a**

CCDC number	1999951
Empirical formula	$C_{18}H_{17}NO_3$
Formula weight	295.32
Temperature	100 K
Wavelength	1.54178 Å
Space group	P 21 21 21
Unit cell dimensions	a=9.0567(8) Å =90º
	b=12.5609(12) Å =90º
	c=29.017(3) Å =90º
Volume	3300.9(5) Å
Z	8
F(000)	1248.0
Completeness to theta = 68.347°	1.75/0.99
Max. and min. transmission	0.753 and 0.665
R indices (all data)	R= 0.0279(5733) wR2(reflections)= 0.0731(6021)
S	1.046
ellipsoid contour % probability levels	50

7d CCDC 2047030

ORTEP plot of the crystal structure of 7d (50% ellipsoid probability)

X-ray crystallographic data of **7d**

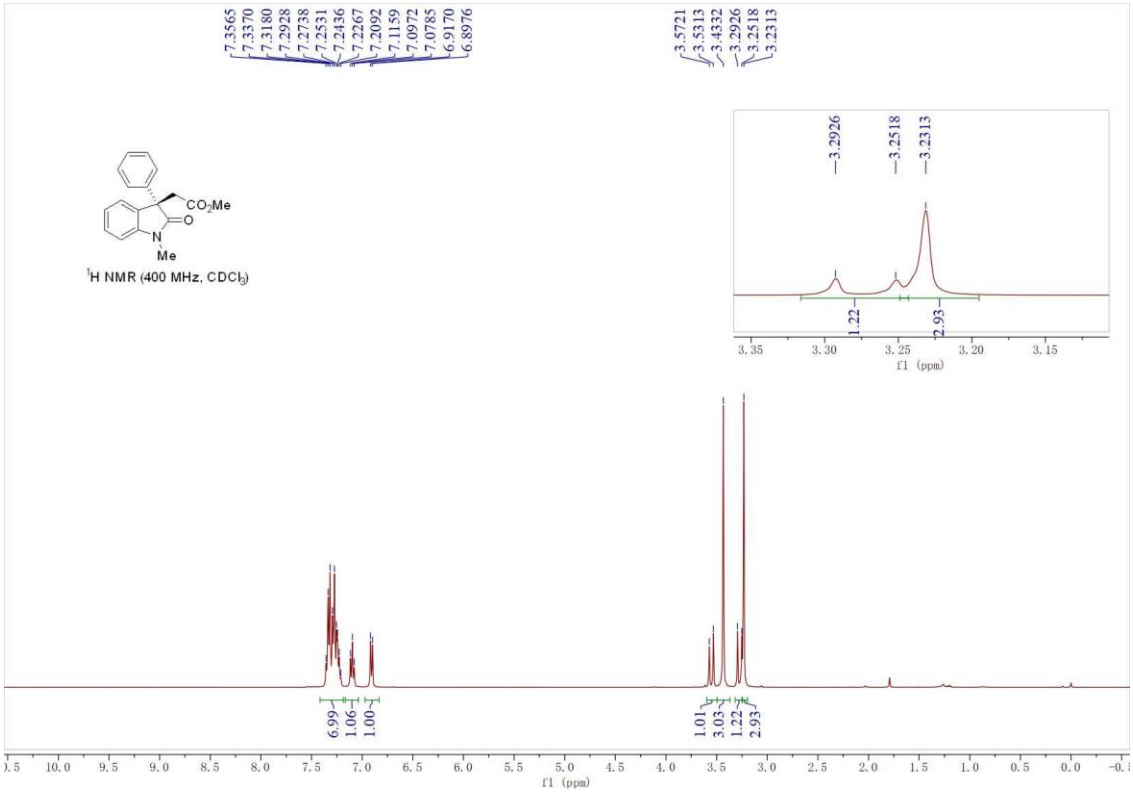
CCDC number	2047030		
Empirical formula	$C_{15}H_{16}F_3NO_3$		
Formula weight	315.29		
Temperature	150 K		
Wavelength	1.54178 Å		
Space group	P 21 21 21		
Unit cell dimensions	a=10.3719 (4)	Å	=90º
	b=19.0789 (8)	Å	=90º
	c=22.6118 (9)	Å	=90º
Volume	4474.5(3) Å		
Z	12		
F(000)	1968.0		
Completeness to theta = 68.347°	1.72/0.96		
Max. and min. transmission	0.959 and 0.904		
R indices (all data)	R= 0.0594(6458) wR2(reflections)= 0.1653(8774)		
S	1.059		
ellipsoid contour % probability levels	50		

8. References

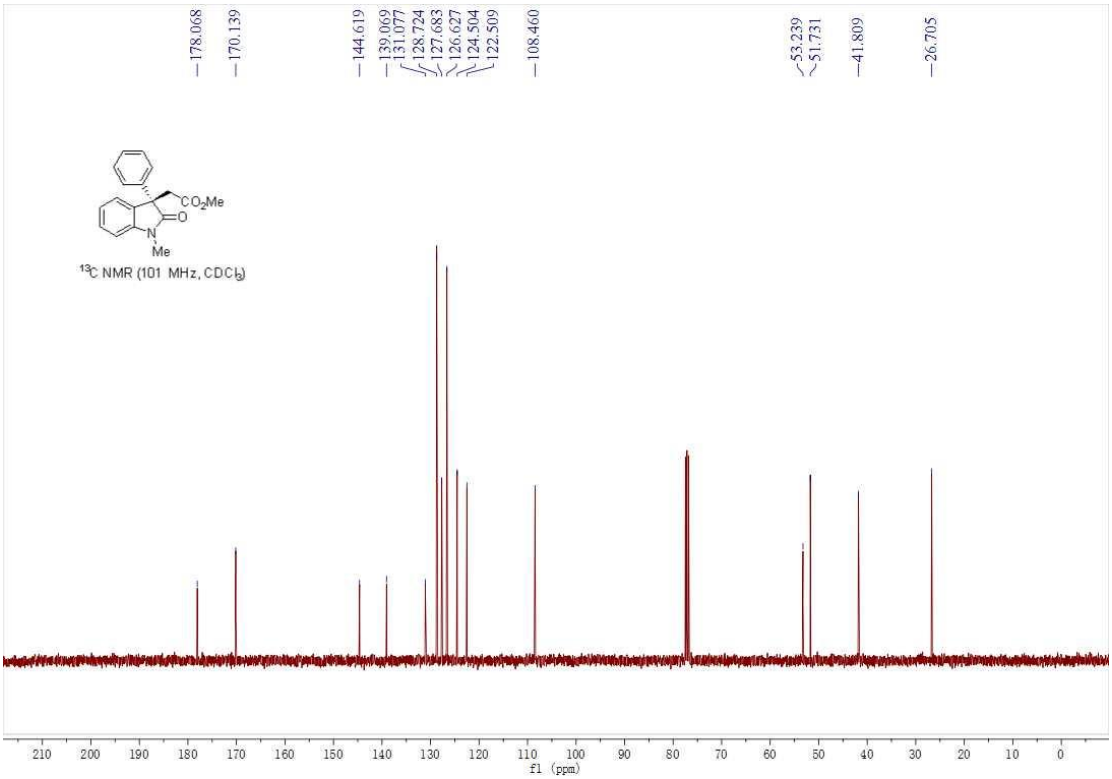
[1] A. Whyte, K. I. Burton, J. Zhang, M. Lautens, *Angew. Chem. Int. Ed.* **2018**, *57*, 13927-13930; *Angew. Chem.* **2018**, *130*, 14123-14126.
[2] P. Fan, Y. Lan, C. Zhang, C. Wang, *J. Am. Chem. Soc.* **2020**, *142*, 2180-2186.
[3] C. Miao, L. Jiang, L. Ren, Q. Xue, F. Yan, W. Shi, X. Li, J. Sheng, S. Kai, *Tetrahedron* **2019**, *75*, 2215-2228.
[4] C. Chen, J. Hu, J. Su, X. Tong, *Tetrahedron Lett.* **2014**, *55*, 3229-3231.

9. NMR Spectra

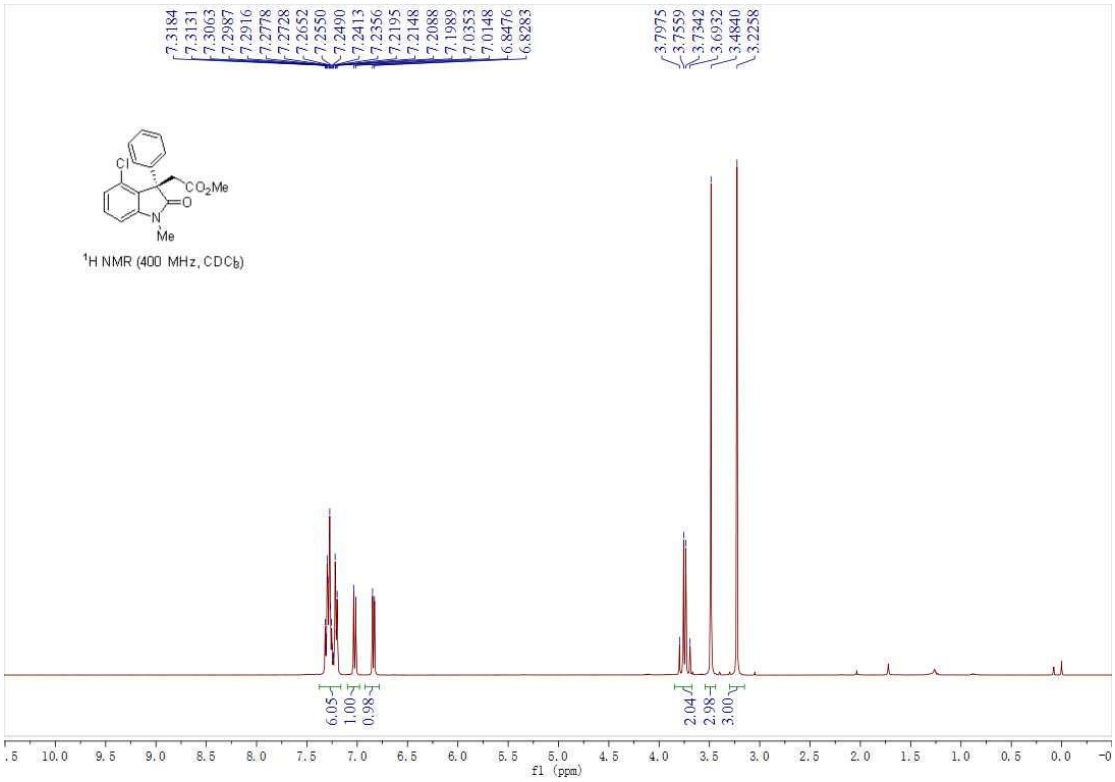
^{1}H NMR of **3a**



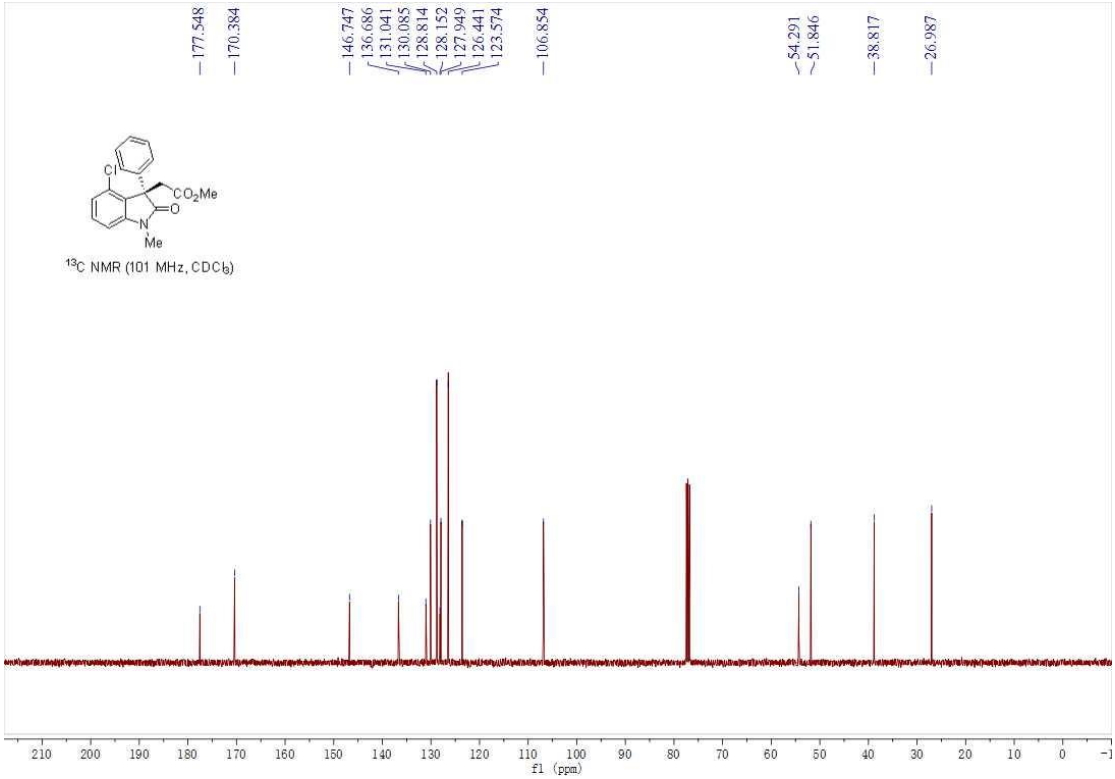
^{13}C NMR of **3a**



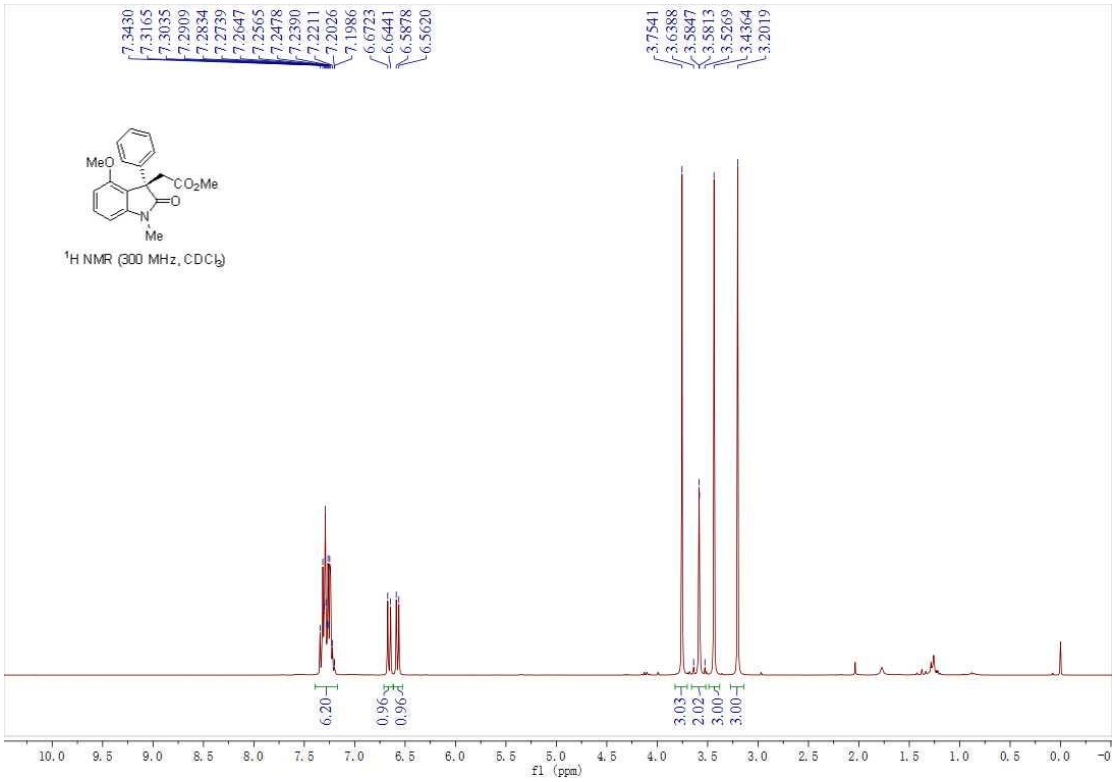
^{1}H NMR of **3b**



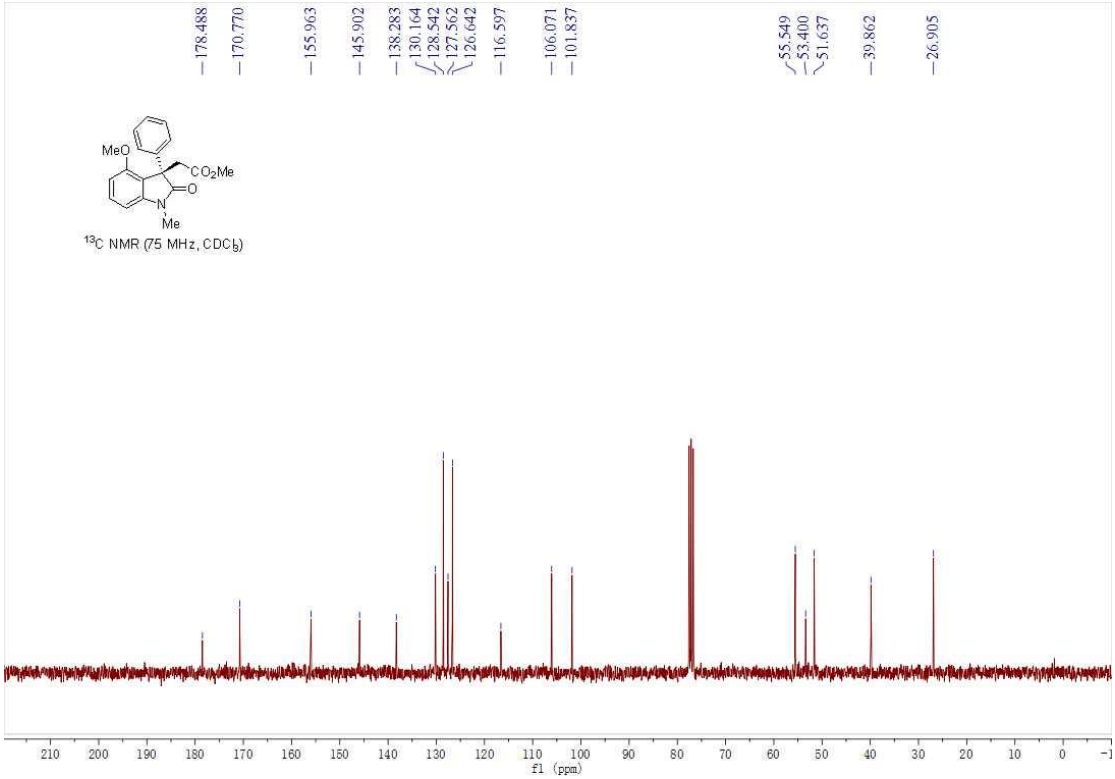
^{13}C NMR of **3b**



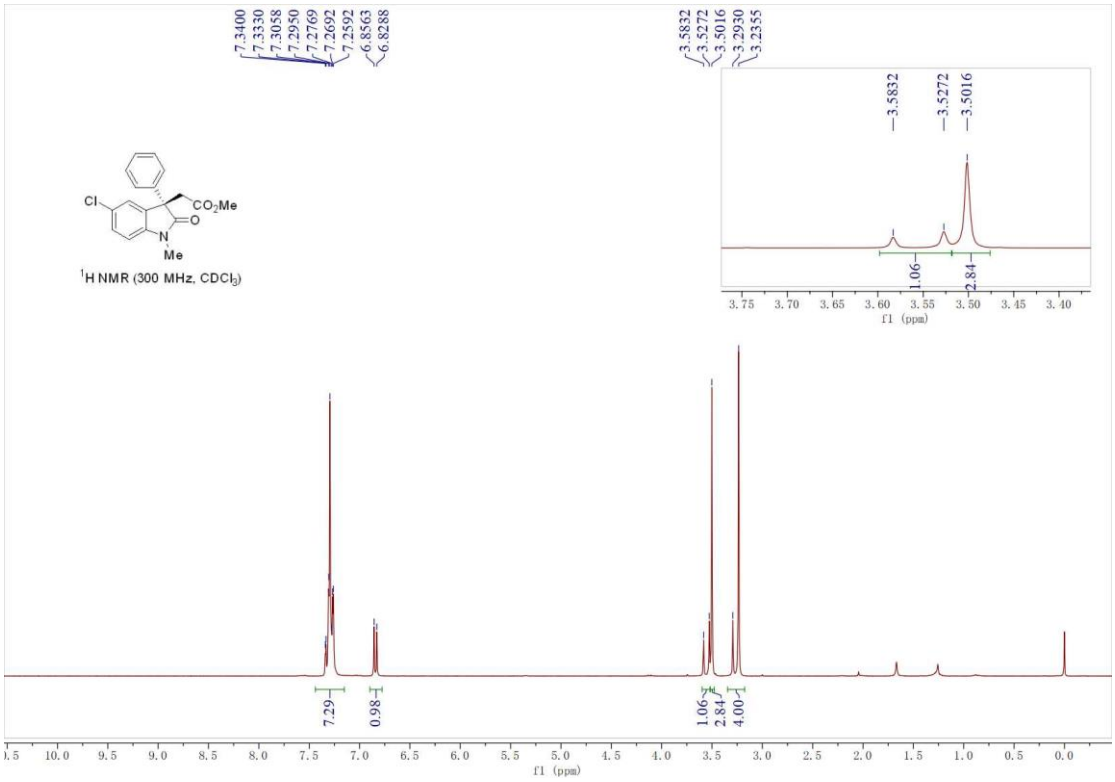
^{1}H NMR of **3c**



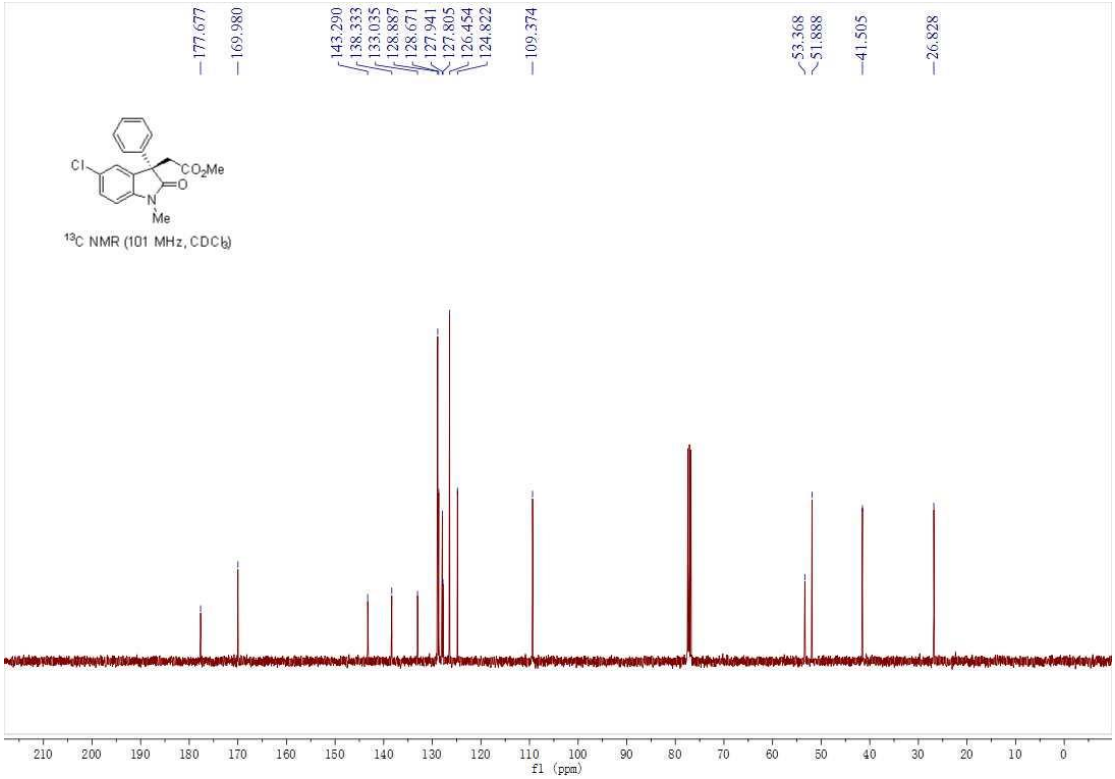
^{13}C NMR of **3c**



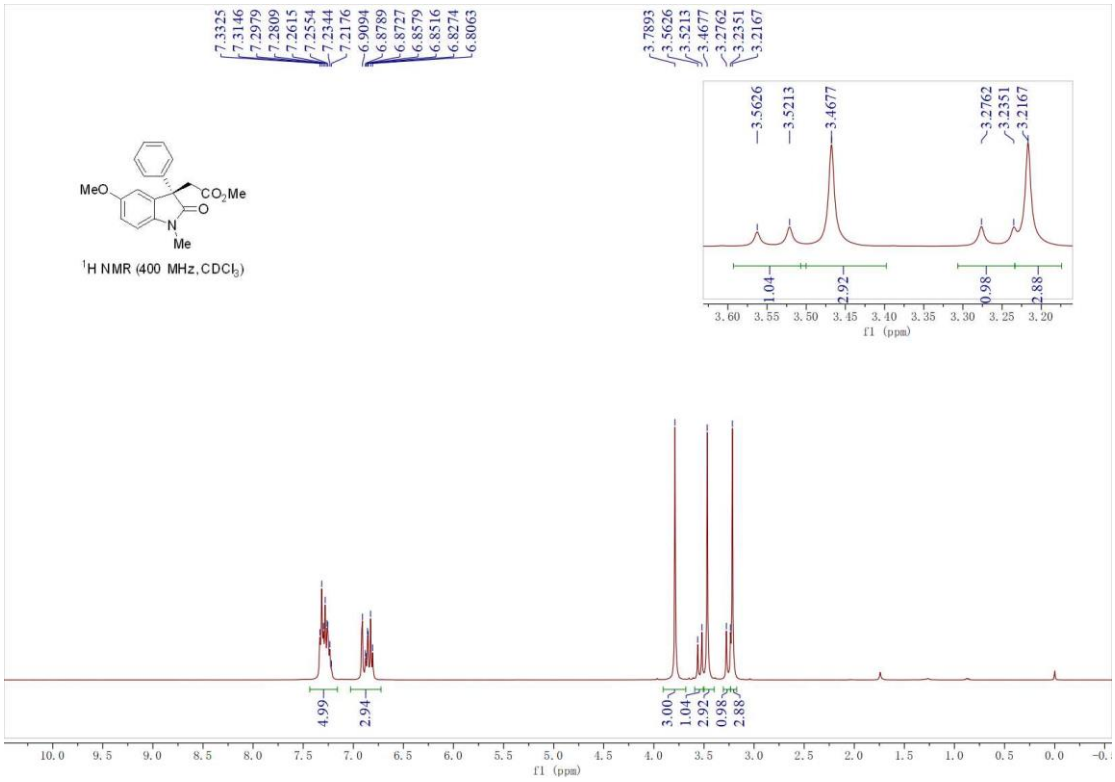
^{1}H NMR of **3d**



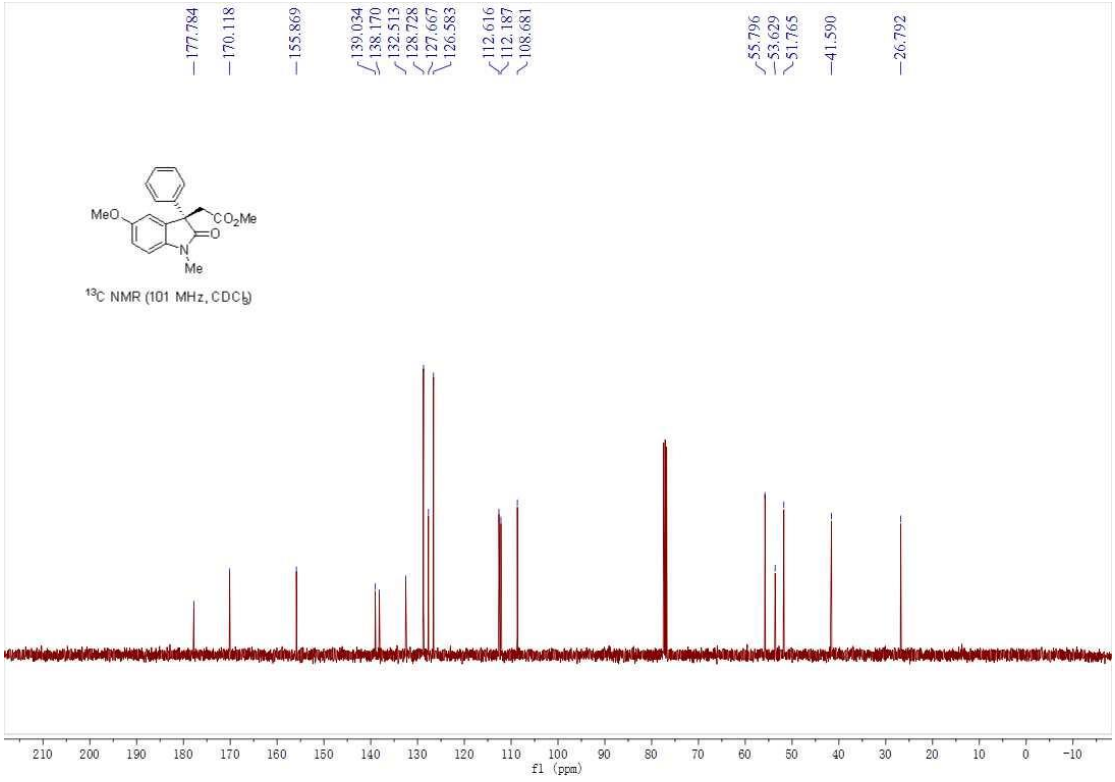
^{13}C NMR of **3d**



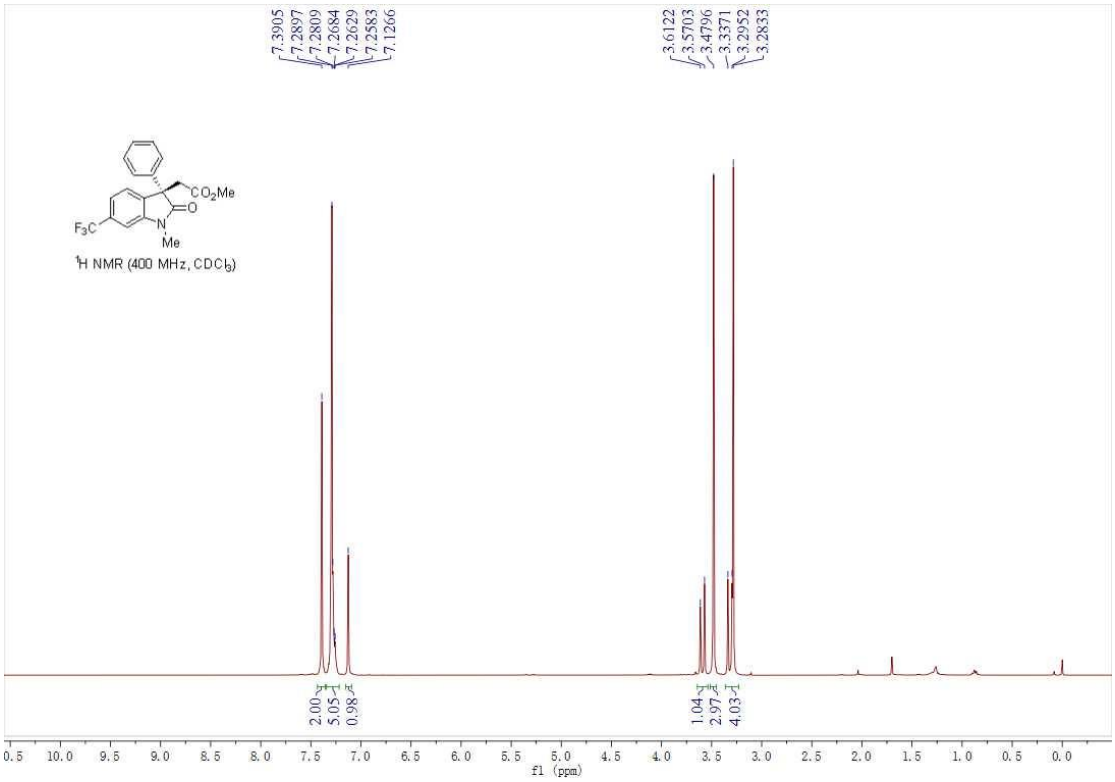
^{1}H NMR of **3e**



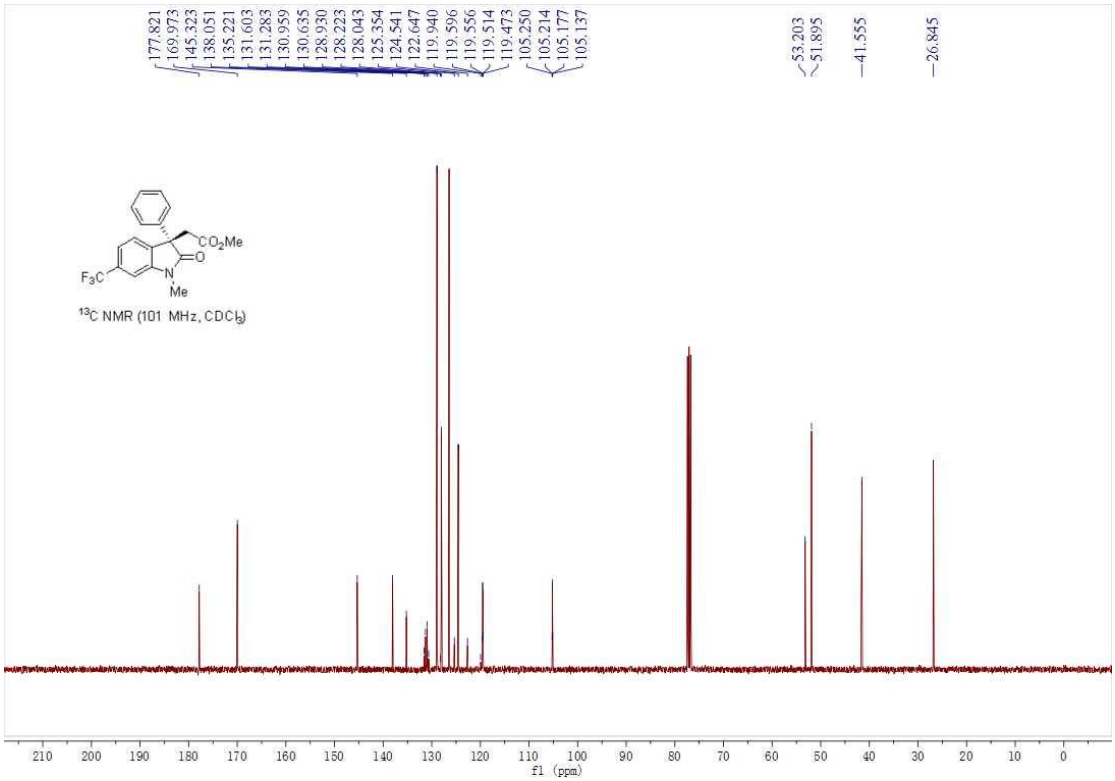
^{13}C NMR of **3e**



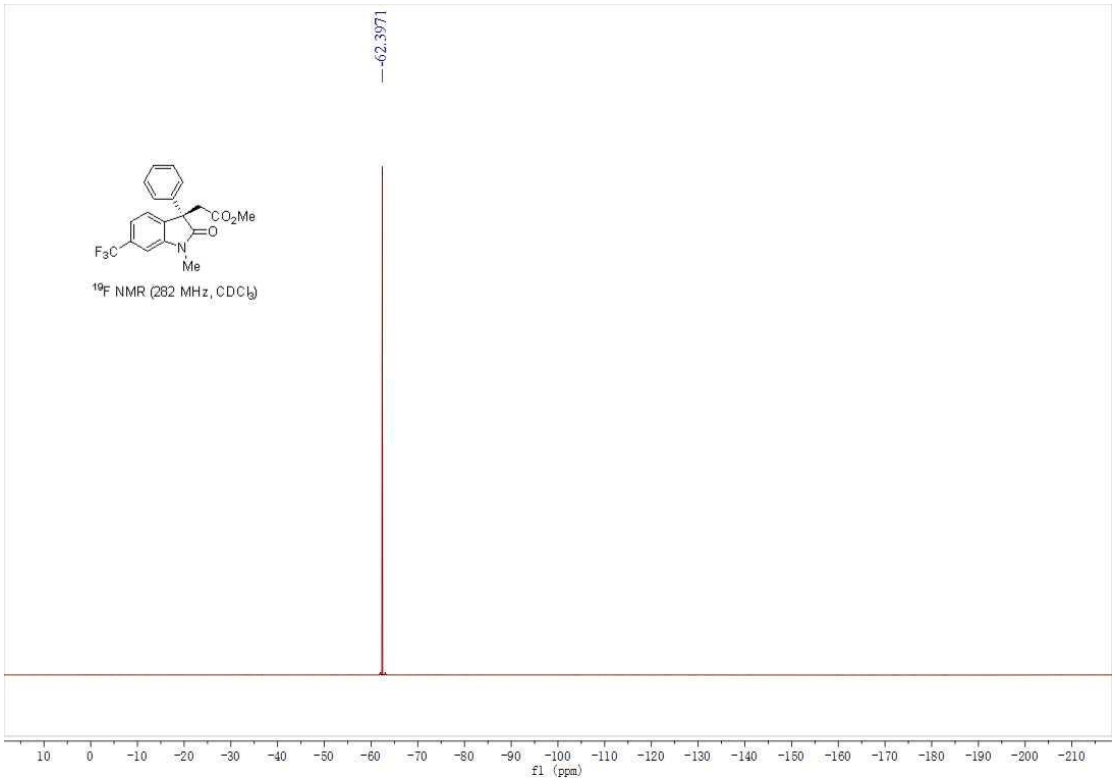
^{1}H NMR of **3f**



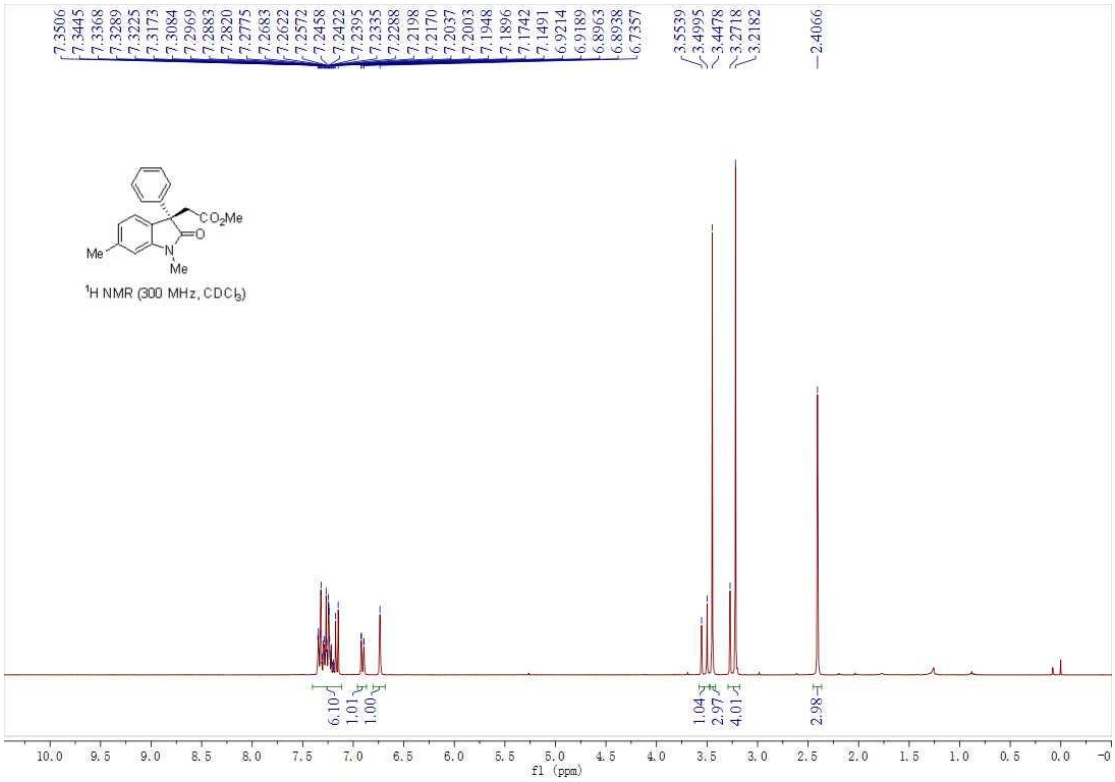
^{13}C NMR of **3f**



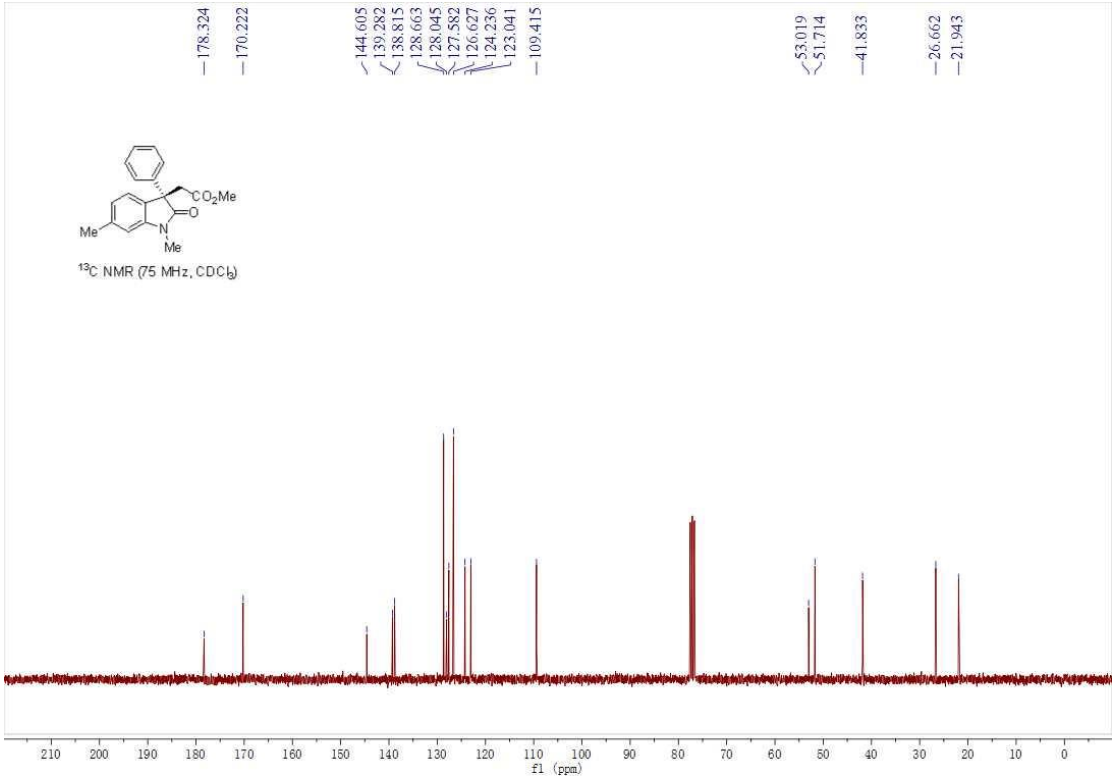
^{19}F NMR of **3f**


-62.3971
CO2Me
F3C
O
N
Me
19F NMR (282 MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

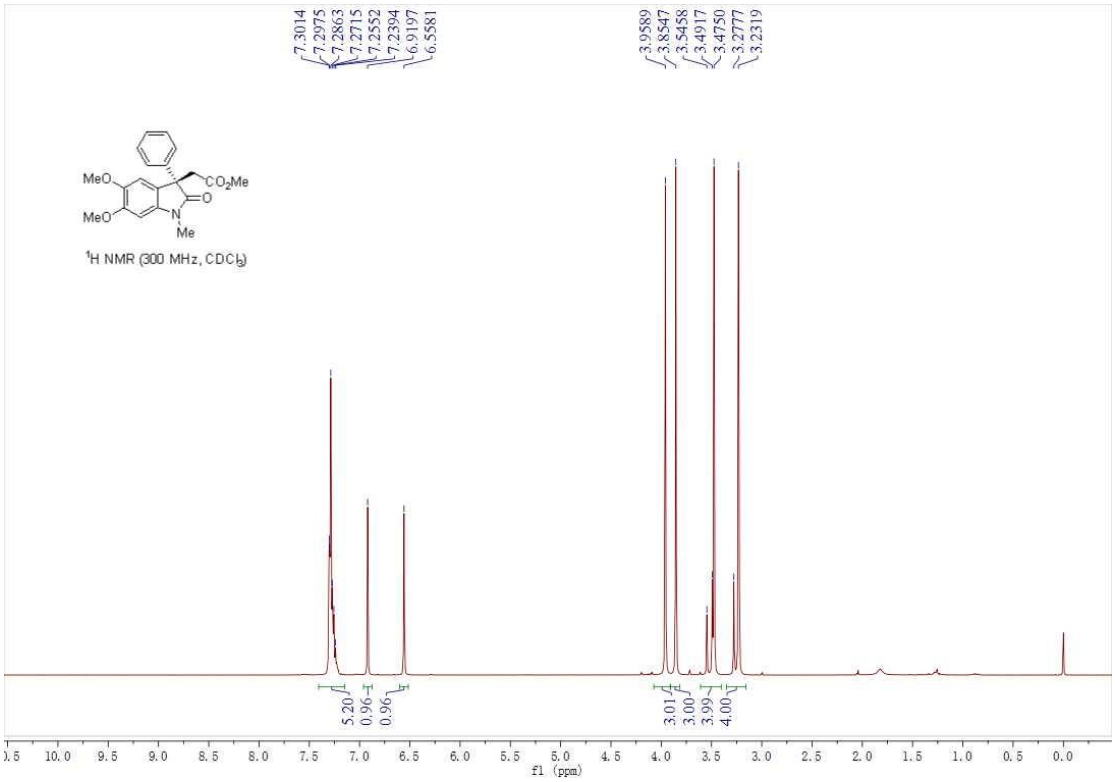
^{1}H NMR of **3g**



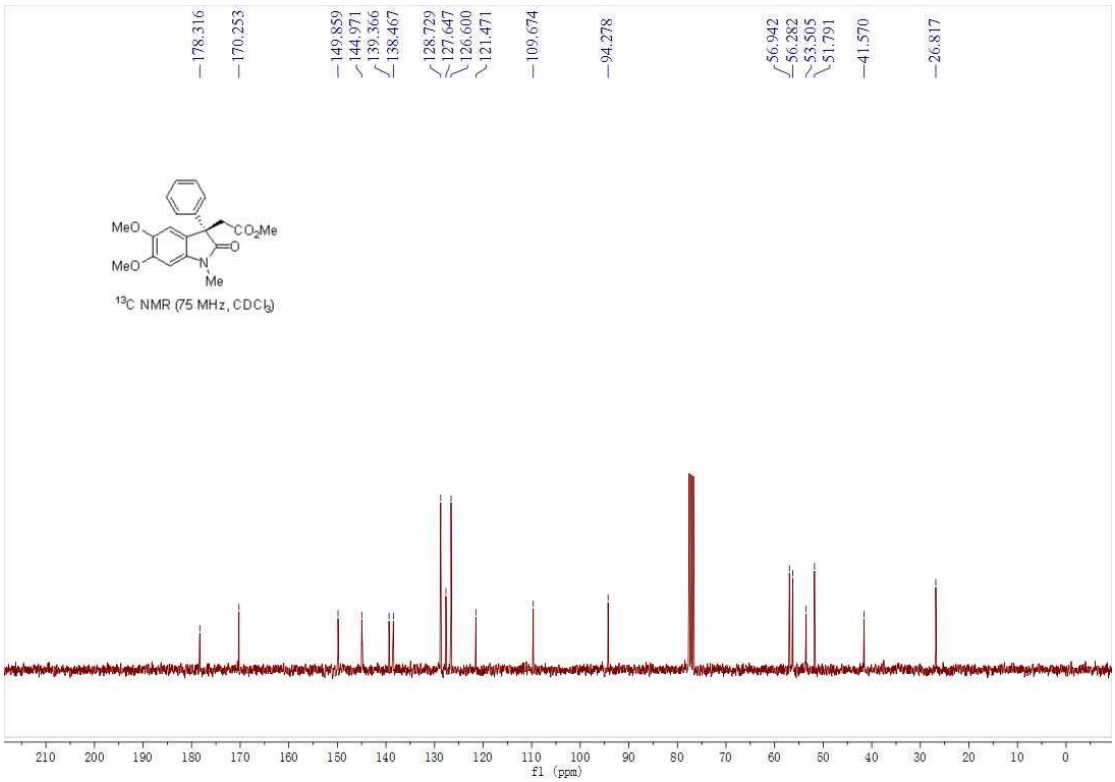
^{13}C NMR of **3g**



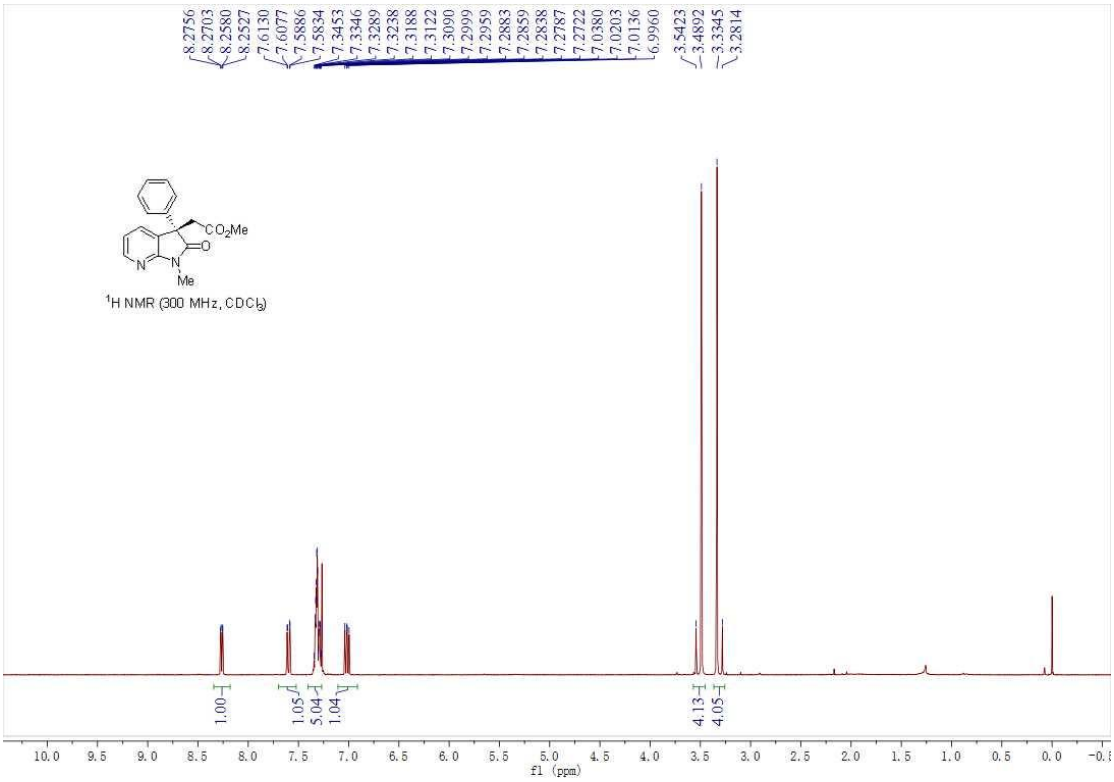
^{1}H NMR of **3h**



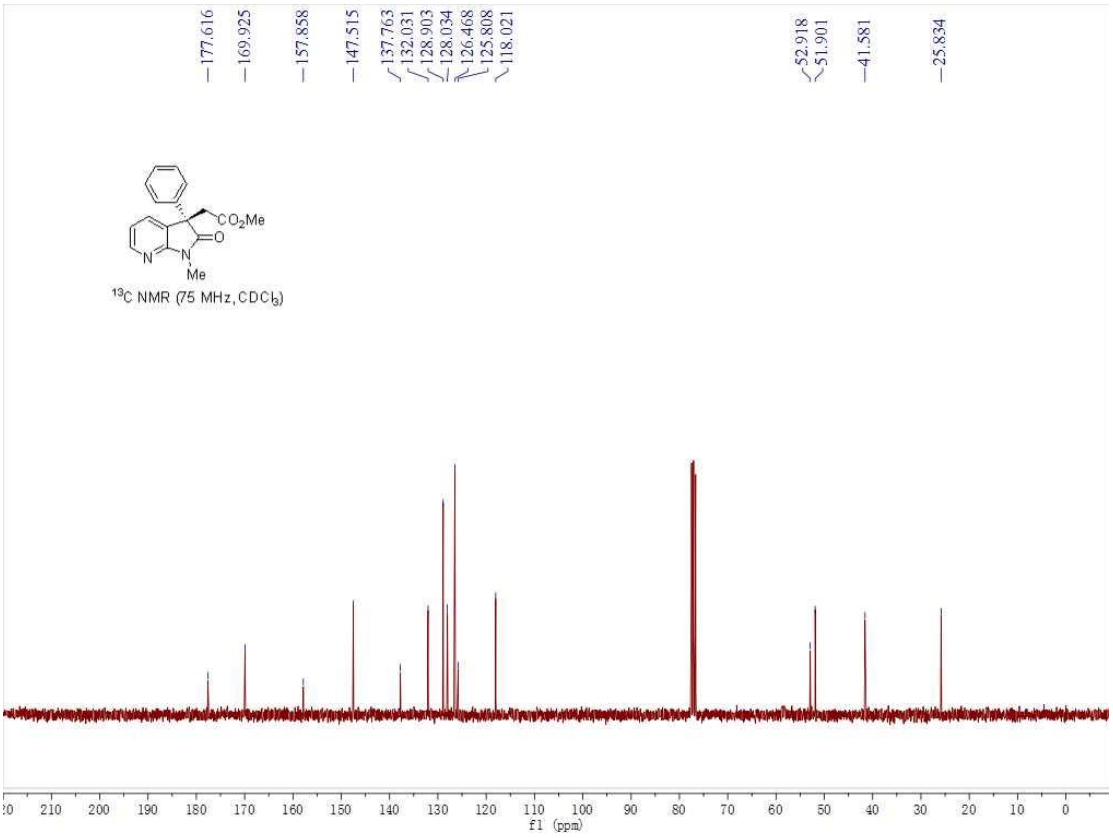
^{13}C NMR of **3h**



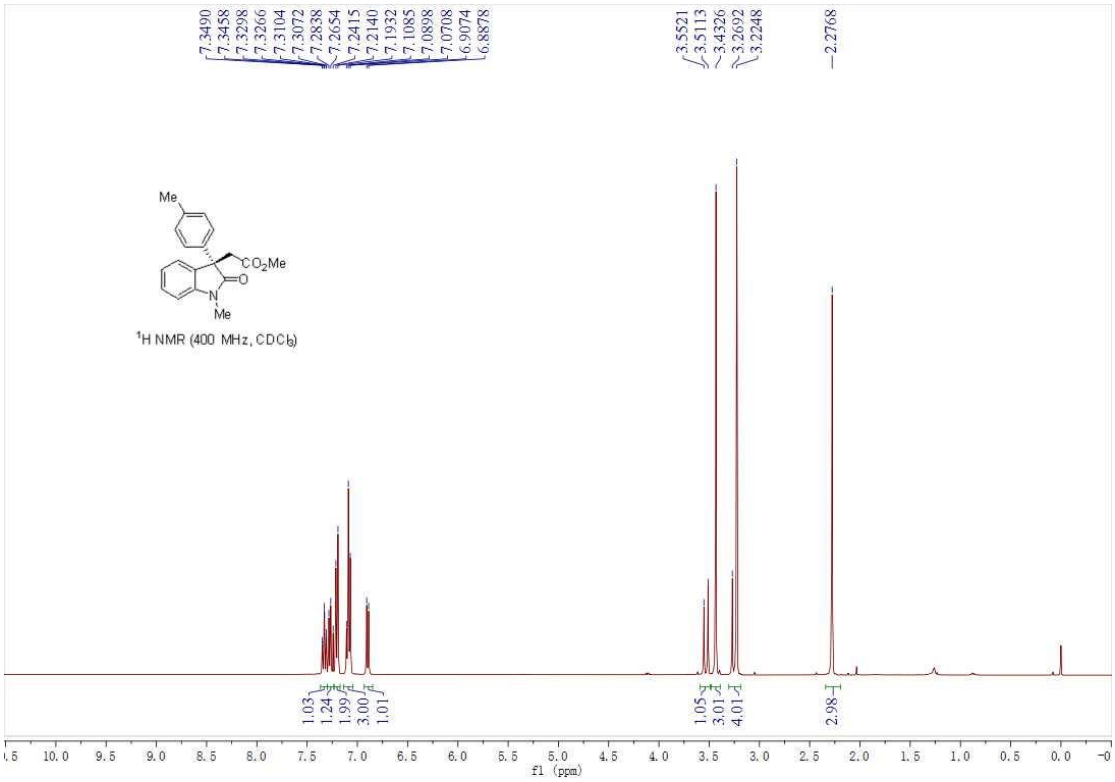
^{1}H NMR of **3i**



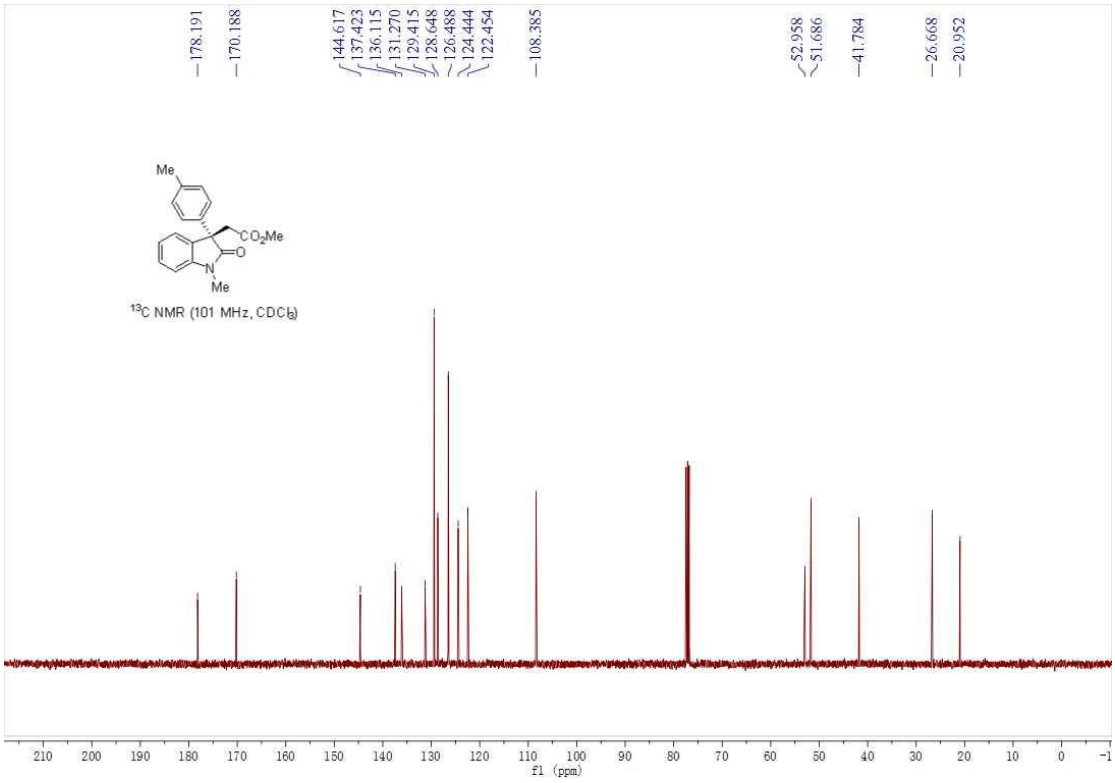
^{13}C NMR of **3i**



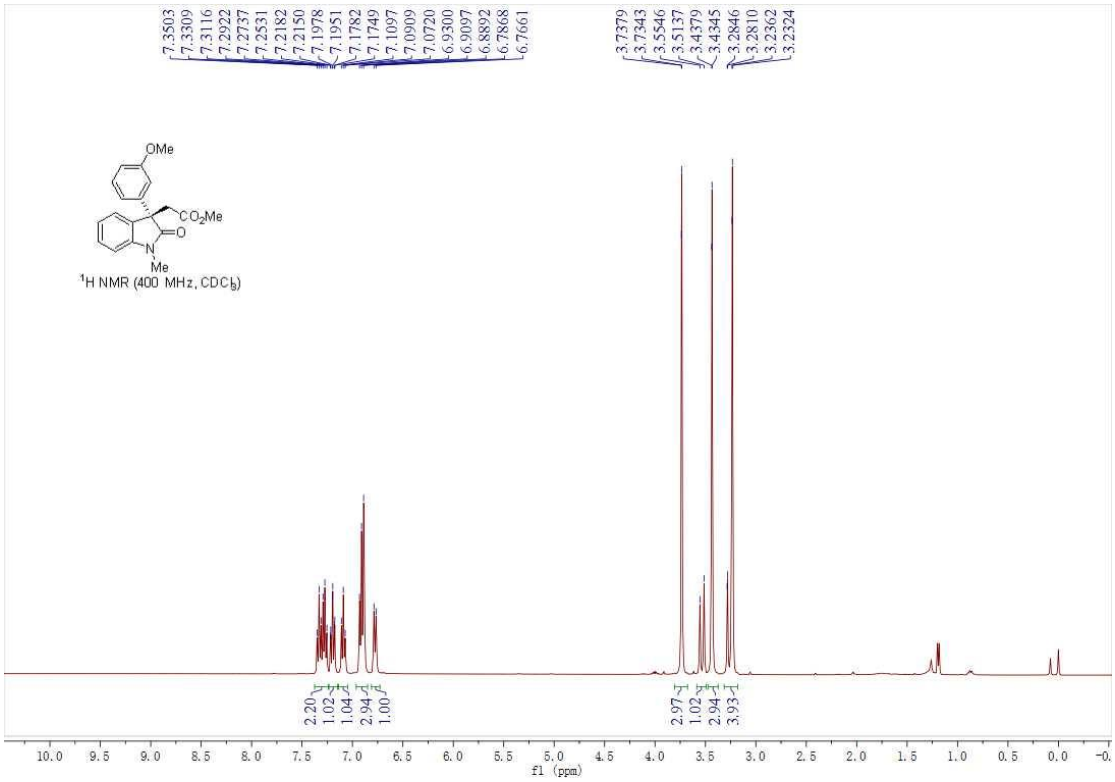
^{1}H NMR of **3j**



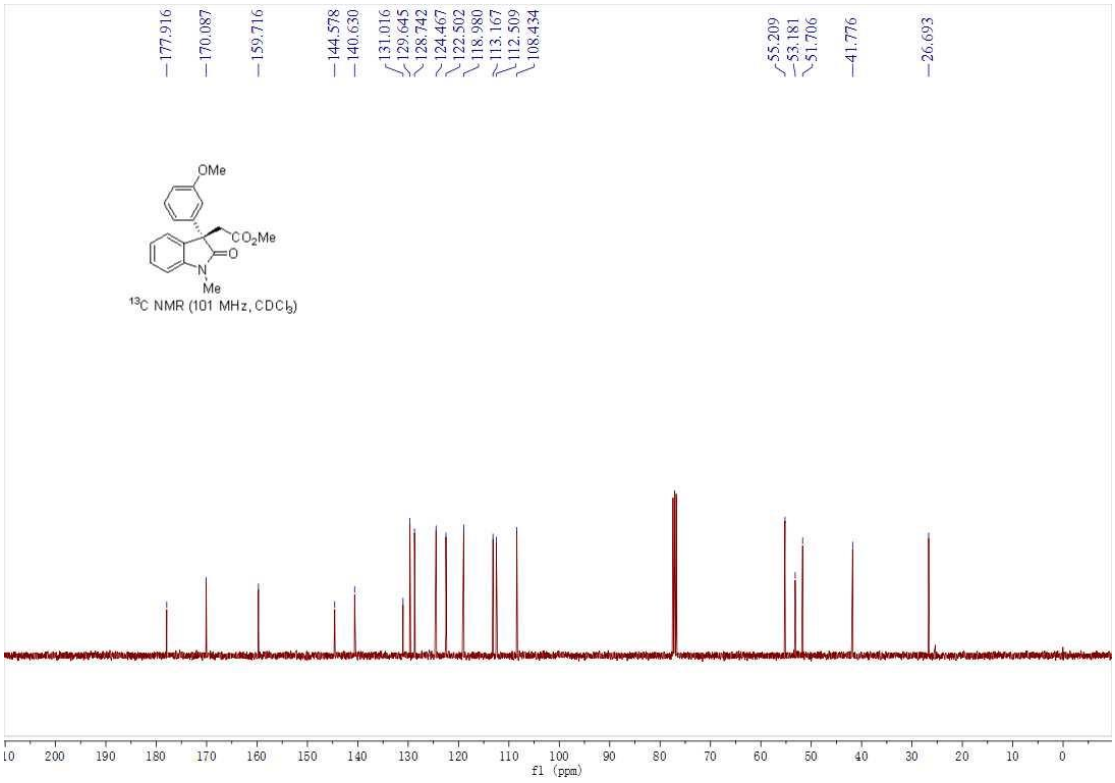
^{13}C NMR of **3j**



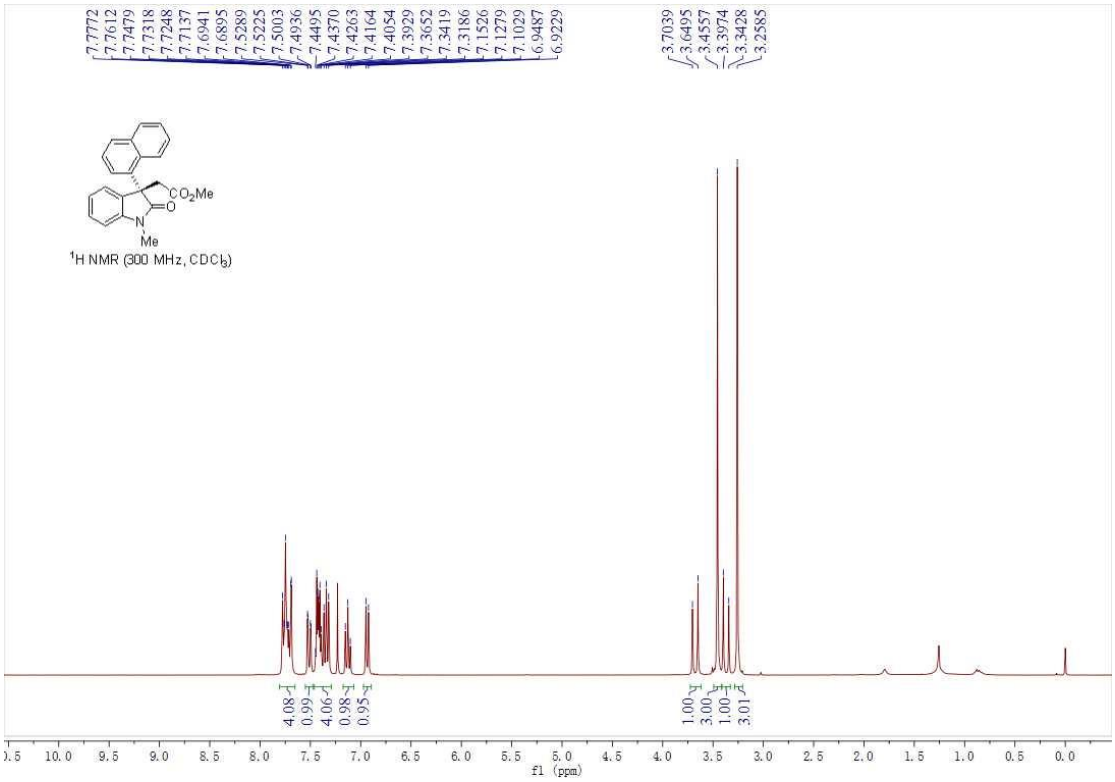
^{1}H NMR of **3k**



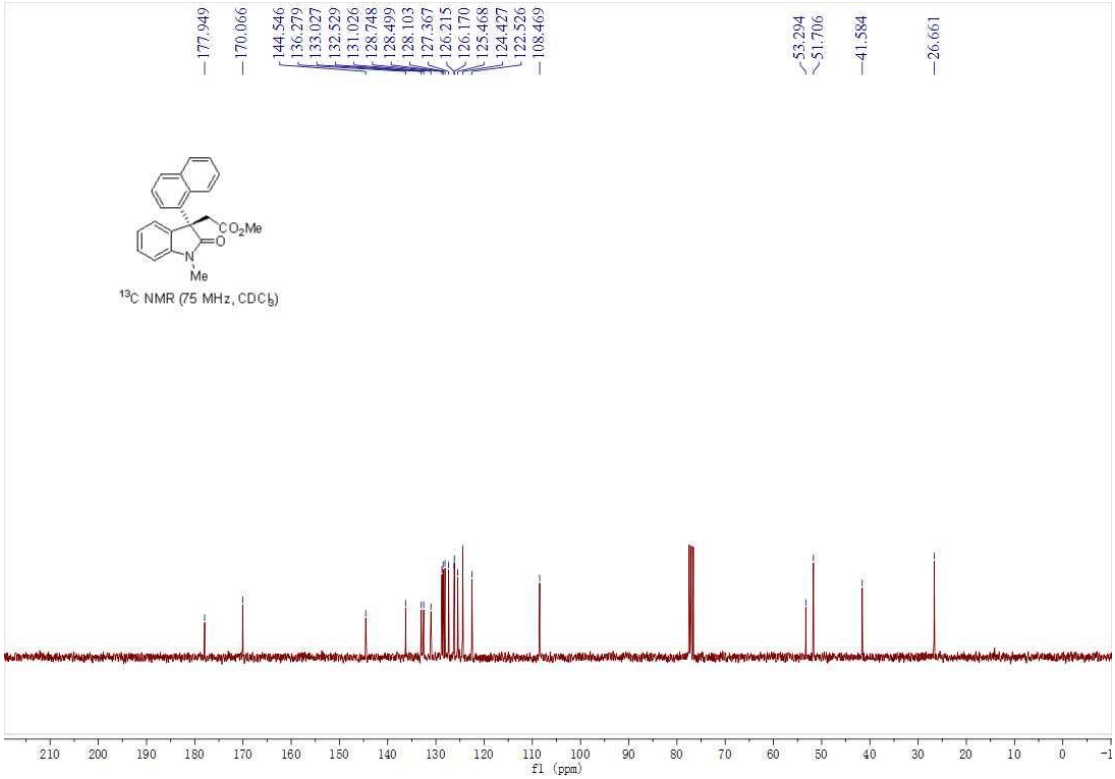
^{13}C NMR of **3k**



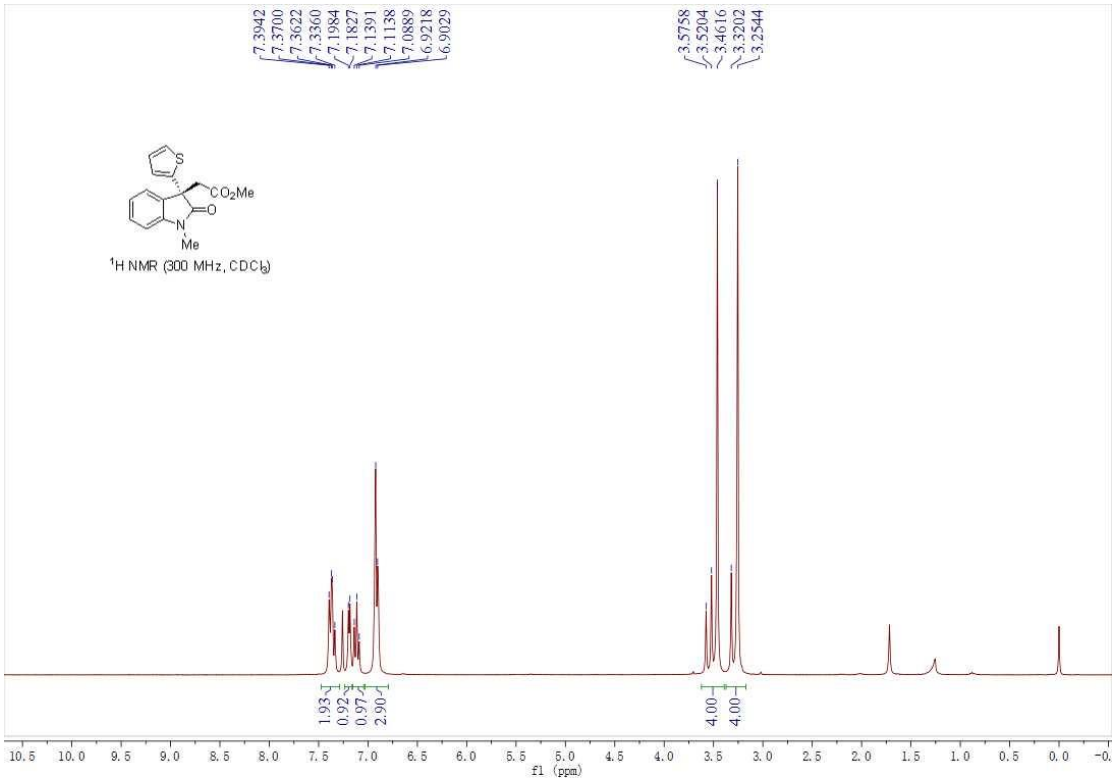
^{1}H NMR of **3l**



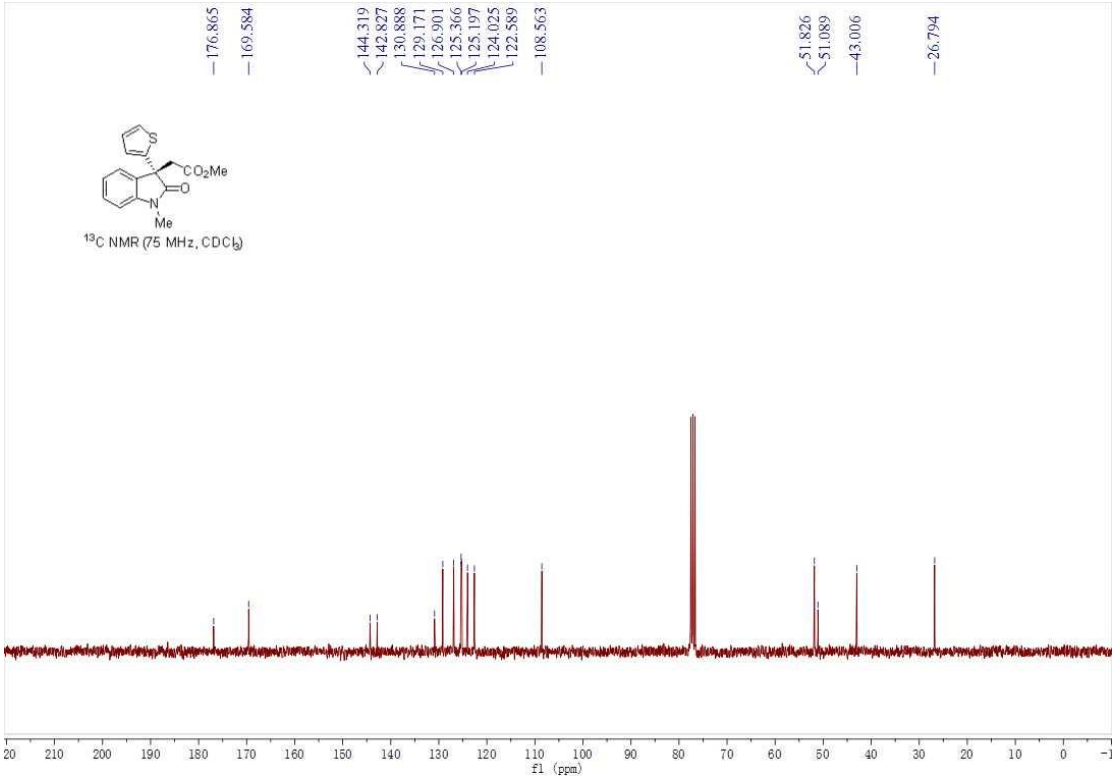
^{13}C NMR of **3l**



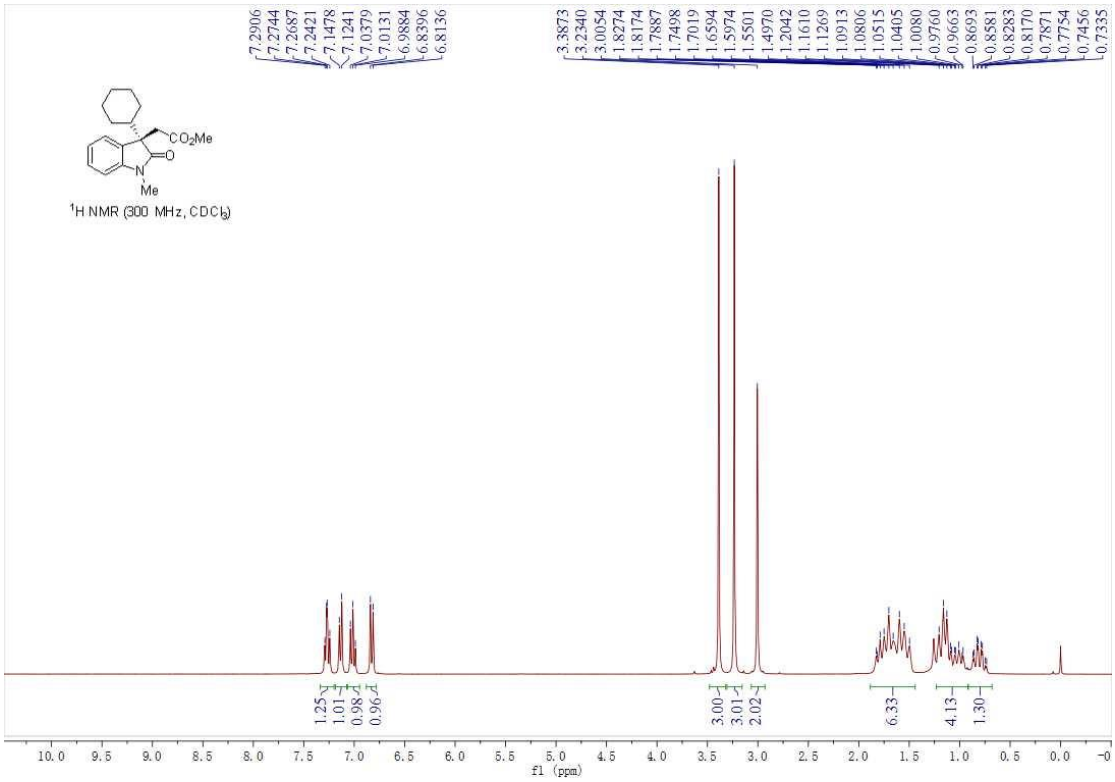
^{1}H NMR of **3m**



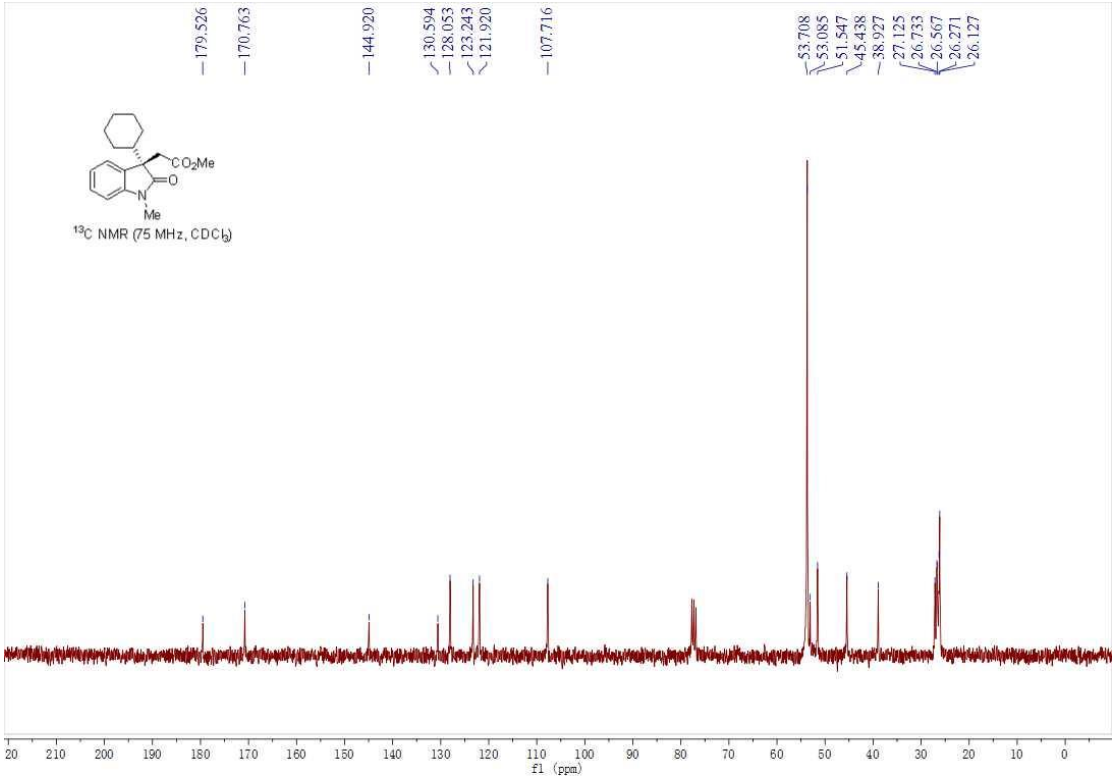
^{13}C NMR of **3m**



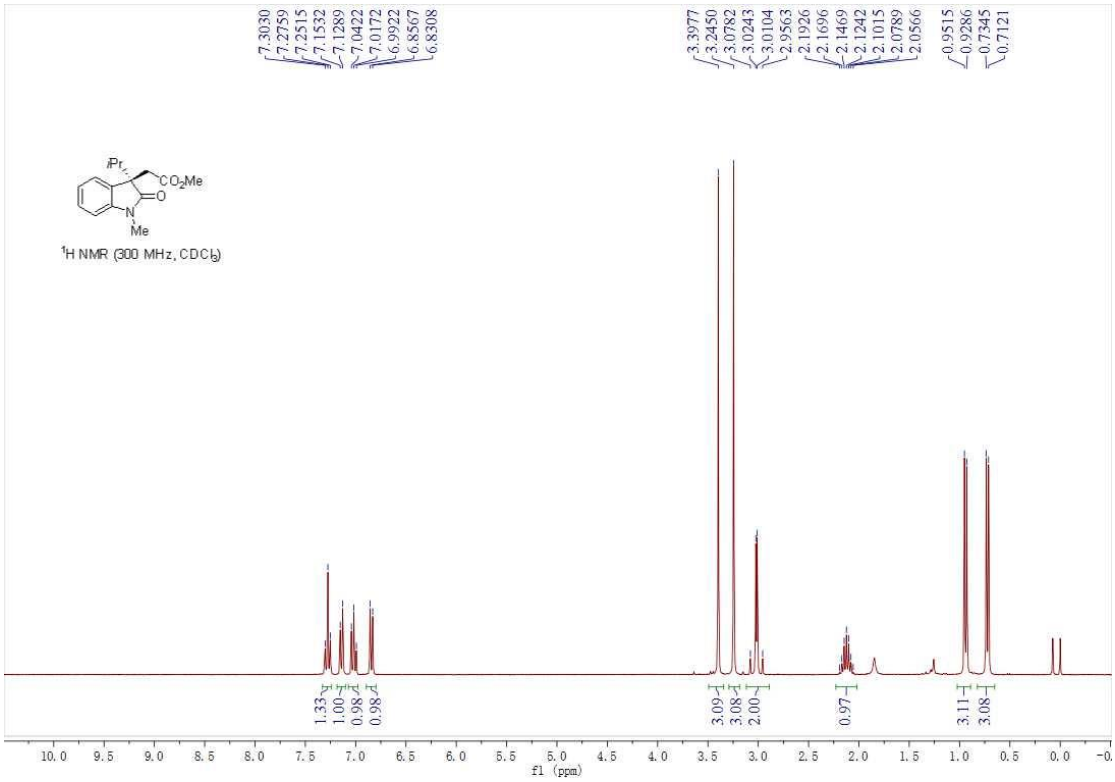
^{1}H NMR of **3n**



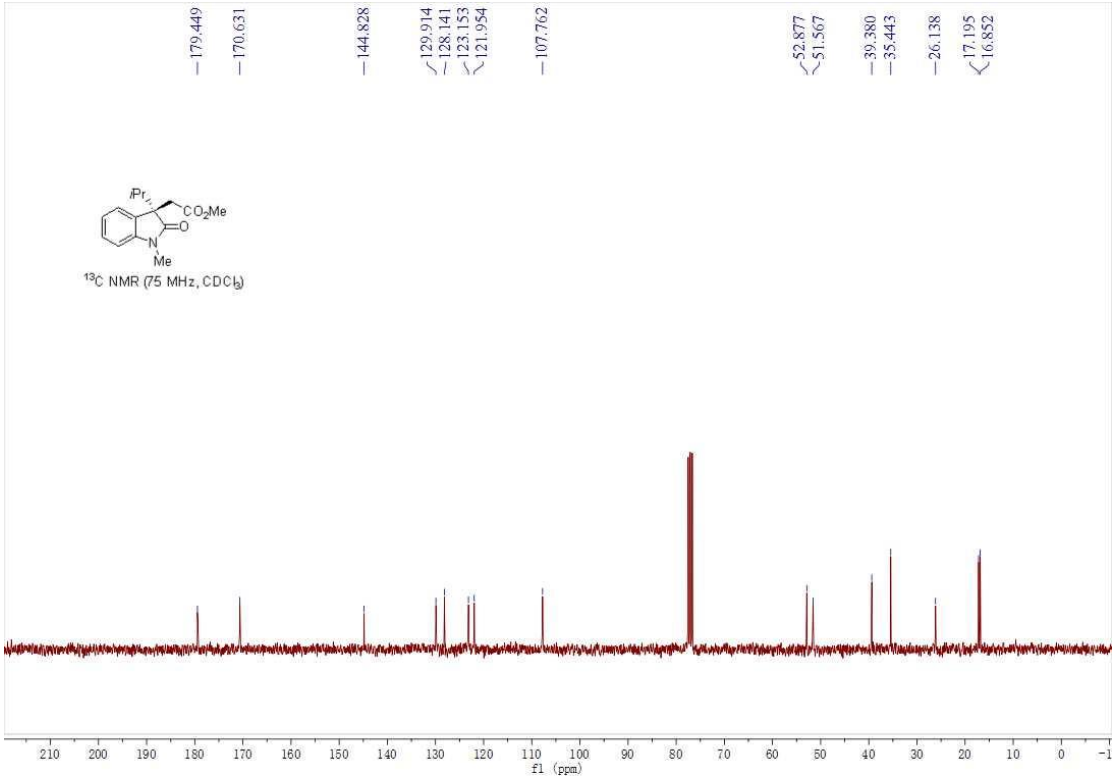
^{13}C NMR of **3n**



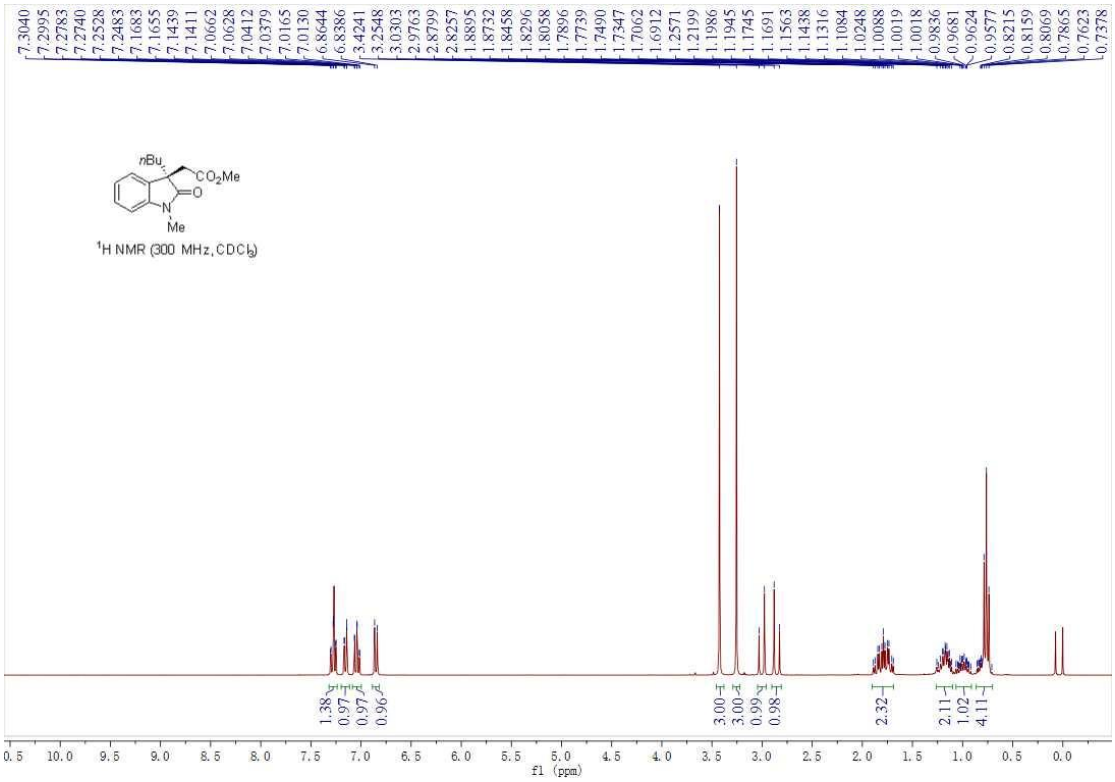
^{1}H NMR of **3o**



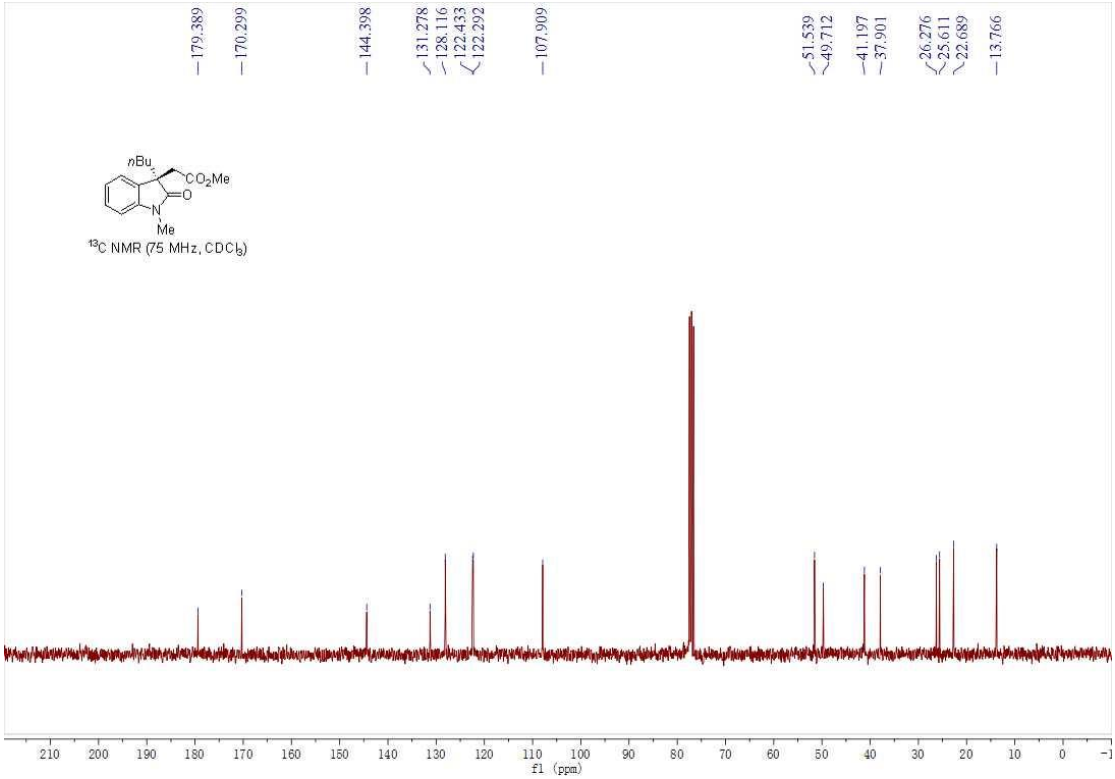
^{13}C NMR of **3o**



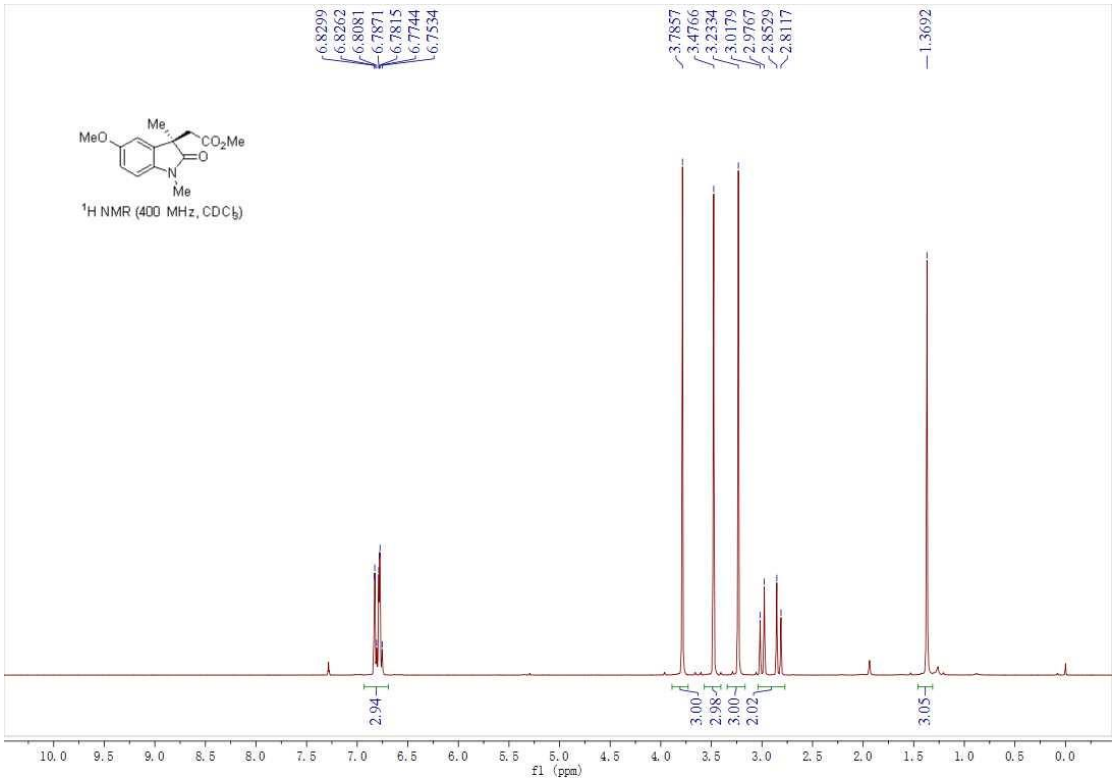
^{1}H NMR of **3p**



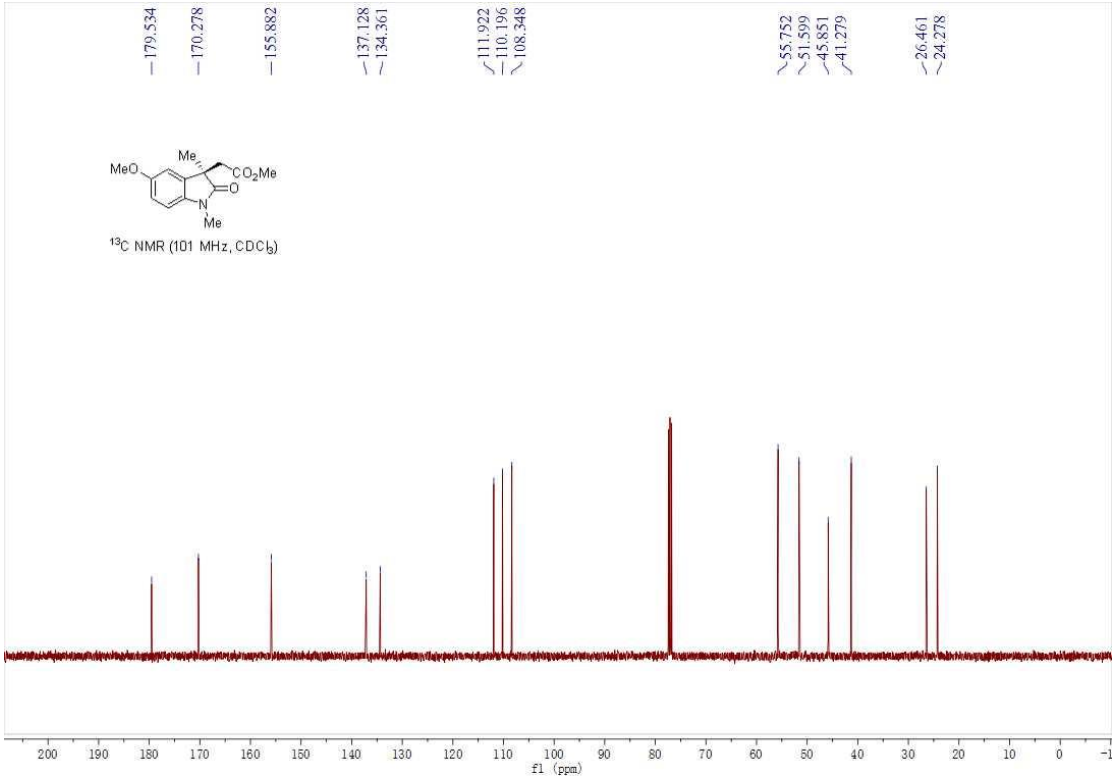
^{13}C NMR of **3p**



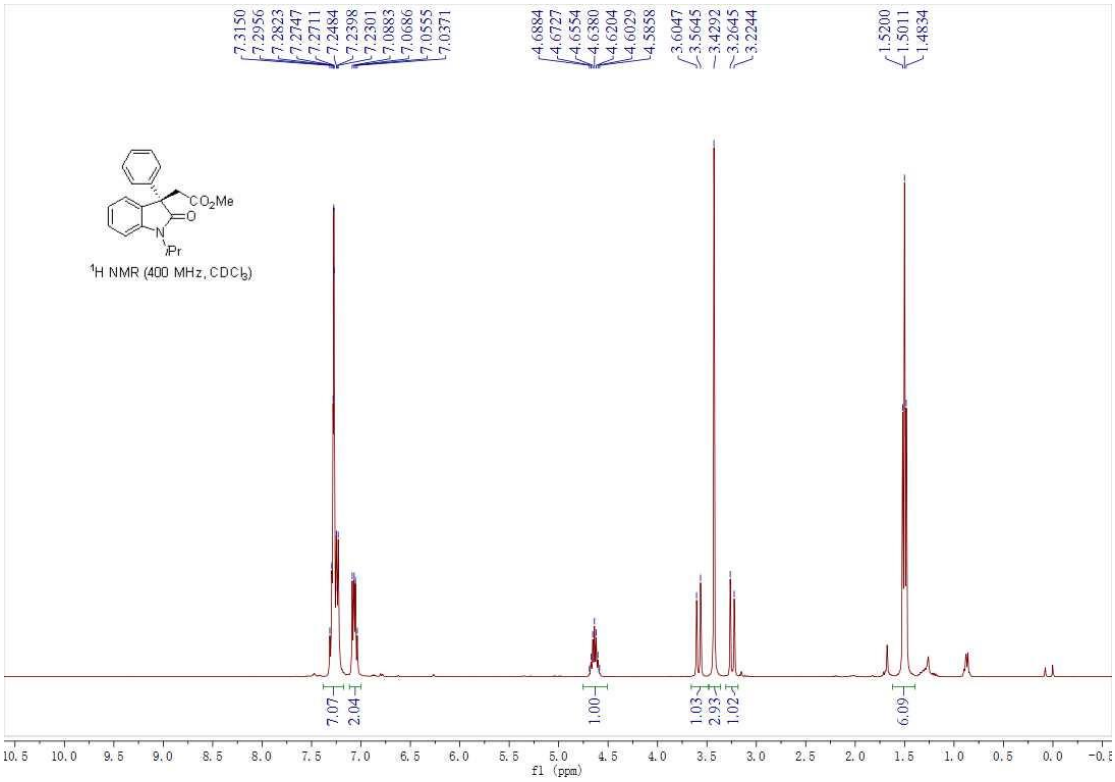
^{1}H NMR of **3q**



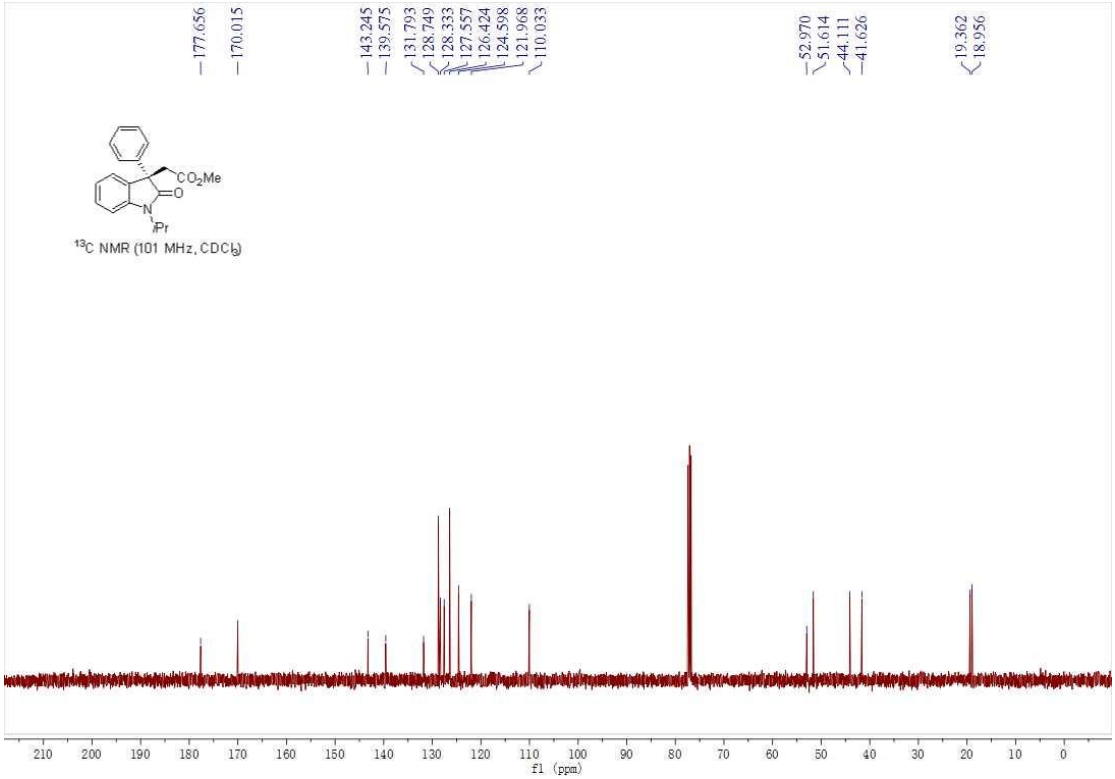
^{13}C NMR of **3q**



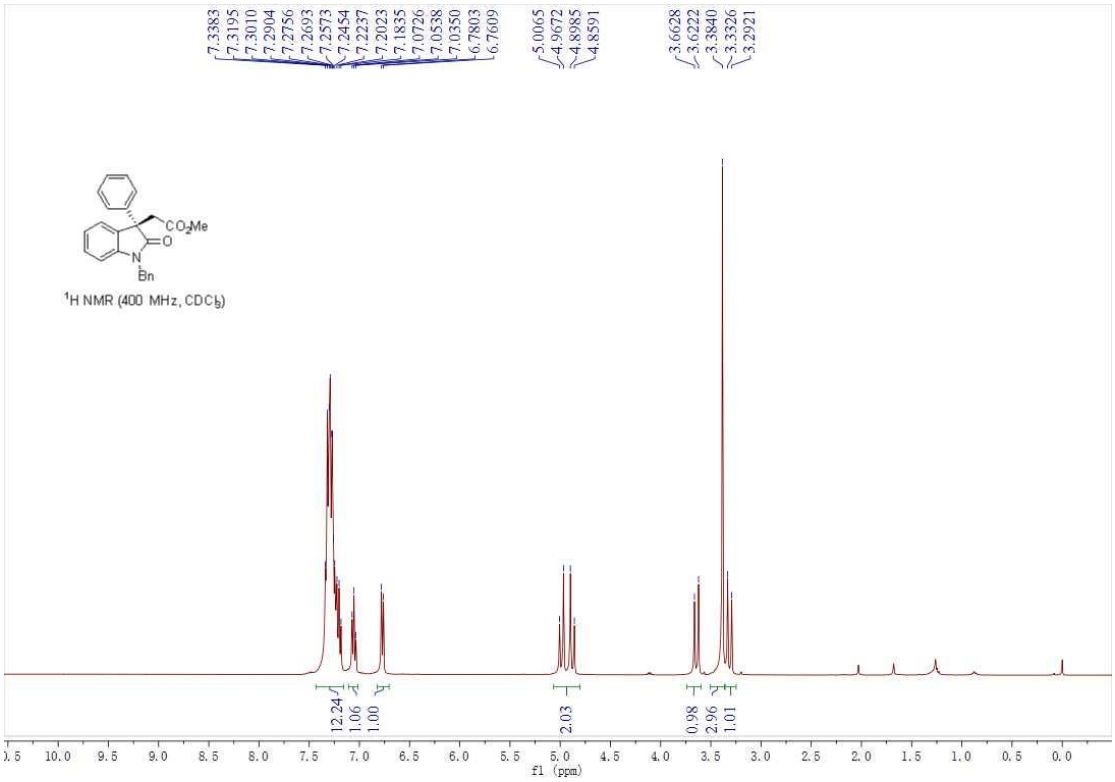
^{1}H NMR of **3r**



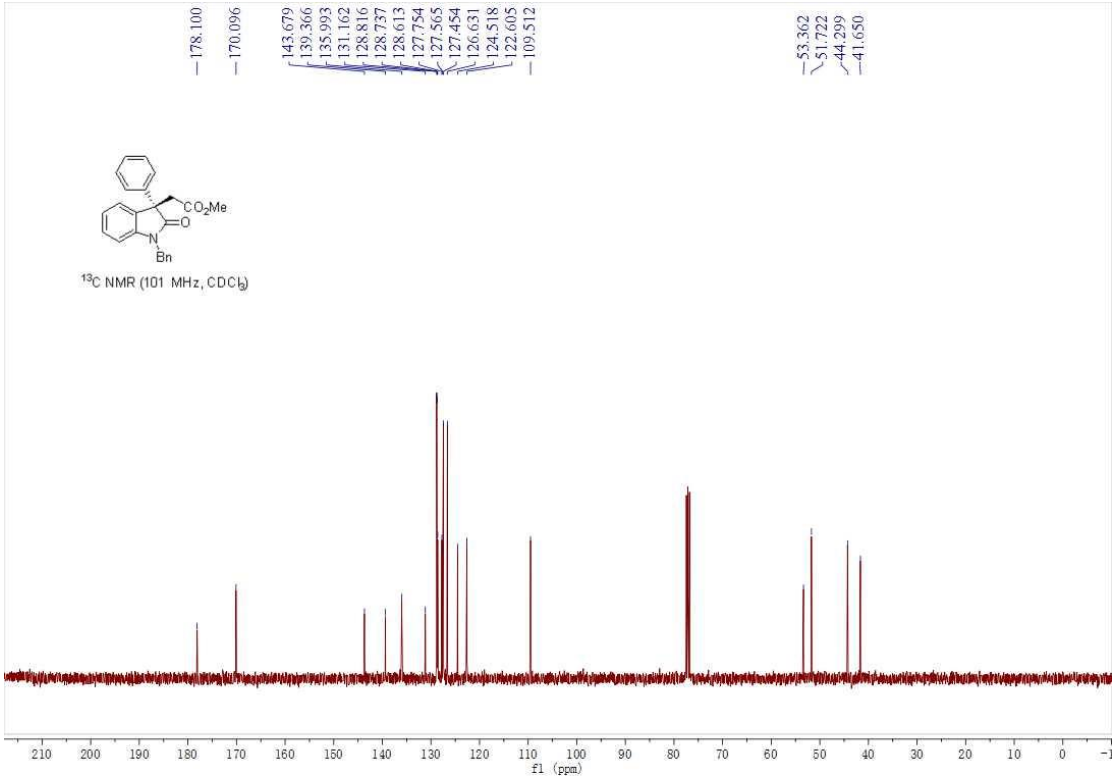
^{13}C NMR of **3r**



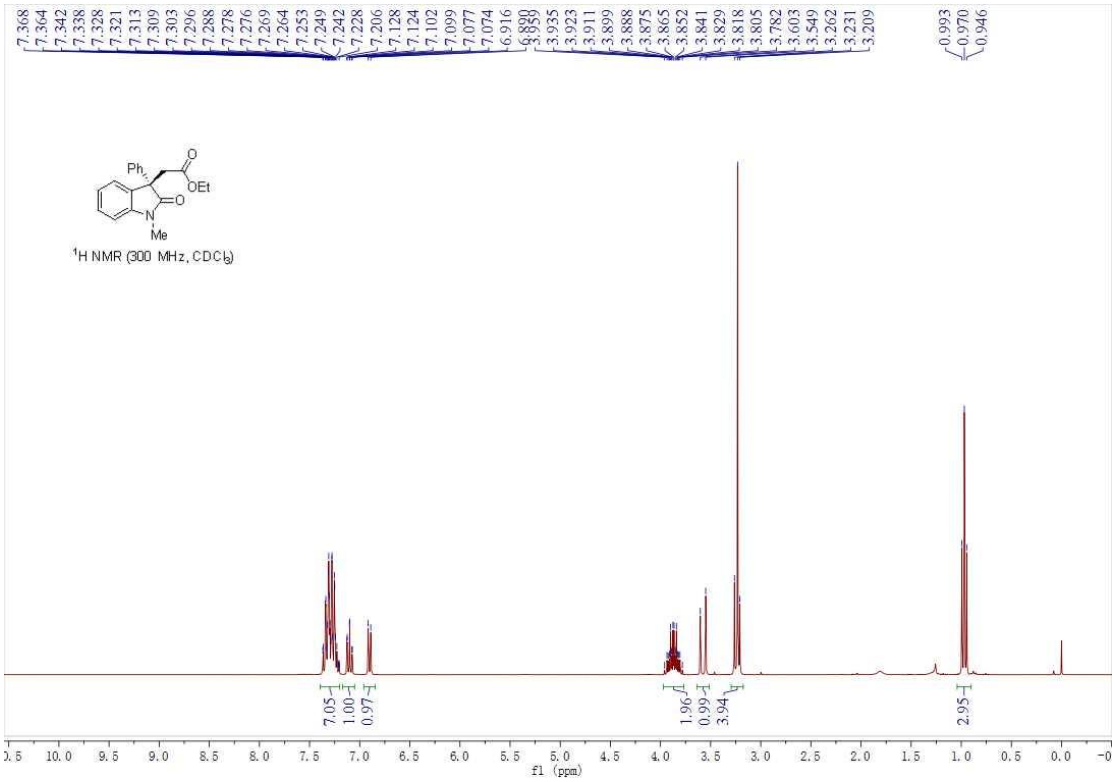
^{1}H NMR of **3s**



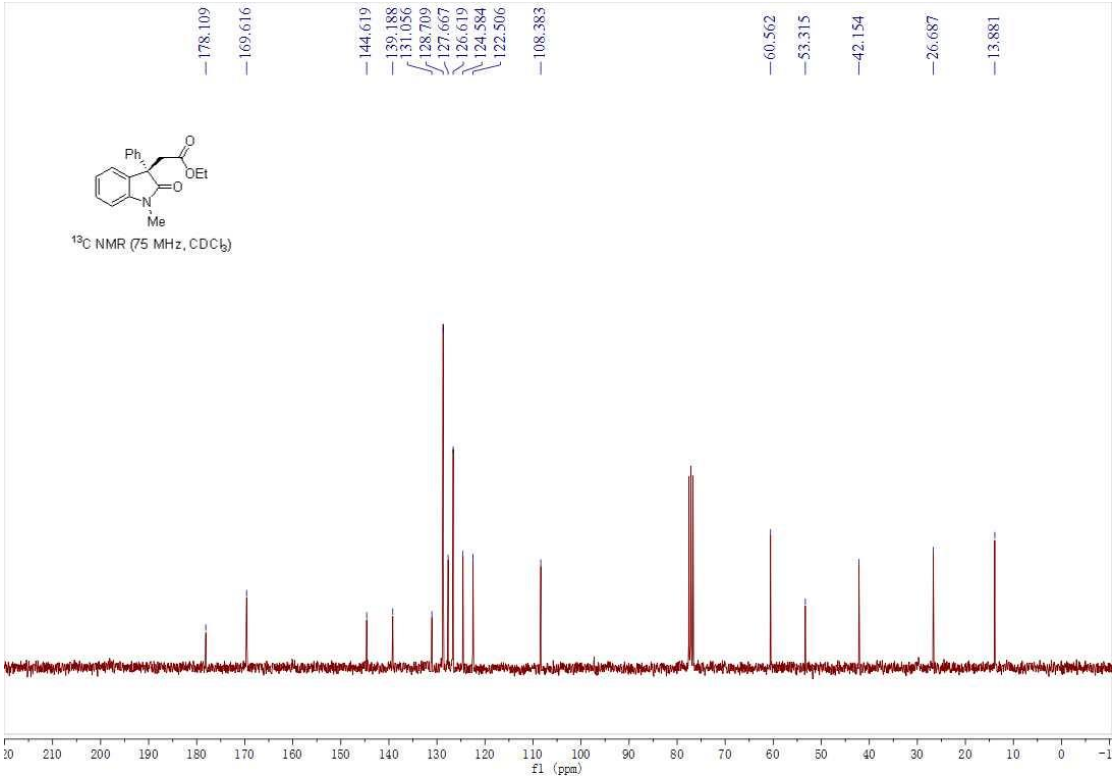
^{13}C NMR of **3s**



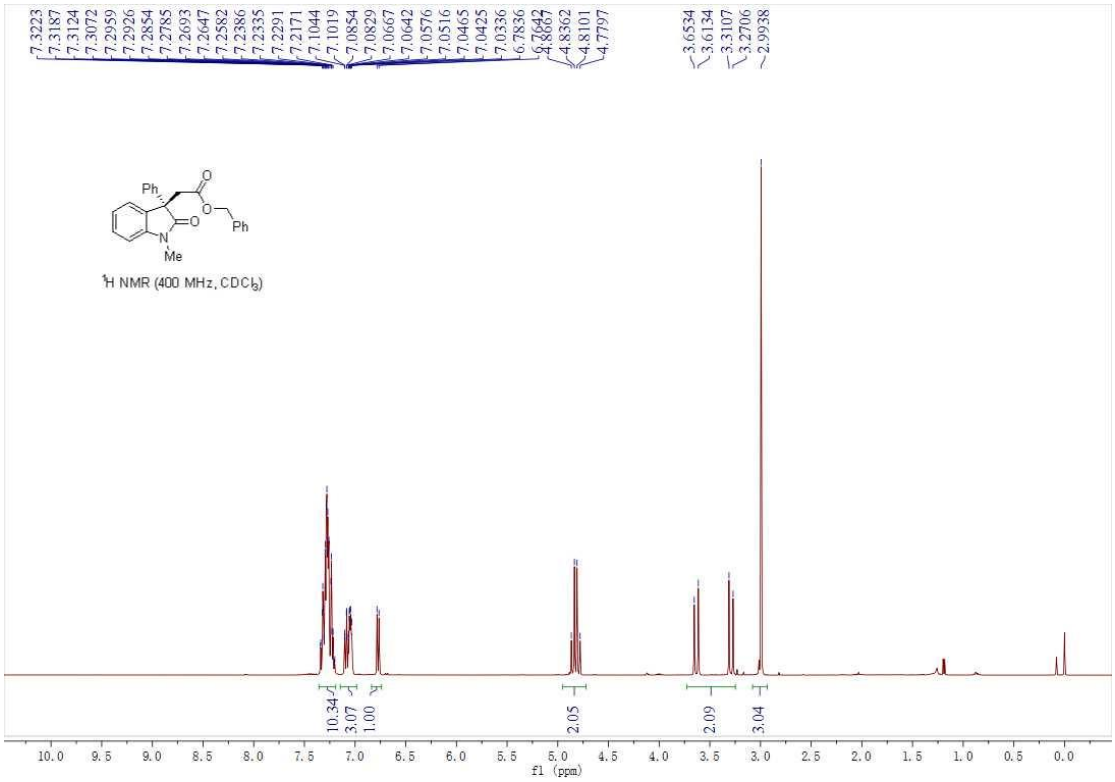
^{1}H NMR of **3t**



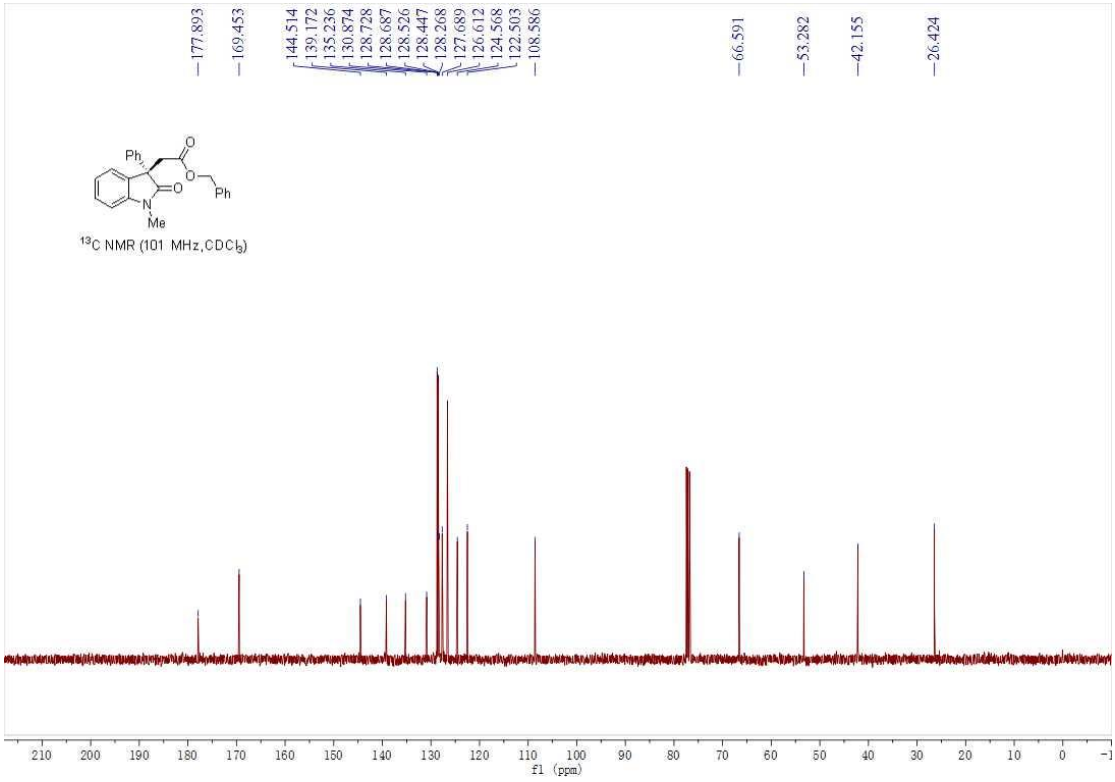
^{13}C NMR of **3t**



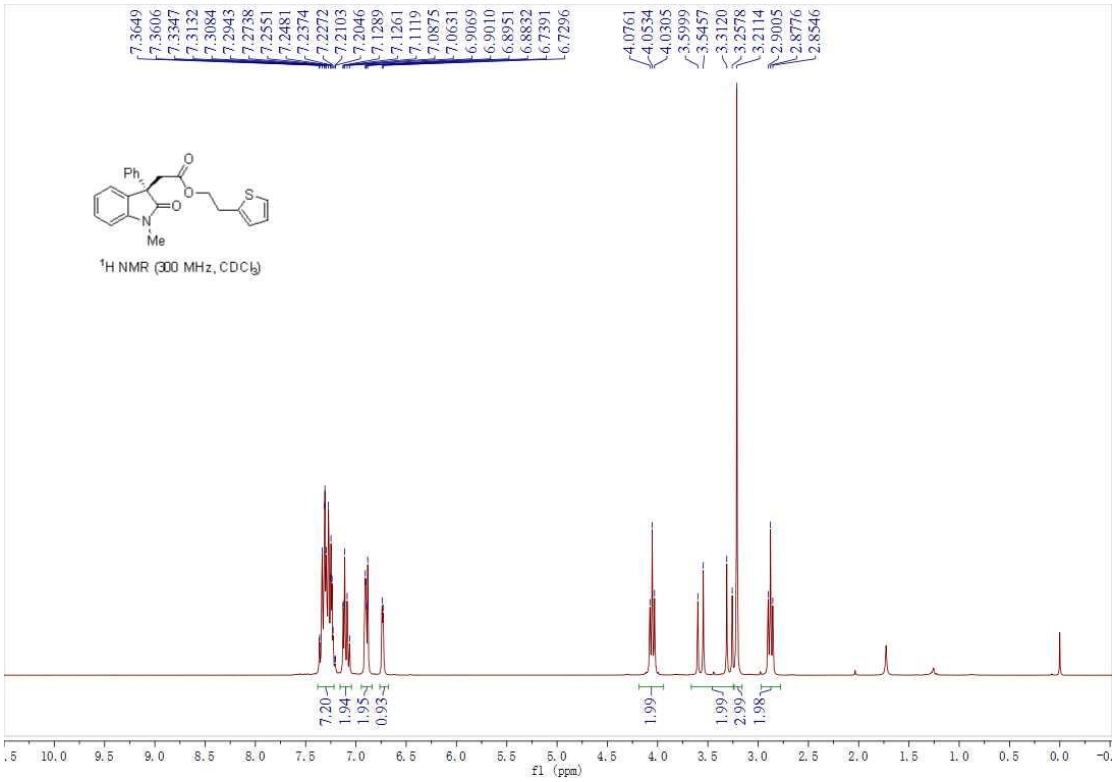
^{1}H NMR of **3u**



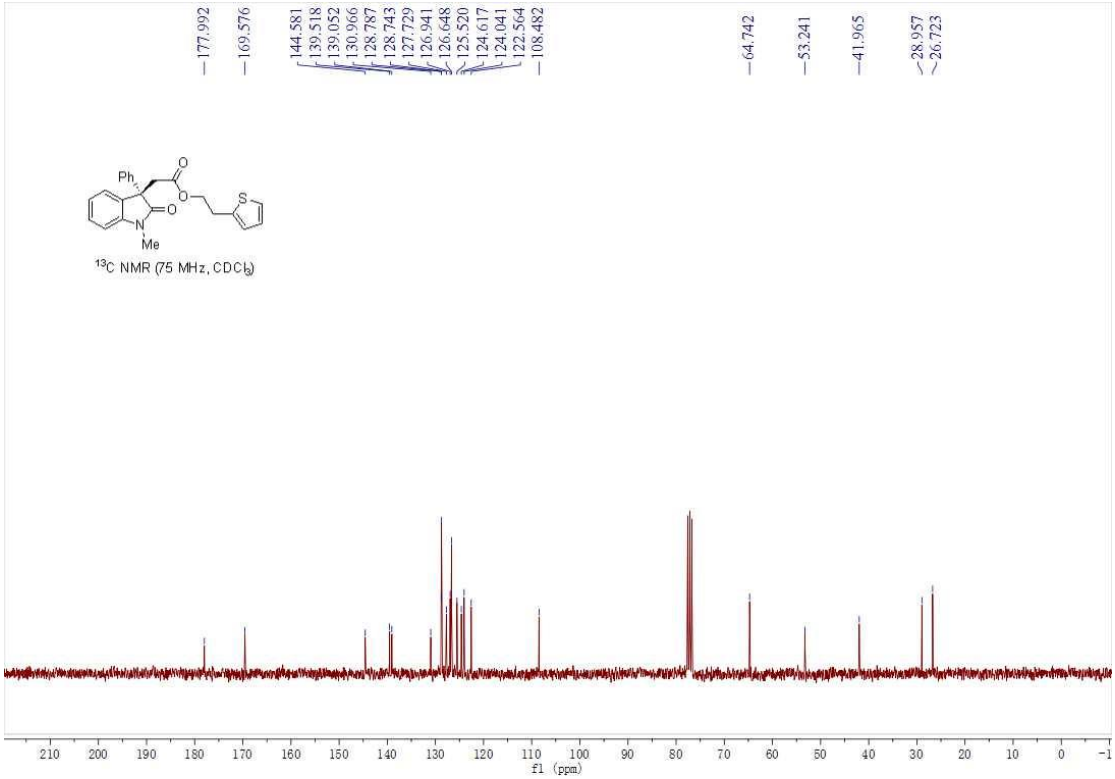
^{13}C NMR of **3u**



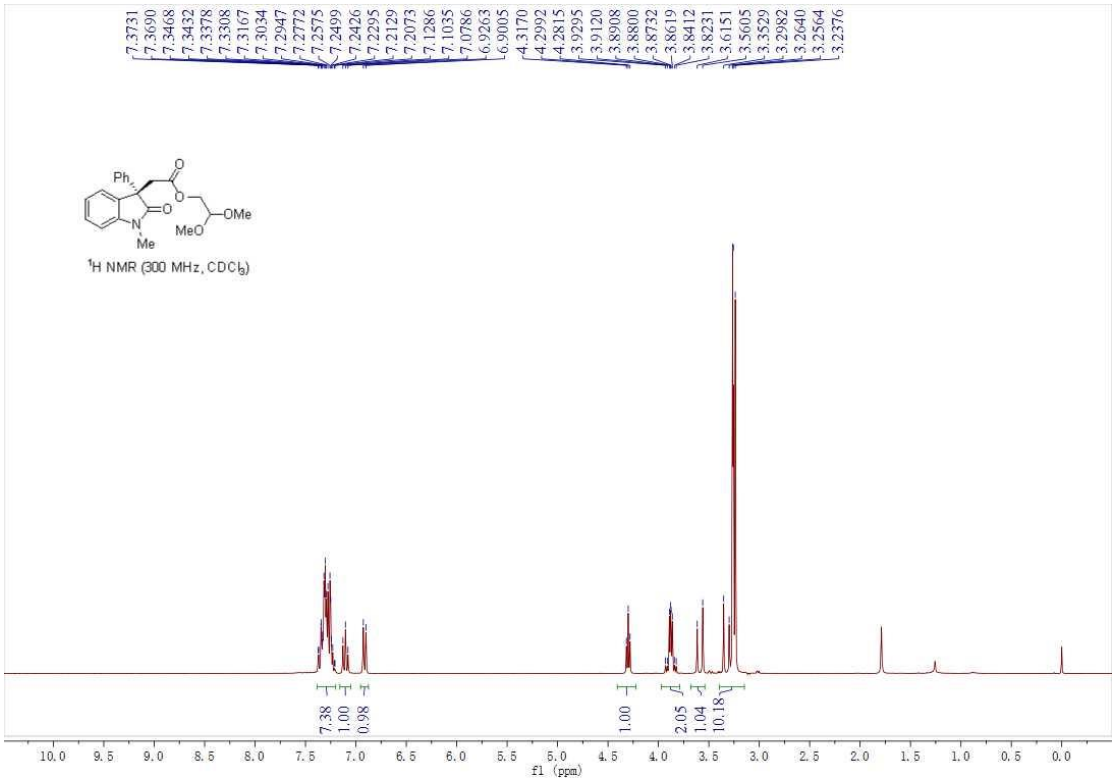
^{1}H NMR of **3v**



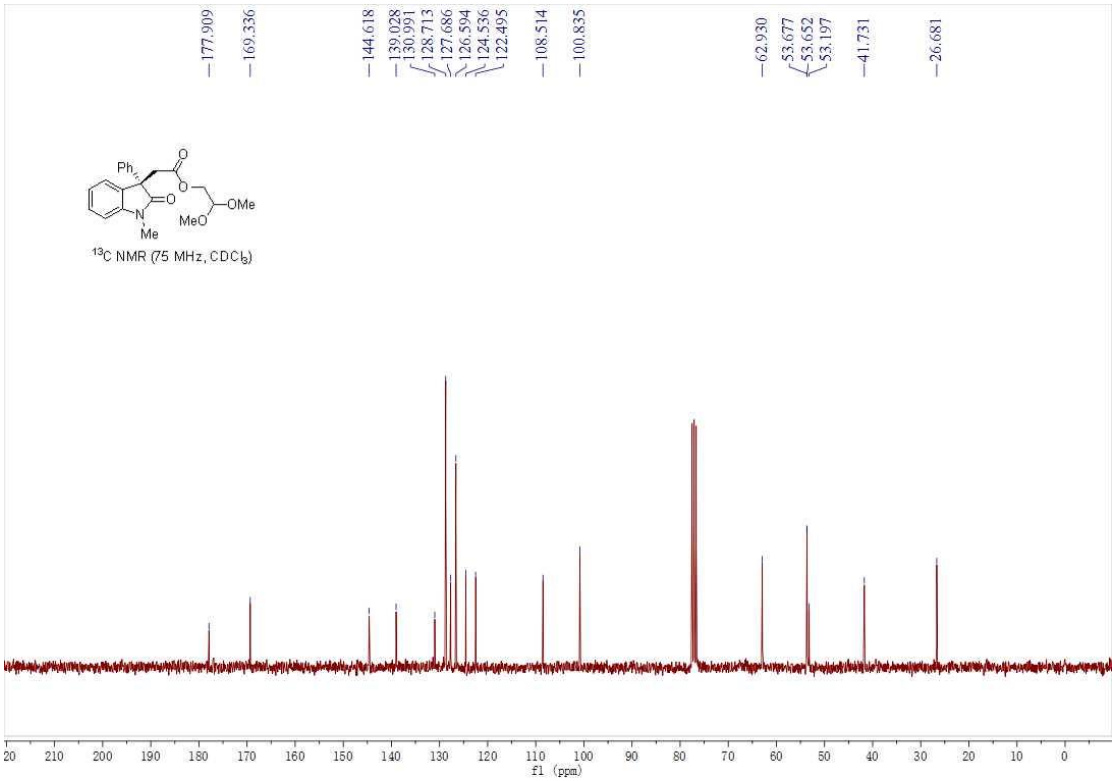
^{13}C NMR of **3v**



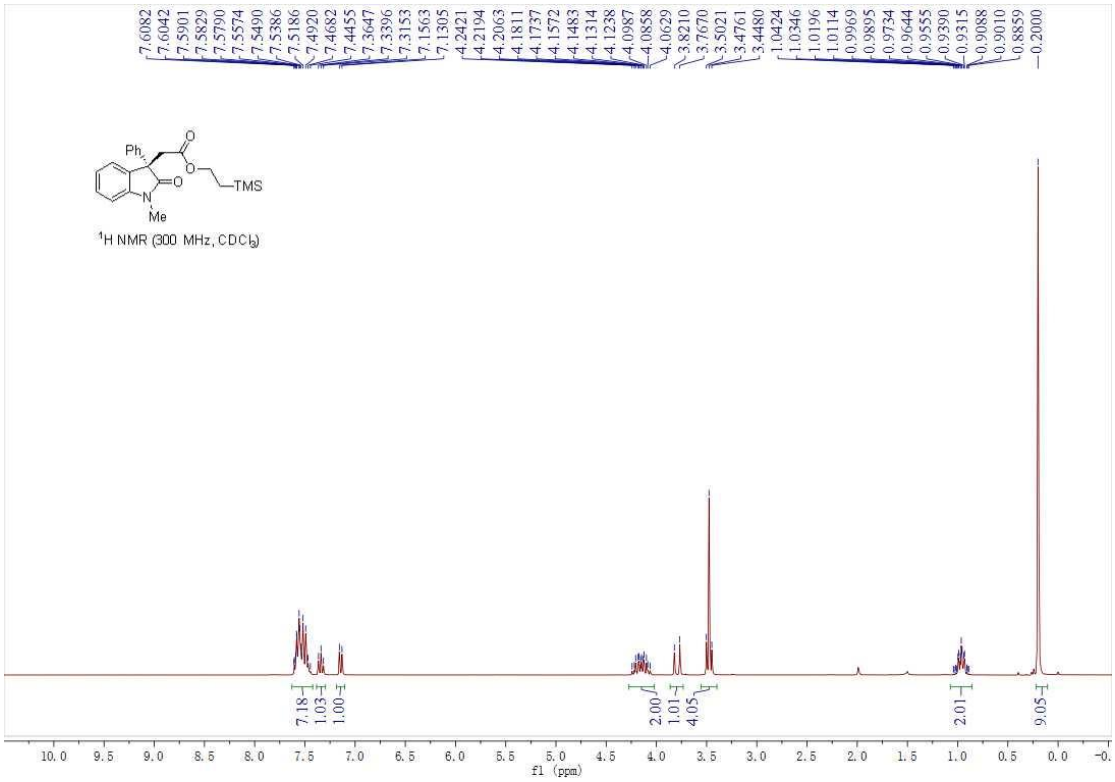
^{1}H NMR of **3w**



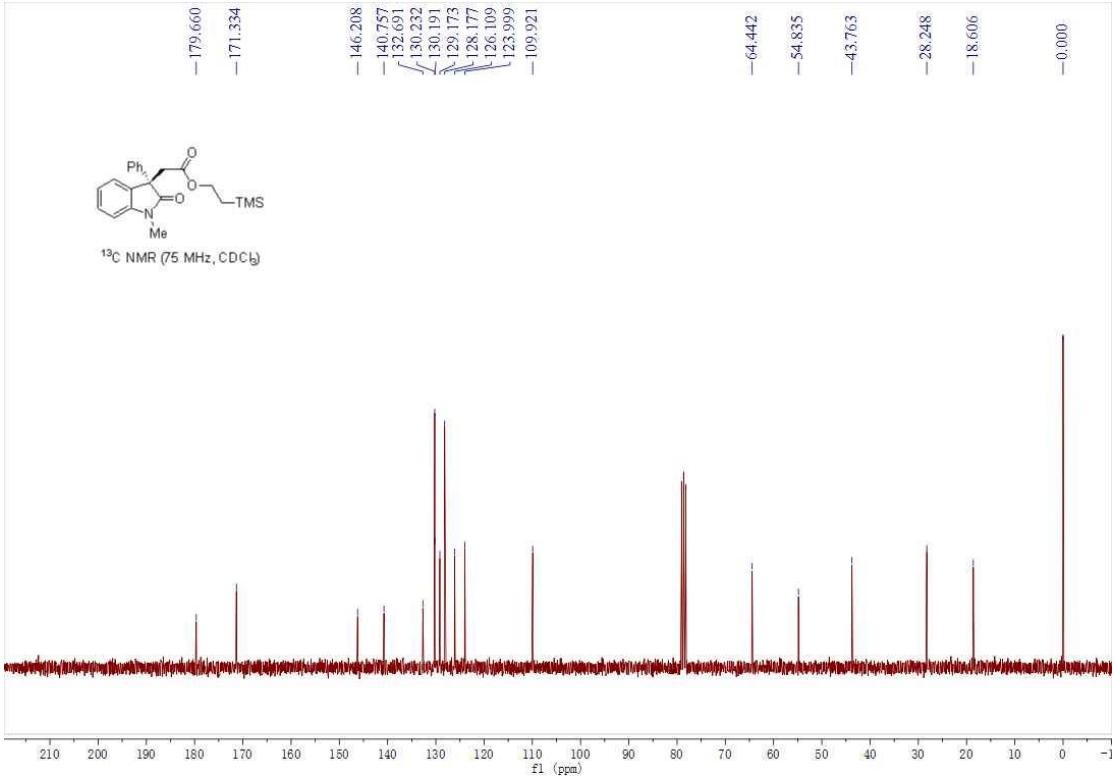
^{13}C NMR of **3w**



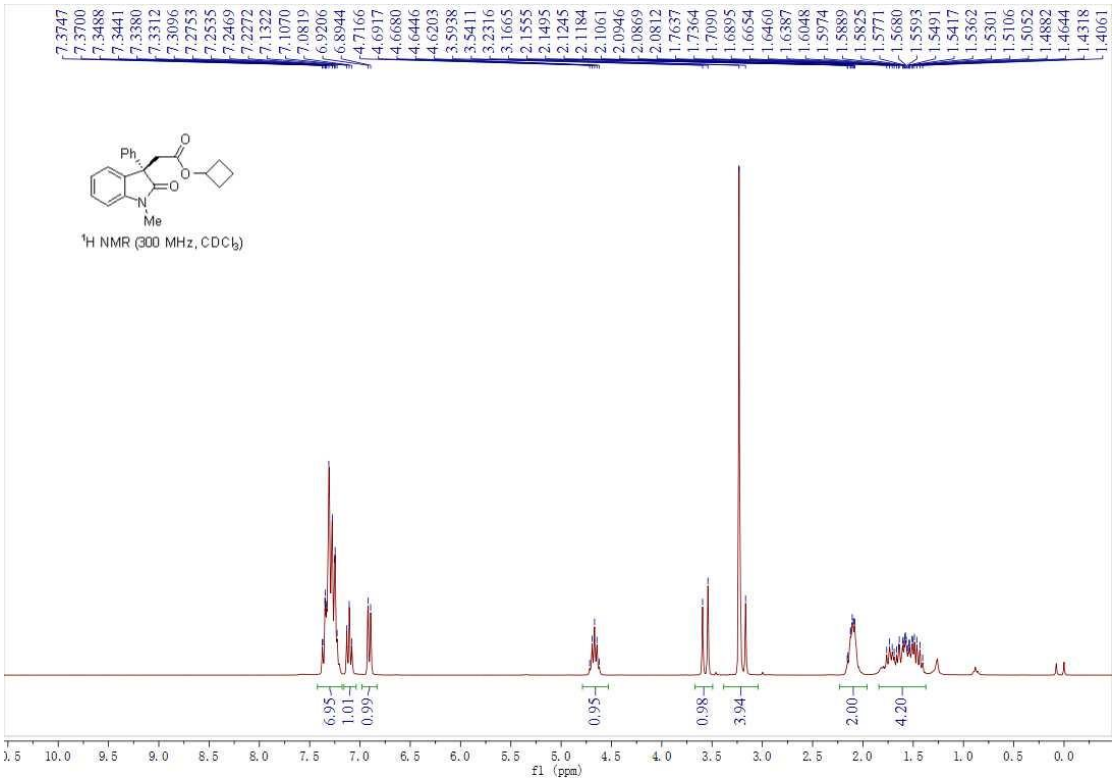
^{1}H NMR of **3x**



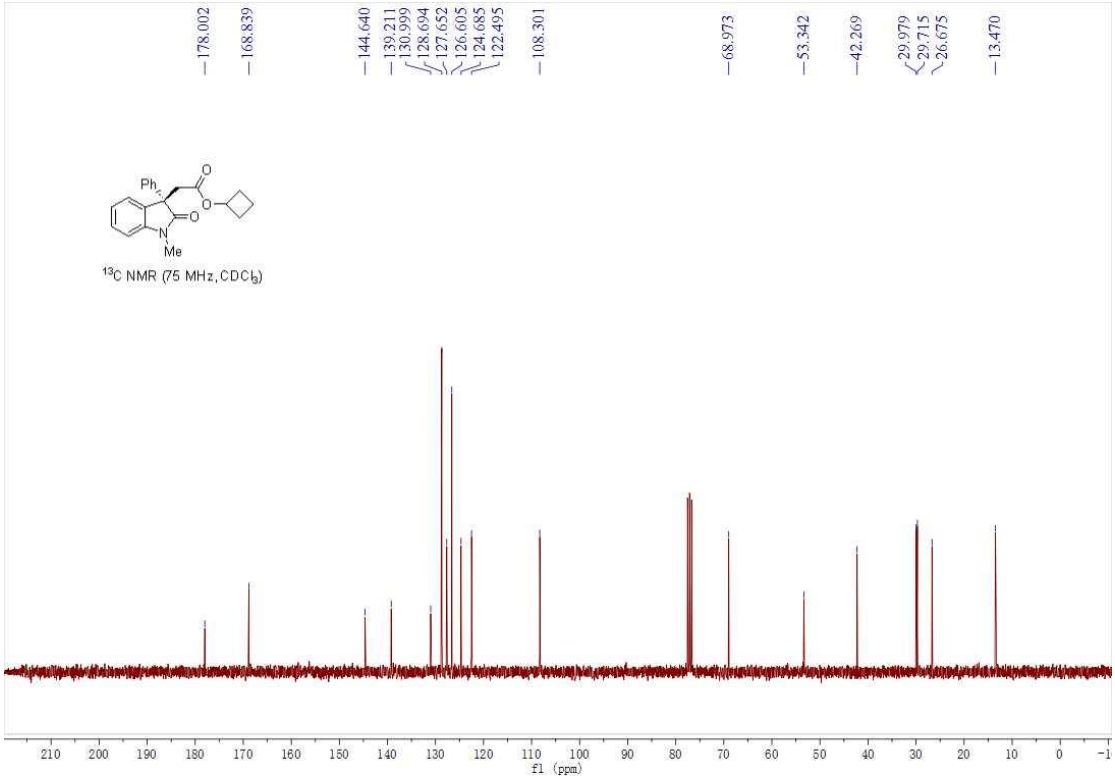
^{13}C NMR of **3x**



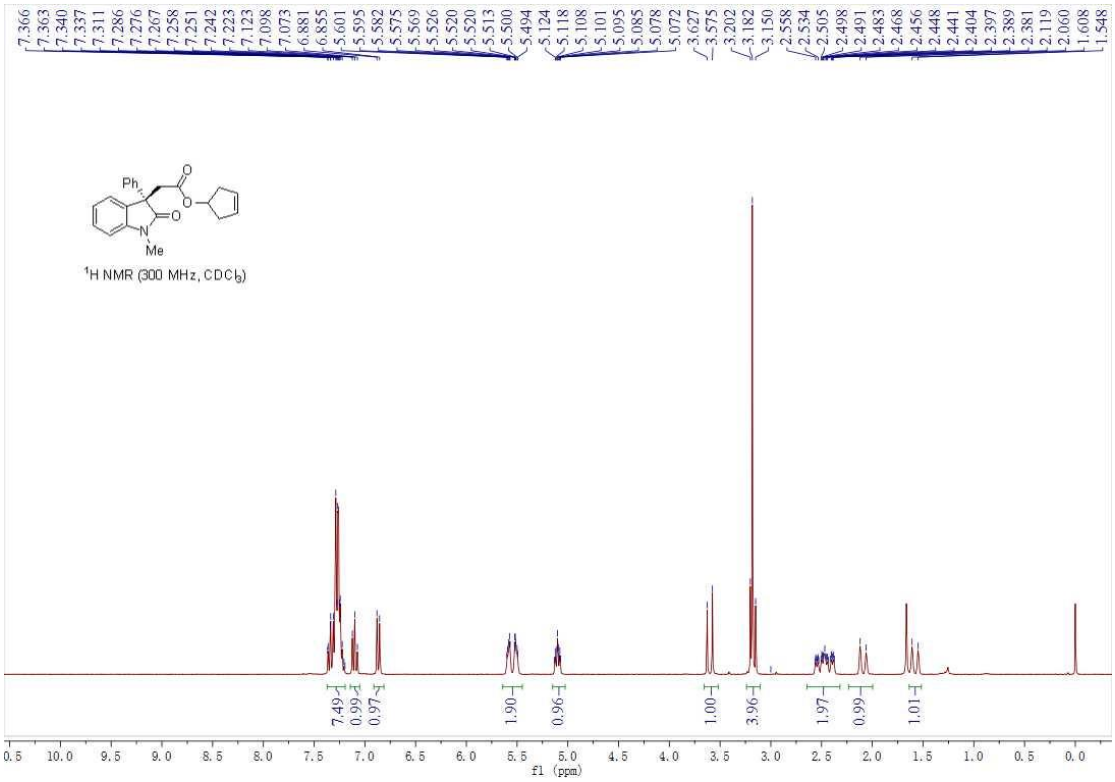
^{1}H NMR of **3y**



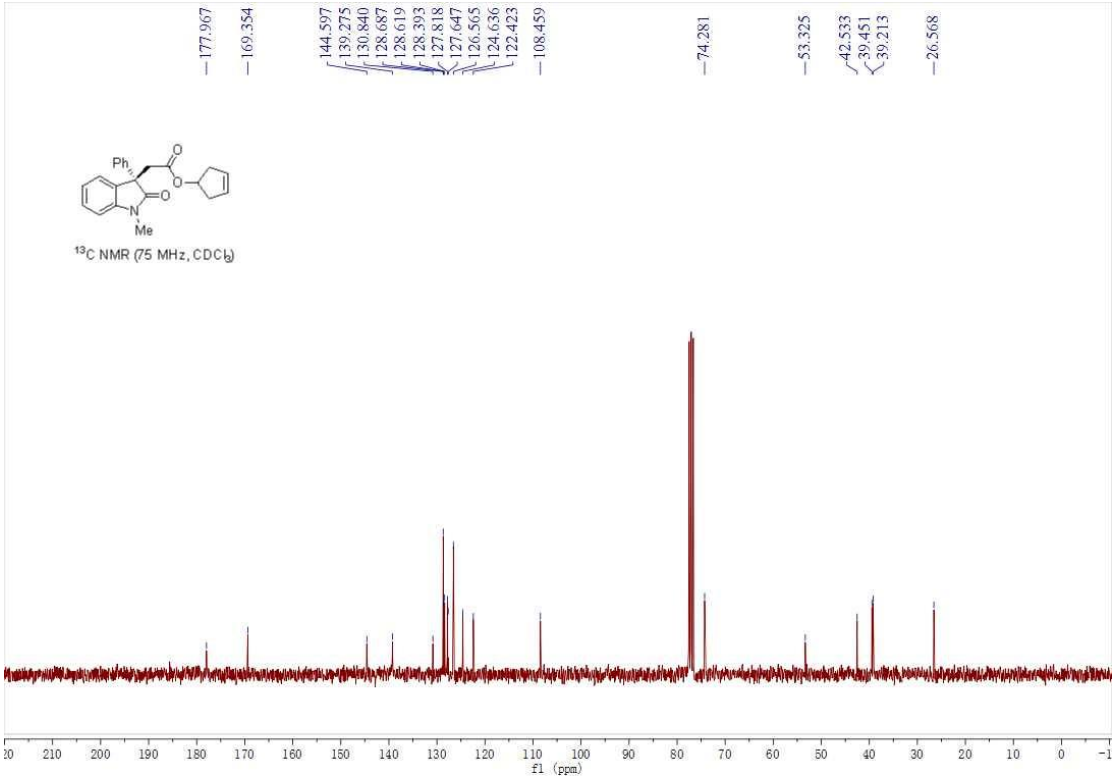
^{13}C NMR of **3y**



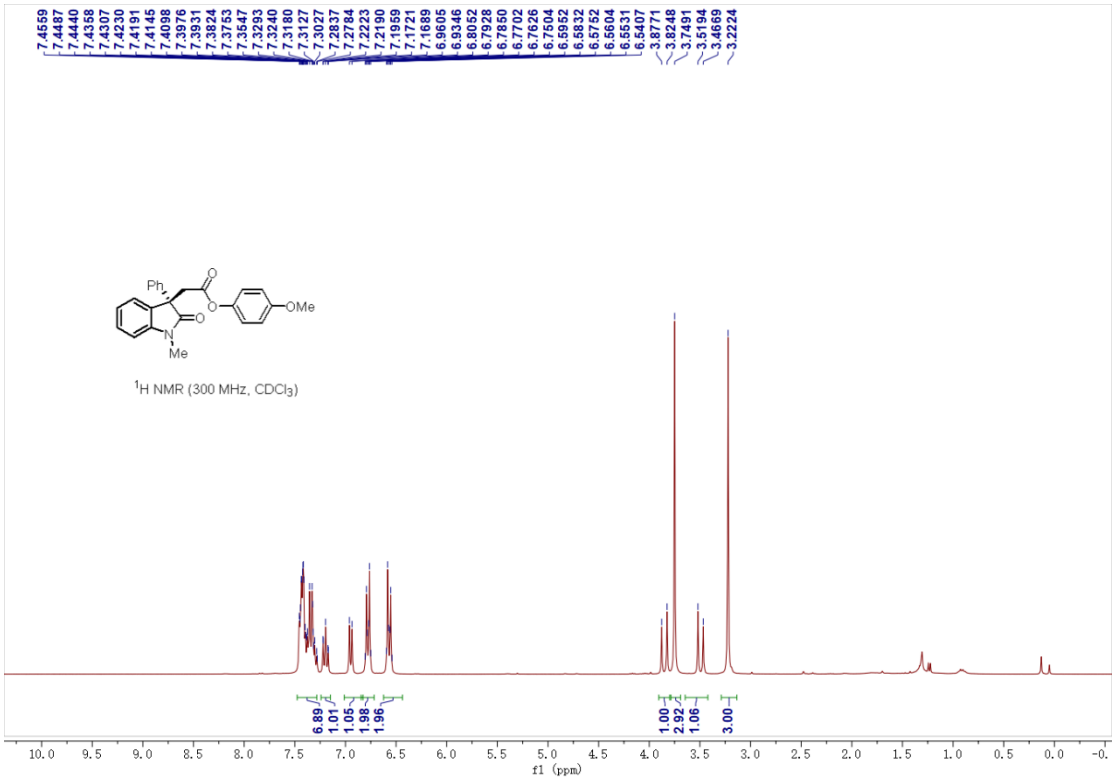
^{1}H NMR of **3z**



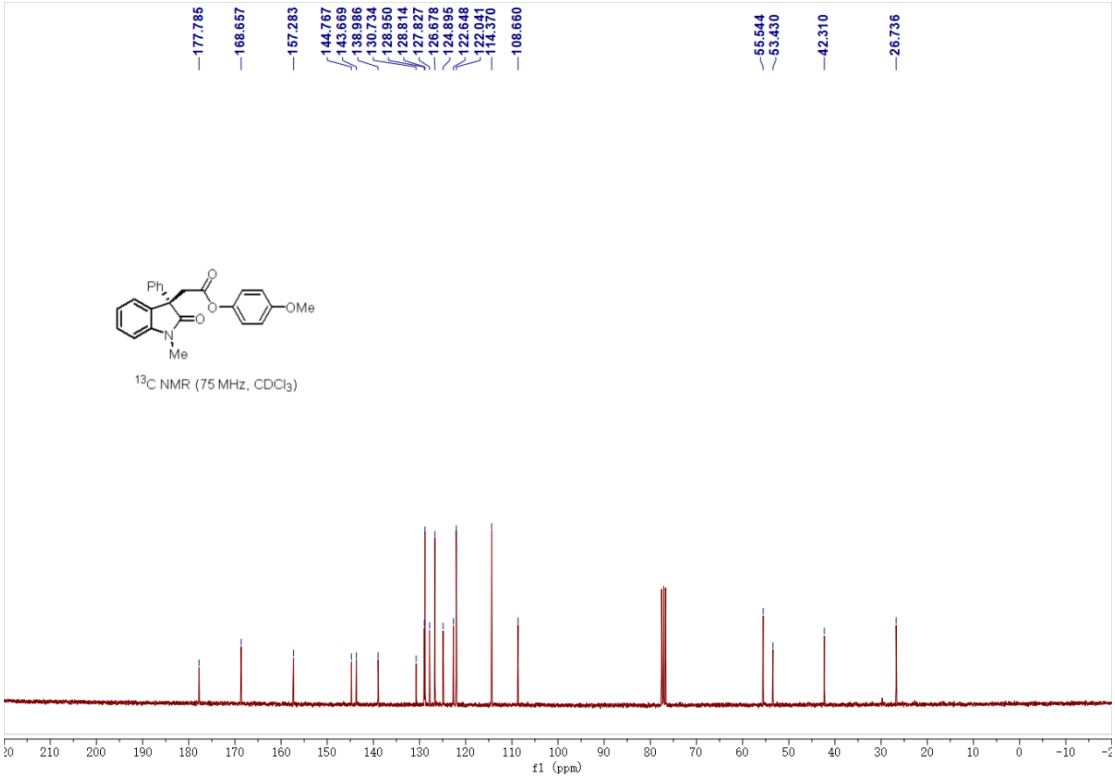
^{13}C NMR of **3z**



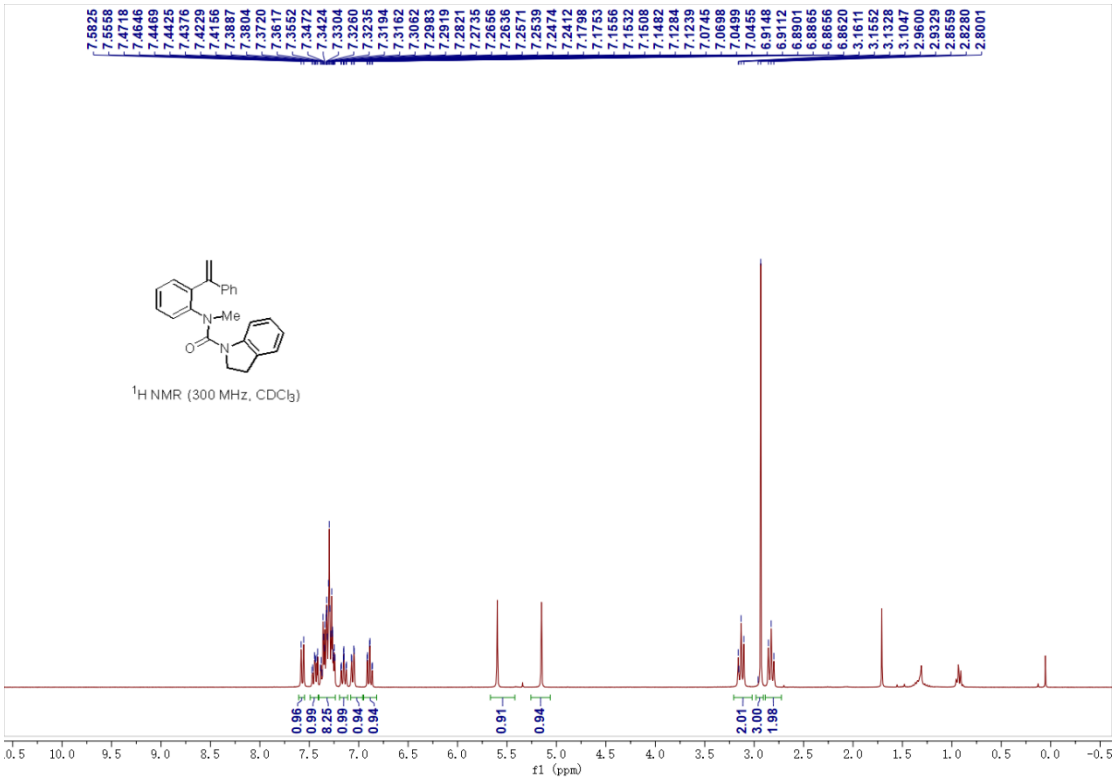
^{1}H NMR of **3aa**



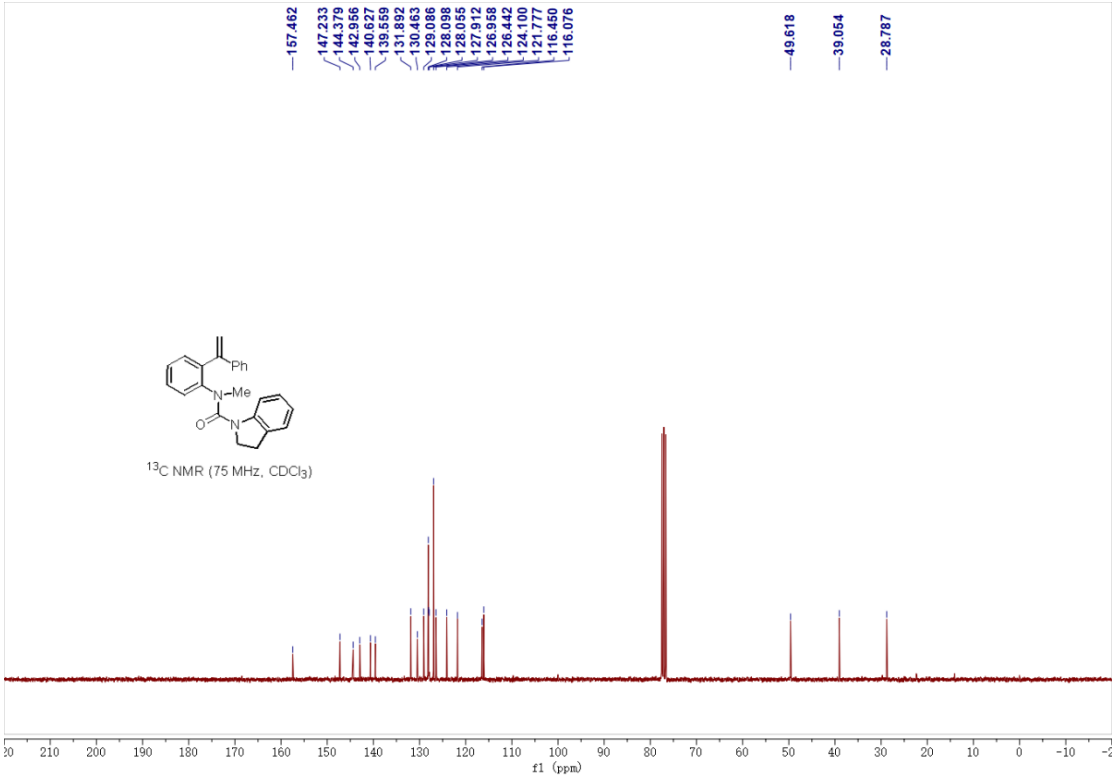
^{13}C NMR of **3aa**



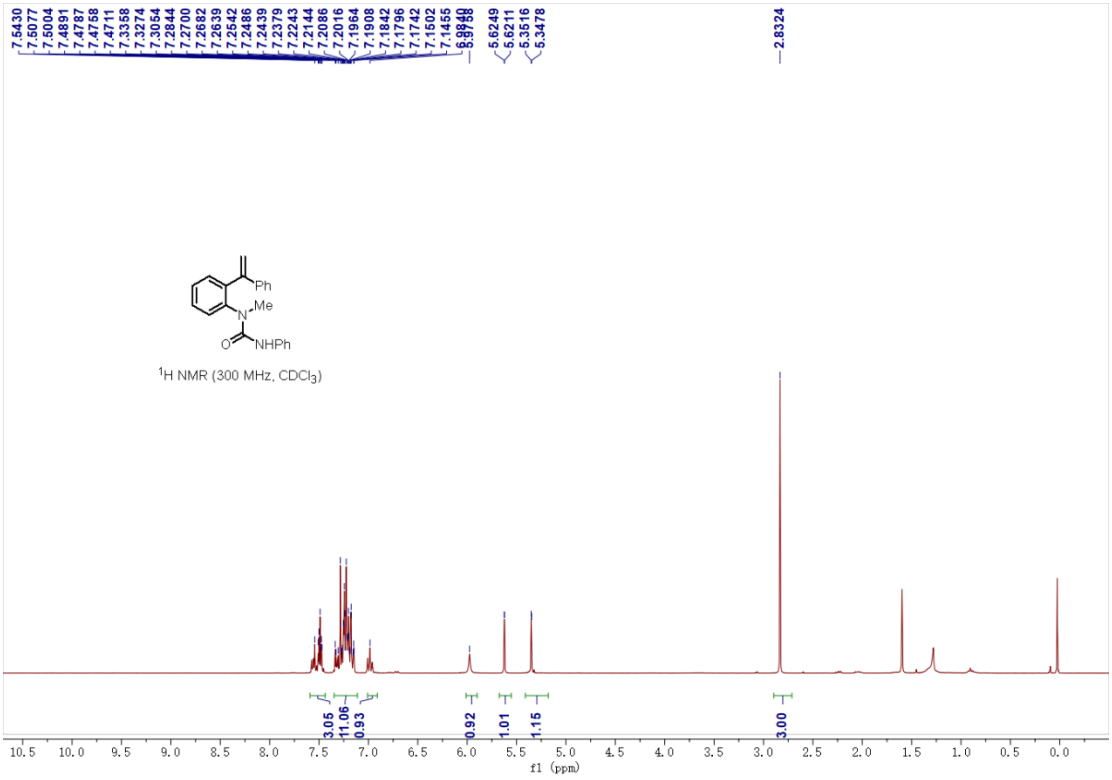
^{1}H NMR of **5b**



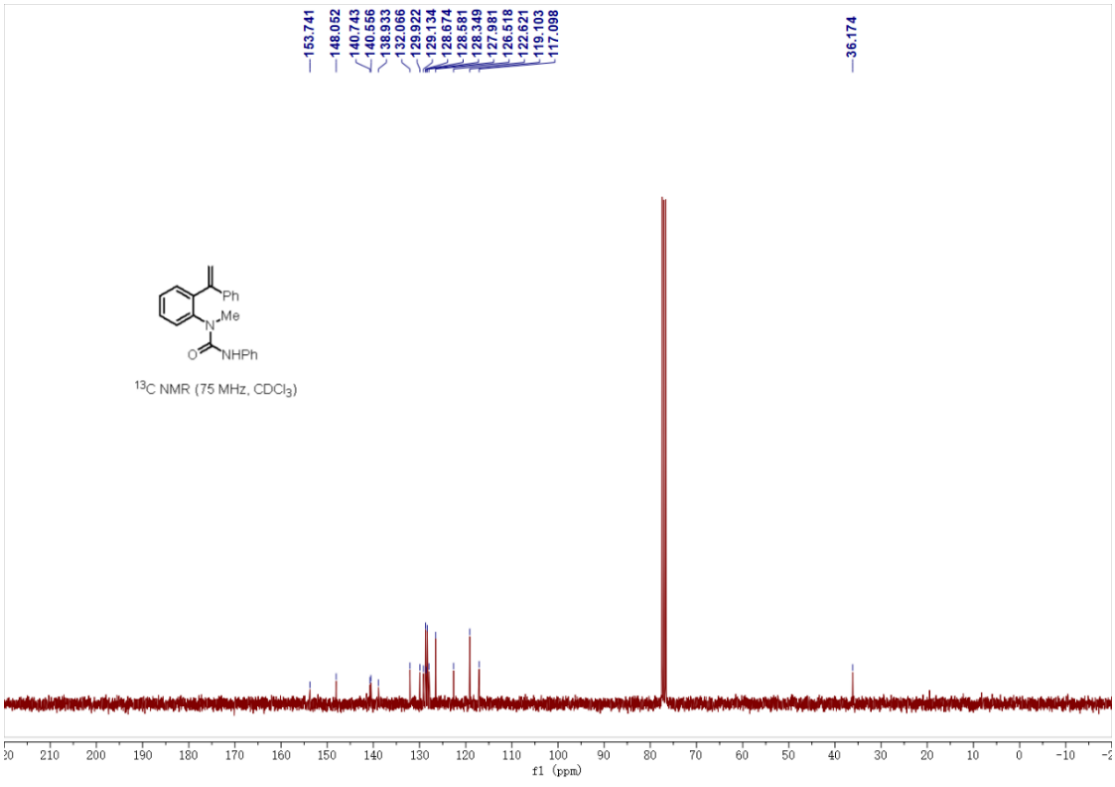
^{13}C NMR of **5b**



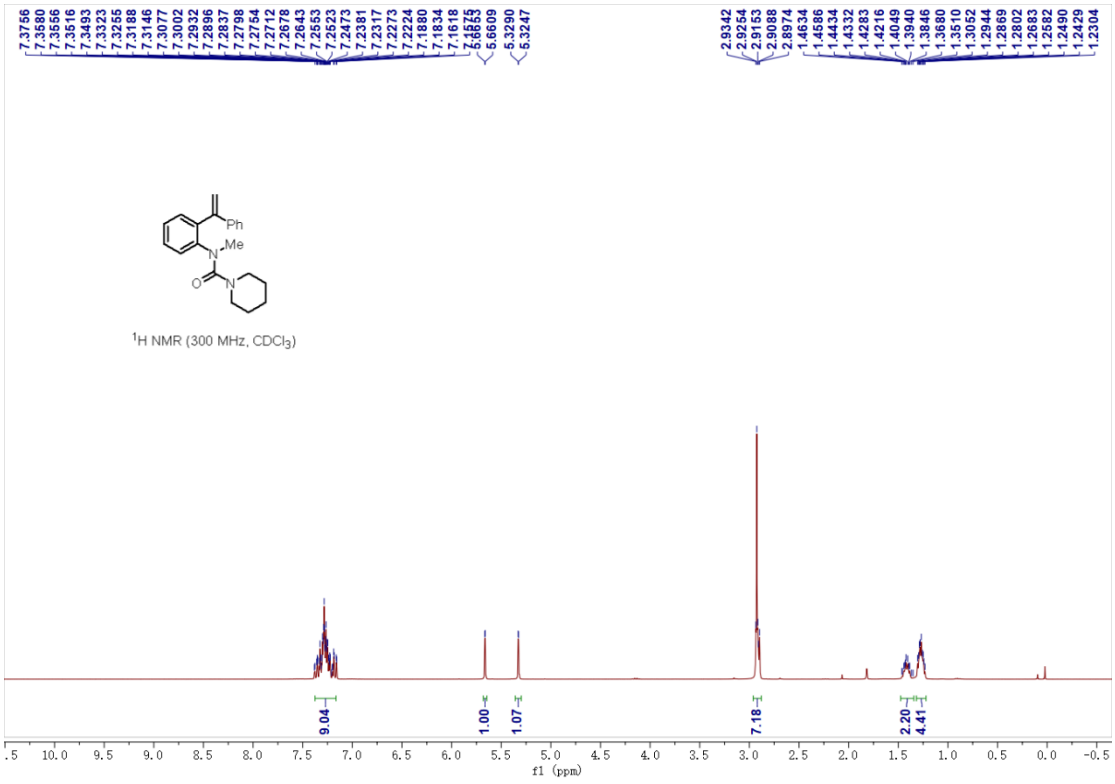
^{1}H NMR of **5c**



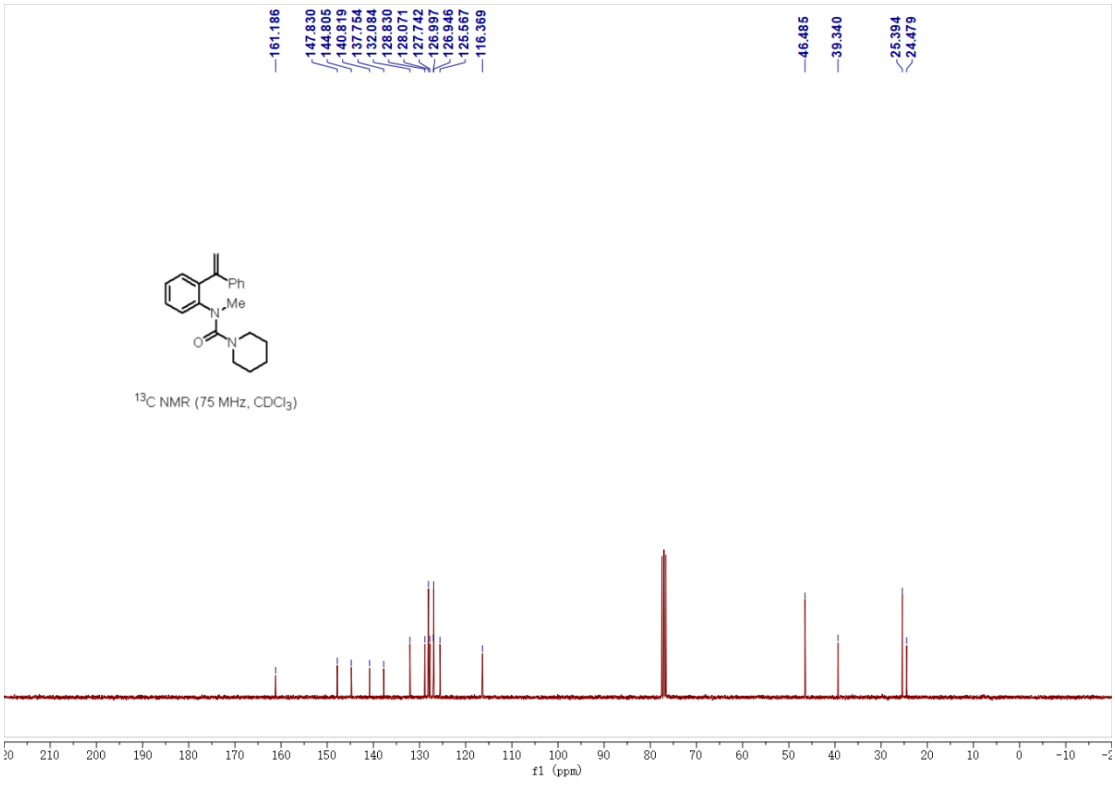
^{13}C NMR of **5c**



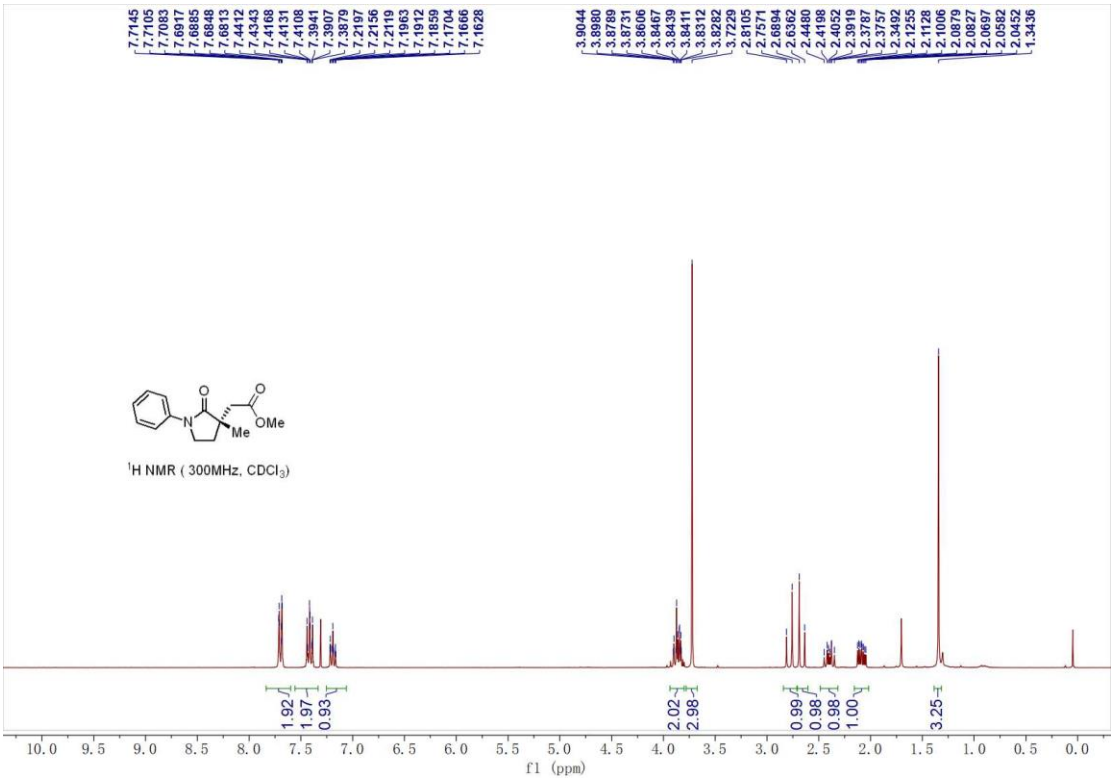
^{1}H NMR of **5d**



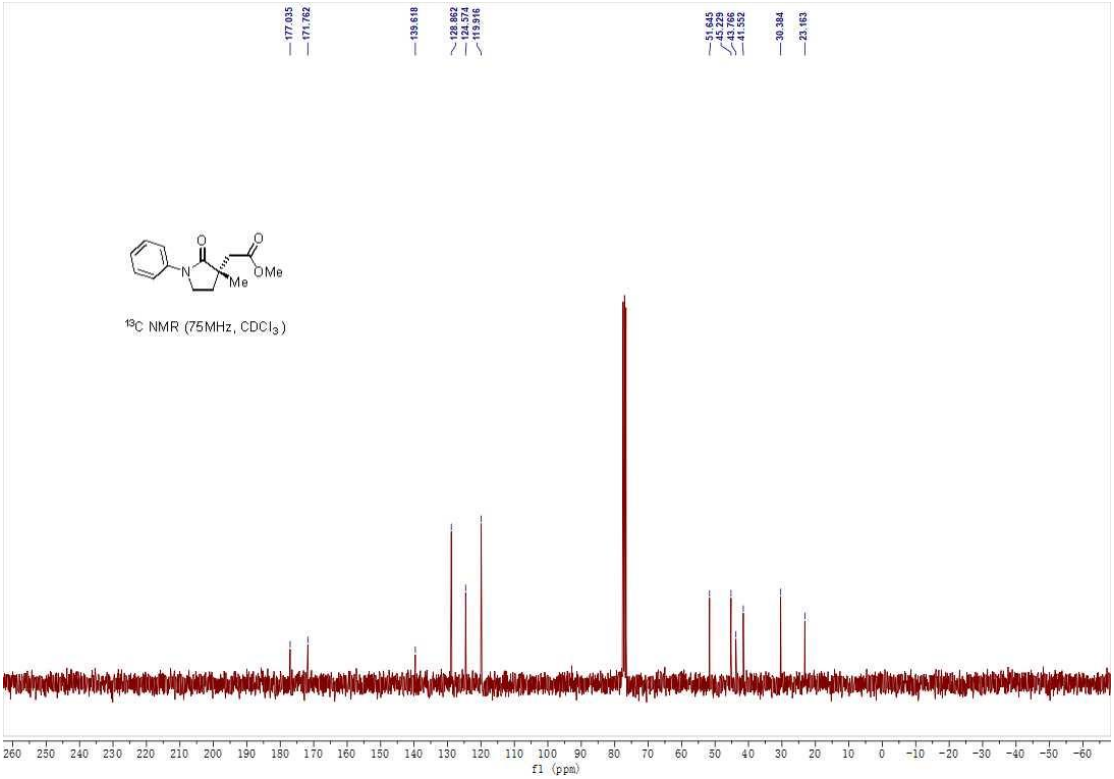
^{13}C NMR of **5d**



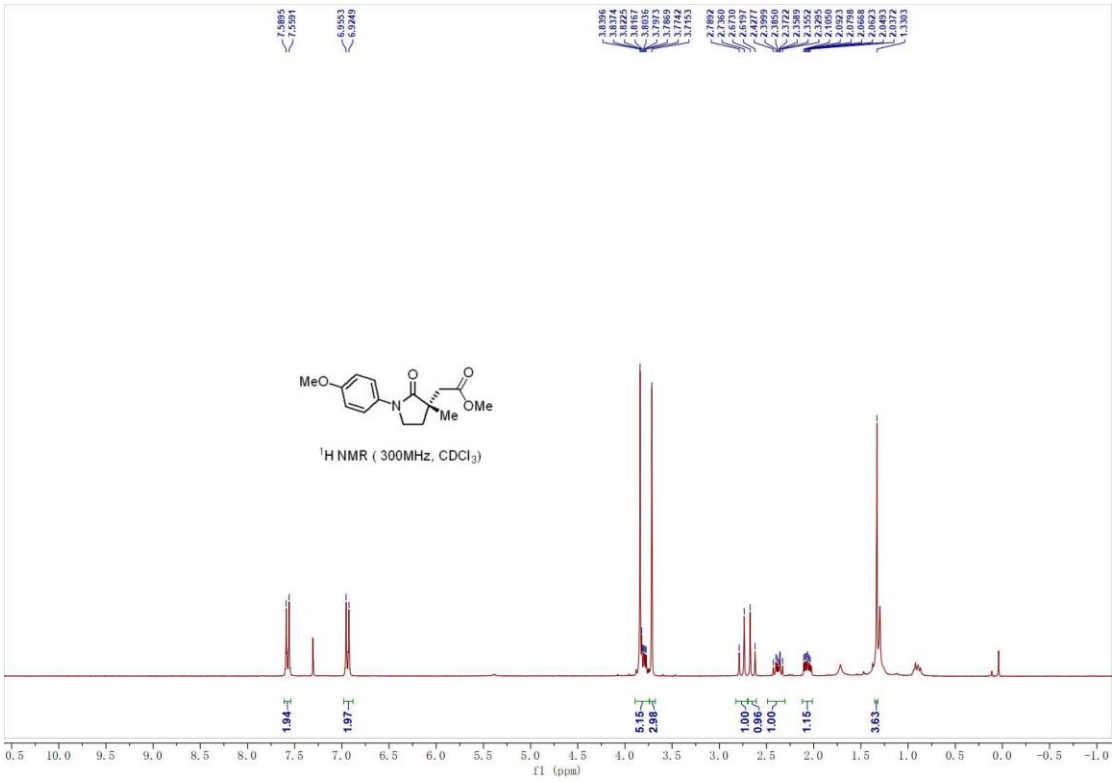
^{1}H NMR of **7a**



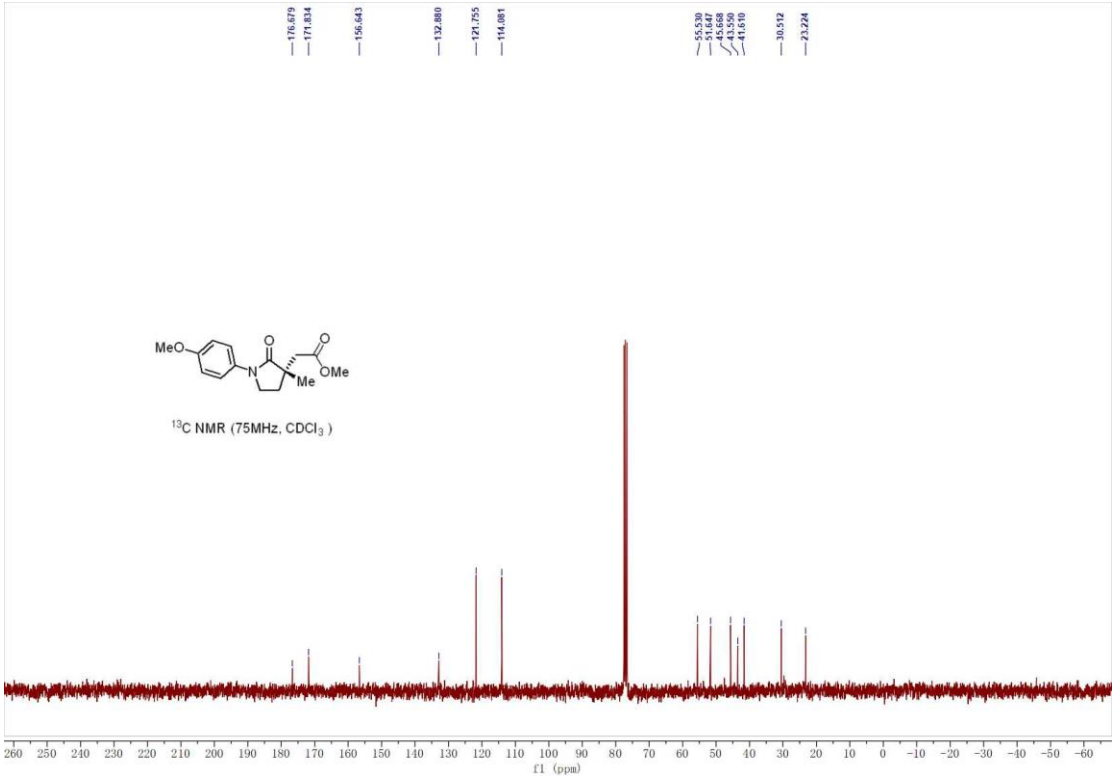
^{13}C NMR of **7a**



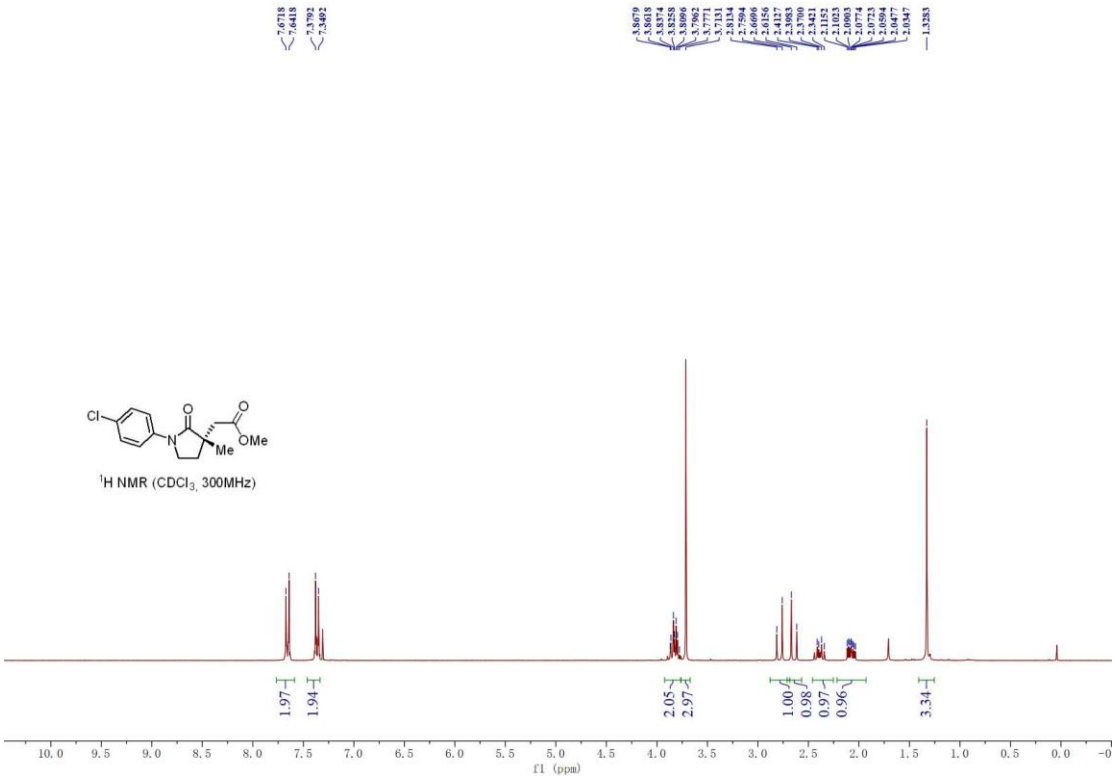
^{1}H NMR of **7b**



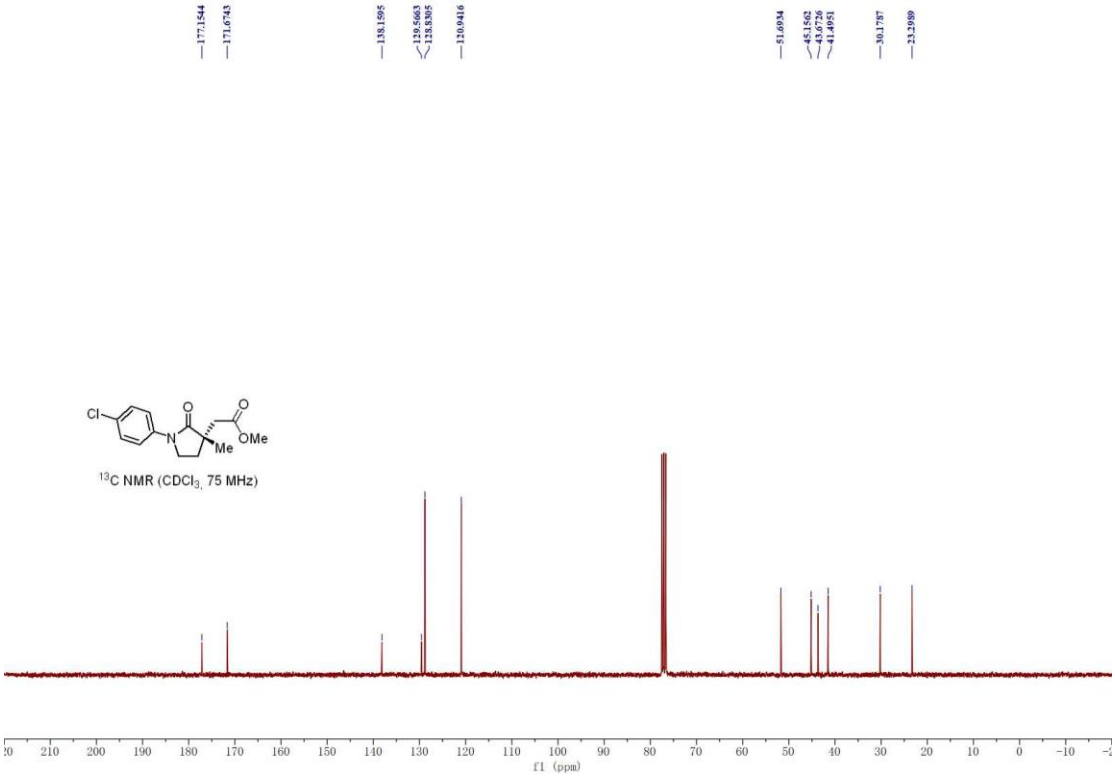
^{13}C NMR of **7b**



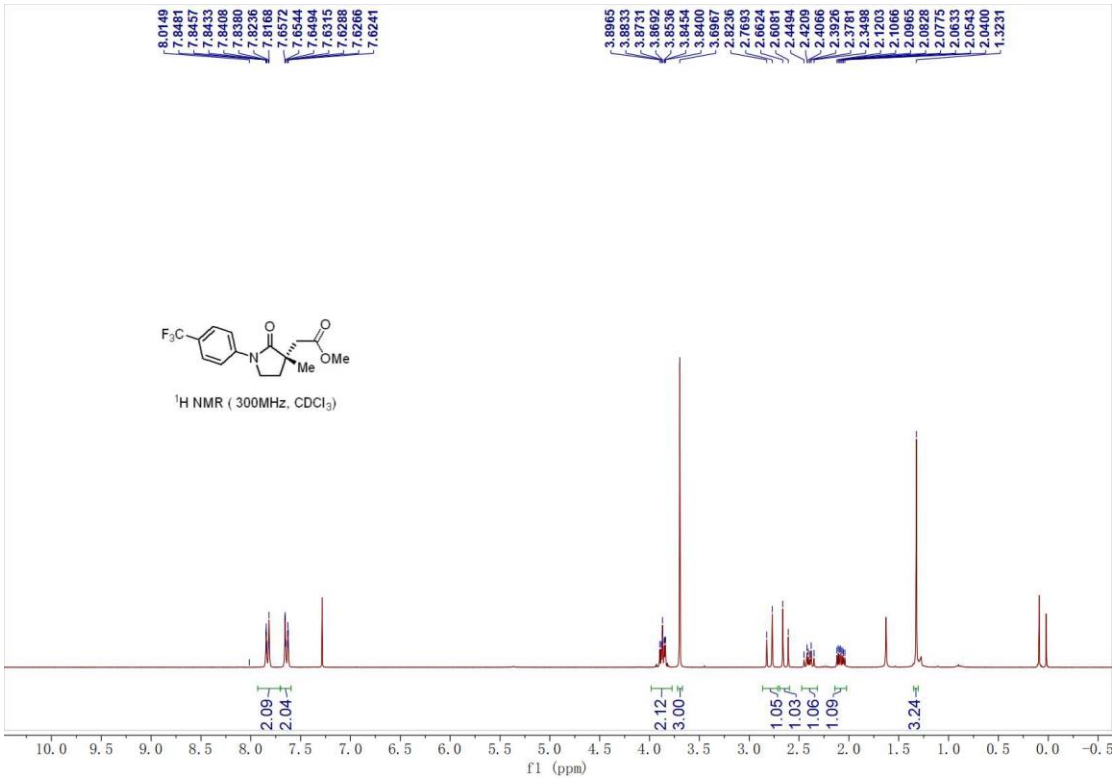
^{1}H NMR of **7c**



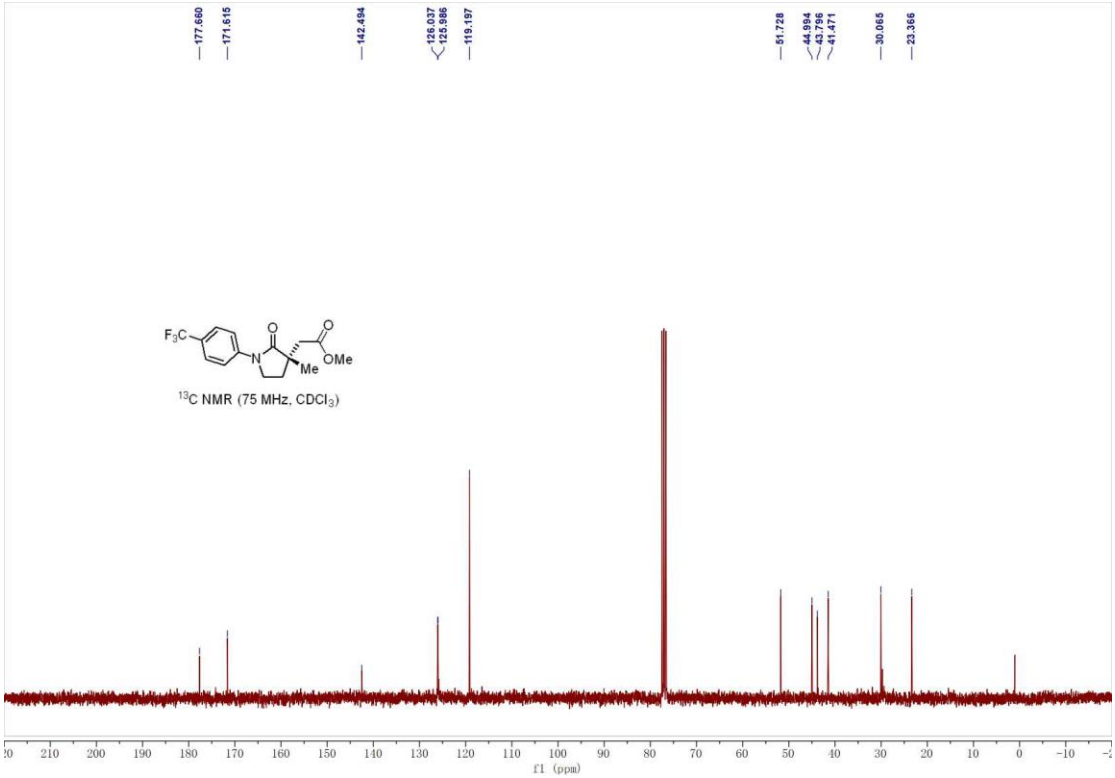
^{13}C NMR of **7c**



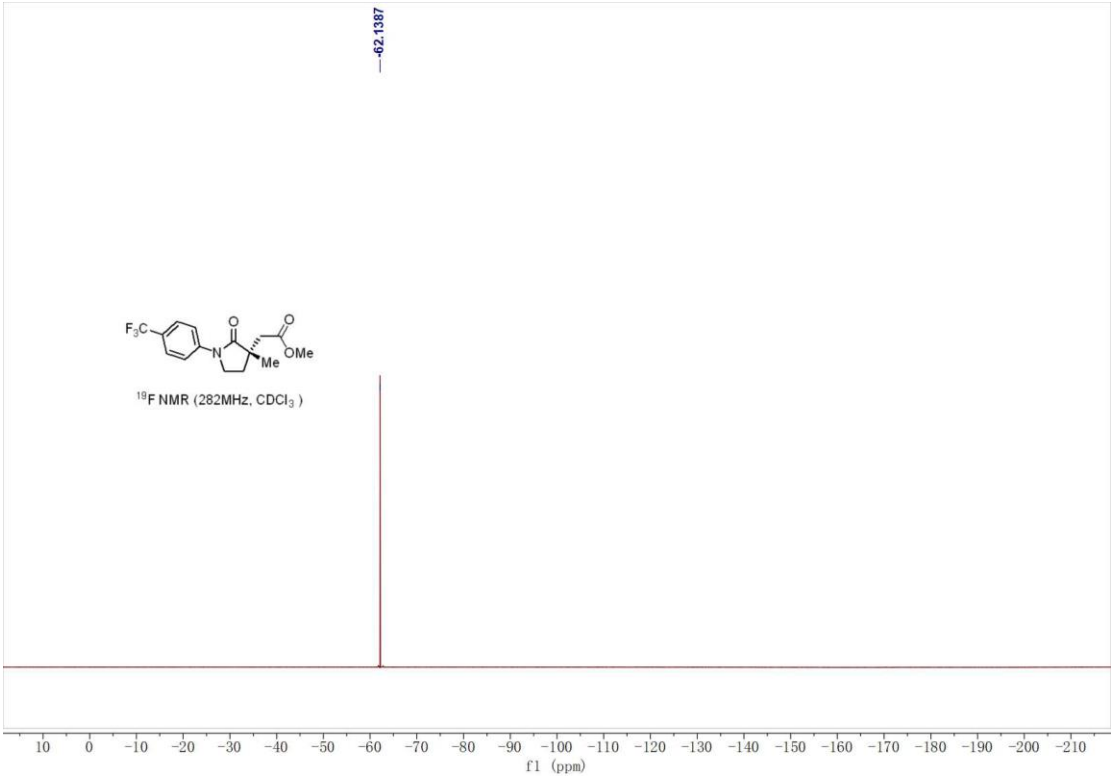
^{1}H NMR of **7d**



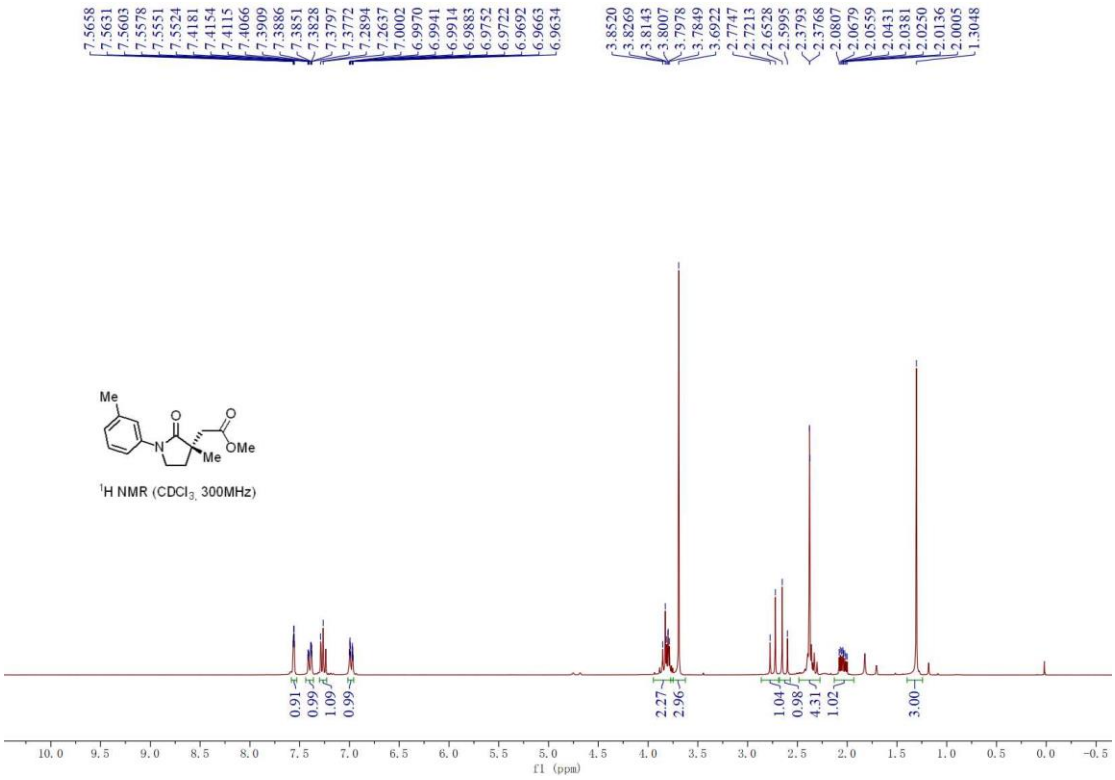
^{13}C NMR of **7d**



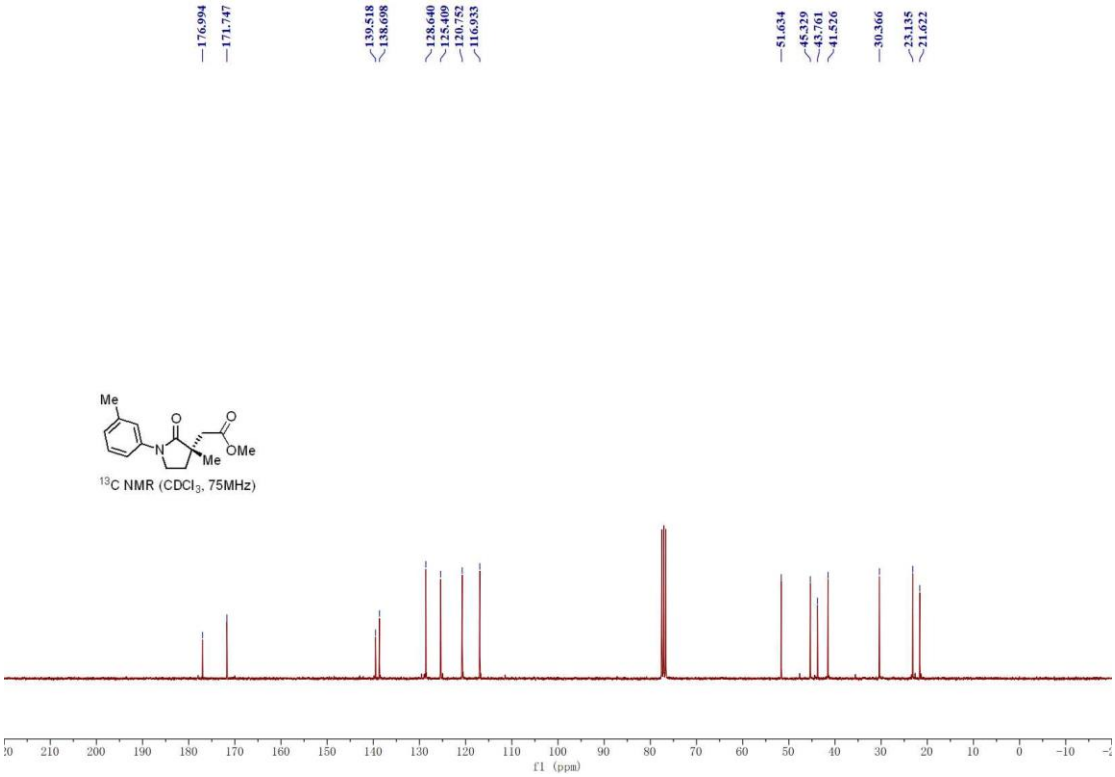
^{19}F NMR of **7d**


-62.1387
F3C
O
N
Me
O
OMe
19F NMR (282MHz, CDCl3)
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

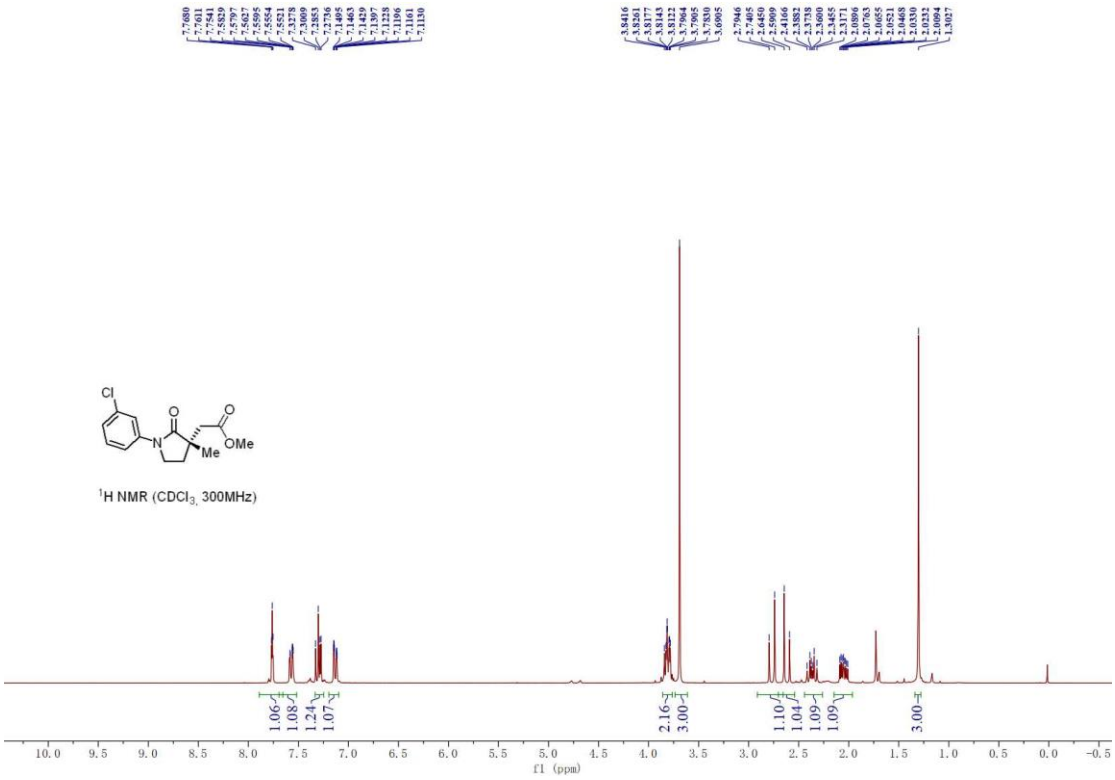
^{1}H NMR of **7e**



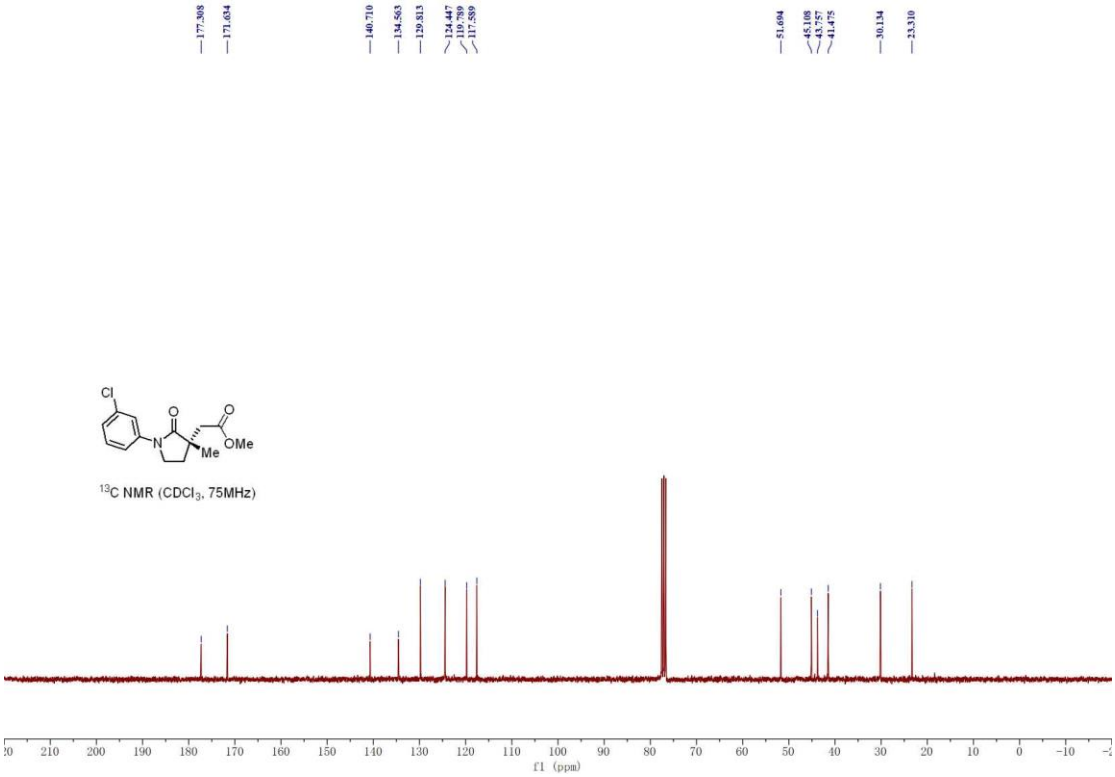
^{13}C NMR of **7e**



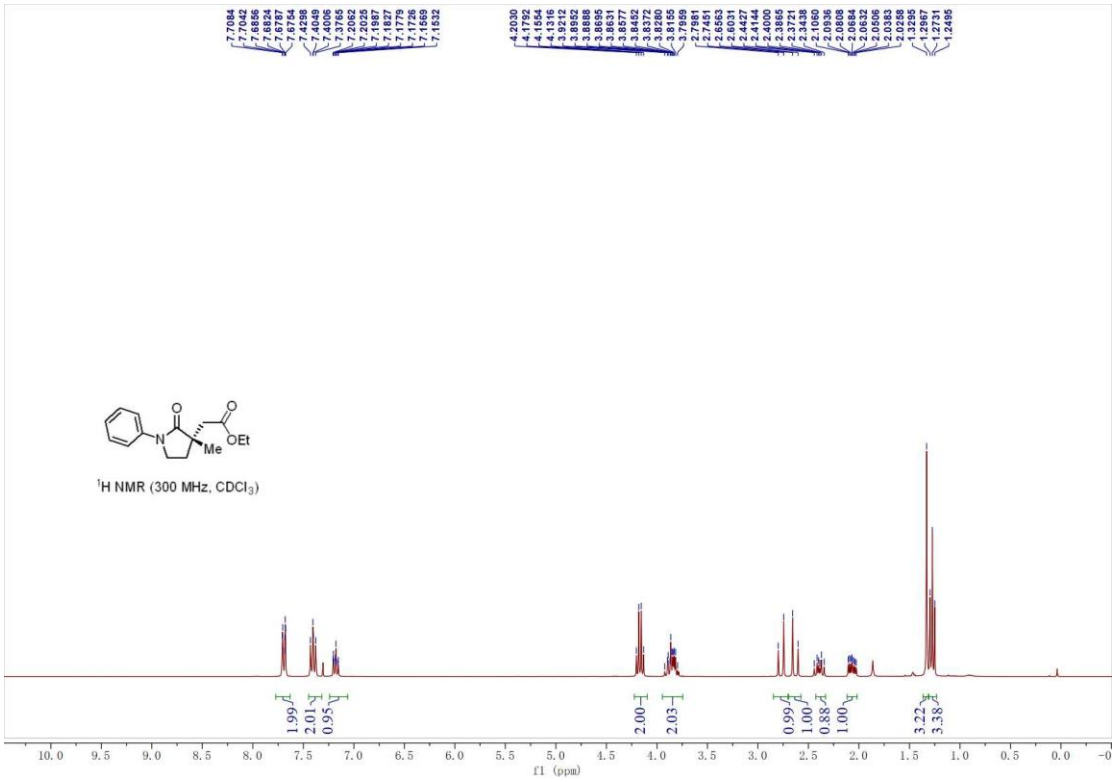
^{1}H NMR of **7f**



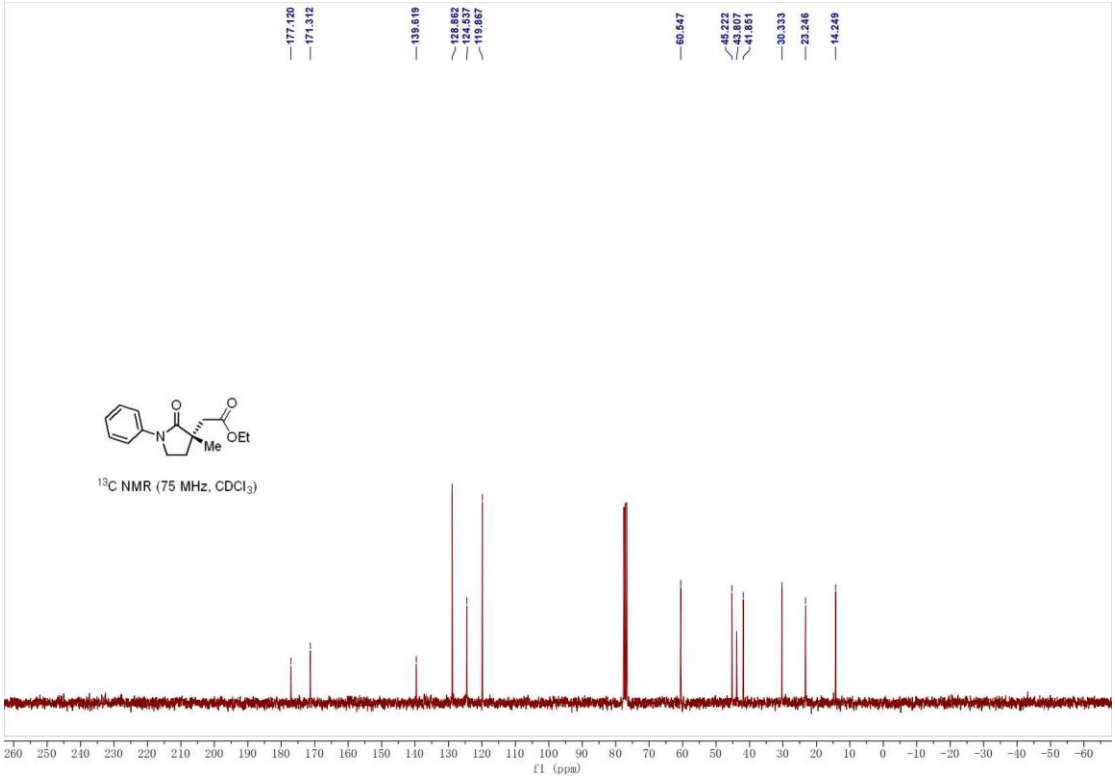
^{13}C NMR of **7f**



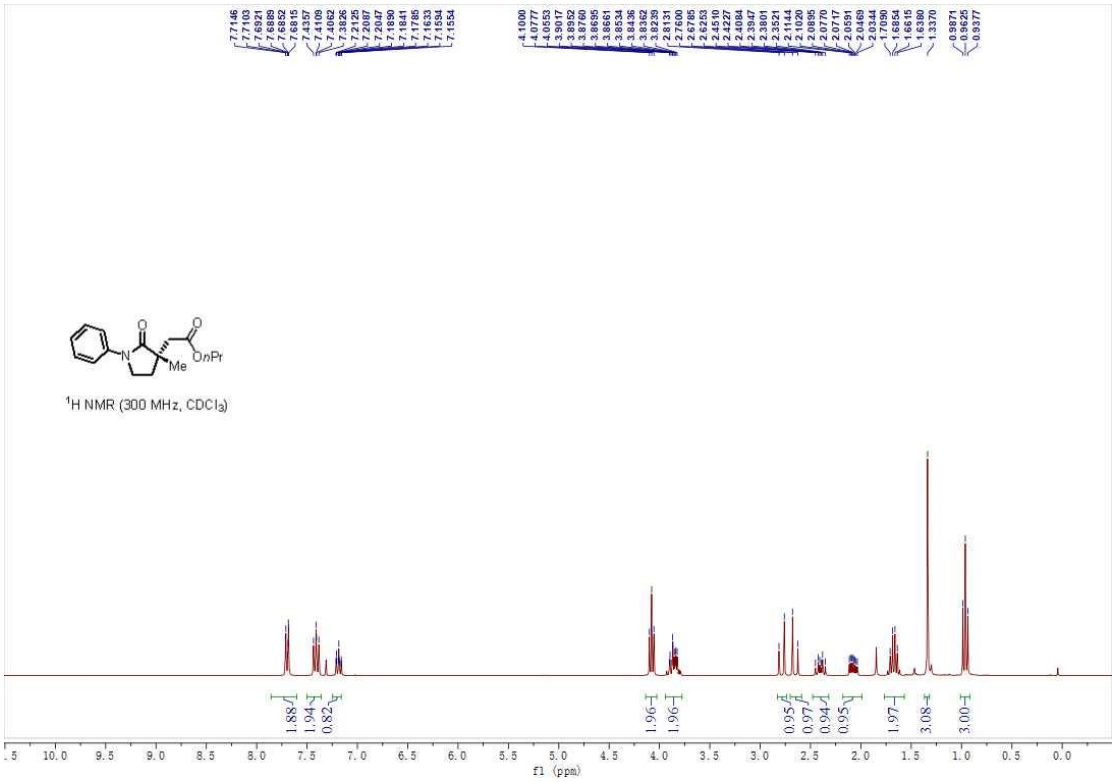
^{1}H NMR of **7g**



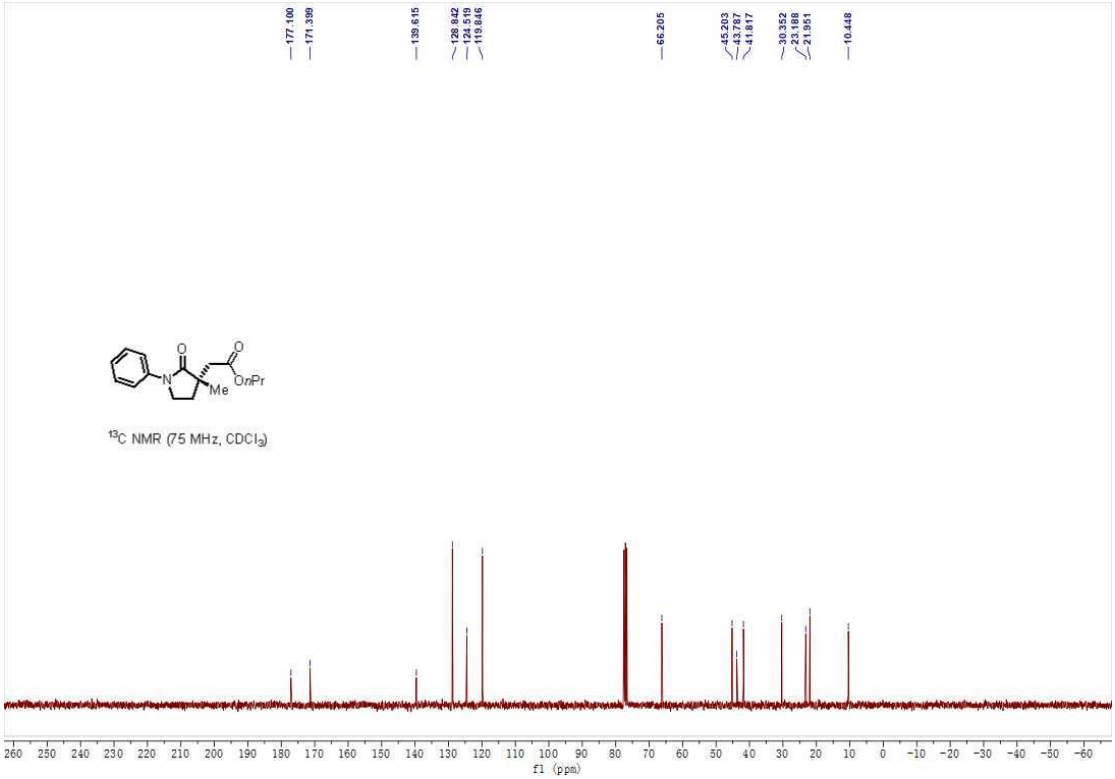
^{13}C NMR of **7g**



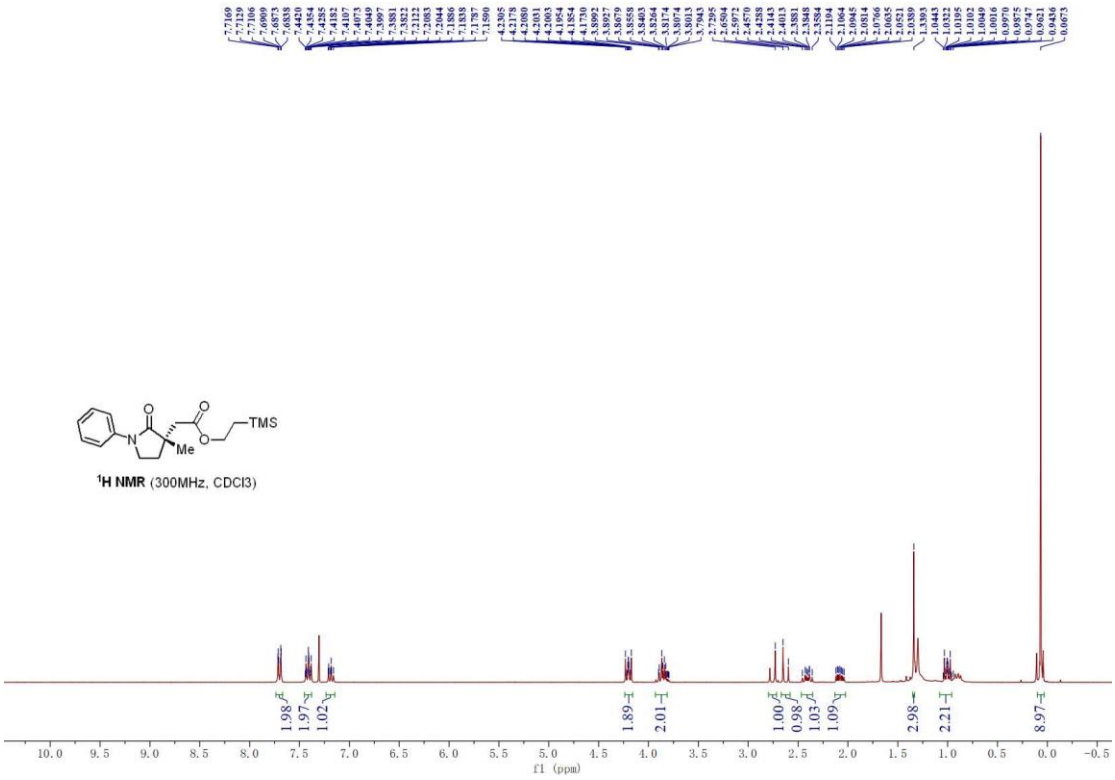
^{1}H NMR of **7h**



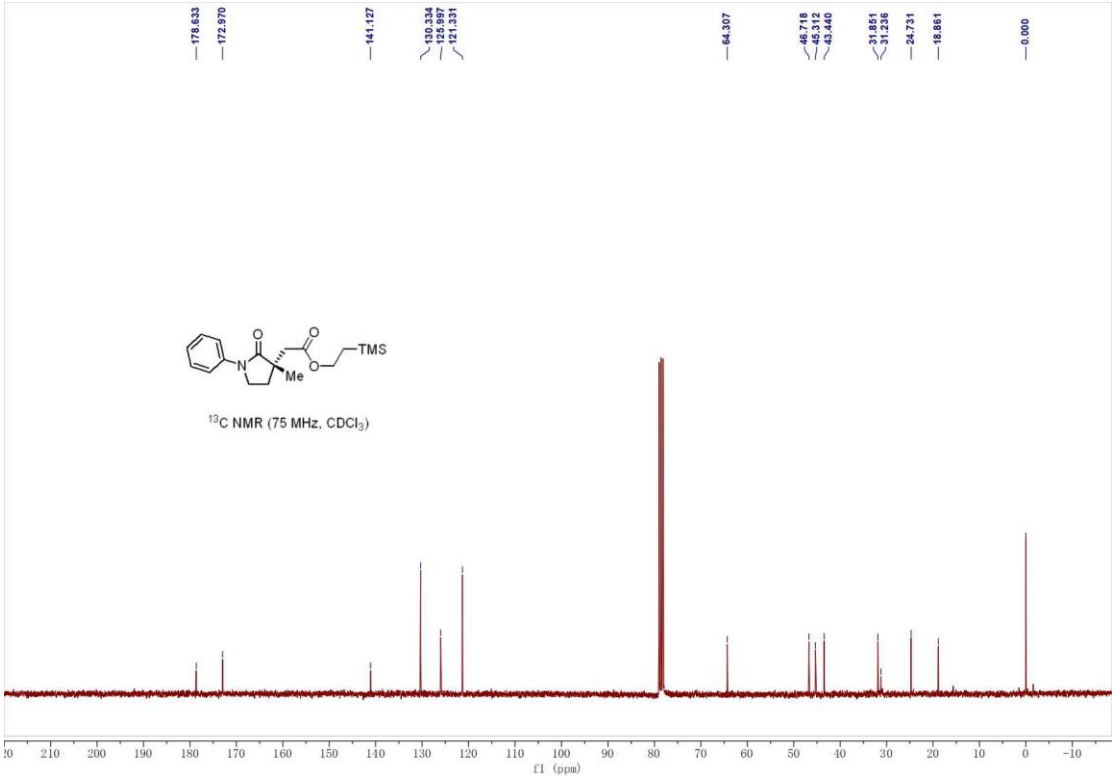
^{13}C NMR of **7h**



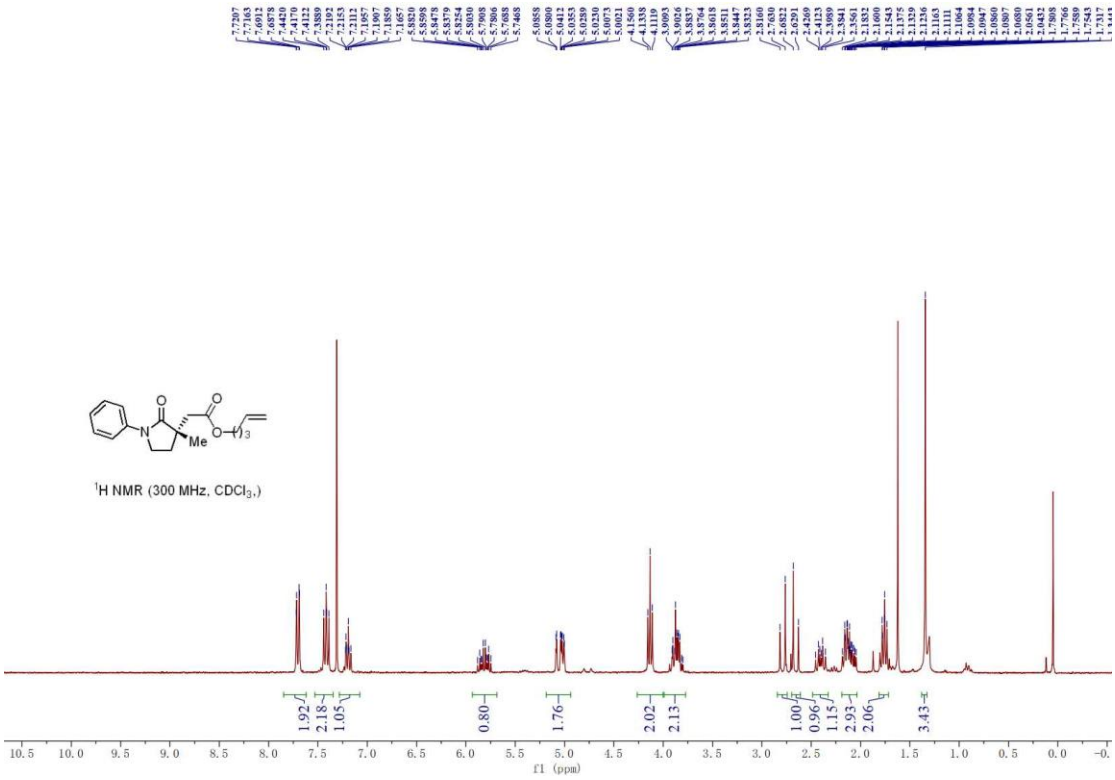
^{1}H NMR of **7i**



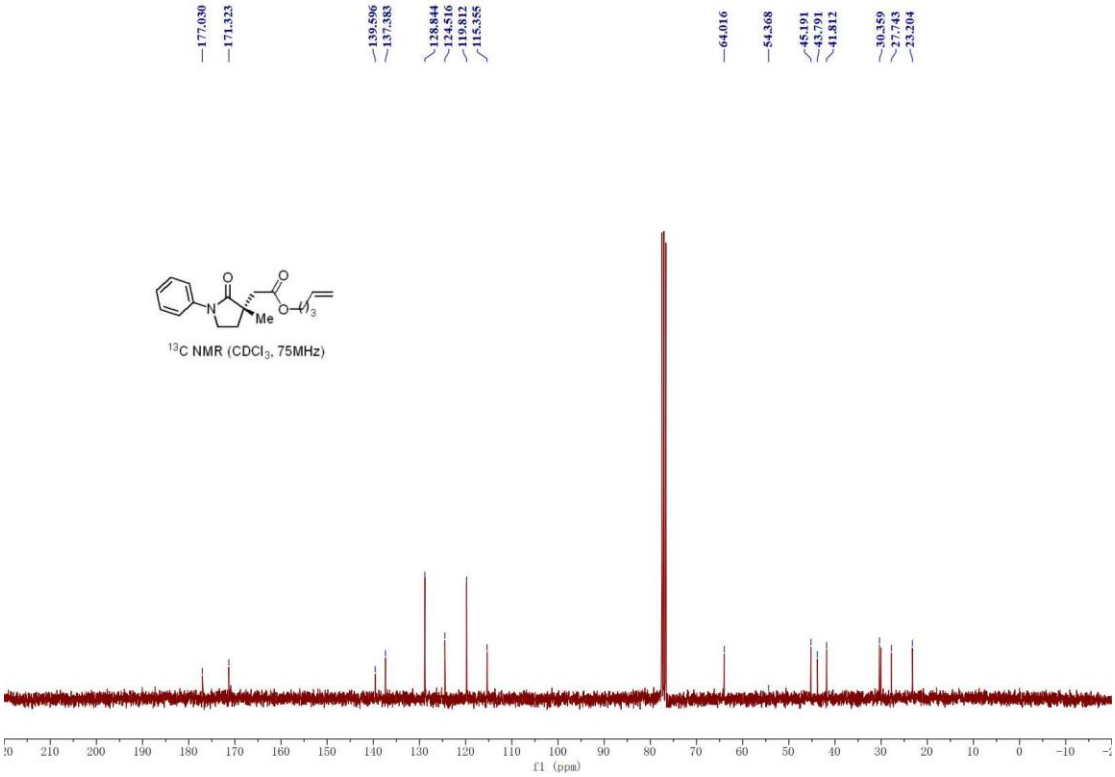
^{13}C NMR of **7i**



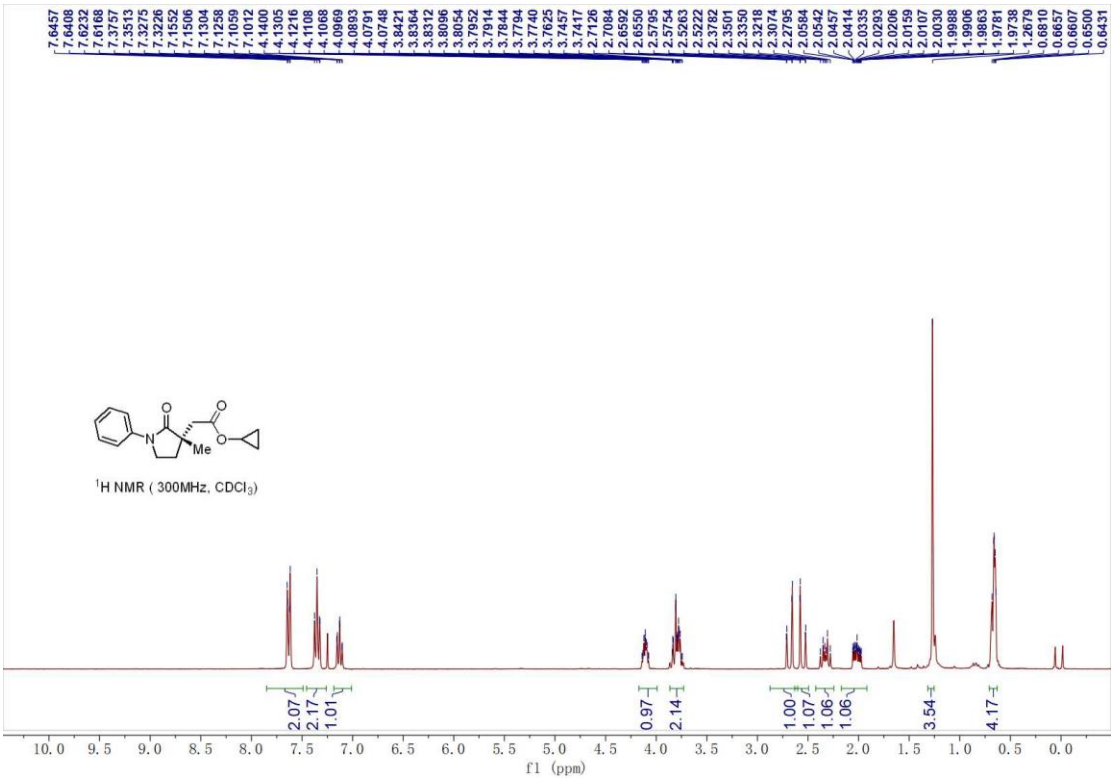
^{1}H NMR of **7j**



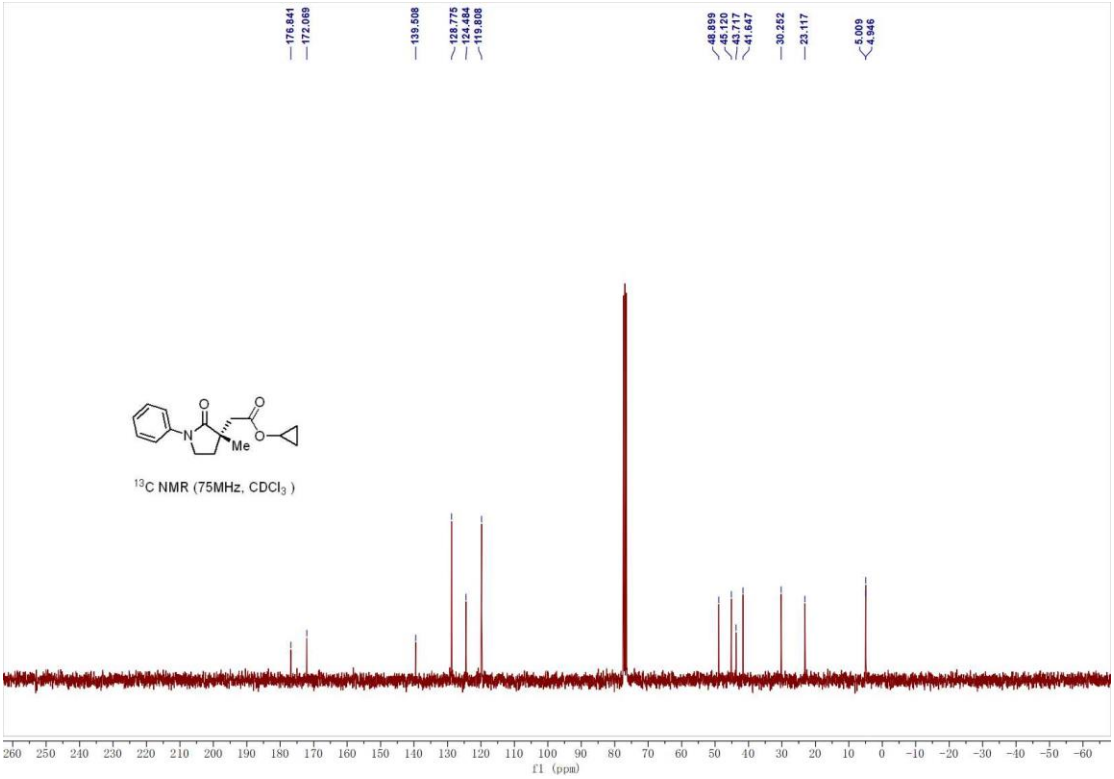
^{13}C NMR of **7j**



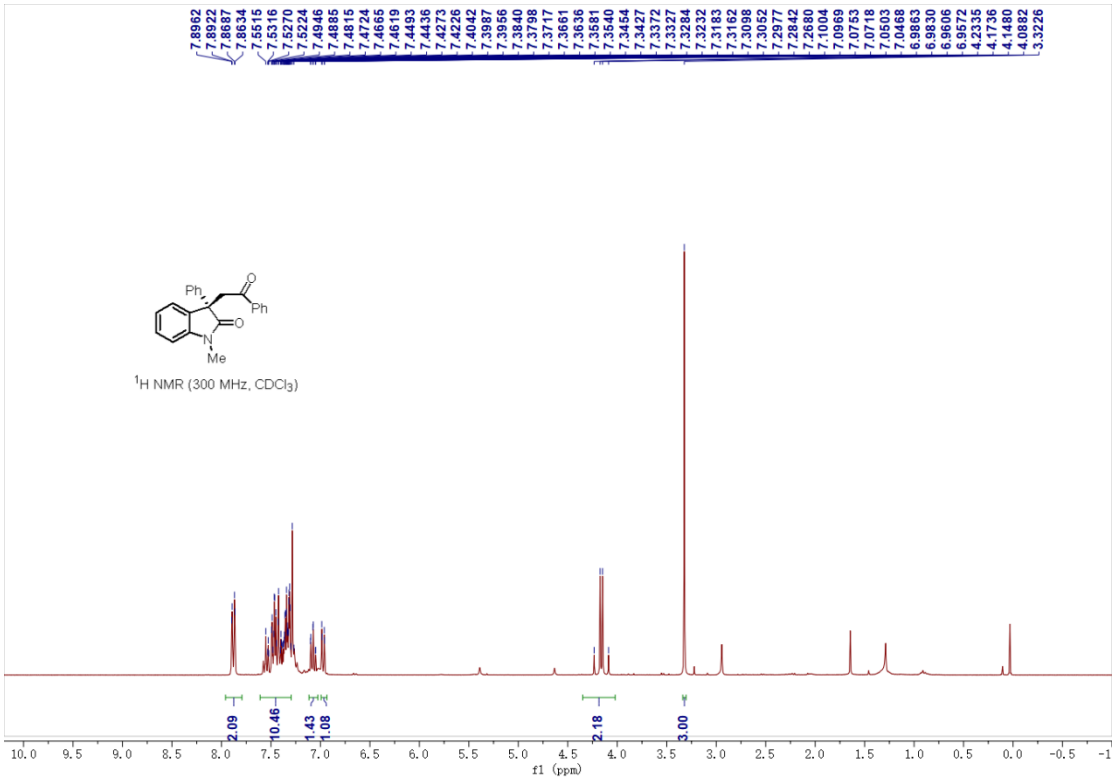
^{1}H NMR of **7k**



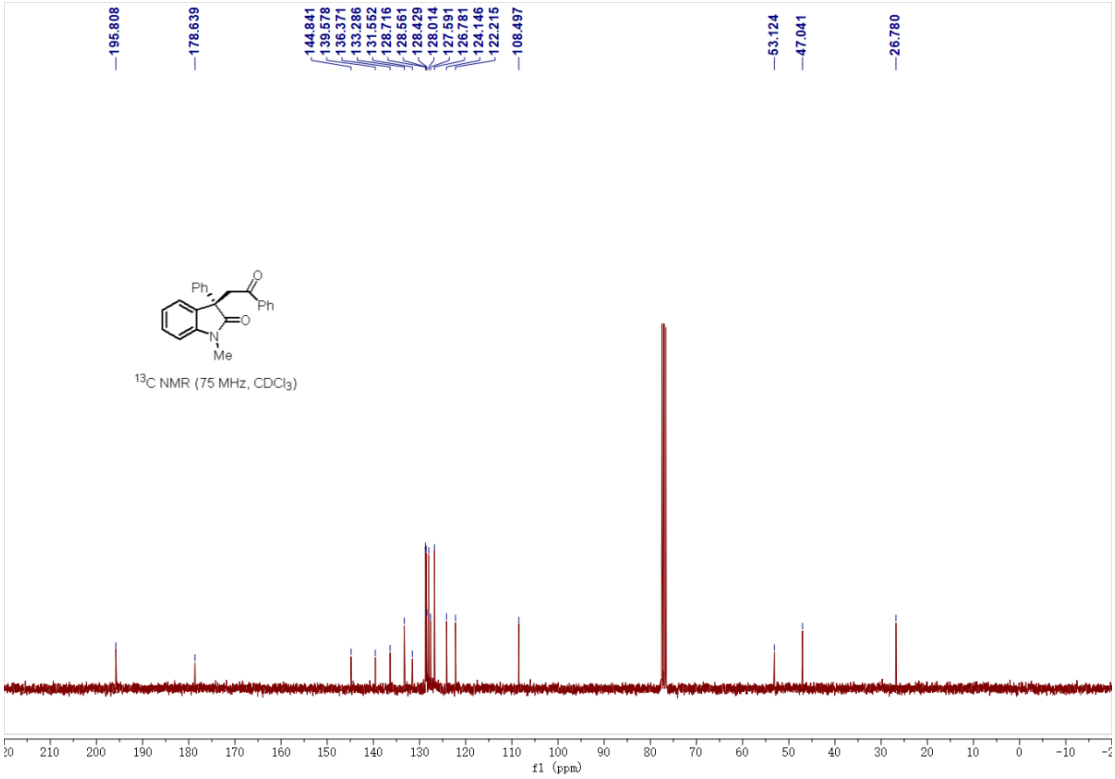
^{13}C NMR of **7k**



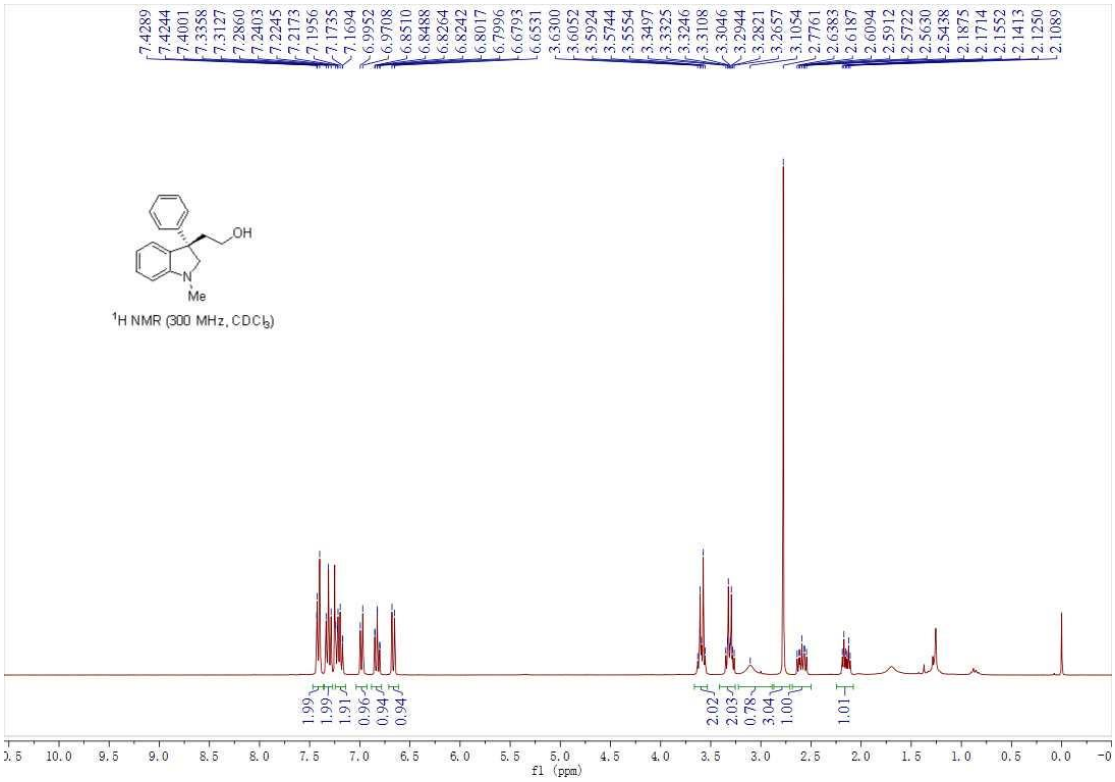
^{1}H NMR of **3ab**



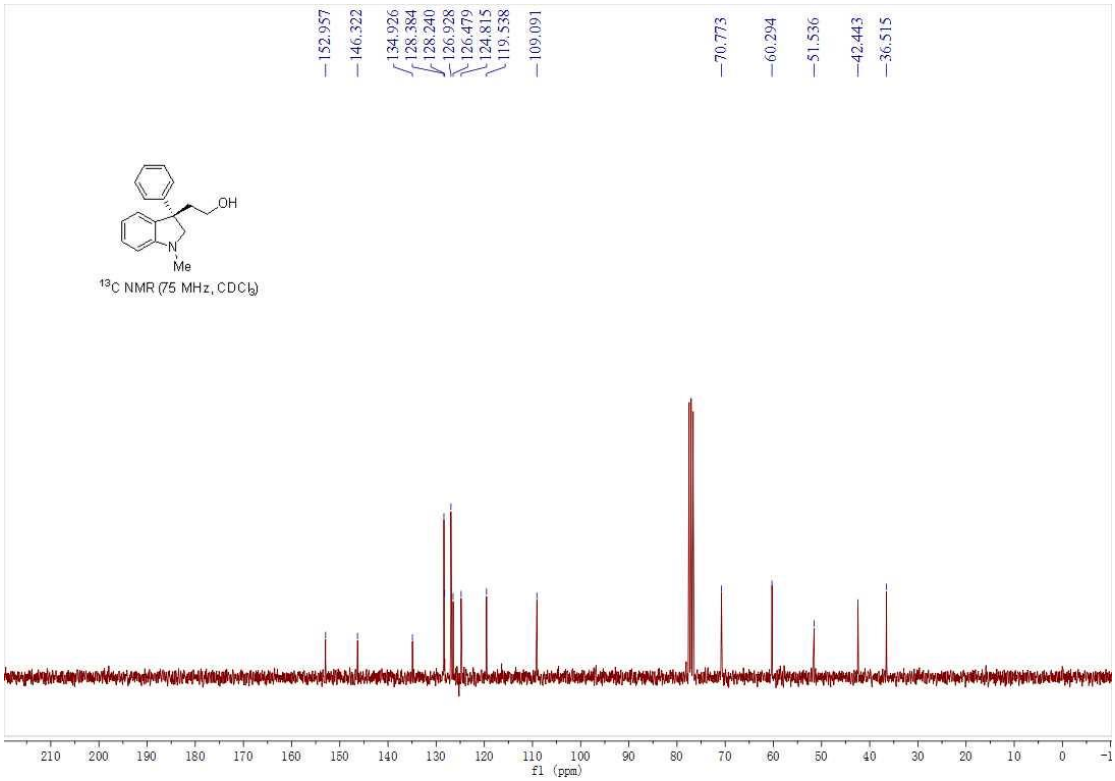
^{13}C NMR of **3ab**



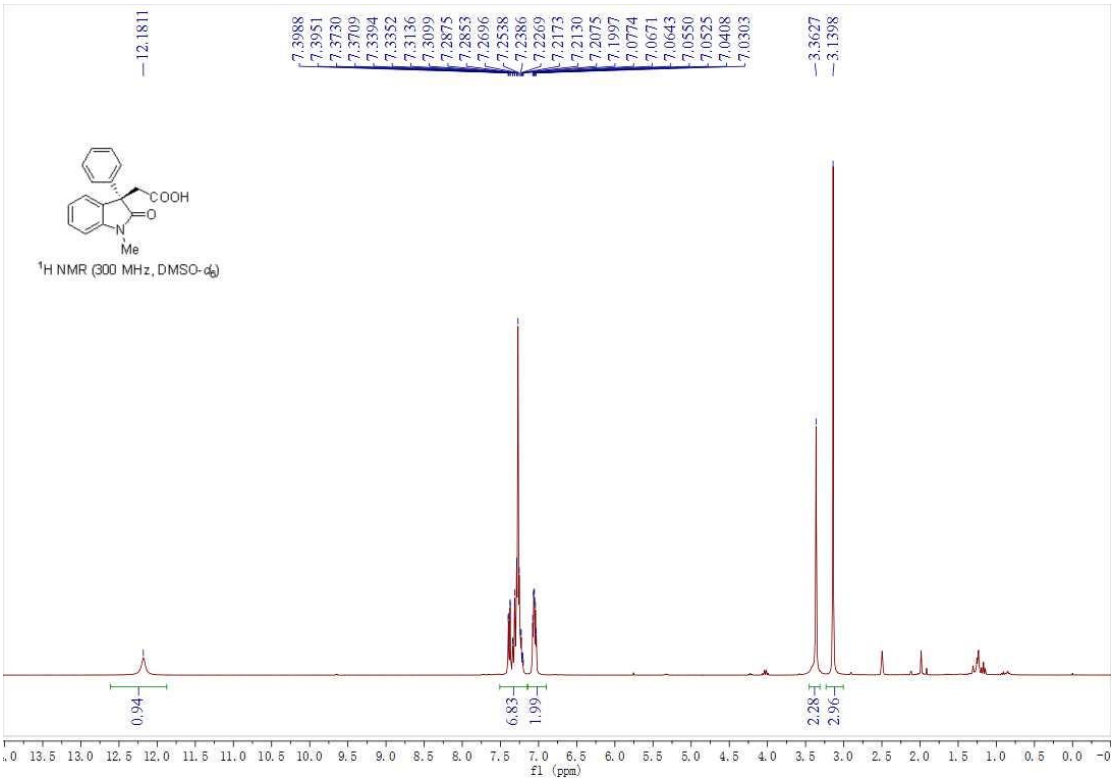
^{1}H NMR of **8**



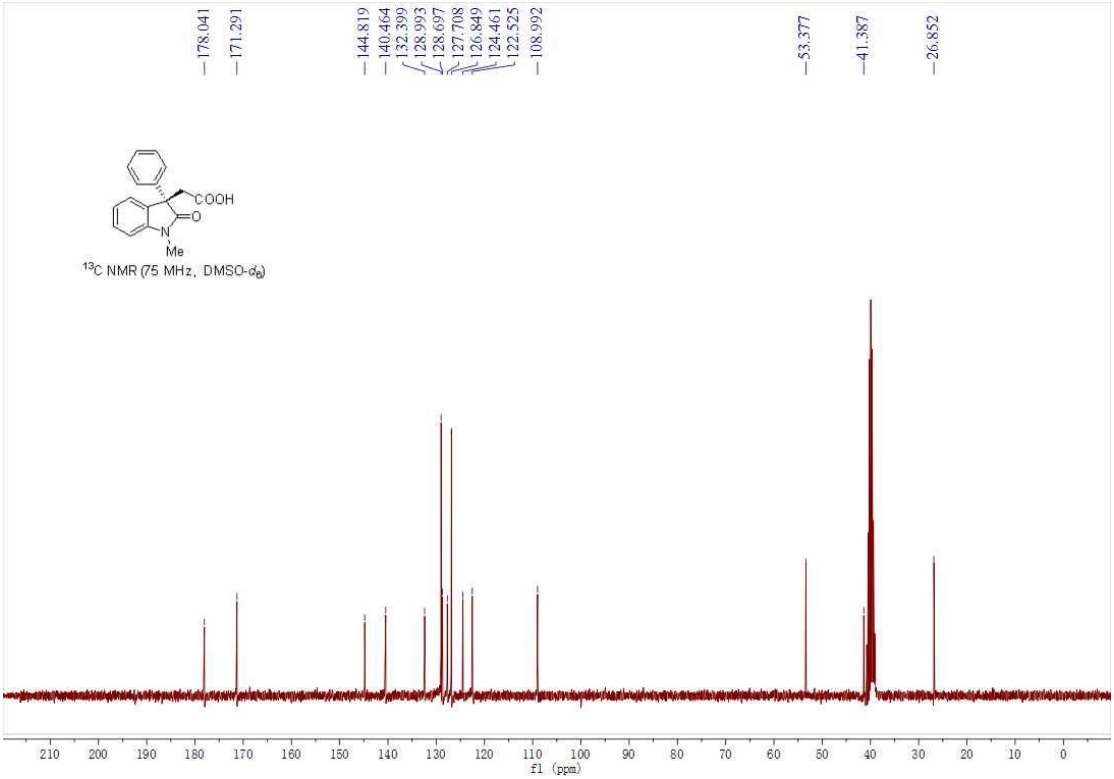
^{13}C NMR of **8**



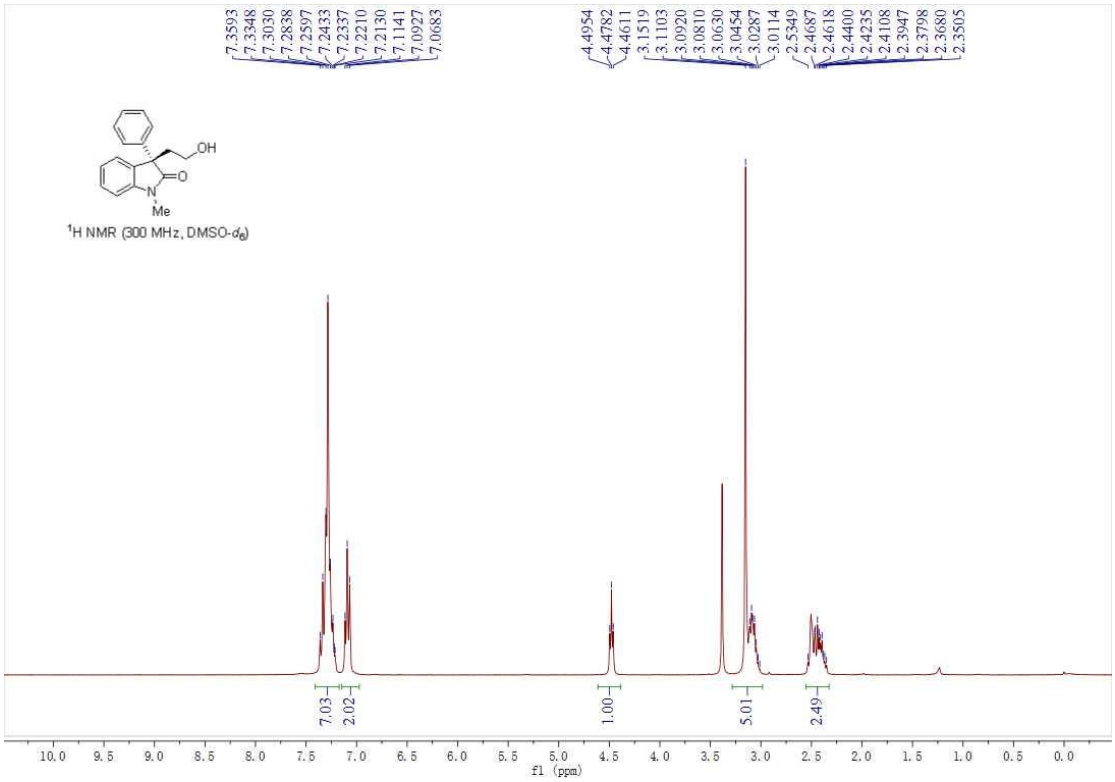
^{1}H NMR of **9**



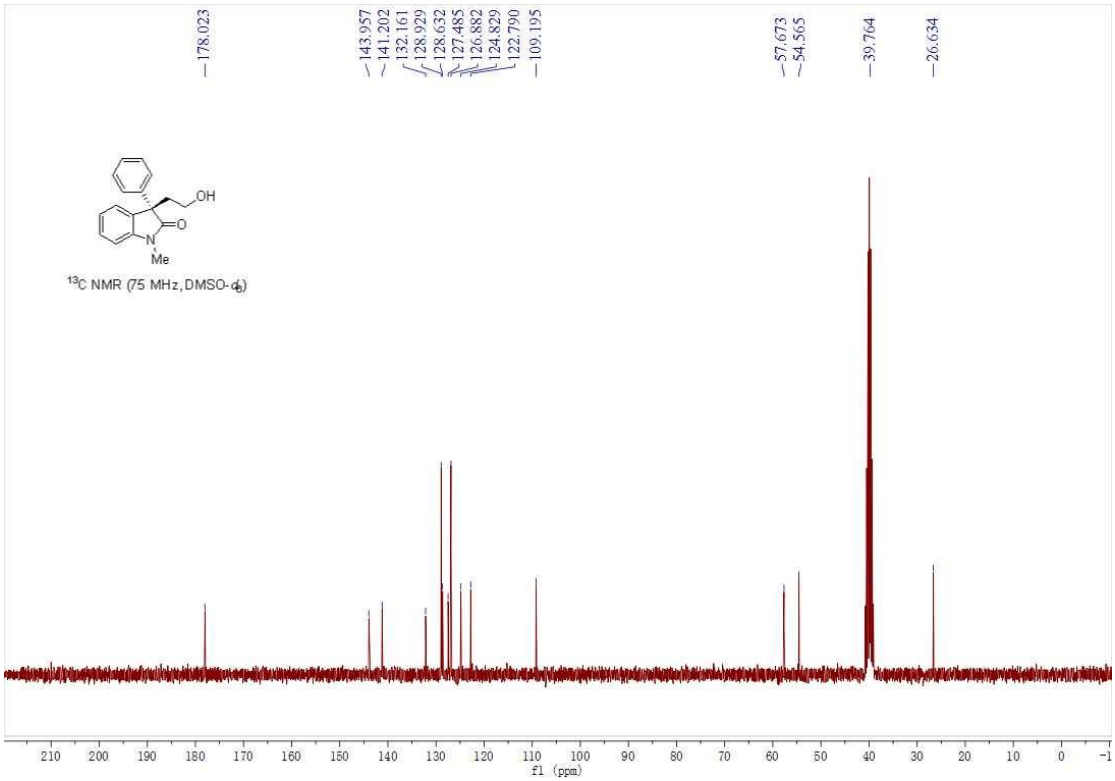
^{13}C NMR of **9**



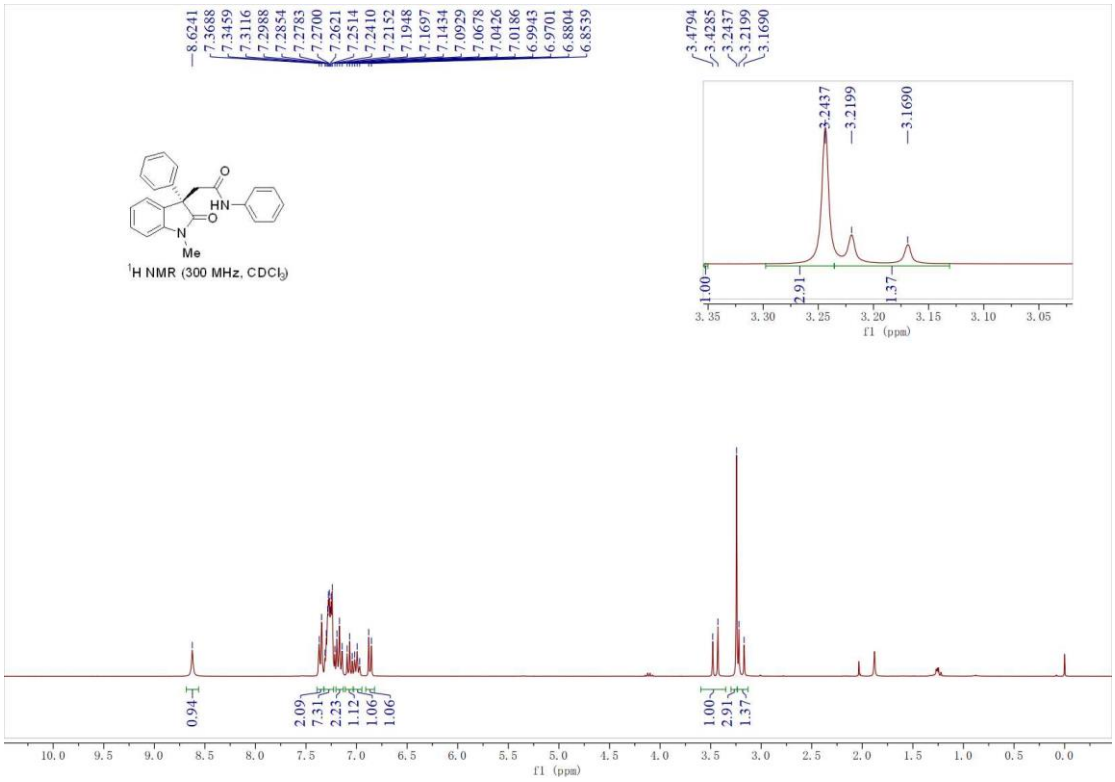
^{1}H NMR of **10**



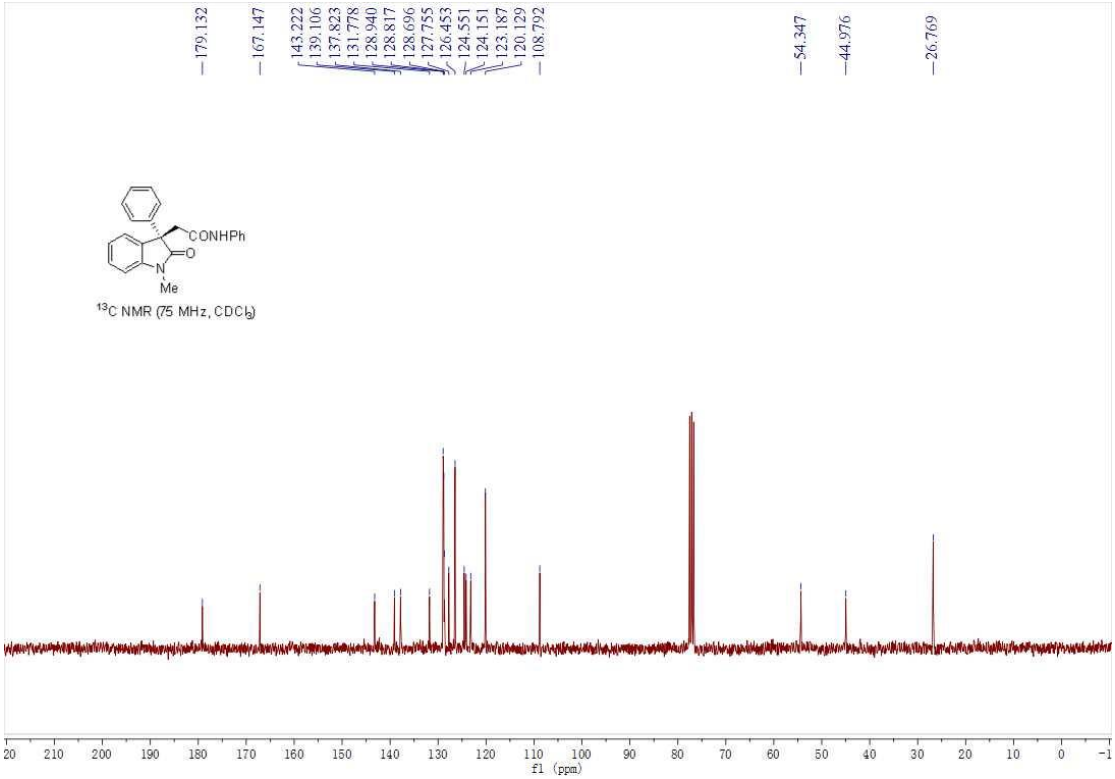
^{13}C NMR of **10**



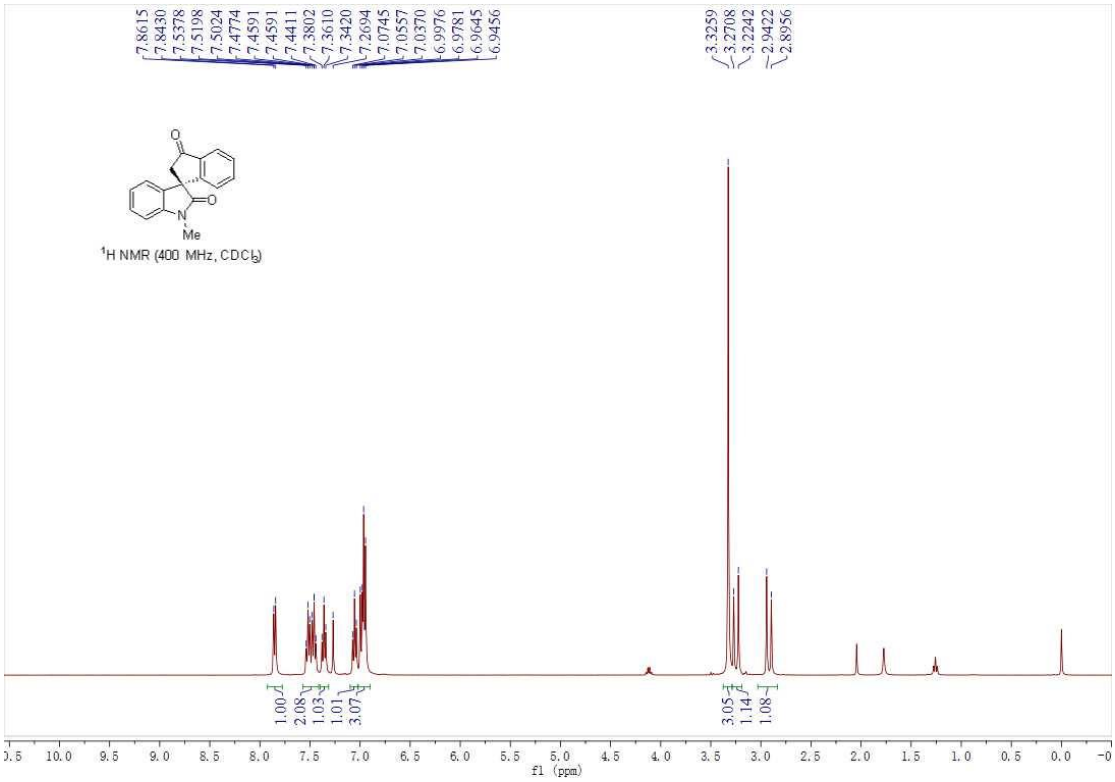
^{1}H NMR of **11**



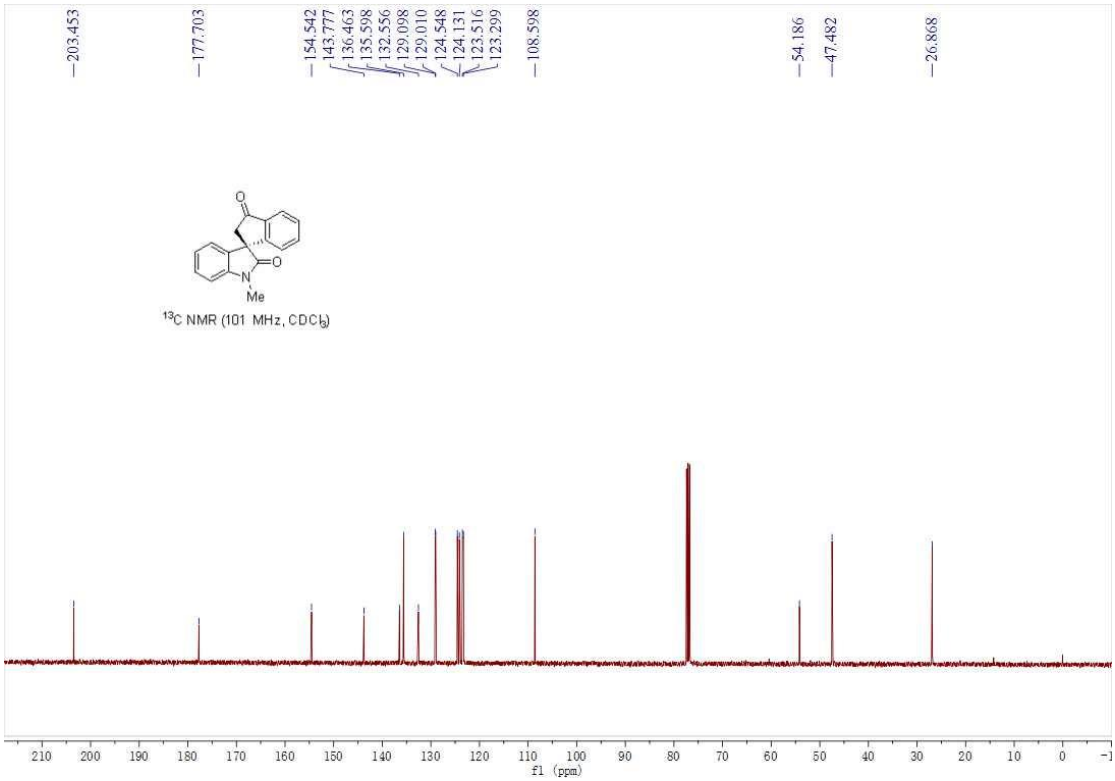
^{13}C NMR of **11**



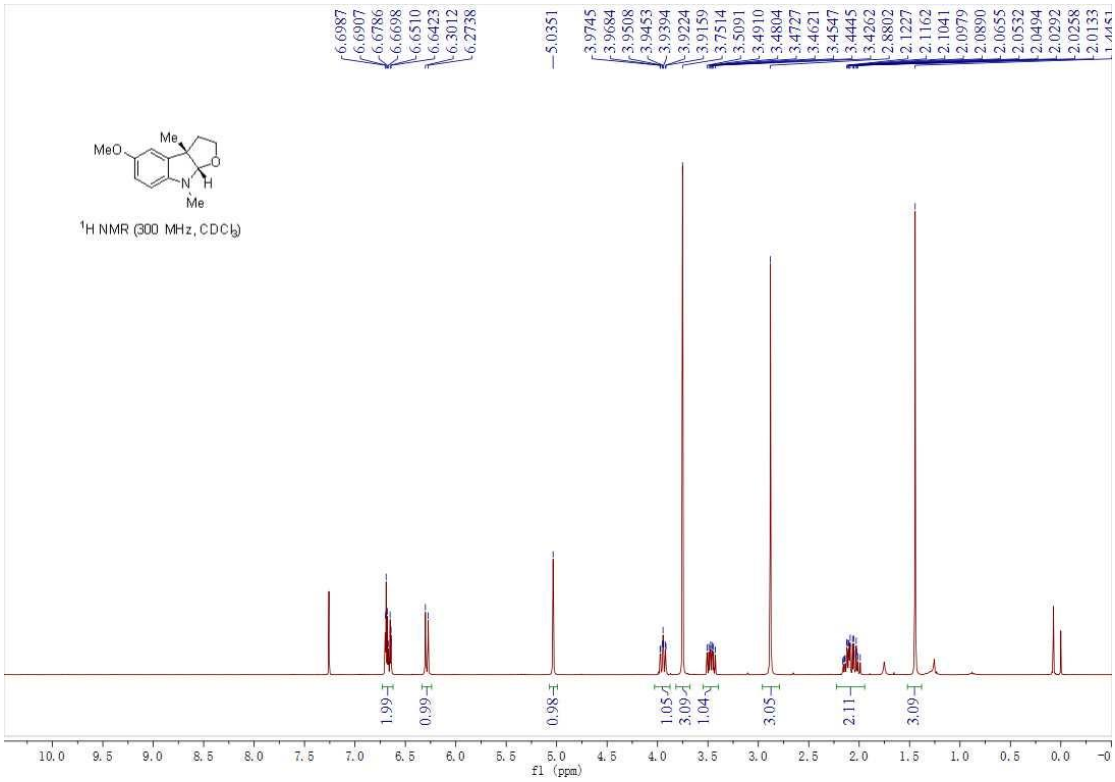
^{1}H NMR of **12**



^{13}C NMR of **12**



^{1}H NMR of **13**



^{13}C NMR of **13**