Supporting Information:

Reversal of Enantioselectivity in Cobalt(II)-Catalyzed Asymmetric Michael–Alkylation Reactions: Synthesis of Spiro-Cyclopropane-Oxindoles

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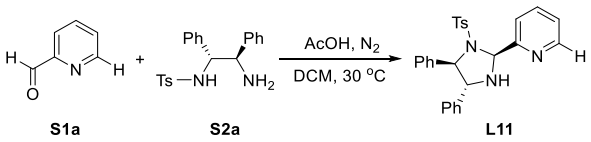
General information

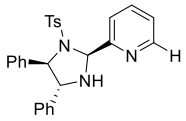
^{1}H NMR spectra were recorded on Bruker Avance III HD 600 or Avance 400 MHz spectrometer. Chemical shifts are recorded in ppm relative to tetramethylsilane and with the solvent resonance as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet; t = triplet; q = quartet; sept = septet; m = multiplet; br = broad), coupling constants (Hz), integration. ^{13}C NMR data were collected on Bruker Avance III HD 150 or Avance 100 MHz spectrometer. Chemical shifts are reported in ppm from the tetramethylsilane with the solvent resonance as internal standard. Enantiomer excesses were determined by chiral HPLC analysis on Chiralcel IE/ID/IG in comparison with the authentic racemates. Chiral HPLC analysis recorded on Thermo scientific Dionex Ultimate 3000 and Agilent Technologies 1260 Infinity. Optical rotations were reported as follows: $[\alpha]_D^T$ (c: g/100 mL, in solvent). Optical rotations recorded on Autopol Automatic Polarimeter. HRMS was recorded on an ABI/Sciex QStar Mass Spectrometer (ESI). EtOAc and DCM were purchased extra dry solvents. Other solvents used for work-up and purification purposes were purchased in technical grade quality and distilled by rotary evaporator before use. Single crystal X-ray crystallography data were obtained on Supernova Atlas S2 CCD detector. These ligands **L1-L10** and **L12** were prepared by previous reported methods.[1-5] The β,γ-unsaturated-α-ketoesters **2a**-**2k** were prepared according to literature precedures.[6] The 2,3-dioxopyrrolidine **5a** were prepared according to literature precedures.[7]

Synthesis of the chiral ligand L11



In a round-bottomed flask containing a stir bar, compound **S1a** (475.0 μL, 5.0 mmol), (*R*,*R*)-TSDPEN **S2a** (1.83 g, 5.0 mmol), AcOH (429.3 μL, 7.5 mmol), and dichloromethane (50.0 mL) were added. Then, the reaction was stirred at 30 °C under N_2 for 6 h. After that, the reaction mixture was quenched by aqueous $NaHCO_3$. The organic layers were extracted with dichloromethane for 3 times, and the collected organic layers were dried over Na_2SO_4. After removing the solvent under reduced pressure, ligand **L11** could be obtained by recrystallization (recrystallization solvent: Pet/EtOAc) as a white solid.

2-((2*S*,4*R*,5*R*)-4,5-Diphenyl-1-tosylimidazolidin-2-yl) pyridine (L11)



White solid: 1.9 g, 83% yield; m.p.: 131.7-134.4 °C; R_f = 0.6 (Pet/EtOAc, 5/1, v/v); $[\alpha]_D^{24}$ = -22.90 (c = 0.91, $CHCl_3$).

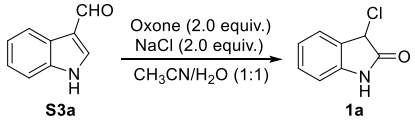
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 4.4 Hz, 1H), 8.05 – 7.98 (m, 1H), 7.85 (td, *J* = 7.6, 1.6 Hz, 1H), 7.65 – 7.60 (m, 2H), 7.34 – 7.29 (m, 1H), 7.25 – 7.15 (m, 10H), 7.03 – 6.98 (m, 2H), 5.95 (s, 1H), 4.66 (d, *J* = 6.8 Hz, 1H), 4.33 (d, *J* = 6.8 Hz, 1H), 3.79 (s, 1H), 2.44 (s, 3H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 149.2, 143.9, 139.8, 139.2, 137.0, 134.4, 129.7, 128.5, 128.4, 128.1, 127.7, 127.6, 127.4, 127.1, 123.9, 123.5, 78.4, 72.1, 69.9, 21.7.

HRMS (ESI): exact mass calcd for $C_{27}H_{25}N_3NaO_2S^+$ $(M+Na)^+$ requires m/z 478.1560, found m/z 478.1559 (Δ = -1 ppm).

General procedures for the preparation of substrates

The substituted 3-chloride oxindoles **1a**-**1h** were prepared according to literature precedures.[8]



In a 250 mL round bottom flask, 1*H*-indole-3-carbaldehyde **S3a** (3.0 g, 20.0 mmol), Oxone (12.7 g, 40.0 mmol) and NaCl (2.4 g, 40.0 mmol) were dissolved in the solvent of CH_3CN/H_2O (1:1). The reaction

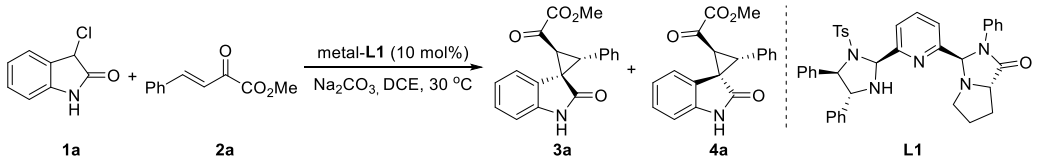
mixture was stirred at 50 °C for 3 h as monitored by TLC. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and then the organic layers were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography to give the desired product **1a**.

S4a **1b-1h**

PIFA (12.0 mmol) was added dropwise to a solution of indoles **S4a** (10.0 mmol) and nBu$_4$NCl·H$_2$O (TBAC) (12.0 mmol) in CH_2Cl_2 with stirring under open-air conditions at room temperature. The resulting solution was stirred for further 5 minutes. After completion of the reaction, the reaction mixture was diluted with ethyl acetate and then the organic layers were dried over Na_2SO_4 and concentrated under vacuum. The residue was purified by flash column chromatography to obtain the products **1b**-**1h**.

Optimization of the reaction conditions

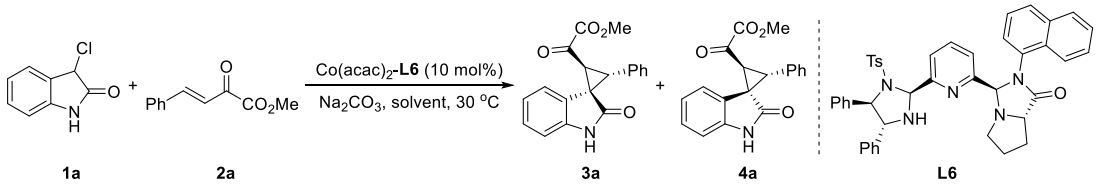
Table S1. Screening of Co(II) salts[a]



entry	metal	yield (**3a**) (%)[b]	**3a:4a**[c]	ee (**3a**) (%)[d]
1	$Co(OAc)_2$	55	79:21	64
2	$CoBr_2$	14	40:60	41
3	$Co(acac)_3$	24	82:18	24
4	$Co(acac)_2$	41	90:10	80
5	$Co(ClO_4)_2·6H_2O$	34	52:48	83
6	$Co(BF_4)_2·6H_2O$	63	82:18	78

[a]Unless otherwise noted, reactions were carried out with metal (10 mol%), **L1** (10 mol%), **1a** (0.1 mmol), **2a** (0.1 mmol), Na_2CO_3 (1.1 equiv.) in DCE (2.0 mL) at 30 °C for 12 h. [b]Isolated yield of **3a**. [c]The ratio of **3a**:**4a** was determined by ^{1}H NMR spectra of the crude product. [d]The ee of **3a** was determined by chiral HPLC analysis.

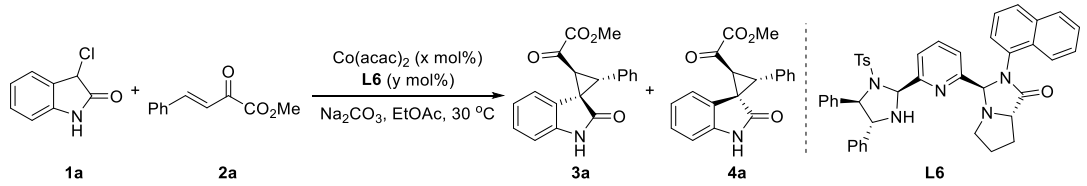
Table S2. Screening of solvents[a]



entry	solvent	yield (**3a**) (%)[b]	**3a:4a**[c]	ee (**3a**) (%)[d]
1	DCM	88	92:8	99
2	THF	34	90:10	97
3	MeCN	86	89:11	96
4	$PhCF_3$	96	93:7	84
5	EtOAc	94	>95:5	99
6	TBME	96	>95:5	92
7	PhCl	86	94:6	99
8	toluene	80	82:18	89

[a]Unless otherwise noted, reactions were carried out with $Co(acac)_2$ (10 mol%), **L6** (10 mol%), **1a** (0.1 mmol), **2a** (0.1 mmol), Na_2CO_3 (1.1 equiv.) in solvent (2.0 mL) at 30 °C for 12 h. [b]Isolated yield of **3a**. [c]The ratio of **3a**:**4a** was determined by ^{1}H NMR spectra of the crude product. [d]The ee of **3a** was determined by chiral HPLC analysis.

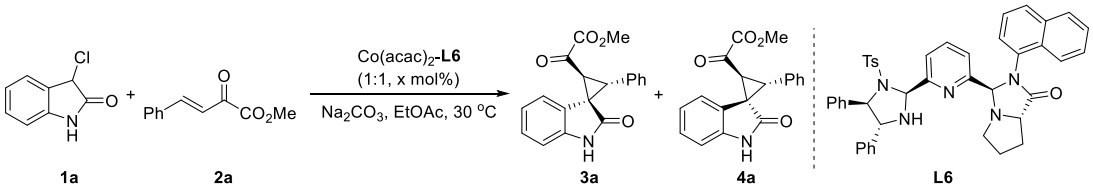
Table S3: Screening of metal/ligand[a]



entry	x	y	yield (**3a**) (%)[b]	**3a:4a**[c]	ee (**3a**) (%)[d]
1	10	10	95	>95:5	99
2	10	11	94	>95:5	99
3	10	12	95	>95:5	99

[a]Unless otherwise noted, reactions were carried out with $Co(acac)_2$ (x mol%), **L6** (y mol%), **1a** (0.1 mmol), **2a** (0.1 mmol), Na_2CO_3 (1.1 equiv.) in EtOAc (2.0 mL) at 30 °C for 12 h. [b]Isolated yield of **3a**. [c]The ratio of **3a**:**4a** was determined by ^1H NMR spectra of the crude product. [d]The ee of **3a** was determined by chiral HPLC analysis.

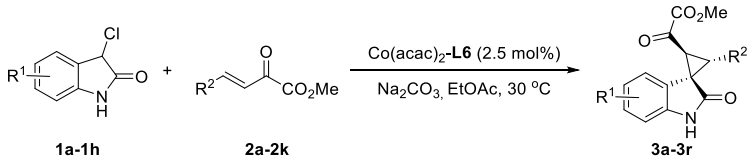
Table S4: Screening the amount of metal and ligand[a]



entry	x	time (h)	yield (**3a**) (%)[b]	**3a:4a**[c]	ee (**3a**) (%)[d]
1	10	12	95	>95:5	99
2	5	36	94	>95:5	99
3	2.5	48	95	>95:5	99
4	1	48	94	>95:5	97
5	0.5	48	87	92:8	93
6	0.25	48	67	74:26	79
7	0.1	48	43	47:53	28

[a]Unless otherwise noted, reactions were carried out with $Co(acac)_2$/**L6** = 1:1 (x mol%), **1a** (0.1 mmol), **2a** (0.1 mmol), Na_2CO_3 (1.1 equiv.) in EtOAc (2.0 mL) at 30 °C. [b]Isolated yield of **3a**. [c]The ratio of **3a**:**4a** was determined by ^1H NMR spectra of the crude product. [d]The ee of **3a** was determined by chiral HPLC analysis.

Catalytic asymmetric Michael–Alkylation reactions

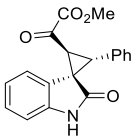


1a-1h **2a-2k** **3a-3r**

Preparation of $Co(acac)_2$ and **L6** solution: in a 2.0 mL volumetric flask, $Co(acac)_2$ (6.4 mg, 0.025 mmol) was added, then THF was added to make the total volume up to 2.0 mL. In a 2.0 mL volumetric flask, **L6** (17.6 mg, 0.025 mmol) was added, then THF was added to make the total volume up to 2.0 mL.

In a dry reaction tube, 200 μL (2.5 mol%) of $Co(acac)_2$ solution and 200 μL (2.5 mol%) of **L6** were added. Then, THF was removed under vacuum. After that, *β*,*γ*-unsaturated-*α*-ketoesters **2** (19.0 mg, 0.1 mmol) and EtOAc (2.0 mL) were added and the reaction was stirred at 30 °C for 0.5 h. Subsequently, 3-chlorooxindoles **1** (16.7 mg, 0.1 mmol) and Na_2CO_3 (11.7 mg, 0.11 mmol) were added and the reaction was stirred at 30 °C until **1** was consumed (detected by TLC, Pet/EtOAc, 1/1, v/v). Finally, the corresponding product **3** was purified directly by flask column chromatography (Pet/EtOAc, 5/1-1/1, v/v).

Methyl 2-oxo-2-((1*R*,2*S*,3*R*)-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl) acetate (3a)



Colorless solid, 30.5 mg, 95% yield, 97:3 dr, 99% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +100.00 (c = 0.77, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

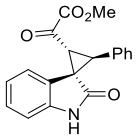
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.418 min (major), 16.940 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.70 (s, 1H), 7.36 – 7.28 (m, 5H), 7.10 (td, *J* = 5.2, 0.8 Hz, 1H), 6.87 (d, *J* = 5.2 Hz, 1H), 6.66 (td, *J* = 5.2, 0.8 Hz, 1H), 6.10 (d, *J* = 5.2 Hz, 1H), 3.91 (d, *J* = 5.6 Hz, 1H), 3.72 (s, 3H), 3.59 (d, *J* = 5.6 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.5, 174.0, 159.9, 142.5, 133.1, 130.0, 128.4, 127.7, 127.6, 125.7, 121.0, 120.8, 109.7, 52.7, 40.1, 38.6, 36.8.

HRMS (ESI): exact mass calcd for $C_{19}H_{15}NNaO_4^+$ $(M+Na)^+$ requires m/z 344.0893, found m/z 344.0892 (Δ = -1 ppm). Known compound.[9]

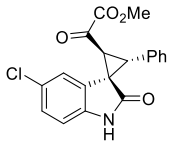
Methyl 2-oxo-2-((1*S*,2*R*,3*S*)-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)acetate (*ent*-3a)



Colorless solid, 29.9 mg, 93% yield, 98:2 dr, 98% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +114.99 (c = 1.25, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.562 min (minor), 16.398 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-5'-chloro-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3b)



Light yellow solid, 30.2 mg, 85% yield, >99:1 dr, 97% ee; m.p.: 126.6-129.3 °C; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +66.03 (c = 1.26, CH_2Cl_2); reaction time: 60 h; reaction temperature: 30 °C.

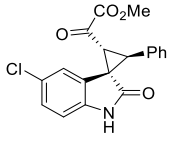
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.542 min (major), 12.155 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.87 (s, 1H), 7.41 – 7.27 (m, 5H), 7.16 (dd, *J* = 8.0, 2.0 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.09 (d, *J* = 2.0 Hz, 1H), 4.04 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.63 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.3, 173.8, 159.8, 141.4, 132.6, 129.6, 128.5, 128.0, 127.8, 127.4, 124.9, 121.1, 111.0, 52.8, 40.0, 38.7, 37.3.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}ClNNaO_4^+$ $(M+Na)^+$ requires m/z 378.0504, found m/z 378.0511 (Δ = +7 ppm).

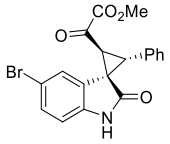
Methyl 2-((1*S*,2*R*,3*S*)-5'-chloro-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3b)



Light yellow solid, 34.4 mg, 97% yield, >99:1 dr, 95% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +60.68 (c = 1.90, CH_2Cl_2); reaction time: 60 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.718 min (minor), 12.053 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-5'-bromo-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3c)



Light yellow oil, 35.9 mg, 90% yield, >99:1 dr, 97% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +54.07 (c = 1.49, CH_2Cl_2); reaction time: 72 h; reaction temperature: 30 °C.

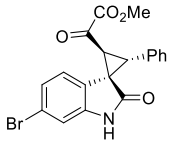
HPLC CHIRALPAK IG, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.233 min (major), 11.855 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.87 (s, 1H), 7.39 – 7.27 (m, 6H), 6.84 (d, *J* = 8.0 Hz, 1H), 6.20 (d, *J* = 2.0 Hz, 1H), 4.03 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.62 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.3, 173.7, 159.8, 141.8, 132.6, 130.2, 129.6, 128.5, 128.2, 128.0, 123.8, 112.6, 111.5, 52.8, 39.9, 38.8, 37.3.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}BrNNaO_4^+$ $(M+Na)^+$ requires m/z 421.9998, found m/z 421.9995 (Δ = -3 ppm).

Methyl 2-((1*R*,2*S*,3*R*)-6'-bromo-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3d)



Yellow solid, 37.9 mg, 95% yield, 99:1 dr, 96% ee; R_f = 0.35 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +91.55 (c = 1.22, CH_2Cl_2); reaction time: 72 h; reaction temperature: 30 °C.

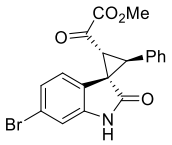
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.550 min (major), 14.337 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.90 (s, 1H), 7.31 (s, 5H), 7.03 (s, 1H), 6.85 (d, *J* = 7.6 Hz, 1H), 6.01 (d, *J* = 7.6 Hz, 1H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.63 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.1, 173.9, 159.8, 144.0, 132.8, 129.5, 128.5, 127.9, 125.1, 123.5, 122.6, 120.3, 112.5, 52.8, 39.8, 38.7, 37.1.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}BrNNaO_4^+$ $(M+Na)^+$ requires m/z 421.9998, found m/z 421.9989 (Δ = -9 ppm). Known compound.[9]

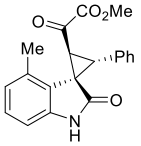
Methyl 2-((1*S*,2*R*,3*S*)-6'-bromo-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3d)



Yellow solid, 38.3 mg, 96% yield, 98:2 dr, 95% ee; R_f = 0.35 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +81.10 (c = 2.27, CH_2Cl_2); reaction time: 72 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.872 min (minor), 14.223 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-4'-methyl-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3e)



Colorless solid, 28.1 mg, 84% yield, 89:11 dr, 97% ee; R_f = 0.5 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +57.23 (c = 1.74, CH_2Cl_2); reaction time: 72 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 13.680 min (major), 16.305 min (minor).

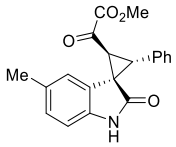
^{1}H NMR (400 MHz, DMSO-d^6) δ 10.76 (s, 1H), 7.37 – 7.23 (m, 3H), 7.23 – 7.12 (m, 2H), 7.05 (t, *J* = 7.6 Hz, 1H), 6.78 (d, *J* = 7.6 Hz, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 4.15 (d, *J* = 8.8 Hz, 1H), 3.72 (s, 3H), 3.38 (d, *J* = 8.4 Hz, 1H), 1.21 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 187.8, 174.8, 159.9, 143.3, 135.4, 133.7, 129.6, 128.6, 127.8, 127.5,

124.4, 122.4, 107.9, 52.7, 40.7, 37.8, 35.5, 18.1.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 358.1050, found m/z 358.1047 (Δ = -3 ppm). Known compound.[9]

Methyl 2-((1*R*,2*S*,3*R*)-5'-methyl-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3f)



Light yellow oil, 31.8 mg, 95% yield, 97:3 dr, 99% ee; R_f = 0.5 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +74.04 (c = 2.42, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

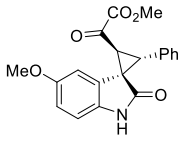
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.418 min (major), 17.948 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.60 (s, 1H), 7.38 – 7.26 (m, 5H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.75 (d, *J* = 8.0 Hz, 1H), 5.91 (s, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 3.71 (s, 3H), 3.57 (d, *J* = 8.4 Hz, 1H), 1.96 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.5, 174.0, 159.9, 140.0, 133.1, 129.54, 129.47, 128.4, 127.8, 127.7, 125.8, 121.8, 109.3, 52.7, 40.2, 38.6, 36.7, 20.7.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 358.1050, found m/z 358.1045 (Δ = -5 ppm). Known compound.[9]

Methyl 2-((1*R*,2*S*,3*R*)-5'-methoxy-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3g)



Light yellow solid, 33.7 mg, 96% yield, 96:4 dr, 99% ee; m.p.: 57.4-60.0 °C; R_f = 0.5 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +93.56 (c = 1.03, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

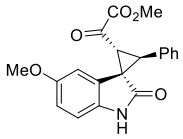
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 19.437 min (major), 24.952 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.53 (s, 1H), 7.45 – 7.23 (m, 5H), 6.77 (d, *J* = 8.4 Hz, 1H), 6.67 (dd, *J* = 8.4, 2.8 Hz, 1H), 5.70 (d, *J* = 2.4 Hz, 1H), 3.91 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.60 (d, *J* = 8.4 Hz, 1H), 3.41 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.5, 173.9, 159.9, 154.0, 135.8, 133.0, 129.6, 128.4, 127.7, 126.9, 112.2, 109.9, 108.1, 55.0, 52.7, 40.4, 38.5, 36.8.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_5^+$ $(M+Na)^+$ requires m/z 374.0999, found m/z 374.0998 (Δ = -1 ppm).

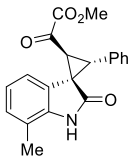
Methyl 2-((1*S*,2*R*,3*S*)-5'-methoxy-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3g)



Light yellow solid, 30.9 mg, 88% yield, 97:3 dr, 98% ee; R_f = 0.5 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +78.70 (c = 1.62, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 19.788 min (minor), 24.232 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-7'-methyl-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3h)



Colorless solid, 32.8 mg, 98% yield, >99:1 dr, 99% ee; m.p.: 69.4-72.0 °C; R_f = 0.55 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +90.67 (c = 2.15, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

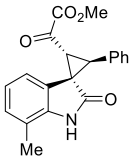
HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.772 min (major), 14.203 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.75 (s, 1H), 7.38 – 7.23 (m, 5H), 6.92 (d, *J* = 7.6 Hz, 1H), 6.57 (t, *J* = 7.6 Hz, 1H), 5.93 (d, *J* = 7.2 Hz, 1H), 3.89 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.58 (d, *J* = 8.4 Hz, 1H), 2.21 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ = 186.5, 174.5, 159.9, 141.0, 133.1, 129.6, 128.9, 128.4, 127.7, 125.3, 120.8, 119.0, 118.3, 52.7, 40.4, 38.6, 36.9, 16.3.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 358.1050, found m/z 358.1044 (Δ = -6 ppm).

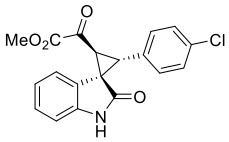
Methyl 2-((1*S*,2*R*,3*S*)-7'-methyl-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3h)



Colorless solid, 32.2 mg, 96% yield, >99:1 dr, 97% ee; R_f = 0.55 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +134.12 (c = 1.32, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 10.985 min (minor), 13.860 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-(4-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3i)



Yellow oil, 34.4 mg, 97% yield, 98:2 dr, 99% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +106.76 (c = 1.73, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.380 min (major), 14.317 min (minor).

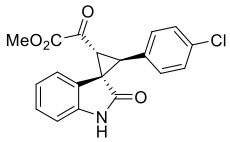
^{1}H NMR (400 MHz, DMSO-d^6) δ 10.73 (s, 1H), 7.43 – 7.30 (m, 4H), 7.12 (td, *J* = 7.6, 1.2 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.70 (td, *J* = 7.6, 1.2 Hz, 1H), 6.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 3.92 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.58(d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.2, 173.9, 159.9, 142.5, 132.4, 132.2, 131.5, 128.5, 127.7, 125.4, 121.0, 109.8, 52.8, 38.6, 36.1.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}ClNNaO_4^+$ $(M+Na)^+$ requires m/z 378.0504, found m/z

378.0508 (Δ = +4 ppm). Known compound.[9]

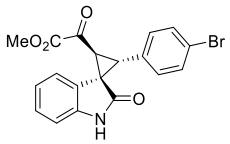
Methyl 2-((1*S*,2*R*,3*S*)-2-(4-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3i)



Yellow oil, 30.5 mg, 86% yield, 98:2 dr, 99% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +90.87 (c = 1.34, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.462 min (minor), 14.080 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-(4-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3j)



Light yellow solid, 37.9 mg, 95% yield, 98:2 dr, 98% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +84.41 (c = 2.12, CH_2Cl_2); reaction time: 60 h; reaction temperature: 30 °C.

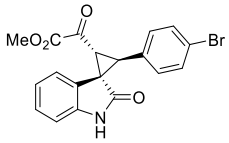
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.910 min (major), 14.915 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.72 (s, 1H), 7.53 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 8.0 Hz, 1H), 6.71 (t, *J* = 7.6 Hz, 1H), 6.14 (d, *J* = 7.2 Hz, 1H), 3.91 (d, *J* = 8.4 Hz, 1H), 3.72 (s, 3H), 3.55 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.2, 173.8, 159.9, 142.5, 132.6, 131.8, 131.4, 127.7, 125.4, 121.00, 120.96, 109.8, 52.8, 40.1, 38.5, 36.1.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}BrNNaO_4^+$ $(M+Na)^+$ requires m/z 421.9998, found m/z 421.9996 (Δ = -2 ppm). Known compound.[9]

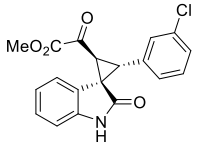
Methyl 2-((1*S*,2*R*,3*S*)-2-(4-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3j)



Light yellow solid, 36.3 mg, 91% yield, 98:2 dr, 98% ee; R_f = 0.4 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +73.68 (c = 1.63, CH_2Cl_2); reaction time: 60 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 12.918 min (minor), 14.455 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-(3-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3k)



Yellow oil, 27.3 mg, 77% yield, >99:1 dr, 98% ee; R_f = 0.35 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +191.27 (c = 1.25, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

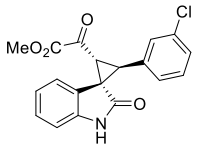
HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.312 min (major), 11.497 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.74 (s, 1H), 7.45 (s, 1H), 7.40 – 7.22 (m, 3H), 7.13 (t, *J* = 7.6 Hz, 1H), 6.89 (d, *J* = 7.6 Hz, 1H), 6.70 (t, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 3.96 (d, *J* = 8.0 Hz, 1H), 3.72 (s, 3H), 3.61 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.1, 173.7, 159.9, 142.5, 135.7, 133.1, 130.2, 129.4, 128.3, 127.8, 125.4, 120.94, 120.91, 109.8, 52.8, 38.5, 36.0.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}ClNNaO_4^+$ $(M+Na)^+$ requires m/z 378.0504, found m/z 378.0508 (Δ = +4 ppm). Known compound.[9]

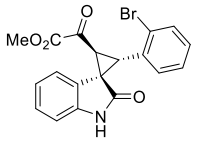
Methyl 2-((1*S*,2*R*,3*S*)-2-(3-chlorophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3k)



Yellow oil, 26.6 mg, 77% yield, 98:2 dr, 97% ee; R_f = 0.35 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +98.59 (c = 1.84, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 9.290 min (minor), 11.132 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-(2-bromophenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3l)



White solid, 23.5 mg, 59% yield, 97:3 dr, 98% ee; R_f = 0.35 (Pet/EtOAc, 1/1, v/v); m.p.: 132.7-135.1 °C; $[\alpha]_D^{23}$ = +46.46 (c = 0.96, CH_2Cl_2); reaction time: 60 h; reaction temperature: 30 °C.

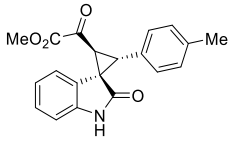
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.197 min (major), 27.780 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.70 (s, 1H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.56 – 7.44 (m, 2H), 7.28 (td, *J* = 7.6, 1.6 Hz, 1H), 7.11 (td, *J* = 7.6, 1.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 6.62 (td, *J* = 7.6, 1.2 Hz, 1H), 5.93 (d, *J* = 7.2 Hz, 1H), 3.98 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.44 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 185.9, 173.7, 159.8, 142.5, 133.2, 132.3, 130.7, 130.0, 127.8, 127.7, 126.2, 125.3, 120.8, 119.9, 109.6, 52.8, 38.0.

HRMS (ESI): exact mass calcd for $C_{19}H_{14}BrNNaO_4^+$ $(M+Na)^+$ requires m/z 421.9998, found m/z 421.9991 (Δ = -7 ppm).

Methyl 2-oxo-2-((1*R*,2*S*,3*R*)-2'-oxo-2-(p-tolyl)spiro[cyclopropane-1,3'-indolin]-3-yl)acetate (3m)



Yellow solid, 31.8 mg, 95% yield, 98:2 dr, 99% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +87.53 (c = 0.97, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

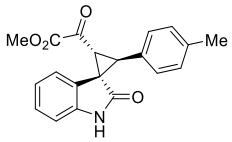
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.913 min (major), 18.173 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.68 (s, 1H), 7.16 (dd, *J* = 16.0, 5.2 Hz, 4H), 7.10 (t, *J* = 5.2 Hz, 1H), 6.87 (d, *J* = 5.2 Hz, 1H), 6.68 (t, *J* = 5.2 Hz, 1H), 6.14 (d, *J* = 5.2 Hz, 1H), 3.88 (d, *J* = 5.6 Hz, 1H), 3.71 (s, 3H), 3.53 (d, *J* = 5.6 Hz, 1H), 2.28 (s, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.5, 174.0, 159.9, 142.4, 136.9, 130.0, 129.4, 129.0, 127.5, 125.7, 121.0, 120.9, 109.6, 52.7, 40.2, 38.7, 36.7, 20.7.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 358.1050, found m/z 358.1056 (Δ = +6 ppm). Known compound.[9]

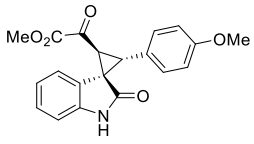
Methyl 2-oxo-2-((1*S*,2*R*,3*S*)-2'-oxo-2-(p-tolyl)spiro[cyclopropane-1,3'-indolin]-3-yl)acetate (*ent*-3m)



Yellow solid, 32.2 mg, 96% yield, 98:2 dr, 99% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +100.90 (c = 1.37, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 15.093 min (minor), 17.580 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-(4-methoxyphenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3n)



Colorless oil, 34.0 mg, 97% yield, 97:3 dr, 96% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +119.46 (c = 0.86, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

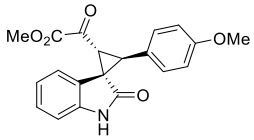
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.880 min (major), 26.883 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.68 (s, 1H), 7.21 (d, *J* = 8.4 Hz, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.92 – 6.83 (m, 3H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.13 (d, *J* = 7.2 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 3.73 (s, 3H), 3.71 (s, 3H), 3.53 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.5, 174.0, 159.9, 158.7, 142.4, 130.7, 127.5, 125.8, 124.8, 121.0, 120.9, 113.8, 109.6, 55.1, 52.7, 40.3, 36.4.

HRMS (ESI): exact mass calcd for $C_{20}H_{17}NNaO_5^+$ $(M+Na)^+$ requires m/z 374.0999, found m/z 374.1004 (Δ = +5 ppm). Known compound.[9]

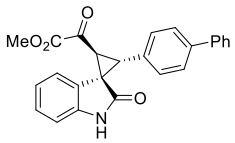
Methyl 2-((1*S*,2*R*,3*S*)-2-(4-methoxyphenyl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-3n)



Colorless oil, 33.0 mg, 94% yield, 97:3 dr, 96% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +77.86 (c = 1.76, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 22.903 min (minor), 25.690 min (major).

Methyl 2-((1*R*,2*S*,3*R*)-2-([1,1'-biphenyl]-4-yl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3o)



White solid, 38.5 mg, 97% yield, 99:1 dr, 99% ee; R_f = 0.5 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +98.96 (c = 2.66, CH_2Cl_2); reaction time: 32 h; reaction temperature: 30 °C.

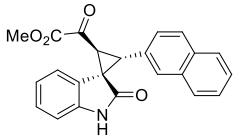
HPLC CHIRALPAK IG, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.165 min (major), 25.285 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.73 (s, 1H), 7.67 (t, *J* = 8.0 Hz, 4H), 7.51 – 7.32 (m, 5H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.88 (d, *J* = 7.6 Hz, 1H), 6.68 (t, *J* = 7.6 Hz, 1H), 6.23 (d, *J* = 7.6 Hz, 1H), 3.97 (d, *J* = 8.8 Hz, 1H), 3.73 (s, 3H), 3.62 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 186.4, 174.0, 159.9, 142.5, 139.4, 139.2, 132.3, 130.1, 129.0, 127.6, 126.6, 125.7, 121.0, 120.9, 109.7, 52.7, 40.3, 38.6, 36.6.

HRMS (ESI): exact mass calcd for $C_{25}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 420.1206, found m/z 420.1201 (Δ = -5 ppm). Known compound.[9]

Methyl 2-((1*R*,2*S*,3*R*)-2-(naphthalen-2-yl)-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3p)



Light yellow solid, 35.2 mg, 95% yield, 98:2 dr, 99% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{24}$ = +100.30 (c = 0.56, CH_2Cl_2); reaction time: 48 h; reaction temperature: 30 °C.

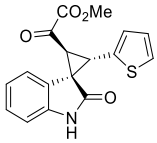
HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.068 min (major), 20.622 min (minor).

^{1}H NMR (400 MHz, CD_3CN) δ 8.73 (s, 1H), 7.89 – 7.83 (m, 3H), 7.80 (d, *J* = 8.4 Hz, 1H), 7.55 – 7.49 (m, 2H), 7.30 (dd, *J* = 8.4, 2.0 Hz, 1H), 7.10 (td, *J* = 8.0, 1.2 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 1H), 6.56 (t, *J* = 7.6 Hz, 1H), 6.08 (d, *J* = 7.6 Hz, 1H), 3.90 (d, *J* = 8.4 Hz, 1H), 3.84 (d, *J* = 8.4 Hz, 1H), 3.78 (s, 3H).

^{13}C NMR (100 MHz, CD_3CN) δ 187.6, 175.0, 161.4, 143.2, 134.1, 133.8, 131.9, 129.2, 129.1, 128.9, 128.8, 128.7, 128.6, 127.5, 127.4, 126.7, 122.21, 122.15, 120.96, 109.8, 53.7, 41.3, 40.4, 38.5.

HRMS (ESI): exact mass calcd for $C_{23}H_{17}NNaO_4^+$ $(M+Na)^+$ requires m/z 394.1050, found m/z 394.1044 (Δ = -6 ppm). Known compound.[9]

Methyl 2-oxo-2-((1*R*,2*S*,3*R*)-2'-oxo-2-(thiophen-2-yl)spiro[cyclopropane-1,3'-indolin]-3-yl) acetate (3q)



Yellow oil, 31.1 mg, 95% yield, 99:1 dr, 97% ee; R_f = 0.45 (Pet/EtOAc, 1/1, v/v); m.p.: 160.2-163.1 °C; $[\alpha]_D^{23}$ = +65.69 (c = 0.75, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IG, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention

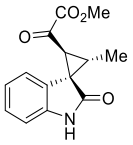
time: 16.750 min (major), 19.067 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.75 (s, 1H), 7.46 (d, *J* = 5.2 Hz, 1H), 7.21 – 7.11 (m, 2H), 7.04 (dd, *J* = 4.8, 3.2 Hz, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 6.74 (t, *J* = 7.6 Hz, 1H), 6.35 (d, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 3.57 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 185.9, 173.6, 159.7, 142.4, 136.1, 128.0, 127.9, 127.0, 126.7, 125.2, 121.1, 120.7, 109.8, 52.8, 40.5, 39.9, 31.5.

HRMS (ESI): exact mass calcd for $C_{17}H_{13}NNaO_4S^+$ $(M+Na)^+$ requires m/z 350.0457, found m/z 350.0459 (Δ = +2 ppm).

Methyl 2-((1*R*,2*S*,3*R*)-2-methyl-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (3r)



Yellow oil, 23.3 mg, 90% yield, 96:4 dr, 98% ee; R_f = 0.55 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{23}$ = +153.71 (c = 0.53, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

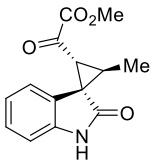
HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.205 min (major), 14.463 min (minor).

^{1}H NMR (400 MHz, DMSO-d^6) δ 10.60 (s, 1H), 7.27 – 7.16 (m, 2H), 6.99 (td, *J* = 7.6, 0.8 Hz, 1H), 6.91 (d, *J* = 7.6 Hz, 1H), 3.67 (s, 3H), 3.16 (d, *J* = 8.0 Hz, 1H), 2.34 – 2.22 (m, 1H), 1.32 (d, *J* = 6.4 Hz, 3H).

^{13}C NMR (100 MHz, DMSO-d^6) δ 187.1, 174.8, 160.0, 142.6, 127.5, 126.4, 122.0, 121.2, 109.8, 52.6, 41.4, 38.9, 28.2, 11.4.

HRMS (ESI): exact mass calcd for $C_{14}H_{13}NNaO_4^+$ $(M+Na)^+$ requires m/z 282.0737, found m/z 282.0730 (Δ = -7 ppm).

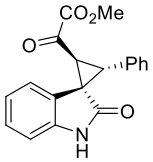
Methyl 2-((1*S*,2*R*,3*S*)-2-methyl-2'-oxospiro[cyclopropane-1,3'-indolin]-3-yl)-2-oxoacetate (*ent*-**3r**)



Yellow oil, 20.7 mg, 80% yield, 99:1 dr, 95% ee; R_f = 0.55 (Pet/EtOAc, 1/1, v/v); $[\alpha]_D^{25}$ = -64.98 (c = 1.01, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK ID, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 11.238 min (minor), 13.540 min (major).

Methyl 2-oxo-2-((1*S*,2*S*,3*R*)-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)acetate (**4a**)

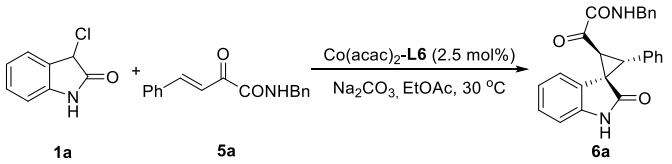


Light yellow oil; R_f = 0.5 (Pet/EtOAc, 1/1, v/v).

^{1}H NMR (600 MHz, DMSO-d^6) δ 10.66 (s, 1H), 7.38 – 7.18 (m, 6H), 7.15 (d, *J* = 7.8 Hz, 1H), 6.96 (t, *J* = 7.8 Hz, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 4.13 (d, *J* = 8.4 Hz, 1H), 3.86 (d, *J* = 8.4 Hz, 1H), 3.76 (s, 3H).

HRMS (ESI): exact mass calcd for $C_{19}H_{15}NNaO_4^+$ $(M+Na)^+$ requires m/z 344.0893, found m/z 344.0892 (Δ = -1 ppm). Known compound.[9]

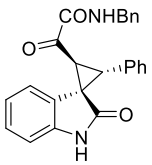
General procedure for the synthesis of spiro-cyclopropane-oxindoles 6a-6c



Preparation of $Co(acac)_2$ and **L6** solution: in a 2.0 mL volumetric flask, $Co(acac)_2$ (6.4 mg, 0.025 mmol) was added, then THF was added to make the total volume up to 2.0 mL. In a 2.0 mL volumetric flask, **L6** (17.6 mg, 0.025 mmol) was added, then THF was added to make the total volume up to 2.0 mL.

In a dry reaction tube, 200 μL (2.5 mol%) of $Co(acac)_2$ solution and 200 μL (2.5 mol%) of **L6** were added. Then, THF was removed under vacuum. After that, *β*,*γ*-unsaturated-*α*- ketoamides **5a** (26.5 mg, 0.1 mmol) and EtOAc (2.0 mL) were added and the reaction was stirred at 30 °C for 0.5 h. Subsequently, 3-chlorooxindoles **1a** (16.7 mg, 0.1 mmol) and Na_2CO_3 (11.7 mg, 0.11 mmol) were added and the reaction was stirred at 30 °C until **1a** was consumed (detected by TLC, Pet/EtOAc, 1/1, v/v). Finally, the corresponding product **6a** was purified directly by flask column chromatography (Pet/EtOAc, 5/1-1/1, v/v).

N-benzyl-2-oxo-2-((1*R*,2*S*,3*R*)-2'-oxo-2-phenylspiro[cyclopropane-1,3'-indolin]-3-yl)acetamide (**6a**)



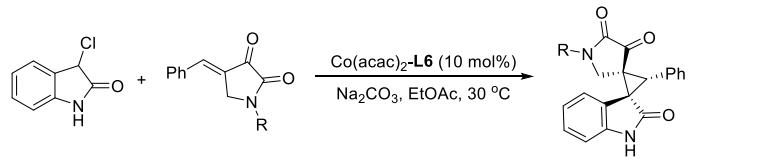
Light yellow oil, 36.0 mg, 91% yield, 95:5 dr, 97% ee; R_f = 0.4 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{25}$ = +82.46 (c = 0.69, CH_2Cl_2); reaction time: 36 h; reaction temperature: 30 °C.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 70/30, flow rate 1.0 mL/min, λ = 254 nm, retention time: 13.143 min (major), 21.757 min (minor).

^{1}H NMR (600 MHz, DMSO-d^6) δ 10.64 (s, 1H), 9.24 (t, *J* = 6.6 Hz, 1H), 7.37 – 7.21 (m, 10H), 7.09 (td, *J* = 7.8, 1.2 Hz, 1H), 6.86 (d, *J* = 7.2 Hz, 1H), 6.65 (t, *J* = 7.8 Hz, 1H), 6.15 (d, *J* = 7.2 Hz, 1H), 4.37 – 4.24 (m, 2H), 4.01 (d, *J* = 9.0 Hz, 1H), 3.58 (d, *J* = 8.4 Hz, 1H).

^{13}C NMR (150 MHz, DMSO-d^6) δ 191.6, 174.0, 160.2, 142.5, 138.6, 133.4, 129.6, 128.4, 128.2, 127.6, 127.4, 127.3, 126.8, 126.0, 121.0, 120.7, 109.5, 42.1, 40.0, 37.8, 36.7.

HRMS (ESI): exact mass calcd for $C_{25}H_{20}N_2NaO_3^+$ $(M+Na)^+$ requires m/z 419.1366, found m/z 419.1373 (Δ = +7 ppm).

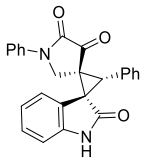


1a R = Ph, **5b**; R = Bn, **5c**

6b R = Ph, 70% yield, 99:1 dr, 99% ee
6c R = Bn, 65% yield, 96:4 dr, 91% ee

In a dry reaction tube, a mixture of 2,3-dioxopyrrolidine **5** (0.1 mmol), $Co(acac)_2$ (2.6 mg, 0.1 mmol, 10 mol%) and ligand **L6** (7.1 mg, 0.1 mmol, 10 mol%) in EtOAc (2.0 mL) were stirred at 30 °C for 0.5 h. After that, 3-chlorooxindole **1a** (16.7 mg, 0.1 mmol) and Na_2CO_3 (11.7 mg, 0.11 mmol) were added. Subsequently, the reaction was stirred at 30 °C for 24 h. After the reaction was complete monitored by TLC (Pet/EtOAc, 3/1, v/v), the reaction was purified by flash column chromatography (Pet/EtOAc, 5/1-3/1, v/v) to give the product **6b** as a light yellow solid (27.6 mg, 70% yield, 99:1 dr, 99% ee) and **6c** as a light yellow solid (26.5 mg, 65% yield, 96:4 dr, 91% ee).

(2'*S*,3*R*,3'*S*)-1'',3'-Diphenyldispiro[indoline-3,1'-cyclopropane-2',3''-pyrrolidine]-2,4'',5''-trione (6b)



Light yellow solid, 27.6 mg, 70% yield, 99:1 dr, 99% ee; R_f = 0.35 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{20}$ = -15.14 (c = 0.78, CH_2Cl_2); reaction time: 24 h; reaction temperature: 30 °C.

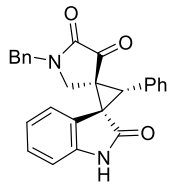
HPLC CHIRALPAK ID, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 19.988 min (major), 26.047 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.65 (s, 1H), 7.90 (d, *J* = 8.4 Hz, 2H), 7.44 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.27 (m, 4H), 7.10 (d, *J* = 7.8 Hz, 1H), 6.99 – 6.92 (m, 3H), 6.88 (t, *J* = 7.8 Hz, 1H), 4.62 (d, *J* = 12.0 Hz, 1H), 4.53 (d, *J* = 12.0 Hz, 1H), 4.02 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 191.6, 174.1, 157.8, 141.0, 138.5, 130.8, 129.5, 128.8, 128.6, 128.5, 128.3, 127.0, 122.4, 121.8, 119.4, 110.0, 48.4, 47.6, 43.3, 41.0.

HRMS (ESI): exact mass calcd for $C_{25}H_{18}N_2NaO_3^+$ $(M+Na)^+$ requires m/z 417.1210, found m/z 417.1206 (Δ = -4 ppm). Known compound.[10]

(2'*S*,3*R*,3'*S*)-1"-benzyl-3'-phenyldispiro[indoline-3,1'-cyclopropane-2',3"-pyrrolidine]-2,4",5"-trione (**6c**)



Light yellow solid, 26.5 mg, 65% yield, 96:4 dr, 91% ee; R_f = 0.35 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{20}$ = -31.88 (c = 0.69, CH_2Cl_2); reaction time: 24 h; reaction temperature: 30 °C.

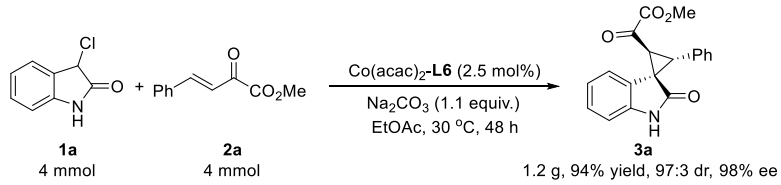
HPLC CHIRALPAK IE, n-hexane/2-propanol = 60/40, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.170 min (major), 21.755 min (minor).

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.73 (s, 1H), 6.86 – 6.78 (m, 5H), 6.77 – 6.71 (m, 3H), 6.64 (t, *J* = 7.2 Hz, 1H), 6.53 (d, *J* = 7.8 Hz, 1H), 6.38 (d, *J* = 8.4 Hz, 1H), 6.34 (d, *J* = 8.4 Hz, 2H), 6.30 (t, *J* = 7.8 Hz, 1H), 4.35 (d, *J* = 14.4 Hz, 1H), 4.08 (d, *J* = 14.4 Hz, 1H), 3.50 (d, *J* = 12.6 Hz, 1H), 3.42 (d, *J* = 13.2 Hz, 1H), 3.28 (s, 1H).

^{13}C NMR (150 MHz, $CDCl_3$) δ 192.2, 174.0, 159.3, 141.5, 134.7, 130.8, 129.2, 128.8, 128.52, 128.47, 128.42, 128.3, 128.1, 121.9, 110.0, 48.8, 47.6, 47.1, 43.3, 41.2.

HRMS (ESI): exact mass calcd for $C_{26}H_{20}N_2NaO_3^+$ $(M+Na)^+$ requires m/z 431.1366, found m/z 431.1366 (Δ = 0 ppm).

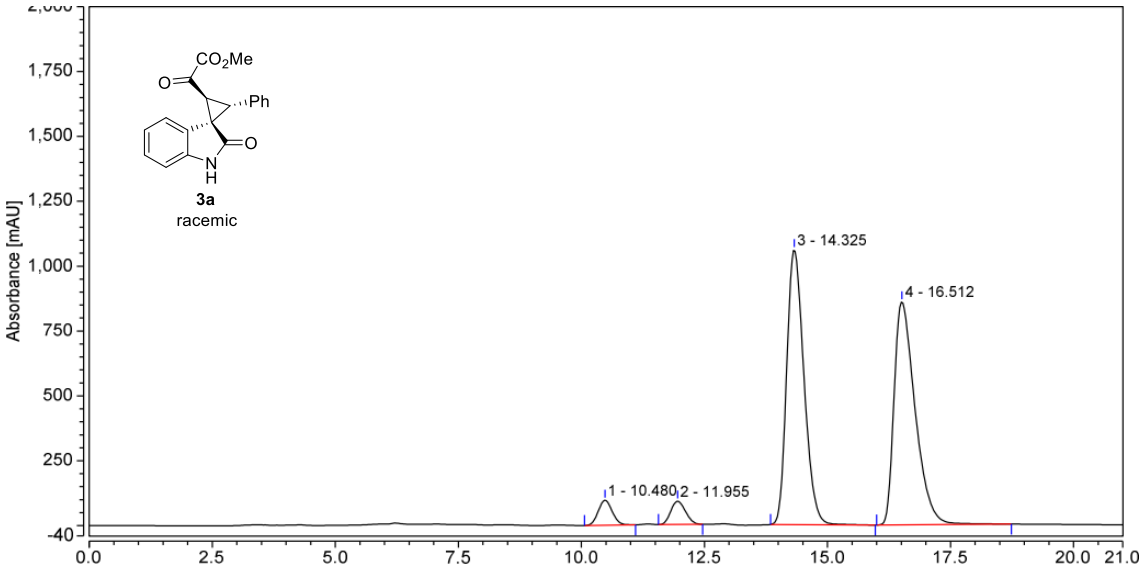
Gram-scale synthesis of 3a



In a dry reaction tube, a mixture of β,γ-unsaturated-α-ketoester **2a** (760.0 mg, 4.0 mmol), $Co(acac)_2$ (25.7 mg, 0.1 mmol, 2.5 mol%) and ligand **L6** (70.5 mg, 0.1 mmol, 2.5 mol%) in EtOAc (80.0 mL) were stirred at 30 °C for 6 h. After that, 3-chlorooxindole **1a** (668.0 mg, 4.0 mmol) and Na_2CO_3 (466.4 mg, 4.4 mmol) were added. Subsequently, the reaction was stirred at 30 °C for 48 h. After the reaction was complete monitored by TLC (R_f = 0.4, Pet/EtOAc, 1/1, v/v), the reaction was purified by flash column chromatography (Pet/EtOAc, 5/1-1/1, v/v) to give the product **3a** as a colorless solid (1.2 g, 94% yield, 97:3 dr, 98% ee).

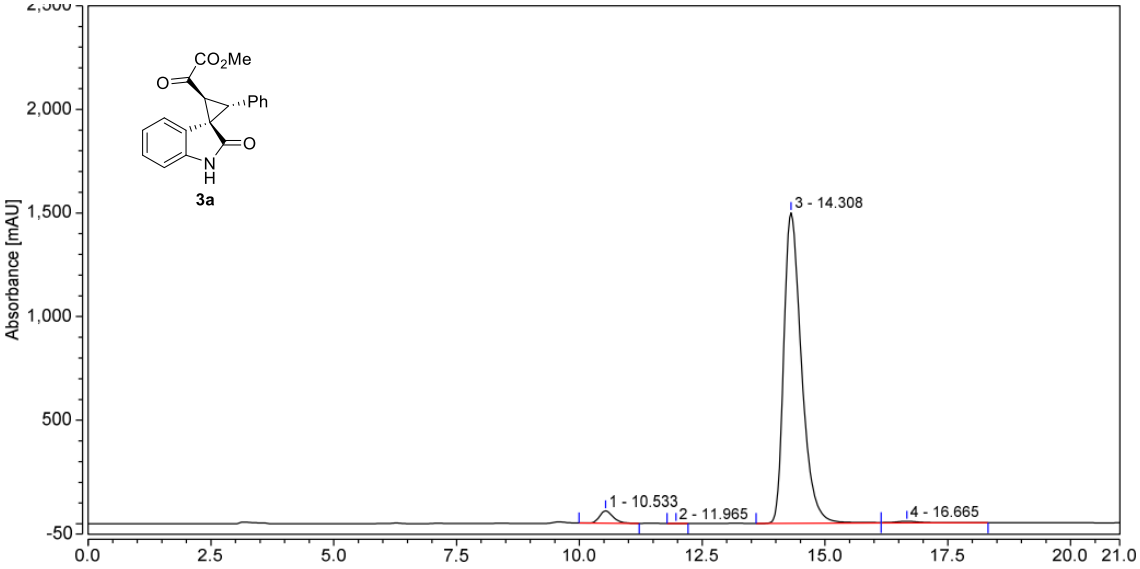
Figure S1. HPLC spectra of **3a** on a gram-scale

HPLC Spectrum of **3a**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.480	31.817	96.448	3.46	4.58
2	11.955	31.078	90.023	3.38	4.27
3	14.325	430.583	1060.196	46.84	50.33
4	16.512	425.876	859.651	46.32	40.81
Total:		**919.354**	**2106.318**	**100.00**	**100.00**

HPLC Spectrum of **3a**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.533	18.845	58.948	2.89	3.76
2	11.965	0.042	0.192	0.01	0.01
3	14.308	627.012	1499.485	96.24	95.69
4	16.665	5.632	8.448	0.86	0.54
Total:		**651.530**	**1567.073**	**100.00**	**100.00**

Nonlinear effect experiment

Nonlinear effect experiment between the ee value of ligand **L6** and product **3a**

a) Preparation of catalyst **L6** solution: in a 5.0 mL volumetric flask, **L6** (35.3 mg, 0.05 mmol) was added, then THF was added to make the total volume up to 5.0 mL.

b) Preparation of catalyst *ent*-**L6** solution: in a 5.0 mL volumetric flask, *ent*-**L6** (35.3 mg, 0.05 mmol) was added, then THF was added to make the total volume up to 5.0 mL.

c) Preparation of metal solution: in a 5.0 mL volumetric flask, $Co(acac)_2$ (12.9 mg, 0.05 mmol) was added, then THF was added to make the total volume up to 5.0 mL.

For 0% ee of **L6**: 250 μL **L6** was mixed with 250 μL *ent*-**L6**;

For 20% ee of **L6**: 300 μL **L6** was mixed with 200 μL *ent*-**L6**;

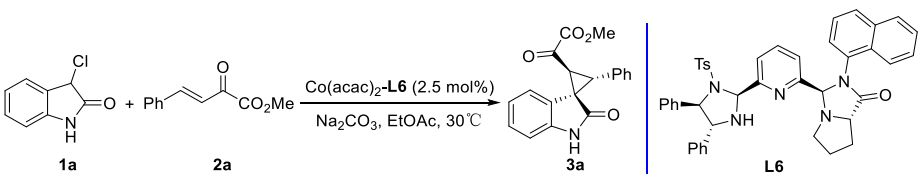
For 40% ee of **L6**: 350 μL **L6** was mixed with 150 μL *ent*-**L6**;

For 60% ee of **L6**: 400 μL **L6** was mixed with 100 μL *ent*-**L6**;

For 80% ee of **L6**: 450 μL **L6** was mixed with 50 μL *ent*-**L6**;

In a dry reaction tube, 2.5 mol % of $Co(acac)_2$ solution and 2.5 mol % of **L6** (0-99% ee) solution were added. Then, THF was removed under vacuum. After that, *β*,*γ*-unsaturated-*α*-ketoester **2a** (0.1 mmol, 19.0 mg) and EtOAc (2.0 mL) were added and the reaction was stirred at 30 °C for 0.5 h. Subsequently, 3-chlorooxindole **1a** (0.1 mmol, 16.7 mg) and Na_2CO_3 (11.7 mg, 0.11 mmol) were added and the reaction was stirred at 30 °C until **1a** was consumed (detected by TLC, Pet/EtOAc, 1/1, v/v). Finally, the corresponding product **3a** was purified directly by flask column chromatography (Pet/EtOAc, 5/1-1/1, v/v).

Table S5: the ee value of ligand **L6** and product **3a**



entry	ee of **L6** (%)	tested ee of **L6** (%)	ee (**3a**) (%)
1	0	11	10
2	20	26	29
3	40	51	47
4	60	73	72
5	80	85	80
6	>99	>99	99

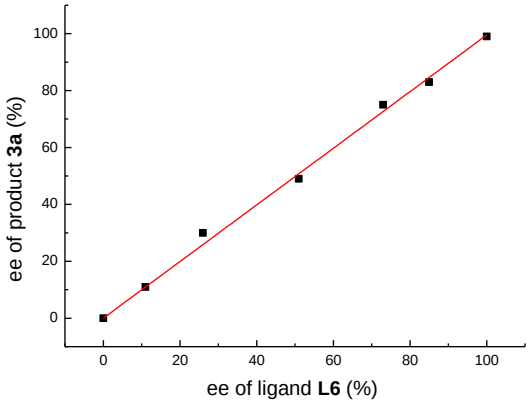
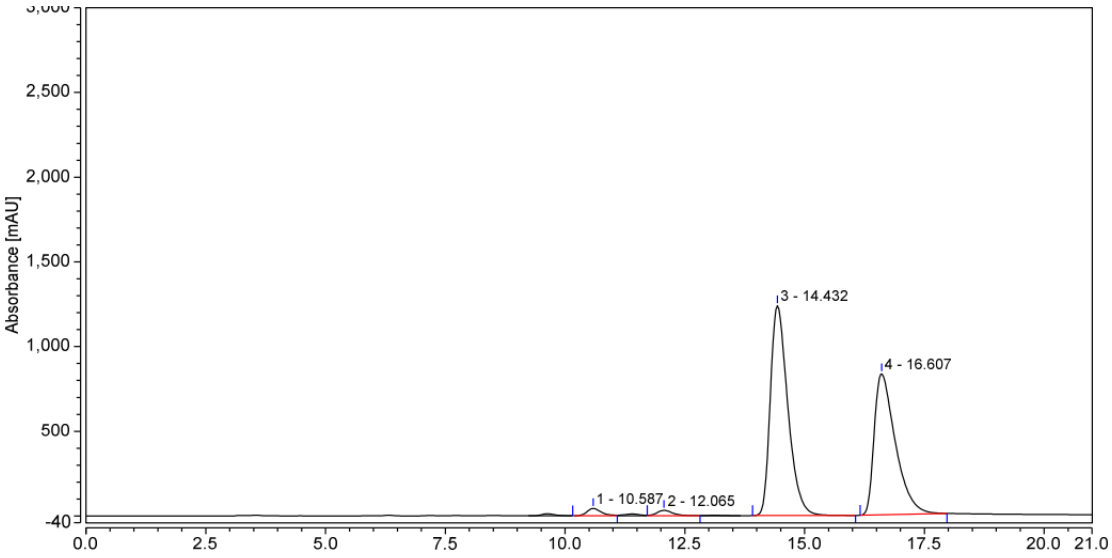


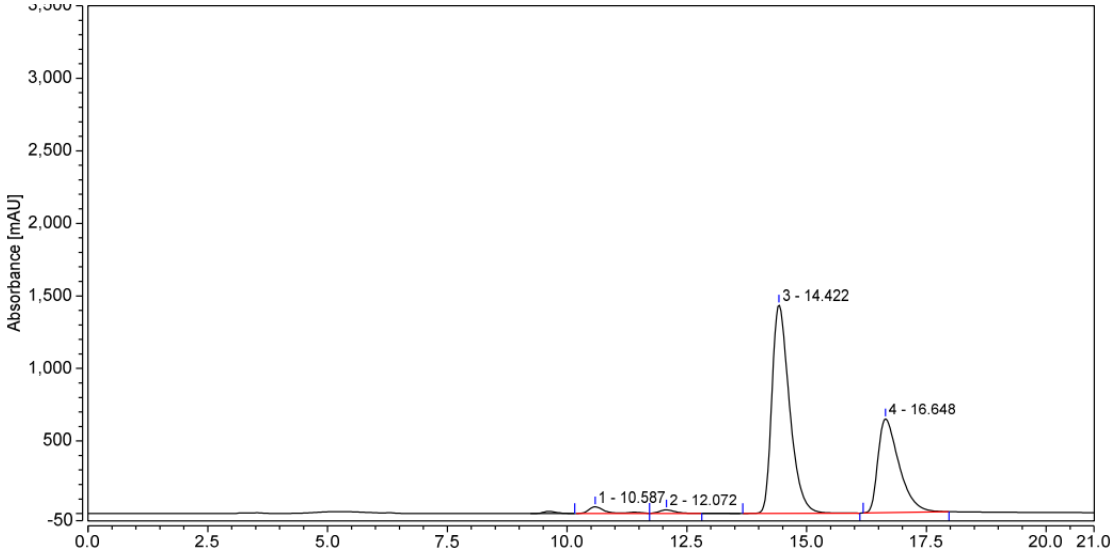
Figure S2. Determination of the linearity between ee values of ligand **L6** and product **3a**.

In the presence of ligand **L6** with 0% ee



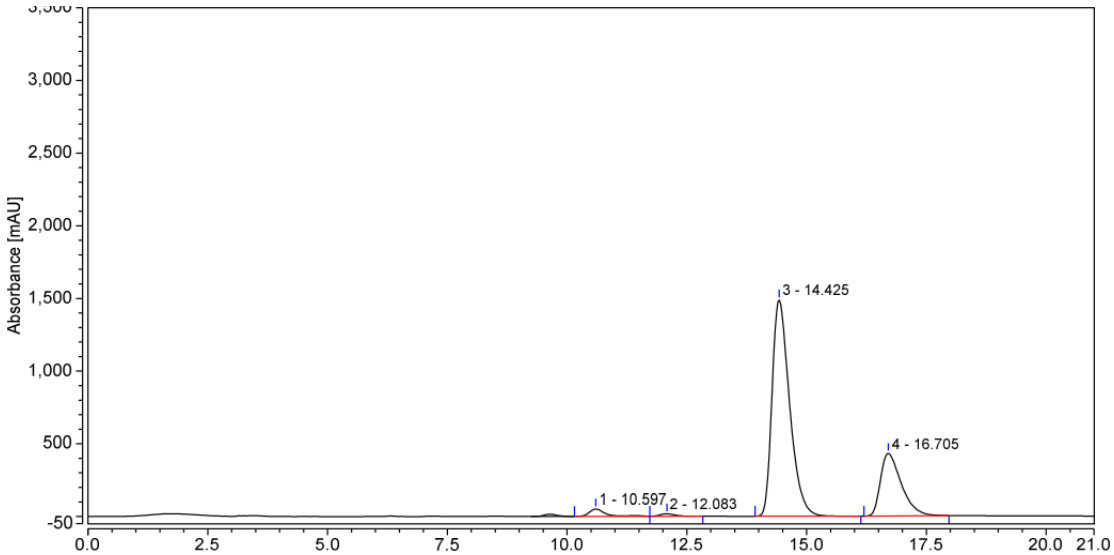
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.587	15.119	43.394	1.54	2.02
2	12.065	12.318	31.715	1.26	1.48
3	14.432	524.446	1238.673	53.58	57.68
4	16.607	427.007	833.556	43.62	38.82
Total:		**978.889**	**2147.338**	**100.00**	**100.00**

In the presence of ligand **L6** with 20% ee



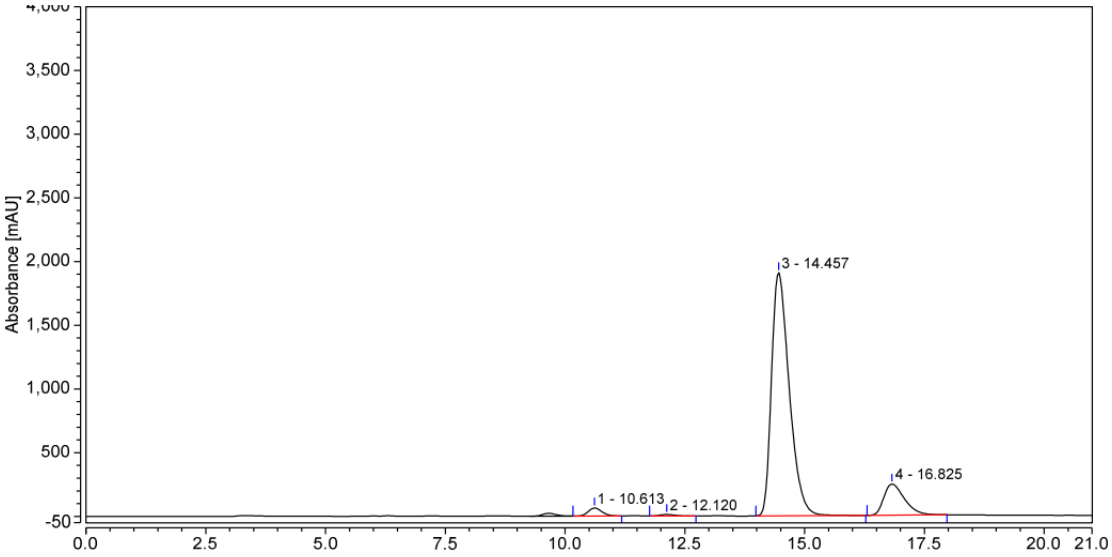
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.587	19.426	46.696	2.00	2.17
2	12.072	9.730	24.806	1.00	1.15
3	14.422	612.766	1436.066	63.04	66.67
4	16.648	330.167	646.575	33.96	30.02
Total:		**972.089**	**2154.143**	**100.00**	**100.00**

In the presence of ligand **L6** with 40% ee



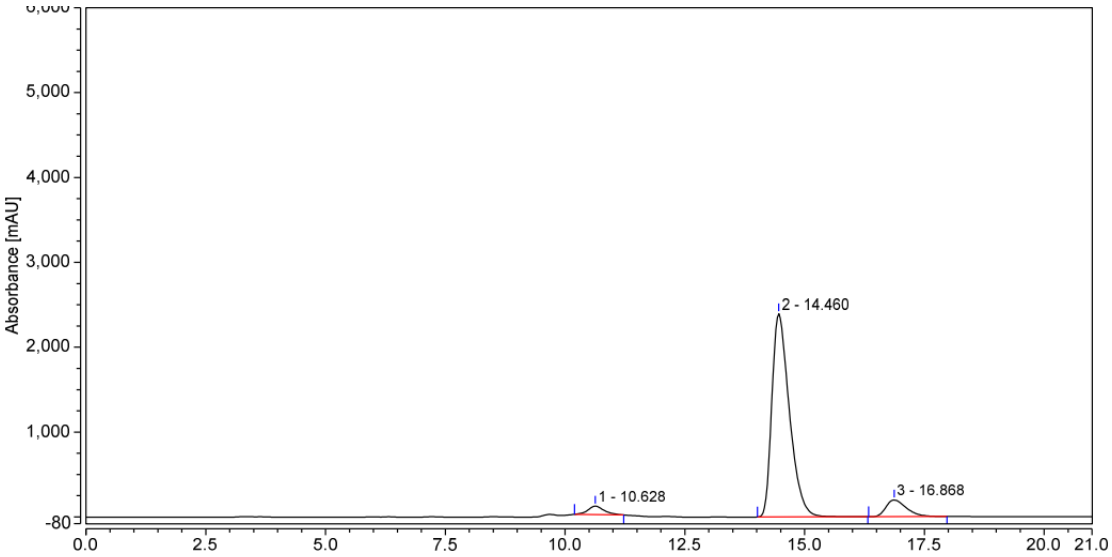
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.597	20.229	50.988	2.31	2.56
2	12.083	6.567	17.891	0.75	0.90
3	14.425	631.607	1489.323	72.16	74.86
4	16.705	216.841	431.175	24.77	21.67
Total:		**875.243**	**1989.377**	**100.00**	**100.00**

In the presence of ligand **L6** with 60% ee



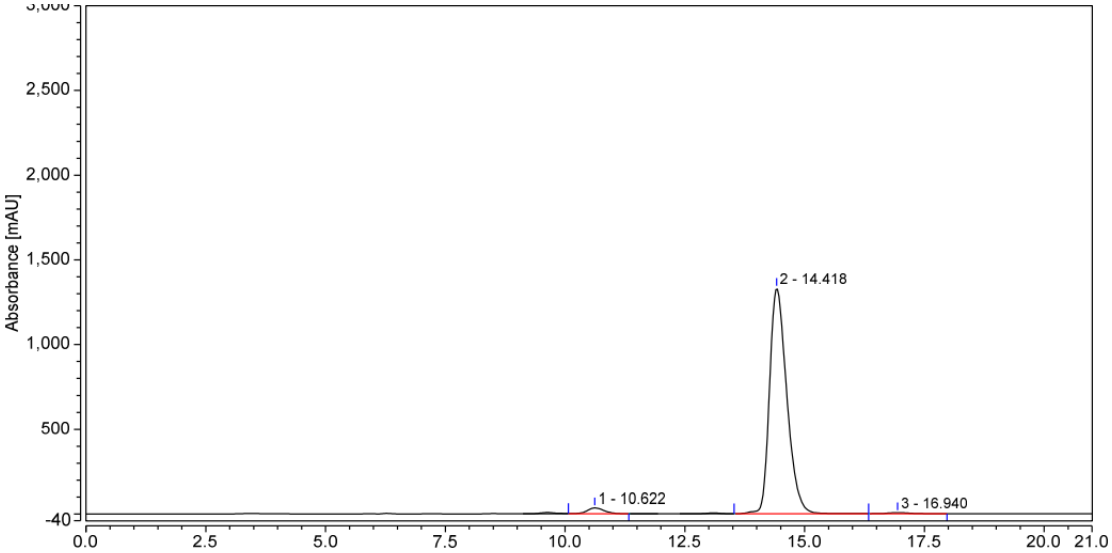
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.613	20.987	62.974	2.17	2.82
2	12.120	4.257	12.086	0.44	0.54
3	14.457	817.797	1909.400	84.73	85.65
4	16.825	122.195	244.728	12.66	10.98
Total:		**965.236**	**2229.188**	**100.00**	**100.00**

In the presence of ligand **L6** with 80% ee



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.628	38.851	99.394	3.37	3.69
2	14.460	1015.852	2394.399	88.17	89.00
3	16.868	97.446	196.413	8.46	7.30
Total:		**1152.150**	**2690.206**	**100.00**	**100.00**

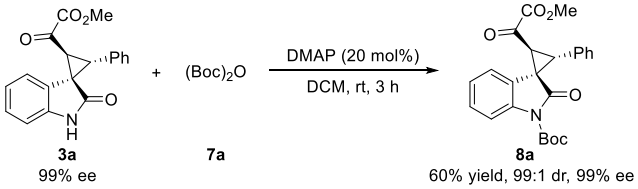
In the presence of ligand **L6** with >99% ee



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.622	14.906	34.933	2.58	2.55
2	14.418	558.423	1330.870	96.81	96.99
3	16.940	3.476	6.402	0.60	0.47
Total:		**576.805**	**1372.205**	**100.00**	**100.00**

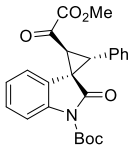
Figure S3. HPLC of **3a** with different ee value of ligand **L6**

Transformation of the product 3a



$(Boc)_2O$ (32.7 mg, 0.15 mmol) and DMAP (2.4 mg, 20 mol%) were added to a solution of **3a** (32.1 mg, 0.1 mmol) in DCM (2.0 mL). Then, the mixture was stirred for 3 h at room temperature until **3a** was consumed (detected by TLC). Finally, the corresponding product **8a** (25.3 mg, 60% yield, 99:1 dr, 99% ee) was purified directly by flask column chromatography (Pet/EtOAc, 50/1-5/1, v/v) as a white solid.

Tert-butyl (1*R*,2*S*,3*R*)-2-(2-methoxy-2-oxoacetyl)-2'-oxo-3-phenylspiro[cyclopropane-1,3'-indoline]-1'-carboxylate (8a)

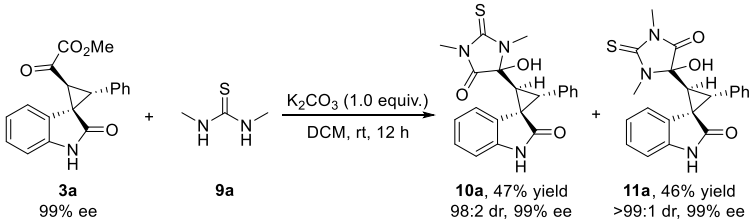


White solid, 25.3 mg, 60% yield, 99:1 dr, 99% ee; R_f = 0.4 (Pet/EtOAc, 5/1, v/v); $[\alpha]_D^{24}$ = +124.49 (c = 1.01, CH_2Cl_2); reaction time: 3 h; reaction temperature: 25 ºC.

HPLC CHIRALPAK IE, n-hexane/2-propanol = 80/20, flow rate 1.0 mL/min, λ = 254 nm, retention time: 14.720 min (major), 16.880 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.0 Hz, 1H), 7.32 – 7.29 (m, 3H), 7.22 (td, *J* = 7.6, 1.2 Hz, 1H), 7.19 – 7.16 (m, 2H), 6.82 (td, *J* = 8.0, 0.8 Hz, 1H), 6.03 (dd, *J* = 7.6, 1.6 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H), 3.86 (s, 3H), 3.51 (d, *J* = 8.4 Hz, 1H), 1.65 (s, 9H).

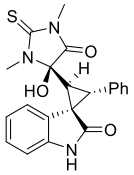
HRMS (ESI): exact mass calcd for $C_{24}H_{23}NNaO_6^+$ $(M+Na)^+$ requires m/z 444.1418, found m/z 444.1424 (Δ = +6 ppm). Known compound.[9]



In a test tube, *N,N'*-dimethylthiourea **9a** (41.7 mg, 0.4 mmol), **3a** (32.1 mg, 0.1 mmol) and K_2CO_3 (13.8 mg, 0.1 mmol) were added. Then, DCM (2.0 mL) was added and the mixture was stirred at room

temperature until **3a** was consumed (determined by TLC). Then the solvent was removed and the mixture was purified by flask column chromatography (Pet/EtOAc, 5/1-3/1, v/v) to afford the products.

(1*R*,2*S*,3*R*)-2-(4-Hydroxy-1,3-dimethyl-5-oxo-2-thioxoimidazolidin-4-yl)-3-phenylspiro[cyclopropane-1,3'-indolin]-2'-one (10a)



White solid, 18.5 mg, 47% yield, 98:2 dr, 99% ee; m.p.: 188.9-191.3 °C; R_f = 0.3 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{23}$ = -35.22 (c = 1.05, CH_2Cl_2); reaction time: 12 h; reaction temperature: 25 °C.

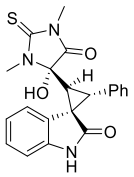
HPLC CHIRALPAK IE, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 35.127 min (major), 48.557 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.84 (s, 1H), 8.10 (s, 1H), 7.39 – 7.29 (m, 3H), 7.23 – 7.16 (m, 2H), 7.08 (td, *J* = 7.6, 1.2 Hz, 1H), 6.91 (d, *J* = 8.0 Hz, 1H), 6.68 (td, *J* = 7.6, 0.8 Hz, 1H), 5.95 (d, *J* = 7.6 Hz, 1H), 4.12 (d, *J* = 8.4 Hz, 1H), 3.47 (s, 3H), 3.24 (s, 3H), 2.56 (d, *J* = 8.0 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.7, 179.5, 173.5, 140.1, 132.4, 129.6, 129.0, 128.5, 127.8, 126.0, 122.6, 120.9, 110.7, 84.1, 39.8, 36.8, 36.4, 29.6, 28.2.

HRMS (ESI): exact mass calcd for $C_{21}H_{19}N_3NaO_3S^+$ $(M+Na)^+$ requires m/z 416.1039, found m/z 416.1045 (Δ = +6 ppm).

(1*R*,2*S*,3*R*)-2-((S)-4-Hydroxy-1,3-dimethyl-5-oxo-2-thioxoimidazolidin-4-yl)-3-phenylspiro [cyclopropane-1,3'-indolin]-2'-one (11a)



Yellow solid, 18.1 mg, 46% yield, >99:1 dr, 99% ee; m.p.: 229.8-232.5 °C; R_f = 0.25 (Pet/EtOAc, 2/1, v/v); $[\alpha]_D^{23}$ = +21.99 (c = 0.69, CH_2Cl_2); reaction time: 12 h; reaction temperature: 25 °C.

HPLC CHIRALPAK IG, n-hexane/2-propanol = 90/10, flow rate 1.0 mL/min, λ = 254 nm, retention time: 18.562 min (major), 25.237 min (minor).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.10 (s, 1H), 7.29 – 7.22 (m, 3H), 7.18 (td, *J* = 7.6, 1.2Hz, 1H), 7.10 – 7.04 (m, 2H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.75 (td, *J* = 7.6, 1.2 Hz, 1H), 5.88 (d, *J* = 7.6 Hz, 1H), 4.12 (d, *J* = 8.8 Hz, 1H), 3.41 (s, 3H), 3.12 (s, 3H), 2.39 (d, *J* = 8.8 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 182.4, 180.2, 171.1, 139.4, 132.3, 130.2, 128.7, 128.3, 128.2, 125.6, 123.1, 122.0, 110.6, 87.2, 40.2, 38.9, 38.3, 28.67, 28.65.

HRMS (ESI): exact mass calcd for $C_{21}H_{19}N_3NaO_3S^+$ $(M+Na)^+$ requires m/z 416.1039, found m/z 416.1041 (Δ = +2 ppm).

X-ray data of 8a

Figure S4. X-Ray crystal structure of **8a** (Recrystallization solvent: DCM/Pet).

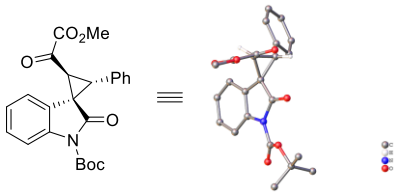
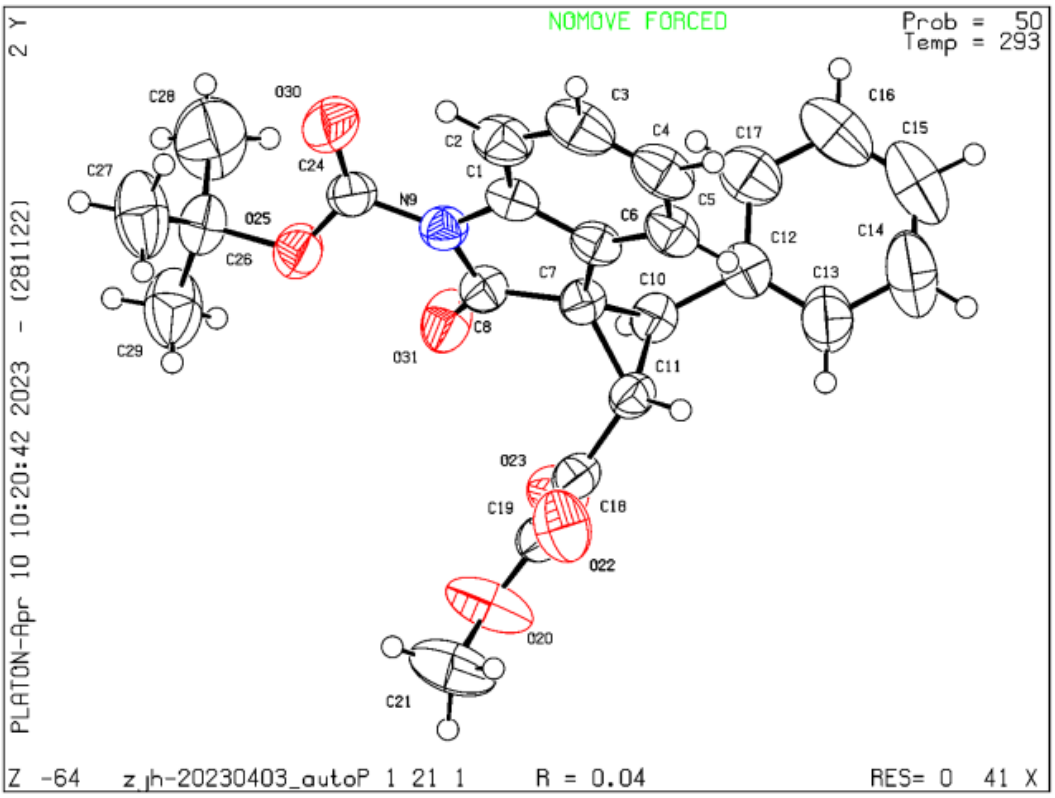


Table S6. Crystal data and structure refinement for (1*R*,2*S*,3*R*)-8a

Identification code	**(1*R*,2*S*,3*R*)-8a**
Empirical formula	$C_{24}H_{23}NO_6$
Formula weight	421.43
Temperature/K	293
Crystal system	monoclinic
Space group	$P2_1$
a/Å	10.51870(10)
b/Å	9.68800(10)
c/Å	10.81100(10)
α/°	90
β/°	93.3660(10)
γ/°	90
Volume/Å^3	1099.796(19)
Z	2
ρ_{calc}g/cm^3	1.273
μ/mm^{-1}	0.758
F(000)	444.0
Crystal size/mm^3	0.15 × 0.08 × 0.06
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.192 to 142.772
Index ranges	-12 ≤ h ≤ 12, -11 ≤ k ≤ 11, -13 ≤ l ≤ 13
Reflections collected	28934
Independent reflections	4237 [R_{int} = 0.0289, R_{sigma} = 0.0145]
Data/restraints/parameters	4237/8/284
Goodness-of-fit on F^2	1.028
Final R indexes [I>=2σ (I)]	R_1 = 0.0442, wR_2 = 0.1176
Final R indexes [all data]	R_1 = 0.0450, wR_2 = 0.1190
Largest diff. peak/hole / e Å^{-3}	0.19/-0.24
Flack parameter	0.03(6)

Datablock zjh-20230403_auto - ellipsoid plot



X-ray data of 10a

Figure S5. X-Ray crystal structure of **10a** (Recrystallization solvent: DCM/Pet). (CCDC: 2322316)

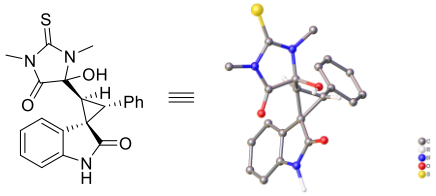
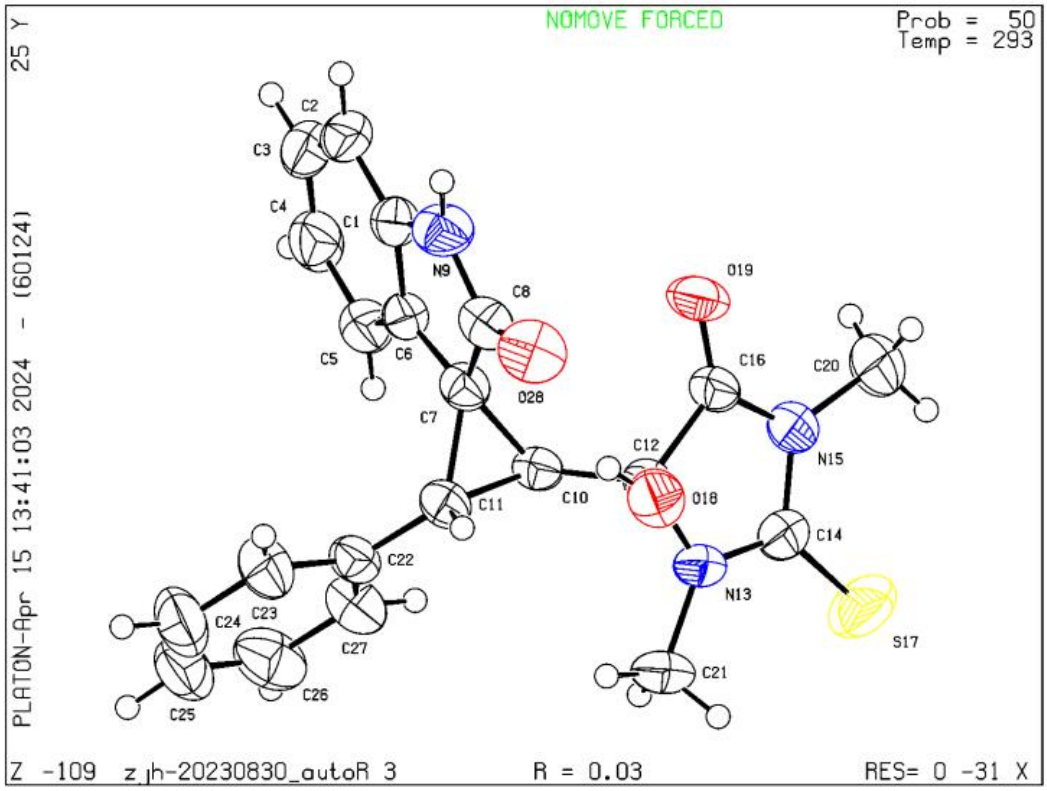


Table S7. Crystal data and structure refinement for (1*R*,2*S*,3*R*)-10a

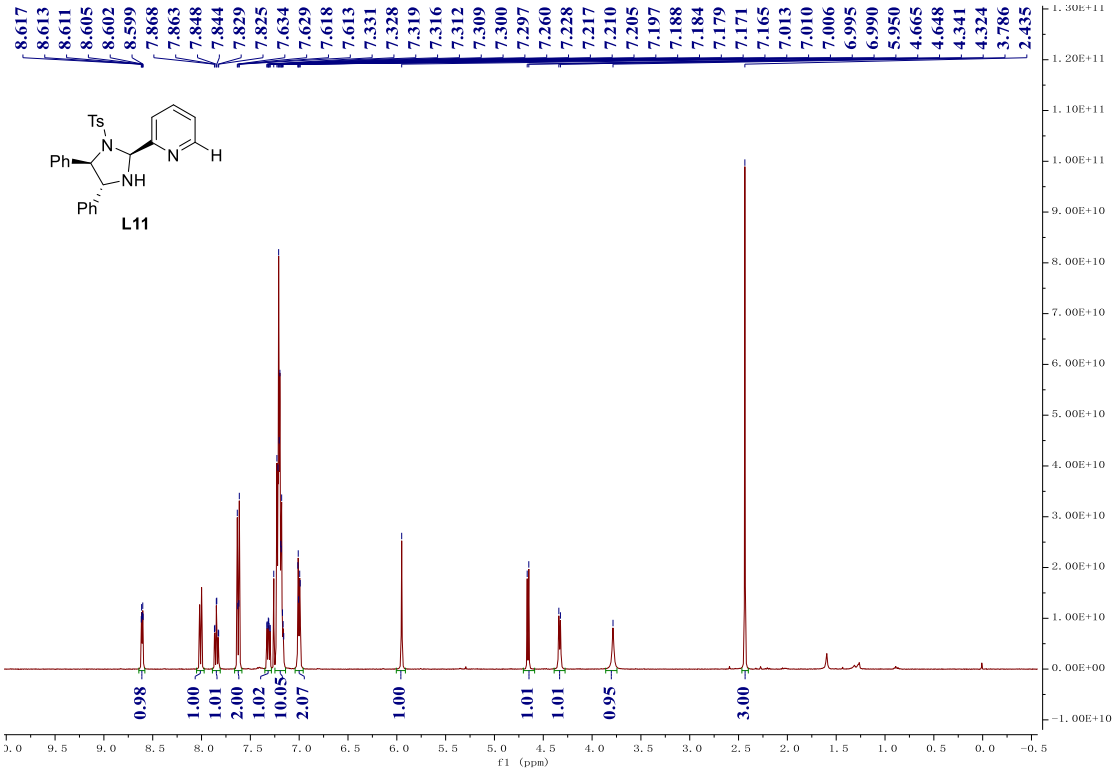
Identification code	**(1*R*,2*S*,3*R*)-10a**
Empirical formula	$C_{21}H_{19}N_3O_3S$
Formula weight	393.45
Temperature/K	293(2)
Crystal system	trigonal
Space group	R3
a/Å	21.7227(2)
b/Å	21.7227(2)
c/Å	11.97970(10)
α/°	90
β/°	90
γ/°	120
Volume/Å^3	4895.58(10)
Z	9
ρcalcg/cm^3	1.201
μ/mm^{-1}	1.526
F(000)	1854.0
Crystal size/mm^3	0.22 × 0.21 × 0.18
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	8.14 to 142.976
Index ranges	-26 ≤ h ≤ 23, -24 ≤ k ≤ 26, -14 ≤ l ≤ 14
Reflections collected	24617
Independent reflections	4218 [Rint = 0.0261, Rsigma = 0.0166]
Data/restraints/parameters	4218/1/259
Goodness-of-fit on F^2	1.029
Final R indexes [I>=2σ (I)]	R1 = 0.0329, wR2 = 0.0930
Final R indexes [all data]	R1 = 0.0334, wR2 = 0.0937
Largest diff. peak/hole / e Å^{-3}	0.15/-0.15
Flack parameter	0.004(11)

Datablock zjh-20230830_auto - ellipsoid plot

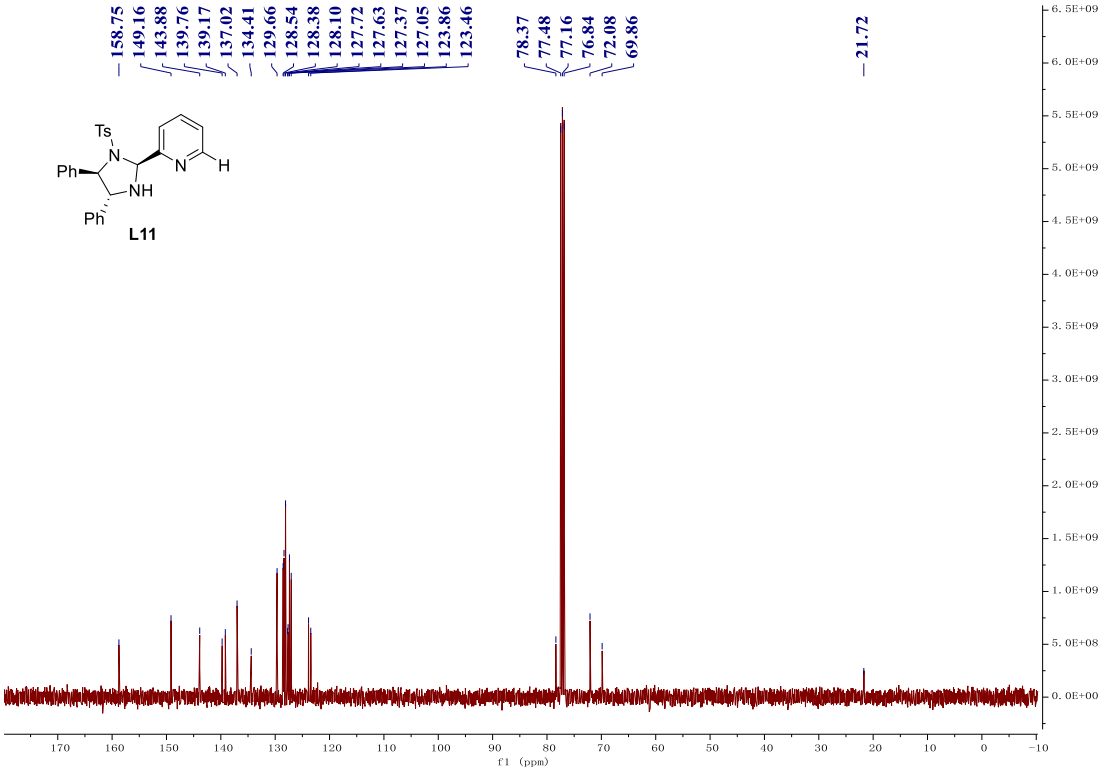


NMR Spectra

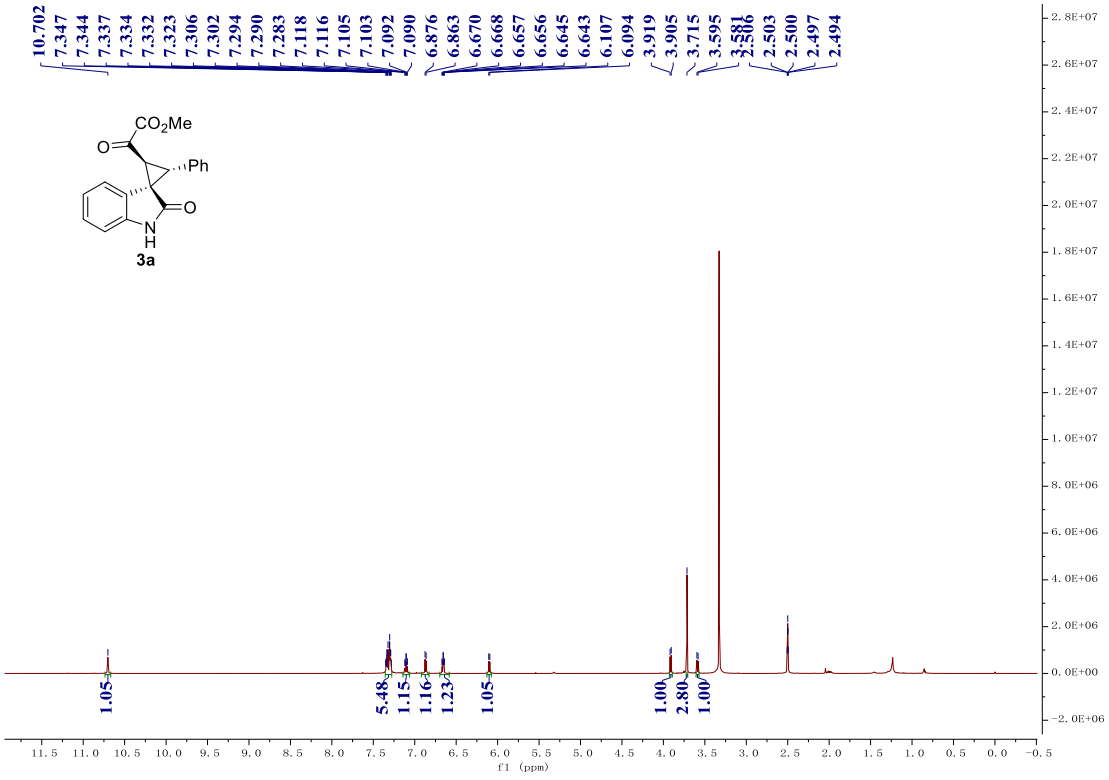
^{1}H NMR Spectrum of **L11** (400 MHz, $CDCl_3$)



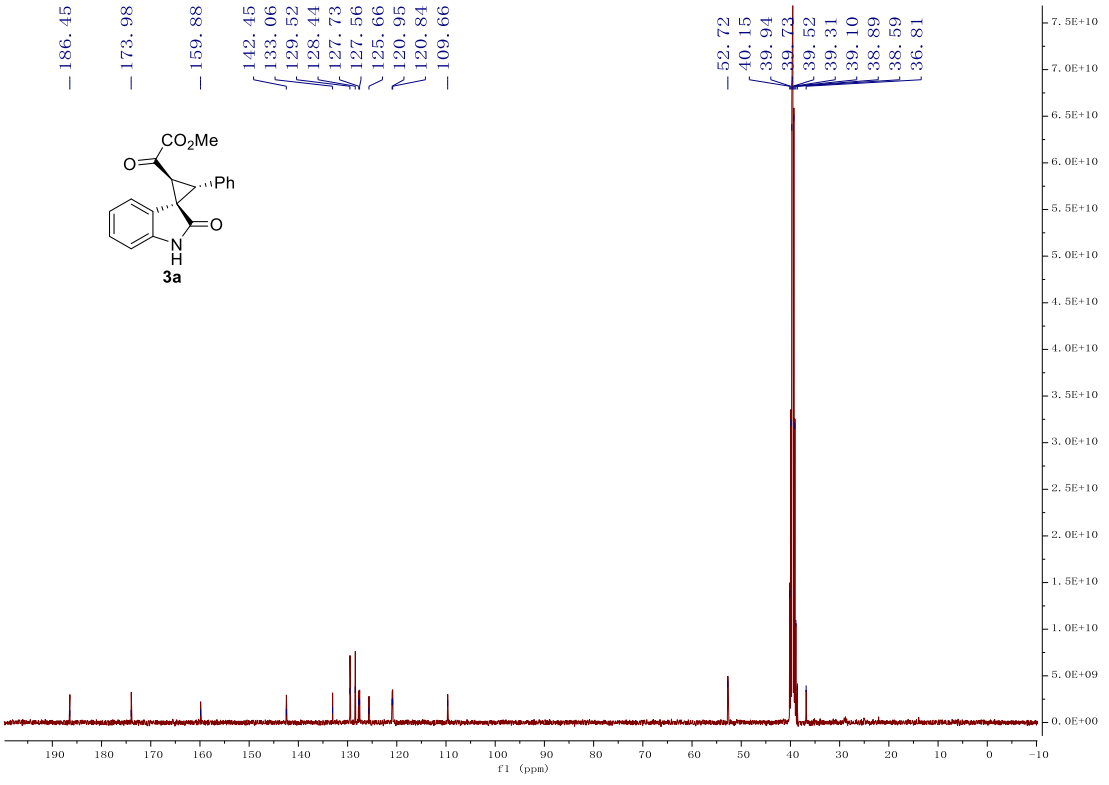
^{13}C NMR Spectrum of **L11** (100 MHz, $CDCl_3$)



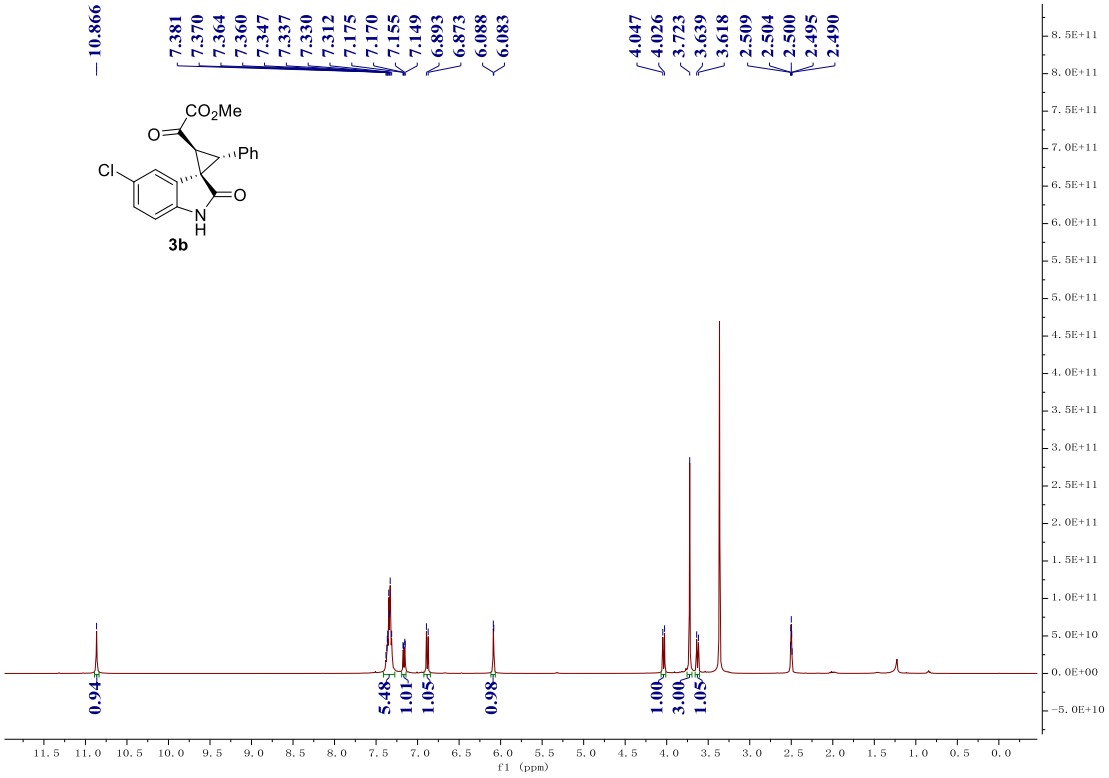
^{1}H NMR Spectrum of **3a** (400 MHz, DMSO-d^{6})



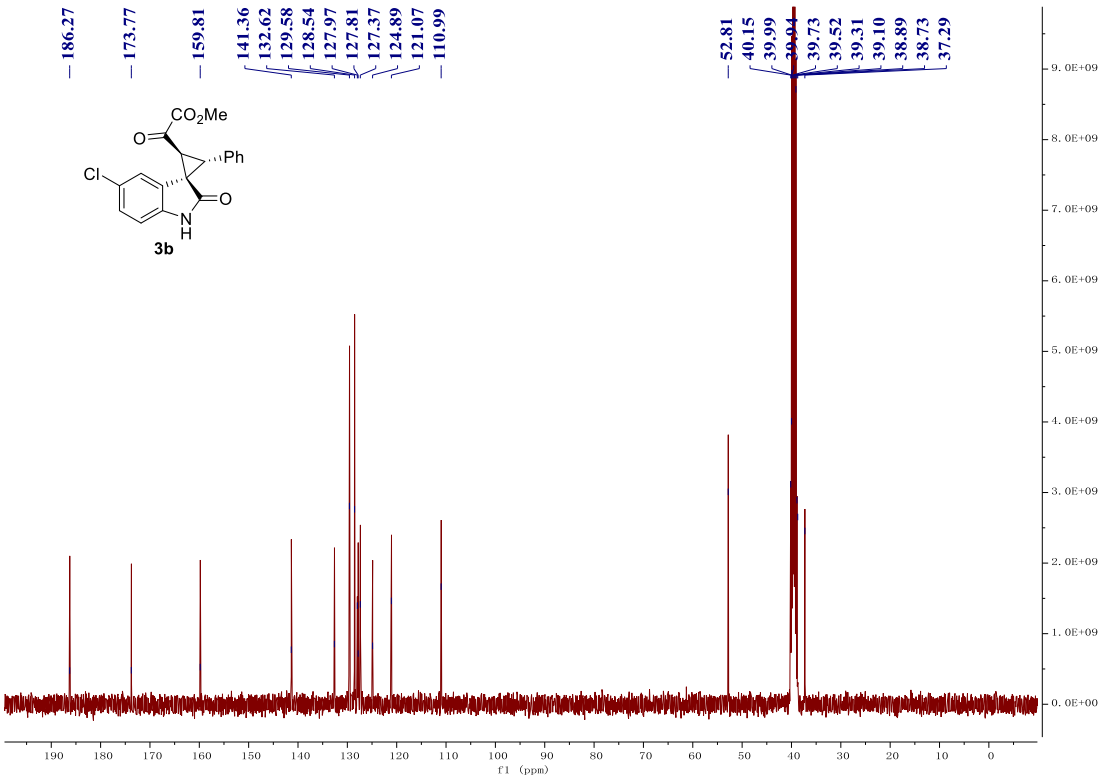
^{13}C NMR Spectrum of **3a** (100 MHz, DMSO-d^{6})



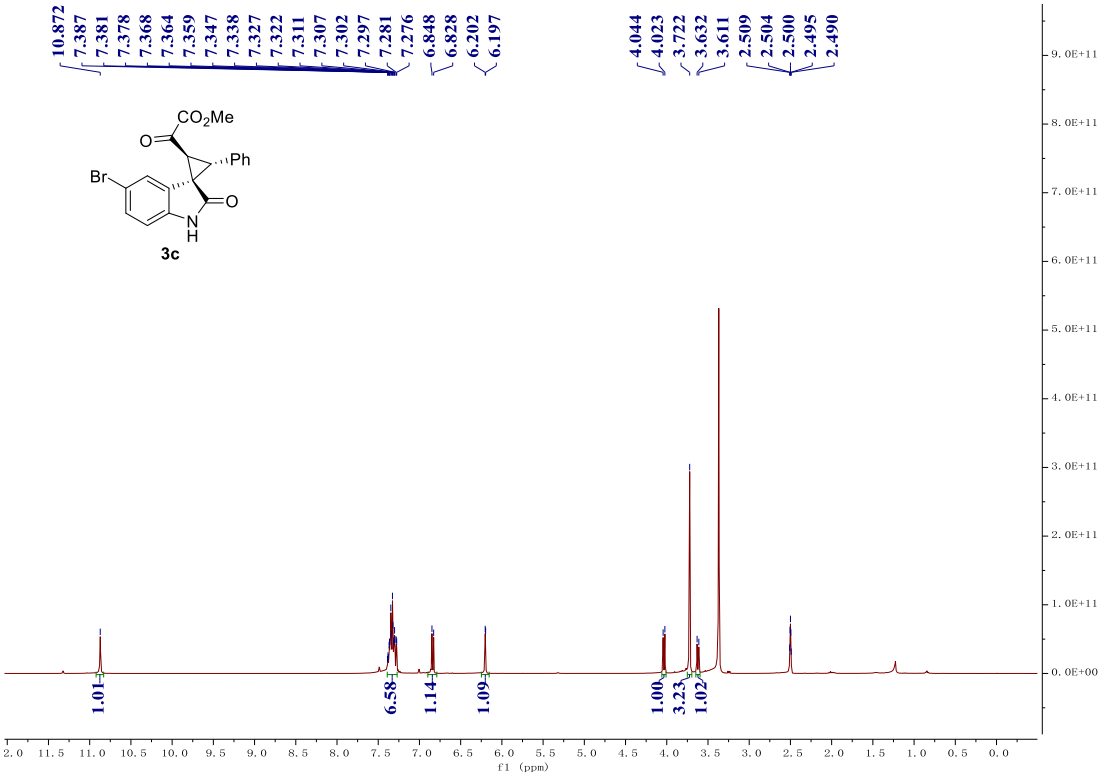
^{1}H NMR Spectrum of **3b** (400 MHz, DMSO-d^{6})



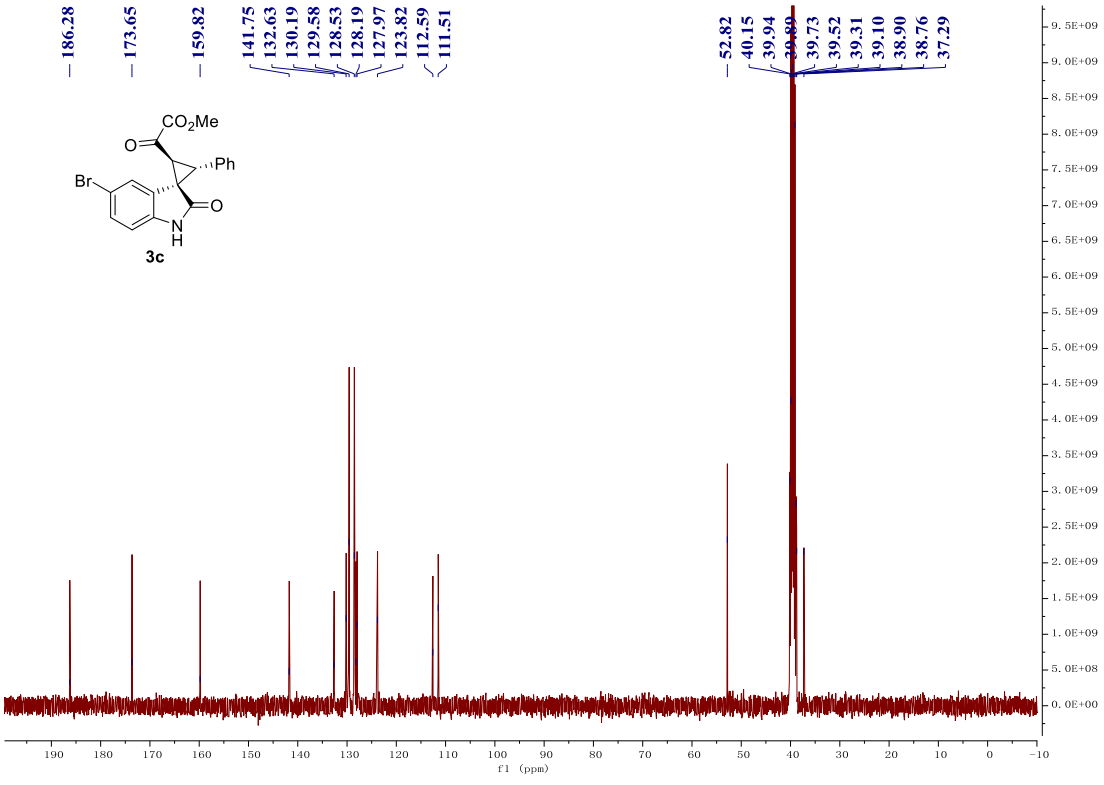
^{13}C NMR Spectrum of **3b** (100 MHz, DMSO-d^{6})



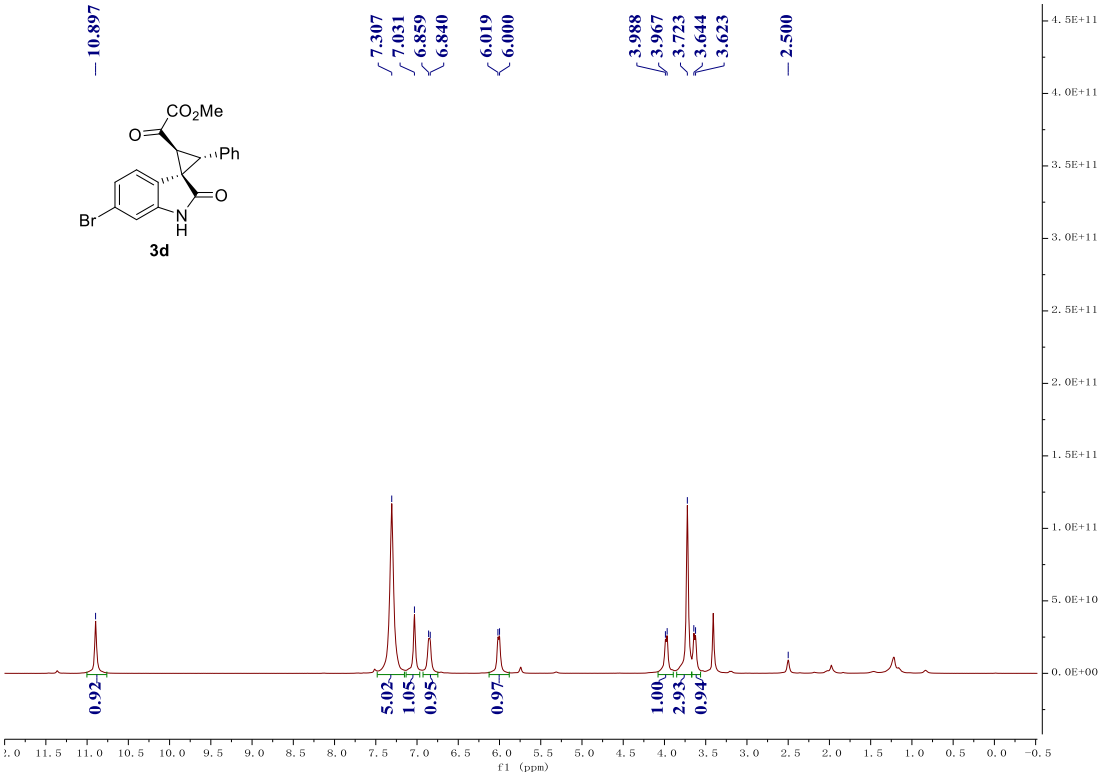
^{1}H NMR Spectrum of **3c** (400 MHz, DMSO-d^{6})



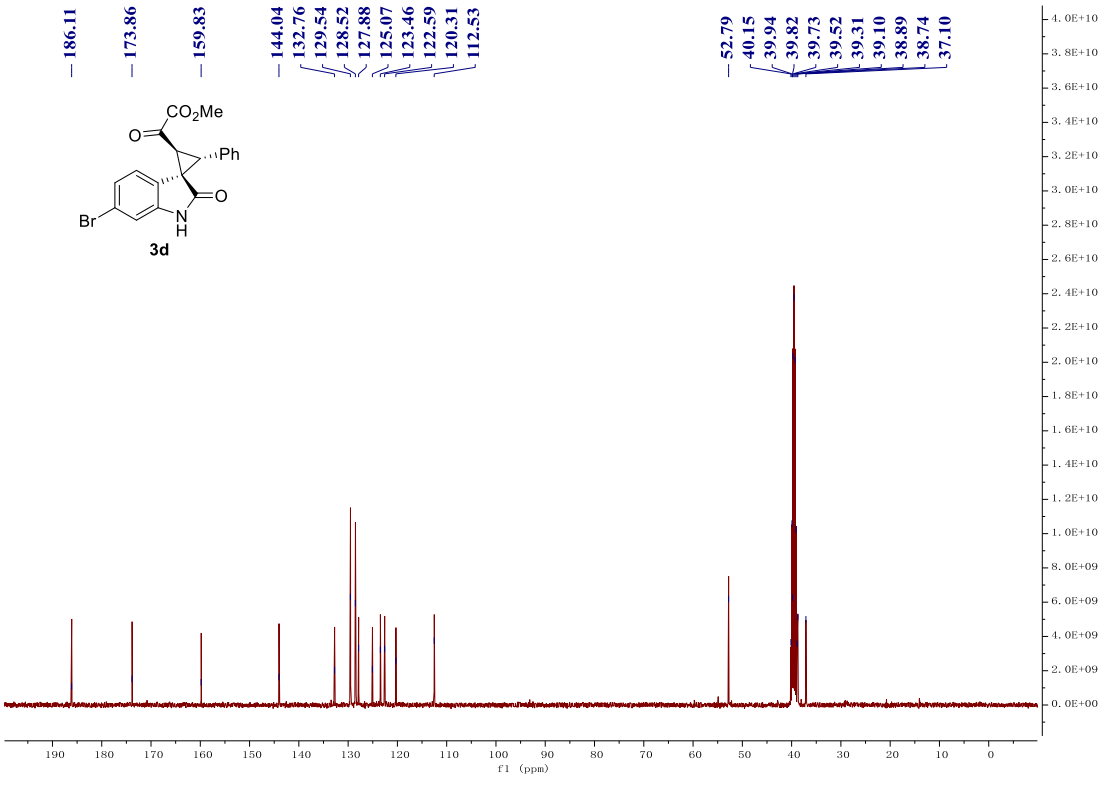
^{13}C NMR Spectrum of **3c** (100 MHz, DMSO-d^{6})



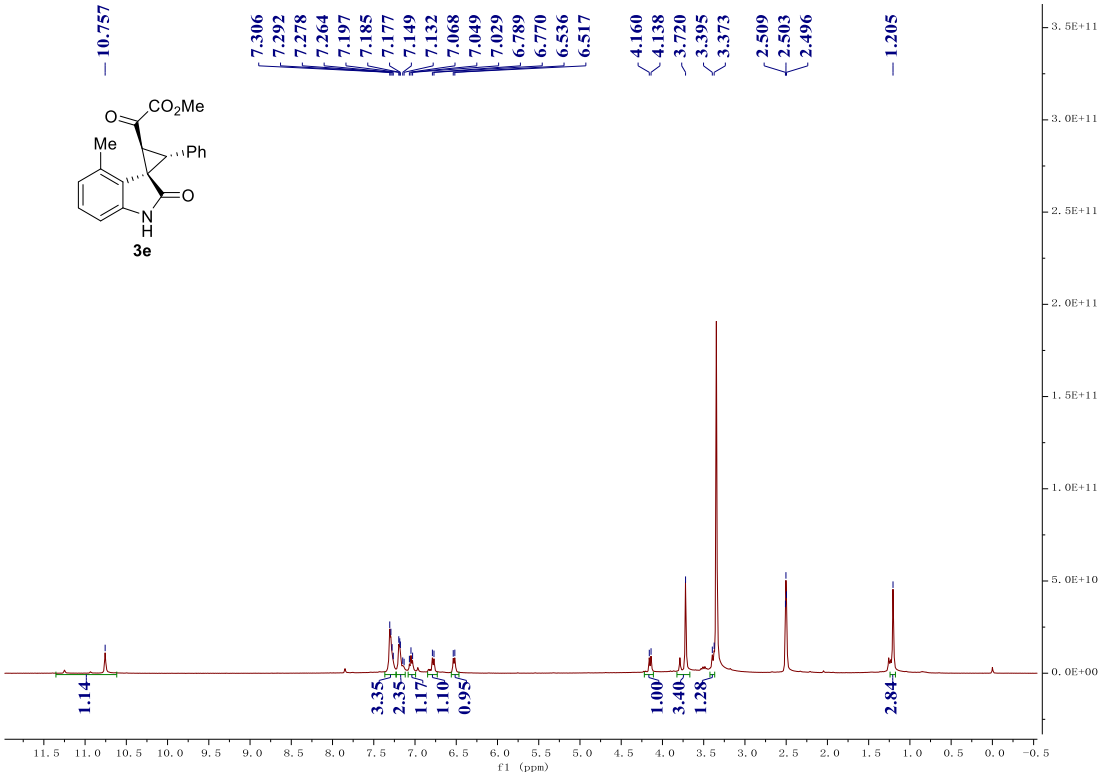
^{1}H NMR Spectrum of **3d** (400 MHz, DMSO-d^{6})



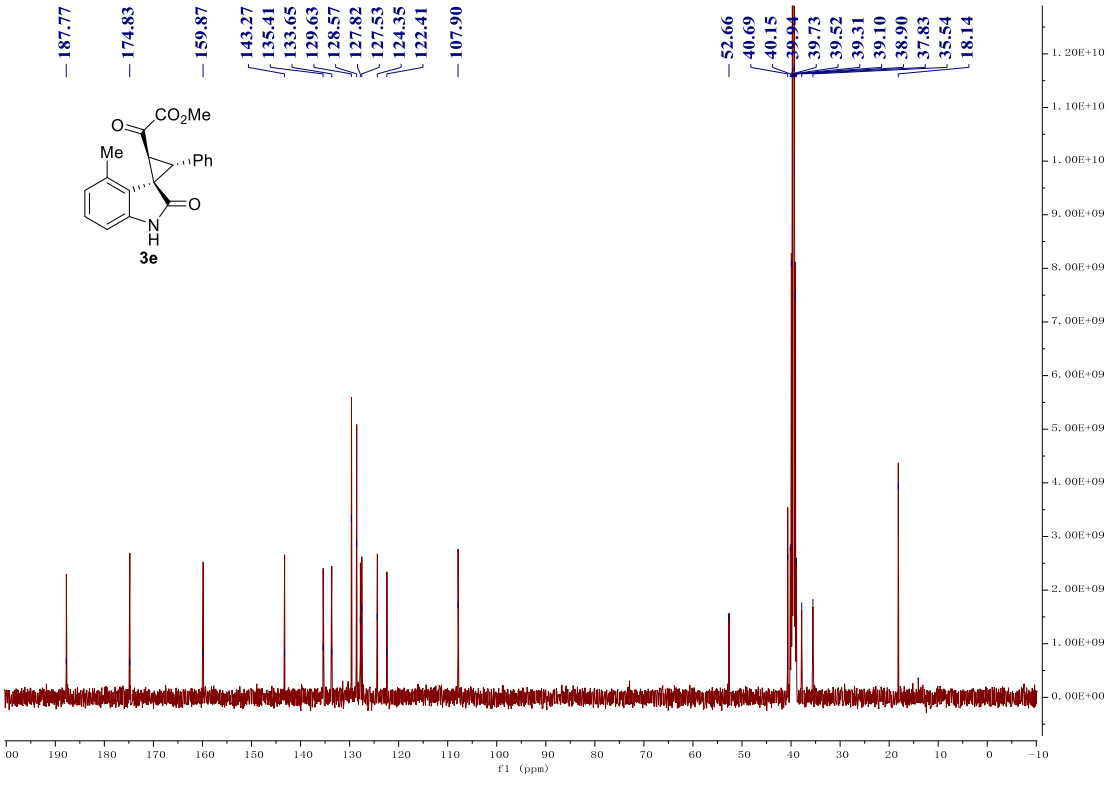
^{13}C NMR Spectrum of **3d** (100 MHz, DMSO-d^{6})



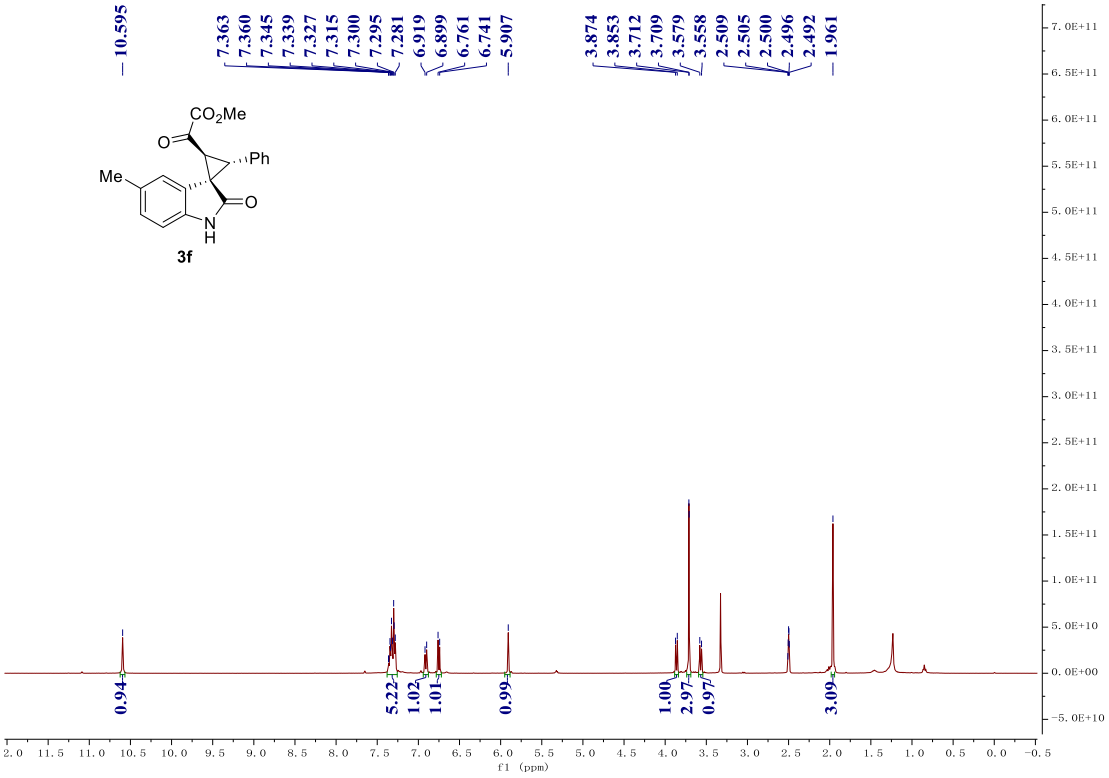
^{1}H NMR Spectrum of **3e** (400 MHz, DMSO-d^{6})



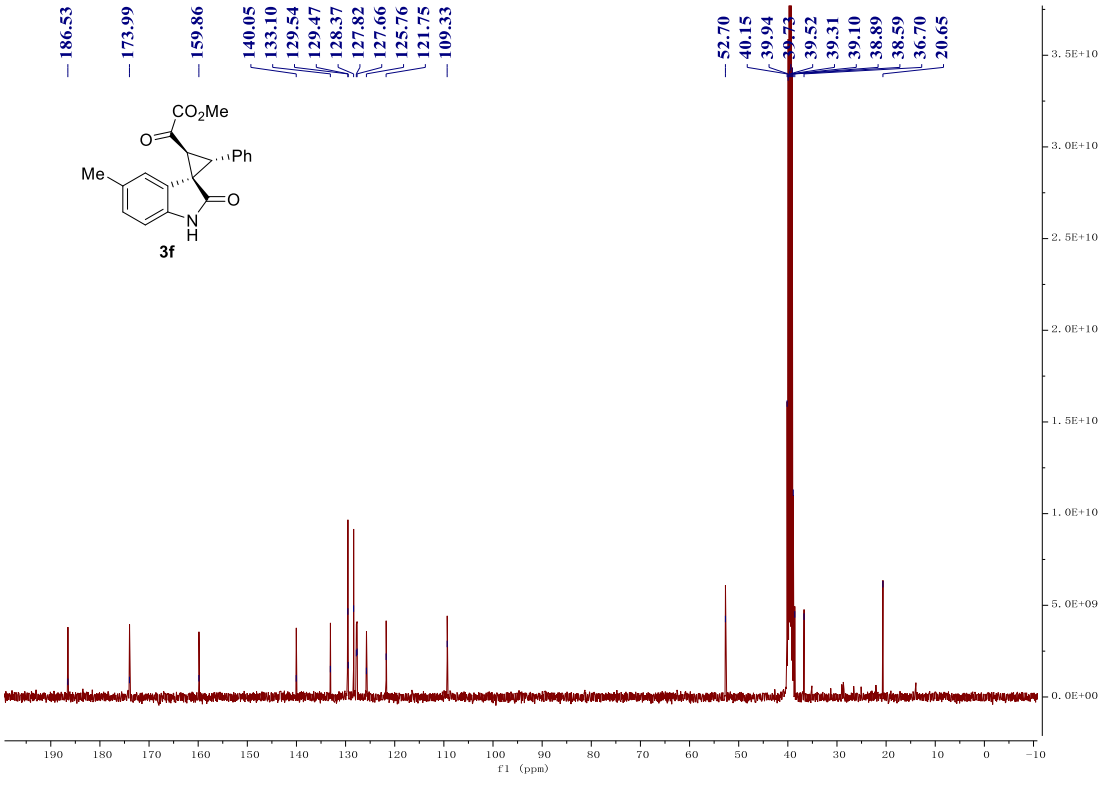
^{13}C NMR Spectrum of **3e** (100 MHz, DMSO-d^{6})



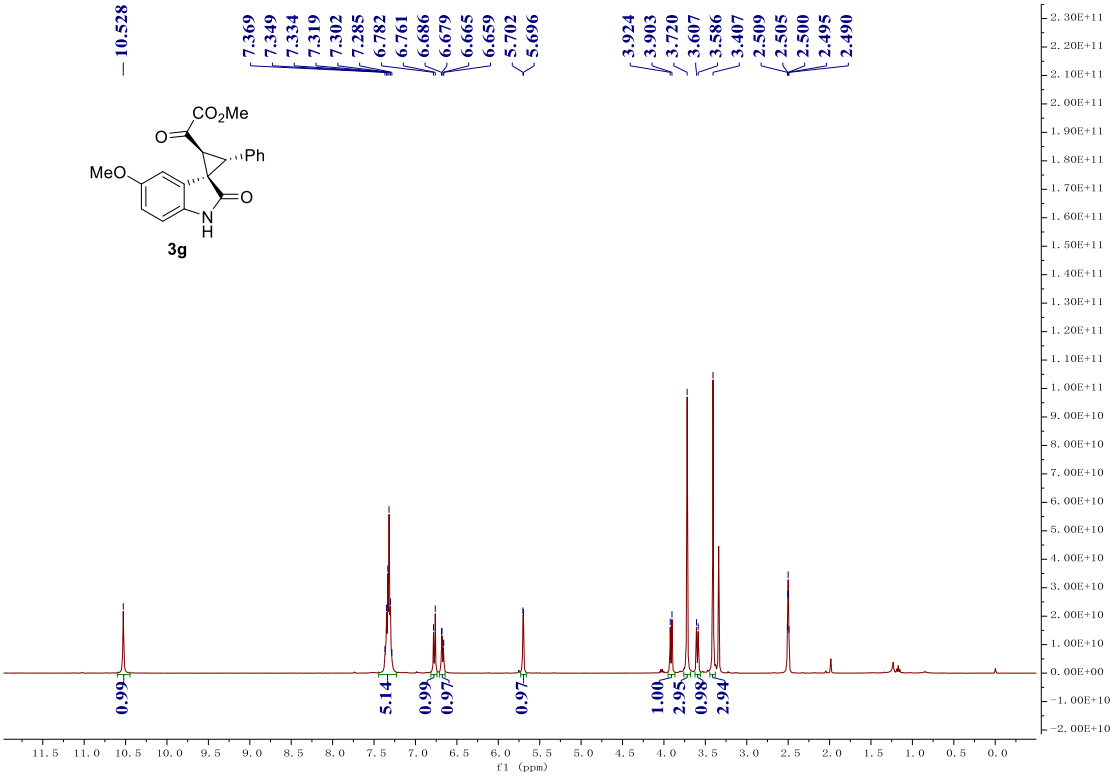
^{1}H NMR Spectrum of **3f** (400 MHz, DMSO-d^{6})



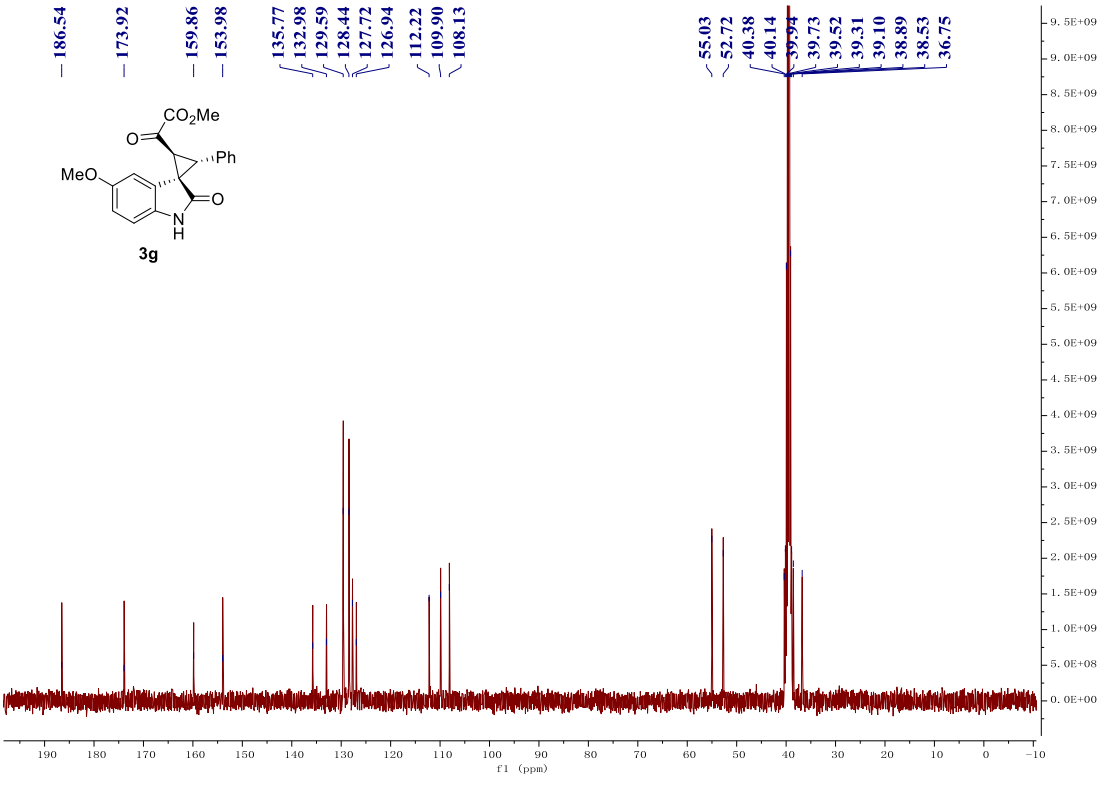
^{13}C NMR Spectrum of **3f** (100 MHz, DMSO-d^{6})



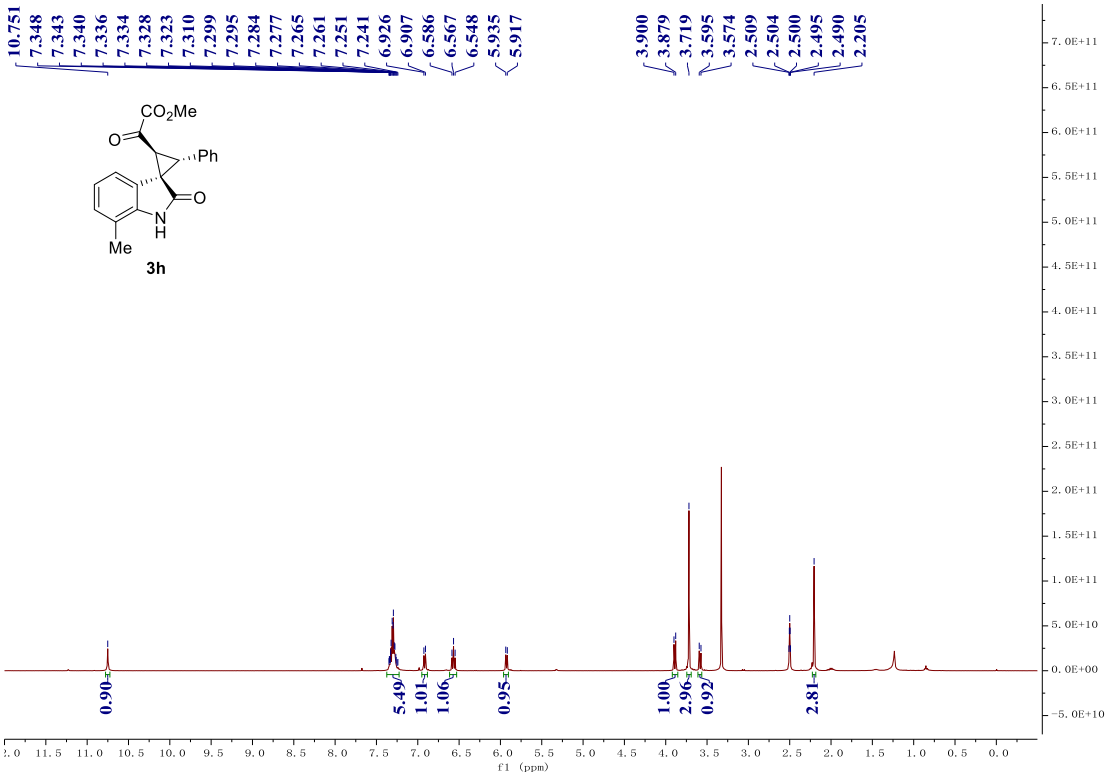
^{1}H NMR Spectrum of **3g** (400 MHz, DMSO-d^{6})



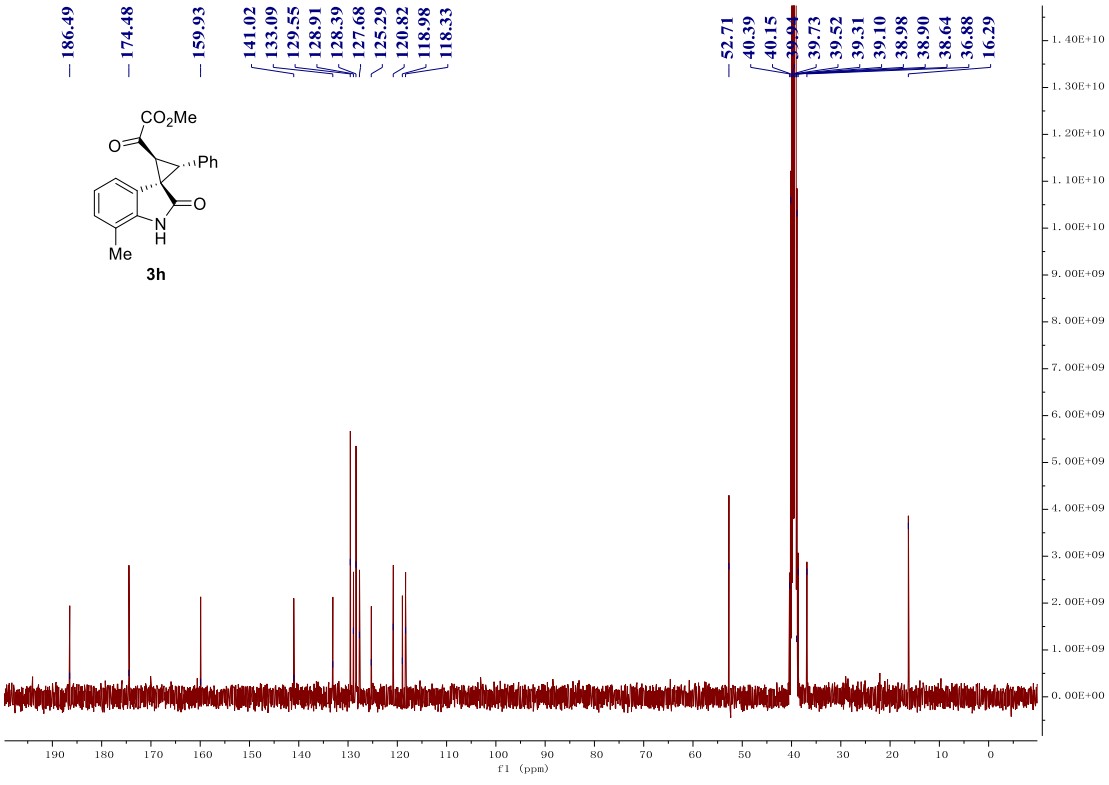
^{13}C NMR Spectrum of **3g** (100 MHz, DMSO-d^{6})



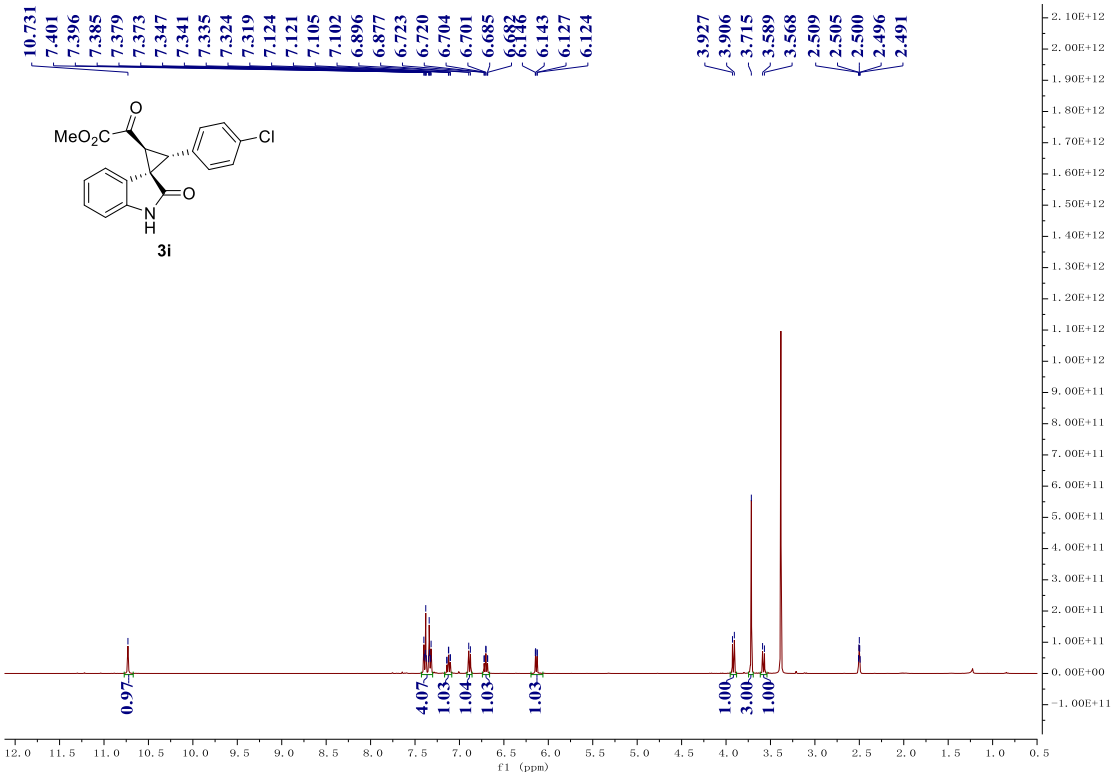
^{1}H NMR Spectrum of **3h** (400 MHz, DMSO-d^{6})



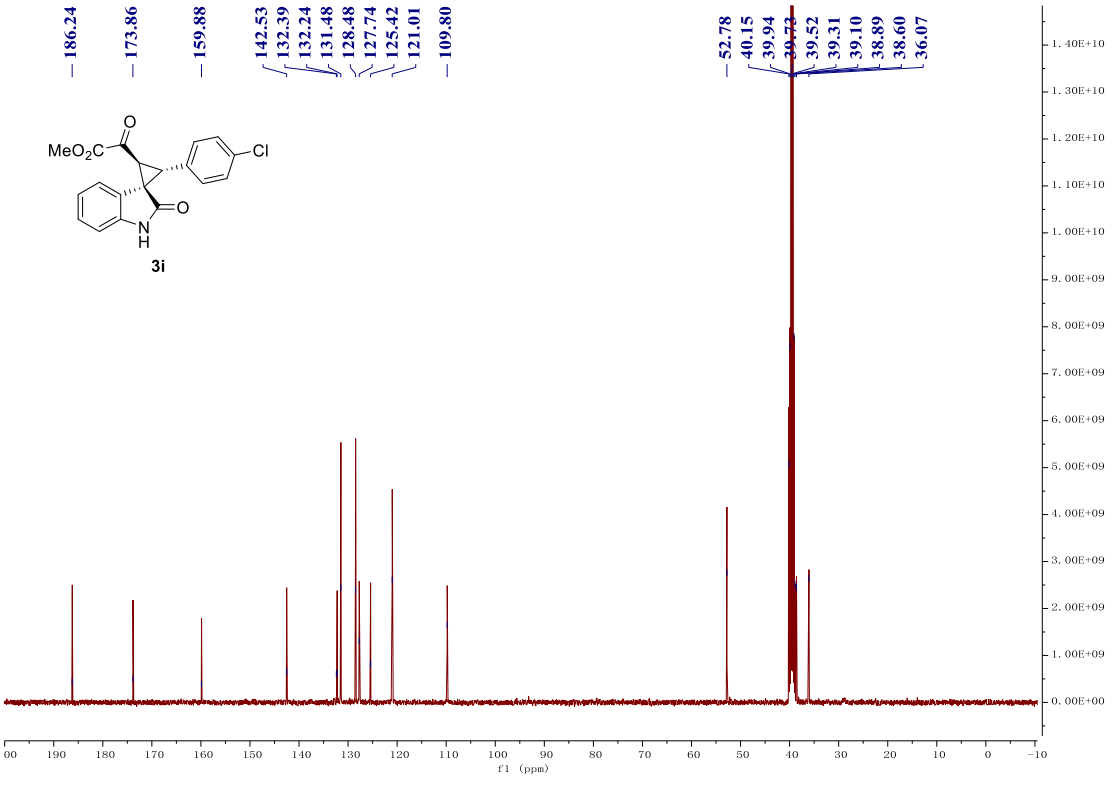
^{13}C NMR Spectrum of **3h** (100 MHz, DMSO-d^{6})



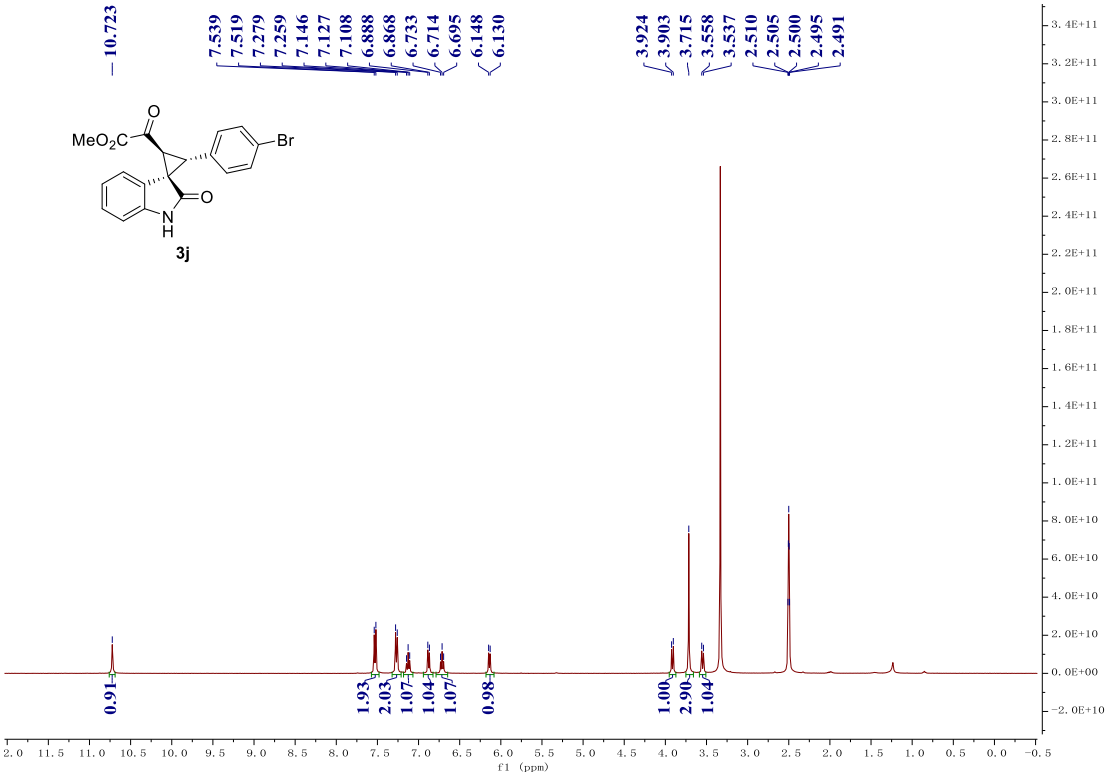
^{1}H NMR Spectrum of **3i** (400 MHz, DMSO-d^{6})



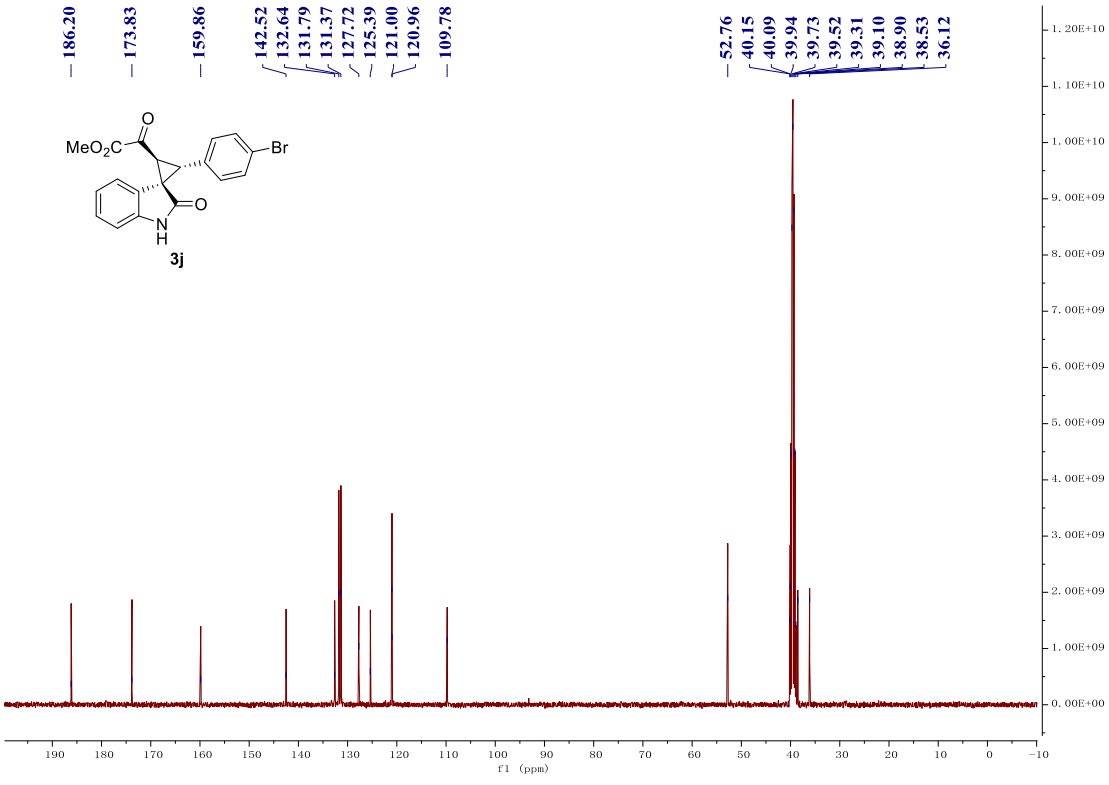
^{13}C NMR Spectrum of **3i** (100 MHz, DMSO-d^{6})



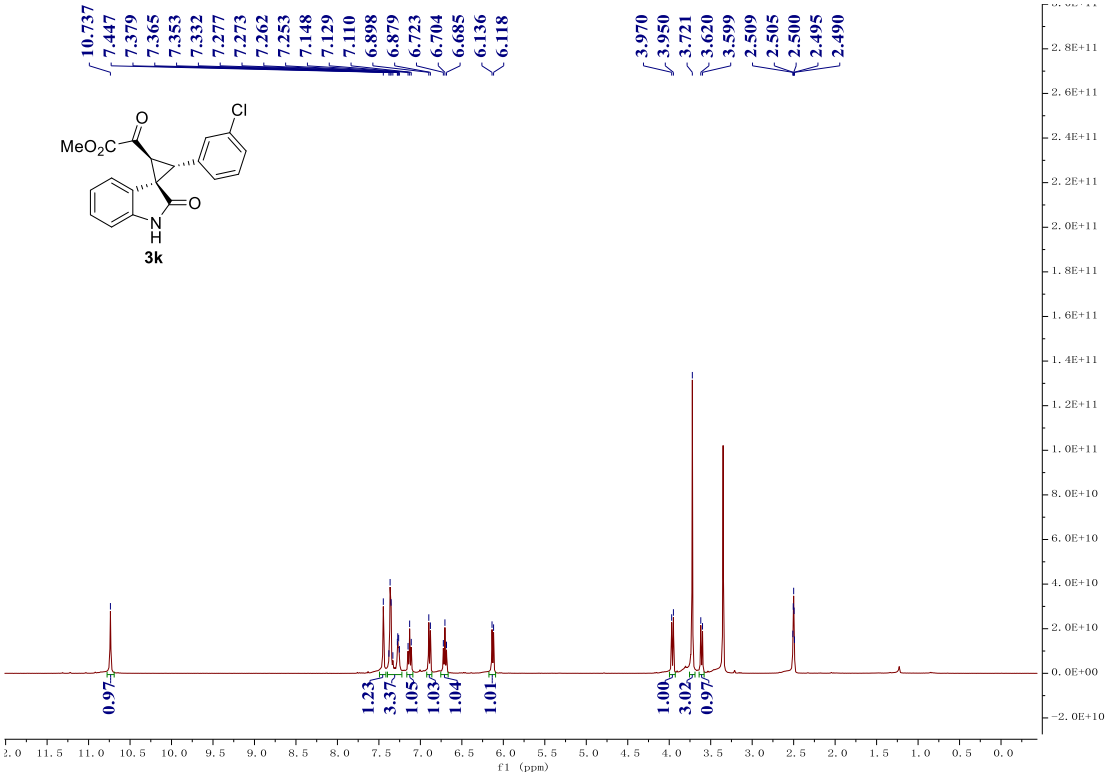
^{1}H NMR Spectrum of **3j** (400 MHz, DMSO-d^{6})



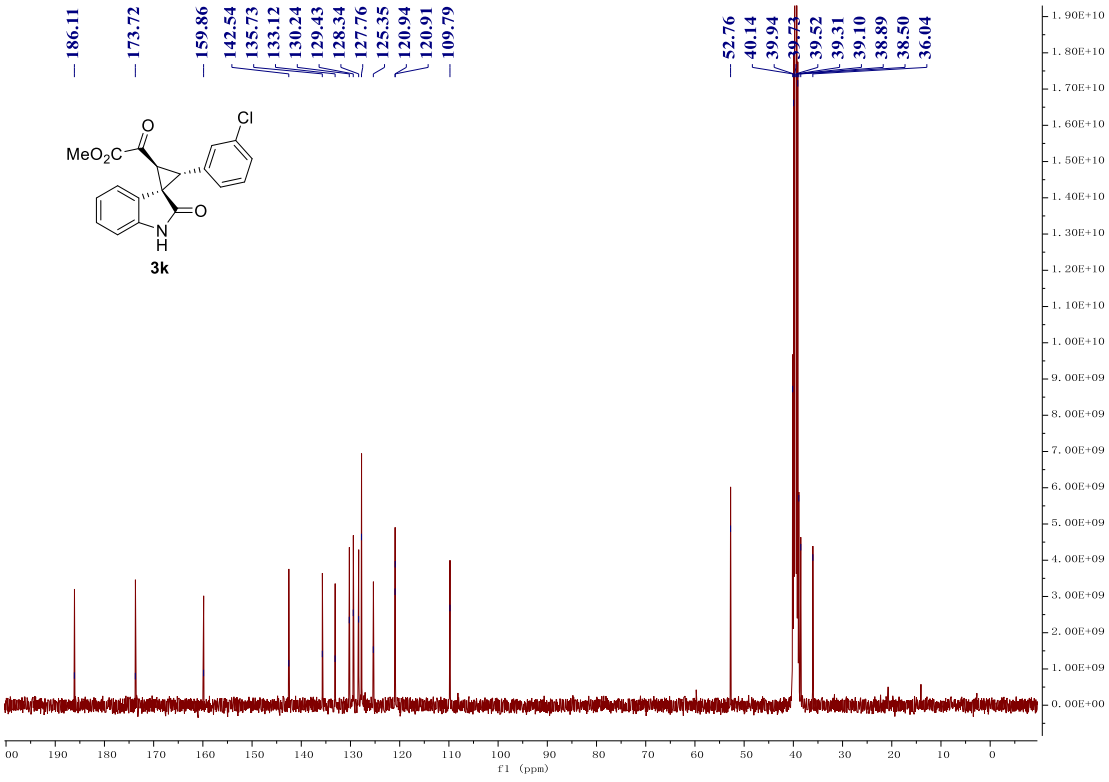
^{13}C NMR Spectrum of **3j** (100 MHz, DMSO-d^{6})



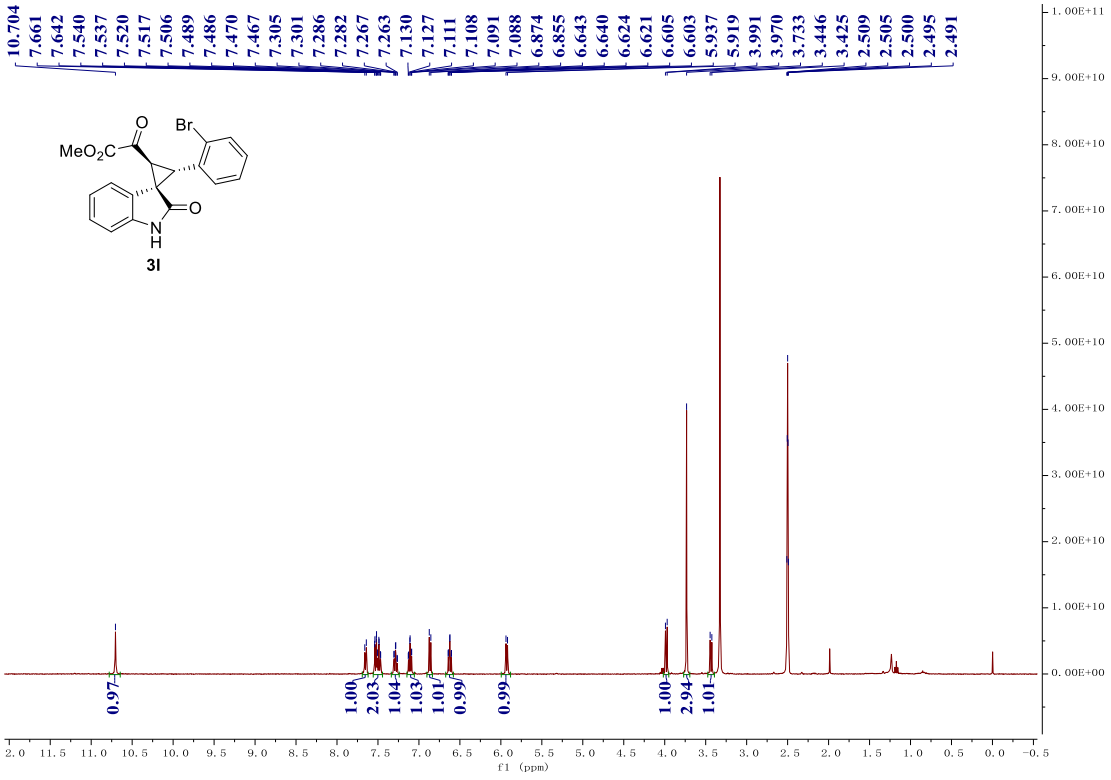
^{1}H NMR Spectrum of **3k** (400 MHz, DMSO-d^{6})



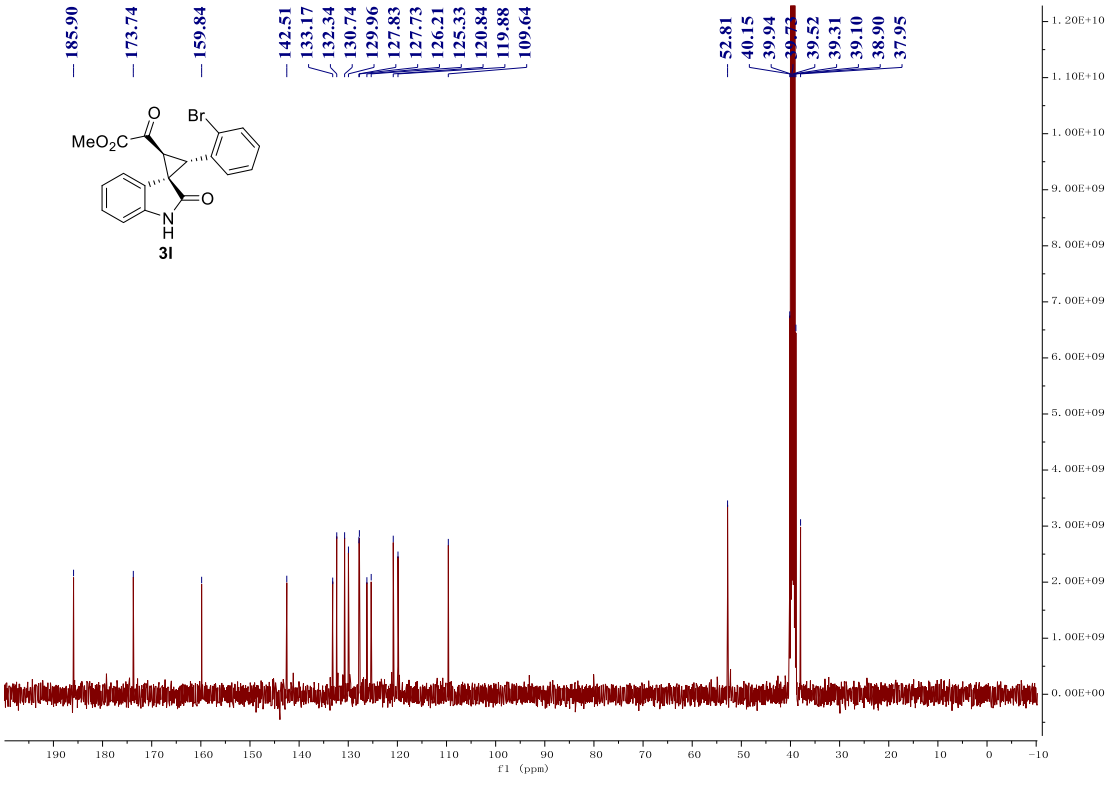
^{13}C NMR Spectrum of **3k** (100 MHz, DMSO-d^{6})



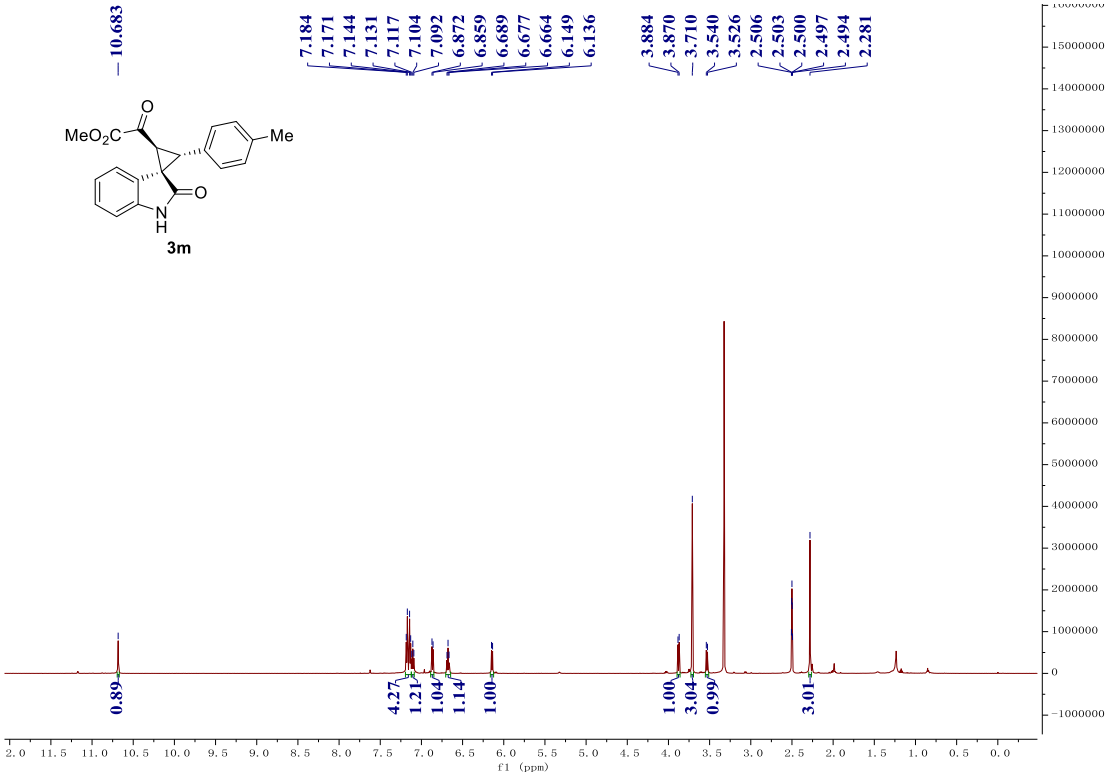
^{1}H NMR Spectrum of **3l** (400 MHz, DMSO-d^{6})



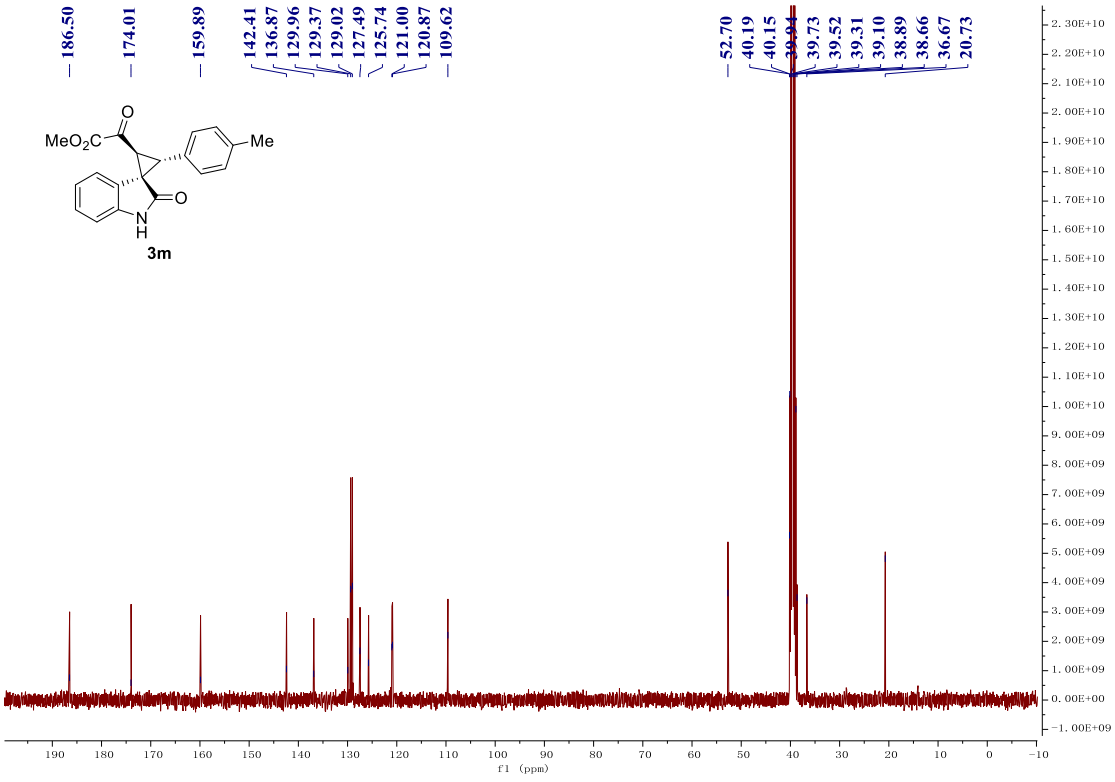
^{13}C NMR Spectrum of **3l** (100 MHz, DMSO-d^{6})



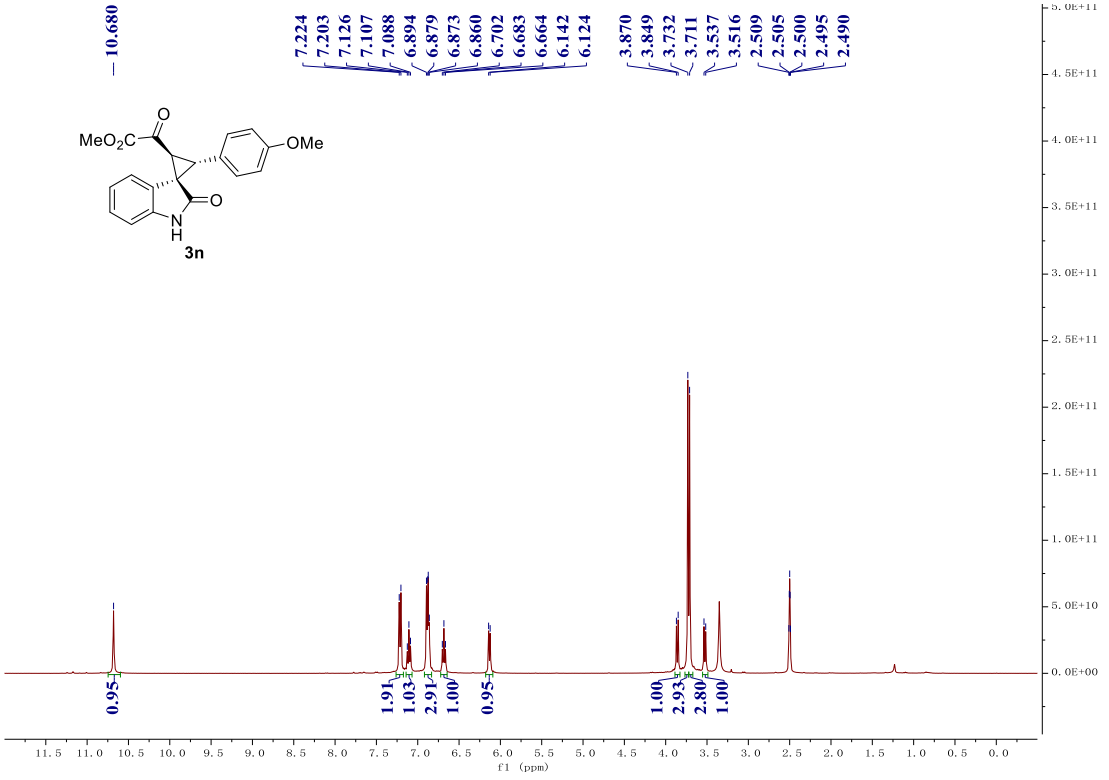
^{1}H NMR Spectrum of **3m** (400 MHz, DMSO-d^{6})



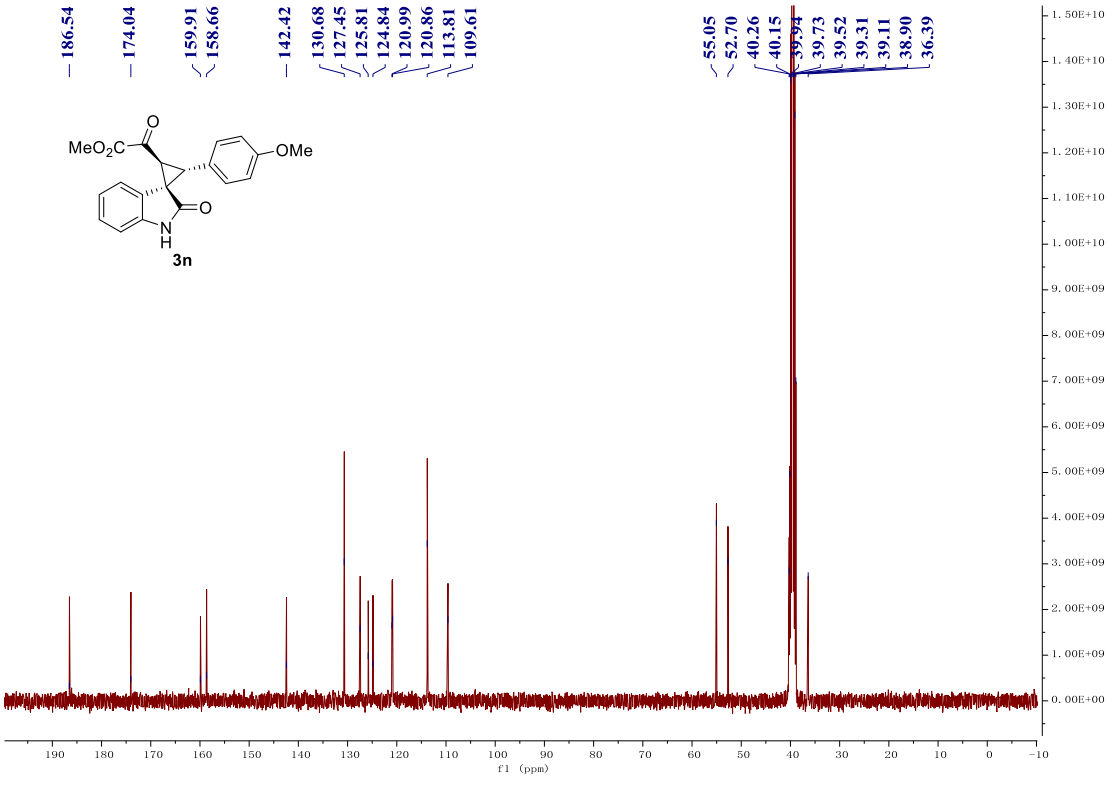
^{13}C NMR Spectrum of **3m** (100 MHz, DMSO-d^{6})



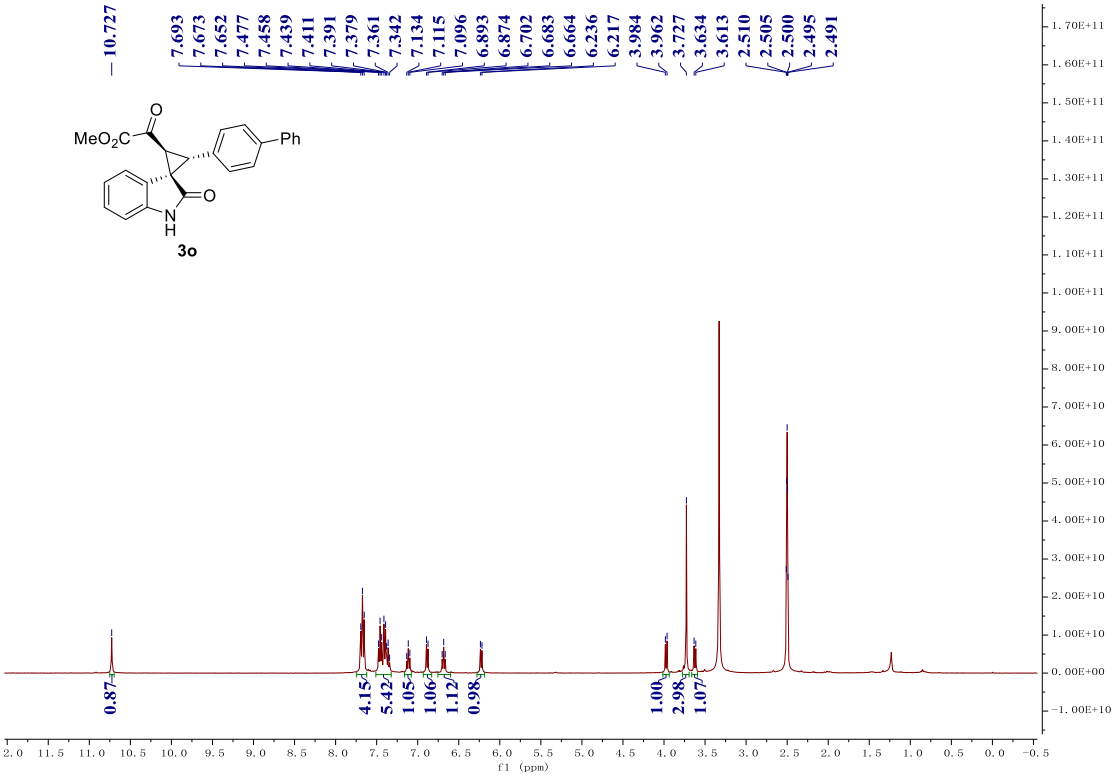
^{1}H NMR Spectrum of **3n** (400 MHz, DMSO-d^{6})



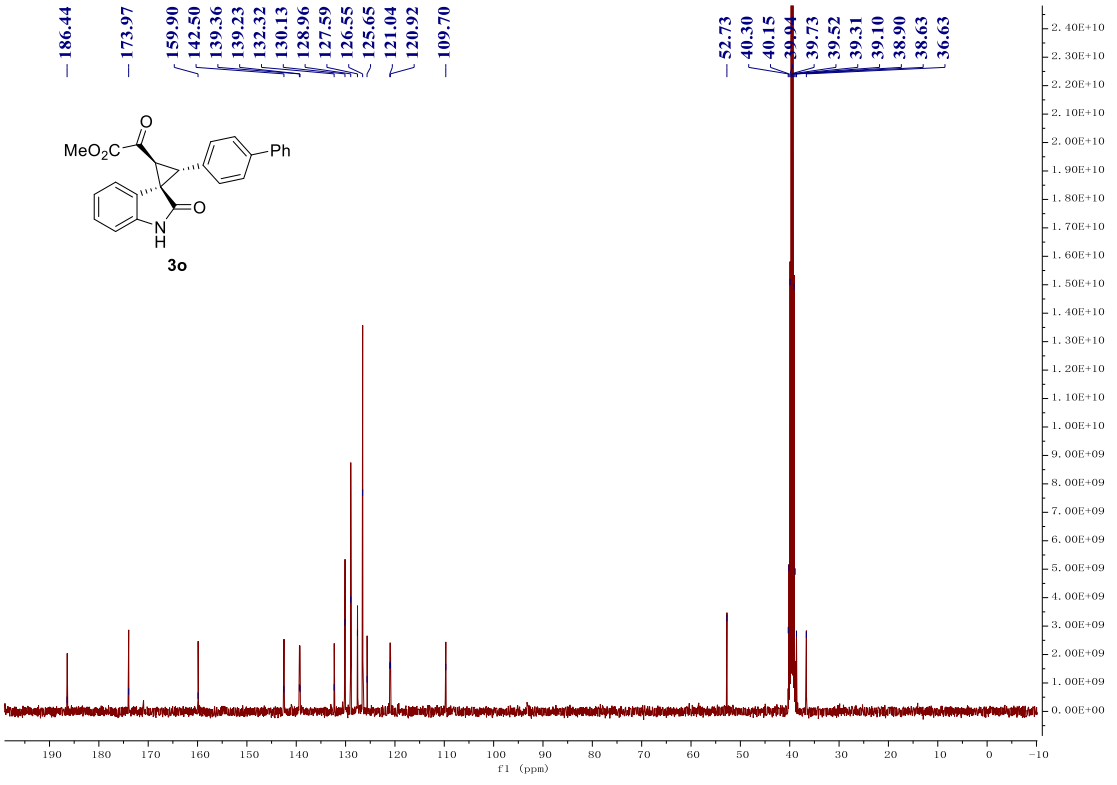
^{13}C NMR Spectrum of **3n** (100 MHz, DMSO-d^{6})



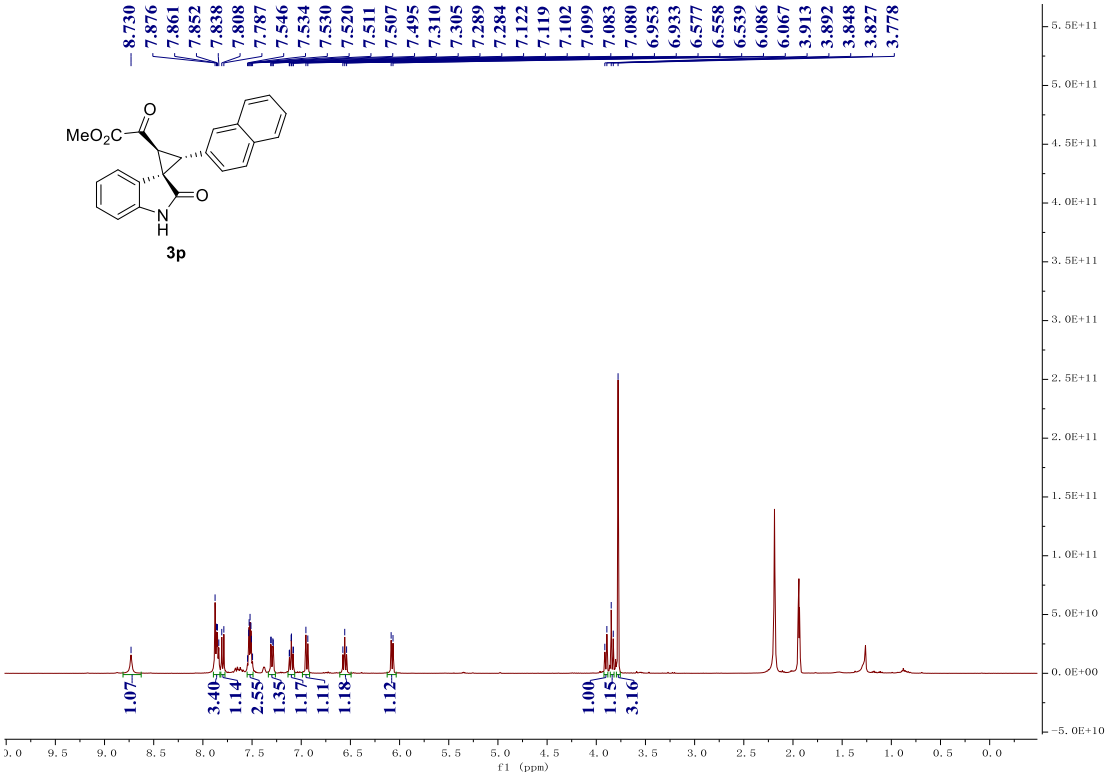
^{1}H NMR Spectrum of **3o** (400 MHz, DMSO-d^{6})



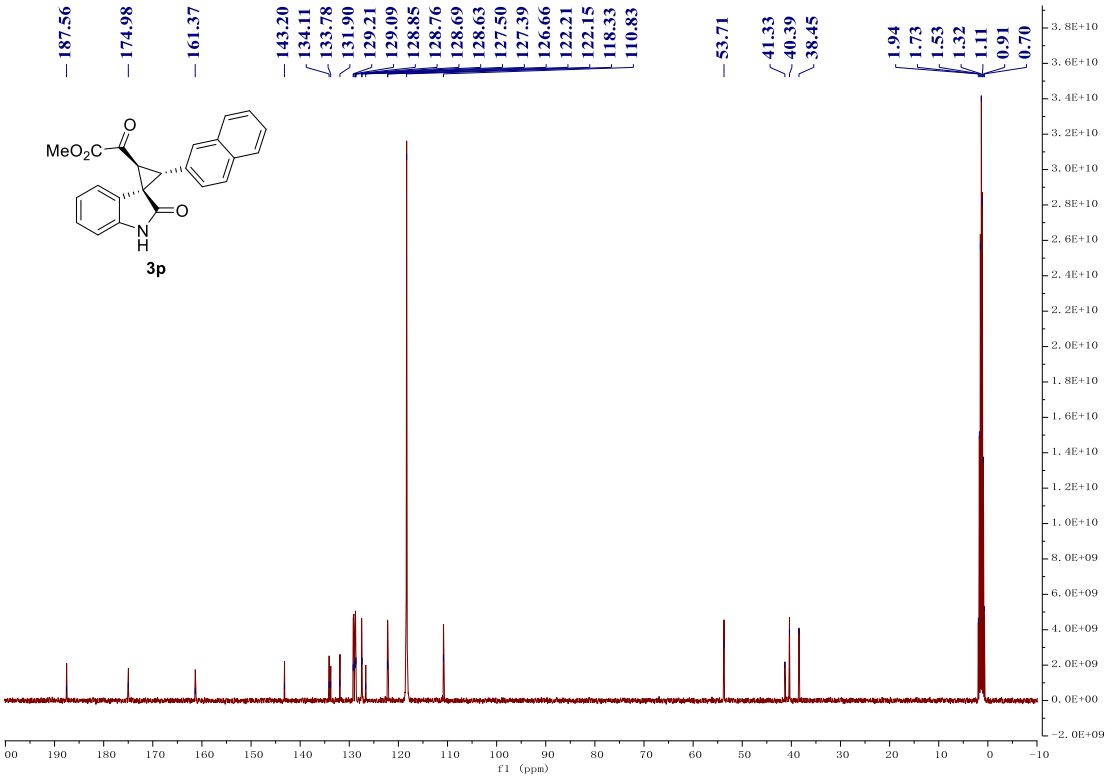
^{13}C NMR Spectrum of **3o** (100 MHz, DMSO-d^{6})



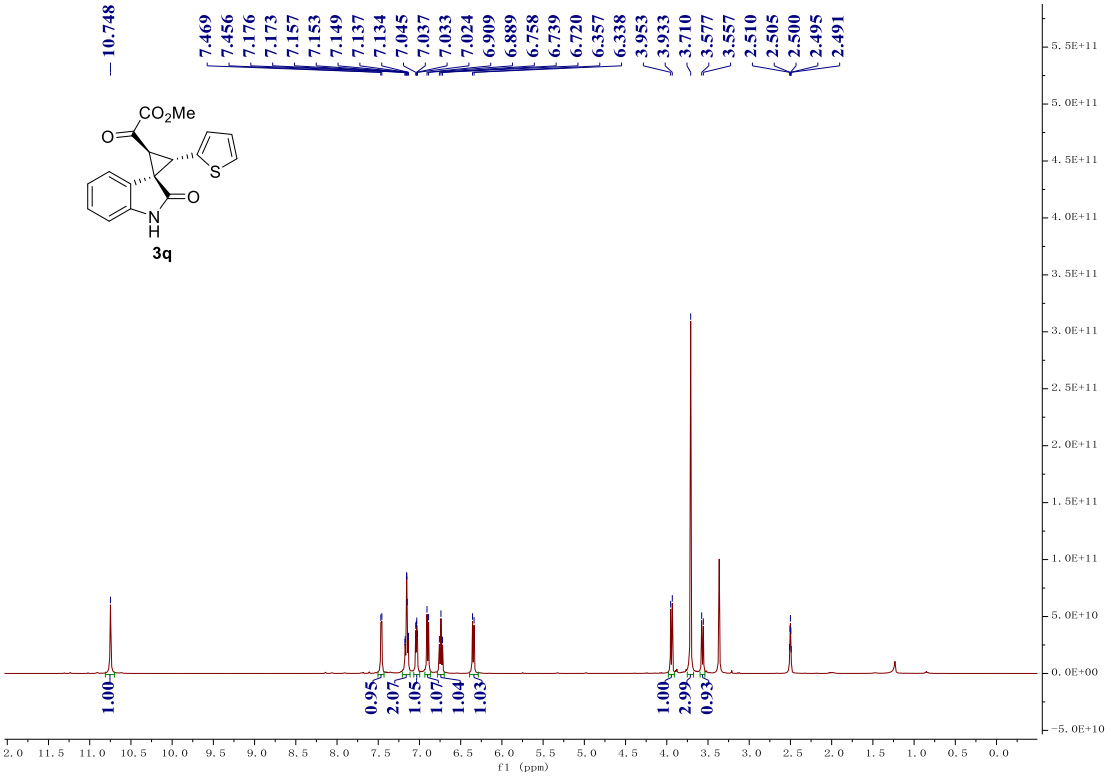
^{1}H NMR Spectrum of **3p** (400 MHz, CD_3CN)



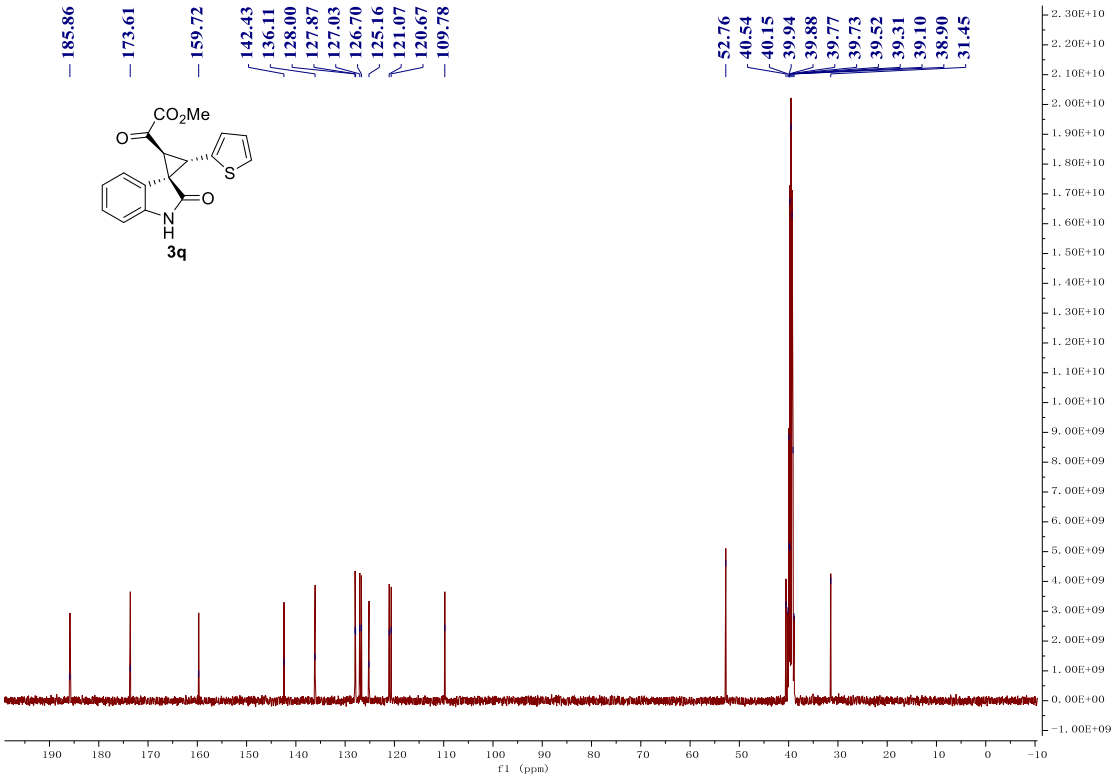
^{13}C NMR Spectrum of **3p** (100 MHz, CD_3CN)



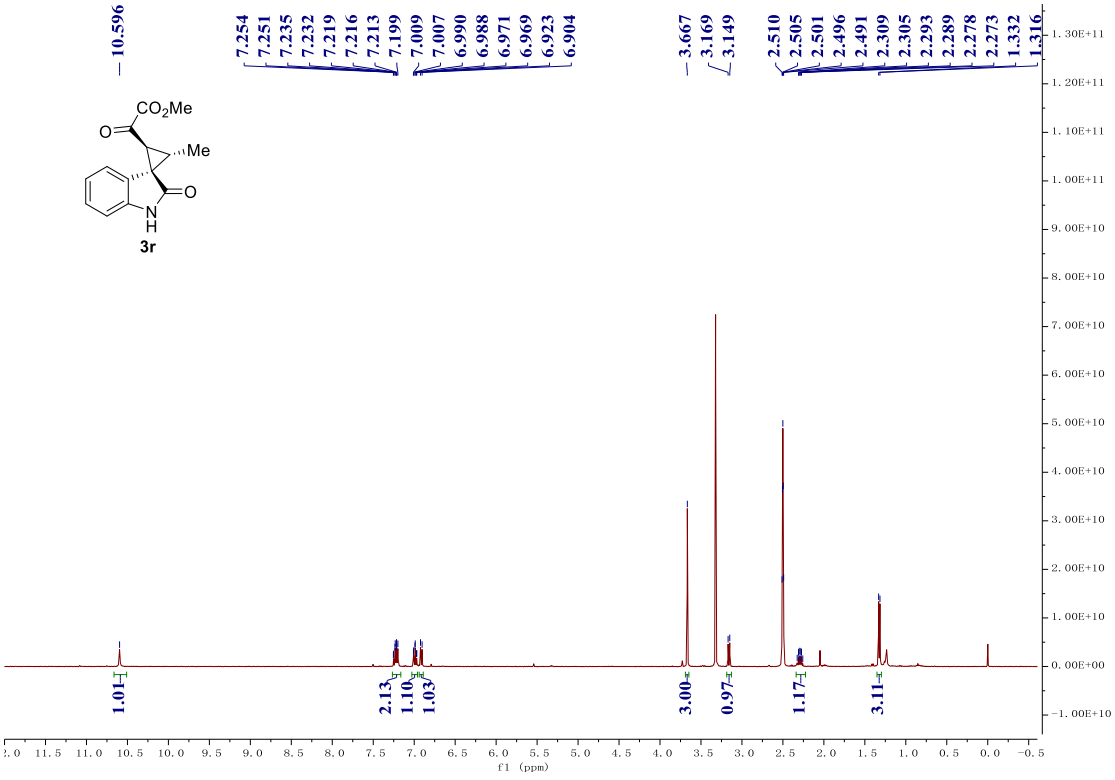
^{1}H NMR Spectrum of **3q** (400 MHz, DMSO-d^{6})



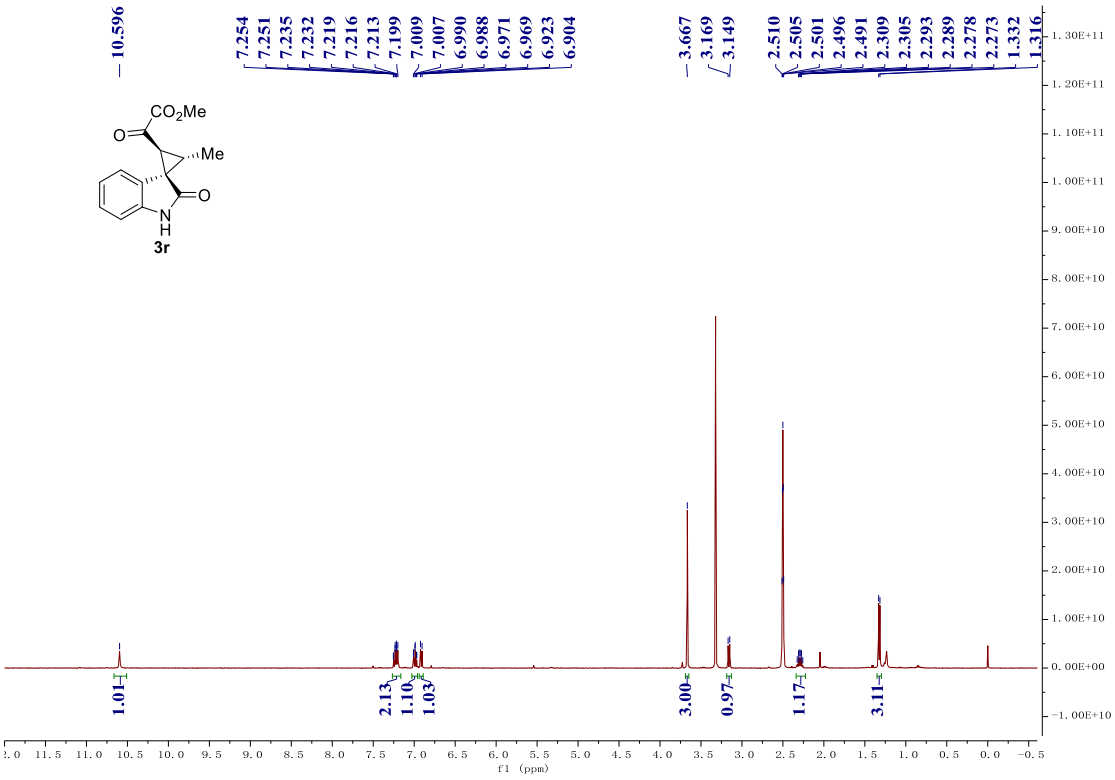
^{13}C NMR Spectrum of **3q** (100 MHz, DMSO-d^{6})



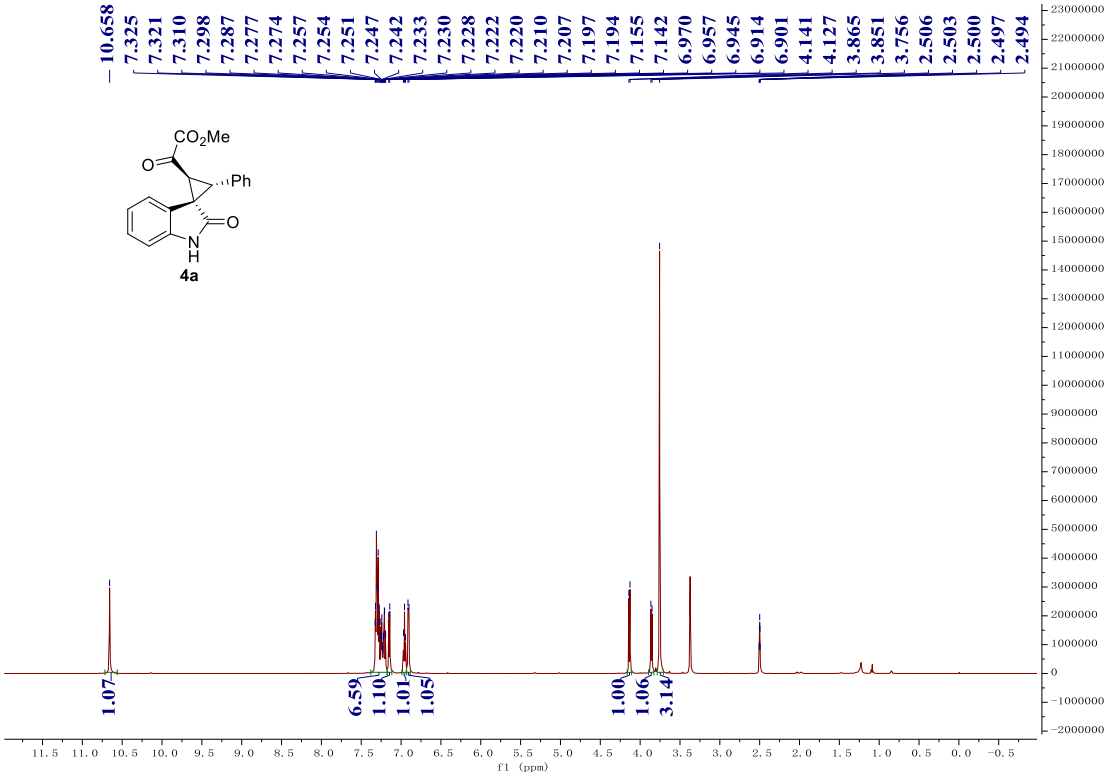
^{1}H NMR Spectrum of **3r** (400 MHz, DMSO-d^{6})



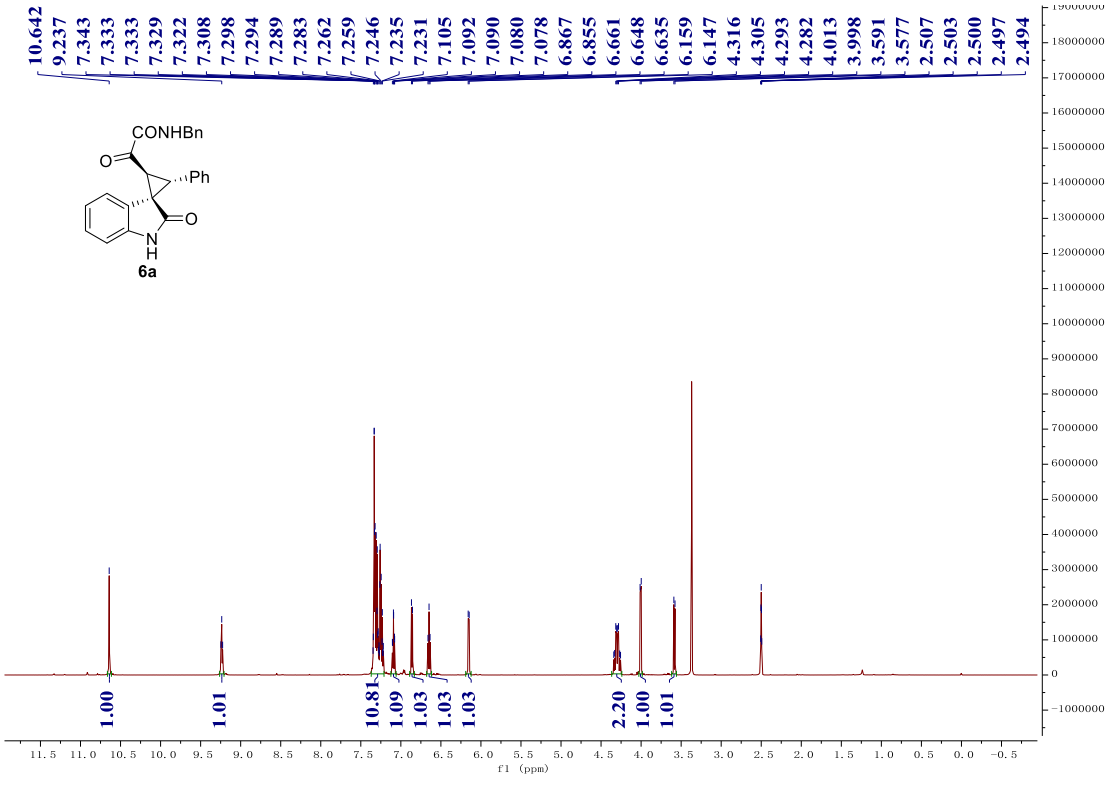
^{13}C NMR Spectrum of **3r** (100 MHz, DMSO-d^{6})



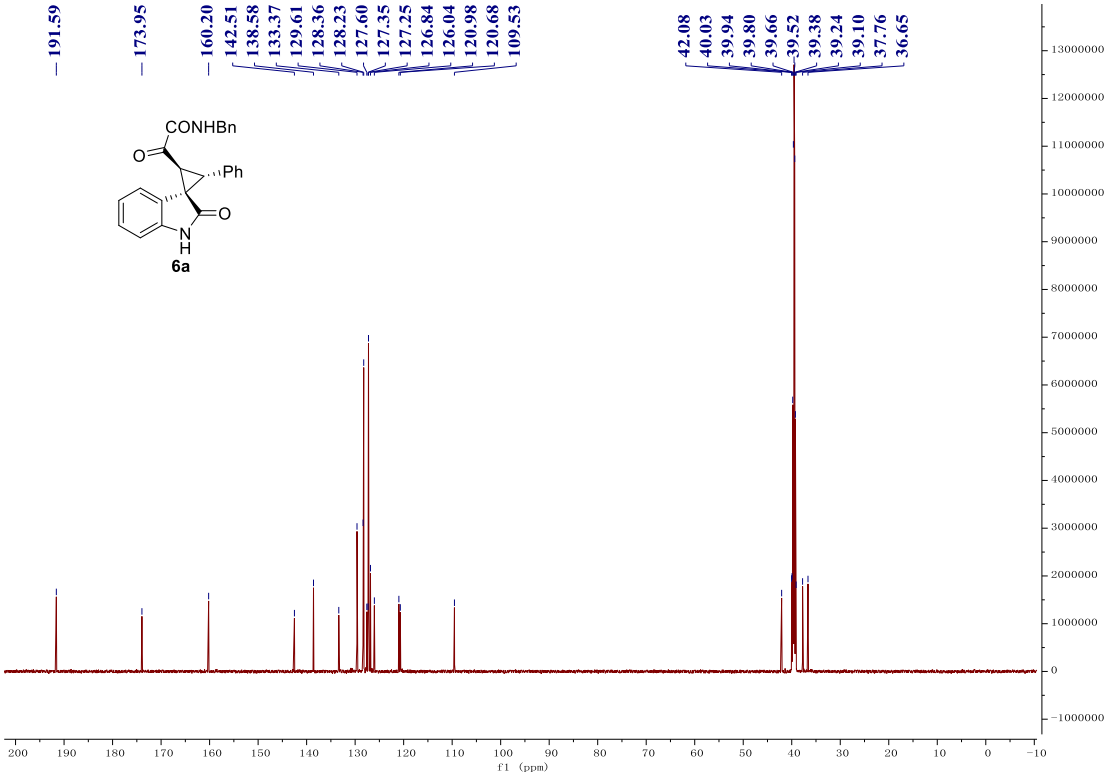
^{1}H NMR Spectrum of **4a** (600 MHz, DMSO-d^{6})



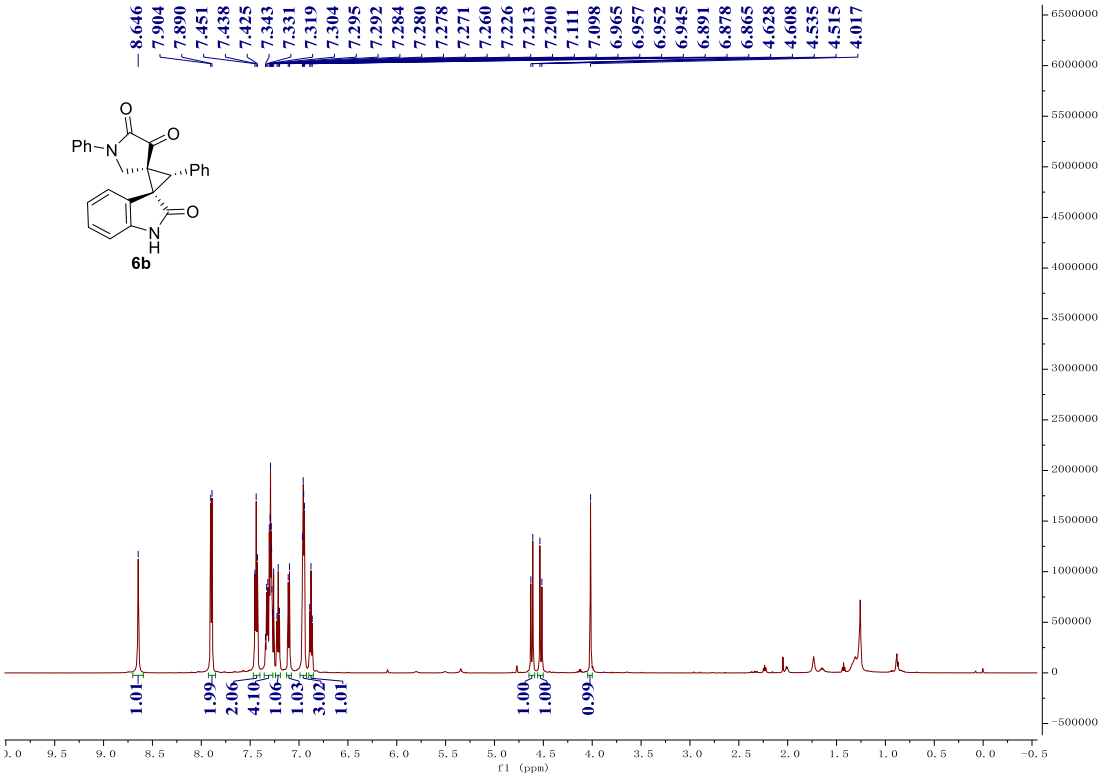
^{1}H NMR Spectrum of **6a** (600 MHz, DMSO-d^{6})



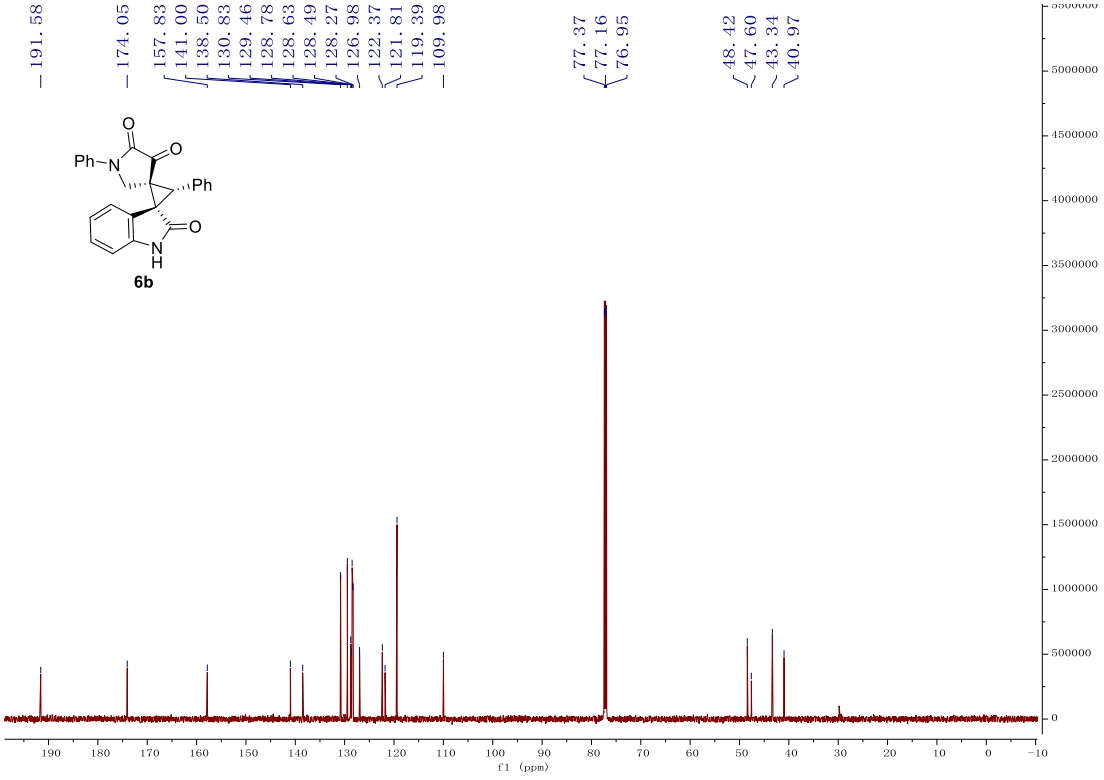
^{13}C NMR Spectrum of **6a** (150 MHz, DMSO-d^{6})



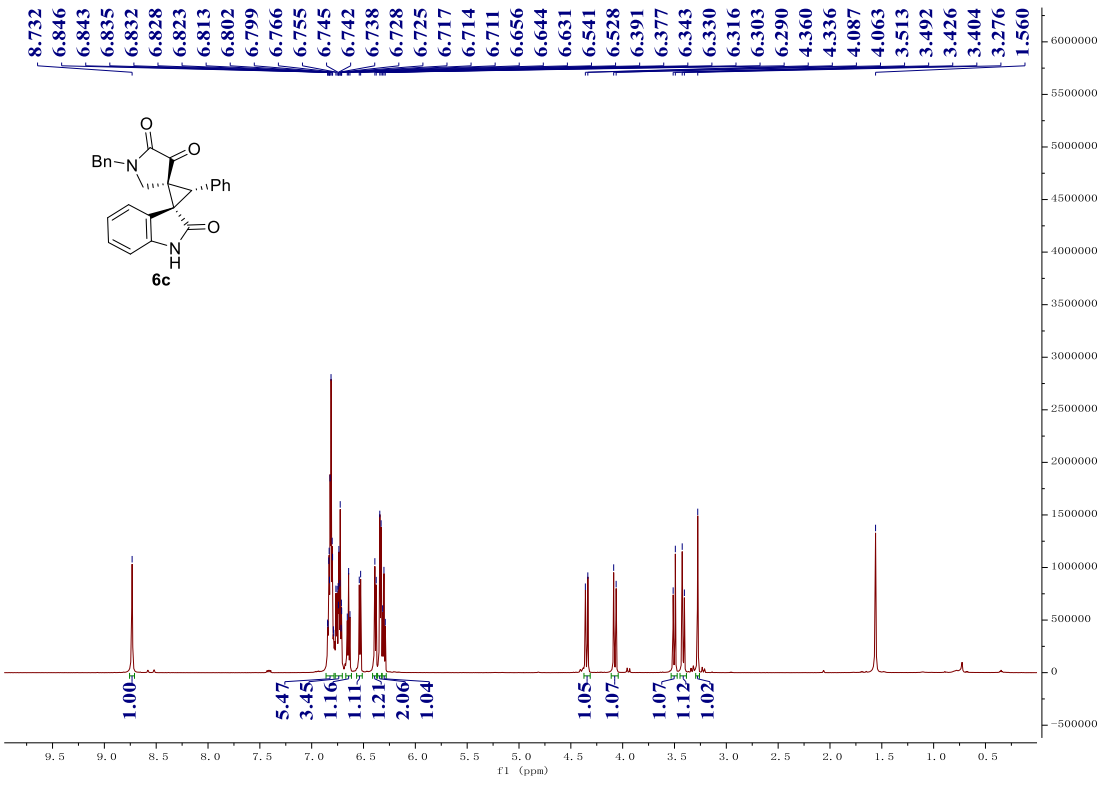
^{1}H NMR Spectrum of **6b** (600 MHz, CDCl$_3$)



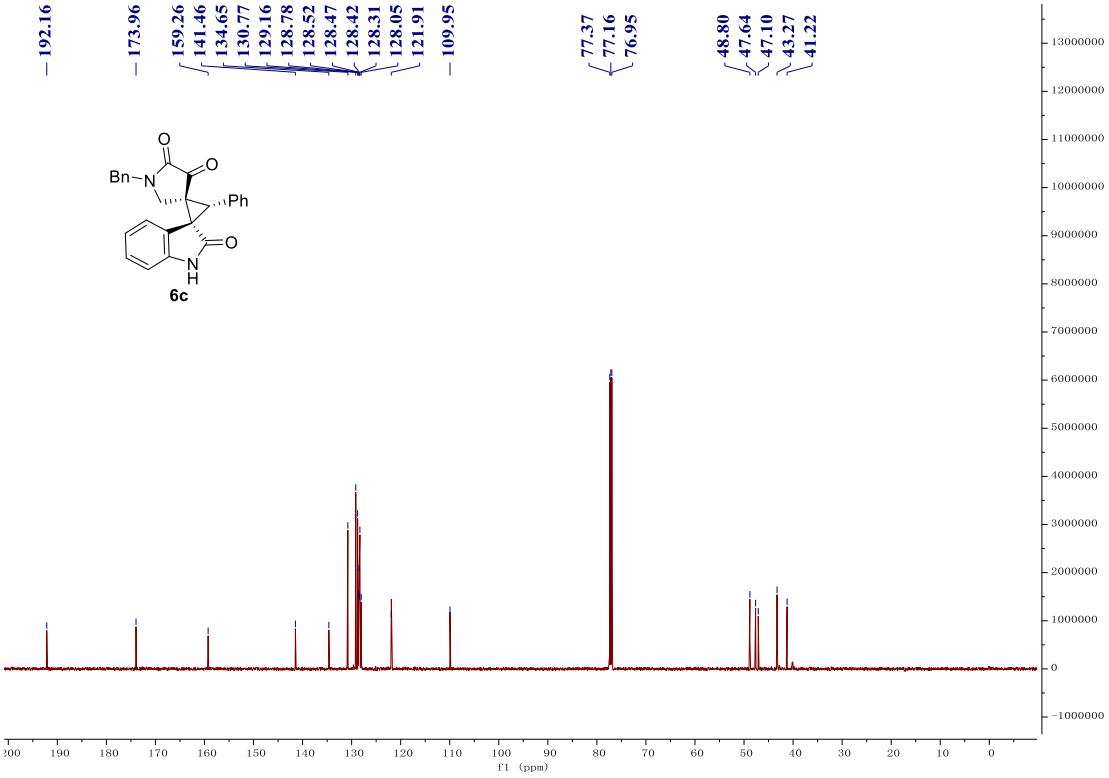
^{13}C NMR Spectrum of **6b** (150 MHz, $CDCl_3$)



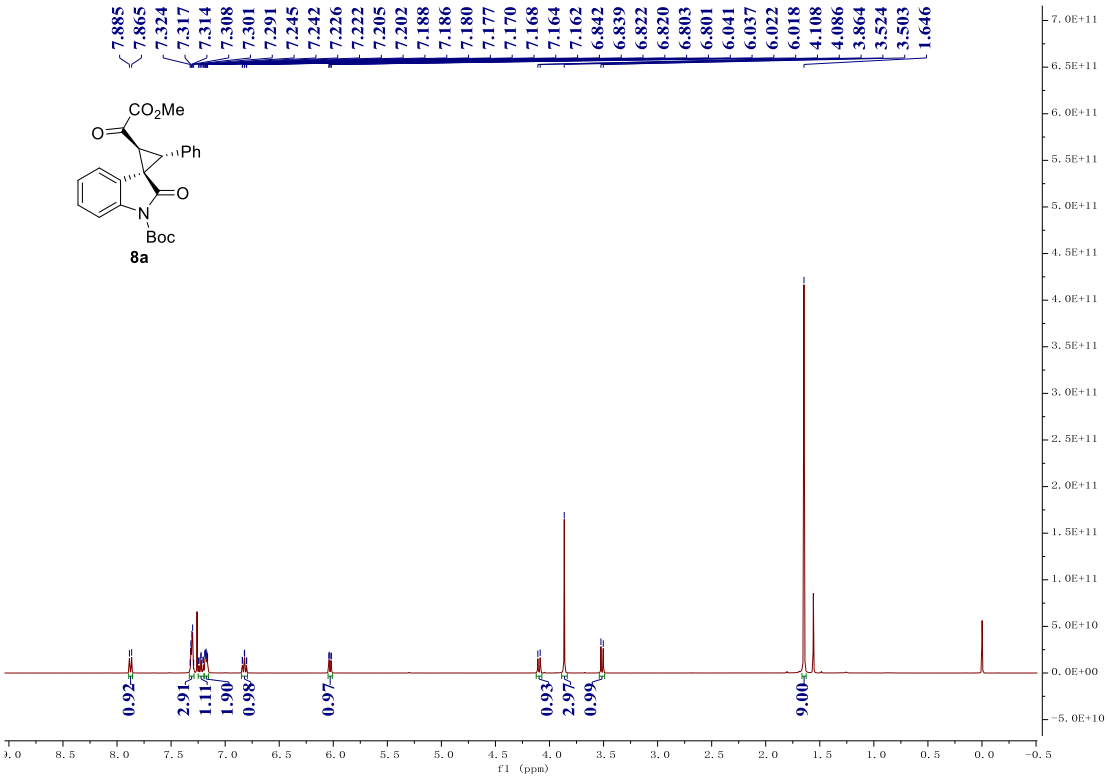
^{1}H NMR Spectrum of **6c** (600 MHz, $CDCl_3$)



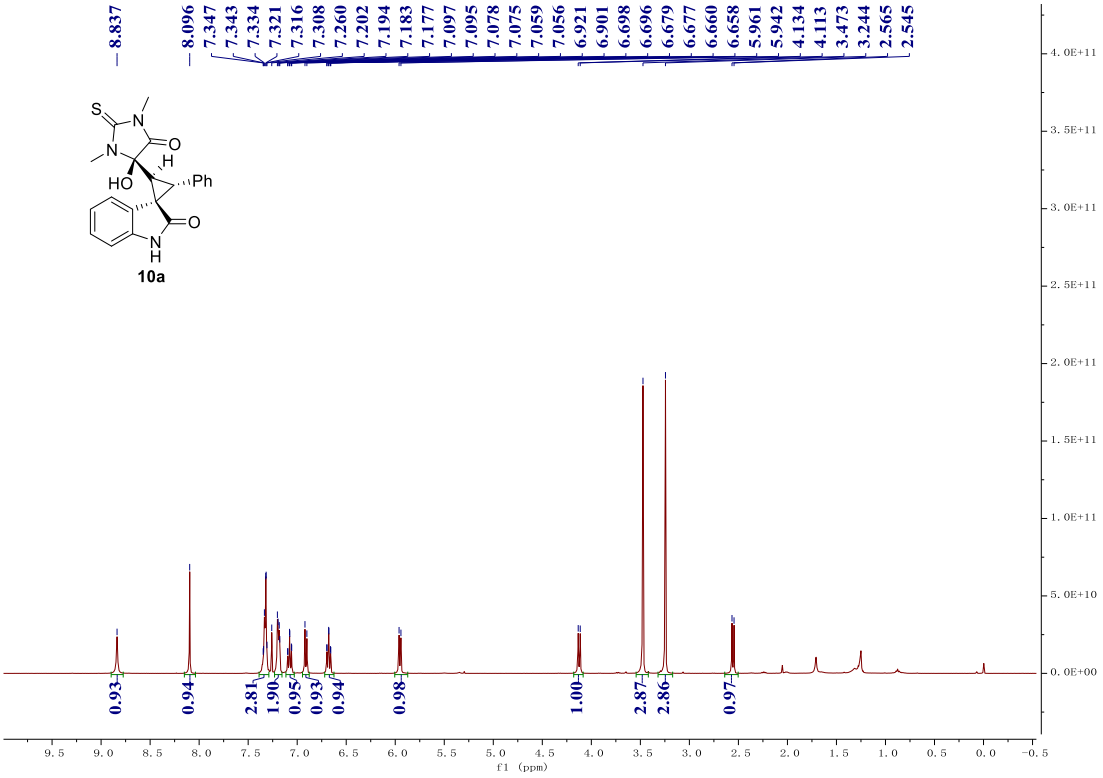
^{13}C NMR Spectrum of **6c** (150 MHz, $CDCl_3$)



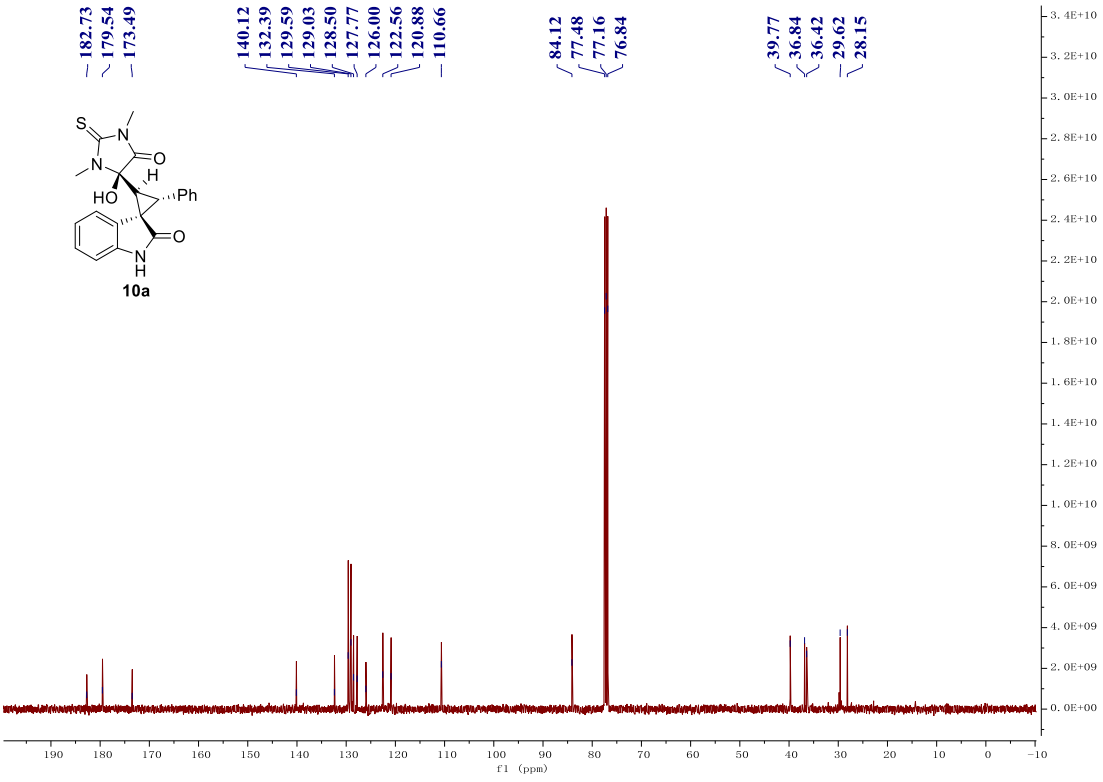
^{1}H NMR Spectrum of **8a** (400 MHz, $CDCl_3$)



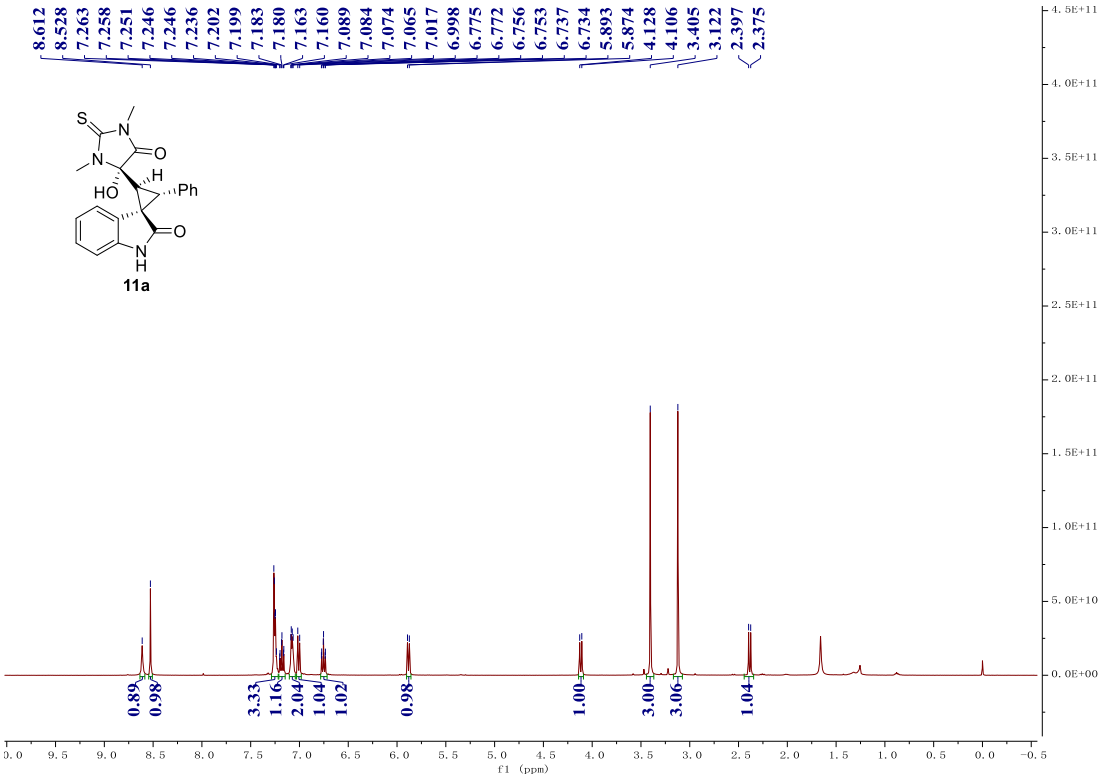
^{1}H NMR Spectrum of **10a** (400 MHz, $CDCl_3$)



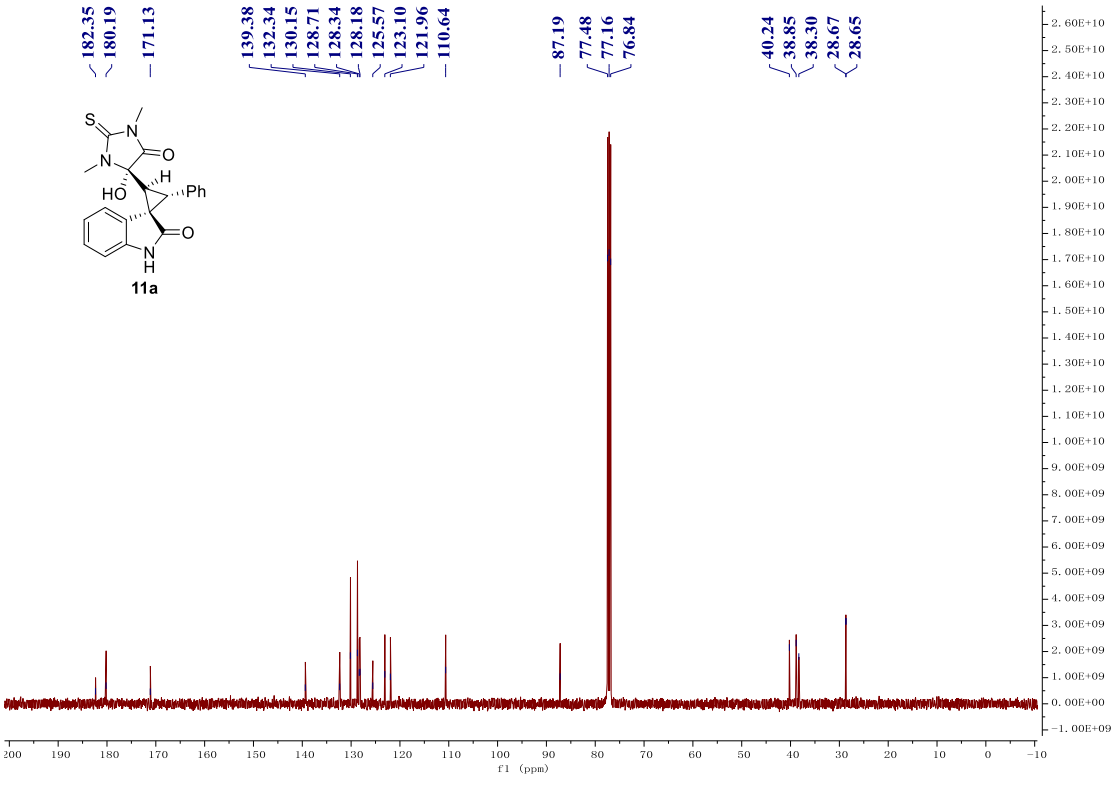
^{13}C NMR Spectrum of **10a** (100 MHz, $CDCl_3$)



^{1}H NMR Spectrum of **11a** (400 MHz, $CDCl_3$)

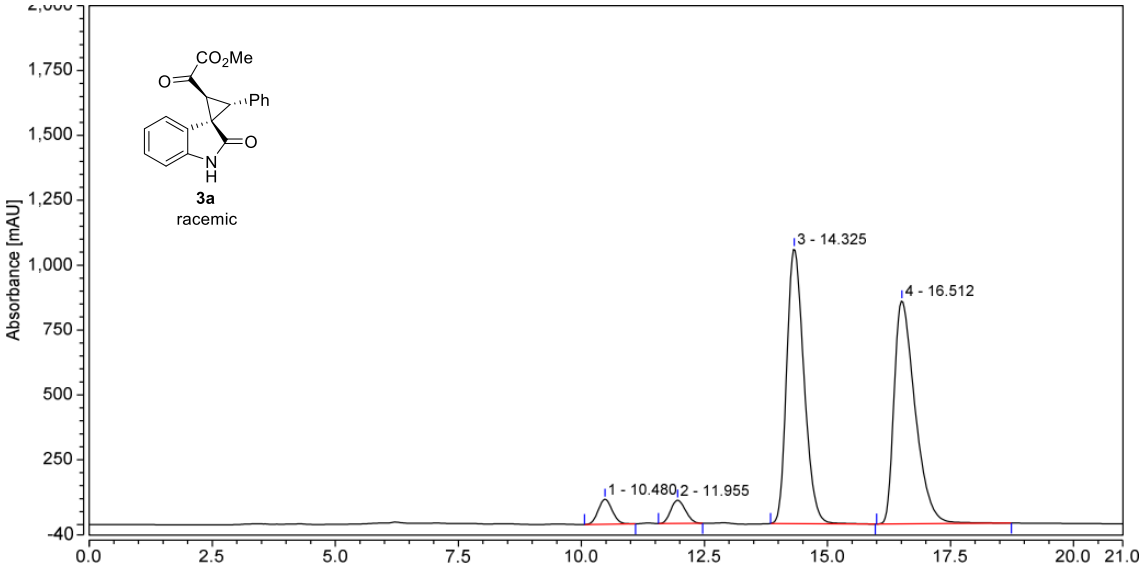


^{13}C NMR Spectrum of **11a** (100 MHz, $CDCl_3$)



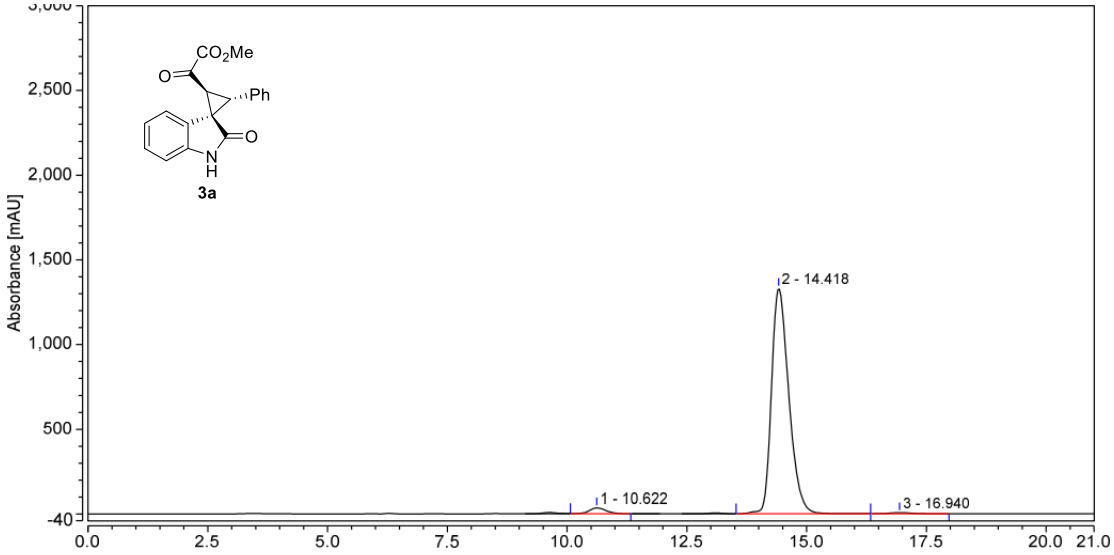
HPLC spectra

HPLC Spectrum of **3a**



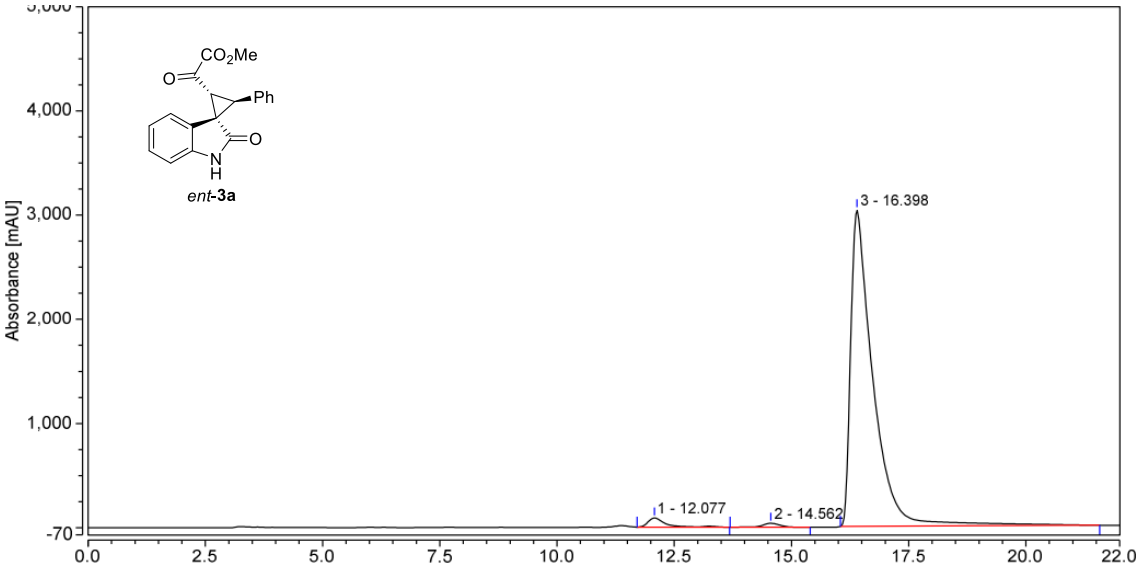
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.480	31.817	96.448	3.46	4.58
2	11.955	31.078	90.023	3.38	4.27
3	14.325	430.583	1060.196	46.84	50.33
4	16.512	425.876	859.651	46.32	40.81
Total:		**919.354**	**2106.318**	**100.00**	**100.00**

HPLC Spectrum of **3a**



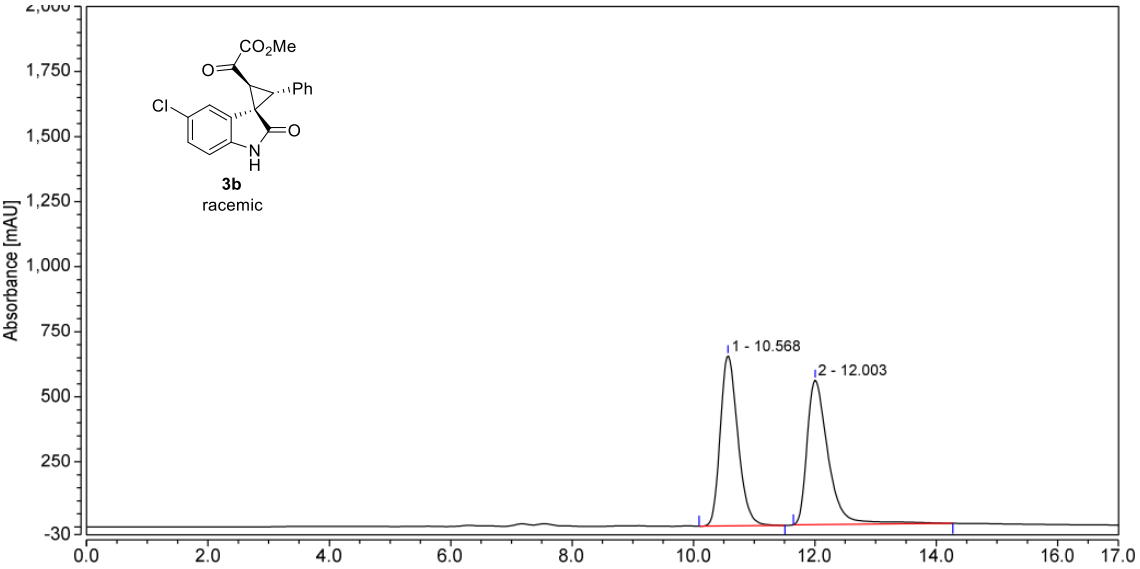
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.622	14.906	34.933	2.58	2.55
2	14.418	558.423	1330.870	96.81	96.99
3	16.940	3.476	6.402	0.60	0.47
Total:		**576.805**	**1372.205**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3a**



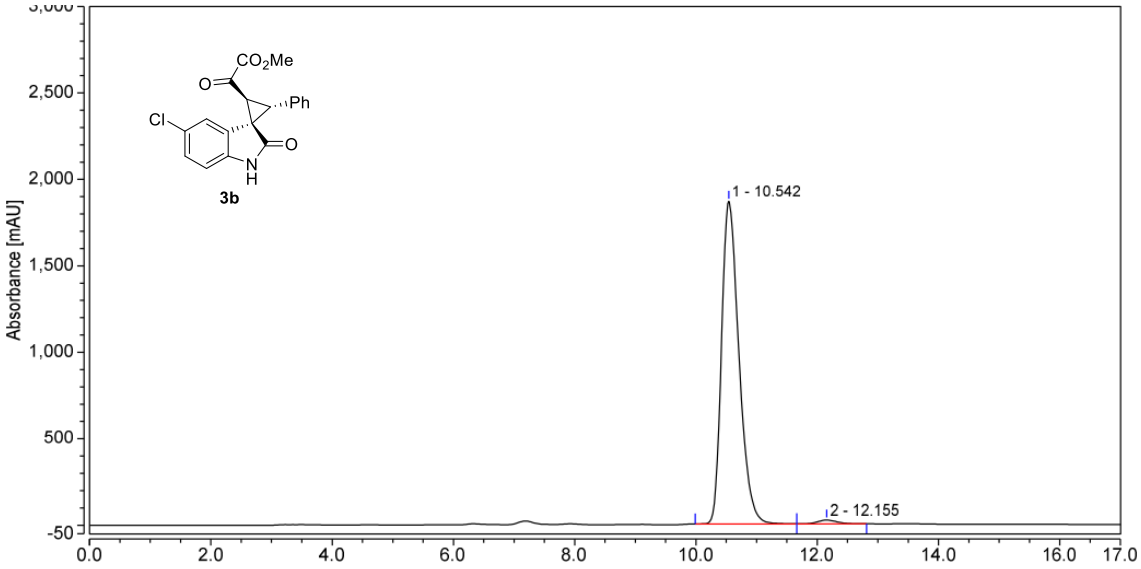
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.077	38.901	87.277	2.24	2.76
2	14.562	16.648	38.202	0.96	1.21
3	16.398	1682.862	3039.956	96.80	96.04
Total:		**1738.411**	**3165.435**	**100.00**	**100.00**

HPLC Spectrum of **3b**



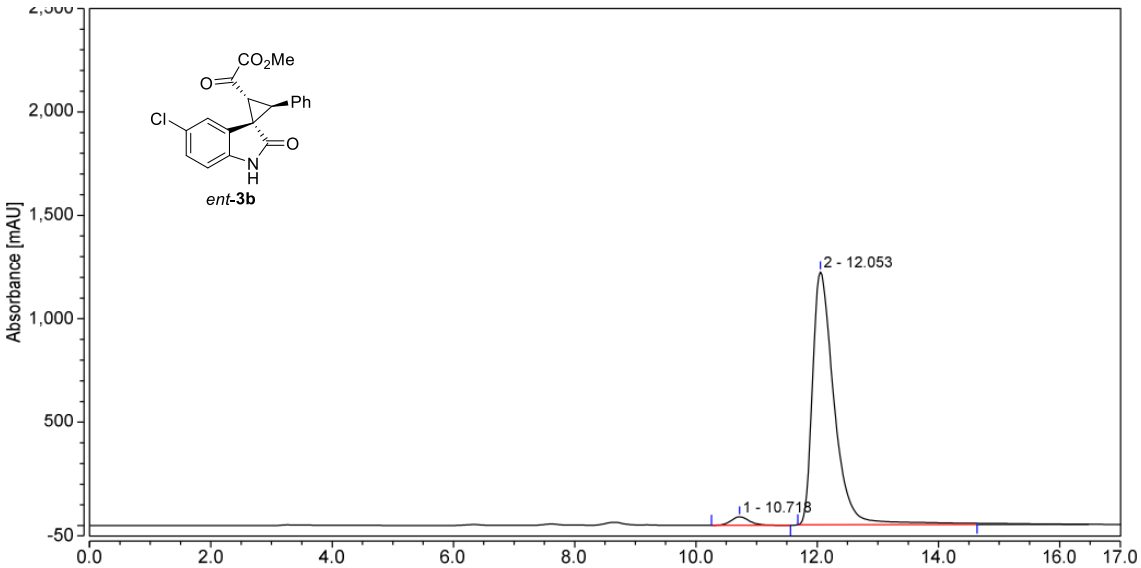
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.568	219.456	654.306	49.50	54.11
2	12.003	223.906	554.951	50.50	45.89
Total		**443.363**	**1209.257**	**100.00**	**100.00**

HPLC Spectrum of **3b**



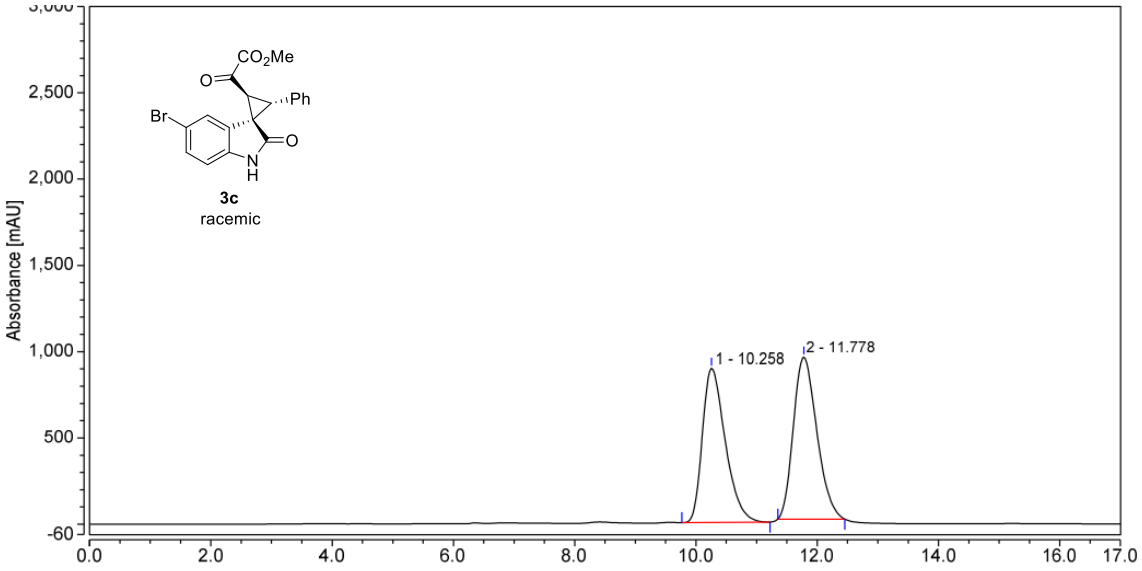
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.542	618.872	1866.345	98.71	98.85
2	12.155	8.057	21.799	1.29	1.15
Total		**626.929**	**1888.144**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3b**



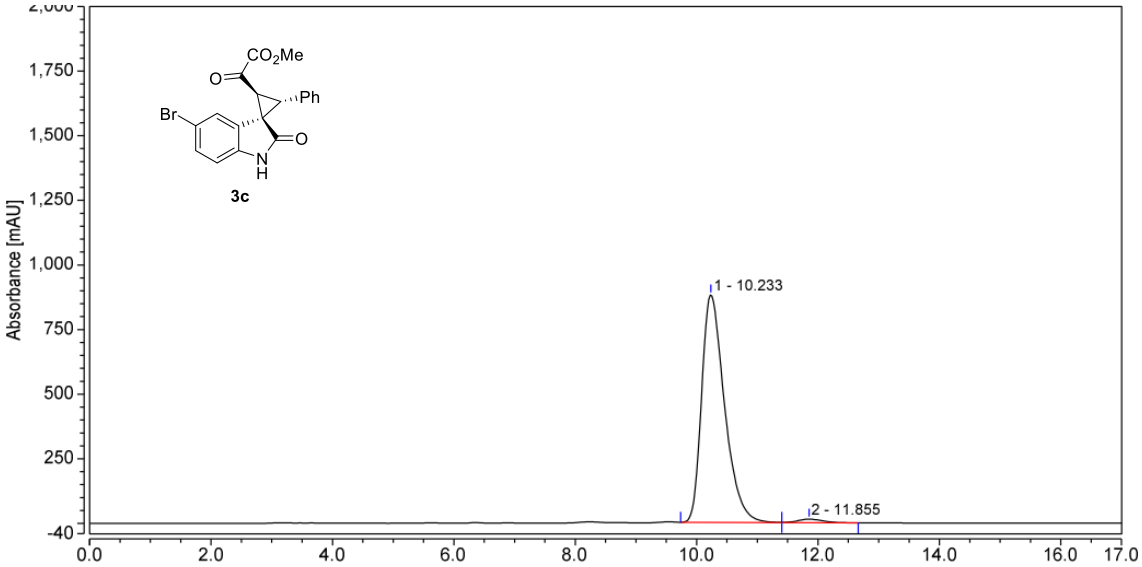
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.718	14.303	40.891	2.74	3.24
2	12.053	507.774	1222.209	97.26	96.76
Total		**522.077**	**1263.100**	**100.00**	**100.00**

HPLC Spectrum of **3c**



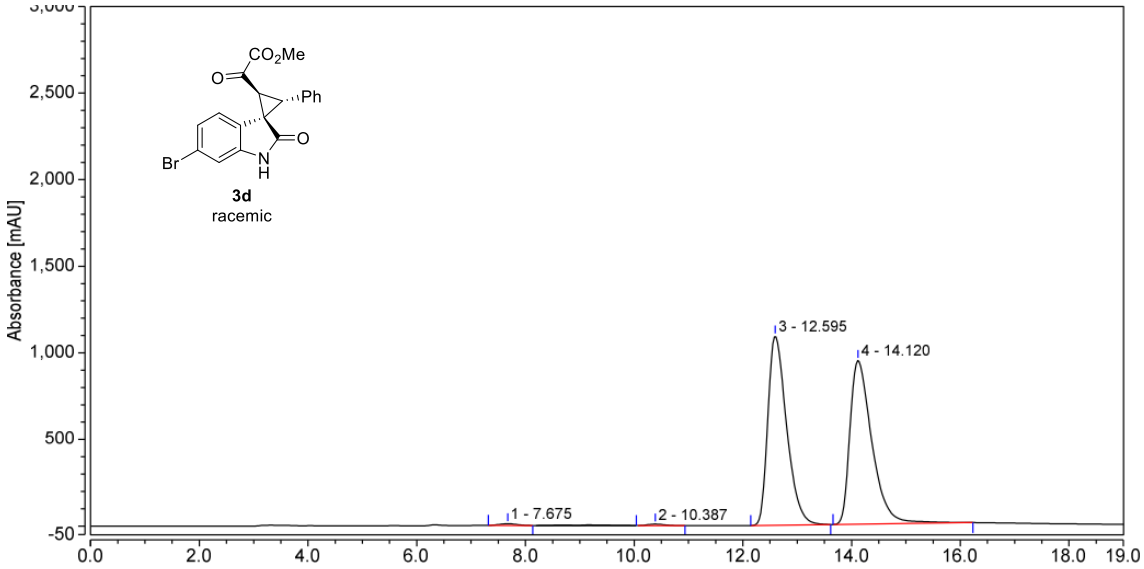
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.258	392.127	893.520	48.19	48.74
2	11.778	421.635	939.800	51.81	51.26
Total		**813.762**	**1833.320**	**100.00**	**100.00**

HPLC Spectrum of **3c**



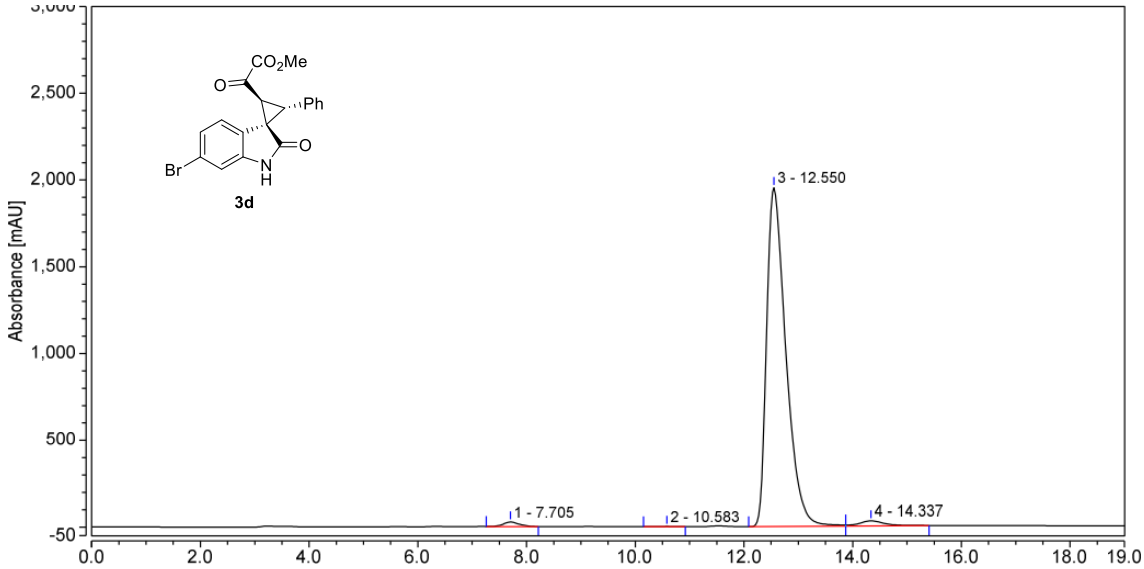
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.233	385.080	880.280	98.33	98.45
2	11.855	6.533	13.888	1.67	1.55
Total		**391.613**	**894.168**	**100.00**	**100.00**

HPLC Spectrum of **3d**



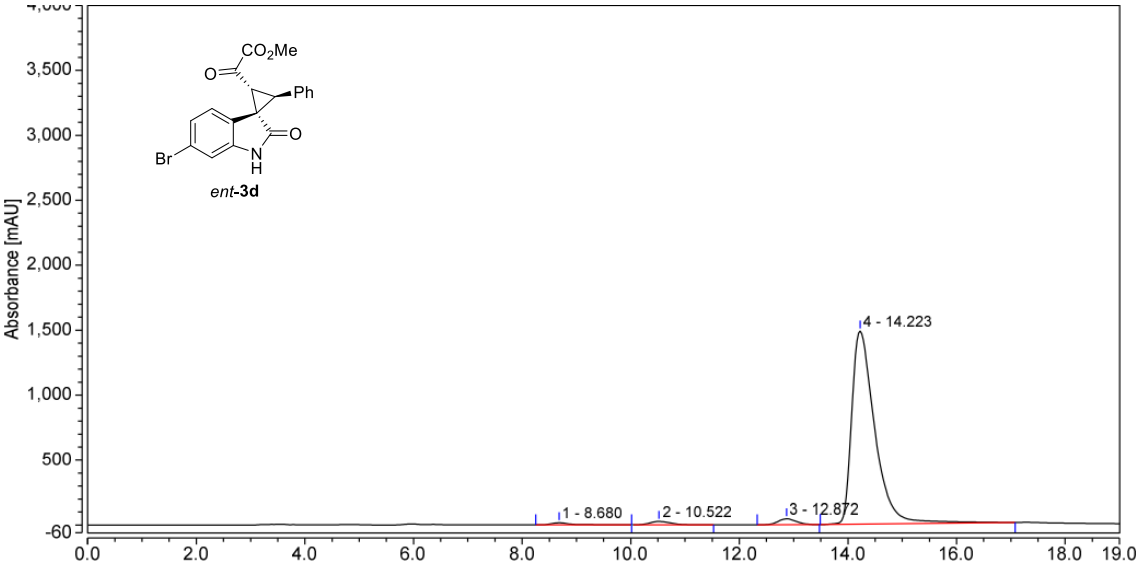
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.675	3.599	9.824	0.41	0.48
2	10.387	3.164	8.833	0.36	0.43
3	12.595	437.768	1093.479	49.33	53.13
4	14.120	442.938	945.913	49.91	45.96
Total		**887.469**	**2058.049**	**100.00**	**100.00**

HPLC Spectrum of **3d**



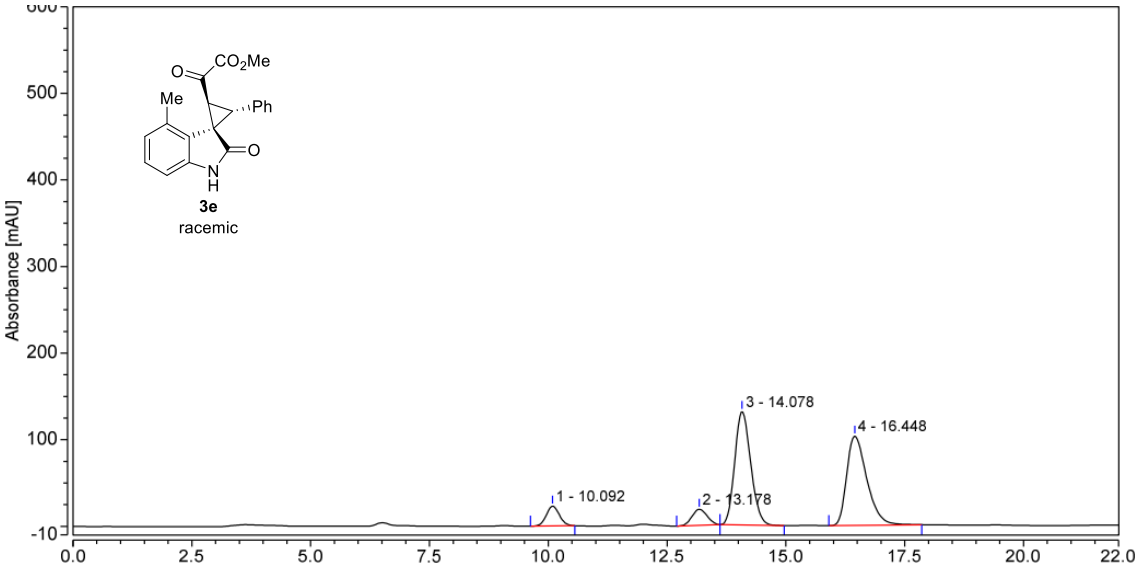
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	7.705	8.817	26.135	1.07	1.30
2	10.583	0.508	1.542	0.06	0.08
3	12.550	802.233	1953.340	96.99	97.16
4	14.337	15.602	29.413	1.89	1.46
Total		**827.161**	**2010.430**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3d**



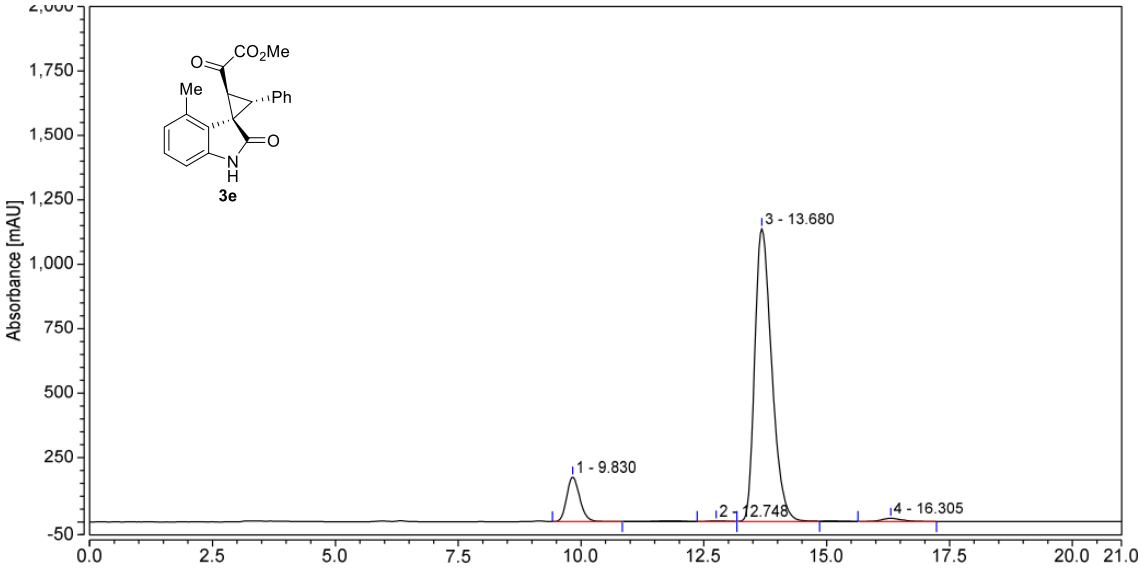
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.680	6.759	16.118	0.88	1.02
2	10.522	11.852	26.330	1.54	1.67
3	12.872	17.985	45.602	2.34	2.90
4	14.223	733.283	1486.080	95.25	94.41
Total		**769.880**	**1574.131**	**100.00**	**100.00**

HPLC Spectrum of **3e**



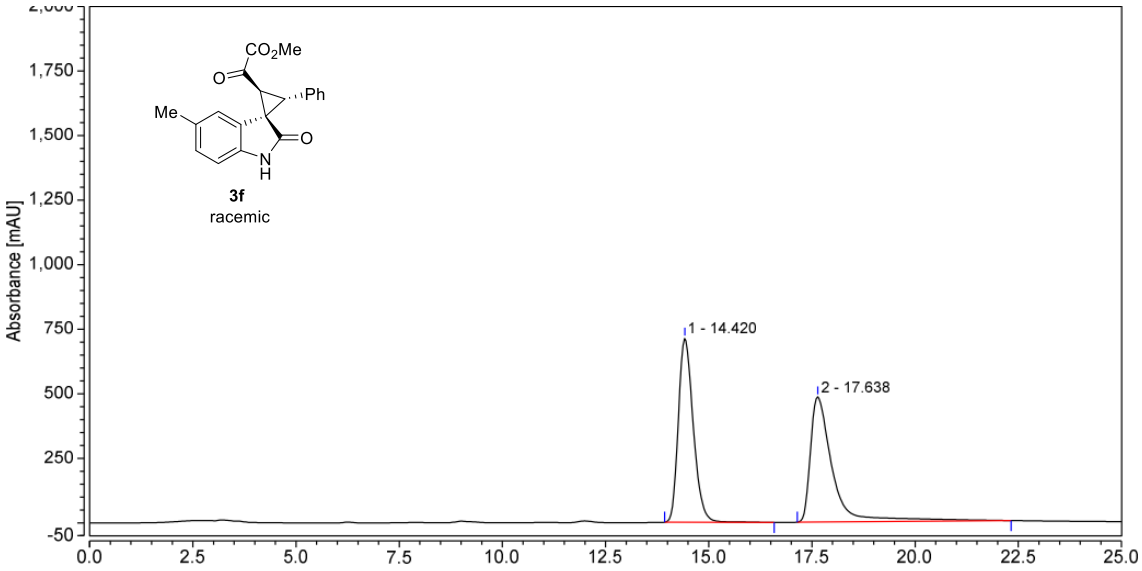
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.092	7.317	22.876	6.30	8.29
2	13.178	6.841	18.580	5.89	6.74
3	14.078	51.321	131.192	44.15	47.56
4	16.448	50.757	103.185	43.67	37.41
Total		**116.236**	**275.832**	**100.00**	**100.00**

HPLC Spectrum of **3e**



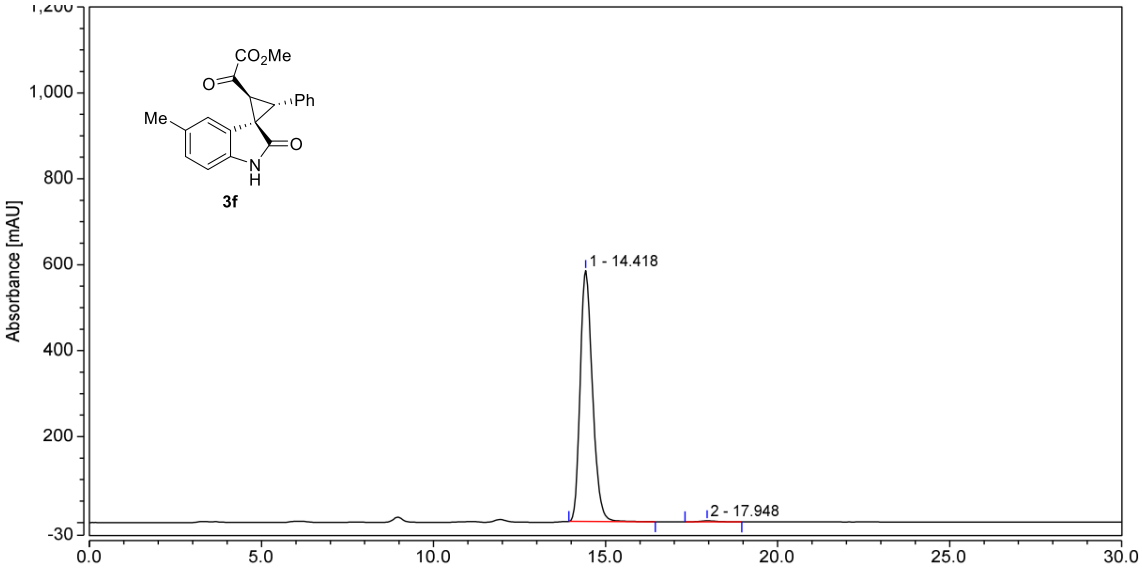
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.830	53.291	173.053	10.30	13.06
2	12.748	1.170	2.496	0.23	0.19
3	13.680	456.936	1137.661	88.31	85.84
4	16.305	6.013	12.132	1.16	0.92
Total		**517.409**	**1325.343**	**100.00**	**100.00**

HPLC Spectrum of **3f**



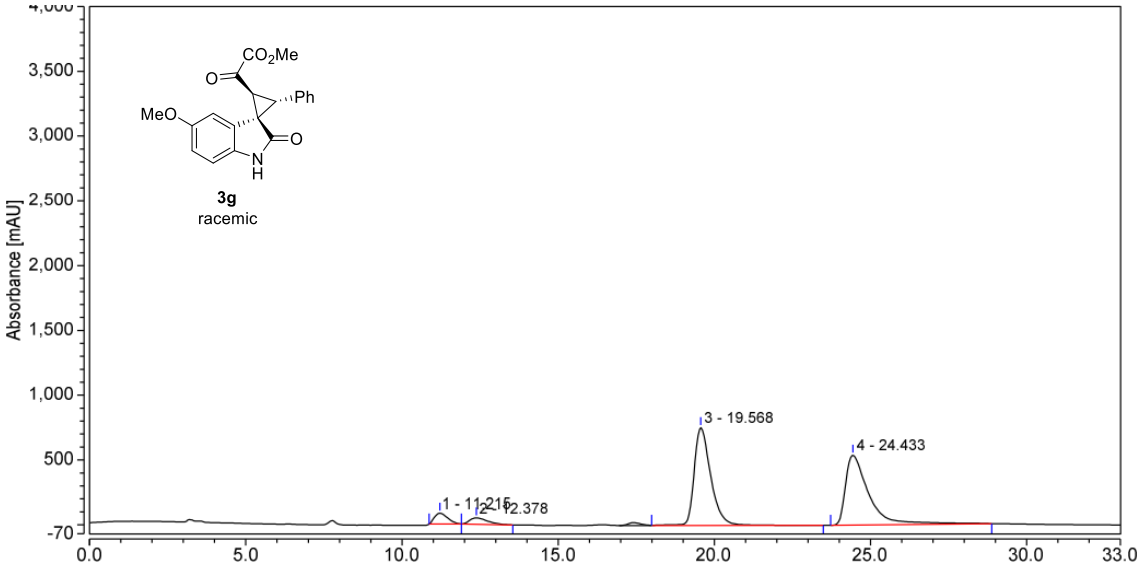
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.420	299.148	713.083	49.88	59.53
2	17.638	300.535	484.850	50.12	40.47
Total		**599.683**	**1197.933**	**100.00**	**100.00**

HPLC Spectrum of **3f**



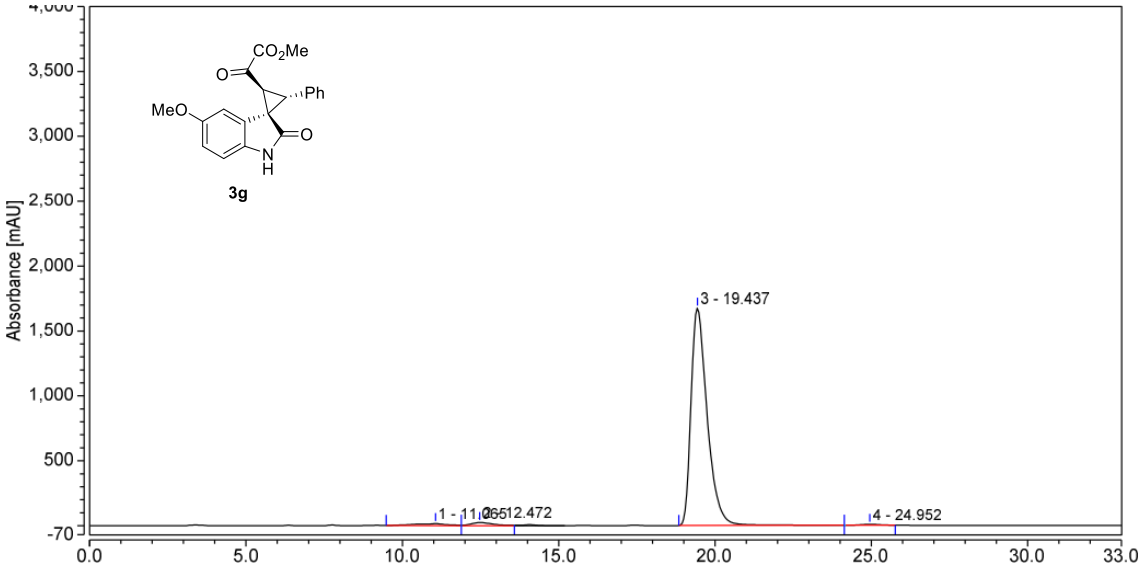
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.418	242.044	584.089	99.46	99.60
2	17.948	1.319	2.365	0.54	0.40
Total		**243.363**	**586.454**	**100.00**	**100.00**

HPLC Spectrum of **3g**



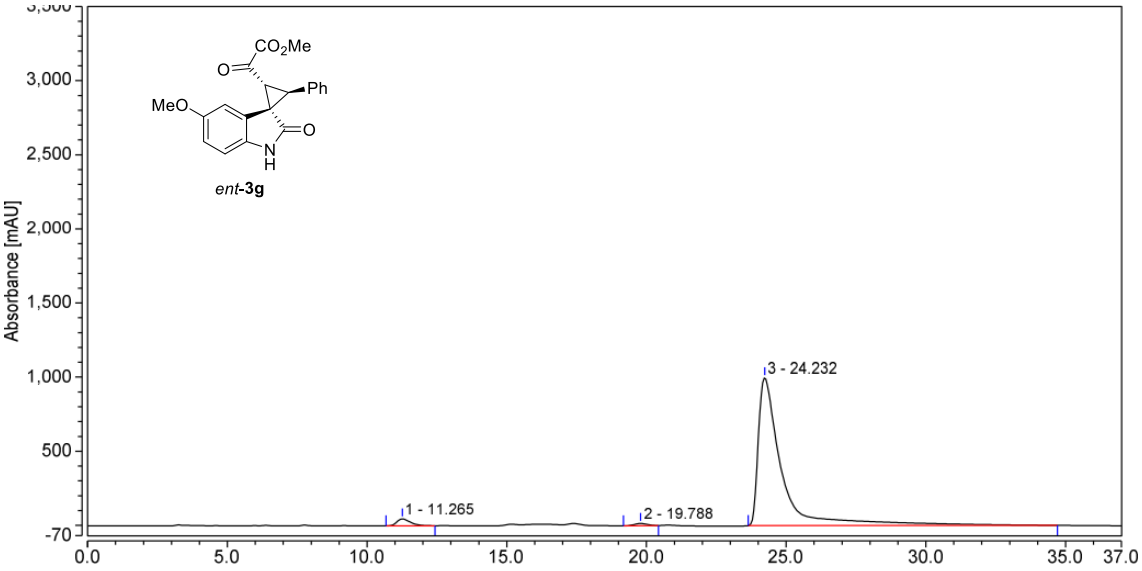
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.215	41.163	83.167	4.10	5.83
2	12.378	32.676	49.338	3.25	3.46
3	19.568	465.466	755.175	46.31	52.93
4	24.433	465.811	538.944	46.34	37.78
Total		**1005.116**	**1426.623**	**100.00**	**100.00**

HPLC Spectrum of **3g**



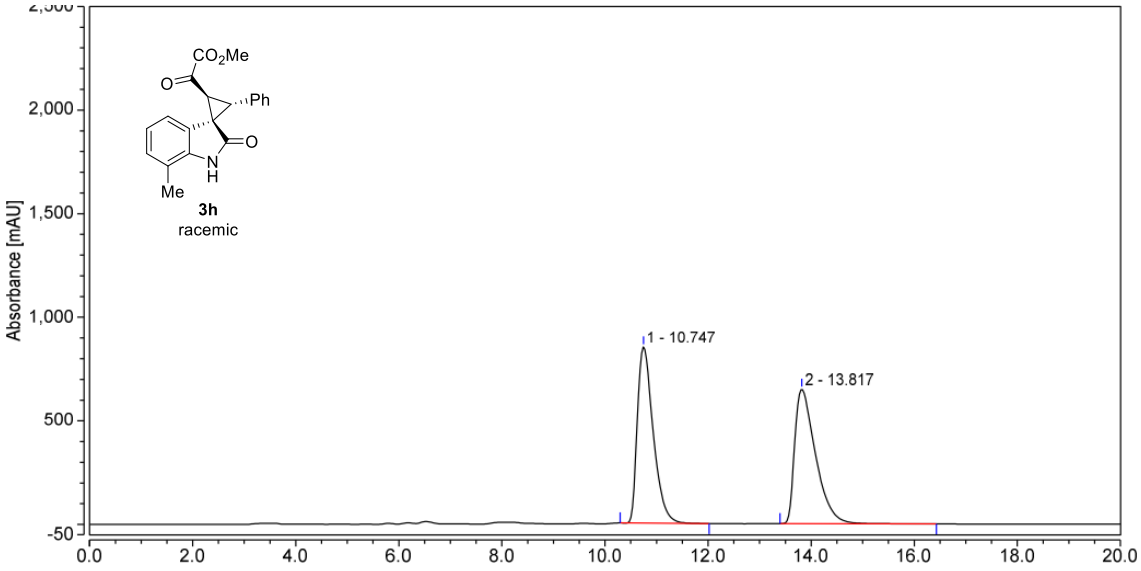
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.065	17.697	14.771	1.69	0.86
2	12.472	19.613	24.360	1.87	1.42
3	19.437	1005.616	1674.406	95.93	97.30
4	24.952	5.302	7.368	0.51	0.43
Total		**1048.228**	**1720.905**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3g**



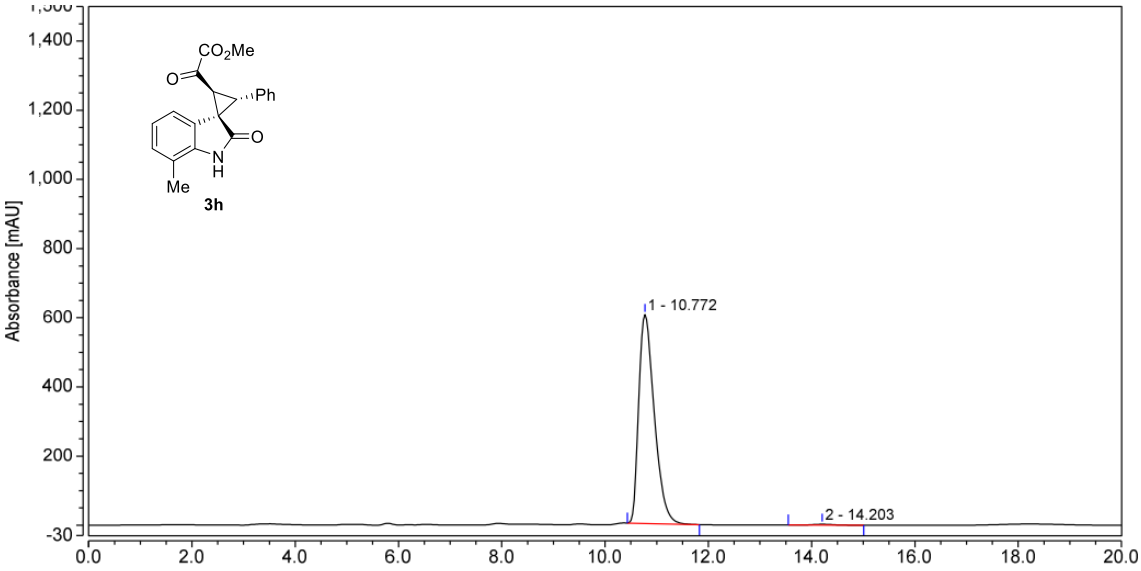
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	11.265	26.315	46.625	2.61	4.40
2	19.788	7.914	15.065	0.78	1.42
3	24.232	975.043	996.900	96.61	94.17
Total		**1009.272**	**1058.590**	**100.00**	**100.00**

HPLC Spectrum of **3h**



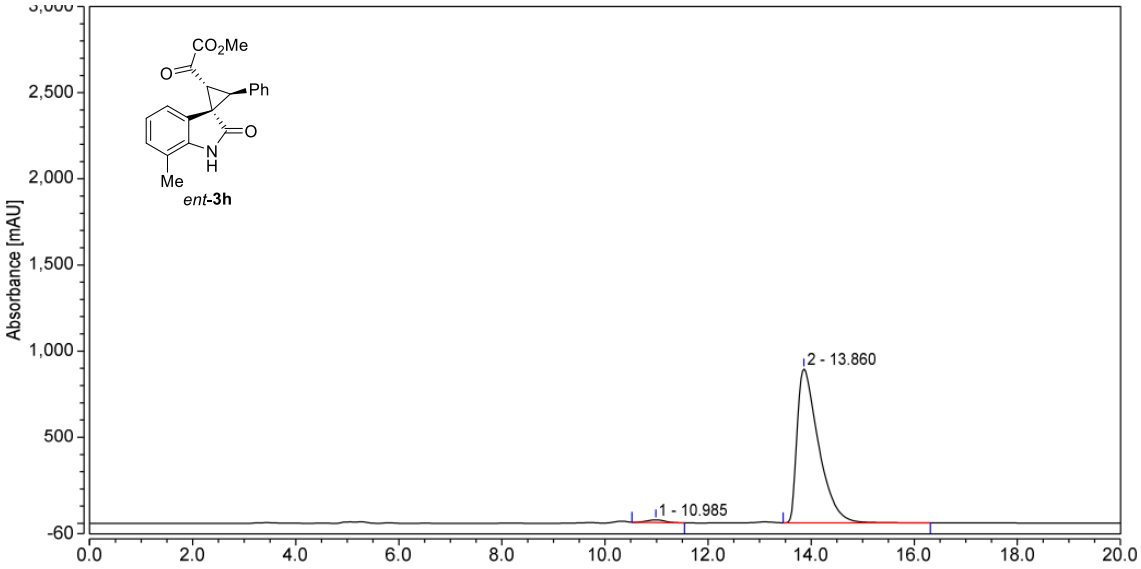
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.747	303.247	851.132	49.90	56.71
2	13.817	304.417	649.591	50.10	43.29
Total		**607.665**	**1500.723**	**100.00**	**100.00**

HPLC Spectrum of **3h**



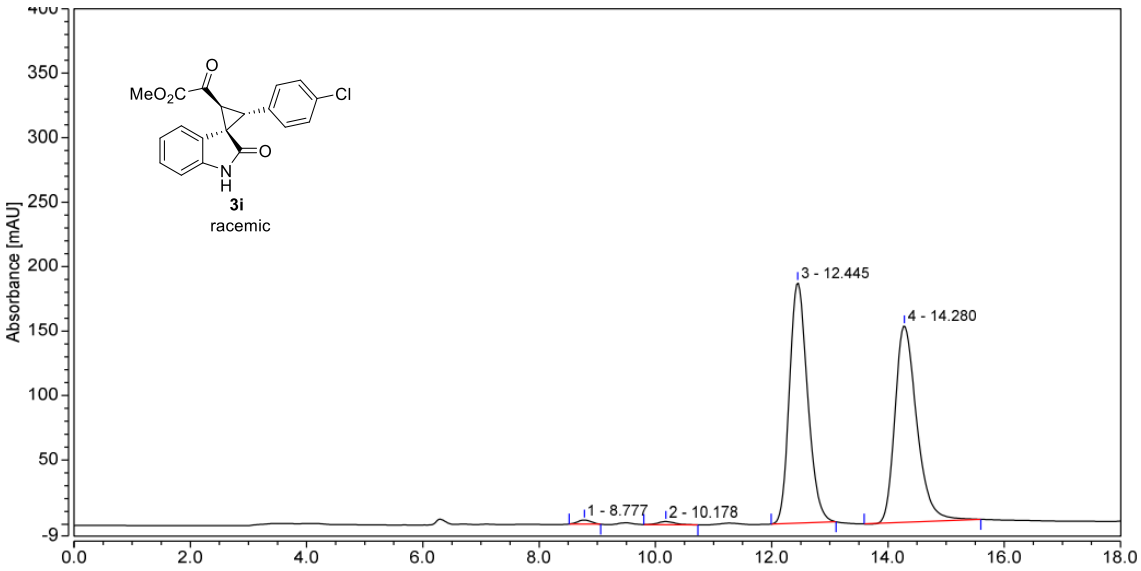
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.772	211.132	604.217	99.45	99.59
2	14.203	1.162	2.496	0.55	0.41
Total		**212.294**	**606.714**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3h**



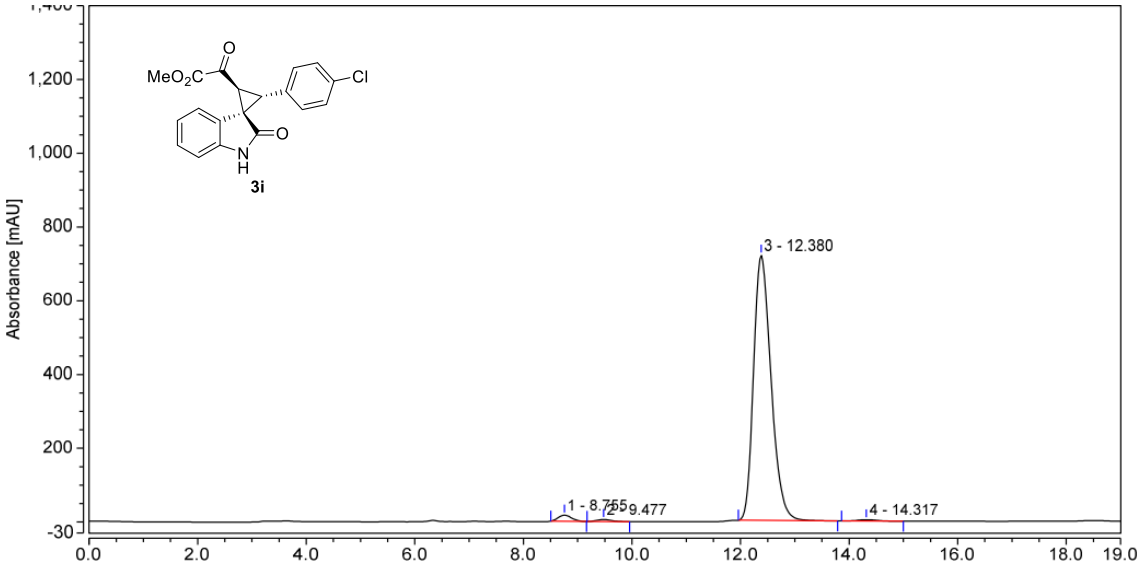
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.985	6.139	15.631	1.40	1.72
2	13.860	431.494	893.074	98.60	98.28
Total		**437.633**	**908.706**	**100.00**	**100.00**

HPLC Spectrum of **3i**



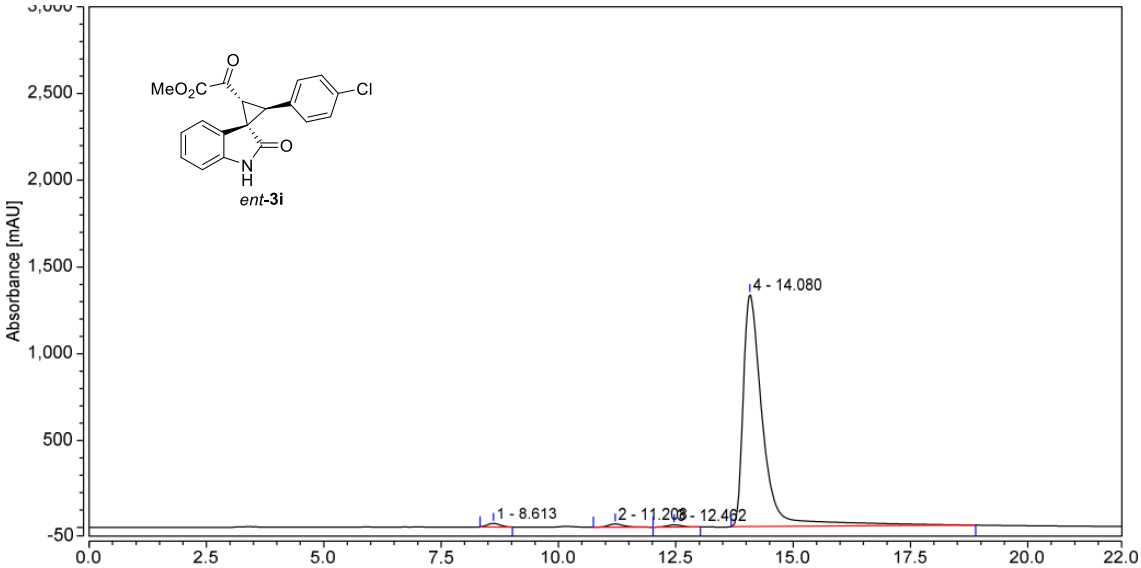
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.777	0.856	3.178	0.63	0.92
2	10.178	0.808	2.434	0.60	0.71
3	12.445	67.617	186.676	49.84	54.15
4	14.280	66.376	152.471	48.93	44.23
Total:		**135.656**	**344.758**	**100.00**	**100.00**

HPLC Spectrum of **3i**



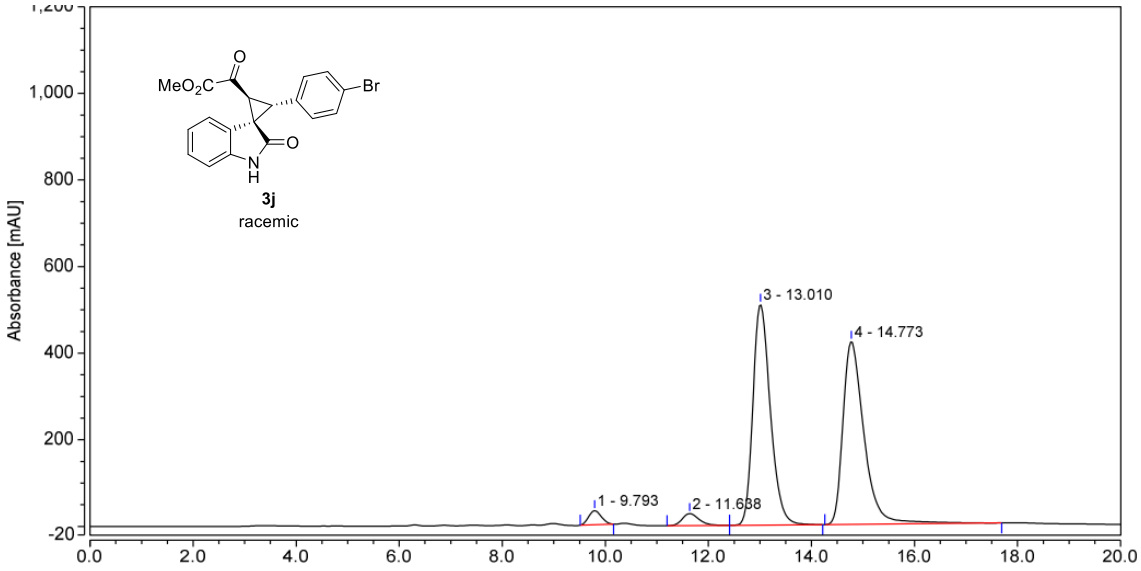
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.755	4.789	16.615	1.73	2.23
2	9.477	1.683	5.590	0.61	0.75
3	12.380	268.371	719.040	97.10	96.52
4	14.317	1.542	3.692	0.56	0.50
Total:		**276.385**	**744.937**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3i**



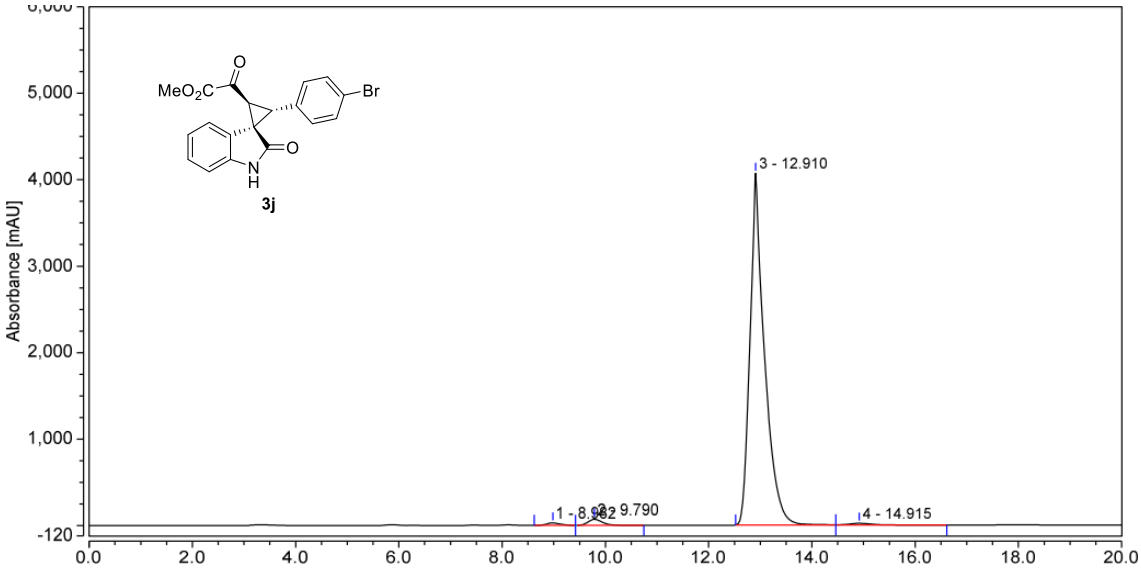
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.613	6.440	20.573	0.96	1.48
2	11.208	6.810	18.277	1.01	1.32
3	12.462	4.539	12.657	0.68	0.91
4	14.080	653.680	1337.479	97.35	96.29
Total:		**671.469**	**1388.986**	**100.00**	**100.00**

HPLC Spectrum of **3j**



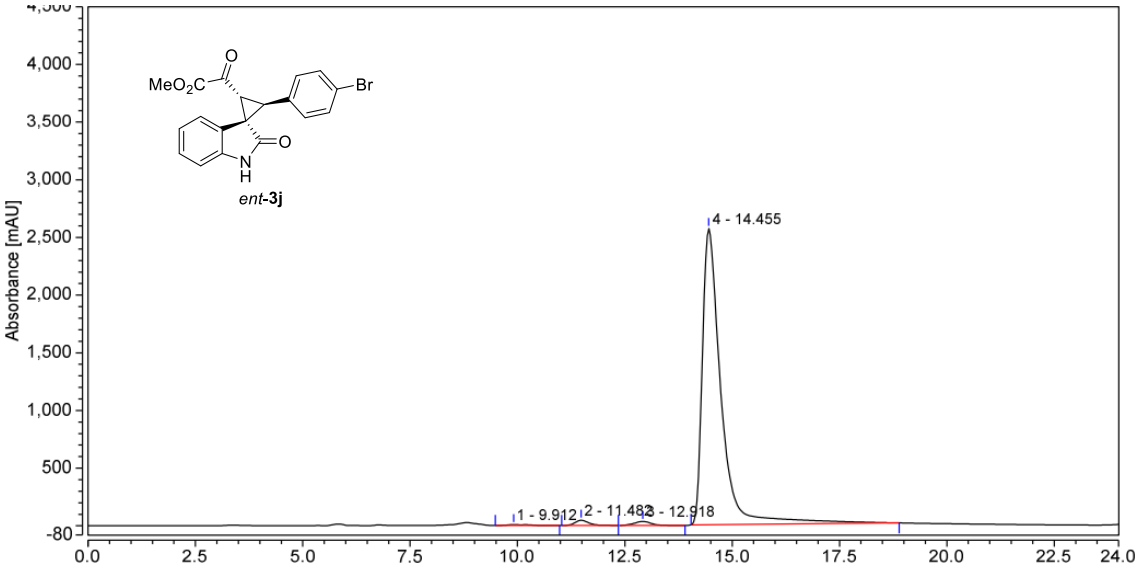
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.793	9.262	32.329	2.20	3.26
2	11.638	10.488	27.727	2.50	2.79
3	13.010	199.877	509.989	47.55	51.38
4	14.773	200.729	422.551	47.75	42.57
Total:		**420.356**	**992.596**	**100.00**	**100.00**

HPLC Spectrum of **3j**



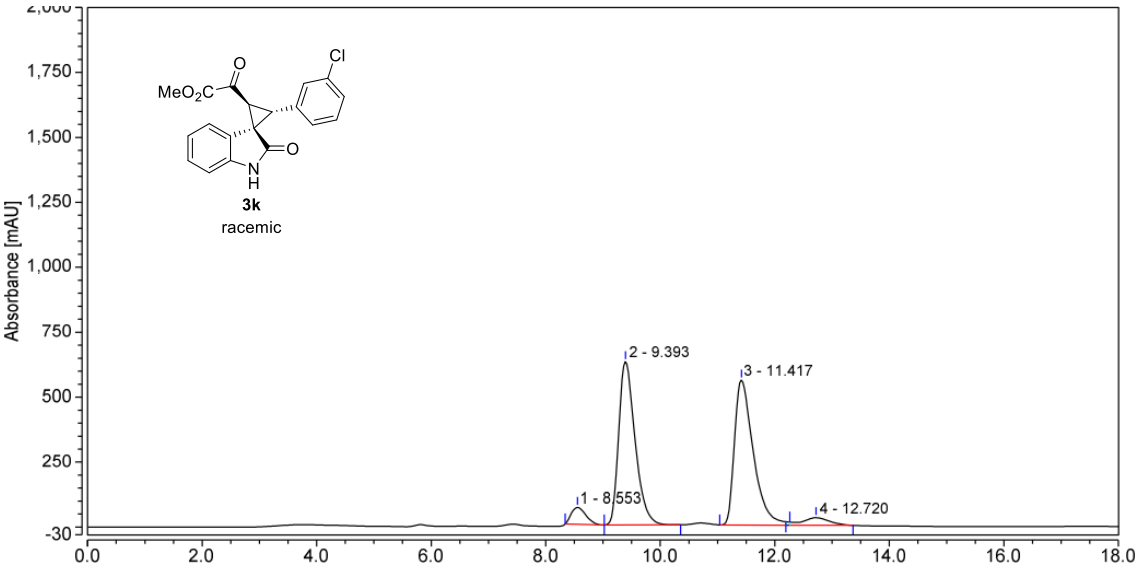
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.982	8.625	28.329	0.63	0.68
2	9.790	22.889	69.575	1.68	1.66
3	12.910	1321.099	4067.522	96.92	97.19
4	14.915	10.500	19.602	0.77	0.47
Total:		**1363.114**	**4185.028**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3j**



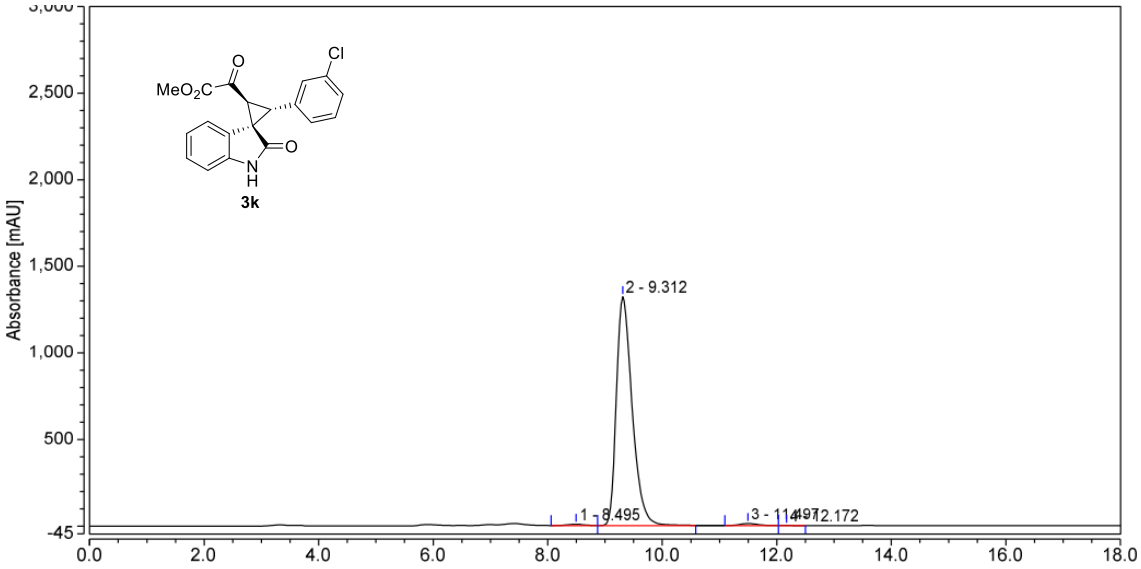
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.912	4.489	7.566	0.34	0.28
2	11.482	17.033	45.071	1.28	1.70
3	12.918	15.426	34.604	1.16	1.30
4	14.455	1296.690	2569.022	97.23	96.72
Total:		**1333.637**	**2656.263**	**100.00**	**100.00**

HPLC Spectrum of **3k**



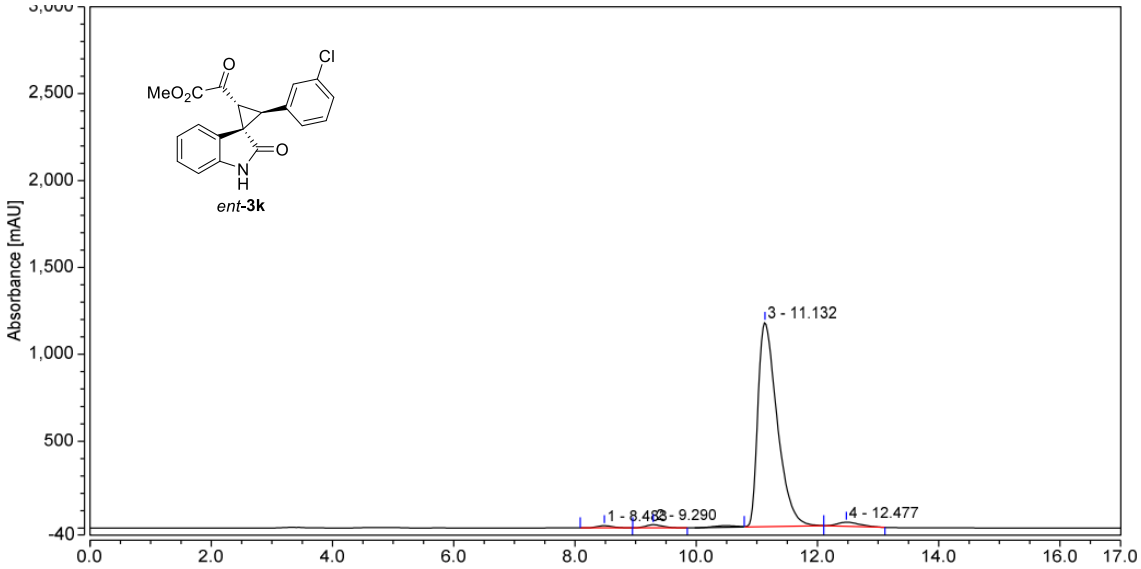
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.553	19.290	65.150	4.23	5.08
2	9.393	208.567	629.074	45.77	49.09
3	11.417	212.051	558.204	46.54	43.56
4	12.720	15.766	29.069	3.46	2.27
Total		**455.674**	**1281.497**	**100.00**	**100.00**

HPLC Spectrum of **3k**



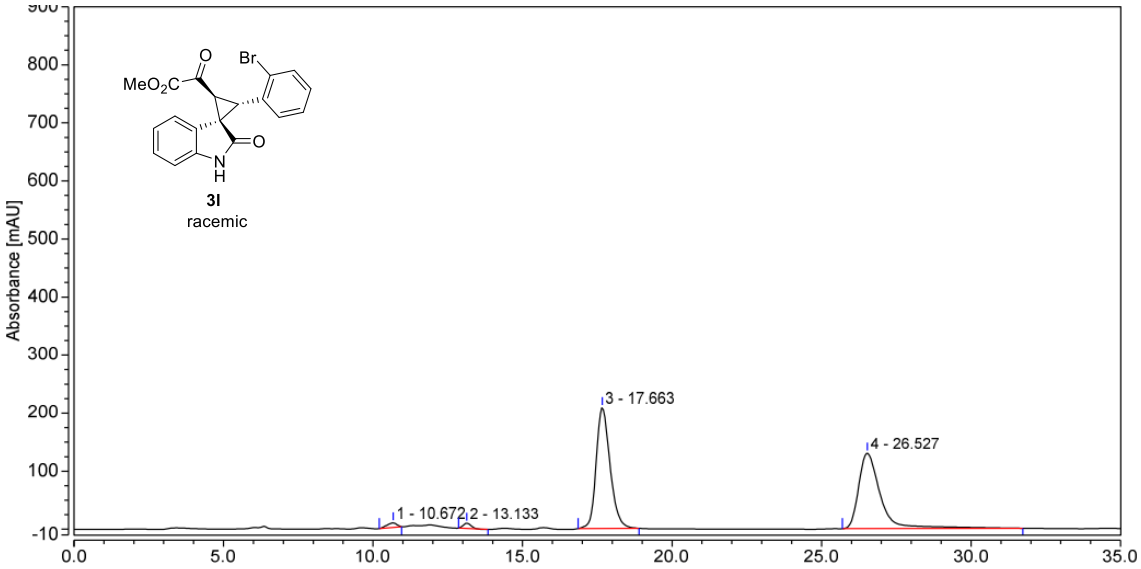
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.495	2.416	7.400	0.56	0.55
2	9.312	422.279	1321.567	98.39	98.53
3	11.497	4.299	11.718	1.00	0.87
4	12.172	0.181	0.622	0.04	0.05
Total		**429.175**	**1341.307**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3k**



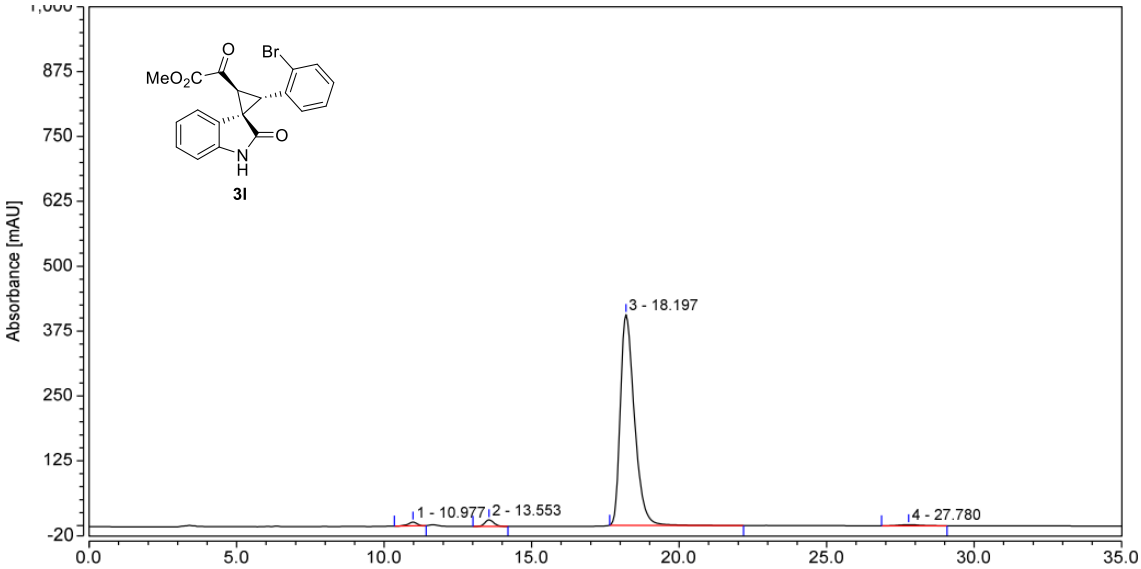
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.483	3.675	12.591	0.81	1.02
2	9.290	5.743	18.248	1.27	1.49
3	11.132	432.445	1174.583	95.69	95.61
4	12.477	10.039	23.148	2.22	1.88
Total:		**451.901**	**1228.570**	**100.00**	**100.00**

HPLC Spectrum of **3l**



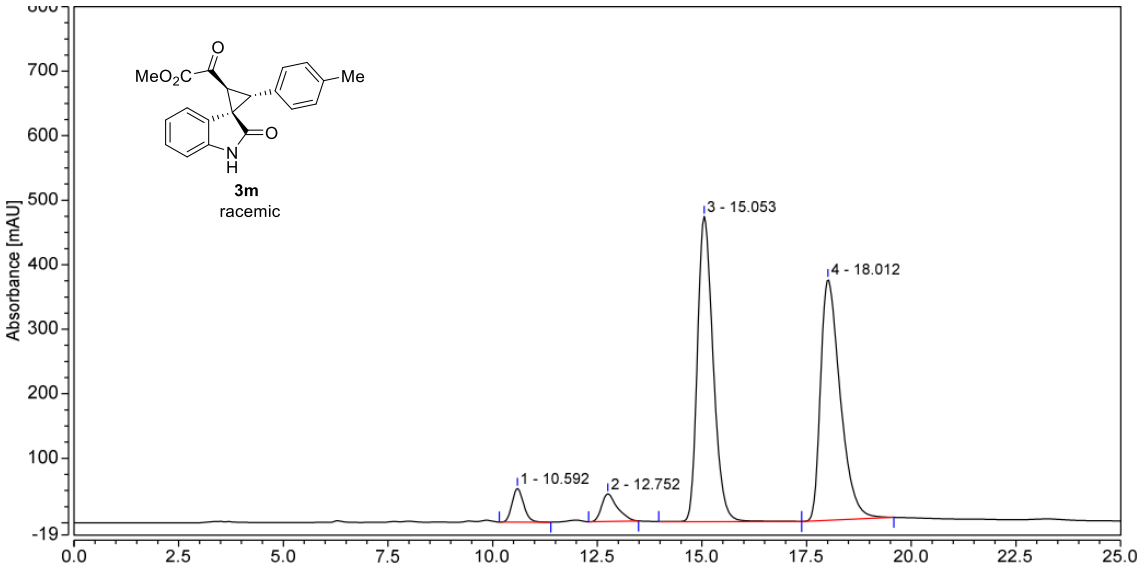
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.672	3.061	7.855	1.34	2.21
2	13.133	2.610	8.923	1.15	2.51
3	17.663	112.254	208.091	49.29	58.64
4	26.527	109.834	130.003	48.22	36.63
Total:		**227.759**	**354.872**	**100.00**	**100.00**

HPLC Spectrum of **3l**



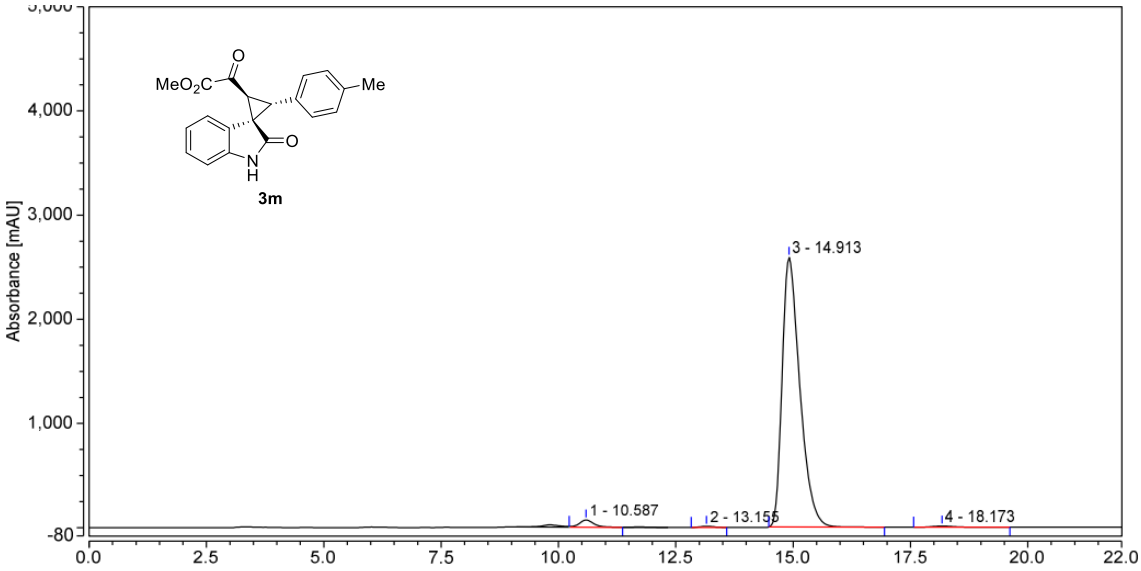
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.977	2.473	7.168	1.06	1.67
2	13.553	4.470	12.645	1.91	2.95
3	18.197	225.104	406.187	96.28	94.87
4	27.780	1.749	2.154	0.75	0.50
Total:		**233.795**	**428.154**	**100.00**	**100.00**

HPLC Spectrum of **3m**



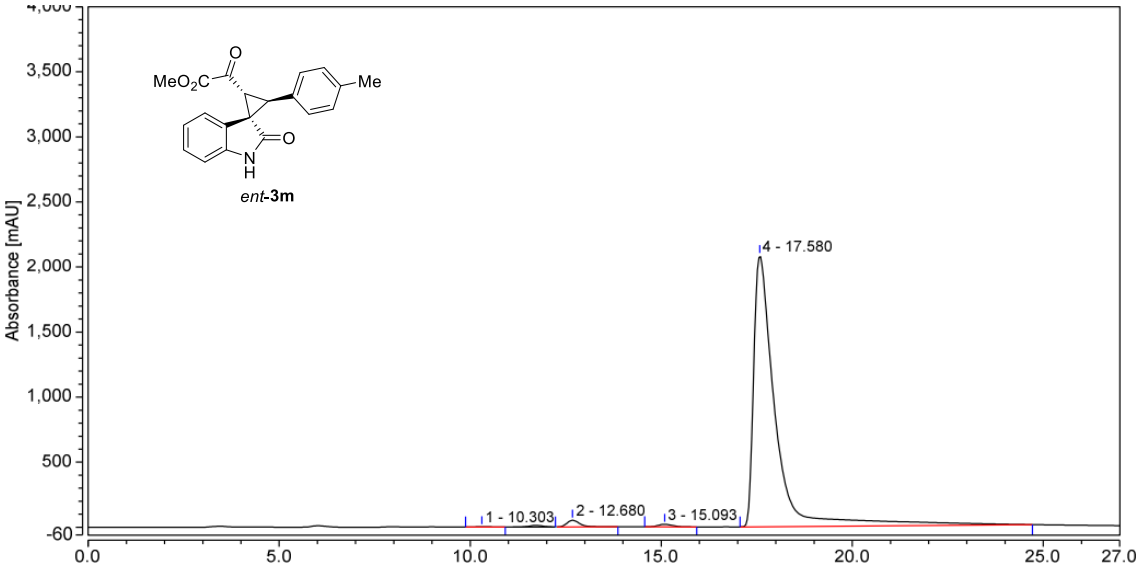
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.592	16.734	52.218	3.76	5.55
2	12.752	18.451	42.681	4.15	4.53
3	15.053	206.503	473.288	46.40	50.27
4	18.012	203.398	373.306	45.70	39.65
Total:		**445.086**	**941.493**	**100.00**	**100.00**

HPLC Spectrum of **3m**



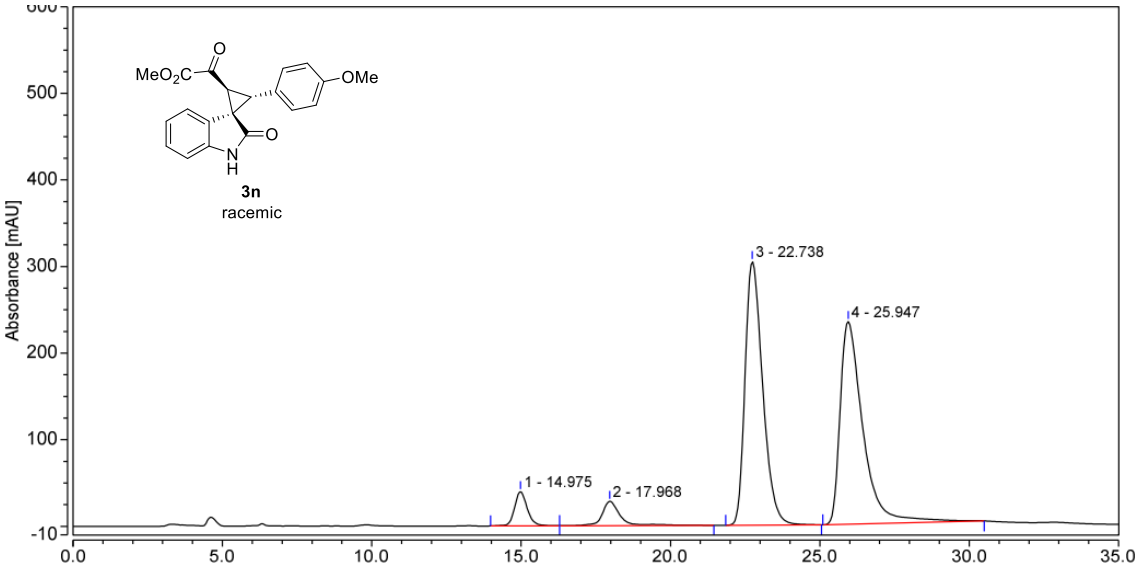
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.587	25.152	69.997	2.16	2.61
2	13.155	3.475	10.983	0.30	0.41
3	14.913	1131.946	2588.045	97.05	96.57
4	18.173	5.823	11.017	0.50	0.41
Total:		**1166.396**	**2680.042**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3m**



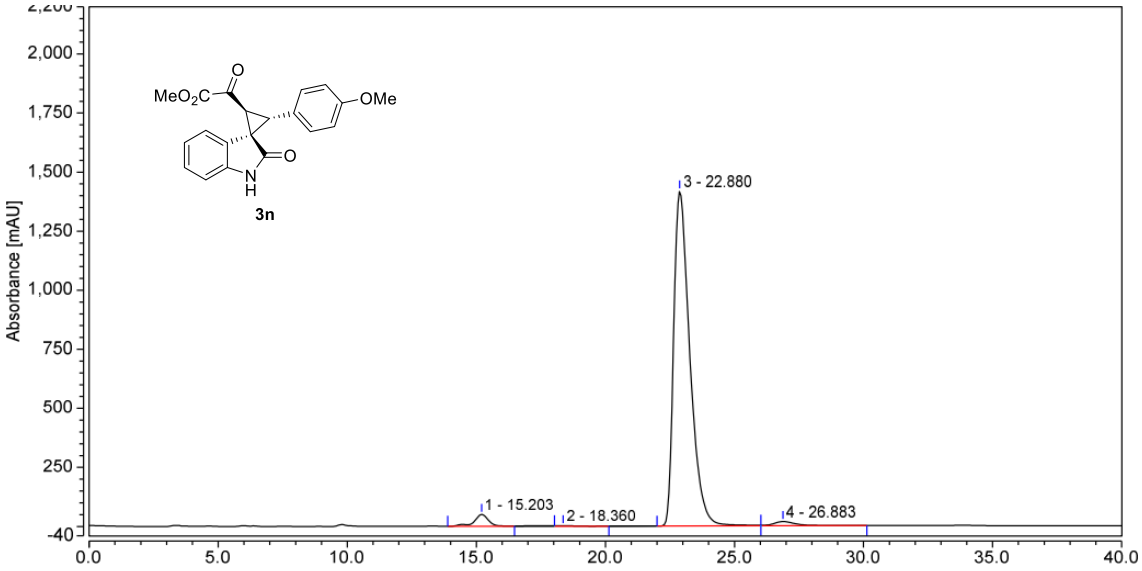
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.303	1.273	2.823	0.09	0.13
2	12.680	20.555	51.533	1.46	2.39
3	15.093	8.506	19.748	0.60	0.92
4	17.580	1378.142	2083.460	97.85	96.57
Total:		**1408.476**	**2157.565**	**100.00**	**100.00**

HPLC Spectrum of **3n**



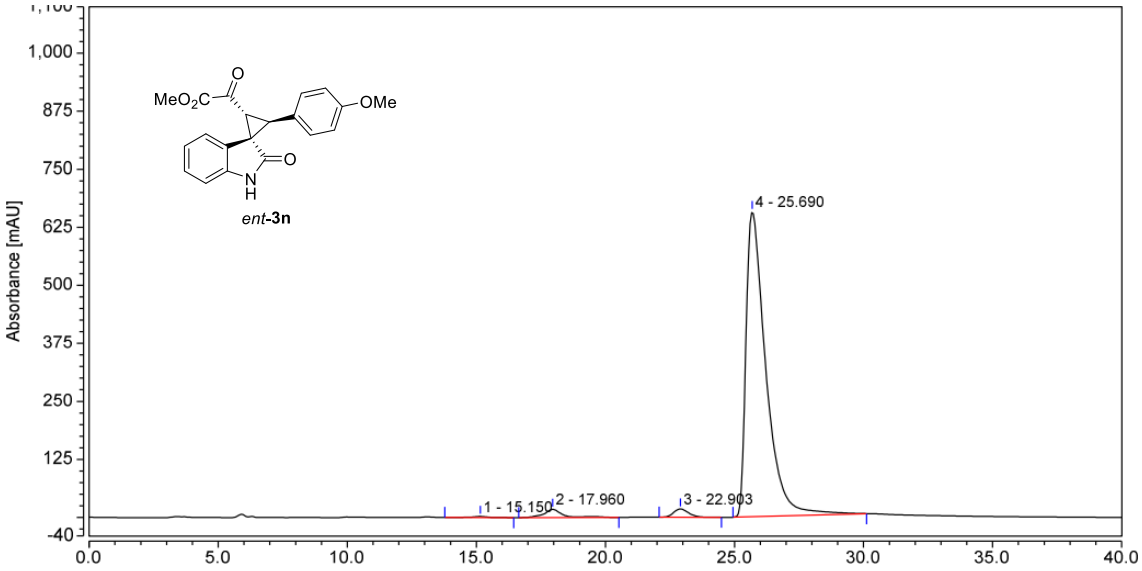
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	14.975	19.419	39.501	4.27	6.52
2	17.968	19.575	28.059	4.31	4.63
3	22.738	208.382	304.266	45.84	50.23
4	25.947	207.180	233.933	45.58	38.62
Total:		**454.556**	**605.759**	**100.00**	**100.00**

HPLC Spectrum of **3n**



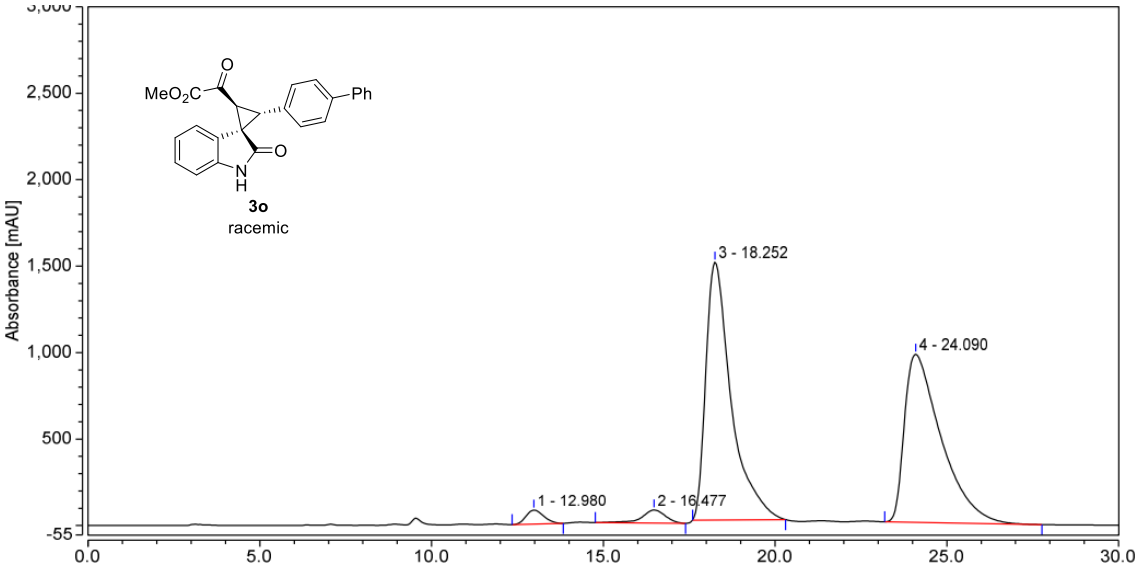
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	15.203	33.021	50.445	3.05	3.39
2	18.360	2.233	2.496	0.21	0.17
3	22.880	1028.630	1418.569	95.03	95.22
4	26.883	18.595	18.345	1.72	1.23
Total:		**1082.479**	**1489.855**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3n**



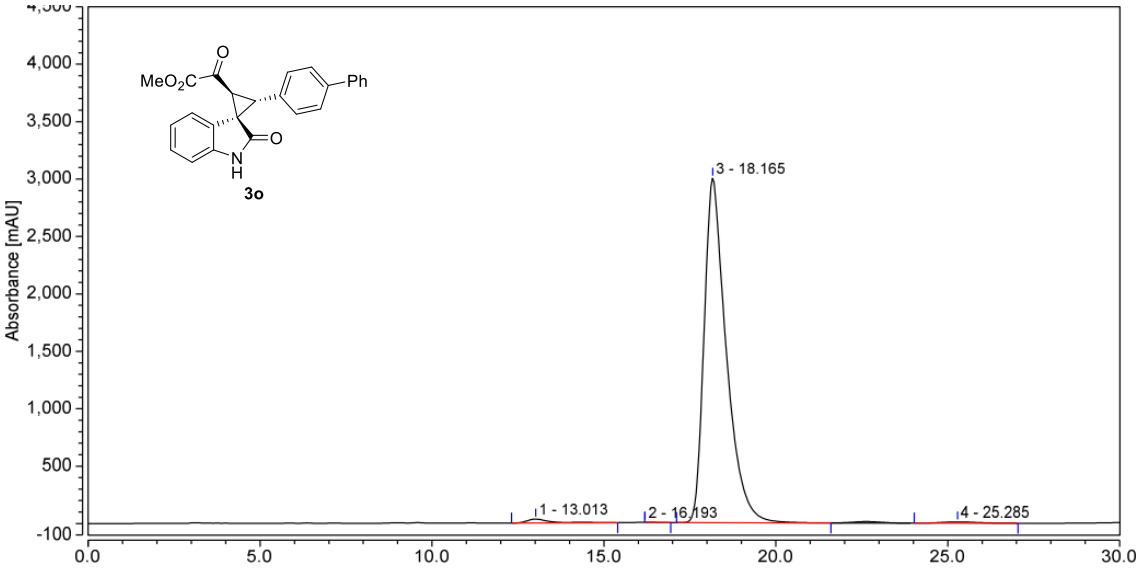
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	15.150	1.806	2.408	0.29	0.35
2	17.960	14.868	17.585	2.42	2.53
3	22.903	12.175	17.908	1.98	2.58
4	25.690	585.795	657.273	95.31	94.55
Total:		**614.643**	**695.175**	**100.00**	**100.00**

HPLC Spectrum of **3o**



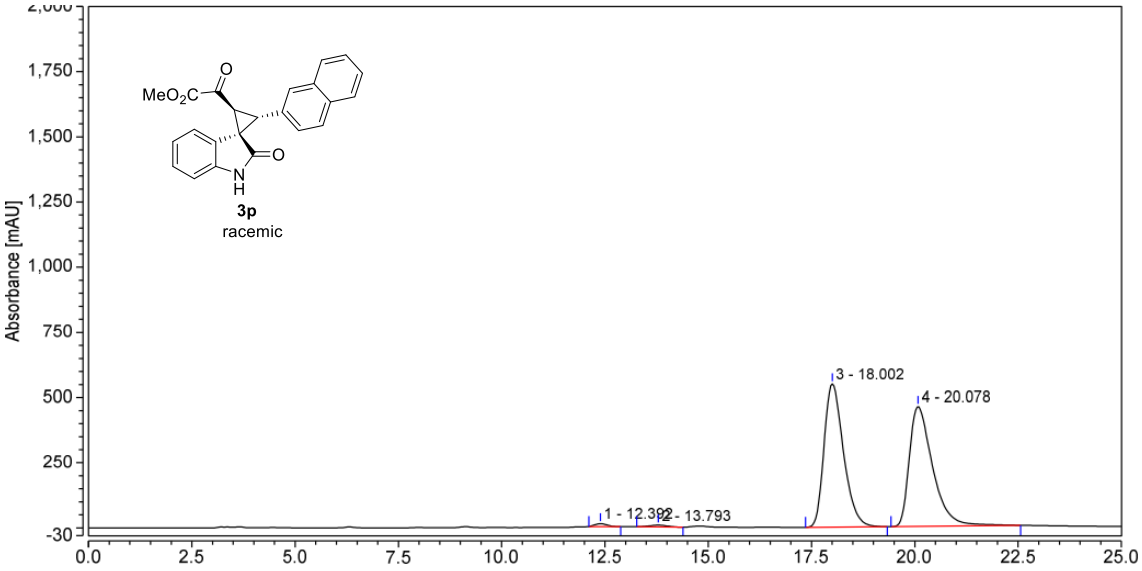
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.980	48.292	80.818	1.86	3.09
2	16.477	60.196	75.851	2.32	2.90
3	18.252	1275.697	1490.950	49.25	56.91
4	24.090	1205.911	972.028	46.56	37.11
Total:		**2590.096**	**2619.647**	**100.00**	**100.00**

HPLC Spectrum of **3o**



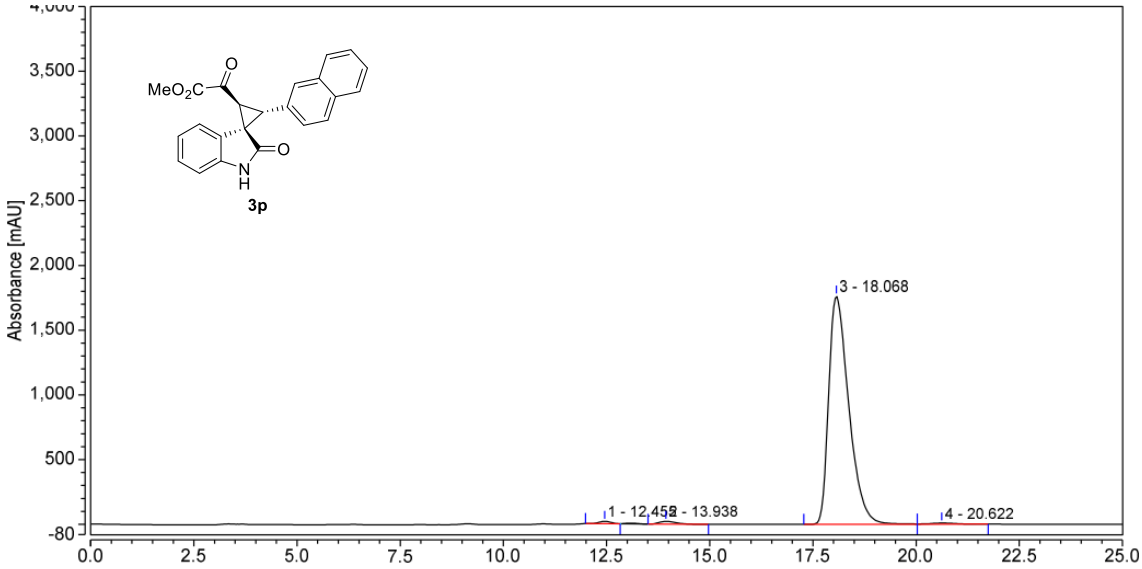
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.013	26.195	33.221	1.15	1.09
2	16.193	0.185	0.009	0.01	0.00
3	18.165	2240.363	3000.318	98.24	98.54
4	25.285	13.783	11.153	0.60	0.37
Total:		**2280.527**	**3044.701**	**100.00**	**100.00**

HPLC Spectrum of **3p**



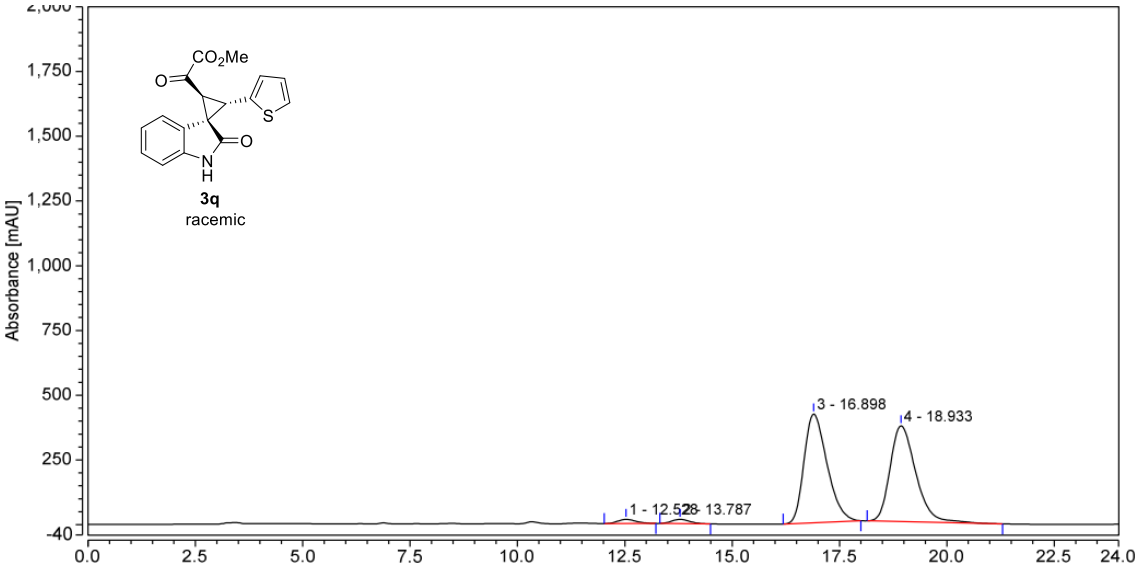
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.392	3.736	11.035	0.61	1.07
2	13.793	3.324	6.808	0.55	0.66
3	18.002	300.635	549.862	49.48	53.51
4	20.078	299.930	459.870	49.36	44.75
Total		**607.625**	**1027.576**	**100.00**	**100.00**

HPLC Spectrum of **3p**



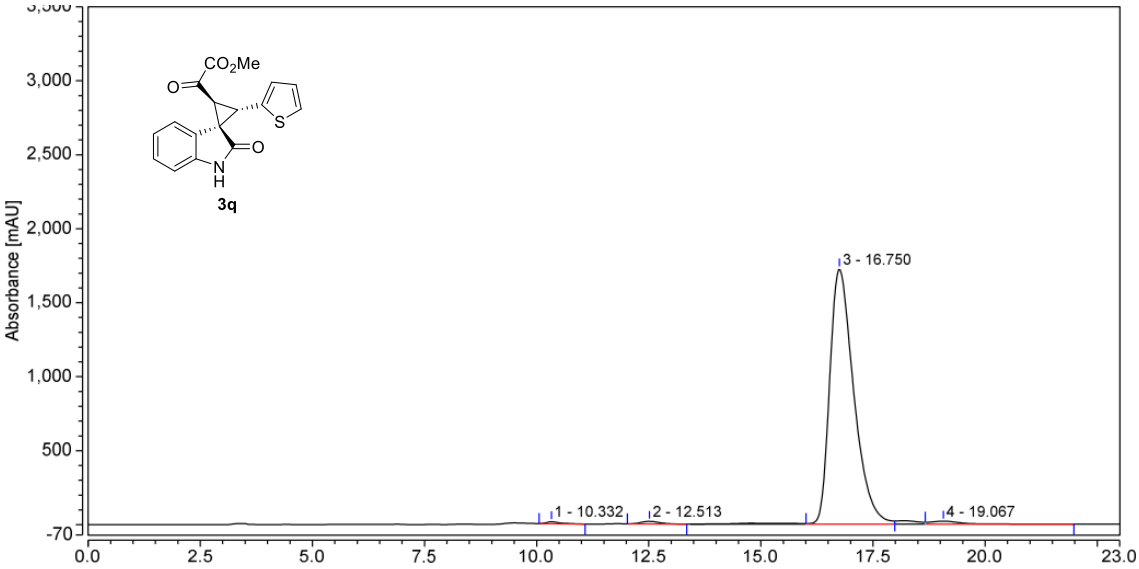
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.455	6.561	18.825	0.64	1.04
2	13.938	11.101	22.703	1.09	1.25
3	18.068	995.333	1762.691	97.63	97.21
4	20.622	6.524	8.995	0.64	0.50
Total		**1019.519**	**1813.214**	**100.00**	**100.00**

HPLC Spectrum of **3q**



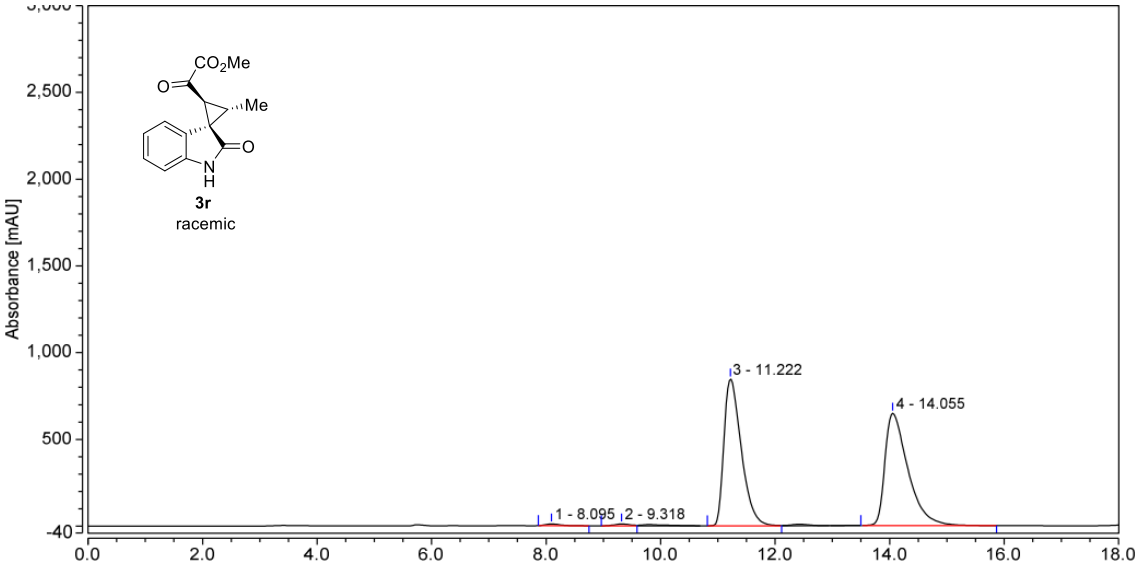
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	12.528	7.918	16.065	1.48	1.95
2	13.787	7.951	16.445	1.49	2.00
3	16.898	261.292	419.874	48.95	51.05
4	18.933	256.684	370.094	48.08	45.00
Total:		**533.845**	**822.480**	**100.00**	**100.00**

HPLC Spectrum of **3q**



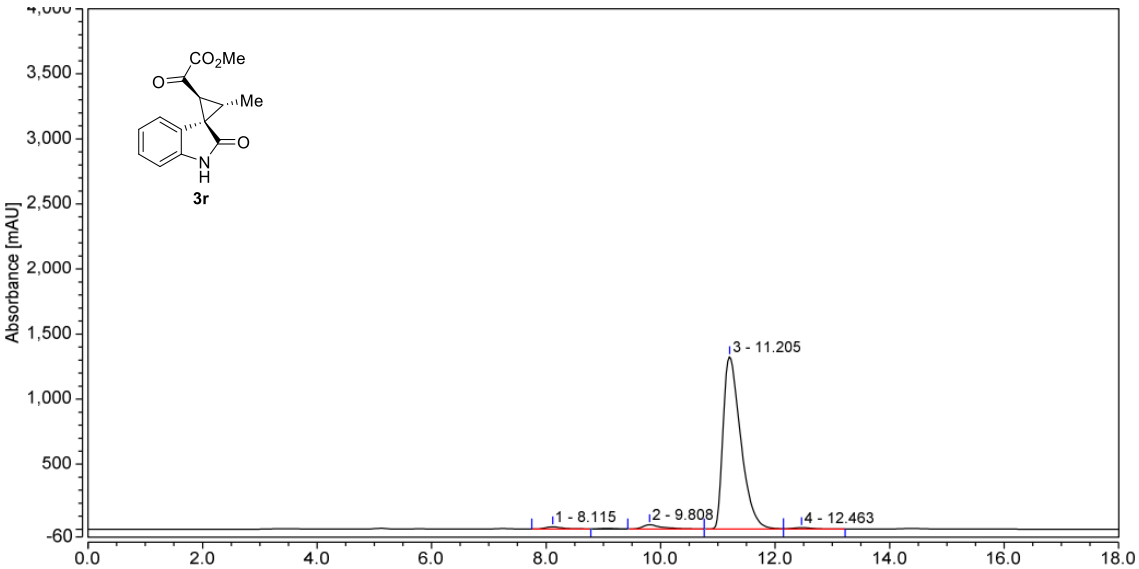
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.332	4.735	13.286	0.43	0.75
2	12.513	8.522	17.513	0.77	0.99
3	16.750	1070.053	1724.310	97.20	97.09
4	19.067	17.555	20.810	1.59	1.17
Total:		**1100.865**	**1775.919**	**100.00**	**100.00**

HPLC Spectrum of **3r**



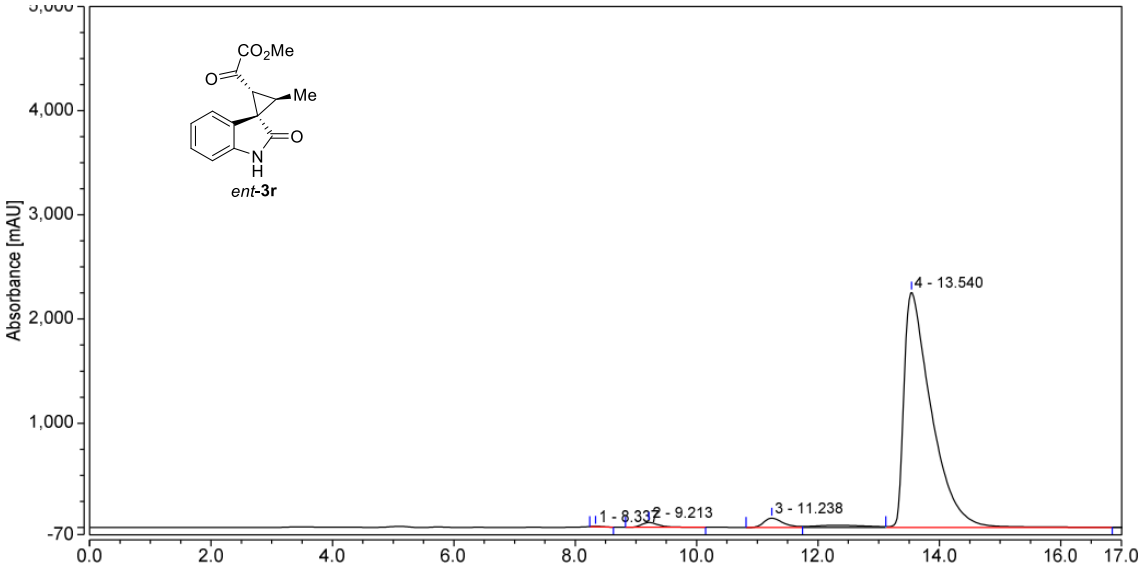
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.095	2.945	9.459	0.49	0.62
2	9.318	3.179	10.291	0.52	0.68
3	11.222	297.409	846.008	49.11	55.88
4	14.055	302.109	648.164	49.88	42.81
Total:		**605.642**	**1513.922**	**100.00**	**100.00**

HPLC Spectrum of **3r**



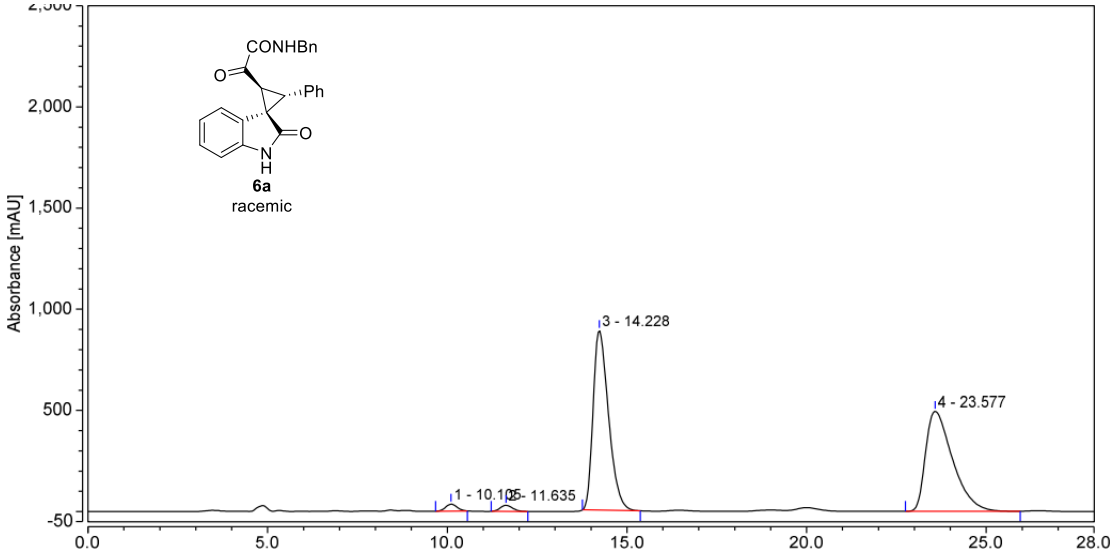
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.115	6.117	17.286	1.23	1.25
2	9.808	13.219	33.065	2.66	2.38
3	11.205	473.939	1325.185	95.21	95.56
4	12.463	4.513	11.212	0.91	0.81
Total:		**497.788**	**1386.747**	**100.00**	**100.00**

HPLC Spectrum of *ent*-**3r**



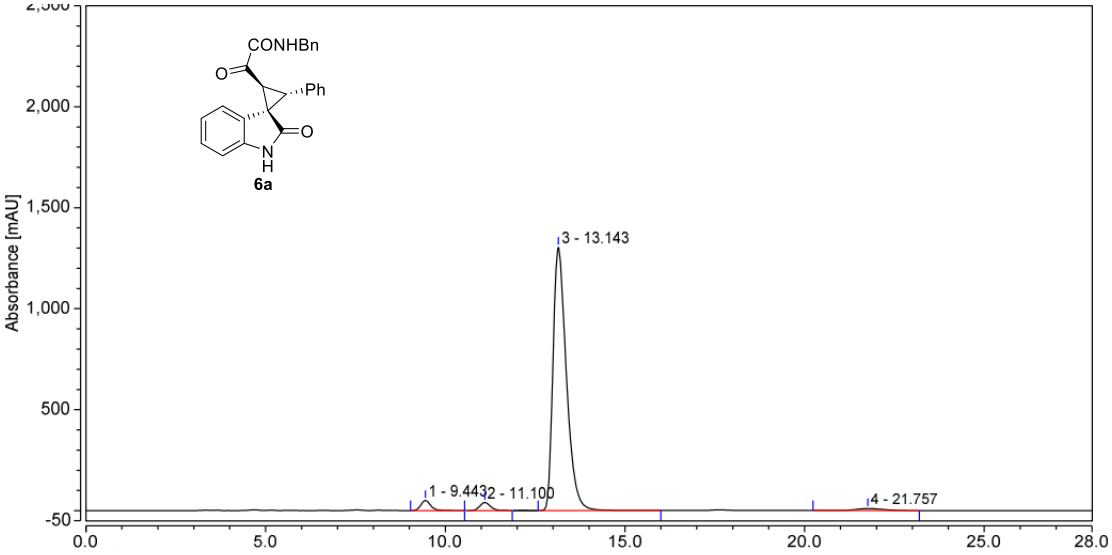
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	8.337	0.766	3.429	0.06	0.14
2	9.213	15.368	45.506	1.25	1.90
3	11.238	32.390	88.902	2.64	3.71
4	13.540	1178.235	2259.194	96.04	94.25
Total		**1226.760**	**2397.032**	**100.00**	**100.00**

HPLC Spectrum of **6a**



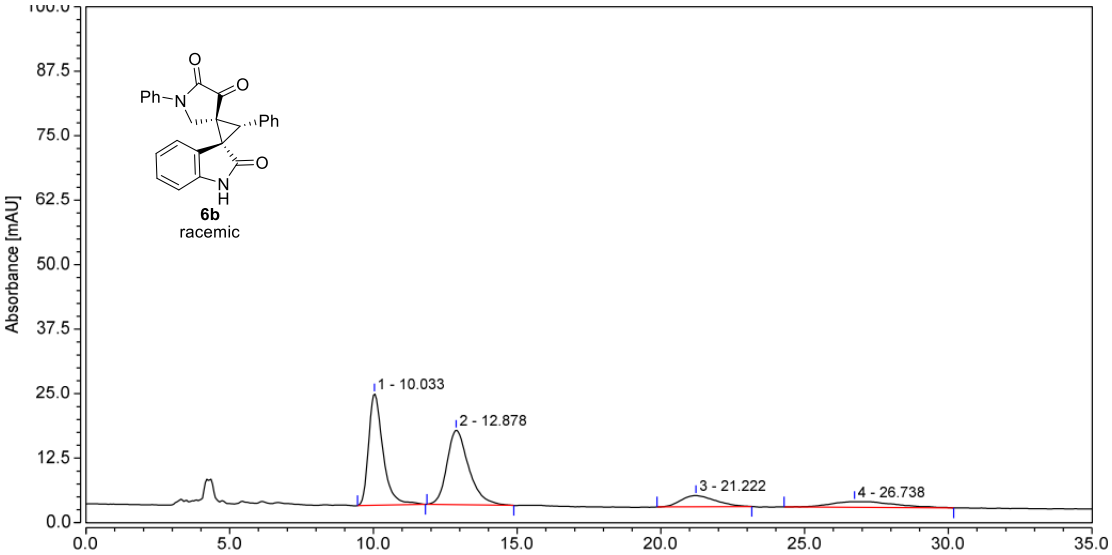
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.105	12.873	34.544	1.43	2.39
2	11.635	11.914	30.372	1.33	2.10
3	14.228	442.511	887.934	49.30	61.35
4	23.577	430.200	494.569	47.93	34.17
Total		**897.498**	**1447.420**	**100.00**	**100.00**

HPLC Spectrum of **6a**



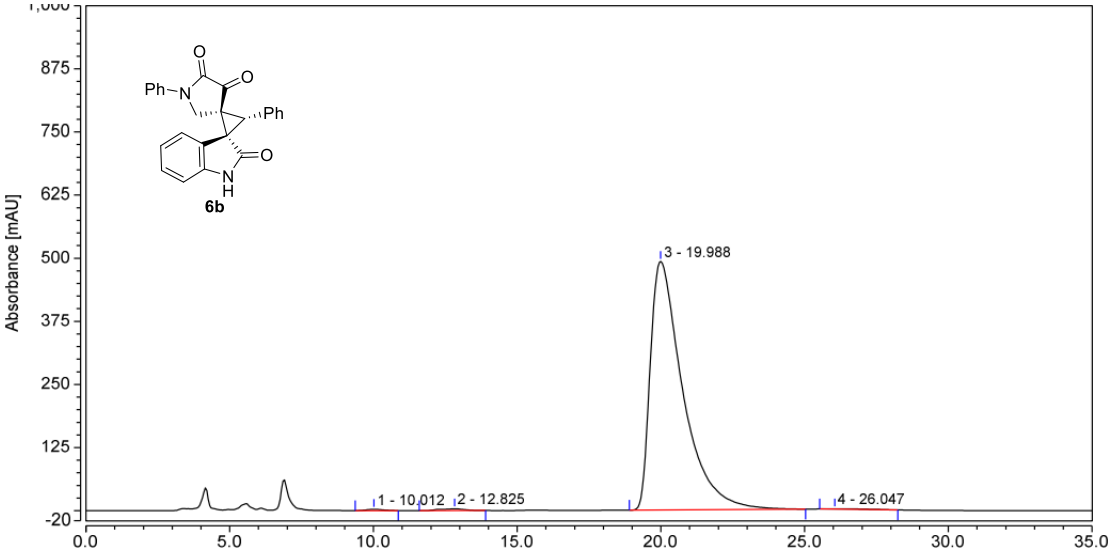
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	9.443	16.225	49.966	2.70	3.56
2	11.100	14.067	40.154	2.34	2.86
3	13.143	562.766	1303.241	93.50	92.87
4	21.757	8.808	10.007	1.46	0.71
Total		**601.866**	**1403.368**	**100.00**	**100.00**

HPLC Spectrum of **6b**



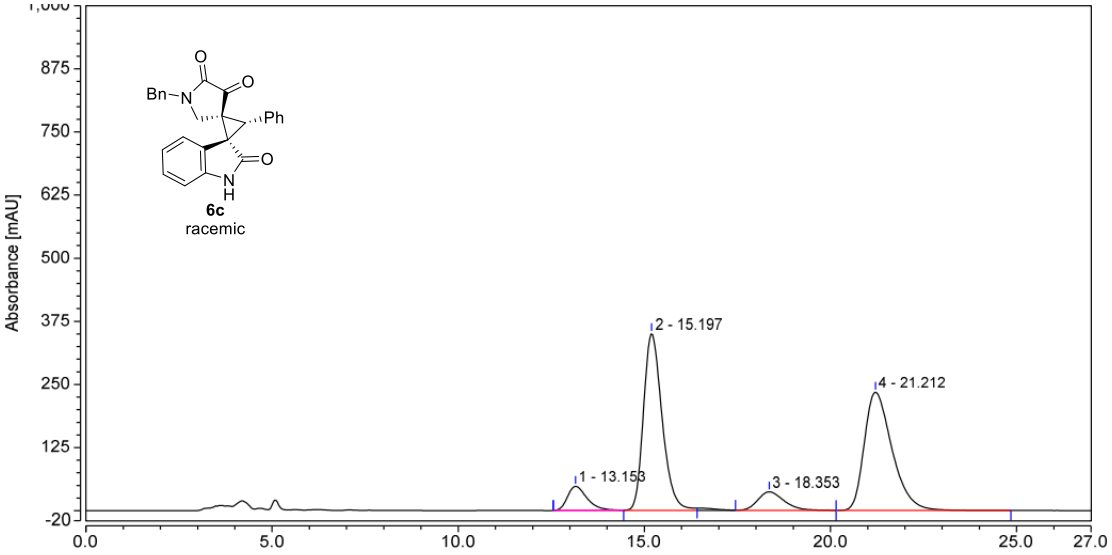
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.033	12.547	21.604	39.84	54.85
2	12.878	12.693	14.430	40.31	36.63
3	21.222	3.314	2.240	10.52	5.69
4	26.738	2.937	1.117	9.33	2.83
Total		**31.491**	**39.390**	**100.00**	**100.00**

HPLC Spectrum of **6b**



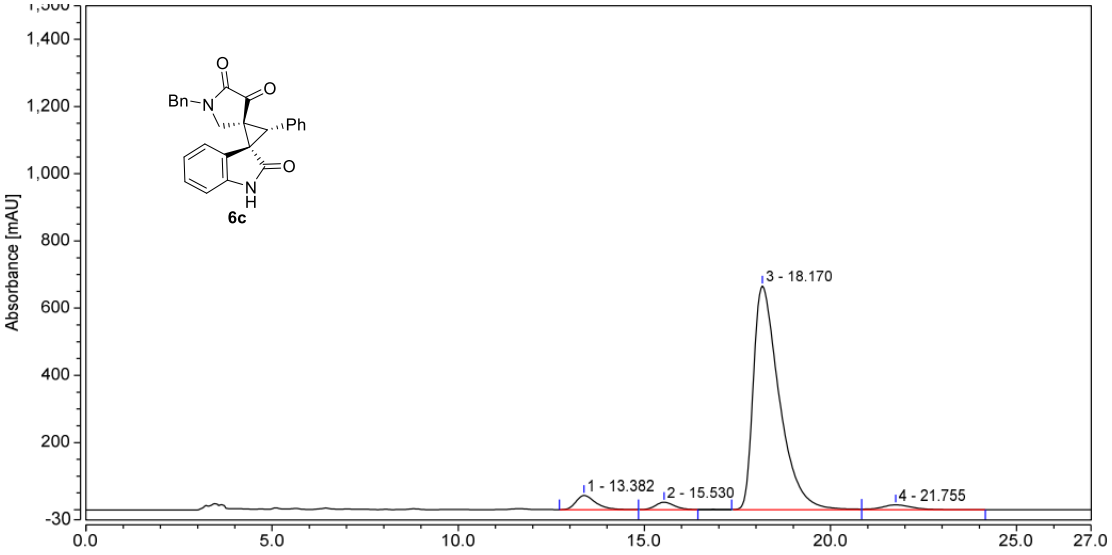
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.012	1.654	2.608	0.25	0.52
2	12.825	3.518	3.538	0.54	0.71
3	19.988	645.205	492.583	98.97	98.61
4	26.047	1.532	0.773	0.23	0.15
Total		**651.909**	**499.501**	**100.00**	**100.00**

HPLC Spectrum of **6c**



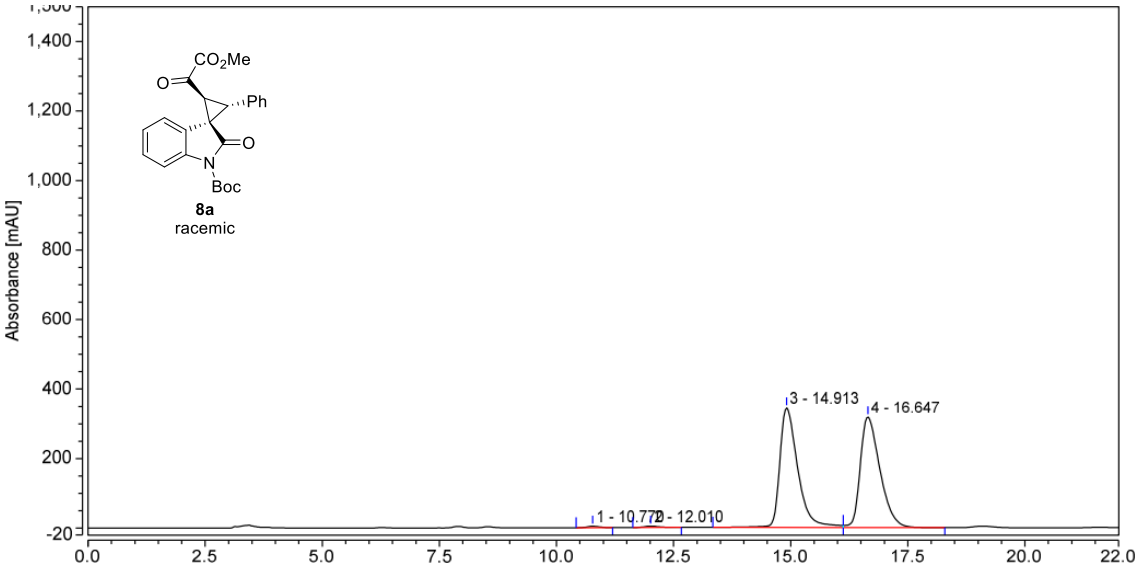
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.153	28.790	47.672	6.16	7.12
2	15.197	204.668	350.351	43.79	52.35
3	18.353	30.700	36.915	6.57	5.52
4	21.212	203.176	234.311	43.48	35.01
Total		**467.334**	**669.249**	**100.00**	**100.00**

HPLC Spectrum of **6c**



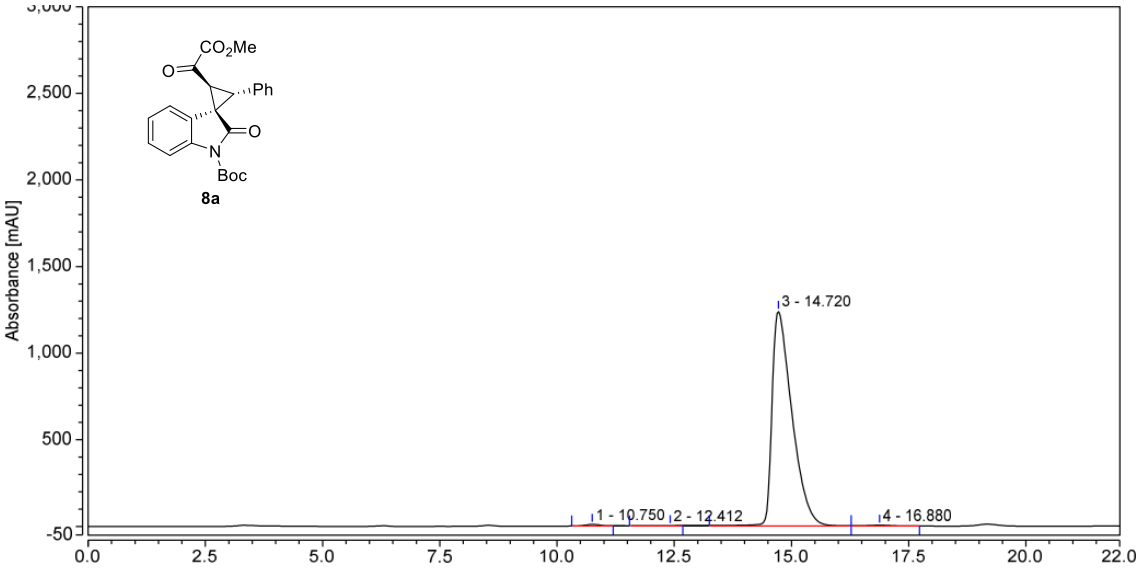
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	13.382	26.086	42.333	4.41	5.68
2	15.530	13.255	22.146	2.24	2.97
3	18.170	537.801	665.749	90.99	89.39
4	21.755	13.913	14.563	2.35	1.96
Total		**591.055**	**744.790**	**100.00**	**100.00**

HPLC Spectrum of **8a**



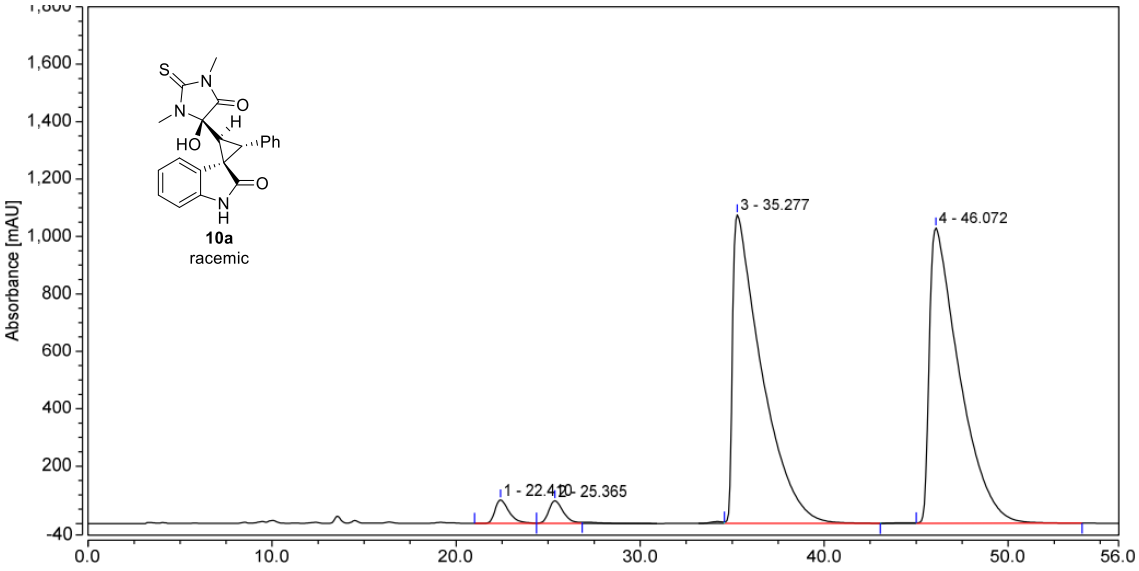
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.770	1.197	4.022	0.39	0.60
2	12.010	1.341	3.837	0.43	0.57
3	14.913	153.076	343.861	49.35	51.32
4	16.647	154.566	318.265	49.83	47.50
Total:		**310.180**	**669.986**	**100.00**	**100.00**

HPLC Spectrum of **8a**



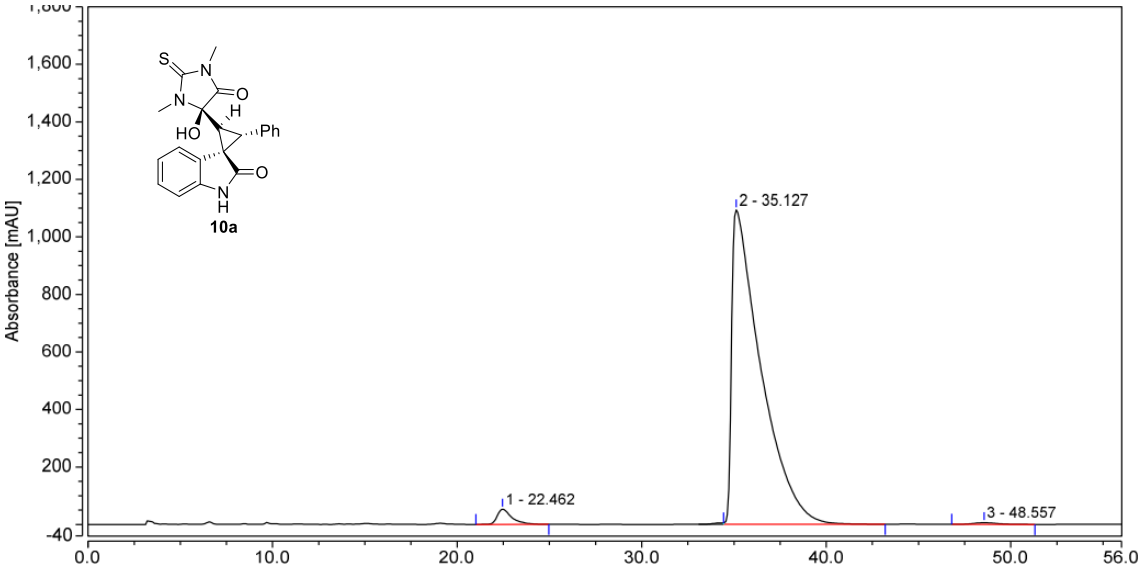
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	10.750	3.846	10.117	0.62	0.80
2	12.412	2.460	2.751	0.39	0.22
3	14.720	614.123	1239.953	98.48	98.58
4	16.880	3.155	4.949	0.51	0.39
Total:		**623.585**	**1257.770**	**100.00**	**100.00**

HPLC Spectrum of **10a**



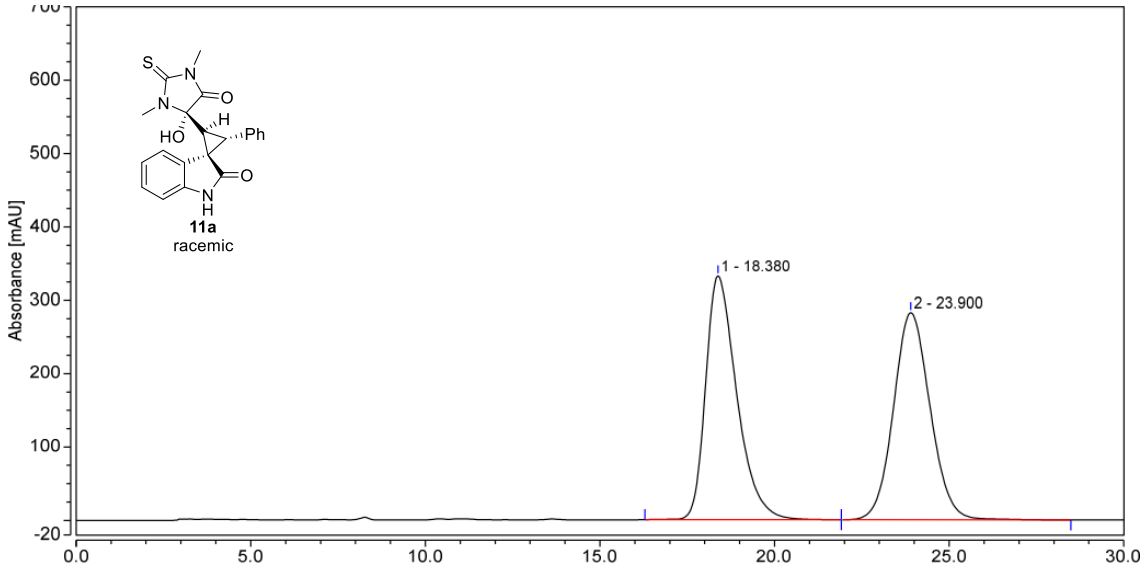
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.410	73.529	82.162	1.81	3.63
2	25.365	72.524	78.873	1.79	3.48
3	35.277	1962.879	1074.605	48.40	47.46
4	46.072	1946.301	1028.626	47.99	45.43
Total:		**4055.234**	**2264.266**	**100.00**	**100.00**

HPLC Spectrum of **10a**



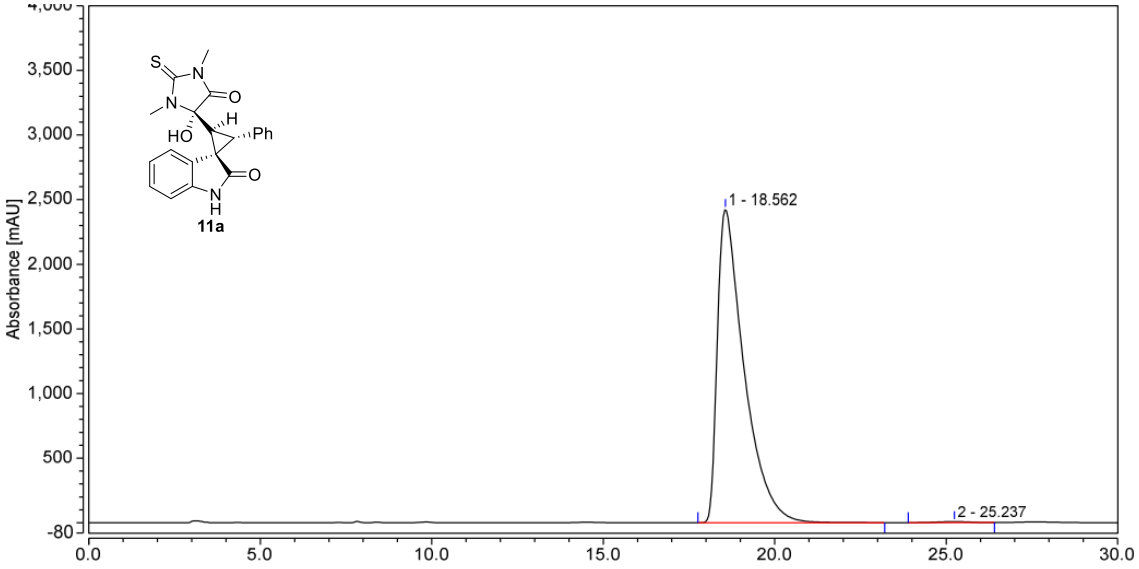
Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	22.462	47.871	52.658	2.32	4.57
2	35.127	2004.918	1093.469	97.27	94.93
3	48.557	8.426	5.753	0.41	0.50
Total:		**2061.215**	**1151.879**	**100.00**	**100.00**

HPLC Spectrum of **11a**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.380	343.193	332.392	49.92	54.07
2	23.900	344.254	282.318	50.08	45.93
Total:		**687.447**	**614.710**	**100.00**	**100.00**

HPLC Spectrum of **11a**



Peak	Retention Time min	Area mAU*min	Height mAU	Area %	Height %
1	18.562	2184.365	2423.788	99.62	99.68
2	25.237	8.405	7.840	0.38	0.32
Total:		**2192.770**	**2431.628**	**100.00**	**100.00**

Quantum chemical calculations

The exchange and correlation electronic effects were considered by employing the density functional theory (DFT)[11] with Gaussian 16 program[12]. The ultrafine grid (99,590), having 99 radial shells and 590 angular points per shell, was used to evaluate the numerical integration accuracy. Geometry optimizations were performed at M06-2X-D3[13] level of theory with the double-zeta basis set Def2-SVP[14]. The harmonic vibrational frequencies were analyzed after the geometry optimizations to characterize the nature of the stationary point as a minimum with all positive frequencies at the same theoretical level.

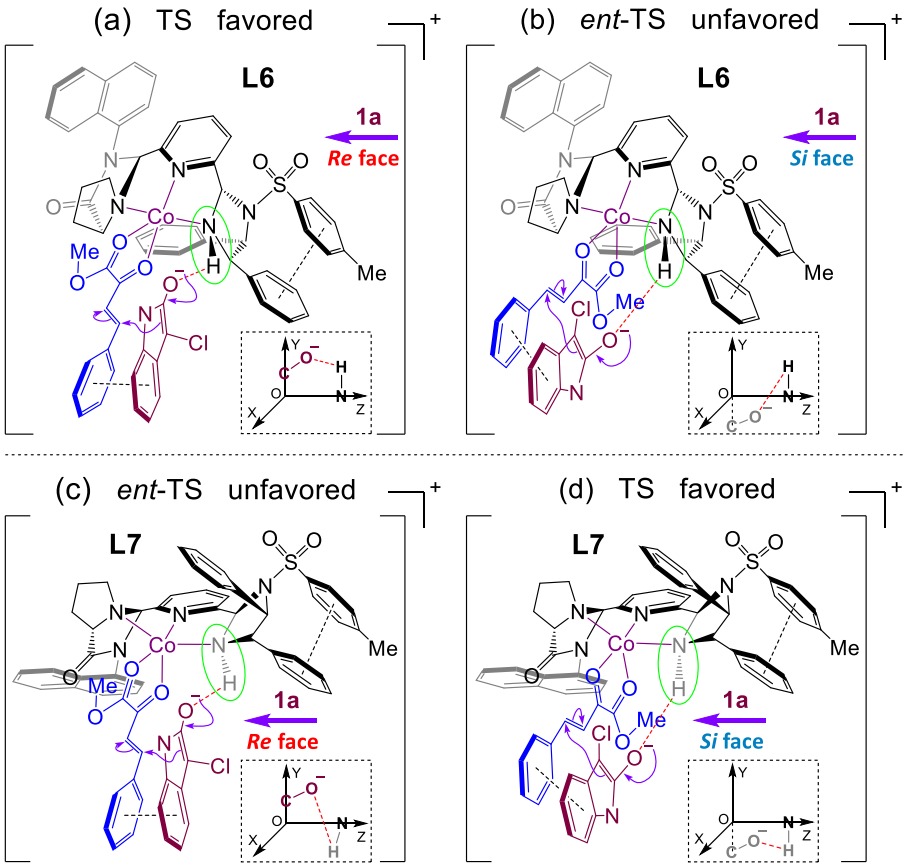


Figure S6. Proposed enantio-determining transition states for two chiral ligands.

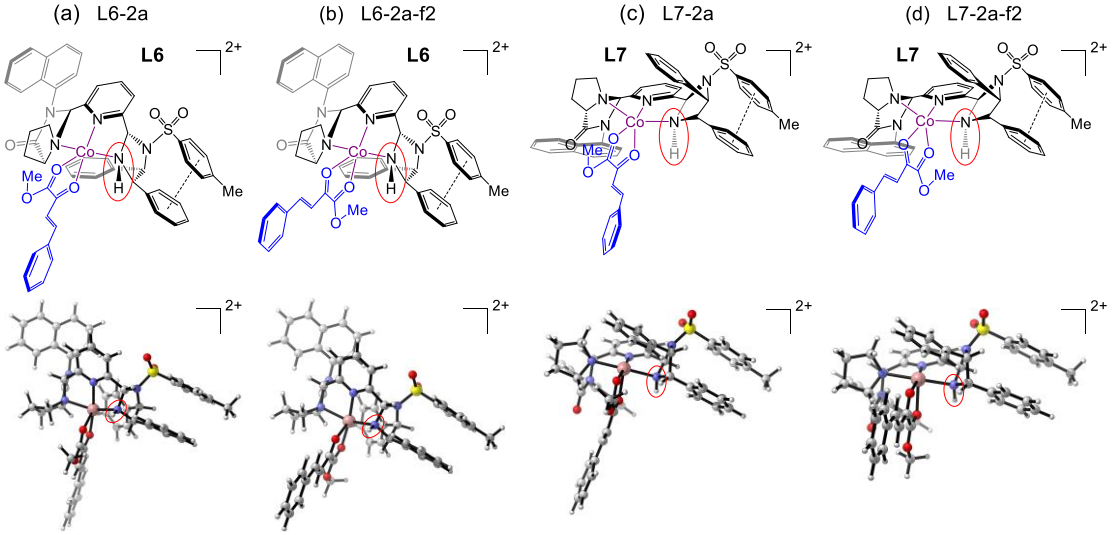


Figure S7. DFT-optimized structures of complexes between chiral ligands and substrate **2a** at the M06-2X-D3/Def2-SVP level.

Cartesian coordinate for DFT calculation

L6-2a

Co	0.43020800	0.44665500	0.76177600
C	-0.78696200	-2.15540200	1.52511200
C	-0.84350300	-3.45462000	2.01943300
C	0.35865900	-4.12087200	2.26171300
C	1.57245400	-3.48434300	2.00311000
C	1.53924900	-2.18439100	1.50793100
H	-1.80693300	-3.93719500	2.17649600
H	0.34750900	-5.14141200	2.64646100
H	2.52733900	-3.98698600	2.16613100
C	-2.00987600	-1.32308100	1.15950200
H	-2.87262400	-1.64815600	1.76523600
N	0.38393700	-1.55862800	1.29062700
N	-2.31424800	-1.37582300	-0.26536100
C	2.78927600	-1.42782700	1.10311400
H	3.60597900	-1.71941000	1.79146500
C	3.68022200	-0.60817400	-0.90894300
C	4.66025500	1.25101500	0.57075100
H	5.55533300	0.97582600	-0.00282900
H	4.56771100	2.34512600	0.53040900
C	-2.37242200	-0.05358700	-0.87121400
N	2.59024100	0.05125500	1.11651400
O	4.23291100	-0.58316100	-1.97215300
C	3.39552300	0.59638100	-0.02692100
H	2.80869700	1.31272700	-0.61845500
N	3.16235600	-1.71134600	-0.26958900
C	4.67730700	0.77093600	2.02566600
H	5.17306100	-0.20775300	2.11762300
C	3.18867600	0.65017400	2.33895000
H	2.75742700	1.65185500	2.47917000
H	2.93483700	0.04592500	3.22122200
H	5.19457400	1.46146600	2.70292600
H	-3.22968000	0.00916800	-1.55926600
C	-2.60050000	0.82844500	0.37659200
H	-2.20271100	1.84340500	0.21376800
N	-1.70725600	0.11656500	1.31396400
H	-1.81920400	0.42517700	2.28070000
S	-3.14286000	-2.68444400	-0.92759500
O	-2.61065100	-2.83499500	-2.26295500
O	-3.01461400	-3.70459500	0.09959600
C	-4.82590000	-2.17230900	-1.04109900
C	-5.30779100	-1.68357400	-2.25388800
C	-5.63805700	-2.25874200	0.09265500
C	-6.62984500	-1.24821600	-2.31980100
H	-4.66000800	-1.67149000	-3.13229400
C	-6.95208100	-1.82155000	0.00234000
H	-5.25135000	-2.69082000	1.01710700
C	-7.46677600	-1.30714700	-1.19928100
H	-7.02324400	-0.87087600	-3.26543700
H	-7.60151200	-1.88823900	0.87765000
C	-8.89876300	-0.85797800	-1.27371800
H	-9.16900900	-0.25741200	-0.39348900
H	-9.09121500	-0.26715900	-2.17762900
H	-9.57135500	-1.72880900	-1.29158400
C	-1.09744500	0.31881700	-1.61463600
C	-0.98142600	1.58435800	-2.20707300
C	-0.05779500	-0.60831500	-1.77891900
C	0.15650600	1.92084800	-2.93546700
H	-1.80017300	2.30409600	-2.11997900
C	1.08411700	-0.26660800	-2.51365000
H	-0.20014800	-1.62592500	-1.41177700
C	1.19835700	1.00096100	-3.08136600
H	0.21995700	2.89996400	-3.41356300
H	1.86624200	-1.00752300	-2.68543700
H	2.08774800	1.25075600	-3.66219200
C	-4.05590300	0.92088900	0.80554700
C	-4.48455700	0.60308000	2.09678800

C	-4.99347700	1.40730900	-0.11439100
C	-5.82192500	0.76771000	2.46386800
H	-3.78779400	0.22386400	2.84831900
C	-6.32590000	1.57464300	0.24986300
H	-4.68198400	1.67267300	-1.12824500
C	-6.74398900	1.25660000	1.54319300
H	-6.13878600	0.51648400	3.47681900
H	-7.04132400	1.95777000	-0.47941600
H	-7.78704900	1.39306000	1.83226700
C	7.12436100	-4.94343500	-0.00013100
C	6.10127600	-5.63561400	-0.59951000
C	4.84657400	-5.01306600	-0.84358800
C	4.66384400	-3.65303500	-0.45555100
C	5.74301900	-2.95868700	0.15560000
C	6.94267400	-3.59038200	0.37851700
H	3.93415200	-6.75057800	-1.76432700
H	8.08370000	-5.42942300	0.17942600
H	6.23804800	-6.67512700	-0.90254500
C	3.77640800	-5.71201700	-1.46789200
C	3.39284300	-3.05363400	-0.70535700
H	5.62601800	-1.90718200	0.42726400
H	7.76790500	-3.04649200	0.83971200
C	2.37655000	-3.75413000	-1.31112200
C	2.56954000	-5.10000800	-1.70166200
H	1.41603300	-3.26371100	-1.48128000
H	1.75770300	-5.64127200	-2.18720700
C	2.36848800	8.67098300	-0.79424400
C	1.97474500	7.44946900	-0.27612100
C	1.97292700	6.29831800	-1.09781600
C	2.37623700	6.41344400	-2.44673700
C	2.77130800	7.63996400	-2.96135100
C	2.76675400	8.76644600	-2.13502500
H	2.36933000	9.55920100	-0.16229100
H	1.66433200	7.38240000	0.76730400
H	2.37760600	5.52591100	-3.08310600
H	3.08338400	7.72514500	-4.00224000
H	3.07642100	9.73255200	-2.53692100
C	1.57653800	5.00658900	-0.61614800
C	1.17559400	4.67282100	0.65533400
H	1.59728500	4.18720300	-1.34468300
H	1.11741700	5.39489600	1.46829100
C	0.82496100	3.32787600	0.93651200
O	0.82230200	2.38020300	0.13061300
C	0.41103200	2.92093600	2.35752900
O	0.20649900	1.73991400	2.58617600
O	0.32058400	3.88100200	3.21794200
C	-0.05660100	3.55251500	4.56982700
H	-1.07339300	3.14211500	4.57277300
H	-0.01449000	4.49132400	5.12591300
H	0.64824400	2.81843300	4.97753000

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Co	-0.33068700	0.74002500	0.41673900
C	-0.02700300	-1.06859300	-1.91512700
C	-0.37115100	-1.69813400	-3.10699000
C	-1.68991300	-1.59234200	-3.55167000
C	-2.62322500	-0.87598800	-2.80257400
C	-2.19604900	-0.27759300	-1.62109600
H	0.37010600	-2.28322800	-3.64919100
H	-1.99154900	-2.07799000	-4.48055900
H	-3.66547600	-0.79399900	-3.11574200
C	1.35095800	-1.14752700	-1.26866000
H	2.11556400	-1.32065800	-2.04471500
N	-0.93135200	-0.37847700	-1.21658000
N	1.41517000	-2.16549300	-0.22667800
C	-3.14001900	0.44374100	-0.67837900
H	-3.91129200	0.95242700	-1.28844000
C	-3.94145100	0.09076600	1.49994400
C	-4.00050600	2.65495000	1.63455200

H	-4.99697200	2.42265200	2.03325600
H	-3.53052200	3.36954600	2.32466500
C	1.85522800	-1.62618100	1.05181500
N	-2.43520200	1.42386600	0.20127100
O	-4.58742000	-0.35068100	2.40750700
C	-3.13577100	1.38012100	1.52791100
H	-2.41652700	1.30387500	2.35553200
N	-3.76258800	-0.47280300	0.25737200
C	-4.00959700	3.21845600	0.21007200
H	-4.80266000	2.75466100	-0.39661500
C	-2.63158300	2.81047800	-0.30206800
H	-1.86200300	3.45598300	0.14438900
H	-2.50000800	2.83932200	-1.39277600
H	-4.16665200	4.30342100	0.17507100
H	2.57031800	-2.31550900	1.52669700
C	2.55924200	-0.33112300	0.59144000
H	2.53857300	0.43002100	1.38818300
N	1.60844900	0.06804700	-0.46638000
H	1.94957500	0.84052300	-1.04045800
S	1.60761900	-3.79345200	-0.61180800
O	0.87088600	-4.51405900	0.40211300
O	1.26577400	-3.83652000	-2.02377600
C	3.32631200	-4.13104900	-0.41324900
C	3.77476700	-4.70427900	0.77505100
C	4.20322300	-3.80852800	-1.45219300
C	5.14031200	-4.93414600	0.93093600
H	3.05811000	-4.98622400	1.54854200
C	5.55847100	-4.04908600	-1.27512000
H	3.82112100	-3.40620800	-2.39183300
C	6.04827400	-4.60980400	-0.08385500
H	5.50497900	-5.39031400	1.85304900
H	6.25609900	-3.80890800	-2.08007500
C	7.51855800	-4.87685100	0.07398400
H	8.11399500	-4.02323100	-0.27998600
H	7.78246300	-5.08321000	1.11845900
H	7.81437200	-5.75035900	-0.52644400
C	0.70561500	-1.35182300	2.01128300
C	0.96442500	-0.77333600	3.26276600
C	-0.60345500	-1.75061300	1.70358700
C	-0.06623900	-0.58189900	4.17925200
H	1.98811900	-0.49881600	3.53347700
C	-1.63538900	-1.56483700	2.63118200
H	-0.77981300	-2.29919400	0.77714300
C	-1.37157500	-0.96868100	3.86270600
H	0.15162600	-0.15370500	5.15908100
H	-2.63984700	-1.92929600	2.41145800
H	-2.18159800	-0.83810900	4.58207900
C	3.99339300	-0.54515600	0.13501700
C	4.45549000	-0.13457300	-1.11779100
C	4.90166300	-1.12258900	1.03158400
C	5.79689500	-0.29726700	-1.47033400
H	3.78347300	0.32635500	-1.84566300
C	6.23934400	-1.28276800	0.68369700
H	4.56828500	-1.44348900	2.02211000
C	6.69165700	-0.86828800	-0.57015800
H	6.14096300	0.03092700	-2.45188800
H	6.93272600	-1.73226300	1.39621400
H	7.74129200	-0.98806500	-0.84233300
C	-8.52771500	-1.22130600	-1.46493600
C	-7.88923700	-2.43344800	-1.55455700
C	-6.53890600	-2.57745700	-1.13344100
C	-5.85274800	-1.44008900	-0.61438800
C	-6.54130000	-0.19981300	-0.52552200
C	-7.84633900	-0.09451600	-0.94232600
H	-6.40377700	-4.68845400	-1.60727300
H	-9.56462400	-1.12270800	-1.78722200
H	-8.41181300	-3.30771200	-1.94659900
C	-5.86252100	-3.82635000	-1.21333000
C	-4.49582700	-1.60996400	-0.20555100

H	-6.03715800	0.66985000	-0.09817400
H	-8.36942100	0.85905400	-0.86090000
C	-3.86802400	-2.83006700	-0.29381800
C	-4.55921800	-3.95530400	-0.80060200
H	-2.82750700	-2.92079100	0.02395700
H	-4.05124800	-4.91781400	-0.85833400
C	2.91233600	8.73094500	-0.79197500
C	2.41064300	7.51692400	-0.35534500
C	2.06030900	6.51660600	-1.29120200
C	2.22947800	6.77315600	-2.66939100
C	2.73175600	7.99224900	-3.10251000
C	3.07237300	8.96908100	-2.16402000
H	3.18346800	9.50223900	-0.07092700
H	2.29031100	7.33855100	0.71388600
H	1.95971700	6.00286100	-3.39481600
H	2.85982000	8.18721500	-4.16725700
H	3.46783100	9.92849400	-2.50145300
C	1.53457600	5.23946800	-0.89749800
C	1.27403800	4.80053600	0.37626600
H	1.31042500	4.53707400	-1.70830100
H	1.44562300	5.41647400	1.25783700
C	0.74411900	3.49684600	0.57611900
O	0.49450400	2.63893300	-0.28327600
C	0.39820400	3.03792200	2.00138800
O	-0.04849100	1.90934800	2.16016800
O	0.60215300	3.88595700	2.95066700
C	0.29009600	3.48161000	4.30049900
H	-0.78012900	3.25268400	4.37198800
H	0.55469300	4.33139400	4.93295900
H	0.88104900	2.59449000	4.55638200

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C	1.09650200	-2.50212900	0.75139900
C	1.07124400	-3.81016400	0.28281100
C	-0.03811800	-4.21721900	-0.46021200
C	-1.07220500	-3.31837100	-0.71796400
C	-0.98140800	-2.03476000	-0.18493700
H	1.91360500	-4.47993400	0.46447900
H	-0.09008800	-5.23350400	-0.85253000
H	-1.94875800	-3.61317500	-1.29222600
C	2.32916900	-1.86946700	1.36413500
H	2.89041400	-2.64420400	1.91761300
C	3.66699800	-0.04647600	0.70458000
C	4.20089000	-0.23410000	3.22626600
H	5.11184400	-0.65838700	2.78322100
H	4.51027800	0.64392100	3.80526800
N	0.07965100	-1.66913000	0.53434800
N	2.01178000	-0.71221500	2.24944800
C	-2.03692100	-0.95110400	-0.38149500
H	-2.49872100	-1.08959700	-1.37708300
O	4.36420100	0.68247600	0.05033400
C	3.18798300	0.18664200	2.12845200
H	2.89301700	1.23661300	2.25361400
N	-1.42573200	0.38713600	-0.21921300
C	-2.50113100	1.30492200	0.20319700
H	-2.04155900	2.17339600	0.70093300
N	3.15168500	-1.26042900	0.32614700
N	-3.06156300	-0.92033300	0.65395000
C	3.44628700	-1.26202600	4.09451700
H	3.80212600	-2.28230500	3.89546900
C	1.97951900	-1.10458100	3.67992100
H	1.50038000	-0.28450400	4.23298600
H	1.36834600	-2.00900800	3.80907000
Co	0.15807700	0.22153200	1.36774300
C	5.56762700	-4.72549700	-0.30146600
C	4.84054500	-3.57875000	-0.08852500
C	4.09186300	-2.99385700	-1.14641200
C	4.12535800	-3.59698200	-2.43838900
C	4.88768300	-4.78326400	-2.62298200

C	5.58573500	-5.33900800	-1.57923900
H	6.14891000	-5.16179200	0.51182100
H	4.86240400	-3.09018700	0.88758900
C	3.29356400	-1.82605100	-0.97552100
C	3.40758500	-2.99533200	-3.50854000
H	4.91241500	-5.24262600	-3.61275400
H	6.16867100	-6.24769100	-1.73207200
C	2.67536900	-1.84902100	-3.31414100
C	2.60576400	-1.26512500	-2.02711000
H	3.45240200	-3.46138000	-4.49455200
H	2.13613100	-1.39394000	-4.14537400
H	2.00186400	-0.37394000	-1.83970800
H	-0.95120400	0.69770000	-1.06964900
C	-3.42599500	1.81535200	-0.88549900
C	-4.38091100	2.77359600	-0.52046900
C	-3.34349400	1.42108200	-2.22185800
C	-5.23009200	3.33112600	-1.47016100
H	-4.45226800	3.10057500	0.52100900
C	-4.20021700	1.97454300	-3.17665300
H	-2.60453400	0.68747400	-2.55125800
C	-5.13892500	2.93263500	-2.80531500
H	-5.95927900	4.08519200	-1.17127500
H	-4.12465800	1.65559200	-4.21723000
H	-5.79548600	3.37615600	-3.55517200
C	-3.18856500	0.40216500	1.25449700
H	-4.24804900	0.66902200	1.37782800
C	-2.49272900	0.49641400	2.60279600
C	-2.58748000	1.68704700	3.33552800
C	-1.78797600	-0.58651700	3.14584700
C	-1.98809000	1.80010300	4.58487800
H	-3.16613500	2.52370300	2.93388600
C	-1.19129200	-0.46859000	4.40980900
H	-1.81200200	-1.54968200	2.63069600
C	-1.28091500	0.72197600	5.12449900
H	-2.09489800	2.72232500	5.15835500
H	-0.70191500	-1.33505800	4.85596200
H	-0.83783900	0.80016500	6.11823200
S	-4.40496700	-1.93829800	0.52893200
O	-3.82915900	-3.21637300	0.15565700
O	-5.13203000	-1.71034700	1.75528300
C	-5.33971900	-1.33211200	-0.83896300
C	-6.26821800	-0.31015500	-0.62731800
C	-5.12568700	-1.87193800	-2.10698800
C	-6.96431000	0.19356700	-1.71826400
H	-6.46286000	0.05571000	0.38249300
C	-5.83654500	-1.35321900	-3.18609000
H	-4.44072200	-2.71117600	-2.23564700
C	-6.75847700	-0.31405100	-3.01086100
H	-7.69619300	0.98948600	-1.56592500
H	-5.68644700	-1.77567500	-4.18134100
C	-7.54321700	0.23014400	-4.17064400
H	-8.56721400	-0.17322700	-4.16003100
H	-7.62451700	1.32441500	-4.11272600
H	-7.08721900	-0.04140000	-5.13081900
H	3.57877000	-1.08668900	5.16882100
C	5.56915900	5.56770700	-2.68293400
C	4.54742900	4.96943000	-1.96600500
C	4.31429500	3.58094200	-2.09317100
C	5.13448400	2.81453800	-2.95008800
C	6.16404000	3.41808300	-3.65815700
C	6.37762700	4.79226200	-3.52592000
H	5.74668800	6.63957200	-2.59438500
H	3.91564900	5.57631900	-1.31591300
H	4.96102000	1.73918400	-3.02905300
H	6.80288500	2.82522500	-4.31269700
H	7.18367300	5.26979800	-4.08545600
C	3.28448500	2.89719000	-1.36982400
C	2.50107600	3.39718200	-0.35256100
H	3.13748100	1.84412000	-1.62460400

H	2.60760600	4.40924000	0.03502500
C	1.61052500	2.52125300	0.30460200
O	1.31881600	1.35177900	-0.01620900
C	0.94930200	2.95783900	1.61855300
O	0.32075300	2.12527900	2.26471100
O	1.10926900	4.18658400	1.97354600
C	0.50605900	4.62024400	3.20924400
H	0.74987700	5.68055700	3.30190100
H	-0.57795700	4.46398200	3.15625900
H	0.92673100	4.04194500	4.04050500

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C	-0.76816400	-2.69233000	-1.21730000
C	-0.31851200	-3.97165500	-1.52076200
C	1.04664900	-4.23339300	-1.39175200
C	1.91043400	-3.22824600	-0.95975100
C	1.38030500	-1.96714900	-0.69954300
H	-1.02371100	-4.75018400	-1.81700900
H	1.43586800	-5.22753200	-1.61451300
H	2.97937400	-3.40597200	-0.85438400
C	-2.23583200	-2.33285000	-1.11251000
H	-2.80877700	-2.94052900	-1.83628000
C	-3.54777100	-1.52880400	0.66617900
C	-4.91461500	-0.94605500	-1.44313600
H	-5.38905800	-1.88663700	-1.13110100
H	-5.67907500	-0.16479400	-1.36387900
N	0.07666400	-1.73076900	-0.84530000
N	-2.48506100	-0.88087000	-1.32322500
C	2.20102200	-0.77855600	-0.21273800
H	3.04304500	-1.15862500	0.39511500
O	-4.04111800	-1.38360900	1.75381000
C	-3.70676400	-0.60750300	-0.53086000
H	-3.74205700	0.44234800	-0.21373000
N	1.33506000	0.15698600	0.53704100
C	1.96473800	1.48861900	0.45232500
H	1.19347700	2.24946500	0.65119300
N	-2.71684800	-2.53775300	0.25134300
N	2.68846700	0.08862000	-1.27666000
C	-4.32227200	-1.05254000	-2.86657900
H	-4.36200300	-2.08748500	-3.23225800
C	-2.87093200	-0.57396400	-2.72090400
H	-2.80409700	0.51597800	-2.83938800
H	-2.16259000	-1.04048900	-3.42034800
Co	-0.66573200	0.17064000	-0.48638700
C	-3.97362100	-6.53867900	-0.55135300
C	-3.62891400	-5.23776300	-0.27157400
C	-2.69033500	-4.94515300	0.75584200
C	-2.13413500	-6.01792300	1.51317600
C	-2.51178800	-7.35173600	1.19592200
C	-3.40284800	-7.60799600	0.18309600
H	-4.70439100	-6.75334900	-1.33211400
H	-4.10582700	-4.41883200	-0.81336700
C	-2.26833700	-3.61962500	1.06747400
C	-1.22983800	-5.73000100	2.57213300
H	-2.08506000	-8.17024200	1.77832200
H	-3.68779200	-8.63435000	-0.04980100
C	-0.87764000	-4.43602100	2.86935600
C	-1.39140100	-3.36786700	2.09687300
H	-0.82443900	-6.56029400	3.15315100
H	-0.19389500	-4.22853500	3.69281100
H	-1.10361600	-2.33409800	2.29850700
H	1.18263600	-0.15012000	1.49973300
C	3.14018800	1.74571300	1.37644000
C	3.68068500	3.03849800	1.38310500
C	3.67359600	0.78811000	2.24069400
C	4.72663600	3.36920800	2.23780100
H	3.26718000	3.80378200	0.71983000
C	4.72961800	1.11584200	3.09481600
H	3.27207100	-0.22678400	2.27924800

C	5.25367100	2.40509000	3.09947100
H	5.12686400	4.38384600	2.23937900
H	5.13693600	0.35607700	3.76344800
H	6.06717000	2.66336200	3.77886100
C	2.32738400	1.48373400	-1.05093100
H	3.18485400	2.14114500	-1.25541300
C	1.15274500	1.92395900	-1.91048700
C	0.70219200	3.24828800	-1.81909400
C	0.54727100	1.05688200	-2.83039100
C	-0.32736700	3.70328200	-2.63450200
H	1.18761400	3.93955300	-1.12499700
C	-0.48756200	1.52409900	-3.65342300
H	0.96488400	0.05768600	-2.97553600
C	-0.92944600	2.83968600	-3.55396500
H	-0.64323100	4.74622900	-2.57571100
H	-0.91032500	0.86409100	-4.41178300
H	-1.71518100	3.20486400	-4.21678200
S	4.11764000	-0.30975800	-2.08557300
O	3.97825400	-1.73127400	-2.33966700
O	4.22059500	0.68740500	-3.12507500
C	5.40962700	-0.08000600	-0.90719700
C	5.96296500	1.19212500	-0.74516200
C	5.83565700	-1.16409400	-0.13981600
C	6.93520700	1.37635600	0.22948400
H	5.65721700	2.01210400	-1.39760100
C	6.81412300	-0.95723200	0.82861500
H	5.43083700	-2.15949400	-0.32787300
C	7.37201000	0.31111500	1.03231200
H	7.37814100	2.36520300	0.36446900
H	7.16437500	-1.80013400	1.42731600
C	8.44457900	0.52813100	2.06170000
H	8.44027500	-0.26246500	2.82257100
H	9.43612100	0.52551900	1.58365000
H	8.32513800	1.50069600	2.55832000
H	-4.86647900	-0.44095400	-3.59598600
C	-5.37879600	6.98525000	1.76639800
C	-4.65885600	5.80629900	1.67391500
C	-3.95860900	5.49497100	0.48571000
C	-4.00483700	6.39914700	-0.59796900
C	-4.72744200	7.57974200	-0.50079900
C	-5.41323500	7.87116200	0.68089300
H	-5.91915600	7.22590300	2.68203900
H	-4.63660400	5.12142700	2.52243900
H	-3.46634500	6.16017600	-1.51748400
H	-4.76101900	8.27527100	-1.33938400
H	-5.98266600	8.79857600	0.76072700
C	-3.19708600	4.28791500	0.33095800
C	-3.02737000	3.28221200	1.25029800
H	-2.69188400	4.14902600	-0.63229900
H	-3.47687500	3.29949800	2.24195200
C	-2.23602900	2.15653500	0.90580800
O	-1.65632700	1.96277400	-0.17993100
C	-2.04585200	1.01744500	1.92068800
O	-1.35248200	0.06555000	1.58491800
O	-2.62875500	1.16536000	3.05563500
C	-2.52109600	0.10425500	4.03445400
H	-3.06363400	0.46358000	4.91117100
H	-2.98314600	-0.79881800	3.61797100
H	-1.46196400	-0.05816200	4.26787500

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