Supporting Information

Asymmetric Oxidative Rearrangement of Indoles Enabled by Dual Catalysis with In Situ Generated Acyl Hypoiodite and Chiral Phosphoric Acid

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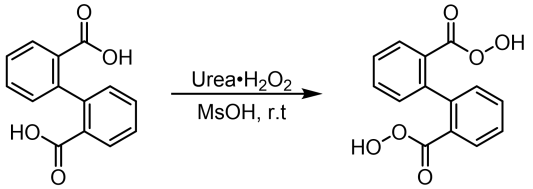
1. General Methods and Materials

All reactions were carried out directly under open air. Commercially available reagents, starting materials and solvents were used without further purification. All reactions were monitored by TLC and visualized by UV lamp (254 nm) or by staining with a solution of 10 g phosphomolybdic acid and 100 mL EtOH followed by heating. Flash column chromatography was performed using 200-300 mesh silica gel. ^{1}H NMR (400 MHz), ^{13}C NMR (101 MHz) and ^{19}F NMR (376 MHz) spectra were obtained on Zhongke-Niujin (Quantum-I Plus 400M). HR-ESI-MS spectra were recorded on a Bruker Esquire LC mass spectrometer and Thermo Scientific LTQ Orbitrap XL using electrospray ionization. Coupling constants are reported in Hertz (Hz). The enantiomeric excesses were determined by HPLC analysis using an Agilent 1260 Infinity II LC system (column Daicel Co. CHIRALCEL; eluent: *n*-hexane/*i*-PrOH). Data for ^{1}H NMR, ^{13}C NMR and ^{19}F NMR spectra were reported as follows: chemical shift (ppm, referenced to protium; s = singlet, br= broad peak, d = doublet, t = triplet, q = quartet, p = quintet, dd = doublet of doublets, td = triplet of doublets, m = multiplet, coupling constant (Hz),

2. General procedure for the preparation of the 2,2'-Diperoxyphenic Acid



Methane sulfonic acid (30 mL) was placed in a round bottom flask equipped with a large magnetic stirrer bar at room temperature. Urea hydrogen peroxide (3.0 eq.) was added in a single portion and stirred for 30 seconds. Diphenic acid (1.0 eq.) was added in a single portion and the reaction stirred vigorously for 24 h. Upon completion, the reaction mixture was poured into a mixture of ice and ethyl acetate. The layers were separated, then the aqueous layer was extracted with ethyl acetate and the combined organics were washed with $NaHCO_3$, brine and dried over Na_2SO_4. Removal of the solvent under reduced pressure to gave 2,2'-diperoxyphenic acid as a pale yellow soild.

^{1}H NMR (400 MHz, $CDCl_3$) δ 11.28 (s, 2H), 8.03 (dd, J = 7.9, 1.3 Hz, 2H), 7.70 (td, J = 7.6, 1.4 Hz, 2H), 7.58 (td, J = 7.7, 1.3 Hz, 2H), 7.32 (dd, J = 7.7, 1.3 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 168.3, 142.1, 133.3, 130.9, 129.9, 128.39, 124.69.

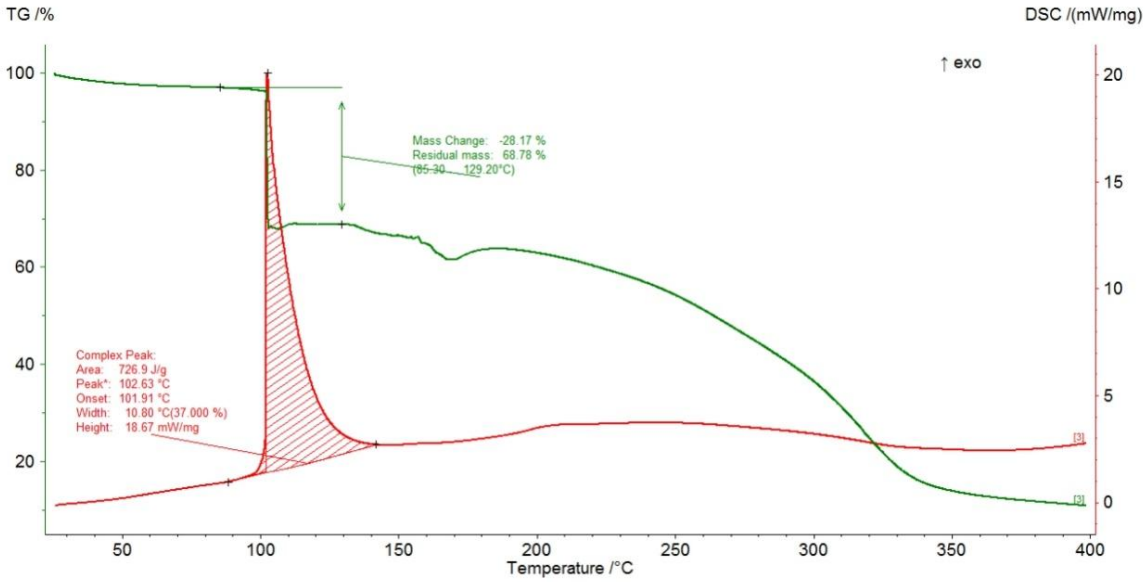
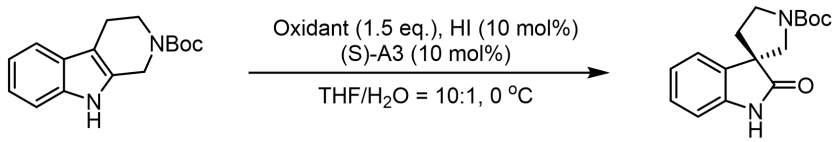


Figure S1. TGA and DSC measurement of 2,2'-DPPA

3. Condition Optimization

3.1. Condition Optimization of 1a

Table S1. Screening of oxidant



1a **2a**

Entry[a]	Oxidant	Yield[b]	*ee*[c]
1	MPO	92%	2%
2	*m*-CPBA	60%	92%
3	2,2'-DPPA (0.7 eq.)	91%	96%
4[d]	2,2'-DPPA (0.7 eq.)	N.P	-
5	H_2O_2	N.R	-
6	BPO	trace	-
7	TBHP (70% wt in water)	N.R	-
8	LPO	N.R	-
9	Oxone	43%	35%
10[d]	Oxone	＜20%	48%

[a] Reaction condition: 1a (0.05 mmol), (S)-A3 (10 mol%), Oxidant (1.5 equiv), solvent (0.5 mL), 0 °C. [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase. [d] NaI (10 mol%) instead of HI (10 mol%).

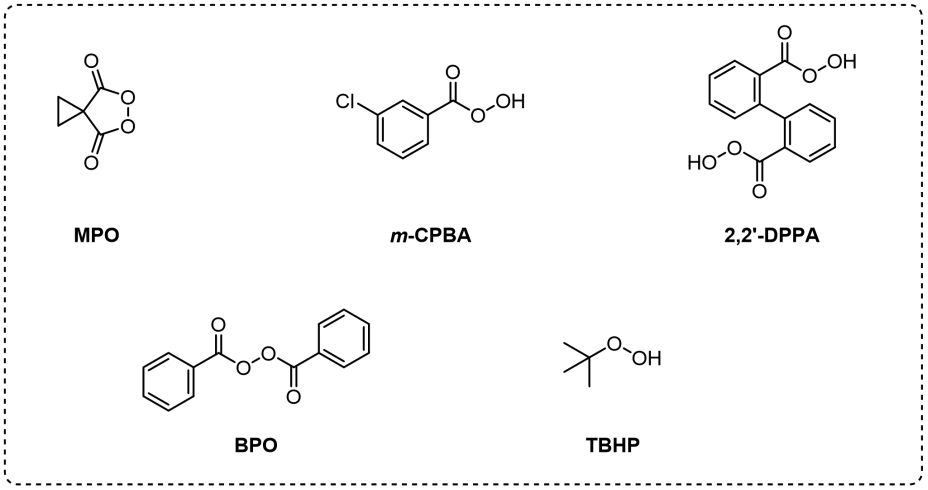
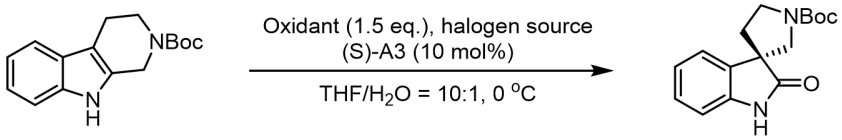


Table S2. Screening of halogen source and loading

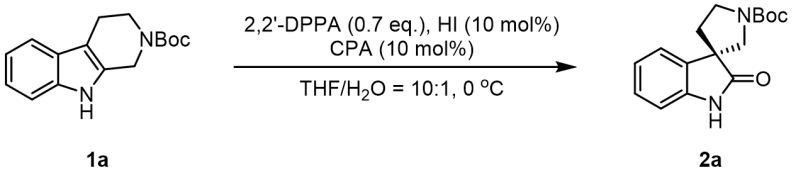


1a **2a**

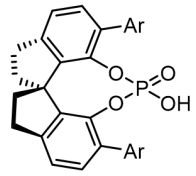
Entry[a]	Oxidant	Halogen Source	Yield[b]	*ee*[c]
1	MPO	LiI (1.5 eq.)	85%	24%
2	MPO	NaI (1.5 eq.)	91%	15%
3	MPO	KI (1.5 eq.)	trace	-
4	MPO	CsI (1.5 eq.)	trace	-
5	MPO	TBAI (1.5 eq.)	63%	20%
6	MPO	HI (1.5 eq.)	90%	12%
7	MPO	HI (10 mol%)	92%	2%
8	*m*-CPBA	HI (1.5 eq.)	63%	86%
9	*m*-CPBA	HI (10 mol%)	60%	92%
10	2,2'-DPPA (0.7 eq.)	HI (1.5 eq.)	89%	91%
11	2,2'-DPPA (0.7 eq.)	HI (10 mol%)	84%	96%
12	2,2'-DPPA (0.7 eq.)	I_2 (1.4 eq.)	82%	83%
13	2,2'-DPPA (0.7 eq.)	HBr (10 mol%)	75%	60%
14	-	I_2 (1.4 eq.)	51%	43%
15	*m*-CPBA/2,2'-DPPA	NaI (10 mol%/1.5 eq.)	N.P	-

[a] Reaction condition: 1a (0.05 mmol), (S)-A3 (10 mol%), Oxidant (1.5 equiv), solvent (0.5 mL), 0 °C. [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase.

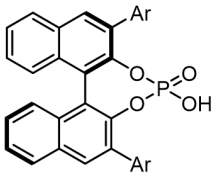
Table S3. Screening of catalysts



1a **2a**



A1: Ar = 2-napthyl
A2: Ar = 9-phenanthrenyl
A3: Ar = 1-pyrenyl
A4: Ar = 2,4,6-^{i}PrC$_6$H$_2$

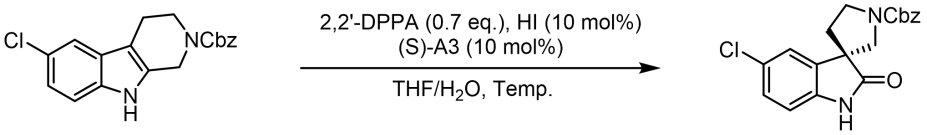


B1: Ar = 1-pryenyl

Entry[a]	Catalyst	Solvent	Yield[b]	*ee*[c]
1	(S)-A1	THF	90%	61%
2	(S)-A2	THF	88%	82%
3	(S)-A3	THF	91%	96%
4[d]	(S)-A4	THF	83%	58%
5	(R)-B1	THF	89%	64%
6	(S)-A3	2-Me-THF	90%	91%
7	(S)-A3	1,4-dioxane	87%	92%
8	(S)-A3	PhMe	25%	60%
9	(S)-A3	acetone	62%	62%
10	(S)-A3	MeCN	79%	40%

[a] Reaction condition: **1a** (0.05 mmol), CPA (10 mol%), 2,2'-DPPA (0.7 eq.), THF (0.5 mL), 0 °C. [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase.

Table S4. Screening of temperature

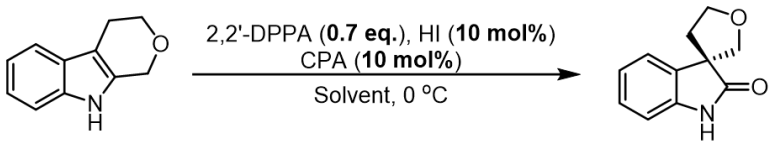


1j **2j**

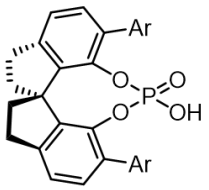
Entry[a]	Temp.	Yield[b]	*ee*[c]
1	r.t (23 °C)	87%	89%
2	0 °C	85%	93%
3	-20 °C	87%	96%
4	-45 °C	60%	57%

[a] Reaction condition: **1j** (0.1 mmol), (S)-A3 (10 mol%), 2,2'-DPPA (0.7 eq.), THF (1.0 mL), H_2O (20 μL). [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase.

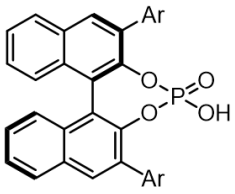
3.2. Condition Optimization of 3a



3a **4a**



A2: Ar = 9-phenanthryl
A3: Ar = 1-pyrenyl
A5: Ar = 1,3-dimethyphenanthren-9-yl

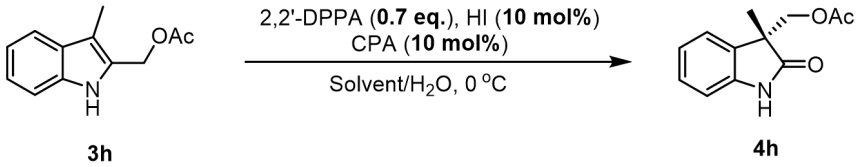


B2: Ar = 1,3-dimethyphenanthren-9-yl
B3: Ar = 9-phenanthryl

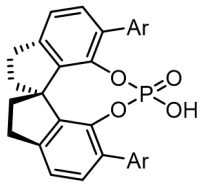
Entry[a]	Catalyst	Solvent	*ee*[c](%)
1	(S)-A2	THF	57
2	(S)-A3	THF	56
3	(R)-B2	THF	67
4	(R)-B3	THF	64
5	(R)-B2	TBME	71
6	(R)-B2	MeCN	60
7	(R)-B2	PhMe	trace,-
8	(R)-B3	1,4-dioxane	74
9	(R)-B2	1,4-dioxane	77
10	(R)-B2	1,4-dioxane:TBME = 1:1	76
11	(R)-B2	DCE:1,4-dioxane = 1:1	77
12	(R)-B2	DCE:1,4-dioxane:TBME = 1:1:1	79
13	(R)-B2	DCE:1,4-dioxane:TBME = 1:1:1	90
14	(R)-B2	DCE:1,4-dioxane:CPME = 1:1:1	89
15	(R)-B2	DCE:1,4-dioxane:TBME = 3:1:1	89
16	(R)-B2	DCE:1,4-dioxane:TBME = 1:3:1	89
17	(R)-B2	DCE:1,4-dioxane:TBME = 1:1:3	89
18	(S)-A5	DCE:1,4-dioxane:TBME = 1:1:3	88
19[c]	(R)-B2	DCE:1,4-dioxane:TBME = 1:1:1	91

[a] Reaction condition: **3a** (0.05mmol), CPA (10 mol%), 2,2'-DPPA (0.7 eq.), solvent (0.6 mL), H_2O (20 μL). [b] The *ee* value was determined by HPLC with a chiral stationary phase. [c] Run with 5 mol% CPA at -20 °C.

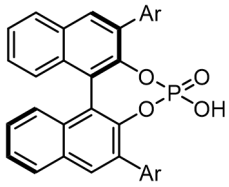
3.3. Condition Optimization of 3h



3h **4h**



A2: Ar = 9-phenanthrenyl

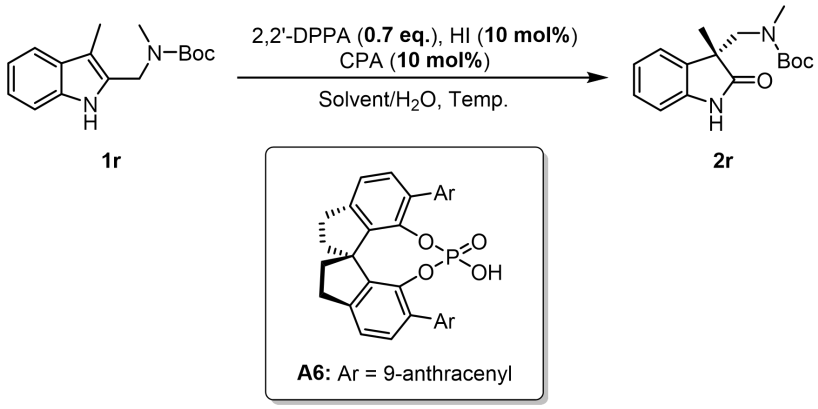


B1: Ar = 1-pryenyl
B2: Ar = 1,3-dimethylphenanthren-9-yl
B3: Ar = 9-phenanthrenyl
B4: Ar = 9-anthracenyl

Entry[a]	CPA	Solvent	Yield[b]	*ee*[c]
1	(R)-B1	THF	36%	15%
2	(R)-B2	THF	75%	60%
3	(R)-B2	THF:DCE = 1:1	74%	55%
4	(R)-B3	THF	60%	50%
5	(R)-B3	1,4-dioxane (27 °C)	78%	33%
6	(R)-B3	1,4-dioxane:DCE = 1:1	68%	45%
7	(S)-A2	1,4-dioxane:DCE = 1:1	71%	6%
8	(R)-B4	THF	70%	77%
9[d]	(R)-B4	THF	65%	87%
10[e]	(R)-B4	THF	61%	91%

[a] Reaction condition: **5** (0.1 mmol), CPA (10 mol%), 2,2'-DPPA (0.7 eq.), THF/H_2O (v/v = 35:1, 0.7 mL), 0 °C. [b] Isolated yield. [c] The ee value was determined by chiral HPLC with a chiral stationary phase. [d] Run at -25 °C. [e] Run at -35 °C.

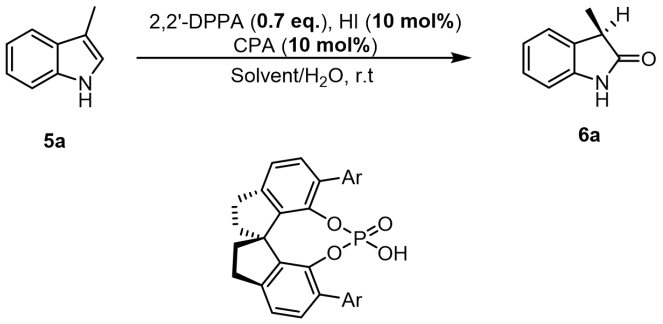
3.4. Condition Optimization of 1r



Entry[a]	Solvent	Temp.	Yield[b]	*ee*[c]
1	1,4-dioxane:PhCl = 1:1	-20 °C	79%	83%
2	THF:PhCl = 1:1	-20 °C	75%	87%
3	THF:PhCl = 1:1	-35 °C	72%	93%
4	THF	-35 °C	70%	90%

[a] Reaction condition: **1r** (0.1 mmol), CPA (10 mol%), 2,2'-DPPA (0.7 eq.), Solvent/H_2O (v/v = 35:1, 0.7 mL) [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase.

3.5. Condition Optimization of 5a



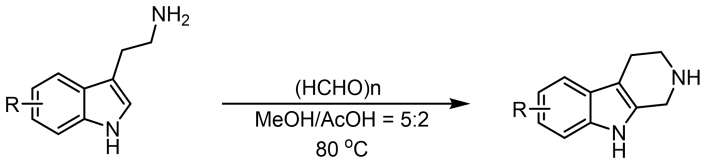
A2: Ar = 9-phenanthrenyl
A3: Ar = 1-pyrenyl
A4: Ar = 9-anthracenyl

Entry[a]	CPA	Solvent	Yield[b]	*ee*[c]
1	(S)-A2	THF	76%	50%
2	(S)-A3	THF	74%	75%
3	(S)-A4	THF	69%	58%
4	(S)-A3	1,4-dioxane	61%	55%
5	(S)-A3	DCE	80%	7%
6	(S)-A3	MeCN	64%	13%
7	(S)-A3	CPME	81%	35%
8	(S)-A3	DME	60%	33%
9	(S)-A3	THF:PhCl = 4:1	72%	55%

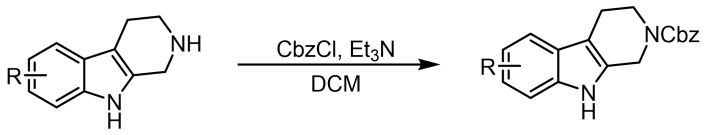
[a] Reaction condition: **5** (0.1 mmol), CPA (10 mol%), 2,2'-DPPA (0.7 eq.), Solvent/H_2O (v/v = 35:1, 0.7 mL) [b] Isolated yield. [c] The *ee* value was determined by chiral HPLC with a chiral stationary phase.

4. Substrate and catalyst preparation

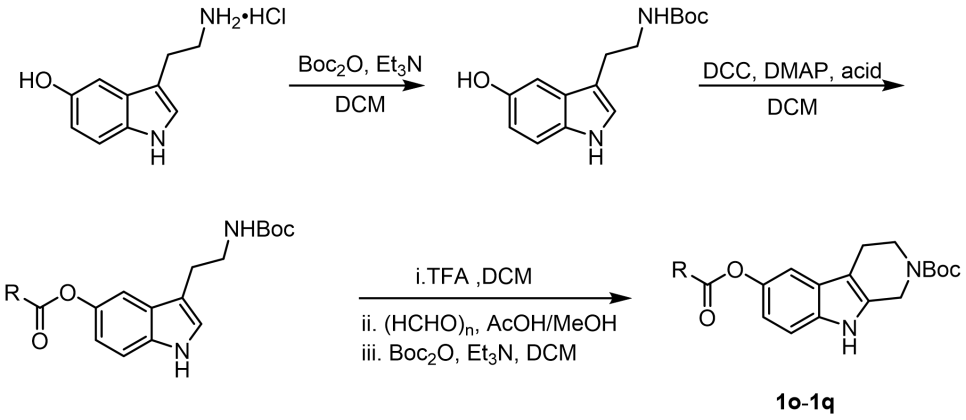
General Procedure A:



To a solution of substituted tryptamine (10 mmol, 1.0 eq.) in a mixture of MeOH/AcOH (v/v = 5:2, 28 mL) was added paraformaldehyde (12 mmol, 1.2 eq.). The mixture was heated to 80 °C for 3 h and then cooled to 0 °C. The mixture was basified to pH 9−10 using aqueous solutions of saturated NaOH and $NaHCO_3$ (with NaOH to pH 4−5 followed by $NaHCO_3$ to pH 8, and then a few drops of the NaOH solution to pH 9−10). Next, the mixture was extracted with DCM. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude 2,3,4,9-tetrahydro-*1H*-pyrido[3,4-*b*]indole.



At 0 °C, to a solution of 2,3,4,9-tetrahydro-*1H*-pyrido[3,4-*b*]indole (1.0 eq.) in DCM were added Et_3N (1.0 eq.) and CbzCl (1.05 eq.). The resulting mixture was allowed to warm to room temperature and stirred at the same temperature. The reaction progress was monitored by TLC. Upon completion, the solvent was evaporated to give the crude product, which was purified by flash column chromatography on silica gel to afford product.



1o-1q

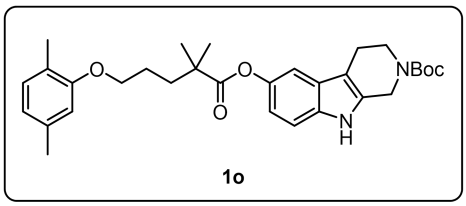
To a solution of 5-Hydroxytryptamine Hydrochloride (5 mmol) in DCM were

added Et_3N (2.0 eq.) and Boc_2O (1.5 eq.). The resulting mixture was stirred at room temperature for 2 h. Upon completion, the solvent was evaporated. The resulting residue was purified by flash column chromatography on silica gel to afford product as a colorless liquid.

Next, the product was dissolved in DCM, then DCC (1.3 eq.), DMAP (20 mol%) and acid (1.3 eq.) was added. The mixture stirred for 2 h and purified by flash column chromatography on silica gel to afford product as a white soild.

The soild was dissolved in DCM, then TFA (5.0 eq.) was slowly added at 0 °C. The mixture was stirred at room temperature for 2 h. Then, the mixture was washed with saturated $NaHCO_3$ and extracted with DCM. The combined organic layers were dried with anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude product. The residue was dissolved in AcOH/MeOH (v/v = 2:5, 15 mL). Next, paraformaldehyde (1.1 eq.) was added. The mixture was heated to 80 °C and stirred for 3 h before it was cooled to 0 °C. The mixture was basified to pH 9−10 using aqueous solutions of saturated NaOH and $NaHCO_3$ (with NaOH to pH 4−5 followed by $NaHCO_3$ to pH 8, and then a few drops of the NaOH solution to pH 9−10). The mixture was then extracted with DCM. The combined organic layers were dried over Na_2SO_4, filtered, and concentrated under reduced pressure to give the crude amine.

The crude amine was dissolved in DCM (15 mL) and treated with Boc_2O (1.2 eq.) and Et_3N (2.0 eq.) at 0 °C. The resulting mixture was stirred at room temperature for 2 h before a solution of saturated aqueous solution of $NaHCO_3$ was added. The layers were separated, and the water layer was extracted with ethyl acetate. The combined organic layers were dried over anhydrous Na_2SO_4, filtered, concentrated. The residue was purified by column chromatography on silica gel to afford the pure product **1o-1q** as a white solid.

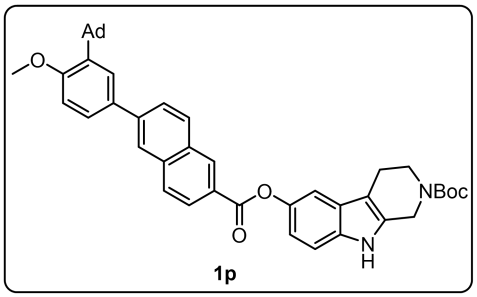


1o

tert-butyl 6-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)-1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indole-2-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.31 (br, 1H), 7.26 – 7.20 (m, 1H), 7.14 (s, 1H), 7.09 – 7.03 (m, 1H), 6.85 – 6.79 (m, 1H), 6.75 – 6.67 (m, 2H), 4.76 – 4.55 (m, 2H), 4.06 (s, 2H), 3.77 (s, 2H), 2.75 (s, 2H), 2.36 (s, 3H), 2.25 (s, 3H), 1.97 (s, 4H), 1.57 (s, 9H), 1.46 (s, 6H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 177.55, 157.05, 144.49, 136.57, 134.06, 130.42, 127.40, 123.73, 120.81, 115.36, 112.07, 111.31, 110.09, 80.23, 68.00, 42.46, 37.31, 28.58, 26.99, 25.44, 25.36, 21.49, 15.92.

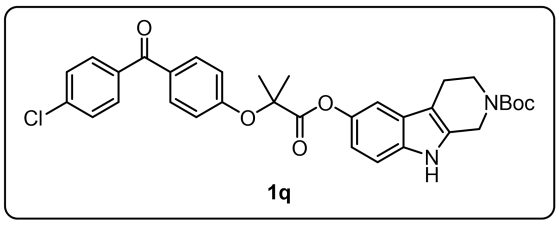


1p

tert-butyl 6-((6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)-1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indole-2-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (s, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.08 (d, *J* = 11.8 Hz, 2H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.87 (d, *J* = 8.5 Hz, 1H), 7.67 (s, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.38 (s, 1H), 7.33 (d, *J* = 7.1 Hz, 1H), 7.06 (t, *J* = 8.0 Hz, 2H), 4.82 – 4.50 (m, 2H), 3.95 (s, 3H), 3.87 – 3.72 (m, 2H), 2.86 – 2.72 (m, 2H), 2.24 (s, 6H), 2.16 (s, 3H), 1.86 (s, 6H), 1.57 (s, 9H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 166.60, 159.05, 144.58, 141.70, 139.11, 136.29, 134.22, 132.58, 131.66, 131.37, 129.93, 128.46, 127.53, 126.76, 126.66, 126.08, 126.01, 125.84, 124.84, 115.58, 112.21, 111.48, 110.50, 80.23, 60.49, 55.25, 40.69, 37.30, 37.21, 34.01, 29.19, 28.58.

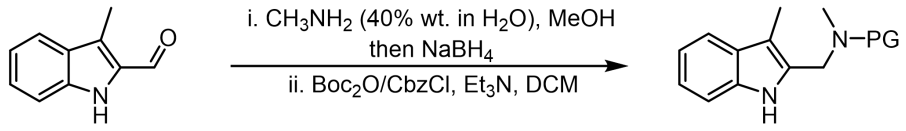


1q

tert-butyl 6-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-1,3,4,9-tetrahydro-2H-pyrido[3,4-b]indole-2-carboxylate

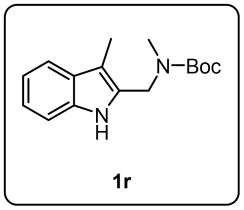
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.54 (br, 1H), 7.84 (d, *J* = 8.7 Hz, 2H), 7.76 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 8.7 Hz, 3H), 6.74 (dd, *J* = 8.7, 2.1 Hz, 1H), 4.64 (s, 2H), 3.80 – 3.72 (m, 2H), 2.78 – 2.70 (m, 2H), 1.89 (s, 6H), 1.55 (s, 9H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 194.41, 173.41, 159.79, 143.92, 138.53, 136.42, 134.27, 132.22, 131.29, 130.62, 128.65, 127.34, 117.53, 114.69, 111.42, 109.71, 108.67, 80.31, 79.66, 60.49, 49.17, 42.58, 41.82, 33.99, 28.56, 25.60, 21.41, 14.26.



To a solution of **S3**[1] in MeOH (10 mL) were added solution CH_3NH_2 (40% in H_2O, 3.0 eq.) and anhydrous sodium sulfate (200 mg). The resulting mixture was stirred at room temperature for 6 h, then was added $NaBH_4$ (1.05 eq.). The reaction mixture was stirred at room temperature overnight, the solvent was evaporated to give the crude amine.

The crude amine was redissolved in DCM (10 mL). To this solution were added Boc_2O/CbzCl (1.5 eq.) and Et_3N (2.0 eq.). The mixture was stirred at room temperature, and the reaction progress was monitored by TLC. Upon completion (~ 2 h), the solvent was evaporated, and the residue was purified by column chromatography on silica gel to afford the pure indole **1r**-**1u** as a white solid.

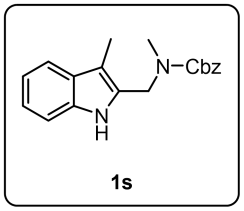


1r

tert-butyl methyl((3-methyl-1H-indol-2-yl)methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (br, 1H), 7.56 (d, *J* = 7.8 Hz, 1H), 7.34 (d, *J* = 8.0 Hz, 1H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.14 (t, *J* = 7.3 Hz, 1H), 4.50 (s, 2H), 2.88 (s, 3H), 2.36 (s, 3H), 1.57 (s, 9H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 157.30, 146.83, 135.62, 131.56, 128.28, 127.67, 122.08, 118.71, 110.85, 85.25, 43.49, 34.53, 27.48, 8.47.

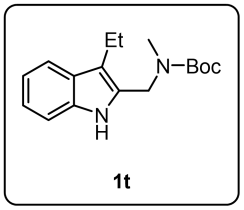


1s

benzyl methyl((3-methyl-1H-indol-2-yl)methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.80 (br, 1H), 7.67 – 7.34 (m, 7H), 7.32 – 7.15 (m, 2H), 5.32 (s, 2H), 4.61 (s, 2H), 3.00 (s, 3H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$): δ 157.73, 136.66, 135.76, 130.84, 129.07, 128.23, 127.92, 122.30, 119.16, 118.82, 110.98, 109.30, 67.63, 44.11, 34.26, 8.56.

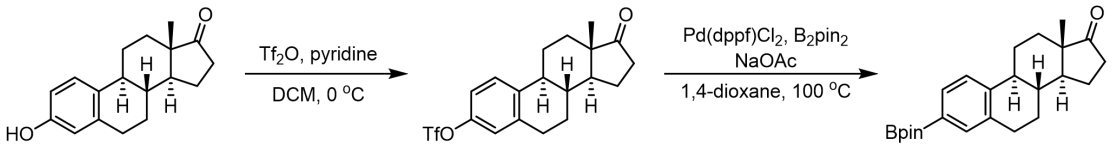


1t

tert-butyl ((3-ethyl-1H-indol-2-yl)methyl)(methyl)carbamate

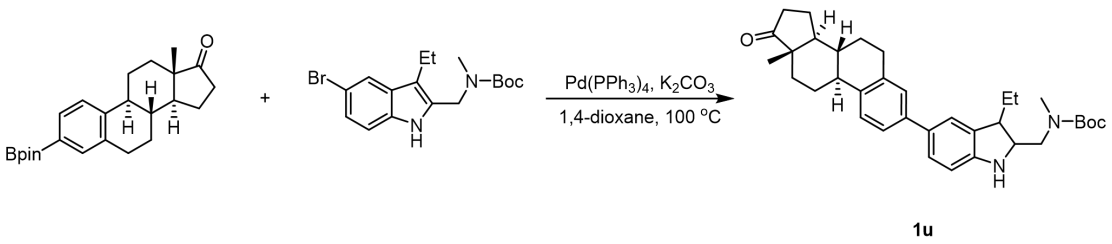
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (br, 1H), 7.63 (d, *J* = 7.8 Hz, 1H), 7.36 (d, *J* = 8.0 Hz, 1H), 7.22 (t, *J* = 7.4 Hz, 1H), 7.14 (t, *J* = 7.4 Hz, 1H), 4.51 (s, 2H), 2.90 (s, 3H), 2.84 (q, *J* = 7.5 Hz, 2H), 1.56 (s, 9H), 1.34 (t, *J* = 7.5 Hz, 3H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 157.40, 135.77, 130.92, 127.37, 122.00, 118.95, 115.78, 110.98, 80.25, 43.52, 34.61, 28.56, 17.42, 16.31.



Estrone (10.0 mmol, 1.0 eq.), and pyridine (12.0 mmol, 1.5 eq.) were dissolved in DCM (30.0 mL) in a flask-round bottom with a stir bar[2]. The reaction mixture was stirred at 0 °C, and Tf_2O (12.0 mmol, 1.2 eq.) was dropwise added into reaction system over 5 min. The reaction mixture was then allowed to warm to room temperature and stirred for 30 min. Upon completion, 4N HCl was added to the reaction. The reaction mixture was then extracted with DCM. The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated under vacuum. The crude product was directly used without further purification.

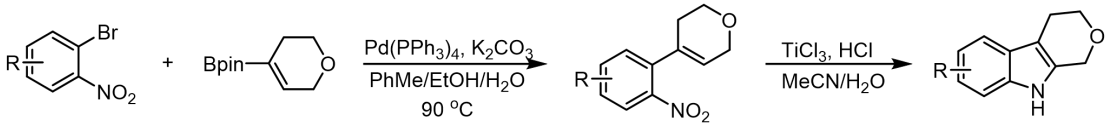
Trifluoromethanesulfonic ester (1.0 eq.), B_2pin_2 (2.0 eq.), $Pd(dppf)Cl_2$ (10 mol%), and NaOAc (3.0 eq.) were dissolved in 1,4-dioxane (20 mL) in a two-neck flask with a stir bar under argon atmosphere. The reaction mixture was stirred at 100 °C for 8 h. Upon completion, water was added to the reaction. The reaction mixture was then extracted with ethyl acetate. The combined organic extracts were dried with anhydrous Na_2SO_4 and concentrated under vacuum. The desired product was obtained through silica gel chromatography.



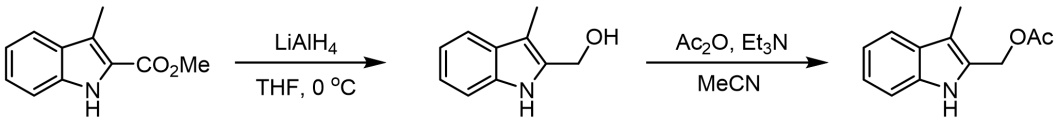
1u

To a two-neck flask with a stir bar were added boronate (1.2 eq.), $Pd(PPh_3)_4$ (15 mol%), tert-butyl ((5-bromo-3-ethyl-1H-indol-2-yl)methyl)(methyl)carbamate (1.0 eq.), K_2CO_3 (6.0 eq.), H_2O (5 mL) and 1,4-dioxane (20 mL) under argon atmosphere. The mixture was heated to refluxed for 16 h. After cooling to room temperature, the mixture was filtered through celite. The filtrate was concentrated under reduced pressure. The residue was purified by flash column chromatography to give **1u** as a white solid.

General Procedure B:



To a solution of substituted 2-bromonitrobenzene (1.0 eq.) and 1-cyclohexen-1-yl-boronic acid pinacol ester (1.2 eq.) in a mixed solvent of toluene, EtOH, and H_2O (v/v/v = 5:2:1) were added $Pd(PPh_3)_4$ (10 mol%) and K_2CO_3 (4.0 eq.). The resultant mixture was then purged with N_2 and heated to 90 °C. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was cooled to room temperature and diluted with water and ethyl acetate. The layers were separated, and the aqueous layer was extracted with ethyl acetate. The combined organic layers were washed with water, dried over Na_2SO_4, and concentrated. The residue was dissolved in acetonitrile and water (v/v = 1:1). A solution of $TiCl_3$ (15-20% in 30% hydrochloric acid) was added. The mixture was stirred at room temperature and the progress was monitored by TLC. Upon completion, the mixture was extracted with ethyl acetate. The combined organic layers were washed with a saturated aqueous $NaHCO_3$ solution and brine, then dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel to afford pure products as a white solid.

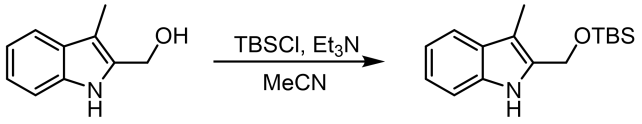


3h

Compound **3h** was prepared from (3-methyl-1H-indol-2-yl)methanol and Ac_2O (3.0 eq.) in the presence of Et_3N (2.5 eq.) and MeCN and purified by flash column chromatography (PE:EA = 5:1) as a white soild[3].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.47 (s, 1H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 8.1 Hz, 1H), 7.28 (t, *J* = 7.5 Hz, 1H), 7.18 (t, *J* = 7.4 Hz, 1H), 5.30 (s, 2H), 2.42 (s, 3H), 2.15 (s, 3H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 172.36, 135.86, 128.92, 128.28, 122.98, 119.41, 111.70, 111.06, 57.65, 21.10, 8.52.



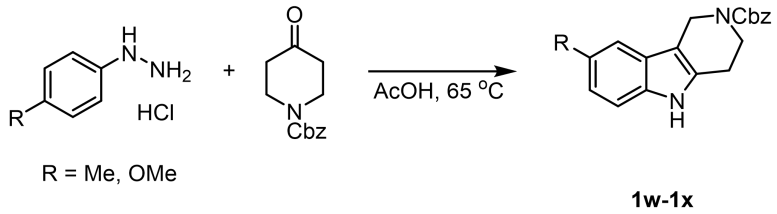
3i

Compound **3i** was prepared from (3-methyl-1H-indol-2-yl)methanol and TBSCl (2.0 eq.) in the presence of Et_3N (3.0 eq.) and MeCN and purified by flash column chromatography (PE:EA = 10:1) as a colorless oil[3].

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.22 (s, 1H), 7.61 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.22 – 7.16 (m, 1H), 4.95 (s, 2H), 2.34 (s, 3H), 1.04 (s, 9H), 0.21 (s, 6H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 135.50, 133.52, 129.27, 121.70, 119.13, 118.64, 110.76, 106.55, 57.50, 26.06, 18.53, 8.48, -5.19.

General Procedure C:

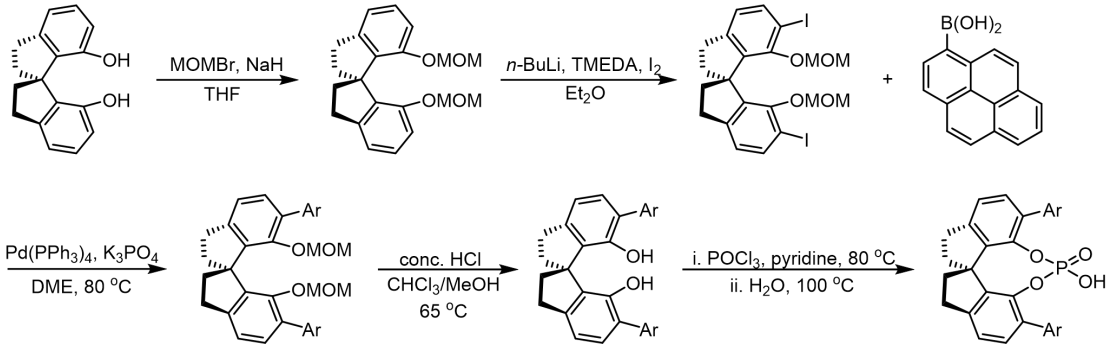


R = Me, OMe

1w-1x

To a solution of benzyl 4-oxopiperidine-1-carboxylate (10 mmol, 1.0 eq.) in AcOH (20 mL) was added *p*-tolylhydrazine hydrochloride (10 mmol, 1.0 eq.). The reaction mixture was heated to 65 °C and stirred for 5 h before it was cooled to room temperature and diluted with water. Then the mixture was extracted with ethyl acetate. The combined organic layers were washed with saturated aqueous $NaHCO_3$ solution and brine, dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel to afford indole **1w-1x** as a pale yellow solid.

Preparation of CPAs

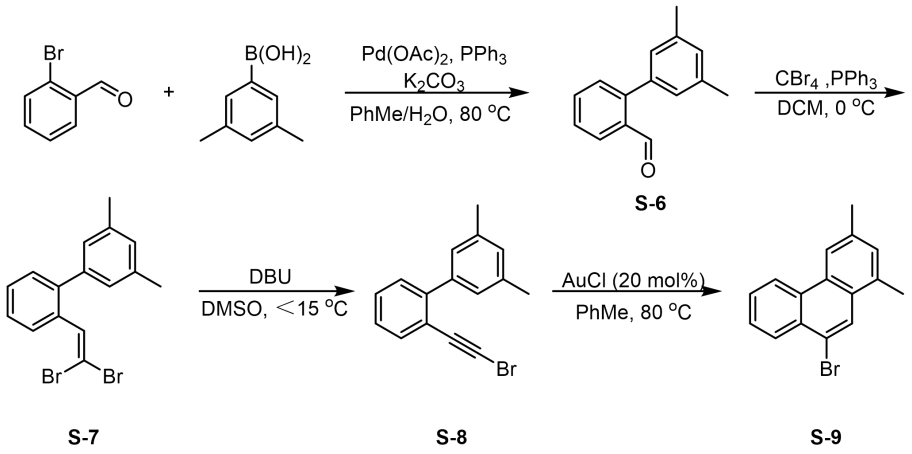


Ar = 1-pyrenyl

Ar = 1-pyrenyl

Ar = 1-pyrenyl

The catalyst (*S*)-A3 was prepared using the procedure according to literature procedure[4].

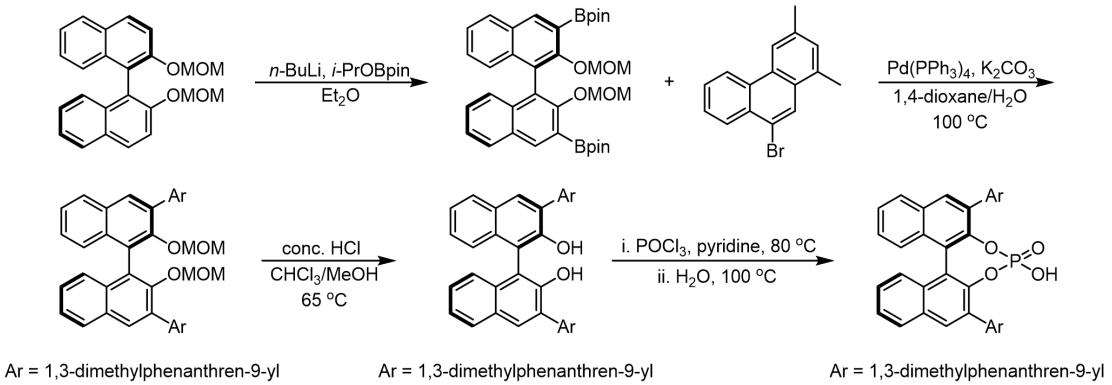


Step 1[5]**:** 2-bromobenzaldehyde (1.0 eq.), 3,5-dimethylphenylboronic acid (1.2 eq.), K_2CO_3 (4.0 eq.), PPh_3 (20 mol%), $Pd(OAc)_2$ (10 mol%) were placed in a round-bottom, which was flushed with argon prior to use. Then toluene and water (v/v = 1:1) was added, and the resulting mixture was stirred at 80 °C for 16 h. After cooling two layers were separated, water layer was extracted with ethyl acetate. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and the crude product was purified by flash column chromatography to obtain **S-6** as a colorless solid.

Step 2: CBr_4 (2.5 eq.) was added portion wise to a solution of PPh_3 (5.0 eq.) in DCM and the resulting yellow mixture was stirred for 10 min at 0 °C. A solution of 2-(3,5-dimethylphenyl)benzaldehyde (1.0 eq.) in DCM was added dropwise and stirring was continued for an additional 1 h at 0 °C. The reaction was then quenched with brine and the aqueous layer was extracted with DCM. The combined organic layers were dried over Na_2SO_4, concentrated under reduced pressure and the crude product was purified by flash column chromatography to obtain **S-7** as a colorless solid.

Step 3: A solution of DBU (3.0 eq.) in DMSO was added to a cooled solution of **S-7** (1.0 eq.) in DMSO at such rate to maintain the internal temperature below 15 °C. The resulting mixture was stirred at 15 °C for 1 h before the reaction was quenched with aq. HCl (1 M) at 0 °C. The aqueous layer was extracted with DCM and the combined organic layers were washed with sat. aq. $NaHCO_3$ solution, water and brine. Afterwards, the organic layer was dried over Na_2SO_4, the solvent was removed under reduced pressure to obtain **S-8** as colorless solid without further purification.

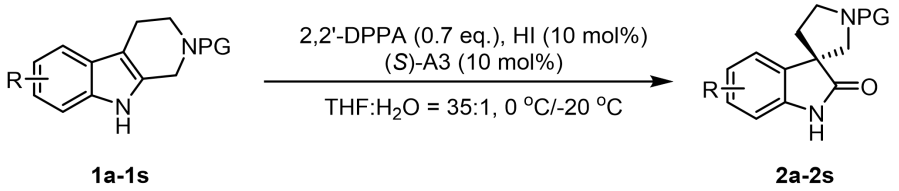
Step 4: In a round-bottom flask under an atmosphere of dry argon, AuCl (20 mol%) and **S-8** (1.0 eq.) in toluene were heated at 100 °C for 1 h. The mixture was then adsorbed on silica gel and purified by flash chromatography to obtain **S-9** as a colorless solid.



The catalyst (*R*)-B2 and (*S*)-A5 was prepared using the procedure according to literature procedure[6].

5. Catalytic Enantioselective Oxidative Rearrangement

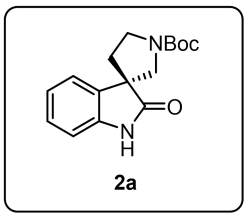
General Procedure D:



1a-1s **2a-2s**

At room temperature, to a 5 mL-vial charged with (*S*)-**A3** (10 mol%) and **1a-1u** (0.1 mmol, 1.0 eq.) were added the solvent of THF/H_2O (v/v = 35:1, 0.7 mL). Then HI (10 mol%) in THF (0.1 mL) was added. The mixture was cooled to 0 °C or –20 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.

Note: Due to the substitution pattern of the amide functionality, each compounds have a mixture of two conformational isomers. All the spectra give the data for the major rotamer.



2a

(*R*)-*tert*-Butyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

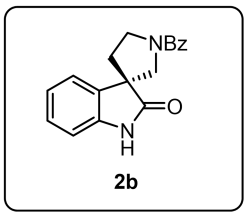
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.22 (br, 1H), 7.29 – 7.16 (m, 2H), 7.12 – 7.03 (m, 1H), 7.02 – 6.95 (m, 1H), 3.97 – 3.71 (m, 3H), 3.63 (m, 1H), 2.50 – 2.38 (m, 1H), 2.17 – 2.08 (m, 1H), 1.52 (s, 9H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 180.20, 154.55, 140.27, 133.15, 128.49, 123.01, 122.79, 110.24, 79.98, 54.41, 53.44, 45.27, 36.41, 35.56, 28.51.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 10.3 min (minor), 13.8 min (major).

$[\alpha]_D^{25}$: -30.3 (*c* = 1.0, CH_2Cl_2).



2b

(*R*)-1'-benzoylspiro[indoline-3,3'-pyrrolidin]-2-one

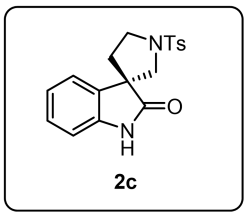
^{1}H NMR (400 MHz, $CDCl_3$): δ 9.35 (br, 1H), 7.50 (m, 5H), 7.19 (m, 2H), 7.11 – 7.01 (m, 1H), 7.00 – 6.88 (m, 1H), 4.27 – 3.87 (m, 4H), 3.87 – 3.55 (m, 1H), 2.65 – 2.51 (m, 1H), 2.47 – 2.30 (m, 1H), 2.24 – 2.13 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.08, 170.32, 140.25, 136.37, 132.25, 131.62, 130.38, 128.51, 127.30, 123.13, 122.73, 110.45, 57.51, 53.57, 45.60 , 34.88.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 25.7 min (minor), 31.6 min (major).

$[\alpha]_D^{25}$: -31.5 (*c* = 1.0, CH_2Cl_2).



2c

(*R*)-1'-tosylspiro[indoline-3,3'-pyrrolidin]-2-one

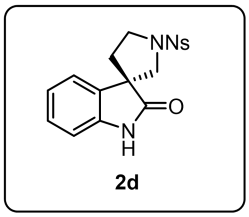
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.13 (s, 1H), 7.80 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.0 Hz, 2H), 7.29 – 7.23 (m, 1H), 7.12 – 7.08 (m, 1H), 7.05 – 6.99 (m, 1H), 6.91 (d, *J* = 7.8 Hz, 1H), 3.77 (dt, *J* = 9.7, 7.4 Hz, 1H), 3.64 – 3.60 (m, 1H), 3.59 – 3.53 (m, 1H), 3.49 (d, *J* = 9.7 Hz, 1H), 2.51 (s, 3H), 2.38 – 2.28 (m, 1H), 2.14 – 2.05 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 178.90, 143.98, 139.64, 133.29, 132.78, 129.94, 128.66, 127.83, 123.29, 109.95, 56.09, 52.85, 47.33, 36.35, 21.68.

HPLC: Daicel column IC; *n*-hexane:*i*-PrOH = 50:50; 1.0 mL/min;

Retention times: 20.7 min (minor), 27.9 min (major).

$[\alpha]_D^{25}$: -42.4 (*c* = 1.0, CH_2Cl_2).



2d

(*R*)-1'-((4-nitrophenyl)sulfonyl)spiro[indoline-3,3'-pyrrolidin]-2-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, *J* = 8.6 Hz, 2H), 8.11 (d, *J* = 7.9 Hz, 2H), 7.94 (br, 1H), 7.28 (d, J = 7.8 Hz, 1H), 7.19 (d, *J* = 7.4 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 3.94 – 3.83 (q, *J* = 8.7, 8.0 Hz, 1H), 3.73 (d, *J* = 10.2 Hz, 1H), 3.66 (q, *J* = 8.8, 8.0 Hz, 1H), 3.55 (d, *J* = 10.2 Hz, 1H), 2.33 (dt, *J* = 13.4, 6.8 Hz, 1H), 2.23 (dt, *J* = 13.5, 7.3 Hz, 1H).

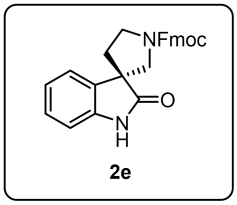
^{13}C NMR(101 MHz, $CDCl_3$): δ 178.89, 150.36, 142.68, 139.87, 131.07, 129.08, 128.87, 124.49, 123.43, 123.06, 110.10, 55.74, 52.61, 47.48, 36.30.

HPLC: Daicel column ID; *n*-hexane:*i*-PrOH = 50:50; 1.0 mL/min;

Retention times: 16.2 min (major), 18.8 min (minor).

$[\alpha]_D^{25}$: -47.6 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{17}H_{15}N_3O_5S + Na]^+$ 396.0625, found 396.0629



2e

(9H-fluoren-9-yl)methyl (*R*)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

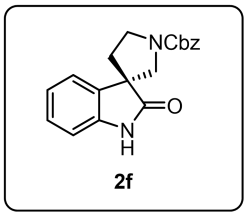
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (br, 1H), 7.83 (d, *J* = 7.5 Hz, 1H), 7.77 (d, *J* = 7.5 Hz, 1H), 7.74 – 7.67 (m, 1H), 7.58 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.43 – 7.35 (m, 2H), 7.31 – 7.24 (m, 3H), 7.16 – 7.05 (m, 2H), 7.04 – 6.95 (m, 1H), 4.59 – 4.43 (m, 2H), 4.38 – 4.24 (m, 1H), 4.00 – 3.69 (m, 4H), 2.57 – 2.44 (m, 1H), 2.26 – 2.11 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.71, 154.83, 144.20, 144.02, 141.47, 141.33, 140.27, 132.71, 132.19, 128.69, 127.81, 127.17, 125.16, 123.20, 122.85, 120.07, 110.29, 67.58, 54.35, 53.38, 47.29, 45.82, 35.59.

HPLC: Daicel column AS-H ; *n*-hexane:*i*-PrOH = 80:20; 1.0 mL/min;

Retention times: 20.1 min (minor), 22.0 min (major).

$[\alpha]_D^{25}$: -32.8 (*c* = 1.0, CH_2Cl_2).



2f

benzyl (*R*)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate.

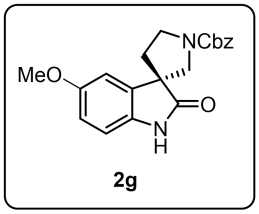
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.96 (br, 1H), 7.47 – 7.27 (m, 5H), 7.27 – 7.23 (m, 1H), 7.23 – 7.14 (m, 1H), 7.11 – 7.03 (m, 1H), 6.94 (d, J = 7.7 Hz, 1H), 5.25 – 5.14 (s, 2H), 4.04 – 3.93 (m, 1H), 3.91– 3.81 (m, 2H), 3.78 – 3.67 (m, 1H), 2.53 – 2.42 (m, 1H), 2.22 – 2.10 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.84, 154.73, 140.09, 136.52, 132.51, 128.50, 128.42, 127.88, 127.76, 122.97, 122.68, 110.14, 67.04, 54.27, 52.29, 45.70, 35.41.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 17.0 min (minor), 22.0 min (major).

$[\alpha]_D^{25}$: -36.5 (*c* = 1.0, CH_2Cl_2).



2g

benzyl (*R*)-5-methoxy-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.01 (br, 1H), 7.53 – 7.30 (m,

5H), 6.89 (d, *J* = 8.9 Hz, 1H), 6.80 (d, *J* = 8.4 Hz, 2H), 5.22 (s, 2H), 4.02 – 3.90 (m, 1H), 3.90 – 3.81 (m, 2H), 3.79 (s, 3H), 3.75 – 3.64 (m, 1H), 2.78 (s, 2H), 2.52 – 2.41 (m, 1H), 2.20 – 2.08 (m, 1H)**.**

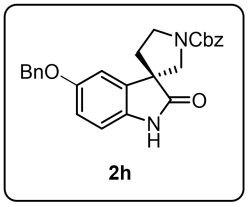
^{13}C NMR(101 MHz, $CDCl_3$): δ 179.99, 178.18, 156.27, 154.83, 136.62, 133.99, 133.65, 133.51, 128.54, 128.06, 127.87, 112.85, 110.65, 110.14, 67.16, 55.91, 54.37, 52.87, 45.80, 35.52, 29.67.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 19.4 min (minor), 26.5 min (major).

$[\alpha]_D^{25}$: -41.9 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_4 + Na]^+$ 375.1315, found 375.1313



2h

benzyl (*R*)-5-(benzyloxy)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.72 (br, 1H), 7.48 – 7.30 (m, 10H), 6.87 (s, 3H), 5.22 (s, 2H), 5.03 (s, 2H), 4.00 – 3.90 (m, 1H), 3.89 – 3.77 (m, 2H), 3.75 – 3.63 (m, 1H), 2.50 – 2.42 (m, 1H), 2.18 – 2.09 (m, 1H).

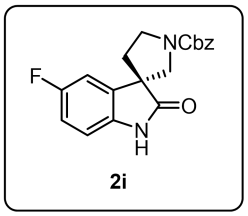
^{13}C NMR(101 MHz, $CDCl_3$): δ 179.65, 155.40, 154.77, 136.81, 134.02, 133.78, 128.70, 128.54, 128.31, 128.15, 128.06, 127.87, 127.61, 114.02, 111.29, 110.54, 70.88, 67.14, 54.08, 53.77, 45.76, 35.53.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 34.4 min (minor), 45.6 min (major).

$[\alpha]_D^{25}$: -54.2 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{26}H_{24}N_2O_4 + Na]^+$ 451.1628, found 451.1630



2i

benzyl (*R*)-5-fluoro-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.98 (br, 1H), 7.46 – 7.27 (m, 5H), 6.99 – 6.84 (m, 3H), 5.19 (s, 2H), 4.05 – 3.93 (m, 1H), 3.87 – 3.75 (m, 2H), 3.74 – 3.67 (m, 1H), 2.51 – 2.38 (m, 1H), 2.21 – 2.08 (m, 1H), 1.91 – 1.80 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.80, 160.59, 158.19, 154.78, 136.71, 136.54, 136.15, 136.06, 133.99 (d, *J* = 22.3 Hz), 128.57, 128.15, 127.91, 114.99 (d, *J* = 23.5 Hz), 110.94 (d, *J* = 22.7 Hz), 67.26, 54.32, 53.98, 52.91, 45.69, 35.42.

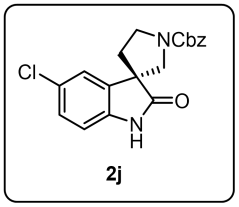
^{19}F NMR (376 MHz, $CDCl_3$): δ -119.49 (d, *J* = 43.9 Hz).

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 17.1 min (minor), 24.8 min (major).

$[\alpha]_D^{25}$: -38.6 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{19}H_{17}FN_2O_3 + Na]^+$ 363.1115, found 363.1111



2j

benzyl (*R*)-5-chloro-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (br, 1H), 7.51 – 7.30 (m, 5H), 7.28 – 7.22 (m, 1H), 7.18 (d, J = 13.0 Hz, 1H), 6.90 (d, J = 8.0 Hz, 1H), 5.23 (s, 2H), 4.05 – 3.91 (m, 1H), 3.90 – 3.78 (m, 2H), 3.76 – 3.62 (m, 1H), 2.55 – 2.40 (m, 1H), 2.22 – 2.10 (m, 1H).

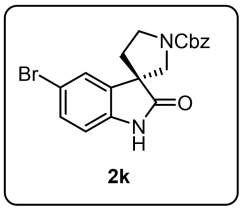
^{13}C NMR(101 MHz, $CDCl_3$): δ 179.33, 154.75, 138.61, 136.52, 134.24, 128.63, 128.17, 127.91, 123.37, 111.18, 67.26, 53.97, 52.61, 45.70, 35.45.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 17.4 min (minor), 26.6 min (major).

$[\alpha]_D^{25}$: -28.4 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{19}H_{17}ClN_2O_3 + Na]^+$ 379.0820, found 379.0821



2k

benzyl (*R*)-5-bromo-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.74 (br, 1H), 7.49 – 7.31 (m, 7H), 6.85 (d, *J* = 8.3 Hz, 1H), 5.23 (s, 2H), 4.03– 3.91 (m, 1H), 3.90– 3.78 (m, 2H), 3.76 – 3.62 (m, 1H), 2.53 – 2.41 (m, 1H), 2.21 – 2.10 (m, 1H).

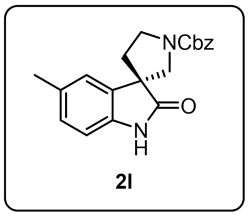
^{13}C NMR(101 MHz, $CDCl_3$): δ 179.17, 154.75, 139.10, 136.52, 134.62, 131.54, 128.64, 128.15, 127.90, 126.12, 115.72, 111.64, 67.26, 53.97, 53.49, 45.71, 35.46.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 17.9 min (minor), 26.4 min (major).

$[\alpha]_D^{25}$: -30.2 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{19}H_{17}BrN_2O_3 + Na]^+$ 423.0315, found 423.0310



2l

benzyl (*R*)-5-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.87 (br, 1H), 7.52 – 7.24 (m, 5H), 7.11 – 6.95 (m, 2H), 6.91 – 6.84 (m, 1H), 5.31 – 5.11 (s, 2H), 4.01 – 3.77 (m, 3H), 3.77 – 3.62 (m, 1H), 2.53 – 2.41 (m, 1H), 2.33 (s, 3H), 2.21– 2.02 (m, 1H).

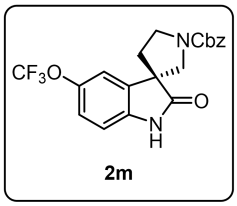
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.19, 154.84, 137.75, 136.86, 132.80, 132.57, 128.86, 128.52, 128.04, 127.82, 123.53, 109.92, 67.10, 54.11, 52.44, 45.83, 35.54, 25.39, 21.20.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 13.2 min (minor), 17.4 min (major).

$[\alpha]_D^{25}$: -43.7 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_3 + Na]^+$ 359.1366, found 359.1360



2m

benzyl (*R*)-2-oxo-5-(trifluoromethoxy)spiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.55 (br, 1H), 7.48 – 7.30 (m, 6H), 7.14 (d, *J* = 8.4 Hz, 1H), 7.07 (d, *J* = 11.2 Hz, 1H), 6.97 (d, *J* = 8.5 Hz, 1H), 5.29 – 5.15 (m, 2H), 4.05 – 3.94 (m, 1H), 3.93 – 3.79 (m, 2H), 3.77 – 3.64 (m, 1H), 2.53 – 2.41 (m, 1H), 2.22 – 2.11 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 180.14, 154.74, 144.95, 139.21, 136.46, 133.76, 128.57, 128.17, 127.91, 121.83, 116.73, 110.92, 67.32, 53.89, 53.72, 45.70, 35.39.

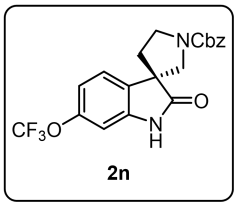
^{19}F NMR (376 MHz, $CDCl_3$): δ -58.26.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 11.5 min (minor), 17.1 min (major).

$[\alpha]_D^{25}$: -30.4 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{17}F_3N_2O_4 + Na]^+$ 429.1033, found 429.1030



2n

benzyl (*R*)-2-oxo-6-(trifluoromethoxy)spiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.24 (br, 1H), 7.52 – 7.30 (m, 5H), 7.23 – 7.10 (m, 1H), 6.99 – 6.82 (m, 2H), 5.22 (s, 2H), 4.05 – 3.92 (m, 1H), 3.92 – 3.77 (m, 2H), 3.76 – 3.65 (m, 1H), 2.53 – 2.41 (m, 1H), 2.20 – 2.10 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.88, 154.84, 149.41, 141.70, 136.69, 130.66, 128.61, 128.16, 128.01, 123.71, 115.22, 104.04, 67.29, 54.05, 53.05, 45.69, 35.44.

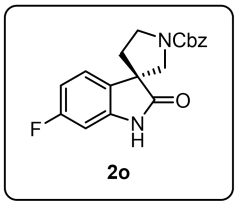
^{19}F NMR (376 MHz, $CDCl_3$):δ -57.85.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 12.8 min (minor), 18.0 min (major).

$[\alpha]_D^{25}$: -31.5 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{17}F_3N_2O_4 + Na]^+$ 429.1033, found 429.1029



2o

benzyl (*R*)-6-fluoro-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.07 (br, 1H), 7.55 – 7.32 (m, 5H), 7.19 – 6.99 (m, 1H), 6.80 – 6.68 (m, 2H), 5.22 (s, 2H), 4.03 – 3.91 (m, 1H), 3.91 – 3.76 (m, 2H), 3.75 – 3.61 (m, 1H), 2.50 – 2.40 (m, 1H), 2.21 – 2.07 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 180.18, 163.04 (d, *J* = 245.8 Hz), 154.84, 141.65, 141.53, 136.56, 128.56, 128.13, 127.91, 123.90, 123.81, 109.33 (d, *J* = 22.7 Hz), 98.97 (d, *J* = 27.3 Hz), 67.24, 54.13, 52.94, 52.00, 45.71, 35.54.

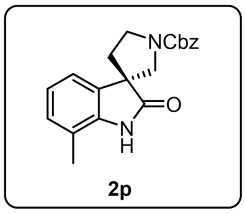
^{19}F NMR (376 MHz, $CDCl_3$): δ -111.51.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 17.9 min (minor), 24.4 min (major).

$[\alpha]_D^{25}$: -36.2 (*c* = 0.9, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{19}H_{17}FN_2O_3 + Na]^+$ 363.1115, found 363.1118



2p

benzyl (*R*)-7-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.90 (br, 1H), 7.51 – 7.29 (m, 5H), 7.14 – 6.95 (m, 3H), 5.23 (s, 2H), 4.03 – 3.94 (m, 1H), 3.94 – 3.80 (m, 2H), 3.78 – 3.64 (m, 1H), 2.55 – 2.42 (m, 1H), 2.34 (s, 3H), 2.23 – 2.10 (m, 1H).

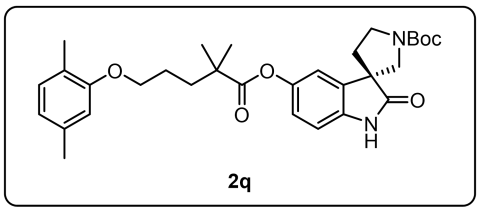
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.84, 154.87, 139.26, 136.68, 132.29, 129.94, 128.61, 128.13, 127.85, 123.05, 120.04, 67.13, 54.42, 53.81, 45.84, 45.38, 35.53, 16.55.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 12.1 min (minor), 19.6 min (major).

$[\alpha]_D^{25}$: -16.4 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_3 + Na]^+$ 359.1366, found 359.1370



2q

tert-butyl (*R*)-5-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.20 (br, 1H), δ 7.03 (d, *J* = 7.4 Hz, 1H), 6.98 – 6.86 (m, 3H), 6.74 – 6.64 (m, 2H), 4.02 (s, 2H), 3.95 – 3.55 (m, 4H), 2.34 (s, 3H), 2.21 (s, 3H), 1.91 (s, 4H), 1.51 (s, 9H), 1.40 (s, 6H).

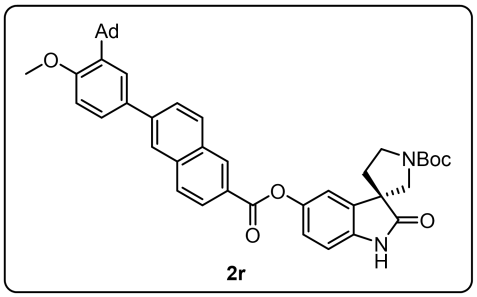
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.26, 176.85, 156.93, 154.56, 146.80, 137.87, 136.56, 133.83, 130.42, 123.62, 121.54, 120.85, 116.81, 112.04, 110.55, 80.11, 67.81, 53.82, 45.23, 42.45, 37.14, 35.48, 28.49, 25.32, 21.46, 15.87.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 6.9 min (major), 7.7 min (minor).

$[\alpha]_D^{25}$: -43.2 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{31}H_{40}N_2O_6 + Na]^+$ 559.2779, found 559.2778



2r

tert-butyl (*R*)-5-((6-(3-((3r,5r,7r)-adamantan-1-yl)-4-methoxyphenyl)-2-naphthoyl)oxy)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.19 (br, 1H), 8.81 (s, 1H), 8.22 (d, *J* = 8.5 Hz, 1H), 8.13 – 8.05 (m, 2H), 8.02 (d, *J* = 8.6 Hz, 1H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.66 (s, 1H), 7.60 (d, *J* = 9.7 Hz, 1H), 7.19 (q, *J* = 11.9, 9.7 Hz, 2H), 7.05 (t, *J* = 7.9 Hz, 2H), 3.95 (s, 3H), 3.90-3.65 (m, 4H), 2.57 – 2.44 (m, 1H), 2.30 – 2.10 (m, 10H), 1.85 (s, 6H), 1.53 (s, 9H).

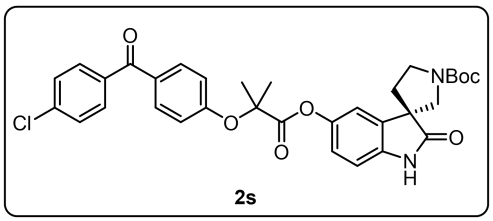
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.12, 165.80, 159.10, 154.54, 146.91, 141.95, 139.13, 138.02, 136.41, 134.16, 132.47, 131.83, 131.30, 129.93, 128.60, 126.80, 126.07, 125.85, 124.84, 121.88, 117.11, 112.22, 110.65, 80.13, 55.24, 53.92, 45.28, 40.69, 37.20, 36.44, 35.61, 33.94, 29.18, 28.54, 25.65, 25.00.

HPLC: Daicel column OX-H; *n*-hexane:*i*-PrOH = 80:20 ; 1.0 mL/min;

Retention times: 14.9 min (minor), 19.2 min (major).

$[\alpha]_D^{25}$: -46.4 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{44}H_{46}N_2O_6 + Na]^+$ 721.3248, found 721.3254



2s

tert-butyl (*R*)-5-((2-(4-(4-chlorobenzoyl)phenoxy)-2-methylpropanoyl)oxy)-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.08 (br, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.74 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 2H), 6.95 - 6.82 (m, 3H), 3.94 – 3.54 (m, 4H), 2.50 – 2.35 (m, 1H), 2.17 – 2.08 (m, 1H), 1.85 (s, 6H), 1.49 (s, 9H).

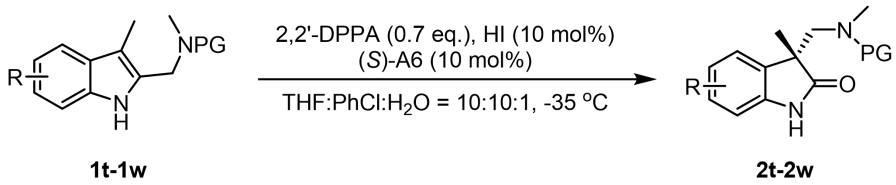
^{13}C NMR(101 MHz, $CDCl_3$): δ 194.33, 179.78, 172.79, 159.51, 154.48, 146.13, 138.60, 136.29, 134.13, 132.21, 131.27, 130.86, 128.66, 121.08, 117.56, 116.44, 110.58, 80.13, 79.52, 53.78, 52.77, 49.24, 45.17, 35.45, 33.95, 28.47, 25.52, 24.98.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 20.3 min (minor), 26.4 min (major).

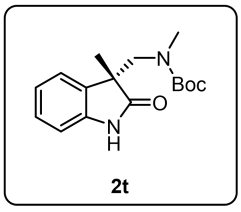
$[\alpha]_D^{25}$: -38.8 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{33}H_{33}ClN_2O_7 + Na]^+$ 627.1869, found 627.1862



1t-1w **2t-2w**

At room temperature, to a 5 mL-vial charged with (*S*)-**A6** (10 mol%) and **1r-1u** (0.1 mmol, 1.0 eq.) were added the solvent of THF/PhCl (v/v = 1:1, 0.8 mL), H_2O (20 μL). Then HI (10 mol%) in THF (0.1 mL) was added. The mixture was cooled to -35 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.



2t

tert-butyl (*R*)-methyl((3-methyl-2-oxoindolin-3-yl)methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.79 (br, 1H), 7.43 – 7.32 (m, 1H), 7.28 – 7.15 (m, 1H), 7.09 – 6.98 (m, 1H), 6.95 – 6.88 (m, 1H), 4.04 (d, *J* = 4.0 Hz, 1H), 3.53 (d, *J* = 13.9 Hz, 1H), 2.73 (s, 3H), 1.40 (s, 9H), 1.29 (s, 3H).

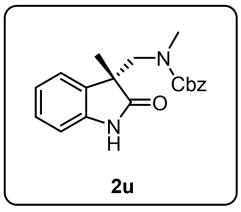
^{13}C NMR(101 MHz, $CDCl_3$): δ 182.35, 155.55, 140.66, 132.23, 127.95, 125.18, 122.29, 109.50, 80.09, 55.18, 50.25, 35.97, 28.22, 22.09, 14.24.

HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 5.5 min (minor), 7.0 min (major).

$[\alpha]_D^{25}$: +1.7 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{16}H_{22}N_2O_3 + H]^+$ 291.1703, found 291.1705



2u

benzyl (*R*)-methyl((3-methyl-2-oxoindolin-3-yl)methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.82 (br, 1H), 7.45 – 7.28 (m, 4H), 7.26 – 7.10 (m, 2H), 7.10 – 6.86 (m, 3H), 5.12 – 4.84 (m,

2H), 4.27 – 3.97 (m, 1H), 3.62 (t, *J* = 15.6 Hz, 1H), 2.81 (d, *J* = 23.1 Hz, 3H), 1.40 (d, *J* = 19.0 Hz, 3H).

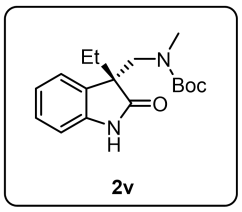
^{13}C NMR(101 MHz, $CDCl_3$): δ 182.78, 156.69, 140.60, 136.87, 131.79, 128.45, 128.17, 127.49, 122.49, 109.99, 66.96, 60.49, 54.67, 50.12, 35.17, 29.75, 22.23, 14.25.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 13.9 min (major), 16.5 min (minor).

$[\alpha]_D^{25}$: +2.2 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{19}H_{20}N_2O_3 + H]^+$ 325.1547, found 325.1542



2v

tert-butyl (*R*)-((3-ethyl-2-oxoindolin-3-yl)methyl)(methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.86 (br, 1H), 7.38 – 7.30 (m, 1H), 7.26 – 7.18 (m, 1H), 7.11 – 6.99 (m, 1H), 6.92 (d, *J* = 7.7 Hz, 1H), 3.40 (d, *J* = 14.2 Hz, 1H), 2.70 (s, 3H), 1.89-1.70 (m, 2H), 1.34 (s, 9H), 0.65 (s, 3H).

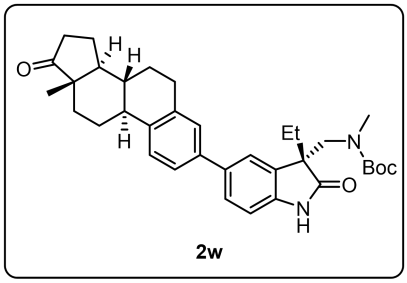
^{13}C NMR(101 MHz, $CDCl_3$): δ 182.56, 155.82, 141.34, 129.81, 127.92, 125.44, 122.25, 109.32, 79.38, 55.58, 53.52, 35.20, 29.11, 28.24, 8.23.

HPLC: Daicel column AS-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 8.4 min (major), 15.2 min (minor).

$[\alpha]_D^{25}$: +2.4 (*c* = 0.7, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{17}H_{24}N_2O_3 + H]^+$ 305.1860, found 305.1861



2w

tert-butyl (((*R*)-3-ethyl-5-((8*R*,9*S*,13*S*,14*S*)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)-2-oxoindolin-3-yl)methyl)(methyl)carbamate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (br, 1H), 7.50 – 7.31 (m, 5H), 6.97 (d, *J* = 7.6 Hz, 1H), 3.06 – 2.97 (m, 2H), 2.81 – 2.70 (m, 3H), 2.61 – 2.47 (m, 2H), 2.42 – 2.33 (m, 1H), 2.27 – 2.19 (m, 1H), 2.18 – 2.09 (m, 2H), 2.05 – 1.83 (m, 4H), 1.75 – 1.47 (m, 8H), 1.37 (s, 1H), 1.30 – 1.23 (m, 9H), 0.96 (s, 3H).

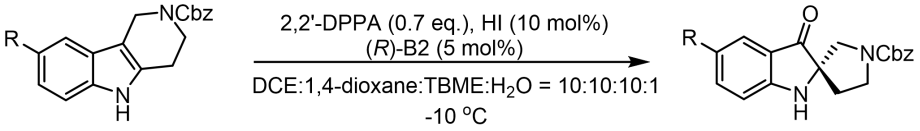
^{13}C NMR(101 MHz, $CDCl_3$): δ 221.09, 182.32, 181.44, 155.88, 140.49, 138.75, 138.57, 138.45, 136.88, 135.35, 130.25, 127.48, 126.97, 126.56, 125.84, 124.42, 109.38, 79.42, 60.48, 55.61, 53.59, 50.59, 48.09, 44.42, 38.30, 35.95, 35.31, 31.68, 29.75, 29.60, 29.57, 29.15, 28.88, 26.63, 25.85, 21.67, 21.12, 14.26, 13.93, 8.51, 8.24.

HPLC: Daicel column AZ-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 23.1 min (minor), 26.2 min (major).

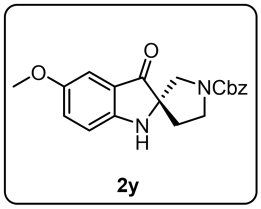
$[\alpha]_D^{25}$: +4.7 (*c* = 0.6, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{35}H_{44}N_2O_4 + H]^+$ 557.3374, found 557.3375



1y-1z **2y-2z**

At room temperature, to a 5 mL-vial charged with (*R*)-**B2** (5 mol%) and **1w-1x** (0.1 mmol, 1.0 eq.) were added the solvent of DCE/1,4-dioxane/TBME (v/v/v = 1:1:1, 0.9 mL), H_2O (20 μL). Then HI (10 mol%) in 1,4-dioxane (0.05 mL) was added. The mixture was cooled to -10 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.



2y

benzyl (*S*)-5-methoxy-3-oxospiro[indoline-2,3'-pyrrolidine] -1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.49 – 7.32 (m, 5H), 7.21 (d, *J* = 8.8 Hz, 1H), 7.09 (s, 1H), 6.88 (d, *J* = 8.8 Hz, 1H), 5.18 (s, 2H), 3.97 – 3.82 (m, 1H), 3.81 (s, 3H), 3.76 – 3.70 (m, 1H), 3.70 – 3.52 (m, 2H), 2.52 – 2.35 (m, 1H), 2.05 – 1.88 (m, 1H).

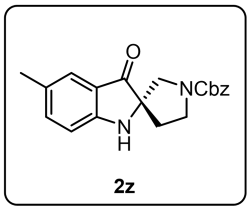
^{13}C NMR(101 MHz, $CDCl_3$): δ 200.02, 155.94, 154.80, 154.03, 128.58, 128.36, 128.15, 128.00, 121.04, 114.48, 104.59, 73.10, 72.18, 67.16, 55.87, 55.72, 45.66, 35.74.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: min (minor), min (major).

$[\alpha]_D^{25}$: +11.4 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_4 + H]^+$ 353.1496, found 353.1495



2z

benzyl (S)-5-methyl-3-oxospiro[indoline-2,3'-pyrrolidine]-1' -carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45 (s, 1H), 7.43 – 7.31 (m, 6H), 6.83 (d, *J* = 8.3 Hz, 1H), 5.17 (s, 2H), 3.96 – 3.82 (m, 1H), 3.75 – 3.69 (m, 1H), 3.69 – 3.50 (m, 2H), 2.45 – 2.36 (m, 1H), 2.33 (s, 3H), 2.02 – 1.88 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 199.91, 158.63, 154.80, 139.16, 136.61, 129.31, 128.57, 128.14, 127.96, 124.19, 120.78, 112.75, 72.46, 67.13, 55.61, 45.64, 35.65, 20.58.

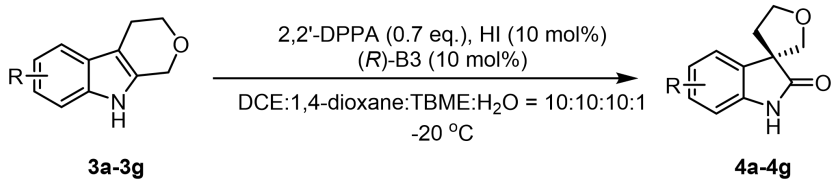
HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 9.3 min (major), 10.8 min (minor).

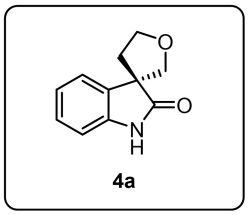
$[\alpha]_D^{25}$: +15.5 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_3 + H]^+$ 337.1547, found 337.1549

General Procedure E:



At room temperature, to a 5 mL-vial charged with (*R*)-**B3** (5 mol%) and the indole **3** (0.1 mmol) were added the mixed solvent DCE/1,4-dioxane/TBME/H_2O (v/v/v/v = 10:10:10:1, 0.9 mL). Then HI (10 mol%) in 1,4-dioxane (0.05 mL) was added. The mixture was cooled to -20 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.



(*R*)-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one

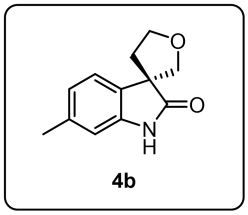
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.91 (br, 1H), 7.29 (d, *J* = 7.4 Hz, 1H), 7.23 (td, *J* = 7.8, 1.4 Hz, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.95 (d, *J* = 7.7 Hz, 1H), 4.23 (t, *J* = 7.1 Hz, 2H), 4.08 (d, *J* = 8.6 Hz, 1H), 3.96 (d, *J* = 8.5 Hz, 1H), 2.56 (dt, *J* = 12.1, 7.2 Hz, 1H), 2.19 (dt, *J* = 13.2, 6.9 Hz, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 181.10, 140.14, 134.07, 128.12, 123.01, 109.90, 69.06, 54.70, 38.64.

HPLC: Daicel column AZ-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 10.5 min (major), 12.0 min (minor).

$[\alpha]_D^{25}$: +27.5 (*c* = 0.8, CH_2Cl_2).



(*R*)-6'-methyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.81 (br, 1H), 7.16 (d, *J* = 7.6

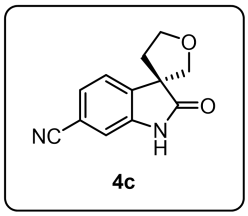
Hz, 1H), 6.87 (d, *J* = 7.6 Hz, 1H), 6.78 (s, 1H), 4.21 (t, *J* = 7.1 Hz, 2H), 4.06 (d, *J* = 8.5 Hz, 1H), 3.93 (d, *J* = 8.5 Hz, 1H), 2.53 (dt, *J* = 12.5, 7.3 Hz, 1H), 2.35 (s, 3H), 2.16 (dt, J = 13.2, 6.9 Hz, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 181.39, 140.21, 138.33, 131.09, 123.51, 122.64, 110.74, 69.04, 54.52, 38.68, 21.56.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 19.5 min (minor), 21.0 min (major).

$[\alpha]_D^{25}$: +29.7 (*c* = 0.8, CH_2Cl_2).



4c

(*R*)-2'-oxo-4,5-dihydro-2*H*-spiro[furan-3,3'-indoline]-6'-carbonitrile

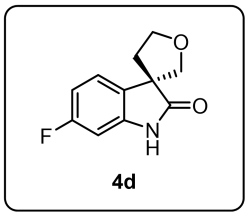
^{1}H NMR (400 MHz, $CDCl_3$): δ 8.64 (br, 1H), 7.39 (s, 2H), 7.19 (s, 1H), 4.23 (tt, *J* = 15.6, 8.3 Hz, 2H), 4.04 (d, *J* = 8.7 Hz, 1H), 3.97 (d, *J* = 8.7 Hz, 1H), 2.68 – 2.54 (m, 1H), 2.29 – 2.18 (m, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 179.57, 140.72, 139.50, 127.64, 123.75, 118.46, 112.42, 111.84, 68.99, 54.77, 38.57.

HPLC: Daicel column OJ-H; *n*-hexane:*i*-PrOH = 80:20; 1.0 mL/min;

Retention times: 15.1 min (major), 18.0 min (minor).

$[\alpha]_D^{25}$: +43.7 (*c* = 0.7, CH_2Cl_2).



4d

(*R*)-6'-fluoro-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.99 (br, 1H), 7.28 – 7.21 (m, 1H), 6.80 – 6.64 (m, 2H), 4.21 (t, *J* = 7.0 Hz, 2H), 4.05 (d, *J* = 8.6 Hz, 1H), 3.93 (d, *J* = 8.6 Hz, 1H), 2.54 (dt, *J* = 14.0, 7.3 Hz, 1H), 2.17 (dt, *J* = 13.3, 6.9 Hz, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 181.40, 162.76 (d, *J* = 245.1 Hz), 141.37 (d, *J* = 11.9 Hz), 129.47 (d, *J* = 2.8 Hz), 123.95 (d, *J* = 9.7 Hz), 109.29 (d, *J* = 22.4 Hz), 98.62 (d, *J* = 27.5 Hz), 68.96, 54.33, 38.63.

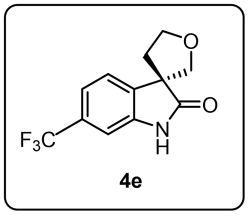
^{19}F NMR (376 MHz, $CDCl_3$) δ -112.27.

HPLC: Daicel column AS-H; *n*-hexane:*i*-PrOH = 60:40; 1.0 mL/min;

Retention times: 23.5 min (major), 29.4 min (minor).

$[\alpha]_D^{25}$: +21.2 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{11}H_{10}FNO_2 + H]^+$ 208.0768, found 208.0770



4e

(*R*)-6'-(trifluoromethyl)-4,5-dihydro-2*H*-spiro[furan-3,3'-ind

olin]-2'-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.77 (s, 1H), 7.47 – 7.37 (m, 2H), 7.22 (s, 1H), 4.35 – 4.21 (m, 2H), 4.10 (d, *J* = 8.6 Hz, 1H), 4.02 (d, *J* = 8.6 Hz, 1H), 2.63 (dt, *J* = 14.0, 7.2 Hz, 1H), 2.24 (dt, *J* = 13.3, 7.1 Hz, 1H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 180.35, 140.59, 138.13, 123.35, 120.28 (q, *J* = 3.8 Hz), 106.75 (d, *J* = 3.8 Hz), 69.10, 54.78, 38.67.

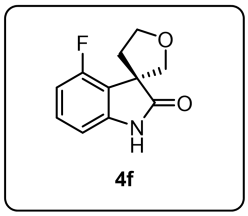
^{19}F NMR (376 MHz, $CDCl_3$): δ -62.44.

HPLC: Daicel column AZ-H; *n*-hexane:*i*-PrOH = 95:5; 1.0 mL/min;

Retention times: 11.6 min (major), 13.2 min (minor).

$[\alpha]_D^{25}$: +17.5 (*c* = 0.6, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{12}H_{10}F_3NO_2 + H]^+$ 258.0736, found 258.0735



4f

(*R*)-4'-fluoro-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2'-on e

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.16 (br, 1H), 7.21 (td, *J* = 8.2, 5.5 Hz, 1H), 6.82 – 6.71 (m, 2H), 4.23 (dq, *J* = 15.1, 7.4 Hz, 2H), 4.12 (q, *J* = 8.8 Hz, 2H), 2.51 – 2.38 (m, 2H).

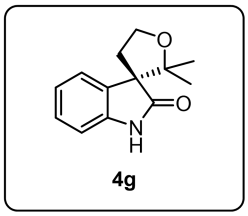
^{13}C NMR(101 MHz, $CDCl_3$): δ 182.05, 158.62 (d, *J* = 247.8 Hz), 142.78 (d, *J* = 9.3 Hz), 130.15 (d, *J* = 8.6 Hz), 118.22 (d, *J* = 19.3 Hz), 110.37 (d, *J* = 20.7 Hz), 106.38 (d, *J* = 3.1 Hz), 75.36, 69.53, 54.07, 37.00.

^{19}F NMR (376 MHz, $CDCl_3$): δ -60.29.

HPLC: Daicel column AS-H; *n*-hexane:*i*-PrOH = 60:40 ; 1.0 mL/min;

Retention times: 16.5 min (major), 20.6 min (minor).

$[\alpha]_D^{25}$: +0.9 (*c* = 0.8, CH_2Cl_2).



4g

(*R*)-2,2-dimethyl-4,5-dihydro-2*H*-spiro[furan-3,3'-indolin]-2' -one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.73 (br, 1H), 7.33 – 7.28 (m, 1H), 7.28 – 7.22 (m, 1H), 7.07 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 4.37 – 4.27 (m, 1H), 4.26 – 4.17 (m, 1H), 2.76 – 2.65 (m, 1H), 2.41 – 2.30 (m, 1H), 1.38 (s, 3H), 1.14 (s, 3H).

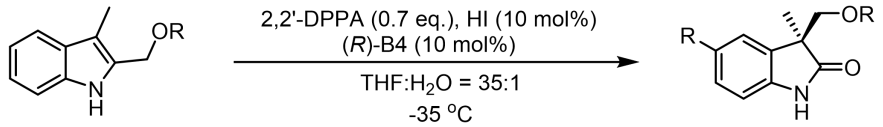
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.26, 140.65, 131.65, 128.10, 124.96, 122.36, 109.77, 84.85, 64.46, 60.02, 35.99, 24.31, 23.31.

HPLC: Daicel column IC; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 9.1 min (major), 13.0 min (minor).

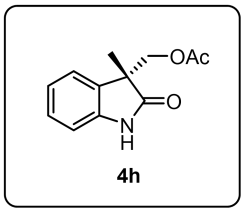
$[\alpha]_D^{25}$: +57.6 (*c* = 0.7, CH_2Cl_2).

General Procedure F:



3h-3i **4h-4i**

At room temperature, to a 5 mL-vial charged with (*R*)-**B4** (10 mol%) and **3h-3i** (0.1 mmol, 1.0 eq.) were added the solvent of THF/H_2O (v/v = 35:1, 0.7 mL). Then HI (10 mol%) in THF (0.1 mL) was added. The mixture was cooled to –35 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.



4h

(*R*)-(3-methyl-2-oxoindolin-3-yl)methyl acetate

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.49 (s, 1H), 7.27 (dd, *J* = 13.3, 7.5 Hz, 2H), 7.09 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 4.55 (d, *J* = 10.8 Hz, 1H), 4.25 (d, *J* = 10.8 Hz, 1H), 1.92 (s, 3H), 1.45 (s, 3H).

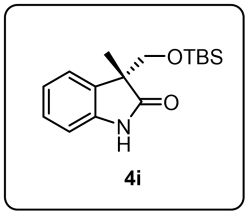
^{13}C NMR(101 MHz, $CDCl_3$): δ 180.64, 170.59, 140.54, 131.79, 128.47, 123.51, 122.72, 109.96, 67.46, 48.55, 29.76, 20.66, 19.77.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 10.5 min (minor), 11.2 min (major).

$[\alpha]_D^{25}$: +7.5 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{12}H_{13}NO_3 + H]^+$ 220.0968, found 220.0969



4i

(*R*)-3-(((tert-butyldimethylsilyl)oxy)methyl)-3-methylindolin-2-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.63 (s, 1H), 7.33 – 7.20 (m, 2H), 7.10 – 7.02 (m, 1H), 6.97 – 6.90 (m, 1H), 3.85 (q, *J* = 9.3 Hz, 2H), 0.78 (s, 9H), -0.02 (s, 3H), -0.08 (s, 3H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 181.95, 140.93, 133.68, 127.81, 123.70, 122.20, 109.56, 68.13, 51.19, 25.66, 18.60, 18.09, -5.53, -5.71.

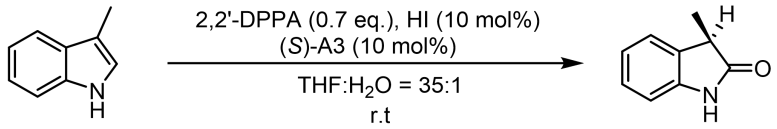
HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 3.9 min (minor), 5.4 min (major).

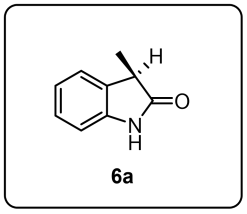
$[\alpha]_D^{25}$: +8.2 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{16}H_{25}NO_2Si + H]^+$ 292.1727, found 292.1725

General Procedure G:



At room temperature, to a 5 mL-vial charged with (*S*)-**3** (10 mol%) and **5a** (0.1 mmol, 1.0 eq.) were added the solvent of THF/H_2O (v/v = 35:1, 0.7 mL). Then HI (10 mol%) in THF (0.1 mL) was added. The mixture was stirred at room temperature followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product.



(*R*)-3-methylindolin-2-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.67 (br, 1H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 7.8 Hz, 1H), 3.51 (q, *J* = 7.6 Hz, 1H), 1.54 (d, *J* = 7.7 Hz, 3H).

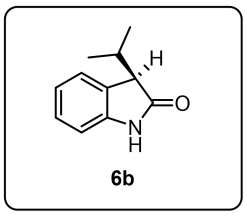
^{13}C NMR(101 MHz, $CDCl_3$): δ 182.16, 141.54, 131.36, 127.96, 123.79, 122.39, 110.03, 41.28, 15.29.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

Retention times: 7.0 min (major), 9.4 min (minor).

$[\alpha]_D^{25}$: -20.5 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_9H_9NO\ H]^+$ 148.0757, found 148.0761



(*R*)-3-isopropylindolin-2-one

^{1}H NMR (400 MHz, $CDCl_3$): δ 9.40 (br, 1H), 7.29 (d, *J* = 7.3 Hz, 1H), 7.24 (t, *J* = 7.7 Hz, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 6.96 (d, *J* = 7.7 Hz, 1H), 3.44 (s, 1H), 2.55 (m, 1H), 1.17 (d, *J* = 7.0 Hz, 3H), 0.95 (d, *J* = 6.8 Hz, 3H).

^{13}C NMR(101 MHz, $CDCl_3$): δ 180.60, 142.26, 128.42, 127.87, 124.66, 122.08, 109.83, 52.33, 30.78, 19.99, 17.99.

HPLC: Daicel column AD-H; *n*-hexane:*i*-PrOH = 90:10 ; 1.0 mL/min;

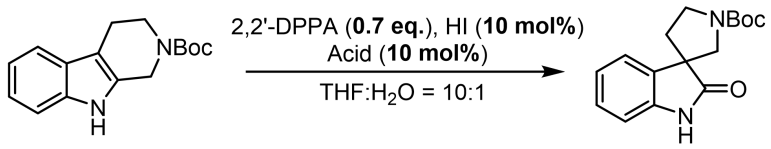
Retention times: 6.0 min (major), 9.3 min (minor).

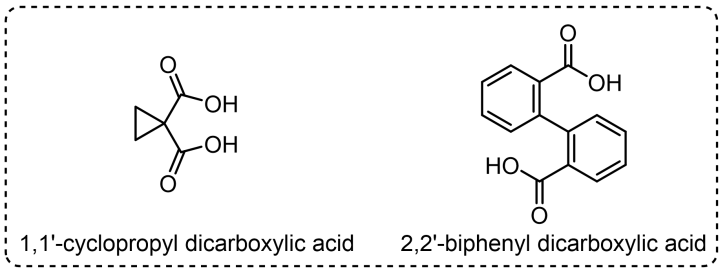
$[\alpha]_D^{25}$: -23.4 (*c* = 0.8, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{11}H_{13}NO + H]^+$ 176.1070, found 176.1073

6. Mechanistic Study

(1) Control Experiment



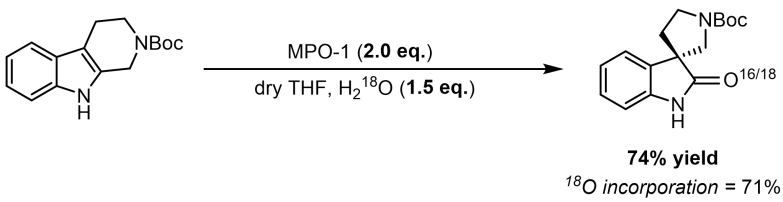


Entry	Acid	Yield (%)
1	1,1'-cyclopropyl dicarboxylic acid	92% (15 min)
2	2,2'-biphenyl dicarboxylic acid	trace (2 h)
3	without CPA and dicarboxylic acid	N.R

Entry 1&2: At room temperature, to a solution of **2a** (0.1 mmol), HI (10 mol%) in THF/H_2O (v/v =10:1) was added 1,1'-cyclopropyl dicarboxylic acid or 2,2'-biphenyl dicarboxylic acid (10 mol%), then 2,2'-DPPA (0.7 eq.) was added. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was directly subjected to silica gel column chromatography to give **3a**.

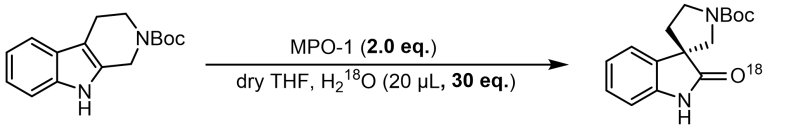
Entry 3: At room temperature, to a solution of **2a** (0.1 mmol), HI (10 mol%) in THF/H_2O (v/v =10:1) was added 2,2'-DPPA (0.7 eq.) was added. The reaction progress was monitored by TLC, **3a** can not be observed from this reaction condition.

(2) Isotopic labeling



At room temperature, to a solution of **2a** in anhydrous THF was added $H_2{}^{18}O$ (1.5 eq.). Then MPO-1 (2.0 eq.) was added. The reaction progress was monitored by

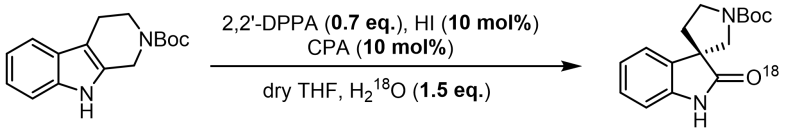
TLC. Upon completion, the reaction mixture was directly subjected to silica gel column chromatography to give **3a**. ^{16}O and ^{18}O incorporation were determined by LC-MS. The ratio of ^{16}O and ^{18}O incorporation is 1:2.5, the result was suggests that there are two reaction mechanisms when MPO was used as oxidant.



74% yield

^{18}O incorporation >98%

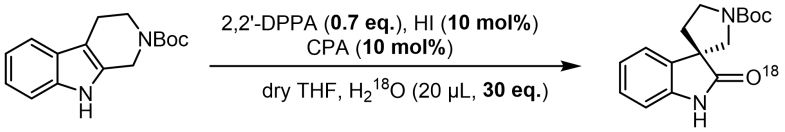
At room temperature, to a solution of **2a** in anhydrous THF was added $H_2{}^{18}O$ (1.5 eq.). Then MPO-1 (2.0 eq.) was added. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was directly subjected to silica gel column chromatography to give **3a**. ^{16}O and ^{18}O incorporation were determined by LC-MS. The insertion rate of ^{18}O is greater than 98%.



93% yield

^{18}O incorporation = 83%

At room temperature, to a solution of **2a** in anhydrous THF was added $H_2{}^{18}O$ (1.5 eq.) and HI (10 mol%). Then 2,2'-DPPA (0.7 eq.) was added. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was directly subjected to silica gel column chromatography to give **3a**. ^{16}O and ^{18}O incorporation were determined by LC-MS. The insertion rate of ^{18}O is 83%. This result ruled out the epoxidation mechanism when 2,2'-DPPA was used as oxidant.

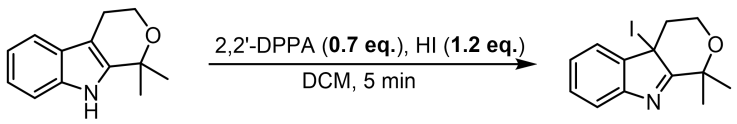


90% yield

^{18}O incorporation >98%

At room temperature, to a solution of **2a** in anhydrous THF was added $H_2{}^{18}O$ (1.5 eq.) and HI (10 mol%). Then 2,2'-DPPA (0.7 eq.) was added. The reaction progress was monitored by TLC. Upon completion, the reaction mixture was directly subjected to silica gel column chromatography to give **3a**. ^{16}O and ^{18}O incorporation were determined by LC-MS. The insertion rate of ^{18}O greater than 98%.

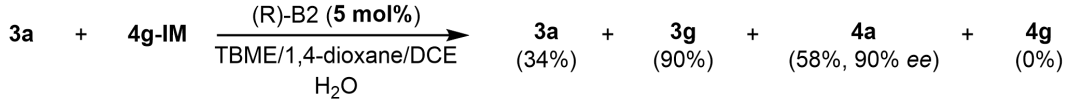
(3) Isolation of Reaction Intermediate and Cross-Over Experiment.



At room temperature, to a solution of 2,2'-DPPA (0.7 eq.) in DCM was slowly added solution of **3g** (1.0 eq.) and HI (1.2 eq.) in DCM. The mixture was stirred at the same temperature for 5 min. The mixture was directly subjected to silica gel column chromatography (eluent: PE/EA = 5:1) to give the pure intermediate **4g-IM**.

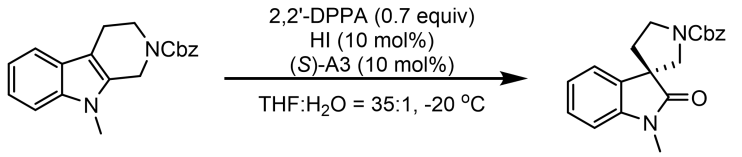
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 7.5 Hz, 1H), 7.55 (d, *J* = 7.3 Hz, 1H), 7.37 (m, 1H), 7.31 (m, 1H), 4.24 (t, *J* = 11.6 Hz, 1H), 3.99 (m, 1H), 2.71 (d, *J* = 15.0 Hz, 1H), 2.10 (s, 3H), 1.67 (s, 3H), 1.62 – 1.50 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 182.82, 149.85, 143.70, 129.36, 126.96, 123.13, 121.78, 76.82, 59.27, 42.80, 37.14, 29.00, 27.23.



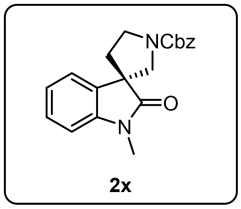
At 0 °C, to a mixture of **4g-IM** (0.1 mmol) and **3a** (0.12 mmol) in mixed solvent DCE/1,4-dioxane/TBME (v/v/v = 1:1:1, 0.6 mL) and H_2O (0.1 mL) was slowly added a solution of (*R*)-B2 (5 mol%) in mixed solvent DCE/1,4-dioxane/TBME (v/v/v = 1:1, 0.3 mL). The reaction mixture was stirred for 1 h, then the mixture was directly subjected to silica gel column chromatograph to form **4a**. The *ee* was determined by HPLC with a chiral stationary phase.

(4) Asymmetric Oxidative Rearrangement of *N*-protected THβC



At room temperature, to a 5 mL-vial charged with (*S*)-**A3** (10 mol%) and **1v** (0.1 mmol, 1.0 eq.) were added the solvent of THF/H_2O (v/v = 35:1, 0.7 mL). Then HI (10 mol%) in THF (0.05 mL) was added. The mixture was cooled to –20 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (0.07 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected

to silica gel column chromatography to afford the pure product. The *ee* was determined by HPLC with a chiral stationary phase.



2x

benzyl (*R*)-1-methyl-2-oxospiro[indoline-3,3'-pyrrolidine]-1'-carboxylate

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 – 7.27 (m, 6H), 7.24 – 7.14 (m, 1H), 7.14 – 7.02 (m, 1H), 6.90 (d, *J* = 7.5 Hz, 1H), 5.28 – 5.14 (m, 2H), 4.04 – 3.91 (m, 1H), 3.90 – 3.77 (m, 2H), 3.75 – 3.61 (m, 1H), 3.26 (s, 3H), 2.52 – 2.39 (m, 1H), 2.17 – 2.00 (m, 1H)**.**

^{13}C NMR(101 MHz, $CDCl_3$): δ 177.24, 154.81, 142.88, 136.67, 132.37, 128.61, 128.12, 128.01, 127.85, 123.16, 122.47, 108.41, 67.10, 54.20, 52.89, 51.96, 45.85, 35.46, 26.50**.**

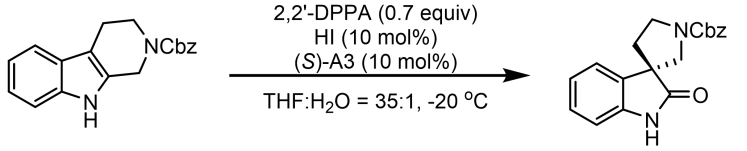
HPLC: Daicel column OD-H; *n*-hexane:*i*-PrOH = 90:10; 1.0 mL/min;

Retention times: 24.2 min (minor), 28.4 min (major).

$[\alpha]_D^{25}$: -30.2 (*c* = 1.0, CH_2Cl_2).

HRMS(ESI): m/z calcd for $[C_{20}H_{20}N_2O_3 + H]^+$ 337.1547, found 337.1550

(5) Gram-scale synthesis of 2f



1f
1.0 g (3.3 mmol)

2f
85% yield, 97% *ee*

At room temperature, to a 5 mL-vial charged with (*S*)-**A3** (10 mol%) and **1f** (1.0 g, 3.3 mmol, 1.0 eq.) were added the solvent of THF/H_2O (v/v = 35:1, 14 mL). Then HI (10 mol%) in THF (0.5 mL) was added. The mixture was cooled to –20 °C and stirred for 5 min followed by slow addition of 2,2'-DPPA (2.3 mmol, 0.7 eq.). The reaction progress was monitored by TLC. Upon completion, the residue was directly subjected to silica gel column chromatography to afford the pure product. The *ee* was determined by HPLC with a chiral stationary phase.

Reference

[1] L. Ding, R.-D. Gao and S.-L. You, Palladium(0)-Catalyzed Intermolecular Asymmetric Cascade Dearomatization Reaction of Indoles with Propargyl Carbonate, *Chem.–Eur. J.*, 2019, **25**, 4330-4334.

[2] C.-M. Zhu, R.-B. Liang, Y. Xiao, W. Zhou, Q.-X. Tong and J.-J. Zhong, Metal-free and site-selective α-C–H functionalization of tetrahydrofuran enabled by the photocatalytic generation of bromine radicals, *Green Chem.*, 2023, **25**, 960-965.

[3] G. Zhao, L. Liang, E. Wang, S. Lou, R. Qi and R. Tong, Fenton chemistry enables the catalytic oxidative rearrangement of indoles using hydrogen peroxide, *Green Chem.*, 2021, **23**, 2300-2307.

[4] W. Yang and J. Sun, Organocatalytic Enantioselective Synthesis of 1,4-Dioxanes and Other Oxa-Heterocycles by Oxetane Desymmetrization, *Angew. Chem. Int. Ed.*, 2016, **55**, 1868-1871.

[5] F. Mandrelli, A. Blond, T. James, H. Kim and B. List, Deracemizing α-Branched Carboxylic Acids by Catalytic Asymmetric Protonation of Bis-Silyl Ketene Acetals with Water or Methanol, *Angew. Chem. Int. Ed.*, 2019, **58**, 11479-11482.

[6] C. Qian, P. Li and J. Sun, Catalytic Enantioselective Synthesis of Spirooxindoles by Oxidative Rearrangement of Indoles, *Angew. Chem. Int. Ed.*, 2021, **60**, 5871-5875.

NMR Spectra and HPLC analysis

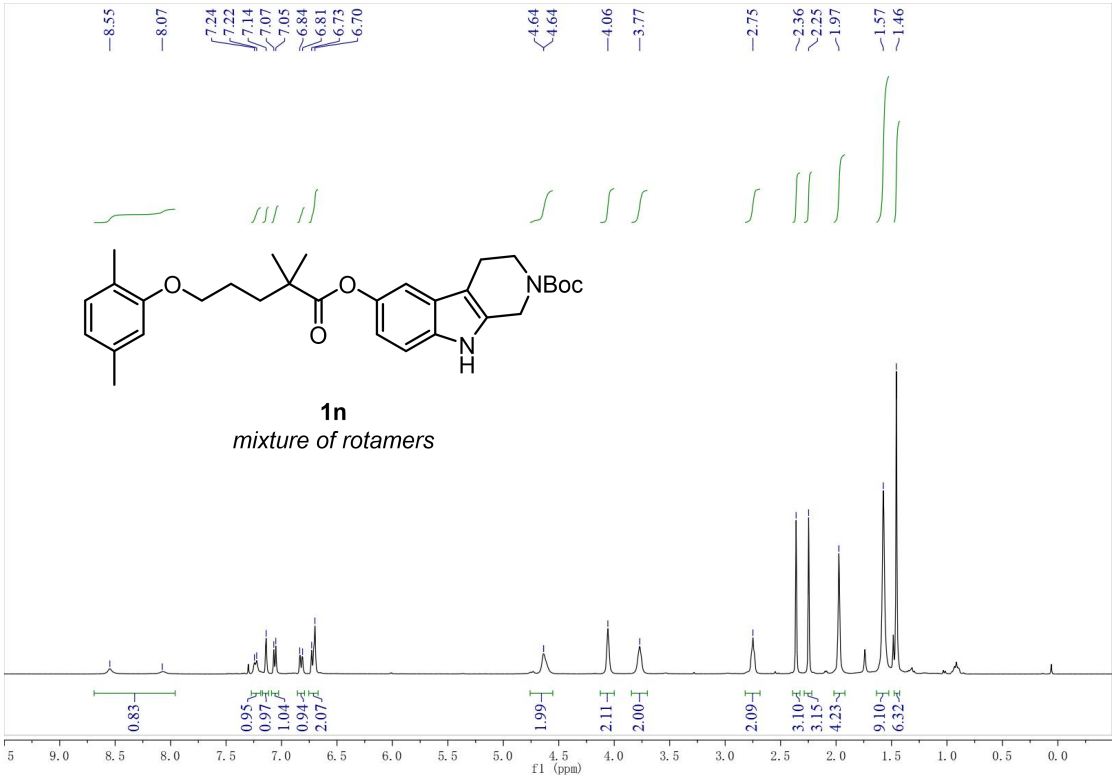


Figure S1. ^{1}H NMR spectra of **1o**

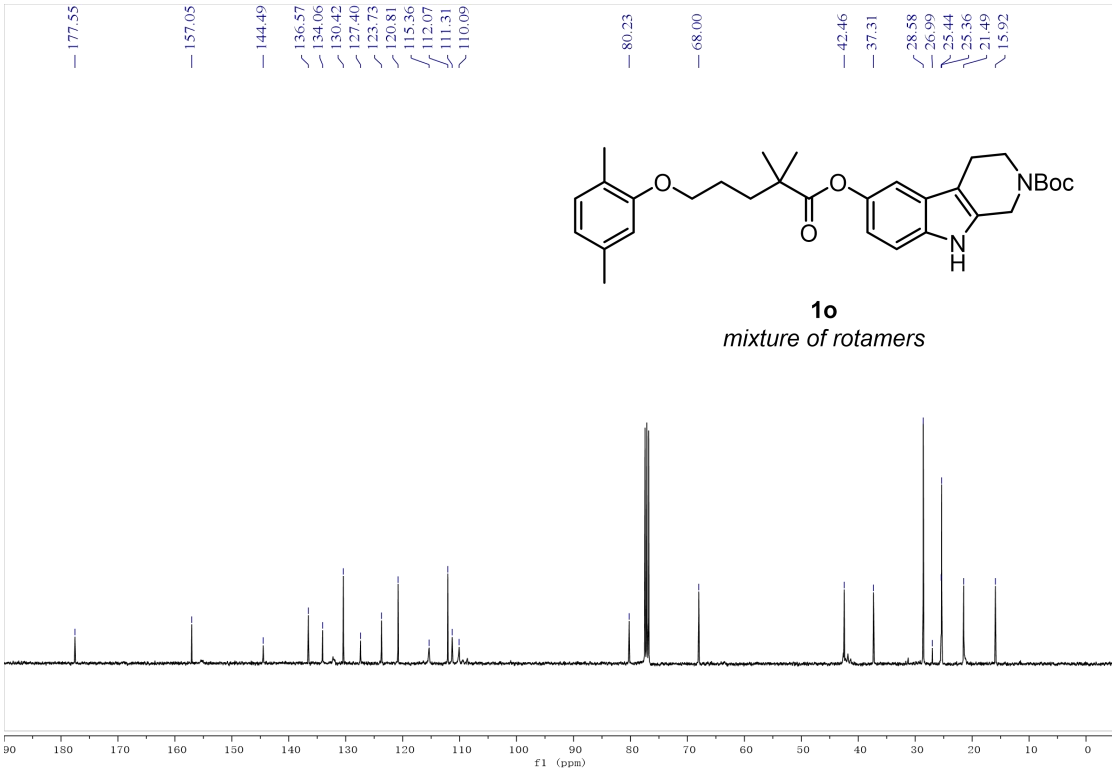


Figure S2. ^{13}C NMR spectra of **1o**

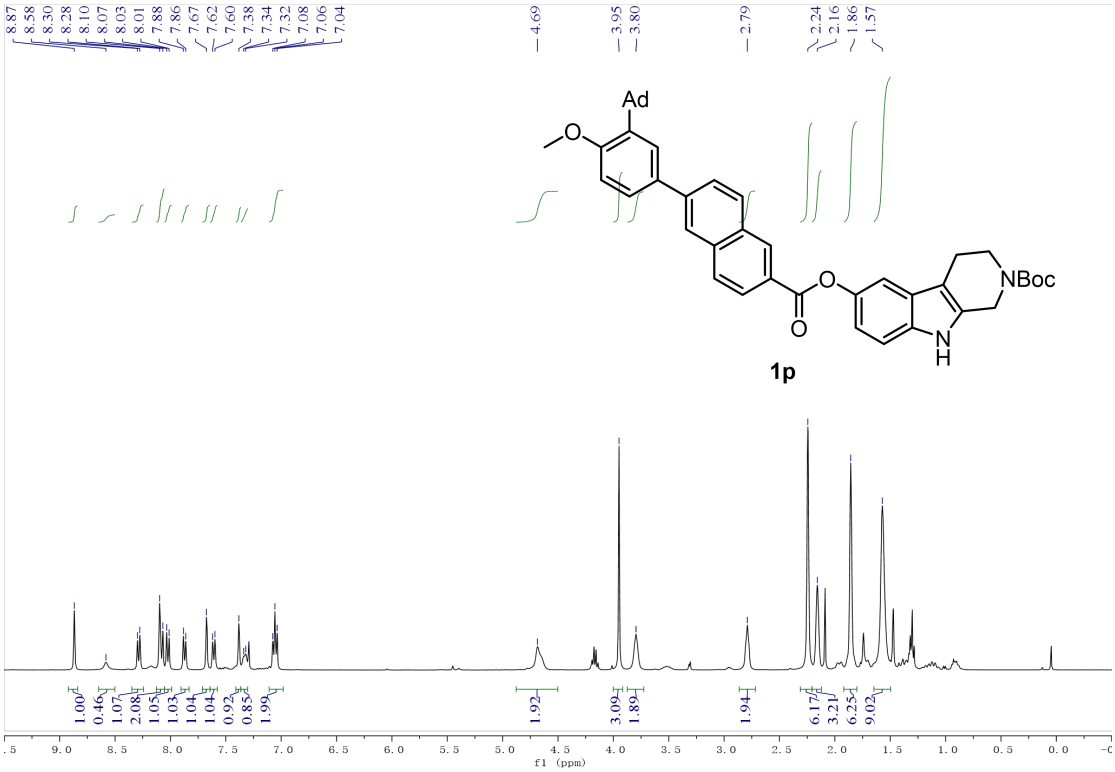


Figure S3. ^{1}H NMR spectra of **1p**

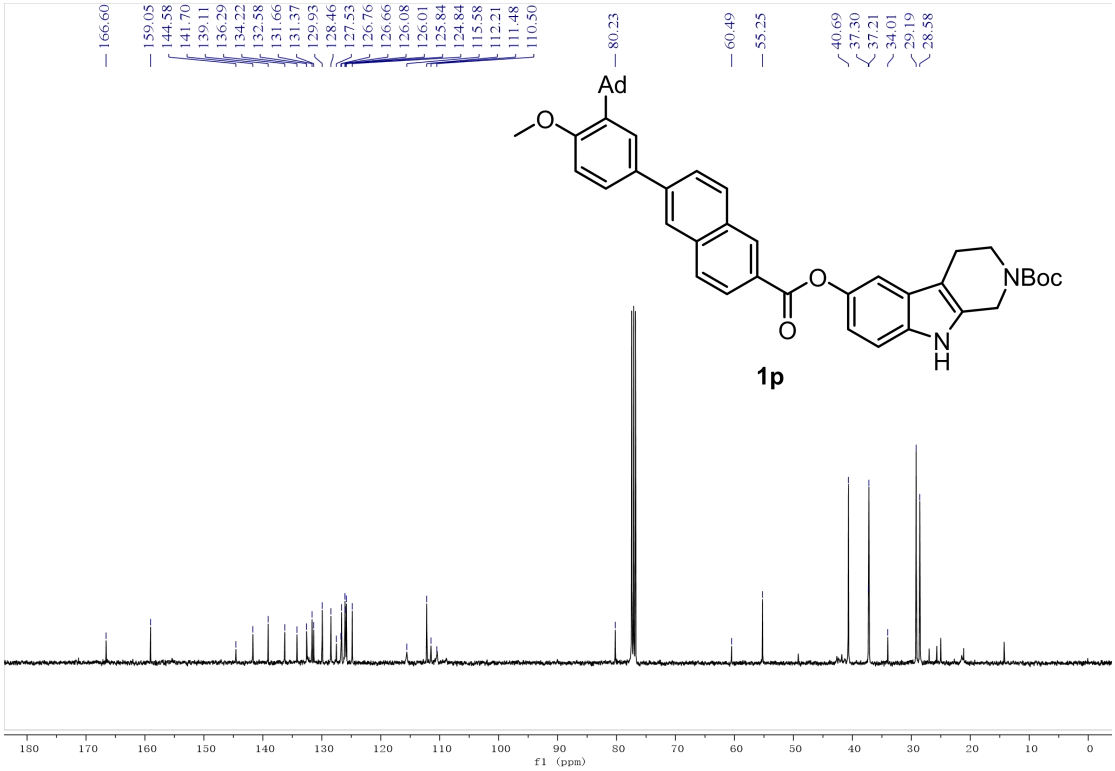


Figure S4. ^{13}C NMR spectra of **1p**

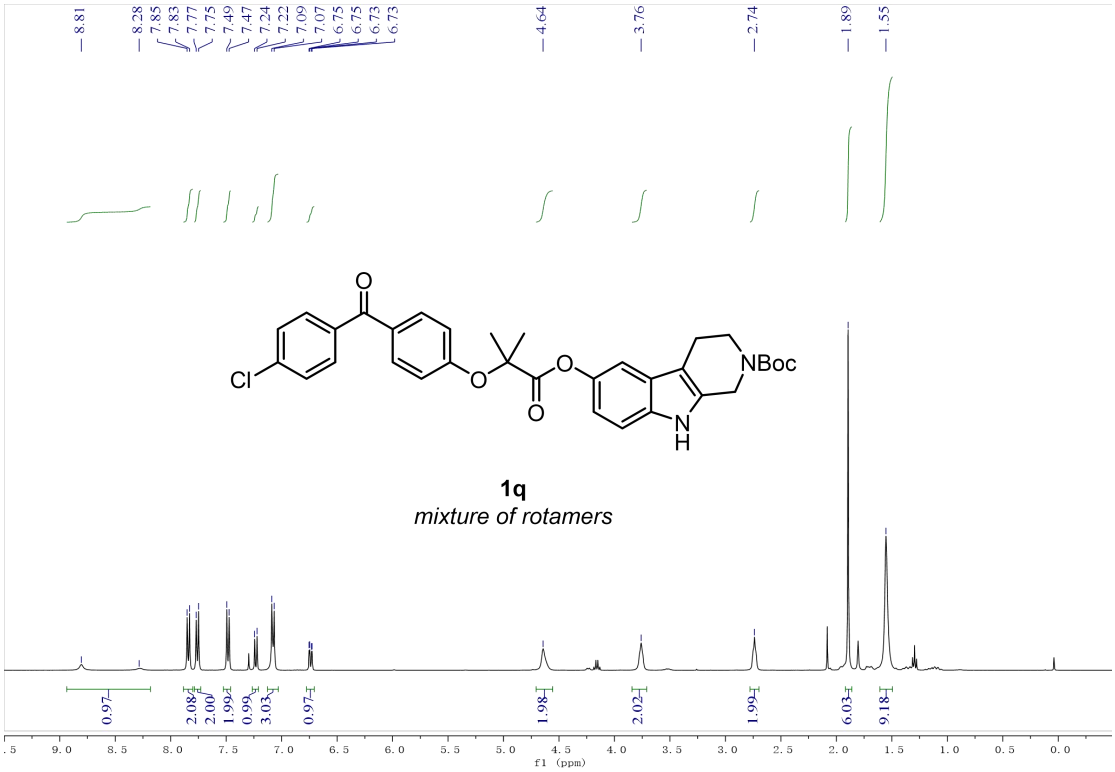


Figure S5. ^{1}H NMR spectra of **1q**

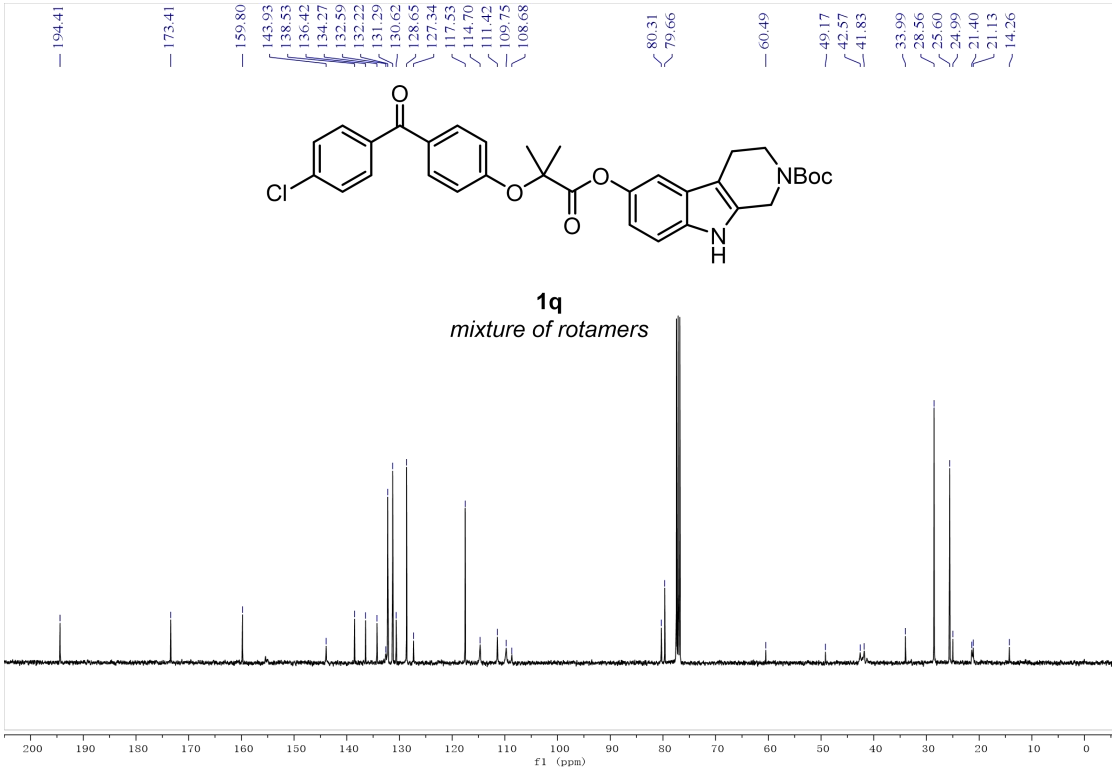


Figure S6. ^{13}C NMR spectra of **1q**

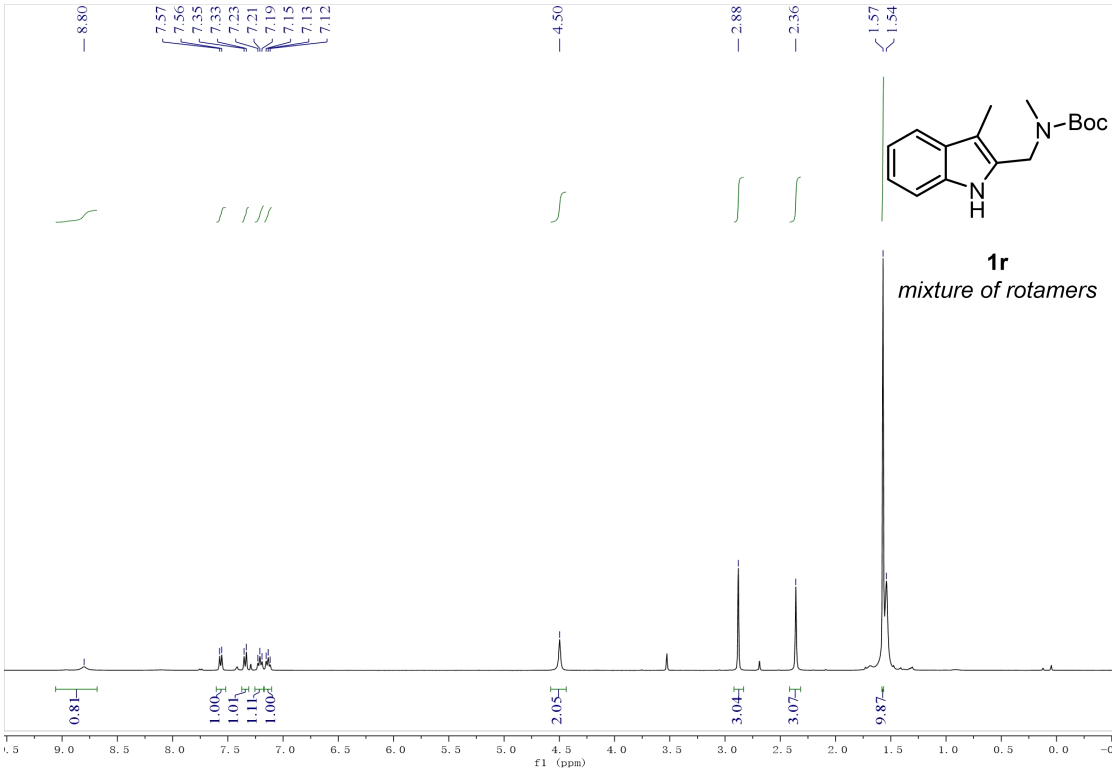


Figure S7. ^{1}H NMR spectra of **1r**

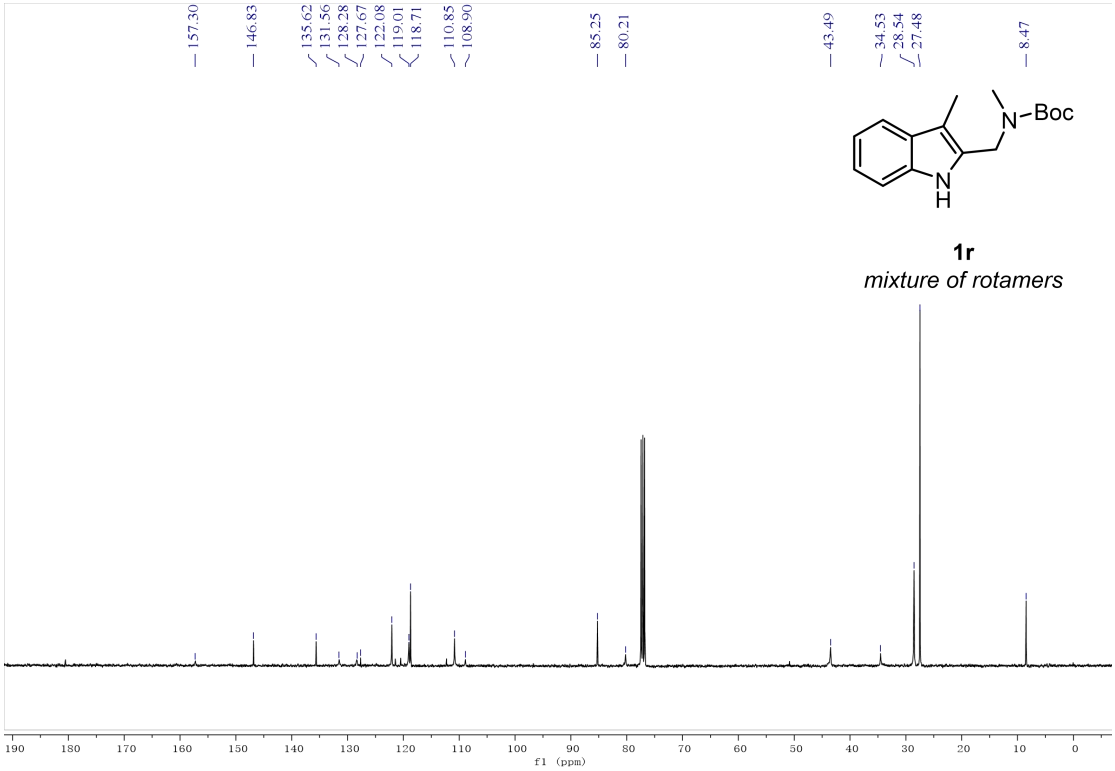


Figure S8. ^{13}C NMR spectra of **1r**

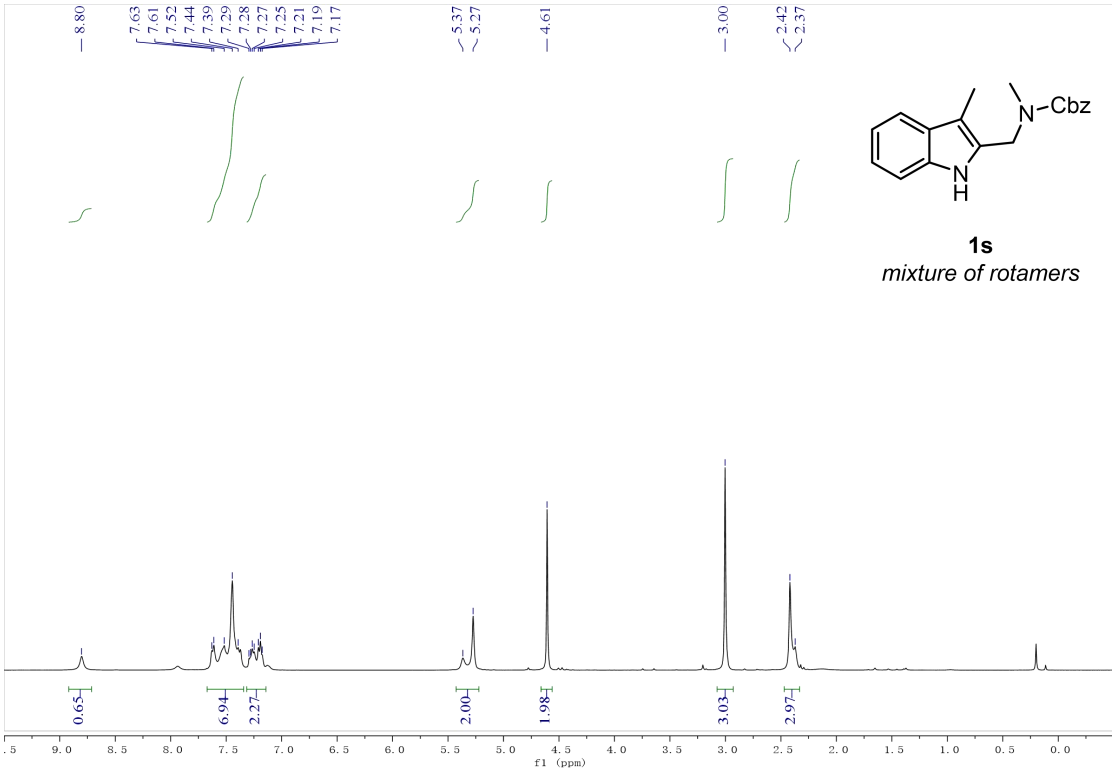


Figure S9. ^{1}H NMR spectra of **1s**

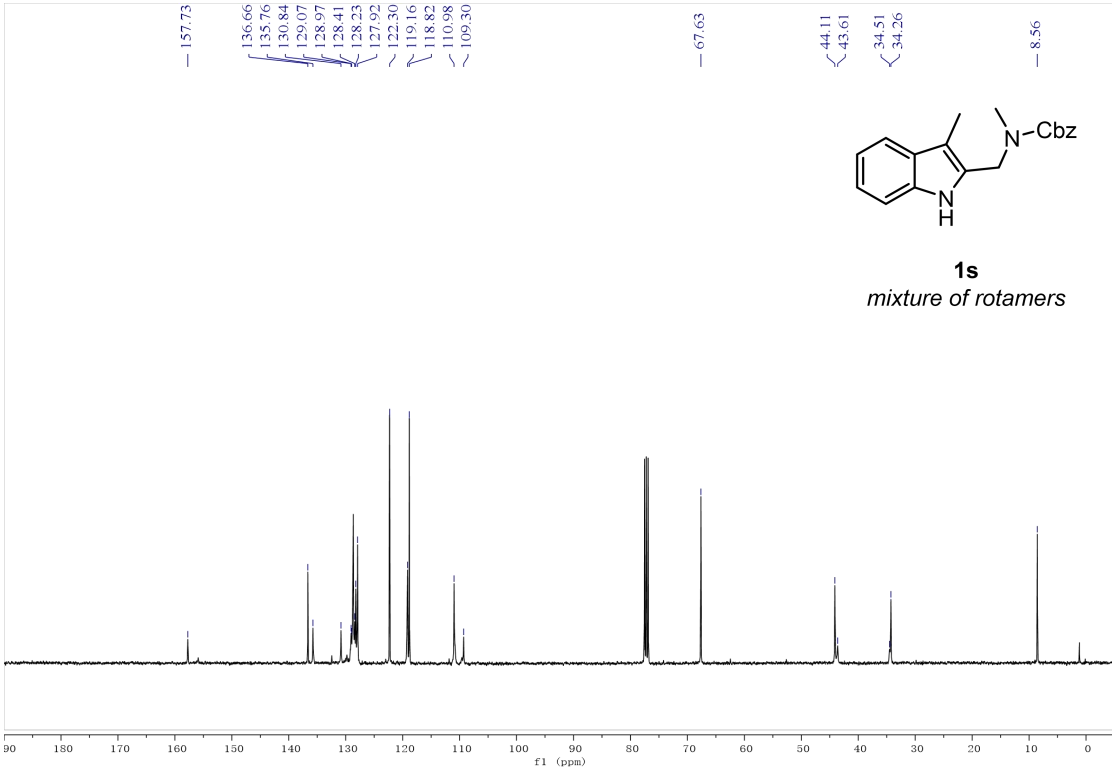


Figure S10. ^{13}C NMR spectra of **1s**

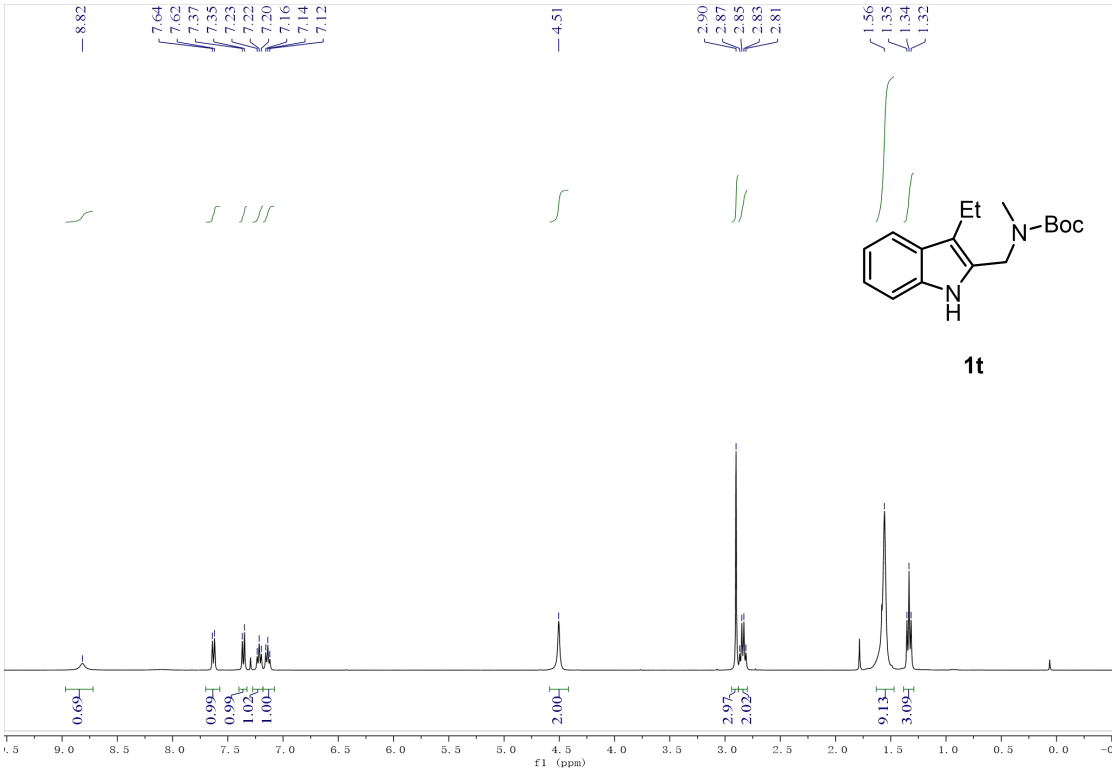


Figure S11. ^{1}H NMR spectra of **1t**

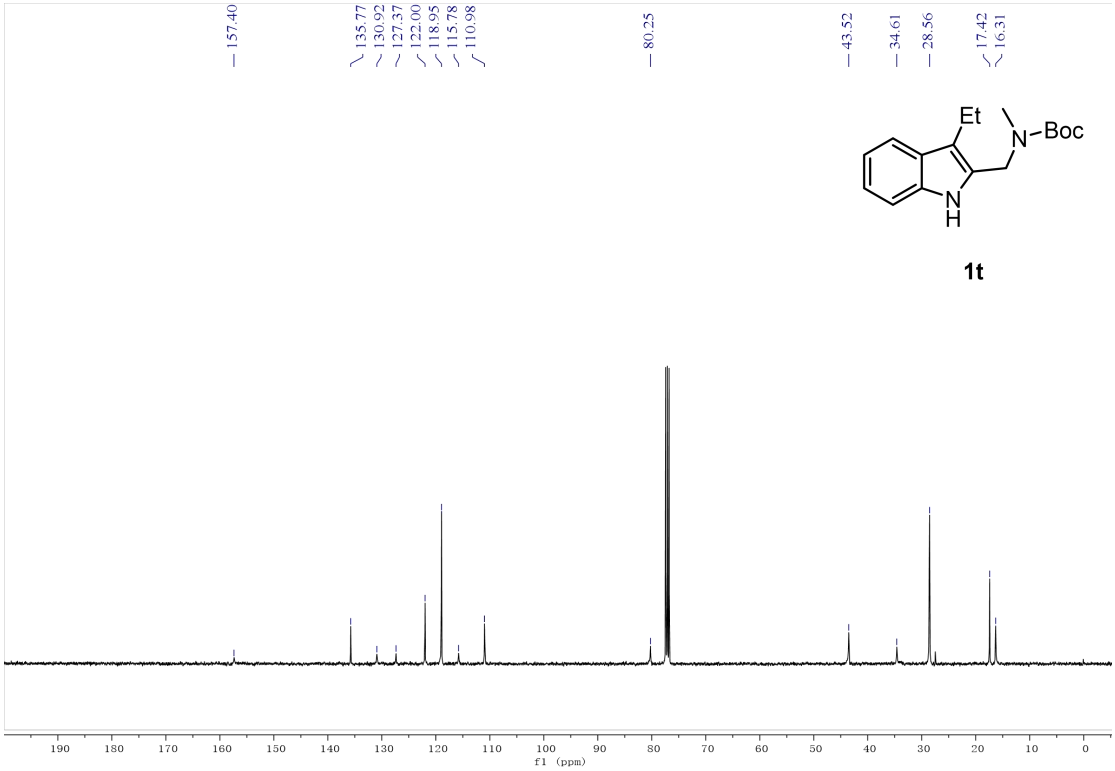


Figure S12. ^{13}C NMR spectra of **1t**

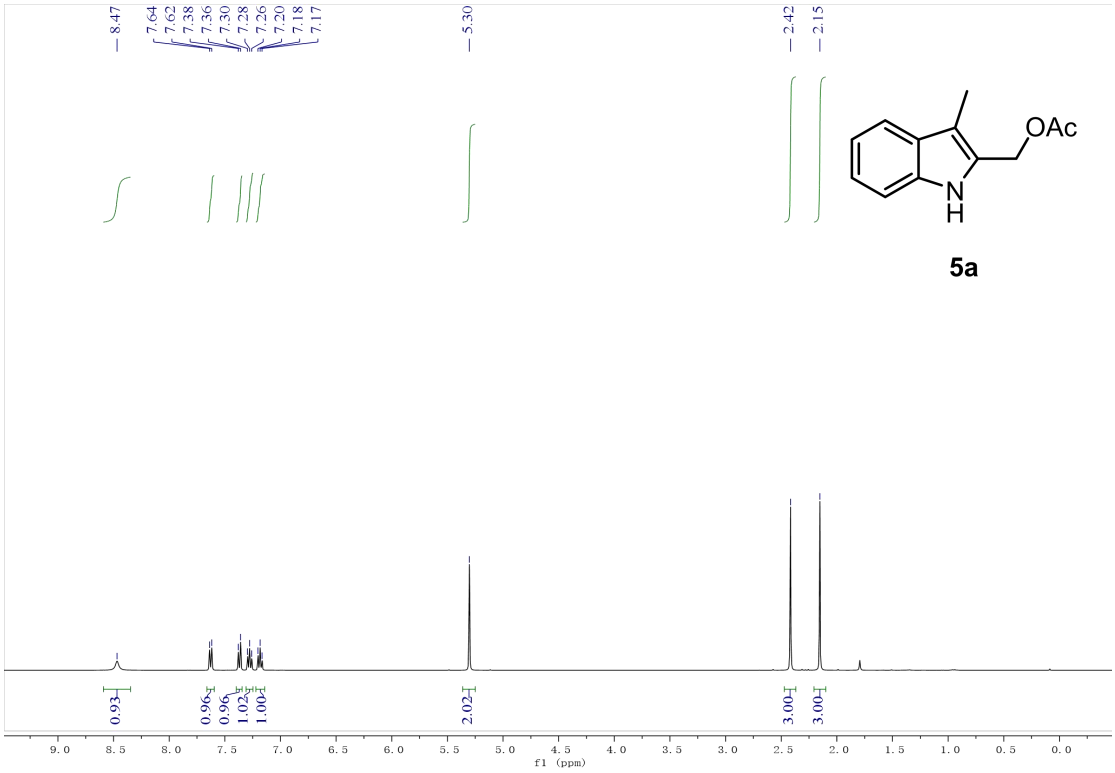


Figure S13. ^{1}H NMR spectra of **5a**

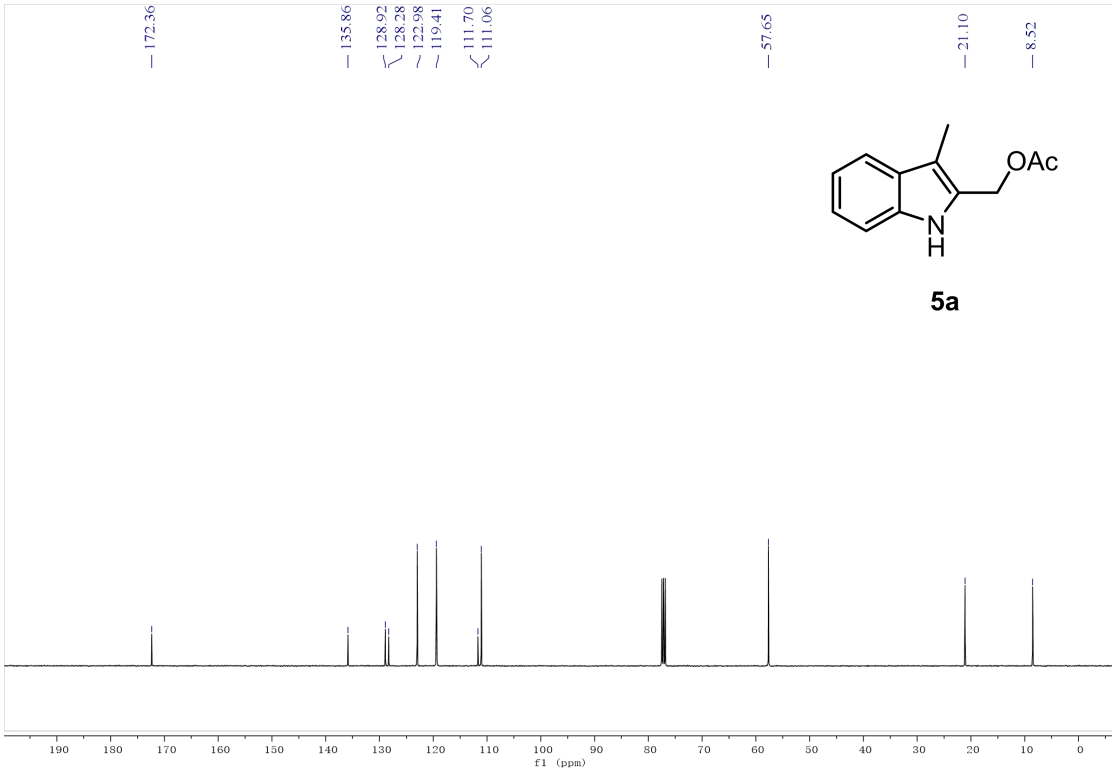


Figure S14. ^{13}C NMR spectra of **5a**

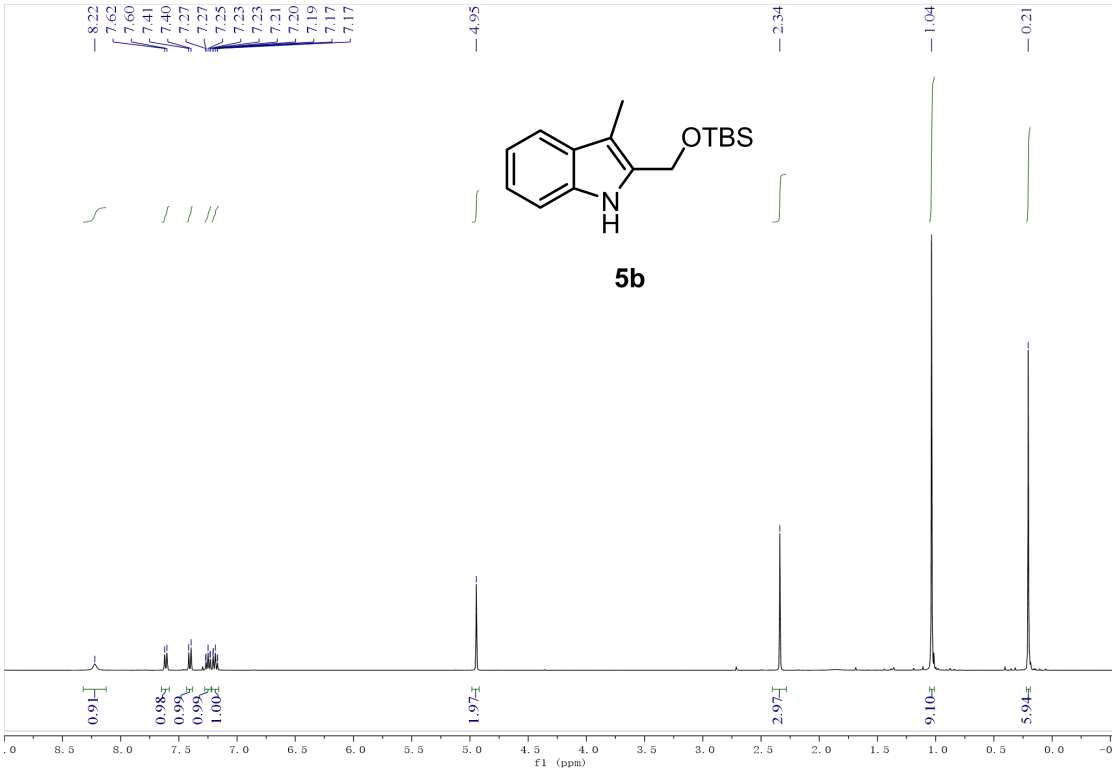


Figure S15. ^{1}H NMR spectra of **5b**

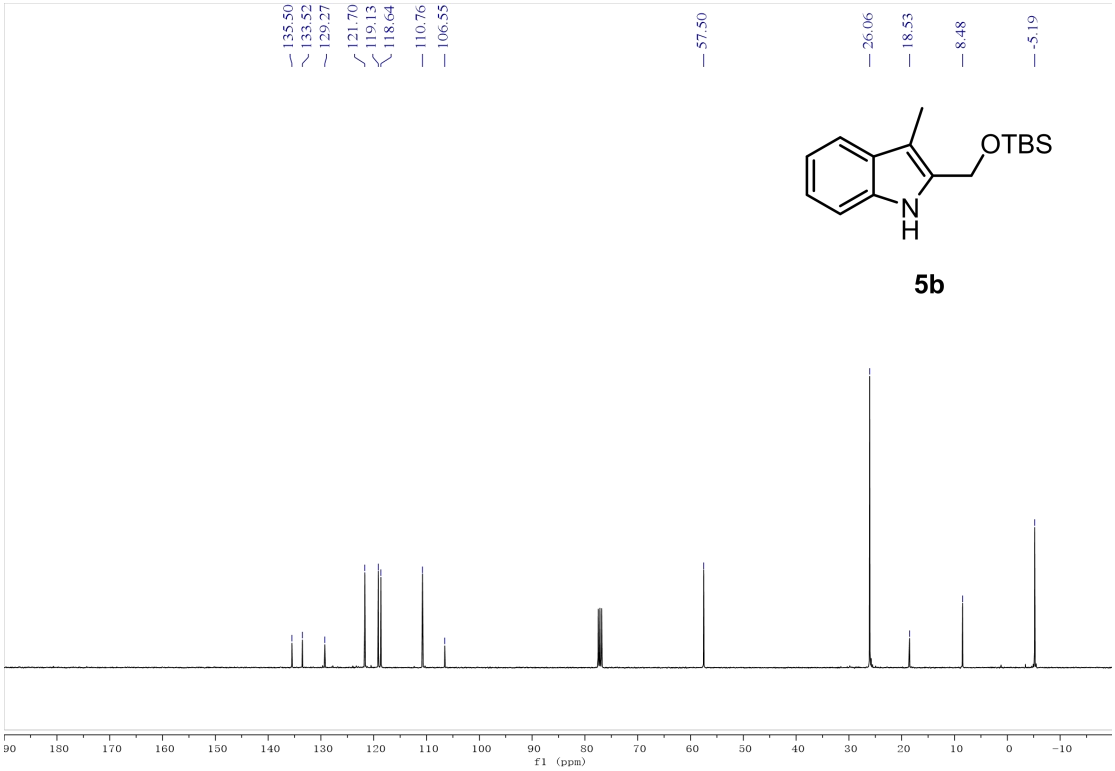


Figure S16. ^{13}C NMR spectra of **5b**

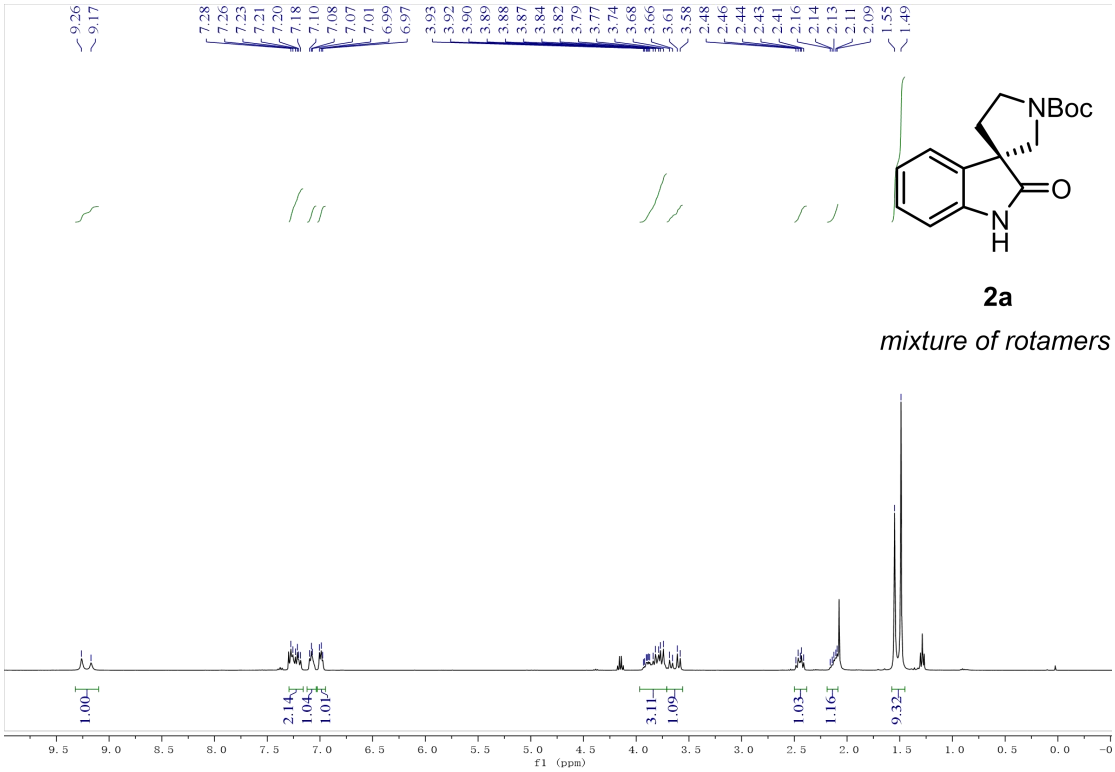


Figure S17. ^{1}H NMR spectra of **2a**

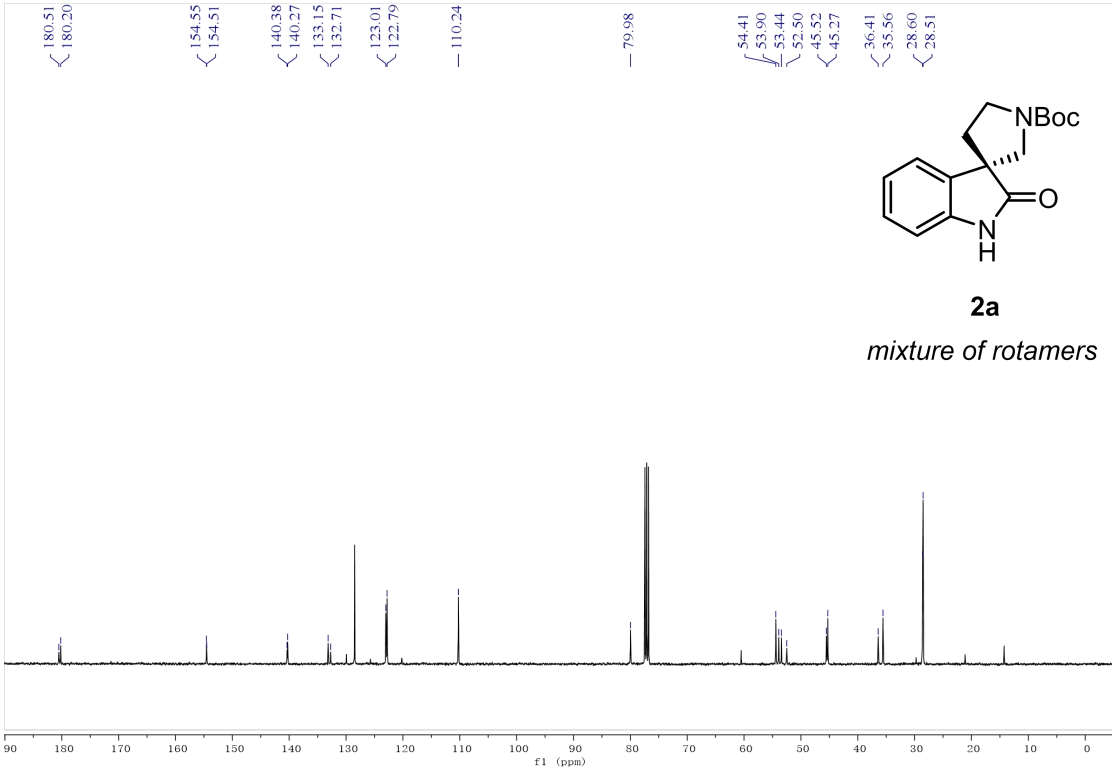


Figure S18. ^{13}C NMR spectra of **2a**

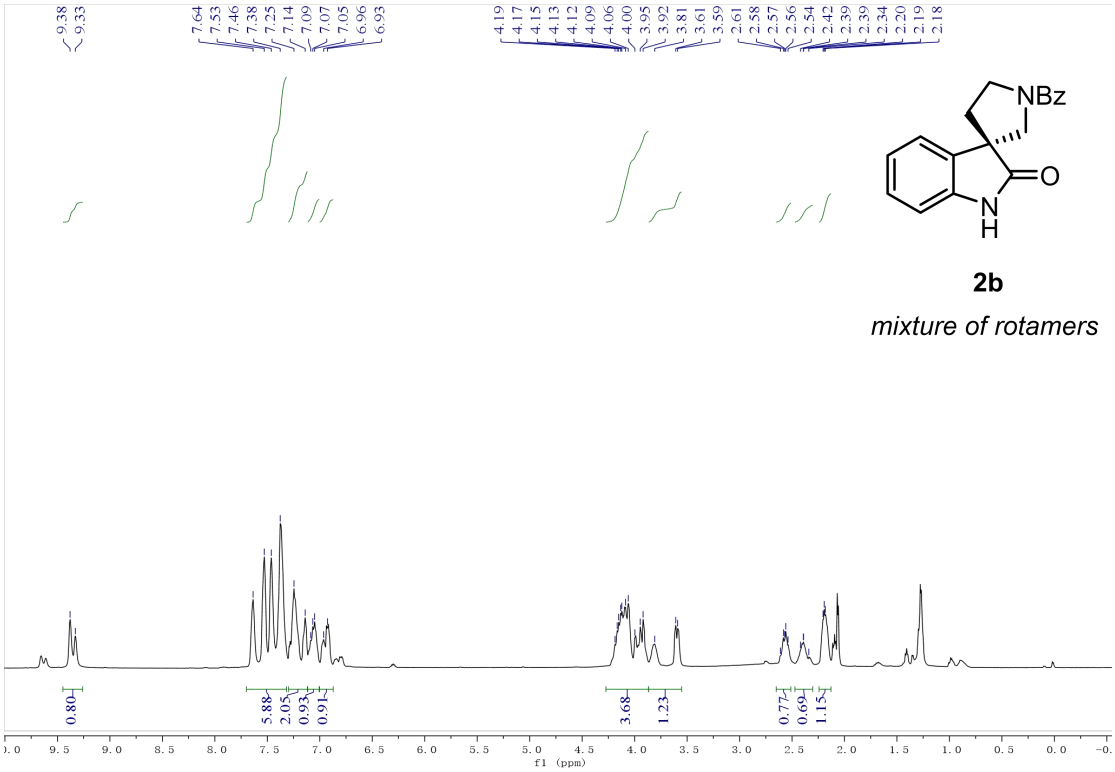


Figure S19. ^{1}H NMR spectra of **2b**

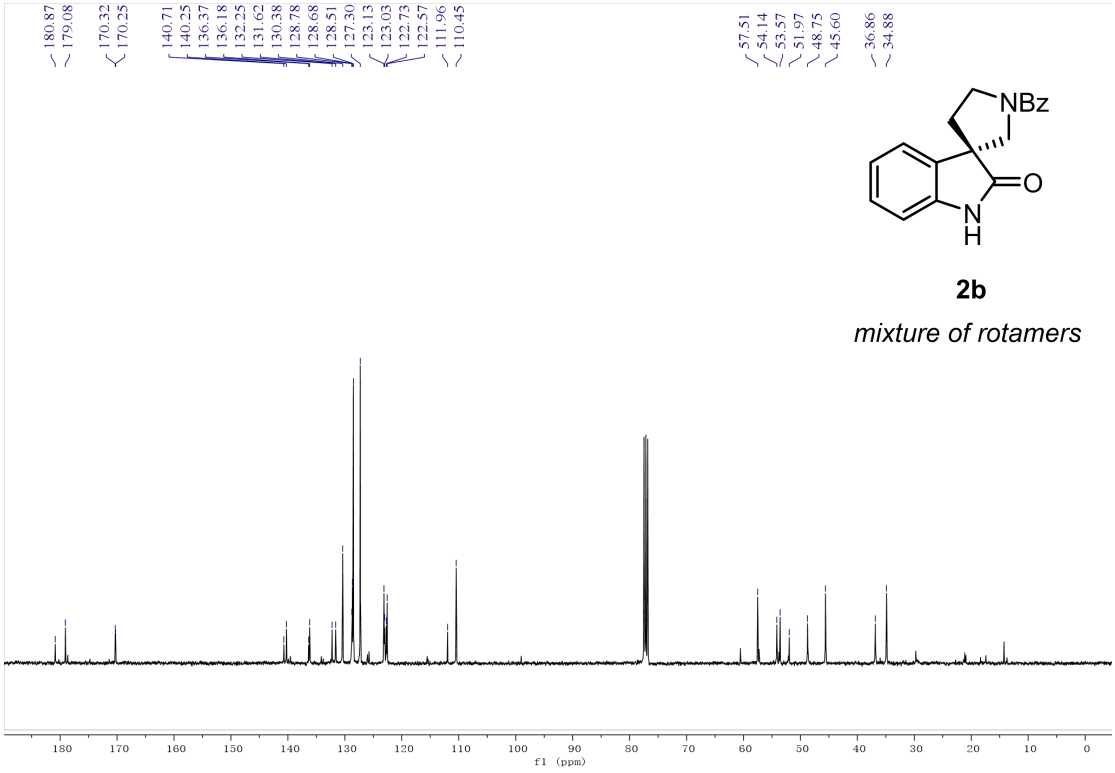


Figure S20. ^{13}C NMR spectra of **2b**

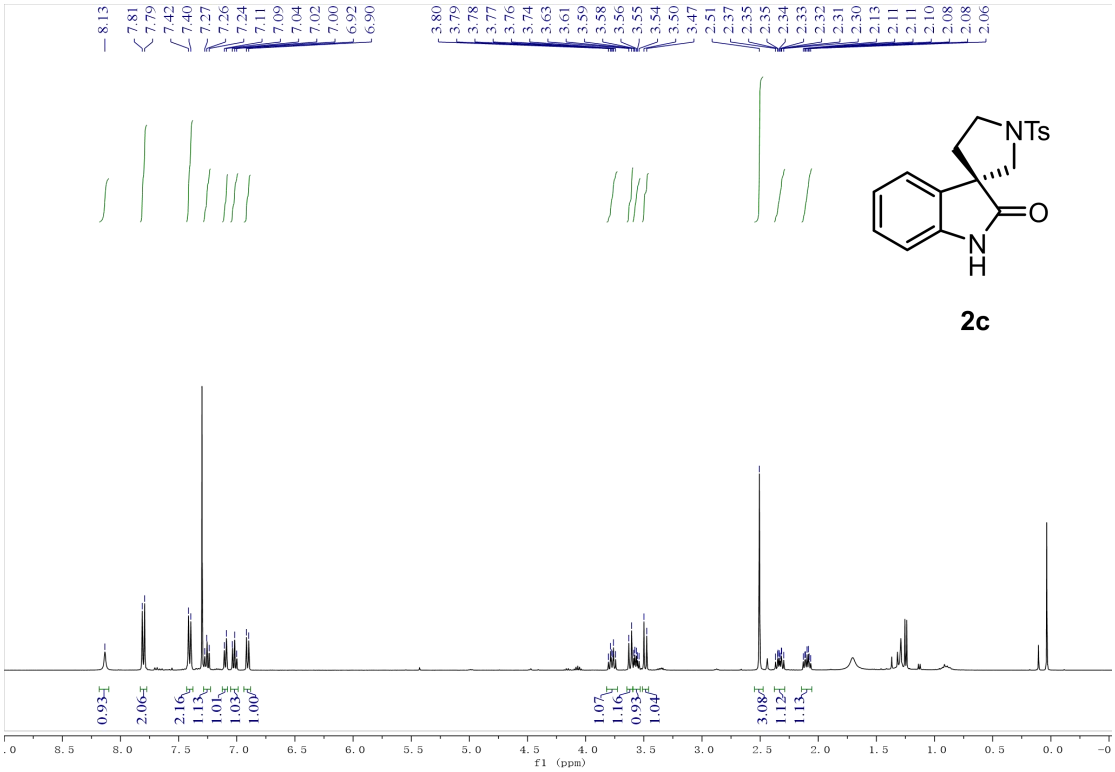


Figure S21. ^{1}H NMR spectra of **2c**

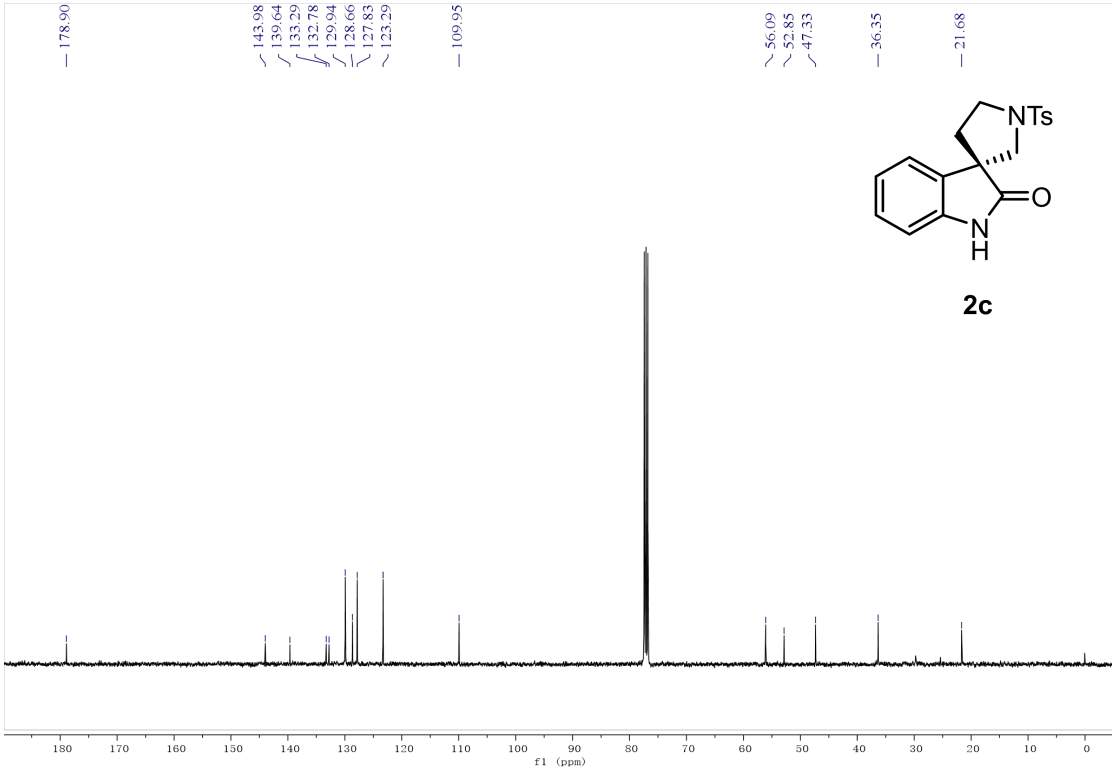


Figure S22. ^{13}C NMR spectra of **2c**

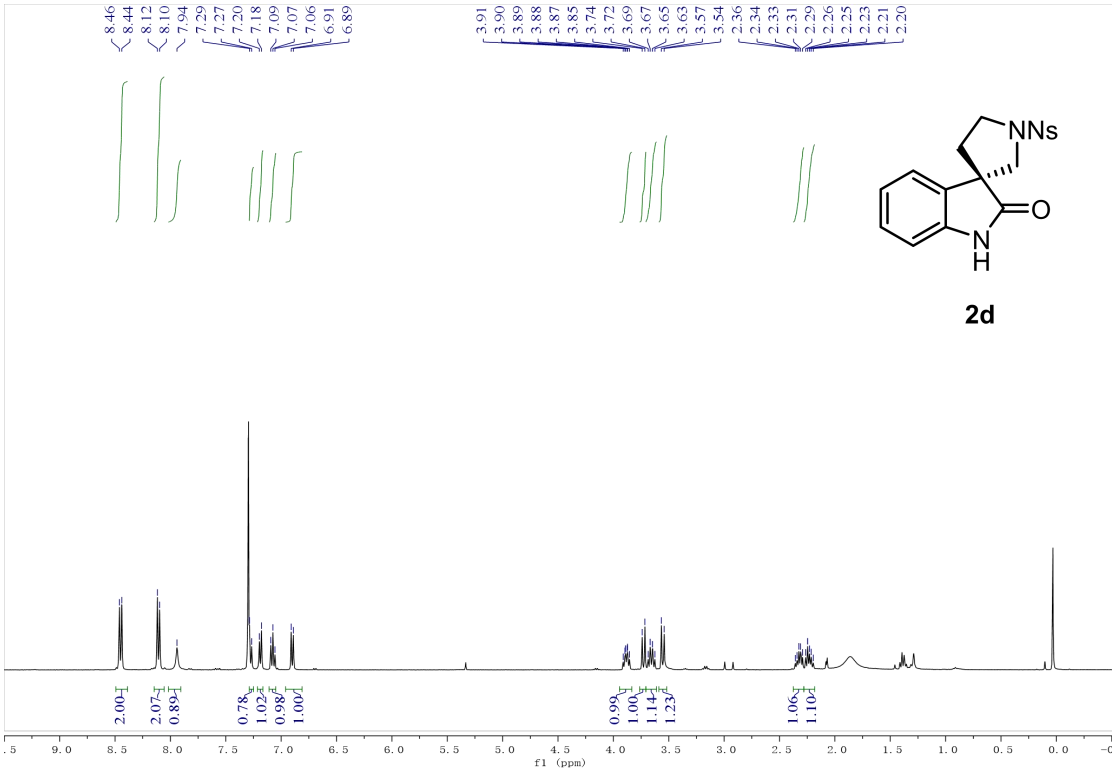


Figure S23. ^{1}H NMR spectra of **2d**

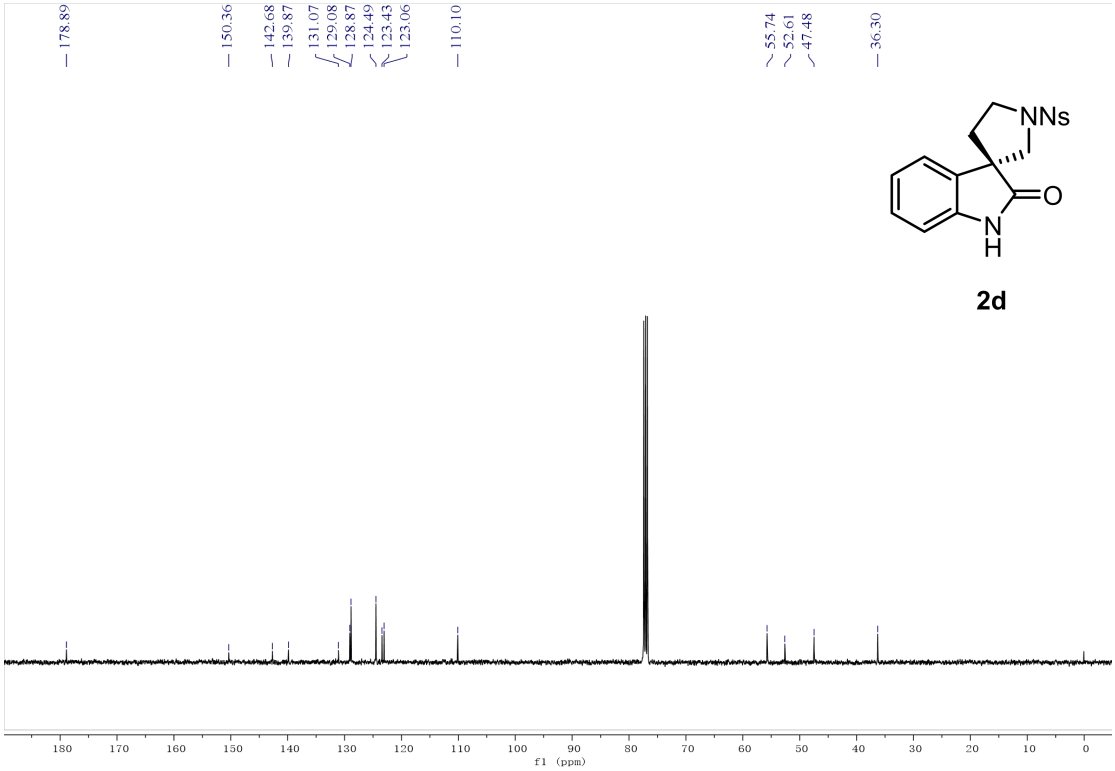


Figure S24. ^{13}C NMR spectra of **2d**

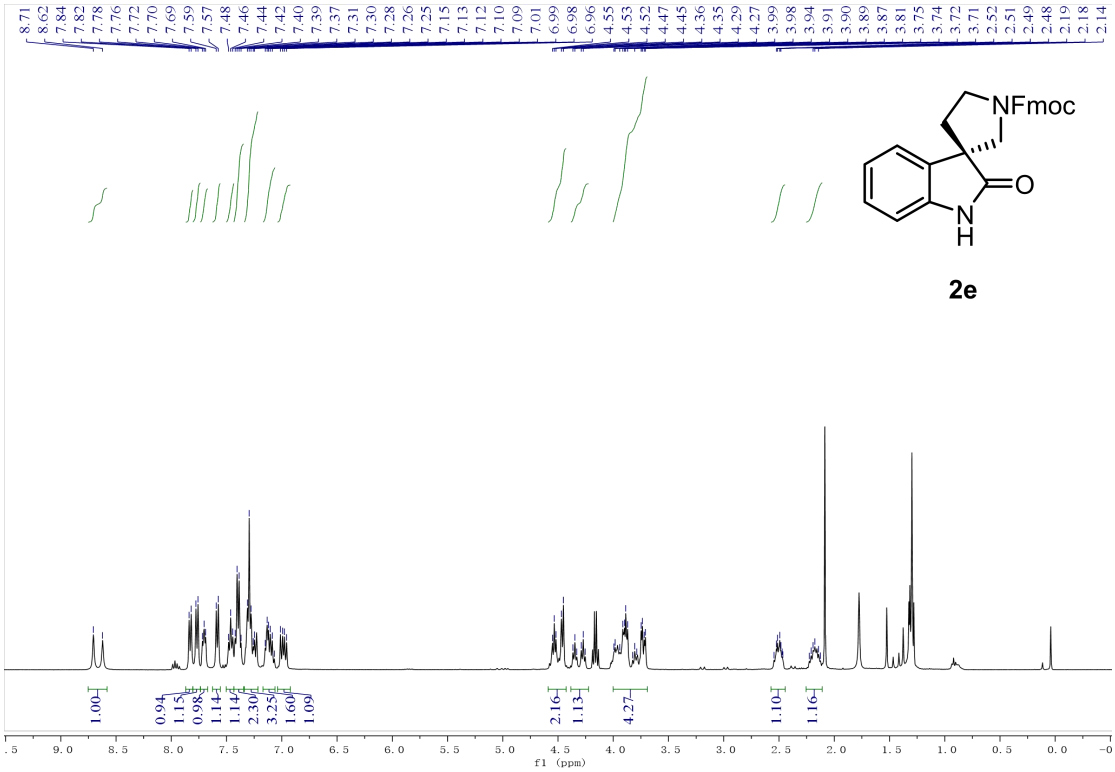


Figure S25. ^{1}H NMR spectra of **2e**

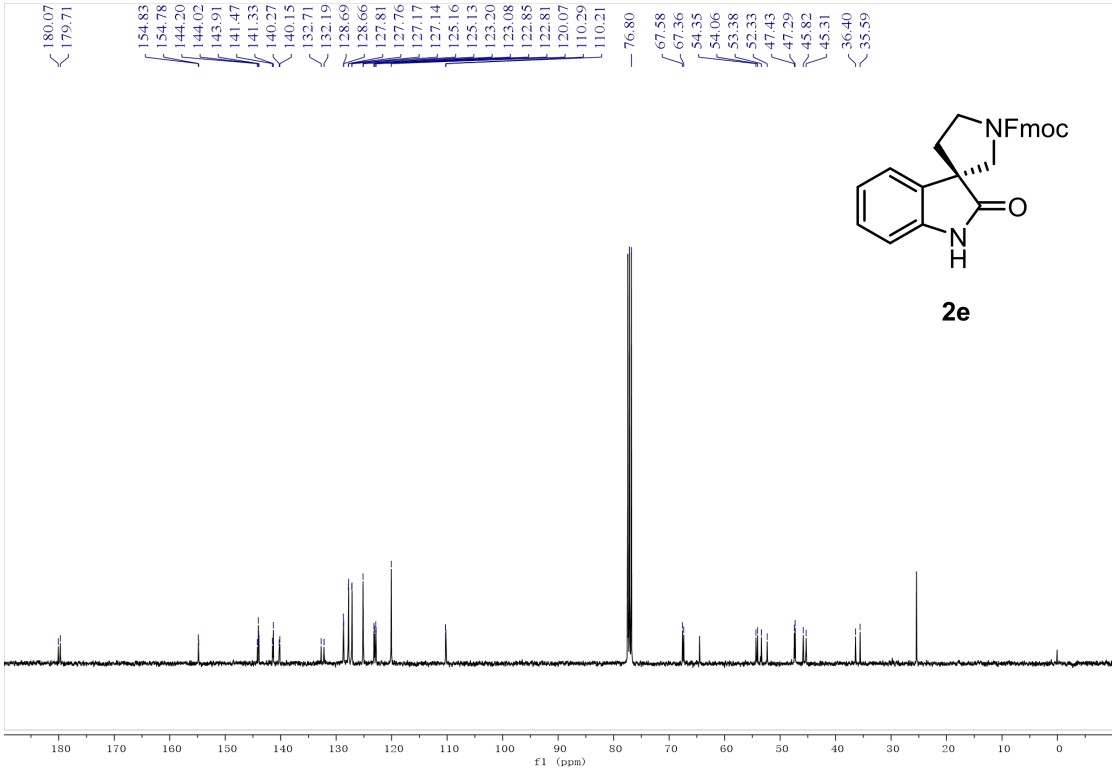


Figure S26. ^{13}C NMR spectra of **2e**

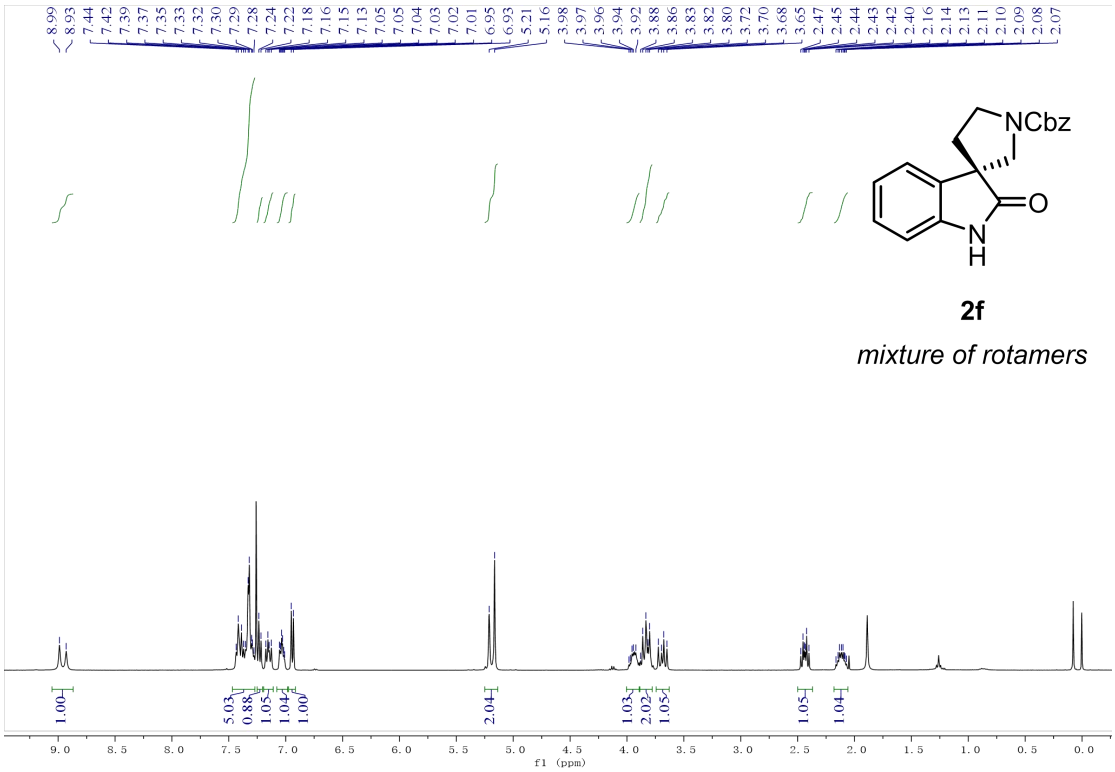


Figure S27. ^{1}H NMR spectra of **2f**

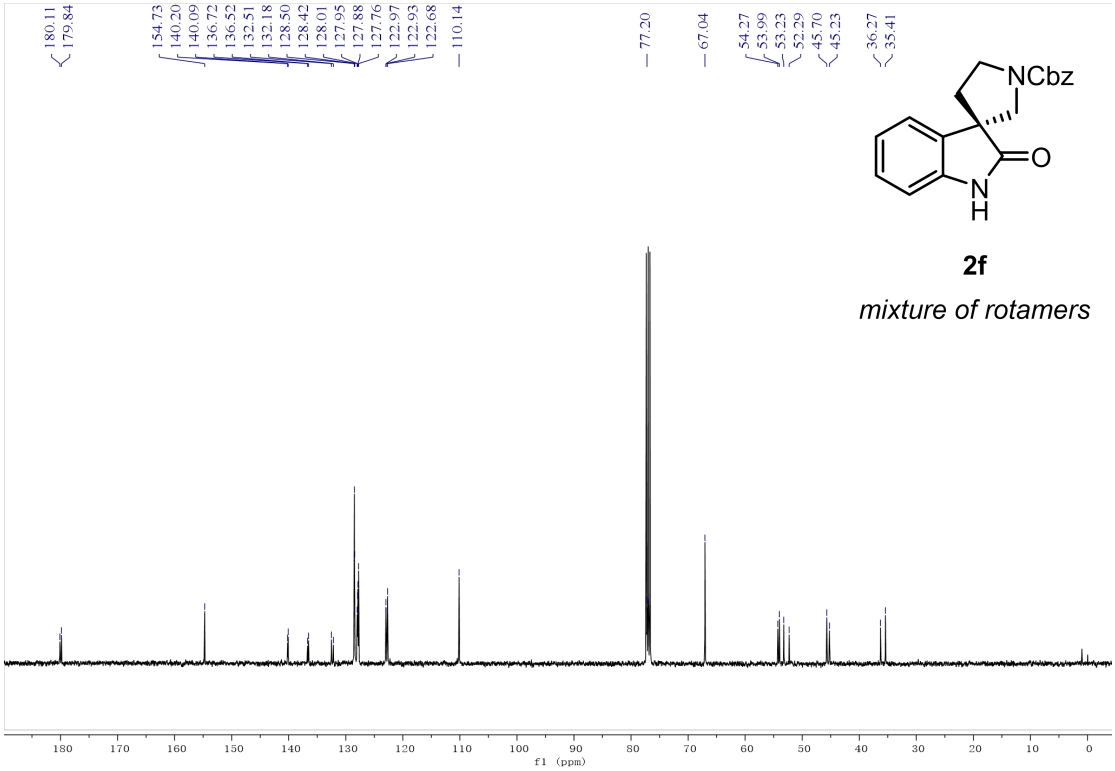


Figure S28. ^{13}C NMR spectra of **2f**

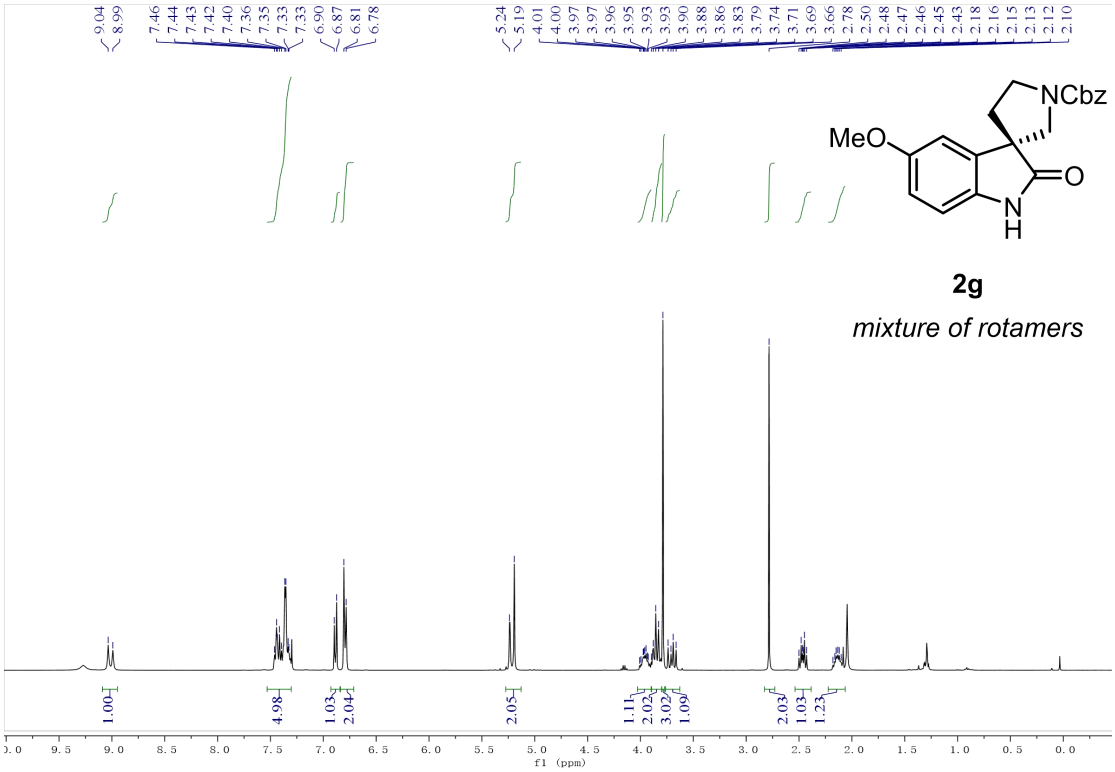


Figure S29. ^{1}H NMR spectra of **2g**

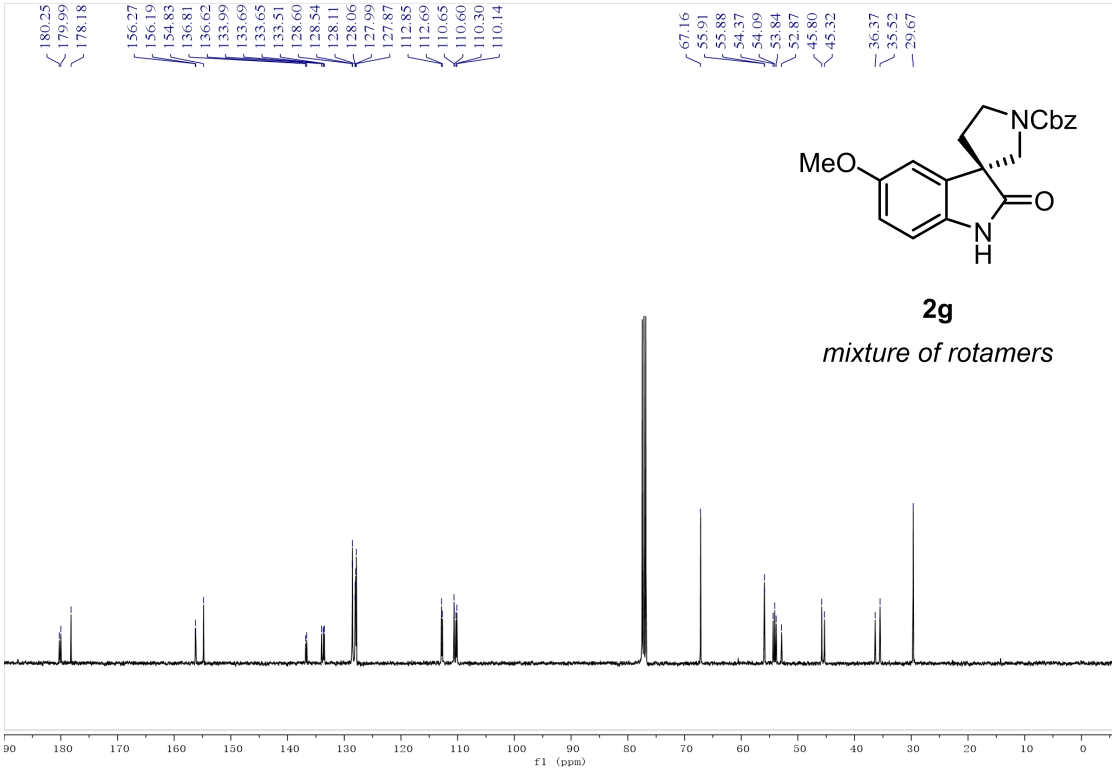


Figure S30. ^{13}C NMR spectra of **2g**

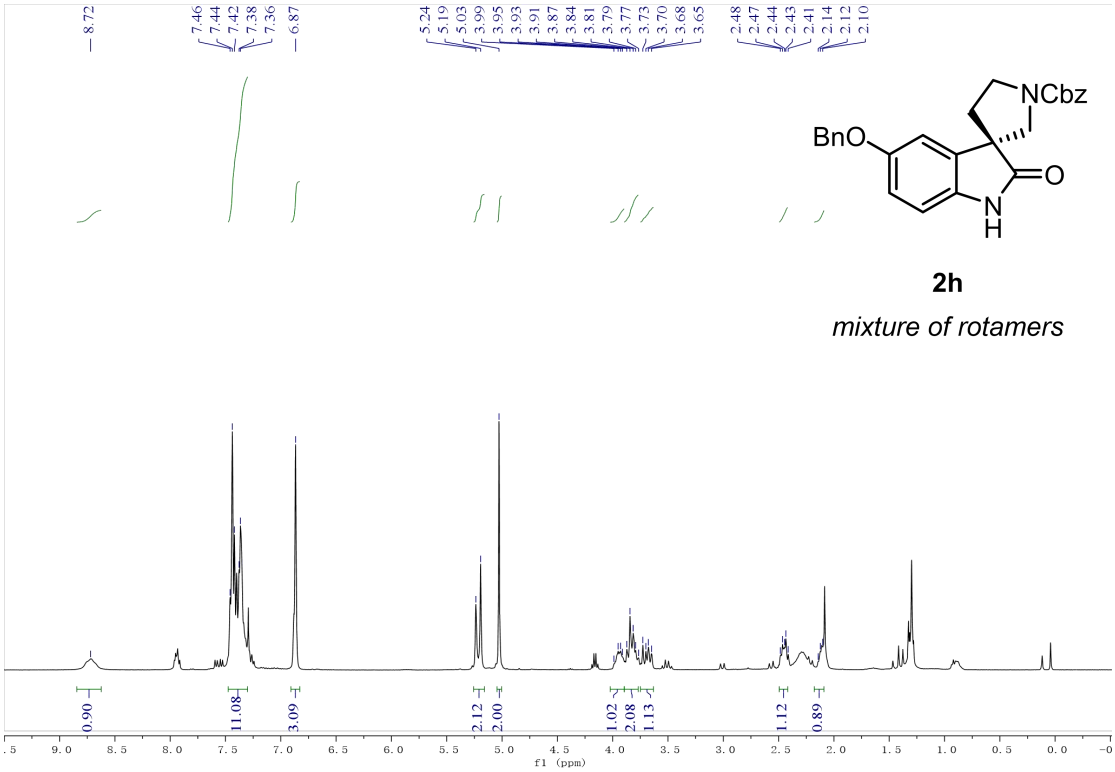


Figure S31. ^{1}H NMR spectra of **2h**

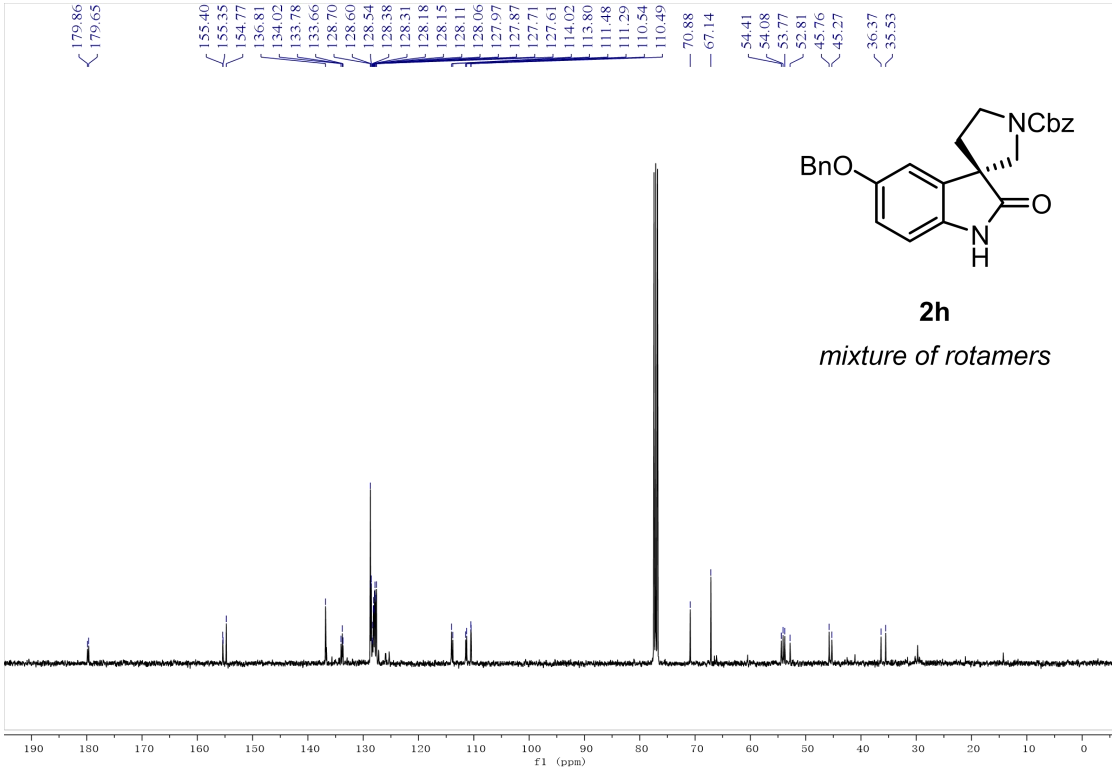


Figure S32. ^{13}C NMR spectra of **2h**

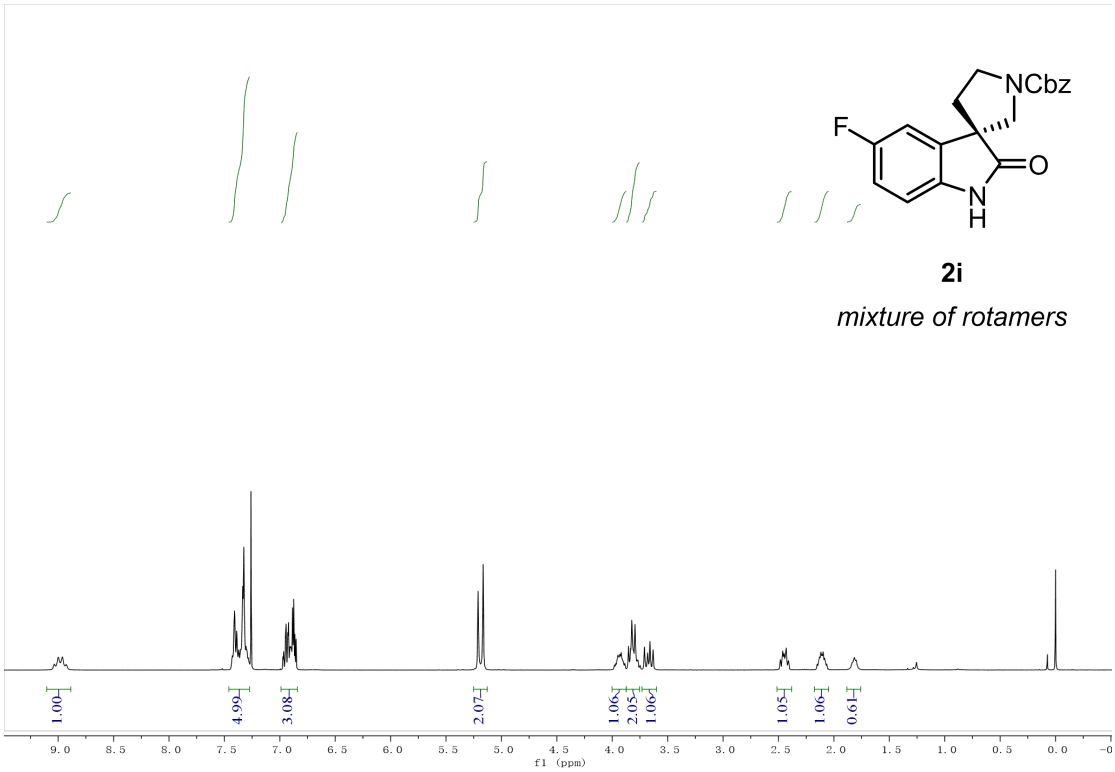


Figure S33. ^{1}H NMR spectra of **2i**

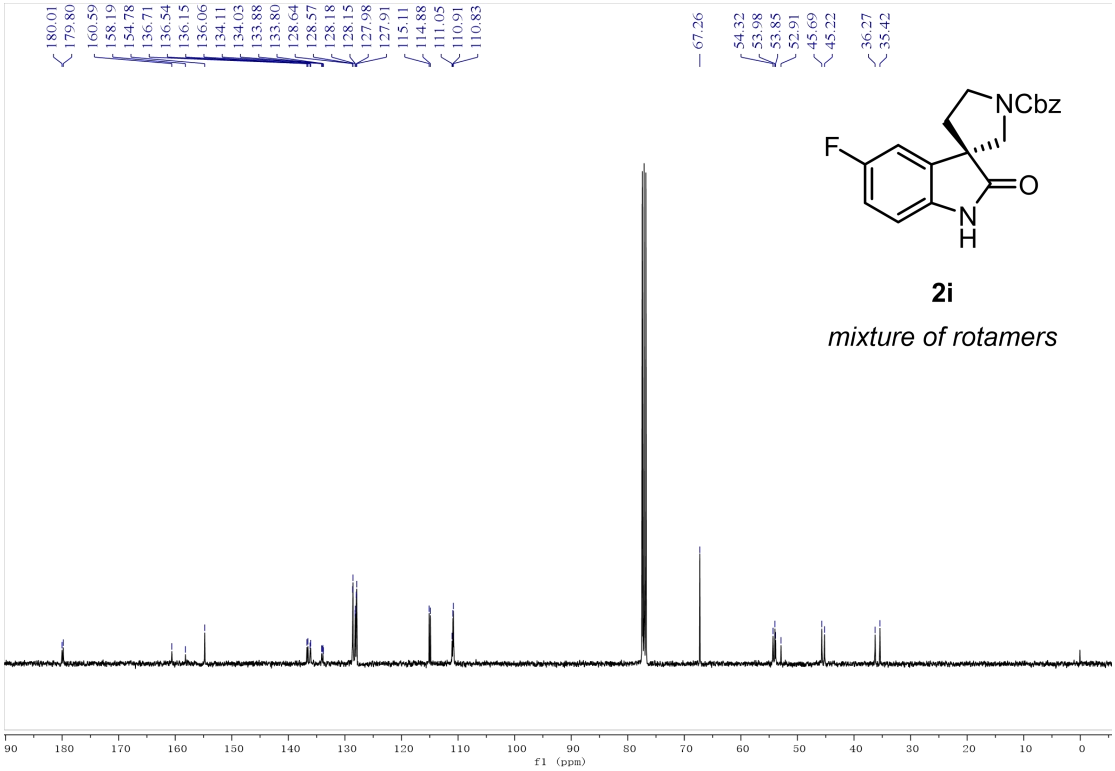


Figure S34. ^{13}C NMR spectra of **2i**

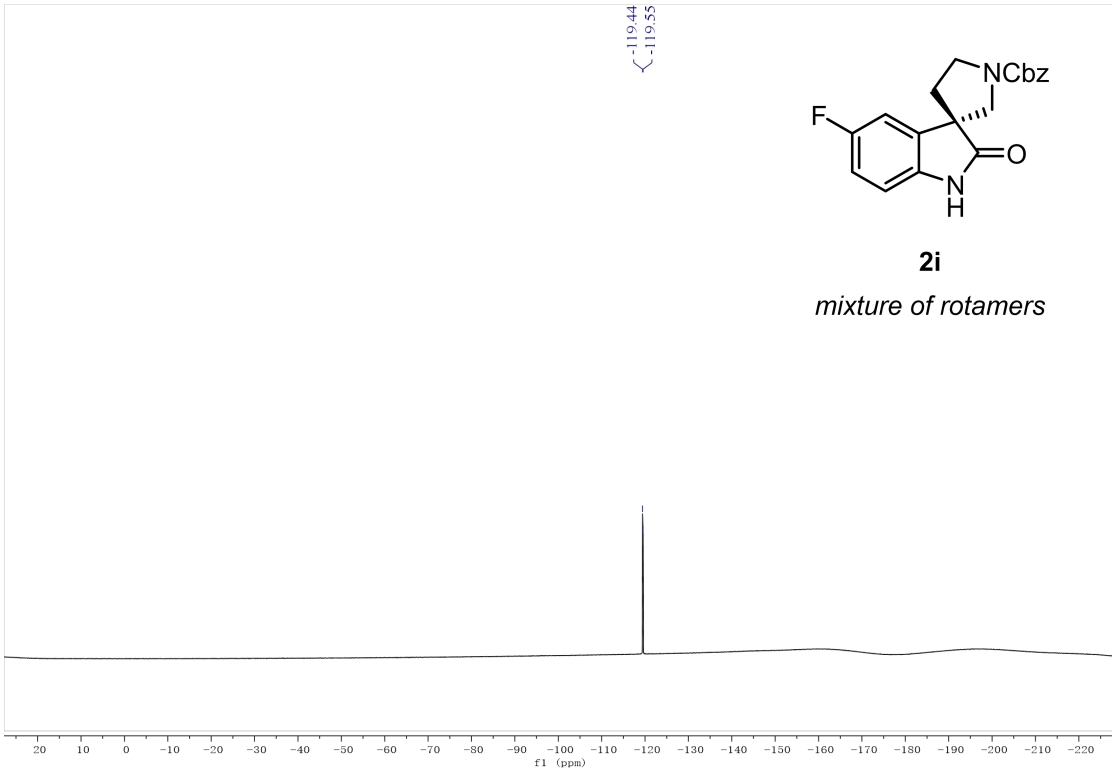


Figure S35. ^{19}F NMR spectra of **2i**

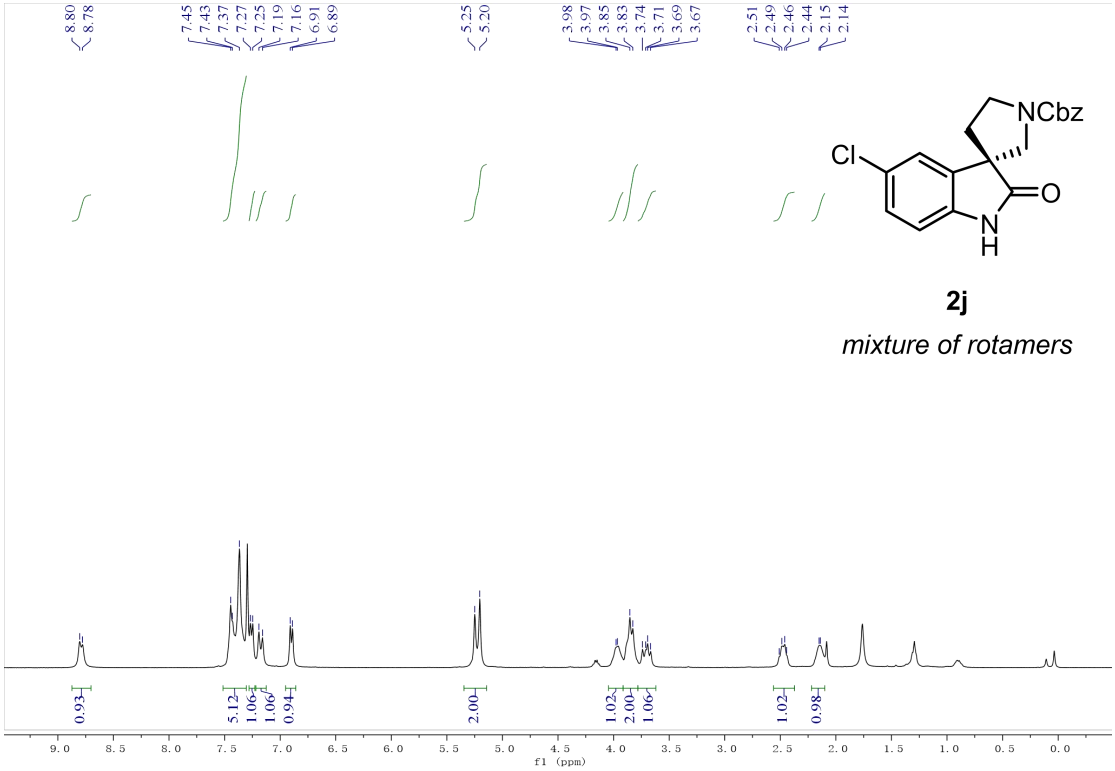


Figure S36. ^{1}H NMR spectra of **2j**

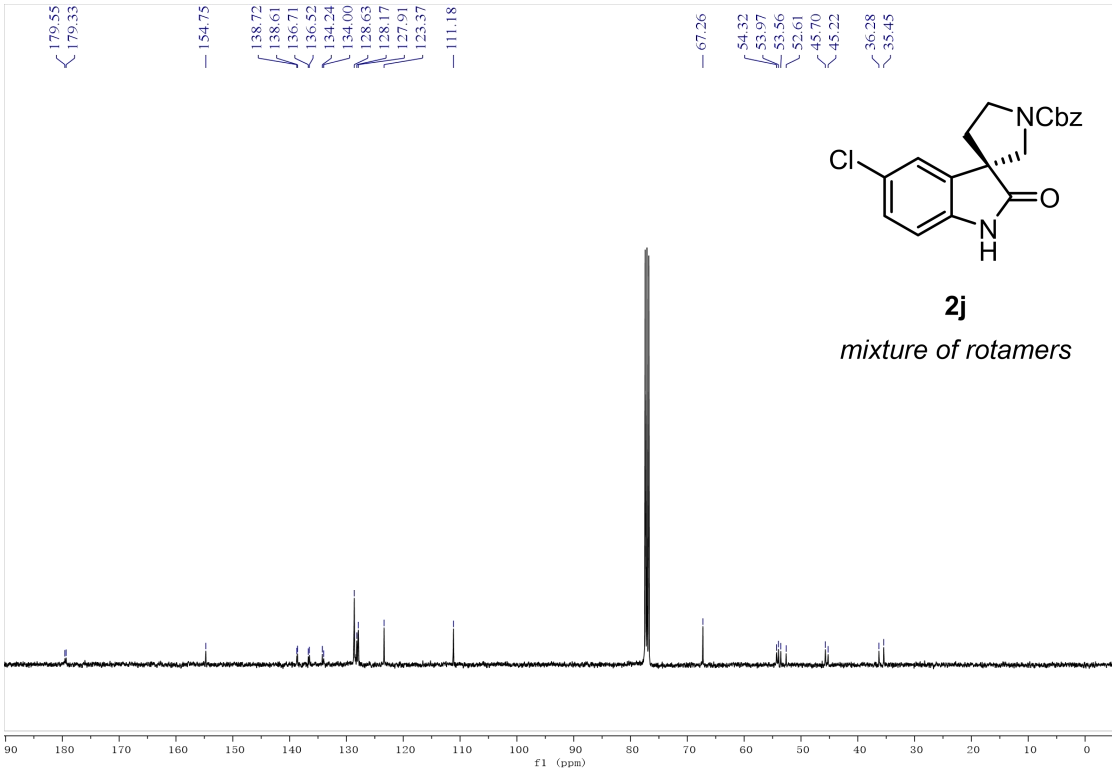


Figure S37. ^{13}C NMR spectra of **2j**

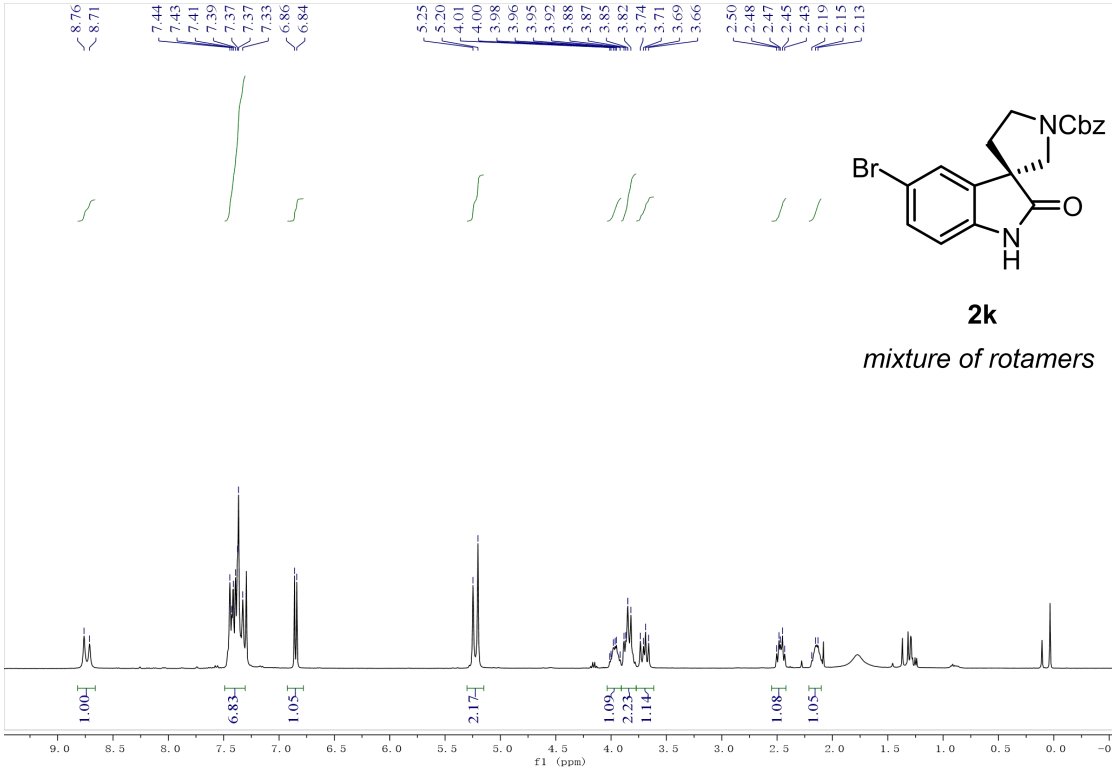


Figure S38. ^{1}H NMR spectra of **2k**

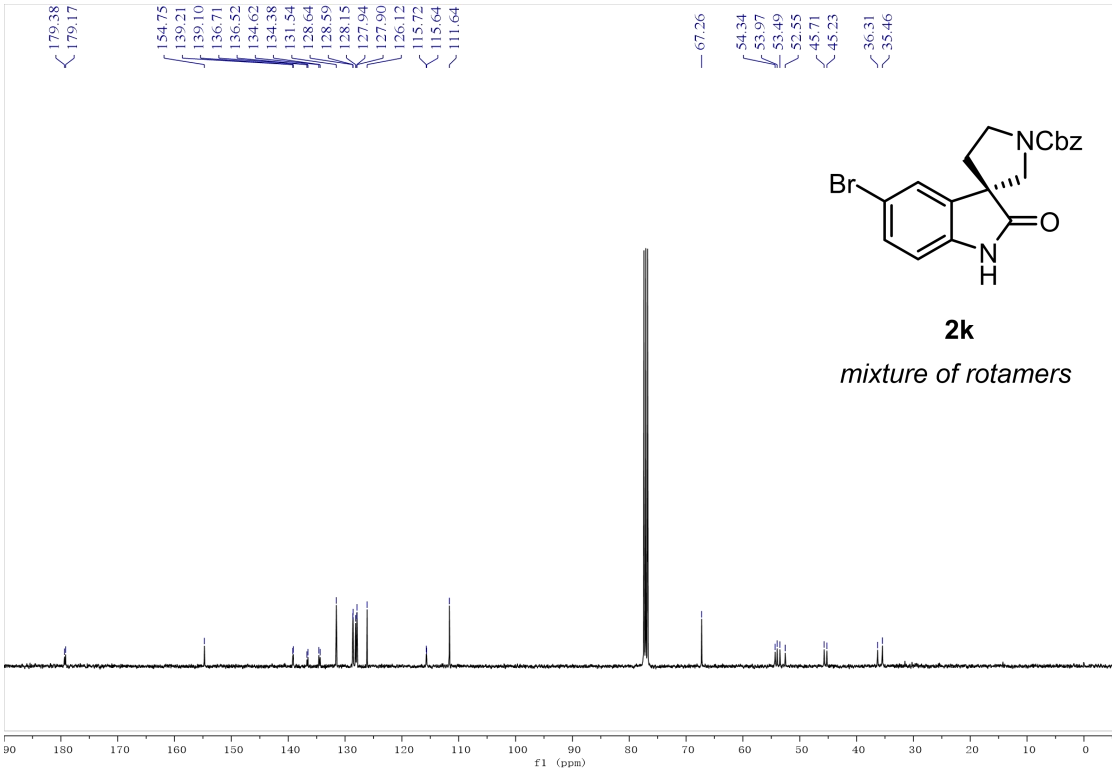


Figure S39. ^{13}C NMR spectra of **2k**

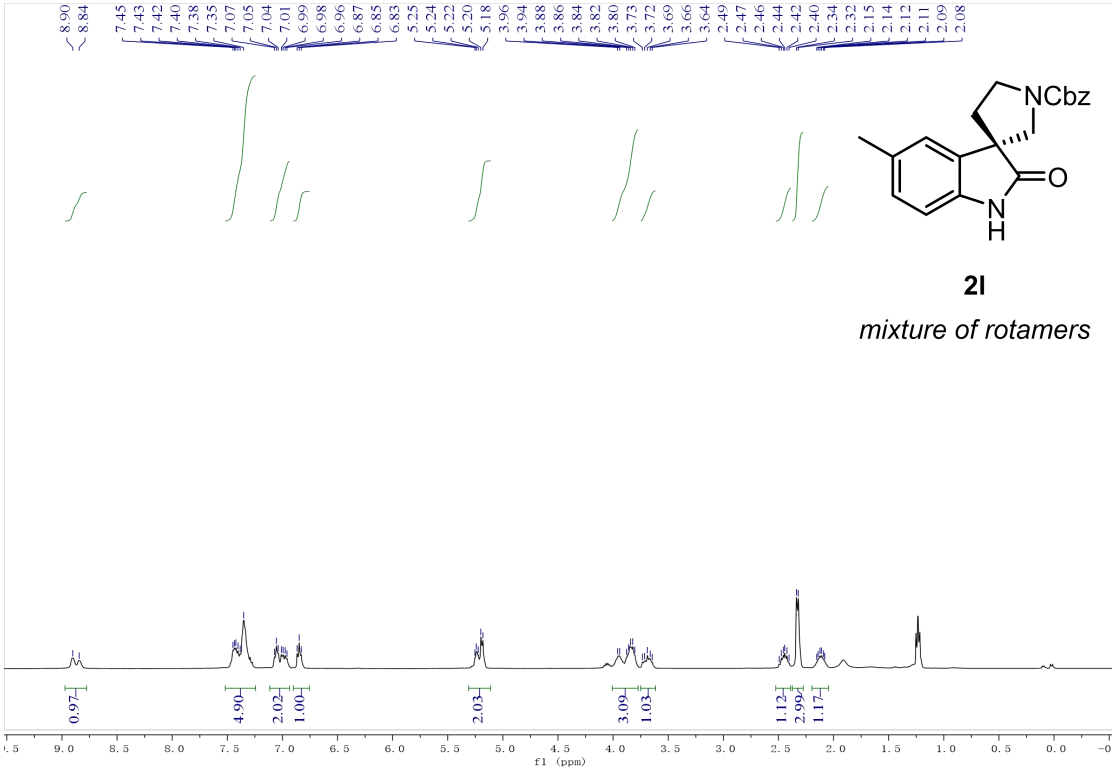


Figure S40. ^{1}H NMR spectra of **2l**

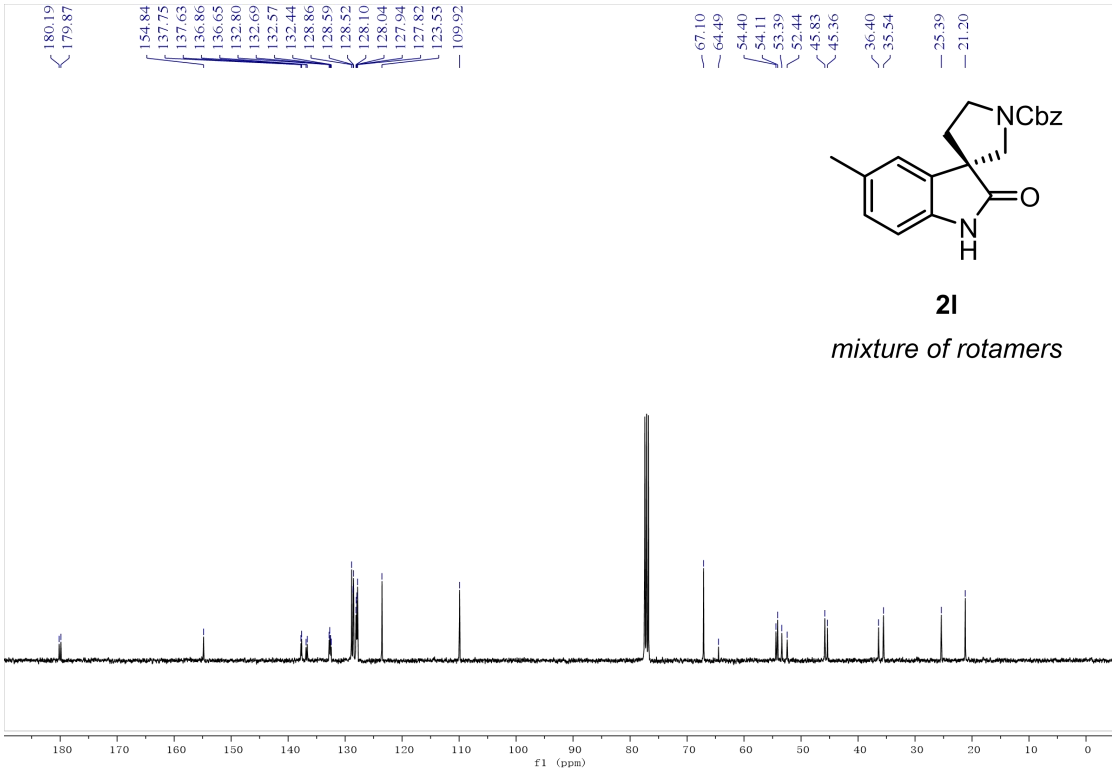


Figure S41. ^{13}C NMR spectra of **2l**

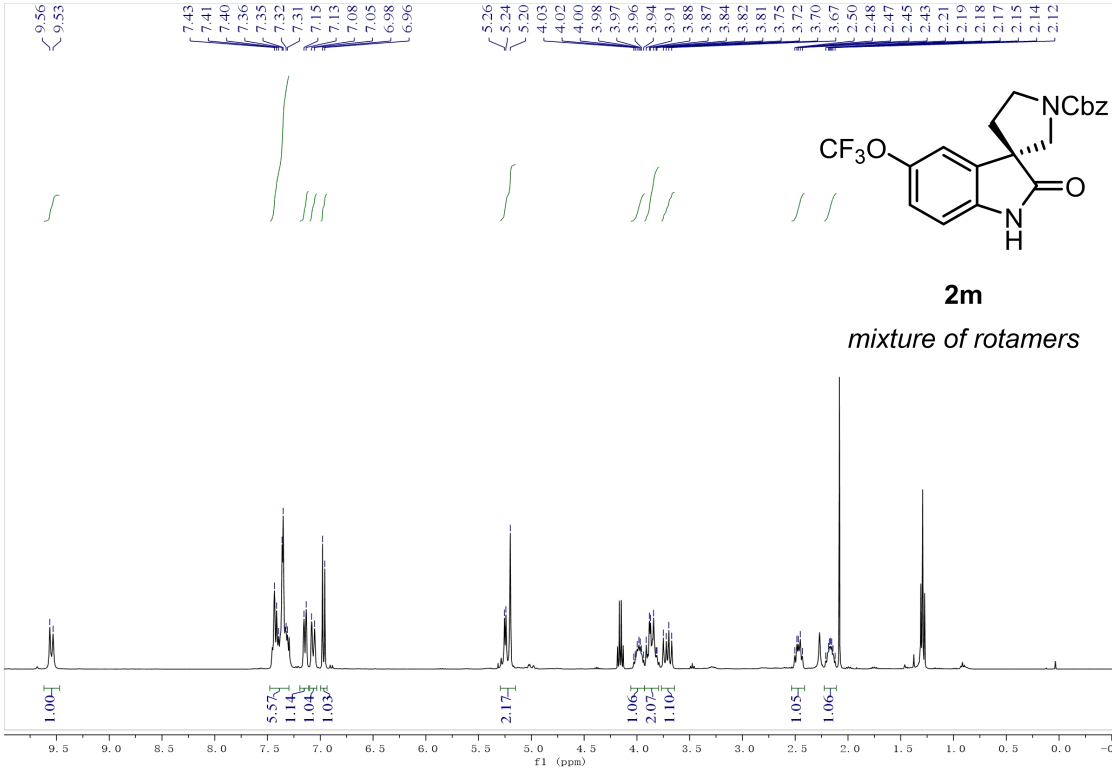


Figure S42. ^{1}H NMR spectra of **2m**

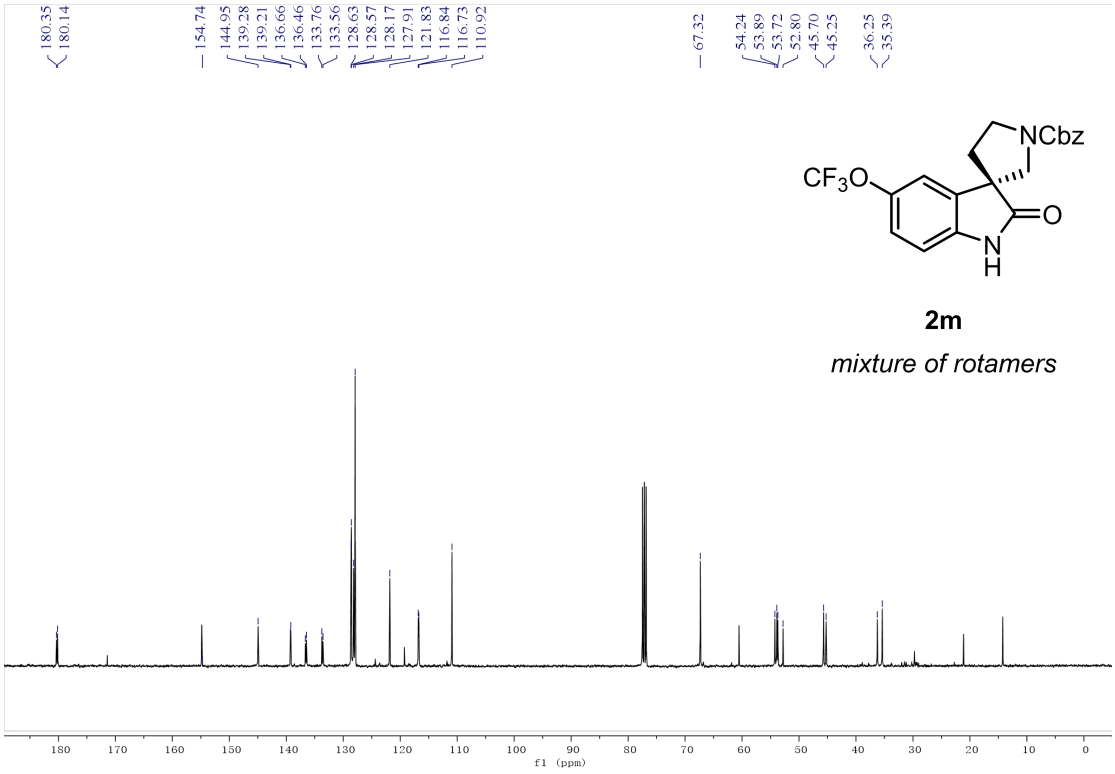


Figure S43. ^{13}C NMR spectra of **2m**

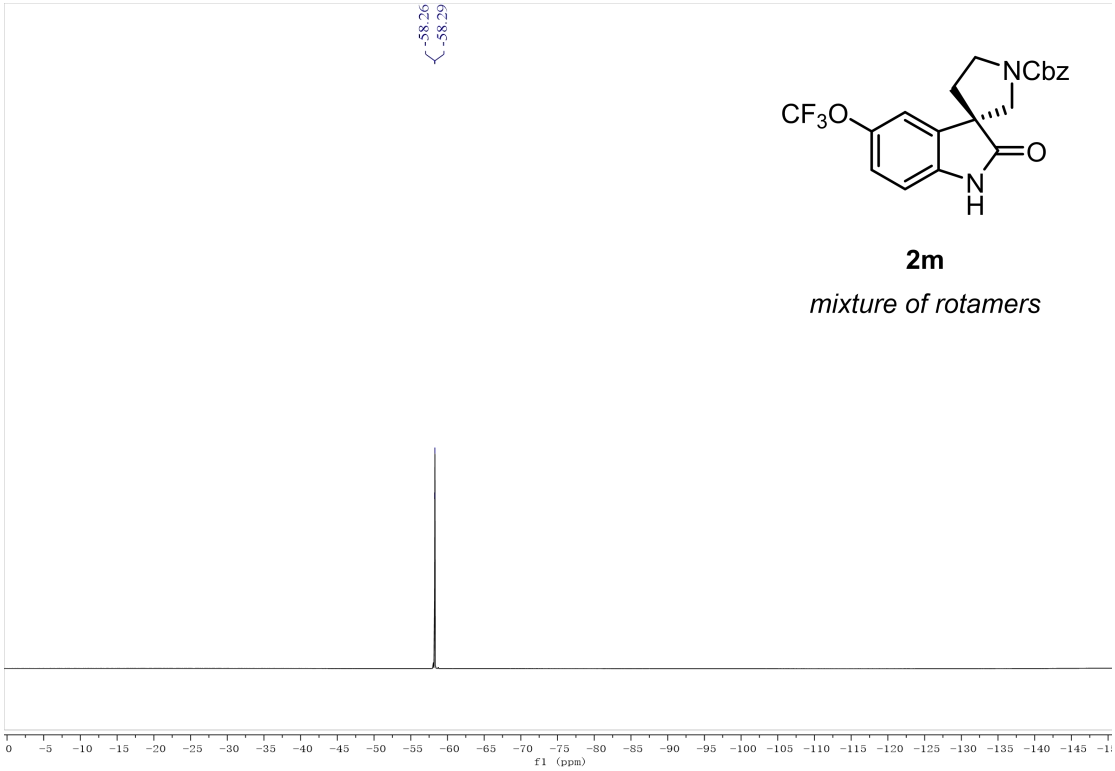


Figure S44. ^{19}F NMR spectra of **2m**

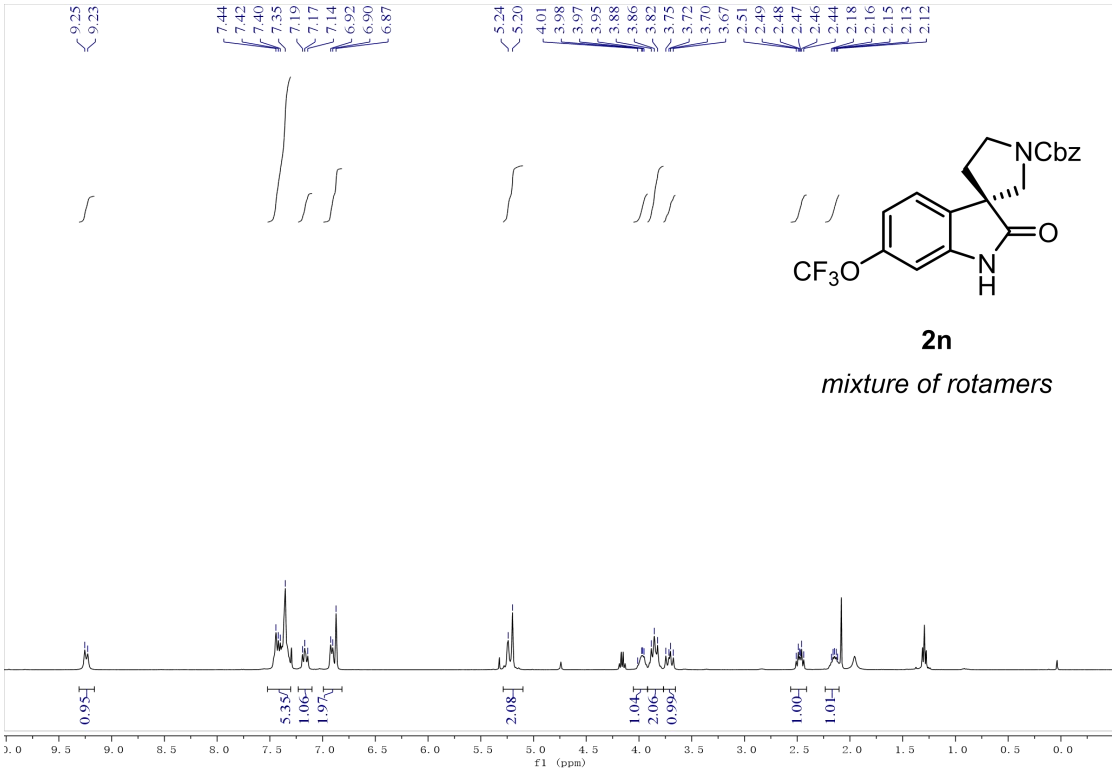


Figure S45. ^{1}H NMR spectra of **2n**

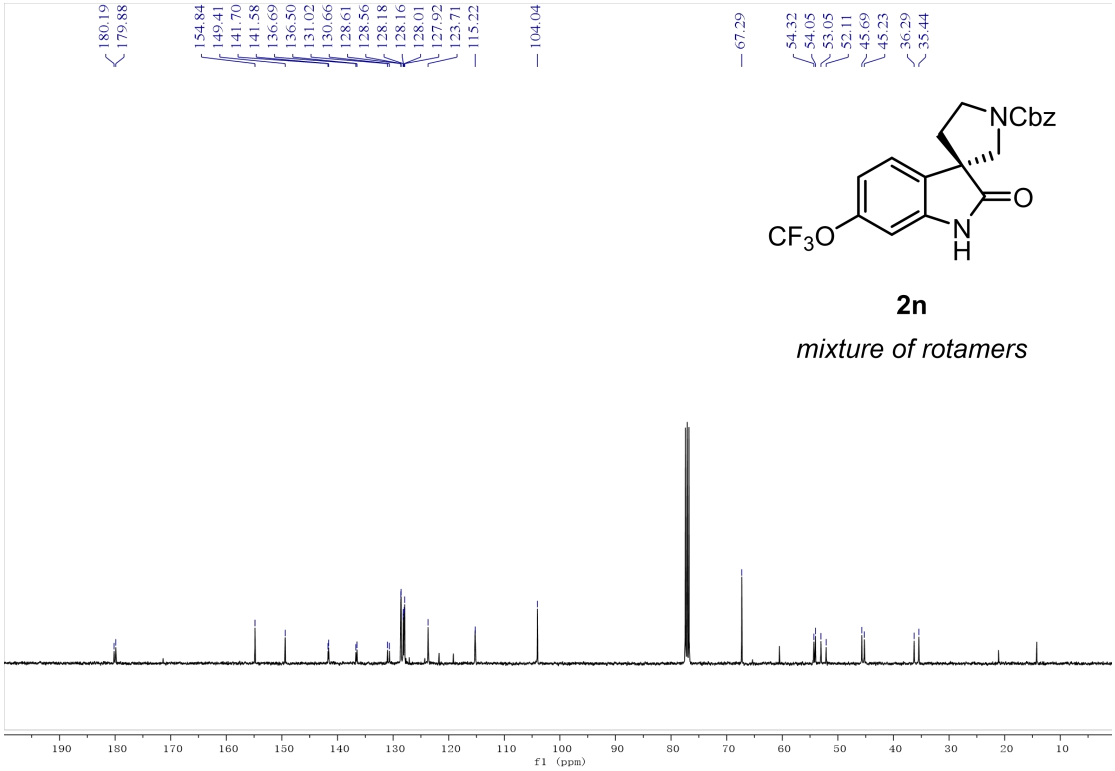


Figure S46. ^{13}C NMR spectra of **2n**

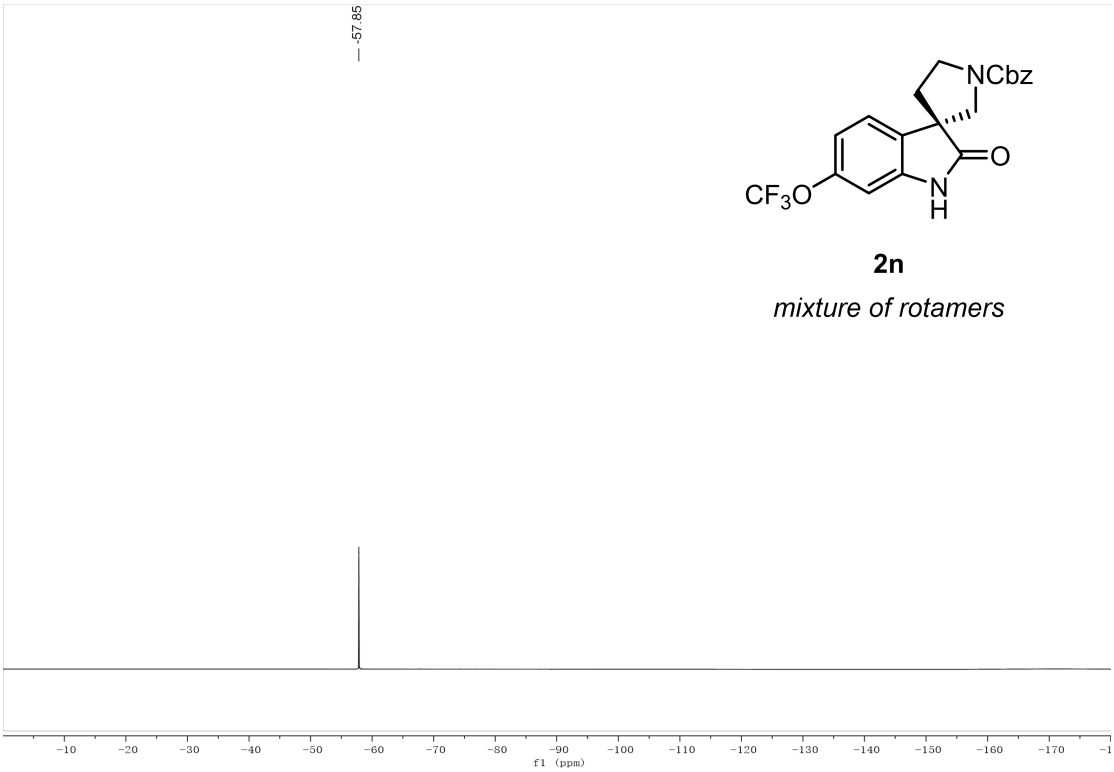


Figure S47. ^{19}F NMR spectra of **2n**

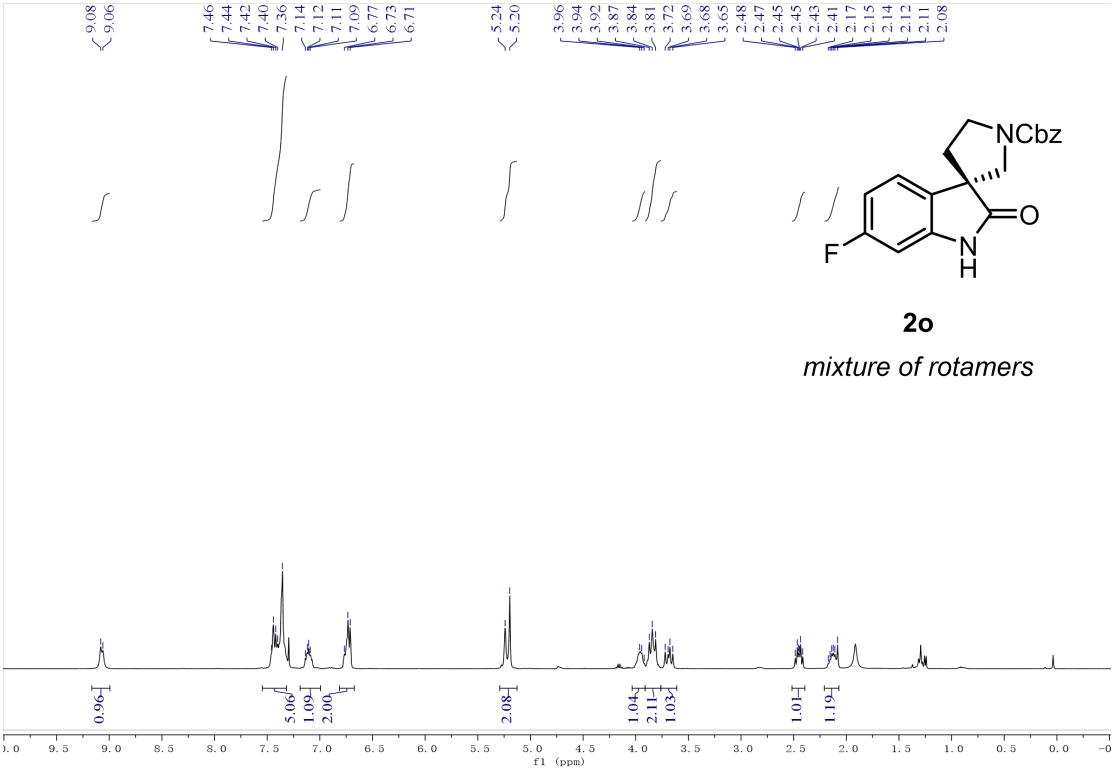


Figure S48. ^{1}H NMR spectra of **2o**

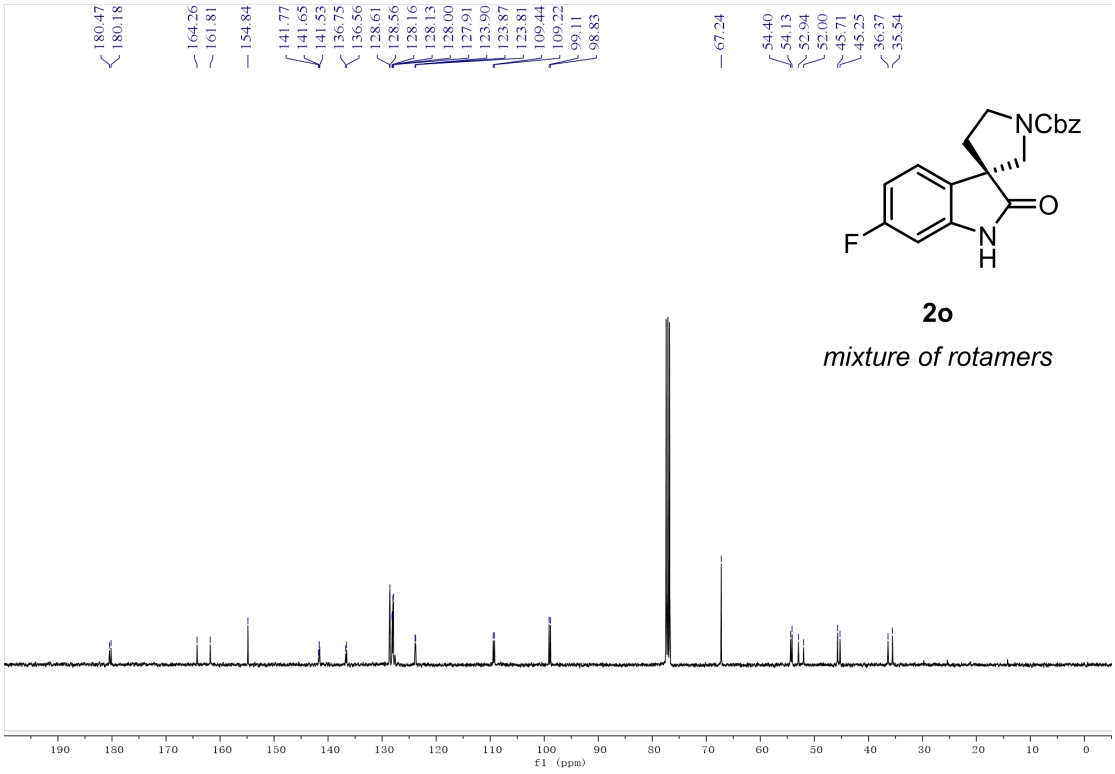


Figure S49. ^{13}C NMR spectra of **2o**

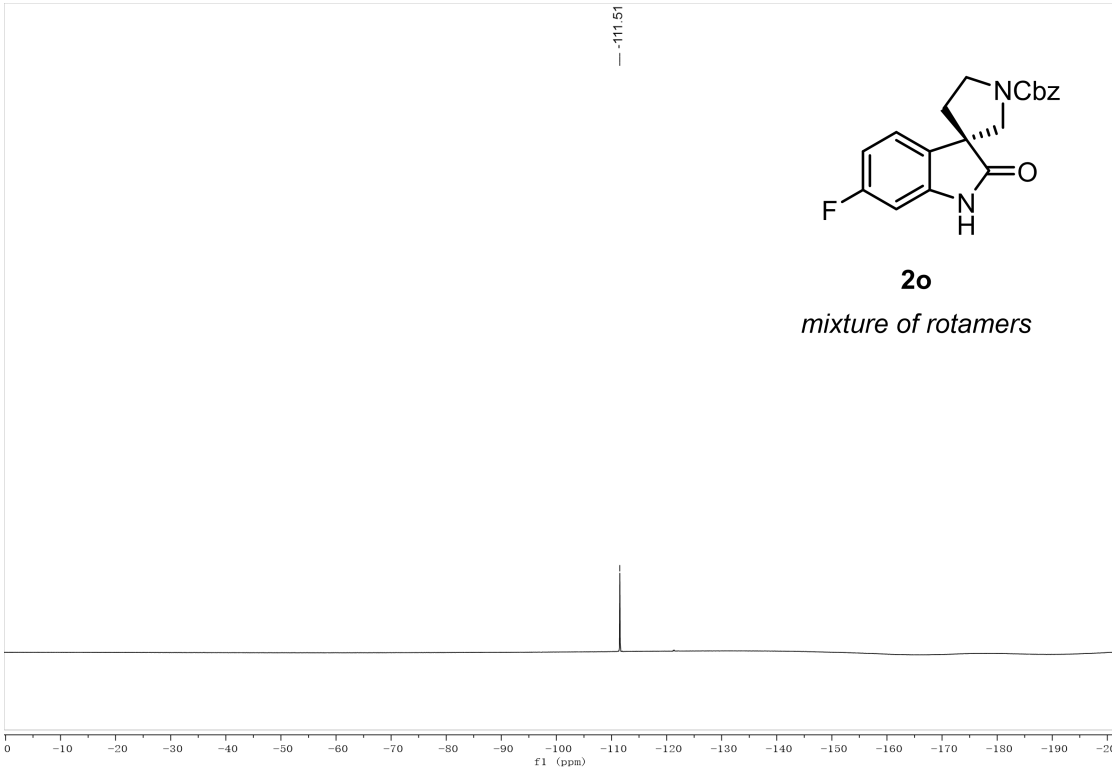


Figure S50. ^{19}F NMR spectra of **2o**

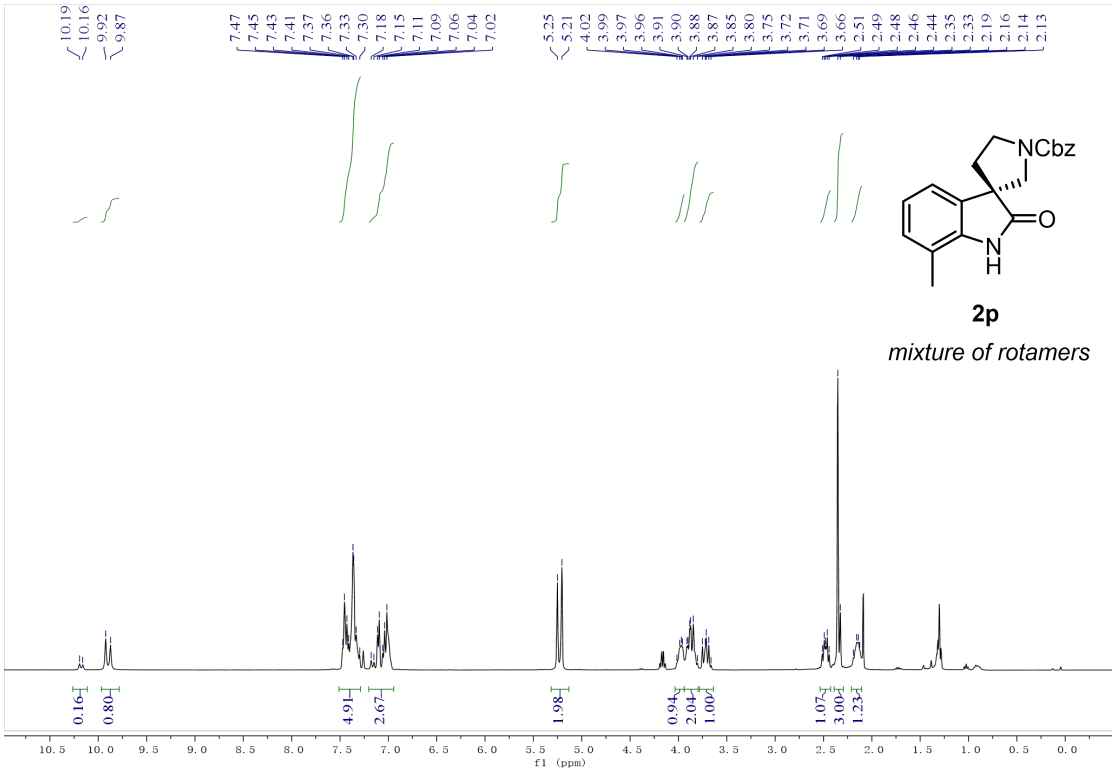


Figure S51. ^{1}H NMR spectra of **2p**

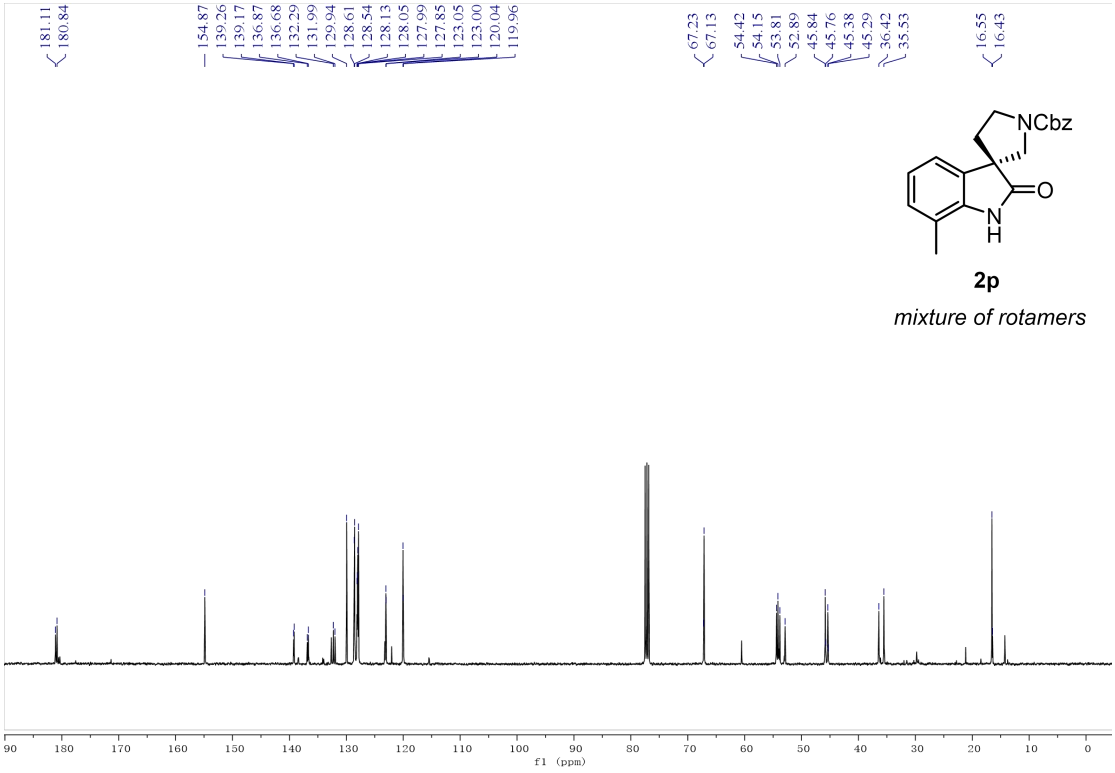


Figure S52. ^{13}C NMR spectra of **2p**

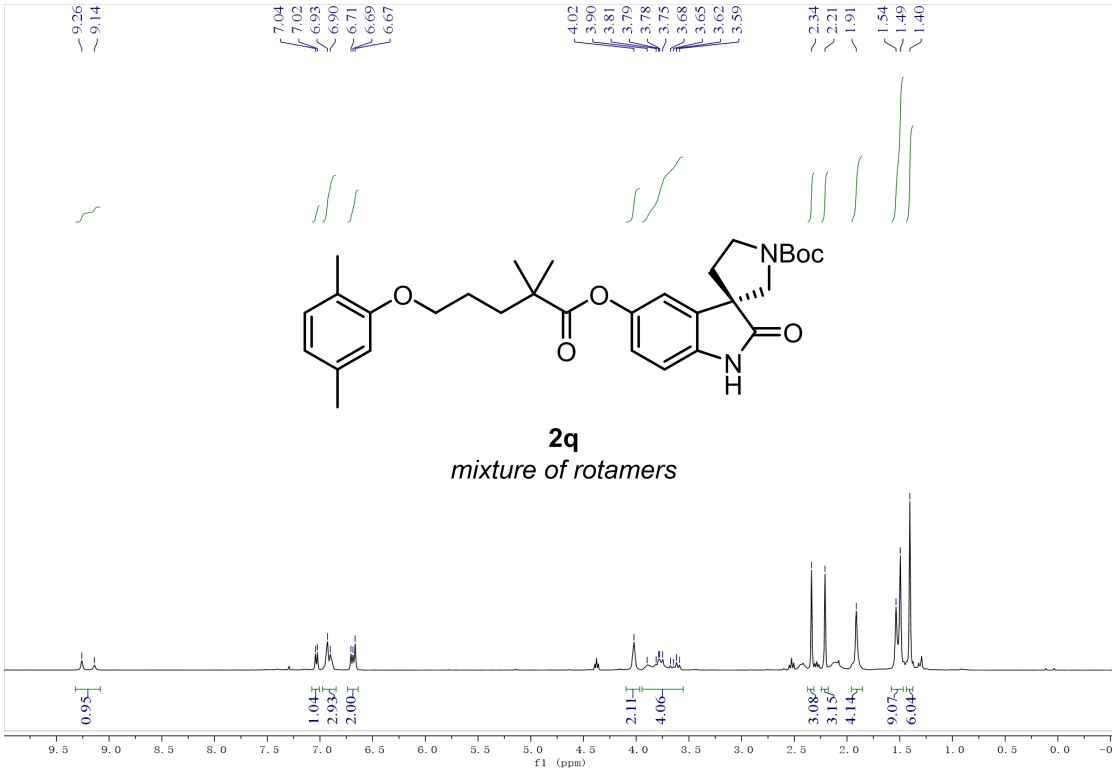


Figure S53. ^{1}H NMR spectra of **2q**

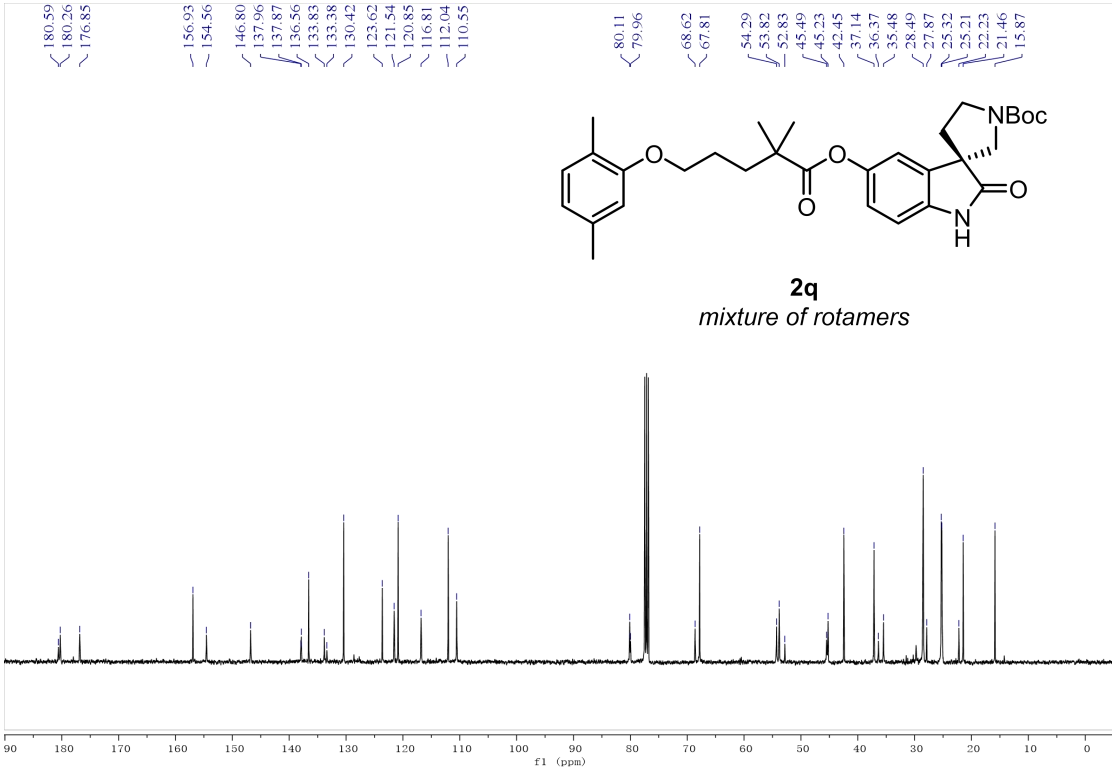


Figure S54. ^{13}C NMR spectra of **2q**

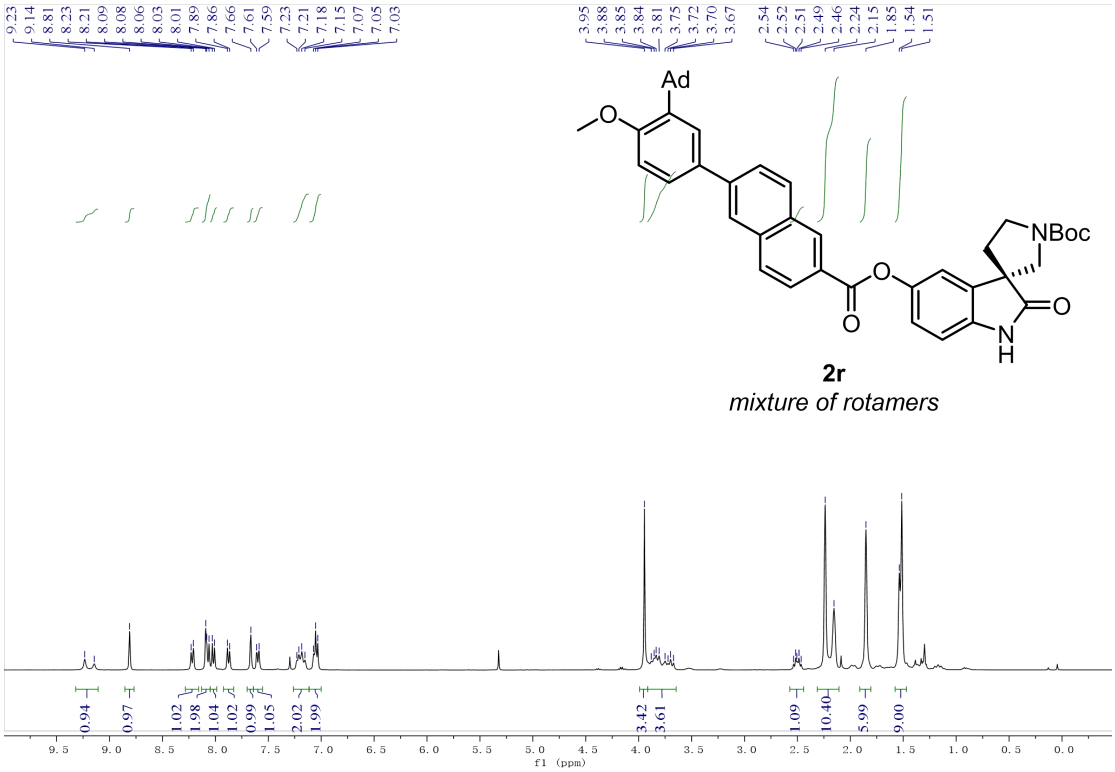


Figure S55. ^{1}H NMR spectra of **2r**

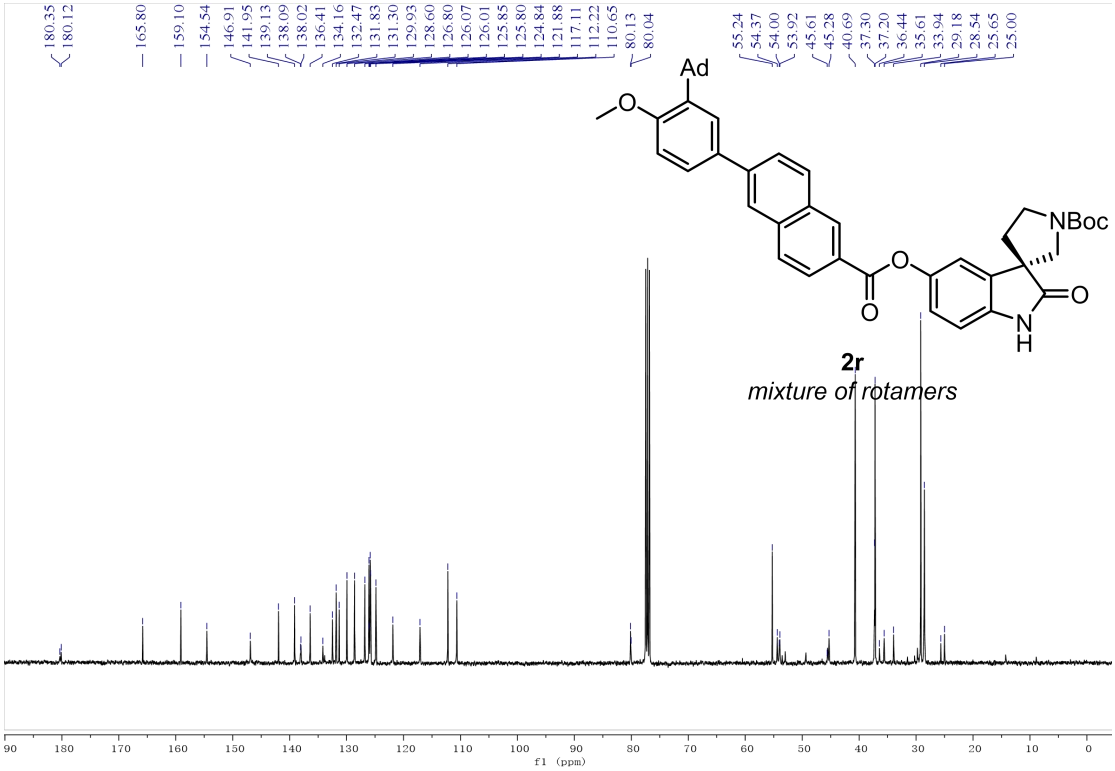


Figure S56. ^{13}C NMR spectra of **2r**

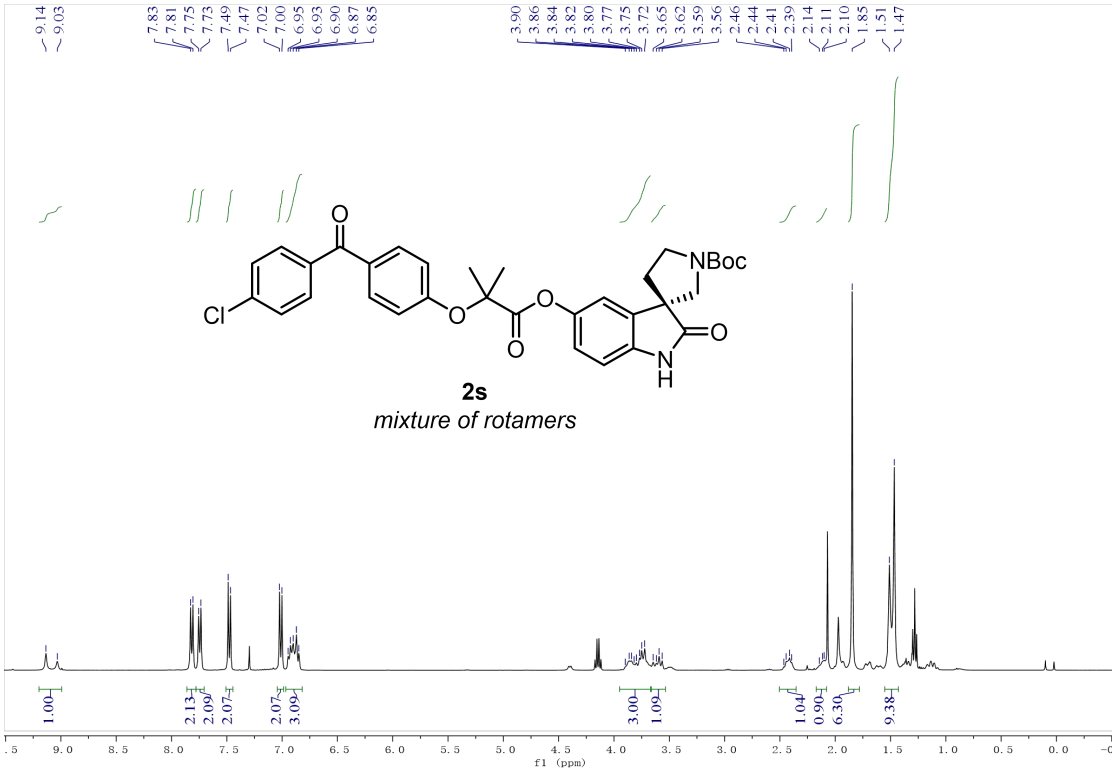


Figure S57. ^{1}H NMR spectra of **2s**

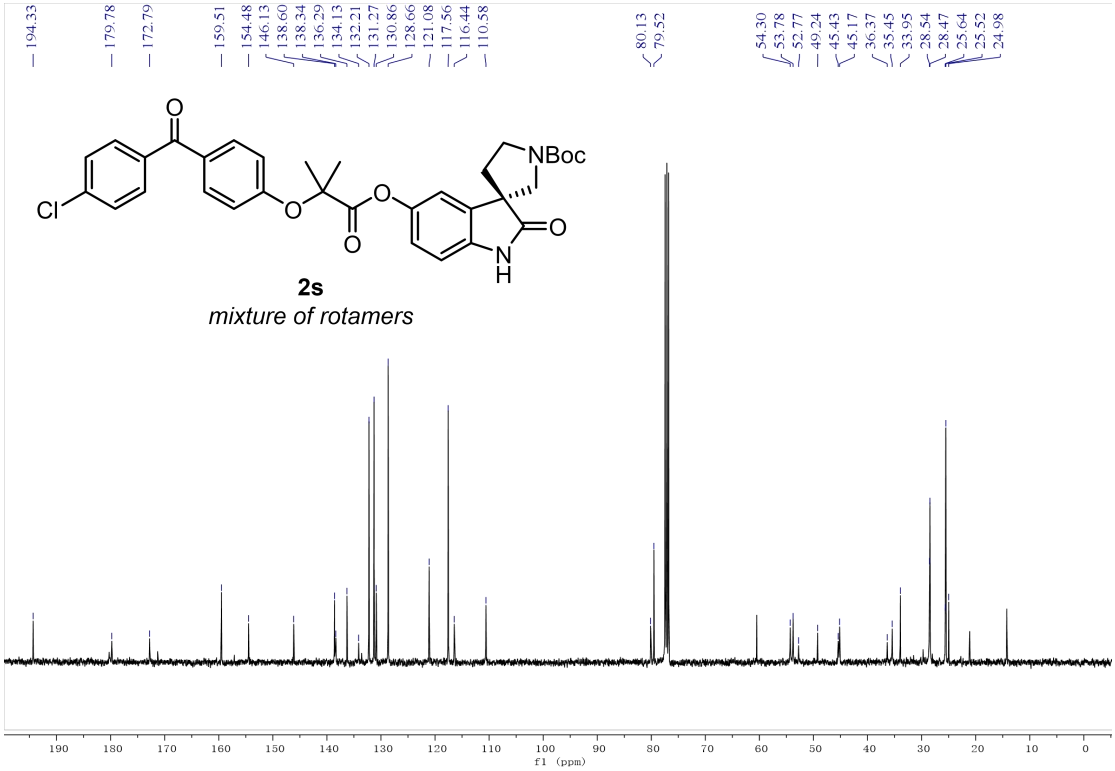


Figure S58. ^{13}C NMR spectra of **2s**

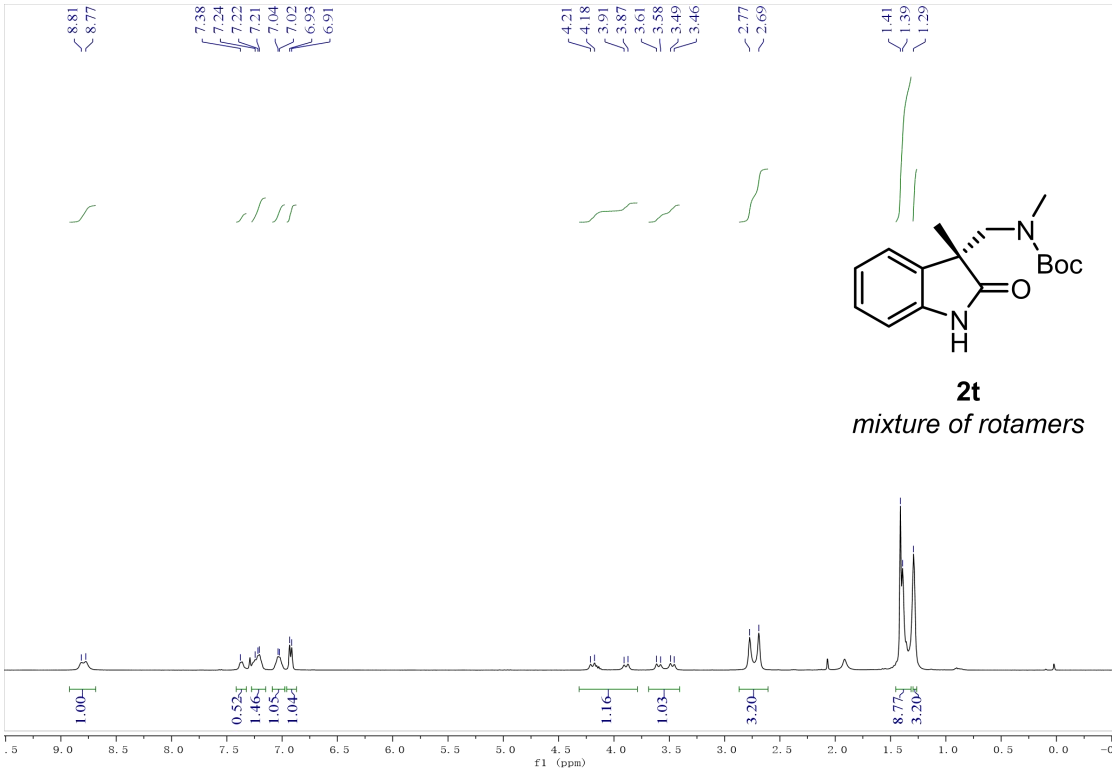


Figure S59. ^{1}H NMR spectra of **2t**

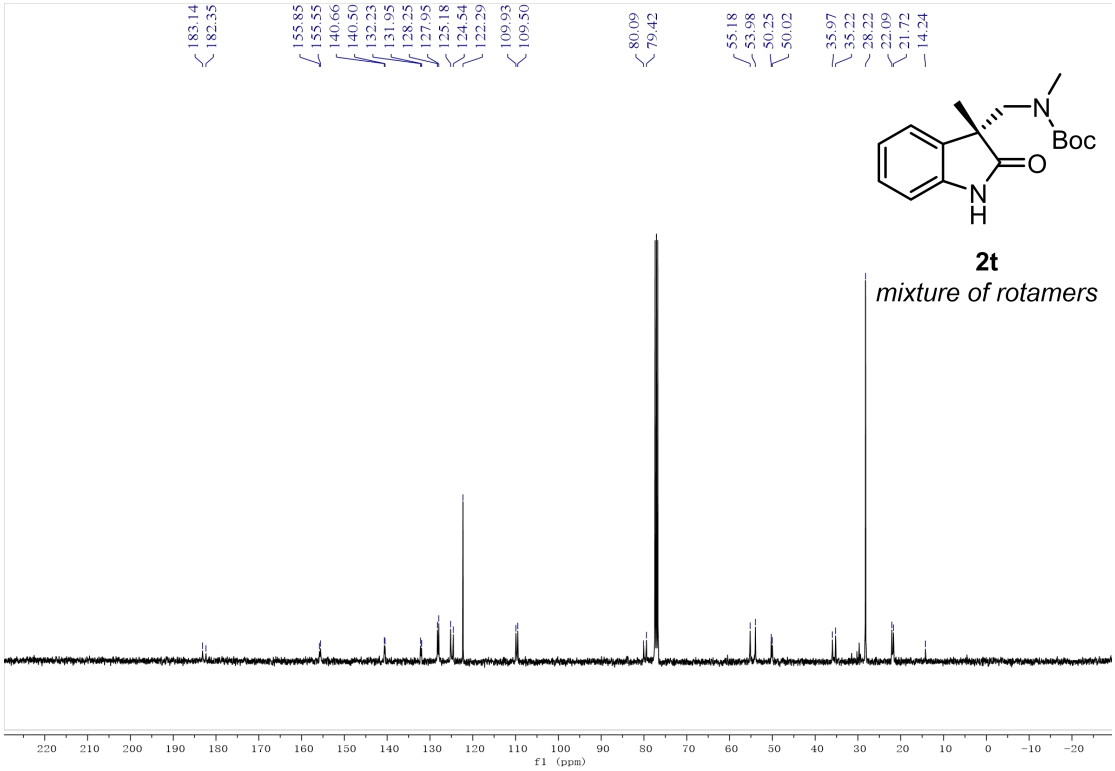


Figure S60. ^{13}C NMR spectra of **2t**

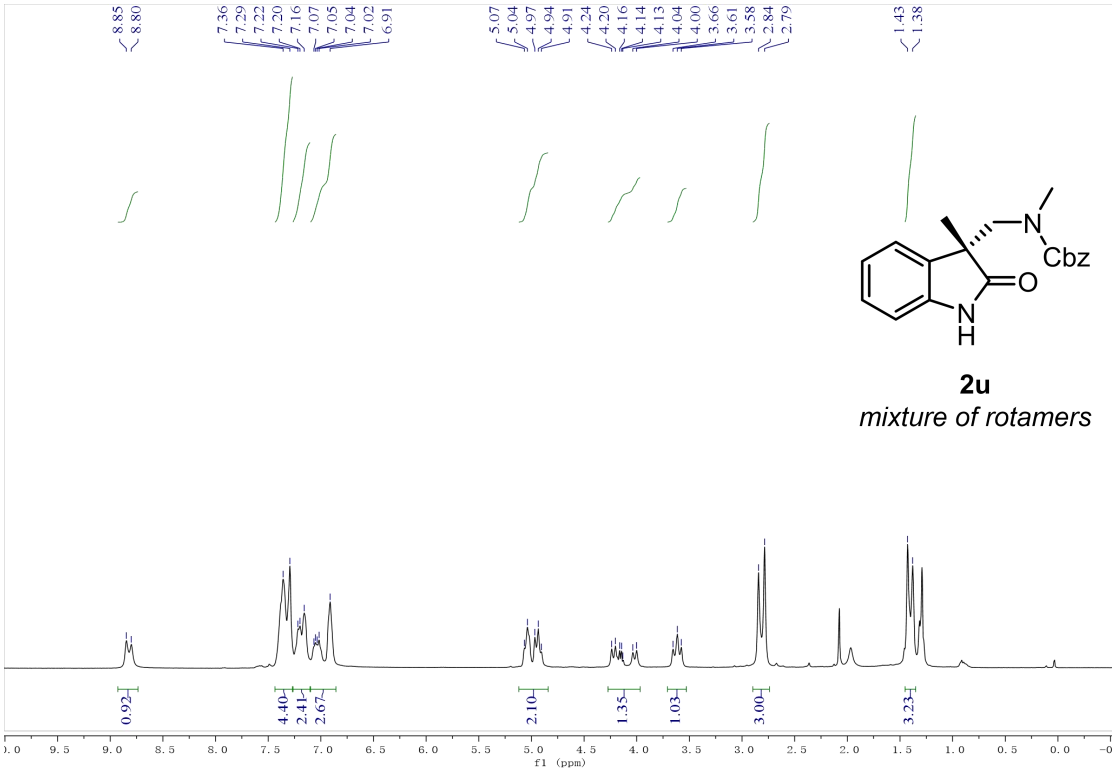


Figure S61. ^{1}H NMR spectra of **2u**

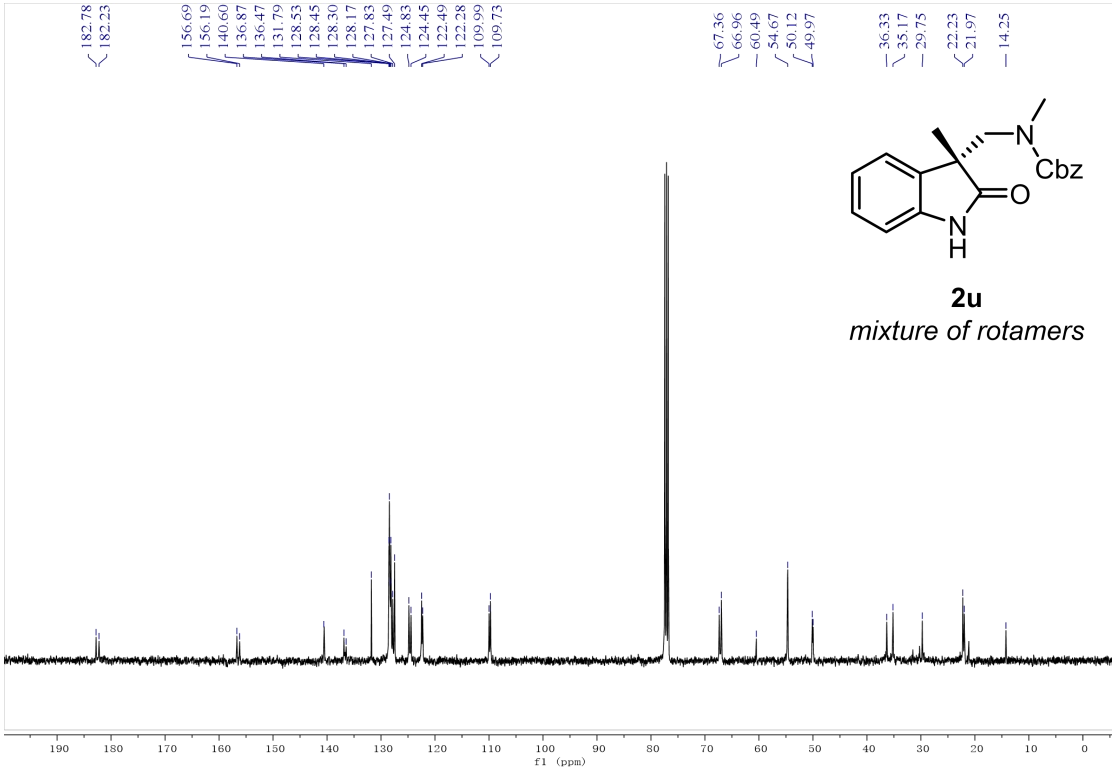


Figure S62. ^{13}C NMR spectra of **2u**

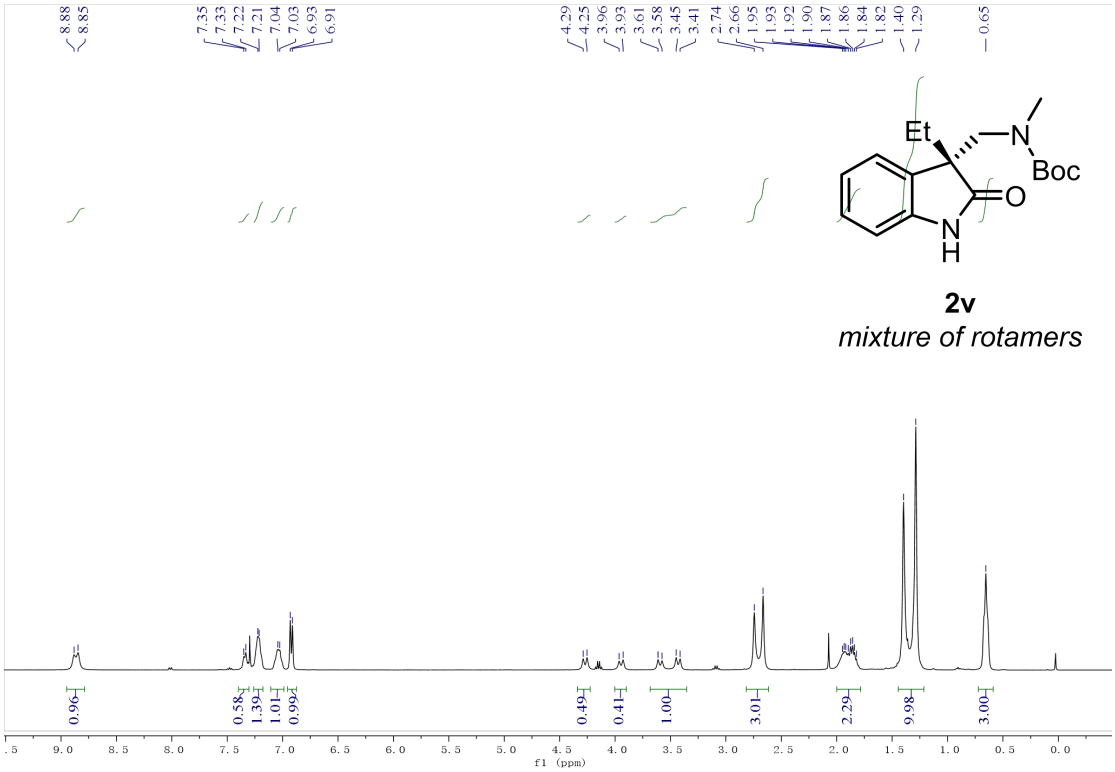


Figure S63. ^{1}H NMR spectra of **2v**

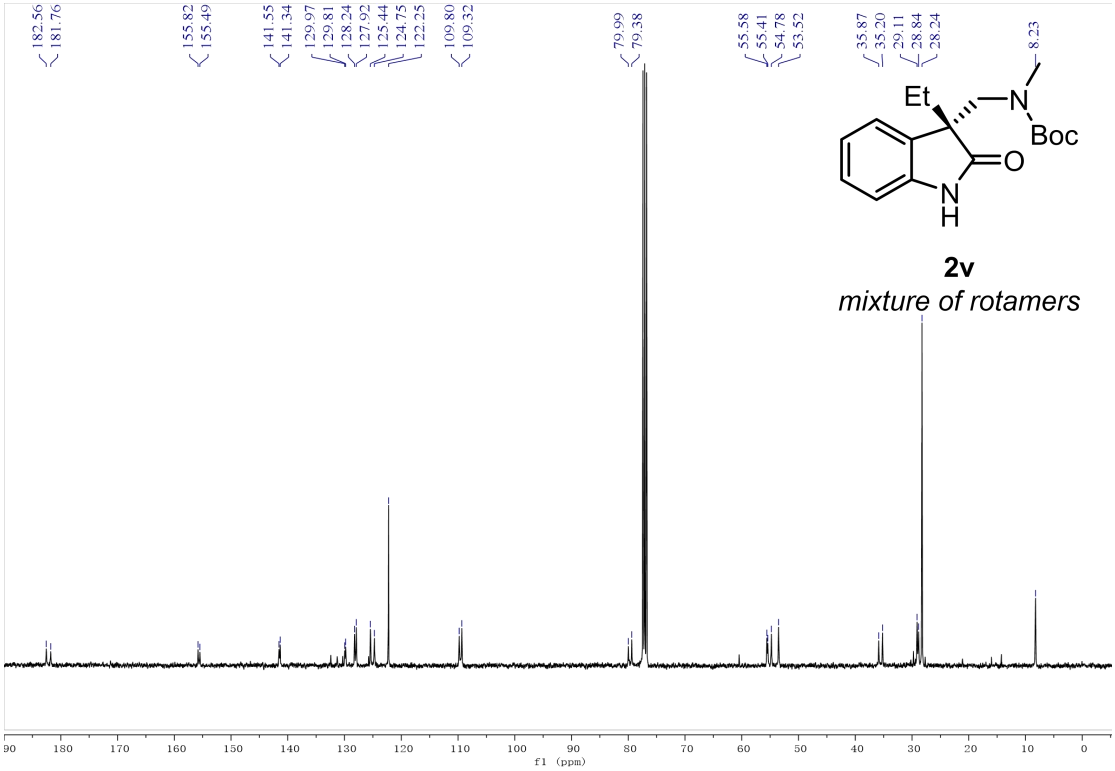


Figure S64. ^{13}C NMR spectra of **2v**

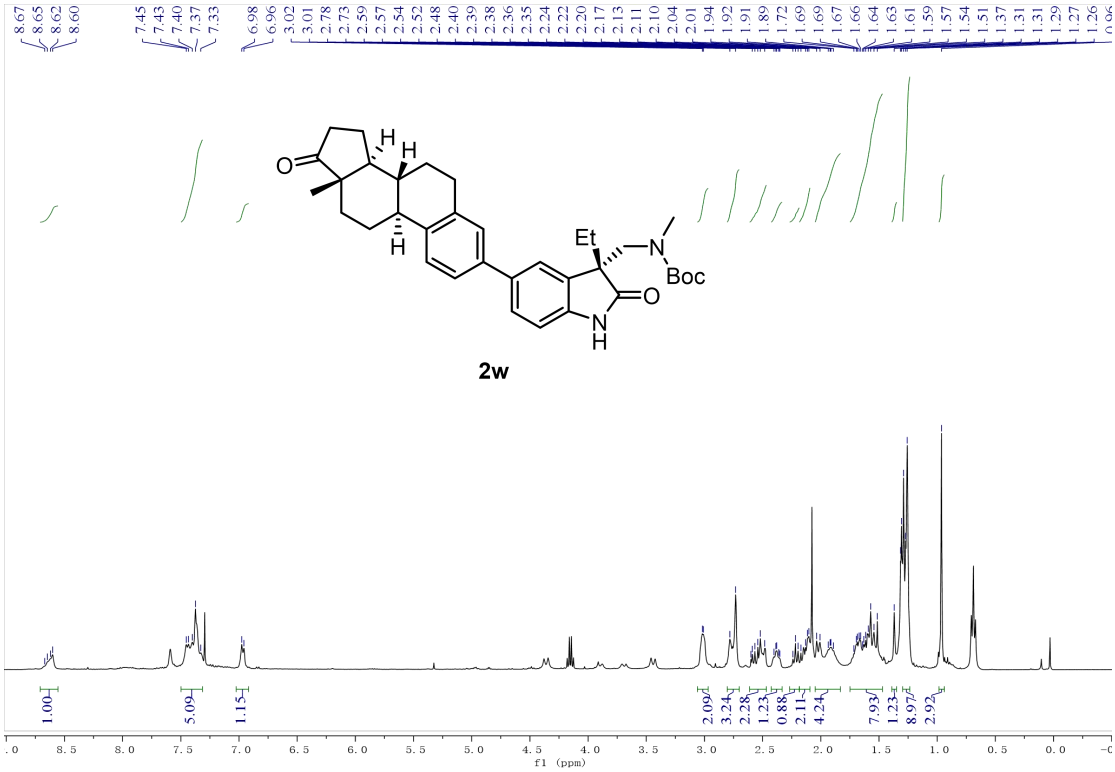


Figure S65. ^{1}H NMR spectra of **2w**

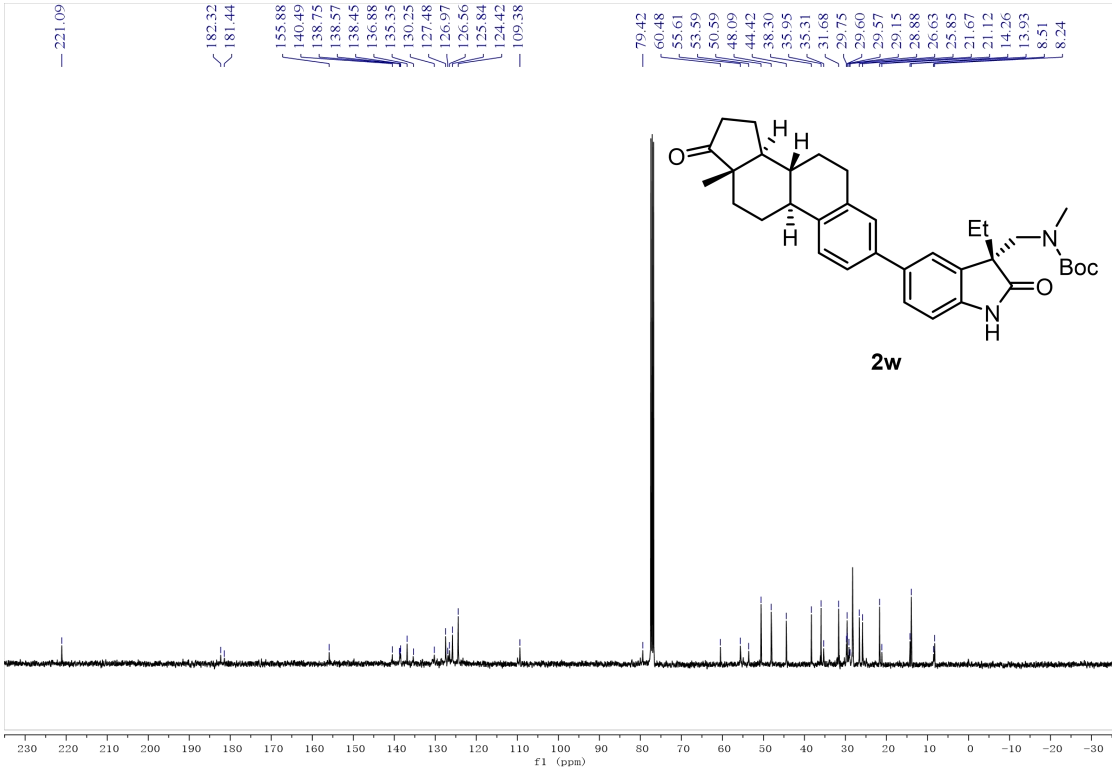


Figure S66. ^{13}C NMR spectra of **2w**

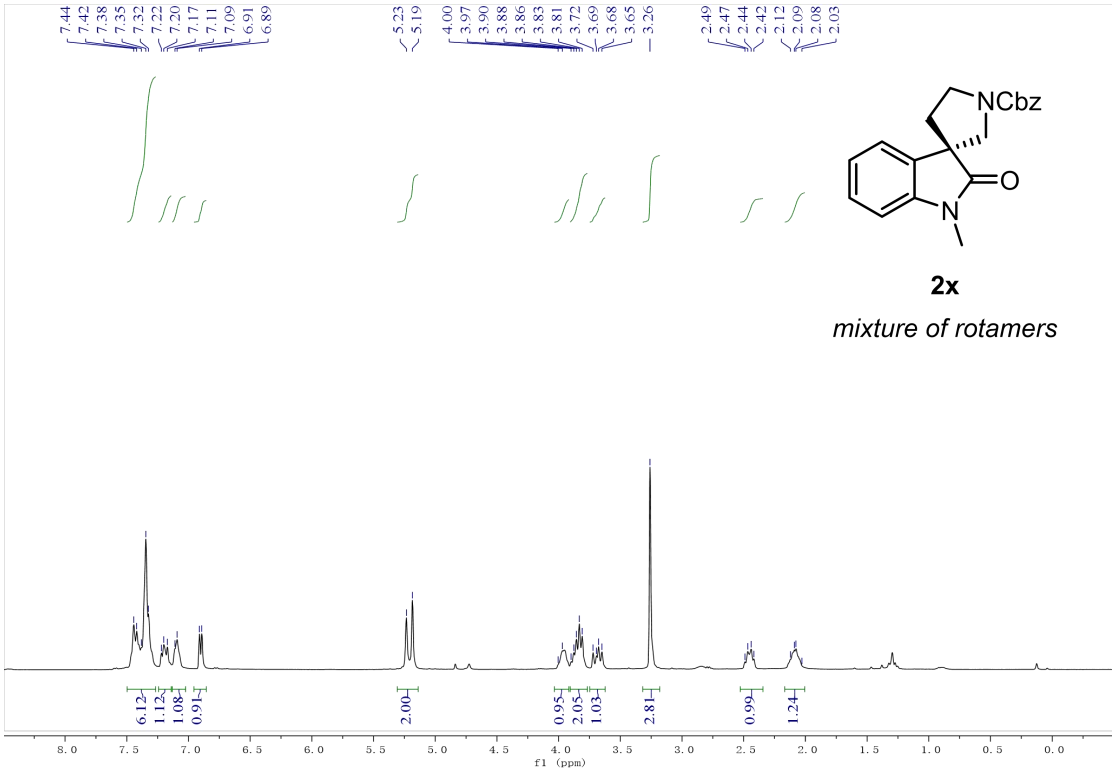


Figure S67. ^{1}H NMR spectra of **2x**

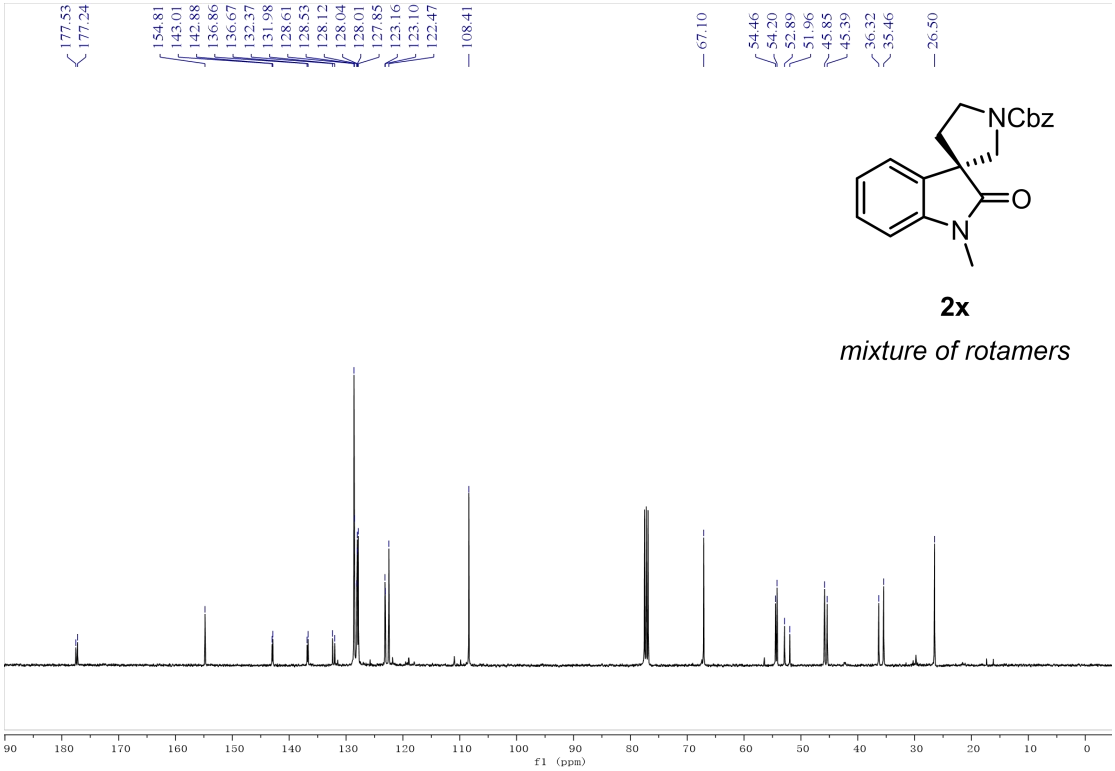


Figure S68. ^{13}C NMR spectra of **2x**

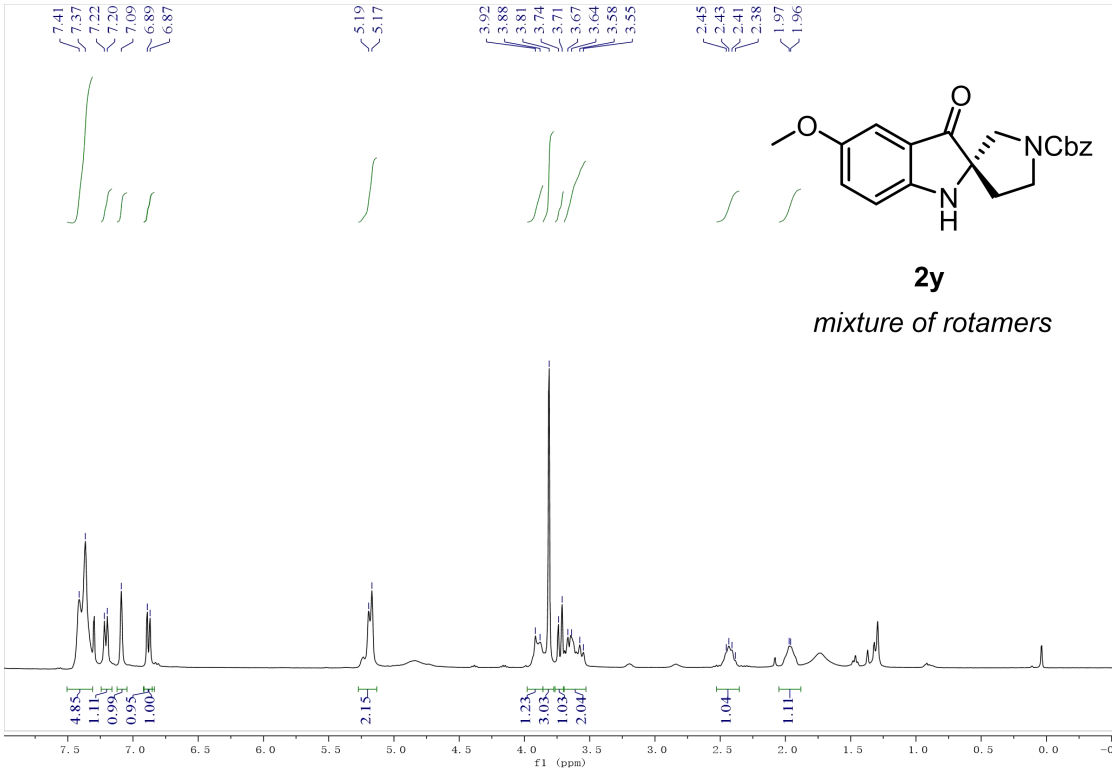


Figure S69. ^{1}H NMR spectra of **2y**

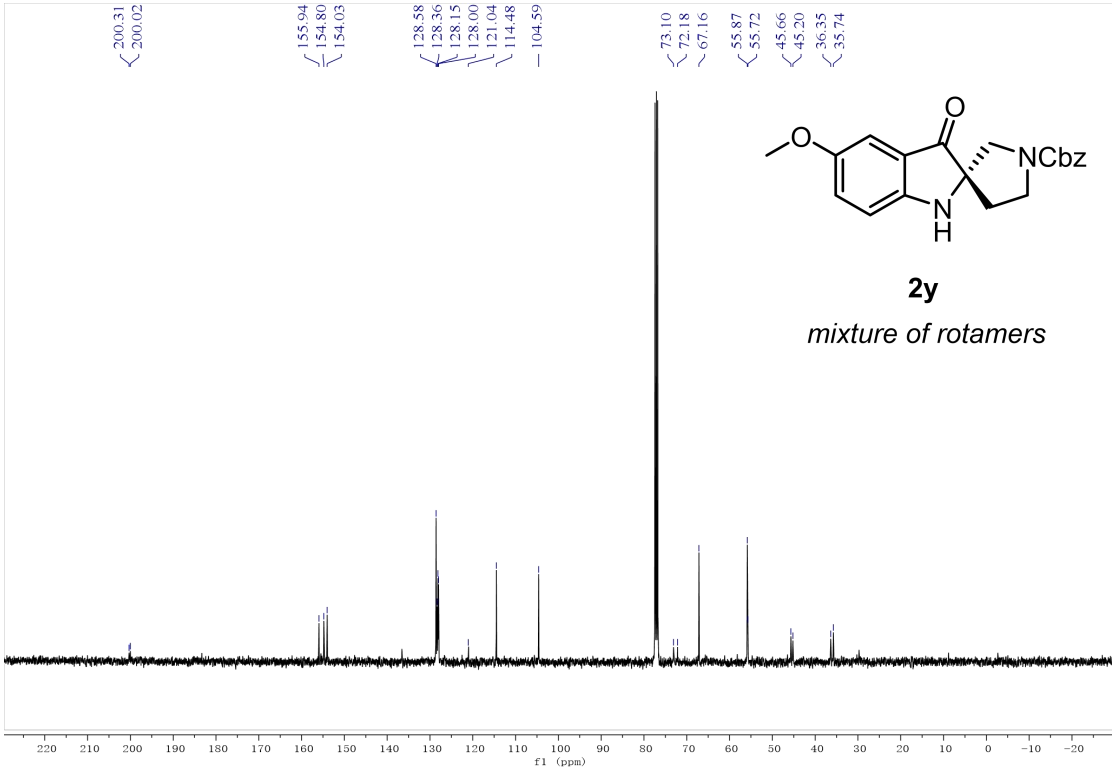


Figure S70. ^{13}C NMR spectra of **2y**

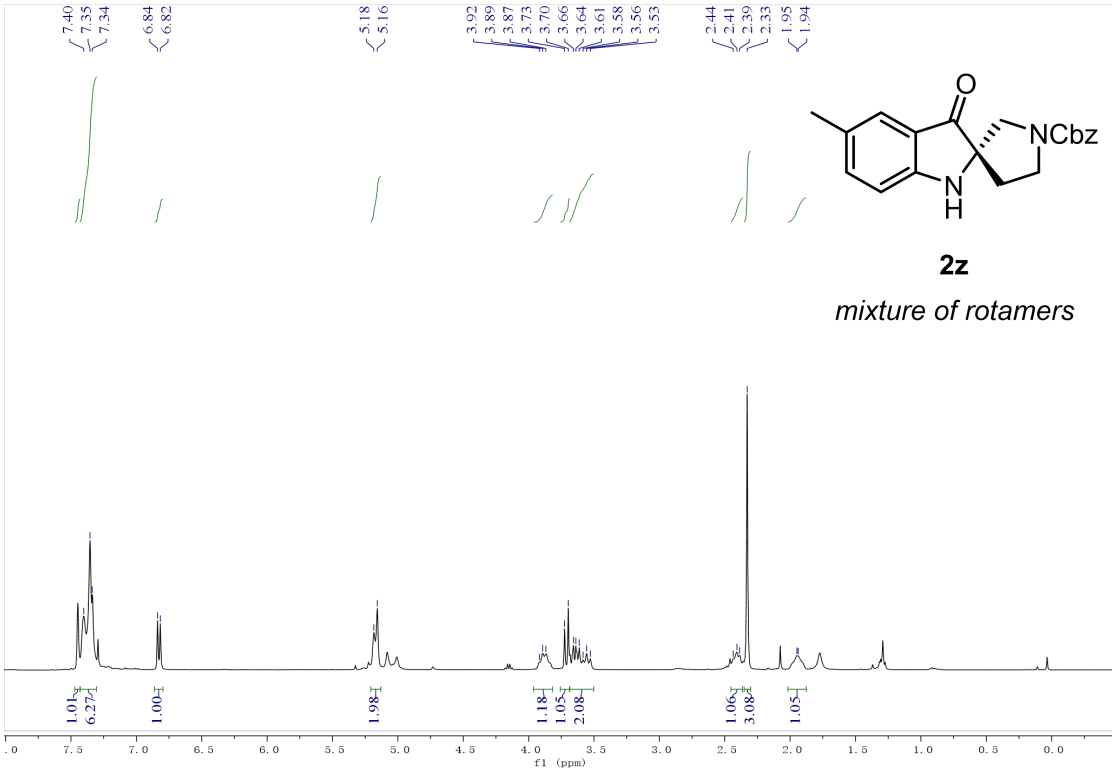


Figure S71. ^{1}H NMR spectra of **2z**

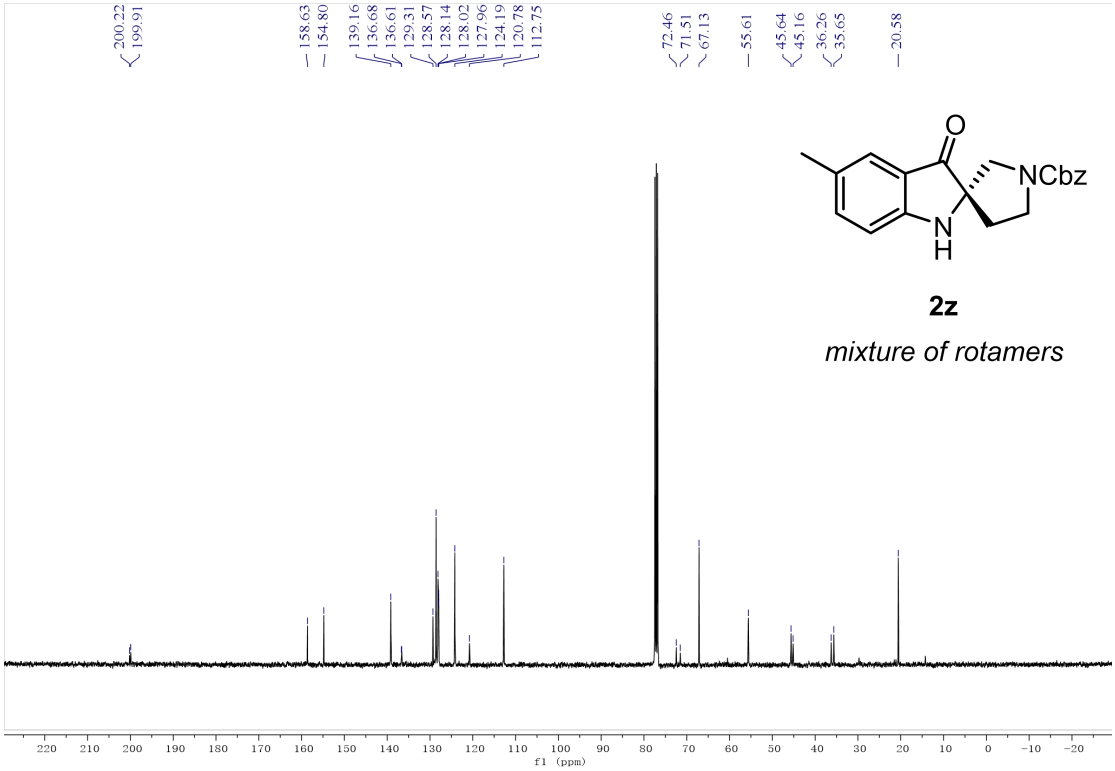


Figure S72. ^{13}C NMR spectra of **2z**

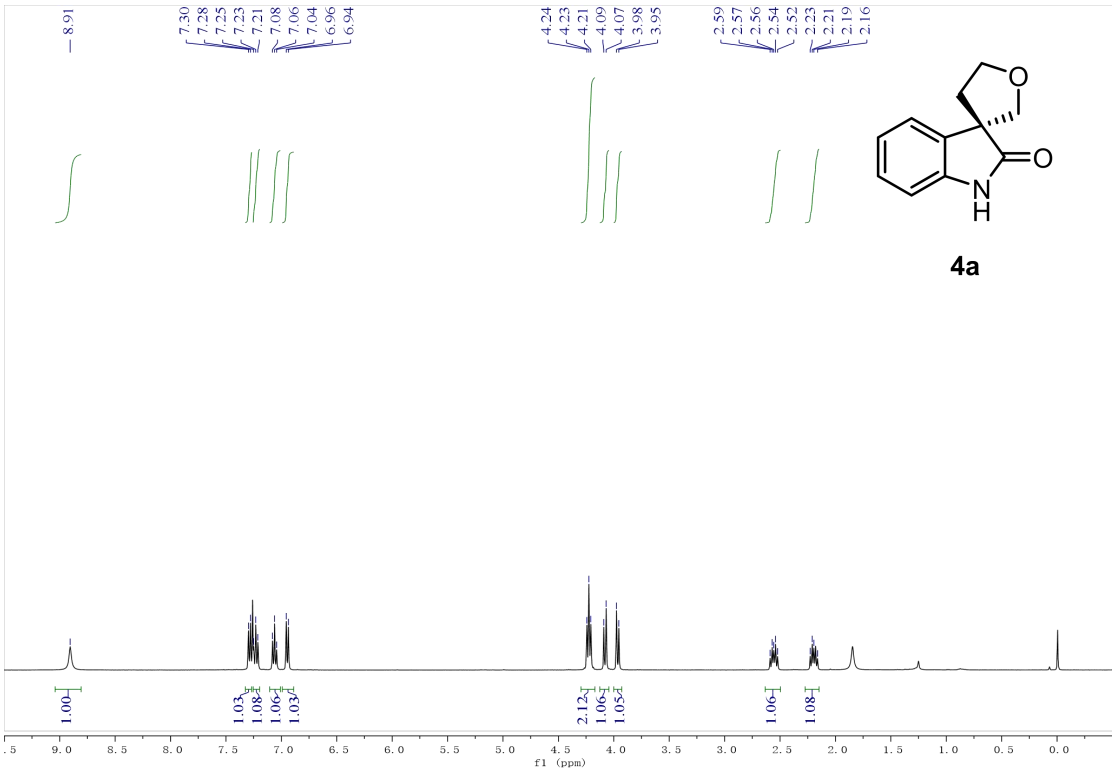


Figure S73. ^{1}H NMR spectra of **4a**

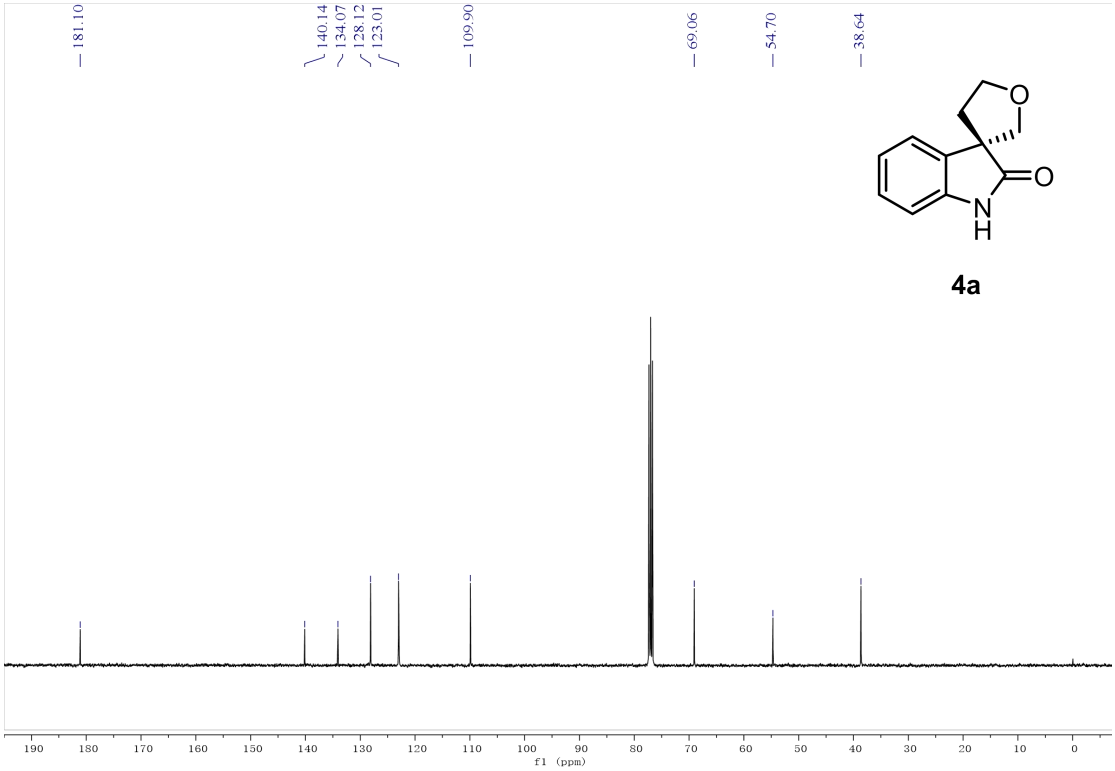


Figure S74. ^{13}C NMR spectra of **4a**

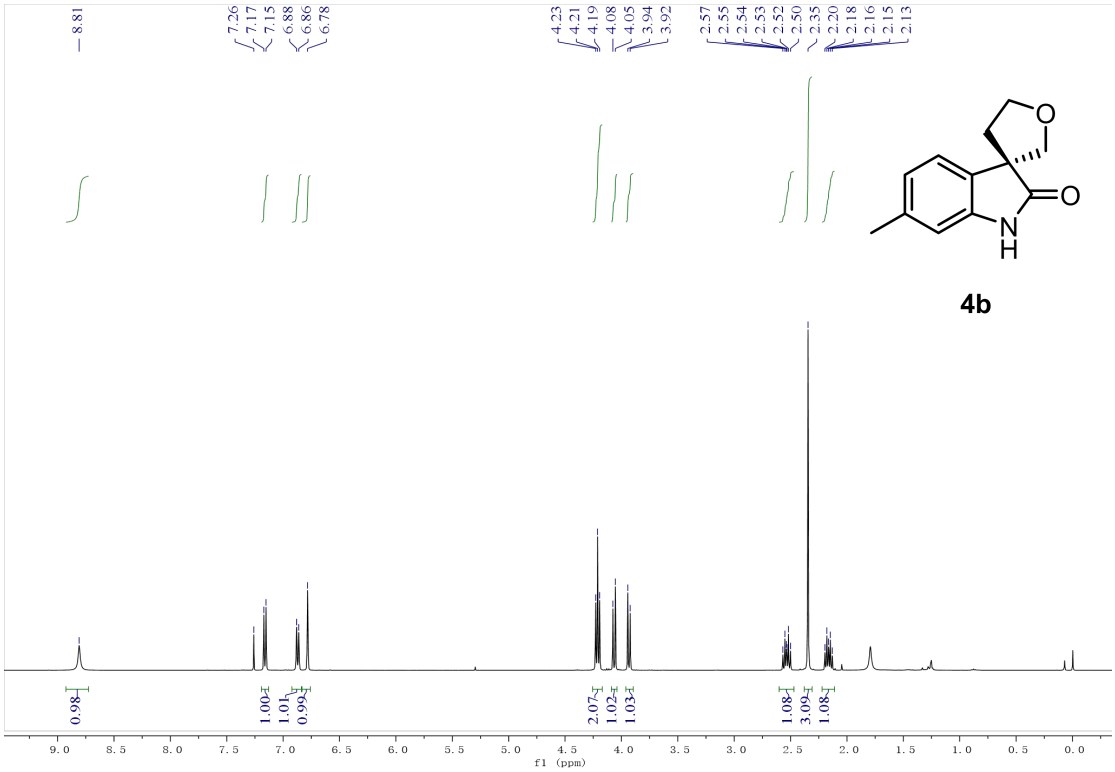


Figure S75. ^{1}H NMR spectra of **4b**

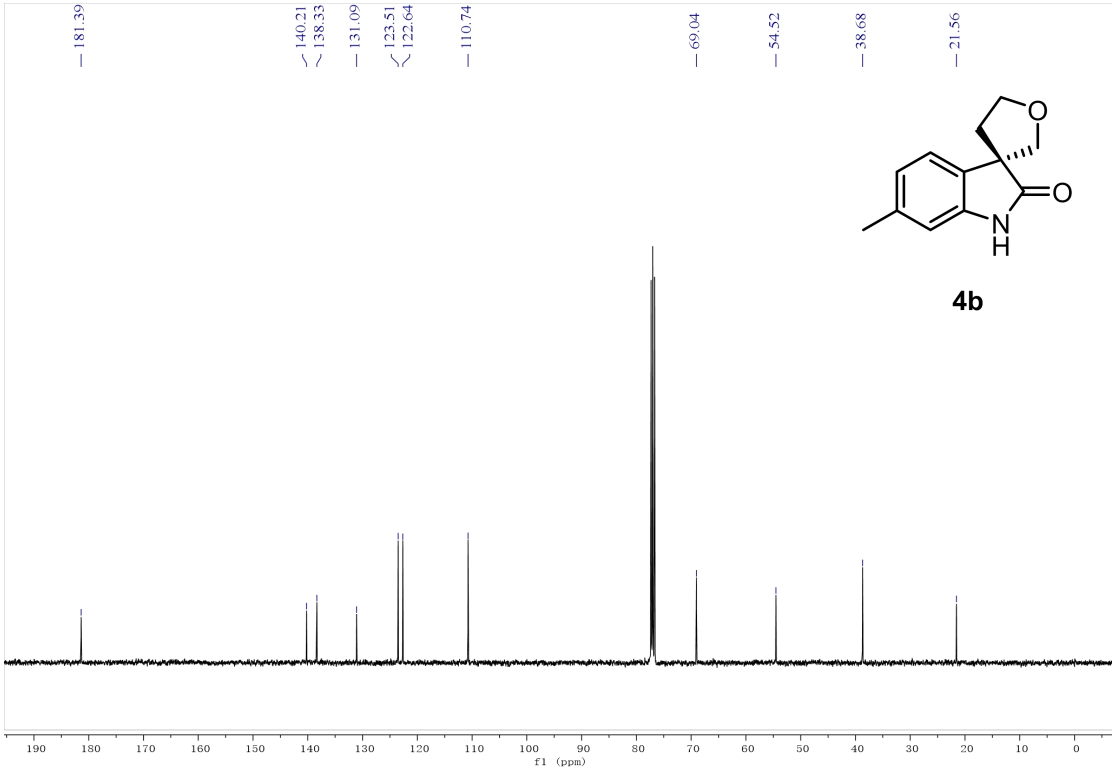


Figure S76. ^{13}C NMR spectra of **4b**

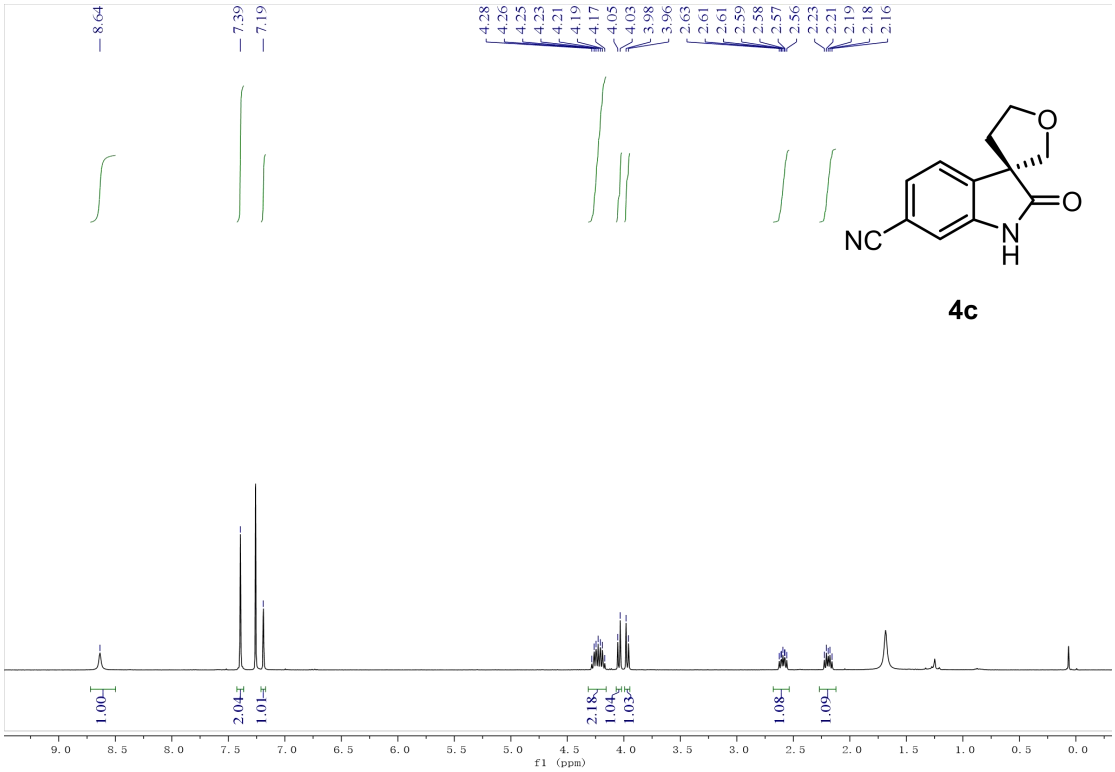


Figure S77. ^{1}H NMR spectra of **4c**

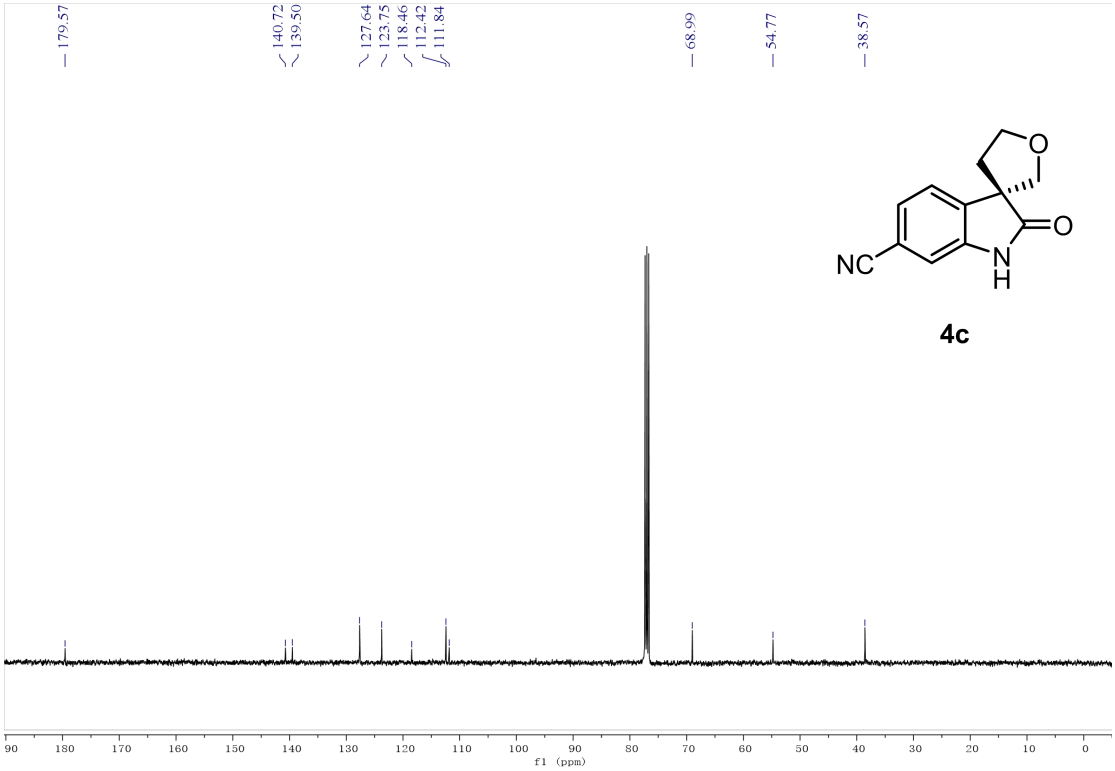


Figure S78. ^{13}C NMR spectra of **4c**

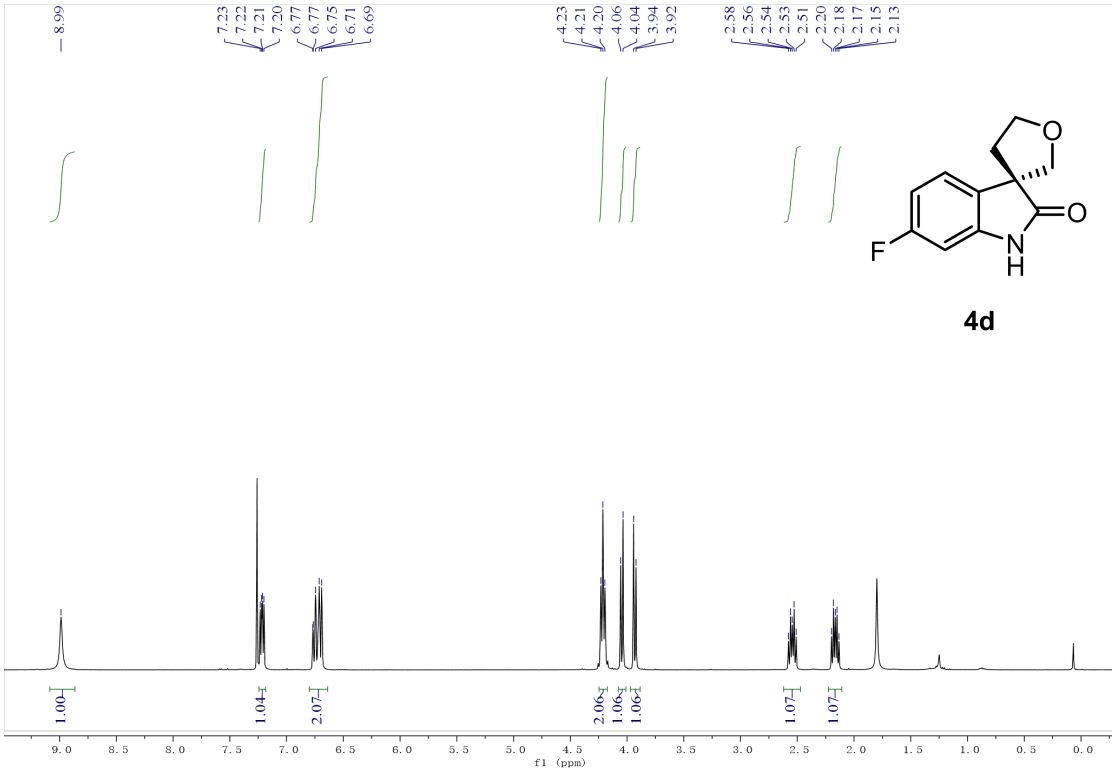


Figure S79. ^{1}H NMR spectra of **4d**

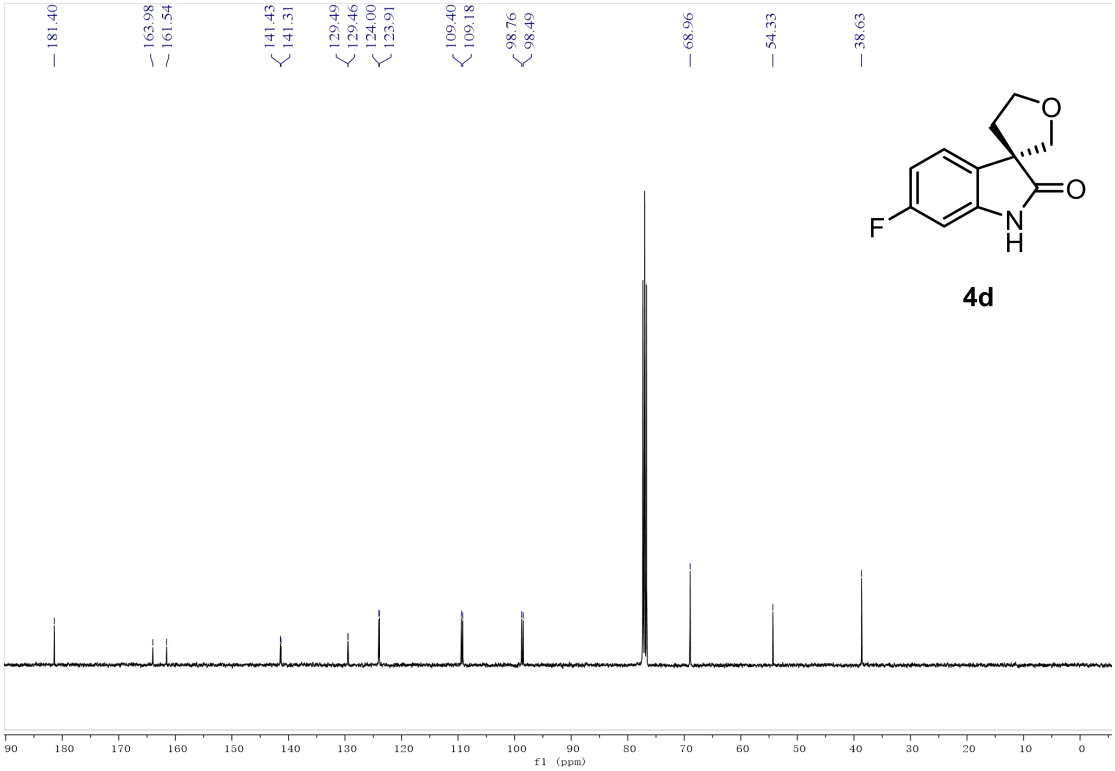


Figure S80. ^{13}C NMR spectra of **4d**

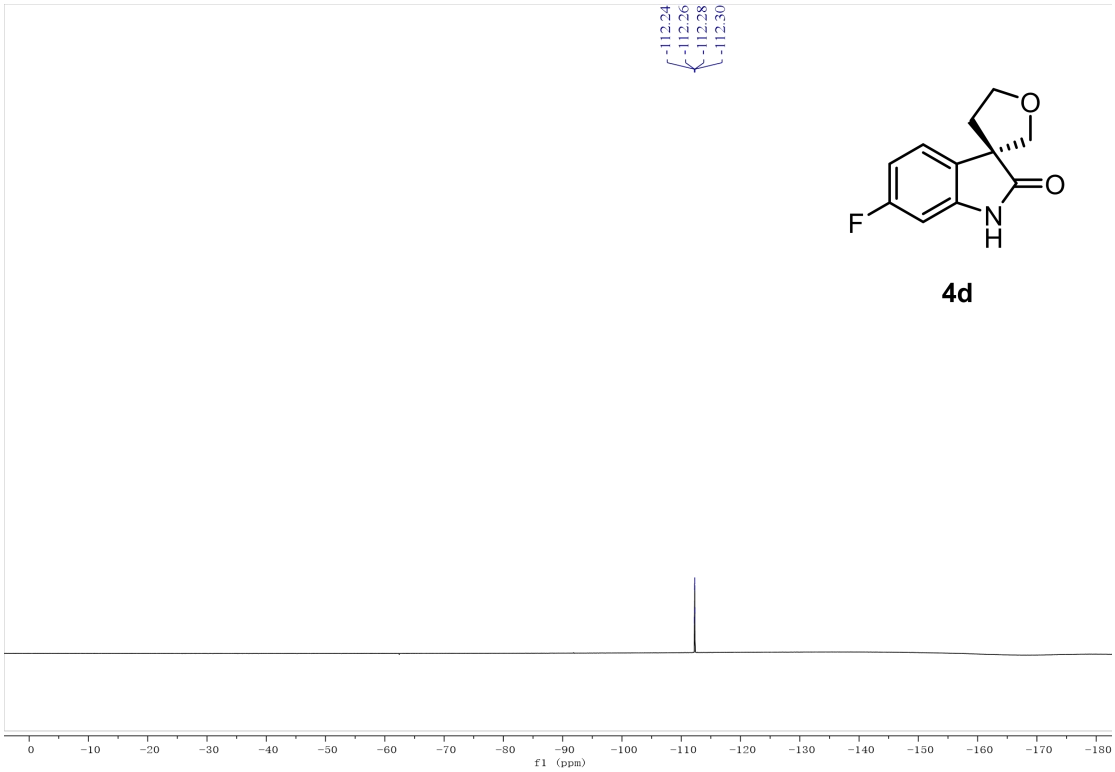


Figure S81. ^{19}F NMR spectra of **4d**

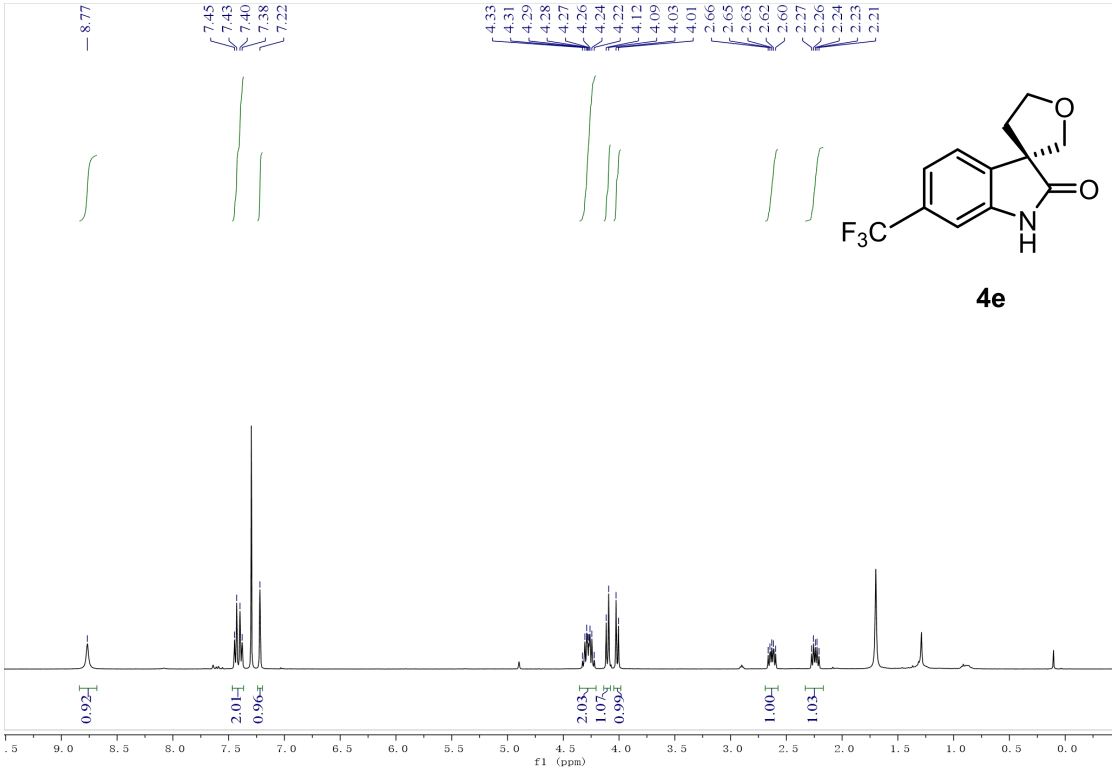


Figure S82. ^{1}H NMR spectra of **4e**

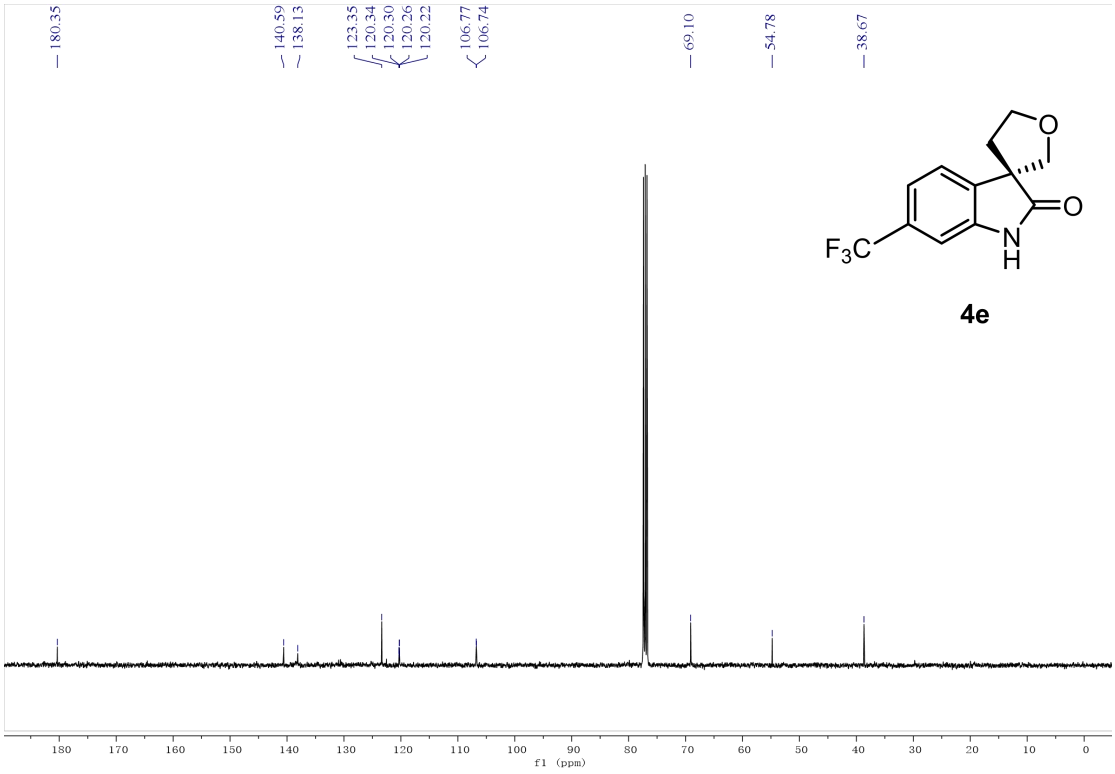


Figure S83. ^{13}C NMR spectra of **4e**

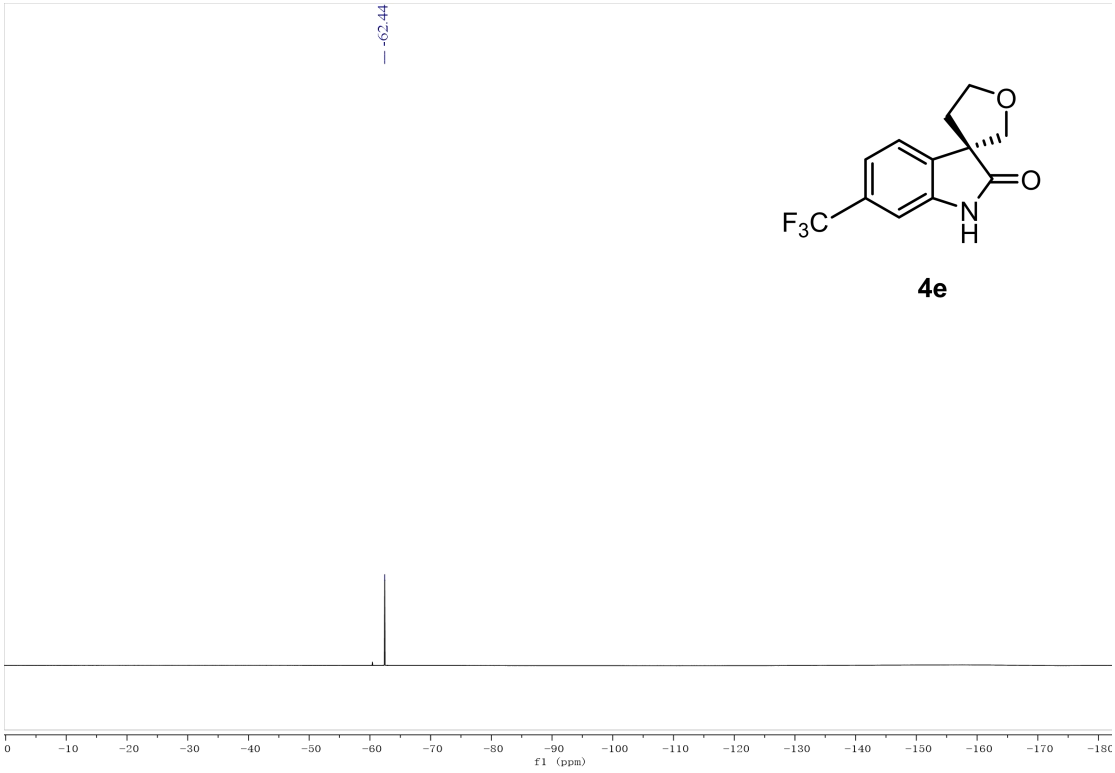


Figure S84. ^{19}F NMR spectra of **4e**

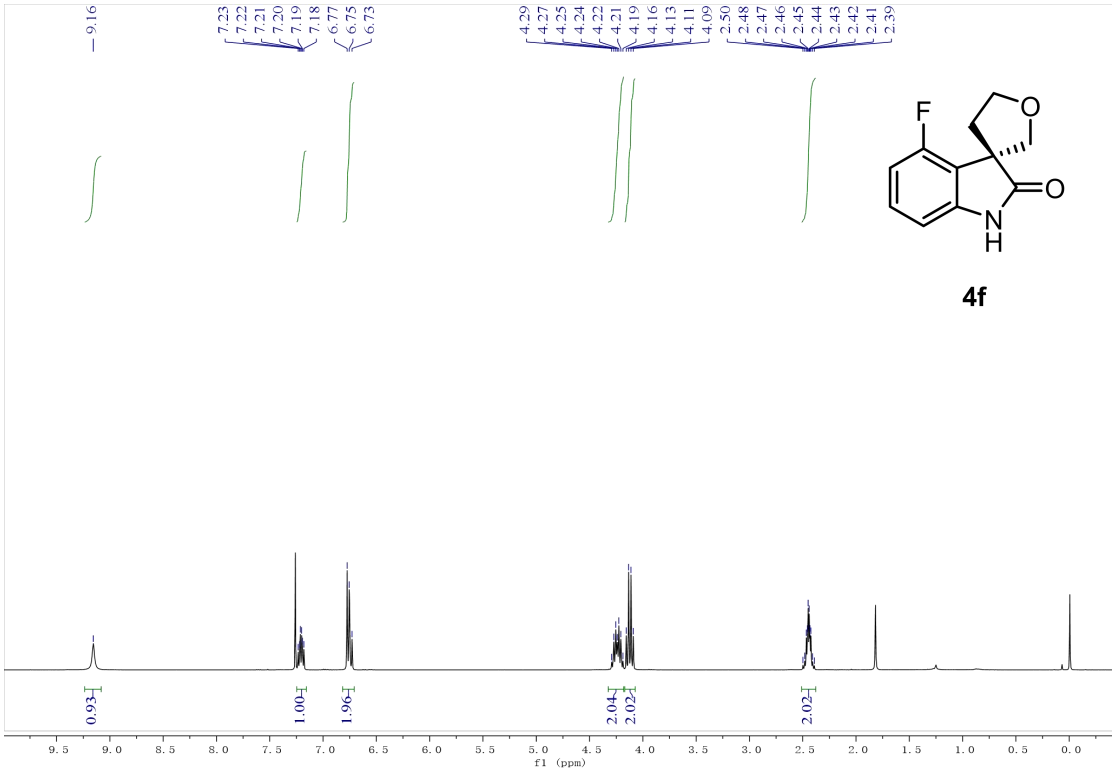


Figure S85. ^{1}H NMR spectra of **4f**

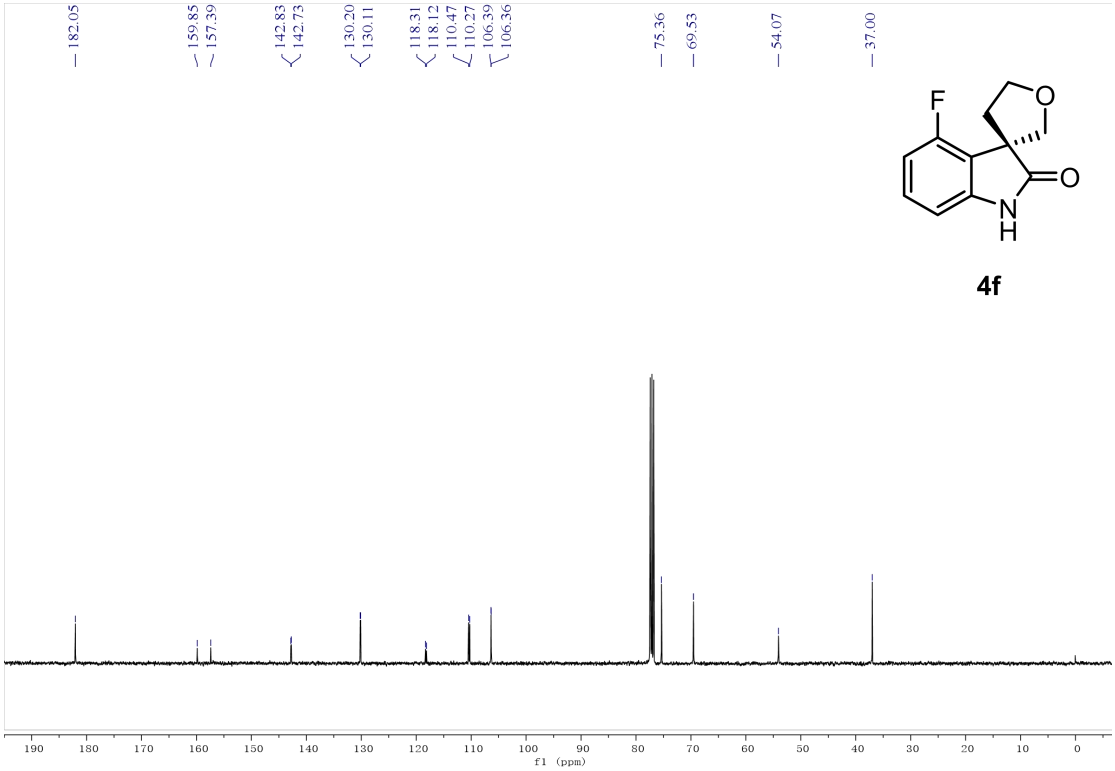


Figure S86. ^{13}C NMR spectra of **4f**

f

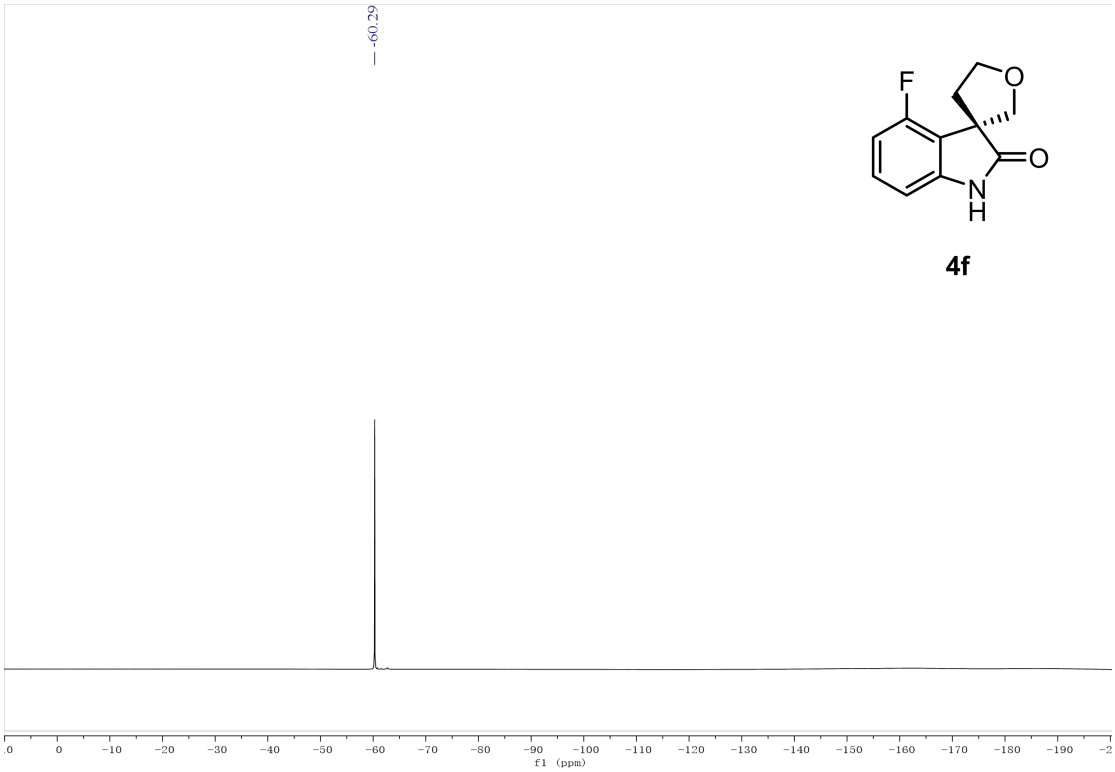


Figure S87. ^{19}F NMR spectra of **4f**

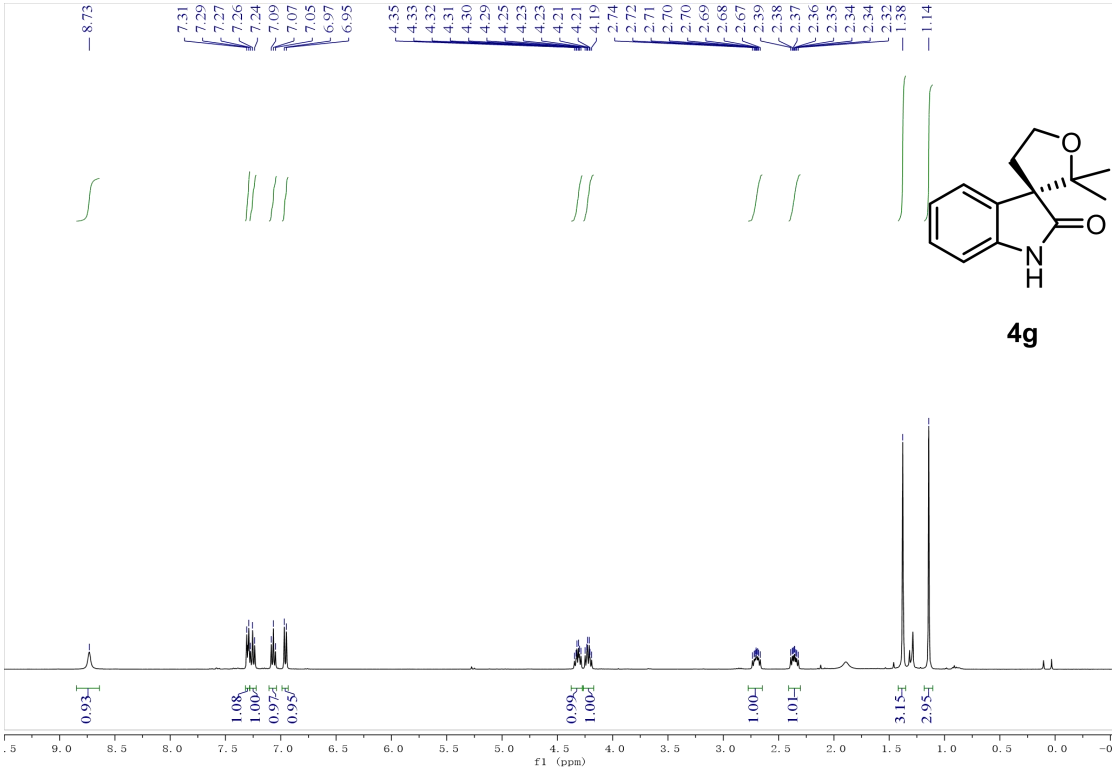


Figure S88. ^{1}H NMR spectra of **4g**

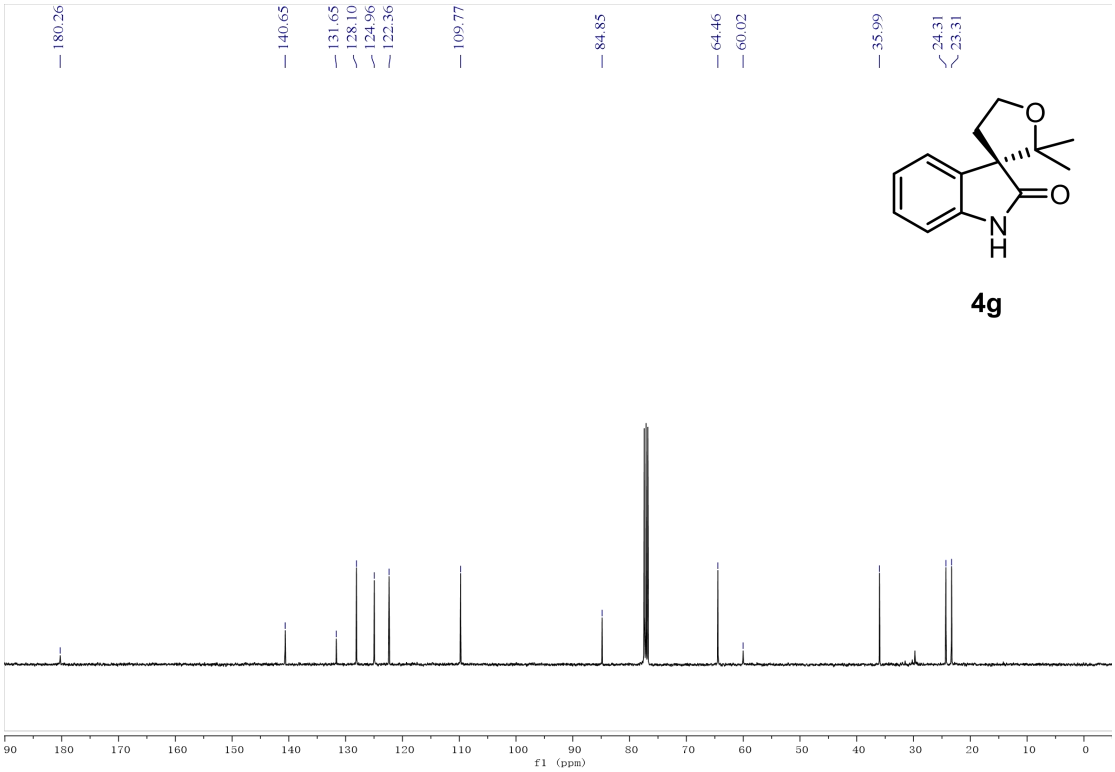


Figure S89. ^{13}C NMR spectra of **4g**

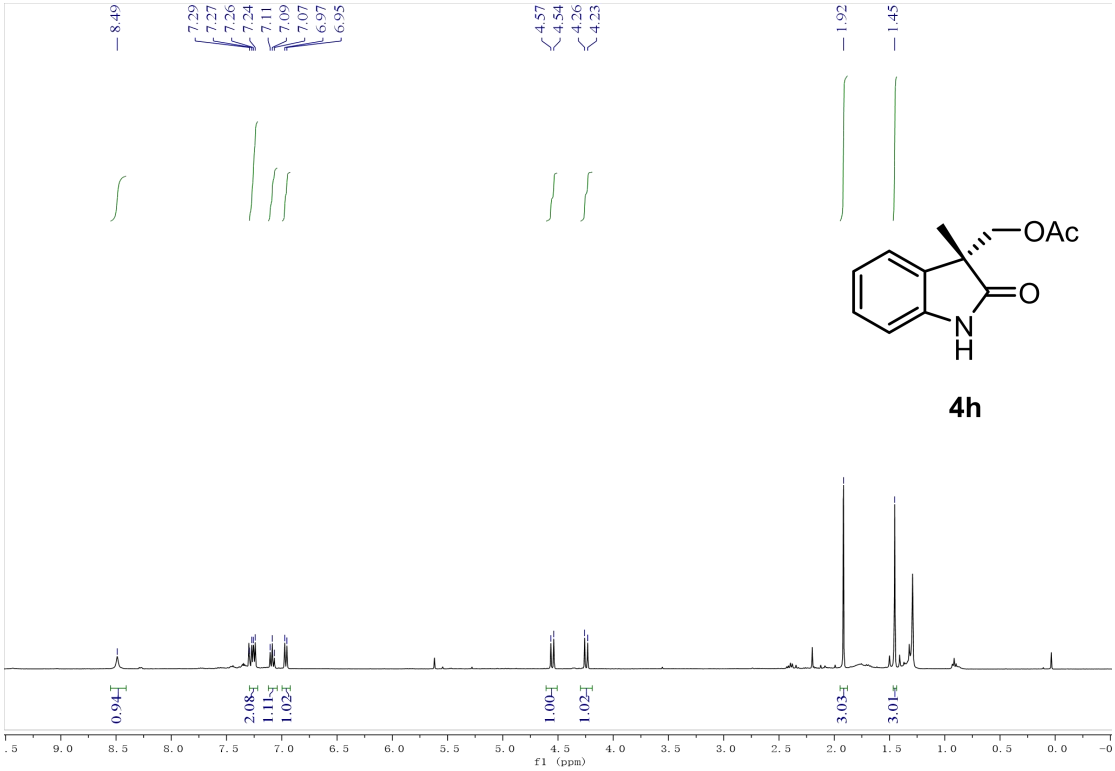


Figure S90. ^{1}H NMR spectra of **4h**

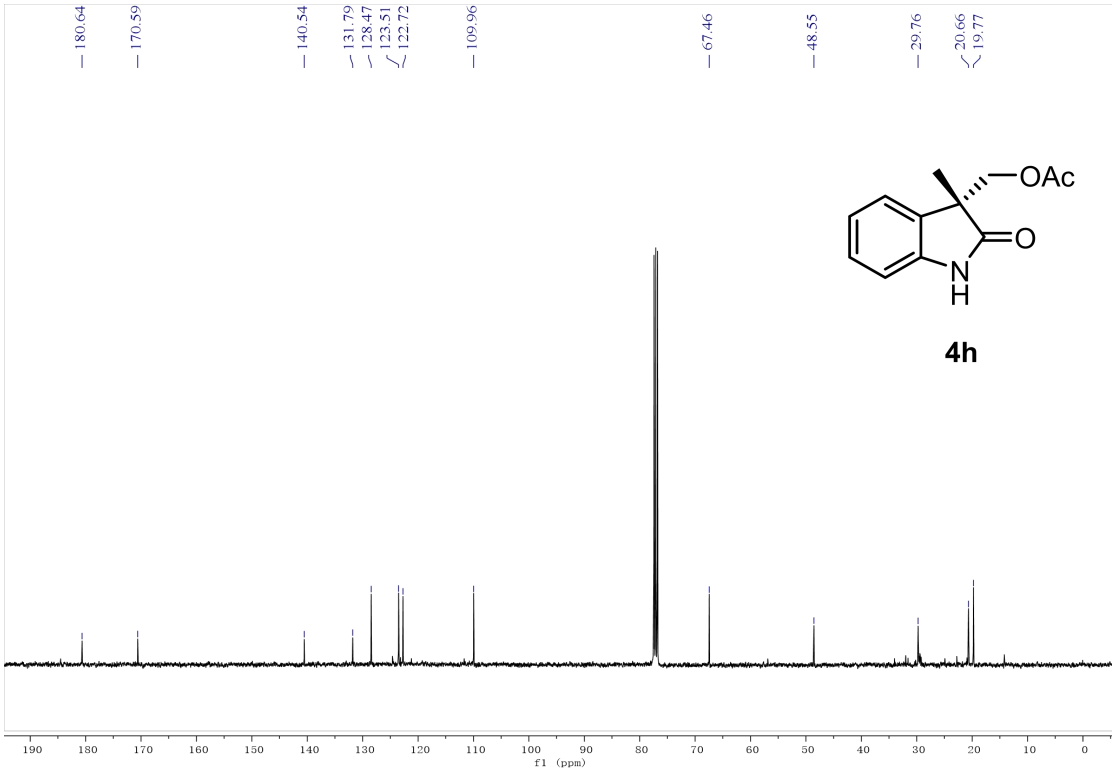


Figure S91. ^{13}C NMR spectra of **4h**

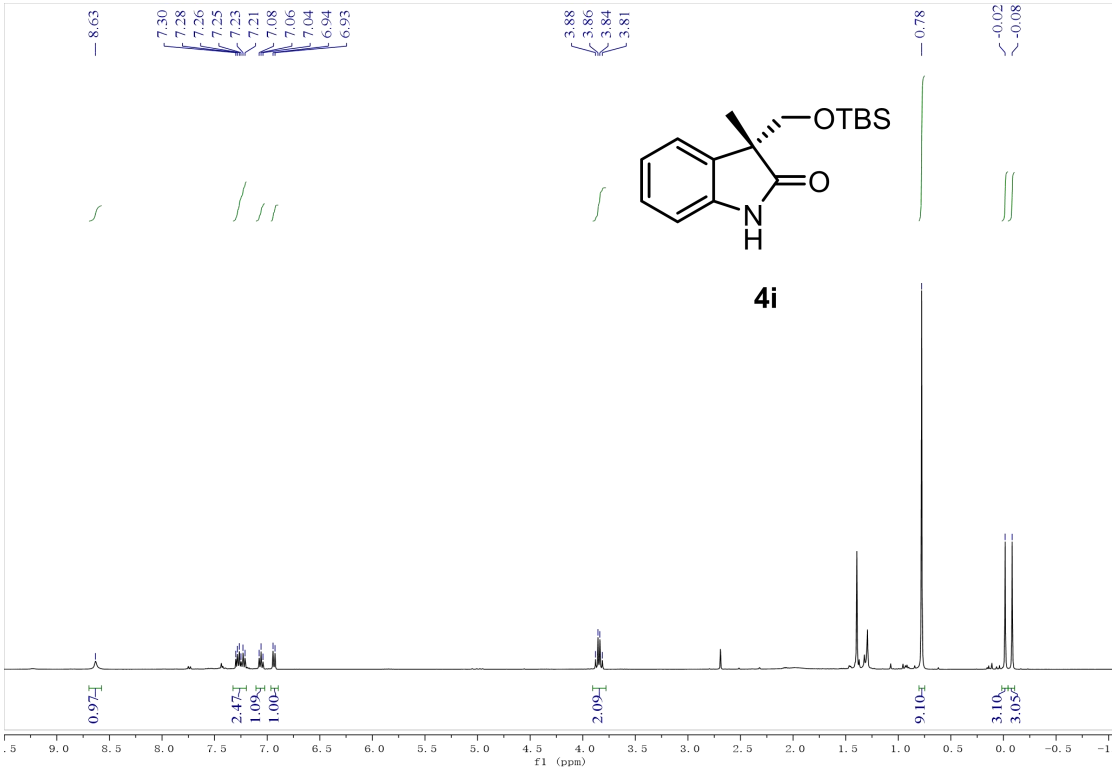


Figure S92. ^{1}H NMR spectra of **4i**

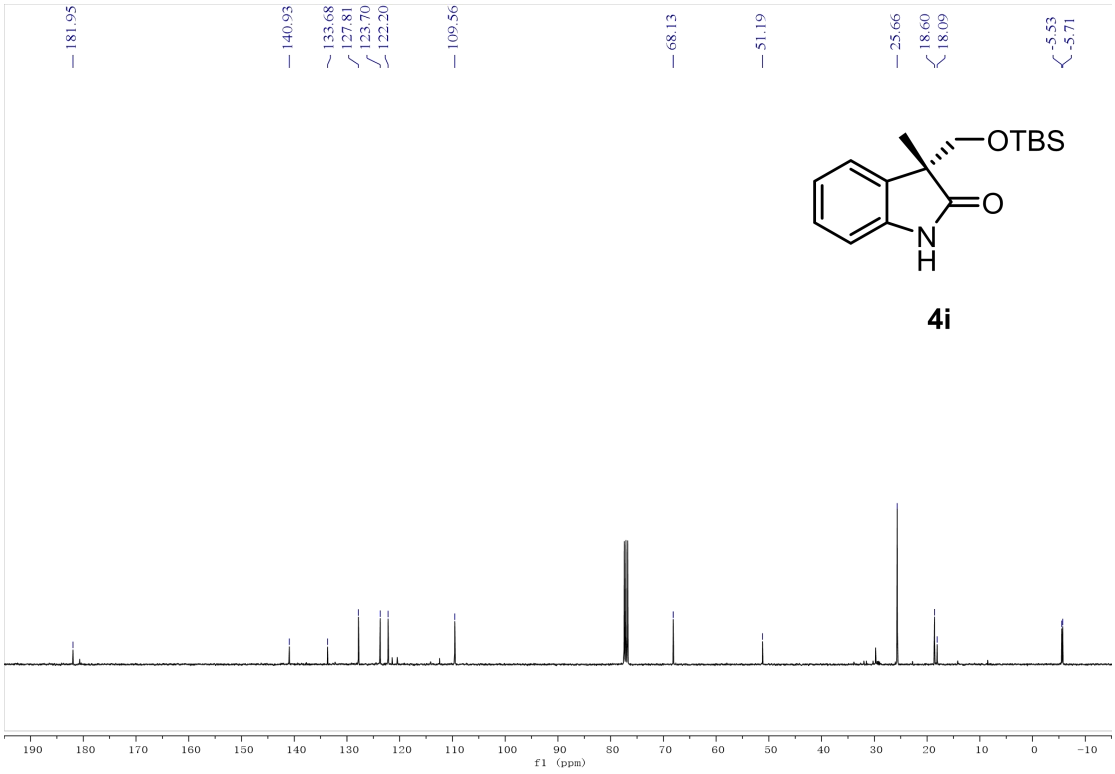


Figure S93. ^{13}C NMR spectra of **4i**

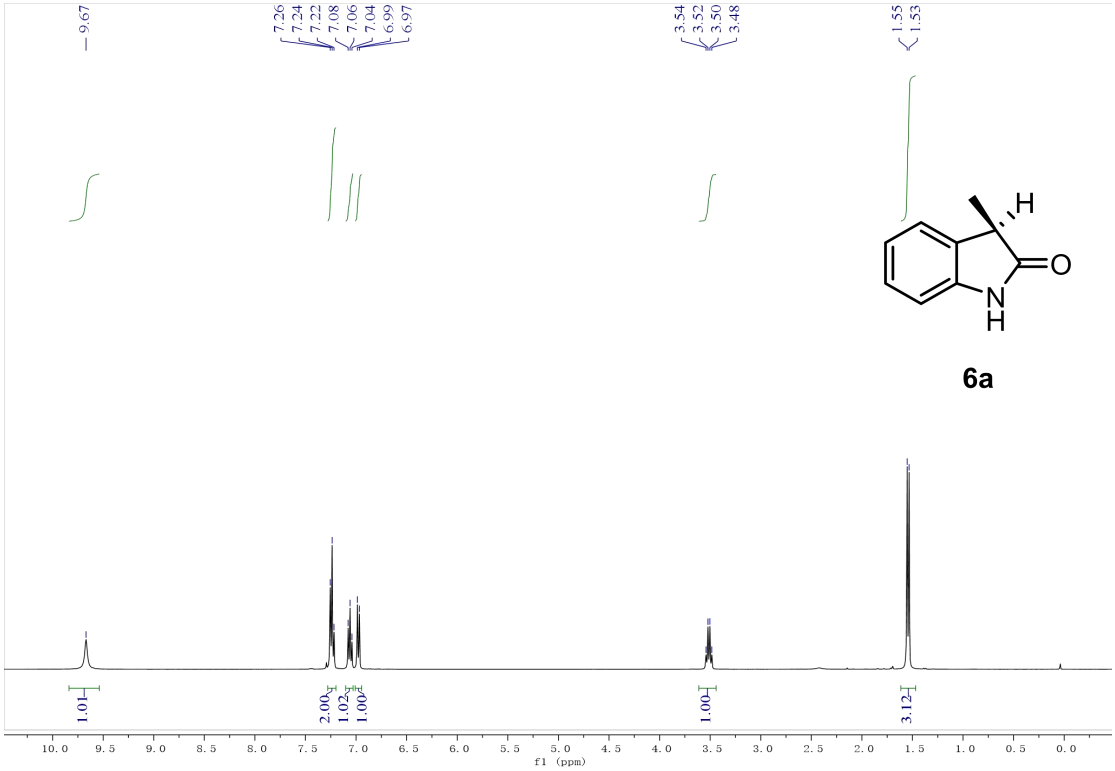


Figure S94. ^{1}H NMR spectra of **6a**

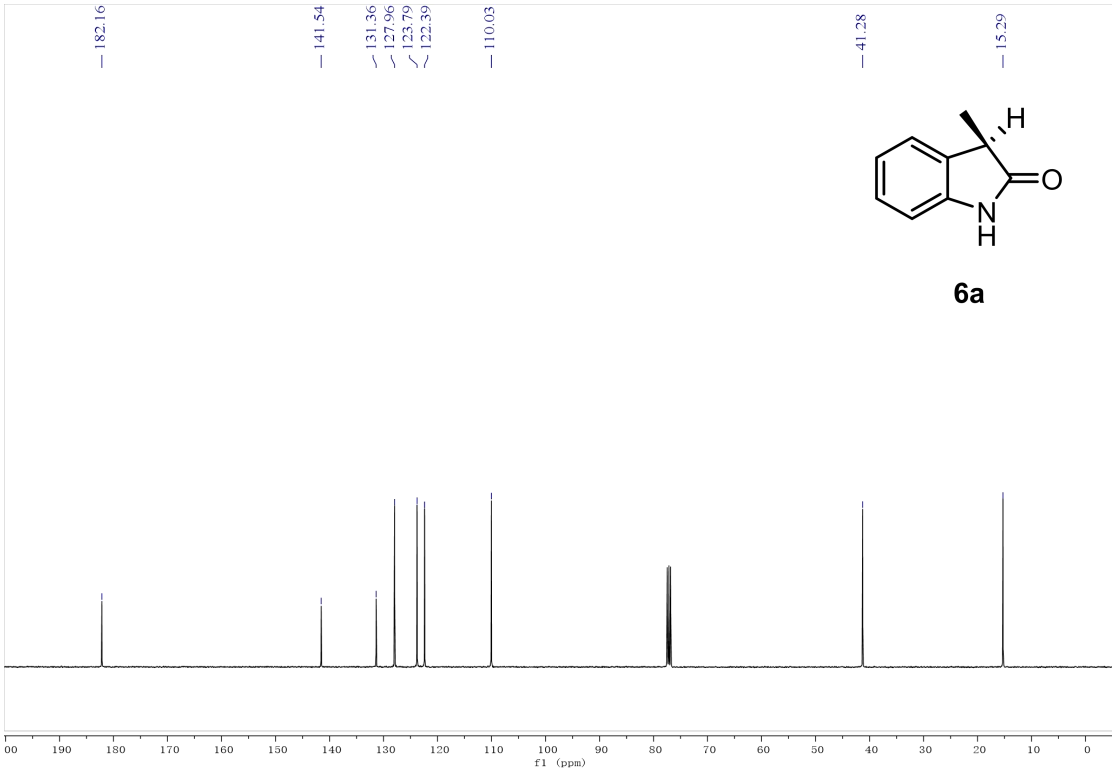


Figure S95. ^{13}C NMR spectra of **6a**

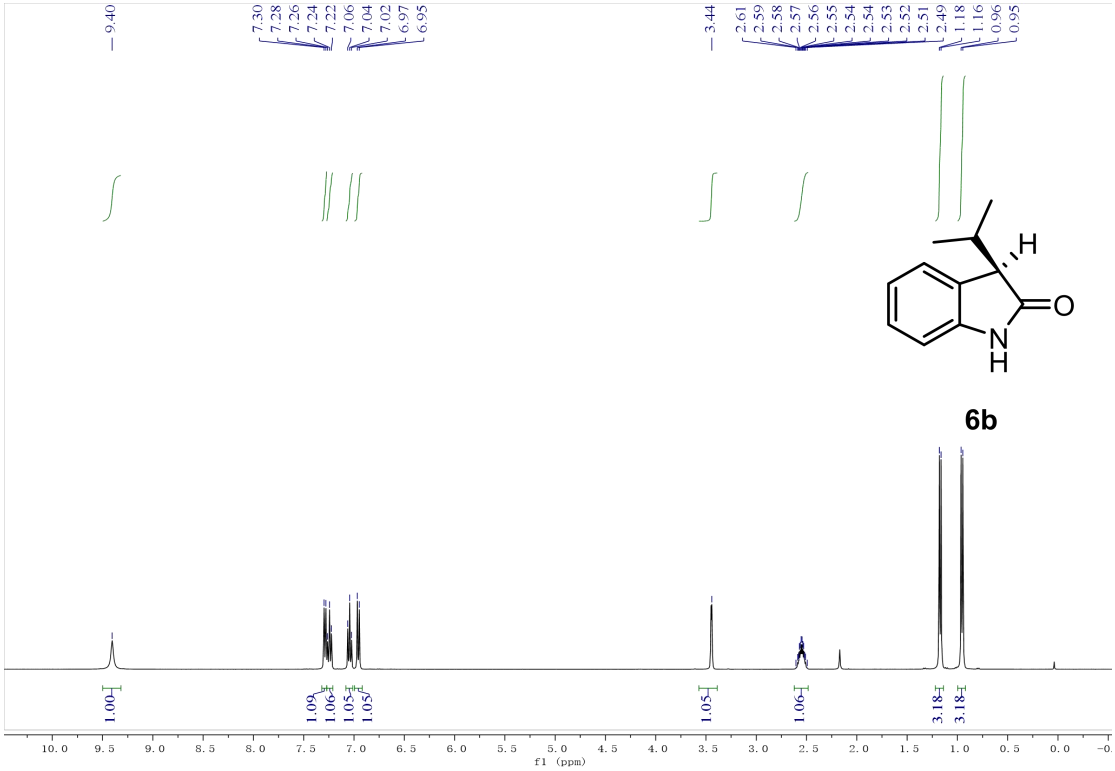


Figure S96. ^{1}H NMR spectra of **6b**

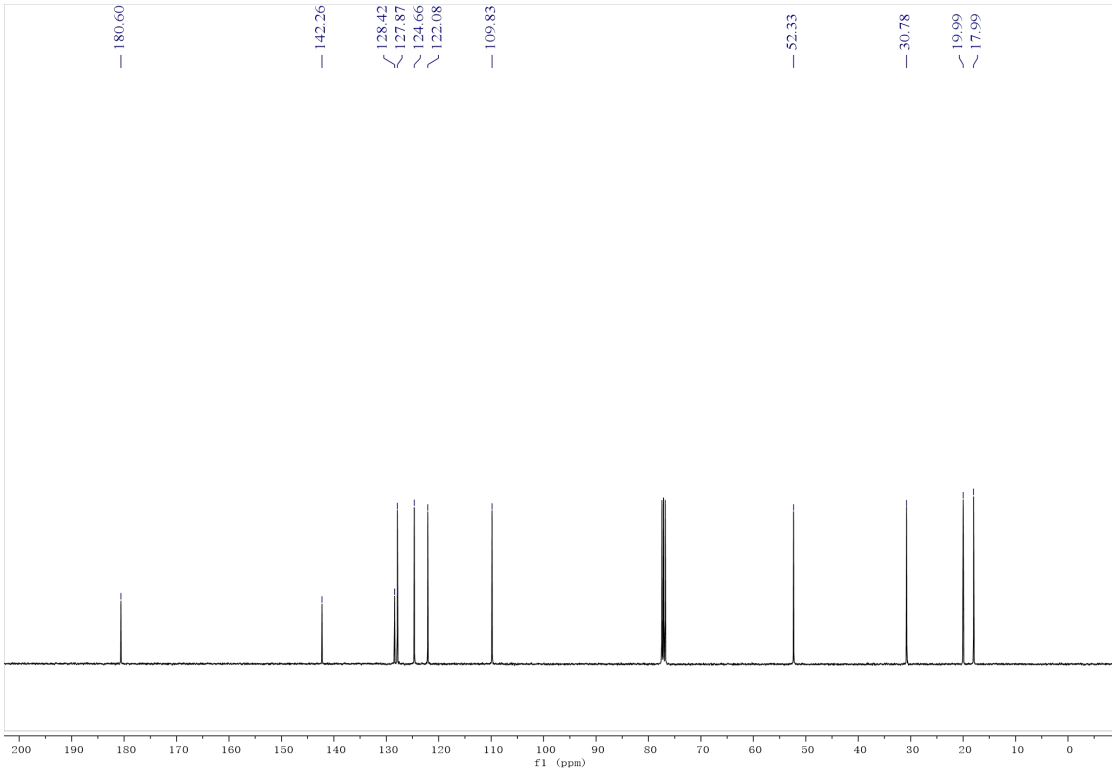


Figure S97. ^{13}C NMR spectra of **6b**

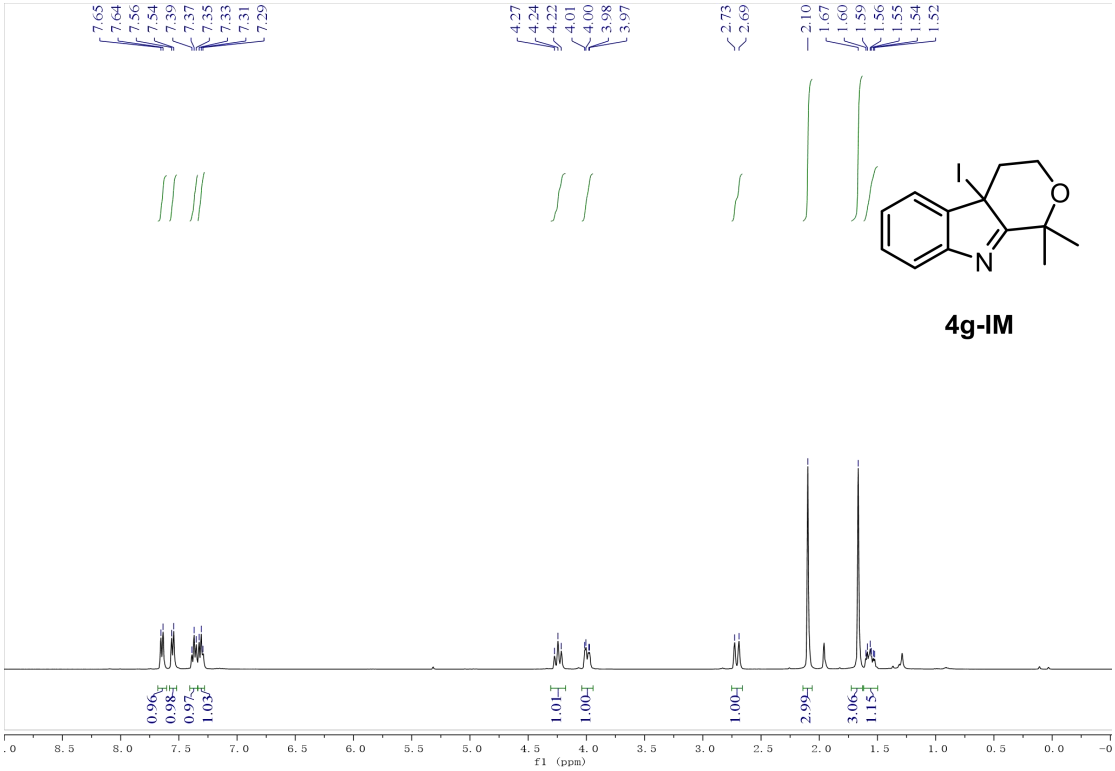


Figure S98. ^{1}H NMR spectra of **4g-IM**

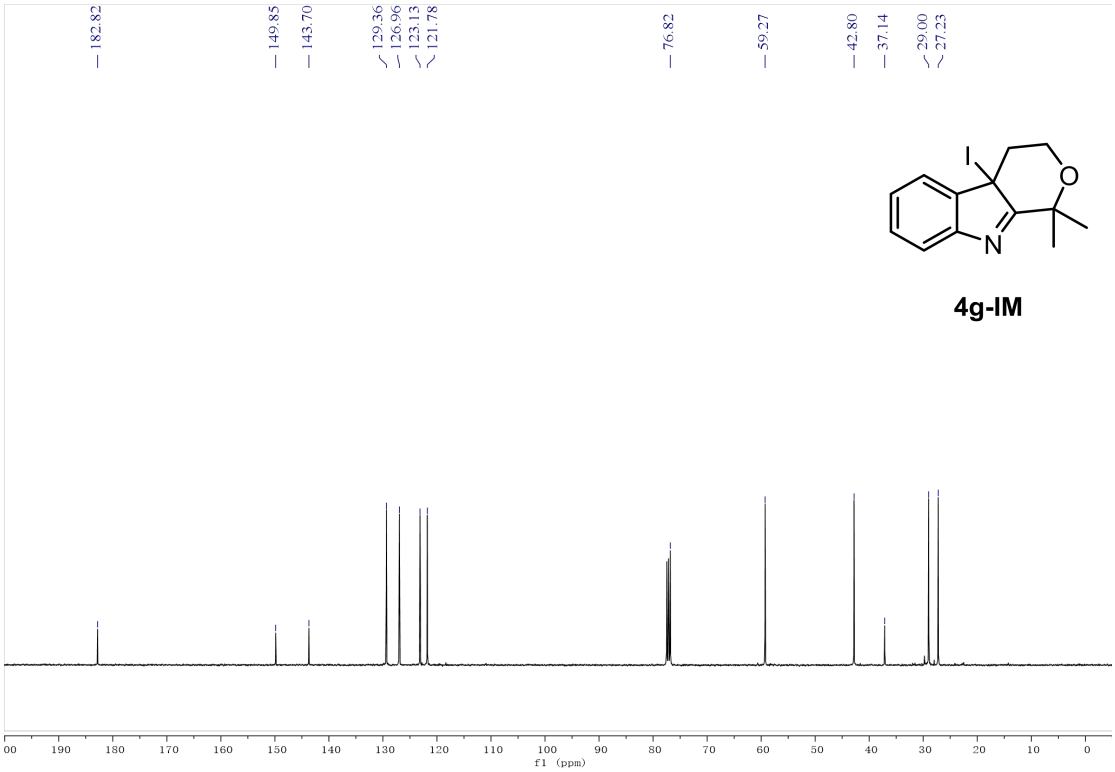
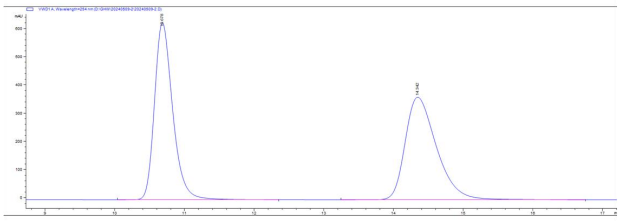


Figure S99. ^{13}C NMR spectra of **4g-IM**

Chiral HPLC spectrum of racemic 2a



信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
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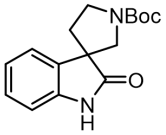
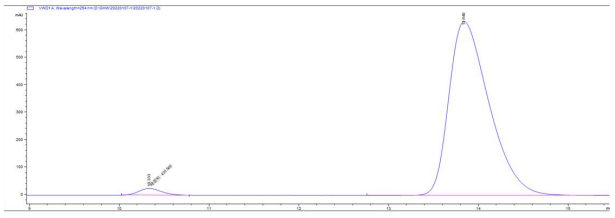
2	14.342	BB	0.4781	1.13107e4	362.40274	49.9534



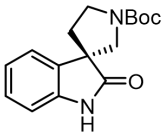
2a-Rac

Chiral HPLC spectrum of 2a



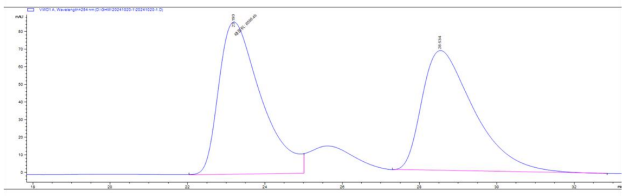
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.333	MM	0.2946	430.56567	24.35566	2.1458
2	13.840	BBA	0.4770	1.96346e4	632.73596	97.8542



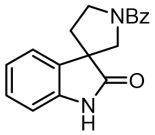
2a

Chiral HPLC spectrum of racemic 2b



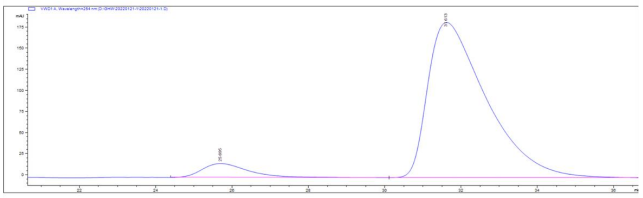
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.193	MM	1.2673	6556.45117	86.22924	50.7448
2	28.534	BBA	1.3987	6363.99170	67.88761	49.2552



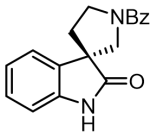
2b-Rac

Chiral HPLC spectrum of 2b



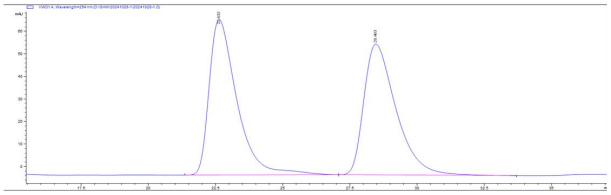
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	25.695	BB	1.2577	1405.67786	16.56951	6.6634
2	31.613	BBA	1.5898	1.96899e4	184.69434	93.3366



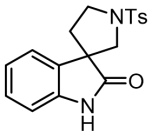
2b

Chiral HPLC spectrum of racemic 2c



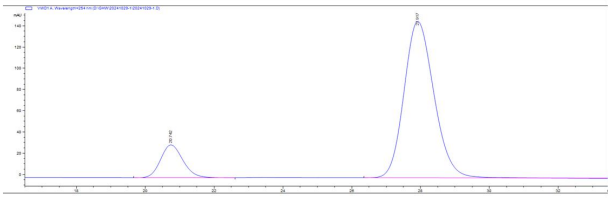
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.632	BB	1.0718	4933.25391	68.86083	50.6082
2	28.463	BB	1.2540	4814.67969	57.91005	49.3918



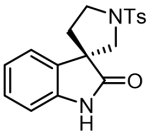
2c-Rac

Chiral HPLC spectrum of 2c



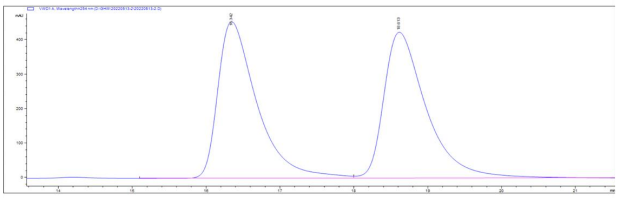
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.742	BB	0.6998	1402.65674	31.00234	13.5427
2	27.917	BB	0.9382	8954.61328	147.71970	86.4573



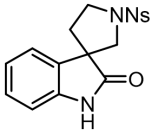
2c

Chiral HPLC spectrum of racemic 2d



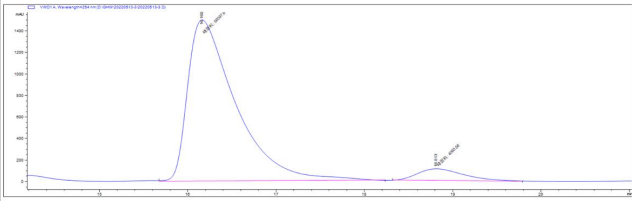
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.342	BV	0.5498	1.67591e4	454.93628	49.7482
2	18.613	VBA	0.5982	1.69288e4	423.67511	50.2518



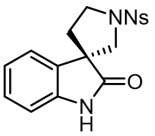
2d-Rac

Chiral HPLC spectrum of 2d



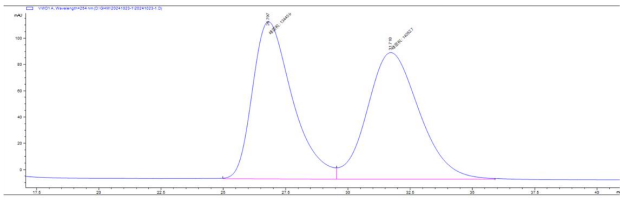
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.160	MM	0.6312	5.65976e4	1494.43750	93.2981
2	18.813	MM	0.6176	4065.57739	109.71777	6.7019



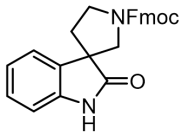
2d

Chiral HPLC spectrum of racemic 2e



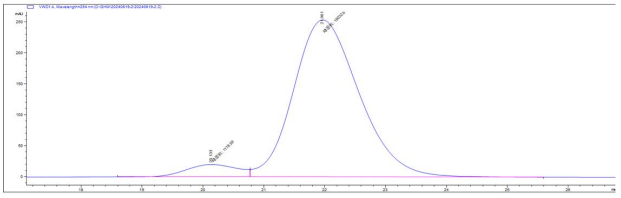
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.797	MM	1.8656	1.34409e4	120.07686	48.8874
2	21.710	MM	2.4235	1.40527e4	96.64259	51.1126



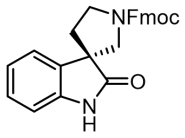
2e-Rac

Chiral HPLC spectrum of 2e



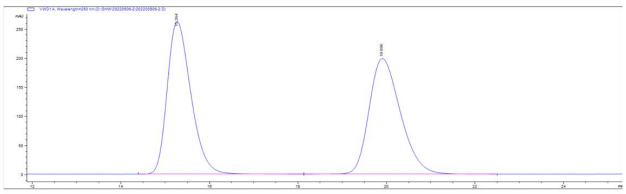
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.133	MM	0.9895	1178.59253	19.85148	5.8314
2	21.961	MM	1.2499	1.90326e4	253.78210	94.1686



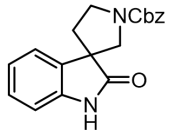
2e

Chiral HPLC spectrum of racemic 2f



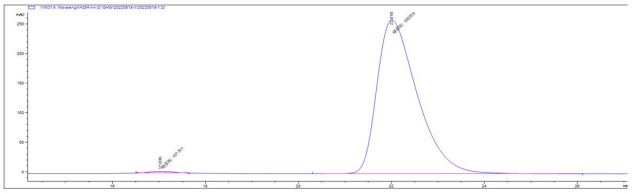
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.264	BB	0.5729	9714.64551	261.82761	49.9619
2	19.896	BB	0.7576	9729.44922	198.22284	50.0381



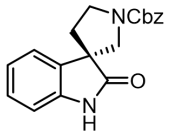
2f-Rac

Chiral HPLC spectrum of 2f



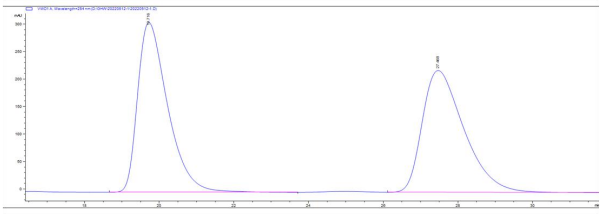
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.036	MM	0.6108	107.81138	2.94201	0.6898
2	22.010	MM	0.9989	1.55209e4	258.95413	99.3102



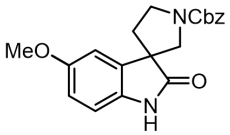
2f

Chiral HPLC spectrum of racemic 2g



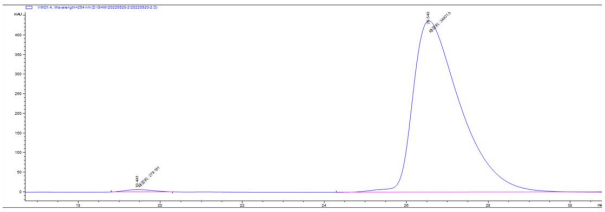
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.716	BB	0.8517	1.72960e4	309.63724	50.0767
2	27.468	BBA	1.1915	1.72430e4	222.16347	49.9233



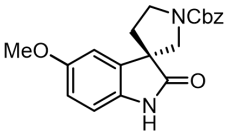
2g-Rac

Chiral HPLC spectrum of 2g



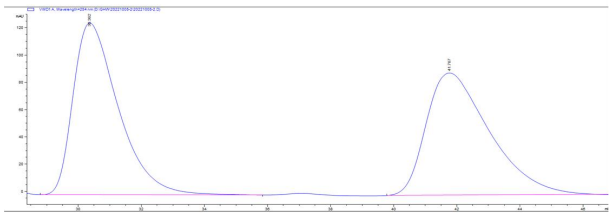
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.441	MM	0.7849	279.18140	5.92802	0.7929
2	26.543	MM	1.3320	3.49315e4	437.08835	99.2071



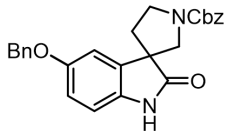
2g

Chiral HPLC spectrum of racemic 2h



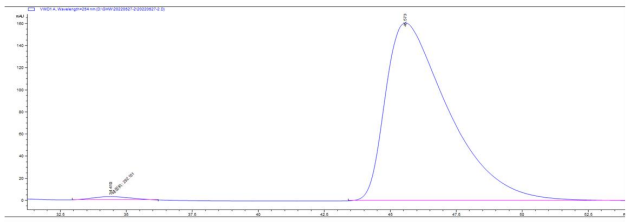
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	30.362	BB	1.5022	1.25574e4	126.05814	50.0609
2	41.767	BBA	1.8854	1.25268e4	89.63661	49.9391



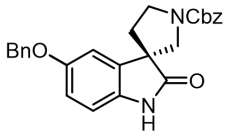
2h-Rac

Chiral HPLC spectrum of 2h



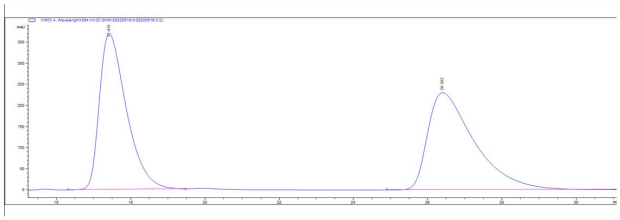
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	34.410	MM	1.6806	292.15094	2.89730	1.0793
2	45.573	BBA	2.2595	2.67762e4	160.57150	98.9207



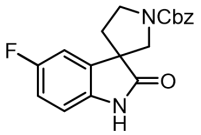
2h

Chiral HPLC spectrum of racemic 2i



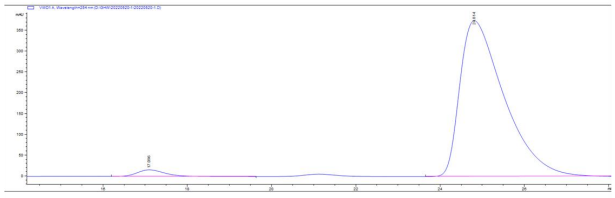
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.415	BB	0.7697	1.86888e4	371.02469	48.0652
2	26.392	BBA	1.3168	2.01934e4	231.24889	51.9348



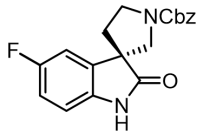
2i-Rac

Chiral HPLC spectrum of 2i



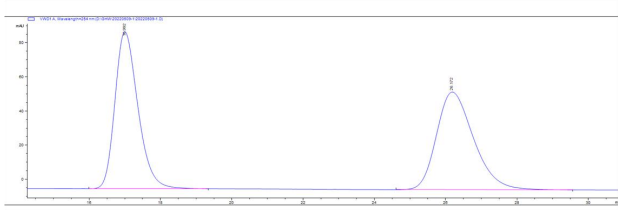
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.096	BB	0.6996	721.14435	15.85482	2.5672
2	24.814	BBA	1.0974	2.73701e4	375.50262	97.4328



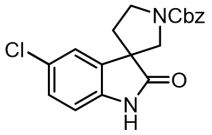
2i

Chiral HPLC spectrum of racemic 2j



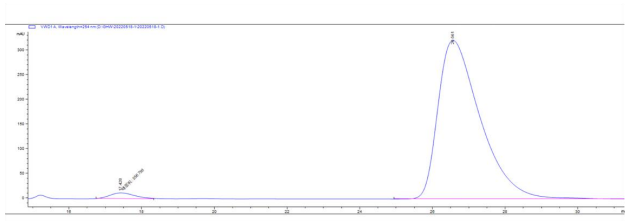
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.992	BB	0.6881	4115.07813	91.95732	49.8539
2	26.172	BB	1.1084	4139.20068	57.19253	50.1461



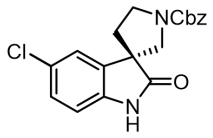
2j-Rac

Chiral HPLC spectrum of 2i



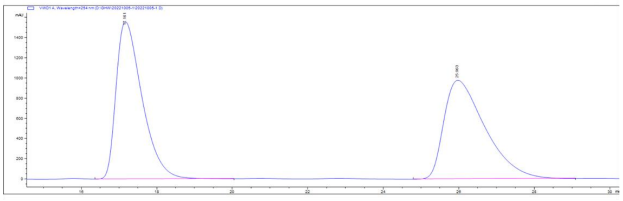
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.428	MM	0.7919	556.75641	11.71755	2.0964
2	26.561	BBA	1.2248	2.60010e4	322.41690	97.9036



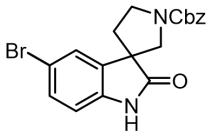
2j

Chiral HPLC spectrum of racemic 2k



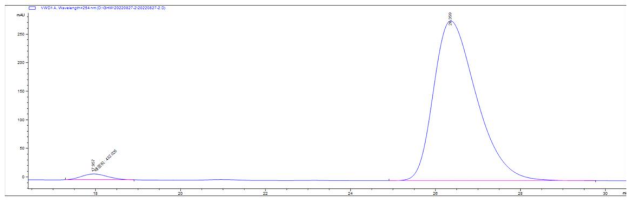
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.161	VB	0.7326	7.47439e4	1566.69385	50.0628
2	25.963	BB	1.1623	7.45563e4	982.49103	49.9372



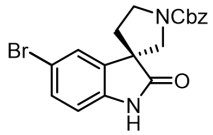
2k-Rac

Chiral HPLC spectrum of 2k



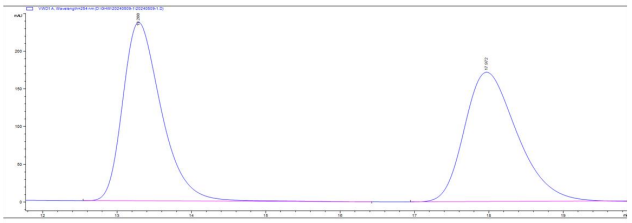
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.957	MM	0.7124	432.02634	10.10699	2.1643
2	26.359	BB	1.0763	1.95299e4	279.12961	97.8357



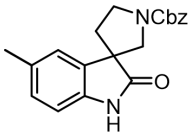
2k

Chiral HPLC spectrum of racemic 2l



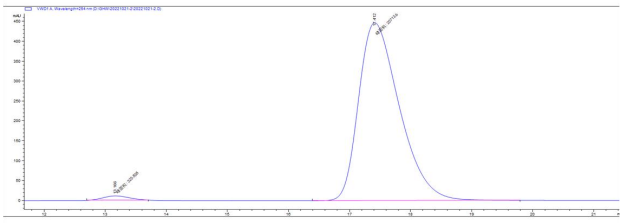
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.288	BB	0.5506	8538.56152	236.83620	50.1881
2	17.972	BBA	0.7589	8474.57227	171.67278	49.8119



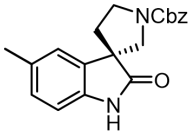
2l-Rac

Chiral HPLC spectrum of 2l



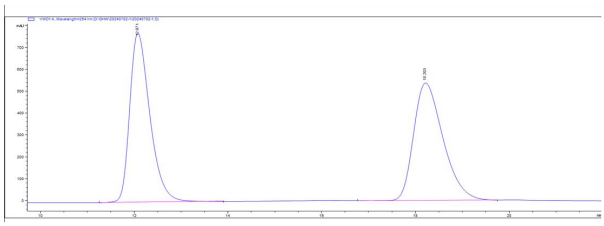
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.166	MM	0.4978	325.83813	10.90849	1.5487
2	17.412	MM	0.7723	2.07136e4	447.03571	98.4513



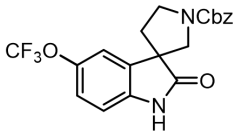
2l

Chiral HPLC spectrum of racemic 2m



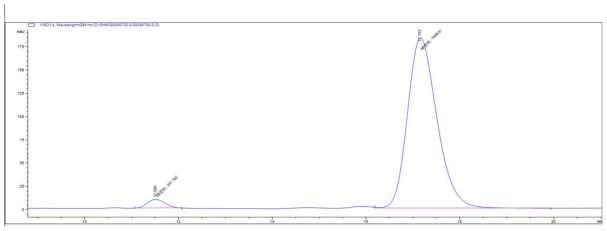
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.071	BB	0.4575	2.31723e4	775.83868	49.7631
2	18.203	BB	0.6711	2.33929e4	538.15381	50.2369



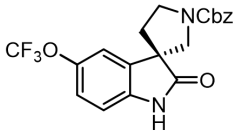
2m-Rac

Chiral HPLC spectrum of 2m



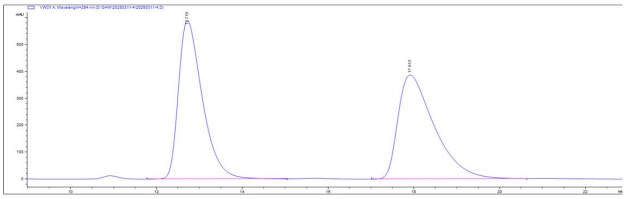
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.506	MM	0.4386	247.19180	9.39301	2.9973
2	17.152	MM	0.7295	7999.86816	182.76161	97.0027



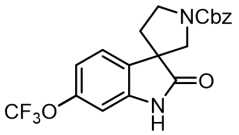
2m

Chiral HPLC spectrum of racemic 2n



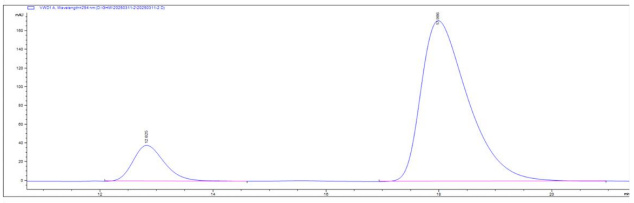
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.719	BB	0.5890	2.27412e4	589.57086	50.0788
2	17.913	BB	0.8809	2.26697e4	386.74014	49.9212



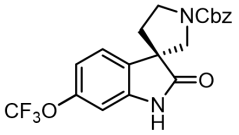
2n-Rac

Chiral HPLC spectrum of 2n



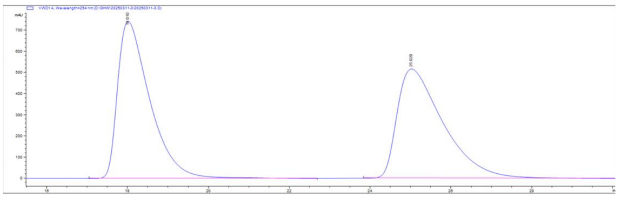
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.825	BB	0.5959	1480.80444	38.23141	13.0535
2	17.986	BB	0.8735	9863.30273	171.61353	86.9465



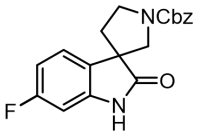
2n

Chiral HPLC spectrum of racemic 2o



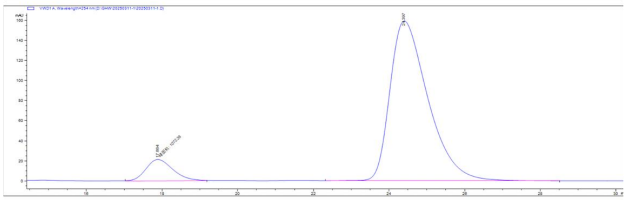
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	18.010	BB	0.8270	4.11628e4	744.53302	50.1426
2	25.020	BB	1.1316	4.09286e4	518.09631	49.8574



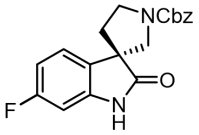
2o-Rac

Chiral HPLC spectrum of 2o



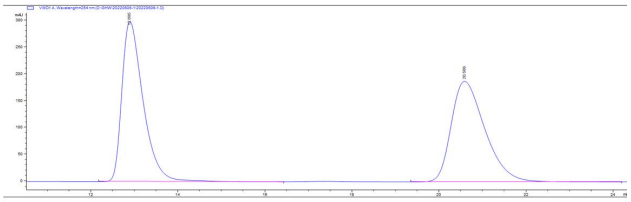
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	17.884	MM	0.8349	1072.39221	21.40817	8.8224
2	24.397	BB	1.0643	1.10829e4	158.97975	91.1776



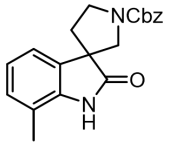
2o

Chiral HPLC spectrum of racemic 2p



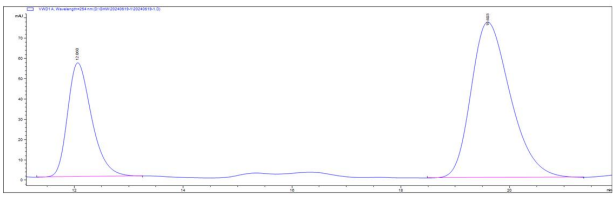
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.895	BB	0.5154	1.01637e4	299.87726	50.0858
2	20.586	BB	0.8270	1.01289e4	188.16982	49.9142



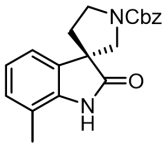
2p-Rac

Chiral HPLC spectrum of 2p



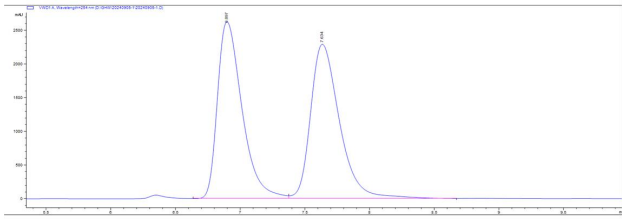
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	12.060	BB	0.4724	1727.49634	56.23013	30.9406
2	19.603	BB	0.7712	3855.76563	76.87331	69.0594



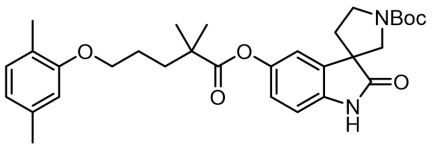
2p

Chiral HPLC spectrum of racemic 2q



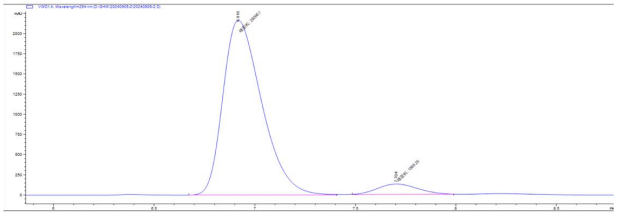
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.897	BV	0.2021	3.47008e4	2627.27710	49.3728
2	7.634	VB	0.2373	3.55824e4	2290.21826	50.6272



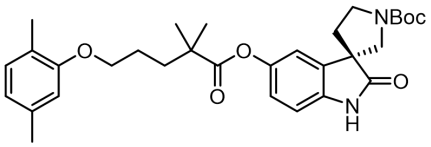
2q-Rac

Chiral HPLC spectrum of 2q



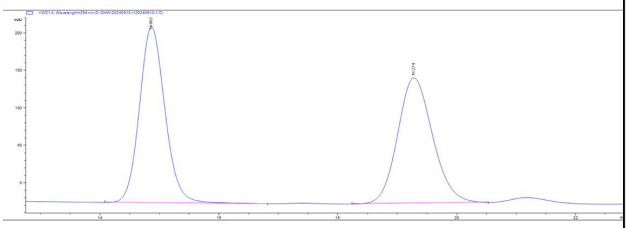
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.918	MM	0.2237	2.90967e4	2168.21606	95.9757
2	7.704	MM	0.2361	1865.25354	131.65709	4.0243



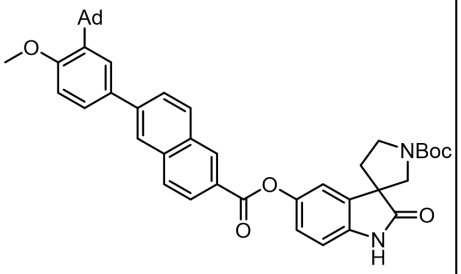
2q

Chiral HPLC spectrum of racemic 2r



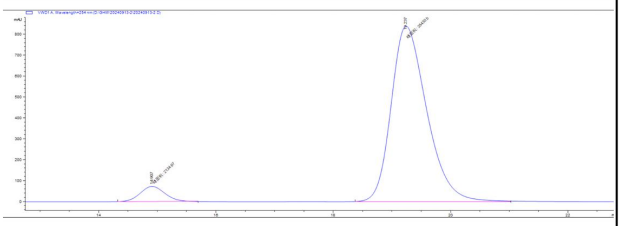
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.862	BB	0.4592	6991.19678	234.90880	50.5876
2	19.274	BB	0.6312	6828.77344	167.28790	49.4124



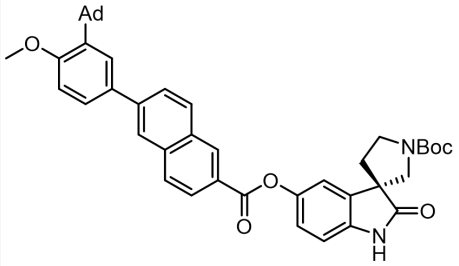
2r-Rac

Chiral HPLC spectrum of 2r



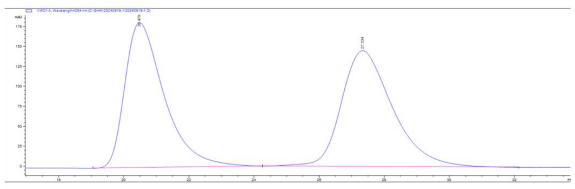
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.907	MM	0.4903	2134.97241	72.57805	5.6833
2	19.237	MM	0.7034	3.54305e4	839.50665	94.3167



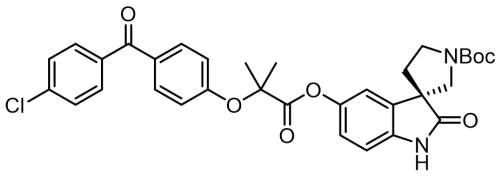
2r

Chiral HPLC spectrum of racemic 2s



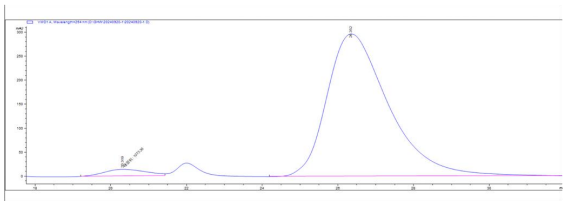
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.479	BB	1.2603	1.52786e4	181.83861	49.0404
2	27.334	BB	1.6726	1.58765e4	145.32629	50.9596



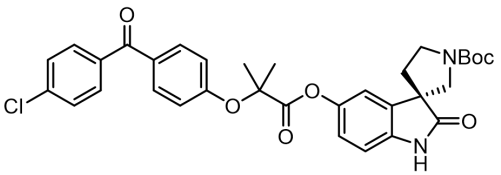
2s-Rac

Chiral HPLC spectrum of 2s



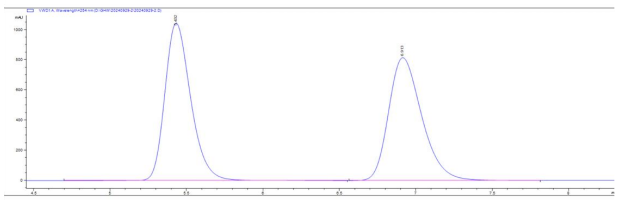
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	20.319	MM	1.2845	1073.35864	13.92653	3.0843
2	26.352	BBA	1.7061	3.37273e4	297.16791	96.9157



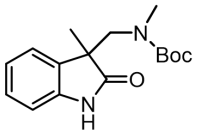
2s

Chiral HPLC spectrum of racemic 2t



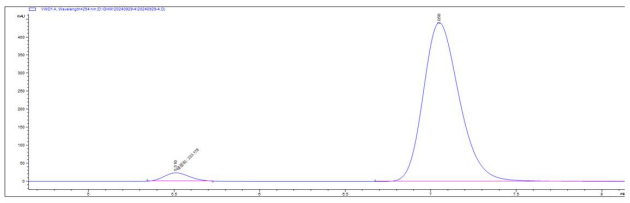
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.432	BV R	0.1801	1.22647e4	1043.67078	50.0071
2	6.913	BB	0.2318	1.22612e4	813.48053	49.9929



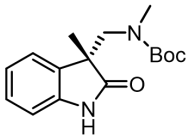
2t-Rac

Chiral HPLC spectrum of 2t



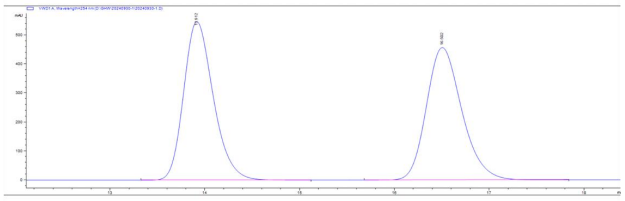
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	5.510	MM	0.1696	233.17805	22.91942	3.4689
2	7.050	BBA	0.2260	6488.70752	442.61182	96.5311



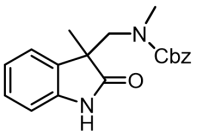
2t

Chiral HPLC spectrum of racemic 2u



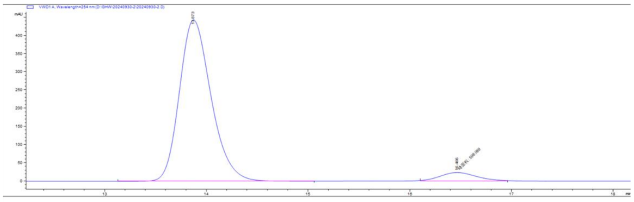
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.912	BB	0.3342	1.19021e4	548.31342	50.0540
2	16.502	BB	0.3987	1.18764e4	457.79059	49.9460



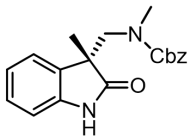
2u-Rac

Chiral HPLC spectrum of 2u



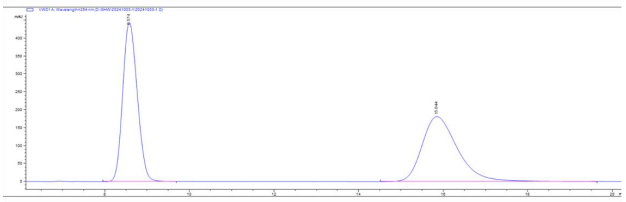
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	13.873	BB	0.3331	9556.41211	442.16470	94.1101
2	16.466	MM	0.4219	598.08911	23.62904	5.8899



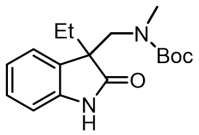
2u

Chiral HPLC spectrum of racemic 2v



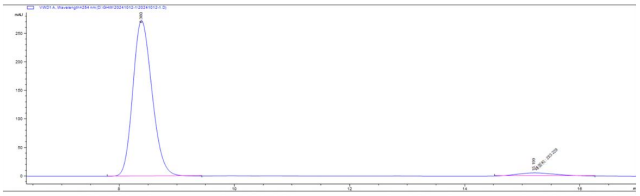
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.574	BB	0.3752	1.05739e4	443.50845	50.1835
2	15.844	BB	0.8905	1.04966e4	181.01067	49.8165



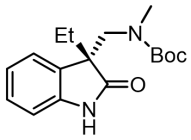
2v-Rac

Chiral HPLC spectrum of 2v



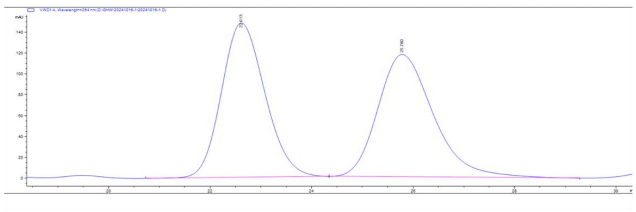
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	8.380	BB	0.3625	6323.20654	272.72812	96.1494
2	15.199	MM	0.7822	253.22919	5.39567	3.8506



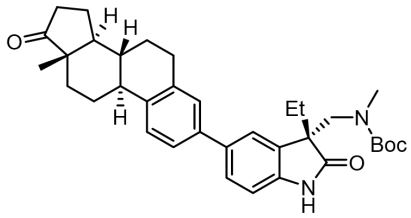
2v

Chiral HPLC spectrum of racemic 2w



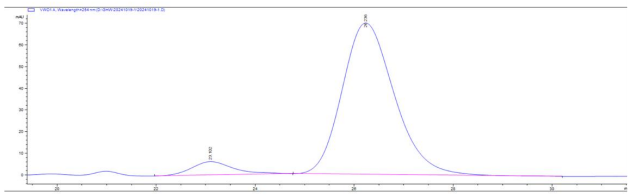
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	22.613	BB	0.9234	8812.37305	148.06740	49.7412
2	25.780	BB	1.1679	8904.07520	117.38663	50.2588



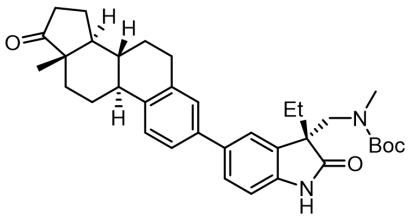
2w-Rac

Chiral HPLC spectrum of 2w



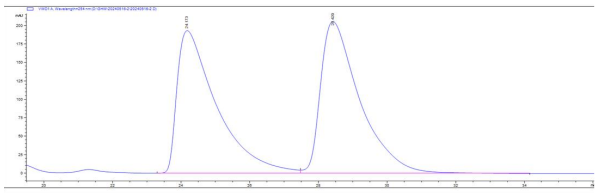
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.102	BB	0.8604	368.24368	6.20432	6.6808
2	26.236	BB	1.1303	5143.76270	69.99585	93.3192



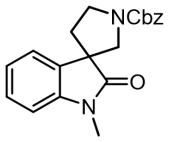
2w

Chiral HPLC spectrum of racemic 2x



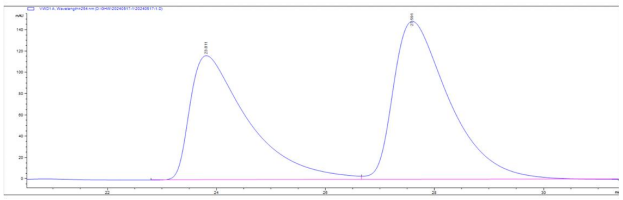
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.811	BV	1.0779	8675.21191	116.47893	44.9643
2	27.591	VBA	1.0747	1.06183e4	148.40999	55.0357



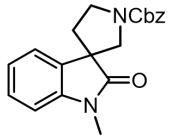
2x-Rac

Chiral HPLC spectrum of 2x



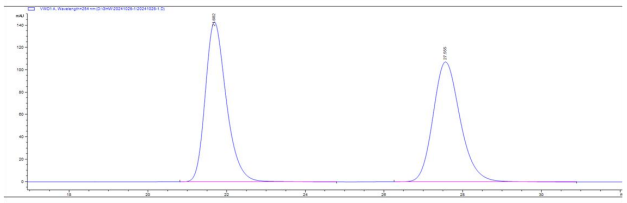
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	24.173	BV	1.1553	1.55289e4	193.48830	48.7221
2	28.420	VB	1.1786	1.63435e4	205.99797	51.2779



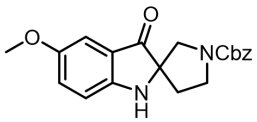
2x

Chiral HPLC spectrum of racemic 2y



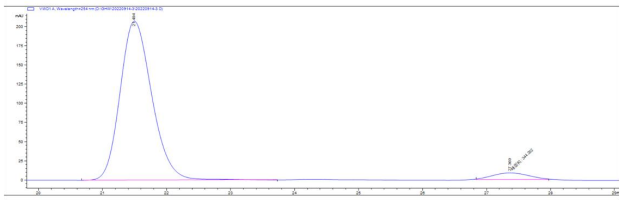
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.682	BB	0.5656	5307.30127	143.14734	50.8116
2	27.555	BB	0.7372	5137.75098	107.38673	49.1884



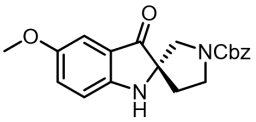
2y-Rac

Chiral HPLC spectrum of 2y



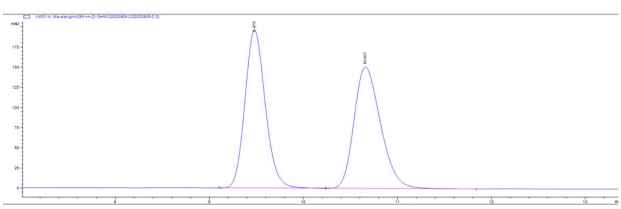
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	21.494	BB	0.5350	7147.30176	206.90802	95.4047
2	27.369	MM	0.6549	344.26233	8.76158	4.5953



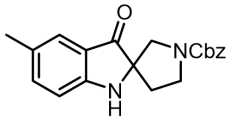
2y

Chiral HPLC spectrum of racemic 2z



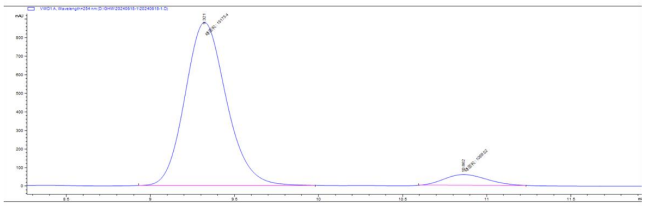
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.478	BB	0.2332	2967.09448	196.49060	49.9833
2	10.657	BB	0.3051	2969.07886	151.16449	50.0167



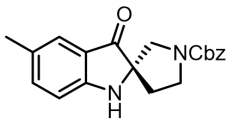
2z-Rac

Chiral HPLC spectrum of 2z



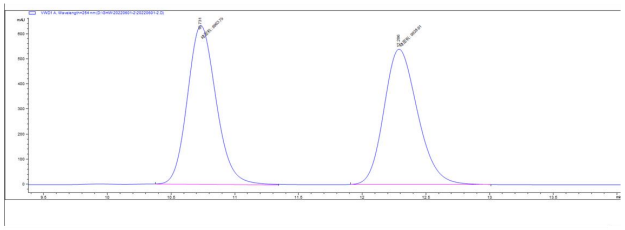
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.321	MM	0.2863	1.51754e4	883.39203	94.4163
2	10.862	MM	0.3010	1069.51697	59.21696	5.5837



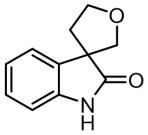
2z

Chiral HPLC spectrum of racemic 4a



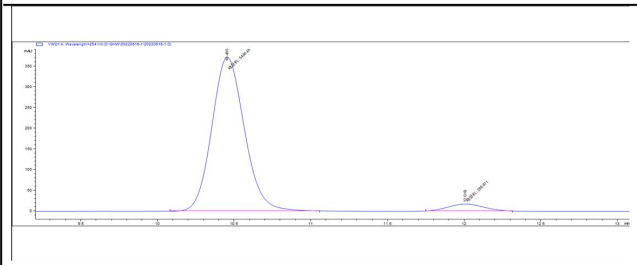
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.731	MM	0.2625	9963.79492	632.72516	50.0625
2	12.286	MM	0.3072	9938.90820	539.21344	49.9375



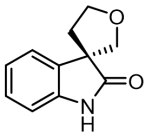
4a-Rac

Chiral HPLC spectrum of 4a



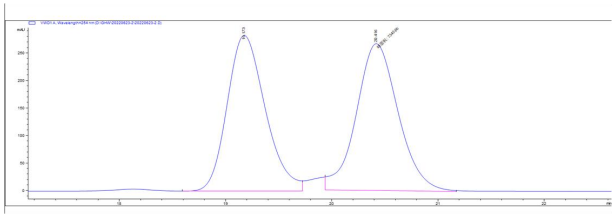
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.455	MM	0.2458	5496.48193	372.65601	95.3728
2	12.010	MM	0.2660	266.67056	16.71038	4.6272



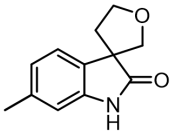
4a

Chiral HPLC spectrum of racemic 4b



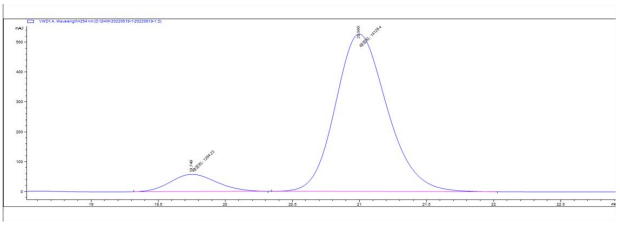
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.173	VV	0.3841	7063.24609	283.06918	49.0370
2	20.416	MM	0.4581	7340.66455	267.07019	50.9630



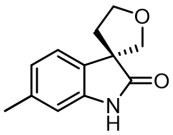
4b-Rac

Chiral HPLC spectrum of 4b



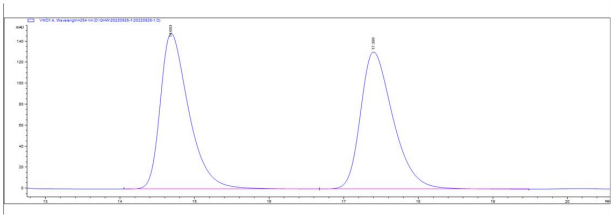
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	19.749	MM	0.4018	1394.22742	57.83347	8.9819
2	20.995	MM	0.4466	1.41284e4	527.19952	91.0181



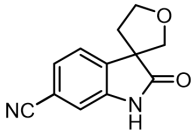
4b

Chiral HPLC spectrum of racemic 4c



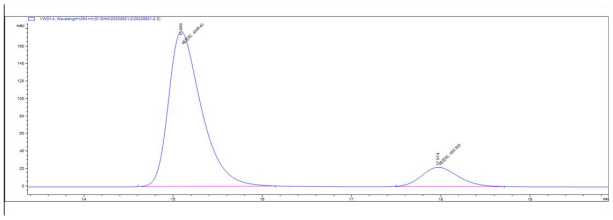
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	14.683	BB	0.4017	3941.97412	148.50507	49.8873
2	17.399	BB	0.4614	3959.79126	130.71968	50.1127



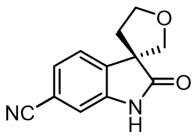
4c-Rac

Chiral HPLC spectrum of 4c



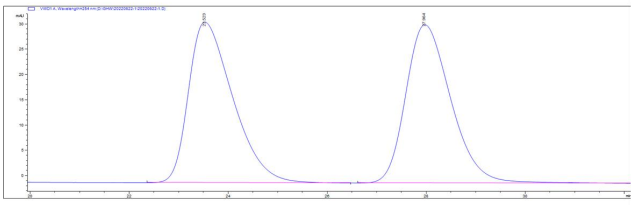
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	15.089	MM	0.4265	4548.42920	177.74770	87.3983
2	17.974	MM	0.4885	655.82471	22.37727	12.6017



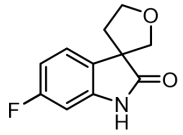
4c

Chiral HPLC spectrum of racemic 4d



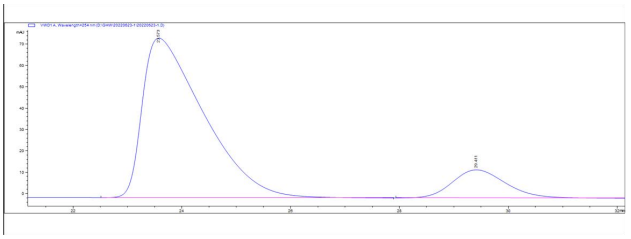
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.523	BB	0.9422	1977.82837	31.81764	49.8907
2	27.964	BBA	0.9759	1986.49463	31.36725	50.1093



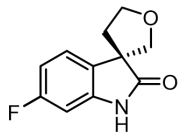
4d-Rac

Chiral HPLC spectrum of 4d



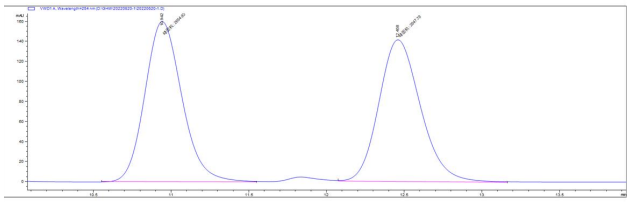
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	23.573	BB	1.1555	5827.54883	74.67470	86.6679
2	29.411	BBA	1.0438	896.44910	13.15836	13.3321



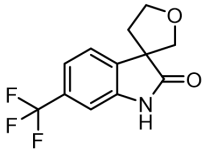
4d

Chiral HPLC spectrum of racemic 4e



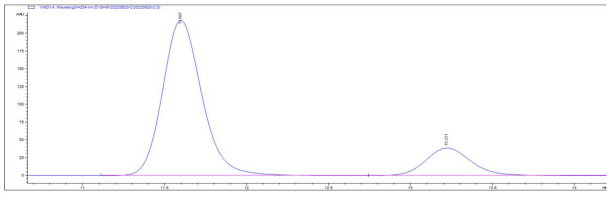
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.942	MM	0.2765	2654.92505	160.00359	50.0673
2	12.458	MM	0.3117	2647.79004	141.56151	49.9327



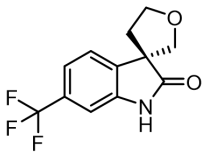
4e-Rac

Chiral HPLC spectrum of 4e



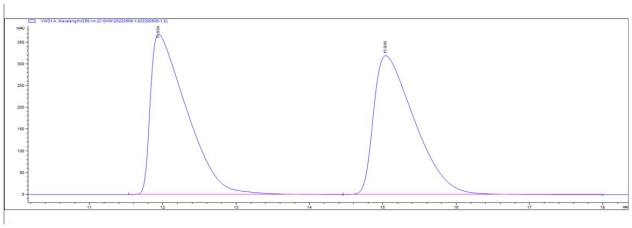
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.597	BB	0.2557	3635.97754	219.00111	83.1228
2	13.221	BB	0.2944	738.24811	38.73265	16.8772



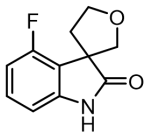
4e

Chiral HPLC spectrum of racemic 4f



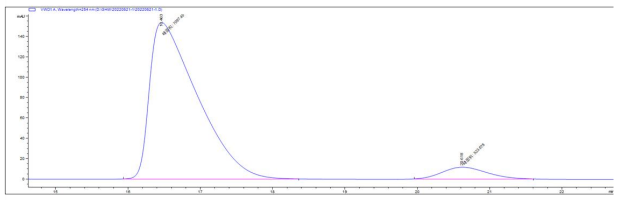
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	11.939	BB	0.5140	1.25862e4	368.94797	50.5319
2	15.036	BB	0.5895	1.23212e4	319.05820	49.4681



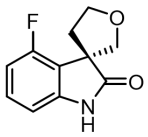
4f-Rac

Chiral HPLC spectrum of 4f



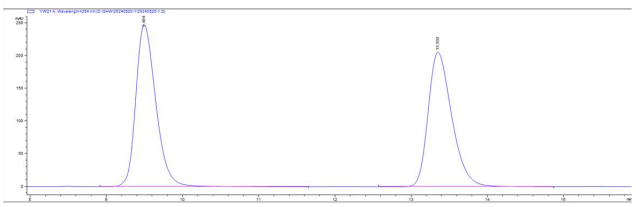
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	16.463	MM	0.7671	7097.45410	154.20624	93.0066
2	20.618	MM	0.7426	533.67761	11.97720	6.9934



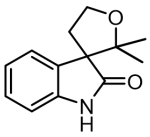
4f

Chiral HPLC spectrum of racemic 4g



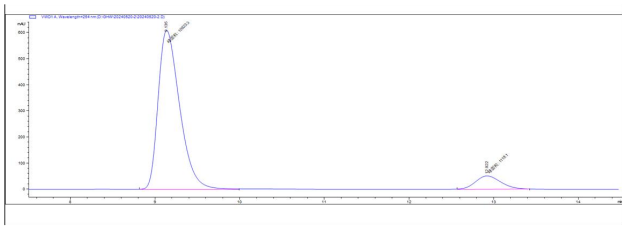
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.494	BB	0.2822	4530.11523	247.88301	50.5255
2	13.350	BB	0.3306	4435.87744	205.68260	49.4745



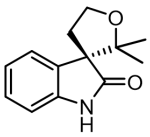
4g-Rac

Chiral HPLC spectrum of 4g



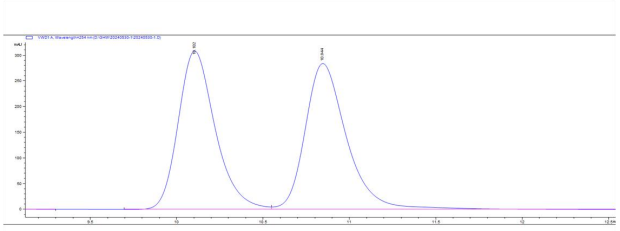
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	9.135	MM	0.2970	1.09233e4	613.03406	90.7145
2	12.922	MM	0.3557	1118.10156	52.38424	9.2855



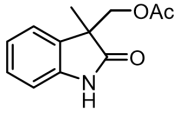
4g

Chiral HPLC spectrum of racemic 4h



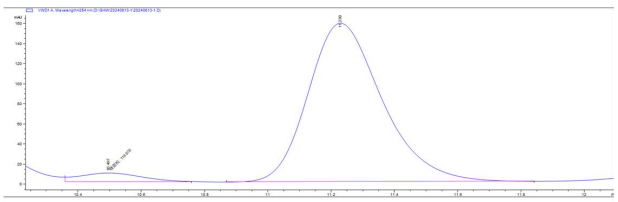
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.102	BV	0.2275	4601.75732	309.41391	49.1385
2	10.844	VB	0.2530	4763.11328	284.93912	50.8615



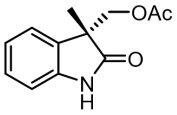
4h-Rac

Chiral HPLC spectrum of 4h



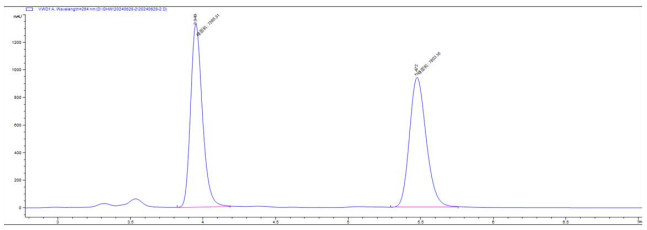
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	10.497	MM	0.2285	119.97564	8.74967	4.4660
2	11.230	BB	0.2487	2566.44678	157.86960	95.5340



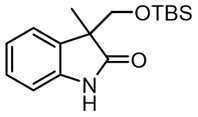
4h

Chiral HPLC spectrum of racemic 4i



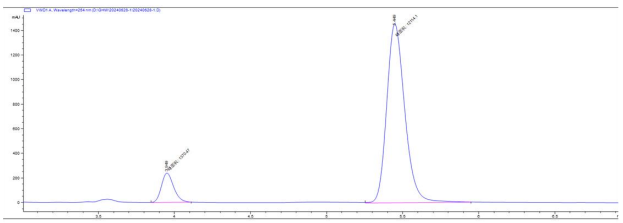
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	3.949	MM	0.0947	7585.30859	1334.34180	49.9412
2	5.472	MM	0.1344	7603.15869	943.18457	50.0588



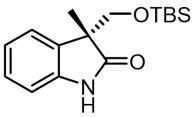
4i-Rac

Chiral HPLC spectrum of 4i



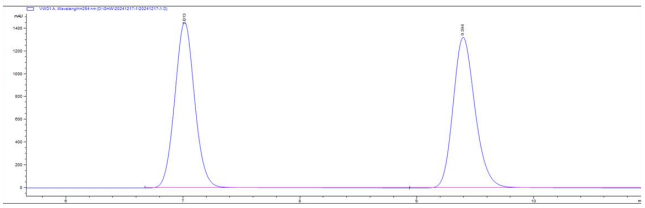
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	3.949	MM	0.0948	1370.46545	240.92621	10.1632
2	5.449	MM	0.1387	1.21141e4	1455.91101	89.8368



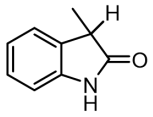
4i

Chiral HPLC spectrum of racemic 6a



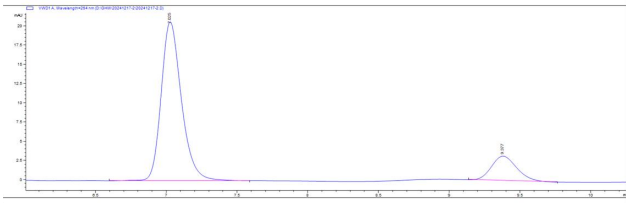
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.013	BV R	0.1825	1.72493e4	1453.35950	49.9897
2	9.394	BBA	0.2016	1.72563e4	1319.16187	50.0103



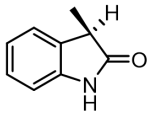
6a-Rac

Chiral HPLC spectrum of 6a



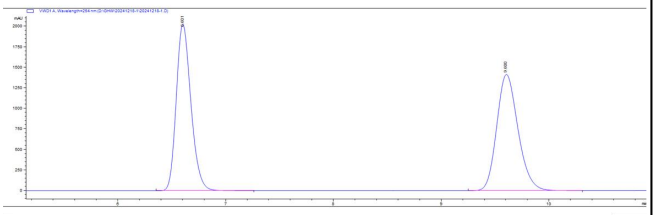
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	7.025	BB	0.1512	216.69173	20.74445	87.7994
2	9.377	BB	0.1927	29.95879	3.20053	12.2006



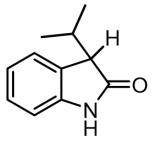
6a

Chiral HPLC spectrum of racemic 6b



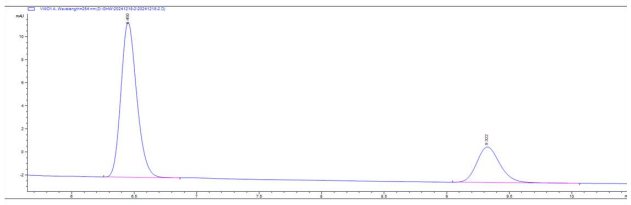
信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.601	BB	0.1460	1.90917e4	2024.75415	49.7196
2	9.600	BB	0.2106	1.93071e4	1411.48889	50.2804



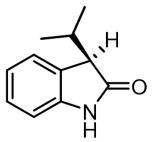
4i-Rac

Chiral HPLC spectrum of 6b



信号 1: VWD1 A, Wavelength=254 nm

峰 #	保留时间 [min]	类型	峰宽 [min]	峰面积 [mAU*s]	峰高 [mAU]	峰面积 %
1	6.450	BB	0.1342	125.08488	13.47376	79.7009
2	9.322	BB	0.1990	32.99206	3.08915	20.2991



6b