Supporting Information for

The Catalytic Asymmetric Dearomatization of Tryptamine for Accessing *meso*-Contiguous Quaternary Carbon Centers of Oligomeric Cyclotryptamine Alkaloids: a Formal Synthesis of Hodgkinsine B

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1. General Information

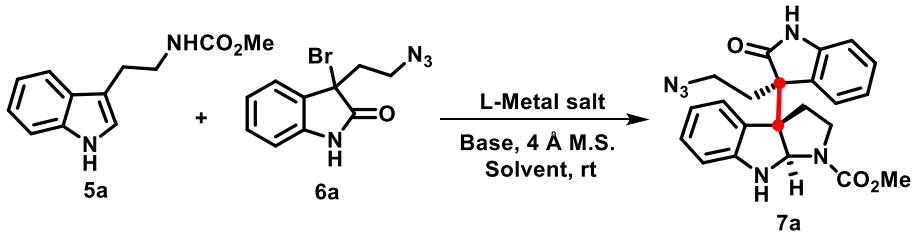
Unless otherwise noted, reagents were obtained from commercial sources and used without further purification. Non-aqueous reaction was conducted under an inert atmosphere of argon in flame-dried glassware. Anhydrous solvents were treated as follow: tetrahydrofuran and diethyl ether were distilledfrom sodium under argon atmosphere, dichloromethane, toluene and ethyl acetate was distilled from calcium hydride under argon atmosphere. Anhydrous DMF, DMA, 1,2-dichloroethane and acetonitrile (Adamas-beta, SafeDry, with molecular sieves) were commercial available. Thin layer chromatography was conducted on Merck 60 F254 pre-coated silica gel plates. Column chromatography was carried out by normal silica gel (40-60 μm, 200-400 mesh, Silicycle P60). NMR data including ^{1}H NMR or ^{13}C NMR spectra were recorded on Bruker AVANCE III 500MHz. All of the 13C NMR spectra were broad band proton-decoupled. ^{1}H NMR Chemical shifts were reported in ppm relative to residual signals of the solvents ($CDCl_3$: 7.26 ppm; $(CD_3)_2CO$: 2.05 ppm; $(CD_3)_2SO$: 2.50 ppm). ^{13}C NMR chemical shifts were reported in ppm relative to the solvent ($CDCl_3$:77.16 ppm; $(CD_3)_2CO$: 206.26 ppm; $(CD_3)_2SO$: 39.52 ppm). Chiral HPLC analyses were performed on Waters 2487 Series using Daicel Chiralpak (AD-H, OD-H, IC, IA and IB-3) column with hexane/iPrOH as the eluent. Optical rotations were measured on Anton Paar MCP 300 polarimeter. High resolution mass spectra were obtained from IonSpec 4.7 Tesla FTMS mass spectrometer (MALDI), Bruker APEXIII 7.0 TESLA FTMS (ESI). The oxindoles **6** were synthesized by the same procedure in the literature.[1-3]

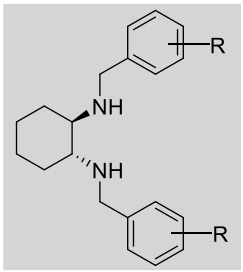
2. Reaction Conditions Optimization of the Reaction

2.1 General Procedure

Reaction was performed with complexing of Oxindole **6a** (0.10 mmol), **Ligand** (0.01 mmol), **Metal slat** (0.01 mmol) and 4Å M.S molecular sieves (10 mg) in solvent (0.5 mL) at 35 °C under Ar for 30 minutes, then **Base** was added at rt, after 10 min a solution of tryptamine **5a** (0.10 mmol) in solvent (0.5 mL) was added, the reaction solution was stirred at room temperature until TLC showed the starting material was no longer consumed. The solution was directly concentrated under reduced pressure and purified by flash column chromatography on silica gel (EtOAc/petroleum ether = 1:10) to afford **7a**.

Table S1. The Screening of conditions for the First Model Reaction

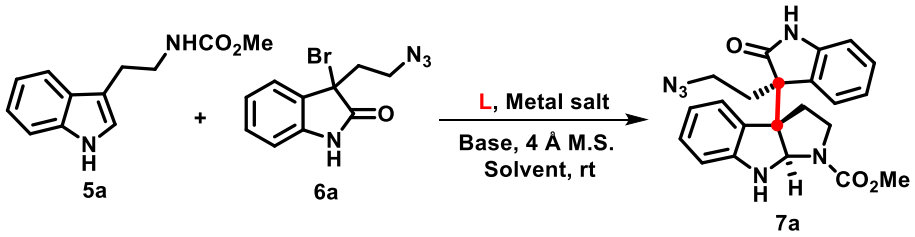


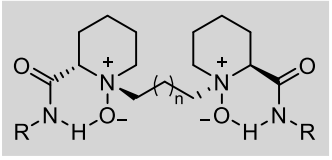


L^1: R=3-OMe
L^2: R=4-OMe
L^3: R=$_4$-Br

Entry	L-Metal salt	Base	Solvent	Yield (%)	ee (%)
1	L^1-Ni(OAc)$_2$·4H$_2$O	Na_2CO_3	THF	80	40
2	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	THF	79	70
3	L^1-Ni(OAc)$_2$·4H$_2$O	TMEDA	THF	39	2
4	L^1-Ni(OAc)$_2$·4H$_2$O	Cs_2CO_3	THF	41	50
5	L^1-Ni(OAc)$_2$·4H$_2$O	Et_3N	THF	52	23
6	L^1-Ni(OAc)$_2$·4H$_2$O	pyridine	THF	50	0
7	L^2- Ni(OAc)$_2$·4H$_2$O	K_2CO_3	THF	85	49
8	L^3-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	THF	70	40
9	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	DCM	49	50
10	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	dioxane	70	50
11	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	DMF	70	30
12	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	CH_3CN	75	49
13	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	DCE	88	11
14	L^1-Ni(OAc)$_2$·4H$_2$O	K_2CO_3	$CHCl_3$	90	41

Table S2. The Screening of Ligands for the First Model Reaction

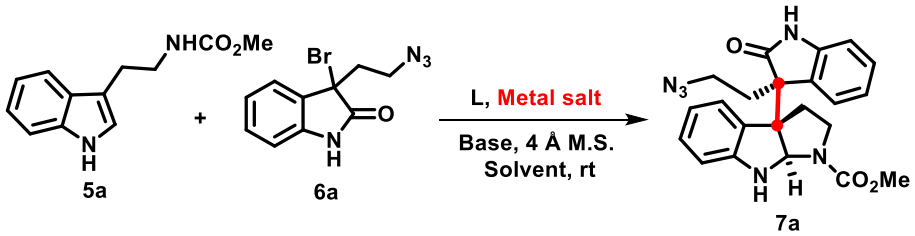




L1: R = Ph, n = 1
L2: R = 2,4,6-Me_3Ph, n = 1
L3: R = 2,6-Et_2-4-MePh, n = 1
L4: R = 2,6-*i*Pr_2Ph, n = 1
L5: R = 2,6-*i*Pr_2Ph, n=0

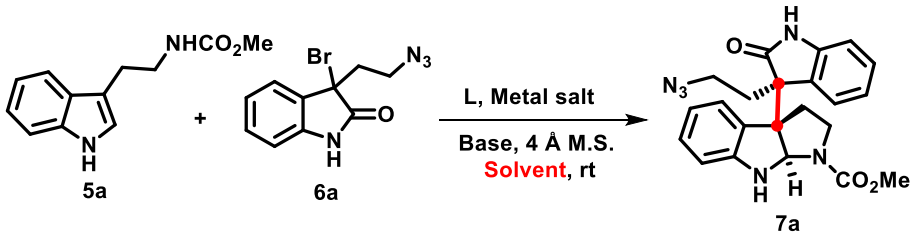
Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L1	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	74	11	6:1
2	L2	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	78	85	4:1
3	L3	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	75	91	5:1
4	L4	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	81	87	4:1
5	L5	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	83	76	>20:1

Table S3. The Screening of Metal salts for the First Model Reaction



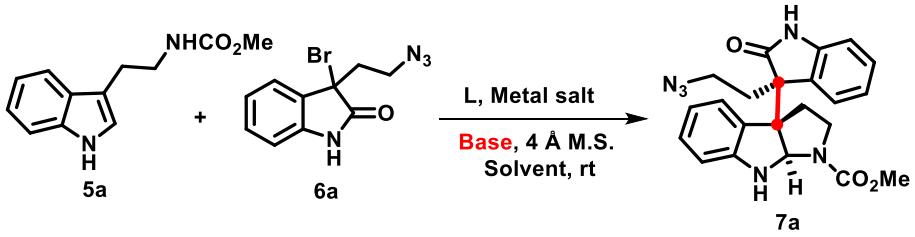
Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L3	DIPEA	$Ni(ClO_4)\cdot 6H_2O$	EtOAc	75	91	5:1
2	L3	DIPEA	$Ni(acac)_2$	EtOAc	65	11	5:1
3	L3	DIPEA	$NiCl_2$	EtOAc	64	0	7:1
4	L3	DIPEA	NiI_2	EtOAc	ND	NA	NA
5	L3	DIPEA	$Ni(BF_4)_2\cdot 6H_2O$	EtOAc	85	95	13:1

Table S4. The Screening of Solvents for the First Model Reaction



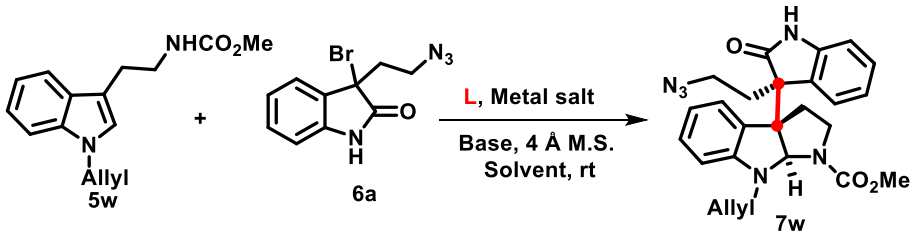
Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	*ee* (%)	*dr*
1	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	85	95	13:1
2	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	Toluene	65	60	16:1
3	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DCM	87	87	16:1
4	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	CH_3CN	75	90	20:1
5	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DMF	77	9	20:1

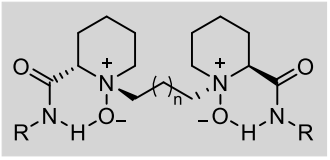
Table S5. The Screening of Bases for the First Model Reaction



Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	85	95	13:1
2	L3	Et_3N	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	82	87	6:1
3	L3	K_2CO_3	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	80	11	6:1
4	L3	TMEDA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	trace	0	3:1
5	L3	DIPA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	85	88	5:1

Table S6. The Screening of Ligands for the Second Model Reaction

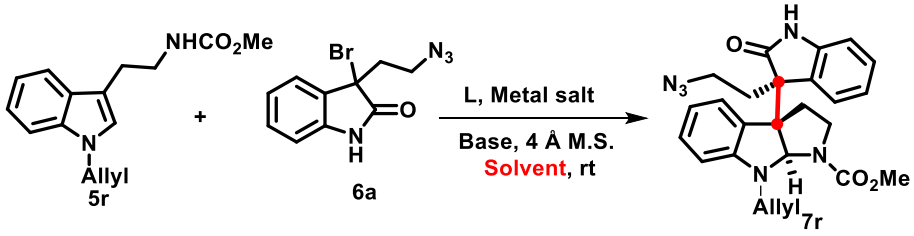




L3: R = 2,6-Et_2-4-MePh, n = 1
L6: R = 2,6-Et_2-4-MePh, n=0
L7: R = 2,4,6-Me_3Ph, n = 0
L8: R = Ph, n = 0
L9: R =2,6-Me_2Ph, n = 0

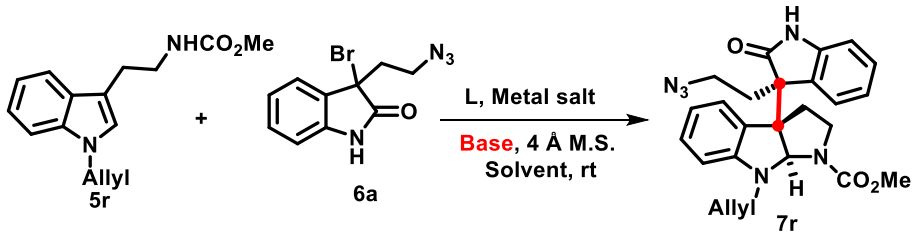
Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	48	82	20:1
2	L9	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	52	79	>20:1
3	L7	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	66	91	>20:1
4	L8	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	27	8	>20:1
5	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	63	91	>20:1

Table S7. The Screening of Solvents for the Second Model Reaction



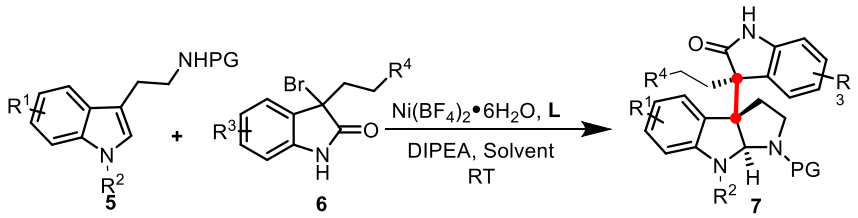
Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L3	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	EtOAc	63	91	>20:1
2	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	THF	15	88	20: 1
3	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	Et_2O	52	68	>20:1
4	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	Toluene	39	36	>20:1
5	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DCM	93	97	>20:1
6	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DMA	11	61	>20:1
7	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	MeCN	41	93	>20:1
8	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DCE	50	94	>20:1

Table S8 The Screening of Bases for the Second Model Reaction



Entry	Ligand	Base	Metal salt	Solvent	Yield (%)	ee (%)	dr
1	L6	DIPEA	$Ni(BF_4)_2{\cdot}6H_2O$	DCM	93	97	>20:1
2	L6	Et_3N	$Ni(BF_4)_2{\cdot}6H_2O$	DCM	41	97	>20:1
3	L6	2,6-Lutidine	$Ni(BF_4)_2{\cdot}6H_2O$	DCM	48	97	>20:1

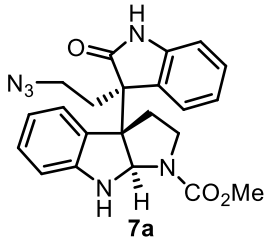
3. Experimental Details and Characterization Data



General procedure A: To a dry tube was charged with **L3** (0.01 mmol), **Nickel slat** (0.01 mmol), Bromo-oxindole **6** (0.1 mmol) and 4Å M.S. molecular sieves (10 mg), the tube was capped with a rubber septum, after evacuated and backfilled argon three times, ethyl acetate (0.5 mL) was added and the mixture was stirred at 35 ºC for 30 min, then **DIPEA** (0.2 mmol) was added via a syringe, finally tryptamine **5** (0.1 mmol) in ethyl acetate (0.5 mL) was added via a syringe. The reaction mixture was allowed to stir for 12h under a Ar atmosphere at room temperature. The reaction mixture was concentrated and purified by column chromatography on silica gel to afford the corresponding product **7**.

General procedure B: To a dry tube was charged with **L6** (0.01 mmol), **Nickel slat** (0.01 mmol), Bromo-oxindole **6** (0.10 mmol) and 4Å M.S. molecular sieves (10 mg), the tube was capped with a rubber septum, After evacuated and backfilled argon three times, dichloromethane (0.5 mL) was added and the mixture was stirred at 35 ºC for 30 min, then **DIPEA** (0.2 mmol) was added via a syringe, finally tryptamine **5** (0.10 mmol) in dichloromethane (0.5 mL) was added via a syringe. The reaction mixture was allowed to stir for 12h under a Ar atmosphere at room temperature. The reaction mixture was concentrated and purified by column chromatography on silica gel to afford the corresponding product **7**.

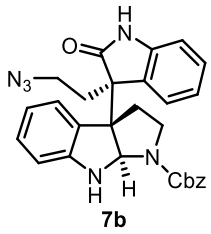
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7a).



This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7a** (35.5 mg, 85% yield) as a white solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 164.86 (*c* 0.0575, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.36 and 8.21 (s, 1H), 7.25-6.98 (m, 3H), 6.89-6.66 (m, 3H), 6.45 (d, *J* = 7.9 Hz, 1H), 6.27 and 6.05 (s, 1H), 5.26 and 5.15 (s, 1H), 4.82 and 4.50 (s, 1H), 3.80 and 3.66 (dd, *J* = 10.5, 8.2 Hz, 1H), 3.69 and 3.62 (s, 3H), 3.26 and 3.12 (td, *J* = 11.9, 8.5 Hz, 1H), 3.00-2.91 (m, 2H), 2.85-2.76 (m, 1H), 2.53-2.47 (m, 1H), 2.44-2.38 (m, 1H), 2.24-2.19 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.8 and 178.7, 155.2 and 154.3, 150.7 and 150.3, 140.9 and 140.7, 129.7, 128.8 and 128.7, 128.6 and 128.5, 127.8 and 127.7, 124.7, 124.5, 122.4 and 122.3, 118.9 and 118.6, 110.0 and 109.9, 109.8, 77.7, 62.6, 61.4, 54.2 and 54.0, 52.6 and 52.3, 47.5, 45.2 and 45.1, 31.6 and 31.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{23}N_6O_3$ 419.1826, found 419.1831. Enantiomeric excess was found to be 95% ee and 13:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 20.92 min, t_{minor} = 10.82 min; minor isomer: t_{major} = 13.78

min, t_{minor} = 8.48 min).

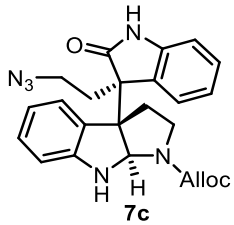
benzyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7b).



7b

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7b** (23.7 mg, 48% yield) as a white solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 270.48 (*c* 0.10, $CHCl_3$).**^{1}H NMR (500 MHz, CDCl$_3$, rotamers)** δ 8.22 and 8.02 (s, 1H), 7.40-7.34 (m, 4H), 7.27-7.12 (m, 3H), 6.88-6.75 (m, 3H), 6.52 and 6.45 (d, 1H), 6.08 and 6.08 (s, 1H), 5.34-5.22 (m, 2H), 5.14-5.05 (m, 2H), 4.88 and 4.48 (s, 1H), 3.85 and 3.75 (t, *J* = 9.4 Hz, 1H), 3.31 and 3.14 (q, *J* = 10.8 Hz, 1H), 3.09-2.96 (m, 2H), 2.89-2.82 (m, 1H), 2.58-2.50 (m, 1H), 2.49-2.40 (m, 1H), 2.29-2.25 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$, rotamers)** δ 178.3, 154.5, 150.7 and 150.6, 150.4 and 150.3, 140.6, 136.5 and 136.4, 131.4, 130.0 and 129.6, 128.6, 128.5, 128.1, 128.0, 127.8, 124.7 and 124.5, 124.4, 122.4, 118.6, 110.8, 110.0 and 109.9, 109.8, 109.6, 77.8, 67.1 and 66.9, 62.8 and 61.5, 54.3 and 54.0, 47.5 and 47.4, 45.3 and 45.2, 31.6 and 31.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{28}H_{27}N_6O_3$ 495.2139, found 495.2141. Enantiomeric excess was found to be 97% and 4:1 dr by chiral HPLC (ChiralPak AD column, hexane/i-PrOH = 70:30, 214 nm, 0.6 mL/min, major isomer: t_{major} = 21.23 min, t_{minor} = 15.62 min; minor isomer: t_{major} = 17.37 min, t_{minor} = 11.80 min).

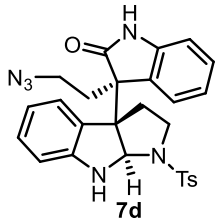
Allyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7c).



7c

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7c** (32.5 mg, 73% yield) as a white solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 169.23 (*c* 0.105, $CHCl_3$). **^{1}H NMR (500 MHz, CDCl$_3$, rotamers)** δ 8.56 and 8.38 (s, 1H), 7.27-7.14 (m, 2H), 7.01-6.72 (m, 3H), 6.55 and 6.51 (d, *J* = 7.7 Hz, 1H), 6.33 and 6.10 (s, 1H), 6.00-5.89 (m, 1H), 5.35-5.20 (m, 3H), 4.70-4.51 (m, 2H), 3.83 and 3.76 (t, *J* = 9.3 Hz, 1H), 3.83 and 3.50 (t, *J* = 6.7 Hz, 1H), 3.31 and 3.17 (q, *J* = 10.6 Hz, 1H), 3.08-2.81 (m, 3H), 2.60-2.37 (m, 2H), 2.35-2.18 (m, 1H), 2.00-1.98 and 1.79-1.73 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$, rotamers)** δ 179.0 and 178.9, 154.4 and 153.6, 150.7 and 150.3, 141.1 and 140.8, 132.9 and 132.7, 129.6, 128.8 and 128.5, 128.6, 127.8 and 127.6, 124.7 and 124.5, 124.4, 122.3 and 123.3, 118.9 and 118.6, 118.1 and 117.6, 109.9, 109.8, 77.7, 66.1 and 65.8, 62.6 and 61.4, 54.2 and 54.0, 47.4, 45.3 and 45.1, 31.6, 30.0. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{24}H_{25}N_6O_3$ 445.1988, found 445.1983. Enantiomeric excess was found to be 84% and 4:1 dr by chiral HPLC (ChiralPak AD column, hexane/i-PrOH = 60:40, 214 nm, 0.6 mL/min, major isomer: t_{major} = 13.43 min, t_{minor} = 59.07 min; minor isomer: t_{major} = 10.38 min, t_{minor} = 71.36 min).

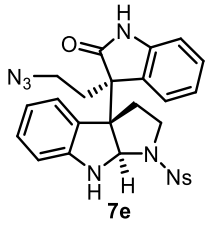
(*S*)-3-(2-azidoethyl)-3-((3a*R*,8a*R*)-1-tosyl-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1H)-yl)indolin-2-one (7d).



7d

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7d** (42.3 mg, 82% yield) as a yellow solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 210.36 (*c* 0.10, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 7.74 (d, *J* = 8.0 Hz, 2H), 7.69 (s, 1H), 7.34 (d, *J* = 8.0 Hz, 2H), 7.26 (td, *J* = 7.7, 1.2 Hz, 1H), 7.13 (t, *J* = 8.0 Hz, 1H), 6.89-6.70 (m, 4H), 6.61(d, *J* = 7.9 Hz, 1H)、6.36 (s, 1H), 5.45 (s, 1H), 4.60 (s, 1H), 3.51 (t, *J* = 8.8 Hz, 1H), 3.05 (td, *J* = 10.5, 5.3 Hz, 1H), 2.98-2.91 (m, 2H), 2.84-2.79 (m, 1H), 2.46 (s, 3H), 2.40-2.27 (m, 2H), 2.19-2.16 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.1, 150.3, 143.6, 140.7, 136.4, 129.7, 129.6, 128.9, 128.3, 127.3, 127.2, 124.4, 124.3, 122.5, 118.9, 110.2, 109.8, 79.8, 62.9, 54.1, 47.4, 46.7, 31.3, 21.6. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{27}H_{27}N_6O_3S$ 515.1860, found 515.1863; Enantiomeric excess was found to be 95% and 16:1 dr by chiral HPLC (ChiralPak AD column, hexane/i-PrOH = 60:40, 214 nm, 0.6 mL/min, major isomer: t_{major} = 20.17 min, t_{minor} = 14.38 min; minor isomer: t_{major} = 10.38 min, t_{minor} = 40.83 min).

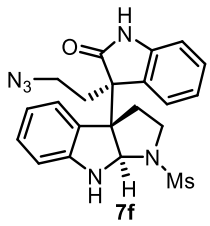
(*S*)-3-(2-azidoethyl)-3-((3a*R*,8a*R*)-1-((4-nitrophenyl)sulfonyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1H)-yl)indolin-2-one (7e).



7e

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7e** (49.6 mg, 91% yield) as a yellow solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 185.06 (*c* 0.14, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.36 (d, *J* = 8.3 Hz, 2H), 8.13 (s, 1H), 8.05 (d, *J* = 8.3 Hz, 2H), 7.27 (t, *J* = 7.7 Hz, 1H), 7.13 (d, *J* = 7.7 Hz, 1H), 6.94-6.68 (m, 3H), 6.47 (d, *J* = 7.6 Hz, 1H), 6.33-6.22 (m, 1H), 5.51 (s, 1H), 4.54 (s, 1H), 3.64 (t, *J* = 8.8 Hz, 1H), 3.23-2.74 (m, 4H), 2.50-2.30 (m, 2H), 2.25 (dd, *J* = 12.2, 5.2 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.4, 150.0, 145.4, 140.7, 130.0, 129.1, 128.6, 128.0, 127.6, 124.4, 124.2, 122.7, 119.8, 110.8, 110.1, 80.1, 63.2, 54.2, 47.3, 46.9, 31.4, 29.7. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{26}H_{24}N_7O_5S$ 546.1554, found 546.1554. Enantiomeric excess was found to be 98% and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 24.35 min, t_{minor} = 11.59 min).

(*S*)-3-(2-azidoethyl)-3-((3a*R*,8a*R*)-1-(methylsulfonyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1H)-yl)indolin-2-one (7f).

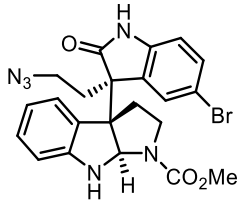


7f

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7f** (26.3 mg, 60% yield) as a white solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 117.23 (*c* 0.07, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.47 (s, 1H), 7.24 (t, *J* = 7.6 Hz, 1H), 7.09 (t, *J* = 7.7 Hz, 1H), 6.90 (d, *J* = 7.8 Hz, 1H), 6.87 (d, *J* = 8.5 Hz, 1H), 6.74-6.61 (m, 2H), 6.58 (d, *J* = 7.8 Hz, 1H), 5.63-5.37 (m, 2H), 3.60 (dd, *J* = 9.8, 7.6 Hz, 1H), 3.29 (td, *J* = 11.8, 7.6 Hz, 1H), 3.04-2.90 (m, 3H), 2.89 (s, 3H), 2.86-2.85 (m, 1H), 2.60-2.54 (m, 1H), 2.51-2.45 (m, 1H), 2.25 (dd, *J* = 12.1, 5.3 Hz, 1H), **^{13}C NMR (126 MHz, Acetone, rotamers)** δ 177.9, 177.8, 151.3, 142.4, 129.2, 128.9, 128.6, 128.3, 124.5, 121.6, 118.2, 109.6, 109.5, 100.0, 79.1, 63.3, 54.2, 47.5, 46.0, 37.8, 31.1. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{21}H_{23}N_6O_3S$ 439.1547, found

439.1549; Enantiomeric excess was found to be 90% ee and 5:1 dr by chiral HPLC (ChiralPak IA column, hexane/i-PrOH = 70:30, 214 nm, 0.7 mL/min, major isomer: t_{major} = 23.65 min, t_{minor} = 27.30 min; minor isomer: t_{major} = 18.94 min, t_{minor} = 30.57 min).

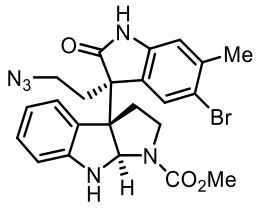
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-5-bromo-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7g).



7g

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7g** (34.6 mg, 70% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 262.14 (*c* 0.0725, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-d6, rotamers)** δ 9.74 and 9.72 (s, 1H), 7.35-7.33 (m, 1H), 7.28-7.26 and 7.19-7.17 (m, 1H), 7.17-7.12 (m, 1H), 6.87 (d, *J* = 8.3 Hz, 1H), 6.76 (dt, *J* = 14.3, 7.4 Hz, 1H), 6.55 and 6.47 (d, *J* = 7.9 Hz, 1H), 6.18 and 6.12 (s, 1H), 5.62 and 5.51(s, 1H), 5.15 and 5.13 (s, 1H), 3.75-3.66 (m, 1H), 3.62-3.60 (m, 3H), 3.37-3.27 (m, 1H), 3.00-2.95 (m, 2H), 2.94-2.90 (m, 1H), 2.57-2.49 (m, 2H), 2.35-2.26 (m, 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 177.6, 154.5 and 153.9, 151.3 and 151.2, 141.3, 131.3 and 131.0, 129.5, 127.6 and 127.5, 124.6 and 124.6, 117.8, 113.8, 111.0, 109.3, 109.0, 77.6 and 76.9, 62.5, 61.4, 54.3 and 54.2, 51.7 and 51.6, 47.4, 45.1, 44.9, 31.4. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{22}H_{22}BrN_6O_3$ 497.0931, found 497.0935; Enantiomeric excess was found to be 88% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.6 mL/min, major isomer: t_{major} = 18.84 min, t_{minor} = 11.41 min).

methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-5-bromo-6-methyl-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7h).

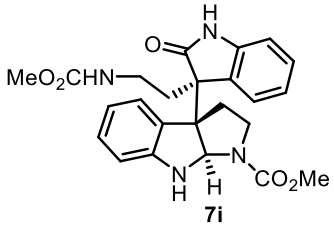


7h

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7h** (40.8 mg, 81% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 221.50 (*c* 0.1775, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.63 (s, 1H), 7.26 and 7.19 (s, 1H), 7.14-7.07 (m, 1H), 6.87 (s, 1H), 6.77-6.71 (m, 1H), 6.51 and 6.44 (d, *J* = 7.9 Hz, 1H), 6.17 and 6.12 (s, 1H), 5.57 and 5.46 (s, 1H), 5.09 (s, 1H), 3.67 (dt, *J* = 17.8, 9.3 Hz, 1H), 3.60 and 3.58 (s, 3H), 3.37-3.15 (m, 1H), 2.97-2.88 (m, 4H), 2.51-2.45 (m, 2H), 2.30 (s, 3H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 177.8, 154.5, 153.8, 151.3 and 151.2, 141.6, 137.5, 129.4, 128.6 and 128.5, 128.2, 127.6 and 127.6, 124.6 and 124.6, 117.8 and 117.7, 116.1, 111.6, 109.2 and 109.0, 77.7 and 76.9, 62.5 and 61.4, 54.0 and 53.9, 51.6 and 51.5, 47.4 and 45.1, 44.9, 31.5, 22.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{24}BrN_6O_3$ 511.1088, found 511.1081. Enantiomeric excess was found to be 81% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 80:20, 214 nm, 0.6 mL/min, major isomer: t_{major} = 58.04 min, t_{minor} = 24.60 min; minor isomer: t_{major} = 35.40 min, t_{minor} = 18.19 min).

methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-((methoxycarbonyl)amino)ethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydrop

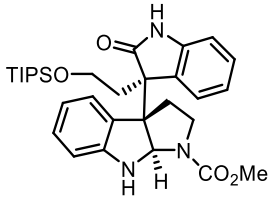
yrrolo[2,3-b]indole-1(2H)-carboxylate (7i).



7i

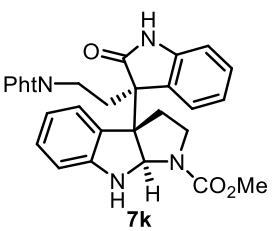
This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7i** (27.0 mg, 60% yield) as a white solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 224.86 (*c* 0.08, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.54 and 9.51 (s, 1H), 7.18 (q, *J* = 7.2 Hz, 1H), 7.06 (dt, *J* = 11.5, 7.4 Hz, 2H), 6.89 (d, *J* = 7.7 Hz, 1H), 6.77 (dt, *J* = 14.8, 7.7 Hz, 1H), 6.65 (dt, *J* = 18.3, 7.6 Hz, 1H), 6.48 and 6.43 (d, *J* = 7.9 Hz, 1H), 6.37 and 6.30 (s, 1H), 6.08-5.78 (m, 1H), 5.55 and 5.45 (s, 1H), 5.33 and 5.29 (s, 1H), 3.73-3.65 (m, 1H), 3.62 and 3.60 (s, 3H), 3.51 (s, 3H), 3.32-3.24 (m, 1H), 2.92-2.87 (m, 1H), 2.86-2.76 (m, 1H), 2.60-2.57 (m, 1H), 2.50-2.47 (m, 1H), 2.41-2.35 (m, 1H), 2.25-2.19 (m, 1H); **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 178.3, 156.5, 154.6 and 154.0, 151.3 and 151.3, 142.2 and 142.1, 129.7 and 129.7, 129.0, 128.2 and 128.2, 124.7 and 124.6, 124.4, 121.5, 117.5 and 117.5, 109.3, 109.0, 108.8, 77.6 and 76.8, 62.6 and 61.4, 54.7, 54.2 and 54.1, 51.6 and 51.5, 50.9, 44.9 and 44.7, 36.9, 32.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{24}H_{27}N_4O_5$ 451.1975, found 451.1976; Enantiomeric excess was found to be 93% ee and >20:1 dr by chiral HPLC (ChiralPak IA column, hexane/i-PrOH = 50:50, 214 nm, 0.7 mL/min, major isomer: t_{major} = 7.85 min, t_{minor} = 19.13 min).

methyl
(3a*R*,8a*R*)-3a-((*S*)-2-oxo-3-(2-((triisopropylsilyl)oxy)ethyl)indolin-3-yl)-3,3a,8,8a-tetrahydropyrro lo[2,3-b]indole-1(2H)-carboxylate (7j).



7j

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7j** (50.0 mg, 91% yield) as a white solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 267.66 (*c* 0.115, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-d6, rotamers)** δ 9.37 and 9.33 (s, 1H), 7.20-6.89 (m, 3H), 6.85 (dd, *J* = 7.8, 2.6 Hz, 1H), 6.75-6.60 (m, 2H), 6.46 and 6.39 (d, *J* = 7.9 Hz, 1H)., 6.34 and 6.24 (s, 1H), 5.50 and 5.39 (s, 1H), 5.33 and 5.25 (s, 1H), 3.73-3.63 (m, 1H), 3.61 and 3.58 (s, 3H), 3.48-3.41 (m, 1H), 3.37-3.16 (m, 2H), 2.90-2.82 (m, 1H), 2.53-2.43 (m, 2H), 2.21 (td, *J* = 12.4, 5.8 Hz, 1H), 0.93 (s, 21H). **^{13}C NMR (126 MHz, Acetone, rotamers)** δ 178.3 and 178.3, 154.5, 153.9, 151.4 and 151.3, 142.4 and 142.3, 129.8, 129.0, 128.4, 127.9 and 127.9, 124.7 and 124.5, 124.4, 121.1 and 121.0, 117.4 and 117.4, 109.1, 109.0 and 108.8, 77.5 and 76.7, 62.7 and 61.4, 59.7, 53.4 and 53.2, 51.5 and 51.4, 44.8 and 44.7, 35.3, 17.4, 11.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{31}H_{44}N_3O_4Si$ 550.3095, found 550.3074. Enantiomeric excess was found to be 93% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 80:20, 214 nm, 0.7 mL/min, major isomer: t_{major} = 13.97 min, t_{minor} = 8.03 min; minor isomer: t_{major} = 9.75 min, t_{minor} = 7.50 min).



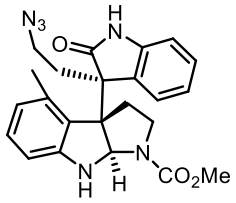
7k

2-(((2-((*S*)-3-((3a*R*,8a*R*)-1-(methoxycarbonyl)-2,3,8,8a-tetrahydropyrro lo[2,3-b]indol-3a(1H)-yl)-2-oxoindolin-3-yl)ethyl)-l2-azanyl)carbonyl)b enzoic acid (7k).

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl

acetate/petroleum ether = 1/10 to afford **7k** (51.1 mg, 98% yield) as a yellow solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 191.07 (*c* 0.08, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.57 and 9.54 (s, 1H), 7.77-7.74 (m, 2H), 7.73-7.69 (m, 2H), 7.12-7.01 (m, 3H), 6.85 (d, *J* = 7.7 Hz, 1H), 6.69-6.54 (m, 2H), 6.48 and 6.41(d, *J* = 7.8 Hz, 1H), 6.32 and 6.23 (s, 1H), 5.53 and 5.44 (s, 1H), 5.31 and 5.26 (s, 1H), 3.77-3.62 (m, 1H), 3.61 and 3.57 (s, 3H), 3.50-3.40 (m, 1H), 3.35-3.21 (m, 2H), 2.91-2.83 (m, 1H), 2.81-2.75 (m, 1H), 2.6-2.57 (m, 1H), 2.25-2.19 (m, 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 178.0, 167.4, 154.4 154.0, 151.3 and 151.2, 142.2 and 142.1, 133.9, 132.1, 129.4 and 129.3, 129.1, 128.1 and 128.0, 124.8 and 124.7, 124.3, 122.7, 121.4 and 121.3, 117.6 and 117.6, 109.5, 109.0, 108.8, 77.6 and 76.8, 62.7 and 61.6, 54.2 and 54.1, 51.7 and 51.6, 44.9 and 44.8, 33.9, 30.0 and 30.0. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{30}H_{27}N_4O_5$ 523.1926, found 523.1980; Enantiomeric excess was found to be 94% ee and >20:1 dr by chiral HPLC (ChiralPak IA column, hexane/i-PrOH = 50:50, 0.7 mL/min, major isomer: t_{major} = 15.56 min, t_{minor} = 48.43 min).

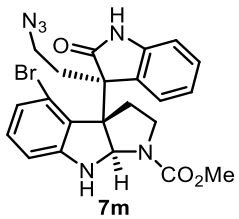
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-4-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7l).



7l

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7l** (40.1 mg, 93% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 283.64 (*c* 0.105, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.71 and 8.65 (s, 1H), 7.21-7.16 (m, 1H), 7.07 (t, *J* = 7.7 Hz, 1H), 6.90 and 6.86 (d, *J* = 7.8 Hz, 1H)., 6.76-6.71 (m, 1H), 6.66 (d, *J* = 7.5 Hz, 1H), 6.28 (d, *J* = 7.8 Hz, 1H), 5.98 and 5.91 (d, *J* = 7.6 Hz, 1H), 4.97 (s, 1H), 4.84 and 4.47 (s, 1H), 3.84 and 3.72 (t, *J* = 9.4 Hz, 1H), 3.69 and 3.64 (s, 3H), 3.45-3.31(m, 1H), 3.15-3.10 (m, 1H), 3.02-2.96 (m, 1H), 2.74-2.69 (m, 2H), 2.66-2.60 (m, 1H), 2.57-2.47 (m, 3H), 2.41-2.36 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 179.0, 155.1 and 154.3, 151.9 and 151.5, 140.5 and 140.4, 135.3 and 135.2, 129.5, 129.1 and 129.0, 128.4, 124.5 and 124.3, 124.2 and 124.1, 122.9 and 122.5, 122.3, 109.5, 108.0, 78.7 and 78.1, 63.7 and 62.7, 55.2, 52.5 and 52.2, 47.4 and 47.3, 46.1 and 45.8, 33.8, 27.2 and 27.0, 20.8 and 20.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{25}N_6O_3$ 433.1983, found 433.1985. Enantiomeric excess was found to be 80% ee and 5:1 dr by chiral HPLC (ChiralPak IA column, hexane/i-PrOH = 70:30, 214 nm, 0.7 mL/min, major isomer: t_{major} = 10.65 min, t_{minor} = 25.40 min; minor isomer: t_{major} = 9.85 min, t_{minor} = 21.80 min).

methyl (3a*S*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-4-bromo-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7m).

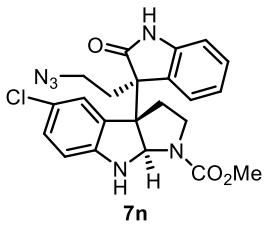


7m

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7m** (40.1 mg, 81% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 262.77 (*c* 0.1625, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.67 (s, 1H), 7.14 (td, *J* = 7.7, 1.3 Hz, 1H), 7.04-6.94 (m, 2H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.64 (t, *J* = 7.6 Hz, 1H), 6.44 and 6.35 (d, *J* = 7.7 Hz, 1H), 5.95 (d, *J* = 7.5 Hz, 1H), 5.79 and 5.64 (s, 1H),

4.93 (s, 1H), 3.76-3.67 (m, 1H), 3.57 (s, 3H), 3.40-3.30 (m, 1H), 3.24 and 3.22 (d, *J* = 5.8 Hz, 1H), 3.03-2.97 (m, 1H), 2.95-2.88 (m, 2H), 2.78-2.69 (m, 1H), 2.62-2.56 (m, 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 177.8, 154.5 and 154.4, 153.7, 141.7, 131.1, 129.0, 128.3, 124.6, 123.8, 123.3, 121.5, 119.5, 109.3, 109.0 and 108.8, 78.9 and 78.2, 64.5 and 63.4, 55.0 and 55.0, 51.5, 47.2, 45.9 and 45.6, 34.5, 26.0 and 25.5. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{22}BrN_6O_3$ 497.0931, found 497.0934. Enantiomeric excess was found to be 55% ee and 6:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 80:20, 214 nm, 0.6 mL/min, major isomer: t_{major} = 32.63 min, t_{minor} = 15.73 min; minor isomer: t_{major} = 18.88 min, t_{minor} = 11.91 min).

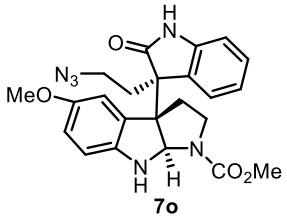
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-5-chloro-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7n).



7n

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7n** (35.3 mg, 78% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 191.55 (*c* 0.16, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.55 and 9.52 (m, 1H), 7.24 (q, *J* = 7.4 Hz, 1H), 7.06-7.01 (m, 1H), 6.93-6.85 (m, 3H), 6.72 and 6.63 (s, 1H), 6.48 and 6.41 (d, *J* = 8.4 Hz, 1H)., 5.81 and 5.74 (s, 1H), 5.54 and 5.48 (s, 1H), 3.74-3.66 (m, 1H), 3.63 and 3.59 (s, 3H), 3.11 (td, *J* = 12.0, 8.0 Hz, 1H), 2.96-2.91 (m, 3H), 2.54-2.49 (m, 1H), 2.46-2.40 (m, 1H), 2.22 (td, *J* = 12.7, 5.8 Hz, 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 177.8, 154.5, 153.9, 150.3 and 150.1, 142.5 and 142.5, 130.1, 128.8, 128.7, 124.9 124.7, 124.4, 121.7 and 121.5, 109.8, 109.7 and 109.6, 77.8 and 76.9, 62.9 and 61.7, 54.0 and 53.9, 51.7 and 51.6, 47.5, 44.7 and 44.6, 31.3 and 31.1, 30.9 and 30.9. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{22}ClN_6O_3$ 453.1436, found 453.1439. Enantiomeric excess was found to be 78% ee and 5:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 80:20, 214 nm, 0.6 mL/min, major isomer: t_{major} = 43.47 min, t_{minor} = 19.94 min; minor isomer: t_{major} = 26.81 min, t_{minor} = 15.87 min).

methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-5-methoxy-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7o).

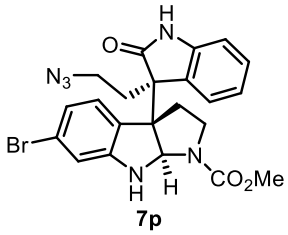


7o

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7o** (29.2 mg, 65% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 178.39 (*c* 0.1125, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.58 and 8.43 (s, 1H), 7.28 and 7.23 (t, *J* = 7.7 Hz, 1H)., 6.95-6.84 (m, 2H), 6.76-6.71 (m, 1H), 6.63-6.61 (m, 1H), 6.46 (d, *J* = 8.5 Hz, 1H), 6.31-6.30 (m, 1H), 5.44 and 5.30 (s, 1H), 4.60 (s, 1H), 3.85-3.81 and 3.73-3.67 (m, 1H), 3.75 and 3.75 (s, 3H), 3.67 (s, 3H), 3.22-2.99 (m, 3H), 2.91-2.82 (m, 1H), 2.52-2.49 (m, 1H), 2.46-2.40 (m, 1H), 2.26-2.17 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.8, 155.1 and 154.5, 153.5 and 153.3, 144.7 and 144.2, 141.2 and 141.0, 129.5 and 129.4, 128.9 and 128.7, 128.7 and 128.5, 124.5, 122.4 and 122.3, 115.2 and 114.8, 111.3 and 111.2, 111.0, 109.9, 78.4 and 77.5, 63.1 and 61.9, 56.0 and 55.8, 54.4 and 54.1, 52.6 and 52.3, 47.5,

44.9, 31.5 and 31.4, 30.4 and 30.3. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{25}N_6O_4$ 449.1932, found 449.1933. Enantiomeric excess was found to be 95% ee and 7:1 dr by chiral HPLC (ChiralPak IB-3 column, hexane/i-PrOH = 80:20, 214 nm, 0.6 mL/min, major isomer: t_{major} = 27.82 min, t_{minor} = 19.97 min; minor isomer: t_{major} = 25.61 min, t_{minor} = 22.35 min).

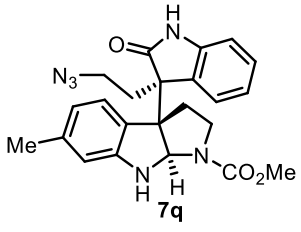
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-6-bromo-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7p).



7p

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7p** (39.6 mg, 80% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 181.83 (*c* 0.065, $CHCl_3$). **^{1}H NMR (500 MHz, CDCl$_3$, rotamers)** δ 8.48 and 8.23 (s, 1H), 7.25 and 7.20 (t, *J* = 7.7 Hz, 1H), 6.95-6.72 (m, 4H), 6.59 (brs, 1H), 6.30 (s, 1H), 5.43 and 5.23 (s, 1H), 5.04 and 4.97 (ss, 1H), 3.80-3.75 and 3.68-3.64 (m, 1H), 3.71 and 33.61 (s, 3H), 3.19-2.91 (m, 3H), 2.89-2.76 (m, 1H), 2.51-2.39 (m, 1H), 2.37-2.30 (m, 1H), 2.19-2.10 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$, rotamers)** δ 178.6 and 178.4, 155.1 and 154.2, 152.0 and 151.6, 141.1 and 140.9, 129.0 and 128.9, 128.4 and 128.2, 126.9 and 126.8, 125.8 and 125.6, 124.3, 123.4 and 123.3, 122.6 and 122.5, 121.5 and 121.3, 112.7 and 112.6, 110.0 and 110.0, 77.8, 62.3 and 61.1, 54.2 and 53.9, 52.7 and 52.4, 47.4, 45.0, 31.4 and 31.3, 30.4. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{22}H_{22}BrN_6O_3$ 497.0936, found 497.0931. Enantiomeric excess was found to be 88% ee and 4:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.6 mL/min, major isomer: t_{major} = 15.78 min, t_{minor} = 10.58 min; minor isomer: t_{major} = 12.16 min, t_{minor} = 9.77 min).

methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-6-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7q).

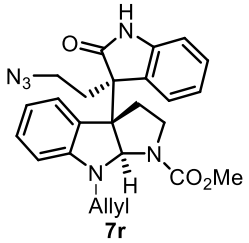


7q

This compound was prepared according to the **general procedure A** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7q** (40.2 mg, 93% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/2, v/v). $[\alpha]_D^{20}$ = 204.79 (*c* 0.14, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-d6, rotamers)** δ 9.55 and 9.51 (s 1H), 7.20 (q, *J* = 7.3 Hz, 1H), 7.10-6.85 (m, 2H), 6.79 (dt, *J* = 14.7, 7.6 Hz, 1H), 6.52-6.40 (m, 2H), 6.33 and 6.26 (s, 1H), 5.46-5.38 (s ,1H), 5.38-5.31 (s, 1H), 3.72-3.65 (m, 1H), 3.63 and 3.57 (s, 3H), 3.22-3.16 (m, 1H), 2.99-2.95 (m, 1H), 2.92-2.84(m, 2H), 2.58-2.42 (m, 2H), 2.23 and 2.21 (s, 3H), 2.21-2.16 (m, 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ 178.1, 154.5 and 154.0, 151.5 and 151.4, 142.3 and 142.2, 138.9 and 138.8, 129.2 and 129.1, 128.3, 125.2, 124.5, 124.4 and 124.3, 121.5, 118.5 and 118.5, 111.0 and 110.9, 109.8, 109.6, 109.4, 77.8 and 77.0, 62.4 and 61.2, 54.0 and 53.9, 51.6 and 51.5, 47.5, 44.8 and 44.7, 31.3, 30.8 and 30.6, 20.8. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{23}H_{25}N_6O_3$ 433.1983, found 433.1988. Enantiomeric excess was found to be 92% ee and 19:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.6 mL/min, major isomer: t_{major} = 26.34 min, t_{minor} = 13.44 min; minor isomer: t_{major} = 11.27 min, t_{minor} = 9.87 min).

methyl

(3a*R*,8a*R*)-8-allyl-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7r).

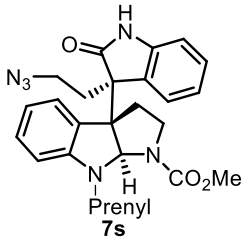


7r

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7r** (42.6 mg, 93% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -222.18 (*c* 0.10, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.55-8.25 (m, 1H), 7.23-7.08 (m, 2H), 6.87-6.83 (m, 2H), 6.75-6.29 (m, 2H), 6.23 (d, *J* = 8.1 Hz, 1H), 6.22-4.66 (m, 5H), 3.84 (dd, *J* = 11.0, 7.9 Hz, 1H), 3.70-3.25 (m, 6H), 2.98 (qd, *J* = 11.9, 6.6 Hz, 2H), 2.84-2.76 (m, 1H), 2.59-2.30 (m, 2H), 2.14-2.10 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.4 and 178.1, 155.5, 154.6, 151.4, 140.8, 134.7 and 134.4, 129.7, 129.7 and 128.7, 127.8, 124.6 and 124.4, 122.5 and 122.4, 117.1 and 116.8, 115.5, 115.1, 109.9 and 109.9, 106.6 and 106.5, 82.0 and 81.8, 62.3 and 61.2, 54.6 and 54.3, 52.5 and 52.5, 48.8, 47.4, 45.1, 31.6, 31.3. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{25}H_{27}N_6O_3$ 459.2139, found 459.2133. Enantiomeric excess was found to be 97% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, t_{major} = 22.98 min, t_{minor} = 10.80 min).

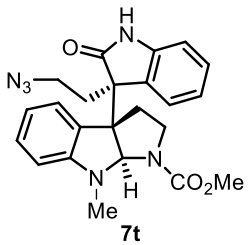
methyl

(3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-8-(3-methylbut-2-en-1-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7s).



7s

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7s** (45.3 mg, 93% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -207.47 (*c* 0.0575, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.25 (s, 1H), 7.29-7.12 (m, 3H), 6.91-6.59 (m, 3H), 6.23-6.19 (m, 1H), 6.00-5.88 (m, 1H), 5.27 (s, 1H), 4.62-4.34 (m, 1H), 3.94 and 3.88 (dd, *J* = 10.9, 7.9 Hz, 1H), 3.73-3.65 (m, 3H), 3.68-3.49 (m, 2H), 3.34-3.21 (m, 1H), 3.06-2.97 (m, 2H), 2.91-72 (m, 1H), 2.58-2.34 (m, 2H), 2.16 2.13 (m, 1H), 1.63-1.59 (m, 6H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.3 and 178.0, 155.5, 154.6, 151.5, 140.6, 132.9 and 132.8, 129.7, 128.9 and 128.8, 128.7 and 128.7, 127.8, 124.7, 124.4 and 124.1, 122.5 and 122.4, 122.1 and 121.5, 116.7 and 116.4, 109.7 and 109.6, 106.1, 82.1 and 81.7, 62.2 and 61.0, 54.5 and 54.2, 52.5, 47.4, 45.1, 43.7, 31.6, 25.6, 17.9. **HRMS (ESI) m/z**: $[M+H]^+$ calcd for $C_{27}H_{31}N_6O_3$ 487.2452, found 487.2445. Enantiomeric excess was found to be 90% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 9.22 min, t_{minor} = 20.28 min).



7t

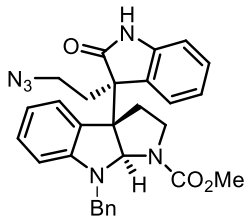
methyl

(3aR,8aR)-3a-((S)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-8-methyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7t).

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7y** (39.3 mg, 91% yield) as a yellow

solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -253.95 (*c* 0.0625, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ 8.46 and 8.38 (s, 1H), 7.28-7.09 (m, 2H), 6.90-6.58(m, 4H), 6.29 (d, *J* = 7.9 Hz, 1H), 6.22-5.88 (m, 1H), 5.42-4.87 (m, 1H), 3.95 and 3.84 (dd, *J* = 10.8, 7.9 Hz, 1H)., 3.77 and 3.70 (s, 3H), 3.27-3.21 (m, 1H), 3.05-2.93 (m, 2H), 2.90-2.81 (m, 1H), 2.75-2.35 (m, 5H), 2.18-2.14 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.6 and 178.4, 155.6 and 154.8, 152.6 and 152.3, 141.0 and 140.7, 129.8 and 129.7, 128.9 and 128.7, 128.7 and 127.9, 124.5 and 124.3, 124.1, 122.4 and 122.2, 117.1, 109.9 and 109.8, 107.0 and 107.8, 83.3 and 82.5, 62.5 and 61.4, 54.7 and 54.5, 52.5 and 52.5, 47.5, 45.1 and 45.0, 33.5 and 33.3, 31.2 and 31.0. **HRMS (ESI) m/z:** $[M+H]^+$calcd for $C_{23}H_{25}N_6O_3$ 433.1983, found 433.1969. Enantiomeric excess was found to be 95% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 11.45 min, t_{minor} = 19.81 min).

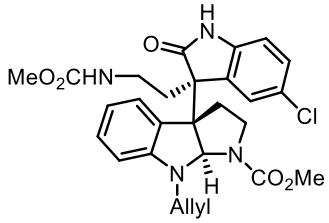
methyl (3a*R*,8a*R*)-3a-((*S*)-3-(2-azidoethyl)-2-oxoindolin-3-yl)-8-benzyl-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7u).



7u

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7u** (40.6 mg, 92% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -172.35 (*c* 0.14, $CHCl_3$). **^{1}H NMR (500 MHz, Acetone-*d*$_6$, rotamers)** δ 9.55 (s, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.28-7.11 (m, 3H), 7.11-6.70 (m, 6H), 6.63 (s, 1H), 6.34 (bs, 1H), 6.10 and 5.98 (d, *J* = 7.9 Hz, 1H), 5.68 (bs, 1H), 4.39-4.11 (m, 2H), 3.94 (t, *J* = 9.3 Hz, 1H), 3.60 and 3.31 (s, 3H), 3.22 (m, 1H), 3.03-2.99 (m, 1H), 2.95-2.84 (m, 2H), 2.61-2.49 (m, 2H), 2.23-2.20 (m 1H). **^{13}C NMR (126 MHz, Acetone-*d*$_6$, rotamers)** δ177.9, 155.4, 154.1, 152.1, 151.7, 139.7 and 139.3, 142.4, 129.3 and 129.2, 128.7 and 128.5, 128.2 and 128.2, 126.4, 126.3, 125.9, 124.6, 124.4, 121.7, 117.2 and 117.0, 109.8, 106.3, 82.9 and 82.6, 62.6 and 61.4, 54.3 and 54.0, 51.8 and 51.4, 49.7, 47.4, 44.9, 31.5 and 31.2. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{29}H_{29}N_6O_3$ 433.1983, found 433.1969. Enantiomeric excess was found to be 93% ee and >20:1 dr by chiral HPLC (ChiralPak IC column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 13.24 min, t_{minor} = 26.53 min).

methyl (3a*R*,8a*R*)-8-allyl-3a-((*S*)-5-chloro-3-(2-((methoxycarbonyl)amino)ethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetrahydropyrrolo[2,3-b]indole-1(2H)-carboxylate (7v).

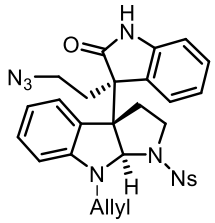


7v

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7v** (51.4 mg, 98% yield) as a yellow solid. R_f = 0.4 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -27.24 (*c* 0.975, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$, rotamers)** δ8.94 (s, 1H), 7.20-6.45 (m, 5H), 6.31 (d, *J* = 7.9 Hz, 1H), 6.27-5.05 (m, 3H), 5.06-4.44 (m, 3H), 3.97-3.93 and 3.89-3.83 (m, 1H), 3.68 (s, 3H), 3.63-3.55 (m, 4H), 3.42-3.25 (m, 1H), 3.01 (dt, *J* = 11.7, 5.7 Hz, 1H), 2.94-2.75 (m, 2H), 2.74-2.21 (m, 3H), 2.15 (dd, *J* = 12.1, 5.4 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$, rotamers)** δ 178.5, 177.8, 156.7, 155.5 and 154.6, 151.3, 139.5, 134.5 and 134.2, 131.2, 130.9, 129.8, 128.8 and

128.4, 127.8 and 127.5, 125.1 and 124.3, 117.2 and 117.0, 115.8 and 115.2, 110.7, 106.6, 82.0, 65.6, 62.3 and 61.2, 55.3, 52.5 and 52.1, 49.6 and 48.8, 45.1, 37.2, 32.3 and 32.1, 30.6. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{27}H_{30}ClN_4O_5$ 525.1899, found 525.1888. Enantiomeric excess was found to be 92% ee and >20:1 dr by chiral HPLC (ChiralPak AD column, hexane/i-PrOH = 80:20, 214 nm, 0.7 mL/min, major isomer: t_{major} = 16.382 min, t_{minor} = 12.85 min).

(*S*)-3-((3a*R*,8a*R*)-8-allyl-1-((4-nitrophenyl)sulfonyl)-2,3,8,8a-tetrahydropyrrolo[2,3-b]indol-3a(1H)-yl)-3-(2-azidoethyl)indolin-2-one (7w).



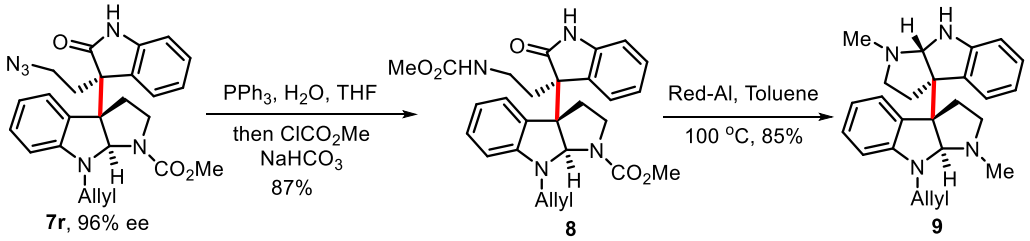
7w

This compound was prepared according to the **general procedure B** The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7w** (50.3 mg, 86% yield) as a yellow solid. R_f = 0.5 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{20}$ = -192.89 (*c* 0.0625, $CHCl_3$). **^{1}H NMR (500 MHz, CDCl$_3$, rotamers)** δ 8.41 (d, *J* = 8.8 Hz, 2H), 8.17 (s, 1H), 8.06 (d, *J* = 8.6 Hz, 2H), 7.26 (t, *J* = 7.6 Hz, 1H), 7.18 (t, *J* = 7.0 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 6.84 (q, *J* = 8.4, 7.9 Hz, 1H), 6.72 (s, 1H), 6.34 (d, *J* = 7.9 Hz, 1H), 6.03 (s, 1H), 5.35 (s, 1H), 5.11 (s, 1H), 4.93 (d, *J* = 10.6 Hz, 2H), 3.86-3.73 (m, 1H), 3.73-3.57 (m, 2H), 3.11-3.05 (m, 1H), 3.02-2.84 (m, 2H), 2.84-2.71 (m, 1H), 2.42-2.23 (m, 2H), 2.16-2.13 (m, 1H). **^{13}C NMR (126 MHz, CDCl$_3$, rotamers)** δ 178.1, 150.8, 150.2, 145.7, 140.6, 133.5, 130.0, 129.0, 128.6, 128.2, 126.7, 124.6, 124.5, 124.3, 122.7, 117.6, 116.5, 110.1, 107.1, 84.9, 62.4, 54.0, 47.7, 47.4, 47.3, 31.7. **HRMS (ESI) m/z:** $[M+H]^+$ calcd for $C_{29}H_{28}N_7O_5S$ 586.1867, found 586.1846. Enantiomeric excess was found to be 89% ee and >20:1 dr by chiral HPLC (ChiralPak AD column, hexane/i-PrOH = 60:40, 214 nm, 0.7 mL/min, major isomer: t_{major} = 8.94 min, t_{minor} = 13.72 min).

Gram scale synthesis of dimer 7r and 7u

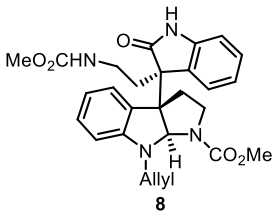
To a dry tube was charged with **L6** (0.77 mmol, 467.0 mg), $Ni(BF_4)_2{\cdot}6H_2O$ (0.77 mmol, 262.1mg), Bromo-oxindole **6a** (11.6 mmol, 3.2 g) and 4Å M.S. molecular sieves (100 mg), the tube was capped with a rubber septum, After evacuated and backfilled argon three times, dichloromethane (80 mL) was added and the mixture was stirred at 35 °C for 30 min, then DIPEA (15.4 mmol, 2.7 mL) was added via a syringe, finally tryptamine **5r** (7.7 mmol, 2.0 g) in dichloromethane (20 mL) was added via a syringe. The reaction mixture was allowed to stir for 12h under a Ar atmosphere at room temperature. The reaction mixture was concentrated and purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7r** (3.2 g, 93% yield) as a yellow solid. Enantiomeric excess was found to be 96% ee and >20:1 dr by chiral HPLC.

To a dry tube was charged with **L6** (1.0 mmol, 606.5 mg), $Ni(BF_4)_2{\cdot}6H_2O$ (1.0 mmol, 340.4mg), Bromo-oxindole **6a** (15.0 mmol, 4.2 g) and 4Å molecular sieves (150 mg), the tube was capped with a rubber septum, After evacuated and backfilled argon three times, dichloromethane (100 mL) was added and the mixture was stirred at 35 °C for 30 min, then DIPEA (20.0 mmol, 3.5mL) was added via a syringe, finally tryptamine **5u** (10.0 mmol, 3.0 g) in dichloromethane (20 mL) was added via a syringe. Upon completion, The residue was purified by flash column chromatography eluting with ethyl acetate/petroleum ether = 1/10 to afford **7u** (4.5 g, 92% yield) as a yellow solid. Enantiomeric excess was found to be 93% ee and >20:1 dr by chiral HPLC.



methyl (3a*R*,8a*R*)-8-allyl-3a-((*S*)-3-(2-((methoxycarbonyl)amino)ethyl)-2-oxoindolin-3-yl)-3,3a,8,8a-tetra hydropyrrolo[2,3-b]indole-1(2H)-carboxylate (8).

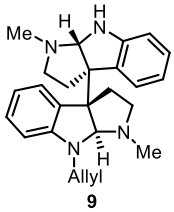
To a solution of **7r** (1.0 mmol, 457.0 mg) in THF (10 mL) was added PPh_3 (1.2 mmol, 283 mg) and H_2O (10.0 mmol, 162 mg), the mixture was then stirred at rt until the starting material completely consumed monitored by TLC, then $NaHCO_3$ (aq) (5 mL) was added to the solution, followed by adding Methyl chloroformate (1.2 mmol, 97.0 μL), the mixture was then stirred at room temperature for 30 min. Upon completion, the reaction mixture was extracted with EtOAc (10 mL× 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography (ethyl acetate/petroleum ether = 1/10, v/v) to afford the corresponding **8** (426.3 mg, 87% yield) as a light yellow solid.



R_f = 0.4 (ethyl acetate/petroleum ether = 1/3, v/v). $[\alpha]_D^{25}$ = 191.74 (*c* 0.65, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 9.14 (s, 1H), 7.86-6.45 (m, 7H), 6.23 (d, *J* = 7.9 Hz, 1H), 5.99-4.99 (m, 3H), 4.98-4.39 (m, 2H), 3.91 and 3.82 (t, *J* = 9.3 Hz, 1H), 3.65 (s, 3H), 3.53 (s, 3H), 3.43-3.09 (m, 2H), 2.95 (td, *J* = 11.4, 5.5 Hz, 1H), 2.78-2.37 (m, 5H), 2.12-2.08 (m, 1H). **^{13}C NMR (126 MHz, $CDCl_3$)** δ 179.4 and 179.2, 156.8, 155.5, 154.7, 151.4, 141.4 and 141.3, 134.8 and 134.6, 129.4, 128.5, 128.1, 124.5, 124.3, 122.2, 117.0 and 116.8, 115.3 and 115.0, 110.0, 106.5 and 106.4, 82.1, 62.3 and 61.1, 55.1 and 54.9, 52.5, 52.0, 49.7, 49.0, 45.0 and 44.9, 37.20, 32.2 and 32.0.

(3a*R*,3'a*S*,8a*S*,8'a*S*)-8-allyl-1,1'-dimethyl-2,2',3,3',8,8a,8',8'a-octahydro-1H,1'H-3a,3'a-bipyrrolo[2,3-b]indole (9).

Red-Al was added to a solution of **8** (0.5 mmol, 256.0 mg) in dry toluene (2 mL) at 0 °C, then the solution was stirred at 100 °C in oil bath for 12h. The reaction mixture was quenched with aqueous potassium sodium tartrate (10 mL) at rt, then extracted with EtOAc (5 mL× 3), the organic layer was dried ($MgSO_4$) and concentrated in vacuo. The residue was purified by flash column chromatography eluting with methanol/dichloromethane =1/30 to afford **9** (164.1 mg, 85% yield) as a off-white solid. R_f = 0.4 (methanol/dichloromethane = 1/7, v/v).



$[\alpha]_D^{25}$ = -15 (*c* 0.4, $CHCl_3$). Literature[4] value: $[\alpha]_D^{25}$ = -16 (*c* = 0.4, $CHCl_3$), (*Angew. Chem. Int. Ed*. **2011**, *50*, 9116-9119).

^{1}H NMR (500 MHz, DMSO-*d*$_6$, 120 °C**)** δ 7.00 (t, *J* = 7.6 Hz, 1H), 6.90 (t, *J* = 7.5 Hz, 1H), 6.78 (s, 1H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.47 (d, *J* = 7.8 Hz, 1H), 6.37-6.32 (m, 2H), 6.22 (s, 1H), 5.80 (s, 1H), 5.46-5.28 (m, 1H), 5.06 (d, *J* = 17.1 Hz, 1H), 4.96 (d, *J* = 10.2 Hz, 1H), 4.73 (s, 1H), 4.44 (s, 1H), 3.63-3.55 (m, 1H), 3.48 (dd, *J* = 15.7, 5.3 Hz, 1H). 2.87 (t, *J* = 7.8 Hz, 1H), 2.77 (t, *J* = 7.3 Hz, 1H), 2.52-2.25 (m, 10H), 2.00-1.94 (m, 2H). **^{13}C NMR (126**

MHz, DMSO-d_6, 120 °C**)** δ 153.5, 152.4, 135.3, 133.6, 132.4, 128.4, 128.2, 124.4, 124.1, 117.7, 117.2, 116.7, 108.2, 107.9, 89.4, 83.7, 63.7, 63.1, 52.5, 52.3, 52.2, 37.1, 36.8, 36.2, 35.6.

Table S9. Comparison of our **^{1}H NMR** data for (-)-*N*-allyl-chimonanthine (**9**) with literature data (**DMSO-d_6**):

Michael C. Willis′s Report[1]: ^{1}H NMR, 250 MHz, DMSO-d_6, 120 °C	This work: ^{1}H NMR, 500 MHz, DMSO-d_6, 120 °C
7.00 (app t, *J* = 7.6 Hz, 1H)	7.00 (t, *J* = 7.6 Hz, 1H)
6.87 (app t, *J* = 7.6 Hz, 1H)	6.90 (t, *J* = 7.5 Hz, 1H)
6.78 (bs, 1H)	6.78 (bs, 1H)
6.53 (app t, *J* = 7.6 Hz, 1H)	6.54 (t, *J* = 7.3 Hz, 1H),
6.45-6.14 (m, 4H),	6.47 (d, *J* = 7.8 Hz, 1H); 6.37-6.32 (m, 2H); 6.22 (s, 1H)
5.62 (bs, 1H)	5.80 (bs, 1H)
5.46-5.23(m, 1H)	5.46-5.28 (m, 1H)
5.06 (d, *J* = 17.2 Hz, 1H)	5.06 (d, *J* = 17.1 Hz, 1H)
4.95 (d, *J* = 10.1 Hz, 1H)	4.96 (d, *J* = 10.2 Hz, 1H),
4.60 (bs, 1H)	4.73 (bs, 1H)
4.39 (bs, 1H)	4.44 (bs, 1H)
3.63 (dd, *J* = 16.2 Hz, 5.2 Hz, 1H)	3.63-3.55 (m, 1H)
3.47 (dd, *J* = 16.2 Hz, 5.2 Hz, 1H)	3.48 (dd, *J* = 15.7, 5.3 Hz, 1H)
2.73 (app t, *J* = 6.7 Hz, 2H)	2.87 (t, *J* = 7.8 Hz, 1H); 2.77 (t, *J* = 7.3 Hz, 1H)
2.48-2.25 (m, 10H)	2.52-2.25 (m, 10H)
2.01-1.82 (m, 2H)	2.00-1.94 (m, 2H)

Table S10. Comparison of our **^{13}C NMR** data for (-)-*N*-allyl-chimonanthine (**9**) with literature data (**DMSO-d_6**):

Michael C. Willis′s Report[1]: ^{1}H NMR, 100 MHz, DMSO-d_6, 120 °C	This work: ^{1}H NMR, 126 MHz, DMSO-d_6, 120 °C
154.1	153.5
153.4	152.4
135.8	135.3
134.5,	133.6,
133.5	132.4
128.6	128.4
128.3	128.2
124.8	124.4
124.5,	124.1,
117.8	117.7
117.3	117.2
117.0	116.7,
108.2	108.2,
108.1	107.9
89.8	89.4
83.9	83.7
64.1	63.7
63.6	63.1
52.8	52.5
52.63	52.3
52.57	52.2
37.7	37.1
37.5	36.8
36.8,	36.2,
36.2	35.6

4. Refernces

[1] Menozzi,C.; Dalko, P. I.; Cossy, J. *Chem. Commun*. **2006**, 4638-4639.
[2] Mizuta, S.; Otaki, H.; Kitagawa, A.; Kitamura, K.; Morii, Y.; Ishihara, J.; Nishi, K. Hashimoto, R.; Usui, T.; Chiba, K.; *Org. Lett*. **2017**, *19*, 2572-2575.
[3] Liao, Y.-H.; Wu, Z.-J.; Han, W.-Y.; Zhang, X.-M.; Yuan, W.-C. *Chem. Eur. J.* **2012**, *18*, 8916-8920;
[4] R. H. Snell, R. L. Woodward and M. C. Willis, *Angew. Chem., Int. Ed*., **2011**, *50*, 9116-9119.

5. HPLC Data

Note: The absolute configuration of **7e** corresponding to major peaks in HPLC spectrums was determined to be (3*S*, 3a*R*, 8a*R*) by the X-ray crystallographic analysis. In addition, the NMR spectral characteristic peaks of the major isomers are similar to these of **7e**. Therefore, the major peaks in HPLC spectrums of other products should correspondingly possess the same configurations as **7e**.

HPLC Report

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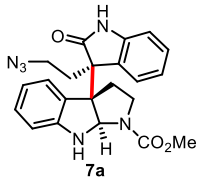

7a

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	8.645	37063.4	747043.1	5.0273	5.0273
2	10.465	275493.7	6752985.2	45.4450	45.4450
3	13.117	22393.2	729277.4	4.9078	4.9078
4	20.015	118878.7	6630378.7	44.6199	44.6199
Total		453829.1	14859684.4	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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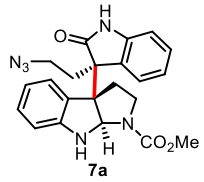

7a

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	8.525	16862.5	376705.1	1.5528	1.5528
2	10.842	23870.8	605085.2	2.4942	2.4942
3	13.742	36631.6	1285052.9	5.2971	5.2971
4	20.943	386192.4	21992890.3	90.6559	90.6559
Total		463557.3	24259733.6	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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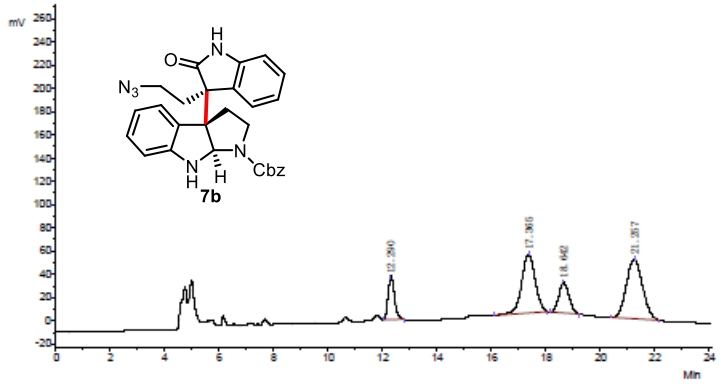

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.290	35497.7	600846.5	11.6757	11.6757
2	17.365	50576.6	1755383.2	34.1108	34.1108
3	18.642	26260.7	676605.1	13.1479	13.1479
4	21.257	51497.8	2113287.0	41.0656	41.0656
Total		163832.7	5146121.9	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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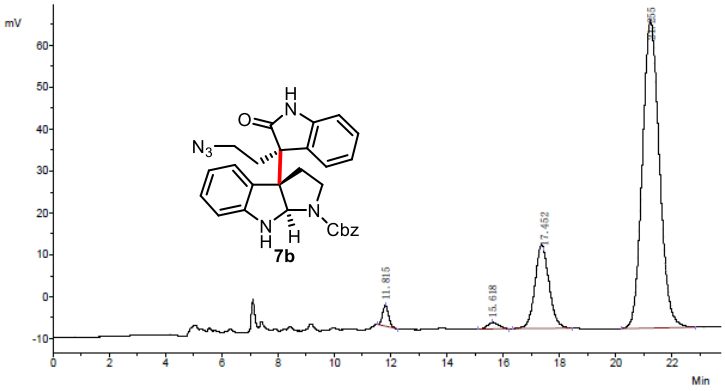

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.815	5076.1	75227.0	1.9325	1.9325
2	15.618	1518.5	43457.6	1.1164	1.1164
3	17.452	18608.2	693935.9	17.8262	17.8262
4	21.255	73177.1	3080160.6	79.1249	79.1249
Total		98380.0	3892781.1	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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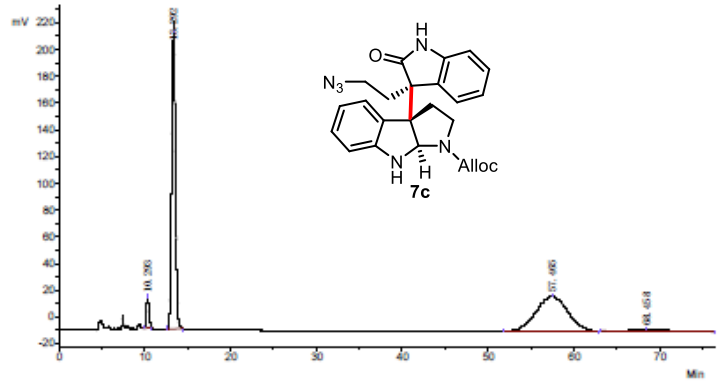

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2	13.292	222100.3	6857722.4	47.8347	47.8347
3	57.465	25780.7	6607021.4	46.0860	46.0860
4	68.458	1100.0	348600.6	2.4316	2.4316
Total		271800.9	14336285.4	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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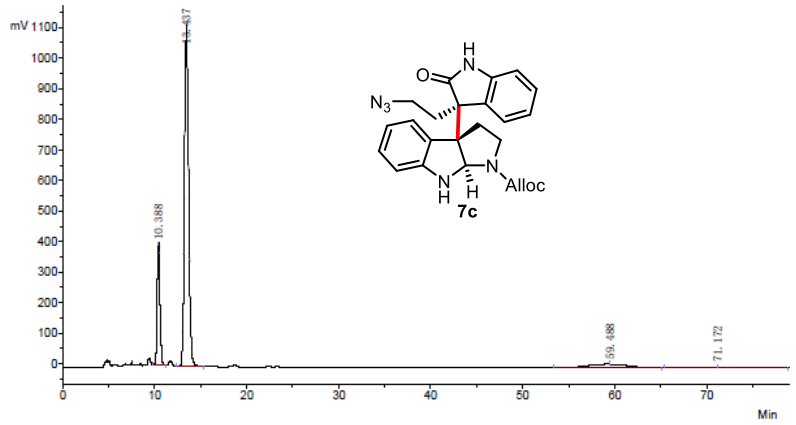

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	10.388	393155.0	8512869.4	18.1029	18.1029
2	13.437	1118534.2	35223464.9	74.9040	74.9040
3	59.488	10754.6	2887212.3	6.1398	6.1398
4	71.172	1119.4	401285.1	0.8533	0.8533
Total		1523563.2	47024831.7	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

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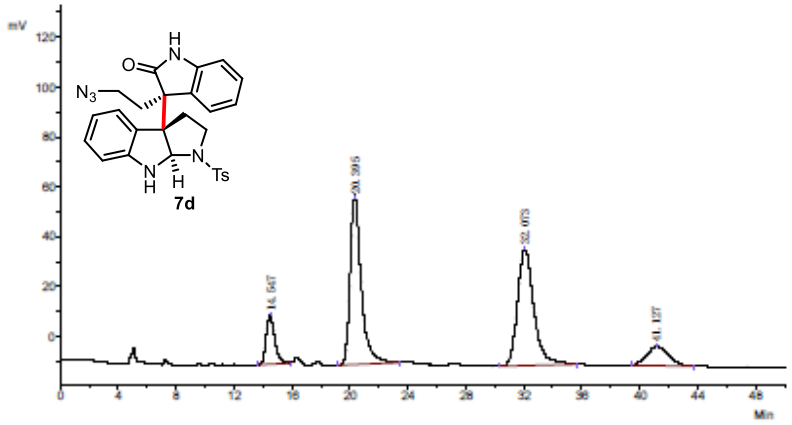

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.547	19195.8	797891.4	8.9810	8.9810
2	20.395	66584.5	3651426.1	41.1003	41.1003
3	32.073	46512.7	3635638.0	40.9226	40.9226
4	41.127	7484.3	799235.0	8.9961	8.9961
Total		139777.4	8884190.5	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

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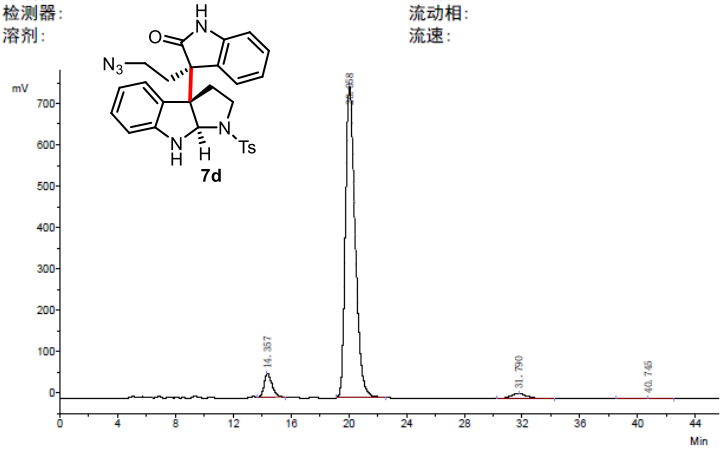
流动相:
流速:

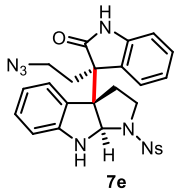


No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	14.357	57032.9	2192403.5	5.7359	5.7359
2	20.058	752542.1	35180906.1	92.0431	92.0431
3	31.790	11151.3	802071.6	2.0984	2.0984
4	40.745	437.7	46828.9	0.1225	0.1225
Total		821164.0	38222210.1	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:



7e

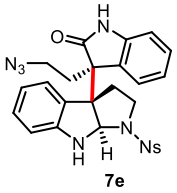
Recording Time:2018.08.08 15:52
色谱柱:
流动相:
流速:

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.065	722475.3	17256690.9	50.1302	50.1302
2	22.557	303765.9	17167026.2	49.8698	49.8698
Total		1026241.3	34423717.1	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3

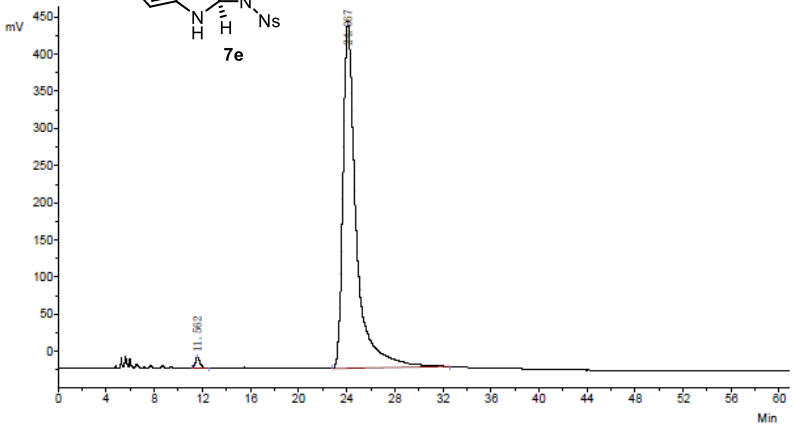
HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:



7e

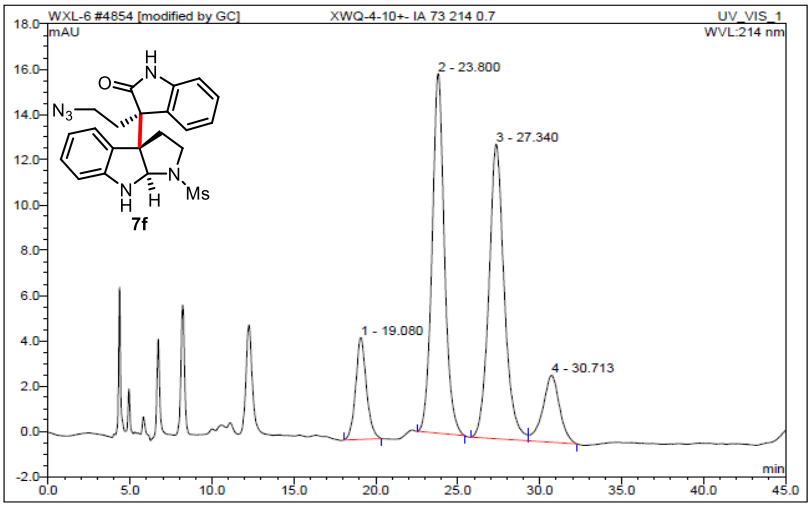
Recording Time:2018.08.07 16:19
色谱柱:
流动相:
流速:



No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.562	13878.3	356023.4	0.9729	0.9729
2	24.067	462328.2	36236149.9	99.0271	99.0271
Total		476206.5	36592173.3	100.0000	100.0000

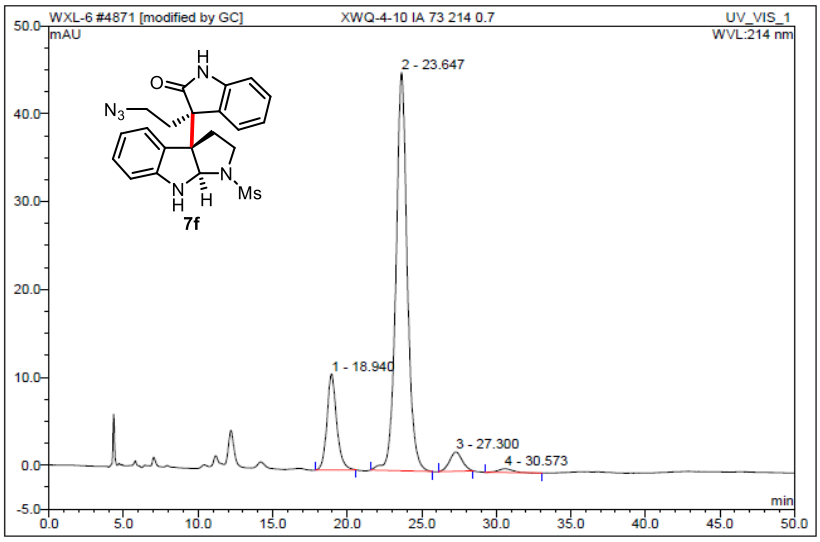
No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

Sample Name:	**XWQ-4-10+- IA 73 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**BC3**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-2**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/2 17:12**	*Sample Weight:*	**1.0000**
Run Time (min):	**45.00**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	19.08	n.a.	4.504	3.431	9.81	n.a.	BMB
2	23.80	n.a.	15.895	13.828	39.55	n.a.	BMB
3	27.34	n.a.	13.026	14.170	40.53	n.a.	BM
4	30.71	n.a.	2.971	3.536	10.11	n.a.	MB
Total:			36.396	34.965	100.00	0.000	

Sample Name:	**XWQ-4-10 IA 73 214 0.7**	*Injection Volume:*	**2.0**
Vial Number:	**BB1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-5**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/3 9:49**	*Sample Weight:*	**1.0000**
Run Time (min):	**50.00**	*Sample Amount:*	**1.0000**

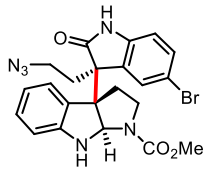


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	18.94	n.a.	10.932	8.244	16.19	n.a.	BMB
2	23.65	n.a.	45.335	40.032	78.60	n.a.	BMB
3	27.30	n.a.	2.196	2.168	4.26	n.a.	BMB
4	30.57	n.a.	0.434	0.489	0.96	n.a.	BMB*
Total:			58.897	50.934	100.00	0.000	

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.12.18 10:33
色谱柱:
流动相:
流速:



7g

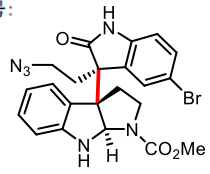
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.480	24289.7	907216.1	50.0417	50.0417
2	19.055	14212.0	905703.4	49.9583	49.9583
Total		38501.7	1812919.5	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

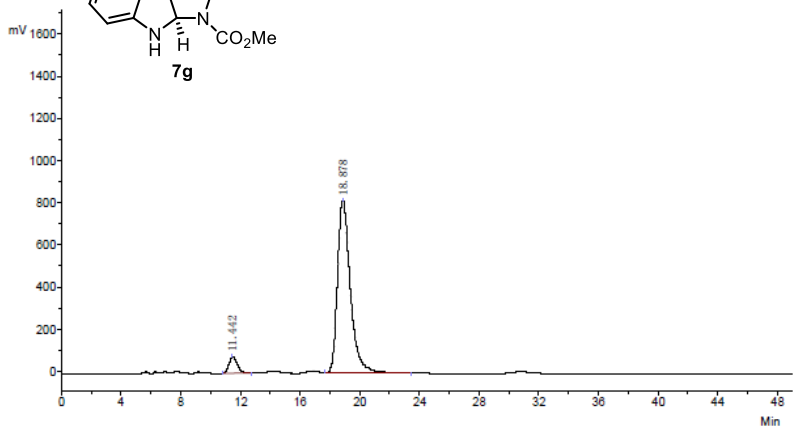
HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.12.18 11:02
色谱柱:
流动相:
流速:



7g



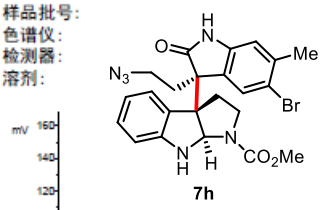
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.442	76174.3	3005083.1	5.8371	5.8371
2	18.878	816700.1	48477579.9	94.1629	94.1629
Total		892874.4	51482663.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

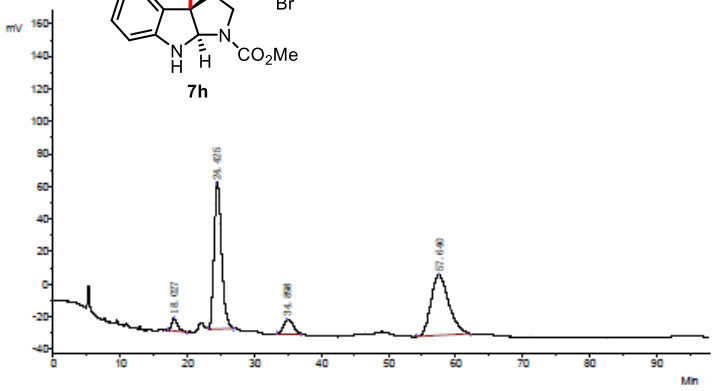
HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.01.10 18:00
色谱柱:
流动相:
流速:



7h



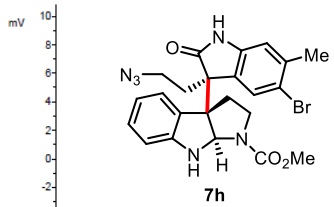
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.027	7823.5	461907.5	3.0537	3.0537
2	24.425	88532.8	6972475.6	46.0958	46.0958
3	34.898	8495.8	862087.5	5.6994	5.6994
4	57.640	36814.0	6829595.3	45.1512	45.1512
Total		141666.1	15126066.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.01.10 19:43
色谱柱:
流动相:
流速:



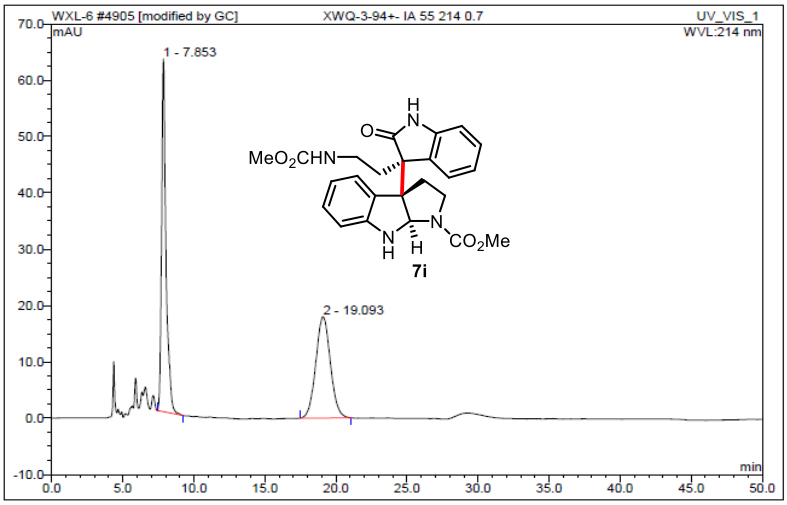
7h

No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	18.323	236.1	14335.9	0.2767	0.2767
2	24.607	5694.2	488468.5	9.4276	9.4276
3	35.535	992.7	107680.7	2.0783	2.0783
4	58.048	21694.2	4570787.9	88.2175	88.2175
Total		28617.3	5181273.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

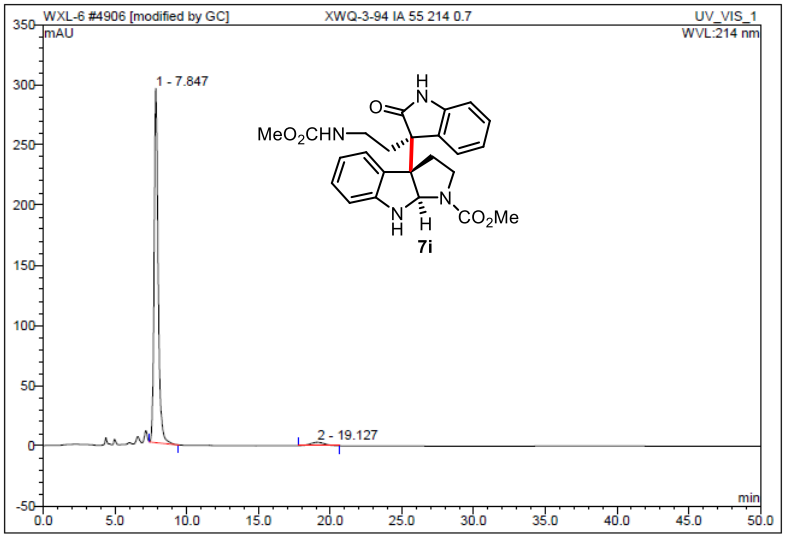
4905 XWQ-3-94+- IA 55 214 0.7

Sample Name:	**XWQ-3-94+- IA 55 214 0.7**	*Injection Volume:*	**2.0**
Vial Number:	**BC5**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-4**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/4 19:18**	*Sample Weight:*	**1.0000**
Run Time (min):	**50.01**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.85	n.a.	62.635	22.461	51.17	n.a.	BMB
2	19.09	n.a.	18.012	21.435	48.83	n.a.	BMB
Total:			80.646	43.895	100.00	0.000	

Sample Name:	**XWQ-3-94 IA 55 214 0.7**	*Injection Volume:*	**2.0**
Vial Number:	**BC6**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-4**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/4 20:09**	*Sample Weight:*	**1.0000**
Run Time (min):	**50.01**	*Sample Amount:*	**1.0000**

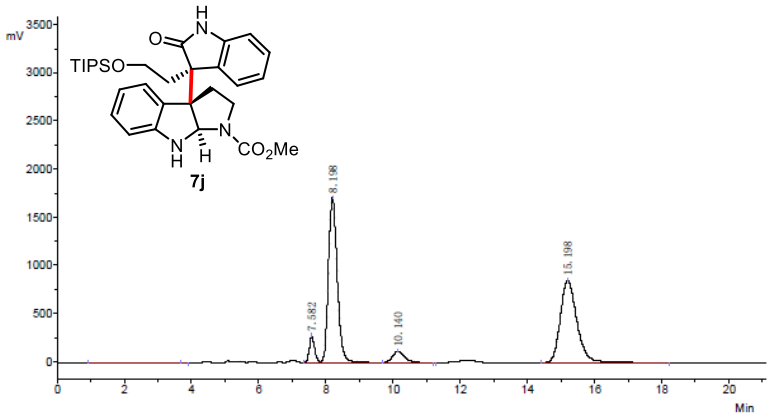


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	7.85	n.a.	294.332	96.164	96.70	n.a.	BMB*
2	19.13	n.a.	2.869	3.282	3.30	n.a.	BMB
Total:			297.200	99.446	100.00	0.000	

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.08.18 22:32
色谱柱:
流动相:
流速:



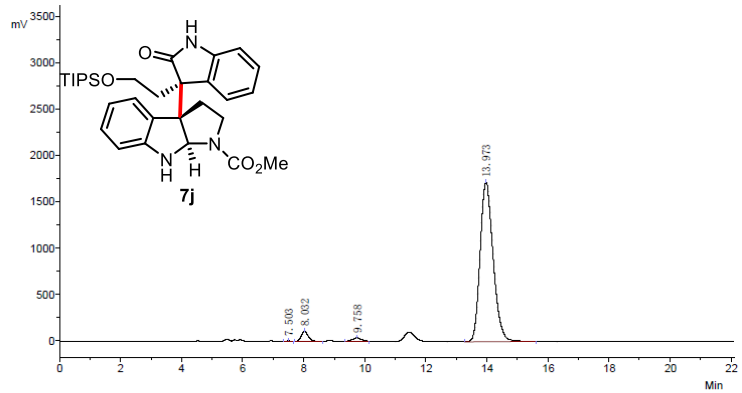
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	7.582	269155.3	3011128.8	4.5586	4.5586
2	8.198	1703890.3	31173848.9	47.1947	47.1947
3	10.140	108649.6	2620584.0	3.9674	3.9674
4	15.198	851373.2	29248182.9	44.2794	44.2794
Total		2933068.4	66053744.6	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

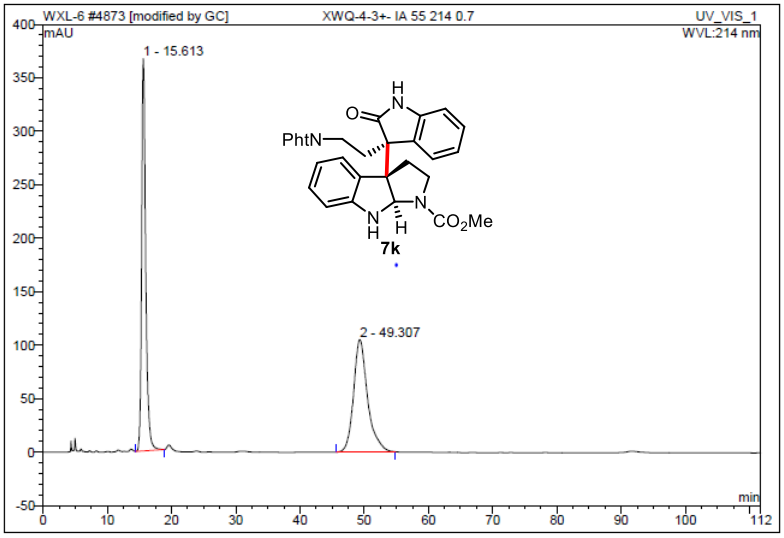
Recording Time:2018.08.18 16:23
色谱柱:
流动相:
流速:



No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	7.503	4857.0	46202.0	0.0859	0.0859
2	8.032	113131.6	1838589.1	3.4178	3.4178
3	9.758	40746.2	870319.8	1.6178	1.6178
4	13.973	1721316.2	51039838.5	94.8785	94.8785
Total		1880051.0	53794949.4	100.0000	100.0000

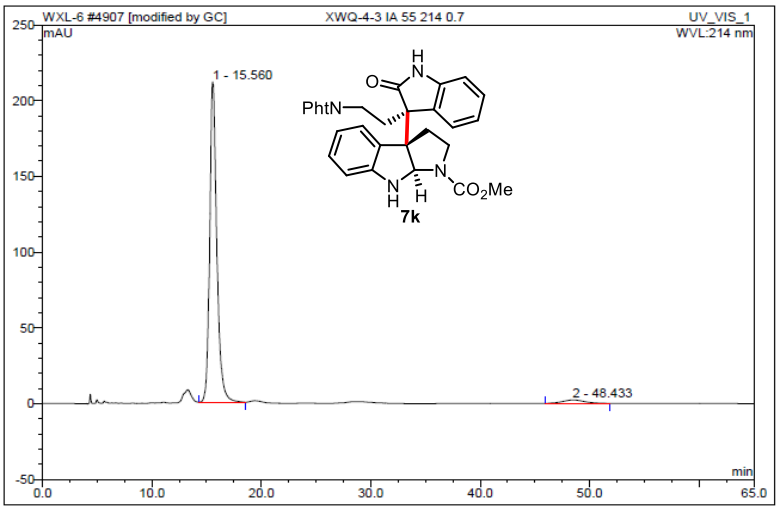
No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

Sample Name:	**XWQ-4-3+- IA 55 214 0.7**	*Injection Volume:*	**4.0**
Vial Number:	**BC4**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-5**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/3 11:44**	*Sample Weight:*	**1.0000**
Run Time (min):	**111.71**	*Sample Amount:*	**1.0000**



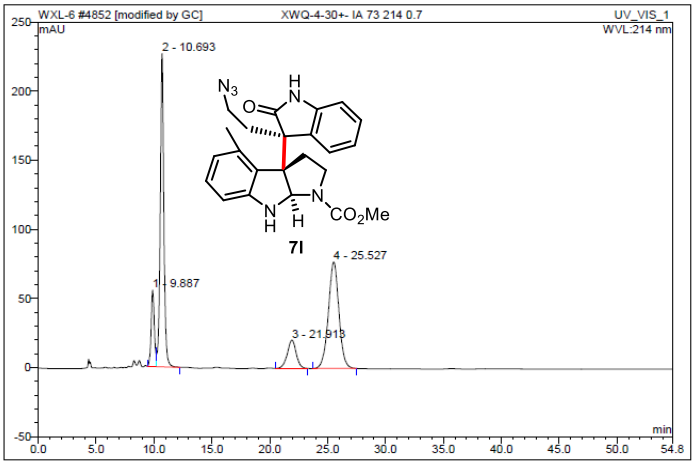
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.61	n.a.	366.989	268.387	50.22	n.a.	BMB*
2	49.31	n.a.	105.164	266.075	49.78	n.a.	BMB
Total:			472.152	534.462	100.00	0.000	

Sample Name:	**XWQ-4-3 IA 55 214 0.7**	*Injection Volume:*	**2.0**
Vial Number:	**BC1**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-5**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/4 21:01**	*Sample Weight:*	**1.0000**
Run Time (min):	**65.01**	*Sample Amount:*	**1.0000**



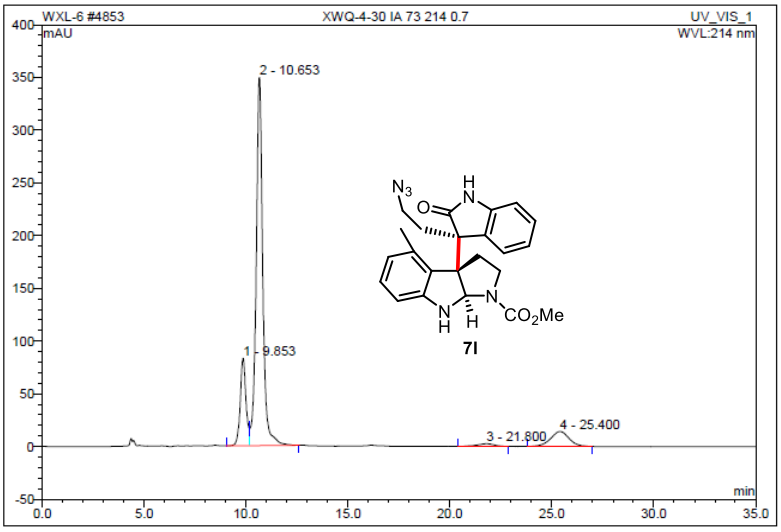
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	15.56	n.a.	211.396	159.146	96.90	n.a.	BMB*
2	48.43	n.a.	2.229	5.087	3.10	n.a.	BMB*
Total:			213.625	164.233	100.00	0.000	

Sample Name:	**XWQ-4-30+- IA 73 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**BC2**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-2**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/2 15:37**	*Sample Weight:*	**1.0000**
Run Time (min):	**54.77**	*Sample Amount:*	**1.0000**



No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.89	n.a.	55.312	17.747	8.89	n.a.	BM
2	10.69	n.a.	226.769	82.148	41.14	n.a.	MB
3	21.91	n.a.	20.584	18.233	9.13	n.a.	BMB
4	25.53	n.a.	77.113	81.547	40.84	n.a.	BMB
Total:			379.779	199.675	100.00	0.000	

Sample Name:	**XWQ-4-30 IA 73 214 0.7**	*Injection Volume:*	**3.0**
Vial Number:	**BD2**	*Channel:*	**UV_VIS_1**
Sample Type:	**unknown**	*Wavelength:*	**214**
Control Program:	**201701-2**	*Bandwidth:*	**n.a.**
Quantif. Method:	**201701**	*Dilution Factor:*	**1.0000**
Recording Time:	**2018/1/2 16:35**	*Sample Weight:*	**1.0000**
Run Time (min):	**35.01**	*Sample Amount:*	**1.0000**

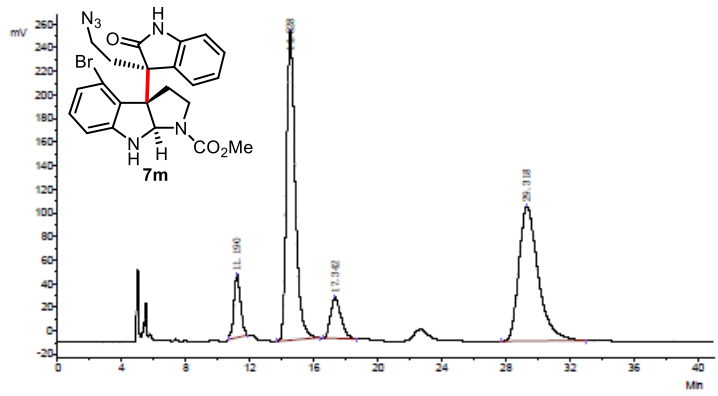


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	9.85	n.a.	83.226	27.257	15.58	n.a.	BM
2	10.65	n.a.	349.344	130.625	74.66	n.a.	MB
3	21.80	n.a.	2.526	2.365	1.35	n.a.	BMB
4	25.40	n.a.	14.095	14.704	8.40	n.a.	BMB
Total:			449.192	174.951	100.00	0.000	

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.11.27 22:05
色谱柱:
流动相:
流速:



7m

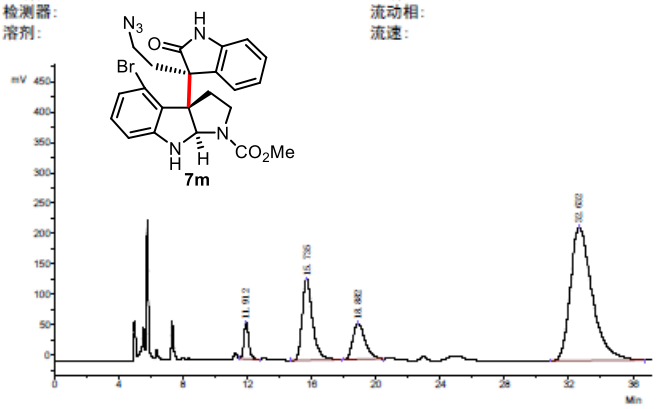
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.190	52242.4	1523246.0	6.7197	6.7197
2	14.528	261748.5	9941968.1	43.8582	43.8582
3	17.342	34334.1	1555490.3	6.8619	6.8619
4	29.318	114293.5	9647730.4	42.5602	42.5602
Total		462618.6	22668434.8	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.12.08 10:06
色谱柱:
流动相:
流速:



7m

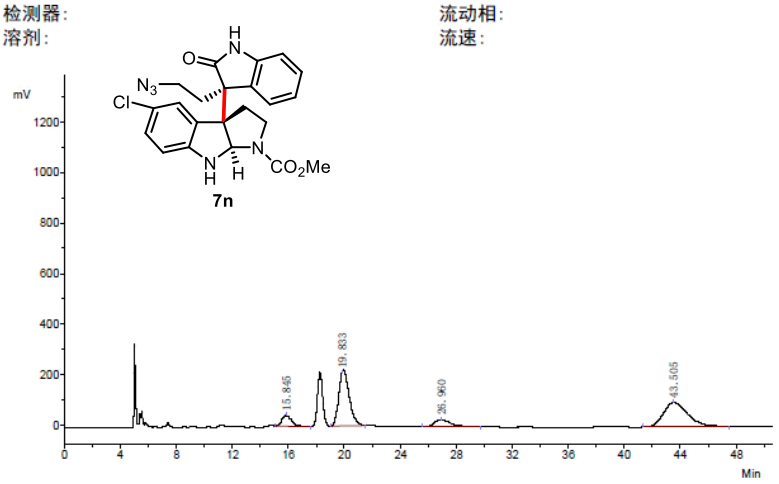
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.912	59401.9	1235012.2	3.9718	3.9718
2	15.735	133864.4	6063576.6	19.5006	19.5006
3	18.882	58906.6	3131238.0	10.0701	10.0701
4	32.632	219634.1	20664493.6	66.4575	66.4575
Total		471807.0	31094320.4	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.12.07 20:38
色谱柱:
流动相:
流速:



7n

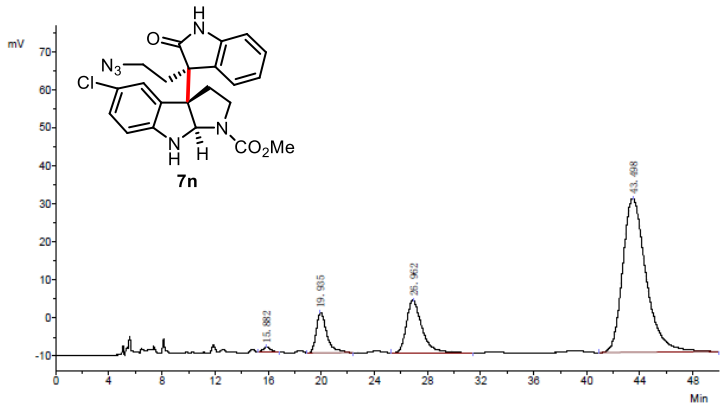
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	15.845	42841.3	2074986.2	7.6115	7.6115
2	19.833	211637.9	11508191.0	42.2146	42.2146
3	26.960	27429.5	2199168.6	8.0670	8.0670
4	43.505	96594.8	11478799.9	42.1068	42.1068
Total		378503.5	27261145.6	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.12.07 21:32
色谱柱:
流动相:
流速:



7n

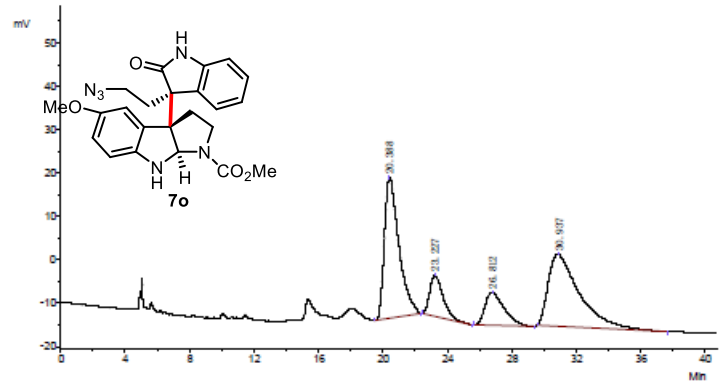
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	15.882	1162.1	51063.6	0.7613	0.7613
2	19.935	10547.1	592630.6	8.8354	8.8354
3	26.962	13627.1	1104986.6	16.4739	16.4739
4	43.498	40407.2	4958802.1	73.9294	73.9294
Total		65743.6	6707483.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.11.28 15:44
色谱柱:
流动相:
流速:



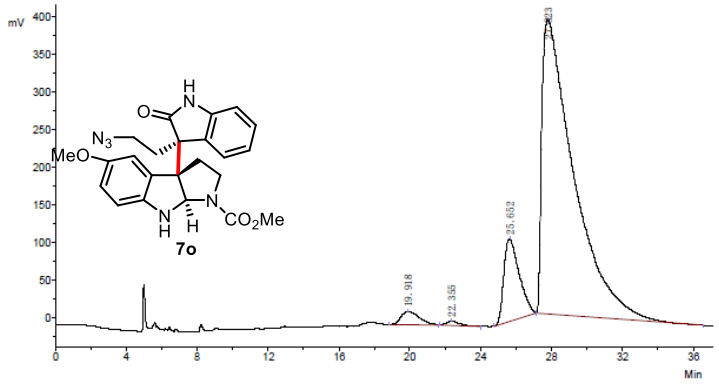
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	20.388	32235.8	2034816.0	37.4645	37.4645
2	23.227	9412.4	548995.4	10.1080	10.1080
3	26.812	7500.6	627564.2	11.5546	11.5546
4	30.937	16488.3	2219940.4	40.8730	40.8730
Total		65637.1	5431316.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2017.11.28 19:27
色谱柱:
流动相:
流速:

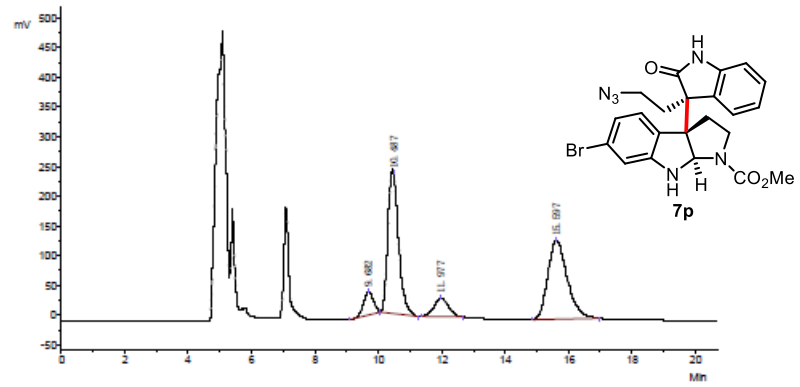


No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	19.918	17280.6	1247571.6	2.1931	2.1931
2	22.355	5049.8	276231.7	0.4856	0.4856
3	25.652	109229.9	6633535.7	11.6609	11.6609
4	27.823	389559.8	48729462.9	85.6604	85.6604
Total		521120.1	56886801.8	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3

HPLC Report

样品批号:　　Recording Time:2017.11.23　21:24

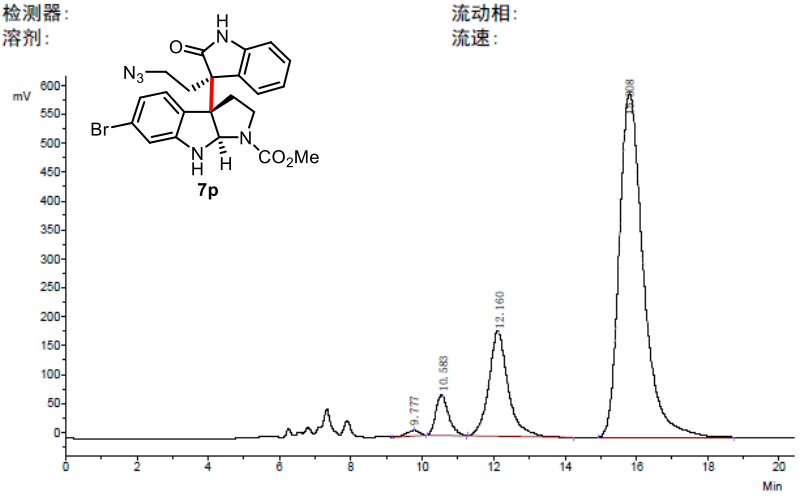


No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	9.682	39493.4	840456.5	6.4098	6.4098
2	10.487	235873.3	5627978.9	42.9222	42.9222
3	11.977	30705.8	993994.4	7.5808	7.5808
4	15.597	132037.2	5649608.1	43.0872	43.0872
Total		438109.8	13112037.9	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:　　Recording Time:2017.11.24　15:29
色谱仪:　　色谱柱:
检测器:　　流动相:
溶剂:　　流速:



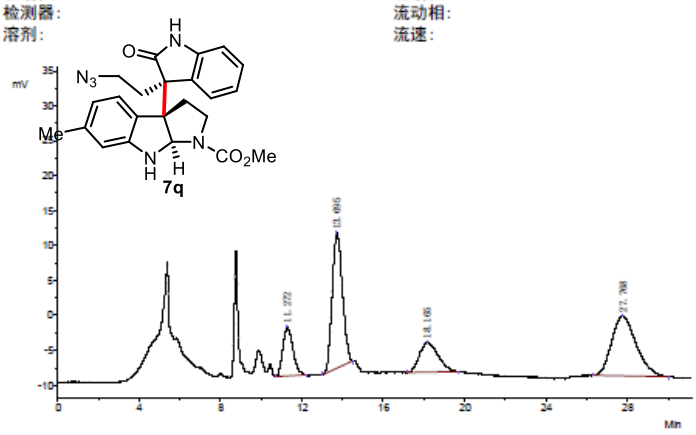
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	9.777	8979.4	229689.1	0.6269	0.6269
2	10.583	66807.0	1725476.2	4.7091	4.7091
3	12.160	177776.2	6788897.3	18.5281	18.5281
4	15.808	594301.2	27897050.3	76.1359	76.1359
Total		847863.7	36641112.9	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.01.12 22:27
色谱柱:
流动相:
流速:



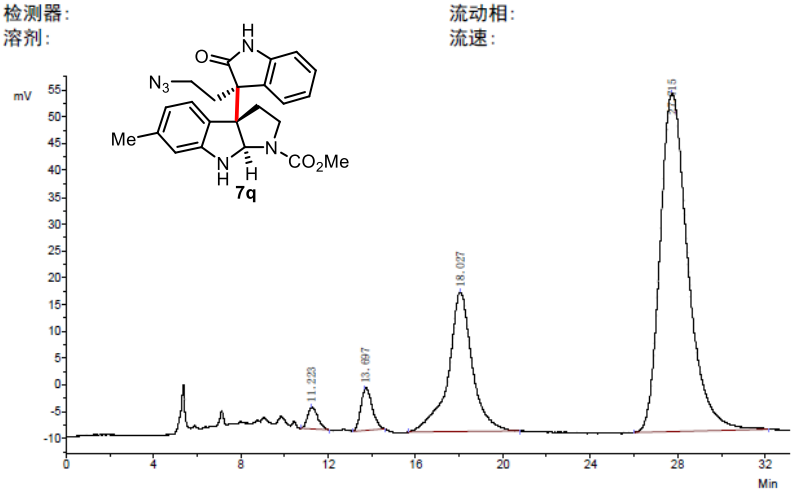
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.272	7019.4	242730.8	12.6873	12.6873
2	13.695	19225.6	678099.2	35.4436	35.4436
3	18.165	4229.4	271115.7	14.1710	14.1710
4	27.768	8562.4	721230.6	37.6981	37.6981
Total		39036.8	1913176.2	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.01.12 23:00
色谱柱:
流动相:
流速:



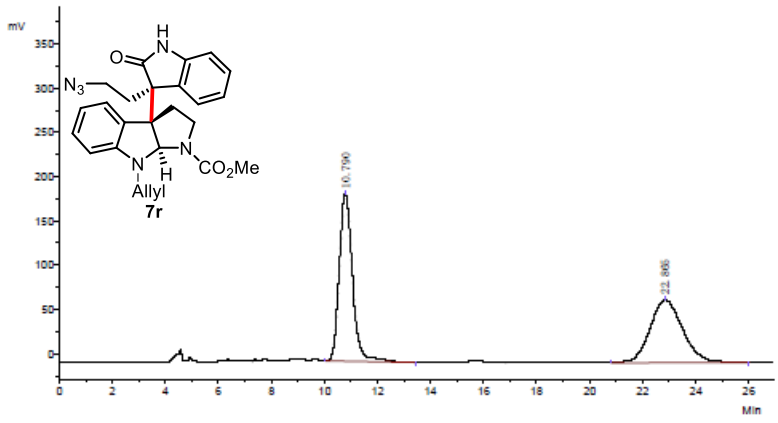
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.223	4059.7	135012.0	1.6929	1.6929
2	13.697	7784.4	284865.2	3.5719	3.5719
3	18.027	26066.6	1986674.3	24.9110	24.9110
4	27.715	62984.8	5568537.7	69.8241	69.8241
Total		100895.5	7975089.2	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.12.28 17:34
色谱柱:
流动相:
流速:



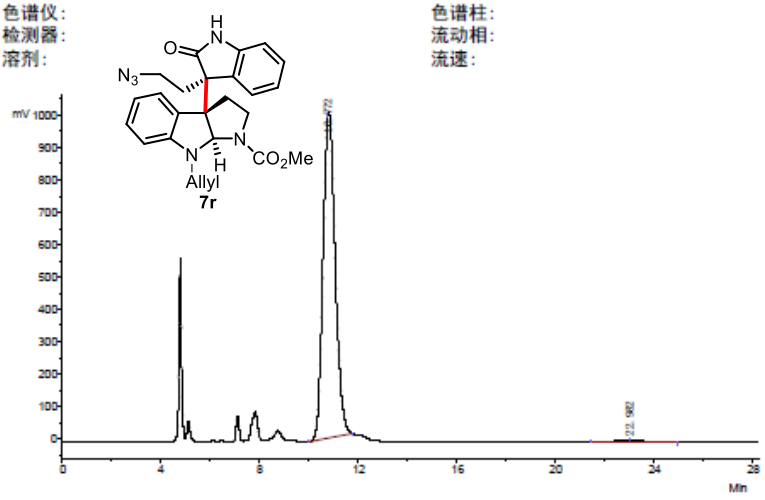
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	10.790	189231.3	6531015.0	51.8095	51.8095
2	22.865	70772.7	6074812.0	48.1905	48.1905
Total		260004.0	12605826.9	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2018.12.28 16:17
色谱柱:
流动相:
流速:



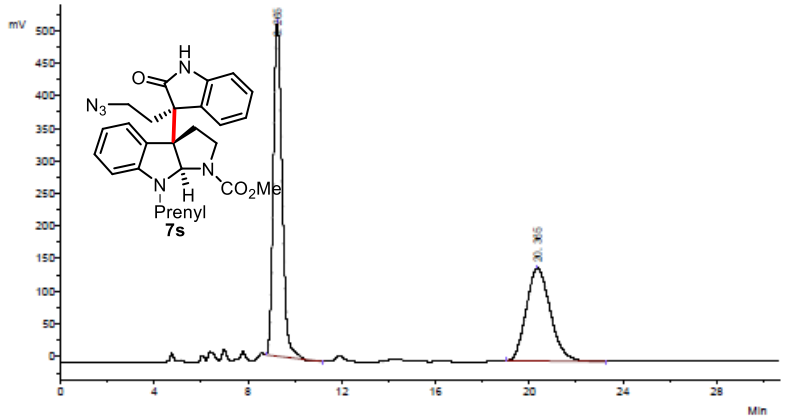
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	10.772	991879.0	34309725.6	98.5757	98.5757
2	22.982	5869.8	495728.6	1.4243	1.4243
Total		997748.8	34805454.1	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.14 22:22
色谱柱:
流动相:
流速:



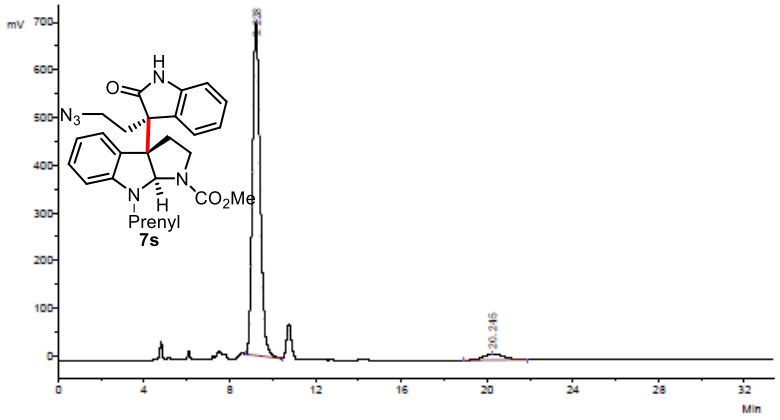
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	9.265	511588.7	13008877.5	56.1114	56.1114
2	20.365	142376.6	10175154.0	43.8886	43.8886
Total		653965.3	23184031.5	100.0000	100.0000

No.	IDName	Mi(ug)	M0(ug)	Cm(ug/m3)	Cc(mg/m3

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.14 21:47
色谱柱:
流动相:
流速:



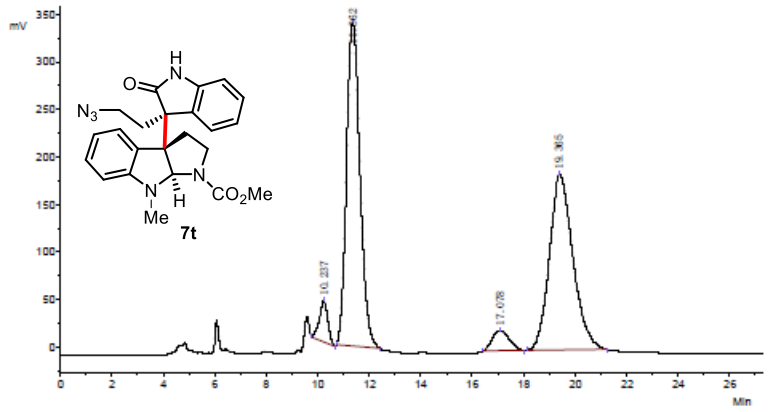
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	9.228	698653.6	17080343.6	94.9333	94.9333
2	20.245	13241.9	911595.1	5.0667	5.0667
Total		711895.6	17991938.7	100.0000	100.0000

No.	IDName	Mi(ug)	M0(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.07 09:51
色谱柱:
流动相:
流速:



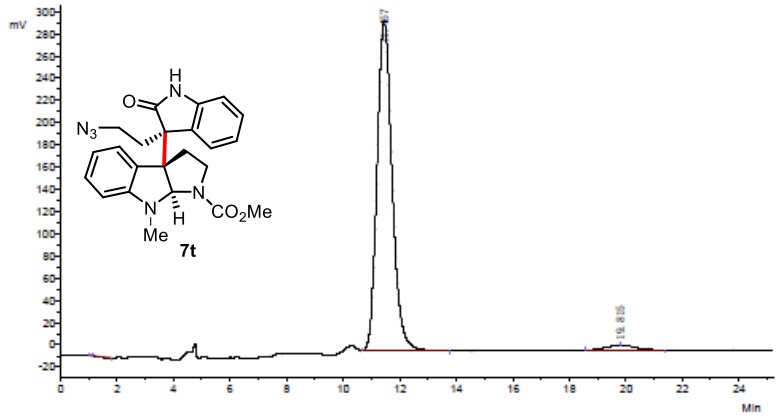
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	10.237	43437.3	999570.1	3.8424	3.8424
2	11.362	340349.0	12358724.5	47.5079	47.5079
3	17.078	21357.8	962001.5	3.6980	3.6980
4	19.365	184581.4	11693730.5	44.9516	44.9516
Total		589725.4	26014026.5	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.02 20:31
色谱柱:
流动相:
流速:



No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	11.457	295531.9	11025365.1	97.4331	97.4331
2	19.815	4193.6	290461.6	2.5669	2.5669
Total		299725.4	11315826.6	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.07 10:20
色谱柱:
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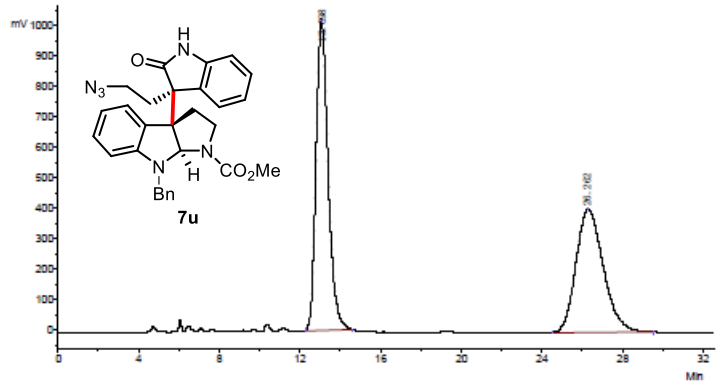


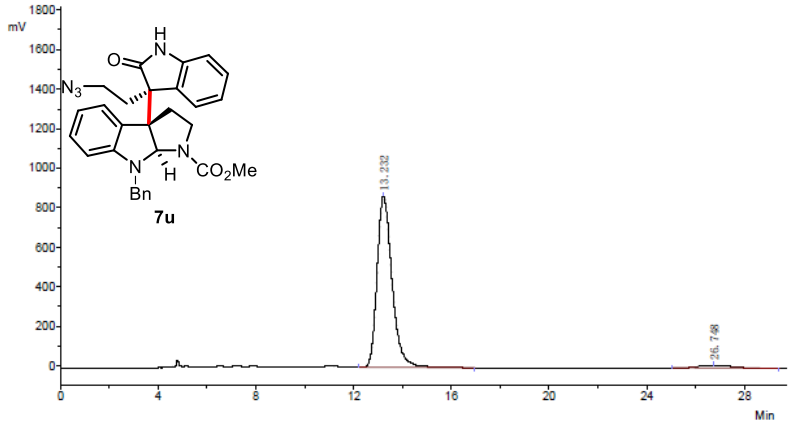
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	13.098	1007823.0	42296317.9	52.6273	52.6273
2	26.262	401102.1	38073255.6	47.3727	47.3727
Total		1408925.1	80369573.5	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.02 21:01
色谱柱:
流动相:
流速:



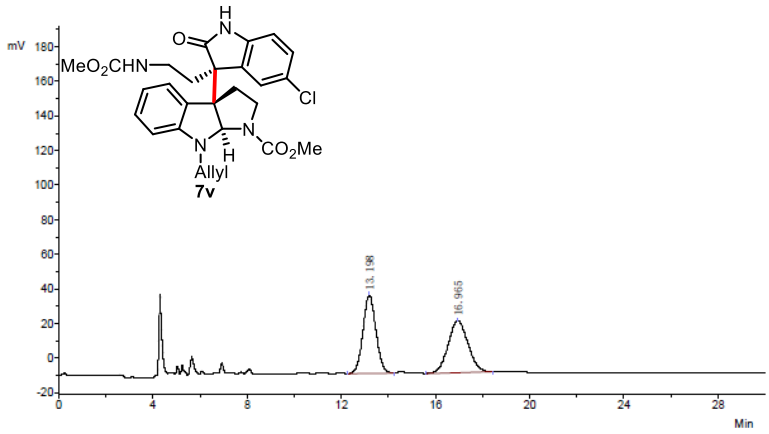
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	13.232	867118.6	36891540.0	96.3839	96.3839
2	26.748	15092.9	1384087.6	3.6161	3.6161
Total		882211.4	38275627.6	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.31 19:17
色谱柱:
流动相:
流速:



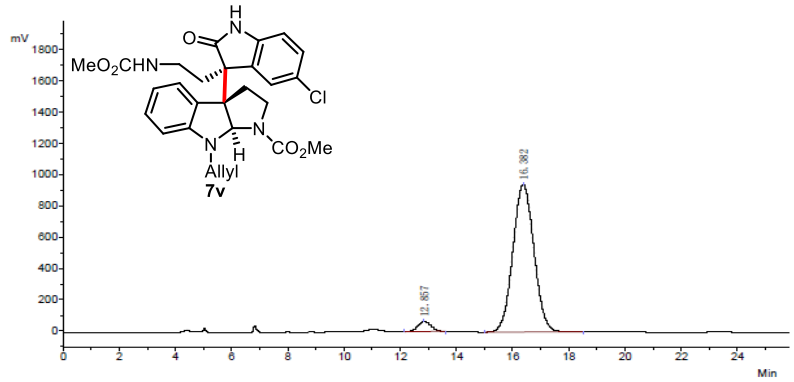
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	13.198	45211.1	1733442.2	49.7929	49.7929
2	16.965	29923.2	1747862.9	50.2071	50.2071
Total		75134.3	3481305.1	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.02.18 10:37
色谱柱:
流动相:
流速:



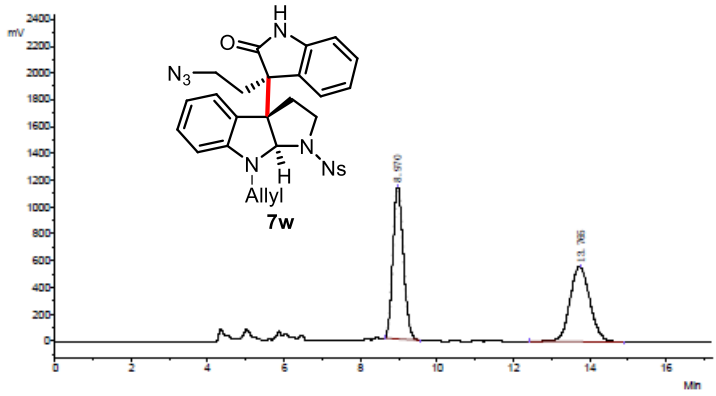
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	12.857	66913.2	2195302.1	4.2759	4.2759
2	16.382	943974.9	49145462.9	95.7241	95.7241
Total		1010888.1	51340765.0	100.0000	100.0000

No.	IDName	Mi(ug)	MO(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.17 16:31
色谱柱:
流动相:
流速:



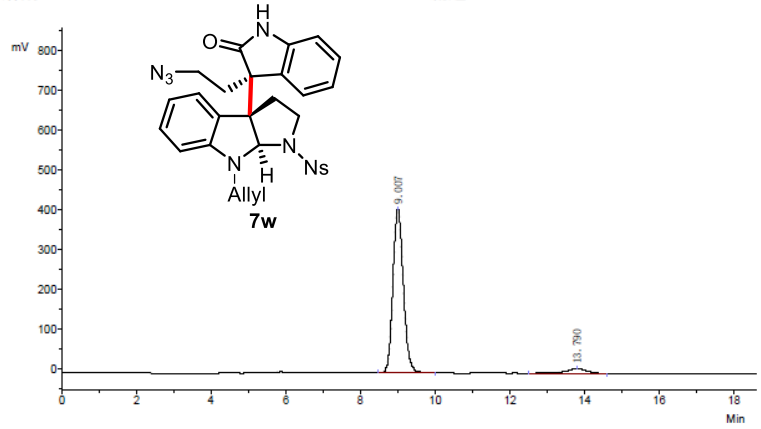
No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	8.970	1131214.1	21653250.9	51.3069	51.3069
2	13.765	558071.4	20550154.7	48.6931	48.6931
Total		1689285.5	42203405.6	100.0000	100.0000

No.	IDName	Mi(ug)	M0(ug)	Cm(ug/m3)	Cc(mg/m3)

HPLC Report

样品批号:
色谱仪:
检测器:
溶剂:

Recording Time:2019.01.17 16:10
色谱柱:
流动相:
流速:

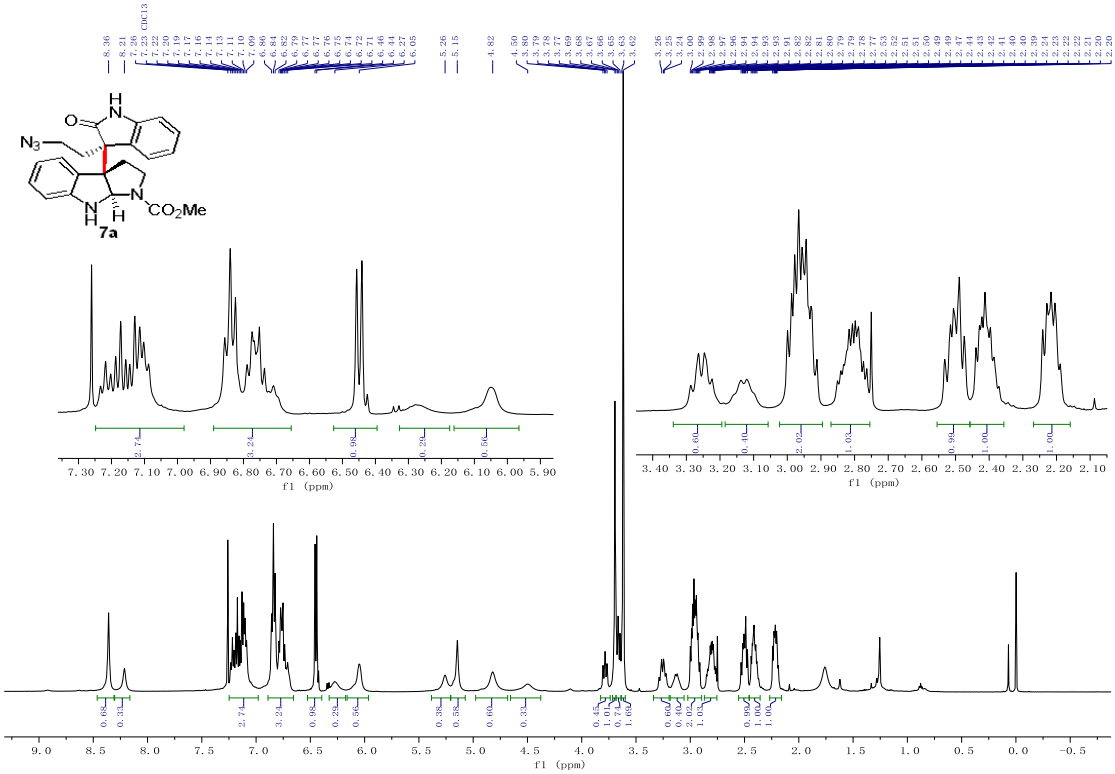


No.	R.Time	PeakHeight	PeakArea	PerCent	Conc
1	9.007	411968.3	7960899.8	95.1521	95.1521
2	13.790	10856.5	405595.8	4.8479	4.8479
Total		422824.8	8366495.6	100.0000	100.0000

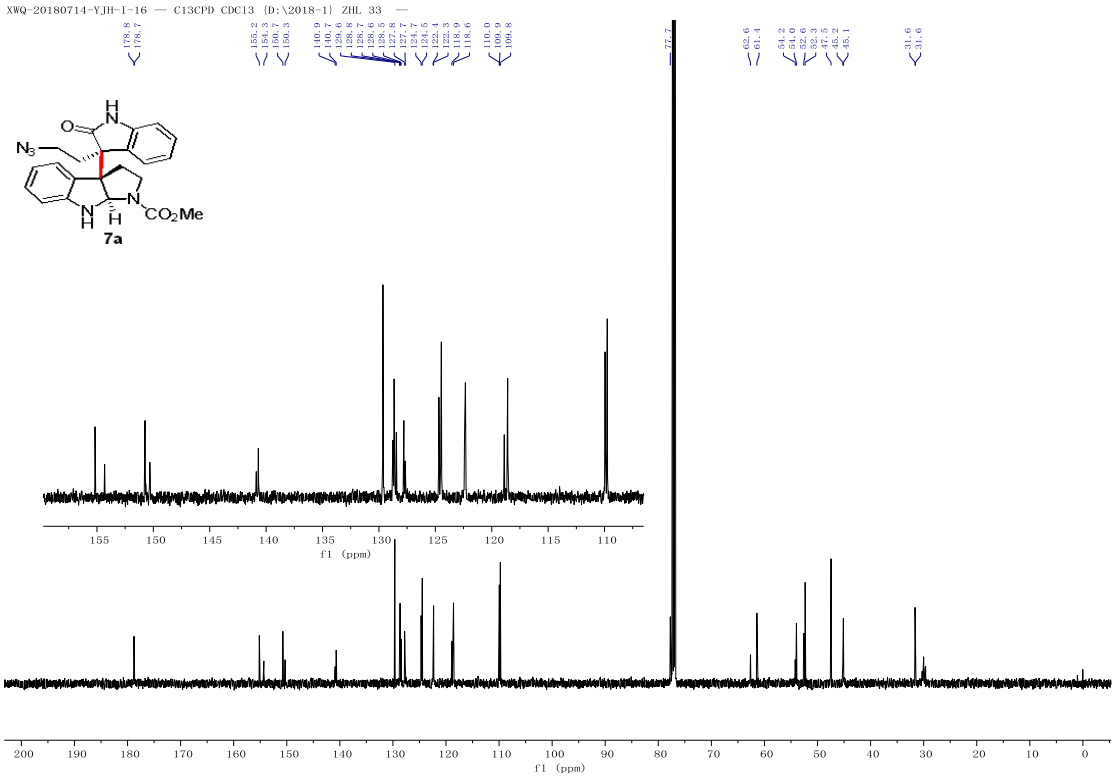
No.	IDName	Mi(ug)	M0(ug)	Cm(ug/m3)	Cc(mg/m3)

6. NMR Spectra

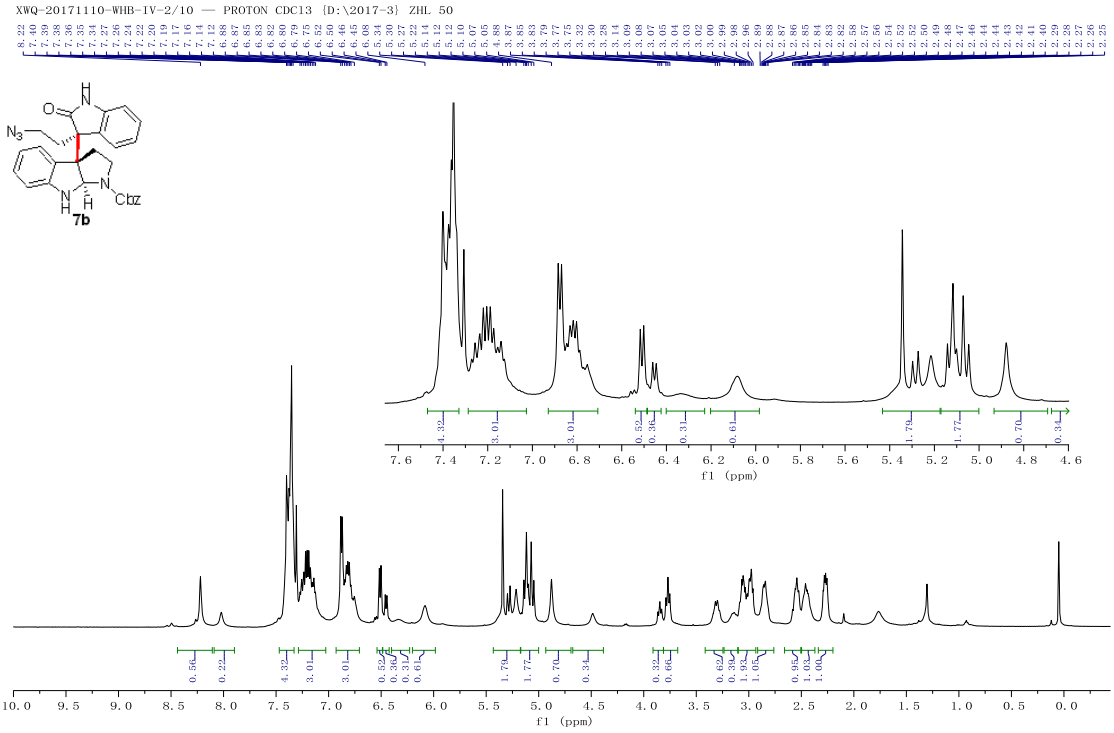
^{1}H NMR Spectrum of **7a** (500 MHz, $CDCl_3$, rotamers)



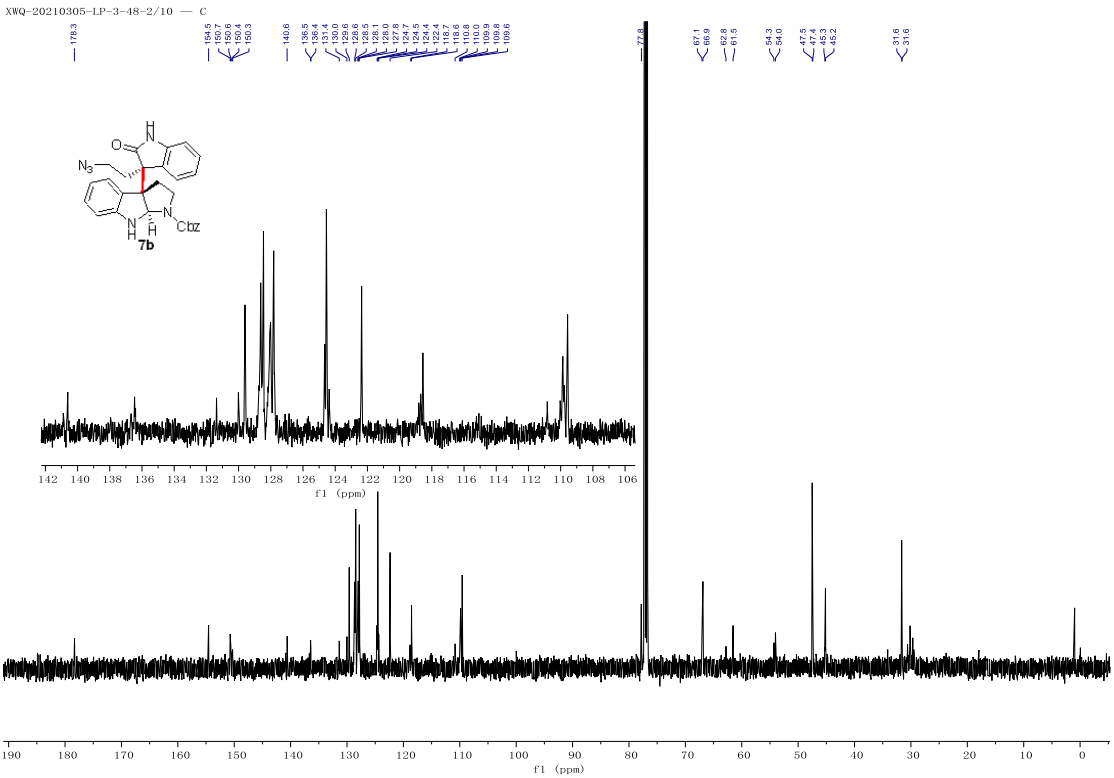
^{13}C NMR Spectrum of **7a** (126 MHz, $CDCl_3$, rotamers)



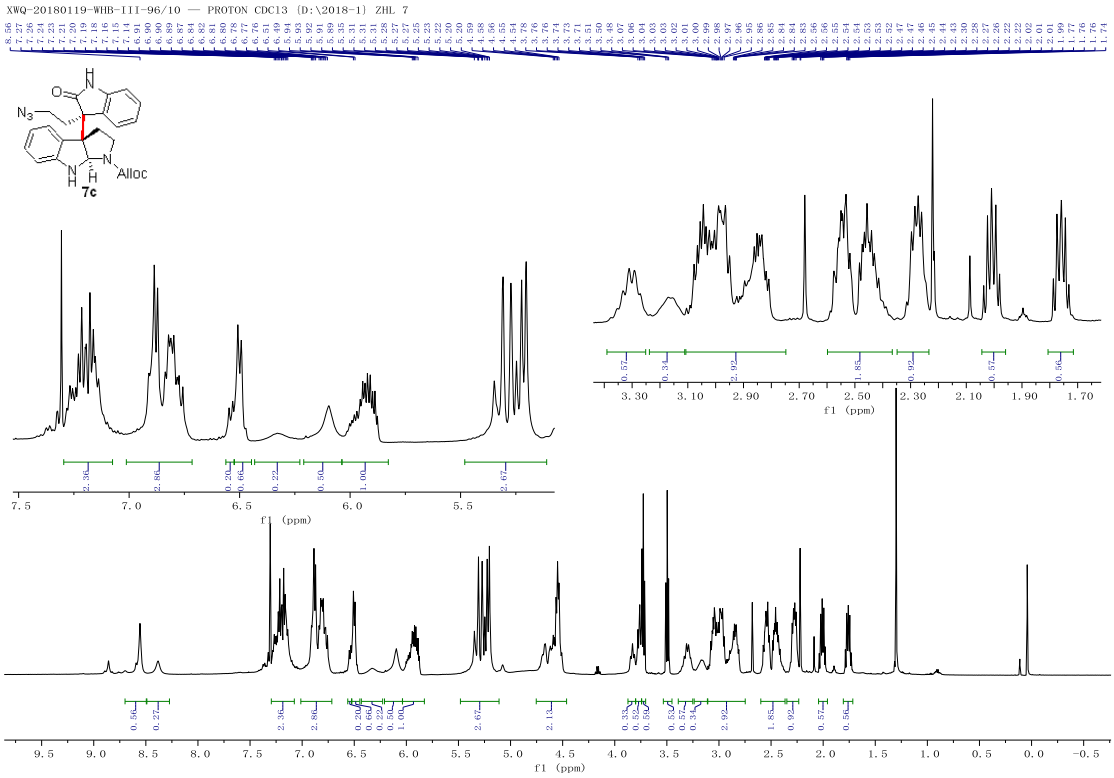
^{1}H NMR Spectrum of **7b** (500 MHz, $CDCl_3$, rotamers)



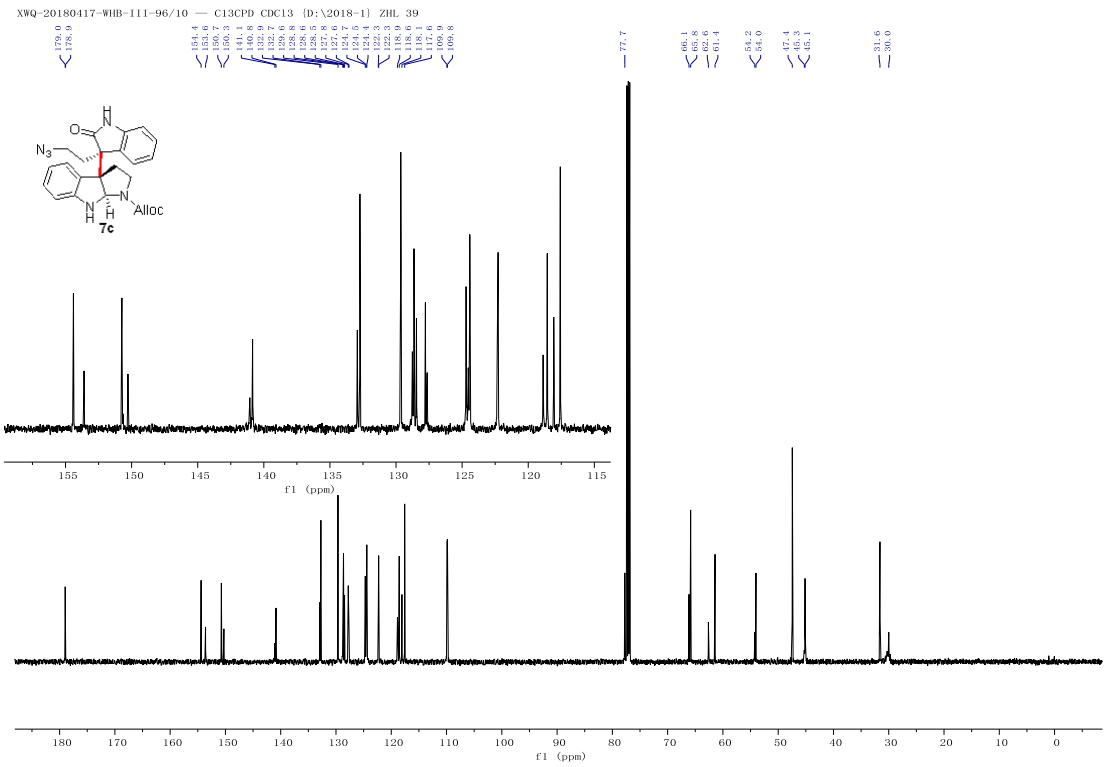
^{13}C NMR Spectrum of **7b** (126 MHz, $CDCl_3$, rotamers)



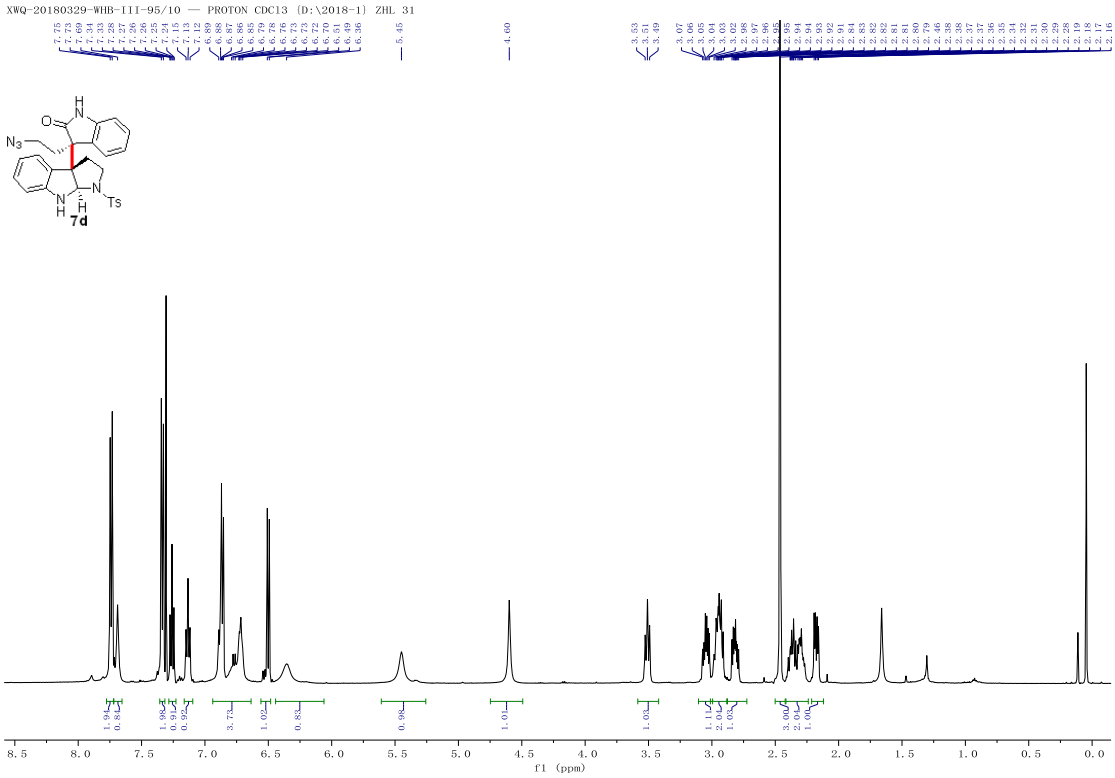
^{1}H NMR Spectrum of **7c** (500 MHz, $CDCl_3$, rotamers)



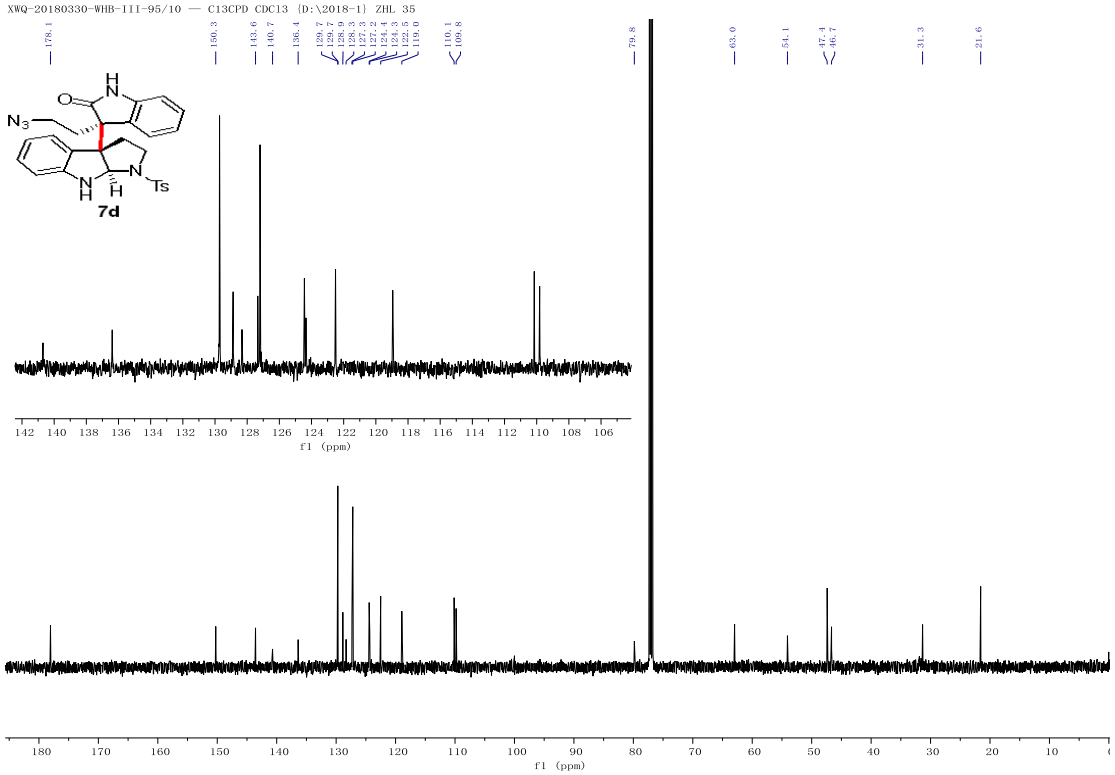
^{13}C NMR Spectrum of **7c** (126 MHz, $CDCl_3$, rotamers)



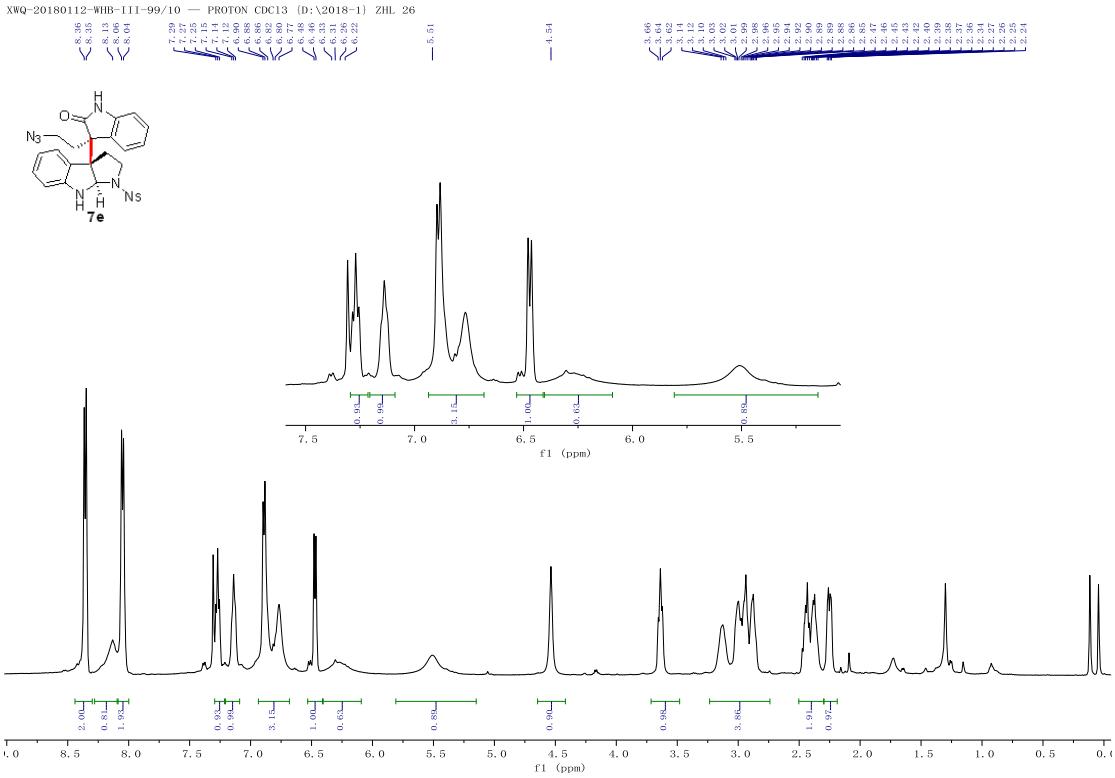
^{1}H NMR Spectrum of **7d** (500 MHz, $CDCl_3$, rotamers)



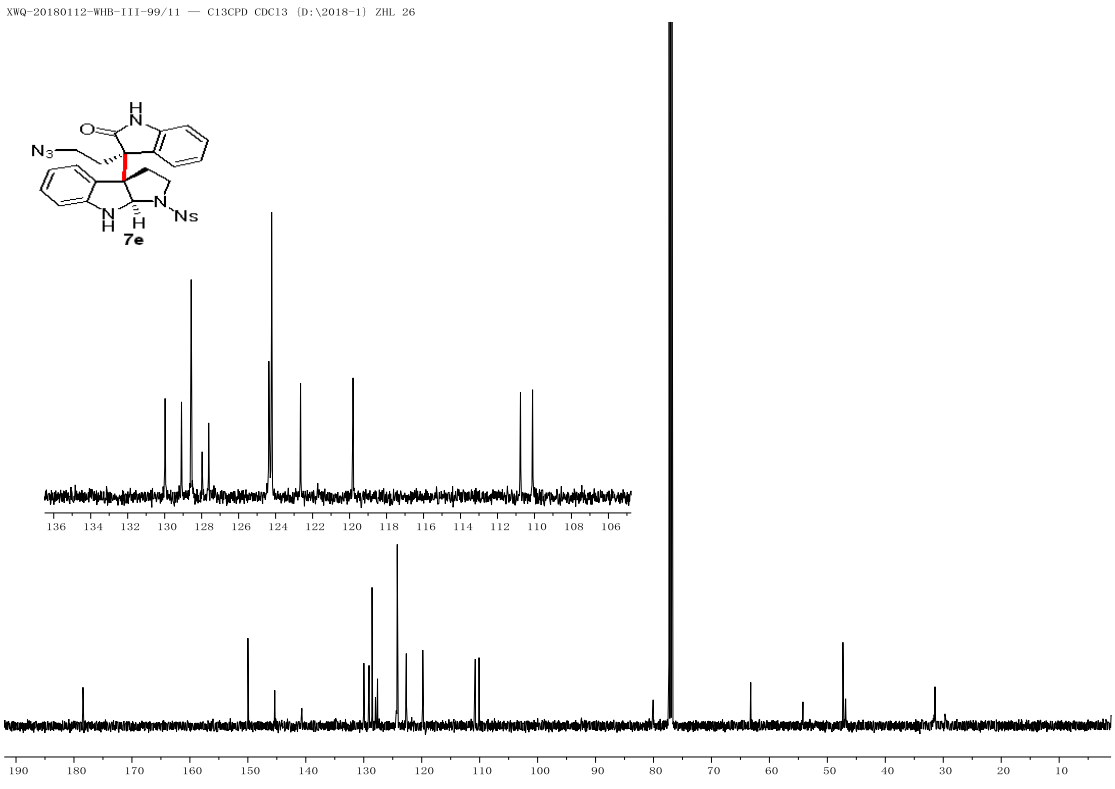
^{13}C NMR Spectrum of **7d** (126 MHz, $CDCl_3$, rotamers)



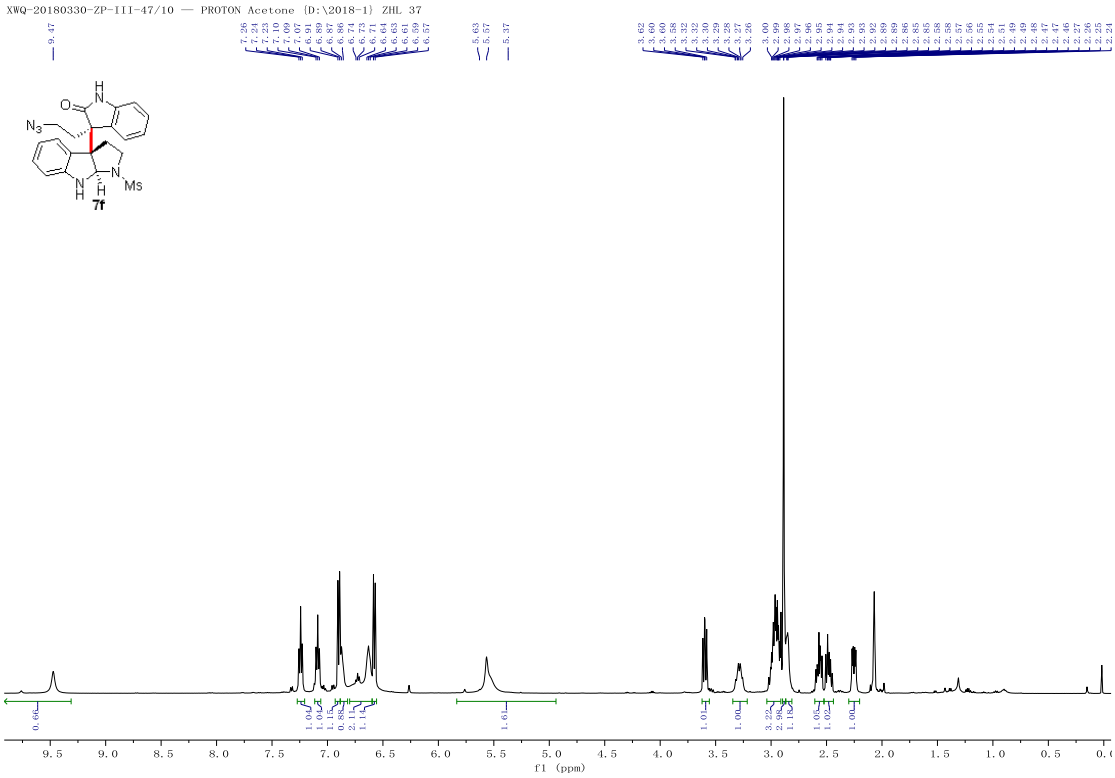
^{1}H NMR Spectrum of **7e** (500 MHz, $CDCl_3$, rotamers)



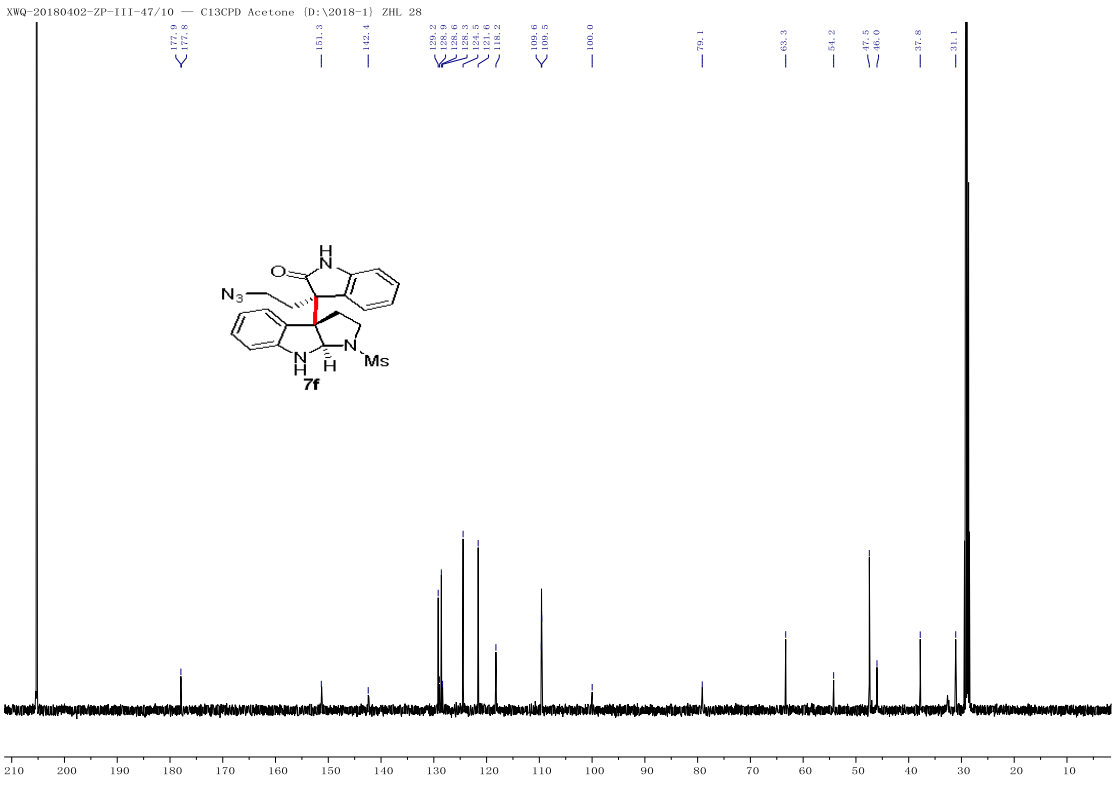
^{13}C NMR Spectrum of **7e** (126 MHz, $CDCl_3$, rotamers)



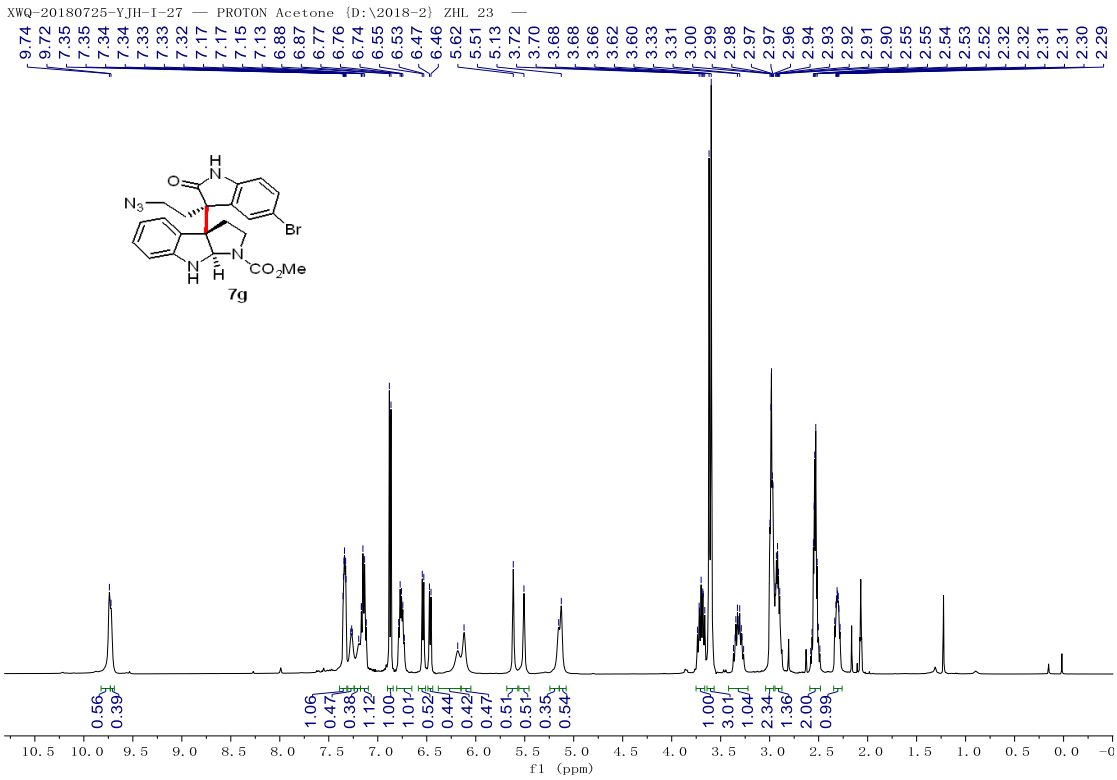
^{1}H NMR Spectrum of **7f** (500 MHz, Acetone-d_6, rotamers)



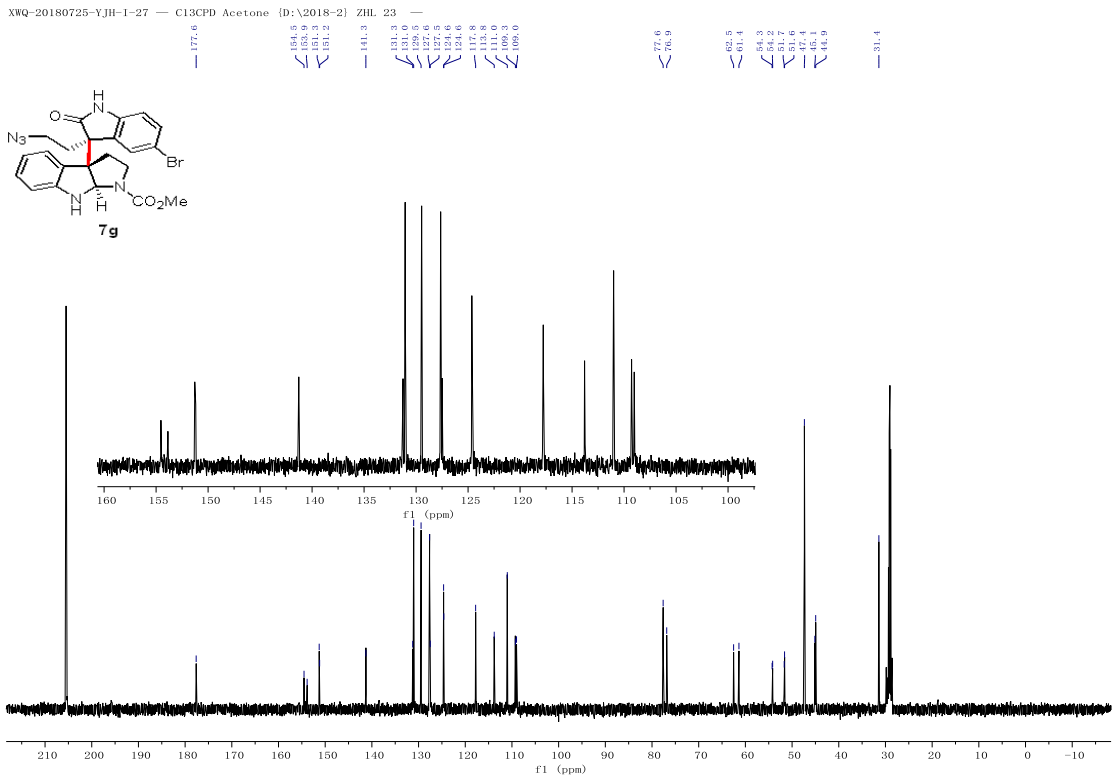
^{13}C NMR Spectrum of **7f** (126 MHz, Acetone-d_6, rotamers)



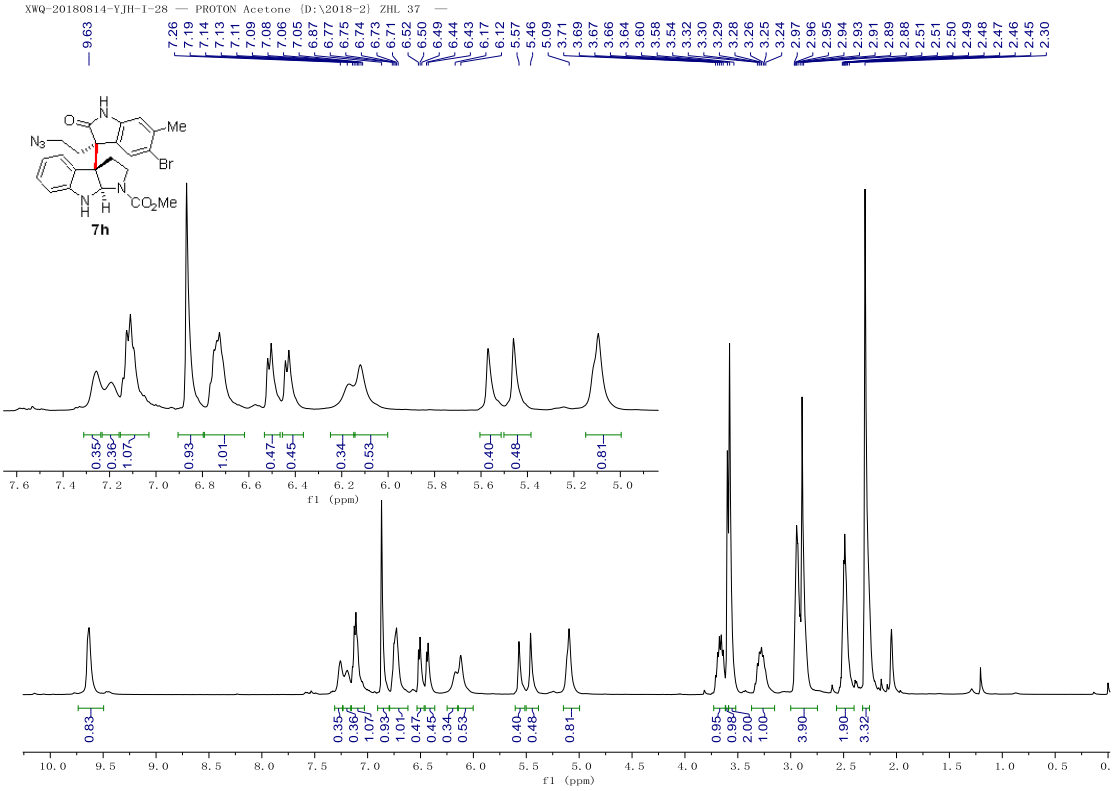
^{1}H NMR Spectrum of **7g** (500 MHz, Acetone-d_6, rotamers)



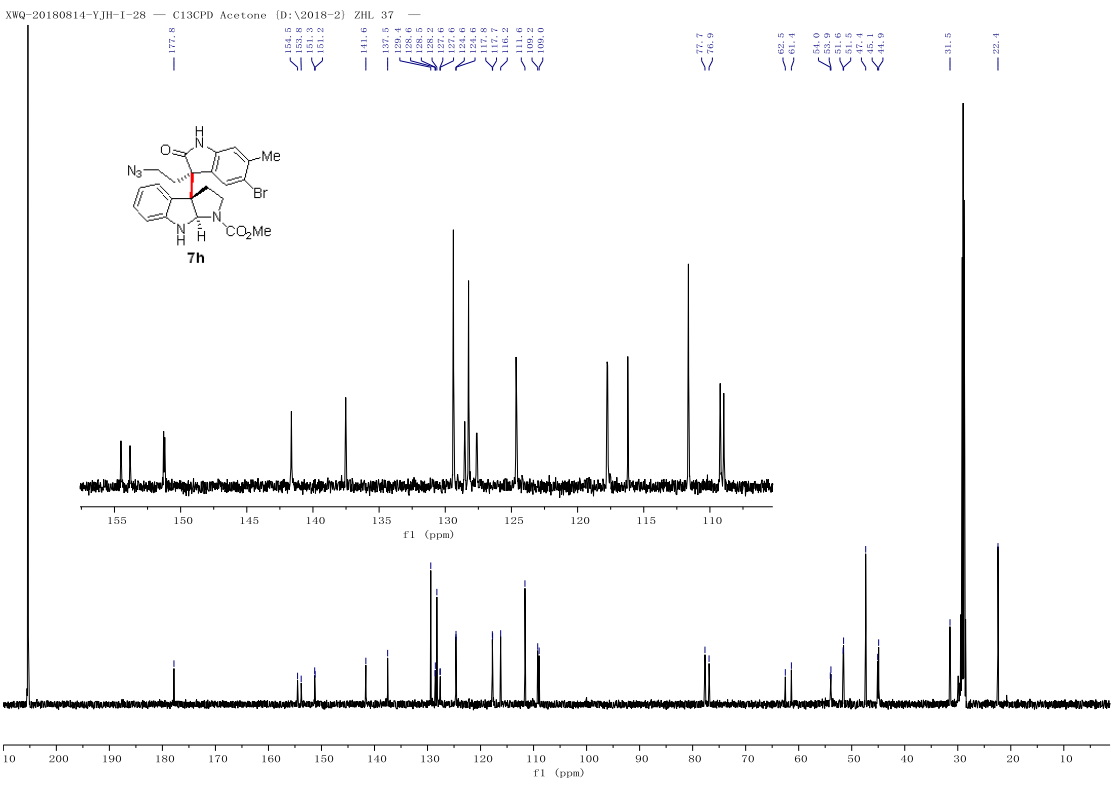
^{13}C NMR Spectrum of **7g** (126 MHz, Acetone-d_6, rotamers)



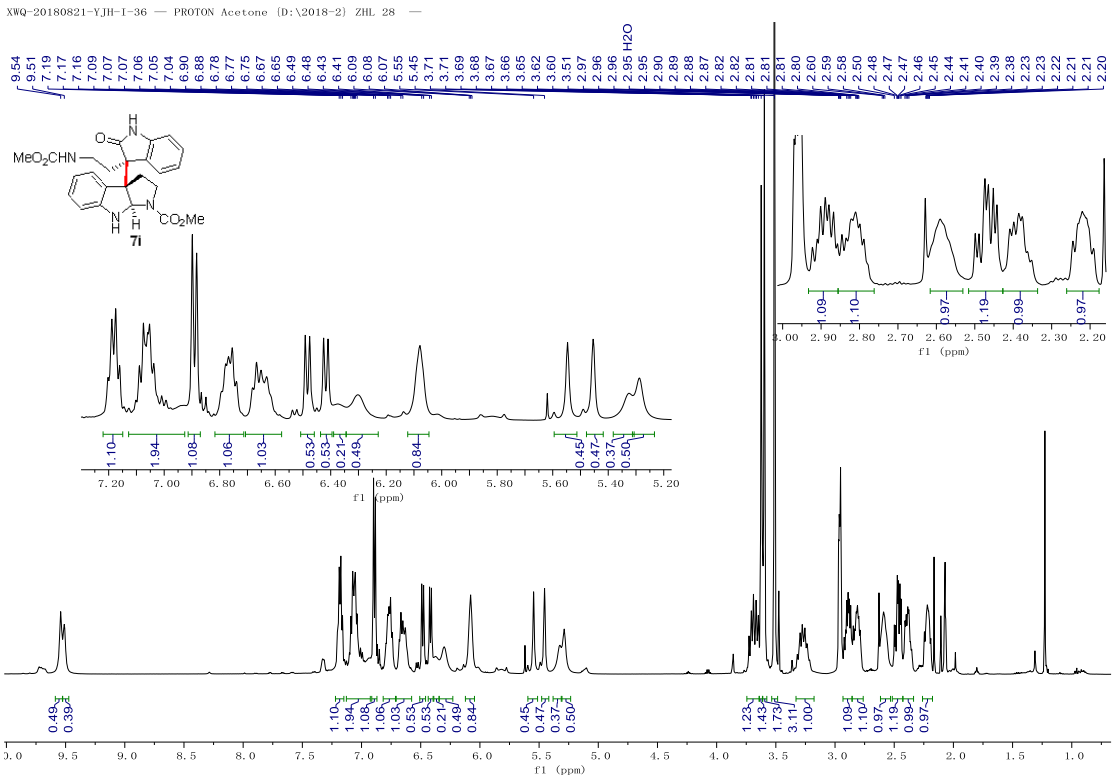
^{1}H NMR Spectrum of **7h** (500 MHz, Acetone-d_6, rotamers)



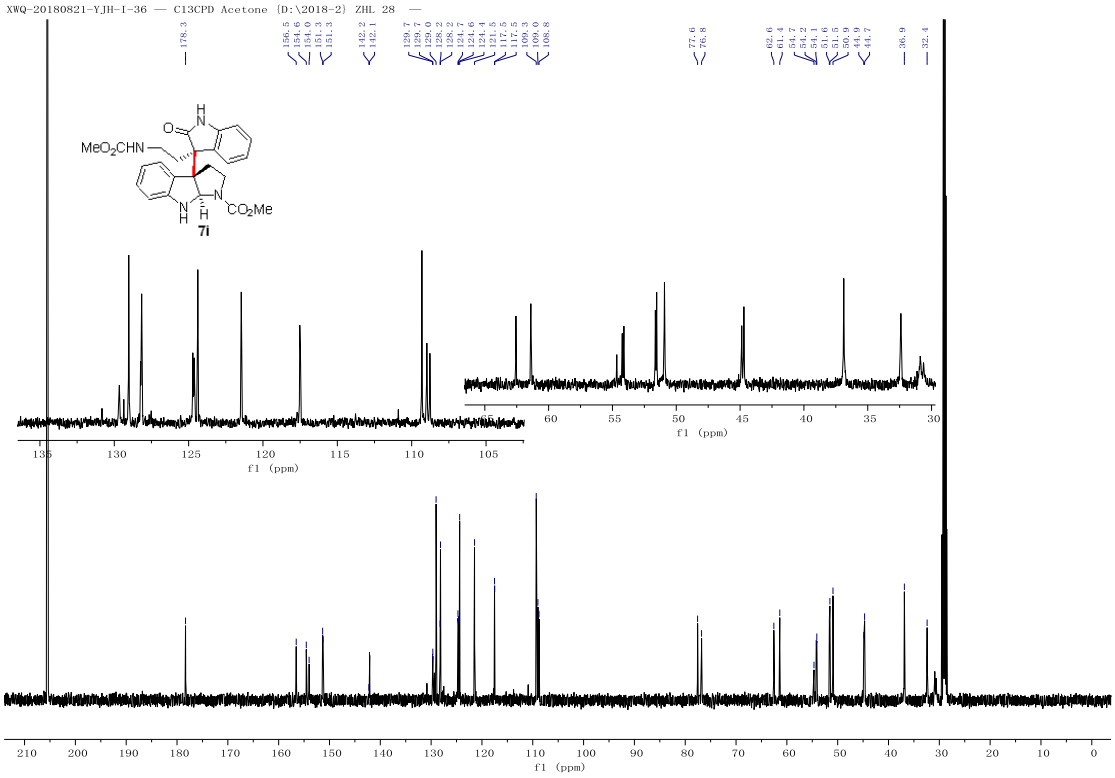
^{13}C NMR Spectrum of **7h** (126 MHz, Acetone-d_6, rotamers)



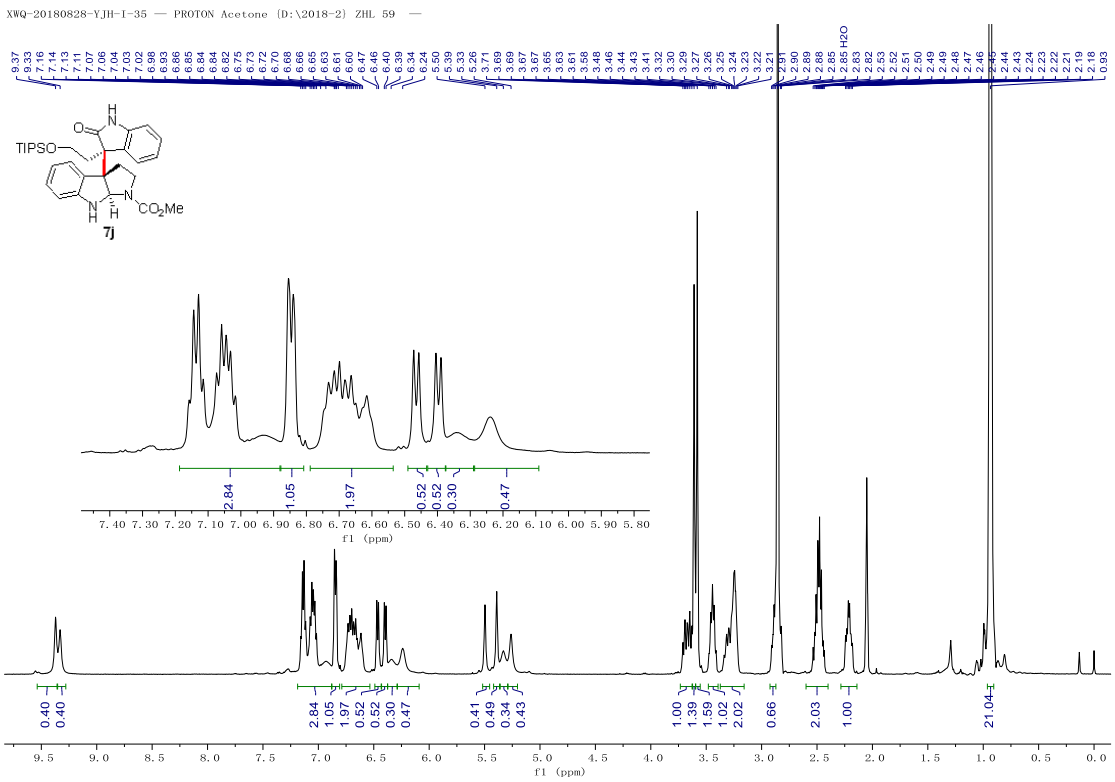
^{1}H NMR Spectrum of **7i** (500 MHz, Acetone-d_6, rotamers)



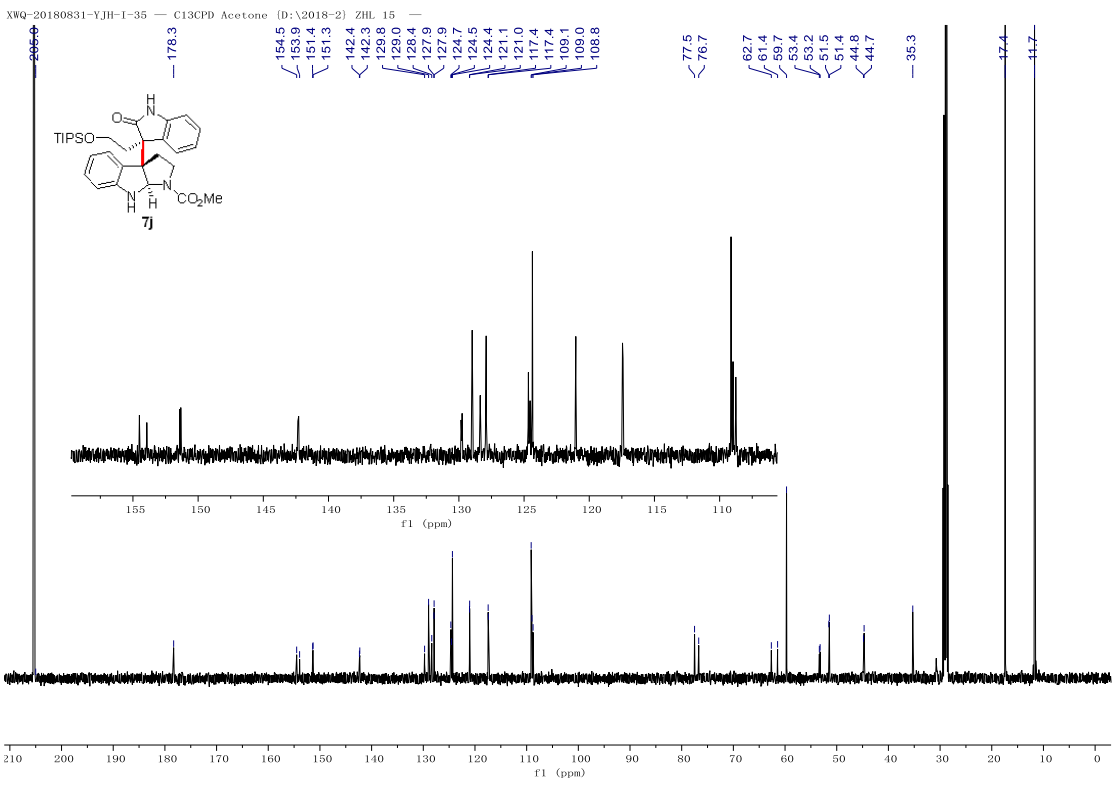
^{13}C NMR Spectrum of **7i** (126 MHz, Acetone-d_6, rotamers)



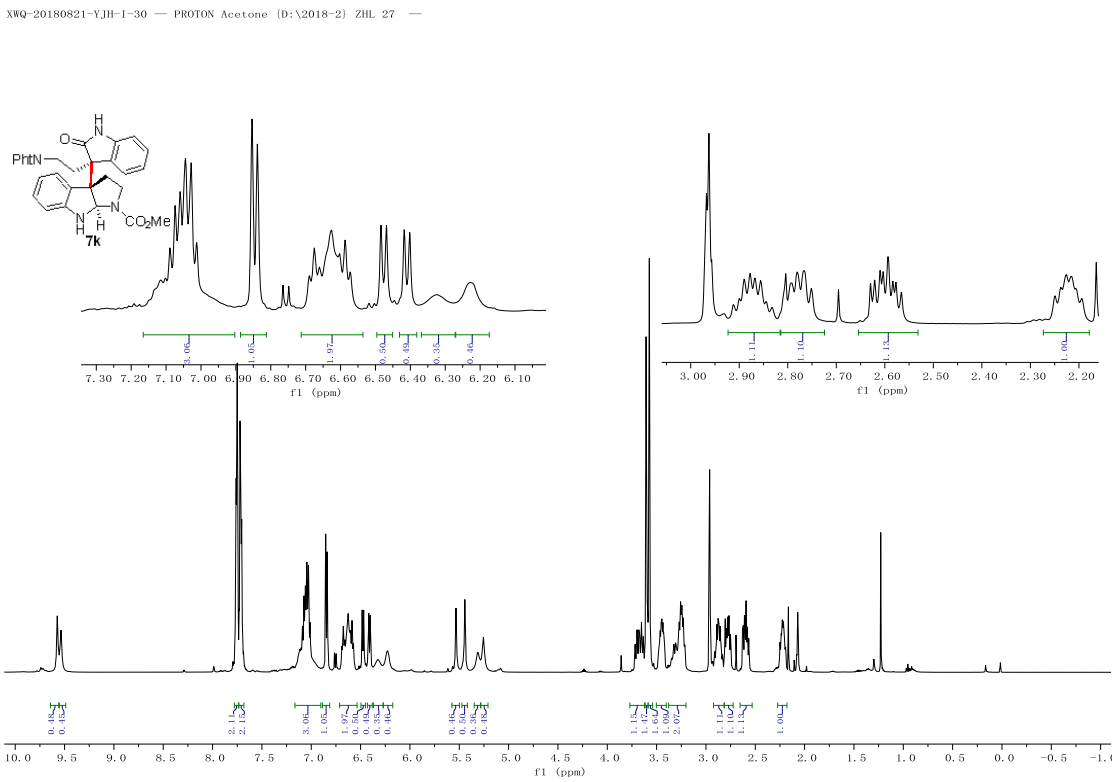
^{1}H NMR Spectrum of **7j** (500 MHz, Acetone-d_6, rotamers)



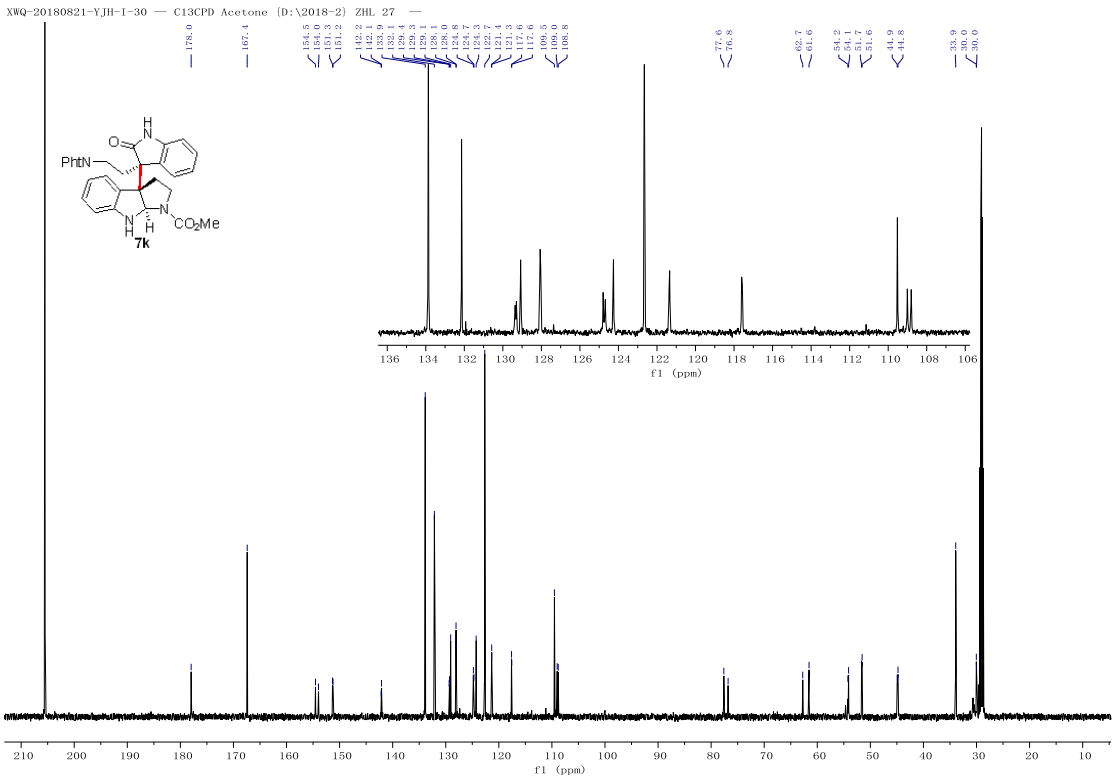
^{13}C NMR Spectrum of **7j** (126 MHz, Acetone-d_6, rotamers)



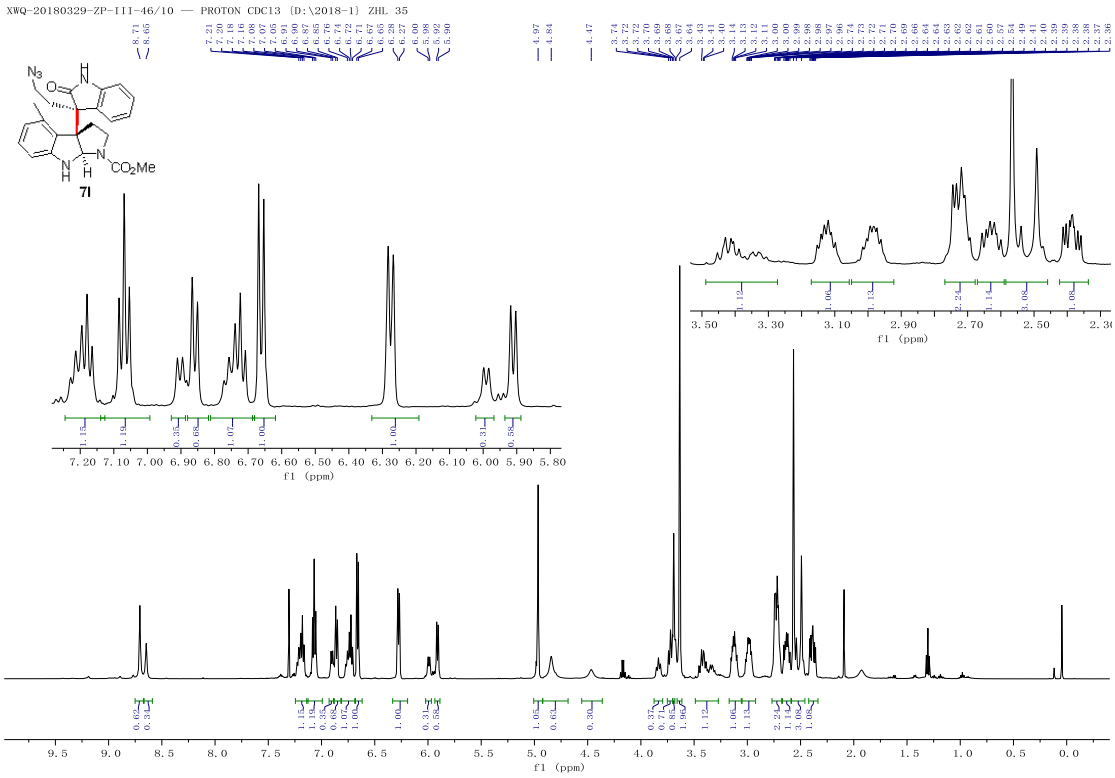
^{1}H NMR Spectrum of **7k** (500 MHz, Acetone-d_6, rotamers)



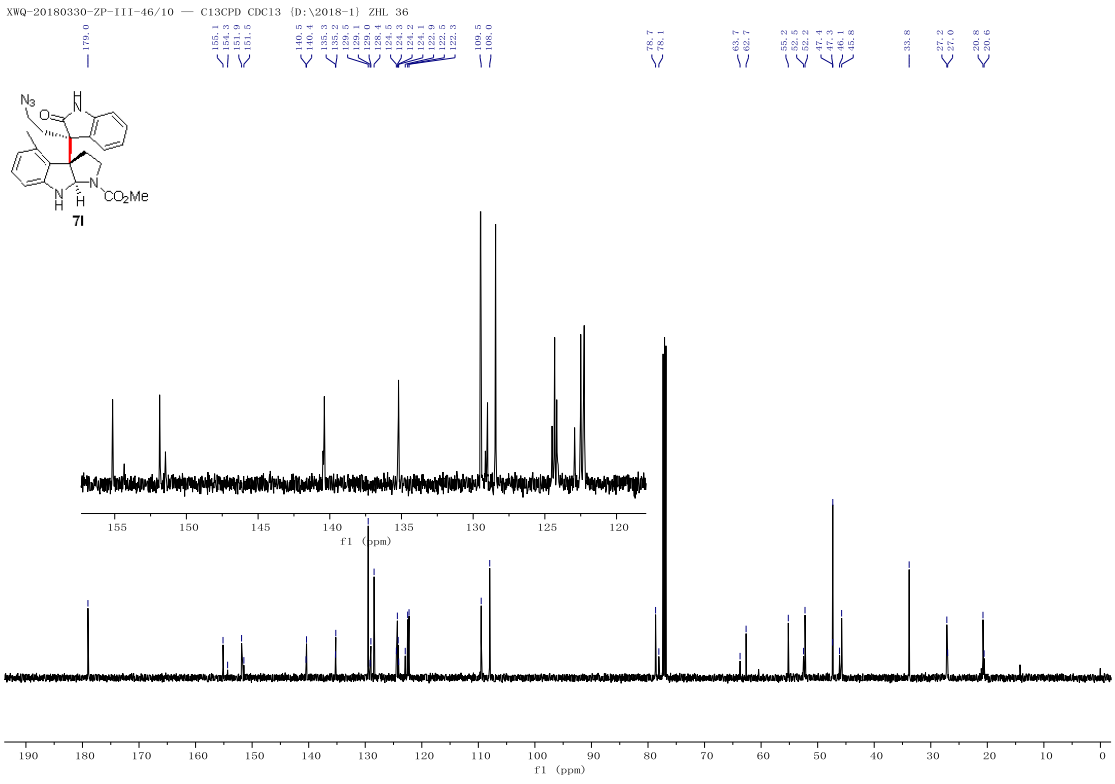
^{13}C NMR Spectrum of **7k** (126 MHz, Acetone-d_6, rotamers)



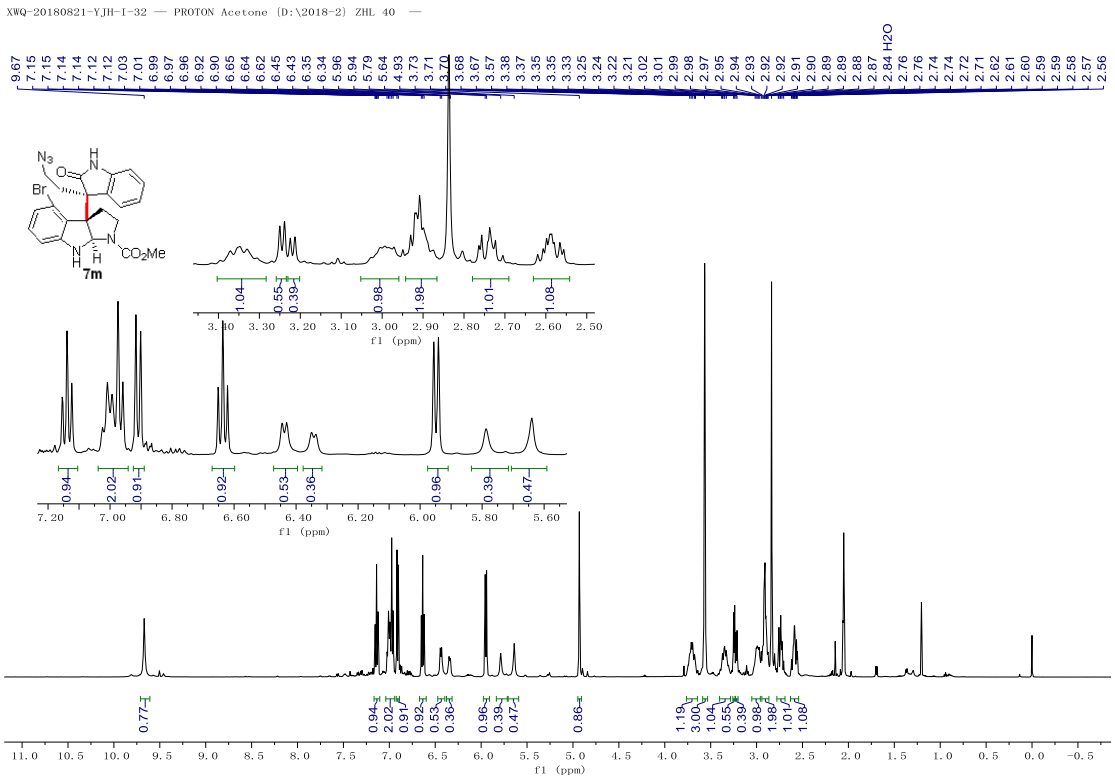
^{1}H NMR Spectrum of **7l** (500 MHz, $CDCl_3$, rotamers)



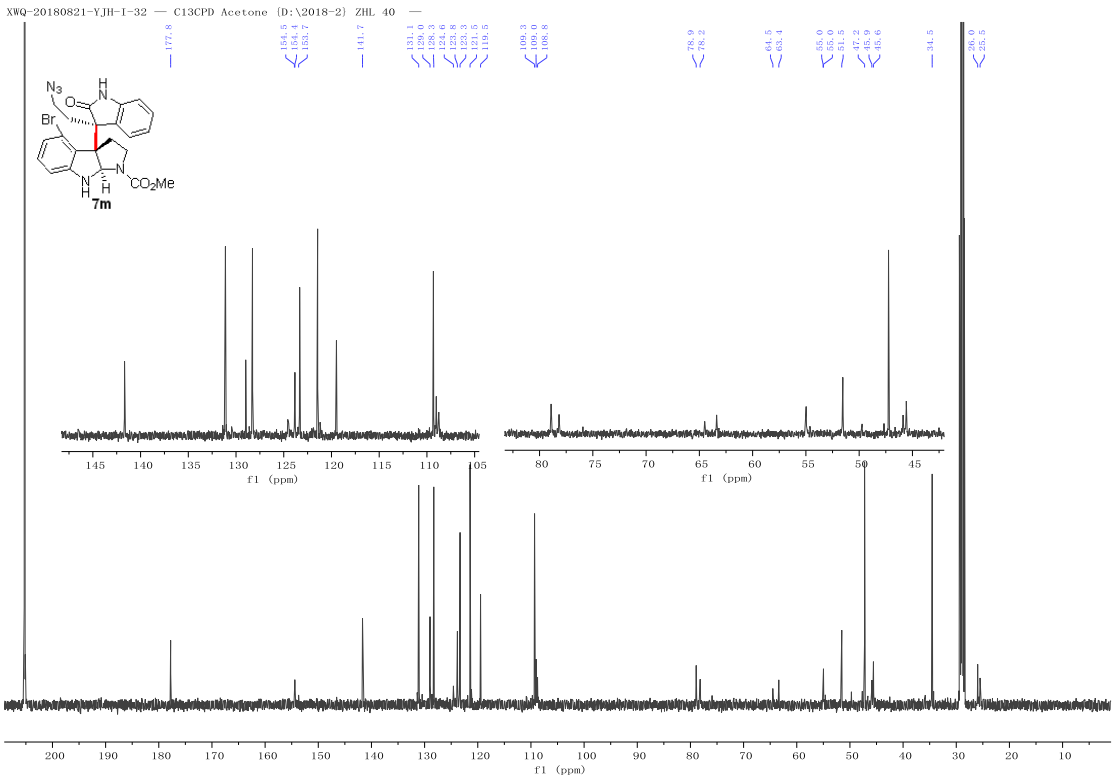
^{13}C NMR Spectrum of **7l** (126 MHz, $CDCl_3$, rotamers)



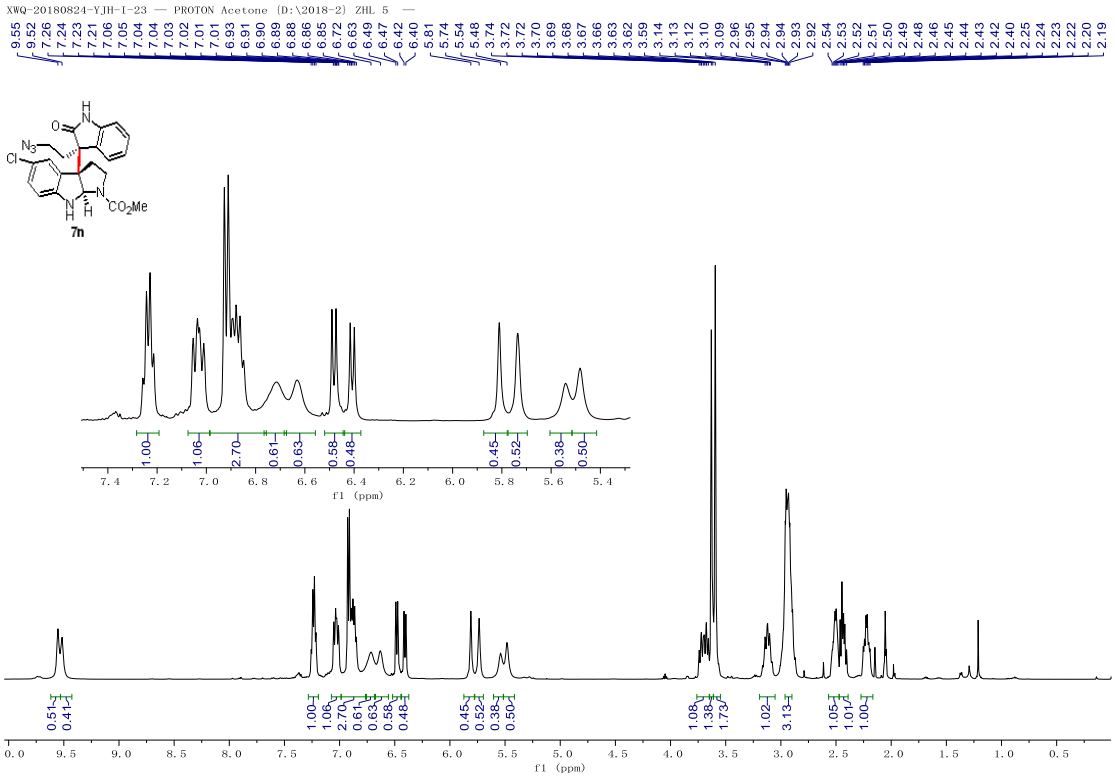
^{1}H NMR Spectrum of **7m** (500 MHz, Acetone-d_6, rotamers)



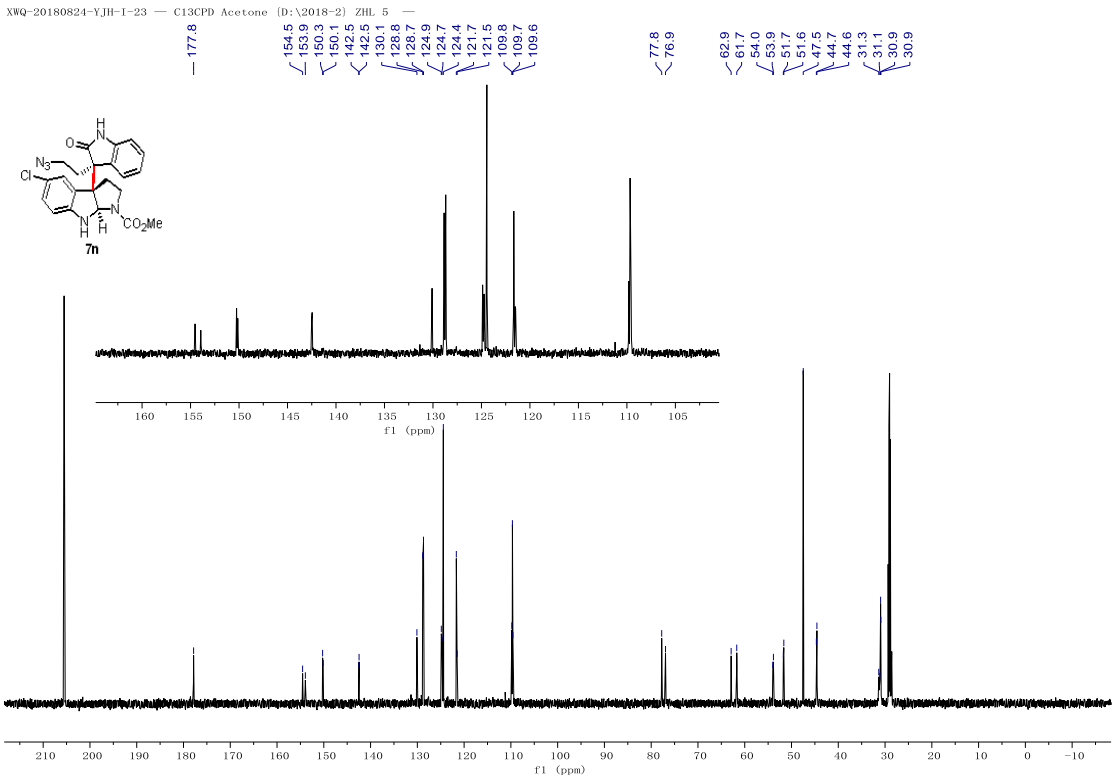
^{13}C NMR Spectrum of **7m** (126 MHz, Acetone-d_6, rotamers)



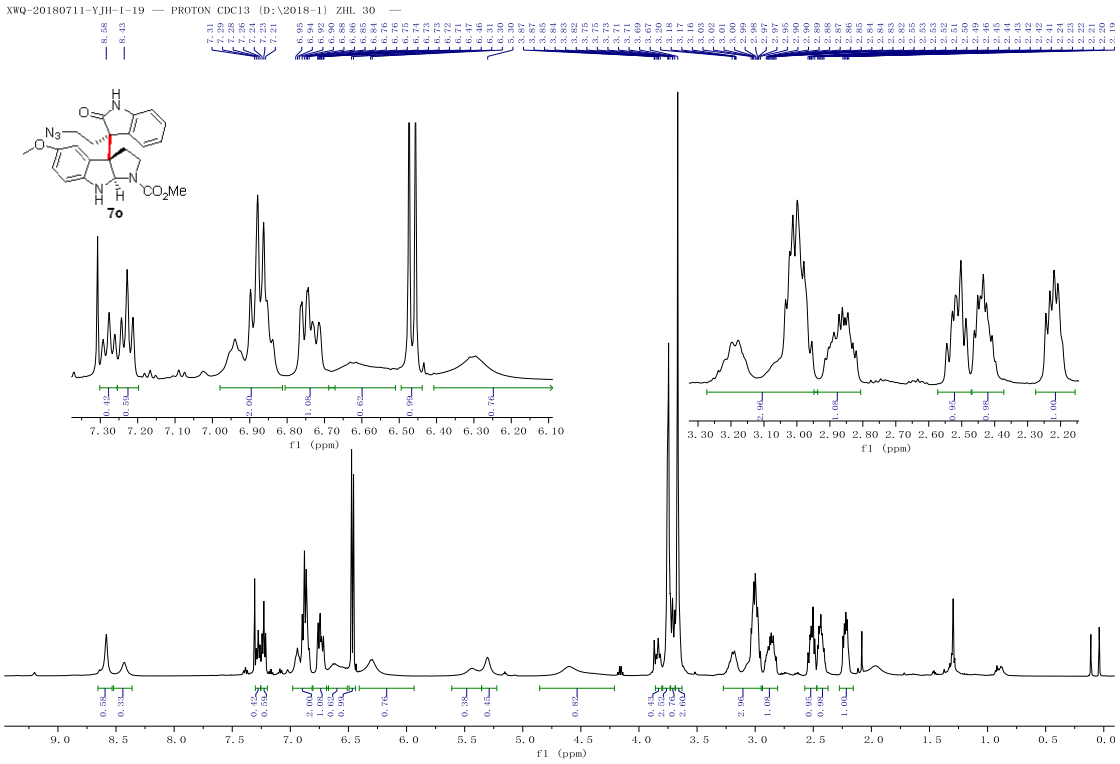
^{1}H NMR Spectrum of **7n** (500 MHz, Acetone-d_6, rotamers)



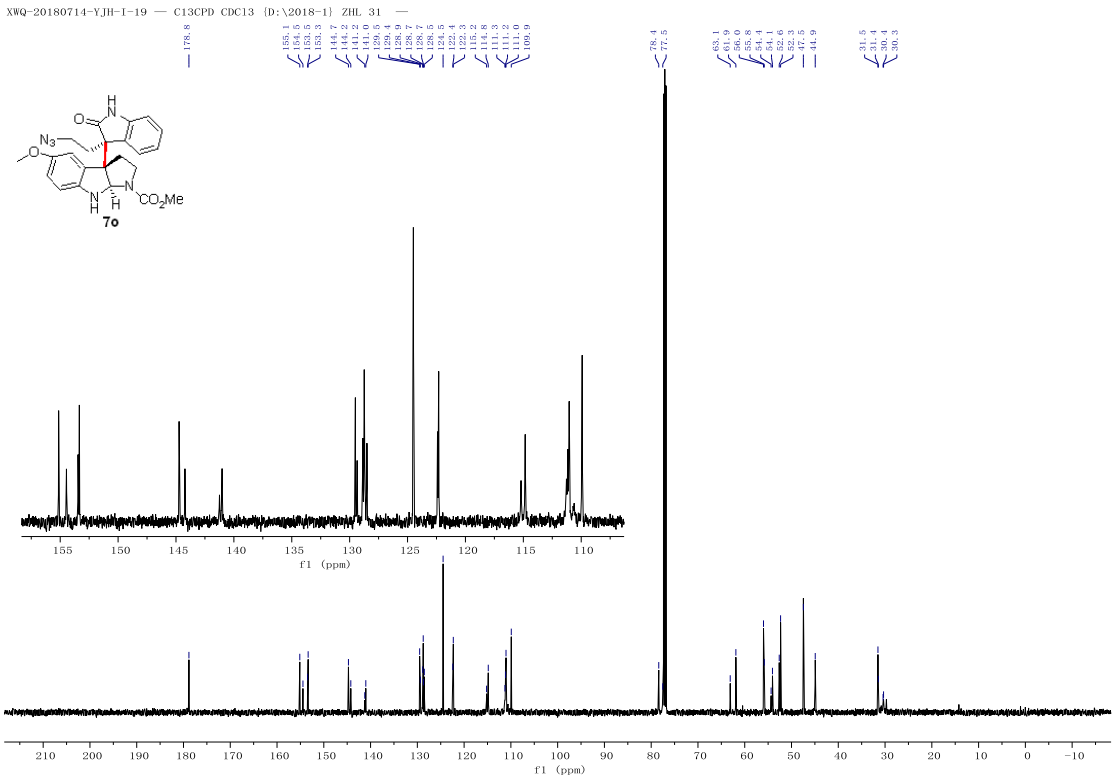
^{13}C NMR Spectrum of **7n** (126 MHz, Acetone-d_6, rotamers)



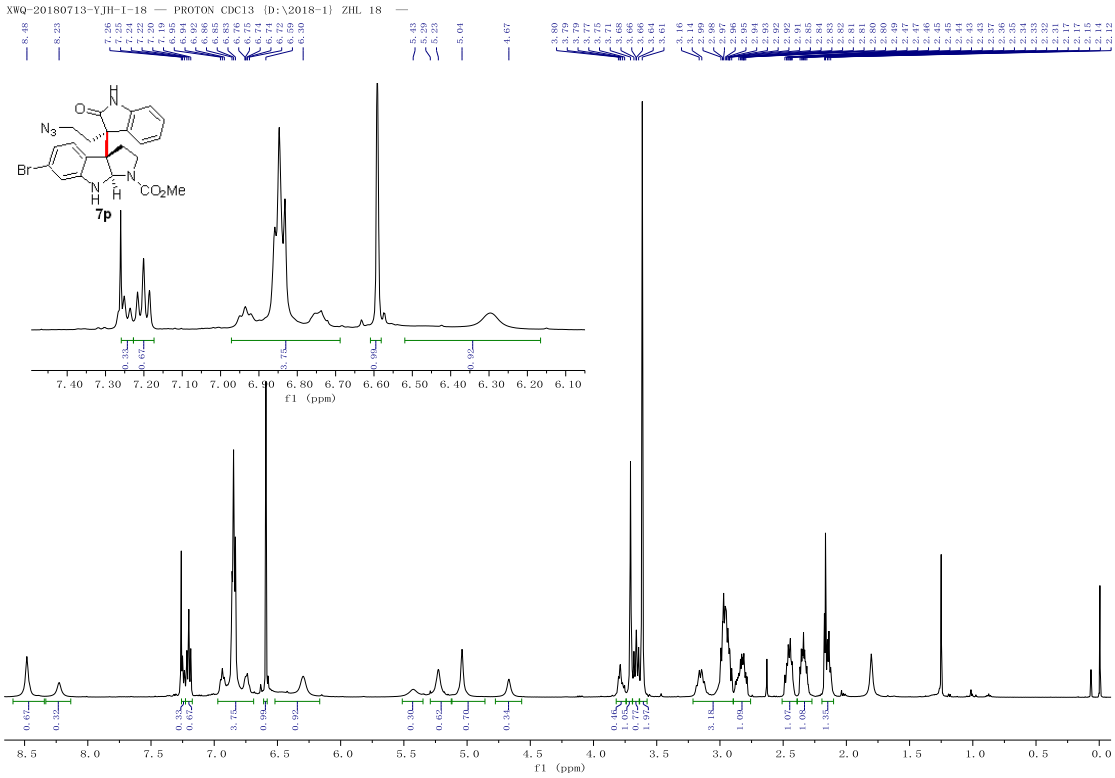
^{1}H NMR Spectrum of **7o** (500 MHz, $CDCl_3$, rotamers)



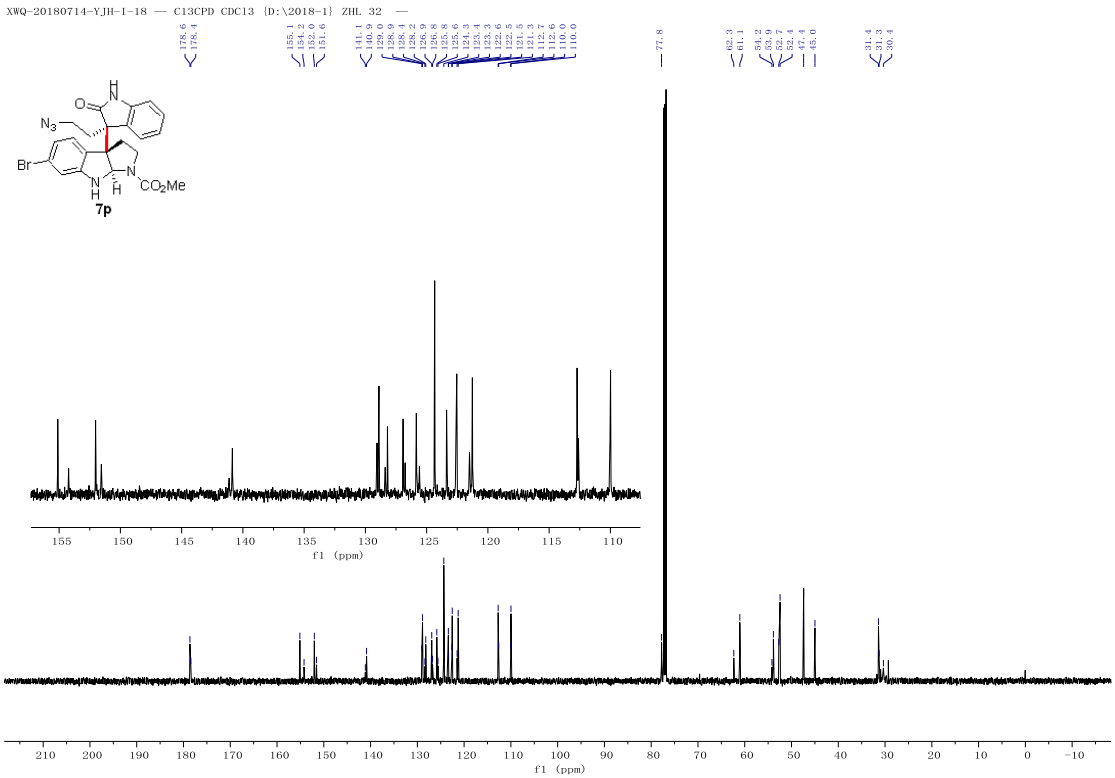
^{13}C NMR Spectrum of **7o** (126 MHz, $CDCl_3$, rotamers)



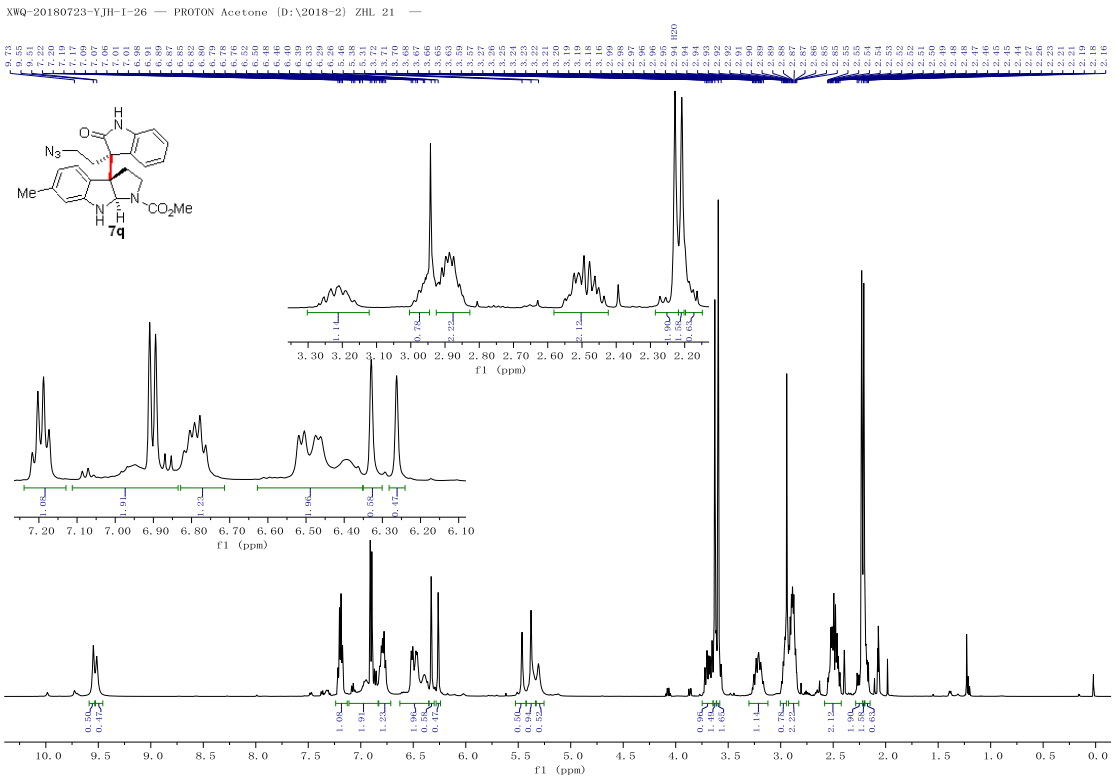
^{1}H NMR Spectrum of **7p** (500 MHz, $CDCl_3$, rotamers)



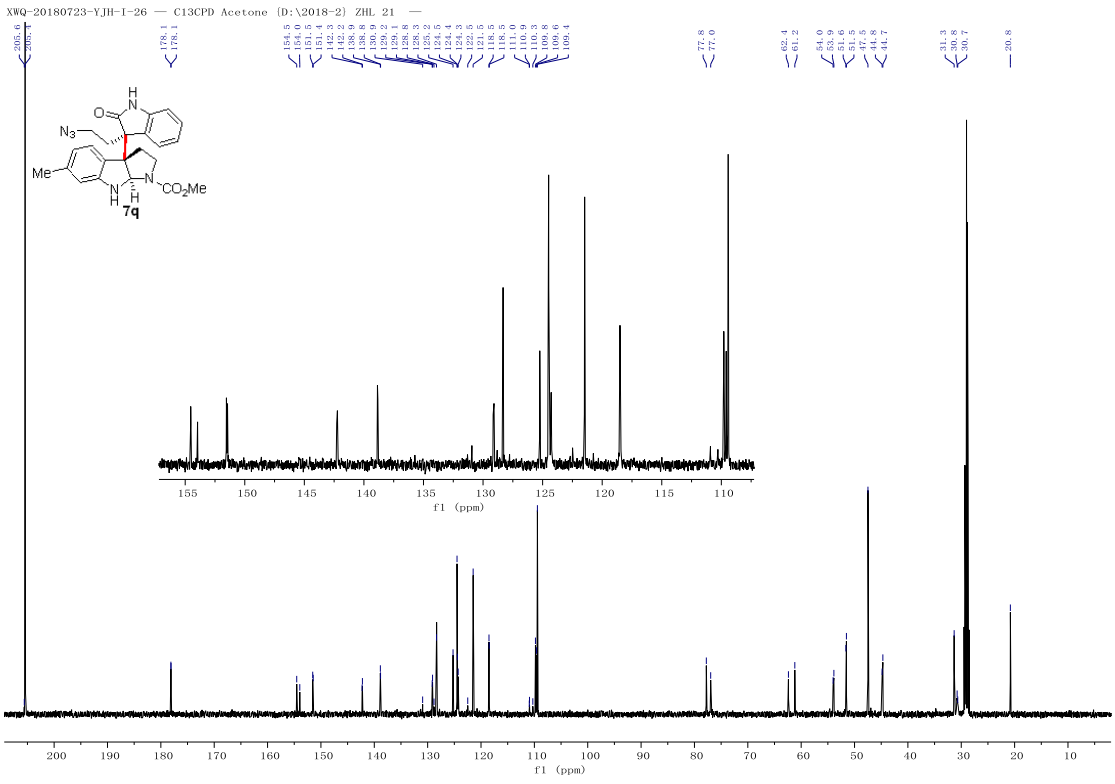
^{13}C NMR Spectrum of **7p** (126 MHz, $CDCl_3$, rotamers)



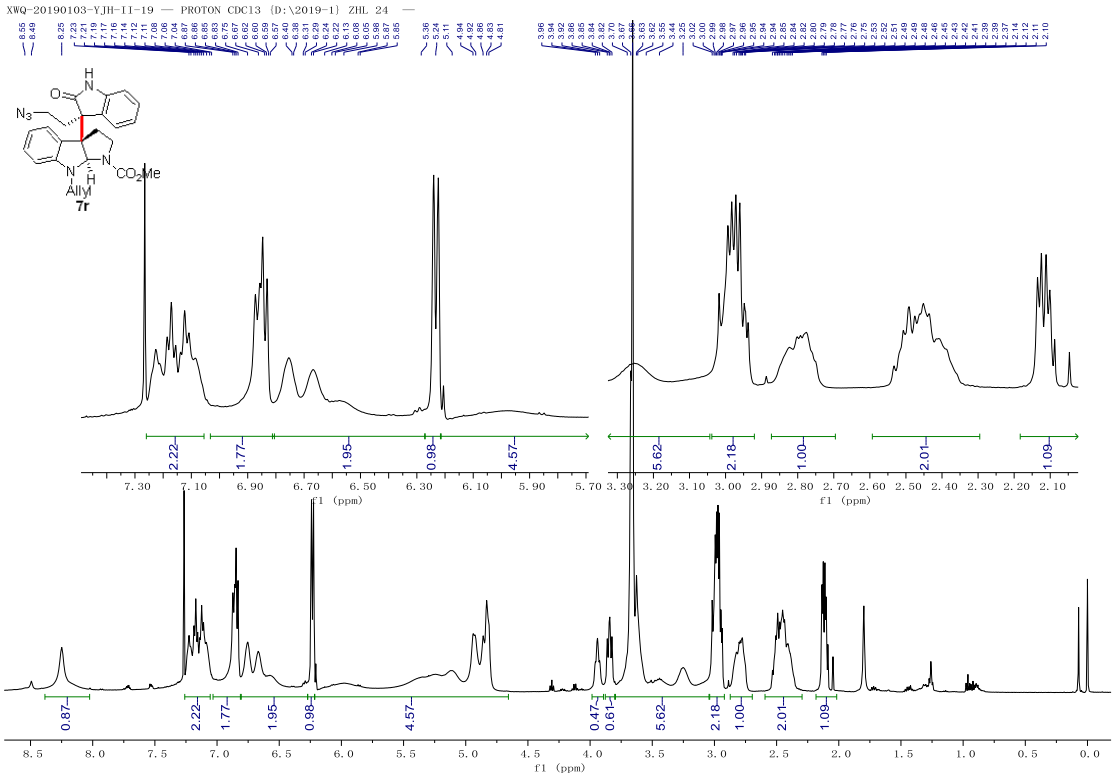
^{1}H NMR Spectrum of **7q** (500 MHz, Acetone-d_6, rotamers)



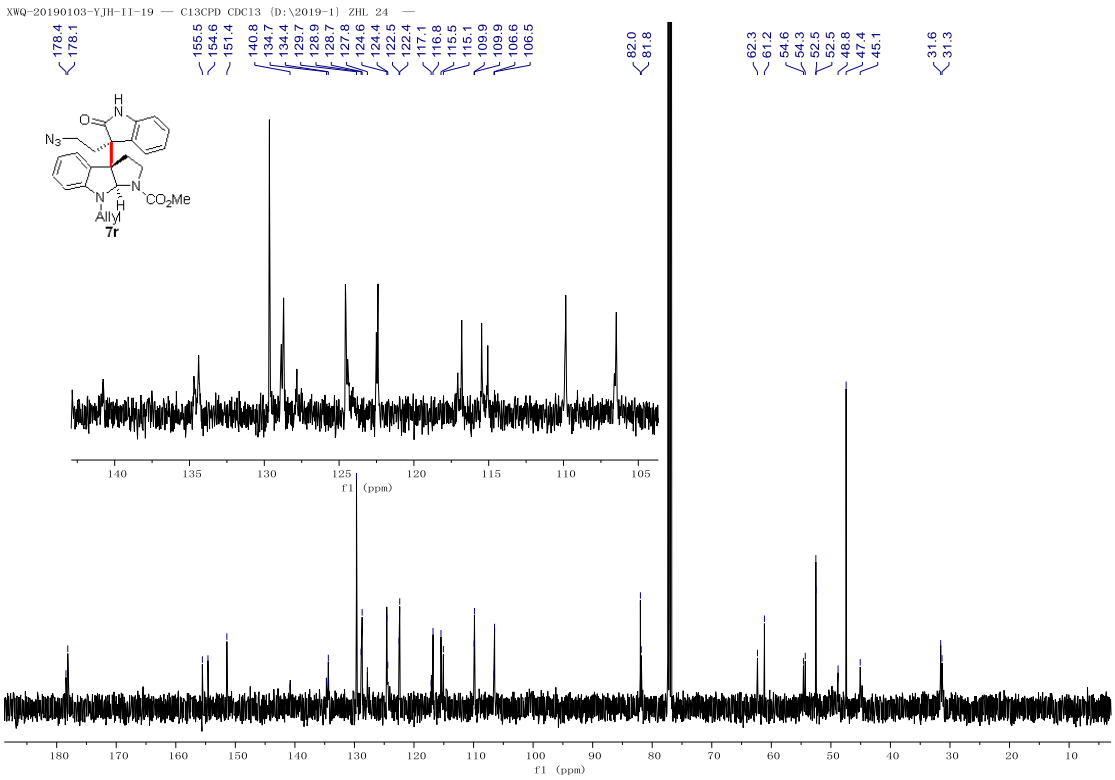
^{13}C NMR Spectrum of **7q** (126 MHz, Acetone-d_6, rotamers)



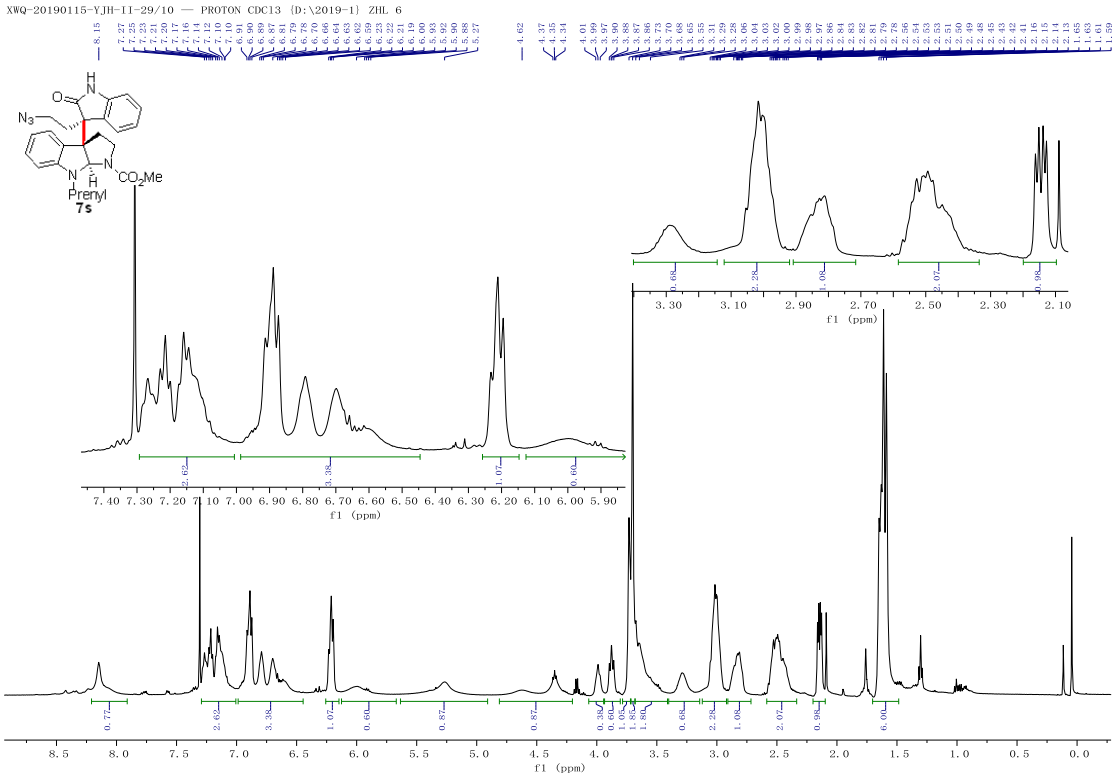
^{1}H NMR Spectrum of **7r** (126 MHz, $CDCl_3$, rotamers)



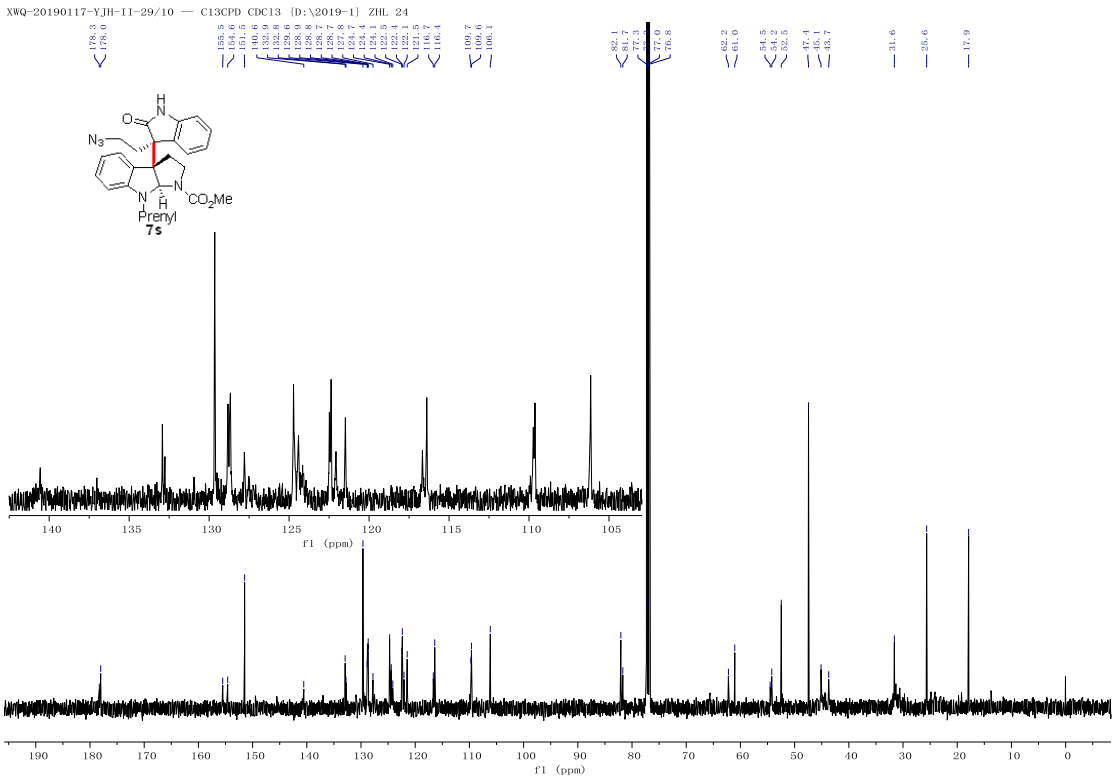
^{13}C NMR Spectrum of **7r** (126 MHz, $CDCl_3$, rotamers)



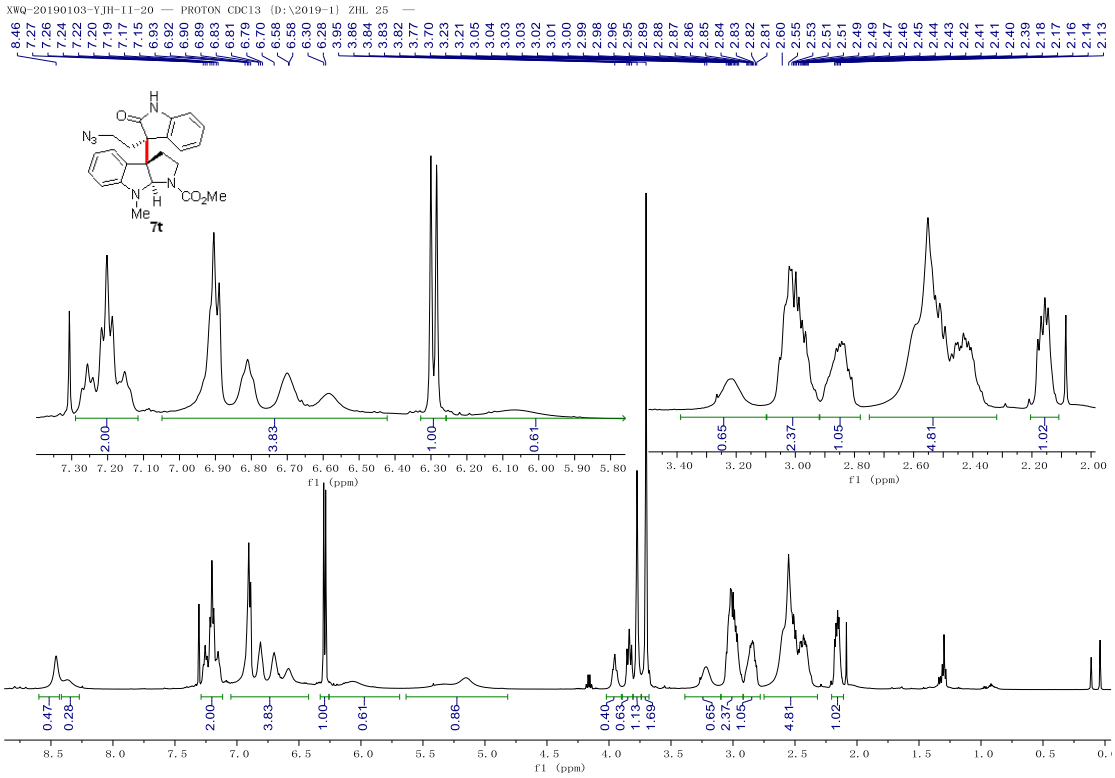
^{1}H NMR Spectrum of **7s** (500 MHz, $CDCl_3$, rotamers)



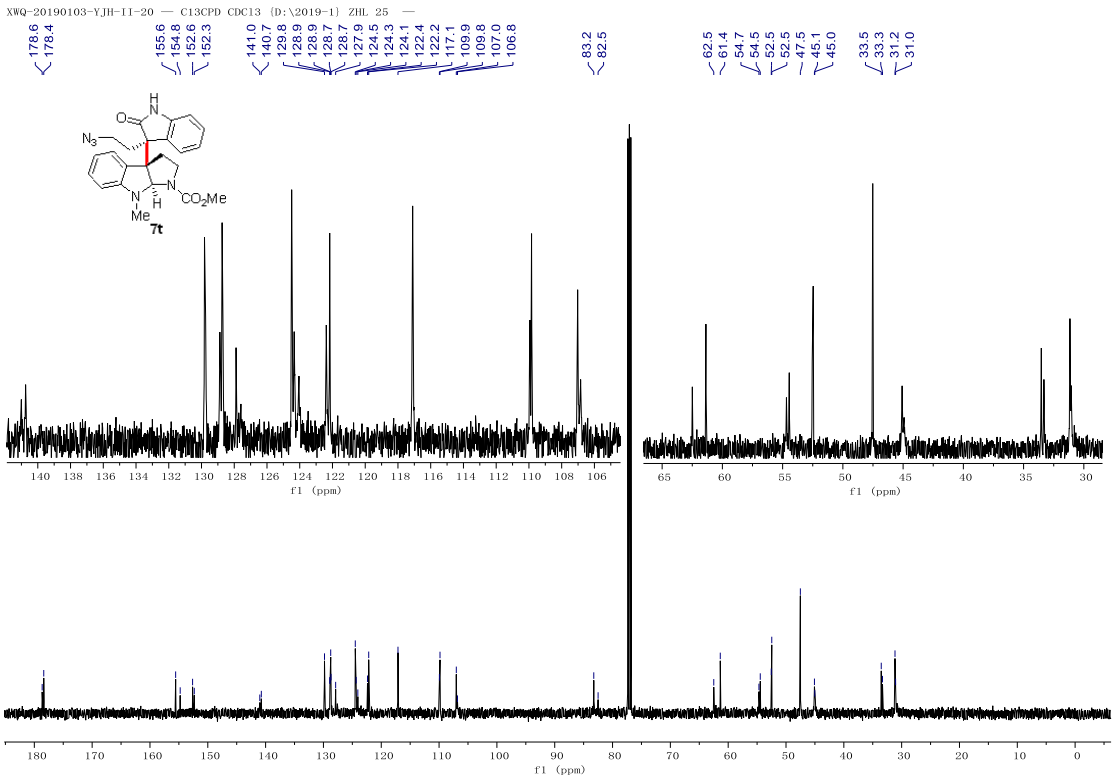
^{13}C NMR Spectrum of **7s** (126 MHz, $CDCl_3$, rotamers)



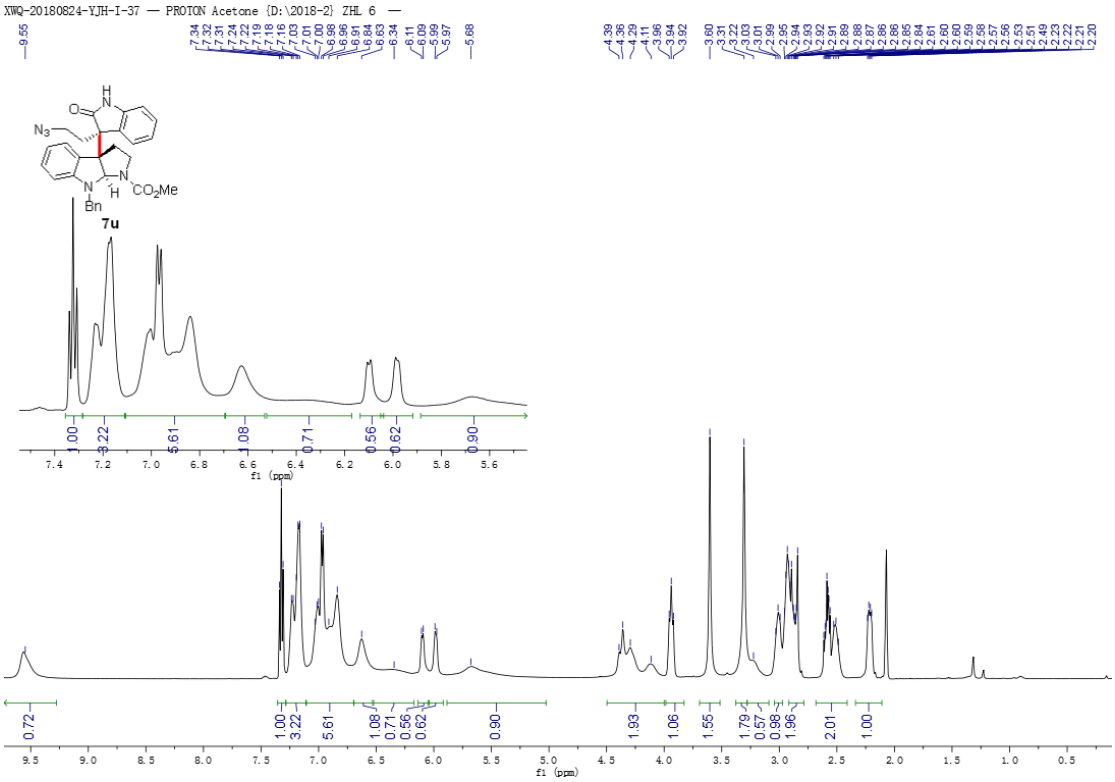
^{1}H NMR Spectrum of **7t** (500 MHz, $CDCl_3$, rotamers)



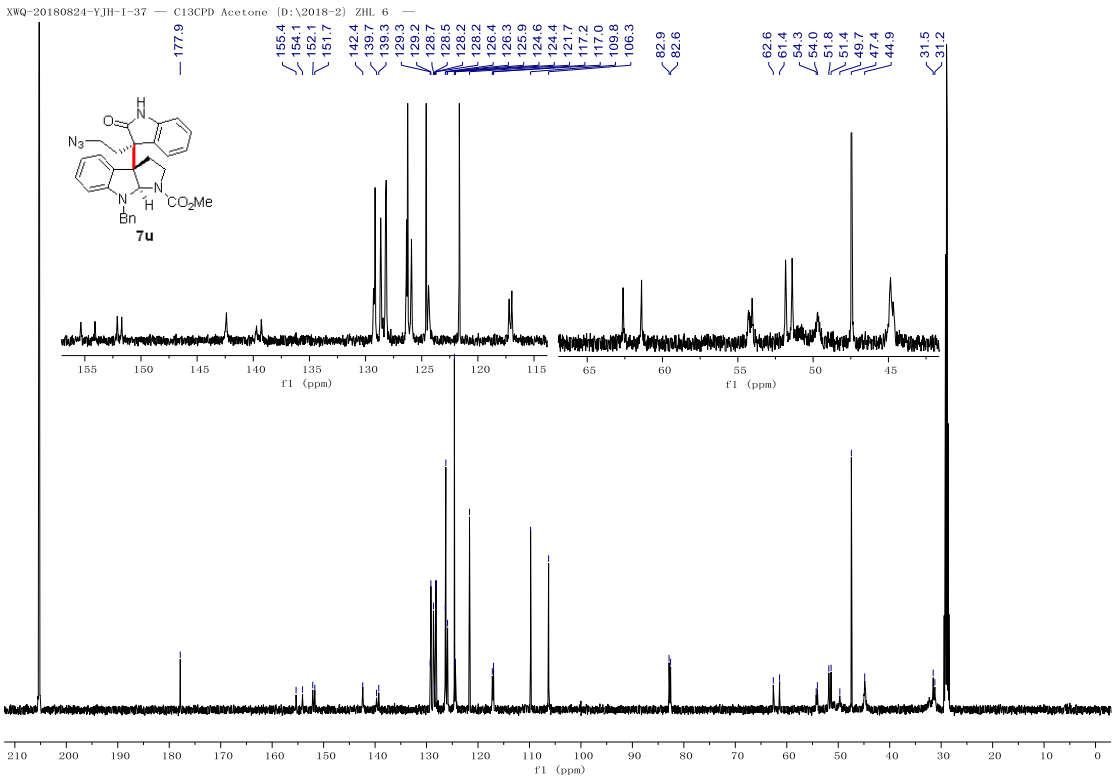
^{13}C NMR Spectrum of **7t** (126 MHz, $CDCl_3$, rotamers)



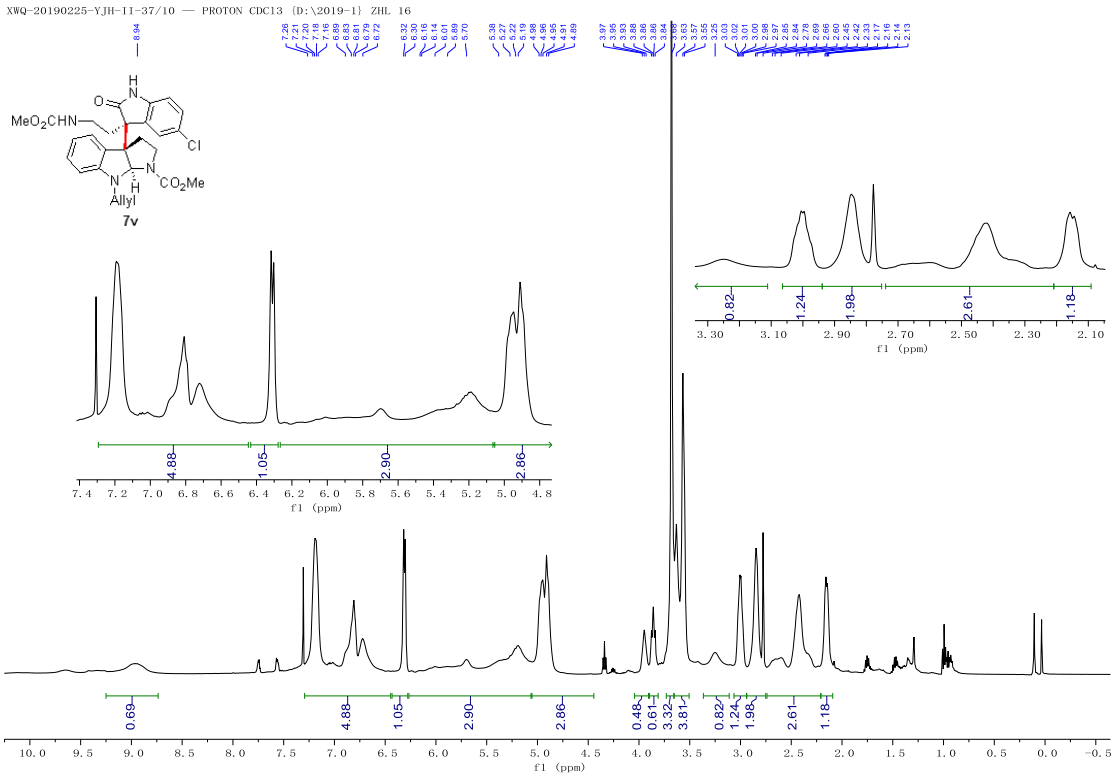
^{1}H NMR Spectrum of **7u** (500 MHz, Acetone-d_6, rotamers)



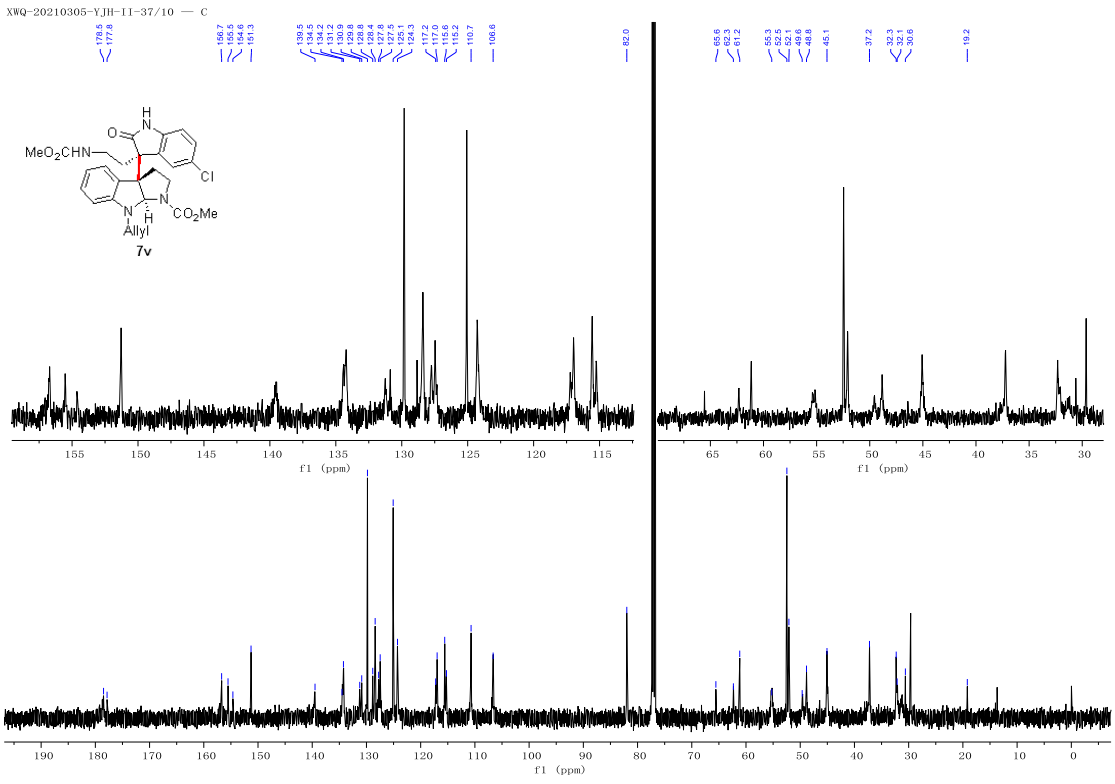
^{13}C NMR Spectrum of **7u** (126 MHz, Acetone-d_6, rotamers)



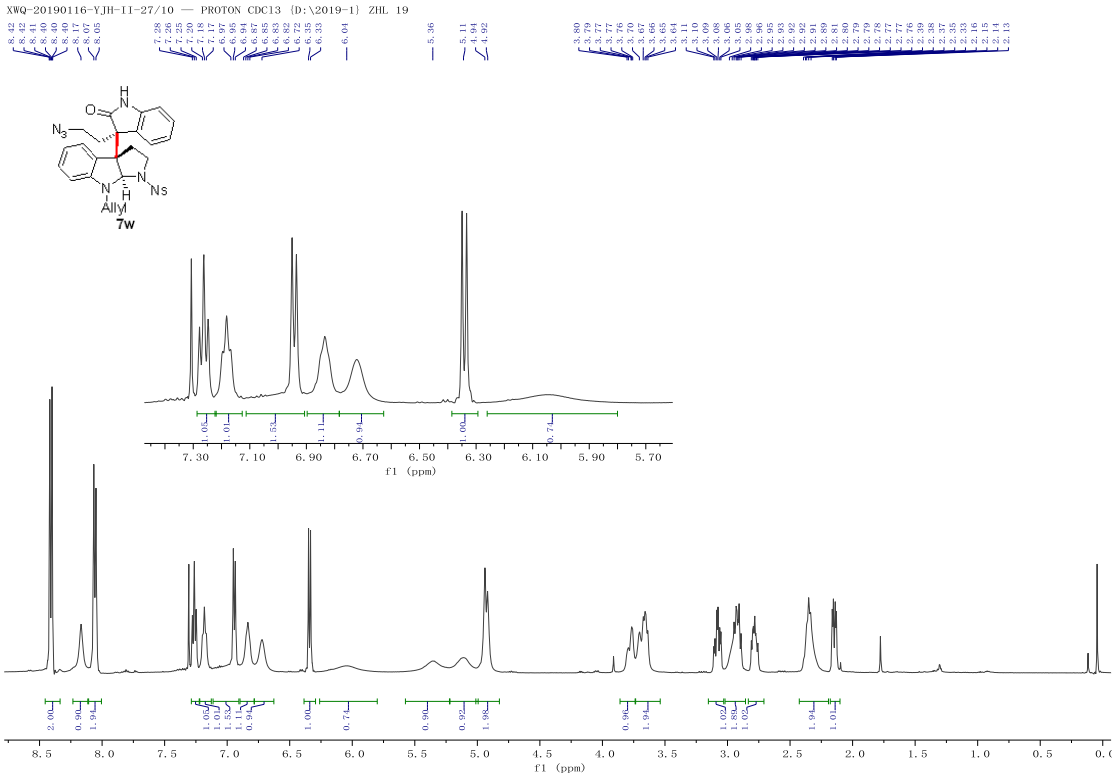
^{1}H NMR Spectrum of **7v** (500 MHz, $CDCl_3$, rotamers)



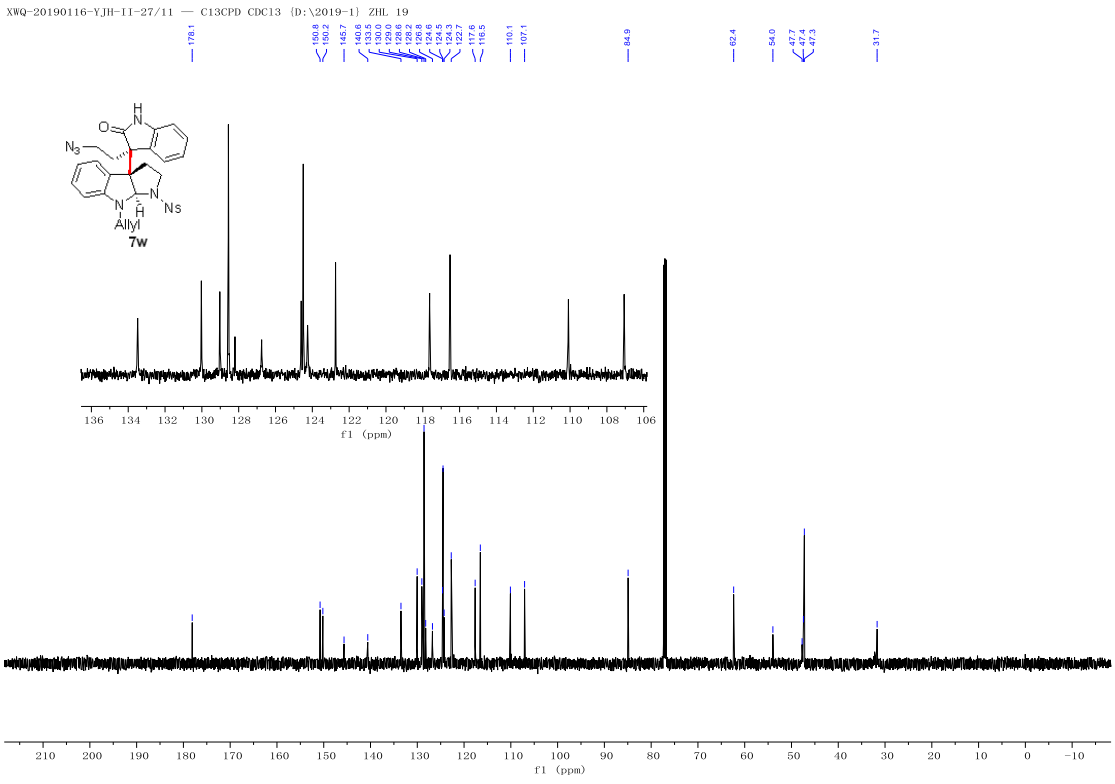
^{13}C NMR Spectrum of **7v** (126 MHz, $CDCl_3$, rotamers)



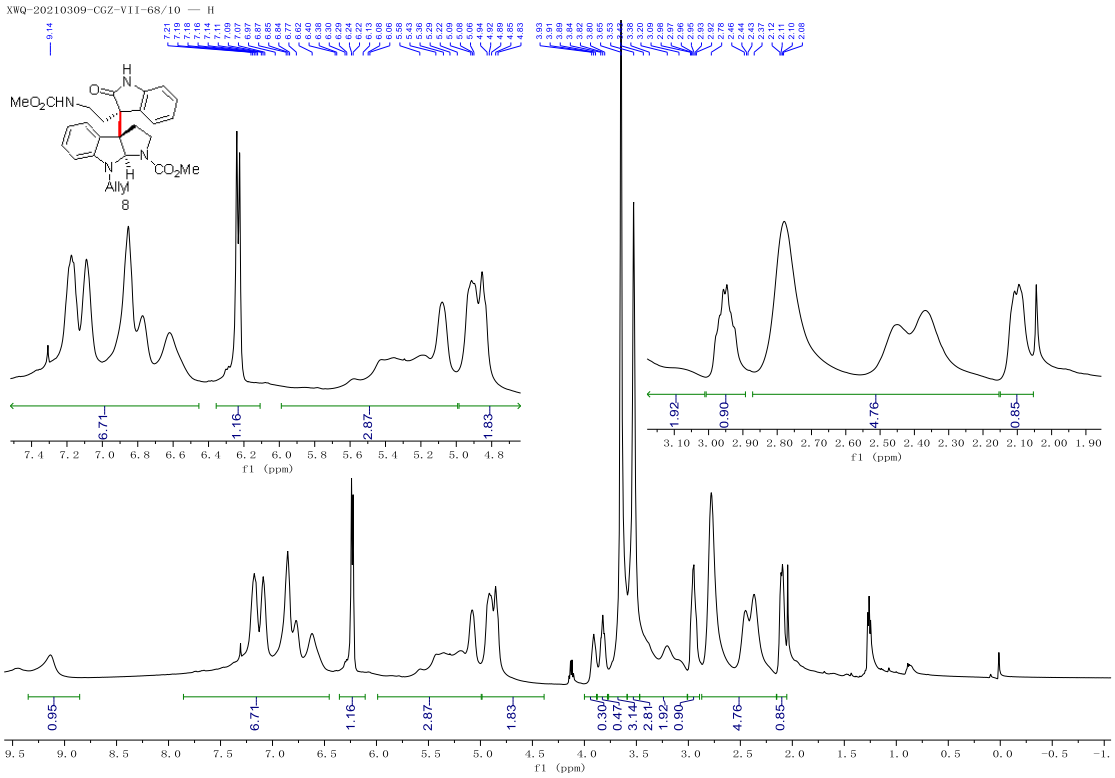
^{1}H NMR Spectrum of **7w** (500 MHz, $CDCl_3$, rotamers)



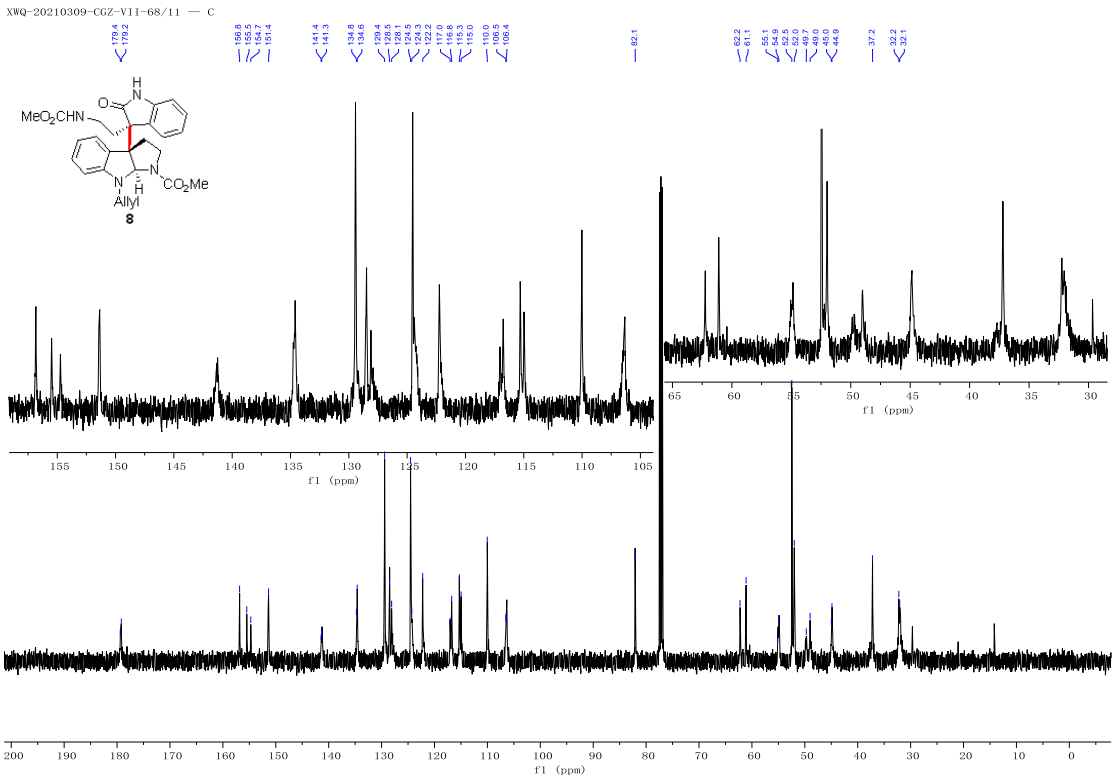
^{13}C NMR Spectrum of **7w** (126 MHz, $CDCl_3$, rotamers)



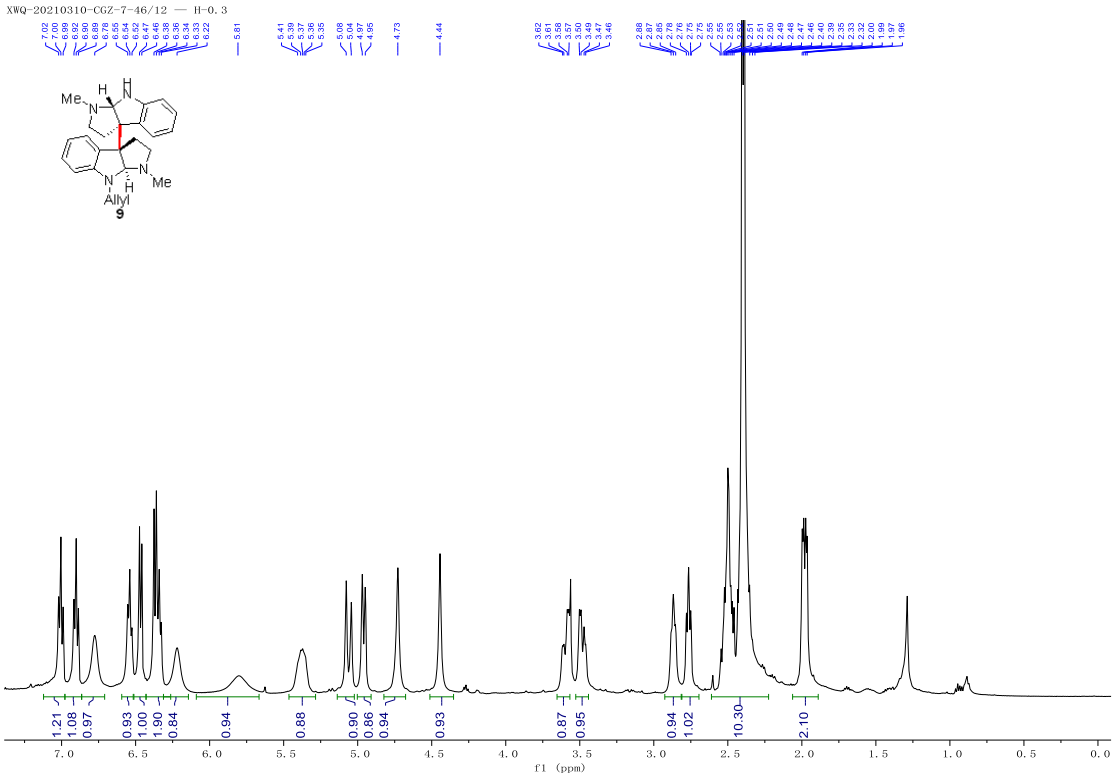
^{1}H NMR Spectrum of **8** (500 MHz, $CDCl_3$, rotamers)



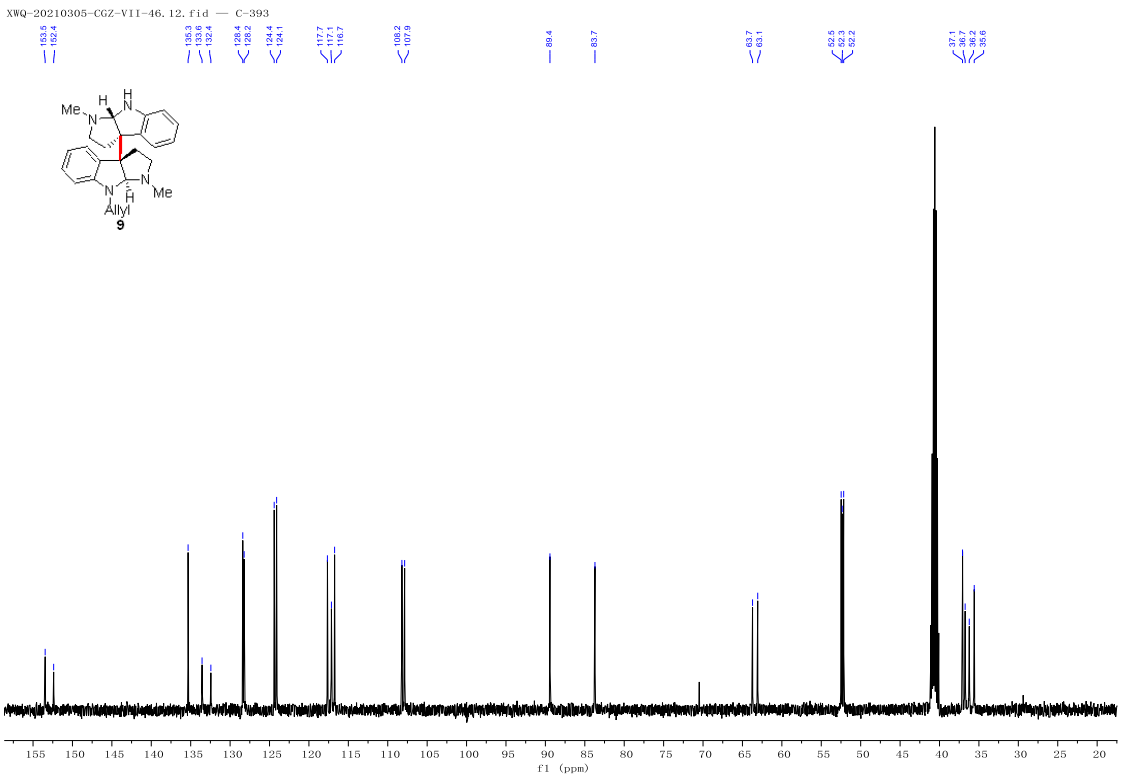
^{13}C NMR Spectrum of **8** (126 MHz, $CDCl_3$, rotamers)



^{1}H NMR Spectrum of **9** (500 MHz, DMSO-d_6, 120 °C)



^{13}C NMR Spectrum of **9** (126 MHz, DMSO-d_6, 120 °C)



7. X-Ray Single Crystal Diffraction Data of Compound 7e

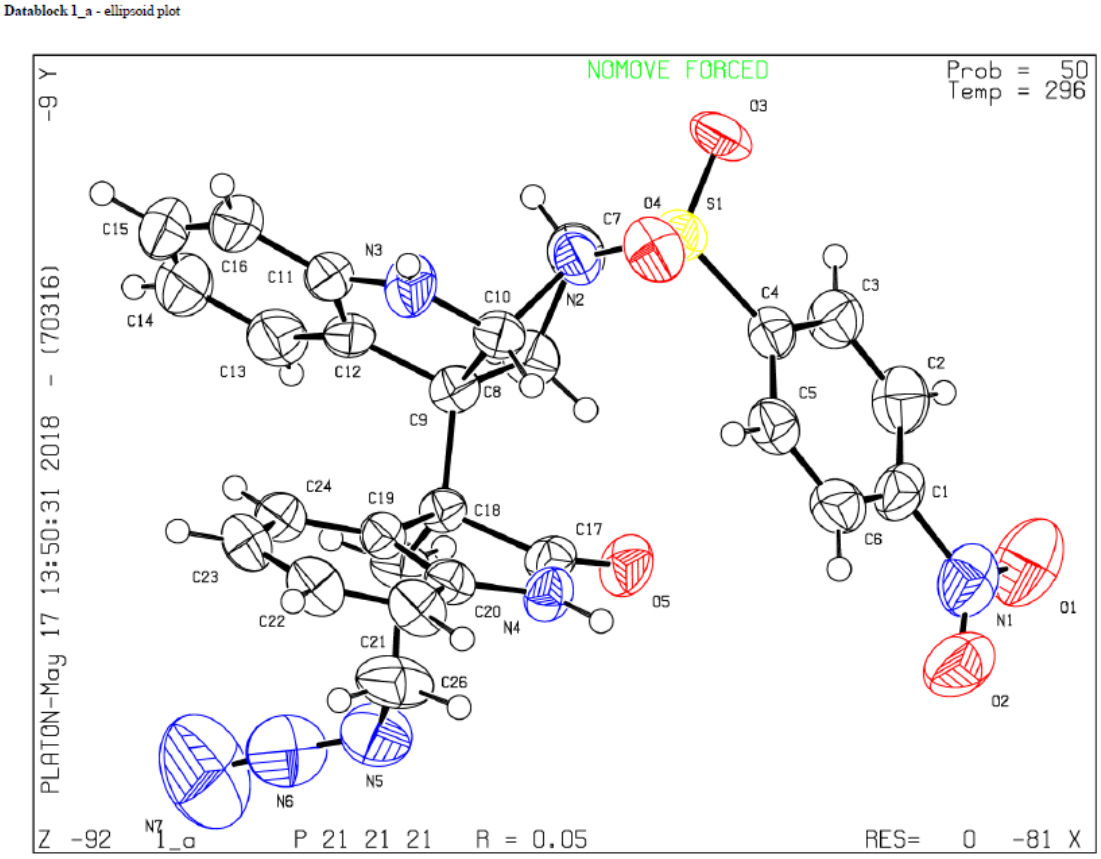


Figure 1. Crystal structure of compound 7e Displacement ellipsoids are drawn at the 50% probability level.

Table S11. Crystal data and structure refinement for **7e.**

Identification code	**7e**	
Empirical formula	C26 H23 N7 O5 S	
Formula weight	545.57	
Temperature	296(2) K	
Wavelength	0.71073 Å	
Crystal system	Orthorhombic	
Space group	$P2_12_12_1$	
Unit cell dimensions	a = 7.98(2) Å	a= 90°.
	b = 13.81(5) Å	b= 90°.
	c = 23.11(7) Å	g = 90°.
Volume	2549(13) $Å^3$	
Z	4	
Density (calculated)	1.422 Mg/m^3	
Absorption coefficient	0.180 mm^{-1}	
F(000)	1136	

Crystal size	0.220 x 0.200 x 0.180 mm^3
Theta range for data collection	2.949 to 25.245°.
Index ranges	-9<=h<=8, -14<=k<=16, -27<=l<=27
Reflections collected	14713
Independent reflections	4507 [R(int) = 0.0945]
Completeness to theta = 25.242°	97.9 %
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4507 / 0 / 352
Goodness-of-fit on F^2	0.980
Final R indices [I>2sigma(I)]	R1 = 0.0550, wR2 = 0.1062
R indices (all data)	R1 = 0.1109, wR2 = 0.1272
Absolute structure parameter	0.07(9)
Extinction coefficient	n/a
Largest diff. peak and hole	0.206 and -0.277 e.$Å^{-3}$

Table S12. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)

for **7e**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	2474(9)	1814(5)	4457(2)	56(2)
C(2)	4068(9)	1430(5)	4449(3)	64(2)
C(3)	5321(8)	1916(4)	4146(3)	56(2)
C(4)	4929(7)	2770(4)	3863(2)	44(2)
C(5)	3305(8)	3159(4)	3891(2)	50(2)
C(6)	2071(8)	2667(5)	4187(3)	56(2)
C(7)	6675(8)	1831(4)	2693(3)	58(2)
C(8)	5128(7)	1456(4)	2382(2)	49(2)
C(9)	4468(7)	2321(4)	2026(2)	39(1)
C(10)	5056(7)	3242(4)	2371(2)	42(1)
C(11)	6140(7)	3371(5)	1439(2)	51(2)
C(12)	5413(7)	2458(4)	1456(2)	44(1)
C(13)	5626(8)	1821(5)	991(3)	64(2)
C(14)	6496(10)	2146(7)	507(3)	83(2)
C(15)	7175(10)	3061(8)	497(3)	88(3)
C(16)	7015(8)	3684(6)	956(3)	72(2)

C(17)	1605(7)	2336(4)	2528(2)	43(1)
C(18)	2509(7)	2328(4)	1932(2)	35(1)
C(19)	1903(6)	3279(4)	1674(2)	36(1)
C(20)	943(7)	3780(4)	2087(2)	41(1)
C(21)	307(8)	4685(4)	1981(2)	49(2)
C(22)	647(8)	5105(4)	1453(3)	51(2)
C(23)	1556(8)	4624(4)	1029(2)	50(2)
C(24)	2192(7)	3701(4)	1142(2)	42(1)
C(25)	1906(6)	1421(4)	1594(2)	45(1)
C(26)	29(8)	1357(5)	1531(3)	72(2)
N(1)	1107(10)	1287(5)	4776(3)	75(2)
N(2)	6307(6)	2877(3)	2792(2)	44(1)
N(3)	5766(7)	3890(4)	1943(2)	55(1)
N(4)	793(5)	3203(3)	2587(2)	46(1)
N(5)	-550(8)	399(4)	1328(3)	81(2)
N(6)	-697(9)	324(4)	812(4)	87(2)
N(7)	-905(15)	168(7)	333(4)	166(5)
O(1)	1533(9)	574(4)	5047(2)	108(2)
O(2)	-336(7)	1592(4)	4735(2)	88(2)
O(3)	8089(5)	3096(3)	3652(2)	65(1)
O(4)	5972(5)	4349(3)	3364(2)	60(1)
O(5)	1594(5)	1685(3)	2892(2)	59(1)
S(1)	6458(2)	3355(1)	3428(1)	47(1)

Table S13. Bond lengths [Å] and angles [°] for 7e

C(1)-C(6)	1.371(9)
C(1)-C(2)	1.378(10)
C(1)-N(1)	1.506(9)
C(2)-C(3)	1.393(9)
C(2)-H(2)	0.9300
C(3)-C(4)	1.384(8)
C(3)-H(3)	0.9300
C(4)-C(5)	1.405(9)
C(4)-S(1)	1.776(7)
C(5)-C(6)	1.378(8)
C(5)-H(5)	0.9300

C(6)-H(6)	0.9300
C(7)-N(2)	1.492(8)
C(7)-C(8)	1.520(9)
C(7)-H(7A)	0.9700
C(7)-H(7B)	0.9700
C(8)-C(9)	1.544(8)
C(8)-H(8A)	0.9700
C(8)-H(8B)	0.9700
C(9)-C(12)	1.530(8)
C(9)-C(10)	1.573(8)
C(9)-C(18)	1.579(8)
C(10)-N(3)	1.451(7)
C(10)-N(2)	1.483(7)
C(10)-H(10)	0.9800
C(11)-C(16)	1.387(8)
C(11)-C(12)	1.389(9)
C(11)-N(3)	1.399(8)
C(12)-C(13)	1.400(8)
C(13)-C(14)	1.391(10)
C(13)-H(13)	0.9300
C(14)-C(15)	1.376(11)
C(14)-H(14)	0.9300
C(15)-C(16)	1.373(10)
C(15)-H(15)	0.9300
C(16)-H(16)	0.9300
C(17)-O(5)	1.231(7)
C(17)-N(4)	1.369(8)
C(17)-C(18)	1.556(8)
C(18)-C(19)	1.521(8)
C(18)-C(25)	1.552(8)
C(19)-C(24)	1.380(8)
C(19)-C(20)	1.405(7)
C(20)-C(21)	1.372(8)
C(20)-N(4)	1.410(7)
C(21)-C(22)	1.377(8)
C(21)-H(21)	0.9300
C(22)-C(23)	1.388(8)
C(22)-H(22)	0.9300

C(23)-C(24)	1.398(8)
C(23)-H(23)	0.9300
C(24)-H(24)	0.9300
C(25)-C(26)	1.508(9)
C(25)-H(25A)	0.9700
C(25)-H(25B)	0.9700
C(26)-N(5)	1.478(9)
C(26)-H(26A)	0.9700
C(26)-H(26B)	0.9700
N(1)-O(1)	1.215(8)
N(1)-O(2)	1.230(8)
N(2)-S(1)	1.616(6)
N(3)-H(3A)	0.8600
N(4)-H(4)	0.8600
N(5)-N(6)	1.204(9)
N(6)-N(7)	1.139(9)
O(3)-S(1)	1.445(5)
O(4)-S(1)	1.435(6)

C(6)-C(1)-C(2)	122.8(6)
C(6)-C(1)-N(1)	117.9(7)
C(2)-C(1)-N(1)	119.3(7)
C(1)-C(2)-C(3)	118.9(6)
C(1)-C(2)-H(2)	120.6
C(3)-C(2)-H(2)	120.6
C(4)-C(3)-C(2)	119.1(6)
C(4)-C(3)-H(3)	120.5
C(2)-C(3)-H(3)	120.5
C(3)-C(4)-C(5)	120.8(6)
C(3)-C(4)-S(1)	120.0(5)
C(5)-C(4)-S(1)	119.1(5)
C(6)-C(5)-C(4)	119.6(6)
C(6)-C(5)-H(5)	120.2
C(4)-C(5)-H(5)	120.2
C(1)-C(6)-C(5)	118.8(6)
C(1)-C(6)-H(6)	120.6
C(5)-C(6)-H(6)	120.6
N(2)-C(7)-C(8)	104.1(5)

N(2)-C(7)-H(7A)	110.9
C(8)-C(7)-H(7A)	110.9
N(2)-C(7)-H(7B)	110.9
C(8)-C(7)-H(7B)	110.9
H(7A)-C(7)-H(7B)	109.0
C(7)-C(8)-C(9)	105.4(5)
C(7)-C(8)-H(8A)	110.7
C(9)-C(8)-H(8A)	110.7
C(7)-C(8)-H(8B)	110.7
C(9)-C(8)-H(8B)	110.7
H(8A)-C(8)-H(8B)	108.8
C(12)-C(9)-C(8)	112.7(5)
C(12)-C(9)-C(10)	100.9(4)
C(8)-C(9)-C(10)	104.7(5)
C(12)-C(9)-C(18)	111.7(5)
C(8)-C(9)-C(18)	114.6(5)
C(10)-C(9)-C(18)	111.2(4)
N(3)-C(10)-N(2)	113.3(5)
N(3)-C(10)-C(9)	105.6(5)
N(2)-C(10)-C(9)	105.0(4)
N(3)-C(10)-H(10)	110.9
N(2)-C(10)-H(10)	110.9
C(9)-C(10)-H(10)	110.9
C(16)-C(11)-C(12)	121.1(6)
C(16)-C(11)-N(3)	128.1(6)
C(12)-C(11)-N(3)	110.7(5)
C(11)-C(12)-C(13)	119.9(6)
C(11)-C(12)-C(9)	110.0(5)
C(13)-C(12)-C(9)	130.1(6)
C(14)-C(13)-C(12)	118.4(7)
C(14)-C(13)-H(13)	120.8
C(12)-C(13)-H(13)	120.8
C(15)-C(14)-C(13)	120.5(7)
C(15)-C(14)-H(14)	119.8
C(13)-C(14)-H(14)	119.8
C(16)-C(15)-C(14)	121.7(7)
C(16)-C(15)-H(15)	119.1
C(14)-C(15)-H(15)	119.1

C(15)-C(16)-C(11)	118.3(7)
C(15)-C(16)-H(16)	120.8
C(11)-C(16)-H(16)	120.8
O(5)-C(17)-N(4)	124.6(5)
O(5)-C(17)-C(18)	127.1(5)
N(4)-C(17)-C(18)	108.3(5)
C(19)-C(18)-C(25)	113.7(5)
C(19)-C(18)-C(17)	101.1(4)
C(25)-C(18)-C(17)	107.9(4)
C(19)-C(18)-C(9)	112.0(4)
C(25)-C(18)-C(9)	111.8(4)
C(17)-C(18)-C(9)	109.7(5)
C(24)-C(19)-C(20)	119.2(5)
C(24)-C(19)-C(18)	131.3(5)
C(20)-C(19)-C(18)	109.5(5)
C(21)-C(20)-C(19)	122.0(5)
C(21)-C(20)-N(4)	129.1(5)
C(19)-C(20)-N(4)	109.0(5)
C(20)-C(21)-C(22)	117.9(5)
C(20)-C(21)-H(21)	121.0
C(22)-C(21)-H(21)	121.0
C(21)-C(22)-C(23)	121.8(5)
C(21)-C(22)-H(22)	119.1
C(23)-C(22)-H(22)	119.1
C(22)-C(23)-C(24)	119.6(5)
C(22)-C(23)-H(23)	120.2
C(24)-C(23)-H(23)	120.2
C(19)-C(24)-C(23)	119.4(5)
C(19)-C(24)-H(24)	120.3
C(23)-C(24)-H(24)	120.3
C(26)-C(25)-C(18)	113.8(4)
C(26)-C(25)-H(25A)	108.8
C(18)-C(25)-H(25A)	108.8
C(26)-C(25)-H(25B)	108.8
C(18)-C(25)-H(25B)	108.8
H(25A)-C(25)-H(25B)	107.7
N(5)-C(26)-C(25)	113.2(5)
N(5)-C(26)-H(26A)	108.9

C(25)-C(26)-H(26A)	108.9
N(5)-C(26)-H(26B)	108.9
C(25)-C(26)-H(26B)	108.9
H(26A)-C(26)-H(26B)	107.7
O(1)-N(1)-O(2)	125.5(7)
O(1)-N(1)-C(1)	116.2(8)
O(2)-N(1)-C(1)	118.4(7)
C(10)-N(2)-C(7)	111.1(4)
C(10)-N(2)-S(1)	120.6(4)
C(7)-N(2)-S(1)	121.4(4)
C(11)-N(3)-C(10)	109.5(5)
C(11)-N(3)-H(3A)	125.2
C(10)-N(3)-H(3A)	125.2
C(17)-N(4)-C(20)	111.9(5)
C(17)-N(4)-H(4)	124.1
C(20)-N(4)-H(4)	124.1
N(6)-N(5)-C(26)	115.0(6)
N(7)-N(6)-N(5)	173.3(9)
O(4)-S(1)-O(3)	121.1(3)
O(4)-S(1)-N(2)	106.1(3)
O(3)-S(1)-N(2)	106.9(3)
O(4)-S(1)-C(4)	107.9(3)
O(3)-S(1)-C(4)	107.7(3)
N(2)-S(1)-C(4)	106.1(3)

Symmetry transformations used to generate equivalent atoms:

Table S14. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for 7e The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	62(5)	65(5)	40(3)	-14(3)	11(3)	-19(4)
C(2)	81(6)	50(4)	59(4)	6(3)	0(4)	-2(4)
C(3)	58(4)	55(4)	56(4)	10(3)	1(3)	6(3)
C(4)	50(4)	44(3)	38(3)	0(3)	-5(3)	-3(3)
C(5)	54(4)	53(4)	43(3)	-5(3)	-5(3)	8(4)
C(6)	52(4)	67(4)	50(4)	-10(4)	-4(3)	-1(3)

C(7)	60(4)	58(4)	55(4)	-5(3)	-2(3)	20(4)
C(8)	53(4)	36(3)	58(4)	4(3)	-3(3)	9(3)
C(9)	38(3)	33(3)	46(3)	3(3)	2(3)	4(3)
C(10)	40(3)	39(3)	46(3)	-3(3)	-3(3)	-2(3)
C(11)	40(4)	67(4)	46(4)	14(3)	-1(3)	1(3)
C(12)	30(3)	54(4)	47(4)	3(3)	1(3)	8(3)
C(13)	50(4)	81(5)	60(4)	-10(4)	0(3)	18(4)
C(14)	62(5)	136(8)	52(5)	-14(5)	9(4)	15(6)
C(15)	60(5)	153(9)	52(5)	23(5)	12(4)	8(6)
C(16)	58(5)	96(6)	60(5)	30(4)	1(4)	-12(4)
C(17)	39(3)	44(3)	46(3)	-3(3)	3(3)	-12(3)
C(18)	33(3)	32(3)	39(3)	1(2)	1(3)	3(3)
C(19)	37(3)	36(3)	35(3)	-3(3)	-1(2)	3(3)
C(20)	36(3)	44(3)	43(3)	-6(3)	-5(3)	0(3)
C(21)	53(4)	42(4)	53(4)	-14(3)	-7(3)	17(3)
C(22)	60(4)	35(3)	57(4)	-3(3)	-11(3)	12(3)
C(23)	58(4)	47(3)	45(4)	3(3)	-12(3)	4(3)
C(24)	40(3)	42(4)	43(3)	-10(3)	1(3)	9(3)
C(25)	38(3)	39(3)	59(3)	-7(3)	-3(3)	2(2)
C(26)	52(4)	69(5)	94(5)	-39(4)	-9(4)	-7(3)
N(1)	97(6)	69(4)	58(4)	-21(3)	13(4)	-17(4)
N(2)	47(3)	51(3)	35(3)	0(2)	-6(2)	6(3)
N(3)	73(4)	42(3)	50(3)	12(3)	2(3)	-13(3)
N(4)	48(3)	48(3)	42(3)	-4(2)	10(2)	10(2)
N(5)	80(5)	79(4)	85(5)	-15(4)	-8(4)	-31(4)
N(6)	89(5)	69(4)	103(6)	-37(5)	6(5)	1(3)
N(7)	220(12)	162(8)	115(7)	-77(7)	-21(8)	43(7)
O(1)	135(5)	87(4)	102(4)	20(3)	32(4)	-14(4)
O(2)	76(4)	109(4)	81(3)	-31(3)	23(3)	-24(4)
O(3)	44(3)	83(3)	67(3)	9(2)	-24(2)	-4(2)
O(4)	79(3)	39(2)	63(3)	1(2)	-14(2)	-9(2)
O(5)	71(3)	50(2)	55(2)	13(2)	6(2)	-17(3)
S(1)	47(1)	49(1)	46(1)	3(1)	-8(1)	-8(1)

Table S15. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for 7e

	x	y	z	U(eq)
H(2)	4302	856	4643	76
H(3)	6405	1671	4135	68
H(5)	3064	3745	3712	60
H(6)	984	2908	4202	68
H(7A)	6841	1494	3057	69
H(7B)	7667	1752	2455	69
H(8A)	4291	1241	2658	59
H(8B)	5413	919	2131	59
H(10)	4111	3547	2571	50
H(13)	5197	1195	1005	77
H(14)	6618	1742	188	100
H(15)	7759	3263	170	106
H(16)	7481	4301	943	86
H(21)	-334	5006	2257	59
H(22)	257	5727	1379	61
H(23)	1741	4915	672	60
H(24)	2805	3373	861	50
H(25A)	2406	1429	1212	55
H(25B)	2304	846	1792	55
H(26A)	-486	1495	1902	86
H(26B)	-343	1848	1260	86
H(3A)	5932	4500	1991	66
H(4)	256	3376	2893	55

Table S16. Torsion angles [°] for 7e.

C(6)-C(1)-C(2)-C(3)	-1.1(9)
N(1)-C(1)-C(2)-C(3)	179.2(5)
C(1)-C(2)-C(3)-C(4)	0.0(9)
C(2)-C(3)-C(4)-C(5)	1.7(8)
C(2)-C(3)-C(4)-S(1)	-175.1(4)
C(3)-C(4)-C(5)-C(6)	-2.5(8)
S(1)-C(4)-C(5)-C(6)	174.4(4)
C(2)-C(1)-C(6)-C(5)	0.4(9)
N(1)-C(1)-C(6)-C(5)	-179.9(5)

C(4)-C(5)-C(6)-C(1)	1.4(8)
N(2)-C(7)-C(8)-C(9)	31.3(6)
C(7)-C(8)-C(9)-C(12)	81.0(6)
C(7)-C(8)-C(9)-C(10)	-27.8(5)
C(7)-C(8)-C(9)-C(18)	-149.8(5)
C(12)-C(9)-C(10)-N(3)	16.2(5)
C(8)-C(9)-C(10)-N(3)	133.4(5)
C(18)-C(9)-C(10)-N(3)	-102.3(5)
C(12)-C(9)-C(10)-N(2)	-103.8(5)
C(8)-C(9)-C(10)-N(2)	13.4(5)
C(18)-C(9)-C(10)-N(2)	137.7(4)
C(16)-C(11)-C(12)-C(13)	3.0(8)
N(3)-C(11)-C(12)-C(13)	179.6(5)
C(16)-C(11)-C(12)-C(9)	-177.5(5)
N(3)-C(11)-C(12)-C(9)	-0.9(6)
C(8)-C(9)-C(12)-C(11)	-120.8(5)
C(10)-C(9)-C(12)-C(11)	-9.6(5)
C(18)-C(9)-C(12)-C(11)	108.6(5)
C(8)-C(9)-C(12)-C(13)	58.7(8)
C(10)-C(9)-C(12)-C(13)	169.8(6)
C(18)-C(9)-C(12)-C(13)	-72.0(7)
C(11)-C(12)-C(13)-C(14)	-3.4(9)
C(9)-C(12)-C(13)-C(14)	177.2(6)
C(12)-C(13)-C(14)-C(15)	2.2(10)
C(13)-C(14)-C(15)-C(16)	-0.5(12)
C(14)-C(15)-C(16)-C(11)	0.0(11)
C(12)-C(11)-C(16)-C(15)	-1.3(9)
N(3)-C(11)-C(16)-C(15)	-177.2(6)
O(5)-C(17)-C(18)-C(19)	174.7(5)
N(4)-C(17)-C(18)-C(19)	-5.0(5)
O(5)-C(17)-C(18)-C(25)	55.2(7)
N(4)-C(17)-C(18)-C(25)	-124.6(5)
O(5)-C(17)-C(18)-C(9)	-66.9(7)
N(4)-C(17)-C(18)-C(9)	113.3(5)
C(12)-C(9)-C(18)-C(19)	-60.5(6)
C(8)-C(9)-C(18)-C(19)	169.8(4)
C(10)-C(9)-C(18)-C(19)	51.4(6)
C(12)-C(9)-C(18)-C(25)	68.4(6)

C(8)-C(9)-C(18)-C(25)	-61.3(6)
C(10)-C(9)-C(18)-C(25)	-179.7(4)
C(12)-C(9)-C(18)-C(17)	-171.9(4)
C(8)-C(9)-C(18)-C(17)	58.4(6)
C(10)-C(9)-C(18)-C(17)	-60.0(6)
C(25)-C(18)-C(19)-C(24)	-62.2(7)
C(17)-C(18)-C(19)-C(24)	-177.6(5)
C(9)-C(18)-C(19)-C(24)	65.7(7)
C(25)-C(18)-C(19)-C(20)	120.3(5)
C(17)-C(18)-C(19)-C(20)	4.9(5)
C(9)-C(18)-C(19)-C(20)	-111.8(5)
C(24)-C(19)-C(20)-C(21)	-1.2(8)
C(18)-C(19)-C(20)-C(21)	176.7(5)
C(24)-C(19)-C(20)-N(4)	178.9(4)
C(18)-C(19)-C(20)-N(4)	-3.3(6)
C(19)-C(20)-C(21)-C(22)	-0.6(8)
N(4)-C(20)-C(21)-C(22)	179.3(5)
C(20)-C(21)-C(22)-C(23)	2.1(9)
C(21)-C(22)-C(23)-C(24)	-1.9(9)
C(20)-C(19)-C(24)-C(23)	1.4(8)
C(18)-C(19)-C(24)-C(23)	-175.9(5)
C(22)-C(23)-C(24)-C(19)	0.1(8)
C(19)-C(18)-C(25)-C(26)	-56.3(7)
C(17)-C(18)-C(25)-C(26)	55.0(6)
C(9)-C(18)-C(25)-C(26)	175.7(5)
C(18)-C(25)-C(26)-N(5)	-167.2(5)
C(6)-C(1)-N(1)-O(1)	-174.6(5)
C(2)-C(1)-N(1)-O(1)	5.1(9)
C(6)-C(1)-N(1)-O(2)	6.8(9)
C(2)-C(1)-N(1)-O(2)	-173.5(6)
N(3)-C(10)-N(2)-C(7)	-108.6(6)
C(9)-C(10)-N(2)-C(7)	6.2(6)
N(3)-C(10)-N(2)-S(1)	100.1(5)
C(9)-C(10)-N(2)-S(1)	-145.1(4)
C(8)-C(7)-N(2)-C(10)	-23.6(6)
C(8)-C(7)-N(2)-S(1)	127.5(4)
C(16)-C(11)-N(3)-C(10)	-171.4(6)
C(12)-C(11)-N(3)-C(10)	12.4(6)

N(2)-C(10)-N(3)-C(11)	96.4(5)
C(9)-C(10)-N(3)-C(11)	-18.1(6)
O(5)-C(17)-N(4)-C(20)	-176.3(5)
C(18)-C(17)-N(4)-C(20)	3.5(6)
C(21)-C(20)-N(4)-C(17)	179.9(5)
C(19)-C(20)-N(4)-C(17)	-0.2(6)
C(25)-C(26)-N(5)-N(6)	-92.1(8)
C(10)-N(2)-S(1)-O(4)	-30.0(5)
C(7)-N(2)-S(1)-O(4)	-178.4(5)
C(10)-N(2)-S(1)-O(3)	-160.6(4)
C(7)-N(2)-S(1)-O(3)	51.0(5)
C(10)-N(2)-S(1)-C(4)	84.6(5)
C(7)-N(2)-S(1)-C(4)	-63.8(6)
C(3)-C(4)-S(1)-O(4)	-159.3(5)
C(5)-C(4)-S(1)-O(4)	23.8(5)
C(3)-C(4)-S(1)-O(3)	-26.9(5)
C(5)-C(4)-S(1)-O(3)	156.1(4)
C(3)-C(4)-S(1)-N(2)	87.3(5)
C(5)-C(4)-S(1)-N(2)	-89.6(5)

Symmetry transformations used to generate equivalent atoms:

Table S17. Hydrogen bonds for 7e [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)