Chiral Naphthyl-C2-Indole as Scaffold for Phosphine Organocatalysis: Application in Asymmetric Formal [4 + 2] Cycloaddition Reactions

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Supporting Information

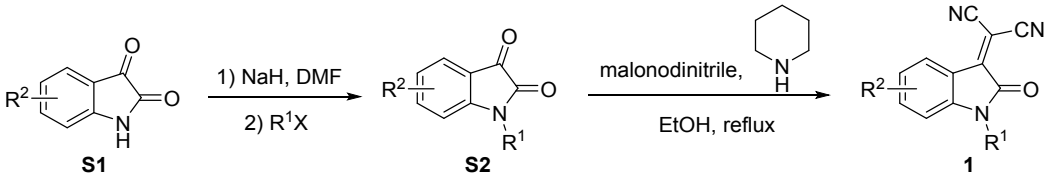
Contents

I. General information

^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on Agilent 400MR DD2 (400 MHz) spectrometer and Agilent 600MR DD2 (600 MHz) spectrometer. Chemical shifts were reported in parts per million (ppm), and tetramethylsilane or the residual solvent peak was used as an internal reference: $CDCl_3$ (^{1}H NMR δ 0.00, ^{13}C NMR δ 77.00), DMSO-d_6 (^{1}H NMR δ 2.50, ^{13}C NMR δ 39.52). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constants (Hz) and integration. Enantiomeric excesses (ee) were determined by HPLC analysis on Hitachi Chromaster using DAICEL CHIRALCEL AD-H, 4.6mm Φ × 250 mmL, DAICEL CHIRALCEL OD-H, 4.6mm Φ ×250 mmL, DAICEL CHIRALCEL ID-H, 4.6mm Φ × 250 mmL, DAICEL CHIRALCEL IA-H, 4.6mm Φ × 250 mmL, DAICEL CHIRALCEL IC-H, 4.6mm Φ × 250 mmL. High resolution mass spectra (HRMS) were performed on Bruker Solarix 7.0T. X-ray crystallography analysis of single crystal was performed on an Agilent SuperNova-CCD X-Ray diffractometer. Optical Rotation was measured on a Rudolph Autopol I polarimeter. Unless otherwise stated, all reagents were purchased from commercial suppliers and used without further purification.

II. General procedure for the synthesis of substrates 1 and *(E)*-2

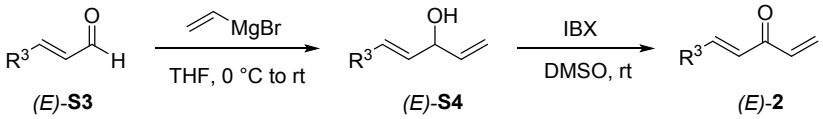
General procedure for the synthesis of substrates 1:



Isatins **S1** (3.0 mmol, 1.0 equiv) was dissolved in anhydrous DMF (15 mL), and the resultant solution was cooled to 0 °C, whereupon sodium hydride (60% dispersion in mineral oil, 3.6 mmol, 1.2 equiv) was added in one portion and stirred for 5-10 minutes. Iodomethane (3.3 mmol, 1.1 equiv) was added and the reaction was stirred at 0 °C for 30 minutes. The reaction was monitored by TLC until **S1** was fully consumed. The reaction mixture was then poured into saturated aqueous NH_4Cl and extracted with ethyl acetate. The combined organic portions were washed with water and brine, dried ($MgSO_4$), filtered, and concentrated to give *N*-substituted isatins **S2** (90%-98% yield).

The preparation of **1** was followed the literature procedure.[1] To a solution of the *N*-substituted isatins **S2** (5.0 mmol, 1.0 equiv) in anhydrous ethanol (10 mL) malonodinitrile (6.0 mmol, 1.2 equiv) was added, as well as one drop piperidine as catalyst. The reaction mixture was refluxed for 1 h (oil bath). After cooling, the precipitated solid was collected by filtration and washed with cold ethanol (10 mL) to afford analytically pure compounds **1** (80%-95% yield).

General procedure for the synthesis of substrates *(E)*-2:

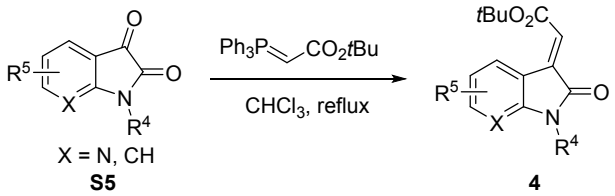


The preparation of *(E)*-**2** was followed the literature procedure.[2] Into a 50 mL oven-dried three-necked bottle under Ar gas protection were added *(E)*-**S3** (10 mmol, 1.0 equiv) and THF (15 mL). The solution was cooled to 0 °C and vinylmagnesium bromide (11 mmol, 1.1 equiv) in THF was added dropwise to the solution within 30 minutes. The mixture was stirred at room temperature overnight and quenched with saturated NH_4Cl. The solution was extracted with ethyl acetate for three times, the combined organic layer was washed with saturated NaCl and dried over Na_2SO_4. The organic layer was

concentrated and purified by column chromatography on silica gel (PE/EA, 5:1). The obtaining alcohol product *(E)*-**S4** (10 mmol, 1.0 equiv) was dissolved in DMSO (20 mL) and IBX (15 mmol, 1.5 equiv) was added, the mixture was stirred at room temperature overnight. The reaction mixture was then diluted with dichloromethane and filtered through celite. The solvent was washed with water for three times and saturated NaCl. After dried over Na_2SO_4, the solvent was concentrated and purified by column chromatography on silica gel (PE/EA, 15:1) to give compounds *(E)*-**2** (80%-95% yield).

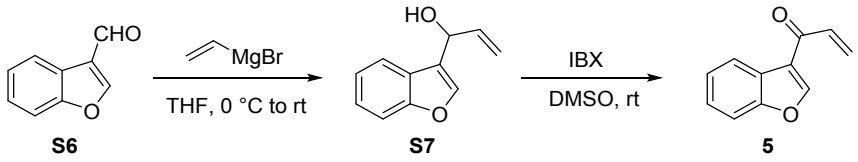
III. General procedure for the synthesis of substrates 4 and 5

General procedure for the synthesis of substrates 4:



The preparation of **4** was followed the literature procedure.[3] To a solution of the *N*-substituted isatins **S5** (2.0 mmol, 2.0 equiv) in $CHCl_3$ (5 mL) was added Wittig reagent (1.0 mmol, 1.0 equiv). The resulting mixture was stirred at room temperature for 10 h or reflux for 6 h (oil bath). Then the mixture was concentrated under reduced pressure and purified by flash chromatography on silica gel (PE/EA, 20:1) to give compounds **4** (70%-90% yield).

General procedure for the synthesis of substrate 5:

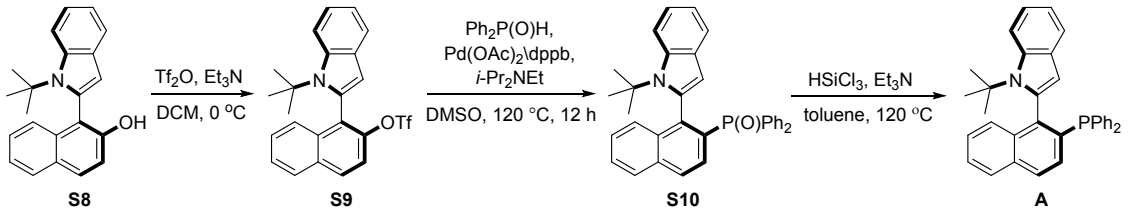


The preparation of **5** was followed the literature procedure.[4] A suspension of benzofuran-3-carbaldehyde **S6** (5.0 mmol, 1.0 equiv) in anhydrous THF (20 mL) was stirred and cooled to 0 °C, and vinylmagnesium bromide (6.0 mmol, 1.2 equiv) was slowly added under argon atmosphere. The resulting yellow suspension was warmed to room temperature and stirred for 6 h. After complete conversion (monitored by TLC), the reaction was quenched with aqueous NH_4Cl and extracted with EtOAc. The combined organic phases were dried (Na_2SO_4), filtered and evaporated. The crude residue was purified by flash chromatography on silica gel (PE/EA, 10:1) to give the alcohol **S7** as a yellow oil in 80% yield. The alcohol **S7** (4.0 mmol, 1.0 equiv) was dissolved in DMSO (10 mL), and IBX (6.0 mmol, 1.5 equiv) was added at room temperature. After complete conversion (monitored by TLC), the mixture was extracted with EtOAc. The combined organic phases were dried over Na_2SO_4. The solvent was removed under reduced pressure, and the residue was purified by flash chromatography on silica gel (PE/EA, 15:1) to give pure compound **5** as a white solid in 97% yield.

IV. General procedure for the synthesis of organocatalysts (A-H)

The organocatalysts were synthesized mainly according to the literature procedures.[5]

Synthesis of organocatalysts A:

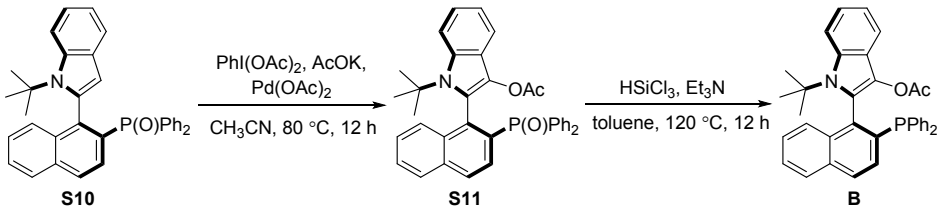


Under argon atmosphere at 0 °C, **S8**[5] (1.0 g, 3.2 mmol, >99% ee) was dissolved in dichloromethane (30 mL), which was added Et_3N (2.7 mL, 19.2 mmol). Then, Tf_2O (1.1 mL, 6.4 mmol) was added dropwise to the reaction mixture at 0 °C, which was further stirred at room temperature for 12 h. After the completion of the reaction indicated by TLC, the reaction mixture was diluted by dichloromethane and quenched by hydrochloric acid (1 M). The resultant mixture was extracted by dichloromethane, and the organic layer was washed successively by saturated $NaHCO_3$ aqueous solution and saturated NaCl aqueous solution. Subsequently, the resultant organic layer was dried by anhydrous Na_2SO_4 and purified by flash column chromatography on silica gel (PE/EA, 15:1) to afford **S9** as a white solid in 85% yield.

A three-necked round-bottom flask charged with a mixture of triflate **S9** (1.0 g, 2.2 mmol), diphenylphosphine oxide (890 mg, 4.4 mmol), 1,4-Bis(diphenylphosphino)butane (dppb) (94 mg, 0.22 mmol), $Pd(OAc)_2$ (49 mg, 0.22 mmol) and diisopropylethylamine (1.8 mL, 11.0 mmol) in 40 mL of DMSO was heated to 120 °C for 12 h (oil bath) under argon atmosphere. The solvent was removed under reduced pressure. To the residue were added water (20 mL) and EtOAc (50 mL), and the organic phase was washed with 10% HCl (3 x 50 mL), brine, and water and finally dried over Na_2SO_4. Evaporation to dryness yielded a crude material which was purified by flash column chromatography on silica gel (PE/EA, 3:1) to yield the pure product **S10** as a colorless solid in 90% yield.

Under argon atmosphere at 0 °C, $HSiCl_3$ (4.0 mL, 40.0 mmol) was carefully added to a mixture of phosphine oxide (1.0 g, 2.0 mmol) and triethylamine (13.3 mL, 96.0 mmol) in toluene (40 mL) in a three-necked round-bottom flask under argon atmosphere. The mixture was heated to reflux for 16-24 h (oil bath). To the cooled mixture was added ether and sodium bicarbonate. Solids were removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA, 15:1) to give the product **A** as a colorless solid in 70% yield.

Synthesis of organocatalysts B:

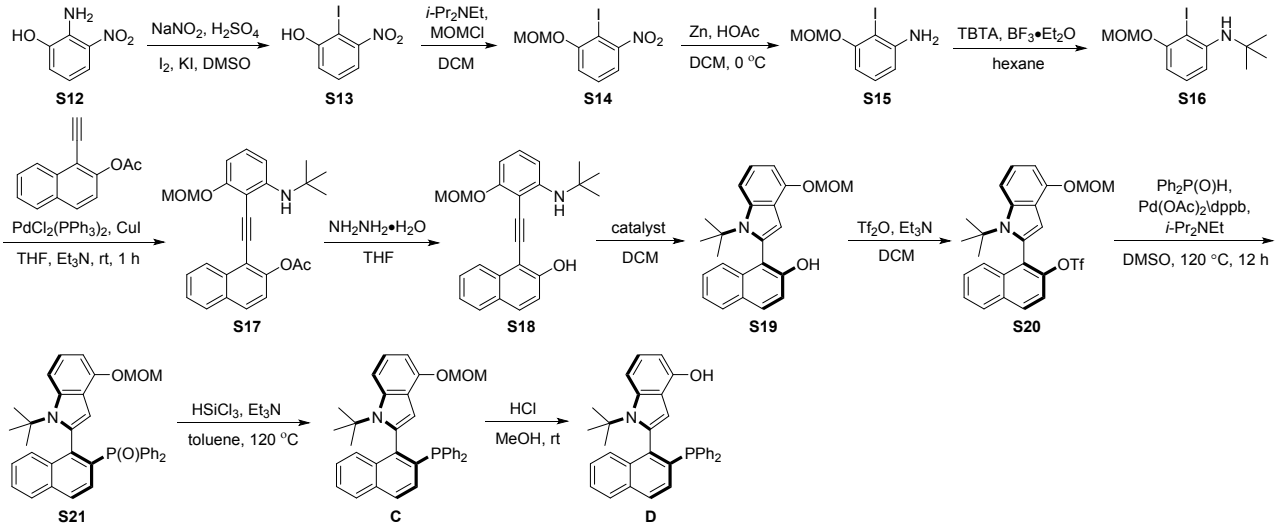


$Pd(OAc)_2$ (898 mg, 4.0 mmol), $PhI(OAc)_2$ (1.3 g, 4.0 mmol), **S10** (1.0 g, 2.0 mmol), and AcOK (196 mg, 2.0 mmol) were loaded into a three-necked round-bottom flask. The flask was evacuated and flushed with nitrogen three times. The solvent acetonitrile (30 mL) was then added with stirring at room temperature for several minutes. The flask was then placed into

a preheated oil bath (80 °C) and stirred for 4 h. After completion of the reaction as judged by TLC, the reaction flask was allowed to cool to room temperature and quenched with sodium bisulfate solution and water. EtOAc was then added for dilution. The organic layer was separated, and the aqueous layer was washed with EtOAc. The filtrate was concentrated under reduced pressure. The crude products were purified by flash column chromatography on silica gel (PE/EA, 2:1) to give the compound **S11** as a yellow solid in 85% yield.

Under argon atmosphere at 0 °C, $HSiCl_3$ (3.6 mL, 36.0 mmol) was carefully added to a mixture of phosphine oxide (1.0 g, 1.8 mmol) and triethylamine (12.0 mL, 86.4 mmol) in toluene (40 mL) in a three-necked round-bottom flask under argon atmosphere. The mixture was heated to reflux for 16-24 h (oil bath). To the cooled mixture was added ether and sodium bicarbonate. Solids were removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel (PE/EA, 15:1) to give the product **B** as a yellow solid in 90% yield.

Synthesis of organocatalysts C and D:



Into a solution of 2-amino-3-nitrophenol **S12** (5.92 g, 38.4 mmol) in DMSO (100 mL) was added 30% H_2SO_4 (200 mL). The mixtures were stirred for 1 h to effect solution, After cooled to 0 °C with an ice-water bath, the mixture was treated with a solution of $NaNO_2$ (3.97 g, 57.6 mmol) in deionized H_2O (20 mL) in 15 minutes. The reaction mixture was stirred at 0 °C for 1 h, after which a solution of KI (9.57 g, 57.6 mmol) and I_2 (7.30 g, 28.8 mmol) in 50 mL of deionized H_2O was added. After 1 h of stirring at room temperature, another batch of KI (3.19 g, 19.2 mmol) and I_2 (3.65 g, 14.4 mmol) in 50 mL of deionized H_2O was then added. The reaction mixture was stirred at room temperature for another 1 h and 80 °C for 2 h (oil bath). EtOAc (250 mL) was added, and the mixture was washed sequentially with brine, 10% $NaHSO_3$, and water. The organic phase was dried over Na_2SO_4, filtered, and concentrated. The residue was purified by flash chromatography on silica gel (hexane/EA, 5:1) to give **S13** as a brown yellow solid in 80% yield.

S13 (3.78 g, 15.0 mmol) was dissolved in CH_2Cl_2 (25 mL) at 0 °C. *N*, *N*-Diisopropylethylamine (4.46 mL, 27.0 mmol) was added slowly to solution, after 10 minutes, methoxymethyl chloride (1.71 mL, 22.5 mmol) was slowly added to solution, then the reaction mixture was warmed up to room temperature and stirred for 30 minutes. The aqueous layer was washed twice with CH_2Cl_2, The organic layer was dried over Na_2SO_4 and evaporated to dryness, which was purified by flash chromathography (PE/EA, 5:1) to yield **S14** as a white solid in 95% yield.

A suspension of **S14** (2.50 g, 8.1 mmol) and zinc dust (15.89 g, 243.0 mmol) in DCM was added HOAc (7.29 mL) dropwise at 0 °C, and allowed to stir at 0 °C for another 10 minutes. The reaction mixture was filtered and washed with DCM. The

filtrate was evaporated to dryness and subjected to flash column chromatography (PE/EA, 4:1) to give **S15** in 85% yield as a yellow oil.

To a stirred solution of **S15** (3.00 g, 10.7 mmol) in hexane at room temperature under argon, were successively added tert-butyl 2,2,2-trichloroacetimidate (TBTA) (4.79 mL, 26.8 mmol) and a few drops of $BF_3 \cdot Et_2O$. The formation of a white precipitate was usually observed. The reaction was monitored by TLC and if needed, extra TBTA and $BF_3 \cdot Et_2O$ were added. When starting material was totally consumed, the solvent was evaporated in vacuo and the resulting crude residue was purified by flash column chromatography (PE/EA, 10:1) to give **S16** in 90% yield as a yellow oil.

$PdCl_2(PPh_3)_2$ (365 mg, 0.52 mmol), CuI (198 mg, 1.04 mmol) and **S16** (3.50 g, 10.44 mmol) were weighed and added into an oven dried flask, evacuated and backfilled with nitrogen (3 times), toluene (25 mL) was injected into the flask, then triethylamine (15 mL) was slowly added. After that, the alkyne (2.63 g, 12.53 mmol) dissolved in toluene (10 mL) was added slowly. The resulting mixture kept stirring at 80 °C for 6 h (oil bath). Then the mixture was filtered through a pad of celite and washed with EA. Removal of solvent under reduced pressure, purified by flash chromatography on silica gel (PE/EA, 8:1) to afford **S17** in 80% yield as a yellow solid.

To a stirred solution of **S17** (2.0 g, 4.8 mmol) in THF (20 mL) was added hydrazine monohydrate (50%, 0.86 mL, 14.4 mmol) dropwise at room temperature. Then, the resulting solution was kept stirring until **S17** was fully consumed. Quenched with NH_4Cl, extracted with EA, washed with brine, dried over Na_2SO_4 and filtered, concentrated under reduced pressure and purified by flash column chromatography (PE/EA, 5:1) to afford the desired product **S18** in 95% yield as a yellow solid.

The asymmetric preparation of **S19** was followed the known literature procedure.[5] A flame-dried Schlenk tube equipped with a magnetic stirring bar was charged with **S18** (751 mg, 2.0 mmol) and quinine-derived thiourea catalyst (119 mg, 0.2 mmol). DCM (30 mL) was injected into the tube at room temperature. After stirring for 24 h, the mixture was purified by silica gel chromatography (PE/EA, 5:1) to afford the chiral product **S19** as a white solid in 90% yield.

Under argon atmosphere at 0 °C, **S19** (1.0 g, 2.7 mmol, >99% ee) was dissolved in dichloromethane (30 mL), which was added Et_3N (2.3 mL, 16.2 mmol). Then, Tf_2O (0.9 mL, 5.4 mmol) was added dropwise to the reaction mixture, which was further stirred at 0 °C for 6 h. After the completion of the reaction indicated by TLC, the reaction mixture was diluted by dichloromethane and quenched by hydrochloric acid (1 M). The resultant mixture was extracted by dichloromethane, and the organic layer was washed successively by saturated $NaHCO_3$ aqueous solution and saturated NaCl aqueous solution. Subsequently, the resultant organic layer was dried by anhydrous Na_2SO_4 and purified by flash column chromatography (PE/EA, 15:1) to afford **S20** as a white solid in 80% yield.

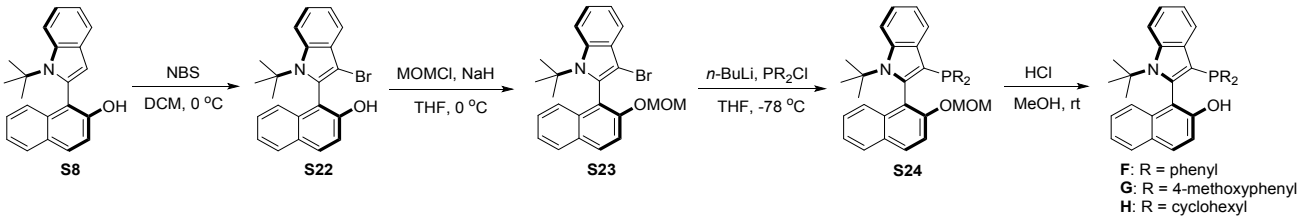
A three-necked round-bottom flask charged with a mixture of triflate **S20** (1.0 g, 2.0 mmol), diphenylphosphine oxide (809 mg, 4.0 mmol), 1,4-Bis(diphenylphosphino)butane (dppb) (85 mg, 0.2 mmol), $Pd(OAc)_2$ (45 mg, 0.2 mmol) and diisopropylethylamine (1.7 mL, 10.0 mmol) in 20 mL of DMSO was heated to 120 °C for 12 h (oil bath) under argon atmosphere. The solvent was removed under reduced pressure. To the residue were added water (20 mL) and EtOAc (50 mL), and the organic phase was washed with 10% HCl (3 x 50 mL), brine, and water and finally dried over Na_2SO_4. Evaporation to dryness yielded a crude material which was purified by flash column chromatography (PE/EA, 2:1) to yield the pure product **S21** as a colorless solid in 90% yield.

Under argon atmosphere at 0 °C, $HSiCl_3$ (3.6 mL, 36.0 mmol) was carefully added to a mixture of phosphine oxide (1.0 g, 1.8 mmol) and triethylamine (12.0 mL, 86.4 mmol) in toluene (40 mL) in a three-necked round-bottom flask under argon atmosphere. The mixture was heated to reflux for 16-24 h (oil bath). To the cooled mixture was added ether and sodium

bicarbonate. Solids were removed by filtration and the solvent was removed under reduced pressure. The residue was purified by flash column chromatography (PE/EA, 10:1) to give the compound **C** as a colorless solid in 90% yield.

C (2.0 mmol) was dissolved in MeOH (25 mL), and then HCl (36%, 13.5 mL) was slowly added. The resulted mixture was stirred at room temperature until deprotection is completed. The acid was neutralized with water. The organic material was extracted with dichloromethane, and dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE/EA, 8:1) to afford the compound **D** as a white solid in 95% yield.

Synthesis of organocatalysts E，F，G and H:



The NBS (605 mg, 3.4 mmol) was dissolved in DCM (20 mL) containing compound **S8**[5] (1.0 g, 3.2 mmol, >99% ee). The resulting mixture was stirred for 8 h at 0 °C. Subsequently, the solvent was removed under reduced pressure to obtain a yellow oily residue, which was purified by column chromatography (PE/EA, 5:1) to afford compound **S22** as a white solid in 95% yield.

To a suspension of NaH (60%, 148 mg, 3.7 mmol) in THF (20 mL) under argon flow were added **S22** (1.0 g, 2.5 mmol) at 0 °C, by small portions. The suspension was kept under stirring for 1 h at room temperature, methoxymethyl chloride (0.34 mL, 4.5 mmol) were added slowly, and the reaction mixture was stirred for 10 additional hours. The reaction was carefully diluted with water and the organic part was extracted with EtOAc. The combined organic extracts were washed with water, brine and dried over anhydrous Na_2SO_4. Concentration and flash chromatography on a silica column (PE/EA, 8:1) afforded compound **S23** as a white solid in 90% yield.

S23 (1.0 g, 2.3 mmol) was dissolved in freshly distilled THF (10 mL) at room temperature under nitrogen atmosphere. The solution was cooled to -78 °C. Then, *n*-BuLi (1.2 mL, 2.5 M in hexane, 3.0 mmol) was added dropwise by syringe. After the reaction mixture was stirred for 30 minutes at -78°C, appropriate chlorodiphenylphosphines (3.5 mmol) in THF (5 mL) was added dropwise. The reaction was allowed to warm to room temperature and stirred overnight. Solvent was removed under reduced pressure. After the solvent was removed under vacuum, the product was successively washing with cold MeOH. The product was then dried under vacuum and flash chromatography on a silica column (PE/EA, 8:1) afforded compounds **S24** as a white solid in 60%-85% yield.

S24 (2.0 mmol) was dissolved in MeOH (25 mL), and then HCl (36%, 13.5 mL) was slowly added. The resulted mixture was stirred at room temperature until deprotection is completed. The acid was neutralized with water. The organic material was extracted with dichloromethane, and dried over anhydrous Na_2SO_4. Removal of solvent under reduced pressure afford a residue which is purified by chromatography on silica gel (PE/EA, 8:1) to afford the pure compounds as white solid in 90%-95% yield.

V. Optimization of the reaction conditions

Optimization of the reaction conditions A:

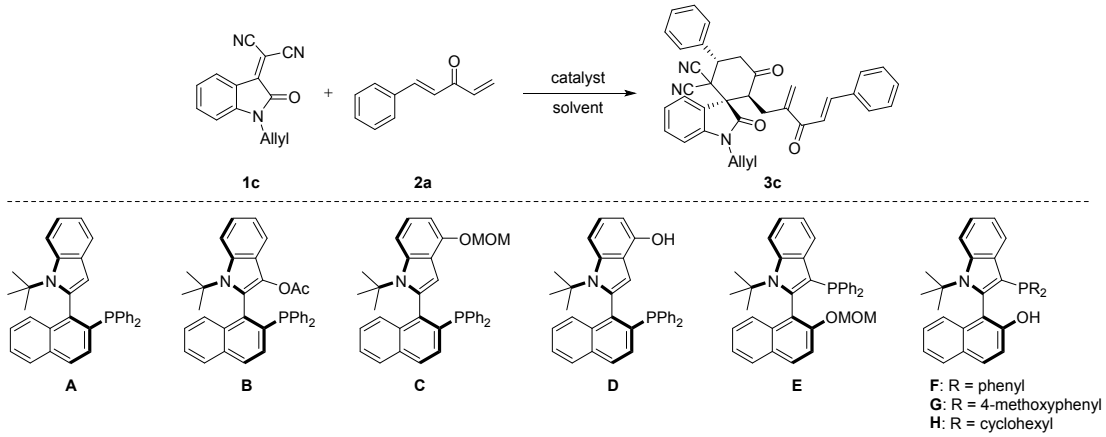


Table 1. Screening of catalyst[a]

entry	catalyst (10 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**A**	toluene	12	25	<10	-79	-
2	**B**	toluene	12	25	<10	-85	-
3	**C**	toluene	12	25	-	-	-
4	**D**	toluene	12	25	<10	-49	-
5	**E**	toluene	12	25	94	5	>20:1
6	**F**	toluene	12	25	95	98	>20:1
7	**G**	toluene	12	25	89	97	18:1
8	**H**	toluene	12	25	90	98	18:1

[a]Reaction conditions: **1c** (0.10 mmol), catalyst (10 mol %) and **2a** (0.25 mmol) in toluene (2.0 mL) at 25 °C for 12 h under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

Table 2. Screening of solvent[a]

entry	catalyst (10 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**F**	toluene	12	25	95	98	>20:1
2	**F**	$PhCF_3$	12	25	93	98	>20:1
3	**F**	DCM	12	25	85	98	15:1
4	**F**	$CHCl_3$	12	25	88	98	18:1
5	**F**	THF	12	25	88	97	15:1
6	**F**	MeCN	12	25	96	93	>20:1

[a]Reaction conditions: **1c** (0.10 mmol), catalyst **F** (10 mol %) and **2a** (0.25 mmol) in solvent (2.0 mL) at 25 °C for 12 h under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

Table 3. Screening of temperature[a]

entry	catalyst (10 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**F**	toluene	24	-10	85	>99	>20:1
2	**F**	toluene	24	0	94	>99	>20:1
3	**F**	toluene	12	10	94	99	>20:1
4	**F**	toluene	12	25	95	98	>20:1
5	**F**	toluene	12	35	95	98	>20:1
6	**F**	toluene	12	50	95	97	>20:1
7[e]	**F**	toluene	24	0	94	96	>20:1

[a]Reaction conditions: **1c** (0.10 mmol), catalyst **F** (10 mol %) and **2a** (0.25 mmol) in toluene (2.0 mL) under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR. [e]With 4 Å MS (40 mg).

Table 4. Catalyst loading screening[a]

entry	catalyst (mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**10**	toluene	24	0	94	>99	>20:1
2	**5**	toluene	24	0	93	>99	>20:1
3	**2.5**	toluene	24	0	65	>99	>20:1

[a]Reaction conditions: **1c** (0.10 mmol), catalyst **F** and **2a** (0.25 mmol) in toluene (2.0 mL) at 0 °C for 24 h under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

Optimization of the reaction conditions B:

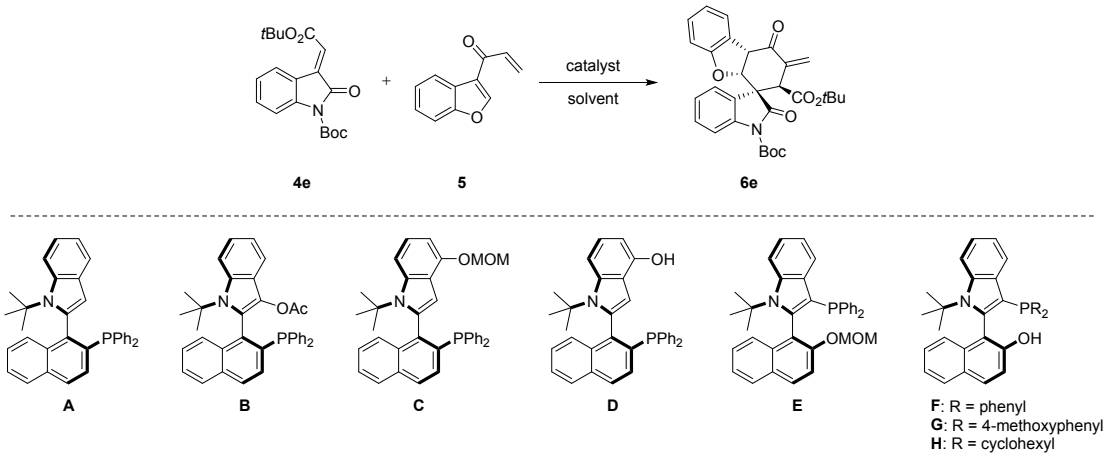


Table 5. Screening of catalyst[a]

entry	catalyst (5 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**A**	toluene	12	25	-	-	-
2	**B**	toluene	12	25	-	-	-

3	**C**	toluene	12	25	-	-	-
4	**D**	toluene	12	25	-	-	-
5	**E**	toluene	12	25	<10	2	-
6	**F**	toluene	12	25	72	>99	>20:1
7	**G**	toluene	12	25	55	>99	18:1
8	**H**	toluene	12	25	39	>99	15:1

[a]Reaction conditions: **4e** (0.075 mmol), catalyst (5 mol %) and **5** (0.05 mmol) in toluene (1.0 mL) at 25 °C for 12 h under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

Table 6. Screening of solvent[a]

entry	catalyst (5 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**F**	toluene	12	25	72	>99	>20:1
2	**F**	$PhCF_3$	12	25	53	>99	15:1
3	**F**	DCM	12	25	40	>99	12:1
4	**F**	$CHCl_3$	12	25	45	>99	15:1
5	**F**	THF	12	25	38	>99	10:1

[a]Reaction conditions: **4e** (0.075 mmol), catalyst **F** (5 mol %) and **5** (0.05 mmol) in solvent (1.0 mL) at 25 °C for 12 h under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

Table 7. Screening of temperature[a]

entry	catalyst (5 mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**F**	toluene	12	0	39	>99	>20:1
2	**F**	toluene	12	15	64	>99	>20:1
3	**F**	toluene	12	25	72	>99	>20:1
4	**F**	toluene	12	35	68	>99	18:1
5	**F**	toluene	12	50	65	>99	15:1
6[e]	**F**	toluene	12	25	80	>99	>20:1
7[e,f]	**F**	toluene	12	25	75	>99	>20:1

[a]Reaction conditions: **4e** (0.075 mmol), catalyst **F** (5 mol %) and **5** (0.05 mmol) in toluene (1.0 mL) under N_2. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR. [e]Substrate **5** was added in two portions. [f]With 4 Å MS (20 mg).

Table 8. Catalyst loading screening[a]

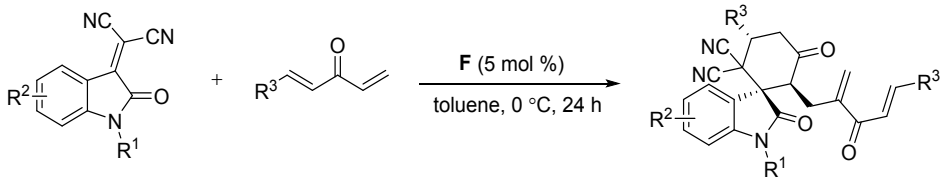
entry	catalyst (mol %)	solvent	time (h)	T (°C)	yield (%)[b]	ee (%)[c]	dr[d]
1	**10**	toluene	12	25	81	>99	>20:1
2	**5**	toluene	12	25	80	>99	>20:1

3	**2.5**	toluene	12	25	58	>99	15:1

[a]Reaction conditions: **4e** (0.075 mmol), catalyst **F** and **5** (0.05 mmol) in toluene (1.0 mL) at 25 °C for 12 h under N_2, substrate **5** was added in two portions. [b]Isolated yield. [c]Determined by HPLC analysis on a chiral stationary phase. [d]Diastereomeric ratio (dr) was determined by ^{1}H NMR.

VI. General procedures for the asymmetric process

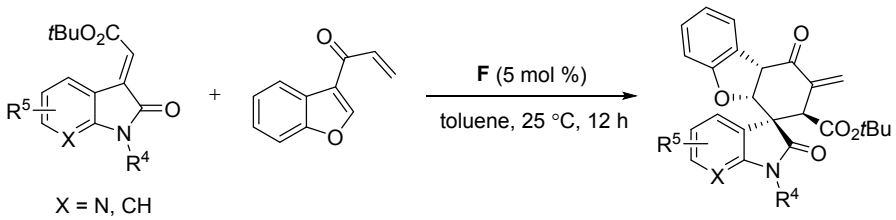
General procedure for the synthesis of compounds 3:



1 **2** **3**

A flame-dried Schlenk tube equipped with a magnetic stirring bar were charged with **1** (0.10 mmol, 1.0 equiv), *(E)*-**2** (0.25 mmol, 2.5 equiv), and catalyst **F** (2.5 mg, 5 mol %), toluene (2.0 mL) was added and the reaction mixture was stirred at 0 °C for 24 h under N_2. After completion, the reaction mixture was purified by flash chromatography on silica gel (EtOAc/ petroleum ether, 1:8 to 1:4) to give the pure products **3**.

General procedure for the synthesis of compounds 6:

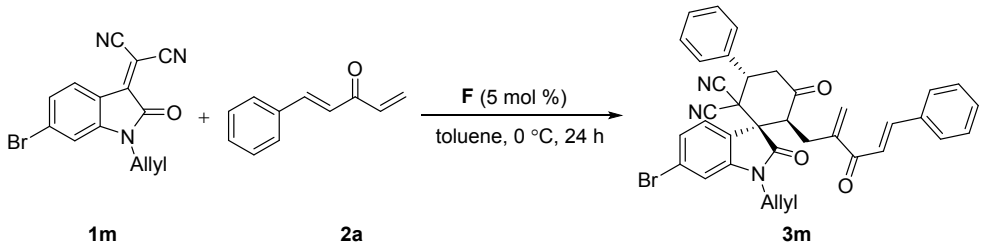


4 **5** **6**

A flame-dried Schlenk tube equipped with a magnetic stirring bar were charged with 3-olefinic oxindole **4** (0.15 mmol, 1.5 equiv), 3-benzofuranyl vinyl ketone **5** (0.1 mmol, 1.0 equiv), and catalyst **F** (2.5 mg, 5 mol %), toluene (2.0 mL) was added and the reaction mixture was stirred at 25 °C for 12 h under N_2, Substrate **5** was added in two portions at 1 h interval. After completion, the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether, 1:10 to 1:4) to give the pure products **6**.

VII. Asymmetric reactions at 1.0 mmol

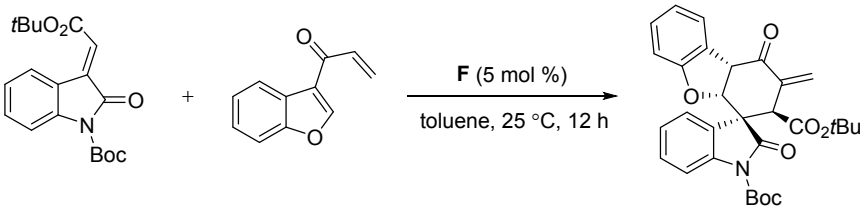
Asymmetric reaction for the synthesis of compound 3m at 1.0 mmol:



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

A flame-dried Schlenk tube equipped with a magnetic stirring bar were charged with **1m** (314 mg, 1.0 mmol), *(E)*-**2a** (396 mg, 2.5 mmol), and catalyst **F** (25 mg, 5 mol %), toluene (20 mL) was added and the reaction mixture was stirred at 0 °C for 24 h under N_2. After completion, the reaction mixture was purified by flash chromatography on silica gel (EtOAc/ petroleum ether, 1:8) to give the pure products **3m**: white solid, 567 mg, 90% yield, 98% ee, >20:1 dr.

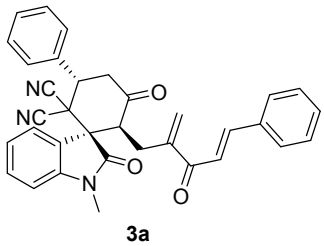
Asymmetric reaction for the synthesis of compound 6e at 1.0 mmol:



4e **5** **6e**

A flame-dried Schlenk tube equipped with a magnetic stirring bar were charged with 3-olefinic oxindole **4e** (518 mg, 1.5 mmol), 3-benzofuranyl vinyl ketone **5** (172 mg, 1.0 mmol), and catalyst **F** (25 mg, 5 mol %), toluene (20 mL) was added and the reaction mixture was stirred at 25 °C for 12 h under N_2, Substrate **5** was added in two portions at 1 h interval. After completion, the reaction mixture was purified by flash chromatography on silica gel (EtOAc/petroleum ether, 1:10) to give the pure products **6e**: white solid, 424 mg, 82% yield, >99% ee, >20:1 dr.

VIII. Analytic data of compounds (3a-3t, 6a-6t)



3a

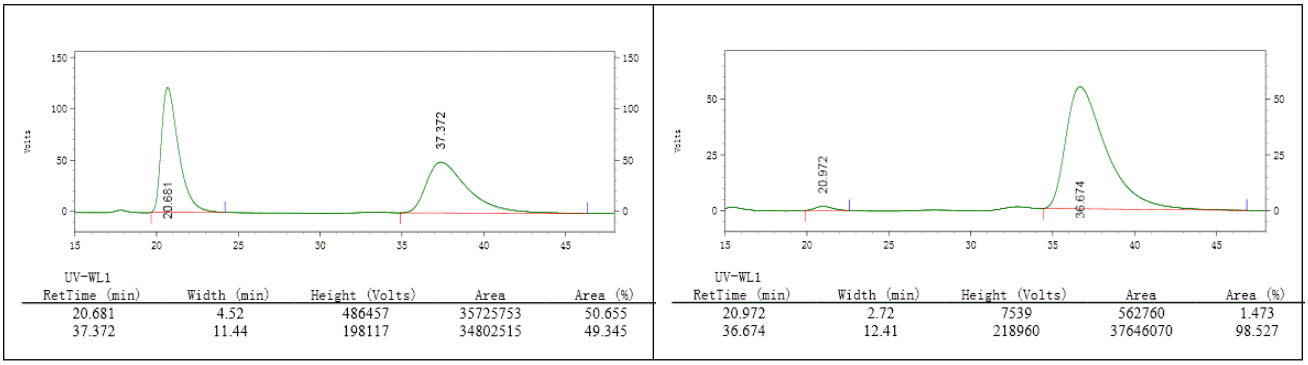
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.33 (m, 12H), 7.26 – 7.20 (m, 1H), 7.06 (d, *J* = 15.7 Hz, 1H), 6.94 (d, *J* = 7.8 Hz, 1H), 5.95 (s, 1H), 5.83 (s, 1H), 4.74 (dd, *J* = 13.9, 3.9 Hz, 1H), 3.77 (dd, *J* = 8.3, 4.0 Hz, 1H), 3.40 – 3.25 (m, 4H), 2.88 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.78 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.86 (dd, *J* = 14.0, 4.1 Hz, 1H).

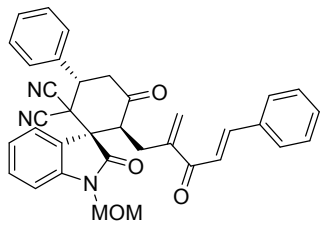
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 190.4, 171.8, 145.3, 143.7, 143.6, 134.5, 134.4, 131.0, 130.3, 129.4, 128.9, 128.8, 128.7, 128.1, 127.3, 125.7, 124.1, 123.9, 120.7, 112.1, 111.6, 109.0, 58.2, 48.5, 48.5, 43.0, 42.4, 27.7, 26.6.

HRMS (ESI) m/z Calcd for $[C_{34}H_{27}N_3NaO_3, M+ Na]^+$: 548.1945, Found: 548.1942.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 20.972 min (minor), t_R = 36.674 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 89.4 ° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 94%, 49.4 mg.





3b

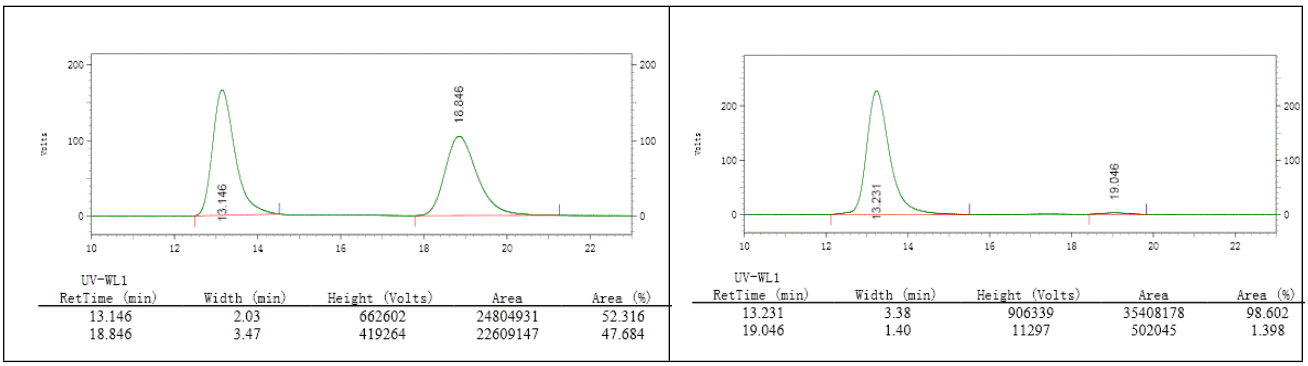
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.35 (m, 12H), 7.29 (t, *J* = 7.7 Hz, 1H), 7.17 (d, *J* = 7.9 Hz, 1H), 7.08 (d, *J* = 15.7 Hz, 1H), 5.98 (s, 1H), 5.87 (s, 1H), 5.22 (q, *J* = 11.0 Hz, 2H), 4.69 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.78 (dd, *J* = 8.4, 3.8 Hz, 1H), 3.45 (s, 3H), 3.35 (t, *J* = 14.3 Hz, 1H), 2.90 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.78 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.88 (dd, *J* = 13.8, 3.8 Hz, 1H).

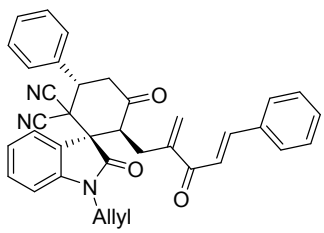
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 190.5, 172.7, 145.2, 143.8, 142.2, 134.6, 134.3, 131.2, 130.4, 129.6, 129.0, 128.8, 128.8, 128.2, 127.5, 125.8, 124.5, 123.8, 120.7, 112.0, 111.8, 110.5, 72.1, 58.8, 57.0, 48.9, 48.6, 43.4, 42.6, 27.7.

HRMS (ESI) m/z Calcd for $[C_{35}H_{29}N_3NaO_4, M+Na]^+$: 578.2050, Found: 578.2047.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 13.231 min (major), t_R = 19.046 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 70.7° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 85%, 47.2 mg.





3c

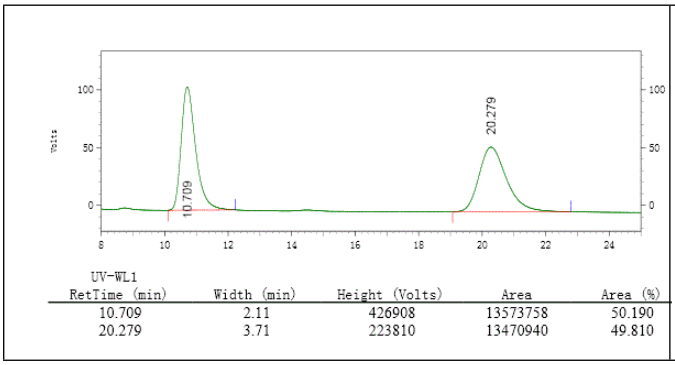
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 7.2 Hz, 1H), 7.63 – 7.29 (m, 12H), 7.20 (t, *J* = 8.1 Hz, 1H), 7.07 (d, *J* = 15.6 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 5.94 (s, 1H), 5.91 – 5.78 (m, 2H), 5.34 (dd, *J* = 40.1, 13.8 Hz, 2H), 4.75 (dd, *J* = 13.8, 3.9 Hz, 1H), 4.53 (dd, *J* = 16.3, 5.2 Hz, 1H), 4.33 (dd, *J* = 16.3, 5.7 Hz, 1H), 3.81 (dd, *J* = 8.0, 4.0 Hz, 1H), 3.33 (t, *J* = 14.3 Hz, 1H), 2.84 (ddd, *J* = 22.8, 15.5, 6.0 Hz, 2H), 1.87 (dd, *J* = 16.0, 4.0 Hz, 1H).

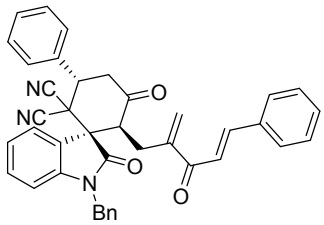
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 190.3, 171.6, 145.2, 143.5, 142.8, 134.4, 134.3, 130.8, 130.2, 130.1, 129.3, 128.8, 128.7, 128.0, 127.2, 125.6, 124.1, 123.8, 120.7, 118.8, 112.1, 111.7, 109.9, 57.9, 48.7, 48.4, 43.1, 42.8, 42.3, 27.5.

HRMS (ESI) m/z Calcd for $[C_{36}H_{29}N_3NaO_3, M+Na]^+$: 574.2101, Found: 574.2073.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.659 min (major), t_R = 20.183 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 81.1° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 93%, 51.3 mg.





3d

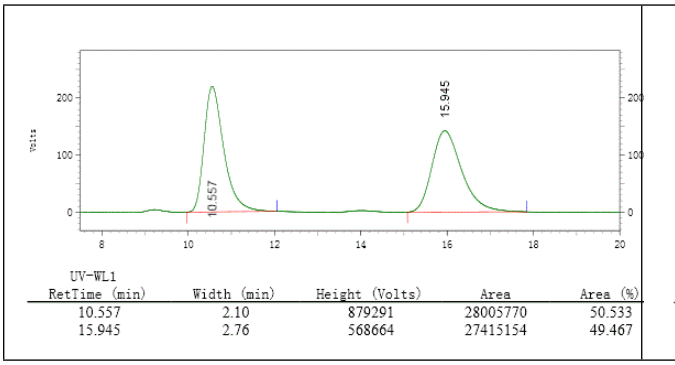
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.24 (m, 17H), 7.17 (t, *J* = 7.7 Hz, 1H), 7.03 (d, *J* = 15.7 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.86 (s, 1H), 5.62 (s, 1H), 5.11 – 4.92 (m, 2H), 4.80 (dd, *J* = 13.8, 3.9 Hz, 1H), 3.83 (dd, *J* = 8.1, 4.2 Hz, 1H), 3.34 (t, *J* = 14.3 Hz, 1H), 2.87 (ddd, *J* = 32.7, 14.3, 6.0 Hz, 2H), 1.85 (dd, *J* = 13.9, 4.2 Hz, 1H).

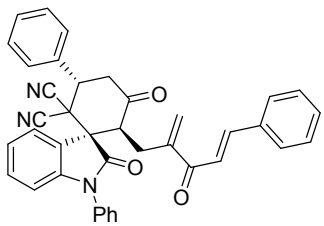
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 190.4, 172.1, 145.2, 143.6, 142.9, 134.5, 134.4, 134.4, 130.9, 130.3, 129.4, 128.9, 128.8, 128.8, 128.1, 128.0, 127.5, 127.3, 125.7, 124.2, 123.9, 120.7, 112.1, 111.8, 110.1, 58.0, 48.9, 48.4, 44.5, 43.2, 42.5, 27.7.

HRMS (ESI) m/z Calcd for $[C_{40}H_{31}N_3NaO_3, M+Na]^+$: 624.2258, Found: 624.2260.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.608 min (major), t_R = 16.097 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 54.8° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 85%, 51.1 mg.





3e

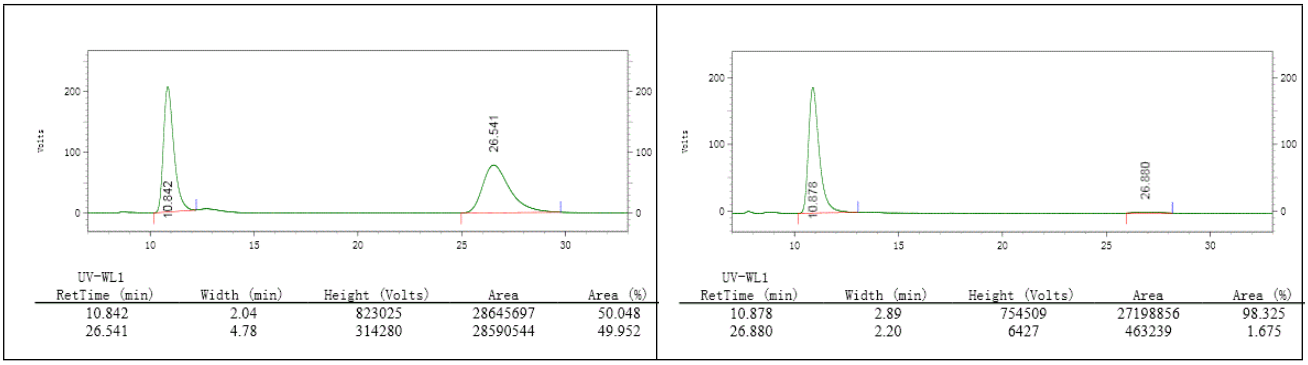
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 7.6 Hz, 1H), 7.64 – 7.43 (m, 10H), 7.43 – 7.31 (m, 7H), 7.25 (t, *J* = 8.7 Hz, 1H), 7.08 (d, *J* = 15.7 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 5.96 (d, *J* = 27.4 Hz, 2H), 4.74 (dd, *J* = 13.9, 3.8 Hz, 1H), 3.86 (dd, *J* = 8.1, 4.3 Hz, 1H), 3.35 (t, *J* = 14.3 Hz, 1H), 2.97 (dd, *J* = 13.9, 8.0 Hz, 1H), 2.88 (dd, *J* = 14.8, 3.9 Hz, 1H), 2.11 (dd, *J* = 13.9, 4.2 Hz, 1H).

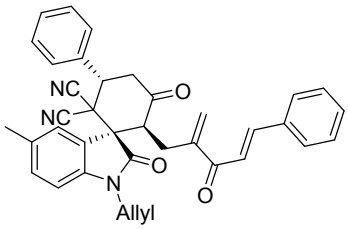
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 190.4, 171.6, 145.4, 144.1, 143.7, 134.5, 134.4, 132.9, 130.9, 130.3, 129.8, 129.4, 129.1, 128.9, 128.8, 128.8, 128.1, 127.4, 126.6, 126.0, 124.3, 123.9, 120.8, 112.0, 111.8, 110.2, 58.3, 48.8, 48.7, 43.1, 42.4, 27.9.

HRMS (ESI) m/z Calcd for $[C_{39}H_{29}N_3NaO_3, M+Na]^+$: 610.2101, Found: 610.2105.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.878 min (major), t_R = 26.880 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 57.4° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 80%, 47.0 mg.





3f

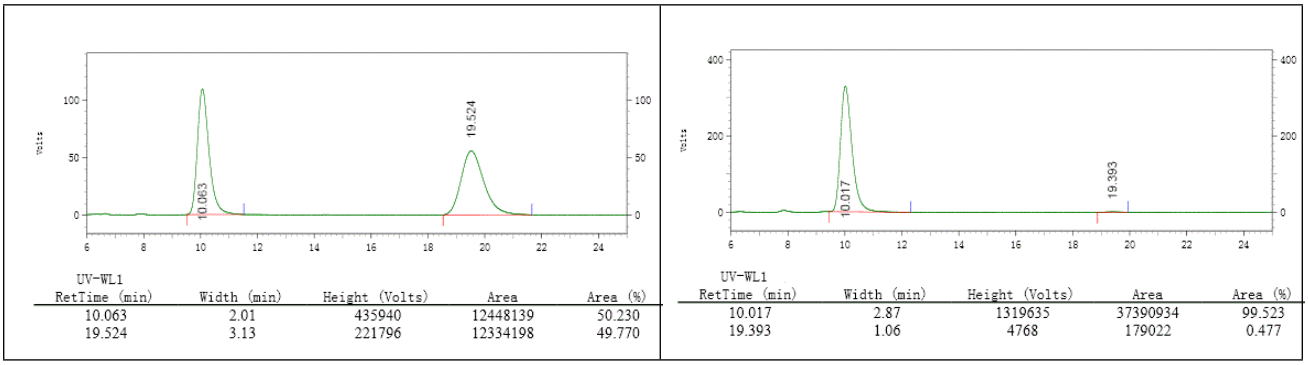
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (s, 1H), 7.62 – 7.45 (m, 5H), 7.47 – 7.33 (m, 6H), 7.20 (d, *J* = 8.1 Hz, 1H), 7.00 (d, *J* = 15.7 Hz, 1H), 6.83 (d, *J* = 8.0 Hz, 1H), 5.92 – 5.80 (m, 2H), 5.74 (s, 1H), 5.40 (d, *J* = 17.1 Hz, 1H), 5.31 (d, *J* = 10.3 Hz, 1H), 4.74 (dd, *J* = 13.8, 3.9 Hz, 1H), 4.53 (dd, *J* = 16.1, 5.3 Hz, 1H), 4.32 (dd, *J* = 16.1, 5.8 Hz, 1H), 3.76 (dd, *J* = 7.7, 4.8 Hz, 1H), 3.33 (t, *J* = 14.3 Hz, 1H), 2.88 (ddd, *J* = 21.5, 14.5, 5.8 Hz, 2H), 2.33 (s, 3H), 1.87 (dd, *J* = 14.2, 4.8 Hz, 1H).

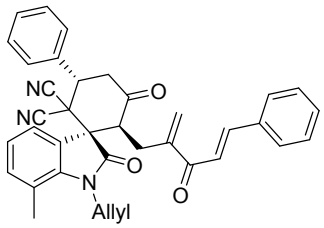
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 190.4, 171.7, 145.6, 143.6, 140.6, 134.7, 134.6, 133.8, 131.3, 130.4, 130.4, 129.5, 129.0, 128.9, 128.2, 126.6, 126.4, 124.4, 120.8, 119.0, 112.2, 111.8, 109.8, , 58.0, 48.8, 48.7, 43.2, 43.1, 42.5, 28.0, 21.3.

HRMS (ESI) m/z Calcd for $[C_{37}H_{31}N_3NaO_3, M+Na]^+$: 588.2258, Found: 588.2254.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.017 min (major), t_R = 19.393 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 83.7° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 92%, 52.0 mg.





3g

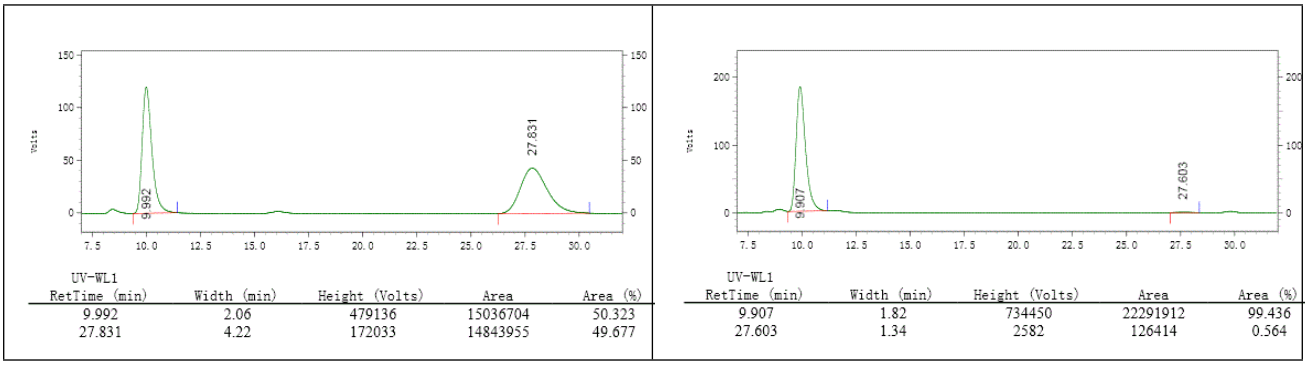
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (dd, *J* = 6.8, 2.1 Hz, 1H), 7.63 – 7.35 (m, 11H), 7.22 – 7.12 (m, 2H), 7.09 (d, *J* = 15.7 Hz, 1H), 6.02 (s, 1H), 6.01 – 5.93 (m, 1H), 5.91 (s, 1H), 5.31 (dd, *J* = 13.9, 10.2 Hz, 2H), 4.78 – 4.59 (m, 3H), 3.69 (dd, *J* = 8.8, 3.4 Hz, 1H), 3.32 (t, *J* = 14.3 Hz, 1H), 2.88 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.70 (dd, *J* = 13.7, 8.8 Hz, 1H), 2.54 (s, 3H), 1.90 (dd, *J* = 13.7, 3.4 Hz, 1H).

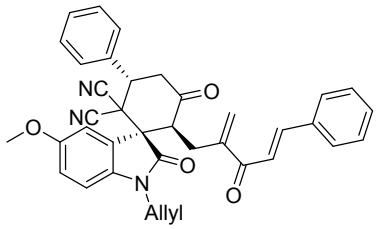
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.9, 190.8, 172.8, 145.7, 143.8, 141.2, 135.1, 134.7, 134.6, 132.6, 130.4, 129.5, 129.0, 129.0, 128.9, 128.3, 127.4, 125.0, 124.0, 123.7, 121.1, 120.6, 117.3, 112.3, 111.9, 57.5, 49.3, 48.9, 44.6, 43.5, 42.7, 27.5, 18.6.

HRMS (ESI) m/z Calcd for $[C_{37}H_{31}N_3NaO_3, M+Na]^+$: 588.2258, Found: 588.2255.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.907 min (major), t_R = 27.603 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 75.4° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 88%, 49.8 mg.





3h

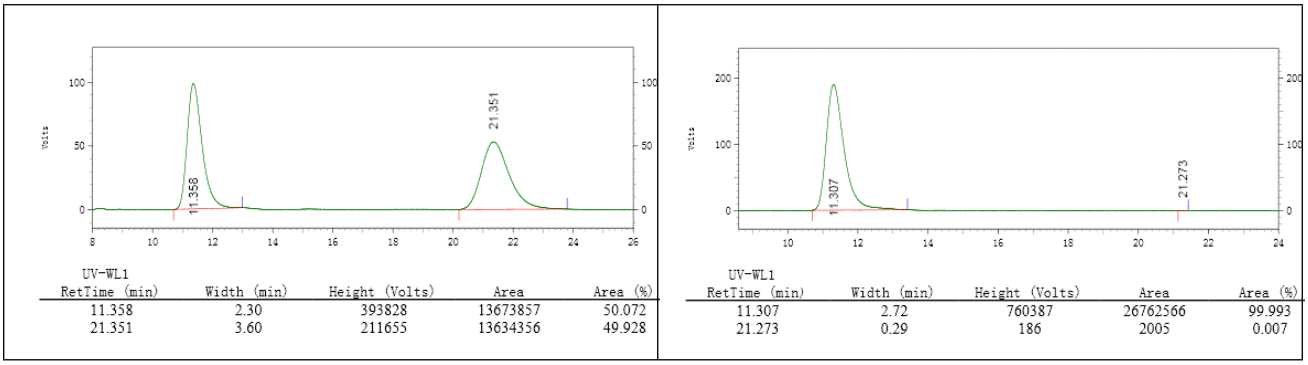
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 – 7.52 (m, 3H), 7.51 – 7.45 (m, 3H), 7.45 – 7.35 (m, 6H), 7.02 (d, *J* = 15.7 Hz, 1H), 6.93 (dd, *J* = 8.6, 2.5 Hz, 1H), 6.86 (d, *J* = 8.6 Hz, 1H), 5.90 (s, 1H), 5.89 – 5.81 (m, 1H), 5.79 (s, 1H), 5.40 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.3 Hz, 1H), 4.75 (dd, *J* = 13.8, 3.9 Hz, 1H), 4.52 (dd, *J* = 16.0, 5.3 Hz, 1H), 4.32 (dd, *J* = 16.2, 5.7 Hz, 1H), 3.77 (s, 3H), 3.73 (dd, *J* = 7.8, 4.7 Hz, 1H), 3.32 (t, *J* = 14.3 Hz, 1H), 2.88 (ddd, *J* = 21.9, 14.5, 5.9 Hz, 2H), 1.88 (dd, *J* = 14.1, 4.6 Hz, 1H).

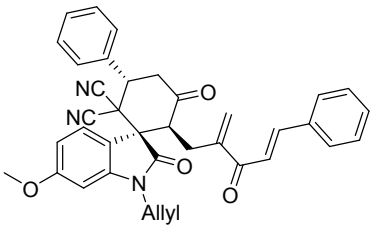
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.6, 190.5, 171.5, 156.6, 145.6, 143.8, 136.2, 134.7, 134.6, 130.5, 130.4, 129.5, 129.0, 128.9, 128.2, 126.9, 125.4, 120.9, 119.0, 116.2, 112.3, 112.2, 111.8, 110.7, 58.3, 55.7, 48.8, 48.7, 43.3, 43.2, 42.6, 28.0.

HRMS (ESI) m/z Calcd for $[C_{37}H_{31}N_3NaO_4, M+Na]^+$: 604.2207, Found: 604.2205.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.307 min (major), t_R = 21.273 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 71.3° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 97%, 56.4 mg.





3i

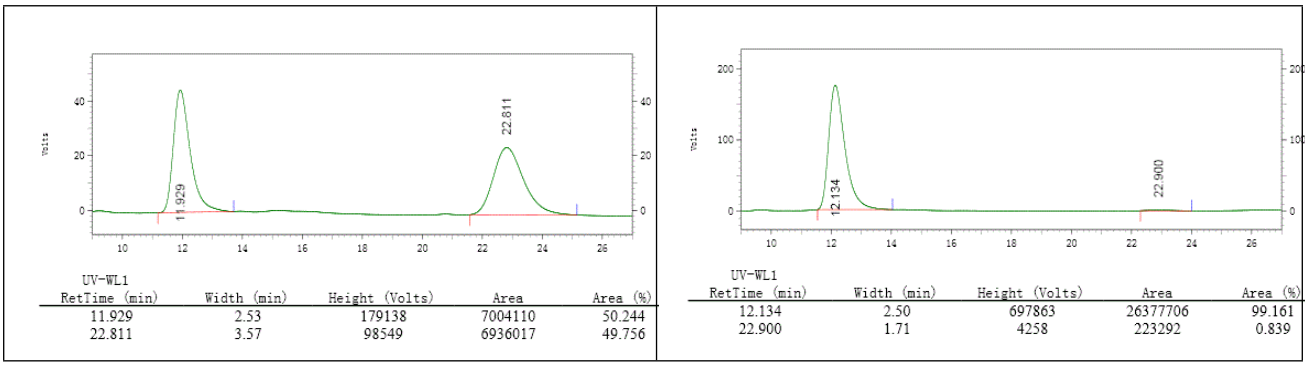
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.5 Hz, 1H), 7.63 – 7.53 (m, 3H), 7.51 – 7.46 (m, 2H), 7.43 – 7.36 (m, 6H), 7.10 (d, *J* = 15.7 Hz, 1H), 6.71 (dd, *J* = 8.5, 2.3 Hz, 1H), 6.53 (d, *J* = 2.2 Hz, 1H), 6.02 (s, 1H), 5.90 (s, 1H), 5.89 – 5.81 (m, 1H), 5.41 (d, *J* = 17.2 Hz, 1H), 5.32 (d, *J* = 10.3 Hz, 1H), 4.71 (dd, *J* = 13.8, 3.9 Hz, 1H), 4.53 (ddd, *J* = 16.3, 5.4, 2.5 Hz, 1H), 4.37 – 4.28 (m, 1H), 3.78 (s, 3H), 3.75 (dd, *J* = 8.5, 4.0 Hz, 1H), 3.32 (t, *J* = 14.3 Hz, 1H), 2.89 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.76 (dd, *J* = 13.8, 8.4 Hz, 1H), 1.94 (dd, *J* = 13.8, 3.9 Hz, 1H).

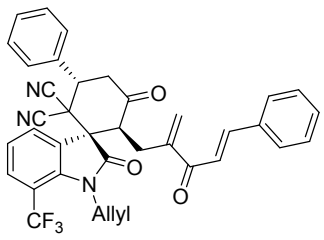
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.8, 190.5, 172.2, 161.9, 145.5, 144.3, 143.6, 134.6, 134.5, 130.3, 130.2, 129.4, 128.9, 128.8, 128.8, 128.1, 127.4, 126.8, 120.9, 118.9, 115.9, 112.3, 111.9, 107.5, 98.0, 57.9, 55.4, 49.1, 49.0, 43.2, 43.0, 42.5, 27.6.

HRMS (ESI) m/z Calcd for $[C_{37}H_{31}N_3NaO_4, M+Na]^+$: 604.2207, Found: 604.2211.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.134 min (major), t_R = 22.900 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 108.4° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 75%, 43.6 mg.





3j

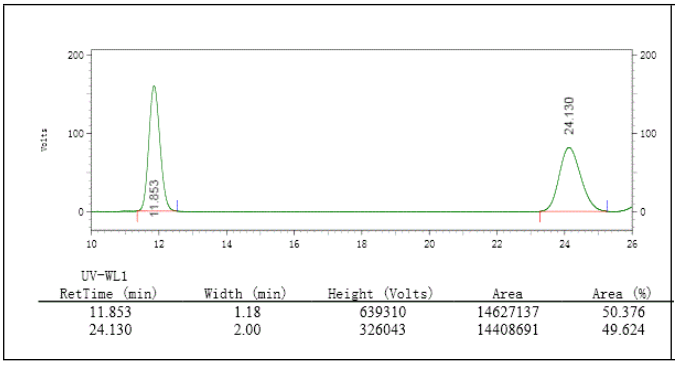
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (d, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.2 Hz, 1H), 7.62 – 7.34 (m, 12H), 7.10 (d, *J* = 15.7 Hz, 1H), 6.05 (s, 1H), 5.99 (s, 1H), 5.94 – 5.81 (m, 1H), 5.33 (dd, *J* = 30.9, 13.7 Hz, 2H), 4.71 – 4.59 (m, 3H), 3.76 (dd, *J* = 8.6, 3.5 Hz, 1H), 3.32 (t, *J* = 14.3 Hz, 1H), 2.90 (dd, *J* = 14.9, 4.0 Hz, 1H), 2.70 (dd, *J* = 13.5, 8.6 Hz, 1H), 1.85 (dd, *J* = 13.5, 3.5 Hz, 1H).

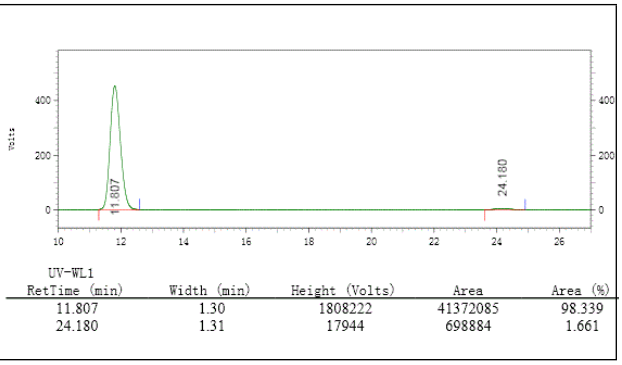
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 190.6, 173.3, 145.1, 144.1, 141.3, 134.6, 134.2, 130.6, 130.5, 129.7, 129.1, 128.9, 128.9, 128.5, 128.3, 126.9, 124.3, 123.4, 121.6, 120.6, 118.9, 113.8, 113.5, 112.0, 111.3, 56.5, 48.7, 48.7, 45.6, 45.6, 43.3, 42.6, 28.0.

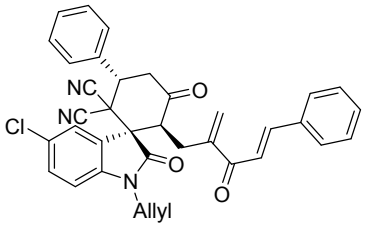
HRMS (ESI) m/z Calcd for $[C_{37}H_{28}F_3N_3NaO_3, M+Na]^+$: 642.1975, Found: 642.1980.

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH) = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.807 min (major), t_R = 24.180 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 73.6° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 82%, 50.8 mg.







3k

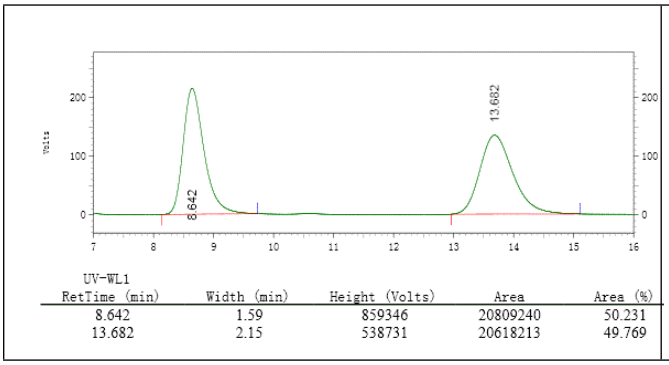
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.66 – 7.52 (m, 3H), 7.51 – 7.33 (m, 9H), 7.07 (d, *J* = 15.6 Hz, 1H), 6.89 (d, *J* = 8.4 Hz, 1H), 5.95 (s, 1H), 5.90 – 5.81 (m, 1H), 5.79 (s, 1H), 5.37 (dd, *J* = 26.3, 13.7 Hz, 2H), 4.70 (dd, *J* = 13.9, 3.8 Hz, 1H), 4.53 (dd, *J* = 16.4, 5.3 Hz, 1H), 4.34 (dd, *J* = 16.5, 5.5 Hz, 1H), 3.72 (dd, *J* = 7.6, 4.6 Hz, 1H), 3.33 (t, *J* = 14.4 Hz, 1H), 2.88 (ddd, *J* = 25.2, 14.5, 5.8 Hz, 2H), 1.85 (dd, *J* = 14.1, 4.4 Hz, 1H).

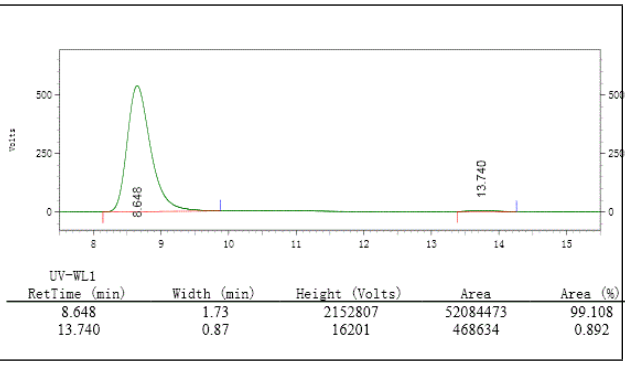
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 190.3, 171.4, 145.5, 144.2, 141.7, 134.7, 134.3, 131.1, 130.4, 130.0, 129.7, 129.7, 129.1, 128.8, 128.3, 127.0, 126.4, 125.9, 120.6, 119.4, 112.0, 111.6, 111.1, 58.1, 48.9, 48.4, 43.3, 42.5, 27.7.

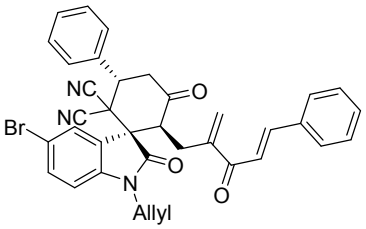
HRMS (ESI) m/z Calcd for $[C_{36}H_{28}ClN_3NaO_3, M+Na]^+$: 608.1711, Found: 608.1708.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 8.648 min (major), t_R = 13.740 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 97.3° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 82%, 48.1 mg.







3l

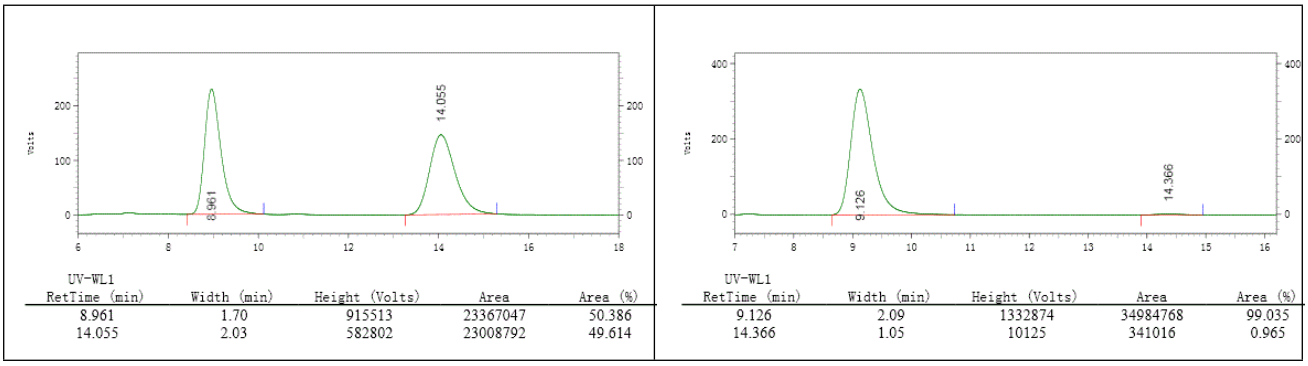
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, *J* = 1.8 Hz, 1H), 7.66 – 7.51 (m, 4H), 7.50 – 7.35 (m, 8H), 7.07 (d, *J* = 15.7 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 1H), 5.94 (s, 1H), 5.91 – 5.79 (m, 1H), 5.77 (s, 1H), 5.40 (d, *J* = 17.1 Hz, 1H), 5.33 (d, *J* = 10.3 Hz, 1H), 4.70 (dd, *J* = 13.8, 3.9 Hz, 1H), 4.53 (dd, *J* = 16.2, 5.3 Hz, 1H), 4.33 (dd, *J* = 16.2, 5.9 Hz, 1H), 3.72 (dd, *J* = 7.5, 4.8 Hz, 1H), 3.33 (t, *J* = 14.3 Hz, 1H), 2.98 – 2.80 (m, 2H), 1.85 (dd, *J* = 14.1, 4.7 Hz, 1H).

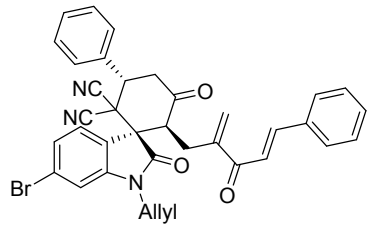
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 190.2, 171.3, 145.6, 144.2, 142.1, 134.7, 134.3, 134.0, 130.4, 129.9, 129.6, 129.1, 128.8, 128.4, 126.8, 126.2, 120.6, 119.5, 119.4, 119.4, 116.9, 111.9, 111.6, 111.5, 58.1, 48.9, 48.9, 48.4, 43.2, 42.5, 27.7.

HRMS (ESI) m/z Calcd for $[C_{36}H_{28}BrN_3NaO_3, M+ Na]^+$: 652.1206, Found: 652.1210.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 9.126 min (major), t_R = 14.366 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 92.0° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 80%, 50.4 mg.





3m

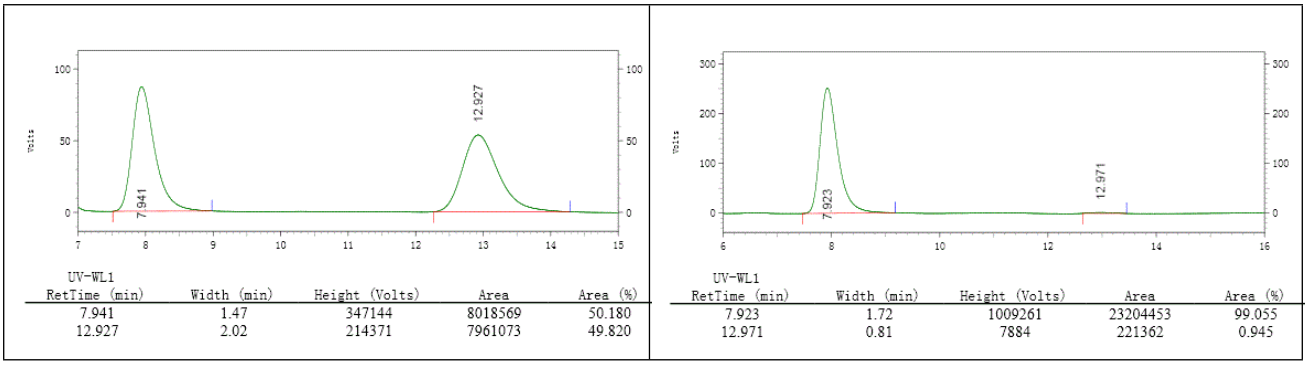
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.2 Hz, 1H), 7.65 – 7.34 (m, 12H), 7.10 (dd, *J* = 8.7, 7.0 Hz, 2H), 6.06 (s, 1H), 5.97 (s, 1H), 5.91 – 5.77 (m, 1H), 5.45 – 5.28 (m, 2H), 4.67 (dd, *J* = 13.9, 3.9 Hz, 1H), 4.58 – 4.47 (m, 1H), 4.33 (dd, *J* = 16.2, 5.7 Hz, 1H), 3.72 (dd, *J* = 8.7, 3.5 Hz, 1H), 3.31 (t, *J* = 14.3 Hz, 1H), 2.89 (dd, *J* = 14.8, 4.0 Hz, 1H), 2.70 (dd, *J* = 13.6, 8.7 Hz, 1H), 1.87 (dd, *J* = 13.6, 3.5 Hz, 1H).

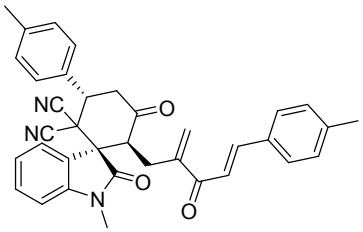
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 190.6, 171.7, 145.3, 144.3, 144.0, 134.6, 134.3, 130.5, 129.8, 129.6, 129.1, 128.9, 128.8, 128.3, 128.2, 127.3, 127.0, 125.1, 123.1, 120.7, 119.5, 113.5, 112.1, 111.7, 58.1, 48.7, 48.4, 43.4, 43.2, 42.6, 27.7.

HRMS (ESI) m/z Calcd for $[C_{36}H_{28}BrN_3NaO_3, M+ Na]^+$: 652.1206, Found: 652.1203.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.923 min (major), t_R = 12.971 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 116.6° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 85%, 53.6 mg.





3n

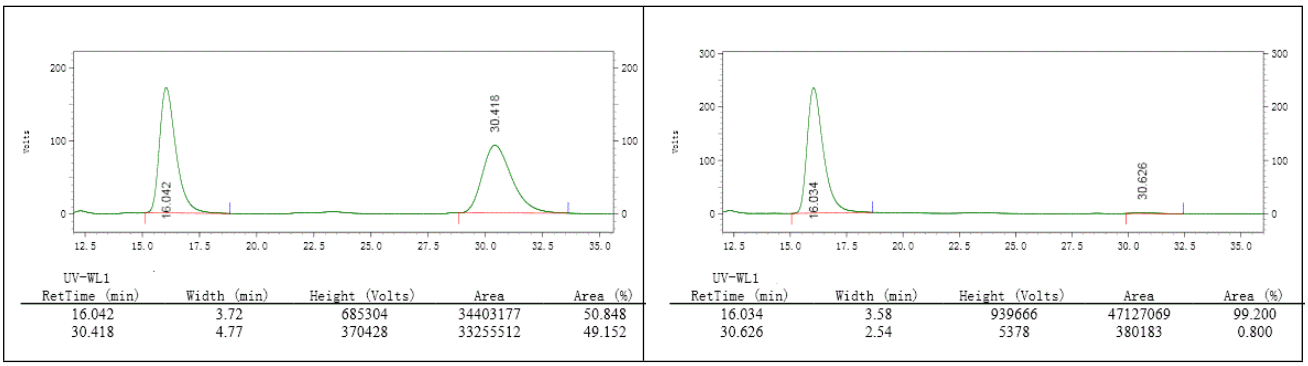
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 15.7 Hz, 1H), 7.46 – 7.31 (m, 5H), 7.23 – 7.13 (m, 5H), 7.01 (d, *J* = 15.6 Hz, 1H), 6.93 (d, *J* = 7.8 Hz, 1H), 5.92 (s, 1H), 5.78 (s, 1H), 4.70 (dd, *J* = 13.9, 3.8 Hz, 1H), 3.77 (dd, *J* = 8.2, 4.1 Hz, 1H), 3.35 – 3.22 (m, 4H), 2.82 (ddd, *J* = 27.5, 14.4, 6.1 Hz, 2H), 2.33 (d, *J* = 12.3 Hz, 6H), 1.85 (dd, *J* = 14.0, 4.1 Hz, 1H).

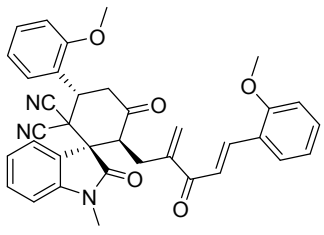
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 190.4, 171.8, 145.4, 143.6, 143.6, 140.7, 139.2, 131.7, 131.4, 130.9, 129.5, 129.4, 128.5, 128.1, 126.8, 125.6, 124.2, 123.8, 119.8, 112.2, 111.7, 108.9, 58.1, 48.7, 48.5, 42.7, 42.5, 27.7, 26.6, 21.3, 20.9.

HRMS (ESI) m/z Calcd for $[C_{36}H_{31}N_3NaO_3, M+Na]^+$: 576.2258, Found: 576.2261.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 16.034 min (major), t_R = 30.626 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 99.1° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 96%, 53.2 mg.





3o

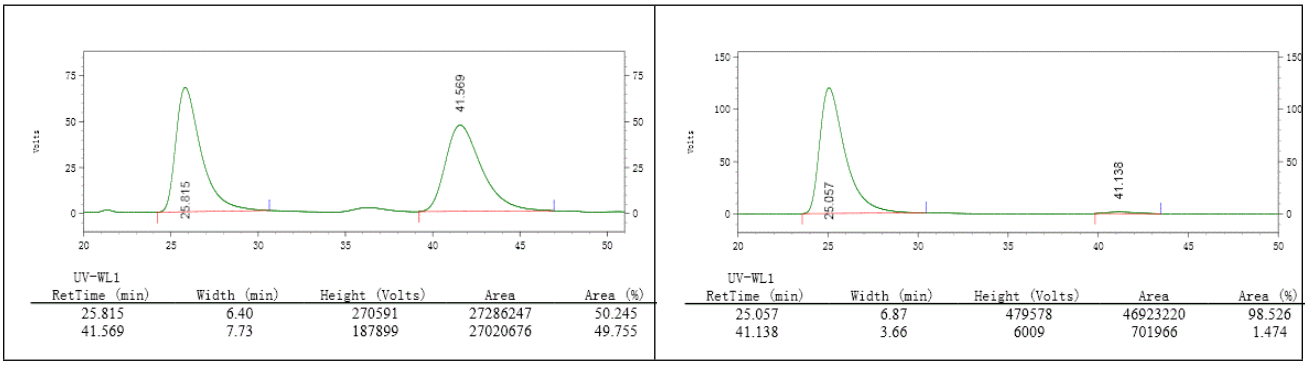
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 – 7.85 (m, 2H), 7.58 – 7.48 (m, 2H), 7.45 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.31 (m, 2H), 7.23 (t, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 15.8 Hz, 1H), 7.03 (t, *J* = 7.5 Hz, 1H), 6.94 (dt, *J* = 14.6, 7.7 Hz, 4H), 5.93 (s, 1H), 5.79 (s, 1H), 5.56 (dd, *J* = 14.1, 3.8 Hz, 1H), 3.88 (s, 3H), 3.80 (s, 3H), 3.76 (dd, *J* = 8.3, 4.1 Hz, 1H), 3.36 – 3.23 (m, 4H), 2.78 (td, *J* = 14.6, 6.1 Hz, 2H), 1.86 (dd, *J* = 14.0, 3.7 Hz, 1H).

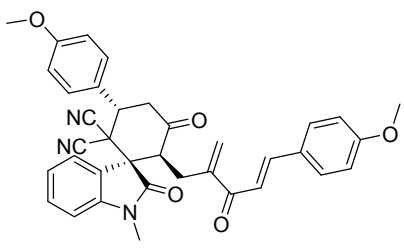
^{13}C NMR (100 MHz, $CDCl_3$) δ 202.0, 191.1, 171.7, 158.5, 157.1, 145.6, 143.8, 139.1, 131.5, 130.9, 130.2, 128.8, 128.0, 126.8, 125.7, 124.4, 123.8, 123.6, 123.2, 121.7, 120.7, 120.6, 112.7, 111.6, 111.1, 111.0, 108.8, 58.2, 55.4, 48.8, 47.9, 42.5, 34.2, 27.8, 26.6.

HRMS (ESI) m/z Calcd for $[C_{36}H_{31}N_3NaO_5, M+Na]^+$: 608.2156, Found: 608.2160.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 25.057 min (major), t_R = 41.138 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 129.2° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 94%, 55.1 mg.





3p

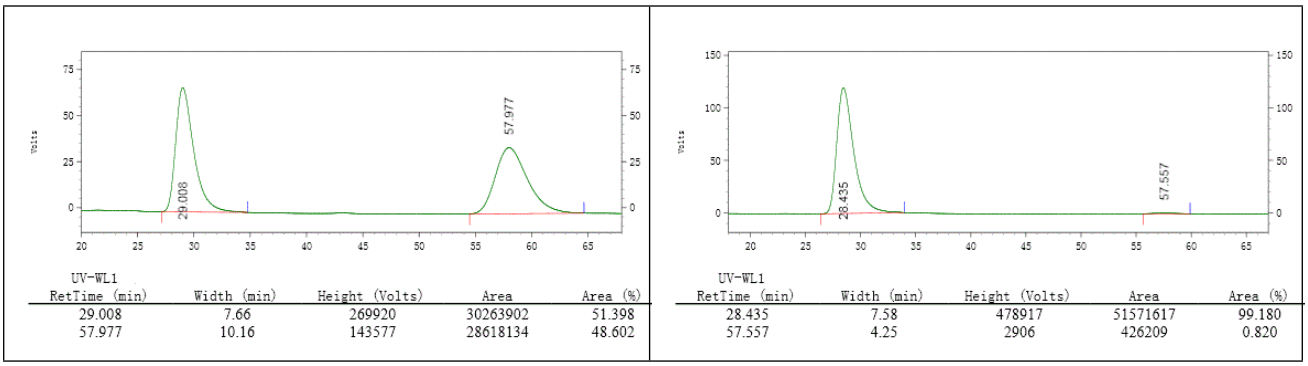
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.58 – 7.36 (m, 6H), 7.23 (t, *J* = 7.7 Hz, 1H), 6.99 – 6.86 (m, 6H), 5.92 (s, 1H), 5.78 (s, 1H), 4.69 (dd, *J* = 13.9, 3.9 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.76 – 3.70 (m, 1H), 3.35 – 3.23 (m, 4H), 2.86 (dd, *J* = 14.7, 4.0 Hz, 1H), 2.77 (dd, *J* = 13.9, 8.3 Hz, 1H), 1.85 (dd, *J* = 15.1, 4.7 Hz, 1H).

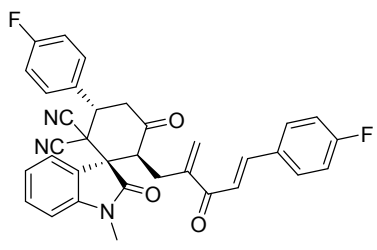
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.7, 190.5, 171.9, 161.4, 160.2, 145.5, 143.7, 143.5, 131.0, 129.9, 127.3, 126.6, 126.4, 125.7, 124.3, 123.9, 118.6, 114.2, 112.3, 111.8, 109.0, 58.2, 55.2, 55.1, 48.9, 48.6, 42.8, 42.6, 27.8, 26.6.

HRMS (ESI) m/z Calcd for $[C_{36}H_{31}N_3NaO_5, M+Na]^+$: 608.2156, Found: 608.2155.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 28.435 min (major), t_R = 57.557 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 119.4° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 85%, 51.1 mg.





3q

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.39 (m, 6H), 7.30 – 7.23 (m, 1H), 7.10 (dt, *J* = 12.5, 8.5 Hz, 4H), 7.02 – 6.94 (m, 2H), 5.91 (d, *J* = 42.3 Hz, 2H), 4.74 (dd, *J* = 13.9, 3.9 Hz, 1H), 3.73 (dd, *J* = 8.5, 3.8 Hz, 1H), 3.33 (s, 3H), 3.27 (t, *J* = 14.3 Hz, 1H), 2.88 (dd, *J* = 14.7, 3.9 Hz, 1H), 2.74 (dd, *J* = 13.8, 8.5 Hz, 1H), 1.85 (dd, *J* = 13.8, 3.8 Hz, 1H).

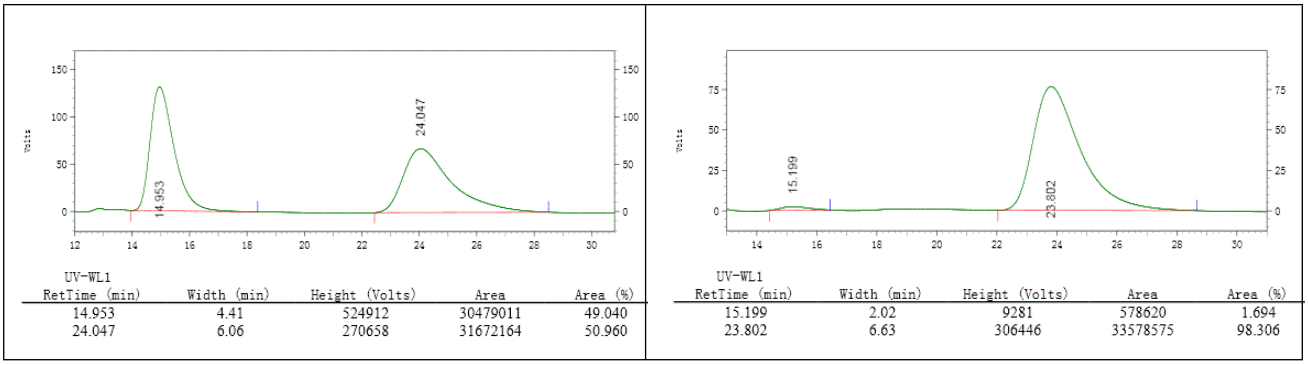
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.4, 190.4, 171.9, 163.9 (d, *J* = 260.0 Hz), 163.2 (d, *J* = 250.0 Hz), 145.4, 143.8, 142.5, 131.2, 130.9 (d, *J* = 3.0 Hz), 130.7 (d, *J* = 10.0

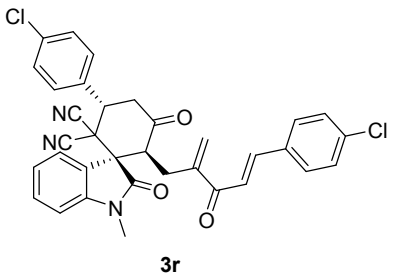
Hz), 130.4 (d, J = 3.0 Hz), 130.2 (d, J = 10.0 Hz), 127.4, 125.8, 124.2, 124.1, 120.6, 120.5, 116.2 (d, J = 5.0 Hz), 116.0 (d, J = 5.0 Hz), 112.1, 111.6, 109.1, 58.2, 48.7, 42.7, 42.5, 27.7, 26.8.

HRMS (ESI) m/z Calcd for $[C_{34}H_{25}F_2N_3NaO_3, M+Na]^+$: 584.1756, Found: 584.1750.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 15.199 min (minor), t_R = 23.802 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 82.8° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 91%, 51.1 mg.





3r

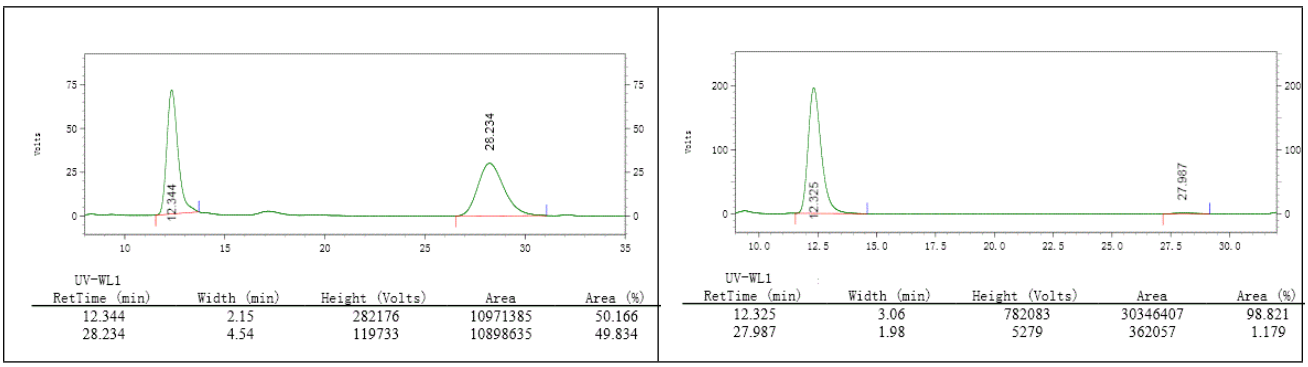
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 7.6 Hz, 1H), 7.55 – 7.31 (m, 10H), 7.25 (d, J = 7.7 Hz, 1H), 7.06 – 6.93 (m, 2H), 5.89 (d, J = 43.5 Hz, 2H), 4.73 (dd, J = 13.8, 3.9 Hz, 1H), 3.75 (dd, J = 8.5, 4.0 Hz, 1H), 3.37 – 3.21 (m, 4H), 2.87 (dd, J = 14.8, 3.9 Hz, 1H), 2.76 (dd, J = 14.0, 8.3 Hz, 1H), 1.84 (dd, J = 13.7, 4.3 Hz, 1H).

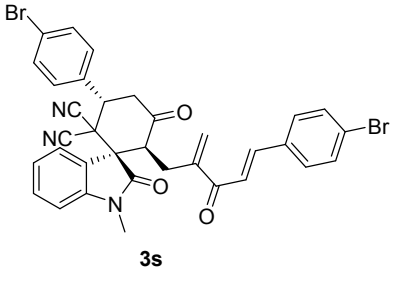
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.2, 190.1, 171.7, 145.3, 143.7, 142.2, 136.1, 135.4, 133.0, 132.9, 131.1, 130.1, 129.3, 129.2, 129.0, 127.5, 125.6, 124.0, 124.0, 121.1, 112.0, 111.5, 109.1, 58.1, 48.6, 48.4, 42.5, 42.3, 27.6, 26.7.

HRMS (ESI) m/z Calcd for $[C_{34}H_{25}Cl_2N_3NaO_3, M+Na]^+$: 616.1165, Found: 616.1160.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.325 min (major), t_R = 27.987 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 99.7° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 88%, 52.3 mg.





3s

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J = 7.6 Hz, 1H), 7.58 – 7.42 (m, 6H), 7.36 (dd, J = 10.9, 8.3 Hz, 4H), 7.24 (t, J = 8.7 Hz, 1H), 7.06 – 6.93 (m, 2H), 5.89 (d, J = 43.6 Hz, 2H), 4.72 (dd, J = 13.8, 3.9 Hz, 1H), 3.75 (dd, J = 8.3, 4.0 Hz, 1H), 3.38

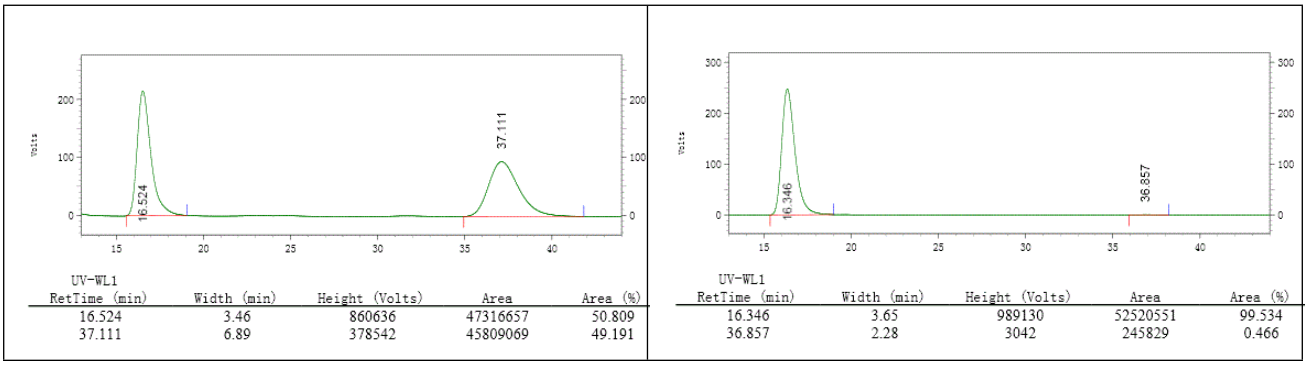
– 3.20 (m, 4H), 2.86 (dd, J = 14.8, 4.0 Hz, 1H), 2.76 (dd, J = 14.0, 8.3 Hz, 1H), 1.84 (dd, J = 16.0, 4.0 Hz, 1H).

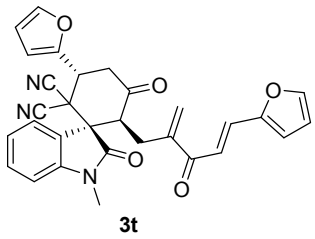
^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1, 190.1, 171.7, 145.2, 143.6, 142.2, 133.4, 132.1, 131.9, 131.1, 130.3, 129.5, 127.5, 125.6, 124.5, 124.0, 123.7, 121.2, 111.9, 111.4, 109.0, 58.1, 48.5, 48.2, 42.5, 42.2, 27.6, 26.7.

HRMS (ESI) m/z Calcd for $[C_{34}H_{25}Br_2N_3NaO_3, M+Na]^+$: 704.0155, Found: 704.0154.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 16.346 min (major), t_R = 36.857 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 111.1° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 88%, 60.1 mg.





3t

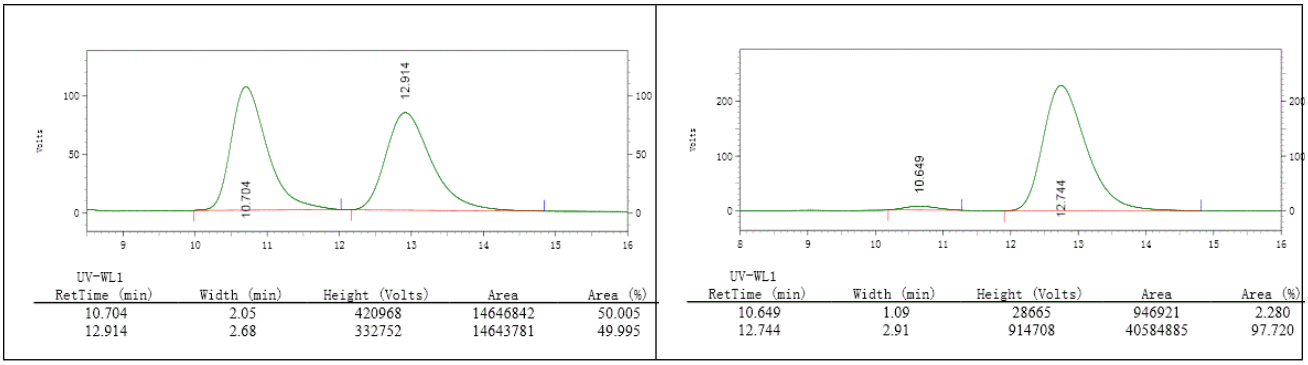
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J = 7.5 Hz, 1H), 7.52 – 7.42 (m, 3H), 7.33 (d, J = 15.4 Hz, 1H), 7.29 – 7.21 (m, 1H), 6.99 – 6.91 (m, 2H), 6.65 (d, J = 3.4 Hz, 1H), 6.48 (dt, J = 3.5, 2.3 Hz, 2H), 6.40 (dd, J = 3.3, 1.8 Hz, 1H), 5.93 (s, 1H), 5.77 (s, 1H), 4.86 (dd, J = 13.6, 4.2 Hz, 1H), 3.70 (dd, J = 8.2, 4.1 Hz, 1H), 3.31 (s, 3H), 3.24 (d, J = 14.2 Hz, 1H), 2.96 (dd, J = 15.2, 4.3 Hz, 1H), 2.74 (dd, J = 13.9, 8.2 Hz, 1H), 1.81 (dd, J = 14.0, 4.2 Hz, 1H).

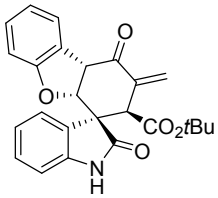
^{13}C NMR (100 MHz, $CDCl_3$) δ 200.8, 190.0, 171.8, 151.3, 148.4, 145.4, 144.7, 143.7, 143.7, 131.2, 129.8, 127.0, 125.7, 124.1, 124.1, 118.3, 115.9, 112.5, 111.9, 111.7, 110.7, 110.1, 109.1, 57.8, 48.7, 46.8, 41.3, 38.2, 27.6, 26.7.

HRMS (ESI) m/z Calcd for $[C_{30}H_{23}N_3NaO_5, M+Na]^+$: 528.1530, Found: 528.1526.

HPLC analysis: Chiralcel OD-H (Hexane/*i*-PrOH) = 60:40, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.649 min (minor), t_R = 12.744 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 99.7° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid; **Yield:** 75%, 37.9 mg.





6a

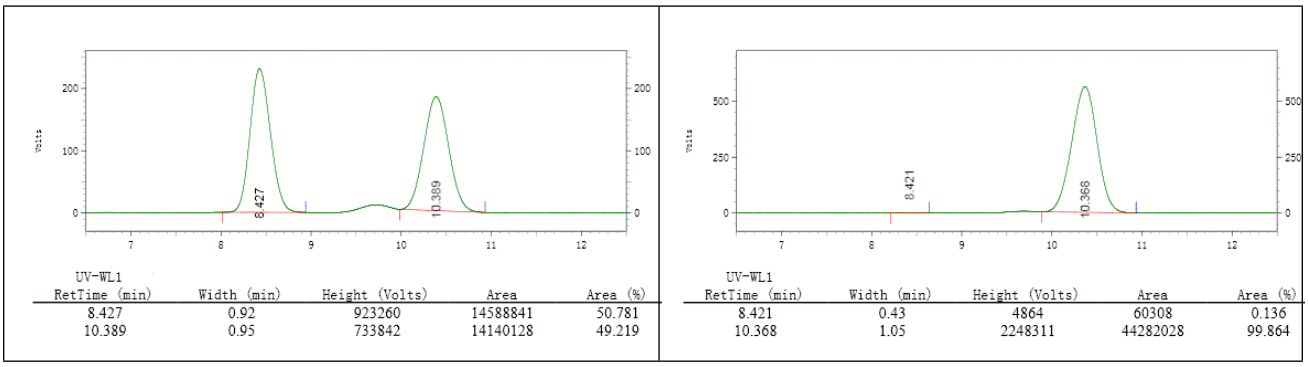
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.85 (s, 1H), 7.42 (d, J = 7.4 Hz, 1H), 7.30 (t, J = 7.7 Hz, 1H), 7.26 – 7.16 (m, 2H), 7.04 (t, J = 7.6 Hz, 1H), 6.97 (d, J = 8.0 Hz, 1H), 6.92 (t, J = 7.8 Hz, 2H), 6.16 (d, J = 3.2 Hz, 1H), 5.20 (d, J = 2.8 Hz, 1H), 5.12 (d, J = 9.4 Hz, 1H), 4.46 (d, J = 9.4 Hz, 1H), 4.12 (t, J = 3.0 Hz, 1H), 1.04 (s, 9H).

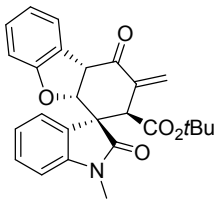
^{13}C NMR (100 MHz, DMSO-d_6) δ 190.1, 175.9, 167.2, 158.9, 142.6, 137.3, 129.8, 129.1, 128.1, 125.8, 125.1, 124.4, 122.6, 121.4, 121.4, 109.7, 82.9, 81.6, 79.2, 51.1, 50.2, 49.3, 26.7.

HRMS (ESI) m/z Calcd for $[C_{25}H_{23}NNaO_5, M+Na]^+$: 440.1468, Found: 440.1471.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 8.421 min (minor), t_R = 10.368 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 11.5° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 70%, 29.2 mg.





6b

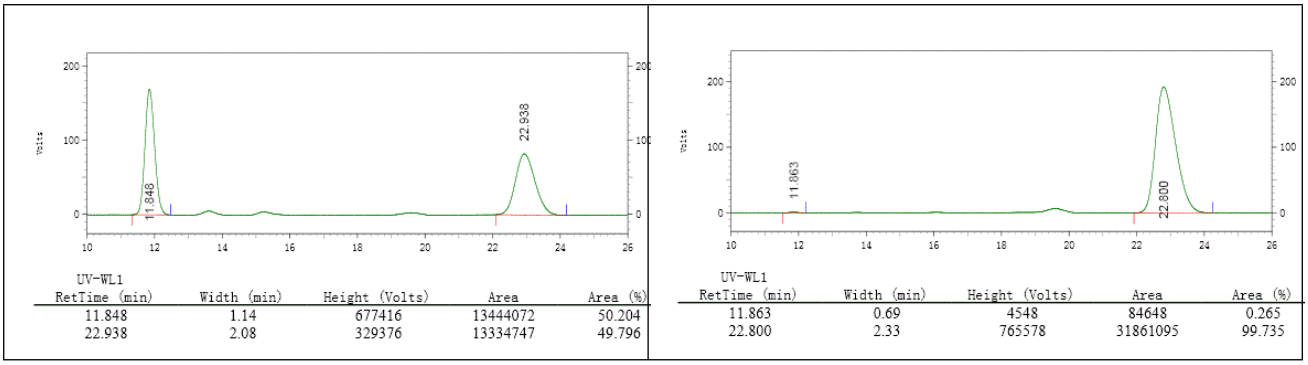
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.4 Hz, 1H), 7.43 – 7.32 (m, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.15 (t, J = 7.5 Hz, 1H), 6.91 (q, J = 8.5, 7.7 Hz, 3H), 6.42 (d, J = 3.1 Hz, 1H), 5.30 (d, J = 2.9 Hz, 1H), 4.91 (d, J = 9.4 Hz, 1H), 4.51 (d, J = 9.4 Hz, 1H), 4.37 (t, J = 3.1 Hz, 1H), 3.25 (s, 3H), 1.05 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 174.9, 167.7, 159.1, 144.0, 137.1, 129.8, 129.3, 127.7, 126.1, 125.8, 124.3, 123.7, 122.7, 121.7, 109.7, 108.1, 83.3, 81.9, 51.9, 50.7, 49.8, 27.2, 26.3.

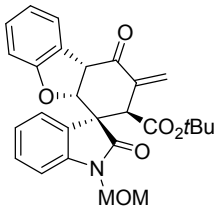
HRMS (ESI) m/z Calcd for $[C_{26}H_{25}NNaO_5, M+Na]^+$: 454.1625, Found: 454.1620.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.863 min (minor), t_R = 22.800 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 21.1° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 93%, 40.1 mg.



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, J = 7.5 Hz, 1H), 7.36 (dd, J = 7.8, 3.5 Hz, 2H), 7.19 (dt, J = 15.7, 7.7 Hz, 2H), 7.10 (d, J = 7.8 Hz, 1H), 6.91 (q, J = 7.9 Hz, 2H), 6.43 (d, J = 3.1 Hz, 1H), 5.32 (d, J = 2.8 Hz, 1H), 5.22 (d, J = 10.9 Hz, 1H), 5.07 (d, J = 11.0 Hz, 1H), 4.96 (d, J = 9.2 Hz, 1H), 4.52 (d, J = 9.5 Hz, 1H), 4.38 (d, J = 3.0 Hz, 1H), 3.40 (s, 3H), 1.09 (s, 9H).



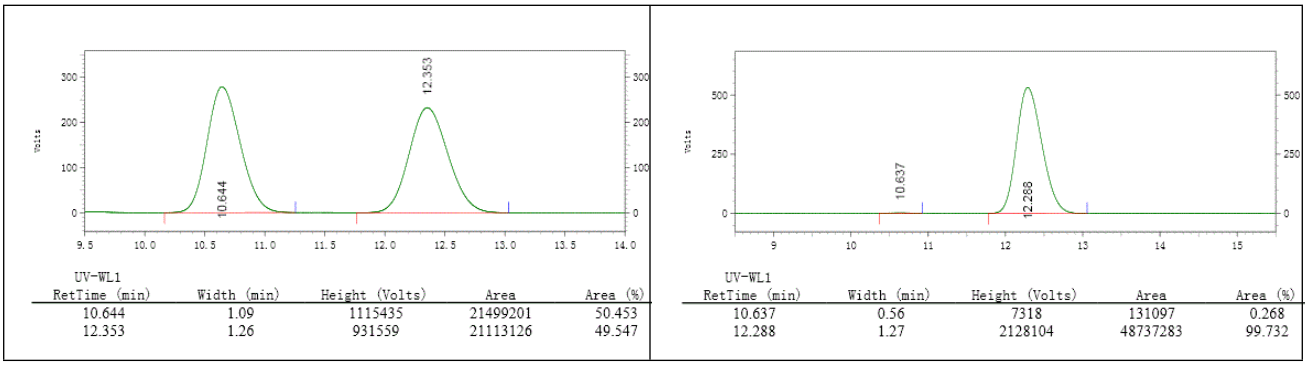
6c

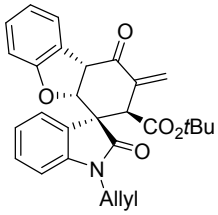
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 175.6, 167.9, 159.0, 142.4, 137.0, 129.8, 129.4, 127.1, 126.3, 125.7, 124.2, 123.0, 121.8, 109.7, 109.6, 83.4, 82.2, 71.6, 56.6, 51.8, 51.2, 49.8, 27.9, 27.3.

HRMS (ESI) m/z Calcd for $[C_{27}H_{27}NNaO_6, M+ Na]^+$: 484.1731, Found: 484.1727.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.637min (minor), t_R = 12.288 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 15.1° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 74%, 34.2 mg.





6d

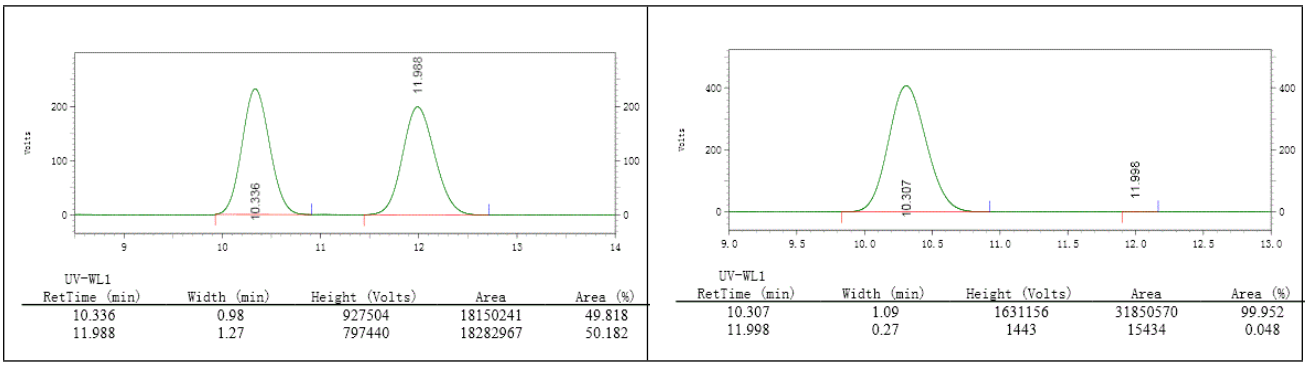
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, J = 7.5 Hz, 1H), 7.35 (dt, J = 10.6, 5.2 Hz, 2H), 7.21 (t, J = 7.8 Hz, 1H), 7.13 (t, J = 7.5 Hz, 1H), 6.95 – 6.85 (m, 3H), 6.43 (d, J = 3.1 Hz, 1H), 5.86 (ddt, J = 16.0, 10.5, 5.3 Hz, 1H), 5.34 – 5.21 (m, 3H), 4.93 (d, J = 9.3 Hz, 1H), 4.58 – 4.49 (m, 2H), 4.36 (d, J = 3.2 Hz, 1H), 4.19 (dd, J = 16.3, 5.5 Hz, 1H), 1.08 (s, 9H).

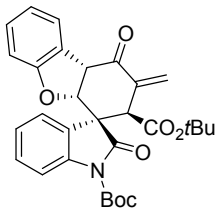
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.6, 174.6, 167.9, 159.1, 143.2, 137.1, 131.1, 129.7, 129.2, 127.6, 126.2, 125.8, 124.3, 124.0, 122.5, 121.7, 117.9, 109.7, 109.1, 83.4, 82.0, 51.8, 50.7, 49.7, 42.5, 27.3.

HRMS (ESI) m/z Calcd for $[C_{28}H_{27}NNaO_5, M+ Na]^+$: 480.1781, Found: 480.1784.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.307 min (major), t_R = 11.998 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 14.2° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 71%, 32.5 mg.





6e

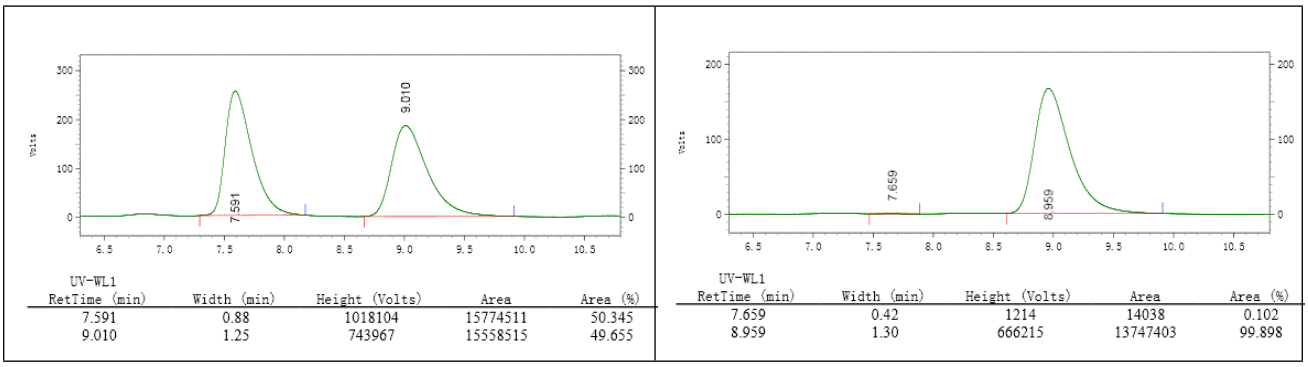
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 1H), 7.61 (d, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.3 Hz, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.26 – 7.20 (m, 2H), 6.95 – 6.87 (m, 2H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.35 (d, *J* = 2.9 Hz, 1H), 5.00 (d, *J* = 9.2 Hz, 1H), 4.52 (d, *J* = 9.3 Hz, 1H), 4.37 (s, 1H), 1.63 (s, 9H), 1.06 (s, 9H).

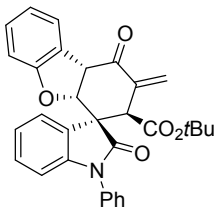
^{13}C NMR (150 MHz, $CDCl_3$) δ 190.4, 173.3, 167.0, 158.9, 148.9, 140.1, 136.4, 129.9, 129.5, 126.7, 126.0, 125.8, 124.6, 124.2, 124.1, 121.9, 114.9, 109.8, 84.9, 83.0, 82.6, 51.7, 50.8, 50.7, 28.0, 27.0.

HRMS (ESI) m/z Calcd for $[C_{30}H_{31}NNaO_7, M+Na]^+$: 540.1993, Found: 540.1972.

HPLC analysis: Chiralcel ID-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.659 min (minor), t_R = 8.959 min (major).

Optical Rotation: $[\alpha]_D^{25}$ = 47.1° (c = 1.1, $CHCl_3$); **Physical properties:** white solid; **Yield:** 80%, 41.4 mg.





6f

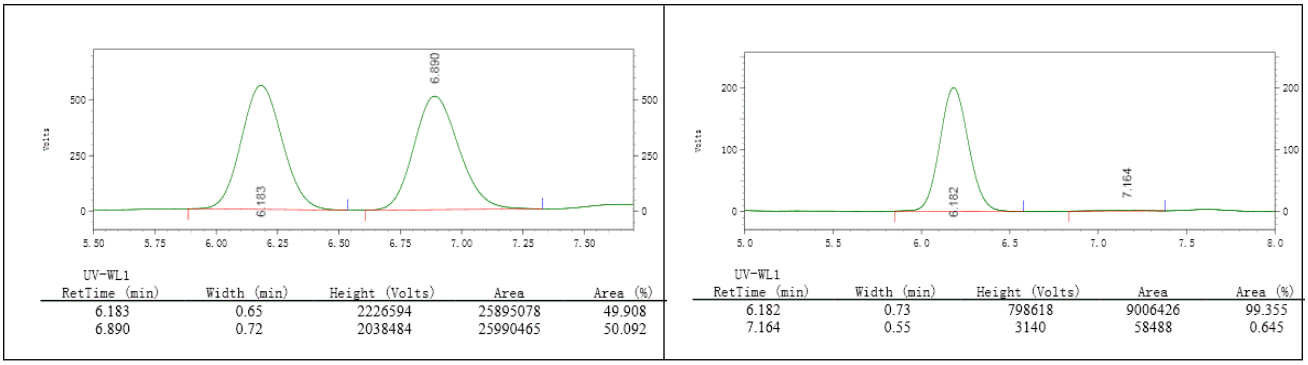
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 12.6, 7.4 Hz, 1H), 7.55 – 7.44 (m, 4H), 7.43 – 7.29 (m, 3H), 7.24 – 7.15 (m, 2H), 7.00 – 6.86 (m, 3H), 6.44 (dd, *J* = 12.3, 3.2 Hz, 1H), 5.34 (dd, *J* = 12.3, 2.9 Hz, 1H), 5.06 (dd, *J* = 12.6, 9.3 Hz, 1H), 4.57 – 4.42 (m, 2H), 1.09 (d, *J* = 12.4 Hz, 9H).

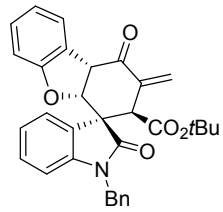
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 174.3, 168.1, 159.0, 143.9, 136.9, 133.8, 129.7, 129.4, 129.2, 128.0, 127.5, 126.5, 126.1, 125.8, 124.3, 124.2, 123.1, 121.8, 109.7, 109.7, 83.3, 82.2, 51.7, 50.8, 50.1, 27.4.

HRMS (ESI) m/z Calcd for $[C_{31}H_{27}NNaO_5, M+Na]^+$: 516.1781, Found: 516.1774.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.182 min (major), t_R = 7.164 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 24.5° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 81%, 40.0 mg.





6g

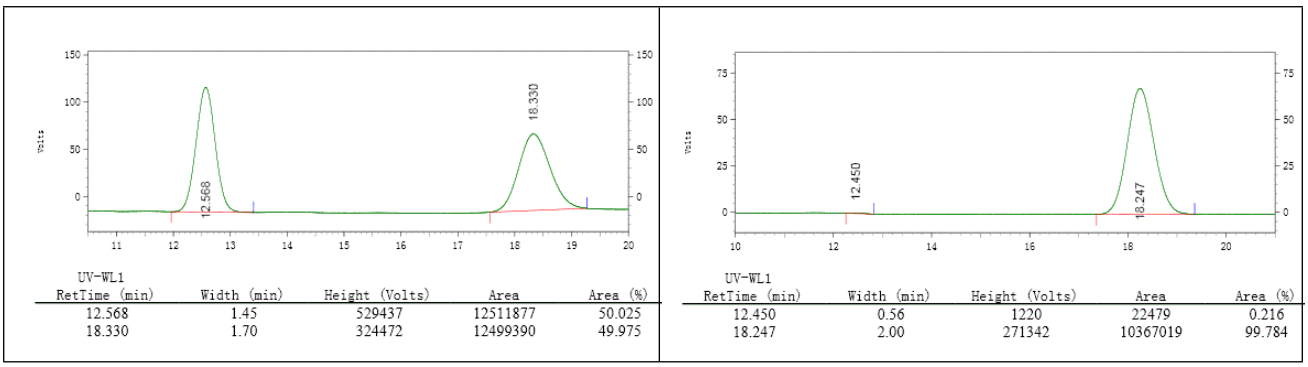
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, *J* = 7.5 Hz, 1H), 7.40 – 7.26 (m, 7H), 7.19 (t, *J* = 7.8 Hz, 1H), 7.09 (t, *J* = 7.6 Hz, 1H), 6.95 – 6.85 (m, 2H), 6.78 (d, *J* = 7.8 Hz, 1H), 6.46 (d, *J* = 3.1 Hz, 1H), 5.35 (d, *J* = 2.8 Hz, 1H), 5.19 (d, *J* = 15.6 Hz, 1H), 4.96 (d, *J* = 9.4 Hz, 1H), 4.67 (d, *J* = 15.7 Hz, 1H), 4.56 (d, *J* = 9.4 Hz, 1H), 4.39 (d, *J* = 3.1 Hz, 1H), 1.10 (s, 9H).

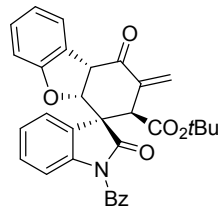
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 175.0, 167.9, 159.1, 143.1, 137.1, 135.4, 129.7, 129.2, 128.7, 127.7, 127.6, 127.3, 126.2, 125.7, 124.3, 124.1, 122.5, 121.7, 109.7, 109.2, 83.4, 82.1, 51.8, 50.8, 49.7, 43.9, 27.3.

HRMS (ESI) m/z Calcd for $[C_{32}H_{29}NNaO_5, M+Na]^+$: 530.1938, Found: 530.1940.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.450 min (minor), t_R = 18.247 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 37.7° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 65%, 33.0 mg.





6h

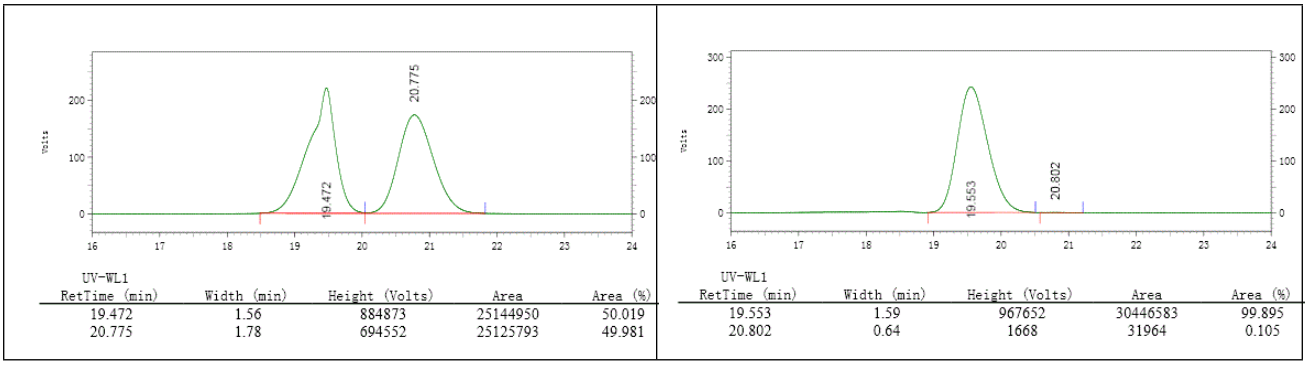
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.0, 3.5 Hz, 3H), 7.69 (d, *J* = 7.6 Hz, 1H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.45 (td, *J* = 8.0, 2.5 Hz, 3H), 7.37 – 7.28 (m, 2H), 7.22 (t, *J* = 8.0 Hz, 1H), 6.92 (dd, *J* = 8.0, 5.9 Hz, 2H), 6.39 (d, *J* = 3.1 Hz, 1H), 5.37 (d, *J* = 2.8 Hz, 1H), 5.07 (d, *J* = 9.3 Hz, 1H), 4.45 – 4.40 (m, 2H), 1.15 (s, 9H).

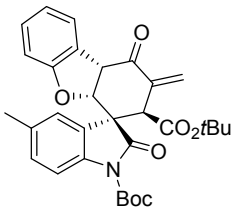
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 174.6, 169.0, 168.1, 158.8, 140.6, 136.5, 133.6, 133.1, 129.9, 129.7, 129.6, 128.2, 127.1, 126.2, 125.8, 124.8, 124.7, 124.1, 121.9, 114.9, 109.8, 82.9, 82.8, 51.6, 51.4, 50.7, 27.3.

HRMS (ESI) m/z Calcd for $[C_{32}H_{27}NNaO_6, M+Na]^+$: 544.1731, Found: 544.1725.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 19.553 min (major), t_R = 20.802 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 6.2° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 60%, 31.3 mg.





6i

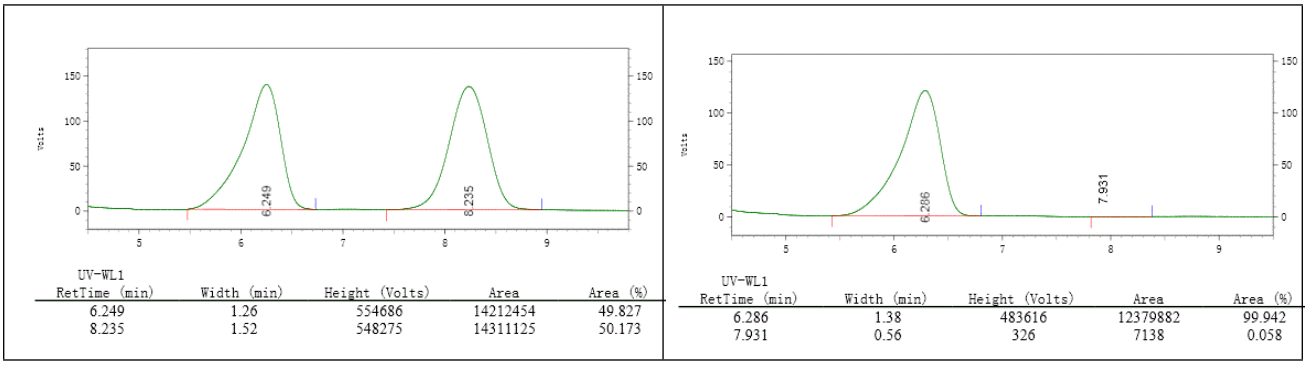
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.4 Hz, 1H), 7.41 (s, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.18 (m, 2H), 6.92 (t, *J* = 7.8 Hz, 2H), 6.42 (d, *J* = 3.2 Hz, 1H), 5.34 (d, *J* = 2.9 Hz, 1H), 4.98 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.35 (t, *J* = 3.0 Hz, 1H), 2.41 (s, 3H), 1.62 (s, 9H), 1.06 (s, 9H).

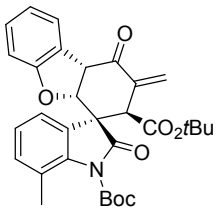
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 173.4, 167.0, 158.9, 148.9, 137.6, 136.5, 134.2, 129.9, 129.8, 126.6, 126.3, 125.7, 124.1, 124.0, 121.8, 114.6, 109.7, 84.6, 83.1, 82.4, 51.6, 50.8, 50.6, 28.0, 26.9, 21.1.

HRMS (ESI) m/z Calcd for $[C_{31}H_{33}NNaO_7, M+Na]^+$: 554.2149, Found: 554.2153.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.286 min (major), t_R = 7.931 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 30.8° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 68%, 36.1 mg.





6j

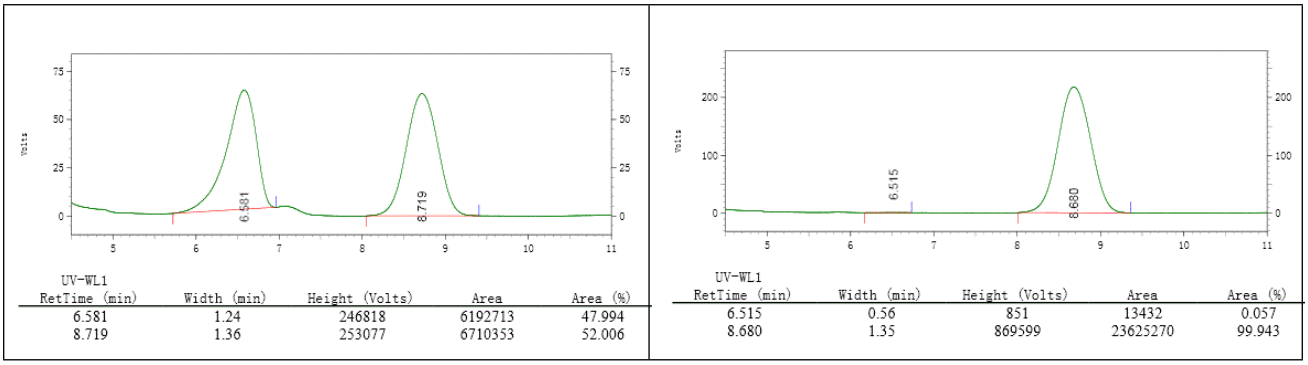
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.3 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.18 (dq, *J* = 15.0, 7.5 Hz, 3H), 6.90 (q, *J* = 7.7 Hz, 2H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.37 – 5.30 (m, 1H), 5.00 (d, *J* = 9.6 Hz, 1H), 4.51 (d, *J* = 9.4 Hz, 1H), 4.32 (d, *J* = 3.2 Hz, 1H), 2.28 (s, 3H), 1.61 (s, 9H), 1.09 (s, 9H).

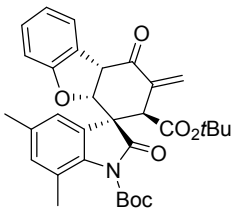
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.7, 173.7, 167.2, 158.9, 148.9, 138.4, 136.6, 132.3, 129.8, 127.6, 125.6, 124.3, 124.2, 124.1, 123.7, 122.9, 121.8, 109.7, 85.1, 83.2, 82.4, 51.7, 51.2, 50.3, 27.7, 27.1, 19.5.

HRMS (ESI) m/z Calcd for $[C_{31}H_{33}NNaO_7, M+Na]^+$: 554.2149, Found: 554.2155.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.515 min (minor), t_R = 8.680 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 44.0° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 78%, 41.5 mg.





6k

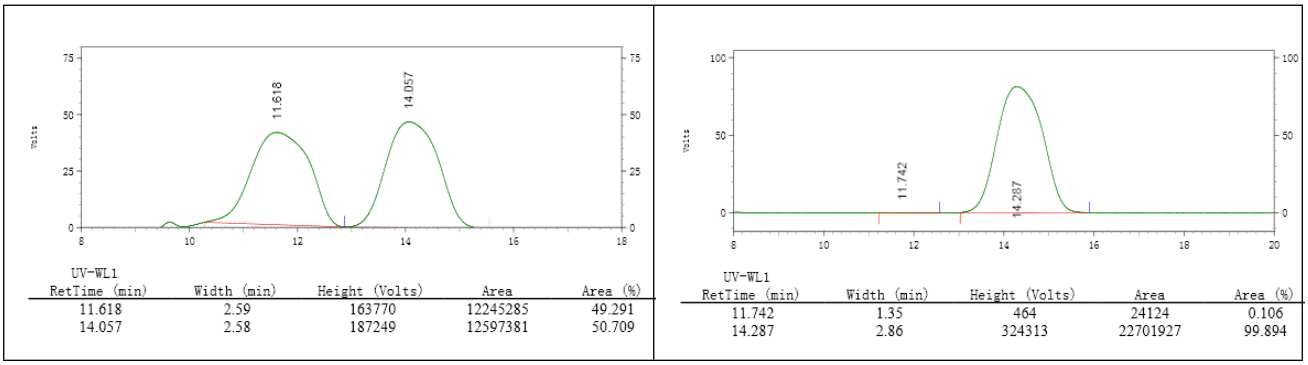
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (dt, *J* = 7.5, 1.3 Hz, 1H), 7.25 – 7.18 (m, 2H), 7.01 (d, *J* = 1.7 Hz, 1H), 6.94 – 6.87 (m, 2H), 6.42 (d, *J* = 3.2 Hz, 1H), 5.34 (d, *J* = 2.9 Hz, 1H), 4.98 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.31 (t, *J* = 3.0 Hz, 1H), 2.37 (s, 3H), 2.24 (s, 3H), 1.60 (s, 9H), 1.09 (s, 9H).

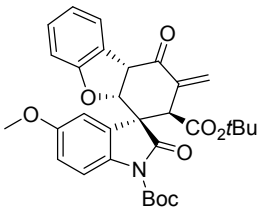
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.8, 173.8, 167.2, 158.9, 148.9, 136.6, 136.0, 133.9, 132.8, 129.8, 127.5, 125.6, 124.3, 124.1, 124.1, 122.7, 121.7, 109.8, 85.0, 83.2, 82.3, 51.6, 51.2, 50.2, 27.7, 27.1, 21.0, 19.5.

HRMS (ESI) m/z Calcd for $[C_{32}H_{35}NNaO_7, M+Na]^+$: 568.2306, Found: 568.2314.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.742 min (minor), t_R = 14.287 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 26.2° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 60%, 32.7 mg.





6l

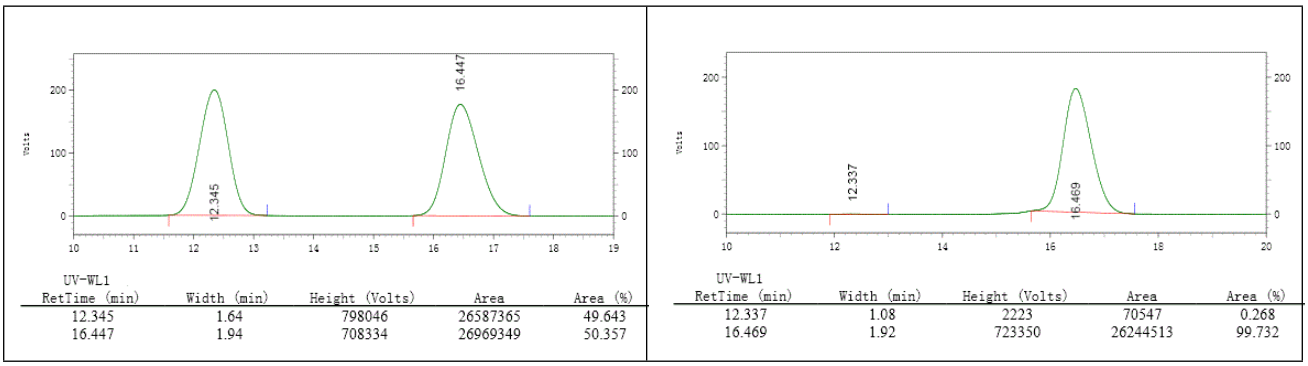
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (dd, *J* = 8.9, 1.4 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.23 – 7.15 (m, 2H), 6.95 – 6.86 (m, 3H), 6.41 (t, *J* = 2.3 Hz, 1H), 5.35 (d, *J* = 2.7 Hz, 1H), 4.99 (dd, *J* = 9.3, 1.5 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.33 (d, *J* = 2.9 Hz, 1H), 3.84 (s, 3H), 1.62 (s, 9H), 1.09 (s, 9H).

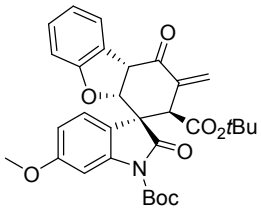
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.3, 173.2, 166.9, 158.8, 156.7, 148.9, 136.4, 133.3, 129.8, 127.9, 125.7, 124.1, 121.8, 115.7, 114.0, 112.4, 109.7, 84.6, 83.0, 82.5, 55.7, 51.6, 50.9, 50.6, 28.0, 27.0.

HRMS (ESI) m/z Calcd for $[C_{31}H_{33}NNaO_8, M+Na]^+$: 570.2098, Found: 570.2094.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 12.337 min (minor), t_R = 16.469 min (major).

Optical Rotation: $[\alpha]_D^{20}$ = 14.6° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 75%, 41.1 mg.





6m

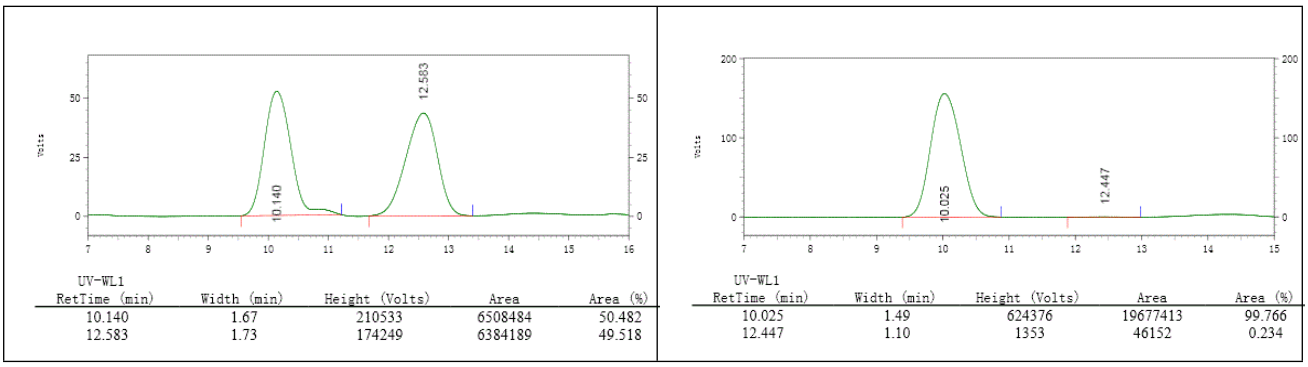
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 (d, *J* = 2.4 Hz, 1H), 7.50 (d, *J* = 8.4 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.21 (t, *J* = 7.8 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.78 (dd, *J* = 8.4, 2.4 Hz, 1H), 6.41 (d, *J* = 3.2 Hz, 1H), 5.33 (d, *J* = 2.8 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.32 (t, *J* = 3.1 Hz, 1H), 3.86 (s, 3H), 1.62 (s, 9H), 1.10 (s, 9H).

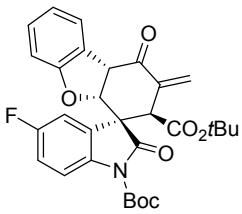
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.5, 173.7, 167.1, 160.8, 158.9, 148.9, 141.1, 136.6, 129.8, 126.6, 125.7, 124.1, 124.1, 121.8, 118.4, 109.8, 109.7, 101.9, 84.9, 83.3, 82.5, 55.6, 51.7, 50.8, 50.4, 28.0, 27.1.

HRMS (ESI) m/z Calcd for $[C_{31}H_{33}NNaO_8, M+Na]^+$: 570.2098, Found: 570.2096.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.025 min (major), t_R = 12.447 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 39.0° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 61%, 33.4 mg.





6n

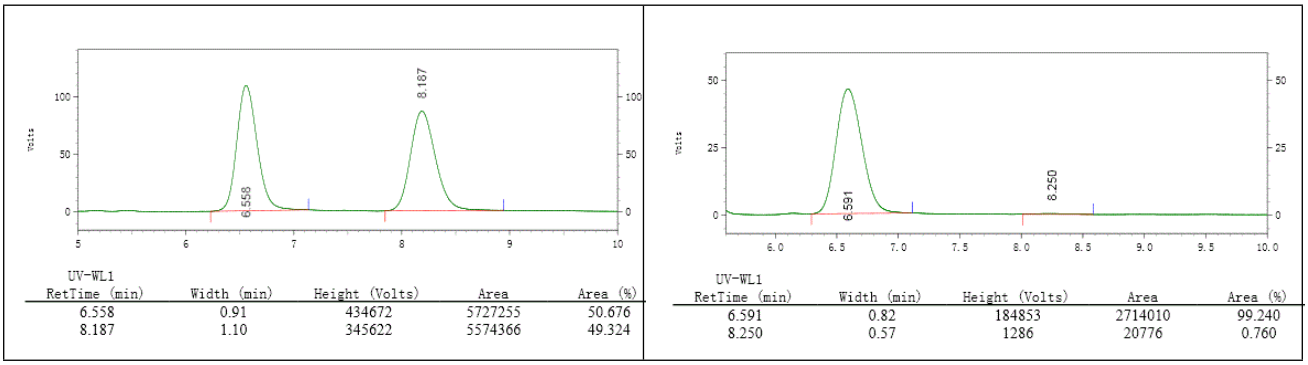
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97 (td, *J* = 9.3, 4.5 Hz, 1H), 7.37 (td, *J* = 9.2, 8.5, 6.0 Hz, 2H), 7.28 – 7.22 (m, 1H), 7.15 (tt, *J* = 9.8, 4.9 Hz, 1H), 6.97 – 6.88 (m, 2H), 6.48 – 6.40 (m, 1H), 5.42 – 5.34 (m, 1H), 5.00 (t, *J* = 9.4 Hz, 1H), 4.52 (t, *J* = 9.2 Hz, 1H), 4.34 (dt, *J* = 9.9, 3.0 Hz, 1H), 1.63 (d, *J* = 9.3 Hz, 9H), 1.12 (d, *J* = 9.3 Hz, 9H).

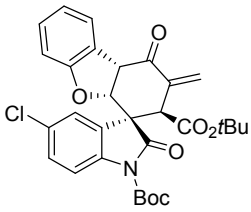
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.1, 172.7, 166.7, 159.6 (d, *J* = 243.0 Hz), 158.6, 148.8, 136.0, 129.9, 128.4 (d, *J* = 9.0 Hz), 125.7, 124.4, 123.8, 122.0, 116.1, 116.1, 115.8, 113.6 (d, *J* = 25.0 Hz), 109.8, 85.0, 82.7, 82.7, 51.5, 50.8, 50.5, 27.9, 27.0.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}FNNaO_7, M+Na]^+$: 558.1899, Found: 558.1877.

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.591 min (major), t_R = 8.250 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 34.2° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 69%, 37.0 mg.





6o

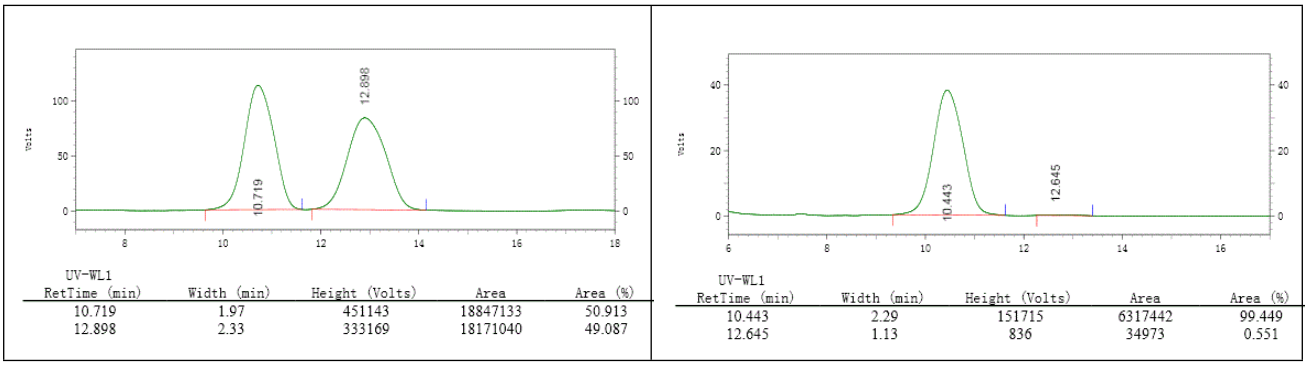
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.8 Hz, 1H), 7.59 (d, *J* = 2.2 Hz, 1H), 7.42 – 7.31 (m, 2H), 7.22 (t, *J* = 7.8 Hz, 1H), 6.94 (dd, *J* = 7.9, 5.3 Hz, 2H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.36 (d, *J* = 2.8 Hz, 1H), 4.98 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.36 – 4.27 (m, 1H), 1.62 (s, 9H), 1.11 (s, 9H).

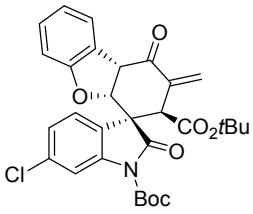
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 172.5, 166.8, 158.7, 148.8, 138.7, 136.1, 130.0, 130.0, 129.4, 128.4, 126.1, 125.7, 124.5, 123.9, 122.1, 116.1, 109.9, 85.2, 82.8, 82.7, 51.6, 50.8, 50.5, 28.0, 27.1.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}ClNNaO_7, M+ Na]^+$: 574.1603, Found: 574.1611.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 10.443 min (major), t_R = 12.645 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 27.4° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 45%, 24.8 mg.





6p

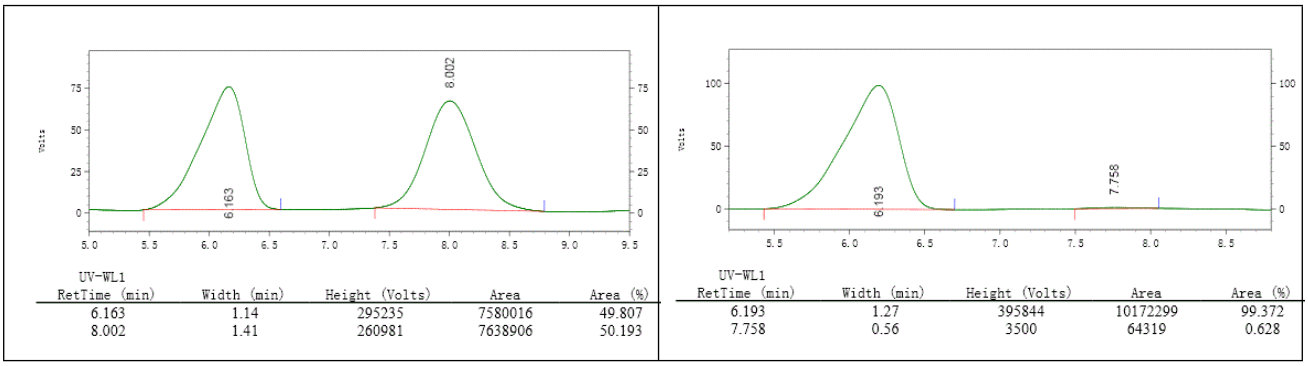
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 1.9 Hz, 1H), 7.54 (d, *J* = 8.1 Hz, 1H), 7.34 (d, *J* = 7.4 Hz, 1H), 7.26 – 7.19 (m, 2H), 6.96 – 6.85 (m, 2H), 6.44 (d, *J* = 3.2 Hz, 1H), 5.36 (d, *J* = 2.9 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 4.51 (d, *J* = 9.3 Hz, 1H), 4.33 (t, *J* = 3.0 Hz, 1H), 1.63 (s, 9H), 1.11 (s, 9H).

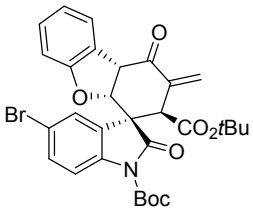
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 172.7, 166.8, 158.7, 148.7, 140.9, 136.0, 135.4, 129.9, 126.8, 125.7, 125.0, 124.6, 124.5, 123.9, 122.0, 115.6, 109.8, 85.4, 82.8, 82.8, 51.6, 50.6, 50.5, 28.0, 27.1.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}ClNNaO_7, M+ Na]^+$: 574.1603, Found: 574.1607.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.193 min (major), t_R = 7.758 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 38.4° (c = 1.0, $CHCl_3$); **Physical properties:** yellow solid; **Yield:** 75%, 41.4 mg.





6q

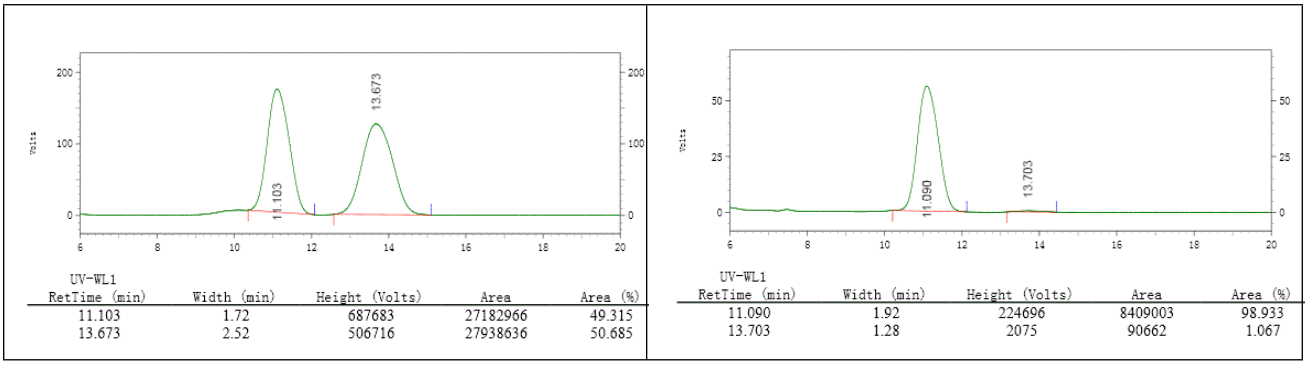
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.7 Hz, 1H), 7.73 (d, *J* = 2.1 Hz, 1H), 7.55 (dd, *J* = 8.8, 2.1 Hz, 1H), 7.35 (d, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 8.0 Hz, 1H), 6.94 (dt, *J* = 7.5, 3.4 Hz, 2H), 6.43 (d, *J* = 3.1 Hz, 1H), 5.36 (d, *J* = 2.8 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 4.49 (d, *J* = 9.4 Hz, 1H), 4.33 (d, *J* = 3.0 Hz, 1H), 1.62 (s, 9H), 1.11 (s, 9H).

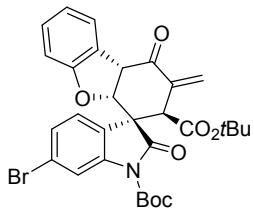
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 172.4, 166.8, 158.7, 148.7, 139.2, 136.1, 132.4, 130.0, 128.9, 128.8, 125.7, 124.5, 123.9, 122.1, 117.5, 116.5, 109.9, 85.3, 82.8, 82.7, 51.6, 50.8, 50.5, 28.0, 27.1.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}BrNNaO_7, M+ Na]^+$: 618.1098, Found: 618.1095.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 98:2, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 11.090 min (major), t_R = 13.703 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 11.4° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 46%, 27.4 mg.





6r

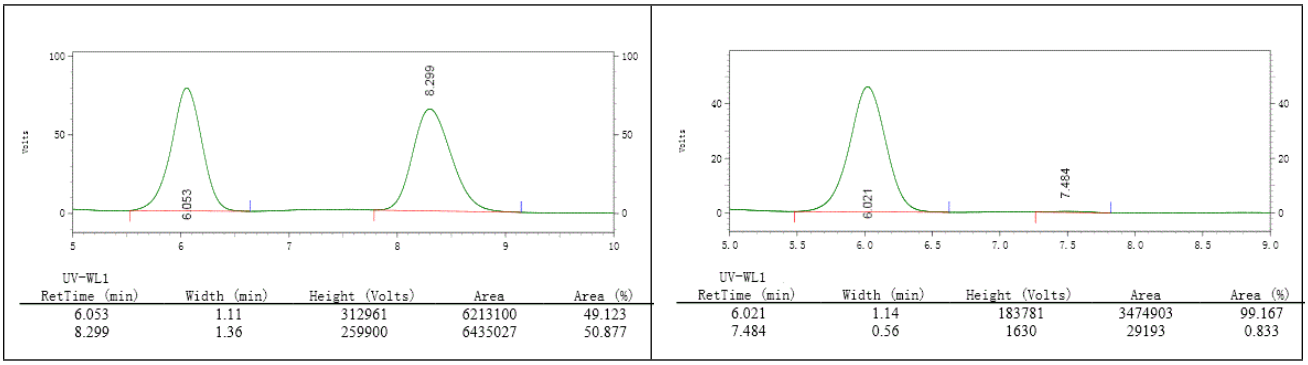
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, *J* = 1.7 Hz, 1H), 7.47 (d, *J* = 8.1 Hz, 1H), 7.40 (dd, *J* = 8.2, 1.7 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.7 Hz, 1H), 6.96 – 6.86 (m, 2H), 6.43 (d, *J* = 3.2 Hz, 1H), 5.35 (d, *J* = 2.9 Hz, 1H), 4.97 (d, *J* = 9.3 Hz, 1H), 4.50 (d, *J* = 9.3 Hz, 1H), 4.33 (t, *J* = 3.0 Hz, 1H), 1.62 (s, 9H), 1.11 (s, 9H).

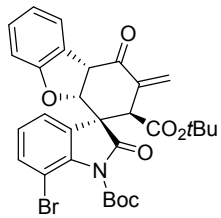
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 172.6, 166.8, 158.7, 148.7, 141.1, 136.1, 129.9, 127.5, 127.1, 125.7, 125.6, 124.4, 123.9, 123.3, 122.0, 118.3, 109.7, 85.4, 82.8, 82.7, 51.6, 50.6, 50.5, 28.0, 27.1.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}BrNNaO_7, M+Na]^+$: 618.1098, Found: 618.1093.

HPLC analysis: Chiralcel AD-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 6.021 min (major), t_R = 7.484 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 24.4° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 51%, 30.4 mg.





6s

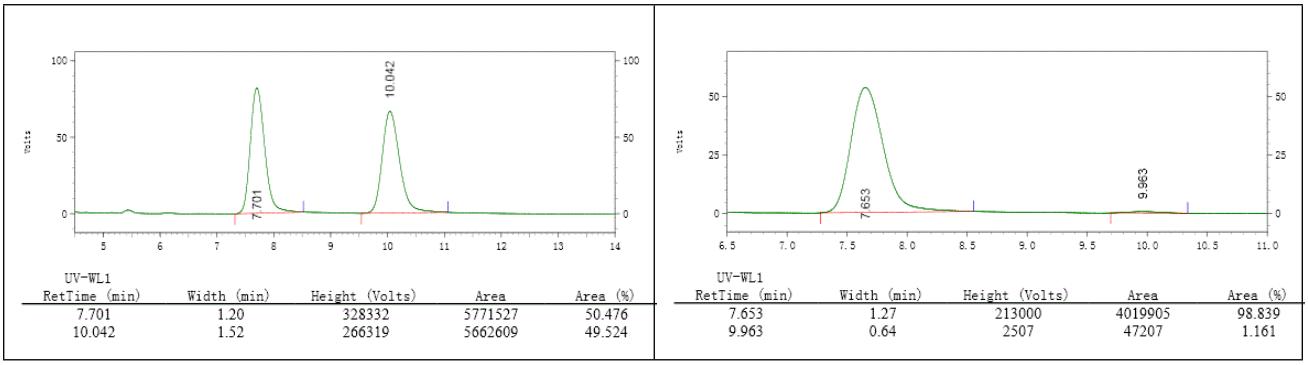
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.52 (m, 2H), 7.35 – 7.31 (m, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.13 (td, *J* = 7.9, 1.4 Hz, 1H), 6.95 – 6.86 (m, 2H), 6.45 (dd, *J* = 3.3, 1.4 Hz, 1H), 5.36 (d, *J* = 2.7 Hz, 1H), 5.02 (dd, *J* = 9.4, 1.5 Hz, 1H), 4.52 (d, *J* = 9.4 Hz, 1H), 4.35 – 4.27 (m, 1H), 1.63 (s, 9H), 1.13 (s, 9H).

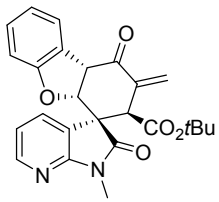
^{13}C NMR (100 MHz, $CDCl_3$) δ 190.4, 173.2, 166.8, 158.8, 147.5, 138.7, 136.1, 134.1, 130.1, 129.9, 125.7, 125.4, 125.2, 124.7, 123.8, 122.0, 109.7, 105.9, 85.9, 83.0, 82.7, 51.7, 51.6, 50.2, 27.6, 27.1.

HRMS (ESI) m/z Calcd for $[C_{30}H_{30}BrNNaO_7, M+Na]^+$: 618.1098, Found: 618.1096.

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH) = 95:5, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.653 min (major), t_R = 9.963 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 11.9° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 46%, 27.4 mg.





6t

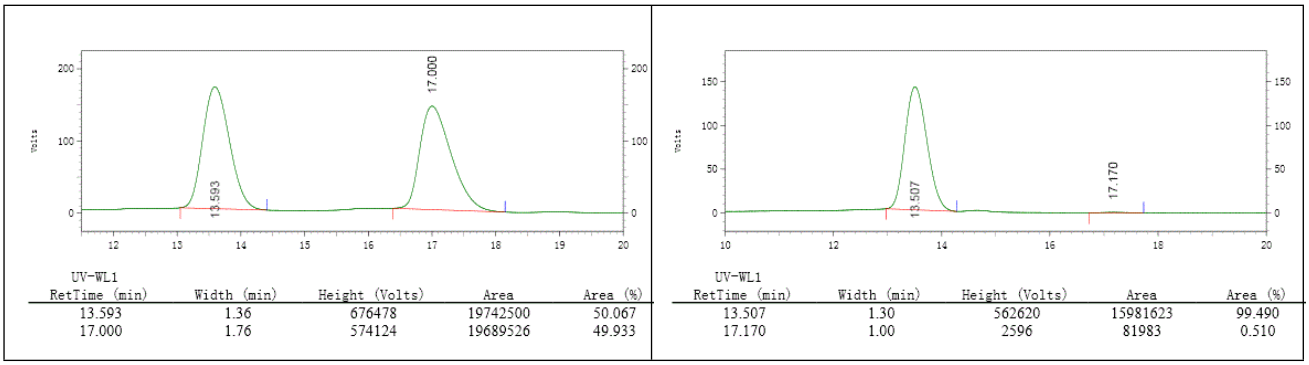
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (dd, *J* = 5.3, 1.6 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.35 (d, *J* = 7.5 Hz, 1H), 7.22 (t, *J* = 7.8 Hz, 1H), 7.06 (dd, *J* = 7.3, 5.3 Hz, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 6.44 (d, *J* = 3.1 Hz, 1H), 5.32 (d, *J* = 2.9 Hz, 1H), 4.95 (d, *J* = 9.5 Hz, 1H), 4.53 (d, *J* = 9.4 Hz, 1H), 4.34 (t, *J* = 3.0 Hz, 1H), 3.33 (s, 3H), 1.09 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 190.2, 174.6, 167.3, 158.9, 157.1, 148.0, 136.5, 133.5, 129.9, 125.8, 124.0, 122.6, 122.0, 118.3, 109.7, 82.7, 82.5, 51.8, 50.5, 49.7, 27.3, 25.5.

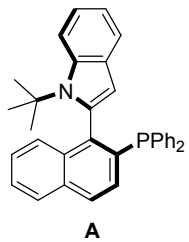
HRMS (ESI) m/z Calcd for $[C_{25}H_{24}N_2NaO_5, M+Na]^+$: 455.1577, Found: 455.1563.

HPLC analysis: Chiralcel IA-H (Hexane/*i*-PrOH) = 85:15, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 13.507 min (major), t_R = 17.170 min (minor).

Optical Rotation: $[\alpha]_D^{20}$ = 8.6° (c = 1.0, $CHCl_3$); **Physical properties:** white solid; **Yield:** 91%, 39.4 mg.



IX. Analytical data of organocatalysts (A-H)



A

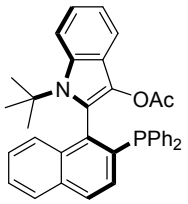
^{1}H NMR (400 MHz, DMSO-d_6) δ 7.94 (t, *J* = 8.0 Hz, 2H), 7.86 (d, *J* = 8.6 Hz, 1H), 7.55 (t, *J* = 7.5 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 1H), 7.42 – 7.31 (m, 7H), 7.23 – 7.16 (m, 4H), 7.15 – 7.07 (m, 3H), 7.01 (t, *J* = 7.4 Hz, 1H), 5.85 (s, 1H), 1.52 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 142.5, 139.0, 138.8, 137.5, 137.4, 136.9, 136.8, 136.5, 135.9, 135.8, 135.0, 134.9, 134.0, 133.8, 133.4, 133.2, 132.8, 129.6, 129.0, 128.5, 128.4, 128.4, 128.3, 128.2, 128.2, 127.7, 127.0, 127.0, 126.6, 120.6, 118.9, 114.9, 109.1, 109.1, 59.0, 30.6.

^{31}P NMR (243 MHz, $CDCl_3$) δ -12.85.

HRMS (ESI) m/z Calcd for $[C_{34}H_{31}NP, M+H]^+$: 484.2189, Found: 484.2167.

Physical properties: white solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -221.1° (c = 1.0, $CHCl_3$).



B

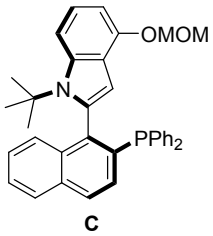
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 – 7.78 (m, 3H), 7.48 (td, *J* = 7.2, 3.6 Hz, 2H), 7.42 – 7.36 (m, 2H), 7.33 – 7.24 (m, 12H), 7.13 (td, *J* = 7.4, 1.9 Hz, 1H), 1.58 (d, *J* = 1.8 Hz, 3H), 1.52 (d, *J* = 2.2 Hz, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 168.5, 139.3, 139.0, 138.4, 138.3, 137.5, 137.4, 137.1, 137.0, 134.5, 134.5, 134.1, 133.9, 133.8, 133.4, 133.2, 133.0, 130.2, 130.2, 130.1, 128.8, 128.5, 128.4, 128.3, 128.3, 128.1, 128.1, 127.6, 127.2, 127.0, 126.8, 121.6, 121.5, 119.2, 117.9, 115.0, 59.3, 30.6, 20.0.

^{31}P NMR (243 MHz, $CDCl_3$) δ -14.27.

HRMS (ESI) m/z Calcd for $[C_{36}H_{33}NO_2P, M+H]^+$: 542.2243, Found: 542.2243.

Physical properties: yellow solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -152.2° (c = 1.0, $CHCl_3$).



C

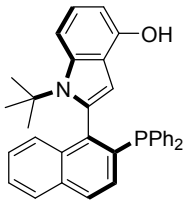
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 9.2 Hz, 2H), 7.50 – 7.40 (m, 2H), 7.36 – 7.17 (m, 13H), 7.11 (t, *J* = 8.1 Hz, 1H), 6.72 (d, *J* = 7.6 Hz, 1H), 6.04 (s, 1H), 5.13 (d, *J* = 6.2 Hz, 1H), 5.03 (d, *J* = 6.1 Hz, 1H), 3.31 (s, 3H), 1.60 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 150.1, 142.8, 142.4, 138.9, 138.8, 138.2, 137.5, 137.4, 135.9, 135.8, 135.8, 135.7, 135.0, 134.9, 133.9, 133.7, 133.4, 133.2, 132.8, 129.6, 128.5, 128.4, 128.3, 128.2, 128.2, 128.1, 127.7, 127.1, 127.1, 126.6, 121.2, 120.8, 109.6, 106.0, 103.9, 94.6, 59.1, 55.8, 30.6.

^{31}P NMR (243 MHz, $CDCl_3$) δ -12.74.

HRMS (ESI) m/z Calcd for $[C_{36}H_{35}NO_2P, M+H]^+$: 544.2400, Found: 544.2390.

Physical properties: white solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -233.6° (c = 1.0, $CHCl_3$).



D

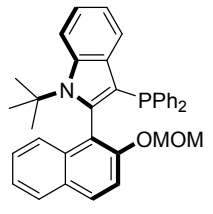
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (t, *J* = 8.8 Hz, 2H), 7.44 (dt, *J* = 8.1, 3.9 Hz, 1H), 7.39 (d, *J* = 8.6 Hz, 1H), 7.36 – 7.20 (m, 13H), 7.06 (t, *J* = 8.1 Hz, 1H), 6.52 (d, *J* = 7.6 Hz, 1H), 5.83 (s, 1H), 4.96 (s, 1H), 1.59 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 148.5, 142.5, 142.1, 138.6, 138.5, 138.2, 137.6, 137.5, 136.1, 136.0, 135.8, 135.7, 135.0, 134.9, 134.1, 133.9, 133.4, 133.2, 132.8, 129.5, 128.5, 128.4, 128.4, 128.3, 128.3, 127.7, 126.9, 126.7, 126.6, 121.6, 118.5, 108.2, 104.4, 104.3, 103.6, 59.2, 30.5.

^{31}P NMR (243 MHz, $CDCl_3$) δ -12.60.

HRMS (ESI) m/z Calcd for $[C_{34}H_{31}NOP, M+H]^+$: 500.2138, Found: 500.2132.

Physical properties: white solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -187.4° (c = 1.0, $CHCl_3$).



E

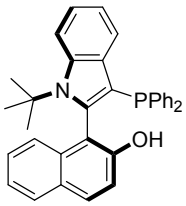
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.83 (dd, *J* = 14.7, 8.1 Hz, 2H), 7.47 (dd, *J* = 9.1, 1.9 Hz, 1H), 7.38 – 7.26 (m, 5H), 7.24 – 7.09 (m, 9H), 7.01 (d, *J* = 8.1 Hz, 1H), 6.87 (t, *J* = 7.6 Hz, 1H), 4.91 (dd, *J* = 7.2, 2.0 Hz, 1H), 4.71 (dd, *J* = 7.1, 2.0 Hz, 1H), 3.21 (s, 3H), 1.57 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 154.1, 144.2, 143.7, 138.5, 138.4, 138.1, 137.9, 137.8, 135.4, 135.4, 132.8, 132.6, 132.2, 132.0, 131.0, 131.0, 130.7, 128.7, 127.9, 127.8, 127.7, 127.3, 127.1, 126.8, 125.4, 123.9, 122.0, 120.6, 120.6, 120.5, 119.2, 115.2, 115.1, 106.9, 94.8, 59.5, 55.7, 30.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ -28.84.

HRMS (ESI) m/z Calcd for $[C_{36}H_{35}NO_2P, M+H]^+$: 544.2400, Found:544.2397.

Optical Rotation: $[\alpha]_D^{20}$ = -60.6° (c = 1.0, $CHCl_3$); **Physical properties:** white solid



F

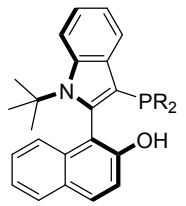
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87 (dd, *J* = 8.8, 3.0 Hz, 2H), 7.82 – 7.76 (m, 1H), 7.44 (dq, *J* = 7.4, 2.4, 2.0 Hz, 2H), 7.30 – 7.20 (m, 7H), 7.18 – 7.08 (m, 7H), 6.93 (t, *J* = 7.5 Hz, 1H), 5.09 (s, 1H), 1.54 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 152.1, 140.7, 140.2, 138.9, 138.9, 137.6, 137.5, 137.5, 137.4, 135.3, 132.8, 132.6, 132.3, 132.1, 131.1, 130.7, 130.7, 128.3, 128.3, 128.1, 127.9, 127.9, 127.8, 127.4, 127.0, 124.7, 123.5, 122.4, 121.6, 119.8, 116.9, 116.6, 116.5, 115.6, 110.3, 110.3, 60.0, 30.4.

^{31}P NMR (243 MHz, $CDCl_3$) δ -28.98.

HRMS (ESI) m/z Calcd for $[C_{34}H_{31}NOP, M+H]^+$: 500.2138, Found: 500.2136.

Physical properties: white solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -55.6° (c = 1.0, $CHCl_3$).



R=4-methoxyphenyl

G

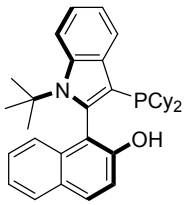
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 8.7 Hz, 2H), 7.80 – 7.74 (m, 1H), 7.35 (t, *J* = 7.7 Hz, 2H), 7.27 – 7.17 (m, 5H), 7.11 – 7.01 (m, 3H), 6.95 (t, *J* = 7.6 Hz, 1H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.67 (d, *J* = 8.1 Hz, 2H), 5.14 (s, 1H), 3.75 (s, 3H), 3.70 (s, 3H), 1.52 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 159.1, 152.1, 140.1, 139.6, 138.9, 138.8, 135.3, 134.3, 134.1, 133.7, 133.5, 131.0, 130.8, 130.7, 128.8, 128.8, 128.7, 128.3, 128.0, 126.9, 124.7, 123.4, 122.4, 121.5, 119.7, 116.9, 116.7, 116.7, 115.5, 114.0, 114.0, 113.6, 113.6, 111.3, 59.9, 55.1, 55.0, 30.3.

^{31}P NMR (243 MHz, $CDCl_3$) δ -30.87.

HRMS (ESI) m/z Calcd for $[C_{36}H_{35}NO_3P, M+H]^+$: 560.2349, Found: 560.2346.

Physical properties: white solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -52.5° (c = 1.0, $CHCl_3$).



H

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.0 Hz, 1H), 7.86 (t, *J* = 8.0 Hz, 2H), 7.77 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.33 – 7.25 (m, 3H), 7.24 – 7.17 (m, 2H), 7.08 (dd, *J* = 6.4, 3.4 Hz, 1H), 5.18 (s, 1H), 2.36 (tdt, *J* = 11.9, 5.8, 3.1 Hz, 1H), 2.19 – 2.08 (m, 1H), 1.83 (d, *J* = 13.1 Hz, 1H), 1.73 (d, *J* = 12.2 Hz, 1H), 1.64 – 1.40 (m, 15H), 1.36 – 1.22 (m, 2H), 1.21 – 1.06 (m, 5H), 1.06 – 0.68 (m, 5H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 151.4, 138.6, 135.4, 130.9, 128.2, 128.0, 126.2, 125.6, 123.3, 122.1, 121.4, 119.5, 116.9, 115.6, 59.7, 34.8, 34.7, 33.8, 33.8, 32.6, 32.3, 32.1, 31.9, 30.7, 30.7, 30.6, 30.5, 30.3, 27.5, 27.4, 27.3, 27.3, 27.2, 27.1, 27.1, 26.2, 26.1.

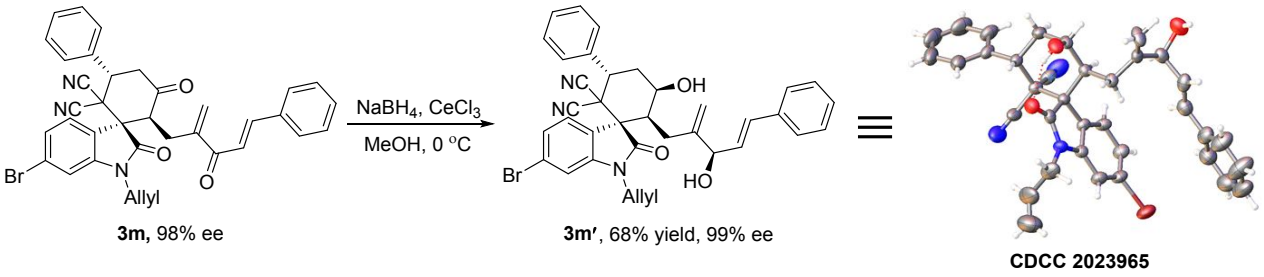
^{31}P NMR (243 MHz, $CDCl_3$) δ -17.84.

HRMS (ESI) m/z Calcd for $[C_{34}H_{43}NOP, M+H]^+$: 512.3077, Found: 512.3080.

Physical properties: yellow solid; **Optical Rotation:** $[\alpha]_D^{20}$ = -51.2° (c = 1.0, $CHCl_3$).

X. Determination of absolute configuration of products 3m and 6e

Determination of absolute configuration of product 3m:

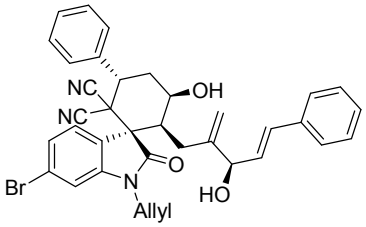


3m, 98% ee

3m′, 68% yield, 99% ee

CDCC 2023965

The absolute configuration of **3m** was determined by X-ray crystallography analysis of its dihydroxyl derivative **3m'**. The preparation of **3m'** was followed the literature procedure.[2] Into a 50 mL oven-dried three-necked bottle under nitrogen protection were added **3m** (200 mg, 0.32 mmol, 98% ee), $CeCl_3$ (158 mg , 0.64 mmol) and methanol (12 mL). The solution was cooled to 0 °C and $NaBH_4$ (36 mg, 0.96 mmol) was added in batches to the solution. The mixture was stirred at room temperature overnight and quenched with water. The solution was extracted with ethyl acetate for three times, the combined organic layer was washed with saturated NaCl and dried over anhydrous Na_2SO_4. The organic layer was concentrated and purified by column chromatography on silica gel (PE/EA,4:1) to give **3m'** (138 mg, 68% yield, 99% ee).



3m′

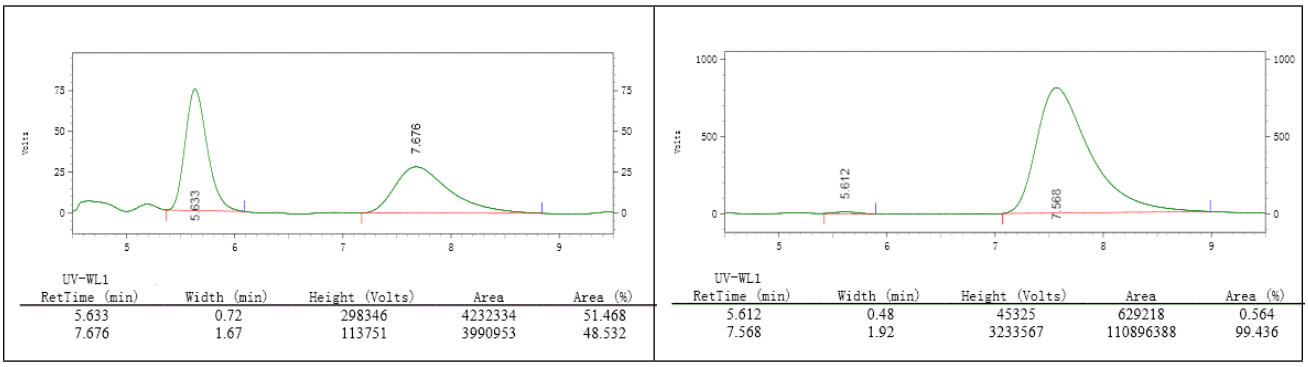
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (d, J = 8.1 Hz, 1H), 7.49 – 7.36 (m, 5H), 7.32 – 7.22 (m, 6H), 7.05 (s, 1H), 6.46 (d, J = 15.8 Hz, 1H), 5.98 (dd, J = 15.9, 5.7 Hz, 1H), 5.72 (ddt, J = 16.1, 10.5, 5.4 Hz, 1H), 5.36 (s, 1H), 5.29 – 5.18 (m, 2H), 5.12 (d, J = 10.5 Hz, 1H), 5.06 (s, 1H), 4.68 (s, 1H), 4.44 – 4.29 (m, 4H), 3.36 (s, 1H), 2.57 (t, J = 11.4 Hz, 2H), 2.40 (d, J = 14.7 Hz, 1H), 2.18 (t, J = 12.8 Hz, 1H), 1.49 (d, J = 13.4 Hz, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 175.0, 145.1, 143.8, 136.2, 135.5, 130.4, 130.3, 129.2, 129.2, 129.0, 128.9, 128.6, 127.7, 127.4, 126.4, 125.7, 124.8, 124.7, 119.4, 115.2, 114.0, 112.2, 112.0, 75.7, 75.6, 64.8, 57.0, 48.5, 43.4, 41.4, 38.1, 34.8, 27.2.

HRMS (ESI) m/z Calcd for $[C_{36}H_{32}BrN_3NaO_3$, M+ Na$]^+$: 656.1519, Found: 656.1517.

HPLC analysis: Chiralcel IC-H (Hexane/*i*-PrOH) = 70:30, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 5.612 min (minor), t_R = 7.568 min (major).

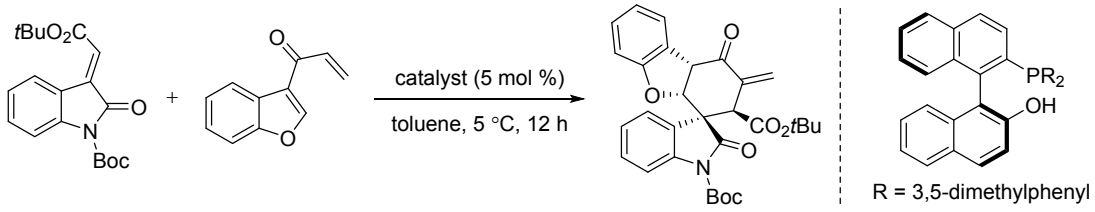
Optical Rotation: $[\alpha]_D^{20}$ = -43.4° (c = 1.0, CH_2Cl_2); **Physical properties:** white solid.



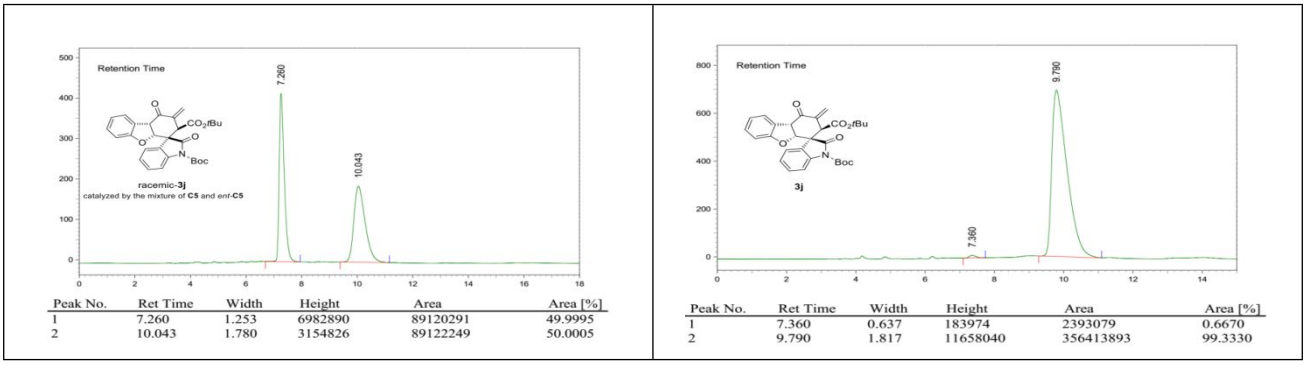
Determination of absolute configuration of product 6e:

The procedure were conducted according to the literature procedures.[4]

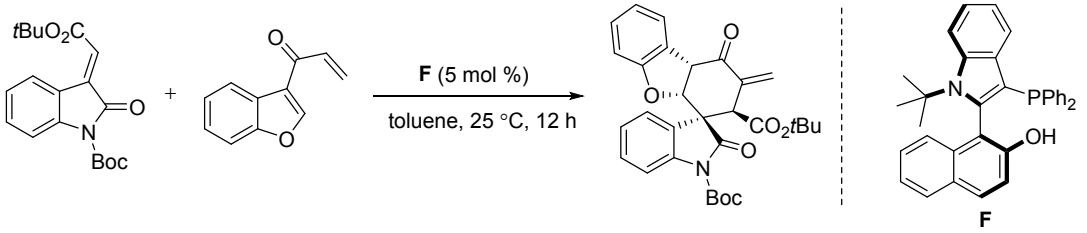
Reported work[4]:



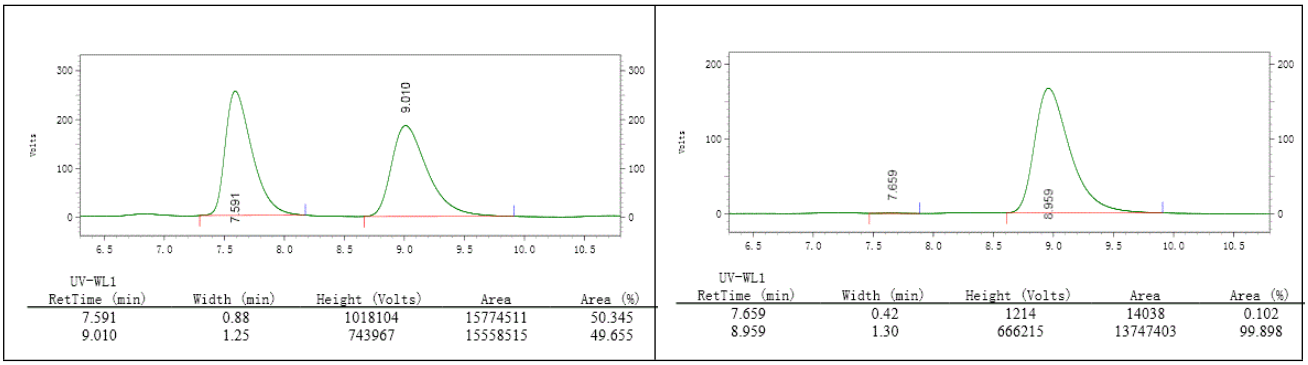
HPLC analysis: Chiralcel ID-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.360 min (minor), t_R = 9.790 min (major). **Optical Rotation:** $[\alpha]_D^{25}$ = 34.7° (c = 1.1, $CHCl_3$).



Our work:

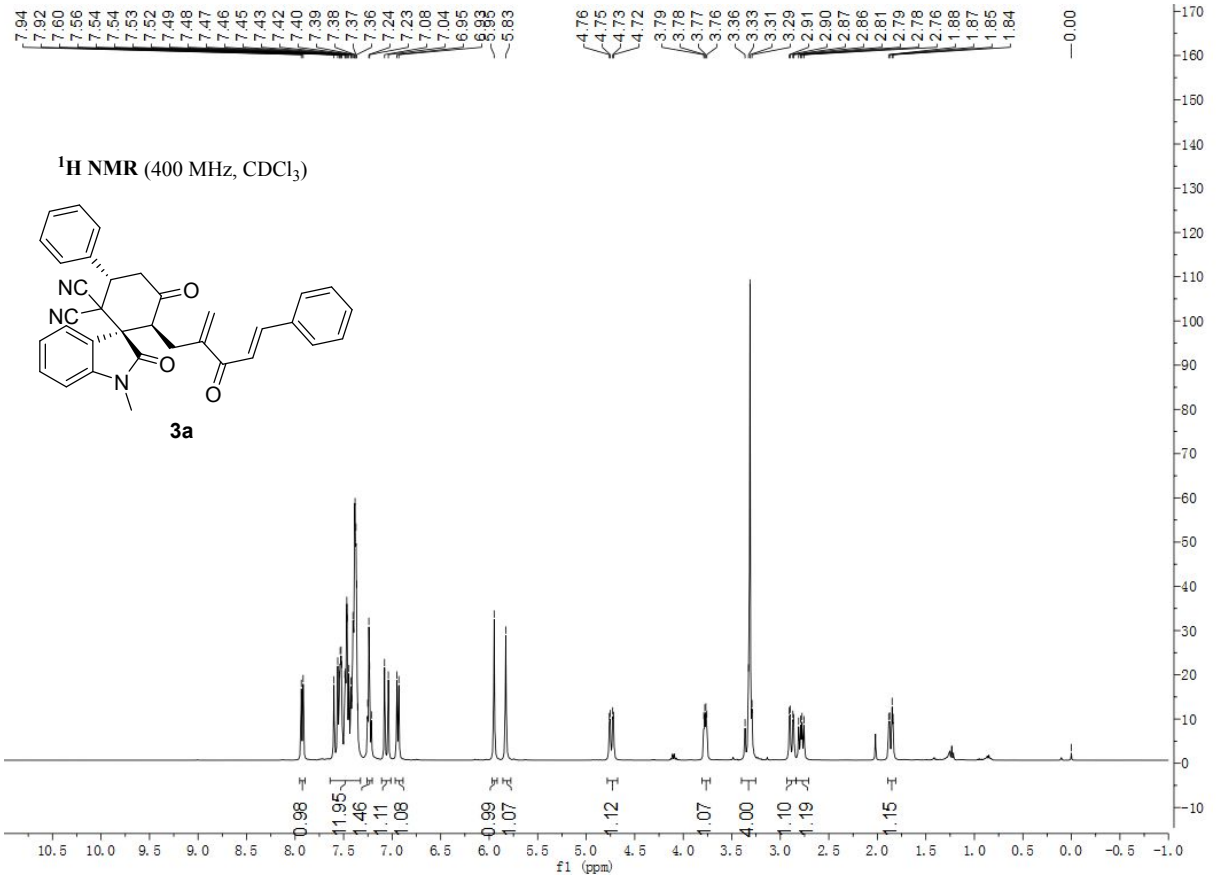


HPLC analysis: Chiralcel ID-H (Hexane/*i*-PrOH) = 80:20, flow rate = 1.0 mL/min, wave length = 254 nm, t_R = 7.659 min (minor), t_R = 8.959 min (major). **Optical Rotation:** $[\alpha]_D^{25}$ = 47.1° (c = 1.1, $CHCl_3$)



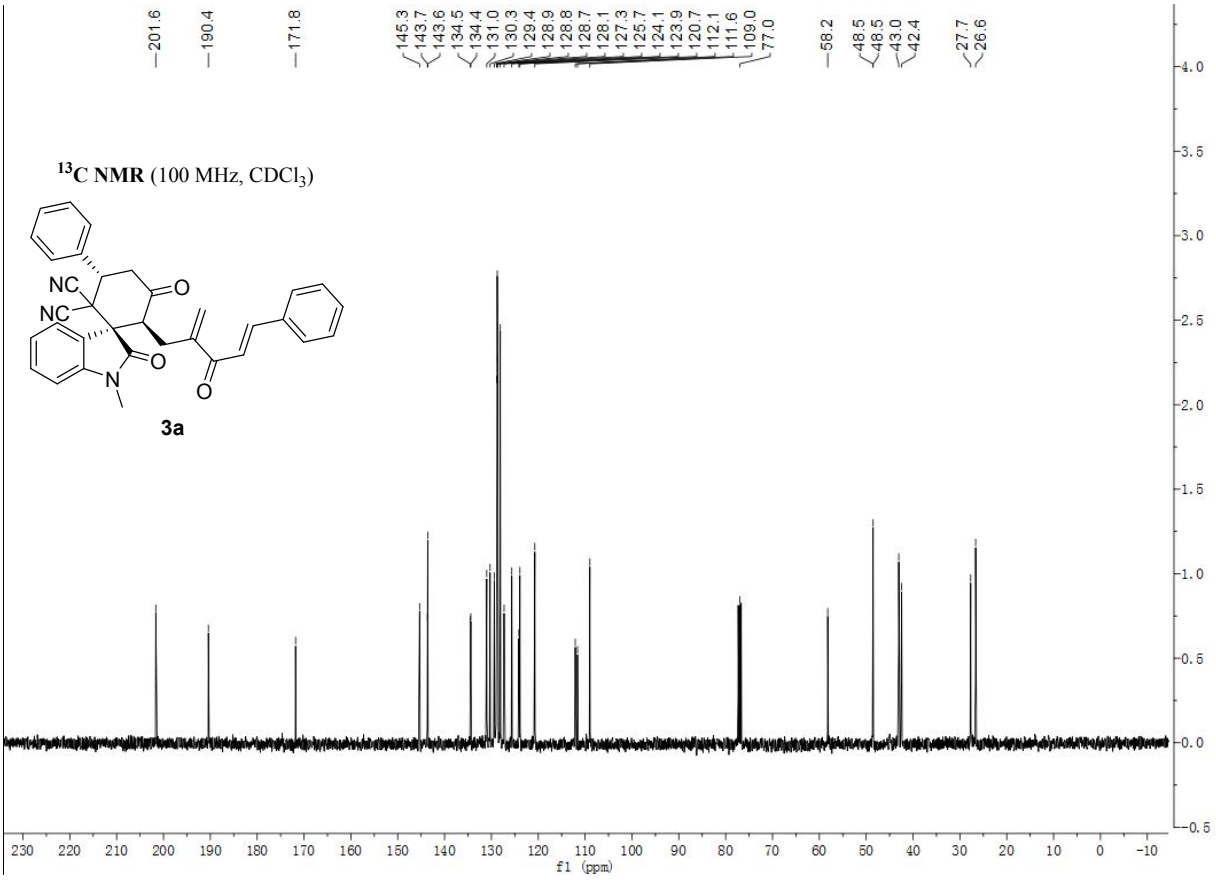
Notify: The racemic sample used in the left spectrum was prepared according to the exact same procedure of reported work[4].

XI. ^{1}H and ^{13}C NMR spectra of compounds (3a-3t, 6a-6t)



^{1}H NMR (400 MHz, $CDCl_3$)

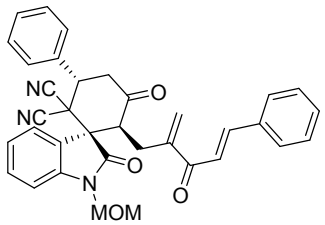
3a



^{13}C NMR (100 MHz, $CDCl_3$)

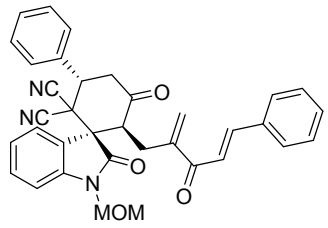
3a

^{1}H NMR (400 MHz, $CDCl_3$)

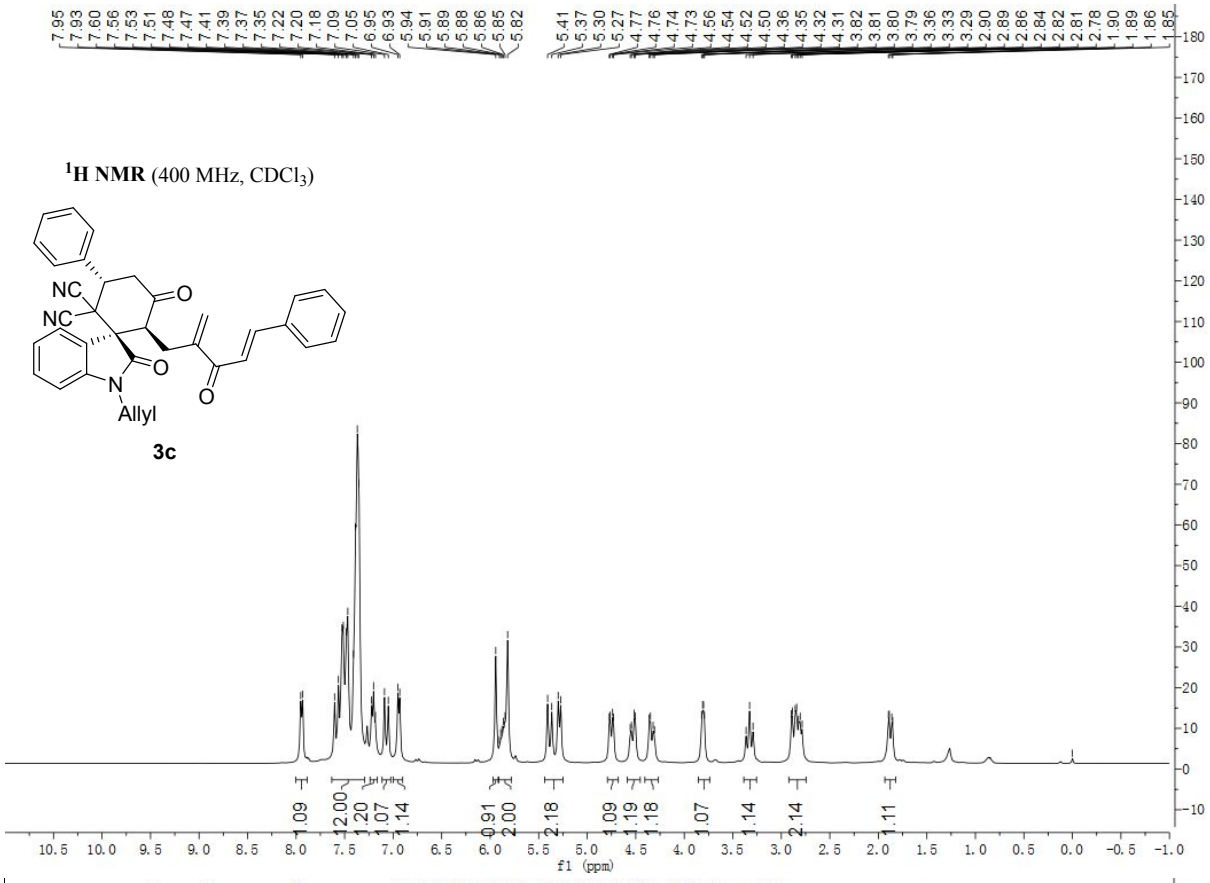


3b

^{13}C NMR (100 MHz, $CDCl_3$)

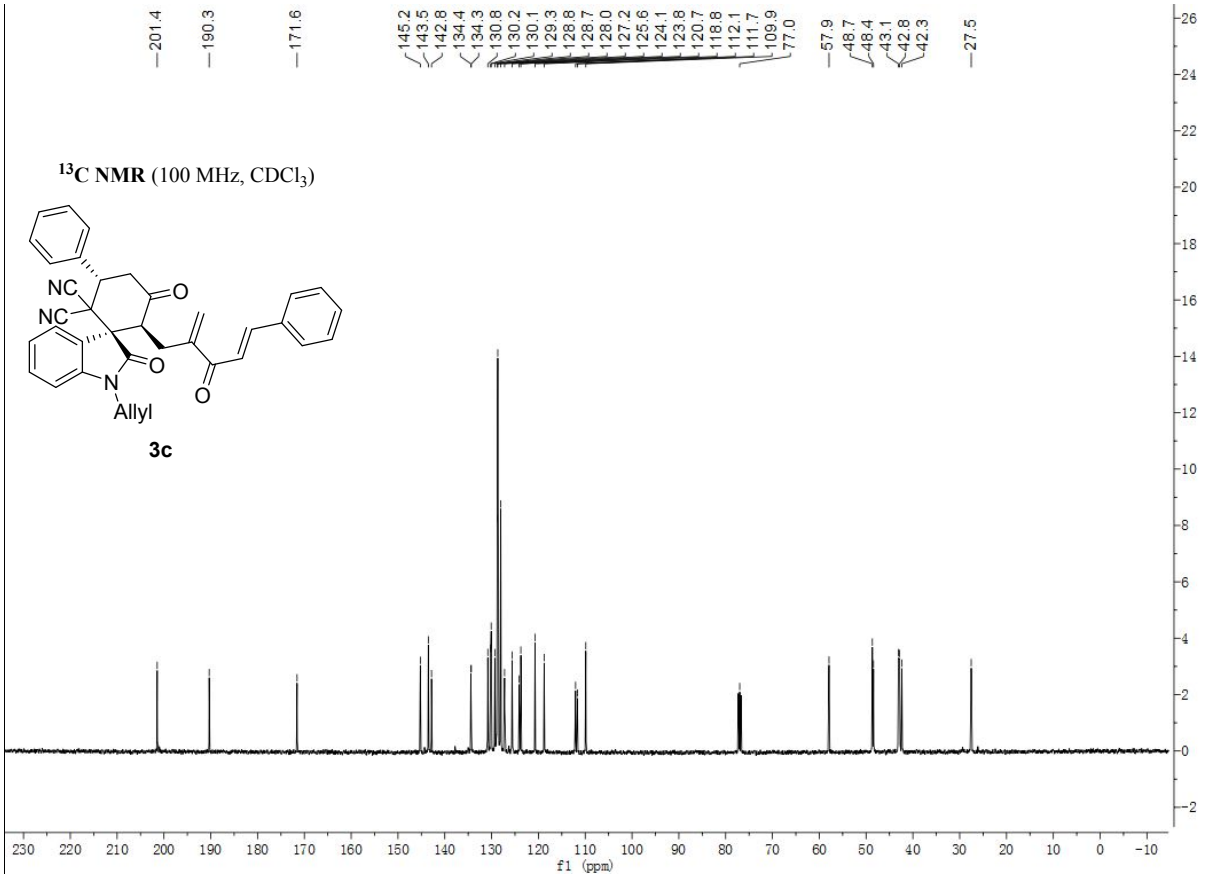


3b



^{1}H NMR (400 MHz, $CDCl_3$)

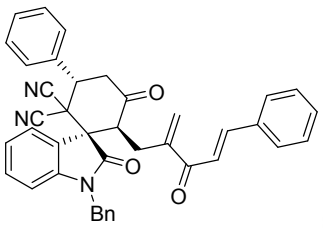
3c



^{13}C NMR (100 MHz, $CDCl_3$)

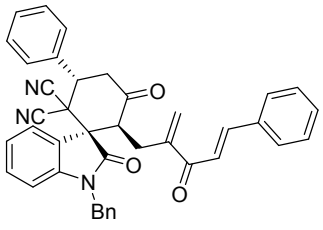
3c

^{1}H NMR (400 MHz, $CDCl_3$)

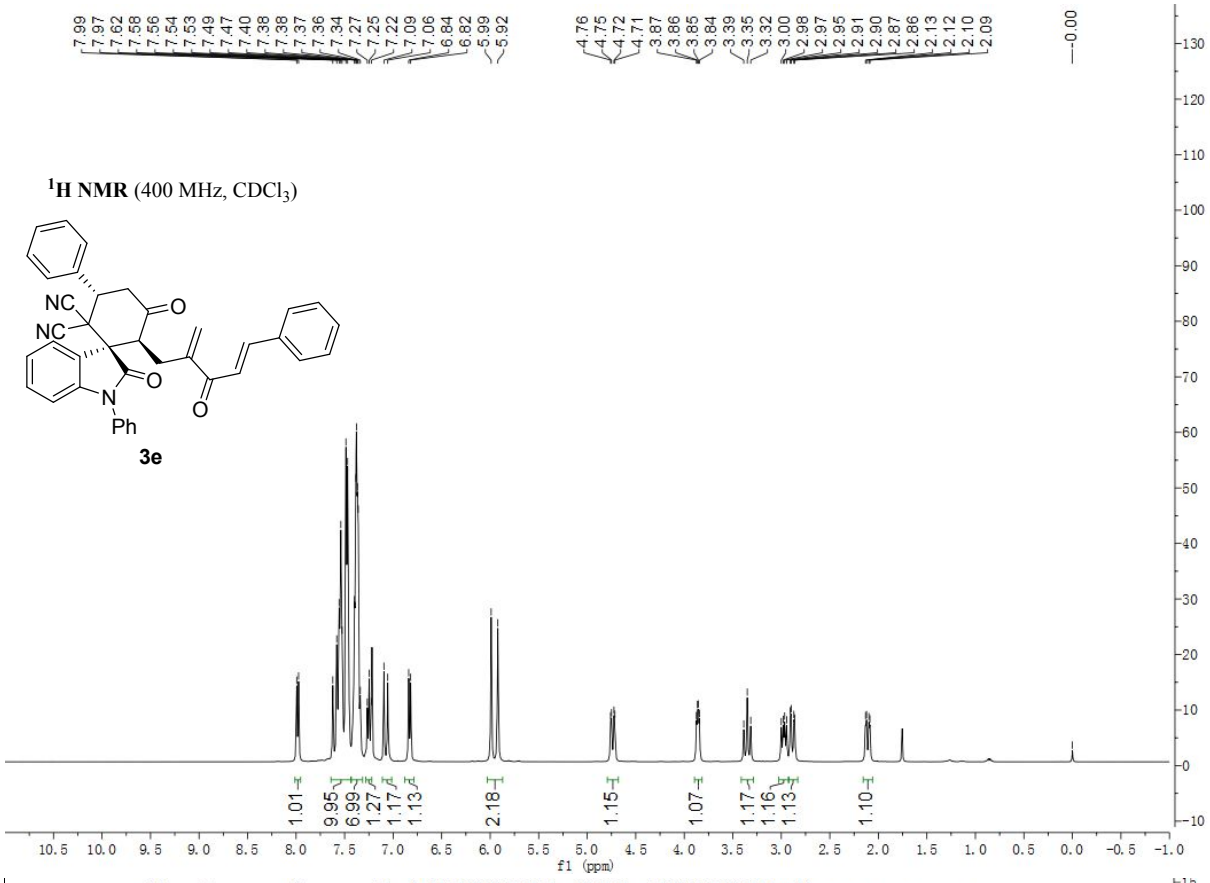


3d

^{13}C NMR (100 MHz, $CDCl_3$)

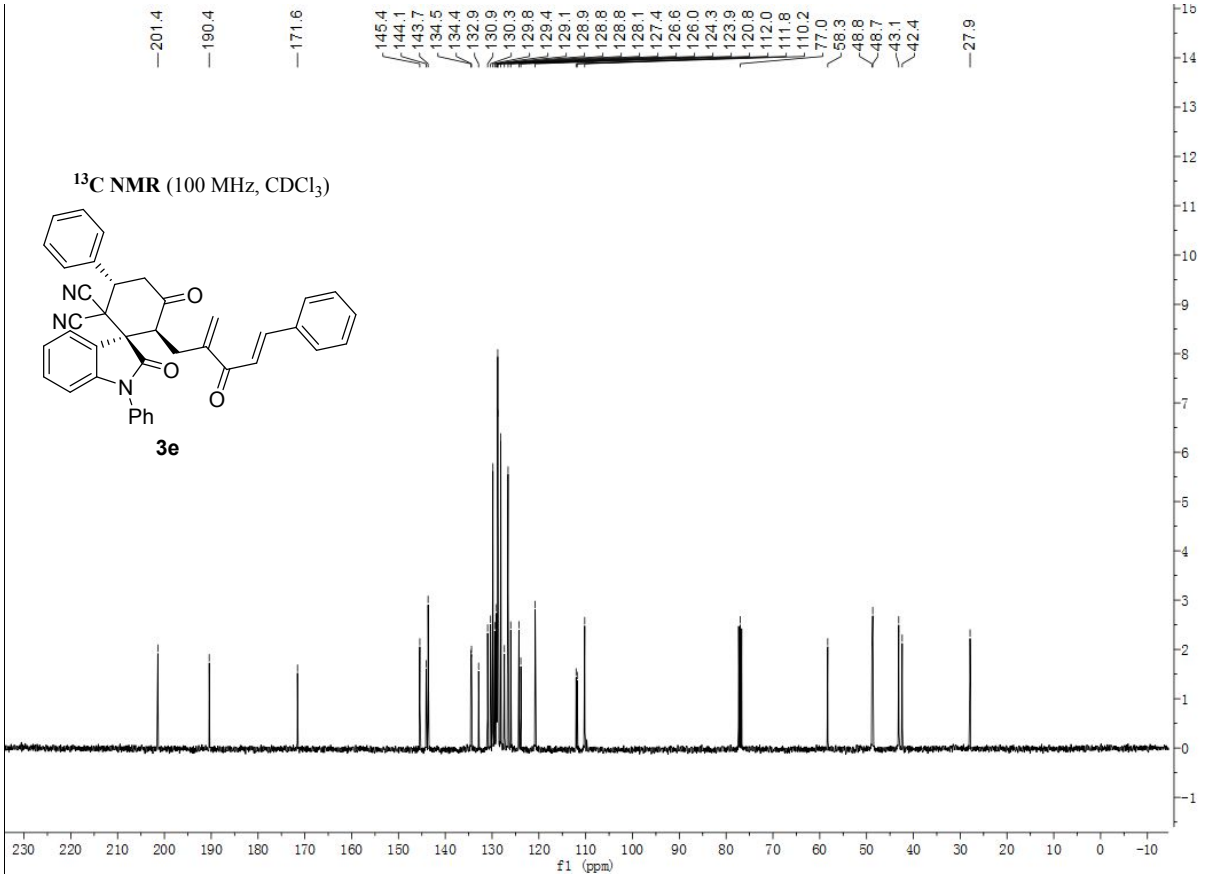


3d



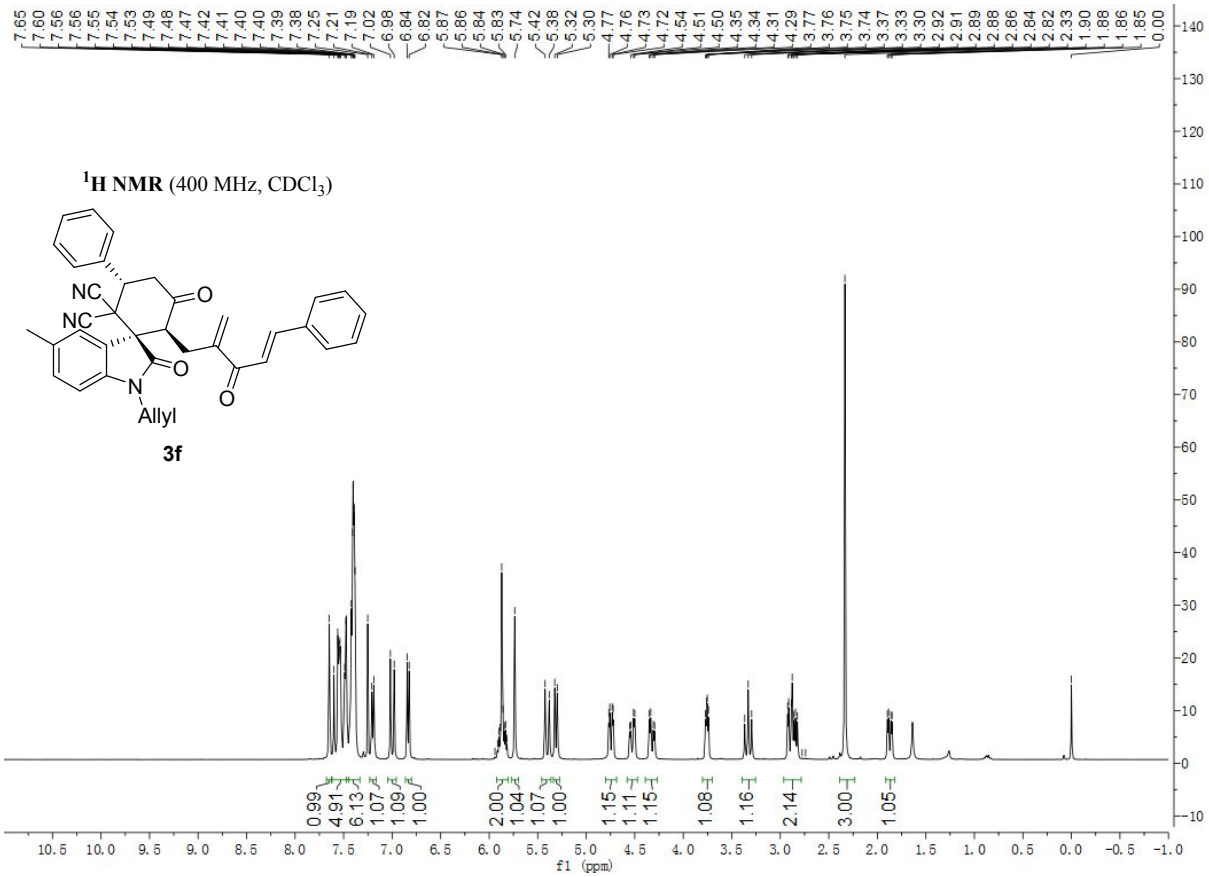
^{1}H NMR (400 MHz, $CDCl_3$)

3e



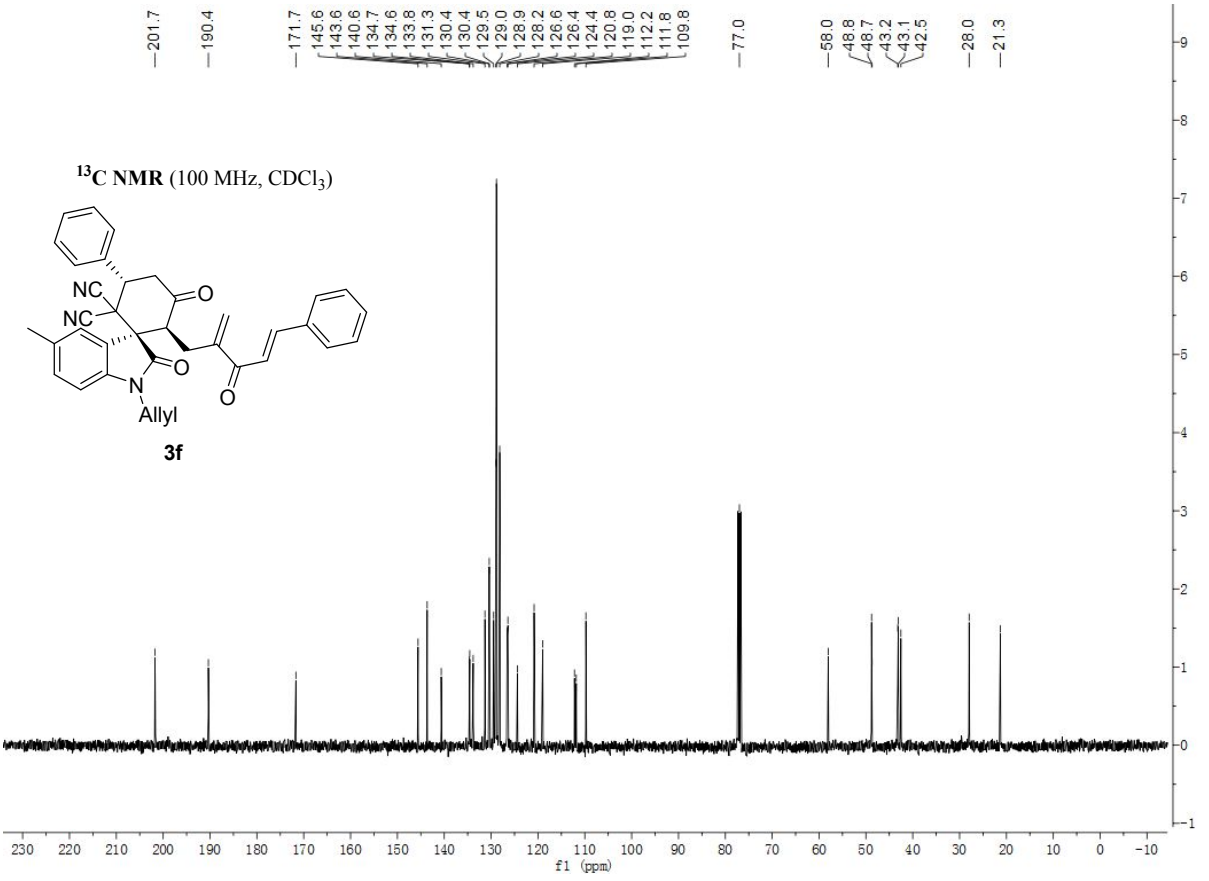
^{13}C NMR (100 MHz, $CDCl_3$)

3e



^{1}H NMR (400 MHz, $CDCl_3$)

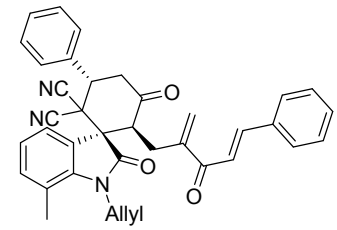
3f



^{13}C NMR (100 MHz, $CDCl_3$)

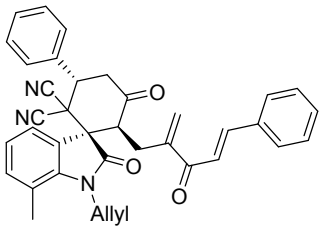
3f

^{1}H NMR (400 MHz, $CDCl_3$)

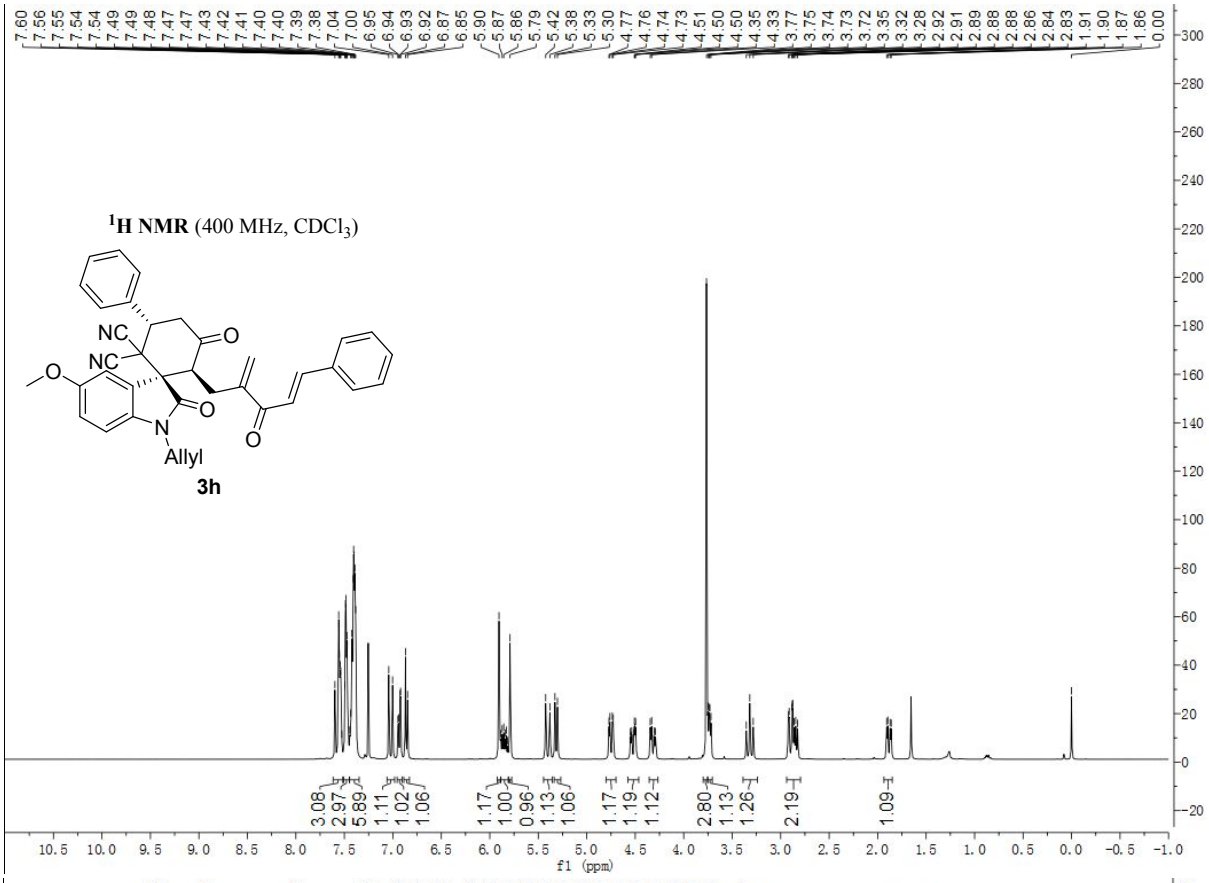


3g

^{13}C NMR (100 MHz, $CDCl_3$)

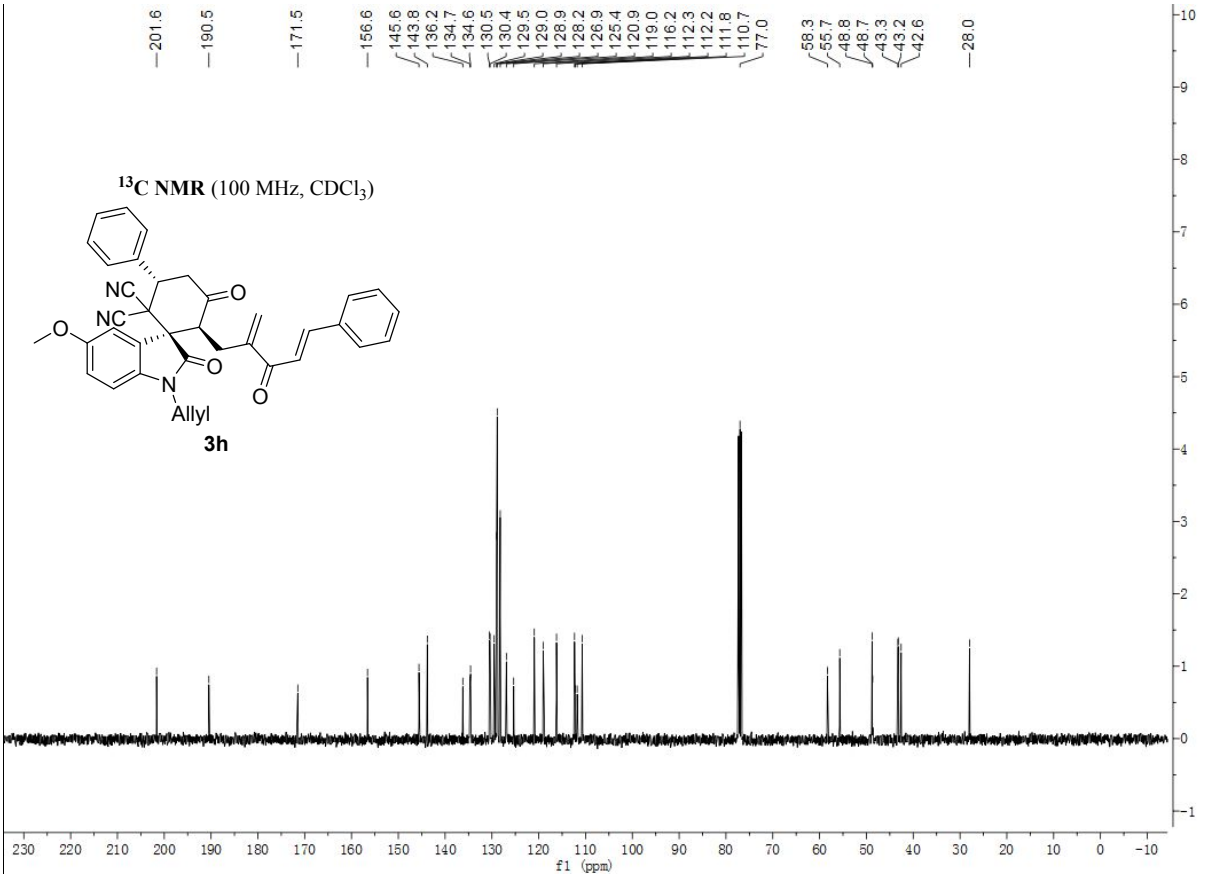


3g



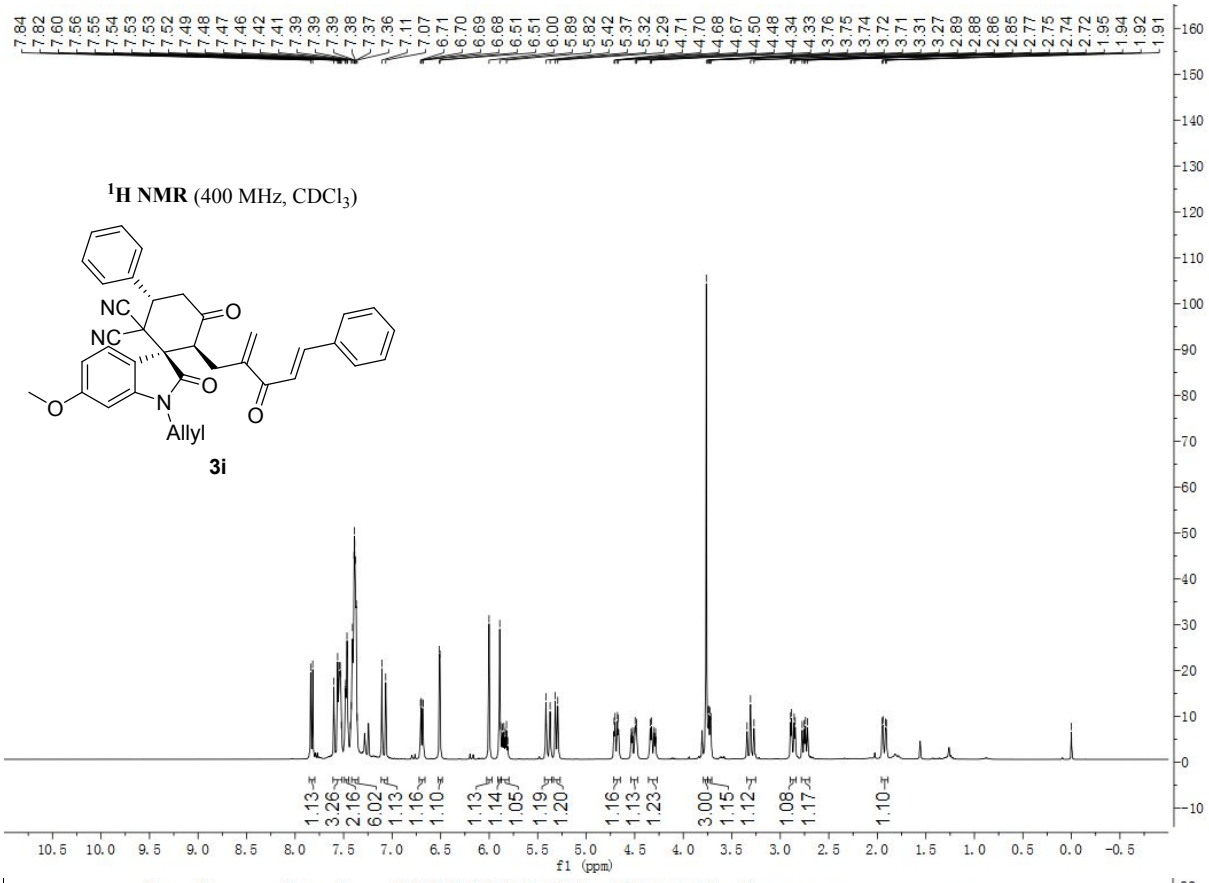
^{1}H NMR (400 MHz, $CDCl_3$)

3h



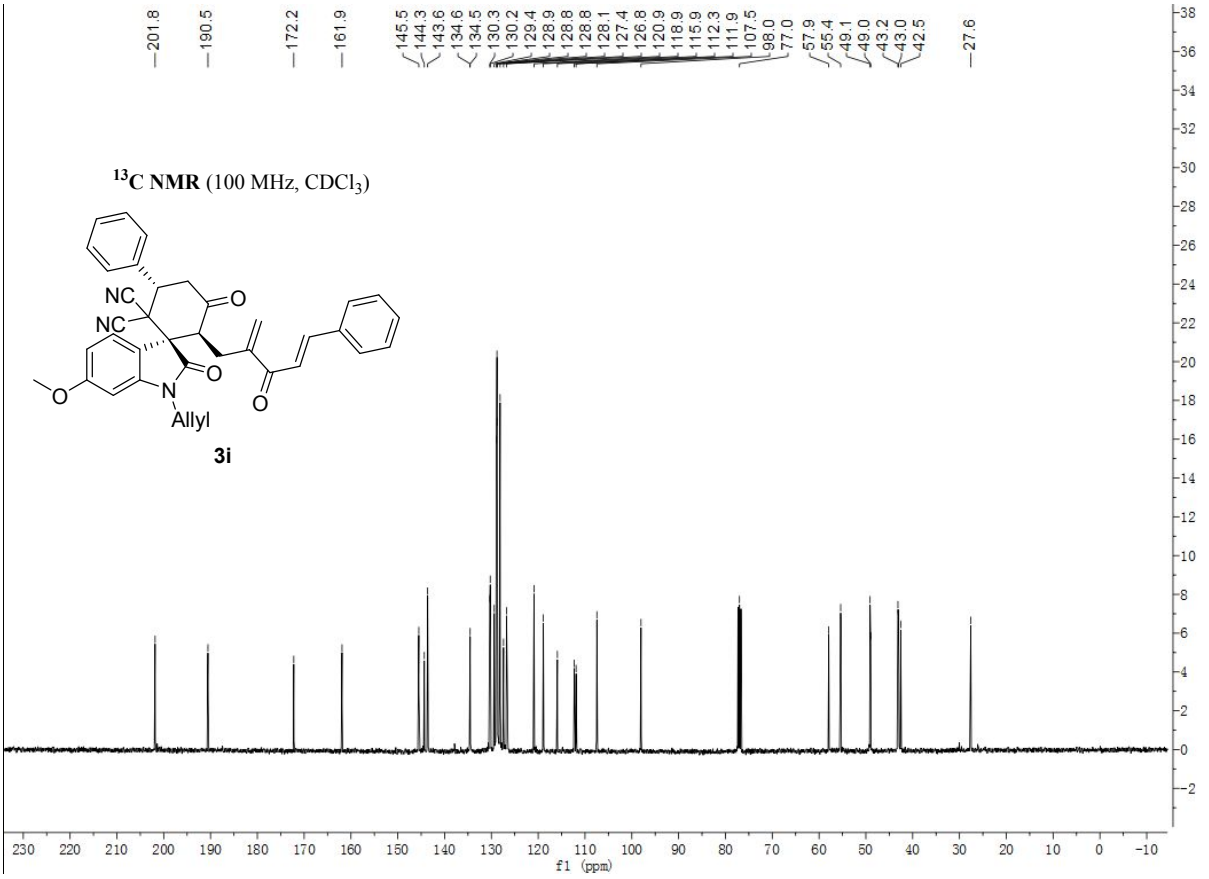
^{13}C NMR (100 MHz, $CDCl_3$)

3h



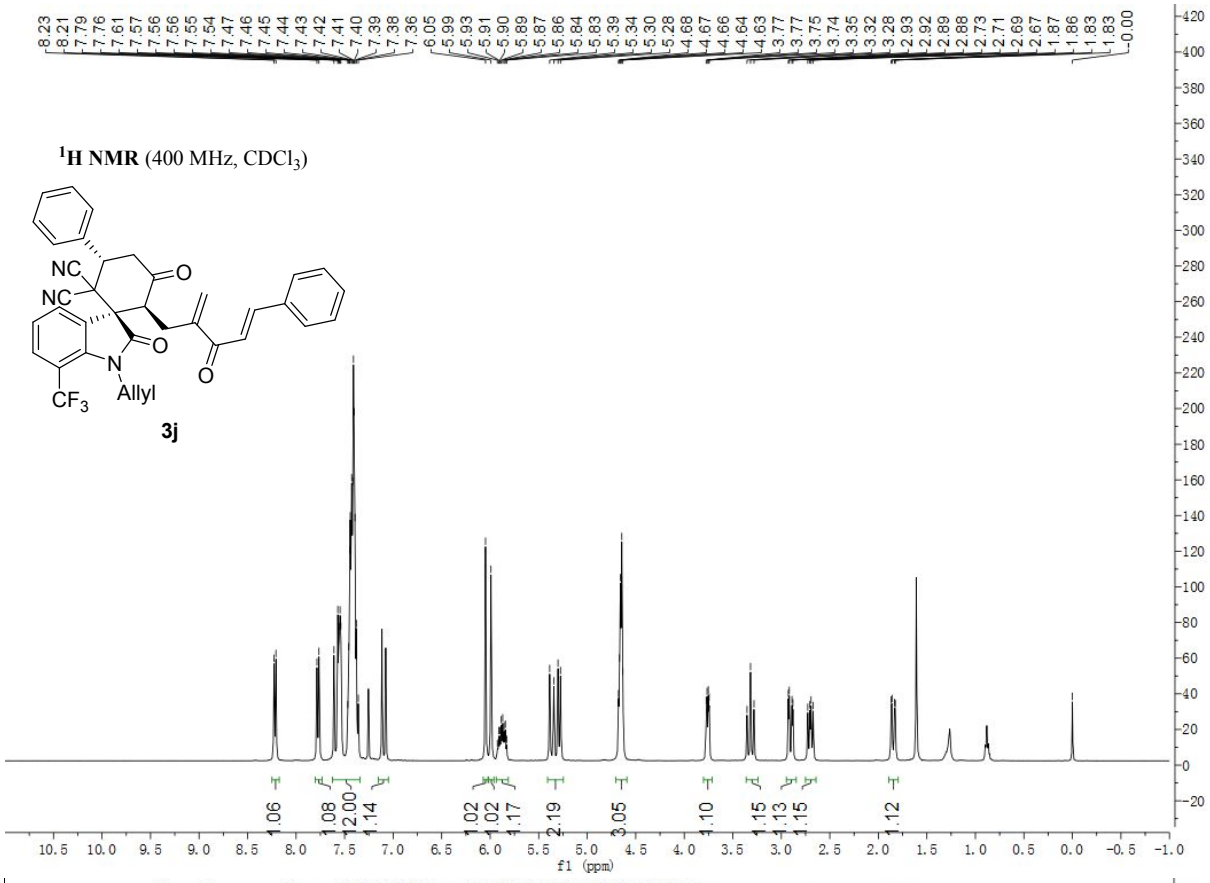
^{1}H NMR (400 MHz, $CDCl_3$)

3i



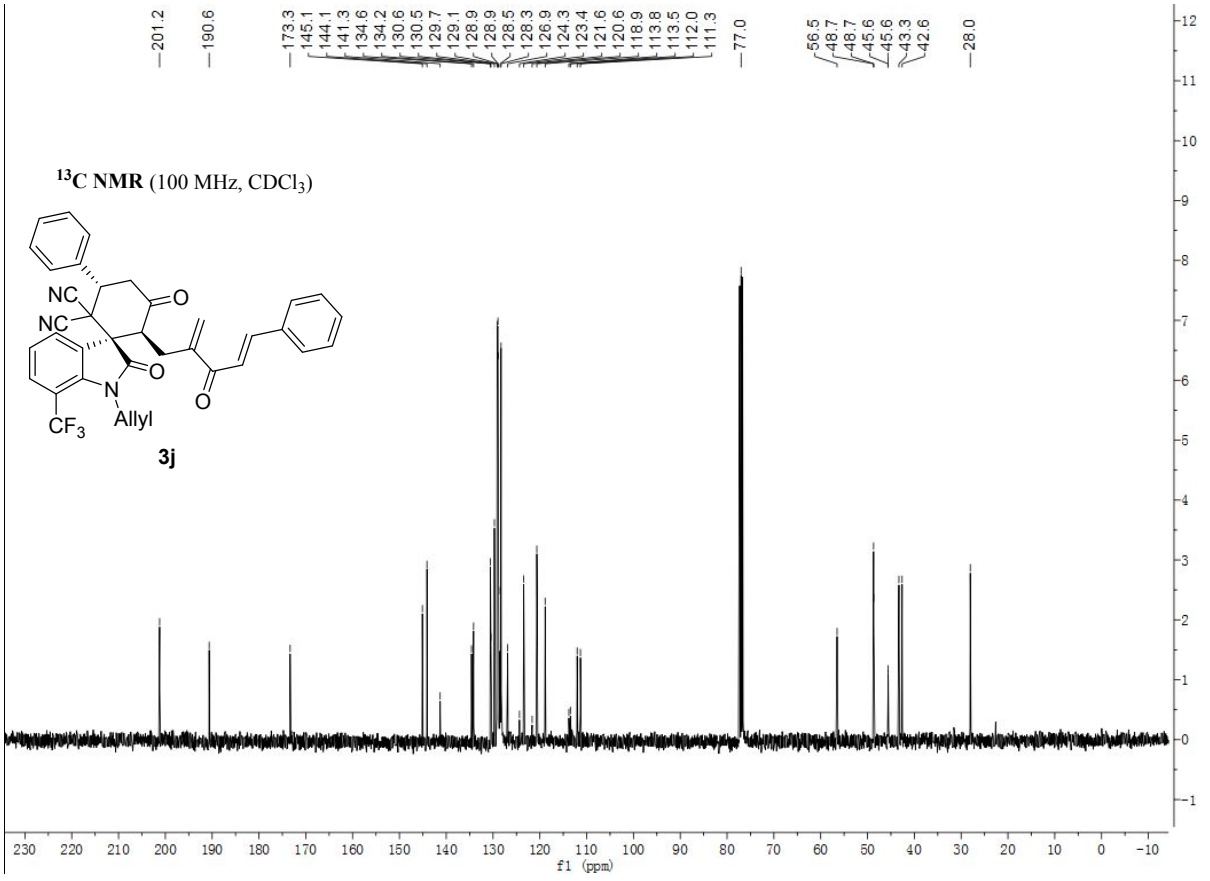
^{13}C NMR (100 MHz, $CDCl_3$)

3i



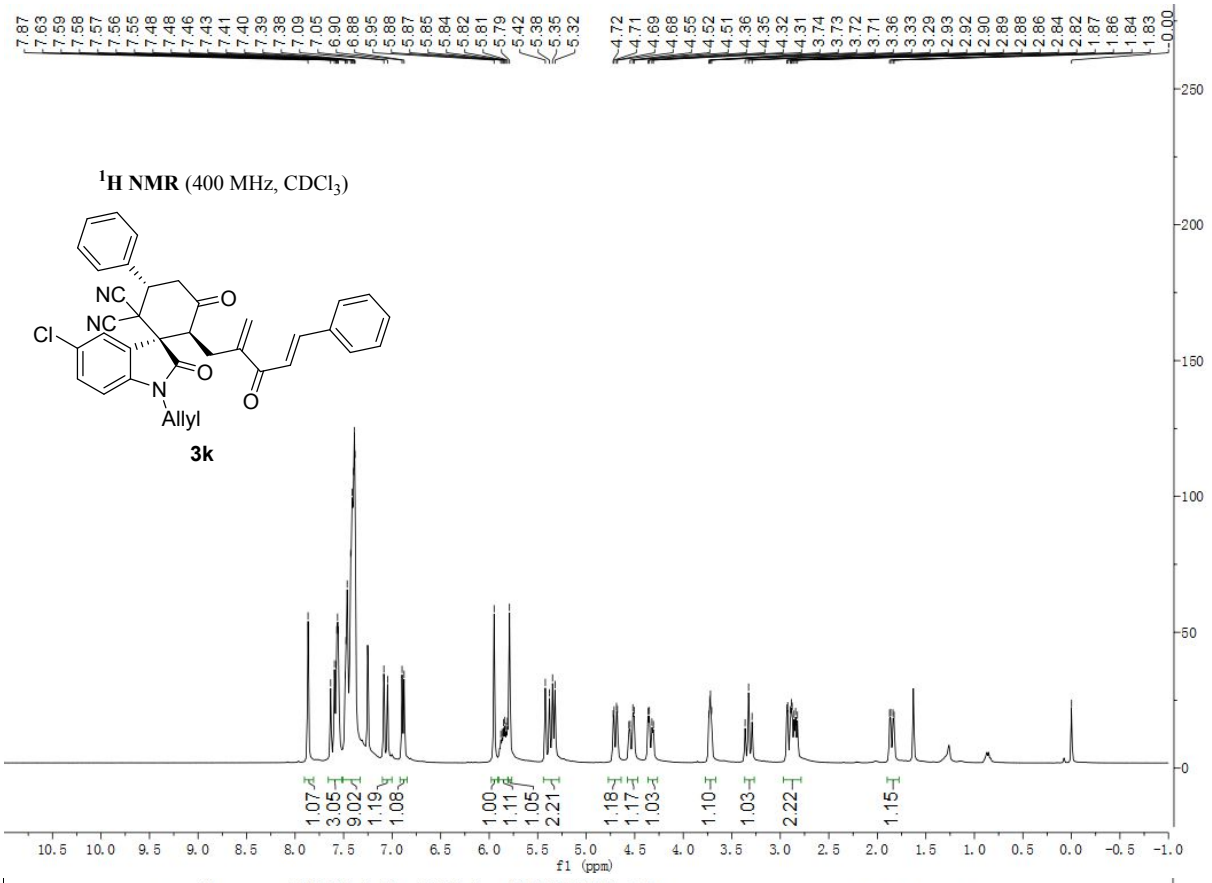
^{1}H NMR (400 MHz, $CDCl_3$)

3j



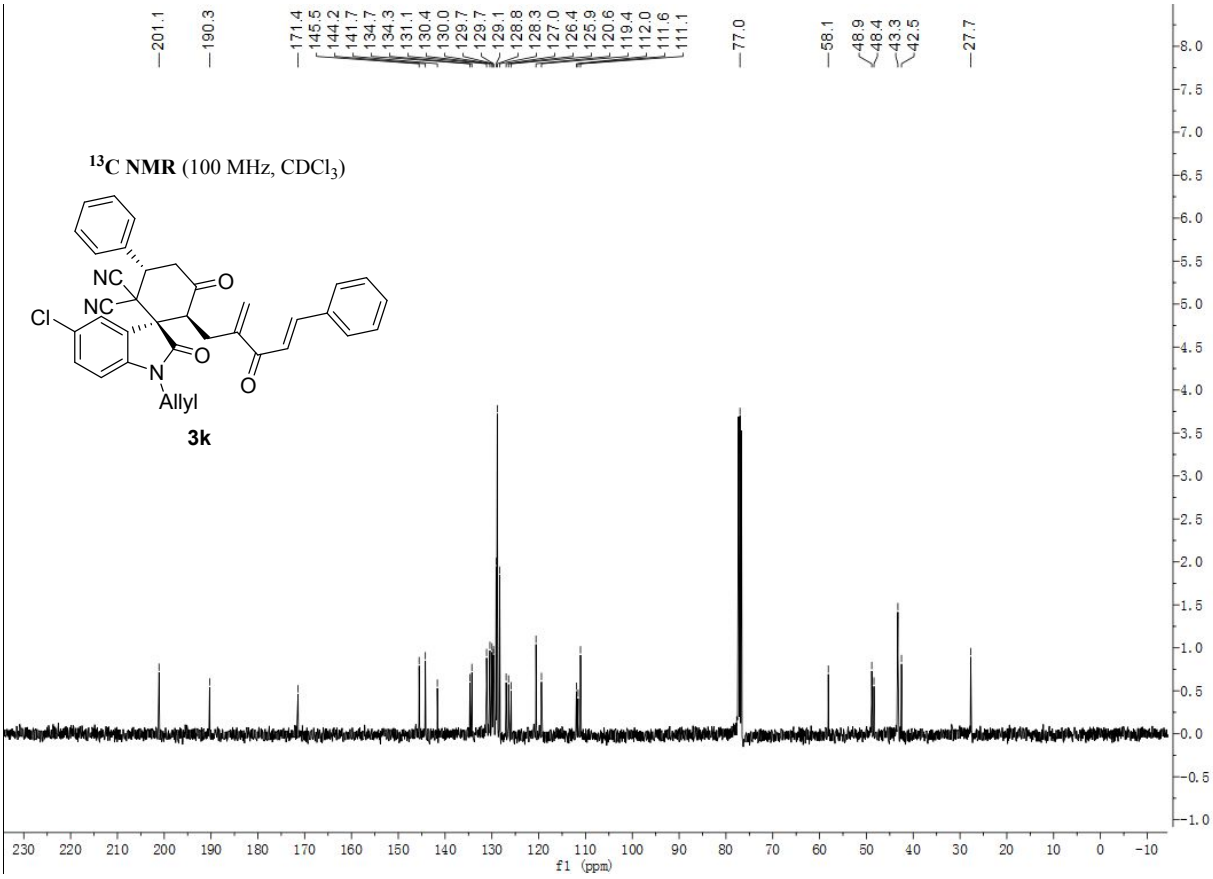
^{13}C NMR (100 MHz, $CDCl_3$)

3j



^{1}H NMR (400 MHz, $CDCl_3$)

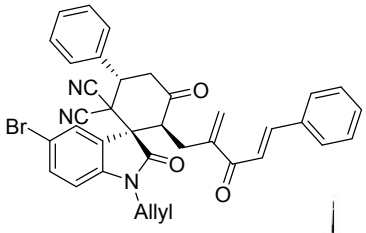
3k



^{13}C NMR (100 MHz, $CDCl_3$)

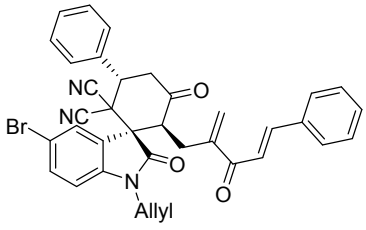
3k

^{1}H NMR (400 MHz, $CDCl_3$)

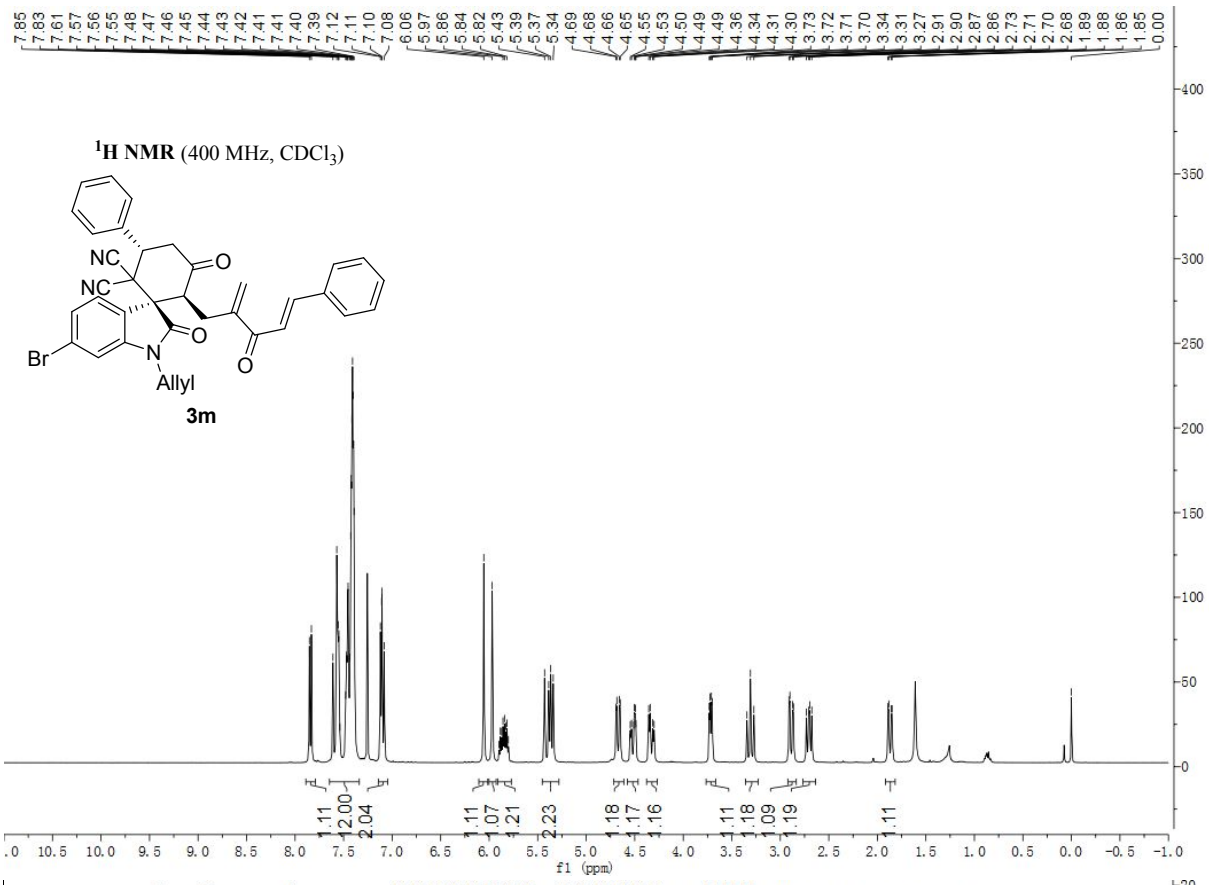


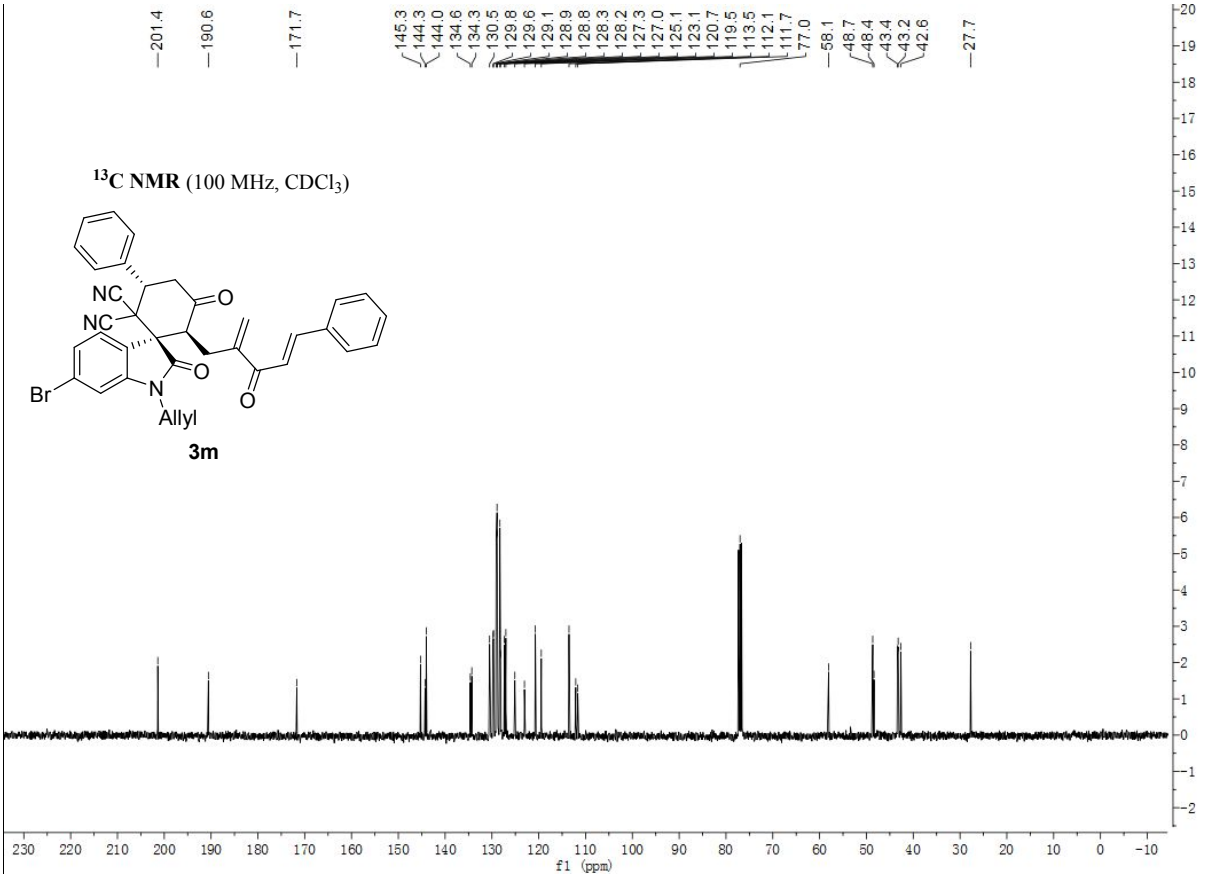
3l

^{13}C NMR (100 MHz, $CDCl_3$)

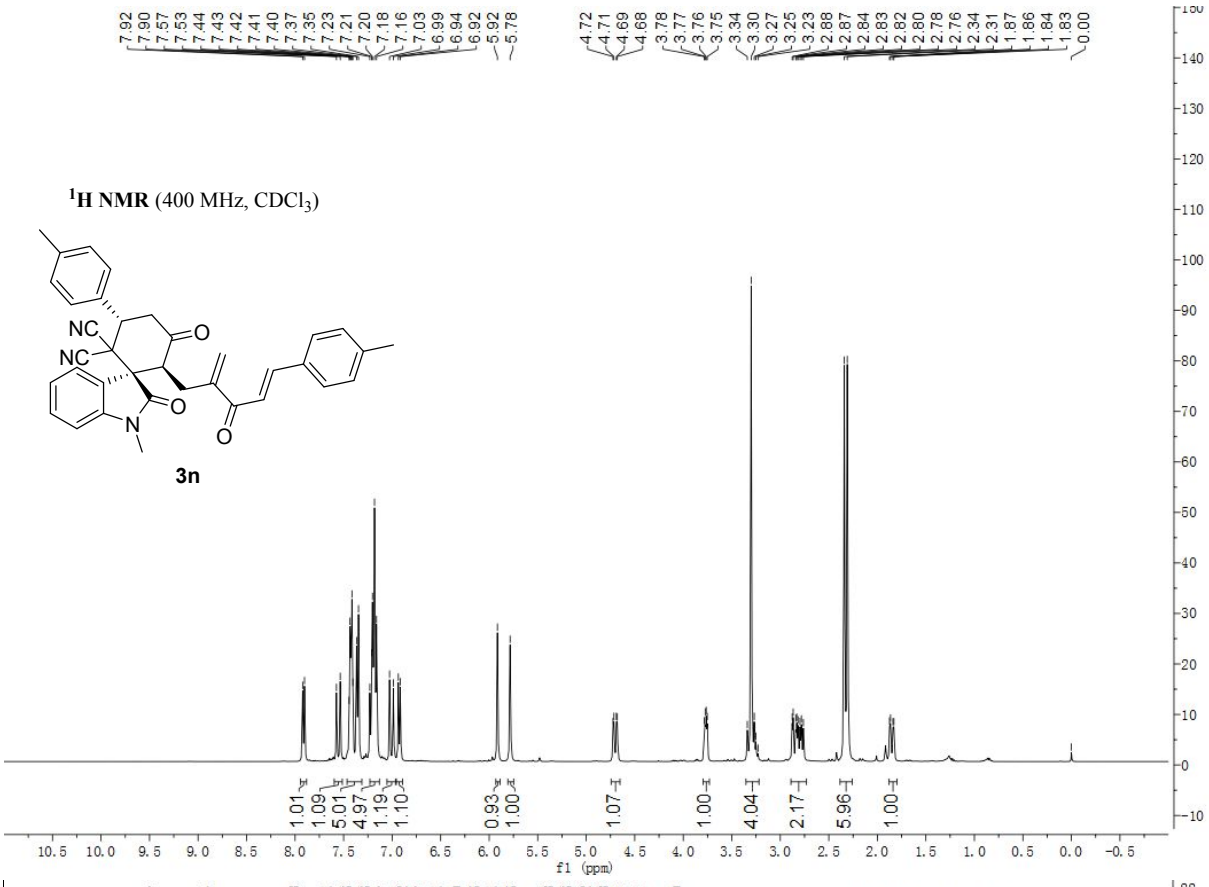


3l

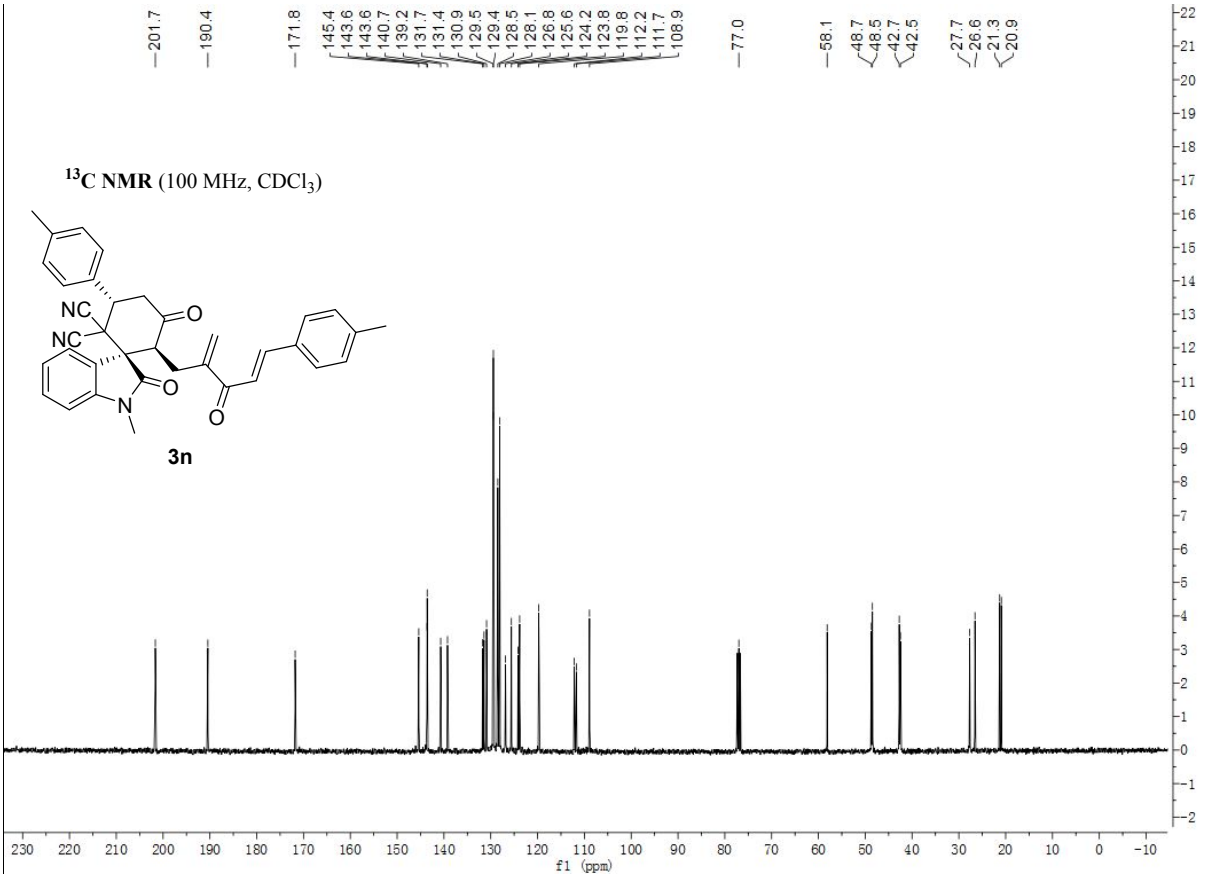

7.85 7.83 7.61 7.57 7.56 7.55 7.48 7.47 7.46 7.45 7.44 7.43 7.42 7.41 7.41 7.40 7.39 7.12 7.11 7.10 7.08 6.06 5.97 5.86 5.84 5.82 5.43 5.39 5.37 5.34 4.69 4.68 4.66 4.65 4.55 4.53 4.50 4.49 4.49 4.36 4.34 4.31 4.30 3.73 3.72 3.71 3.70 3.34 3.31 3.27 2.91 2.90 2.87 2.86 2.73 2.71 2.70 2.68 1.89 1.88 1.86 1.85 0.00
1H NMR (400 MHz, CDCl3)
NC
NC
O
O
O
O
N
Br
Allyl
3m
1.11 2.00 2.04 1.11 1.07 1.21 2.23 1.18 1.17 1.16 1.11 1.18 1.09 1.19 1.11
f1 (ppm)

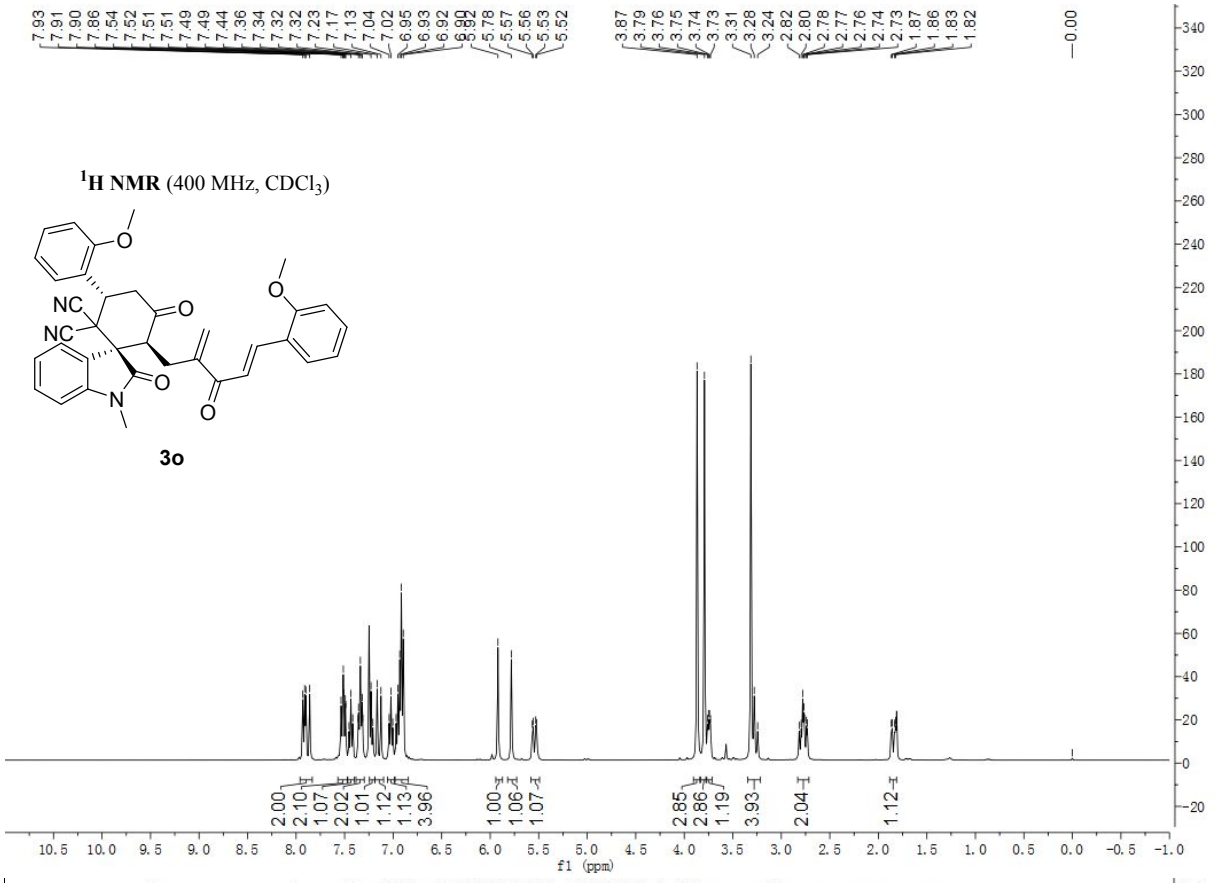

201.4 190.6 171.7 145.3 144.3 144.0 134.6 134.3 130.5 129.8 129.6 129.1 128.9 128.8 128.3 128.2 127.3 127.0 125.1 123.1 120.7 119.5 113.5 112.1 111.7 77.0 58.1 48.7 48.4 43.4 43.2 42.6 27.7
13C NMR (100 MHz, CDCl3)
NC
NC
O
O
O
O
N
Br
Allyl
3m
f1 (ppm)

^{1}H NMR (400 MHz, $CDCl_3$)



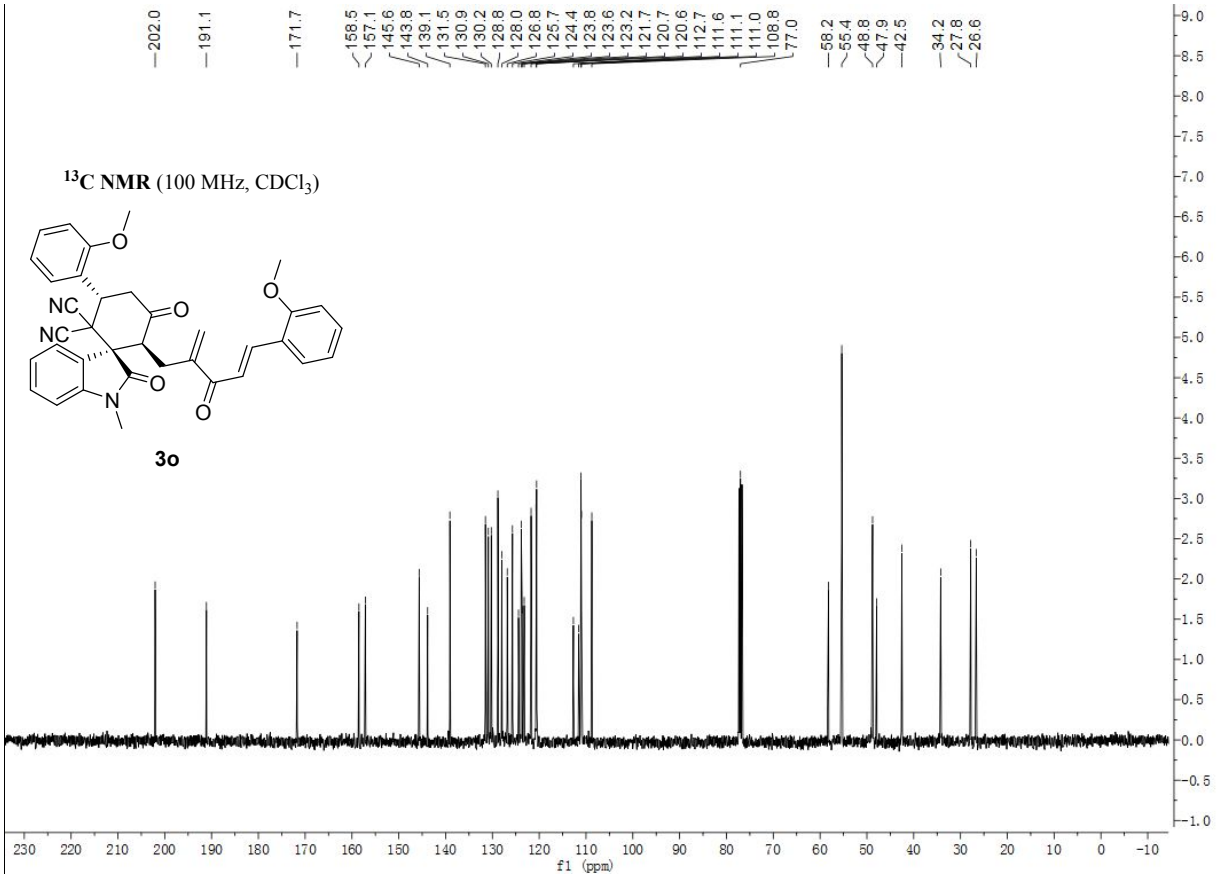
^{13}C NMR (100 MHz, $CDCl_3$)





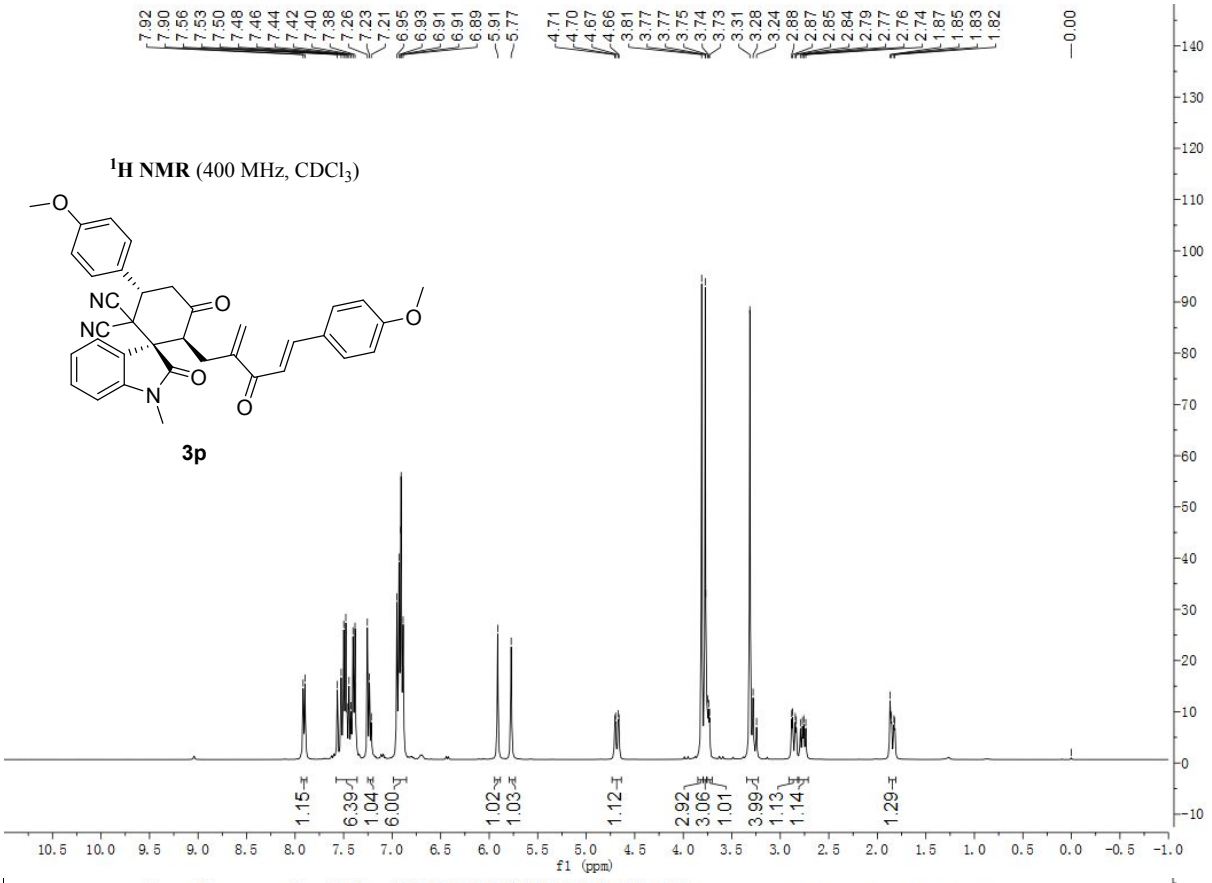
^{1}H NMR (400 MHz, $CDCl_3$)

3o



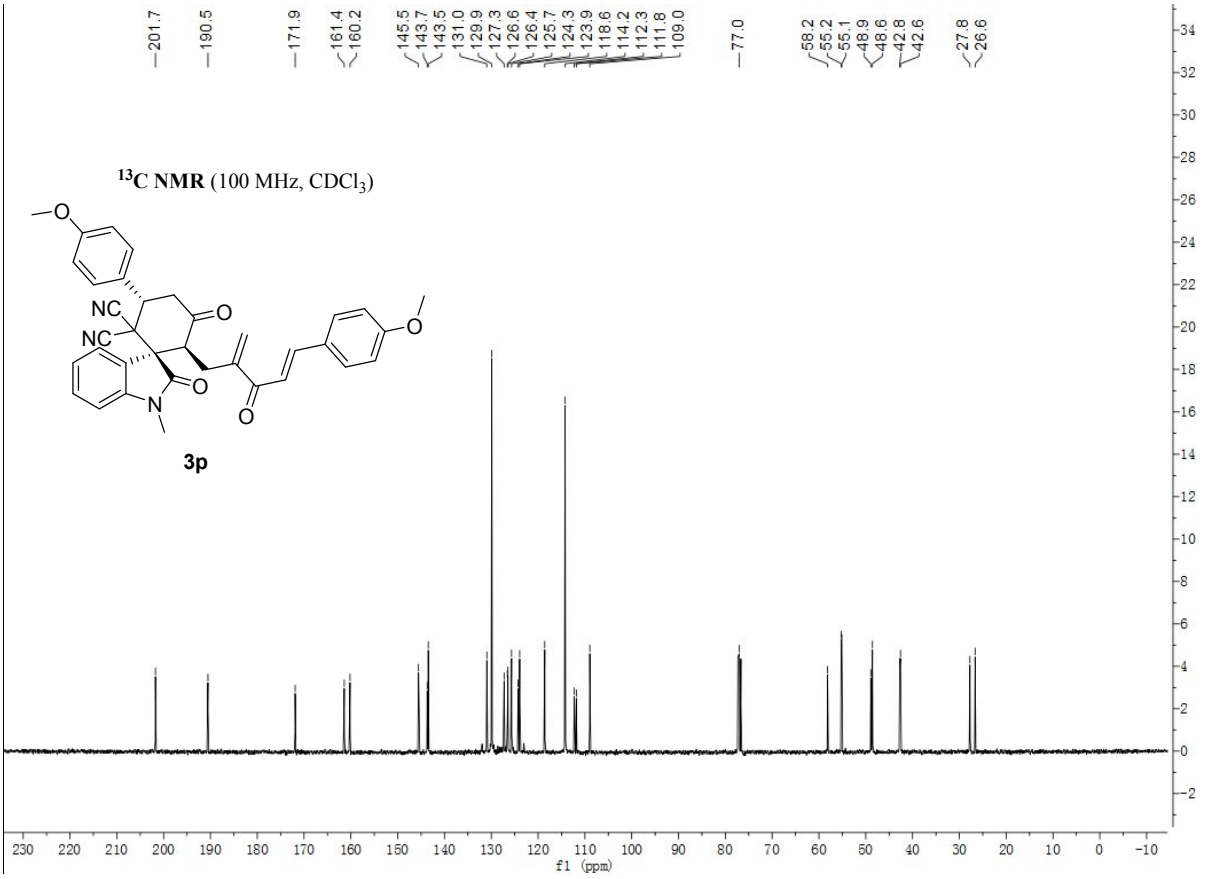
^{13}C NMR (100 MHz, $CDCl_3$)

3o



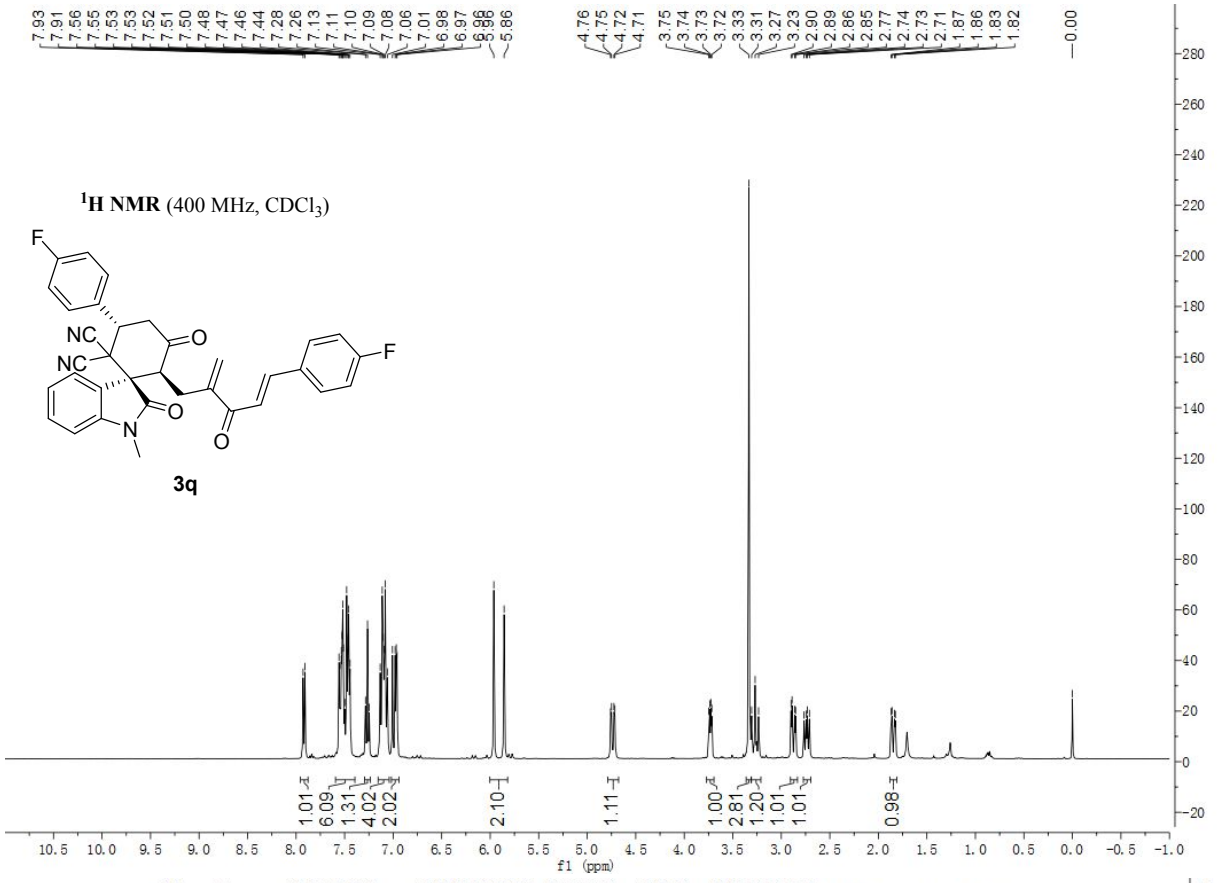
^{1}H NMR (400 MHz, $CDCl_3$)

3p



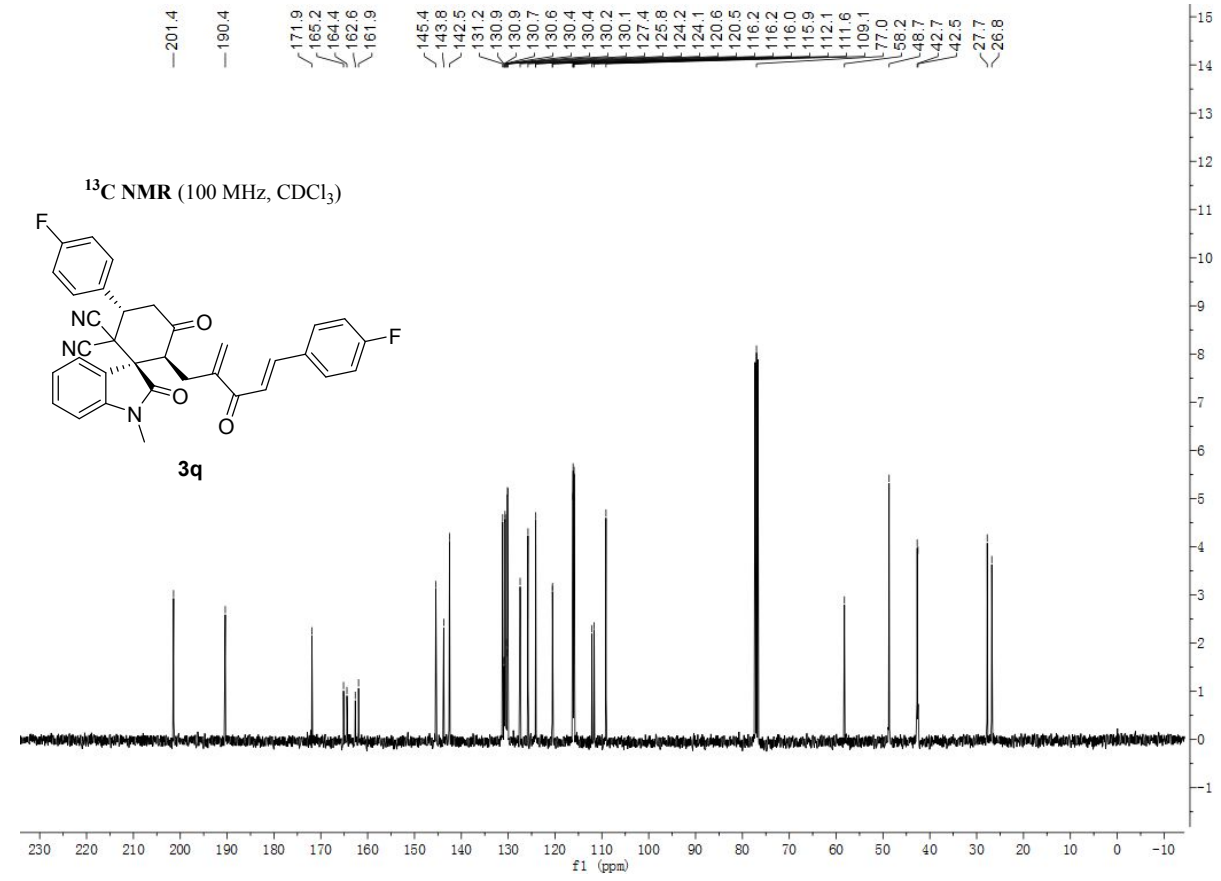
^{13}C NMR (100 MHz, $CDCl_3$)

3p



^{1}H NMR (400 MHz, $CDCl_3$)

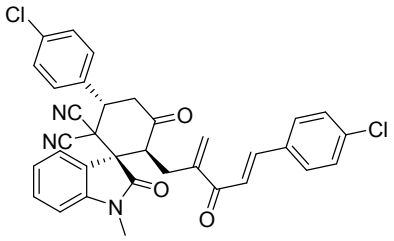
3q



^{13}C NMR (100 MHz, $CDCl_3$)

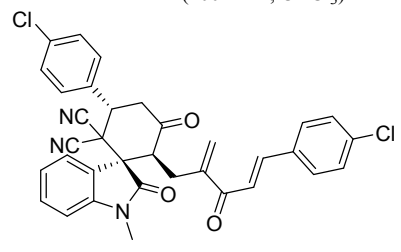
3q

^{1}H NMR (400 MHz, $CDCl_3$)

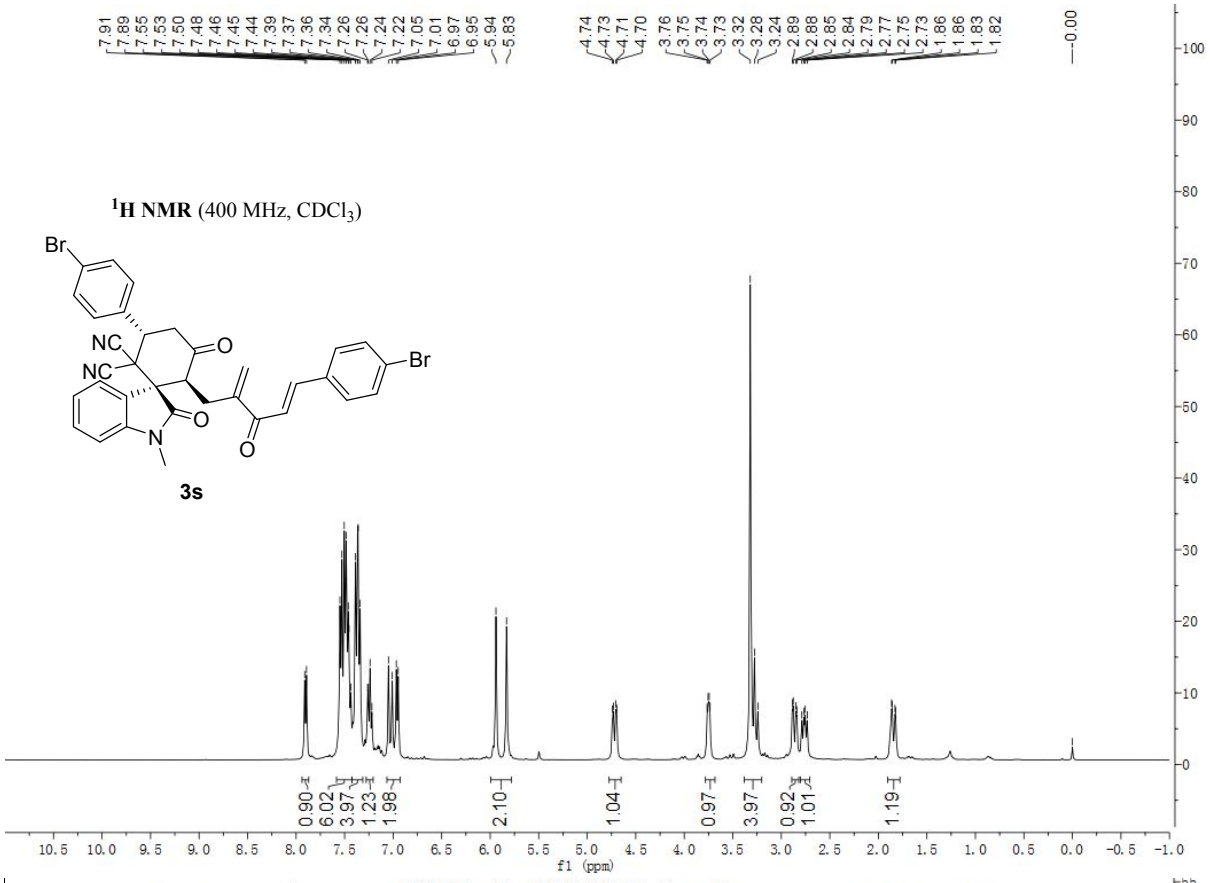


3r

^{13}C NMR (100 MHz, $CDCl_3$)

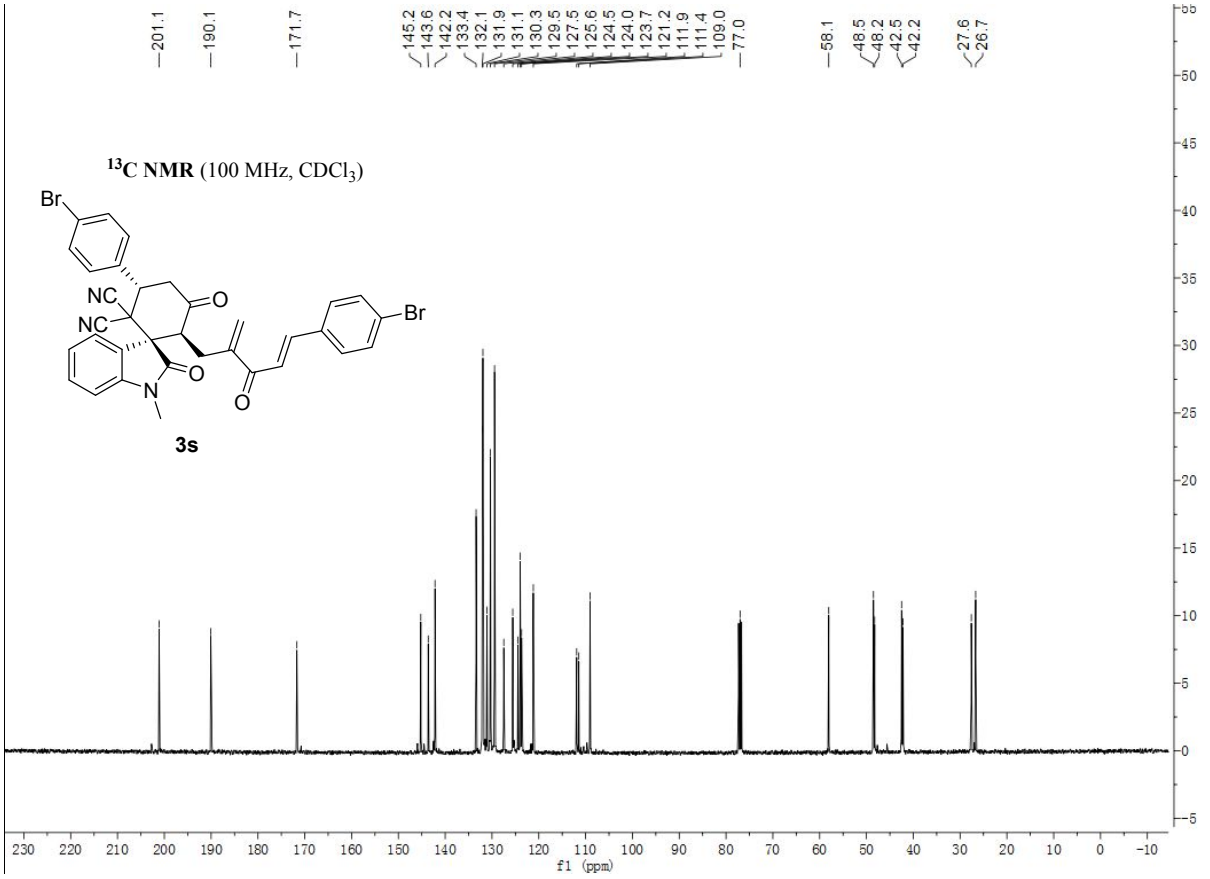


3r



^{1}H NMR (400 MHz, $CDCl_3$)

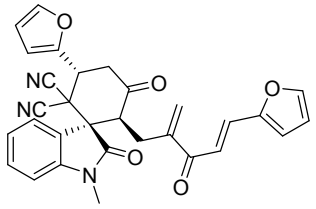
3s



^{13}C NMR (100 MHz, $CDCl_3$)

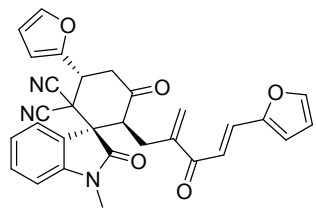
3s

^{1}H NMR (400 MHz, $CDCl_3$)



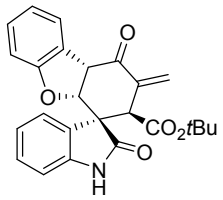
3t

^{13}C NMR (100 MHz, $CDCl_3$)



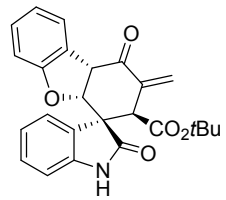
3t

^{1}H NMR (400 MHz, DMSO-d_6)

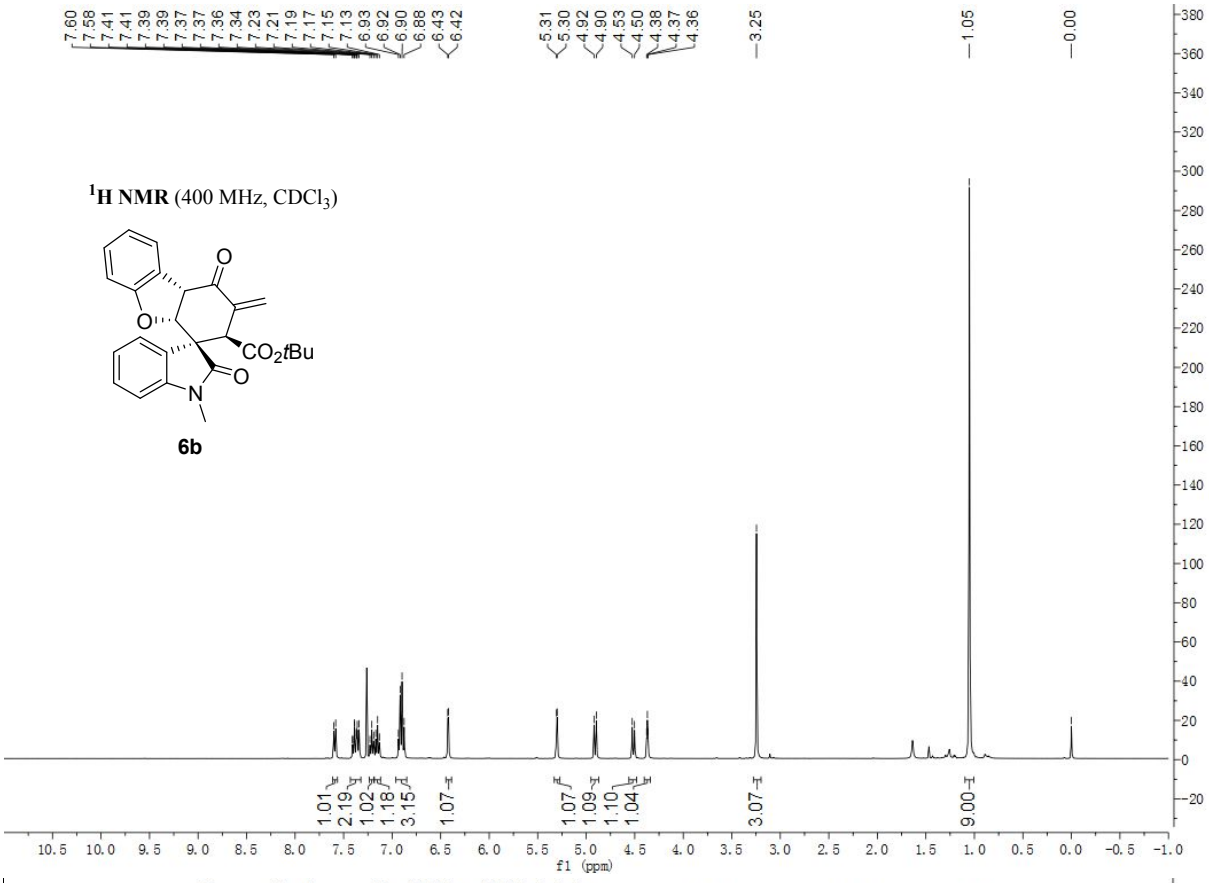


6a

^{13}C NMR (100 MHz, DMSO-d_6)

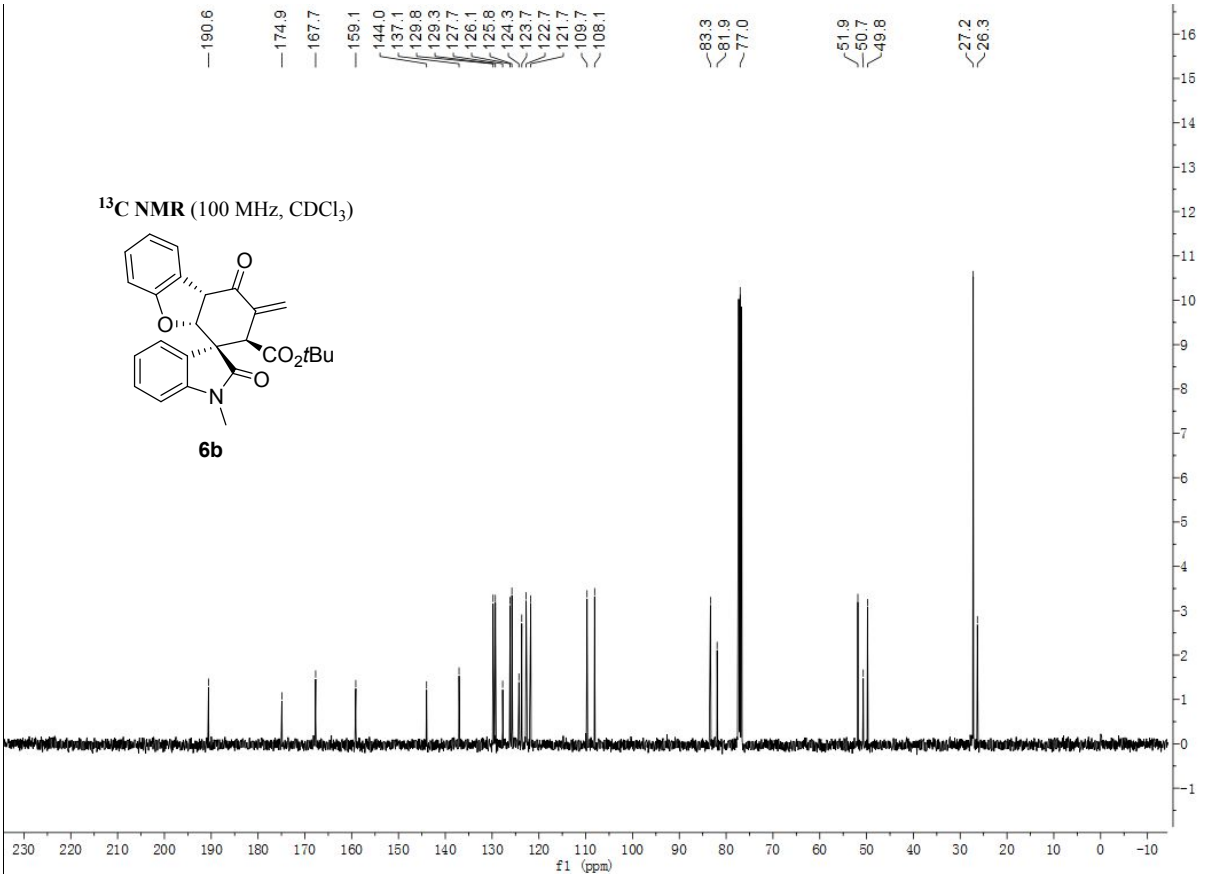


6a



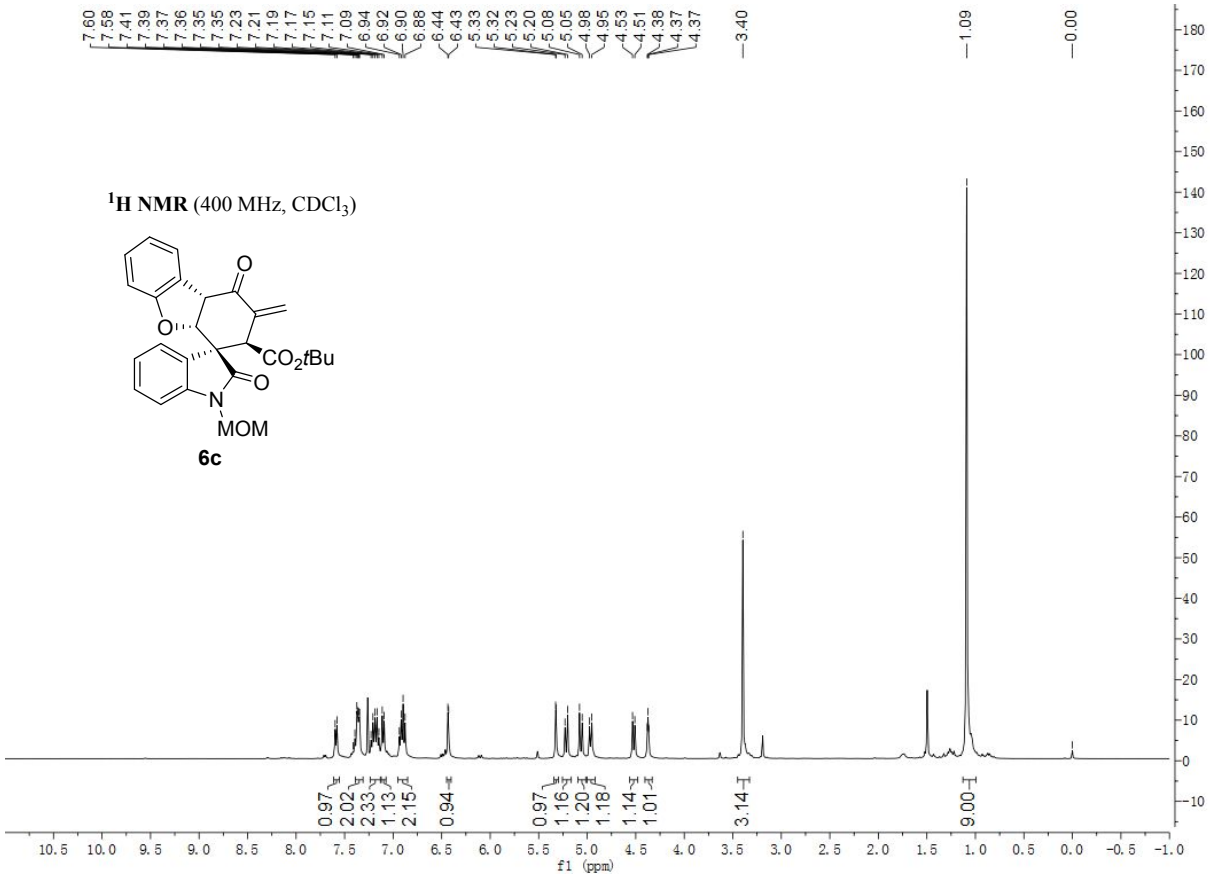
^{1}H NMR (400 MHz, $CDCl_3$)

6b



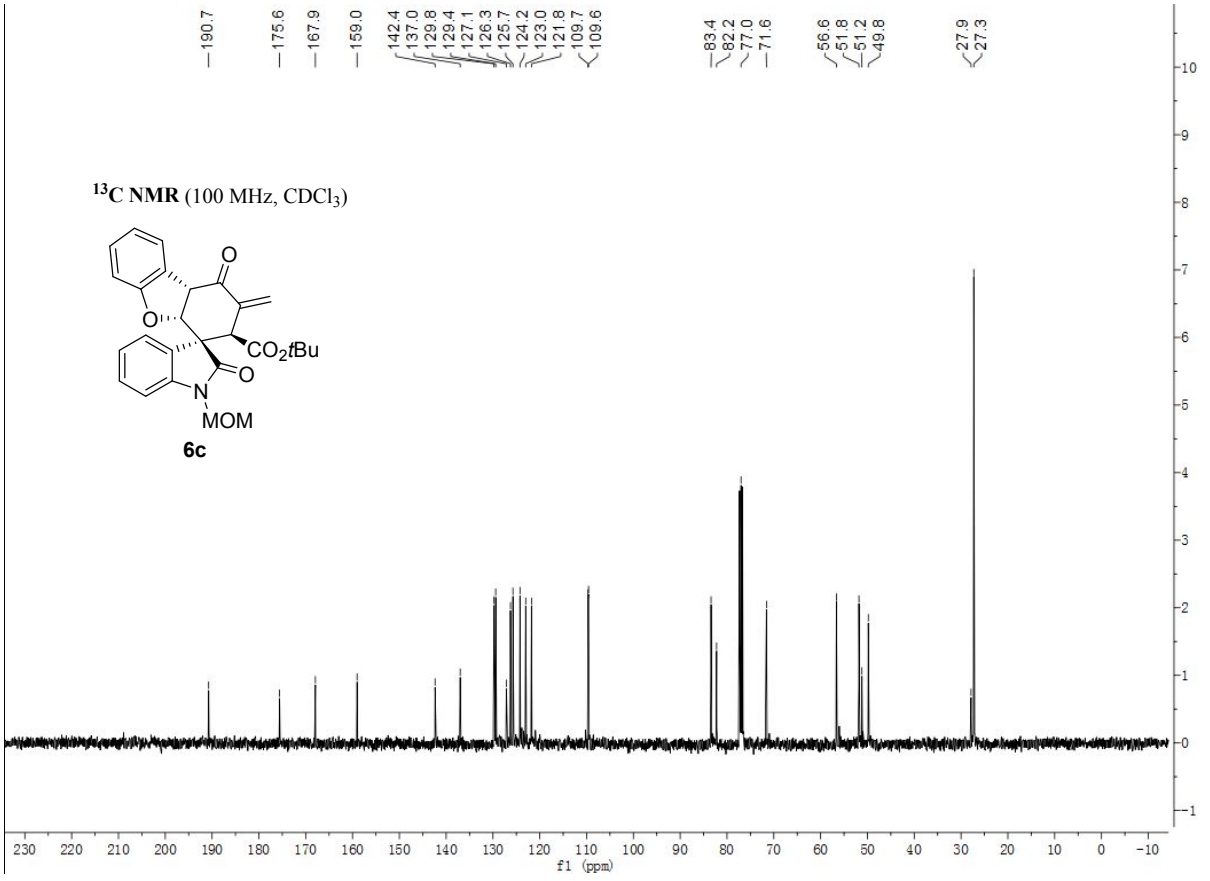
^{13}C NMR (100 MHz, $CDCl_3$)

6b



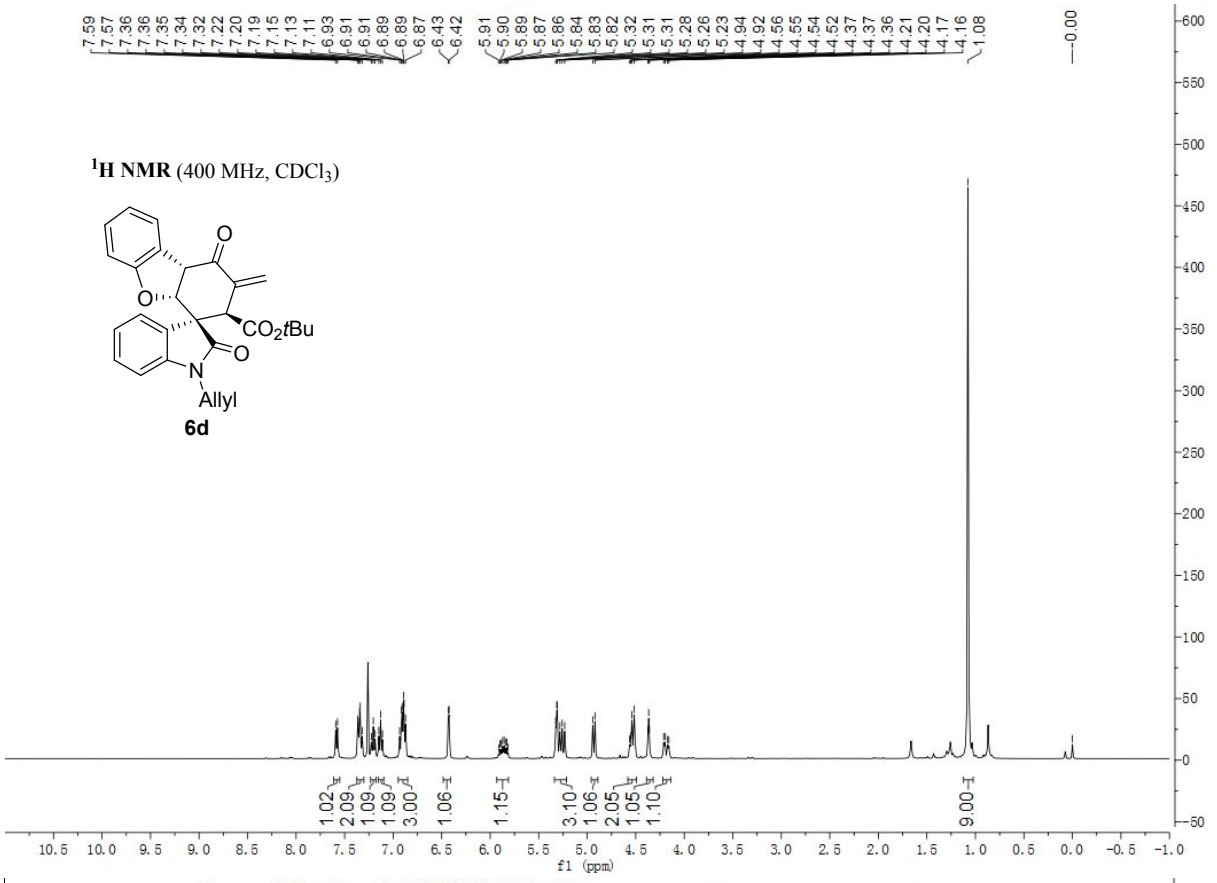
^{1}H NMR (400 MHz, $CDCl_3$)

6c



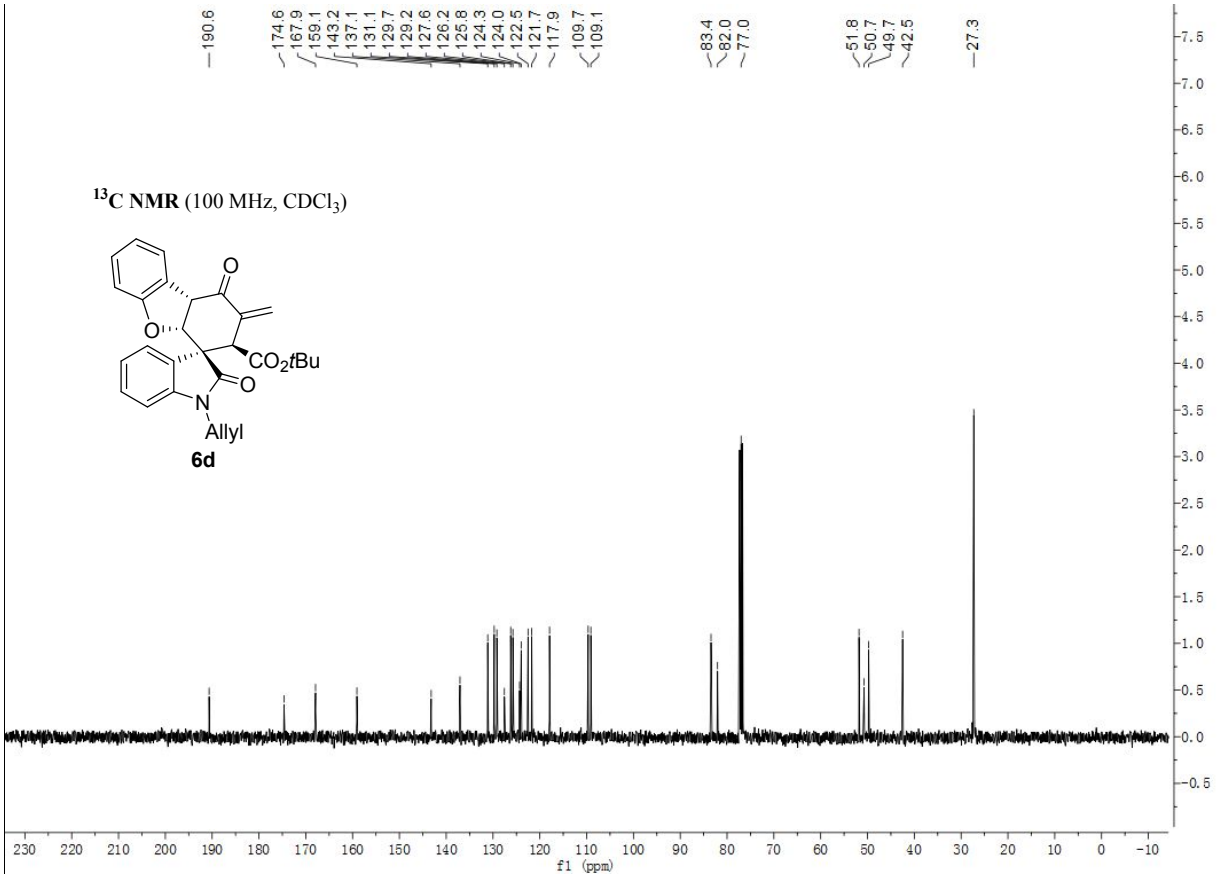
^{13}C NMR (100 MHz, $CDCl_3$)

6c



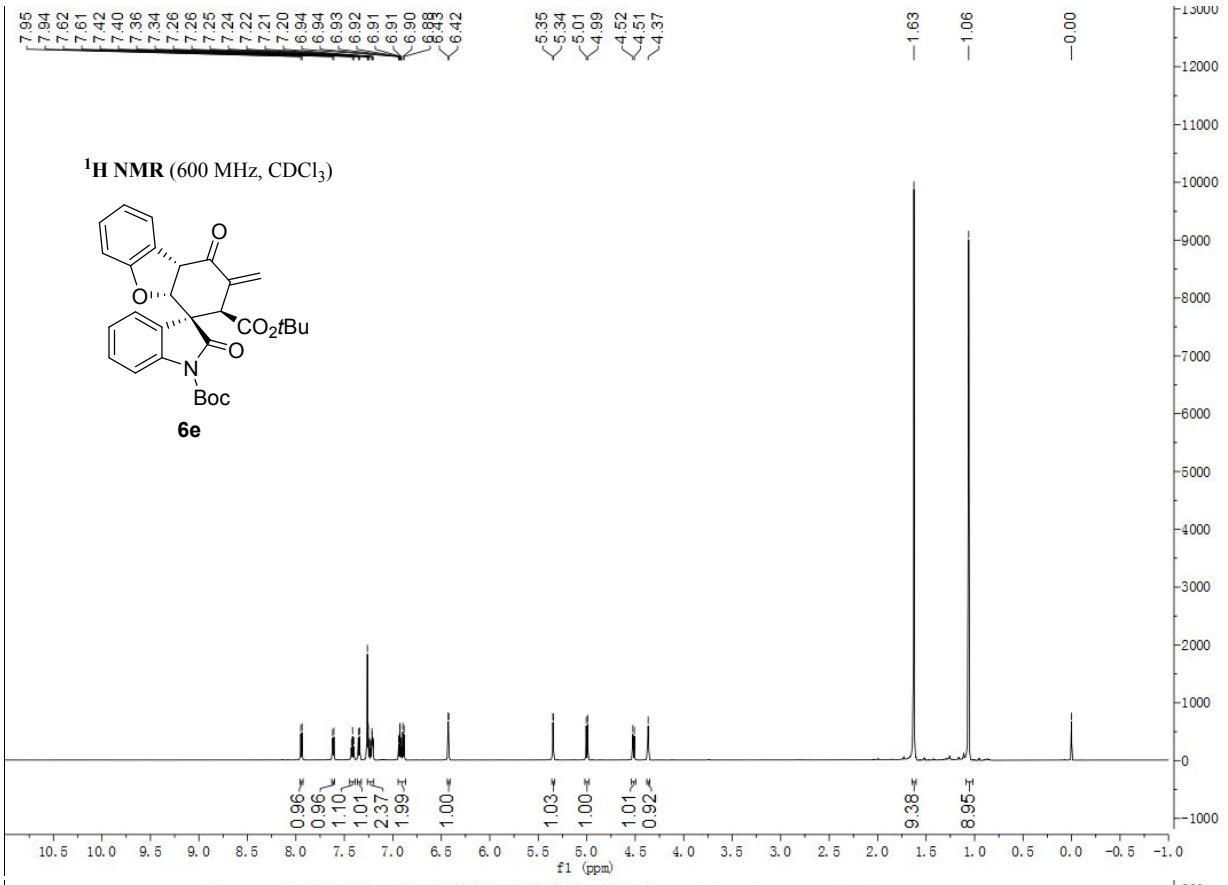
^{1}H NMR (400 MHz, $CDCl_3$)

6d



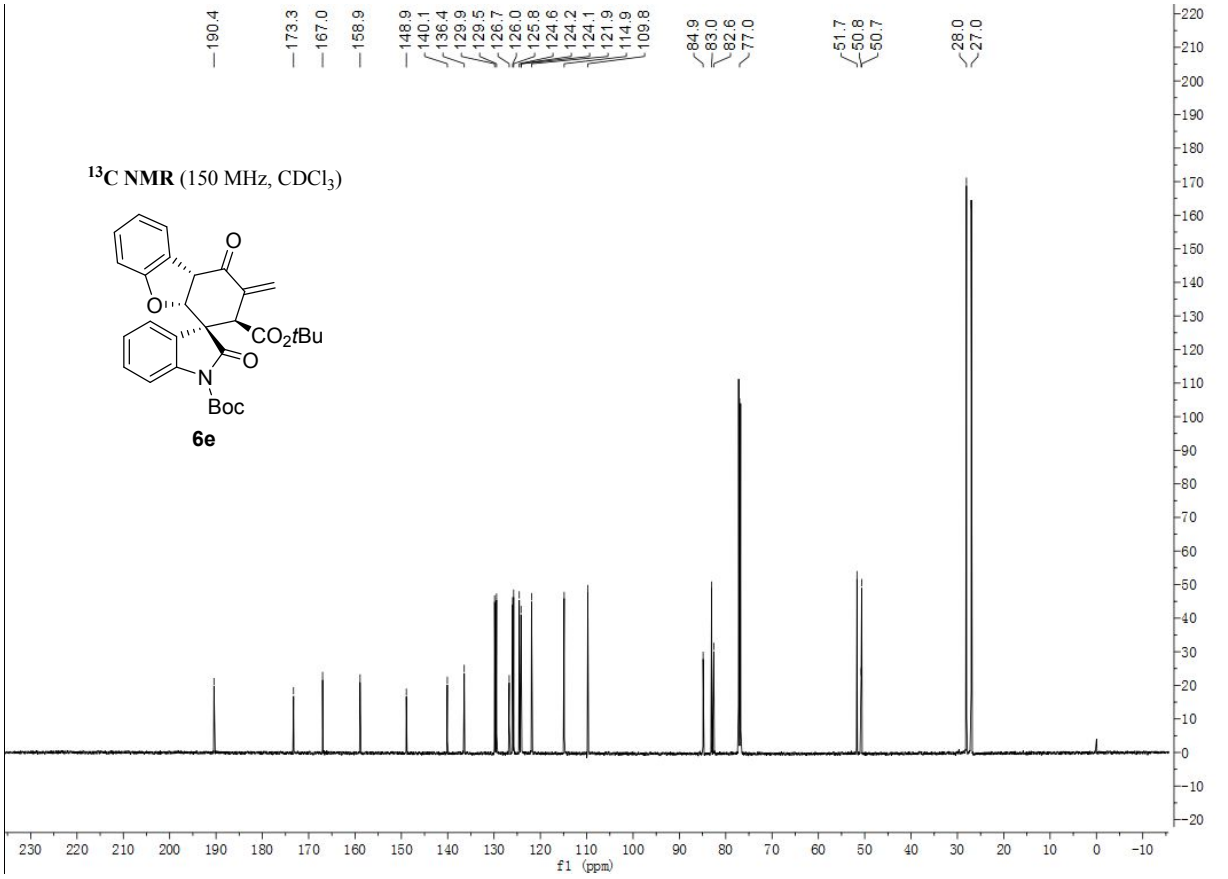
^{13}C NMR (100 MHz, $CDCl_3$)

6d



^{1}H NMR (600 MHz, $CDCl_3$)

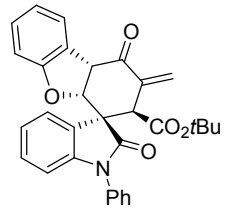
6e



^{13}C NMR (150 MHz, $CDCl_3$)

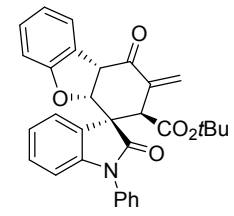
6e

^{1}H NMR (400 MHz, $CDCl_3$)

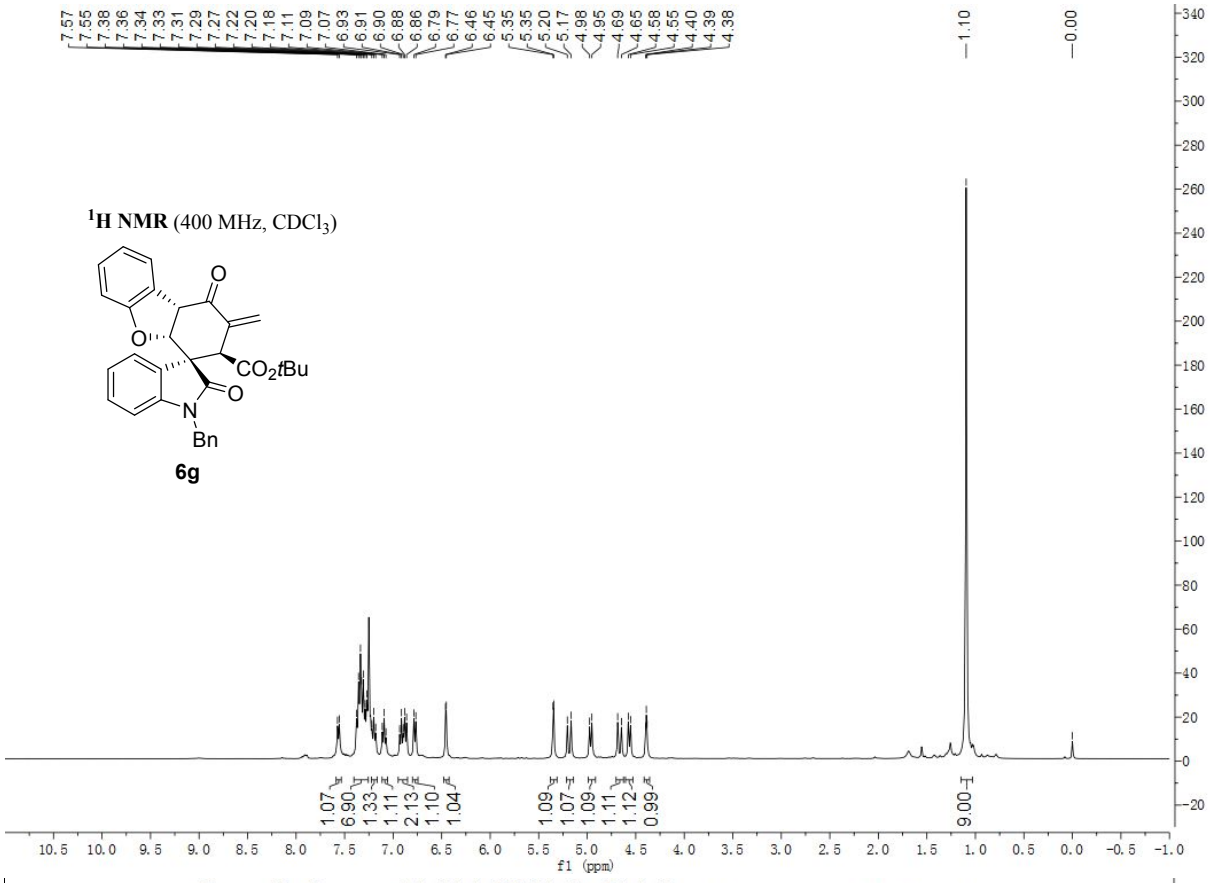


6f

^{13}C NMR (100 MHz, $CDCl_3$)

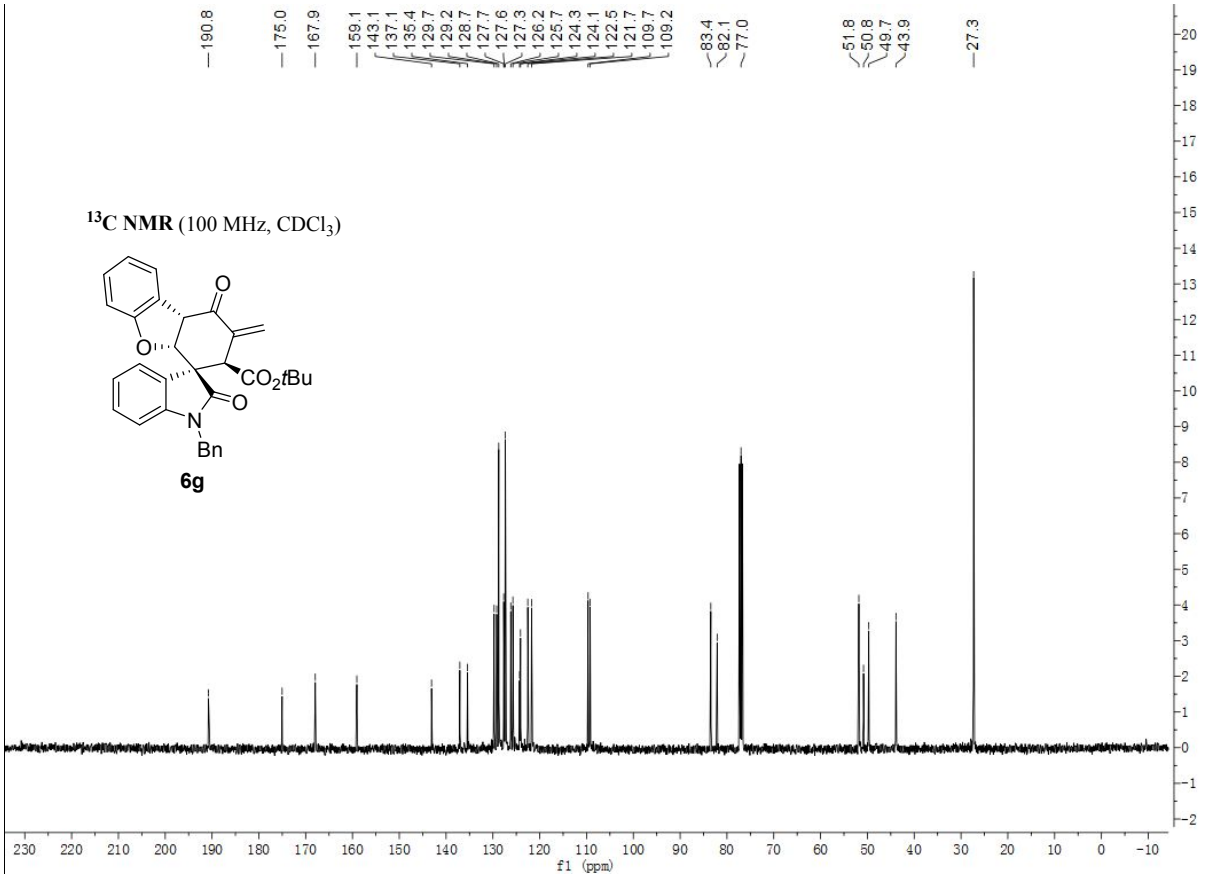


6f



^{1}H NMR (400 MHz, $CDCl_3$)

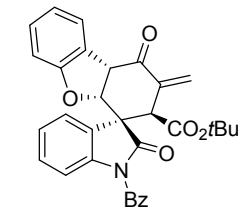
6g



^{13}C NMR (100 MHz, $CDCl_3$)

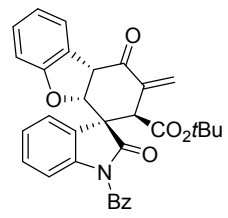
6g

^{1}H NMR (400 MHz, $CDCl_3$)



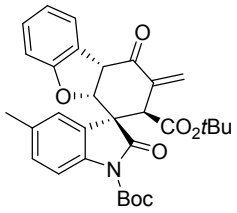
6h

^{13}C NMR (100 MHz, $CDCl_3$)



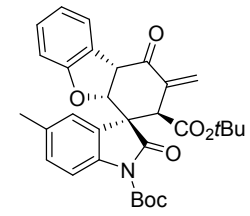
6h

^{1}H NMR (400 MHz, $CDCl_3$)



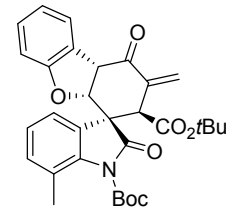
6i

^{13}C NMR (100 MHz, $CDCl_3$)



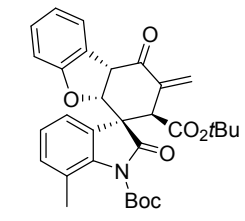
6i

^{1}H NMR (400 MHz, $CDCl_3$)



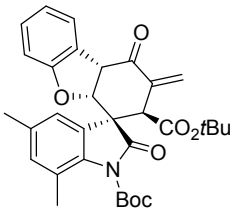
6j

^{13}C NMR (100 MHz, $CDCl_3$)



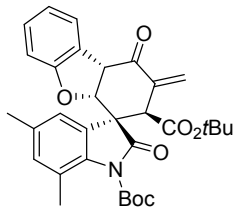
6j

^{1}H NMR (400 MHz, $CDCl_3$)



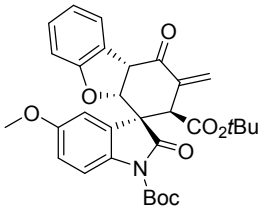
6k

^{13}C NMR (100 MHz, $CDCl_3$)



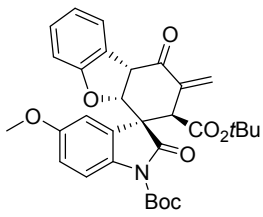
6k

^{1}H NMR (400 MHz, $CDCl_3$)



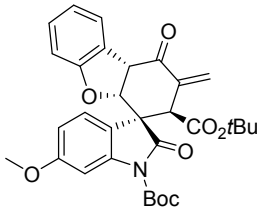
6l

^{13}C NMR (100 MHz, $CDCl_3$)



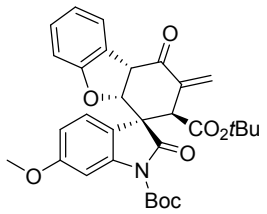
6l

^{1}H NMR (400 MHz, $CDCl_3$)



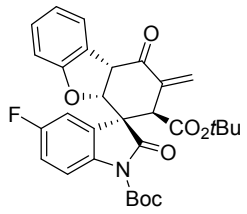
6m

^{13}C NMR (100 MHz, $CDCl_3$)



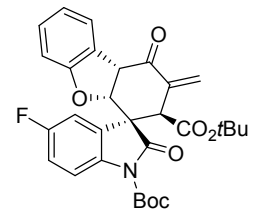
6m

^{1}H NMR (400 MHz, $CDCl_3$)



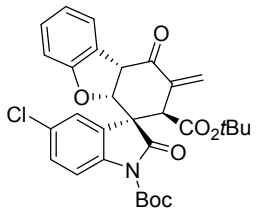
6n

^{13}C NMR (100 MHz, $CDCl_3$)



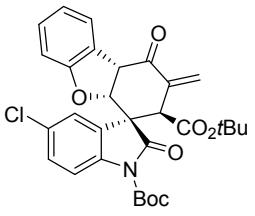
6n

^{1}H NMR (400 MHz, $CDCl_3$)

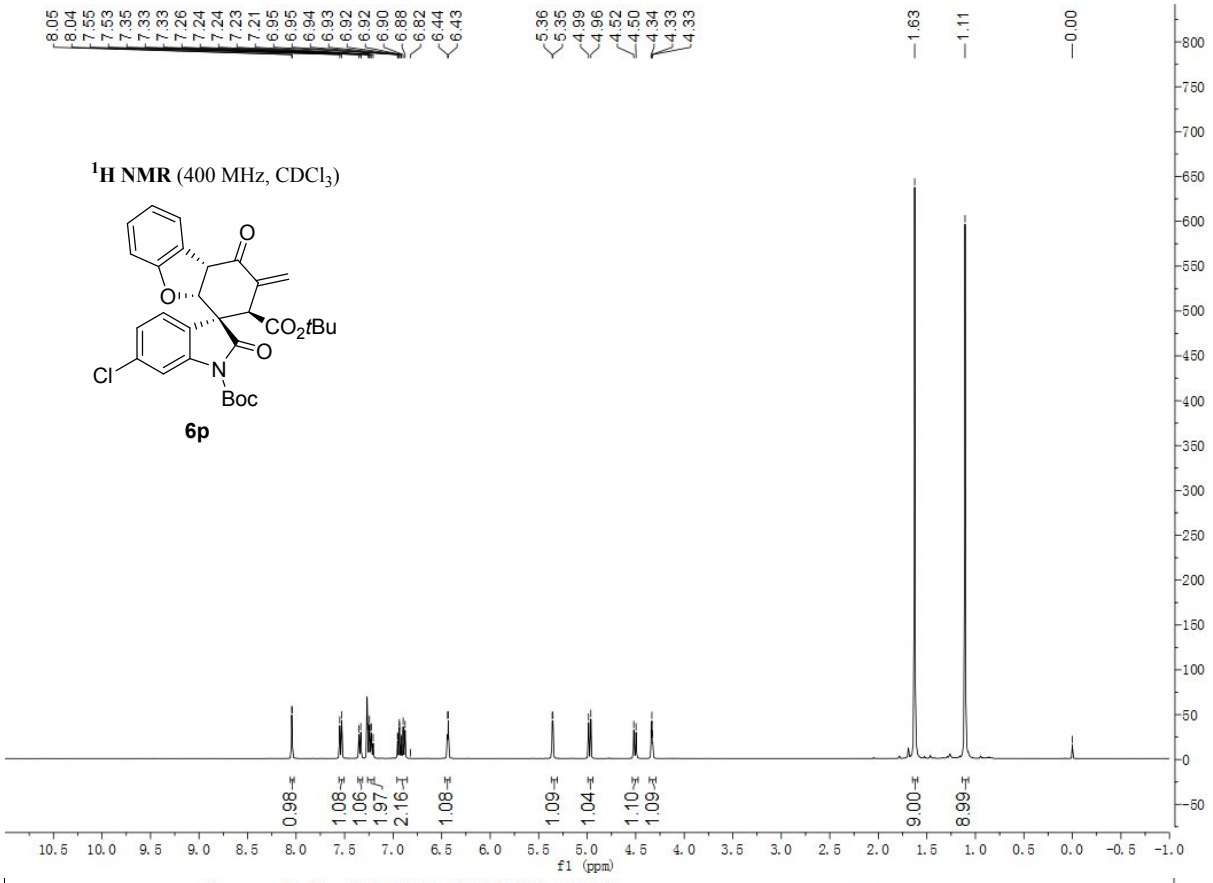


6o

^{13}C NMR (100 MHz, $CDCl_3$)

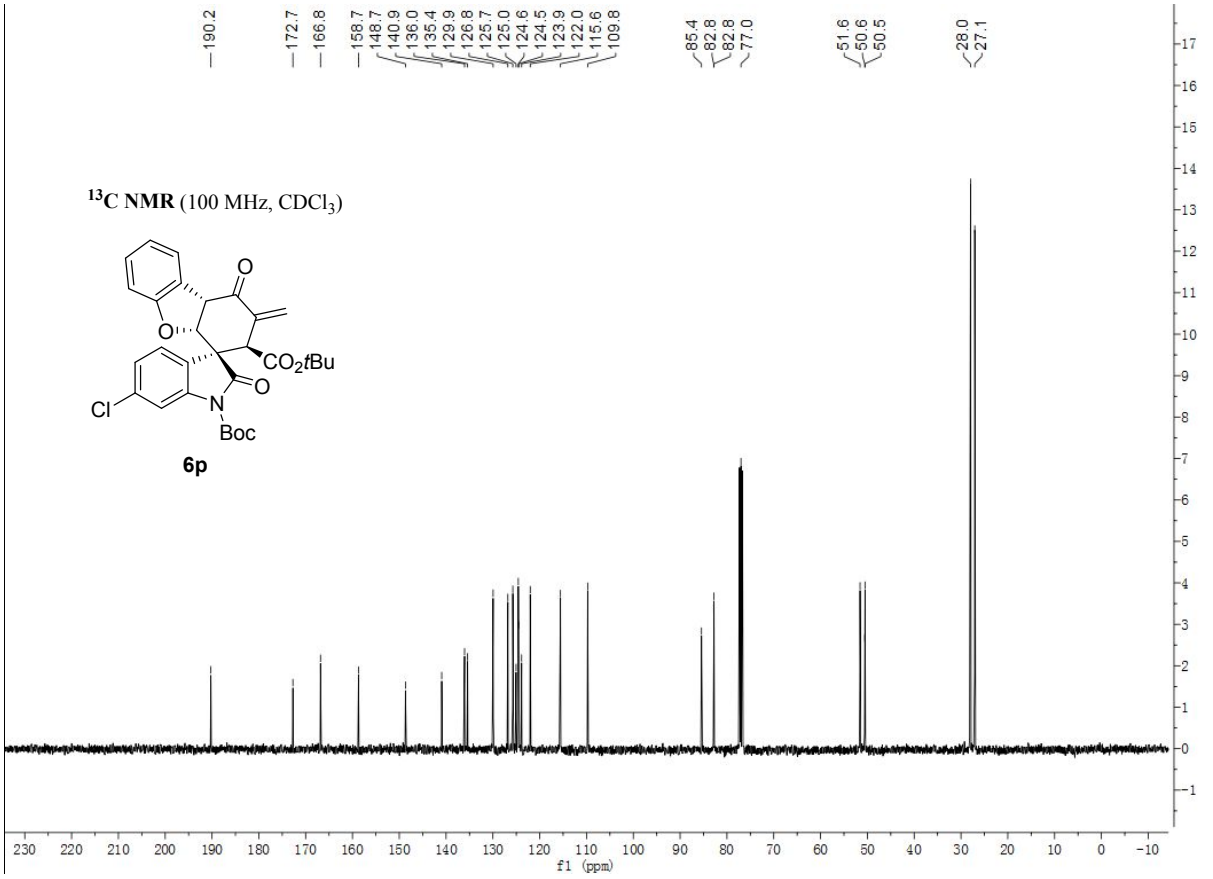


6o



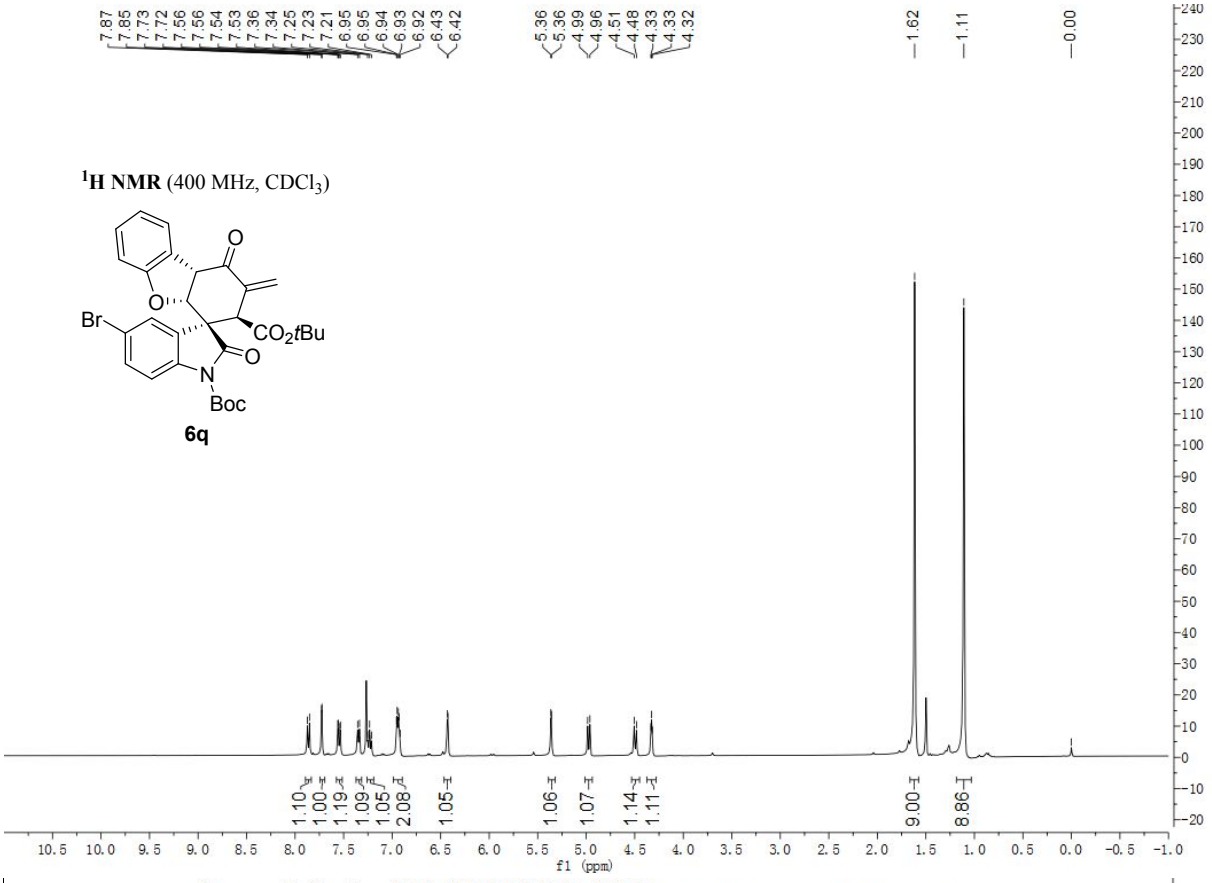
^{1}H NMR (400 MHz, $CDCl_3$)

6p



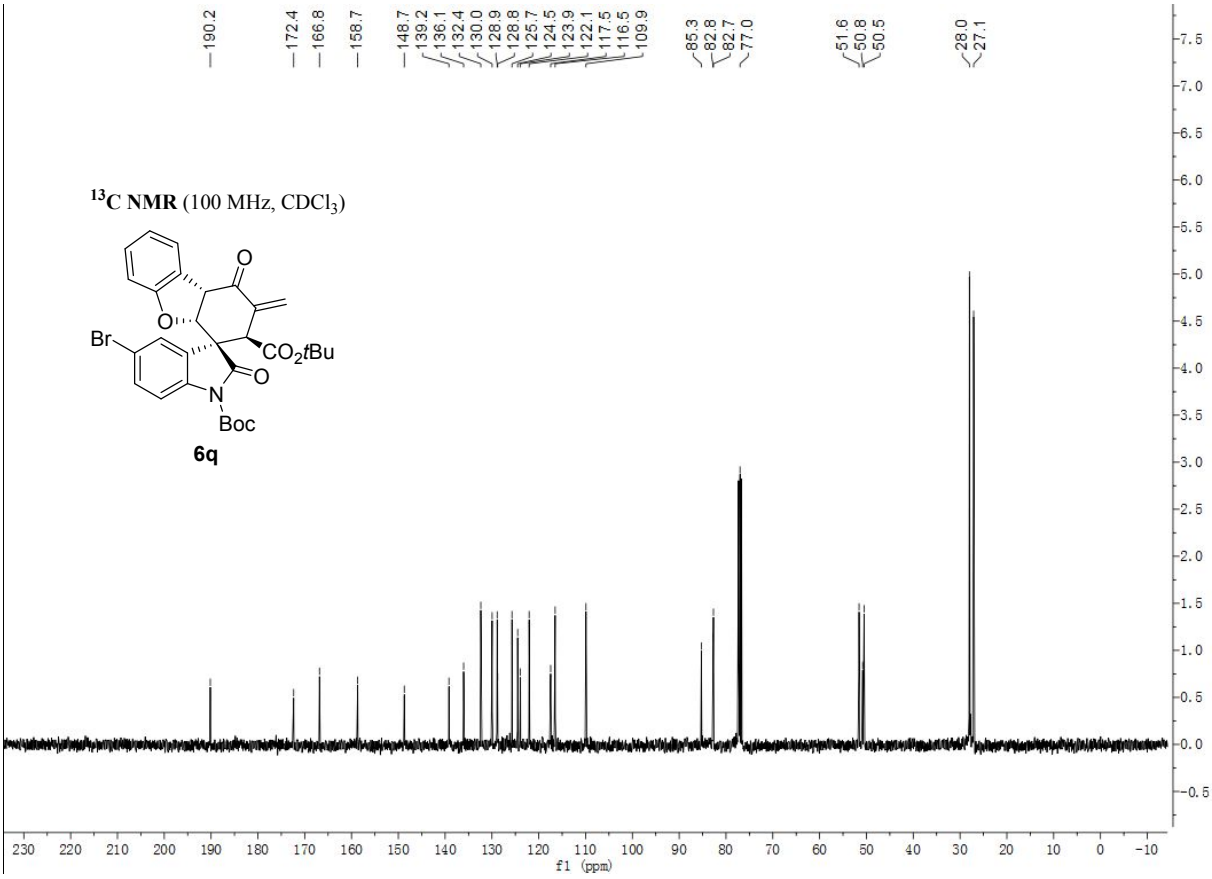
^{13}C NMR (100 MHz, $CDCl_3$)

6p



^{1}H NMR (400 MHz, $CDCl_3$)

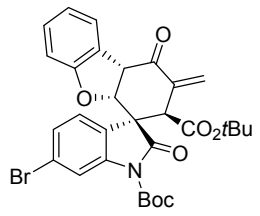
6q



^{13}C NMR (100 MHz, $CDCl_3$)

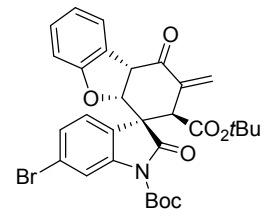
6q

^{1}H NMR (400 MHz, $CDCl_3$)



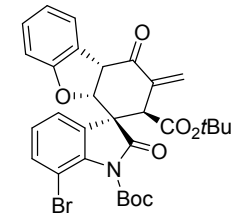
6r

^{13}C NMR (100 MHz, $CDCl_3$)



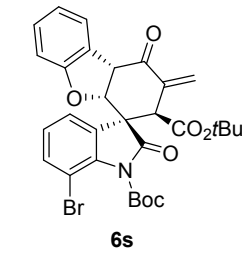
6r

^{1}H NMR (400 MHz, $CDCl_3$)



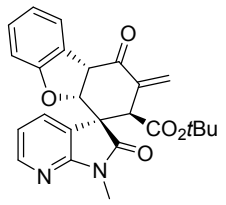
6s

^{13}C NMR (100 MHz, $CDCl_3$)



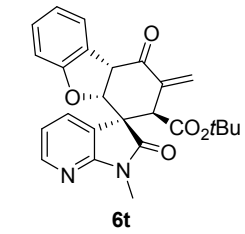
6s

^{1}H NMR (400 MHz, $CDCl_3$)



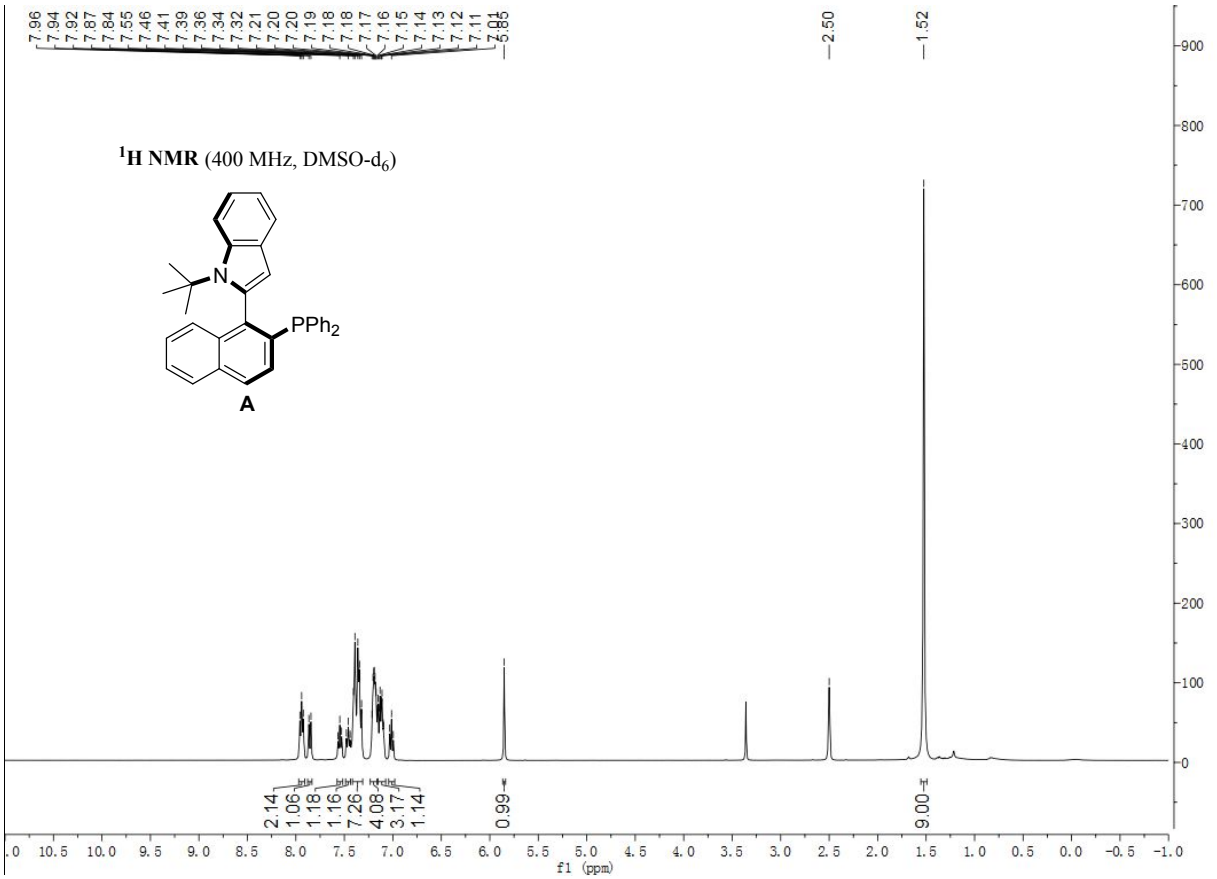
6t

^{13}C NMR (100 MHz, $CDCl_3$)



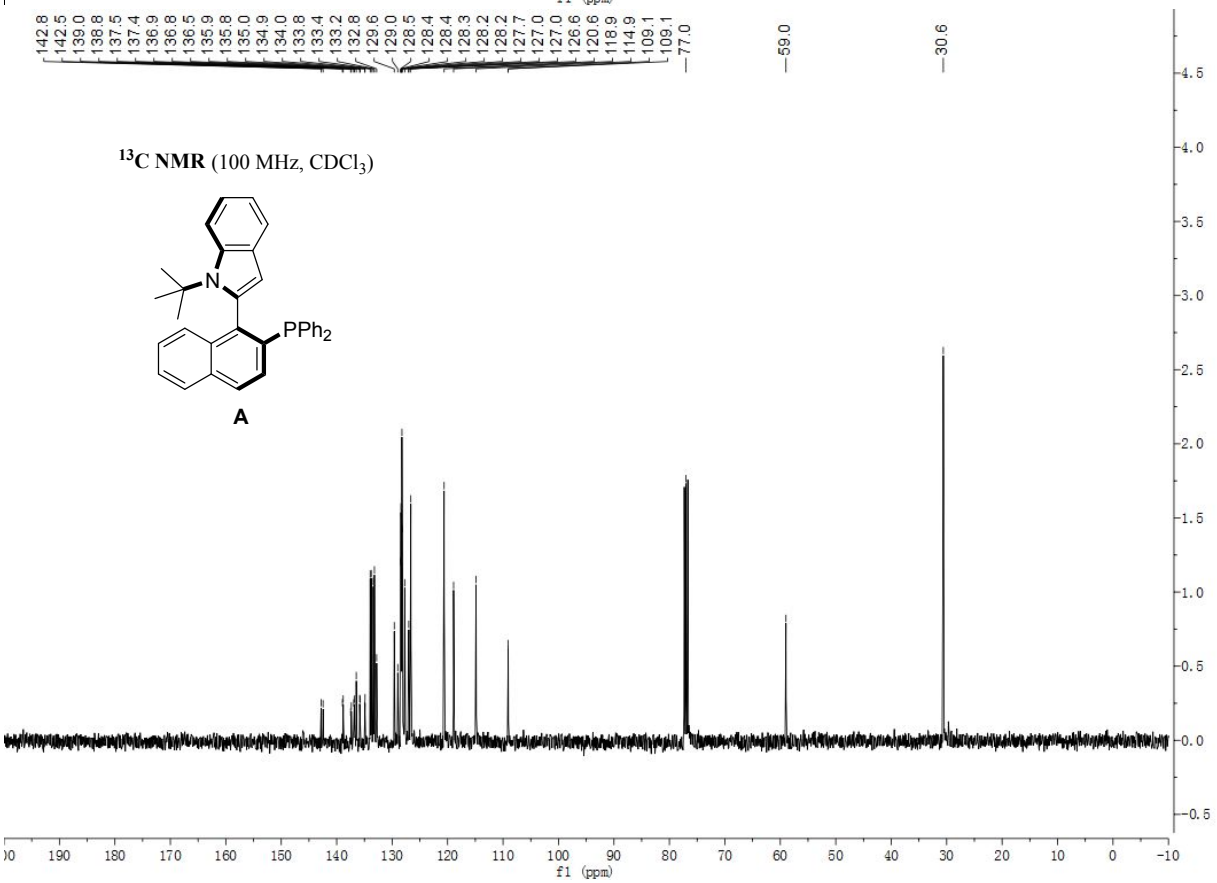
6t

XII. ^{1}H, ^{13}C and ^{31}P NMR spectra of organocatalysts (A-H)



^{1}H NMR (400 MHz, DMSO-d_6)

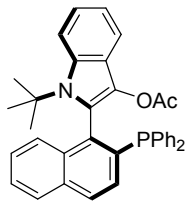
A



^{13}C NMR (100 MHz, $CDCl_3$)

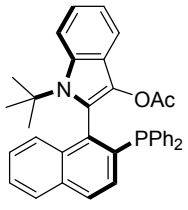
A

^{1}H NMR (400 MHz, $CDCl_3$)



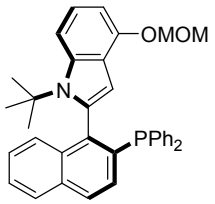
B

^{13}C NMR (100 MHz, $CDCl_3$)



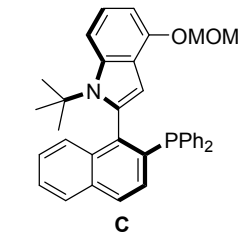
B

^{1}H NMR (400 MHz, $CDCl_3$)



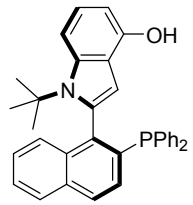
C

^{13}C NMR (100 MHz, $CDCl_3$)



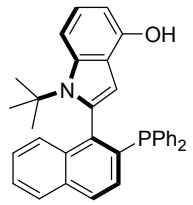
C

^{1}H NMR (400 MHz, $CDCl_3$)



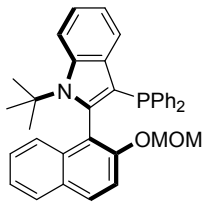
D

^{13}C NMR (100 MHz, $CDCl_3$)



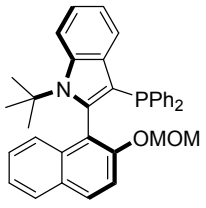
D

^{1}H NMR (400 MHz, $CDCl_3$)

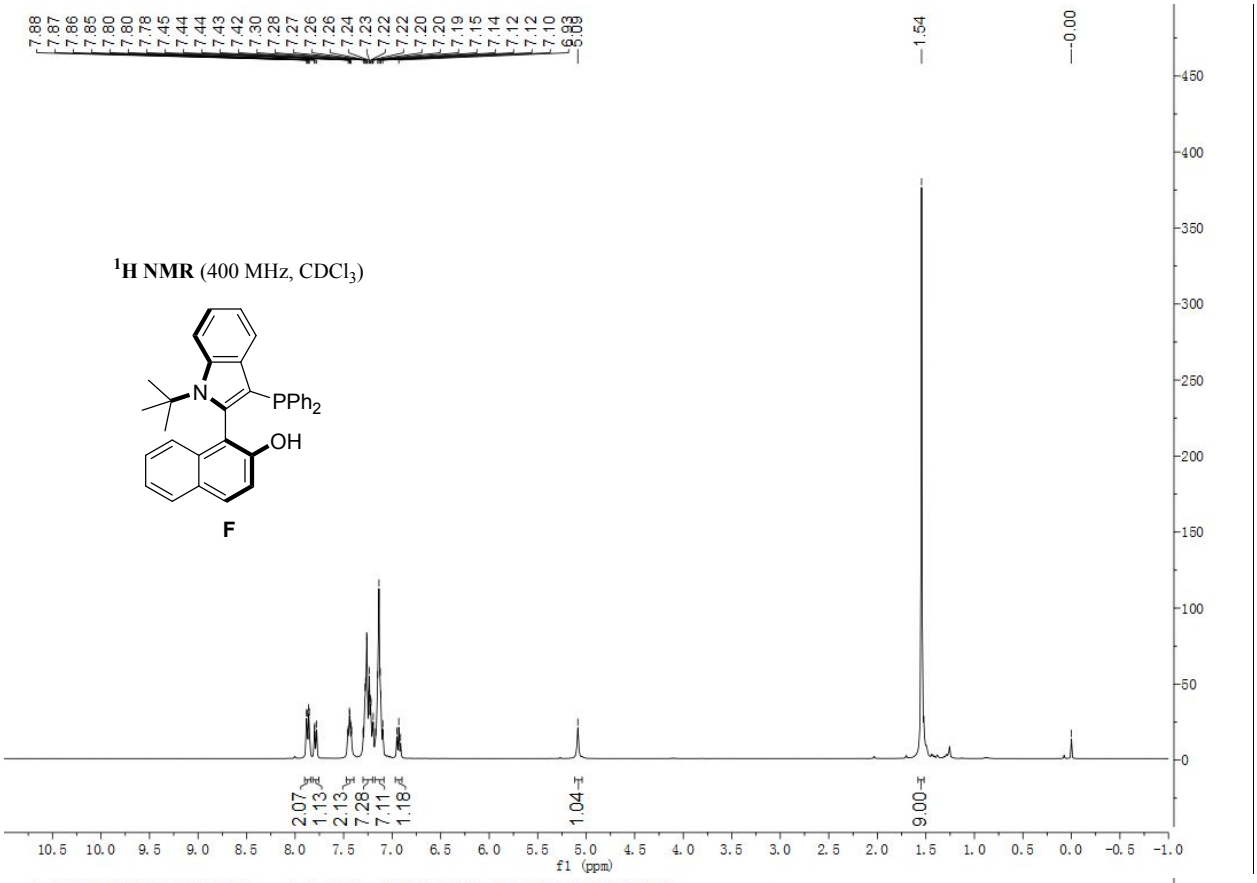


E

^{13}C NMR (100 MHz, $CDCl_3$)

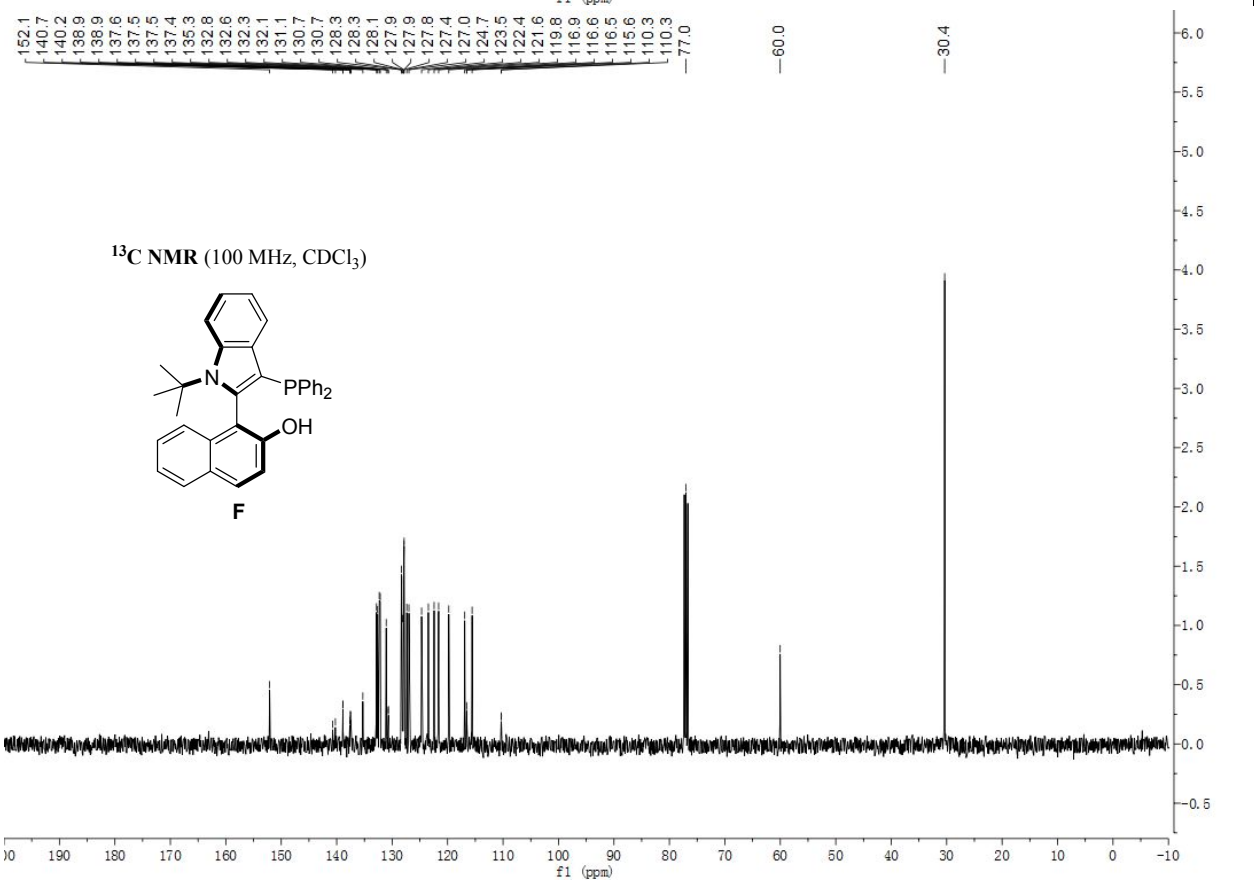


E



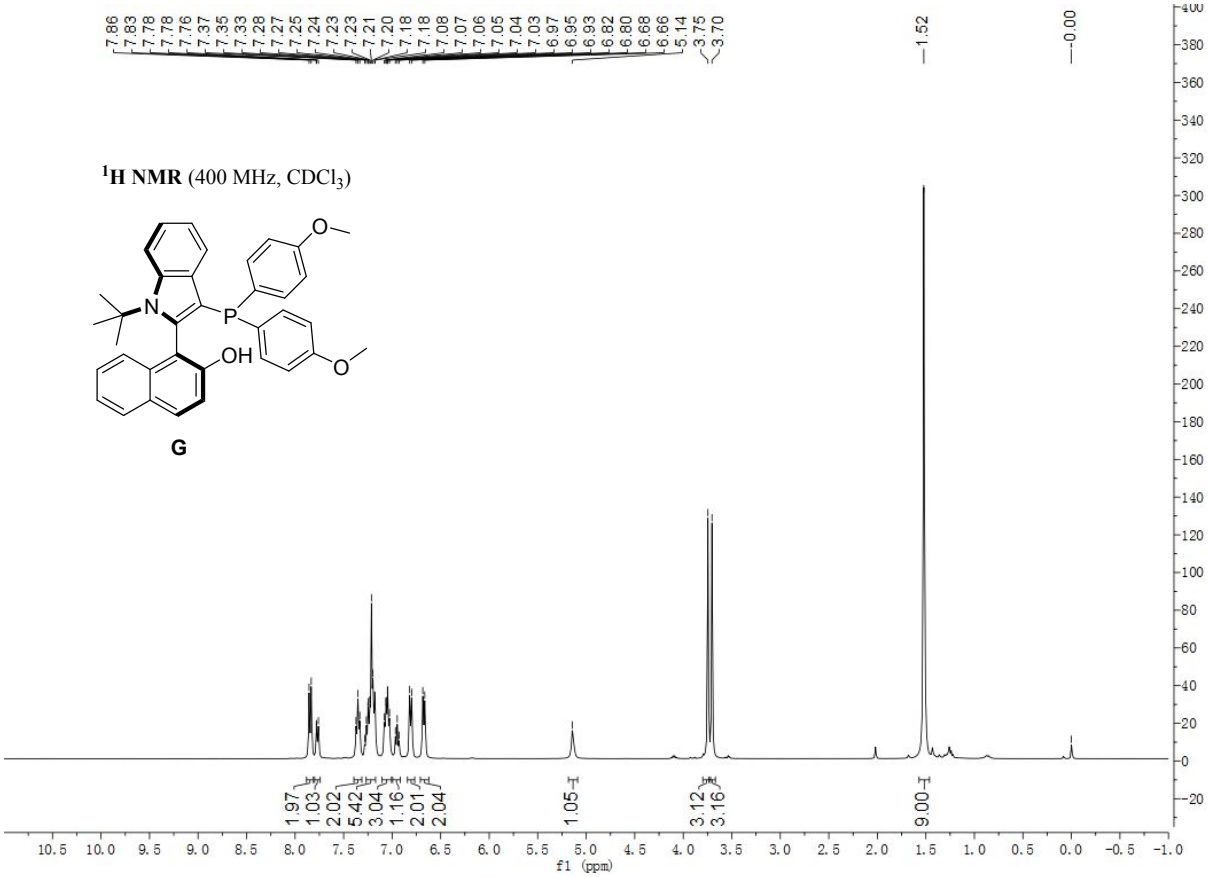
^{1}H NMR (400 MHz, $CDCl_3$)

F



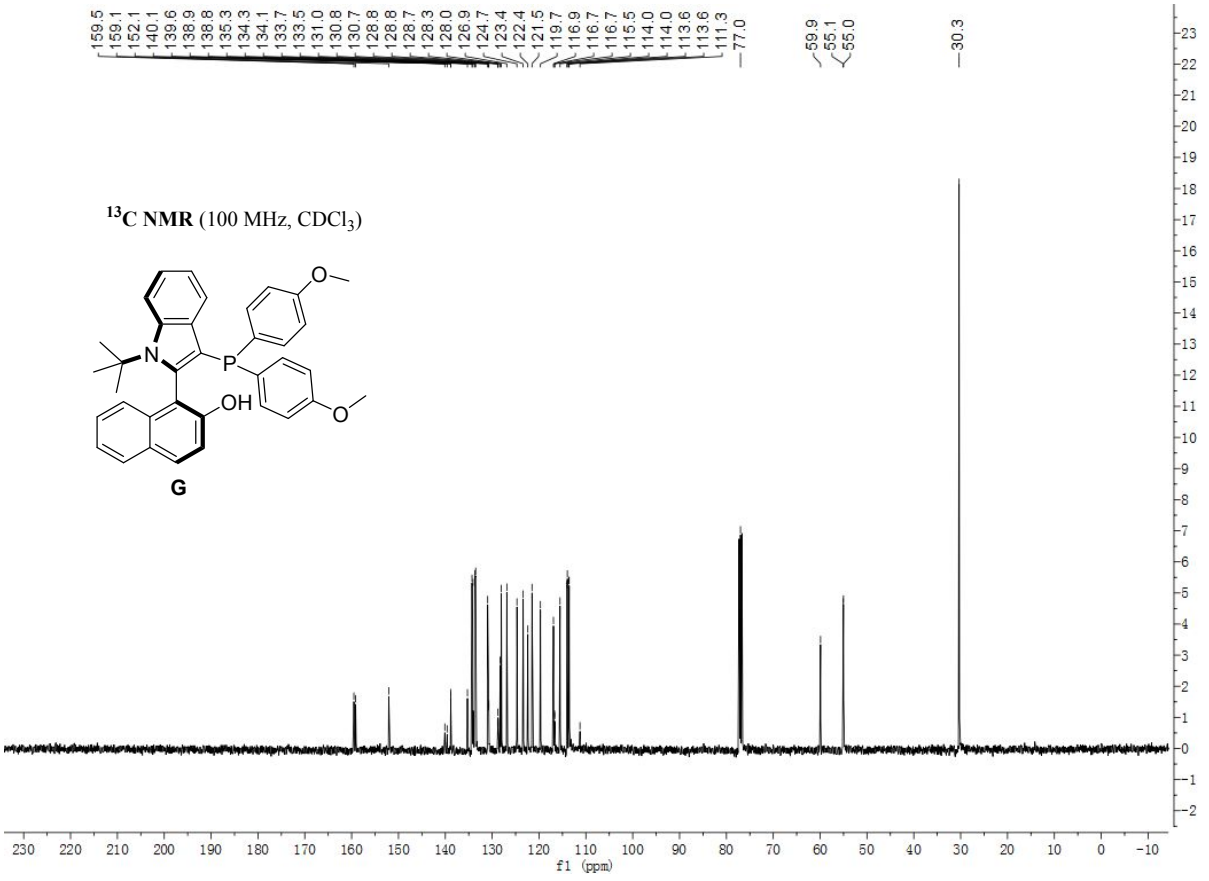
^{13}C NMR (100 MHz, $CDCl_3$)

F



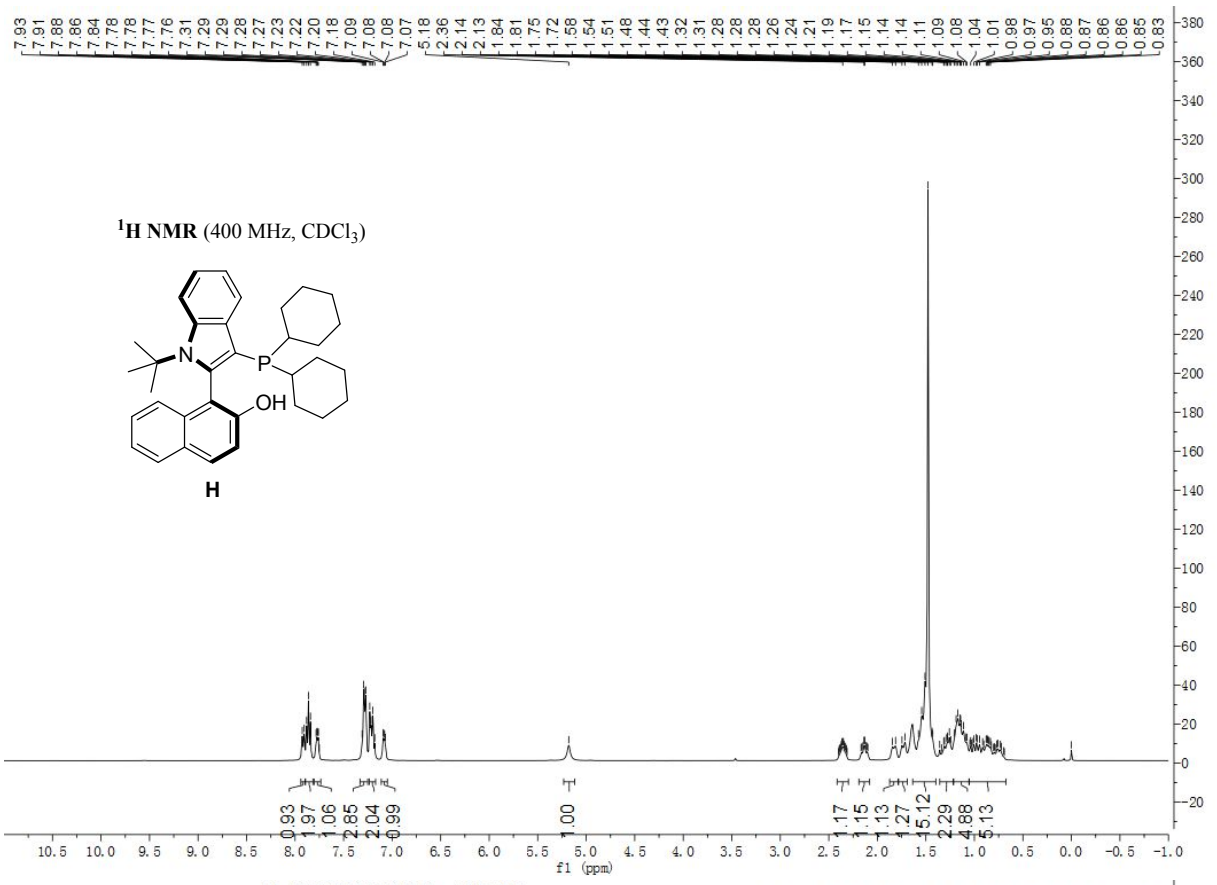
^{1}H NMR (400 MHz, $CDCl_3$)

G



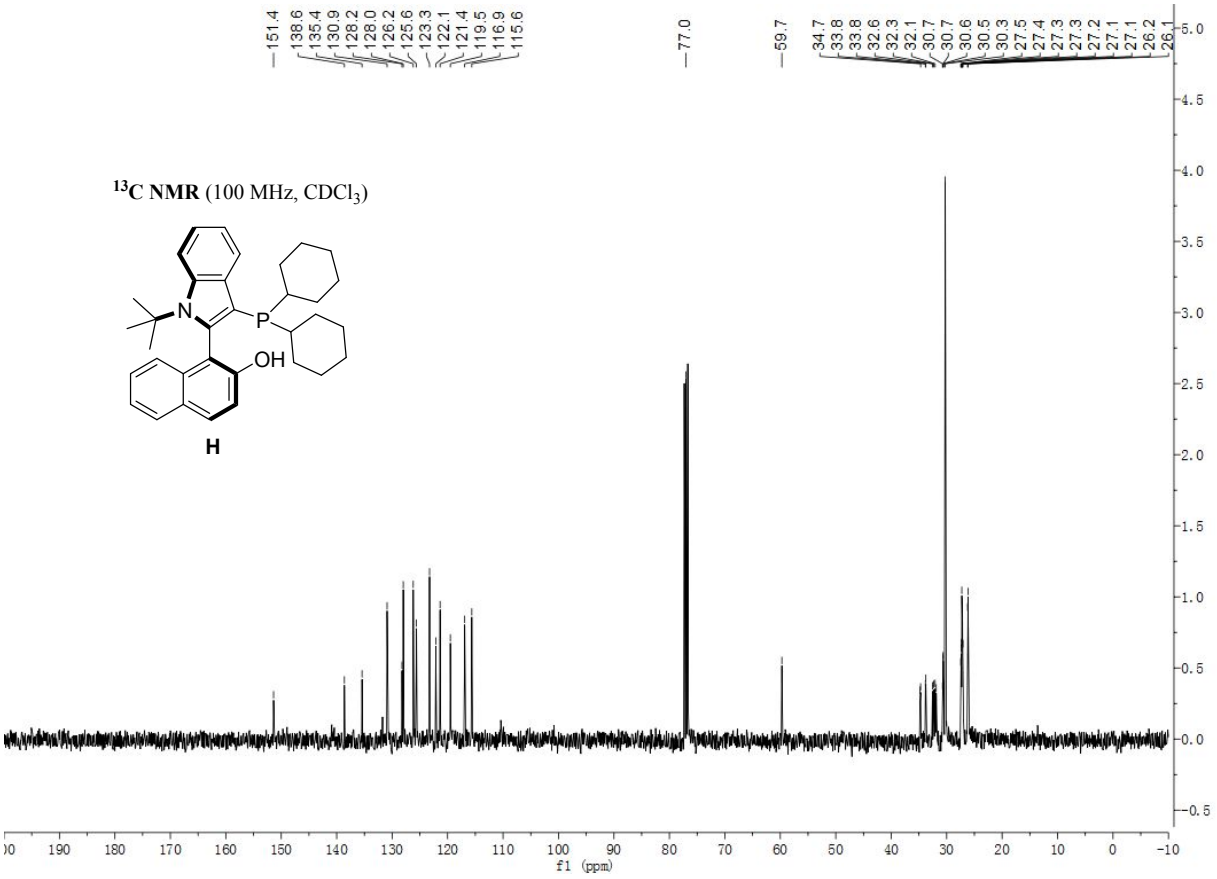
^{13}C NMR (100 MHz, $CDCl_3$)

G



^{1}H NMR (400 MHz, $CDCl_3$)

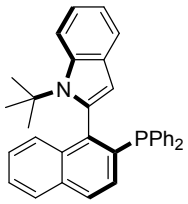
H



^{13}C NMR (100 MHz, $CDCl_3$)

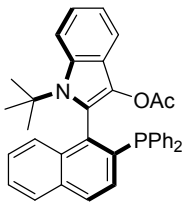
H

^{31}P NMR (243 MHz, $CDCl_3$)



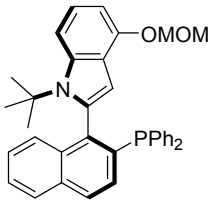
A

^{31}P NMR (243 MHz, $CDCl_3$)



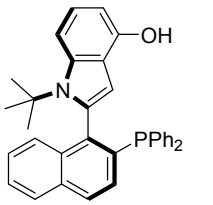
B

^{31}P NMR (243 MHz, $CDCl_3$)



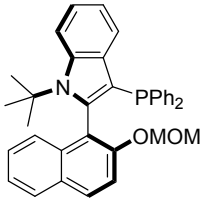
C

^{31}P NMR (243 MHz, $CDCl_3$)



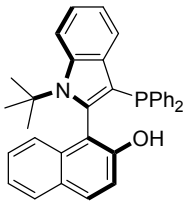
D

^{31}P NMR (243 MHz, $CDCl_3$)



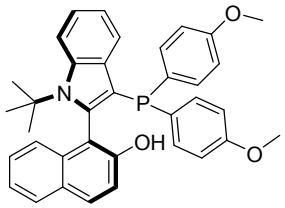
E

^{31}P NMR (243 MHz, $CDCl_3$)



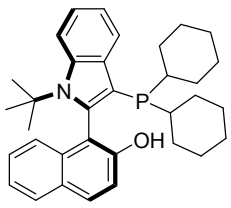
F

^{31}P NMR (243 MHz, $CDCl_3$)



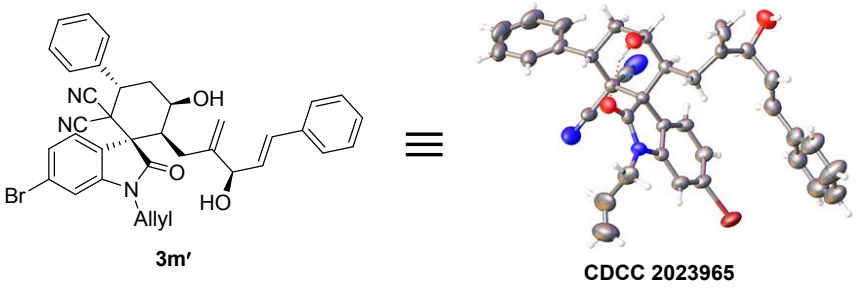
G

^{31}P NMR (243 MHz, $CDCl_3$)



H

XIII. X-ray crystallographic information (3m')



Bond precision:	C-C = 0.0089 A		Wavelength = 0.71073
Cell:	a = 10.4884 (7)	b = 15.3832 (11)	c = 18.9253 (10)
	alpha = 90	beta = 90	gamma = 90
Temperature:	295 K		
	Calculated	Reported	
Volume	3053.5 (3)	3053.5 (3)	
Space group	P 21 21 21	P 21 21 21	
Hall group	P 2ac 2ab	P 2ac 2ab	
Moiety formula	C36 H32 Br N3 O3	C36 H32 Br N3 O3	
Sum formula	C36 H32 Br N3 O3	C36 H32 Br N3 O3	
Mr	634.55	634.55	
Dx, g cm-3	1.380	1.380	
Z	4	4	
Mu (mm-1)	1.387	1.387	
F000	1312.0	1312.0	
F000’	1311.33		
h, k,lmax	14,21,25	14,20,25	
Nref	8186 [4556]	6971	
Tmin, Tmax	0.622, 0.642	0.608, 1.000	
Tmin’	0.609		

Correction method = # Reported T Limits: Tmin = 0.608 Tmax = 1.000

AbsCorr = MULTI-SCAN

Data completeness = 1.53/0.85 Theta (max) = 29.079

R (reflections) = 0.0526 (4145) wR2 (reflections) = 0.1155 (6971)

S = 1.017 Npar = 398

XIV. References

[1] Li, T.; Xie, J.; Jiang, Y.; Sha, F.; Wu, X. *Adv. Synth. Catal.* **2015***, 357,* 3507-3511.

[2] Hu, F.-L.; Wei, Y.; Shi, M. *Adv. Synth. Catal.* **2014**, *356*, 736-742.

[3] Tan, B.; Hernández-Torres, G.; Barbas, C. F. III. *J. Am. Chem. Soc.* **2011**, *133*, 12354-12357.

[4] Xiao, B.-X.; Jiang, B.; Song, X.; Du, W.; Chen, Y.-C. *Chem. Commun.* **2019**, *55*, 3097-3100.

[5] Peng, L.; Li, K.; Xie, C.; Li, S.; Xu, D.; Qin, W.; Yan, H. *Angew. Chem. Int. Ed.* **2019**, *58*, 17199-17204.