Supporting Information

Linear Paired Electrolysis Enabled Dearomative [3 + 2] Cycloadditions of Indoles and Benzofurans with Vinyl Azides†

Shaoxiong Yang,‡ Yanren Zhu,‡ Enfan Pu, Piaopiao Jiang, Xiong Li, Hongbin Zhang,* Jingbo Chen*

Key Laboratory of Medicinal Chemistry for Natural Resource, Ministry of Education, Yunnan Key Laboratory of Research and Development for Natural Products, School of Chemical Science and Technology, School of Pharmacy, Yunnan University, Kunming, 650500, P. R. China.

*Corresponding author. Email: zhanghb@ynu.edu.cn, chenjb@ynu.edu.cn

‡These authors contributed equally to this work.

Table of Contents

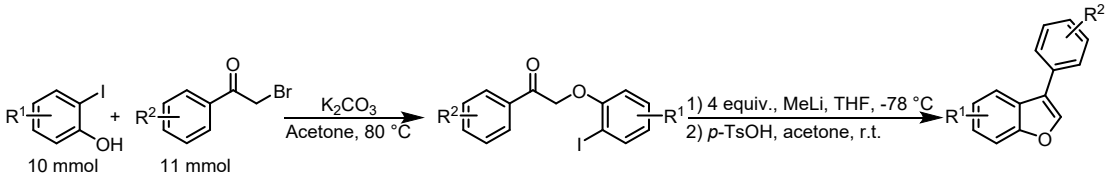
1.General information

Unless otherwise stated, commercially available chemicals were used without treatment. analytical grade solvents and commercially available reagents were used without further purification. All compounds were characterized by **^{1}H NMR**, **^{13}C NMR** and **HRMS**. **^{1}H NMR** and **^{13}C NMR** spectra were recorded on Bruker Avance 400 spectrometers. Chemical shifts are reported in parts per million (δ) referenced to tetramethylsilane (0.0 ppm), chloroform-*d* (7.26 ppm or 77.16 ppm). Data for **^{1}H NMR** and **^{13}C NMR** spectroscopy are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad), coupling constant (Hz), integration. X-Ray Single Crystal Diffraction Data were recorded on Bruker D8 QUEST and Bruker APEX DUO. High Resolution Mass spectra were taken on AB QSTAR Pulsar mass spectrometer or Aglient LC/MSD TOF mass spectrometer. Optical rotations were recorded on a JASCO P-2000 polarimeter. Melting points were measured on a Hanon MP 430 auto melting-point system and are uncorrected. Silica gel (200-300 mesh) for column chromatography and silica GF254 for TLC were obtained from Merck Chemicals Co. Ltd. (Shanghai). The boiling range of petroleum ether for column chromatography is 60-90 ℃. Electrolysis was performed using a SW-3211A dual display potentiostat (Guangzhou Swevy Instruments Co., China). All the electrochemical oxidations were performed in an oven-dried three-necked undivided cell equipped with a carbon felt anode (15 mm × 10 mm × 0.2 mm) and a carbon felt cathode (15 mm × 10 mm × 0.2 mm) unless otherwise noted. The indole, benzofuran and vinyl azide derivatives used as substrates were synthesized following established methods.

2. Experimental procedures

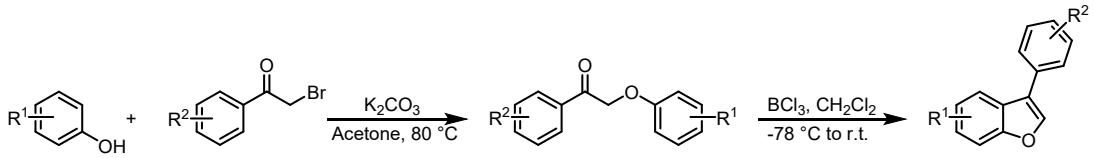
2.1. Synthesis of substrates

Synthesis of benzofuran derivatives:



According to the previous literature procedure,[1] a 250 mL round bottom flask was charged with a magnetic stir bar, then 2-iodophenol (10 mmol, 1.0 equiv.), 11 mmol 1- bromoacetophenone (1.1 equiv.) and 15 mmol K_2CO_3 (1.5 equiv.) were dissolved in 40 mL acetone. The reaction mixture was heated to 80 ℃ and stirred overnight. Cooled it to room temperature when the reaction was finished, and then the mixture was filtered through celite and the filtrate was concentrated to afford quantitative conversion to 1-(*o*-iodophenoxy)-acetophenone and used without further purification.

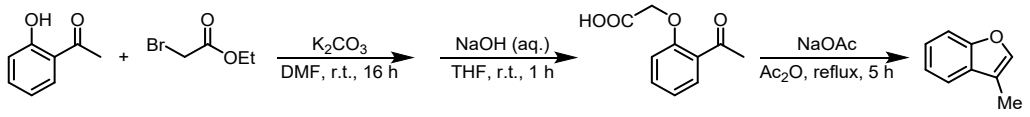
An oven-dried 250 mL two necked round-bottom flask was charged with a magnetic stir bar, 40 mL THF and 33 mL CH_3Li (1.3 M in THF, 4.0 equiv.). The flask was cooled to -78 ℃, and the product obtained from the last step was dissolved in 10 mL THF and added dropwise. The reaction was stirred for 30 minutes at -78 ℃ and then allowed to warm to room temperature. The reaction mixture was slowly hydrolyzed with concentrated NH_4Cl aqueous solution, followed by the addition of 80 mL H_2O. The reaction was extracted with ethyl acetate (3 x 40 mL), the organic layers were combined and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was dissolved in acetone and added *p*-toluenesulfonic acid (0.1 equiv.). The reaction was stirred overnight at room temperature. Following solvent evaporation, the crude product was purified by column chromatography on silica to obtain the desired 3-arylbenzofuran derivates (**1aa, 1ba-1bd, 1bi-1bk, 1bn**).



According to the previous literature procedure,[2] a 250 mL round bottom flask was charged with a magnetic stir bar, then phenol (10 mmol, 1.0 equiv.), 1- bromoacetophenone (11 mmol, 1.1 equiv.) and 15 mmol K_2CO_3 (1.5 equiv.) were dissolved in 40 mL acetone. The reaction mixture was heated

to 80 ℃ and stirred overnight. Cooled it to room temperature when the reaction was finished, and then the mixture was filtered through celite and the filtrate was concentrated to afford quantitative conversion to 1-(*o*-iodophenoxy)-acetophenone and used without further purification.

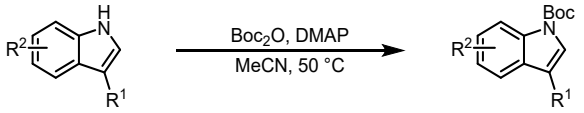
To a stirred solution of the product obtained from the last step in CH_2Cl_2 (33 mL) was added BCl_3 (1.2 equiv., 1.0 M solution in CH_2Cl_2) at -78 ℃. After being stirred at rt for 1 h, the reaction mixture was quenched with cold H_2O. The mixture was extracted with CH_2Cl_2 two times. The combined organic layers were dried over Na_2SO_4, and concentrated under reduced pressure. The resulting residue was purified by silica gel column chromatography to give the benzofuran or naphthofuran derivates (**1be-1bh, 1bk, 1bm, 1bo,1bp**).



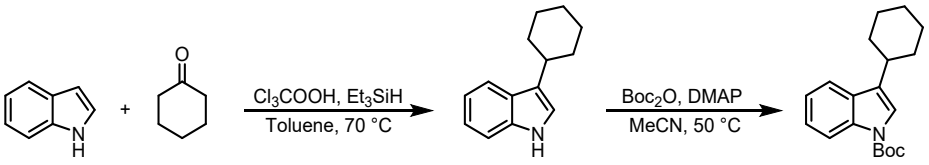
3-methylbenzofuran: According to the previous literature procedure,[1b] a 250 mL round bottom flask was charged with a magnetic stir bar, then 2-hydroxy acetophenone (12 mmol, 1.2 equiv.), and K_2CO_3 (1.0 equiv.) were dissolved in 40 mL DMF. ethyl bromoacetate (10 mmol, 1.0 equiv.) was added dropwise. The reaction mixture was stirred for 16 h. After adding 20 mL H_2O, the reaction mixture was stirred for another 30 minutes. The precipitate was filtered, washed with water and dried over Na_2SO_4. After removal of the solvent in vacuo, the intermediate product was afforded as a white solid. Dissolved the white solid in 30 mL THF, and 4 M NaOH aqueous solution was added. The mixture was stirred for 1 h, and THF was removed in vacuo. The residue was acidified with 3 M HCl solution and precipitate was filtered, washed with water and extracted with ethyl acetate (3 x 40 mL). The organic layers were combined and dried over Na_2SO_4. After removal of the solvent in vacuo, the product was afforded without further purification.

Dissolved the product obtained from the last step in 50 mL acetic anhydride, and added NaOAc (40 mmol, 4.0 equiv.). The mixture was stirred under reflux for 5 h. And the reaction mixture was cooled to room temperature and poured into 80 mL ice water. Extracted with ethyl acetate (3 x 40mL), the organic layers were combined and dried over Na_2SO_4. After removal of the solvent in vacuo, the residue was purified by column chromatography on silica to obtain the desired 3-methylbenzofuran (**1bl**).

Synthesis of indole derivatives:

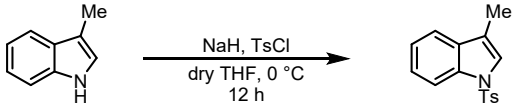


According to the previous literature procedure.[3] To a solution of indoles (5 mmol, 1.0 equiv.) in CH_3CN (5 mL) was added Boc_2O (5 mmol, 1.0 equiv.) and 4-dimethylamino pyridine (DMAP, 0.01 mmol). The mixture was stirred at 50 ℃ for 1 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure to afford a crude residue. The crude product was purified by silica gel column chromatography (petroleum ether/ EtOAc) to give *N*-Boc indoles (**4aa-4ak, 4am, 4an**).



According to the previous literature procedure.[4] Into a 100 mL three-neck flask equipped with a magnetic stir bar, glass stopper and dropping funnel, dry toluene (7.5 mL), Et_3SiH (38.4 mmol, 3.0 equiv.) and Cl_3CCOOH (19.2 mmol, 1.5 equiv.) were added under N_2 atmosphere. The mixture was heated to 70 ºC and treated with a solution of cyclohexanone (14.1 mmol, 1.1 equiv.) and indole (12.8 mmol, 1.0 equiv.) in toluene (5 mL) dropwise. The reaction mixture was then stirred for 2 h at this temperature. After cooling to room temperature, the mixture was quenched with saturated Na_2CO_3, extracted with Et_2O. The combined organic layer was dried over anhydrous Na_2SO_4, filtrated, concentrated under vacuum, and the residue was purified by flash column chromatography (petroleum ether/ EtOAc) to give a white solid.

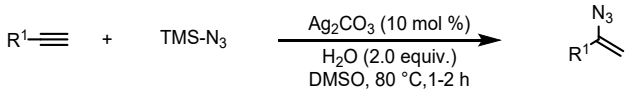
The indoles (5 mmol, 1.0 equiv.) obtained from the last step was dissolved in CH_3CN (5 mL), and then Boc_2O (5 mmol, 1.0 equiv.) and 4-dimethylaminopyridine (DMAP, 0.01 mmol) were added. The mixture was stirred at 50 ℃ for 1 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure to afford a crude residue. The crude product was purified by silica gel column chromatography (petroleum ether/ EtOAc) to give *N*-Boc indoles (**4al**).



According to the previous literature procedure.[5] To a stirred solution of the indole (5 mmol, 1.0

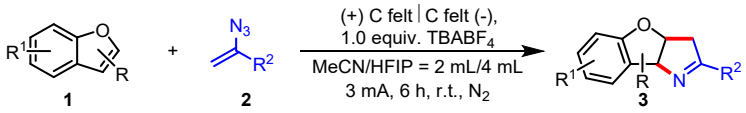
equiv.) in THF at 0 °C under a nitrogen atmosphere was added NaH (6 mmol, 1.2 equiv., 60% in oil). After stirring for 20 min at 0 °C, TsCl (7.5 mmol, 1.5 equiv.) was added dropwise, and the resulting mixture was stirred for 16 h at 25 °C. The reaction mixture was treated with water (15 mL) and EtOAc (20 mL) and transferred to a 125 mL separatory funnel. The organic layer was collected, and the aqueous layer was extracted with EtOAc (25 mL x 2). The combined organic layers were washed with brine (20 mL), dried over Na_2SO_4, and filtered. The filtrate was concentrated, and the residue was purified by flash column chromatography to afford the desired indole.

Synthesis of vinyl azides derivative:



According to the previous literature procedure.[6] To a solution of the corresponding alkyne (0.5 mmol, 1.0 equiv.), TMS-N_3 (1.0 mmol, 2.0 equiv.) and H_2O (1.0 mmol, 2.0 equiv.) in DMSO (2 mL) at 80 °C, Ag_2CO_3 (0.05 mmol, 0.1 equiv.) was added. The mixture was then stirred for 1-2 h until substrate alkyne consumed as indicated by TLC. The resulting mixture was concentrated and taken up by dichloromethane (3 x 15 mL). The organic layer was washed with brine (3 x 40 mL), dried over Na_2SO_4 and concentrated. Purification of the crude product with flash column chromatography (petroleum ether) and concentrated in vacuo to afford vinyl azides derivatives.

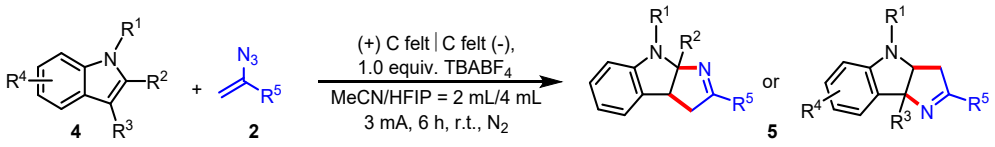
2.2 General procedure for electrochemical induced dearomative [3 + 2] annulation of benzofurans.



$TBABF_4$ (0.2 mmol, 1 equiv.) were placed in an oven-dried undivided three-necked bottle (15 mL). The bottle was equipped with a stir bar, two carbon felts (10 mm × 15 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (2 mL), benzofuran derivatives **1** (0.2 mmol, 1 equiv.), vinyl azides species **2** (0.4 mmol, 2.0 equiv.) and commercially available hexafluoroisopropanol (HFIP, 4 mL) were added. The reaction was stirred and electrolyzed at a constant current of 3.0 mA at room temperature for 6 h. After completion of the reaction, the product was identified by TLC. The solvent was

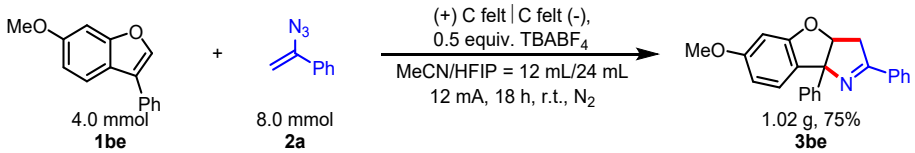
removed under reduced pressure by rotary evaporator, and then the pure product **3** was obtained by flash column chromatography on silica gel.

2.3 General procedure for electrochemical induced dearomative [3 + 2] annulation of indoles.



$TBABF_4$ (0.2 mmol, 1.0 equiv.) were placed in an oven-dried undivided three-necked bottle (15 mL). The bottle was equipped with a stir bar, two carbon felts (15 mm × 10 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (2 mL), indole derivatives **4** (0.2 mmol, 1 equiv.), vinyl azides species **2** (0.4 mmol, 2.0 equiv.) and commercially available hexafluoroisopropanol (HFIP, 4 mL) were added. The reaction was stirred and electrolyzed at a constant current of 3.0 mA at room temperature for 6 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by rotary evaporator, and then the pure product **5** was obtained by flash column chromatography on silica gel.

2.4 General procedure for the gram-scale electrochemical induced dearomative [3 + 2] annulation of benzofuran derivative (1be).



$TBABF_4$ (2.0 mmol, 0.5 equiv.) were placed in an oven-dried undivided two-necked bottle (50 mL). The bottle was equipped with a stir bar, two carbon felts (30 mm × 10 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (12 mL), benzofuran derivative **1be** (896.0 mg, 4.0 mmol, 1 equiv.), vinyl azides species **2a** (8.0 mmol, 2.0 equiv.) and commercially available hexafluoroisopropanol (HFIP, 24 mL) were added. The reaction was stirred and electrolyzed at a constant current of 12 mA at room temperature for 18 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by rotary evaporator, and then 1.02 g pure product

3be (yield = 75%) was obtained by flash column chromatography on silica gel (petroleum ether/ EtOAc = 20:1).

The green chemistry metrics of this protocol

$$\text{E-factor} = \frac{\text{Mass of waste}}{\text{Mass of product}} \qquad \text{Atom Economy (\%)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

$$\text{Process Management Index} = \frac{\text{Total mass of input material in the whole process}}{\text{Mass of product}}$$

Atom Efficiency (%) = Atom Economy (%) x Yield (%) x 100

$$\text{Carbon Efficiency (\%)} = \frac{\text{Total no. of C in reactants}}{\text{Total no. of C in products}} \times 100$$

$$\text{Reaction mass Economy (\%)} = \frac{\text{Mass of desired product}}{\text{Mass of all reactants}} \times 100$$

Reactant 1	**1be**	0.896g	4.0 mmol	FW 224.26
Reactant 2	**2a**	1.16g	8.0 mmol	FW 145.16
Electrolyte	$TBABF_4$	0.658g	2.0 mmol	FW 329.27
Solvent	CH_3CN + HFIP	9.432g (12 mL) + 38.304g (24 mL)		
Product	**3be**	1.02g	3.0 mmol	FW 341.41

Product yield = 75%

E-factor = (0.896 + 1.16 + 0.658 + 9.432 + 38.304 - 1.02) / 1.02 = 48.46 Kg waste / 1Kg product

Atom Economy = (341.41 / 369.42) x 100 = 92.4%

Process Management Index = (0.896 + 1.16 + 0.658 + 9.432 + 38.304) / 1.02 = 49.46

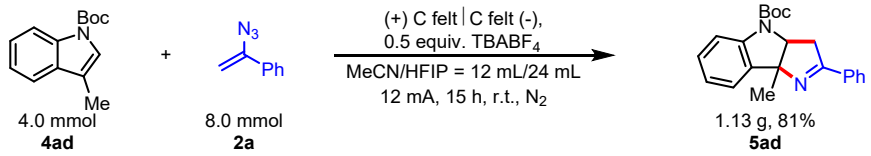
Atom Efficiency = 75% x 92.4% x 100 = 69.3%

Carbon Efficiency = 23 / 23 x 100 = 100%

Reaction mass Economy = 1.02 / (0.896 + 1.16) x 100 = 49.6%

2.5 General procedure for the gram-scale electrochemical induced dearomative [3 + 2]

annulation of indole derivative (4ad).



$TBABF_4$ (2.0 mmol, 0.5 equiv.) were placed in an oven-dried undivided two-necked bottle (50 mL). The bottle was equipped with a stir bar, two carbon felts (30 mm × 10 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (12 mL), indole derivative **4ad** (925.0 mg, 4.0 mmol, 1 equiv.), vinyl azides species **2a** (8.0 mmol, 2.0 equiv.) and commercially available hexafluoroisopropanol (HFIP, 24 mL) were added. The reaction was stirred and electrolyzed at a constant current of 12 mA at room temperature for 15 h. After completion of the reaction, the product was identified by TLC. The solvent was removed under reduced pressure by rotary evaporator, and then 1.13 g pure product **5ad** (yield = 81%) was obtained by flash column chromatography on silica gel (petroleum ether/ EtOAc = 15:1).

The green chemistry metrics of this protocol

$$\text{E-factor} = \frac{\text{Mass of waste}}{\text{Mass of product}} \qquad \text{Atom Economy (\%)} = \frac{\text{Molecular mass of desired product}}{\text{Molecular mass of all reactants}} \times 100$$

$$\text{Process Management Index} = \frac{\text{Total mass of input material in the whole process}}{\text{Mass of product}}$$

Atom Efficiency (%) = Atom Economy (%) x Yield (%) x 100

$$\text{Carbon Efficiency (\%)} = \frac{\text{Total no. of C in reactants}}{\text{Total no. of C in products}} \times 100$$

$$\text{Reaction mass Economy (\%)} = \frac{\text{Mass of desired product}}{\text{Mass of all reactants}} \times 100$$

Reactant 1	**4ad**	0.925g	4.0 mmol	FW 231.29
Reactant 2	**2a**	1.16g	8.0 mmol	FW 145.16
Electrolyte	$TBABF_4$	0.658g	2.0 mmol	FW 329.27
Solvent	CH_3CN + HFIP	9.432g (12 mL) + 38.304g		

		(24 mL)		
Product	**5ad**	1.13g	3.3 mmol	FW 348.45

Product yield = 81%

E-factor = (0.925 + 1.16 + 0.658 + 9.432 + 38.304 - 1.13) / 1.13 = 43.67 Kg waste / 1Kg product

Atom Economy = (348.45 / 376.45) x 100 = 92.6%

Process Management Index = (0.925 + 1.16 + 0.658 + 9.432 + 38.304) / 1.13 = 44.67

Atom Efficiency = 81% x 92.6% x 100 = 75.0%

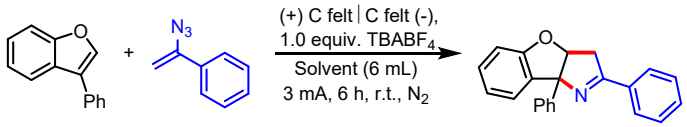
Carbon Efficiency = 22 / 22 x 100 = 100%

Reaction mass Economy = 1.13 / (0.925 + 1.16) x 100 = 54.2%

Experimental setup diagram for the gram scale reaction

2.6 Optimization of reaction conditions

Table 1. Solvent screening[a]

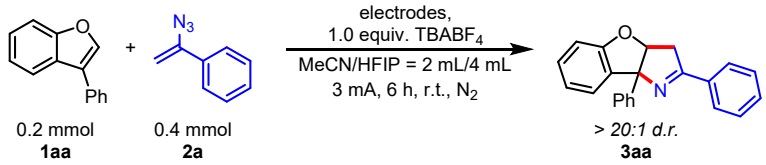


Entry	Solvent	Yield (%)[b]
1	CH_3CN	23
2	DCM	10
3	HFIP	35
4	THF	<5
5	CH_3CN/ HFIP = 2:1	65

6	**CH_3CN/ HFIP = 1:2**	**82**
7	CH_3CN/ HFIP = 1:5	73
8[c]	CH3CN/ HFIP = 1:2	63
9	MeOH	0
10	TFE	0

[a]Reaction conditions: carbon felt electrodes (15 mm × 10 mm × 2.0 mm, distance: 10 mm), **1aa** (0.20 mmol), **2a** (2.0 equiv.), $^{n}Bu_4NBF_4$ (1.0 equiv.), solvent (6mL), undivided cell, N_2, room temperature, constant current = 3.0 mA, 6 h. [b]Isolated yields were shown. [c]CH_3CN/ HFIP = 4 mL/8 mL. HFIP: hexafluoroisopropanol.

Table 2. Optimization of electrodes[a]

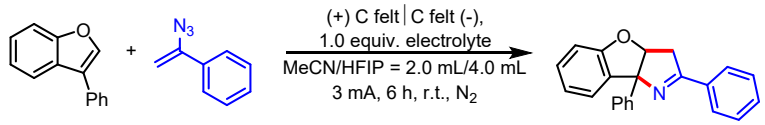


0.2 mmol **1aa** | 0.4 mmol **2a** | *> 20:1 d.r.* **3aa**

Entry	Anode/Cathode	Yield (%)[b]
1	C rod/C felt	45
2	Pt/C felt	32
3	C cloth/C felt	76
4	**C felt/C felt**	**82**
5	C felt/Pt	65
6	C felt/C rod	50
7	C felt/Ni foam	23
8	C felt/Zn	10

[a]Reaction conditions: electrodes, **1aa** (0.20 mmol), **2a** (2.0 equiv.), $^{n}Bu_4NBF_4$ (1.0 equiv.), solvent (CH_3CN/HFIP = 2 mL/4 mL), undivided cell, N_2, room temperature, constant current = 3.0 mA, 6 h. [b]Isolated yields were shown.

Table 3. electrolyte screening[a]

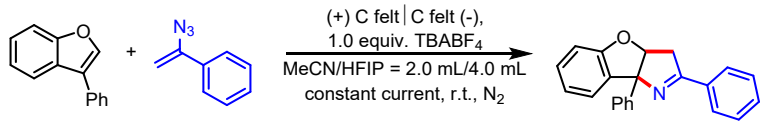


0.2 mmol **1aa** | 0.4 mmol **2a** | *> 20:1 d.r.* **3aa**

Entry	Electrolyte	Yield (%)[b]
1	$LiClO_4$	25
2	$TBAPF_6$	74
3	**$TBABF_4$**	**82**
4	TBAOAc	32
5	$TBAClO_4$	48
6	TBAI	8

[a]Reaction conditions: carbon felt electrodes (15 mm × 10 mm × 2.0 mm, distance: 10 mm), **1aa** (0.20 mmol), **2a** (2.0 equiv.), electrolyte (1.0 equiv.), solvent (CH_3CN/HFIP = 2 mL/4 mL), undivided cell, N_2, room temperature, constant current = 3.0 mA, 6 h. [b]Isolated yields were shown.

Table 4. Optimization of constant current[a]

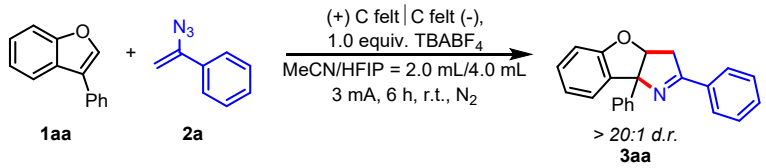


0.2 mmol **1aa** | 0.4 mmol **2a** | *> 20:1 d.r.* **3aa**

Entry	Constant current (mA), reaction time	Yield (%)[b]
1	0 mA, 24 h	0
2	1.0 mA, 12 h	68
3	2.0 mA, 10 h	72
4	**3.0 mA, 6 h**	**82**
5	5.0 mA, 3.2 h	81
6	3.0 mA, 6 h, air	70

[a]Reaction conditions: carbon felt electrodes (15 mm × 10 mm × 2.0 mm, distance: 10 mm), **1aa** (0.20 mmol), **2a** (2.0 equiv.), $^nBu_4NBF_4$ (1.0 equiv.), solvent (CH_3CN/HFIP = 2 mL/4 mL), undivided cell, N_2, room temperature, constant current. [b]Isolated yields were shown.

Table 5. Optimization of substrate loading[a]



Entry	1a/2a (mmol)	Yield (%)[b]
1	0.2/0.2	52
2	0.2/0.3	76
3	**0.2/0.4**	**82**
4	0.2/0.5	82

[a]Reaction conditions: carbon felt electrodes (15 mm × 10 mm × 2.0 mm, distance: 10 mm), **1aa** (0.20 mmol), **2a** (x mmol), $^{n}Bu_4NBF_4$ (1.0 equiv.), solvent (CH_3CN/HFIP = 2 mL/4 mL), undivided cell, N_2, room temperature, constant current = 3.0 mA, 6 h. [b]Isolated yields were shown.

3. Mechanistic Experiments

3.1 Electrochemical Procedures for Cyclic Voltammetry

Cyclic voltammetry experiments were performed in a three-electrode cell connected to three-necked bottles under nitrogen at room temperature. The working electrode was a steady glassy carbon disk electrode (Φ = 3 mm), the counter electrode was a platinum wire. The distance of working electrode and counter electrode was 10 mm. The reference was an Hg/Hg_2Cl_2 electrode submerged in saturated aqueous KCl solution. 0.1 M $TBABF_4$ was used as the supporting electrolyte and CH_3CN/HFIP = 2 mL/4 mL was used as the solvent. The scan rate was 0.05 V/s.

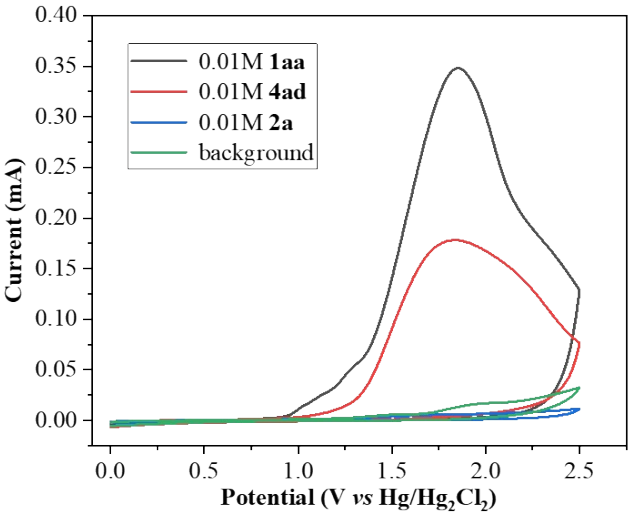


Figure S1 Cyclic voltammograms of background, **1aa**, **4ad** and **2a** (initial scan polarity: **positive**). Int E = 0 V; High E = 2.5 V; Low E = 0 V; Final E = 0 V.

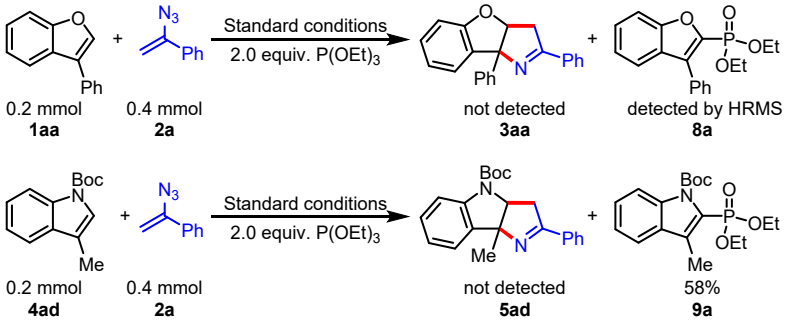
Background (the green line): 0.6 mmol $TBABF_4$ in CH_3CN/HFIP = 2 mL/4 mL.

0.01 M **1aa** (the black line): 0.6 mmol $TBABF_4$ and 0.06 mmol **1aa** in CH_3CN/HFIP = 2 mL/4 mL.

0.01 M **4ad** (the red line): 0.6 mmol $TBABF_4$ and 0.06 mmol **4ad** in CH_3CN/HFIP = 2 mL/4 mL.

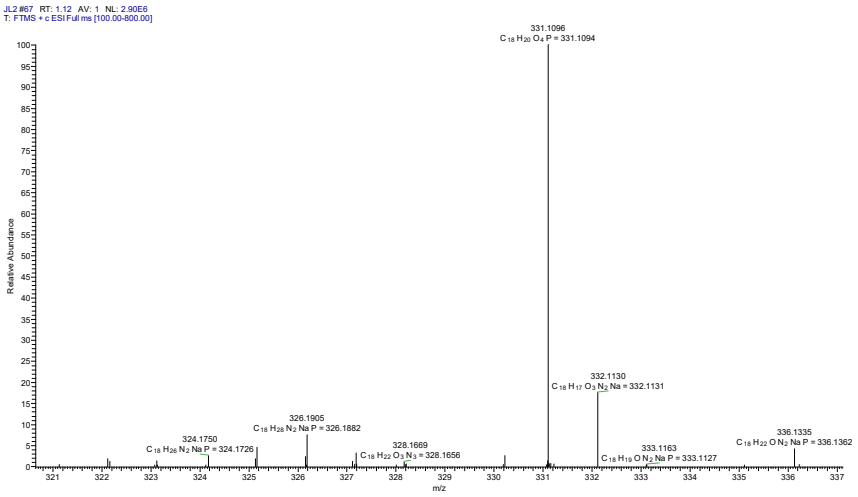
0.02 M **2a** (the blue line): 0.6 mmol TBABF4 and 0.12 mmol **2a** in CH_3CN/HFIP = 2 mL/4 mL.

3.2 Radical cation trapping experiment by $P(OEt)_3$.



Radical cation trapping experiment of 3-phenylbenzofuran (**1aa**). $TBABF_4$ (0.2 mmol, 1.0 equiv.) were placed in an oven-dried undivided two-necked bottle (15 mL). The bottle was equipped with a stir bar, two carbon felts (10 mm × 15 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (2 mL), 3-phenylbenzofuran **1aa** (0.2 mmol, 1.0 equiv.), α-tolyl vinyl azide **2a** (0.4 mmol, 2.0 equiv.), commercially available hexafluoroisopropanol (HFIP, 4 mL) and $P(OEt)_3$ (0.4 mmol, 2.0 equiv.) were added. The reaction was stirred and electrolyzed at a constant current of 3 mA at room

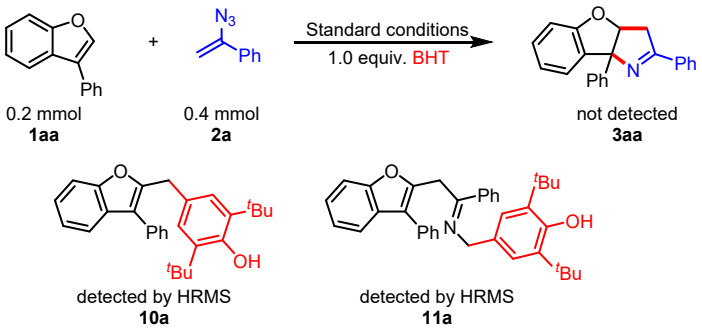
temperature for 6 h. After completion of the reaction. The reaction solution was detected by HRMS, the desired [3 + 2] annulation product **3aa** was not observed. Instead, the benzofuran phosphorylation product **8a** was detected.



benzofuran phosphorylation product 8a was detected by HRMS

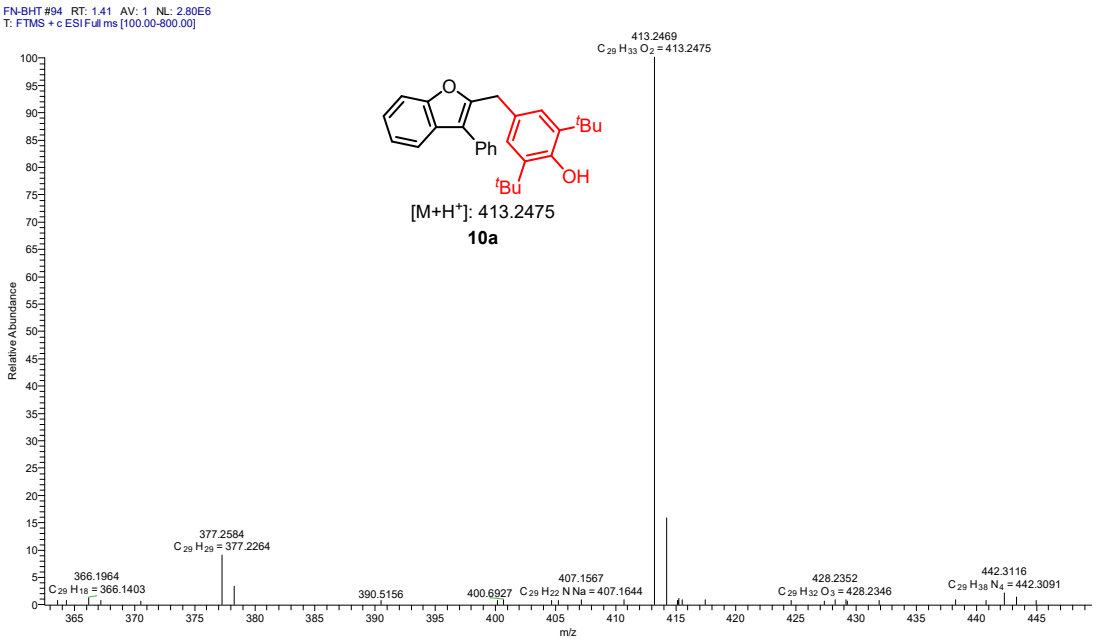
Radical cation trapping experiment of 3-methyl *N*-Boc indoles (**4ad**). $TBABF_4$ (0.2 mmol, 1.0 equiv.) were placed in an oven-dried undivided three-necked bottle (15 mL). The bottle was equipped with a stir bar, two carbon felts (10 mm × 15 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (2 mL), 3-methyl *N*-Boc indoles **4ad** (0.2 mmol, 1.0 equiv.), *α*-tolyl vinyl azide **2a** (0.4 mmol, 2.0 equiv.), commercially available hexafluoroisopropanol (HFIP, 4 mL) and $P(OEt)_3$ (0.4 mmol, 2.0 equiv.) were added. The reaction was stirred and electrolyzed at a constant current of 3 mA at room temperature for 6 h. After completion of the reaction. The desired [3 + 2] annulation product **5ad** was not observed. Instead, the indole phosphorylation product **9a** was isolated in 58% yield.

3.3 Radical trapping experiment by BHT.

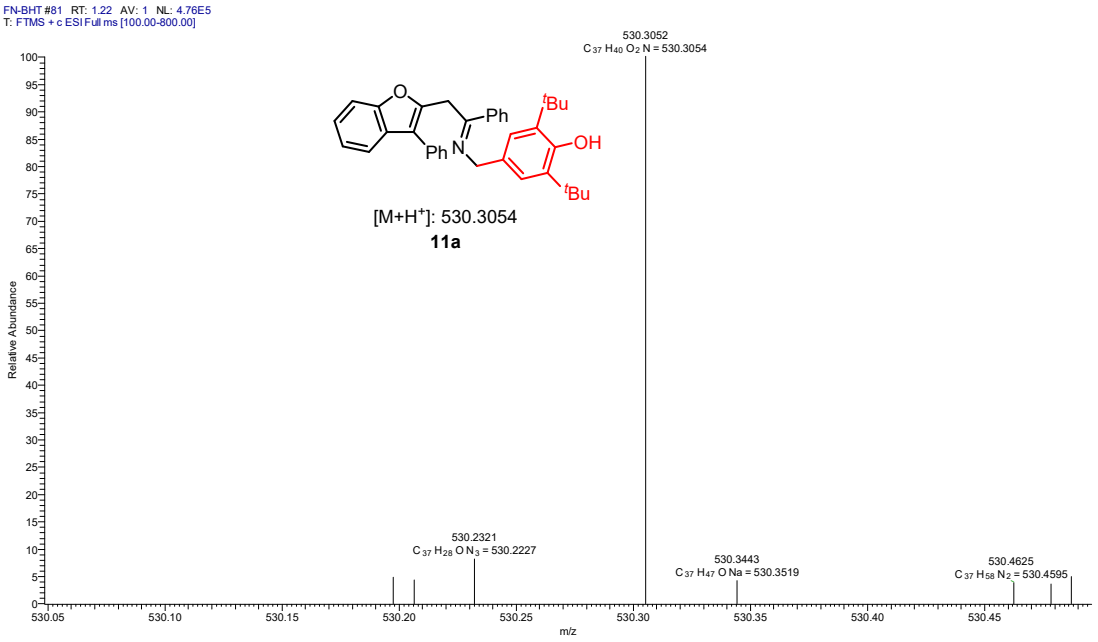


Radical trapping experiment of 3-phenylbenzofuran (**1aa**). $TBABF_4$ (0.2 mmol, 1.0 equiv.) were

placed in an oven-dried undivided two-necked bottle (15 mL). The bottle was equipped with a stir bar, two carbon felts (10 mm × 15 mm) were used as two electrodes and the distance of two electrodes is 10 mm. The bottle was flushed with nitrogen. Degased dry CH_3CN (2 mL), 3-phenylbenzofuran **1aa** (0.2 mmol, 1.0 equiv.), *α*-tolyl vinyl azide **2a** (0.4 mmol, 2.0 equiv.), BHT (0.2 mmol, 1.0 equiv.) and commercially available hexafluoroisopropanol (HFIP, 4 mL) were added. The reaction was stirred and electrolyzed at a constant current of 3 mA at room temperature for 6 h. After completion of the reaction. The reaction solution was detected by HRMS, the desired [3 + 2] annulation product **3aa** was not observed. Instead, the two radical intermediates (**10a, 11a**) that were trapped by BHT was detected.

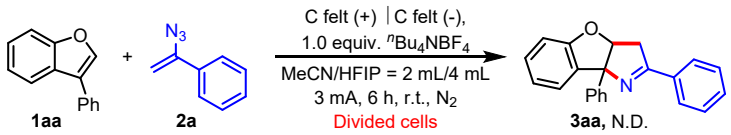


radical intermediates 10a



radical intermediates 11a

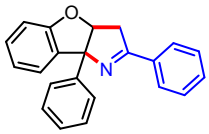
3.4 Control experiments using divided cells



The experiment was conducted in divided cells separated by an anionexchange membrane. A magnetic stir bar and a carbon felt (15 mm × 10 mm × 0.2 mm) electrode were placed in each cell, and then the same solvent containing 0.2 mmol **1aa**, 0.4 mmol **2a**, 0.2 mmol $TBABF_4$, 2 mL CH_3CN and 4 mL HFIP was added into each cell. The reaction was stirred and electrolyzed at aconstant current of 3 mA at room temperature for 6 h. After completion of the reaction, there was noproduct detected by TLC.

4. Characterization Data of Products

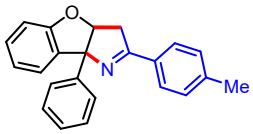
2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3aa)



Pale yellow solid, 51.1 mg, 82% yield, melting point: 122.3 – 124.1 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.32

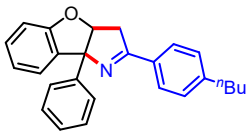
– 7.27 (m, 2H), 7.25 – 7.20 (m, 1H), 6.98 – 6.92 (m, 1H), 6.87 (dd, *J* = 8.1, 1.0 Hz, 1H), 5.31 (dd, *J* = 6.0, 1.4 Hz, 1H), 3.56 – 3.39 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 160.2, 142.7, 133.8, 131.2, 130.8, 129.7, 128.7, 128.6, 128.4, 127.5, 126.7, 126.0, 121.5, 109.9, 92.0, 91.9, 43.3. **HRMS (ESI)** calculated for $C_{22}H_{18}NO^+$, $[M+H]^+$: 312.1383; found: 312.1377.

8b-phenyl-2-(p-tolyl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ab)



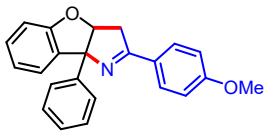
Colorless oil, 55.3 mg, 85% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.84 (d, *J* = 8.0 Hz, 2H), 7.36 – 7.31 (m, 4H), 7.31 – 7.27 (m, 2H), 7.25 – 7.19 (m, 3H), 6.96 – 6.91 (m, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.28 (dd, *J* = 5.9, 1.2 Hz, 1H), 3.52 – 3.35 (m, 2H), 2.39 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.0, 160.2, 142.8, 141.6, 131.1, 130.9, 129.6, 129.4, 128.5, 128.4, 127.5, 126.7, 126.0, 121.4, 109.9, 92.0, 91.9, 43.2, 21.7. **HRMS (ESI)** calculated for $C_{23}H_{20}NO^+$, $[M+H]^+$: 326.1539; found: 326.1542.

2-(4-butylphenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ac)



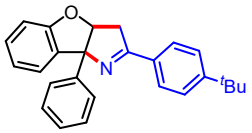
Colorless oil, 58.8 mg, 80% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.87 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 4.3 Hz, 4H), 7.30 – 7.27 (m, 2H), 7.25 (d, *J* = 9.0 Hz, 2H), 7.22 – 7.19 (m, 1H), 6.97 – 6.90 (m, 1H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.29 (dd, *J* = 6.0, 1.4 Hz, 1H), 3.53 – 3.37 (m, 2H), 2.67 – 2.62 (m, 2H), 1.66 – 1.61 (m, 2H), 1.35 – 1.30 (m, 4H), 0.89 (q, *J* = 3.4 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.1, 160.2, 146.6, 142.9, 131.4, 130.9, 129.6, 128.8, 128.6, 128.5, 128.4, 127.5, 126.8, 126.0, 121.4, 109.9, 92.0, 43.2, 36.0, 31.5, 31.1, 22.7, 14.2. **HRMS (ESI)** calculated for $C_{26}H_{26}NO^+$, $[M+H]^+$: 368.2009; found: 368.2005.

2-(4-methoxyphenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ad)



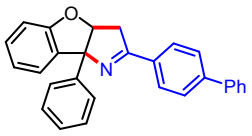
Yellow solid, 53.9 mg, 79% yield, melting point: 156.7 – 158.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 (d, *J* = 8.8 Hz, 2H), 7.33 (d, *J* = 3.9 Hz, 4H), 7.31 – 7.26 (m, 2H), 7.24 – 7.19 (m, 1H), 6.97 – 6.91 (m, 3H), 6.85 (d, *J* = 8.0 Hz, 1H), 5.28 (dd, *J* = 6.0, 1.4 Hz, 1H), 3.85 (s, 3H), 3.50 – 3.35 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.4, 162.0, 160.2, 142.9, 131.0, 130.1, 129.6, 128.5, 127.5, 126.8, 126.6, 126.0, 121.5, 114.0, 109.9, 92.0, 91.8, 55.5, 43.1. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1484.

2-(4-(tert-butyl)phenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ae)



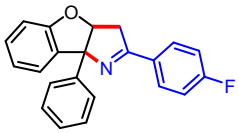
Colorless oil, 61.0 mg, 83% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.90 (d, *J* = 8.5 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 4.1 Hz, 4H), 7.30 – 7.26 (m, 2H), 7.24 – 7.18 (m, 1H), 6.96 – 6.90 (m, 1H), 6.84 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.28 (dd, *J* = 6.0, 1.3 Hz, 1H), 3.55 – 3.36 (m, 2H), 1.34 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.0, 160.3, 154.7, 142.8, 131.1, 130.9, 129.6, 128.5, 128.2, 127.5, 126.8, 126.0, 125.6, 121.4, 109.9, 92.0, 92.0, 43.2, 35.1, 31.3. **HRMS (ESI)** calculated for $C_{26}H_{26}NO^+$, $[M+H]^+$: 368.2009; found: 368.2006.

2-([1,1'-biphenyl]-4-yl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3af)



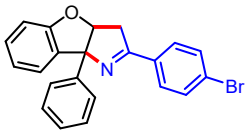
Yellow solid, 67.4 mg, 87% yield, melting point: 178.8 – 179.2 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.04 (d, *J* = 8.0 Hz, 2H), 7.72 – 7.63 (m, 4H), 7.48 (t, *J* = 7.5 Hz, 2H), 7.43 – 7.35 (m, 5H), 7.34 – 7.29 (m, 2H), 7.23 (d, *J* = 7.5 Hz, 1H), 7.01 – 6.84 (m, 2H), 5.33 (d, *J* = 5.9 Hz, 1H), 3.62 – 3.40 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.8, 160.2, 143.9, 142.7, 140.4, 132.7, 130.8, 129.7, 129.0, 128.9, 128.6, 128.0, 127.5, 127.3, 127.3, 126.7, 126.0, 121.5, 110.0, 92.0, 91.9, 43.3. **HRMS (ESI)** calculated for $C_{28}H_{22}NO^+$, $[M+H]^+$: 388.1696; found: 388.1693.

2-(4-fluorophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ag)



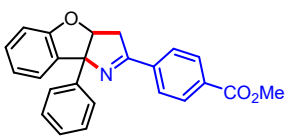
White solid, 49.4 mg, 75% yield, melting point: 134.7 – 136.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 – 7.91 (m, 2H), 7.39 – 7.26 (m, 6H), 7.26 – 7.20 (m, 1H), 7.12 (t, *J* = 8.6 Hz, 2H), 6.95 (t, *J* = 7.5 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.31 (dd, *J* = 5.8, 1.6 Hz, 1H), 3.51 – 3.37 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 164.7 (d, *J* = 251.6 Hz), 160.1, 142.6, 130.7, 130.5, 130.5, 130.1 (d, *J* = 3.3 Hz), 129.7, 128.6, 127.6, 126.7, 126.0, 121.5, 115.9, 115.6, 110.0, 92.0, 91.9, 43.3. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -108.72. **HRMS (ESI)** calculated for $C_{22}H_{17}FNO^+$, $[M+H]^+$: 330.1289; found: 330.1287.

2-(4-bromophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ah)



Yellow solid, 54.6 mg, 70% yield, melting point: 176.4 – 1176.8 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.5 Hz, 2H), 7.38 – 7.26 (m, 6H), 7.23 (t, *J* = 7.9 Hz, 1H), 6.94 (t, *J* = 7.4 Hz, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.31 (dd, *J* = 5.8, 1.7 Hz, 1H), 3.50 – 3.35 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.2, 160.1, 142.5, 132.7, 131.9, 130.6, 129.9, 129.8, 128.6, 127.6, 126.6, 126.0, 125.8, 121.6, 110.0, 92.1, 91.8, 43.2. **HRMS (ESI)** calculated for $C_{22}H_{17}BrNO^+$, $[M+H]^+$: 390.0448; found: 390.0445.

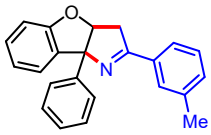
methyl 4-(8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrol-2-yl)benzoate (3ai)



White solid, 54.7 mg, 74% yield, melting point: 145.2 – 147.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.14 – 8.08 (m, 2H), 8.05 – 8.00 (m, 2H), 7.38 – 7.28 (m, 6H), 7.26 – 7.21 (m, 1H), 6.98 – 6.93 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.34 (dd, *J* = 5.7, 1.6 Hz, 1H), 3.95 (s, 3H), 3.55

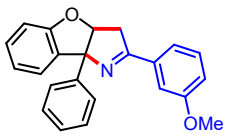
– 3.41 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.4, 166.6, 160.1, 142.4, 137.7, 132.3, 130.5, 129.9, 129.8, 128.6, 128.3, 127.6, 126.6, 126.0, 121.6, 110.0, 92.3, 91.7, 52.5, 43.4. **HRMS (ESI)** calculated for $C_{24}H_{20}NO_3^+$, $[M+H]^+$: 370.1438; found: 370.1436.

8b-phenyl-2-(m-tolyl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3aj)



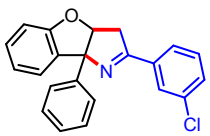
Yellow solid, 48.8 mg, 75% yield, melting point: 160.4 – 162.1 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 (s, 1H), 7.70 (d, *J* = 7.4 Hz, 1H), 7.37 – 7.28 (m, 8H), 7.25 – 7.20 (m, 1H), 6.98 – 6.92 (m, 1H), 6.86 (dd, *J* = 8.1, 0.9 Hz, 1H), 5.29 (dd, *J* = 6.0, 1.4 Hz, 1H), 3.53 – 3.39 (m, 2H), 2.40 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.4, 160.3, 142.7, 138.5, 133.8, 132.1, 130.8, 129.7, 128.8, 128.6, 128.6, 127.5, 126.8, 126.1, 125.7, 121.5, 109.9, 92.0, 91.9, 43.3, 21.5. **HRMS (ESI)** calculated for $C_{23}H_{20}NO^+$, $[M+H]^+$: 326.1539; found: 326.1542.

2-(3-methoxyphenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ak)



Colorless oil, 52.6 mg, 77% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.58 (s, 1H), 7.47 (dd, *J* = 7.7, 1.3 Hz, 1H), 7.38 – 7.29 (m, 7H), 7.25 – 7.21 (m, 1H), 7.05 – 7.01 (m, 1H), 6.98 – 6.93 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.29 (dd, *J* = 5.9, 1.5 Hz, 1H), 3.86 (s, 3H), 3.52 – 3.39 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.1, 160.3, 159.8, 142.6, 135.2, 130.7, 129.7, 129.7, 128.6, 127.6, 126.7, 126.1, 121.5, 121.1, 117.6, 112.8, 110.0, 92.0, 91.9, 55.6, 43.4. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1484.

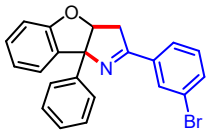
2-(3-chlorophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3al)



White solid, 56.7 mg, 82% yield, melting point: 159.5 – 161.2 ℃. **^{1}H NMR (400 MHz,**

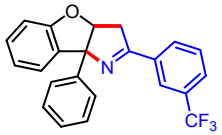
Chloroform-*d*) δ 8.01 (s, 1H), 7.79 (dd, *J* = 7.6, 1.4 Hz, 1H), 7.48 – 7.42 (m, 1H), 7.40 – 7.27 (m, 7H), 7.26 – 7.20 (m, 1H), 6.99 – 6.92 (m, 1H), 6.87 (d, *J* = 8.1 Hz, 1H), 5.33 (dd, *J* = 5.8, 1.6 Hz, 1H), 3.52 – 3.35 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.0, 160.1, 142.4, 135.5, 134.8, 131.2, 130.5, 129.9, 129.8, 128.6, 128.3, 127.6, 126.6, 126.5, 126.0, 121.6, 110.0, 92.1, 91.7, 43.3. **HRMS (ESI)** calculated for $C_{22}H_{17}ClNO^+$, $[M+H]^+$: 346.0993; found: 346.0990.

2-(3-bromophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3am)



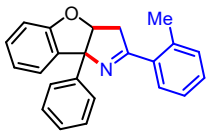
Pale yellow solid, 66.4 mg, 85% yield, melting point: 164.9 – 165.9 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.17 (s, 1H), 7.83 (d, *J* = 7.8 Hz, 1H), 7.60 (dd, *J* = 8.3, 2.0 Hz, 1H), 7.39 – 7.28 (m, 7H), 7.26 – 7.21 (m, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.32 (dd, *J* = 5.8, 1.6 Hz, 1H), 3.51 – 3.36 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 160.1, 142.4, 135.8, 134.1, 131.2, 130.5, 130.2, 129.8, 128.6, 127.6, 127.0, 126.6, 126.0, 123.0, 121.6, 110.0, 92.1, 91.7, 43.2. **HRMS (ESI)** calculated for $C_{22}H_{17}BrNO^+$, $[M+H]^+$: 390.0488; found: 390.0495.

8b-phenyl-2-(3-(trifluoromethyl)phenyl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3an)



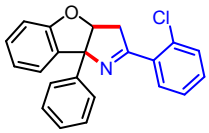
Colorless oil, 60.7 mg, 80% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.24 (s, 1H), 8.13 (d, *J* = 7.9 Hz, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.8 Hz, 1H), 7.40 – 7.29 (m, 6H), 7.26 – 7.23 (m, 1H), 6.97 (t, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 8.1 Hz, 1H), 5.35 (d, *J* = 5.7 Hz, 1H), 3.57 – 3.41 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 160.1, 142.3, 134.6, 131.6, 131.2 (q, *J* = 32.7 Hz), 130.5, 129.9, 129.2, 128.7, 127.7 (q, *J* = 4.8 Hz), 127.7, 126.6, 126.0, 125.1 (q, *J* = 3.8 Hz), 124.0 (d, *J* = 272.5 Hz), 121.6, 110.1, 92.2, 91.7, 43.3. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.59. **HRMS (ESI)** calculated for $C_{23}H_{17}F_3NO^+$, $[M+H]^+$: 380.1257; found: 380.1254.

8b-phenyl-2-(o-tolyl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ao)



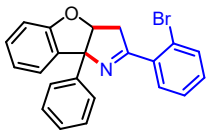
White solid, 50.8 mg, 78% yield, melting point: 158.6 – 159.2 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.50 (d, *J* = 7.8 Hz, 1H), 7.43 – 7.35 (m, 4H), 7.33 – 7.28 (m, 2H), 7.26 – 7.20 (m, 4H), 6.95 – 6.85 (m, 2H), 5.31 (dd, *J* = 4.3, 3.2 Hz, 1H), 3.48 – 3.42 (m, 2H), 2.57 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.8, 160.0, 142.9, 138.1, 133.8, 131.6, 131.3, 129.8, 129.5, 129.4, 128.6, 127.5, 126.7, 125.9, 125.8, 121.4, 109.9, 92.7, 91.4, 46.4, 22.3. **HRMS (ESI)** calculated for $C_{23}H_{20}NO^+$, $[M+H]^+$: 326.1539; found: 326.1538.

2-(2-chlorophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ap)



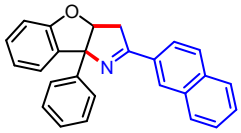
Colorless oil, 51.9 mg, 75% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.69 (dd, *J* = 7.6, 1.9 Hz, 1H), 7.44 – 7.35 (m, 6H), 7.34 – 7.26 (m, 3H), 7.26 – 7.22 (m, 1H), 6.98 – 6.92 (m, 1H), 6.90 (d, *J* = 8.0 Hz, 1H), 5.31 (dd, *J* = 5.9, 1.3 Hz, 1H), 3.68 – 3.51 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.2, 160.3, 142.0, 134.3, 132.7, 131.2, 131.0, 130.5, 130.4, 129.8, 128.6, 127.6, 127.0, 126.8, 126.1, 121.5, 110.0, 92.1, 91.6, 46.4. **HRMS (ESI)** calculated for $C_{22}H_{17}ClNO^+$, $[M+H]^+$: 346.0993; found: 346.0992.

2-(2-bromophenyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3aq)



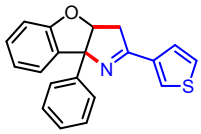
Colorless oil, 54.6 mg, 70% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.62 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.45 – 7.31 (m, 6H), 7.29 – 7.24 (m, 3H), 6.99 – 6.87 (m, 2H), 5.32 (d, *J* = 6.1 Hz, 1H), 3.66 (dd, *J* = 18.9, 6.1 Hz, 1H), 3.50 (d, *J* = 18.9 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.5, 160.3, 142.1, 136.8, 133.5, 131.0, 130.6, 130.5, 129.8, 128.6, 127.6, 127.6, 126.8, 126.1, 121.5, 121.1, 110.0, 92.1, 92.0, 46.5. **HRMS (ESI)** calculated for $C_{22}H_{17}BrNO^+$, $[M+H]^+$: 390.0488; found: 390.0493.

2-(naphthalen-2-yl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ar)



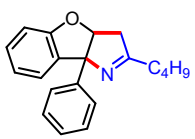
Pale yellow solid, 52.1 mg, 72% yield, melting point: 168.0 – 169.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.24 (s, 1H), 8.19 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.91 – 7.83 (m, 3H), 7.55 – 7.48 (m, 2H), 7.38 – 7.27 (m, 6H), 7.21 (dd, *J* = 7.7, 1.5 Hz, 1H), 6.99 – 6.91 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.34 (dd, *J* = 6.1, 1.3 Hz, 1H), 3.66 – 3.49 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 160.2, 142.7, 134.8, 133.0, 131.4, 130.8, 129.7, 129.1, 128.9, 128.6, 128.4, 127.9, 127.6, 126.7, 126.7, 126.1, 125.0, 121.5, 110.0, 92.1, 92.0, 43.3. **HRMS (ESI)** calculated for $C_{26}H_{20}NO^+$, $[M+H]^+$: 362.1539; found: 362.1534.

8b-phenyl-2-(thiophen-3-yl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3as)



Pale yellow solid, 28.6 mg, 45% yield, melting point: 138.9 – 139.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.76 (dd, *J* = 2.9, 1.3 Hz, 1H), 7.70 (dd, *J* = 5.0, 1.3 Hz, 1H), 7.38 – 7.26 (m, 7H), 7.25 – 7.19 (m, 1H), 6.94 (t, *J* = 7.5 Hz, 1H), 6.85 (d, *J* = 8.1 Hz, 1H), 5.26 (dd, *J* = 5.1, 2.3 Hz, 1H), 3.47 – 3.36 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 166.5, 160.2, 142.6, 137.2, 130.7, 129.7, 128.6, 128.5, 127.5, 127.2, 126.7, 126.5, 126.0, 121.5, 110.0, 92.0, 91.8, 44.0. **HRMS (ESI)** calculated for $C_{20}H_{16}NOS^+$, $[M+H]^+$: 318.0947; found: 318.0941.

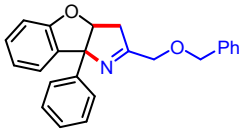
2-butyl-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3at)



Colorless oil, 51.9 mg, 89% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.28 – 7.18 (m, 5H), 7.16 – 7.09 (m, 2H), 6.86 – 6.80 (m, 1H), 6.77 (d, *J* = 8.0 Hz, 1H), 5.07 (dd, *J* = 5.8, 1.6 Hz, 1H), 2.99 – 2.85 (m, 2H), 2.50 – 2.36 (m, 2H), 1.63 – 1.55 (m, 2H), 1.36 – 1.27 (m, 2H), 0.86 (t, *J* = 7.3 Hz,

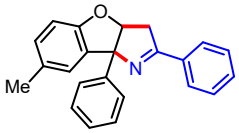
3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 177.2, 160.1, 142.6, 131.0, 129.5, 128.5, 127.4, 126.6, 125.8, 121.4, 109.8, 92.1, 91.5, 45.1, 33.8, 28.8, 22.7, 14.0. **HRMS (ESI)** calculated for $C_{20}H_{22}NO^+$, $[M+H]^+$: 292.1696; found: 292.1692.

2-((benzyloxy)methyl)-8b-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3au)



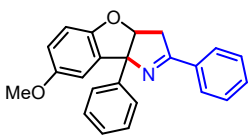
Colorless oil, 47.6 mg, 67% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.37 – 7.27 (m, 10H), 7.24 – 7.17 (m, 2H), 6.94 – 6.89 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.20 (dd, *J* = 4.1, 3.3 Hz, 1H), 4.58 (d, *J* = 1.5 Hz, 2H), 4.40 (q, *J* = 13.8 Hz, 2H), 3.15 (d, *J* = 3.7 Hz, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.9, 160.2, 142.2, 137.5, 130.5, 129.7, 128.6, 128.6, 128.1, 128.1, 127.6, 126.6, 125.9, 121.5, 110.0, 92.0, 91.4, 73.4, 69.9, 43.9. **HRMS (ESI)** calculated for $C_{24}H_{22}NO_2^+$, $[M+H]^+$: 356.1645; found: 356.1644.

7-methyl-2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3ba)



Colorless oil, 48.8 mg, 75% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (dd, *J* = 8.0, 1.8 Hz, 2H), 7.49 – 7.41 (m, 3H), 7.35 (d, *J* = 4.3 Hz, 4H), 7.32 – 7.27 (m, 1H), 7.08 (s, 1H), 7.01 (dd, *J* = 8.2, 1.9 Hz, 1H), 6.75 (d, *J* = 8.1 Hz, 1H), 5.30 (dd, *J* = 6.1, 1.3 Hz, 1H), 3.54 – 3.36 (m, 2H), 2.26 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 158.1, 142.9, 133.9, 131.2, 130.8, 130.8, 130.2, 128.7, 128.5, 128.4, 127.5, 126.7, 126.3, 109.5, 92.1, 43.3, 20.9. **HRMS (ESI)** calculated for $C_{23}H_{20}NO^+$, $[M+H]^+$: 326.1539; found: 326.1536.

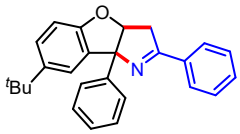
7-methoxy-2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bb)



Colorless oil, 58.0 mg, 85% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 (dd, *J* = 7.4, 2.1 Hz, 2H), 7.51 – 7.43 (m, 3H), 7.36 (d, *J* = 4.2 Hz, 4H), 7.34 – 7.28 (m, 1H), 6.87 (d, *J* = 2.5 Hz, 1H),

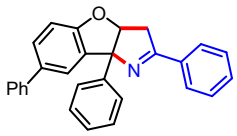
6.80 (d, *J* = 2.4 Hz, 2H), 5.34 – 5.28 (m, 1H), 3.73 (s, 3H), 3.55 – 3.37 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.4, 154.8, 154.3, 142.6, 133.8, 131.3, 131.2, 128.7, 128.6, 128.4, 127.5, 126.7, 116.1, 110.7, 110.1, 92.3, 92.2, 56.1, 43.3. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1492.

7-(tert-butyl)-2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bc)



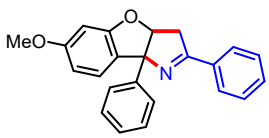
Pale yellow solid, 61.0 mg, 83% yield, melting point: 176.7 – 178.1 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (d, *J* = 7.5 Hz, 2H), 7.48 – 7.40 (m, 3H), 7.37 – 7.24 (m, 7H), 6.82 – 6.75 (m, 1H), 5.24 (dd, *J* = 5.9, 1.7 Hz, 1H), 3.53 – 3.36 (m, 2H), 1.26 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 158.2, 144.5, 142.8, 133.9, 131.2, 130.0, 128.6, 128.6, 128.4, 127.5, 126.8, 126.7, 122.9, 109.1, 92.3, 92.1, 43.3, 34.6, 31.8. **HRMS (ESI)** calculated for $C_{26}H_{26}NO^+$, $[M+H]^+$: 368.2009; found: 368.2006.

2,7,8b-triphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bd)



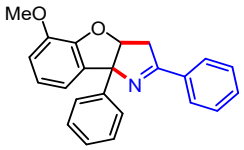
Colorless oil, 62.0 mg, 80% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.56 – 7.51 (m, 3H), 7.51 – 7.44 (m, 4H), 7.37 (q, *J* = 7.6 Hz, 6H), 7.33 – 7.26 (m, 2H), 6.94 (d, *J* = 8.3 Hz, 1H), 5.37 (dd, *J* = 6.1, 1.3 Hz, 1H), 3.60 – 3.40 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 159.9, 142.5, 141.1, 135.0, 133.8, 131.5, 131.3, 128.8, 128.7, 128.6, 128.4, 127.6, 127.0, 126.8, 126.7, 124.8, 110.1, 92.5, 92.0, 43.2. **HRMS (ESI)** calculated for $C_{28}H_{22}NO^+$, $[M+H]^+$: 388.1696; found: 388.1695.

6-methoxy-2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3be)



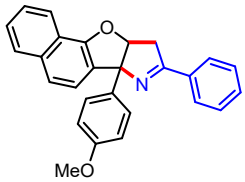
Colorless oil, 56.0 mg, 82% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.97 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.50 – 7.42 (m, 3H), 7.35 (d, *J* = 4.4 Hz, 4H), 7.32 – 7.27 (m, 1H), 7.18 (d, *J* = 8.3 Hz, 1H), 6.52 (dd, *J* = 8.3, 2.3 Hz, 1H), 6.44 (d, *J* = 2.3 Hz, 1H), 5.32 (dd, *J* = 6.0, 1.3 Hz, 1H), 3.79 (s, 3H), 3.54 – 3.37 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.7, 161.6, 161.6, 142.8, 133.9, 131.2, 128.6, 128.5, 128.3, 127.5, 126.7, 126.1, 123.1, 107.5, 96.1, 92.8, 91.6, 55.6, 43.1. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1485.

5-methoxy-2,8b-diphenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bf)



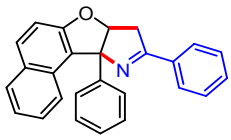
Colorless oil, 55.3 mg, 81% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.50 – 7.41 (m, 3H), 7.34 (d, *J* = 4.3 Hz, 4H), 7.32 – 7.27 (m, 1H), 6.94 – 6.89 (m, 2H), 6.83 (p, *J* = 3.7 Hz, 1H), 5.38 (dd, *J* = 6.2, 1.1 Hz, 1H), 3.91 (s, 3H), 3.61 (dd, *J* = 18.4, 1.2 Hz, 1H), 3.42 (dd, *J* = 18.4, 6.2 Hz, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 148.7, 144.6, 142.5, 133.8, 131.8, 131.2, 128.6, 128.6, 128.4, 127.5, 126.7, 122.1, 117.9, 111.9, 92.6, 92.5, 56.0, 43.2. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1486.

6b-(4-methoxyphenyl)-8-phenyl-6b,9a-dihydro-9*H*-naphtho[2',1':4,5]furo[3,2-*b*]pyrrole (3bg)



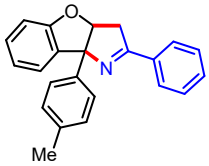
Colorless oil, 53.2 mg, 68% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.05 – 7.99 (m, 1H), 7.99 – 7.93 (m, 2H), 7.83 (dd, *J* = 6.2, 3.3 Hz, 1H), 7.51 – 7.39 (m, 7H), 7.28 (d, *J* = 8.8 Hz, 2H), 6.89 (d, *J* = 8.7 Hz, 2H), 5.47 (dd, *J* = 6.2, 1.3 Hz, 1H), 3.81 (s, 3H), 3.67 – 3.49 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.8, 159.0, 155.9, 135.1, 134.9, 134.0, 131.1, 128.6, 128.4, 128.1, 127.9, 126.5, 125.6, 124.1, 123.0, 121.8, 121.4, 120.8, 113.9, 92.7, 92.6, 55.4, 43.4. **HRMS (ESI)** calculated for $C_{27}H_{22}NO_2^+$, $[M+H]^+$: 392.1465; found: 392.1460.

9,10a-diphenyl-7a,10a-dihydro-8*H*-naphtho[1',2':4,5]furo[3,2-*b*]pyrrole (3bh)



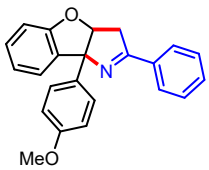
White solid, 57.1 mg, 79% yield, melting point: 221.8 – 223.7 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.99 – 7.94 (m, 2H), 7.79 – 7.70 (m, 3H), 7.41 (q, *J* = 6.9, 6.3 Hz, 3H), 7.36 – 7.23 (m, 7H), 7.14 (d, *J* = 8.8 Hz, 1H), 5.37 (dd, *J* = 6.1, 2.3 Hz, 1H), 3.59 – 3.44 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.4, 157.9, 143.6, 134.0, 131.3, 131.1, 130.5, 130.2, 128.7, 128.6, 128.6, 128.4, 127.4, 127.0, 126.4, 123.8, 123.2, 121.3, 112.3, 93.1, 92.9, 43.6. **HRMS (ESI)** calculated for $C_{26}H_{20}NO^+$, $[M+H]^+$: 362.1539; found: 362.1534.

2-phenyl-8b-(p-tolyl)-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bi)



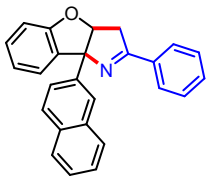
Colorless oil, 46.9 mg, 72% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.00 – 7.93 (m, 2H), 7.50 – 7.42 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.25 – 7.15 (m, 5H), 6.97 – 6.92 (m, 1H), 6.86 (d, *J* = 8.1 Hz, 1H), 5.29 (dd, *J* = 5.9, 1.4 Hz, 1H), 3.55 – 3.37 (m, 2H), 2.36 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.0, 160.2, 139.7, 137.2, 133.9, 131.2, 130.9, 129.6, 129.2, 128.7, 128.4, 126.6, 126.0, 121.4, 109.9, 91.9, 91.8, 43.2, 21.2. **HRMS (ESI)** calculated for $C_{27}H_{22}NO_2^+$, $[M+H]^+$: 326.1539; found: 362.1536.

8b-(4-methoxyphenyl)-2-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bj)



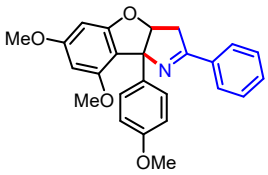
Colorless oil, 44.4 mg, 65% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (dd, *J* = 8.0, 1.7 Hz, 2H), 7.51 – 7.41 (m, 3H), 7.32 – 7.28 (m, 1H), 7.28 – 7.17 (m, 4H), 6.97 – 6.91 (m, 1H), 6.86 (dd, *J* = 10.0, 8.3 Hz, 3H), 5.26 (dd, *J* = 5.9, 1.4 Hz, 1H), 3.80 (s, 3H), 3.53 – 3.38 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.9, 160.2, 159.0, 134.8, 133.9, 131.2, 130.9, 129.6, 128.7, 128.4, 127.9, 126.0, 121.4, 113.9, 109.9, 91.8, 91.6, 55.4, 43.2. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_2^+$, $[M+H]^+$: 342.1489; found: 342.1485.

8b-(naphthalen-2-yl)-2-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bk)



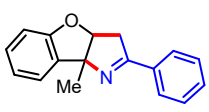
Colorless oil, 54.2 mg, 75% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.08 – 8.00 (m, 2H), 7.90 (s, 1H), 7.88 – 7.79 (m, 3H), 7.54 – 7.46 (m, 5H), 7.44 – 7.37 (m, 1H), 7.31 (dd, *J* = 7.5, 1.6 Hz, 1H), 7.28 (d, *J* = 7.7 Hz, 1H), 7.01 – 6.90 (m, 2H), 5.42 (d, *J* = 5.9 Hz, 1H), 3.61 – 3.42 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.3, 160.2, 140.0, 133.9, 133.2, 132.7, 131.3, 130.9, 129.8, 128.7, 128.4, 128.3, 127.7, 126.4, 126.2, 126.0, 125.3, 125.0, 121.6, 110.0, 92.2, 91.7, 43.3. **HRMS (ESI)** calculated for $C_{26}H_{20}NO^+$, $[M+H]^+$: 362.1539; found: 362.1535.

6,8-dimethoxy-8b-(4-methoxyphenyl)-2-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bl)



Pale yellow solid, 61.0 mg, 76% yield, melting point: 162.7 – 164.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.95 (dd, *J* = 7.9, 1.8 Hz, 2H), 7.50 – 7.40 (m, 3H), 7.26 – 7.21 (m, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.82 (s, 1H), 6.47 (s, 1H), 5.21 (dd, *J* = 5.9, 1.5 Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 3.79 (s, 3H), 3.50 – 3.35 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.8, 159.0, 154.5, 150.7, 144.3, 134.8, 133.9, 131.1, 128.6, 128.3, 127.8, 120.6, 113.9, 108.5, 94.7, 92.5, 92.1, 56.7, 56.2, 55.4, 43.1. **HRMS (ESI)** calculated for $C_{25}H_{24}NO_4^+$, $[M+H]^+$: 402.1700; found: 402.1699.

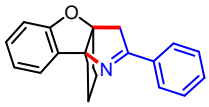
8b-methyl-2-phenyl-3a,8b-dihydro-3*H*-benzofuro[3,2-*b*]pyrrole (3bm)



Colorless oil, 38.9 mg, 78% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.81 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.51 (dd, *J* = 7.3, 1.4 Hz, 1H), 7.45 – 7.36 (m, 3H), 7.22 – 7.16 (m, 1H), 6.99 – 6.93 (m, 1H),

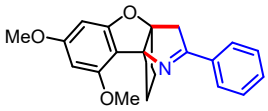
6.78 (d, *J* = 8.1 Hz, 1H), 5.09 (dd, *J* = 4.9, 2.6 Hz, 1H), 3.53 – 3.41 (m, 2H), 1.74 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.0, 159.5, 134.0, 130.9, 130.8, 129.4, 128.6, 128.1, 124.3, 121.1, 109.9, 89.5, 85.8, 43.3, 23.6. **HRMS (ESI)** calculated for $C_{17}H_{15}NO^+$, $[M+H]^+$: 250.1226; found: 250.1223.

11-phenyl-6,7,8,9-tetrahydro-9a,5a-(azenoethan[2]yl[1]ylidene)dibenzo[b,d]furan (3bn)



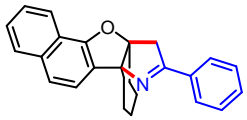
White solid, 40.5 mg, 70% yield, melting point: 168.2 – 169.6 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 – 7.77 (m, 2H), 7.54 – 7.48 (m, 1H), 7.44 – 7.35 (m, 3H), 7.25 – 7.16 (m, 1H), 6.98 (t, *J* = 7.4 Hz, 1H), 6.77 (d, *J* = 8.1 Hz, 1H), 3.58 (d, *J* = 17.8 Hz, 1H), 3.26 (d, *J* = 17.8 Hz, 1H), 2.83 – 2.73 (m, 1H), 2.40 – 2.29 (m, 1H), 1.77 – 1.62 (m, 3H), 1.56 – 1.44 (m, 1H), 1.31 – 1.19 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.9, 159.4, 134.2, 130.8, 129.6, 129.6, 128.5, 128.0, 124.2, 121.0, 110.3, 94.6, 84.0, 46.2, 32.0, 31.6, 20.8, 20.0. **HRMS (ESI)** calculated for $C_{20}H_{20}NO^+$, $[M+H]^+$: 290.1539; found: 290.1535.

1,3-dimethoxy-11-phenyl-6,7,8,9-tetrahydro-9a,5a-(azenoethan[2]yl[1]ylidene)-dibenzo[b,d]furan (3bo)



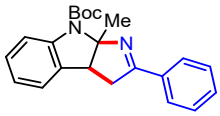
Pale yellow solid, 49.6 mg, 71% yield, melting point: 172.7 – 174.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.86 – 7.79 (m, 2H), 7.42 – 7.34 (m, 3H), 6.02 (dd, *J* = 29.8, 2.0 Hz, 2H), 3.87 (s, 3H), 3.74 (s, 3H), 3.48 (d, *J* = 17.8 Hz, 1H), 3.20 (d, *J* = 17.8 Hz, 1H), 2.29 – 2.20 (m, 1H), 1.81 – 1.60 (m, 4H), 1.43 – 1.27 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.4, 162.7, 161.7, 158.4, 134.5, 130.6, 128.4, 128.1, 108.3, 95.2, 91.9, 88.8, 85.0, 55.7, 55.6, 46.0, 31.4, 30.6, 20.4, 19.8. **HRMS (ESI)** calculated for $C_{22}H_{24}NO_3^+$, $[M+H]^+$: 350.1751; found: 350.1746.

14-phenyl-8,9,10,11-tetrahydro-7*H*-6b,11a-(azenoethan[2]yl[1]ylidene)cyclohepta[b]naphtho[2,1-*d*]furan (3bp)



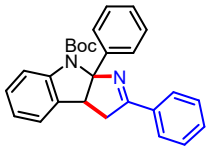
Colorless oil, 52.3 mg, 74% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.06 – 7.99 (m, 1H), 7.86 – 7.80 (m, 1H), 7.80 – 7.75 (m, 2H), 7.52 (d, *J* = 8.3 Hz, 1H), 7.48 – 7.42 (m, 3H), 7.41 – 7.34 (m, 3H), 3.70 (d, *J* = 18.7 Hz, 1H), 3.46 (d, *J* = 18.6 Hz, 1H), 2.72 – 2.47 (m, 2H), 2.15 (t, *J* = 14.6, 10.5 Hz, 1H), 2.06 – 1.99 (m, 1H), 1.71 – 1.63 (m, 1H), 1.61 – 1.49 (m, 3H), 1.47 – 1.31 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.9, 154.0, 134.8, 134.2, 130.7, 128.5, 128.0, 127.8, 126.2, 125.2, 124.1, 122.2, 121.9, 120.7, 120.6, 99.3, 91.7, 52.0, 37.5, 36.1, 31.1, 25.0, 24.2. **HRMS (ESI)** calculated for $C_{22}H_{24}NO_3^+$, $[M+H]^+$: 354.1852; found: 354.1847.

tert-butyl 8a-methyl-2-phenyl-3a,8a-dihydropyrrolo[2,3-*b*]indole-8(3*H*)-carboxylate (5aa)



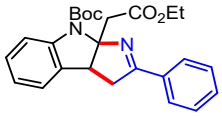
Colorless oil, 45.3 mg, 65% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.88 – 7.84 (m, 2H), 7.55 – 7.33 (m, 4H), 7.21 – 7.11 (m, 2H), 6.99 – 6.93 (m, 1H), 3.74 (d, *J* = 8.7 Hz, 1H), 3.54 (dd, *J* = 17.1, 8.8 Hz, 1H), 3.22 (d, *J* = 17.1, 2.0 Hz, 1H), 1.94 (s, 3H), 1.66 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 152.9, 142.6, 134.0, 131.8, 131.1, 128.5, 128.4, 128.3, 124.3, 122.7, 116.0, 100.3, 81.4, 50.0, 42.7, 28.7, 26.1. **HRMS (ESI)** calculated for $C_{22}H_{25}N_2O_2^+$, $[M+H]^+$: 349.1911; found: 349.1913.

tert-butyl 2,8a-diphenyl-3a,8a-dihydropyrrolo[2,3-*b*]indole-8(3*H*)-carboxylate (5ab)



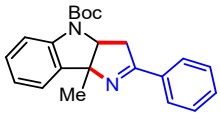
Pale yellow solid, 55.8 mg, 68% yield, melting point: 166.5 – 167.8 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 (d, *J* = 6.8 Hz, 3H), 7.52 – 7.43 (m, 3H), 7.37 – 7.26 (m, 6H), 7.16 (d, *J* = 7.4 Hz, 1H), 7.03 (t, *J* = 7.4 Hz, 1H), 3.97 (d, *J* = 8.5 Hz, 1H), 3.44 (dd, *J* = 17.1, 8.6 Hz, 1H), 3.28 (dd, *J* = 17.2, 2.0 Hz, 1H), 1.27 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.2, 152.5, 145.2, 142.8, 133.8, 131.6, 131.4, 128.6, 128.5, 128.2, 127.1, 124.8, 124.3, 122.9, 115.6, 102.8, 80.9, 53.0, 42.7, 28.1. **HRMS (ESI)** calculated for $C_{27}H_{27}N_2O_2^+$, $[M+H]^+$: 411.2067; found: 411.2069.

tert-butyl 8a-(2-ethoxy-2-oxoethyl)-2-phenyl-3a,8a-dihydropyrrolo[2,3-*b*]indole-8(3*H*)-carboxylate (5ac)



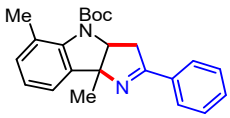
Colorless oil, 50.5 mg, 60% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.98 – 7.66 (m, 3H), 7.45 – 7.35 (m, 3H), 7.20 – 7.12 (m, 2H), 6.96 (t, *J* = 7.4 Hz, 1H), 4.23 (d, *J* = 9.2, 2.3 Hz, 1H), 4.05 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 15.5 Hz, 1H), 3.64 (dd, *J* = 17.2, 9.2 Hz, 1H), 3.21 (dd, *J* = 17.3, 2.4 Hz, 2H), 1.66 (s, 9H), 1.11 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.6, 170.2, 152.4, 142.3, 133.7, 132.0, 131.3, 128.5, 128.4, 128.3, 124.3, 122.9, 115.9, 100.3, 81.7, 60.5, 47.5, 44.0, 42.4, 28.6, 14.2. **HRMS (ESI)** calculated for $C_{25}H_{29}N_2O_4^+$, $[M+H]^+$: 421.2122; found: 421.2125

tert-butyl 8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ad)



Pale yellow solid, 62.7 mg, 90% yield, melting point: 168.9 – 169.7 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.96 – 7.44 (m, 4H), 7.44 – 7.34 (m, 3H), 7.26 – 7.20 (m, 1H), 7.06 (t, *J* = 7.5 Hz, 1H), 4.75 – 4.51 (m, 1H), 3.68 (s, 1H), 3.48 – 3.21 (m, 1H), 1.75 (s, 3H), 1.62 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.5, 151.7, 141.8, 135.4, 134.0, 130.8, 128.9, 128.5, 128.0, 124.0, 123.0, 115.0, 83.9, 83.0, 82.2, 81.1, 67.6, 45.0, 28.6, 26.3. **HRMS (ESI)** calculated for $C_{22}H_{25}N_2O_2^+$， $[M+H]^+$: 349.1911; found: 349.1910.

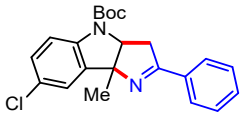
tert-butyl 5,8b-dimethyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ae)



Colorless oil, 61.6 mg, 85% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.78 (d, 2H), 7.43 – 7.34 (m, 3H), 7.30 (d, *J* = 6.5, 2.3 Hz, 1H), 7.08 – 7.01 (m, 2H), 4.72 (dd, *J* = 9.1, 4.9 Hz, 1H), 3.70 (dd, *J* = 18.2, 9.1 Hz, 1H), 3.09 (dd, *J* = 18.2, 4.9 Hz, 1H), 2.30 (s, 3H), 1.79 (s, 3H), 1.58 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.9, 153.9, 139.6, 137.5, 134.1, 131.4, 130.8, 128.5, 127.9,

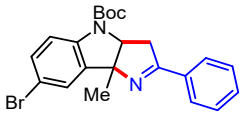
127.7, 124.8, 121.3, 84.3, 70.3, 44.9, 28.5, 26.7, 20.8. **HRMS (ESI)** calculated for $C_{23}H_{27}N_2O_2^+$, $[M+H]^+$: 363.2067; found: 363.2068.

tert-butyl 7-chloro-8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5af)



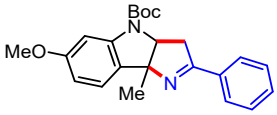
Pale yellow solid, 65.9 mg, 86% yield, melting point: 195.1 – 196.7 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 – 7.36 (m, 7H), 7.22 – 7.14 (m, 1H), 4.60 (s, 1H), 3.66 (s, 1H), 3.43 – 3.23 (m, 1H), 1.72 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 151.9, 140.4, 136.4, 133.8, 131.0, 128.8, 128.6, 128.0, 127.9, 124.3, 116.0, 83.6, 83.6, 82.7, 67.9, 45.0, 28.6, 26.2. **HRMS (ESI)** calculated for $C_{22}H_{24}ClN_2O_2^+$, $[M+H]^+$: 3383.1521; found: 3383.1521.

tert-butyl 7-bromo-8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ag)



Pale yellow solid, 75.2 mg, 88% yield, melting point: 200.1 – 201.6 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.82 – 7.30 (m, 8H), 4.59 (s, 1H), 3.73 – 3.59 (m, 1H), 3.43 – 3.21 (m, 1H), 1.72 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 152.0, 140.9, 136.8, 133.7, 131.7, 131.0, 128.6, 128.0, 127.2, 116.5, 115.3, 82.7, 81.5, 67.8, 45.0, 28.6, 26.2. **HRMS (ESI)** calculated for $C_{22}H_{24}BrN_2O_2^+$, $[M+H]^+$: 427.1016; found: 427.1013.

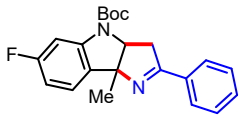
tert-butyl 6-methoxy-8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ah)



Colorless oil, 62.1 mg, 82% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.79 (d, *J* = 7.6, 1.9 Hz, 2H), 7.55 (s, 0.5H), 7.45 – 7.33 (m, 4H), 7.12 (s, 0.5H), 6.61 (dd, *J* = 8.3, 2.4 Hz, 1H), 4.61 (s, 1H), 3.79 (s, 3H), 3.73 – 3.59 (m, 1H), 3.43 – 3.22 (m, 1H), 1.72 (s, 3H), 1.62 (s, 9H). **^{13}C NMR (101**

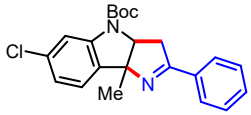
MHz, Chloroform-*d*) δ 169.5, 169.1, 160.7, 152.0, 143.1, 142.3, 134.0, 130.8, 128.5, 127.9, 127.1, 124.3, 109.7, 108.5, 101.4, 100.4, 83.4, 82.5, 82.3, 81.1, 68.3, 55.6, 45.0, 44.5, 28.6, 26.4, 26.1. **HRMS (ESI)** calculated for $C_{23}H_{27}N_2O_3^+$, $[M+H]^+$: 379.2016; found: 379.2014.

tert-butyl 6-fluoro-8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ai)



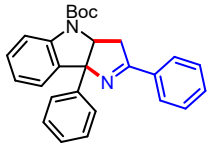
Pale yellow solid, 62.3 mg, 85% yield, melting point: 151.6 – 152.7 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.85 – 7.76 (m, 2H), 7.64 (s, 0.5H), 7.48 – 7.35 (m, 4H), 7.21 – 7.14 (m, 0.5H), 6.73 (t, 1H), 4.63 (s, 1H), 3.66 (s, 1H), 3.30 (m, 1H), 1.72 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 163.6 (d, J = 242.8 Hz), 152.4, 143.2, 133.9, 130.9, 128.5, 128.0, 124.8, 109.5 (d, J = 23.3 Hz), 103.2, 102.9, 83.4, 82.9, 82.5, 81.6, 68.3, 44.9, 28.6, 26.2. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -112.84. **HRMS (ESI)** calculated for $C_{22}H_{24}FN_2O_2^+$, $[M+H]^+$: 367.1816; found: 367.1816.

tert-butyl 6-chloro-8b-methyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5aj)



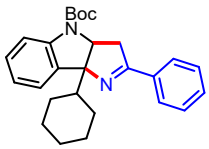
White solid, 60.5 mg, 79% yield, melting point: 185.2 – 186.7 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.97 – 7.34 (m, 7H), 7.01 (d, J = 8.0, 1.9 Hz, 1H), 4.61 (s, 1H), 3.65 (s, 1H), 3.44 – 3.22 (m, 1H), 1.72 (s, 3H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.8, 151.9, 143.0, 134.7, 133.8, 133.4, 131.0, 128.6, 128.0, 124.8, 123.0, 115.5, 83.4, 81.7, 68.1, 44.9, 28.6, 26.2. **HRMS (ESI)** calculated for $C_{22}H_{24}ClN_2O_2^+$, $[M+H]^+$: 383.1521; found: 383.1521.

tert-butyl 2,8b-diphenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5ak)



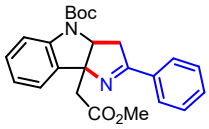
Pale yellow solid, 64.0 mg, 78% yield, melting point: 170.9 – 171.5 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.01 – 7.54 (m, 3H), 7.50 – 7.41 (m, 3H), 7.39 – 7.26 (m, 7H), 7.03 (t, *J* = 7.5 Hz, 1H), 4.98 – 4.75 (m, 1H), 3.74 – 3.60 (m, 1H), 3.43 (m, 1H), 1.61 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.8, 152.3, 144.9, 142.5, 134.9, 133.9, 131.1, 129.2, 128.6, 128.6, 128.2, 127.4, 126.4, 123.3, 115.0, 89.7, 81.6, 70.1, 45.0, 28.6. **HRMS (ESI)** calculated for $C_{27}H_{27}N_2O_2^+$, $[M+H]^+$: 411.2067; found: 411.2065.

tert-butyl 8b-cyclohexyl-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5al)



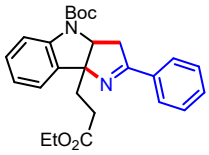
White solid, 58.3 mg, 70% yield, melting point: 182.5 – 184.1 ℃. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 – 7.35 (m, 7H), 7.21 (t, *J* = 7.8 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.90 – 4.65 (m, 1H), 3.63 – 3.41 (m, 1H), 3.35 – 3.15 (m, 1H), 2.38 (t, *J* = 12.3 Hz, 1H), 1.81 – 1.66 (m, 4H), 1.63 (s, 9H), 1.47 – 1.11 (m, 4H), 1.02 – 0.78 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.1, 152.3, 141.9, 134.0, 133.2, 130.7, 128.7, 128.5, 128.4, 127.9, 124.6, 124.2, 122.9, 114.9, 91.1, 90.4, 82.3, 81.1, 61.9, 45.8, 44.3, 28.7, 28.1, 26.6, 26.5, 26.4, 26.2. **HRMS (ESI)** calculated for $C_{27}H_{33}N_2O_2^+$, $[M+H]^+$: 417.2537; found: 417.2533.

tert-butyl 8b-(2-methoxy-2-oxoethyl)-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5am)



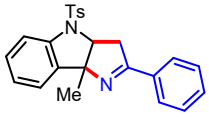
Colorless oil, 61.0 mg, 75% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.93 – 7.45 (m, 4H), 7.43 – 7.34 (m, 3H), 7.26 – 7.20 (m, 1H), 7.04 (t, *J* = 7.5 Hz, 1H), 5.19 – 5.10 (m, 1H), 3.92 – 3.79 (m, 1H), 3.58 (s, 3H), 3.46 – 3.19 (m, 2H), 3.04 (d, *J* = 16.2 Hz, 1H), 1.62 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 172.3, 170.9, 152.0, 141.7, 133.8, 132.8, 130.9, 129.5, 128.5, 128.0, 124.1, 122.9, 115.2, 84.7, 81.2, 65.4, 51.7, 46.5, 42.8, 28.6. **HRMS (ESI)** calculated for $C_{24}H_{27}N_2O_2^+$, $[M+H]^+$: 407.1965; found: 407.1967.

tert-butyl 8b-(3-ethoxy-3-oxopropyl)-2-phenyl-3a,8b-dihydropyrrolo[3,2-*b*]indole-4(3*H*)-carboxylate (5an)



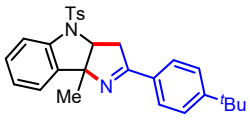
Colorless oil, 66.9 mg, 77% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.91 – 7.48 (m, 4H), 7.44 – 7.33 (m, 3H), 7.25 (t, *J* = 10.2 Hz, 1H), 7.04 (t, *J* = 7.4 Hz, 1H), 4.70 (m, 1H), 4.15 – 4.02 (m, 2H), 3.60 (m, 1H), 3.28 (m, 1H), 2.54 – 2.23 (m, 4H), 1.62 (s, 9H), 1.20 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.1, 171.0, 170.5, 152.8, 151.9, 141.9, 133.7, 133.1, 131.0, 129.2, 128.5, 128.0, 124.7, 124.3, 123.0, 115.1, 86.7, 85.8, 82.4, 81.3, 64.9, 60.6, 45.5, 34.0, 29.6, 28.6, 14.2. **HRMS (ESI)** calculated for $C_{26}H_{31}N_2O_4^+$, $[M+H]^+$: 435.2278; found: 435.2279.

8b-methyl-2-phenyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ao)



Colorless oil, 70.8 mg, 88% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.72 – 7.68 (m, 2H), 7.64 – 7.57 (m, 3H), 7.36 – 7.27 (m, 4H), 7.18 – 7.12 (m, 3H), 7.03 – 6.98 (m, 1H), 4.30 (dd, *J* = 7.1, 3.4 Hz, 1H), 3.65 – 3.53 (m, 2H), 2.28 (s, 3H), 1.28 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 170.2, 144.5, 140.9, 135.5, 134.2, 133.7, 131.0, 129.8, 129.2, 128.5, 128.0, 127.4, 124.6, 124.5, 115.4, 84.7, 69.7, 45.3, 26.2, 21.6. **HRMS (ESI)** calculated for $C_{24}H_{23}N_2O_2S^+$, $[M+H]^+$: 403.1475; found: 403.1474.

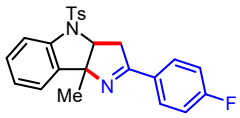
2-(4-(tert-butyl)phenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ap)



Pale yellow solid, 80.7 mg, 88% yield, melting point: 184.1 – 186.0 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.75 – 7.66 (m, 5H), 7.44 – 7.38 (m, 3H), 7.28 – 7.23 (m, 3H), 7.08 (t, *J* = 7.5, 1.1 Hz, 1H), 4.38 (dd, *J* = 7.1, 3.5 Hz, 1H), 3.73 – 3.61 (m, 2H), 2.37 (s, 3H), 1.36 (s, 3H), 1.31 (s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.9, 154.5, 144.4, 140.9, 135.7, 134.2, 130.9, 129.8,

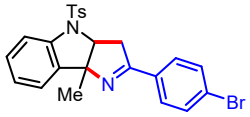
129.2, 127.8, 127.4, 125.5, 124.6, 124.5, 115.4, 84.6, 69.8, 45.3, 35.0, 31.2, 26.3, 21.6. **HRMS (ESI)** calculated for $C_{28}H_{31}N_2O_2S^+$, $[M+H]^+$: 459.2101; found: 459.2100.

2-(4-fluorophenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5aq)



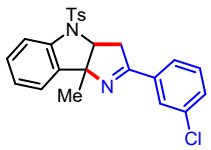
Colorless oil, 67.3 mg, 80% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.80 – 7.74 (m, 2H), 7.70 – 7.63 (m, 3H), 7.40 – 7.36 (m, 1H), 7.25 – 7.20 (m, 3H), 7.09 – 7.00 (m, 3H), 4.35 (dd, *J* = 6.9, 3.6 Hz, 1H), 3.69 – 3.57 (m, 2H), 2.35 (s, 3H), 1.34 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.0, 164.5 (d, *J* = 251.4 Hz), 144.5, 140.9, 135.4, 134.1, 130.2, 130.1, 130.0 (d, *J* = 3.3 Hz), 129.9, 129.3, 127.4, 124.6, 124.5, 115.7, 115.5, 115.4, 84.7, 69.8, 45.3, 26.2, 21.7. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -109.01. **HRMS (ESI)** calculated for $C_{24}H_{22}FN_2O_2S^+$, $[M+H]^+$: 421.1381; found: 421.1383.

2-(4-bromophenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ar)



Colorless oil, 81.8 mg, 85% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.74 – 7.63 (m, 5H), 7.50 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 7.5, 1.4 Hz, 1H), 7.29 – 7.24 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.40 (dd, *J* = 6.9, 3.5 Hz, 1H), 3.72 – 3.59 (m, 2H), 2.37 (s, 3H), 1.38 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.1, 144.5, 140.9, 135.2, 134.0, 132.6, 131.7, 129.8, 129.5, 129.3, 127.3, 125.5, 124.6, 124.5, 115.3, 84.8, 69.7, 45.2, 26.1, 21.6. **HRMS (ESI)** calculated for $C_{24}H_{22}BrN_2O_2S^+$, $[M+H]^+$: 481.0580; found: 481.0577.

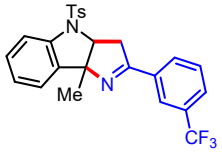
2-(3-chlorophenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5as)



Colorless oil, 65.5 mg, 75% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.83 (s, 1H), 7.72 – 7.65 (m, 3H), 7.61 (d, *J* = 7.6 Hz, 1H), 7.43 – 7.36 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.27 – 7.23 (m, 3H),

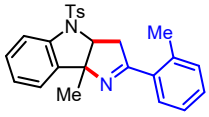
7.09 (t, *J* = 7.5, 1.0 Hz, 1H), 4.37 (dd, *J* = 6.7, 3.8 Hz, 1H), 3.71 – 3.59 (m, 2H), 2.37 (s, 3H), 1.37 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.1, 144.6, 140.9, 135.4, 135.1, 134.7, 134.1, 131.0, 129.9, 129.9, 129.4, 128.0, 127.4, 126.2, 124.6, 124.5, 115.4, 84.8, 69.7, 45.3, 26.1, 21.7. **HRMS (ESI)** calculated for $C_{24}H_{22}ClN_2O_2S^+$, $[M+H]^+$: 437.1085; found: 437.1084.

8b-methyl-4-tosyl-2-(3-(trifluoromethyl)phenyl)-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5at)



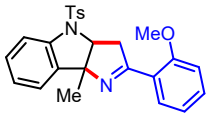
Colorless oil, 65.9 mg, 70% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.09 (s, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.73 – 7.66 (m, 4H), 7.51 (t, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 7.5, 1.3 Hz, 1H), 7.30 – 7.24 (m, 3H), 7.10 (t, *J* = 7.5 Hz, 1H), 4.40 (dd, *J* = 6.5, 3.9 Hz, 1H), 3.76 – 3.64 (m, 2H), 2.38 (s, 3H), 1.39 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 168.9, 144.6, 141.0, 135.1, 134.5, 134.1, 131.3, 131.1 (q, *J* = 32.5 Hz), 129.9, 129.4, 129.1, 127.5 (d, *J* = 3.7 Hz), 127.4, 124.8 (q, *J* = 3.8 Hz), 124.7, 124.6, 124.0 (d, *J* = 272.6 Hz), 115.4, 85.0, 69.7, 45.3, 26.1, 21.7. **^{19}F NMR (376 MHz, Chloroform-*d*)** δ -62.65. **HRMS (ESI)** calculated for $C_{25}H_{22}F_3N_2O_2S^+$, $[M+H]^+$: 471.1349; found: 471.1347.

8b-methyl-2-(o-tolyl)-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5au)



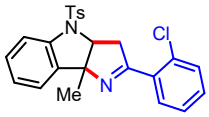
Pale yellow solid, 66.7 mg, 80% yield, melting point: 144.3 – 146.1 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.76 – 7.71 (m, 3H), 7.43 – 7.38 (m, 2H), 7.33 – 7.26 (m, 4H), 7.23 – 7.19 (m, 2H), 7.11 (t, *J* = 7.5 Hz, 1H), 4.38 (dd, *J* = 7.5, 3.0 Hz, 1H), 3.73 – 3.58 (m, 2H), 2.43 (s, 3H), 2.40 (s, 3H), 1.41 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.9, 144.5, 140.9, 137.5, 135.6, 134.2, 133.7, 131.4, 129.8, 129.6, 129.2, 128.9, 127.4, 125.7, 124.6, 124.5, 115.4, 85.1, 69.5, 48.3, 26.2, 21.7, 21.6. **HRMS (ESI)** calculated for $C_{25}H_{25}N_2O_2S^+$, $[M+H]^+$: 417.1631; found: 417.1629.

2-(2-methoxyphenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5av)



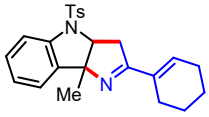
Pale yellow solid, 67.5 mg, 78% yield, melting point: 89.5 – 89.9 °C. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.74 – 7.65 (m, 4H), 7.42 (d, *J* = 7.5, 1.4 Hz, 1H), 7.38 – 7.32 (m, 1H), 7.28 – 7.22 (m, 3H), 7.08 (t, *J* = 7.5, 1.0 Hz, 1H), 6.93 – 6.87 (m, 2H), 4.36 (dd, *J* = 8.0, 2.7 Hz, 1H), 3.88 – 3.81 (m, 4H), 3.67 (dd, *J* = 19.4, 2.7 Hz, 1H), 2.37 (s, 3H), 1.35 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.1, 158.4, 144.4, 141.0, 135.7, 134.4, 132.0, 130.5, 129.8, 129.1, 127.4, 124.6, 124.5, 123.4, 120.7, 115.5, 111.2, 82.9, 70.4, 55.5, 48.2, 26.1, 21.7. **HRMS (ESI)** calculated for $C_{25}H_{25}N_2O_3S^+$, $[M+H]^+$: 433.1580; found: 433.1583.

2-(2-chlorophenyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5aw)



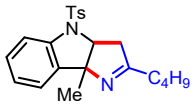
Colorless oil, 61.2 mg, 70% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.74 – 7.67 (m, 3H), 7.48 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.42 – 7.35 (m, 2H), 7.32 – 7.23 (m, 5H), 7.12 – 7.07 (m, 1H), 4.39 (dd, *J* = 7.8, 2.5 Hz, 1H), 3.87 (dd, *J* = 19.2, 7.9 Hz, 1H), 3.65 (d, *J* = 19.2, 2.6 Hz, 1H), 2.38 (s, 3H), 1.40 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.2, 144.5, 141.2, 134.9, 134.2, 134.1, 132.6, 131.0, 130.5, 130.3, 129.9, 129.4, 127.4, 126.9, 124.6, 115.4, 84.2, 70.1, 48.2, 25.8, 21.7. **HRMS (ESI)** calculated for $C_{24}H_{22}ClN_2O_2S^+$, $[M+H]^+$: 437.1085; found: 437.1085.

2-(cyclohex-1-en-1-yl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ax)



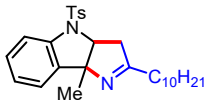
Colorless oil, 58.5 mg, 72% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.65 (t, *J* = 8.7 Hz, 3H), 7.37 (d, *J* = 7.5, 1.4 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 3H), 7.05 (t, *J* = 7.4 Hz, 1H), 6.29 (s, 1H), 4.22 (dd, *J* = 6.4, 4.4 Hz, 1H), 3.42 – 3.36 (m, 2H), 2.36 (s, 3H), 2.30 (s, 2H), 2.18 (d, *J* = 4.5 Hz, 2H), 1.66 – 1.55 (m, 4H), 1.27 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.6, 144.4, 140.8, 136.4, 136.0, 134.4, 134.3, 129.8, 129.1, 127.4, 124.5, 124.5, 115.4, 84.1, 69.6, 44.2, 26.4, 26.2, 25.1, 22.2, 22.0, 21.7. **HRMS (ESI)** calculated for $C_{24}H_{27}N_2O_2S^+$, $[M+H]^+$: 407.1788; found: 407.1784.

2-butyl-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ay)



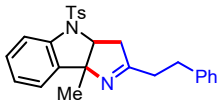
Colorless oil, 65.0 mg, 85% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.69 – 7.62 (m, 3H), 7.35 – 7.30 (m, 1H), 7.26 – 7.20 (m, 3H), 7.09 – 7.02 (m, 1H), 4.20 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.29 – 3.10 (m, 2H), 2.36 (s, 3H), 2.32 – 2.26 (m, 2H), 1.54 – 1.46 (m, 2H), 1.33 – 1.26 (m, 2H), 1.25 (s, 3H), 0.87 (t, *J* = 7.3 Hz, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.1, 144.4, 140.9, 135.5, 134.2, 129.8, 129.1, 127.3, 124.5, 124.3, 115.3, 84.0, 69.8, 47.0, 33.4, 28.7, 26.1, 22.6, 21.7, 13.9. **HRMS (ESI)** calculated for $C_{22}H_{27}N_2O_2S^+$, $[M+H]^+$: 383.1788; found: 383.1791.

2-decyl-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5az)



Colorless oil, 76.5 mg, 82% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 8.0 Hz, 3H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.25 – 7.17 (m, 3H), 7.07 – 7.00 (m, 1H), 4.19 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.22 (dd, *J* = 19.0, 7.6 Hz, 1H), 3.13 (dd, *J* = 19.1, 2.8 Hz, 1H), 2.36 – 2.31 (m, 3H), 2.30 – 2.24 (m, 2H), 1.50 (t, *J* = 7.5 Hz, 2H), 1.28 – 1.18 (m, 17H), 0.89 – 0.82 (m, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.9, 144.3, 140.8, 135.4, 134.1, 129.7, 129.0, 127.2, 124.4, 124.3, 115.2, 83.9, 69.7, 46.9, 33.6, 31.9, 29.5, 29.5, 29.3, 29.3, 29.3, 26.4, 26.0, 22.7, 21.5, 14.1. **HRMS (ESI)** calculated for $C_{28}H_{39}N_2O_2S^+$, $[M+H]^+$: 467.2727; found: 467.2723.

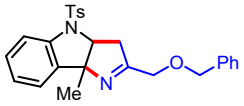
8b-methyl-2-phenethyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5ba)



Colorless oil, 76.6 mg, 89% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.67 (dd, *J* = 8.2, 6.2 Hz, 3H), 7.36 – 7.32 (m, 1H), 7.28 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.25 – 7.20 (m, 4H), 7.18 – 7.10 (m, 3H), 7.09 – 7.04 (m, 1H), 4.19 (dd, *J* = 7.2, 3.2 Hz, 1H), 3.24 – 3.08 (m, 2H), 2.92 – 2.82 (m, 2H), 2.66 – 2.56 (m, 2H), 2.35 (s, 3H), 1.25 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 175.0, 144.4, 140.9, 140.7, 135.3, 134.1, 129.7, 129.1, 128.5, 128.3, 127.3, 126.2, 124.5, 124.3, 115.3, 84.1, 69.7,

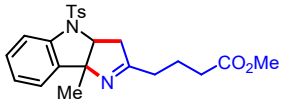
47.6, 34.9, 32.6, 25.9, 21.6. **HRMS (ESI)** calculated for $C_{26}H_{27}N_2O_2S^+$, $[M+H]^+$: 431.1788; found: 431.1785.

2-((benzyloxy)methyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5bb)



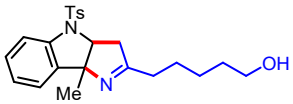
Colorless oil, 78.6 mg, 88% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.66 (dd, *J* = 8.4, 1.9 Hz, 3H), 7.35 – 7.27 (m, 6H), 7.25 (d, *J* = 8.1 Hz, 1H), 7.22 (d, *J* = 8.2 Hz, 2H), 7.10 – 7.04 (m, 1H), 4.52 (s, 2H), 4.25 (dd, *J* = 7.7, 2.8 Hz, 1H), 4.17 (d, *J* = 2.2 Hz, 2H), 3.41 – 3.22 (m, 2H), 2.36 (s, 3H), 1.28 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 173.5, 144.4, 141.0, 137.4, 134.9, 134.2, 129.8, 129.3, 128.6, 128.0, 127.3, 124.5, 124.4, 115.4, 84.5, 73.4, 69.6, 69.3, 45.7, 25.9, 21.6. **HRMS (ESI)** calculated for $C_{26}H_{27}N_2O_3S^+$, $[M+H]^+$: 447.1737; found: 447.1733.

methyl 4-(8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indol-2-yl)butanoate (5bc)



Colorless oil, 75.1 mg, 88% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.68 – 7.61 (m, 3H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.26 – 7.18 (m, 3H), 7.07 – 7.01 (m, 1H), 4.23 – 4.16 (m, 1H), 3.62 (s, 3H), 3.24 (dd, *J* = 19.0, 7.7 Hz, 1H), 3.13 (dd, *J* = 19.0, 2.8 Hz, 1H), 2.37 – 2.27 (m, 7H), 1.93 – 1.82 (m, 2H), 1.23 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 174.8, 173.5, 144.4, 140.9, 135.3, 134.1, 129.8, 129.2, 127.3, 124.5, 124.3, 115.3, 84.2, 69.7, 51.6, 47.3, 33.4, 32.7, 26.0, 21.6, 21.5. **HRMS (ESI)** calculated for $C_{23}H_{27}N_2O_4S^+$, $[M+H]^+$: 427.1686; found: 427.1685.

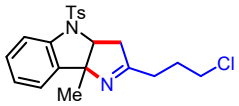
5-(8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indol-2-yl)pentan-1-ol (5bd)



Colorless oil, 67.7 mg, 82% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 7.64 (d, *J* = 8.3 Hz, 3H), 7.32 (d, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 7.9, 5.7 Hz, 3H), 7.04 (t, *J* = 7.5 Hz, 1H), 4.19 (dd, *J* = 7.6, 2.9 Hz, 1H), 3.61 – 3.52 (m, 2H), 3.22 (dd, *J* = 19.0, 7.6 Hz, 1H), 3.13 (dd, *J* = 19.0, 2.9 Hz, 1H), 2.71 (s, 1H), 2.34 (s, 3H), 2.28 (t, *J* = 7.4 Hz, 2H), 1.60 – 1.47 (m, 4H), 1.37 – 1.29 (m, 2H), 1.24 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 176.0, 144.5, 140.8, 135.3, 134.0, 129.8, 129.2,

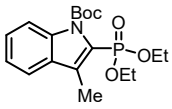
127.3, 124.6, 124.4, 115.3, 84.0, 69.7, 62.2, 47.3, 33.2, 32.0, 26.0, 25.4, 25.3, 21.6. **HRMS (ESI)** calculated for $C_{23}H_{29}N_2O_3S^+$, $[M+H]^+$: 413.1893; found: 413.1889.

2-(3-chloropropyl)-8b-methyl-4-tosyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (5be)



Colorless oil, 66.9 mg, 83% yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.65 (d, *J* = 8.4 Hz, 3H), 7.31 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.23 (dd, *J* = 8.1, 6.3 Hz, 3H), 7.09 – 7.03 (m, 1H), 4.20 (dd, *J* = 7.7, 2.8 Hz, 1H), 3.56 – 3.49 (m, 2H), 3.25 (dd, *J* = 19.0, 7.7 Hz, 1H), 3.15 (dd, *J* = 19.0, 2.9 Hz, 1H), 2.47 – 2.40 (m, 2H), 2.36 (s, 3H), 2.08 – 2.01 (m, 2H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 174.3, 144.5, 140.9, 135.3, 134.2, 129.8, 129.2, 127.3, 124.6, 124.4, 115.4, 84.3, 69.7, 47.7, 44.5, 30.7, 29.0, 26.0, 21.6. **HRMS (ESI)** calculated for $C_{21}H_{24}N_2O_2SCl^+$, $[M+H]^+$: 403.1242; found: 403.1241.

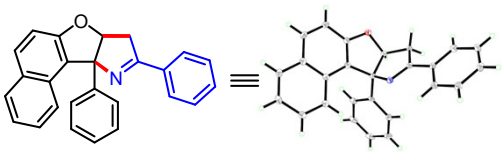
tert-butyl 2-(diethoxyphosphoryl)-3-methyl-1*H*-indole-1-carboxylate (9a)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 8.5 Hz, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.42 – 7.36 (m, 1H), 7.24 (t, *J* = 7.5 Hz, 1H), 4.24 – 4.07 (m, 4H), 2.56 (d, *J* = 2.3 Hz, 3H), 1.66 (s, 9H), 1.33 (t, *J* = 7.1 Hz, 6H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 149.9, 138.0, 137.9, 132.1, 131.9, 130.0, 129.8, 127.3, 123.3, 122.7, 122.7, 121.1, 120.2, 115.3, 115.3, 84.9, 62.4, 62.4, 28.1, 16.5, 16.4, 11.0. ^{31}P NMR (162 MHz, Chloroform-*d*) δ 9.53. **HRMS (ESI)** calculated for $C_{18}H_{27}NO_5P^+$, $[M+H]^+$: 368.1621; found: 368.1622.

5. X-ray Structure and Data

5.1 X-ray Structure and Data for Product 3bh (CCDC number: 2457376)



3bh **CCDC**:2457376

Table 6. Crystal data and structure refinement for 3bh.

Chemical formula	$C_{26}H_{19}NO$	
Formula weight	361.42 g/mol	
Wavelength	0.71073 Å	
Crystal size	0.070 x 0.160 x 0.210 mm	
Crystal system	monoclinic	
Space group	P 1 21/n 1	
Unit cell dimensions	a = 9.8144(9) Å	α = 90°
	b = 8.2022(7) Å	β = 100.027(4)°
	c = 22.949(2) Å	γ = 90°
Volume	1819.2(3) $Å^3$	
Z	4	
Density (calculated)	1.320 g/cm^3	
Absorption coefficient	0.080 mm^{-1}	
F(000)	760	
Theta range for data collection	2.14 to 27.54°	
Index ranges	-12<=h<=12, -9<=k<=10, -29<=l<=29	
Reflections collected	27788	
Independent reflections	4195 [R(int) = 0.0897]	
Max. and min. transmission	0.7456 and 0.6525	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL 2018/3 (Sheldrick, 2015)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	4195 / 0 / 253	
Goodness-of-fit on F2	1.114	
Final R indices	3005 data; I>2σ(I)	R1 = 0.0626, wR2 = 0.1121

	all data	R1 = 0.1026, wR2 = 0.1303
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0323P)^2+1.4675P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.270 and -0.296 eÅ^{-3}	
R.M.S. deviation from mean	0.057 eÅ^{-3}	

5.2 X-ray Structure and Data for Product 3bn (CCDC number: 2457379)

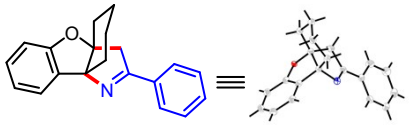


Table 7. Crystal data and structure refinement for 3bn.

Chemical formula	$C_{20}H_{19}NO$	
Formula weight	289.36 g/mol	
Wavelength	0.71073 Å	
Crystal size	0.170 x 0.200 x 0.210 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 18.0371(7) Å	α = 90°
	b = 10.3994(4) Å	β = 117.2320(10)°
	c = 17.8291(6) Å	γ = 90°
Volume	2973.62(19) Å^3	
Z	8	
Density (calculated)	1.293 g/cm^3	
Absorption coefficient	0.079 mm^{-1}	
F(000)	1232	
Theta range for data collection	2.29 to 27.54°	
Index ranges	-23<=h<=23, -13<=k<=13, -23<=l<=23	
Reflections collected	41911	

Independent reflections	6844 [R(int) = 0.0625]	
Max. and min. transmission	0.7456 and 0.6572	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL 2018/3 (Sheldrick, 2015)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	6844 / 0 / 397	
Goodness-of-fit on F2	1.051	
Δ/σmax	0.001	
Final R indices	5494 data; I>2σ(I)	R1 = 0.0507, wR2 = 0.1077
	all data	R1 = 0.0691, wR2 = 0.1193
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0407P)^2+1.9519P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.324 and -0.254 eÅ^{-3}	
R.M.S. deviation from mean	0.052 eÅ^{-3}	

5.3 X-ray Structure and Data for Product 5ab (CCDC number: 2457377)

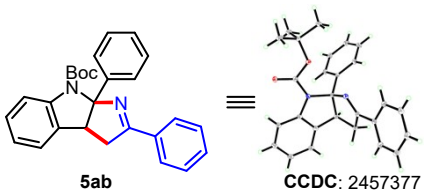
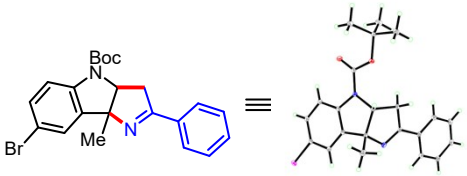


Table 8. Crystal data and structure refinement for 5ab.

Chemical formula	$C_{27}H_{26}N_2O_2$
Formula weight	410.50 g/mol
Wavelength	0.71073 Å
Crystal size	0.180 x 0.220 x 0.240 mm
Crystal system	monoclinic
Space group	C 1 2/c 1

Unit cell dimensions	a = 23.3054(7) Å	α = 90°
	b = 9.0717(3) Å	β = 111.9950(10)°
	c = 21.5229(8) Å	γ = 90°
Volume	4219.2(2) $Å^3$	
Z	8	
Density (calculated)	1.292 g/cm^3	
Absorption coefficient	0.082 mm^{-1}	
F(000)	1744	
Theta range for data collection	2.04 to 28.33°	
Index ranges	-28<=h<=30, -12<=k<=10, -27<=l<=28	
Reflections collected	31646	
Independent reflections	5254 [R(int) = 0.0553]	
Max. and min. transmission	0.7457 and 0.6304	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	
Refinement program	SHELXL 2018/3 (Sheldrick, 2015)	
Function minimized	Σ w(Fo2 - Fc2)2	
Data / restraints / parameters	5254 / 0 / 283	
Goodness-of-fit on F2	1.053	
Δ/σmax	0.001	
Final R indices	4338 data; I>2σ(I)	R1 = 0.0460, wR2 = 0.0980
	all data	R1 = 0.0623, wR2 = 0.1073
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0377P)^2+4.8237P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.355 and -0.260 $eÅ^{-3}$	
R.M.S. deviation from mean	0.049 $eÅ^{-3}$	

5.4 X-ray Structure and Data for Product 5ag (CCDC number: 2457378)



5ag **CCDC**: 2457378

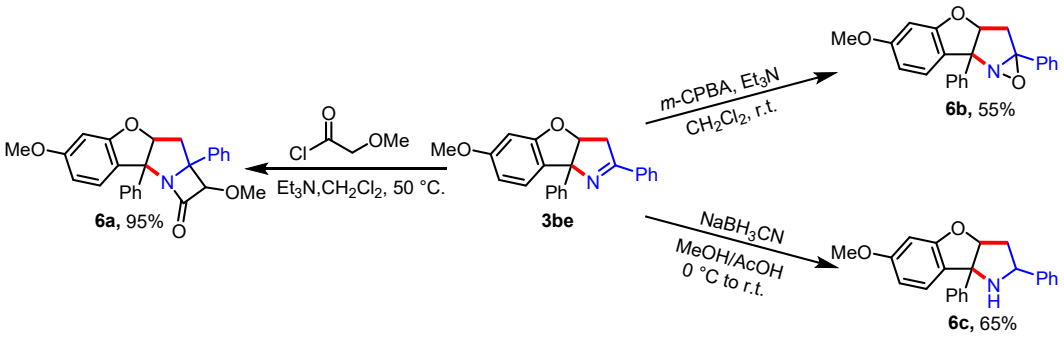
Table 9. Crystal data and structure refinement for 5ag.

Chemical formula	$C_{22}H_{23}BrN_2O_2$	
Formula weight	427.33 g/mol	
Wavelength	0.71073 Å	
Crystal size	0.050 x 0.160 x 0.280 mm	
Crystal system	monoclinic	
Space group	P 1 21/c 1	
Unit cell dimensions	a = 10.7771(5) Å	α = 90°
	b = 15.1534(6) Å	β = 105.628(2)°
	c = 12.5418(5) Å	γ = 90°
Volume	1972.48(14) $Å^3$	
Z	4	
Density (calculated)	1.439 g/cm^3	
Absorption coefficient	2.103 mm^{-1}	
F(000)	880	
Theta range for data collection	1.96 to 28.35°	
Index ranges	-14<=h<=14, -20<=k<=20, -16<=l<=16	
Reflections collected	28385	
Independent reflections	4926 [R(int) = 0.0520]	
Max. and min. transmission	0.7457 and 0.5795	
Structure solution technique	direct methods	
Structure solution program	SHELXT 2018/2 (Sheldrick, 2018)	
Refinement method	Full-matrix least-squares on F2	

Refinement program		SHELXL 2018/3 (Sheldrick, 2015)
Function minimized		Σ w(Fo2 - Fc2)2
Data / restraints / parameters		4926 / 0 / 248
Goodness-of-fit on F2		1.032
Δ/σmax		0.001
Final R indices	4259 data; I>2σ(I)	R1 = 0.0283, wR2 = 0.0598
	all data	R1 = 0.0378, wR2 = 0.0641
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0116P)^2+1.8755P]$ where $P=(F_o^2+2F_c^2)/3$	
Largest diff. peak and hole	0.429 and -0.408 eÅ^{-3}	
R.M.S. deviation from mean	0.065 eÅ^{-3}	

6. Cycloaddition Product Diversification

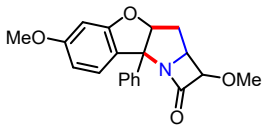
6.1 Diversification of benzofuran.



Formation of 6a

According to literature report, **3be** (34.1 mg, 0.10 mmol), Et_3N (30.4 mg, 0.30 mmol), and CH_2Cl_2 (1.0 mL) was added into a 10 mL Schlenk tube equipped with a stirring bar. 2-Methoxyacetyl chloride (32.6 mg, 0.30 mmol, in 1.0 mL CH_2Cl_2) was added to the mixture dropwise at room temperature. Then the tube was sealed and heated at 50 ℃ for 16 h. Completion of the reaction was analysed by TLC. The mixture was concentrated under reduced pressure and the crude residue was subjected to **^{1}H NMR** to determine the d.r. value, only one single diastereoisomer (>20:1 d.r.) was observed. Then target product **6a** was isolated by flash chromatography (pentane/EtOAc) in 95% yield (39.3 mg).

1,6-dimethoxy-3a,9a-diphenyl-3a,8a,9,9a-tetrahydroazeto[1,2-*a*]benzofuro[2,3-*d*]pyrrol-2(1*H*)-one (6a)

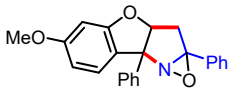


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.14 (m, 11H), 6.39 (d, *J* = 10.1 Hz, 2H), 5.54 – 5.42 (m, 1H), 4.51 (s, 1H), 3.67 (s, 3H), 3.16 – 2.98 (m, 4H), 2.54 – 2.41 (m, 1H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 171.4, 162.0, 159.1, 141.6, 138.1, 128.8, 128.4, 127.8, 127.7, 126.9, 125.6, 121.1, 107.7, 99.0, 97.3, 90.9, 72.8, 58.2, 55.6, 43.3. **HRMS (ESI)** calculated for $C_{26}H_{24}NO_4^+$, $[M+H]^+$: 414.1700; found: 414.1703.

Formation of 6b

Following the literature procedure, to a stirred solution of **3be** (68.3 mg, 0.20 mmol) in dry CH_2Cl_2 (2.0 mL), *m*-CPBA (44.9 mg, 0.26 mmol) was discharged at room temperature and the reaction was stirred overnight. Then, Et_3N (42 μL, 0.30 mmol) was added to the reaction mixture. Completion of the reaction was analysed by TLC. The resulting mixture was purified by flash chromatography (pentane/EtOAc) to obtain the intended product **6b** (39.3 mg, 55%). only one single diastereoisomer (>20:1 d.r.) was observed.

5-methoxy-2a,8a-diphenyl-2a,7a,8,8a-tetrahydrobenzofuro[2,3-*d*][1,2]oxazireno-[2,3-*a*]pyrrole (6b)



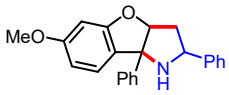
^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.51 – 8.41 (m, 2H), 7.50 – 7.45 (m, 4H), 7.41 – 7.34 (m, 3H), 7.32 – 7.27 (m, 2H), 6.64 – 6.57 (m, 1H), 6.46 (s, 1H), 5.20 (dd, *J* = 5.5, 1.6 Hz, 1H), 3.80 (s, 3H), 3.68 – 3.54 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 163.1, 162.5, 137.7, 137.2, 130.9, 129.1, 129.0, 128.7, 128.6, 127.8, 127.7, 126.8, 117.6, 108.1, 96.1, 93.0, 86.8, 55.8, 36.0. **HRMS (ESI)** calculated for $C_{23}H_{20}NO_3^+$, $[M+H]^+$: 358.1438; found: 358.1435.

Formation of 6c

The **3be** (68.3 mg, 0.20 mmol) was dissolved into MeOH (2.0 mL) under Ar atmosphere. The

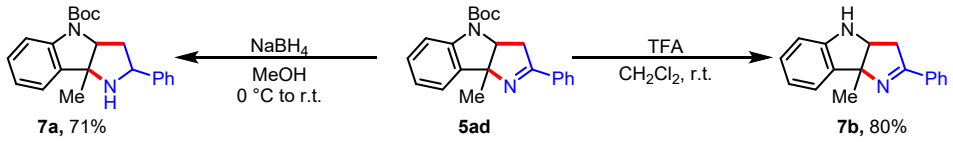
mixture was cooled to 0 ℃ for 10 min. To the resulting mixture, AcOH (200 μL), $NaBH_3CN$ (37.7 mg, 0.6 mmol) were added. Then, the resulting mixture was stirred at room temperature for 4 h until the completion of reaction as monitored by TLC analysis. MeOH was removed under vacuum. 20 mL $NaHCO_3$ (aq.) and 20 mL CH_2Cl_2 were added, the layers were separated, and the aqueous layer extracted with DCM (3 × 20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was purified by flash column chromatography directly to give the desired product **6c** (44.7 mg) in 65% yield. only one single diastereoisomer (>20:1 d.r.) was observed.

6-methoxy-2,8b-diphenyl-2,3,3a,8b-tetrahydro-1*H*-benzofuro[3,2-*b*]pyrrole (6c)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.71 – 7.64 (m, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.37 (q, *J* = 7.5 Hz, 4H), 7.32 – 7.26 (m, 2H), 6.86 (d, *J* = 8.0 Hz, 1H), 6.54 – 6.45 (m, 2H), 5.09 (d, *J* = 5.2 Hz, 1H), 4.42 – 4.32 (m, 1H), 3.83 (s, 3H), 2.49 – 2.39 (m, 1H), 2.16 – 1.94 (m, 2H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 162.6, 161.3, 145.5, 142.8, 128.5, 128.2, 127.5, 127.2, 127.1, 127.0, 125.9, 124.5, 107.5, 96.4, 95.5, 75.7, 60.0, 55.7, 43.0. **HRMS (ESI)** calculated for $C_{23}H_{22}NO_2^+$, $[M+H]^+$: 344.1645; found: 344.1644.

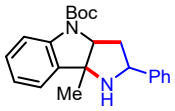
6.2 Diversification of indole.



Formation of 7a

Following the modified literature procedure, sodium borohydride ($NaBH_4$, 37.8 mg, 1.00 mmol) was gradually added to the **5ad** (69.7 mg, 0.20 mmol) in MeOH (2.0 mL) at 0°C. The mixture was stirred 12 h at room temperature. After the consumption of the reactant, water (10 mL) was added, and the mixture was extracted with EtOAc (2 x 10 mL). The organic layer was separated, and the combined organic extracts were washed with brine, and then dried over Na_2SO_4. The solvent was removed under reduced pressure, yielding the pure product 7a (49.8 mg, 71%). only one single diastereoisomer (>20:1 d.r.) was observed.

tert-butyl 8b-methyl-2-phenyl-2,3,3a,8b-tetrahydropyrrolo[3,2-*b*]indole-4(1*H*)-carboxylate (7a)

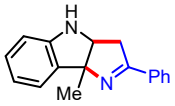


^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.95 – 7.23 (m, 8H), 7.03 (t, *J* = 7.4 Hz, 1H), 4.56 – 4.26 (m, 2H), 3.16 – 2.88 (m, 1H), 2.00 (s, 1H), 1.83 (t, *J* = 12.2, 7.4 Hz, 1H), 1.59 (s, 3H), 1.56(s, 9H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 152.5, 149.1, 141.3, 136.5, 129.1, 128.6, 127.6, 126.8, 123.4, 122.9, 115.3, 81.0, 72.2, 69.0, 61.1, 46.0, 28.6, 27.1. **HRMS (ESI)** calculated for $C_{22}H_{27}N_2O_2^+$, $[M+H]^+$: 351.2067; found: 351.2067.

Formation of 7b

Following the modified literature procedure, the **5ad** (68.3 mg, 0.20 mmol) was dissolved into CH_2Cl_2 (2.0 mL), TFA (200 μL) were added. Then, the resulting mixture was stirred at room temperature for 2 h until the completion of reaction as monitored by TLC analysis. 20 mL $NaHCO_3$ (aq.) and 20 mL CH_2Cl_2 were added, the layers were separated, and the aqueous layer extracted with CH_2Cl_2 (3×20 mL). The combined organic layers were dried over Na_2SO_4, filtered, and concentrated in vacuo. The product was without purified, directly to give the desired product **7b** (39.7 mg) in 65% yield.

8b-methyl-2-phenyl-3,3a,4,8b-tetrahydropyrrolo[3,2-*b*]indole (7b)



^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.81 (d, *J* = 7.9, 1.8 Hz, 2H), 7.46 (d, *J* = 7.4, 1.3 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.09 (t, *J* = 7.6, 1.3 Hz, 1H), 6.81 (t, *J* = 7.4, 1.0 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 1H), 4.25 (dd, *J* = 6.4, 1.5 Hz, 1H), 3.35 (dd, *J* = 17.4, 6.4 Hz, 1H), 3.18 (d, *J* = 17.4, 1.5 Hz, 1H), 1.68 (s, 3H). **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 169.5, 150.2, 134.5, 131.9, 130.6, 128.9, 128.4, 128.1, 124.3, 119.1, 109.4, 86.4, 66.0, 44.5, 24.8. **HRMS (ESI)** calculated for $C_{17}H_{17}N_2^+$, $[M+H]^+$: 249.1386; found: 249.1381.

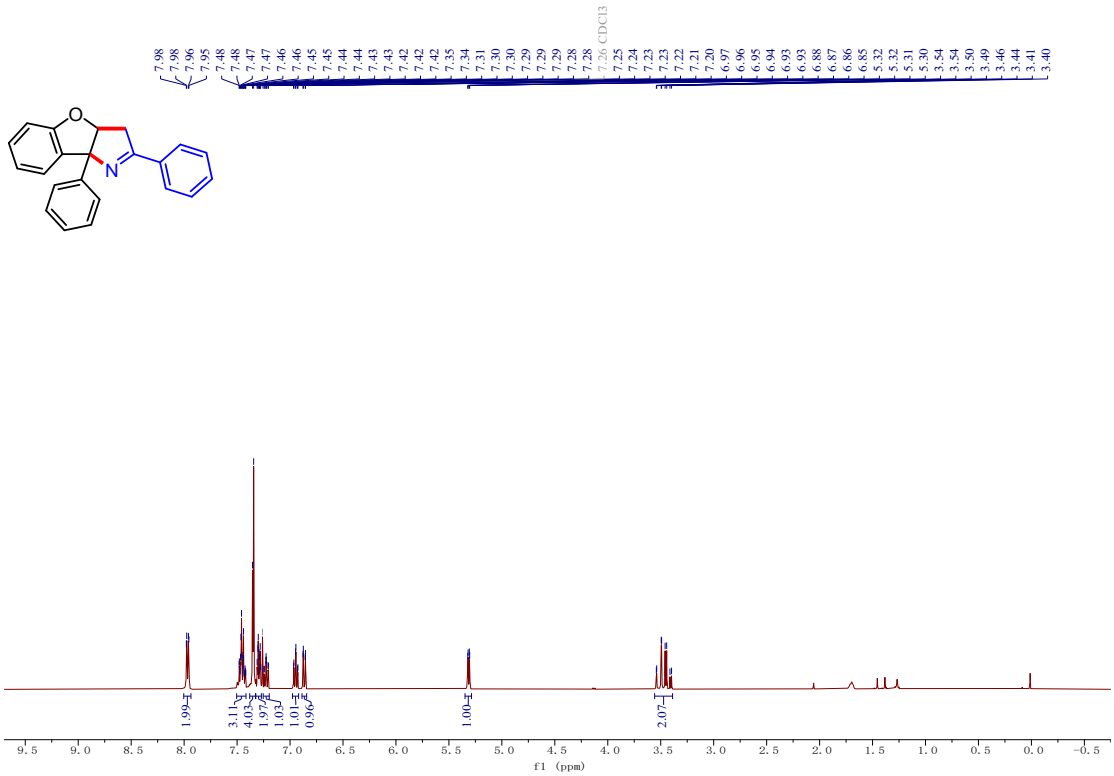
7. References

1 (a) G. A. Kraus* and J. D. Schroeder, *Synlett*, 2005, 2504-2506; (b) L. Nie, J. Yang, Z. Liu, S.

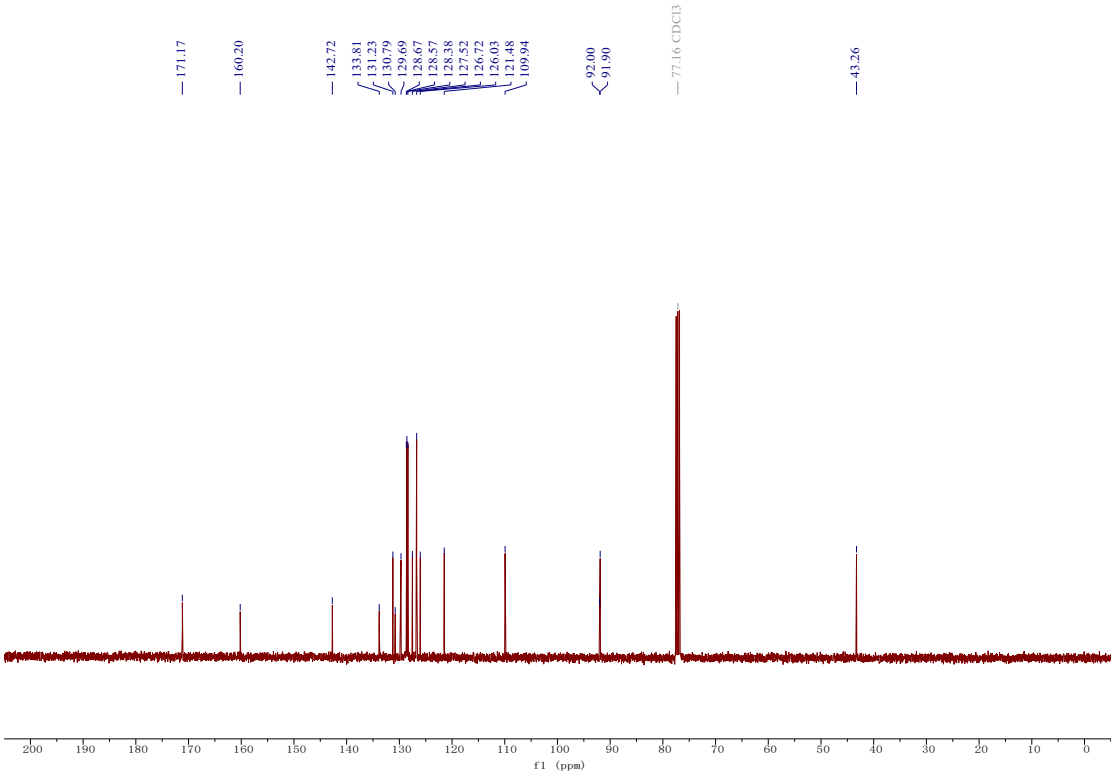
Zhou, S. Chen, X. Qi, A. Lei and H. Yi, *J. Am. Chem. Soc.*, 2024, **146**, 31330-31338.
2 I. Kim, S.-H. Lee and S. Lee, *Tetrahedron Lett.*, 2008, **49**, 6579-6584.
3 F. Zhang, H. S. Sasmal, C. G. Daniliuc and F. Glorius, *J. Am. Chem. Soc.*, 2023, **145**, 15695-15701.
4 J. Wu, Z. Peng, T. Shen and Z.-Q. Liu, *Adv. Synth. Catal.*, 2022, **364**, 2565-2570.
5 S. Yadav and S. S. V. Ramasastry, *Chem. Commun.*, 2021, **57**, 77-80.
6 Z. Liu, P. Liao and X. Bi, *Org. Lett.*, 2014, **16**, 3668-3671.

8. Spectra Data

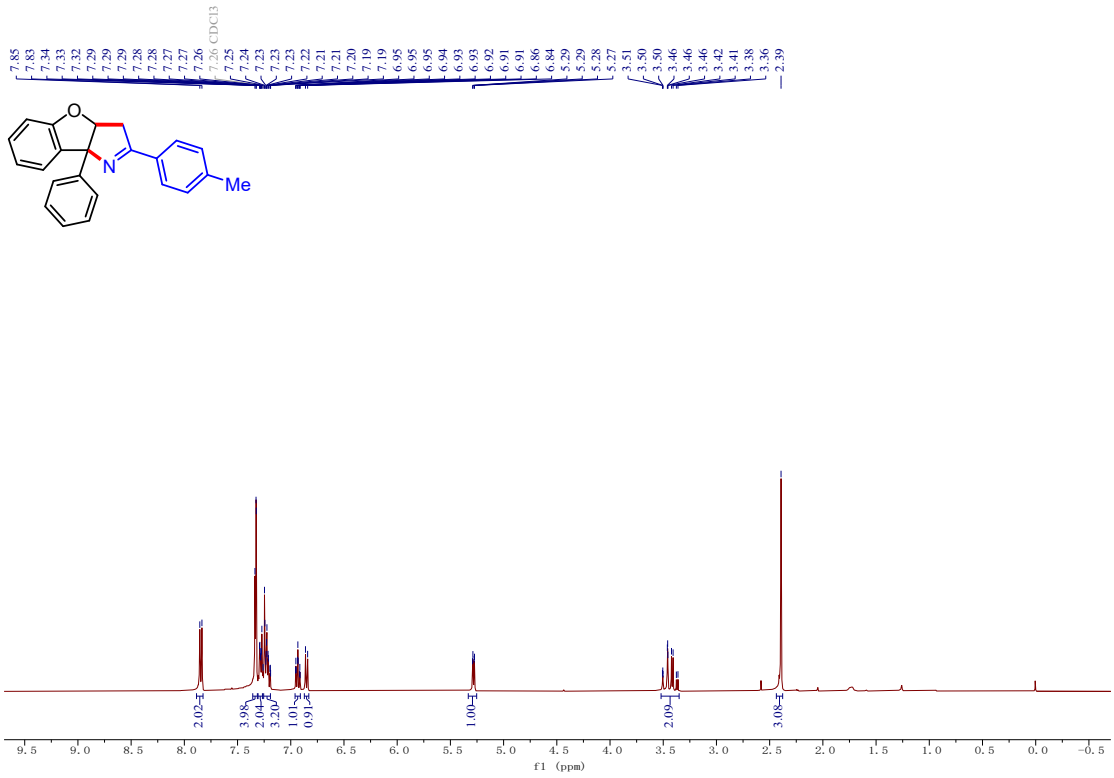
^{1}H NMR spectra of 3aa ($CDCl_3$, 400 MHz)



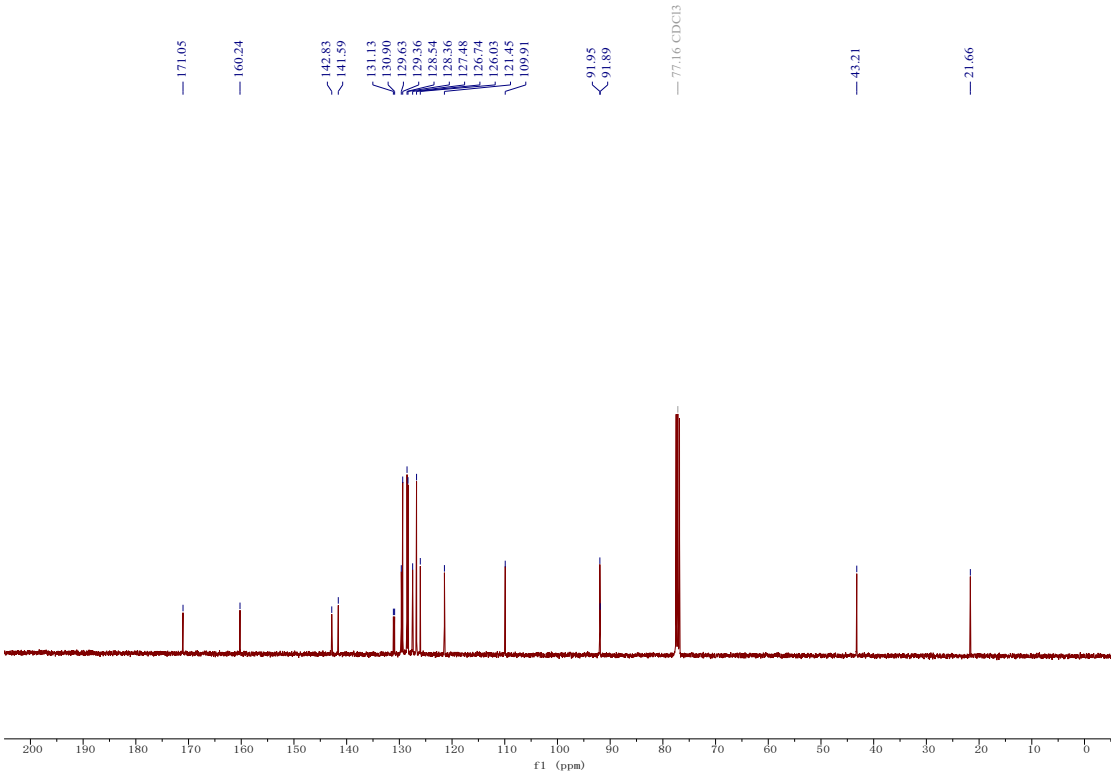
^{13}C NMR spectra of 3aa ($CDCl_3$, 101 MHz)



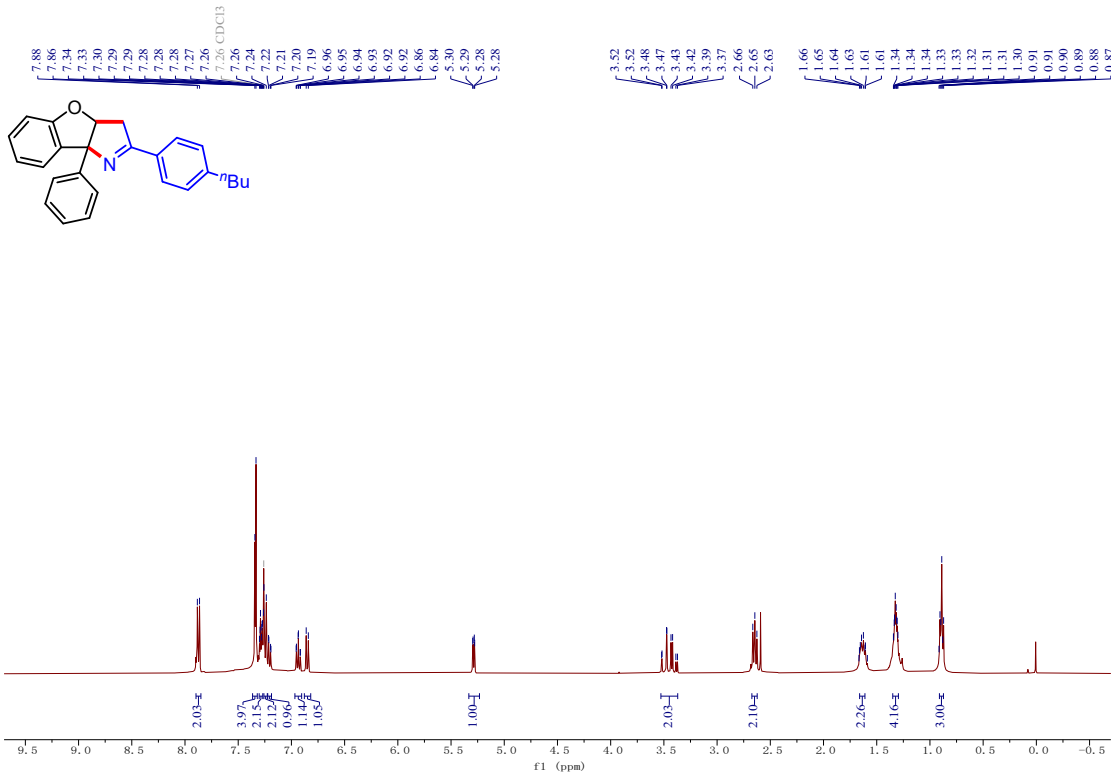
^{1}H NMR spectra of 3ab ($CDCl_3$, 400 MHz)



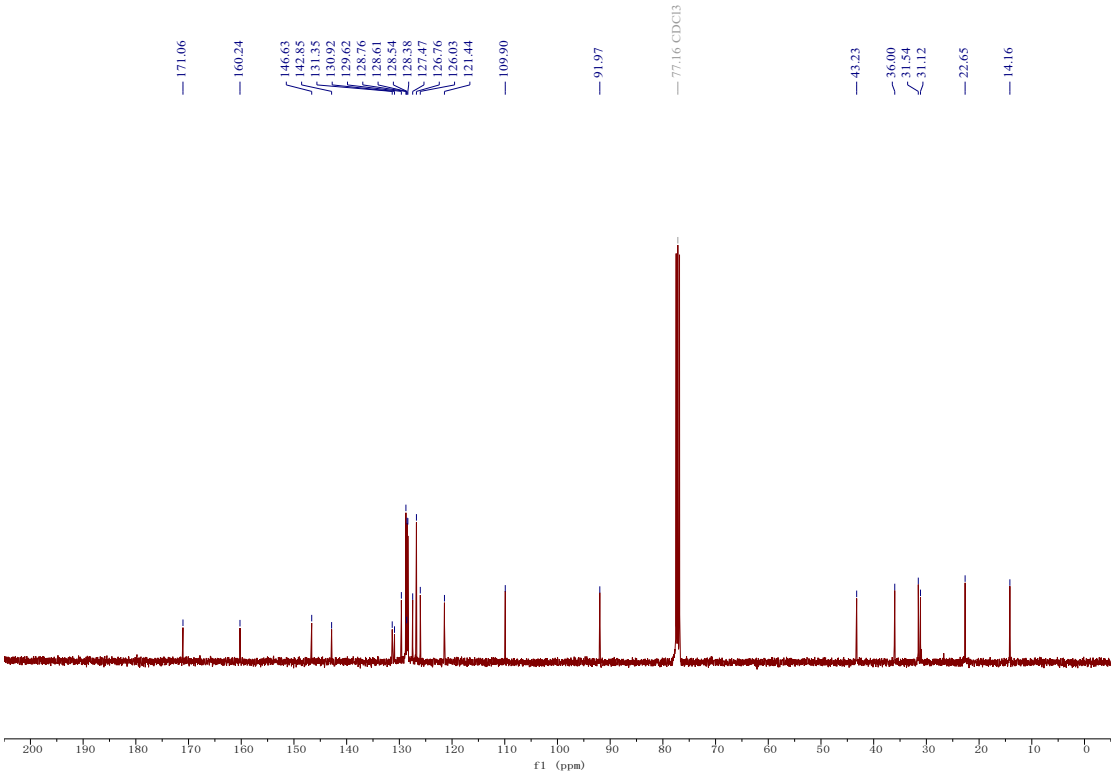
^{13}C NMR spectra of 3ab ($CDCl_3$, 101 MHz)



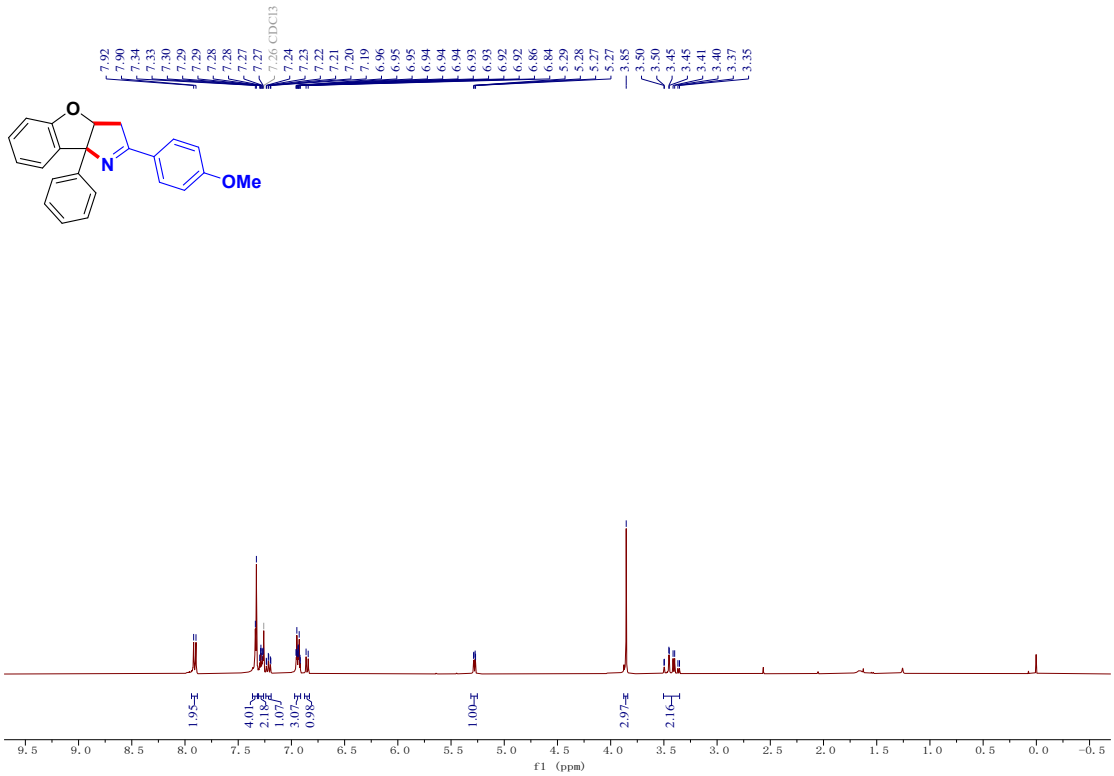
^{1}H NMR spectra of 3ac ($CDCl_3$, 400 MHz)



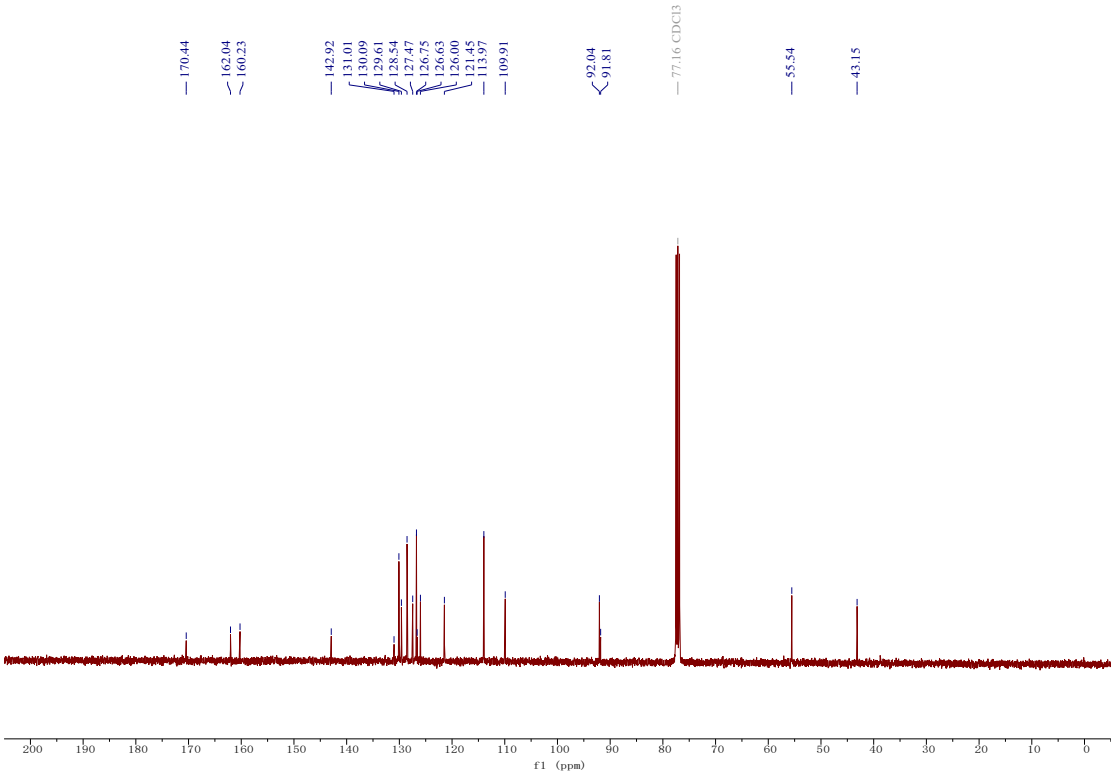
^{13}C NMR spectra of 3ac ($CDCl_3$, 101 MHz)



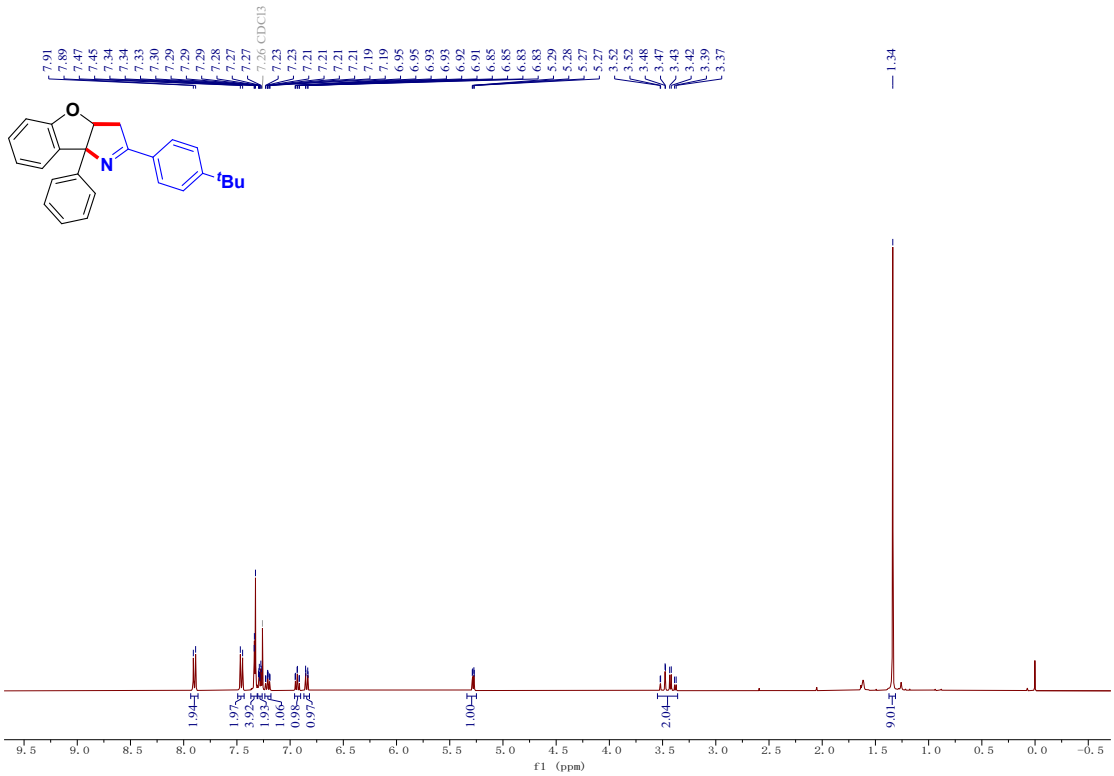
^{1}H NMR spectra of 3ad ($CDCl_3$, 400 MHz)



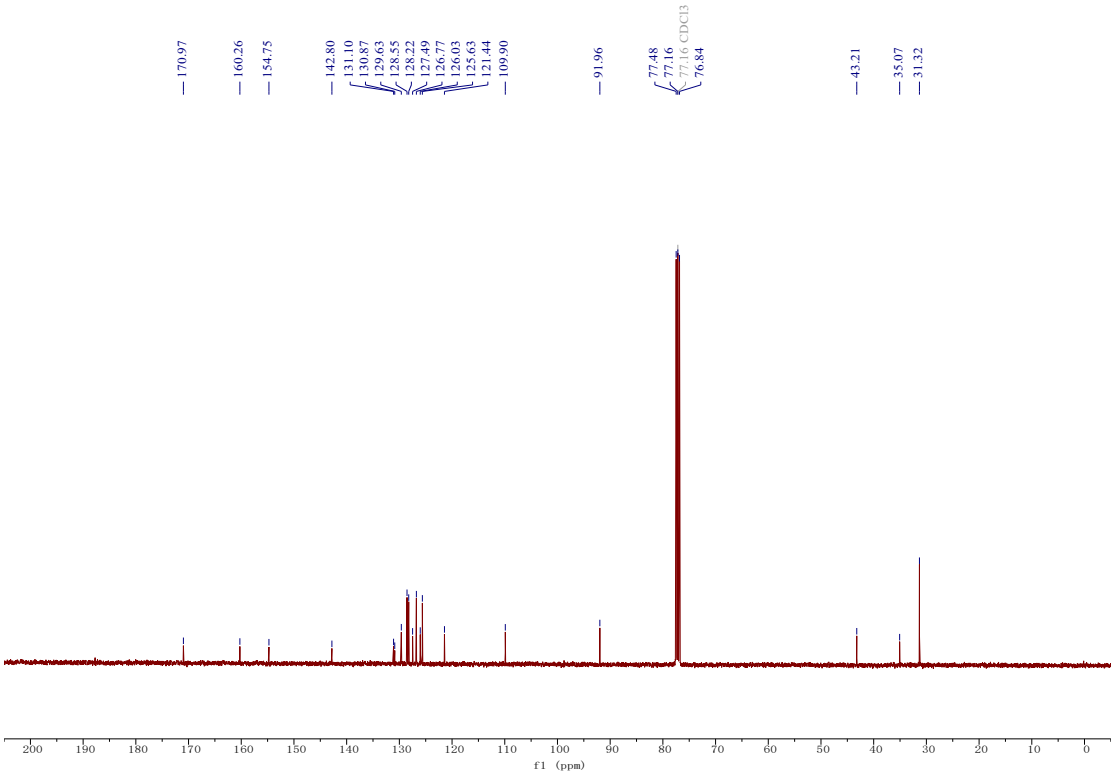
^{13}C NMR spectra of 3ad ($CDCl_3$, 101 MHz)



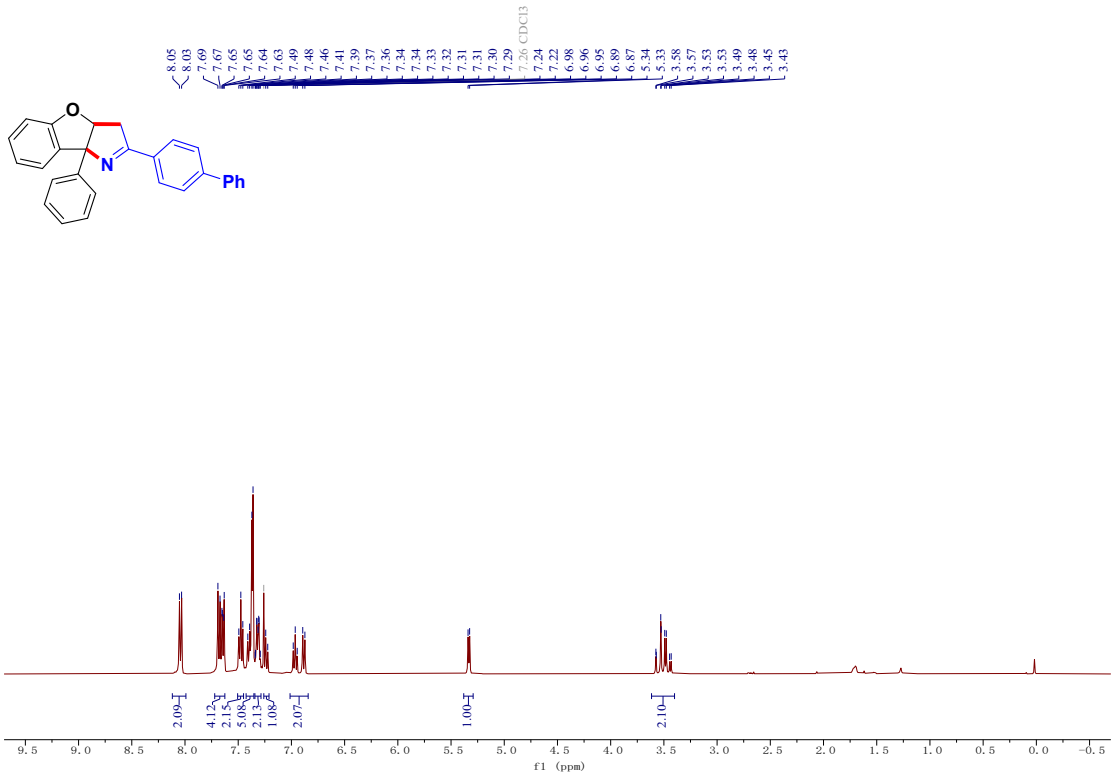
^{1}H NMR spectra of 3ae ($CDCl_3$, 400 MHz)



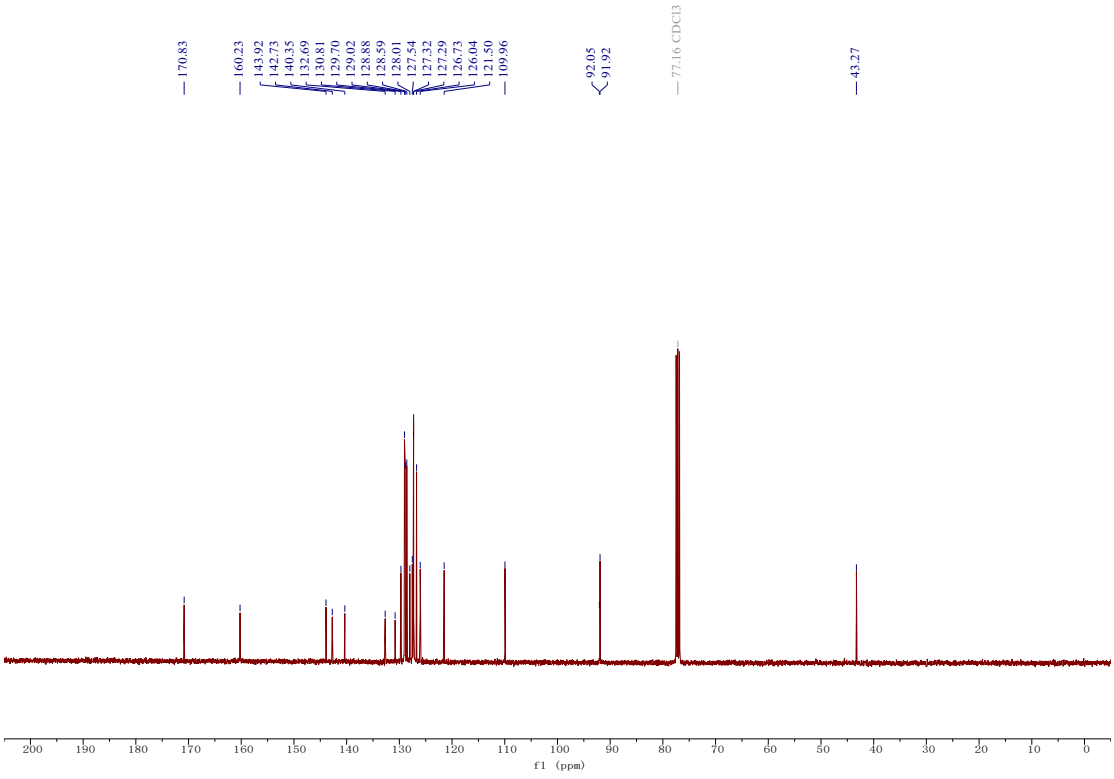
^{13}C NMR spectra of 3ae ($CDCl_3$, 101 MHz)



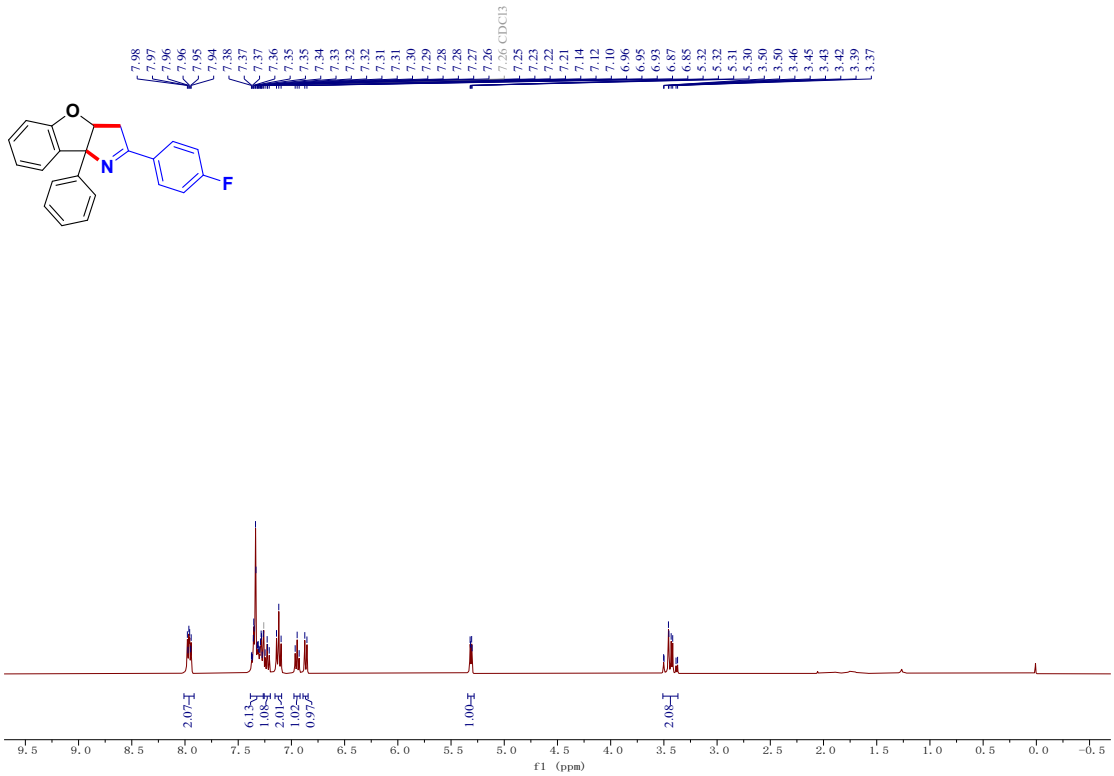
^{1}H NMR spectra of 3af ($CDCl_3$, 400 MHz)



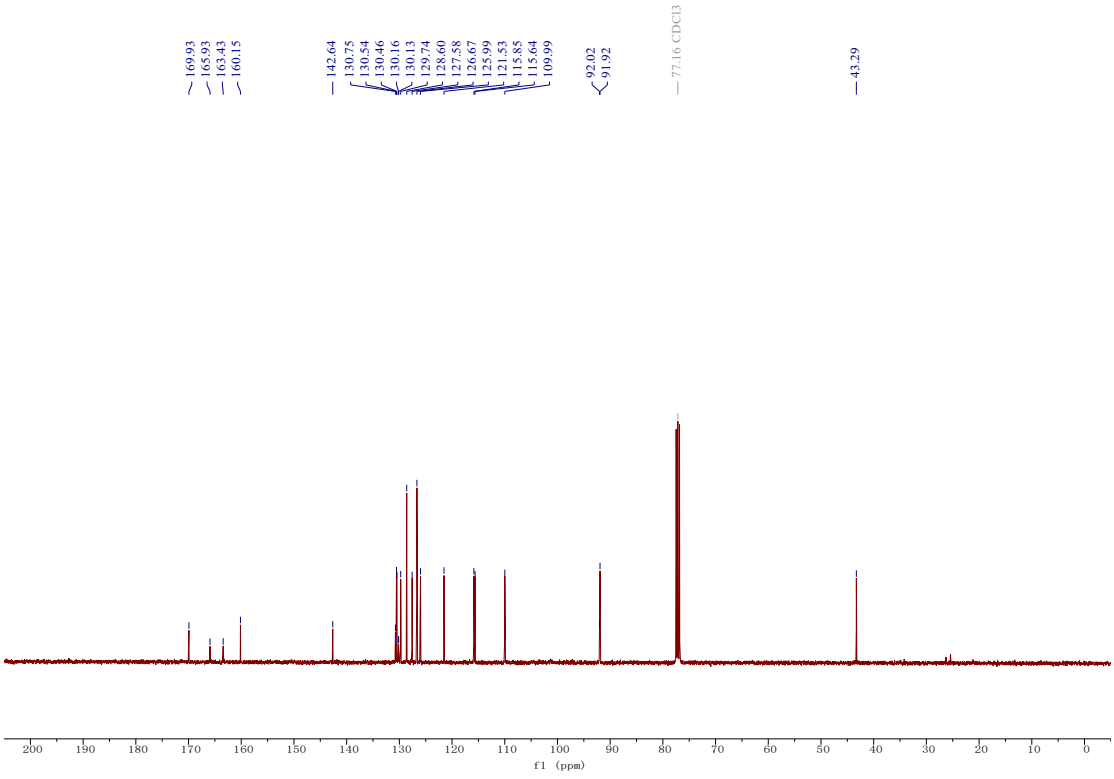
^{13}C NMR spectra of 3af ($CDCl_3$, 101 MHz)



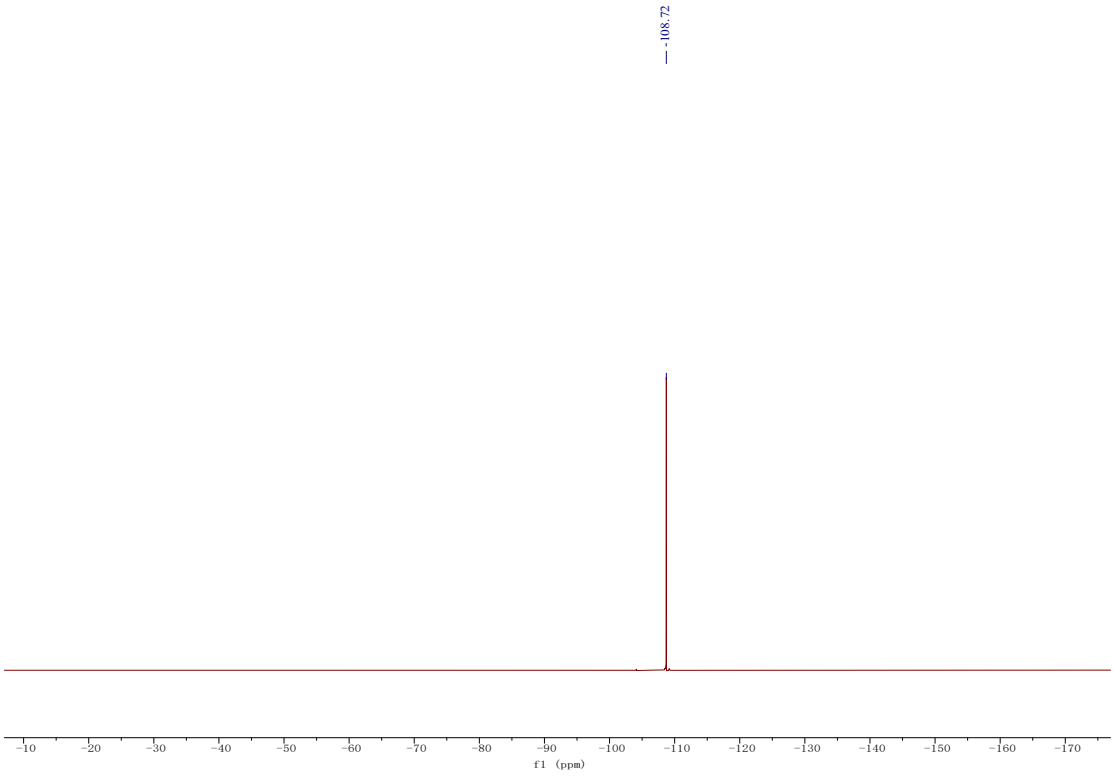
^{1}H NMR spectra of 3ag ($CDCl_3$, 400 MHz)



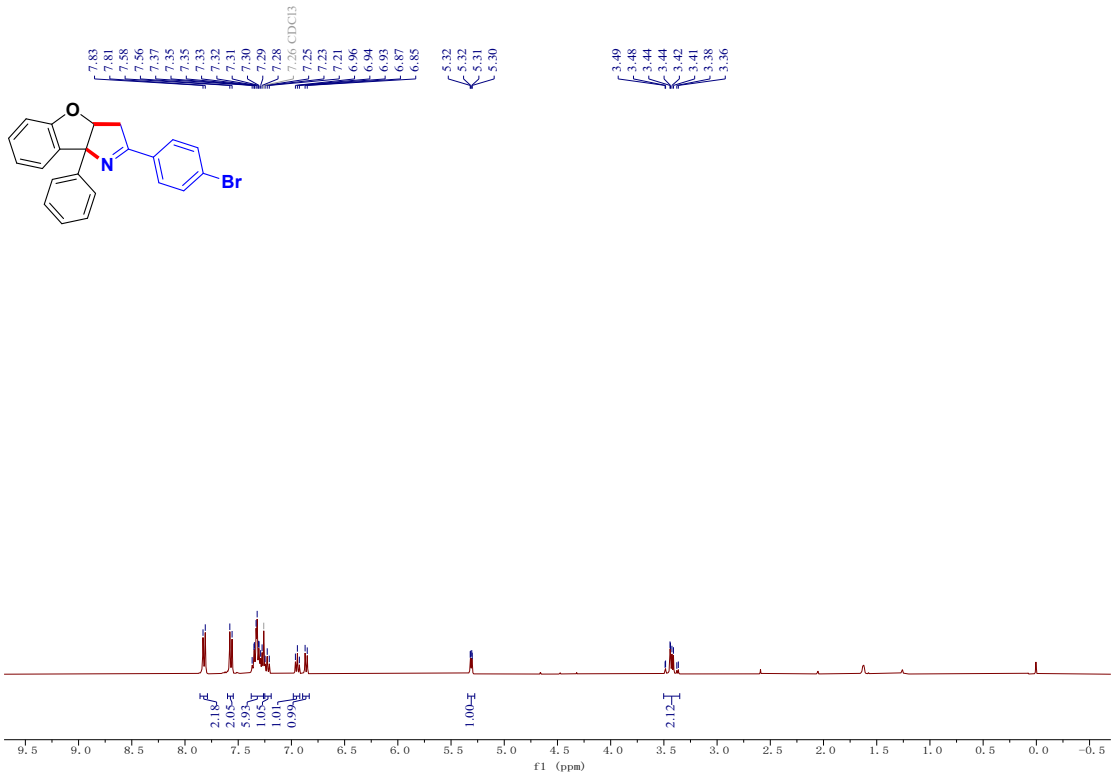
^{13}C NMR spectra of 3ag ($CDCl_3$, 101 MHz)



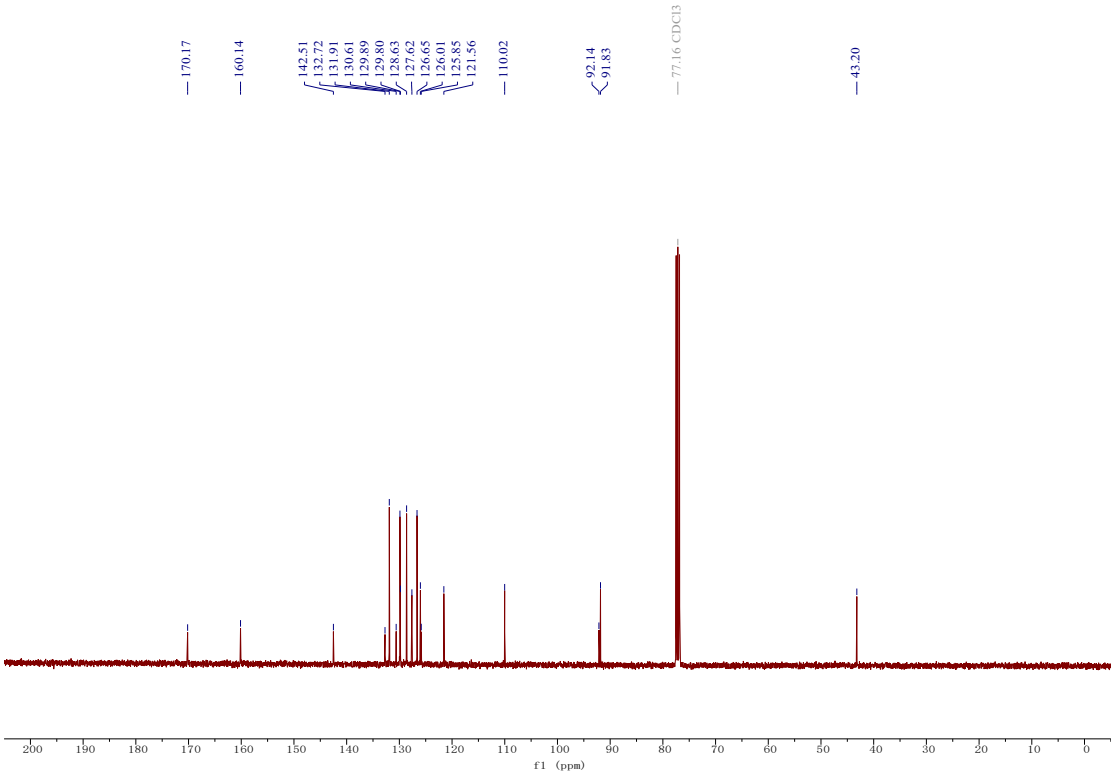
^{19}F NMR spectra of 3ag ($CDCl_3$, 376 MHz)



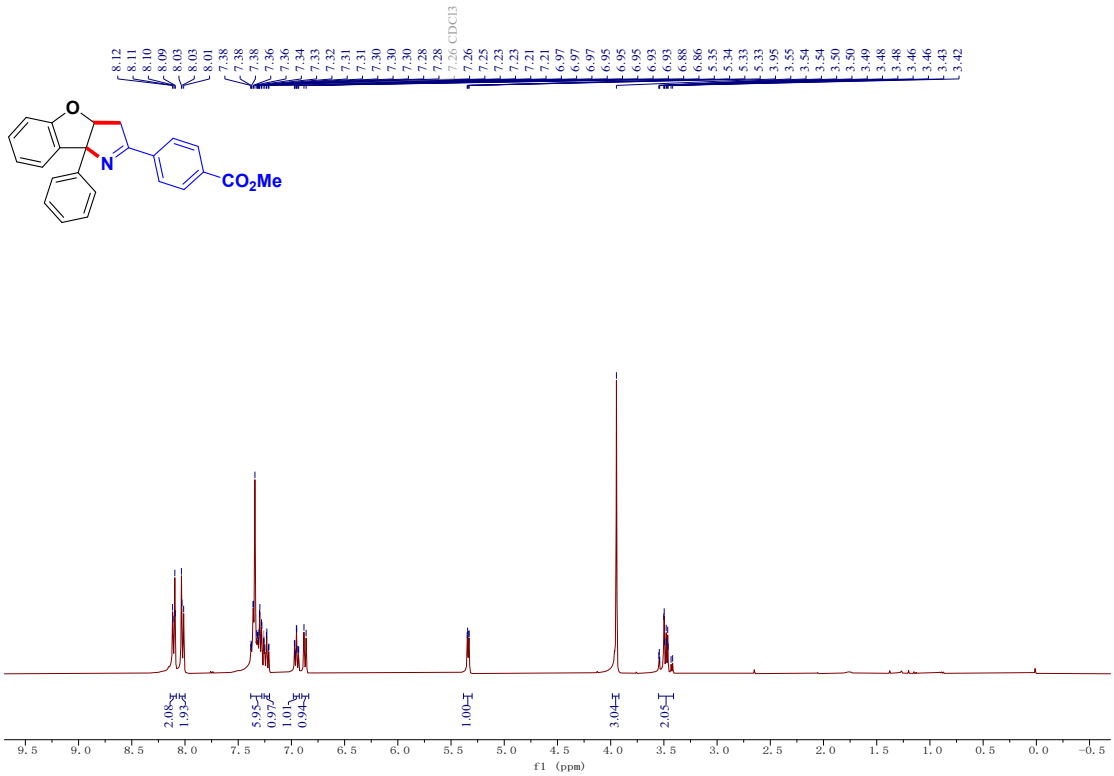
^{1}H NMR spectra of 3ah ($CDCl_3$, 400 MHz)



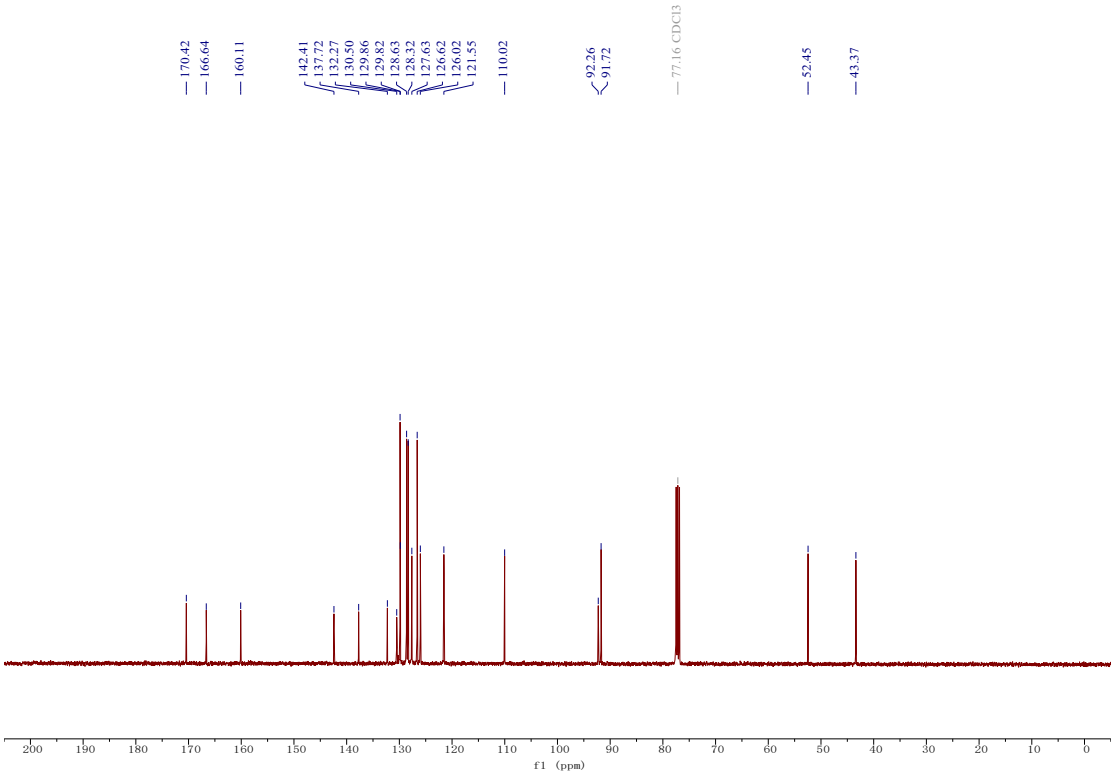
^{13}C NMR spectra of 3ah ($CDCl_3$, 101 MHz)



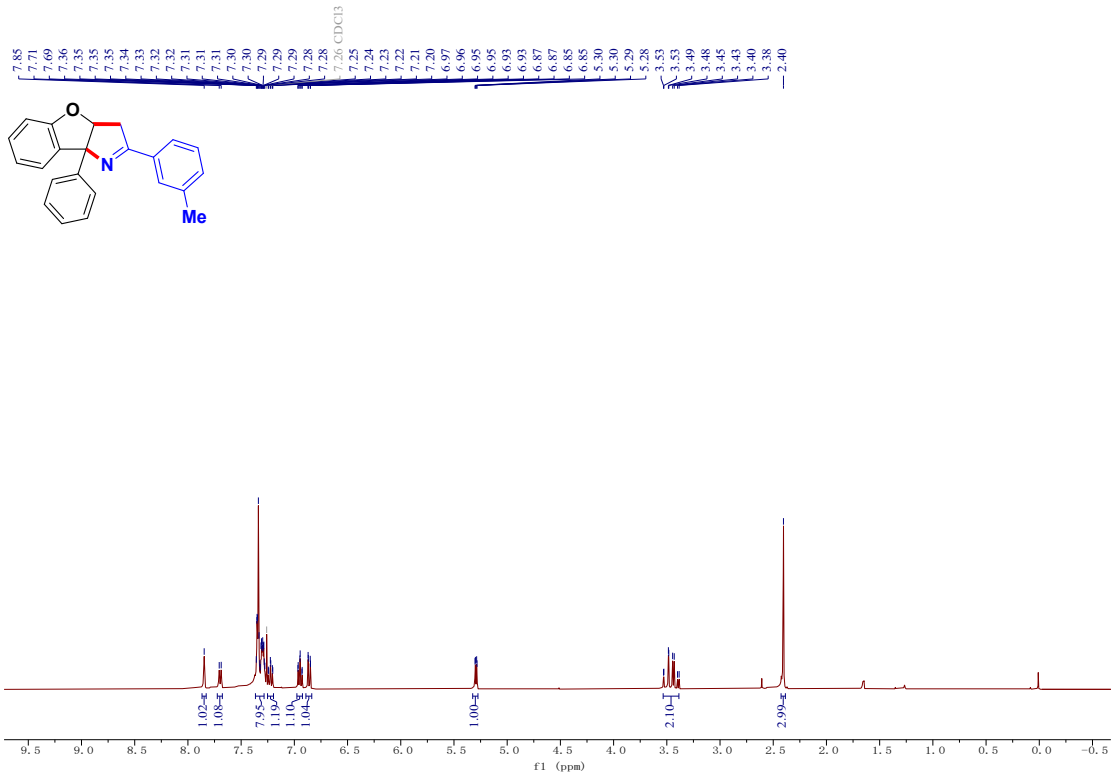
^{1}H NMR spectra of 3ai ($CDCl_3$, 400 MHz)



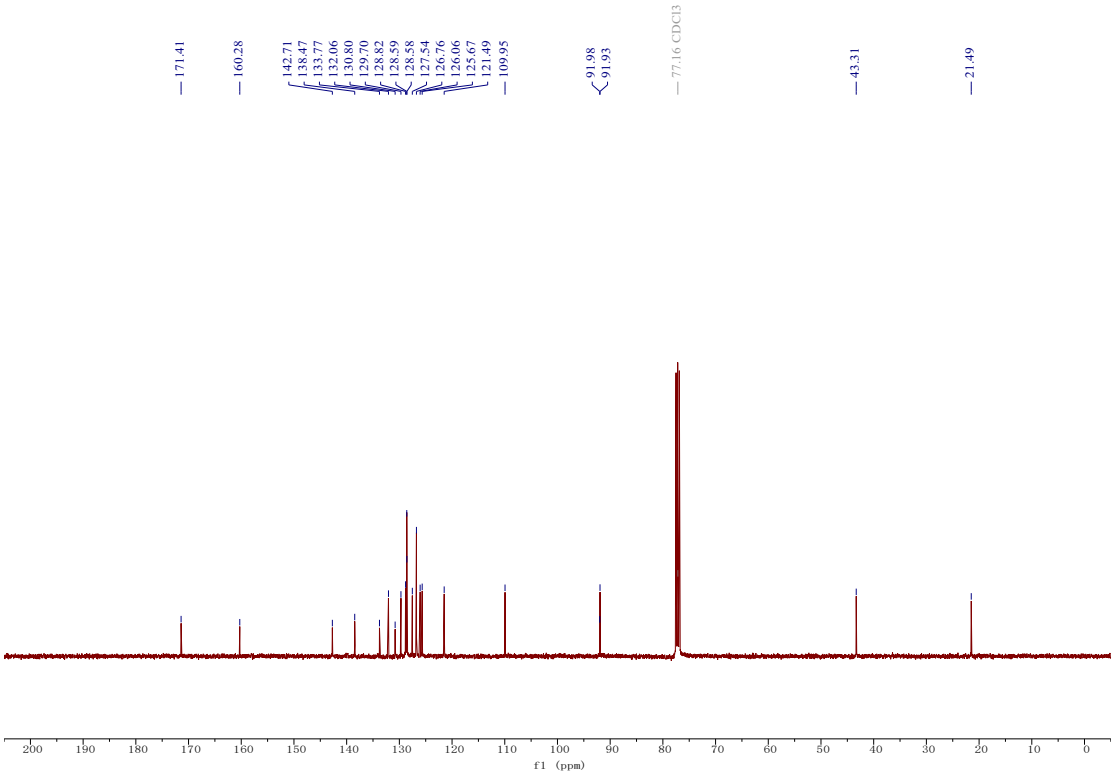
^{13}C NMR spectra of 3ai ($CDCl_3$, 101 MHz)



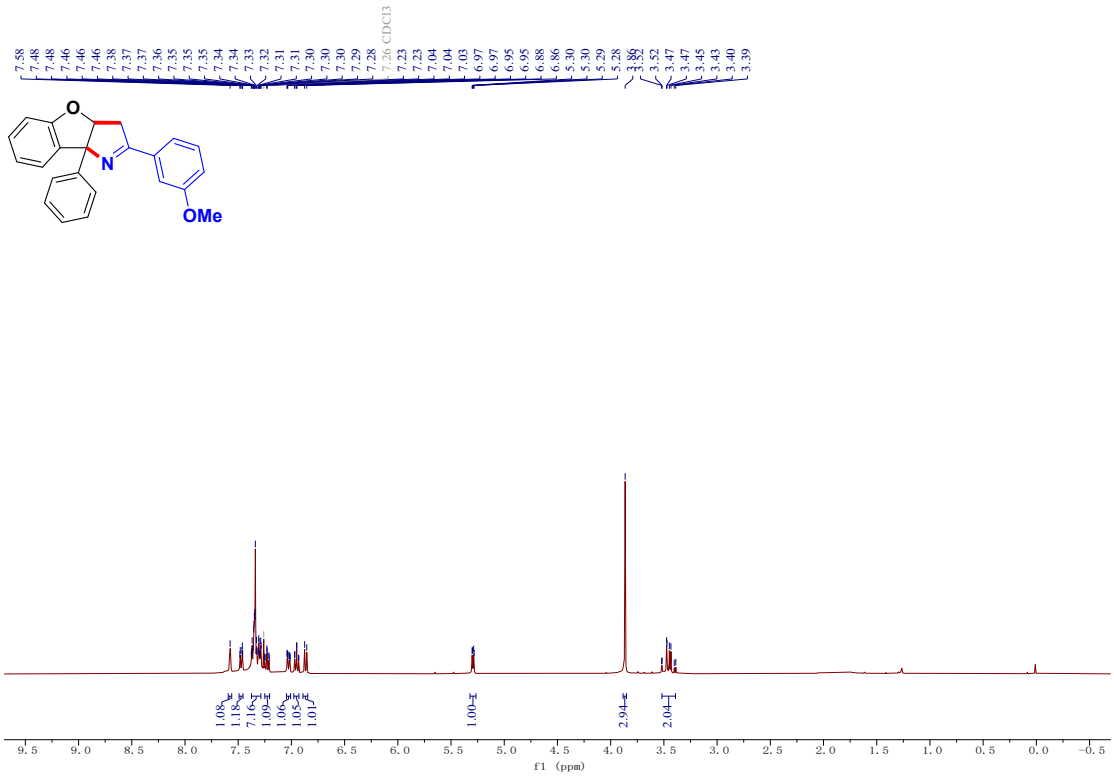
^{1}H NMR spectra of 3aj ($CDCl_3$, 400 MHz)



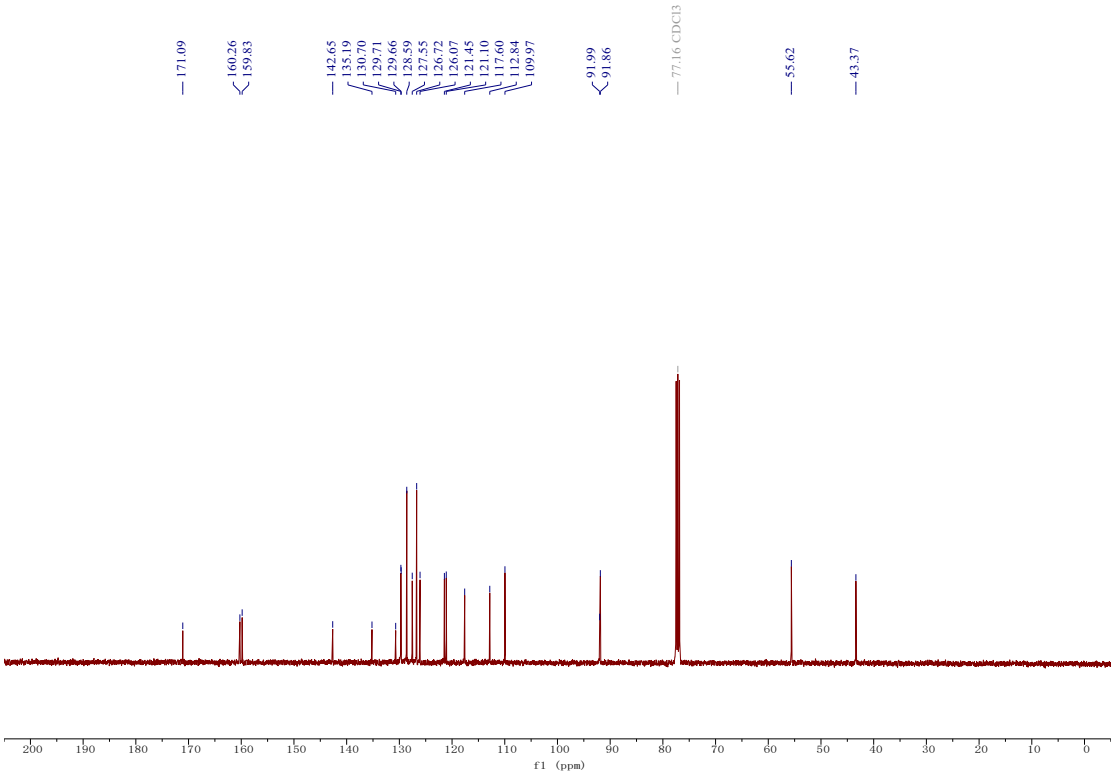
^{13}C NMR spectra of 3aj ($CDCl_3$, 101 MHz)



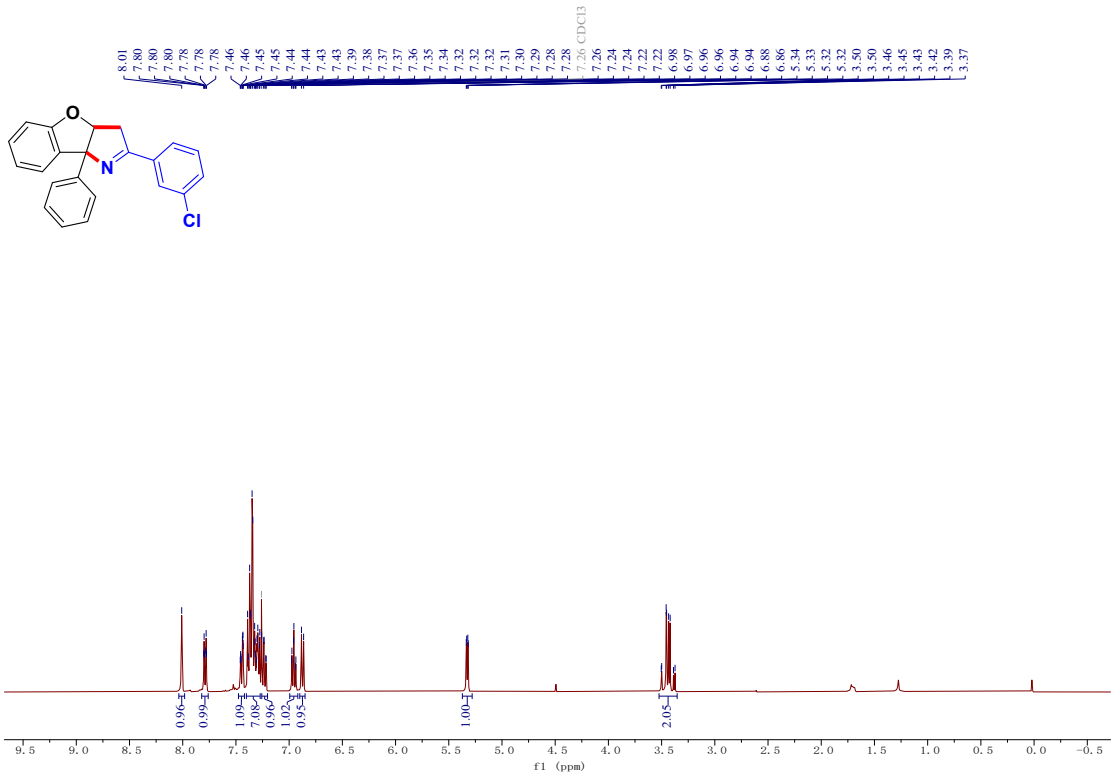
^{1}H NMR spectra of 3ak ($CDCl_3$, 400 MHz)



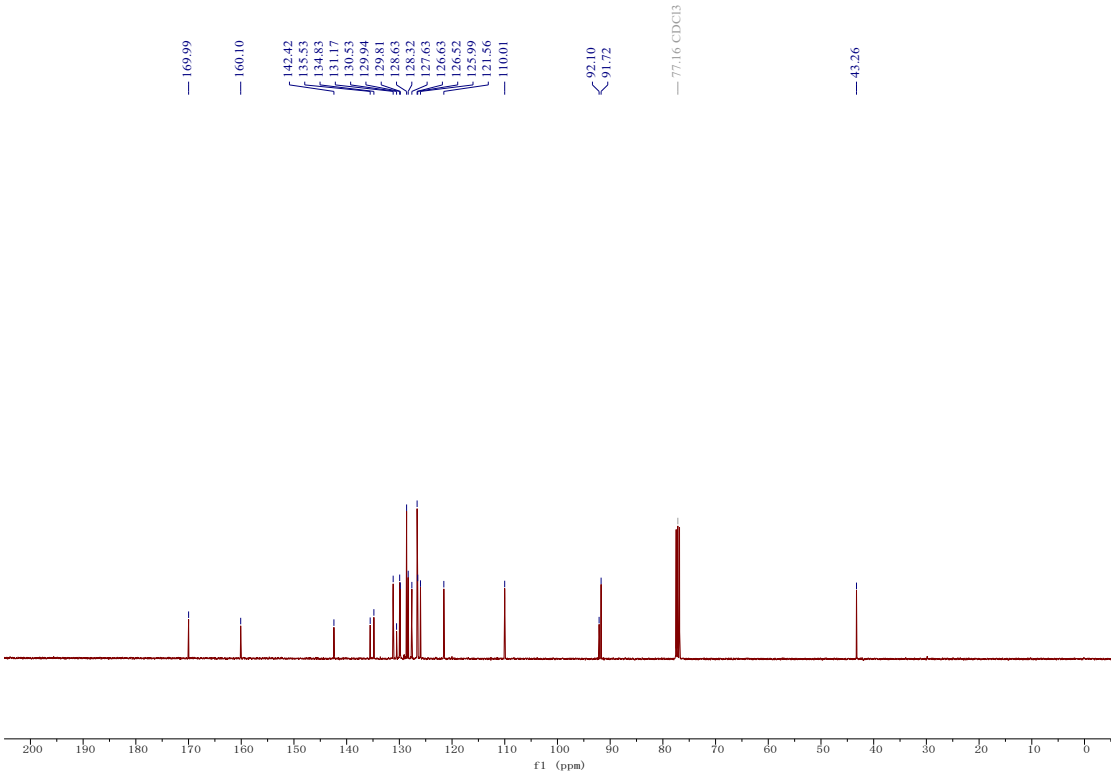
^{13}C NMR spectra of 3ak ($CDCl_3$, 101 MHz)



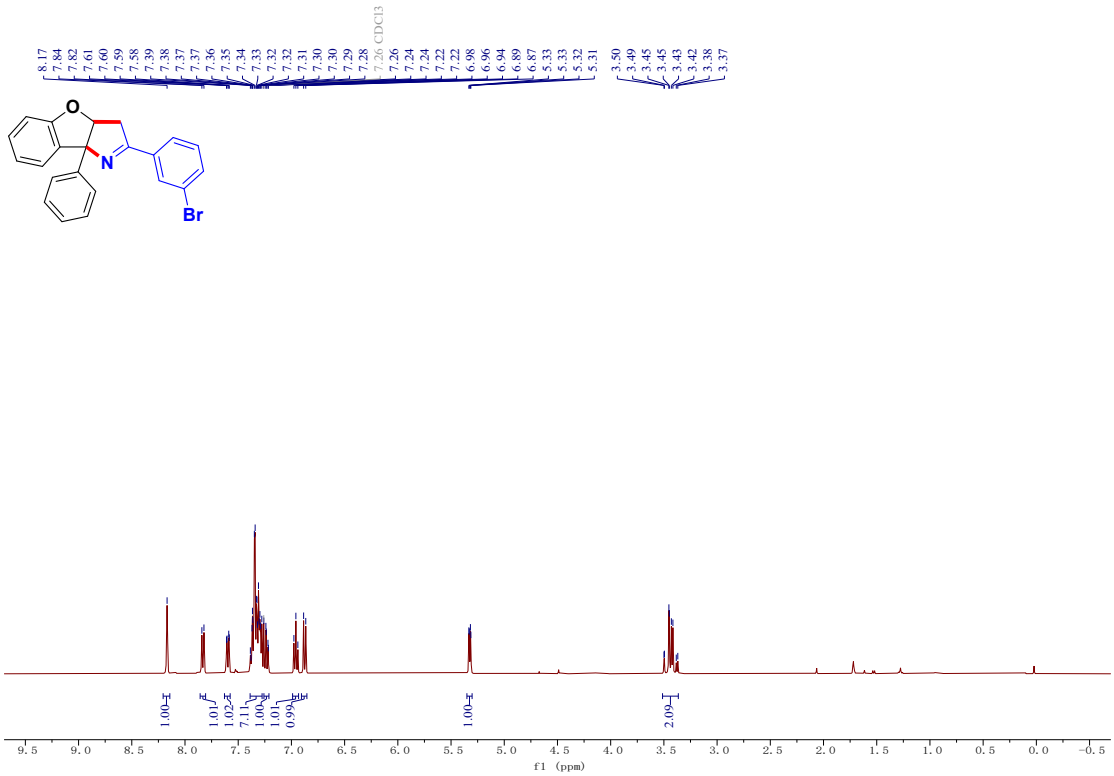
^{1}H NMR spectra of 3al ($CDCl_3$, 400 MHz)



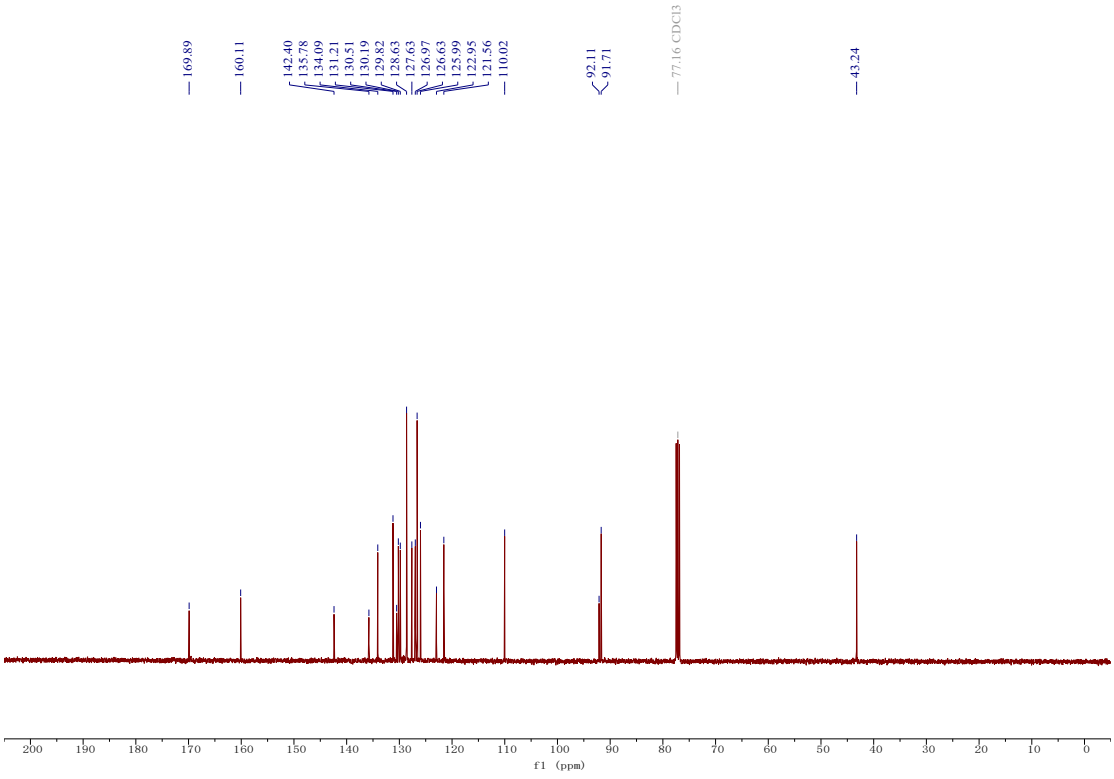
^{13}C NMR spectra of 3al ($CDCl_3$, 101 MHz)



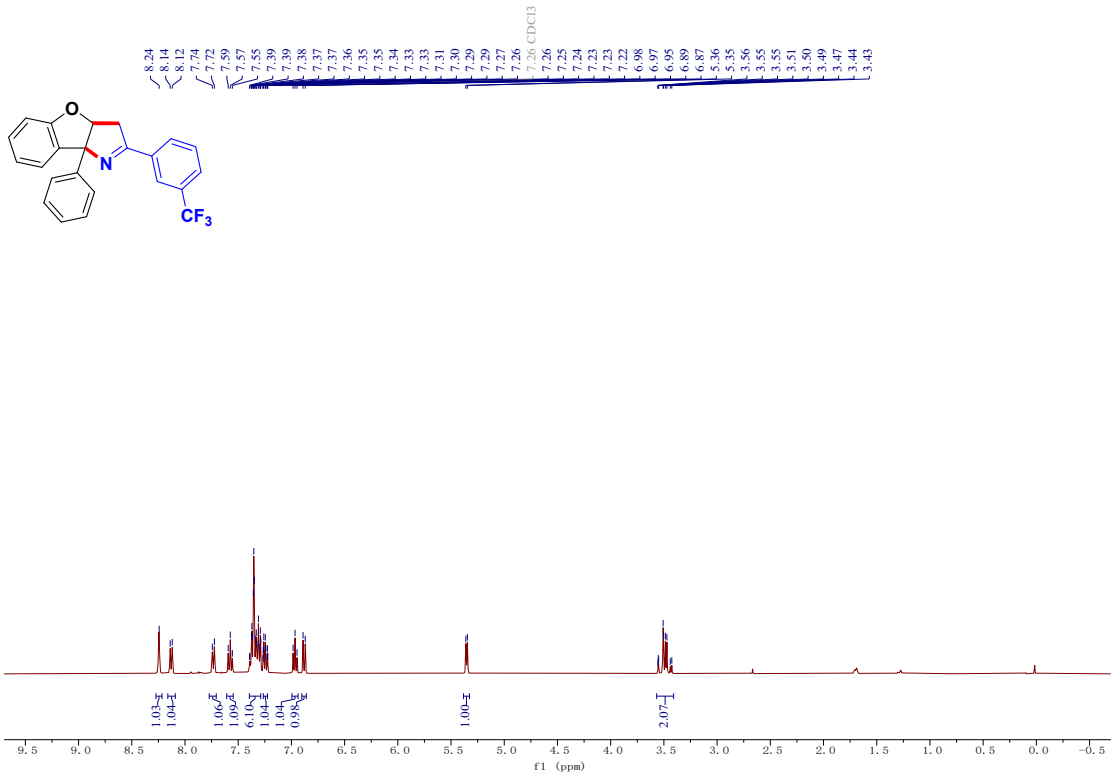
^{1}H NMR spectra of 3am ($CDCl_3$, 400 MHz)



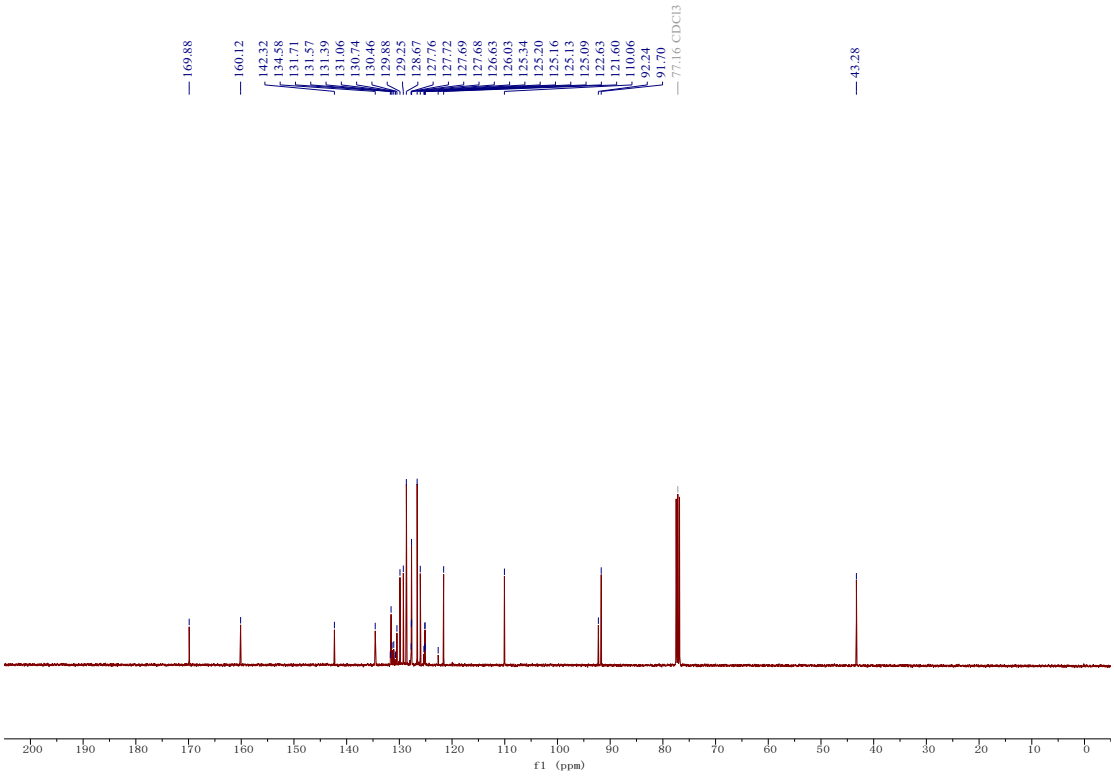
^{13}C NMR spectra of 3am ($CDCl_3$, 101 MHz)



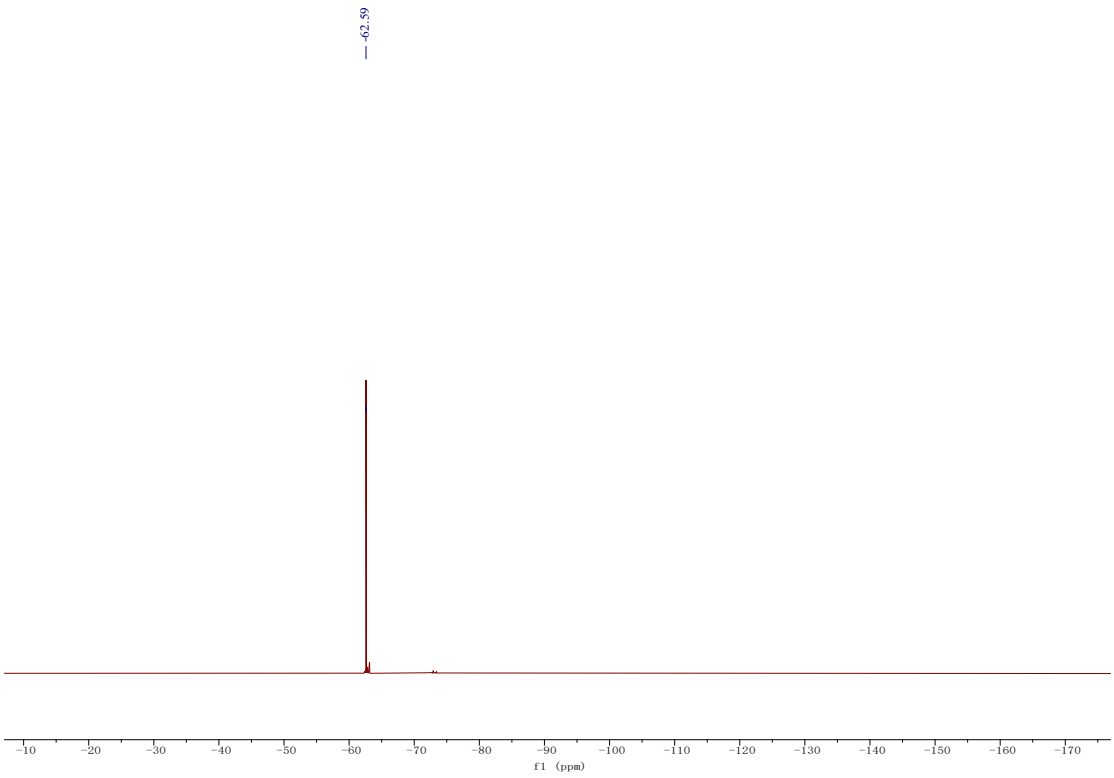
^{1}H NMR spectra of 3an ($CDCl_3$, 400 MHz)



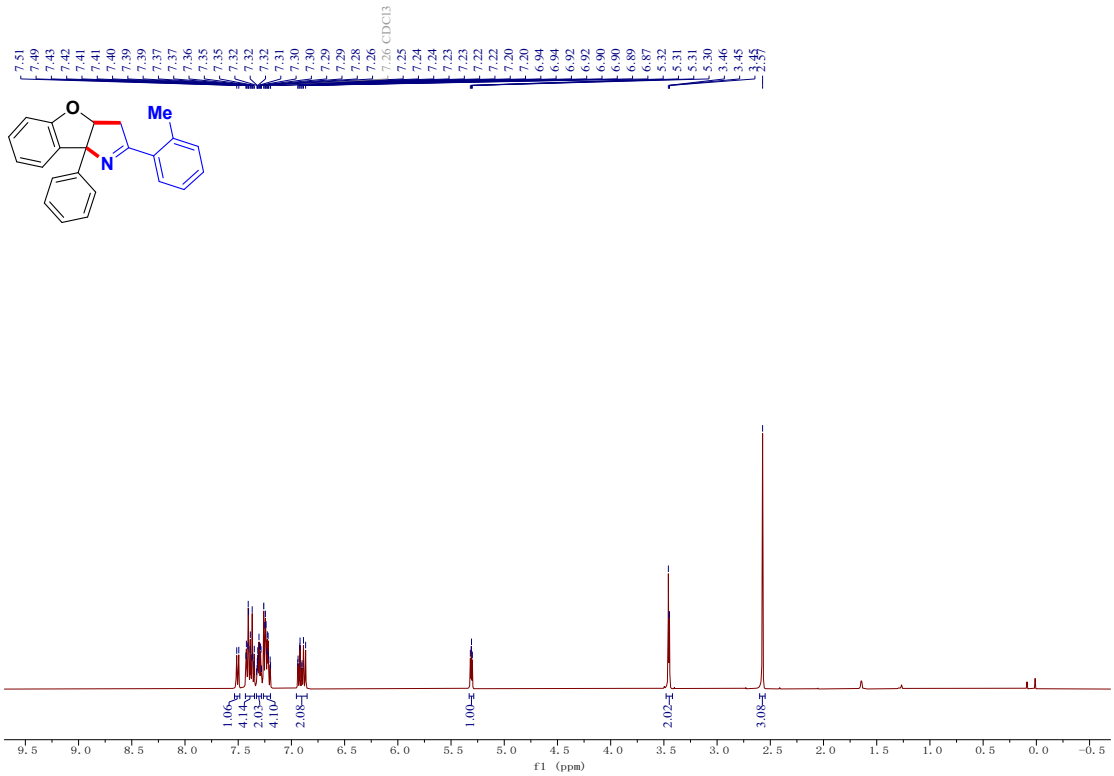
^{13}C NMR spectra of 3an ($CDCl_3$, 101 MHz)



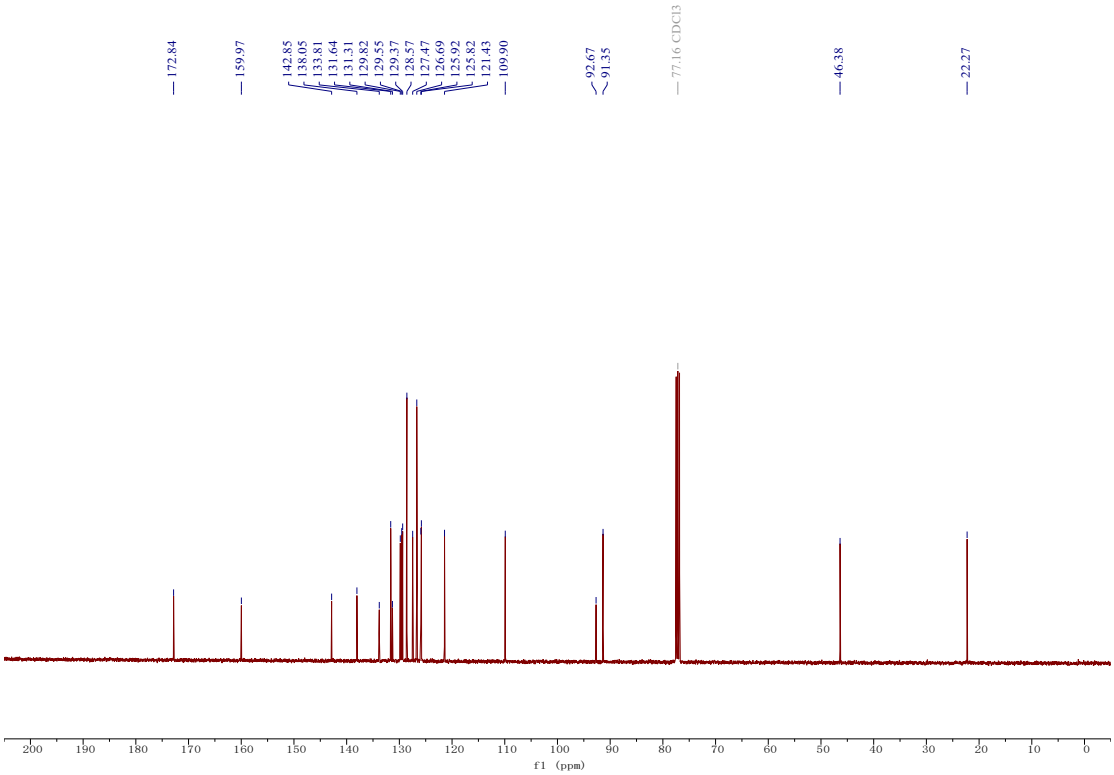
^{19}F NMR spectra of 3an ($CDCl_3$, 376 MHz)



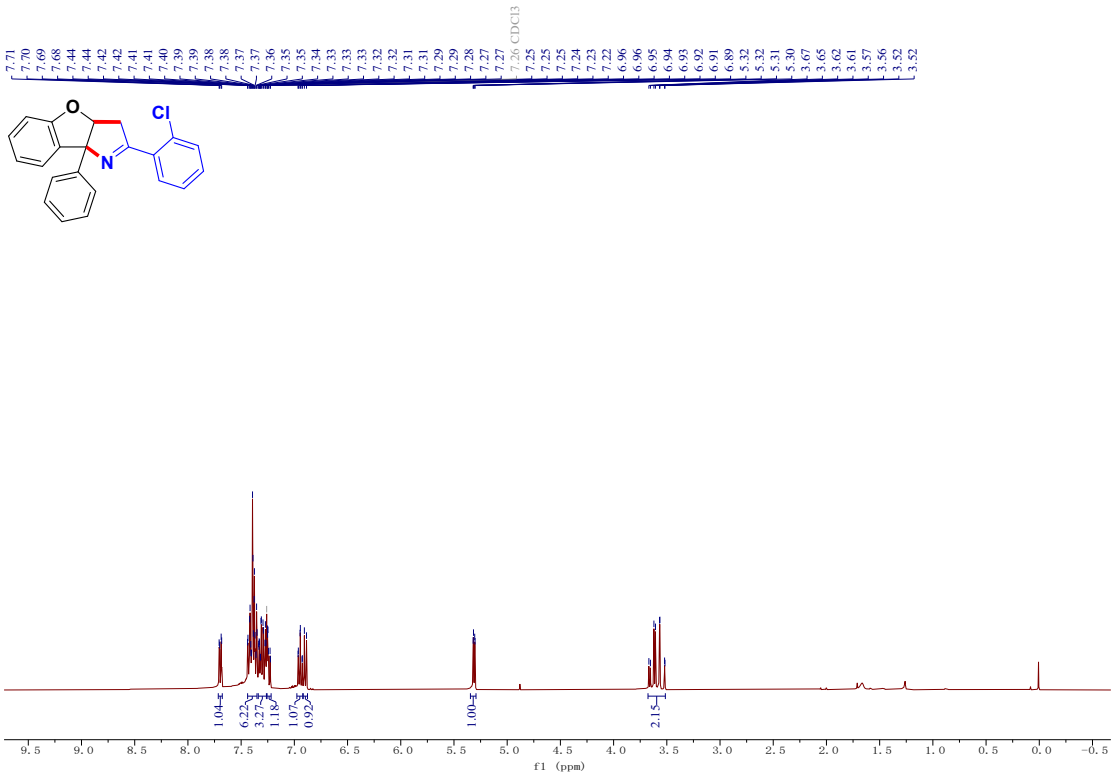
^{1}H NMR spectra of 3ao ($CDCl_3$, 400 MHz)



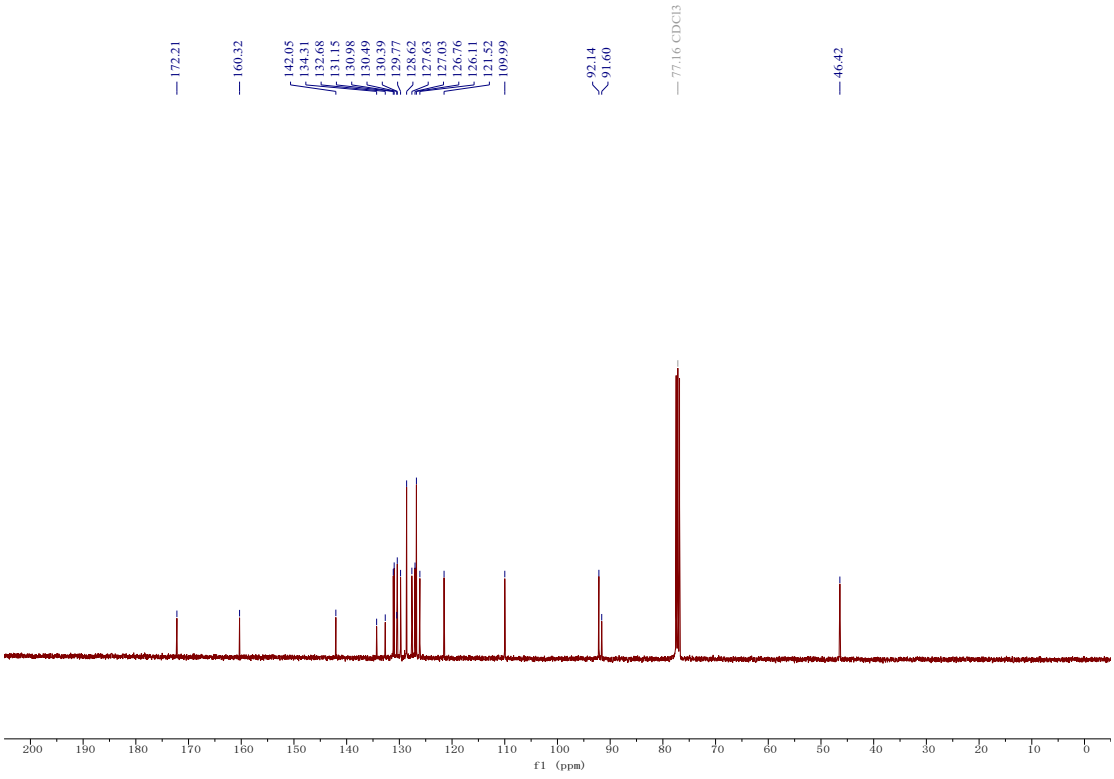
^{13}C NMR spectra of 3ao ($CDCl_3$, 101 MHz)



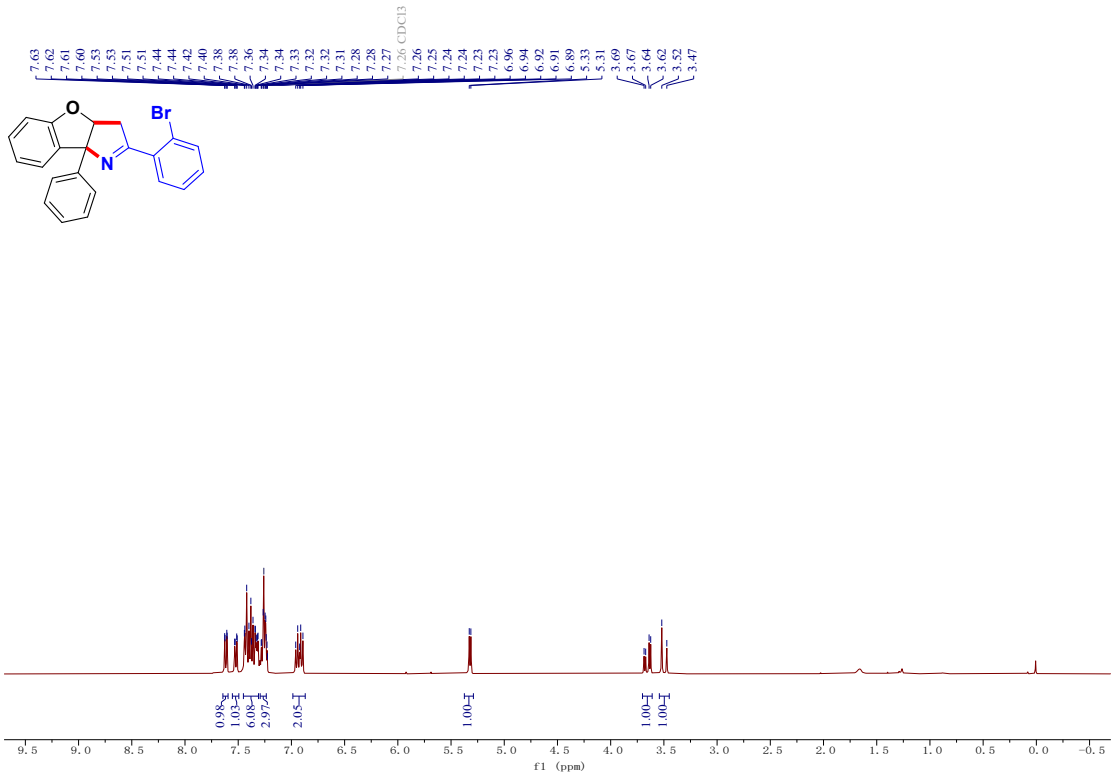
^{1}H NMR spectra of 3ap ($CDCl_3$, 400 MHz)



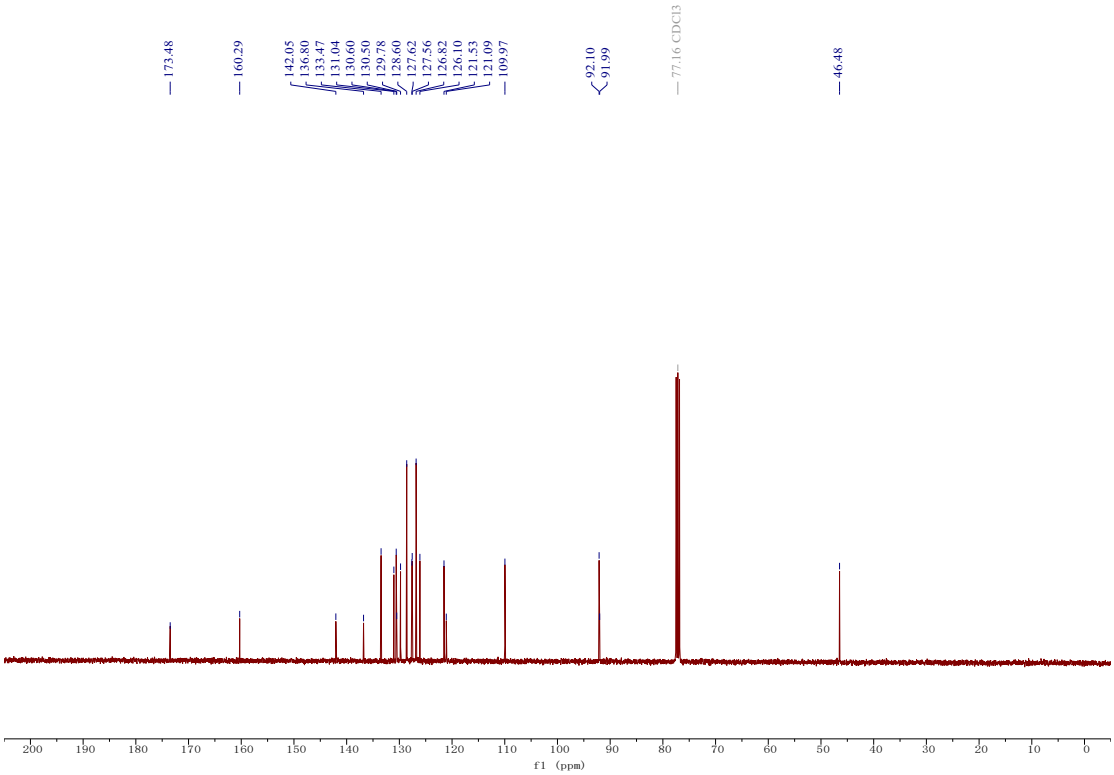
^{13}C NMR spectra of 3ap ($CDCl_3$, 101 MHz)



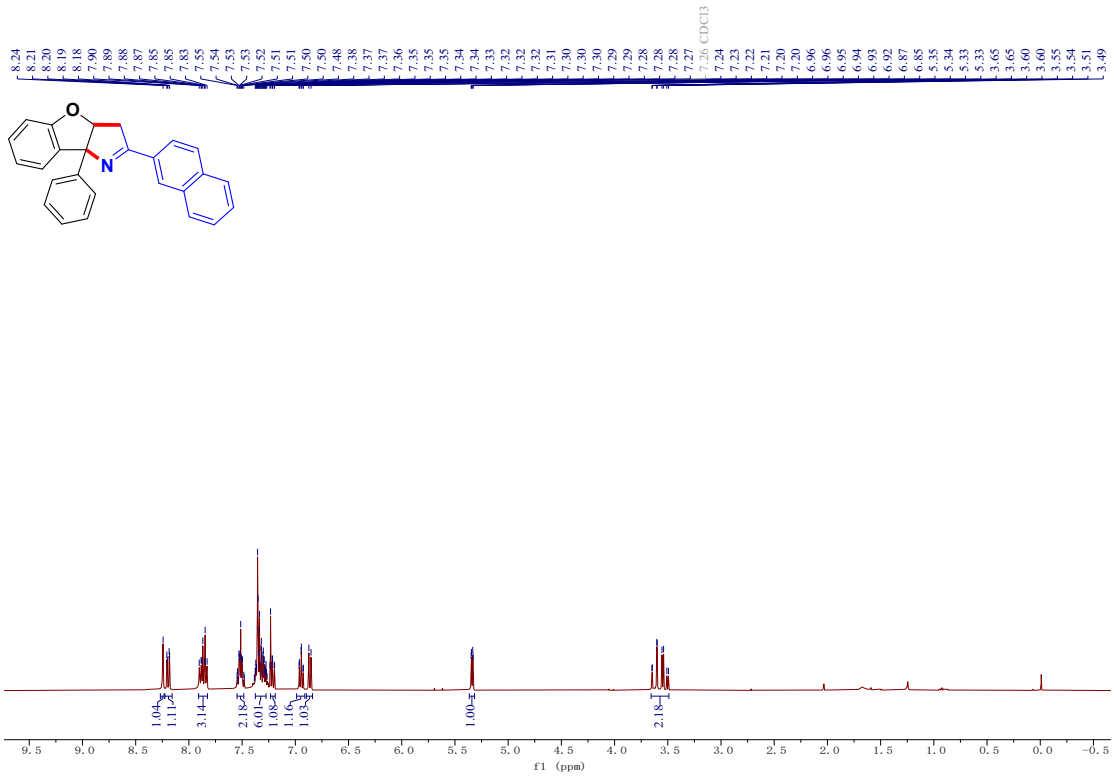
^{1}H NMR spectra of 3aq ($CDCl_3$, 400 MHz)



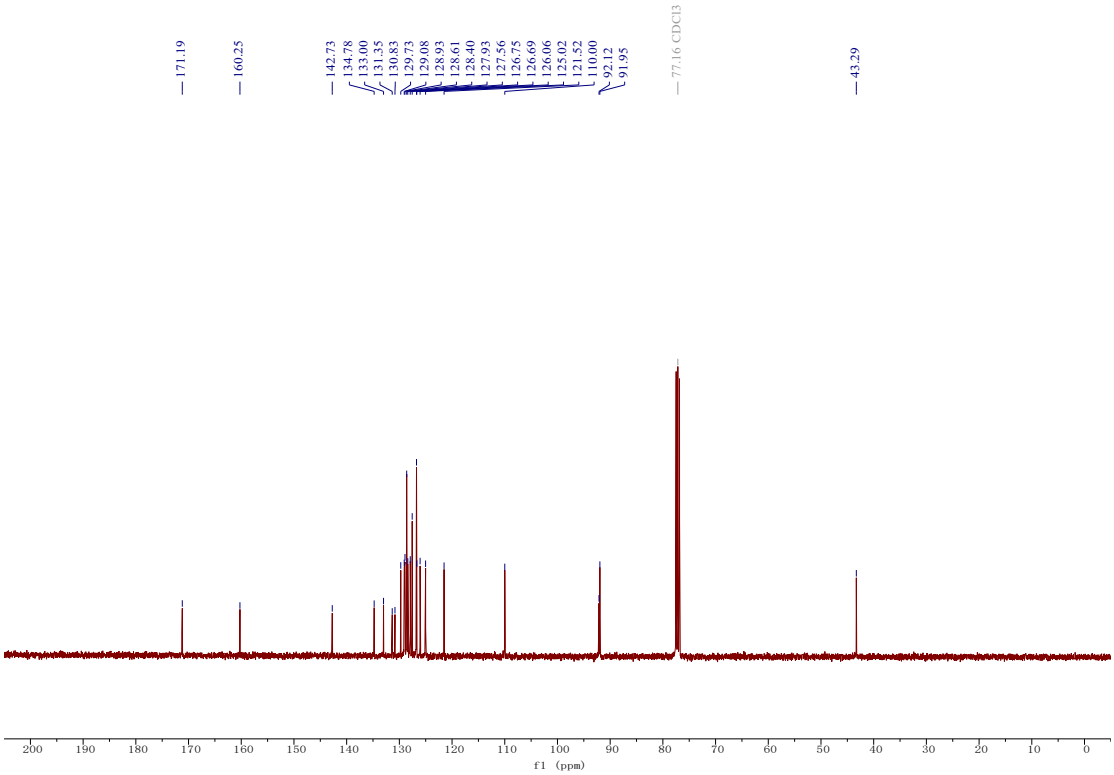
^{13}C NMR spectra of 3aq ($CDCl_3$, 101 MHz)



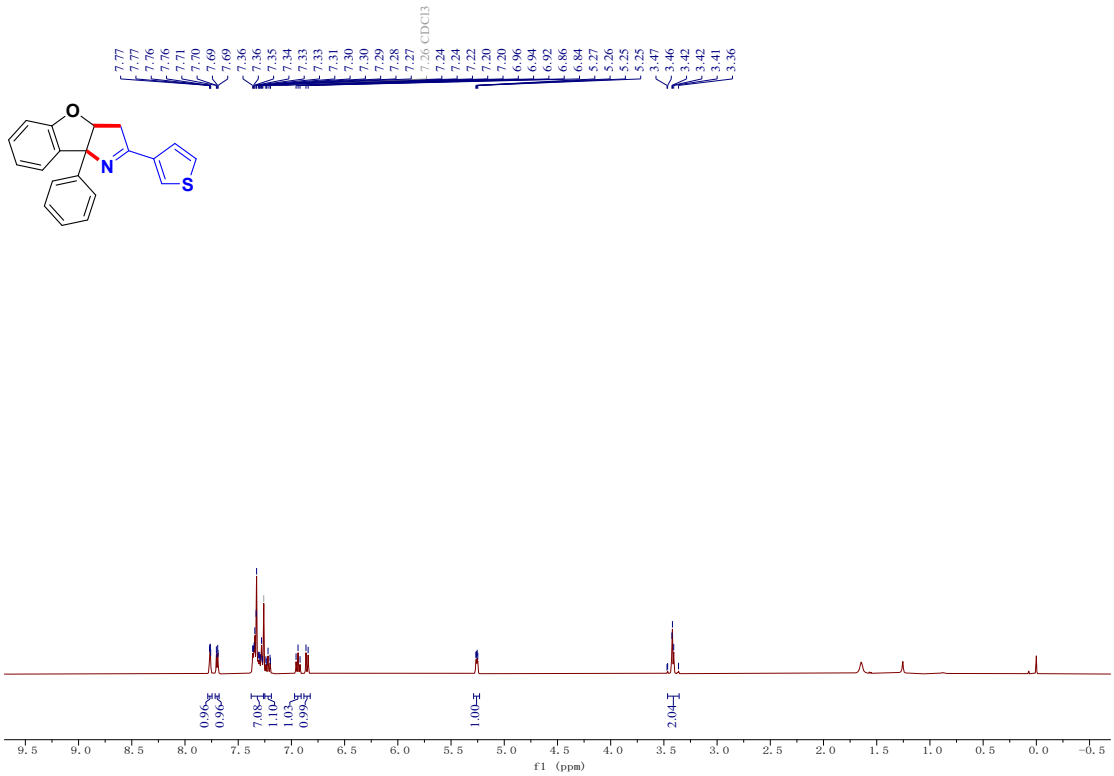
^{1}H NMR spectra of 3ar ($CDCl_3$, 400 MHz)



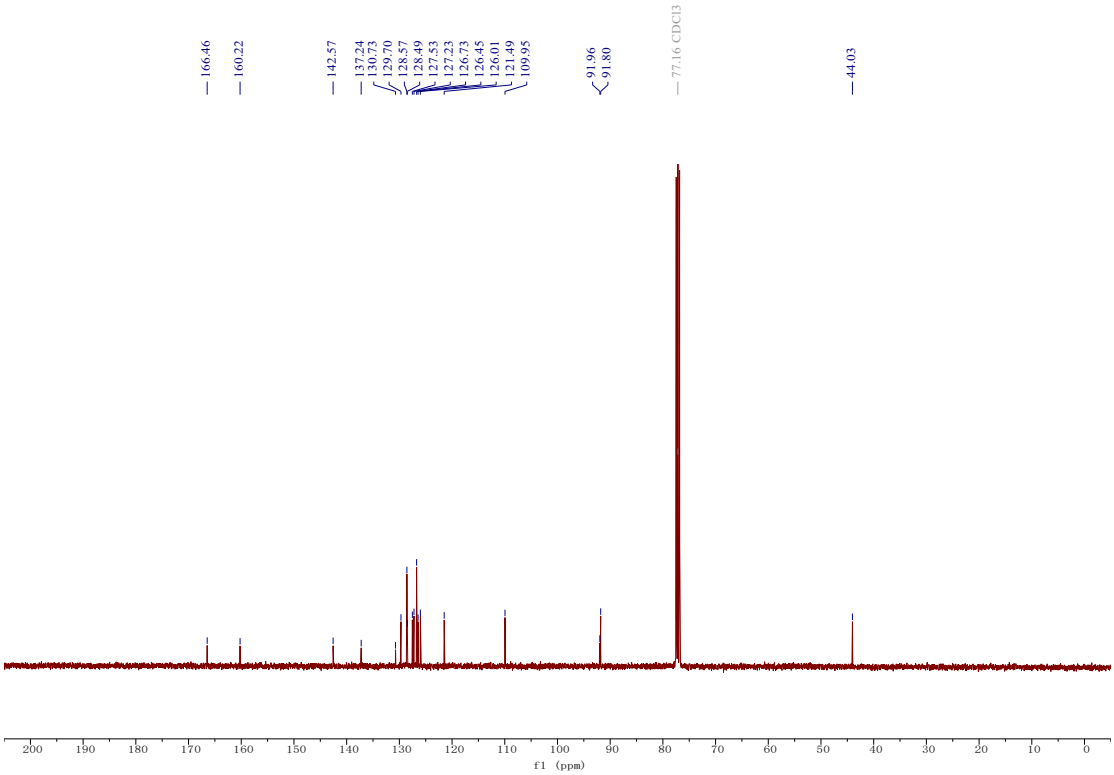
^{13}C NMR spectra of 3ar ($CDCl_3$, 101 MHz)



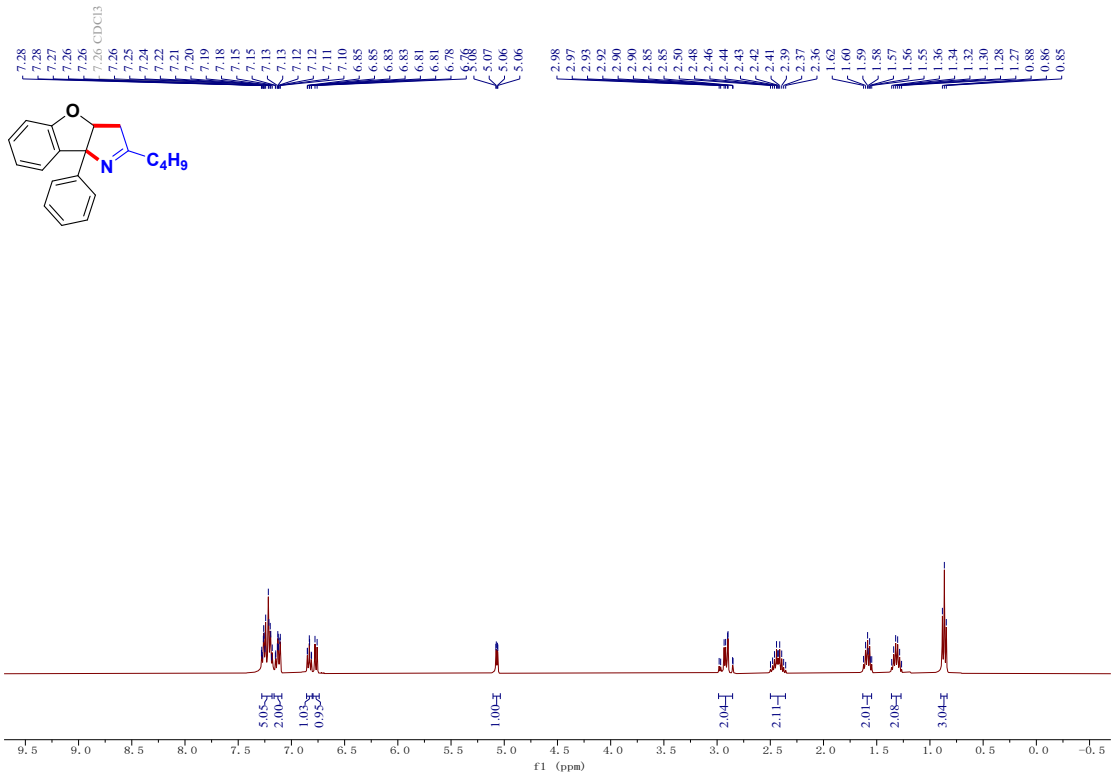
^{1}H NMR spectra of 3as ($CDCl_3$, 400 MHz)



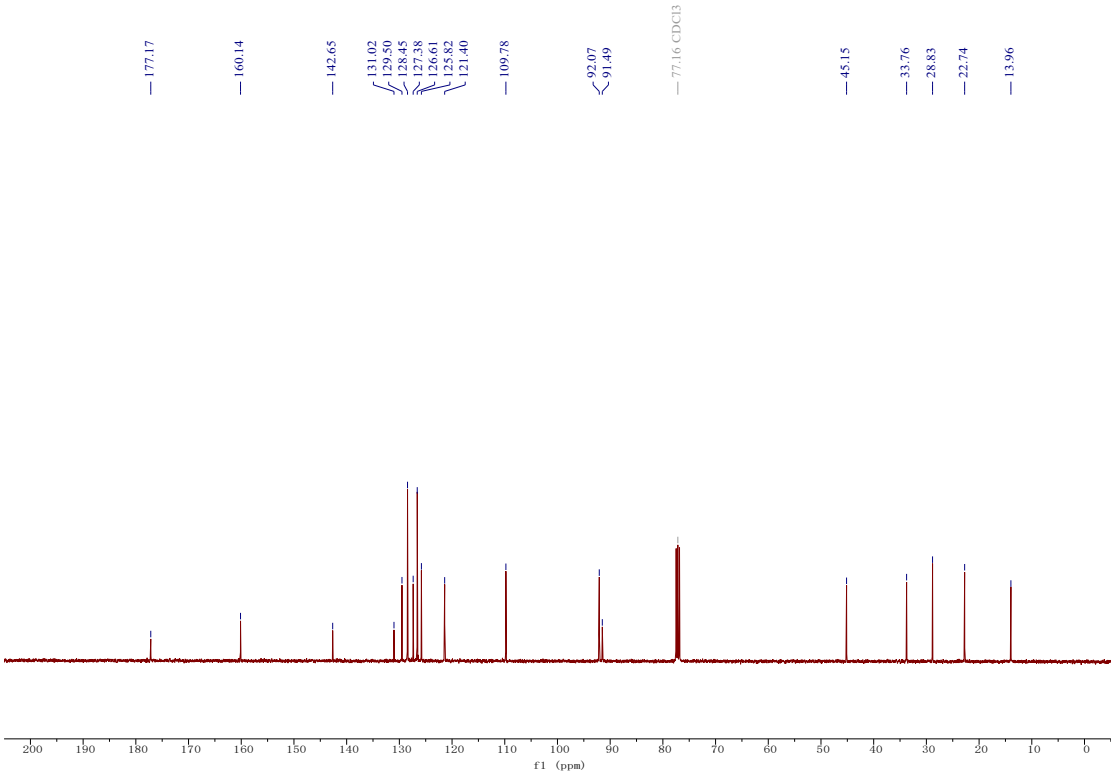
^{13}C NMR spectra of 3as ($CDCl_3$, 101 MHz)



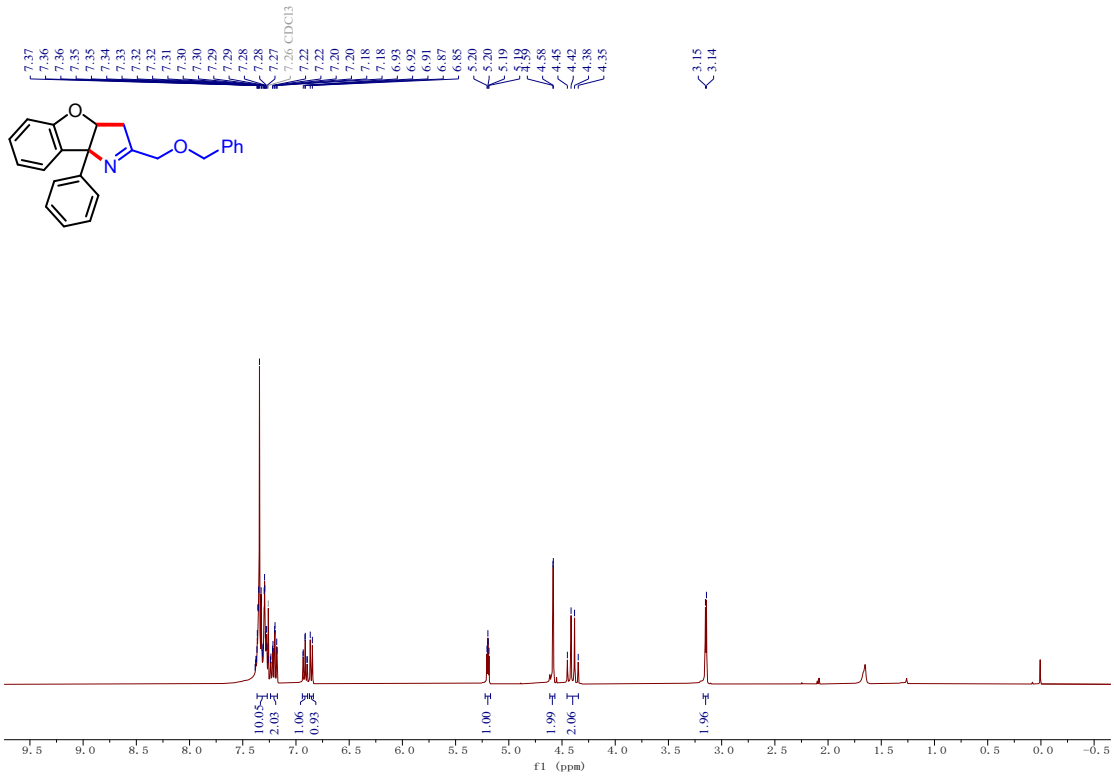
^{1}H NMR spectra of 3at ($CDCl_3$, 400 MHz)



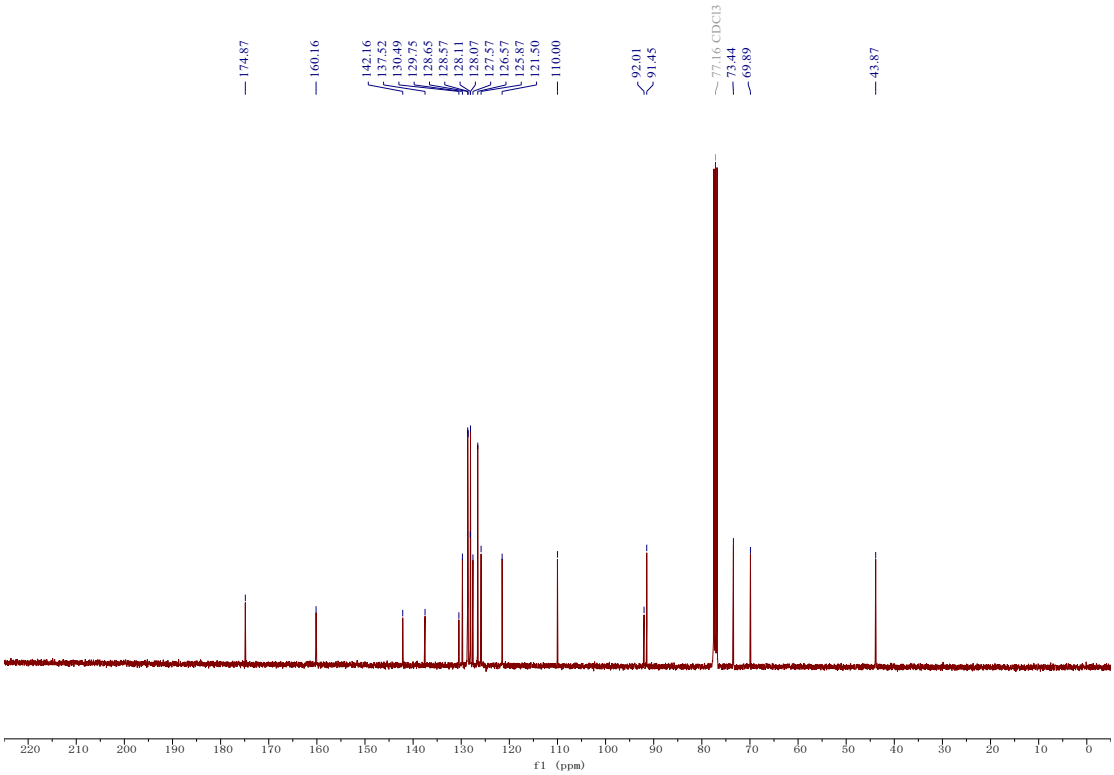
^{13}C NMR spectra of 3at ($CDCl_3$, 101 MHz)



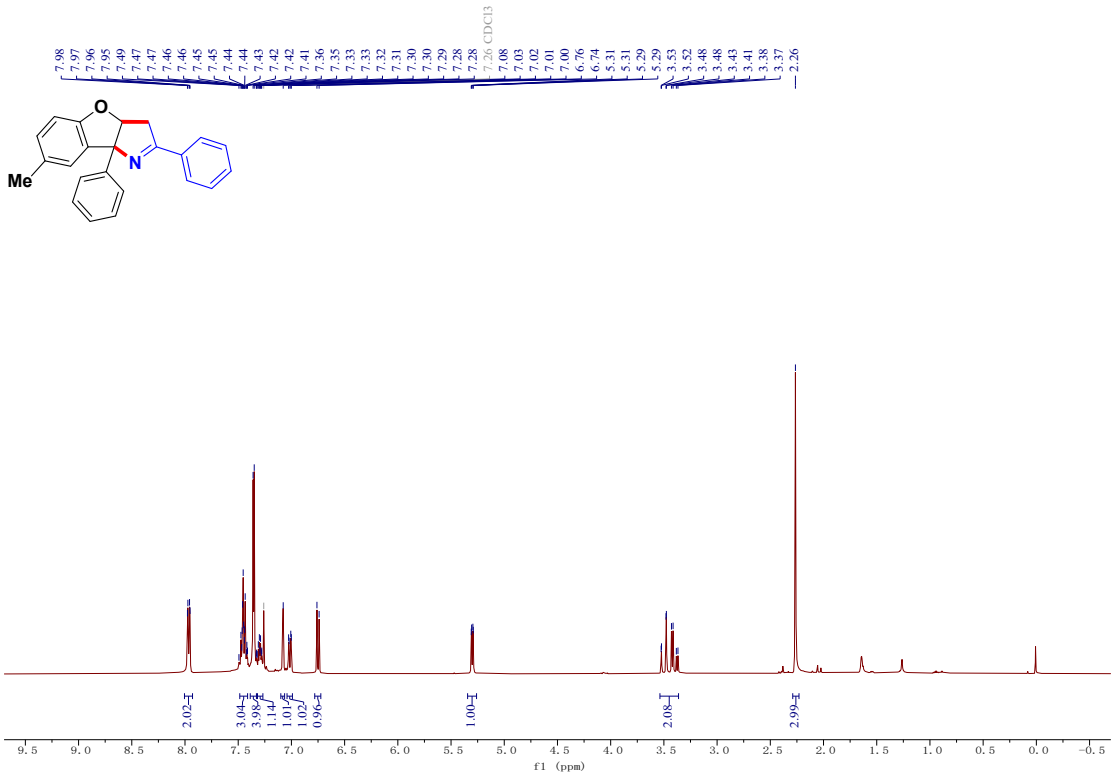
^{1}H NMR spectra of 3au ($CDCl_3$, 400 MHz)



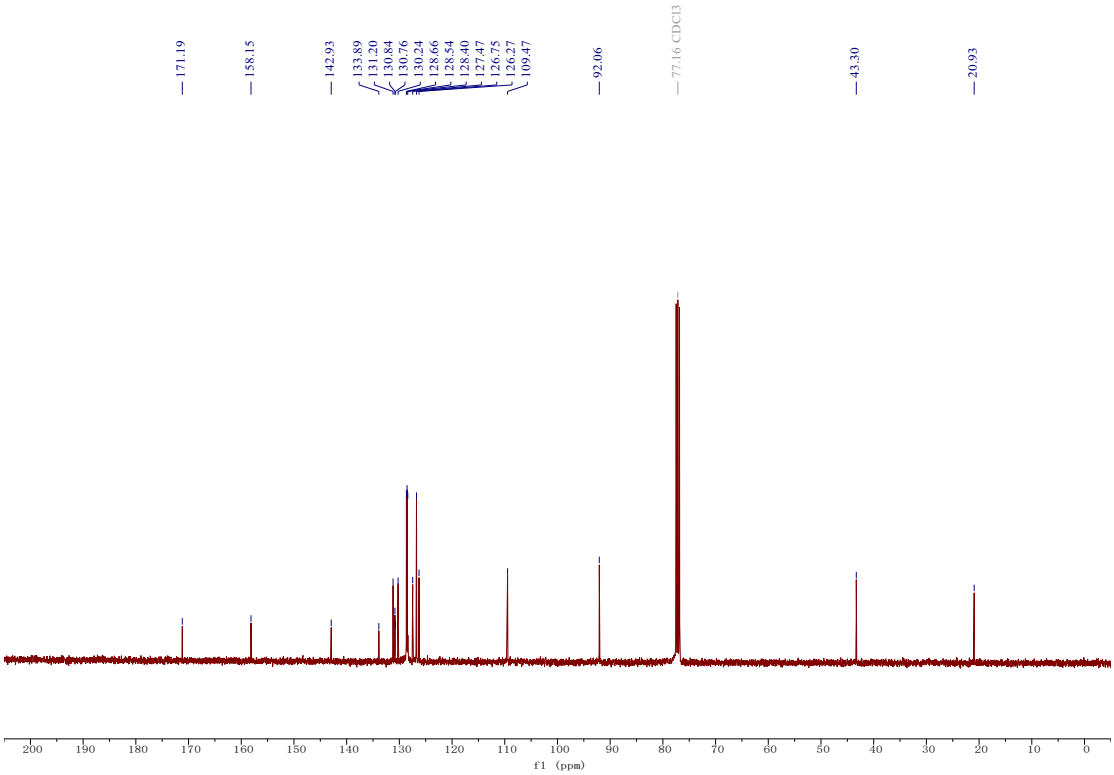
^{13}C NMR spectra of 3au ($CDCl_3$, 101 MHz)



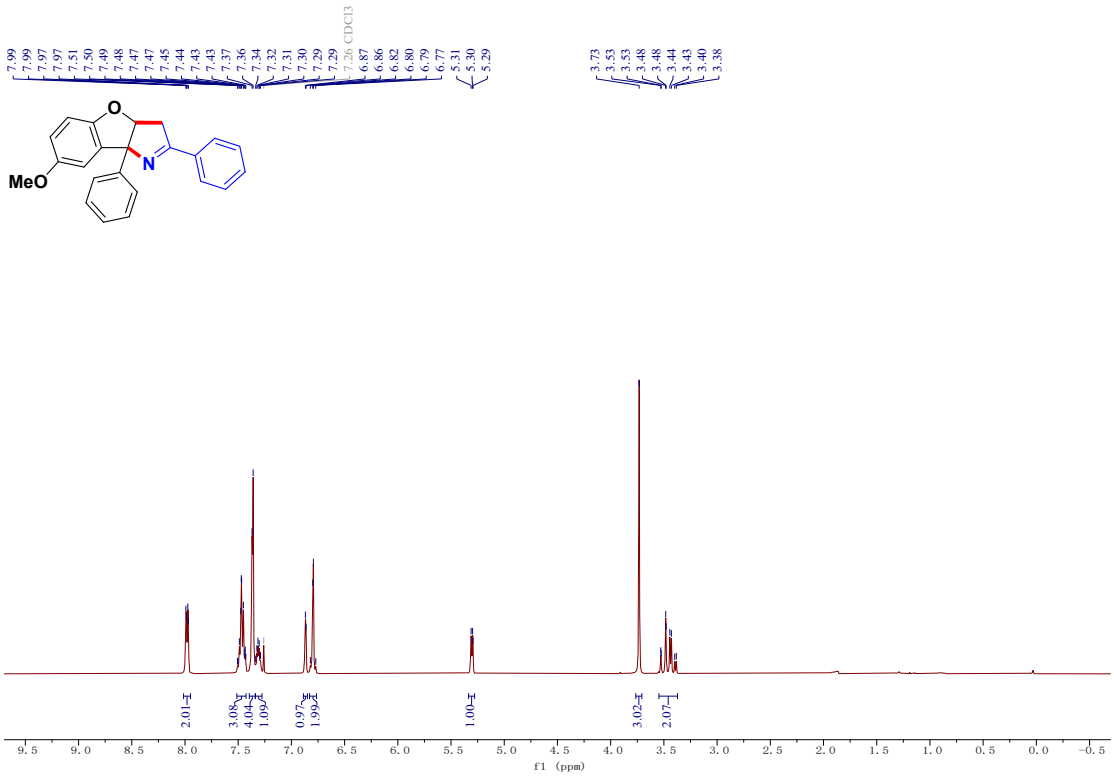
^{1}H NMR spectra of 3ba ($CDCl_3$, 400 MHz)



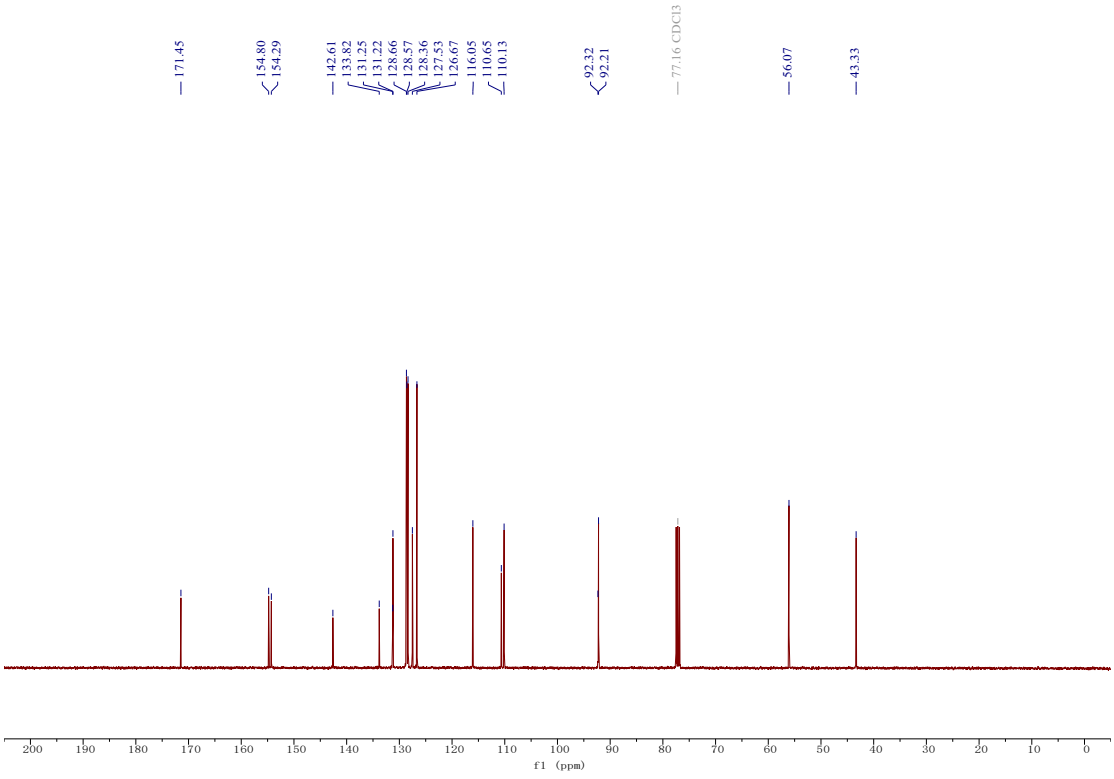
^{13}C NMR spectra of 3ba ($CDCl_3$, 101 MHz)



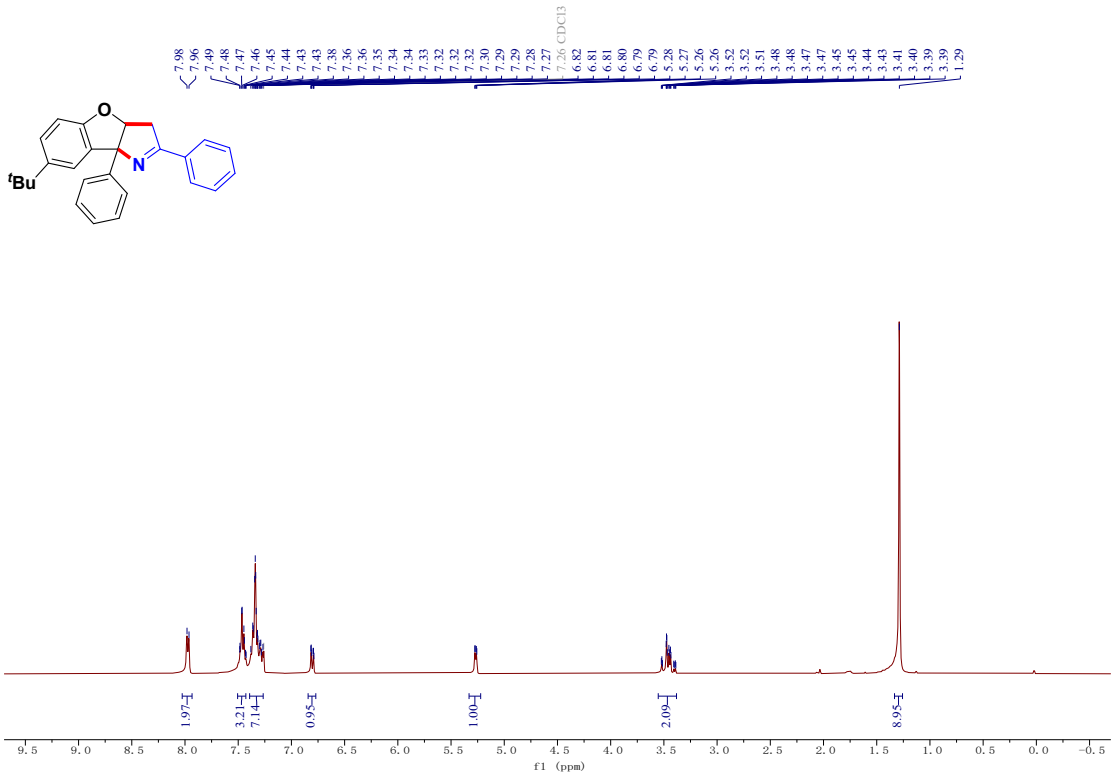
^{1}H NMR spectra of 3bb ($CDCl_3$, 400 MHz)



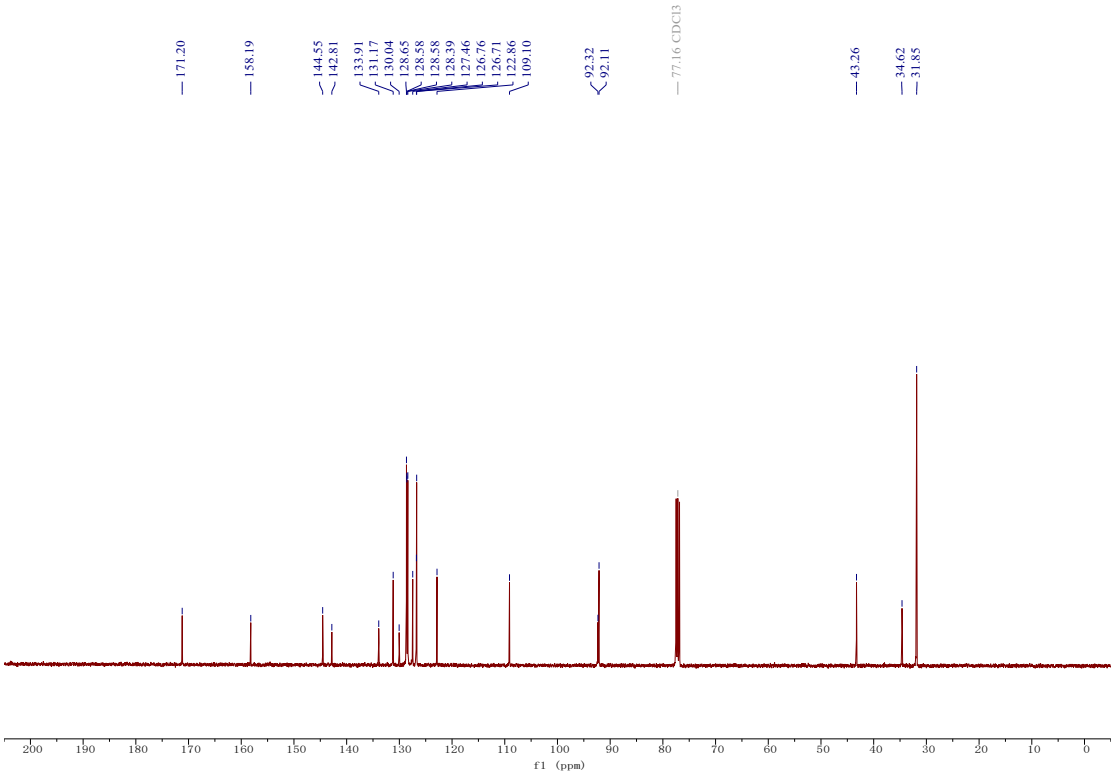
^{13}C NMR spectra of 3bb ($CDCl_3$, 101 MHz)



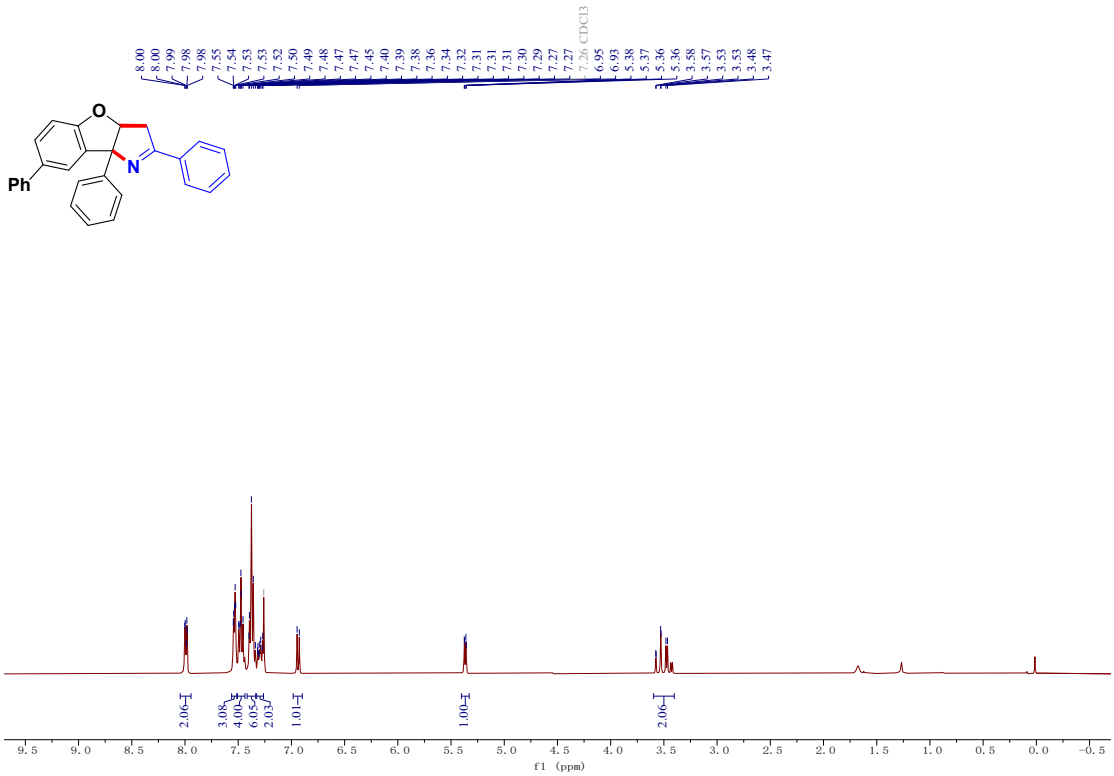
^{1}H NMR spectra of 3bc ($CDCl_3$, 400 MHz)



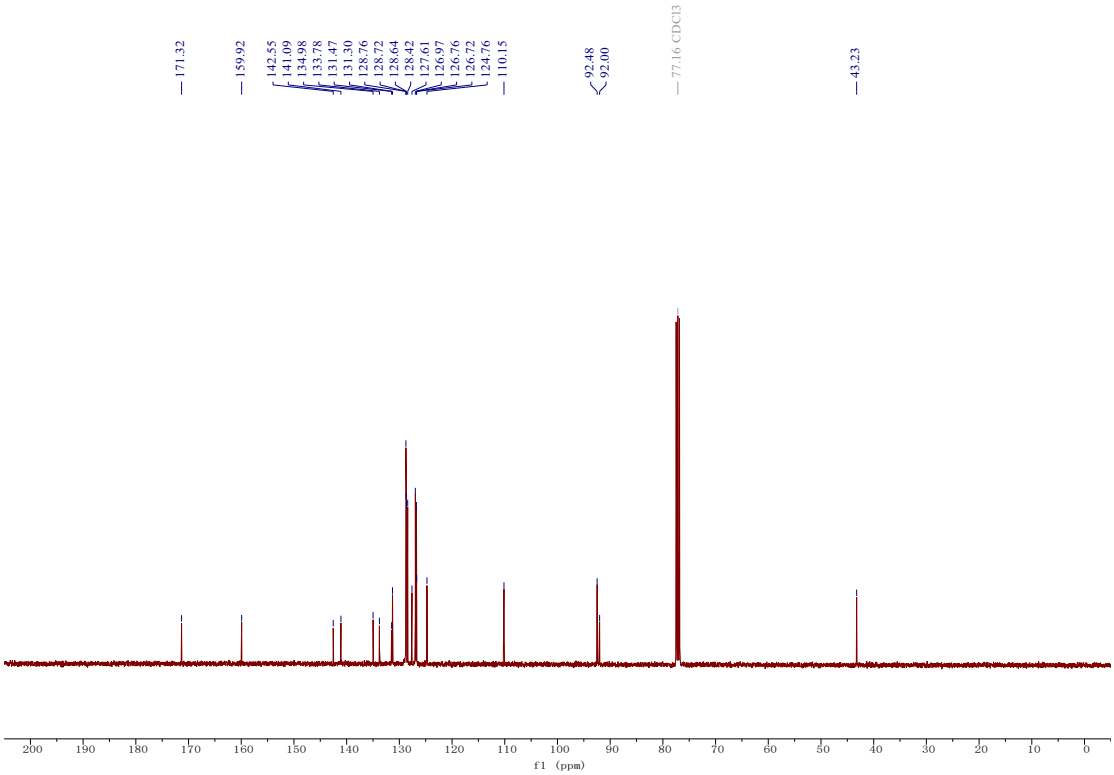
^{13}C NMR spectra of 3bc ($CDCl_3$, 101 MHz)



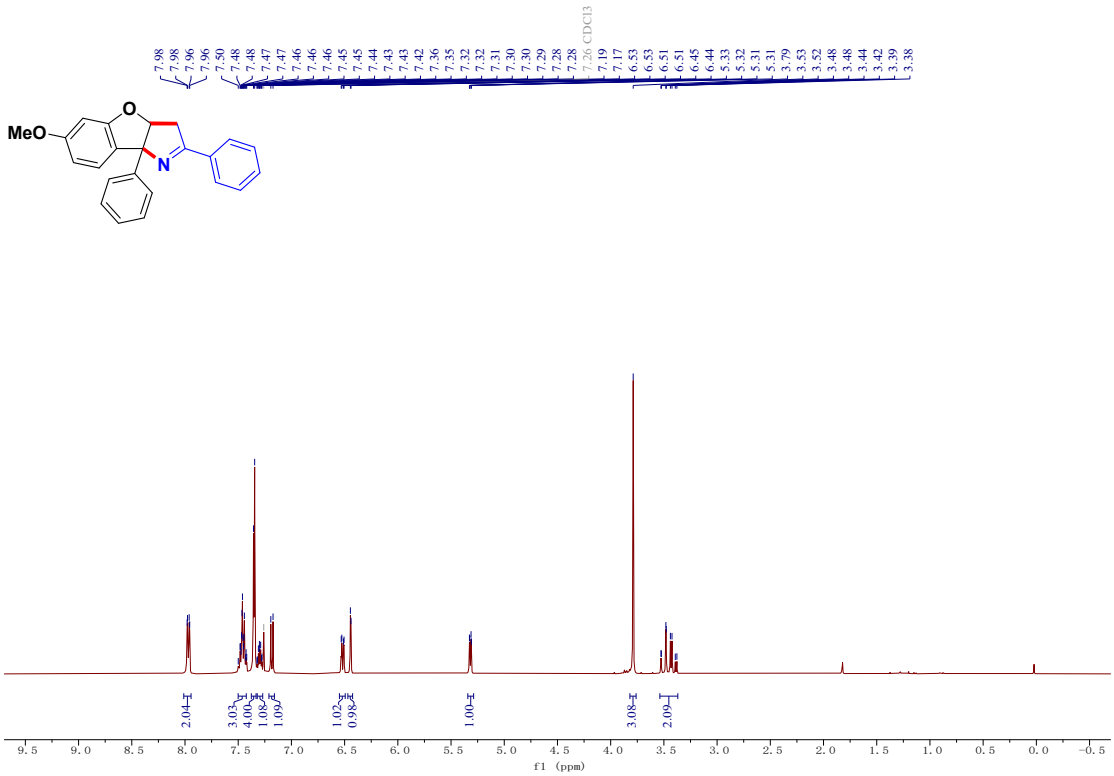
^{1}H NMR spectra of 3bd ($CDCl_3$, 400 MHz)



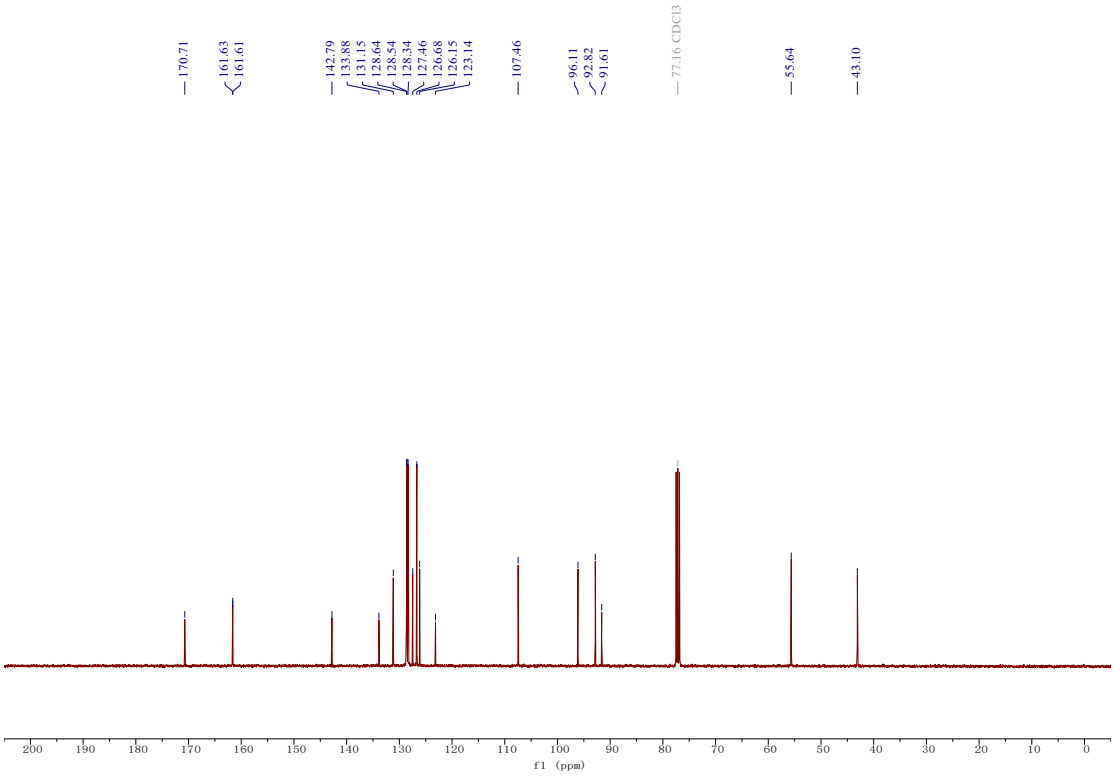
^{13}C NMR spectra of 3bd ($CDCl_3$, 101 MHz)



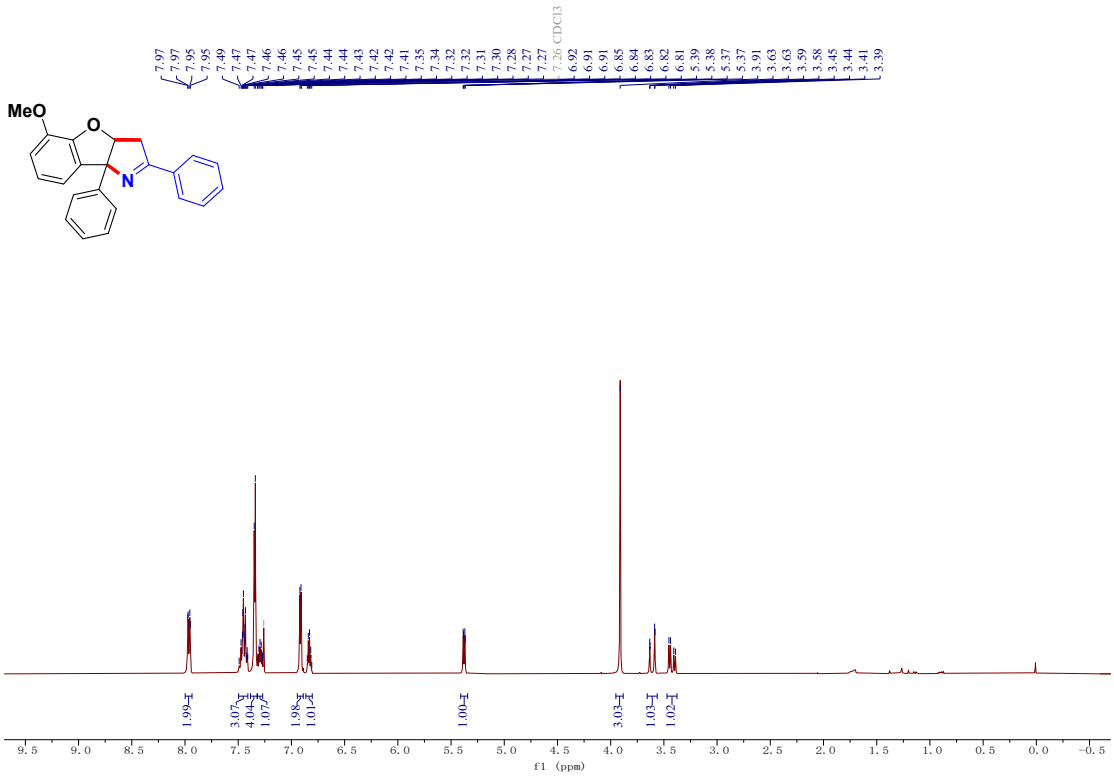
^{1}H NMR spectra of 3be ($CDCl_3$, 400 MHz)



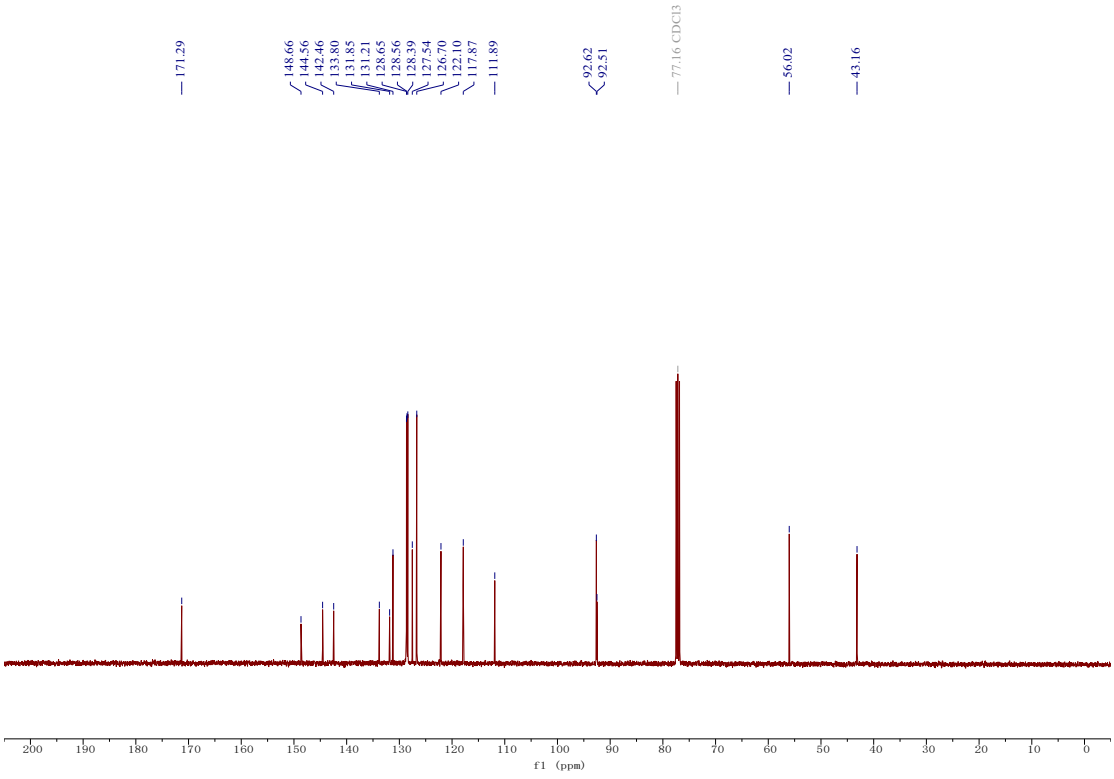
^{13}C NMR spectra of 3be ($CDCl_3$, 101 MHz)



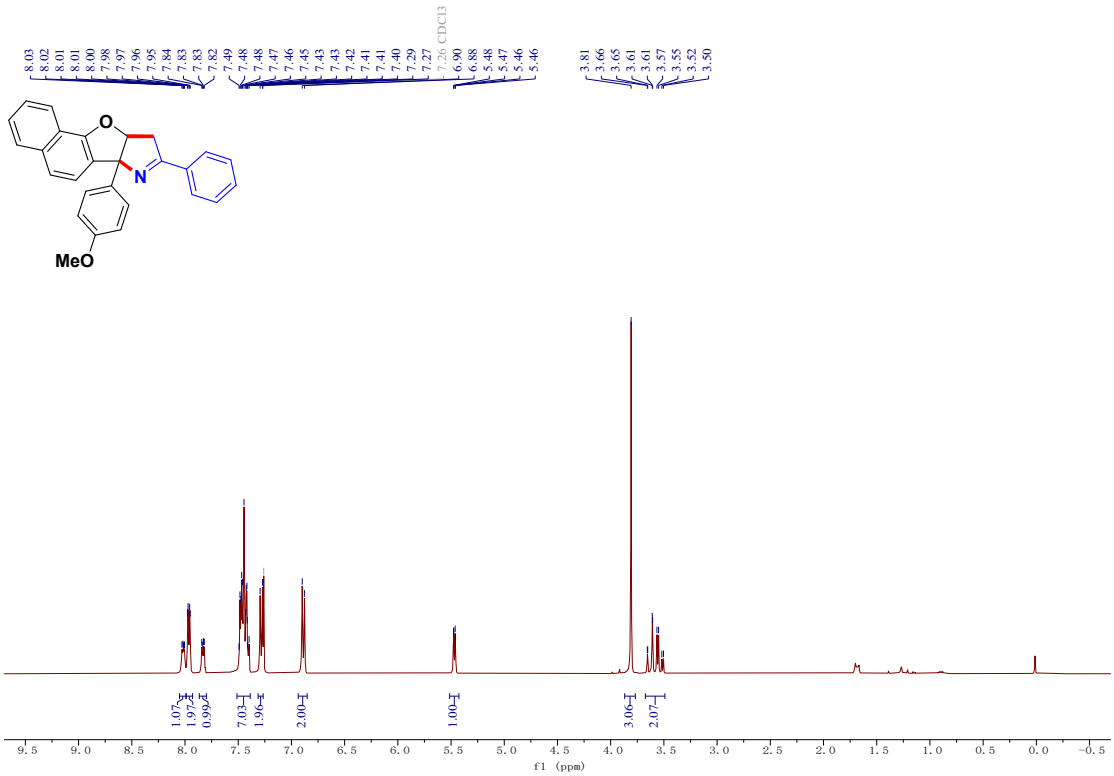
^{1}H NMR spectra of 3bf ($CDCl_3$, 400 MHz)



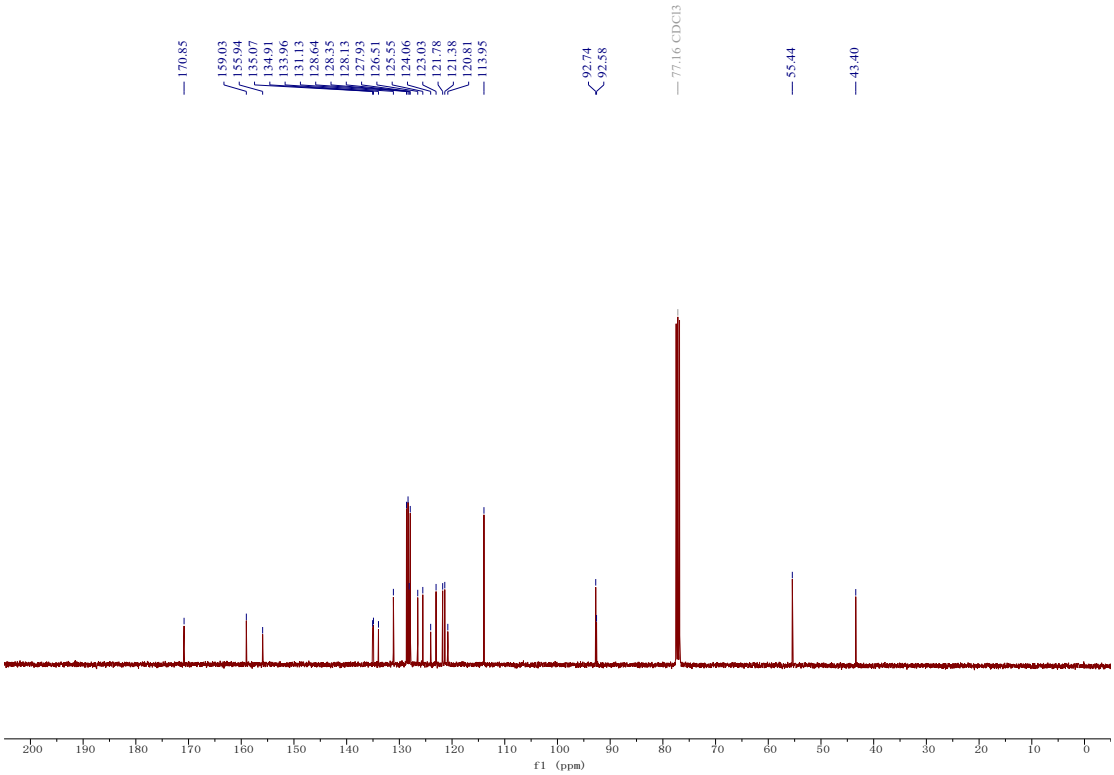
^{13}C NMR spectra of 3bf ($CDCl_3$, 101 MHz)



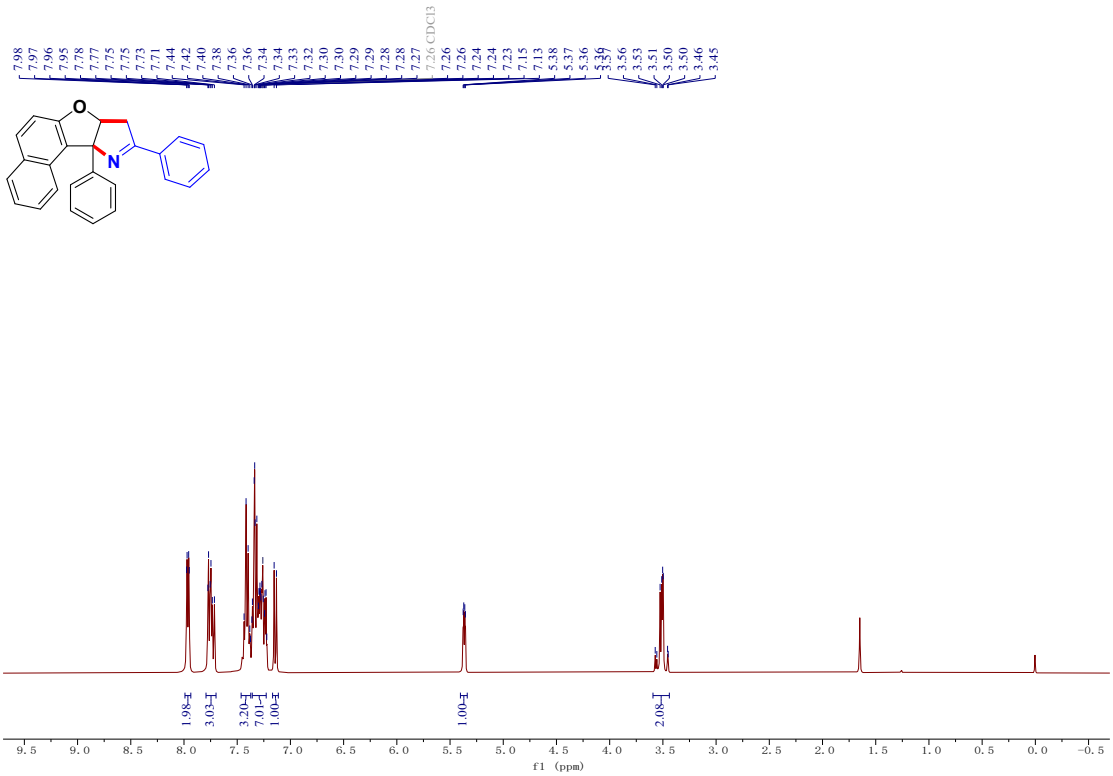
^{1}H NMR spectra of 3bg ($CDCl_3$, 400 MHz)



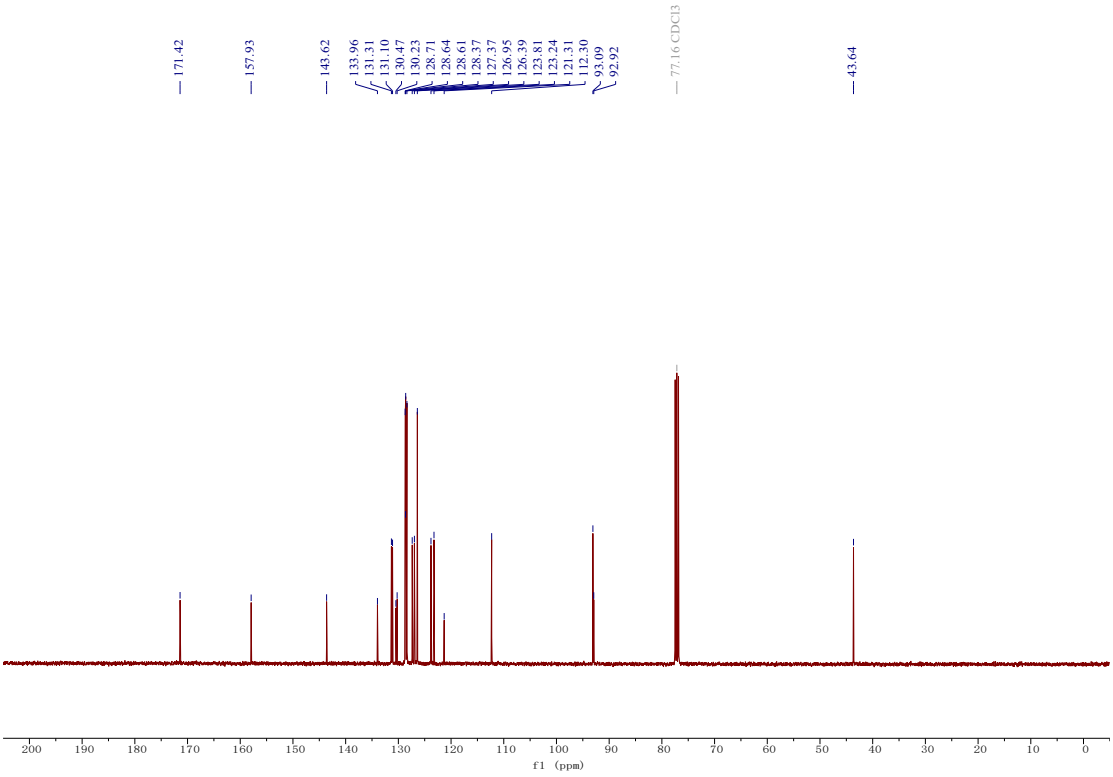
^{13}C NMR spectra of 3bg ($CDCl_3$, 101 MHz)



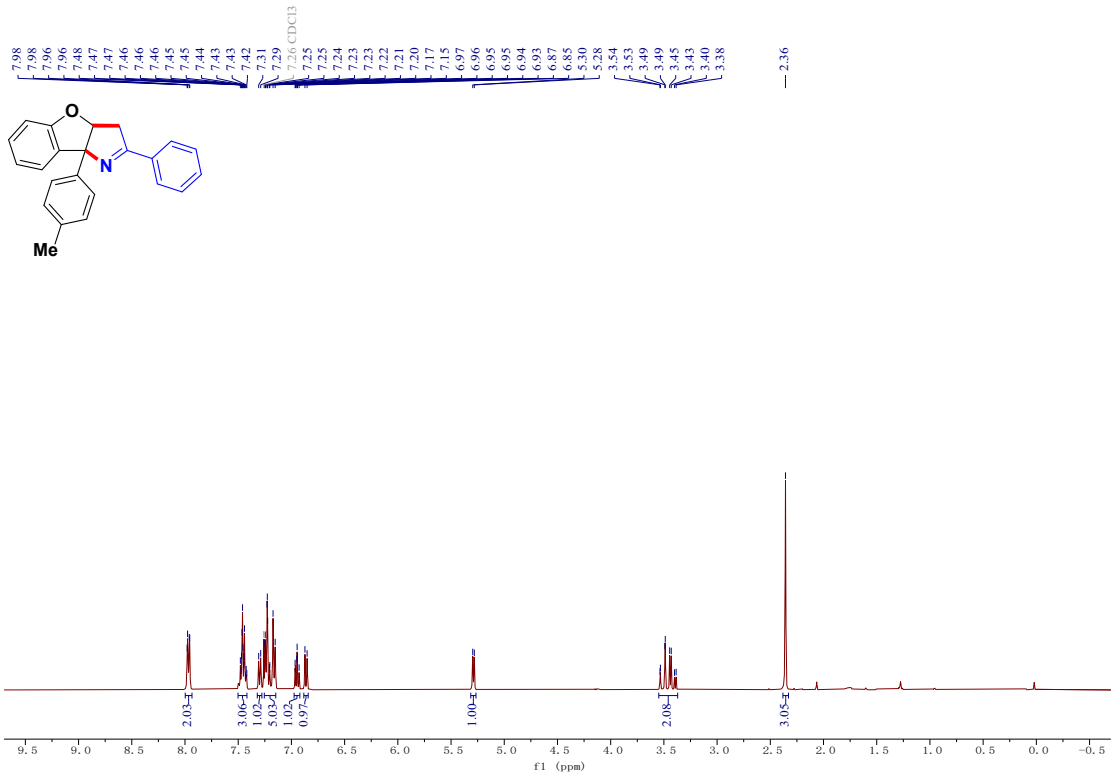
^{1}H NMR spectra of 3bh ($CDCl_3$, 400 MHz)



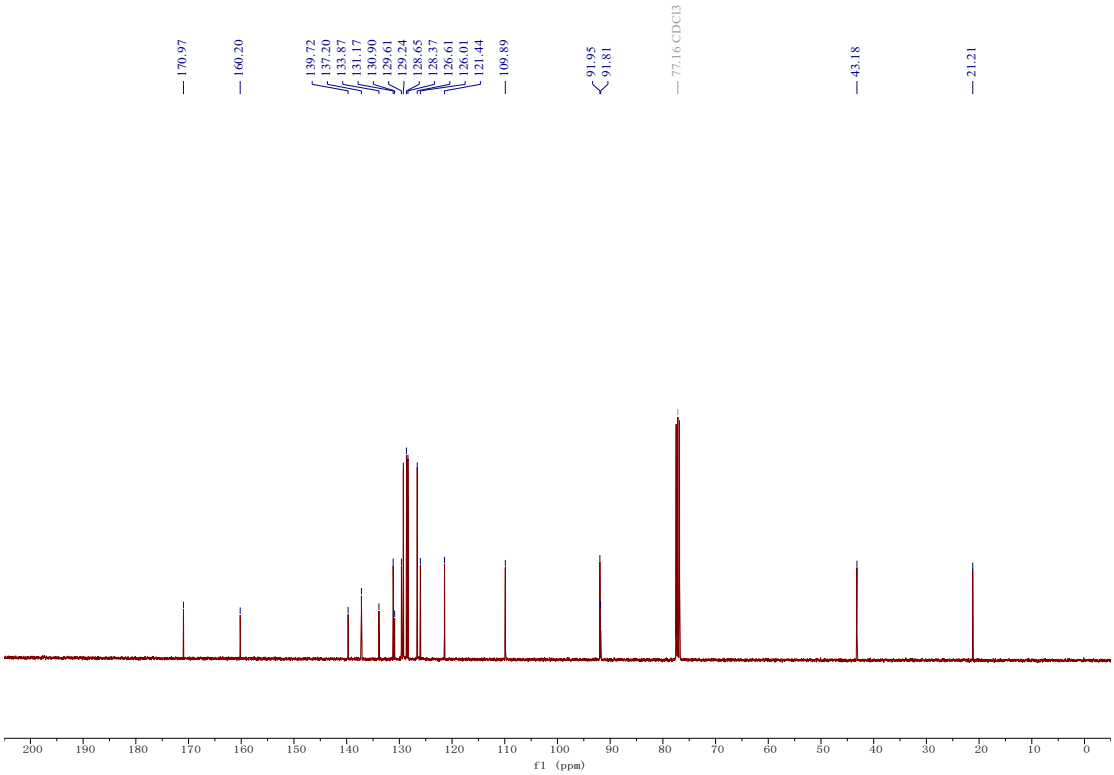
^{13}C NMR spectra of 3bh ($CDCl_3$, 101 MHz)



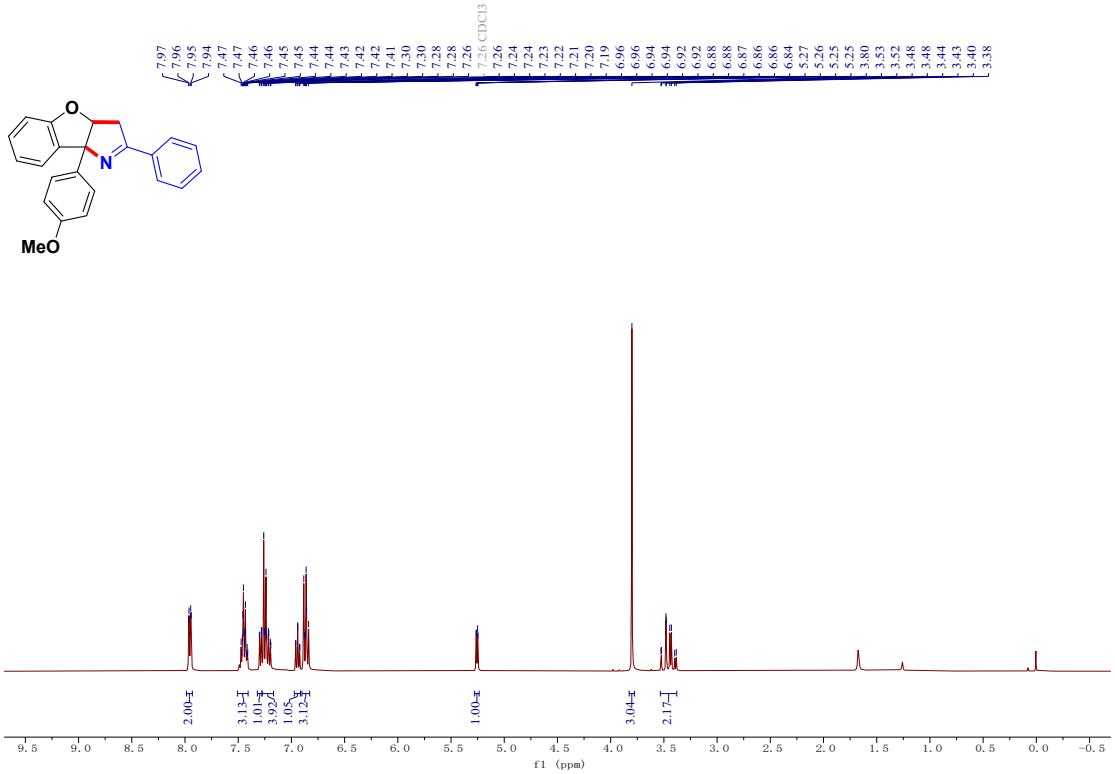
^{1}H NMR spectra of 3bi ($CDCl_3$, 400 MHz)



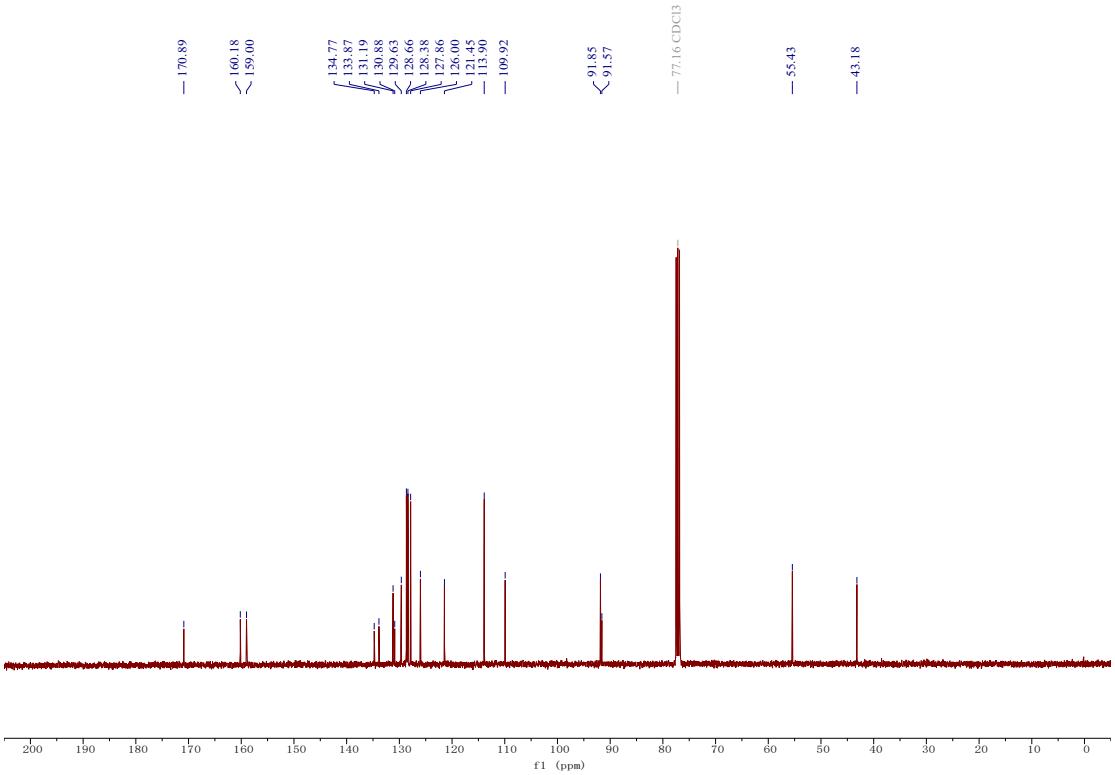
^{13}C NMR spectra of 3bi ($CDCl_3$, 101 MHz)



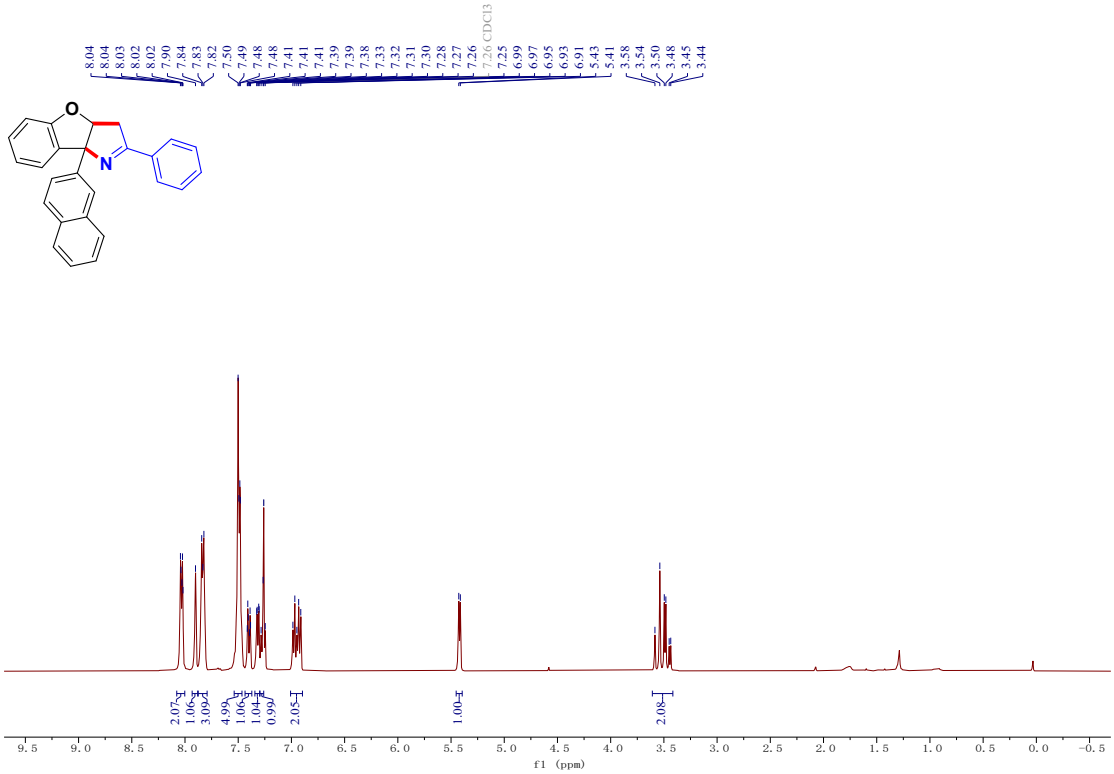
^{1}H NMR spectra of 3bj ($CDCl_3$, 400 MHz)



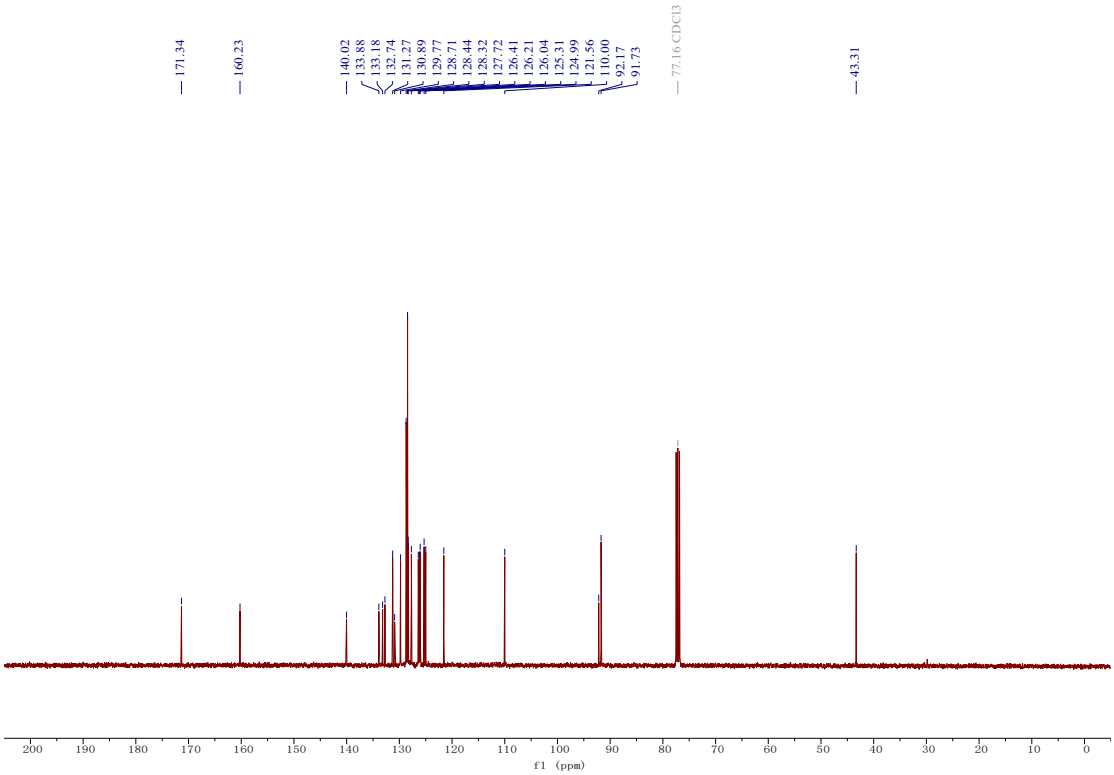
^{13}C NMR spectra of 3bj ($CDCl_3$, 101 MHz)



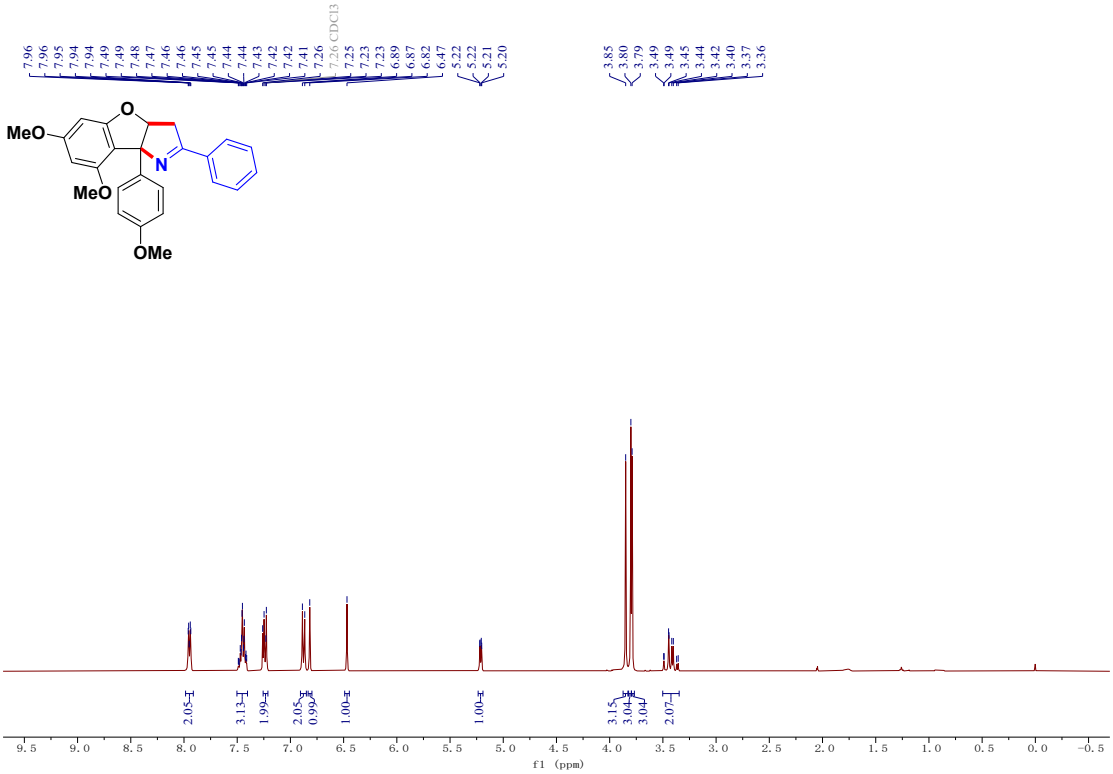
^{1}H NMR spectra of 3bk ($CDCl_3$, 400 MHz)



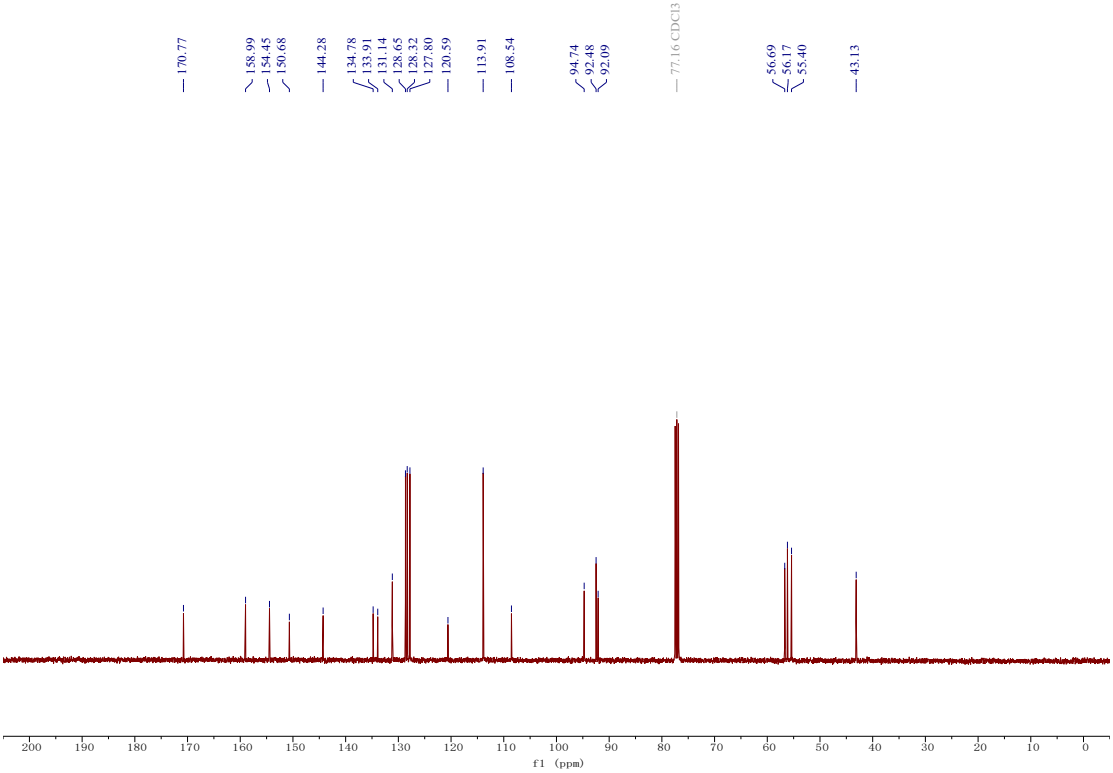
^{13}C NMR spectra of 3bk ($CDCl_3$, 101 MHz)



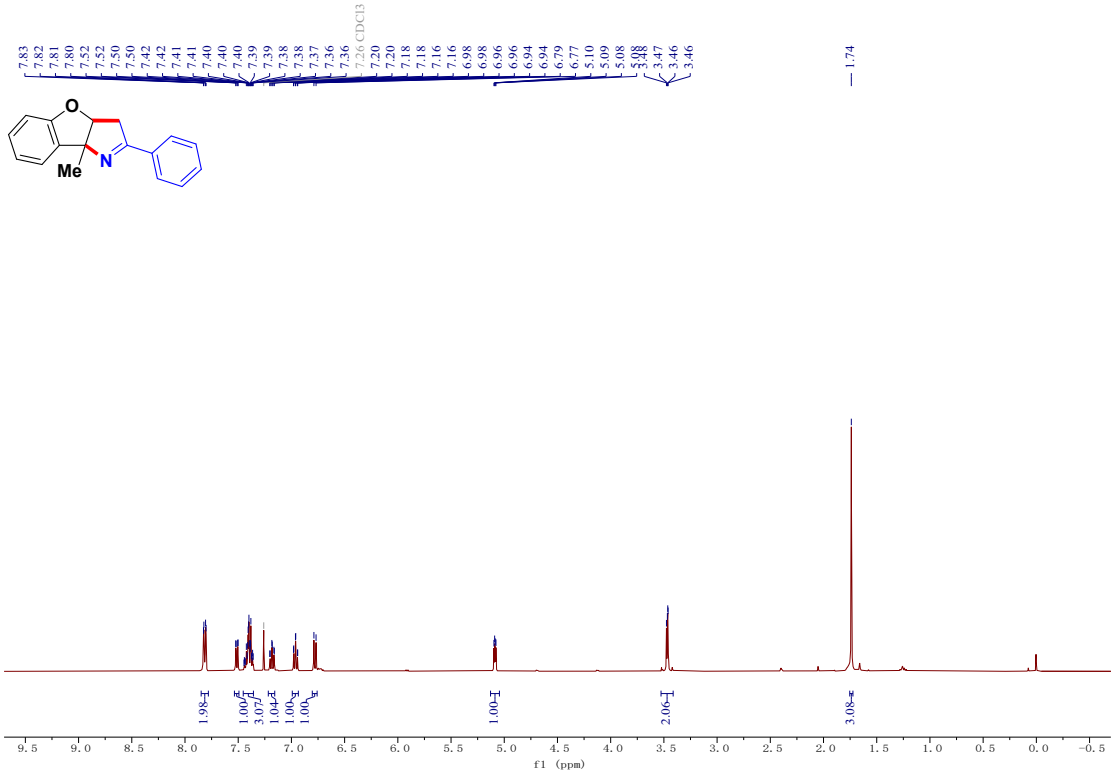
^{1}H NMR spectra of 3bl ($CDCl_3$, 400 MHz)



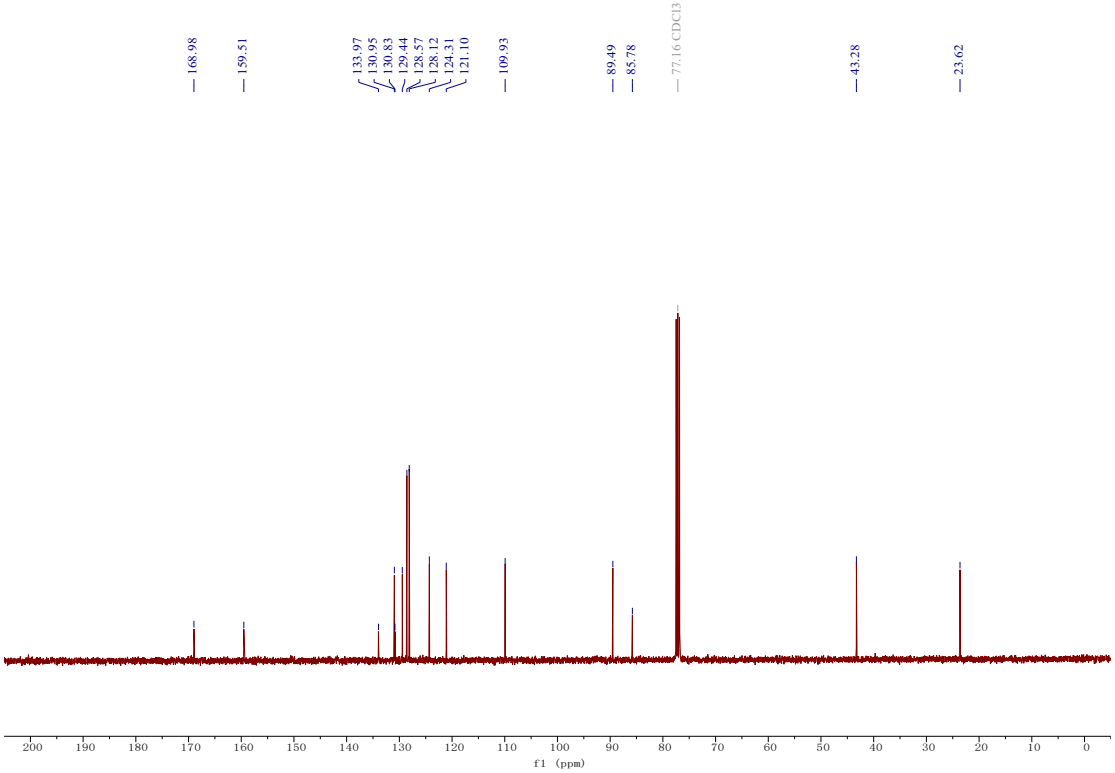
^{13}C NMR spectra of 3bl ($CDCl_3$, 101 MHz)



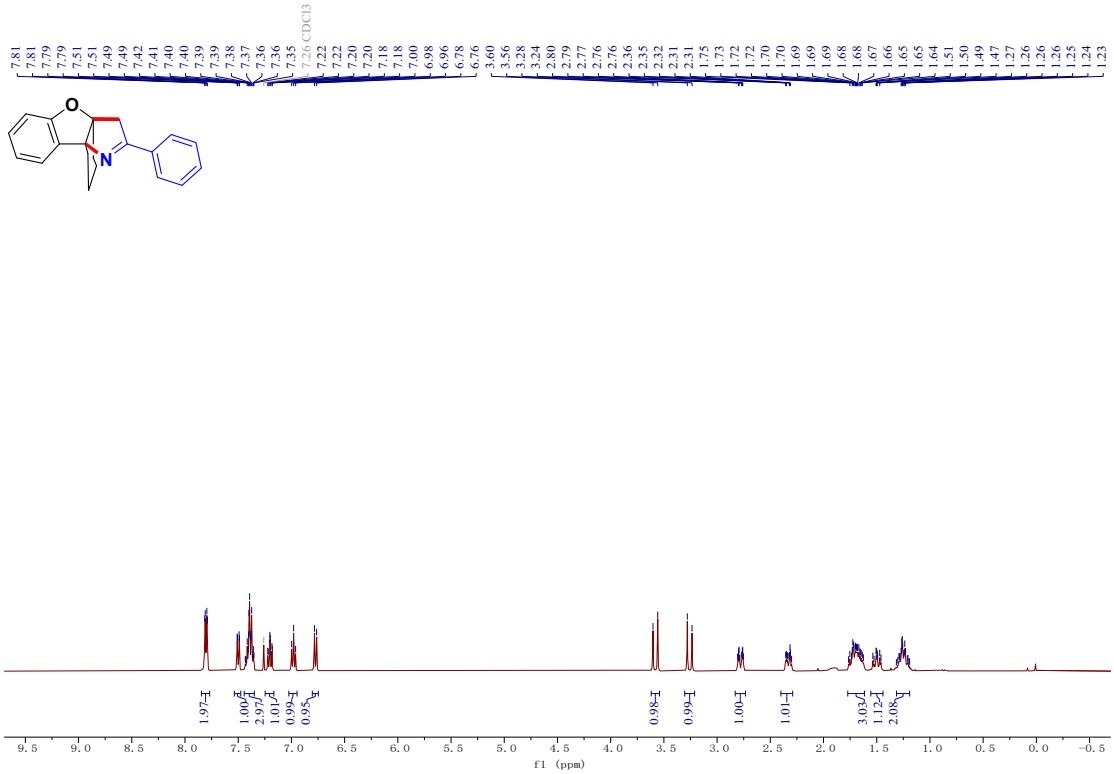
^{1}H NMR spectra of 3bm ($CDCl_3$, 400 MHz)



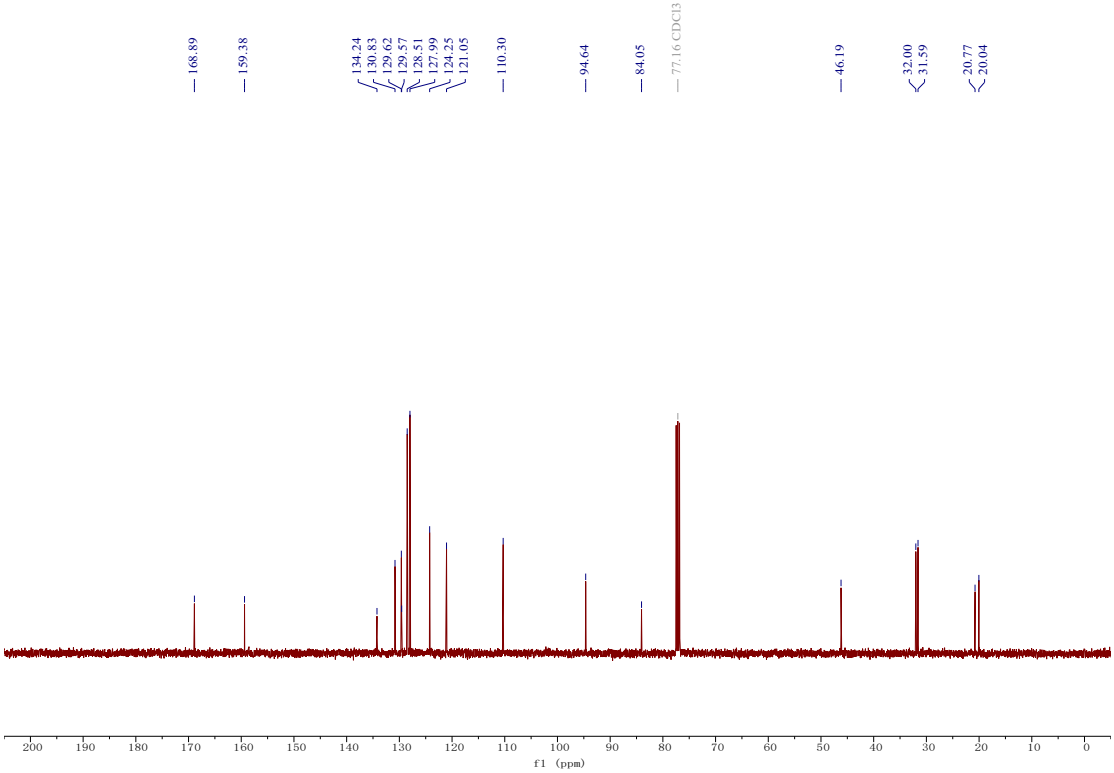
^{13}C NMR spectra of 3bm ($CDCl_3$, 101 MHz)



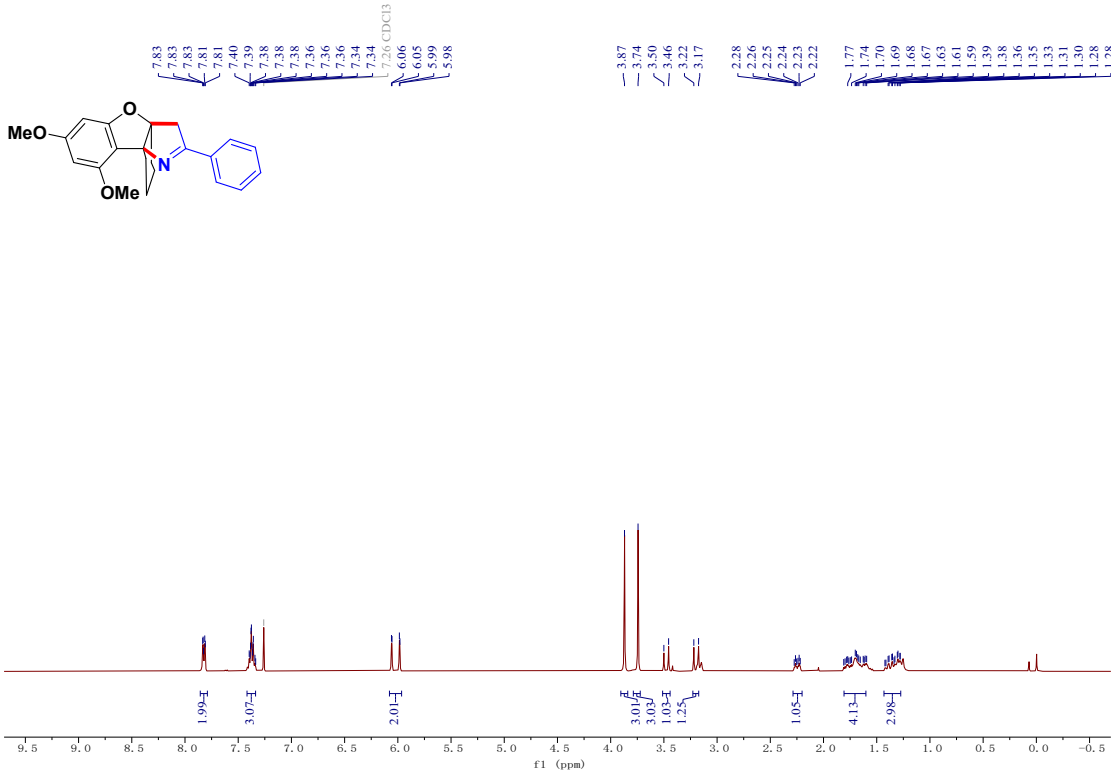
^{1}H NMR spectra of 3bn ($CDCl_3$, 400 MHz)



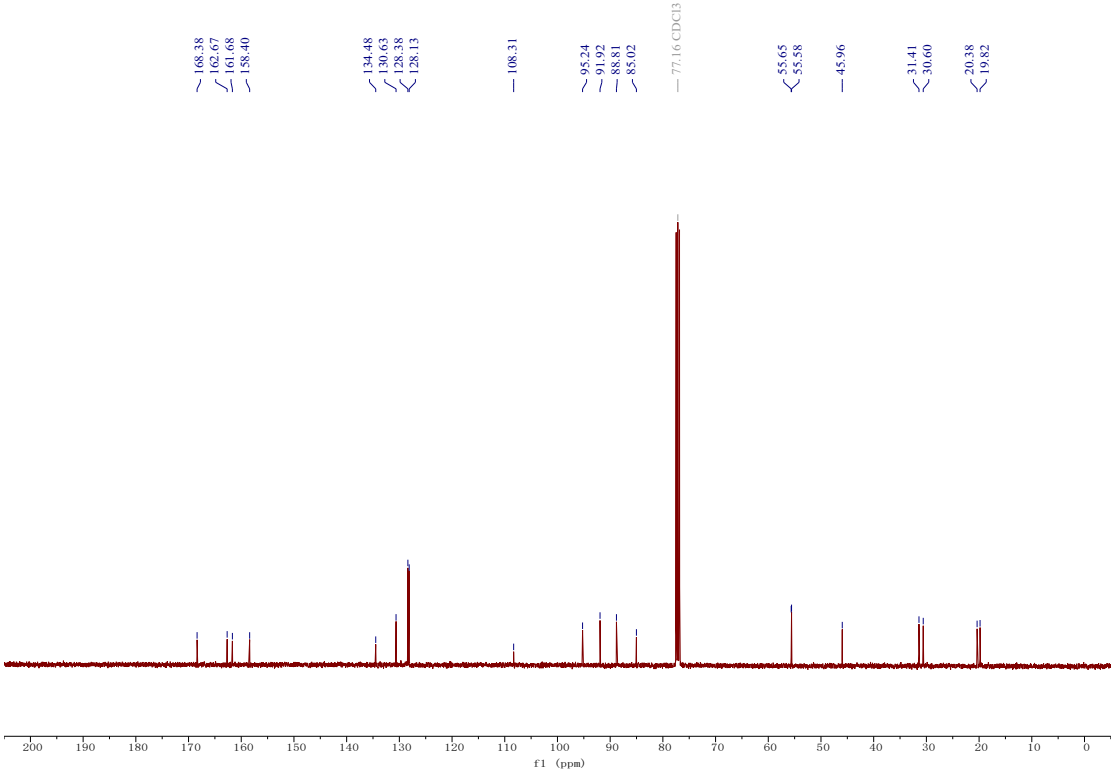
^{13}C NMR spectra of 3bn ($CDCl_3$, 101 MHz)



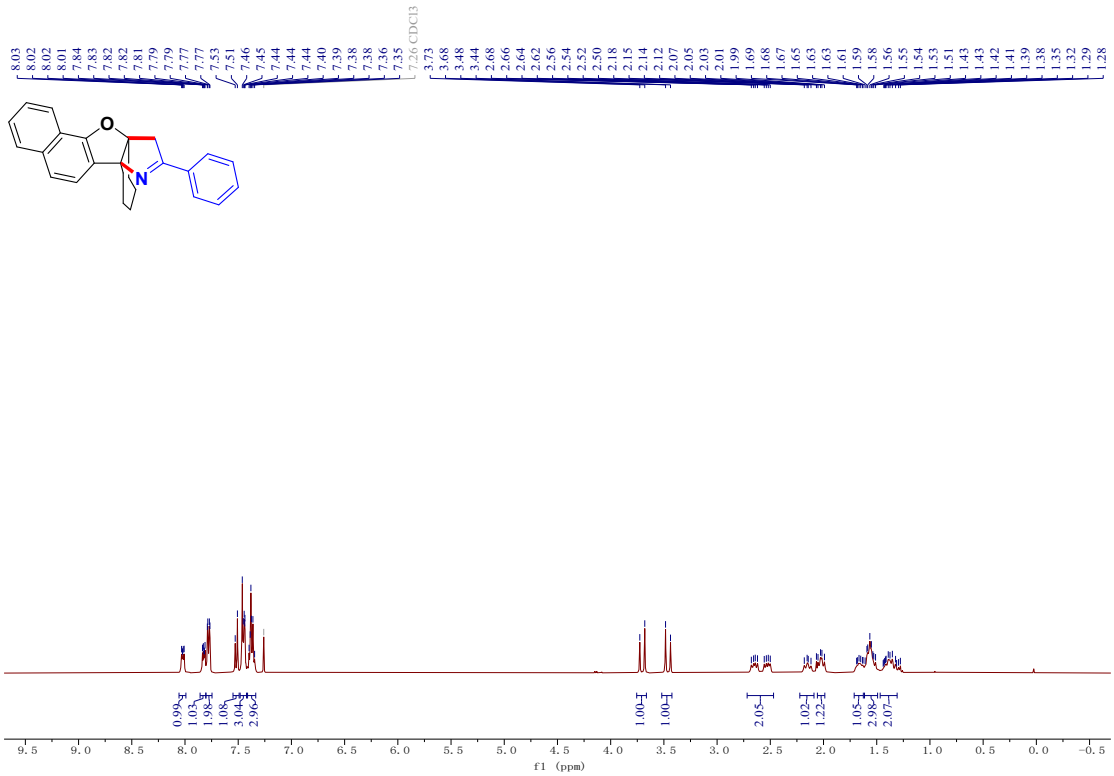
^{1}H NMR spectra of 3bo ($CDCl_3$, 400 MHz)



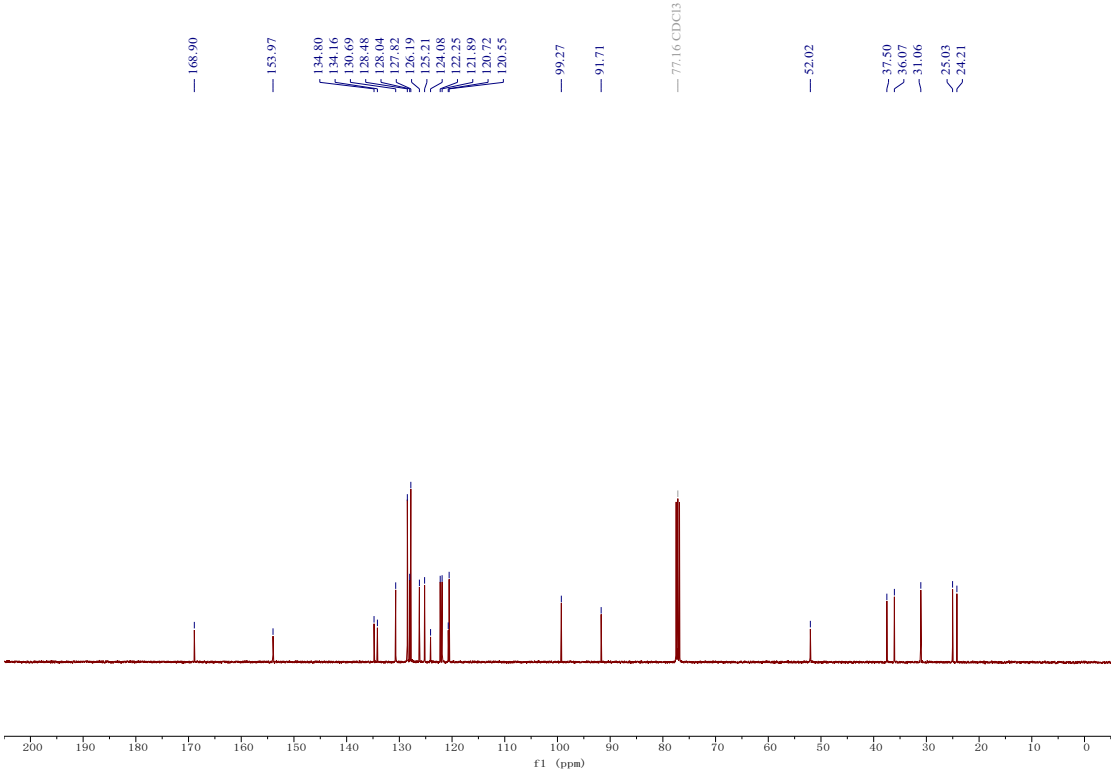
^{13}C NMR spectra of 3bo ($CDCl_3$, 101 MHz)



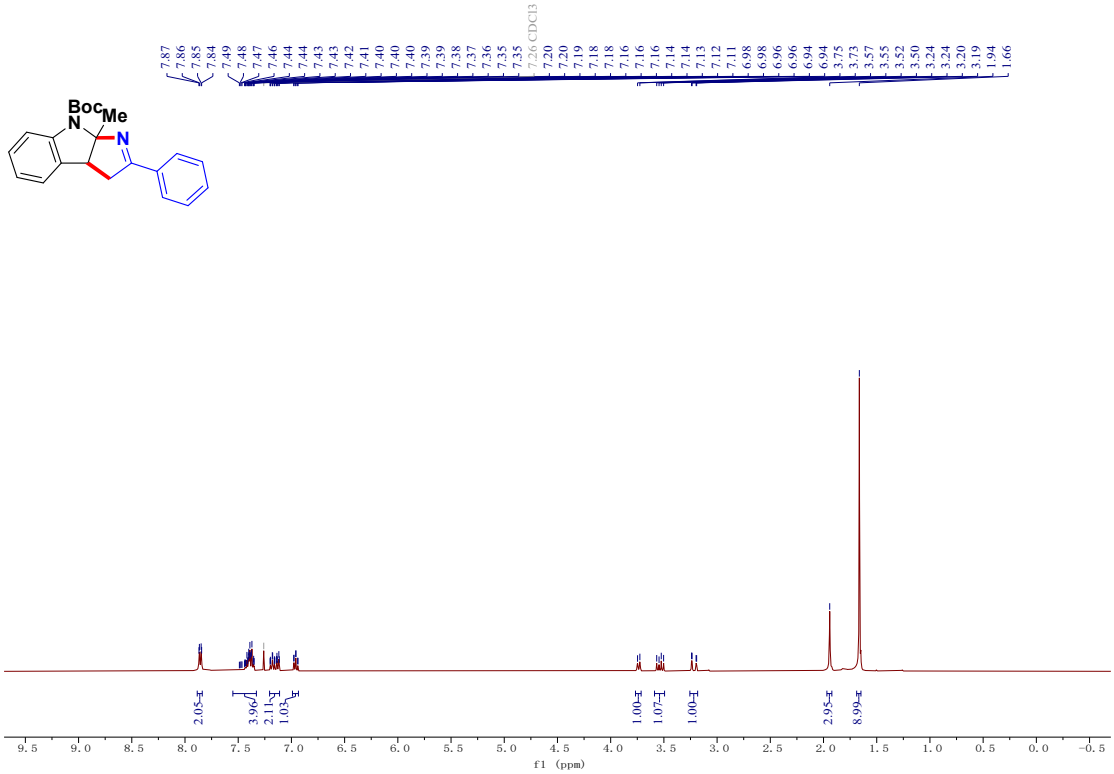
^{1}H NMR spectra of 3bp ($CDCl_3$, 400 MHz)



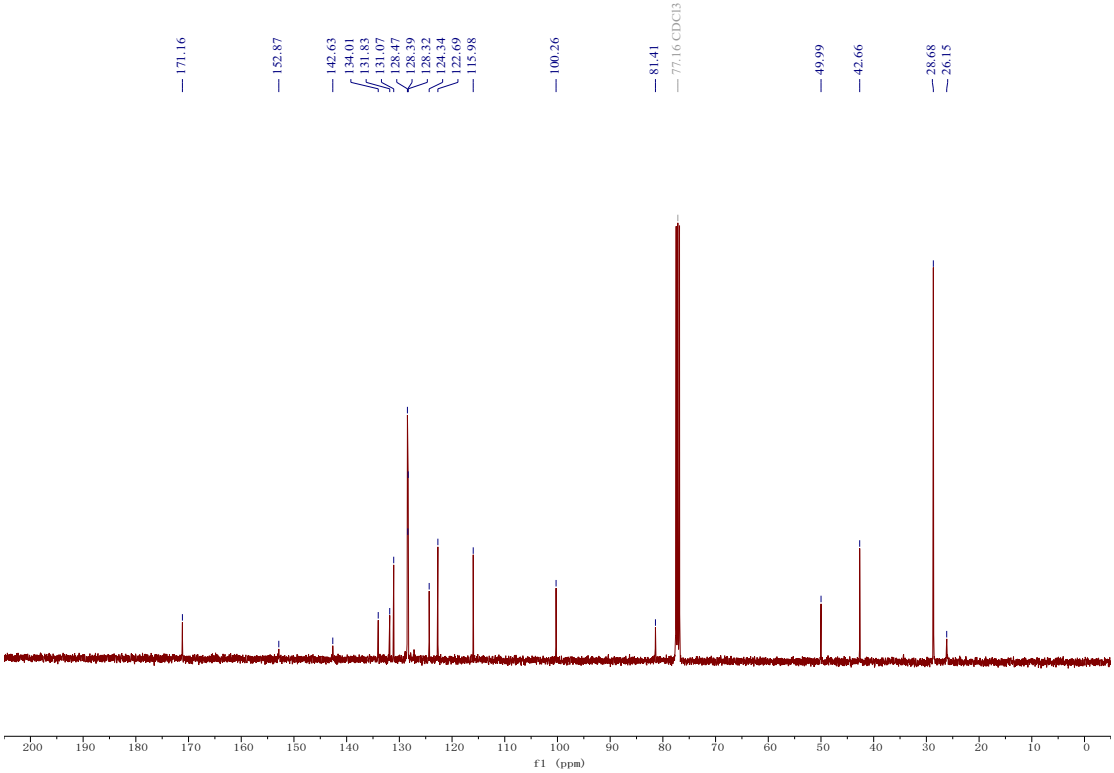
^{13}C NMR spectra of 3bp ($CDCl_3$, 101 MHz)



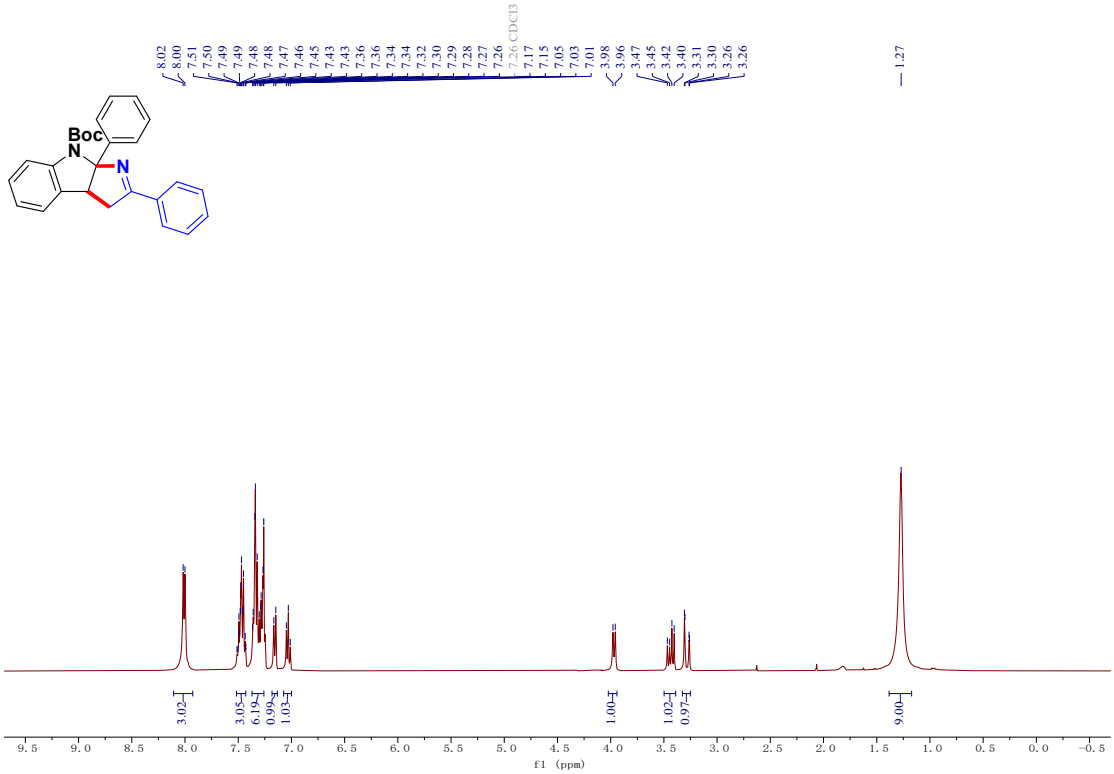
^{1}H NMR spectra of 5aa ($CDCl_3$, 400 MHz)



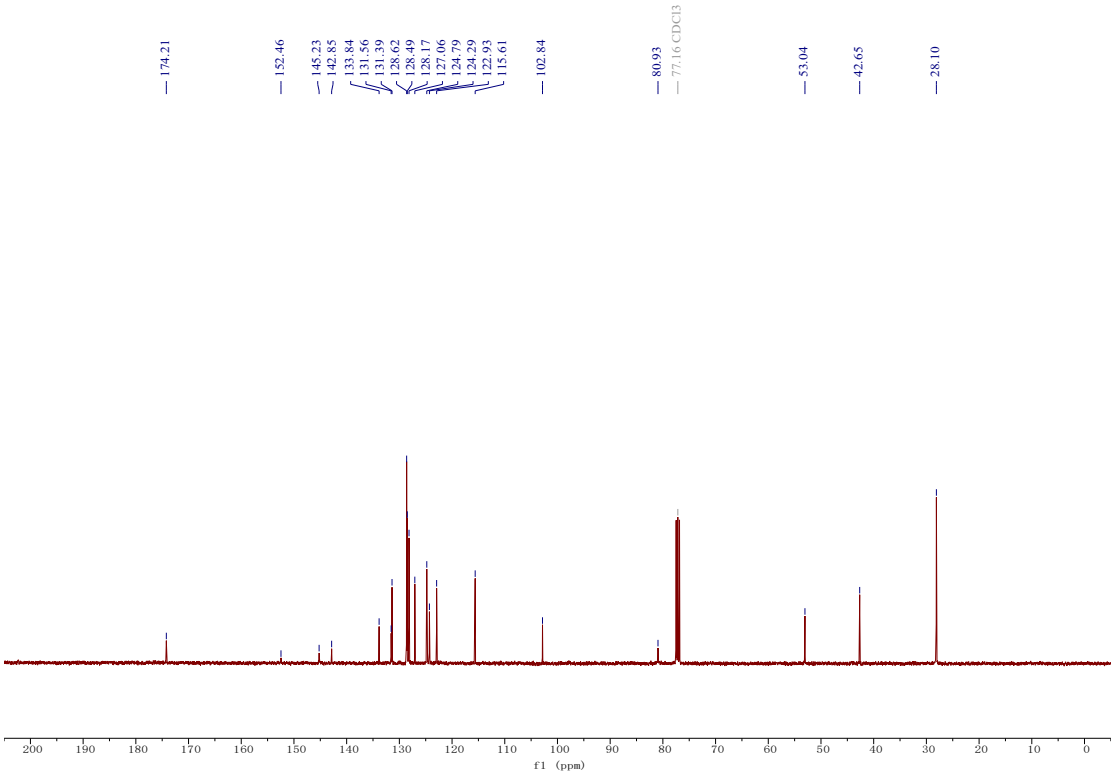
^{13}C NMR spectra of 5aa ($CDCl_3$, 101 MHz)



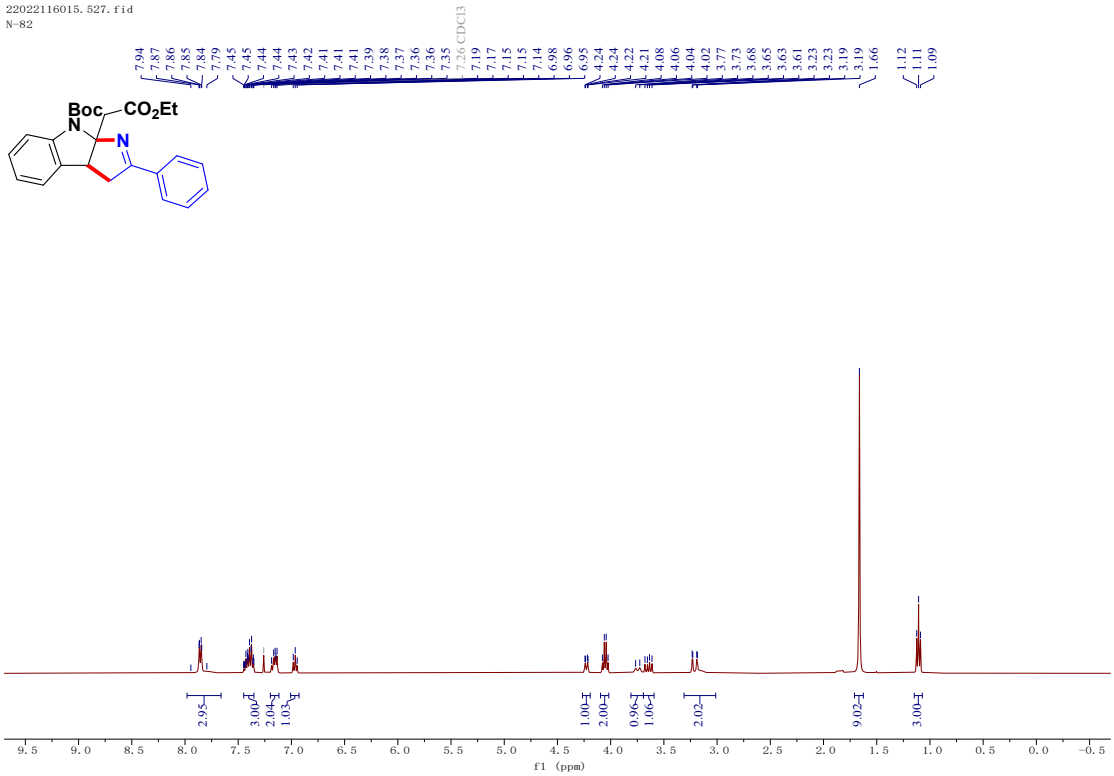
^{1}H NMR spectra of 5ab ($CDCl_3$, 400 MHz)



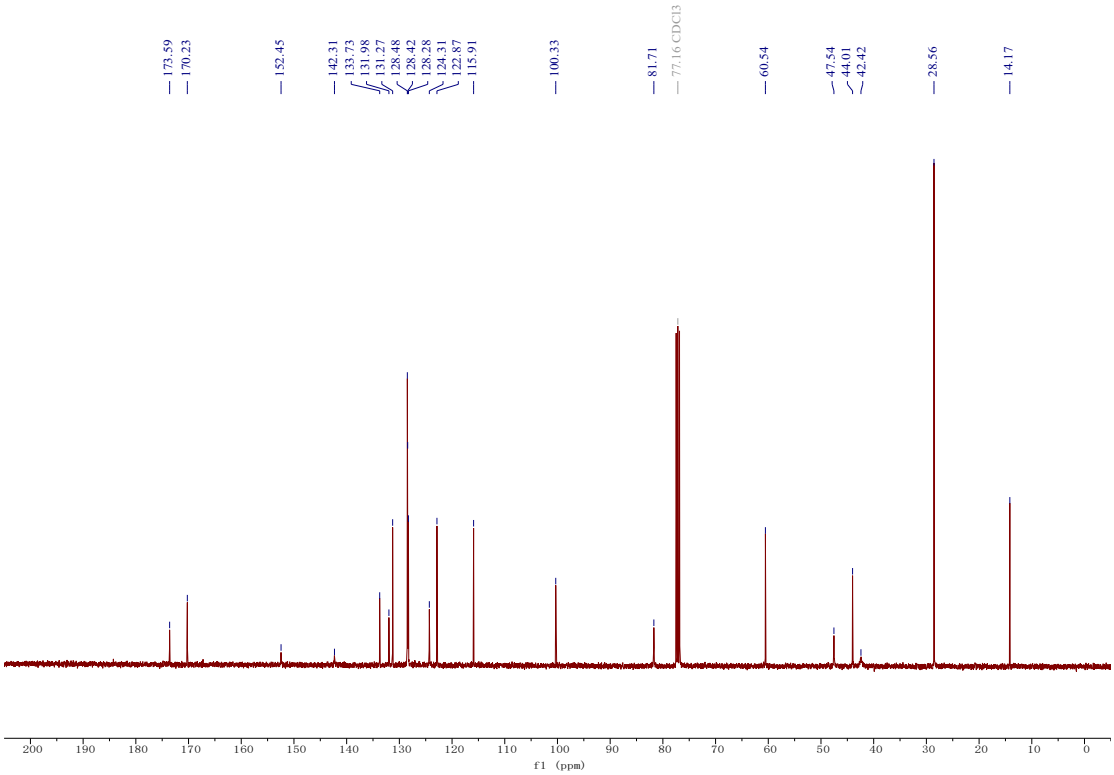
^{13}C NMR spectra of 5ab ($CDCl_3$, 101 MHz)



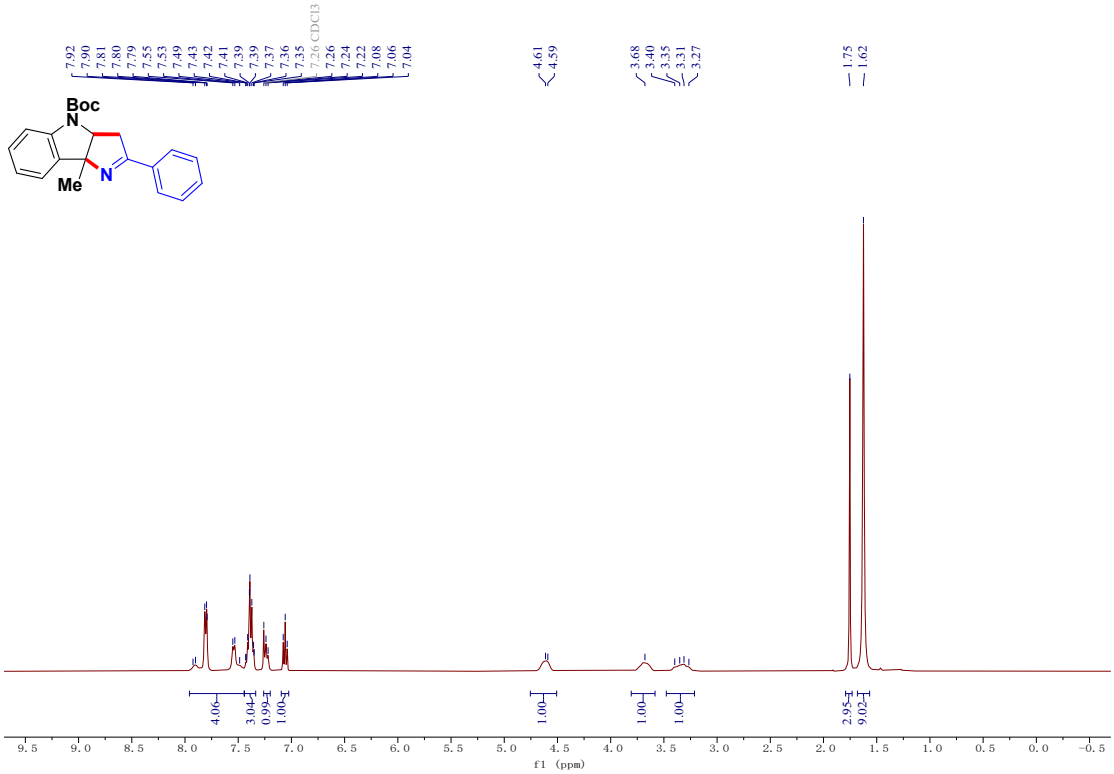
^{1}H NMR spectra of 5ac ($CDCl_3$, 400 MHz)



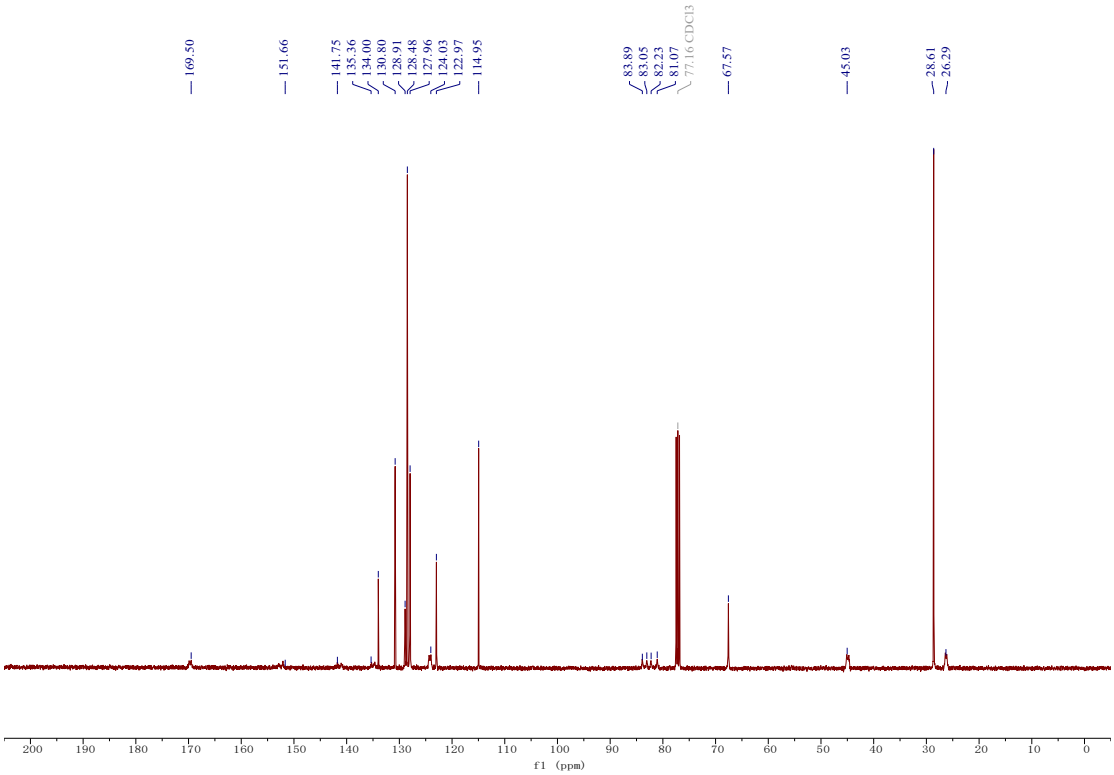
^{13}C NMR spectra of 5ac ($CDCl_3$, 101 MHz)



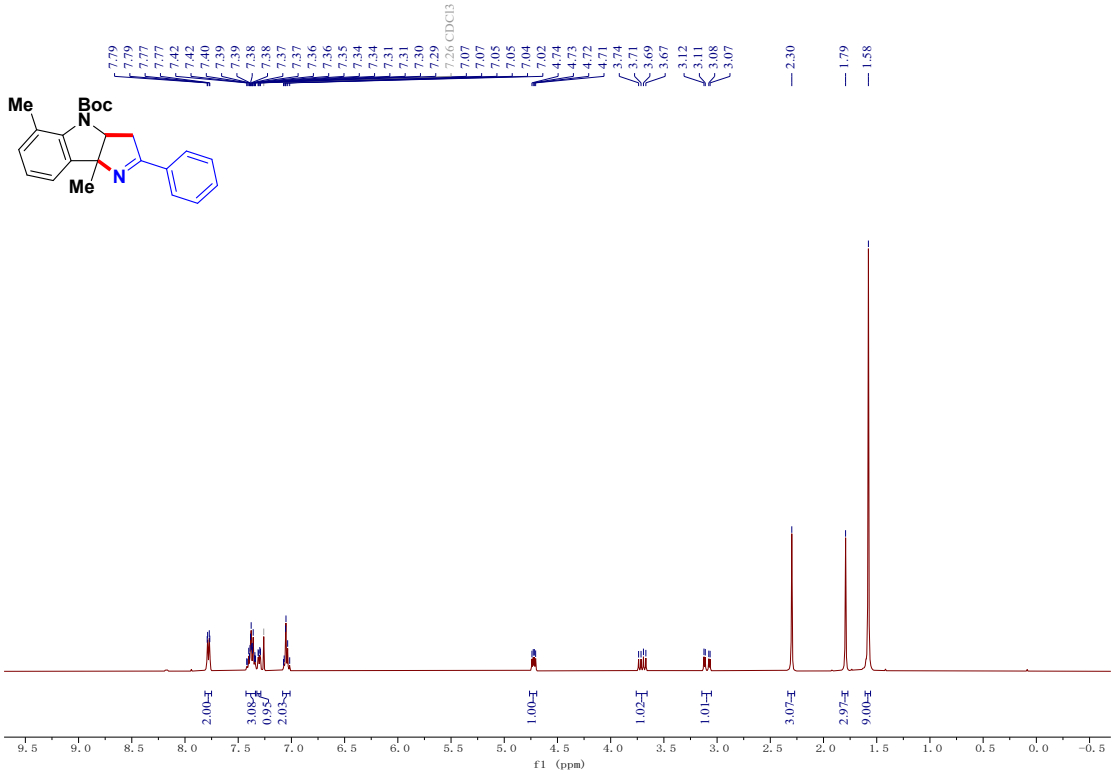
^{1}H NMR spectra of 5ad ($CDCl_3$, 400 MHz)



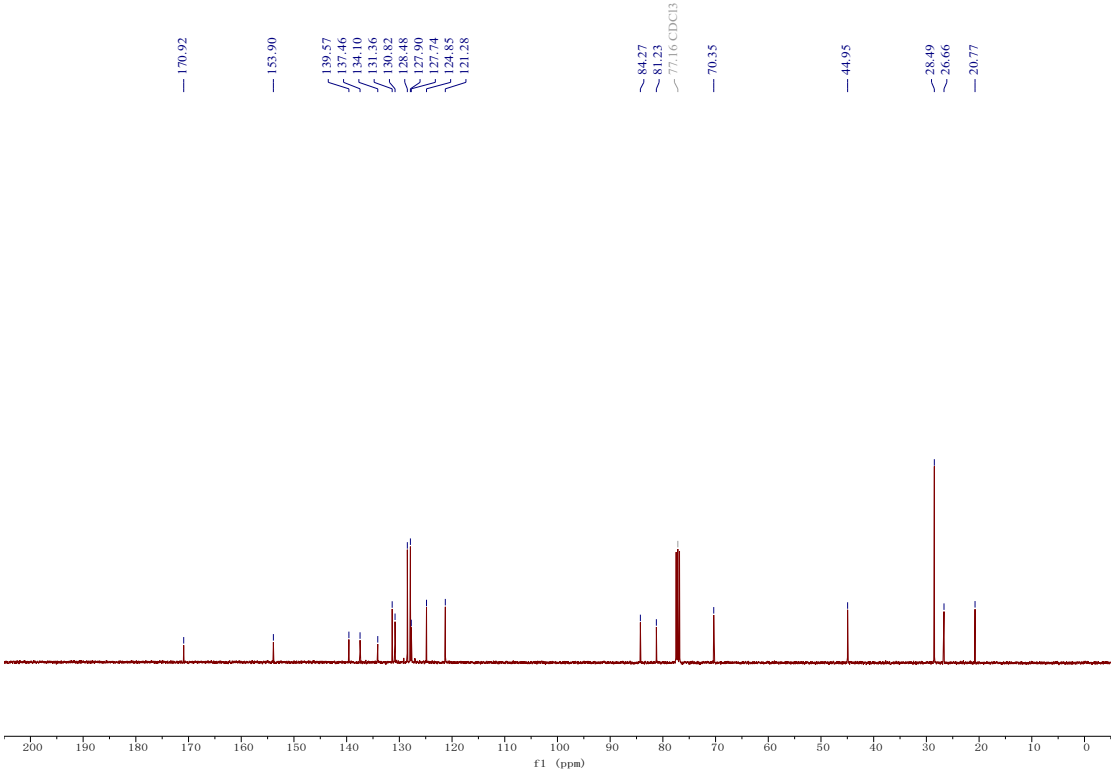
^{13}C NMR spectra of 5ad ($CDCl_3$, 101 MHz)



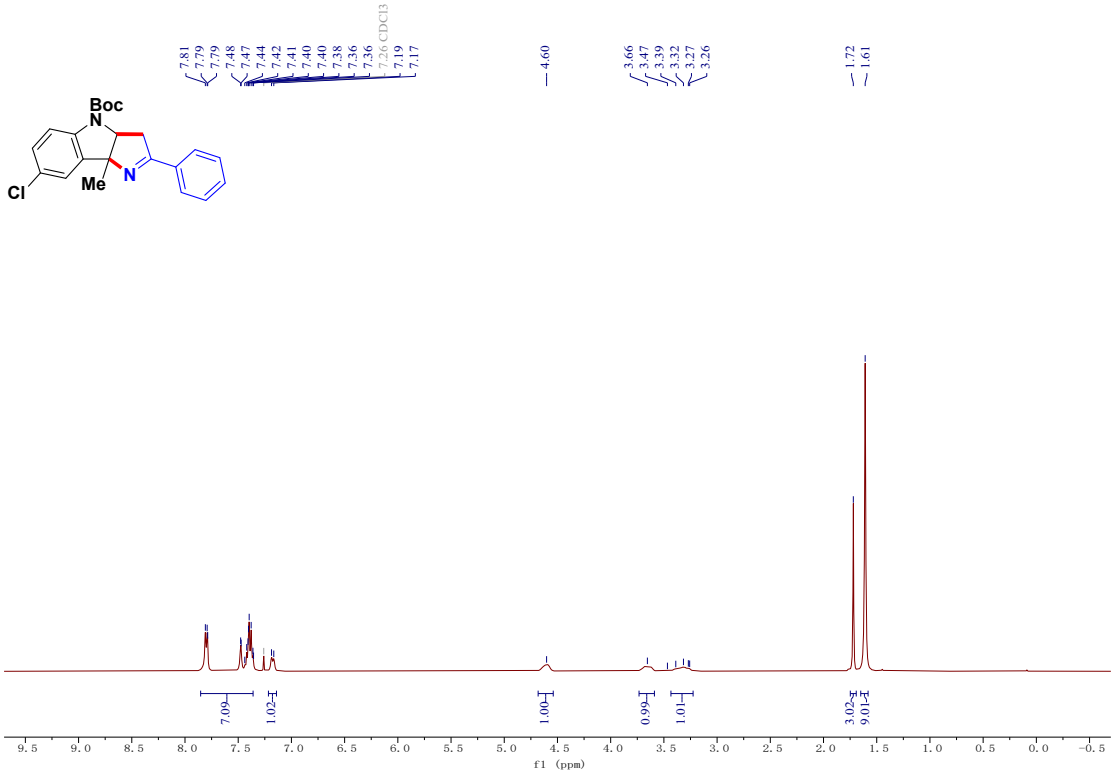
^{1}H NMR spectra of 5ae ($CDCl_3$, 400 MHz)



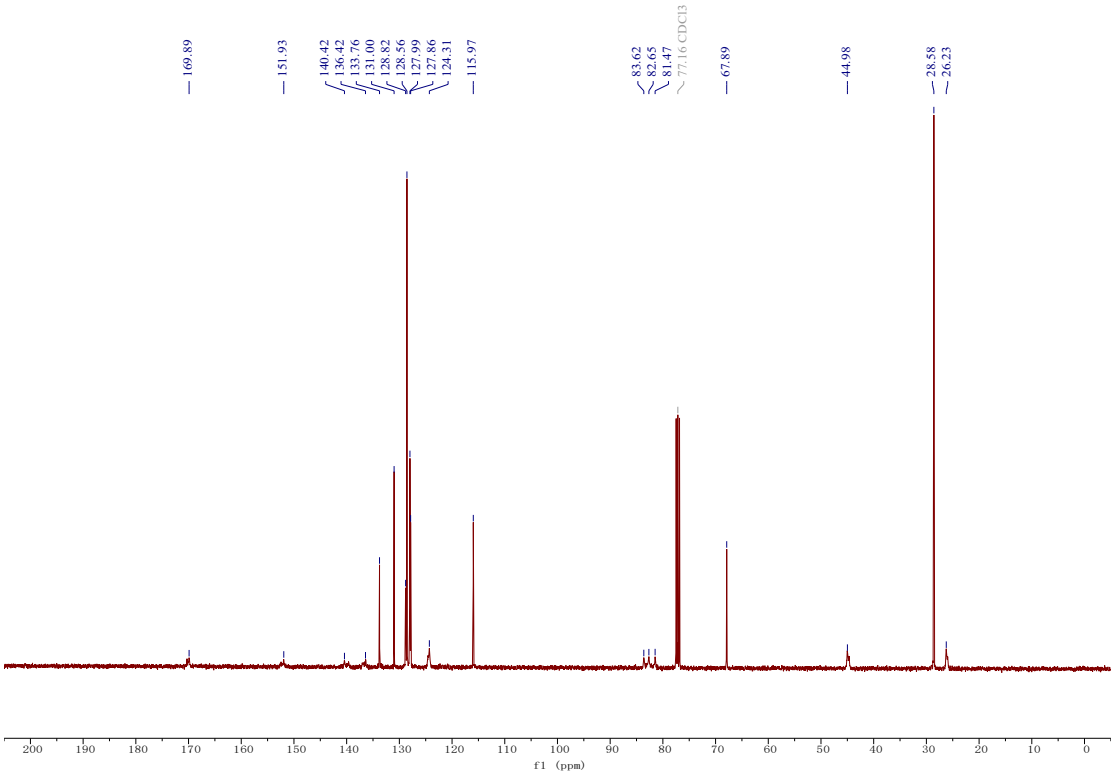
^{13}C NMR spectra of 5ae ($CDCl_3$, 101 MHz)



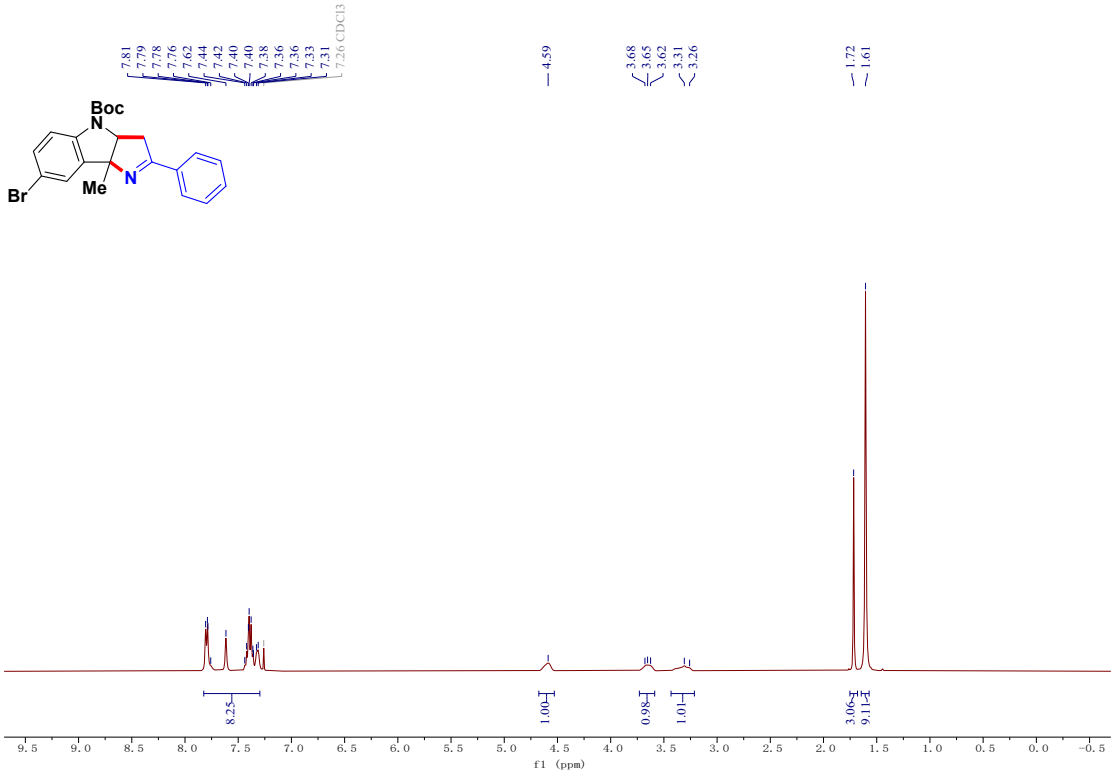
^{1}H NMR spectra of 5af ($CDCl_3$, 400 MHz)



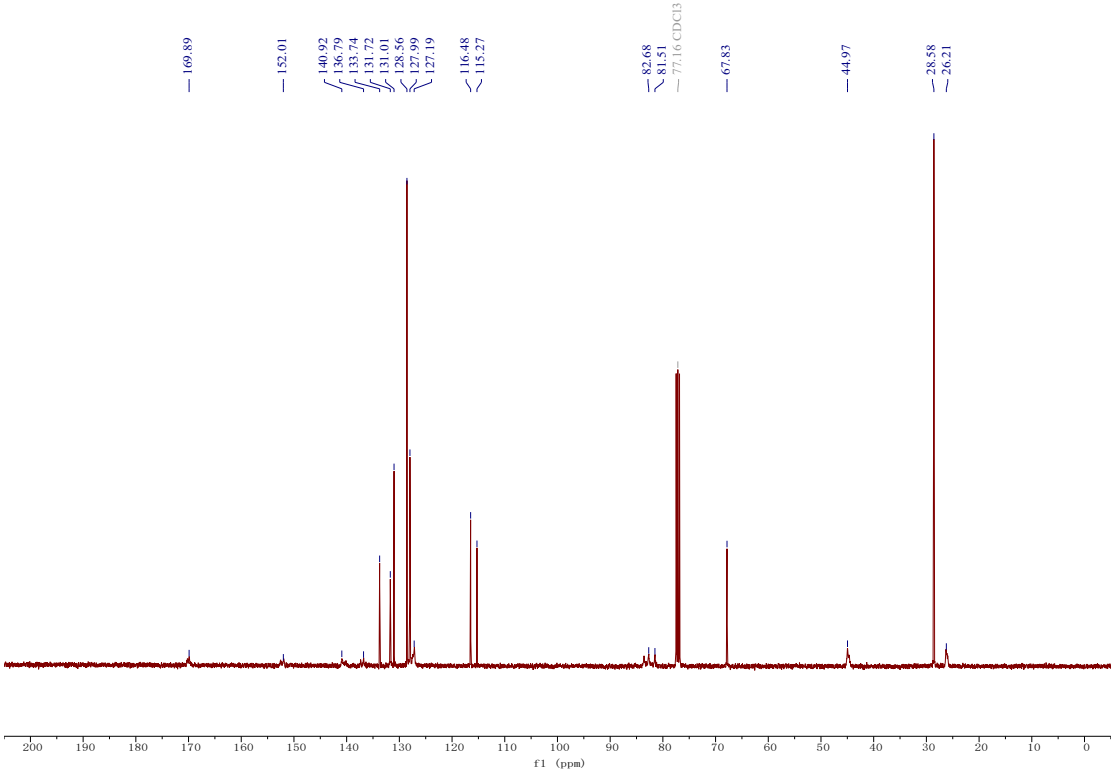
^{13}C NMR spectra of 5af ($CDCl_3$, 101 MHz)



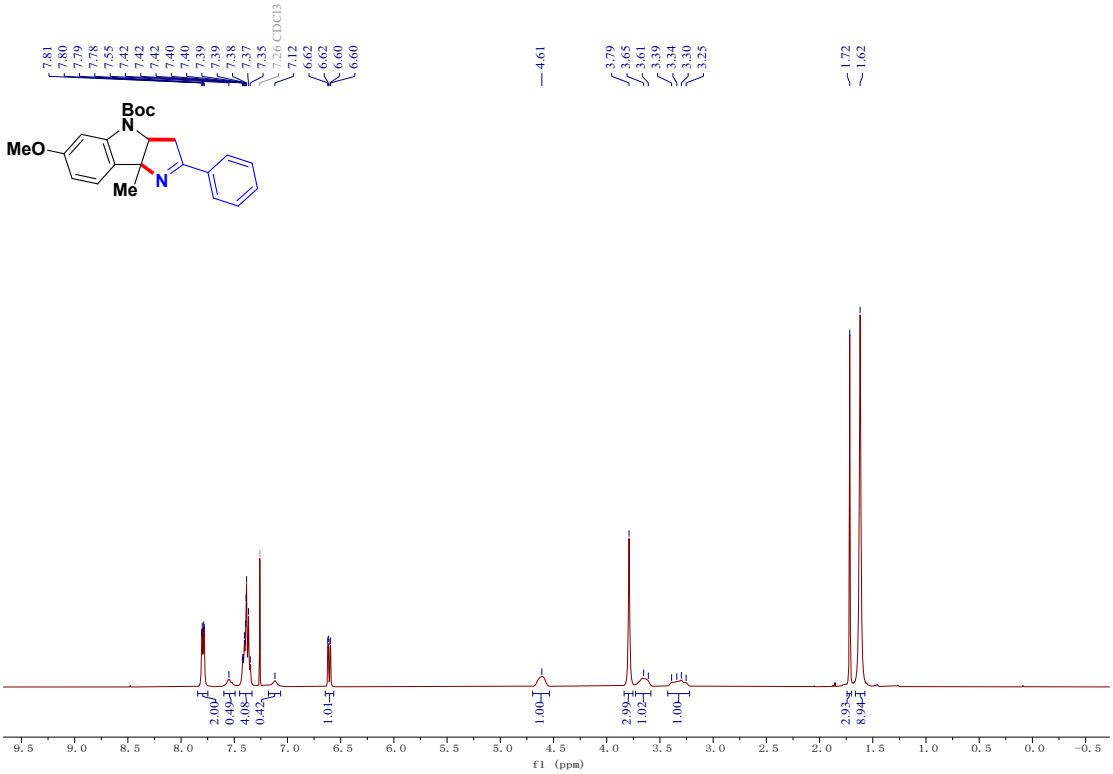
^{1}H NMR spectra of 5ag ($CDCl_3$, 400 MHz)



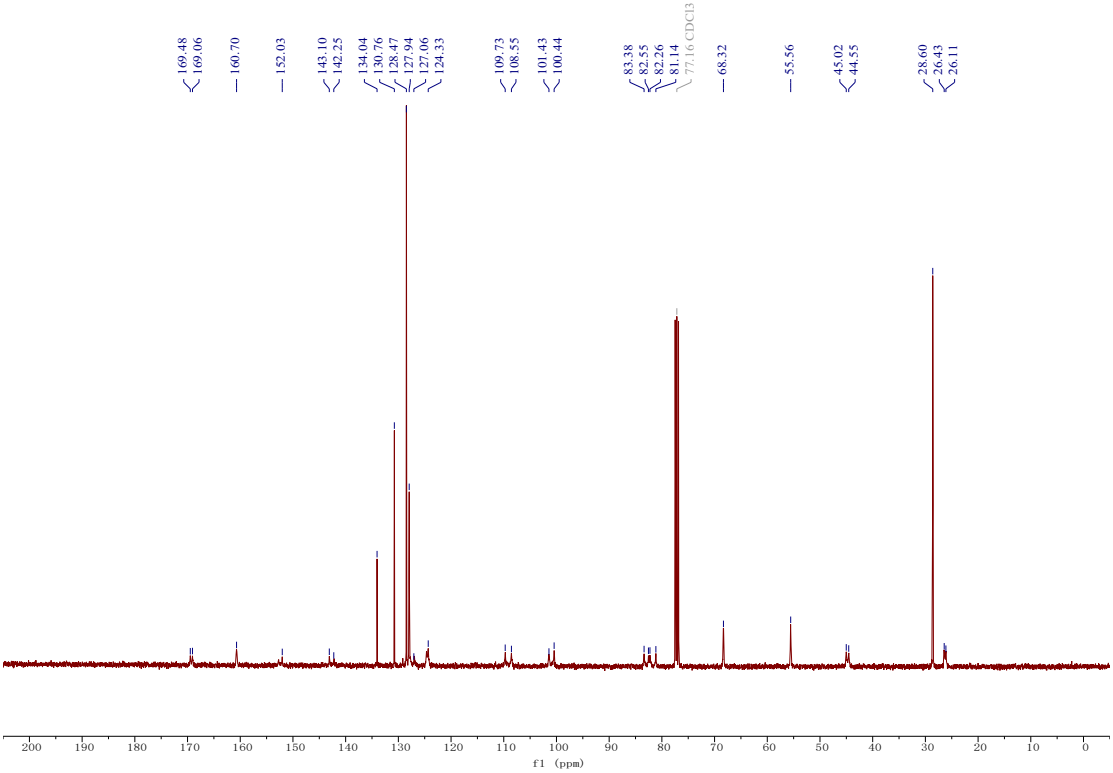
^{13}C NMR spectra of 5ag ($CDCl_3$, 101 MHz)



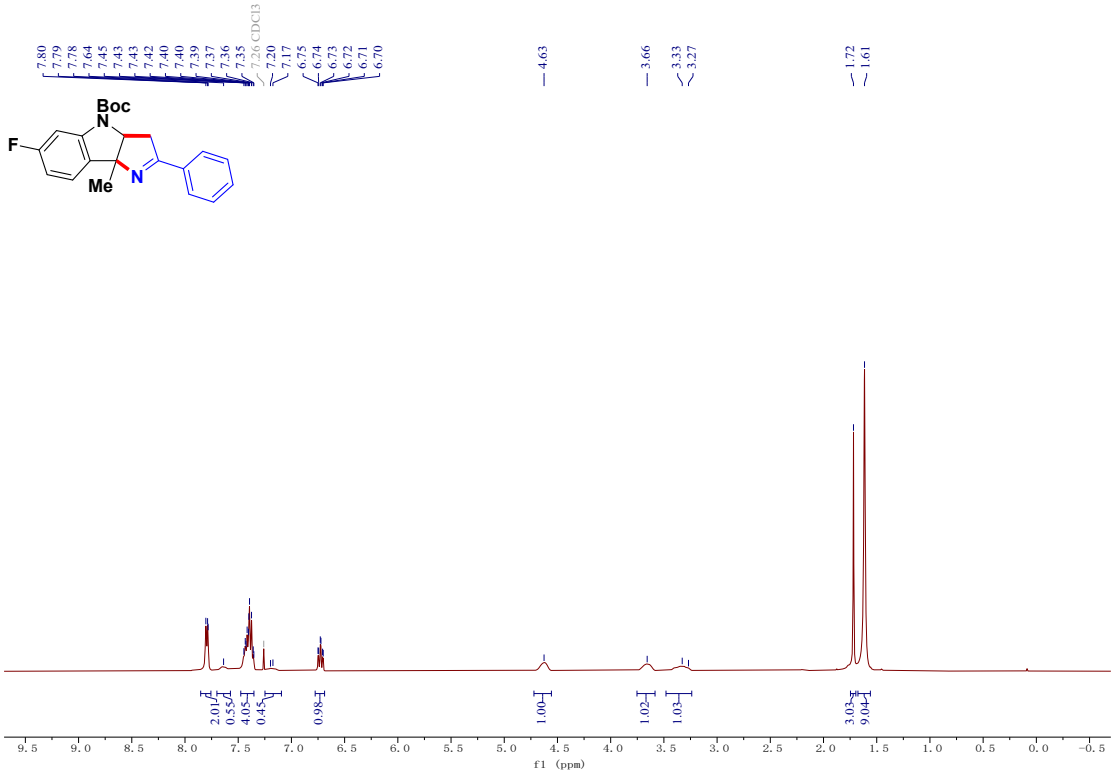
^{1}H NMR spectra of 5ah ($CDCl_3$, 400 MHz)



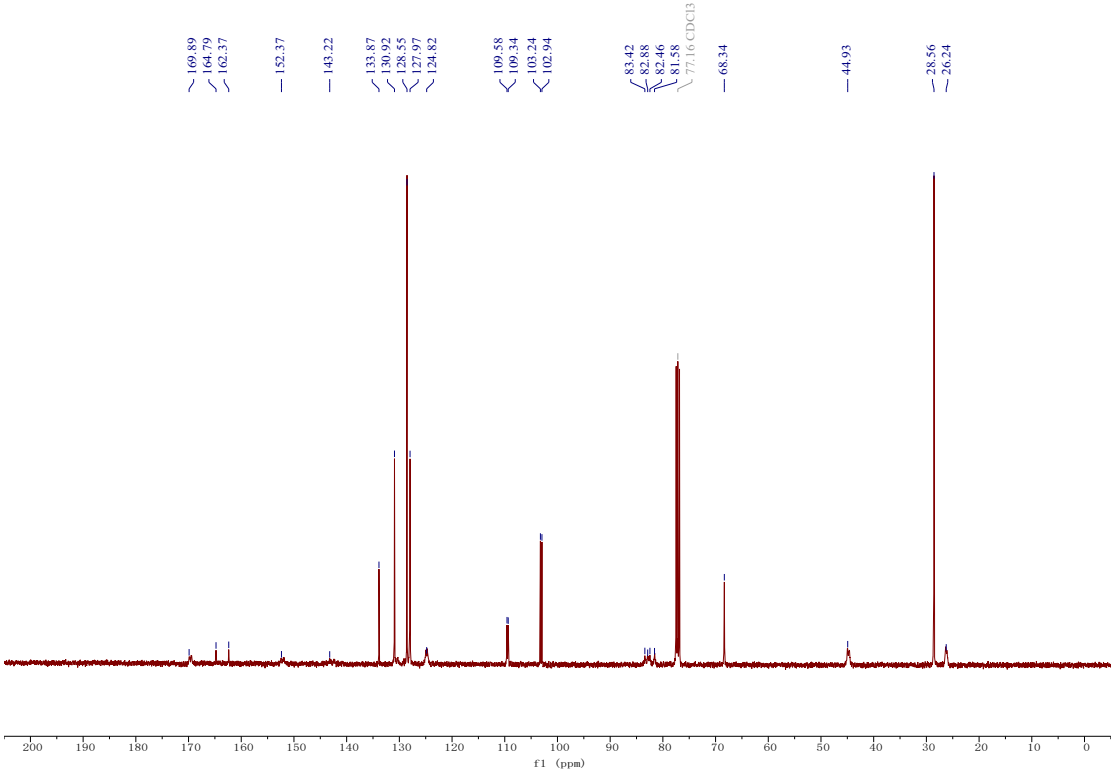
^{13}C NMR spectra of 5ah ($CDCl_3$, 101 MHz)



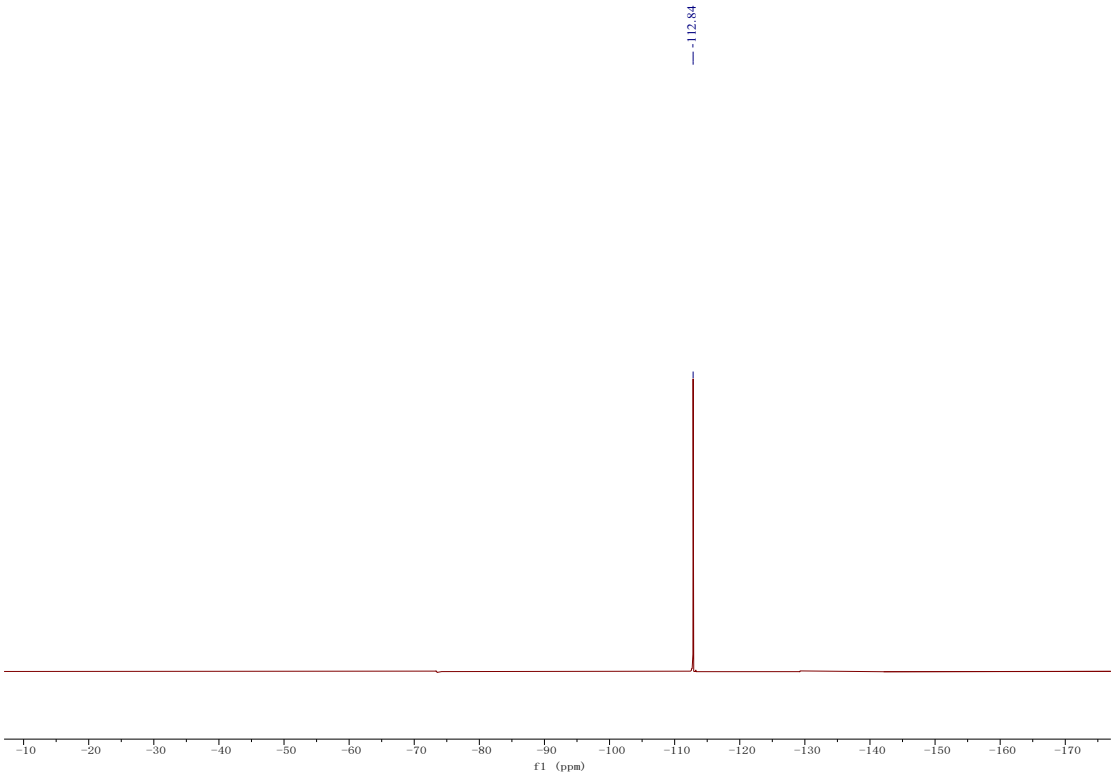
^{1}H NMR spectra of 5ai ($CDCl_3$, 400 MHz)



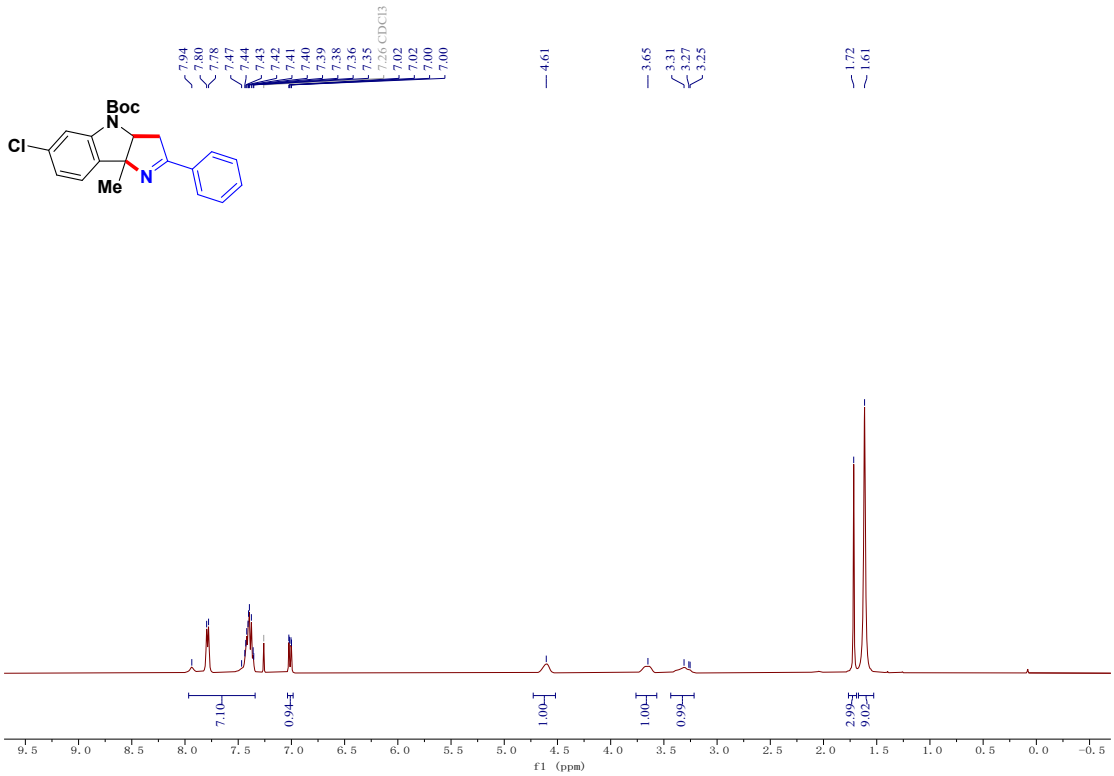
^{13}C NMR spectra of 5ai ($CDCl_3$, 101 MHz)



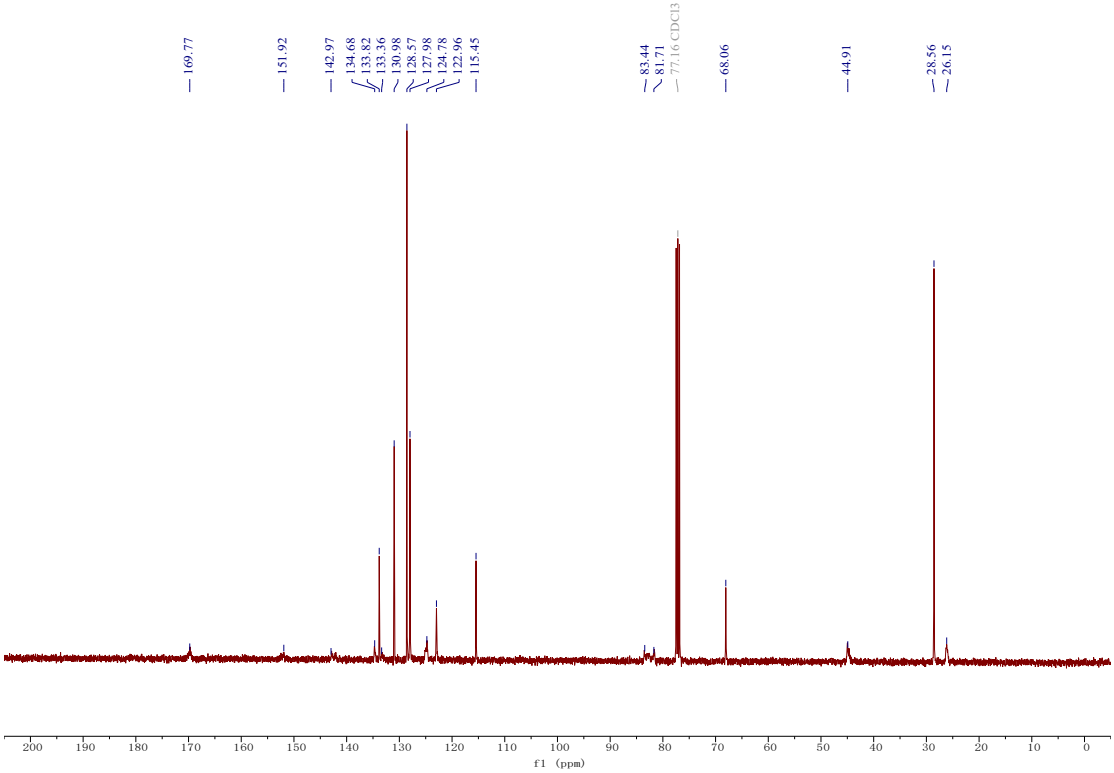
^{19}F NMR spectra of 5ai ($CDCl_3$, 376 MHz)



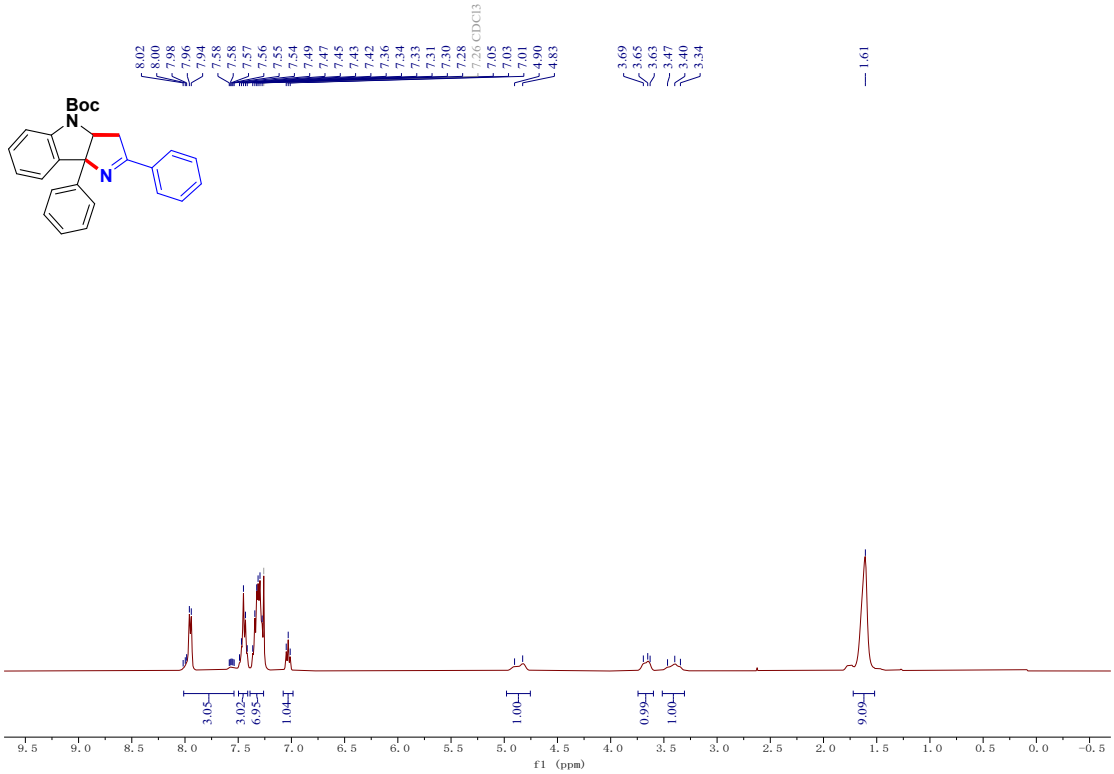
^{1}H NMR spectra of 5aj ($CDCl_3$, 400 MHz)



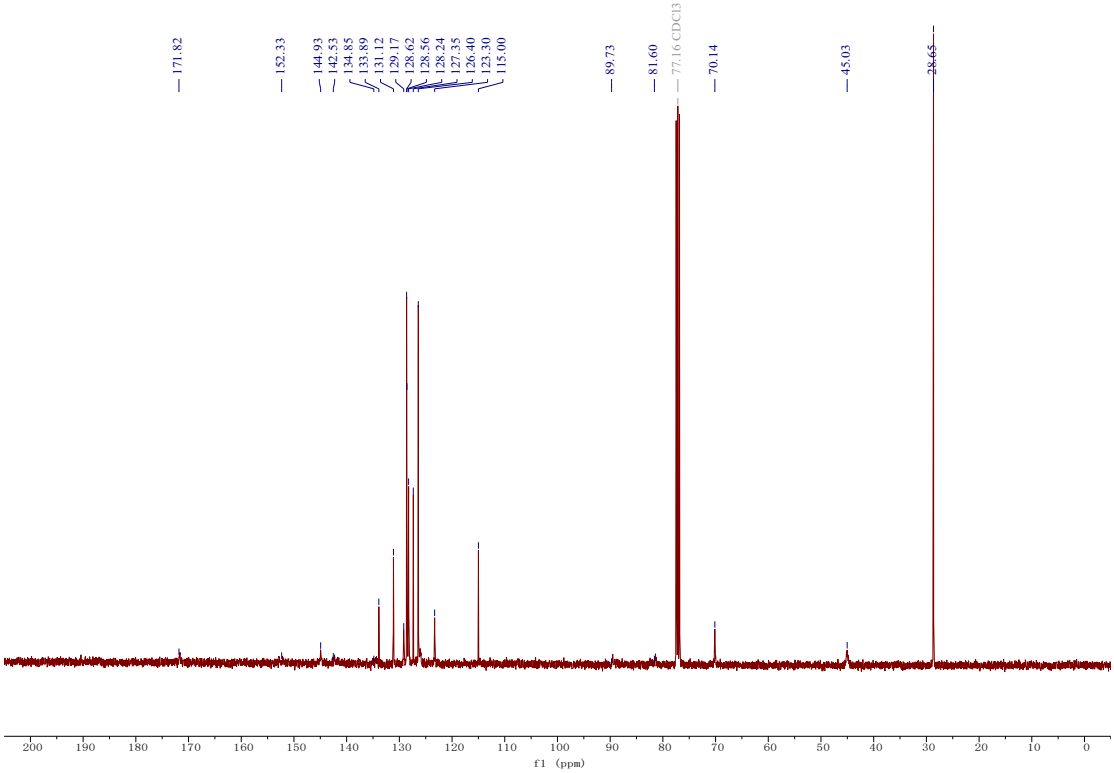
^{13}C NMR spectra of 5aj ($CDCl_3$, 101 MHz)



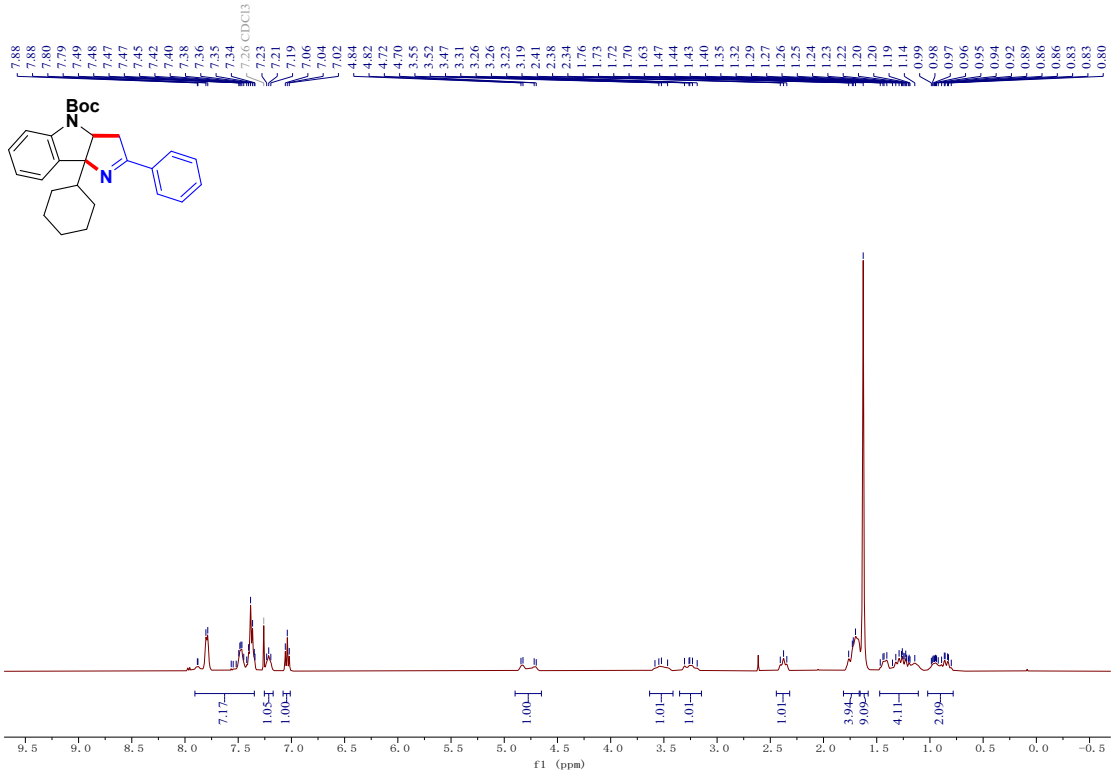
^{1}H NMR spectra of 5ak ($CDCl_3$, 400 MHz)



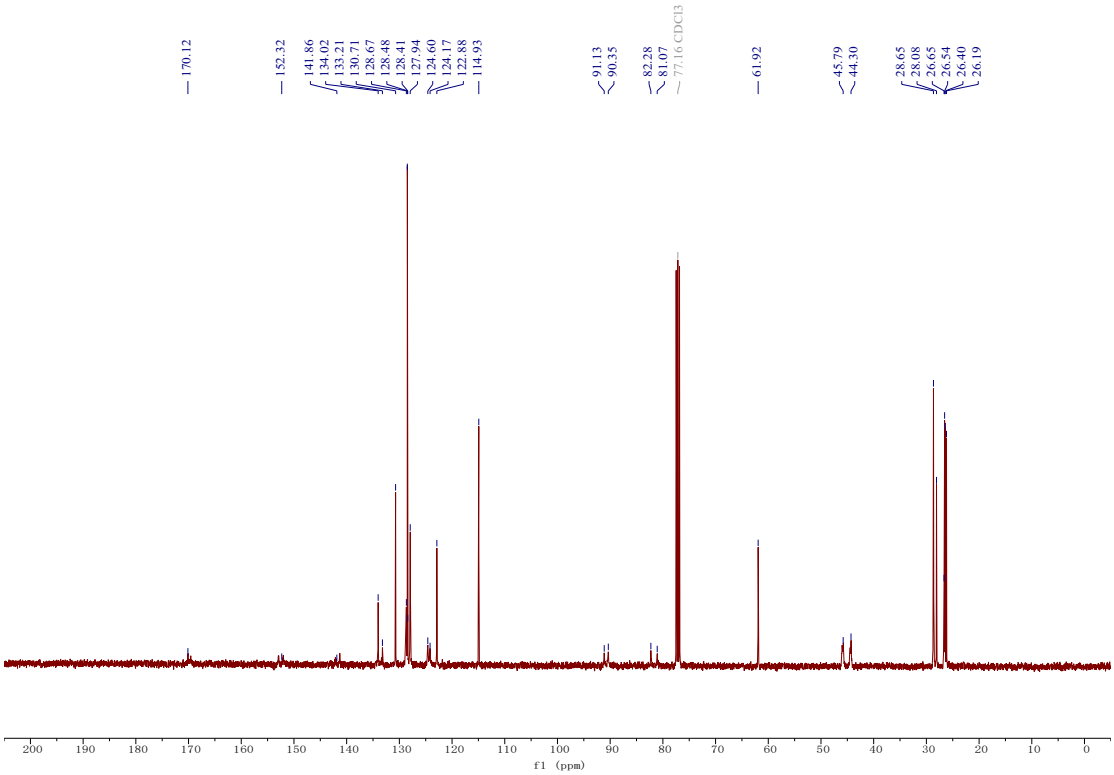
^{13}C NMR spectra of 5ak ($CDCl_3$, 101 MHz)



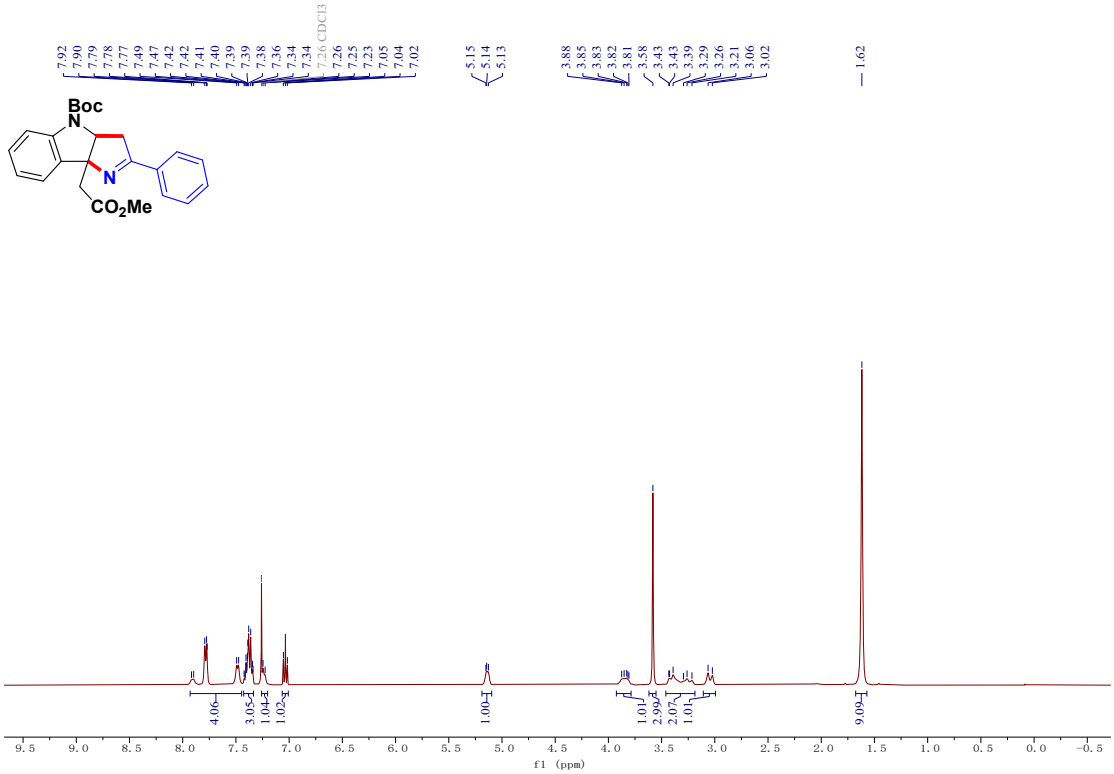
^{1}H NMR spectra of 5al ($CDCl_3$, 400 MHz)



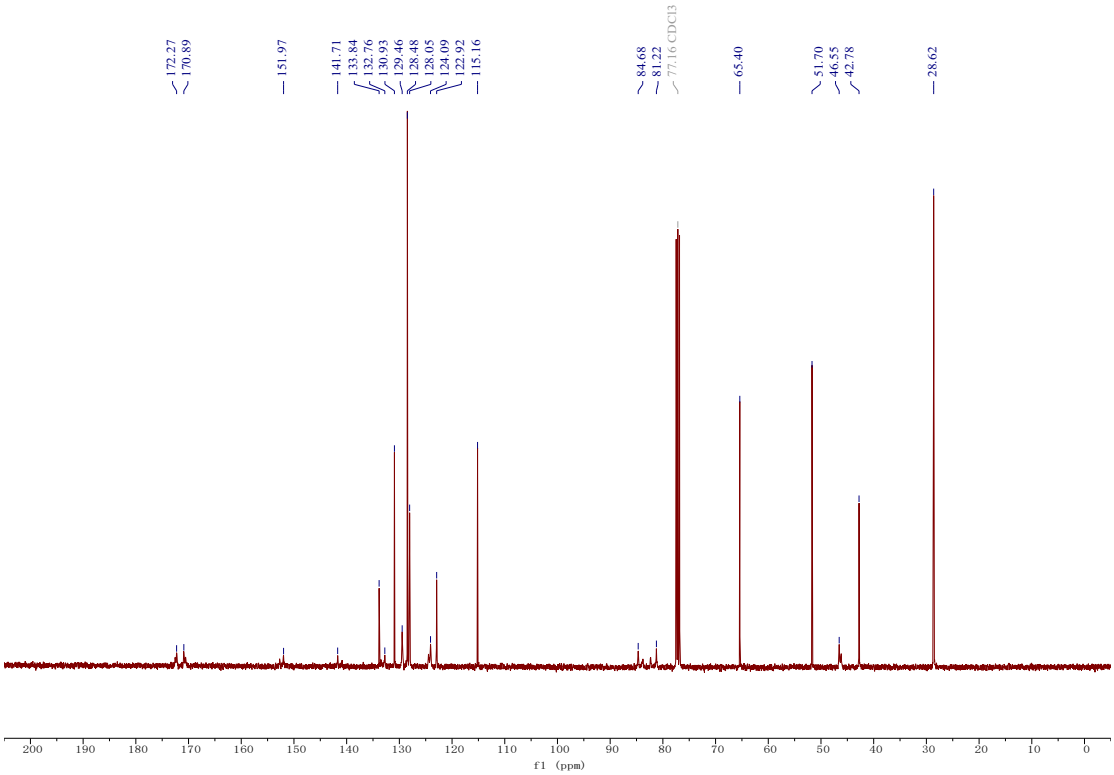
^{13}C NMR spectra of 5al ($CDCl_3$, 101 MHz)



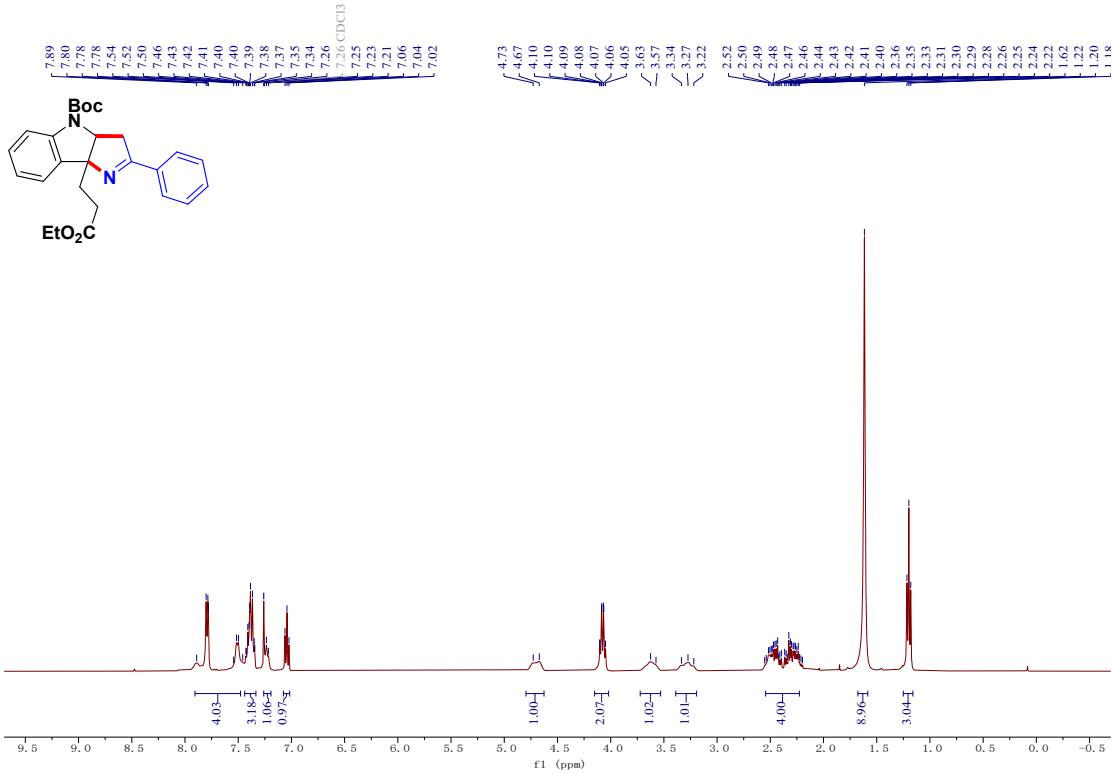
^{1}H NMR spectra of 5am ($CDCl_3$, 400 MHz)



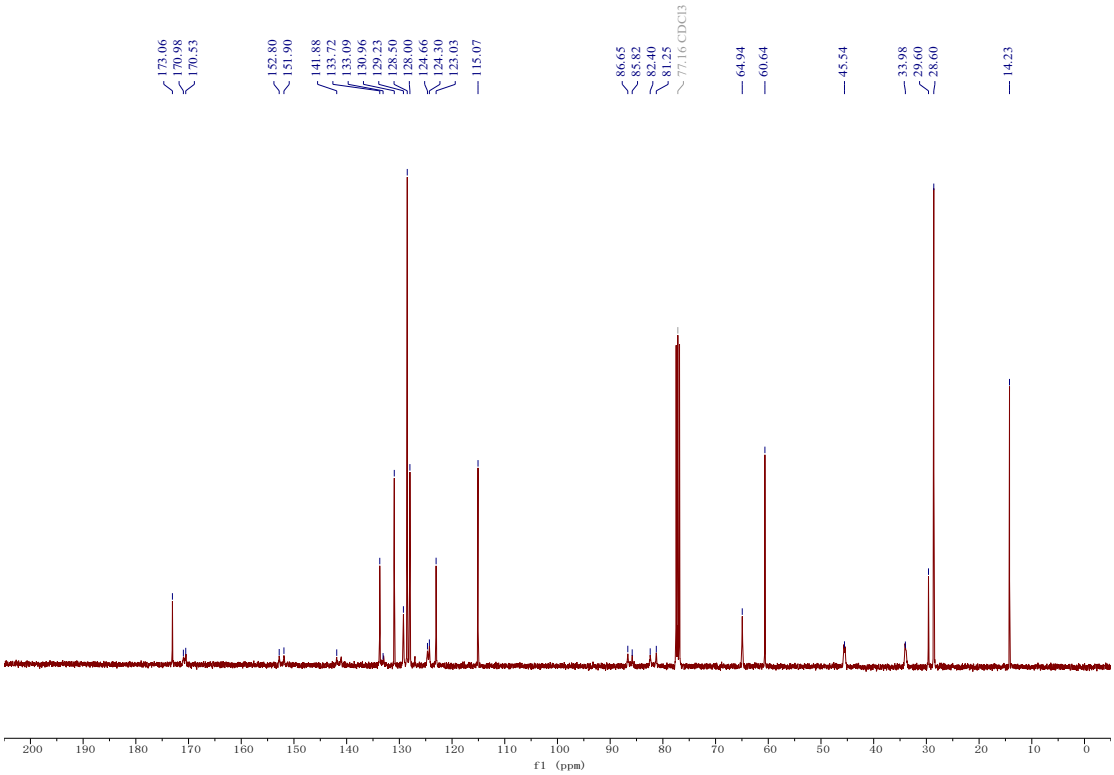
^{13}C NMR spectra of 5am ($CDCl_3$, 101 MHz)



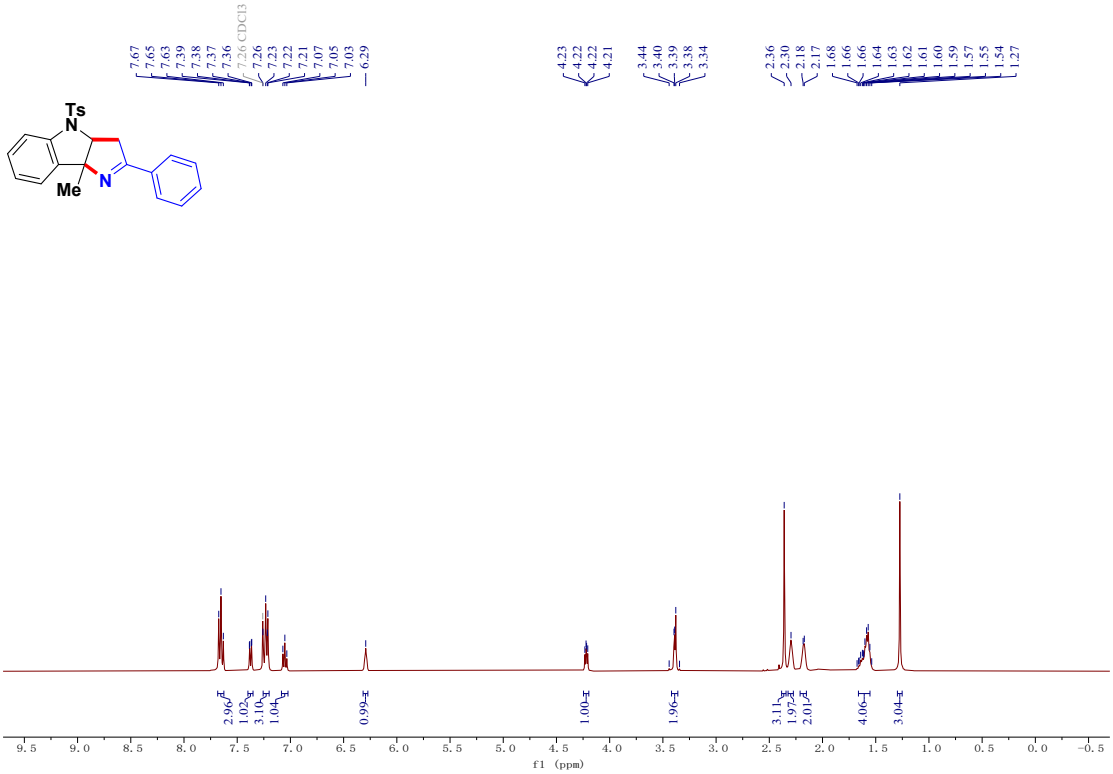
^{1}H NMR spectra of 5an ($CDCl_3$, 400 MHz)



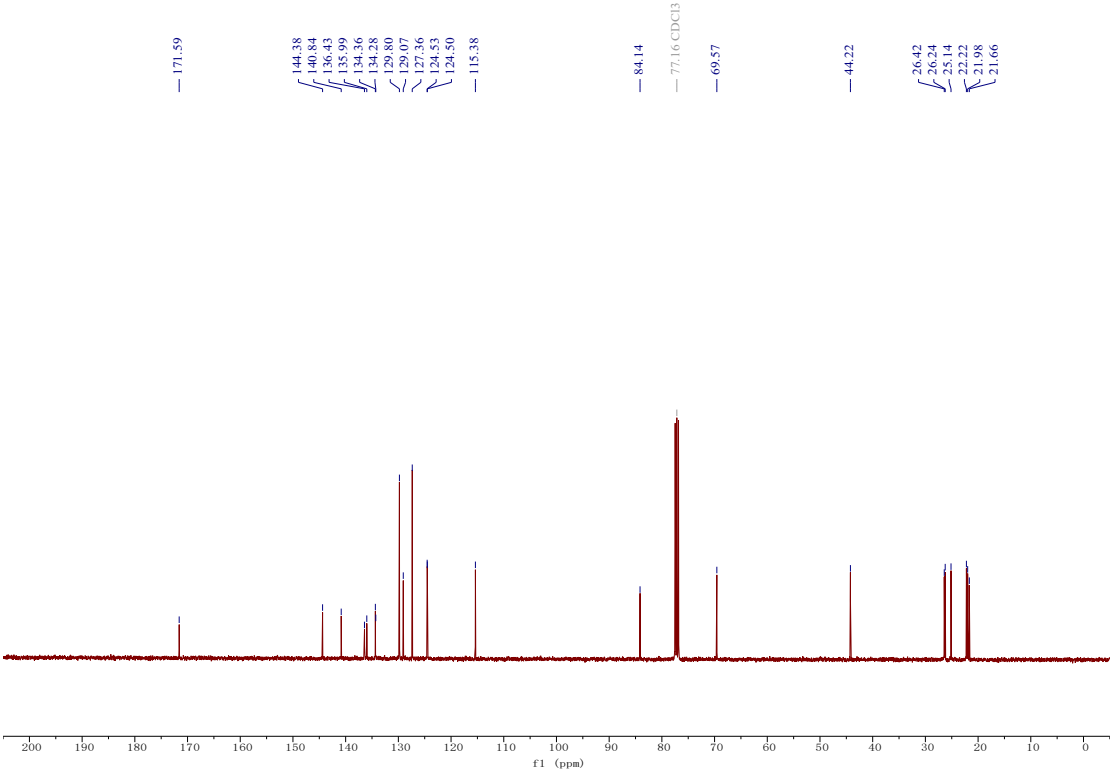
^{13}C NMR spectra of 5an ($CDCl_3$, 101 MHz)



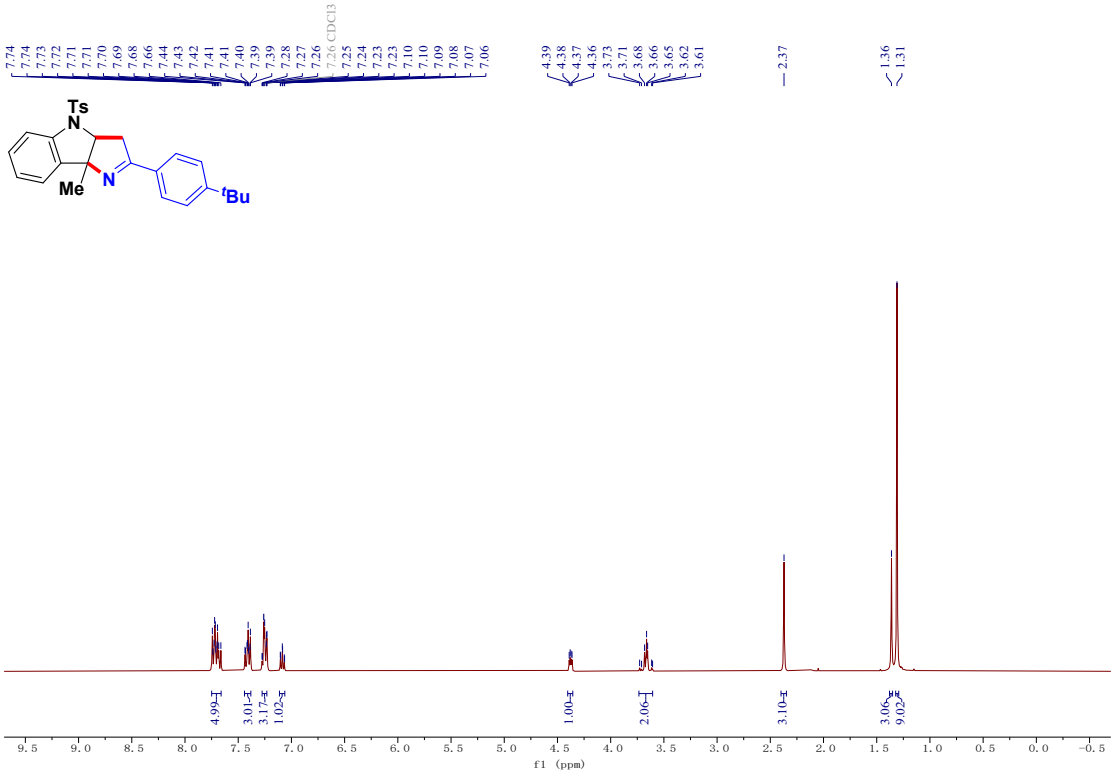
^{1}H NMR spectra of 5ao ($CDCl_3$, 400 MHz)



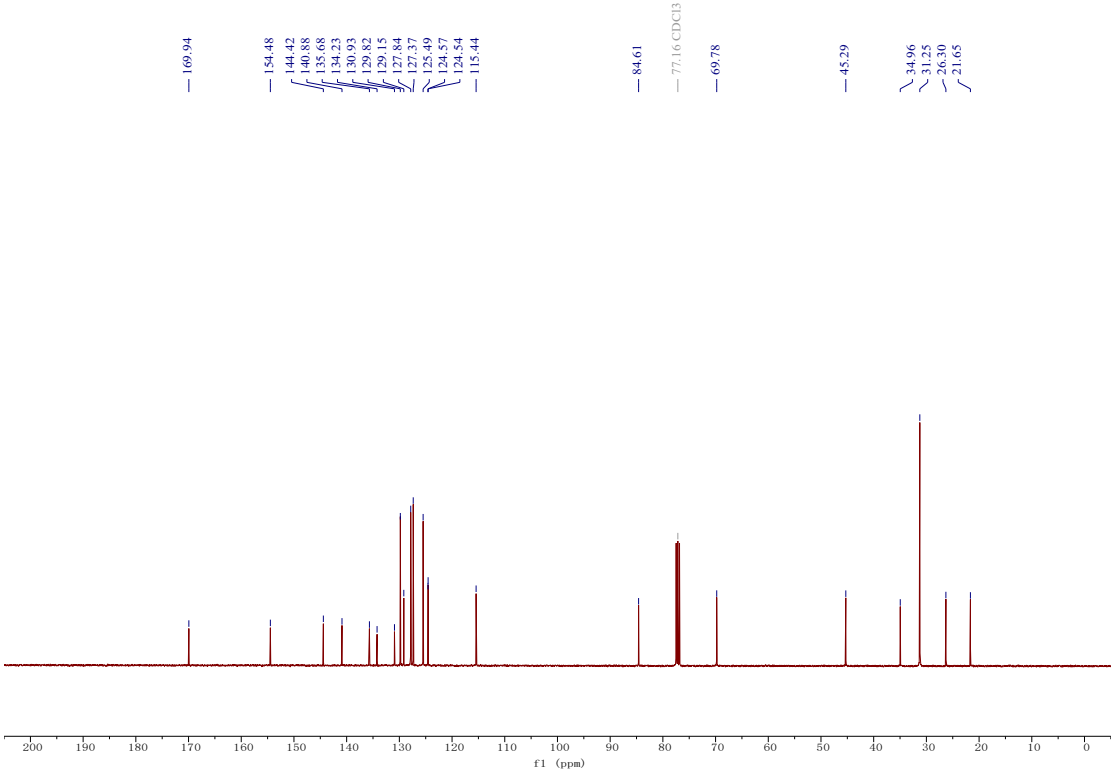
^{13}C NMR spectra of 5ao ($CDCl_3$, 101 MHz)



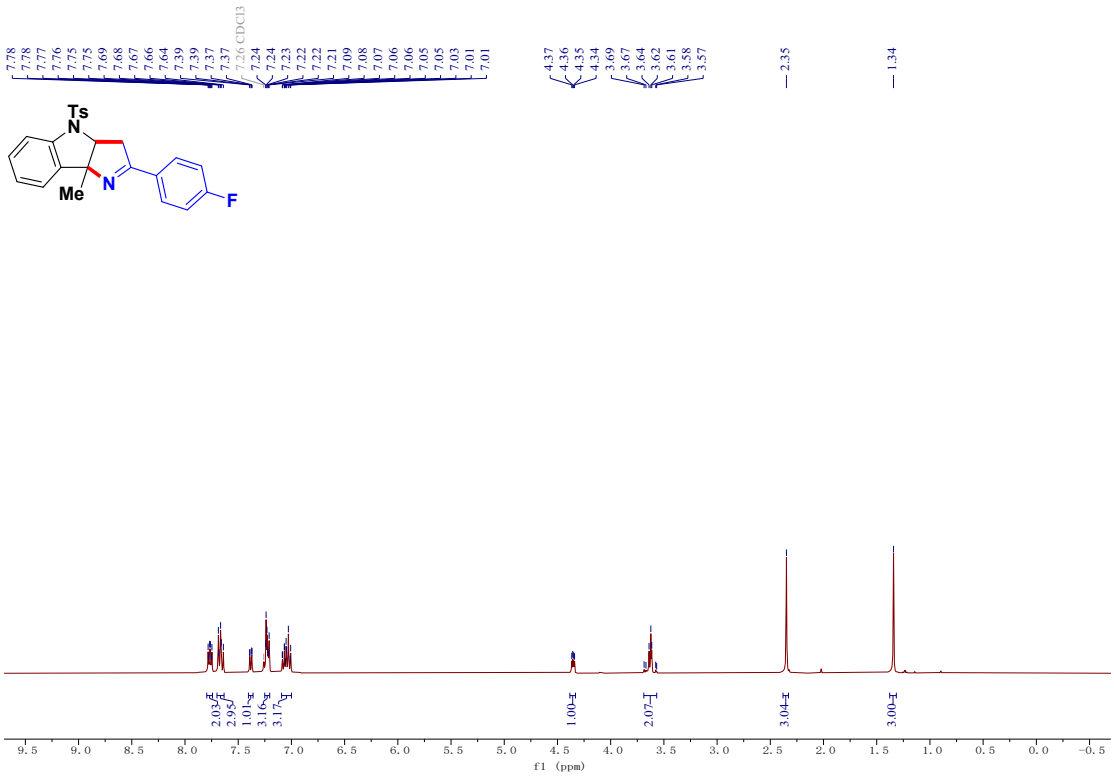
^{1}H NMR spectra of 5ap ($CDCl_3$, 400 MHz)



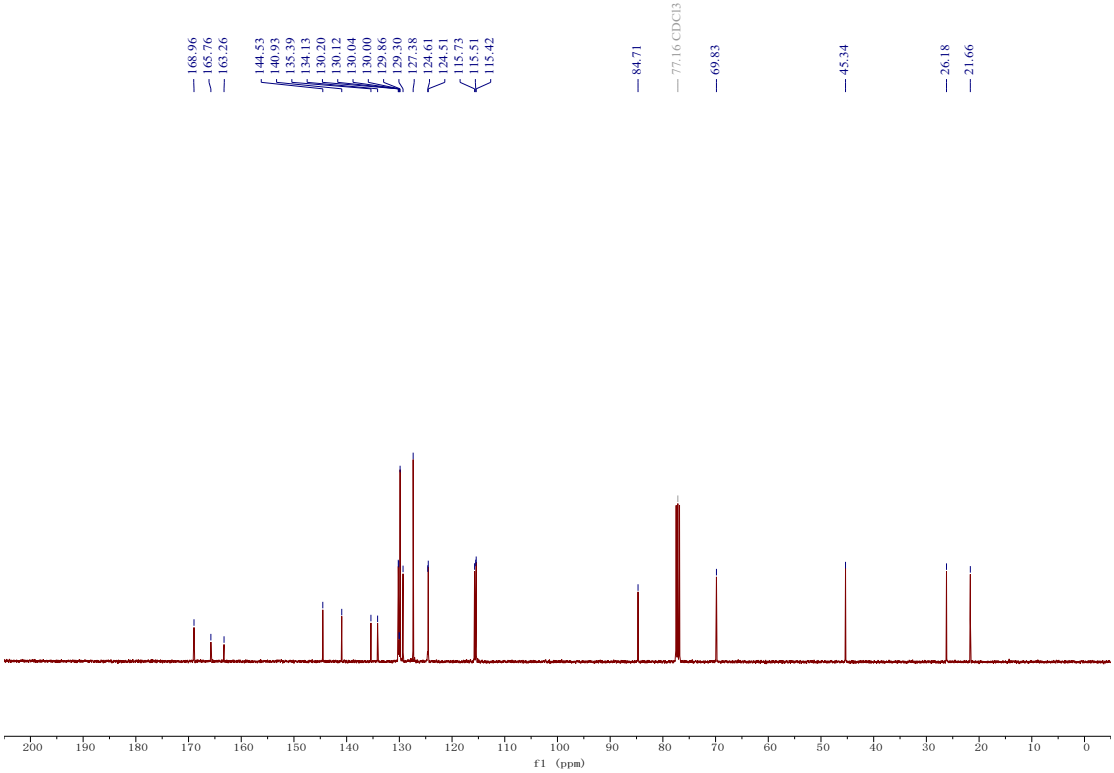
^{13}C NMR spectra of 5ap ($CDCl_3$, 101 MHz)



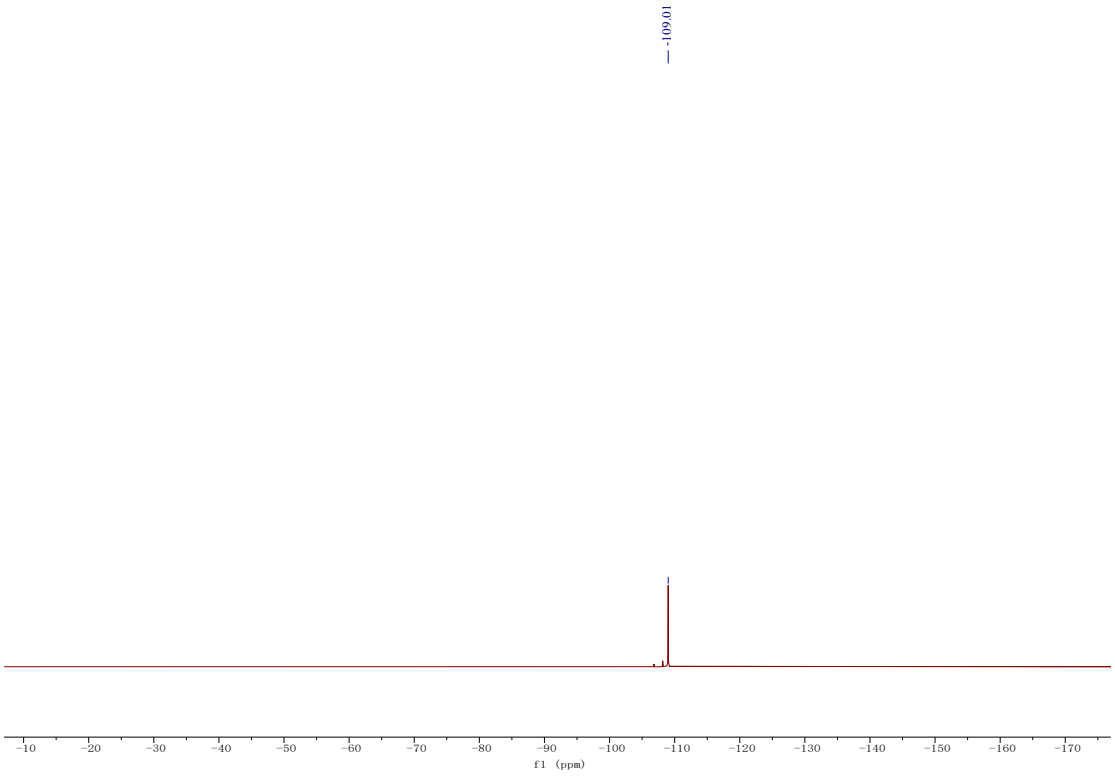
^{1}H NMR spectra of 5aq ($CDCl_3$, 400 MHz)



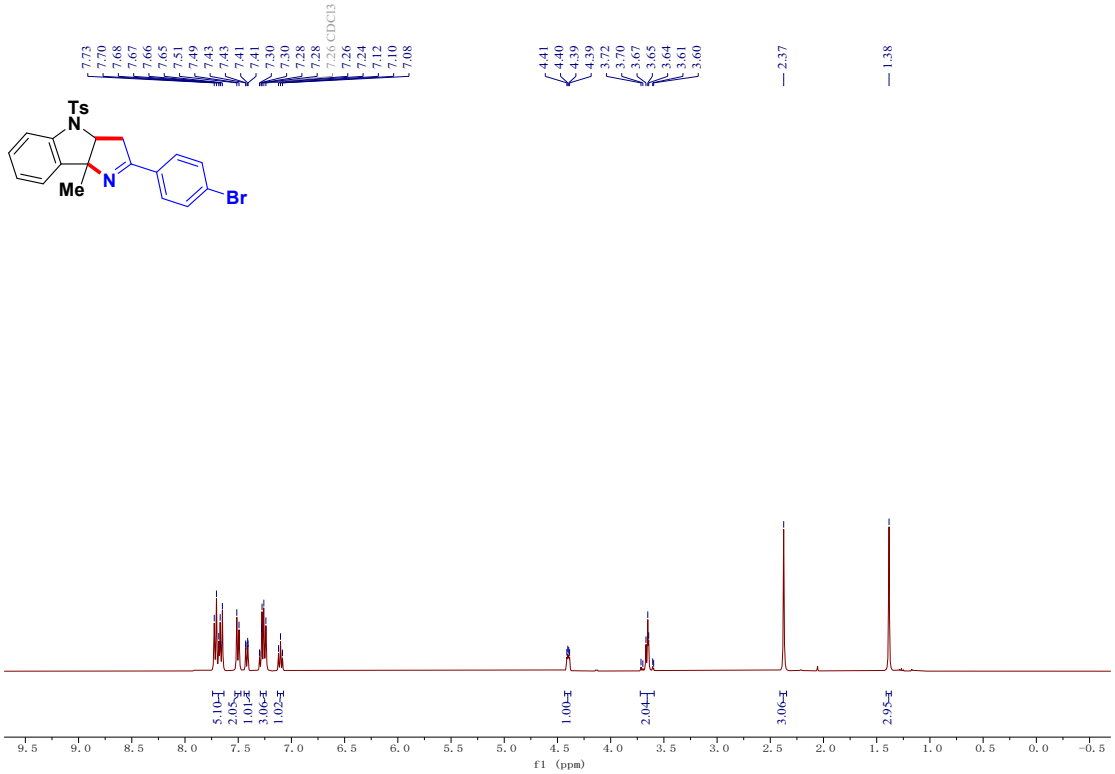
^{13}C NMR spectra of 5aq ($CDCl_3$, 101 MHz)



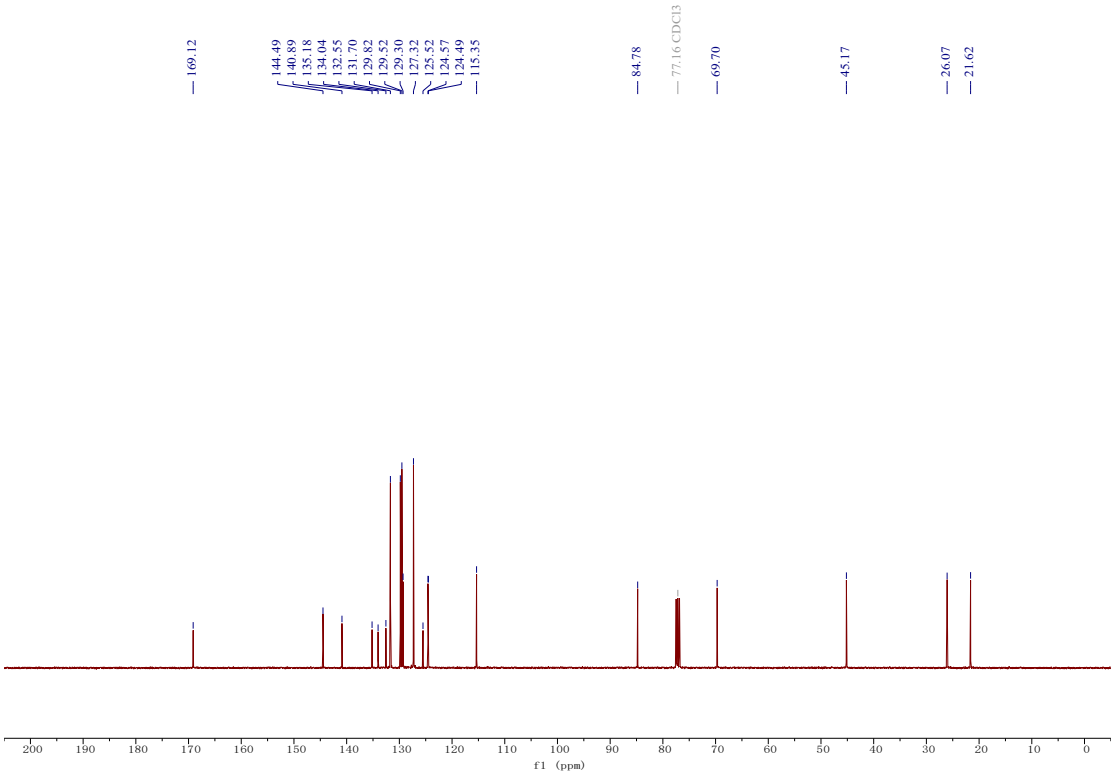
^{19}F NMR spectra of 5aq ($CDCl_3$, 376 MHz)



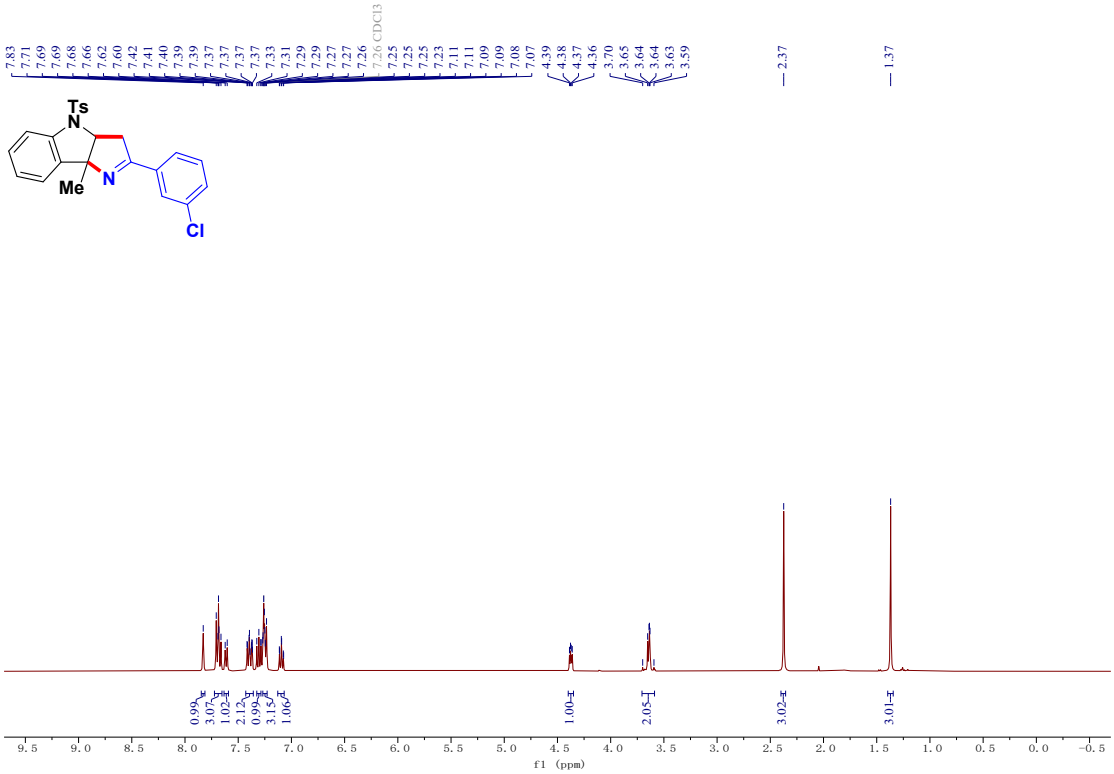
^{1}H NMR spectra of 5ar ($CDCl_3$, 400 MHz)



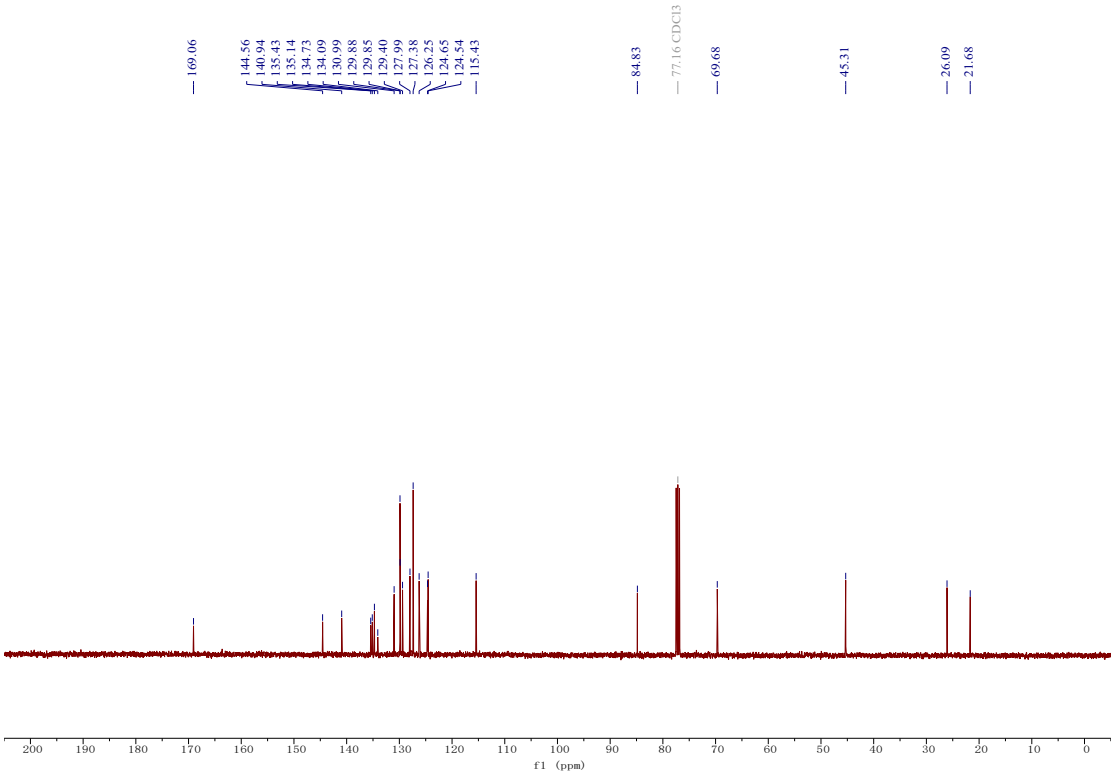
^{13}C NMR spectra of 5ar ($CDCl_3$, 101 MHz)



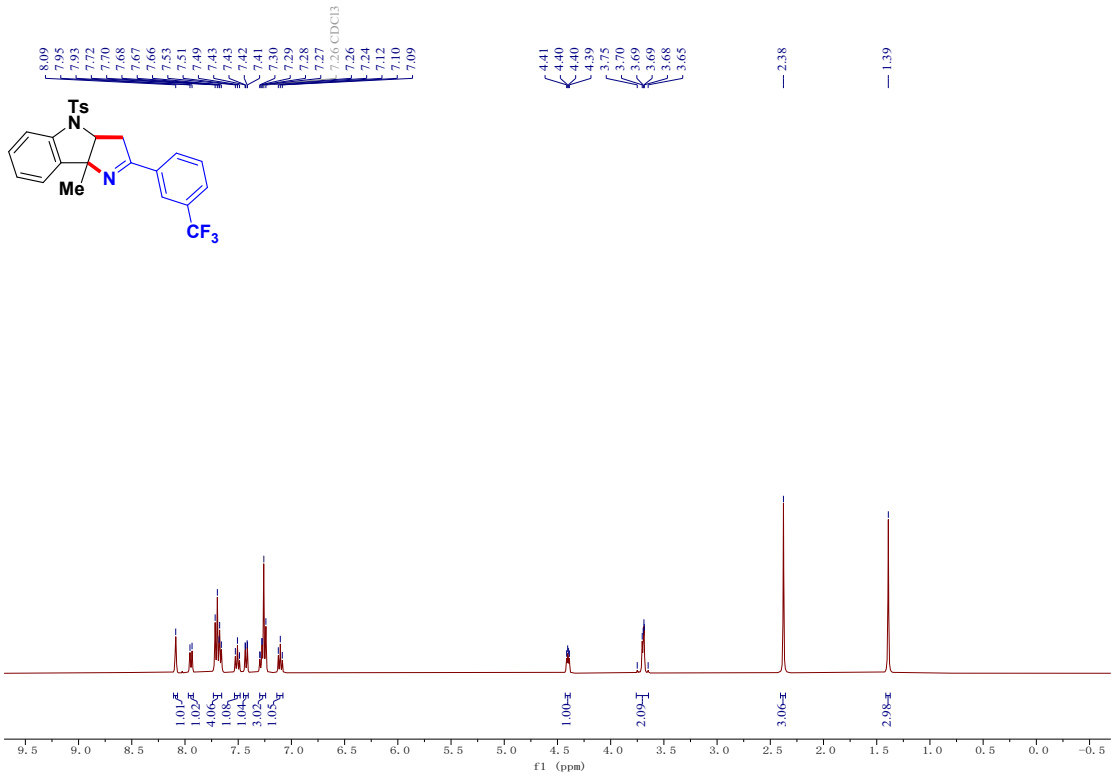
^{1}H NMR spectra of 5as ($CDCl_3$, 400 MHz)



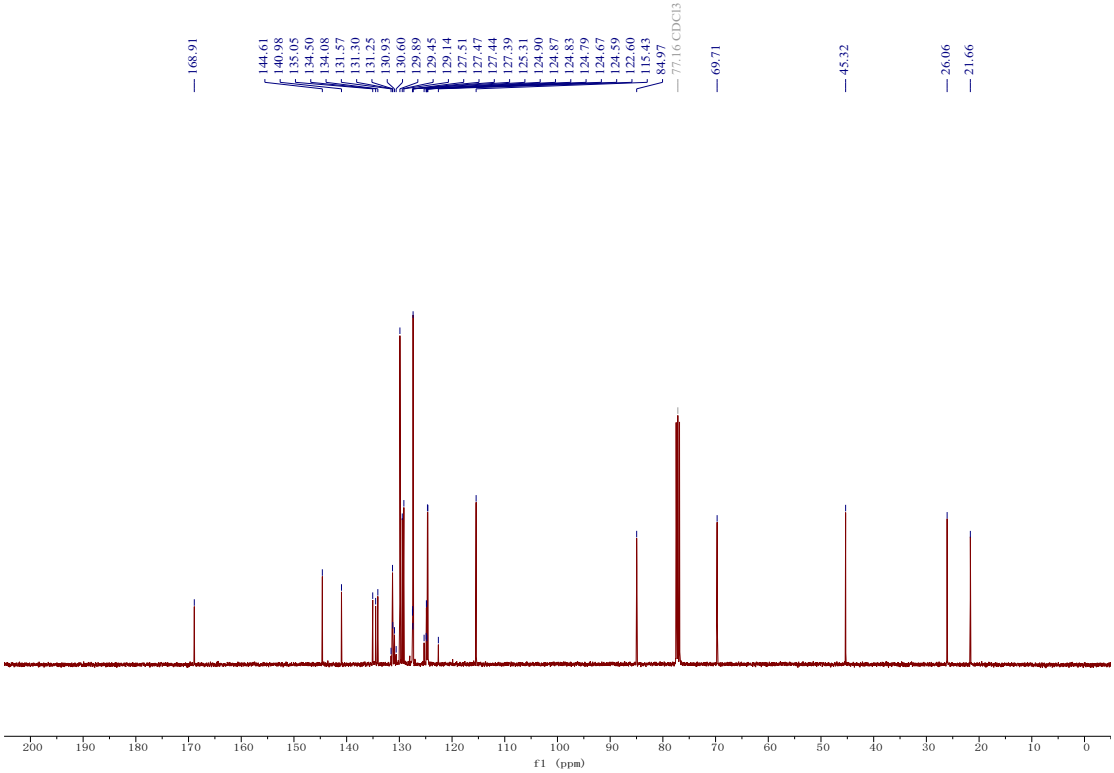
^{13}C NMR spectra of 5as ($CDCl_3$, 101 MHz)



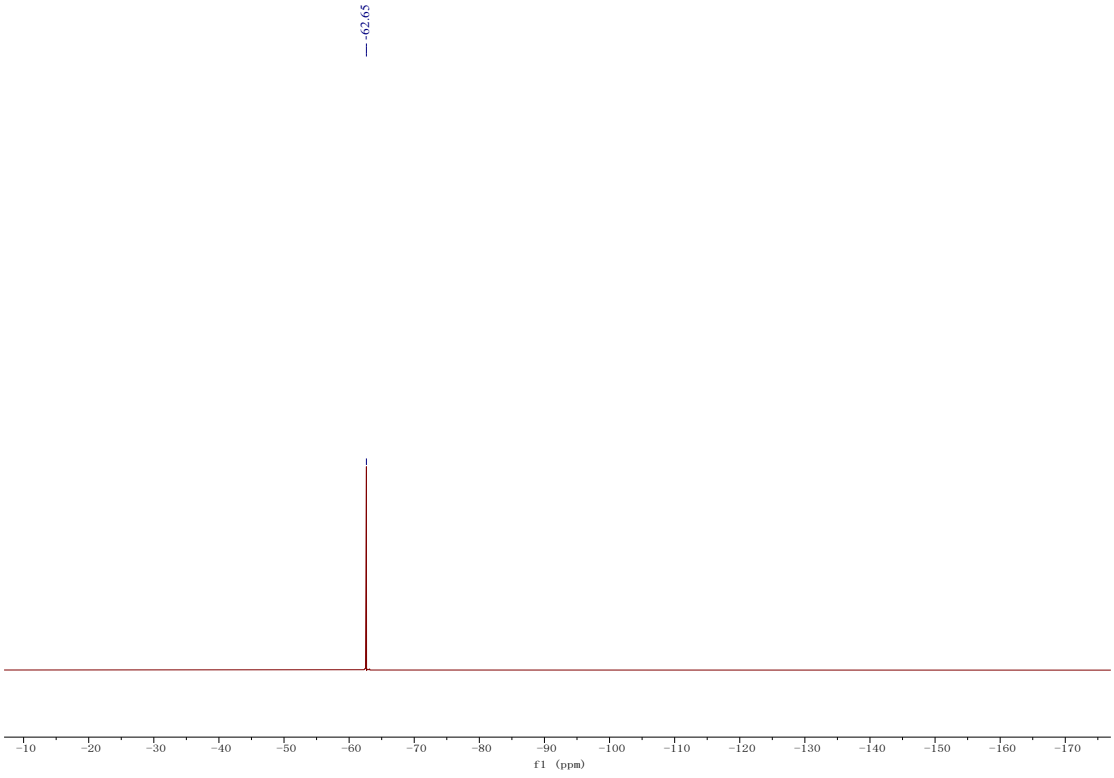
^{1}H NMR spectra of 5at ($CDCl_3$, 400 MHz)



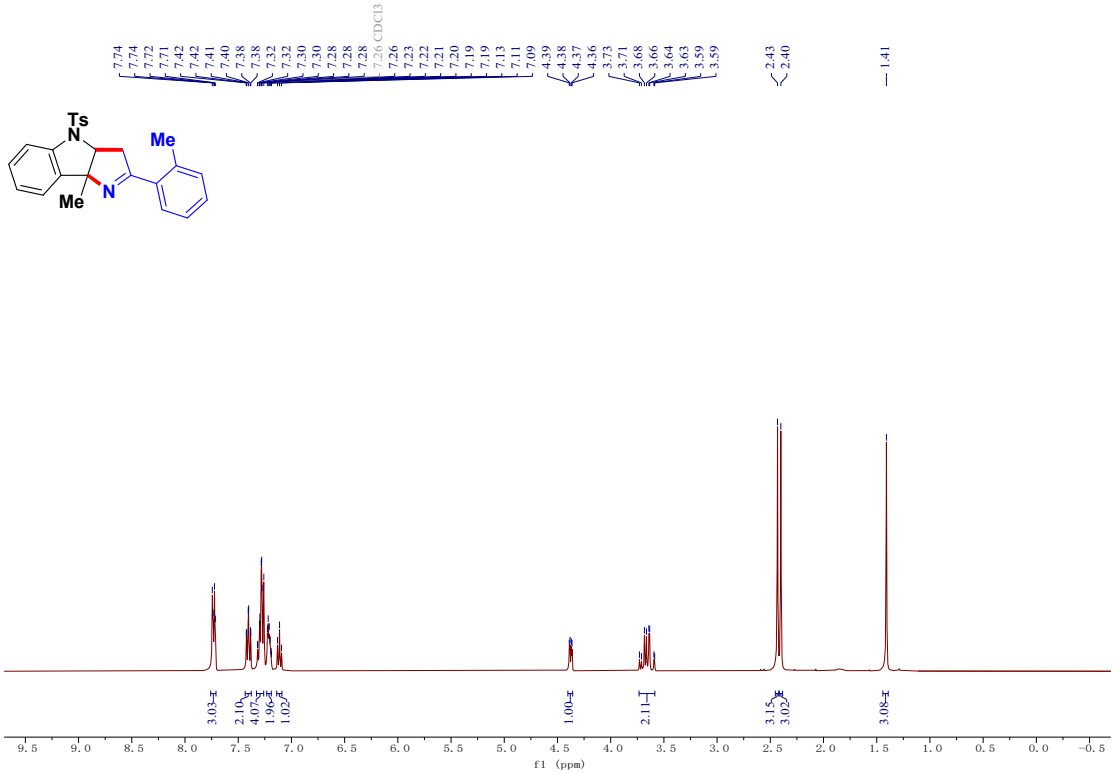
^{13}C NMR spectra of 5at ($CDCl_3$, 101 MHz)



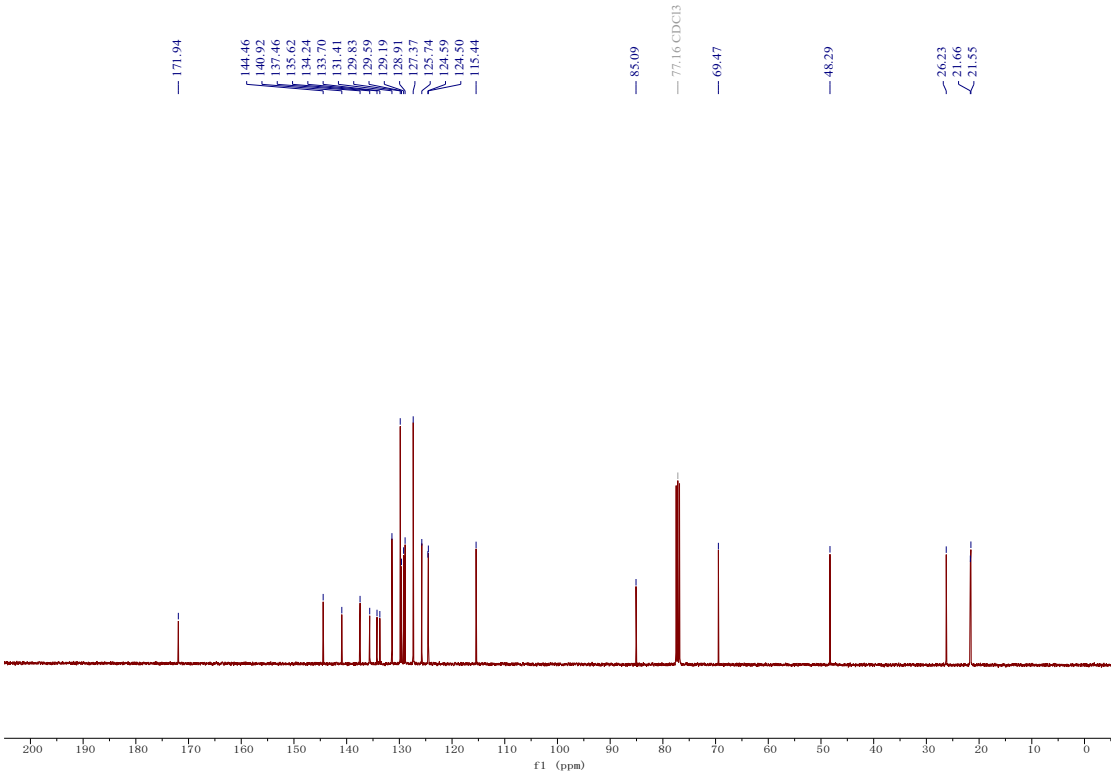
^{19}F NMR spectra of 5at ($CDCl_3$, 376 MHz)



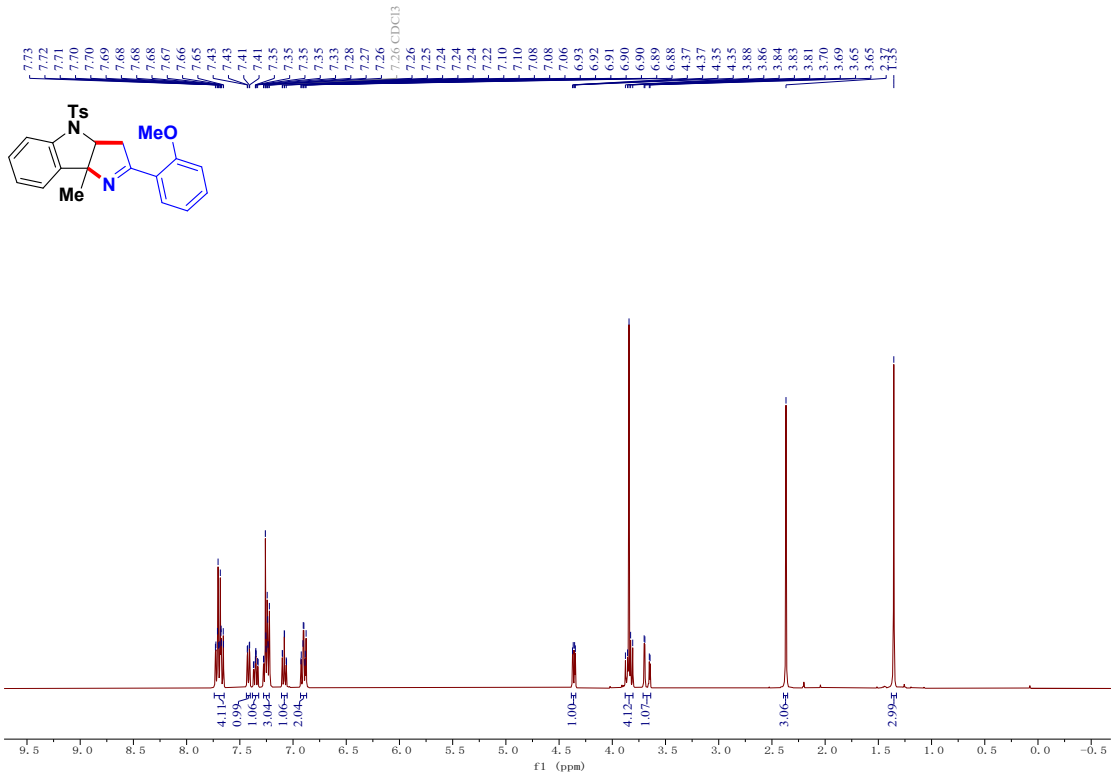
^{1}H NMR spectra of 5au ($CDCl_3$, 400 MHz)



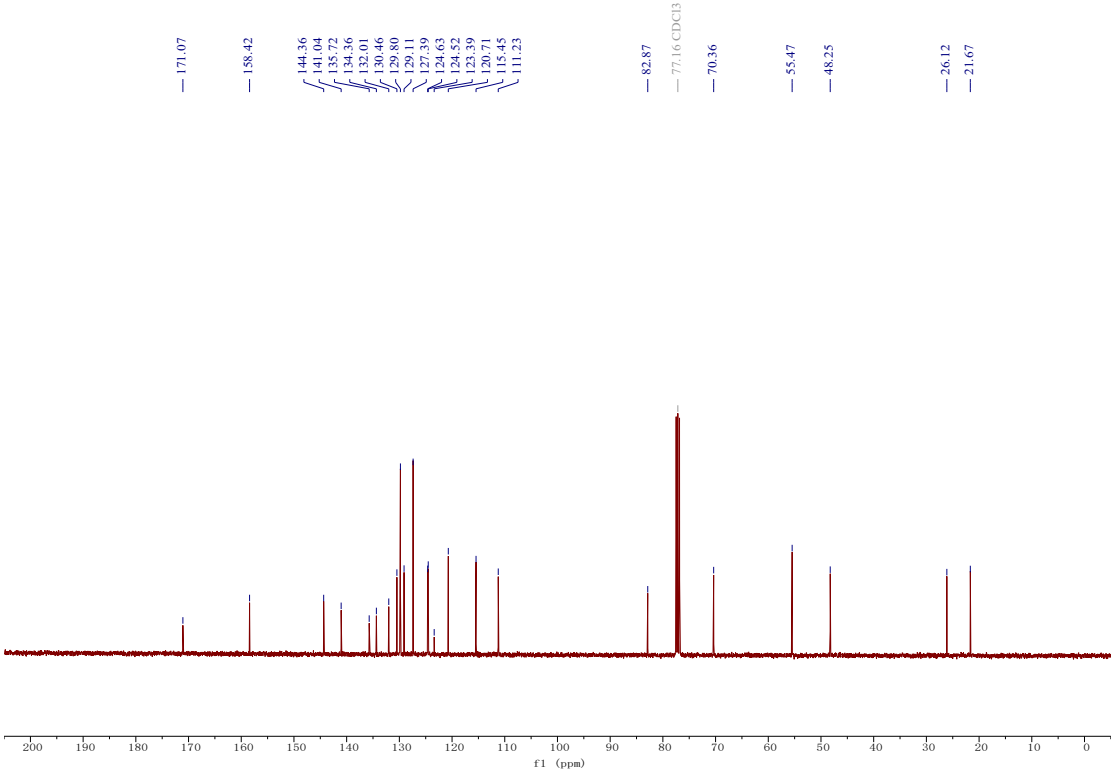
^{13}C NMR spectra of 5au ($CDCl_3$, 101 MHz)



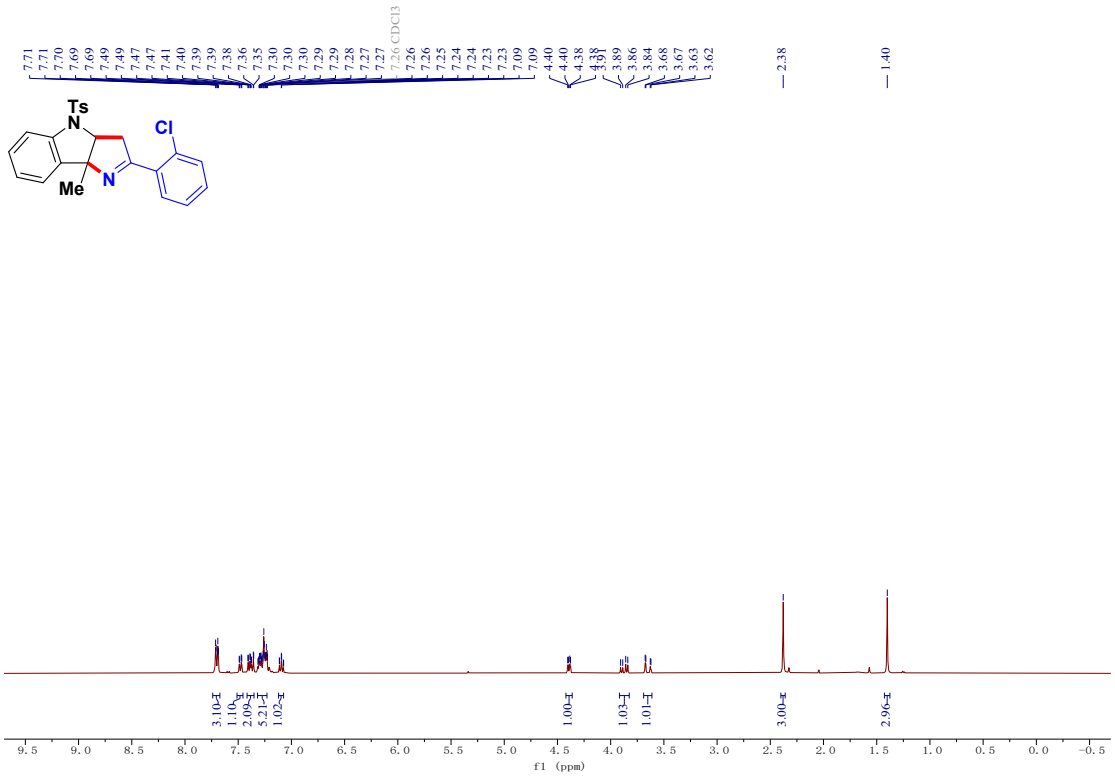
^{1}H NMR spectra of 5av ($CDCl_3$, 400 MHz)



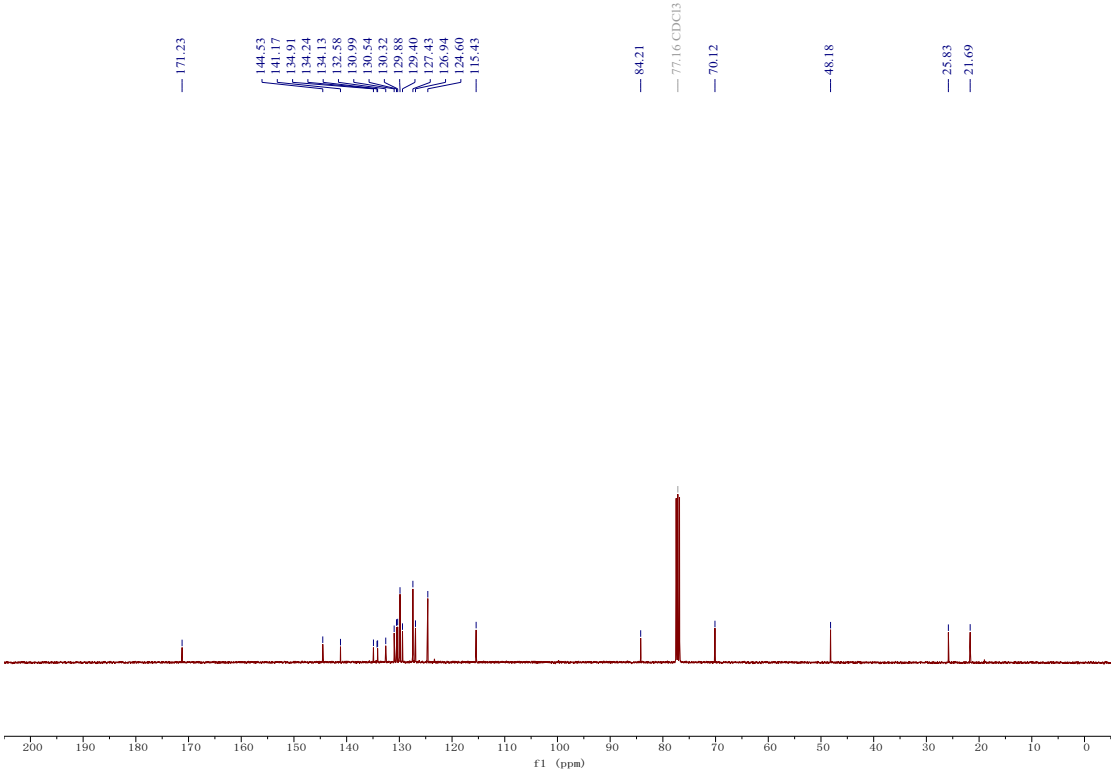
^{13}C NMR spectra of 5av ($CDCl_3$, 101 MHz)



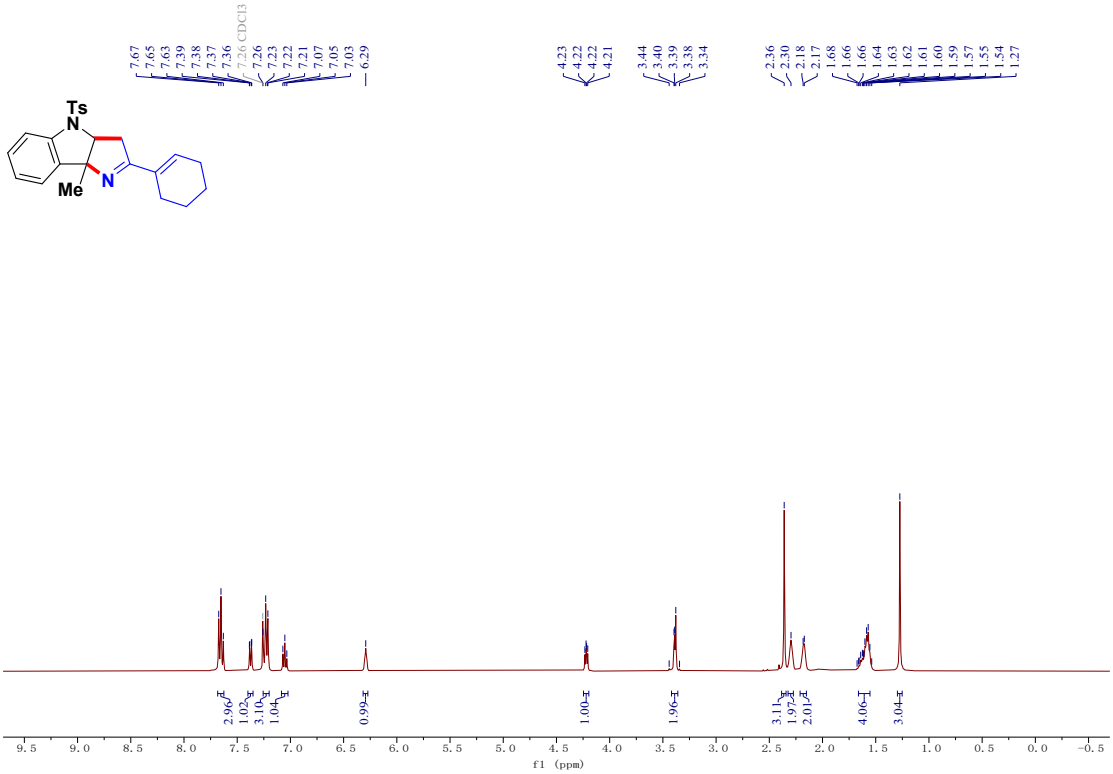
^{1}H NMR spectra of 5aw ($CDCl_3$, 400 MHz)



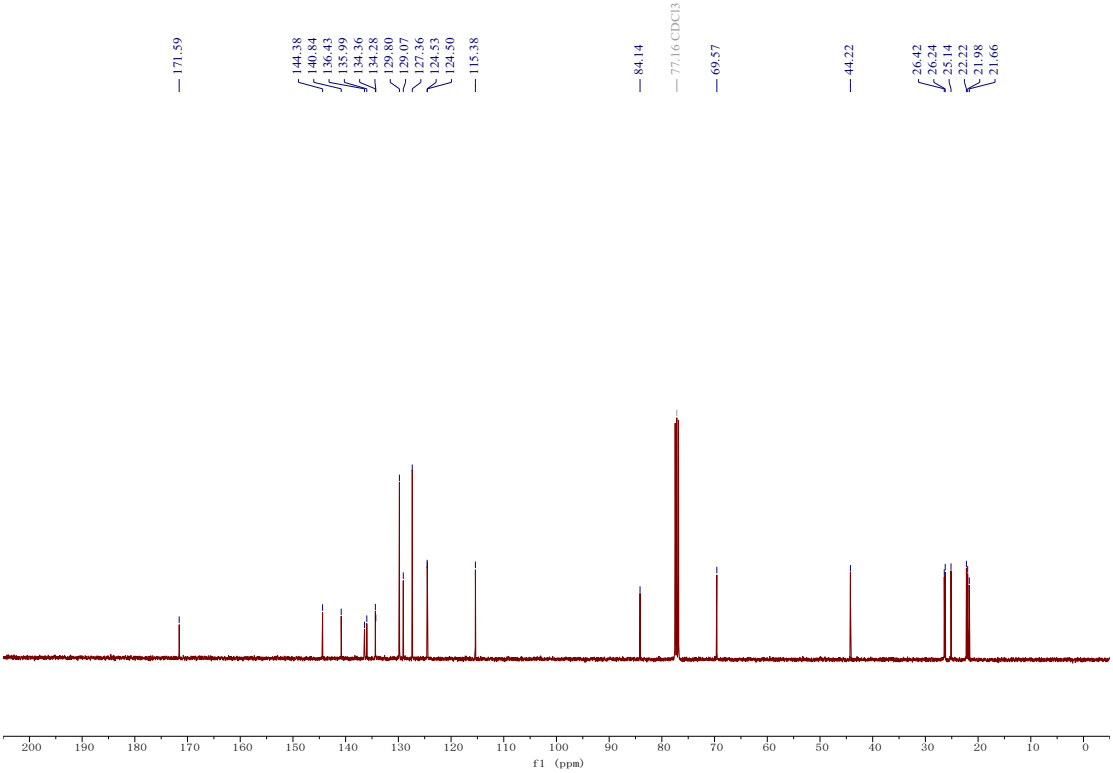
^{13}C NMR spectra of 5aw ($CDCl_3$, 101 MHz)



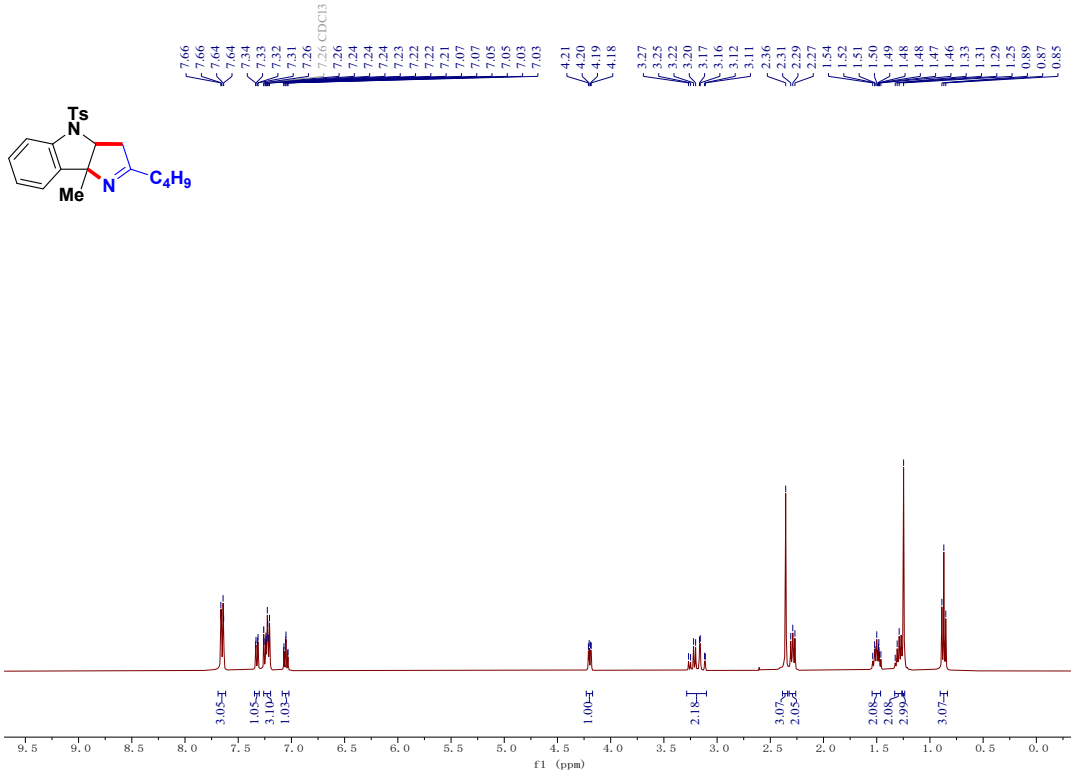
^{1}H NMR spectra of 5ax ($CDCl_3$, 400 MHz)



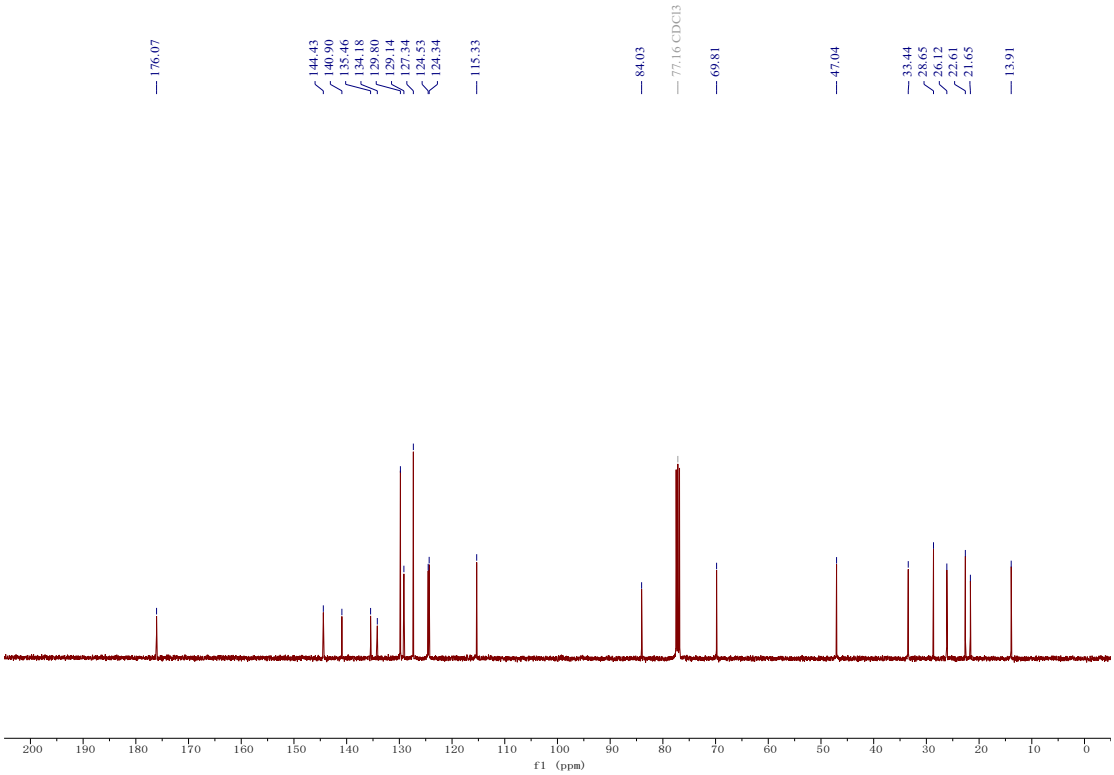
^{13}C NMR spectra of 5ax ($CDCl_3$, 101 MHz)



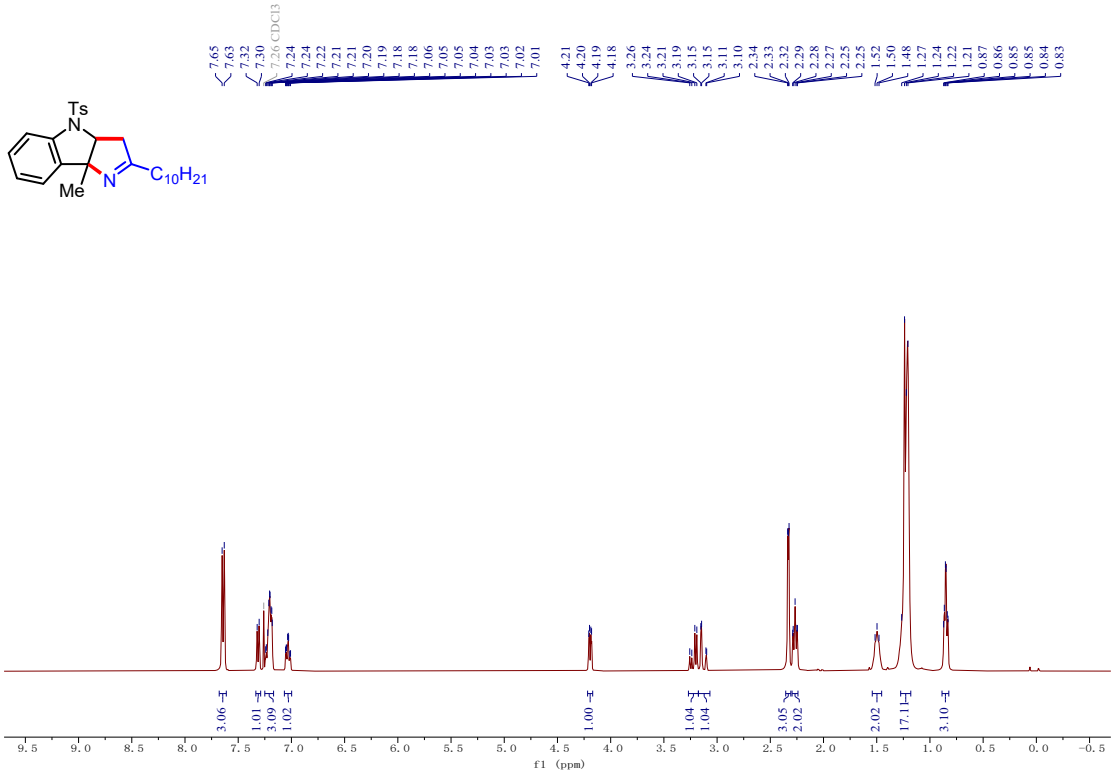
^{1}H NMR spectra of 5ay ($CDCl_3$, 400 MHz)



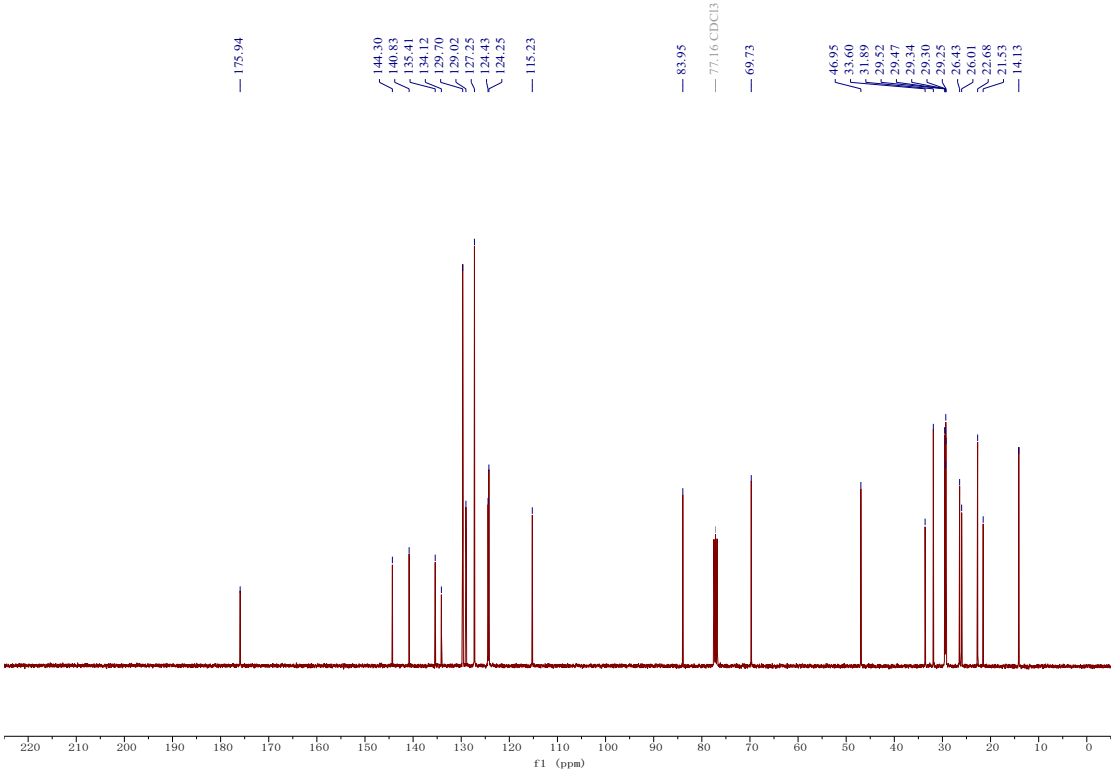
^{13}C NMR spectra of 5ay ($CDCl_3$, 101 MHz)



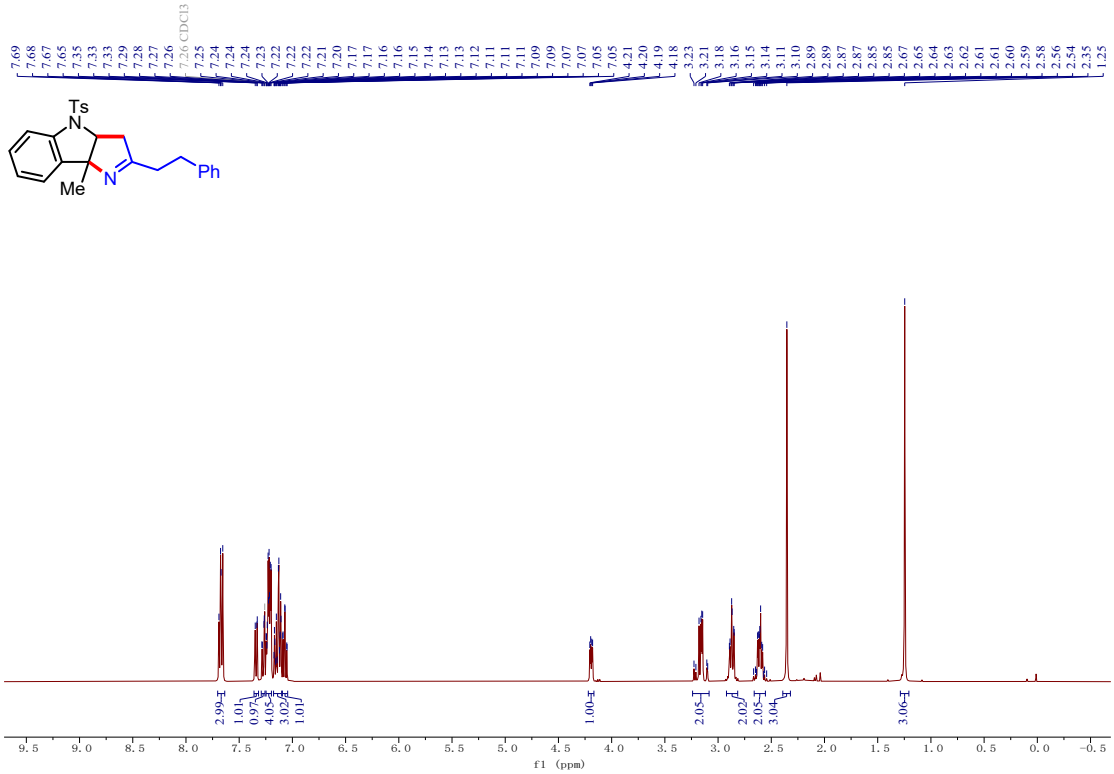
^{1}H NMR spectra of 5az ($CDCl_3$, 400 MHz)



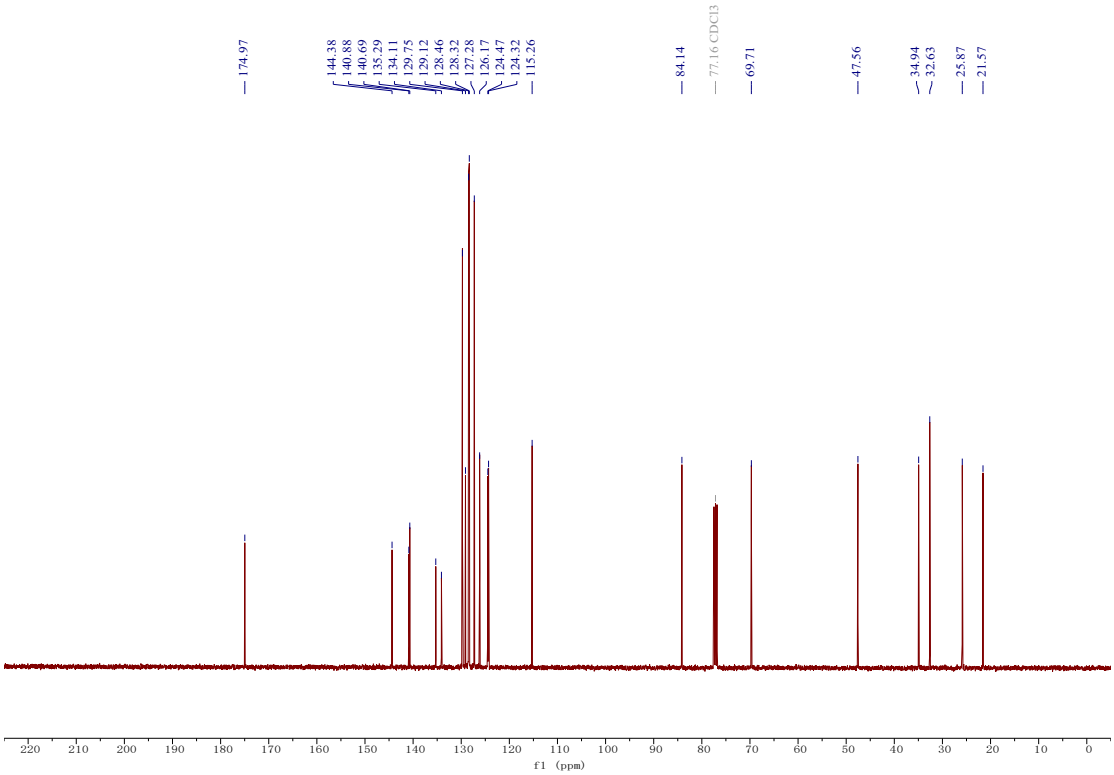
^{13}C NMR spectra of 5az ($CDCl_3$, 101 MHz)



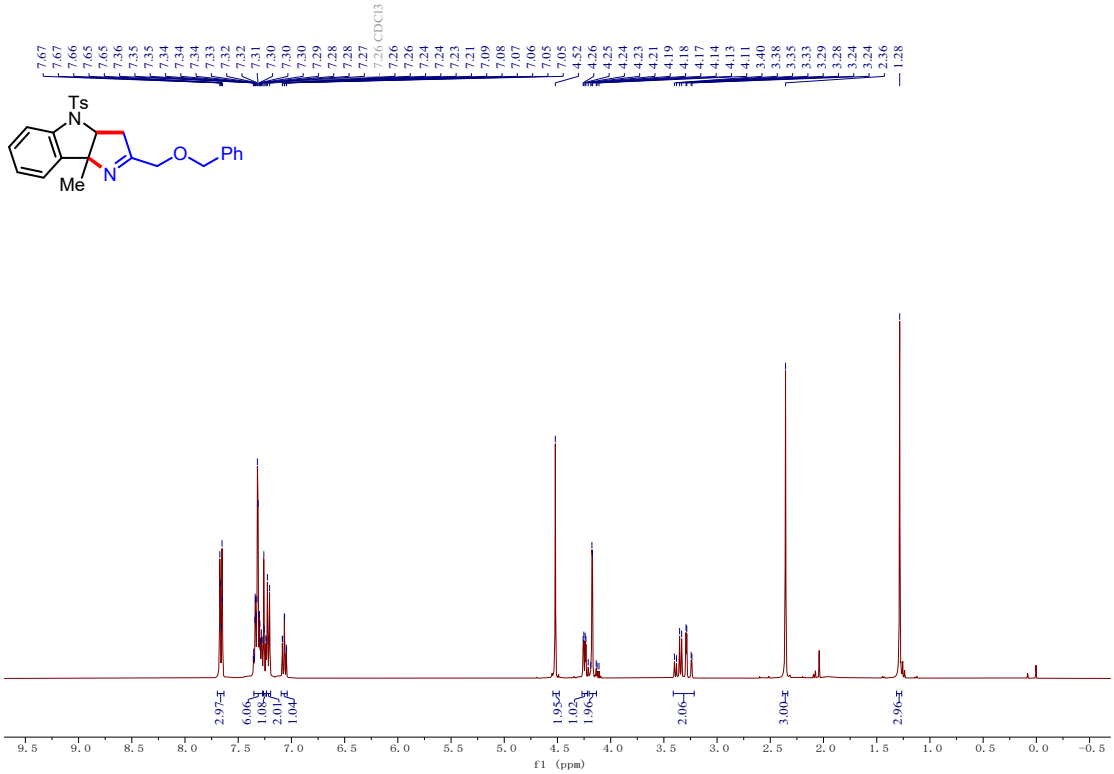
^{1}H NMR spectra of 5ba ($CDCl_3$, 400 MHz)



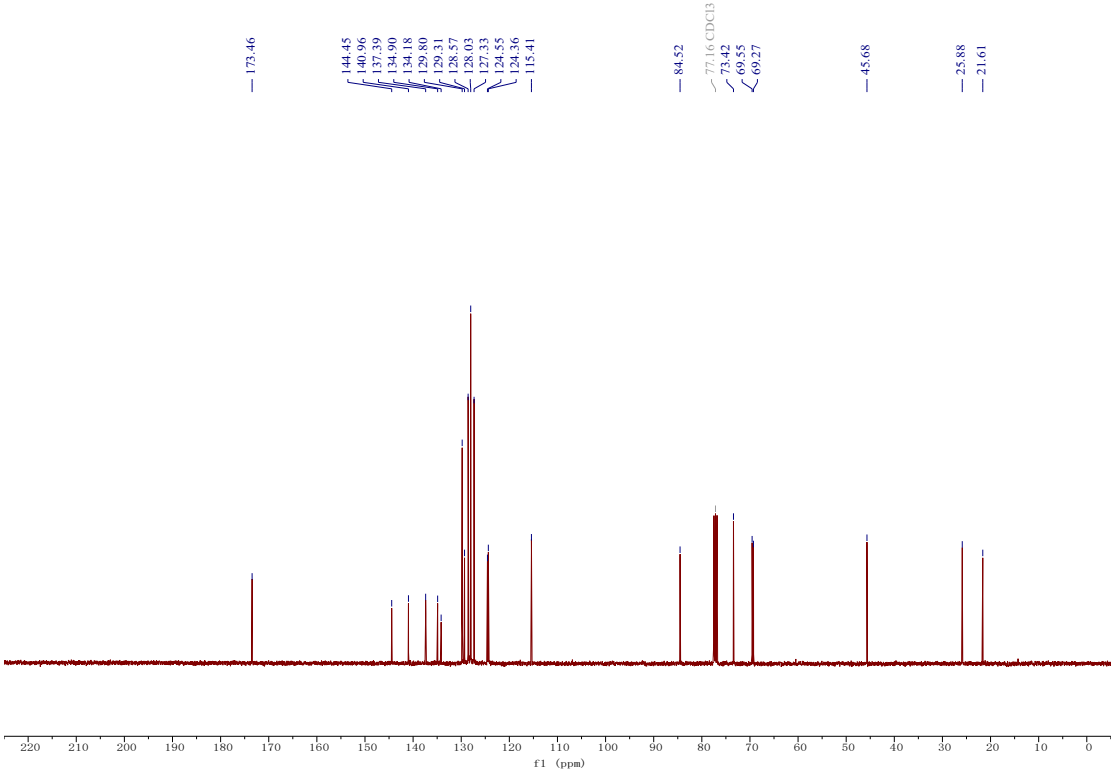
^{13}C NMR spectra of 5ba ($CDCl_3$, 101 MHz)



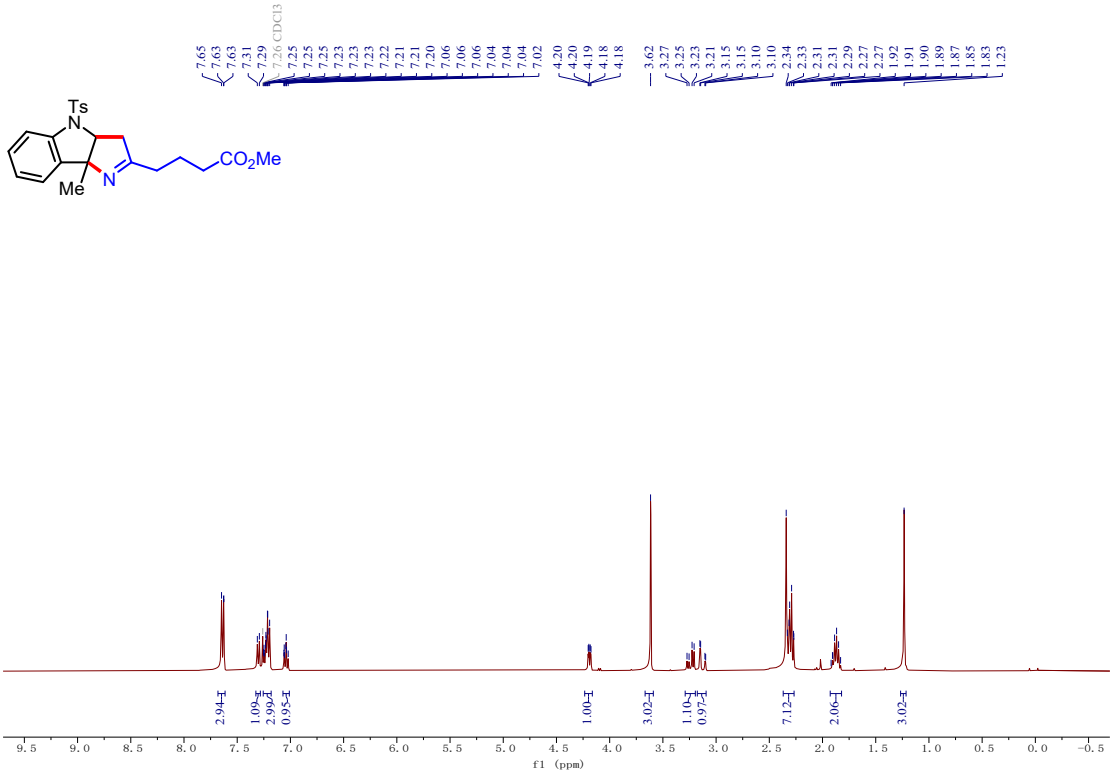
^{1}H NMR spectra of 5bb ($CDCl_3$, 400 MHz)



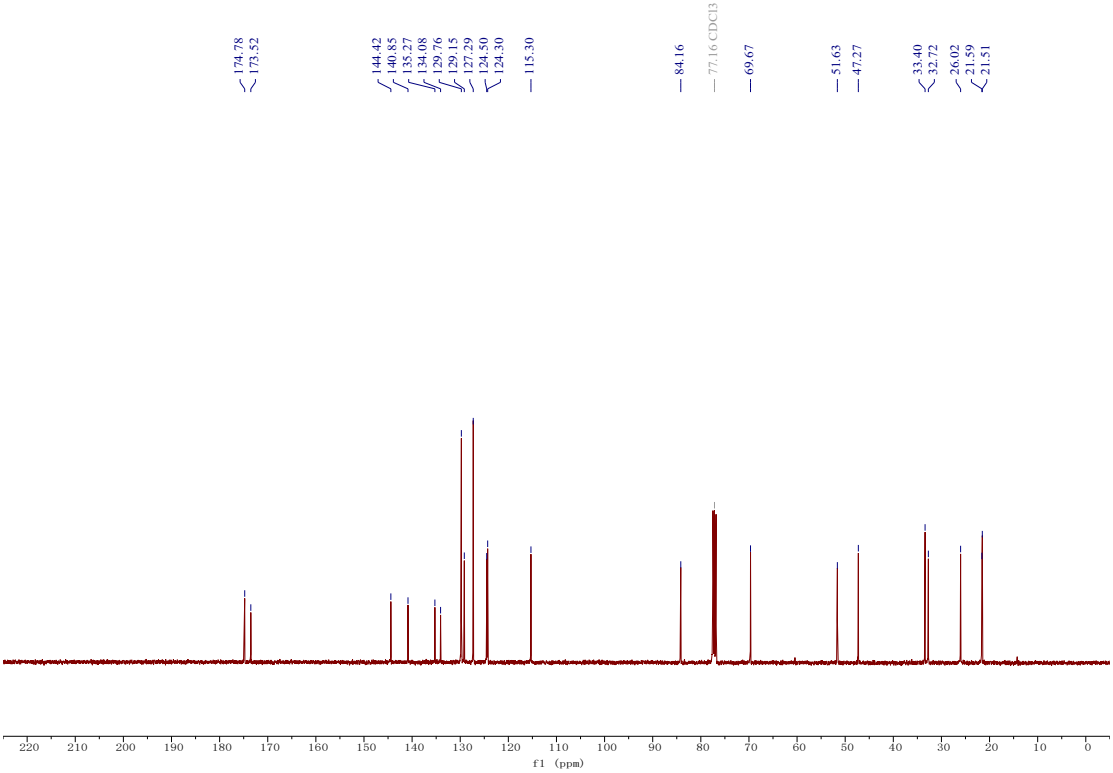
^{13}C NMR spectra of 5bb ($CDCl_3$, 101 MHz)



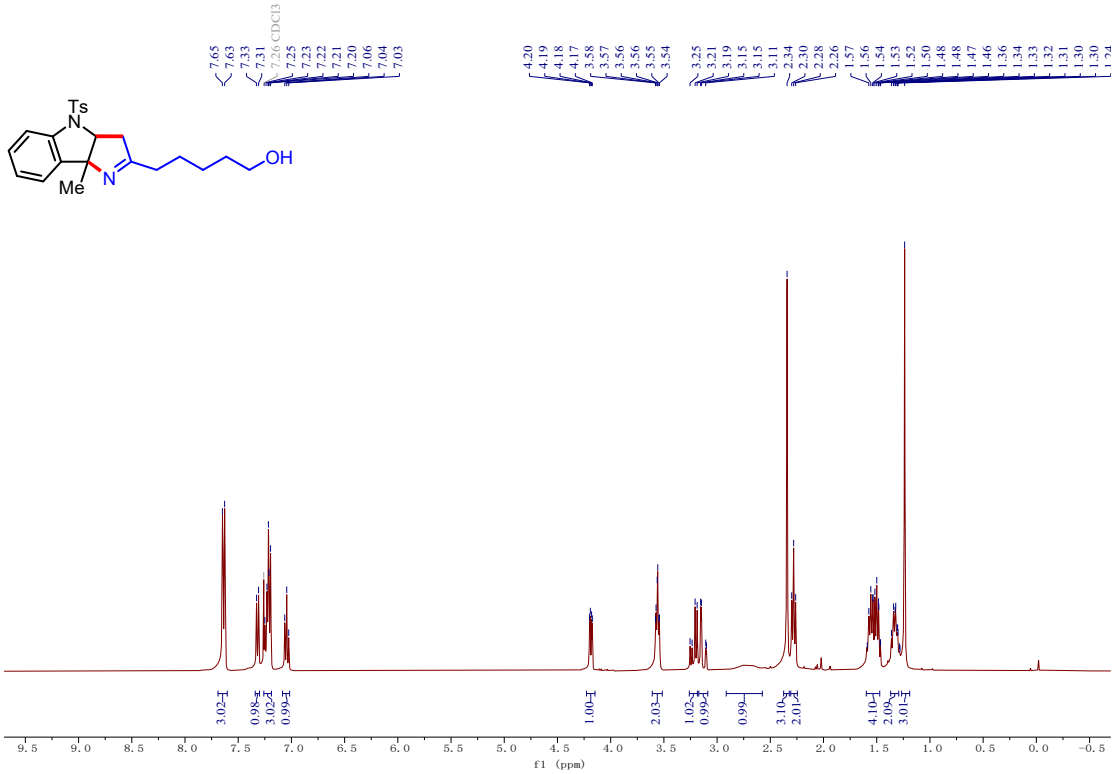
^{1}H NMR spectra of 5bc ($CDCl_3$, 400 MHz)



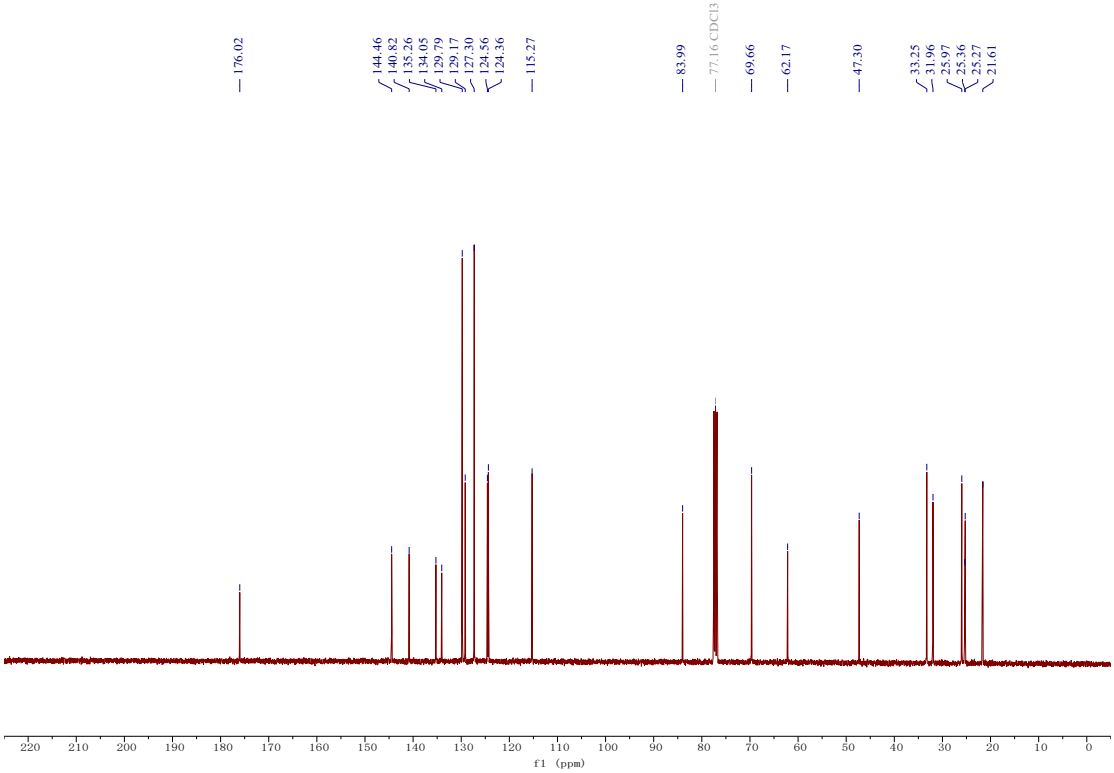
^{13}C NMR spectra of 5bc ($CDCl_3$, 101 MHz)



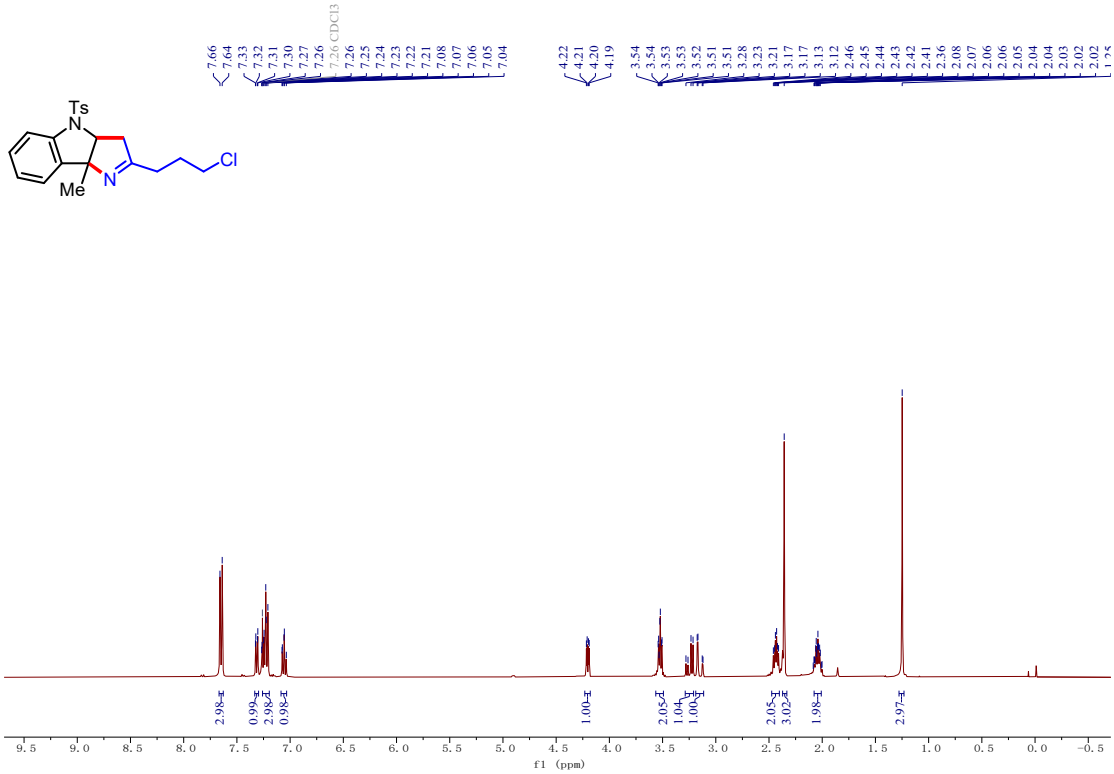
^{1}H NMR spectra of 5bd ($CDCl_3$, 400 MHz)



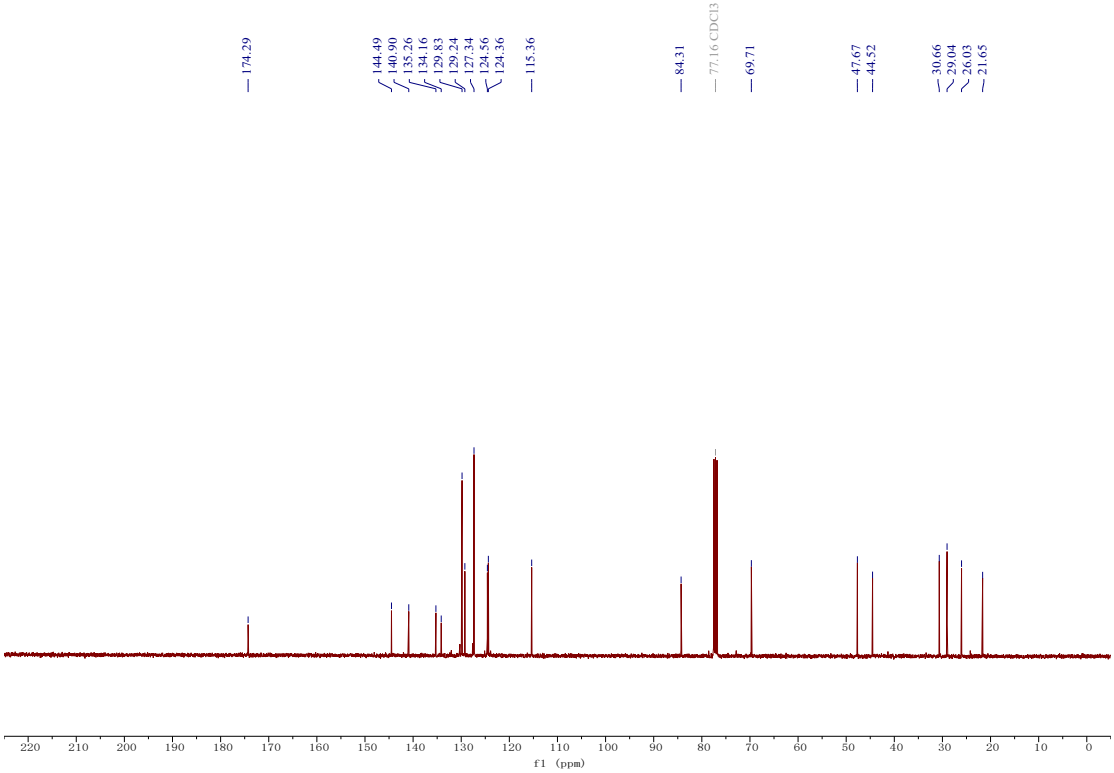
^{13}C NMR spectra of 5bd ($CDCl_3$, 101 MHz)



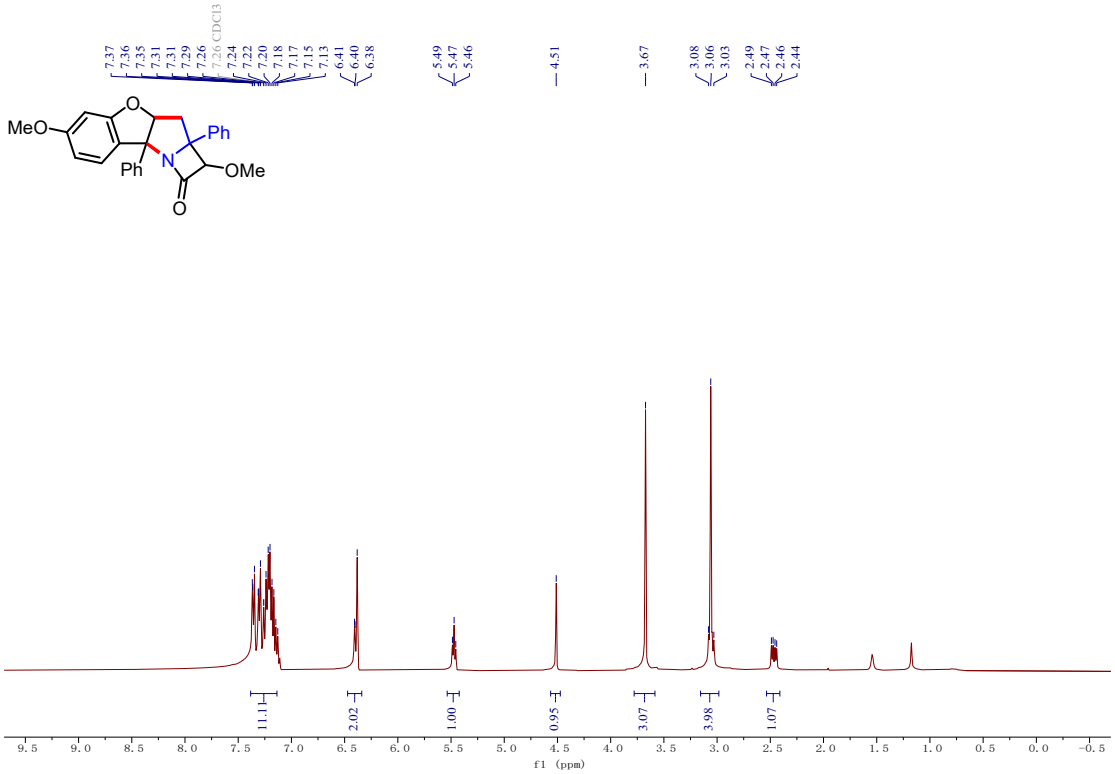
^{1}H NMR spectra of 5be ($CDCl_3$, 400 MHz)



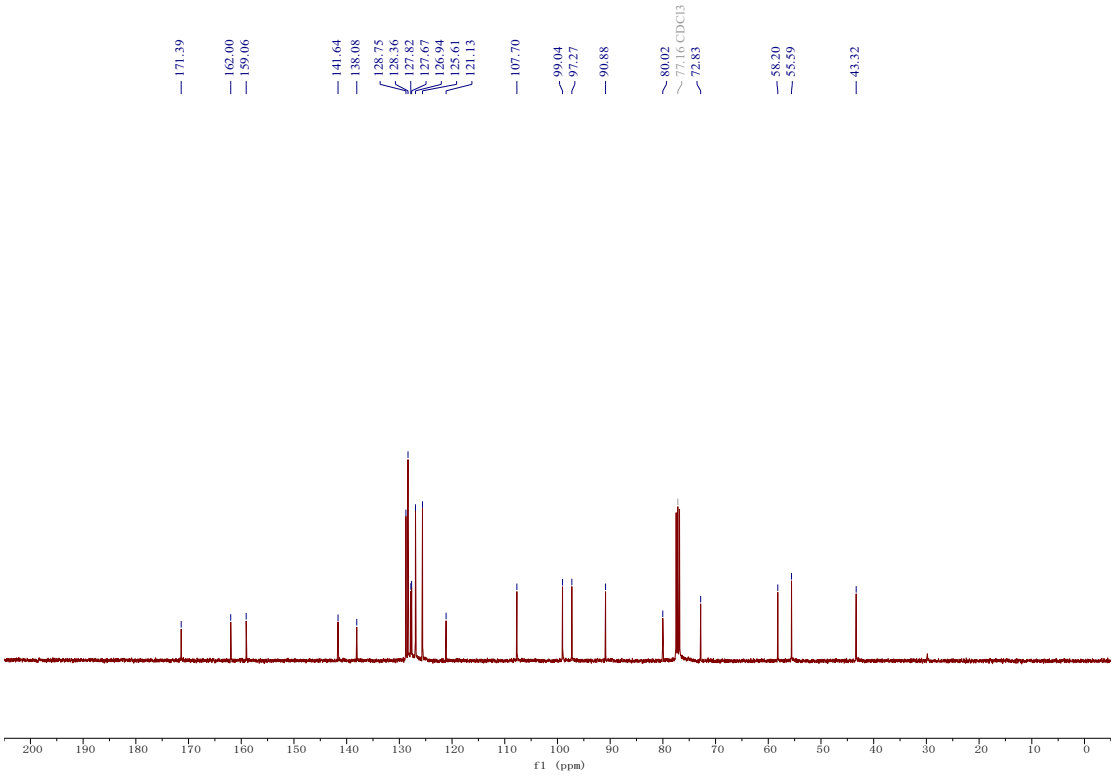
^{13}C NMR spectra of 5be ($CDCl_3$, 101 MHz)



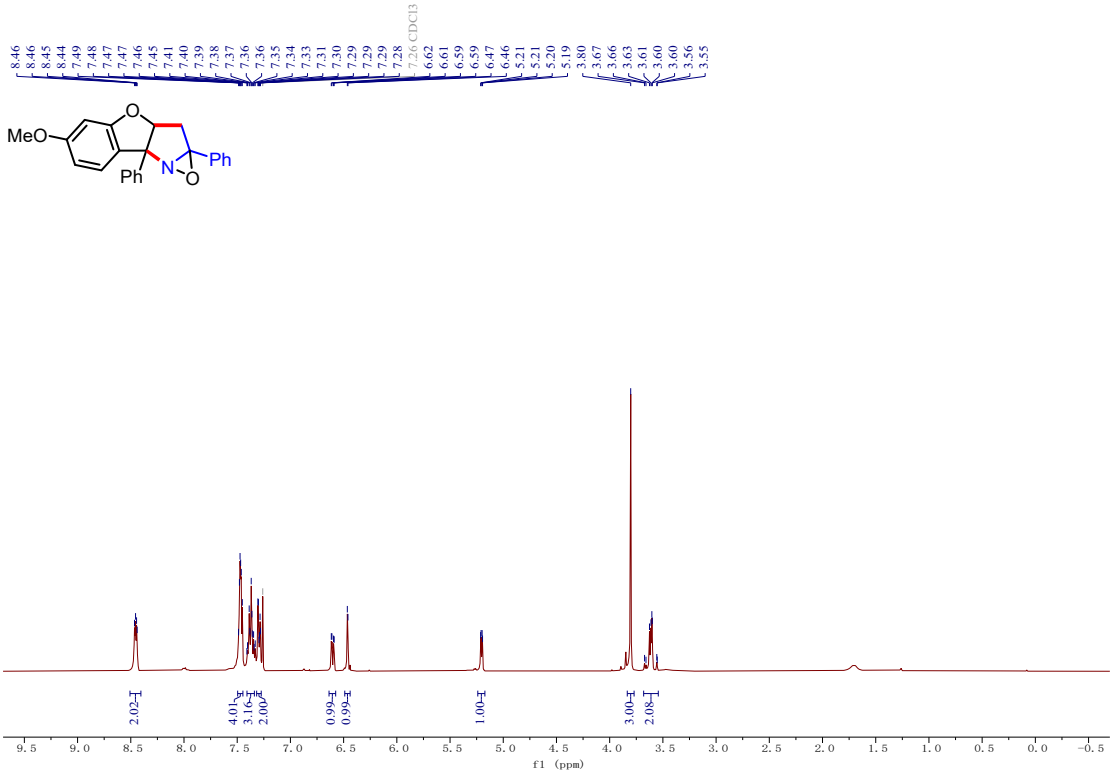
^{1}H NMR spectra of 6a ($CDCl_3$, 400 MHz)



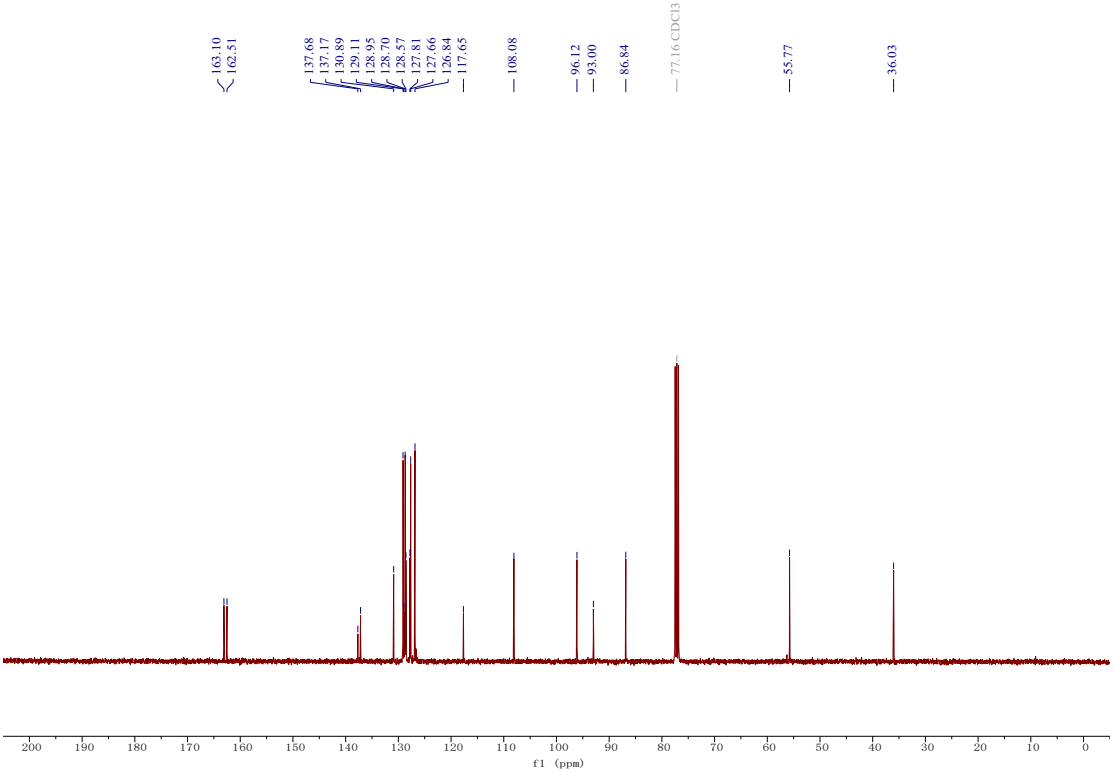
^{13}C NMR spectra of 6a ($CDCl_3$, 101 MHz)



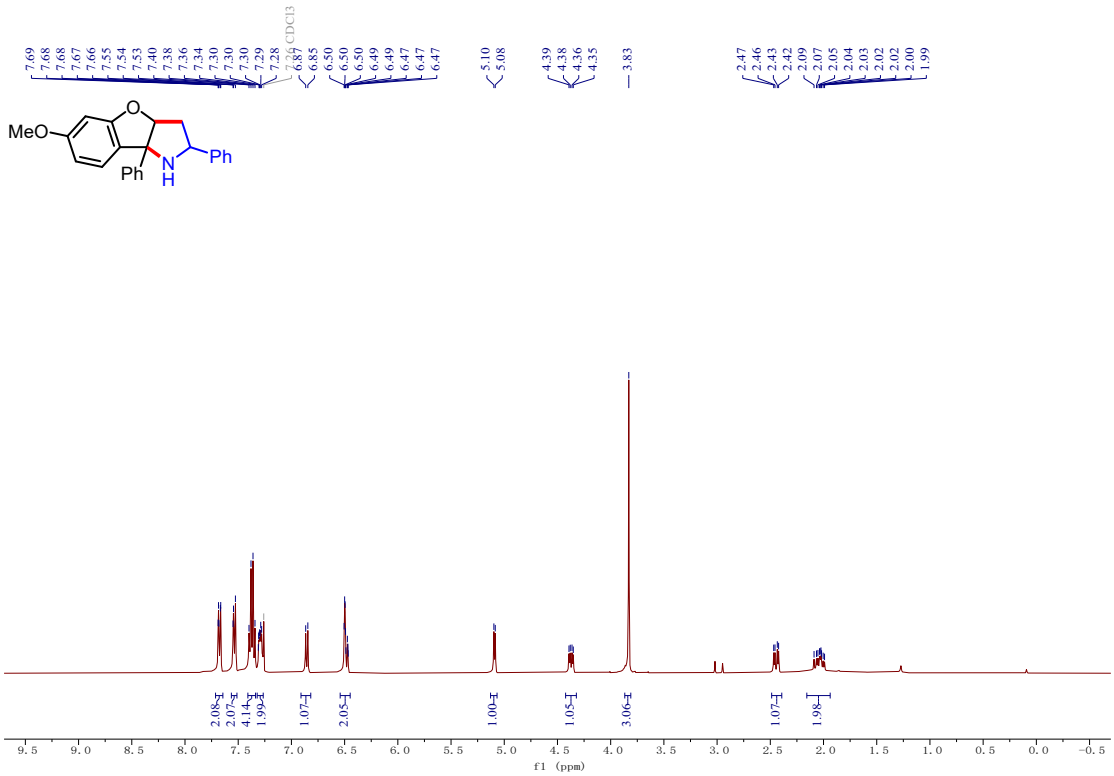
^{1}H NMR spectra of 6b ($CDCl_3$, 400 MHz)



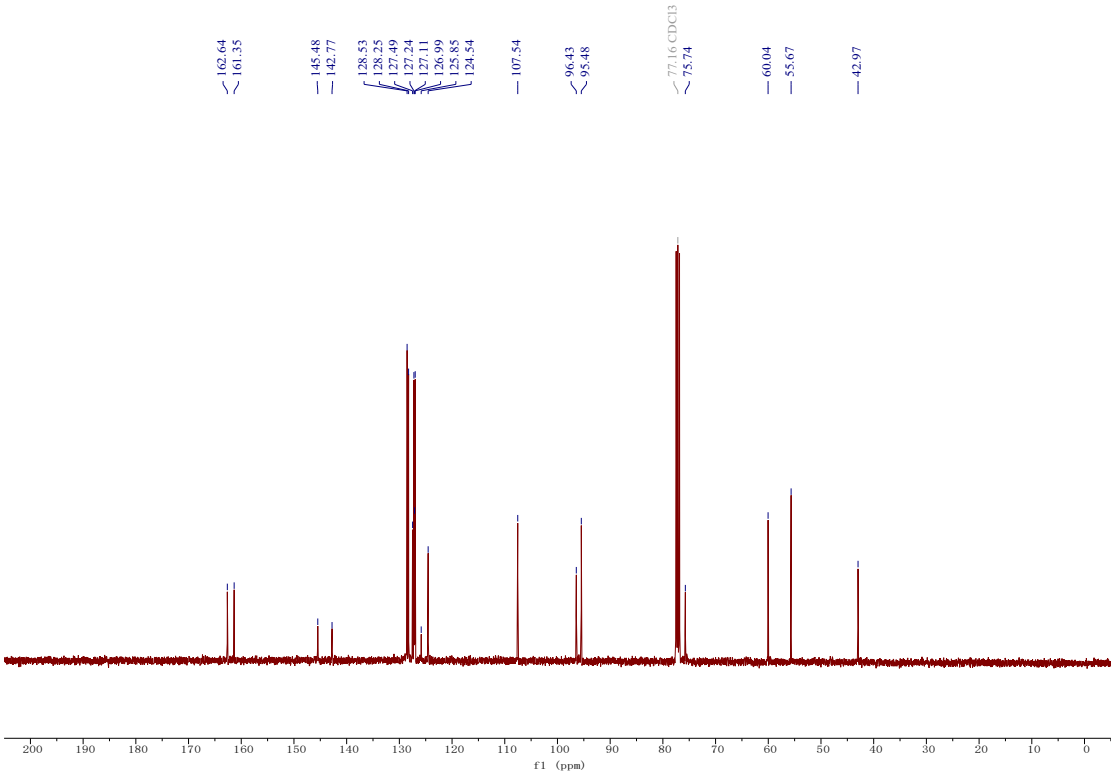
^{13}C NMR spectra of 6b ($CDCl_3$, 101 MHz)



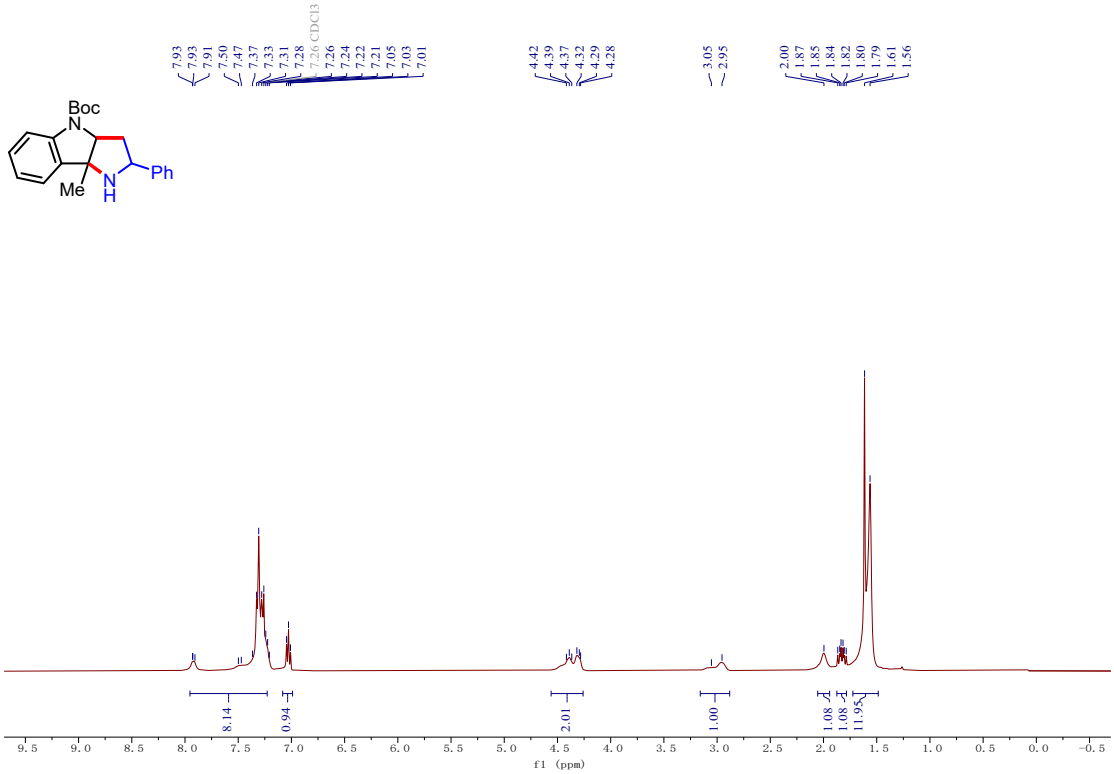
^{1}H NMR spectra of 6c ($CDCl_3$, 400 MHz)



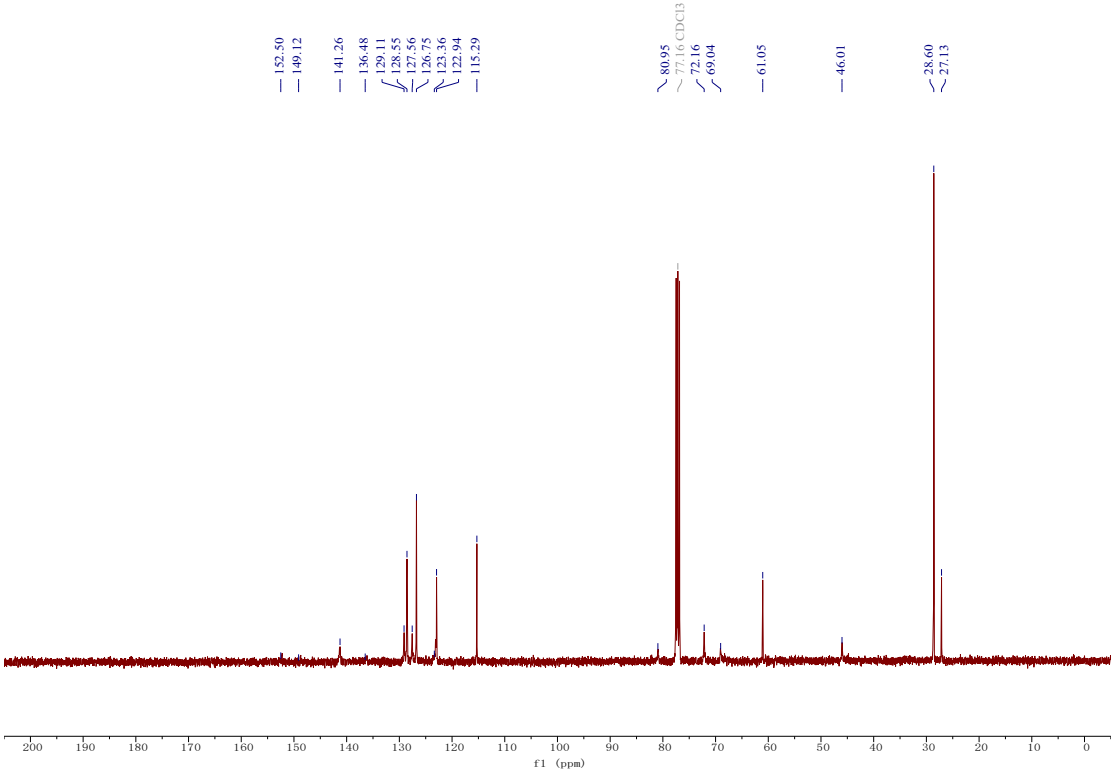
^{13}C NMR spectra of 6c ($CDCl_3$, 101 MHz)



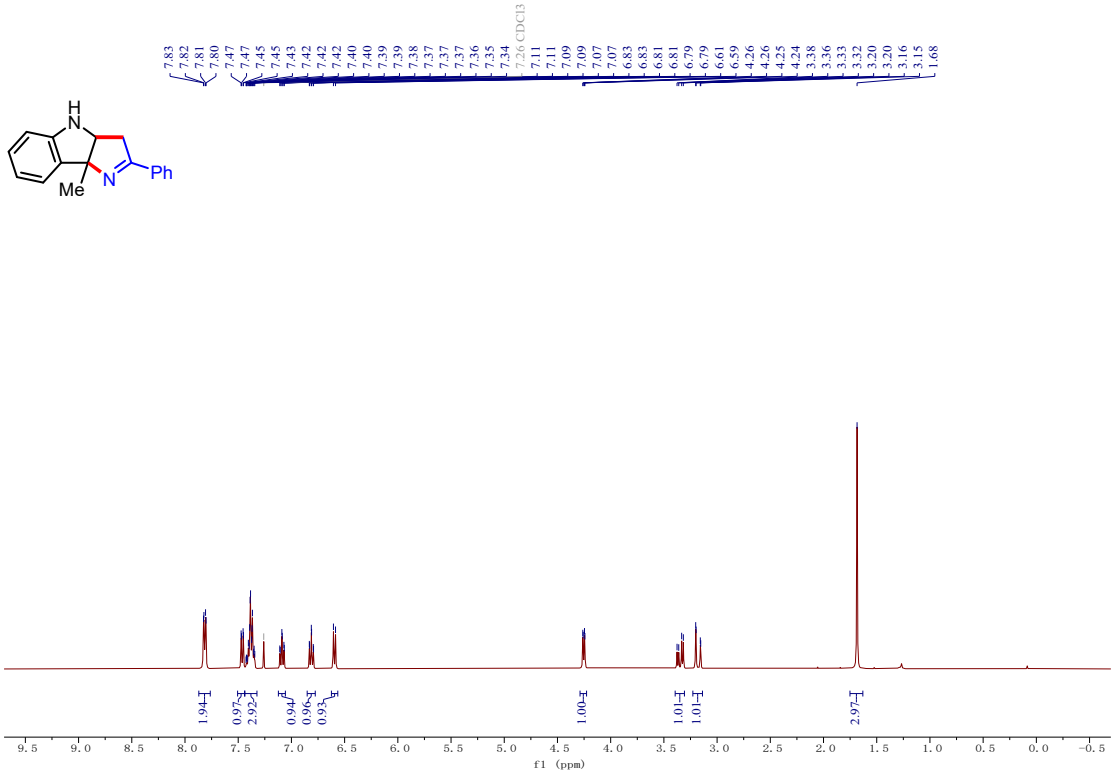
^{1}H NMR spectra of 7a ($CDCl_3$, 400 MHz)



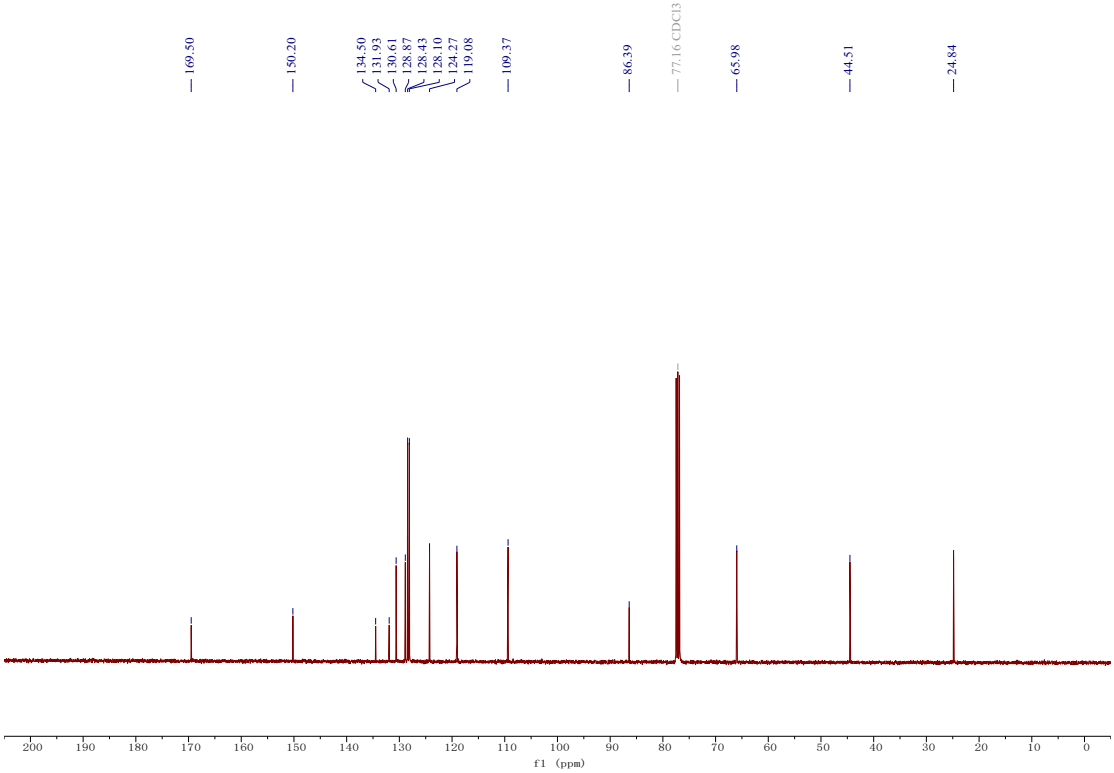
^{13}C NMR spectra of 7a ($CDCl_3$, 101 MHz)



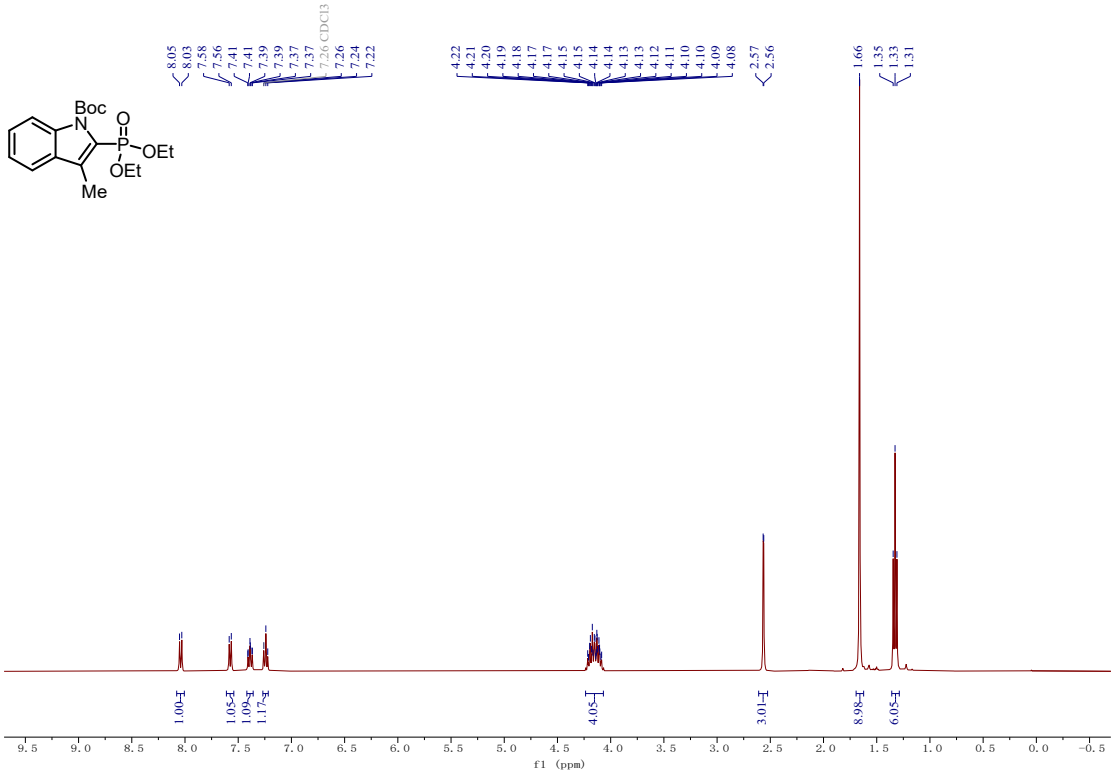
^{1}H NMR spectra of 7b ($CDCl_3$, 400 MHz)



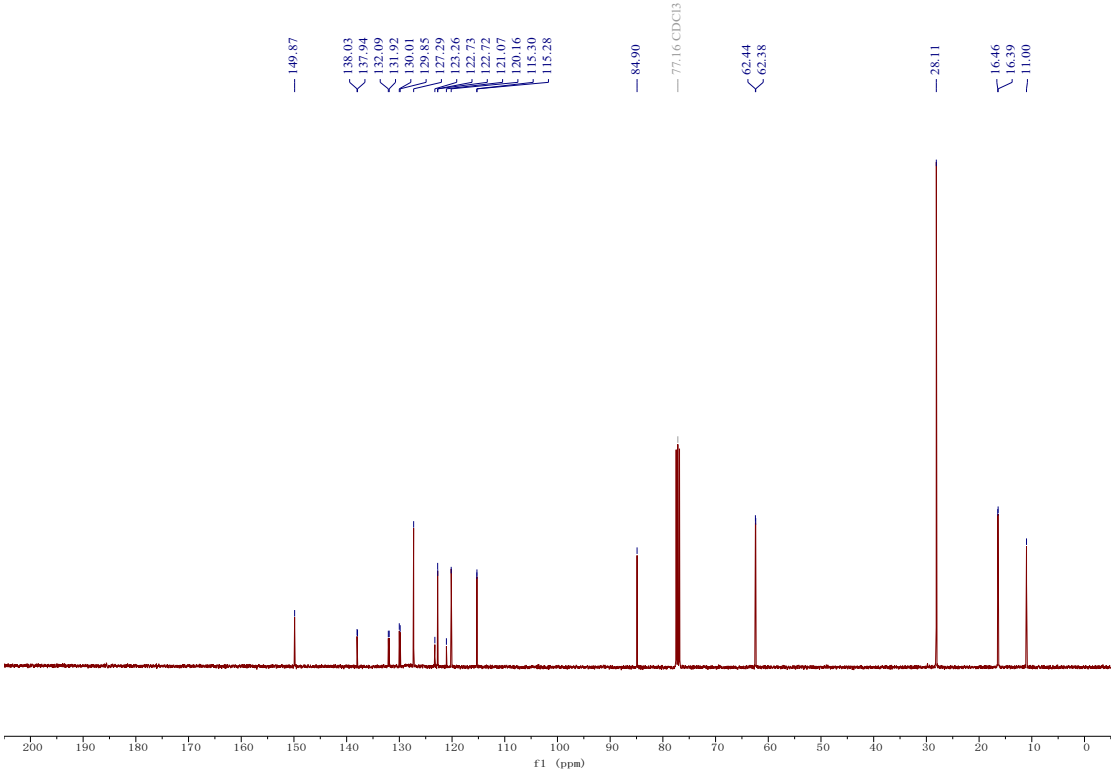
^{13}C NMR spectra of 7b ($CDCl_3$, 101 MHz)



^{1}H NMR spectra of 9a ($CDCl_3$, 400 MHz)



^{13}C NMR spectra of 9a ($CDCl_3$, 101 MHz)



^{31}P NMR spectra of 9a ($CDCl_3$, 162 MHz)