

*Electronic Supplementary Information*

**All-in-one Rh(III)-covalent organic framework for  
sustainable and regioselective C(sp<sup>2</sup>)-H bond  
functionalization**

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## I. Materials and methods

### 1. Materials

Unless specifically described, solvents and experimental reagents were purchased from Energy Chemical or Bidepharm. The monomer of 4,4',4'',4'''-(1,9-dihydropyrene-1,3,6,8-tetrayl)tetraaniline and [2,2'-bipyridine]-5,5'-dicarbaldehyde were purchased from Leyan. All chemicals were used without further purification.

### 2. Methods

Unless otherwise specified, all reactions were performed under air. The unknown products were additionally characterized by high-resolution mass spectrometry (HRMS).

**NMR:**  $^1\text{H}$  NMR spectra were recorded on Bruker 400, 500, or 600MHz spectrometer with  $\text{CDCl}_3$  as the solvent;  $^{13}\text{C}$  NMR spectra were recorded on Bruker 101 or 126 MHz spectrometer with  $\text{CDCl}_3$  as the solvent;  $^{19}\text{F}$  NMR spectra were recorded on Bruker 471 MHz spectrometer with  $\text{CDCl}_3$  as the solvent. Chemical shifts were reported in parts per million( $\delta$ ) with TMS (0 ppm) as the internal standard. The peak patterns are indicated as follows: s (singlet), d (doublet), dd (doublet of doublets), t (triplet), q (quartet), and m (multiplet). The coupling constants ( $J$ ) are reported in Hertz (Hz).

**Powder X-ray diffraction:** Powder X-ray diffraction (PXRD) patterns of the as-prepared samples were obtained on a powder Xray diffractometer (Cu  $K\alpha$  radiation source, Ultima IV, Rigaku), from  $2\theta = 1.5^\circ$  up to  $40^\circ$  with  $0.04^\circ$  increment.

**UV-Vis diffuse reflectance spectroscopy:** UV-Vis diffuse reflectance spectra were recorded on a Hitachi UH4150 spectrophotometer in the wavelength range of 200 ~ 800 nm,  $\nu = 200$  nm/min, and  $\text{BaSO}_4$  was used as a reference.

**Fourier-transform infrared spectroscopy:** Fourier-transform infrared (FT-IR) spectra were collected in the range of 400 ~ 4000  $\text{cm}^{-1}$  on a Bruker IFS 66  $\nu/\text{s}$  Fourier transform infrared spectrometer.

**Nitrogen sorption isotherms:** The nitrogen adsorption and desorption isotherms were measured at 77 K using a Micromeritics ASAP 2460 instrument.

**Scanning electron microscopy:** Scanning electron microscopy (SEM) images were captured on a ZEISS Gemini 300, microscope operated at an accelerating voltage of 0.02-30 kV.

**Transmission electron microscopy:** Transmission electron microscopy (TEM) images were captured on a JEOL JEM-F200 microscope at an accelerating voltage of 200 kV. The samples were prepared by drop-casting sonicated ethyl alcohol suspensions of the materials onto a copper grid.

**$^{13}\text{C}$  CP/MAS NMR:** The solid phases  $^{13}\text{C}$  CP/MAS NMR spectra were collected on a Bruker Avance III 400 MHz WB solid-state NMR spectrometer.

**Thermogravimetric analysis:** Thermogravimetric analysis (TGA) was performed on an STA449 F5/QMS 403D instrument from 30  $^\circ\text{C}$  to 800  $^\circ\text{C}$  at a 10  $^\circ\text{C}/\text{min}$  rate under an argon atmosphere.

**X-ray photoelectron spectroscopy:** X-ray photoelectron spectroscopy (XPS) was performed on a Thermo Scientific K-Alpha system (excitation source is Al  $K\alpha$  ray, 1486.6 eV). All measurements were performed in the CAE mode with the reference of C 1s (284.8 eV).

**Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM):** Aberration-corrected high-angle annular dark-field scanning transmission

electron microscopy (ACHAADF-STEM) images were captured on a JEOL 2100FCs microscope at an accelerating voltage of 200 kV. The samples were prepared by drop-casting sonicated ethyl alcohol suspensions of the materials onto a copper grid.

**Inductively coupled plasma mass spectrometry:** Inductively coupled plasma mass spectrometry (ICP-MS) was performed on an Agilent 5110 instrument. The amount of Rh content was calculated using the following equation.

$$C_x(\mu\text{g}/\text{kg}) = \frac{C_0(\mu\text{g}/\text{L}) \times f \times V_0(\text{mL}) \times 10^{-3}}{m(\text{g}) \times 10^{-3}} = \frac{C_1(\mu\text{g}/\text{L}) \times V_0(\text{mL}) \times 10^{-3}}{m(\text{g}) \times 10^{-3}}$$

$$W\% = \frac{C_x(\mu\text{g}/\text{kg})}{10^9} \times 100\%$$

**Ultraviolet photoelectron spectroscopy:** Ultraviolet photoelectron spectroscopy (UPS) was performed on a PHI5000 VersaProbe III (Scanning ESCA Microprobe) SCA (Spherical Analyzer) with He I, 21.2 eV (80 mA, 530 V,  $5.0 \times 10^{-2}$  mbar) as UV light source. And the sample bias is -10 V.

**Electrochemical measurements:** Electrochemical measurements were carried out on a three-electrode system with a CHI660E electrochemical workstation. Indium-tin oxide (ITO) glasses were cleaned by sonication in acetone for 15 min and dried under a UV lamp. 5 mg of RhCOF-SYNU-1 powder was mixed with 0.2 mL of Ethanol (EtOH) and 0.2 mL 5 wt% Nafion to get slurry, which was spreading on the surface of ITO glass, and the boundary was protected by Scotch tape. Then, put it in the vacuum oven at 80 °C for 5 h. After cooling down to room temperature, remove the Scotch tape. The measurements were carried out in a 0.1 mol L<sup>-1</sup> Sodium sulfate, Ag/AgCl electrode (saturated KCl) as reference electrode, a platinum wire as the counter electrode for photocurrent responses collection, electrochemical impedance spectra recording, and Mott-Schottky (M-S) experiments. A 300 W xenon lamp provided visible light irradiation with a  $\lambda = 420$  nm cut-off filter. The applied potentials vs. Ag/AgCl were converted to NHE or RHE potentials using the following equations:

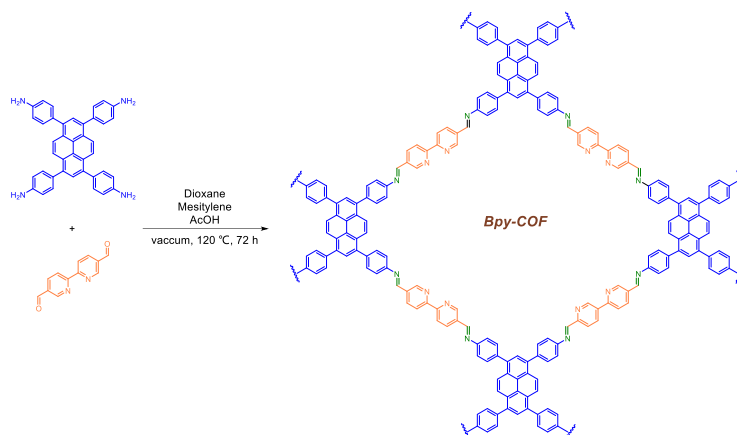
$$E_{NHE} = E_{Ag/AgCl} + E_{Ag/AgCl}^{\theta} (E_{Ag/AgCl}^{\theta} = 0.199V)$$

$$E_{RHE} = E_{Ag/AgCl} + 0.0591pH + E_{Ag/AgCl}^{\theta} (E_{Ag/AgCl}^{\theta} = 0.199V)$$

Vacuum level values were converted to electrochemical potentials according to -4.44 eV vs. vacuum level, equal to -0.4 V vs. NHE at pH 6.8.<sup>1</sup>

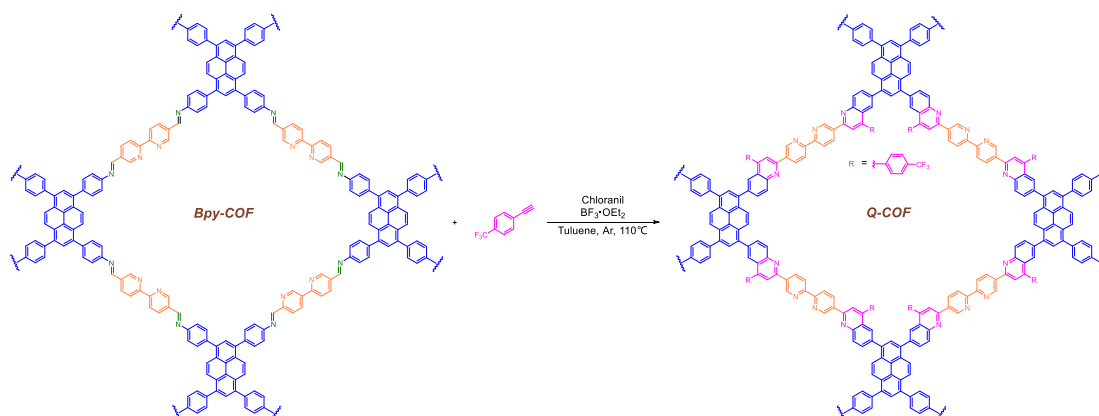
## II. General procedures for the synthesis of COFs

### 1. Preparation of BPy-COF



A glass ampoule was charged with 4,4',4'',4'''-(1,9-dihydropyrene-1,3,6,8-tetrayl)tetraaniline (85 mg, 0.15 mmol), [2,2'-bipyridine]-5,5'-dicarbaldehyde (64 mg, 0.3 mmol), dioxane (1.5 mL), and mesitylene (1.5 mL). Next, the tube was immersed in an ultrasonic bath for 30 min. Following sonication, 0.5 mL of 3 M aqueous acetic acid was added, and the reaction mixture was degassed by three freeze-pump-thaw cycles. The tube was then sealed off, heated at 120 °C, and left undisturbed for 72 h, yielding a solid at the bottom. Upon completion, the precipitate was isolated by filtration and washed with tetrahydrofuran (3×20 mL) and acetone (3×20 mL). The resulting powder was dried at 80 °C under vacuum for 12 h to yield Bpy-COF as an orange powder (135 mg, 97%).

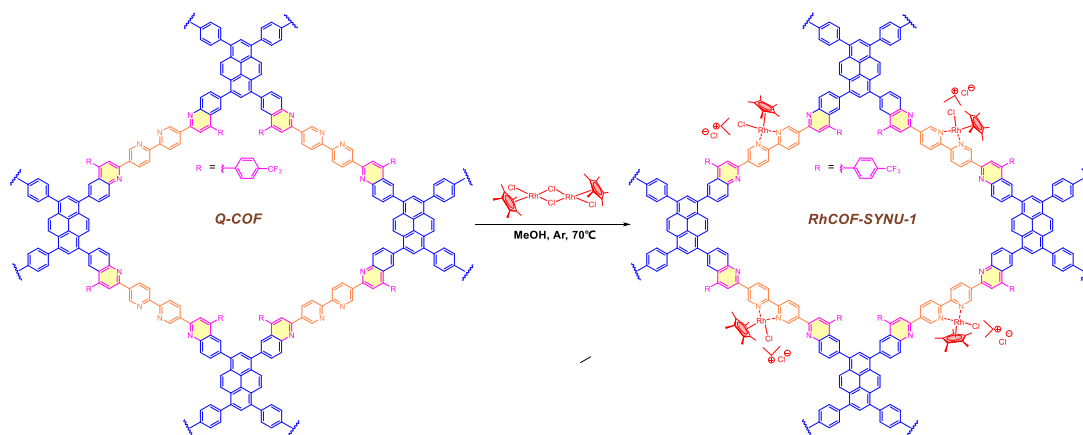
### 2. Preparation of Q-COF



A 25 mL Schlenk tube was charged with Bpy-COF (24 mg) and chloranil (40 mg), followed by the addition of 4'-trifluoromethylphenylacetylene (40  $\mu$ L), BF<sub>3</sub>·OEt<sub>2</sub> (20  $\mu$ L) and toluene (5 mL). After three freeze-pump-thaw cycles, the Schlenk tube was sealed and heated under an argon atmosphere at 110 °C for 72 h. After cooling to room temperature, the reaction was quenched with saturated NaHCO<sub>3</sub>. The solid residue was isolated by filtration and washed with *N,N*-

dimethylformamide (3×10 mL), water (3×10 mL), and methanol (3×10 mL), respectively. Then, the resulting solid was dried at 80 °C under vacuum for 12 h to yield Q-COF as a brown powder (39 mg, 95%).

### 3. Preparation of RhCOF-SYNU-1



A 25 mL Schlenk tube was charged with Q-COF (41 mg) and  $[Cp^*RhCl_2]_2$  (16 mg), followed by the addition of methanol (5 mL), and the reaction was stirred under an argon atmosphere at 70 °C for 24 h. Upon completion, the precipitate was isolated by filtration and washed with methanol (3×10 mL) and dichloromethane (3×10 mL), respectively. The resulting solid was then dried at 60 °C under vacuum for 12 h to yield RhCOF-SYNU-1 as a dark red powder (43 mg).

### III. Characterizations and photoelectrochemical measurements of COFs

#### 1. Characterizations of Bpy-COF

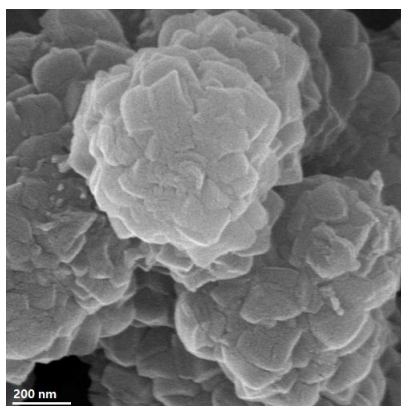


Figure S1. The SEM image of BPy-COF

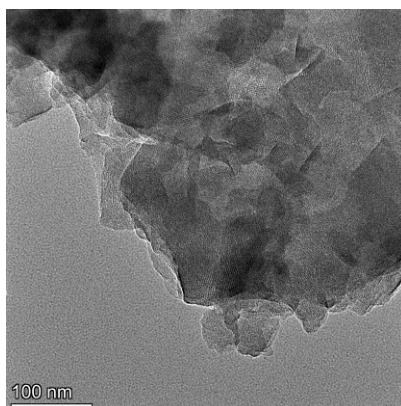


Figure S2. The TEM image of BPy-COF

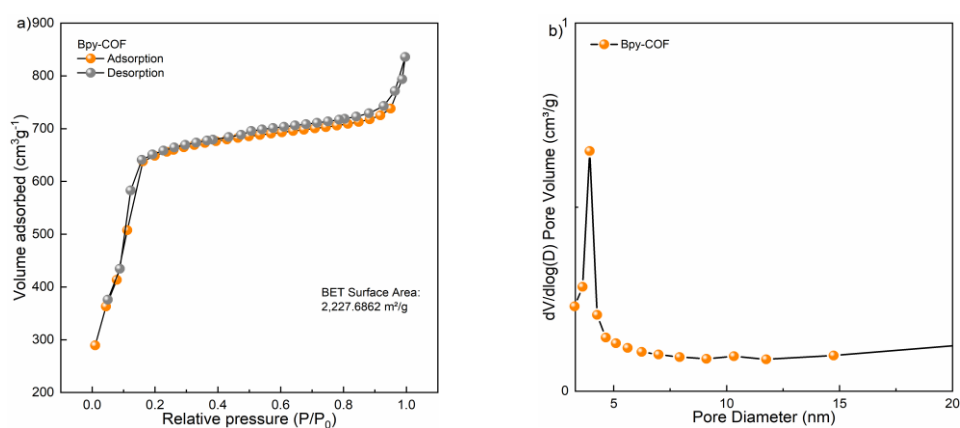


Figure S3. a)  $N_2$  adsorption and desorption isotherms of BPy-COF measured at 77 K; b) Pore size distributions of BPy-COF

## 2. Characterizations of Q-COF

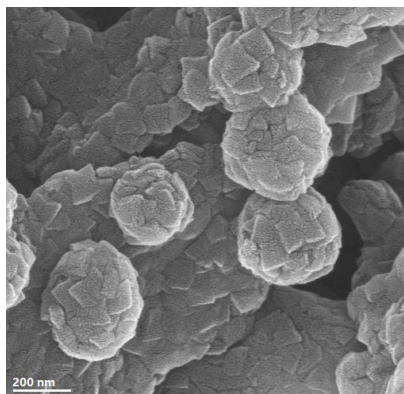


Figure S4. The SEM image of Q-COF

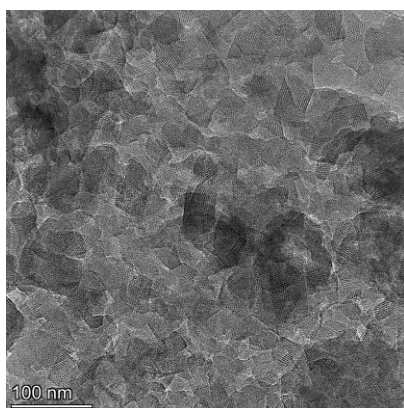


Figure S5. The TEM image of Q-COF

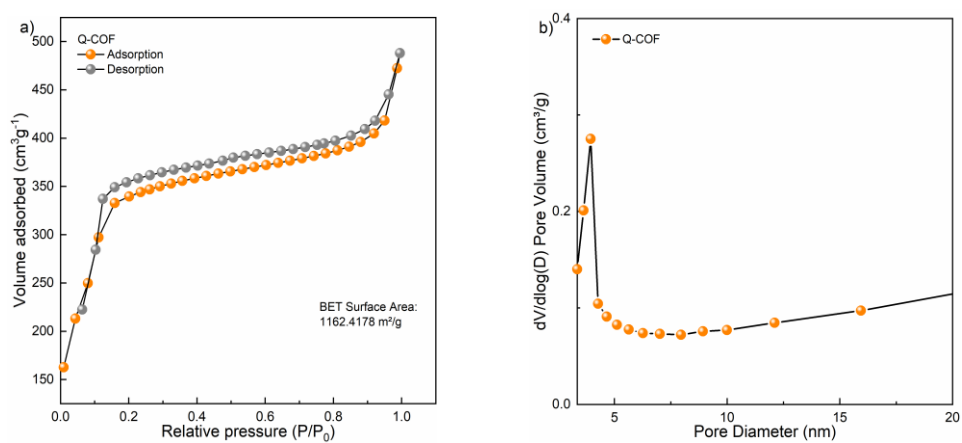


Figure S6. a)  $N_2$  adsorption and desorption isotherms of Q-COF measured at 77 K; b) Pore size distributions of Q-COF



### 3. Characterizations and photoelectrochemical measurements of RhCOF-SYNU-1

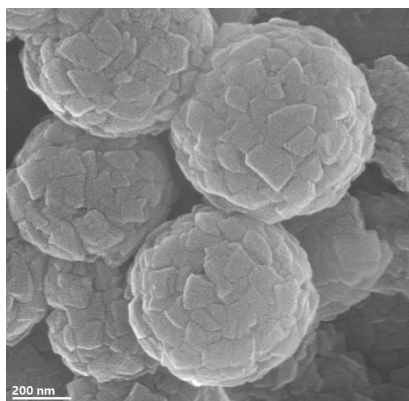


Figure S7. The SEM image of RhCOF-SYNU-1

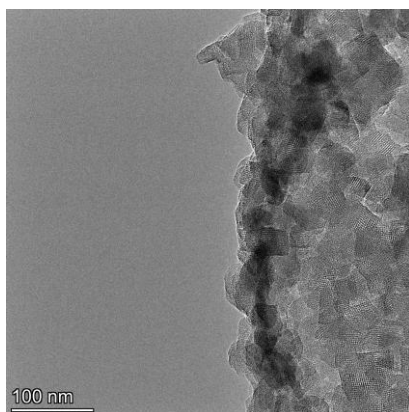


Figure S8. The TEM image of RhCOF-SYNU-1

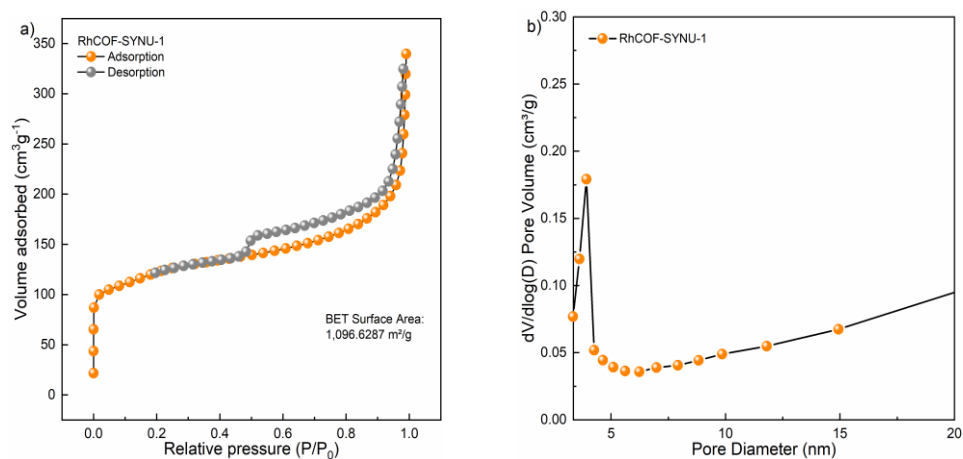
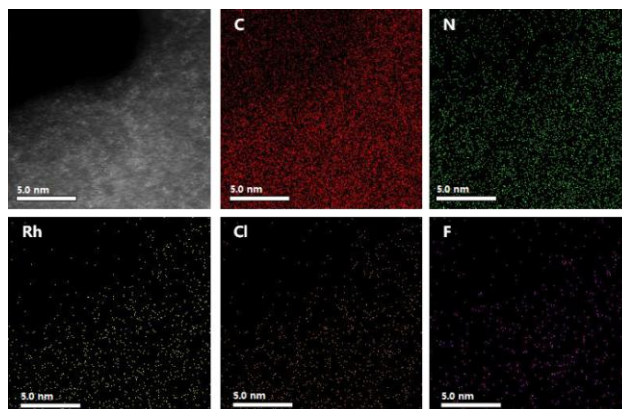
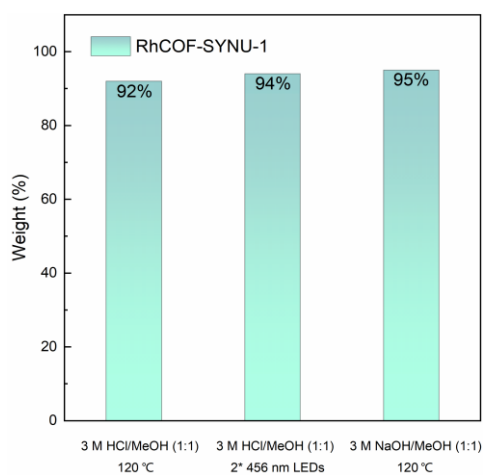


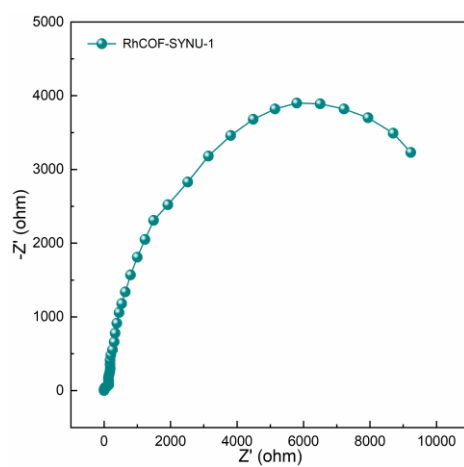
Figure S9. a) N<sub>2</sub> adsorption and desorption isotherms of RhCOF-SYNU-1 measured at 77 K; b) Pore size distributions of RhCOF-SYNU-1



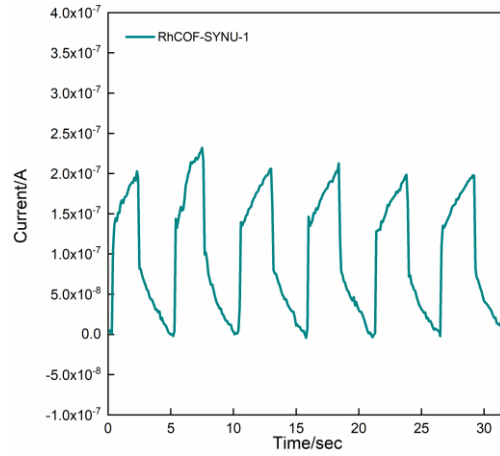
**Figure S10.** EDX mapping images of RhCOF-SYNU-1



**Figure S11.** The weight remaining of RhCOF-SYNU-1 under different simulated conditions



**Figure S12.** The electrochemical impedance spectrum of RhCOF-SYNU-1



**Figure S13.** Photocurrent responses of RhCOF-SYNU-1

#### 4. ICP-MS for RhCOF-SYNU-1

The amount of Rh content for RhCOF-SYNU-1 was calculated using the following equation.

$$m = 0.0555 \text{ (g)} \quad V_0 = 25 \text{ (mL)}, \quad C_0 = 2.461 \text{ (mg/L)}, \quad f = 100, \quad C_1 = 246.079672 \text{ (mg/kg)}$$

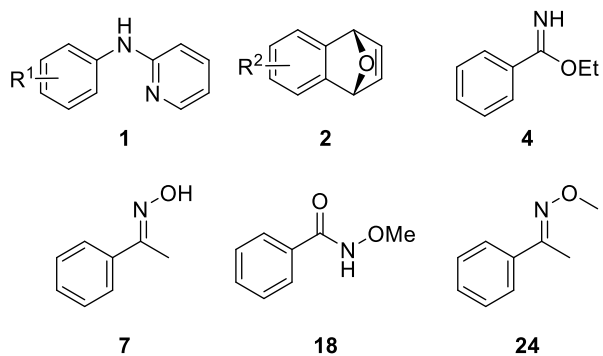
$$C_X(\text{mg/kg}) = \frac{C_0(\text{mg/L}) \times f \times V_0(\text{mL}) \times 10^{-3}}{m(\text{g}) \times 10^{-3}} = \frac{C_1(\text{mg/L}) \times V_0(\text{mL}) \times 10^{-3}}{m(\text{g}) \times 10^{-3}}$$

$$W\% = \frac{C_X(\text{mg/kg})}{10^6} \times 100\%$$

$$C_X(\text{mg/kg}) = \frac{2.461 \text{ (mg/L)} \times 100 \times 25 \text{ (mL)} \times 10^{-3}}{0.0555 \text{ (g)} \times 10^{-3}} = 110811 \text{ (mg/kg)}$$

$$\text{The amount of Rh content} = \frac{110811 \text{ (mg/kg)}}{10^6} \times 100\% = 11.08\%$$

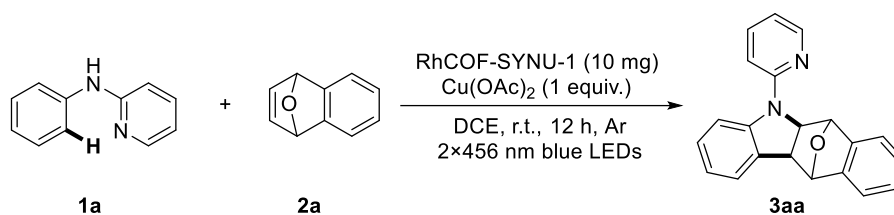
#### IV. General procedures for the synthesis of starting materials



The starting materials (**1**<sup>2</sup>, **2**<sup>2</sup>, **4**<sup>3</sup>, **7**<sup>4</sup>, **18**<sup>5</sup>, and **24**<sup>6</sup>) were synthesized using previously reported methods.

## V. Optimization of the reaction conditions for the reaction of **1a** with **2a**

**Table S1.** Screening of the reaction conditions.<sup>a</sup>

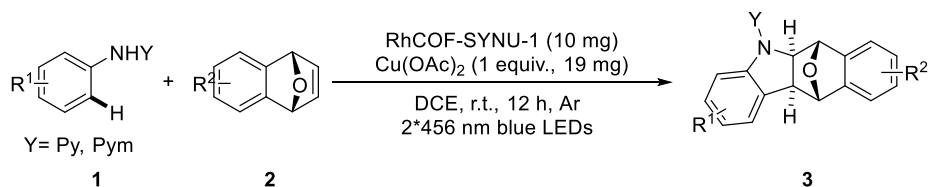


Entry	Variation	Yield of <b>3aa</b> (%) <sup>b</sup>
<b>1</b>	-	<b>93</b>
2	AgOAc instead of Cu(OAc) <sub>2</sub>	93
3	TFE instead of DCE	33
4	THF instead of DCE	88
5	7 mg RhCOF-SYNU-1	64
6	15 mg RhCOF-SYNU-1	91
7	Without RhCOF-SYNU-1	NR
8	Under dark	NR
9	Without Cu(OAc) <sub>2</sub>	trace
10	Under air	78

<sup>a</sup>Reaction conditions: **1a** (0.1 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), Cu(OAc)<sub>2</sub> (0.1 mmol), DCE (2 mL), room temperature, Ar, 12 h, 2x456 nm blue LEDs. <sup>b</sup>Isolated yield. NR denotes no reaction.

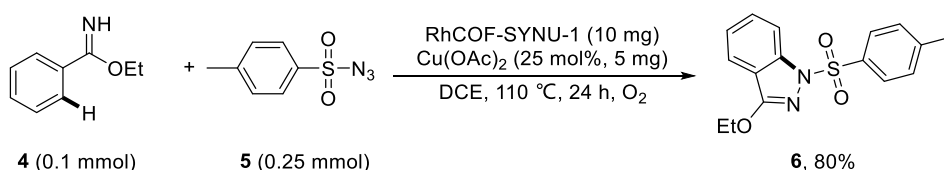
## VI. General procedures for the synthesis of compounds **3**, **6**, **9**, **11**, **13**, **16**, **17**, **20**, **23**, and **26**

### General procedure for the synthesis of compounds **3**



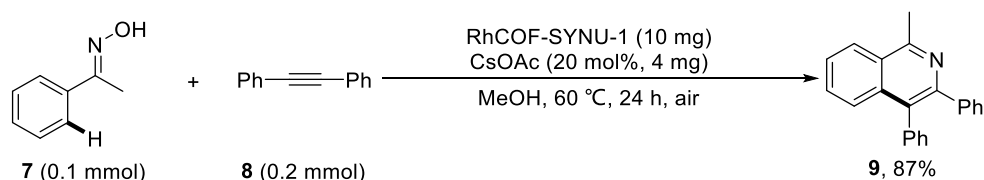
A 10 mL glass tube was charged with *N*-protected amine **1** (0.10 mmol), bicyclic alkene **2** (0.12 mmol), RhCOF-SYNU-1 (10 mg), Cu(OAc)<sub>2</sub> (0.1 mmol, 19 mg), and DCE (2 mL). The resulting mixture was stirred at 1000 rpm under an argon atmosphere and subjected to blue light irradiation (using two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. After the reaction was complete, the remaining solid was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was purified *via* silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 7/1) to yield the desired product **3**.

### General procedure for the synthesis of compound **6**



A 10 mL glass tube was charged with ethyl benzimidate **4** (0.10 mmol), 4-methylbenzenesulfonyl azide **5** (0.25 mmol), RhCOF-SYNU-1 (10 mg), Cu(OAc)<sub>2</sub> (0.025 mmol, 5 mg), and DCE (2 mL). The mixture was stirred at 1000 rpm and heated to 110 °C under an oxygen atmosphere for 24 hours. Upon completion, the remaining solid was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 10/1) to yield the desired product **6**.

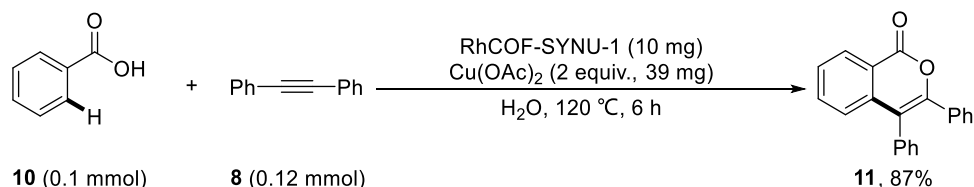
### General procedure for the synthesis of compound **9**



A 10 mL glass tube was charged with 1-phenylethan-1-one oxime **7** (0.10 mmol), 1,2-diphenylethyne **8** (0.2 mmol), RhCOF-SYNU-1 (10 mg), CsOAc (0.02 mmol, 4 mg), and MeOH (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated to 60 °C under air for 24 hours. Upon completion, the remaining solid was removed by filtration, and the solvent was

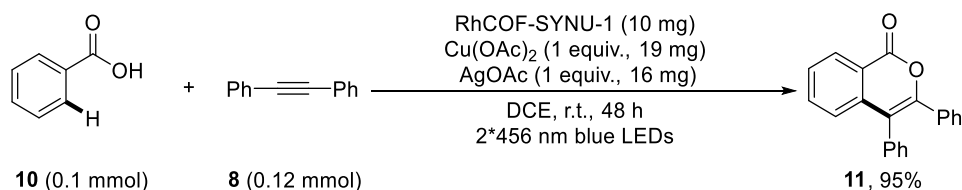
evaporated under reduced pressure. The residue was purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 15/1) to yield the desired product **9**.

**General procedure for the synthesis of compound 11 under thermal conditions**



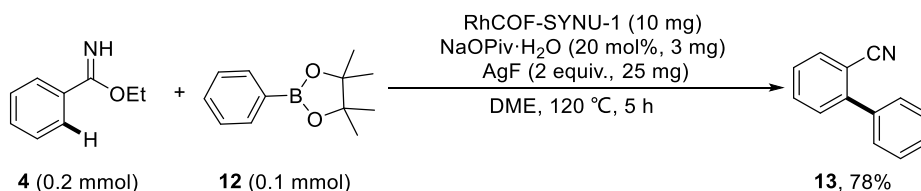
A 10 mL glass tube was charged with benzoic acid **10** (0.10 mmol), 1,2-diphenylethyne **8** (0.12 mmol), RhCOF-SYNU-1 (10 mg), Cu(OAc)<sub>2</sub> (0.2 mmol, 39 mg), and H<sub>2</sub>O (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated to 120 °C for 6 hours. Upon completion, the RhCOF-SYNU-1 was removed by filtration. The resulting mixture was extracted with diethyl ether (5 mL × 3). The organic layers were combined and dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The residue was then purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 10/1) to yield the desired product **11**.

**General procedure for the synthesis of compound 11 under visible-light-irradiation**



A 10 mL glass tube was charged with benzoic acid **10** (0.10 mmol), 1,2-diphenylethyne **8** (0.12 mmol), RhCOF-SYNU-1 (10 mg), Cu(OAc)<sub>2</sub> (0.1 mmol, 19 mg), AgOAc (0.1 mmol, 16mg), and DCE (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and irradiated with blue light (using two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 48 hours at room temperature. Upon completion, the remaining solid was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 10/1) to yield the desired product **11**.

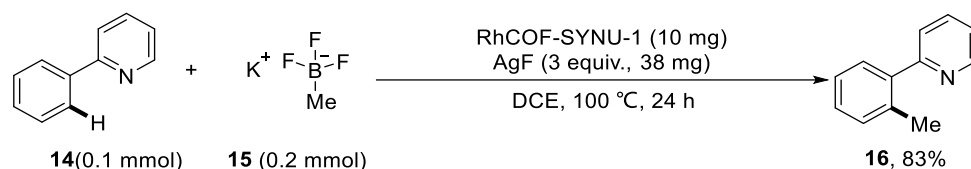
**General procedure for the synthesis of compound 13**



A 10 mL glass tube was charged with ethyl benzimidate **4** (0.20 mmol), 4,4,5,5-tetramethyl-2-

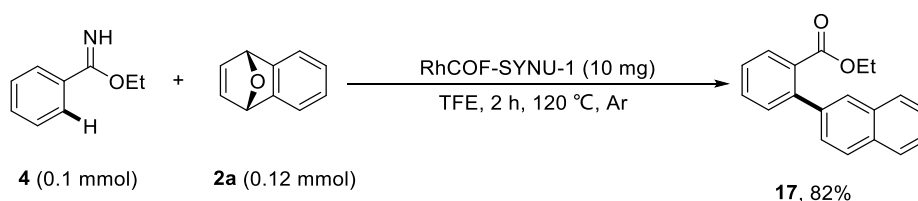
phenyl-1,3,2-dioxaborolane **12** (0.10 mmol), RhCOF-SYNU-1 (10 mg), NaOPiv·H<sub>2</sub>O (0.02 mmol, 3 mg), AgF (0.2 mmol, 25 mg), and DME (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated to 120 °C for 5 hours. Upon completion, the remaining solid was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 100/1) to yield the desired product **13**.

#### General procedure for the synthesis of compound 16



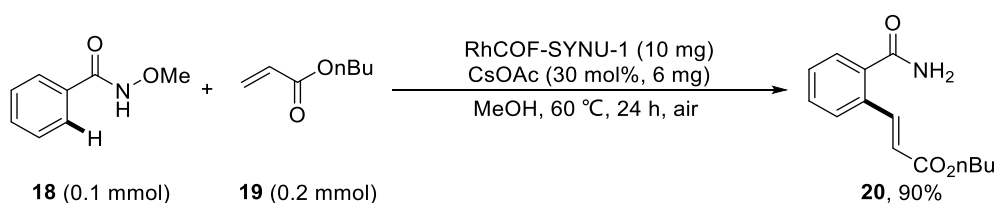
A 10 mL glass tube was charged with 2-phenylpyridine **14** (0.10 mmol), potassium methyltrifluoroborate **15** (0.2 mmol), RhCOF-SYNU-1 (10 mg), AgF (0.30 mmol, 38 mg), and DCE (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated to 100 °C for 24 hours. Upon completion, the remaining solid was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was then purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 20/1) to yield the desired product **16**.

#### General procedure for the synthesis of compound 17



A 10 mL glass tube was charged with ethyl benzimidate **4** (0.10 mmol), 1,4-dihydro-1,4-epoxynaphthalene **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and TFE (2 mL). The mixture was stirred at 1000 rpm and heated under an argon atmosphere at 120 °C for 2 hours. Upon completion, RhCOF-SYNU-1 was removed by filtration, and the solvent was evaporated under reduced pressure. The residue was then purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 15/1) to yield the desired product **17**.

#### General procedure for the synthesis of compound 20

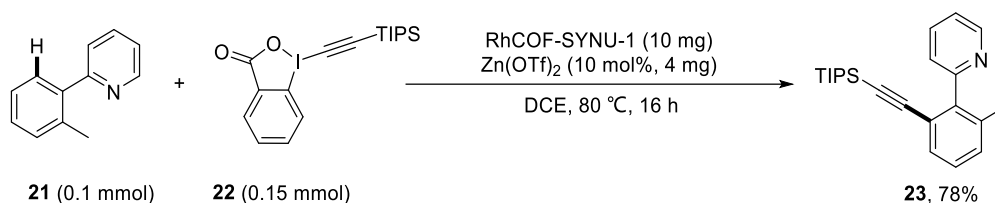


A 10 mL glass tube was charged with the *N*-methoxybenzamide **18** (0.10 mmol), butyl acrylate



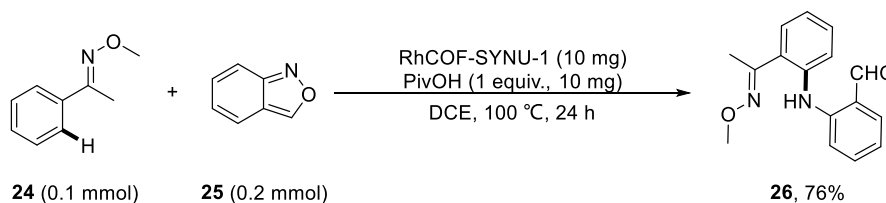
**19** (0.20 mmol), RhCOF-SYNU-1 (10 mg), CsOAc (0.03 mmol, 6 mg) and MeOH (2 mL). The tube was sealed, and the mixture was stirred (1000 rpm) and heated under air at 60 °C for 24 hours. Upon completion, the remaining solid was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography (PE/EA = 1/1) to afford the desired product **20**.

**General procedure for the synthesis of compound 23**



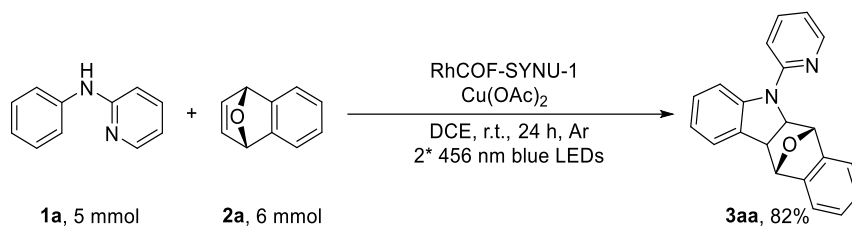
A 10 mL glass tube was charged with the 2-(*o*-tolyl)pyridine **21** (0.10 mmol), 1-[(triisopropylsilyl)ethynyl]-1,2-benziodoxol-3(*1H*)-one **22** (0.15 mmol), RhCOF-SYNU-1 (10 mg), Zn(OTf)<sub>2</sub> (0.01 mmol, 4 mg) and DCE (2 mL). The tube was sealed, and the mixture was stirred (1000 rpm) and heated at 80 °C for 16 hours. Upon completion, the remaining solid was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography (PE/EA = 20/1) to afford the desired product **23**.

**General procedure for the synthesis of compound 23**

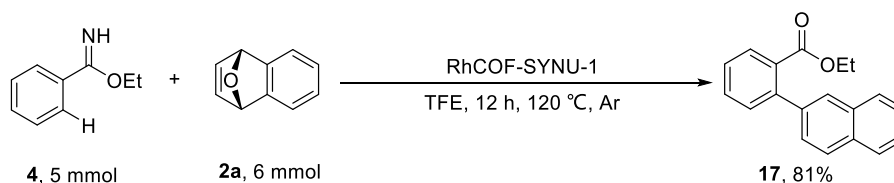


A 10 mL glass tube was charged with the 1-phenylethan-1-one *O*-methyl oxime **24** (0.10 mmol), 2,1-benzisoxazole **25** (0.20 mmol), RhCOF-SYNU-1 (10 mg), PivOH (0.10 mmol, 10 mg) and DCE (2 mL). The tube was sealed, and the mixture was stirred (1000 rpm) and heated at 100 °C for 24 h. Upon completion, the RhCOF-SYNU-1 was filtered while the solvent was removed under the reduced pressure. The residue was then purified by silica gel flash chromatography (PE/EA = 20/1) to afford the desired product **26**.

## VII. Scale-up experiments



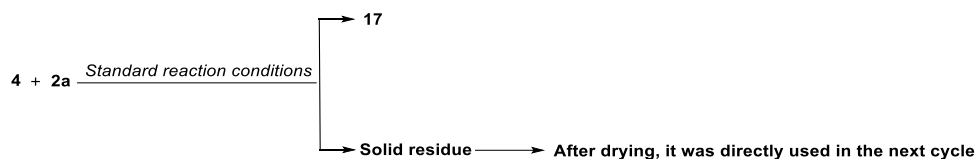
A round-bottom flask (100 mL) that contained **1a** (5 mmol, 845 mg), bicyclic alkene **2a** (6 mmol, 864 mg), RhCOF-SYNU-1 (300 mg), Cu(OAc)<sub>2</sub> (5 mmol, 950 mg) was evacuated and purged with argon gas five times. Then, DCE (50 mL) was added into the system, and the mixture was stirred under the blue LED irradiation (Two Kessil PR160L blue LEDs, 456 nm, 40 W, the distance between the reactor and lamp is approximately 5 cm.) for 24 hours at room temperature. Upon completion, the remaining solid was filtered, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa** (1260 mg, 82%).



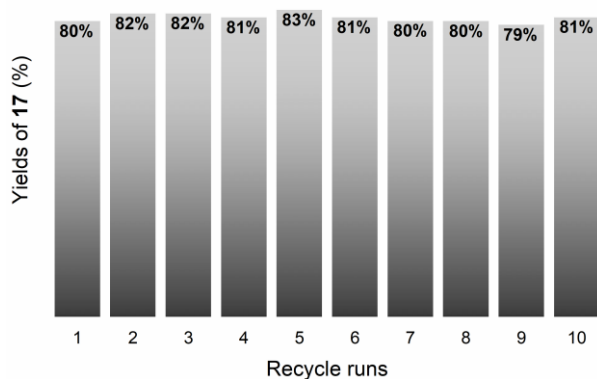
A 25 mL Schlenk tube was charged with **1a** (5 mmol, 745 mg), bicyclic alkene **2a** (6 mmol, 864 mg), and RhCOF-SYNU-1 (300 mg), followed by the addition of TFE (10 mL). After three freeze-pump-thaw cycles, the Schlenk tube was sealed and heated under an argon atmosphere at 120 °C for 12 hours. Upon completion, the RhCOF-SYNU-1 was filtered, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 20/1) to afford the desired product **3aa** (1120 mg, 81%).

## VIII. Catalyst and metal oxidant recycling experiments

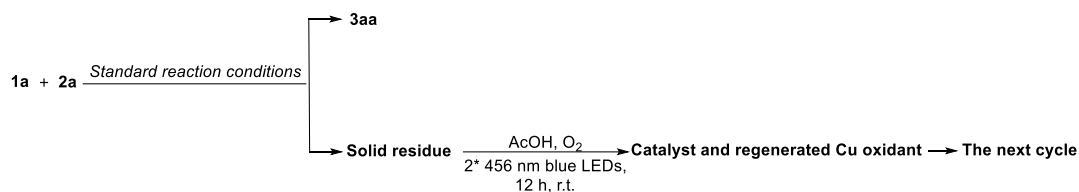
### 1. Catalyst recycling experiments for the synthesis of compound **17**



A 10 mL glass tube was charged with ethyl benzimidate **4** (0.10 mmol), 1,4-dihydro-1,4-epoxynaphthalene **2a** (0.12 mmol), RhCOF-SYNU-1 (50 mg), and TFE (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated under an argon atmosphere at 120 °C for 2 hours. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 15/1) to afford the desired product **17**. The solid was then dried at 80 °C under vacuum for 1 h, yielding the recycled RhCOF-SYNU-1 directly used for the next cycle.

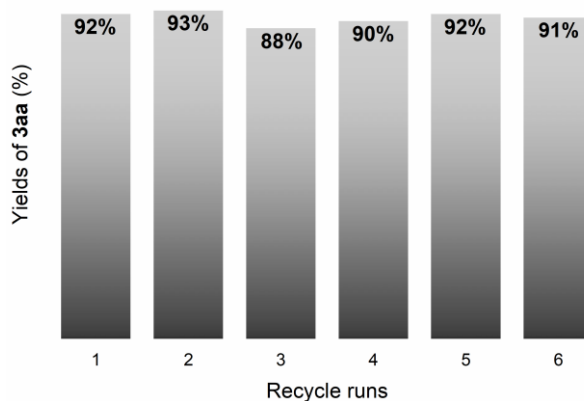


## 2. Catalyst and oxidant recycling experiments for the synthesis of compound **3aa** under visible-light-irradiation

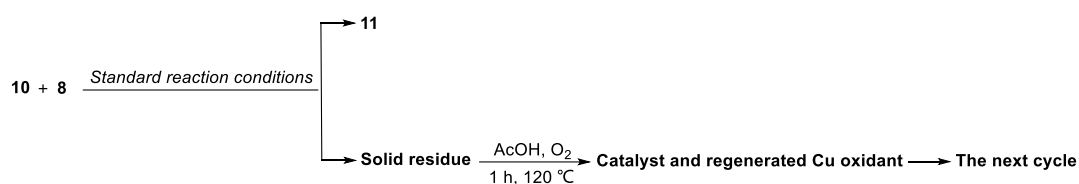


A 10 mL glass tube was charged with **1a** (0.10 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (50 mg), and Cu(OAc)<sub>2</sub> (0.15 mmol, 30 mg). The tube was evacuated and purged with argon gas three times. DCE (2 mL) was then added, and the mixture was stirred under blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa**.

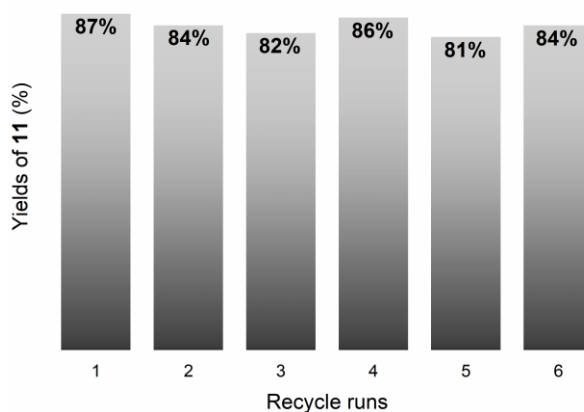
The solid reaction residue was then transferred into 1 mL of acetic acid. This mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W; positioned approximately 5 cm from the reactor) under an oxygen atmosphere (oxygen balloon) for 12 hours at room temperature. Subsequently, the acetic acid was removed under reduced pressure, and the solid was dried at 80 °C under vacuum for 1 h. This process yielded the regenerated catalyst and oxidant, which were directly used for the next cycle.



### 3. Catalyst and oxidant recycling experiments for the synthesis of compound **11** under thermal conditions



A 10 mL glass tube was charged with benzoic acid **10** (0.10 mmol), 1,2-diphenylethyne **8** (0.12 mmol), RhCOF-SYNU-1 (50 mg), Cu(OAc)<sub>2</sub> (0.3 mmol, 60 mg), and H<sub>2</sub>O (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated to 120 °C under an air atmosphere for 6 hours. Upon completion, the resulting mixture was extracted with diethyl ether (5 mL × 3). The organic layers were combined and dried over MgSO<sub>4</sub> and filtered. The solvent was removed under reduced pressure. The residue was then purified by silica gel flash chromatography using a mixture of petroleum ether and ethyl acetate (PE/EA = 10/1) to yield the desired product **11**. Meanwhile, 5 mmol of acetic acid was added to the remaining aqueous phase. The tube was sealed, and the above mixture was heated at 120 °C for 1 hour under an oxygen atmosphere. This process yielded the regenerated catalyst and oxidant-containing suspension, which were directly used for the next cycle by adding fresh reactants **10** and **8**.

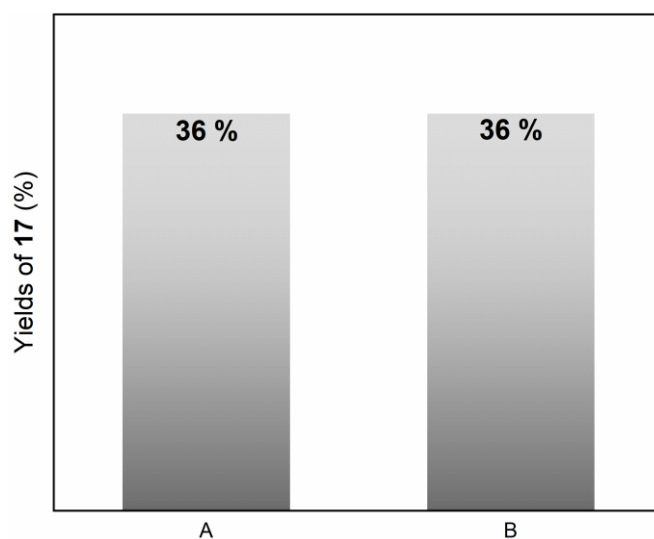


## IX. Hot filtration test

A hot filtration test was performed to ensure the catalytic activity of RhCOF-SYNU-1 originates from the undamaged RhCOF-SYNU-1.

Firstly, a 10 mL glass tube was charged with ethyl benzimidate **4** (0.10 mmol), 1,4-dihydro-1,4-epoxynaphthalene **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and TFE (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated at 120 °C under an argon atmosphere for 10 minutes (labeled as A). After the isolation, the typical reaction yield was determined to be 36%.

Then, a parallel reaction was conducted. A 10 mL glass tube was charged with ethyl benzimidate **4** (0.10 mmol), 1,4-dihydro-1,4-epoxynaphthalene **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and TFE (2 mL). The tube was sealed, and the mixture was stirred at 1000 rpm and heated at 120 °C under an argon atmosphere. The reaction was interrupted after 10 minutes. The catalyst RhCOF-SYNU-1 was then removed immediately by filtration. The filtrate was then put back into the oil bath for 2 hours. Upon isolation, no increase in yield of **17** was obtained. The outcome for B was still 36%.



## X. The Characterizations of Recycled RhCOF-SYNU-1

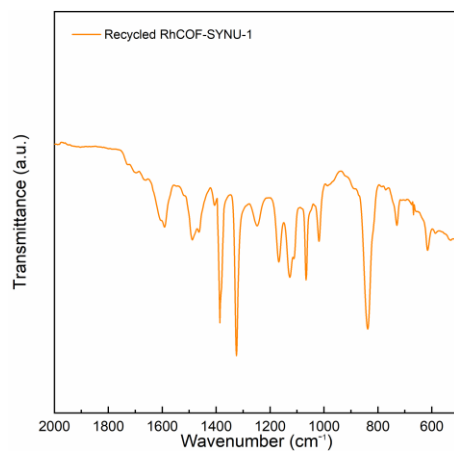


Figure S14. The FT-TR spectrum of Recycled RhCOF-SYNU-1

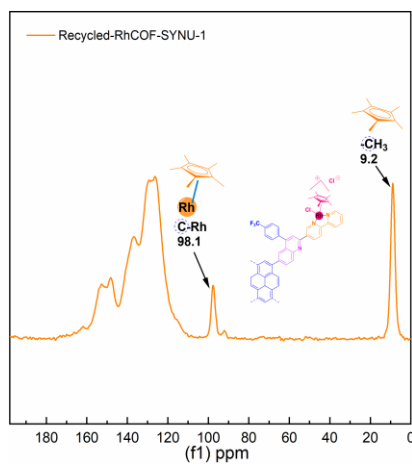


Figure S15. Solid-state <sup>13</sup>C NMR spectrum of Recycled RhCOF-SYNU-1

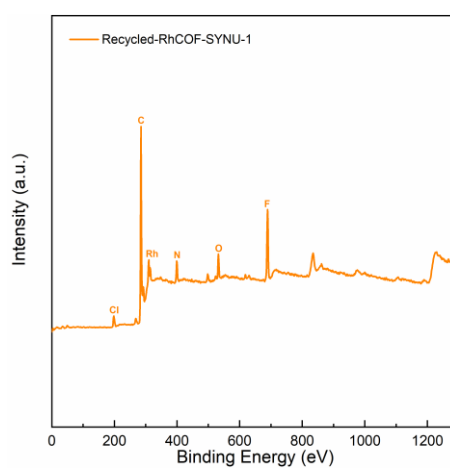
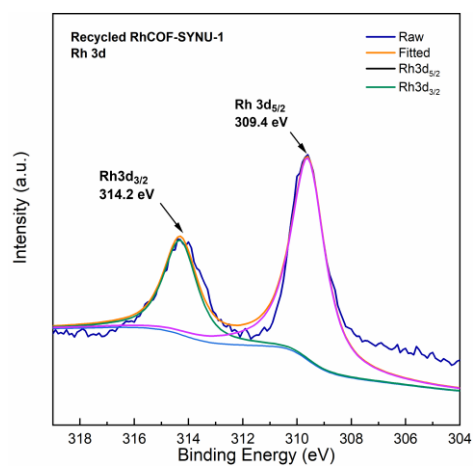
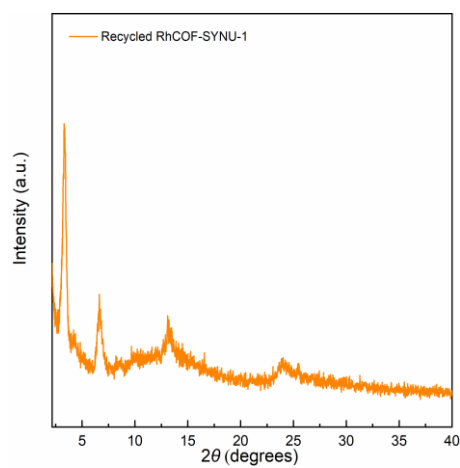


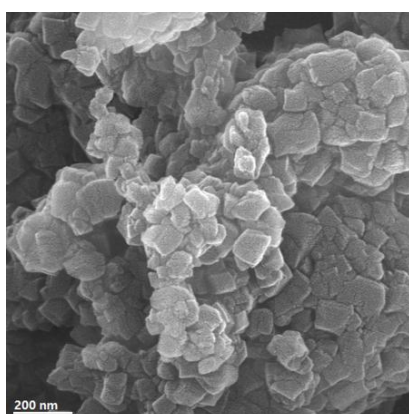
Figure S16. XPS full spectrum of Recycled RhCOF-SYNU-1



**Figure S17.** The Rh 3d XPS spectrum of Recycled RhCOF-SYNU-1

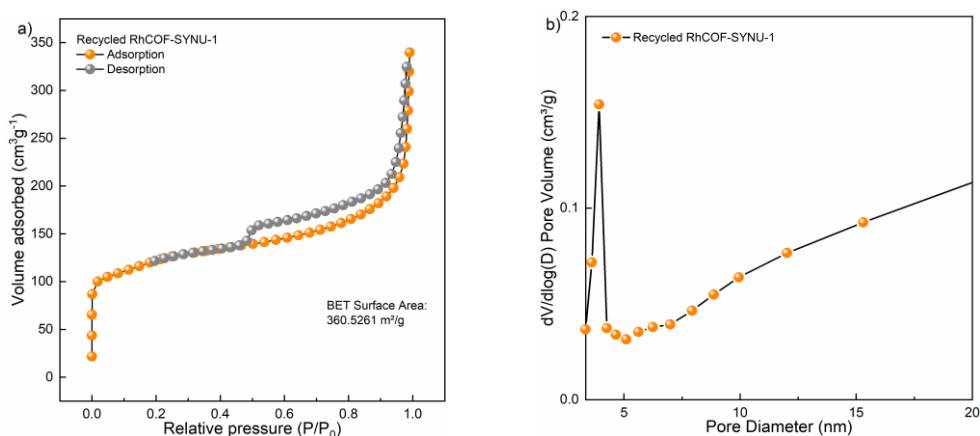


**Figure S18.** The PXRD pattern of Recycled RhCOF-SYNU-1

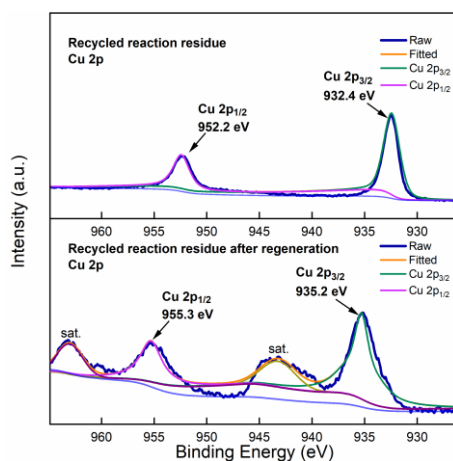


**Figure S19.** The SEM image of Recycled RhCOF-SYNU-1





**Figure S20.** a)  $N_2$  adsorption and desorption isotherms of Recycled RhCOF-SYNU-1 measured at 77 K b) Pore size distribution of Recycled RhCOF-SYNU-1



**Figure S21.** Cu 2p XPS spectrum of recycled reaction residue before and after regeneration

#### ICP-MS for Recycled RhCOF-SYNU-1

The amount of Rh content for Recycled RhCOF-SYNU-1 was calculated using the following equation.

$$m = 0.0403 \text{ (g)} \quad V_0 = 25 \text{ (mL)}, \quad C_0 = 0.177543 \text{ (mg/L)}, \quad f = 1000, \quad C_1 = 177.543 \text{ (mg/kg)}$$

$$C_x \text{ (mg/kg)} = \frac{C_0 \text{ (mg/L)} \times f \times V_0 \text{ (mL)} \times 10^{-3}}{m \text{ (g)} \times 10^{-3}} = \frac{C_1 \text{ (mg/L)} \times V_0 \text{ (mL)} \times 10^{-3}}{m \text{ (g)} \times 10^{-3}}$$

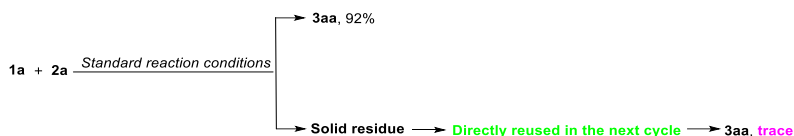
$$W\% = \frac{C_x \text{ (mg/kg)}}{10^6} \times 100\%$$

$$C_x \text{ (mg/kg)} = \frac{0.177543 \text{ (mg/L)} \times 1000 \times 25 \text{ (mL)} \times 10^{-3}}{0.0403 \text{ (g)} \times 10^{-3}} = 110138 \text{ (mg/kg)}$$

$$\text{The amount of Rh content} = \frac{110138 \text{ (mg/kg)}}{10^6} \times 100\% = 11.01\%$$

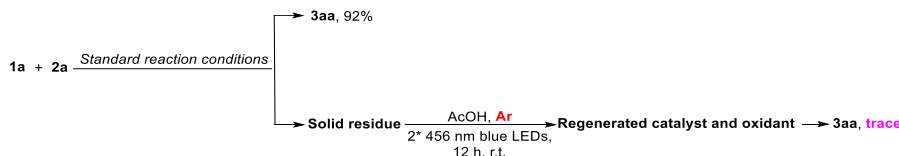
## XI. Control experiments for the Cu oxidant regeneration under visible-light-irradiation

### 1. Reuse without the Cu oxidant regeneration



A 10 mL glass tube was charged with **1a** (0.10 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and Cu(OAc)<sub>2</sub> (0.1 mmol, 20 mg). The tube was evacuated and purged with argon gas three times. DCE (2 mL) was then added, and the mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa**. The solid reaction residue was directly used for the reaction of **1a** with **2a** without regeneration. Under standard reaction conditions, only a trace amount of **3aa** was observed.

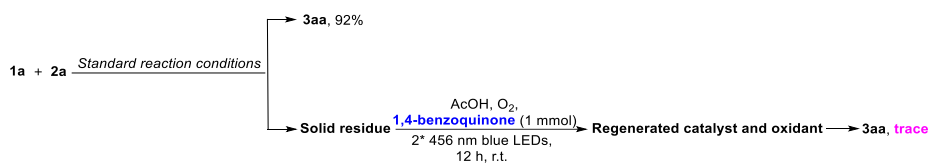
### 2. Reuse with the Cu oxidant regeneration under argon atmosphere



A 10 mL glass tube was charged with **1a** (0.10 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and Cu(OAc)<sub>2</sub> (0.1 mmol, 20 mg). The tube was evacuated and purged with argon gas three times. DCE (2 mL) was then added, and the mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa**.

The solid reaction residue was then transferred into 1 mL of acetic acid. This mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W; positioned approximately 5 cm from the reactor) under an argon atmosphere for 12 hours at room temperature. Subsequently, the acetic acid was removed under reduced pressure, and the solid was dried at 80 °C under vacuum for 1 h. The yielded solids were directly used for the reaction of **1a** with **2a**. Under standard reaction conditions, only a trace amount of **3aa** was observed.

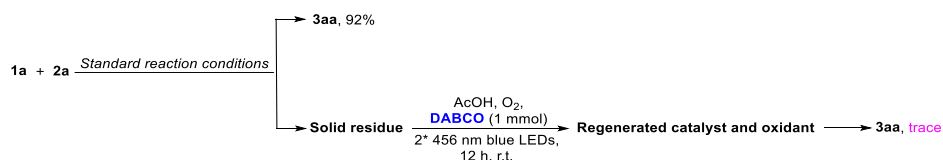
### 3. Reuse with the Cu oxidant regeneration in the presence of 1,4-benzoquinone



A 10 mL glass tube was charged with **1a** (0.10 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and Cu(OAc)<sub>2</sub> (0.1 mmol, 20 mg). The tube was evacuated and purged with argon gas three times. DCE (2 mL) was then added, and the mixture was stirred under blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa**.

The solid reaction residue was then transferred into 1 mL of acetic acid, then 10 equiv. 1,4-benzoquinone (1 mmol) was added. This mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W; positioned approximately 5 cm from the reactor) under an oxygen atmosphere (oxygen balloon) for 12 hours at room temperature. Subsequently, the acetic acid was removed under reduced pressure, and the solid was dried at 80 °C under vacuum for 1 h. The yielded solids were directly used for the reaction of **1a** with **2a**. Under standard reaction conditions, only a trace amount of **3aa** was observed.

### 4. Reuse with the Cu oxidant regeneration in the presence of DABCO

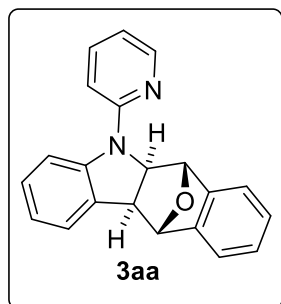


A 10 mL glass tube was charged with **1a** (0.10 mmol), **2a** (0.12 mmol), RhCOF-SYNU-1 (10 mg), and Cu(OAc)<sub>2</sub> (0.1 mmol, 20 mg). The tube was evacuated and purged with argon gas three times. DCE (2 mL) was then added, and the mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W, positioned approximately 5 cm from the reactor) for 12 hours at room temperature. Upon completion, diethyl ether (3×5 mL) was added, and the mixture was centrifuged to separate the solid in the reaction solution. Meanwhile, the solvent was removed under reduced pressure, and the residue was purified by silica gel flash chromatography (PE/EtOAc = 10/1) to afford the desired product **3aa**.

The solid reaction residue was then transferred into 1 mL of acetic acid, then 10 equiv. DABCO (1,4-diazabicyclo[2.2.2]octane, 1 mmol) was added. This mixture was stirred with the blue LED irradiation (two Kessil PR160L blue LEDs, 456 nm, 40 W; positioned approximately 5 cm from the reactor) under an oxygen atmosphere (oxygen balloon) for 12 hours at room temperature. Subsequently, the acetic acid was removed under reduced pressure, and the solid was dried at 80 °C under vacuum for 1 h. The yielded solids were directly used for the reaction of **1a** with **2a**. Under standard reaction conditions, only a trace amount of **3aa** was observed.

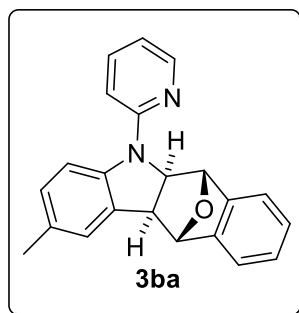
## XII. Characterization data of compounds

### 5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (**3aa**)<sup>2</sup>



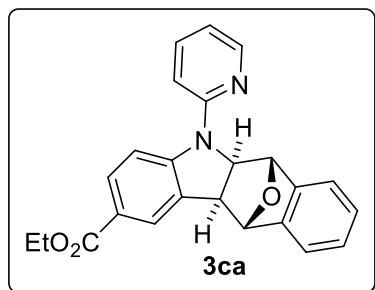
According to the general procedure (PE/EtOAc = 7/1), **3aa** was obtained in 93% yield (29 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 5.1, 1.9 Hz, 1H), 8.01 (d, *J* = 8.1 Hz, 1H), 7.66 – 7.58 (m, 1H), 7.47 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.40 – 7.32 (m, 2H), 7.26 – 7.20 (m, 3H), 7.04 (d, *J* = 8.5 Hz, 1H), 6.93 (td, *J* = 7.4, 1.0 Hz, 1H), 6.81 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.67 (s, 1H), 5.38 (s, 1H), 4.59 (d, *J* = 7.7 Hz, 1H), 3.73 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.9, 148.5, 147.2, 145.7, 143.1, 137.4, 130.3, 128.3, 127.5, 127.2, 124.4, 120.9, 120.5, 119.7, 115.1, 113.6, 108.7, 85.0, 83.6, 67.9, 49.6. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>17</sub>N<sub>2</sub>O 313.1336, found 313.1335.

### 2-methyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (**3ba**)<sup>2</sup>



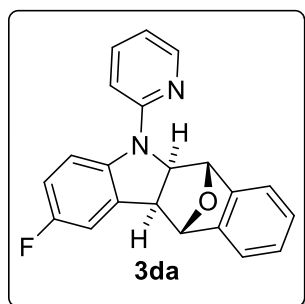
According to the general procedure (PE/EtOAc = 7/1), **3ba** was obtained in 90% yield (29 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.37 (dd, *J* = 5.2, 1.9 Hz, 1H), 7.89 (d, *J* = 8.2 Hz, 1H), 7.60 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.47 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.37 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.24 (dd, *J* = 5.2, 2.9 Hz, 2H), 7.18 (s, 1H), 7.06 – 6.98 (m, 2H), 6.78 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.67 (s, 1H), 5.38 (s, 1H), 4.57 (d, *J* = 7.7 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.5, 145.7, 144.9, 143.1, 137.3, 130.3, 130.3, 128.7, 127.5, 127.2, 125.1, 120.5, 119.7, 114.7, 113.4, 108.4, 85.0, 83.6, 68.0, 49.6, 20.9. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O 327.1494, found 327.1492.

### ethyl 5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole-2-carboxylate (**3ca**)<sup>2</sup>



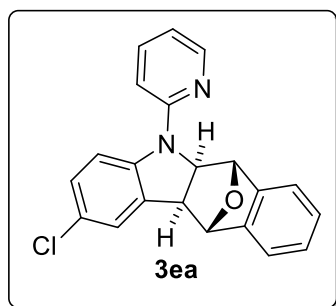
According to the general procedure (PE/EtOAc = 7/1), **3ca** was obtained in 76% yield (29 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.45 – 8.43 (m, 1H), 8.04 (m, 2H), 7.99 – 7.95 (m, 1H), 7.72 – 7.67 (m, 1H), 7.49 – 7.46 (m, 1H), 7.43 – 7.40 (m, 1H), 7.29 – 7.25 (m, 2H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.92 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.68 (s, 1H), 5.45 (s, 1H), 4.69 (d, *J* = 7.6 Hz, 1H), 4.38 (q, *J* = 7.1 Hz, 2H), 3.75 (d, *J* = 7.6 Hz, 1H), 1.41 (t, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 166.6, 154.3, 151.1, 148.6, 145.5, 142.8, 137.7, 131.1, 130.3, 127.7, 127.3, 125.8, 122.5, 120.5, 119.8, 116.3, 112.5, 109.5, 85.1, 83.4, 68.6, 60.6, 49.2, 14.5. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>24</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> 385.1549, found 385.1547.

### 2-fluoro-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[b]carbazole (**3da**)<sup>2</sup>



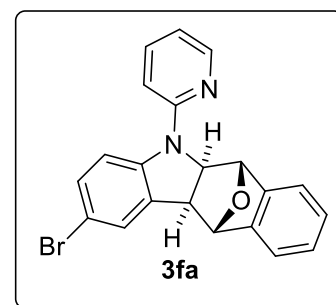
According to the general procedure (PE/EtOAc = 7/1), **3da** was obtained in 78% yield (26 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.37 – 8.35 (m, 1H), 8.11 (dd, *J* = 8.9, 4.7 Hz, 1H), 7.62 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.46 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.39 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.29 – 7.22 (m, 2H), 7.05 (ddd, *J* = 8.0, 2.8, 1.0 Hz, 1H), 6.94 – 6.88 (m, 2H), 6.81 (dd, *J* = 7.1, 4.9 Hz, 1H), 5.64 (s, 1H), 5.38 (s, 1H), 4.55 (d, *J* = 7.7 Hz, 1H), 3.71 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.7 (d, *J* = 239.4 Hz), 154.8, 148.4, 145.4, 143.5, 142.8, 137.5, 131.6 (d, *J* = 7.6 Hz), 127.7, 127.4, 120.4, 119.8, 114.9, 114.7 (d, *J* = 7.6 Hz), 114.3 (d, *J* = 22.7 Hz), 111.3 (d, *J* = 24.0 Hz), 108.1, 84.8, 83.5, 68.2, 49.7. <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -123.25. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>FN<sub>2</sub>O 331.1240, found 331.1241.

### 2-chloro-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[b]carbazole (**3ea**)<sup>2</sup>



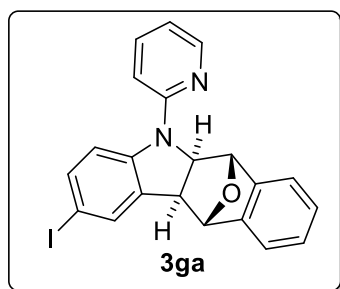
According to the general procedure (PE/EtOAc = 7/1), **3ea** was obtained in 91% yield (31 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.07 (d, *J* = 8.7 Hz, 1H), 7.64 (ddd, *J* = 8.9, 7.3, 2.0 Hz, 1H), 7.46 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.40 – 7.37 (m, 1H), 7.30 (s, 1H), 7.28 – 7.24 (m, 2H), 7.17 (dd, *J* = 8.7, 2.3 Hz, 1H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.84 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.65 (s, 1H), 5.39 (s, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 3.70 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.7, 148.5, 146.1, 145.4, 142.9, 137.7, 132.1, 128.1, 127.8, 127.5, 125.4, 124.5, 120.5, 119.9, 115.4, 115.0, 108.6, 85.0, 83.5, 68.2, 49.6. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>ClN<sub>2</sub>O 347.0947, found 347.0946.

### 2-bromo-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[b]carbazole (**3fa**)<sup>2</sup>



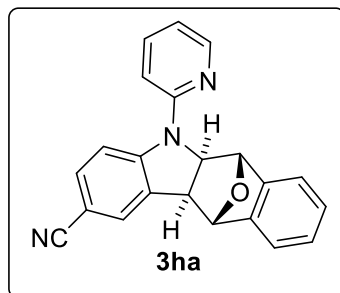
According to the general procedure (PE/EtOAc = 7/1), **3fa** was obtained in 67% yield (26 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.37 (dd, *J* = 4.9, 1.9 Hz, 1H), 8.02 (d, *J* = 8.7 Hz, 1H), 7.68 – 7.60 (m, 1H), 7.47 – 7.43 (m, 2H), 7.40 – 7.35 (m, 1H), 7.31 (dd, *J* = 8.7, 2.1 Hz, 1H), 7.27 – 7.25 (m, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.64 (s, 1H), 5.38 (s, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 3.70 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.4, 148.3, 146.3, 145.2, 142.6, 137.4, 132.3, 130.8, 127.6, 127.2, 127.1, 120.3, 119.7, 115.3, 115.2, 112.3, 108.4, 84.7, 83.2, 67.9, 49.3. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>BrN<sub>2</sub>O 391.0443, found 391.0441.

### 2-iodo-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (**3ga**)<sup>2</sup>



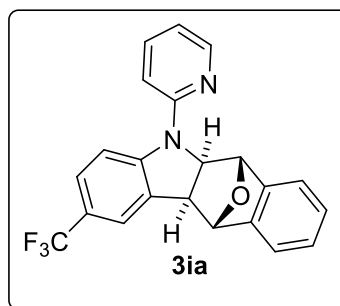
According to the general procedure (PE/EtOAc = 7/1), **3ga** was obtained in 90% yield (39mg). White solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 5.1, 2.2 Hz, 1H), 7.89 (d, *J* = 8.6 Hz, 1H), 7.66 – 7.61 (m, 2H), 7.50 – 7.44 (m, 2H), 7.38 – 7.35 (m, 1H), 7.26 (dd, *J* = 5.3, 3.0 Hz, 2H), 6.94 (d, *J* = 8.4 Hz, 1H), 6.84 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.64 (s, 1H), 5.38 (s, 1H), 4.55 (d, *J* = 7.7 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.5, 148.4, 147.1, 145.3, 142.7, 137.6, 136.9, 133.0, 132.9, 127.7, 127.4, 120.5, 119.8, 116.0, 115.4, 108.7, 84.9, 83.4, 82.2, 68.0, 49.3. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>IN<sub>2</sub>O 439.0301, found 439.0302.

### 5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole-2-carbonitrile (**3ha**)<sup>2</sup>



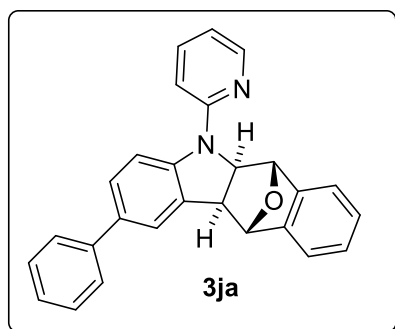
According to the general procedure (PE/EtOAc = 3/1), **3ha** was obtained in 57% yield (19 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.44 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.20 (d, *J* = 8.5 Hz, 1H), 7.73 (ddd, *J* = 8.8, 7.3, 2.0 Hz, 1H), 7.59 (s, 1H), 7.53 (dd, *J* = 8.6, 1.8 Hz, 1H), 7.48 (dd, *J* = 5.7, 2.5 Hz, 1H), 7.42 (dd, *J* = 5.8, 2.5 Hz, 1H), 7.31 – 7.28 (m, 2H), 7.03 (d, *J* = 8.4 Hz, 1H), 6.96 (dd, *J* = 7.3, 4.8 Hz, 1H), 5.66 (s, 1H), 5.41 (s, 1H), 4.67 (d, *J* = 7.7 Hz, 1H), 3.75 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.0, 150.8, 148.6, 145.1, 142.5, 137.9, 133.6, 131.1, 127.9, 127.7, 127.6, 120.5, 120.0, 119.9, 116.8, 113.8, 109.5, 102.8, 85.0, 83.2, 68.4, 49.2. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>16</sub>N<sub>3</sub>O 338.1289, found 338.1288.

### 5-(pyridin-2-yl)-2-(trifluoromethyl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (**3ia**)<sup>2</sup>



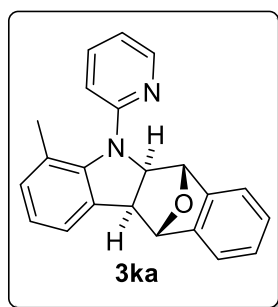
According to the general procedure (PE/EtOAc = 7/1), **3ia** was obtained in 88% yield (34mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (m, 1H), 8.16 (d, *J* = 8.5 Hz, 1H), 7.68-7.65 (m, 1H), 7.57 (s, 1H), 7.48-7.44 (m, 2H), 7.42-7.36 (m, 1H), 7.27-7.26 (m, 2H), 6.99 (d, *J* = 8.4 Hz, 1H), 6.89 (dd, *J* = 7.3, 4.9 Hz, 1H), 5.66 (s, 1H), 5.42 (s, 1H), 4.62 (d, *J* = 7.7 Hz, 1H), 3.74 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.4, 150.0, 148.5, 145.3, 142.7, 137.7, 130.6, 127.8, 127.5, 126.1 (q, *J* = 2.5 Hz), 124.8 (q, *J* = 271.4 Hz), 122.4 (q, *J* = 32.8 Hz), 121.3 (q, *J* = 15.1 Hz), 120.5, 119.9, 116.1, 113.3, 109.1, 85.0, 83.4, 68.4, 49.4. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>16</sub>F<sub>3</sub>N<sub>2</sub>O 381.1210, found 381.1209.

### 2-phenyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ja)<sup>2</sup>



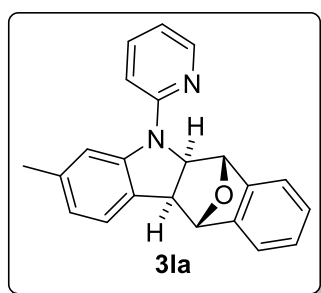
According to the general procedure (PE/EtOAc = 7/1), **3ja** was obtained in 82% yield (32mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 5.0, 1.8 Hz, 1H), 8.10 (d, *J* = 8.4 Hz, 1H), 7.65 - 7.59 (m, 4H), 7.49 - 7.39 (m, 5H), 7.32 - 7.23 (m, 3H), 7.04 (d, *J* = 8.4 Hz, 1H), 6.86 - 6.80 (m, 1H), 5.70 (s, 1H), 5.46 (s, 1H), 4.63 (d, *J* = 7.6 Hz, 1H), 3.78 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.8, 148.5, 146.7, 145.6, 143.0, 141.3, 137.5, 134.1, 131.0, 128.8, 127.6, 127.3, 127.2, 126.7, 126.6, 123.1, 120.5, 119.8, 115.2, 113.9, 108.8, 85.1, 83.6, 68.2, 49.7. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>21</sub>N<sub>2</sub>O 389.1649, found 389.1648.

### 4-methyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ka)<sup>2</sup>



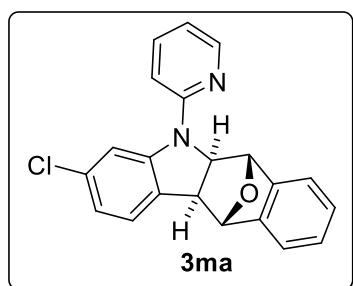
According to the general procedure (PE/EtOAc = 7/1), **3ka** was obtained in 85% yield (25mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.35 (m, 1H), 7.53 - 7.50 (m, 1H), 7.47 (d, *J* = 4.6 Hz, 1H), 7.35 - 7.29 (m, 1H), 7.24 - 7.17 (m, 3H), 7.04 (d, *J* = 7.5 Hz, 1H), 6.96 (t, *J* = 7.4 Hz, 1H), 6.85 (dd, *J* = 8.3, 4.9 Hz, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 5.72 (s, 1H), 5.26 (s, 1H), 4.34 (d, *J* = 7.2 Hz, 1H), 3.78 (d, *J* = 7.2 Hz, 1H), 2.02 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.4, 148.5, 146.6, 145.7, 143.6, 136.9, 132.0, 131.0, 127.4, 127.1, 124.3, 122.7, 121.9, 120.7, 119.6, 117.1, 112.8, 86.2, 84.4, 72.3, 50.5, 20.4. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O 327.1494, found 327.1492.

### 3-methyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3la)<sup>2</sup>



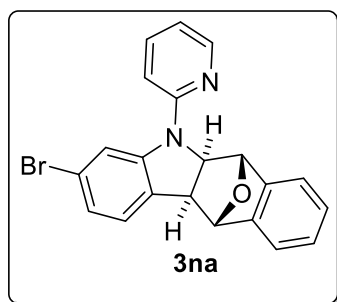
According to the general procedure (PE/EtOAc = 7/1), **3la** was obtained in 96% yield (31mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.83 (s, 1H), 7.66 - 7.59 (m, 1H), 7.47 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.38 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.26 - 7.22 (m, 3H), 7.05 (d, *J* = 8.5 Hz, 1H), 6.81 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.77 (d, *J* = 7.4 Hz, 1H), 5.67 (s, 1H), 5.36 (s, 1H), 4.59 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 2.38 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.1, 148.6, 147.4, 145.8, 143.2, 138.2, 137.4, 127.6, 127.6, 127.2, 124.1, 121.7, 120.5, 119.8, 115.0, 114.4, 108.9, 85.1, 83.7, 68.3, 49.3, 22.1. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>19</sub>N<sub>2</sub>O 327.1493, found 327.1492.

### 3-chloro-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ma)<sup>2</sup>



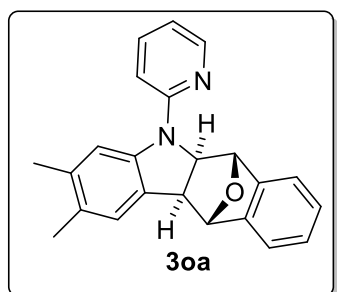
According to the general procedure (PE/EtOAc = 7/1), **3ma** was obtained in 84% yield (29 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 4.9, 1.8 Hz, 1H), 8.18 (s, 1H), 7.71 – 7.63 (m, 1H), 7.46 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.39 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.28 – 7.22 (m, 3H), 6.95 (d, *J* = 8.5 Hz, 1H), 6.93 – 6.84 (m, 2H), 5.64 (s, 1H), 5.37 (s, 1H), 4.59 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.4, 148.5, 148.3, 145.4, 142.7, 137.6, 133.9, 128.7, 127.7, 127.4, 124.7, 120.6, 120.4, 119.8, 115.6, 114.3, 108.7, 85.0, 83.3, 68.4, 49.3. HR-MS<sup>7</sup> (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>ClN<sub>2</sub>O 347.0946, found 347.0946.

### 3-bromo-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3na)



According to the general procedure (PE/EtOAc = 7/1), **3na** was obtained in 82% yield (32mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (m, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.68 - 7.63 (m, 1H), 7.50 - 7.44 (m, 2H), 7.42 - 7.36 (m, 1H), 7.35 - 7.29 (m, 1H), 7.28 - 7.25 (m, 2H), 6.94 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.65 (s, 1H), 5.40 (s, 1H), 4.58 (d, *J* = 7.6 Hz, 1H), 3.72 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.4, 148.5, 148.5, 145.4, 142.7, 137.6, 129.2, 127.7, 127.4, 125.2, 123.6, 122.0, 120.4, 119.8, 117.0, 115.6, 108.7, 84.9, 83.3, 68.3, 49.3. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>16</sub>BrN<sub>2</sub>O 391.0440, found 391.0441.

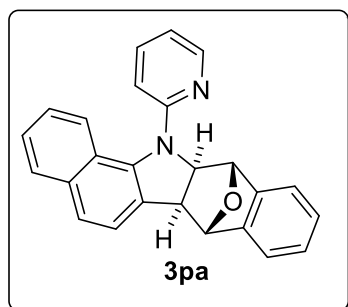
### 2,3-dimethyl-5-(pyridin-2-yl)-5a,-6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbaole (3oa)



According to the general procedure (PE/EtOAc = 7/1), **3oa** was obtained in 89% yield (30mg). White solid. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 8.38 (m, 1H), 7.80 (s, 1H), 7.63-7.60 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.47 (dd, *J* = 5.3, 3.1 Hz, 1H), 7.37 (dd, *J* = 5.2, 3.1 Hz, 1H), 7.25 - 7.23 (m, 2H), 7.14 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.79 (dd, *J* = 7.1, 4.9 Hz, 1H), 5.66 (s, 1H), 5.36 (s, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 2.27 (d, *J* = 18.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.5, 145.7, 145.3, 143.2, 137.3, 136.3, 128.8, 127.7, 127.4, 127.1, 125.5, 120.5, 119.7, 115.0, 114.6, 108.5, 85.0, 83.7, 68.1, 49.3, 20.5, 19.5. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O 341.1650, found 341.1648.

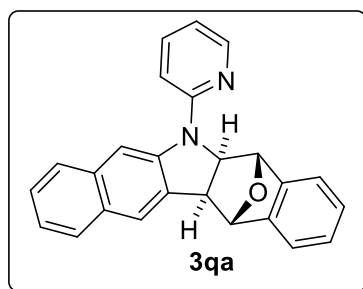


**13-(pyridin-2-yl)-6b,12,12a,13-tetrahydro-7H-7,12-epoxydibenzo[*a,h*]carbazole (3pa)<sup>2</sup>**



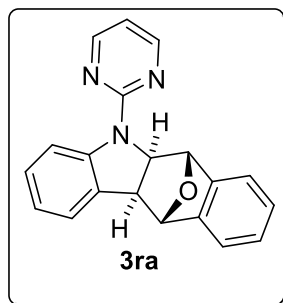
According to the general procedure (PE/EtOAc = 5/1), **3pa** was obtained in 81% yield (29 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.85 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.2 Hz, 1H), 7.58 – 7.51 (m, 2H), 7.48 – 7.34 (m, 4H), 7.29 (t, *J* = 7.6 Hz, 1H), 7.25 – 7.22 (m, 2H), 6.89 (dd, *J* = 7.2, 4.9 Hz, 1H), 6.71 (d, *J* = 8.3 Hz, 1H), 5.87 (s, 1H), 5.33 (s, 1H), 4.57 (d, *J* = 7.2 Hz, 1H), 3.97 (d, *J* = 7.1 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.0, 148.5, 145.7, 143.7, 143.0, 136.6, 134.6, 128.8, 127.5, 127.4, 127.1, 125.2, 125.1, 124.5, 123.7, 122.8, 122.4, 120.8, 119.6, 117.2, 113.0, 86.3, 83.8, 72.7, 51.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O 363.1491, found 363.1492.

**6-(pyridin-2-yl)-5a,6,12b,13-tetrahydro-5H-5,13-epoxydibenzo[*b,h*]carbazole (3qa)<sup>2</sup>**



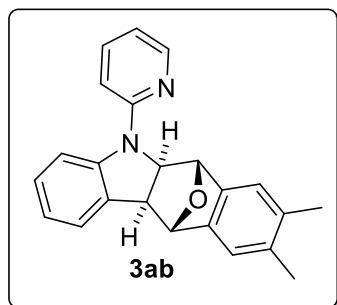
According to the general procedure (PE/EtOAc = 7/1), **3qa** was obtained in 71% yield (26 mg). White solid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.53 (dd, *J* = 5.1, 1.9 Hz, 1H), 8.30 (s, 1H), 7.86 – 7.70 (m, 4H), 7.55 (s, 1H), 7.50 – 7.38 (m, 2H), 7.38 – 7.27 (m, 4H), 6.98 – 6.89 (m, 1H), 5.75 (s, 1H), 5.52 (s, 1H), 4.79 (d, *J* = 7.3 Hz, 1H), 3.88 (dd, *J* = 7.4, 1.2 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.7, 148.6, 145.5, 145.1, 143.1, 137.5, 134.7, 132.9, 129.5, 127.6, 127.3, 127.3, 127.3, 125.9, 123.4, 123.2, 120.6, 119.8, 115.5, 109.3, 108.2, 85.6, 83.5, 68.1, 48.8. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>25</sub>H<sub>19</sub>N<sub>2</sub>O 363.1492, found 363.1492.

**5-(pyrazin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ra)<sup>2</sup>**



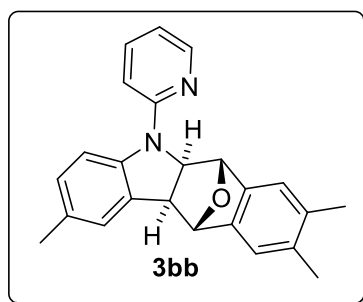
According to the general procedure (PE/EtOAc = 7/1), **3ra** was obtained in 78% yield (24 mg). Yellow solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.54 (d, *J* = 4.7 Hz, 2H), 8.46 (d, *J* = 8.5 Hz, 1H), 7.51 (dd, *J* = 5.7, 2.7 Hz, 1H), 7.41 - 7.36 (m, 2H), 7.29 (d, *J* = 6.6 Hz, 1H), 7.26 - 7.24 (m, 2H), 7.01 (t, *J* = 6.9 Hz, 1H), 6.75 (t, *J* = 4.7 Hz, 1H), 5.76 (s, 1H), 5.39 (s, 1H), 4.82 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 159.2, 157.5, 146.2, 145.8, 143.4, 130.7, 128.3, 127.4, 127.1, 124.2, 121.8, 120.9, 119.5, 115.9, 112.0, 85.2, 83.8, 67.2, 49.1. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>20</sub>H<sub>16</sub>N<sub>3</sub>O 314.1287, found 314.1288.

**8,9-dimethyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ab)<sup>2</sup>**



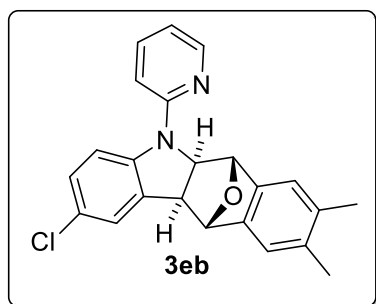
According to the general procedure (PE/EtOAc = 7/1), **3ab** was obtained in 80% yield (27mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (dd, *J* = 5.0, 1.9 Hz, 1H), 8.06 (d, *J* = 8.1 Hz, 1H), 7.63 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.35 – 7.32 (m, 1H), 7.26 (s, 1H), 7.25 – 7.20 (m, 1H), 7.18 (s, 1H), 7.02 (d, *J* = 8.5 Hz, 1H), 6.97 – 6.90 (m, 1H), 6.82 (dd, *J* = 7.1, 4.8 Hz, 1H), 5.61 (s, 1H), 5.33 (s, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 3.71 (d, *J* = 7.6 Hz, 1H), 2.30 (d, *J* = 4.0 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.4, 147.2, 143.6, 140.8, 137.3, 135.6, 135.3, 130.4, 128.2, 124.3, 121.7, 121.1, 120.8, 114.9, 113.8, 108.7, 85.0, 83.4, 68.1, 50.0, 20.1, 20.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O 341.1648, found 341.1648.

**2,8,9-trimethyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3bb)<sup>2</sup>**



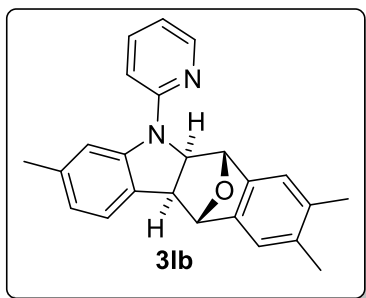
According to the general procedure (PE/EtOAc = 7/1), **3bb** was obtained in 87% yield (31mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 4.9, 1.9 Hz, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.26 (s, 1H), 7.16 (d, *J* = 3.2 Hz, 2H), 7.03 (dd, *J* = 8.2, 1.8 Hz, 1H), 6.98 (d, *J* = 8.5 Hz, 1H), 6.79 (dd, *J* = 7.2, 4.9 Hz, 1H), 5.60 (s, 1H), 5.33 (s, 1H), 4.54 (d, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 7.6 Hz, 1H), 2.34 (s, 3H), 2.30 (d, *J* = 3.6 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.4, 144.9, 143.6, 140.9, 137.2, 135.6, 135.3, 130.5, 130.2, 128.6, 125.0, 121.7, 121.0, 114.5, 113.6, 108.4, 84.9, 83.5, 68.2, 50.0, 20.9, 20.1, 20.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O 355.1806, found 355.1805.

**2-chloro-8,9-dimethyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3eb)<sup>2</sup>**



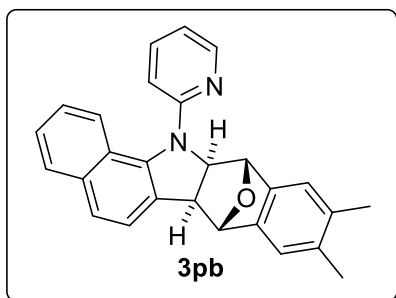
According to the general procedure (PE/EtOAc = 7/1), **3eb** was obtained in 90% yield (33mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (dd, *J* = 4.9, 1.9 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 7.66 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.30 (s, 1H), 7.26 (s, 1H), 7.20 – 7.15 (m, 2H), 6.93 (d, *J* = 8.5 Hz, 1H), 6.85 (dd, *J* = 7.2, 4.8 Hz, 1H), 5.59 (s, 1H), 5.34 (s, 1H), 4.54 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H), 2.31 (d, *J* = 3.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.6, 148.4, 145.9, 143.2, 140.5, 137.5, 135.9, 135.5, 132.2, 127.9, 125.2, 124.3, 121.7, 121.1, 115.2, 115.0, 108.5, 84.8, 83.2, 68.4, 49.9, 20.1, 20.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>20</sub>ClN<sub>2</sub>O 375.1260, found 375.1259.

**3,8,9-trimethyl-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (31b)<sup>2</sup>**



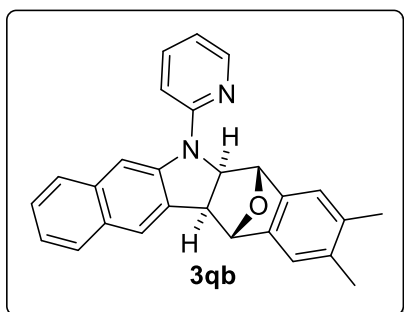
According to the general procedure (PE/EtOAc = 7/1), **31b** was obtained in 80% yield (28 mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 5.1, 1.9 Hz, 1H), 7.89 (s, 1H), 7.64 (ddd, *J* = 8.9, 7.1, 2.0 Hz, 1H), 7.26 (s, 1H), 7.22 (d, *J* = 7.5 Hz, 1H), 7.17 (s, 1H), 7.03 (d, *J* = 8.5 Hz, 1H), 6.85 – 6.72 (m, 2H), 5.61 (s, 1H), 5.31 (s, 1H), 4.55 (d, *J* = 7.6 Hz, 1H), 3.67 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H), 2.30 (d, *J* = 4.3 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.4, 147.3, 143.6, 140.8, 138.1, 137.3, 135.6, 135.2, 127.7, 123.9, 121.7, 121.6, 121.1, 114.8, 114.5, 108.7, 85.0, 83.5, 68.5, 49.6, 22.1, 20.1, 20.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>24</sub>H<sub>23</sub>N<sub>2</sub>O 355.1805, found 355.1805.

**9,10-dimethyl-13-(pyridin-2-yl)-6b,12,12a,13-tetrahydro-7H-7,12-epoxydibenzo[*α, h*]carbazole (3pb)<sup>2</sup>**



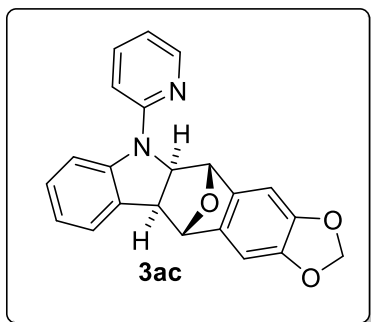
According to the general procedure (PE/EtOAc = 7/1), **3pb** was obtained in 80% yield (31mg). White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (d, *J* = 5.1, 1.9 Hz, 1H), 7.83-7.80 (m, 1H), 7.58-7.49 (m, 2H), 7.45-7.33 (m, 4H), 7.30 (s, 1H), 7.14 (s, 1H), 6.89-6.83 (m, 1H), 6.69 (d, *J* = 8.3 Hz, 1H), 5.78 (s, 1H), 5.25 (s, 1H), 4.51 (d, *J* = 7.2 Hz, 1H), 3.91 (d, *J* = 7.1 Hz, 1H), 2.26 (d, *J* = 4.6 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 158.8, 148.3, 143.4, 142.7, 141.2, 136.4, 135.3, 135.0, 134.4, 128.6, 127.6, 125.0, 124.9, 124.3, 123.5, 122.7, 122.2, 121.9, 120.7, 116.9, 112.8, 86.0, 83.6, 72.8, 51.2, 19.9, 19.9. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>O 391.1806, found 391.1805.

**2,3-dimethyl-6-(pyridin-2-yl)-5a,6-12b,13-tetrahydro-5H-5,13-epoxydibenzo[*b, h*]carbazole (3qb)<sup>2</sup>**



According to the general procedure (PE/EtOAc = 7/1), **3qb** was obtained in 79% yield (30mg) White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 5.0, Hz, 1H), 8.25 (s, 1H), 7.69 - 7.60 (m, 4H), 7.31 - 7.28 (m, 1H), 7.22 - 7.19 (m, 2H), 7.16 - 7.09 (m, 2H), 6.80 (dd, *J* = 7.1, 4.8 Hz, 1H), 5.55 (s, 1H), 5.33 (s, 1H), 4.57 (d, *J* = 7.4 Hz, 1H), 3.71 (dd, *J* = 7.3, 1.2 Hz, 1H), 2.22 (d, *J* = 2.4 Hz, 6H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.8, 148.5, 145.1, 143.4, 140.8, 137.4, 135.7, 135.4, 134.7, 133.1, 129.6, 127.4, 127.2, 125.8, 123.4, 123.1, 121.8, 121.1, 115.4, 109.3, 108.4, 85.5, 83.3, 68.3, 49.3, 20.1, 20.1. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>27</sub>H<sub>23</sub>N<sub>2</sub>O 391.1805, found 391.1805.

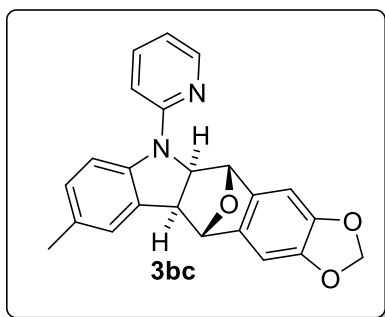
**6-(pyridin-2-yl)-5a,6,10b,11-tetrahydro-5H-5,11-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]carbazole (3ac)<sup>2</sup>**



According to the general procedure (PE/EtOAc = 7/1), **3ac** was obtained in 80% yield (30mg) White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.39 (m, 1H), 7.98 (d, *J* = 8.0 Hz, 1H), 7.63 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.27 – 7.20 (m, 1H), 7.06 – 7.03 (m, 1H), 6.99 (s, 1H), 6.97 – 6.90 (m, 1H), 6.91 (s, 1H), 6.86 – 6.79 (m, 1H), 5.99 (dd, *J* = 12.7, 1.5 Hz, 2H), 5.60 (s, 1H), 5.31 (s, 1H), 4.56 (d, *J* = 7.6 Hz, 1H), 3.69 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.9, 148.5, 147.1, 147.1, 146.8, 139.4, 137.4, 136.7, 130.2, 128.3, 124.3, 120.8, 115.1,

113.5, 108.7, 102.6, 102.0, 101.4, 85.1, 83.7, 68.0, 49.8. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub> 357.1234, found 357.1234.

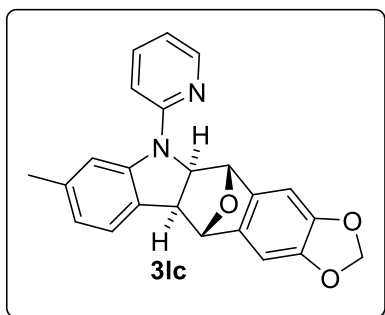
**9-methyl-6-(pyridin-2-yl)-5a,6,10b,11-tetrahydro-5H-5,11-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]carbazole (3bc)**



According to the general procedure (PE/EtOAc = 7/1), **3bc** was obtained in 87% yield (32mg) White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.38 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.86 (d, *J* = 8.2 Hz, 1H), 7.61 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.17 (s, 1H), 7.06 – 7.00 (m, 2H), 6.99 (s, 1H), 6.90 (s, 1H), 6.80 (dd, *J* = 7.1, 4.9 Hz, 1H), 5.99 (dd, *J* = 13.8, 1.6 Hz, 2H), 5.59 (s, 1H), 5.30 (s, 1H), 4.54 (d, *J* = 7.6 Hz, 1H), 3.65 (d, *J* = 7.6 Hz, 1H), 2.35 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.5, 147.0, 146.8, 144.8, 139.4, 137.3, 136.7, 130.3, 130.2, 128.6, 125.1, 114.7, 113.3,

108.4, 102.6, 102.0, 101.4, 85.0, 83.7, 68.1, 49.8, 20.9. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> 371.1390, found 371.1390.

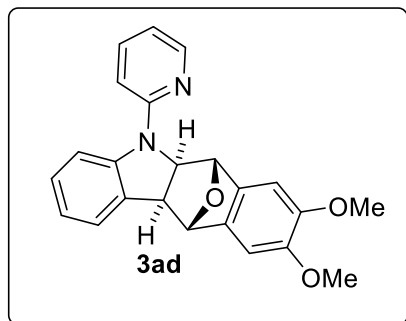
**8-methyl-6-(pyridin-2-yl)-5a,6,10b,11-tetrahydro-5H-5,11-epoxy[1,3]dioxolo[4',5':4,5]benzo[1,2-b]carbazole (3lc)<sup>2</sup>**



According to the general procedure (PE/EtOAc = 7/1), **3lc** was obtained in 80% yield (30mg) White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 5.0, 1.9 Hz, 1H), 7.81 (s, 1H), 7.63 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.22 (d, *J* = 7.4 Hz, 1H), 7.06 (d, *J* = 8.5 Hz, 1H), 6.99 (s, 1H), 6.90 (s, 1H), 6.85 – 6.81 (m, 1H), 6.77 (d, *J* = 6.9 Hz, 1H), 5.98 (dd, *J* = 13.6, 1.6 Hz, 2H), 5.60 (s, 1H), 5.28 (s, 1H), 4.55 (d, *J* = 7.5 Hz, 1H), 3.64 (d, *J* = 7.6 Hz, 1H), 2.39 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 155.0, 148.5, 147.2, 147.0, 146.8, 139.5, 138.1, 137.3, 136.7, 127.5, 124.0, 121.6, 115.0,

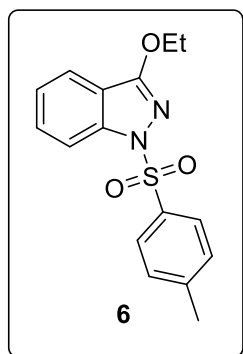
114.2, 108.8, 102.6, 102.0, 101.4, 85.1, 83.7, 68.4, 49.4, 22.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>19</sub>N<sub>2</sub>O<sub>3</sub> 357.1234, found 357.1234.

**8,9-dimethoxy-5-(pyridin-2-yl)-5a,6,11,11a-tetrahydro-5H-6,11-epoxybenzo[*b*]carbazole (3ad)<sup>2</sup>**



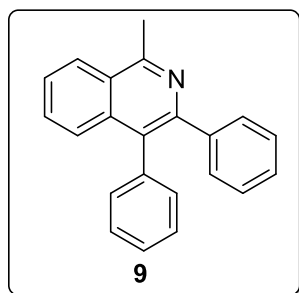
According to the general procedure (PE/EtOAc = 3/1), **3ad** was obtained in 75% yield (28mg) White solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (m, 1H), 8.00 (d, *J* = 8.1 Hz, 1H), 7.64 (ddd, *J* = 8.9, 7.2, 2.0 Hz, 1H), 7.34 (dt, *J* = 7.3, 1.2 Hz, 1H), 7.26 – 7.21 (m, 1H), 7.07 (d, *J* = 9.8 Hz, 2H), 7.02 (s, 1H), 6.94 (td, *J* = 7.4, 1.0 Hz, 1H), 6.86 – 6.80 (m, 1H), 5.65 (s, 1H), 5.35 (s, 1H), 4.57 (d, *J* = 7.6 Hz, 1H), 3.94 (d, *J* = 12.2 Hz, 6H), 3.70 (d, *J* = 7.6 Hz, 1H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 154.9, 148.5, 148.5, 148.3, 147.1, 138.0, 137.4, 135.2, 130.3, 128.2, 124.3, 120.8, 115.1, 113.5, 108.8, 105.0, 104.3, 85.3, 83.8, 68.2, 56.4, 56.3, 50.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>21</sub>N<sub>2</sub>O<sub>3</sub> 373.1549, found 373.1547.

**3-Ethoxy-1-tosyl-1H-indazole (6)<sup>7</sup>**



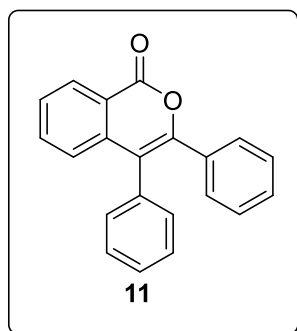
According to the general procedure (PE/EtOAc = 10/1), **6** was obtained in 80% yield (25 mg). Yellow Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.12 (d, *J* = 8.5 Hz, 1H), 7.73 (d, *J* = 8.4 Hz, 2H), 7.58 – 7.51 (m, 2H), 7.29 – 7.26 (m, 1H), 7.17 (d, *J* = 8.0 Hz, 2H), 4.47 (q, *J* = 7.1 Hz, 2H), 2.33 (s, 3H), 1.43 (t, *J* = 7.1 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 161.6, 144.8, 143.1, 133.8, 130.0, 129.5, 127.5, 124.1, 120.2, 118.3, 114.3, 65.6, 21.6, 14.4. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>16</sub>H<sub>17</sub>N<sub>2</sub>O<sub>3</sub>S 317.0954 found 317.0954.

**1-methyl-3,4-diphenylisoquinoline (9)<sup>4</sup>**



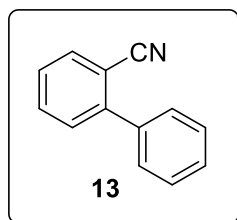
According to the general procedure (PE/EtOAc = 15/1), **9** was obtained in 87% yield (25 mg). White Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.21 (dd, *J* = 6.8, 3.1 Hz, 1H), 7.69 – 7.65 (m, 1H), 7.60 (dd, *J* = 6.3, 3.4 Hz, 2H), 7.39 – 7.31 (m, 5H), 7.26 – 7.22 (m, 2H), 7.18 (dd, *J* = 9.8, 6.9 Hz, 3H), 3.09 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 157.8, 149.5, 141.0, 137.6, 136.0, 131.4, 130.3, 129.9, 129.2, 128.2, 127.6, 127.1, 126.9, 126.5, 126.3, 126.2, 125.6, 22.8. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>22</sub>H<sub>18</sub>N 296.1433, found 296.1434.

### 3,4-diphenyl-1*H*-isochromen-1-one (**11**)<sup>8,9</sup>



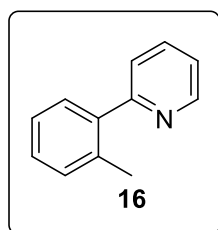
According to the general procedure (PE/EtOAc = 15/1), **11** was obtained in 82% yield (20 mg). Yellow Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.41 (dd, *J* = 7.9, 1.3 Hz, 1H), 7.68 - 7.61 (m, 1H), 7.56 - 7.50 (m, 1H), 7.46 - 7.39 (m, 3H), 7.36 - 7.31 (m, 2H), 7.28 - 7.23 (m, 3H), 7.22 - 7.17 (m, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 162.3, 151.0, 138.9, 134.6, 134.3, 132.9, 131.3, 129.6, 129.2, 129.1, 129.0, 128.1, 128.1, 127.9, 125.4, 120.5, 116.9. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>21</sub>H<sub>15</sub>O<sub>2</sub> 299.1066 found 299.1067.

### [1,1'-biphenyl]-2-carbonitrile (**13**)<sup>10</sup>



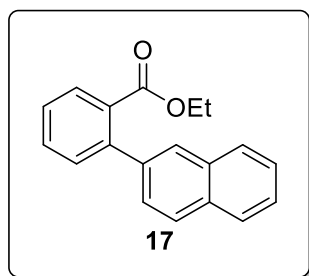
According to the general procedure (PE/EtOAc = 100/1), **13** was obtained in 83% yield (15 mg). Yellow Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.77 (dd, *J* = 7.8, 1.4 Hz, 1H), 7.65 (td, *J* = 7.7, 1.4 Hz, 1H), 7.58 - 7.55 (m, 2H), 7.54 - 7.48 (m, 3H), 7.47 - 7.43 (m, 2H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 145.5, 138.2, 133.8, 132.8, 130.1, 128.8, 128.8, 128.7, 127.6, 118.7, 111.3. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>13</sub>H<sub>10</sub>N 180.0965 found 180.0964.

### 2-(*o*-tolyl)pyridine (**16**)<sup>11</sup>



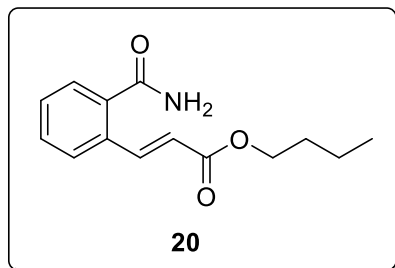
According to the general procedure (PE/EtOAc = 20/1), **16** was obtained in 82% yield (14 mg). Yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.73 (d, *J* = 4.9 Hz, 1H), 7.76 (m, 1H), 7.46 - 7.39 (m, 2H), 7.36 - 7.28 (m, 3H), 7.28 - 7.22 (m, 1H), 2.40 (s, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 160.1, 149.2, 140.5, 136.1, 135.8, 130.8, 129.6, 128.3, 125.9, 124.1, 121.6, 20.3. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>12</sub>H<sub>12</sub>N 170.0965, found 170.0964.

### ethyl 2-(naphthalen-2-yl) benzoate (**17**)<sup>3</sup>



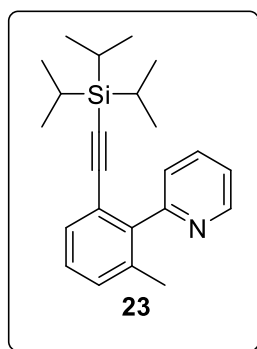
According to the general procedure (PE/EtOAc = 15/1), **17** was obtained in 82% yield (20 mg). Yellow Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 7.90 - 7.83 (m, 4H), 7.79 (s, 1H), 7.59 - 7.55 (m, 1H), 7.51 - 7.46 (m, 4H), 7.45 (m, 1H), 4.07 (q, *J* = 7.2 Hz, 2H), 0.90 (t, *J* = 7.2 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 168.8, 142.4, 139.1, 133.2, 132.5, 131.4, 131.3, 131.0, 129.9, 128.1, 127.7, 127.4, 127.3, 127.1, 126.9, 126.2, 126.0, 61.0, 13.7. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>19</sub>H<sub>17</sub>O<sub>2</sub> 277.1221 found 277.1223.

### 3-(2-carbamoylphenyl)acrylate (**20**)<sup>5</sup>



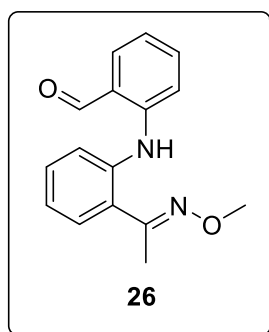
According to the general procedure (PE/EtOAc = 1/1), **20** was obtained in 90% yield (22 mg). White Solid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.03 (d, *J* = 15.9 Hz, 1H), 7.58 (d, *J* = 7.9 Hz, 1H), 7.54 - 7.48 (m, 1H), 7.44 - 7.32 (m, 2H), 6.34 (d, *J* = 16.0 Hz, 1H), 5.99 (s, 1H), 5.81 (s, 1H), 4.13 (t, *J* = 6.7 Hz, 2H), 1.65 - 1.57 (m, 2H), 1.40 - 1.31 (m, 2H), 0.89 (t, *J* = 7.4 Hz, 3H). <sup>13</sup>C NMR (126 MHz, CDCl<sub>3</sub>) δ 170.5, 166.6, 141.8, 135.8, 133.1, 130.8, 129.8, 127.8, 127.4, 121.2, 64.6, 30.7, 19.2, 13.8. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>14</sub>H<sub>18</sub>NO<sub>3</sub> 247.1208, found 247.1208.

### 2-(2-methyl-6-((triisopropylsilyl)ethynyl)phenyl)pyridine (**23**)<sup>12</sup>



According to the general procedure (PE/EtOAc = 20/1), **23** was obtained in 78% yield (27 mg). Yellow liquid. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 8.68 (ddd, *J* = 4.9, 1.9, 1.0 Hz, 1H), 7.71 (td, *J* = 7.7, 1.8 Hz, 1H), 7.43 (dd, *J* = 5.0, 4.0 Hz, 1H), 7.41 - 7.34 (m, 1H), 7.23 - 7.21 (m, 3H), 2.11 (s, 3H), 0.92 (m, 21H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 158.9, 149.2, 142.9, 136.4, 136.0, 130.4, 130.3, 127.7, 125.1, 122.9, 121.9, 105.9, 93.8, 20.1, 18.5, 11.1. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>23</sub>H<sub>32</sub>NSi 350.2299 found 350.2299.

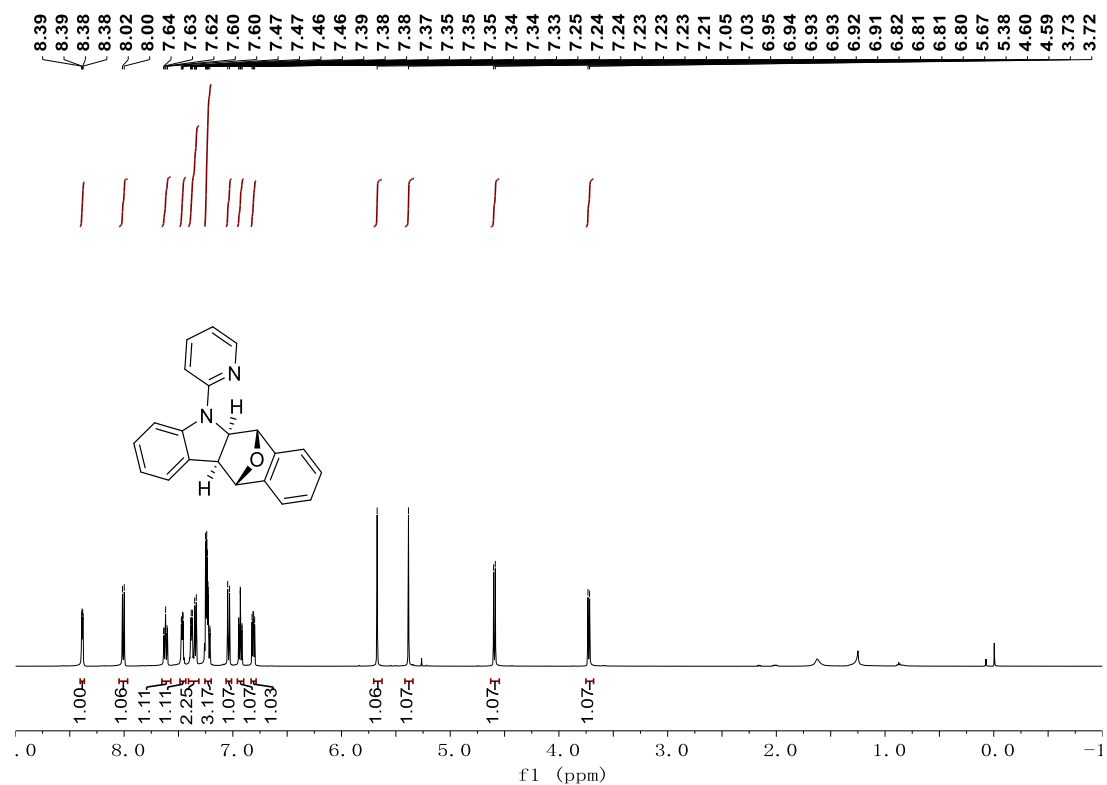
### 2-((2-(1-(methoxyimino)ethyl)phenyl)amino)benzaldehyde (**26**)<sup>6</sup>



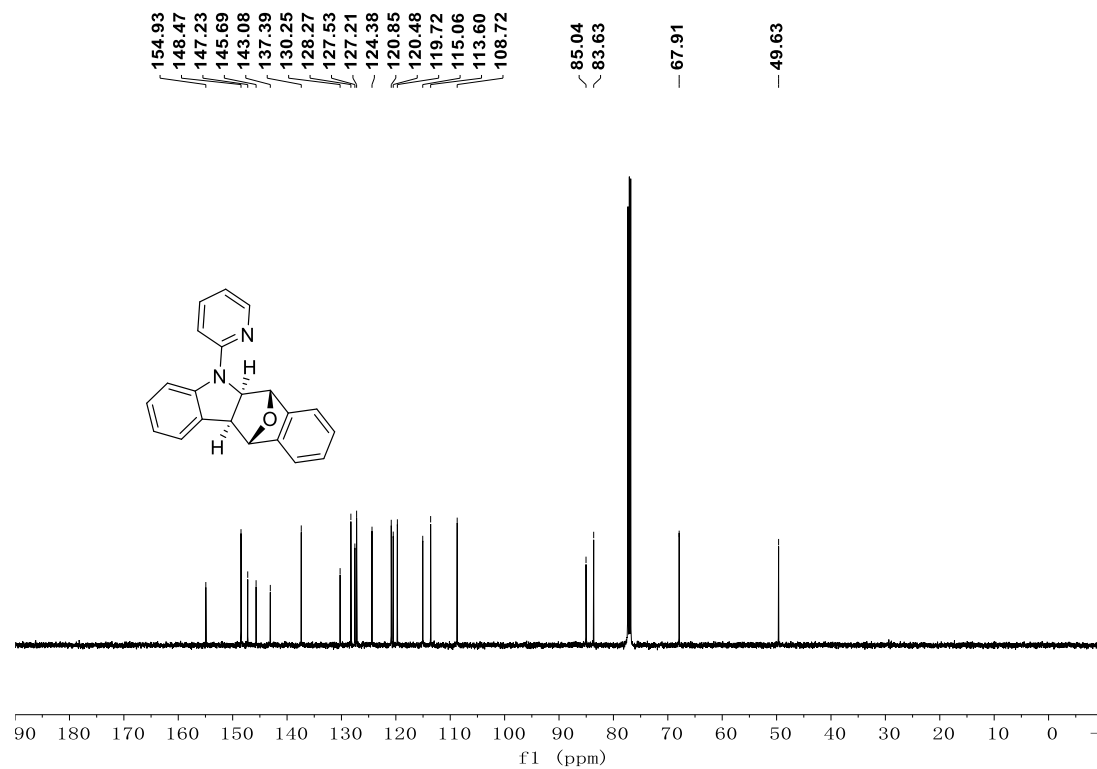
According to the general procedure (PE/EtOAc = 20/1), **26** was obtained in 76% yield (20 mg). Yellow liquid. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 10.72 (s, 1H), 9.97 (s, 1H), 7.61 (dd, *J* = 7.8, 1.7 Hz, 1H), 7.56 (d, *J* = 6.9 Hz, 1H), 7.46 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.40 - 7.29 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 1H), 7.20 - 7.13 (m, 1H), 4.14 (s, 3H), 2.22 (s, 3H). <sup>13</sup>C NMR (101 MHz, CDCl<sub>3</sub>) δ 193.4, 154.3, 146.7, 137.6, 136.4, 135.1, 130.2, 129.4, 128.9, 123.8, 123.5, 120.7, 117.7, 114.0, 62.2, 15.0. HR-MS (ESI)[M+H]<sup>+</sup> *m/z* calcd for C<sub>16</sub>H<sub>16</sub>N<sub>2</sub>O<sub>2</sub> 269.1282 found 269.1282.

### XIII. The $^1\text{H}$ , $^{13}\text{C}$ , and $^{19}\text{F}$ NMR spectra of compounds

The  $^1\text{H}$  NMR spectrum of **3aa** (500 MHz,  $\text{CDCl}_3$ )

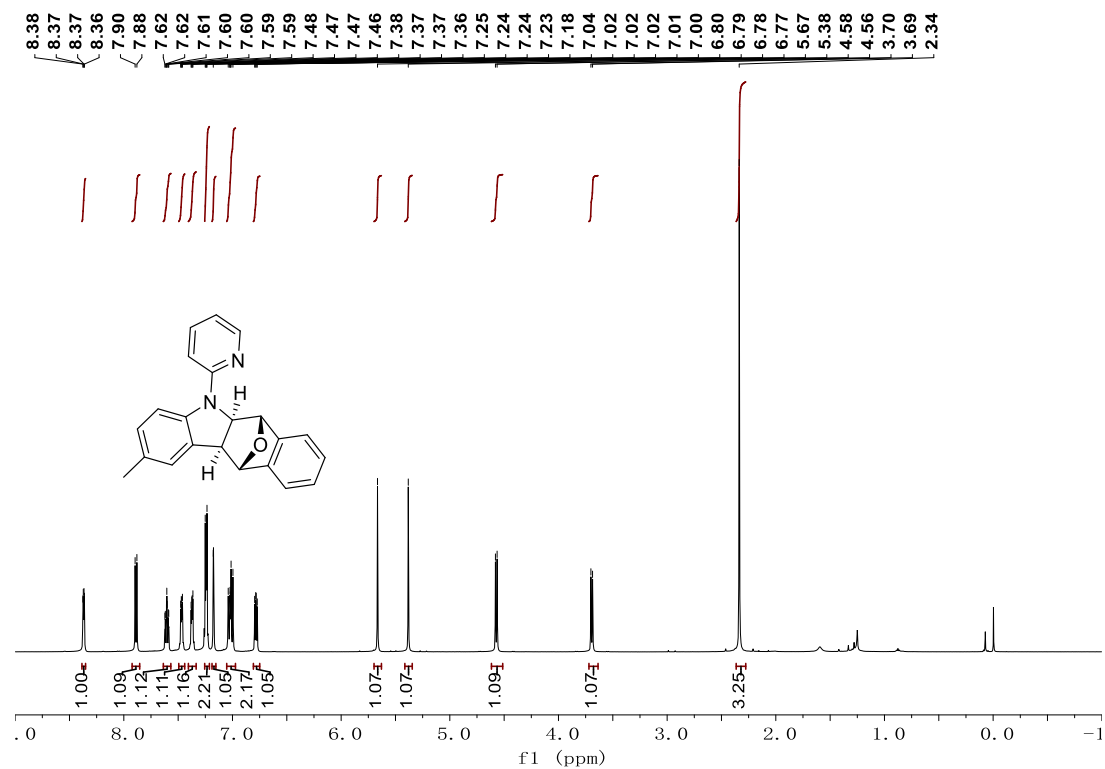


The  $^{13}\text{C}$  NMR spectrum of **3aa** (126 MHz,  $\text{CDCl}_3$ )

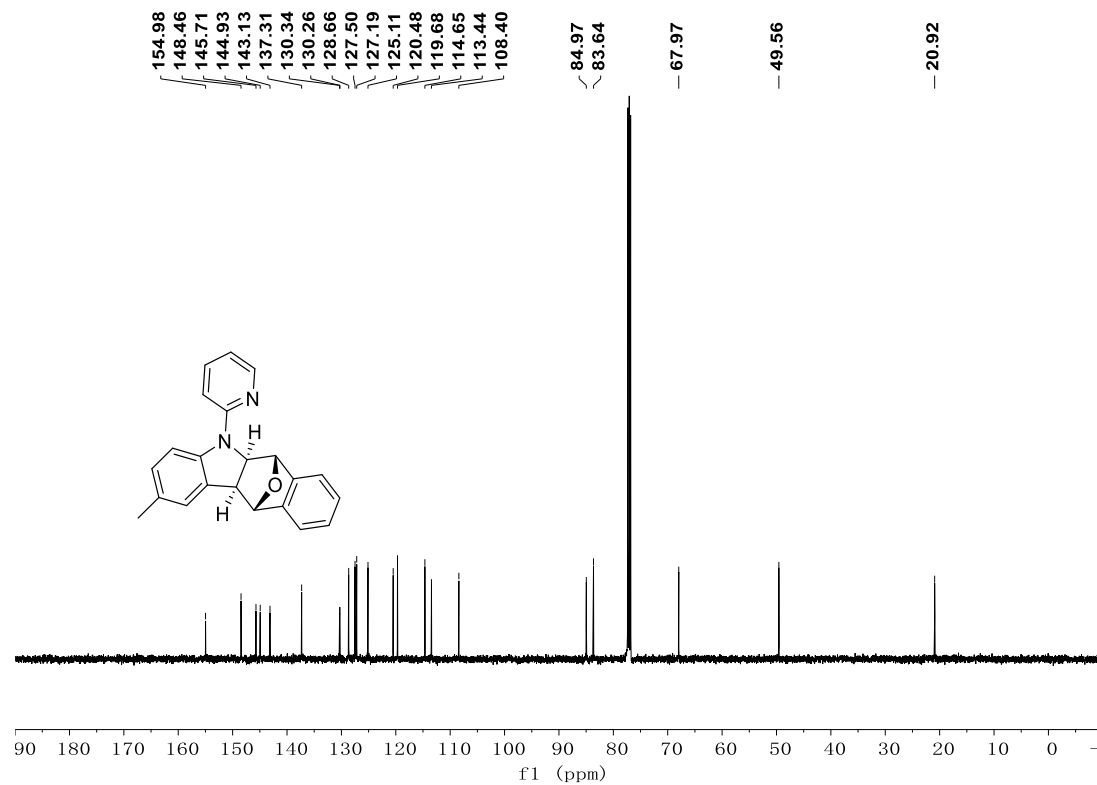




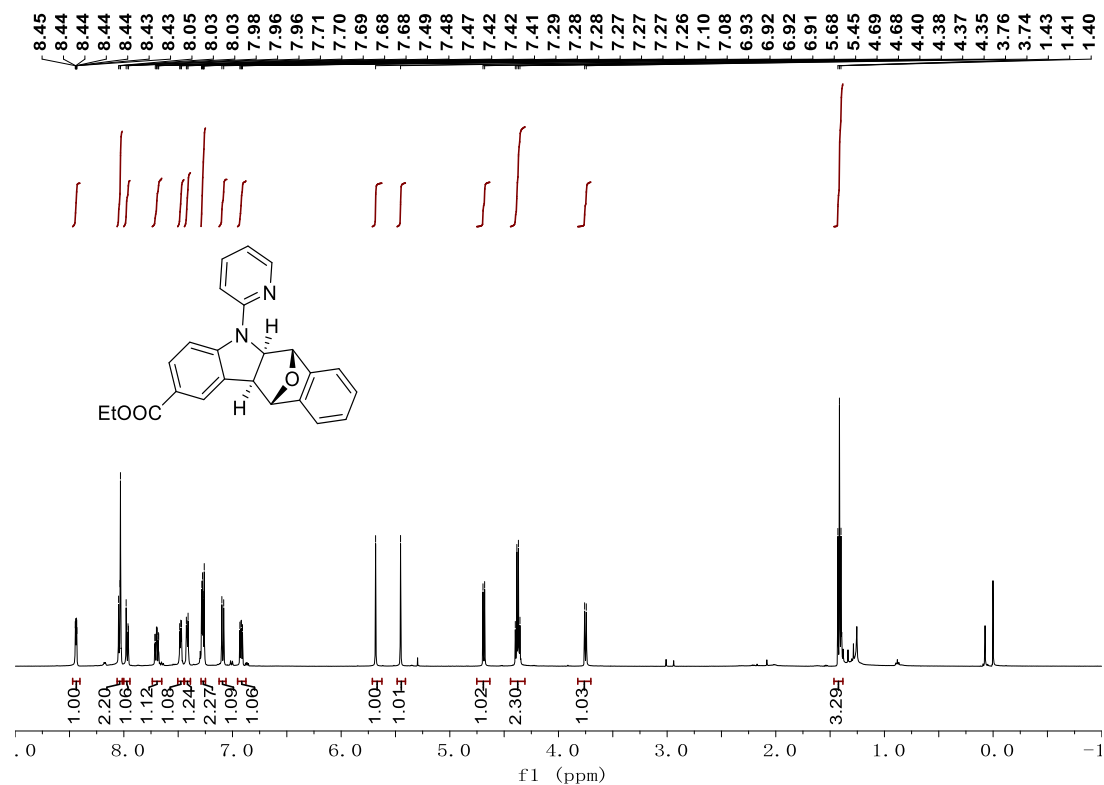
The  $^1\text{H}$  NMR spectrum of **3ba** (500 MHz,  $\text{CDCl}_3$ )



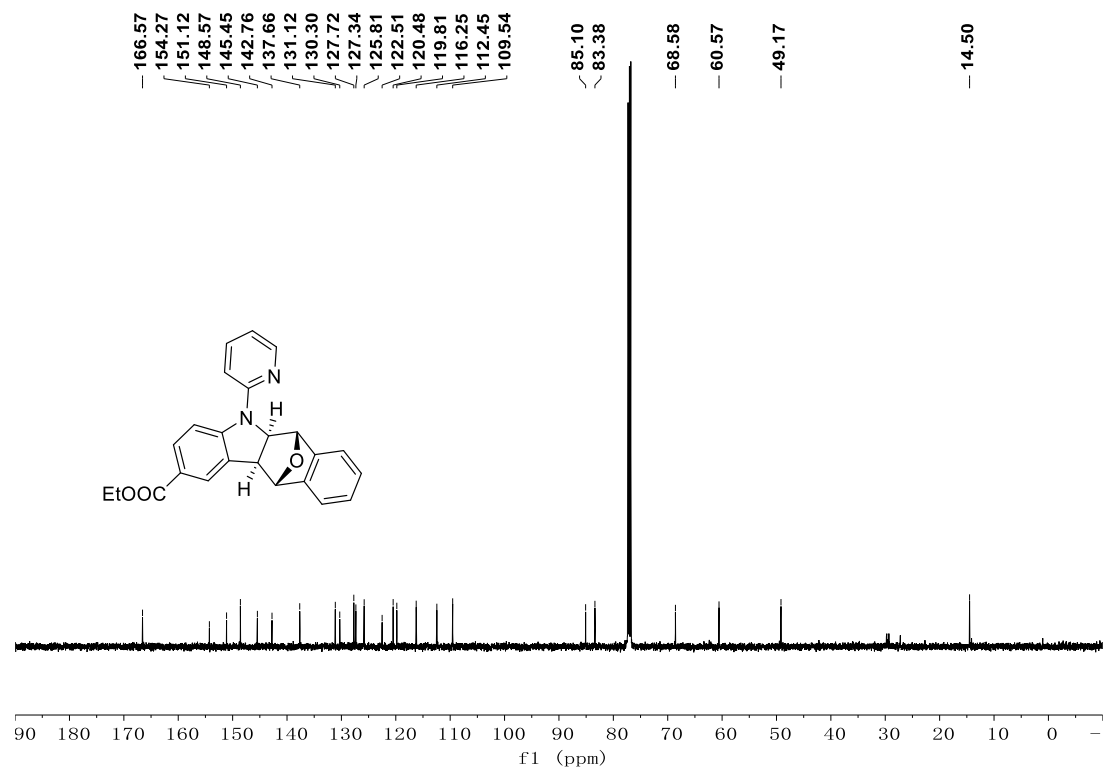
The  $^{13}\text{C}$  NMR spectrum of **3ba** (126 MHz,  $\text{CDCl}_3$ )



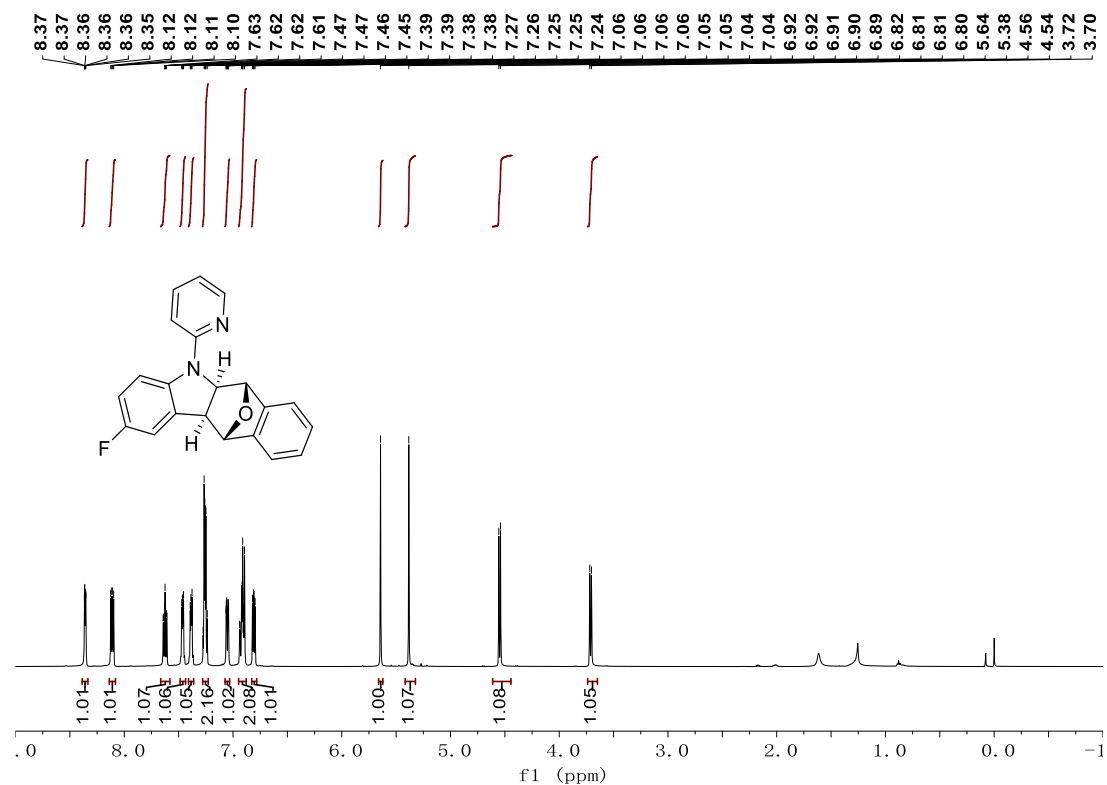
The  $^1\text{H}$  NMR spectrum of **3ca** (500 MHz,  $\text{CDCl}_3$ )



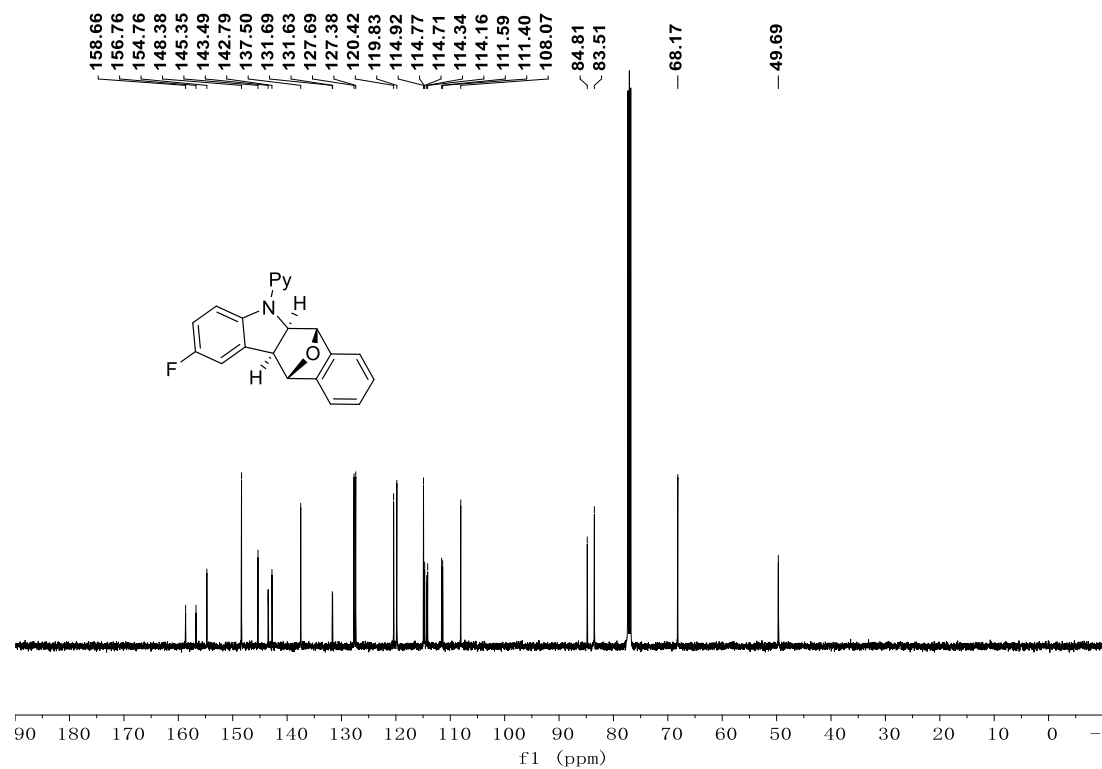
The  $^{13}\text{C}$  NMR spectrum of **3ca** (126 MHz,  $\text{CDCl}_3$ )



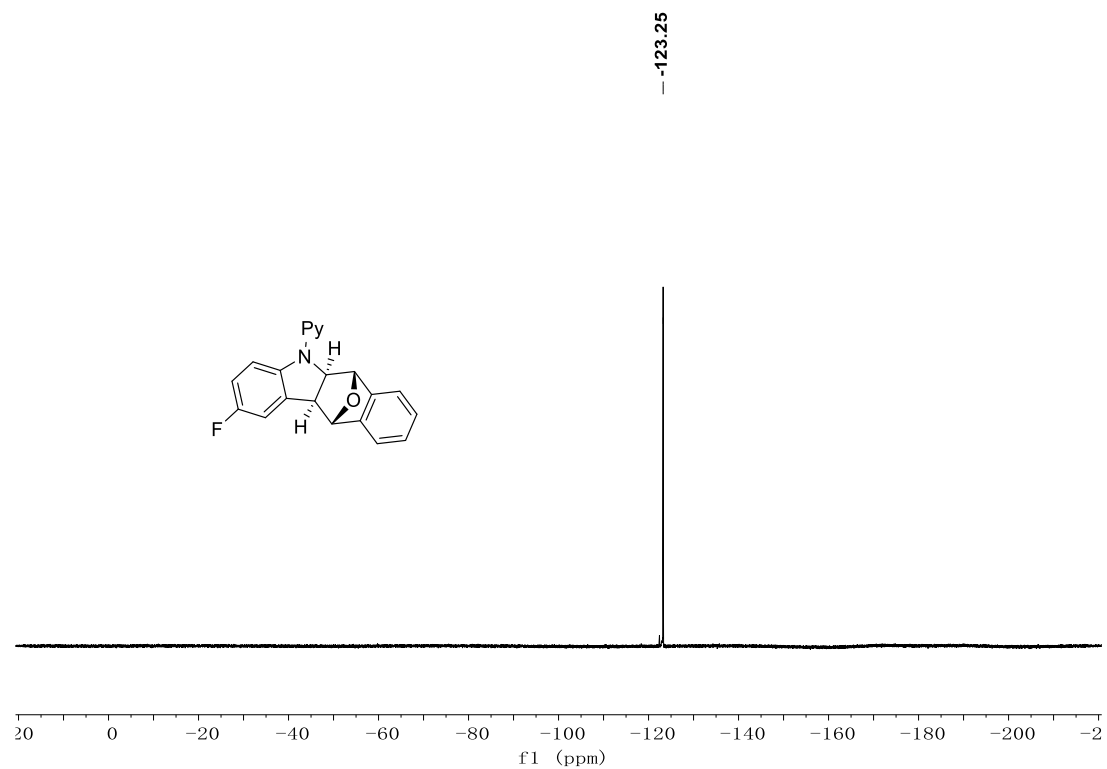
The  $^1\text{H}$  NMR spectrum of **3da** (500 MHz,  $\text{CDCl}_3$ )



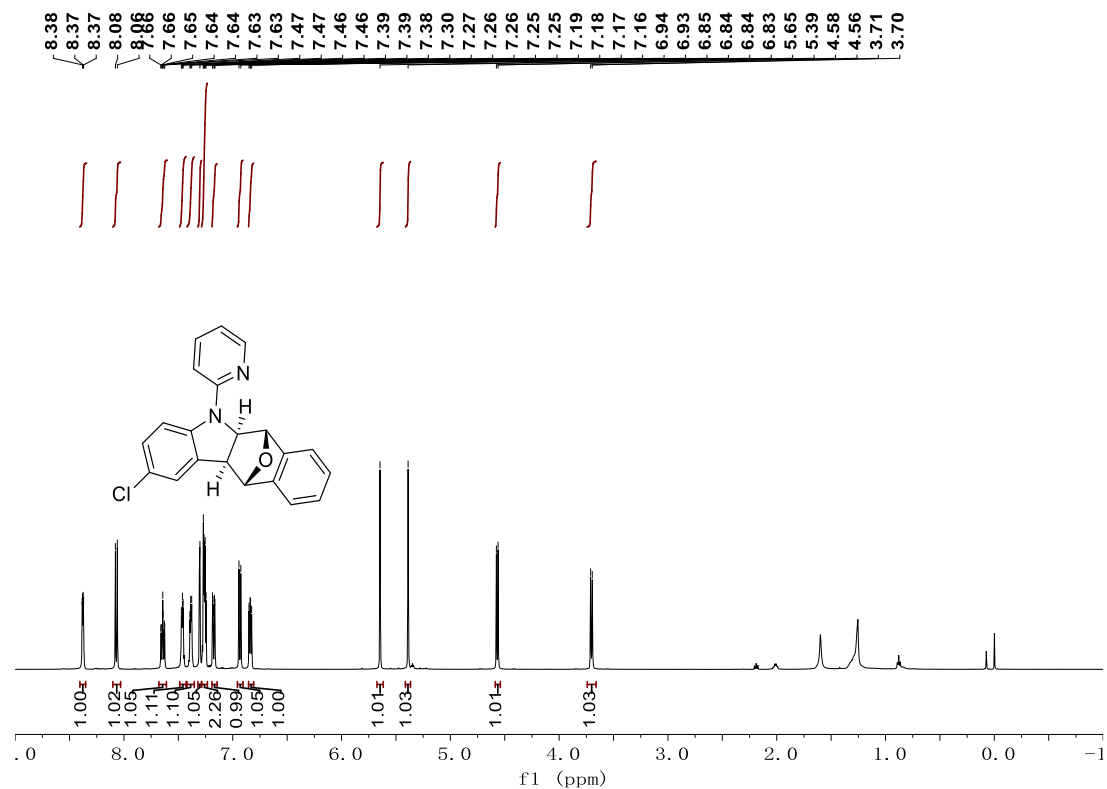
The  $^{13}\text{C}$  NMR spectrum of **3da** (126 MHz,  $\text{CDCl}_3$ )



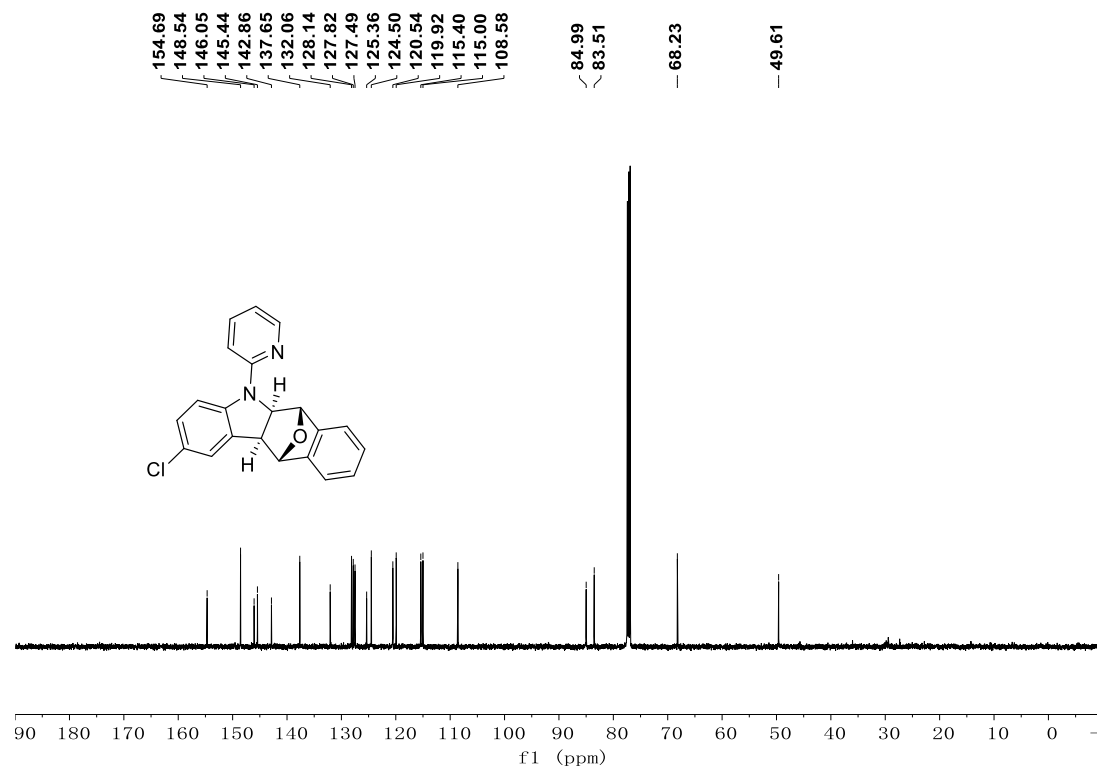
The  $^{19}\text{F}$  NMR spectrum of **3da** (471 MHz,  $\text{CDCl}_3$ )



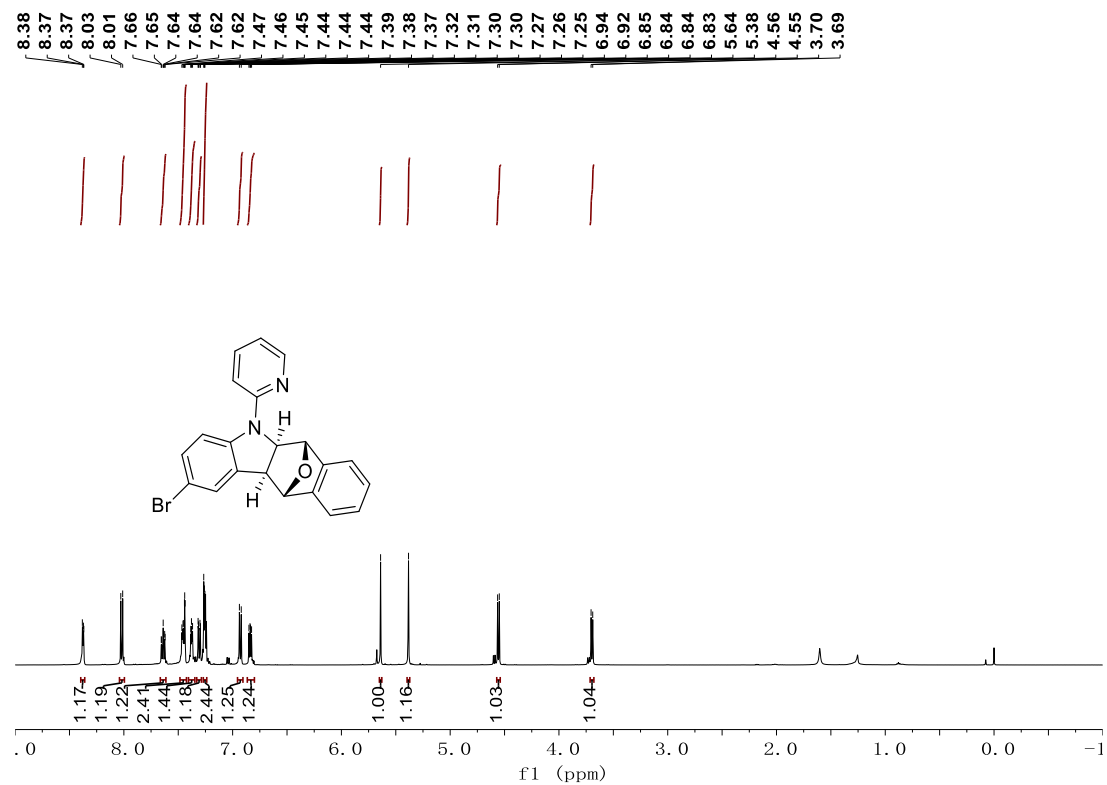
The  $^1\text{H}$  NMR spectrum of **3ea** (500 MHz,  $\text{CDCl}_3$ )



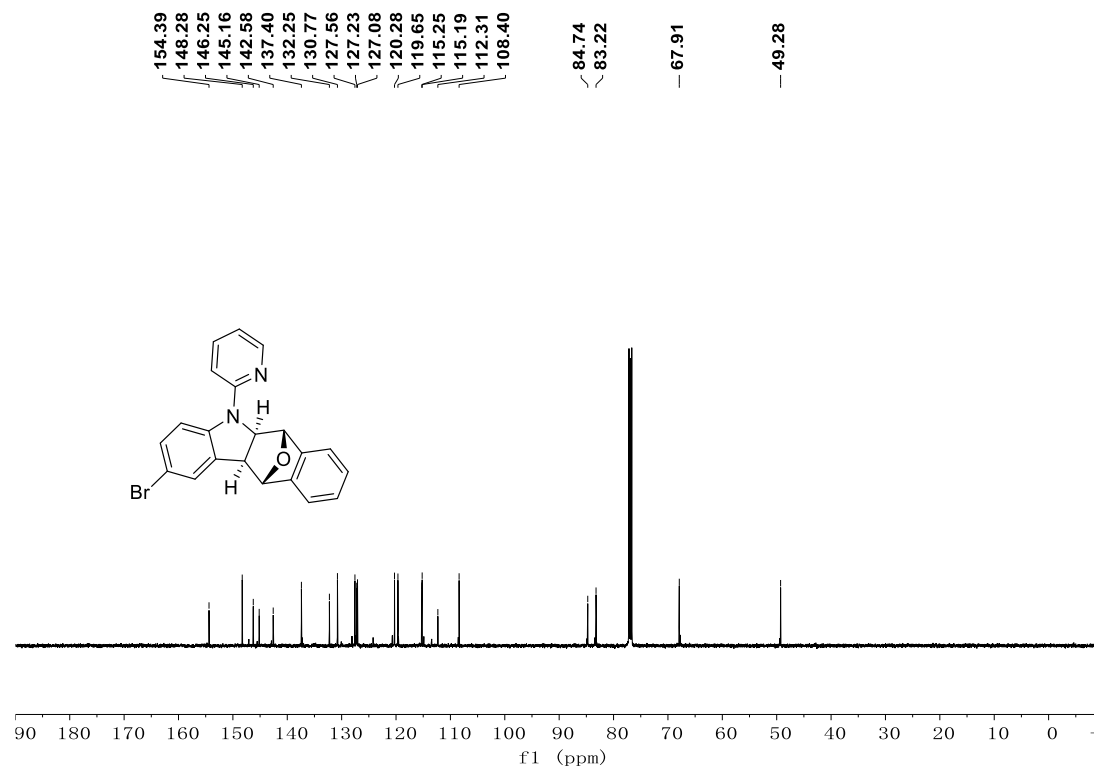
The  $^{13}\text{C}$  NMR spectrum of **3ea** (126 MHz,  $\text{CDCl}_3$ )



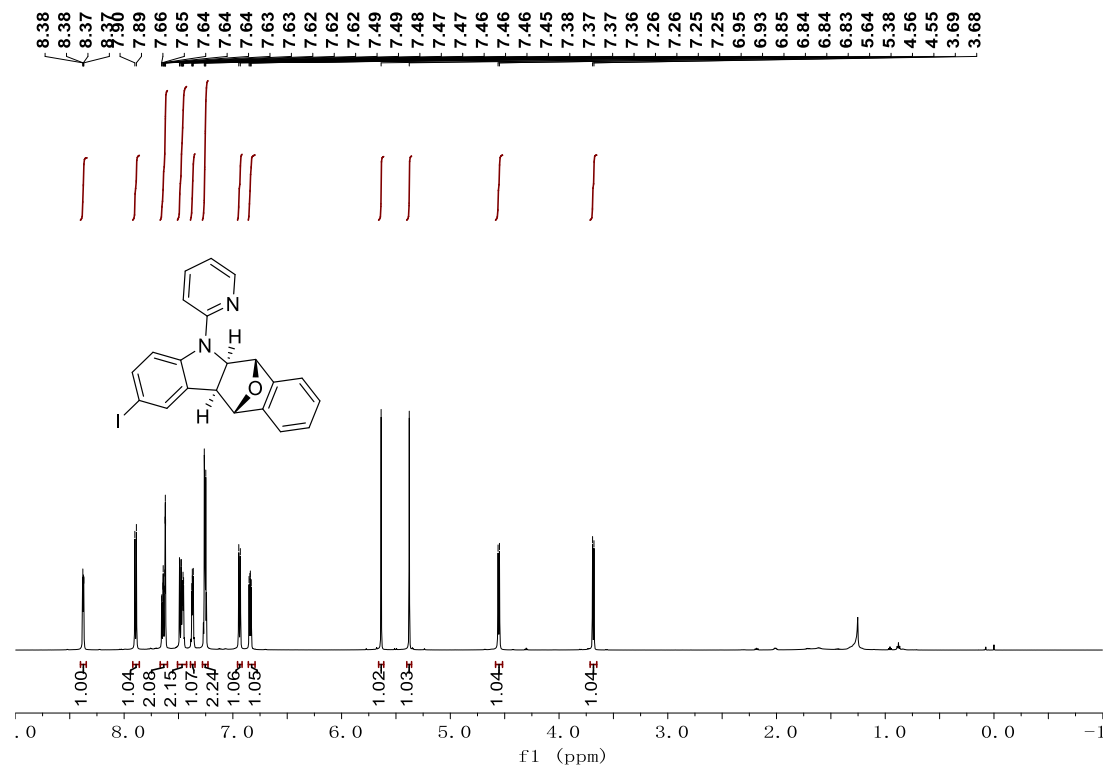
The  $^1\text{H}$  NMR spectrum of **3fa** (500 MHz,  $\text{CDCl}_3$ )



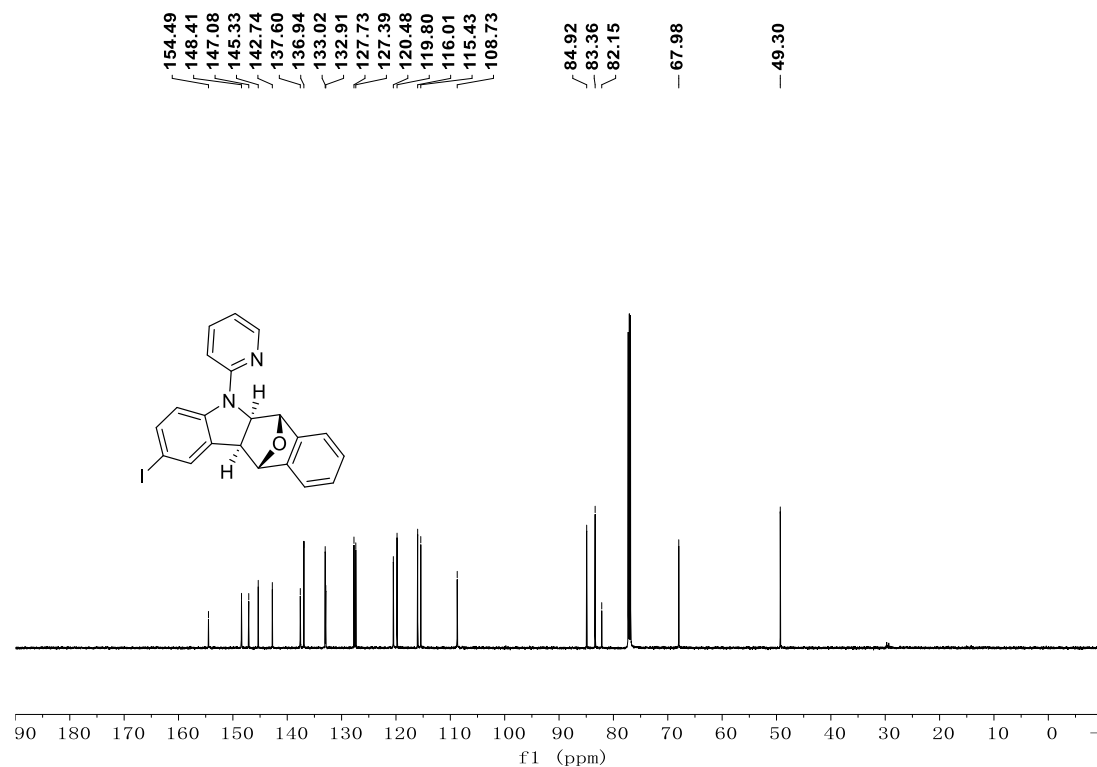
The  $^{13}\text{C}$  NMR spectrum of **3fa** (126 MHz,  $\text{CDCl}_3$ )



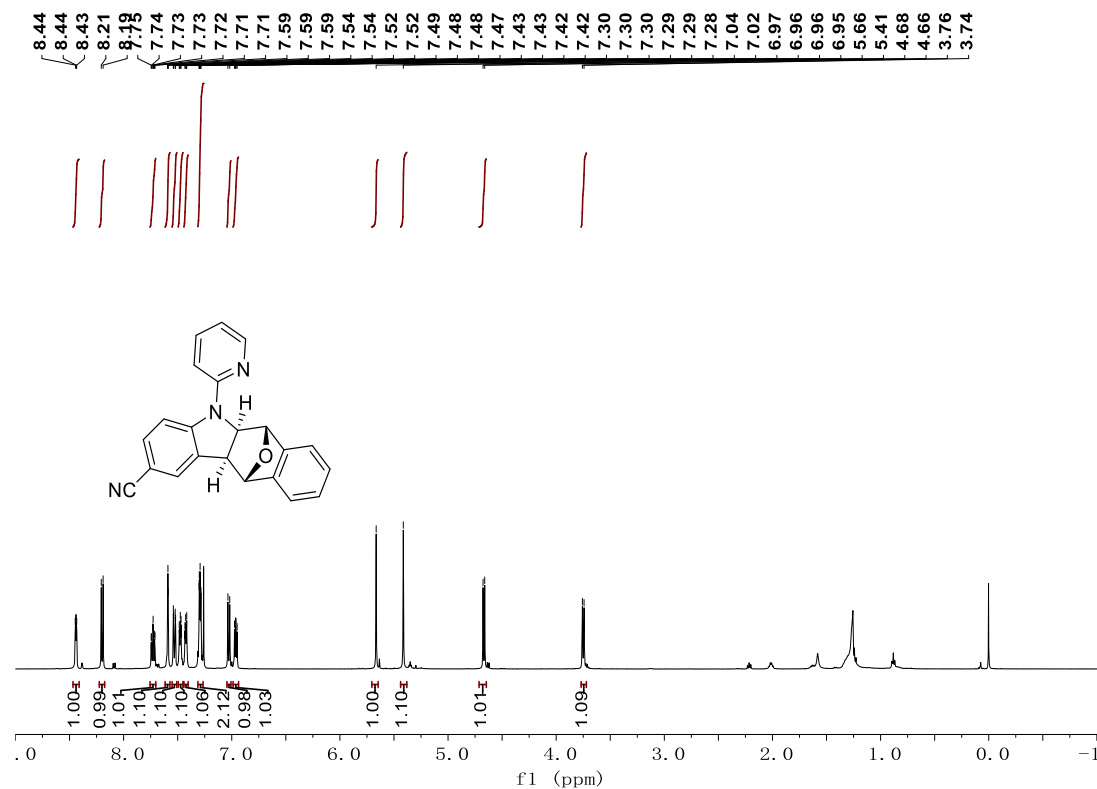
The  $^1\text{H}$  NMR spectrum of **3ga** (600 MHz,  $\text{CDCl}_3$ )



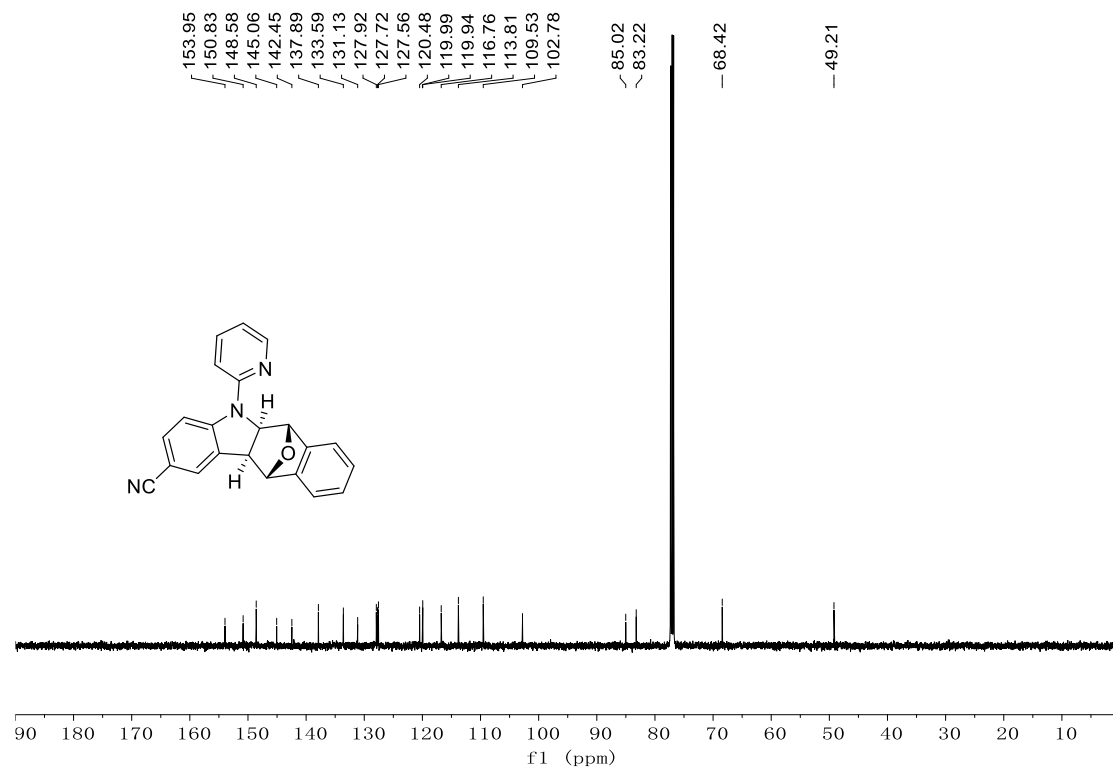
The  $^{13}\text{C}$  NMR spectrum of **3ga** (126 MHz,  $\text{CDCl}_3$ )



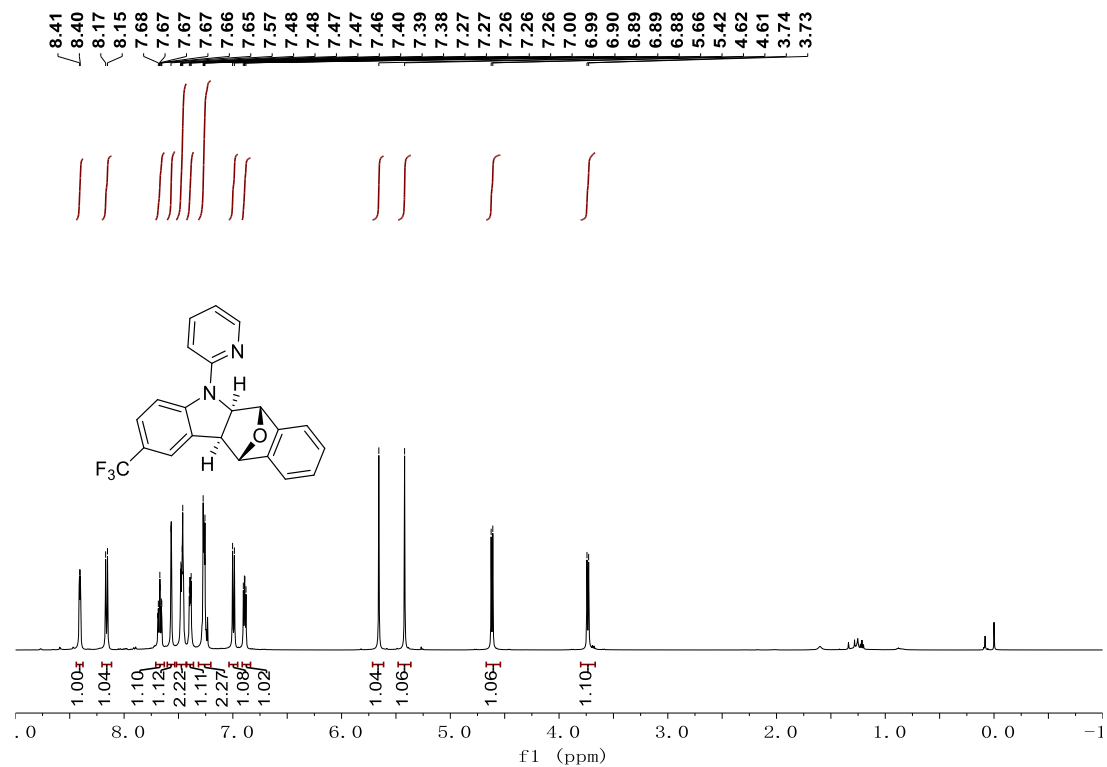
The  $^1\text{H}$  NMR spectrum of **3ha** (500 MHz,  $\text{CDCl}_3$ )



The  $^{13}\text{C}$  NMR spectrum of **3ha** (126 MHz,  $\text{CDCl}_3$ )

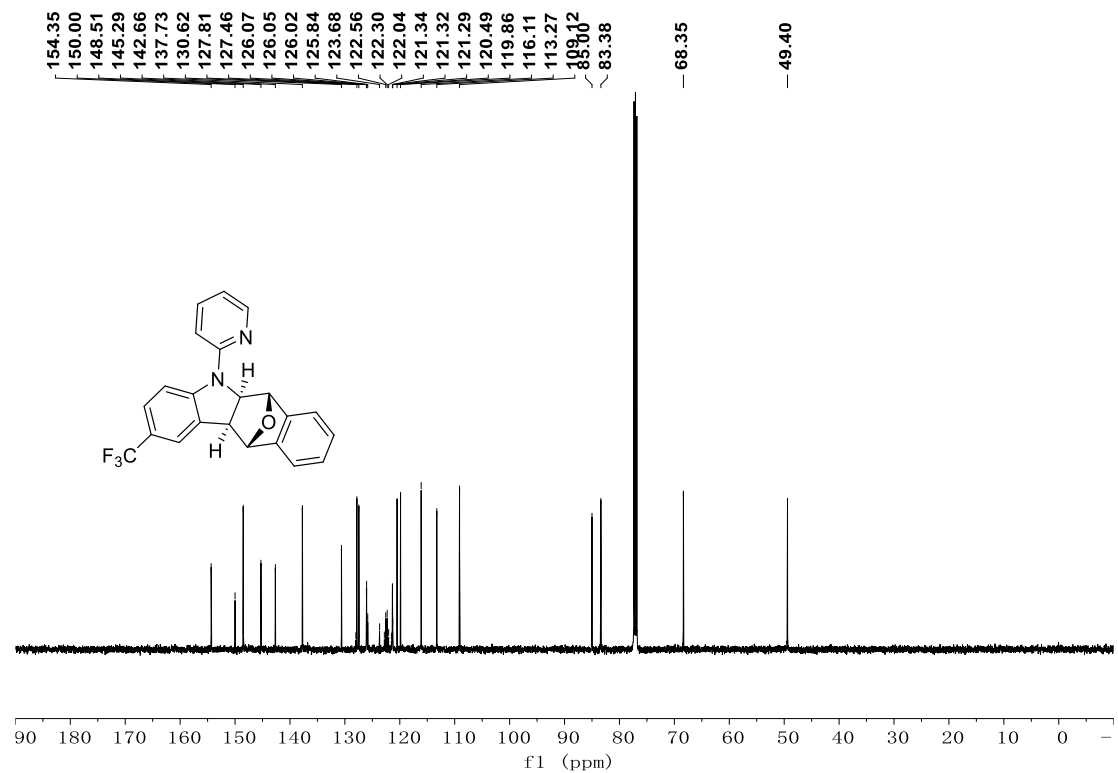


The  $^1\text{H}$  NMR spectrum of **3ia** (500 MHz,  $\text{CDCl}_3$ )

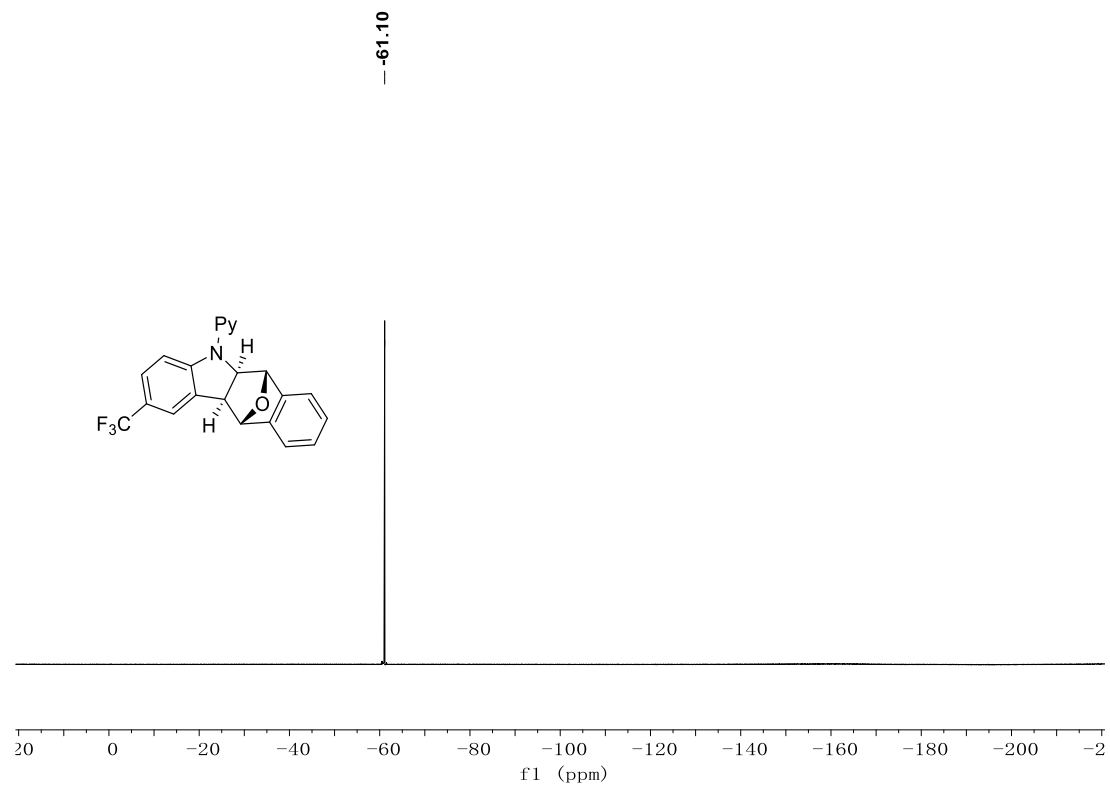




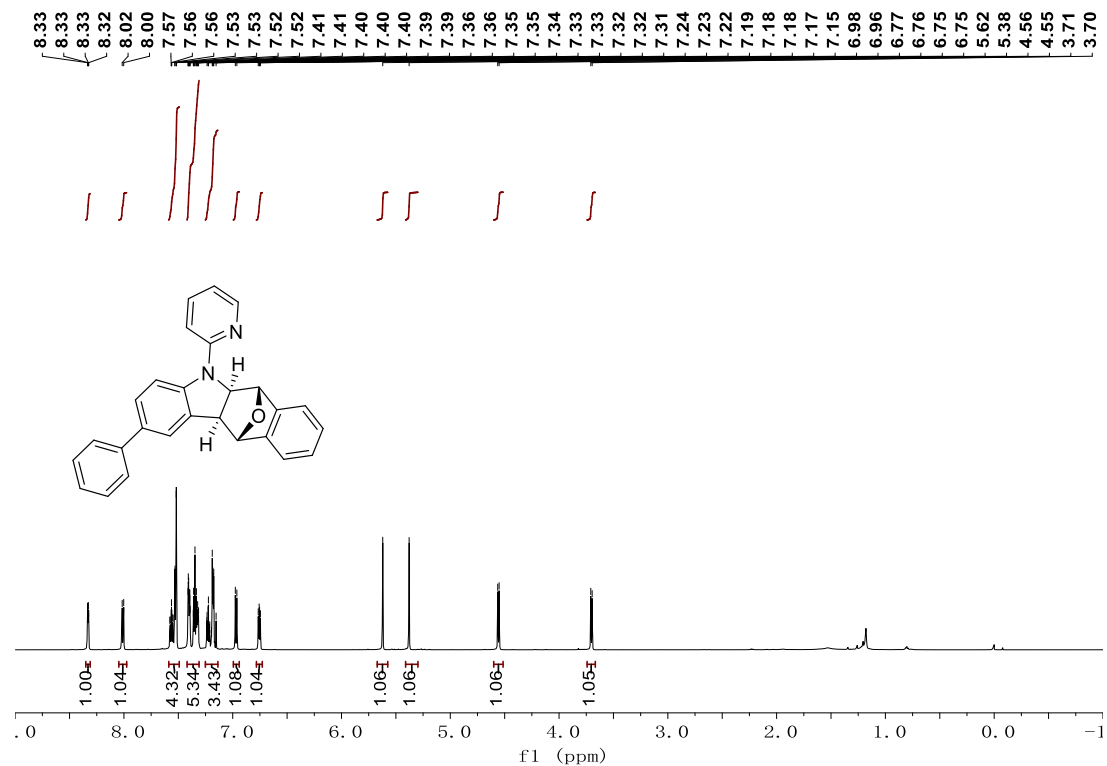
The  $^{13}\text{C}$  NMR spectrum of **3ia** (126 MHz,  $\text{CDCl}_3$ )



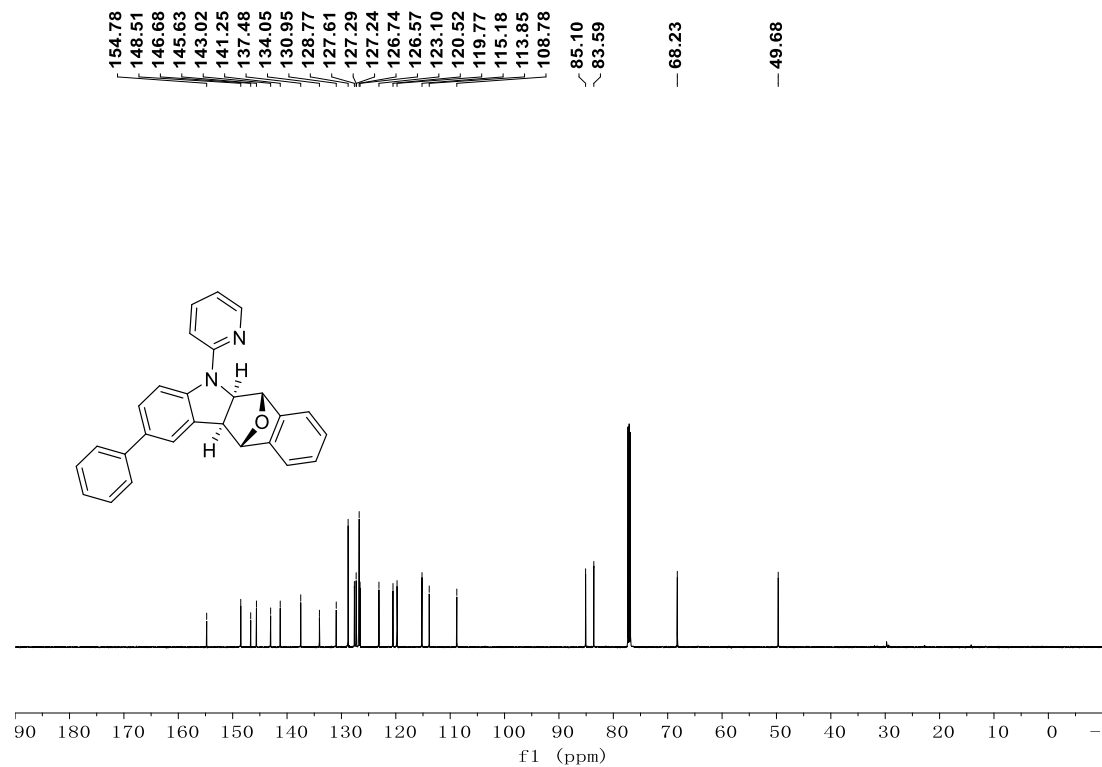
The  $^{19}\text{F}$  NMR spectrum of **3ia** (471 MHz,  $\text{CDCl}_3$ )



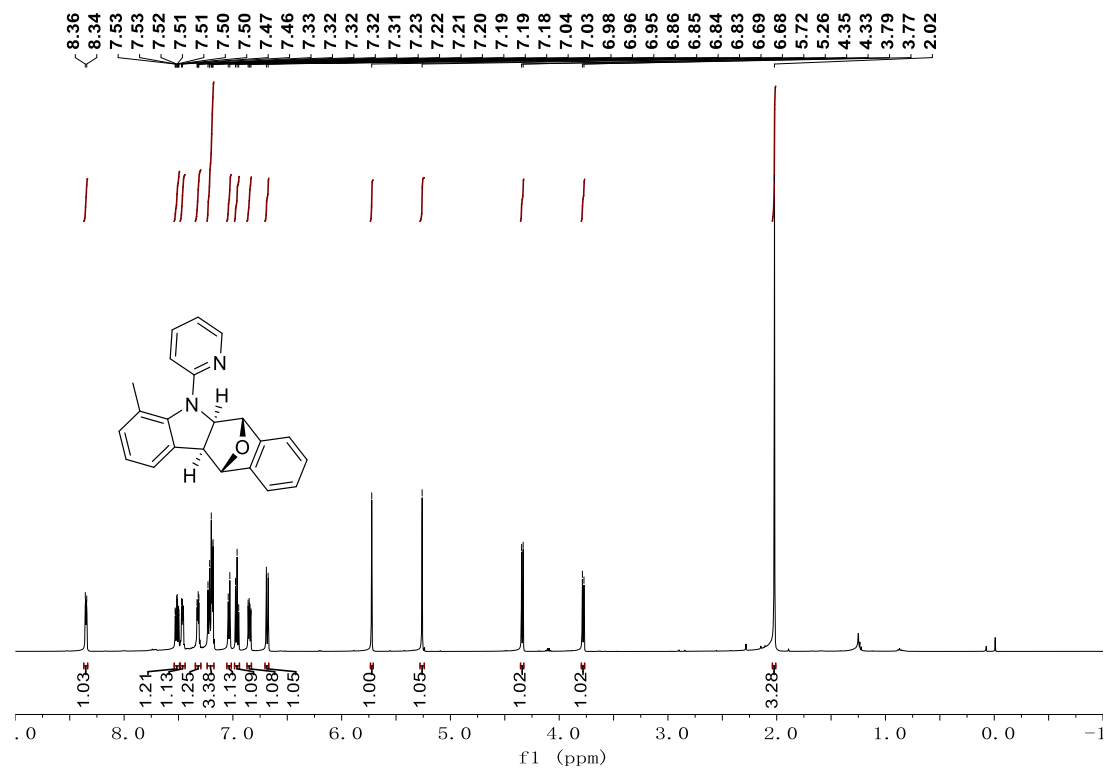
The  $^1\text{H}$  NMR spectrum of **3ja** (500 MHz,  $\text{CDCl}_3$ )



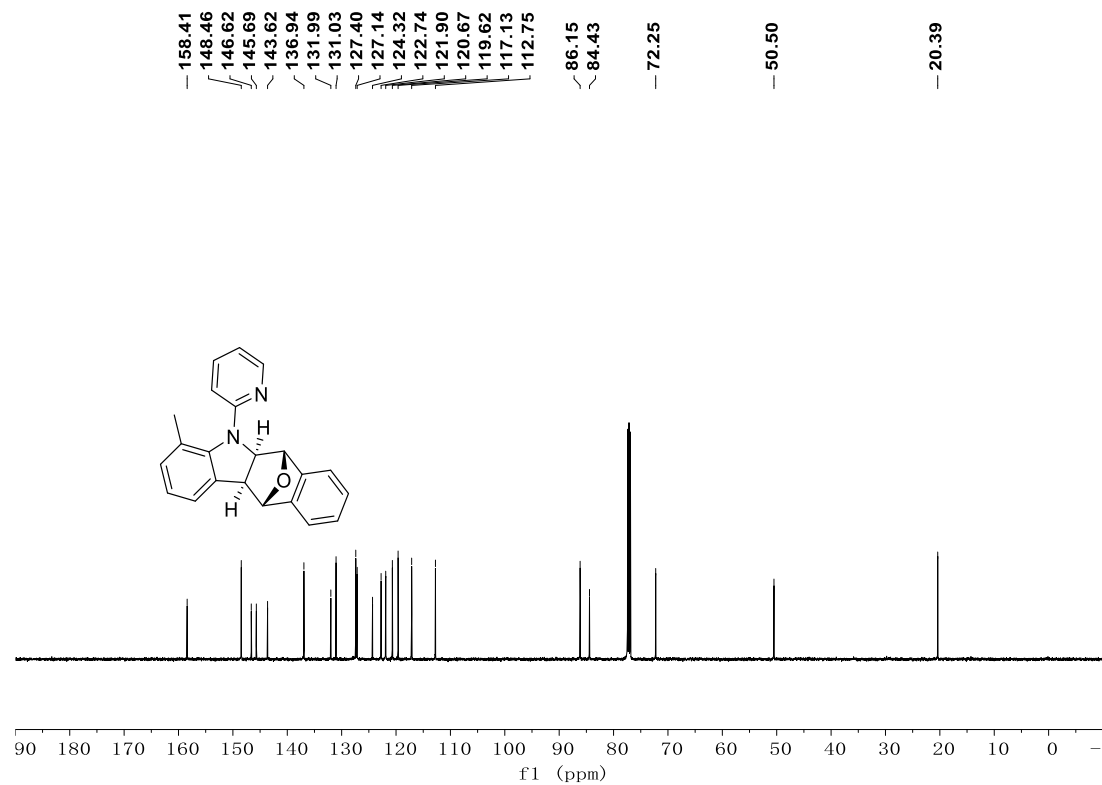
The  $^{13}\text{C}$  NMR spectrum of **3ja** (126 MHz,  $\text{CDCl}_3$ )



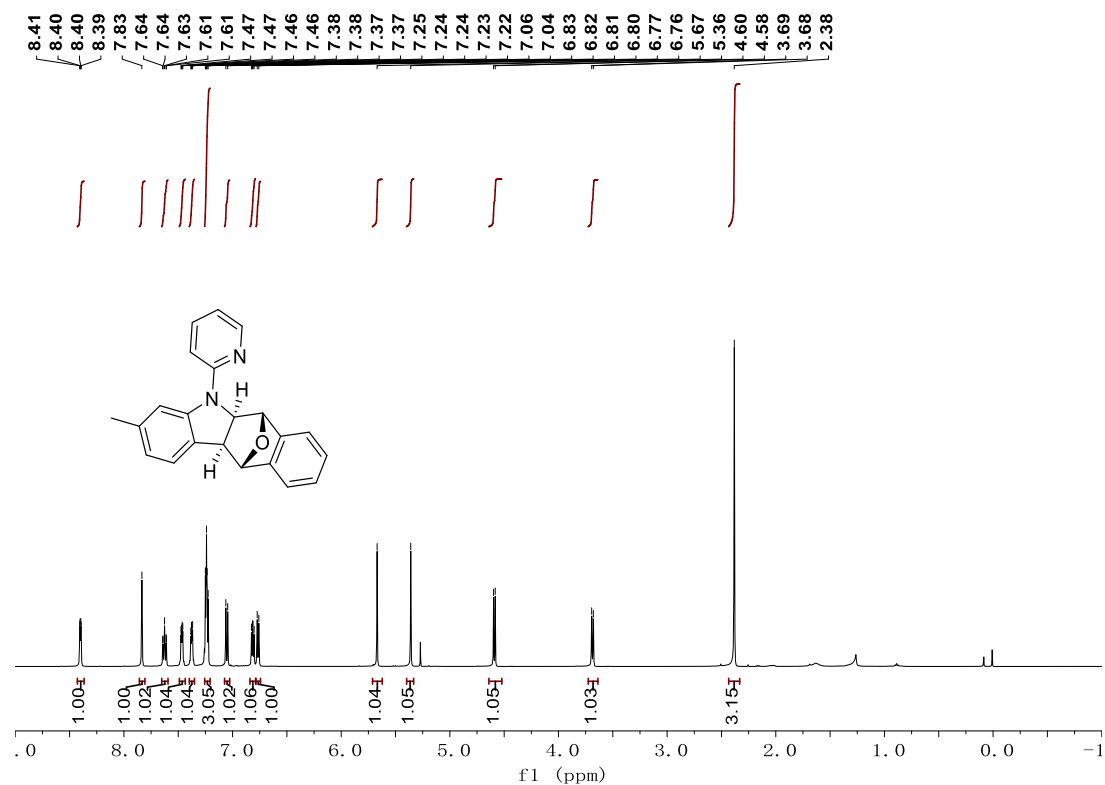
The  $^1\text{H}$  NMR spectrum of **3ka** (500 MHz,  $\text{CDCl}_3$ )



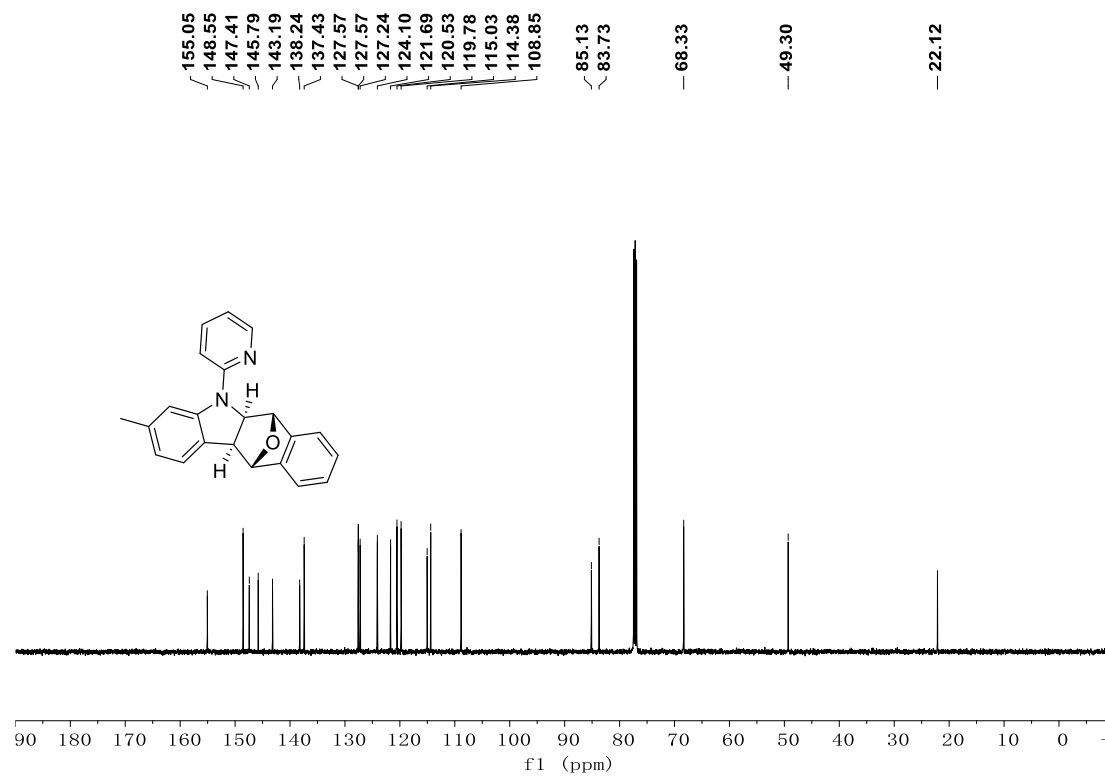
The  $^{13}\text{C}$  NMR spectrum of **3ka** (126 MHz,  $\text{CDCl}_3$ )



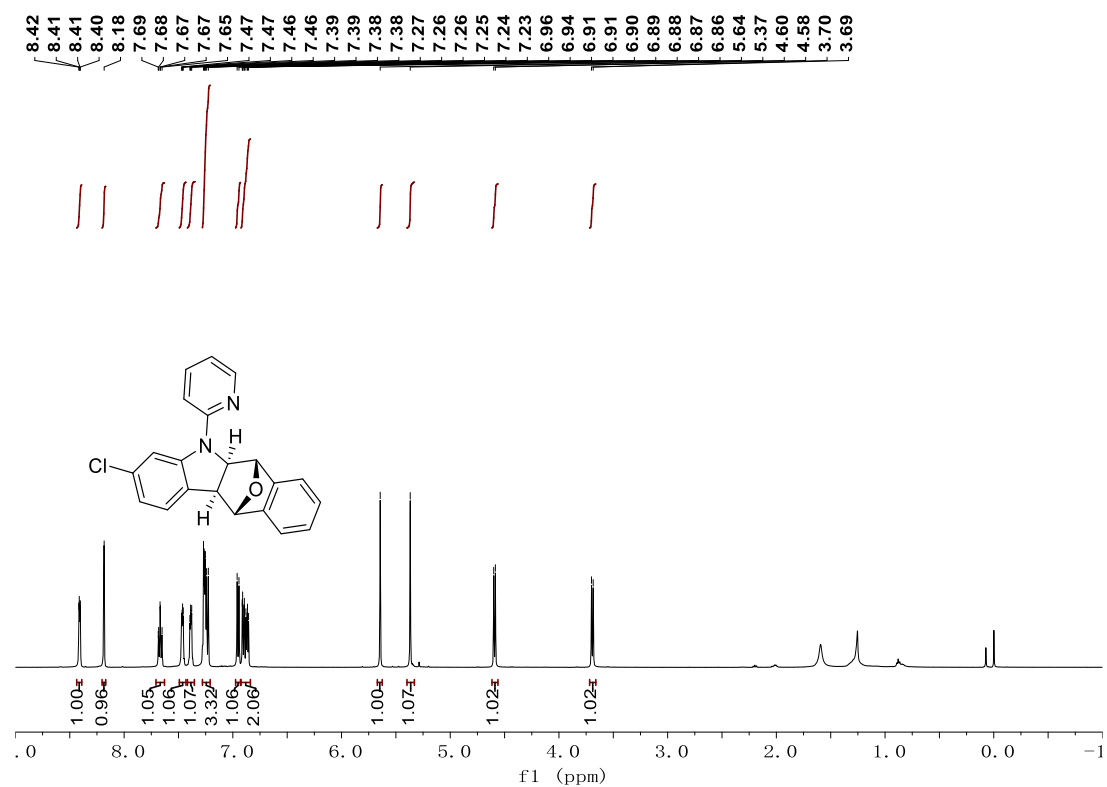
The  $^1\text{H}$  NMR spectrum of **3la** (500 MHz,  $\text{CDCl}_3$ )



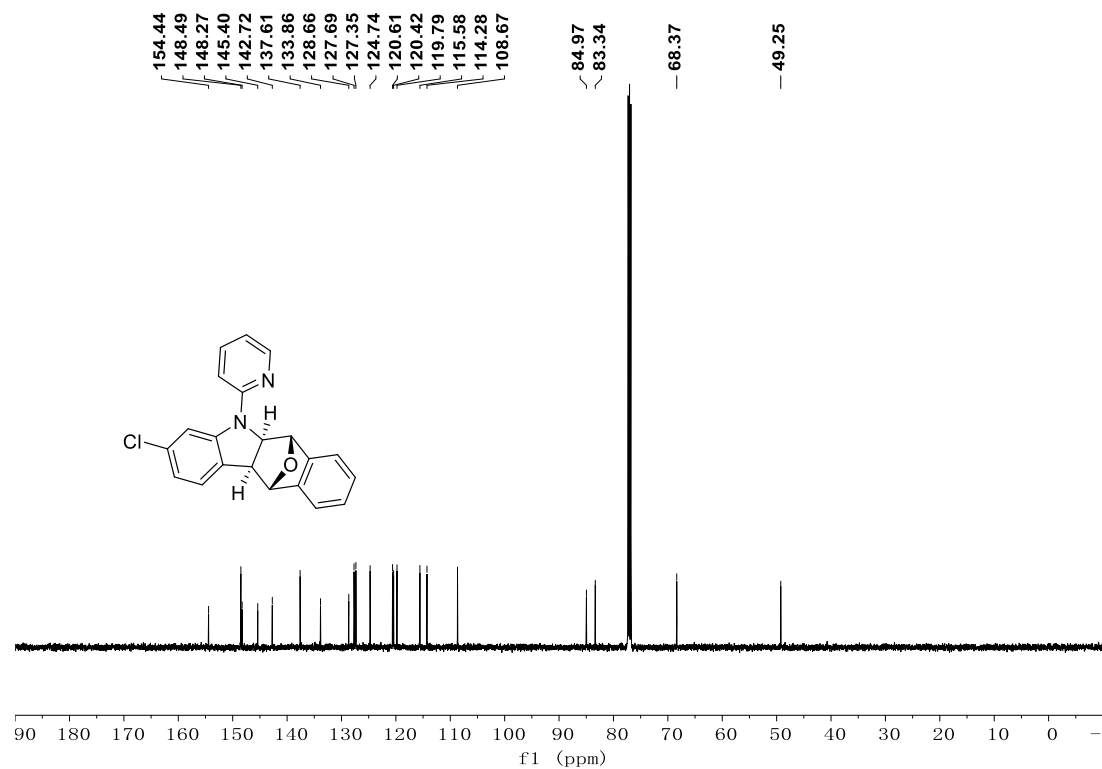
The  $^{13}\text{C}$  NMR spectrum of **3la** (126 MHz,  $\text{CDCl}_3$ )



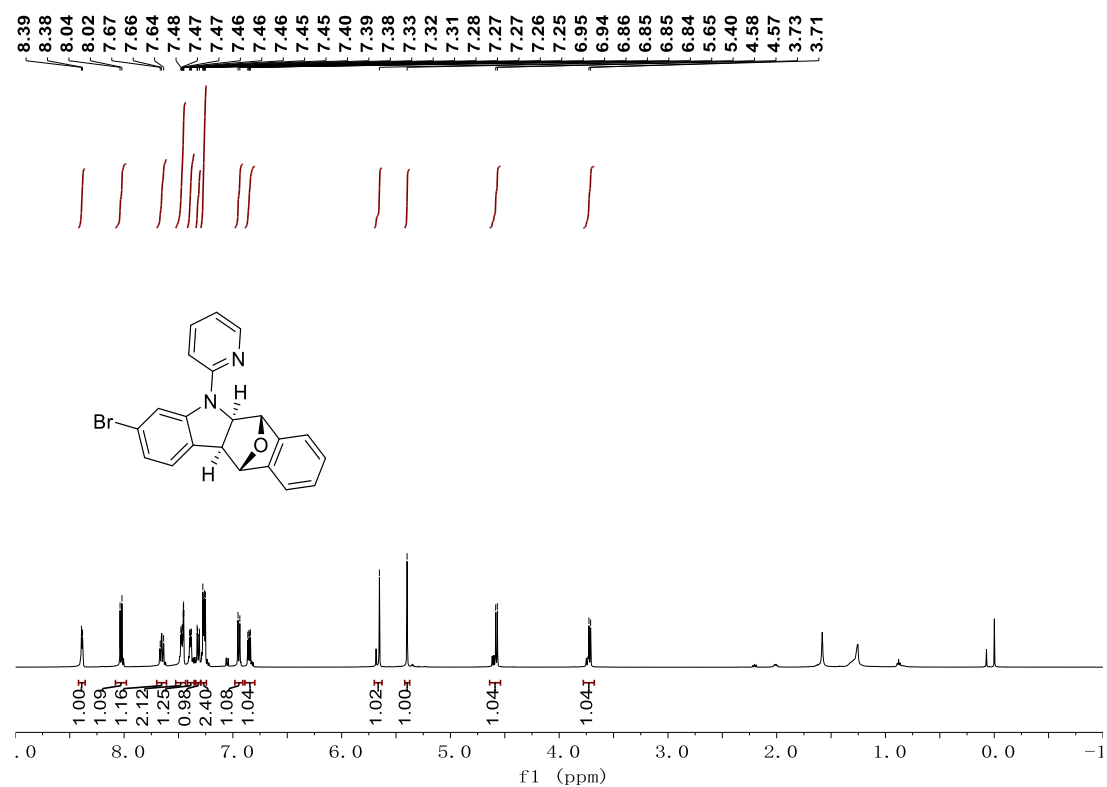
The  $^1\text{H}$  NMR spectrum of **3ma** (500 MHz,  $\text{CDCl}_3$ )



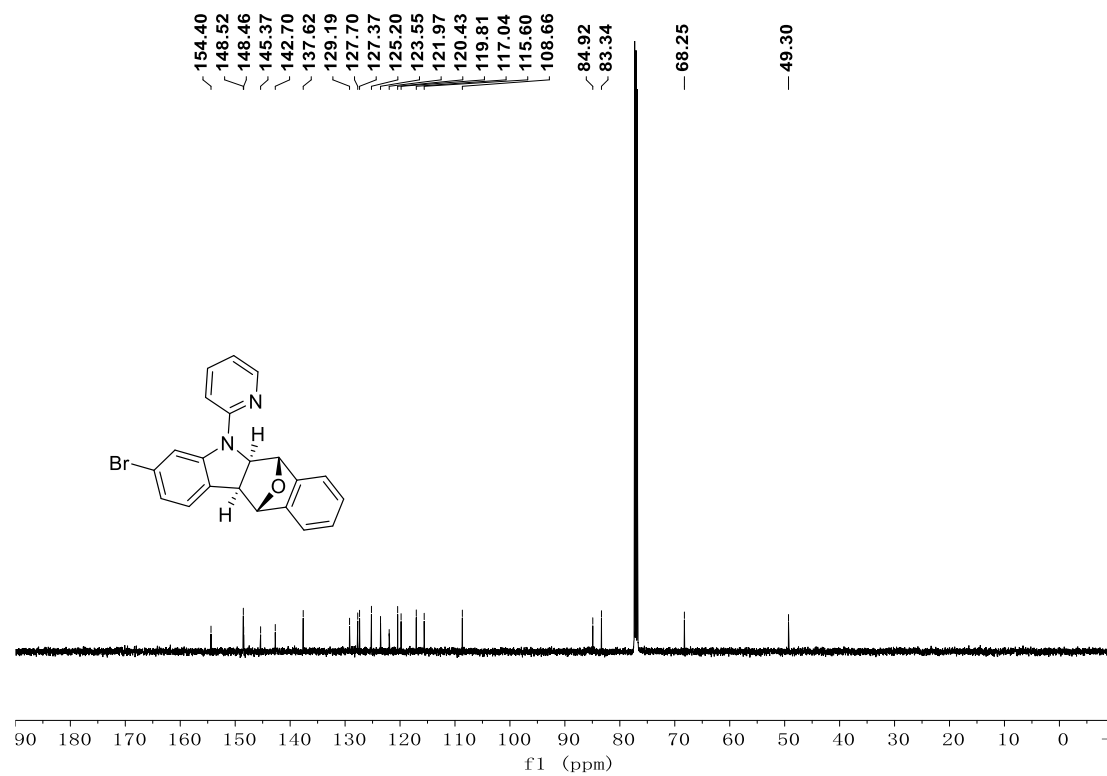
The  $^{13}\text{C}$  NMR spectrum of **3ma** (126 MHz,  $\text{CDCl}_3$ )



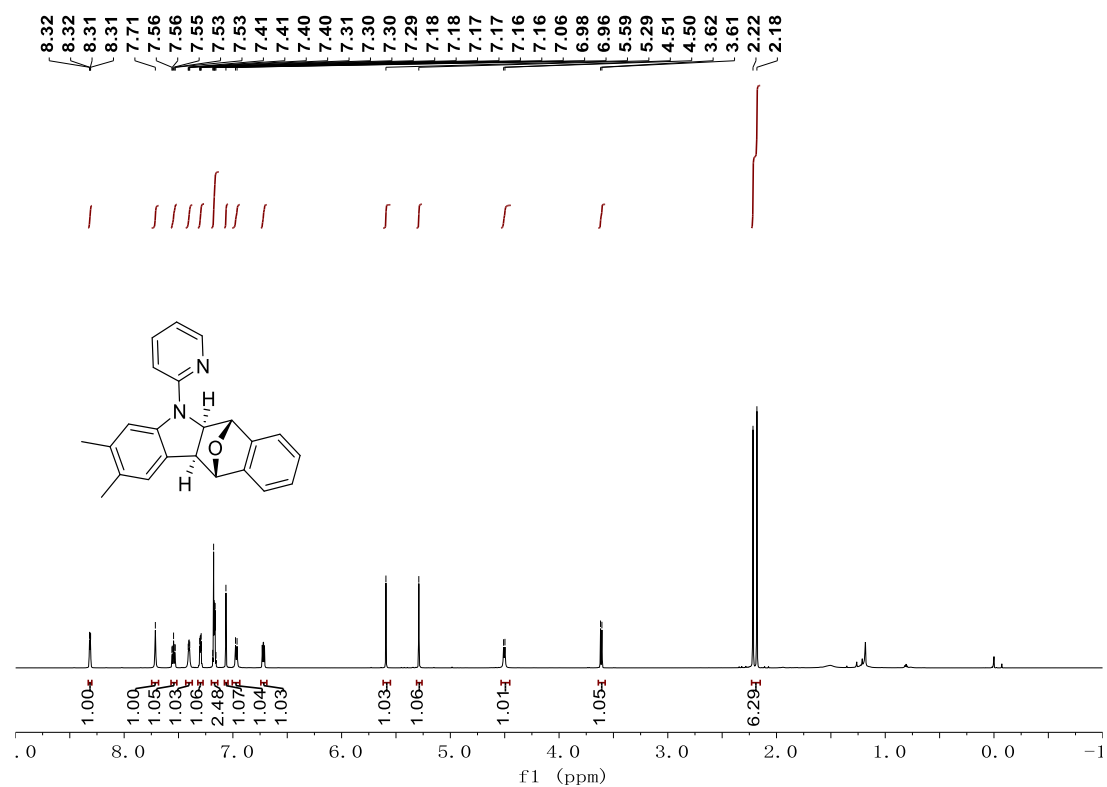
The  $^1\text{H}$  NMR spectrum of **3na** (500 MHz,  $\text{CDCl}_3$ )



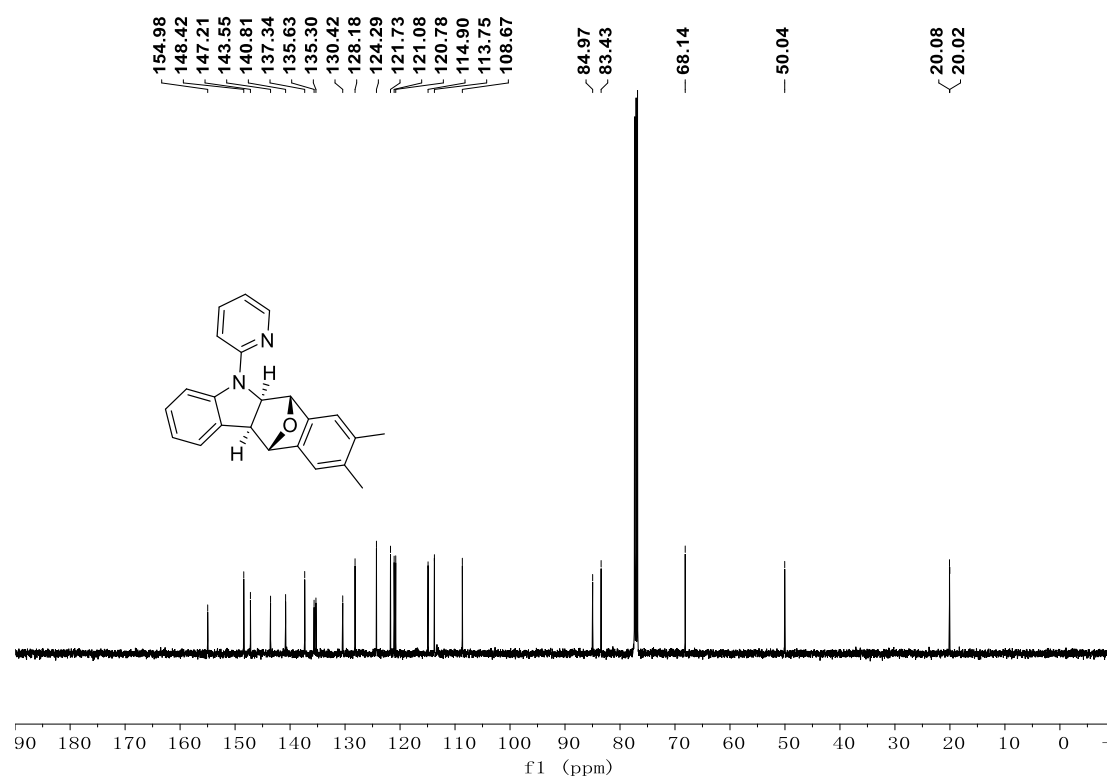
The  $^{13}\text{C}$  NMR spectrum of **3na** (126 MHz,  $\text{CDCl}_3$ )



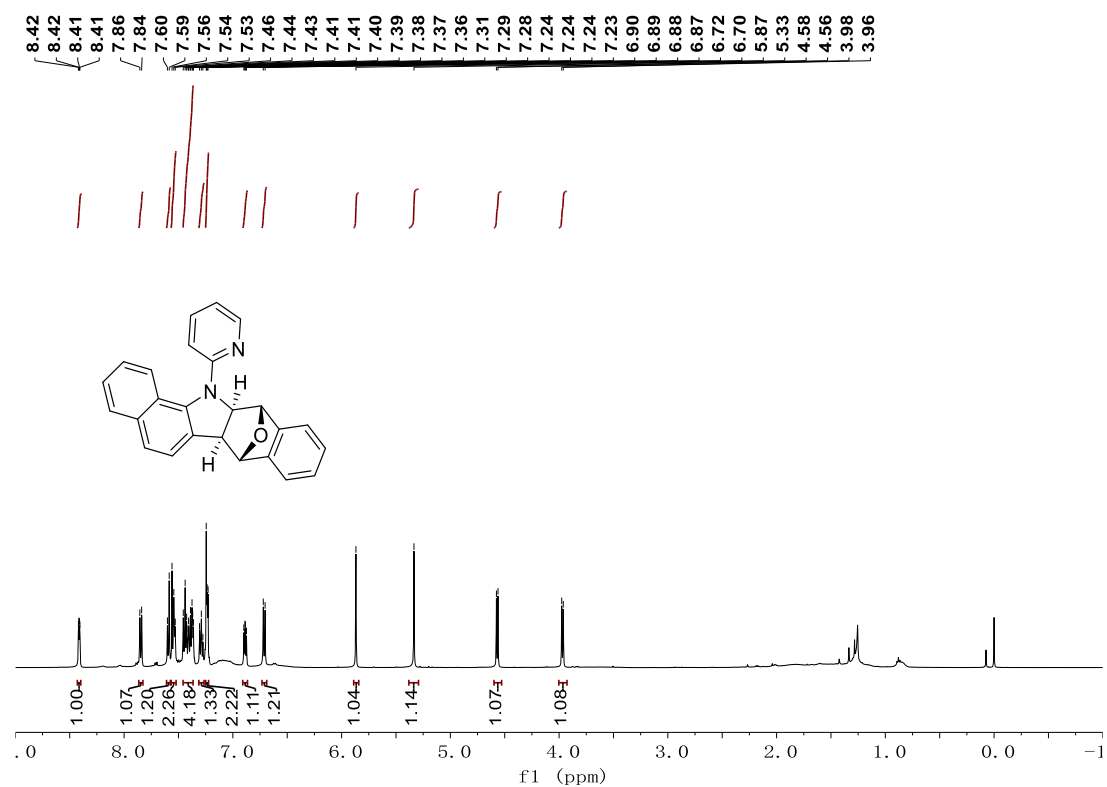
The  $^1\text{H}$  NMR spectrum of **3oa** (600 MHz,  $\text{CDCl}_3$ )



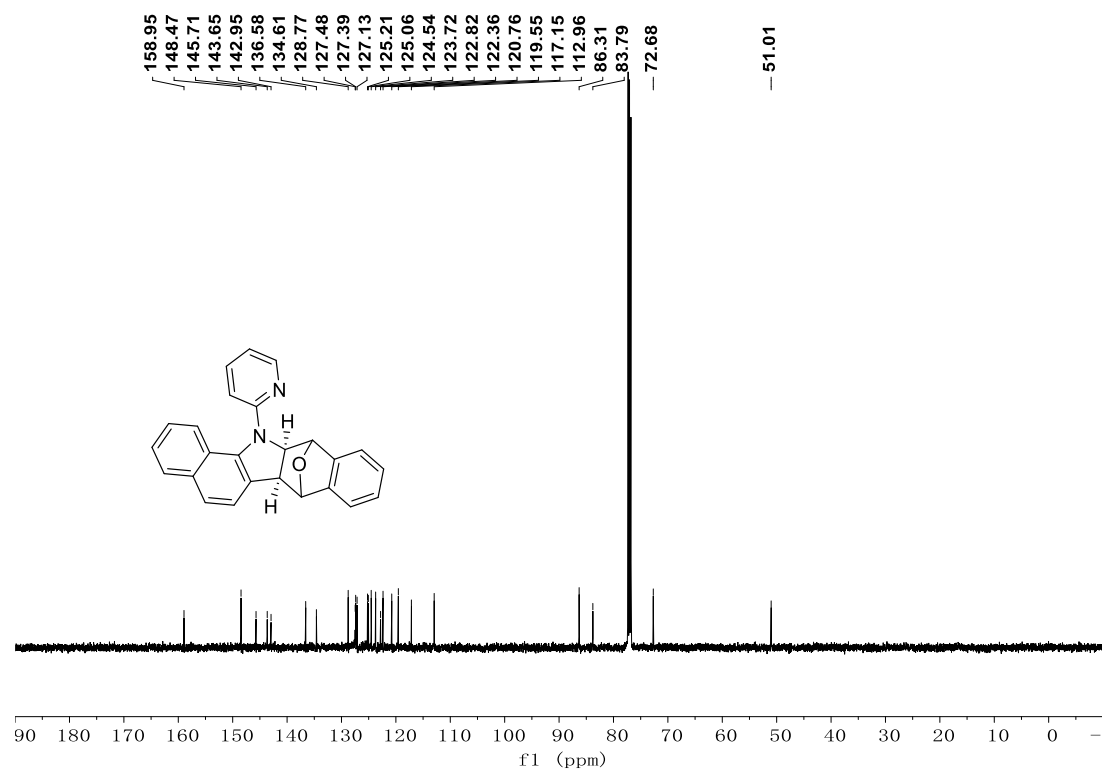
The  $^{13}\text{C}$  NMR spectrum of **3oa** (126 MHz,  $\text{CDCl}_3$ )



The  $^1\text{H}$  NMR spectrum of **3pa** (500 MHz,  $\text{CDCl}_3$ )

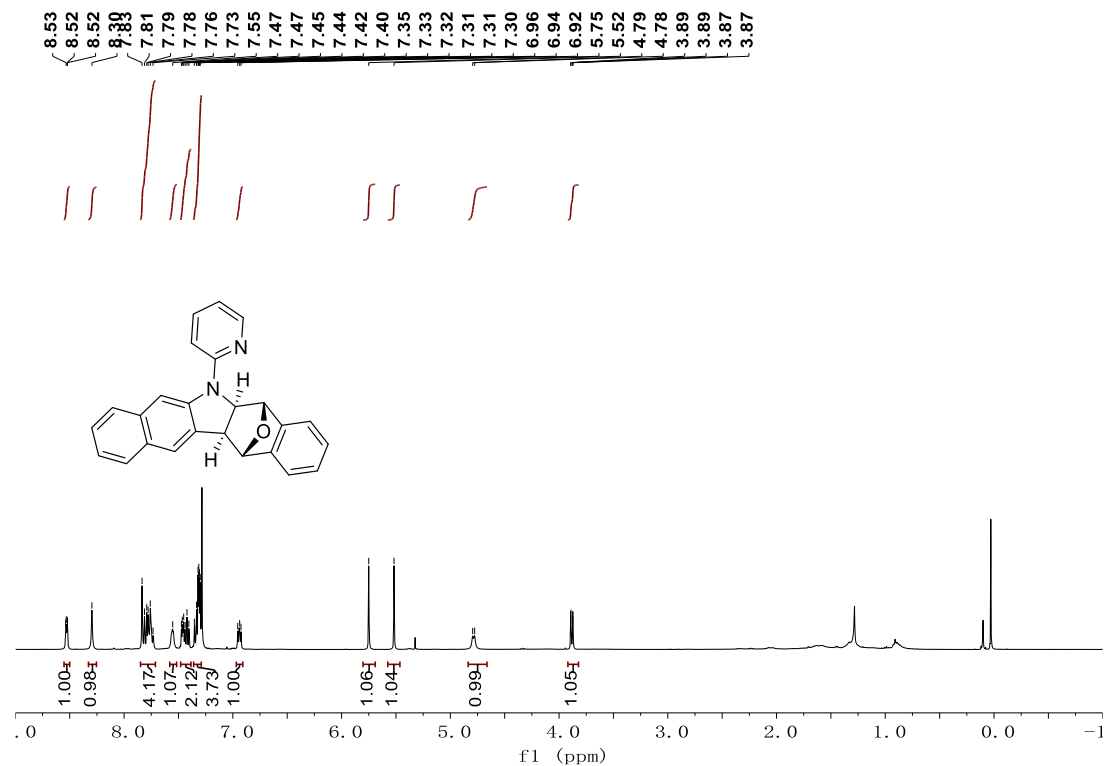


The  $^{13}\text{C}$  NMR spectrum of **3pa** (126 MHz,  $\text{CDCl}_3$ )

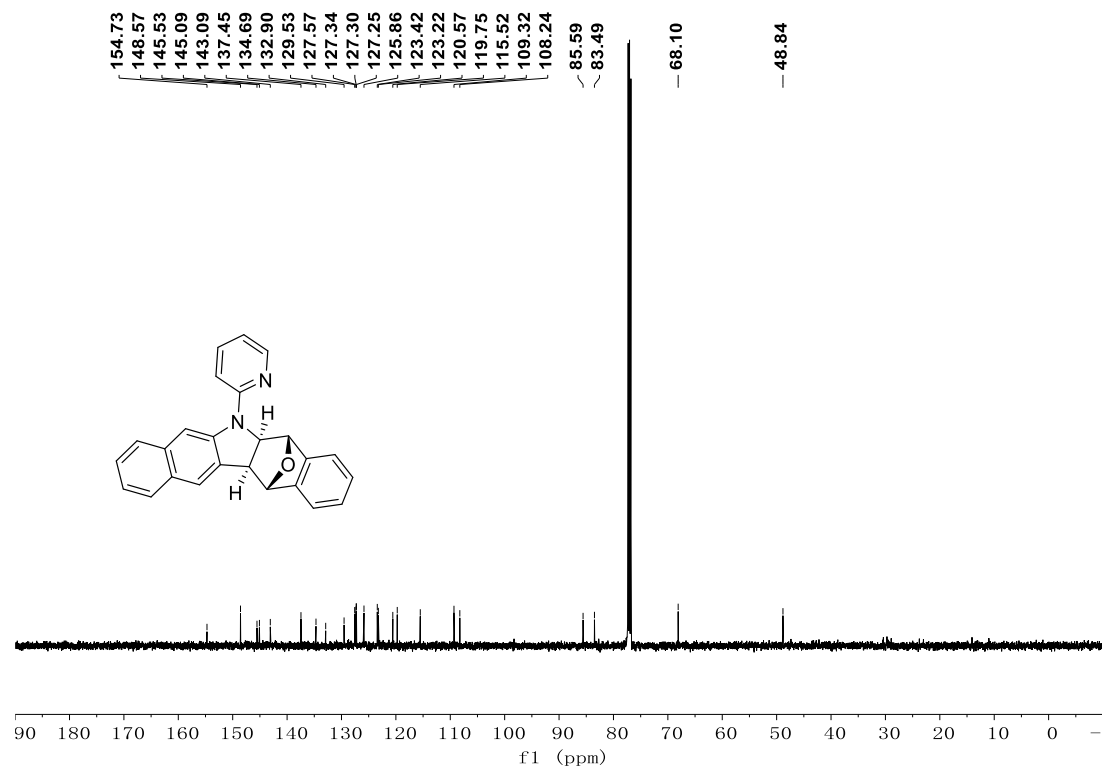




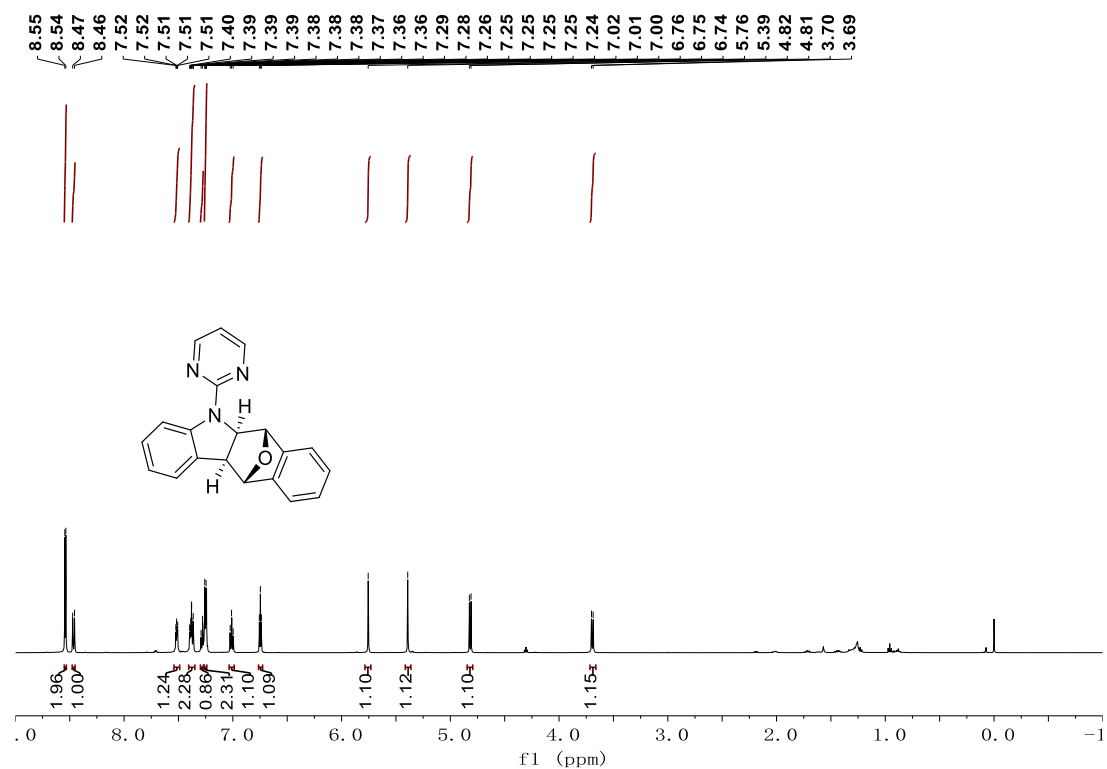
The  $^1\text{H}$  NMR spectrum of **3qa** (400 MHz,  $\text{CDCl}_3$ )



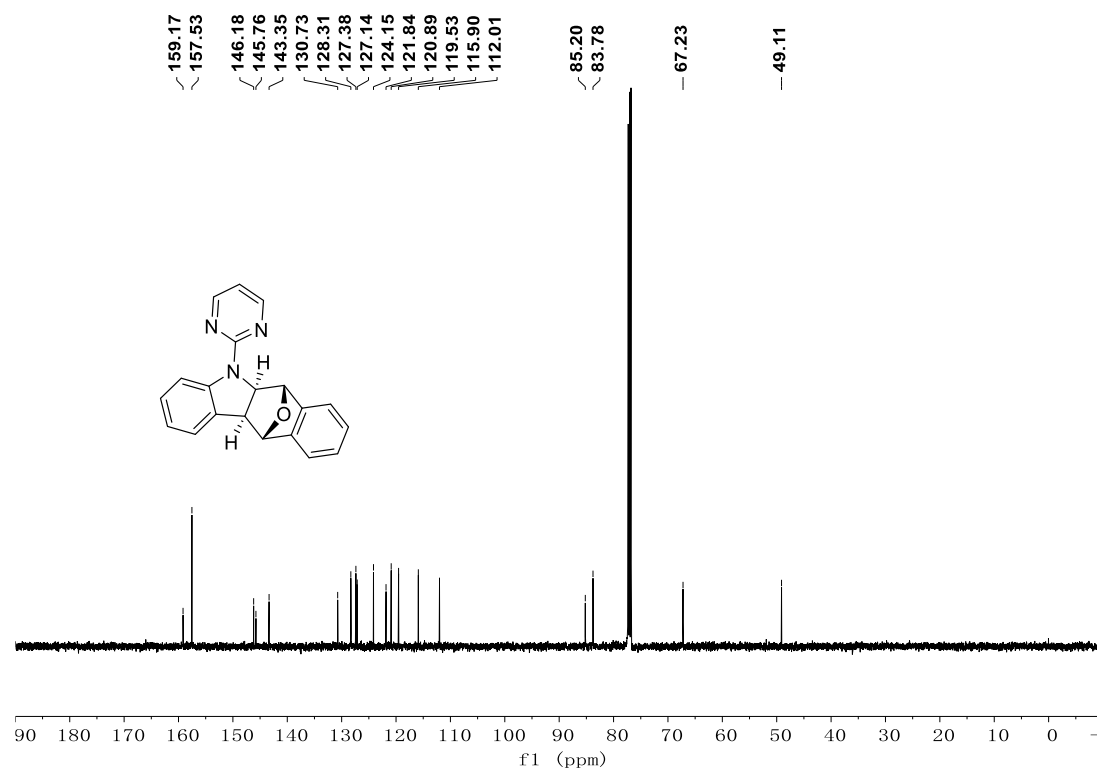
The  $^{13}\text{C}$  NMR spectrum of **3qa** (126 MHz,  $\text{CDCl}_3$ )



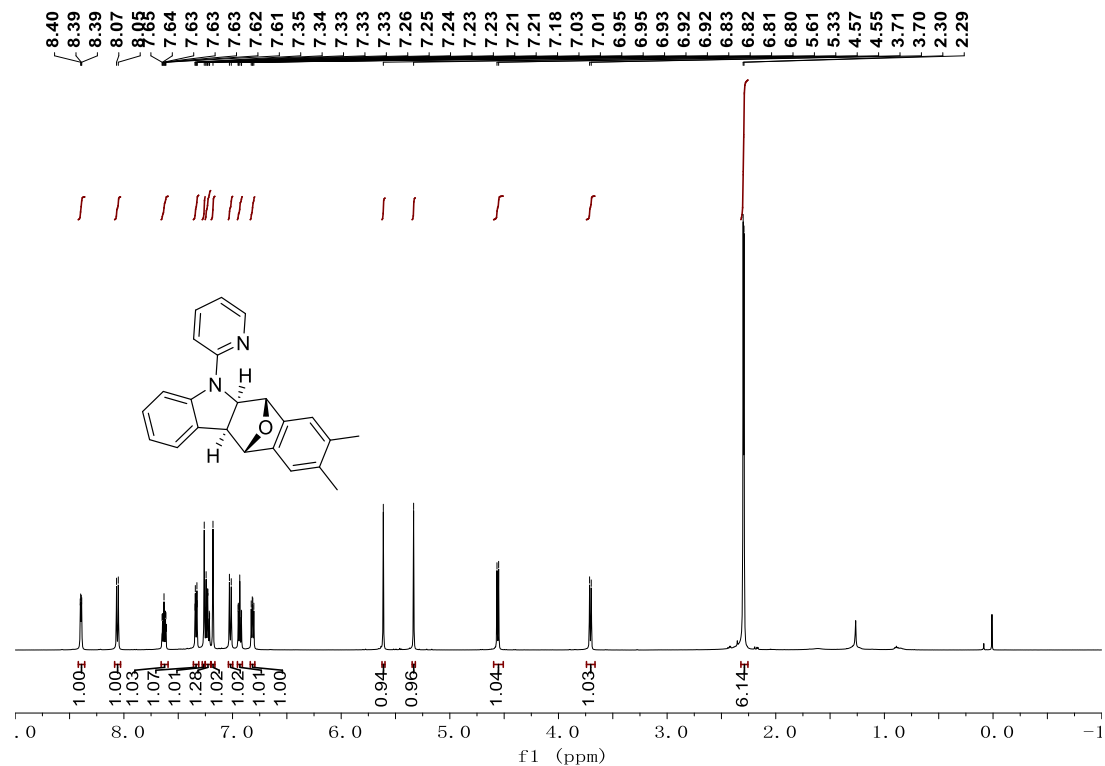
The  $^1\text{H}$  NMR spectrum of **3ra** (500 MHz,  $\text{CDCl}_3$ )



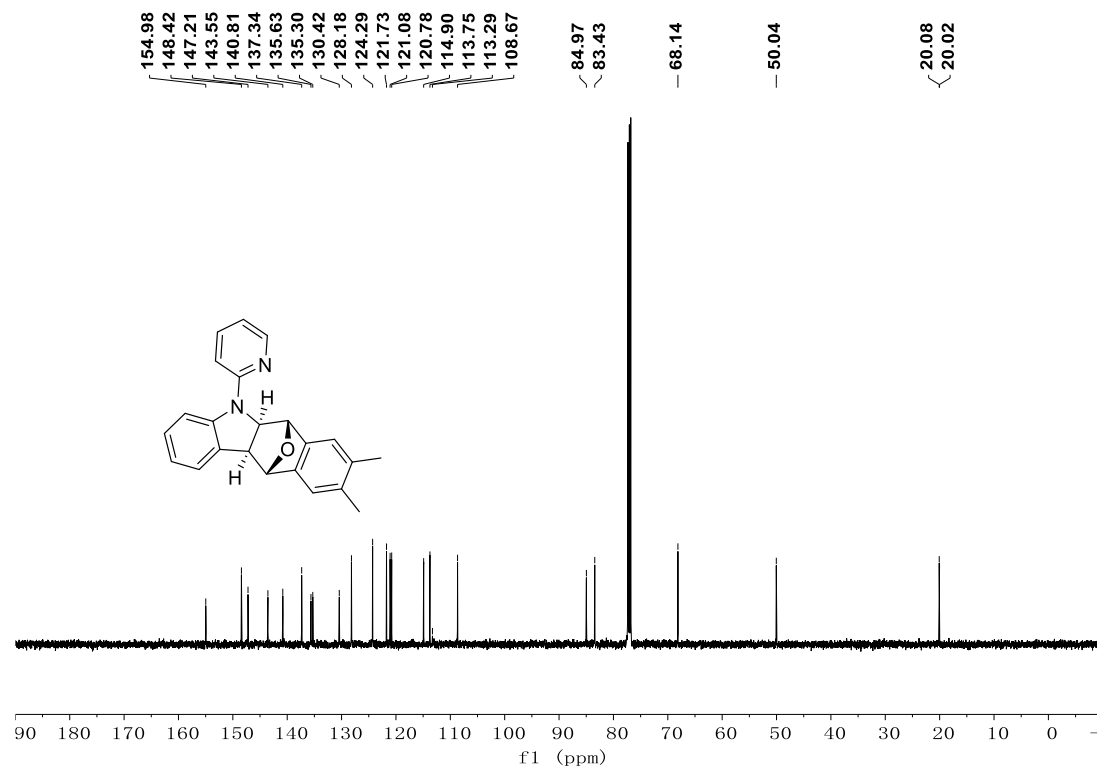
The  $^{13}\text{C}$  NMR spectrum of **3ra** (126 MHz,  $\text{CDCl}_3$ )



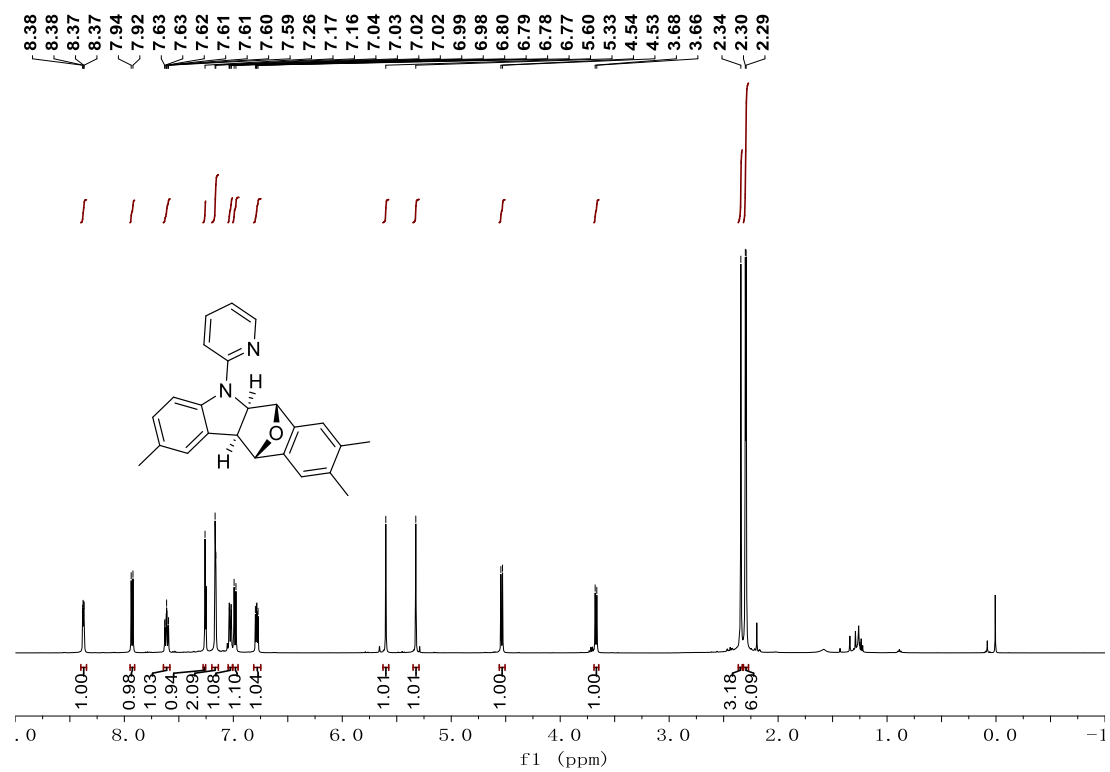
The  $^1\text{H}$  NMR spectrum of **3ab** (500 MHz,  $\text{CDCl}_3$ )



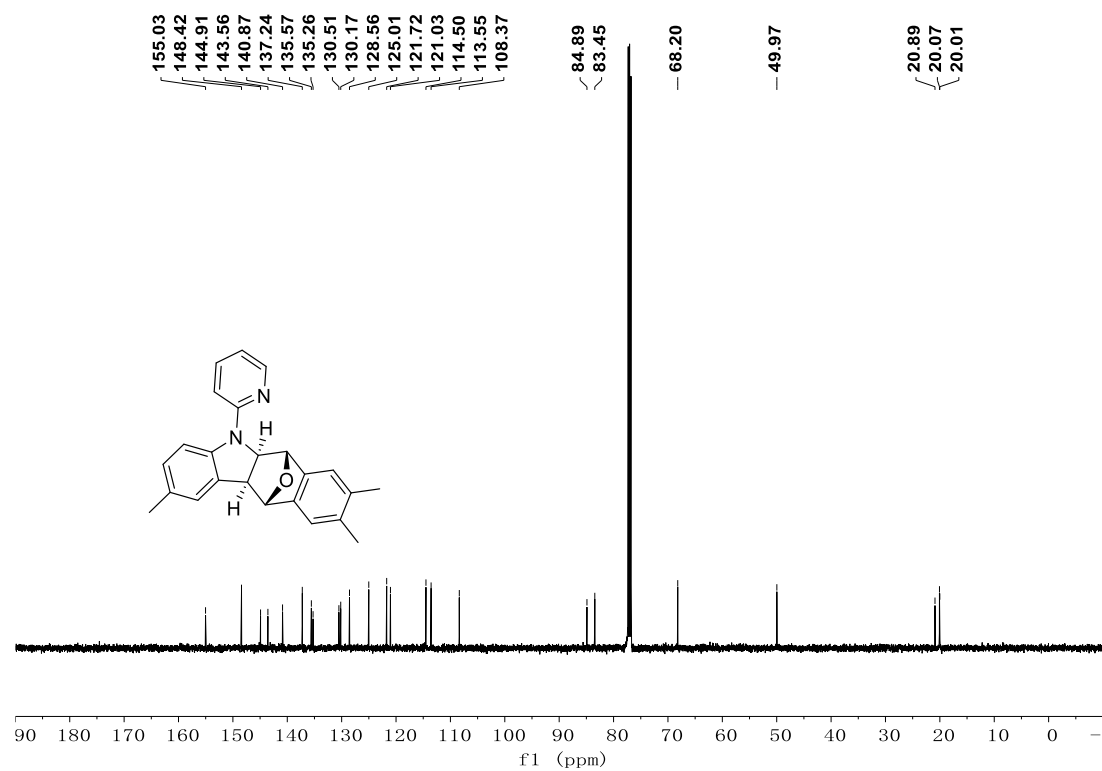
The  $^{13}\text{C}$  NMR spectrum of **3ab** (126 MHz,  $\text{CDCl}_3$ )



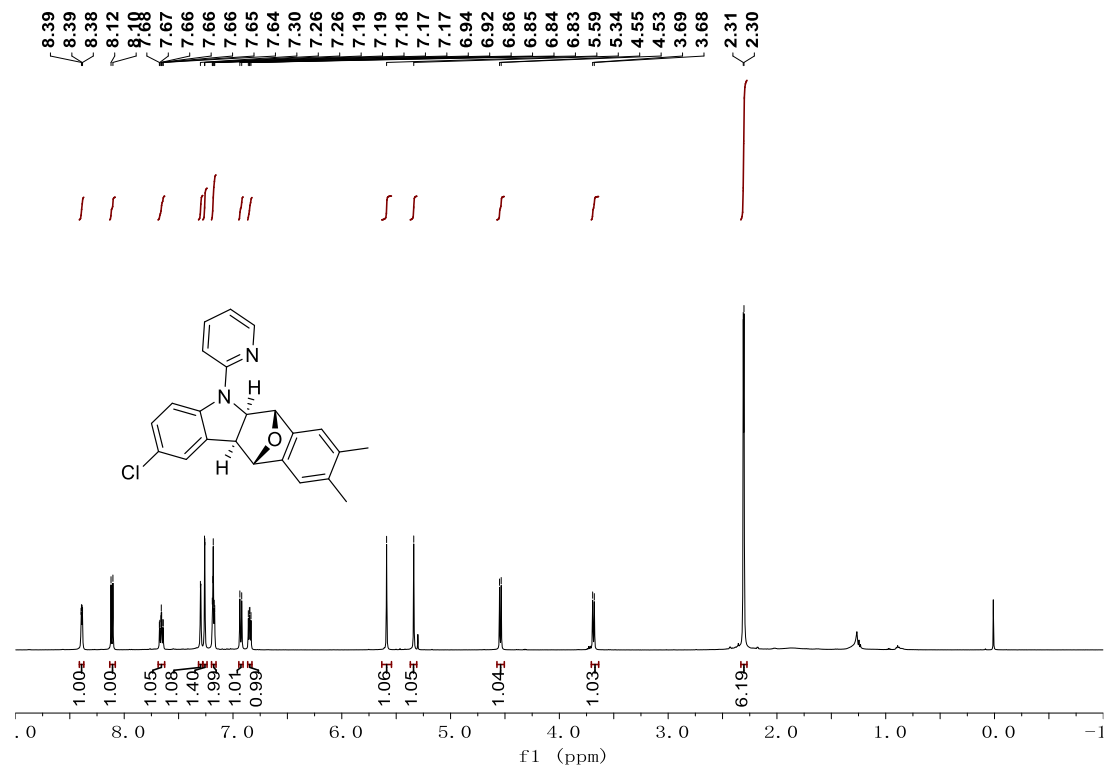
The  $^1\text{H}$  NMR spectrum of **3bb** (500 MHz,  $\text{CDCl}_3$ )



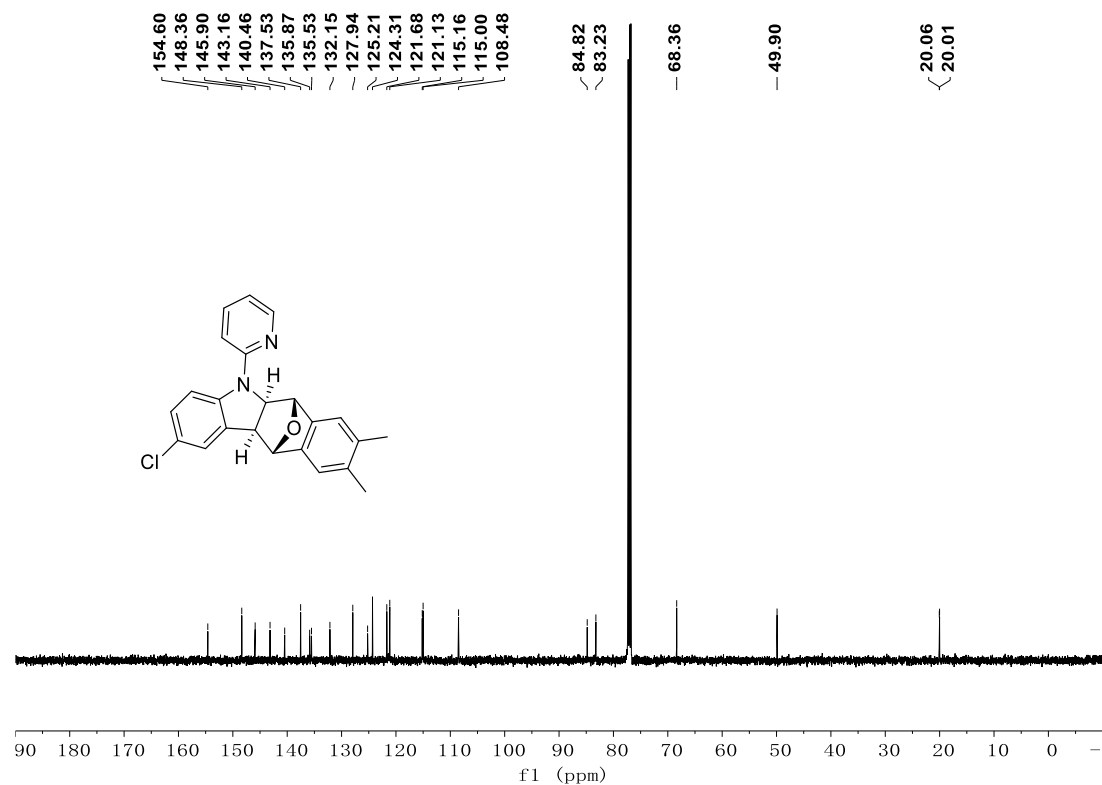
The  $^{13}\text{C}$  NMR spectrum of **3bb** (126 MHz,  $\text{CDCl}_3$ )



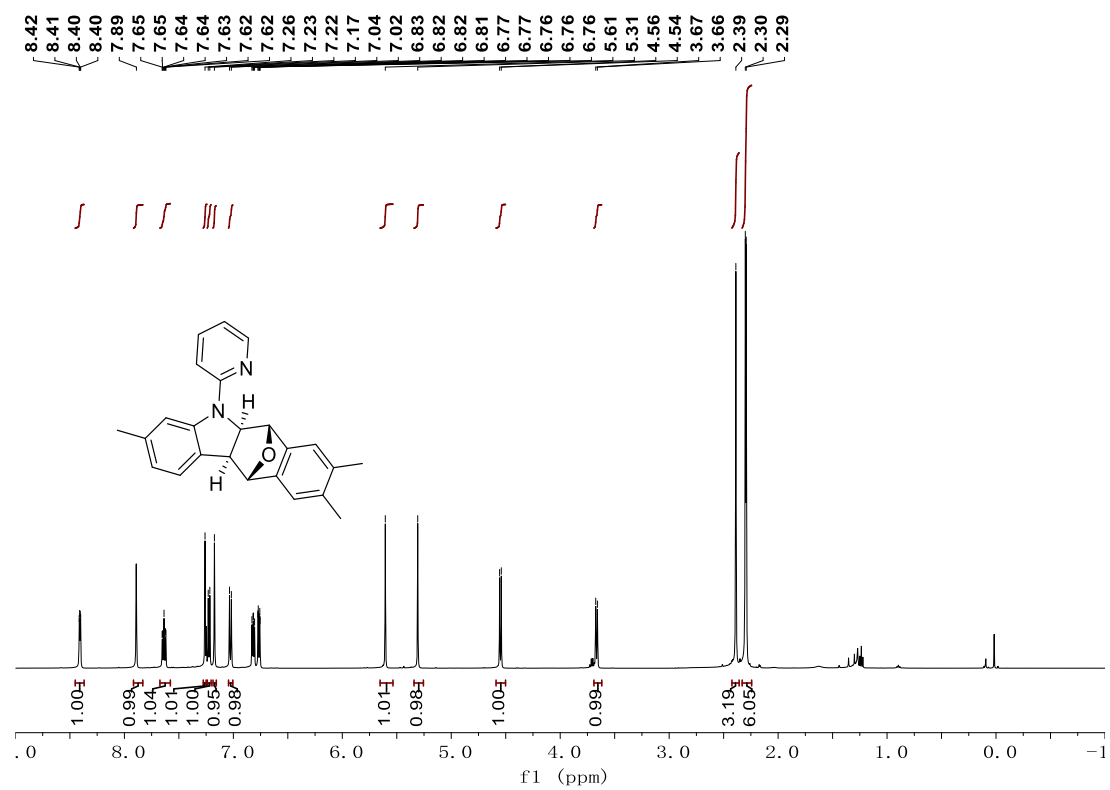
The  $^1\text{H}$  NMR spectrum of **3eb** (500 MHz,  $\text{CDCl}_3$ )



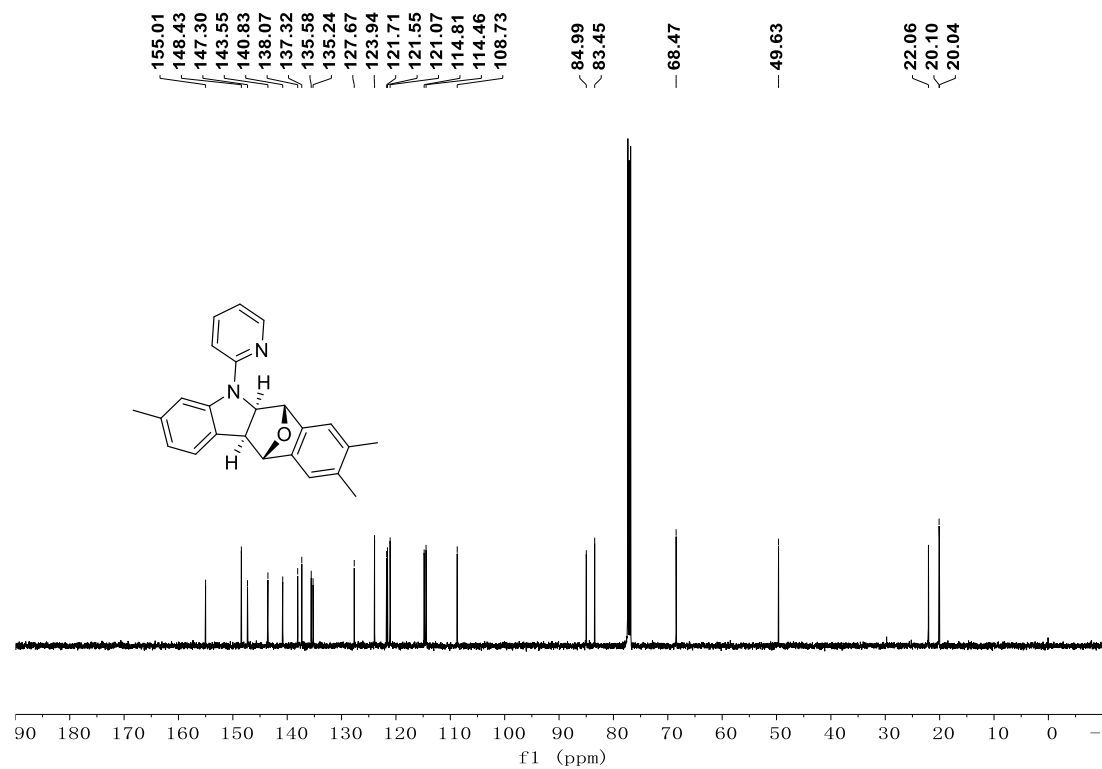
The  $^{13}\text{C}$  NMR spectrum of **3eb** (126 MHz,  $\text{CDCl}_3$ )



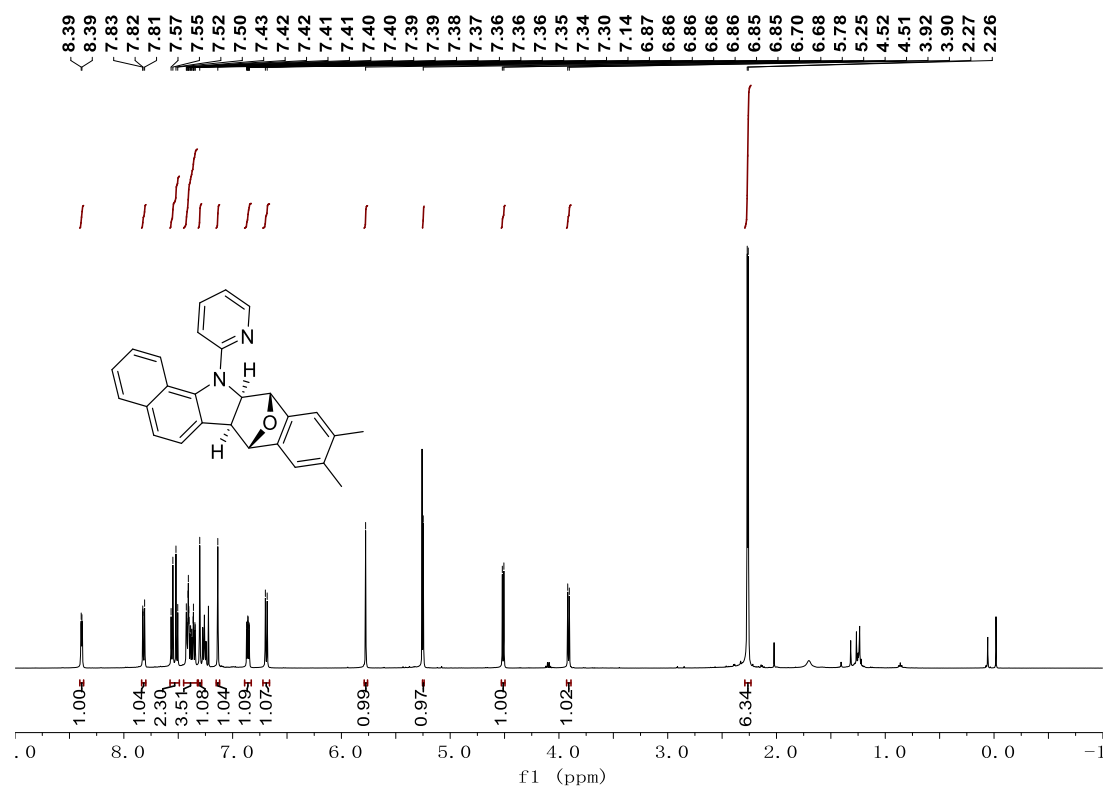
The  $^1\text{H}$  NMR spectrum of **3b** (500 MHz,  $\text{CDCl}_3$ )



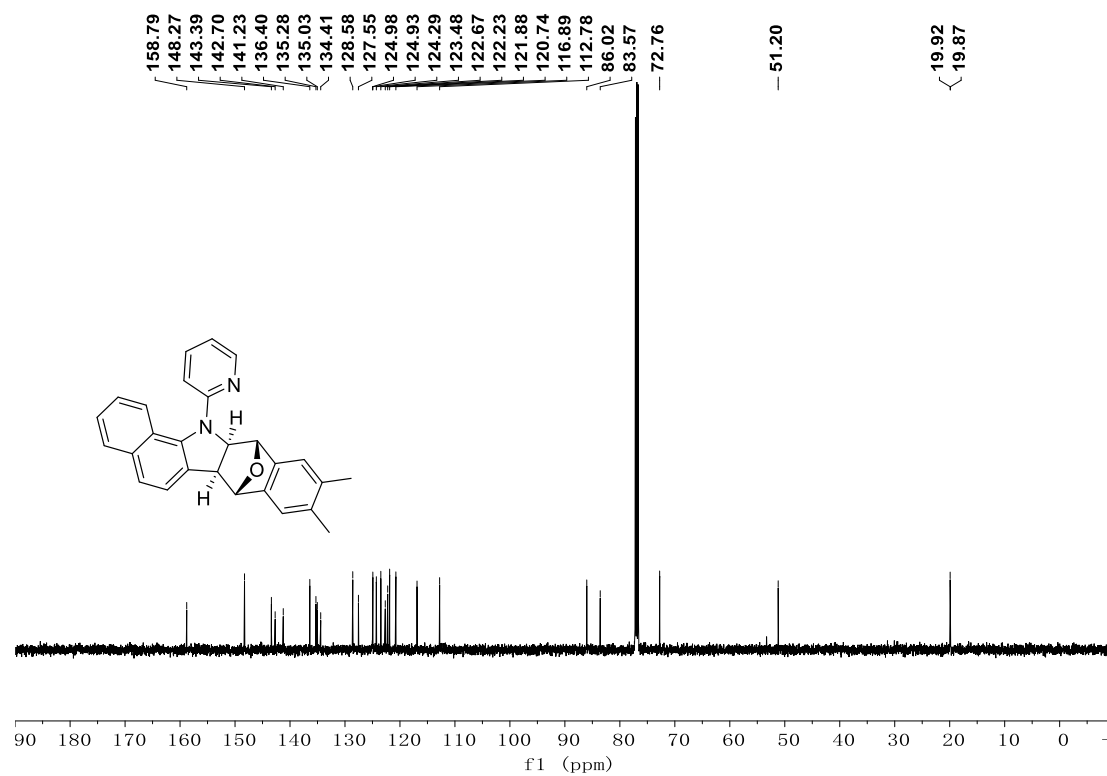
The  $^{13}\text{C}$  NMR spectrum of **3b** (126 MHz,  $\text{CDCl}_3$ )



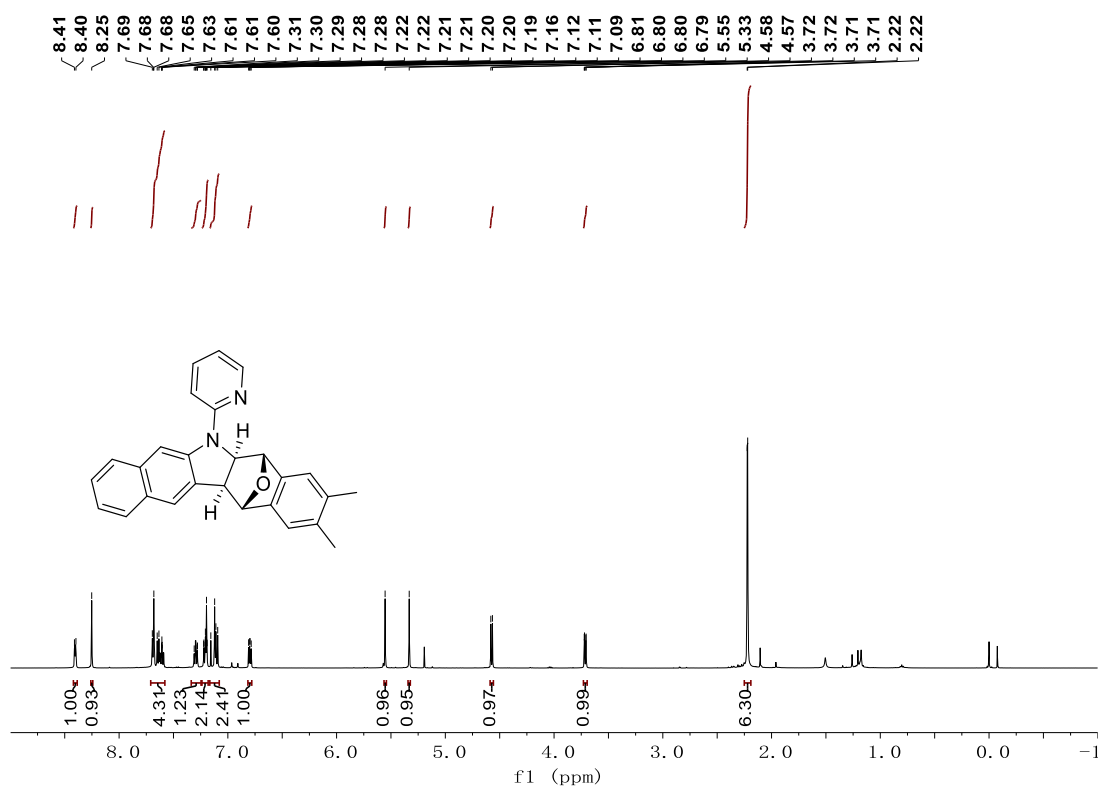
The  $^1\text{H}$  NMR spectrum of **3pb** (500 MHz,  $\text{CDCl}_3$ )



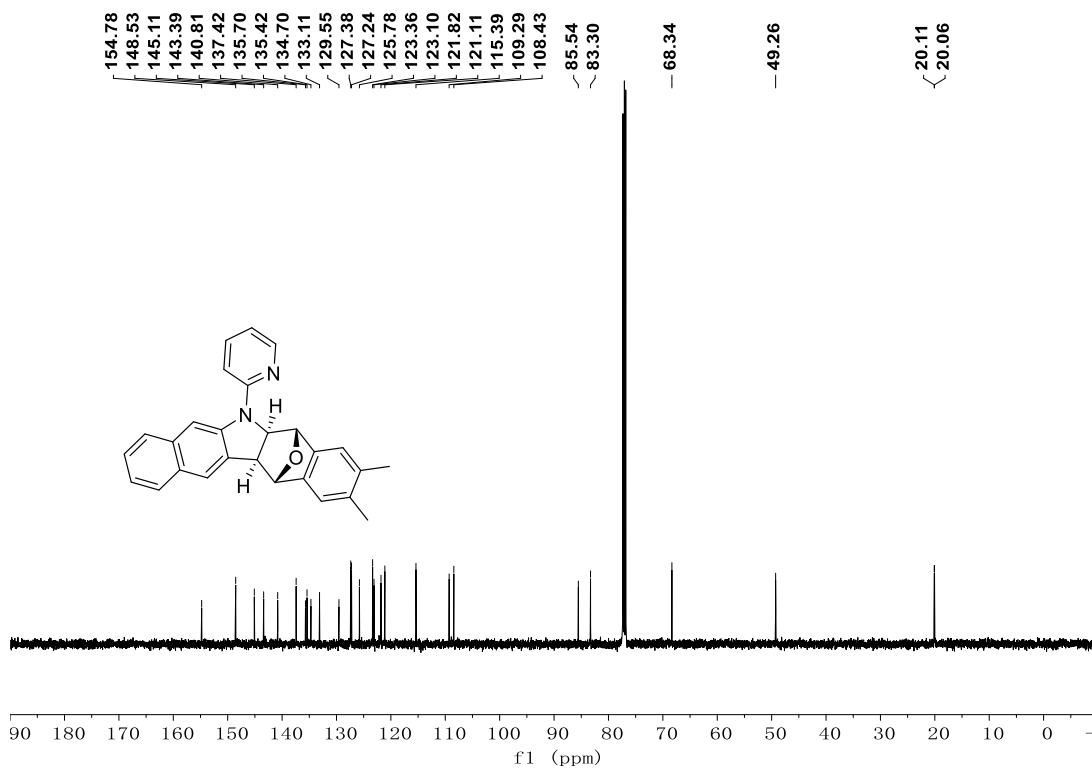
The  $^{13}\text{C}$  NMR spectrum of **3pb** (126 MHz,  $\text{CDCl}_3$ )



The  $^1\text{H}$  NMR spectrum of **3qb** (500 MHz,  $\text{CDCl}_3$ )

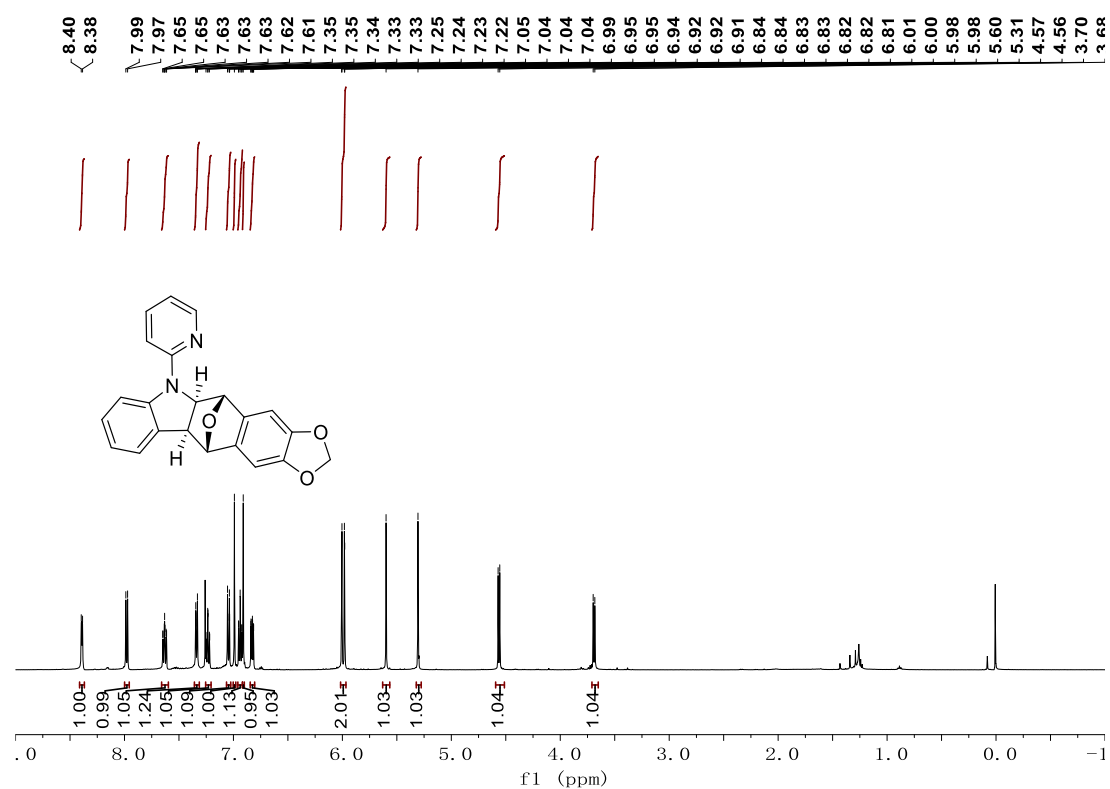


The  $^{13}\text{C}$  NMR spectrum of **3qb** (126 MHz,  $\text{CDCl}_3$ )

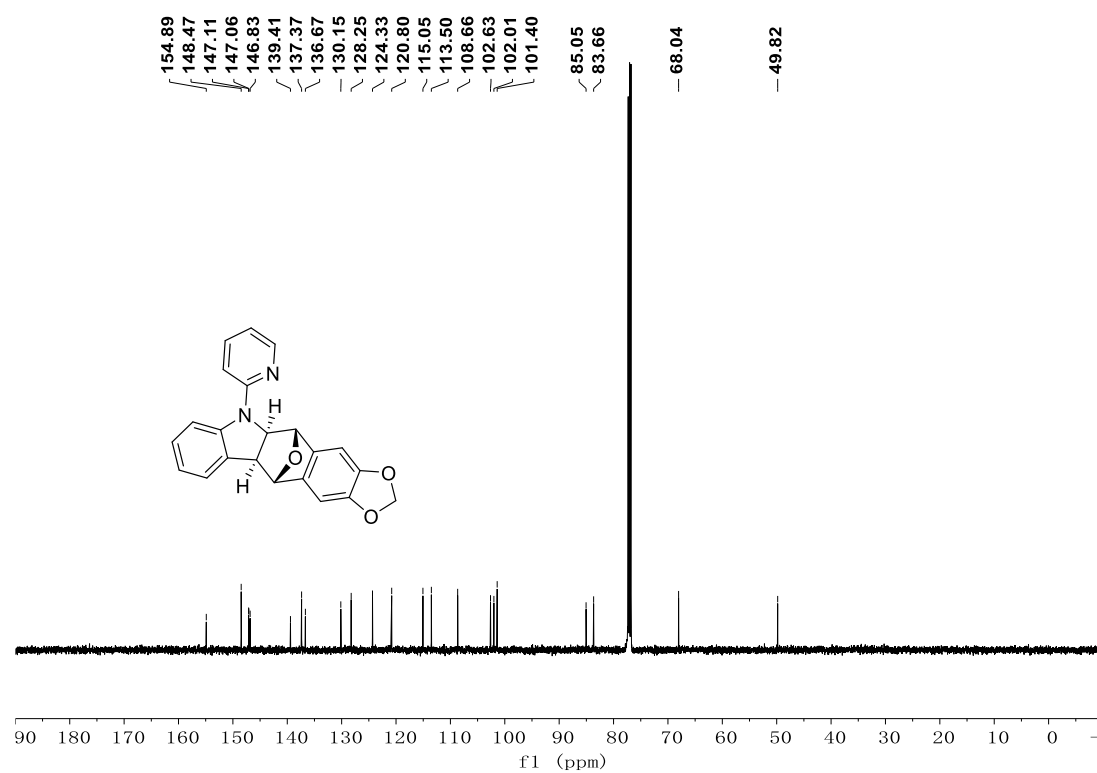




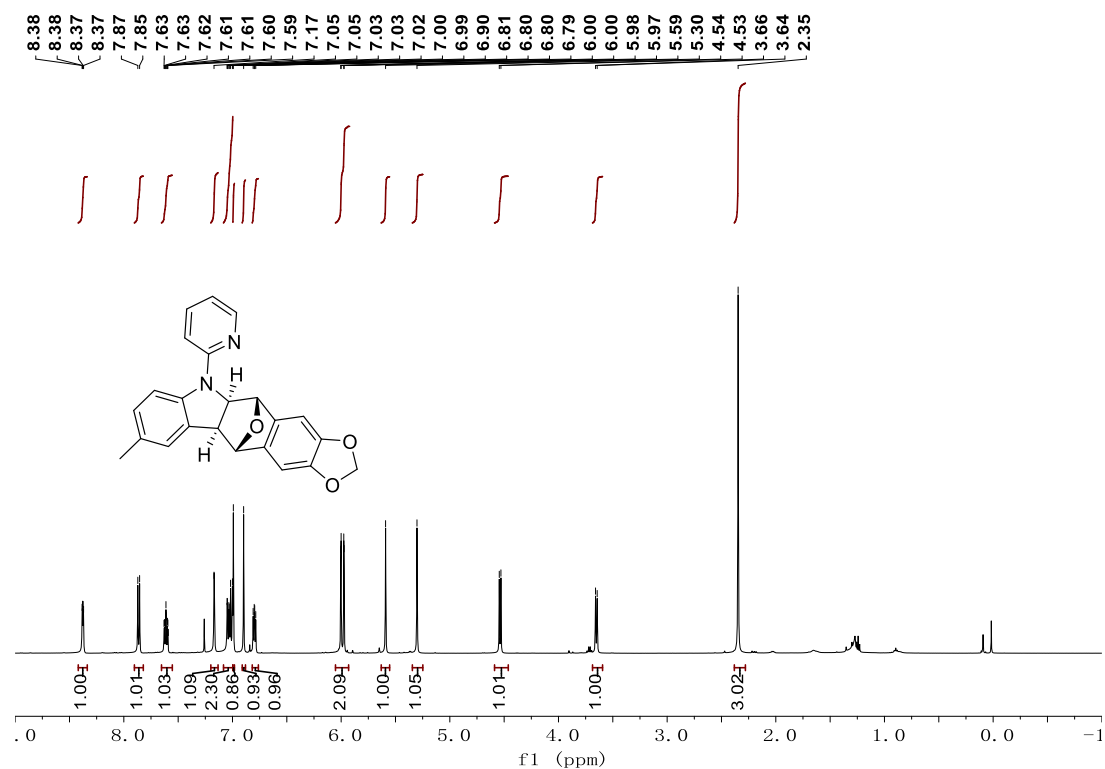
The  $^1\text{H}$  NMR spectrum of **3ac** (500 MHz,  $\text{CDCl}_3$ )



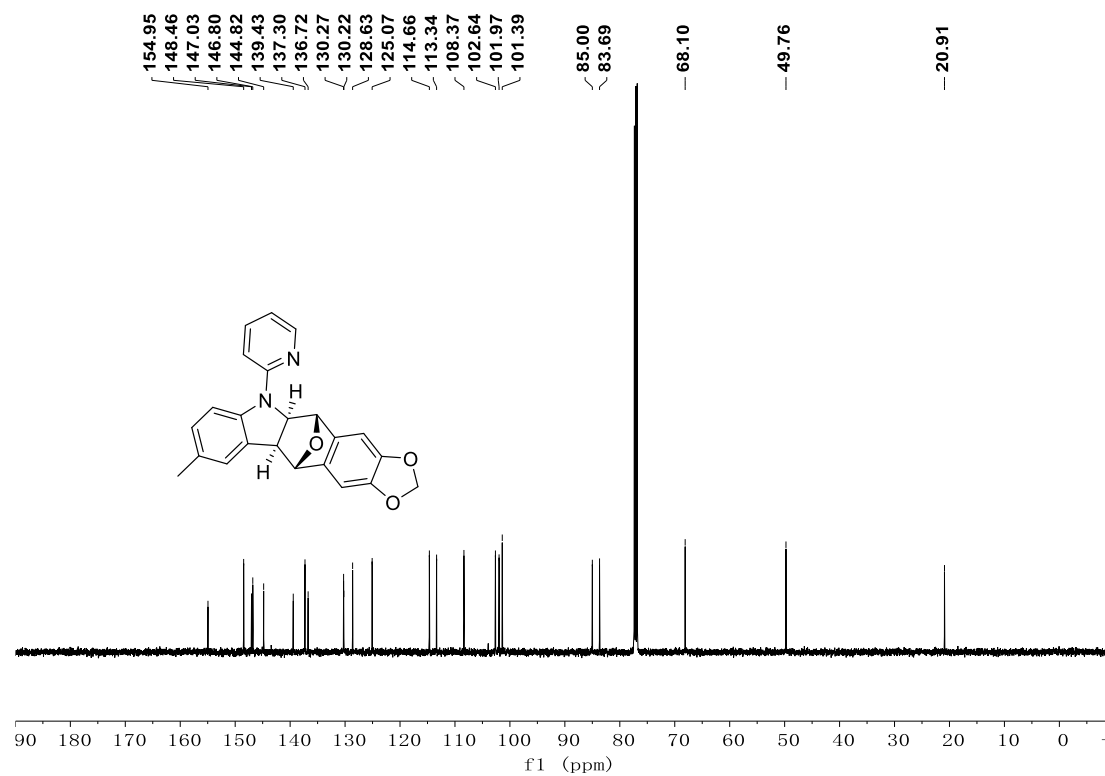
The  $^{13}\text{C}$  NMR spectrum of **3ac** (126 MHz,  $\text{CDCl}_3$ )



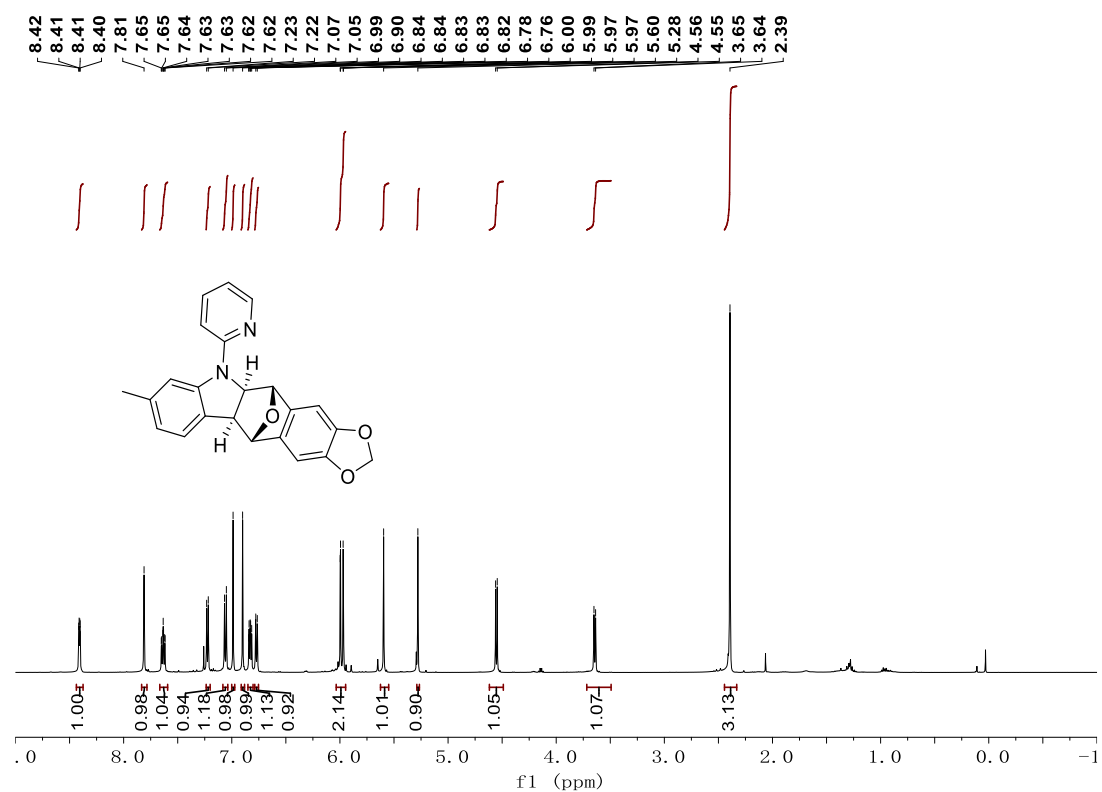
The  $^1\text{H}$  NMR spectrum of **3bc** (500 MHz,  $\text{CDCl}_3$ )



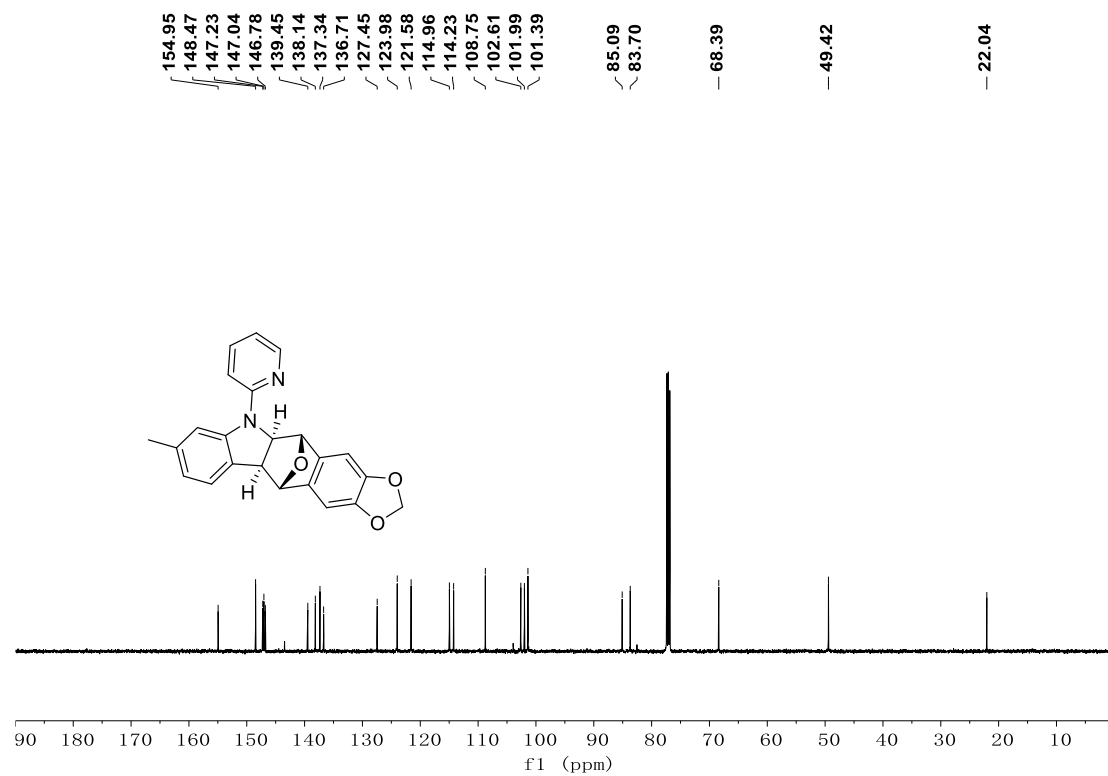
The  $^{13}\text{C}$  NMR spectrum of **3bc** (126 MHz,  $\text{CDCl}_3$ )



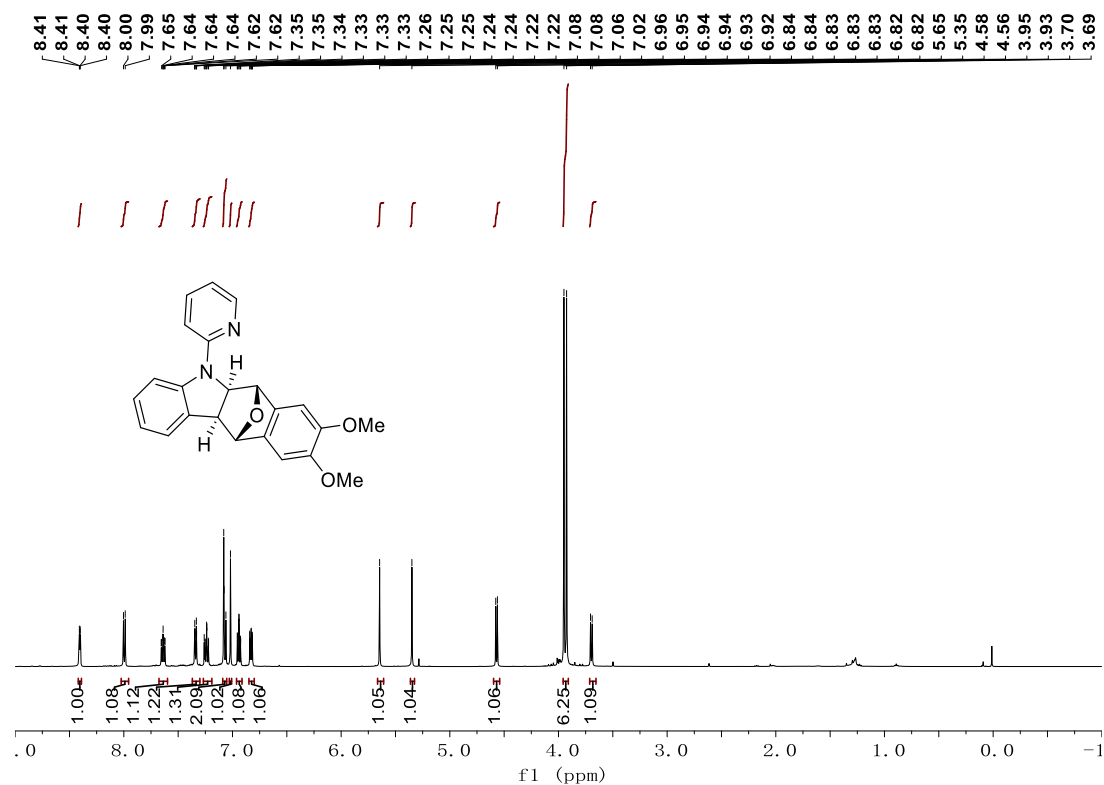
The  $^1\text{H}$  NMR spectrum of **3lc** (500 MHz,  $\text{CDCl}_3$ )



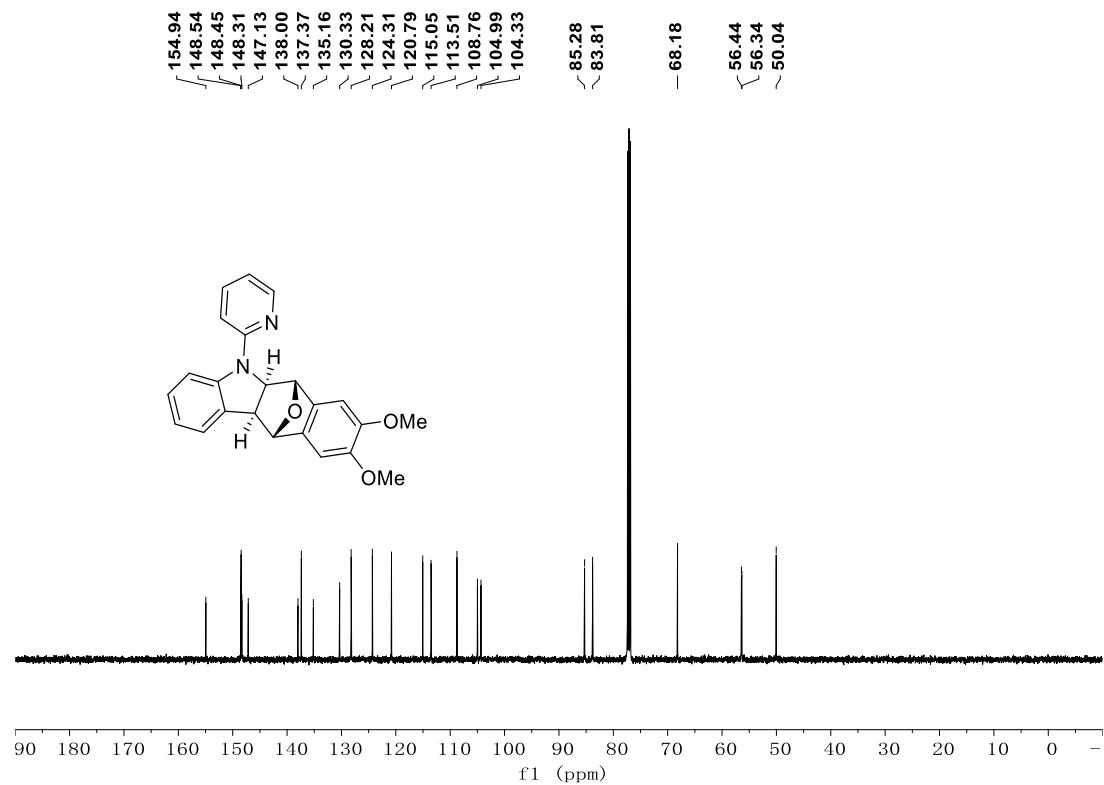
The  $^{13}\text{C}$  NMR spectrum of **3lc** (126 MHz,  $\text{CDCl}_3$ )



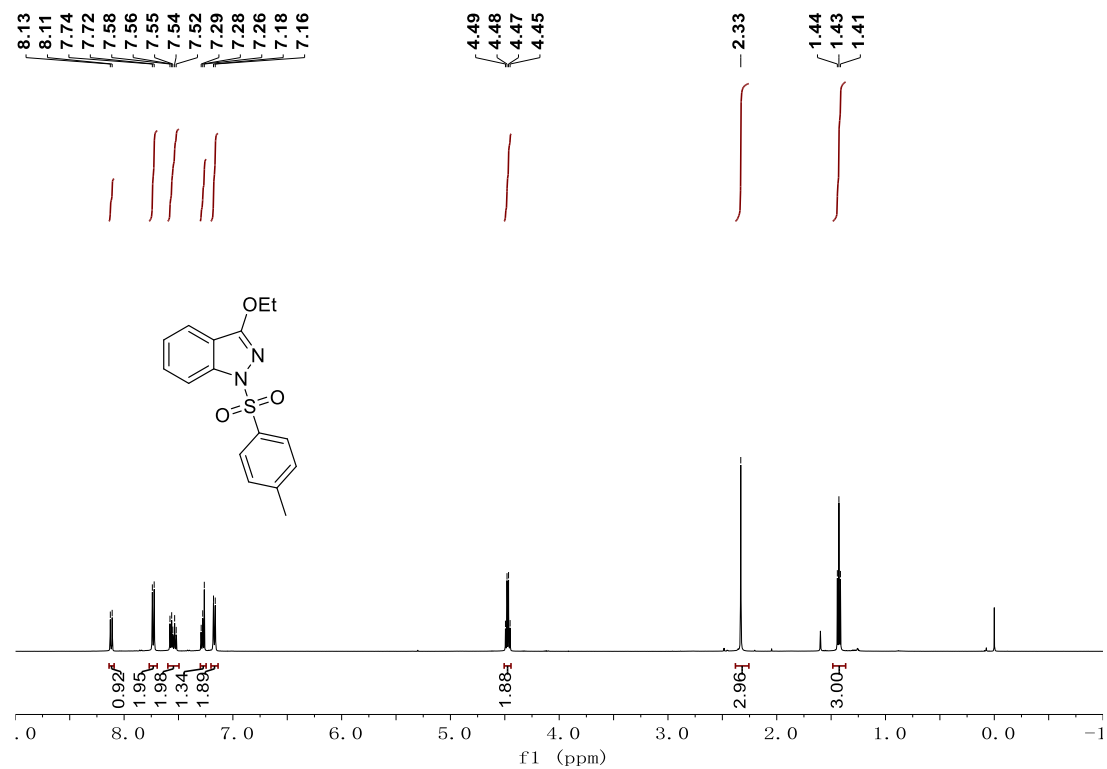
The  $^1\text{H}$  NMR spectrum of **3ad** (500 MHz,  $\text{CDCl}_3$ )



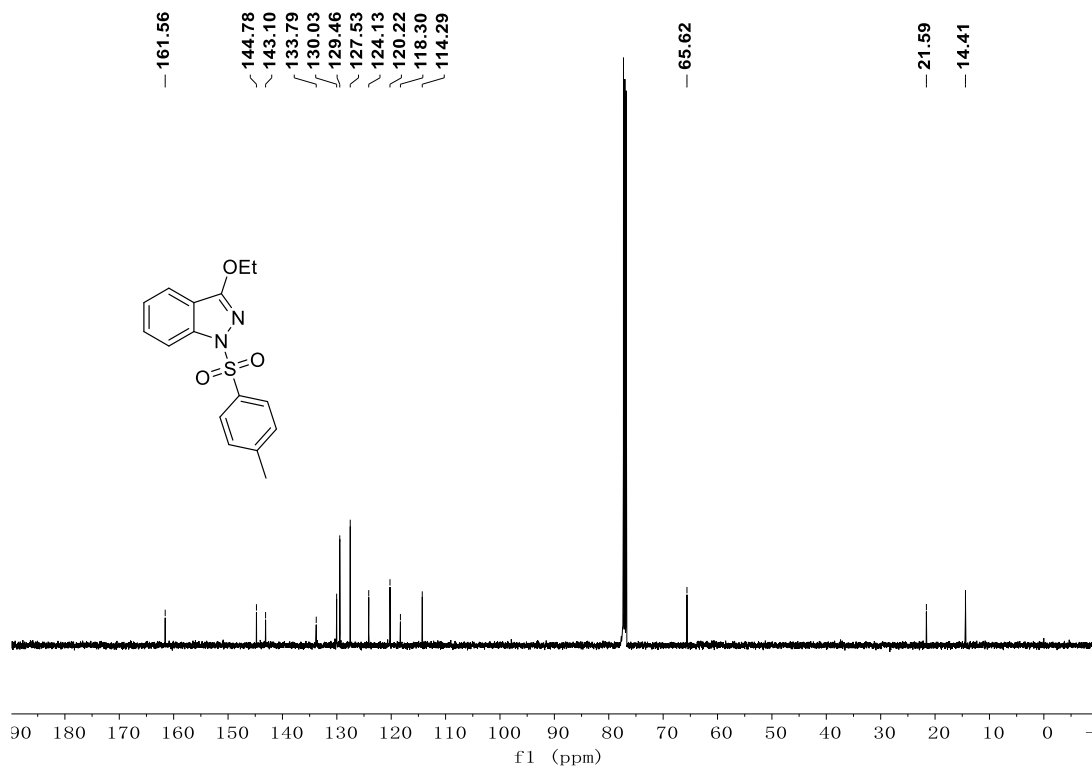
The  $^{13}\text{C}$  NMR spectrum of **3ad** (126 MHz,  $\text{CDCl}_3$ )



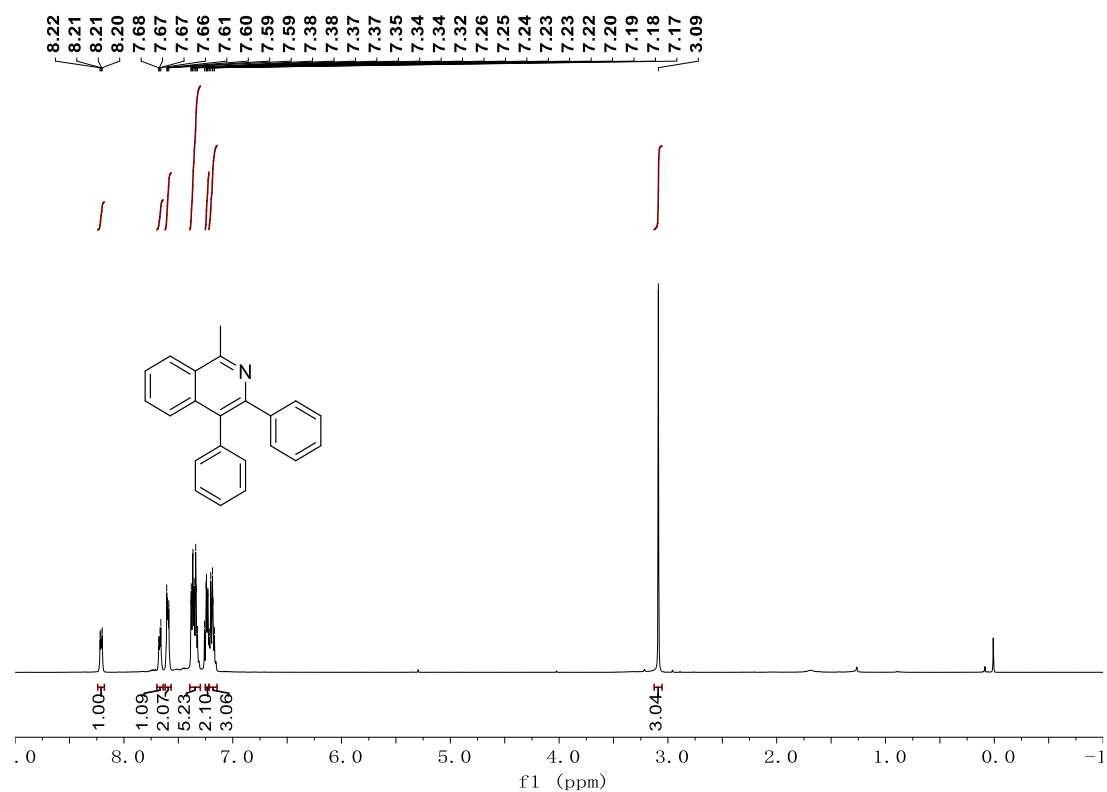
The  $^1\text{H}$  NMR spectrum of **6** (500 MHz,  $\text{CDCl}_3$ )



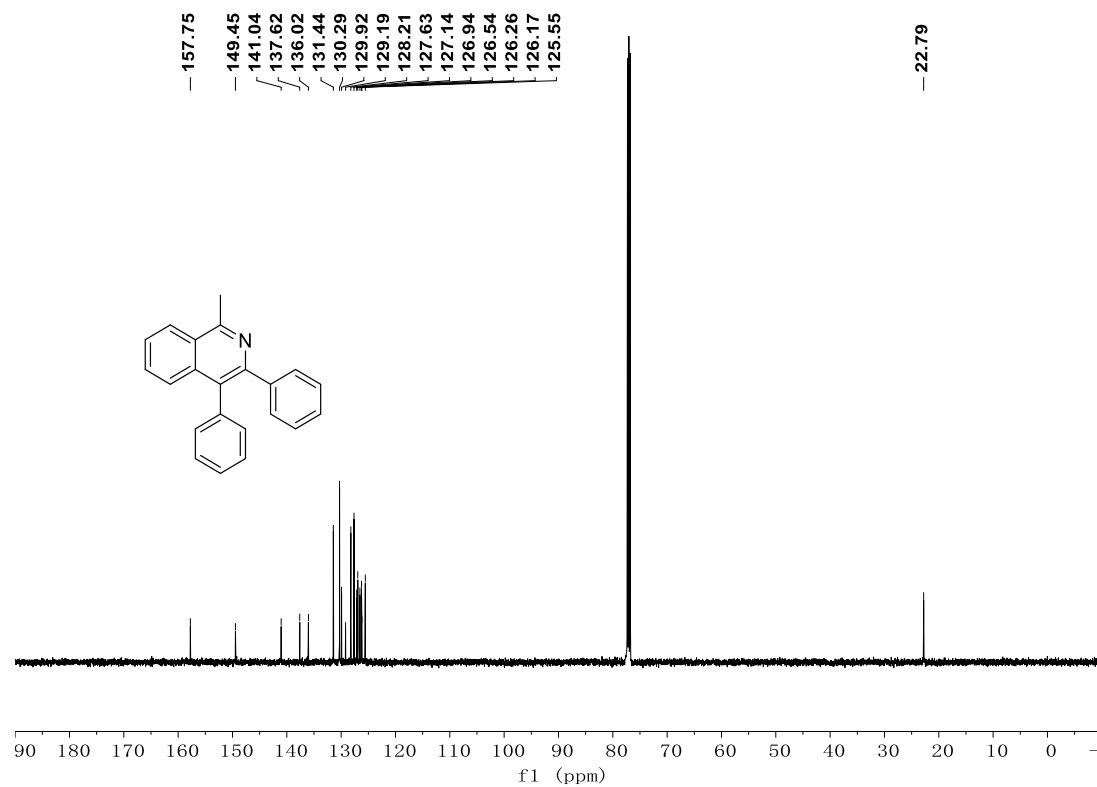
The  $^{13}\text{C}$  NMR spectrum of **6** (126 MHz,  $\text{CDCl}_3$ )



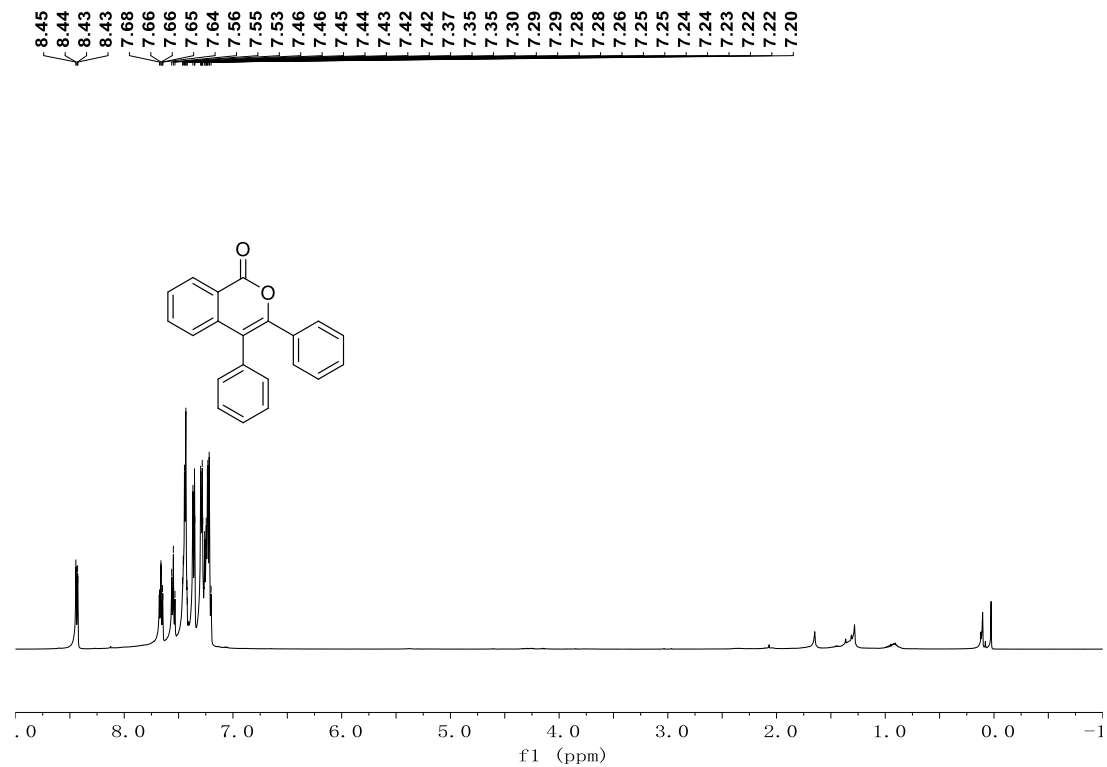
The  $^1\text{H}$  NMR spectrum of **9** (500 MHz,  $\text{CDCl}_3$ )



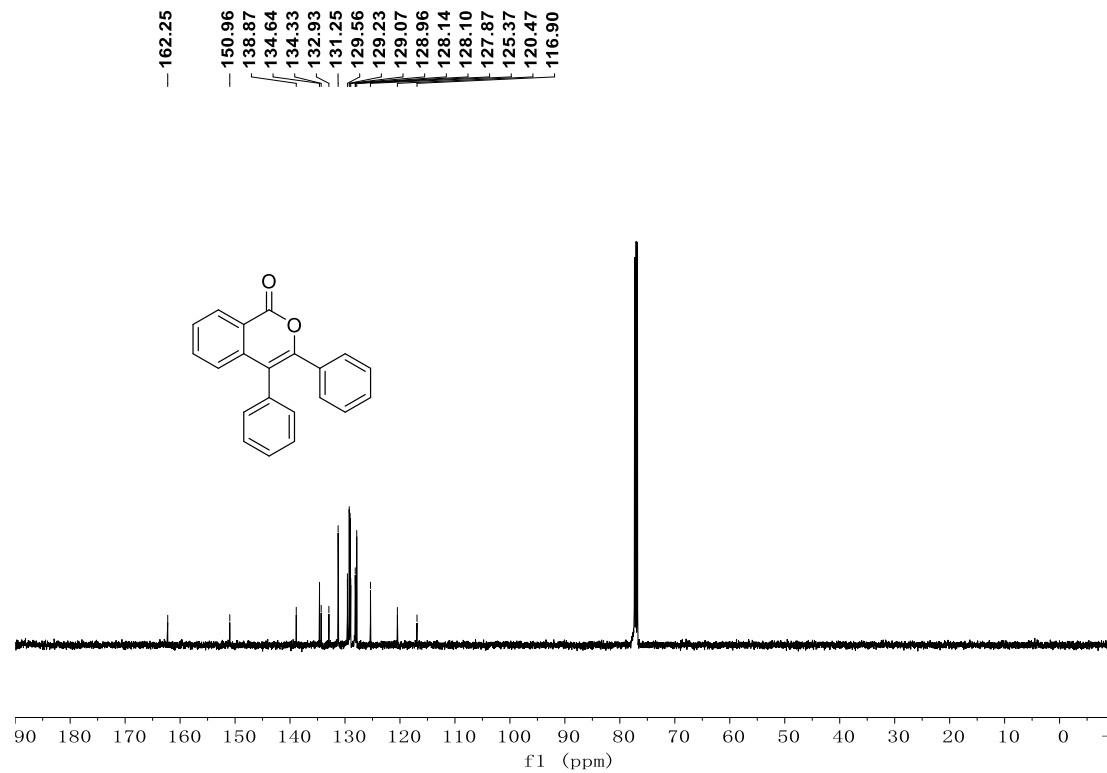
The  $^{13}\text{C}$  NMR spectrum of **9** (126 MHz,  $\text{CDCl}_3$ )



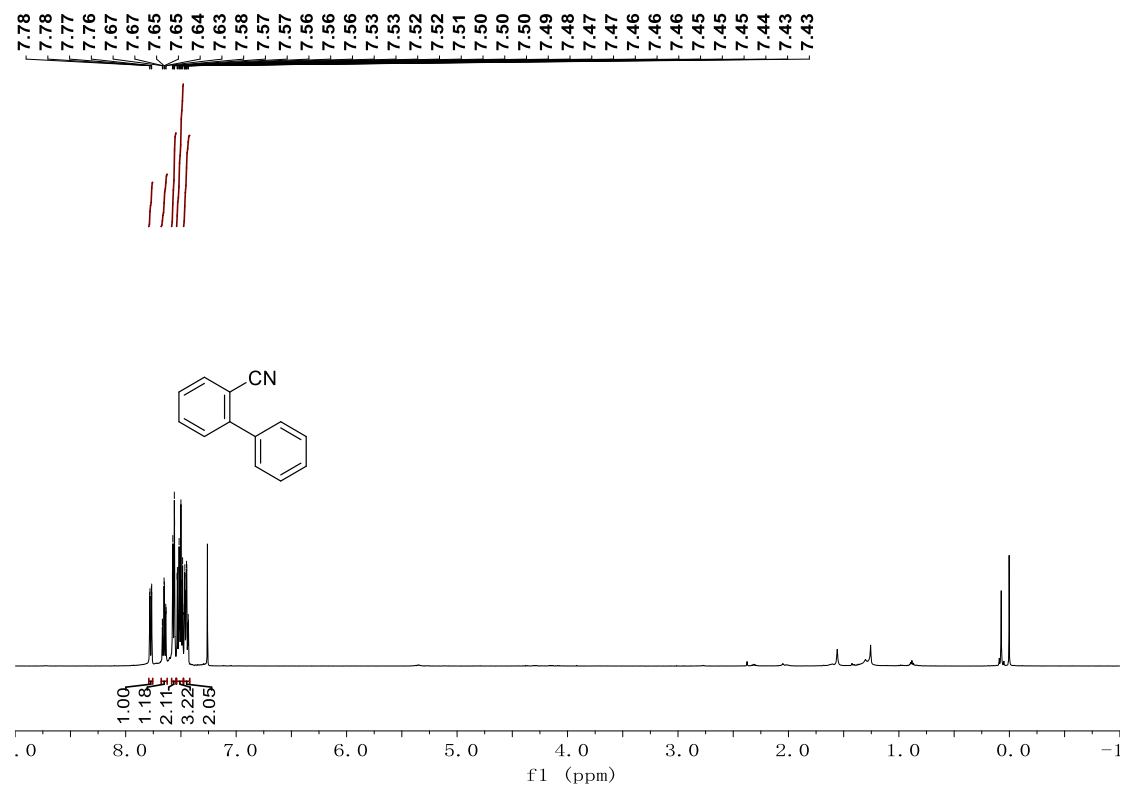
The  $^1\text{H}$  NMR spectrum of **11** (500 MHz,  $\text{CDCl}_3$ )



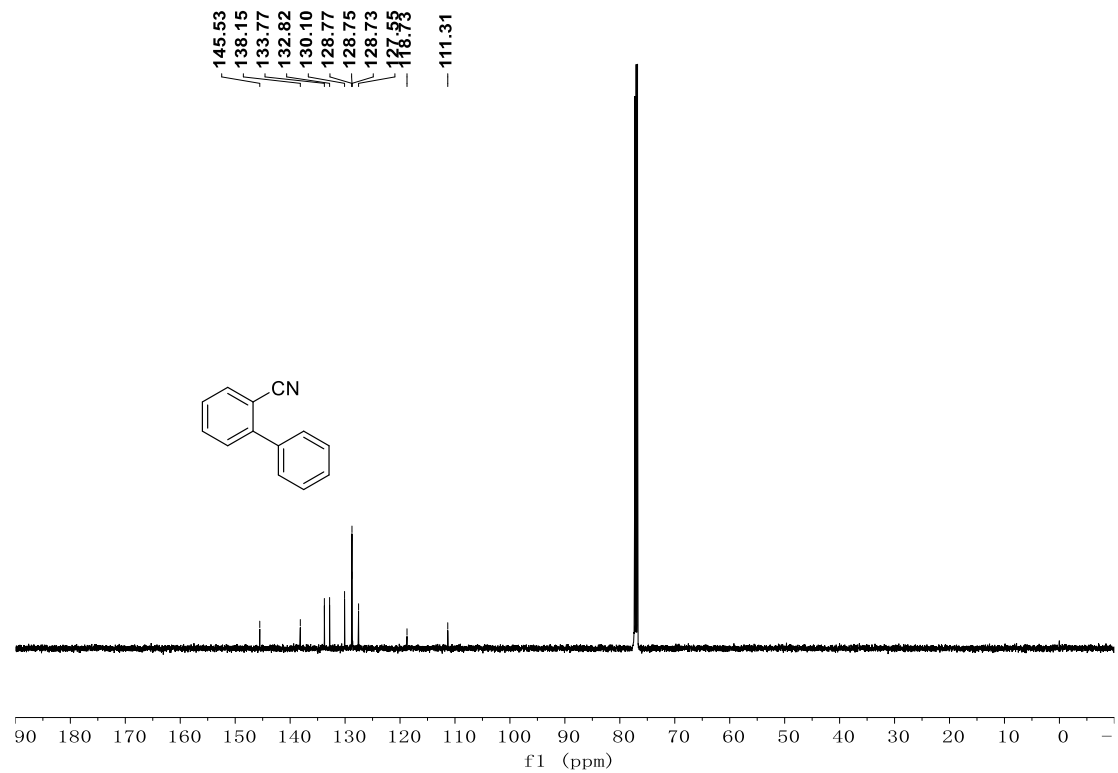
The  $^{13}\text{C}$  NMR spectrum of **11** (126 MHz,  $\text{CDCl}_3$ )



The  $^1\text{H}$  NMR spectrum of **13** (500 MHz,  $\text{CDCl}_3$ )

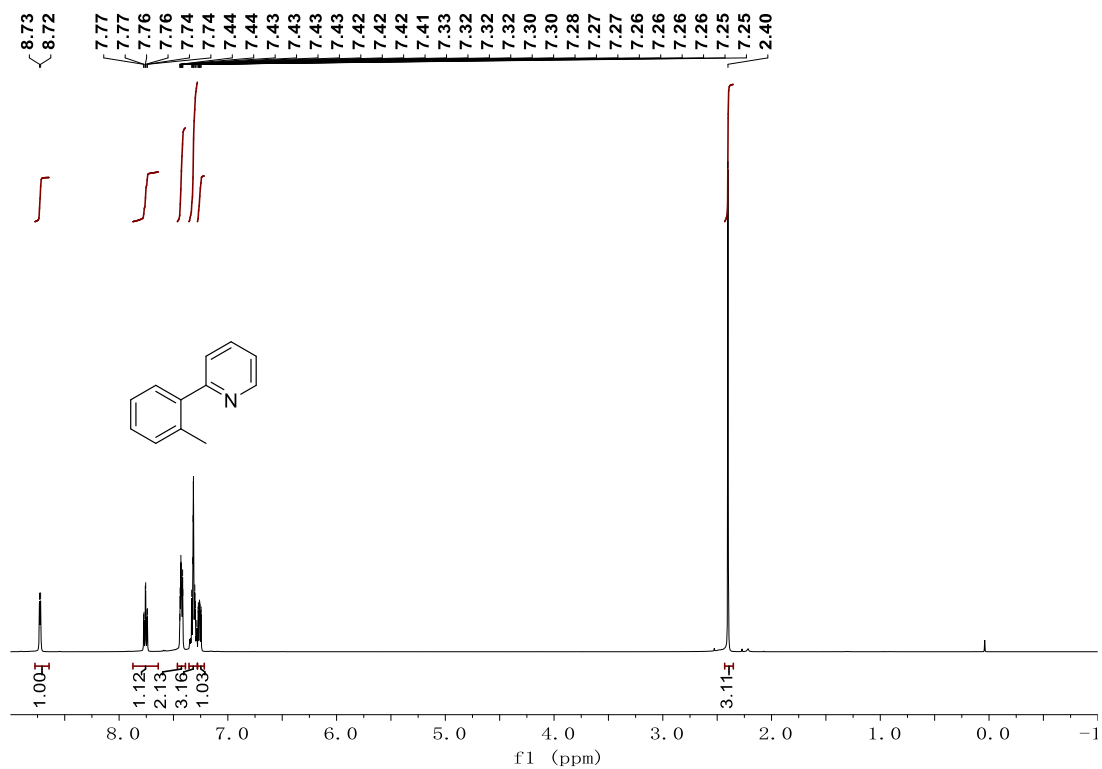


The  $^{13}\text{C}$  NMR spectrum of **13** (126 MHz,  $\text{CDCl}_3$ )

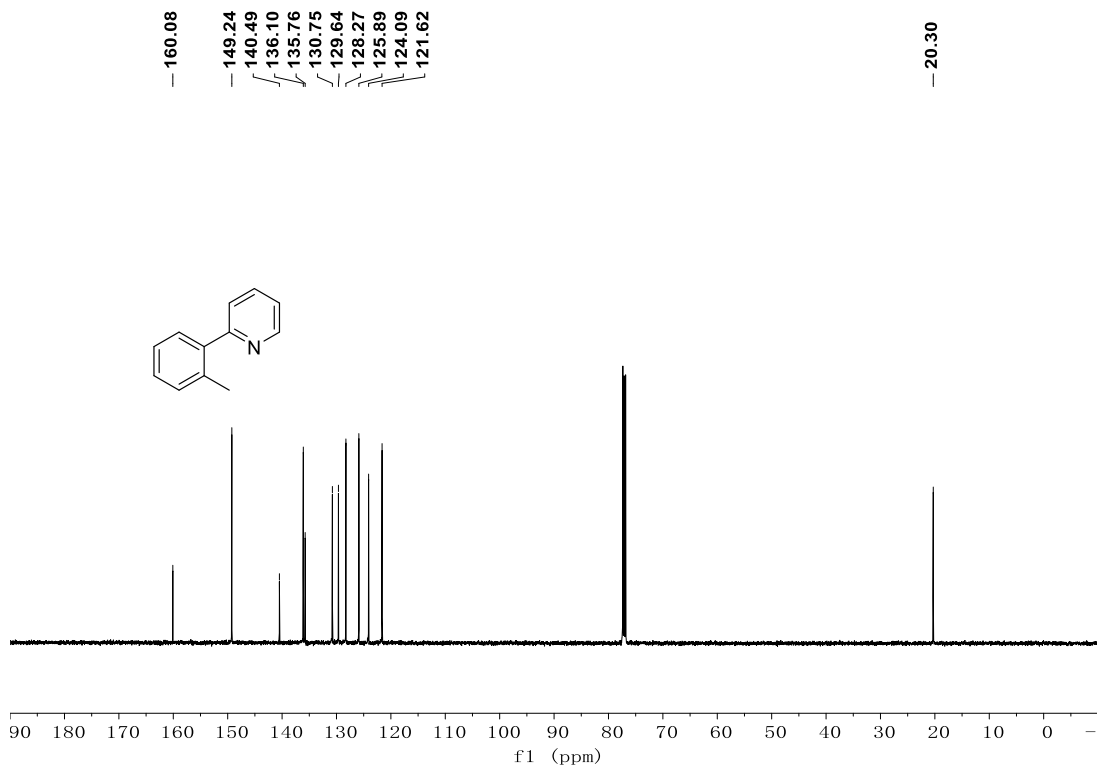




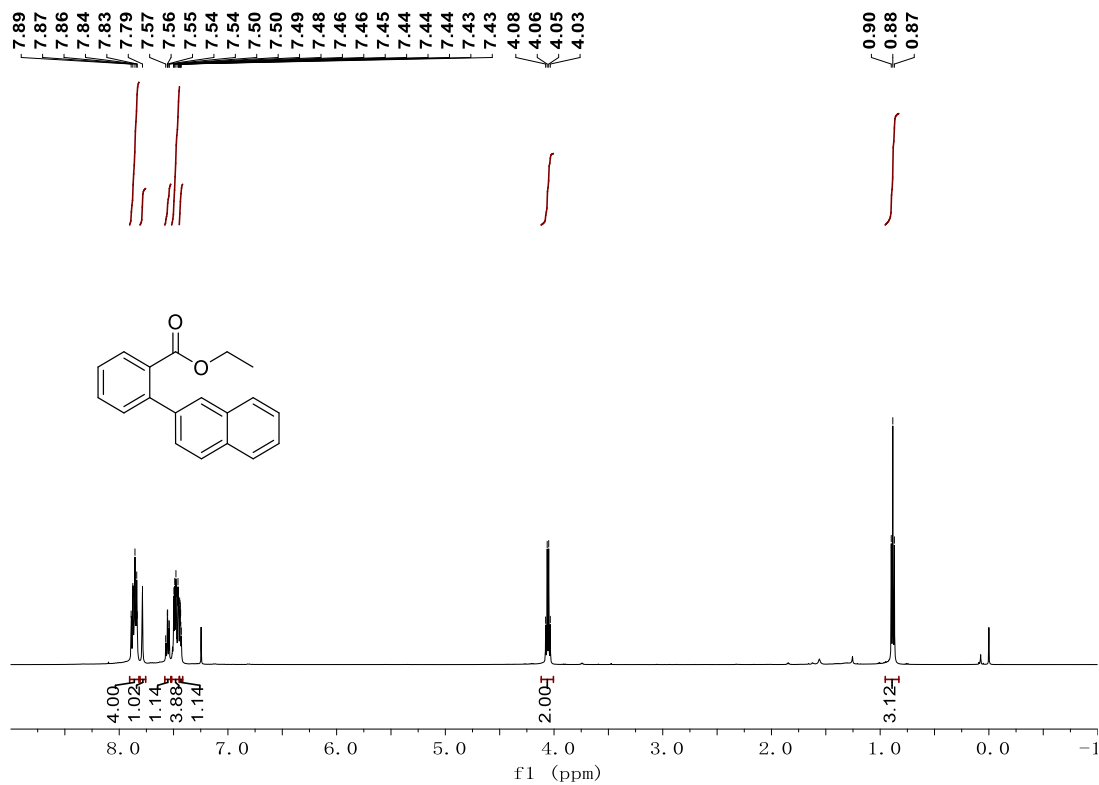
The  $^1\text{H}$  NMR spectrum of **16** (500 MHz,  $\text{CDCl}_3$ )



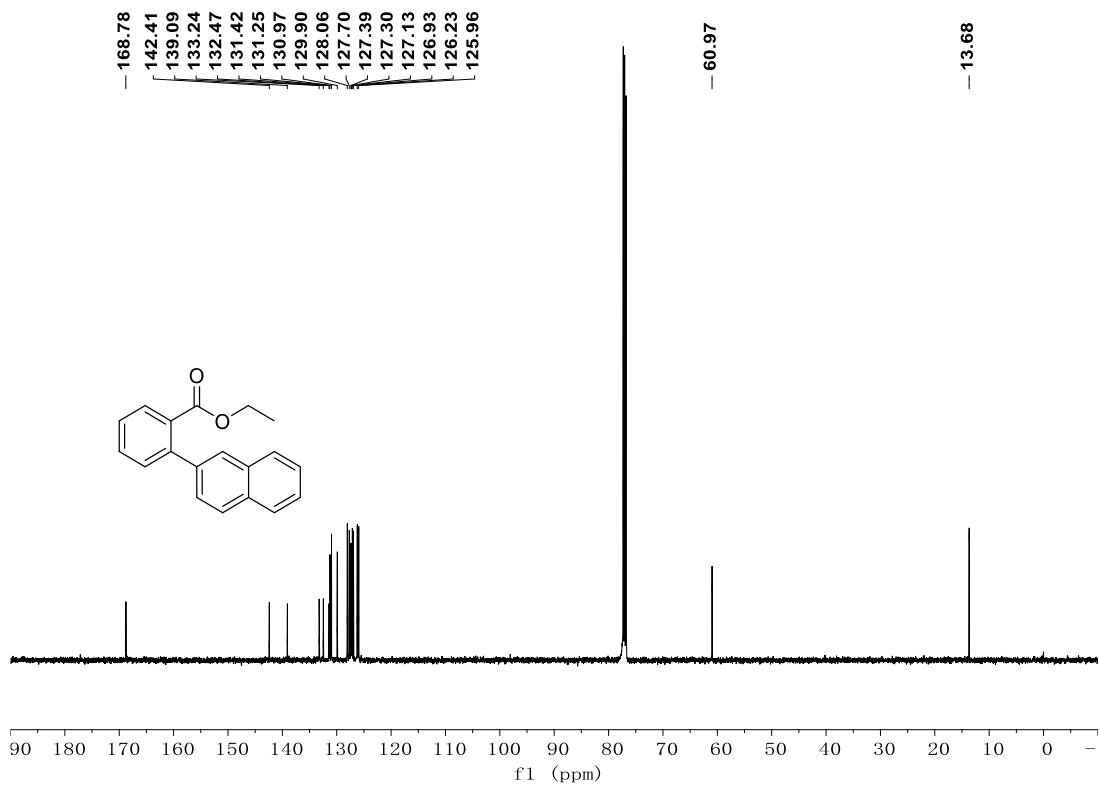
The  $^{13}\text{C}$  NMR spectrum of **16** (126 MHz,  $\text{CDCl}_3$ )



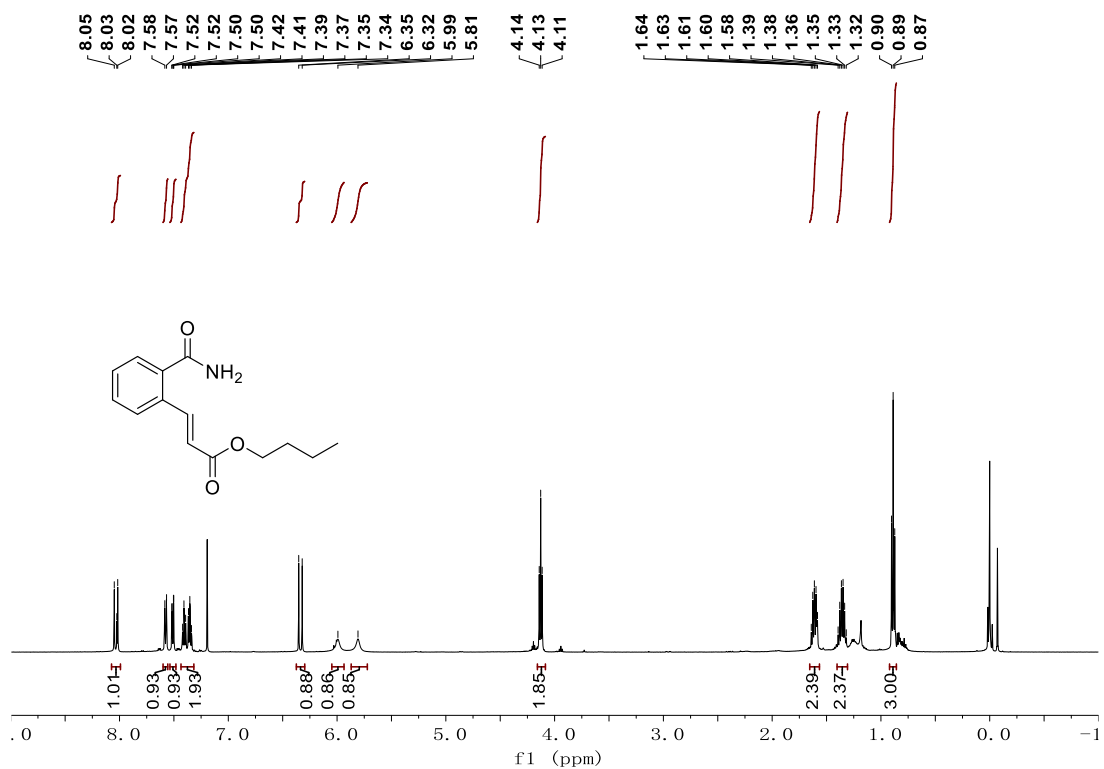
The  $^1\text{H}$  NMR spectrum of **17** (500 MHz,  $\text{CDCl}_3$ )



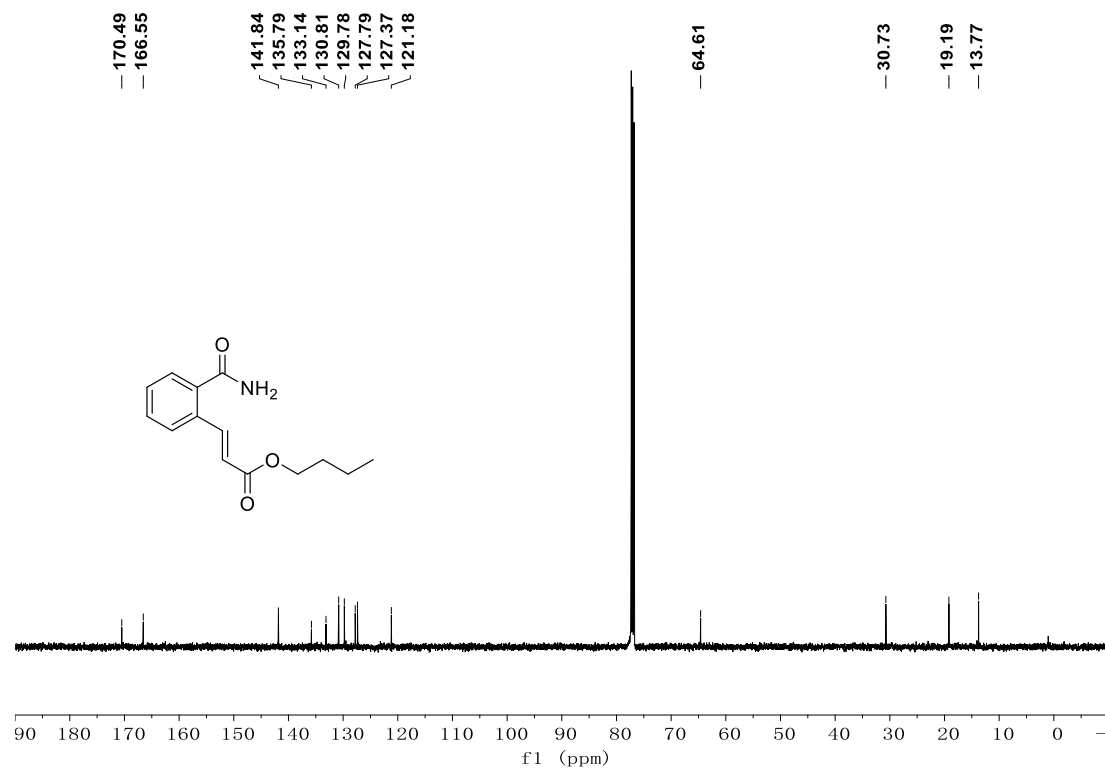
The  $^{13}\text{C}$  NMR spectrum of **17** (126 MHz,  $\text{CDCl}_3$ )



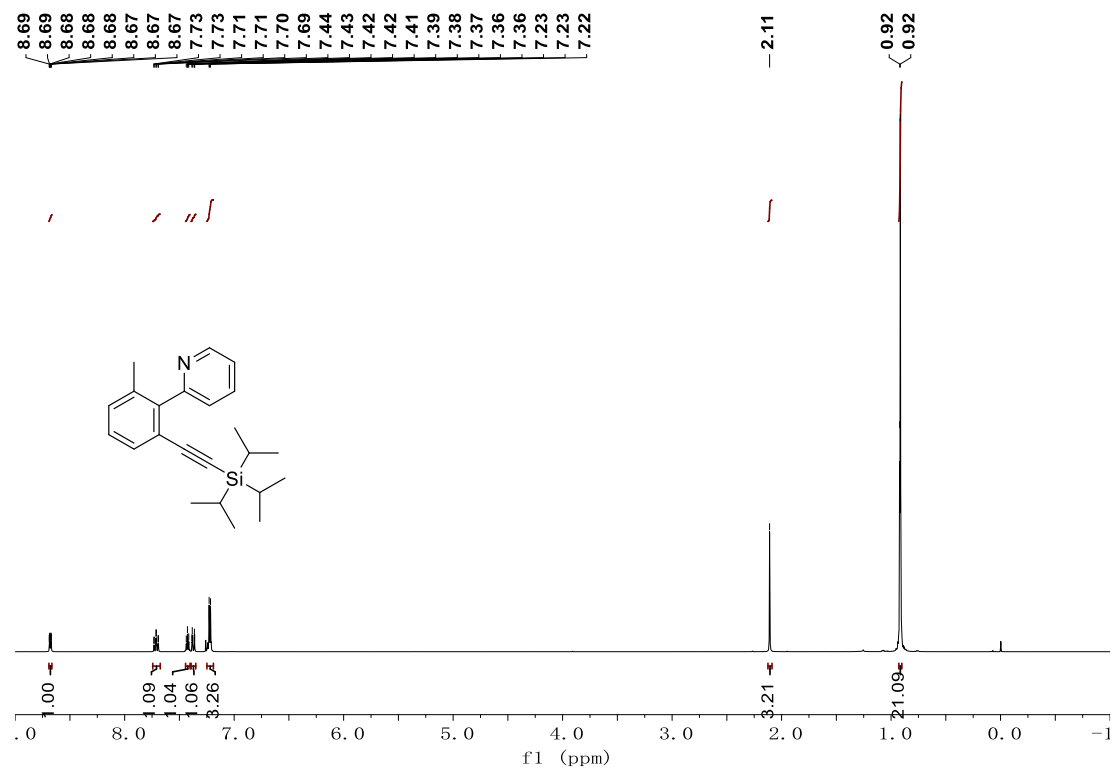
The  $^1\text{H}$  NMR spectrum of **20** (500 MHz,  $\text{CDCl}_3$ )



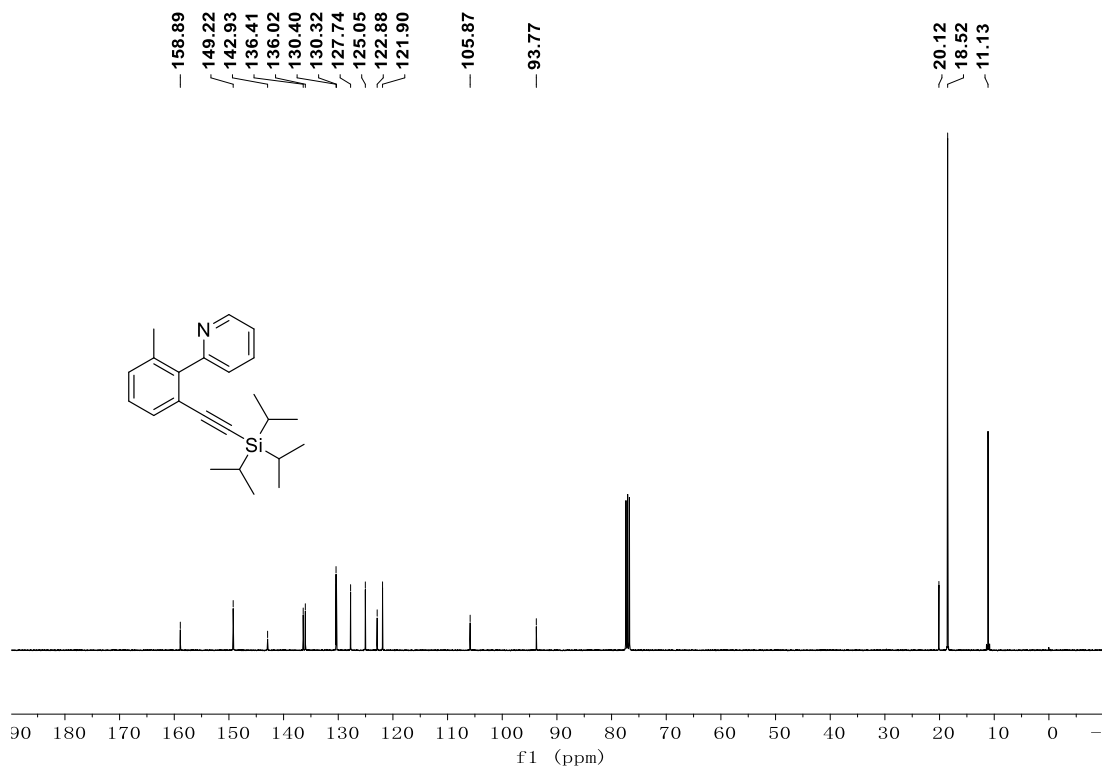
The  $^{13}\text{C}$  NMR spectrum of **20** (126 MHz,  $\text{CDCl}_3$ )



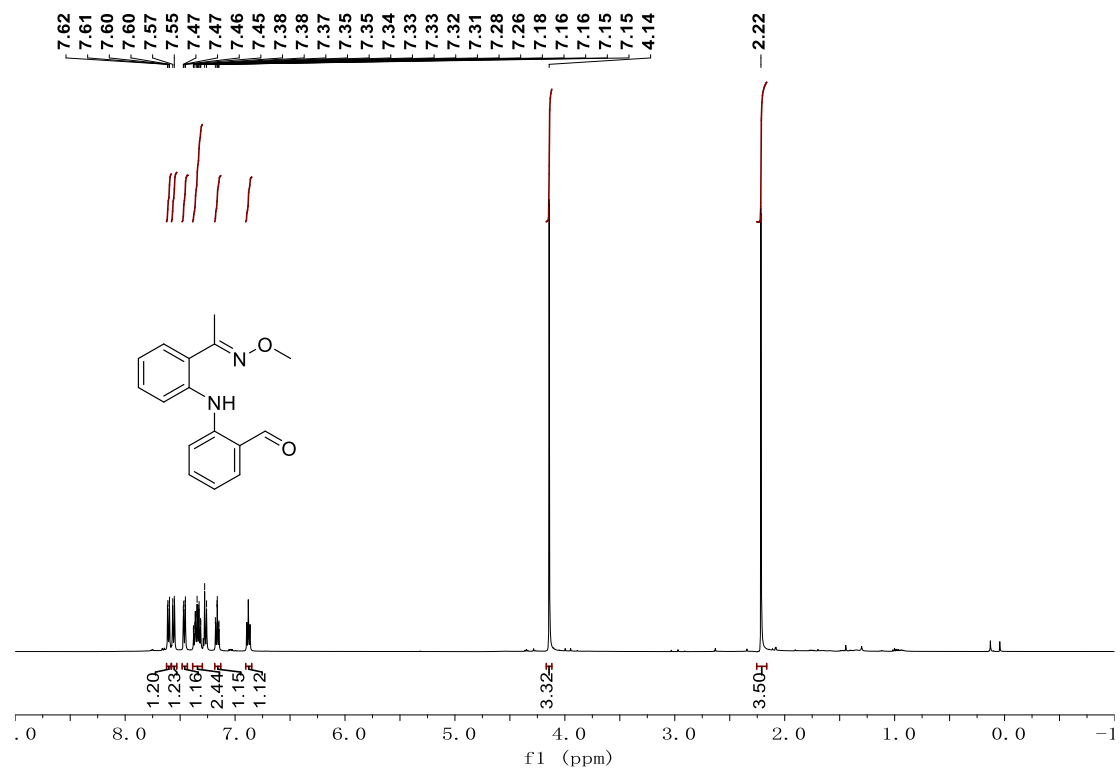
The  $^1\text{H}$  NMR spectrum of **23** (400 MHz,  $\text{CDCl}_3$ )



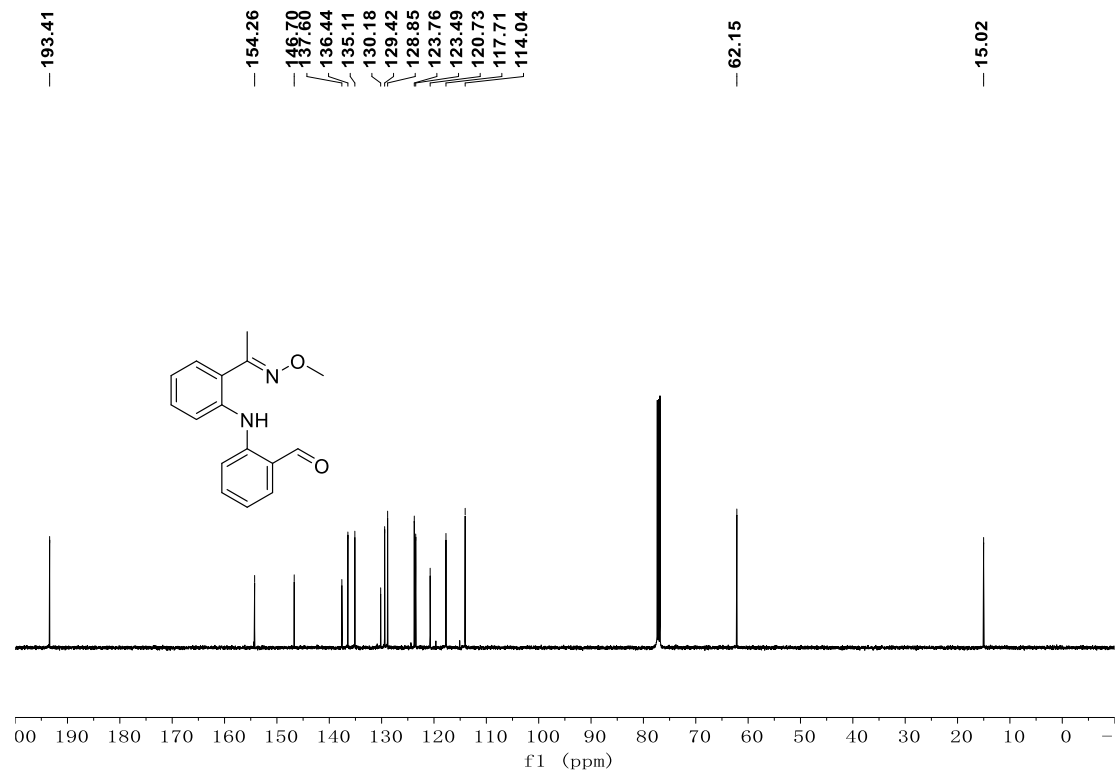
The  $^{13}\text{C}$  NMR spectrum of **23** (101 MHz,  $\text{CDCl}_3$ )



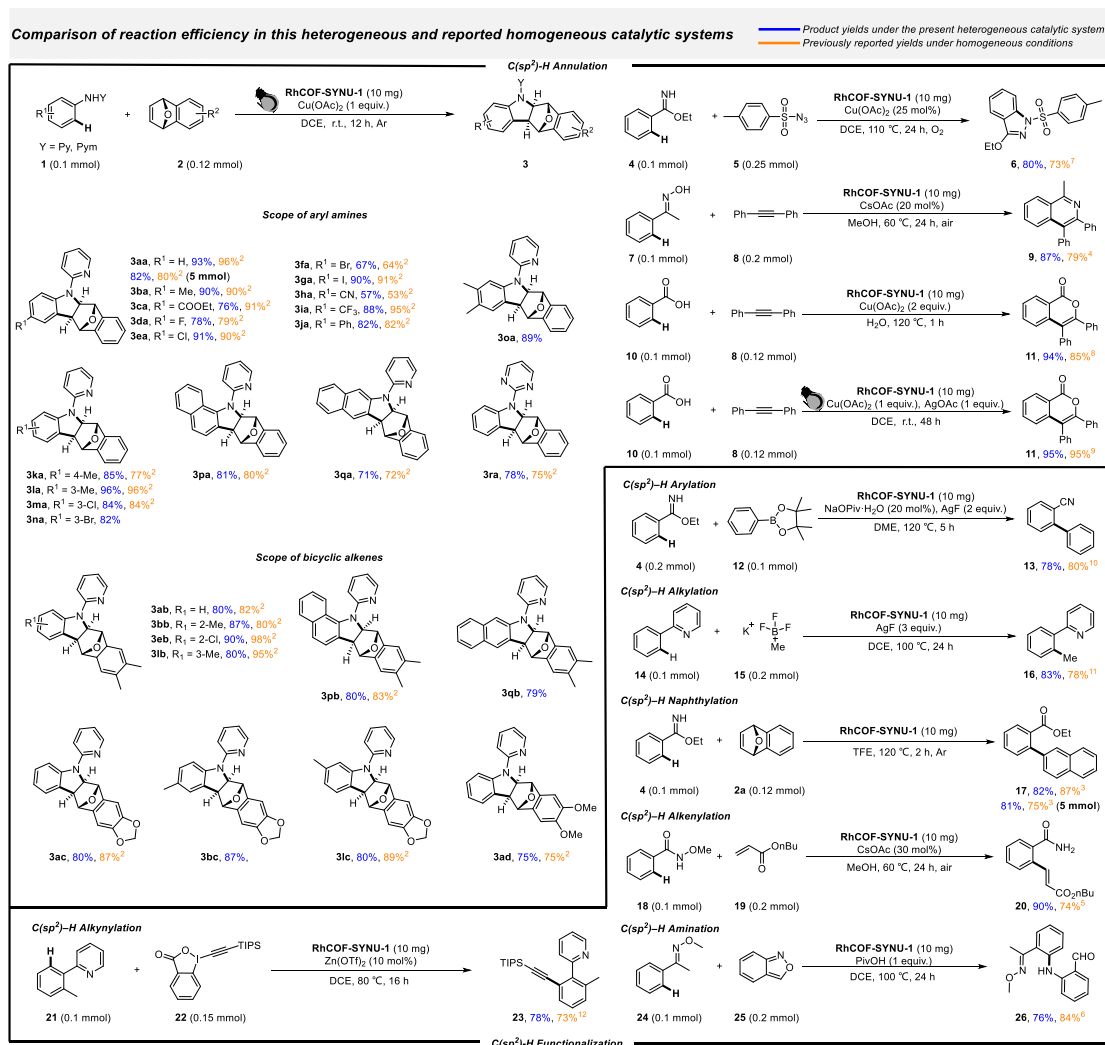
The  $^1\text{H}$  NMR spectrum of **26** (500 MHz,  $\text{CDCl}_3$ )



The  $^{13}\text{C}$  NMR spectrum of **26** (101 MHz,  $\text{CDCl}_3$ )



## XIV. Comparison of reaction efficiency



**Figure S14.** Comparison of reaction efficiency between our heterogeneous catalytic system and previously reported homogeneous cases

## XV. References

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