Supporting Information

Pyridine-Oriented Transannular C-H Functionalization of Arene

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1. General Information

All reactions were carried out under an argon atmosphere with magnetic stirring unless otherwise noted. DCM was distilled over CaH_2, THF was distilled over Na/benzophenone. Toluene and $CHCl_3$ were commercially purchased analytical pure reagent. Glassware was dried in an oven-dried before use. The PPh_3, K_2CO_3, $Pd(PPh_3)_4$, CF_3SO_3H, *n*-BuLi, various boric acids and boron esters, 2-bromonicotinaldehyde, 2-bromo-6-methylnicotinaldehyde, 2-bromo-5-chloronicotinaldehyde and 2-bromo-4-chloronicotinaldehyde are commercially available. All new compounds were characterized by NMR spectroscopy, IR spectroscopy, high-resolution mass spectroscopy (HRMS).

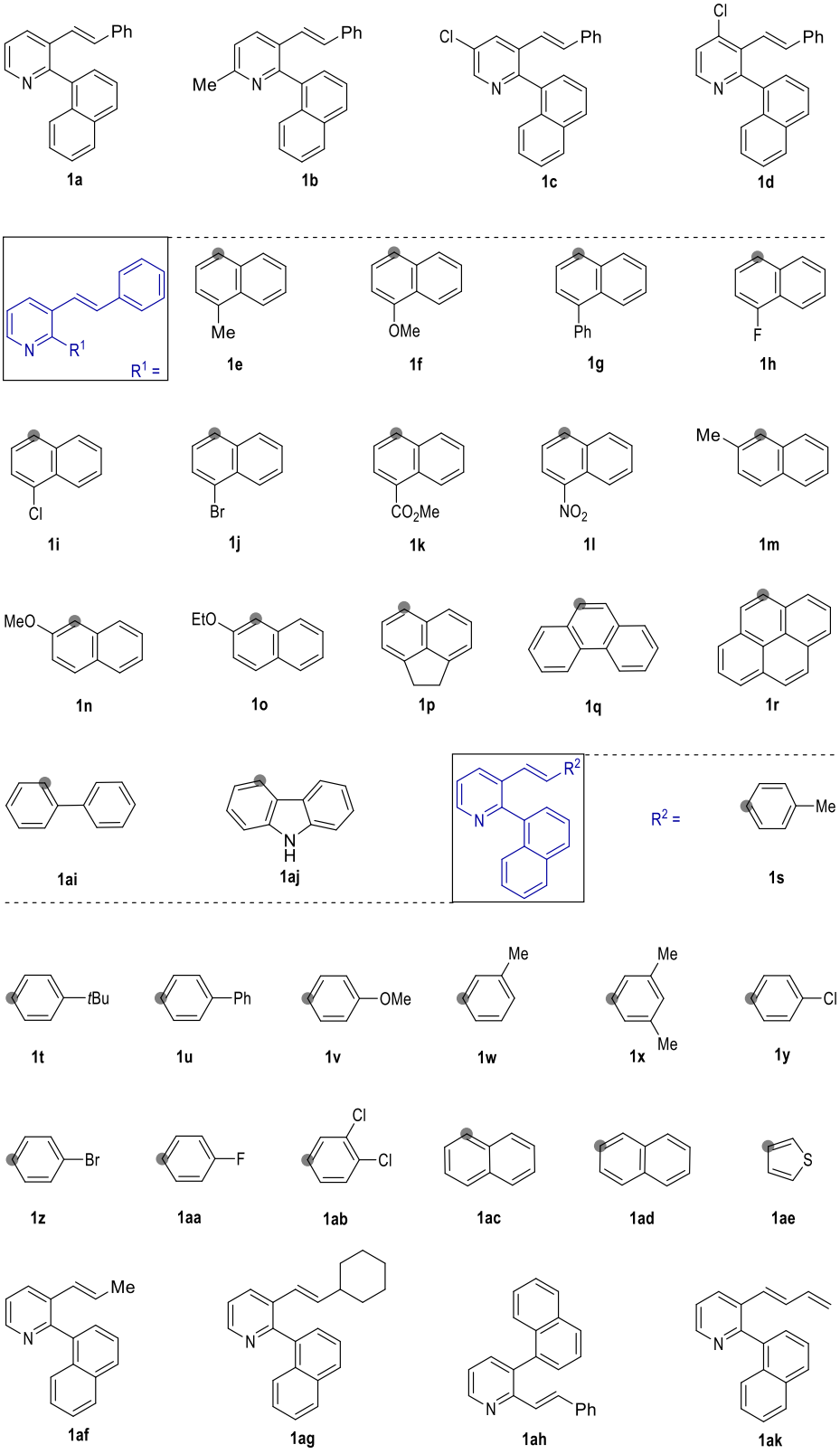
^1H, ^{13}C and ^{19}F NMR spectra were recorded on Bruker 400 spectrometer (^1H at 400 MHz, ^{13}C at 101 MHz and ^{19}F at 377 MHz). Chemical shifts for ^1H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of $SiMe_4$ (δ 0.00 singlet). ^1H NMR splitting patterns are designated as singlet (s), doublet (d), triplet (t), quartet (q), multiplet (m), doublet of doublets (dd), triplet of doublets (td). Coupling constants are reported as a *J* value in Hz. ^{13}C NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.00) and relative to the signal of chloroform-*d* (δ 77.00 triplet). ^{13}C NMR spectra were recorded on the same spectrometer with complete proton decoupling.

Infrared (IR) spectra were measured on Thermofisher Nicolet iN10 FM-IR spectrometer using KBr plates. High resolution mass spectral analysis (HRMS) was recorded on a FT-ICR (Fourier Transform-Ion Cyclotron Resonance) mass spectrometer by using electrospray ionization (ESI) techniques. Single crystal X-ray diffraction measurements were performed on an Agilent SuperNova-CCD X-Ray diffractometer.

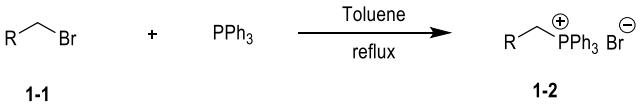
Column chromatographic was performed on 200-300 mesh silica gel and reactions were monitored by thin layer chromatography (TLC) using silica gel GF254 plates. Visualisation was by ultraviolet fluorescene (λ = 254 nm) and staining with phosphomolybdic acid.

2. The preparation of substrates

The preparation method of substrates **1a**[1], **1b**–**1ak** and their characterization data are provided as follows.



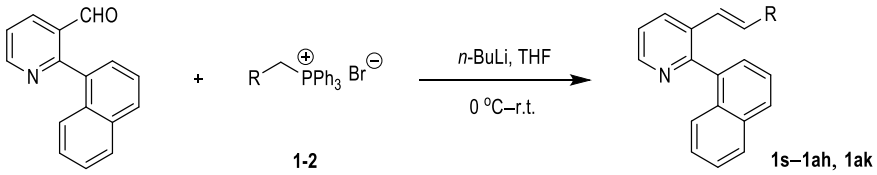
2.1 Procedure A: the synthesis of the phosphine ylides



1-1 1-2

The PPh_3 (20.0 mmol, 1.0 equiv.) was dissolved in toluene (20.0 mL) for a 100.0 mL round bottom flask, following benzyl bromide **1**-**1** (20.0 mmol, 1.0 equiv.) was added into the reaction system. The reaction mixture was refluxed for a period of time. Then, the reaction mixture was cooled to room temperature when the benzyl bromide **1**-**1** was completely consumed by TLC monitoring. The solid materials were isolated by filter through buchner funnel, washed with petroleum ether (PE) and dried under *vacuo* to afford the phosphine ylides[2] **1**-**2**.

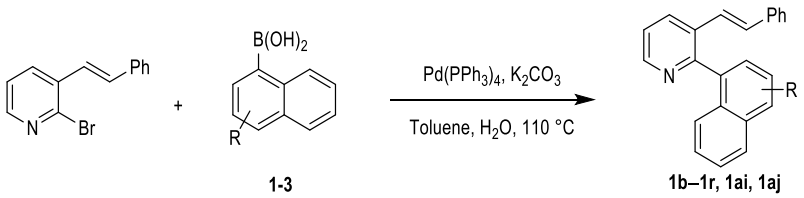
2.2 Procedure B: the synthesis of substrates 1s–1ah, 1ak



1-2 1s–1ah, 1ak

The phosphine ylides[2] **1-2** (3.3 mmol, 1.1 equiv.) was dissolved in dry THF (10.0 mL) for a 100.0 mL round bottom flask. The solution was cooled to 0 ℃, then the *n*-BuLi (1.5 mL, 2.5 M in hexane, 3.6 mmol, 1.2 equiv.) was added dropwise at 0 °C. After 20 minutes, the 2-(naphthalen-1-yl) nicotinaldehyde[3] (3.0 mmol, 1.0 equiv.) was dissolved in dry THF (10.0 mL) and added dropwise to the reaction mixture, the resulting mixture was warmed to room temperature and stirred. The reaction mixture was quenched with saturated aq. NH_4Cl solution when the 2-(naphthalen-1-yl) nicotinaldehyde[3] was completely consumed by TLC monitoring and extracted by DCM (10.0 mL × 3). The organic solution was combined and dried over anhydrous Na_2SO_4, then the organic solution was concentrated under *vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding substrates **1s**–**1ah**, **1ak**.

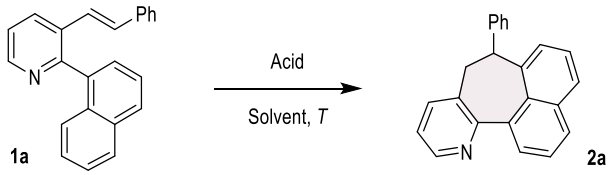
2.3 Procedure C: the synthesis of substrates 1b–1r, 1ai, 1aj



The tetrtriphenylphosphine palladium (2.0 mol%), potassium carbonate (10.0 mmol, 2.0 equiv.) and naphthylboric acid **1-3** (6.0 mmol, 1.2 equiv.) was dissolved in toluene (10.0 mL) under argon for a 100.0 mL oven-dried round bottom flask. Following the 2-bromo-3-styrylpyridine[4] (5.0 mmol, 1.0 equiv.) was dissolved in toluene (10.0 mL) and added to the above reaction, following the distilled water (3.0 ml) was added. Then the reaction mixture was heated to 110 ℃ and stirred at this temperature. The reaction mixture was cooled to room temperature when the raw materials were completely consumed by TLC monitoring and filtered, then combined the organic solution and dried over anhydrous Na_2SO_4. The organic solution was concentrated under *vacuo* and purified by column chromatography on silica gel to afford the corresponding substrates **1b**–**1r**, **1ai**, **1aj**.

3. General procedure for the synthesis of products 2

3.1 Table 1 The reaction condition screening[a]



Entry	Acid	Solvent	*T* (℃)	Yield (%)[b]
1	CH_3COOH	DCE	r.t.	N.R.
2	CF_3COOH	DCE	r.t.	N.R.
3	HCl	DCE	r.t.	N.R.
4	H_2SO_4	DCE	r.t.	23
5	CSA[c]	DCE	r.t.	N.R.
6	TsOH[d]	DCE	r.t.	N.R.
7	CH_3SO_3H	DCE	r.t.	10
8	CF_3SO_3H	DCE	r.t.	92
9	CF_3SO_3H	DCM	r.t.	39
10	**CF_3SO_3H**	**$CHCl_3$**	**r.t.**	**98**
11	CF_3SO_3H	Toluene	r.t.	57
12	CF_3SO_3H	EtOH	r.t.	N.R.
13	CF_3SO_3H	THF	r.t.	N.R.
14	CF_3SO_3H	DMF	r.t.	trace

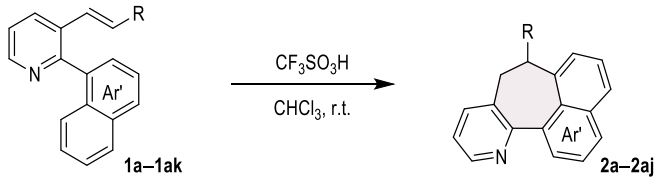
[a]All reactions of **1a** (0.3 mmol) and acid (0.3 mmol, 1.0 equiv.) were performed in solvent (0.5 mL) at room temperature for an oven-dried 10.0 mL Schlenk tube, the reactions were monitored by TLC until the **1a** was completely consumed. [b]Isolated yield, N.R. means no reaction. [c]CSA = Camphorsulfonic acid. [d]TsOH = *p*-Toluenesulfonic acid.

We initiated trials to assess the viability of our design by using 2-aryl-3-vinyl-pyridine and various acids dissolved in solvents. Initially, we selected 2-naphthyl-3-styryl-pyridine **1a** as the model substrate to investigate the possibility of reaction. The solution of 1a in DCE was reacted with the presence of acid (1.0 equiv.) at room temperature.

To screen the reaction conditions, we tested different acids, including CH_3COOH and CF_3COOH (entries 1 and 2, Table 1), these conditions resulted only in the formation of pyridine salts, with no progress in the transannular reactions. Next, we explored the effect of the HCl (entry 3, Table 1) for this reaction, but unfortunately, no product was observed. When we switched to H_2SO_4 (entry 4, Table 1) as the acid

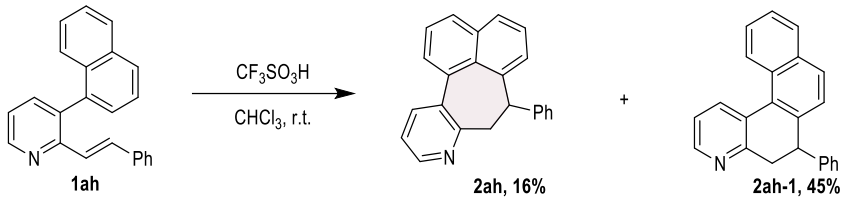
component, we were pleased to obtain the desired pyridine-containing fused seven-membered ring **2a** in 23% yield. Encouraged by this outcome, we explored the feasibility of sulfonic acids, such as CSA and TsOH (entries 5 and 6, Table 1), but were disappointed to find no product from these reactions. Subsequently, we tested CH_3SO_3H (entry 7, Table 1), which yielded only trace amounts of product. When we replaced CH_3SO_3H with CF_3SO_3H (entry 8, Table 1), we achieved an excellent yield of 92% for the expected product. In addition, we screened various solvents, including dichloromethane, chloroform, toluene, ethanol, tetrahydrofuran, and N,N-dimethylformamide (entries 9–14, Table 1). The results indicated that $CHCl_3$ was the optimal solvent for this reaction, affording the expected product 2a in almost quantitative yield (entry 10, Table 1). Consequently, we determined that the optimal reaction conditions involved the use of $CHCl_3$ as the solvent in the presence of CF_3SO_3H at room temperature.

3.2. Procedure D: the synthesis of products 2



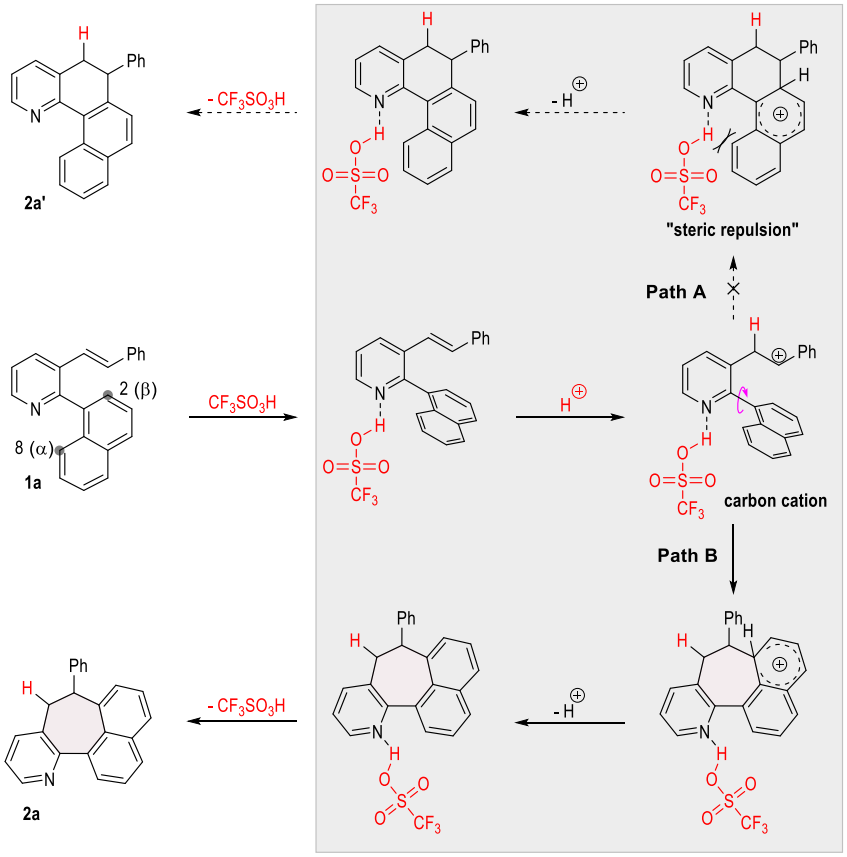
The pyridine **1a**–**1ak** (0.3 mmol, 1.0 equiv.) was dissolved in $CHCl_3$ (0.5 mL) for an oven-dried 10.0 mL Schlenk tube, following the CF_3SO_3H (0.3 mmol, 1.0 equiv.) was added and stirred at room temperature. (For reaction monitoring: the small amount of reaction mixture was taken through the dropper in a small container and neutralized with an appropriate amount of 10M NaOH solution, then extracted with ethyl acetate. The organic phase was monitored by TLC.) After the pyridine **1a**–**1ak** was completely consumed by TLC monitoring, the reaction mixture in the Schlenk tube was slowly poured into ice water, then neutralized with NaOH (10.0 M) solution and extracted with DCM (5.0 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel to afford the corresponding products **2a**–**2aj**. When the alkyl group was substituted with an alkene, the reaction system became a messy system, so the corresponding product **2ak** couldn't be obtained.

3.3. The interchanged experiment of substituents



The **1ah** (0.3 mmol, 1.0 equiv.) was dissolved in $CHCl_3$(0.5 mL) for an oven-dried 10.0 mL Schlenk tube, following the CF_3SO_3H (0.3 mmol, 1.0 equiv.) was added to the above solution and stirred at room temperature. According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 15 : 1) to afford the product **2ah** and **2ah-1** with yields of 16% and 45%, respectively..

4. The mechanistic proposal

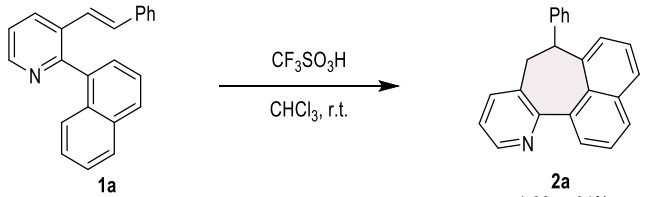


The regioselective electrophilic addition of alkenes can be attributed to the electron-deficient nature of the pyridine salt, which is disfavorable for the stability of the carbon cation. Consequently, this leads to the preferential formation of the benzyl carbon cation. Furthermore, the competitive homoannular reaction (Path A) may be

hindered by the spatial repulsive force arising from the nitrogen-hydrogen bond with the arene ring, prompting a dynamic rotation to favor the conformationally stable transannular reaction (Path B). Additionally, the electrophilic substitution reactivity at the α-position on naphthalene is generally higher than at the β-position. Hence, the transannular Friedel-Crafts alkylation can be efficiently achieved through the orientation facilitated by the pyridine group. Additionally, the electrophilic substitution reactivity at the α-position on naphthalene is generally higher than at the β-position. Hence, the transannular Friedel-Crafts alkylation can be efficiently achieved through the orientation facilitated by the pyridine group.

5. The synthetic transformations of products 2

5.1. Gram-scale syntheses

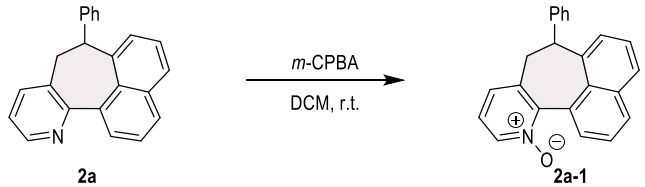


1a
2.0 g, 6.5 mmol

2a
1.62 g, 81%

The **1a** (2.0 g, 6.5 mmol, 1.0 equiv.) was dissolved in $CHCl_3$(1.0 mL) for an oven-dried 50.0 mL round bottom flask, following the CF_3SO_3H (1.2 ml, 13.0 mmol, 2.0 equiv.) was added to the above solution and stirred at room temperature. According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to afford the product **2a** in 81% yield.

5.2. The *m*-CPBA oxidation of 2a to 2a-1

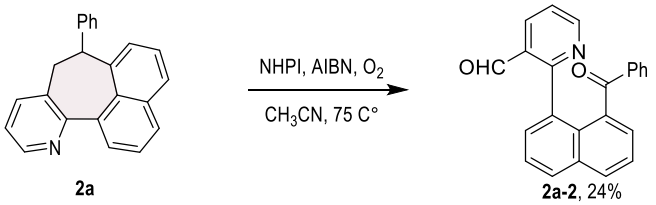


2a **2a-1**

The **2a** (100.0 mg, 0.32 mmol, 1.0 equiv.), *m*-CPBA (113.0 mg, 0.64 mmol, 2.0 equiv.) were dissolved in DCM (2.0 mL) for an oven-dried 10.0 mL Schlenk tube and stirred at room temperature. The reaction mixture was quenched with saturated aq. $NaHCO_3$ solution when the **2a** was completely consumed by TLC monitoring and extracted by DCM (5.0 mL × 3). Then the combined organic phase was dried over

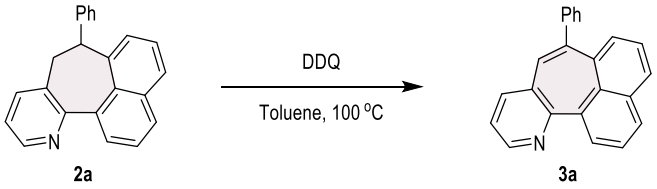
anhydrous Na_2SO_4, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (PE : EA = 1 : 1) to afford the corresponding product **2a-1** in 93% yield.

5.3. The oxidation 2a to diketone 2a-2



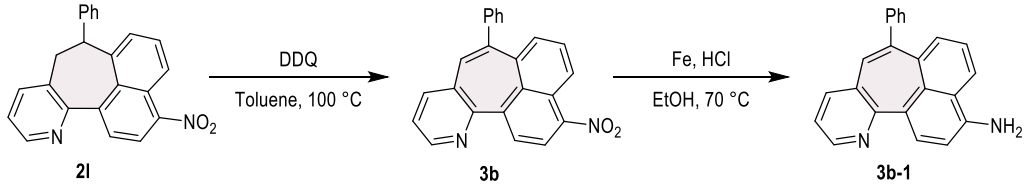
The **2a** (0.35g, 1.0 mmol, 1.0 equiv.), NHPI (0.23g, 1.0 mmol, 1.0 equiv.) and AIBN (8.0 mL) were added to an oven-dried 10 mL Schlenk tube under argon atmosphere and was dissolved in CH_3CN (2.0 mL). The reaction mixture was heated to 75 ℃ (oil bath) for 3h. Then the mixture was cooled to room temperature and handled with an appropriate amount of 0.3 M H_2SO_4 solution for 2h. After completion, the solvent was concentrated in *vacuo*, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to give the product **2a-2** in 24% yield.

5.4. The DDQ oxidation of 2a to 3a



The **2a** (100.0 mg, 0.32 mmol, 1.0 equiv.), DDQ (70.0 mg, 0.30 mmol, 1.0 equiv.) were dissolved in toluene (2.0 mL) for an oven-dried 10.0 mL Schlenk tube. The reaction mixture was heated to 100 ℃ and stirred at this temperature. Then the mixture was cooled to room temperature when the **2a** was completely consumed by TLC monitoring and concentrated under *vacuo*. The residue was purified by column chromatography on silica gel (PE : EA = 50 : 1) to obtain the product **3a** in 57% yield.

5.5. The transformations of 2l



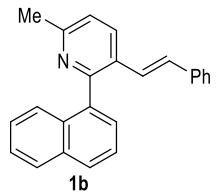
Step 1: The compound **2l** (0.35 g, 1.0 mmol, 1.0 equiv.), DDQ (0.23 g, 1.0 mmol, 1.0 equiv.) were dissolved in toluene (10.0 mL) for an oven-dried 50.0 mL round bottom flask. The reaction mixture was heated to 100 ℃ and stirred for a period of time. The mixture was cooled to room temperature when the **2l** was completely consumed by TLC monitoring and concentrated under *vacuo*, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to give the product **3b** in 45% yield.

Step 2: The activated iron powder (32.0 mg, 0.57 mmol, 2.0 equiv.) and **3b** (100.0 mg, 0.28 mmol, 1.0 equiv.) were added in EtOH (2.0 mL) for an oven-dried 10.0 mL Schlenk tube. The reaction mixture was heated to 70 ℃. Then, the HCl (37.0 μL, content 38%, 1.14 mmol, 4.0 equiv.) was added dropwise to the mixture and stirred at 70 ℃. The reaction mixture was cooled to room temperature when the **3b** was completely consumed by TLC monitoring, then quenched with saturated aq. NaOH solution and extracted by DCM (5.0 mL × 3). The combined organic phase was dried over anhydrous $MgSO_4$, filtered and concentrated in *vacuo*. The residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to afford the corresponding product **3b-1** in 56% yield.

6. Characterization data for key compounds

6.1. Characterization data for substrates 1b–1ak

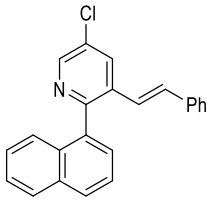
(*E*)-6-methyl-2-(naphthalen-1-yl)-3-styrylpyridine (**1b**)



1b

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1b** as a colorless amorphous solid in 82% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.05 (d, *J* = 8.0 Hz, 1H), 7.92 – 7.87 (m, 2H), 7.57 – 7.52 (m, 2H), 7.48 – 7.44 (m, 2H), 7.39 – 7.35 (m, 1H), 7.25 – 7.21 (m, 1H), 7.20 – 7.10 (m, 5H), 7.00 (d, *J* = 16.0 Hz, 1H), 6.69 (d, *J* = 16.0 Hz, 1H), 2.64 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.1, 156.9, 137.5, 137.0, 133.8, 133.0, 131.9, 129.8, 129.6, 128.6, 128.5, 128.2, 127.8, 127.7, 126.5, 126.3, 126.0, 125.9, 125.3, 122.5, 24.5; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1599.

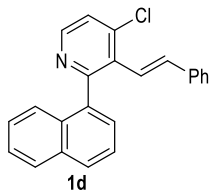
(*E*)-5-chloro-2-(naphthalen-1-yl)-3-styrylpyridine (**1c**)



1c

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 50 : 1) to provide the product **1c** as a colorless amorphous solid in 93% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (d, *J* = 2.4 Hz, 1H), 7.91 (q, *J* = 8.0 Hz, 2H), 7.66 (d, *J* = 2.4 Hz, 1H), 7.60 (d, *J* = 8.0 Hz, 1H), 7.52 – 7.40 (m, 4H), 7.29 – 7.24 (m, 3H), 7.21 – 7.19 (m, 2H), 6.46 (d, *J* = 12.4 Hz, 1H), 6.09 (d, *J* = 12.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.2, 146.9, 136.7, 136.4, 135.8, 134.0, 133.8, 132.7, 131.4, 130.2, 129.0, 128.7, 128.6, 128.4, 127.9, 127.5, 126.5, 126.0, 125.9, 125.4, 125.1; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NCl$, 342.1050, found 342.1053.

(*E*)-4-chloro-2-(naphthalen-1-yl)-3-styrylpyridine (**1d**)

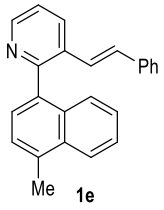


1d

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 50 : 1) to provide the product **1d** as a green oily liquid in 84% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.54 (d, *J* = 5.2 Hz, 1H), 7.93 – 7.88 (m, 2H), 7.58 – 7.42 (m, 6H), 7.20 – 7.14 (m, 3H), 7.03 – 6.90 (m, 2H), 6.88 (d, *J* = 16.4 Hz,

1H), 6.62 (d, *J* = 16.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.3, 147.6, 143.5, 137.8, 136.7, 136.6, 133.7, 132.0, 131.3, 128.8, 128.5, 128.4, 128.1, 127.4, 126.5, 126.5, 126.0, 125.4, 125.2, 124.1, 122.0; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}N$, 308.1439, found 308.1441; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NCl$, 342.1050, found 342.1053.

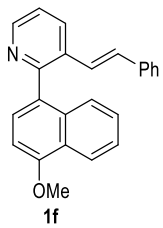
(*E*)-2-(4-methylnaphthalen-1-yl)-3-styrylpyridine (**1e**)



1e

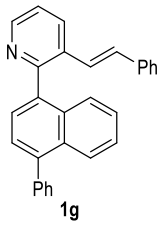
According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1e** as a yellow amorphous solid in 74% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.79 – 7.71 (m, 2H), 7.59 – 7.54 (m, 1H), 7.51 – 7.41 (m, 3H), 7.34 – 7.26 (m, 5H), 7.15 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.46 (d, *J* = 12.0 Hz, 1H), 6.23 (d, *J* = 12.0 Hz, 1H), 2.81 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 148.3, 137.5, 136.5, 136.0, 135.1, 132.9, 131.7, 131.4, 128.9, 128.5, 127.7, 127.5, 127.2, 126.4, 126.1, 126.0, 125.8, 124.5, 121.9, 19.7; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1599.

(*E*)-2-(4-methoxynaphthalen-1-yl)-3-styrylpyridine (**1f**)



1f

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1f** as a yellow amorphous solid in 79% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.40 – 8.32 (dd, J_1 = 8.0 Hz, J_2 =1.2 Hz, 1H), 7.70 – 7.54 (m, 2H), 7.51 – 7.42 (m, 3H), 7.28 – 7.22 (m, 5H), 7.12 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.87 (d, *J* = 8.0 Hz, 1H), 6.44 (d, *J* = 12.0 Hz, 1H), 6.20 (d, *J* = 12.0 Hz, 1H), 4.04 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 155.8, 148.2, 137.5, 136.5, 133.0, 132.5, 131.1, 130.0, 128.8, 128.4, 127.9, 127.8, 127.4, 126.8, 125.7, 125.5, 125.2, 122.2, 121.6, 103.2, 55.6; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1548.



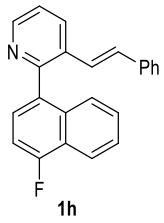
1g

(*E*)-2-(4-phenylnaphthalen-1-yl)-3-styrylpyridine (**1g**)

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product

1g as a colorless oily liquid in 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (d, *J* = 4.8 Hz, 1H), 8.08 – 7.98 (m, 1H), 7.76 – 7.69 (m, 2H), 7.58 – 7.41 (m, 9H), 7.28 – 7.20 (m, 5H), 7.14 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 6.28 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 148.4, 141.0, 140.8, 137.6, 137.2, 136.5, 132.9, 132.1, 131.9, 131.7, 130.2, 128.9, 128.5, 128.4, 127.6, 127.5, 127.4, 127.0, 126.5, 126.3, 126.2, 126.1, 126.0, 122.0; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{22}N$, 384.1752, found 384.1754.

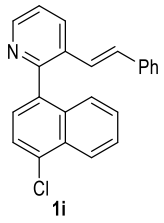
(*E*)-2-(4-fluoronaphthalen-1-yl)-3-styrylpyridine (**1h**)



1h

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1h** as a yellow oily liquid in 75% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.70 – 7.60 (m, 2H), 7.51 – 7.47 (m, 1H), 7.46 – 7.37 (m, 2H), 7.23 – 7.14 (m, 6H), 7.11 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.39 (d, *J* = 12.0 Hz, 1H), 6.13 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 160.2, 157.4 (d, *J* = 27.6 Hz), 148.3, 137.7 (d, *J* = 4.3 Hz), 136.3, 133.7, 133.1,133.0 (d, *J* = 4.6 Hz), 131.7, 128.8, 128.5, 127.6 (d, *J* = 3.6 Hz), 127.5, 127.3 (d, *J* = 5.0 Hz), 126.2, 125.8 (d, *J* = 2.8 Hz), 124.0 (d, *J* = 16.5 Hz), 122.1, 120.8 (d, *J* = 5.6 Hz), 109.0, 108.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -122.00; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NF$, 326.1345, found 326.1349.

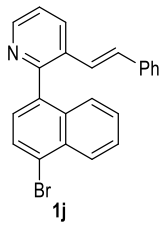
(*E*)-2-(4-chloronaphthalen-1-yl)-3-styrylpyridine (**1i**)



1i

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1i** as an orange amorphous solid in 79% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 4.8 Hz, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.68 – 7.65 (m, 1H), 7.62 – 7.56 (m, 2H), 7.48 – 7.43 (m, 1H), 7.42 – 7.37 (m, 2H), 7.22 – 8.15 (m, 5H), 7.06 (d, *J* = 16.0 Hz, 1H), 6.72 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.6, 148.3, 136.6, 136.6, 132.9, 132.7, 132.5, 131.4, 131.0, 128.6, 128.1, 127.6, 127.2, 127.1, 126.6, 126.4, 125.6, 124.8, 124.8, 123.0; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NCl$, 342.1050, found 342.1053.

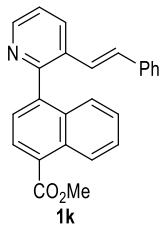
(*E*)-2-(4-bromonaphthalen-1-yl)-3-styrylpyridine (**1j**)



1j

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20: 1) to provide the product **1j** as a yellow amorphous solid in 72% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (d, *J* = 4.8 Hz, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.79 (d, *J* = 7.6 Hz, 1H), 7.66 (d, *J* = 8.0 Hz, 1H), 7.61 (d, *J* = 8.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 1H), 7.41 (t, *J* = 7.6 Hz, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 7.22 – 7.14 (m, 5H), 7.12 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.38 (d, *J* = 12.0 Hz, 1H), 6.10 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 148.3, 137.7, 137.7, 136.3, 133.0, 132.8, 132.2, 132.0, 129.3, 128.8, 128.5, 127.8, 127.6, 127.5, 127.4, 127.1, 127.0, 126.3, 123.5, 122.2; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NBr$, 386.0544, found 386.0547.

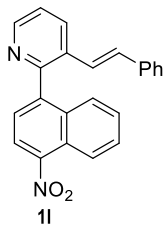
methyl (*E*)-4-(3-styrylpyridin-2-yl)-1-naphthoate (**1k**)



1k

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1k** as a colorless oily liquid in 77% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.02 (d, *J* = 8.4 Hz, 1H), 8.66 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.22 (d, *J* = 7.6 Hz, 1H), 7.70 (dd, J_1 = 7.6 Hz, J_2 =1.6 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.61 (ddd, J_1 = 8.4 Hz, J_2 =6.8 Hz, J_3 =1.4 Hz, 1H), 7.50 (d, *J* = 7.6 Hz, 1H), 7.45 (ddd, J_1 = 8.4 Hz, J_2 =6.8 Hz, J_3 =1.4 Hz, 1H), 7.25 – 7.13 (m, 6H), 6.40 (d, *J* = 12.4 Hz, 1H), 6.11 (d, *J* = 12.4 Hz, 1H), 4.01 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 167.9, 157.3, 148.3, 142.5, 137.6, 136.2, 132.9, 132.1, 131.9, 131.7, 129.4, 128.7, 128.5, 127.6, 127.6, 127.5, 126.7, 126.6, 126.2, 126.1, 126.0, 122.4, 52.2; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}NO_2$, 366.1494, found 366.1498.

(*E*)-2-(4-nitronaphthalen-1-yl)-3-styrylpyridine (**1l**)

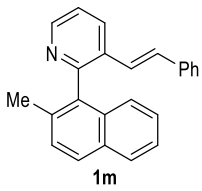


1l

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1l** as a brown amorphous solid in 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 8.61 – 8.52 (m, 1H), 8.17 (d, *J* = 8.0 Hz, 1H), 7.73 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.69 – 7.64 (m, 2H), 7.51 – 7.47 (m, 1H), 7.46 (d, *J* = 8.0 Hz, 1H), 7.25 – 7.18 (m, 4H), 7.13

– 7.06 (m, 2H), 6.41 (d, *J* = 12.0 Hz, 1H), 6.11 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.1, 148.4, 146.7, 144.1, 137.9, 136.0, 133.0, 132.8, 132.5, 129.2, 128.6, 128.5, 127.8, 127.6, 126.5, 126.2, 125.8, 125.4, 123.3, 123.0, 122.8; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}N_2O_2$, 353.1290, found 353.1294.

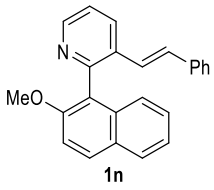
(*E*)-2-(2-methylnaphthalen-1-yl)-3-styrylpyridine (**1m**)



1m

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1m** as a colorless oily liquid in 69% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.71 (d, *J* = 4.8 Hz, 1H), 7.85 (t, *J* = 8.0 Hz, 2H), 7.72 (d, *J* = 8.0 Hz, 1H), 7.46 – 7.33 (m, 3H), 7.28 – 7.21 (m, 6H), 7.13 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.39 (d, *J* = 12.4 Hz, 1H), 6.00 (d, *J* = 12.4 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 148.8, 137.1, 136.5, 135.7, 133.9, 132.8, 132.1, 132.1, 132.0, 128.7, 128.7, 128.5, 128.2, 128.0, 127.6, 126.4, 126.3, 125.1, 125.0, 121.8, 20.1; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1598.

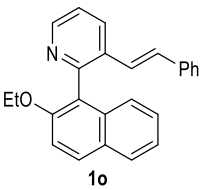
(*E*)-2-(2-methoxynaphthalen-1-yl)-3-styrylpyridine (**1n**)



1n

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1n** as a colorless oily liquid in 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (dd, J_1 = 4.8 Hz, J_2 =2.0 Hz, 1H), 7.95 (d, *J* = 8.8 Hz, 1H), 7.86 – 7.84 (m, 1H), 7.64 (dd, *J* = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.40 – 7.34 (m, 3H), 7.33 – 7.28 (m, 3H), 7.27 – 7.22 (m, 3H), 7.14 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.42 (d, *J* = 12.0 Hz, 1H), 6.11 (d, *J* = 12.0 Hz, 1H), 3.82 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.8, 154.5, 148.5, 137.2, 136.6, 134.2, 133.0, 131.4, 130.2, 129.1, 129.0, 128.3, 128.0, 127.4, 127.3, 126.9, 124.4, 123.6, 122.7, 121.8, 113.1, 56.2; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1548.

(*E*)-2-(2-ethoxynaphthalen-1-yl)-3-styrylpyridine (**1o**)

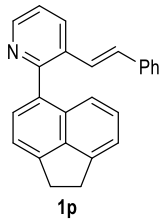


1o

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1o** as a colorless oily liquid in 86% yield. **^{1}H NMR (400**

MHz, $CDCl_3$) δ 8.64 (dd, J_1 = 4.8 Hz, J_2 =2.0 Hz, 1H), 7.88 (d, J = 9.2 Hz, 1H), 7.84 – 7.78 (m, 1H), 7.62 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.33 – 7.29 (m, 3H), 7.27 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 2H), 7.24 – 7.16 (m, 4H), 7.08 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.39 (d, J = 12.0 Hz, 1H), 6.11 (d, J = 12.0 Hz, 1H), 4.13 – 4.09 (m, 2H), 1.22 (t, J = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.0, 153.9, 148.4, 137.1, 136.6, 133.9, 133.1, 131.5, 130.0, 129.1, 129.1, 128.2, 128.0, 127.4, 127.3, 126.8, 124.4, 123.6, 123.4, 121.7, 114.7, 64.9, 15.0; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{22}NO$, 352.1701, found 352.1705.

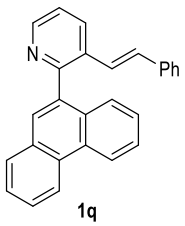
(*E*)-2-(1,2-dihydroacenaphthylen-5-yl)-3-styrylpyridine (**1p**)



1p

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1p** as a yellow amorphous solid in 92% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (dd, J_1 = 4.4 Hz, J_2 =1.6 Hz, 1H), 7.65 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 1H), 7.55 – 7.46 (m, 2H), 7.39 – 7.35 (m, 1H), 7.31 – 7.17 (m, 7H), 7.06 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.42 (d, J = 12.0 Hz, 1H), 6.22 (d, J = 12.0 Hz, 1H), 3.40 (s, 4H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0, 148.3, 146.9, 146.1, 139.6, 137.6, 136.6, 133.0, 132.6, 131.1, 130.0, 129.7, 128.9, 128.5, 128.3, 128.0, 127.4, 121.6, 121.0, 119.4, 118.7, 30.5, 30.3; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}N$, 334.1596, found 334.1597.

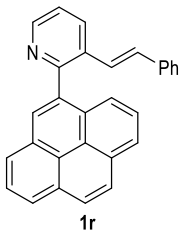
(*E*)-2-(phenanthren-1-yl)-3-styrylpyridine (**1q**)



1q

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1q** as a yellow oily liquid in 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 8.4 Hz, 1H), 8.57 (d, J = 3.2 Hz, 1H), 7.74 (d, J = 8.0 Hz, 1H), 7.63 – 7.60 (m, 2H), 7.59 – 7.46 (m, 4H), 7.42 – 7.38 (m, 1H), 7.17 – 7.06 (m, 6H), 6.29 (d, J = 12.0 Hz, 1H), 6.12 (d, J = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 148.3, 137.6, 136.5, 136.3, 133.1, 131.8, 131.3, 130.7, 130.5, 129.0, 128.8, 128.5, 128.4, 127.5, 127.2, 127.0, 126.8, 126.7, 126.6, 126.5, 123.0, 122.6, 122.1; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$, 358.1596, found 358.1599.

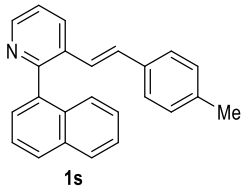
(*E*)-2-(pyren-1-yl)-3-styrylpyridine (**1r**)



1r

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1r** as a yellow amorphous solid in 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.74 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.21 – 8.11 (m, 3H), 8.07 – 7.93 (m, 6H), 7.75 (dd, J_1 = 7.6 Hz, J_2 =1.2 Hz, 1H), 7.28 – 7.17 (m, 6H), 6.35 (d, *J* = 12.4 Hz, 1H), 6.13 (d, *J* = 12.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.5, 148.3, 137.7, 136.4, 134.8, 133.3, 131.7, 131.4, 131.3, 130.9, 129.1, 128.8, 128.5, 127.9, 127.9, 127.6, 127.6, 127.4, 126.0, 125.4, 125.2, 125.0, 124.9, 124.8, 124.6, 122.1; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{20}N$, 382.1596, found 382.1598.

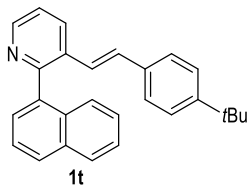
(*E*)-3-(4-methylstyryl)-2-(naphthalen-1-yl)pyridine (**1s**)



1s

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1s** as a colorless amorphous solid in 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (d, *J* = 4.4 Hz, 1H), 7.92 (d, *J* = 6.8 Hz, 2H), 7.75 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.0 Hz, 1H), 7.57 – 7.47 (m, 3H), 7.46 – 7.39 (m, 1H), 7.21 – 7.13 (m, 3H), 7.08 (d, *J* = 8.0 Hz, 2H), 6.41 (d, *J* = 12.0 Hz, 1H), 6.13 (d, *J* = 12.0 Hz, 1H), 2.35 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 148.1, 137.6, 137.5, 137.3, 133.8, 133.5, 133.1, 131.5, 131.5, 129.1, 128.7, 128.7, 128.3, 127.4, 126.6, 126.3, 125.8, 125.7, 125.2, 121.9, 21.3; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1599.

(*E*)-3-(4-(tert-butyl)styryl)-2-(naphthalen-1-yl)pyridine (**1t**)

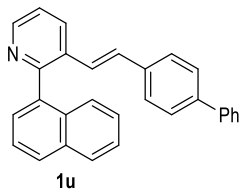


1t

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1t** as a brown amorphous solid in 94% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 – 8.58 (m, 1H), 7.88 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.63 (d, *J* = 8.0 Hz, 1H), 7.60 – 7.40 (m, 3H), 7.41 – 7.37 (m, 1H), 7.28 – 7.23 (m, 2H), 7.19 – 7.13 (m, 3H), 6.36 (d, *J* = 12.0 Hz, 1H), 6.11 (d, *J* = 12.0 Hz, 1H), 1.31 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0, 150.6, 148.1, 137.6, 137.6, 133.8, 133.4, 133.2, 131.5, 131.3, 128.6,

128.5, 128.3, 127.4, 126.7, 126.3, 125.8, 125.7, 125.3, 125.1, 121.9, 34.6, 31.2; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{26}N$, 364.2065, found 364.2065.

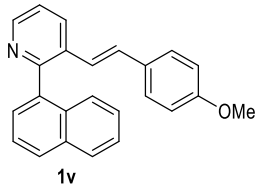
(*E*)-3-(2-([1,1'-biphenyl]-4-yl)vinyl)-2-(naphthalen-1-yl)pyridine (**1u)**



1u

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1u** as a green amorphous solid in 90% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (dd, J_1 = 4.4 Hz, J_2 =1.2 Hz, 1H), 7.97 – 7.92 (m, 2H), 7.81 (d, J = 8.0 Hz, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.63 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 2H), 7.58 – 7.51 (m, 5H), 7.50 – 7.41 (m, 3H), 7.40 – 7.31 (m, 3H), 7.21 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.47 (d, J = 12.2 Hz, 1H), 6.23 (d, J = 12.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 148.3, 140.5, 140.2, 137.6, 135.4, 133.8, 133.0, 131.5, 131.1, 129.3, 128.9, 128.8, 128.7, 128.3, 127.6, 127.5, 127.5, 127.1, 126.9, 126.4, 125.9, 125.7, 125.2, 122.0; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{22}N$, 384.1752, found 384.1754.

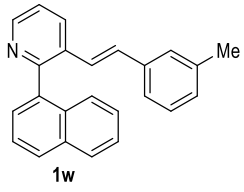
(*E*)-3-(4-methoxystyryl)-2-(naphthalen-1-yl)pyridine (**1v**)



1v

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1v** as a colorless oily liquid in 75% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.63 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 7.89 (d, J = 8.0 Hz, 2H), 7.73 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.62 (d, J = 8.0 Hz, 1H), 7.52 – 7.44 (m, 3H), 7.41 – 7.22 (m, 1H), 7.19 – 7.12 (m, 3H), 6.80 – 6.74 (m, 2H), 6.34 (d, J = 12.0 Hz, 1H), 6.05 (d, J = 12.0 Hz, 1H), 3.78 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.9, 158.1, 148.0, 137.6, 137.5, 133.8, 133.2, 131.5, 131.0, 130.1, 128.9, 128.6, 128.3, 127.4, 126.2, 125.8, 125.7, 125.7, 125.1, 121.9, 113.8, 55.2; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1548.

(*E*)-3-(3-methylstyryl)-2-(naphthalen-1-yl)pyridine (**1w**)

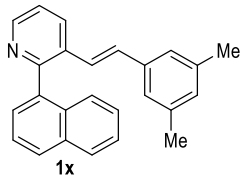


1w

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1w** as a colorless oily liquid in 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (dd, J_1 = 4.8, J_2 =1.8 Hz, 1H), 7.95 – 7.90

(m, 2H), 7.73 (dd, J_1 = 8.0, J_2 =1.8 Hz, 1H), 7.67 (d, J = 8.0 Hz, 1H), 7.57 – 7.48 (m, 3H), 7.46 – 7.21 (m, 1H), 7.19 – 7.13 (m, 2H), 7.07 – 7.04 (m, 3H), 6.42 (d, J = 12.2 Hz, 1H), 6.17 (d, J = 12.2 Hz, 1H), 2.30 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 148.2, 138.0, 137.6, 137.6, 136.4, 133.8, 132.9, 131.7, 131.5, 129.6, 128.7, 128.3, 128.2, 127.5, 127.2, 126.3, 125.8, 125.8, 125.7, 125.1, 121.9, 21.4; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1599.

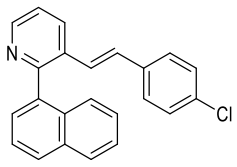
(*E*)-3-(3,5-dimethylstyryl)-2-(naphthalen-1-yl)pyridine (**1x**)



1x

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1x** as a colorless amorphous solid in 93% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (dd, J_1 = 4.8 Hz, J_2 =1.8 Hz, 1H), 7.97 – 7.91 (m, 2H), 7.78 (dd, J_1 = 8.0 Hz, J_2 =1.8 Hz, 1H), 7.71 (d, J = 8.0 Hz, 1H), 7.62 – 7.54 (m, 2H), 7.54 – 7.44 (m, 2H), 7.18 (dd, J_1 = 8.0 Hz, J_2 =4.8 Hz, 1H), 6.89 (d, J = 4.0 Hz, 3H), 6.41 (d, J = 12.0 Hz, 1H), 6.18 (d, J = 12.0 Hz, 1H), 2.27 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.0, 148.1, 137.9, 137.7, 137.6, 136.3, 133.8, 133.1, 131.9, 131.6, 129.2, 128.7, 128.3, 127.6, 127.0, 126.6, 126.3, 125.9, 125.8, 125.2, 121.8, 21.3; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{22}N$, 336.1752, found 336.1754.

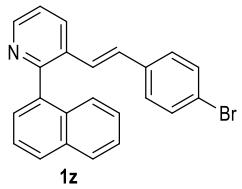
(*E*)-3-(4-chlorostyryl)-2-(naphthalen-1-yl)pyridine (**1y**)



1y

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1y** as a colorless amorphous solid in 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.70 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.13 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.96 (t, J = 8.4 Hz, 2H), 7.62 – 7.55 (m, 2H), 7.53 – 7.47 (m, 2H), 7.45 – 7.37 (m, 2H), 7.17 (d, J = 8.4 Hz, 2H), 7.07 (d, J = 8.4 Hz, 2H), 7.00 (d, J = 16.4 Hz, 1H), 6.74 (d, J = 16.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 148.4, 137.2, 135.3, 133.8, 133.6, 132.8, 132.2, 131.8, 129.7, 128.8, 128.7, 128.3, 127.8, 127.8, 126.5, 126.0, 125.9, 125.8, 125.2, 122.8; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NCl$, 342.1050, found 342.1053.

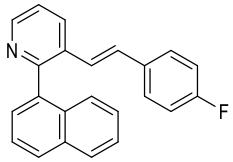
(*E*)-3-(4-bromostyryl)-2-(naphthalen-1-yl)pyridine (**1z**)



1z

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1z** as a colorless amorphous solid in 89% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (d, *J* = 4.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.65 (q, *J* =8.0 Hz, 2H), 7.58 – 7.49 (m, 3H), 7.46 – 7.40 (m, 1H), 7.37 (d, *J* = 8.0 Hz, 2H), 7.18 (dd, J_1 = 8.0 Hz, J_2 = 4.0 Hz, 1H), 7.06 (d, *J* = 8.0 Hz, 2H), 6.33 (d, *J* = 12.0 Hz, 1H), 6.23 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.2, 148.5, 137.4, 135.3, 133.8, 132.4, 131.6, 131.4, 130.3, 130.3, 128.9, 128.8, 128.3, 128.2, 127.4, 126.4, 125.9, 125.6, 125.1, 122.0, 121.4; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NBr$, 386.0544, found 386.0548.

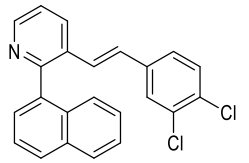
(*E*)-3-(4-fluorostyryl)-2-(naphthalen-1-yl)pyridine (**1aa**)



1aa

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1aa** as a colorless amorphous solid in 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.67 (dd, J_1 = 4.8 Hz, J_2 =2.0 Hz, 1H), 7.92 (d, *J* = 8.0 Hz, 2H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.56 – 7.46 (m, 3H), 7.44 – 7.40 (m, 1H), 7.33– 7.15 (m, 3H), 6.99 – 6.90 (m, 2H), 6.37 (d, *J* = 12.0 Hz, 1H), 6.19 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 163.2, 160.8, 158.2, 148.3, 137.4 (d, *J* = 8.7 Hz), 133.8, 132.6, 132.5(d, *J* = 3.5 Hz), 131.5, 130.5, 130.4, 128.7, 128.3, 127.4, 126.3, 125.9, 125.6, 125.1, 122.0, 115.5, 115.3; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -113.77; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}NF$, 326.1345, found 326.1349.

(*E*)-3-(3,4-dichlorostyryl)-2-(naphthalen-1-yl)pyridine (**1ab**)

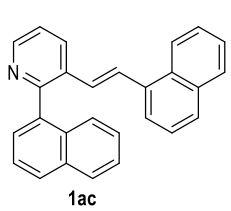


1ab

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1ab** as a colorless oily liquid in 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.15 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 8.04 – 7.97 (m, 2H), 7.65 – 7.59 (m, 2H), 7.55 – 7.52 (m, 2H), 7.48 – 7.42 (m, 2H), 7.31 – 7.26 (m, 2H), 7.00 – 6.94 (m, 2H), 6.78 (d, *J* = 16.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8, 148.7, 137.0, 136.9, 133.8,

133.0, 132.7, 131.9, 131.7, 131.5, 130.5, 129.0, 128.5, 128.4, 128.4, 127.8, 127.2, 126.5, 126.0, 125.7, 125.4, 125.2, 122.8; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{16}NCl_2$, 376.0660, found 376.0663.

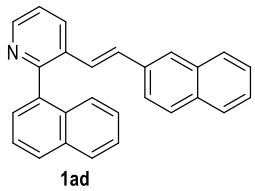
(*E*)-2-(naphthalen-1-yl)-3-(2-(naphthalen-1-yl)vinyl)pyridine (**1ac)**



1ac

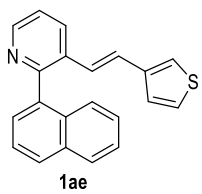
According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 25 : 1) to provide the product **1ac** as a thick liquid in 96% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.61 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.03 – 7.95 (m, 3H), 7.95 – 7.89 (m, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.80 – 7.75 (m, 1H), 7.69 – 7.60 (m, 2H), 7.60 – 7.49 (m, 4H), 7.48 – 7.39 (m, 3H), 6.96 (d, J = 12.0 Hz, 1H), 6.92 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.56 (d, J = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 148.1, 137.9, 137.3, 134.4, 133.9, 133.8, 132.4, 131.8, 131.7, 130.3, 129.2, 128.8, 128.7, 128.5, 128.1, 127.5, 126.5, 126.3, 126.3, 126.1, 125.9, 125.7, 125.4, 124.7, 121.9; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$, 358.1596, found 358.1597.

(*E*)-2-(naphthalen-1-yl)-3-(2-(naphthalen-2-yl)vinyl)pyridine (**1ad**)



1ad

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1ad** as a green amorphous solid in 95% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.68 (dd, J_1 = 4.8 Hz, J_2 = 2.0 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.84 – 7.79 (m, 1H), 7.76 – 7.68 (m, 5H), 7.60 – 7.54 (m, 2H), 7.52 – 7.42 (m, 4H), 7.38 (dd, J_1 = 8.4 Hz, J_2 = 2.0 Hz, 1H), 7.13 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 6.61 (d, J = 12.0 Hz, 1H), 6.29 (d, J = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 148.3, 137.6, 137.6, 134.0, 133.8, 133.5, 132.9, 132.7, 131.6, 131.5, 128.8, 128.3, 128.2, 128.0, 127.9, 127.7, 127.7, 127.5, 126.5, 126.4, 126.3, 126.2, 125.9, 125.7, 125.2, 121.9; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$, 358.1596, found 358.1599.



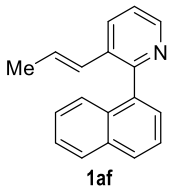
1ae

(*E*)-2-(naphthalen-1-yl)-3-(2-(thiophen-3-yl)vinyl)pyridine (**1ae)**

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 25 : 1) to provide the

product **1ae** as a colorless amorphous solid in 82% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.75 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.94 (d, J = 8.0 Hz, 2H), 7.86 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.69 (d, J = 8.0 Hz, 1H), 7.52 (m, 3H), 7.43 (m, 1H), 7.28 (m, 1H), 7.21 (dd, J_1 = 5.2 Hz, J_2 = 2.8 Hz, 1H), 7.12 (d, J = 2.8 Hz, 1H), 6.94 (d, J = 5.2 Hz, 1H), 6.39 (d, J = 12.0 Hz, 1H), 6.16 (d, J = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 148.4, 137.7, 137.7, 137.6, 133.8, 133.3, 131.5, 128.7, 128.3, 127.6, 127.4, 126.5, 126.3, 125.9, 125.7, 125.7, 125.5, 125.2, 124.6, 122.1; **HRMS**: m/z: [M + H] calculated for $C_{21}H_{16}NS$, 314.1003, found 314.1006.

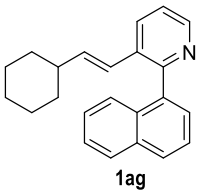
(*E*)-2-(naphthalen-1-yl)-3-(prop-1-en-1-yl)pyridine (**1af**)



1af

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **1af** as a colorless oily liquid in 61% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.88 (d, J = 8.0 Hz, 2H), 7.78 (dd, J_1 = 8.0 Hz, J_2 = 4.8 Hz, 1H), 7.50 – 7.32 (m, 6H), 6.00 (dd, J_1 = 11.6 Hz, J_2 = 1.6 Hz, 1H), 5.63 – 5.54 (m, 1H), 1.79 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 147.5, 137.9, 137.1, 133.6, 132.7, 132.6, 131.5, 128.4, 128.3, 128.2, 127.3, 127.2, 126.1, 125.7, 125.1, 121.9, 14.3; **HRMS**: m/z: [M + H] calculated for $C_{18}H_{16}N$, 246.1283, found 246.1286.

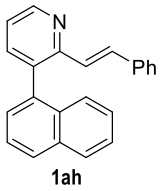
(*E*)-3-(2-cyclohexylvinyl)-2-(naphthalen-1-yl)pyridine(**1ag**)



1ag

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **1ag** as a green oily liquid in 73% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.87 (d, J = 8.0 Hz, 2H), 7.71 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.54 – 7.41 (m, 4H), 7.40 – 7.33 (m, 2H), 5.89 (d, J = 11.6 Hz, 1H), 5.28 (t, J = 10.8 Hz, 1H), 1.70 – 1.46 (m, 5H), 1.21 – 0.98 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.8, 147.6, 140.0, 138.0, 137.0, 133.7, 133.3, 131.5, 128.4, 128.2, 127.2, 126.1, 125.7, 125.1, 124.1, 122.6, 122.1, 41.1, 37.0, 33.0, 32.6, 25.9, 25.5; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{24}N$, 314.1909, found 314.1912.

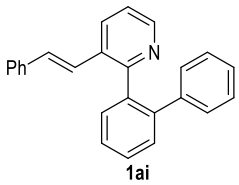
(*E*)-3-(naphthalen-1-yl)-2-styrylpyridine (**1ah**)



1ah

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 25 : 1) to provide the product **1ah** as a colorless oily liquid in 95% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (dd, J_1 = 4.8 Hz, J_2 = 2.0 Hz, 1H), 7.89 (dd, J_1 = 16.8 Hz, J_2 = 8.0 Hz, 2H), 7.65 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.54 – 7.47 (m, 2H), 7.46 – 7.36 (m, 2H), 7.32 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 7.22 – 7.11 (m, 6H), 6.39 (dd, J_1 = 14.8 Hz, J_2 = 12.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.6, 148.6, 138.7, 136.6, 135.5, 133.5, 133.4, 131.5, 129.2, 128.5, 128.4, 128.2, 127.9, 127.6, 127.4, 126.3, 125.9, 125.6, 125.3, 122.1; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}N$, 308.1439, found 308.1441.

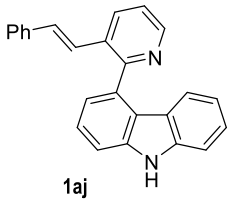
(*E*)-2-([1,1'-biphenyl]-2-yl)-3-styrylpyridine (**1ai**)



1ai

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **1ai** as a colorless oily liquid in 63% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.56 (d, J = 4.8 Hz, 1H), 7.76 (d, J = 8.0 Hz, 1H), 7.54 – 7.43 (m, 4H), 7.30 – 7.25 (m, 2H), 7.24 – 7.18 (m, 4H), 7.09 – 6.99 (m, 5H), 6.60 (dd, J = 20.4, 16.0 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.3, 147.9, 141.5, 140.8, 137.0, 132.8, 131.0, 130.5, 129.8, 129.7, 129.3, 128.8, 128.5, 127.8, 127.7, 127.5, 126.6, 126.5, 125.0, 122.4; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}N$, 334.1596, found 334.1598.

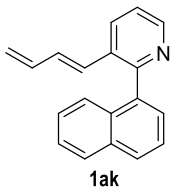
(*E*)-4-(3-styrylpyridin-2-yl)-9H-carbazole(**1aj**)



1aj

According to Procedure C, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **1aj** as a green amorphous solid in 87% yield. **^{1}H NMR (400 MHz, Chloroform-*d*)** δ 8.66 (d, J = 4.4 Hz, 1H), 8.59 (s, 1H), 7.70 (d, J = 8.0 Hz, 1H), 7.35 (t, J = 7.6 Hz, 1H), 7.26 – 7.16 (m, 10H), 7.02 (d, J = 8.0 Hz, 1H), 6.95 (t, J = 7.6 Hz, 1H), 6.40 (d, J = 12.4 Hz, 1H), 6.29 (d, J = 12.4 Hz, 1H); **^{13}C NMR (101 MHz, Chloroform-*d*)** δ 158.5, 148.1, 139.9, 139.9, 137.7, 136.5, 134.5, 132.3, 131.7, 128.9, 128.4, 127.3, 127.3, 125.6, 125.3, 122.5, 122.3, 122.0, 120.9, 120.6, 119.1, 110.7, 110; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{19}N_2$, 347.1548, found 347.1552.

(*E*)-3-(buta-1,3-dien-1-yl)-2-(naphthalen-1-yl)pyridine (**1ak**)

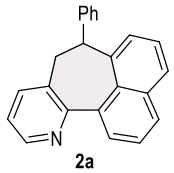


1ak

According to Procedure B, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **1ak** as a brown amorphous solid in 66% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.69 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.90 (dd, J_1 = 8.0 Hz, J_2 = 3.6 Hz, 2H), 7.85 (dd, J_1 = 8.0 Hz, J_2 = 2.0 Hz, 1H), 7.56 – 7.34 (m, 6H), 6.87 – 6.75 (m, 1H), 6.10 (t, J = 11.2 Hz, 1H), 6.01 (d, J = 11.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 158.1, 148.0, 137.7, 137.6, 133.7, 132.6, 132.4, 132.0, 131.4, 128.7, 128.3, 127.7, 127.5, 126.3, 125.9, 125.8, 125.1, 122.0, 120.7; **HRMS**: m/z: [M + H] calculated for $C_{19}H_{16}N$, 258.1283, found 258.1286.

6.2. Characterization data for products

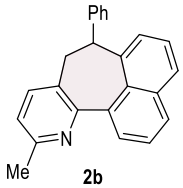
7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2a**)



2a

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **2a** as a colorless solid in 98% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.43 – 8.36 (m, 1H), 8.03 (d, J = 7.6 Hz, 1H), 7.88 (d, J = 8.4 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.39 (s, 2H), 7.03 (s, 4H), 6.94 – 6.66 (m, 3H), 5.02 (s, 1H), 3.67 (s, 1H), 3.24 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 147.5, 136.9, 135.2, 132.4, 131.3, 130.8, 128.9, 128.1, 128.0, 125.8, 125.6, 124.7, 121.4, 53.1; **IR(cm^{-1})**: ν 3055, 2918, 1569, 1493, 1452, 1382, 1068, 835, 787, 776, 702 ; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}N$, 308.1439, found 308.1441.

11-methyl-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2b**)

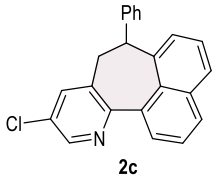


2b

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 50 : 1) to provide the product **2b** as a colorless amorphous solid in 94% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 = 0.8 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.71 (t, J = 7.6 Hz, 1H), 7.38 (s, 2H), 7.03 – 6.76 (m, 7H), 5.02 (s, 1H), 3.64 (s, 1H), 3.22 (s, 1H), 2.56 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.4, 155.9, 137.1, 135.3, 132.4, 131.1, 130.9, 128.8, 128.2, 128.0, 125.7, 124.7, 121.0, 53.2, 24.4; **IR(cm^{-1})**: ν 3052, 2918,

1577, 1445, 1379, 1265, 1072, 836, 782, 735; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1599.

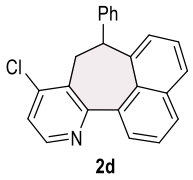
10-chloro-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2c**)



2c

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2c** as a colorless amorphous solid in 89% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.41 (s, 1H), 8.30 (dd, J_1 = 7.6 Hz, J_2 =1.2 Hz, 1H), 8.03 (dd, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 7.87 (d, J = 8.0 Hz, 1H), 7.67 (t, J = 8.0 Hz, 1H), 7.40 (s, 2H), 7.05 (s, 4H), 6.81 (s, 2H), 5.01 (s, 1H), 3.61 (s, 1H), 3.23 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.7, 146.1, 135.8, 135.2, 132.4, 131.6, 130.5, 129.7, 129.0, 128.2, 127.9, 126.1, 125.5, 124.8, 52.7; **IR(cm^{-1})**: ν 3057, 2923, 1494, 1451, 1432, 1135, 836, 776, 705; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}ClN$, 342.1050, found 342.1053.

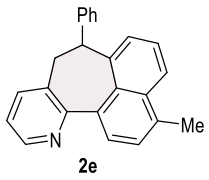
9-chloro-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2d**)



2d

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2d** as an orange oily liquid in 81% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 – 8.21 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.88 (d, J = 8.0 Hz, 1H), 7.68 (t, J = 8.0 Hz, 1H), 7.41 (s, 2H), 7.18 – 6.89 (m, 6H), 5.08 (s, 1H), 4.09 (s, 1H), 3.41 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.6, 147.4, 136.4, 135.0, 132.9, 131.7, 130.5, 129.7, 128.8, 128.2, 127.8, 126.0, 125.5, 124.9, 122.3, 52.4; **IR(cm^{-1})**: ν 3056, 2920, 1555, 1451, 1410, 1380, 988, 826, 781, 768, 700; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}ClN$, 342.1050, found 342.1053.

3-methyl-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2e**)

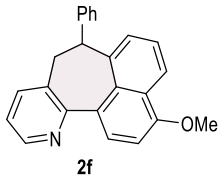


2e

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2e** as a colorless amorphous solid in 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (d, J = 4.8 Hz, 1H), 8.26 (d, J = 7.6 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.59 (d, J = 7.6 Hz, 1H), 7.52 – 7.29 (m, 2H), 7.03 (s, 4H), 6.84 (d, J = 8.0 Hz, 3H), 5.02 (s, 1H), 3.65 (s, 1H), 3.25 (s, 1H), 2.84 (s, 3H);

^{13}C NMR (101 MHz, $CDCl_3$) δ 157.8, 147.5, 136.9, 135.3, 134.0, 132.1, 130.9, 128.2, 128.0, 127.1, 125.7, 124.6, 124.3, 121.2, 53.3, 20.9; **IR(cm^{-1})**: ν 3025, 2922, 1582, 1493, 1450, 1385, 846, 782, 756, 700; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1593.

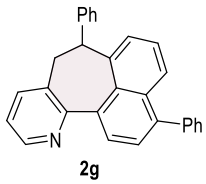
3-methoxy-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2f**)



2f

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2f** as a colorless amorphous solid in 69% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.43 (d, *J* = 9.6 Hz, 2H), 8.32 (d, *J* = 8.4 Hz, 1H), 7.39 (s, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 7.01 (s, 3H), 6.82 (s, 3H), 5.00 (s, 1H), 4.10 (s, 3H), 3.62 (s, 1H), 3.23 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 157.0, 147.3, 132.9, 131.6, 129.2, 128.1, 127.9, 126.7, 125.7, 124.1, 121.9, 120.8, 104.4, 55.8, 53.0; **IR(cm^{-1})**: ν 3058, 2934, 1593, 1515, 1451, 1414, 1315, 1251, 1103, 1038, 781, 701; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1542.

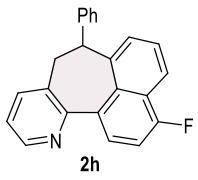
3,7-diphenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2g**)



2g

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2g** as a colorless amorphous solid in 99% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.53 (s, 1H), 8.41 (d, *J* = 7.6 Hz, 1H), 7.97 (d, *J* = 8.4 Hz, 1H), 7.68 (d, *J* = 7.6 Hz, 1H), 7.59 – 7.50 (m, 5H), 7.45 – 7.28 (m, 2H), 7.07 (s, 4H), 6.89 (s, 3H), 5.08 (s, 1H), 3.74 (s, 1H), 3.28 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 147.6, 142.8, 141.6, 136.4, 133.4, 131.8, 131.2, 130.2, 128.3, 128.2, 128.0, 127.4, 127.1, 126.8, 125.8, 124.7, 121.4, 53.4; **IR(cm^{-1})**: ν 3054, 2918, 1600, 1581, 1492, 1450, 1264, 1073, 852, 784, 702; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{22}N$, 384.1752, found 384.1755.

3-fluoro-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2h**)

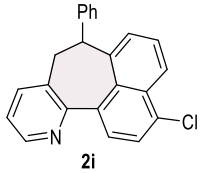


2h

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 25 : 1) to provide the product **2h** as a colorless amorphous solid in 82% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.36 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz,

1H), 8.22 (d, *J* = 8.4 Hz, 1H), 7.62 – 7.29 (m, 3H), 7.02 (s, 4H), 6.87 – 6.79 (m, 3H), 5.02 (s, 1H), 3.63 (s, 1H), 3.24 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 161.3, 158.8, 156.7, 147.5, 133.0 (d, *J* = 4.2 Hz), 132.5 (d, *J* = 8.8 Hz), 132.0 (d, *J* = 3.5 Hz), 128.0, 125.9, 125.0 (d, *J* = 14.5 Hz), 121.4, 120.6 (d, *J* = 8.8 Hz), 109.7, 109.5, 52.8; **^{19}F NMR (377 MHz, $CDCl_3$)** δ -118.58; **IR(cm^{-1})**: ν 3029, 2927, 1602, 1578, 1511, 1452, 1416, 1246, 1094, 835, 782, 757, 700; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}FN$, 326.1345, found 326.1346.

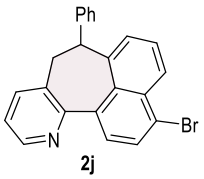
3-chloro-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2i**)



2i

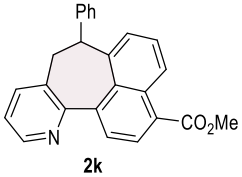
According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2i** as a colorless amorphous solid in 83% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.57 – 8.33 (m, 2H), 8.24 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.2 Hz, 1H), 7.57 – 7.32 (m, 2H), 7.15 – 6.62 (m, 7H), 5.01 (s, 1H), 3.62 (s, 1H), 3.24 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.7, 147.5, 136.8, 134.5, 132.0, 131.9, 131.9, 128.0, 126.3, 125.9, 124.8, 121.7, 53.0; **IR(cm^{-1})**: ν 3053, 2922, 1573, 1505, 1451, 1376, 1052, 781, 702; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}ClN$, 342.1050, found 342.1053.

3-bromo-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2j**)



2j

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2j** as a colorless amorphous solid in 92% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 – 8.43 (m, 2H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.58 – 7.33 (m, 2H), 7.03 (s, 4H), 6.89 (s, 1H), 6.79 (s, 2H), 5.01 (s, 1H), 3.59 (s, 1H), 3.24 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.7, 147.7, 137.0, 132.9, 132.4, 132.0, 130.2, 128.1, 127.9, 126.1, 126.1, 125.9, 121.7, 53.0; **IR(cm^{-1})**: ν 3025, 2919, 1569, 1504, 1451, 1375, 1043, 780, 702, 599; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}BrN$, 386.0544, found 386.0539.



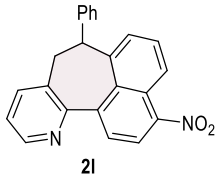
2k

methyl-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine-3-carboxylate (**2k**)

According to Procedure D, the residue was purified by column

chromatography on silica gel (PE : EA = 15 : 1) to provide the product **2k** as a colorless amorphous solid in 50% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.84 (dd, J_1 = 8.8 Hz, J_2 = 1.6 Hz, 1H), 8.48 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.31 (d, J = 7.6 Hz, 1H), 8.23 (d, J = 7.6 Hz, 1H), 7.48 (t, J = 7.6 Hz, 1H), 7.38 (s, 1H), 7.04 – 6.96 (m, 4H), 6.90 (t, J = 6.0 Hz, 1H), 6.78 (d, J = 6.0 Hz, 2H), 4.99 (s, 1H), 4.05 (s, 3H), 3.60 (d, J = 13.2 Hz, 1H), 3.21 (d, J = 13.2 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.7, 156.7, 147.7, 141.1, 136.7, 132.7, 131.2, 131.0, 130.3, 129.9, 128.6, 128.1, 128.0, 126.2, 125.8, 125.7, 122.0, 53.3, 52.4; **IR(cm^{-1})**: ν 3358, 2921, 2851, 1718, 1452, 1258, 1199, 1088, 786, 703; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}NO_2$, 366.1494, found 366.1499.

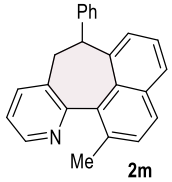
3-nitro-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2l**)



2l

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **2l** as a yellow amorphous solid in 84% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (d, J = 2.8 Hz, 1H), 8.33 (dd, J_1 = 14.8, J_2 = 8.0 Hz, 2H), 8.14 (d, J = 8.0 Hz, 1H), 7.61 – 7.36 (m, 2H), 7.17 – 6.90 (m, 5H), 6.77 (d, J = 4.8 Hz, 2H), 5.02 (s, 1H), 3.62 (d, J = 14.0 Hz, 1H), 3.26 (d, J = 14.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.6, 149.0, 147.9, 142.1, 137.0, 131.5, 131.4, 130.7, 128.2, 128.0, 127.6, 126.2, 126.1, 122.5, 122.4, 121.8, 53.0; **IR(cm^{-1})**: ν 3057, 2921, 1568, 1519, 1452, 1351, 780, 757, 703; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}N_2O_2$, 353.1290, found 353.1294.

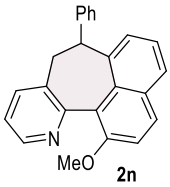
1-methyl-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2m**)



2m

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2m** as a colorless amorphous solid in 58% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.40 (s, 1H), 7.84 (d, J = 8.4 Hz, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.27 (d, J = 7.6 Hz, 2H), 7.02 – 6.91 (m, 4H), 6.79 – 6.72 (m, 3H), 4.90 (s, 1H), 3.77 (s, 1H), 3.04 (s, 1H), 2.45 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 146.7, 137.8, 134.6, 133.1, 131.2, 130.5, 129.9, 129.8, 128.3, 127.8, 125.6, 124.0, 121.3, 53.3, 23.1; **IR(cm^{-1})**: ν 3052, 2920, 1578, 1453, 1365, 1059, 835, 802, 773, 705; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1597.

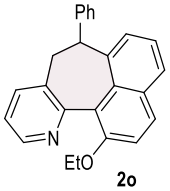
1-methoxy-7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2n**)



2n

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2n** as a colorless amorphous solid in 42% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 (s, 1H), 7.94 (d, *J* = 8.8 Hz, 1H), 7.76 – 7.69 (m, 1H), 7.49 (d, *J* = 8.8 Hz, 1H), 7.47 – 7.23 (m, 2H), 7.22– 6.73 (m, 7H), 4.89 (s, 1H), 3.92 (s, 3H), 3.76 (s, 1H), 3.05 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.6, 155.3, 146.8, 131.9, 131.7, 130.9, 130.3, 128.3, 127.9, 125.6, 123.4, 123.0, 121.2, 116.2, 58.2, 53.2; **IR(cm^{-1})**: ν 3054, 2920, 2849, 1610, 1509, 1455, 1260, 1066, 804, 702; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1542.

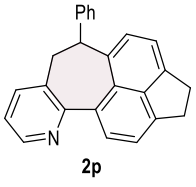
1-ethoxy-7-(naphthalen-2-yl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b] pyridine (**2o**)



2o

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2o** as a colorless amorphous solid in 38% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (s, 1H), 7.92 (d, *J* = 9.2 Hz, 1H), 7.73 – 7.69 (m, 1H), 7.47 (d, *J* = 9.2 Hz, 1H), 7.24 – 7.20 (m, 2H), 7.02 – 6.74 (m, 7H), 4.89 (s, 1H), 4.21 – 4.16 (m, 2H), 3.76 (s, 1H), 3.04 (s, 1H), 1.30 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 155.4, 146.7, 131.8, 130.8, 130.4, 128.3, 127.9, 127.8, 125.6, 124.0, 123.0, 121.2, 117.9, 67.2, 53.1, 15.1; **IR(cm^{-1})**: ν 3054, 2978, 2925, 1596, 1507, 1453, 1256, 1041, 803, 701; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{22}NO$, 352.1701, found 352.1705.

5-phenyl-1,2,5,6-tetrahydroacenaphtho[5',6':5,6,7]cyclohepta[1,2-b]pyridine (**2p**)

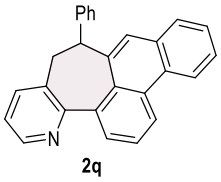


2p

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 35 : 1) to provide the product **2p** as a colorless amorphous solid in 68% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.55 (d, *J* = 7.2 Hz, 1H), 8.48 (s, 1H), 7.55 (d, *J* = 7.2 Hz, 1H), 7.39 (s, 1H), 7.25 (s, 1H), 7.00 (s, 4H), 6.81 (s, 3H), 5.02 (s, 1H), 3.64 (s, 1H), 3.47 (d, *J* = 11.6 Hz, 4H), 3.26 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.9, 148.9, 147.3, 145.7, 140.5, 138.0, 133.2, 132.7, 130.7, 129.2, 127.9, 125.6, 121.0, 120.1, 118.9, 51.8, 40.3, 30.3, 30.1; **IR(cm^{-1})**: ν 3025, 2920, 2851, 1601, 1581, 1451, 1422, 1286, 1090, 850, 781, 701; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}N$,

334.1596, found 334.1593.

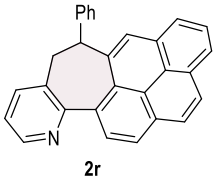
9-phenyl-8,9-dihydrophenanthro[10',1':5,6,7]cyclohepta[1,2-b]pyridine (**2q**)



2q

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2q** as a colorless oily liquid in 97% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.80 (d, *J* = 8.0 Hz, 1H), 8.74 (d, *J* = 8.0 Hz, 1H), 8.59 (s, 1H), 8.56 – 8.47 (m, 1H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.68 (m, 2H), 7.55 (t, *J* = 8.0 Hz, 1H), 7.44 (d, *J* = 8.0 Hz, 1H), 7.04 (m, 4H), 6.89 (m, 3H), 5.03 (s, 1H), 3.70 (d, *J* = 12.0 Hz, 1H), 3.22 (d, *J* = 12.0 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7, 147.6, 136.6, 135.3, 133.7, 131.9, 131.4, 131.4, 130.9, 129.6, 129.5, 128.3, 128.0, 127.5, 126.8, 125.8, 125.4, 122.9, 122.5, 121.7, 53.1; **IR(cm^{-1})**: ν 3054, 2921, 1583, 1492, 1449, 1105, 787, 757, 703; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$,358.1596, found 358.1598.

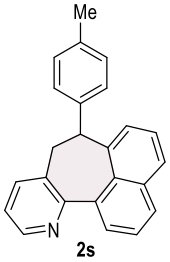
8-phenyl-1,5,8,9-tetrahydropyreno[1',10':5,6,7]cyclohepta[1,2-b]pyridine (**2r**)



2r

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2r** as a colorless amorphous solid in 65% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.87 (d, *J* = 8.0 Hz, 1H), 8.58 (s, 1H), 8.41 (d, *J* = 8.0 Hz, 1H), 8.39 – 8.16 (m, 3H), 8.10 – 7.80 (m, 3H), 7.11– 6.93 (m, 7H), 5.19 (s, 1H), 3.70 (s, 1H), 3.36 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7, 147.7, 134.7, 132.4, 131.8, 131.4, 130.1, 129.3, 128.1, 128.0, 127.8, 126.2, 126.0, 125.9, 125.5, 124.9, 124.2, 121.2, 53.9; **IR(cm^{-1})**: ν 3043, 2921, 1582, 1445, 1427, 1268, 849, 734, 700; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{20}N$, 382.1596, found 382.1601.

7-(p-tolyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2s**)

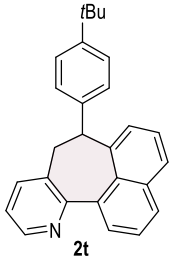


2s

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2s** as a colorless amorphous solid in 99% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (s, 1H), 8.40 (d, *J* = 7.6 Hz, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.70 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 2H), 7.11 – 6.63 (m, 6H), 4.99 (s, 1H), 3.66 (s, 1H), 3.22 (s, 1H), 2.21 (s,

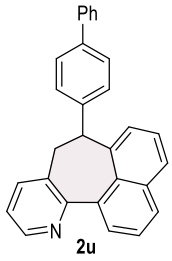
3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 147.5, 136.9, 135.2, 132.4, 131.3, 130.8, 128.7, 128.0, 125.6, 124.7, 121.5, 52.8, 20.9; **IR(cm^{-1})**: ν 3048, 2919, 1568, 1511, 1445, 1379, 1072, 836, 787, 775; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1596.

7-(4-(tert-butyl)phenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2t**)

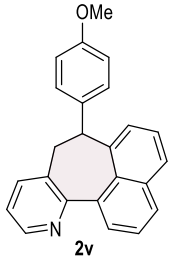


According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2t** as a colorless amorphous solid in 86% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 8.38 (dd, J_1 = 7.2 Hz, J_2 = 1.6 Hz, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 7.69 (t, J = 8.0 Hz, 1H), 7.38 (s, 2H), 7.04 – 6.73 (m, 6H), 4.99 (s, 1H), 3.63 (s, 1H), 3.23 (s, 1H), 1.22 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.3, 147.4, 136.9, 135.2, 132.3, 131.2, 130.7, 128.7, 127.7, 125.5, 124.8, 124.7, 121.2, 52.6, 34.2, 31.3; **IR(cm^{-1})**: ν 3052, 2960, 2866, 1569, 1508, 1455, 1445, 1363, 1268, 1108, 836, 787, 559; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{26}N$, 364.2065, found 364.2064.

7-([1,1'-biphenyl]-4-yl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine(**2u**)



According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2u** as a colorless amorphous solid in 95% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.42 (d, J = 8.0 Hz, 1H), 8.05 (d, J = 8.0 Hz, 1H), 7.90 (d, J = 8.0 Hz, 1H), 7.73 (t, J = 8.0 Hz, 1H), 7.66 – 7.26 (m, 9H), 7.09 – 6.85 (m, 4H), 5.06 (s, 1H), 3.71 (s, 1H), 3.27 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 147.6, 140.7, 136.9, 135.3, 132.5, 131.3, 130.8, 128.9, 128.7, 128.5, 127.1, 126.9, 126.6, 125.7, 124.8, 121.5, 52.8; **IR(cm^{-1})**: ν 3052, 2922, 1568, 1487, 1445, 1072, 836, 776, 742, 698; **HRMS**: m/z: [M + H] calculated for $C_{29}H_{22}N$, 384.1752, found 384.1757.

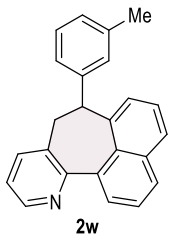


7-(4-methoxyphenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b] pyridine (**2v**)

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product

2v as a colorless oily liquid in 75% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.48 (s, 1H), 8.35 (d, *J* = 7.2 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.67 (t, *J* = 8.0 Hz, 1H), 7.38 (s, 2H), 7.04 (s, 1H), 6.90 (s, 1H), 6.70 (s, 2H), 6.56 (s, 2H), 4.97 (s, 1H), 3.66 (s, 4H), 3.19 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.3, 147.5, 136.8, 135.2, 132.3, 131.2, 130.7, 129.0, 128.7, 125.5, 124.7, 121.5, 113.3, 55.1, 52.3; **IR(cm^{-1})**: ν 3053, 2931, 1583, 1510, 1445, 1250, 1177, 1035, 836, 788; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}NO$, 338.1545, found 338.1544.

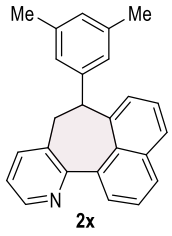
7-(m-tolyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2w**)



2w

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2w** as a colorless oily liquid in 98% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.39 – 8.36 (m, 1H), 8.03 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.72 – 7.67 (m, 1H), 7.38 (s, 2H), 6.99 – 6.63 (m, 6H), 4.98 (s, 1H), 3.66 (s, 1H), 3.22 (s, 1H), 2.13 (s, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5, 147.5, 136.9, 135.2, 132.3, 131.3, 130.8, 128.8, 127.9, 126.5, 125.6, 125.2, 124.7, 121.4, 53.1, 21.3; **IR(cm^{-1})**: ν 3050, 2917, 1569, 1445, 1379, 1071, 835, 784, 706; **HRMS**: m/z: [M + H] calculated for $C_{24}H_{20}N$, 322.1596, found 322.1598.

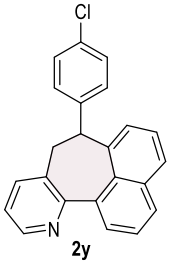
7-(3,5-dimethylphenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2x**)



2x

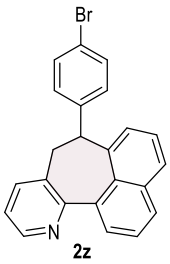
According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2x** as a colorless amorphous solid in 85% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 8.33 (dd, J_1 = 7.6 Hz, J_2 =1.2 Hz, 1H), 8.01 (dd, J_1 = 8.0 Hz, J_2 =1.2 Hz, 1H), 7.86 (d, *J* = 8.0 Hz, 1H), 7.68 (t, *J* = 7.6 Hz, 1H), 7.38 (s, 2H), 7.06 – 6.92 (m, 2H), 6.68 – 6.46 (m, 3H), 4.93 (s, 1H), 3.64 (s, 1H), 3.18 (s, 1H), 2.09 (s, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5, 147.5, 136.9, 135.1, 132.2, 131.2, 130.7, 128.6, 127.4, 126.0, 125.5, 124.7, 121.4, 53.1, 21.1; **IR(cm^{-1})**: ν 3051, 2918, 1601, 1445, 1379, 1073, 850, 835, 787, 775, 738; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{22}N$, 336.1752, found 336.1750.

7-(4-chlorophenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2y**)



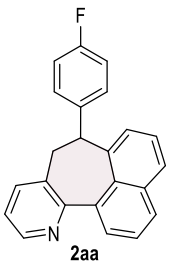
According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2y** as a colorless liquid in 80% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 (s, 1H), 8.36 (d, *J* = 7.2 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.38 – 7.36 (m, 2H), 7.26 – 6.91 (m, 4H), 6.72 (s, 2H), 4.97 (s, 1H), 3.66 (s, 1H), 3.19 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 147.7, 136.6, 135.2, 132.5, 131.3, 130.6, 129.4, 129.1, 128.1, 125.7, 124.7, 121.6, 52.5; **IR(cm^{-1})**: ν 3053, 2921, 1576, 1489, 1445, 1091, 1014, 837, 789, 732; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}ClN$, 342.1050, found 342.1046.

7-(4-bromophenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2z**)



According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2z** as a colorless amorphous liquid in 83% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.39 (s, 1H), 8.25 (d, *J* = 7.6 Hz, 1H), 7.90 (d, *J* = 8.0 Hz, 1H), 7.76 (d, *J* = 8.0 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.39 – 7.26 (m, 2H), 7.10 – 6.75 (m, 4H), 6.56 (s, 2H), 4.84 (s, 1H), 3.54 (s, 1H), 3.07 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 147.7, 136.6, 135.2, 132.5, 131.3, 131.0, 130.6, 129.8, 129.1, 125.7, 124.7, 121.6, 52.6; **IR(cm^{-1})**: ν 3053, 2920, 1575, 1486, 1445, 1072, 1010, 836, 788, 776, 668; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}BrN$, 386.0544, found 386.0544.

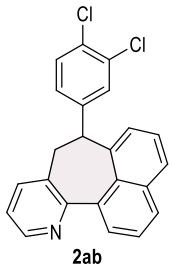
7-(4-fluorophenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2aa**)



According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2aa** as a colorless amorphous solid in 46% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.49 (s, 1H), 8.35 (d, *J* = 7.4 Hz, 1H), 8.02 (d, *J* = 8.0 Hz, 1H), 7.87 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 7.09 – 6.60 (m, 6H), 5.00 (s, 1H), 3.67 (s, 1H), 3.19 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.3, 147.6, 136.7, 135.2, 132.5, 131.3, 130.6, 129.4 (d, *J* = 7.6 Hz), 129.0, 125.7, 124.7, 121.5, 114.8, 114.6, 52.3; **^{19}F NMR (377 MHz,**

$CDCl_3$) δ -117.41; **IR(cm^{-1})**: ν 3052, 2920, 1600, 1507, 1446, 1220, 1158, 836, 789, 777; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}FN$, 326.1345, found 326.1349.

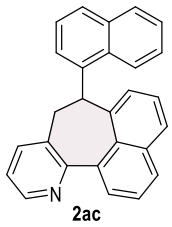
7-(3,4-dichlorophenyl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2ab**)



2ab

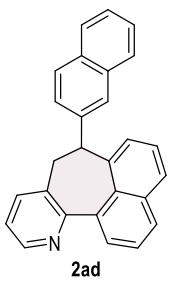
According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 10 : 1) to provide the product **2ab** as a colorless amorphous liquid in 40% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (d, *J* = 4.0 Hz, 1H), 8.37 (dd, J_1 = 7.6 Hz, J_2 =1.6 Hz, 1H), 8.02 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.69 (t, *J* = 8.0 Hz, 1H), 7.53 – 7.26 (m, 2H), 7.13 – 6.86 (m, 4H), 6.54 (s, 1H), 4.93 (s, 1H), 3.65 (s, 1H), 3.19 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 147.9, 136.5, 135.3, 132.6, 131.4, 130.4, 129.9, 129.4, 127.6, 125.8, 124.7, 121.7, 52.3; **IR(cm^{-1})**: ν 3053, 2922, 1568, 1471, 1445, 1132, 1030, 835,788, 776; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{16}Cl_2N$, 376.0660, found 376.0662.

7-(naphthalen-1-yl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2ac**)



2ac

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2ac** as a colorless amorphous solid in 95% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.45 (d, *J* = 7.2 Hz, 2H), 8.08 (s, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.75 – 7.59 (m, 2H), 7.56 – 7.32 (m, 4H), 7.02 – 6.22 (m, 4H), 5.78 (s, 1H), 3.72 (s, 1H), 3.57 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 147.5, 141.0, 136.9, 135.9, 135.3, 133.6, 132.5, 131.4, 129.1, 129.0, 127.7, 126.6, 126.1, 125.7, 125.3, 124.9, 123.2, 121.3, 49.6; **IR(cm^{-1})**: ν 3048, 2920, 2850, 1575, 1509, 1445, 1394, 1264, 837, 777, 736 ; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$, 358.1596, found 358.1591.



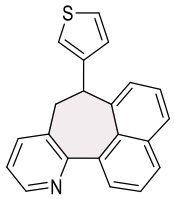
2ad

7-(naphthalen-2-yl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]py ridine (**2ad**)

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2ad** as a colorless amorphous solid in 58% yield. **^{1}H NMR (400 MHz,**

$CDCl_3$) δ 8.68 – 8.24 (m, 2H), 8.06 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 7.2 Hz, 1H), 7.72 (t, *J* = 8.0 Hz, 2H), 7.59 – 6.30 (m, 6H), 7.23 – 6.55 (m, 4H), 5.17 (s, 1H), 3.75 (s, 1H), 3.35 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.4, 147.6, 136.9, 135.3, 133.2, 132.4, 131.8, 131.3, 130.8, 128.9, 127.7, 127.4, 127.0, 126.4, 125.8, 125.7, 125.3, 124.7, 121.5, 53.3; **IR(cm^{-1})**: ν 3052, 2920, 1568, 1506, 1445, 1264, 835, 778, 756; **HRMS**: m/z: [M + H] calculated for $C_{27}H_{20}N$, 358.1596, found 358.1598.

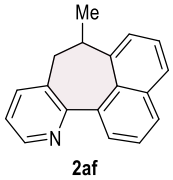
7-(thiophen-3-yl)-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**2ae**)



2ae

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2ae** as a colorless liquid in 65% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.51 (s, 1H), 8.35 (d, *J* = 7.6 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.87 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.40 (s, 2H), 7.17 (s, 1H), 7.04 – 6.95 (m, 2H), 6.68 (s, 1H), 6.34 (s, 1H), 5.00 (s, 1H), 3.60 (s, 1H), 3.26 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.3, 147.5, 136.7, 135.3, 132.5, 131.2, 130.1, 128.9, 127.0, 125.6, 125.2, 124.6, 121.8, 121.4, 48.9; **IR(cm^{-1})**: ν 3056, 2920, 1600, 1572, 1470, 1451, 1376, 1070, 835, 777, 701; **HRMS**: m/z: [M + H] calculated for $C_{21}H_{16}NS$, 314.1003, found 314.1005.

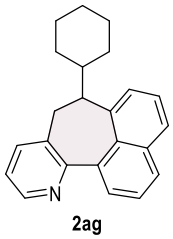
6-methyl-5,6-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine(**2af**)



2af

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2af** as a colorless oily liquid in 30% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.66 (dd, J_1 = 4.8 Hz, J_2 = 1.2 Hz, 1H), 8.35 (dd, J_1 = 7.2 Hz, J_2 = 5.6 Hz, 1H), 7.96 – 7.92 (m, 1H), 7.82 – 7.76 (m, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.54 – 7.50 (m, 1H), 7.41 – 7.36 (m, 2H), 7.22 – 7.16 (dd, J_1 = 7.6 Hz, J_2 = 4.8 Hz, 1H), 3.72 – 3.61 (m, 1H), 3.41 (d, *J* = 14.0 Hz, 1H), 2.93 – 2.83 (dd, J_1 = 14.0 Hz, J_2 = 6.8 Hz, 1H), 1.00 (d, *J* = 7.2 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.7, 147.6, 143.9, 137.2, 136.5, 135.3, 132.2, 131.2, 129.5, 128.3, 125.4, 124.6, 121.6, 41.3, 21.9; **IR(cm^{-1})**: ν 3053, 2960, 2924, 2864, 1583, 1567, 1444, 1384,1290, 1097, 832, 772, 626; **HRMS**: m/z: [M + H] calculated for $C_{18}H_{16}N$, 246.1283, found 246.1282.

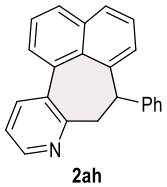
6-cyclohexyl-5,6-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine(**2ag**)



2ag

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 30 : 1) to provide the product **2ag** as a colorless oily liquid in 10% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.65 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 8.48 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.94 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.80 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.61 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 8.0 Hz, 1H), 7.36 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 6.8 Hz, 1H), 7.18 (dd, J_1 = 7.6 Hz, J_2 = 4.4 Hz, 1H), 3.34 (d, J = 13.6 Hz, 1H), 3.19 – 3.08 (m, 2H), 1.87 – 1.41 (m, 5H), 1.15 – 0.7 (m, 6H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.5, 147.3, 141.4, 137.6, 136.5, 135.7, 133.7, 132.8, 131.4, 129.9, 129.8, 128.5, 125.3, 124.0, 121.1, 53.3, 38.8, 36.0, 32.2, 31.0, 26.4, 26.1, 26.0; **IR(cm^{-1})**: ν 3055, 2918, 2850, 1565, 1447, 1428, 1385, 1069, 837, 784, 770, 639; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{24}N$, 314.1909, found 314.1910.

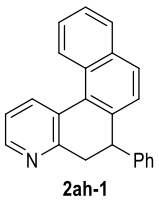
7-phenyl-7,8-dihydronaphtho[1',8':3,4,5]cyclohepta[1,2-b]pyridine (**2ah**)



2ah

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **2ah** as a colorless amorphous solid in 16% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.18 (s, 1H), 7.97 (dd, J_1 = 7.2 Hz, J_2 = 2.0 Hz, 1H), 7.86 (d, J = 8.4 Hz, 1H), 7.66 (d, J = 7.6 Hz, 1H), 7.62 – 7.55 (m, 2H), 7.51 – 7.30 (m, 2H), 7.13 – 6.74 (m, 6H), 5.04 (s, 1H), 3.88 (s, 1H), 3.71 (s, 1H),; **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.3, 138.5, 135.5, 135.2, 130.9, 130.8, 130.5, 128.5, 128.3, 127.7, 125.6, 125.4, 125.3, 121.6, 52.2; **IR(cm^{-1})**: ν 3054, 2920, 1575, 1492, 1450, 1382, 1181, 1102, 837, 801, 776, 699; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}N$, 308.1439, found 308.1437.

6-phenyl-5,6-dihydronaphtho[1,2-f]quinoline (**2ah-1**)

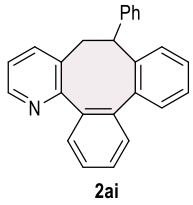


2ah-1

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **2ah-1** as a colorless oily liquid in 45% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.44 – 8.37 (m, 2H), 8.21 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), δ 7.90 – 7.85 (m, 1H), 7.73 (d, J = 8.4 Hz, 1H), δ 7.56 – 7.46 (m, 2H), 7.27 – 7.15 (m, 5H), 7.06 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 2H), 4.35 (t, J = 6.4 Hz, 1H), 3.44 (d, J = 6.4 Hz, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 157.2, 147.3, 142.0, 139.0,

135.1, 133.7, 130.3, 129.9, 129.2, 128.9, 128.7, 128.5, 128.3, 126.7, 126.6, 126.5, 125.6, 124.9, 121.4, 45.3, 39.8; **IR(cm^{-1})**: ν 3056, 3025, 2956, 2894, 2363, 1574, 1492, 1442, 1420, 1211, 1103, 910, 818, 732, 699; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}N$, 308.1439, found 308.1444.

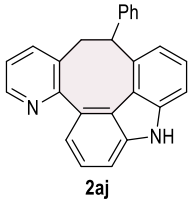
10-phenyl-9,10-dihydrodibenzo[5,6:7,8]cycloocta[1,2-b]pyridine (**2ai**)



2ai

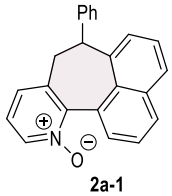
According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **2ai** as a colorless solid in 87% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.42 (dd, J_1 = 4.8 Hz, J_2 = 1.6 Hz, 1H), 7.60 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.54 – 7.42 (m, 4H), 7.23 – 7.10 (m, 6H), 7.07– 7.02 (m, 3H), 7.00 – 6.95 (m, 1H), 4.47 (dd, J_1 = 12.4 Hz, J_2 = 7.6 Hz, 1H), 3.14 – 2.98 (m, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 159.7, 147.5, 145.8, 142.4, 139.9, 139.2, 138.9, 135.5, 134.6, 133.9, 131.6, 130.9, 128.7, 128.6, 128.1, 127.7, 127.3, 126.4, 126.3, 122.7, 55.6, 39.9; **IR(cm^{-1})**: ν 3058, 2925, 1573, 1493, 1449, 1426, 1023, 770, 750, 699; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{20}N$, 334.1596, found 334.1600.

5-phenyl-5,6-dihydro-1H-pyrido[2',3':5,6]cycloocta[1,2,3,4-def]carbazole (**2aj**)



2aj

According to Procedure D, the residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **2aj** as a green oily liquid in 55% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.02 (d, J = 8.0 Hz, 1H), 8.69 (d, J = 5.2 Hz, 1H), 8.21 (s, 1H), 7.40 (d, J = 7.6 Hz, 1H), 7.35 (t, J = 8.0 Hz, 1H), 7.21 – 7.07 (m, 7H), 7.04 (d, J = 7.6 Hz, 2H), 6.98 (d, J = 8.0 Hz, 1H), 4.32 (t, J = 6.0 Hz, 1H), 3.31 (dd, J_1 = 14.8 Hz, J_2 = 5.2 Hz, 1H), 3.14 (dd, J_1 = 14.8 Hz, J_2 = 6.8 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 154.1, 147.0, 143.5, 140.7, 140.4, 135.7, 134.0, 131.7, 131.2, 128.3, 128.3, 126.4, 126.3, 126.1, 123.3, 122.4, 120.1, 118.8, 111.9, 110.3, 44.9, 37.3; **IR(cm^{-1})**: ν 3408, 3240, 3054, 2927, 1601, 1492, 1439, 1325, 1148, 812, 772, 740, 701; **HRMS**: m/z: [M + H] calculated for $C_{25}H_{19}N_2$, 347.1548, found 347.1552.



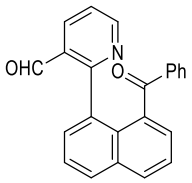
2a-1

7-phenyl-7,8-dihydronaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine 12-oxide (**2a-1**)

The residue was purified by column chromatography on silica gel (PE :

EA = 1 : 1) to provide the product **2a-1** as a yellowish-green oily liquid in 93% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.50 – 8.47 (m, 1H), 8.07 (d, *J* = 6.4 Hz, 1H), 8.01 (d, *J* = 8.0 Hz, 1H), 7.83 (d, *J* = 7.2 Hz, 1H), 7.63 (t, *J* = 8.0 Hz, 1H), 7.39 – 7.33 (m, 2H), 7.09 (t, *J* = 7.2 Hz, 2H), 7.01 (t, *J* = 7.2 Hz, 1H), 6.85 (d, *J* = 7.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 6.50 (d, *J* = 8.0 Hz, 1H), 4.94 (d, *J* = 6.4 Hz, 1H), 3.58 (d, *J* = 13.6 Hz, 1H), 3.12 (dd, J_1 = 13.6 Hz, J_2 = 6.4 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 147.6, 143.4, 138.8, 138.5, 137.7, 135.2, 132.7, 132.1, 130.8, 130.2, 128.7, 128.2, 128.1, 126.5, 125.9, 124.7, 124.7, 124.1, 122.9, 52.5, 39.0; **IR(cm^{-1})**: ν 3056, 2923, 1597, 1491, 1450, 1420, 1266, 1227, 1064, 962, 828, 771, 702, 570; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{18}NO$, 324.1388, found 324.1393.

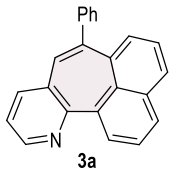
2-(8-benzoylnaphthalen-1-yl)nicotinaldehyde (**2a-2**)



2a-2

The residue was purified by column chromatography on silica gel (PE : EA = 15 : 1) to provide the product **2a-2** as a colorless oily liquid in 24% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 9.91 (s, 1H), 8.16 – 8.07 (m, 4H), 7.64 – 7.53 (m, 5H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.15 (dd, J_1 = 7.6 Hz, J_1 = 4.8 Hz, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 197.0, 191.2, 163.6, 152.6, 137.7, 137.1, 135.5, 135.1, 134.3, 133.0, 132.9, 131.6, 130.7, 130.0, 129.9, 129.8, 129.5, 128.0, 125.4, 125.1, 122.5; **IR(cm^{-1})**: ν 2922, 2851, 1694, 1660, 1578, 1448, 1271, 828, 778, 712; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{16}NO_2$, 338.1181, found 338.1182.

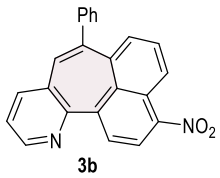
7-phenylnaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**3a**)



3a

The residue was purified by column chromatography on silica gel (PE : EA = 50 : 1) to provide the product **3a** as a yellowish-green oily liquid in 57% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.59 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 8.33 (dd, J_1 = 4.8 Hz, J_2 =1.6 Hz, 1H), 7.77 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.63 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.46 (dd, J_1 = 8.0 Hz, J_2 =1.6 Hz, 1H), 7.45 – 7.33 (m, 3H), 7.25 – 7.20 (m, 2H), 7.19 – 7.12 (m, 2H), 7.00 (dd, J_1 = 7.6 Hz, J_2 = 0.8 Hz, 1H), 6.52 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 155.6, 149.9, 147.4, 146.6, 139.5, 138.2, 137.6, 135.8, 134.8, 132.8, 130.9, 130.3, 129.7, 129.1, 129.1, 128.6, 128.4, 127.4, 126.3, 124.5, 122.3; **IR(cm^{-1})**: ν 3052, 2924, 1558, 1491, 1443, 1073, 831, 781, 767, 747, 701, 634; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{16}N$, 306.1283, found 306.1286.

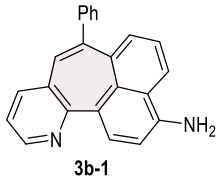
3-nitro-7-phenylnaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridine (**3b**)



3b

The residue was purified by column chromatography on silica gel (PE : EA = 20 : 1) to provide the product **3b** as an orange-red amorphous solid in 45% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.64 (dd, J_1 = 4.4 Hz, J_2 = 1.6 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.28 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 8.16 (d, J = 8.4 Hz, 1H), 7.59 (dd, J_1 = 7.6 Hz, J_2 = 1.6 Hz, 1H), 7.40 (dd, J_1 = 8.4 Hz, J_2 = 7.6 Hz, 1H), 7.37 – 7.32 (m, 3H), 7.27 – 7.24 (m, 1H), 7.22 – 7.15 (m, 3H), 6.68 (s, 1H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 153.3, 150.3, 147.4, 146.6, 145.9, 142.9, 139.9, 138.1, 136.0, 132.7, 131.7, 129.0, 128.8, 128.5, 128.5, 127.8, 127.2, 125.9, 123.4, 123.3, 122.5; **IR (cm^{-1})**: ν 3359, 2921, 2851, 1633, 1514, 1343, 1322, 1073, 779, 701; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{15}N_2O_2$, 351.1134, found 351.1137.

7-phenylnaphtho[1',8':5,6,7]cyclohepta[1,2-b]pyridin-3-amine (**3b-1**)



3b-1

The residue was purified by column chromatography on silica gel (PE : EA = 8 : 1) to provide the product **3b-1** as a yellowish-green amorphous solid in 56% yield. **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.52 (dd, J_1 = 4.8, J_2 = 1.6 Hz, 1H), 8.17 (d, J = 8.0 Hz, 1H), 7.58 (dd, J_1 = 8.0, J_2 = 1.2 Hz, 1H), 7.40 (dd, J_1 = 7.6, J_2 = 1.6 Hz, 1H), 7.35 – 7.30 (m, 3H), 7.22 – 7.18 (m, 2H), 7.16 – 7.11 (m, 1H), 7.05 (dd, J_1 = 7.6, J_2 = 4.8 Hz, 1H), 6.97 – 6.93 (m, 2H), 6.51 (s, 1H), 4.18 (s, 2H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 156.5, 149.7, 147.0, 146.9, 143.2, 141.3, 137.8, 136.6, 131.9, 131.2, 131.1, 129.5, 129.1, 128.6, 128.3, 127.2, 124.3, 123.8, 121.2, 120.5, 110.8; **IR (cm^{-1})**: ν 3359, 2923, 2853, 1632, 1567, 1443, 1420, 1261, 776, 701; **HRMS**: m/z: [M + H] calculated for $C_{23}H_{17}N_2$, 321.1392, found 321.1395.

7. X-ray structures of 2a and 2ai

The single crystal was obtained by slow evaporation of a saturated solution in ethyl acetate in a lossely capped vial. Structure information was deposited at the Cambridge Crystallographic Data Center (CCDC)

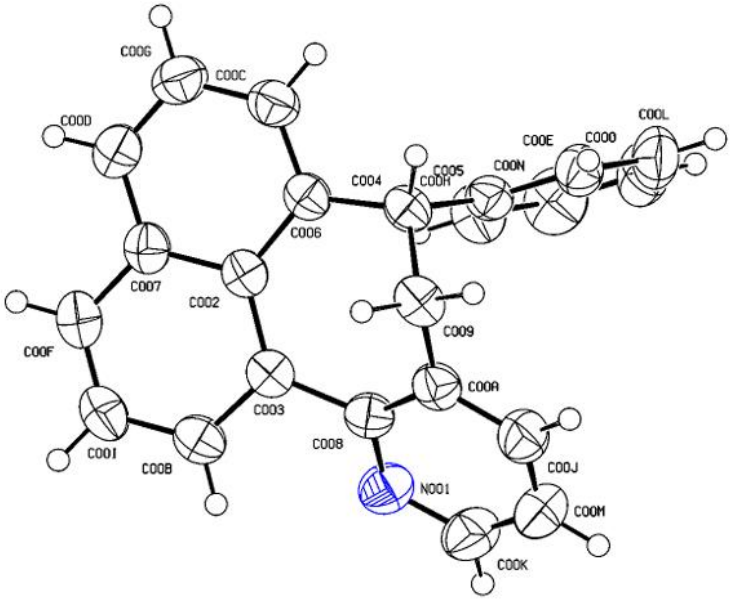


Figure S1. The X-ray crystallographic structure of **2a**

Figure S1. X-ray crystallographic structure of **2a** (CCDC 2380484) showing thermal ellipsoid probability at 50%. A suitable crystal **2a** was selected and mounted on a **SuperNova, Dual, Cu at home/near, Eos** diffractometer. The crystal was kept at 293(2) K during data collection. Using Olex2[5], the structure was solved with the SHELXT[6] structure solution program using Intrinsic Phasing and refined with the SHELXL[7] refinement package using Least Squares minimisation.

Crystal Data for $C_{23}H_{17}N$ (M =307.38 g/mol): monoclinic, space group $P2_1/c$ (no. 14), a = 9.70210(10) Å, b = 7.22330(10) Å, c = 23.9872(3) Å, β = 94.7610(10) °, V = 1675.25(4) Å^3, Z = 4, T = 293(2) K, μ(Cu Kα) = 0.538 mm^{-1}, *Dcalc* = 1.219 g/cm^3, 15651 reflections measured (7.396° ≤ 2Θ ≤ 141.248°), 3207 unique (R_{int} = 0.0190, R_{sigma} = 0.0123) which were used in all calculations. The final R_1 was 0.0354 (I > 2σ(I)) and wR_2 was 0.0984 (all data).

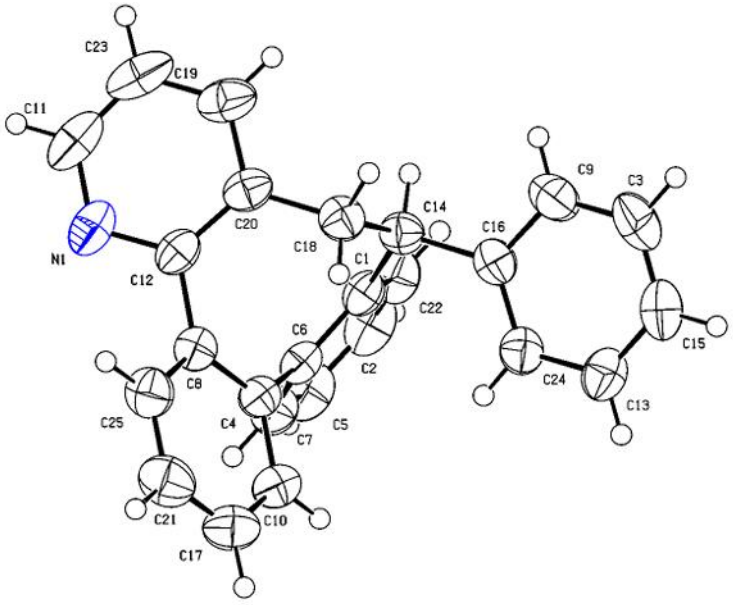


Figure S2. The X-ray crystallographic structure of **2ai**

Figure S2. X-ray crystallographic structure of **2ai** (CCDC 2380480) showing thermal ellipsoid probability at 50%. A suitable crystal **2ai** was selected and mounted on a **XtaLAB Synergy R, DW system, HyPix** diffractometer. The crystal was kept at 302.34(10) K during data collection. Using Olex2[5], the structure was solved with the SHELXT[6] structure solution program using Intrinsic Phasing and refined with the SHELXL[7] refinement package using Least Squares minimisation.

Crystal Data for $C_{25}H_{19}N$ (M =333.41 g/mol): triclinic, space group P-1 (no. 2), a = 7.7811(4) Å, b = 9.7347(4) Å, c = 13.6565(7) Å, α = 100.211(4)°, β = 100.569(4)°, γ = 109.946(4)°, V = 923.13(8) Å^3, Z = 2, T = 302.34(10) K, μ(Cu Kα) = 0.527 mm^{-1}, *Dcalc* = 1.199 g/cm^3, 10212 reflections measured (6.818° ≤ 2Θ ≤ 152.426°), 3621 unique (R_{int} = 0.0178, R_{sigma} = 0.0172) which were used in all calculations. The final R_1 was 0.0392 (I > 2σ(I)) and wR_2 was 0.1067 (all data).

8. References

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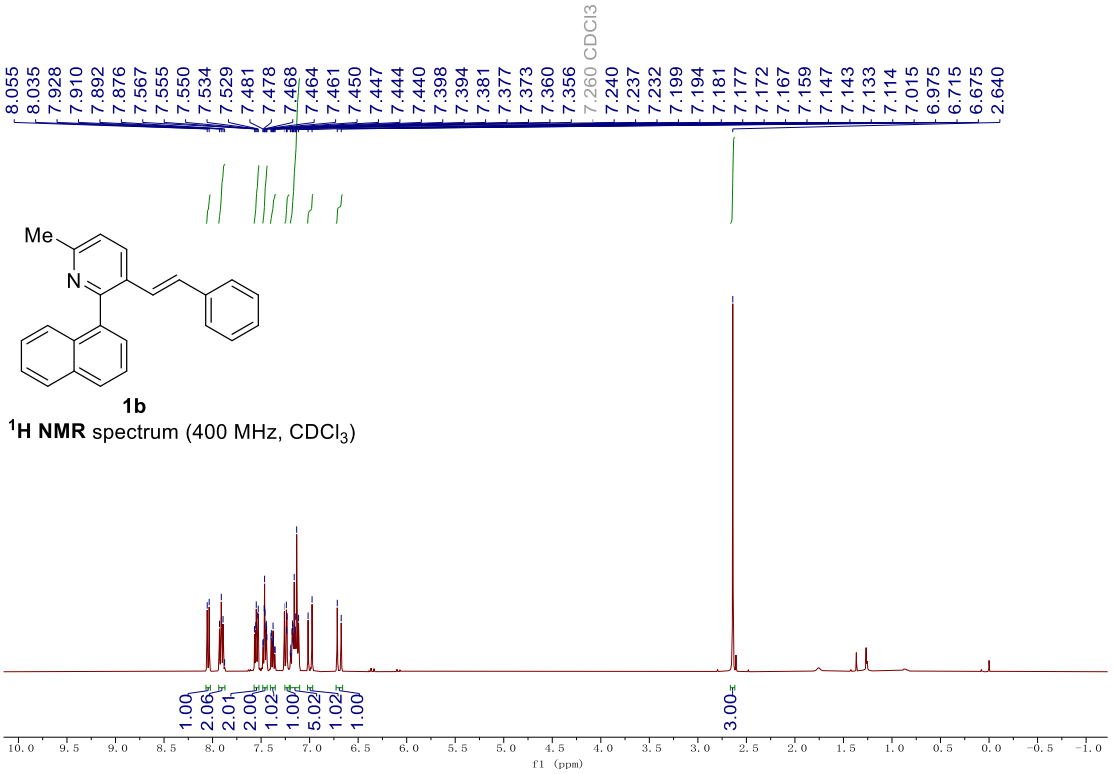
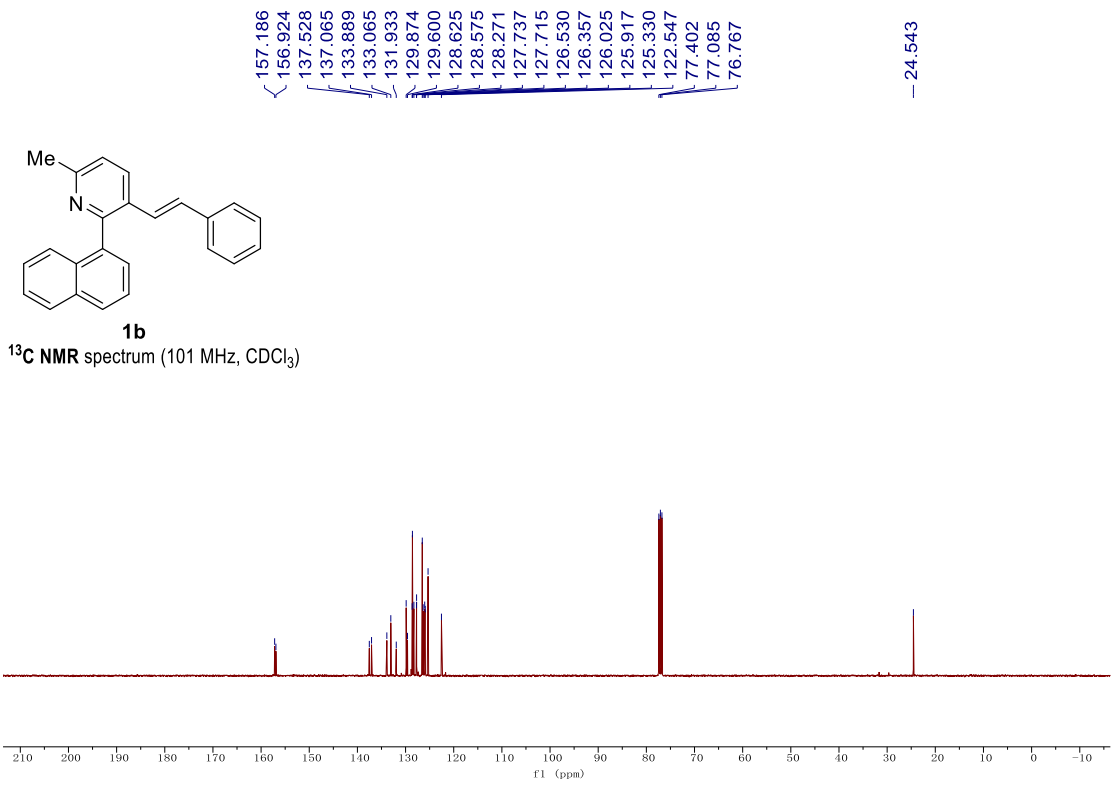
9. Copies of NMR spectra



1b

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



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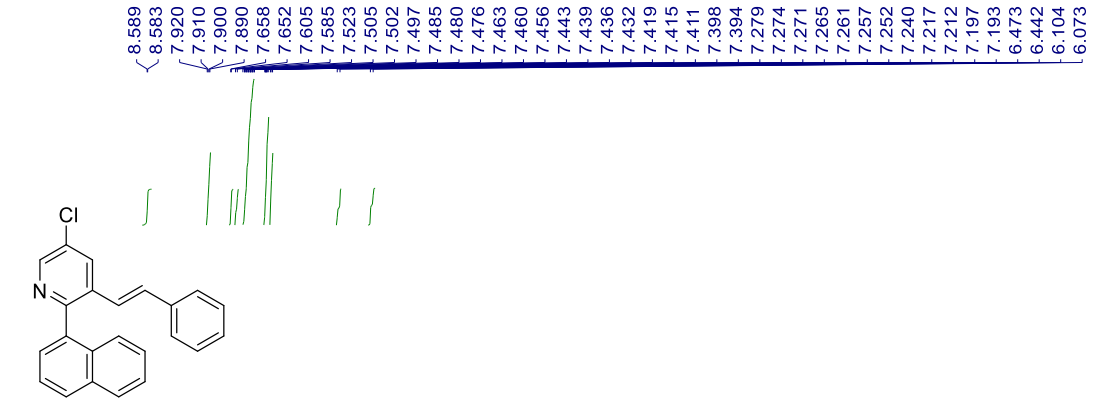
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



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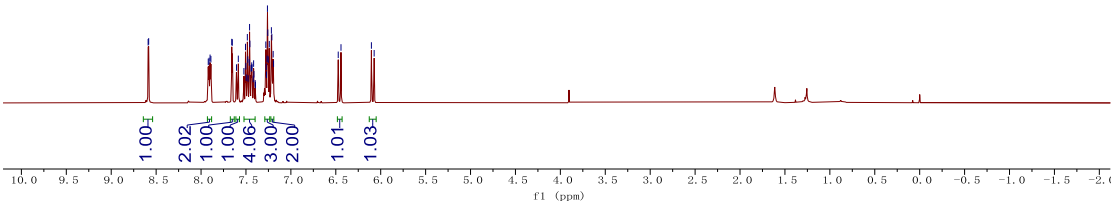
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



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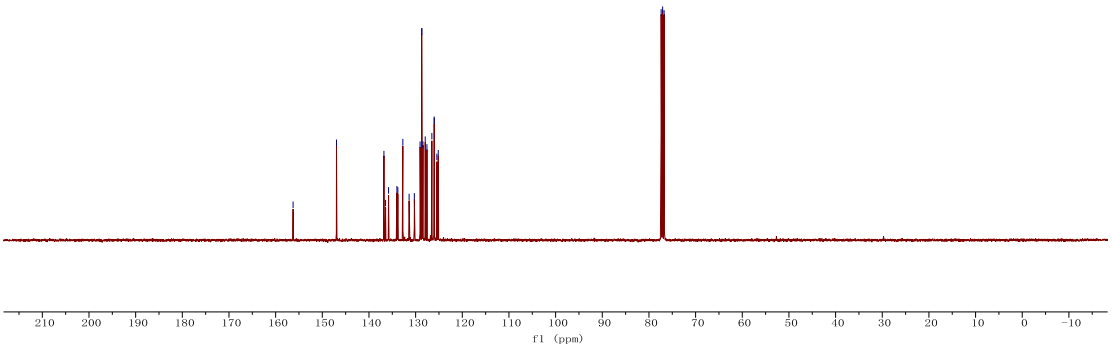
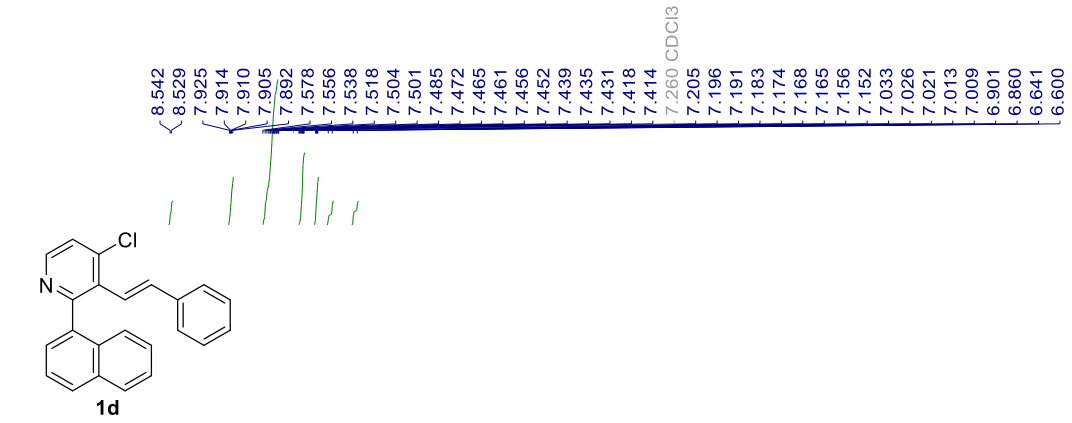
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





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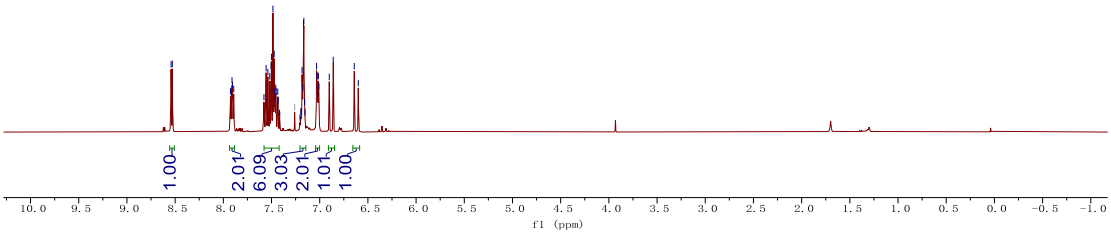

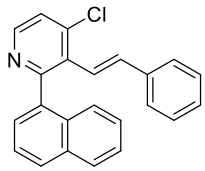

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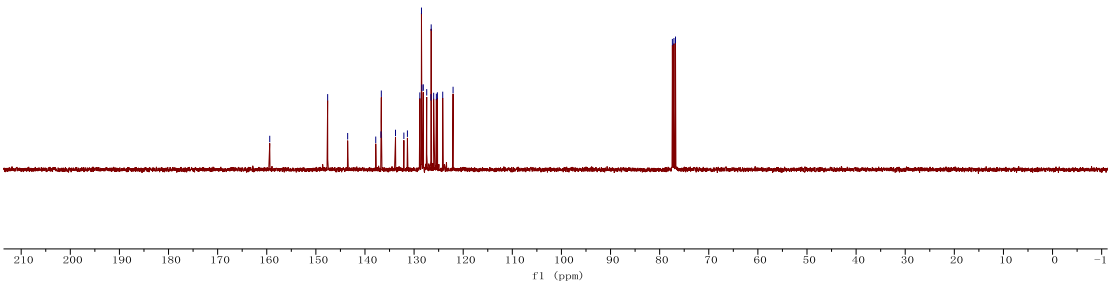
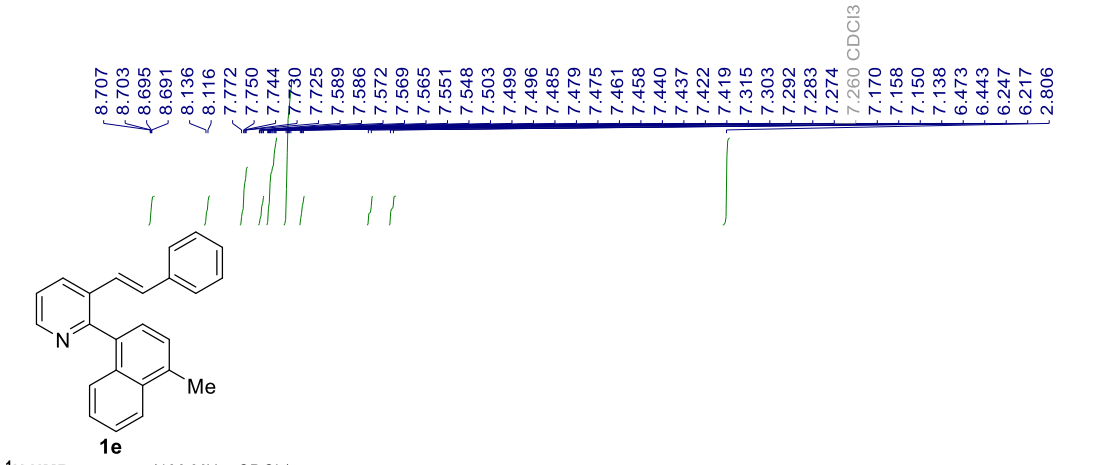
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





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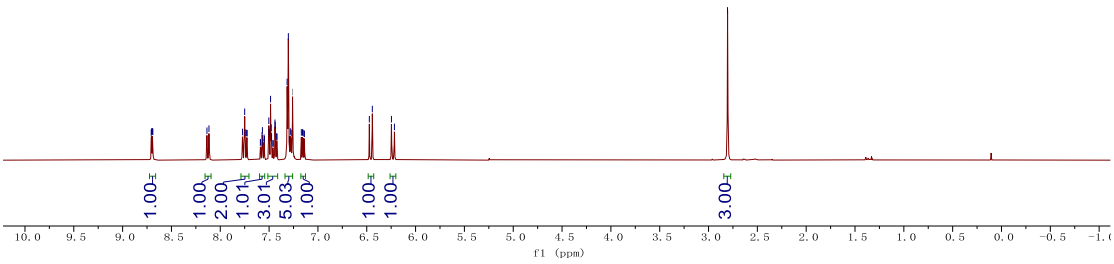
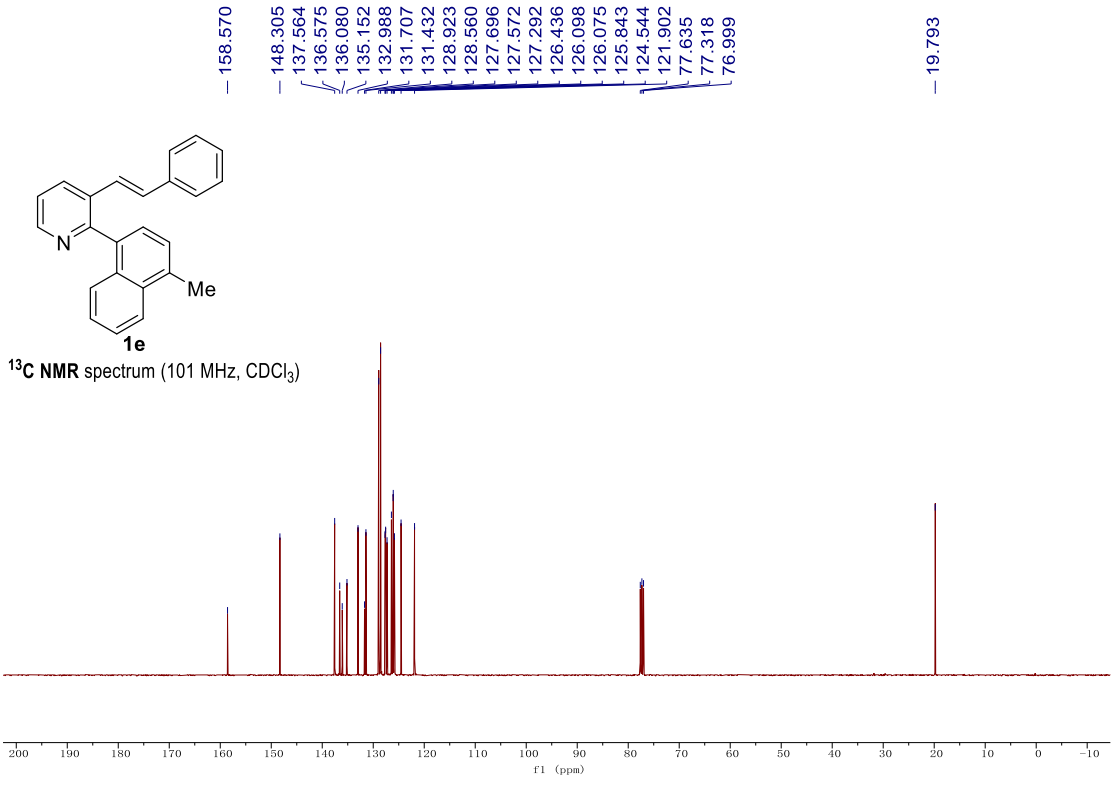
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





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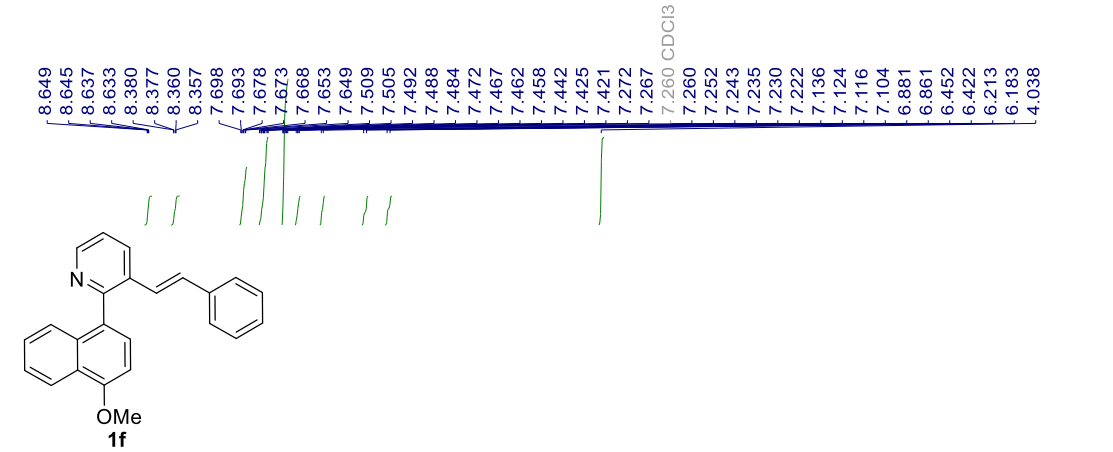
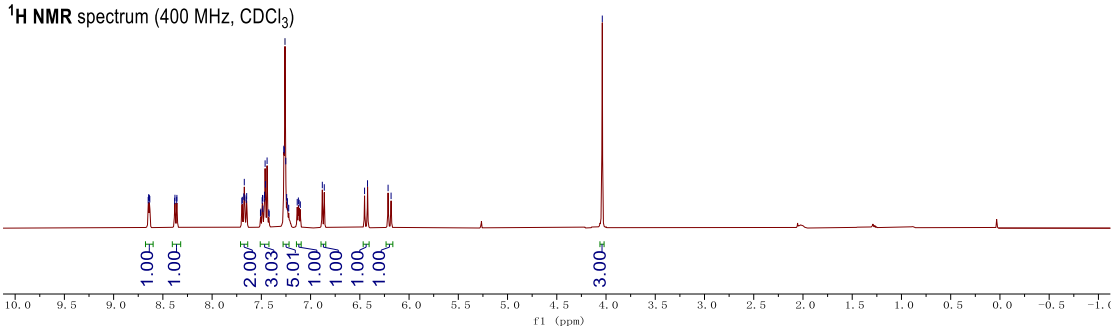
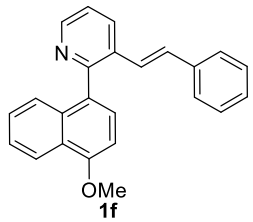
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1f

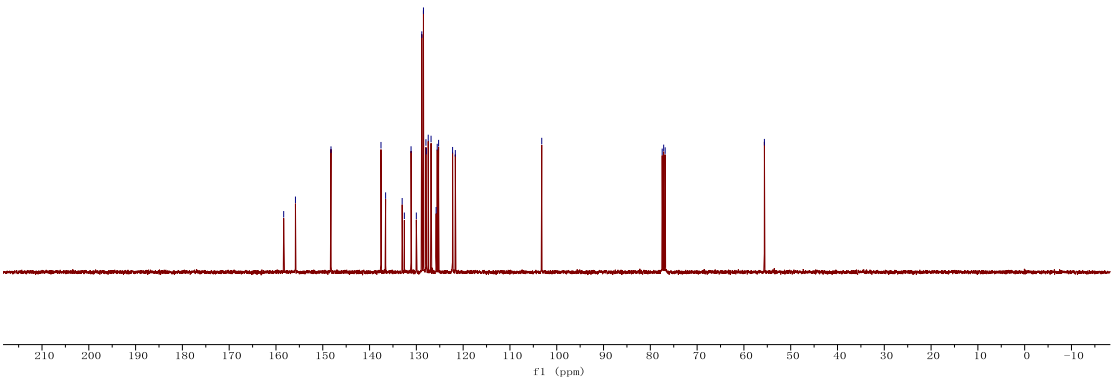
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

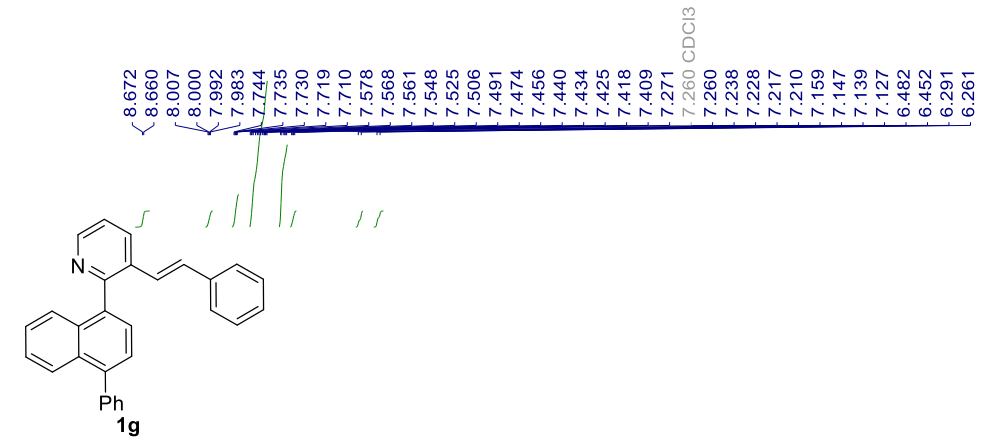




1f

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)





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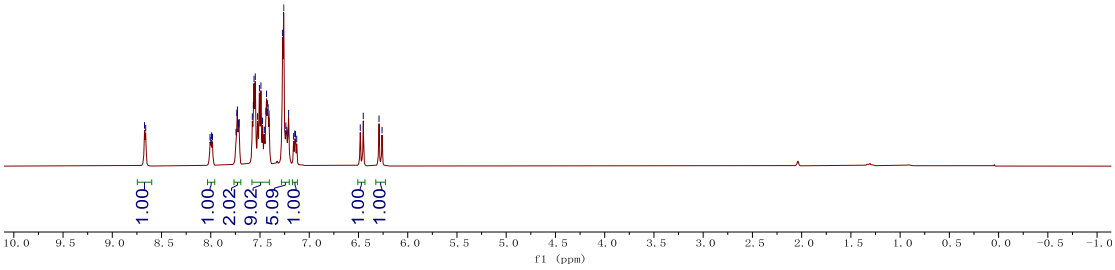
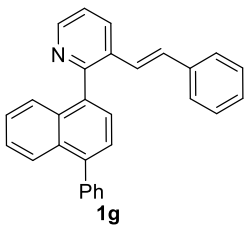
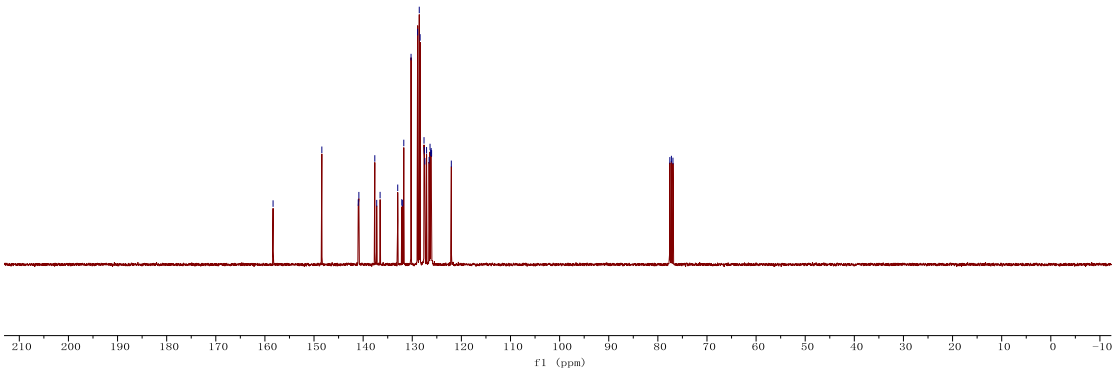
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

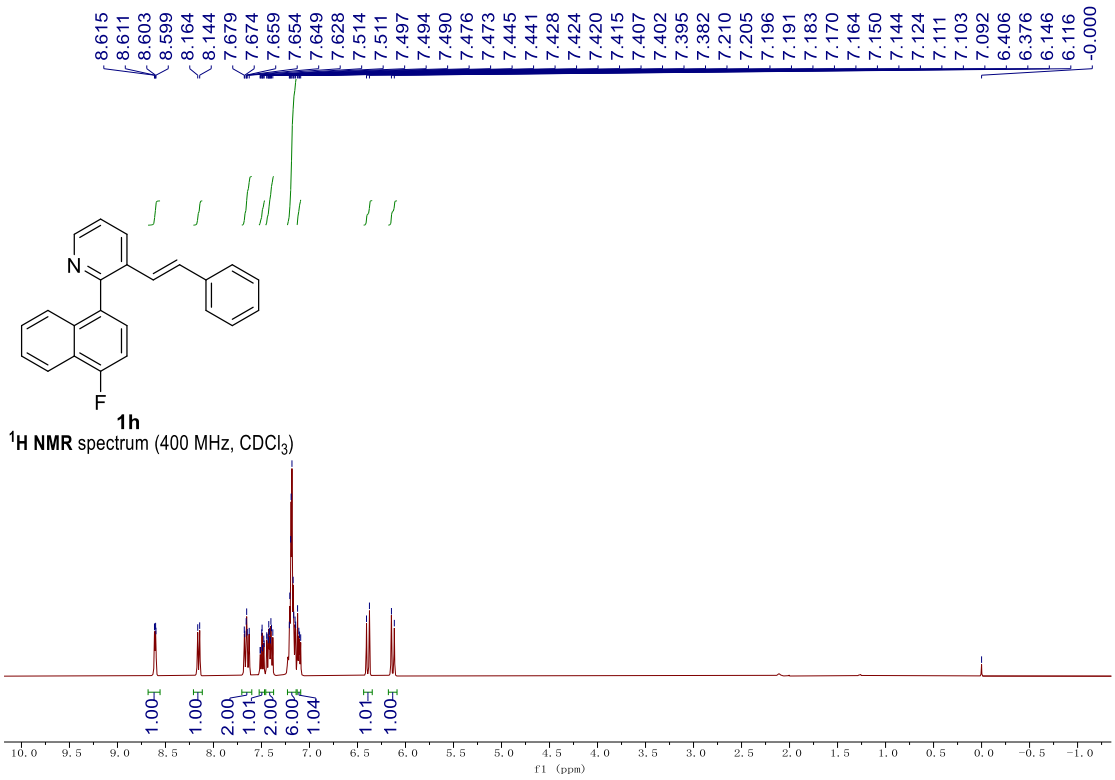




1g

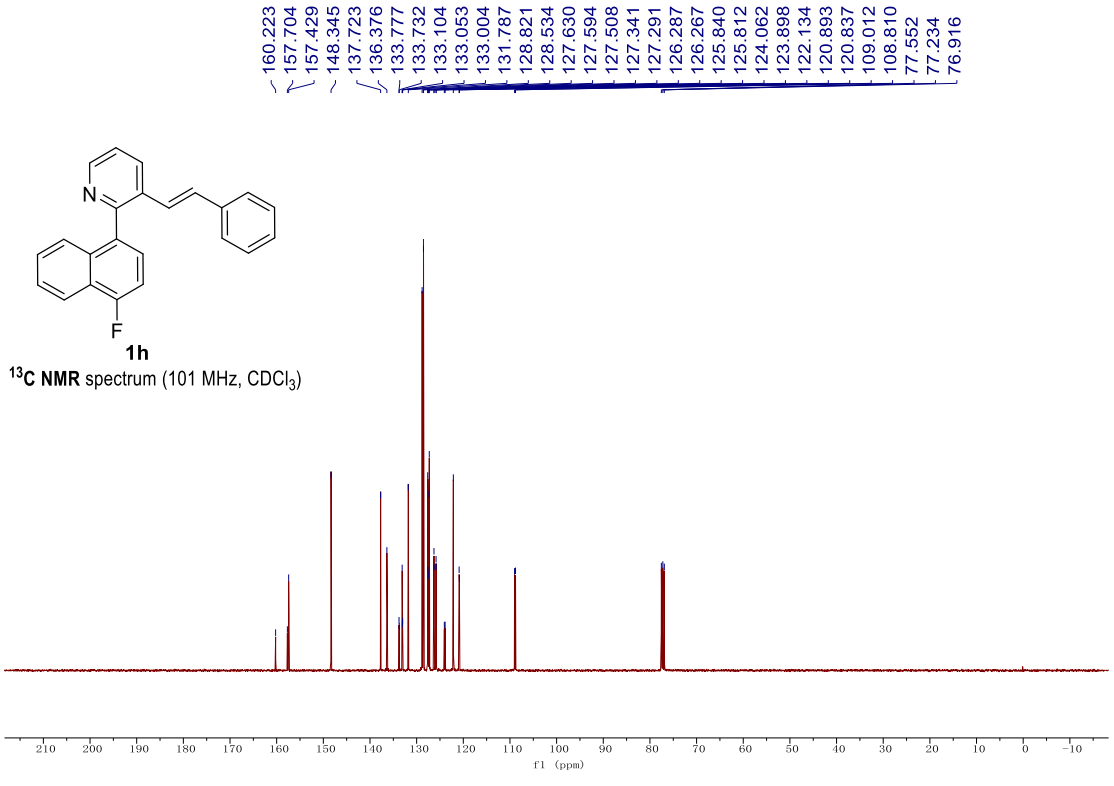
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





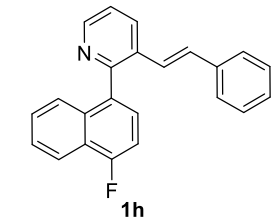
1h

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



1h

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)



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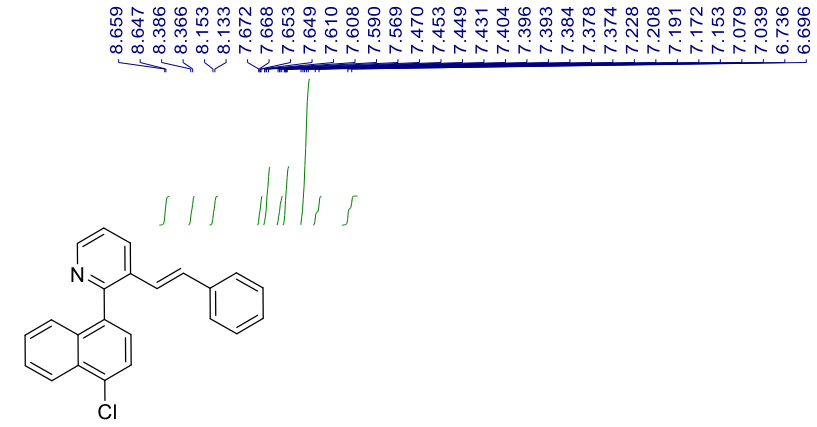
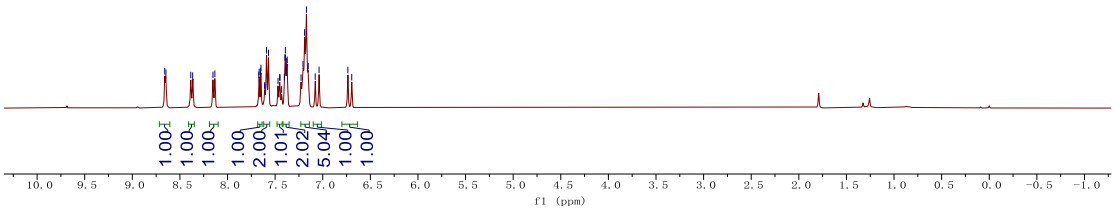
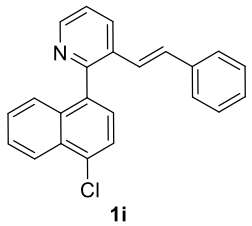
^{19}F NMR spectrum (377 MHz, $CDCl_3$)



1i

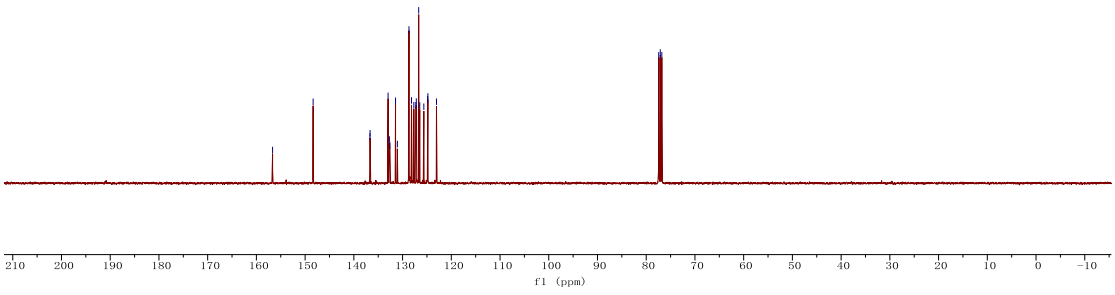
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

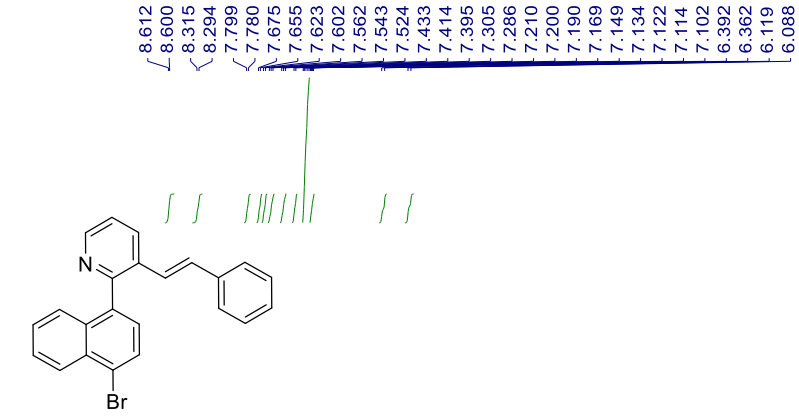




1i

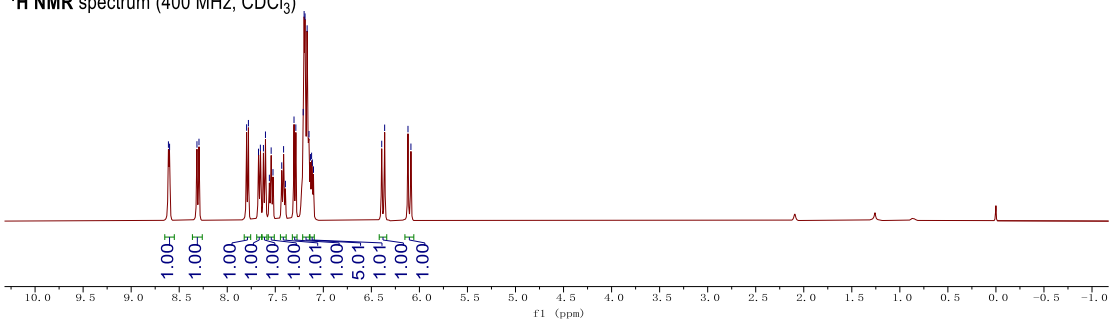
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

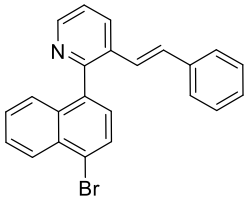




1j

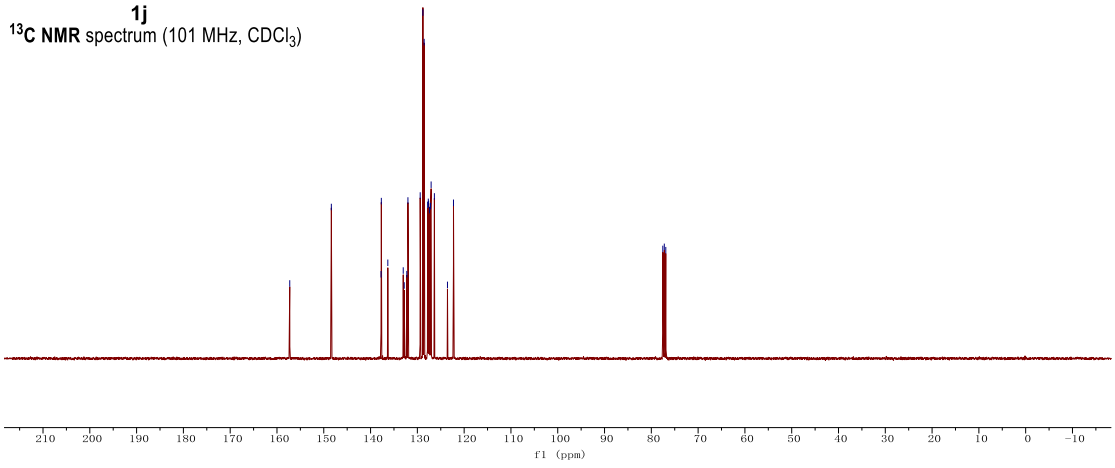
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

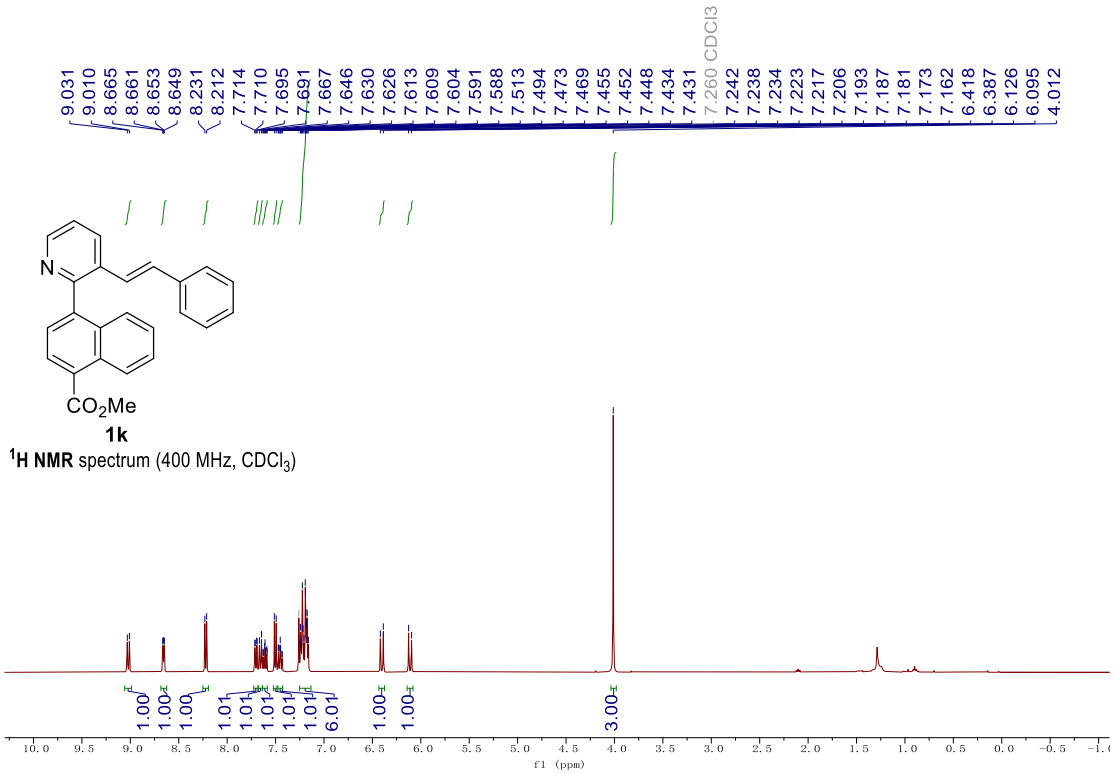




1j

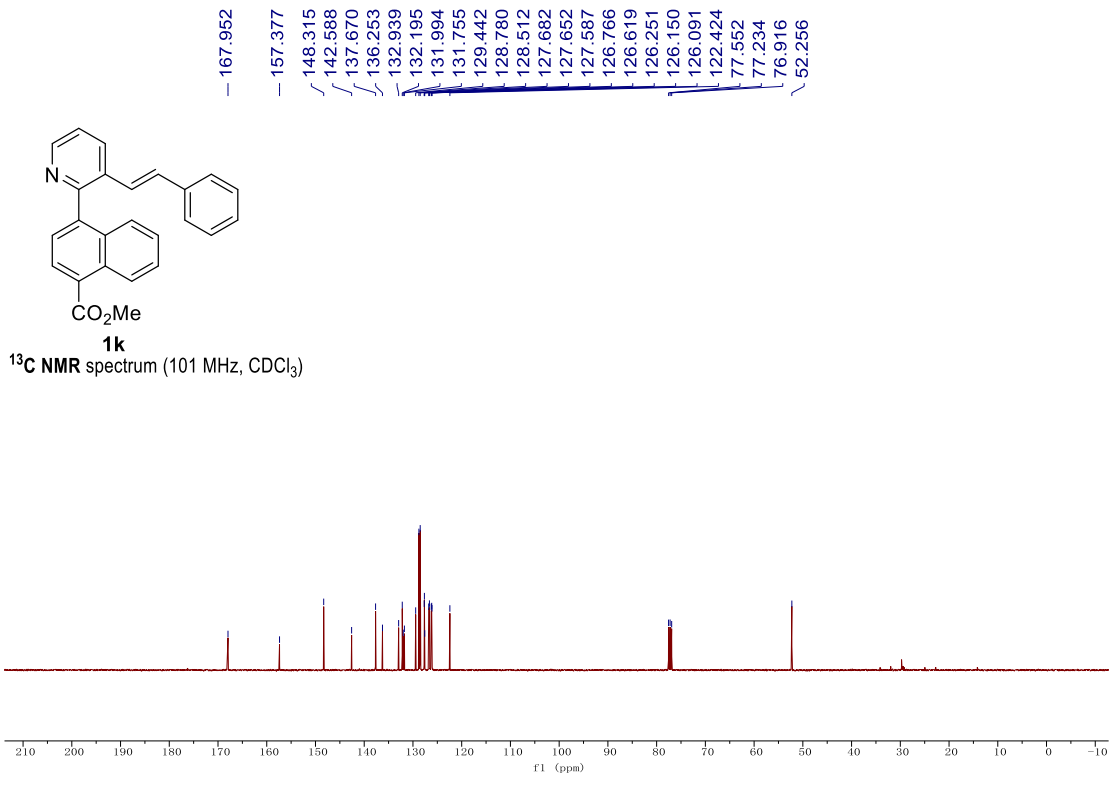
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





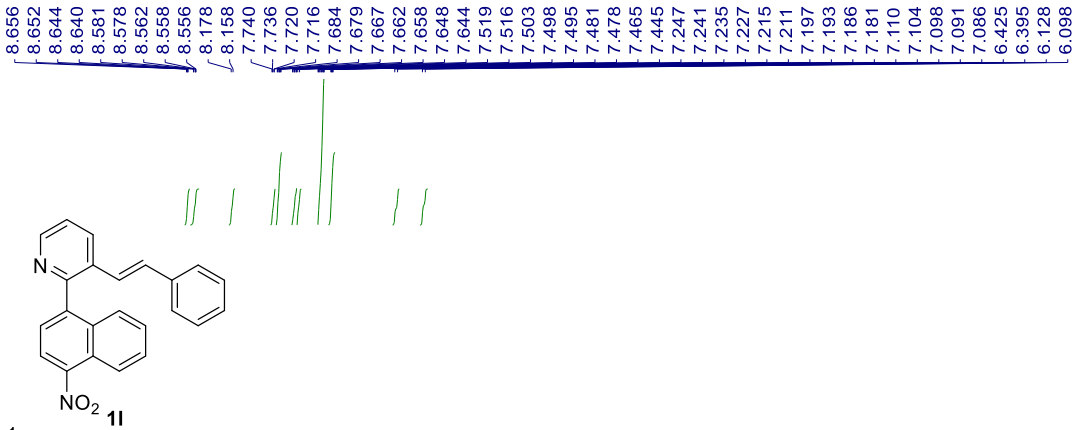
1k

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



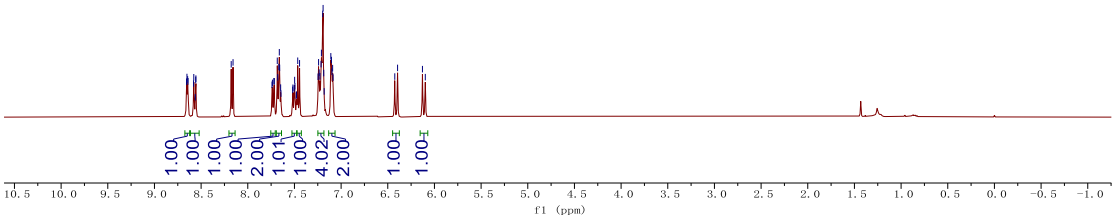
1k

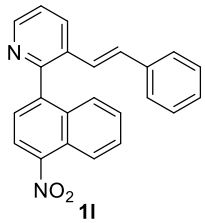
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1l

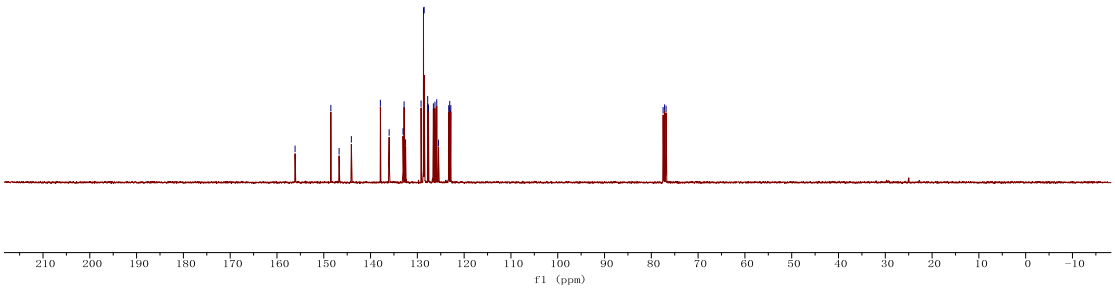
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

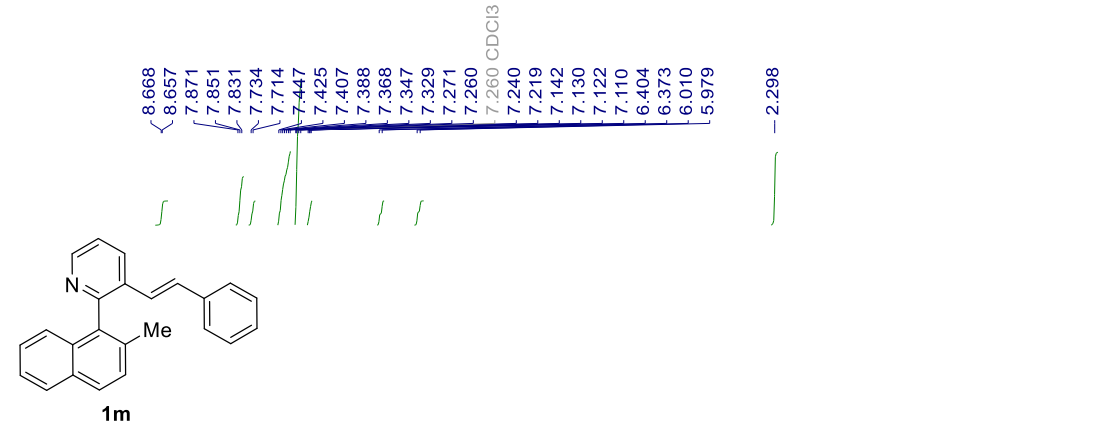




1l

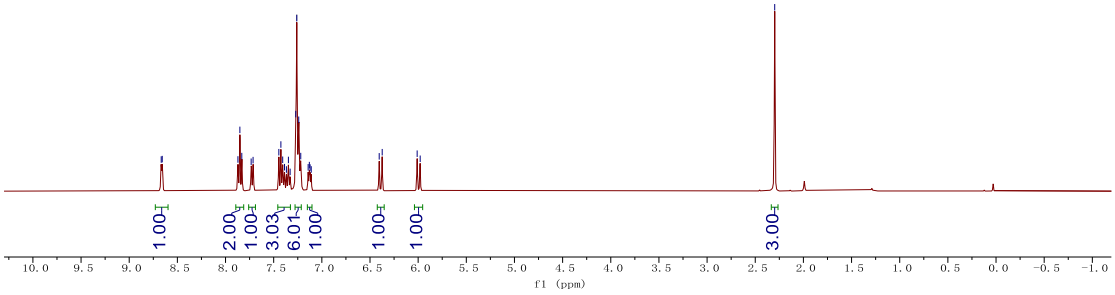
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

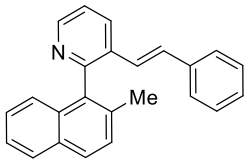




1m

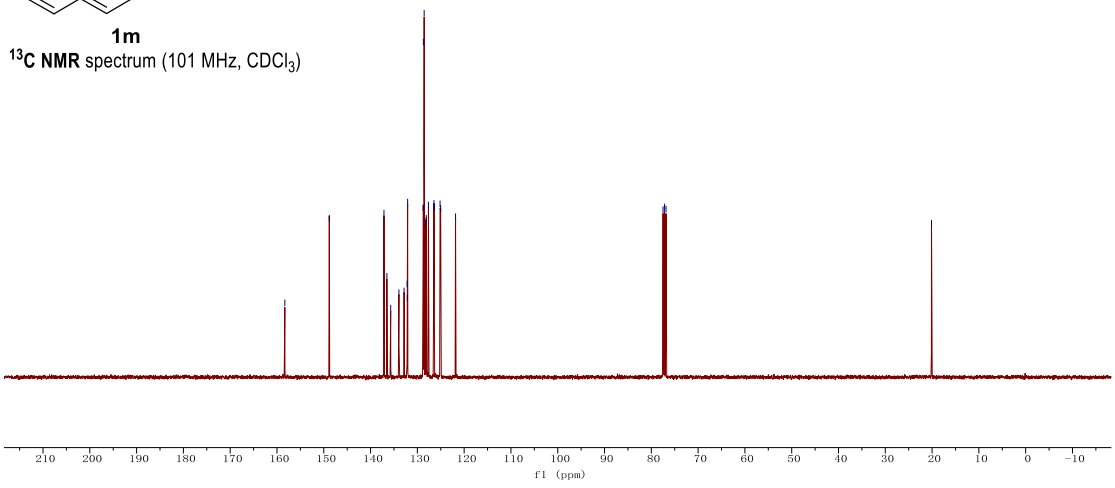
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

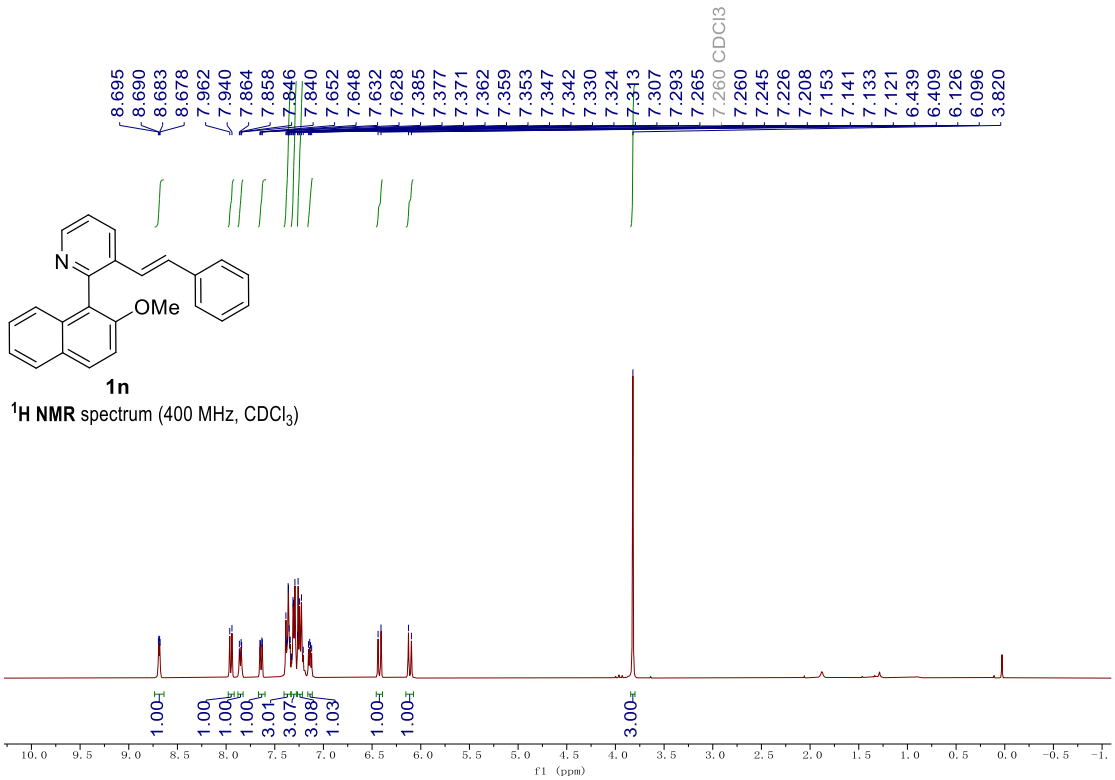




1m

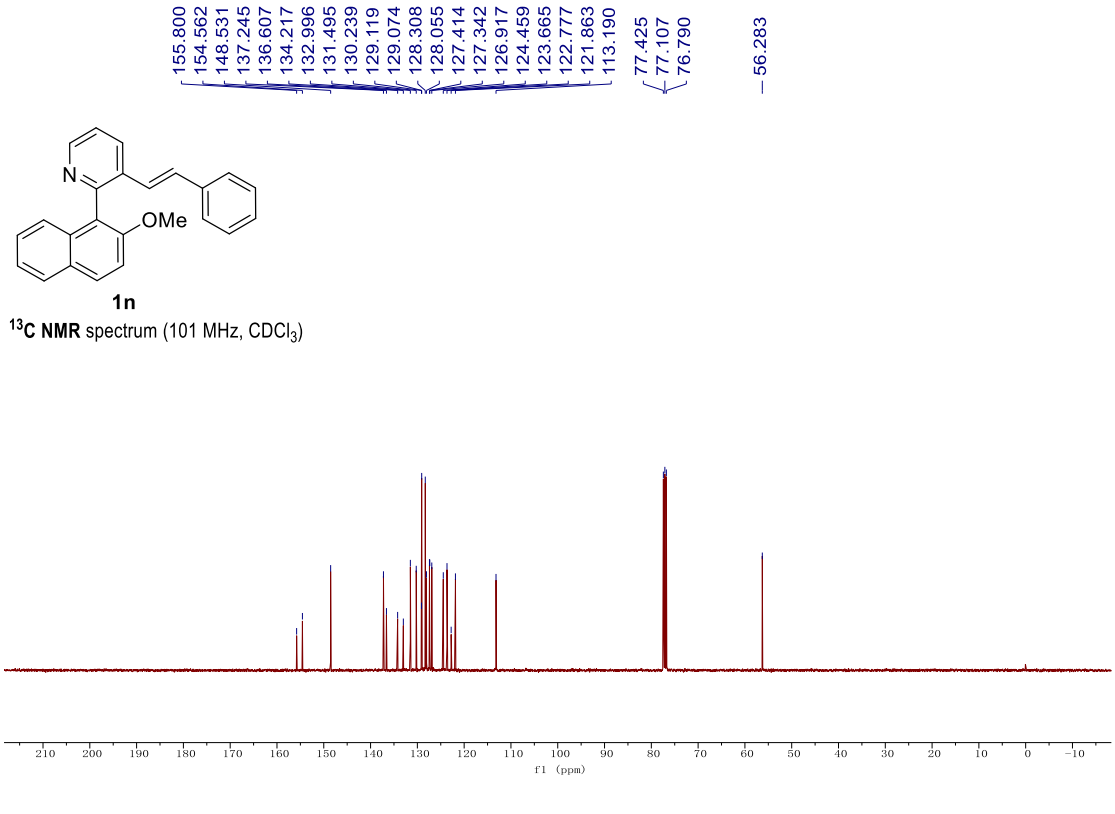
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





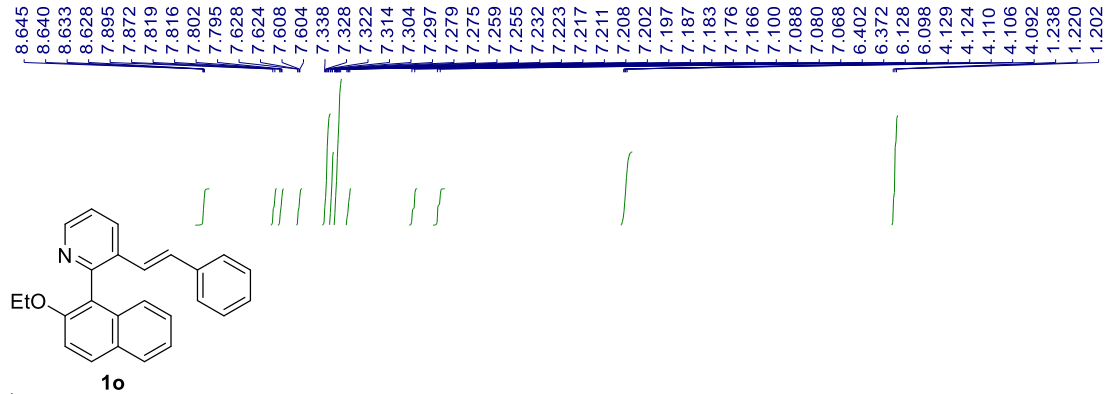
1n

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



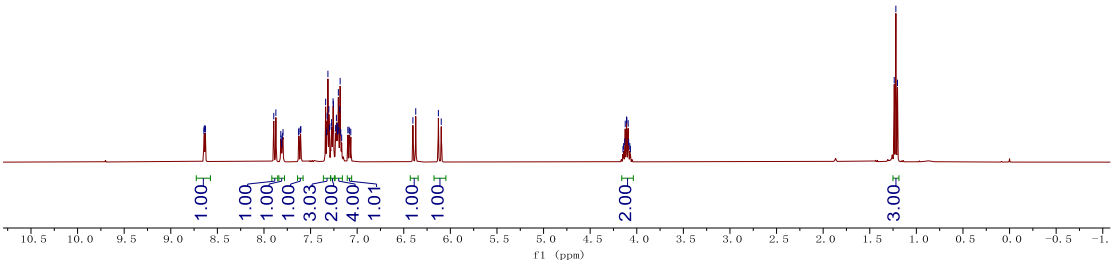
1n

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



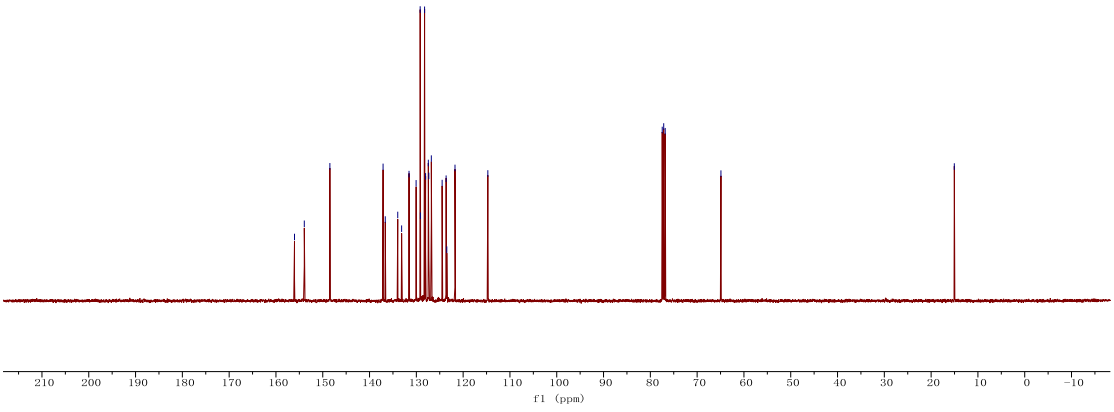
1o

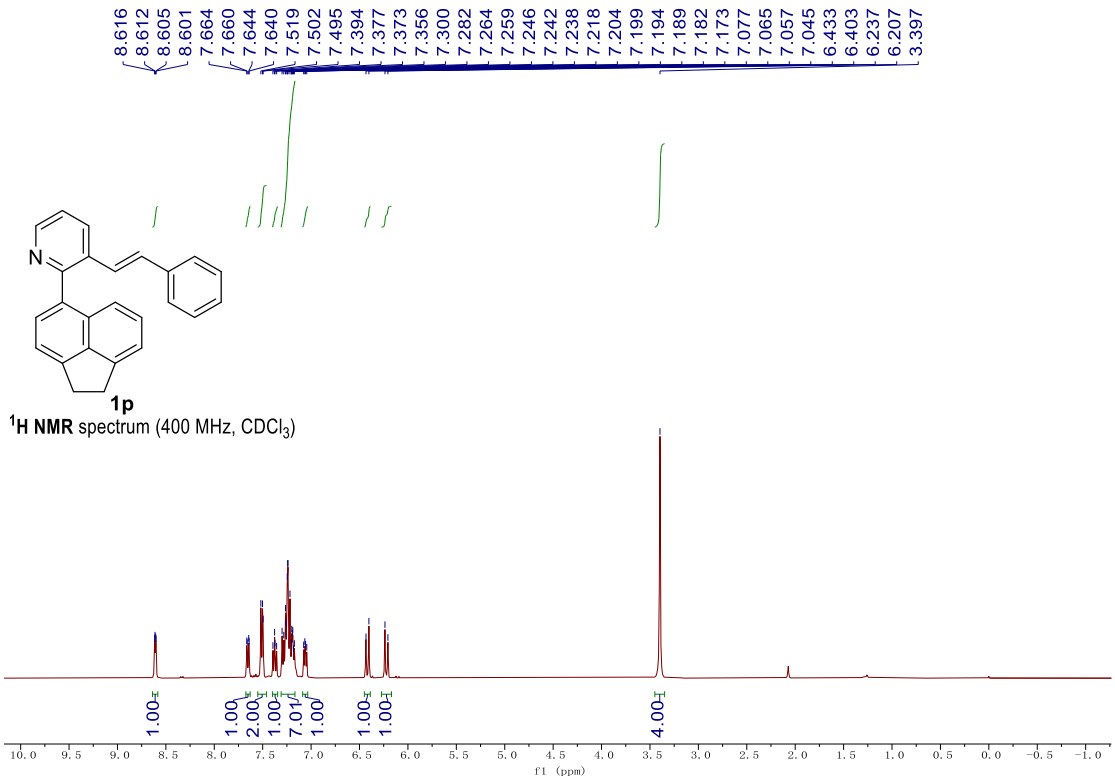
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



1o

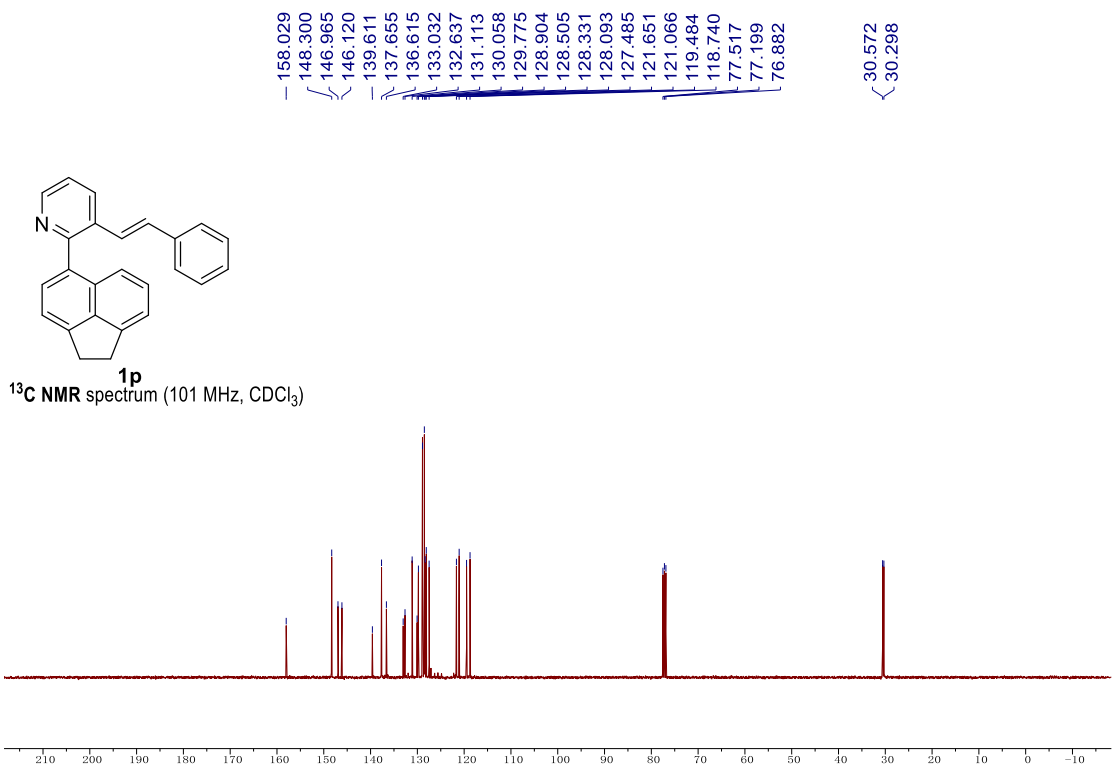
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





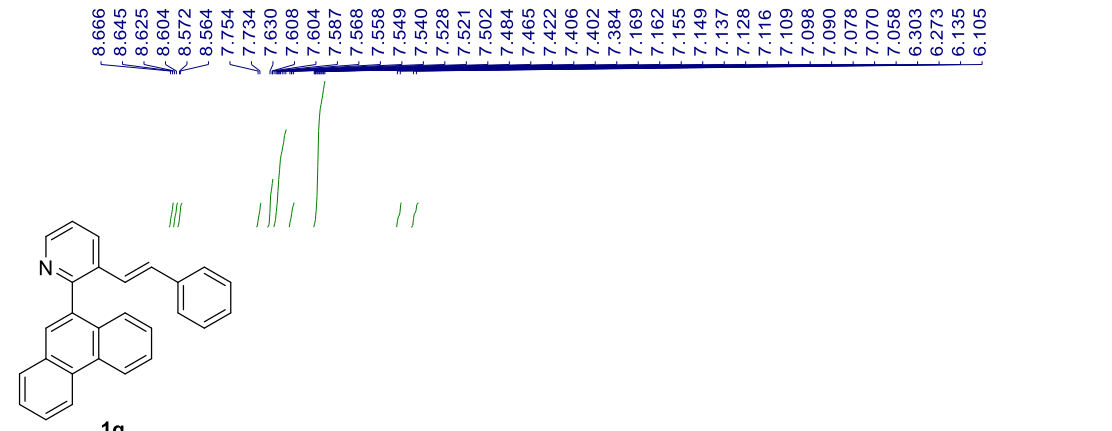
1p

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



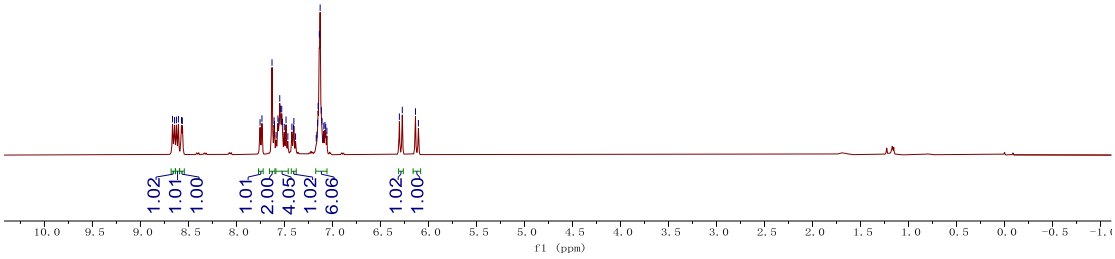
1p

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



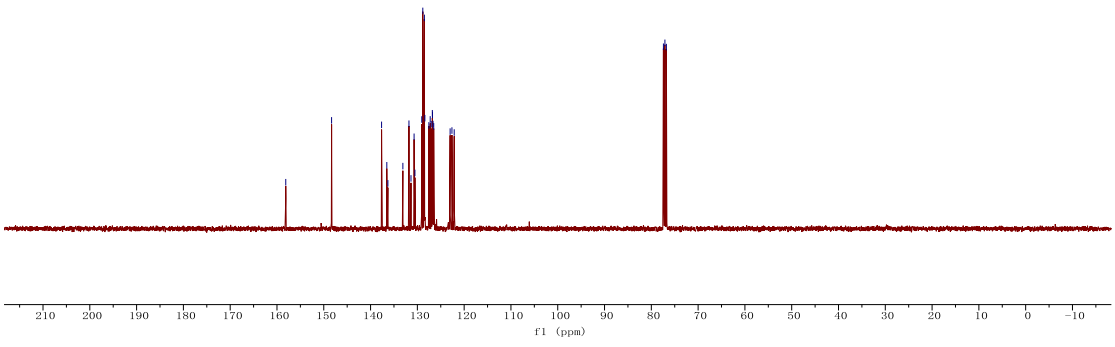
1q

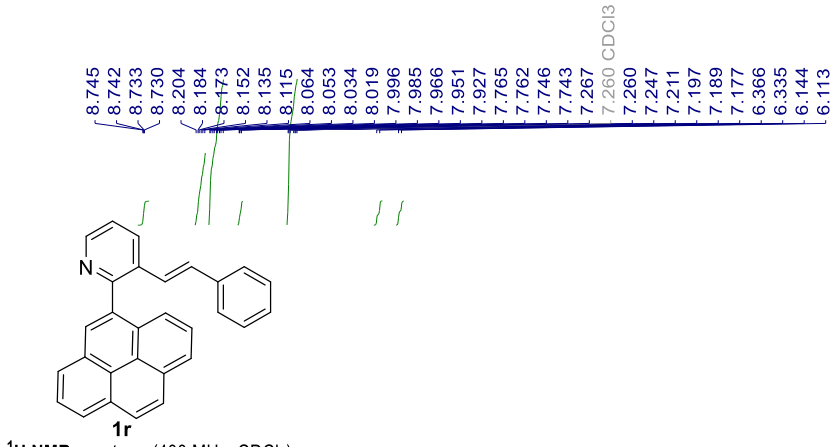
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



1q

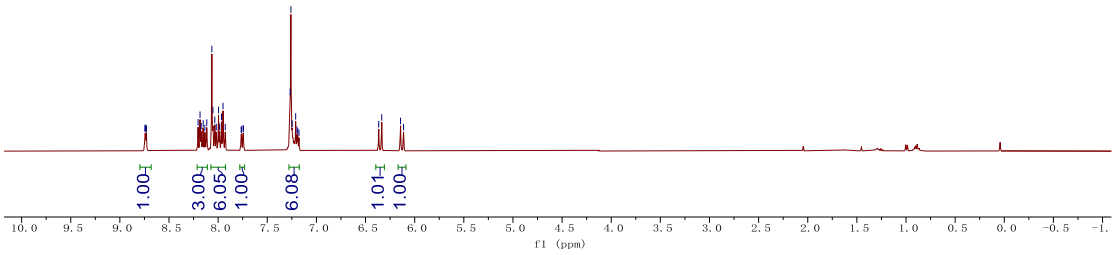
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

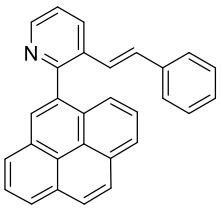




1r

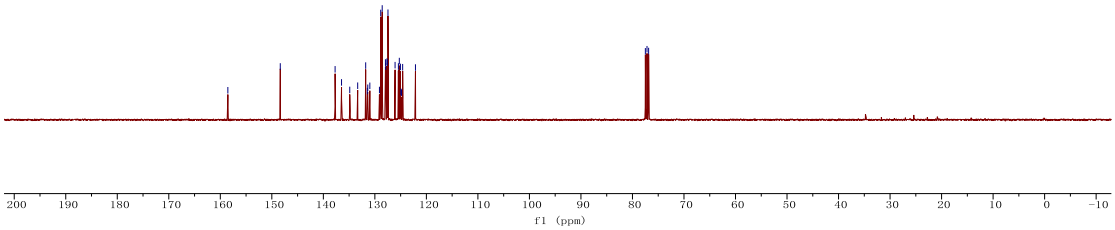
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

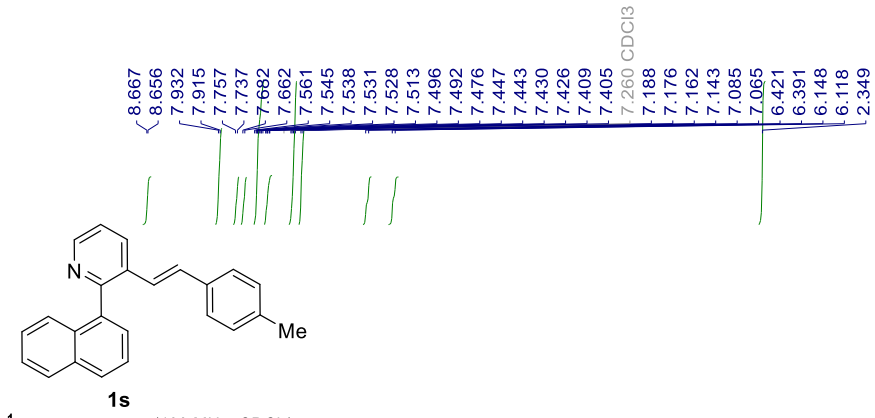




1r

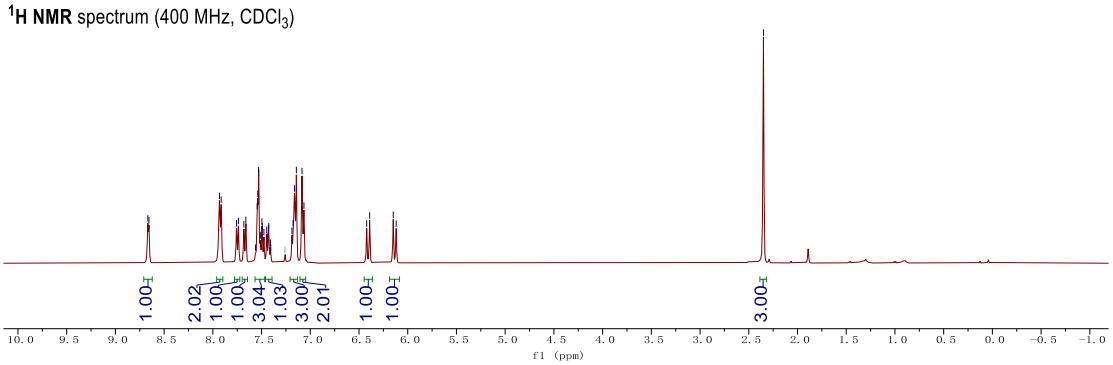
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

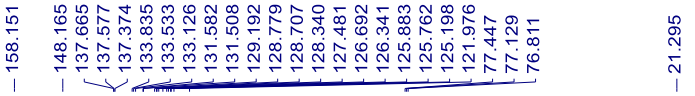


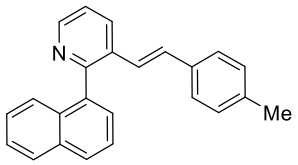


1s

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

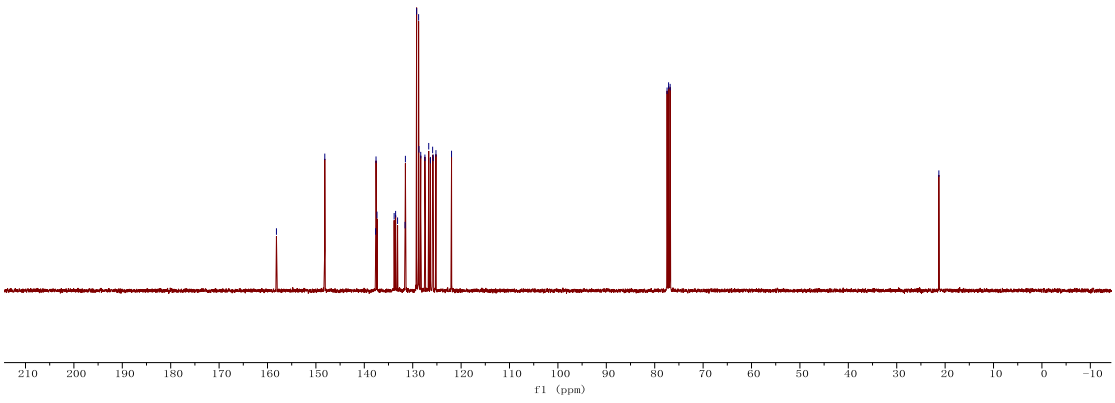


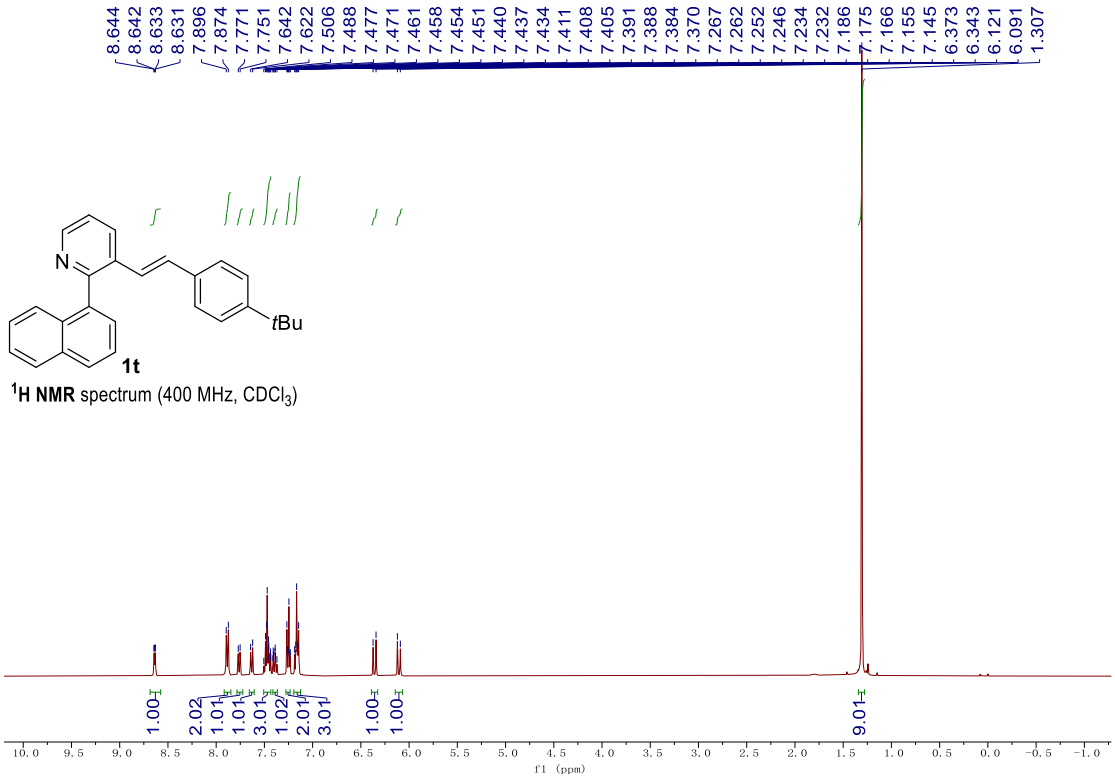




1s

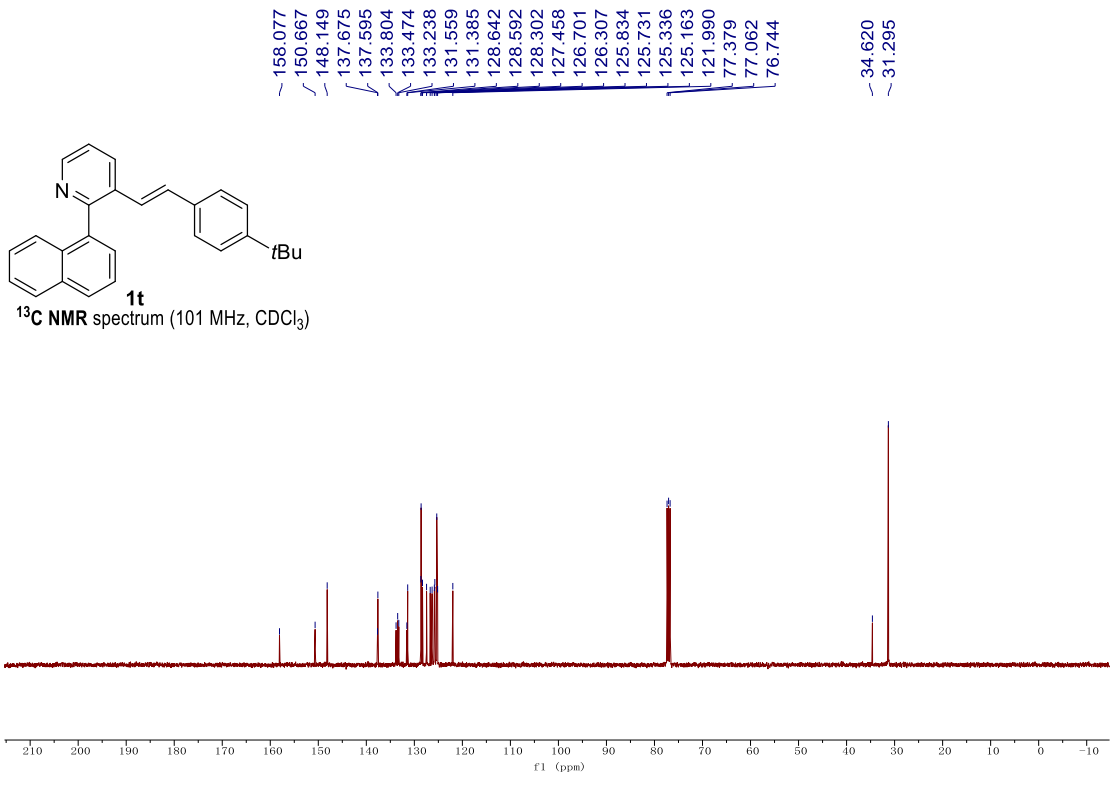
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





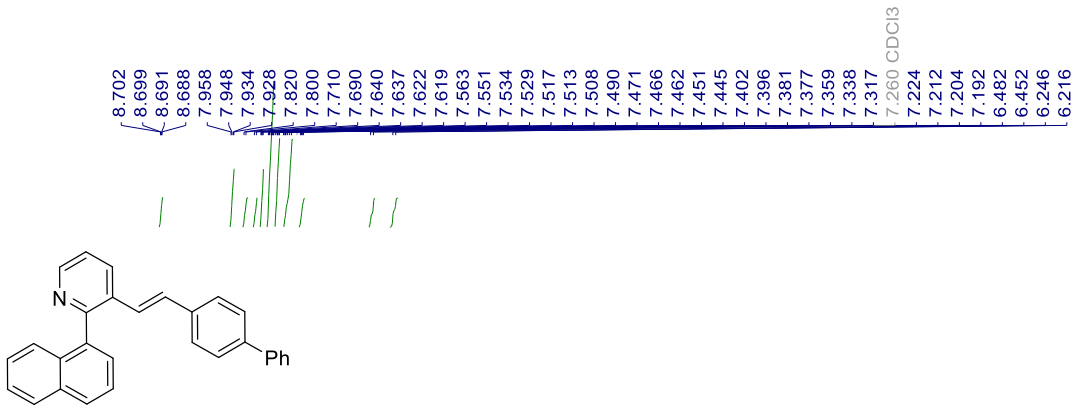
1t

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



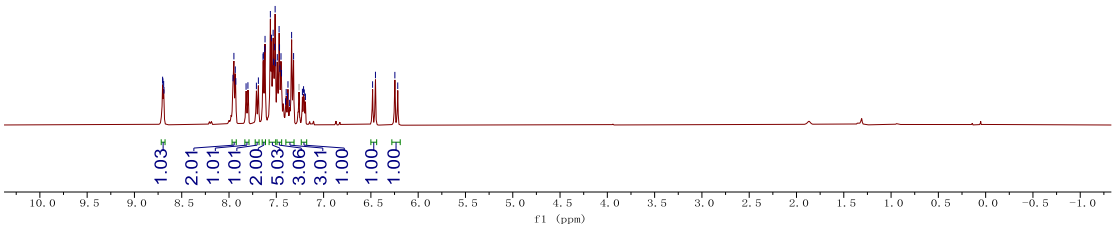
1t

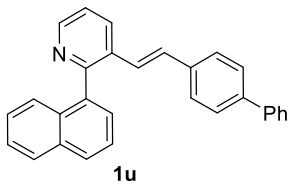
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1u

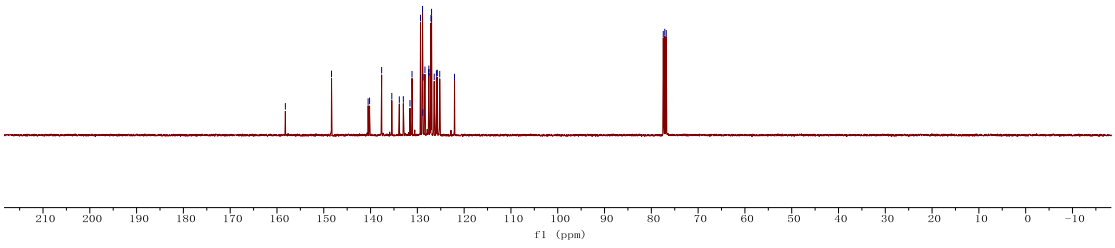
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

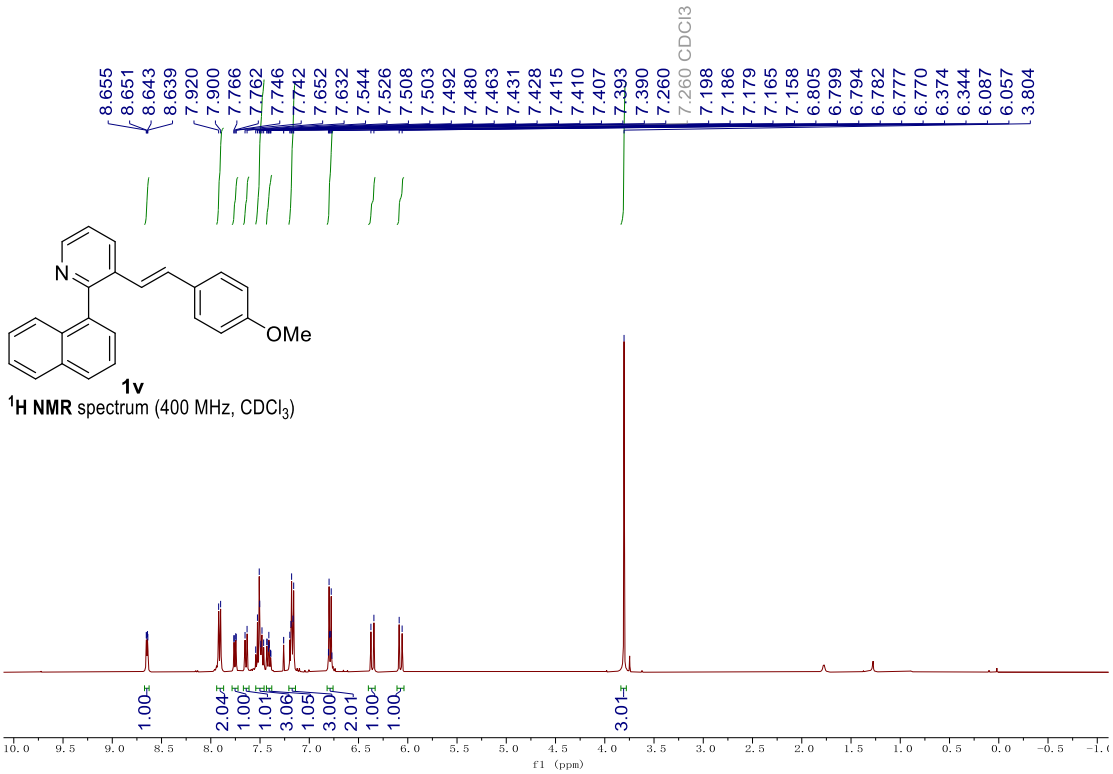




1u

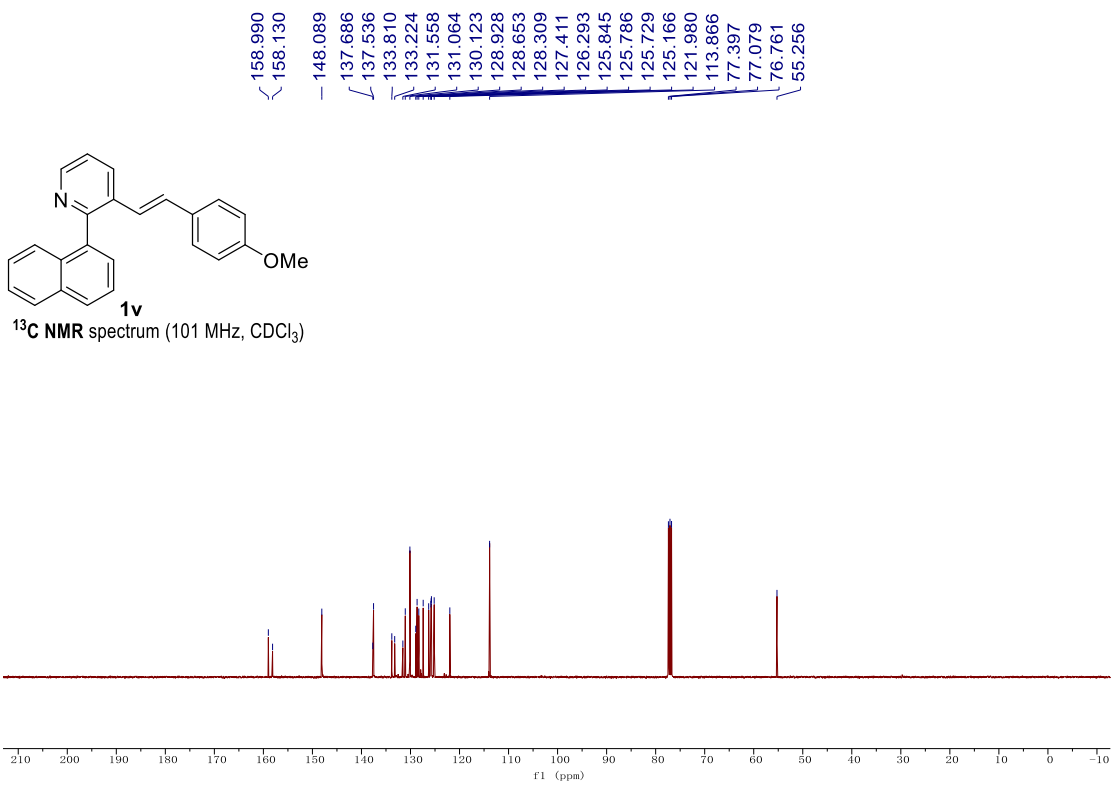
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)





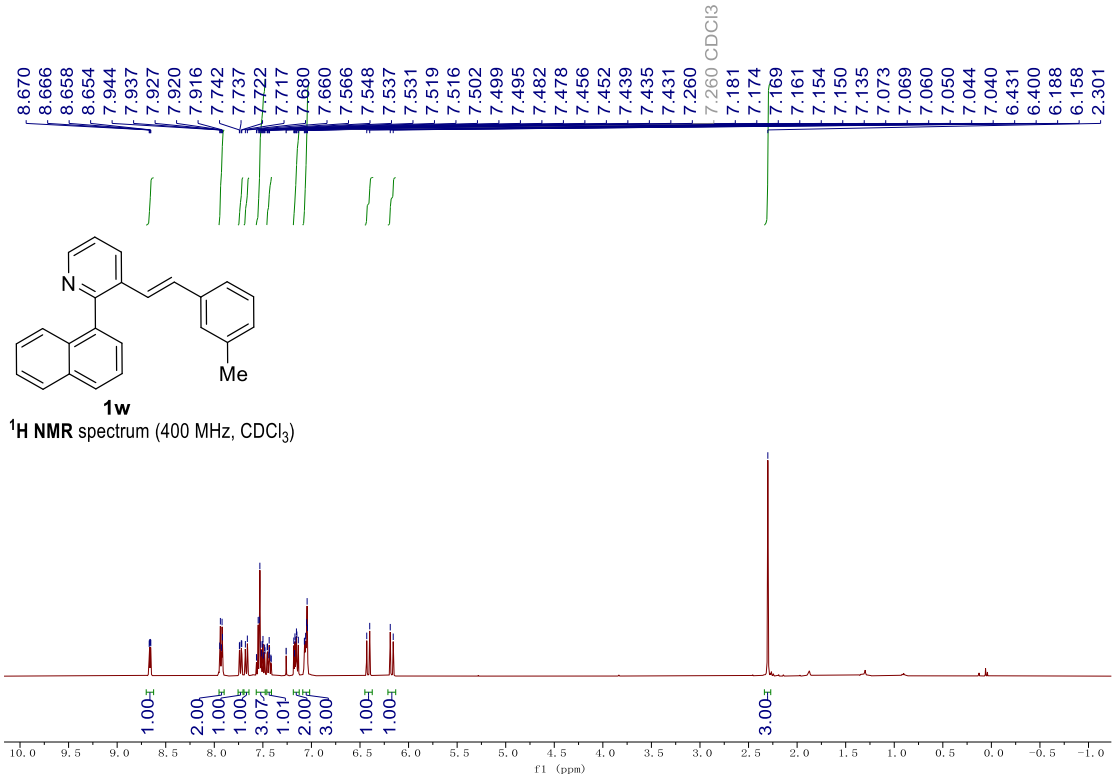
1v

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



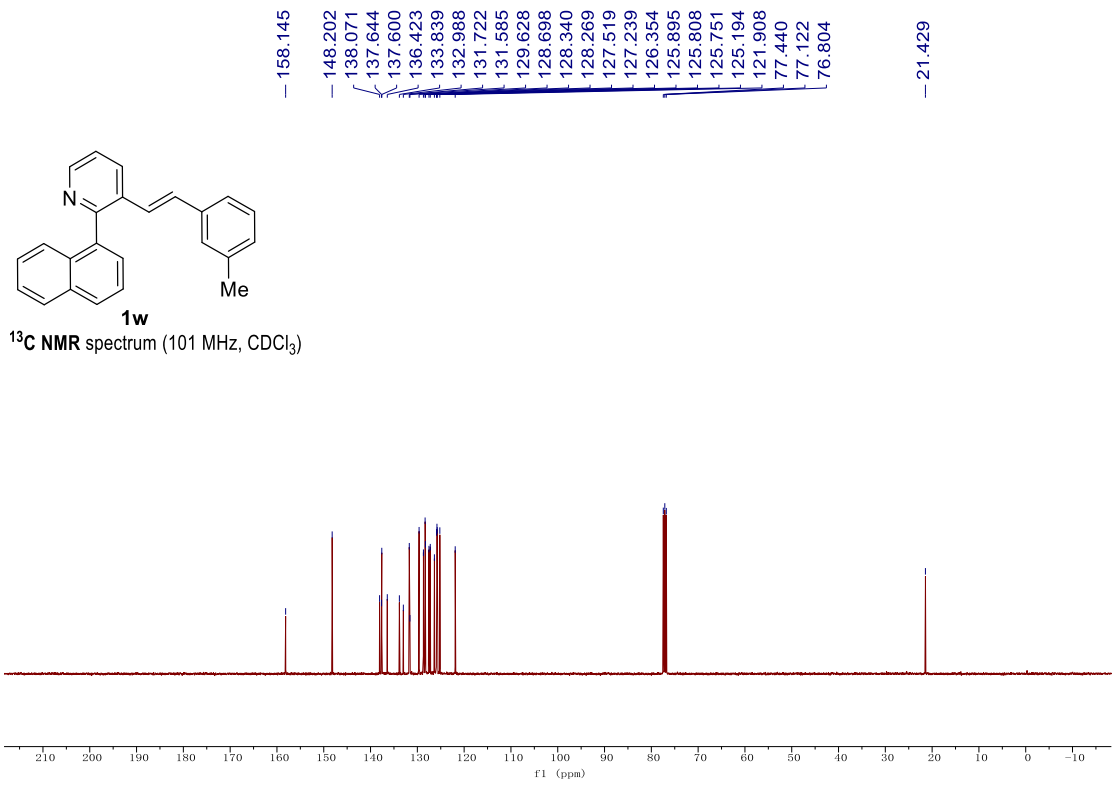
1v

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



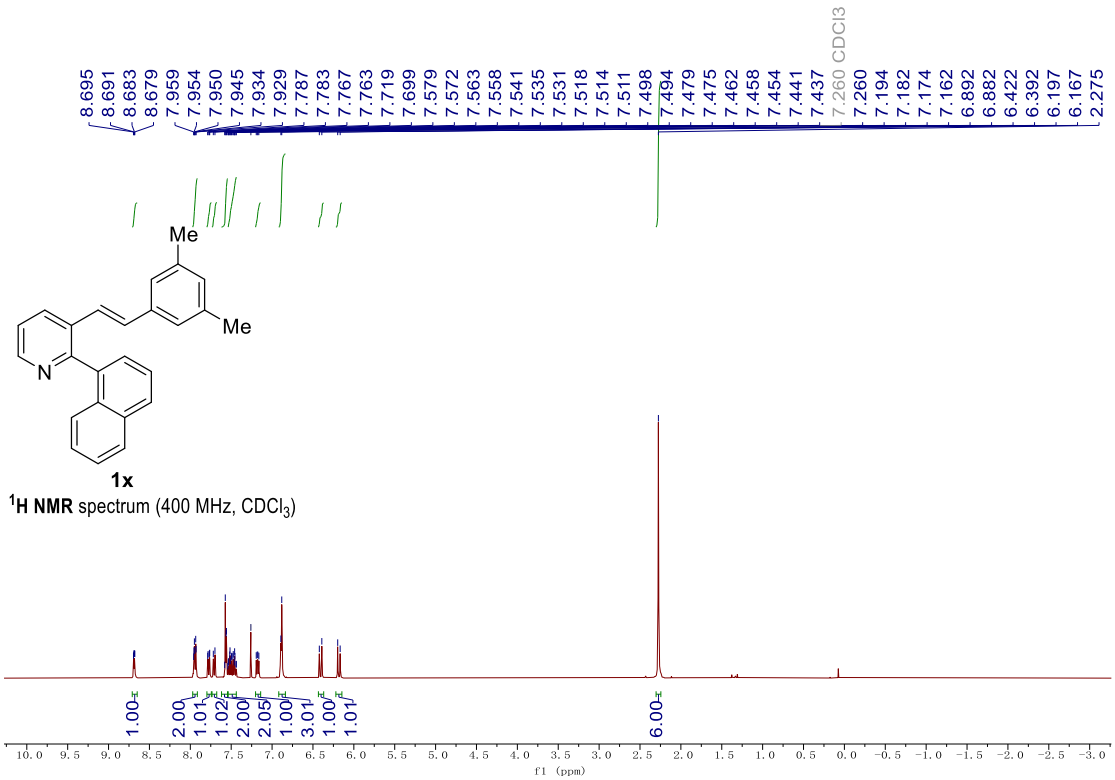
1w

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



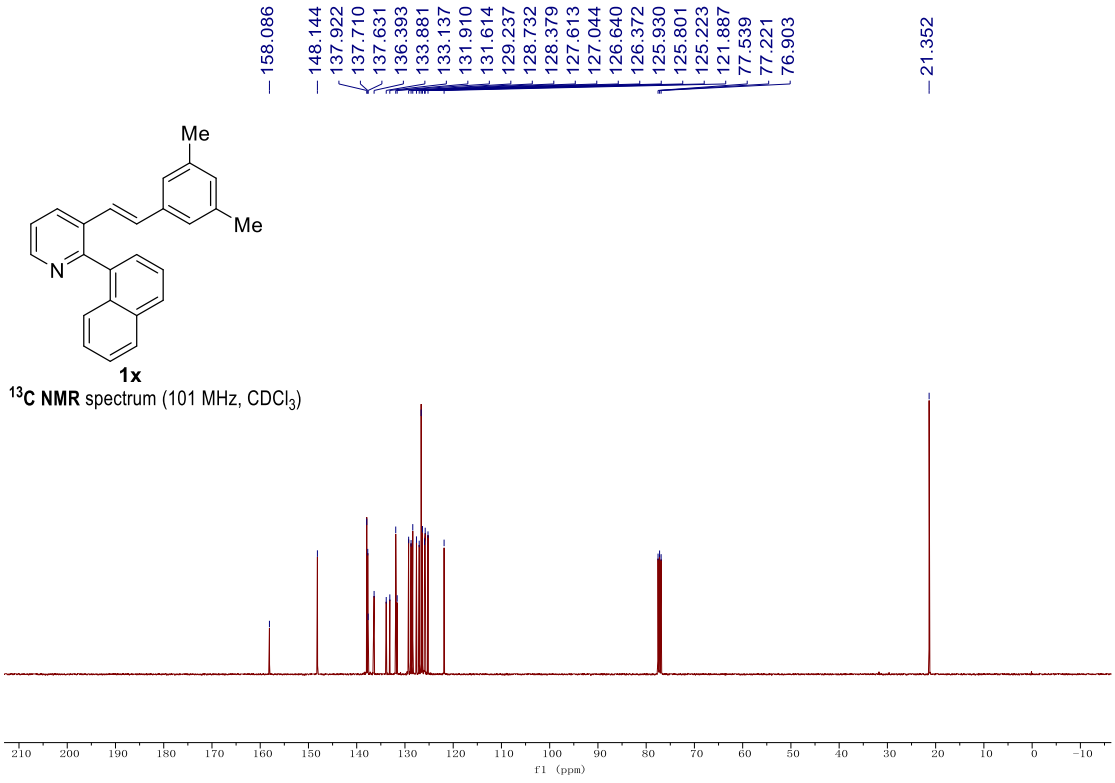
1w

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



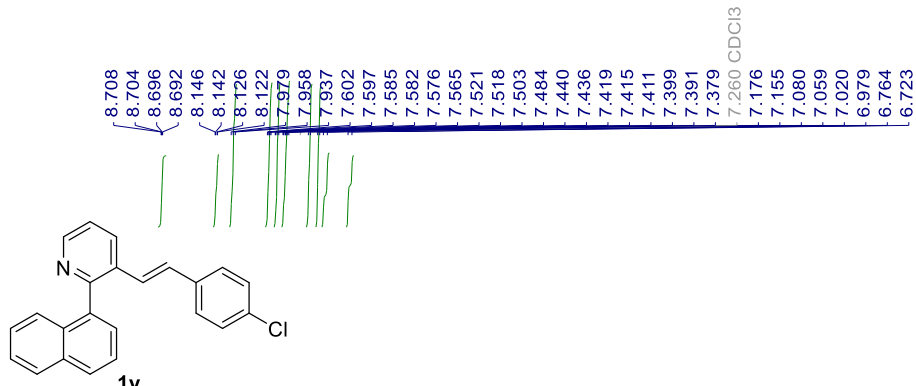
1x

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



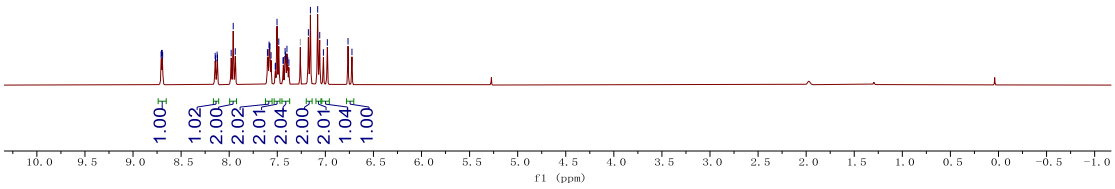
1x

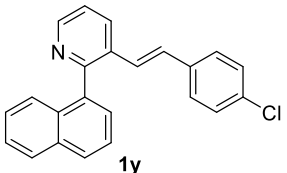
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1y

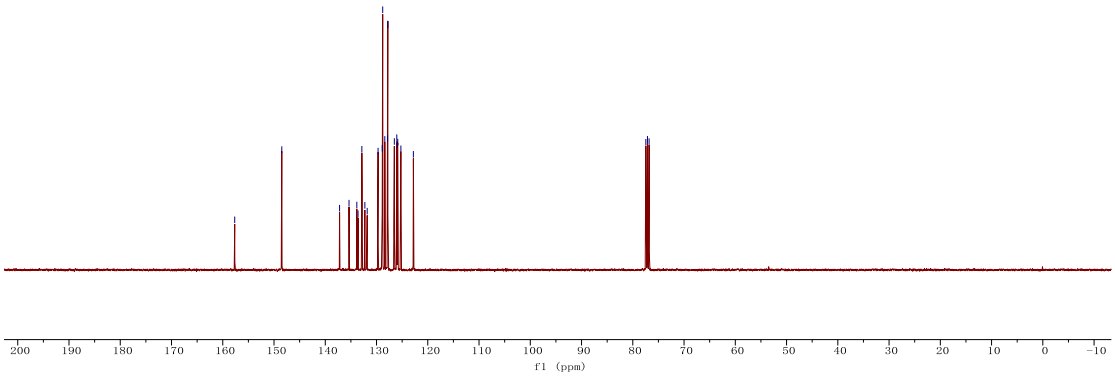
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

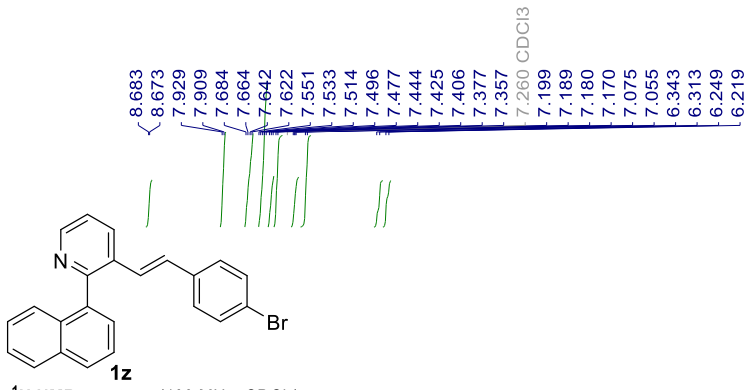




1y

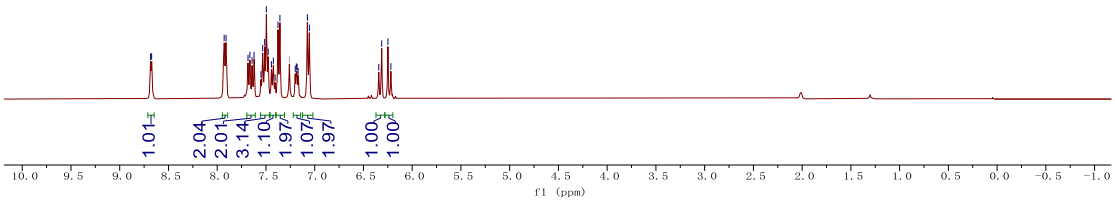
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

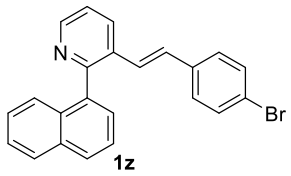




1z

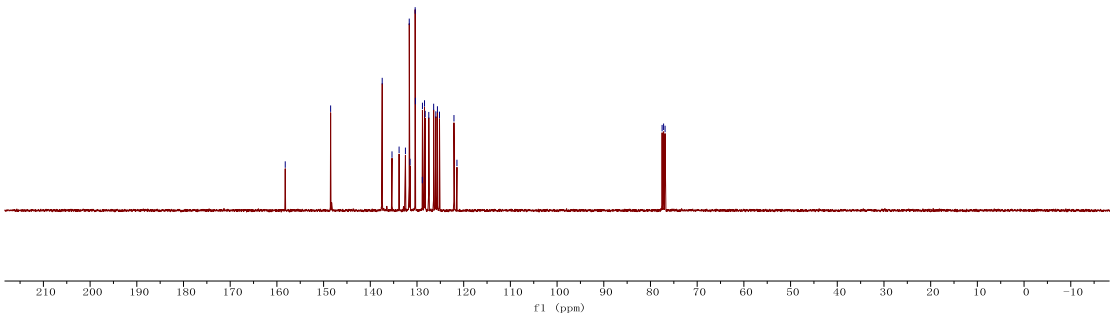
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

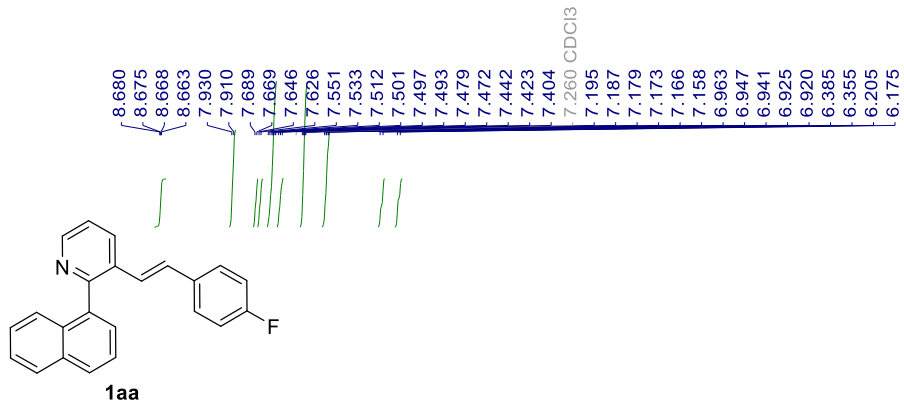




1z

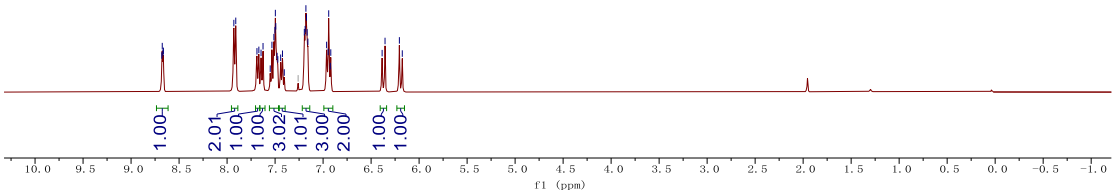
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

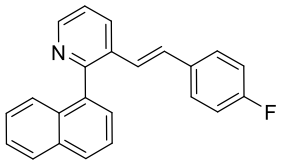




1aa

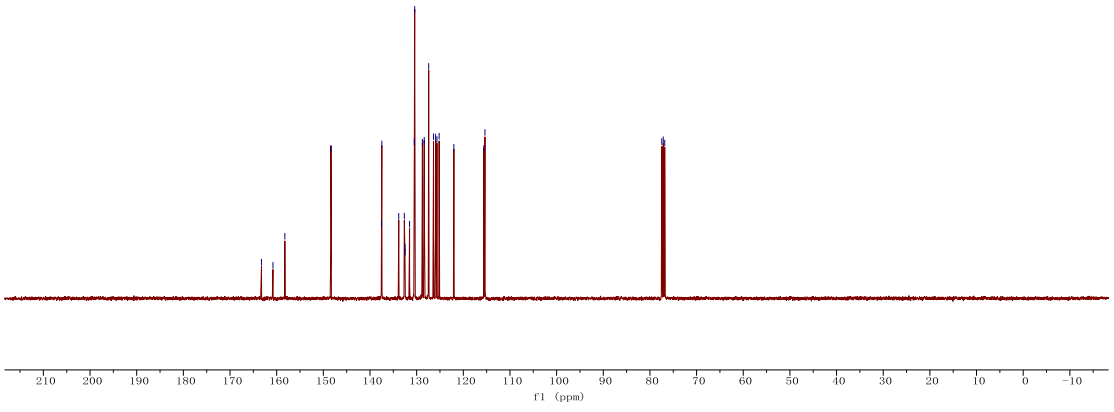
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

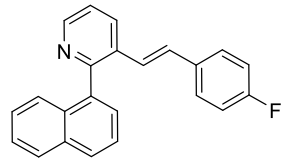




1aa

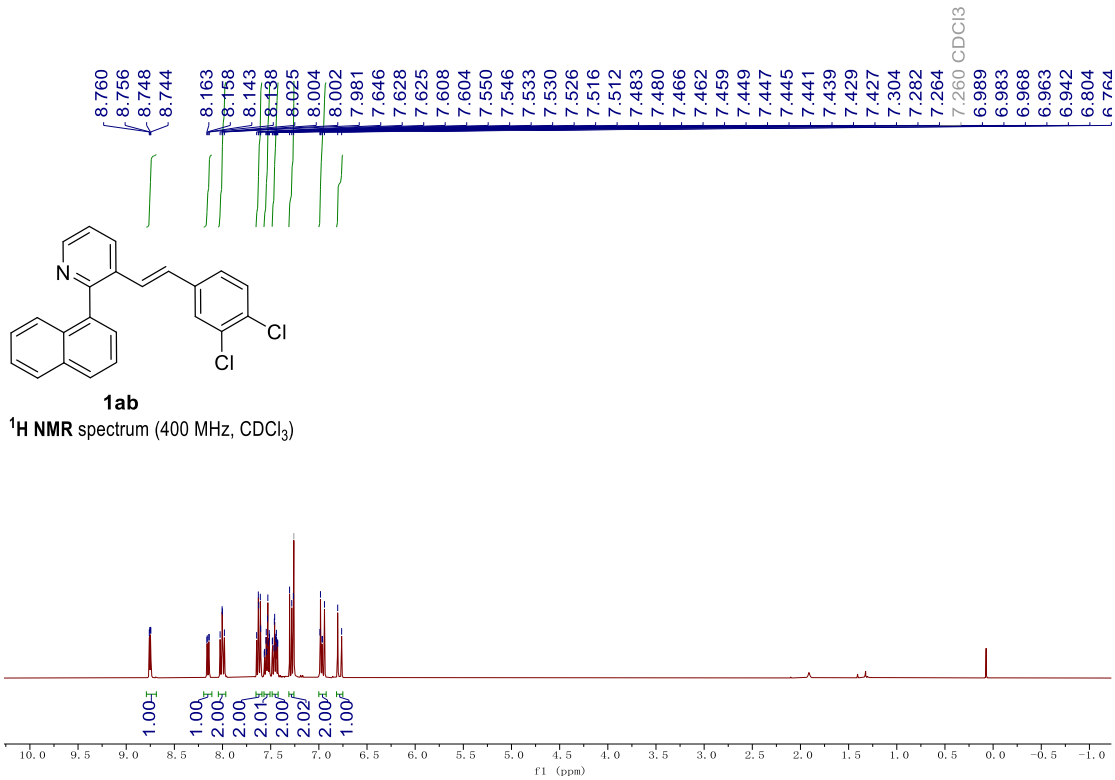
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





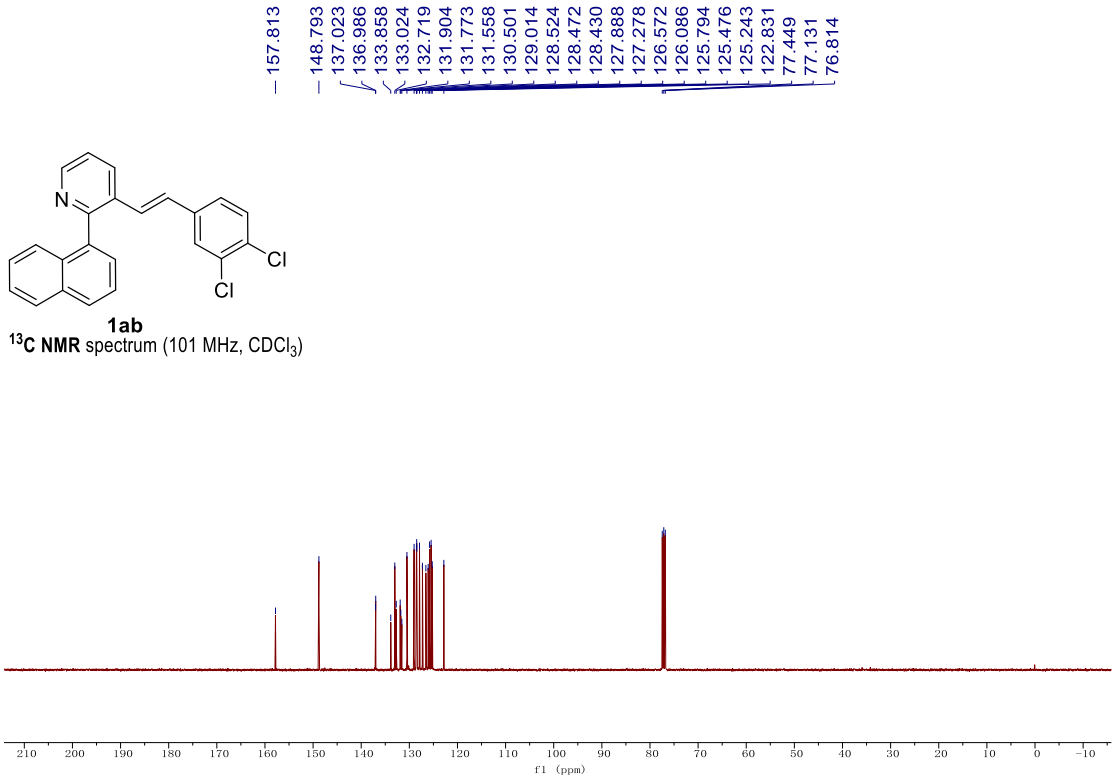
1aa

^{19}F NMR spectrum (377 MHz, $CDCl_3$)



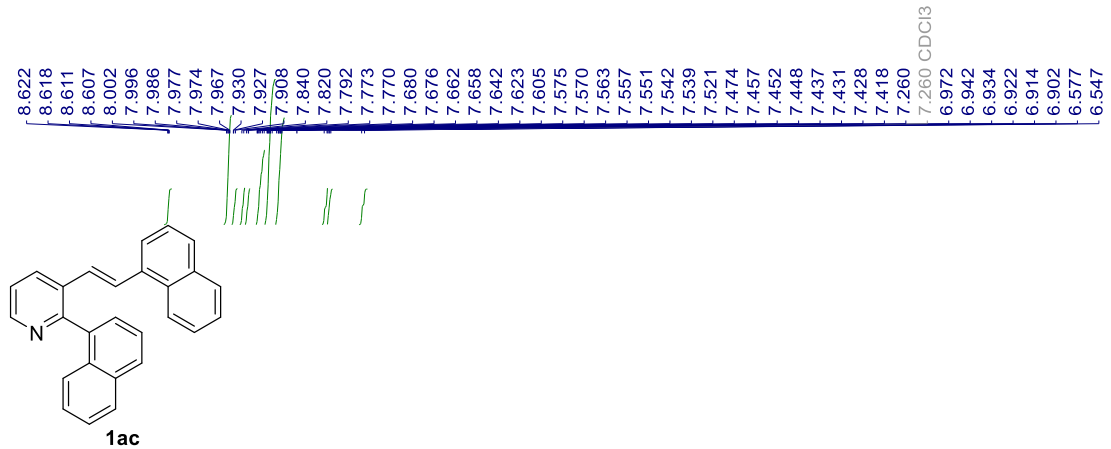
1ab

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



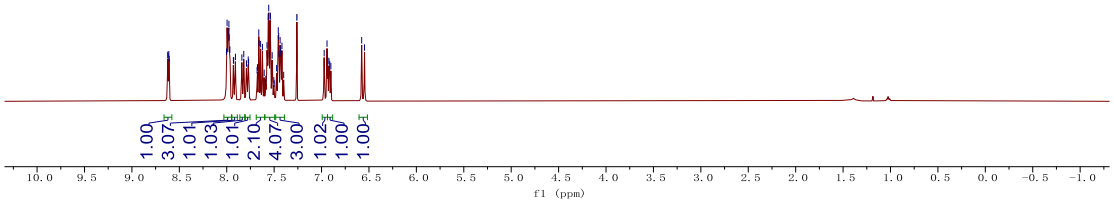
1ab

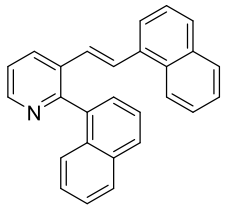
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1ac

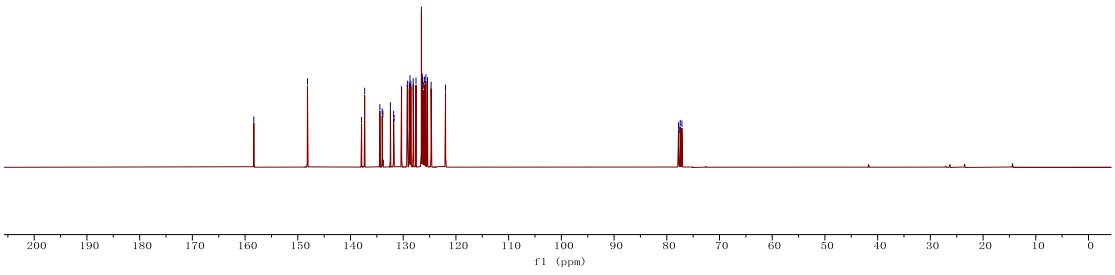
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

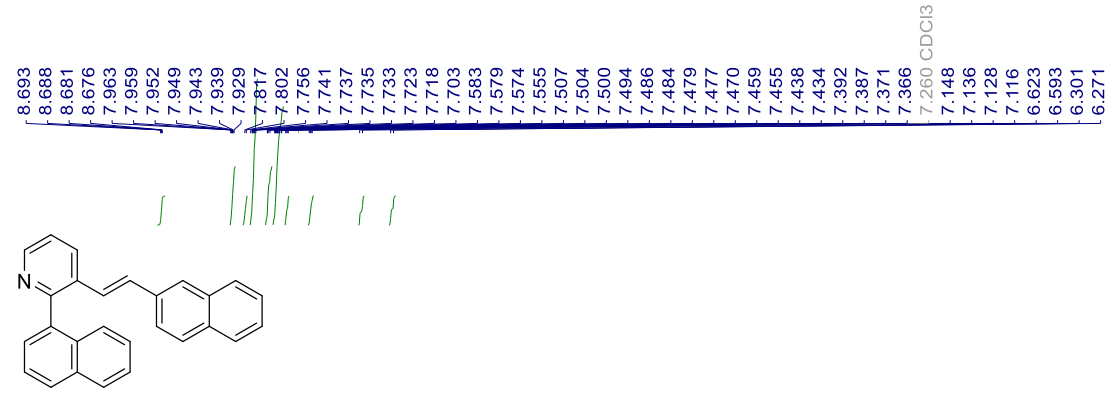




1ac

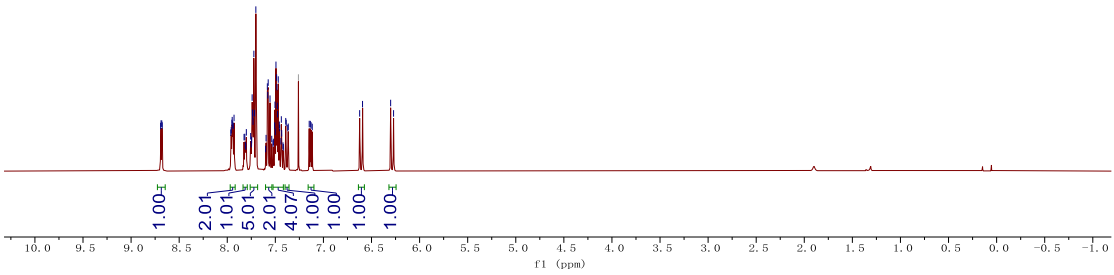
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

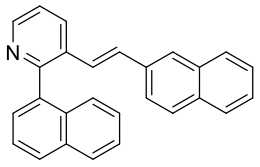




1ad

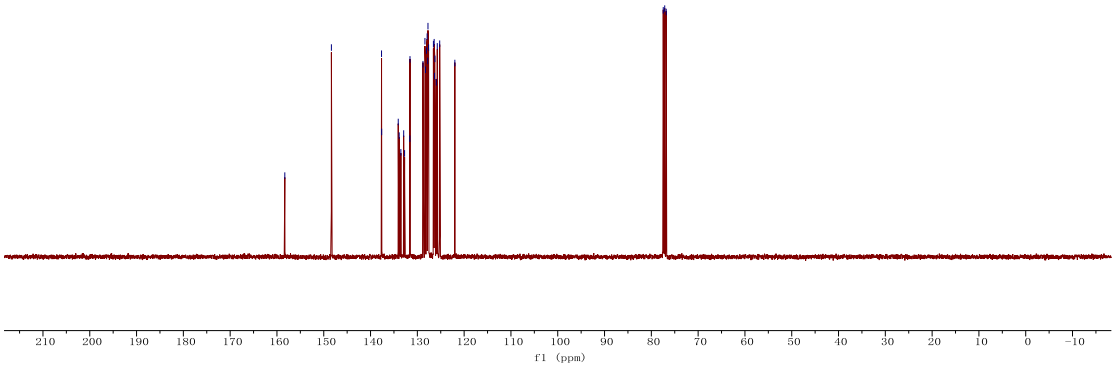
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

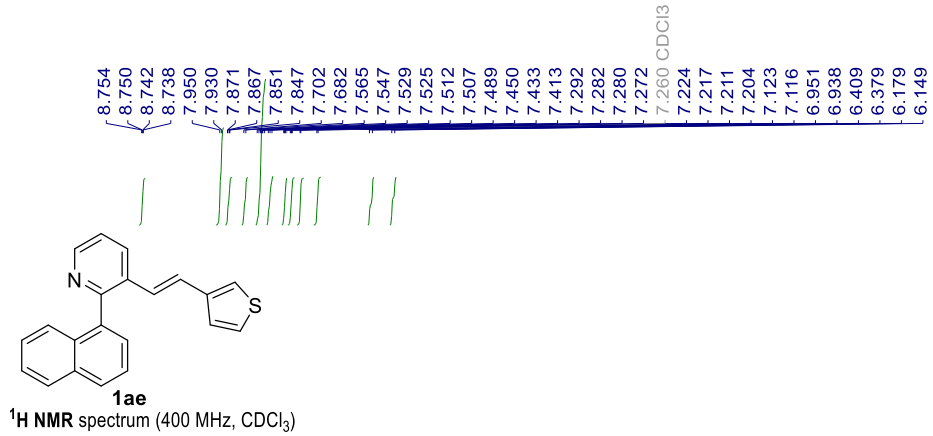




1ad

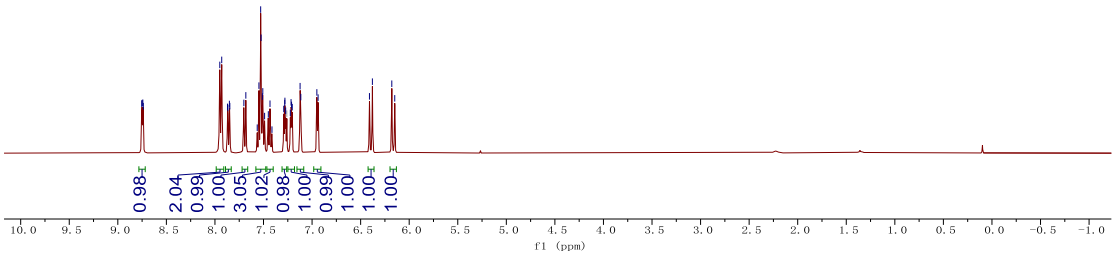
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

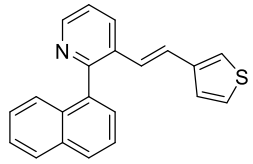




1ae

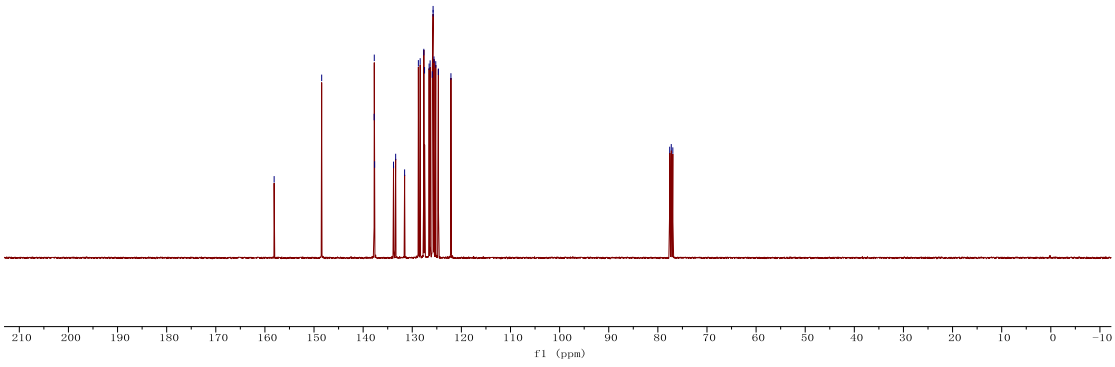
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

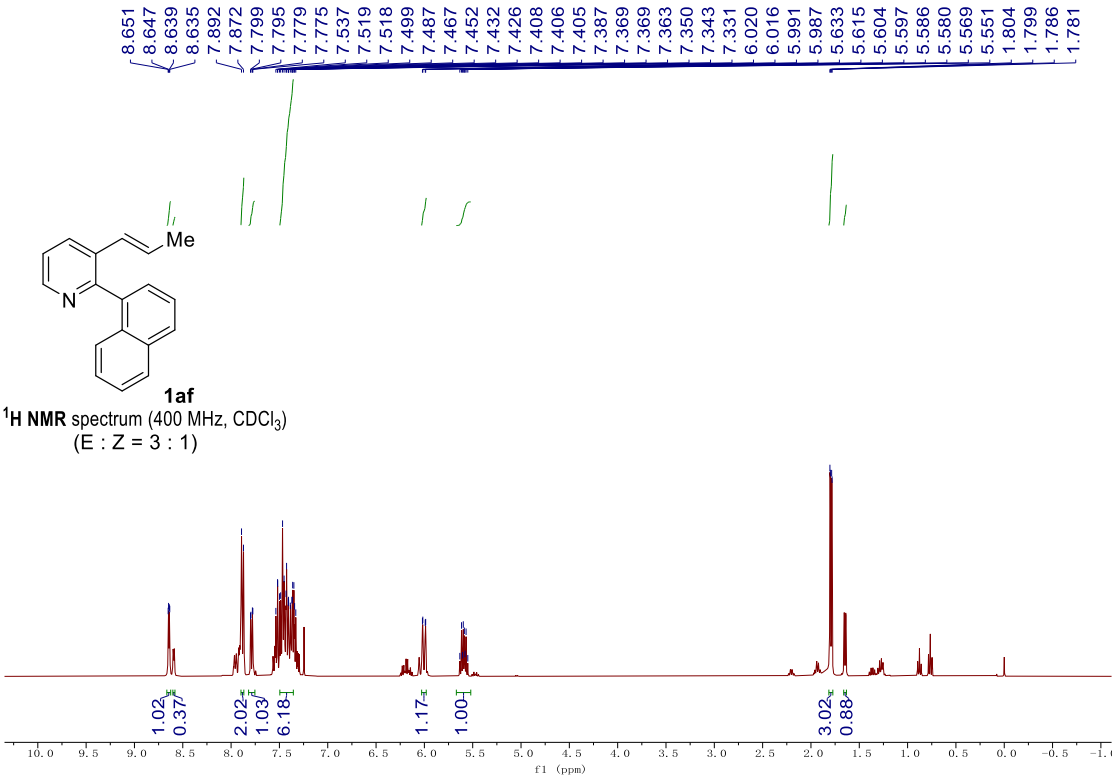




1ae

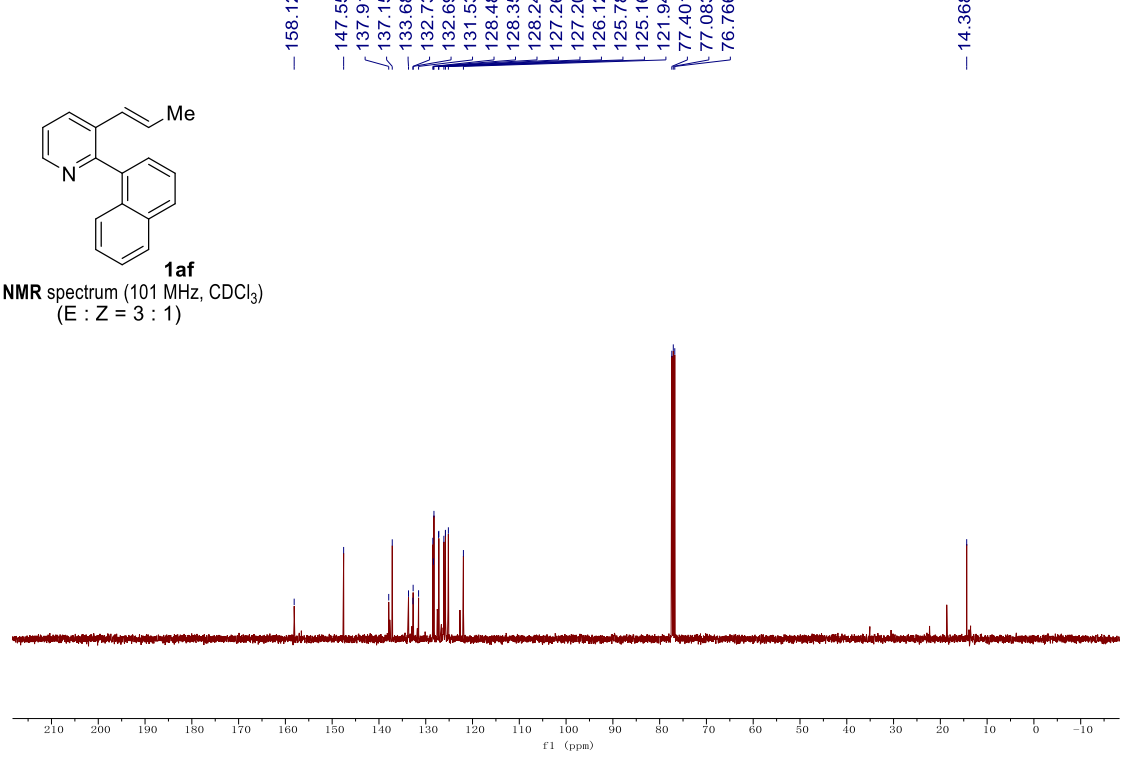
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





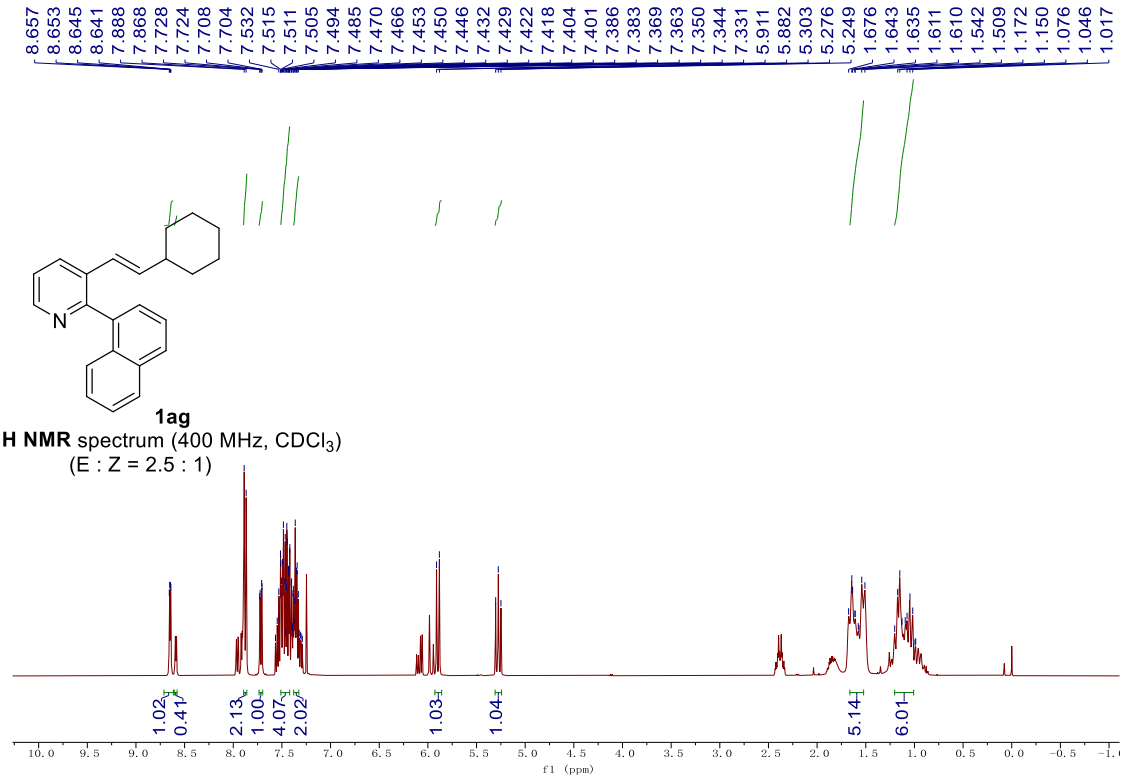
1af

^{1}H NMR spectrum (400 MHz, $CDCl_3$)
(E : Z = 3 : 1)



1af

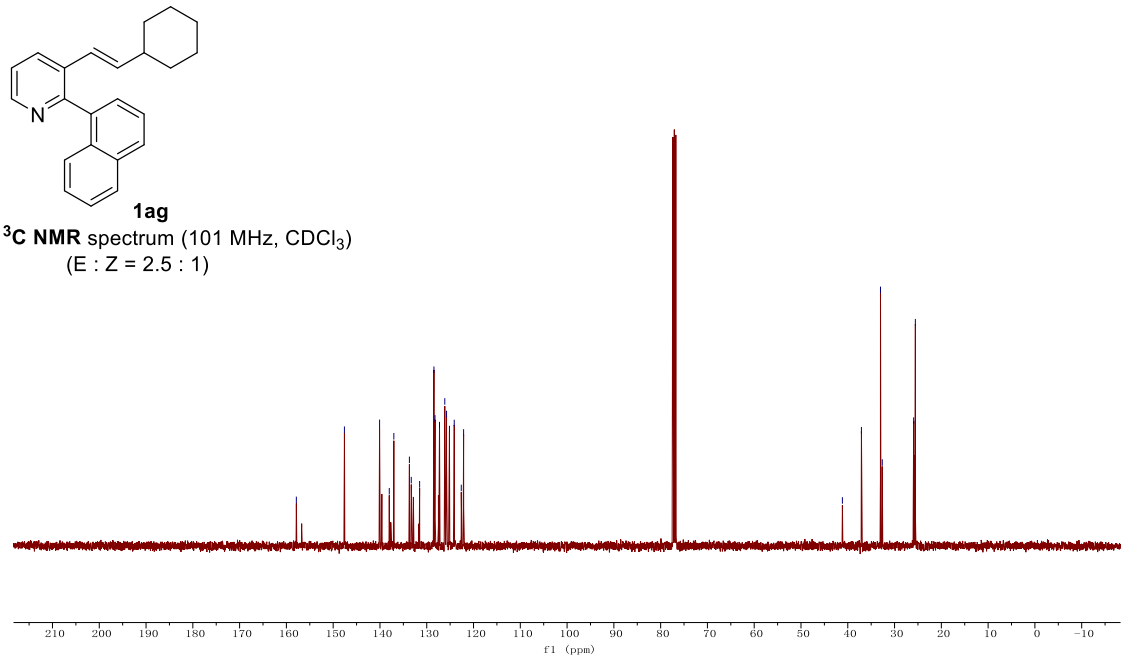
^{13}C NMR spectrum (101 MHz, $CDCl_3$)
(E : Z = 3 : 1)



1ag

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

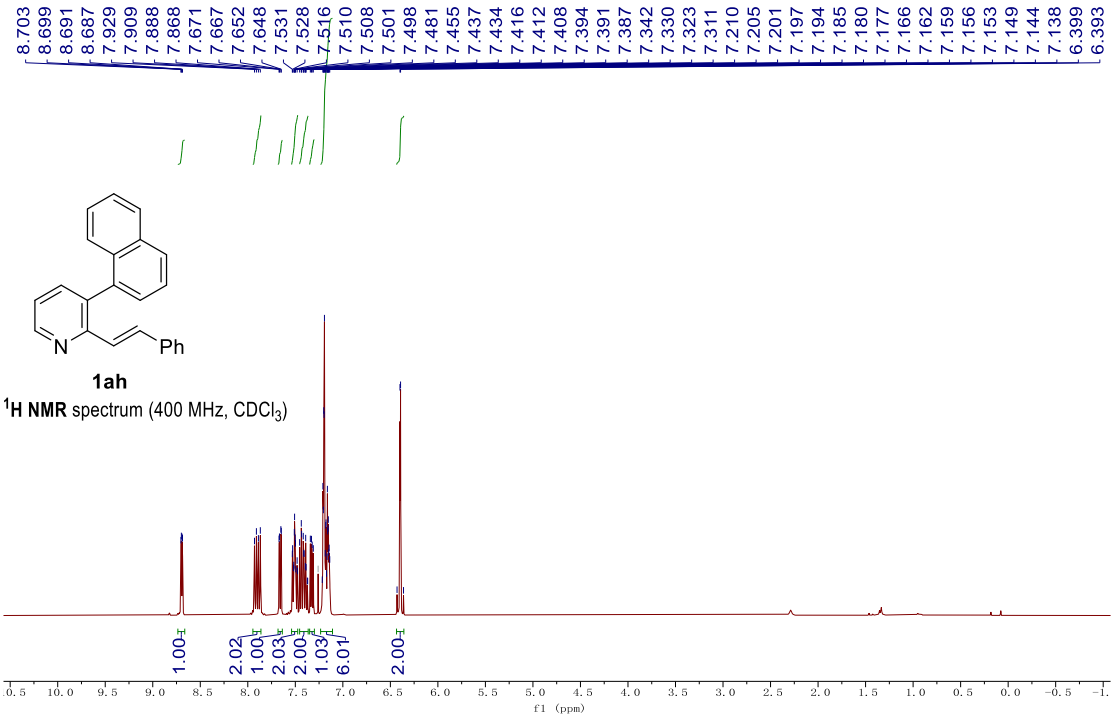
(E : Z = 2.5 : 1)



1ag

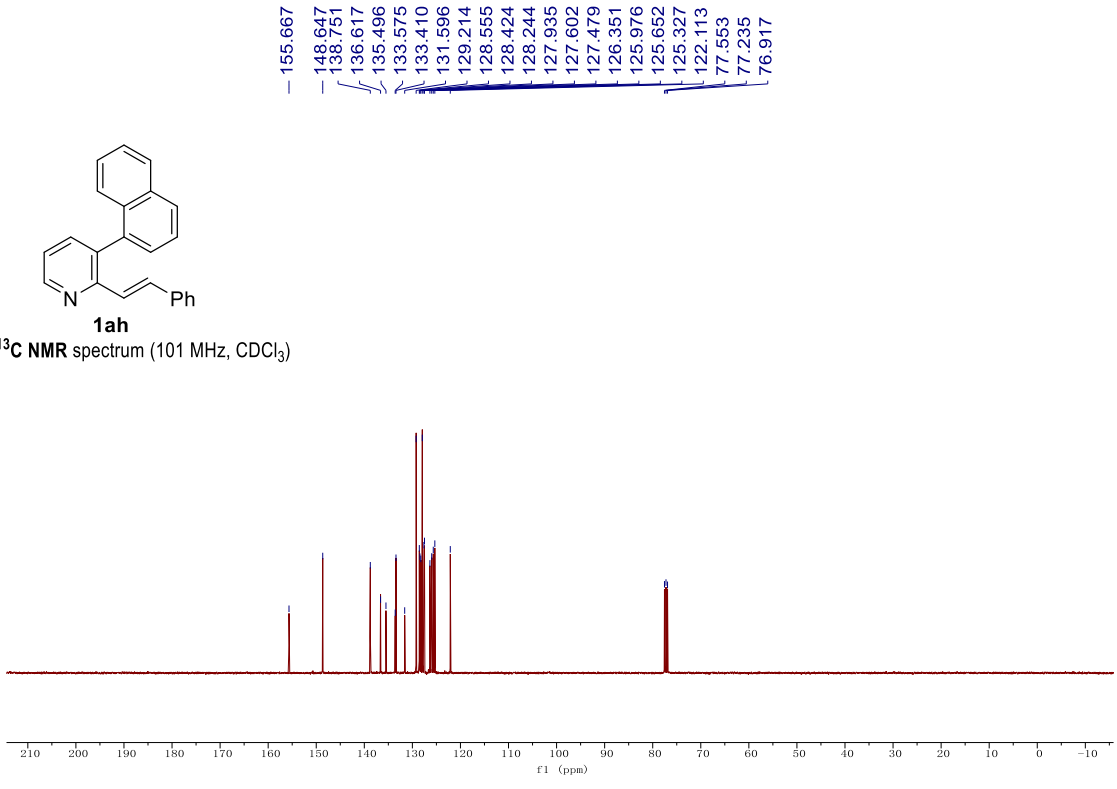
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

(E : Z = 2.5 : 1)



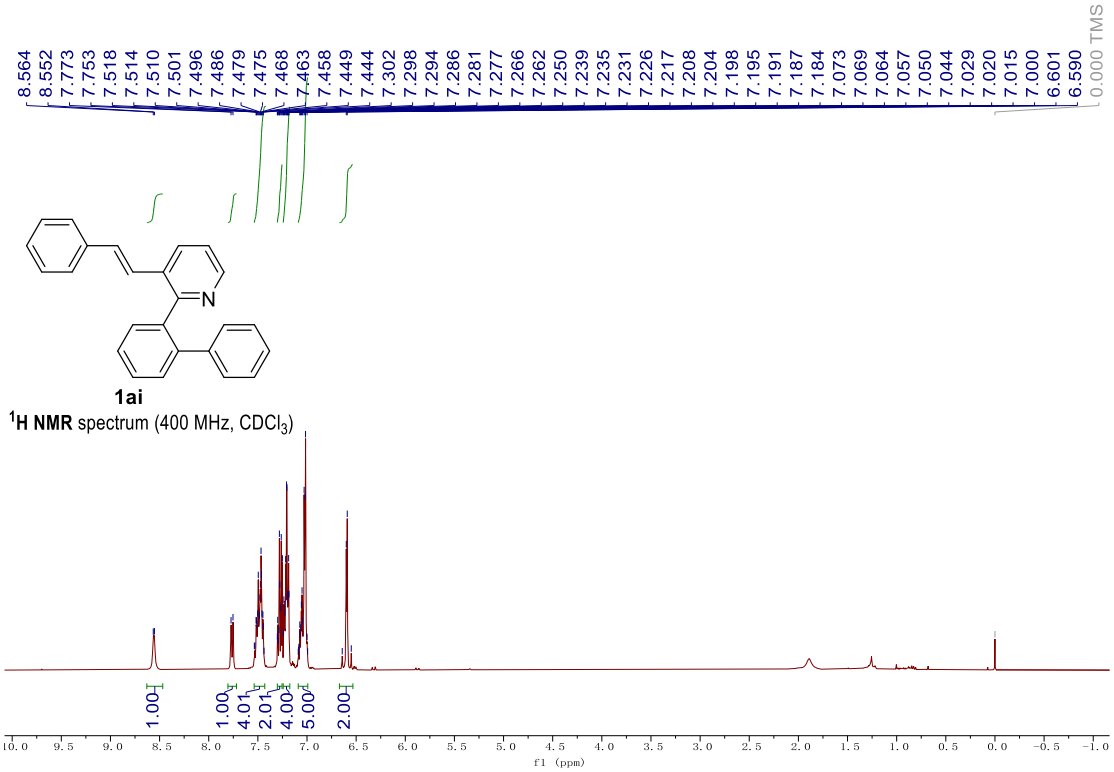
1ah

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



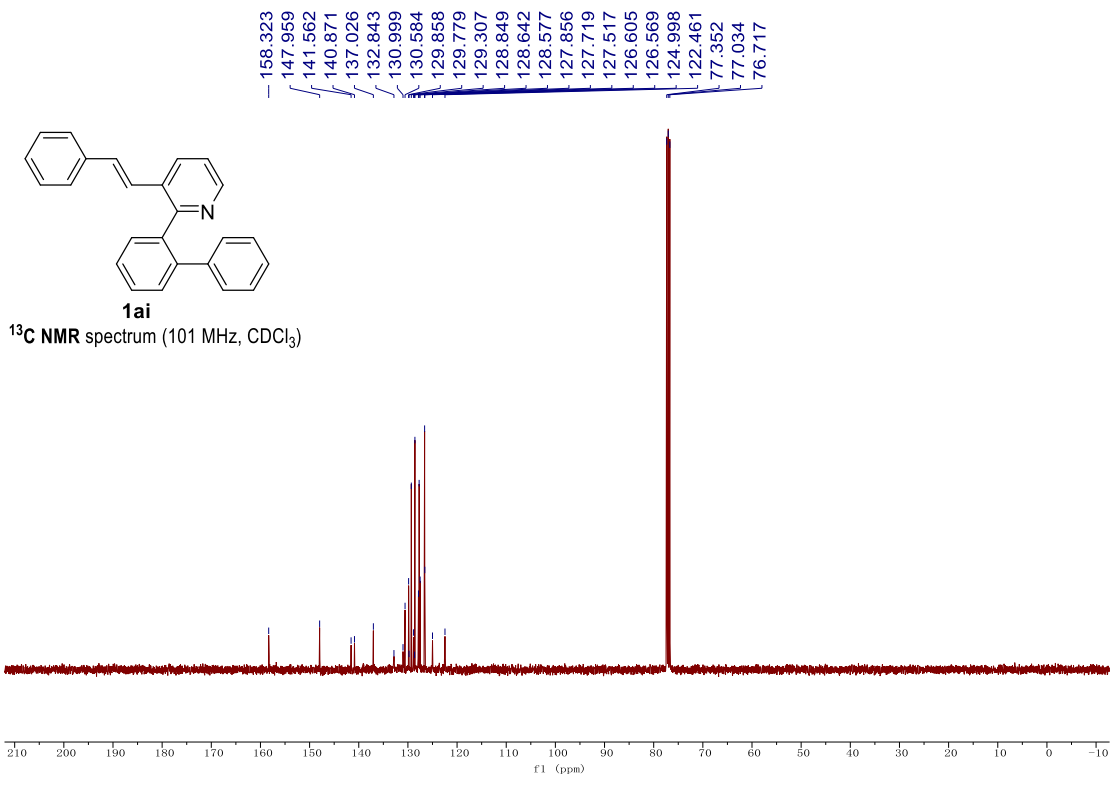
1ah

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



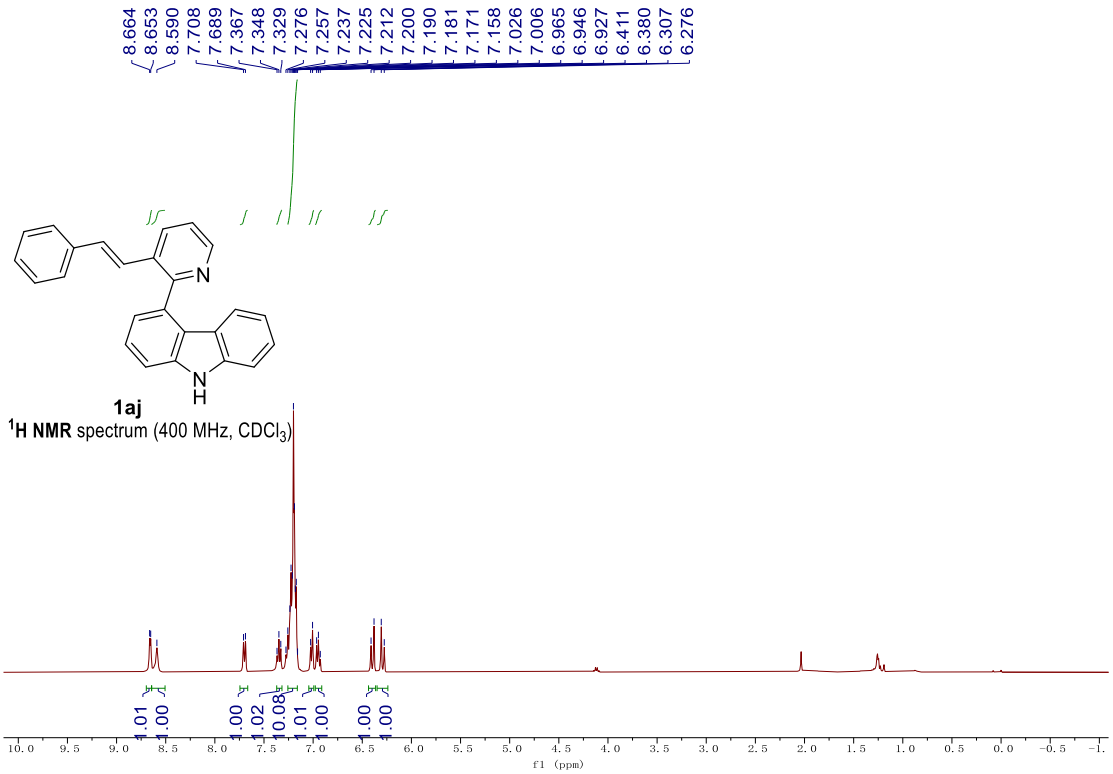
1ai

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



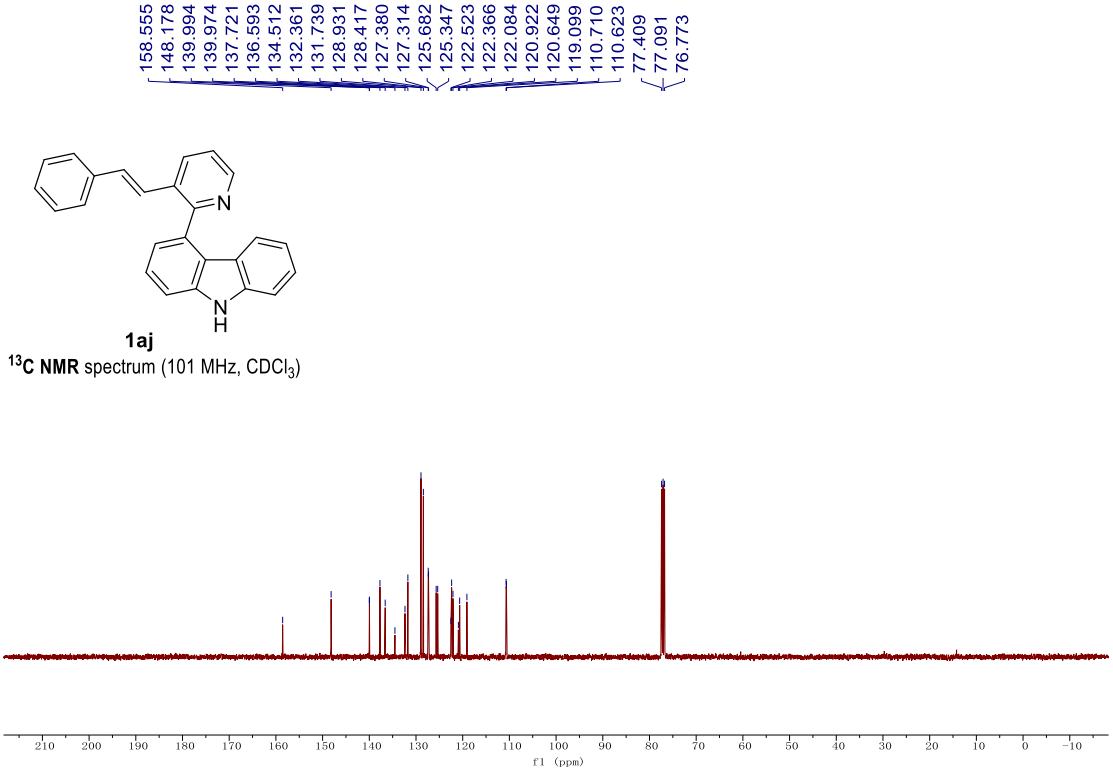
1ai

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



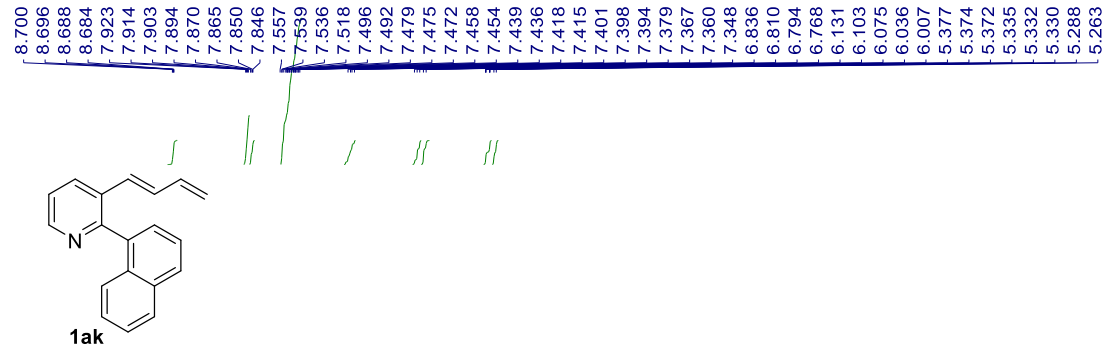
1aj

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



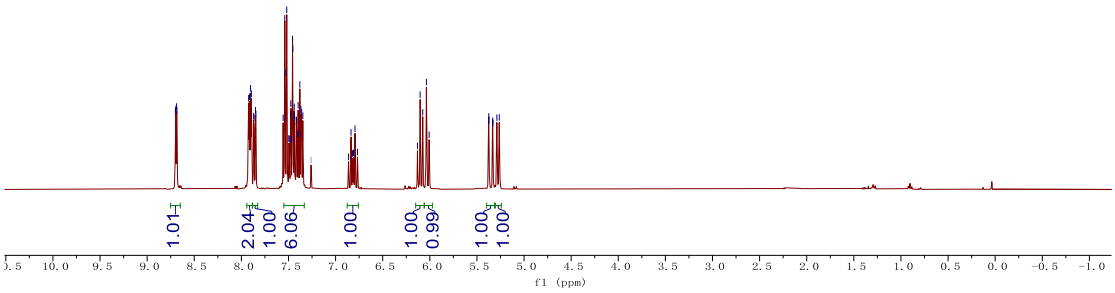
1aj

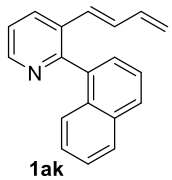
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



1ak

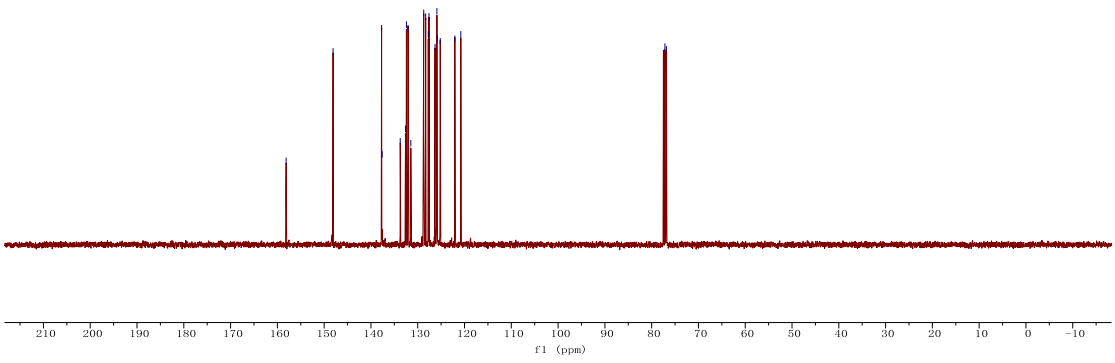
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

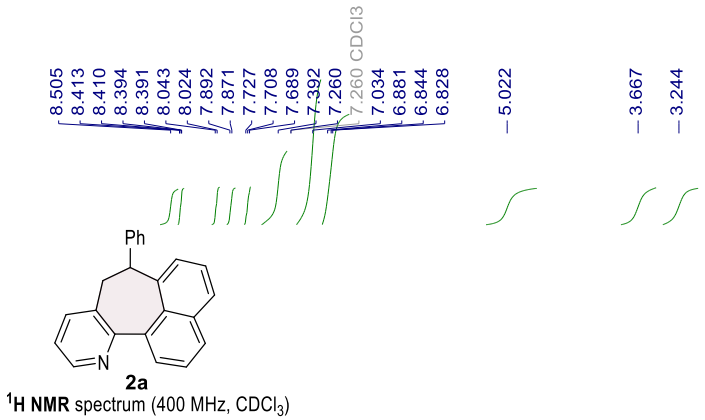




1ak

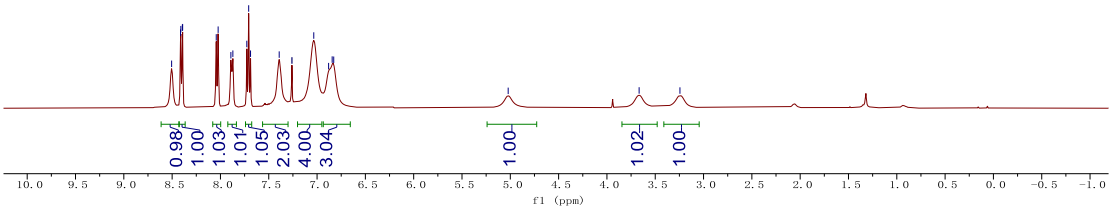
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

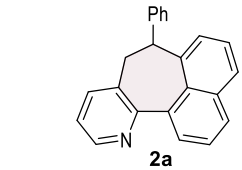




2a

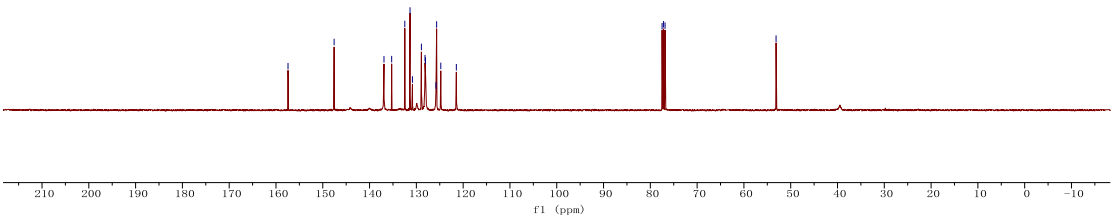
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

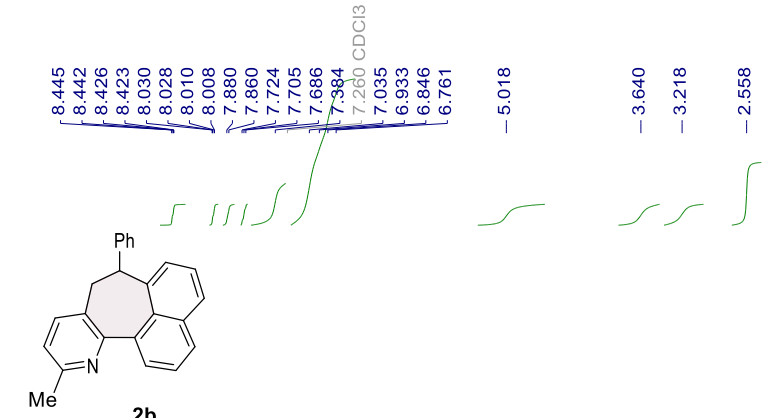




2a

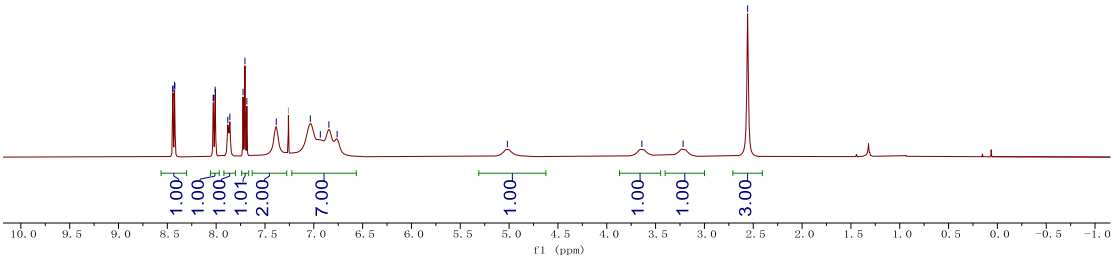
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

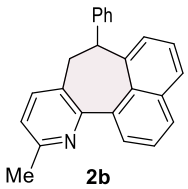




2b

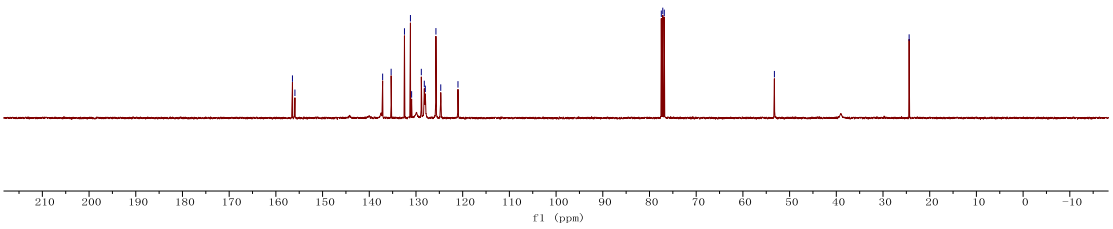
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

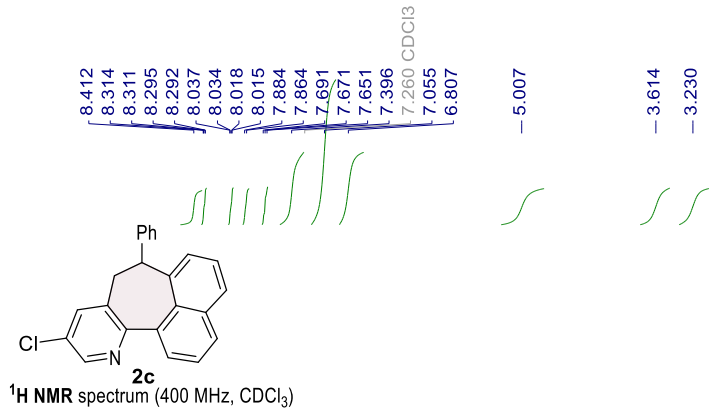




2b

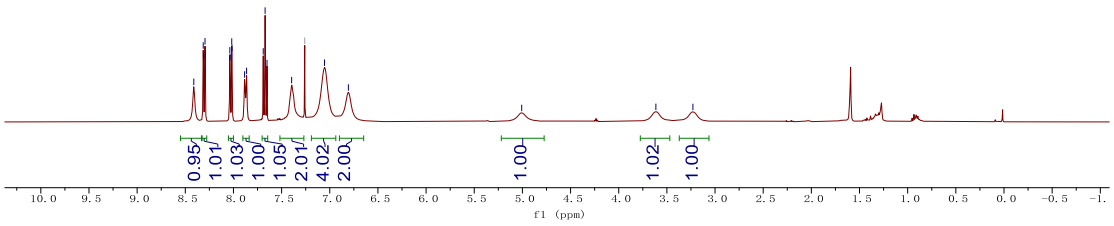
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

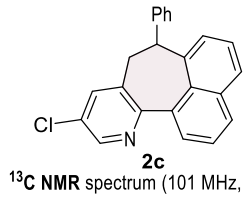




2c

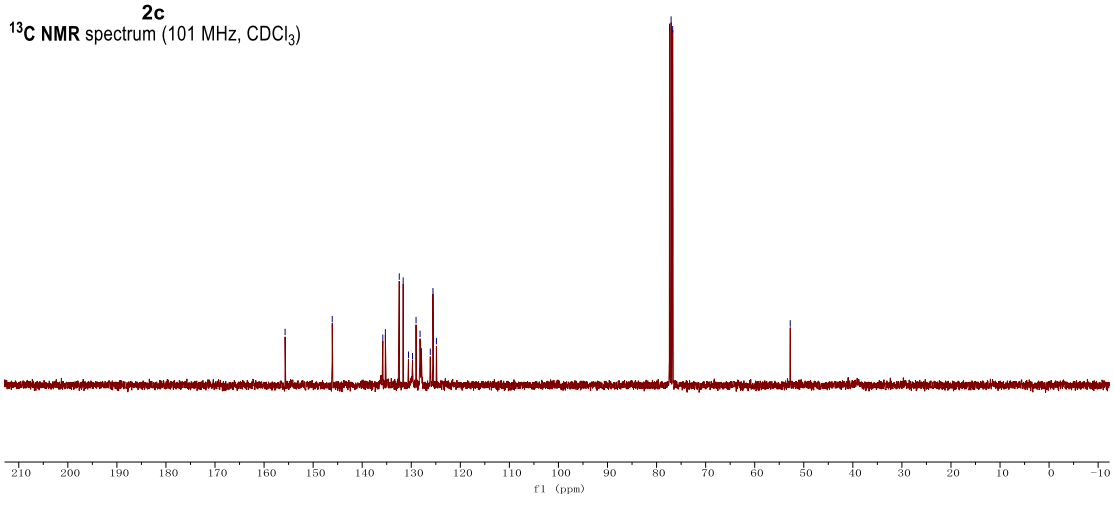
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

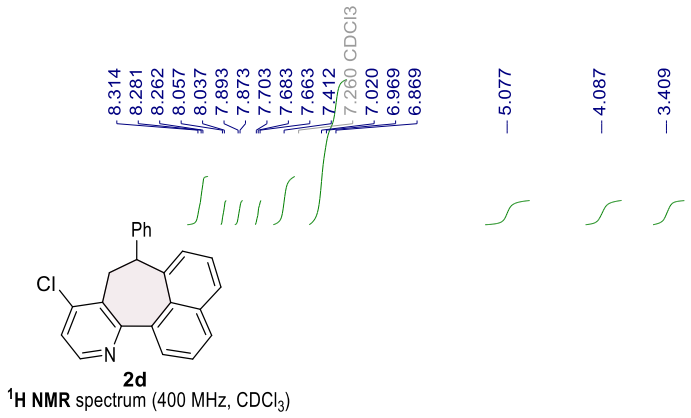




2c

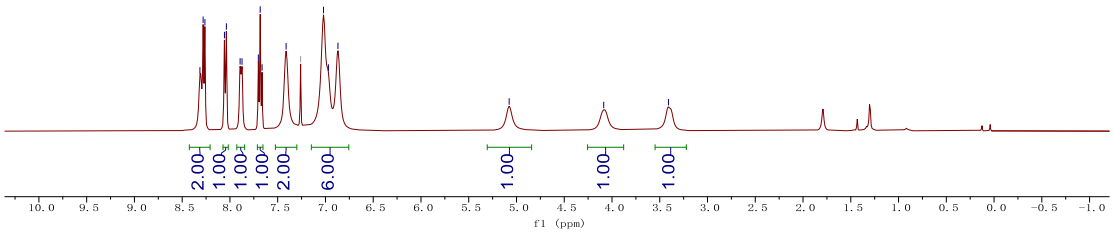
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

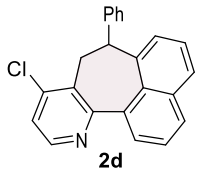




2d

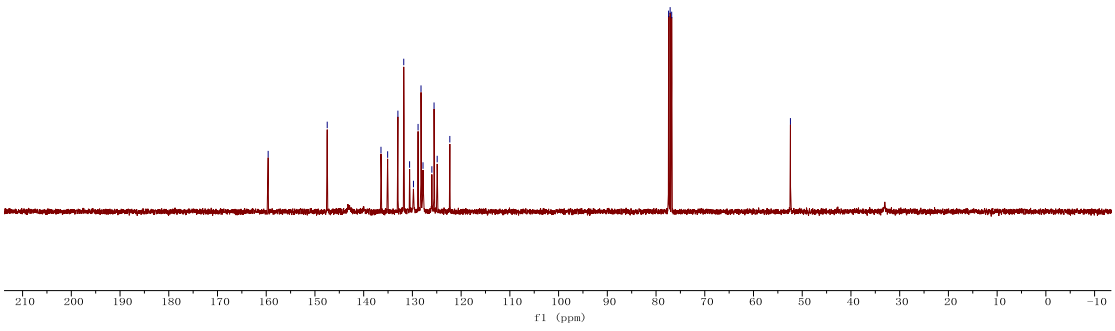
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

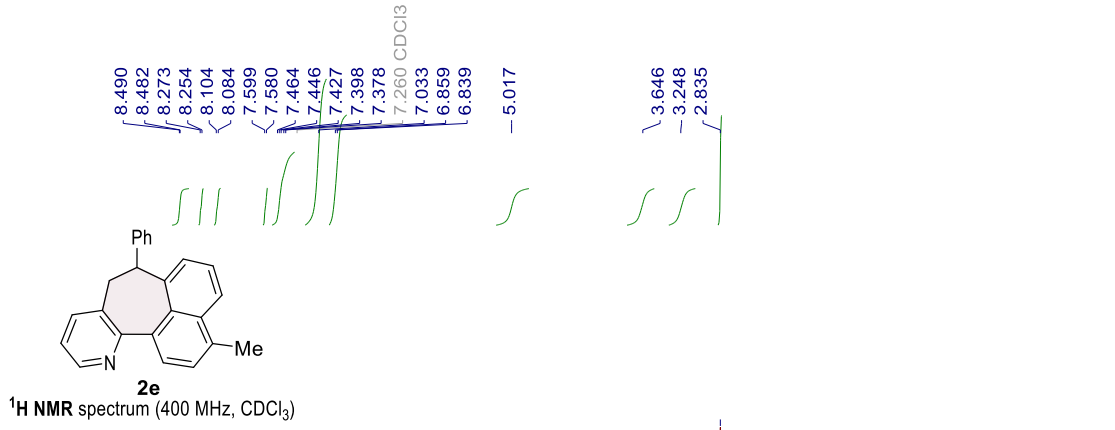




2d

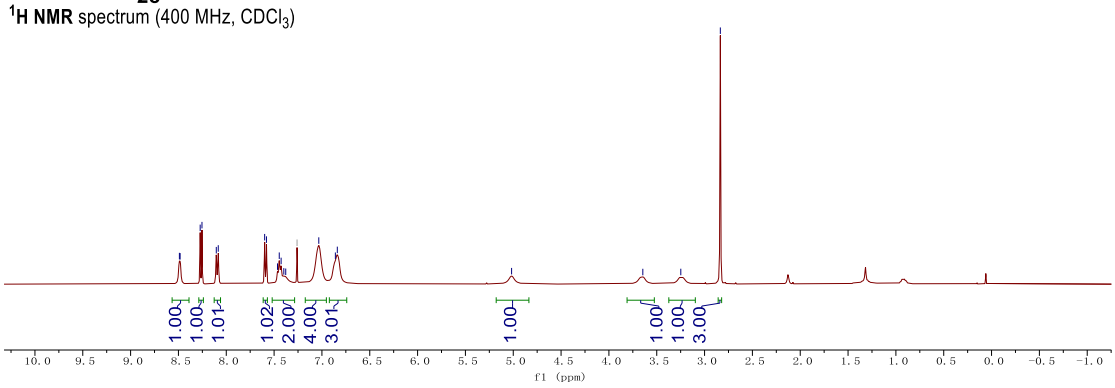
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

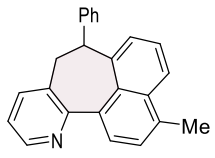




2e

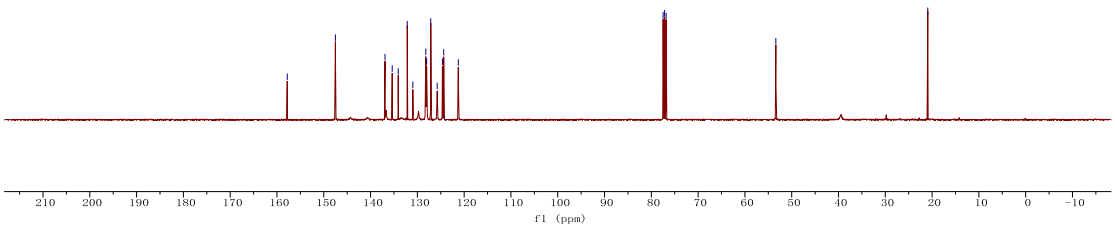
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

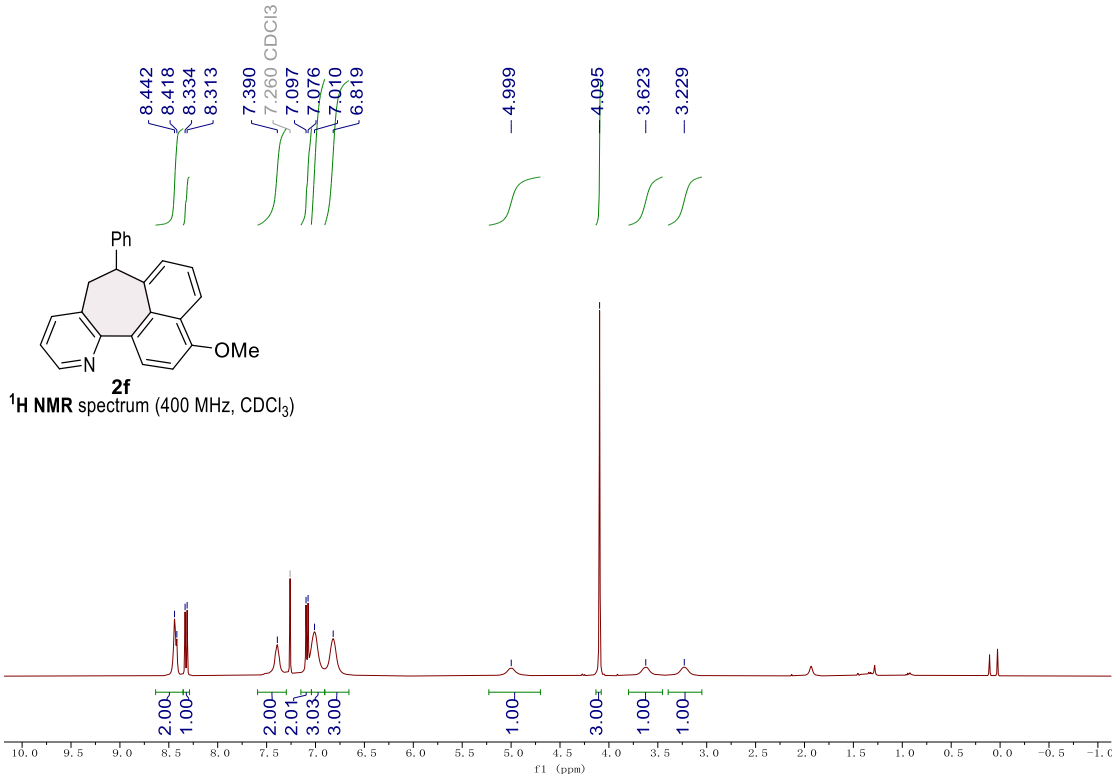




2e

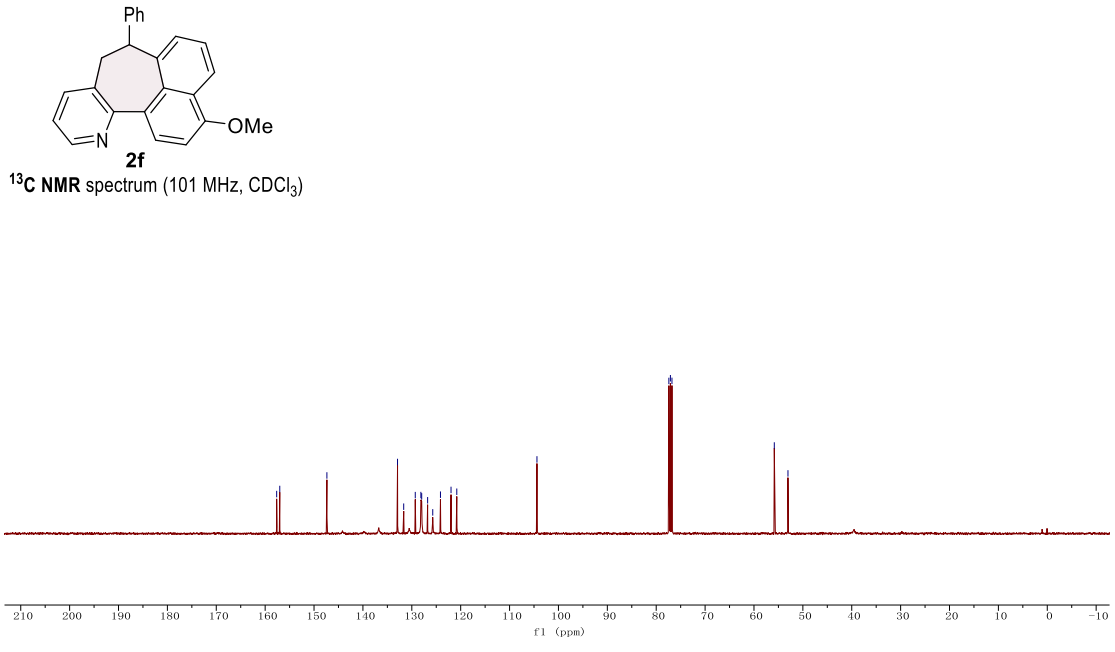
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





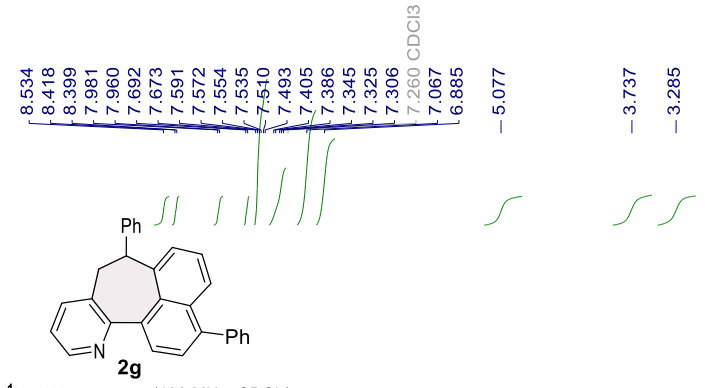
2f

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



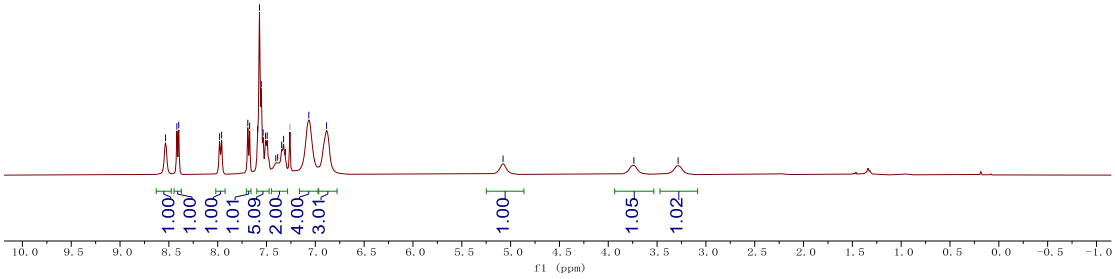
2f

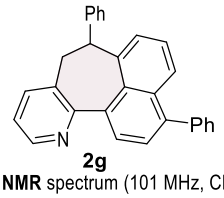
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2g

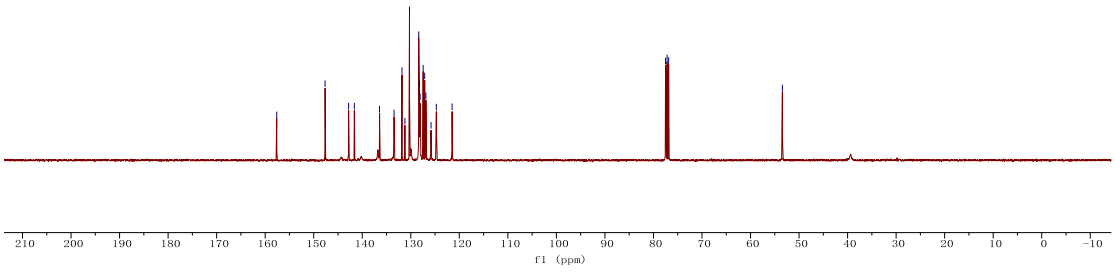
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

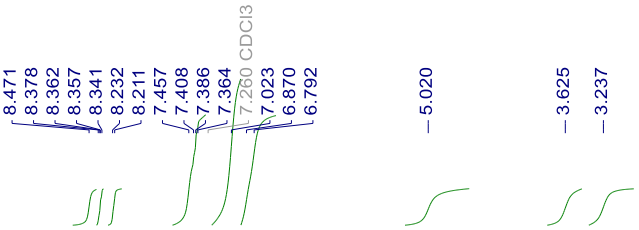


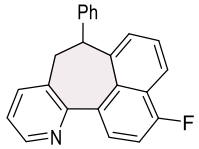


2g

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

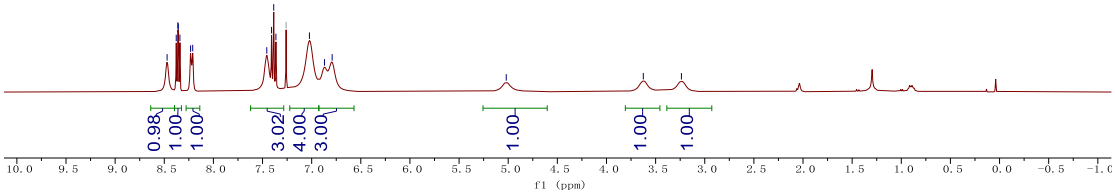


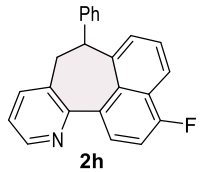




2h

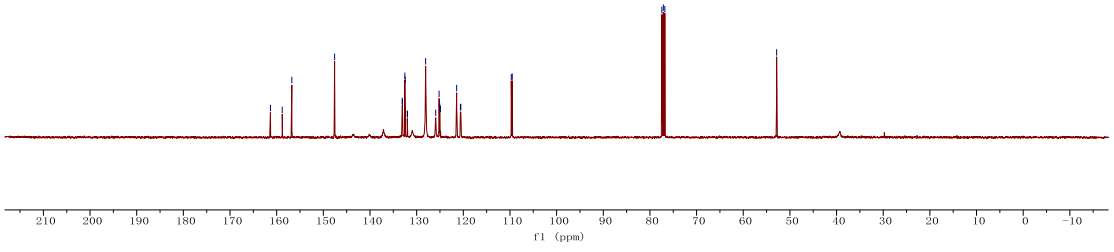
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

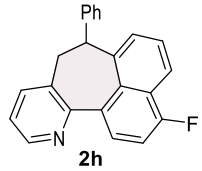




2h

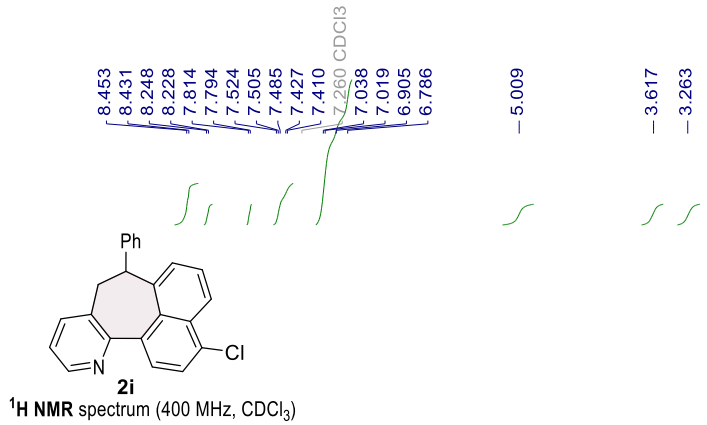
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





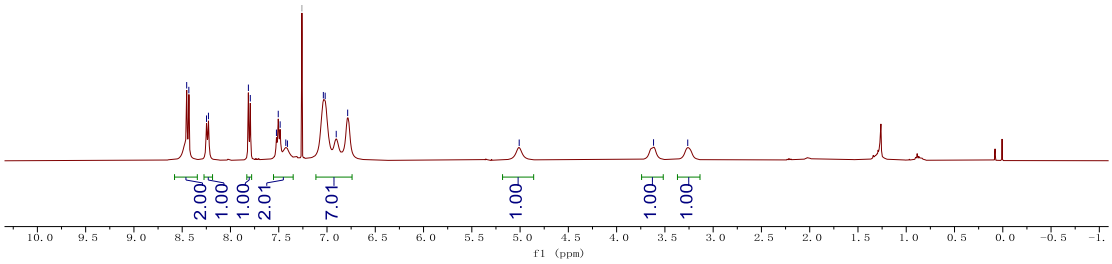
2h

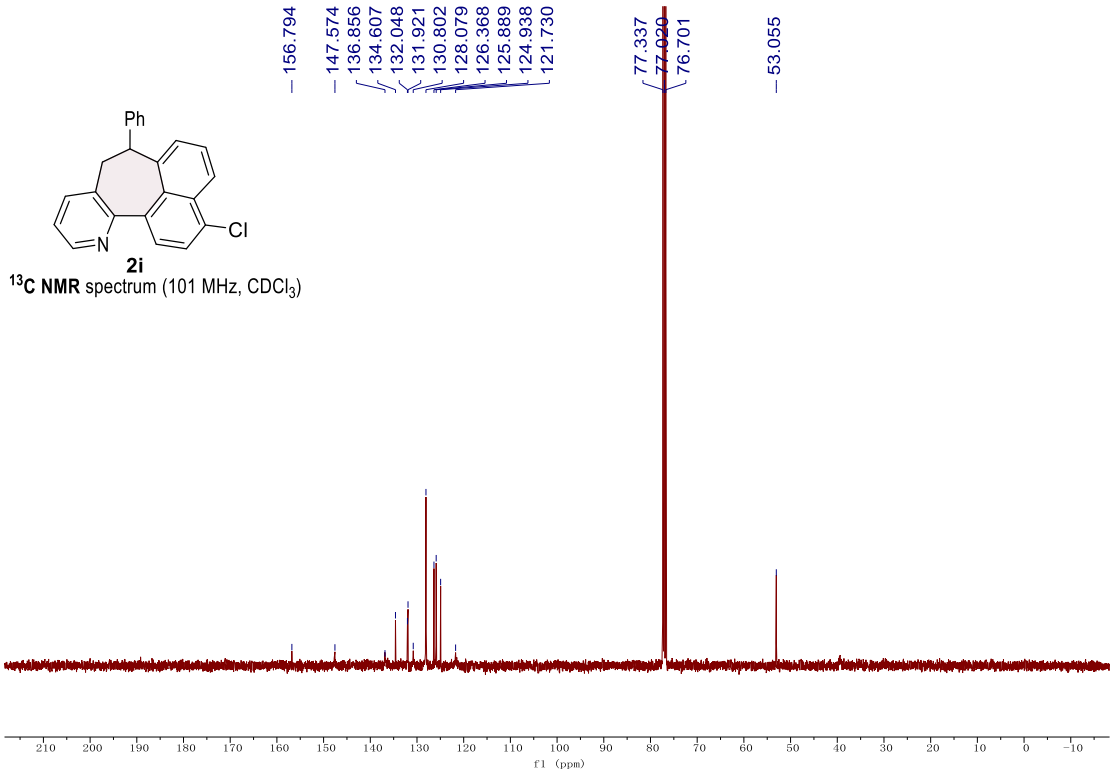
^{19}F NMR spectrum (377 MHz, $CDCl_3$)



2i

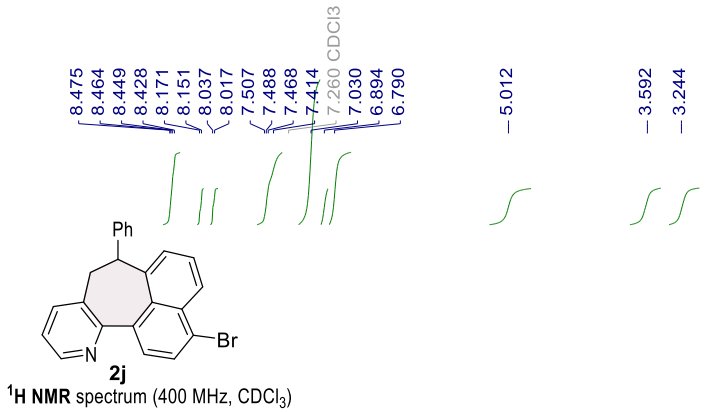
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





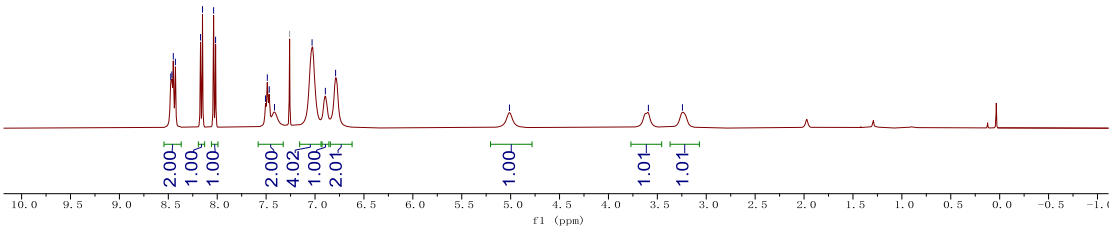
2i

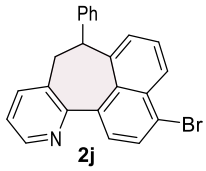
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2j

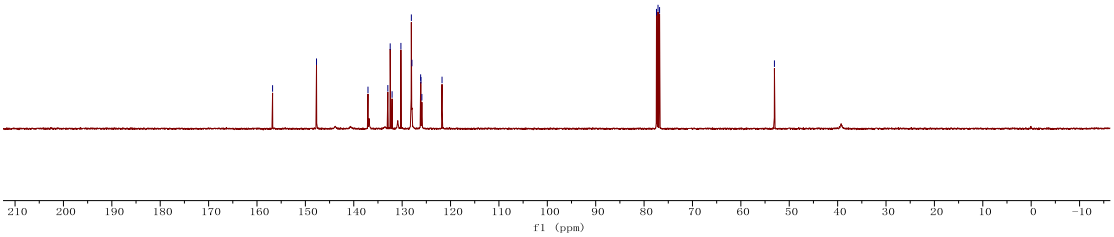
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

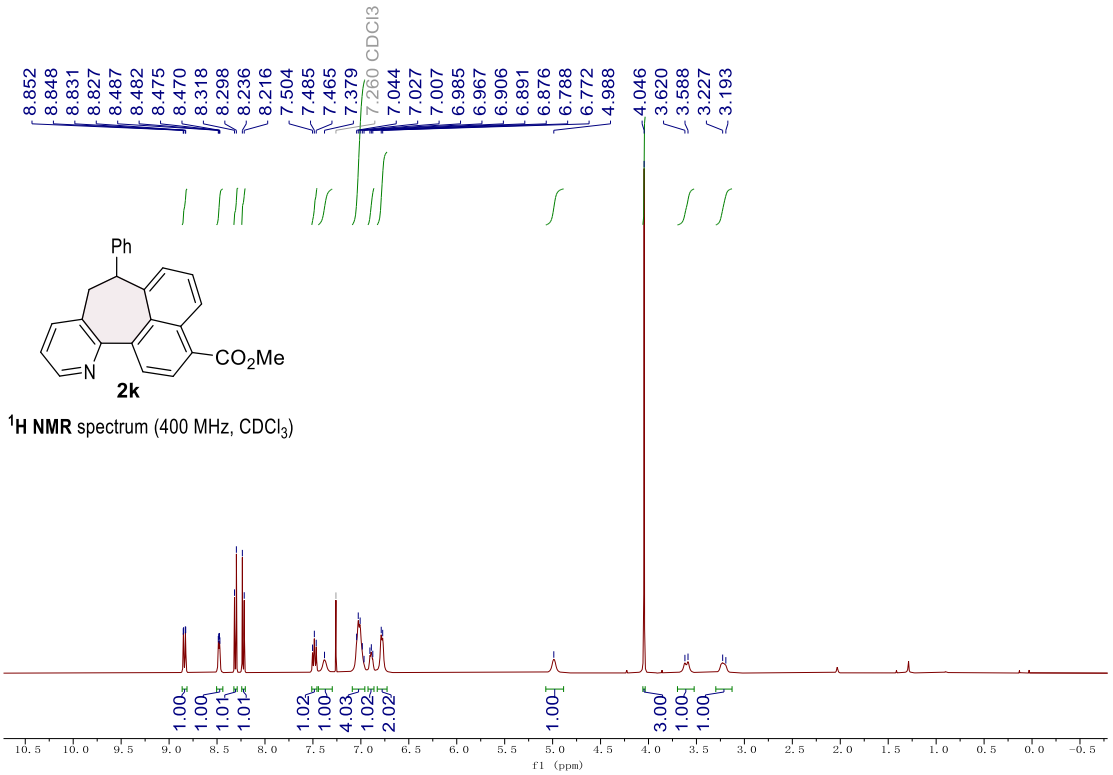




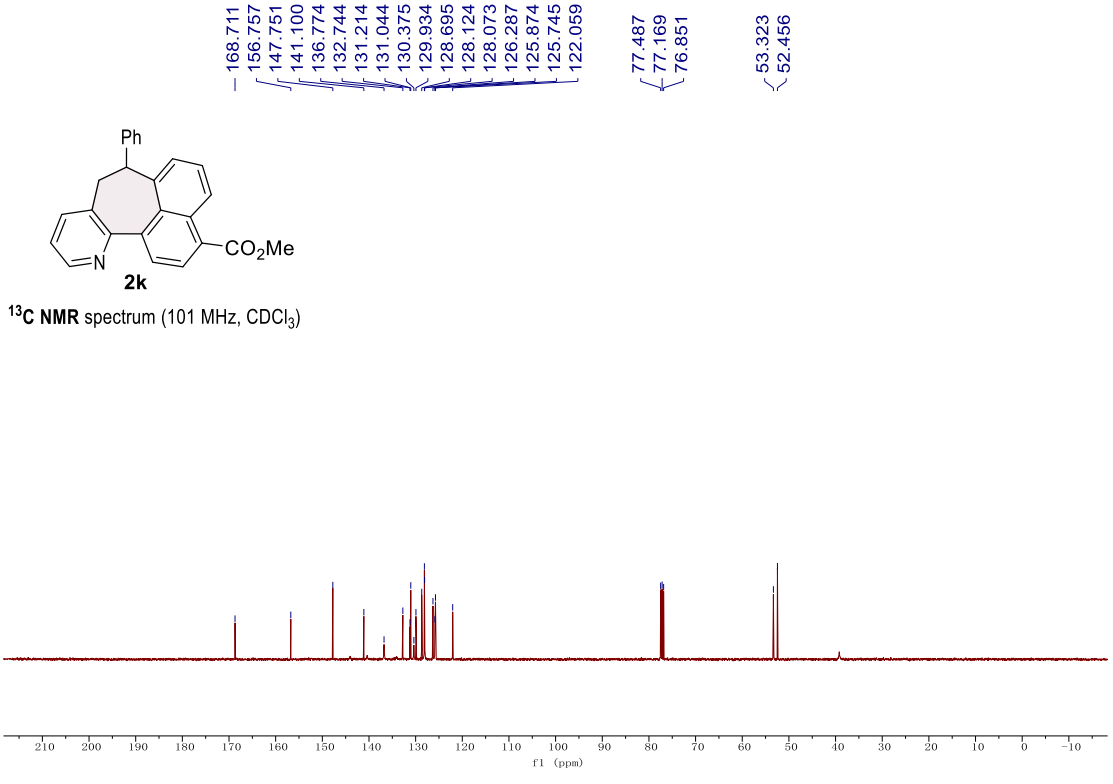
2j

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

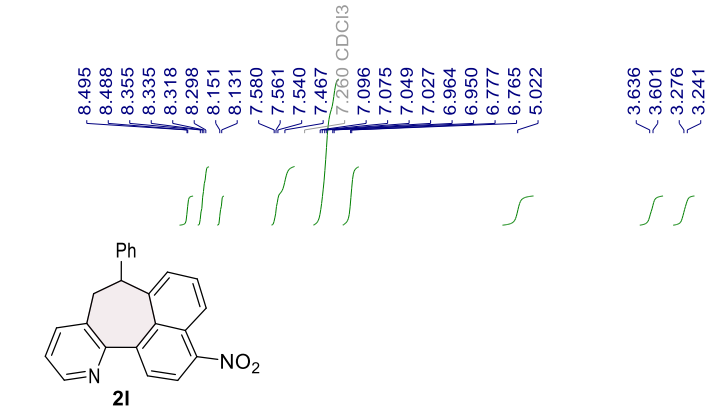




^{1}H NMR spectrum (400 MHz, $CDCl_3$)

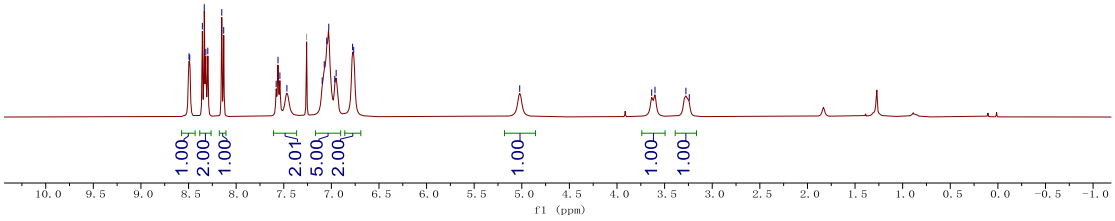


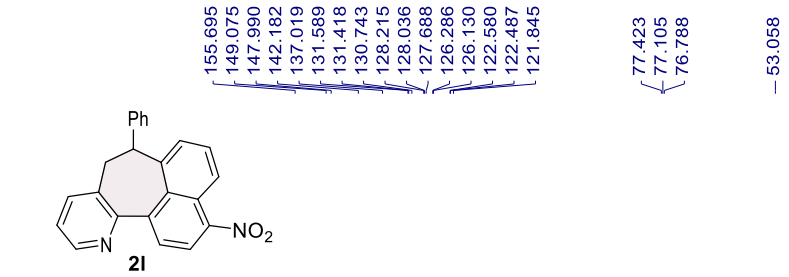
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2l

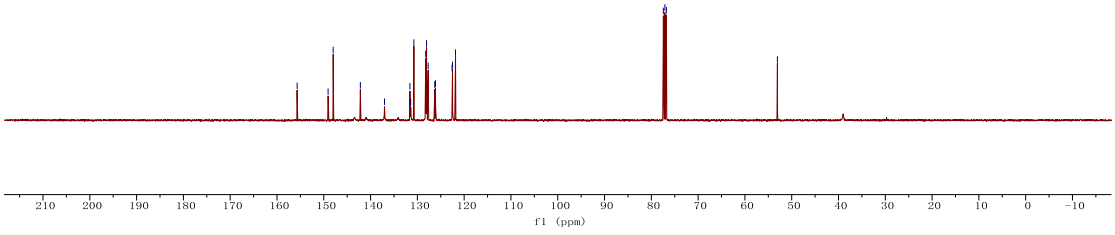
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

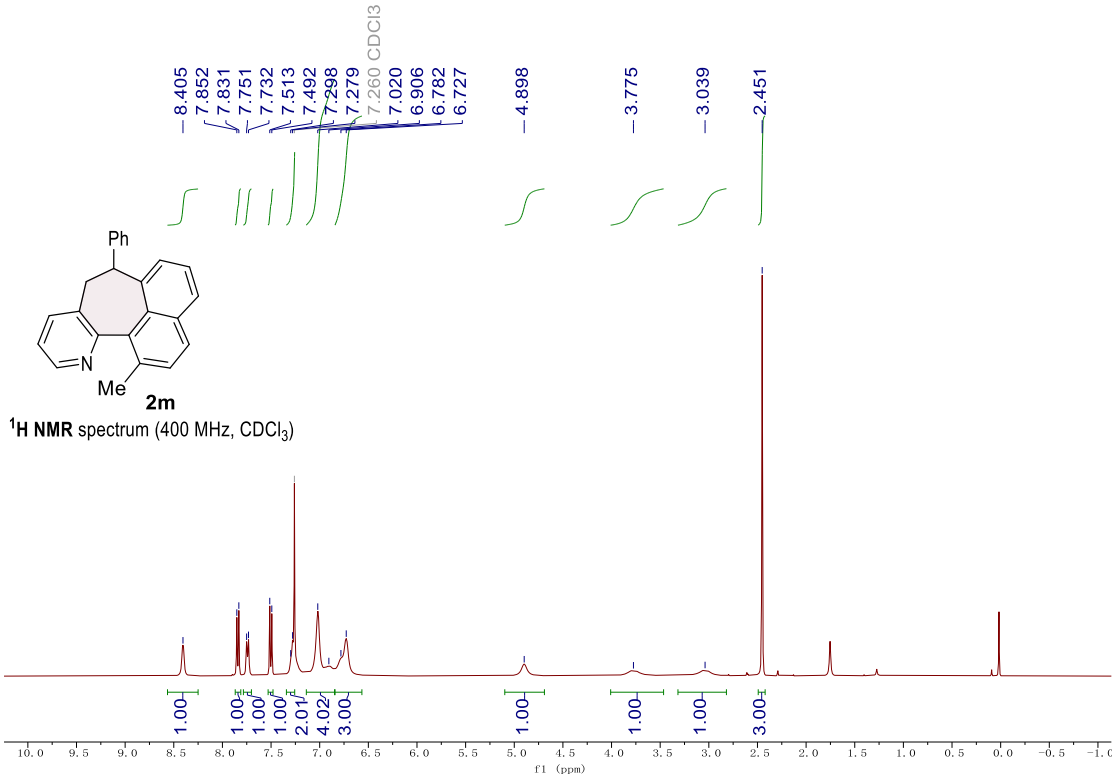




2l

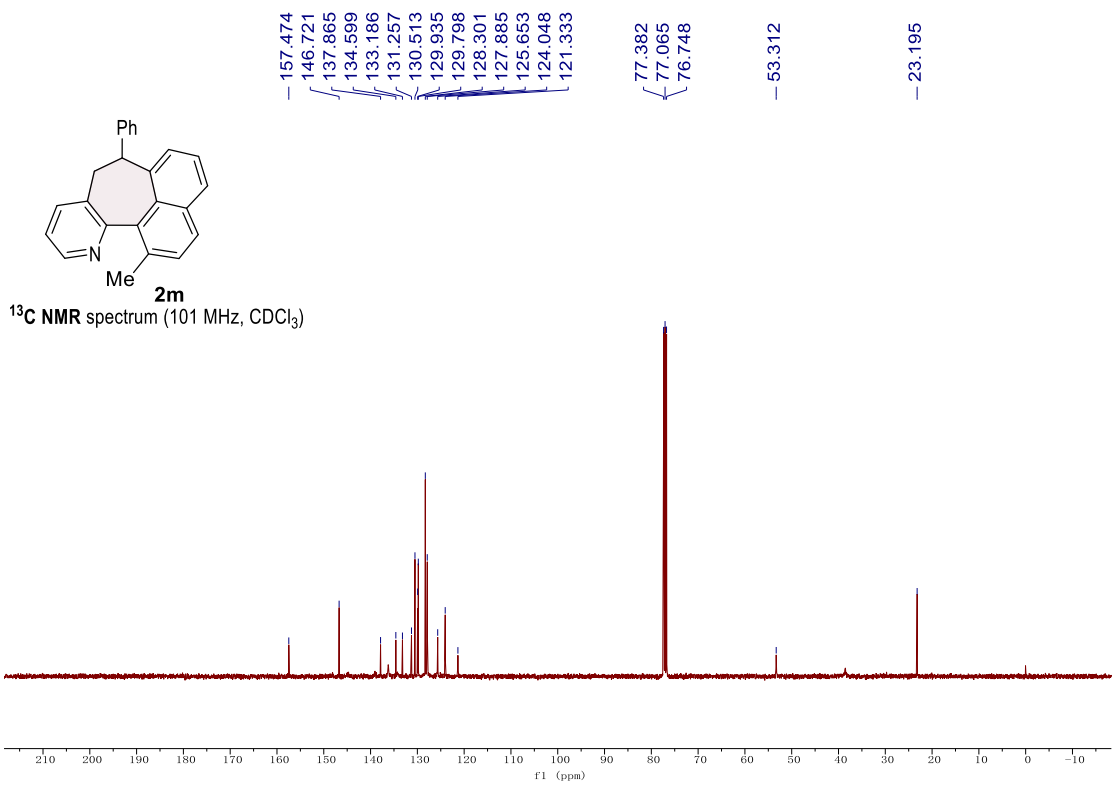
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





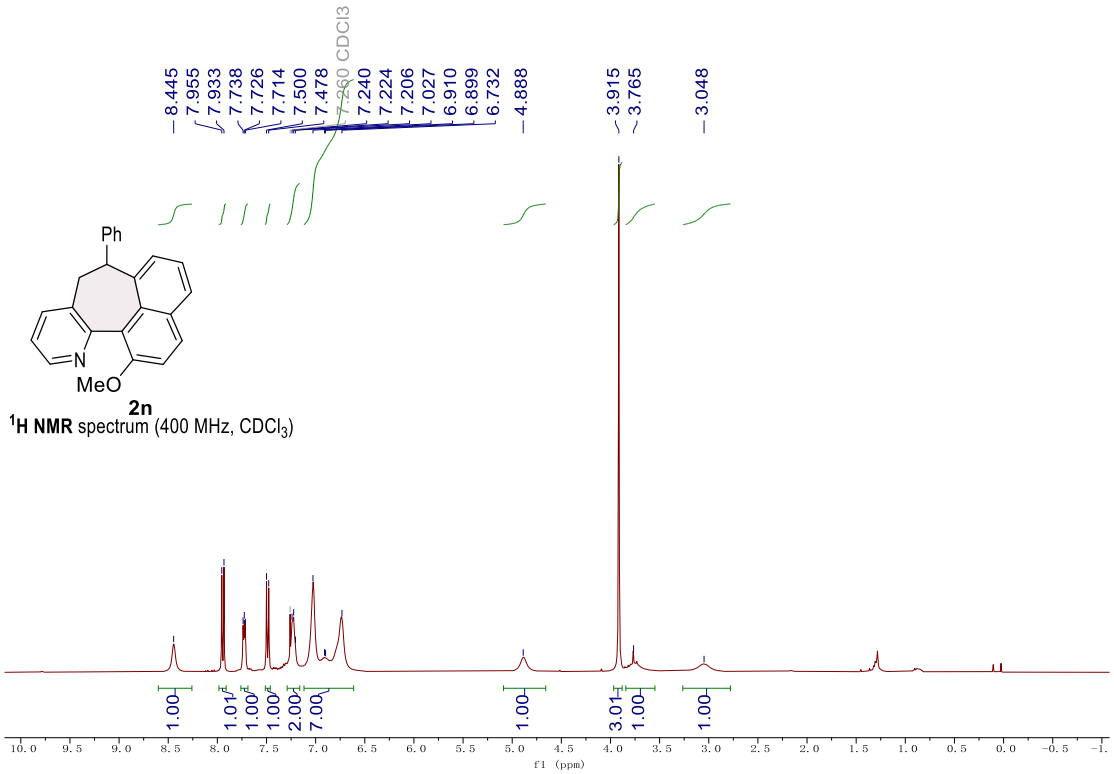
2m

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



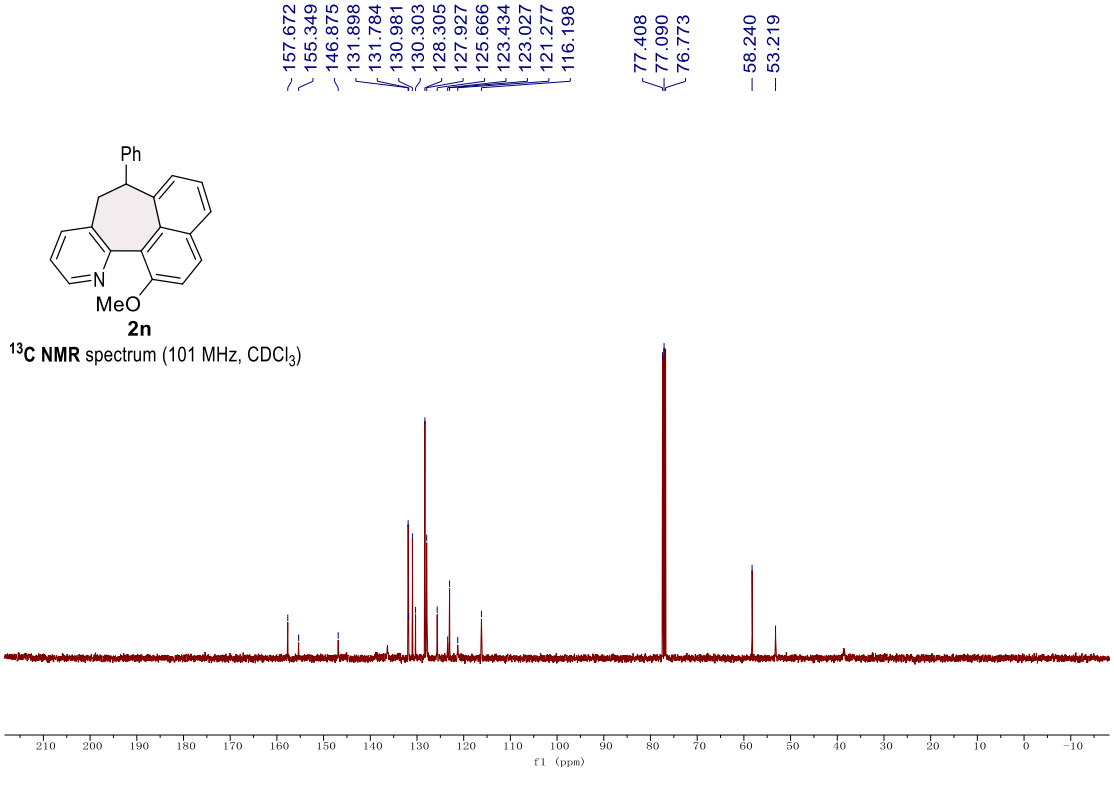
2m

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



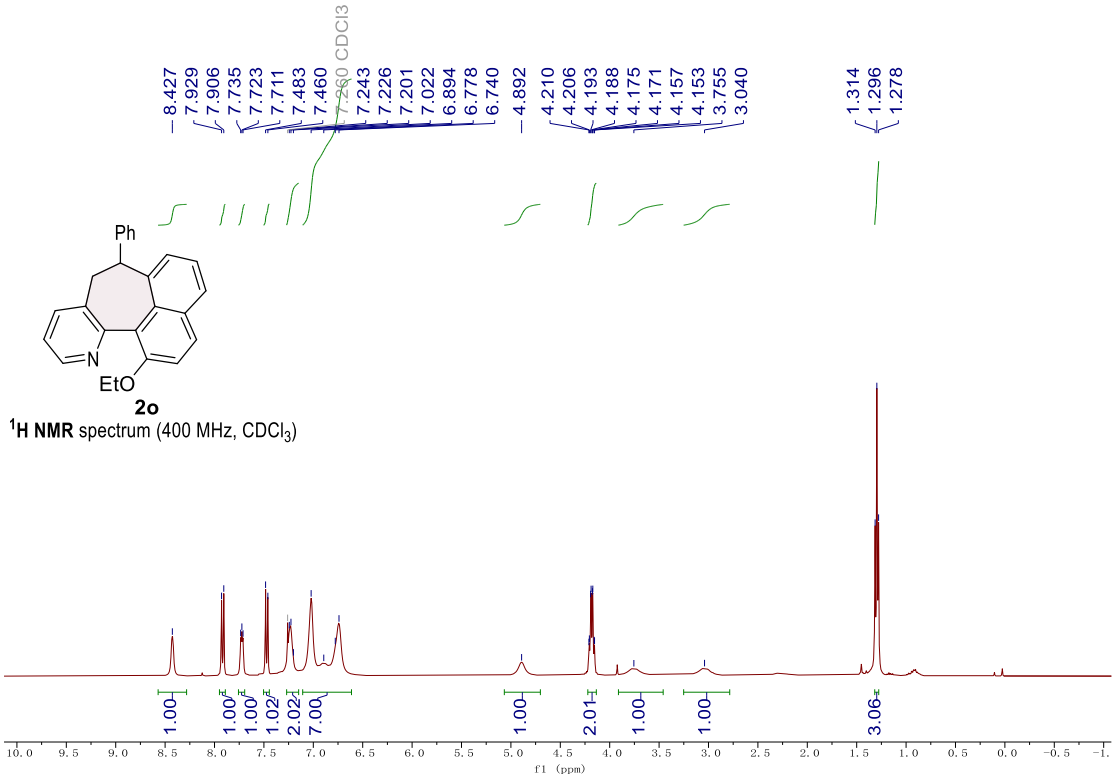
2n

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



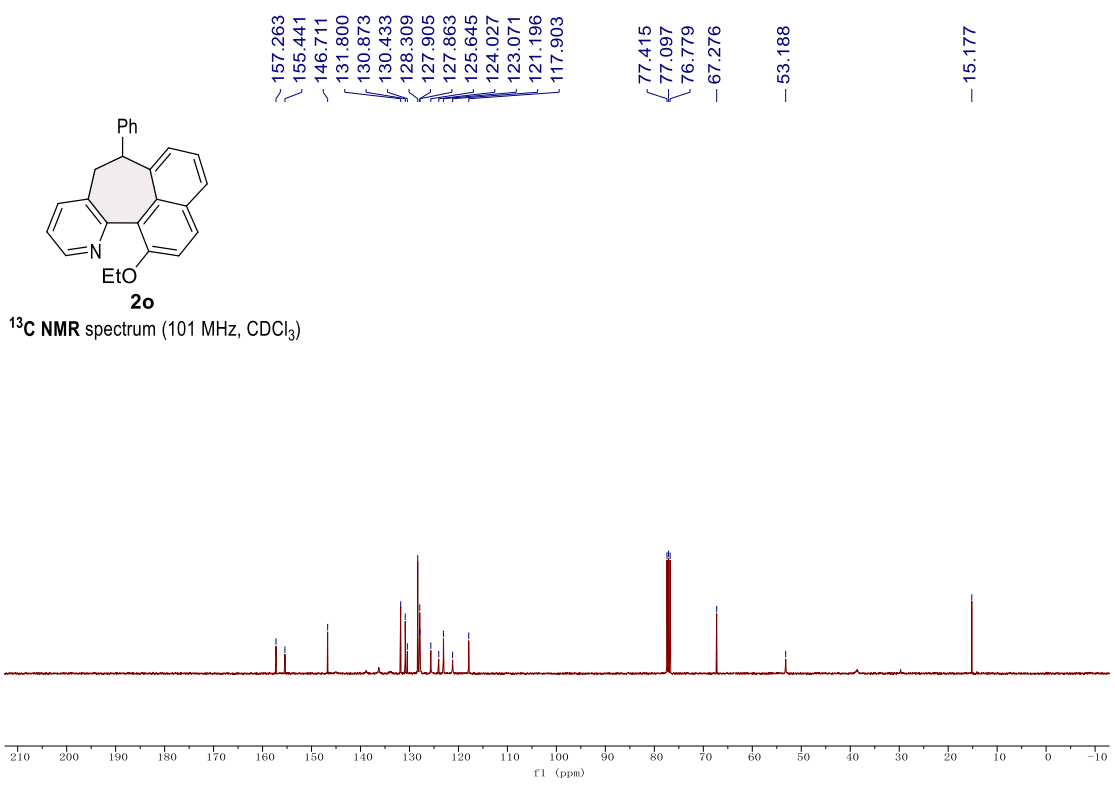
2n

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



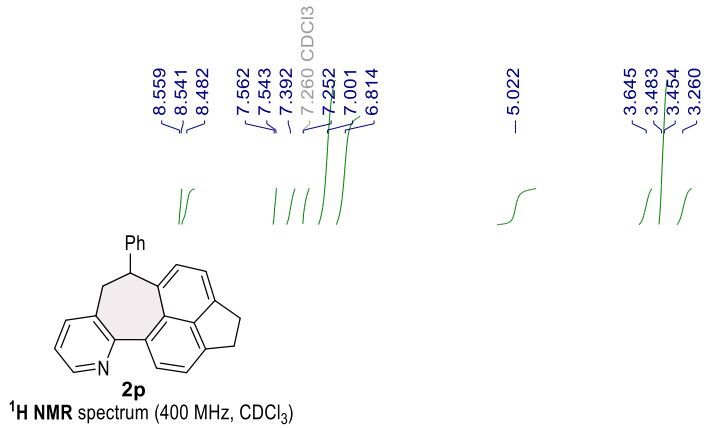
2o

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



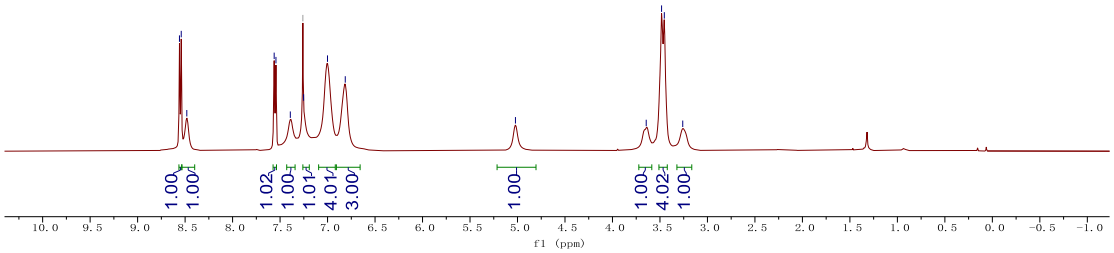
2o

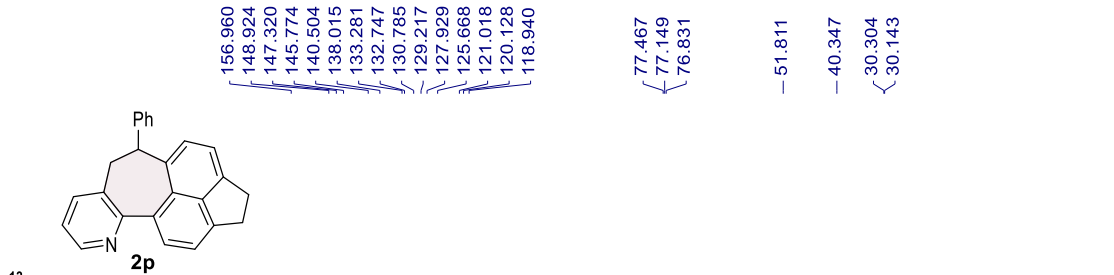
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2p

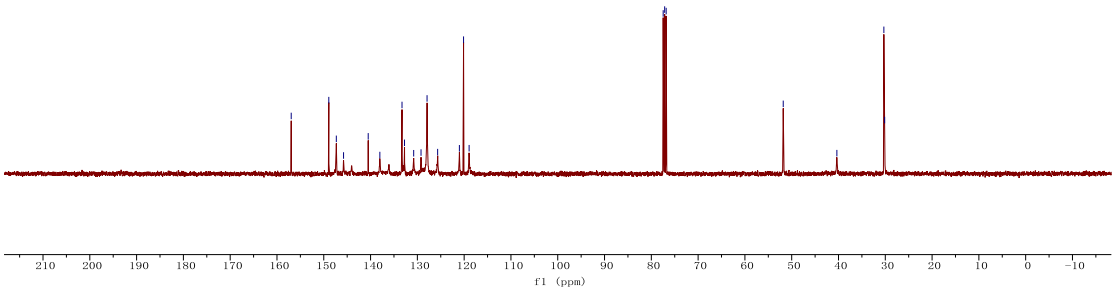
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

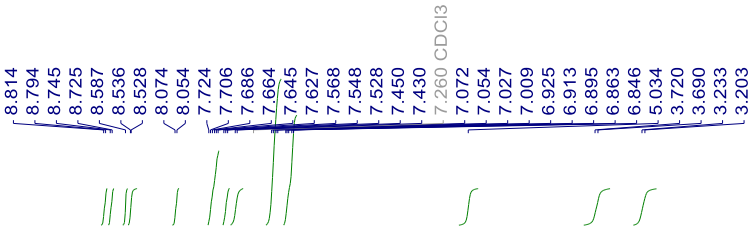


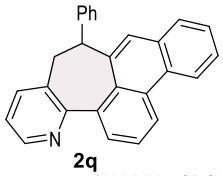


2p

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

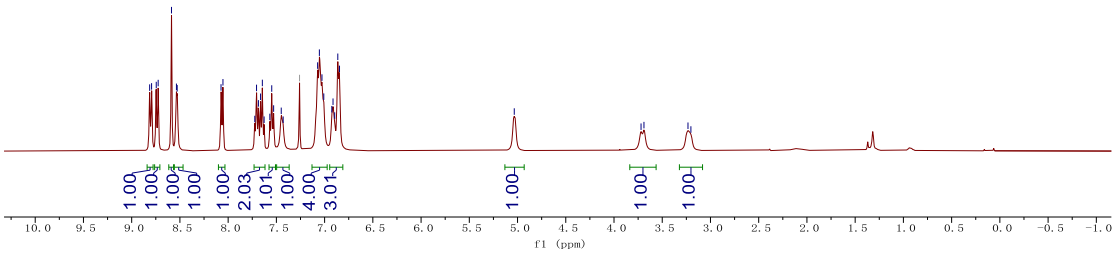


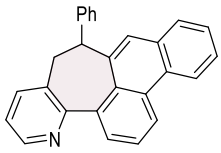




2q

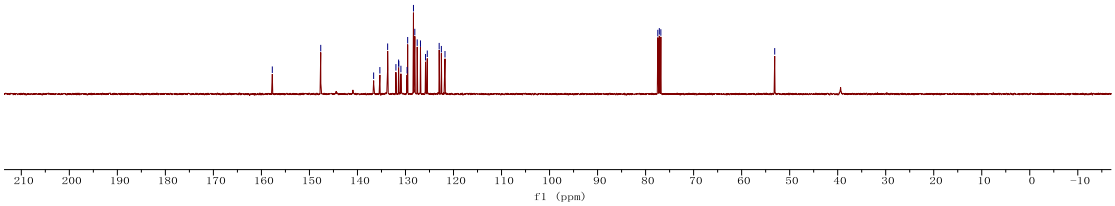
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

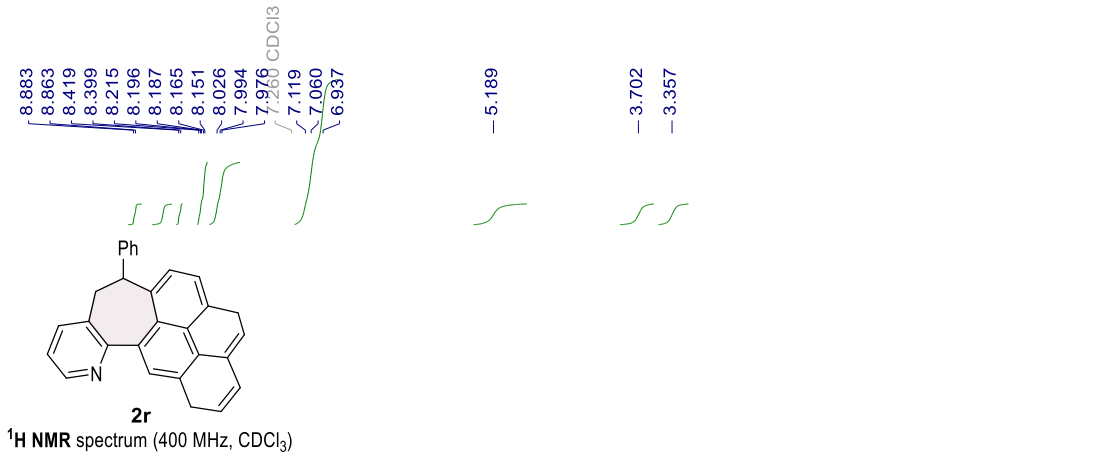




2q

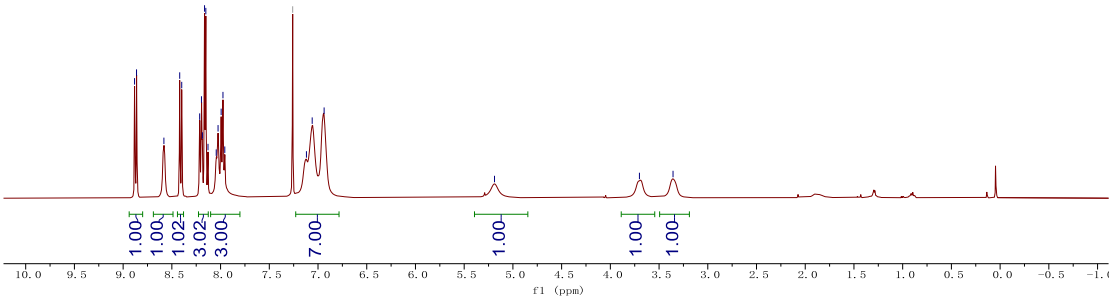
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

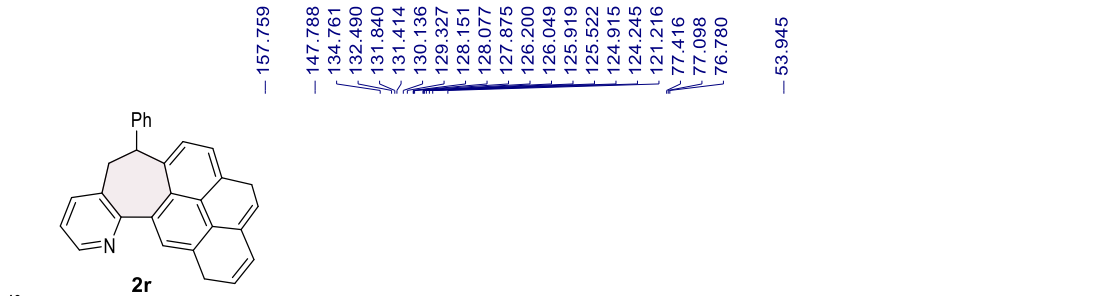




2r

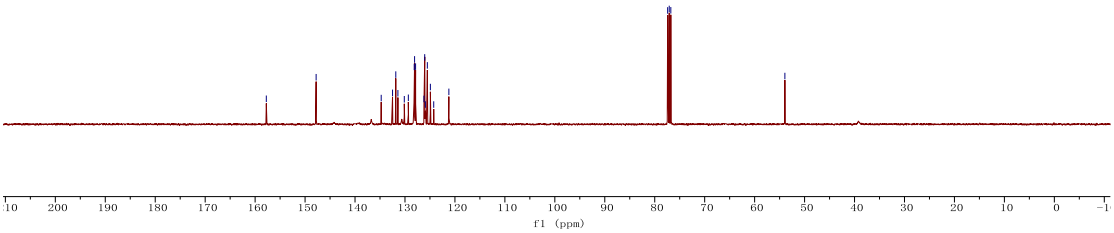
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

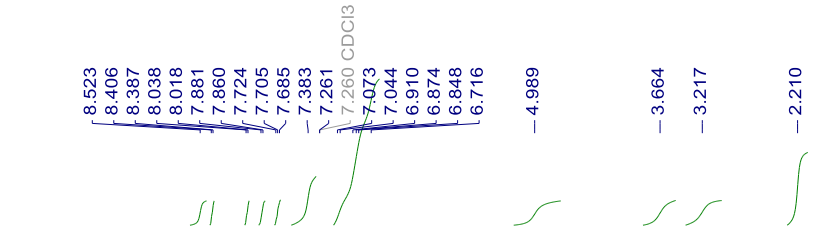


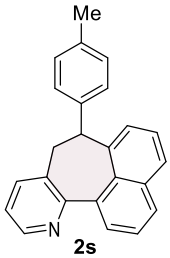


2r

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

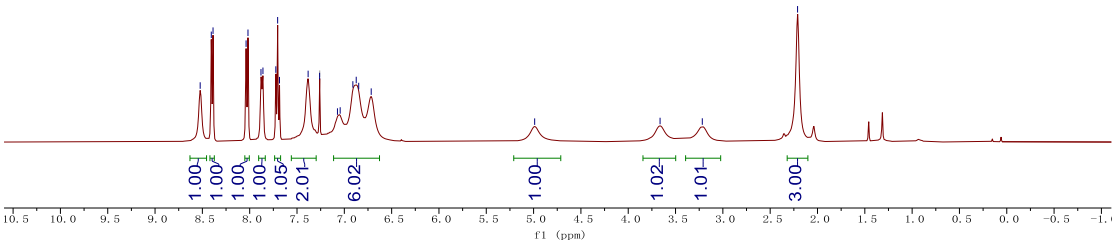


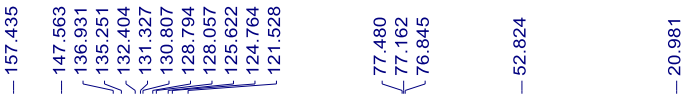


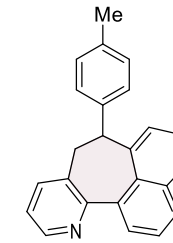


2s

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

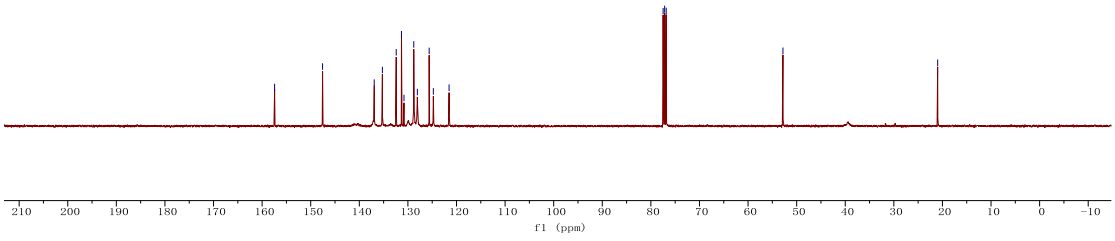


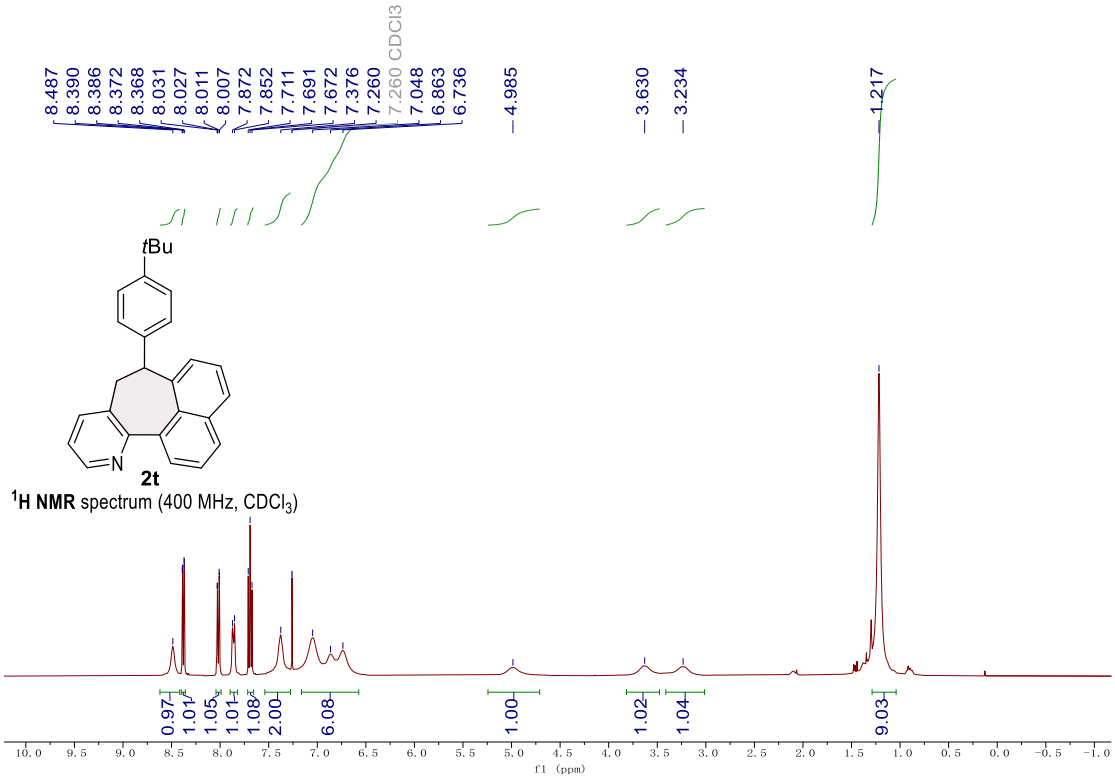




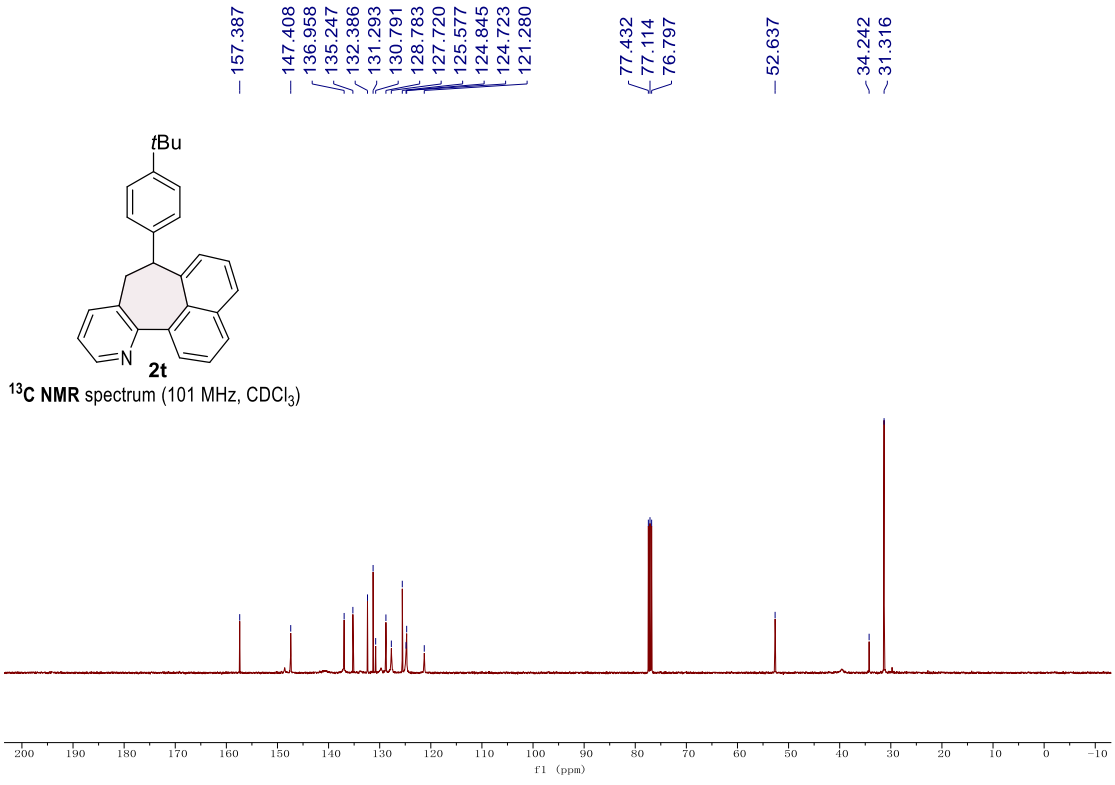
2s

^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)

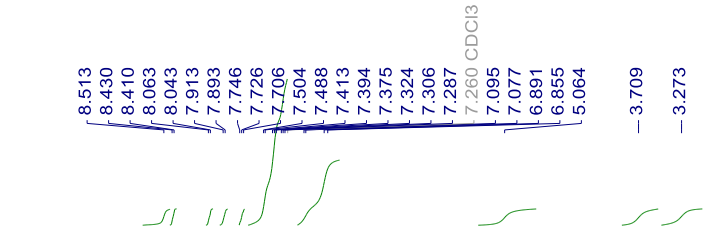


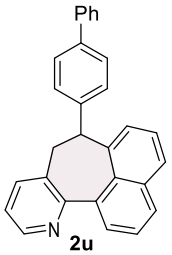


^{1}H NMR spectrum (400 MHz, $CDCl_3$)



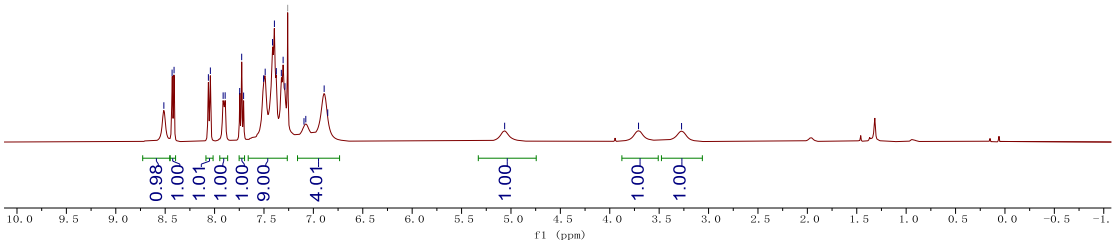
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

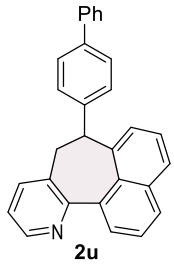




2u

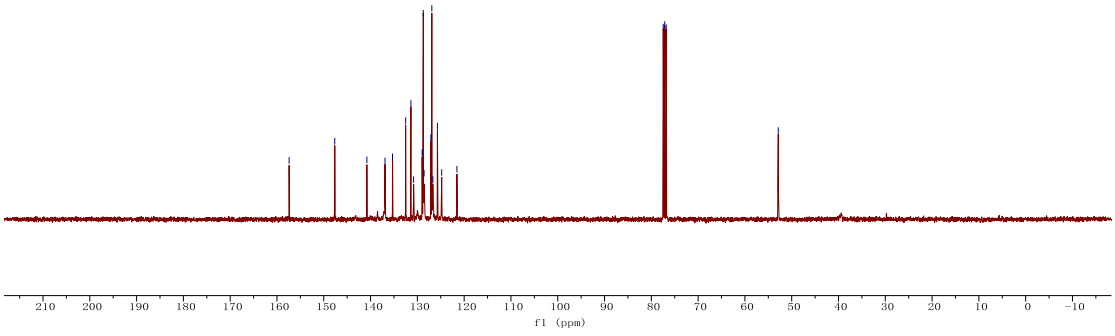
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

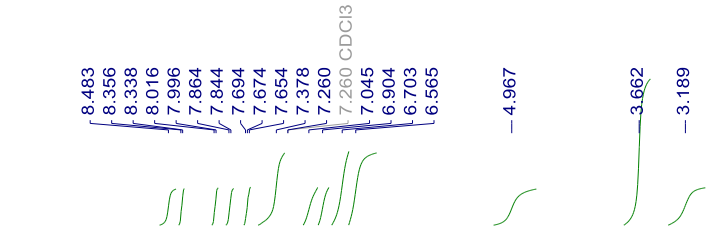


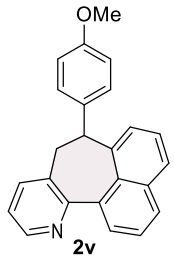


2u

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

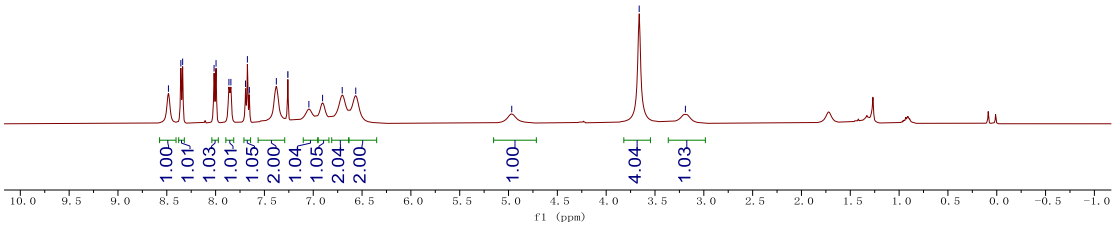


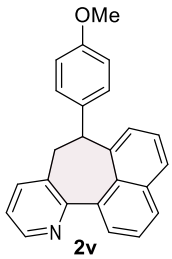




2v

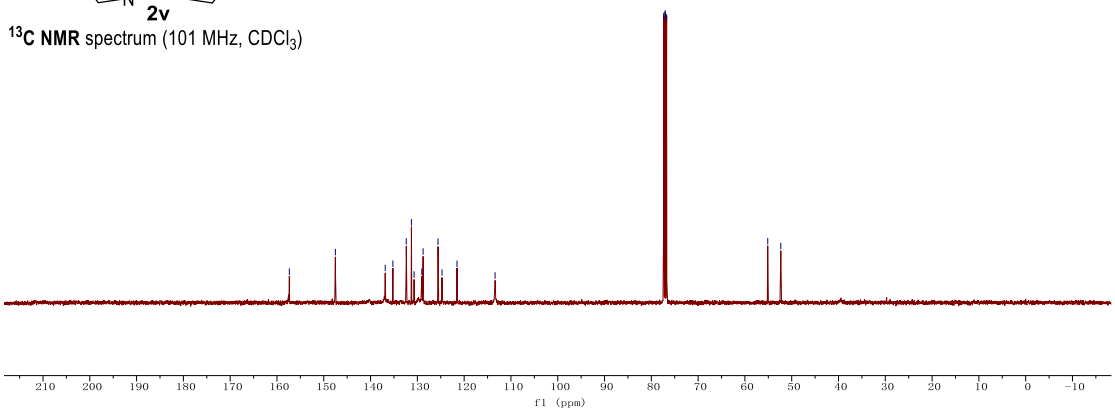
^{1}**H NMR** spectrum (400 MHz, $CDCl_3$)

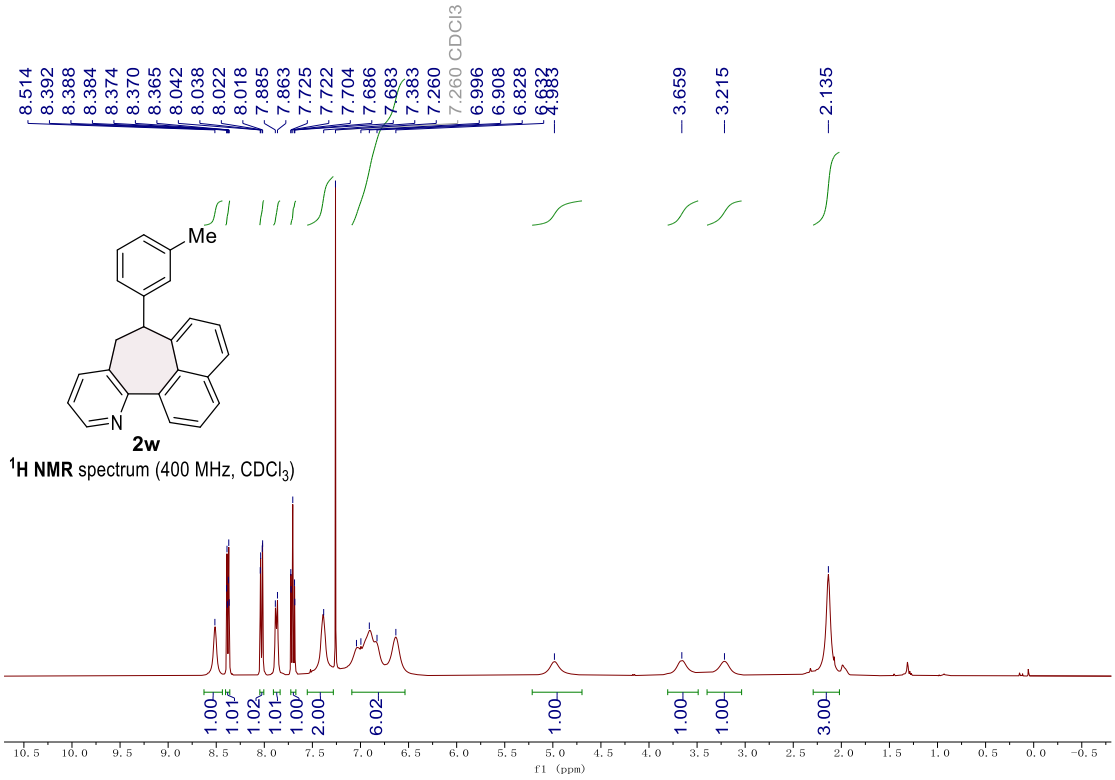




2v

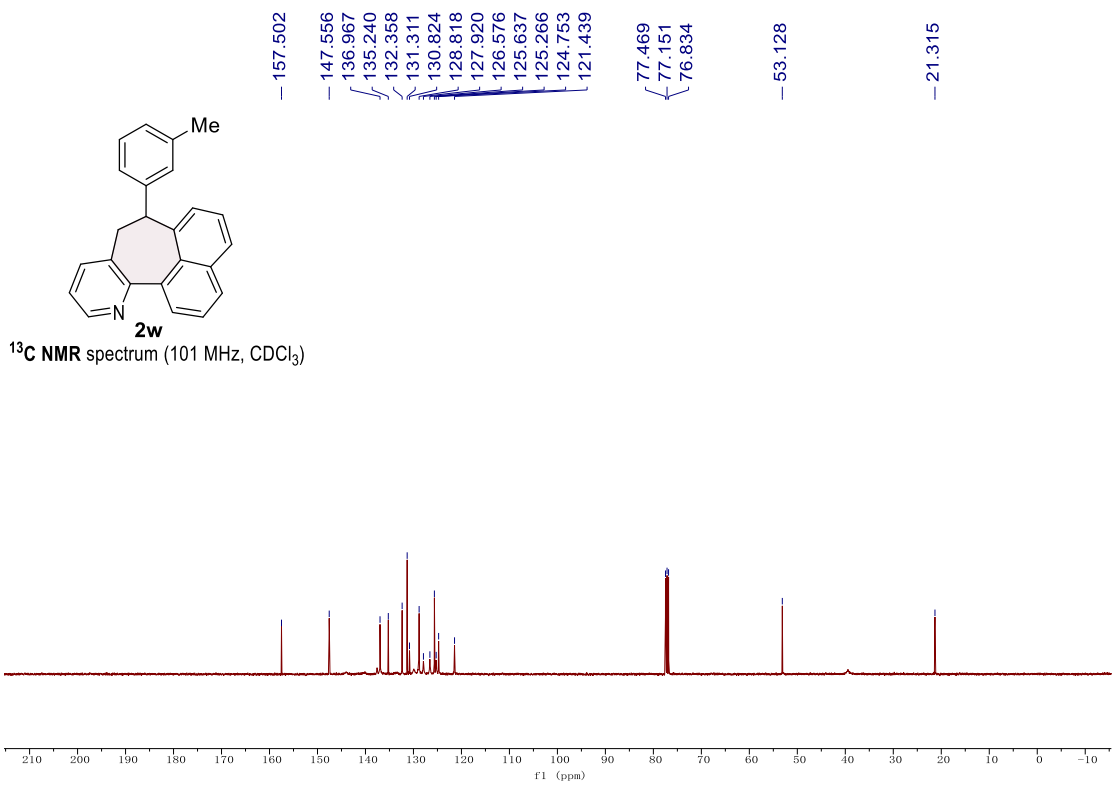
^{13}**C NMR** spectrum (101 MHz, $CDCl_3$)





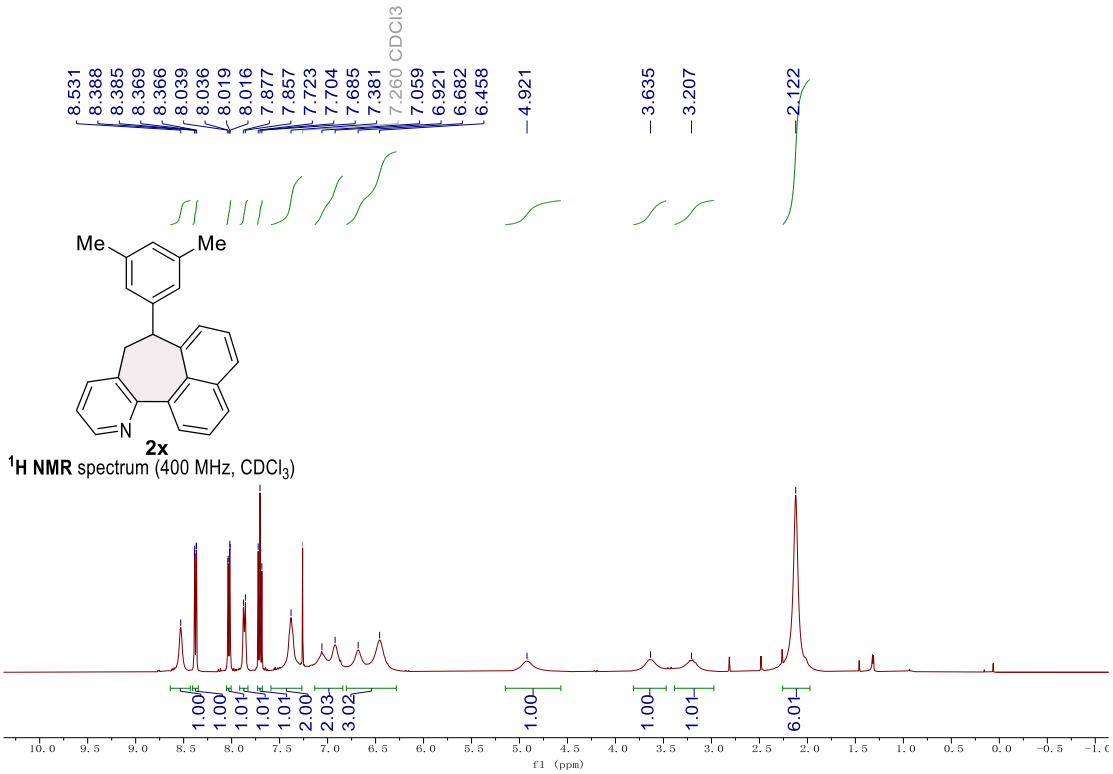
2w

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



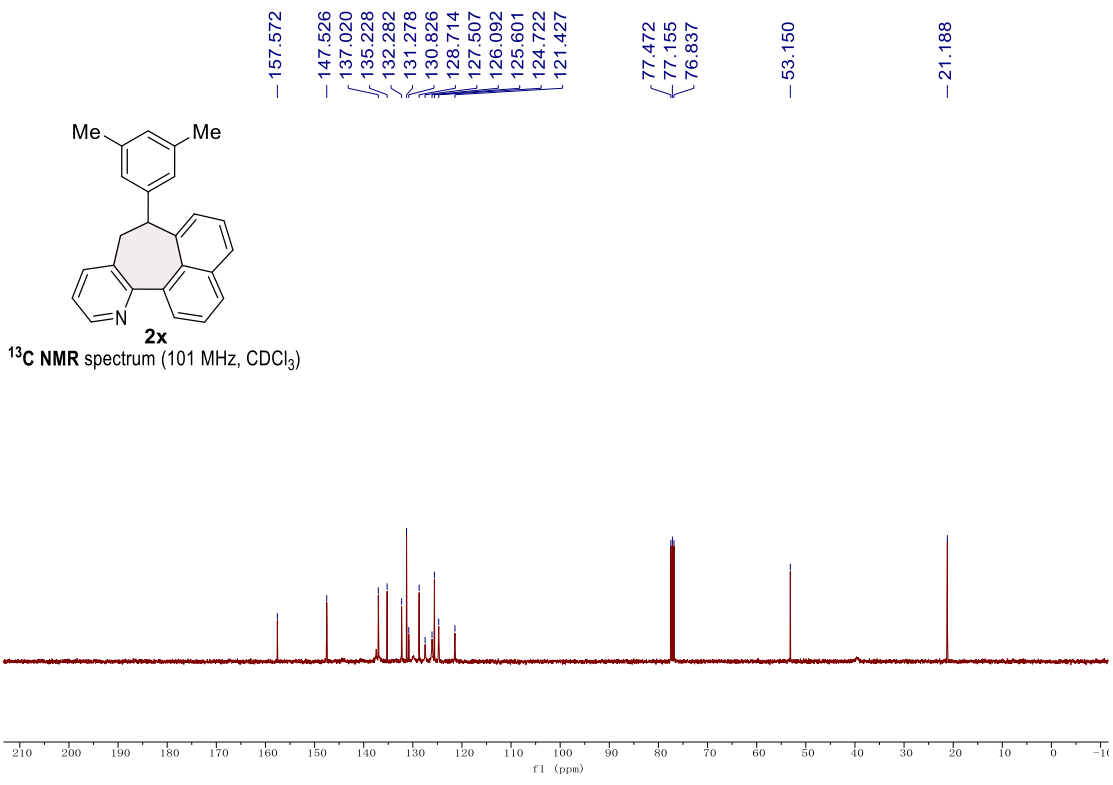
2w

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



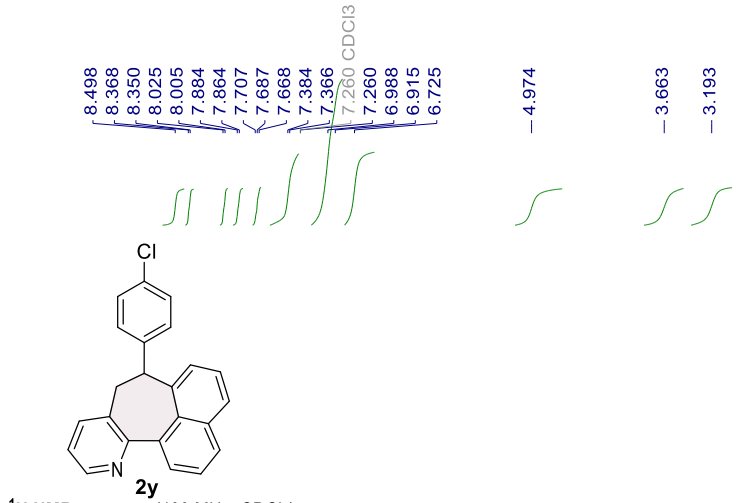
2x

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



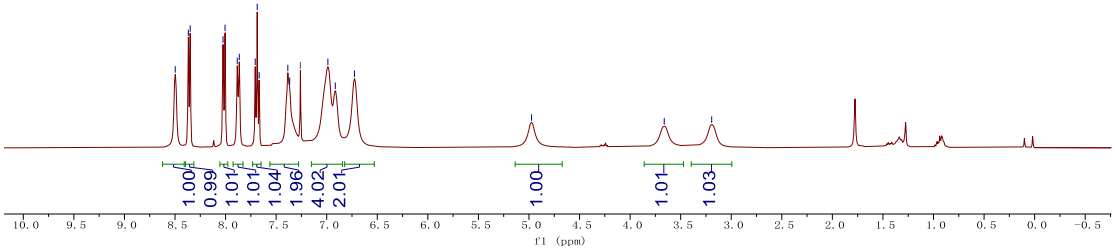
2x

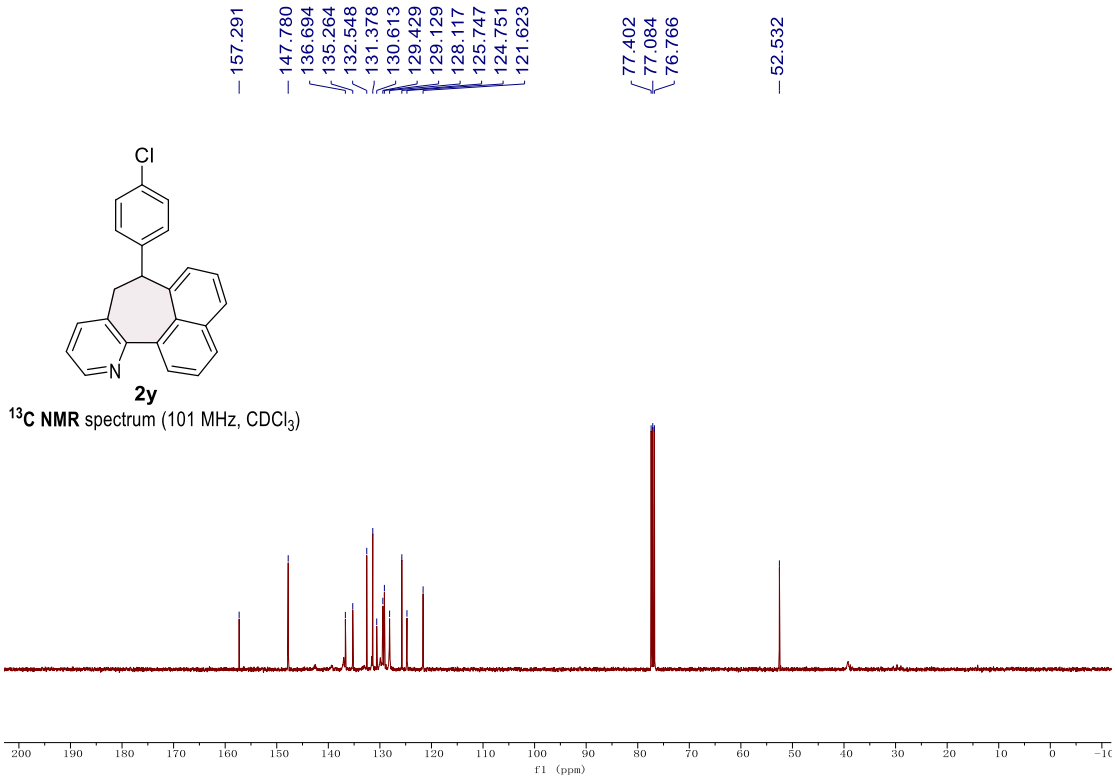
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2y

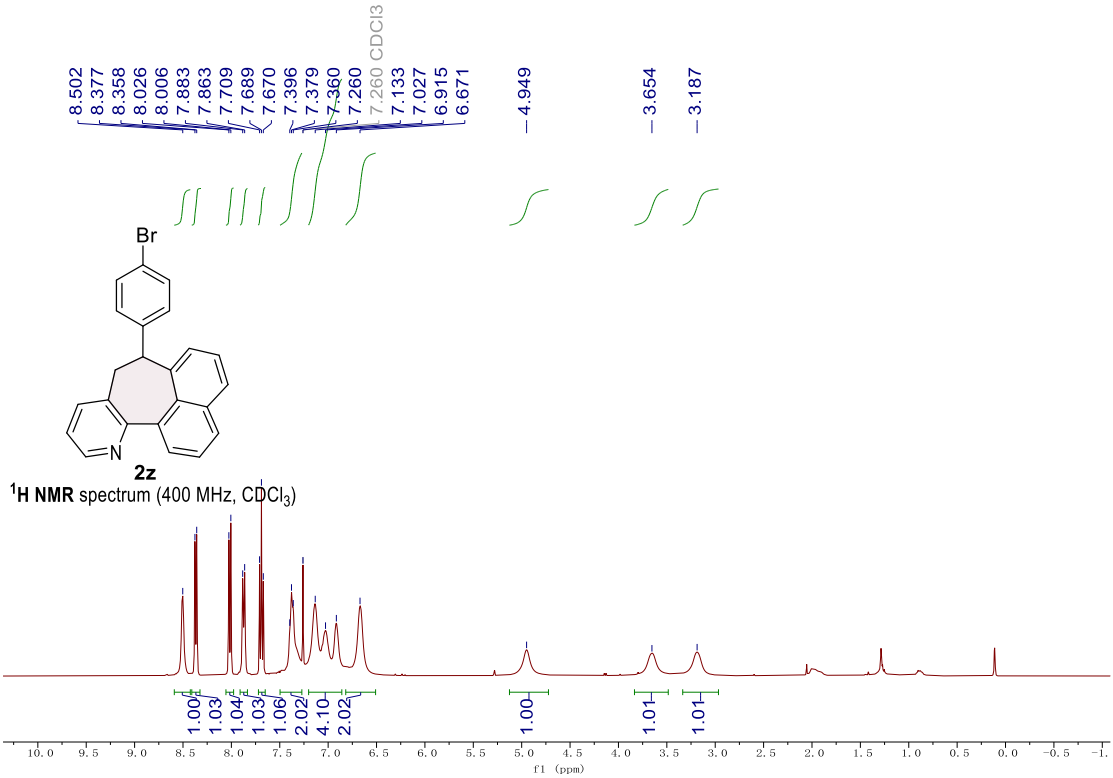
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





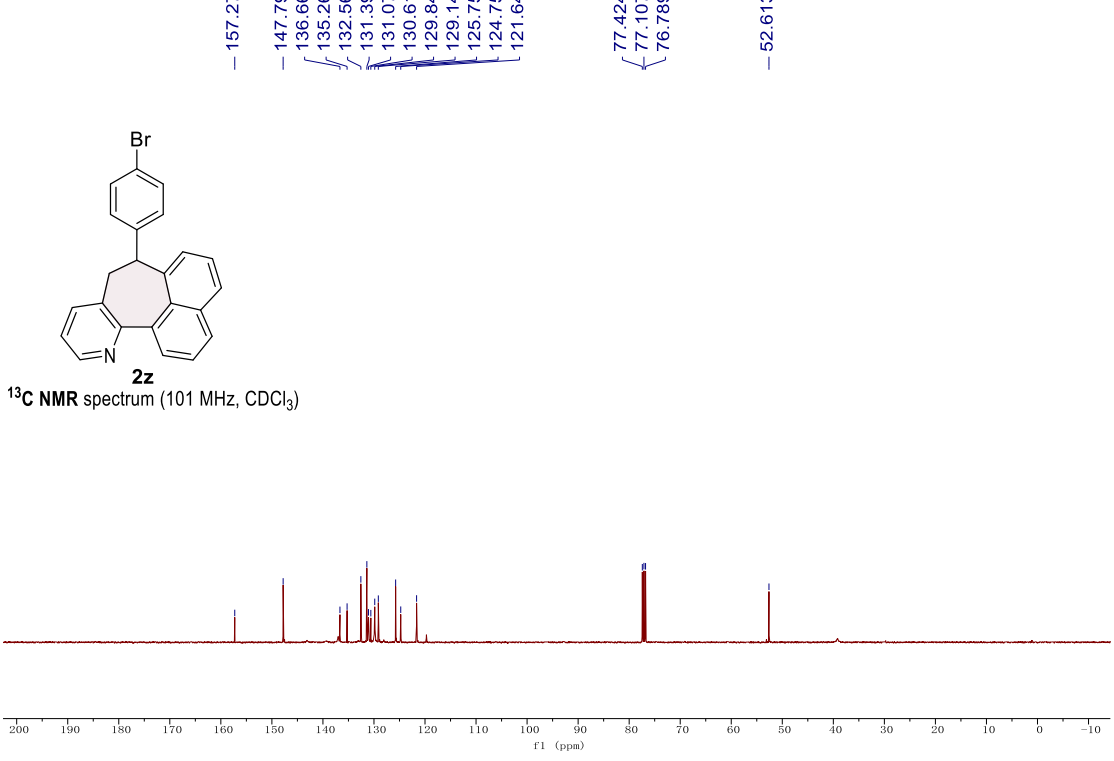
2y

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



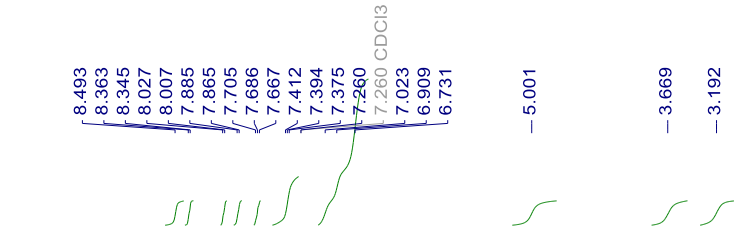
2z

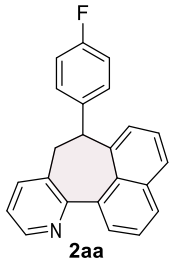
^{1}H NMR spectrum (400 MHz, $CDCl_3$)



2z

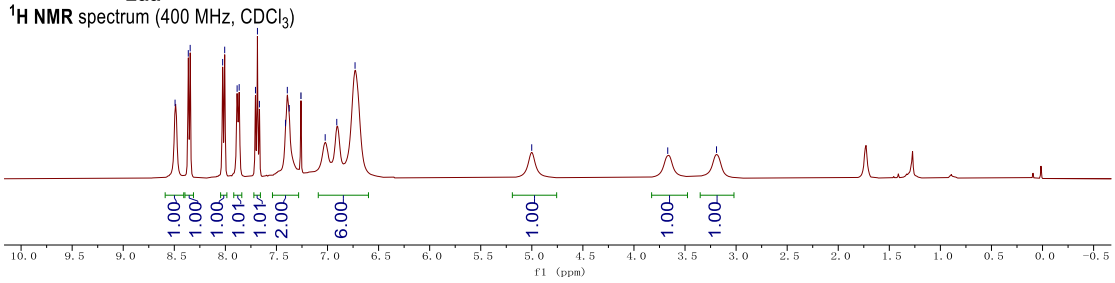
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

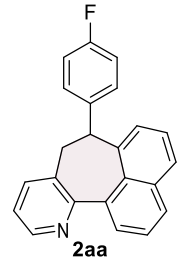




2aa

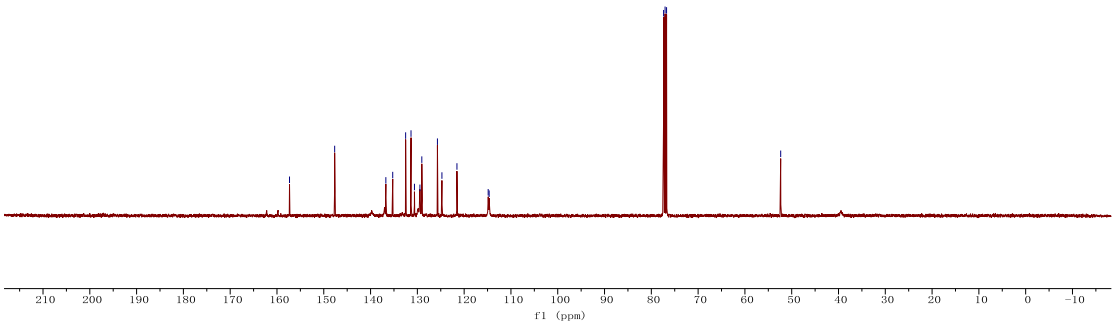
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

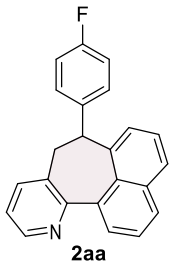




2aa

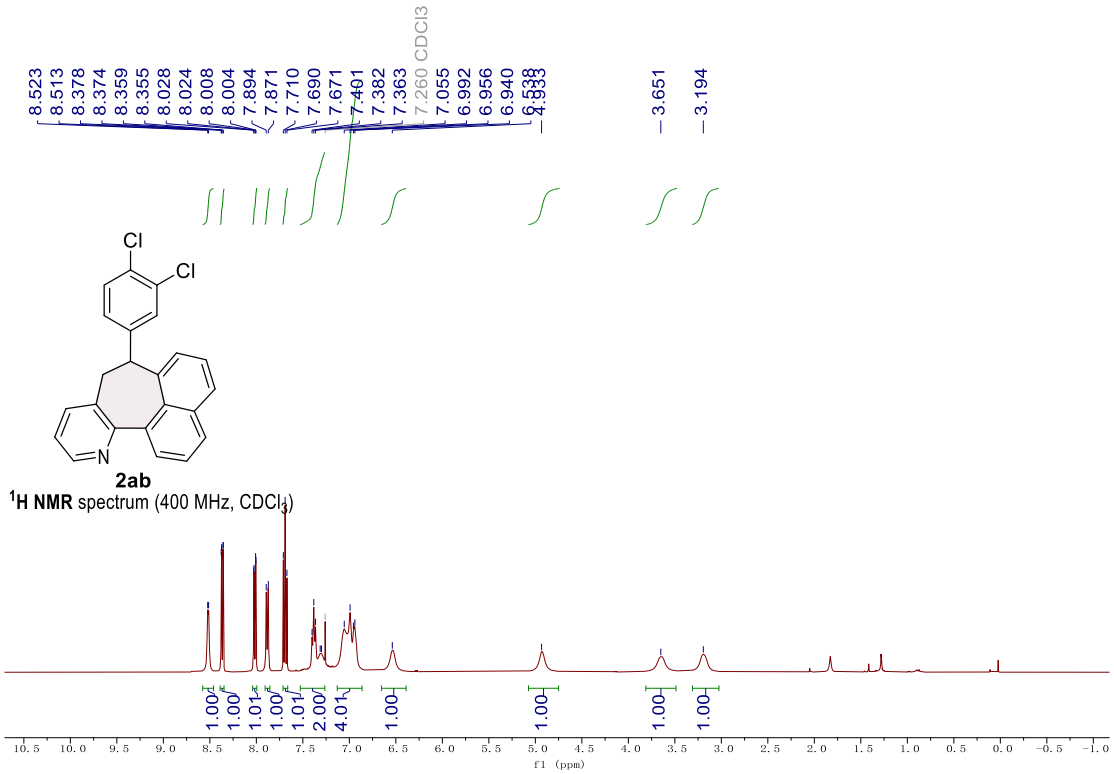
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





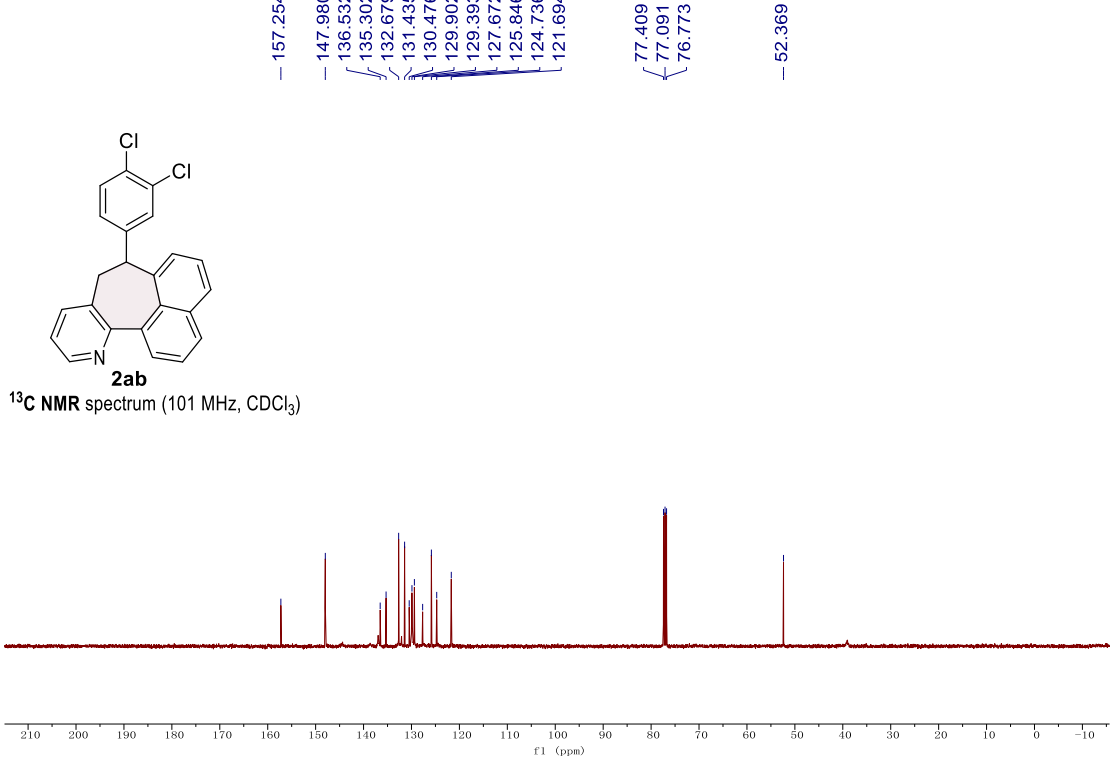
2aa

^{19}F NMR spectrum (377 MHz, $CDCl_3$)



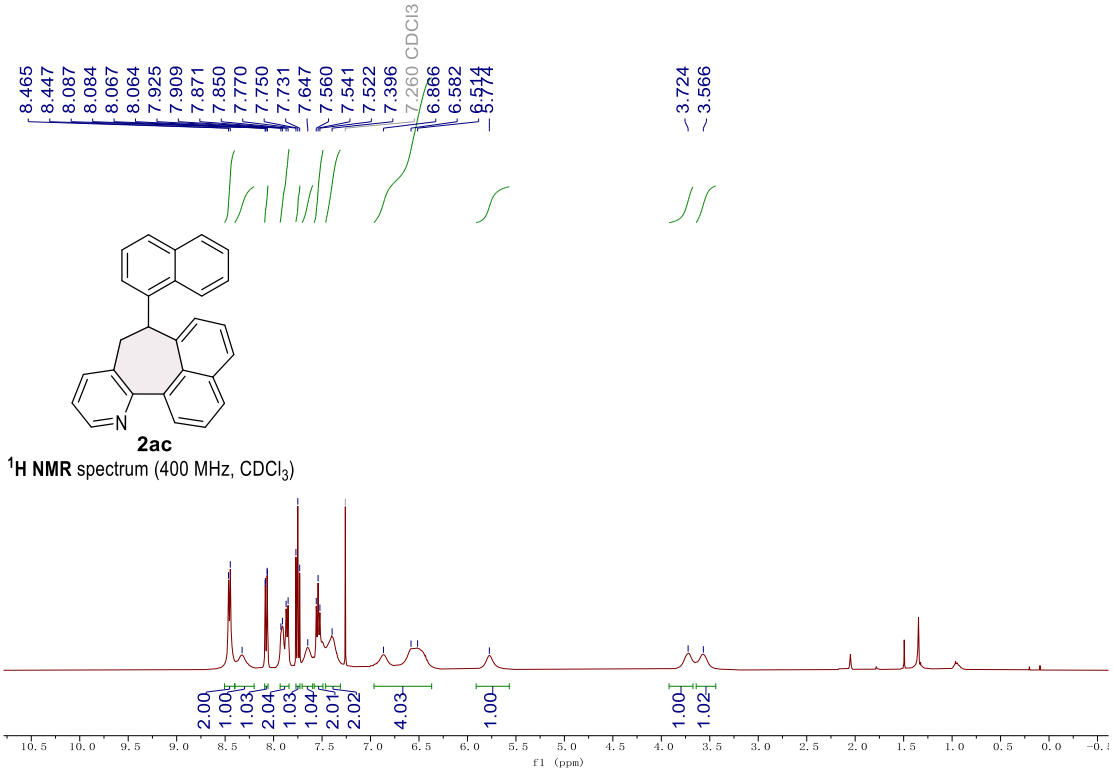
2ab

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



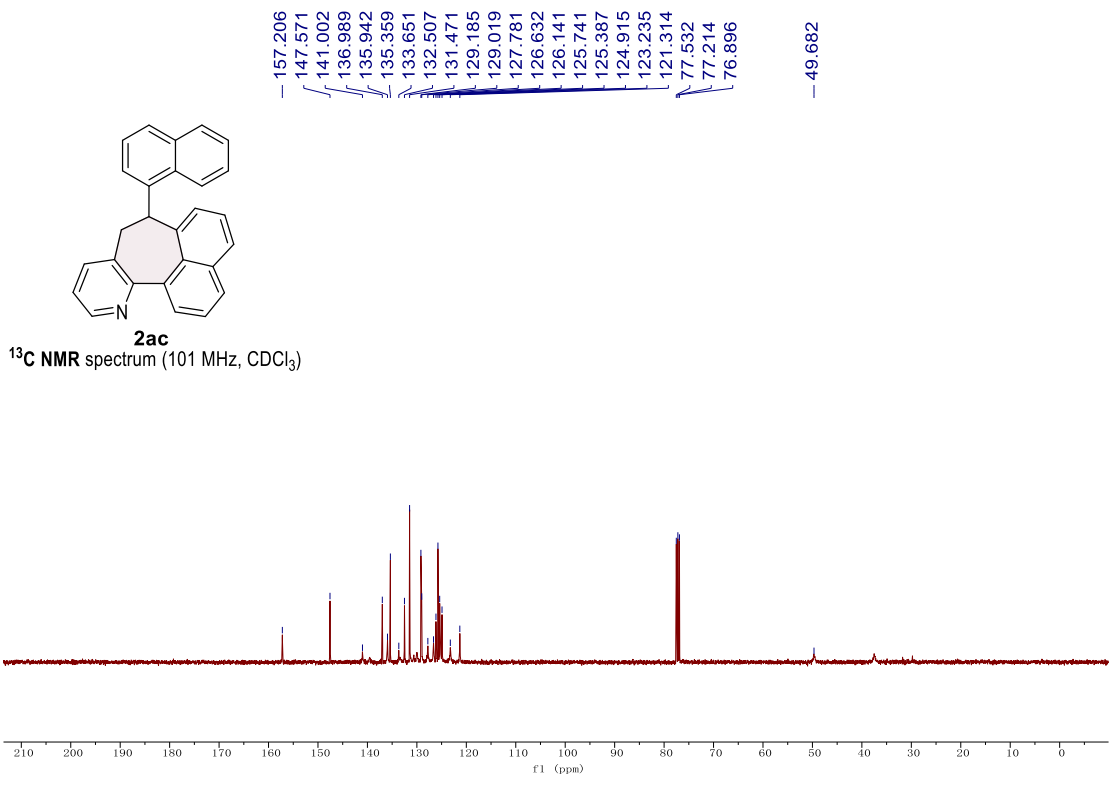
2ab

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



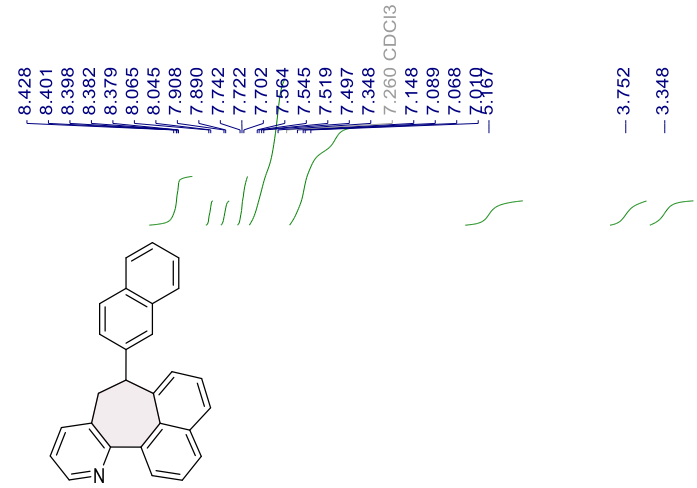
2ac

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



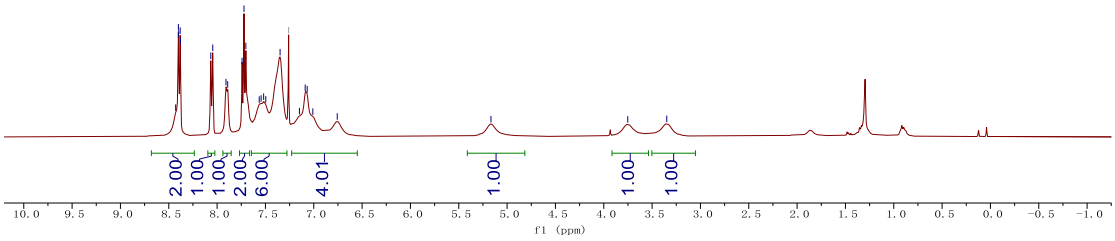
2ac

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



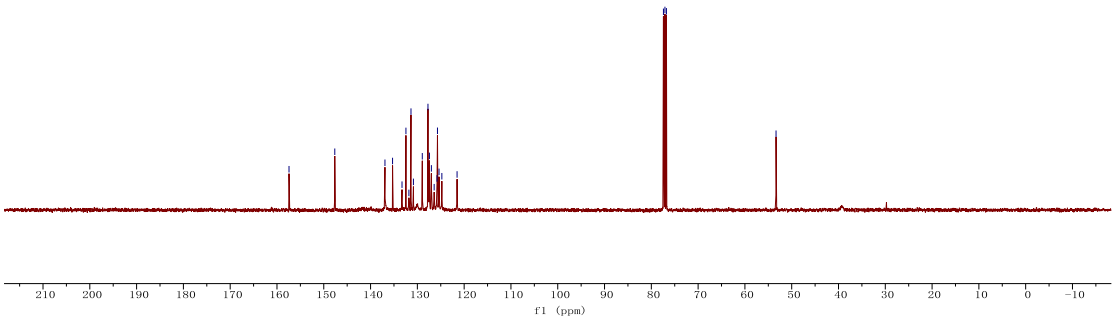
2ad

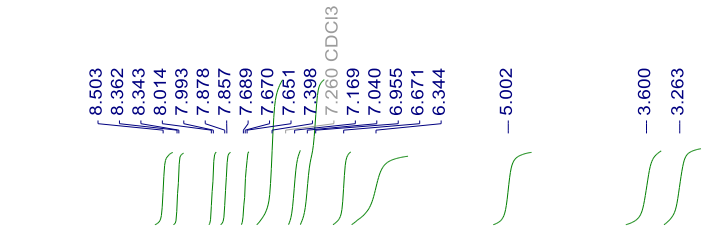
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

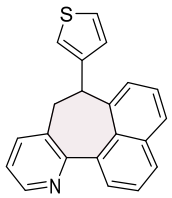


2ad

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

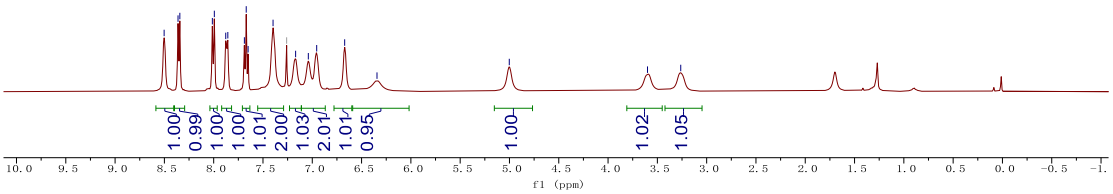


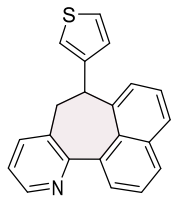




2ae

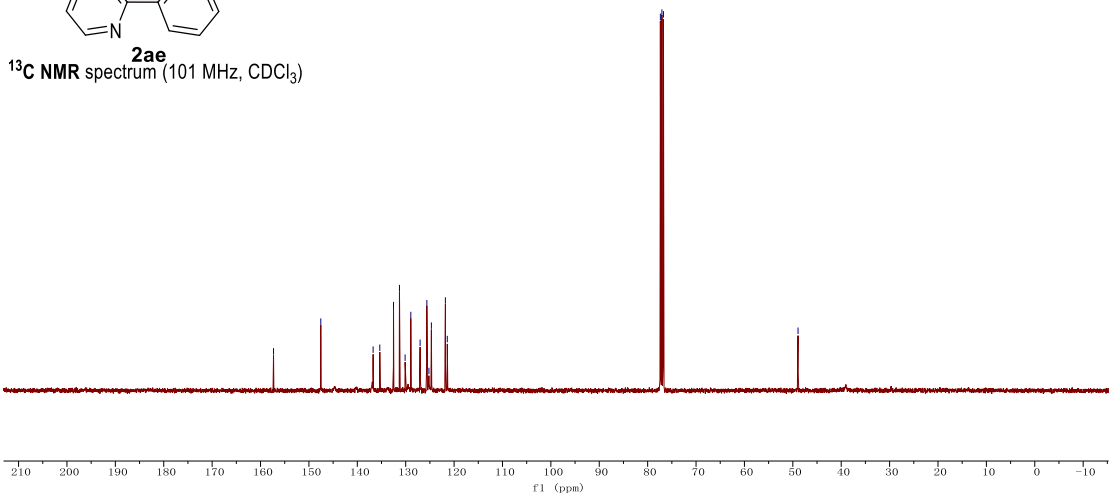
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

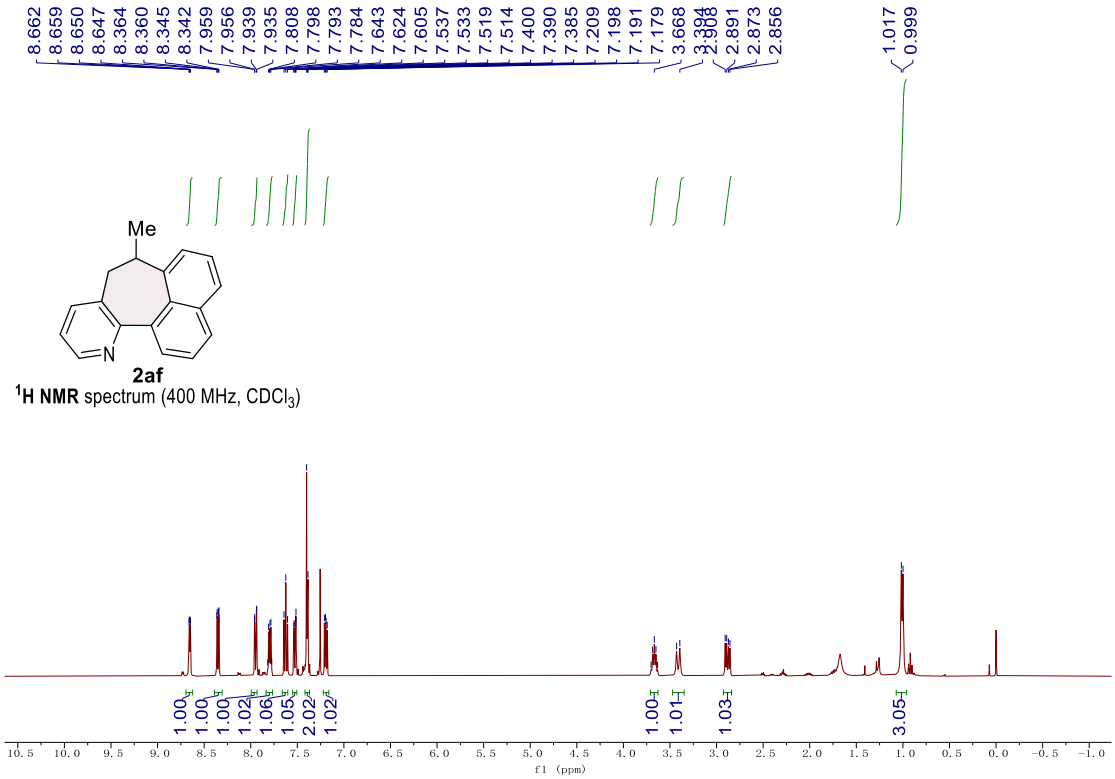




2ae

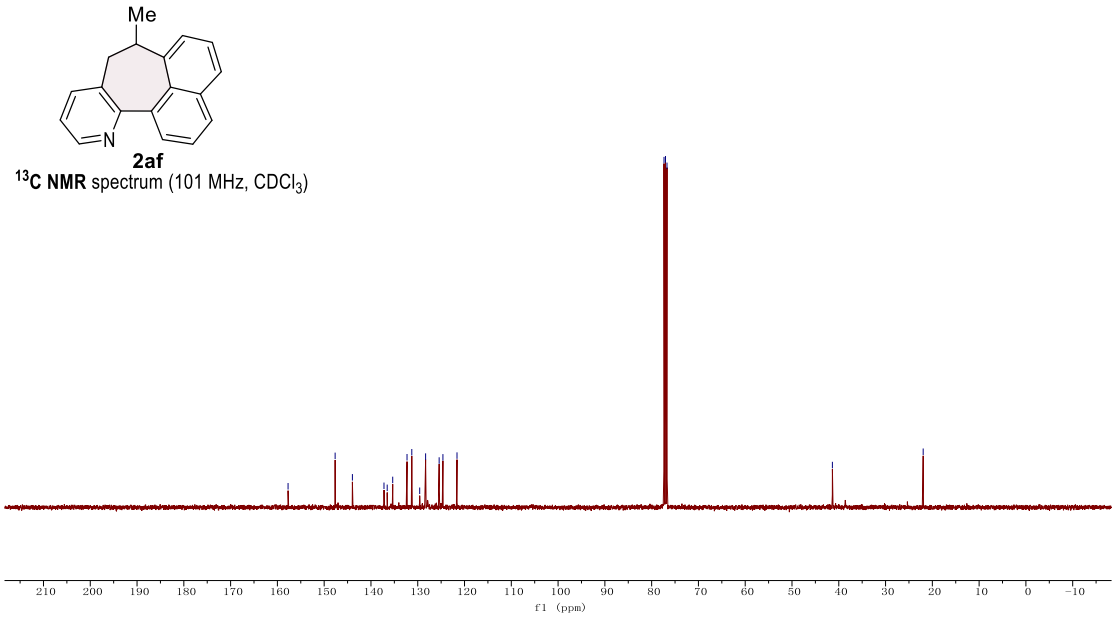
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





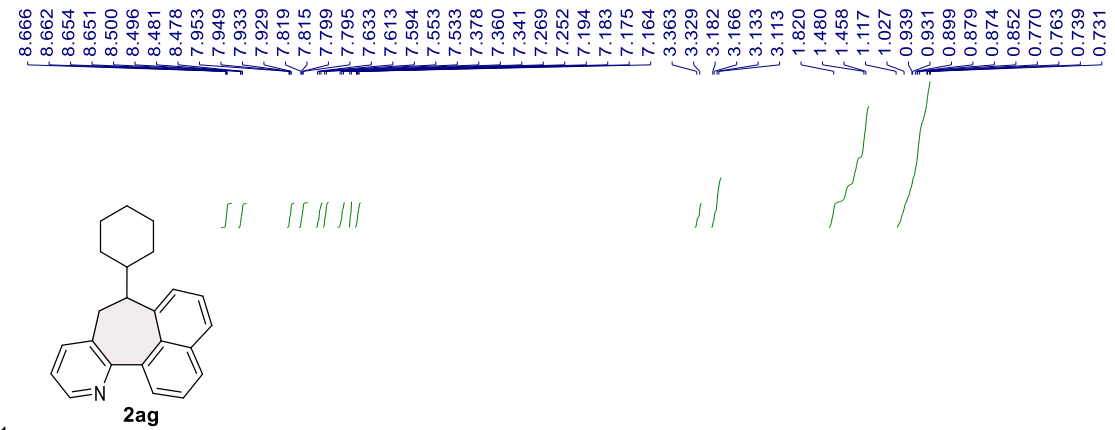
2af

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



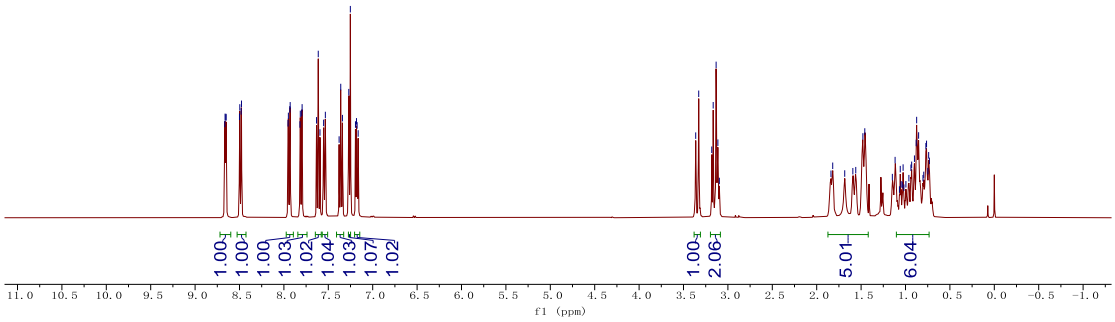
2af

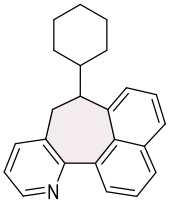
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2ag

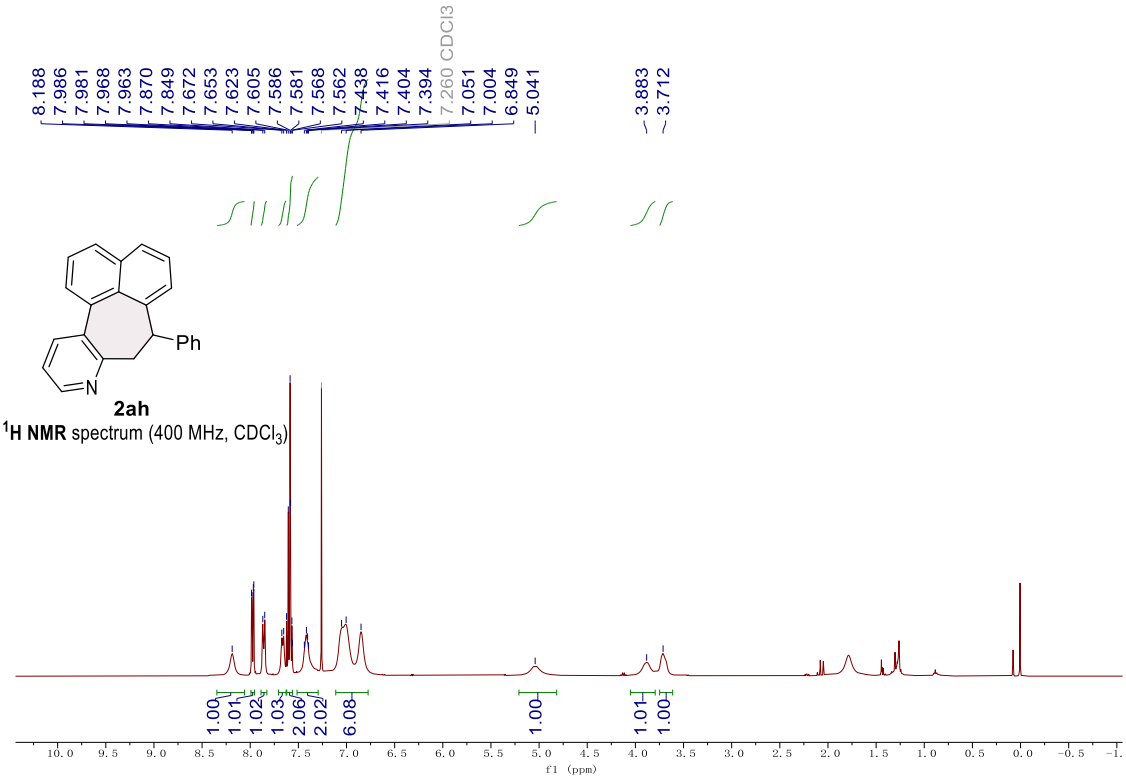
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





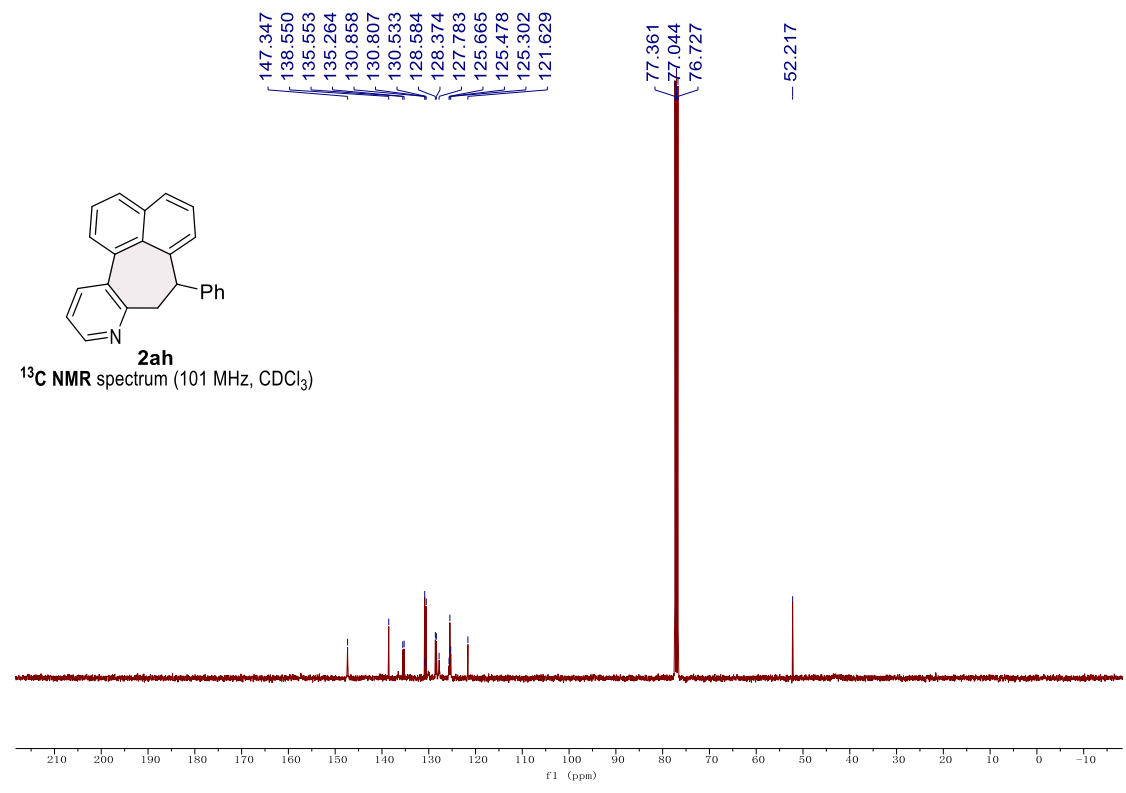
2ag

^{13}C NMR spectrum (101 MHz, $CDCl_3$)



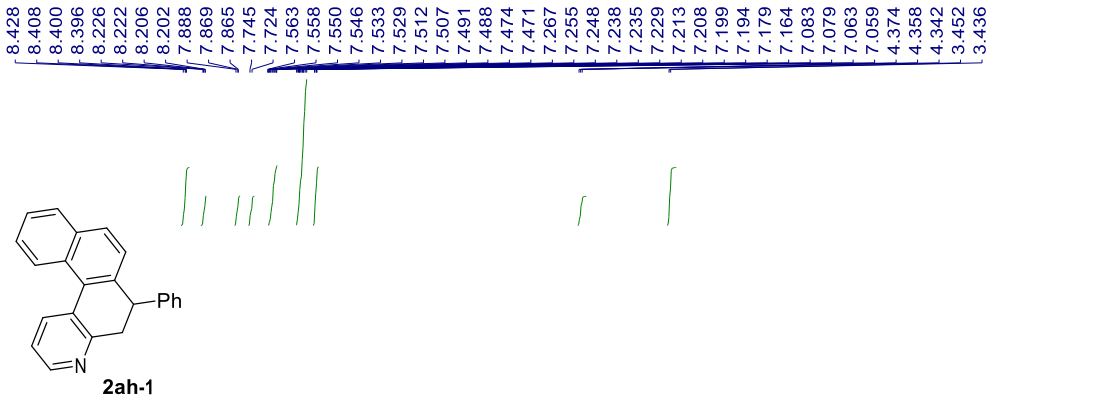
2ah

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



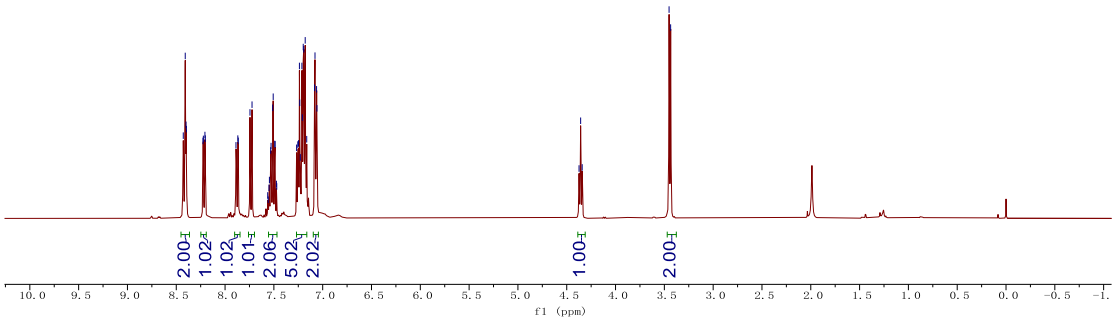
2ah

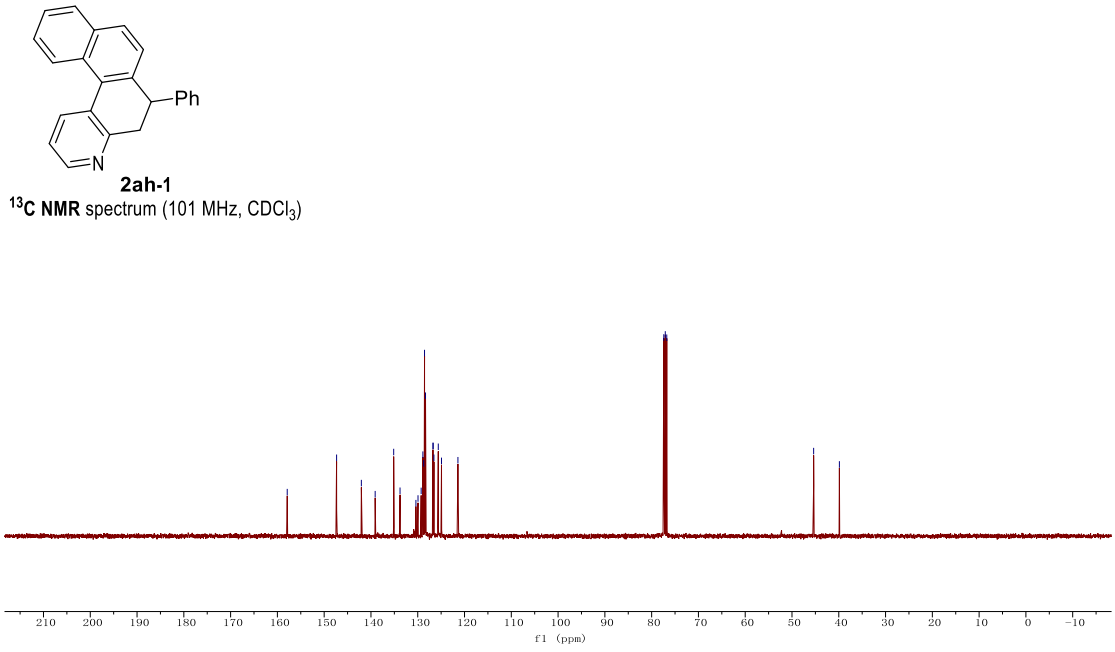
^{13}C NMR spectrum (101 MHz, $CDCl_3$)



2ah-1

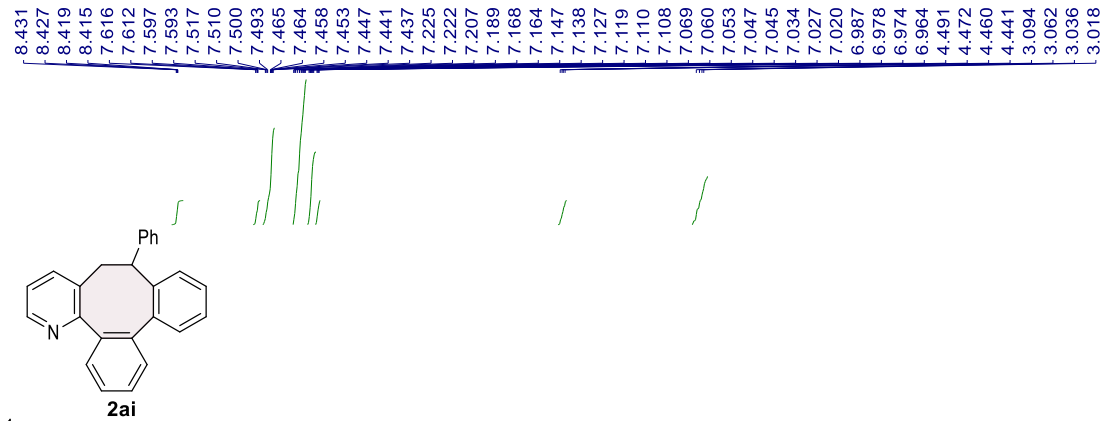
^{1}H NMR spectrum (400 MHz, $CDCl_3$)





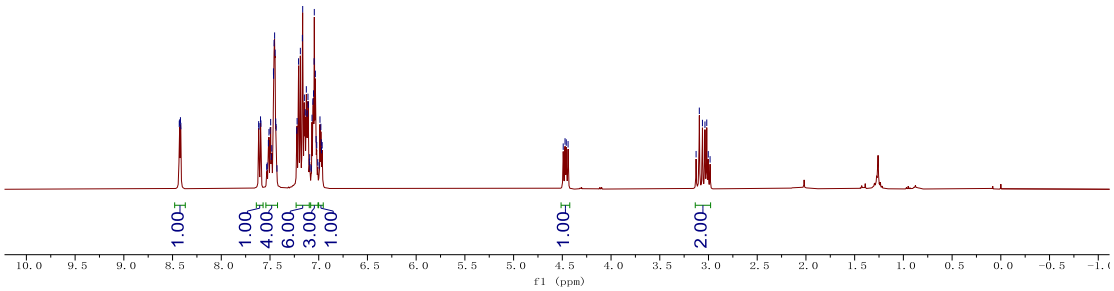
2ah-1

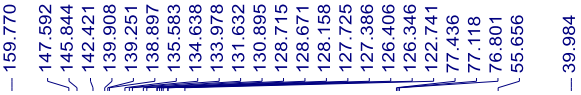
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

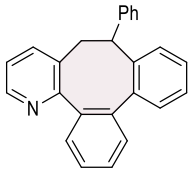


2ai

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

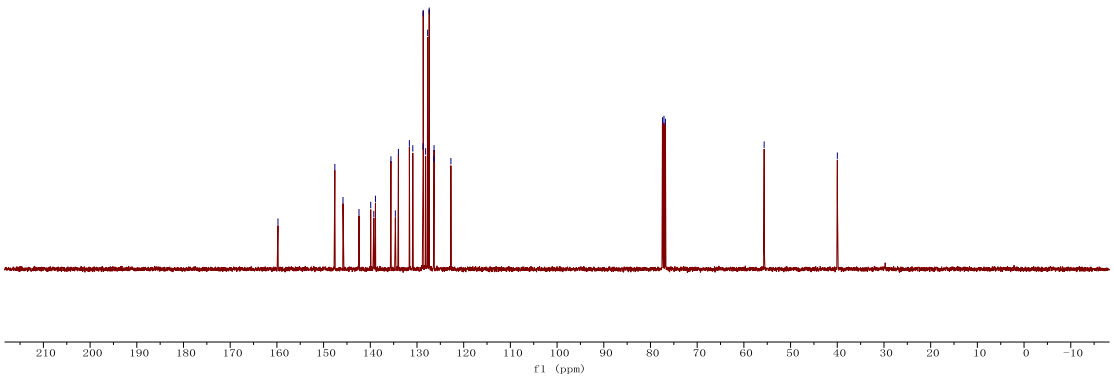


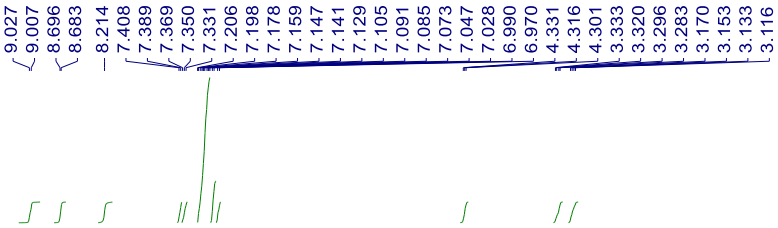


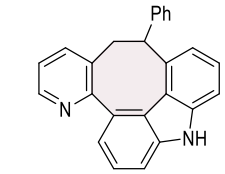


2ai

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

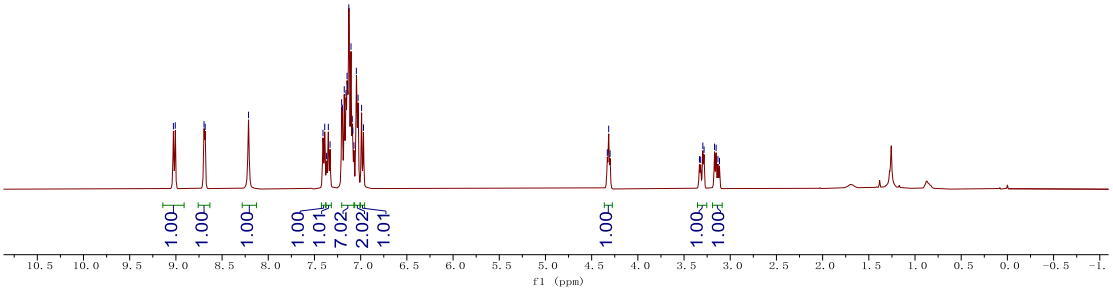


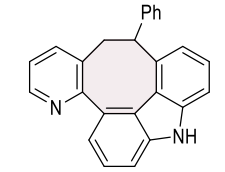




2aj

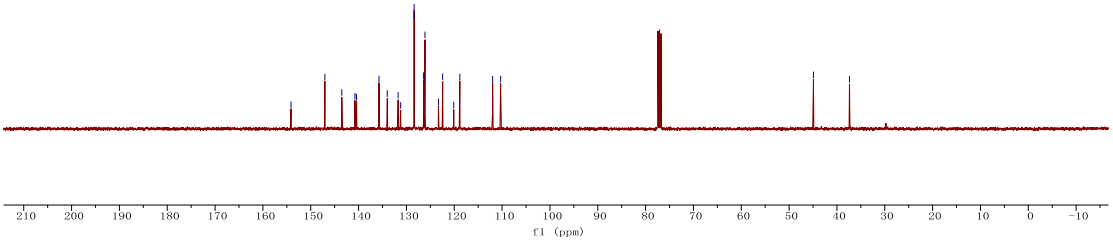
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

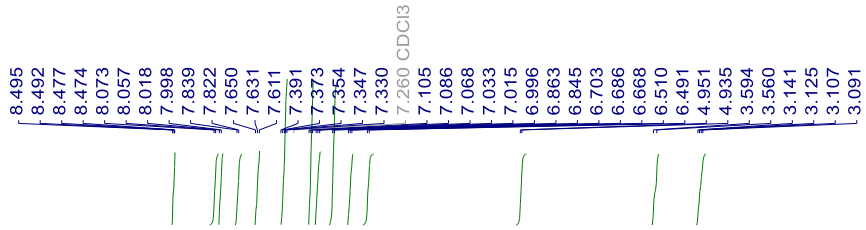


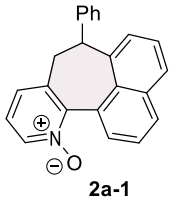


2aj

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

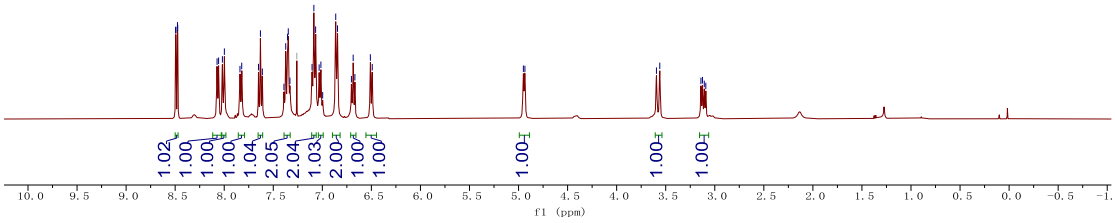


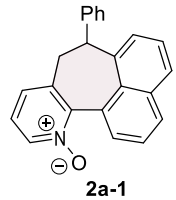




2a-1

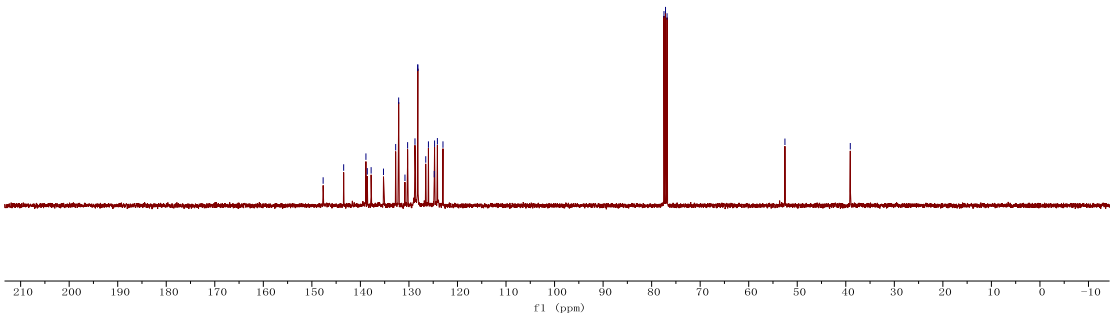
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

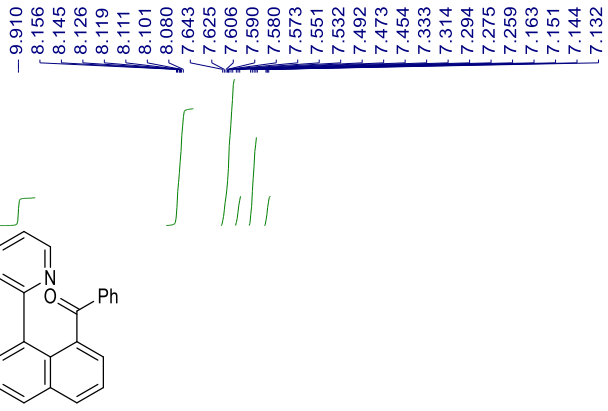




2a-1

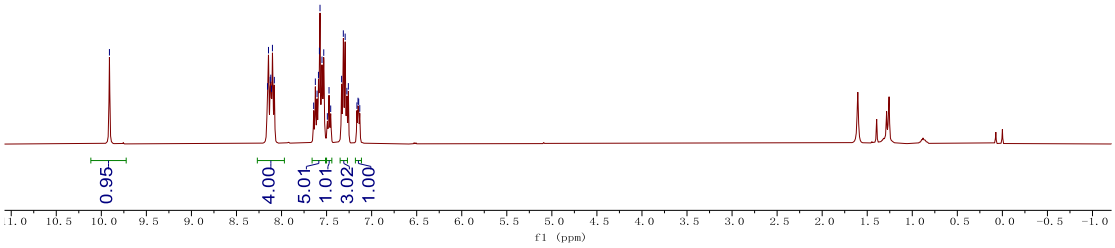
^{13}C NMR spectrum (101 MHz, $CDCl_3$)

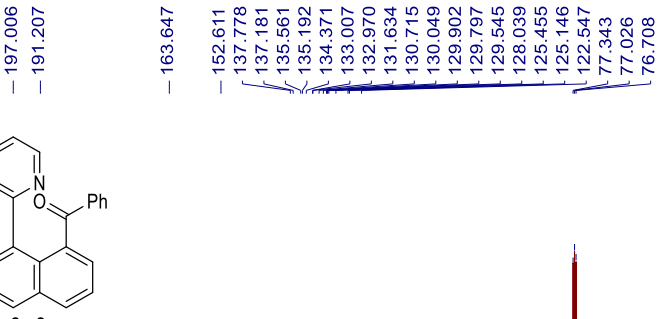




2a-2

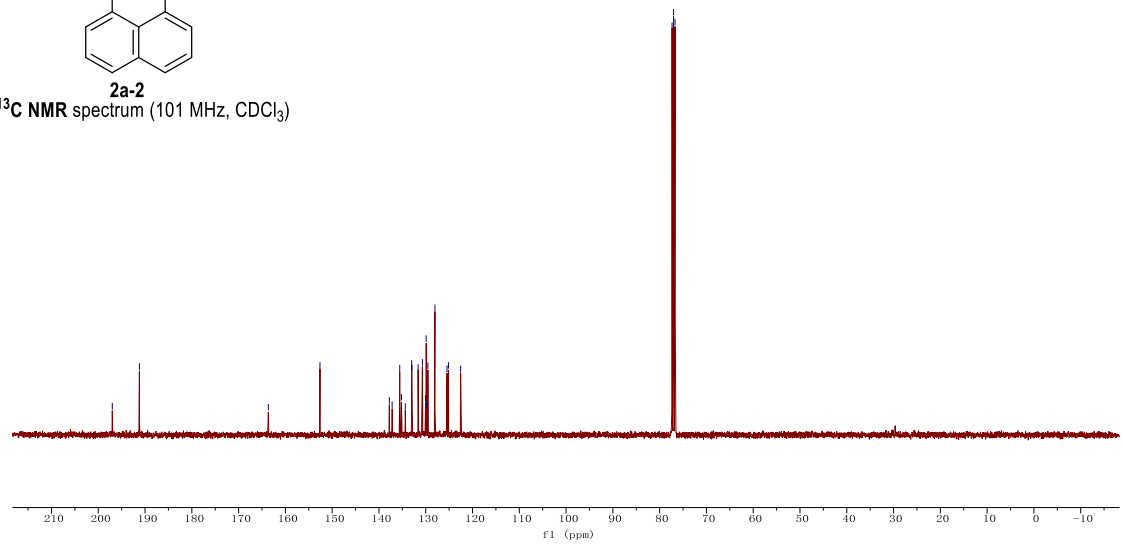
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

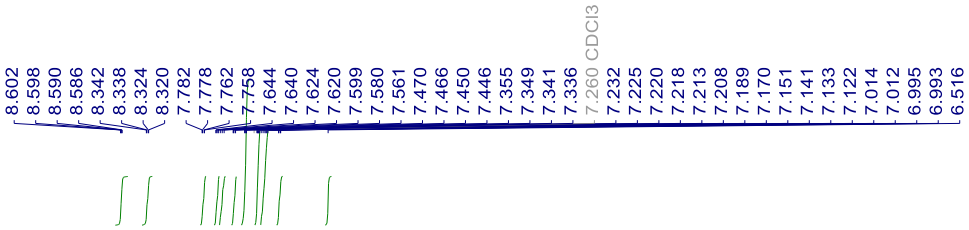


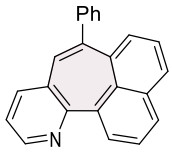


2a-2

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

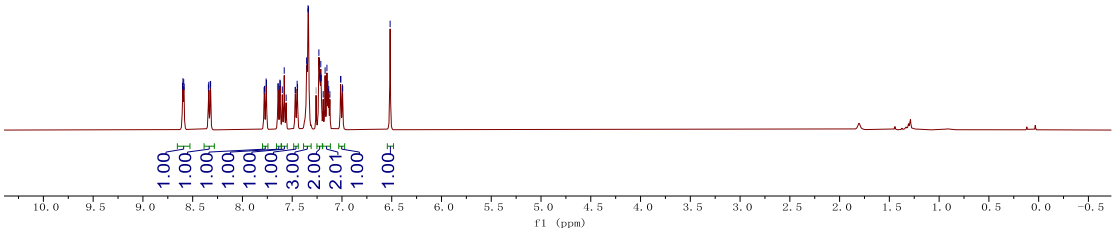


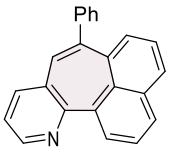




3a

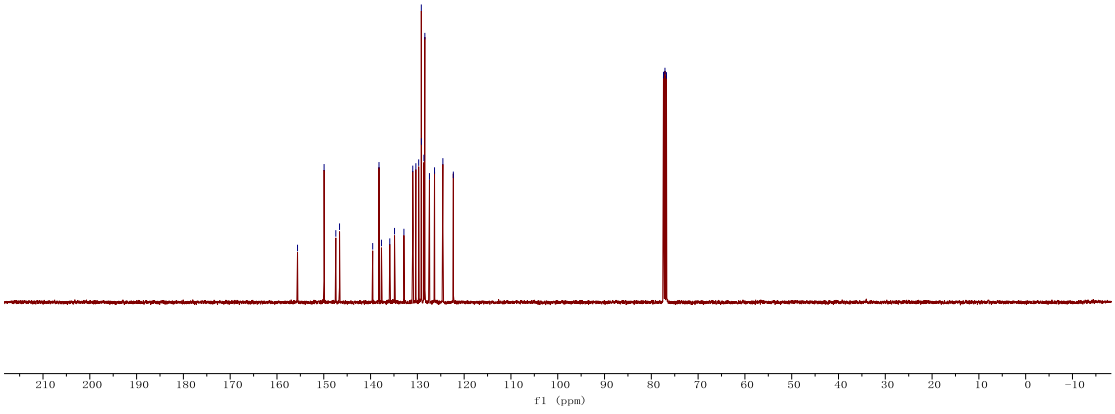
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

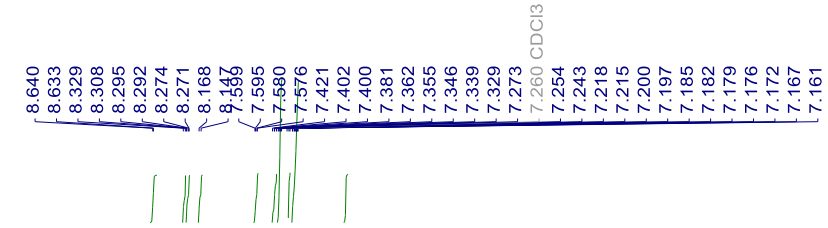


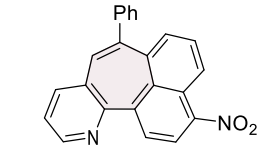


3a

^{13}C NMR spectrum (101 MHz, $CDCl_3$)

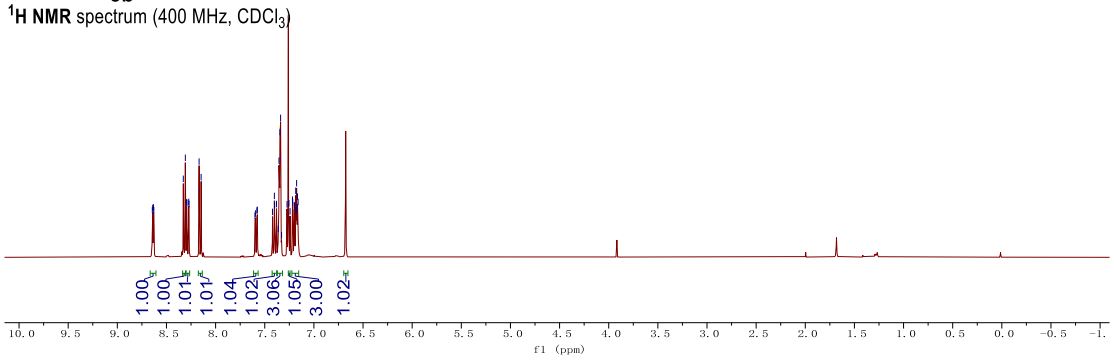


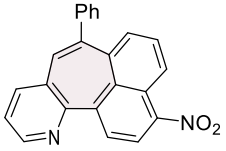




3b

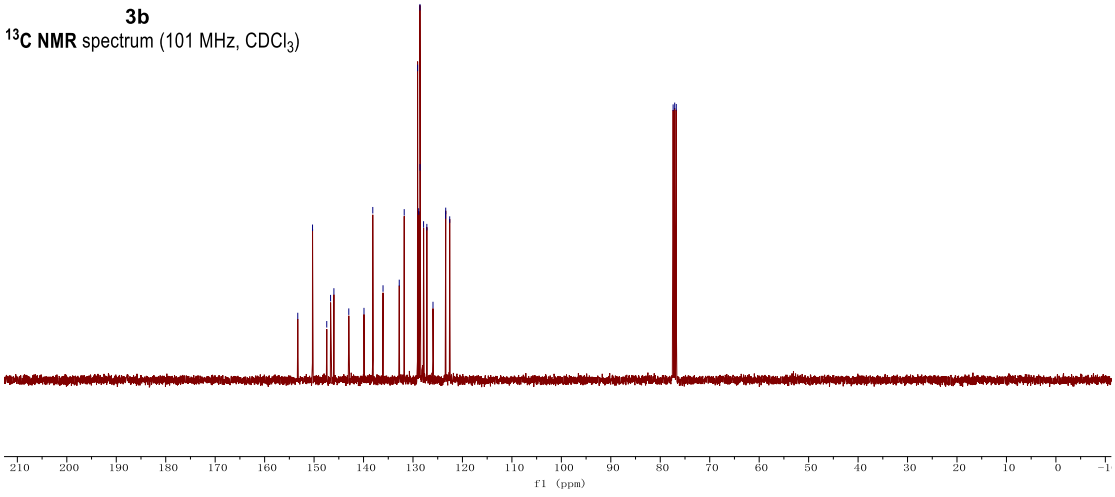
^{1}H NMR spectrum (400 MHz, $CDCl_3$)

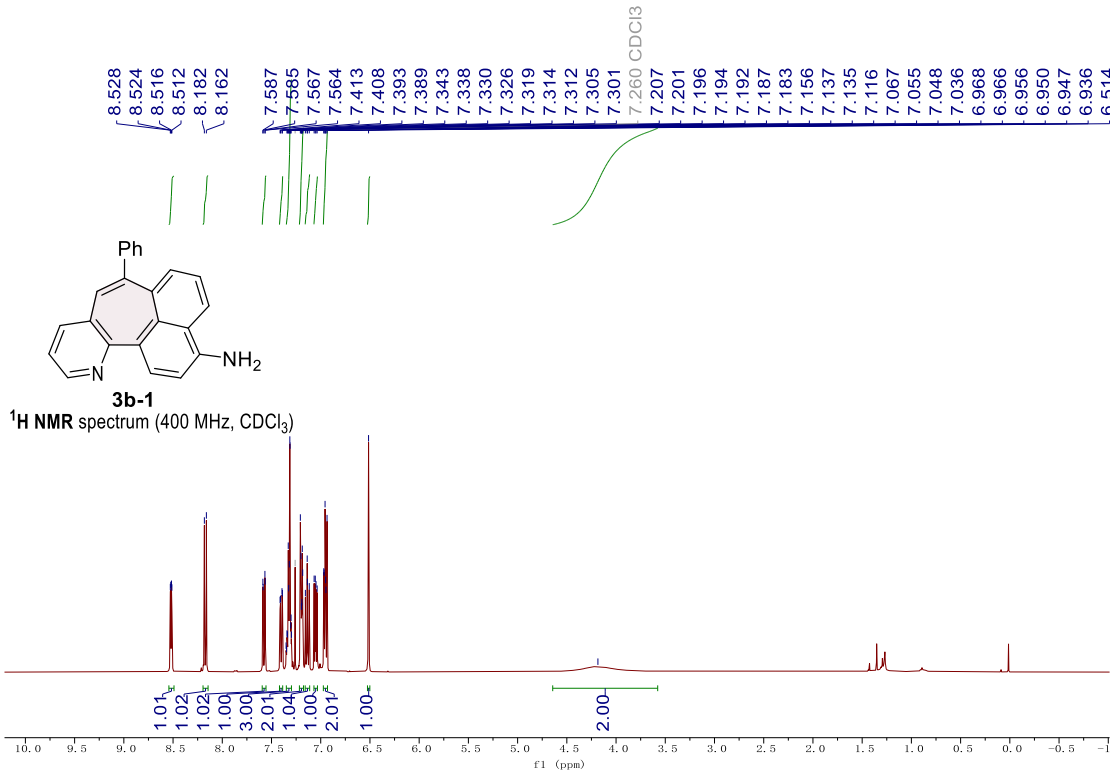




3b

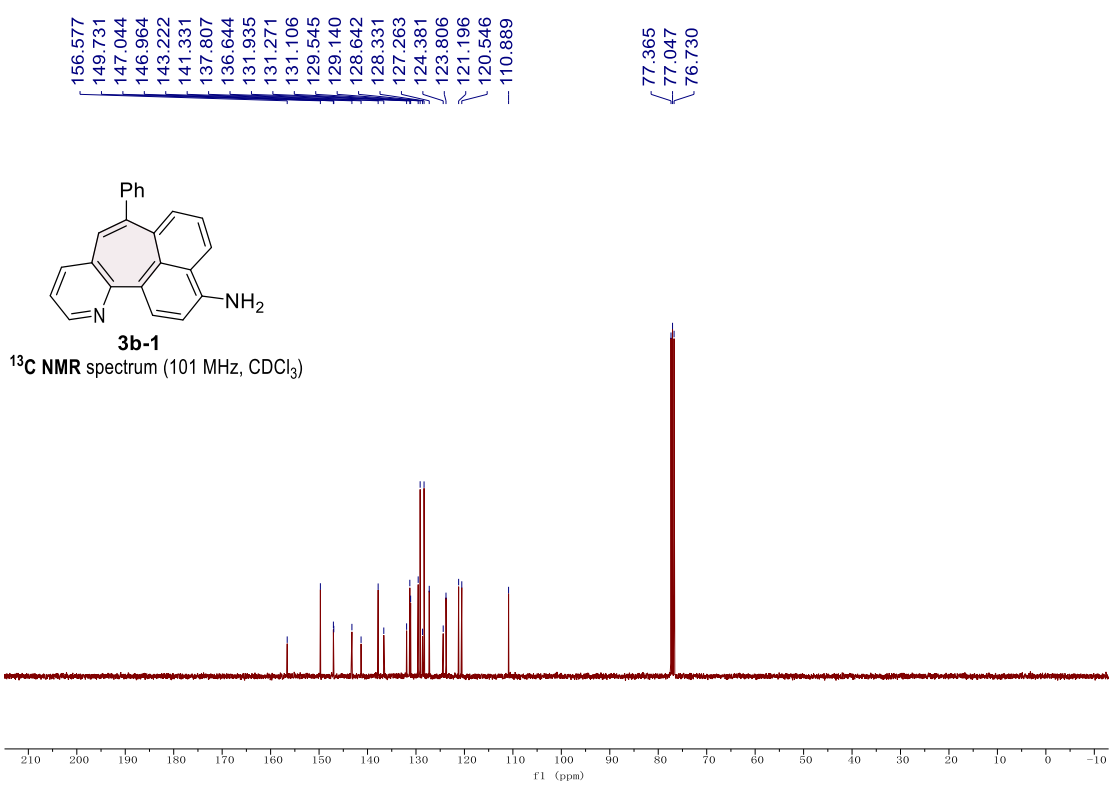
^{13}C NMR spectrum (101 MHz, $CDCl_3$)





3b-1

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



3b-1

^{13}C NMR spectrum (101 MHz, $CDCl_3$)