Supporting Information

Visible Light-induced Reductive Aza-6π Electrocyclization Access to 6-Substituted Phenanthridines

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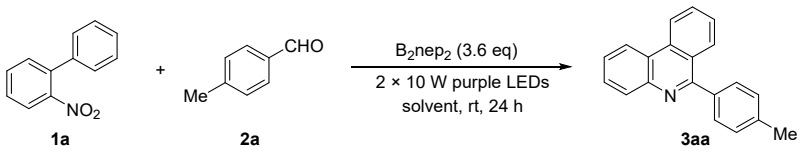
1. General information

General Methods. ^{1}H NMR spectra were recorded on 500 MHz spectrophotometers. Chemical shifts (δ) are reported in ppm from the resonance of tetramethyl silane as the internal standard (TMS: 0.00 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), coupling constants (Hz) and integration. All NMR spectra were recorded on a Bruker spectrometer at 500 MHz (^{1}H NMR), 125 MHz (^{13}C NMR) and 500 MHz (^{19}F NMR). HRMS was recorded on Bruker micrOTOF II ESI-TOF. All air- and moisture-sensitive reactions were performed under an atmosphere of Nitrogen in fire dried glassware. Flash column chromatography was performed using 200-300 mesh silica gel. The heat source used in all heating reactions are oil bath. Unless otherwise noted, all reagents and solvents were obtained from commercial sources. Phenanthridine **3aa**[1], **3ab**[2], **3ac**[3], **3ad**[4], **3ae**[5], **3af**[3], **3ag**[6], **3ai**[6], **3aj**[3], **3ak**[7], **3an**[1], **3ao**[8], **3ap**[9], **3aq**[10], **3ar**[5], **3as**[11], **3ba**[12], **3da**[13], were known compounds, and their spectral data matched literature values. The wavelength of purple LEDs chosen in the manuscript is 385 nm

2. Experimental section of phenanthridines construction

2.1 Optimization of reaction conditions

Table S1. Screening of solvents[a]

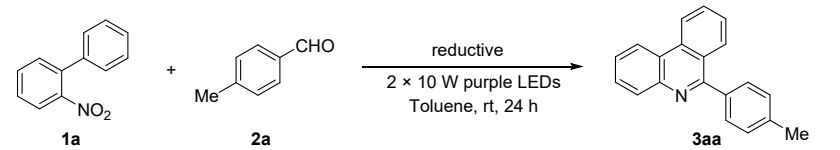


1a 2a 3aa

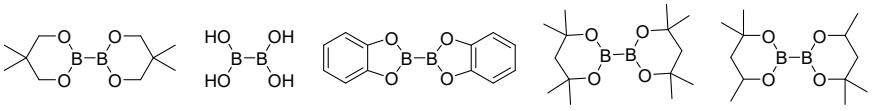
Entry	solvent	Yield of **3aa** (%)[b]
1	EtOH	52
2	CH_3CN	43
3	THF	N.R.
4	Toluene	63
5	DCE	26
6	PhCl	40
7	EA	41
8	HFIP	trace
9	Dioxane	N.R.
10	H_2O	trace
11	IPA	49

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.2 eq, 0.24 mmol, 28.8 mg) and B1 (3.6 eq, 0.72 mmol, 162.8 mg) were added in solvent (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S2. Screening of reductants[a]



1a 2a 3aa



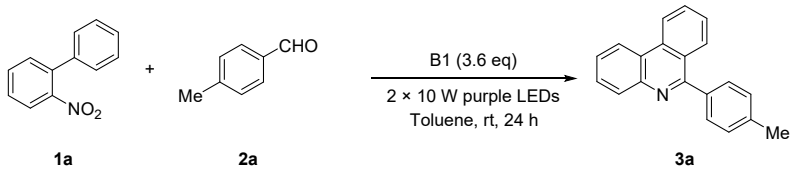
B1 B2 B3 B4 B5

Entry	reductants	Yield of **3aa** (%)[b]
1	B1	63
2	B2	N.R.
3	B3	N.R.
4	B4	56
5	B5	45

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.2 eq, 0.24 mmol, 28.8 mg) and reductive

(3.6 eq, 0.72 mmol, 162.8 mg) were added in Toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S3. Screening of aldehyde and nitroarenes ratios and equivalent of B1[a]

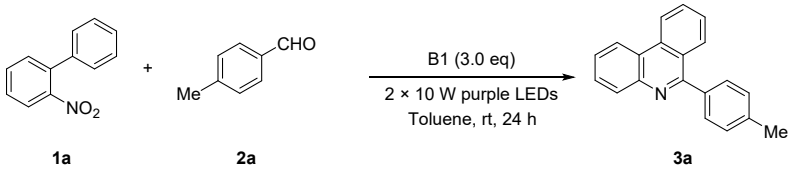


1a **2a** **3a**

Entry	**1a** (x eq)	**2a** (y eq)	B1 (z eq)	Yield of **3aa** (%)[b]
1	1	1	3.6	56
2	1	1.2	3.6	63
3	1	1.5	3.6	71
4	1	2.0	3.6	71
5	1	1.5	2	52
6	1	1.5	3	78

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.2 eq, 0.24 mmol, 28.8 mg) and B1 (3.6 eq, 0.72 mmol, 162.8 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S4. Screening of light sources[a]

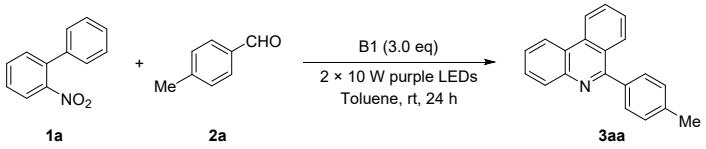


1a **2a** **3a**

Entry	light source	Yield of **3aa** (%)[b]
1	2 × 10 W purple LEDs	78
2	2 × 3 W purple LEDs	20
3	2 × 3 W blue LEDs	N.R.
4	2 × 3 W green LEDs	N.R.

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.5 eq, 0.3 mmol, 36.0 mg) and B1 (3.0 eq, 0.6 mmol, 135.7 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S5. Screening of the concentration of the reaction solution[a]

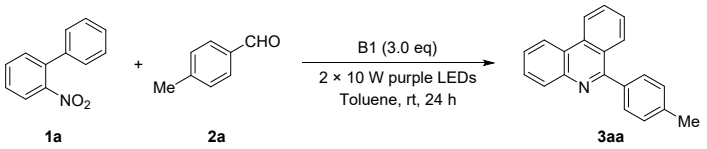


1a 2a 3aa

Entry	**Toluene (x mL)**	Yield of **3aa** (%)[b]
1	1.0	/
2	1.5	/
3	2.0	78
4	3.0	78
5	4.0	79

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.5 eq, 0.3 mmol, 36.0 mg) and B1 (3.0 eq, 0.6 mmol, 135.7 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S6. Control experiment[a]

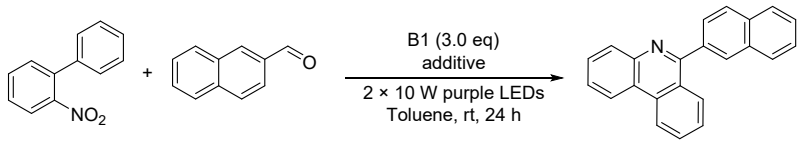


1a 2a 3aa

Entry	Deviation from the standard conditions	Yield of **3aa** (%)[b]
1	dark	N.R.
2	N_2	75
3	air	78

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2a** (1.5 eq, 0.3 mmol, 36.0 mg) and B1 (3.0 eq, 0.6 mmol, 135.7 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S7. Screening of additives[a]

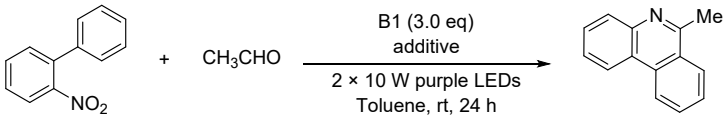


1a 2n 3an

Entry	Additive	Equivalent	Yield of **3an** (%)[b]
1	/	/	27
2	CF_3SO_3H	0.2	trace
3	$MeSO_3H$	0.2	trace
4	CF_3COOH	0.2	66
5	PhCOOH	0.2	25
6	C_6F_5COOH	0.2	44
7	PivOH	0.2	58
8	HFIP	2.0	75
9	4CzIPN	0.01	26
10	Mes-Acr^+ ClO_4^-	0.01	20
11	$(Ir[dF(CF_3)ppy]_2(dtbpy))PF_6$	0.01	18
12	Eosin Y	0.01	16
13	$[Ru(bpy)_3]Cl_2$	0.01	14

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2n** (1.5 eq, 0.3 mmol, 46.8 mg) and B1 (3.0 eq , 0.6mmol, 135.7 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

Table S8. Screening of additives when the aldehyde is 3 equivalent[a]



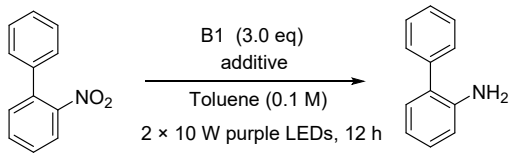
1a 2r 3ar

Entry	Additive	Equivalent (eq)	Yield of **3ar** (%)[b]
1	/	/	15
2	HFIP	2.0	21
3	4CzIPN	0.01	46

[a]A mixture of **1a** (1.0 eq, 0.2 mmol, 39.8 mg), **2r** (3.0 eq, 0.6 mmol, 26.4 mg) and B1 (3.0 eq, 0.6 mmol, 135.7 mg) were added in toluene (2.0 mL, 0.1 M) and stirred at rt for 24 h under irradiation of 2 ×10 W LEDs. [b]isolted yields.

In order to explain the role of HFIP in the reaction, we performed control experiments in the absence of nitroaromatics

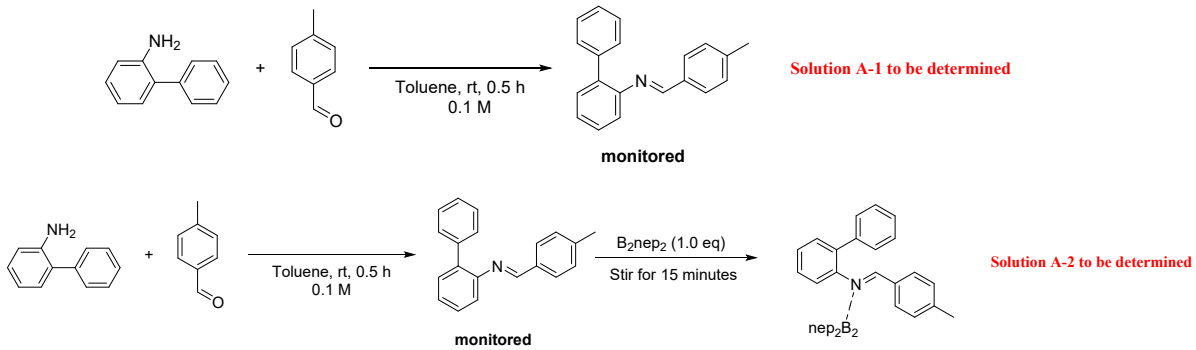
Table S9. Control experiments



2a **I**

Entry	Additive	Yield of **I**	Time
1	/	50%	12 h
2	4CZIPN (1 mol%)	52%	12 h
3	HFIP (3.0 eq)	80%	12 h
4	HFIP (3.0 eq)	76%	6 h

In order to test whether B-reactants, in addition to acting as a reducing agent, acts as a Lewis acid ligated with imine to assist in the completion of the subsequent electrocyclisation, we carried out the following experiments.



Scheme S1 Stepwise synthesis.

When a large amount of imine generation was monitored in reaction solution 1, UV

absorption experiments were performed. Similar to **A-1**, UV-visible absorption experiments were carried out after the addition of B_2nep_2 and continuous stirring for 15 min following the detection of large amounts of imine formation in reaction **A-2**. As shown in Fig. S1

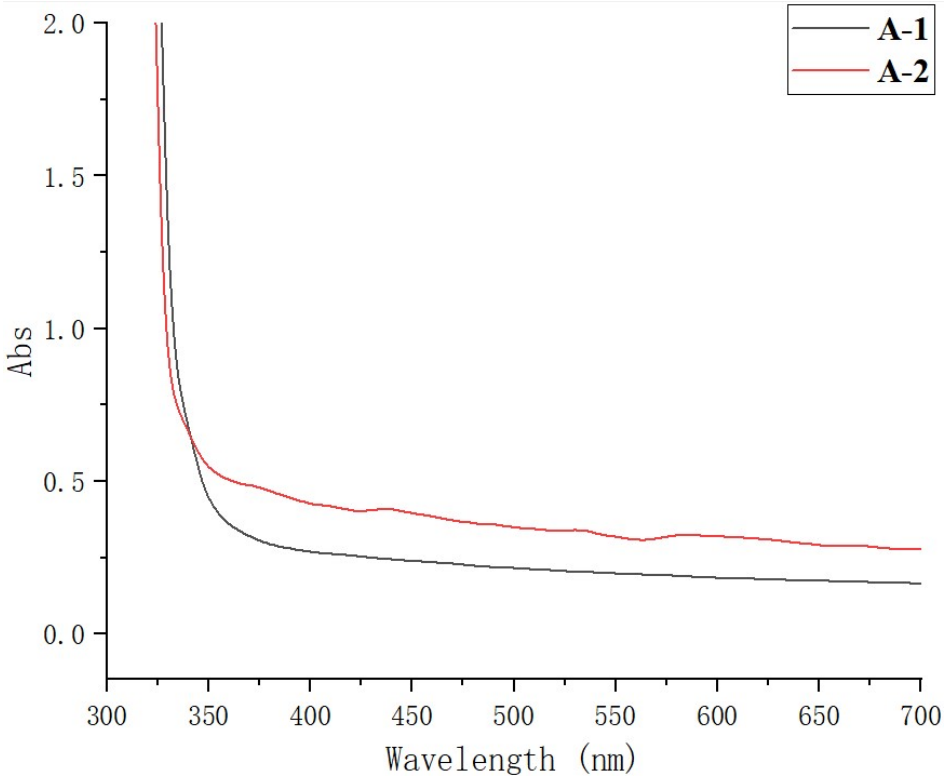


Fig. S1 UV absorption spectra

It can be seen in the figure that the UV absorption in the reaction solution was weakly enhanced at 380 nm under the condition of B_2nep_2 addition, which indicated that B_2nep_2 not only acted as a reducing agent, but also acted as a Lewis acid ligated with imine to assist the subsequent electrocyclisation reaction.

2.2 General procedures and characterization

General procedure A

In a dry Schlenk tube, a mixture of 2-nitrobiphenyl (1.0 eq , 0.2 mmol, 39.8 mg), benzaldehyde (1.5 eq, 0.3 mmol, 36.0 mg) and B1 (3.0 eq, 0.6 mmol, 135.7 mg) in toluene (2.0 mL), was stirred under 2 × 10 W purple LEDs for 24 hours until the 2-nitrobiphenyl was consumed completely, which was determined by TLC analysis. The residue was purified by column chromatography on silica gel to afford the desired

product.

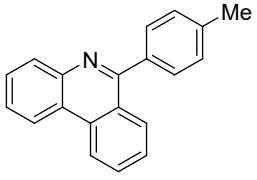
General procedure B

In a dry Schlenk tube, a mixture of 2-nitrobiphenyl (1.0 eq, 0.2 mmol, 39.8 mg), benzaldehyde (1.5 eq, 0.3 mmol, 36.0 mg), B1 (3.0 eq , 0.6 mmol, 135.7 mg) and HFIP (2.0 eq, 0.4 mmol, 67.2 mg) in toluene (2.0 mL), was stirred under 2 × 10 W purple LEDs for 24 hours until the 2-nitrobiphenyl was consumed completely, which was determined by TLC analysis. The residue was purified by column chromatography on silica gel to afford the desired product.

General procedure C

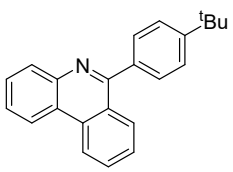
In a dry Schlenk tube, a mixture of 2-nitrobiphenyl (1.0 eq, 0.2 mmol, 39.8 mg), benzaldehyde (3.0 eq, 0.6 mmol, 36.0 mg), B1 (3.0 eq, 0.6 mmol, 135.7 mg) and 4CzIPN (1 mol%) in toluene (2.0 mL), was stirred under 2 × 10 W purple LEDs for 24 hours until the 2-nitrobiphenyl was consumed completely, which was determined by TLC analysis. The residue was purified by column chromatography on silica gel to afford the desired product.

6-(*p*-Tolyl)phenanthridine (3aa)[1]



According to **procedure A**. Light yellow solid, 78% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.2 Hz, 1H), 7.88 – 7.82 (m, 1H), 7.78 – 7.73 (m, 1H), 7.67 (dd, *J* = 19.9, 8.0 Hz, 3H), 7.63 – 7.59 (m, 1H), 7.38 (d, *J* = 7.6 Hz, 2H), 2.49 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.3, 143.9, 138.6, 137.0, 133.5, 130.5, 130.4, 129.7, 129.1, 129.0, 128.8, 127.1, 126.8, 125.4, 123.7, 122.2, 121.9, 21.4.

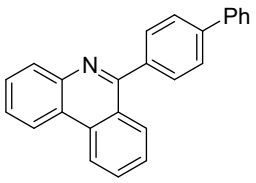
6-(4-(*tert*-Butyl)phenyl)phenanthridine (3ab)[2]



According to **procedure A**. Yellow solid, 62% yield. **^{1}H NMR**

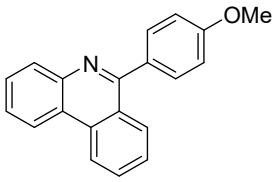
(500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.20 (d, *J* = 8.4 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.5 Hz, 1H), 7.72 – 7.66 (m, 3H), 7.65 – 7.56 (m, 3H), 1.42 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 151.8, 143.9, 136.9, 133.5, 130.5, 130.4, 129.5, 129.1, 128.8, 127.1, 126.8, 125.4, 125.3, 123.7, 122.2, 121.9, 34.8, 31.4.

6-([1,1'-Biphenyl]-4-yl)phenanthridine (3ac)[3]



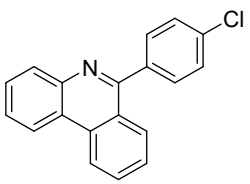
According to **procedure A**. White solid, 65% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.29 (d, *J* = 8.2 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.76 (m, 6H), 7.72 (d, *J* = 7.6 Hz, 3H), 7.65 (t, *J* = 7.7 Hz, 1H), 7.51 (t, *J* = 7.6 Hz, 2H), 7.41 (t, *J* = 7.4 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 143.9, 141.7, 140.9, 138.8, 133.5, 130.6, 130.4, 130.3, 128.9, 128.9, 127.6, 127.3, 127.3, 127.2, 127.0, 125.3, 123.8, 122.3, 122.0.

6-(4-Methoxyphenyl)phenanthridine (3ad)[4]



According to **procedure A**. Light yellow solid, 78% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, J = 8.3 Hz, 1H), 8.60 (d, J = 8.2 Hz, 1H), 8.24 (d, J = 8.2 Hz, 1H), 8.17 (d, J = 8.3 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.78 – 7.70 (m, 3H), 7.67 (t, J = 7.6 Hz, 1H), 7.62 (t, J = 7.6 Hz, 1H), 7.10 (d, J = 8.6 Hz, 2H), 3.92 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.9, 160.2, 143.9, 133.5, 132.3, 131.2, 130.5, 130.3, 129.0, 128.8, 127.1, 126.8, 125.4, 123.6, 122.2, 121.9, 113.9, 55.5.

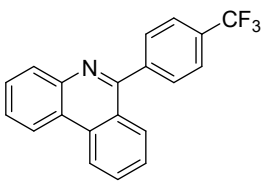
6-(4-Chlorophenyl)phenanthridine (3ae)[5]



According to **procedure A**. White solid, 52% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.3 Hz, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 7.6 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.70 (d, *J* = 8.1 Hz, 3H), 7.63 (t, *J* = 7.7 Hz, 1H), 7.55 (d, *J* = 8.1 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 143.7, 138.2, 134.9, 133.5, 131.2, 130.7, 130.4, 129.0, 128.7, 128.5, 127.3, 127.2,

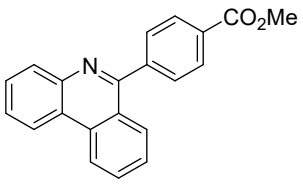
125.0, 123.8, 122.4, 122.0.

6-(4-(Trifluoromethyl)phenyl)phenanthridine (3af)[3]



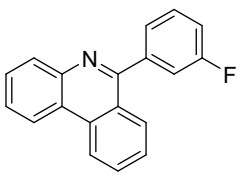
According to **procedure A**. White solid, 51% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.03 (d, *J* = 8.6 Hz, 1H), 7.93 – 7.81 (m, 5H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.65 (t, *J* = 7.6 Hz, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -62.58. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.7, 143.7, 143.4, 133.5, 130.85 (q, *J* = 32.8 Hz), 130.42, 130.18, 129.09, 128.34, 127.41, 125.47 (q, *J* = 3.8 Hz), 124.91 (q, *J* = 272.7 Hz), 122.43, 122.04.

Methyl 4-(phenanthridin-6-yl)benzoate (3ag)[6]



According to **procedure B**. Light yellow solid, 40% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.74 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.1 Hz, 1H), 8.27 (dd, *J* = 14.6, 8.0 Hz, 3H), 8.04 (d, *J* = 8.2 Hz, 1H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.83 (d, *J* = 7.9 Hz, 2H), 7.79 (t, *J* = 7.5 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.7 Hz, 1H), 3.99 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.9, 160.2, 144.3, 143.7, 133.5, 130.8, 130.4, 130.3, 129.9, 129.7, 129.0, 128.5, 127.3, 127.3, 125.0, 123.9, 122.4, 122.0, 52.3.

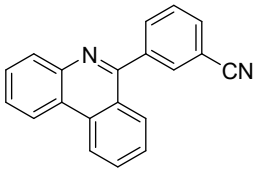
6-(3-Fluorophenyl)phenanthridine (3ah)



According to **procedure A**. White solid, 59% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.2 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.71 (t, *J* = 7.6 Hz, 1H), 7.64 (t, *J* = 7.6 Hz, 1H), 7.57 – 7.51 (m, 2H), 7.48 (dd, *J* = 9.5, 2.6 Hz, 1H), 7.26 – 7.21 (m, 1H). **^{19}F NMR** (471 MHz, $CDCl_3$) δ -112.80. **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.8 (d, *J* = 246.8 Hz), 159.8 (d, *J* = 2.3 Hz), 143.6, 141.9 (d, *J* = 7.3 Hz), 133.5, 130.8, 130.4, 130.1 (d, *J* = 8.2 Hz), 129.0, 128.6, 127.3 (d, *J* = 8.9 Hz), 125.6 (d, *J* = 3.0 Hz), 125.0, 123.9, 122.3, 122.0, 116.9 (d, *J* = 22.3 Hz), 115.7 (d, *J* = 21.0 Hz).**HRMS** (ESI) m/z:

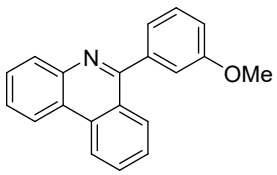
$[M+H]^+$ calcd for $C_{19}H_{12}FN$ 274.1027, found 274.1024.

3-(Phenanthridin-6-yl)benzonitrile (3ai)[6]



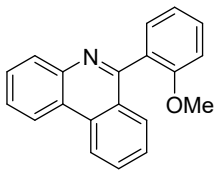
According to **procedure A**. White solid, 55% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.2 Hz, 1H), 8.23 (d, *J* = 8.4 Hz, 1H), 8.08 (s, 1H), 8.04 – 7.96 (m, 2H), 7.94 – 7.89 (m, 1H), 7.85 – 7.77 (m, 2H), 7.77 – 7.72 (m, 1H), 7.68 (dt, *J* = 10.6, 7.4 Hz, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.6, 143.6, 141.1, 134.2, 133.6, 133.4, 132.3, 131.0, 130.4, 129.4, 129.2, 128.0, 127.6, 127.5, 124.7, 123.9, 122.6, 122.1, 118.6, 112.9.

6-(3-Methoxyphenyl)phenanthridine (3aj)[3]



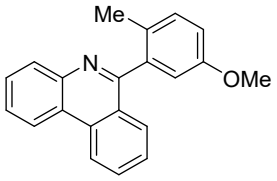
According to **procedure A**. Light yellow solid, 73% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 8.2 Hz, 1H), 8.29 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.77 (t, *J* = 7.6 Hz, 1H), 7.69 (t, *J* = 7.6 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 7.4 Hz, 2H), 7.09 (dd, *J* = 7.7, 2.2 Hz, 1H), 3.89 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 159.7, 143.4, 140.7, 133.5, 130.8, 130.2, 129.5, 129.1, 129.0, 127.2, 127.1, 125.2, 123.8, 122.3, 122.2, 122.0, 115.1, 114.9, 55.5.

6-(2-Methoxyphenyl)phenanthridine (3ak)[7]



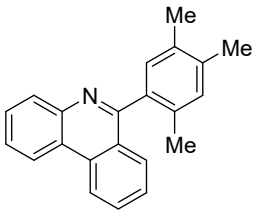
According to **procedure A**. Light yellow solid, 65% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.62 (d, *J* = 8.3 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 7.85 – 7.80 (m, 1H), 7.79 – 7.73 (m, 2H), 7.71 – 7.66 (m, 1H), 7.59 – 7.54 (m, 1H), 7.53 – 7.46 (m, 2H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.08 (d, *J* = 8.3 Hz, 1H), 3.69 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.0, 157.4, 144.0, 132.8, 130.9, 130.5, 130.4, 130.2, 129.0, 128.7, 127.1, 126.9, 126.9, 126.2, 124.1, 122.0, 121.9, 121.1, 111.2, 55.6.

6-(5-Methoxy-2-methylphenyl)phenanthridine (3al)



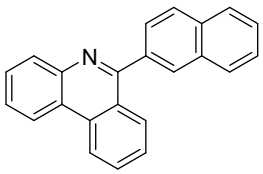
According to **procedure A**. Light yellow solid, 72% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.64 (d, *J* = 6.7 Hz, 1H), 8.27 (d, *J* = 8.1 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.80 – 7.69 (m, 3H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.27 (d, *J* = 9.6 Hz, 1H), 6.98 (d, *J* = 7.9 Hz, 2H), 3.82 (s, 3H), 2.03 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.8, 157.7, 143.8, 140.0, 133.0, 131.4, 130.7, 130.4, 128.9, 128.7, 128.5, 127.4, 127.0, 125.7, 123.9, 122.1, 122.0, 114.8, 114.4, 55.4, 18.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}NO$ 300.1383, found 300.1390.

6-(2,4,5-Trimethylphenyl)phenanthridine (3am)



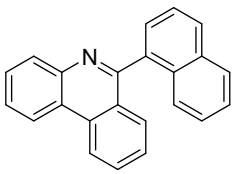
According to **procedure B**. Light yellow gum, 66% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.63 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.77 (d, *J* = 8.0 Hz, 2H), 7.70 (t, *J* = 7.9 Hz, 1H), 7.57 (t, *J* = 7.6 Hz, 1H), 7.19 (s, 1H), 7.14 (s, 1H), 2.35 (s, 3H), 2.30 (s, 3H), 2.05 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 162.3, 143.9, 136.8, 136.7, 133.9, 133.5, 133.0, 131.6, 130.6, 130.4, 130.4, 128.9, 128.8, 127.3, 126.8, 126.0, 123.8, 122.1, 122.0, 19.6, 19.3, 19.3. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}N$ 298.1590, found 298.1587.

6-(Naphthalen-2-yl)phenanthridine (3an)[1]



According to **procedure B**. White solid, 75% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.73 (d, *J* = 8.3 Hz, 1H), 8.65 (d, *J* = 8.3 Hz, 1H), 8.30 (d, *J* = 8.2 Hz, 1H), 8.25 (s, 1H), 8.17 (d, *J* = 8.2 Hz, 1H), 8.05 (d, *J* = 8.3 Hz, 1H), 8.00 – 7.93 (m, 2H), 7.91 – 7.84 (m, 2H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.72 (t, *J* = 7.6 Hz, 1H), 7.64 – 7.55 (m, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.2, 143.9, 137.3, 133.5, 133.4, 133.3, 130.6, 130.4, 129.3, 129.0, 128.9, 128.5, 128.1, 127.8, 127.4, 127.2, 127.0, 126.6, 126.5, 125.4, 123.8, 122.3, 122.0.

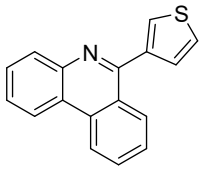
6-(Naphthalen-1-yl)phenanthridine (3ao)[8]



According to **procedure B**. White solid, 71% yield. **^{1}H NMR** (500

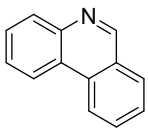
MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.70 (d, *J* = 8.2 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.03 (dd, *J* = 7.2, 2.4 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.83 – 7.79 (m, 1H), 7.78 – 7.73 (m, 1H), 7.70 – 7.63 (m, 3H), 7.52 – 7.46 (m, 2H), 7.44 (d, *J* = 8.5 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 143.8, 137.1, 133.8, 133.1, 132.3, 130.9, 130.4, 129.2, 129.1, 129.0, 128.9, 128.3, 127.4, 127.3, 127.2, 126.6, 126.4, 126.1, 126.0, 125.4, 124.0, 122.1.

6-(Thiophen-3-yl)phenanthridine (3ap)[9]



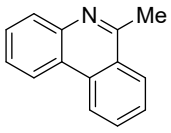
According to **procedure B**. Yellow gum, 54% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.60 (d, *J* = 6.9 Hz, 1H), 8.30 (d, *J* = 7.1 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.0 Hz, 1H), 7.80 – 7.73 (m, 2H), 7.67 (dt, *J* = 13.1, 7.5 Hz, 2H), 7.59 (d, *J* = 4.9 Hz, 1H), 7.52 (dd, *J* = 5.0, 3.0 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 156.5, 143.9, 140.9, 133. 4, 130.6, 130.3, 129.3, 128.9, 128.5, 127.3, 127.0, 126.4, 125.8, 125.5, 123.7, 122.2, 122.0.

Phenanthridine (3aq)[10]



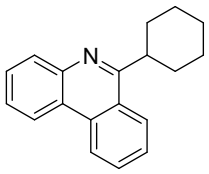
According to **procedure C**. White solid, 33% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.29 (s, 1H), 8.60 (dd, *J* = 15.1, 8.2 Hz, 2H), 8.20 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.87 (t, *J* = 7.7 Hz, 1H), 7.78 – 7.67 (m, 3H). **^{13}C NMR** (12 6 MHz, $CDCl_3$) δ 153.6, 144.5, 132.6, 131.0, 130.2, 128.8, 128.7, 127.5, 127.1, 126.4, 124.1, 122.2, 121.9.

6-Methylphenanthridine (3ar)[5]



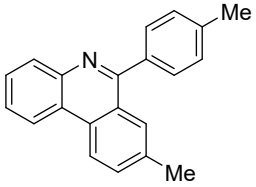
According to **procedure C**. Light yellow solid, 45% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.22 (d, *J* = 8.2 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.81 (m, 1H), 7.74 – 7.67 (m, 2H), 7.62 (t, *J* = 7.6 Hz, 1H), 3.05 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 158.9, 143.7, 132.6, 130.5, 129.4, 128.7, 127.3, 126.6, 126.4, 126.0, 123.8, 122.3, 122.0, 23.4.

6-Cyclohexylphenanthridine (3as)[11]



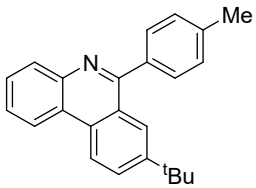
According to **procedure C**. Yellow gum, 41% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.66 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.32 (d, *J* = 8.3 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.69 (q, *J* = 7.0 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 3.62 (t, *J* = 11.4 Hz, 1H), 2.08 (d, *J* = 12.0 Hz, 2H), 2.01 – 1.91 (m, 4H), 1.85 (d, *J* = 12.7 Hz, 1H), 1.57 (t, *J* = 12.8 Hz, 2H), 1.45 (t, *J* = 12.8 Hz, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 165.3, 143.9, 133.0, 130.0, 129.9, 128.4, 127.1, 126.1, 125.6, 124.8, 123.4, 122.6, 121.8, 42.0, 32.3, 26.9, 26.3.

8-Methyl-6-(p-tolyl)phenanthridine (3ba)[12]



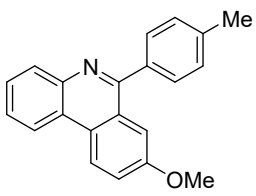
According to **procedure B**. Light yellow gum, 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 – 8.55 (m, 2H), 8.23 (d, *J* = 8.2 Hz, 1H), 7.91 (s, 1H), 7.75 – 7.70 (m, 1H), 7.66 (dd, *J* = 13.8, 8.3 Hz, 4H), 7.39 (d, *J* = 7.6 Hz, 2H), 2.51 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 143.6, 138.5, 137.1, 137.1, 132.2, 131.3, 130.3, 129.7, 129.1, 128.3, 128.3, 126.7, 125.5, 123.8, 122.1, 121.8, 21.8, 21.4.

8-(*tert*-Butyl)-6-(p-tolyl)phenanthridine (3ca)



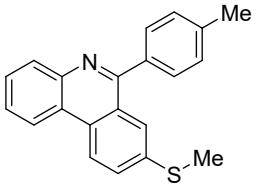
According to **procedure B**. Light yellow solid, 43% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.7 Hz, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.18 (d, *J* = 2.0 Hz, 1H), 7.94 (dd, *J* = 8.7, 2.0 Hz, 1H), 7.75 – 7.63 (m, 4H), 7.39 (d, *J* = 7.5 Hz, 2H), 2.50 (s, 3H), 1.39 (s, 9H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.4, 150.1, 143.7, 138.6, 137.0, 131.4, 130.2, 129.8, 129.1, 128.8, 128.4, 126.7, 125.2, 124.7, 123.7, 122.1, 121.8, 35.1, 31.3, 21.5. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{23}N$ 326.1903, found 326.1911.

8-Methoxy-6-(*p*-tolyl)phenanthridine (3da)[13]



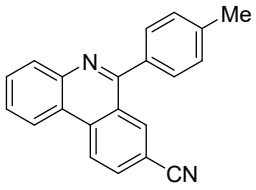
According to **procedure B**. Light yellow solid, 58% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.61 (d, *J* = 9.0 Hz, 1H), 8.52 (d, *J* = 7.8 Hz, 1H), 8.21 (d, *J* = 8.3 Hz, 1H), 7.68 (dd, *J* = 19.2, 7.4 Hz, 4H), 7.53 – 7.46 (m, 2H), 7.37 (d, *J* = 7.6 Hz, 2H), 3.84 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5, 158.5, 143.1, 138.6, 137.0, 130.3, 129.5, 129.2, 127.9, 127.8, 126.9, 126.7, 123.9, 123.8, 121.4, 121.0, 109.1, 55.5, 21.4.

8-(Methylthio)-6-(*p*-tolyl)phenanthridine (3ea)



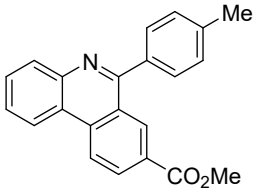
According to **procedure B**. Light yellow gum, 20% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.7 Hz, 1H), 8.54 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.95 (d, *J* = 2.0 Hz, 1H), 7.75 – 7.70 (m, 2H), 7.68 – 7.62 (m, 3H), 7.37 (d, *J* = 7.7 Hz, 2H), 2.50 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5, 143.6, 138.7, 138.1, 136.7, 130.9, 130.4, 129.6, 129.4, 129.2, 128.5, 127.0, 125.8, 125.1, 123.6, 122.7, 121.7, 21.4, 15.8. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{17}NS$ 316.1154, found 316.1166.

6-(*p*-Tolyl)phenanthridine-8-carbonitrile (3fa)



According to **procedure A**. White solid, 58% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.6 Hz, 1H), 8.59 (d, *J* = 8.2 Hz, 1H), 8.49 (d, *J* = 1.7 Hz, 1H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.01 (d, *J* = 8.3 Hz, 1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.74 (t, *J* = 7.0 Hz, 1H), 7.61 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 7.8 Hz, 2H), 2.51 (s, 3H).**^{13}C NMR** (126 MHz, $CDCl_3$) δ 160.5, 144.8, 139.5, 136.1, 135.6, 134.4, 131.7, 130.7, 130.6, 129.7, 129.5, 127.7, 124.8, 123.6, 122.5, 122.4, 118.6, 110.6, 21.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{21}H_{14}N_2$ 295.1230, found 295.1233.

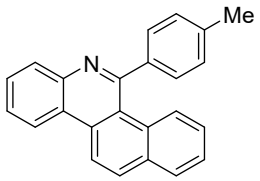
Methyl 6-(*p*-tolyl)phenanthridine-8-carboxylate (3ga)



According to **procedure A**. White solid, 53% yield. **^{1}H NMR**

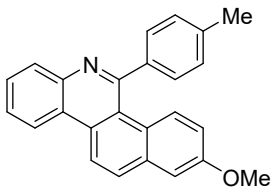
(500 MHz, $CDCl_3$) δ 8.86 (d, *J* = 1.7 Hz, 1H), 8.69 (d, *J* = 8.7 Hz, 1H), 8.58 (d, *J* = 8.2 Hz, 1H), 8.42 (dd, *J* = 8.6, 1.8 Hz, 1H), 8.24 (d, *J* = 6.7 Hz, 1H), 7.79 (t, *J* = 6.9 Hz, 1H), 7.69 (d, *J* = 6.9 Hz, 1H), 7.67 – 7.64 (m, 2H), 7.40 (d, *J* = 7.8 Hz, 2H), 3.94 (s, 3H), 2.50 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 166.6, 161.6, 144.7, 139.0, 136.5, 136.4, 131.2, 130.5, 130.2, 129.9, 129.8, 129.3, 128.6, 127.2, 124.7, 122.8, 122.6, 122.5, 52.4, 21.5. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{17}NO_2$ 328.1332, found 328.1345.

5-(*p*-Tolyl)benzo[i]phenanthridine (3ha)



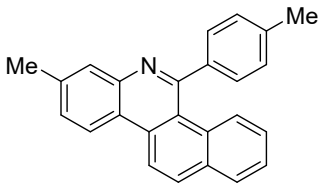
According to **procedure B**. Light yellow solid, 43% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.65 (dd, *J* = 8.7, 4.3 Hz, 2H), 8.27 (d, *J* = 8.2 Hz, 1H), 8.17 (d, *J* = 8.9 Hz, 1H), 7.94 (d, *J* = 8.1 Hz, 1H), 7.90 (d, *J* = 8.7 Hz, 1H), 7.81 – 7.76 (m, 1H), 7.72 – 7.67 (m, 1H), 7.53 (d, *J* = 8.1 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.32 (d, *J* = 7.8 Hz, 2H), 7.24 (t, *J* = 7.1 Hz, 1H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.4, 144.2, 141.8, 138.3, 134.3, 133.2, 132.3, 130.4, 130.0, 129.8, 129.0, 128.8, 128.4, 128.4, 126.7, 126.4, 125.8 123.6, 122.4, 121.5, 119.9, 21.5. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{24}H_{17}N$ 320.1434, found 320.1444.

2-Methoxy-5-(*p*-tolyl)benzo[i]phenanthridine (3la)



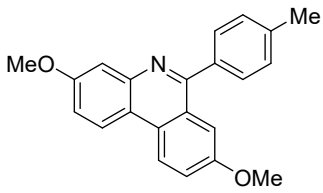
According to **procedure B**.Light yellow solid, 49% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.62 (t, *J* = 8.2 Hz, 2H), 8.25 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.9 Hz, 1H), 7.80 – 7.72 (m, 2H), 7.70 – 7.65 (m, 1H), 7.52 (d, *J* = 7.6 Hz, 2H), 7.31 (d, *J* = 7.6 Hz, 2H), 7.28 (d, *J* = 2.8 Hz, 1H), 6.88 (dd, *J* = 9.5, 2.8 Hz, 1H), 3.93 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 159.1, 157.7, 143.8, 141.8, 138.2, 134.9, 132.8, 131.5, 129.9, 129.9, 129.8, 128.8, 128.5, 126.7, 124.9, 123.7, 122.2, 121.8, 120.5, 116.8, 107.8, 55.3, 21.5. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}NO$ 350.1539, found 350.1549.

5-(*p*-Tolyl)benzo[i]phenanthridine (3ja)



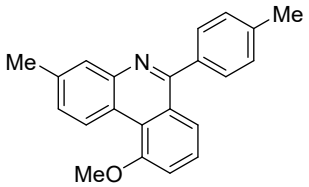
According to **procedure B**. Light yellow solid, 60% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.9 Hz, 1H), 8.51 (d, *J* = 8.5 Hz, 1H), 8.13 (d, *J* = 9.0 Hz, 1H), 8.07 (s, 1H), 7.91 (d, *J* = 8.0 Hz, 1H), 7.88 (d, *J* = 8.7 Hz, 1H), 7.54 – 7.46 (m, 4H), 7.31 (d, *J* = 7.8 Hz, 2H), 7.25 – 7.20 (m, 1H), 2.61 (s, 3H), 2.48 (s, 3H).13C NMR (126 MHz, CDCl3) δ 159.36, 144.25, 141.82, 139.24, 138.18, 134.40, 133.03, 132.19, 130.49, 129.72, 129.23, 128.82, 128.70, 128.40, 128.31, 126.16, 125.76, 122.21, 121.38, 121.07, 119.92, 21.63, 21.47. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{25}H_{19}N$ 334.1590, found 334.1581.

3,8-Dimethoxy-6-(*p*-tolyl)phenanthridine (3ka)



According to **procedure B**. Light yellow solid, 22% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 8.45 (d, *J* = 9.0 Hz, 1H), 8.36 (d, *J* = 9.1 Hz, 1H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.62 (d, *J* = 2.7 Hz, 1H), 7.46 (d, *J* = 2.6 Hz, 1H), 7.42 (dd, *J* = 9.0, 2.7 Hz, 1H), 7.37 (d, *J* = 7.8 Hz, 2H), 7.27 (dd, *J* = 8.9, 2.5 Hz, 1H), 3.96 (s, 3H), 3.81 (s, 3H), 2.48 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.0, 159.5, 157.6, 144.6, 138.5, 137.2, 129.5, 129.2, 128.2, 125.6, 123.3, 122.6, 121.3, 118.1, 117.9, 109.9, 108.8, 55. 6, 55.4, 21.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}NO_2$ 330.1489, found 330.1498.

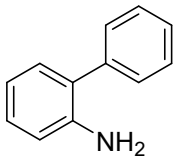
10-Methoxy-3-methyl-6-(*p*-tolyl)phenanthridine (3la)



According to **procedure B**. Near white solid, 35% yield. **^{1}H NMR** (500 MHz, $CDCl_3$) δ 9.40 (d, *J* = 8.7 Hz, 1H), 8.05 (s, 1H), 7.72 (d, *J* = 8.2 Hz, 1H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.53 – 7.46 (m, 2H), 7.35 (d, *J* = 7.7 Hz, 2H), 7.30 (d, *J* = 8.0 Hz, 1H), 4.16 (s, 3H), 2.59 (s, 3H), 2.47 (s, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 161.1, 158.0, 144.6, 138.3, 138.1, 137.7, 129.7, 129.6, 129.0, 128.3, 127.6, 127.3, 126.5,

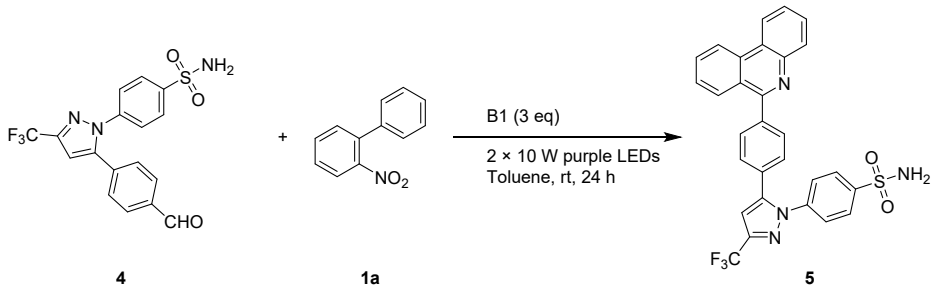
124.1, 121.5, 121.1, 111.4, 55.9, 21.4. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{22}H_{19}NO$ 314.1539, found 314.1548.

2-Aminobiphenyl (I)



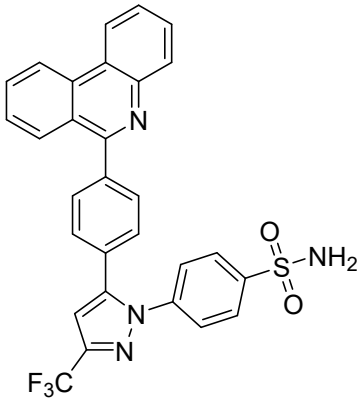
White solid, 80% yield. **^{1}H NMR** (500 MHz, Chloroform-d) δ 7.52 – 7.46 (m, 4H), 7.42 – 7.36 (m, 1H), 7.23 – 7.15 (m, 2H), 6.87 (td, J = 7.4, 1.2 Hz, 1H), 6.81 (dd, J = 7.9, 1.2 Hz, 1H), 3.77 (s, 2H). **^{13}C NMR** (126 MHz, $CDCl_3$) δ 143.53, 139.59, 130.46, 129.11, 128.81, 128.50, 127.68, 127.16, 118.65, 115.61. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{12}H_{11}N$ 170.0964, found 170.0967.

3. Modification of celecoxib



4 1a 5

4-(5-(4-(Phenanthridin-6-yl)phenyl)-3-(trifluoromethyl)-1H-pyrazol-1-yl)benzenesulfonamide (5)



According to **procedure A**. White solid, 61% yield. **^{1}H NMR** (500 MHz, DMSO-d6) δ 8.93 (d, *J* = 8.0 Hz, 1H), 8.83 (d, *J* = 8.3 Hz, 1H), 8.10 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.95 (dd, *J* = 15.6, 8.2 Hz, 4H), 7.80 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.77 – 7.72 (m, 4H), 7.69 – 7.64 (m, 2H), 7.53 (d, *J* = 8.2 Hz, 4H), 7.36 (s, 1H). **^{19}F NMR** (471 MHz, DMSO-d6) δ -60.81. **^{13}C NMR** (126 MHz, DMSO- d6) δ 159.99, 145.28, 144.64, 143.60, 142.83 (q, *J* = 37.9 Hz), 141.56, 140.52, 133.30, 130.20, 130.0 (q, *J* = 152.5 Hz), 129.66, 129.04, 128.33, 127.95, 127.45, 126.59, 124.66, 123.78, 123.41, 123.19, 121.78 (q, *J* = 268.4 Hz), 107.31. **HRMS** (ESI) m/z: $[M+H]^+$ calcd for $C_{29}H_{19}F_3N_4O_2S$ 545.1254, found 545.1249.

4. Reference

1, Kobayashi, E.; Kishi, A.; Togo, H. 6-Arylphenanthridines from Aryl *o*-Biaryl Ketones with 1, 1, 1, 3, 3, 3-Hexamethyldisilazane and Molecular Iodine. *Eur. J. Org. Chem*. **2019**, *2019*, 7335-7347.

2, Li, J.; Wang, H.; Sun, J.; Yang, Y.; Liu, L. Synthesis of phenanthridine derivatives via cascade annulation of diaryliodonium salts and nitriles. *Org. Biomol. Chem.* **2014**, *12*, 7904-7908.

3, Jaiswal, Y.; Kumar, Y.; Pal, J. Subramanian, R.; Kumar, A. Rapid Synthesis of Polysubstituted Phenanthridines from Simple Aliphatic/Aromatic Nitriles and Iodo Arenes via Pd(II) Catalyzed Domino C–C/C–C/C–N Bond Formation. *Chem. Comm*. **2018**, *54*, 7207-7210.

4, Lu, R.; Cao, L.; Guan, H.; Liu, L. Iron-catalyzed aerobic dehydrogenative kinetic resolution of cyclic secondary amines. *J. Am. Chem. Soc.* **2019**, *141*, 6318-6324.

5, Kishi, A.; Moriyama, K.; Togo, H. Preparation of phenanthridines from *o*-cyanobiaryls via addition of organic lithiums to nitriles and imino radical cyclization with iodine. *J. Org. Chem*. **2018**, *83*, 11080-11088.

6, Korotvička, A.; Frejka, D.; Hampejsová, Z.; Císařová, I.; Kotora, M. Synthesis of Phenanthridines via a Rhodium-Catalyzed C–C Bond Cleavage Reaction of Biphenylene with Nitriles. *Synthesis*. **2016**, *48*, 987-996.

7, Pawlas, J.; Begtrup, M. A one-pot access to 6-substituted phenanthridines from fluoroarenes and nitriles via 1, 2-arynes. *Org. Lett*. **2002**, *4*, 2687-2690.

8, Chen, Y.-F.; Hsieh, J.-C. Synthesis of Polysubstituted Phenanthridines via Ligand-Free Copper-Catalyzed Annulation. *Org. Lett*. **2014**, *16*, 4642-4645.

9, Ramanathan, M.; Liu, S.-T. Preparation of Substituted Phenanthridines from the Coupling of Aryldiazonium Salts with Nitriles: A Metal Free Approach. *J. Org. Chem*. **2015**, *80*, 5329-5336.

10, Kim, K. D.; Lee, J. H. Visible-Light Photocatalyzed Deoxygenation of N-Heterocyclic N-Oxides. *Org. Lett*. **2018**, *20*, 7712-7716.

11, Huang, C.; Wang, J.-H. Qiao, J.; Fan, X.-W.; Chen, B.; Tung, C.-H.; Wu, L.-Z.

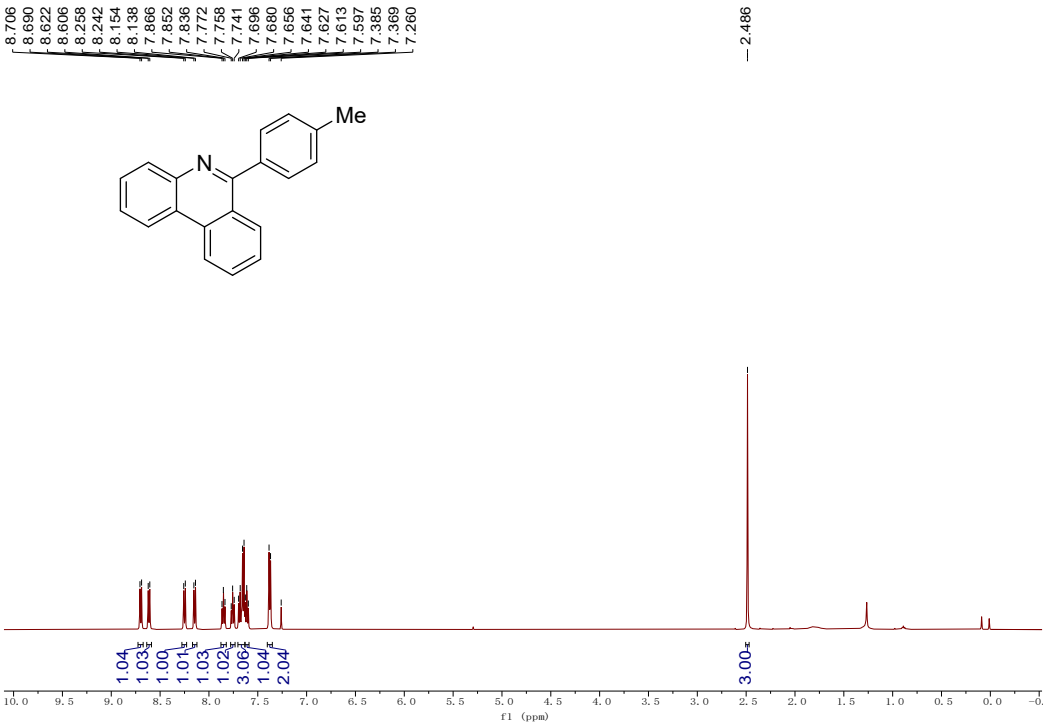
Direct Arylation of Unactivated Alkanes with Heteroarenes by Visible-Light Catalysis. *J. Org. Chem*. **2019**, *84*, 12904-12912.

12, Maiti, D.; Halder, A.; De Sarkar, S. Base-Promoted Aerobic Oxidation/Homolytic Aromatic Substitution Cascade toward the Synthesis of Phenanthridines. *Adv. Synth. Catal.* **2019**, *361*, 4941-4948.

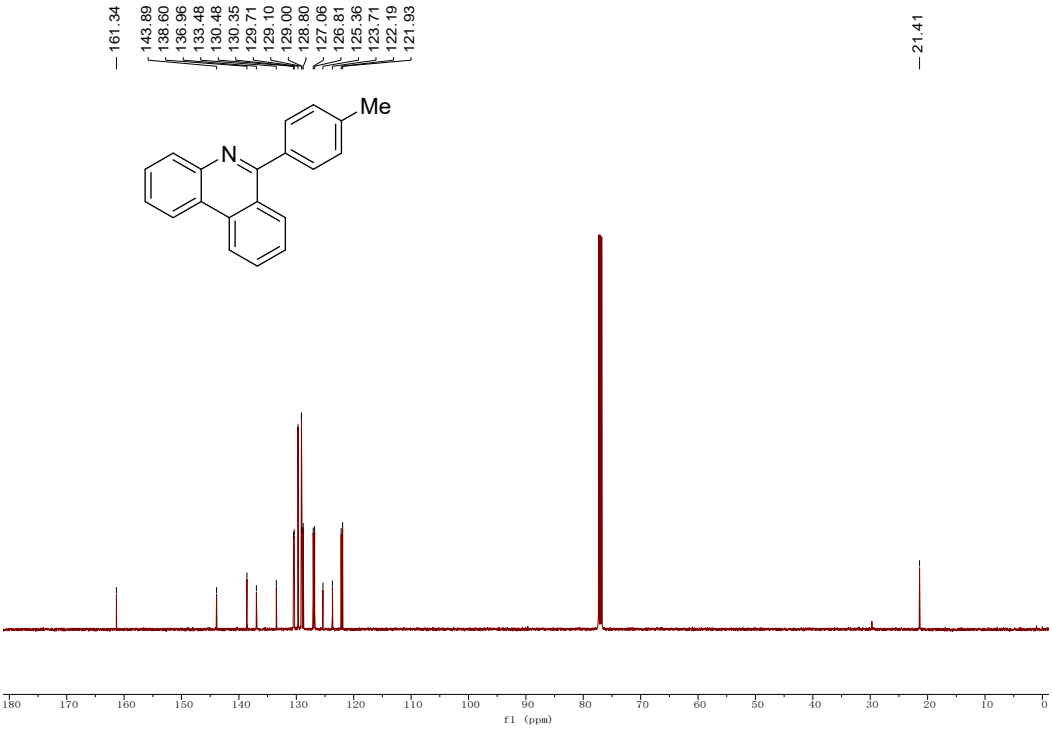
13, Liu, S.; Pan, W.; Wu, S.; Bu, X.; Xin, S.; Yu, J.; Xu, H.; Yang, X. Visible-Light-Induced Tandem Radical Addition–Cyclization of 2-Aryl Phenyl Isocyanides Catalysed by Recyclable Covalent Organic Frameworks. *Green Chem*. **2019**, *21*, 2905-2910.

5. NMR Spectra of compounds.

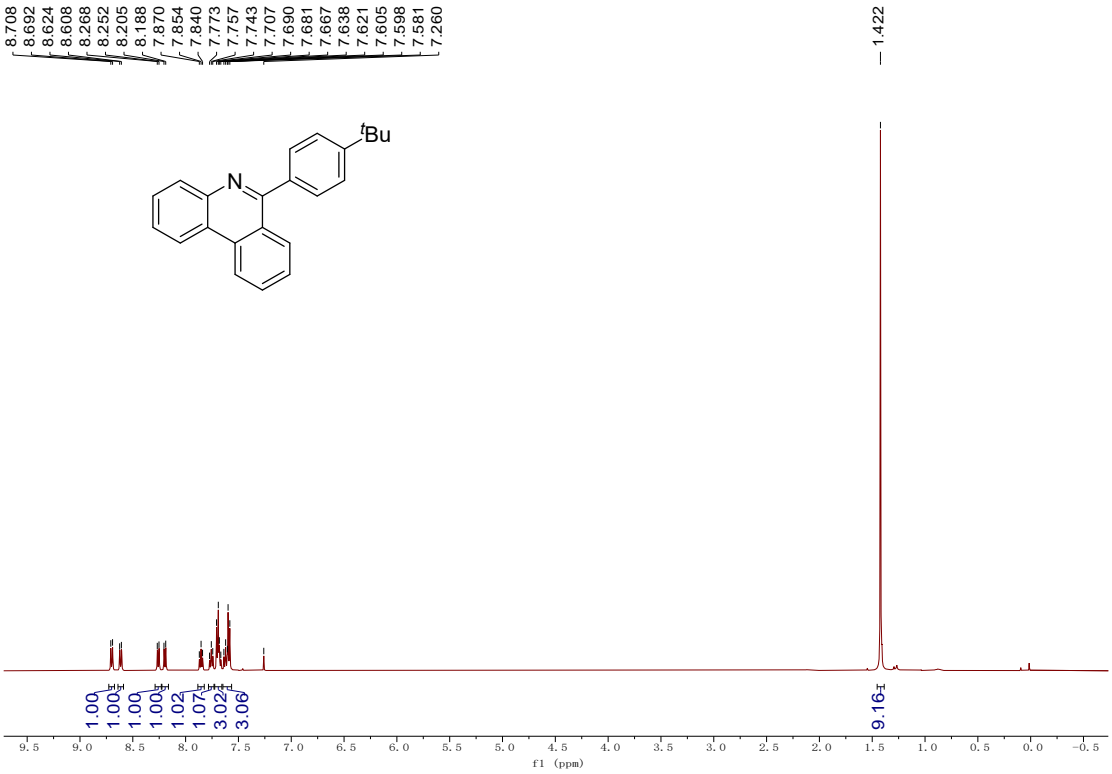
500 Hz ^{1}H NMR spectrum of **3aa** in $CDCl_3$



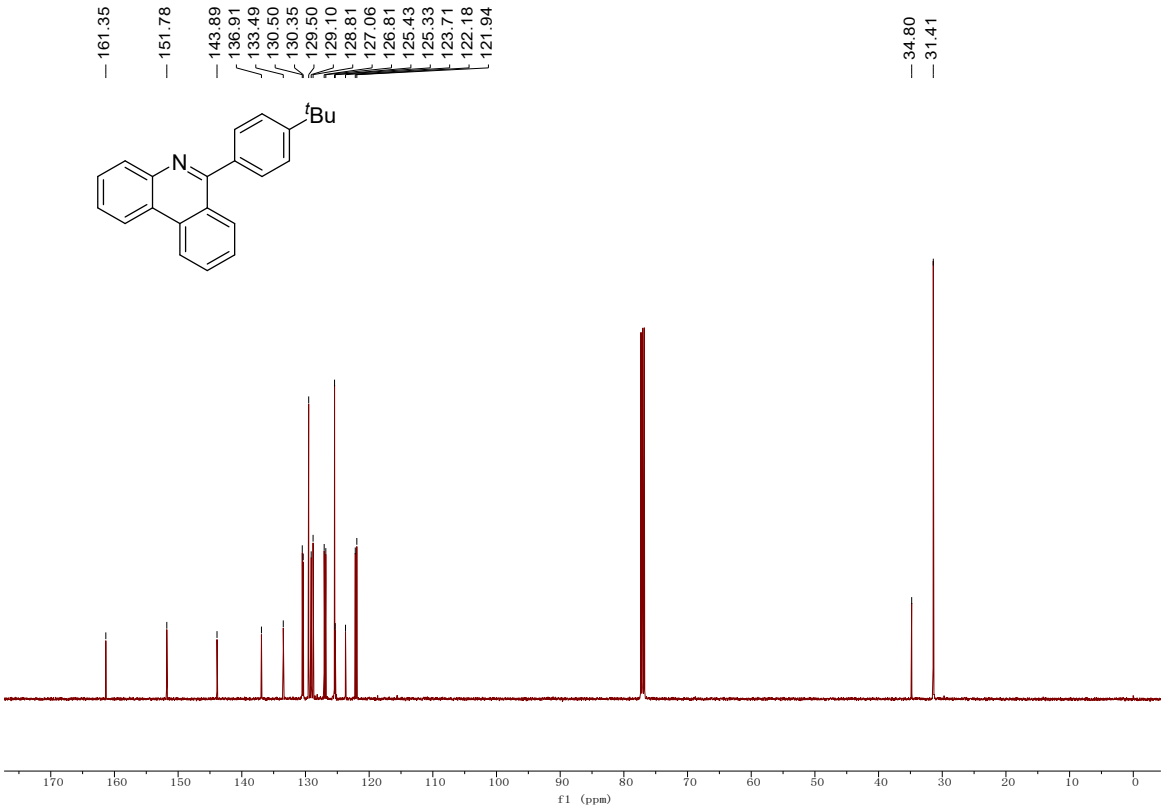
126 Hz ^{13}C {^{1}H} NMR spectrum of **3aa** in $CDCl_3$



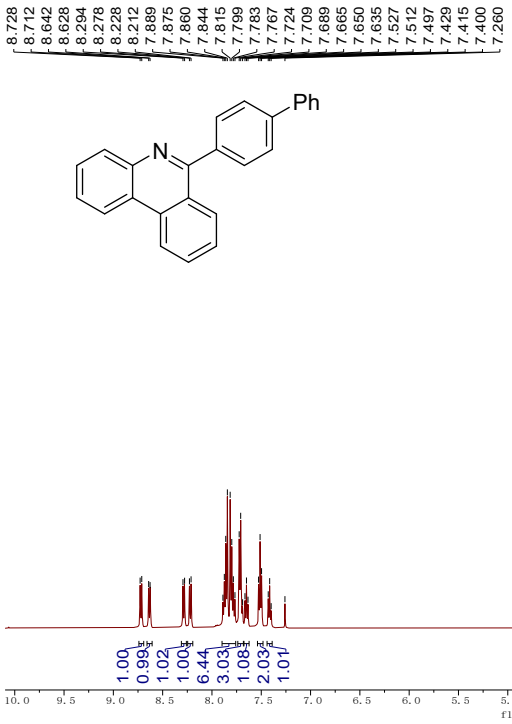
500 Hz ^{1}H NMR spectrum of **3ab** in $CDCl_3$



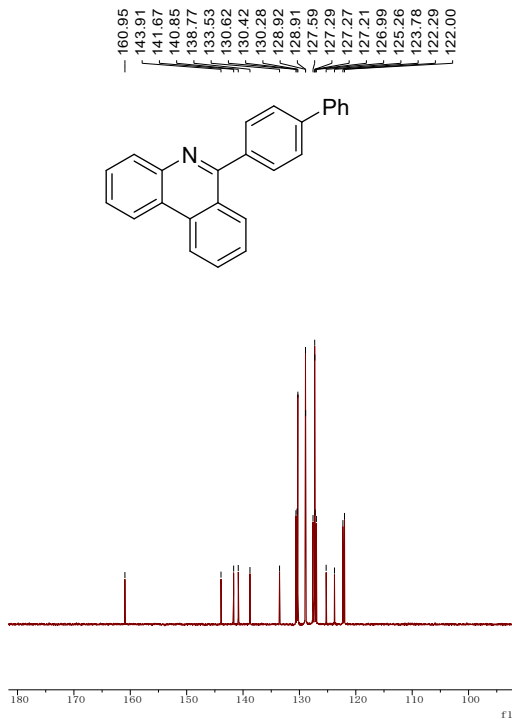
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ab** in $CDCl_3$



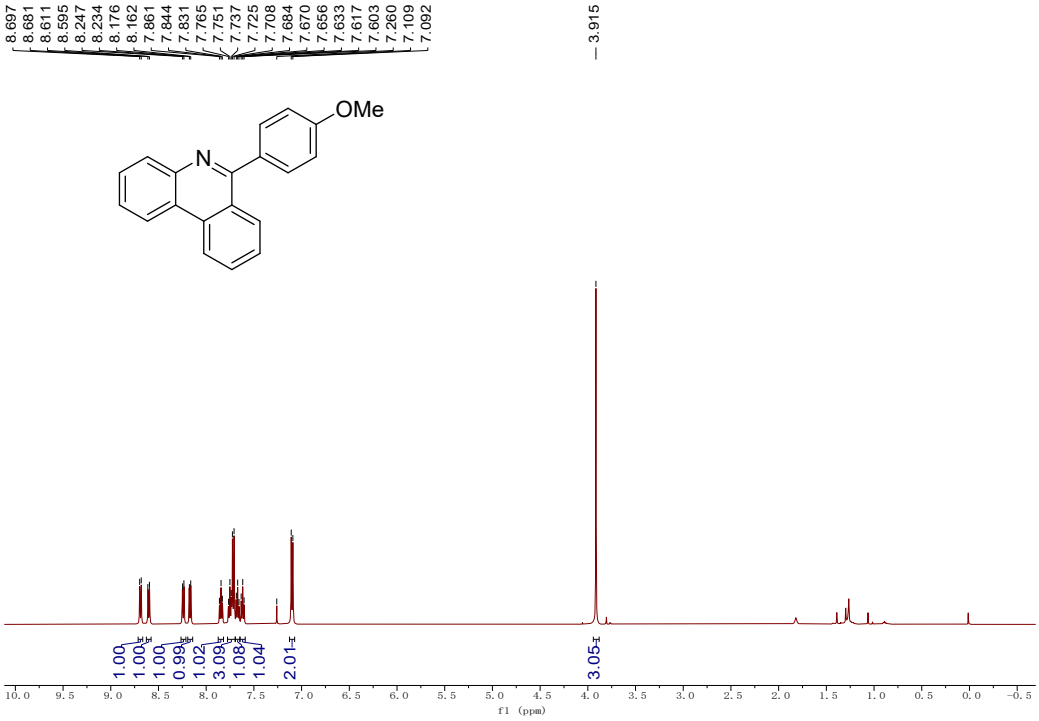
500 Hz ^{1}H NMR spectrum of **3ac** in $CDCl_3$



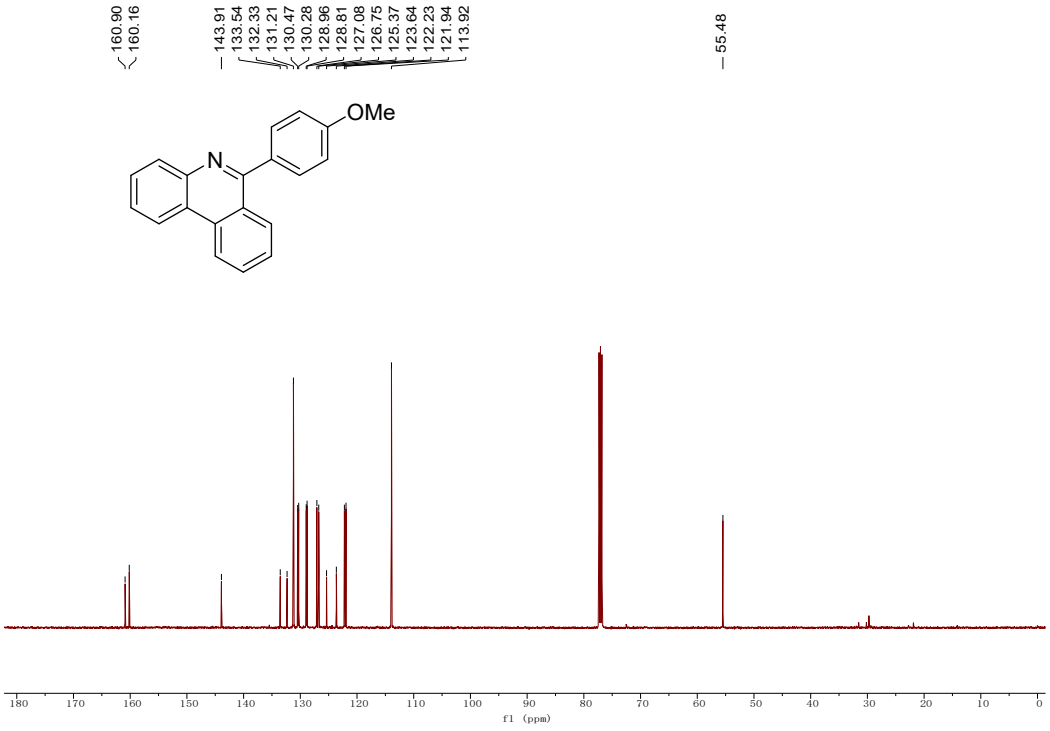
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ac** in $CDCl_3$



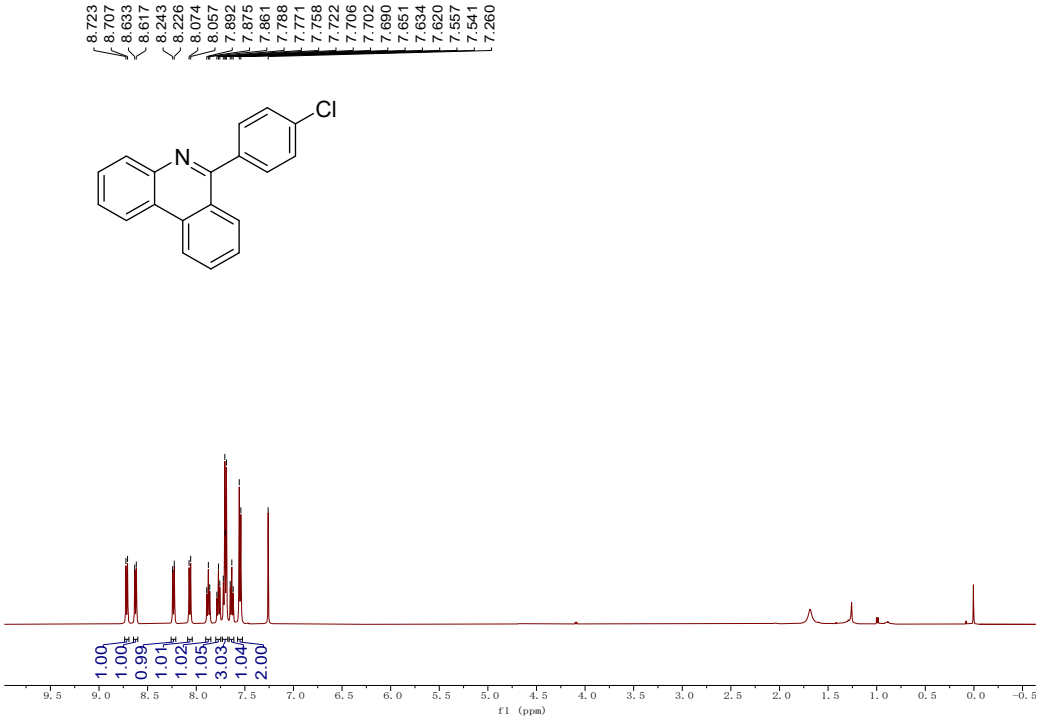
500 Hz ^{1}H NMR spectrum of **3ad** in $CDCl_3$



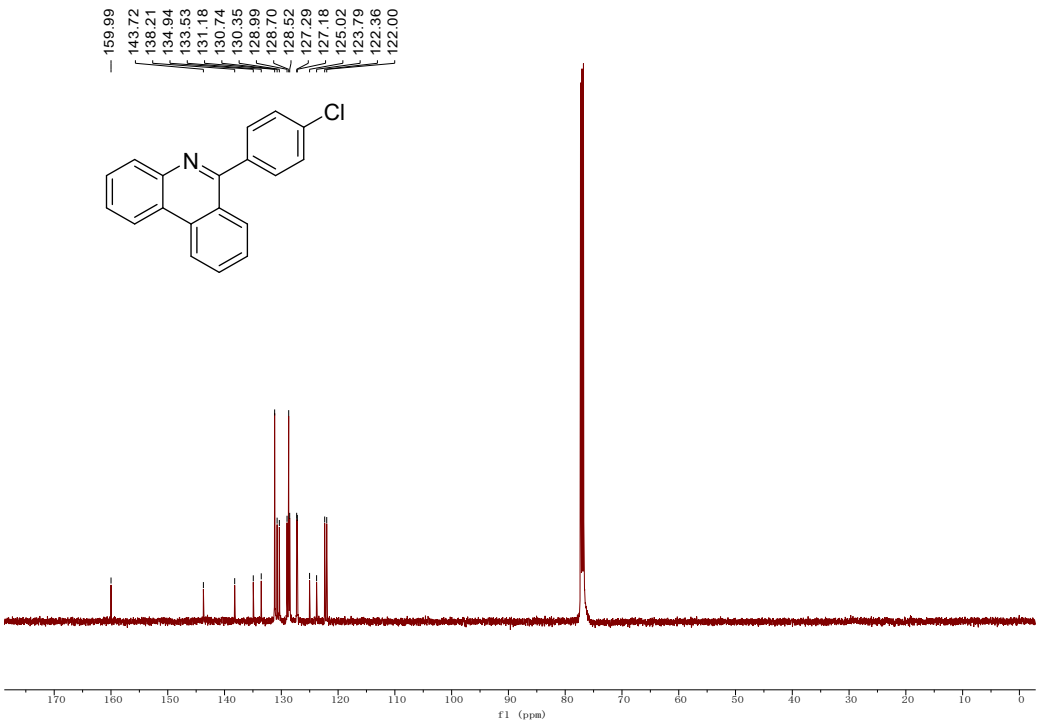
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ad** in $CDCl_3$



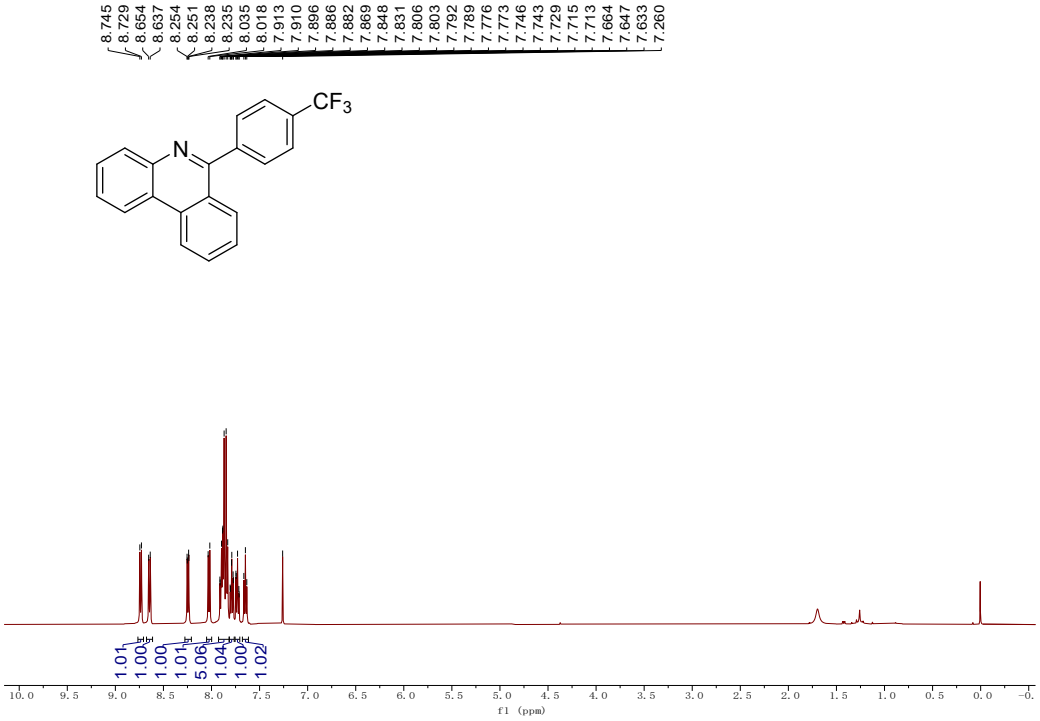
500 Hz ^{1}H NMR spectrum of **3ae** in $CDCl_3$



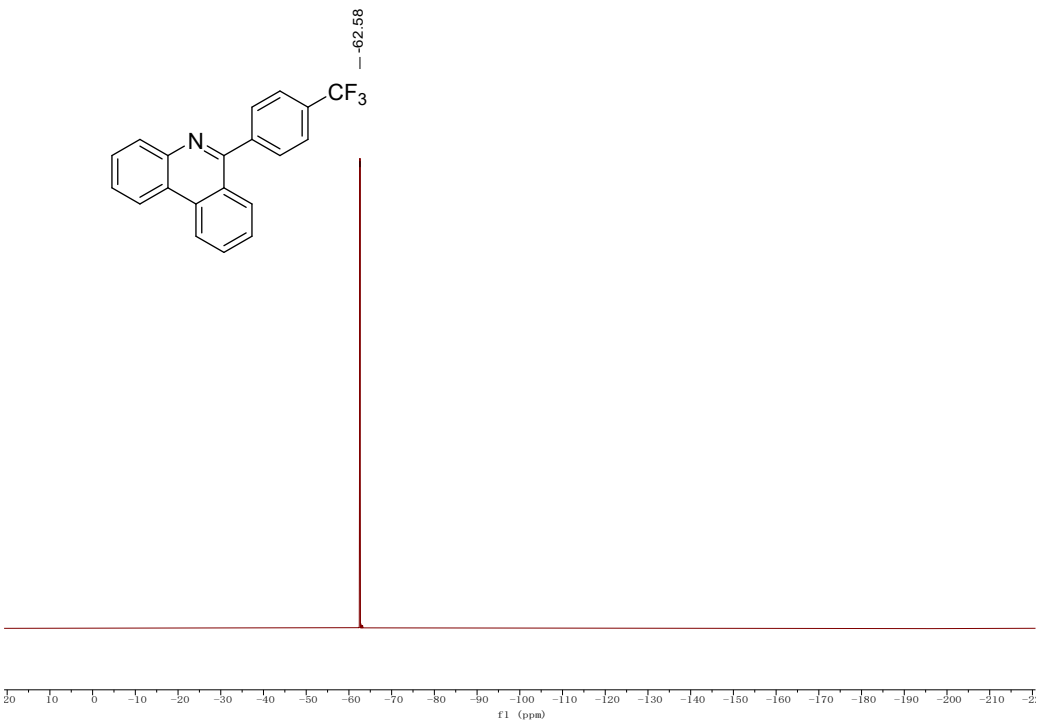
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ae** in $CDCl_3$



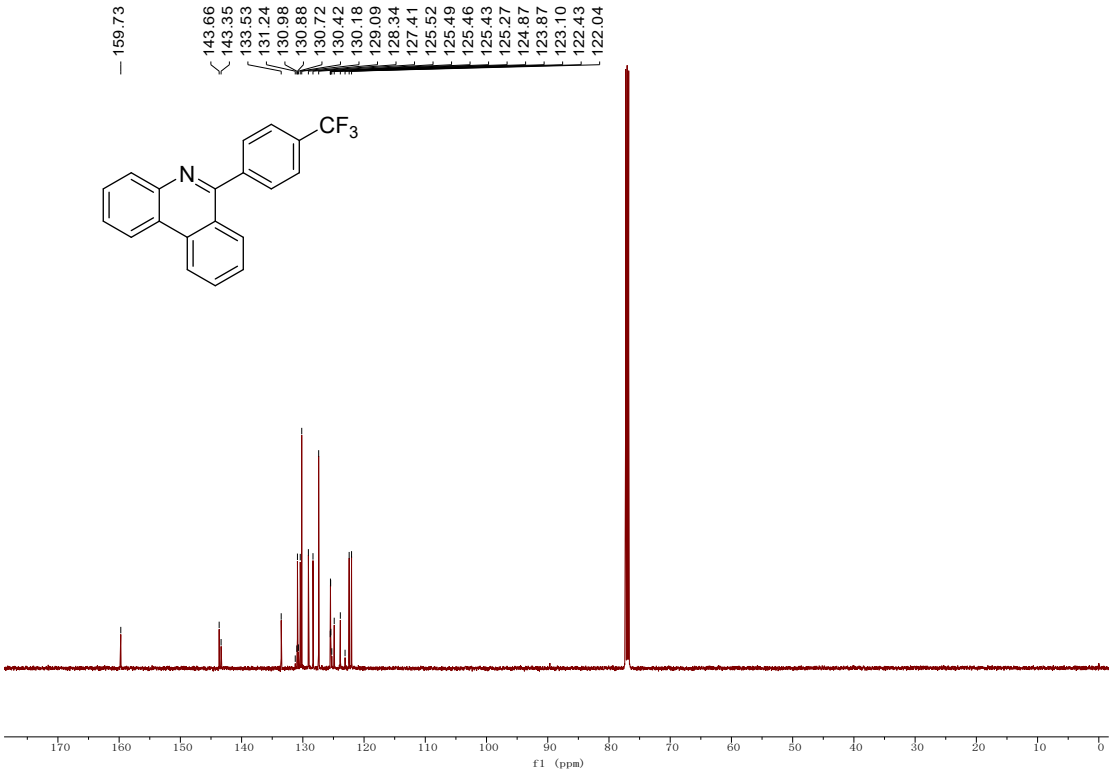
500 Hz ^{1}H NMR spectrum of **3af** in $CDCl_3$



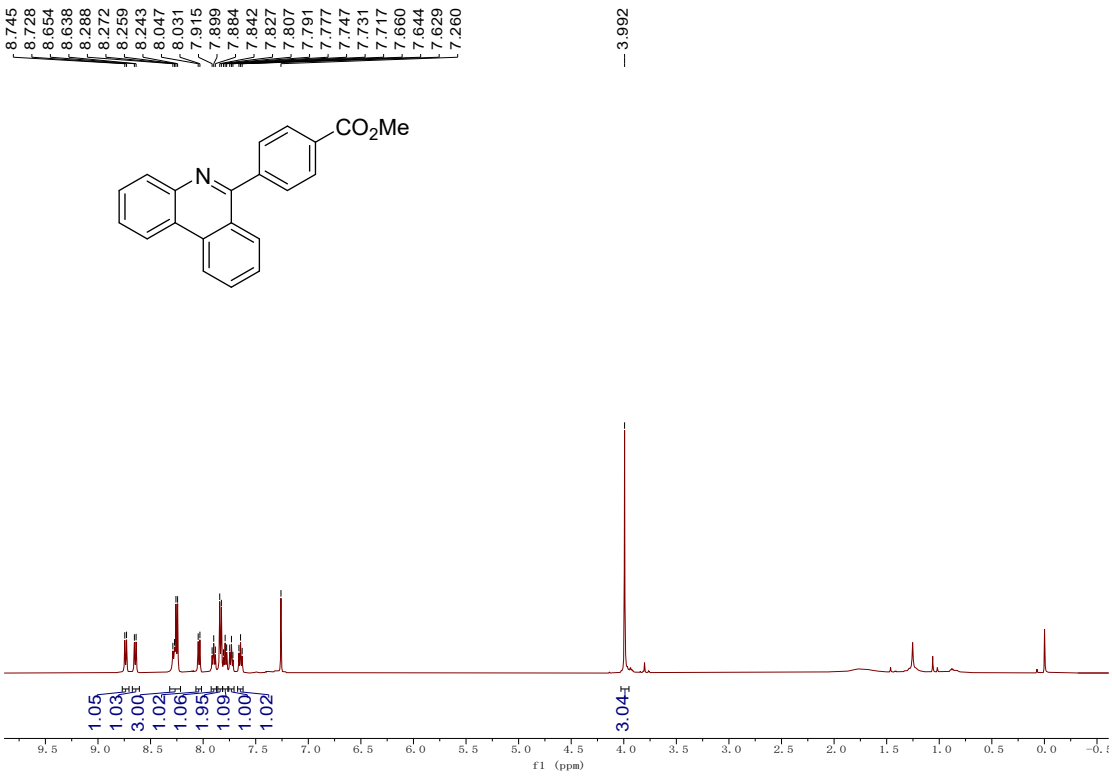
471 Hz ^{19}F {^{1}H} NMR spectrum of **3af** in $CDCl_3$



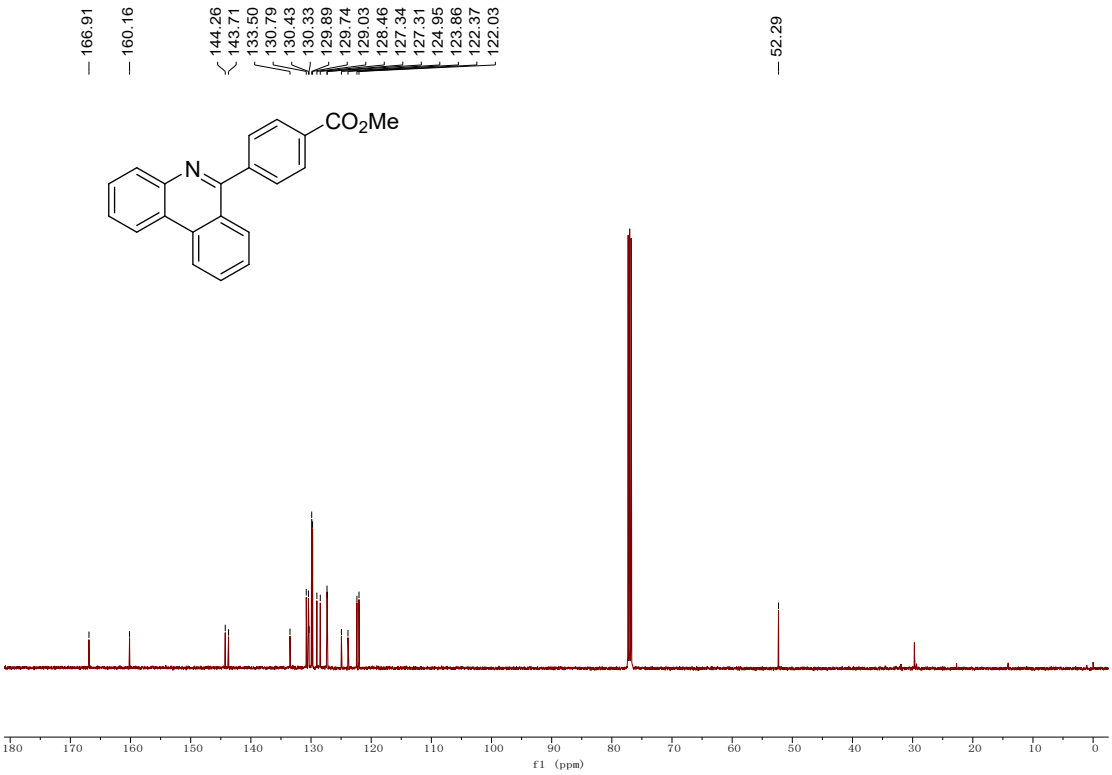
126 Hz ^{13}C {^{1}H} NMR spectrum of **3af** in $CDCl_3$



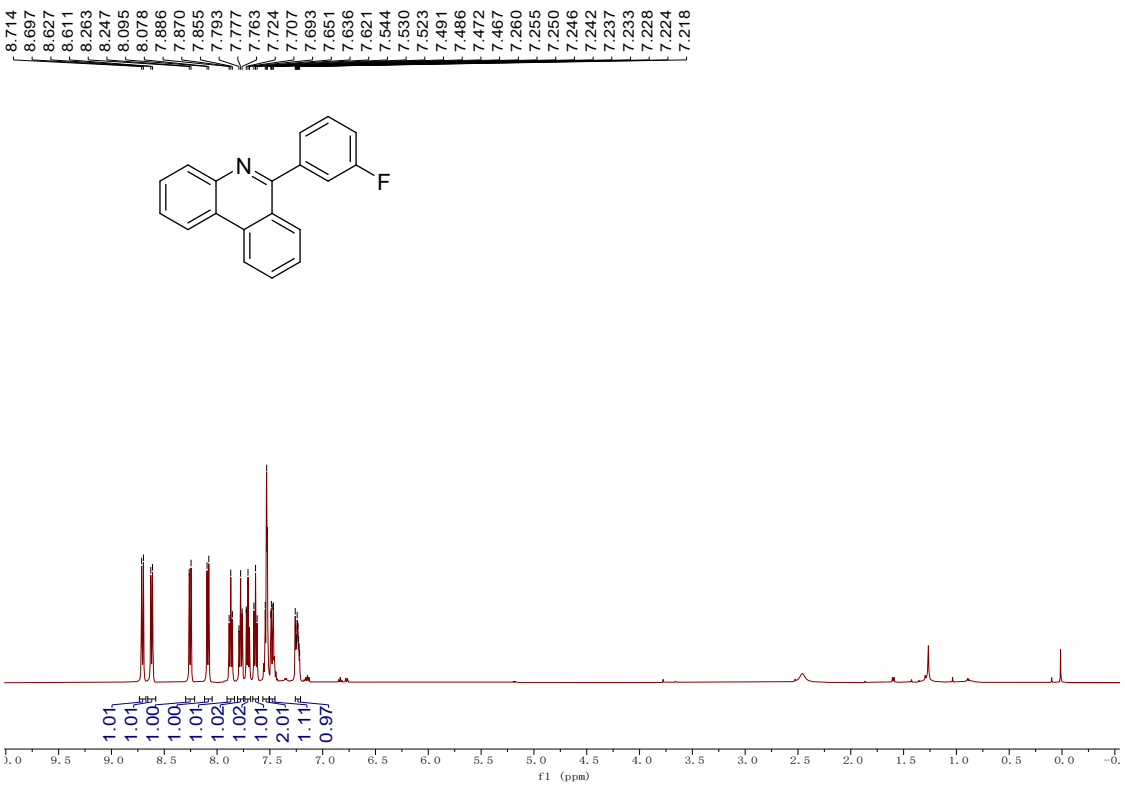
500 Hz ^{1}H NMR spectrum of **3ag** in $CDCl_3$



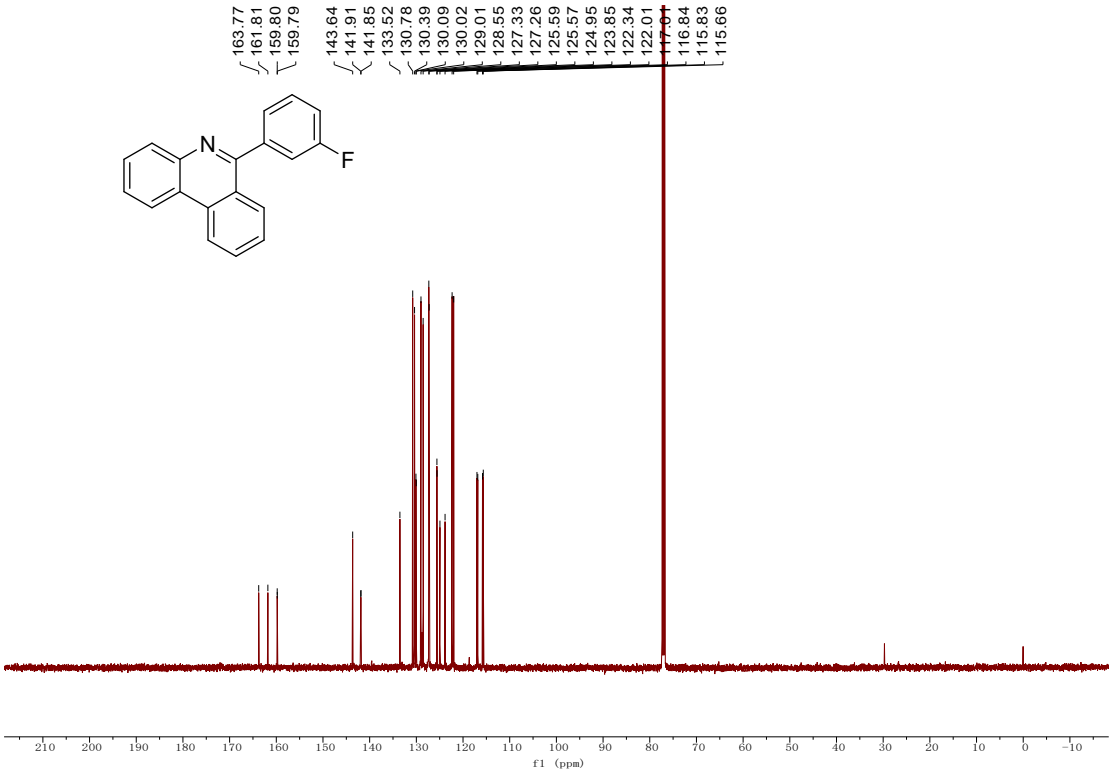
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ag** in $CDCl_3$



500 Hz ^{1}H NMR spectrum of **3ah** in $CDCl_3$

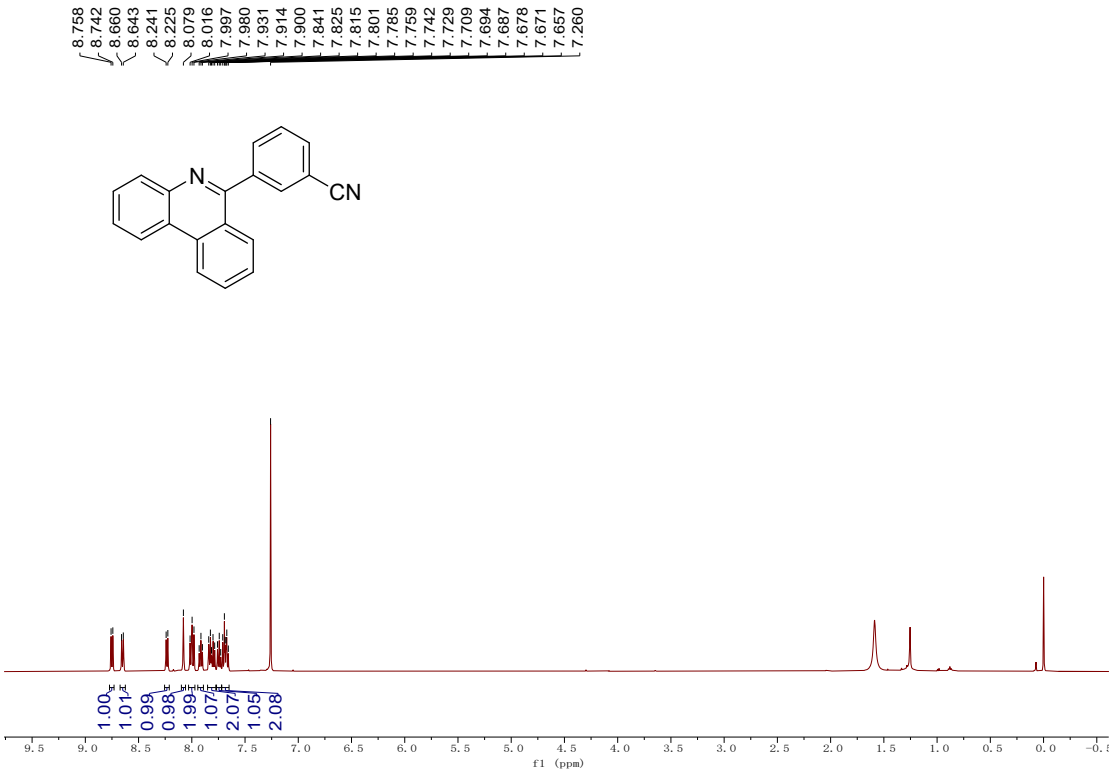


126 Hz ^{13}C {^{1}H} NMR spectrum of **3ah** in $CDCl_3$

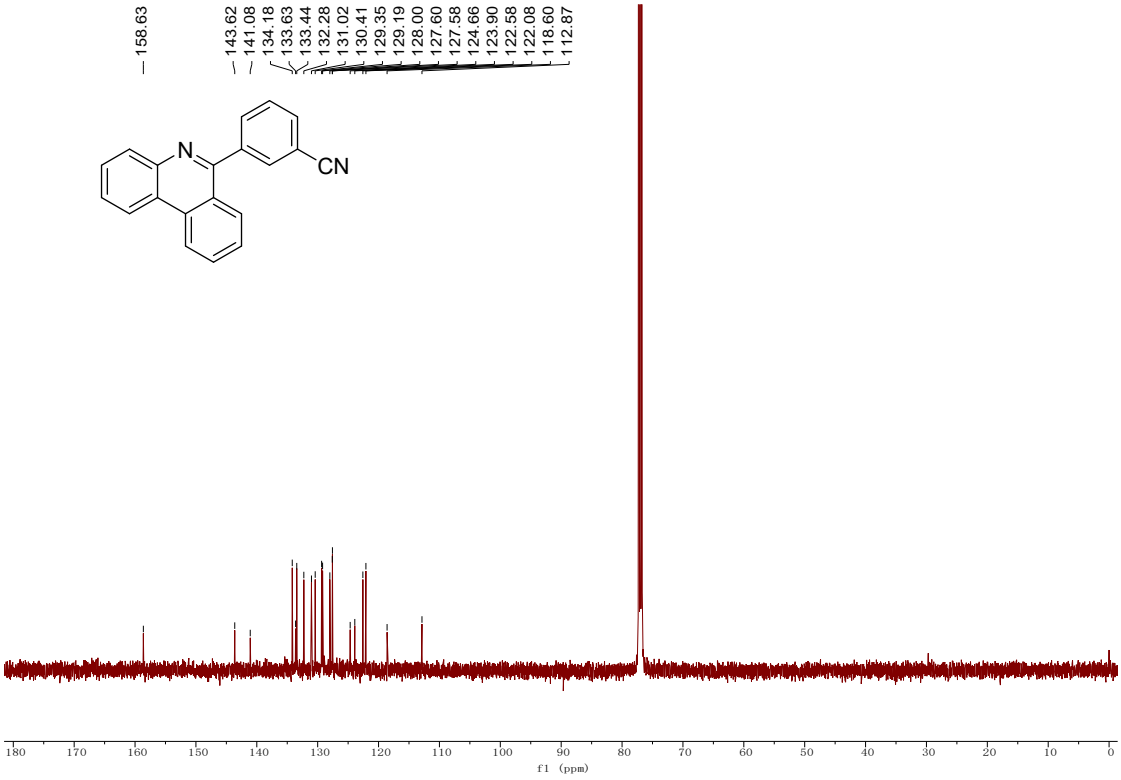


471 Hz ^{19}F {^{1}H} NMR spectrum of **3ah** in $CDCl_3$

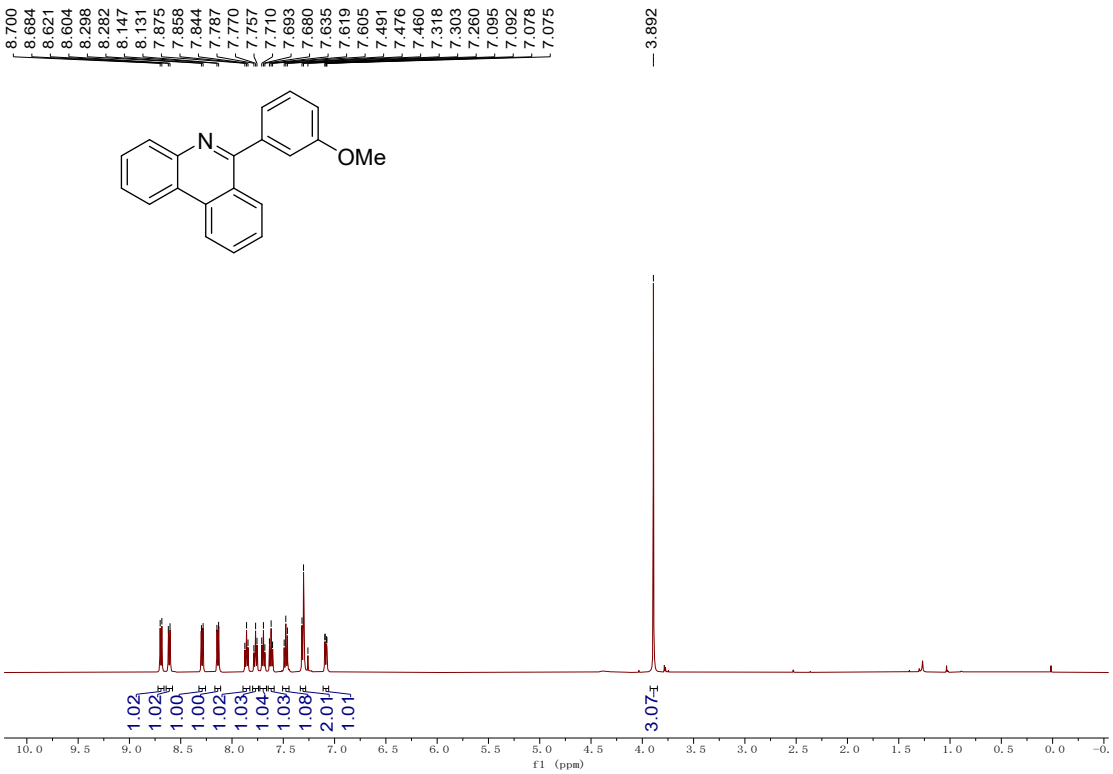
500 Hz ^{1}H NMR spectrum of **3ai** in $CDCl_3$



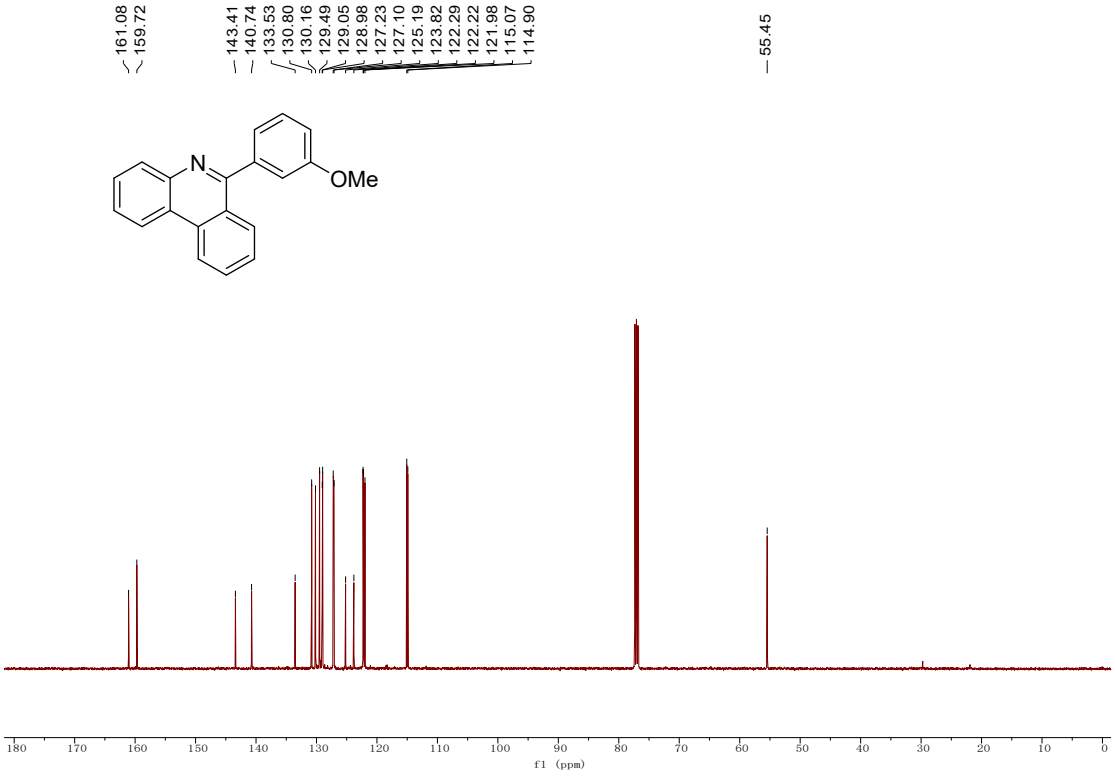
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ai** in $CDCl_3$



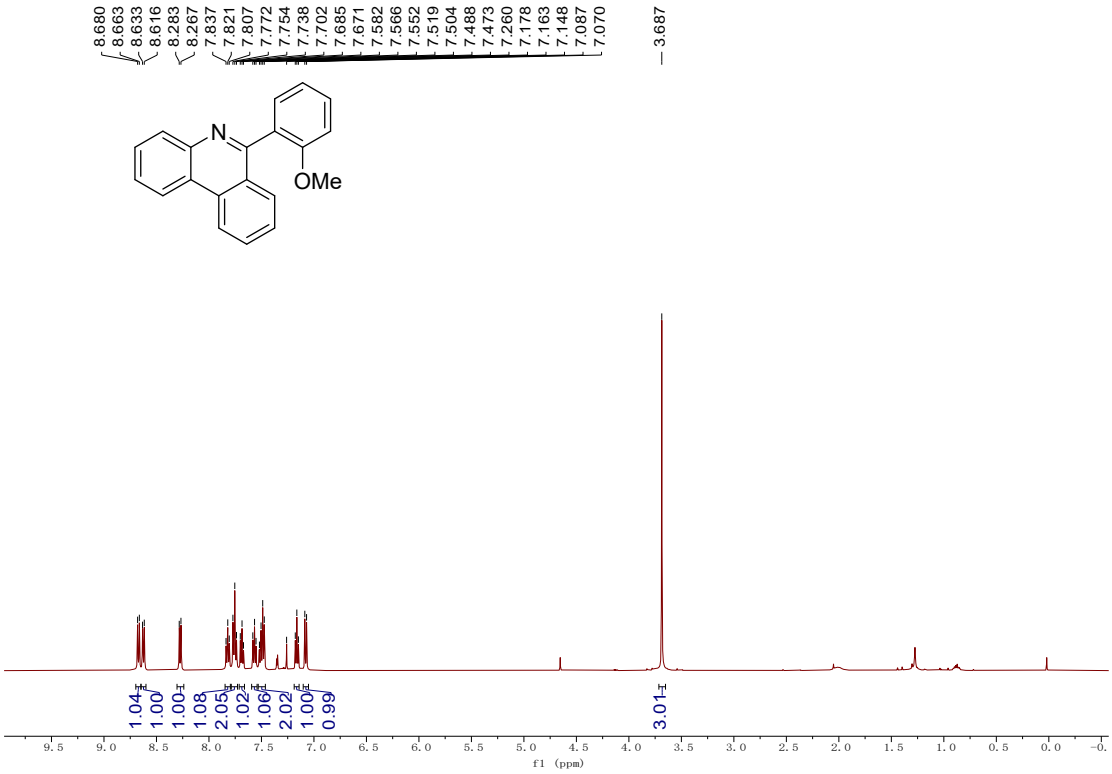
500 Hz ^{1}H NMR spectrum of **3aj** in $CDCl_3$



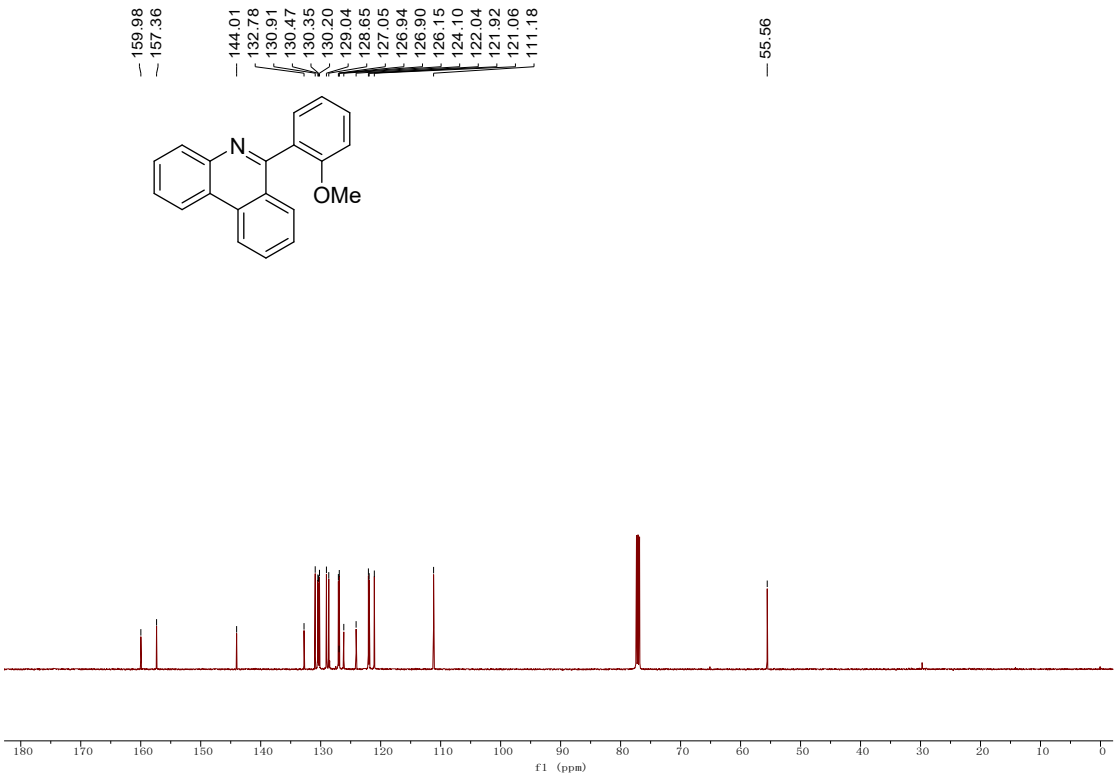
126 Hz ^{13}C {^{1}H} NMR spectrum of **3aj** in $CDCl_3$



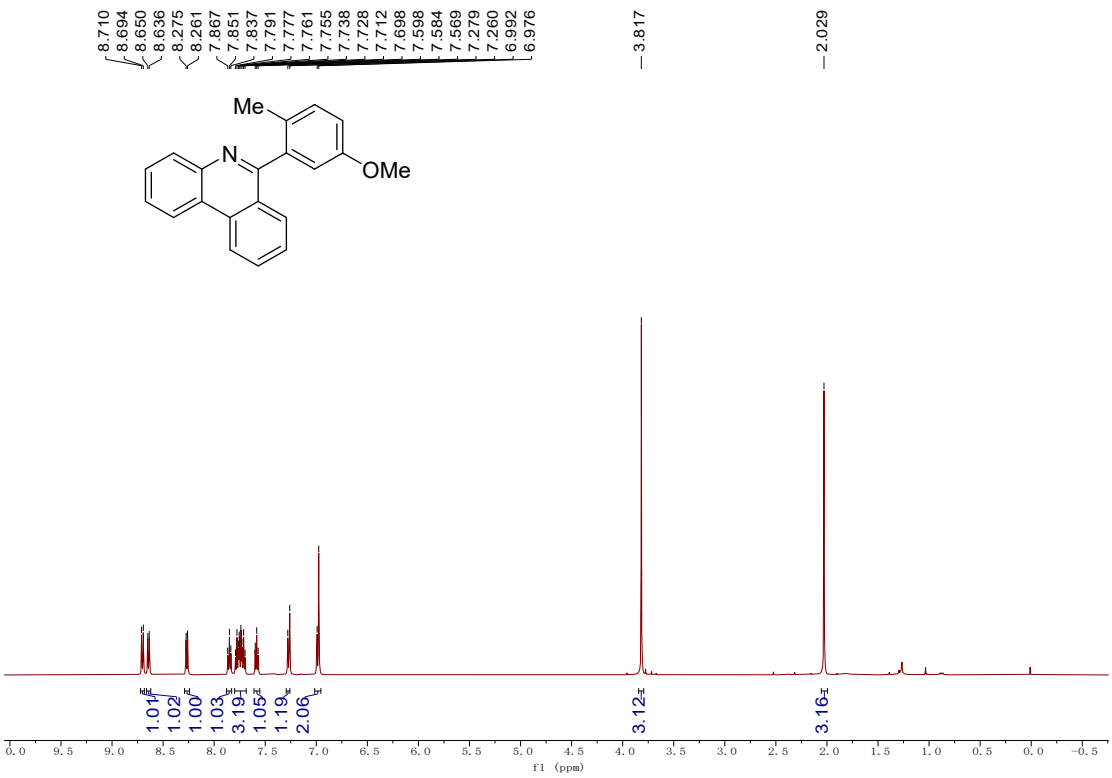
500 Hz ^{1}H NMR spectrum of **3ak** in $CDCl_3$



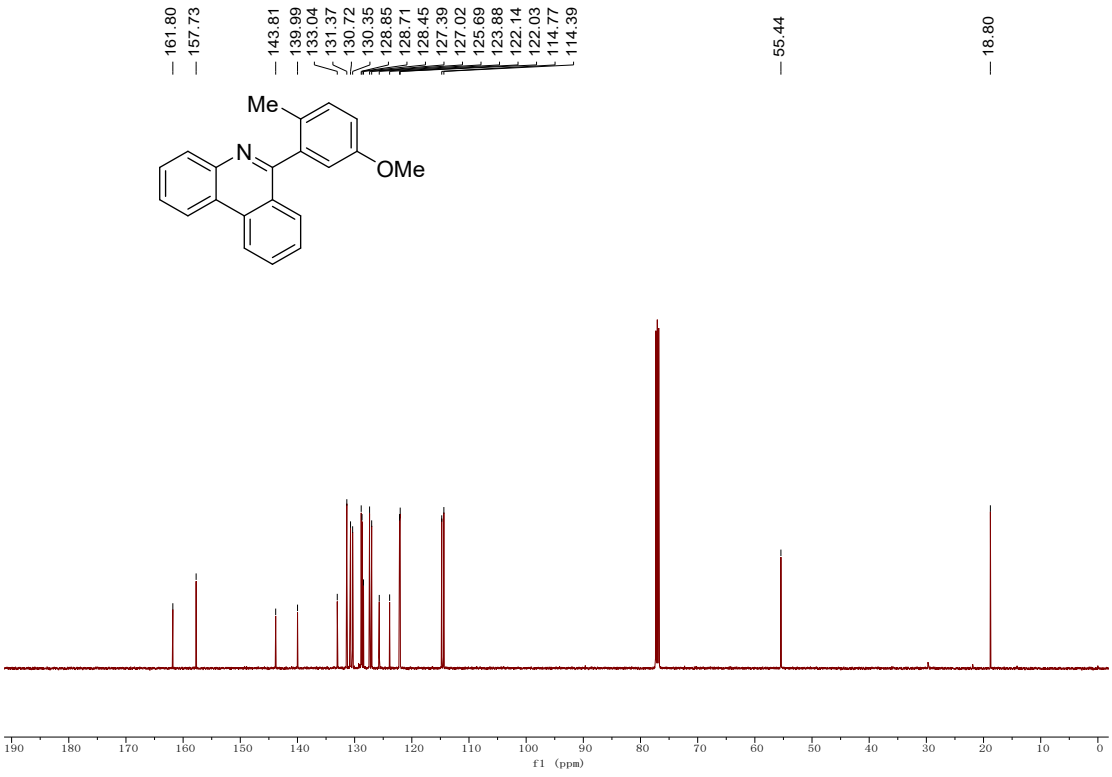
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ak** in $CDCl_3$



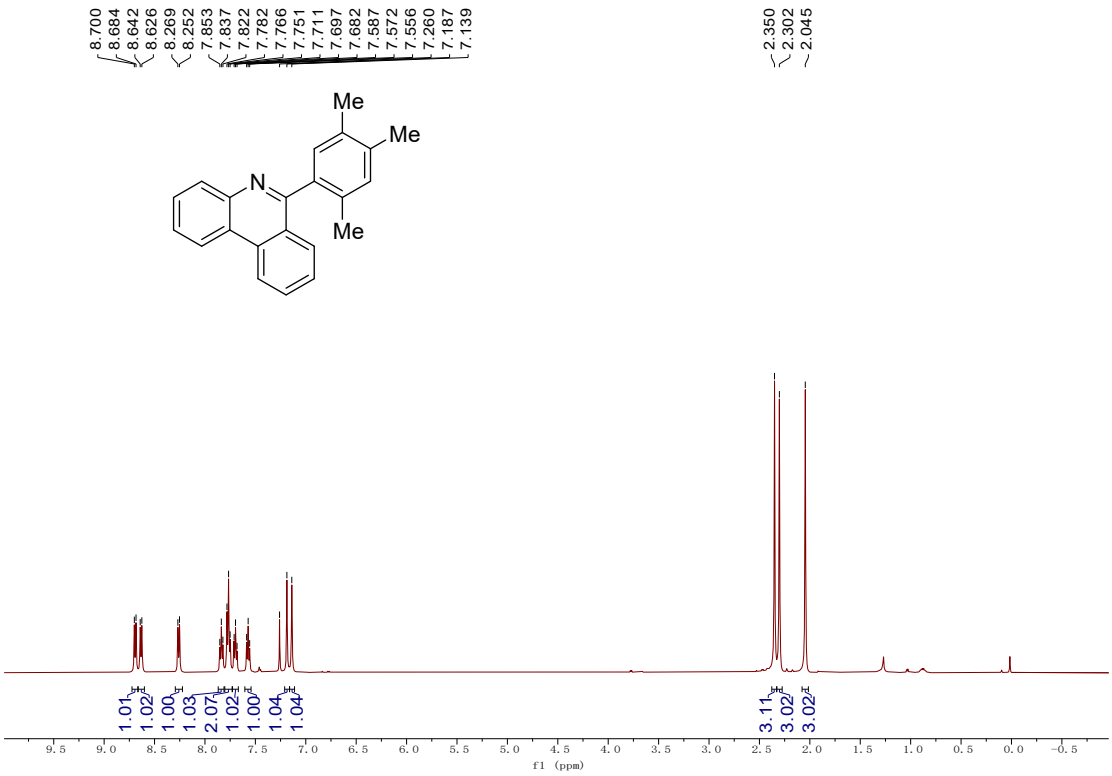
500 Hz ^{1}H NMR spectrum of **3al** in $CDCl_3$



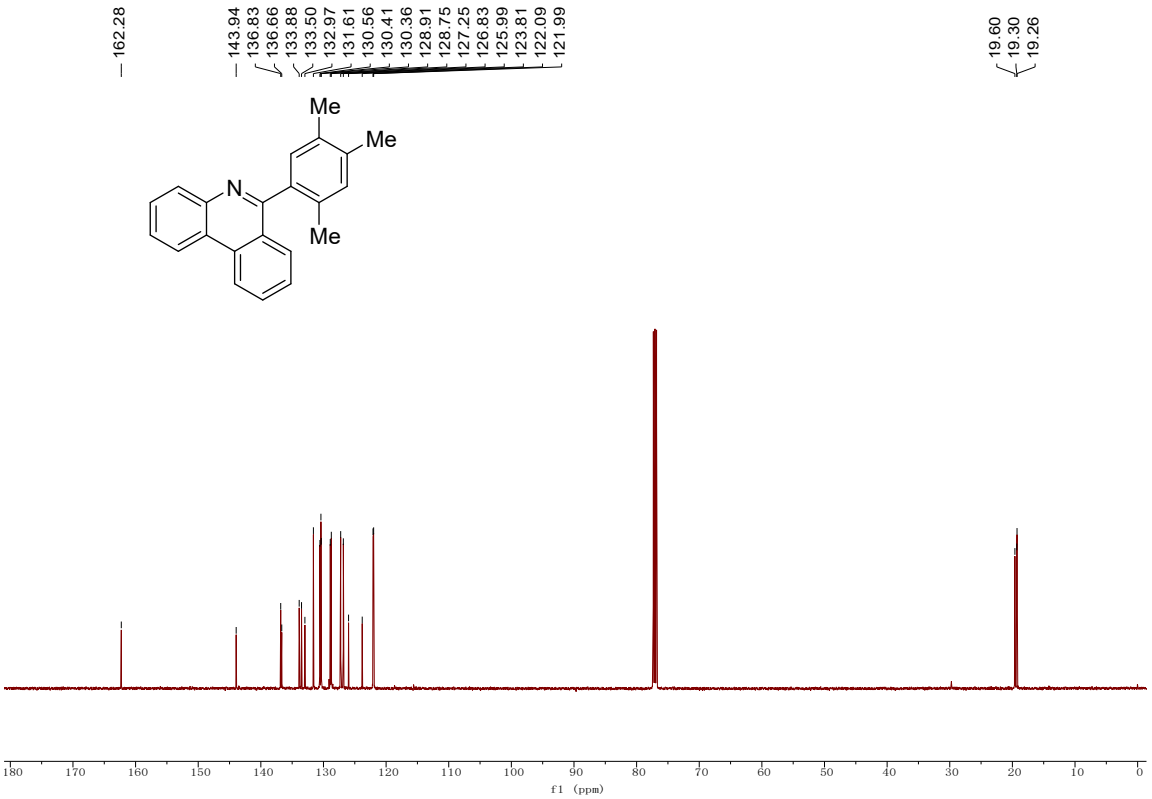
126 Hz ^{13}C {^{1}H} NMR spectrum of **3al** in $CDCl_3$



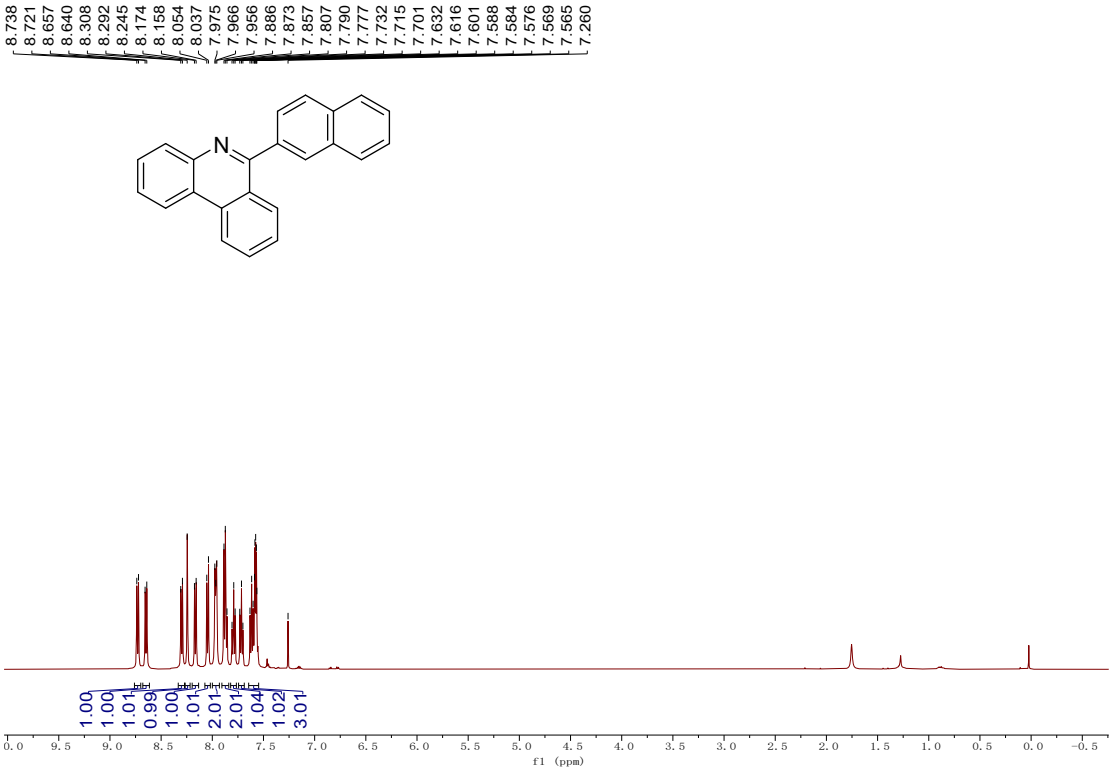
500 Hz ^{1}H NMR spectrum of **3am** in $CDCl_3$



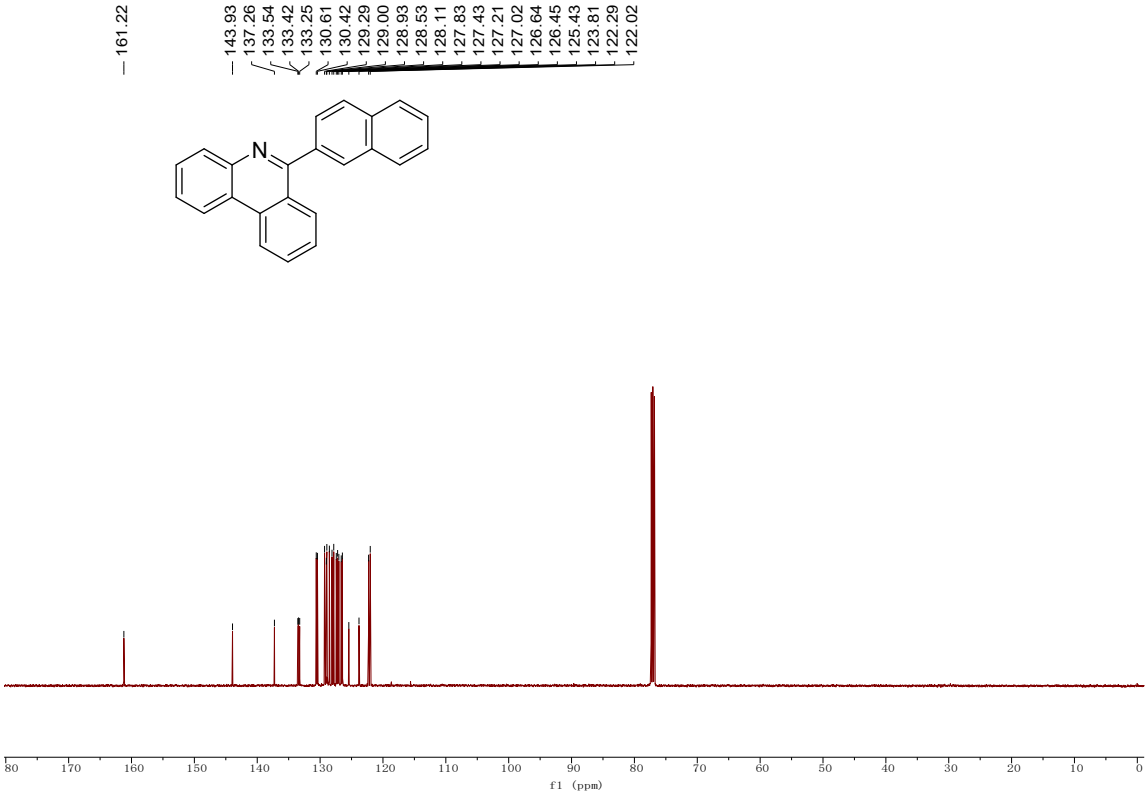
126 Hz ^{13}C {^{1}H} NMR spectrum of **3am** in $CDCl_3$



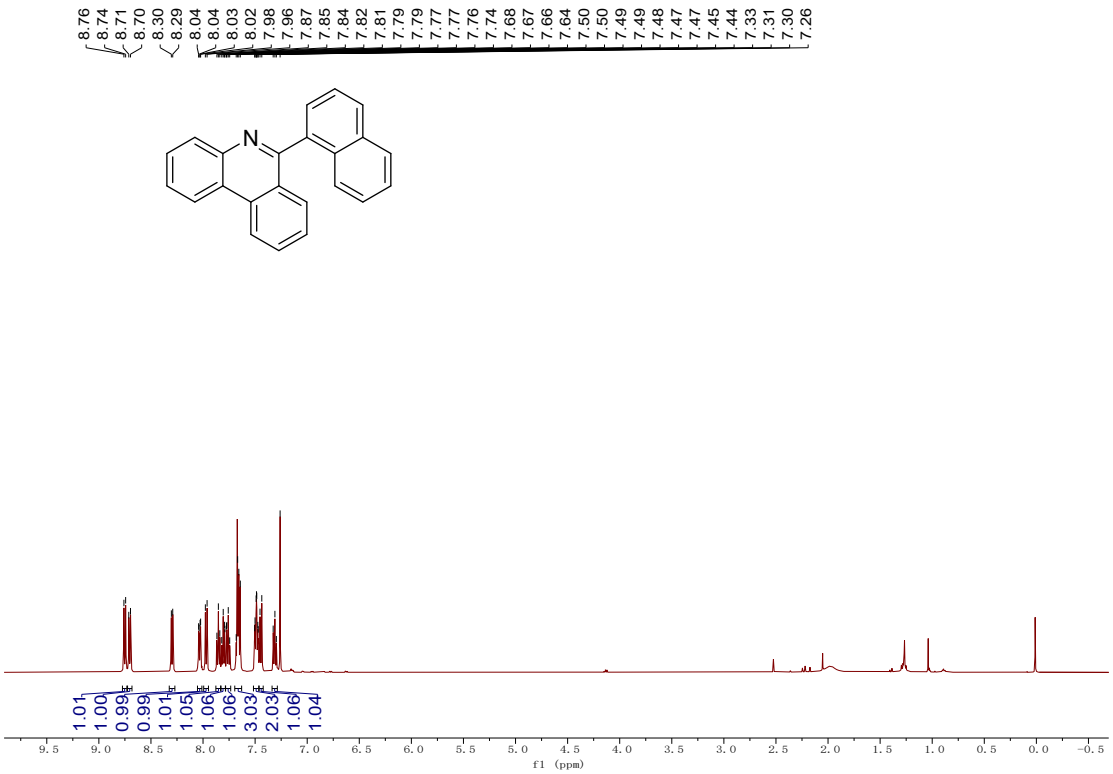
500 Hz ^{1}H NMR spectrum of **3an** in $CDCl_3$



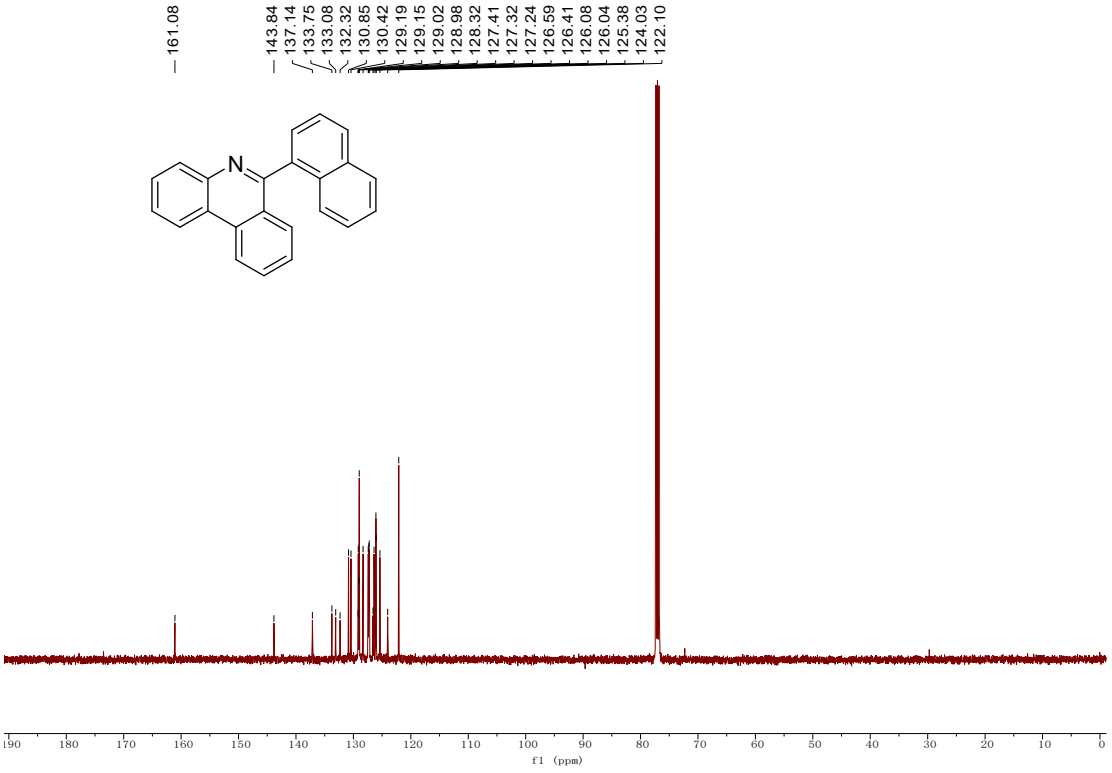
126 Hz ^{13}C {^{1}H} NMR spectrum of **3an** in $CDCl_3$



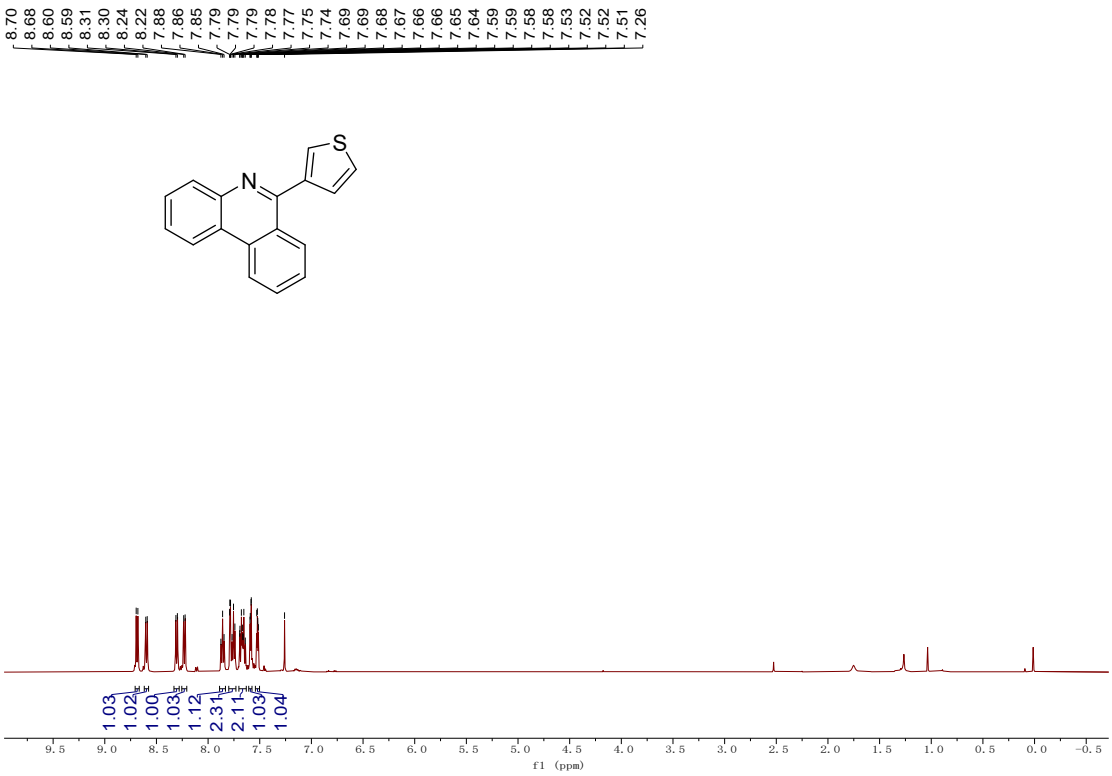
500 Hz ^{1}H NMR spectrum of **3ao** in $CDCl_3$



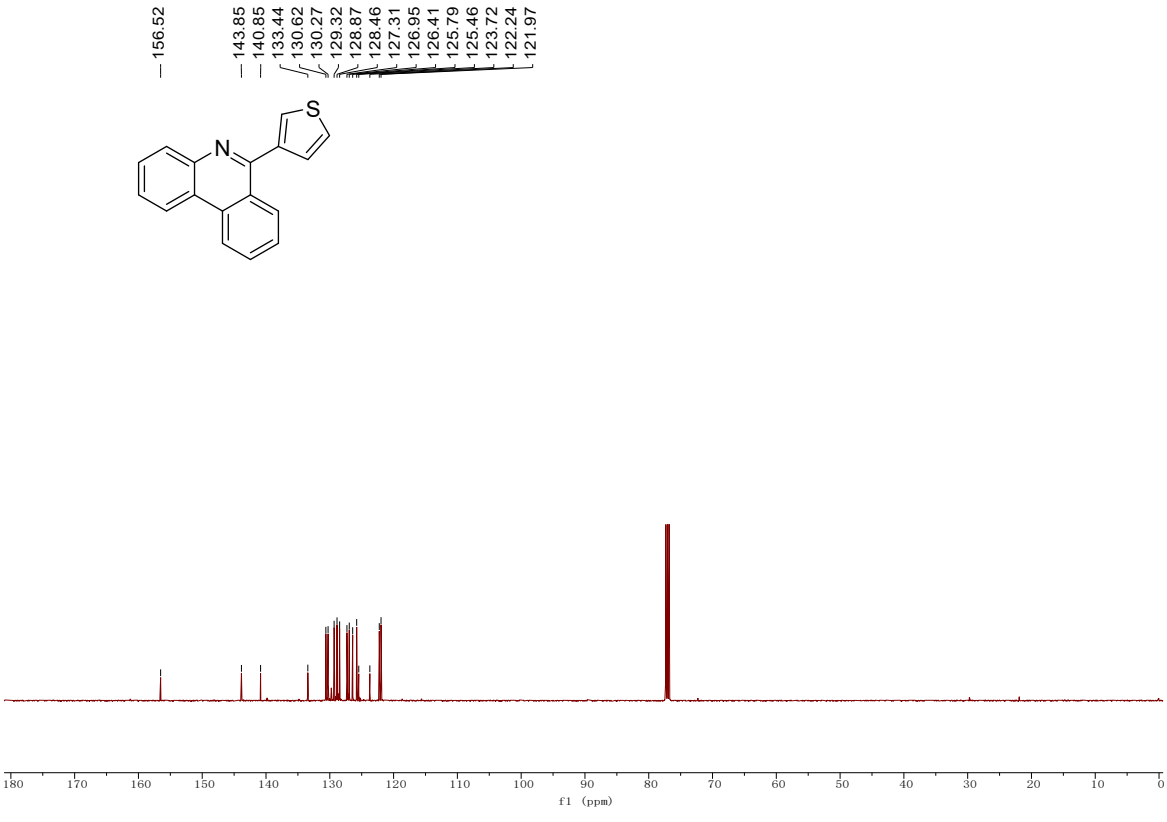
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ao** in $CDCl_3$



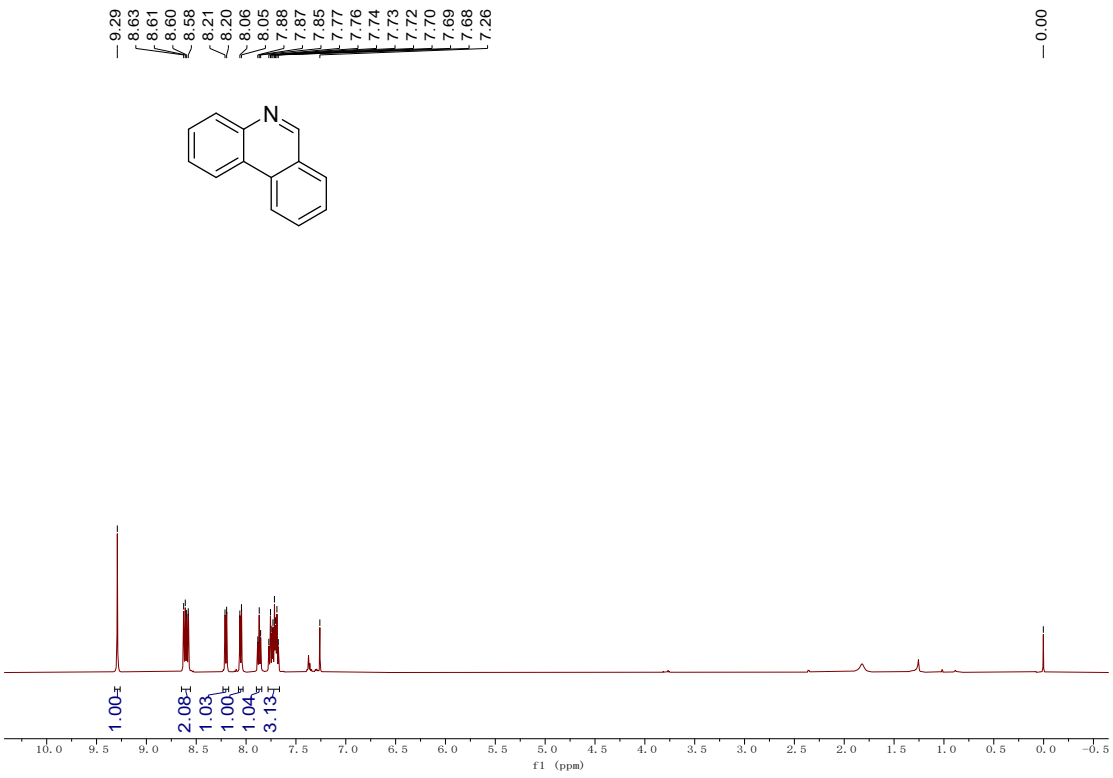
500 Hz ^{1}H NMR spectrum of **3ap** in $CDCl_3$



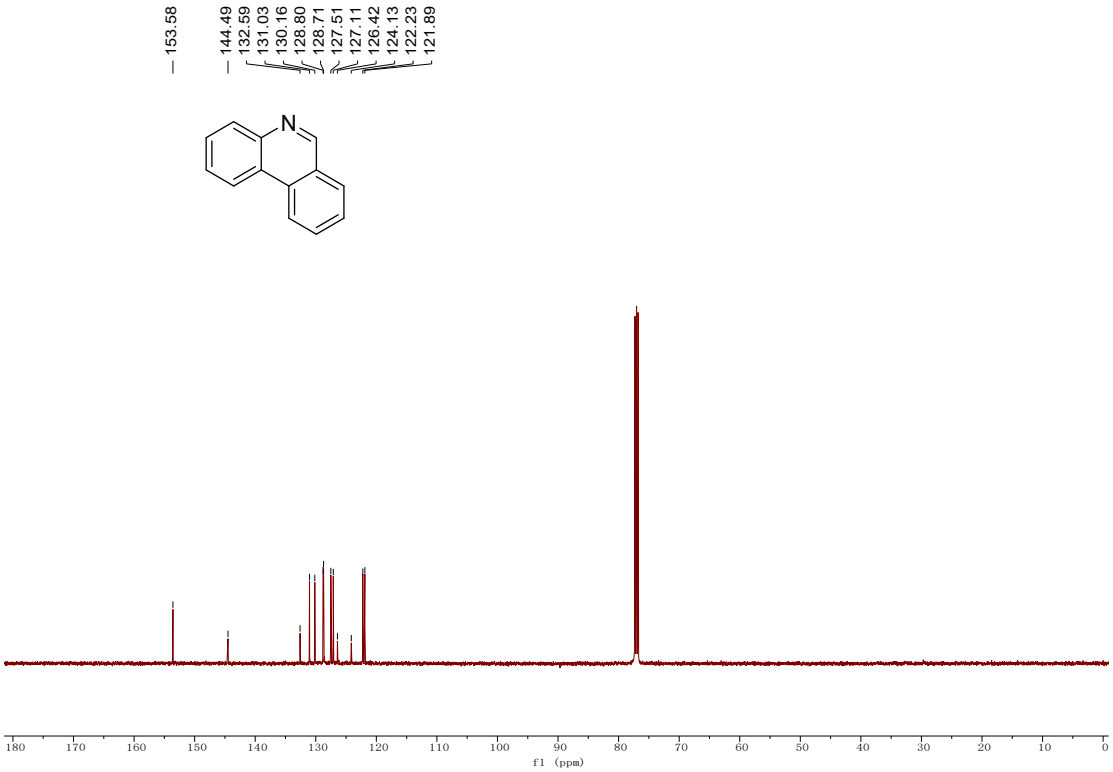
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ap** in $CDCl_3$



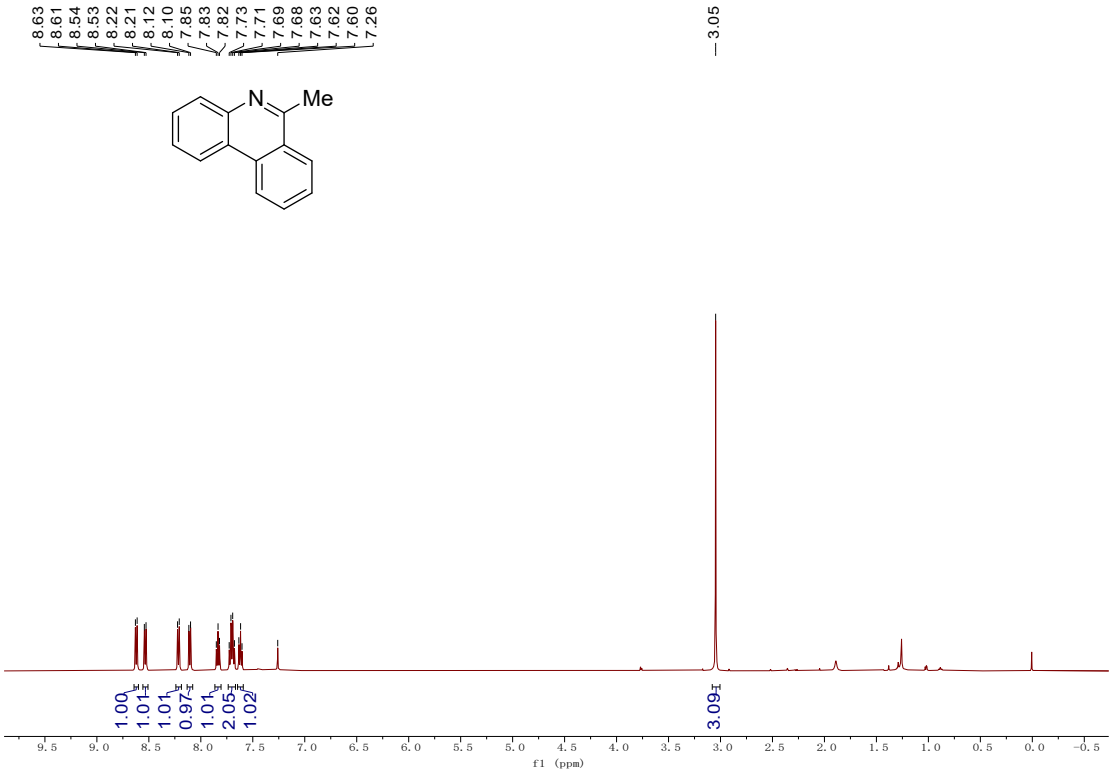
500 Hz ^{1}H NMR spectrum of **3aq** in $CDCl_3$



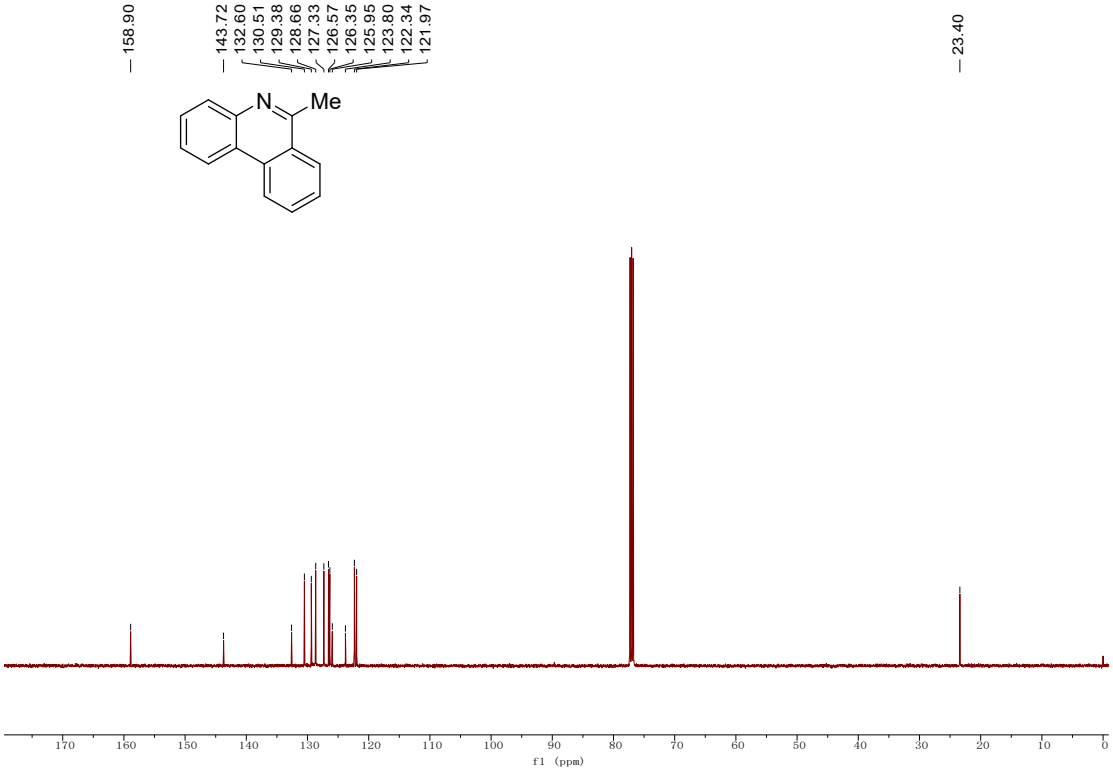
126 Hz ^{13}C {^{1}H} NMR spectrum of **3aq** in $CDCl_3$



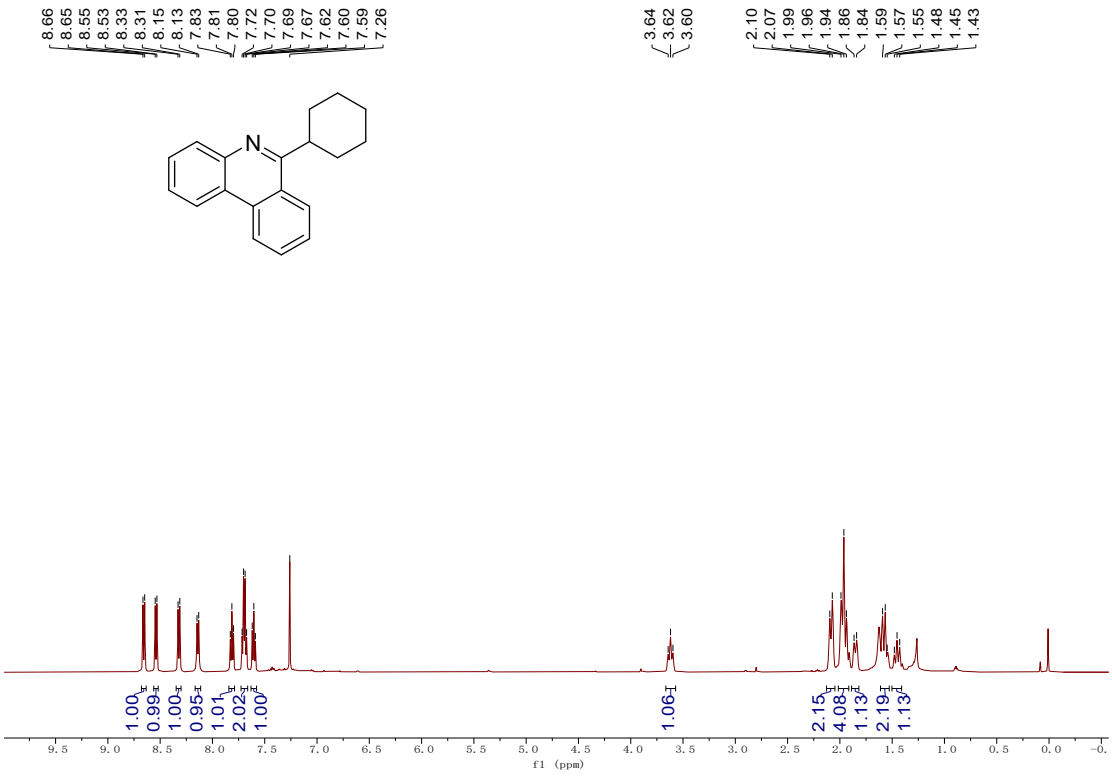
500 Hz ^{1}H NMR spectrum of **3ar** in $CDCl_3$



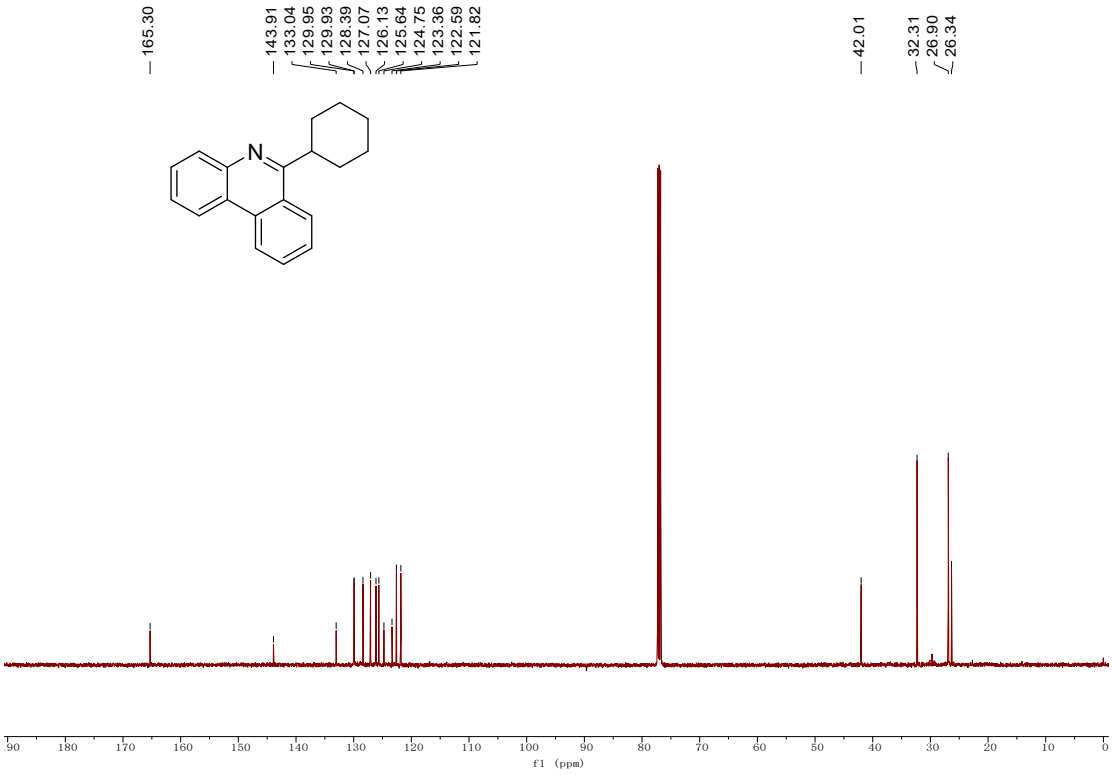
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ar** in $CDCl_3$



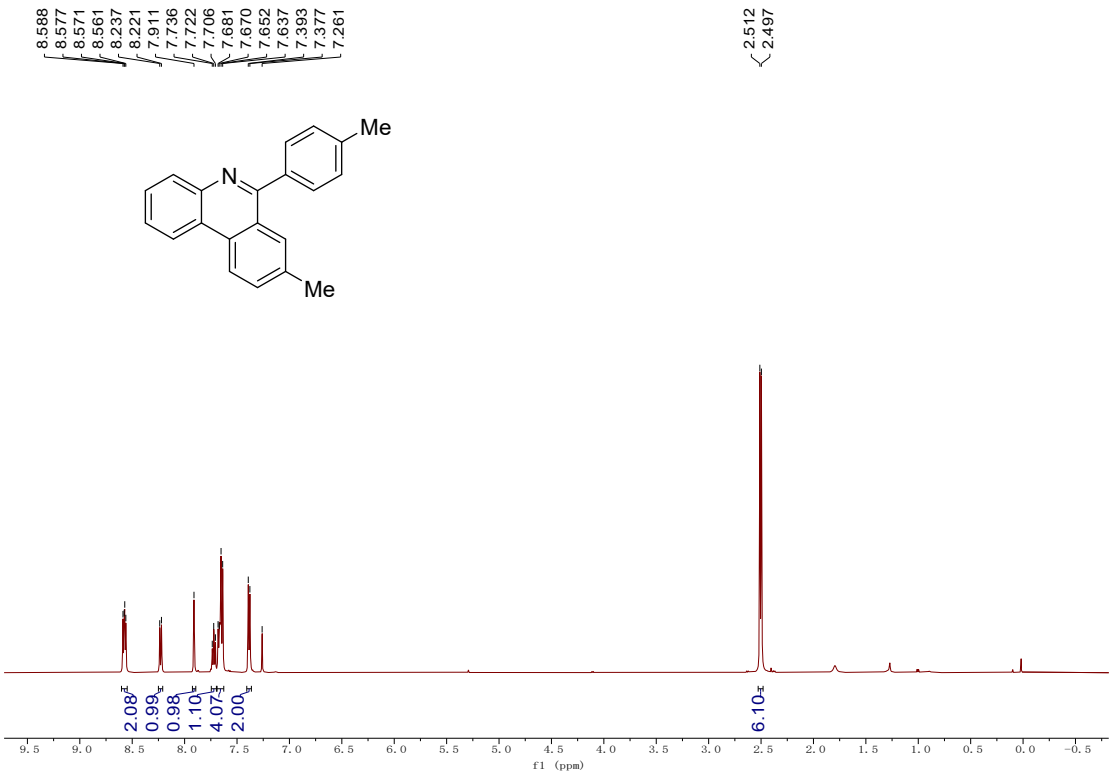
500 Hz ^{1}H NMR spectrum of **3as** in $CDCl_3$



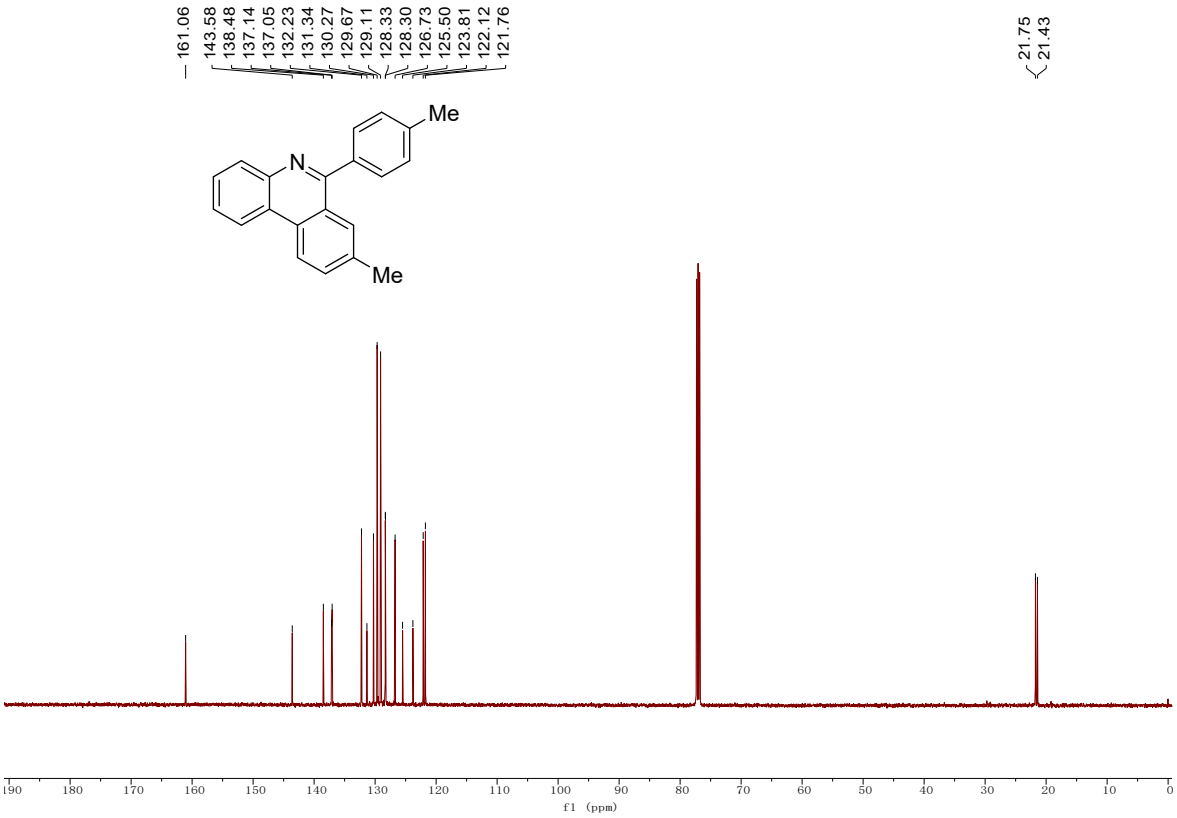
126 Hz ^{13}C {^{1}H} NMR spectrum of **3as** in $CDCl_3$



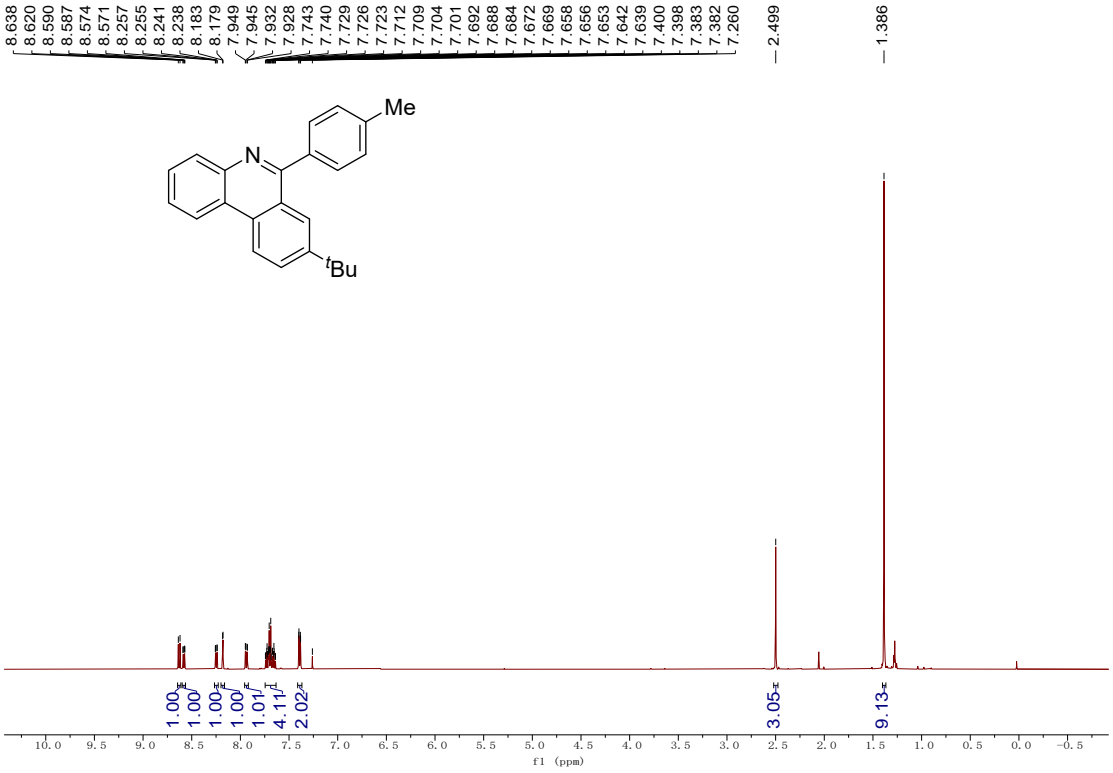
500 Hz ^{1}H NMR spectrum of **3ba** in $CDCl_3$



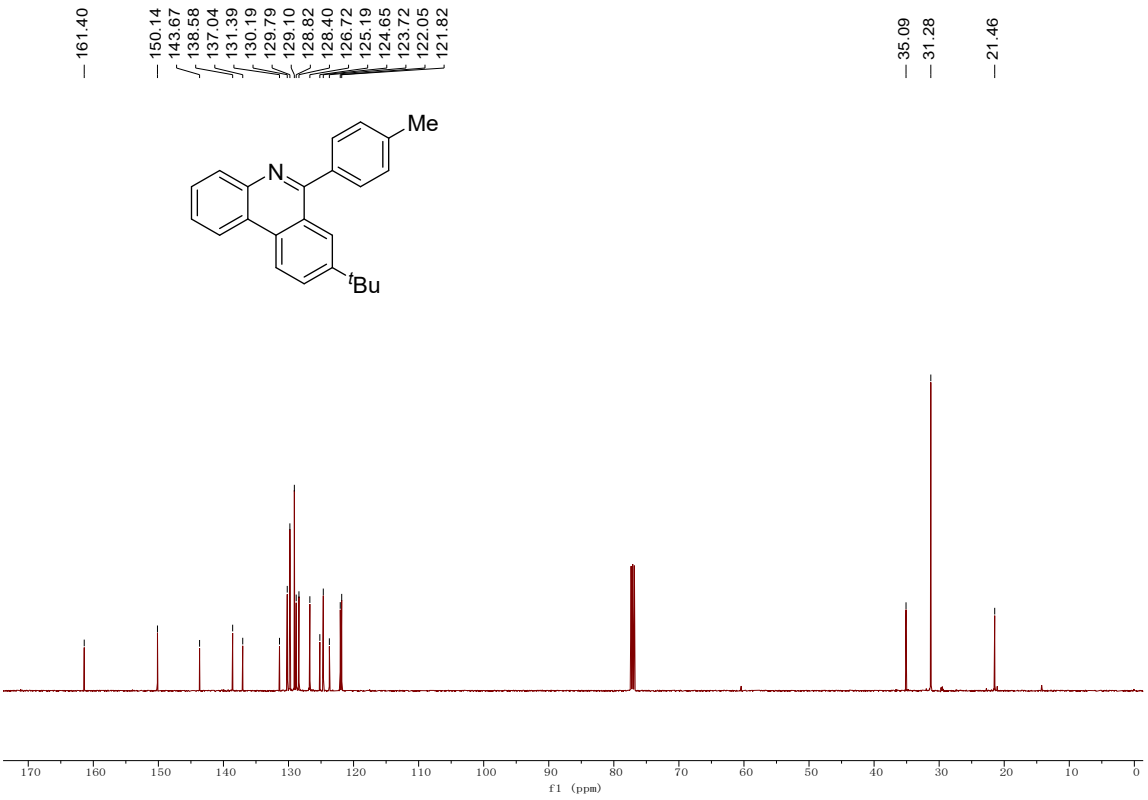
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ba** in $CDCl_3$



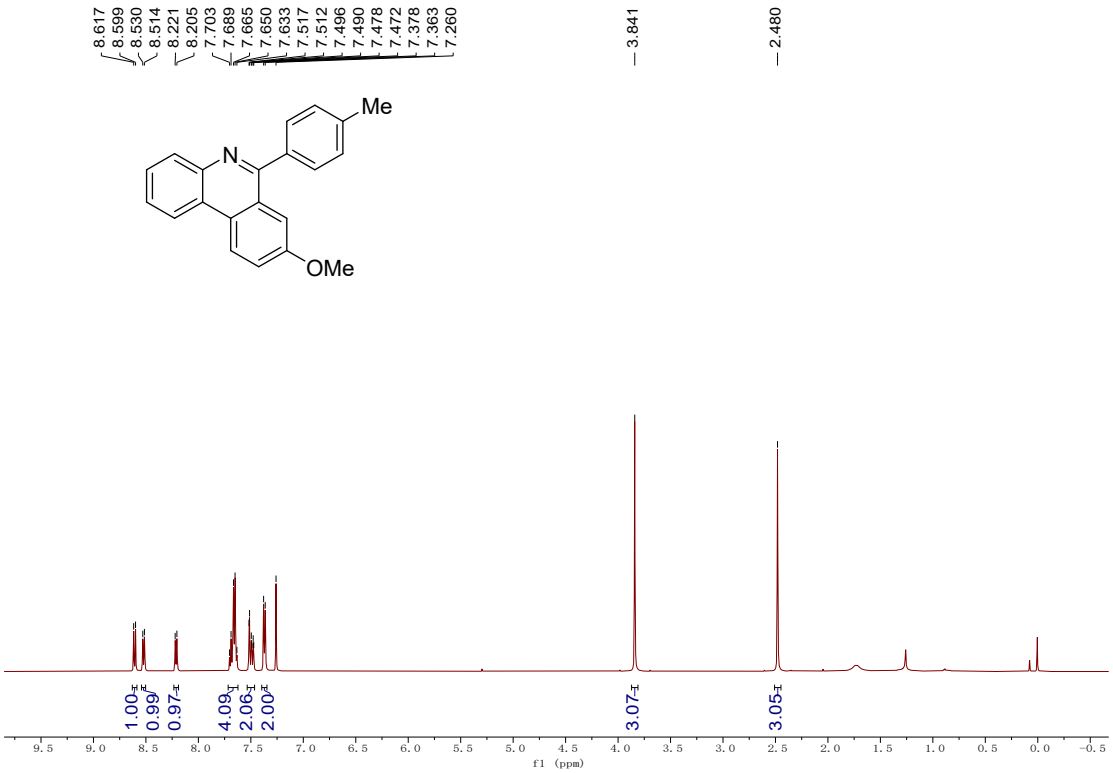
500 Hz ^{1}H NMR spectrum of **3ca** in $CDCl_3$



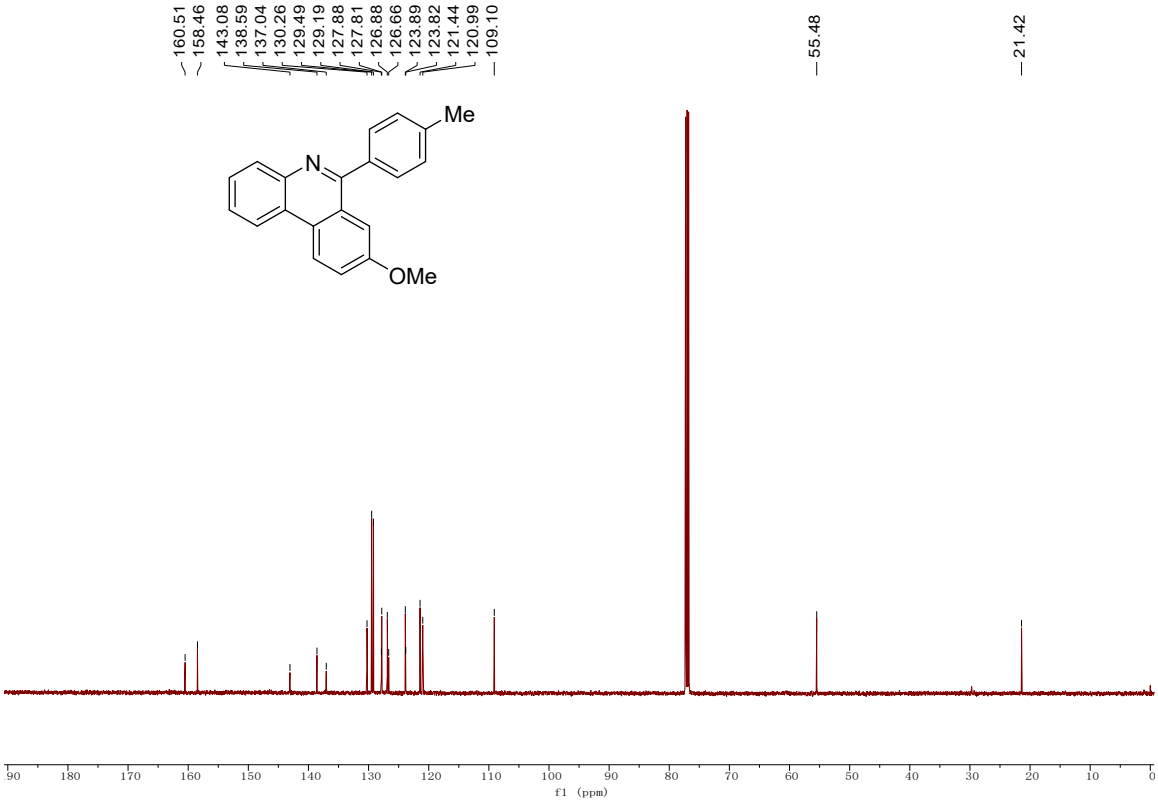
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ca** in $CDCl_3$



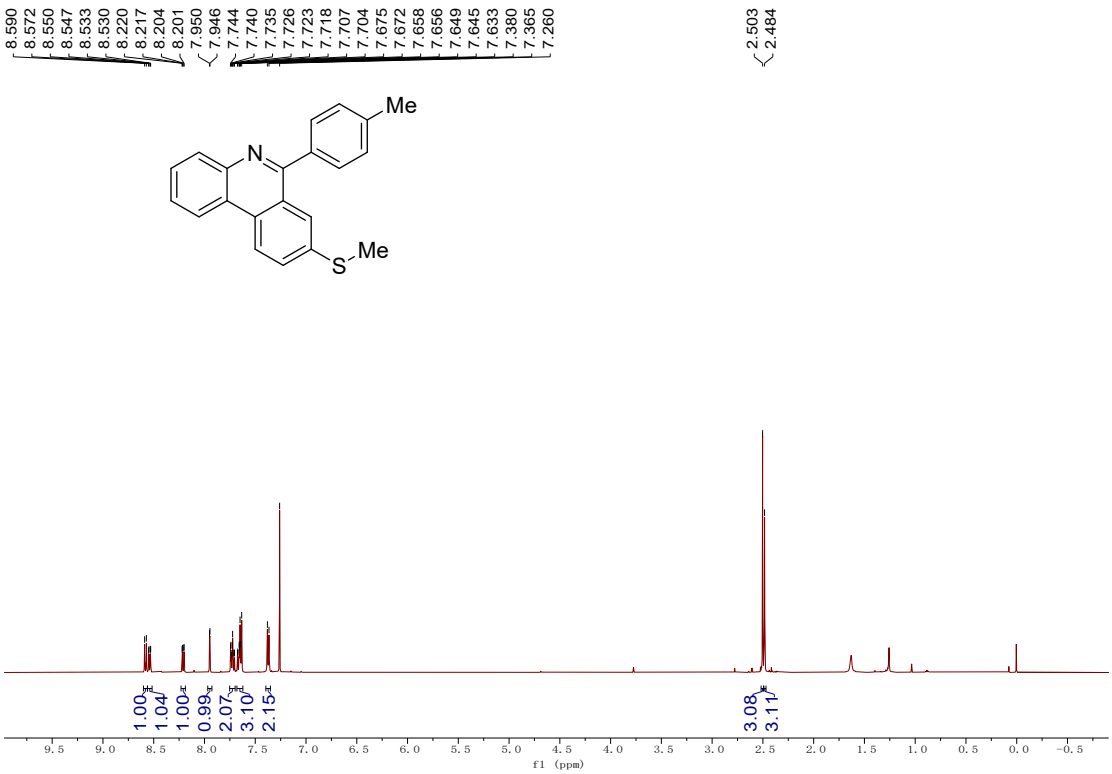
500 Hz ^{1}H NMR spectrum of **3da** in $CDCl_3$



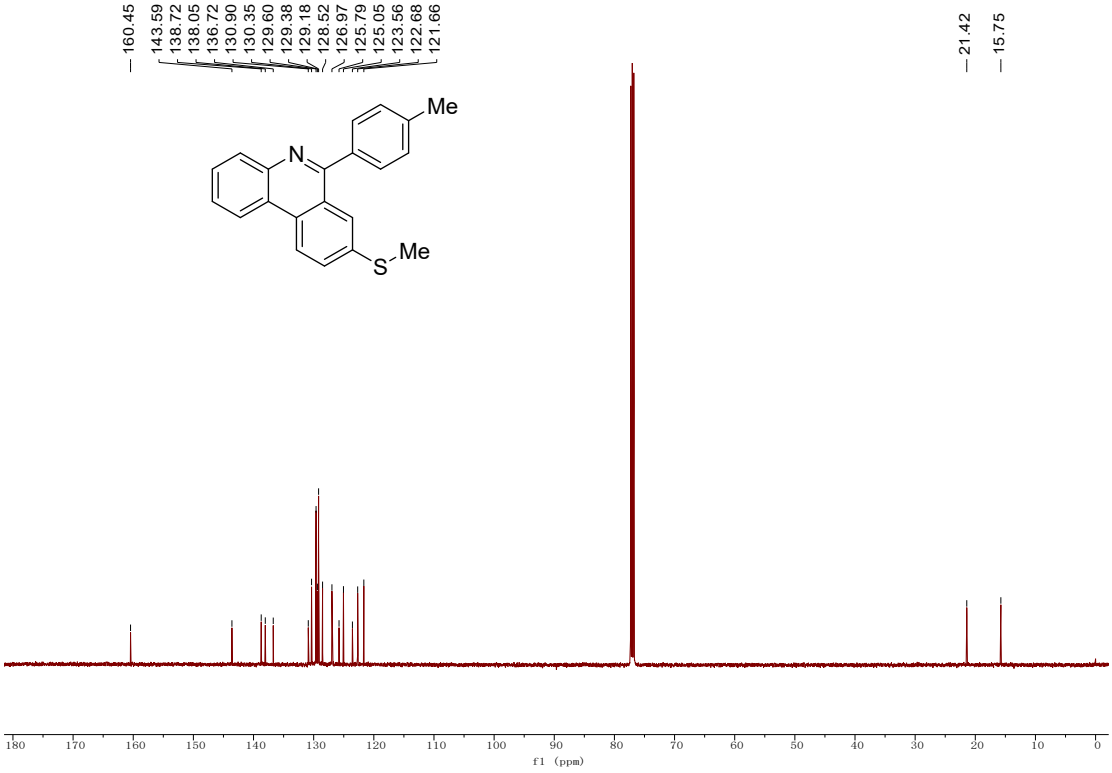
126 Hz ^{13}C {^{1}H} NMR spectrum of **3da** in $CDCl_3$



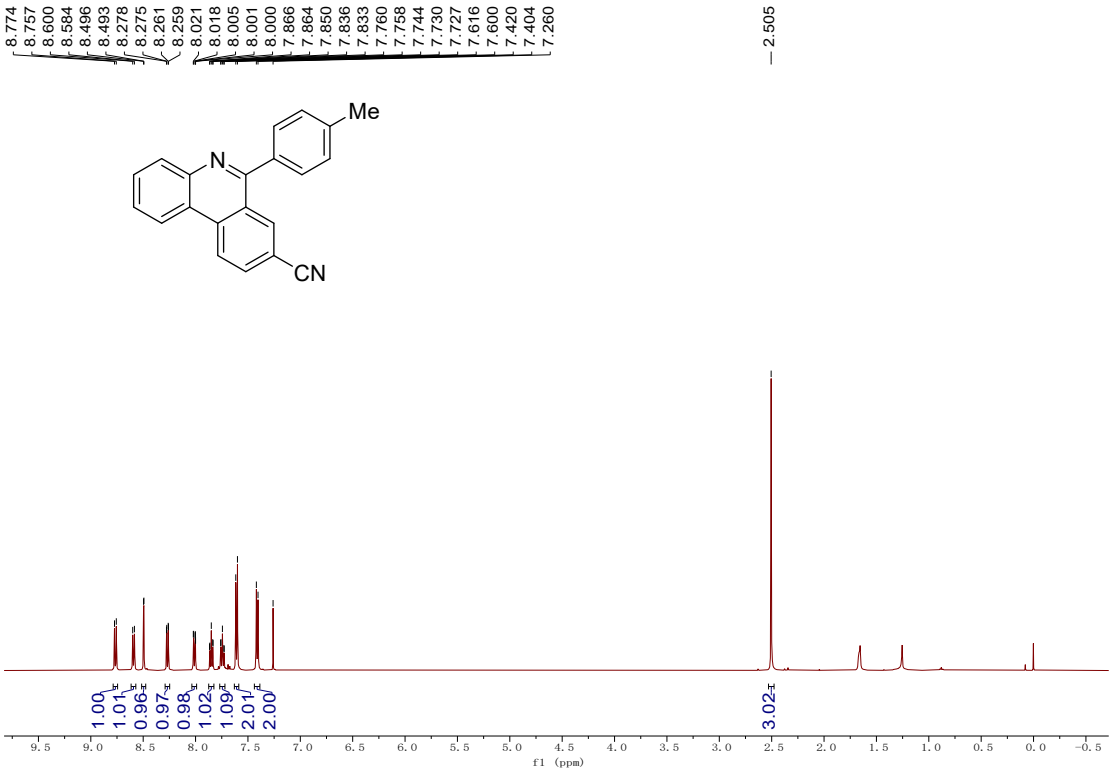
500 Hz ^{1}H NMR spectrum of **3ea** in $CDCl_3$



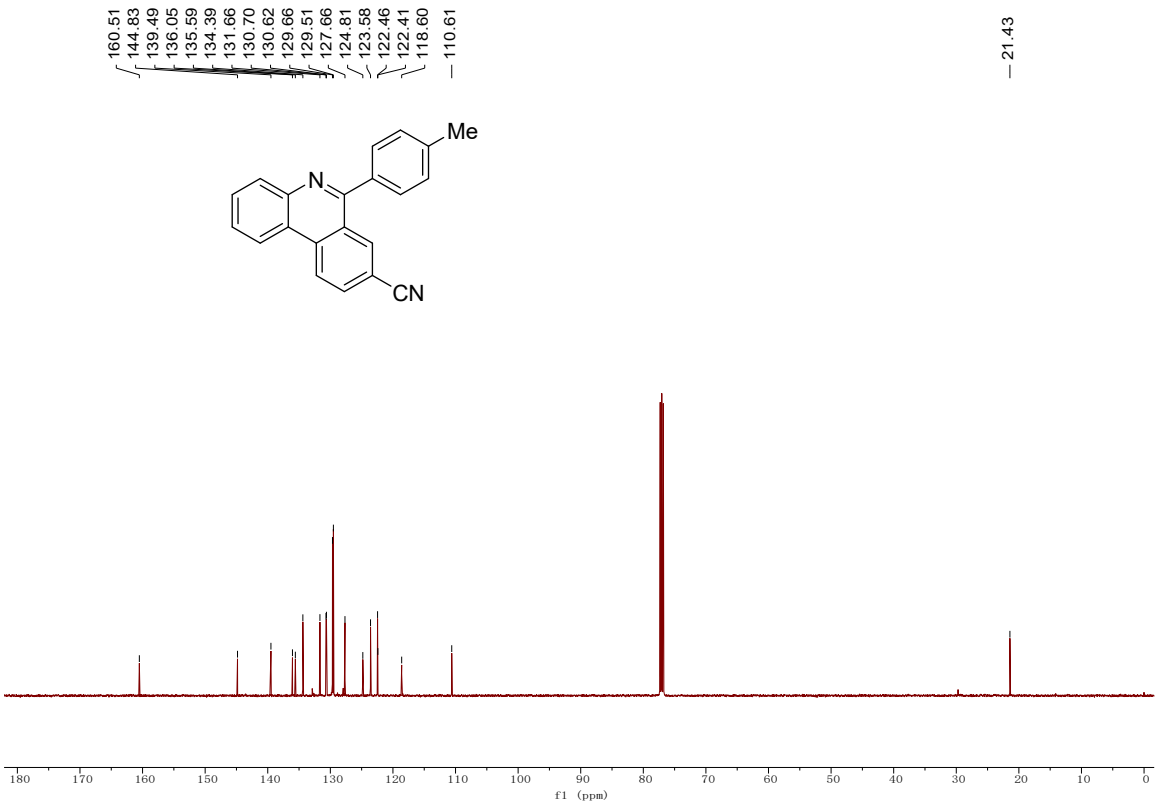
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ea** in $CDCl_3$



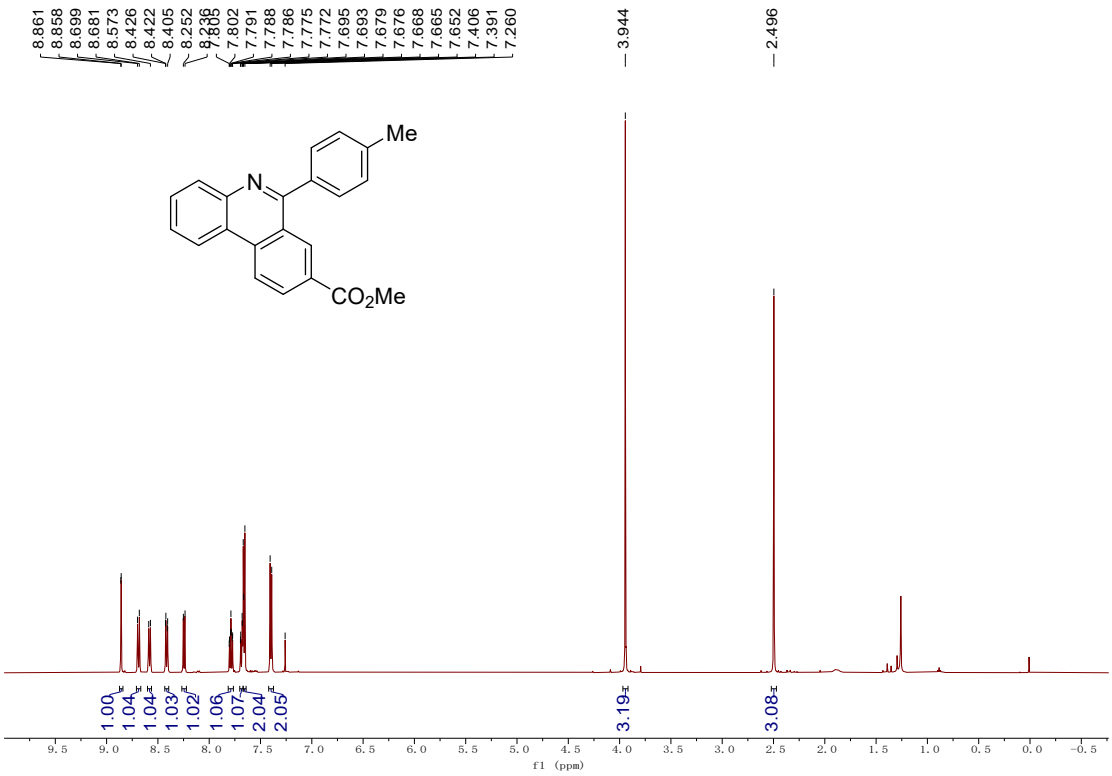
500 Hz ^{1}H NMR spectrum of **3fa** in $CDCl_3$



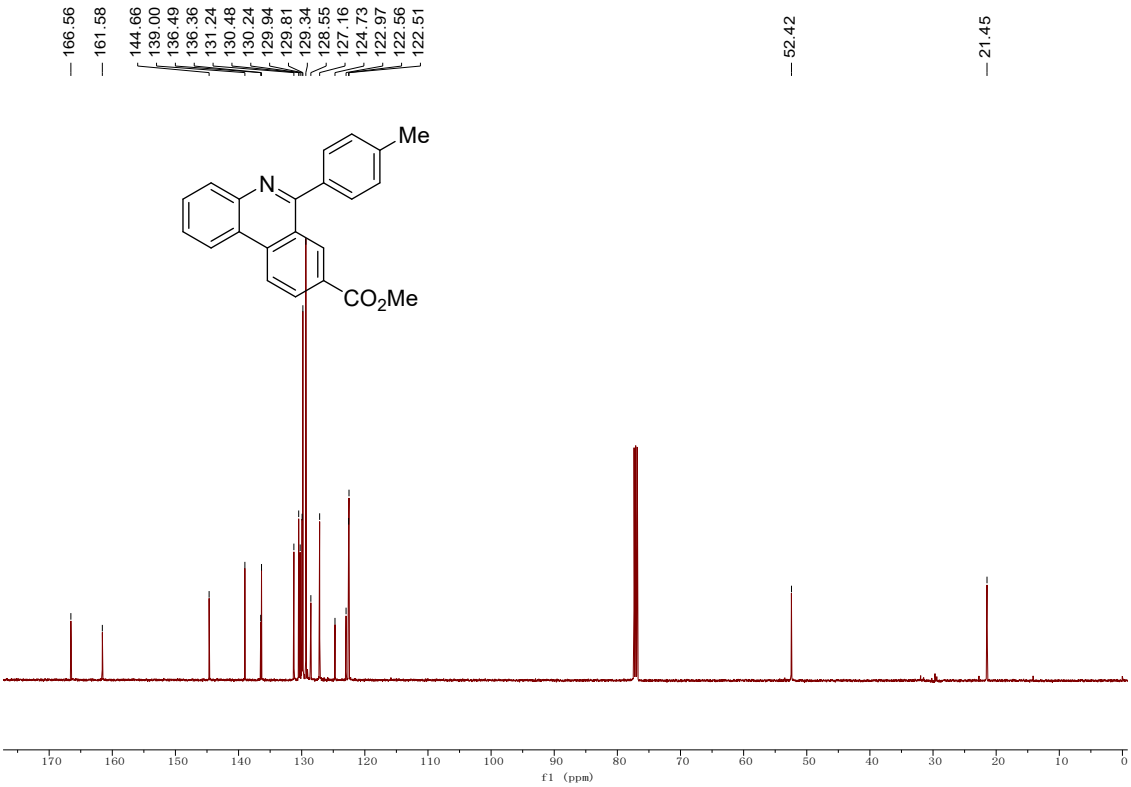
126 Hz ^{13}C {^{1}H} NMR spectrum of **3fa** in $CDCl_3$



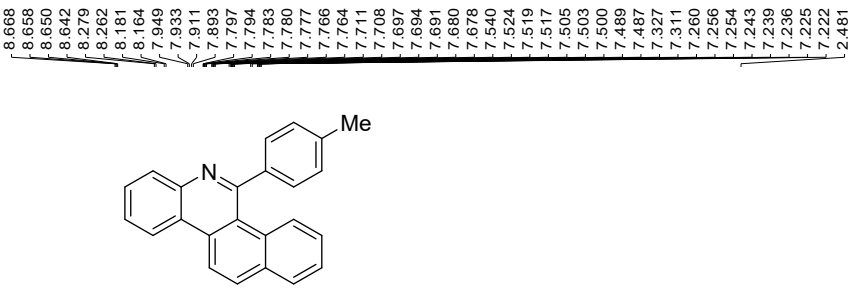
500 Hz ^{1}H NMR spectrum of **3ga** in $CDCl_3$

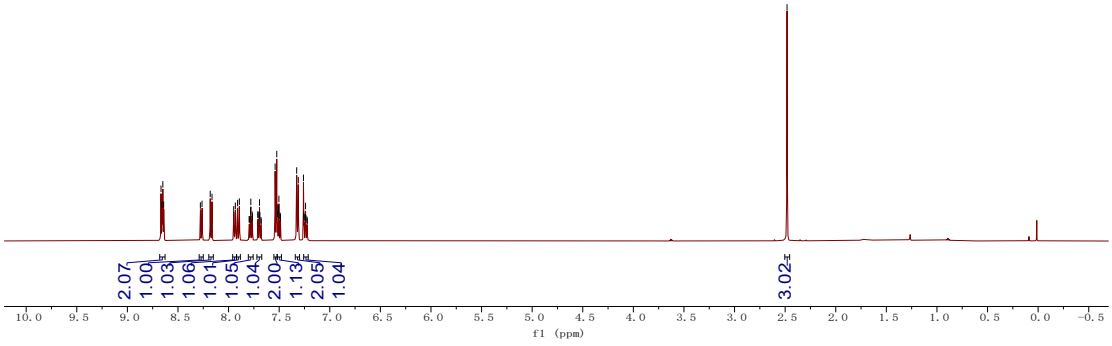


126 Hz ^{13}C {^{1}H} NMR spectrum of **3ga** in $CDCl_3$

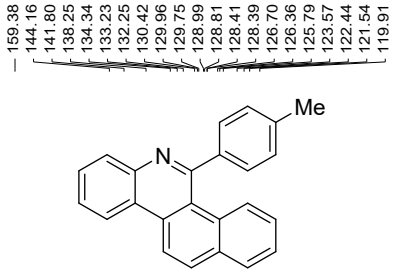


500 Hz ^{1}H NMR spectrum of **3ha** in $CDCl_3$

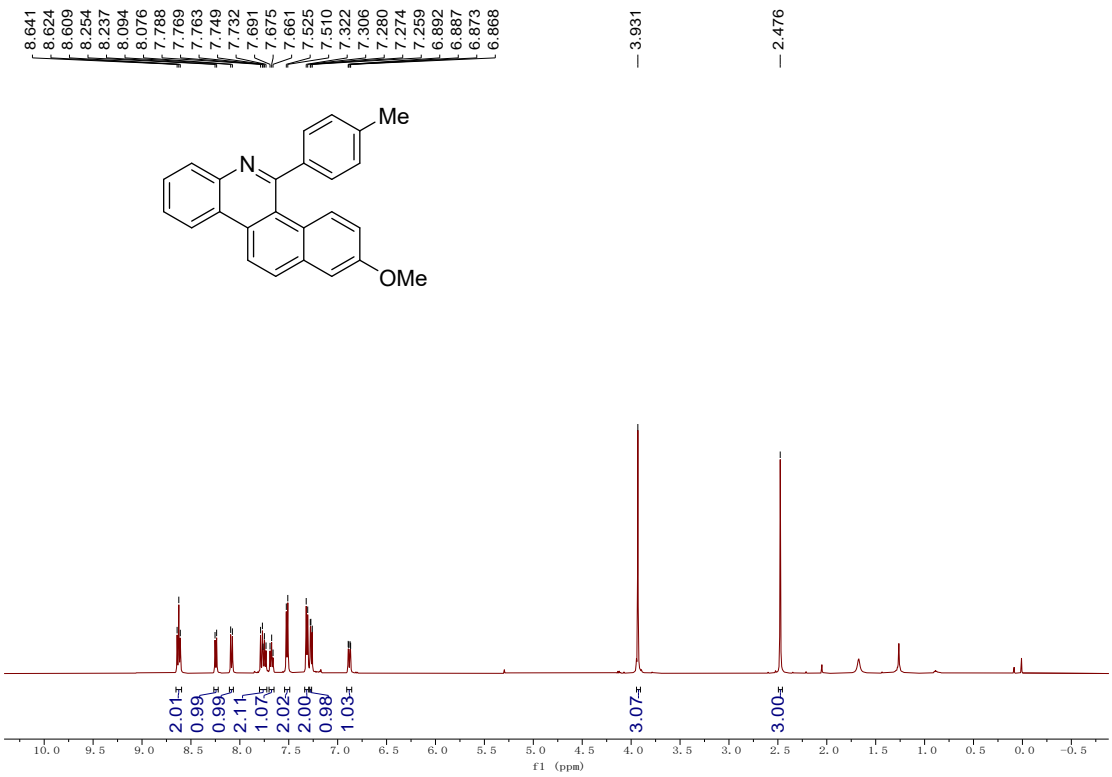




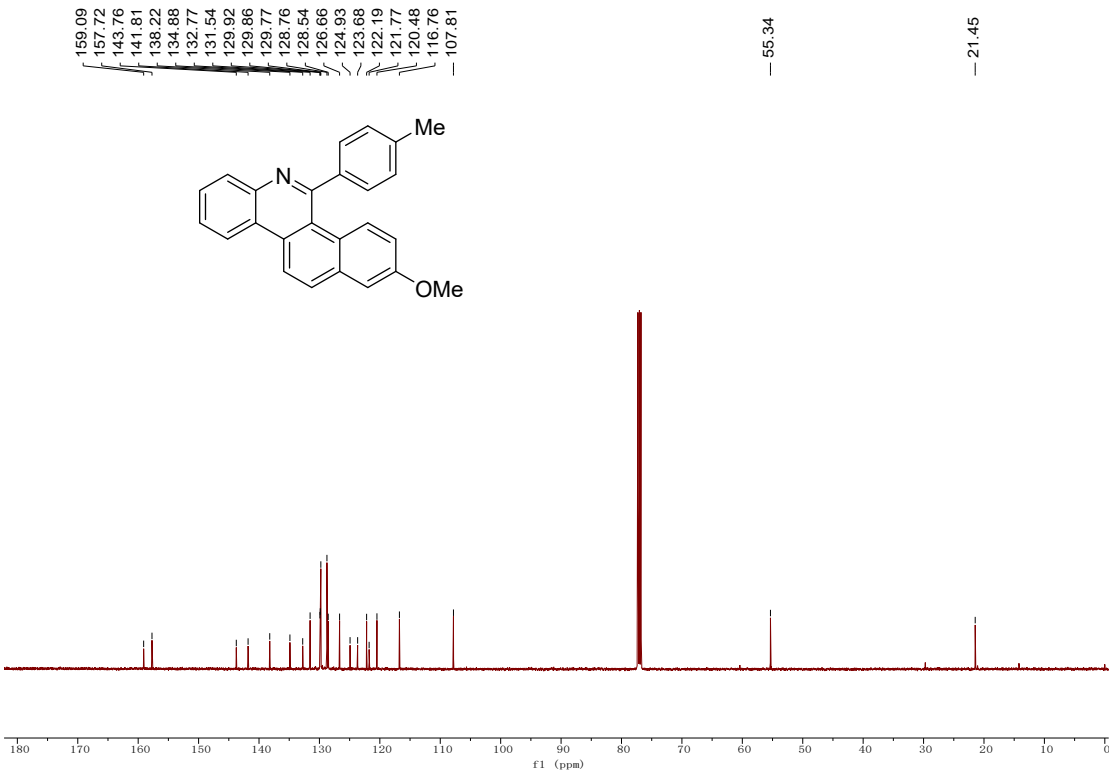
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ha** in $CDCl_3$



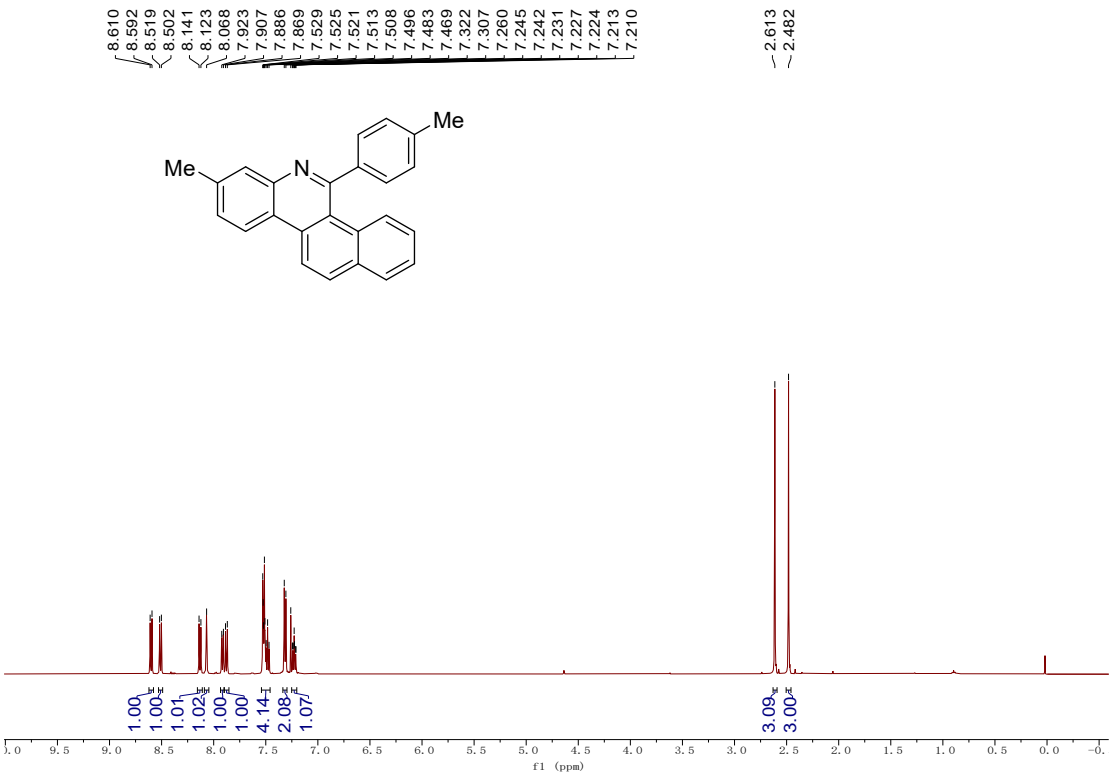
500 Hz ^{1}H NMR spectrum of **3ia** in $CDCl_3$



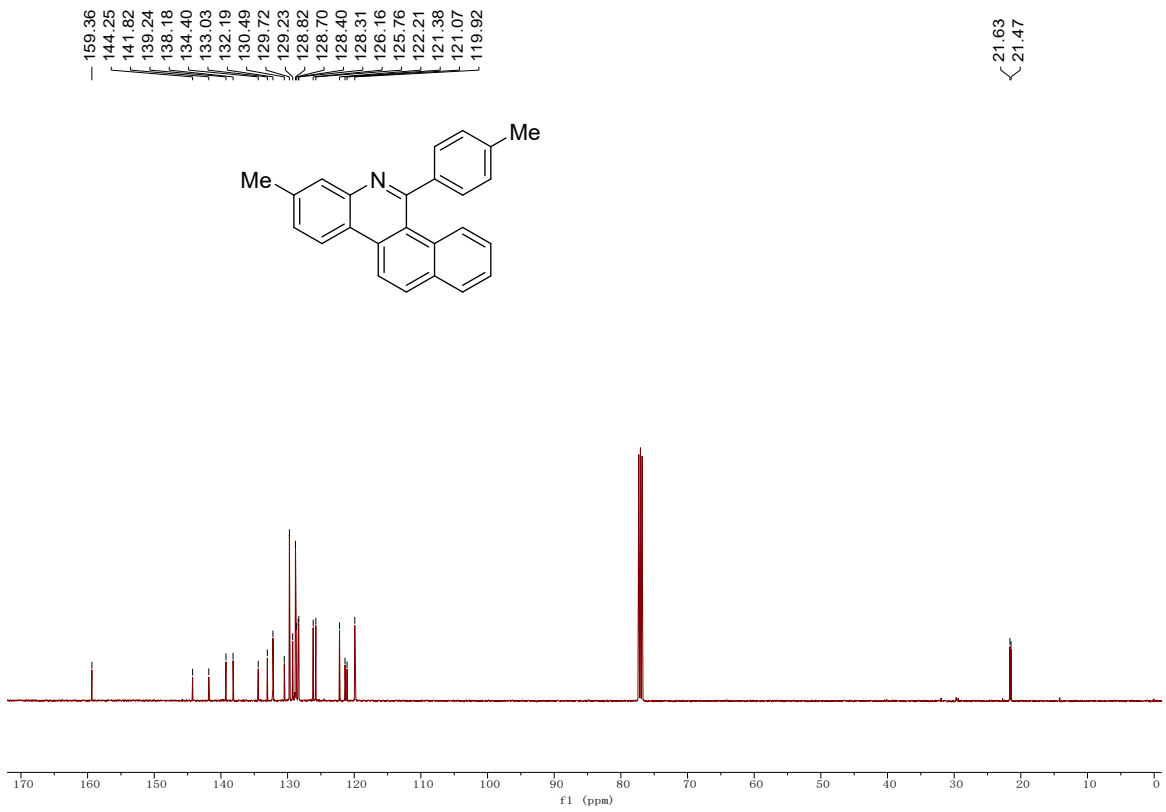
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ia** in $CDCl_3$



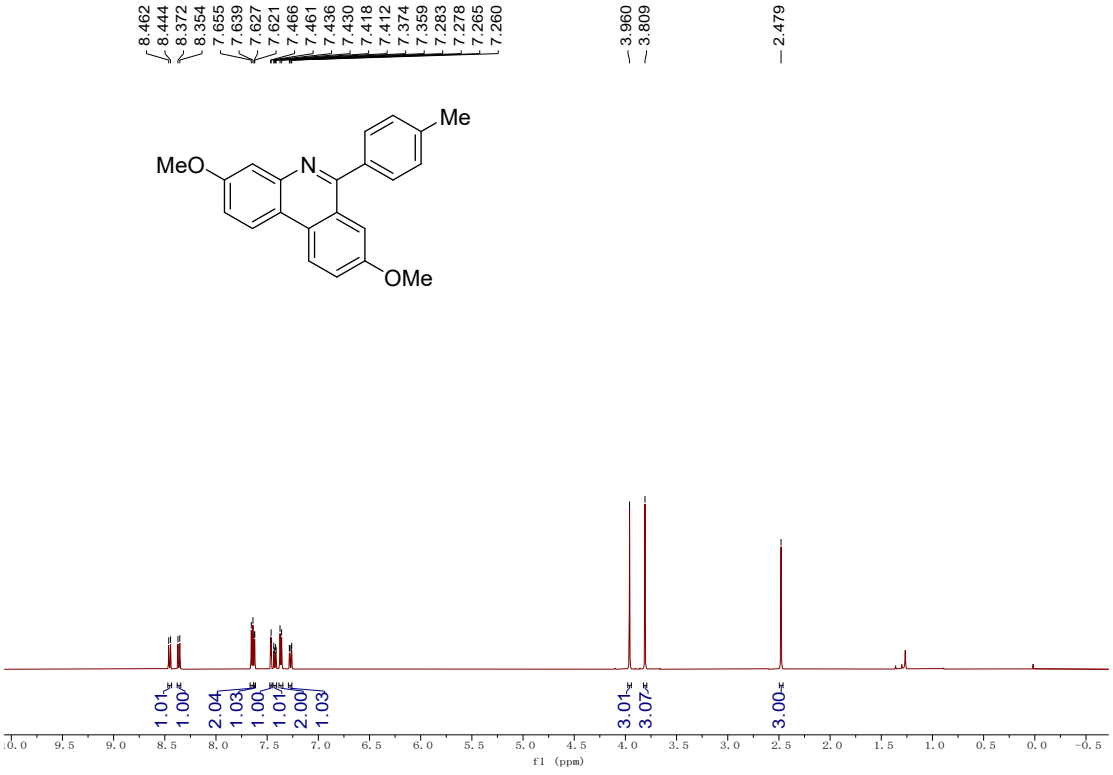
500 Hz ^{1}H NMR spectrum of **3ja** in $CDCl_3$



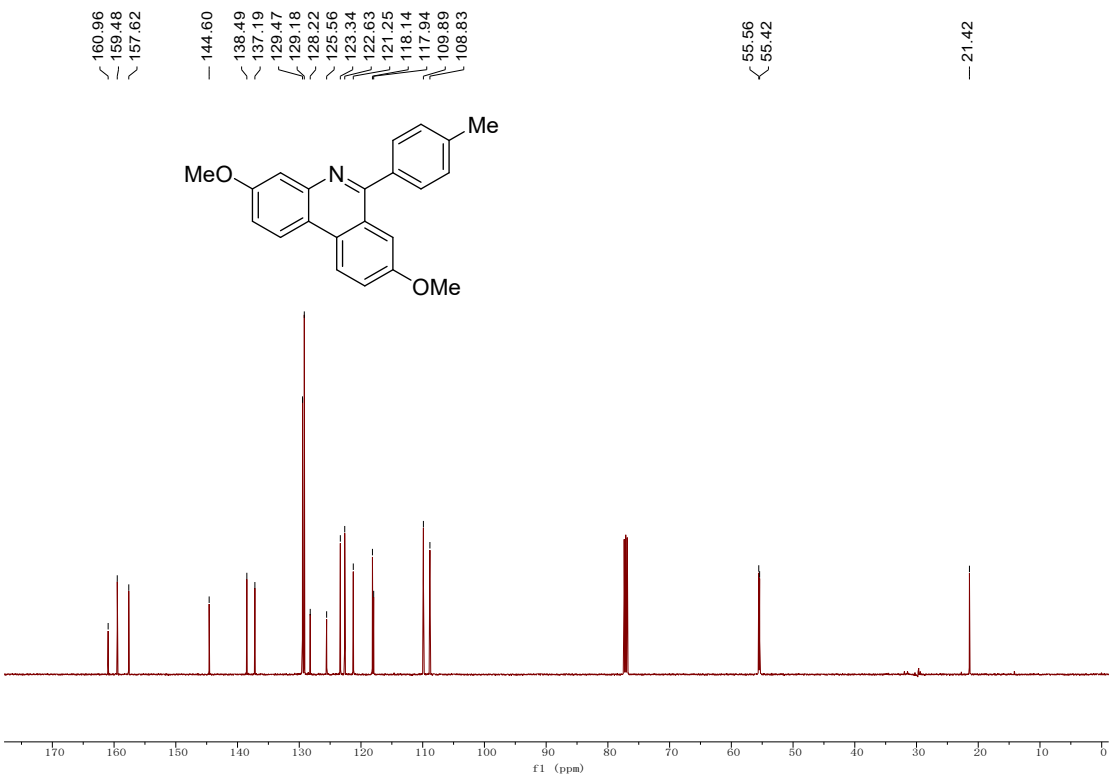
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ja** in $CDCl_3$



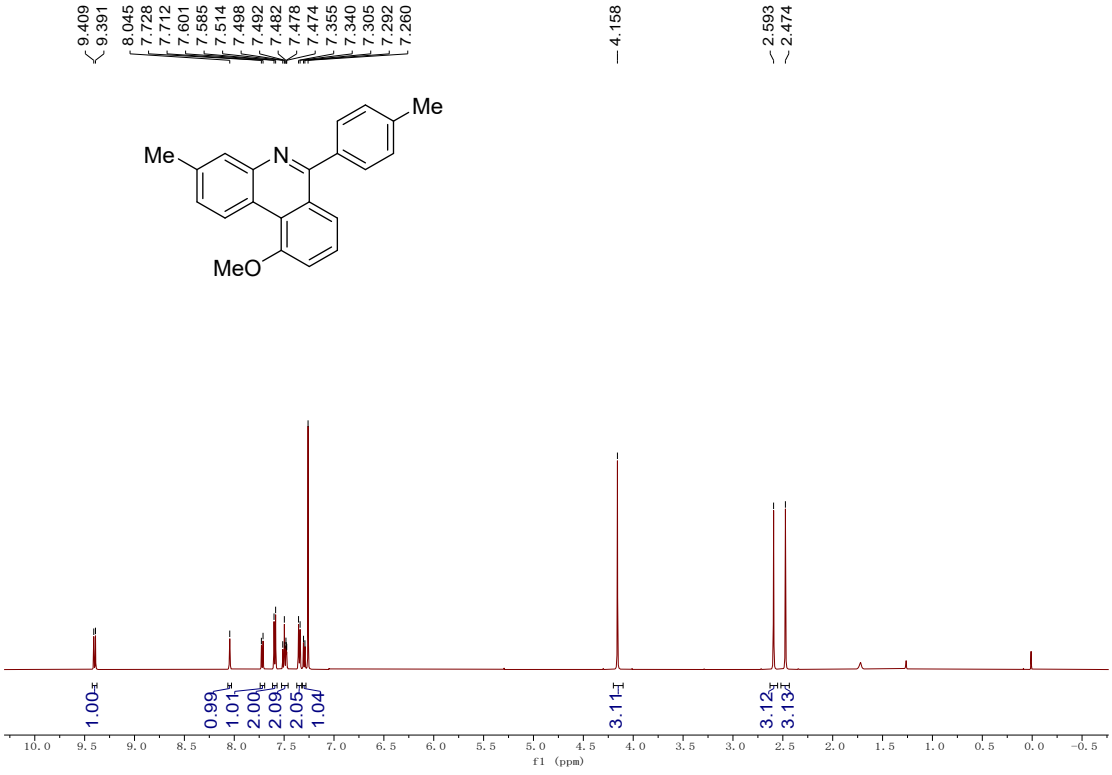
500 Hz ^{1}H NMR spectrum of **3ka** in $CDCl_3$



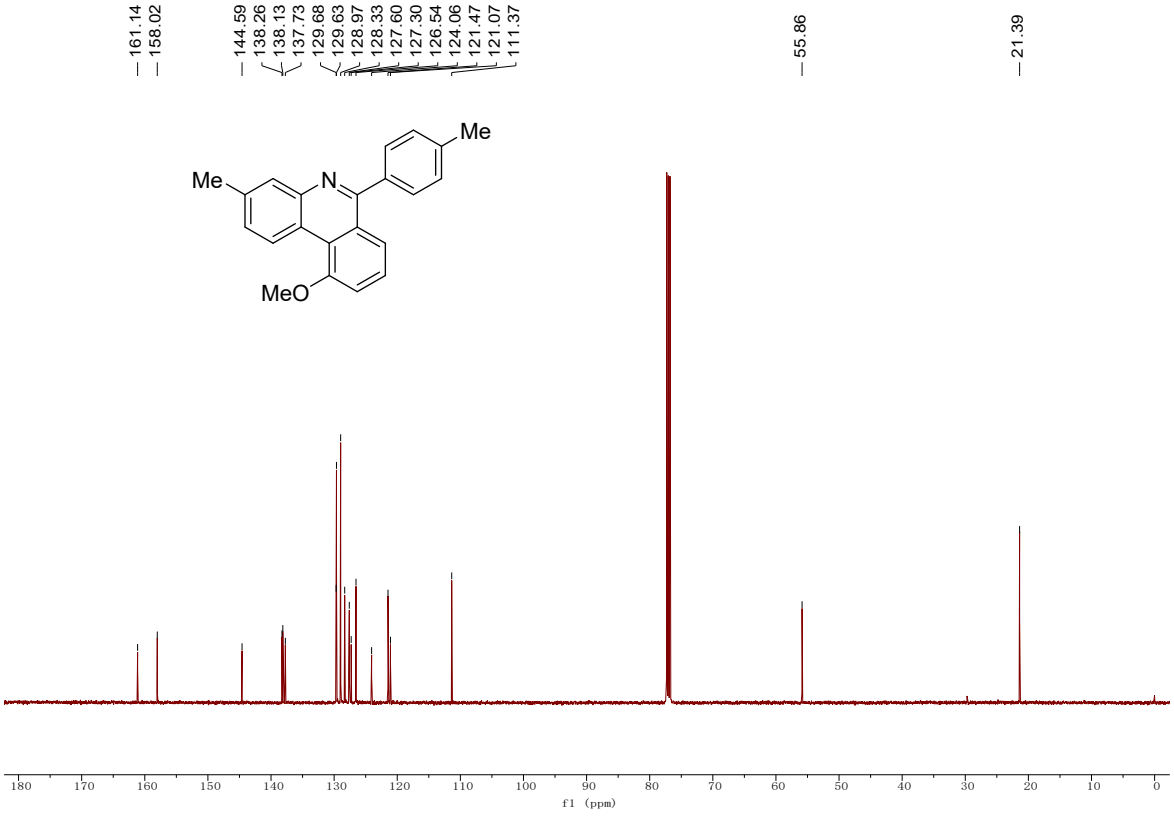
126 Hz ^{13}C {^{1}H} NMR spectrum of **3ka** in $CDCl_3$



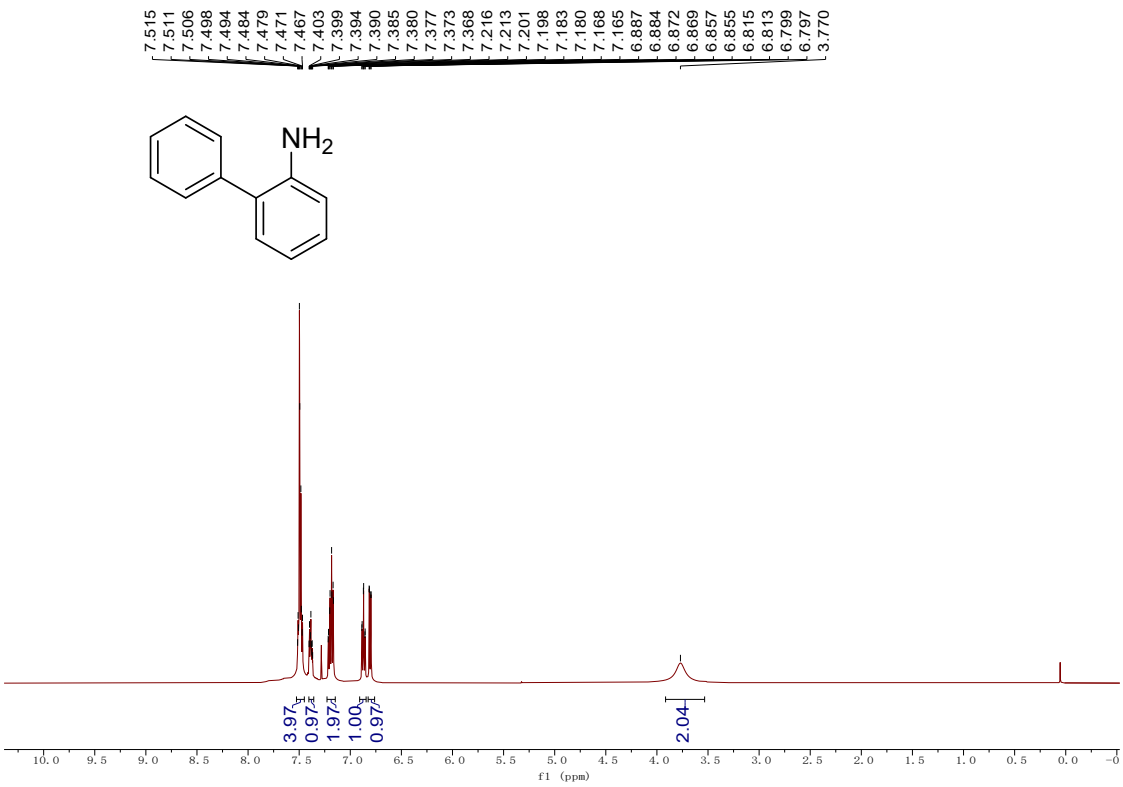
500 Hz ^{1}H NMR spectrum of **3la** in $CDCl_3$



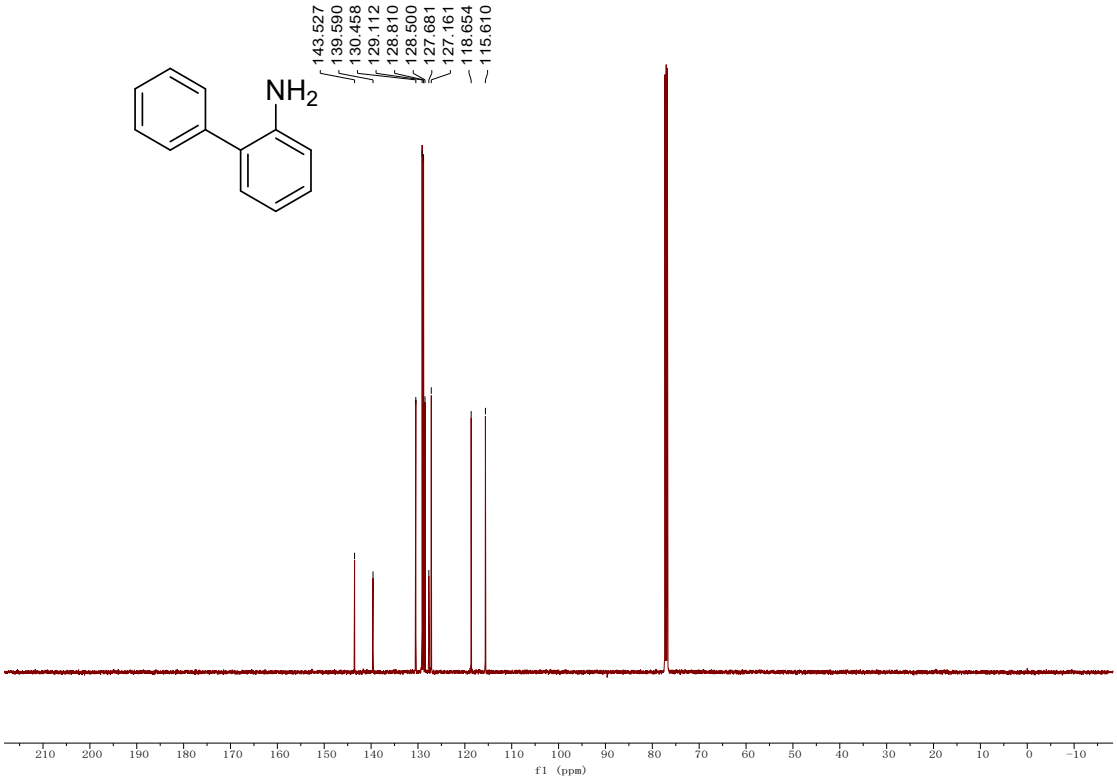
126 Hz ^{13}C {^{1}H} NMR spectrum of **3la** in $CDCl_3$



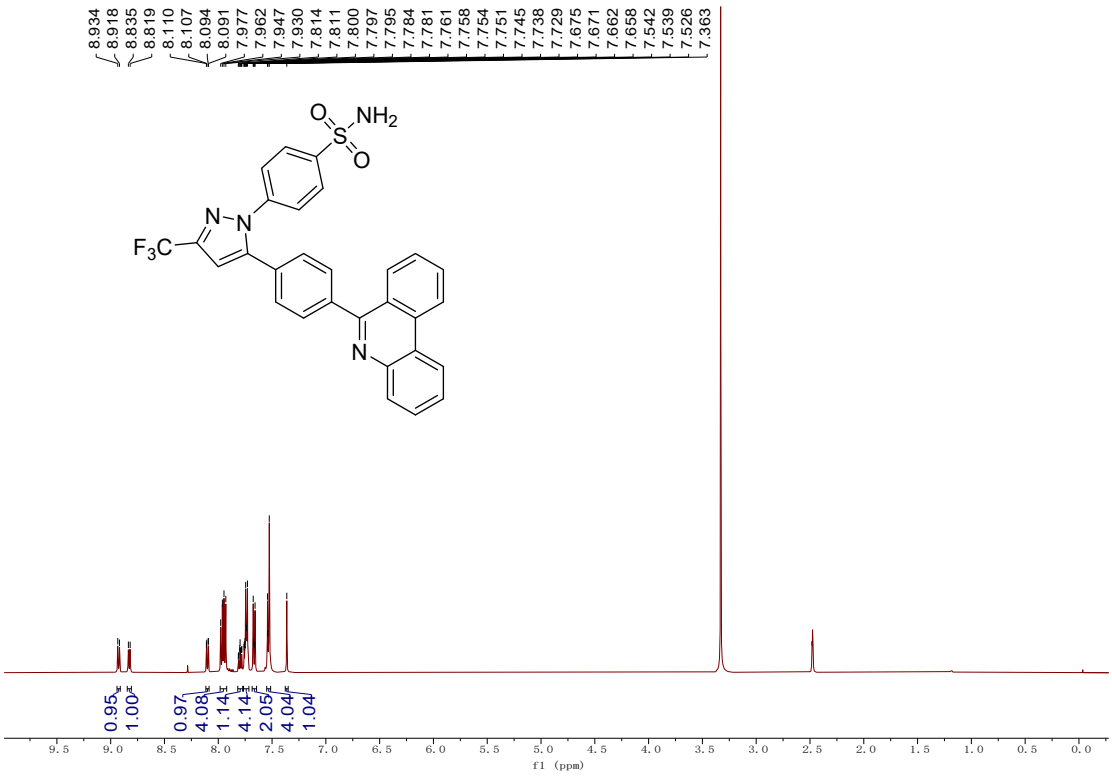
500 Hz ^{1}H NMR spectrum of **I** in $CDCl_3$



126 Hz ^{13}C {^{1}H} NMR spectrum of **I** in $CDCl_3$



500 Hz ^{1}H NMR spectrum of **5** in $CDCl_3$



471 Hz ^{19}F {^{1}H} NMR spectrum of **5** in $CDCl_3$

126 Hz ^{13}C {^{1}H} NMR spectrum of **5** in $CDCl_3$