Supporting Information

Bromide-promoted cascade annulation of isocyano-biaryls with aldehydes through photoredox catalysis

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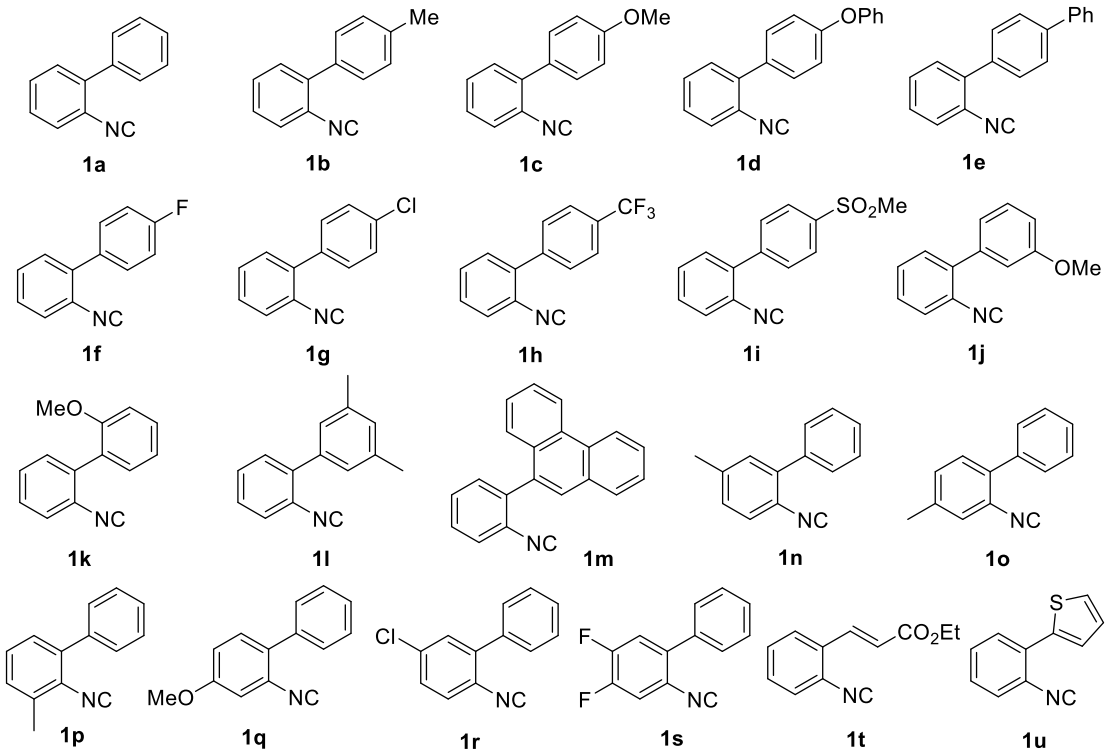
1. General information

Reactions via general procedure were carried out under argon atmosphere unless otherwise noted. Column chromatography was performed using silica gel (200-300 mesh) or preparative thin layer chromatography was performed using silica gel (GF254). ^{1}H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument using $CDCl_3$ as solvent. Chemical shift values are reported in δ (ppm) relative to $CDCl_3$ (^{1}H NMR, δ = 7.26; ^{13}C NMR, δ = 77.00), respectively. In order to indicate the signal multiplicity, the following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet) and m (multiplet) as well as combinations of them. High-resolution mass spectra (ESI) were obtained with the Thermo Scientific LTQ Orbitrap XL mass spectrometer. Melting points were measured with a YUHUA X-5 melting point instrument and were uncorrected. A commercially available blue LED (35W, HIPAR30) was purchased from Shenzhen Jing Feng Times Lighting Technology Co., Ltd as the light source. All irradiation reactions were carried out in a borosilicate glass vessel. The distance from the light source to the irradiation vessel is around 4-5 cm. Unless otherwise noted, all photocatalysts and other reagents were obtained from commercial suppliers and used without further purification.

2. Procedures for the preparation of 2-isocyanobiaryls

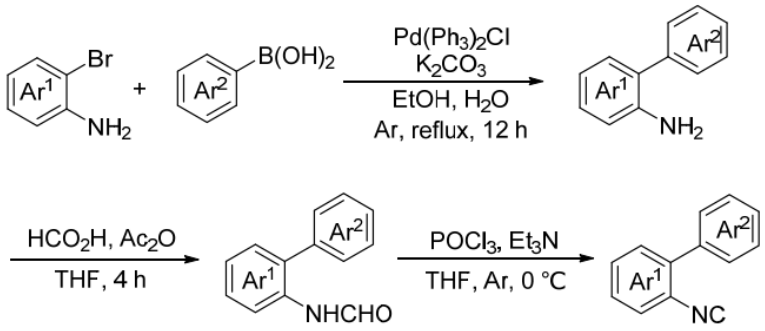


2-Bromoarylamine (10.0 mmol), aryl boronic acid (12.0 mmol), K_2CO_3 (6.2 g, 45.0 mmol) and $Pd(PPh_3)_2Cl_2$ (140.4 mg, 0.2 mmol) were added to a mixture of EtOH (20 mL) and water (20 mL) at room temperature. The mixture was heated to reflux for 12 h under Ar. After cooled to room temperature, the mixture was extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford 2-aryl aniline.

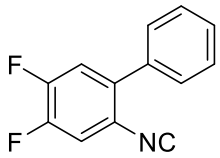
Then, acetic formic anhydride (18.0 mmol), which was newly prepared from the reaction of acetic anhydride (1.7 mL, 18.0 mmol) with formic acid (0.8 mL, 20.0 mmol) at 55 °C for 2 h, was added dropwise to a mixture of 2-aryl aniline (3.0 mmol) in 6.0 mL THF at 0 °C. After the addition was completed, the mixture was warmed to room temperature and stirred for 4 h. Then, the reaction was quenched with saturated $NaHCO_3$ and extracted with EtOAc. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo to give the corresponding formamides.

These formamides were used for the subsequent dehydration reaction without further purification. $POCl_3$ (0.8 mL, 9.0 mmol) was added via syringe pump to a mixture of Et_3N (3.8 mL, 27.0 mmol) and formamides (3.0 mmol) in THF (6 mL) at 0 °C within 2 hours. After the addition was completed, the resulting mixture was stirred at 0 °C for another 2 hours. Then, the mixture was

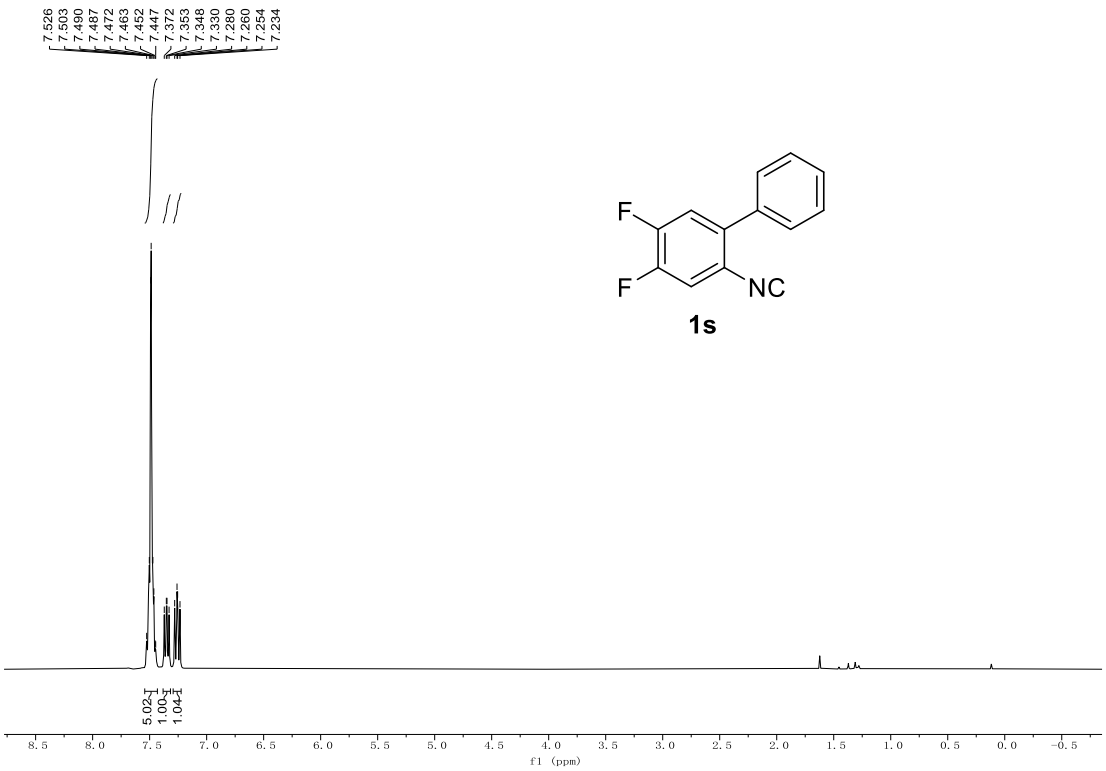
quenched with sat. $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layer was washed with brine, dried over anhydrous Na_2SO_4 and concentrated in vacuo. The residue was purified by chromatography on silica gel using petroleum ether/ethyl acetate as eluent to afford 2-isocyanobiaryls.



Substrates (**1a-1c**, **1e**, **1g-1h**, **1k**, **1t**)[1], **1d**[2], (**1f**, **1i-1j**, **1n-1o**)[3], (**1l**, **1r**)[4], (**1m**, **1q**)[5], **1p**[6], and **1u**[7] are known compounds, Substrate **1s** is a new compound, and the characterization data and NMR spectra are provided.



4,5-difluoro-2-isocyano-1,1'-biphenyl (1s): According to the procedure, **1s** was purified by flash column chromatography on silica gel using petroleum ether and ethyl acetate (10:1) as an eluent and obtained in 75% yield (1.6 g). Yellow solid. mp: 88 – 92 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.54 – 7.43 (m, 5H), 7.35 (dd, *J* = 9.6, 7.3 Hz, 1H), 7.26 (dd, *J* = 10.4, 8.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.0, 150.6 (dd, *J* = 255.5, 12.5 Hz), 159.1(dd, *J* = 253.5, 13.9 Hz), 136.5 (dd, *J* = 6.4, 4.2 Hz), 135.2, 129.0, 128.9, 120.3 (m), 119.2 (d, *J* = 18.9 Hz), 117.2 (d, *J* = 20.6 Hz); ^{19}F NMR (376 MHz, Chloroform-*d*) δ -132.69 (d, *J* = 21.9 Hz), -135.84 (d, *J* = 21.8 Hz). HRMS (ESI) m/z calcd for $C_{13}H_8NF_2$ $(M+H)^+$ 216.0619, found 216.0621.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7.463
7.452
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7.348
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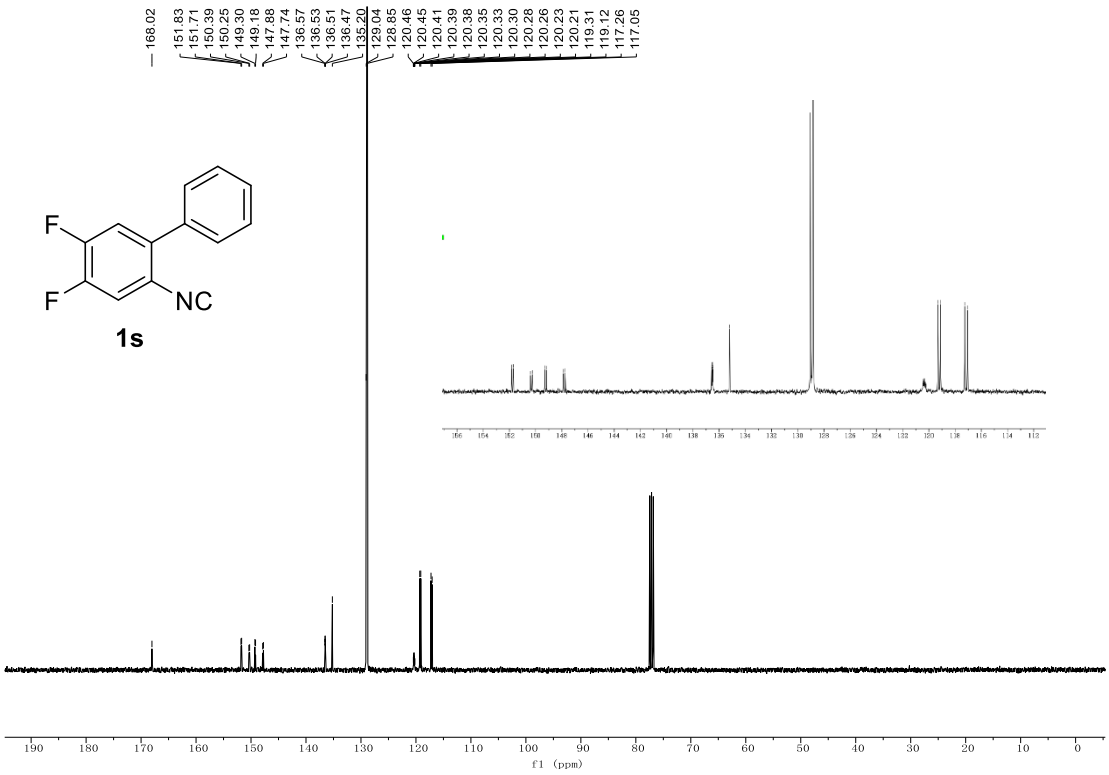
1.00
1.04
F
F
NC
1s
f1 (ppm)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151.83
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150.39
150.25
149.30
149.18
147.88
147.74
136.57
136.53
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135.20
129.04
128.85
120.46
120.45
120.41
120.39
120.38
120.35
120.33
120.30
120.28
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117.26
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F
F
NC
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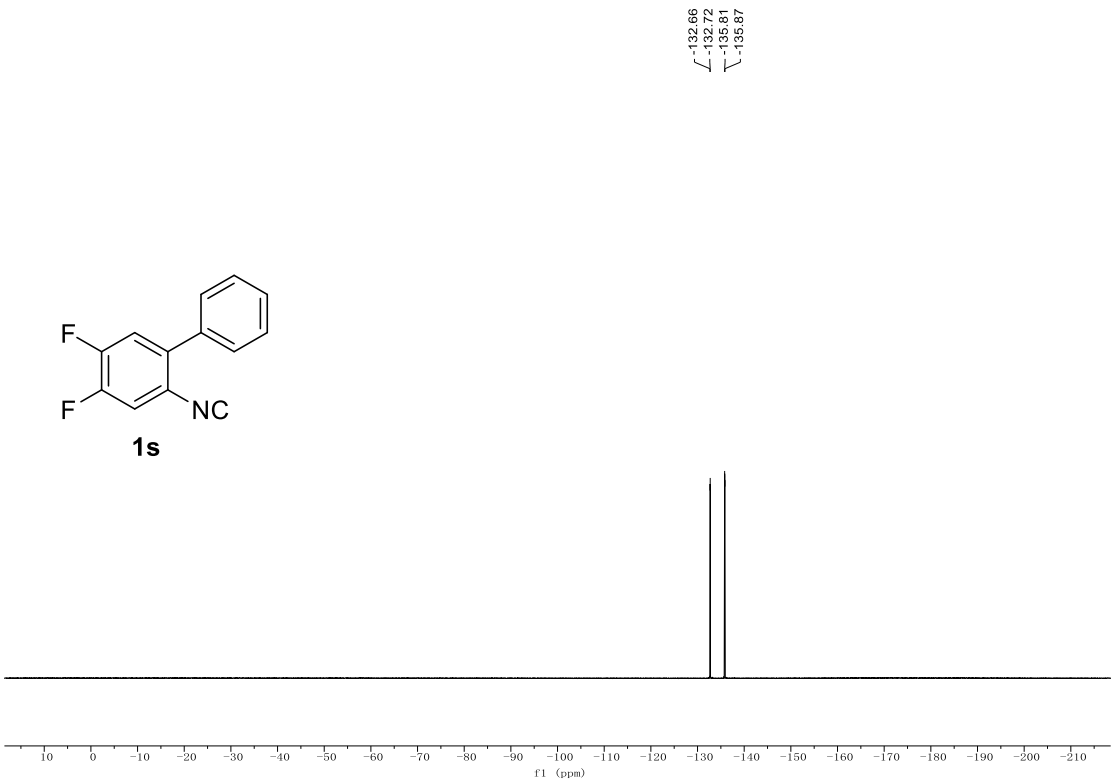
f1 (ppm)



3. General procedure for the synthesis of 3a

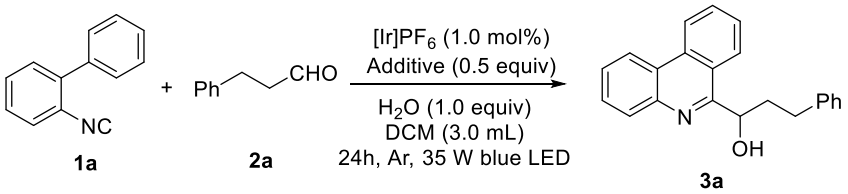
Standard conditions: A 10 mL reaction vessel was charged with 2-isocyano-1,1'-biphenyl (**1a**, 0.2 mmol, 35.8 mg), phenylpropyl aldehyde (**2a**, 0.4 mmol, 53.1 μL), NH_4Br (0.06 mmol, 5.9 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2.3 mg), H_2O (0.2 mmol, 3.6 μL), and DCM (3.0 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The resulting mixture was stirred at 35 °C for 24 hours under irradiation with a 35 W blue LED. The reaction was monitored by TLC. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with ethyl acetate (3×10 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. Preparative thin layer chromatography was performed using silica gel (GF254) to give product **3a**.

Gram-scale experiment: A 250 mL reaction vessel was charged with 2-isocyano-1,1'-biphenyl (**1a**, 6.0 mmol, 1075 mg), phenylpropyl aldehyde (**2a**, 12.0 mmol, 1.6 mL), NH_4Br (1.8 mmol, 177 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.06 mmol, 69 mg), H_2O (6.0 mmol, 108 μL), and DCM (60 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The resulting mixture was stirred at 35 °C for 24 hours under irradiation

with two 35 W blue LEDs. The crude reaction mixture was quenched with saturated sodium carbonate and extracted with acetate (3 × 20 mL). The extracts were combined, dried over sodium sulfate, filtered and the volatiles were removed under reduced pressure. The reaction yields were quantified by separation, and column chromatography was performed using silica gel (200-300 mesh) to give product **3a**, 1.03 g, 55% yield.

4. Optimization of the reaction conditions

Table 1. The effect of additive on this reaction

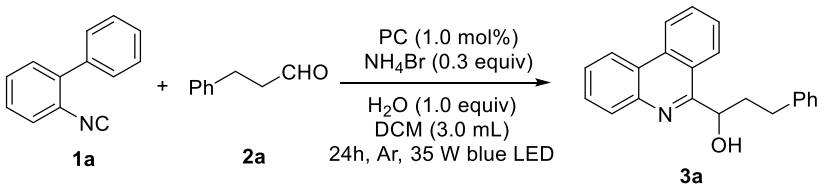


1a **2a** **3a**

Entry	Additive	Yield of **3a** (%)
1	NaBr	44
2	NH_4Br	53
3	LiCl	7
4	LiBr	48
5	KI	trace
6	NiCl	trace
7	NaI	nd
8	KBr	45
9 [b]	NH_4Br	58
10 [b]	TBABr	44
11 [c]	TBABr	50

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), [Ir]PF_6 (1 mol %), additive (0.5 equiv), H_2O (1 equiv), DCM (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield. [b] Additive (0.3 equiv). [c] In the absence of H_2O.

Table 2. The effect of photocatalyst on this reaction



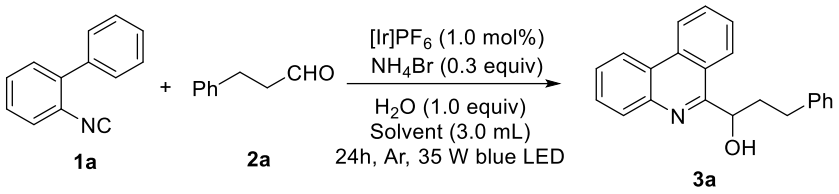
1a **2a** **3a**

Entry	PC	Yield of **3a** (%) [b]
1	4CzIPN	36
2	Rose Bengal	34

3	$[Ru(bpy)_3](PF_6)_2$	trace
4	9-Fluorenone	19
5	Eosin B	trace
6	$Ir(ppy)_3$	trace
7	$Ir[dF(Me)ppy]_2(dtbbpy)PF_6$	14
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	57
9	Eosin Y	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), PC (1 mol %), NH_4Br (0.3 equiv), H_2O (1 equiv), DCM (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

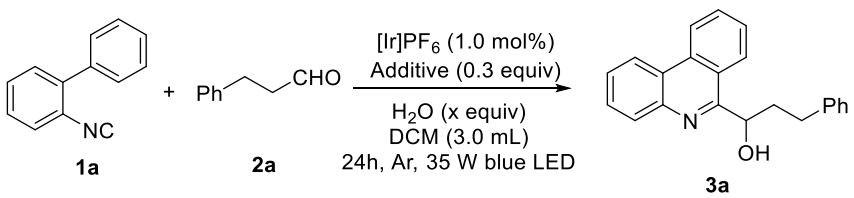
Table 3. The effect of solvent on this reaction



Entry	Solvent	Yield of **3a** (%) [b]
1	DCM	58
2	MeCN	trace
3	PhCl	53
4	EA	50
5	Acetone	25
6	DCE	50
7	THF	16
8	toluene	20
9	PhBr	39
10	EtOH	18
11	DMF	trace
12	Et_2O	22
13	DMSO	trace
14	Cyclohexane	19
15	$CHCl_3$	21

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ir]PF_6$ (1 mol %), NH_4Br (0.3 equiv), H_2O (1 equiv), solvent (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

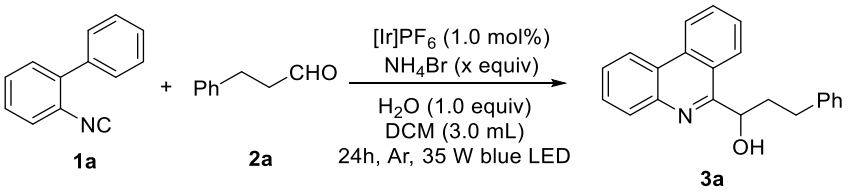
Table 4. The effect of H_2O on this reaction



Entry	H_2O	Yield of **3a** (%) [b]
1	0	50
2	0.5	51
3	1	58
4	2	53
5	10	42

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ir]PF_6$ (1 mol %), NH_4Br (0.3 equiv), H_2O (x equiv), DCM (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

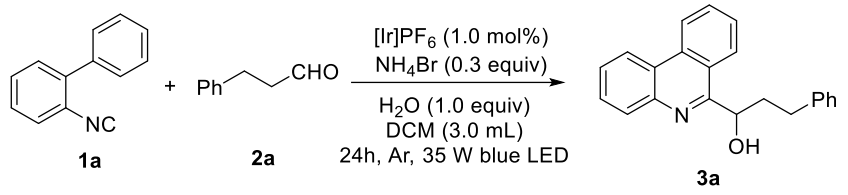
Table 5. The effect of NH_4Br on this reaction



Entry	NH_4Br	Yield of **3a** (%) [b]
1	0	32
2	0.1	50
3	0.3	58
4	0.5	55
5	0.7	55
6	1	50

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ir]PF_6$ (1 mol %), NH_4Br (x equiv), H_2O (1 equiv), DCM (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

Table 6. The effect of feed ratio on this reaction



Entry	**1a:2a**	Yield of **3a** (%) [b]
1	1:3	50
2	1:2	58
3	1:1	38
4	2:1	30

[a] Reaction conditions: $[Ir]PF_6$ (1 mol %), NH_4Br (0.3 equiv), H_2O (1 equiv), solvent (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

Table 7. Control experiments

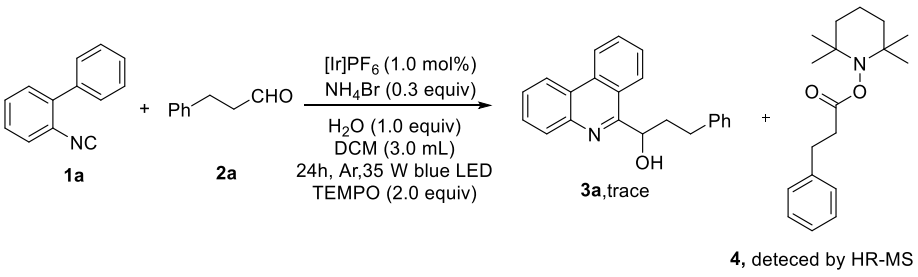
Entry	variation of standard condition	Yield of **3a** (%) [b]
1	none	58
2	without $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	0
3	without NH_4Br	trace
4	In dark	trace

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), $[Ir]PF_6$ (1 mol %), NH_4Br (0.3 equiv), H_2O (1 equiv), DCM (3 mL), Ar, 35 W blue LED, 35 °C, 24 h. [b] Isolated yield.

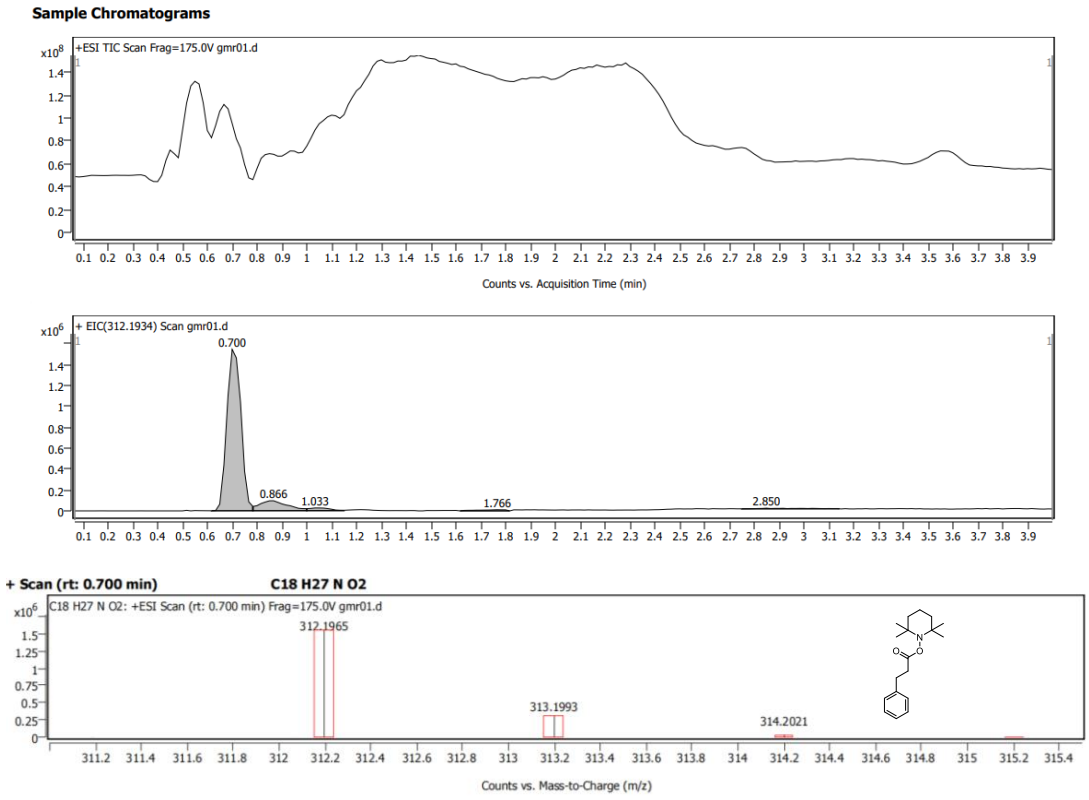
5. Mechanistic Investigations

5.1. Radical trapping experiments

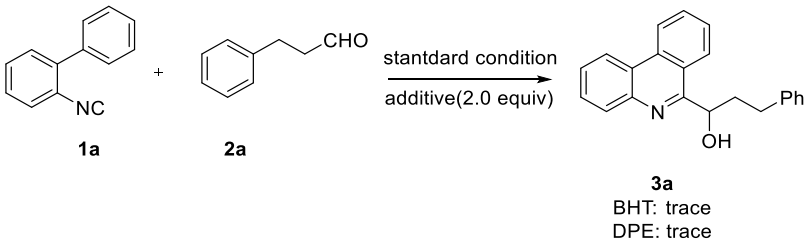
The following reaction was carried out under standard condition: A 10 mL reaction vessel was charged with 2-isocyano-1,1'-biphenyl (**1a**, 0.2 mmol, 35.8 mg), phenylpropyl aldehyde (**2a**, 0.4 mmol, 53.1 μL), NH_4Br (0.06 mmol, 5.9 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2.3 mg), H_2O (0.2 mmol, 3.6 μL), 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) (0.4 mmol, 2.0 equiv, 62.8 mg) and DCM (3.0 mL). The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The resulting mixture was stirred at 35 °C for 24 hours under irradiation with a 35 W blue LED. The formation of **3a** was suppressed. Meanwhile, the TEMPO-trapped product (**4**) was detected by HR-MS.



HRMS (ESI): m/z calcd for $C_{18}H_{27}NNaO_2$ $(M+Na)^+$ 312.1934, found 312.1965.



2-isocyano-1,1'-biphenyl (**1a**, 0.2 mmol, 35.8 mg), phenylpropyl aldehyde (**2a**, 0.4 mmol, 53.1μL), NH_4Br (0.06 mmol, 5.9 mg), $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.002 mmol, 2.3 mg), H_2O (0.2 mmol, 3.6 μL), butylated hydroxytoluene (BHT) (0.4 mmol, 2.0 equiv, 88.2 mg) or 1,1-Diphenylethylene (DPE) (0.4 mmol, 2.0 equiv, 72 μL), and DCM (3.0 mL) were placed in a 10 mL reaction tube. The reaction mixture was stirred under air using a 35 W blue LED for 24 h. The formation of **3a** was suppressed.



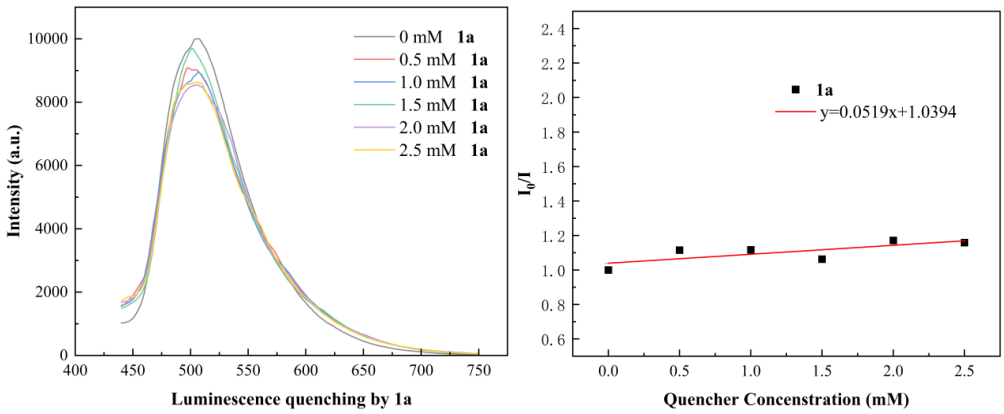
5.2. Stern–Volmer Quenching

Formulation solution: 2-isocyano-1,1'-biphenyl (2.5 mmol, 447.5 mg) was dissolved in DCM in a 25 mL volumetric flask to set the concentration to be 0.1 M. Phenylpropyl aldehyde (2.5 mmol, 332 μL) was dissolved in DCM in a 25 mL volumetric flask to set the concentration to be 0.1 M. NH_4Br (1.25 mmol, 122.9 mg) was dissolved in acetone in a 25 mL volumetric flask to set the concentration

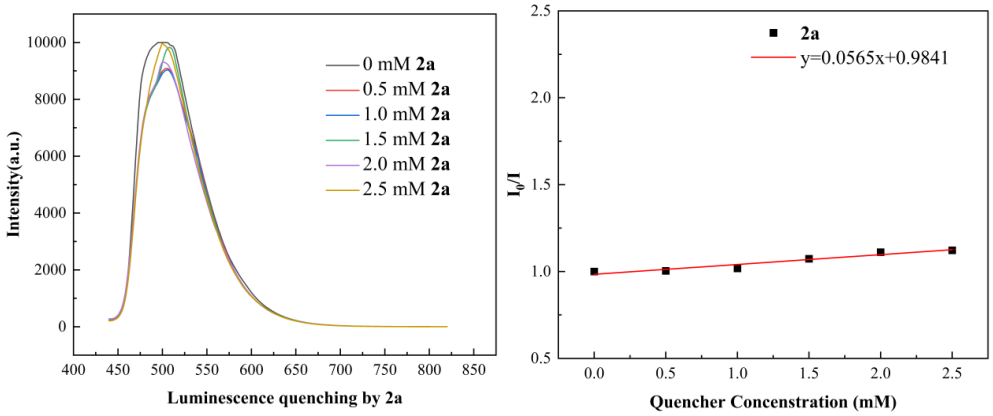
to be 0.05 M (acetone was used as solvent for NH_4Br due to its' poor solubility in DCM). TBABr (1.25 mmol, 80.6 mg) was dissolved in DCM in a 25 mL volumetric flask to set the concentration to be 0.01 M. $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ (0.0025 mol, 2.8 mg) was dissolved in DCM (25.0 mL) to set the concentration to be 0.1 mM.

Experimental procedure: The resulting 0.1 mM $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ solution (50 μL) was added to a cuvette, which was then diluted to a volume of 2.0 mL by adding further solvent (DCM) to prepare a 2.5 μM solution. 10.0 μL of 2-isocyano-1,1'-biphenyl (**1a**) was successively added, uniformly stirred and the resulting mixture was bubbled with nitrogen for 3 minutes and irradiated at 420 nm. Fluorescence emission spectra of 0 μL, 10.0 μL, 20.0 μL, 30.0 μL, 40.0 μL, 50.0 μL fluorescence intensity. Follow this method and make changes to the amount of other compound to obtain the Stern–Volmer relationship in turn.

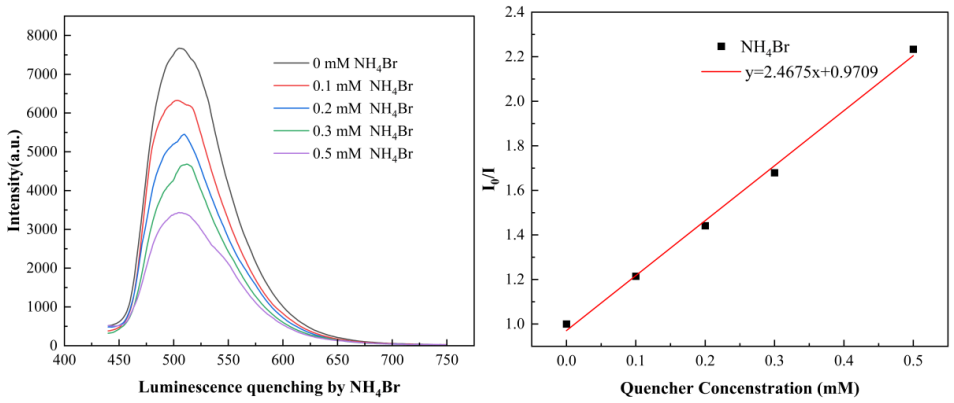
(a) Fluorescence of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by 2-isocyano-1,1'-biphenyl (**1a**).



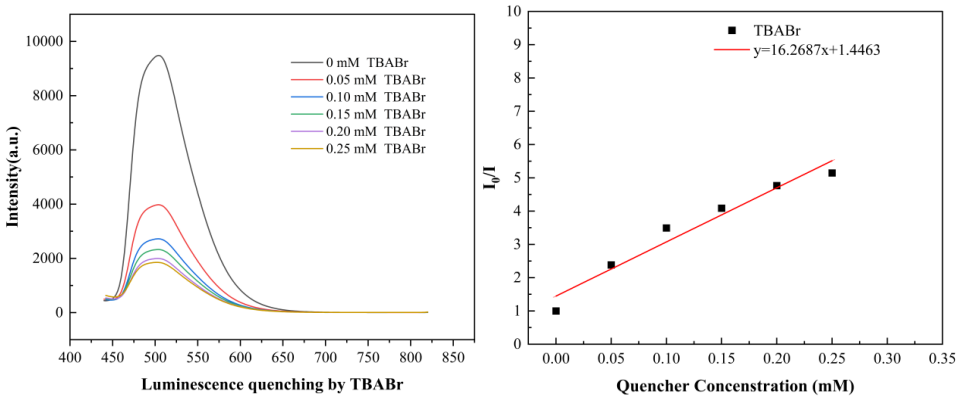
(b) Fluorescence of $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ quenched by phenylpropyl aldehyde (**2a**).



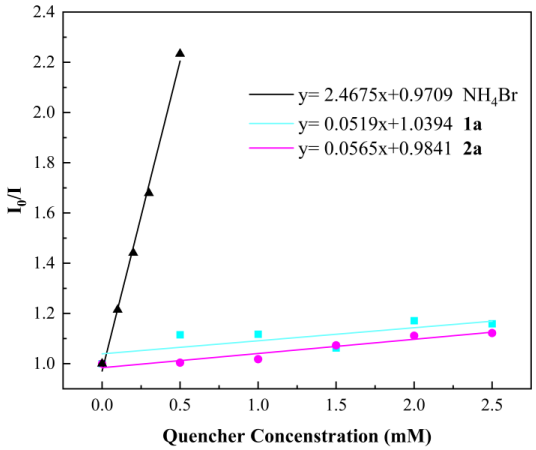
(c) Fluorescence of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 quenched by NH_4Br in acetone.



(d) Fluorescence of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 quenched by TBABr in DCM.



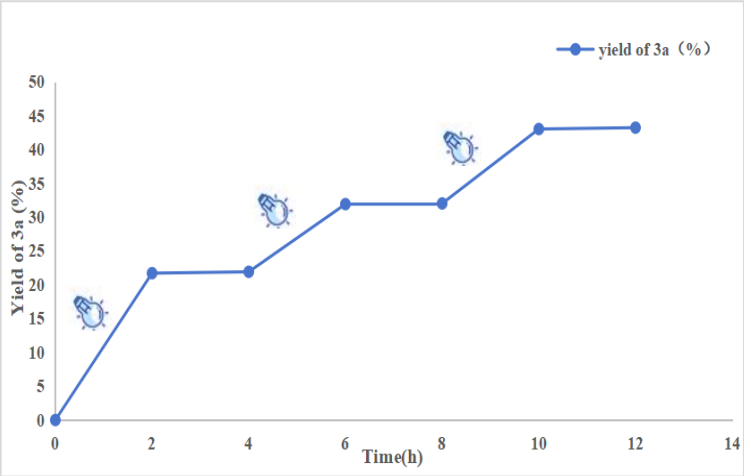
(e) Stern-Volmer plots of Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6.



5.3 Switched light on/off experiment

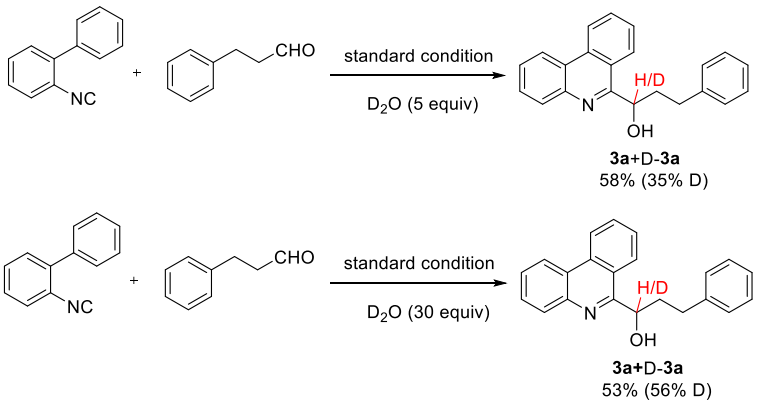
Six 10 ml reaction vessels, numbered 1, 2, 3, 4, 5, 6, were charged with 2-isocyano-1,1'-biphenyl (**1a**, 0.2 mmol, 35.8 mg), phenylpropyl aldehyde (**2a**, 0.4 mmol, 53.1 μL), NH_4Br (0.06

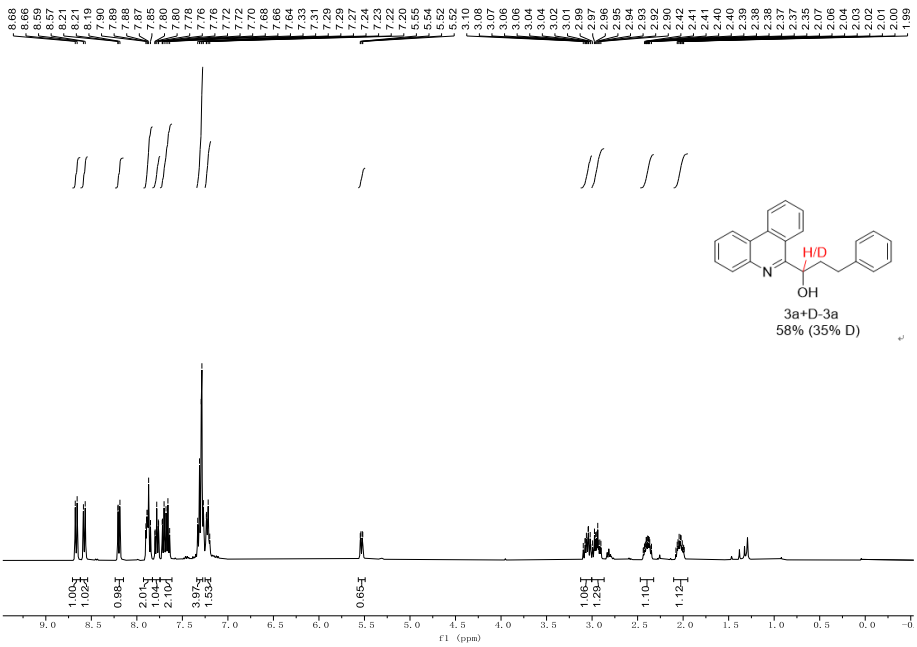
mmol, 5.9 mg), Ir[dF(CF_3)ppy]$_2$(dtbbpy)PF_6 (0.002 mmol, 2.3 mg), H_2O (0.2 mmol, 3.6 μL), and DCM (3.0 mL) respectively. The atmosphere was exchanged by applying vacuum and backfilling with Ar (this process was conducted for three times). The mixture was stirring at 35 °C for sequential periods (2 hours) under irradiation with a 35 W blue LED and followed by stirring in the dark for 2 hours, and so on. At each time point, one reaction vessel was taken out, and the isolated yield of **3a** was obtained. As shown in the figure, continuous light irradiation was essential for the process.

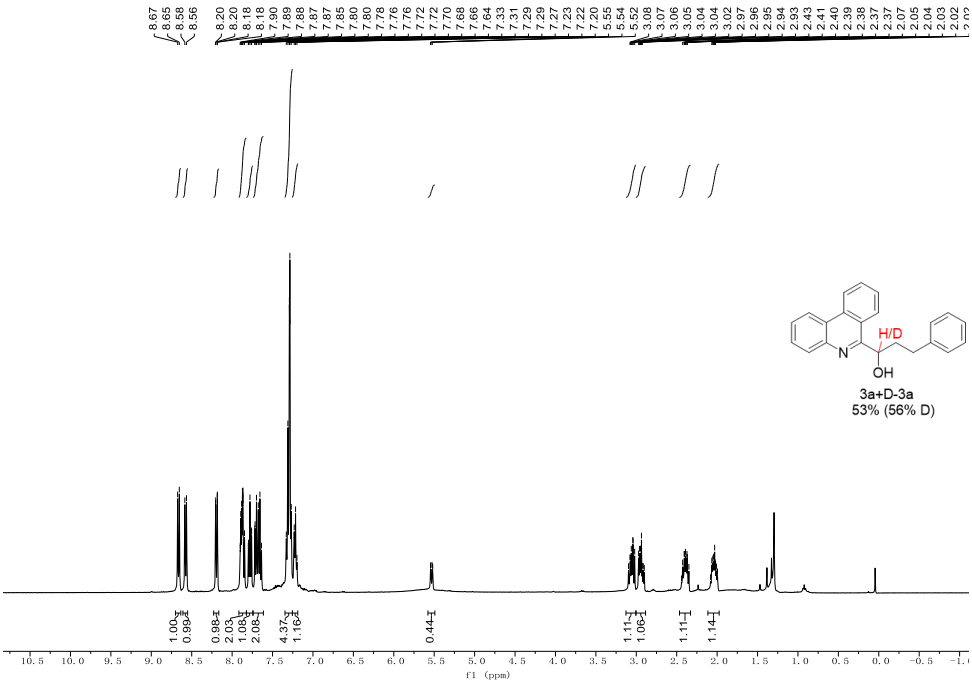


5.4 Deuteration experiment

Using D_2O under standard condition

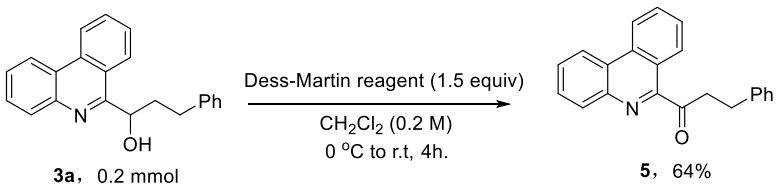






6. Late-stage modification of product 3a

6.1 Oxidation

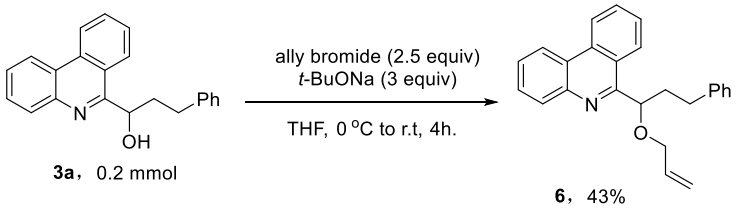


3a，0.2 mmol　　**5**，64%

To a 10 mL reaction vessel was charged successively with **3a** (0.2 mmol, 62.2 mg), Dess-Martin reagent (0.3 mmol, 127.3 mg) and CH_2Cl_2 (0.2 M) at 0 °C. The reaction mixture was stirred at room temperature for 4 h. The reaction was monitored by TLC. The crude reaction mixture was quenched with $NaHCO_3$ (aq, 10%, 5 mL). Then the mixture was extracted with ethyl acetate for three times (3×10 mL). The organic solution was dried over sodium sulfate, and filtered. The crude material was purified by silica gel to deliver the product **5** (39.8 mg, 64%).

1-(phenanthridin-6-yl)-3-phenylpropan-1-one (5)[8]: yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (d, *J* = 8.2 Hz, 1H), 8.67 (d, *J* = 8.3 Hz, 1H), 8.65 – 8.57 (m, 1H), 8.27 – 8.21 (m, 1H), 7.93 – 7.85 (m, 1H), 7.85 – 7.69 (m, 3H), 7.36 (d, *J* = 6.8 Hz, 4H), 7.30 – 7.21 (m, 1H), 3.85 – 3.78 (m, 2H), 3.22 (t, *J* = 7.7 Hz, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 203.8, 154.1, 142.5, 141.4, 133.5, 131.0, 130.8, 129.0, 128.8, 128.6, 128.5, 128.1, 127.8, 126.1, 125.3, 123.1, 122.1, 122.1, 42.0, 30.2.

6.2 Allylation



3a，0.2 mmol　　**6**，43%

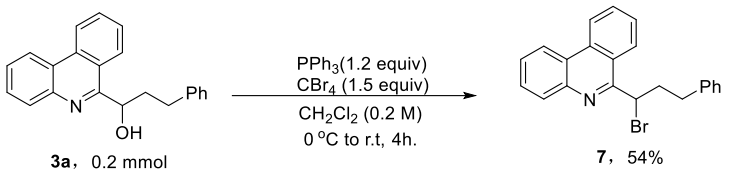
To a solution of **3a** (0.2 mmol, 62.2 mg) and allyl bromide (0.5 mmol, 43 μL) in THF (2 mL) at 0 °C was added t-BuONa (0.6 mmol, 58 mg) and the mixture was vigorously stirred at room temperature. After 4 hours the reaction was quenched with water (3.0 mL) and diluted with EtOAc (5.0 mL). The aqueous phase was extracted with EtOAc (3×5 mL). Combined organic extracts were washed with water (3.0 mL), brine, dried over $MgSO_4$ and concentrated. The diene product **6** was purified by short column chromatography.

6-(1-(allyloxy)-3-phenylpropyl)phenanthridine (6): yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.78 (d, *J* = 8.3 Hz, 1H), 8.69 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 8.1 Hz, 1H), 8.25 (d, *J* = 8.1 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.78 (t, *J* = 7.5 Hz, 1H), 7.69 (q, *J* = 7.6 Hz, 2H), 7.29 (dt, *J* = 13.3, 7.3 Hz, 5H), 7.21 (t, *J* = 7.0 Hz, 1H), 5.99 (ddt, *J* = 16.1, 10.7, 5.6 Hz, 1H), 5.36 – 5.24 (m, 1H), 5.18 (dt, *J* = 8.3, 4.1 Hz, 2H), 4.14 – 3.95 (m, 2H), 3.05 (ddd, *J* = 14.5, 10.1, 5.1 Hz, 1H), 2.91 – 2.76 (m, 1H), 2.60 (dtd, *J* = 14.3, 9.4, 5.2 Hz, 1H), 2.46 – 2.28 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.7, 143.3, 141.8, 134.8, 133.4, 130.6, 130.1, 128.7, 128.6, 128.4, 127.2, 127.1, 126.7, 125.9,

124.4, 124.1, 122.5, 122.0, 117.0, 84.0, 70.4, 37.6, 32.7. HRMS (ESI) m/z calcd for $C_{25}H_{24}NO$ $(M+H)^+$ 354.1852, found 354.1849.

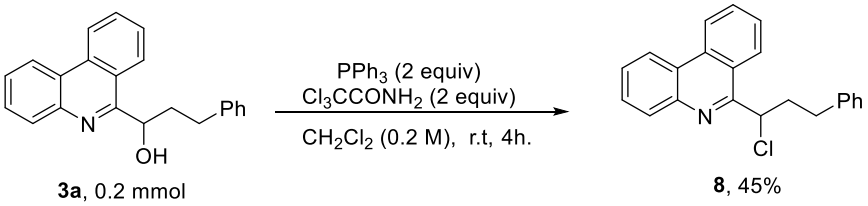
6.3 Bromination and Chlorination

Bromination: To a 10 mL reaction vessel was charged successively with **3a** (0.2 mmol, 62.2 mg), CBr_4 (0.3 mmol, 99.5 mg), CH_2Cl_2 (1.0 mL), and PPh_3 (1.2 equiv, 62.9 mg) in an ice bath. After the reaction mixture was stirred for 4 h at room temperature, the reaction solution was concentrated under reduced pressure. The residue was purified by silica gel flash column chromatography to give the corresponding compound **7** (39.2 mg, 54% yield).



6-(1-bromo-3-phenylpropyl)phenanthridine (7): white solid. mp: 149 – 151 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.71 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 7.8 Hz, 1H), 8.31 (d, *J* = 8.2 Hz, 1H), 8.28 – 8.22 (m, 1H), 7.92 – 7.84 (m, 1H), 7.83 – 7.69 (m, 3H), 7.40 – 7.27 (m, 5H), 5.83 (t, *J* = 6.9 Hz, 1H), 3.15 – 3.05 (m, 2H), 2.99 (ddd, *J* = 20.9, 7.6, 5.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.5, 143.4, 141.1, 133.5, 130.6, 130.5, 128.8, 128.7, 128.6, 127.6, 127.4, 126.2, 125.5, 124.1, 124.1, 122.7, 122.0, 49.5, 37.5, 34.2. HRMS (ESI) m/z calcd for $C_{22}H_{19}NBr$ $(M+H)^+$ 376.0695, found 376.0688.

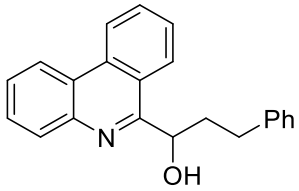
Chlorination: To a stirred solution of **3a** (0.2 mmol, 62.2 mg) and PPh_3 (0.4 mmol, 104.8 mg) in dry CH_2Cl_2 (0.5 mL) was added Cl_3CCONH_2 (0.4 mmol, 64.8 mg) at room temperature under an N_2 atmosphere. After reaction completion (TLC), the reaction was quenched with cold water and extracted with dichloromethane. The combined organic layer was washed with brine, dried over anhydrous $MgSO_4$ and filtered. The filtrate was concentrated in vacuum. Purification by silica-gel chromatography (hexane/AcOEt = 60/1) gave the corresponding product **8** (30.0 mg, 45% yield).



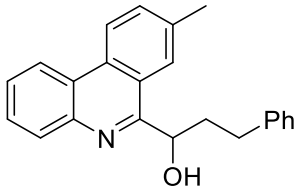
6-(1-chloro-3-phenylpropyl)phenanthridine (8): yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.0 Hz, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.21 (d, *J* = 8.0 Hz,

1H), 7.85 (t, *J* = 7.6 Hz, 1H), 7.80 – 7.66 (m, 3H), 7.28 (tq, *J* = 16.1, 7.3 Hz, 5H), 5.72 (t, *J* = 6.5 Hz, 1H), 3.01 (q, *J* = 5.7, 4.0 Hz, 1H), 2.95 (ddd, *J* = 8.7, 6.9, 4.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.2, 143.2, 141.1, 133.5, 130.6, 130.6, 128.8, 128.7, 128.5, 127.6, 127.4, 126.2, 125.6, 124.2, 124.1, 122.7, 122.0, 58.4, 37.3, 33.2. HRMS (ESI) m/z calcd for $C_{22}H_{19}NCl$ $(M+H)^+$ 322.1201, found 322.1196.

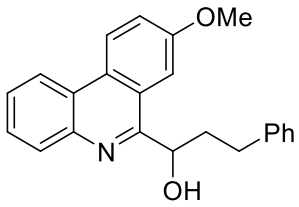
7. Characterization data of products



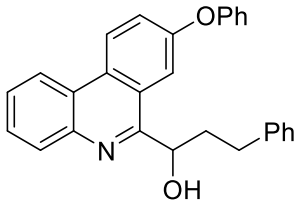
1-(phenanthridin-6-yl)-3-phenylpropan-1-ol (3a)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3a** (36.4 mg, 58%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.24 – 8.10 (m, 1H), 7.95 – 7.81 (m, 2H), 7.81 – 7.71 (m, 1H), 7.72 – 7.58 (m, 2H), 7.31 – 7.22 (m, 4H), 7.18 (ddd, *J* = 6.8, 3.9, 1.9 Hz, 1H), 5.60 (s, 1H), 5.50 (d, *J* = 8.4 Hz, 1H), 3.09 – 2.97 (m, 1H), 2.90 (ddd, *J* = 13.9, 9.5, 4.8 Hz, 1H), 2.43 – 2.31 (m, 1H), 2.00 (dtd, *J* = 13.8, 9.0, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 142.1, 141.9, 133.3, 130.8, 129.5, 128.9, 128.7, 128.4, 127.4, 127.0, 125.9, 125.0, 124.2, 123.1, 122.8, 122.1, 68.8, 40.8, 32.0.



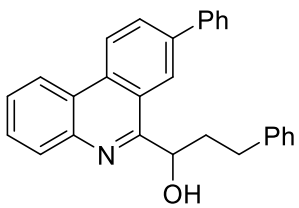
1-(8-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3b)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3b** (30.8 mg, 47%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.3 Hz, 2H), 8.14 (d, *J* = 9.1 Hz, 1H), 7.76 – 7.68 (m, 1H), 7.64 (d, *J* = 13.6 Hz, 2H), 7.49 (s, 1H), 7.32 (d, *J* = 6.5 Hz, 4H), 7.23 (t, *J* = 7.5 Hz, 1H), 5.58 (s, 1H), 5.45 (s, 1H), 3.06 (dt, *J* = 13.8, 8.3 Hz, 1H), 2.92 (ddd, *J* = 13.6, 8.4, 4.8 Hz, 1H), 2.49 (s, 3H), 2.44 – 2.26 (m, 1H), 1.99 (ddt, *J* = 17.0, 8.4, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.8, 142.0, 141.7, 137.4, 132.6, 131.1, 129.3, 128.9, 128.5, 128.4, 126.9, 126.0, 124.5, 124.3, 123.1, 122.6, 121.9, 68.4, 40.8, 32.0, 21.8.



1-(8-methoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3c): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3c** (37.7mg, 55%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.46 (d, *J* = 9.1 Hz, 1H), 8.40 (d, *J* = 7.7 Hz, 1H), 8.15 – 8.09 (m, 1H), 7.71 – 7.58 (m, 2H), 7.39 (dd, *J* = 9.1, 2.5 Hz, 1H), 7.33 (q, *J* = 4.5, 3.7 Hz, 4H), 7.22 (tt, *J* = 5.4, 2.4 Hz, 1H), 6.93 (d, *J* = 2.5 Hz, 1H), 5.58 (s, 1H), 5.35 (dd, *J* = 9.2, 1.7 Hz, 1H), 3.69 (s, 3H), 3.19 – 3.05 (m, 1H), 2.91 (ddd, *J* = 13.2, 7.3, 4.9 Hz, 1H), 2.35 – 2.23 (m, 1H), 1.97 (dddd, *J* = 11.4, 9.1, 5.7, 3.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.2, 158.6, 142.0, 141.3, 129.3, 129.0, 128.5, 127.9, 127.5, 127.0, 125.9, 124.3, 124.2, 124.2, 121.6, 121.6, 104.6, 68.1, 55.4, 40.5, 32.0. HRMS (ESI) m/z calcd for $C_{23}H_{21}NNaO$ $(M+Na)^+$ 366.1465, found 366.1459.

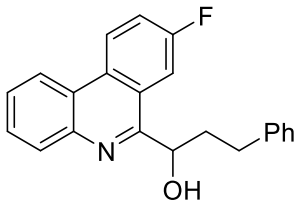


1-(8-phenoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3d): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3d** (42.1 mg, 52%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 9.1 Hz, 1H), 8.49 (d, *J* = 7.6 Hz, 1H), 8.19 – 8.12 (m, 1H), 7.76 – 7.64 (m, 2H), 7.58 (dd, *J* = 9.0, 2.4 Hz, 1H), 7.49 – 7.39 (m, 3H), 7.22 (dd, *J* = 13.9, 5.8 Hz, 3H), 7.17 – 7.07 (m, 5H), 5.56 (s, 1H), 5.30 (d, *J* = 8.5 Hz, 1H), 2.88 (t, *J* = 7.9 Hz, 2H), 2.27 (dtd, *J* = 16.7, 8.6, 2.4 Hz, 1H), 1.92 (dq, *J* = 15.0, 8.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3, 156.6, 156.5, 141.8, 141.6, 130.2, 129.5, 129.1, 128.6, 128.5, 128.4, 127.3, 125.8, 124.9, 124.3, 124.2, 124.1, 123.4, 121.8, 119.2, 112.5, 69.1, 40.5, 32.1. HRMS (ESI) m/z calcd for $C_{28}H_{24}NO_2$ $(M+H)^+$ 406.1802, found 406.1801.

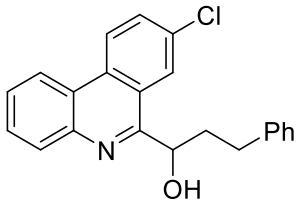


3-phenyl-1-(8-phenylphenanthridin-6-yl)propan-1-ol (3e): yellow oil. Purification by

preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3e** (41.3 mg, 53%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.6 Hz, 1H), 8.54 (d, *J* = 7.6 Hz, 1H), 8.21 – 8.14 (m, 1H), 8.07 (dd, *J* = 8.6, 1.7 Hz, 1H), 7.96 (d, *J* = 1.5 Hz, 1H), 7.75 (ddd, *J* = 8.2, 7.0, 1.4 Hz, 1H), 7.67 (ddd, *J* = 8.3, 7.0, 1.4 Hz, 1H), 7.63 – 7.50 (m, 4H), 7.50 – 7.42 (m, 1H), 7.33 – 7.26 (m, 4H), 7.22 (ddd, *J* = 8.4, 5.1, 2.3 Hz, 1H), 5.63 – 5.43 (m, 1H), 3.11 (dt, *J* = 13.8, 8.3 Hz, 1H), 2.91 (ddd, *J* = 13.3, 7.8, 4.8 Hz, 1H), 2.45 – 2.33 (m, 1H), 2.03 (dtt, *J* = 16.7, 7.9, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.3, 142.1, 141.8, 140.1, 139.8, 132.3, 130.0, 129.5, 129.1, 128.9, 128.9, 128.6, 128.1, 127.4, 127.1, 126.0, 124.0, 123.4, 123.3, 122.8, 122.2, 68.2, 40.8, 31.8. HRMS (ESI) m/z calcd for $C_{28}H_{24}NO$ $(M+H)^+$ 390.1852, found 390.1859.

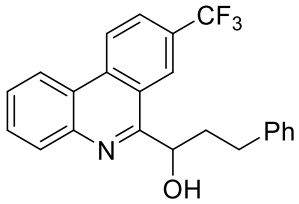


1-(8-fluorophenanthridin-6-yl)-3-phenylpropan-1-ol (3f)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3f** (35.8 mg, 54%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.577 (dd, J= 9.2, 5.2 Hz, 1H), 8.439 (d, J= 8 Hz, 1H), 8.132 (d, J= 8 Hz, 1H), 7.739-7.702 (m, 1H), 7.648 (t, J= 7.6 Hz, 1H), 7.572-7.522 (m, 1H), 7.395 (dd, J= 9.6, 2.8 Hz, 1H), 7.321-7.268 (m, 2H), 7.255-7.231 (m, 1H), 7.203-7.167 (m, 1H), 5.437 (s, 1H), 5.341 (d, J= 8.8 Hz, 1H), 3.042-2.967 (m, 1H), 2.932-2.864 (m, 1H), 2.344-2.268 (m, 1H), 2.042-1.922 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.2 (d, *J* = 249.4 Hz), 160.2 (d, *J* = 4.2 Hz), 141.7, 141.6, 129.9, 129.5, 128.7, 128.6, 128.4, 127.3, 125.9, 125.3 (d, *J* = 8.6 Hz), 124.1 (d, *J* = 7.9 Hz), 123.7, 121.8, 120.0 (d, *J* = 23.7 Hz), 109.7 (d, *J* = 21.8 Hz), 68.8, 40.4, 31.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -111.00.

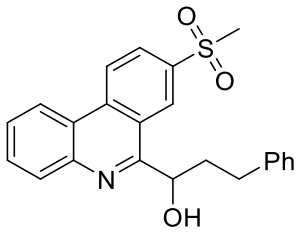


1-(8-chlorophenanthridin-6-yl)-3-phenylpropan-1-ol (3g)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3g** (31.2 mg, 45%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.50 (d, *J* = 8.8 Hz, 1H), 8.44 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 7.73 (dd, *J* = 13.6, 5.0 Hz, 3H), 7.65 (t, *J* = 7.5 Hz, 1H), 7.29 (dt, *J* = 12.8, 7.2 Hz, 4H), 7.20 (t, *J* = 7.0 Hz, 1H), 5.34 (d, *J* = 7.4 Hz, 1H), 3.02 (dt, *J* = 14.0, 8.3 Hz, 1H),

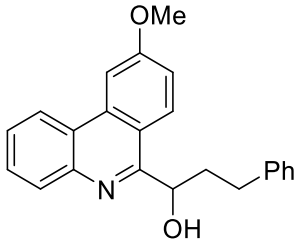
2.90 (ddd, *J* = 13.6, 8.7, 4.8 Hz, 1H), 2.31 (dt, *J* = 15.0, 8.2 Hz, 1H), 1.97 (ddt, *J* = 18.5, 8.5, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.1, 142.0, 141.6, 133.5, 131.6, 131.4, 129.6, 129.2, 128.7, 128.5, 127.4, 126.0, 124.5, 124.4, 123.9, 123.6, 122.0, 68.6, 40.6, 31.9.



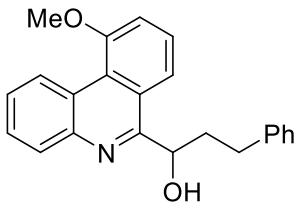
3-phenyl-1-(8-(trifluoromethyl)phenanthridin-6-yl)propan-1-ol (3h): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3h** (36.6 mg, 48%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.713 (d, J= 8.4 Hz, 1H), 8.532 (d, J= 8.4 Hz, 1H), 8.168 (d, J= 8.4 Hz, 1H), 8.050 (s, 1H), 8.001 (d, J= 8.4 Hz, 1H), 7.804 (dd, J= 8, 7.2 Hz, 1H), 7.721-7.683 (m, 1H), 7.306-7.268 (m, 3H), 7.224-7.157 (m, 1H), 7.243 (s, 1H), 5.403 (d, J= 8.8 Hz, 1H),5.348 (s, 1H), 3.077-3.001 (m, 1H), 2.933-2.867 (m, 1H), 2.354-2.275 (m, 1H), 2.014-1.925 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.2, 142.8, 141.3, 135.4, 130.1, 129.7, 129.2 (q, J = 33.0 Hz), 128.7, 128.6, 127.6, 126.7 (q, J=3.0 Hz), 126.1, 123.9, 123.8 (q, J = 257 Hz), 123.2, 122.5, 122.4, 68.4, 40.8, 31.8; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -62.19. HRMS (ESI) m/z calcd for $C_{23}H_{18}NONaF_3$ $(M+Na)^+$ 404.1233, found 404.1244.



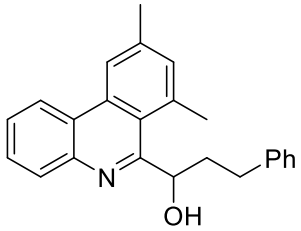
1-(6-(1-hydroxy-3-phenylpropyl)phenanthridin-8-yl)ethan-1-one (3i): white solid. mp: 88 – 90 °C. Purification by preparative thin layer chromatography was performed (PE/EA: 3/1) to yield **3i** (36.0 mg, 46%) as a white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.64 – 8.50 (m, 2H), 8.37 – 8.28 (m, 1H), 8.23 (d, *J* = 8.1 Hz, 1H), 7.87 (t, *J* = 7.6 Hz, 1H), 7.76 (t, *J* = 7.6 Hz, 1H), 7.23 (t, *J* = 7.5 Hz, 4H), 7.14 (t, *J* = 6.6 Hz, 1H), 5.56 – 5.48 (m, 1H), 5.34 (s, 1H), 3.12 (s, 3H), 3.02 (dt, *J* = 14.3, 8.2 Hz, 1H), 2.89 (ddd, *J* = 13.8, 8.8, 5.0 Hz, 1H), 2.39 (dtd, *J* = 16.5, 8.9, 2.4 Hz, 1H), 2.04 (ddd, *J* = 16.4, 8.1, 3.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 143.0, 141.3, 139.2, 136.6, 130.8, 129.7, 128.6, 128.6, 128.0, 127.9, 125.9, 125.5, 124.6, 123.0, 122.8, 122.6, 68.8, 44.6, 40.7, 31.6. HRMS (ESI) m/z calcd for $C_{23}H_{22}NSO_3$ $(M+H)^+$ 392.1315, found 392.1311.



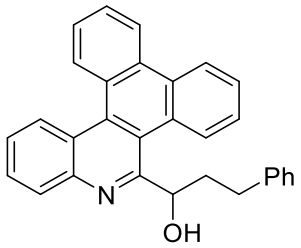
1-(9-methoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3j): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3j** (22.6 mg, 33%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.0 Hz, 1H), 8.25 (d, *J* = 8.2 Hz, 1H), 8.22 – 8.07 (m, 1H), 7.84 – 7.70 (m, 2H), 7.70 – 7.61 (m, 1H), 7.37 – 7.24 (m, 4H), 7.24 – 7.14 (m, 1H), 7.07 (d, *J* = 8.0 Hz, 1H), 5.82 (dd, *J* = 8.9, 1.9 Hz, 1H), 3.76 (s, 3H), 3.04 (dtt, *J* = 17.8, 8.5, 4.9 Hz, 2H), 2.32 – 2.20 (m, 1H), 1.69 (ddt, *J* = 18.3, 8.9, 5.3 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 158.0, 142.85, 141.8, 135.9, 131.4, 129.1, 129.0, 128.9, 128.3, 126.8, 125.6, 123.7, 122.6, 115.2, 114.8, 108.3, 72.0, 55.3, 41.6, 33.0. HRMS (ESI) m/z calcd for $C_{23}H_{21}NNaO_2$ $(M+Na)^+$ 366.1465, found 366.1468.



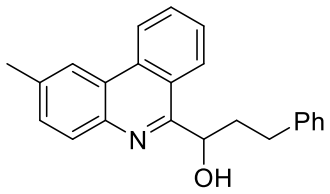
1-(10-methoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3k): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3k** (28.8 mg, 42%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.49 (d, *J* = 8.5 Hz, 1H), 8.18 (d, *J* = 8.0 Hz, 1H), 7.74 (t, *J* = 7.4 Hz, 1H), 7.66 (t, *J* = 7.7 Hz, 1H), 7.59 (t, *J* = 8.0 Hz, 1H), 7.49 (d, *J* = 8.1 Hz, 1H), 7.32 (d, *J* = 7.9 Hz, 1H), 7.26 (p, *J* = 7.3 Hz, 4H), 7.18 (t, *J* = 6.8 Hz, 1H), 5.47 (d, *J* = 7.9 Hz, 1H), 4.15 (s, 3H), 3.01 (dt, *J* = 14.1, 8.2 Hz, 1H), 2.88 (ddd, *J* = 14.0, 9.7, 4.7 Hz, 1H), 2.42 – 2.28 (m, 1H), 1.98 (ddt, *J* = 18.4, 9.0, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.6, 158.6, 142.0, 131.0, 129.1, 128.7, 128.4, 128.3, 128.0, 127.7, 126.9, 125.8, 125.1, 124.0, 123.9, 117.2, 111.9, 69.0, 55.9, 40.6, 32.0. HRMS (ESI) m/z calcd for $C_{23}H_{22}NO_2$ $(M+H)^+$344.1645, found 344.1641.



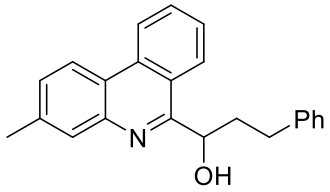
1-(6,8-dimethylphenanthren-9-yl)-3-phenylpropan-1-ol (3l): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3l** (20.5 mg, 30%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.2 Hz, 1H), 8.34 (s, 1H), 8.09 (d, *J* = 8.0 Hz, 1H), 7.70 (t, *J* = 7.5 Hz, 1H), 7.61 (t, *J* = 7.6 Hz, 1H), 7.29 – 7.17 (m, 5H), 7.14 (t, *J* = 6.9 Hz, 1H), 6.31 (s, 1H), 5.73 – 5.65 (m, 1H), 2.99 – 2.91 (m, 2H), 2.67 (s, 3H), 2.56 (s, 3H), 2.11 – 1.99 (m, 1H), 1.70 – 1.56 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.8, 142.1, 141.0, 140.6, 135.7, 135.3, 133.9, 128.8, 128.7, 128.7, 128.4, 126.8, 125.8, 124.4, 122.40 121.6, 120.9, 71.0, 42.1, 32.47, 24.7, 21.9. HRMS (ESI) m/z calcd for $C_{24}H_{24}NO_2$ $(M+H)^+$ 342.1852, found 342.1852.



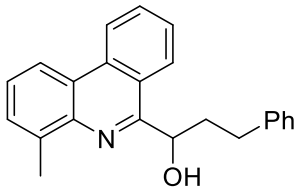
1-(dibenzo[i,k]phenanthridin-5-yl)-3-phenylpropan-1-ol (3m): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3m** (37.2 mg, 45%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.75 (d, *J* = 8.2 Hz, 1H), 8.71 – 8.59 (m, 3H), 8.26 – 8.17 (m, 2H), 7.77 (q, *J* = 7.2 Hz, 2H), 7.72 – 7.57 (m, 3H), 7.43 (t, *J* = 7.6 Hz, 1H), 7.15 (dq, *J* = 14.3, 7.1 Hz, 3H), 7.04 (d, *J* = 6.9 Hz, 2H), 5.88 (dd, *J* = 8.8, 2.6 Hz, 1H), 2.83 (dt, *J* = 13.9, 8.2 Hz, 1H), 2.72 (ddd, *J* = 13.6, 8.7, 5.0 Hz, 1H), 2.20 (dtd, *J* = 13.7, 8.4, 2.7 Hz, 1H), 1.90 (dtd, *J* = 13.8, 8.7, 5.1 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.2, 144.0, 141.7, 135.6, 132.3, 130.4, 130.0, 128.9, 128.8, 128.7, 128.5, 128.3, 128.1, 128.0, 127.6, 127.6, 127.4, 127.1, 127.0, 126.4, 125.8, 123.8, 123.6, 123.4, 121.4, 71.7, 39.6, 32.1. HRMS (ESI) m/z calcd for $C_{30}H_{23}NNaO$ $(M+Na)^+$ 36.1672, found 436.1659.



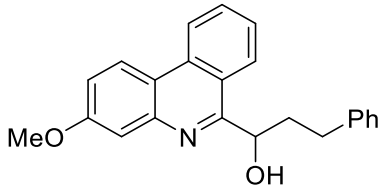
1-(2-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3n)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3n** (25.5 mg, 39%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 8.3 Hz, 1H), 8.31 (s, 1H), 8.04 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.76 (m, 2H), 7.64 – 7.52 (m, 2H), 7.33 – 7.22 (m, 4H), 7.22 – 7.14 (m, 1H), 5.62 (s, 1H), 5.47 (dd, *J* = 8.5, 2.2 Hz, 1H), 3.01 (ddd, *J* = 13.8, 9.2, 7.5 Hz, 1H), 2.88 (td, *J* = 9.5, 4.8 Hz, 1H), 2.62 (s, 3H), 2.36 (tdd, *J* = 13.9, 8.5, 2.3 Hz, 1H), 1.98 (dtd, *J* = 13.8, 9.1, 4.8 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.0, 142.0, 140.4, 136.9, 133.1, 130.6, 130.6, 129.2, 128.7, 128.4, 127.2, 125.9, 125.0, 124.0, 123.1, 122.7, 121.8, 68.8, 40.8, 32.0, 22.0.



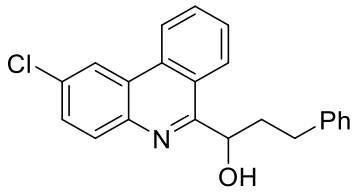
1-(3-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3o)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3o** (26.8 mg, 41%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.3 Hz, 1H), 8.41 (d, *J* = 8.3 Hz, 1H), 7.95 (s, 1H), 7.90 – 7.75 (m, 2H), 7.58 (t, *J* = 7.6 Hz, 1H), 7.49 (d, *J* = 8.3 Hz, 1H), 7.26 (q, *J* = 6.7, 6.3 Hz, 4H), 7.19 (d, *J* = 5.0 Hz, 1H), 5.65 (s, 1H), 5.48 (d, *J* = 8.4 Hz, 1H), 3.02 (dt, *J* = 15.7, 8.2 Hz, 1H), 2.95 – 2.82 (m, 1H), 2.60 (t, *J* = 2.2 Hz, 3H), 2.46 – 2.28 (m, 1H), 1.99 (ddt, *J* = 18.4, 9.2, 3.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 142.2, 142.0, 139.2, 133.4, 130.8, 129.0, 128.8, 128.7, 128.4, 126.9, 125.9, 125.0, 122.7, 122.6, 121.9, 121.8, 68.8, 40.8, 32.0, 21.6.



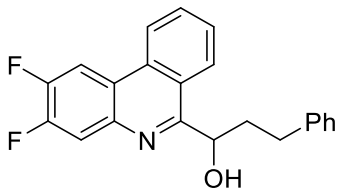
1-(4-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3p)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3p** (30.1 mg, 46%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.0 Hz, 1H), 7.90 – 7.79 (m, 2H), 7.66 – 7.53 (m, 3H), 7.27 (p, *J* = 7.2, 6.6 Hz, 4H), 7.18 (t, *J* = 6.8 Hz, 1H), 5.81 (s, 1H), 5.51 (d, *J* = 6.8 Hz, 1H), 3.10 – 2.98 (m, 1H), 2.89 (s, 4H), 2.40 (ddt, *J* = 14.2, 7.3, 3.7 Hz, 1H), 2.00 (dtd, *J* = 13.8, 9.0, 4.9 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 159.5, 141.9, 140.5, 137.0, 133.7, 130.7, 129.7, 128.7, 128.4, 127.2, 126.7, 125.9, 124.9, 124.0, 123.0, 122.7, 120.0, 69.0, 40.8, 32.0, 18.4.



1-(3-methoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3q)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3q** (28.2 mg, 42%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.52 (d, *J* = 8.3 Hz, 1H), 8.41 (d, *J* = 9.0 Hz, 1H), 7.86 – 7.75 (m, 2H), 7.56 (d, *J* = 7.8 Hz, 2H), 7.29 (dt, *J* = 17.6, 9.1 Hz, 5H), 7.19 (t, *J* = 6.4 Hz, 1H), 5.49 (d, *J* = 7.6 Hz, 1H), 4.01 (s, 3H), 3.03 (dt, *J* = 16.4, 8.3 Hz, 1H), 2.91 (td, *J* = 14.0, 11.7, 4.7 Hz, 1H), 2.36 (dt, *J* = 14.8, 8.2 Hz, 1H), 2.00 (dtd, *J* = 13.8, 8.9, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.6, 160.3, 143.6, 141.9, 133.5, 130.9, 128.7, 128.4, 126.3, 125.9, 125.0, 123.4, 122.3, 122.0, 118.2, 118.0, 109.3, 68.9, 55.6, 40.8, 32.0.

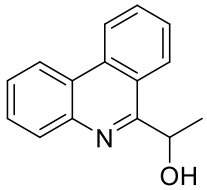


1-(2-chlorophenanthridin-6-yl)-3-phenylpropan-1-ol (3r): white solid. mp: 169 – 172 °C. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3r** (38.2 mg, 55%) as a white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.47 (d, *J* = 8.7 Hz, 1H), 8.42 (d, *J* = 2.0 Hz, 1H), 8.03 (d, *J* = 8.7 Hz, 1H), 7.81 (dt, *J* = 7.2, 3.0 Hz, 2H), 7.69 – 7.59 (m, 2H), 7.31 – 7.21 (m, 4H), 7.18 (t, *J* = 6.9 Hz, 1H), 5.44 (d, *J* = 8.3 Hz, 1H), 3.01 (dt, *J* = 14.0, 8.3 Hz, 1H), 2.90 (ddd, *J* = 13.8, 9.3, 4.8 Hz, 1H), 2.32 (dt, *J* = 16.2, 8.5 Hz, 1H), 1.97 (ddt, *J* = 18.1, 8.9, 5.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.4, 141.8, 140.4, 132.9, 132.2, 131.1, 130.8, 129.4, 128.7, 128.4, 128.1, 126.0, 125.2, 125.1, 123.1, 122.7, 121.8, 68.9, 40.7, 32.0. HRMS (ESI) m/z calcd for $C_{22}H_{18}NOClNa$ $(M+Na)^+$ 370.0969, found 370.0965.

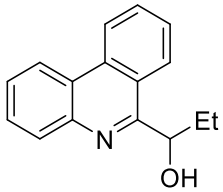


1-(2-chlorophenanthridin-6-yl)-3-phenylpropan-1-ol (3s): white solid. mp: 104 – 107 °C. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **3s** (35.0 mg, 50%) as a white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.375 (d, J= 8 Hz, 1H), 8.184

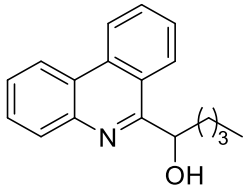
(dd, J= 11.6, 8 Hz, 1H), 7.887-7.815 (m, 3H), 7.645 (t, J= 7.6 Hz, 1H), 7.313-7.264 (m, 3H), 7.243 (s, 1H), 7.224-7.185 (m, 1H), 5.455 (d, J= 8 Hz, 1H), 5.308 (s, 1H), 3.060-2.985 (m, 1H), 2.955-2.885 (m, 1H), 2.370-2.288 (m, 1H), 2.026-1.935 (m, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 152.4 (d, *J* = 14.3 Hz), 151.3 (d, *J* = 14.4 Hz), 149.9 (d, *J* = 15.0 Hz), 148.8 (d, *J* = 14.5 Hz), 141.7, 139.1 (d, *J* = 9.8 Hz), 132.3, 131.2, 128.6 (d, *J* = 28.4 Hz), 127.8, 126.0, 125.2, 122.6, 121.1 (d, *J* = 6.0 Hz), 116.4 (d, *J* = 16.5 Hz), 109.3 (d, *J* = 19.0 Hz), 68.9, 40.7, 32.0; ^{19}F NMR (376 MHz, Chloroform-*d*) δ -134.33 (d, *J* = 21.9 Hz), -135.73 (d, *J* = 21.8 Hz). HRMS (ESI) m/z calcd for $C_{22}H_{17}NOF_2Na$ $(M+Na)^+$ 372.1170, found 372.1169.



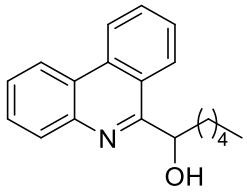
1-(phenanthridin-6-yl)ethan-1-ol (4a)[10]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4a** (25.0 mg, 56%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.4 Hz, 1H), 8.18 – 8.09 (m, 2H), 7.91 – 7.83 (m, 1H), 7.79 – 7.63 (m, 3H), 5.64 (q, *J* = 6.5 Hz, 2H), 1.66 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 162.1, 142.1, 133.4, 130.9, 129.4, 129.0, 127.5, 127.0, 125.3, 124.2, 123.0, 122.8, 122.1, 66.0, 25.3.



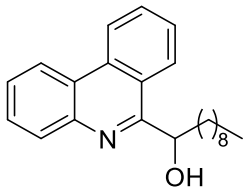
1-(phenanthridin-6-yl)propan-1-ol (4b): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4b** (25.6 mg, 54%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.61 (d, *J* = 8.3 Hz, 1H), 8.51 (d, *J* = 8.1 Hz, 1H), 8.14 (d, *J* = 8.1 Hz, 1H), 8.08 (d, *J* = 8.2 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.77 – 7.60 (m, 3H), 5.54 (s, 1H), 5.51 – 5.41 (m, 1H), 2.15 (dqd, *J* = 14.6, 7.4, 2.8 Hz, 1H), 1.74 (dp, *J* = 14.5, 7.3 Hz, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 142.0, 133.2, 130.8, 129.5, 128.9, 127.4, 127.0, 125.2, 124.1, 123.2, 122.7, 122.1, 70.7, 31.8, 9.9. HRMS (ESI) m/z calcd for $C_{16}H_{16}NO$ $(M+H)^+$ 238.1227, found 238.1226.



1-(phenanthridin-6-yl)propan-1-ol (4c): white solid. mp: 90 – 93 °C. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4c** (23.3 mg, 44%) as a white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 7.9 Hz, 1H), 8.13 (dd, *J* = 19.7, 7.8 Hz, 2H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.79 – 7.61 (m, 3H), 5.55 – 5.46 (m, 1H), 2.14 – 1.99 (m, 1H), 1.68 (ddq, *J* = 17.5, 10.1, 5.7, 5.1 Hz, 2H), 1.52 (dddd, *J* = 17.7, 11.6, 7.7, 2.3 Hz, 1H), 1.46 – 1.37 (m, 1H), 1.37 – 1.28 (m, 1H), 0.90 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 142.1, 133.3, 130.9, 129.4, 128.9, 127.4, 127.0, 125.2, 124.1, 123.1, 122.8, 122.1, 69.7, 38.8, 27.9, 22.8, 14.1. HRMS (ESI) m/z calcd for $C_{18}H_{20}NO$ $(M+H)^+$ 266.1539, found 266.1511.

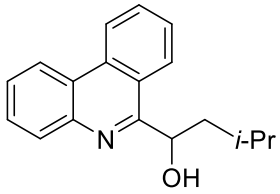


1-(phenanthridin-6-yl)hexan-1-ol (4d): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4d** (13.4 mg, 24%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.16 (d, *J* = 8.1 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.88 (t, *J* = 7.7 Hz, 1H), 7.72 (ddd, *J* = 19.4, 11.2, 8.1 Hz, 3H), 5.51 (d, *J* = 4.9 Hz, 1H), 2.06 (t, *J* = 10.4 Hz, 1H), 1.68 (dq, *J* = 17.9, 10.3 Hz, 2H), 1.62 – 1.48 (m, 1H), 1.35 – 1.27 (m, 4H), 0.88 (t, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 142.1, 133.3, 130.9, 129.4, 128.9, 127.4, 127.0, 125.2, 124.1, 123.1, 122.8, 122.1, 69.8, 39.1, 31.9, 25.5, 22.7, 14.1. HRMS (ESI) m/z calcd for $C_{19}H_{21}NONa$ $(M+Na)^+$ 302.1515, found 302.1524.

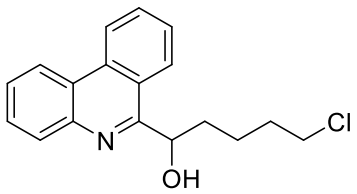


1-(phenanthridin-6-yl)decan-1-ol (4e): white solid. mp: 65 – 69 °C. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4e** (26.8 mg, 40%) as a white solid; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.65 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.6 Hz, 1H), 7.79 – 7.61 (m, 3H), 5.56 – 5.47 (m, 1H), 2.06 (t, *J* = 10.1 Hz, 1H), 1.75 – 1.61 (m, 2H), 1.38 (dd, *J* = 13.9, 8.9 Hz, 1H), 1.24 (s,

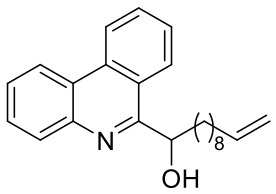
12H), 0.87 (t, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 142.0, 133.3, 130.9, 129.4, 128.9, 127.4, 127.0, 125.2, 124.1, 123.1, 122.8, 122.1, 69.8, 39.1, 31.9, 29.6, 29.6, 29.4, 25.8, 22.7, 14.2. HRMS (ESI) m/z calcd for $C_{23}H_{30}NO$ $(M+H)^+$ 336.2322, found 336.2293.



5-chloro-1-(phenanthridin-6-yl)pentan-1-ol (4f)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4f** (36.6 mg, 69%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.52 (d, *J* = 8.1 Hz, 1H), 8.13 (d, *J* = 8.1 Hz, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.75 – 7.60 (m, 3H), 5.56 (d, *J* = 9.4 Hz, 1H), 5.44 (s, 1H), 2.26 (dqt, *J* = 13.3, 6.6, 4.2 Hz, 1H), 1.74 (ddd, *J* = 13.6, 10.0, 1.6 Hz, 1H), 1.57 (ddd, *J* = 14.1, 8.4, 3.8 Hz, 1H), 1.24 (d, *J* = 6.6 Hz, 3H), 0.96 (d, *J* = 6.8 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.9, 142.1, 133.1, 130.8, 129.4, 128.9, 127.4, 126.9, 125.1, 124.1, 123.0, 1228, 122.1, 68.2, 48.6, 25.5, 24.0, 21.6.

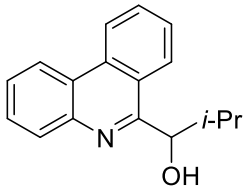


5-chloro-1-(phenanthridin-6-yl)pentan-1-ol (4g): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4g** (35.9 mg, 60%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.64 (d, *J* = 8.3 Hz, 1H), 8.54 (d, *J* = 8.1 Hz, 1H), 8.17 – 8.11 (m, 1H), 8.07 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.82 (m, 1H), 7.78 – 7.63 (m, 3H), 5.51 (dd, *J* = 7.7, 2.4 Hz, 1H), 3.53 (t, *J* = 6.4 Hz, 2H), 2.18 – 2.03 (m, 1H), 1.83 (dddd, *J* = 19.8, 13.5, 10.4, 6.8 Hz, 3H), 1.76 – 1.59 (m, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.9, 142.0, 133.3, 130.9, 129.5, 129.0, 127.5, 127.1, 125.0, 124.1, 123.0, 122.9, 122.1, 69.5, 45.0, 38.2, 32.6, 23.3. HRMS (ESI) m/z calcd for $C_{18}H_{18}NOClNa$ $(M+Na)^+$ 322.0969, found 322.0969.

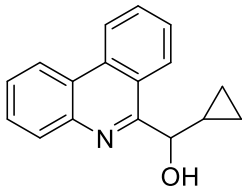


1-(phenanthridin-6-yl)undec-10-en-1-ol (4h): yellow oil. Purification by preparative thin layer

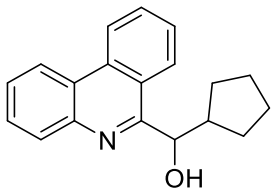
chromatography was performed (PE/EA: 10/1) to yield **4h** (13.2 mg, 19%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.18 – 8.13 (m, 1H), 8.10 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.83 (m, 1H), 7.77 – 7.64 (m, 3H), 5.80 (ddt, *J* = 16.9, 10.2, 6.7 Hz, 1H), 5.51 (d, *J* = 4.8 Hz, 1H), 5.04 – 4.89 (m, 2H), 2.02 (dt, *J* = 14.4, 6.2 Hz, 3H), 1.66 (td, *J* = 11.3, 3.5 Hz, 2H), 1.37 – 1.32 (m, 2H), 1.27 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.5, 142.1, 139.3, 133.3, 130.8, 129.5, 128.9, 127.4, 127.0, 125.2, 124.1, 123.2, 122.8, 122.1, 114.1, 69.8, 39.1, 33.8, 29.6, 29.6, 29.4, 29.1, 28.9, 25.8. HRMS (ESI) m/z calcd for $C_{24}H_{29}NNaO$ $(M+Na)^+$ 370.2141, found 370.2156.



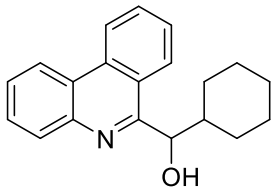
2-ethyl-1-(phenanthridin-6-yl)hexan-1-ol (4i): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4i** (17.6 mg, 35%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.1 Hz, 1H), 8.17 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.86 (t, *J* = 7.7 Hz, 1H), 7.71 (dq, *J* = 22.2, 7.3 Hz, 3H), 5.43 (s, 1H), 5.38 (s, 1H), 2.40 – 2.26 (m, 1H), 1.32 (d, *J* = 6.9 Hz, 3H), 0.63 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.0, 142.1, 133.3, 130.8, 129.5, 128.9, 127.4, 127.0, 125.6, 124.1, 123.4, 122.7, 122.1, 69.0, 17.72, 2.7, 0.9. HRMS (ESI) m/z calcd for $C_{17}H_{18}NNaO$ $(M+Na)^+$ 274.1202, found 274.1182.



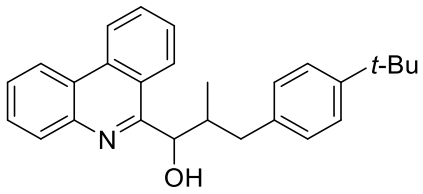
cyclopropyl(phenanthridin-6-yl)methanol (4j)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4j** (15.0 mg, 30%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (d, *J* = 8.3 Hz, 1H), 8.49 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.86 – 7.78 (m, 1H), 7.76 – 7.58 (m, 3H), 5.49 (d, *J* = 4.3 Hz, 1H), 5.41 (s, 1H), 1.36 (tq, *J* = 9.6, 5.2 Hz, 1H), 0.81 (dq, *J* = 9.1, 5.1, 3.8 Hz, 1H), 0.54 (ddt, *J* = 14.5, 9.6, 5.0 Hz, 2H), 0.31 (ddd, *J* = 12.7, 6.3, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.7, 141.9, 133.3, 130.8, 129.5, 128.9, 127.3, 127.0, 125.4, 124.0, 123.4, 122.8, 122.1, 73.6, 34.6, 21.0, 14.6.



cyclopentyl(phenanthridin-6-yl)methanol (4k): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4k** (11.1 mg, 20%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 7.8 Hz, 1H), 8.22 – 8.12 (m, 2H), 7.90 – 7.83 (m, 1H), 7.77 – 7.62 (m, 3H), 5.60 (d, *J* = 2.8 Hz, 1H), 5.44 (s, 1H), 2.53 (pd, *J* = 8.5, 2.9 Hz, 1H), 1.92 (ddt, *J* = 11.3, 7.8, 3.5 Hz, 2H), 1.74 (dq, *J* = 12.1, 7.3, 6.4 Hz, 1H), 1.62 (tdd, *J* = 12.7, 5.9, 2.6 Hz, 1H), 1.51 (dtd, *J* = 12.6, 7.9, 4.2 Hz, 2H), 1.45 – 1.33 (m, 1H), 0.96 (dtd, *J* = 11.8, 7.6, 4.4 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 161.1, 142.0, 133.3, 130.8, 129.5, 128.8, 127.3, 126.9, 125.3, 124.1, 123.3, 122.7, 122.1, 70.9, 46.2, 30.1, 26.1, 25.9, 24.7. HRMS (ESI) m/z calcd for $C_{19}H_{20}NO$ $(M+H)^+$ 278.1539, found 278.1507.



cyclohexyl(phenanthridin-6-yl)methanol (4l)[9]: yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4l** (14.0 mg, 24%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.66 (d, *J* = 8.3 Hz, 1H), 8.56 (d, *J* = 8.0 Hz, 1H), 8.19 – 8.10 (m, 2H), 7.90 – 7.83 (m, 1H), 7.78 – 7.62 (m, 3H), 5.43 – 5.35 (m, 1H), 1.93 (dd, *J* = 14.7, 5.1 Hz, 2H), 1.83 (d, *J* = 12.9 Hz, 1H), 1.72 (qd, *J* = 12.8, 3.4 Hz, 1H), 1.59 (d, *J* = 9.8 Hz, 2H), 1.33 – 1.24 (m, 2H), 1.16 (dt, *J* = 13.0, 3.4 Hz, 1H), 1.04 (d, *J* = 13.2 Hz, 1H), 0.95 (dt, *J* = 12.3, 3.2 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.6, 141.9, 133.2, 130.8, 129.5, 128.9, 127.4, 126.9, 125.4, 124.0, 123.5, 122.8, 122.1, 73.6, 44.9, 31.2, 26.8, 26.3, 26., 25.1.



3-(4-(tert-butyl)phenyl)-2-methyl-1-(phenanthridin-6-yl)propan-1-ol (4m): yellow oil. Purification by preparative thin layer chromatography was performed (PE/EA: 10/1) to yield **4m** (19.2 mg, 25%) as a yellow oil; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.53 (d, *J* = 8.3 Hz, 1H), 8.16 (d, *J* = 8.9 Hz, 1H), 8.12 (d, *J* = 8.2 Hz, 1H), 7.90 – 7.81 (m, 1H), 7.80 –

7.63 (m, 3H), 6.91 (d, *J* = 8.3 Hz, 2H), 6.64 (d, *J* = 8.2 Hz, 2H), 5.52 (d, *J* = 2.4 Hz, 1H), 2.54 (tdd, *J* = 11.2, 5.7, 3.4 Hz, 1H), 2.49 – 2.31 (m, 2H), 1.29 (s, 3H), 1.14 (s, 9H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 160.3, 147.9, 141.8, 137.6, 133.2, 130.8, 129.5, 128.9, 128.5, 127.3, 127.0, 125.2, 124.5, 124.1, 123.5, 122.8, 122.1, 73.7, 41.8, 35.1, 34.1, 31.3, 18.4. HRMS (ESI) m/z calcd for $C_{27}H_{30}NO$ $(M+H)^+$384.2322, found 384.2323.

8. Reference

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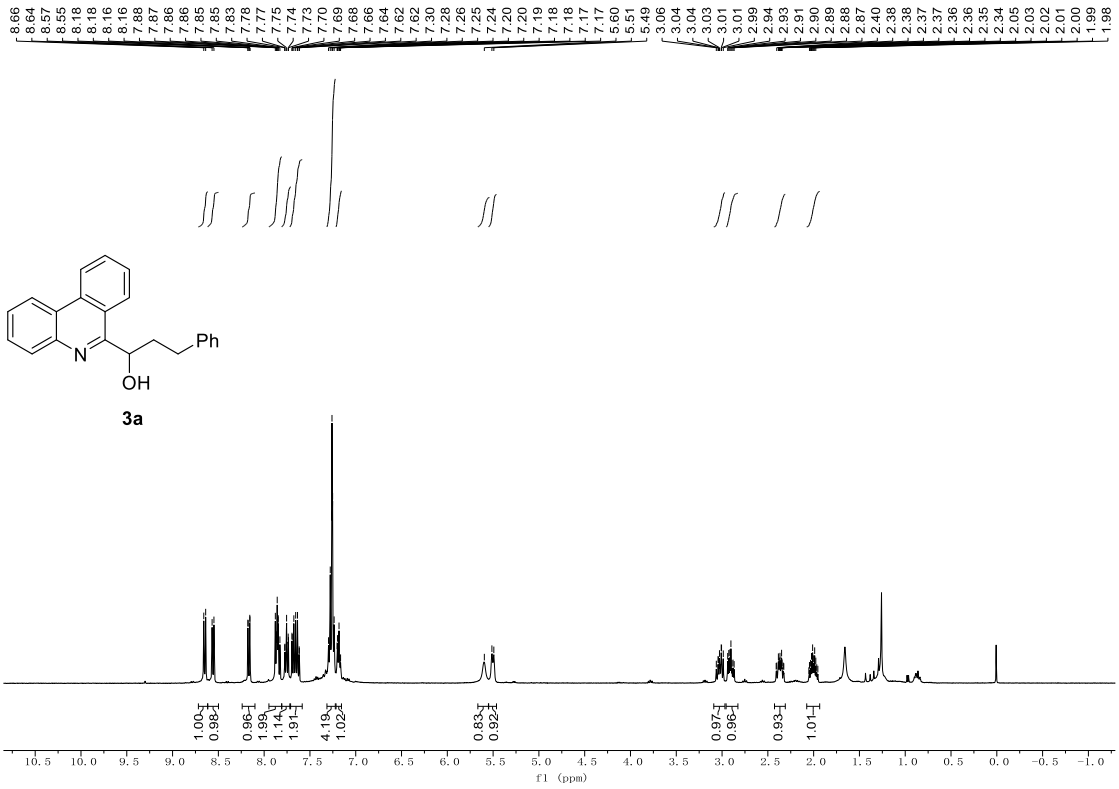
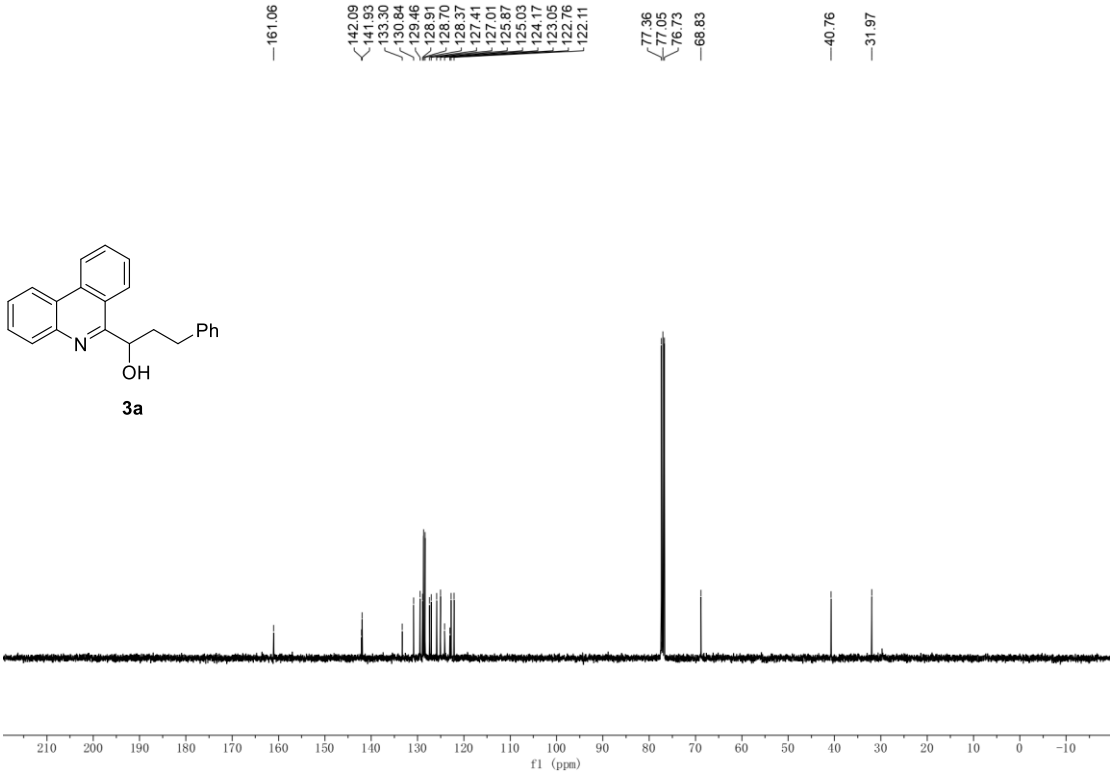
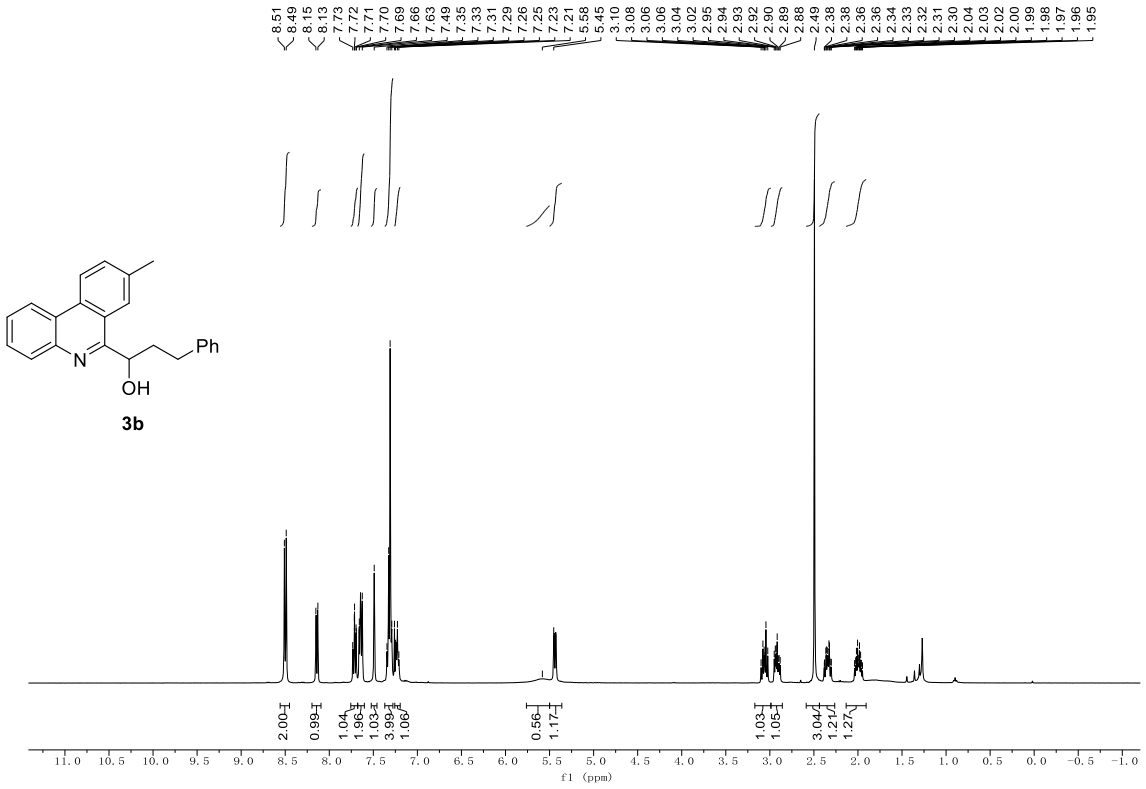
9. NMR Spectra

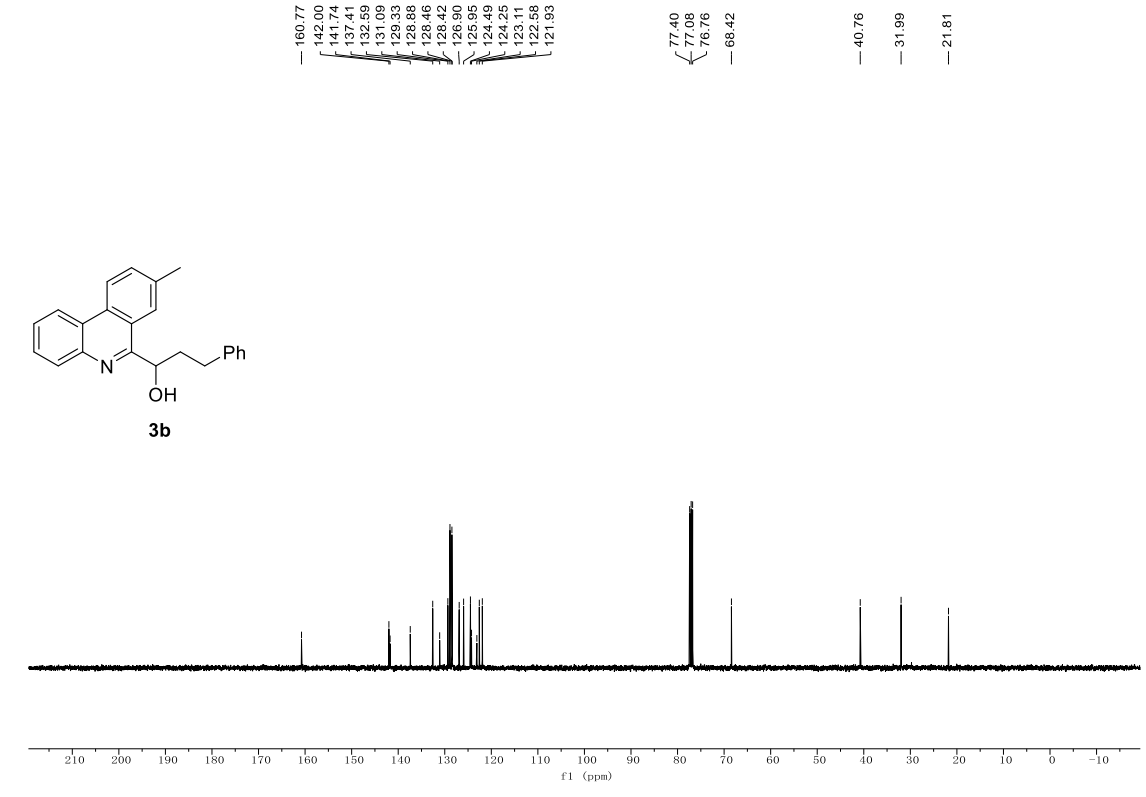
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3a



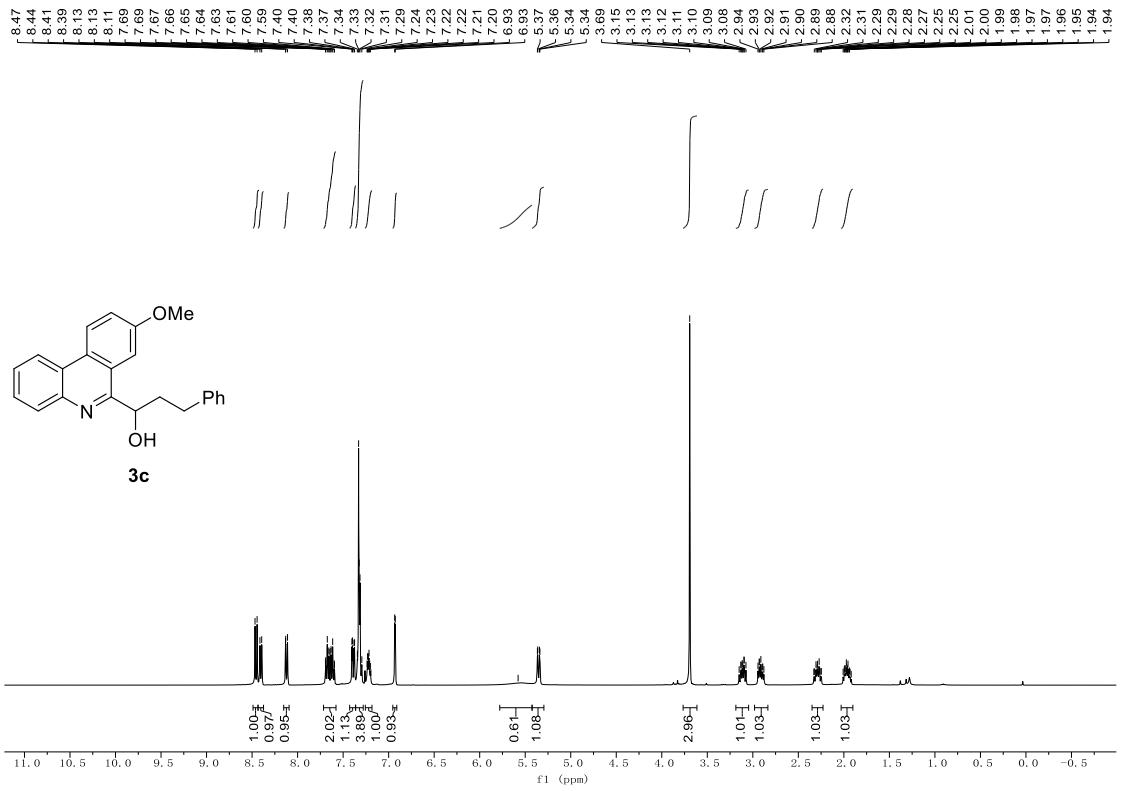


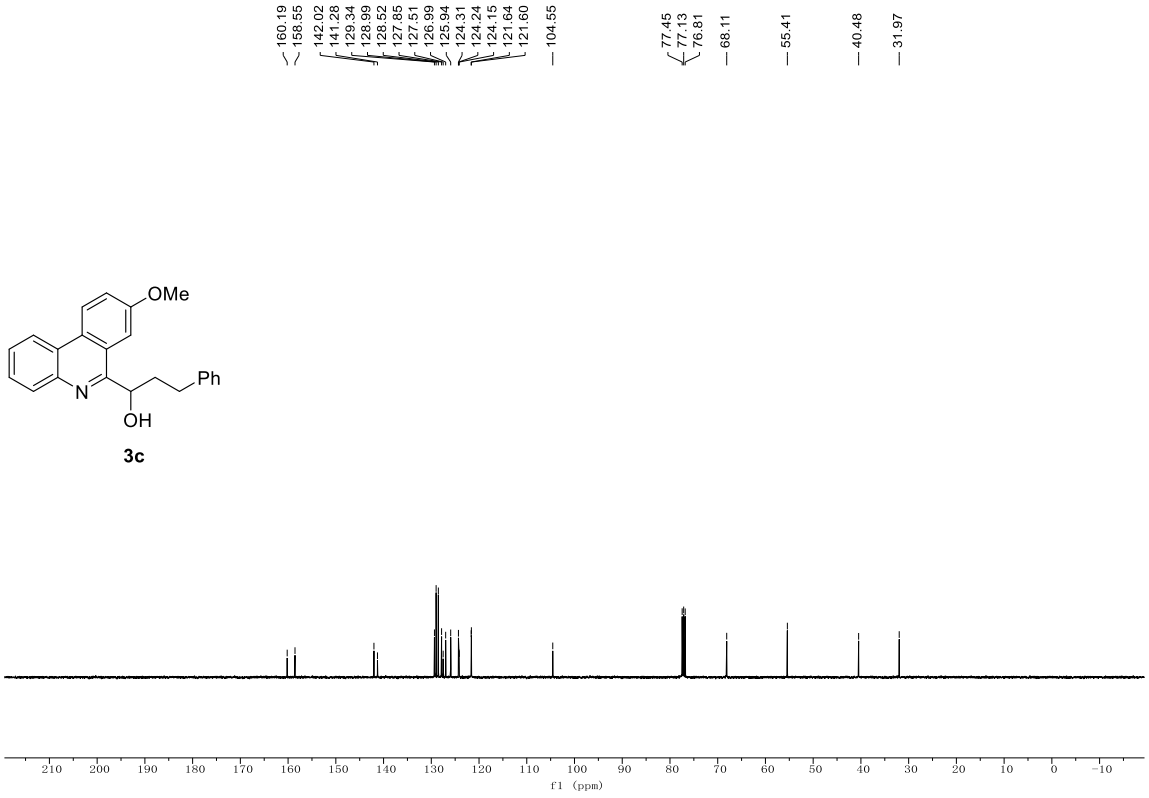
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3b



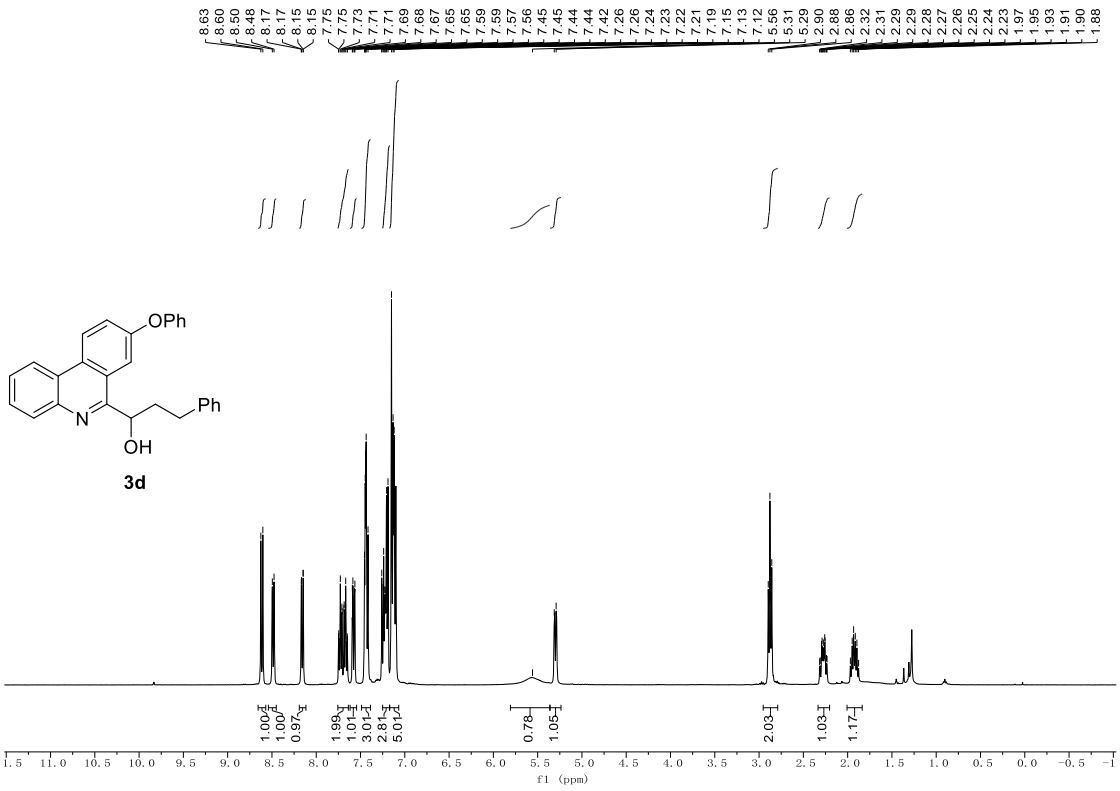


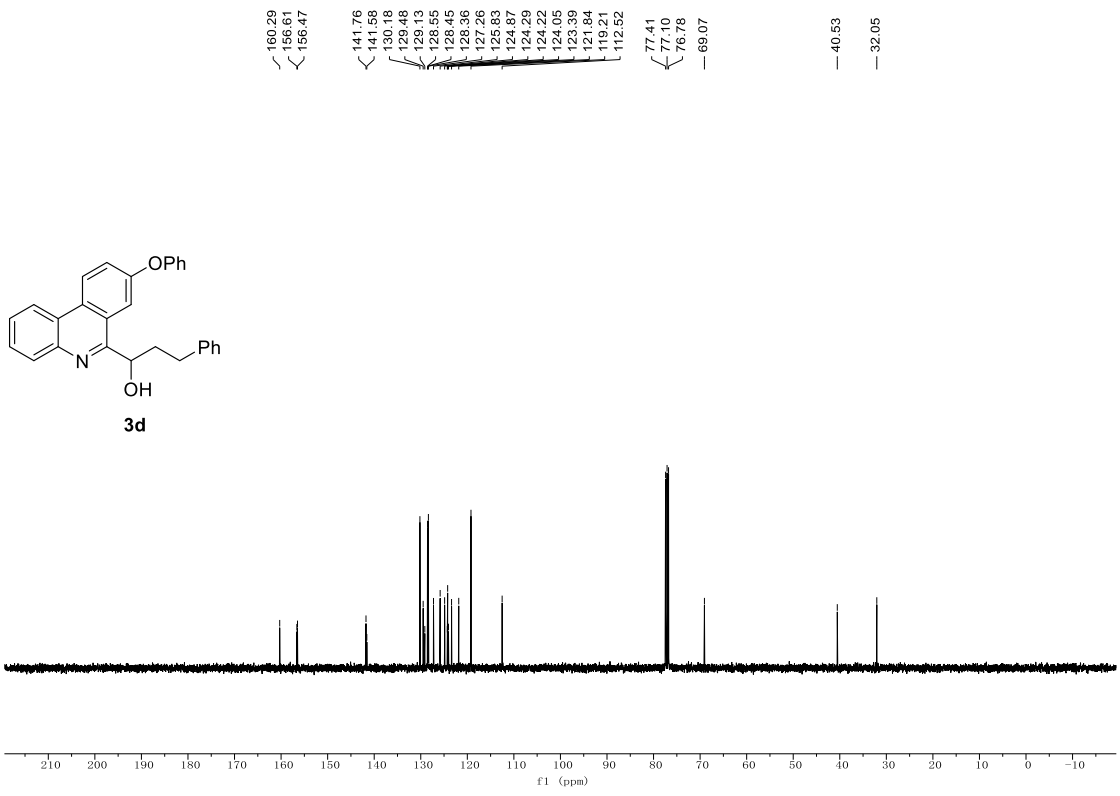
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3c



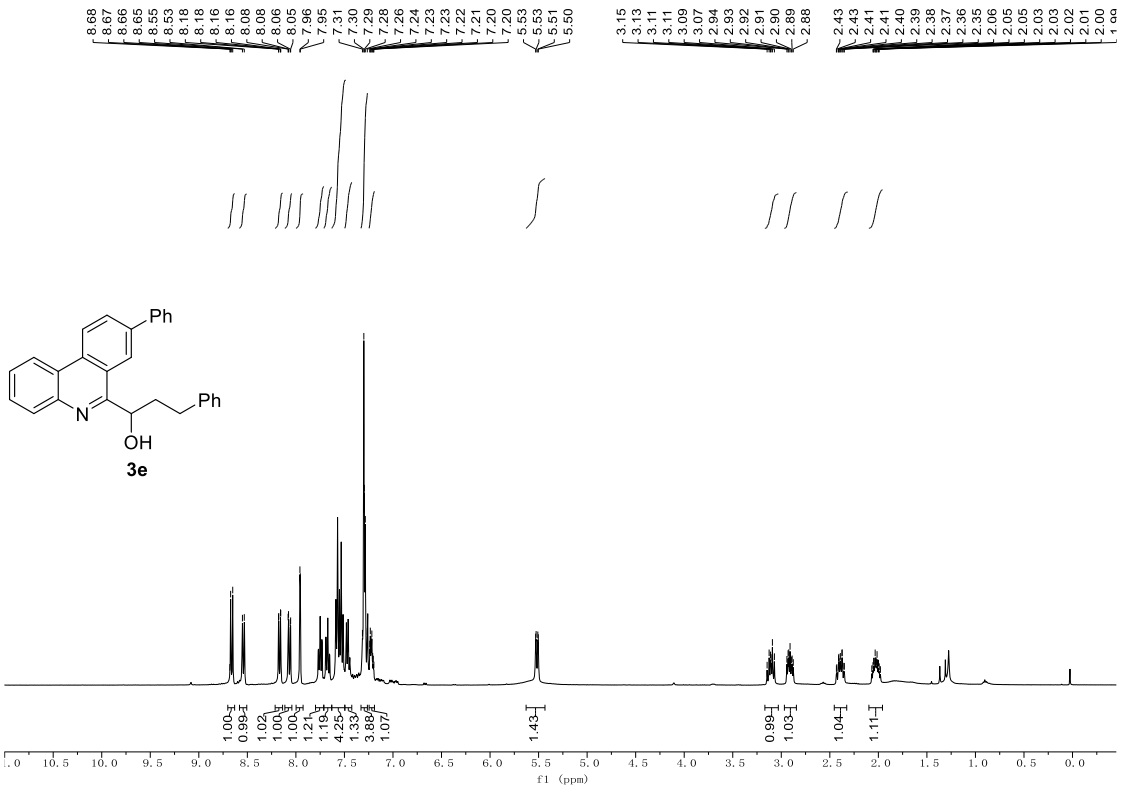


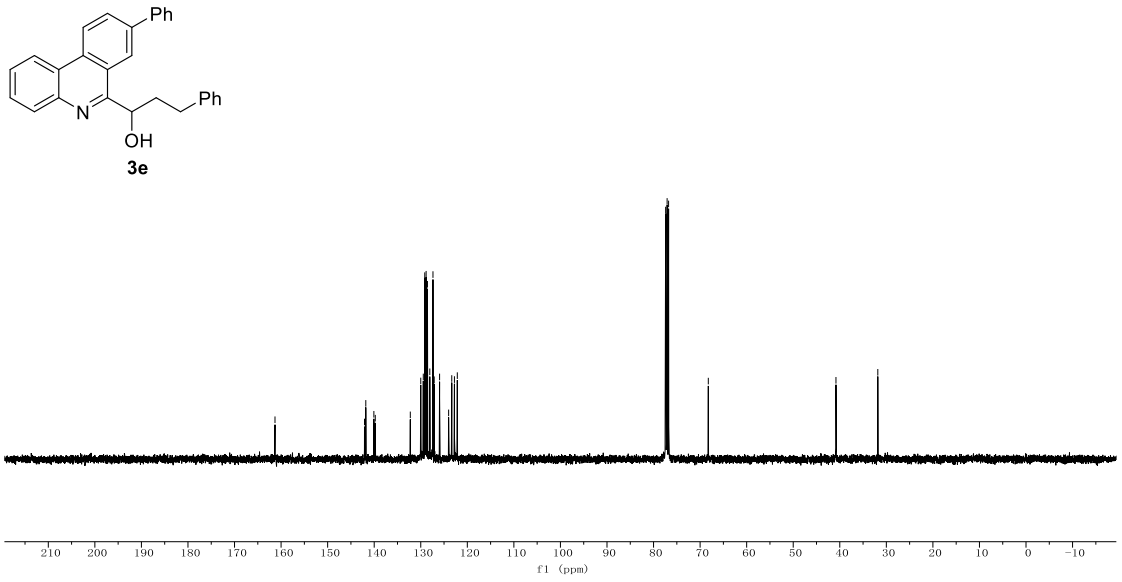
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3d



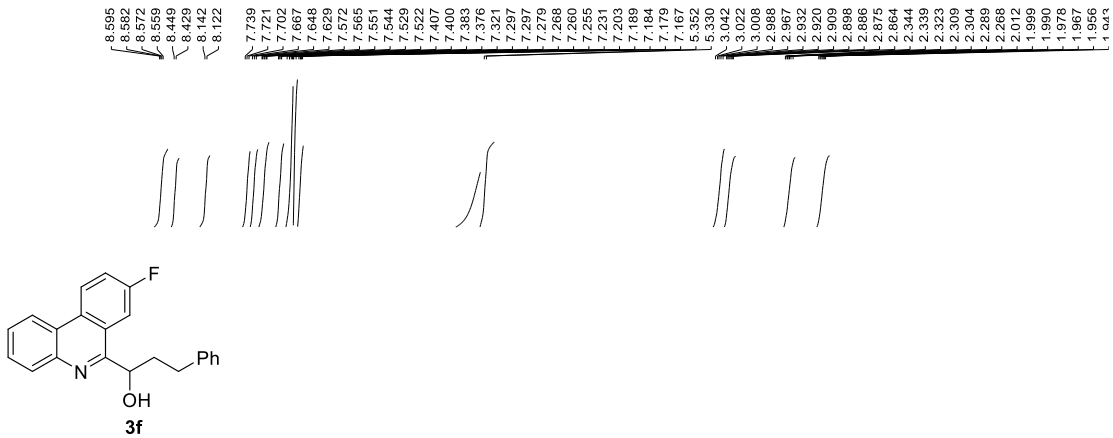


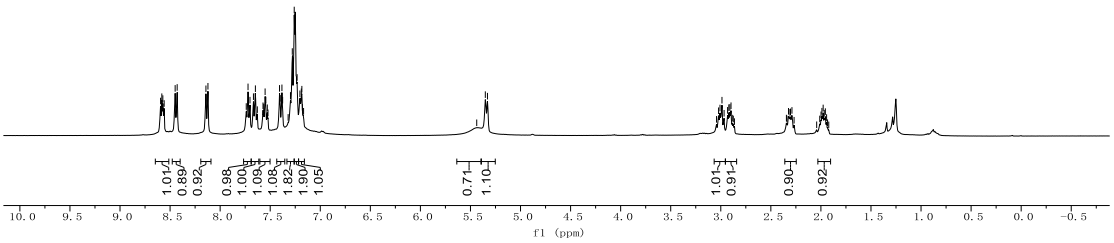
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3e

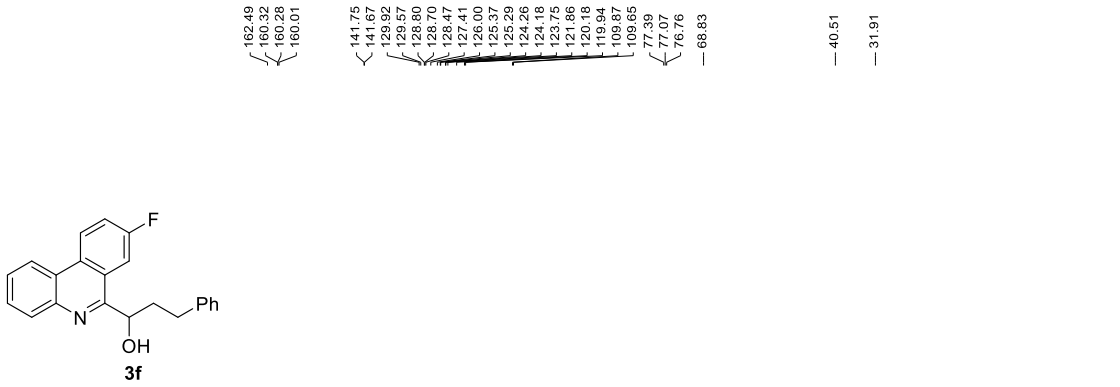


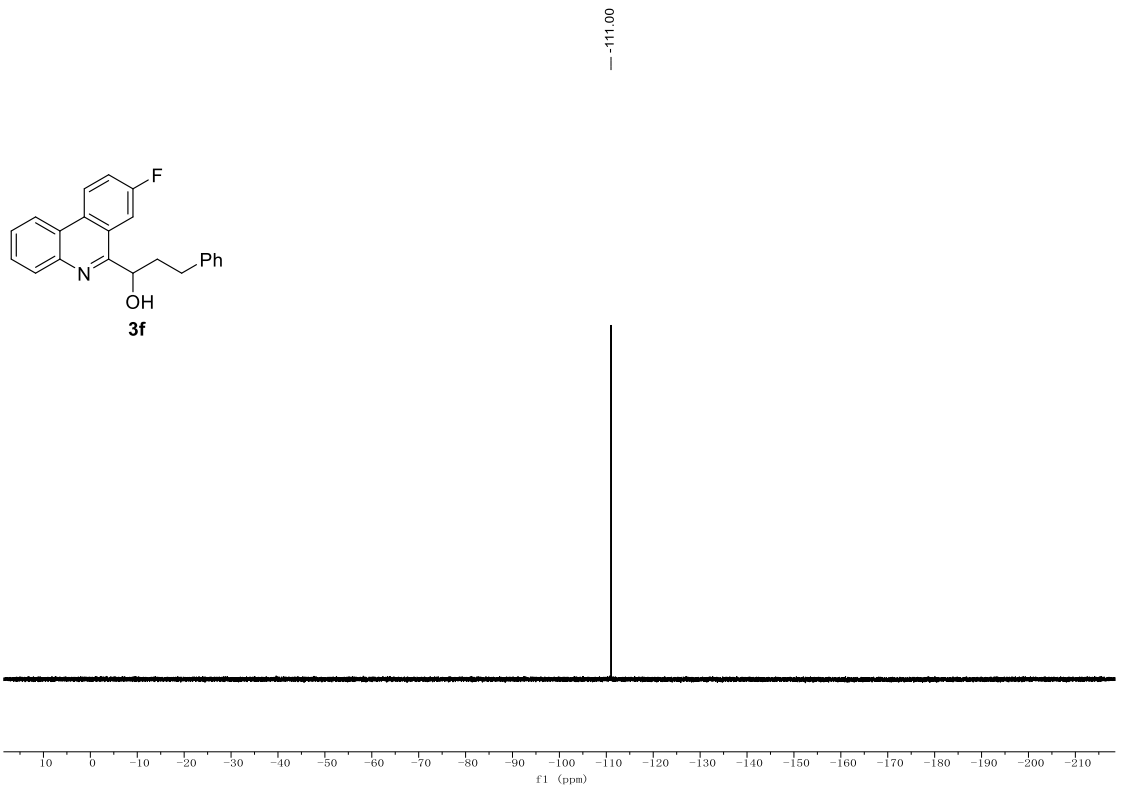


^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3f

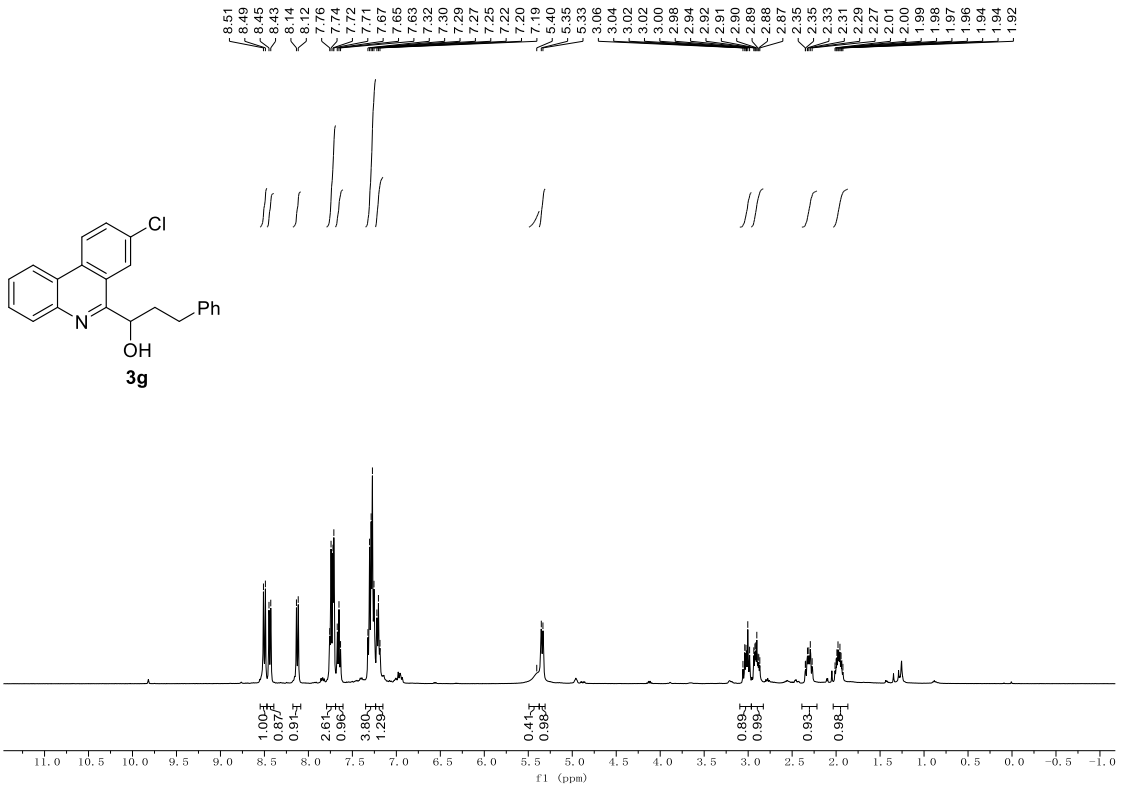


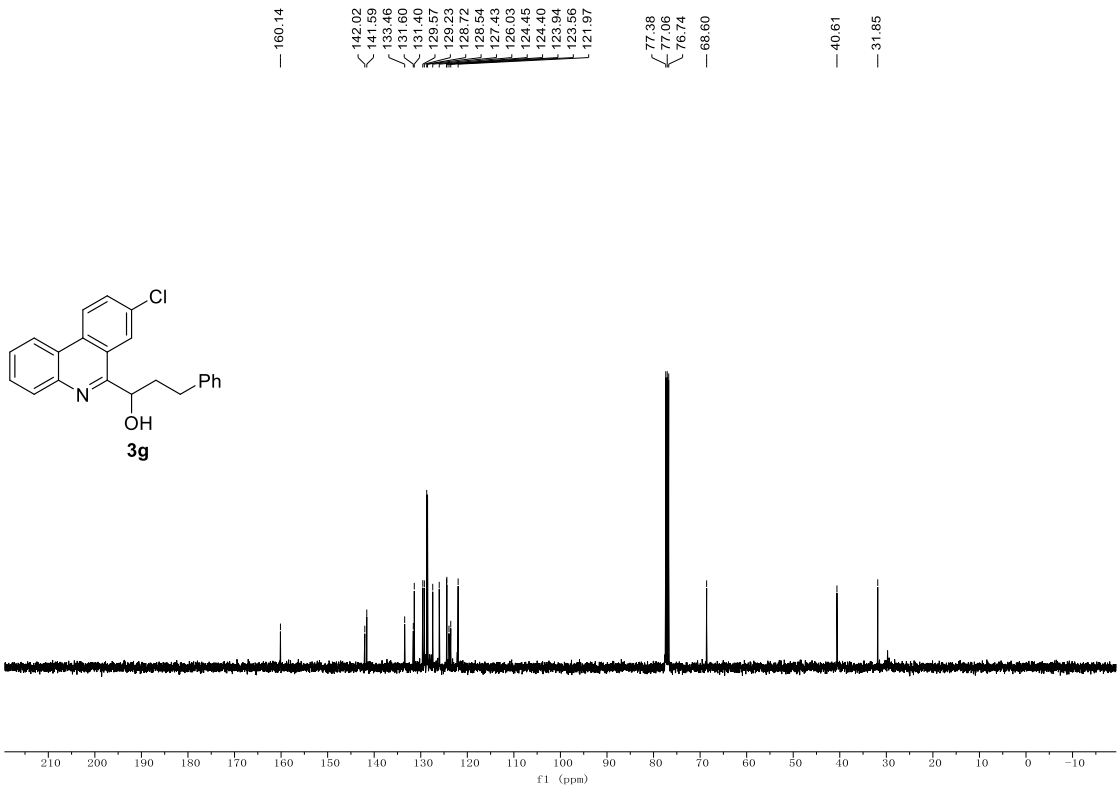




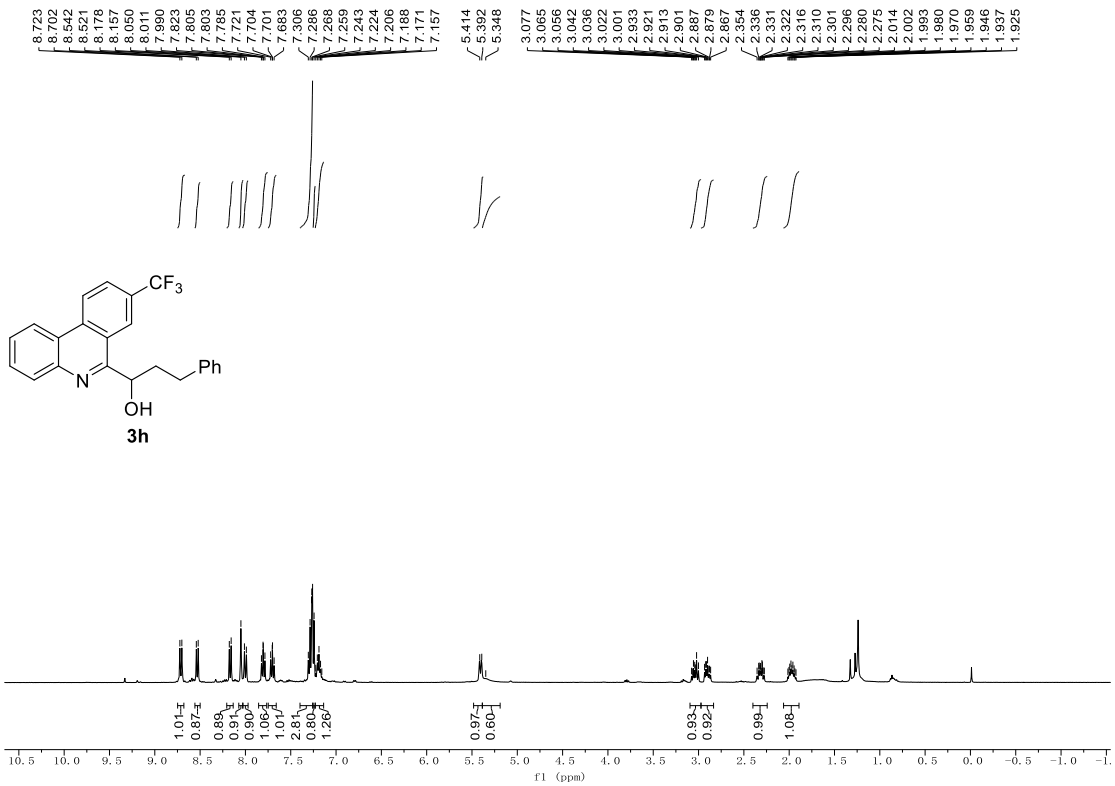


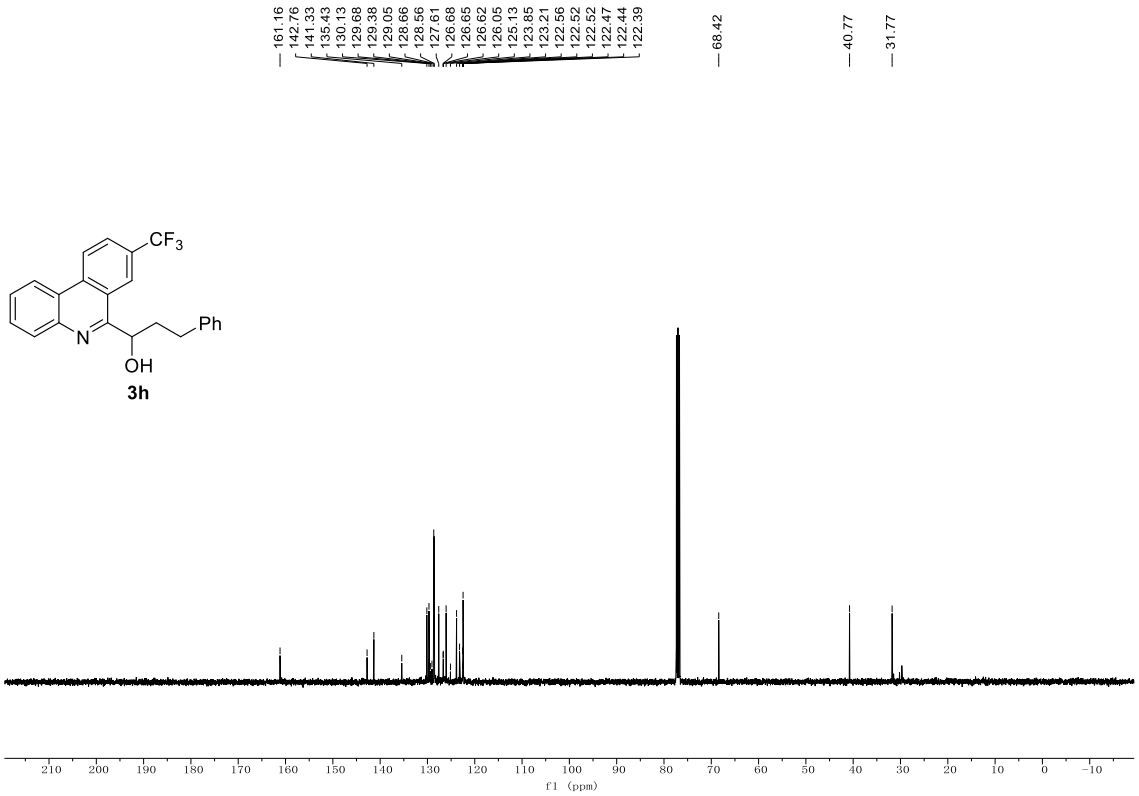
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3g





^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3h

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141.33
135.43
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129.68
129.38
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127.61
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126.62
126.05
125.13
123.85
123.21
122.56
122.52
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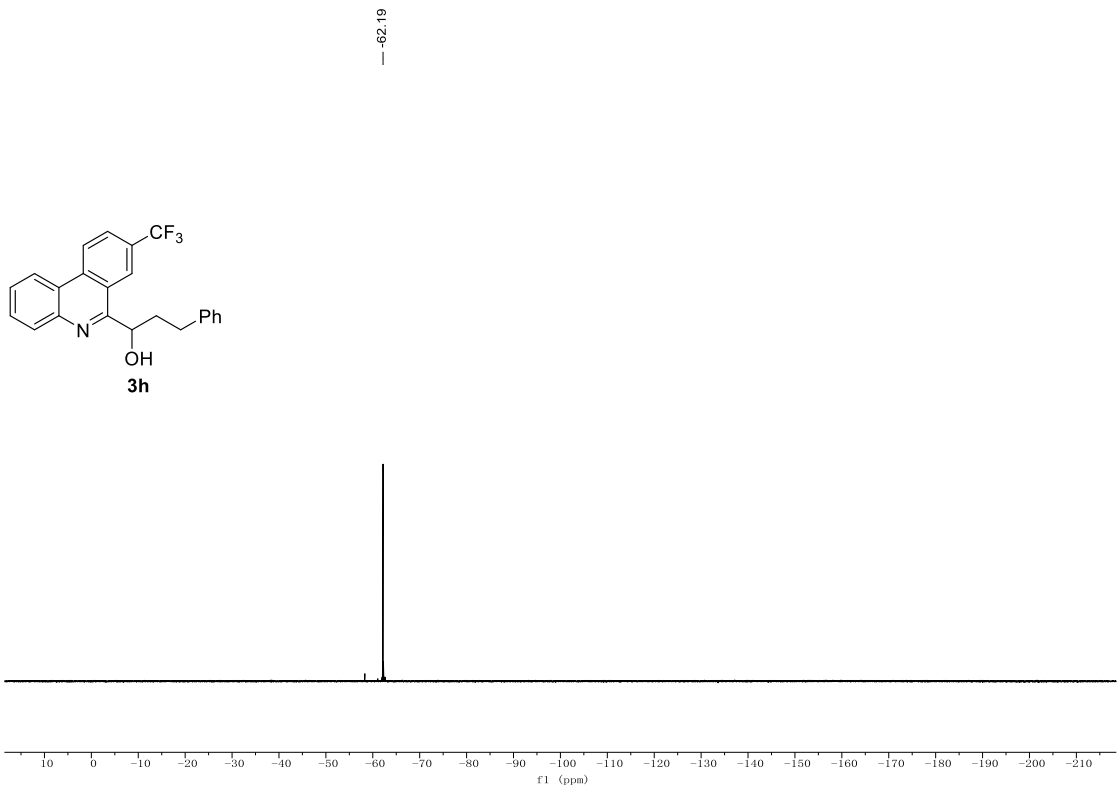
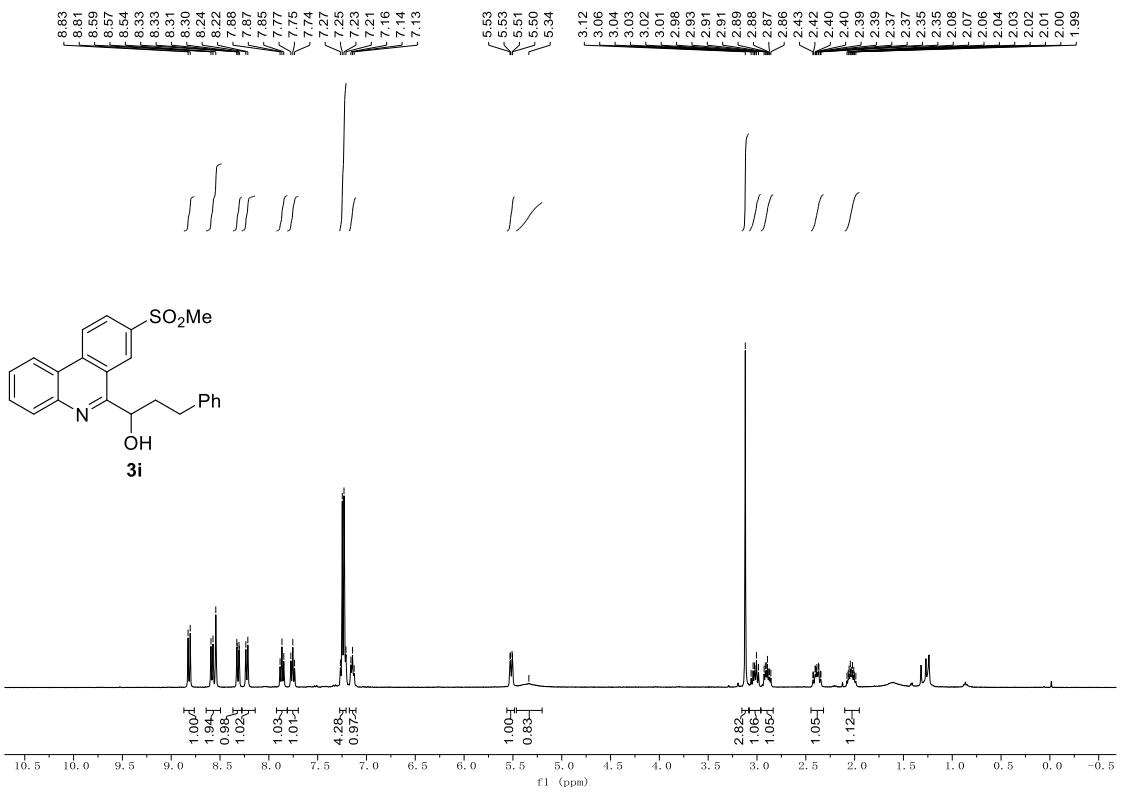
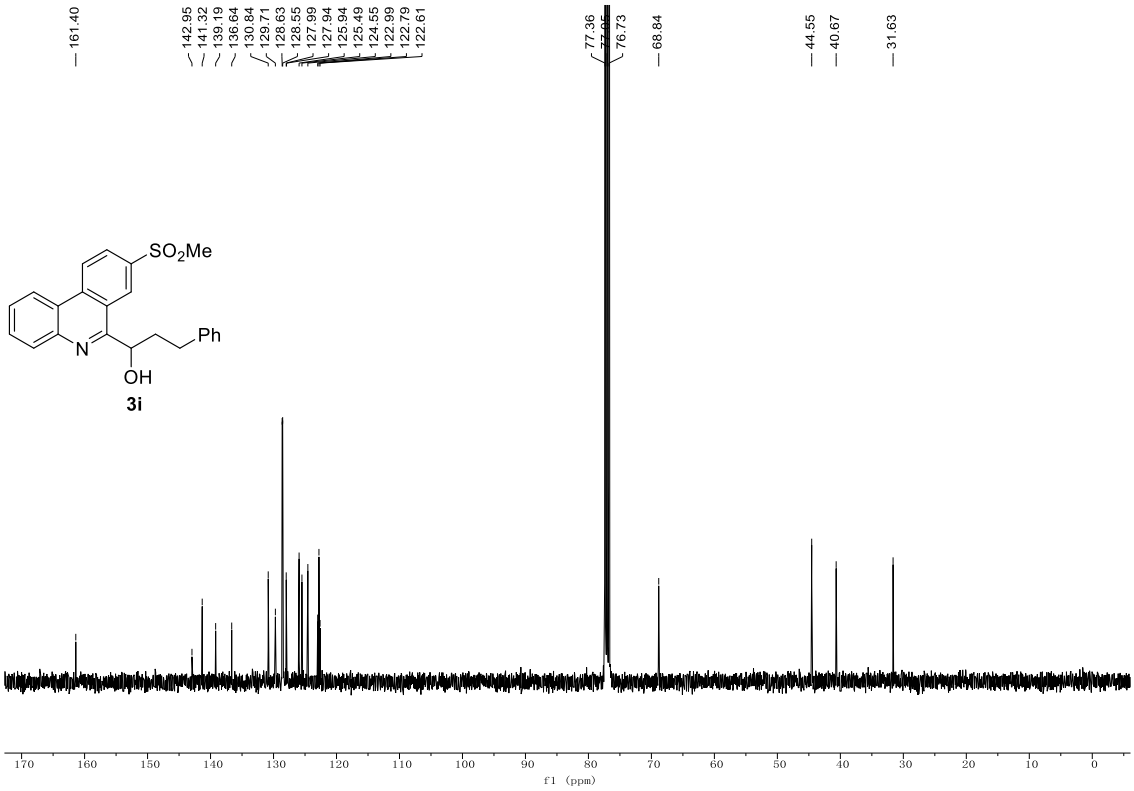
122.47
122.44
122.39
68.42
40.77
31.77
CF3
Ph
N
OH
3h
f1 (ppm)

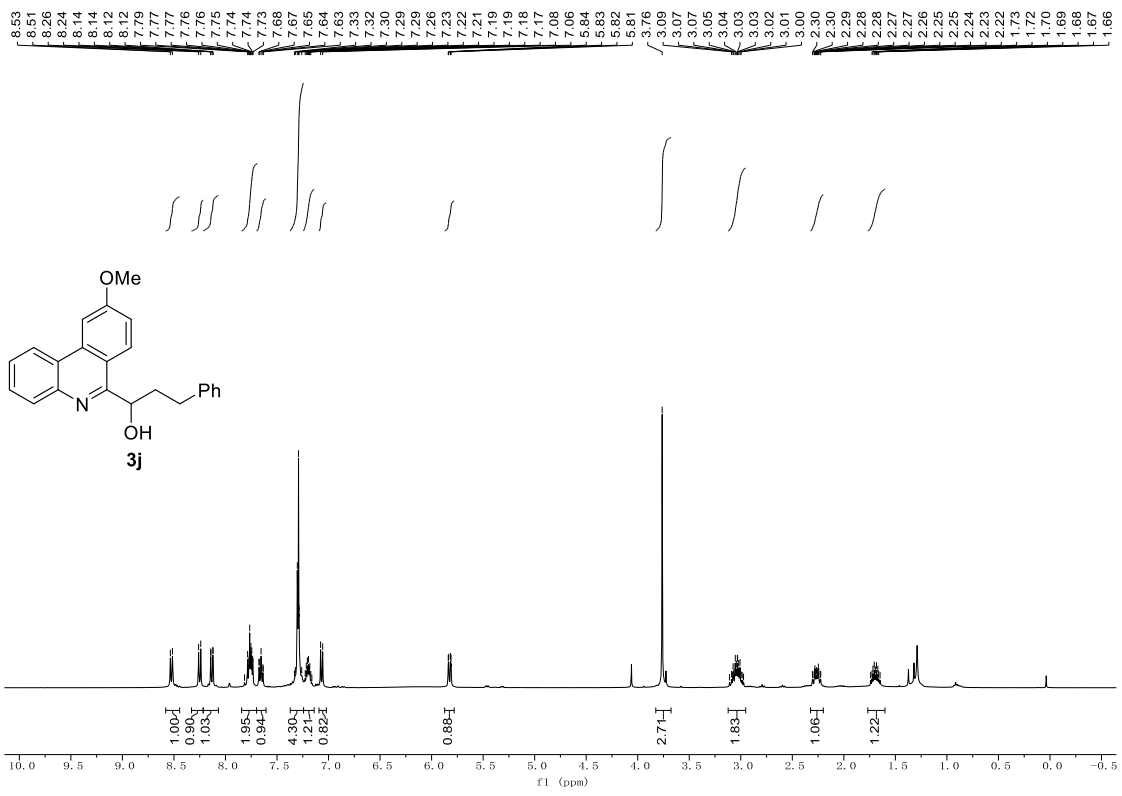

-62.19
CF3
Ph
N
OH
3h
f1 (ppm)

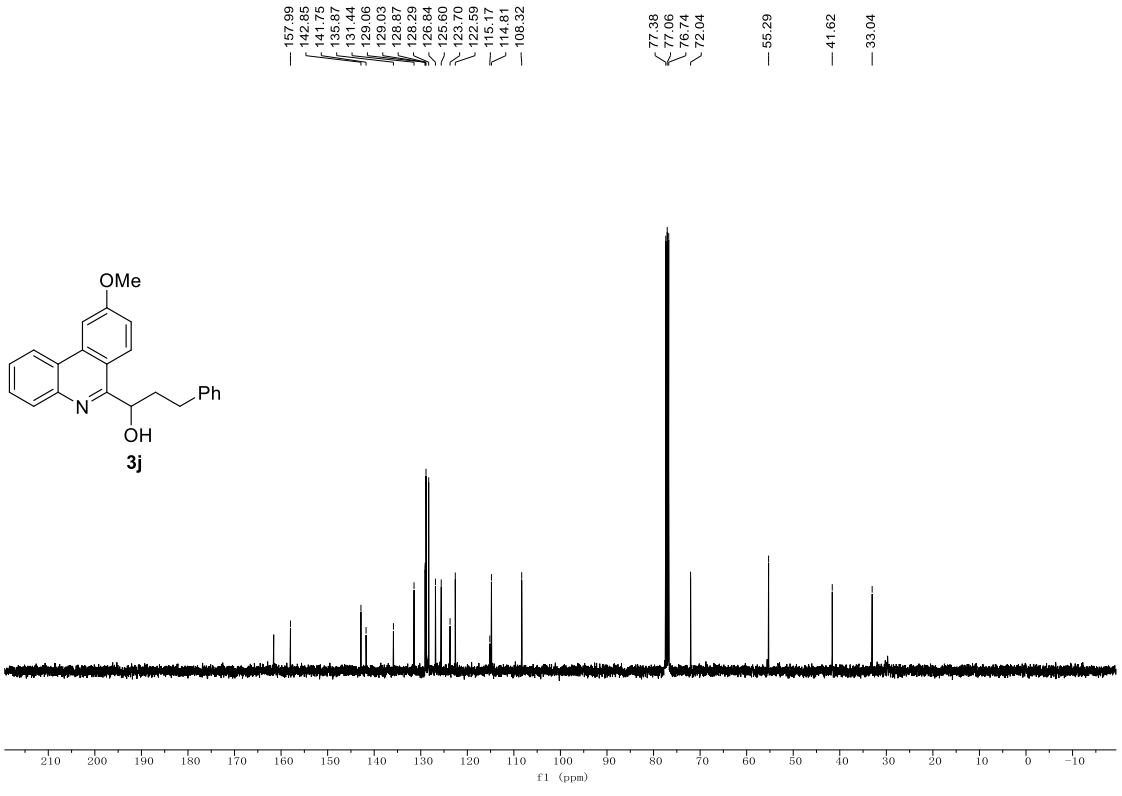
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3i



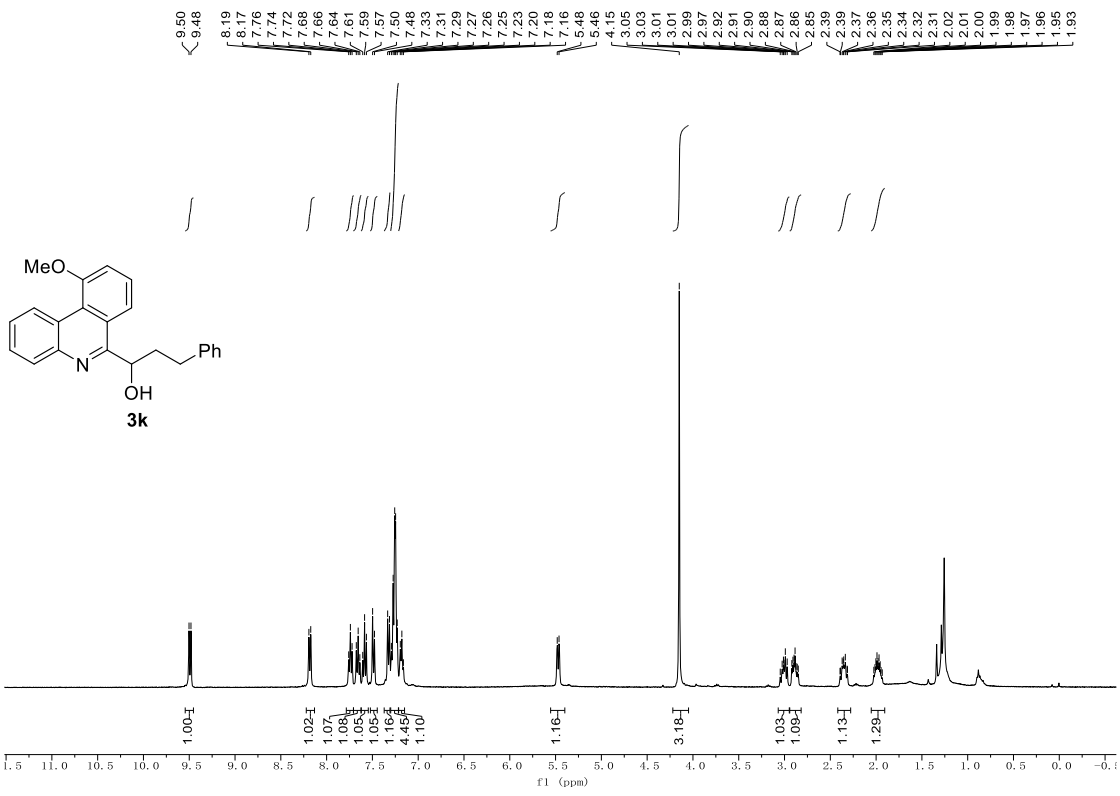


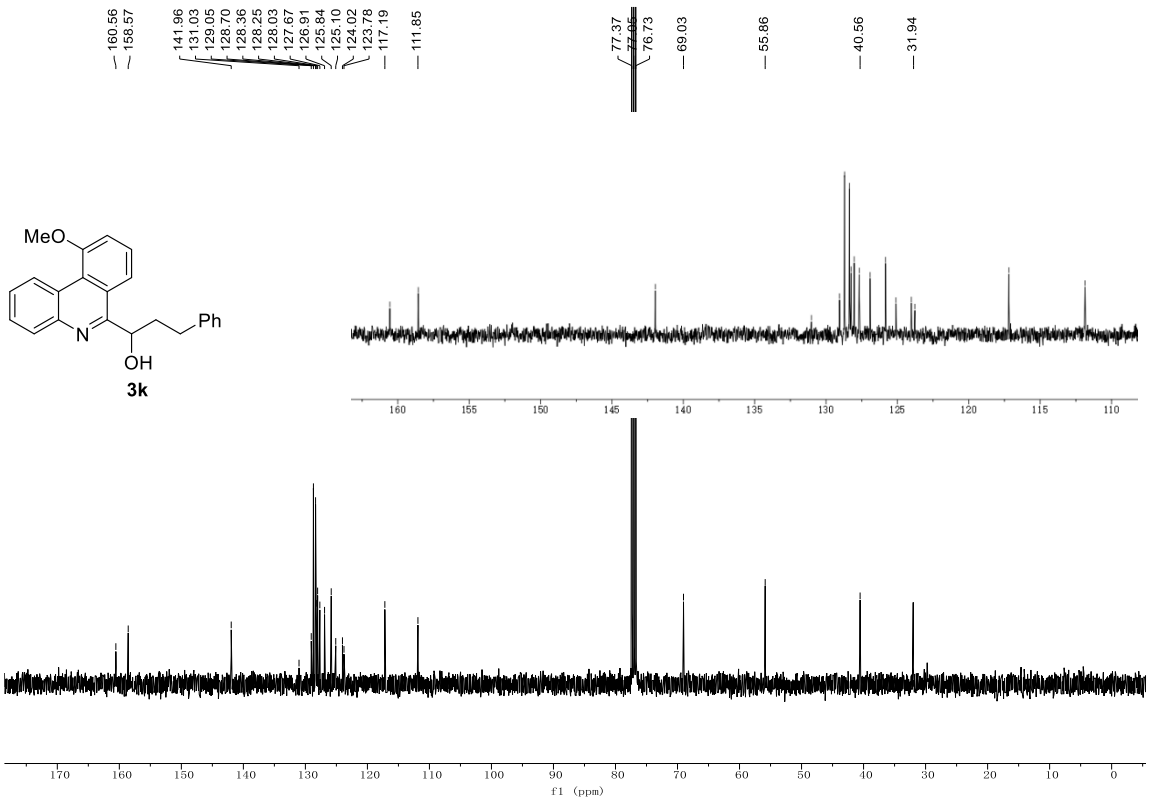
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3j



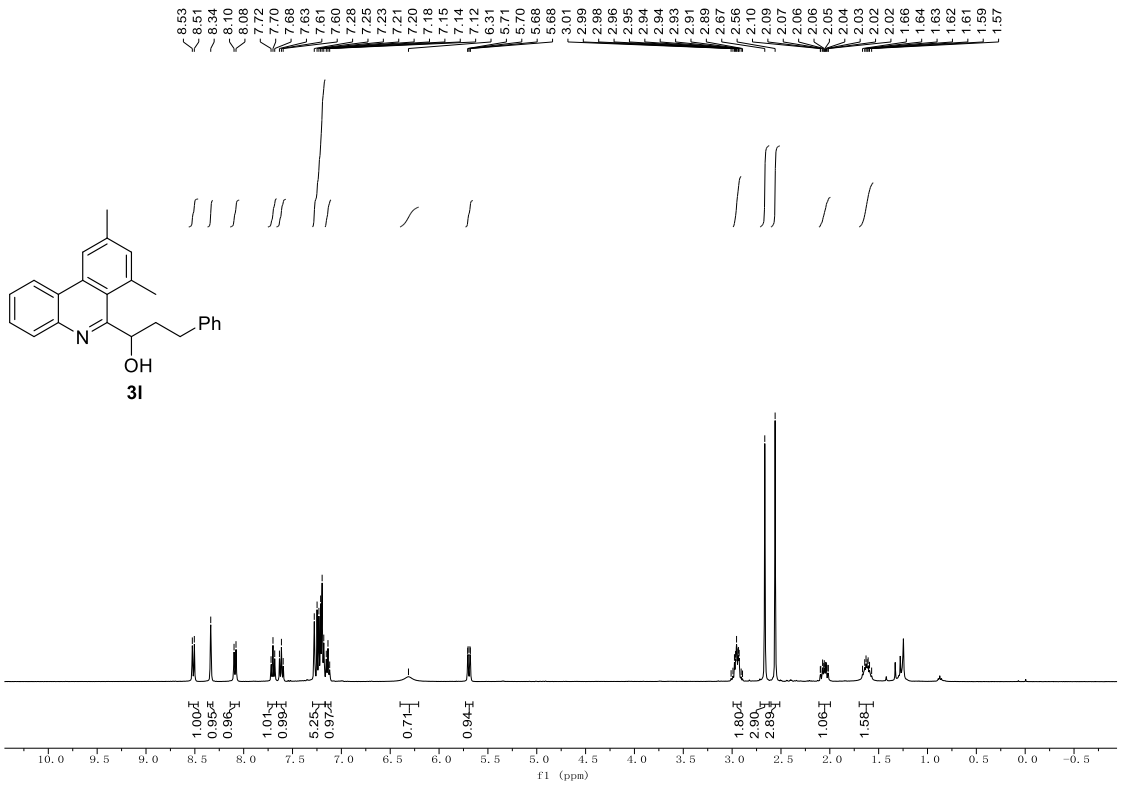


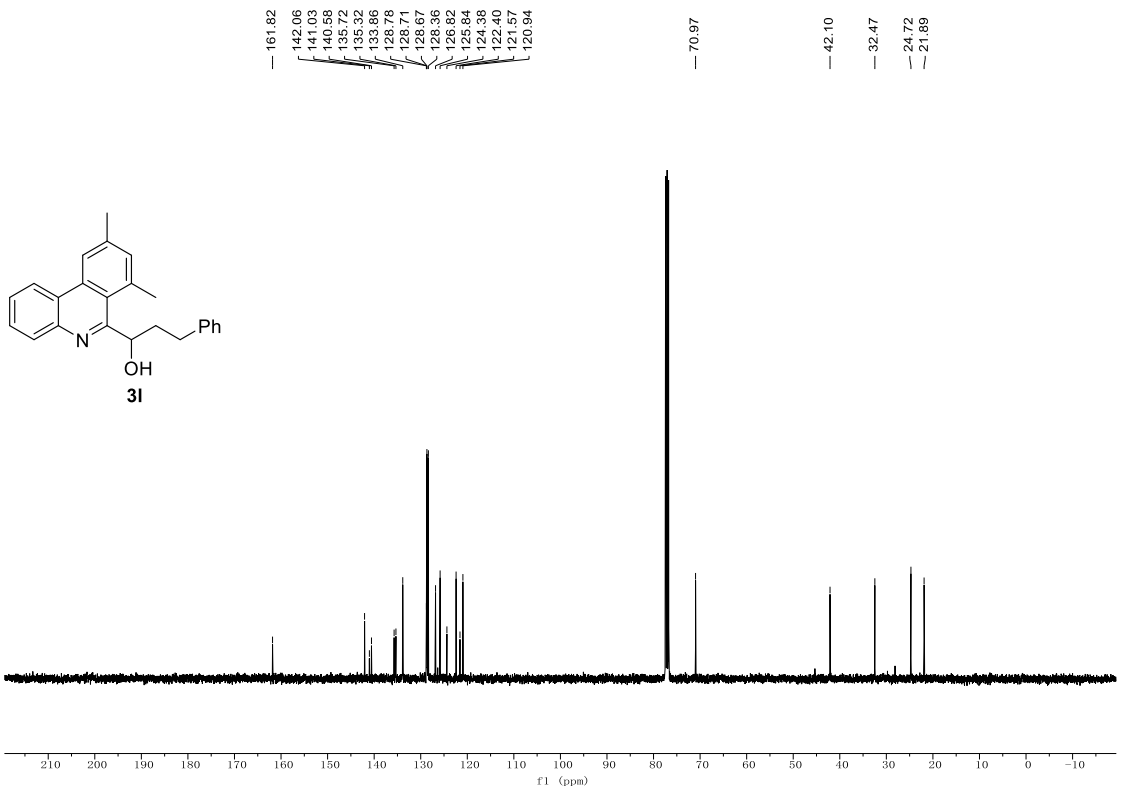
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3k



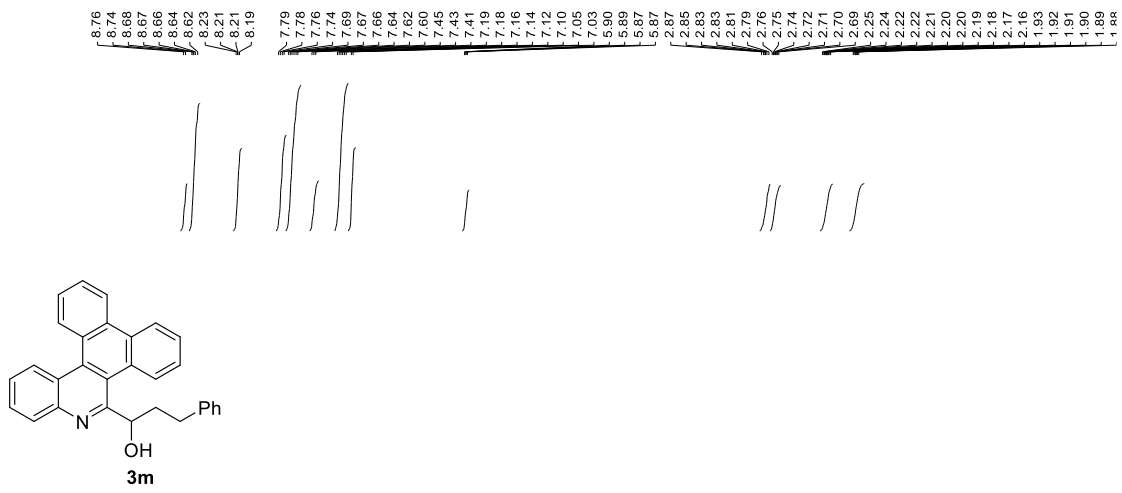


^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3l

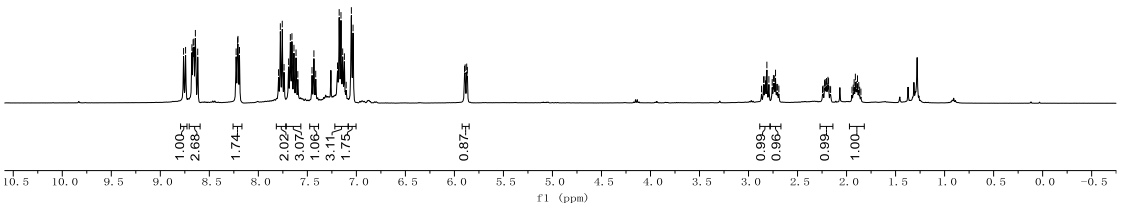


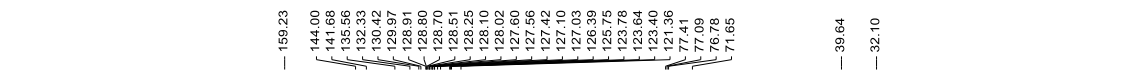


^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3m

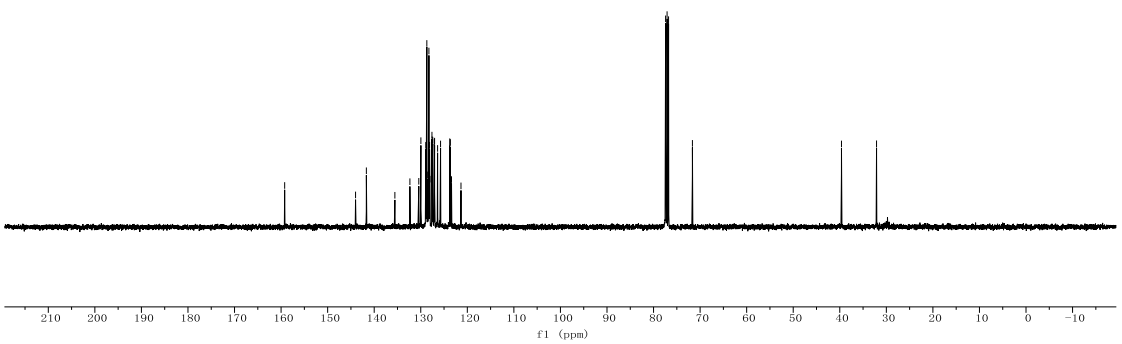


3m

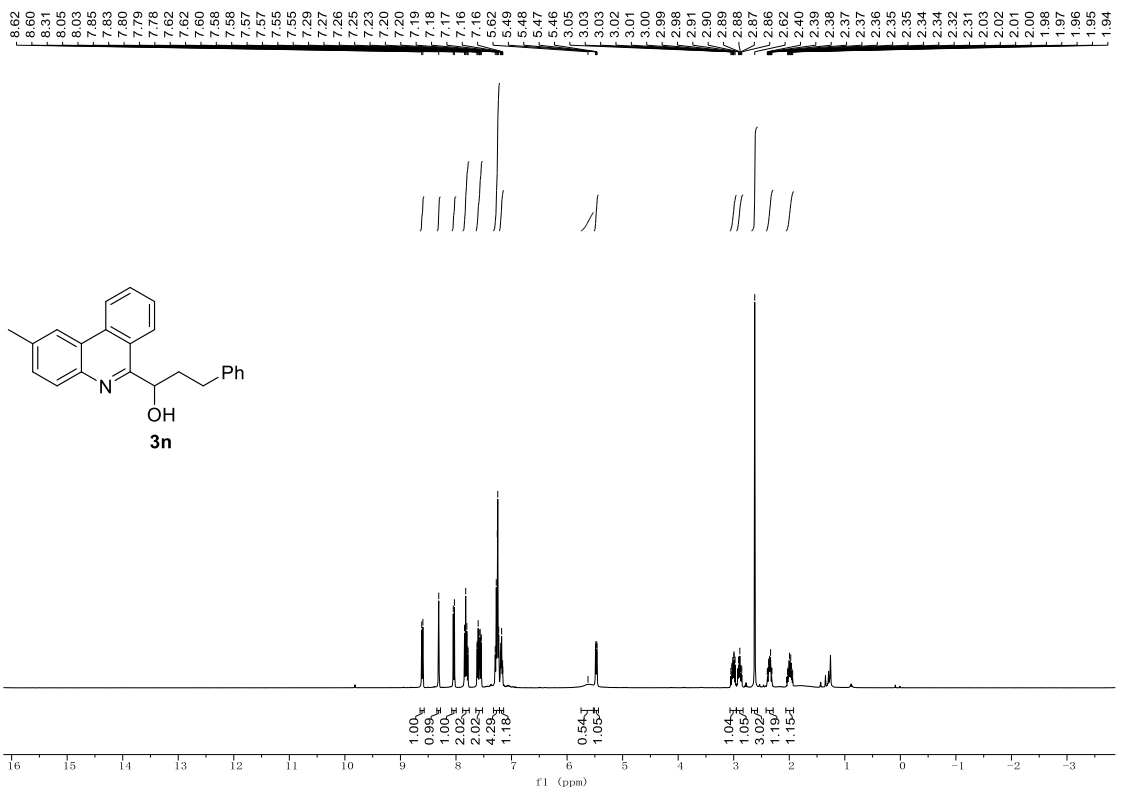


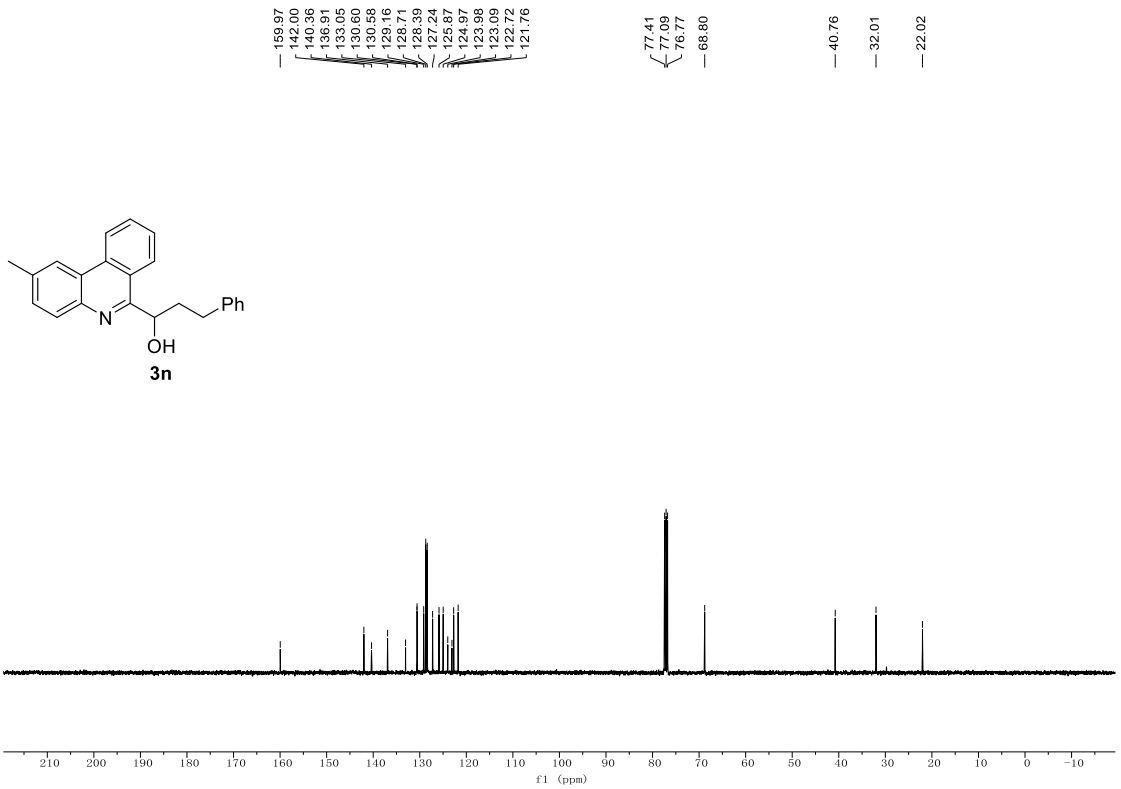


3m

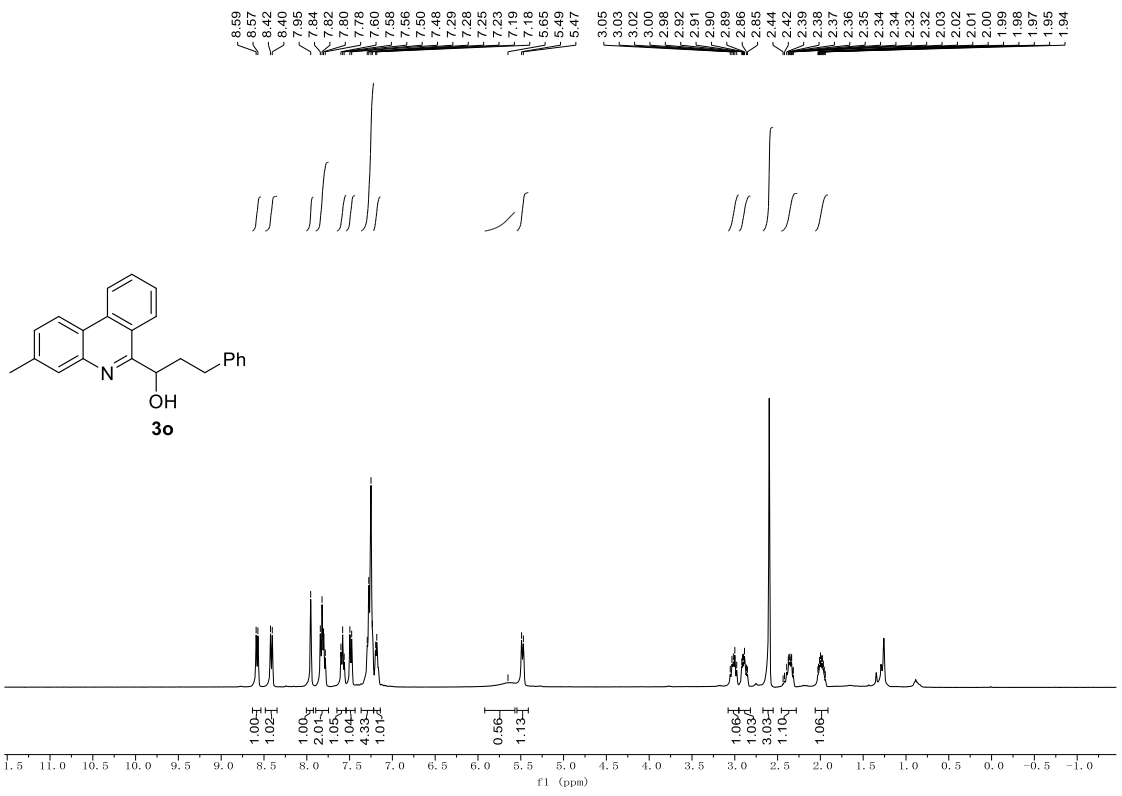


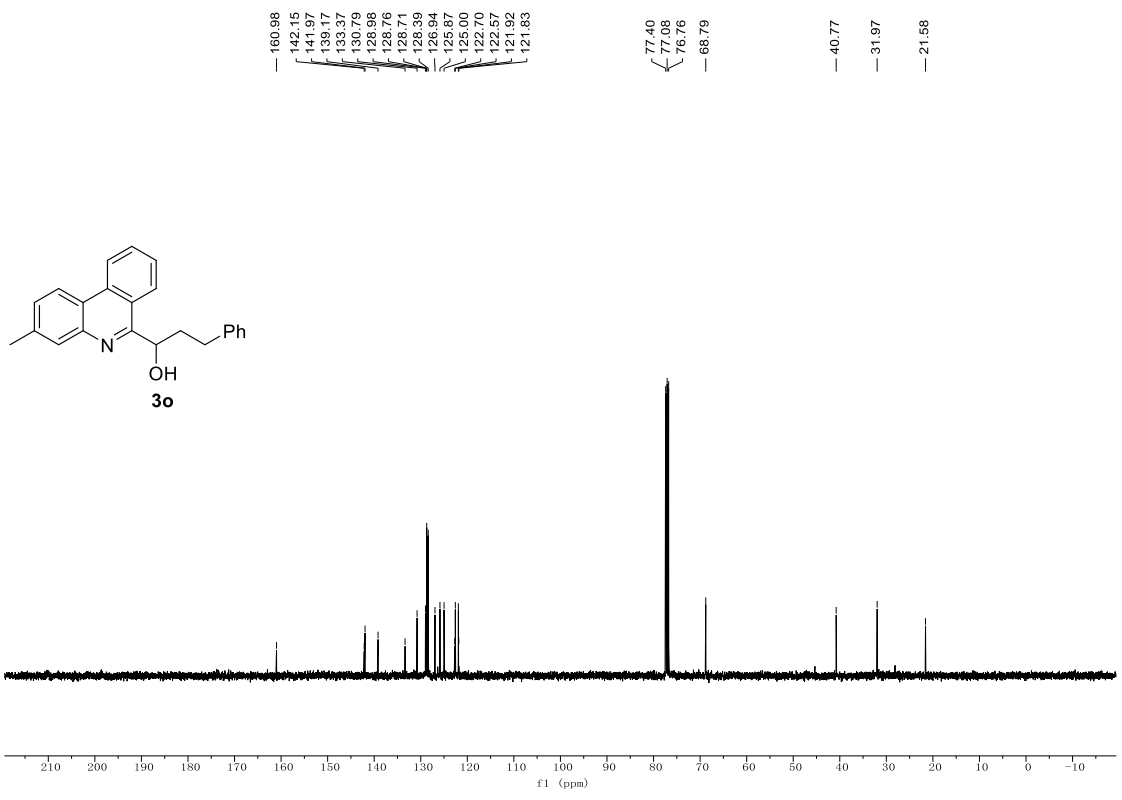
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3n



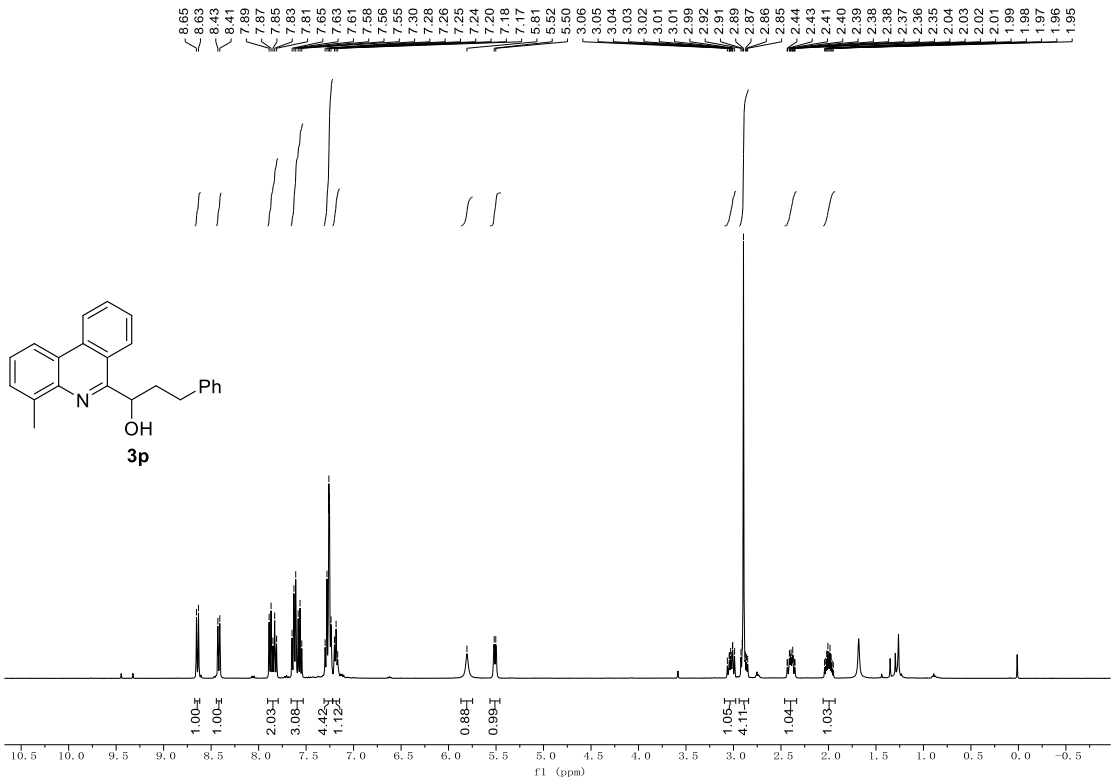


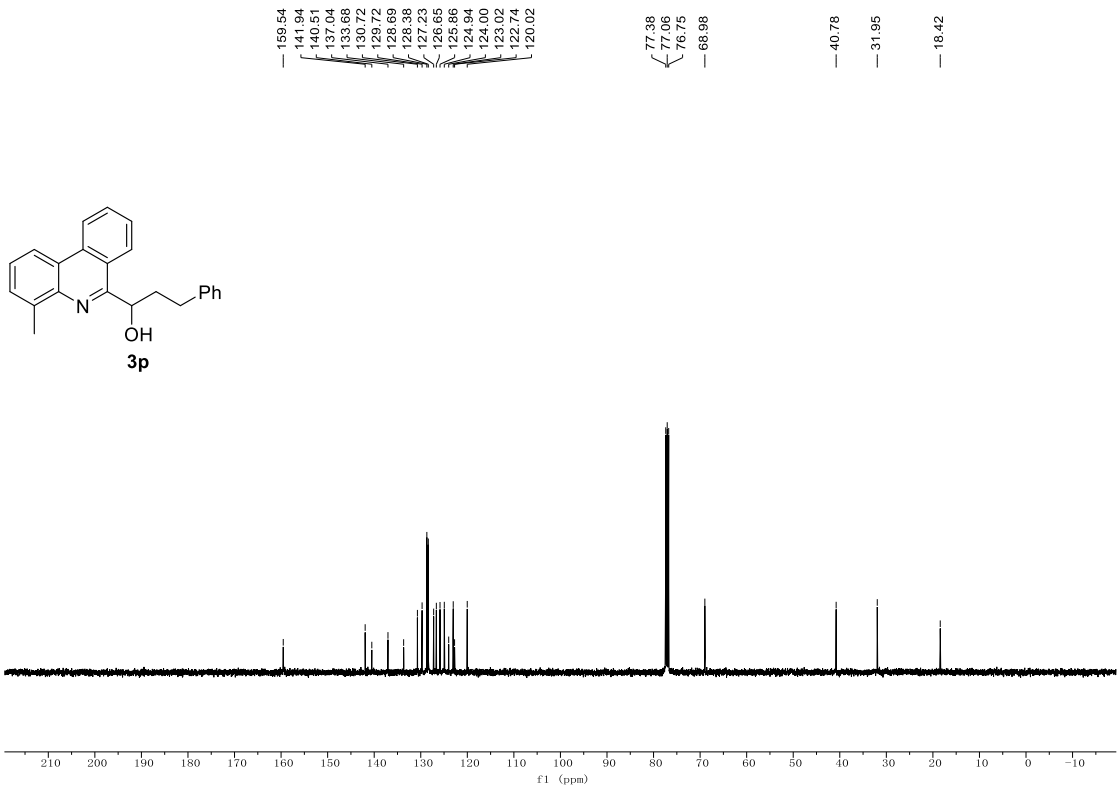
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3o



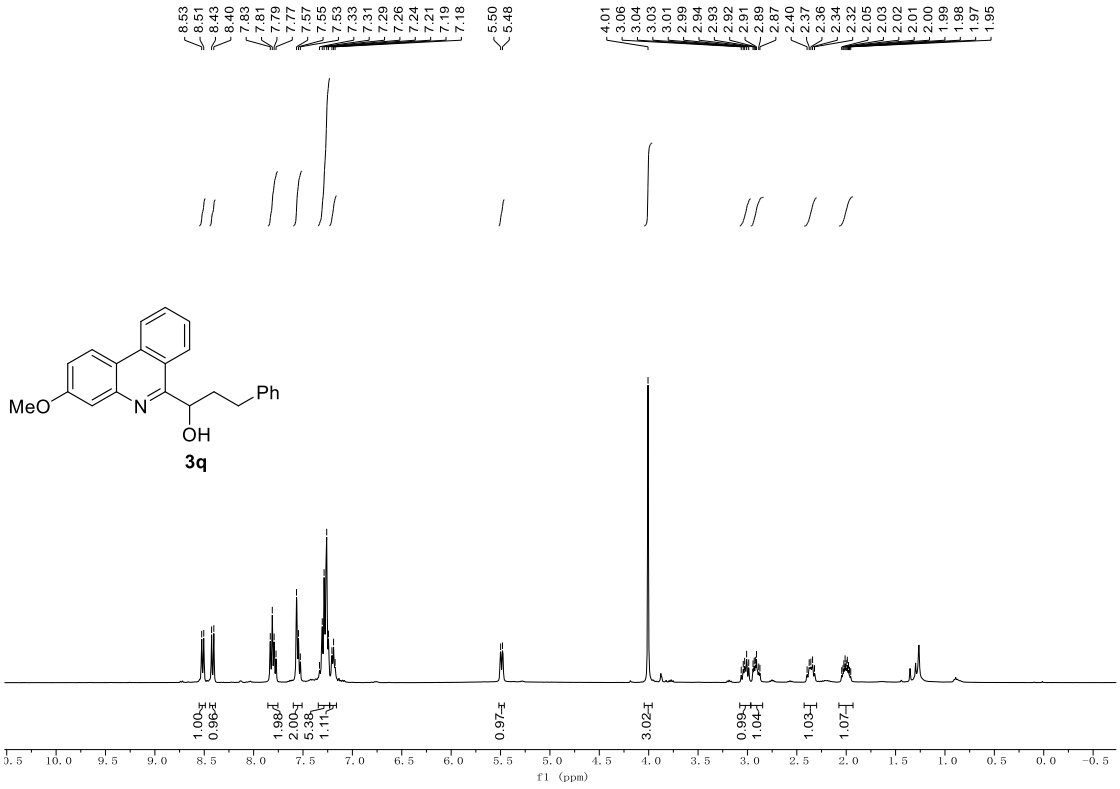


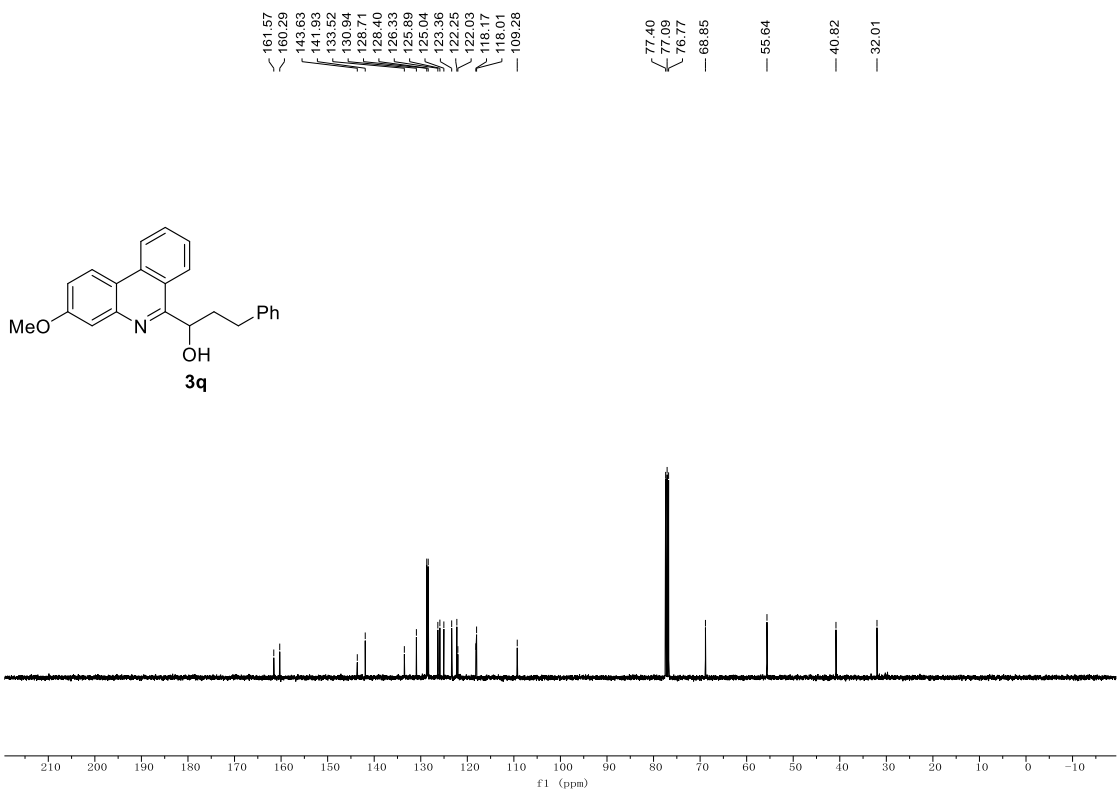
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3p



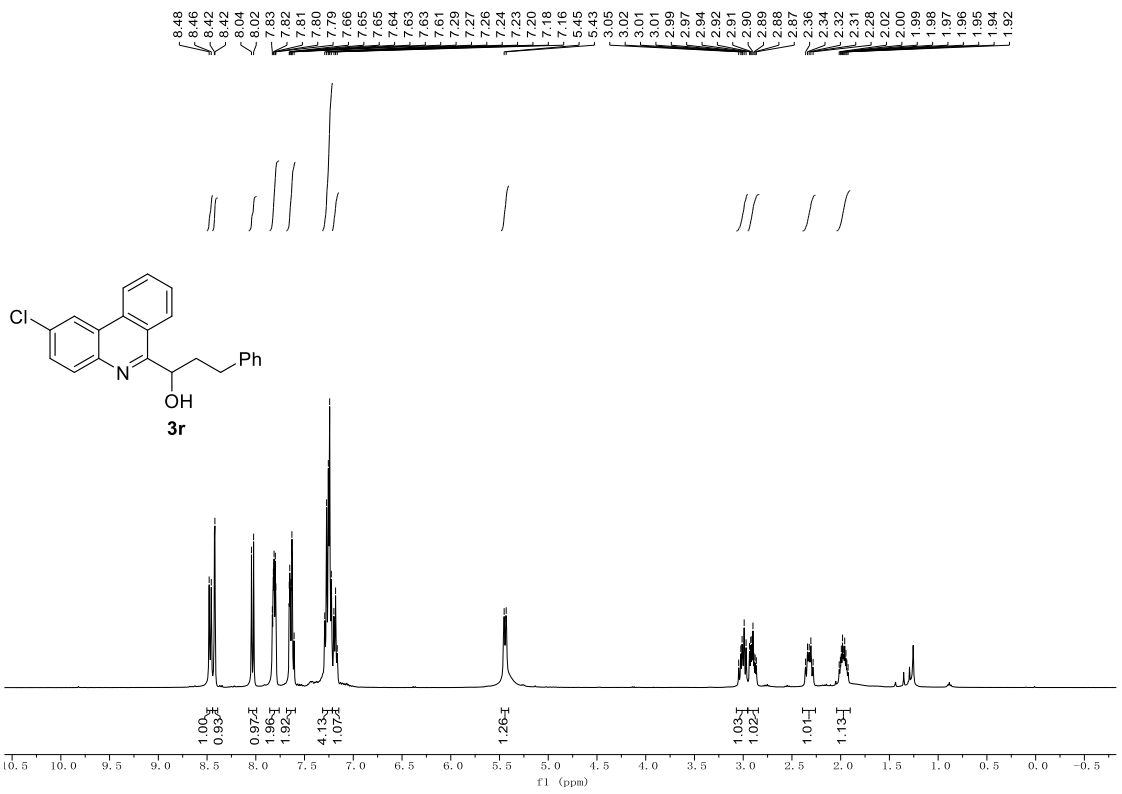


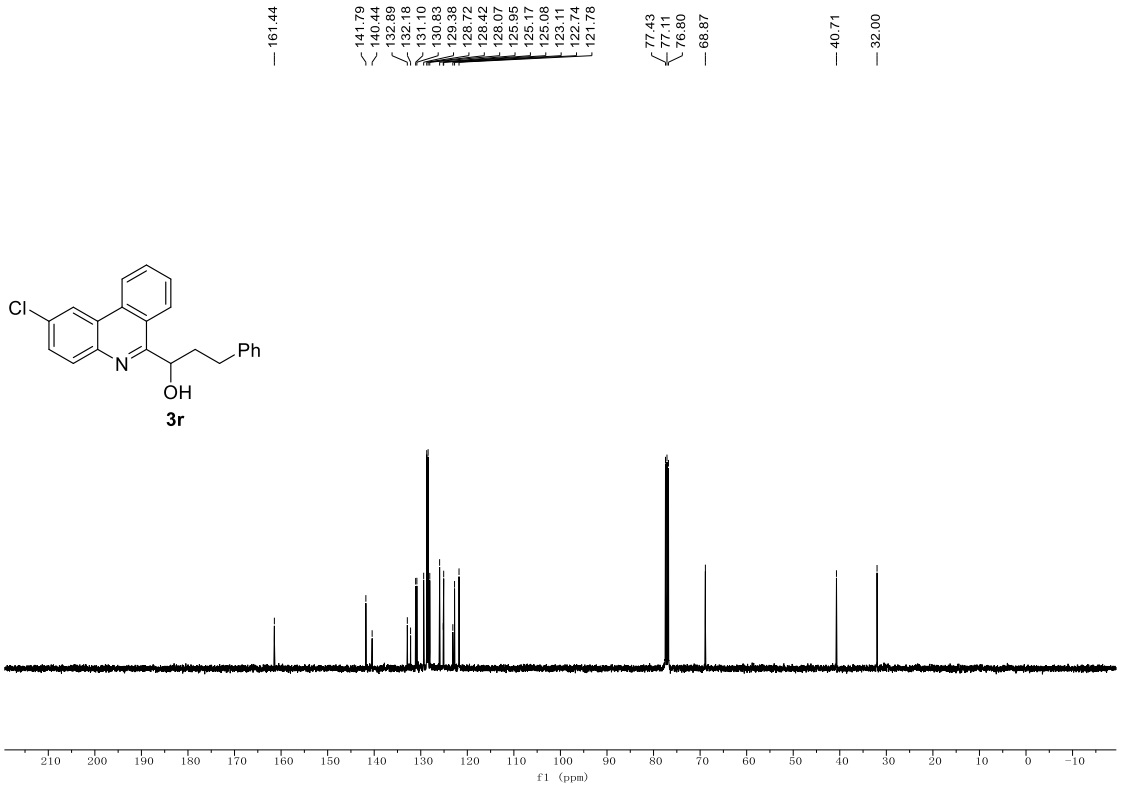
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3q



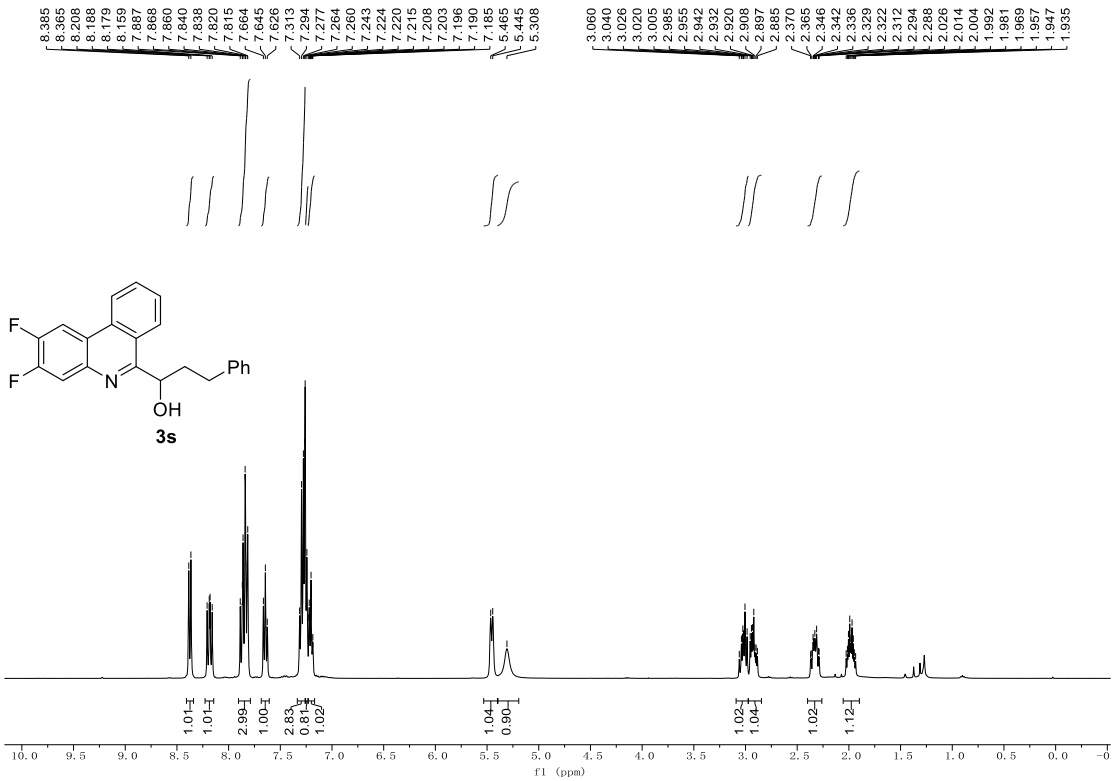


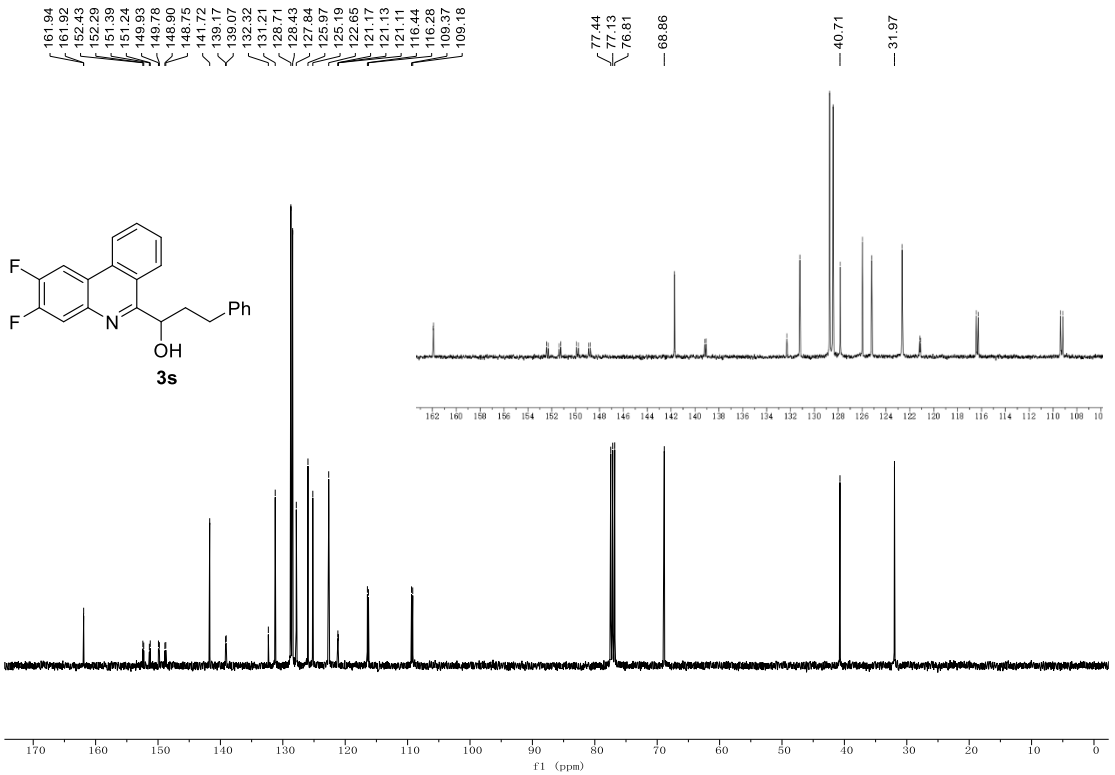
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3r

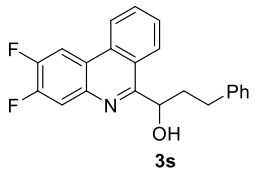




^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 3s

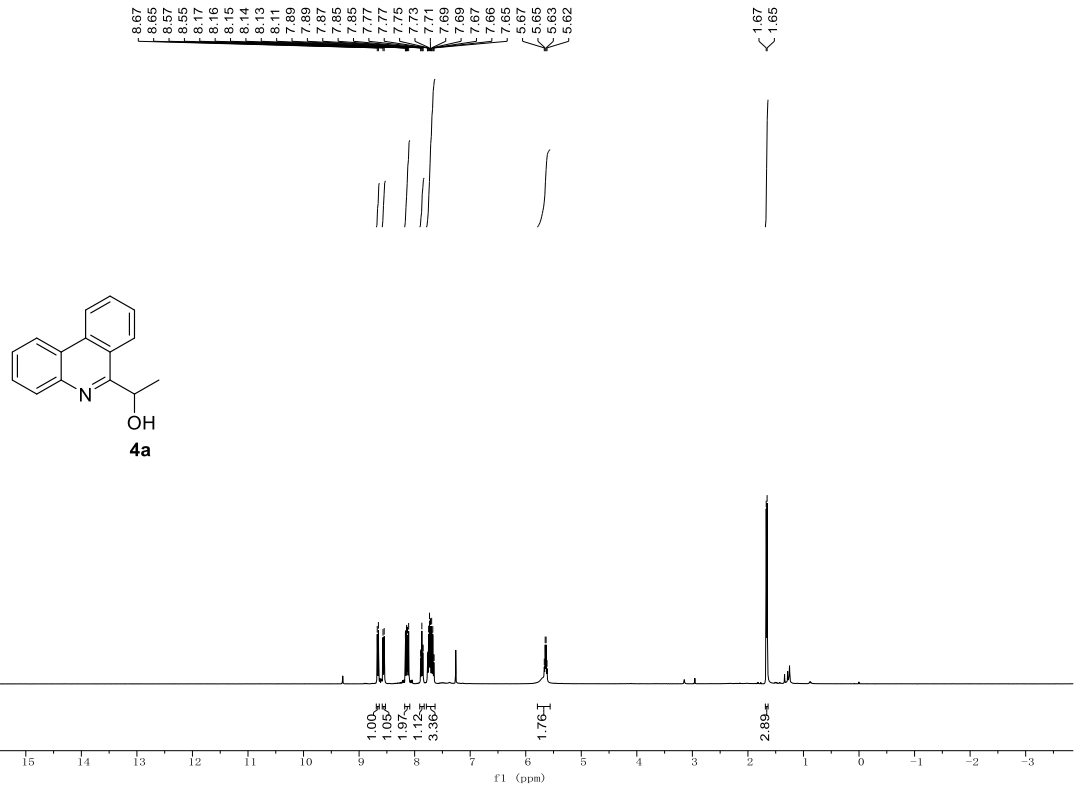




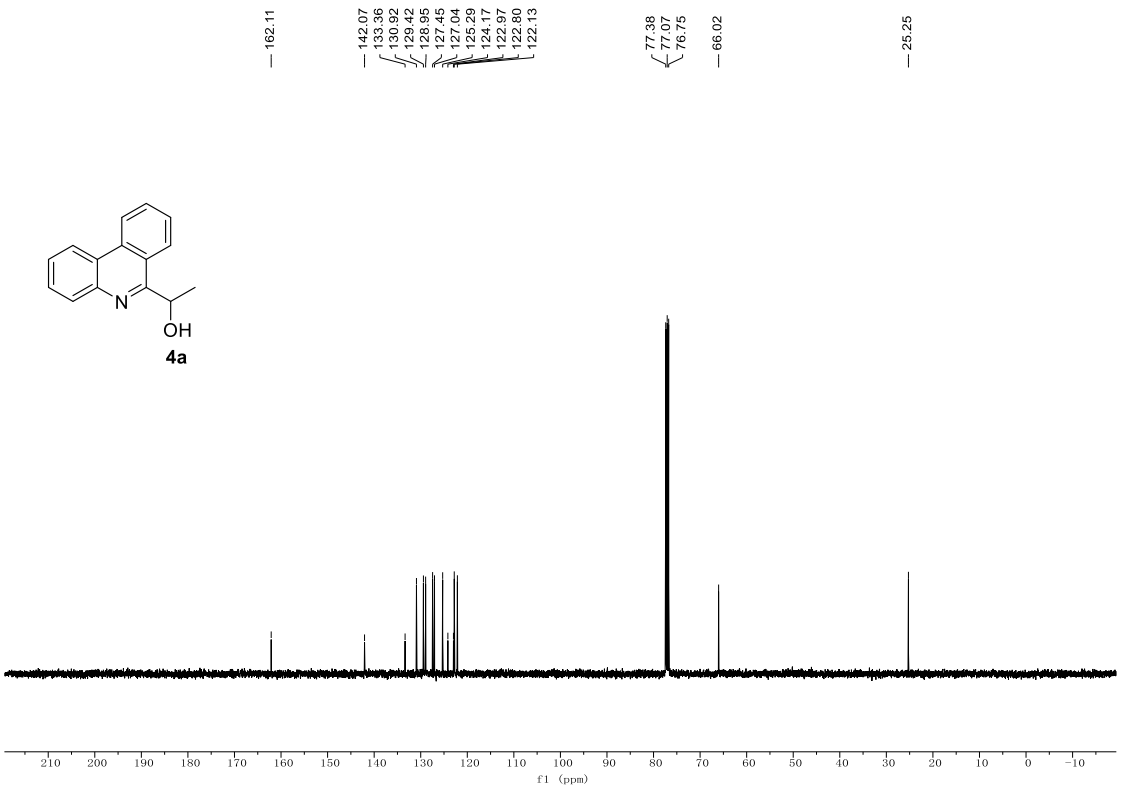


3s

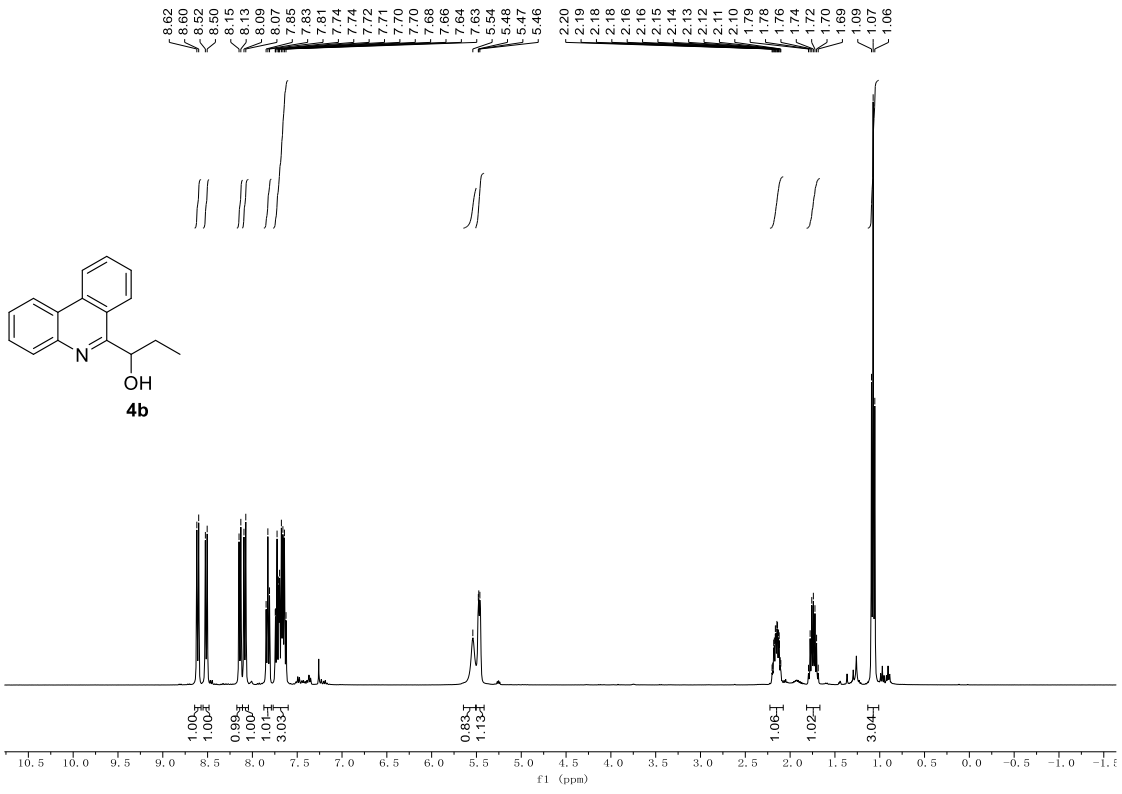
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4a

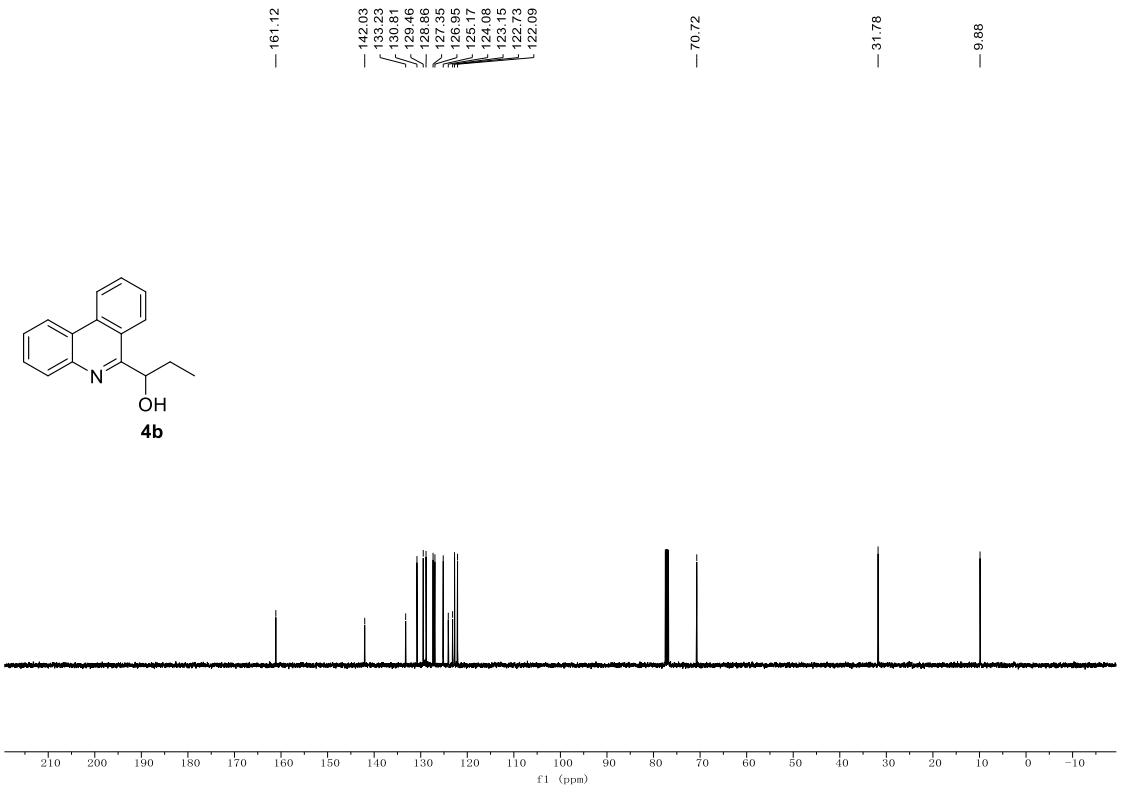


4a

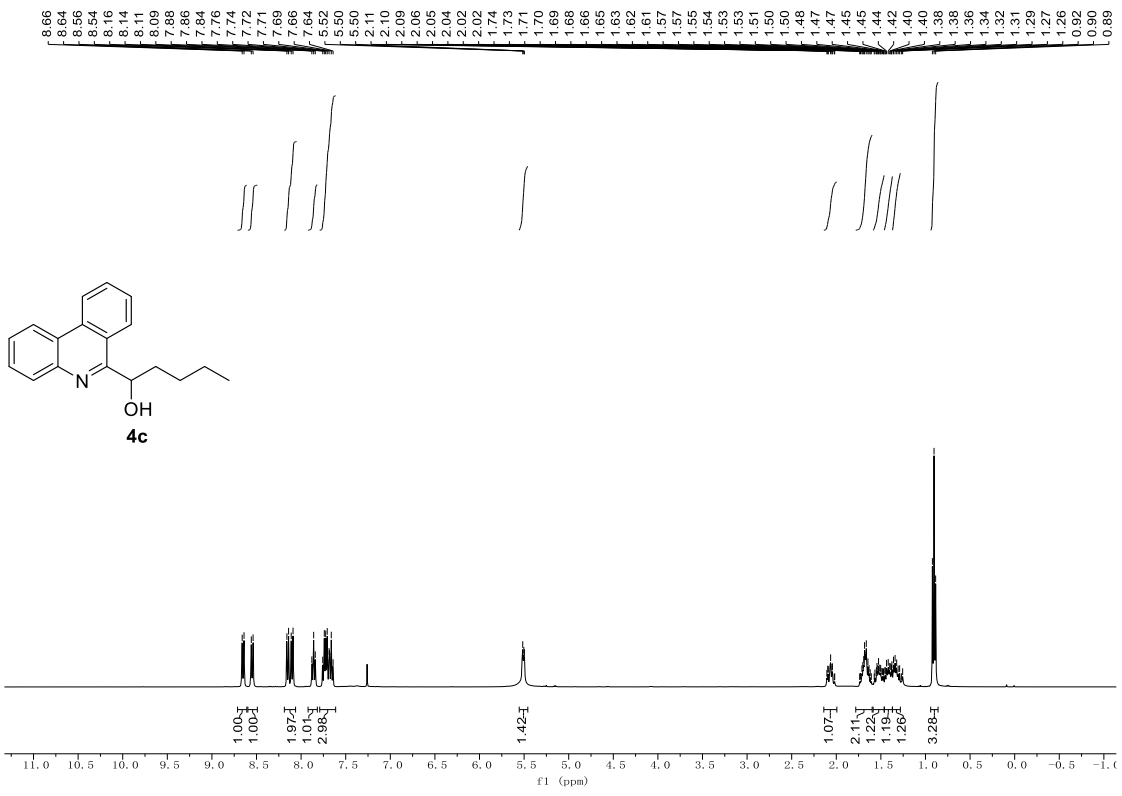


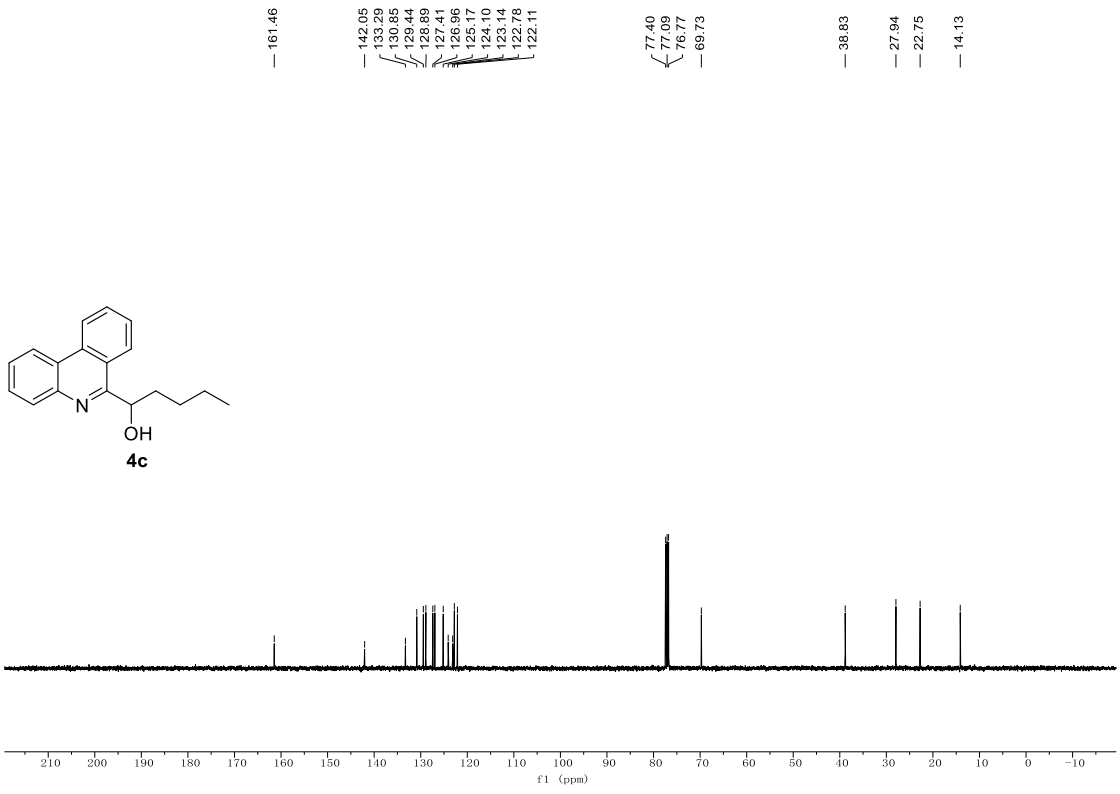
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4b



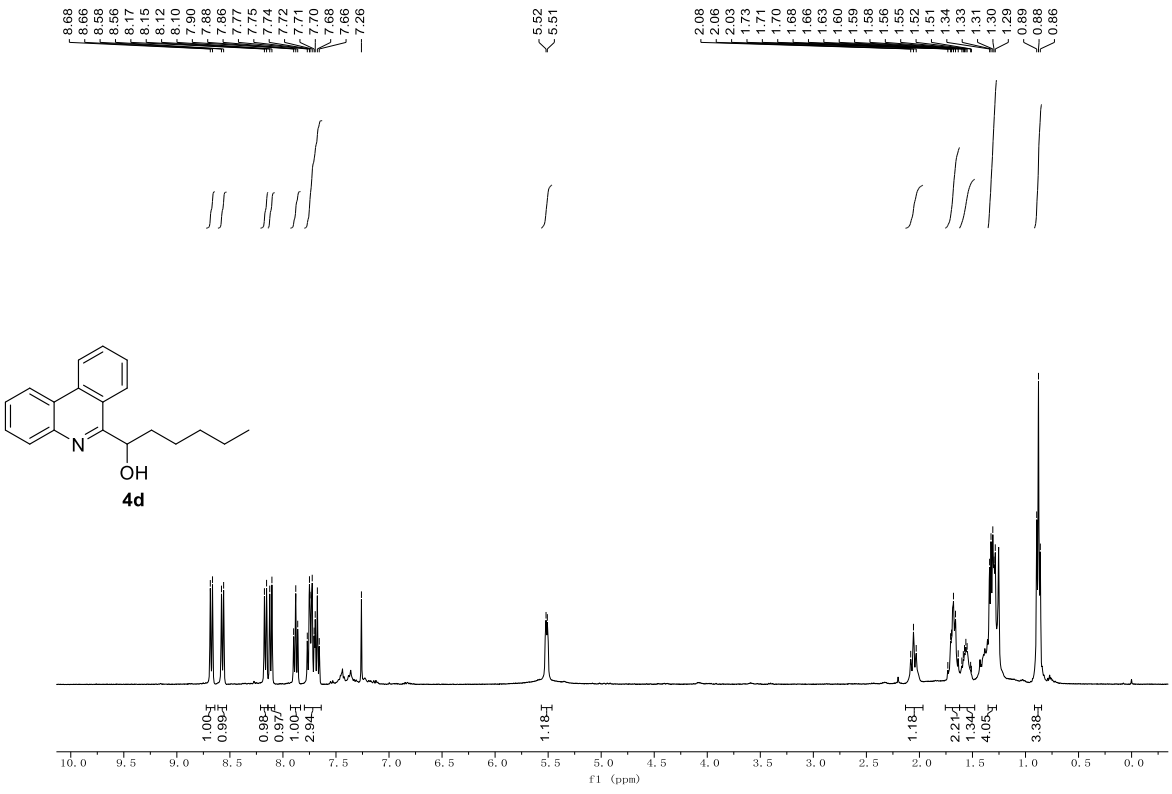


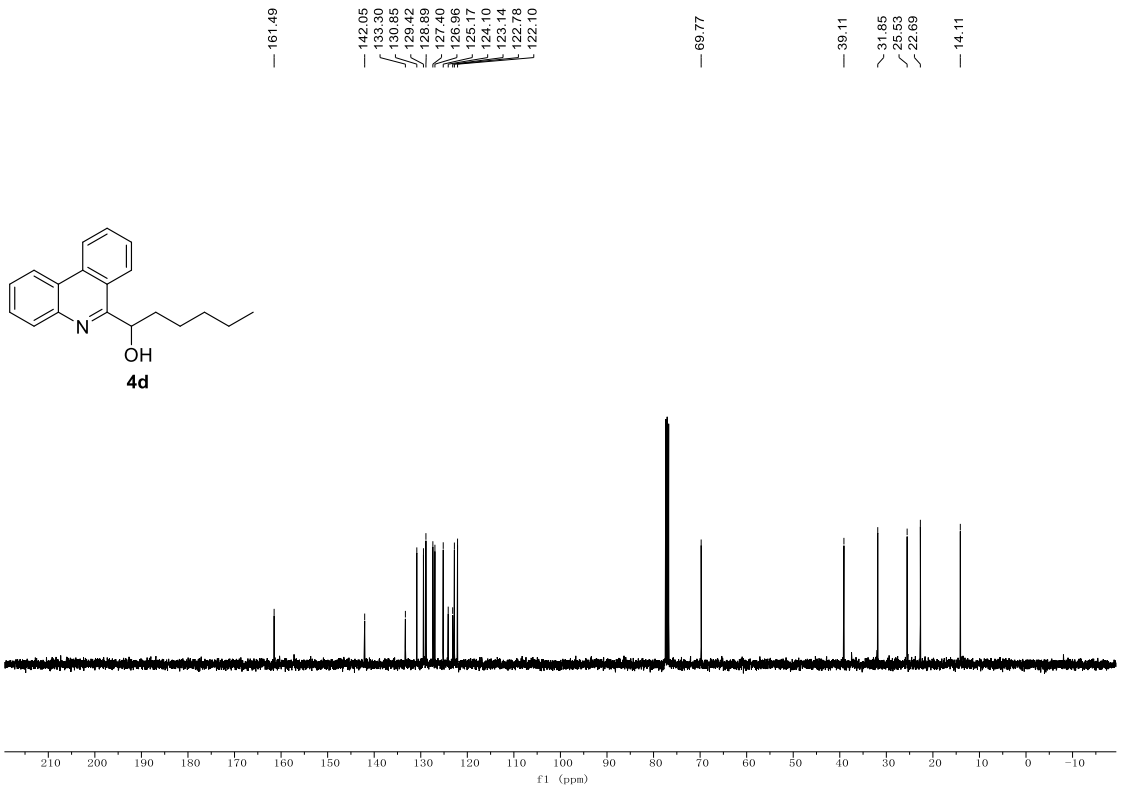
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4c



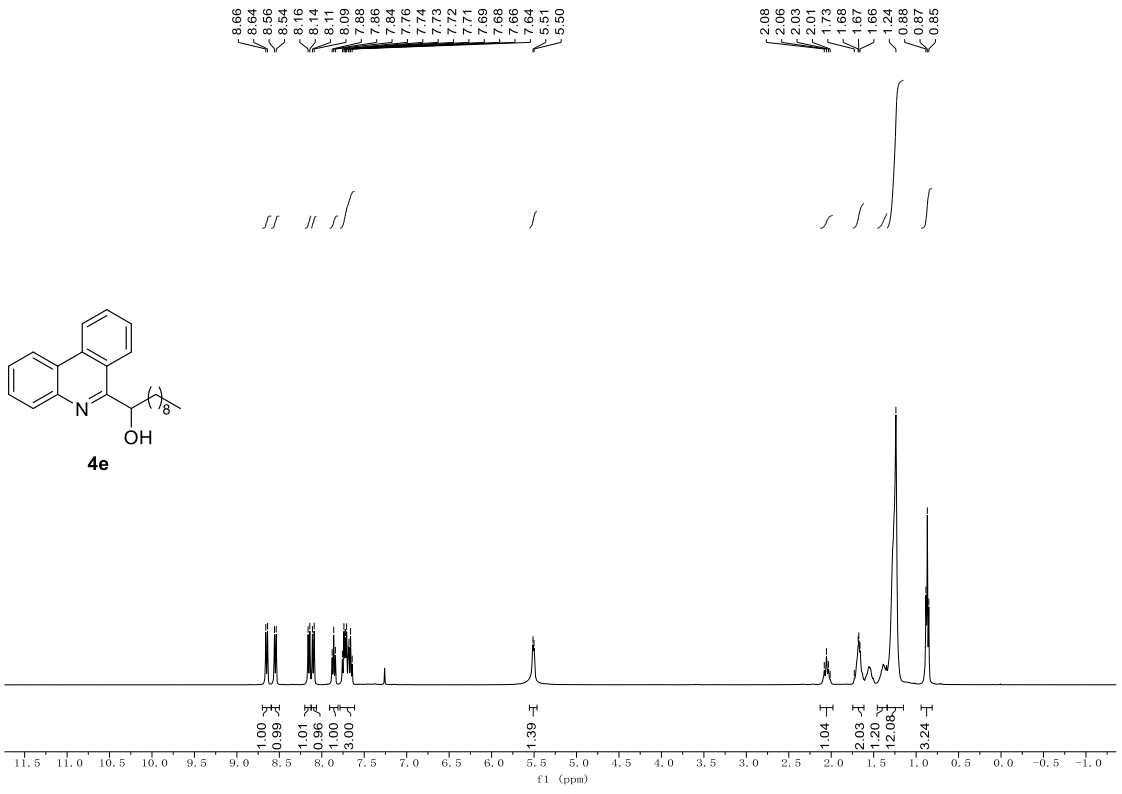


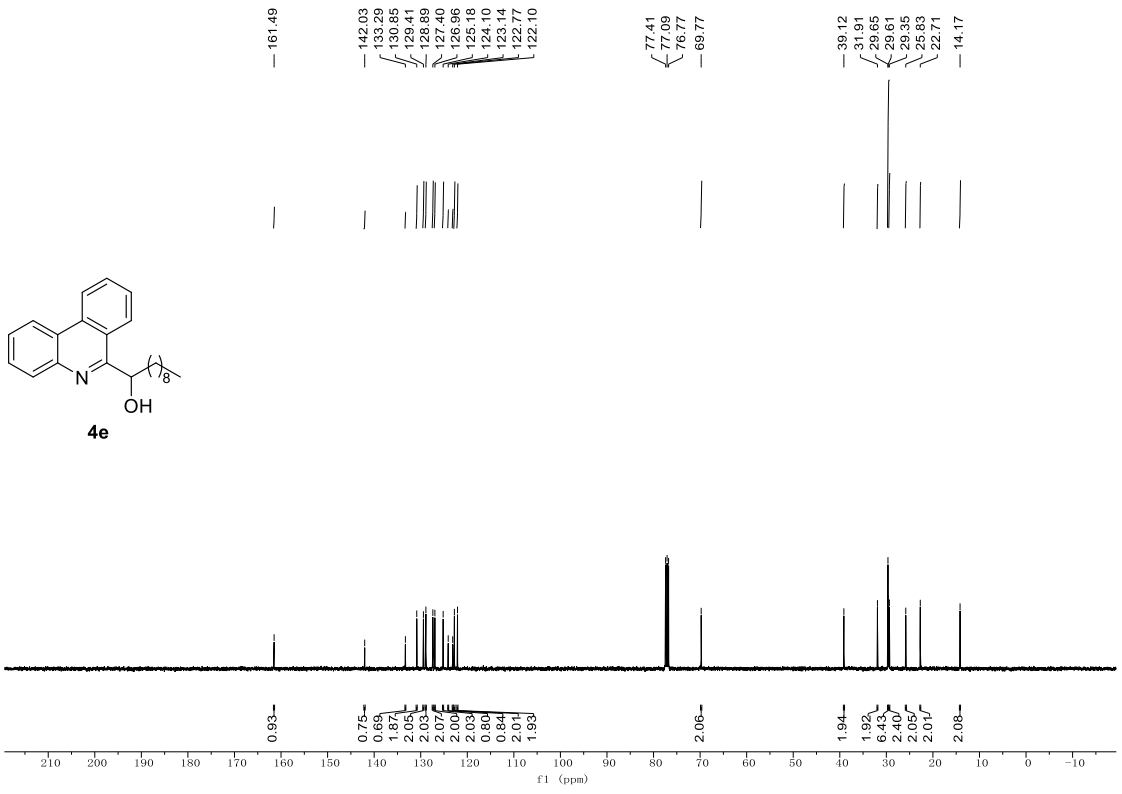
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4d



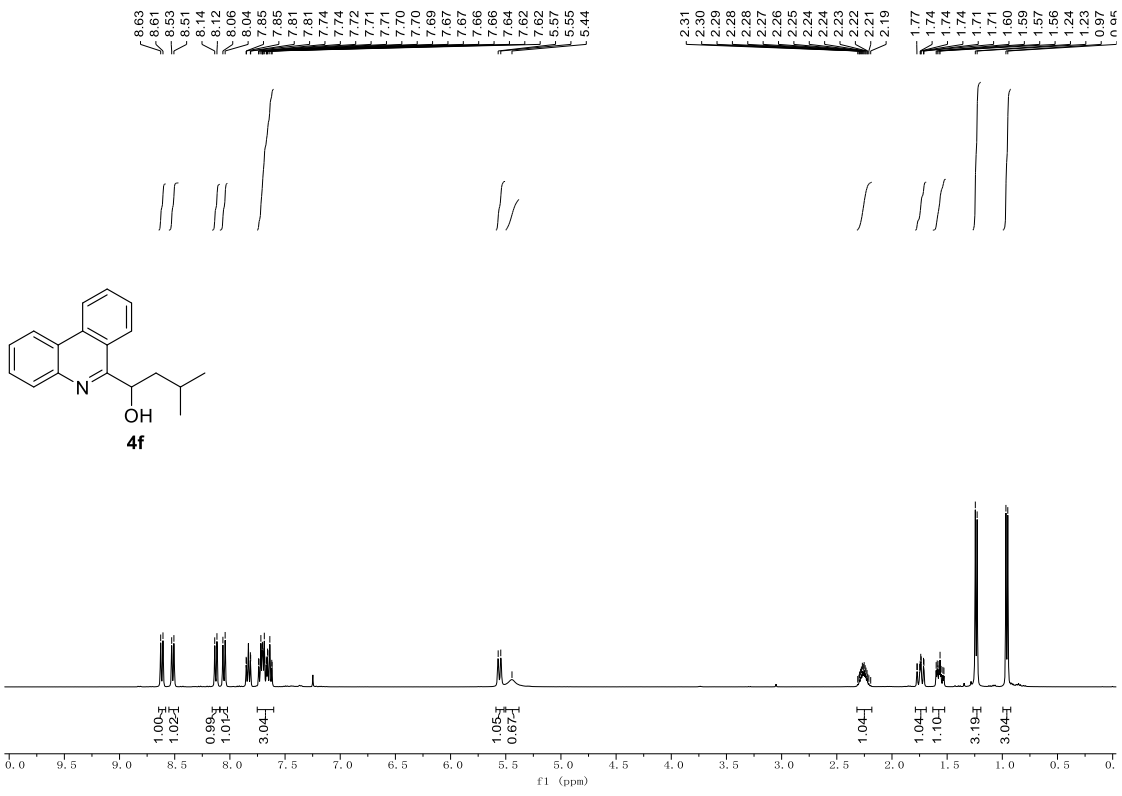


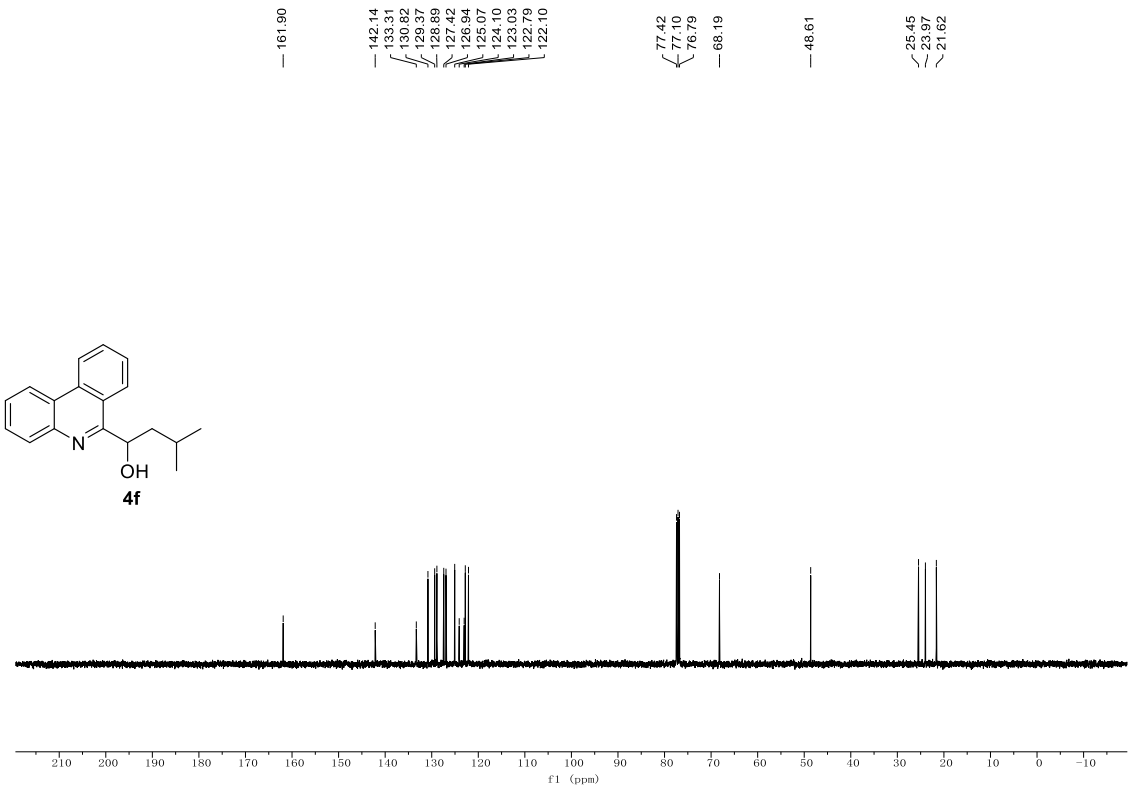
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4e



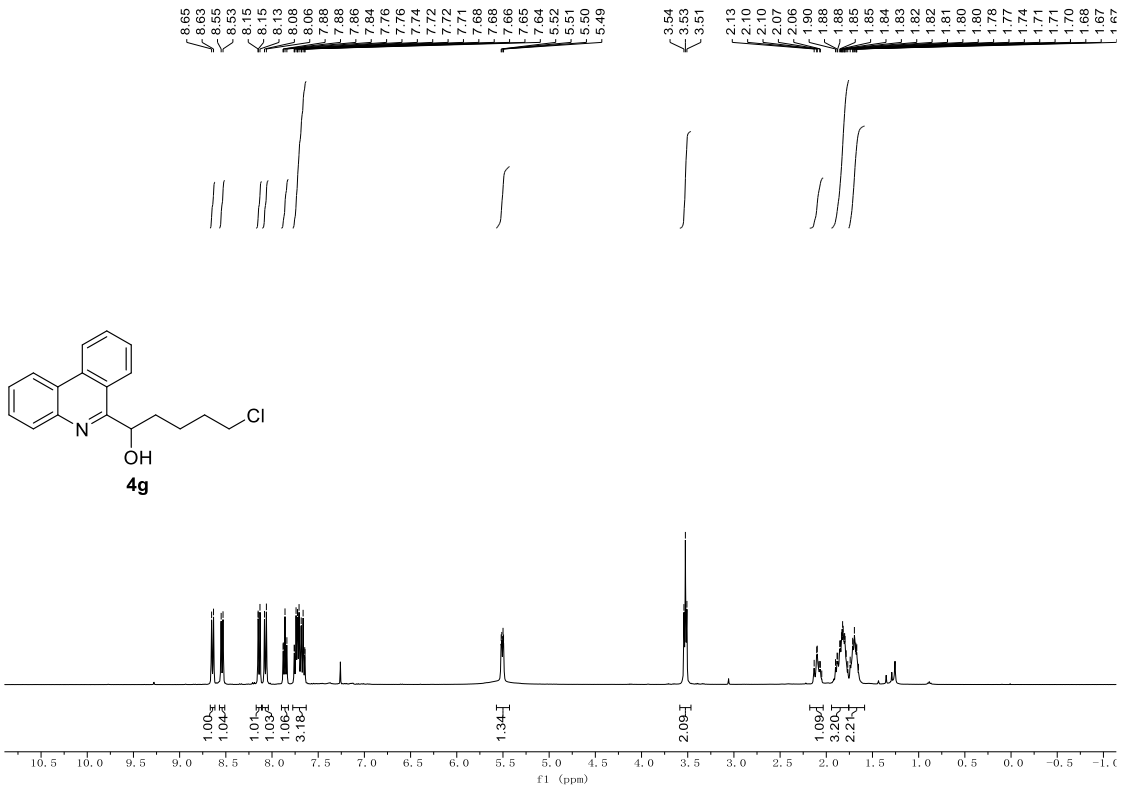


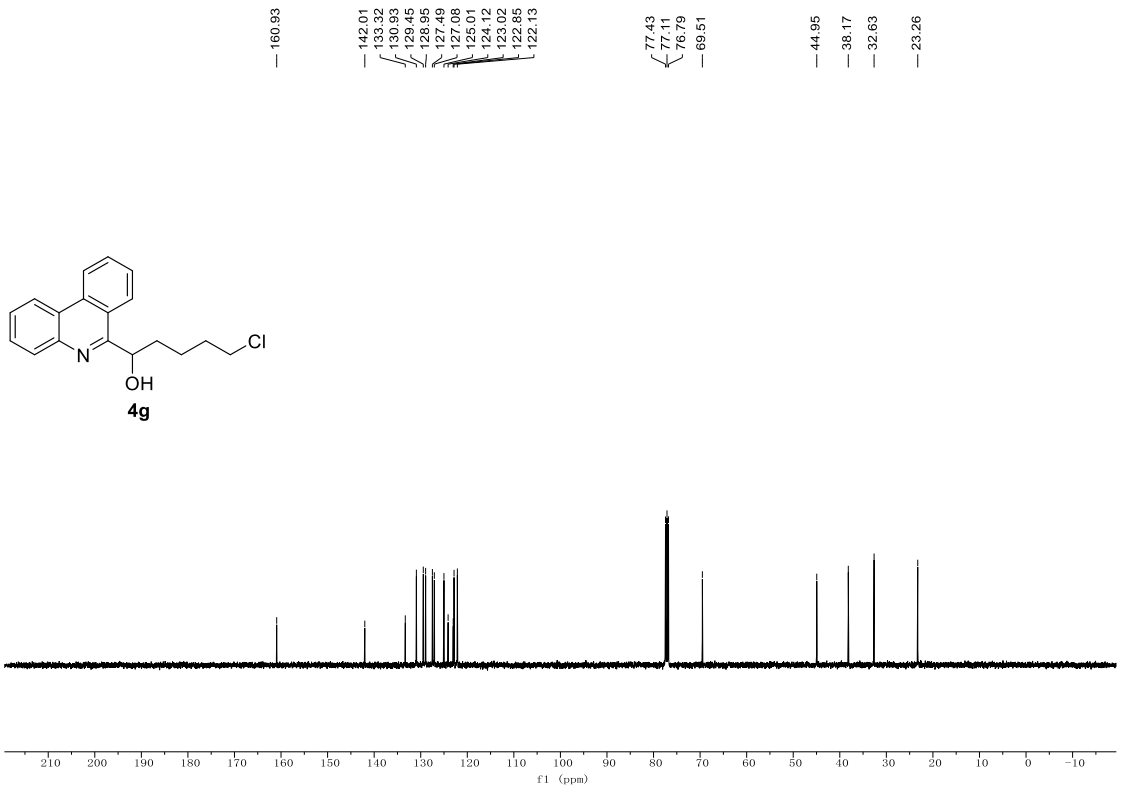
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4f



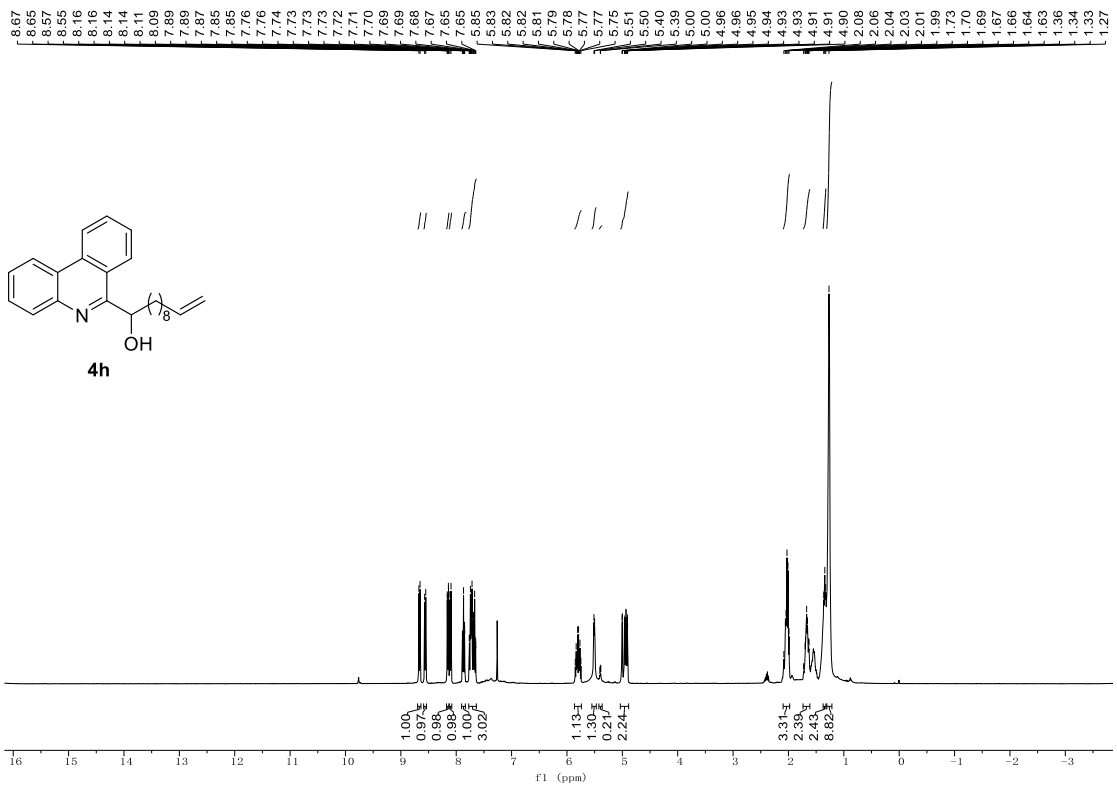


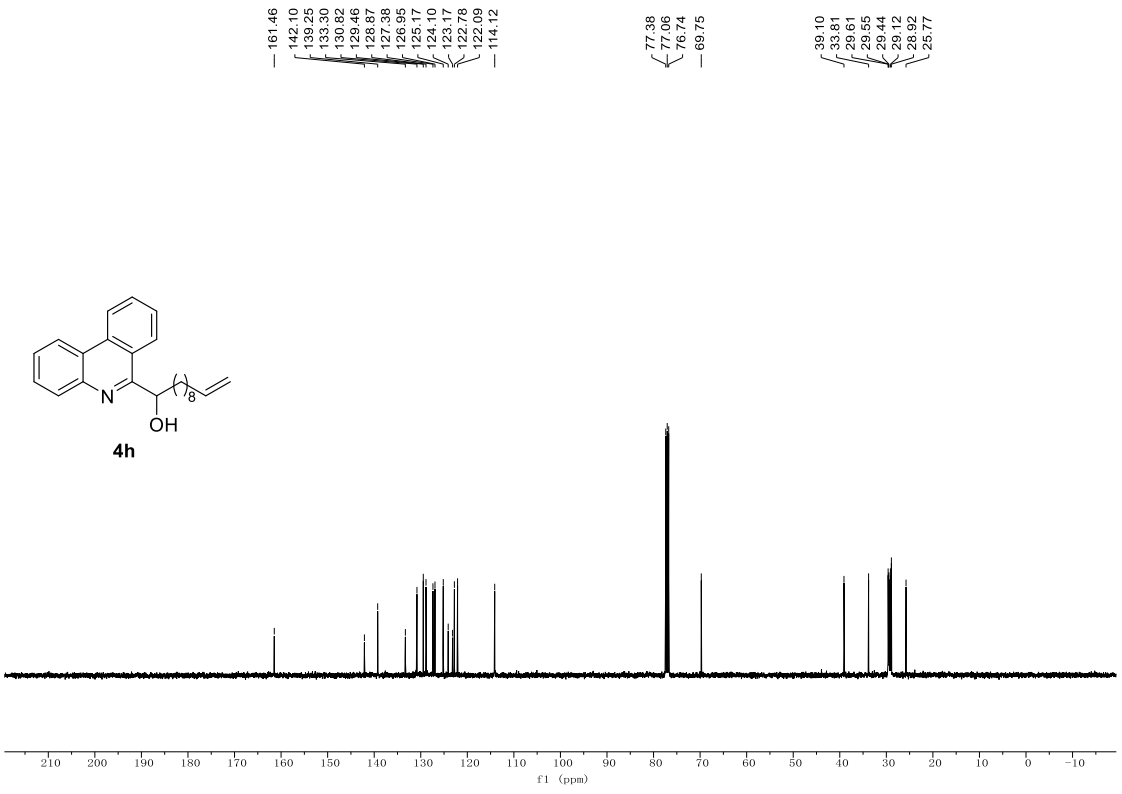
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4g





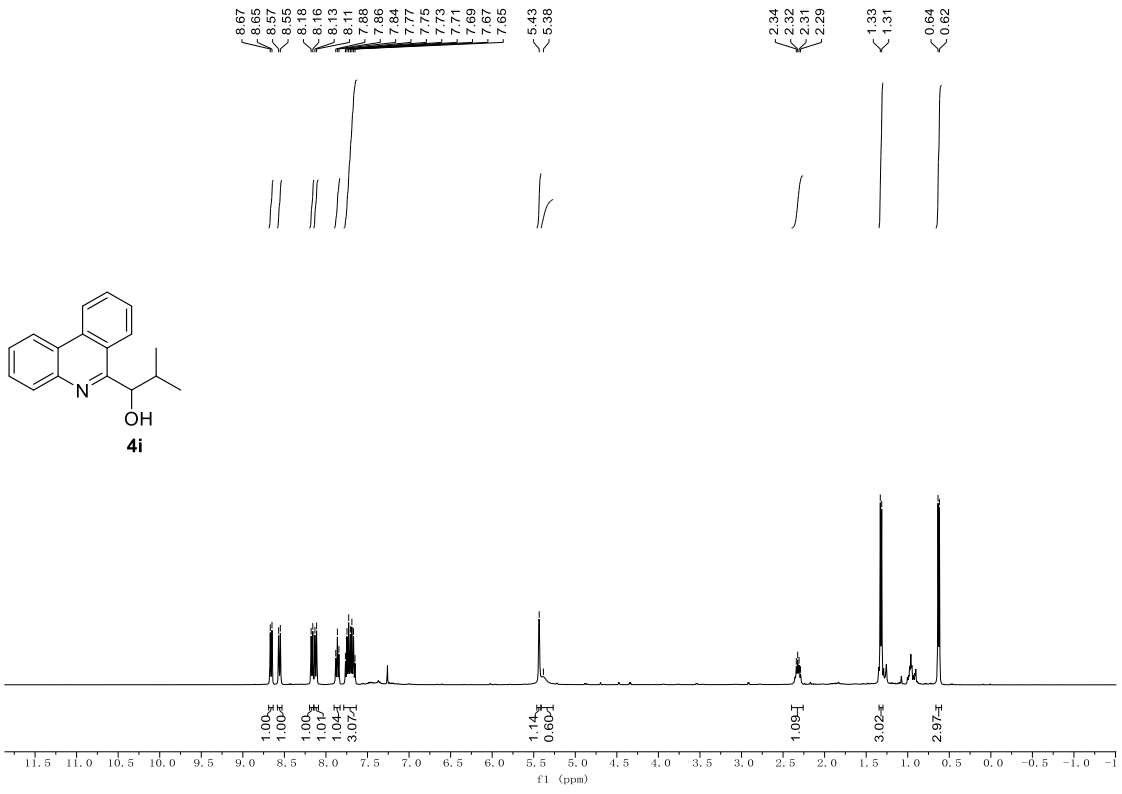
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4h



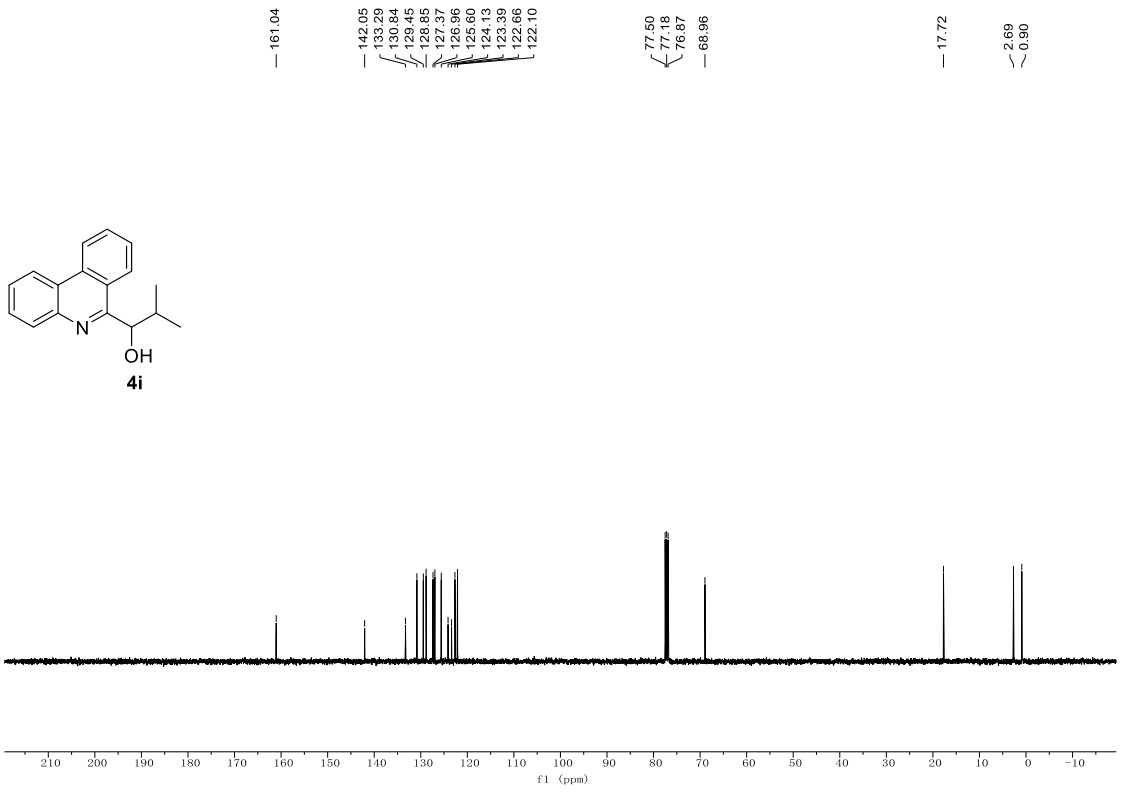


4h

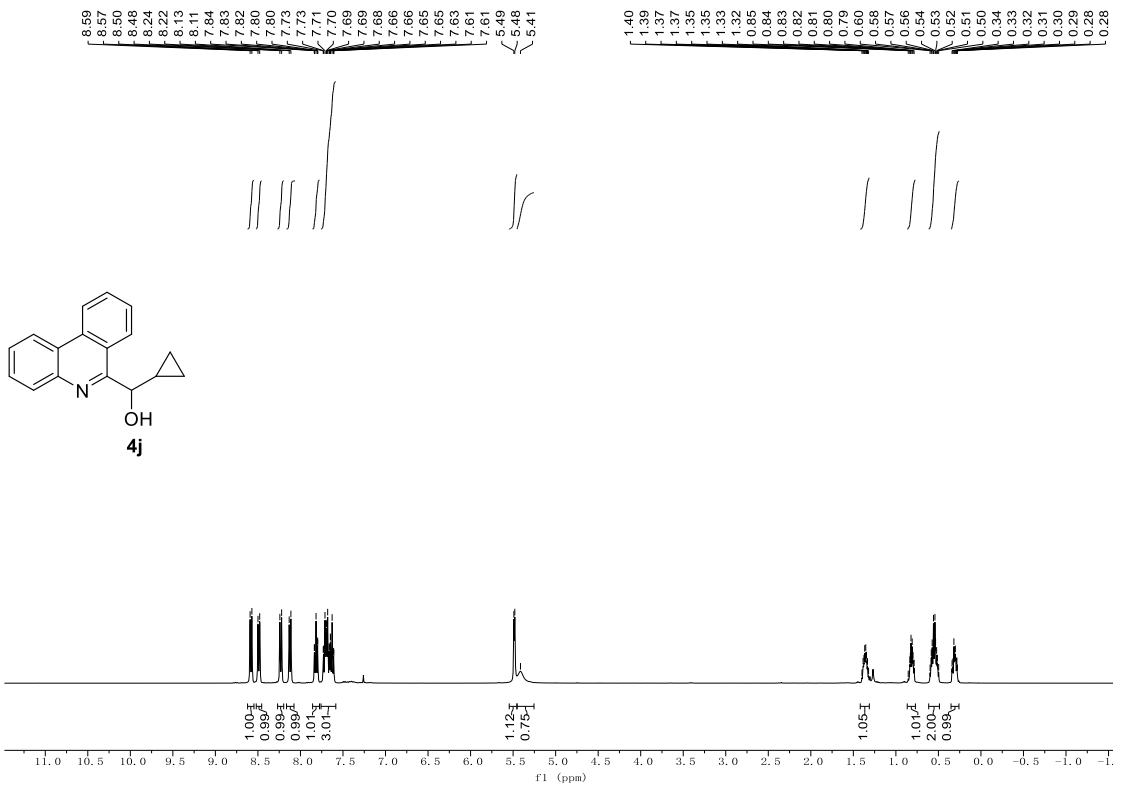
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4i

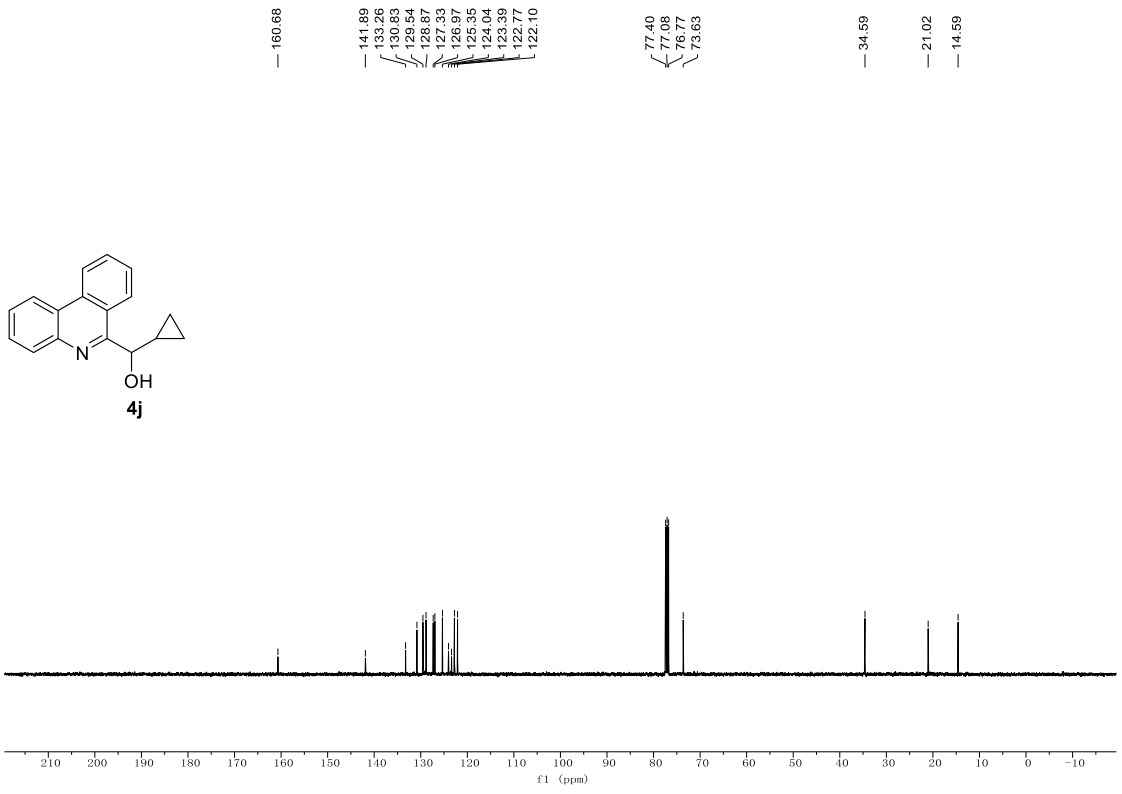


4i

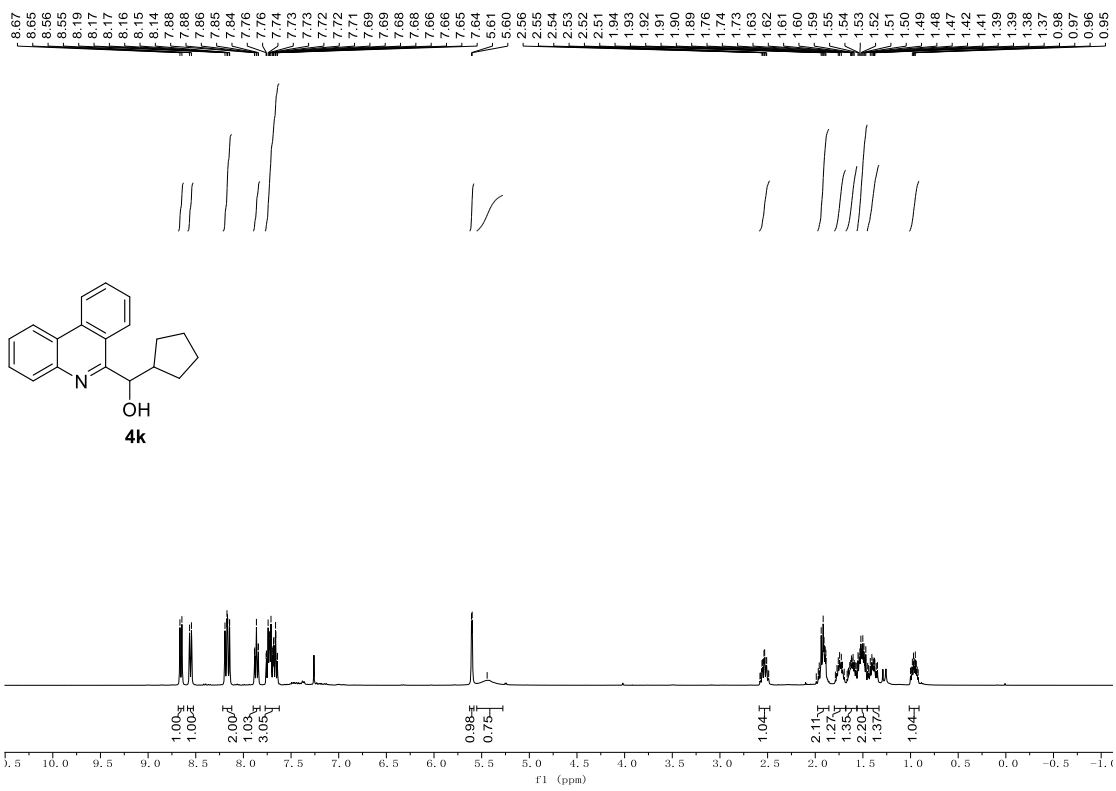


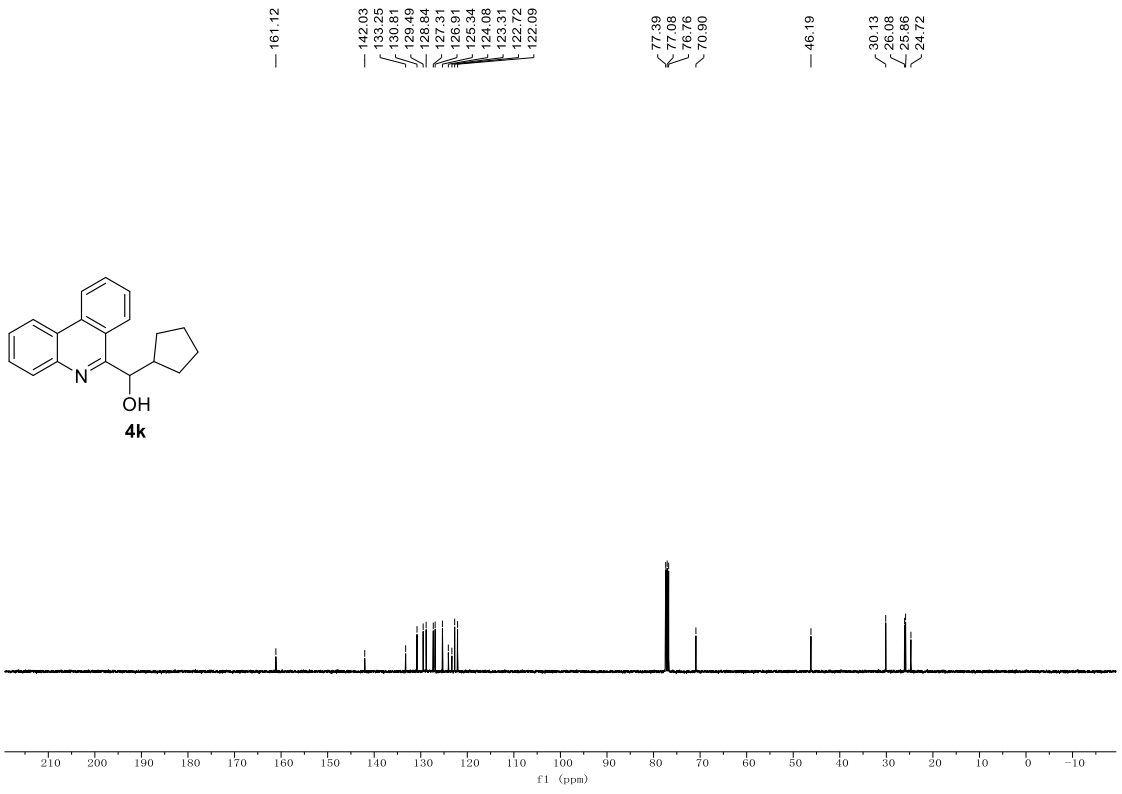
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4j



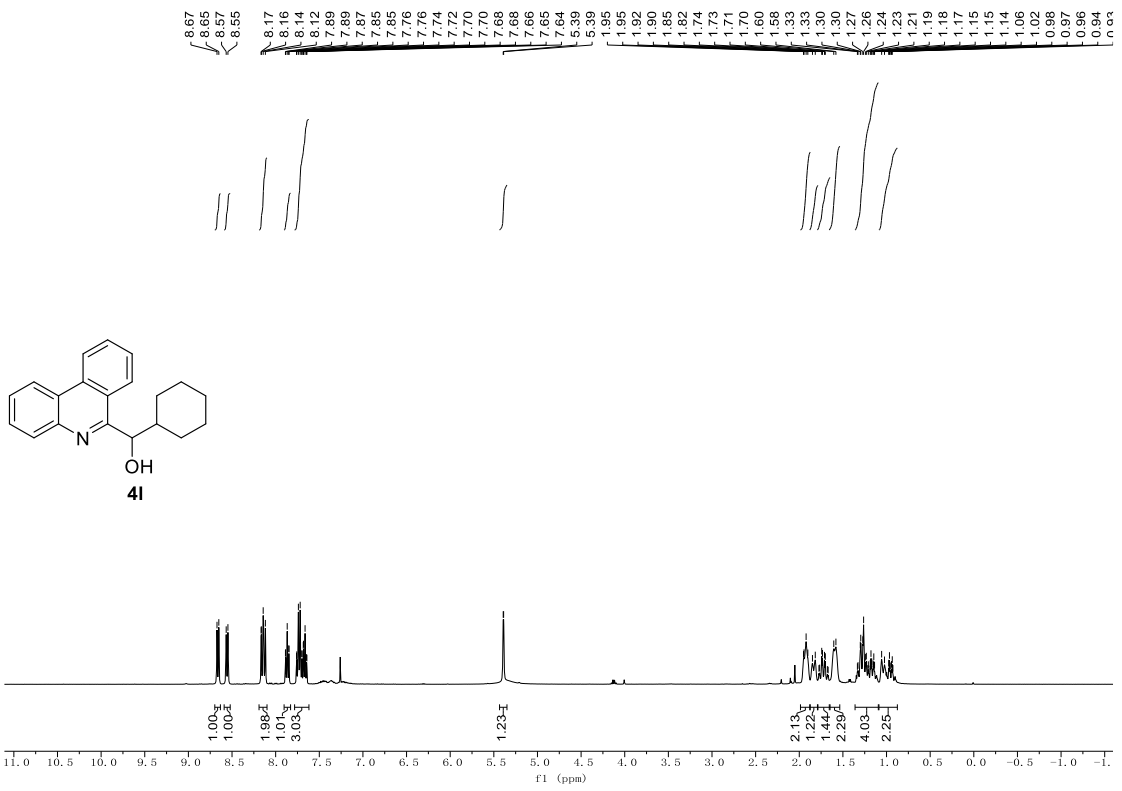


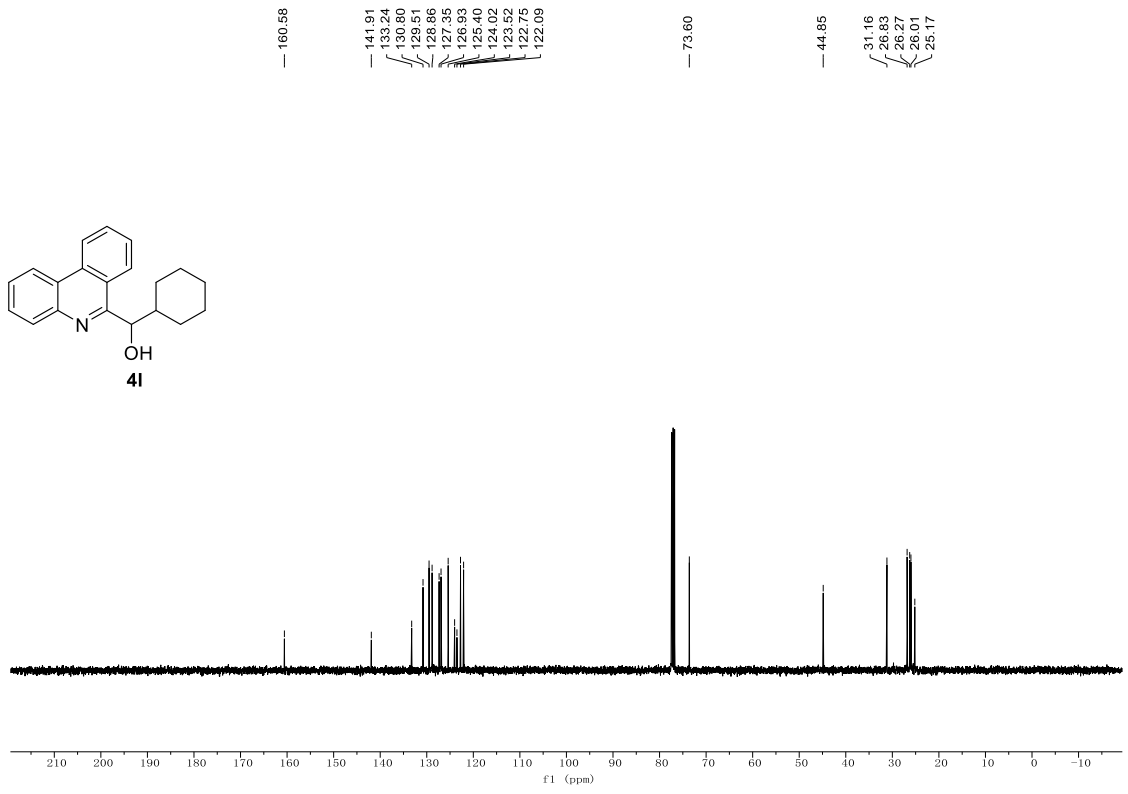
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4k



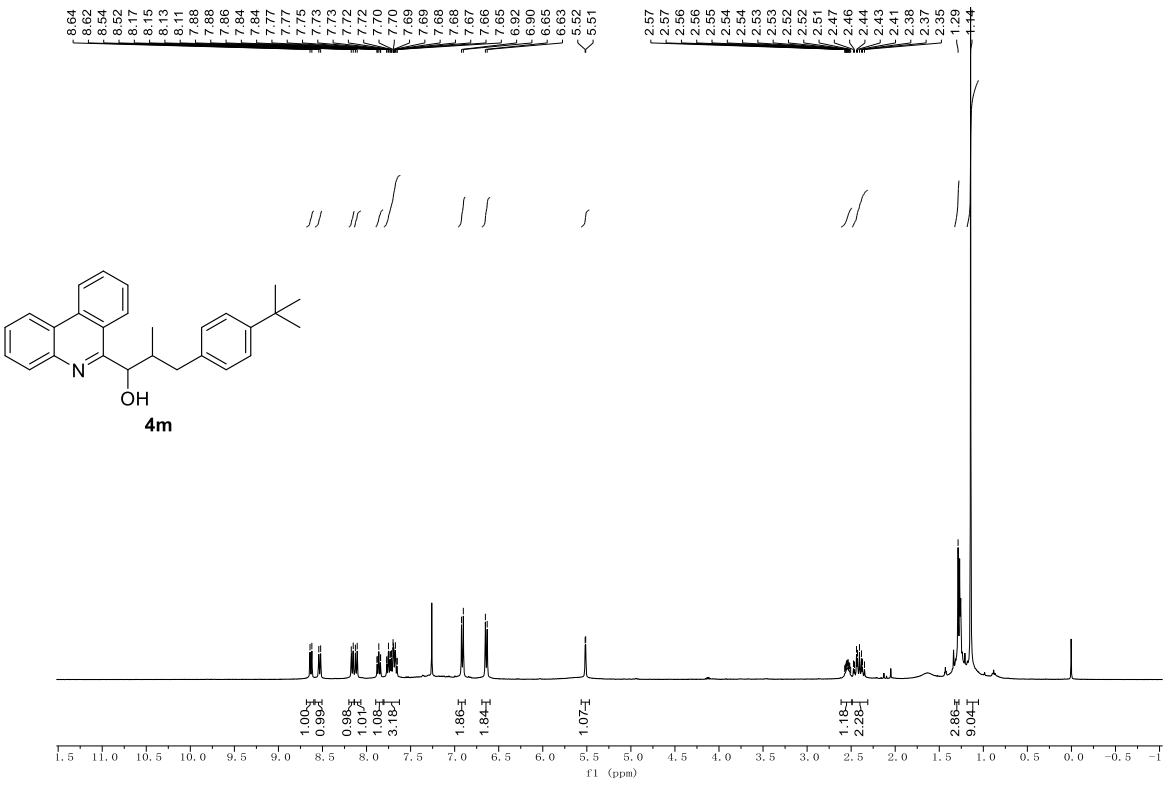


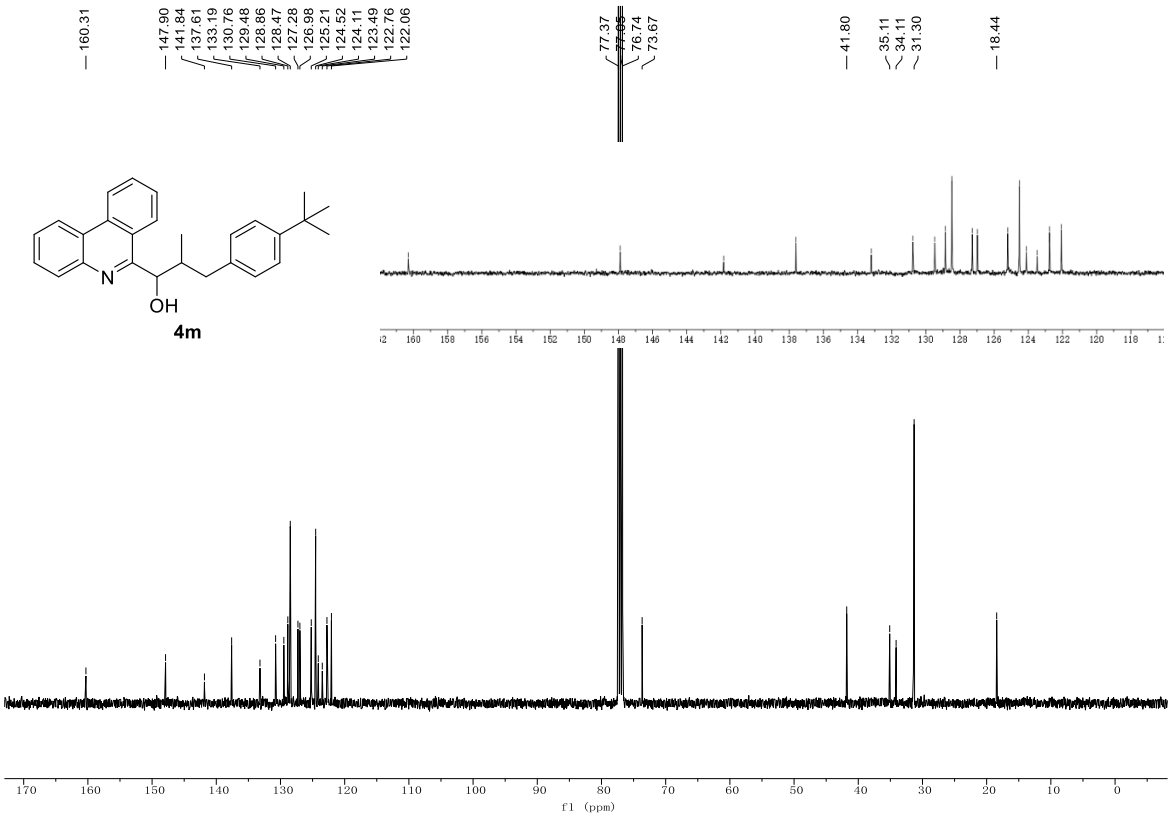
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4l



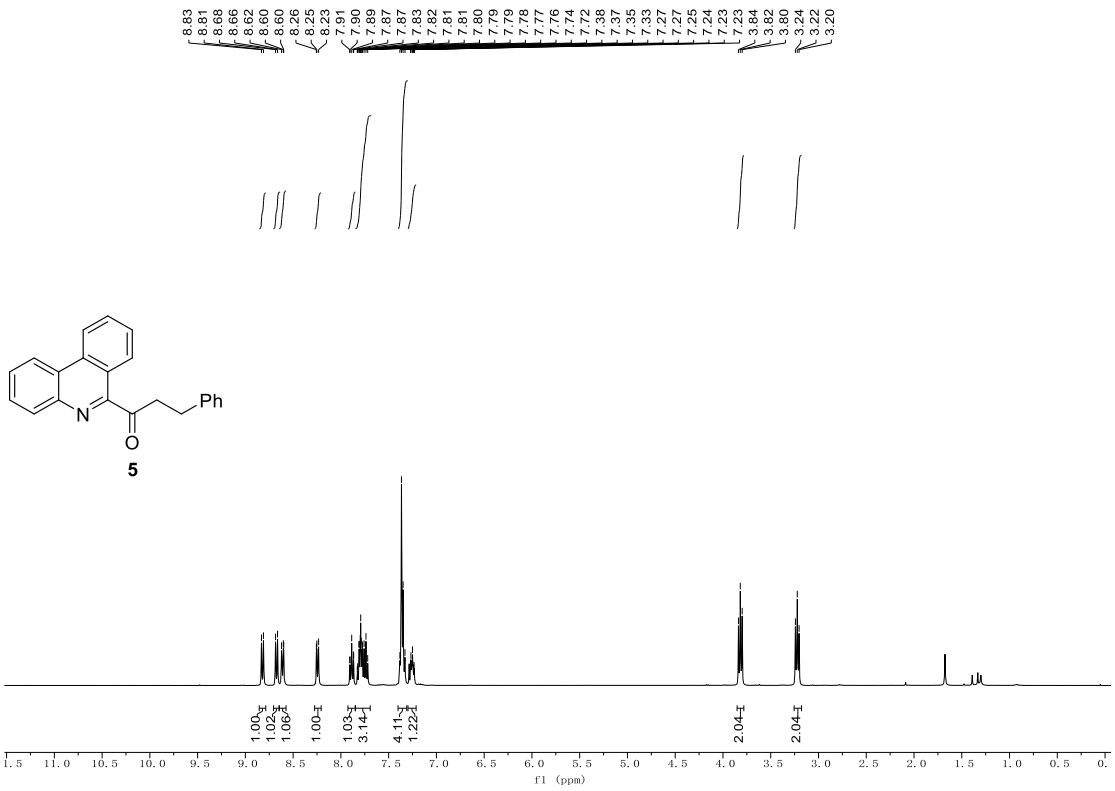


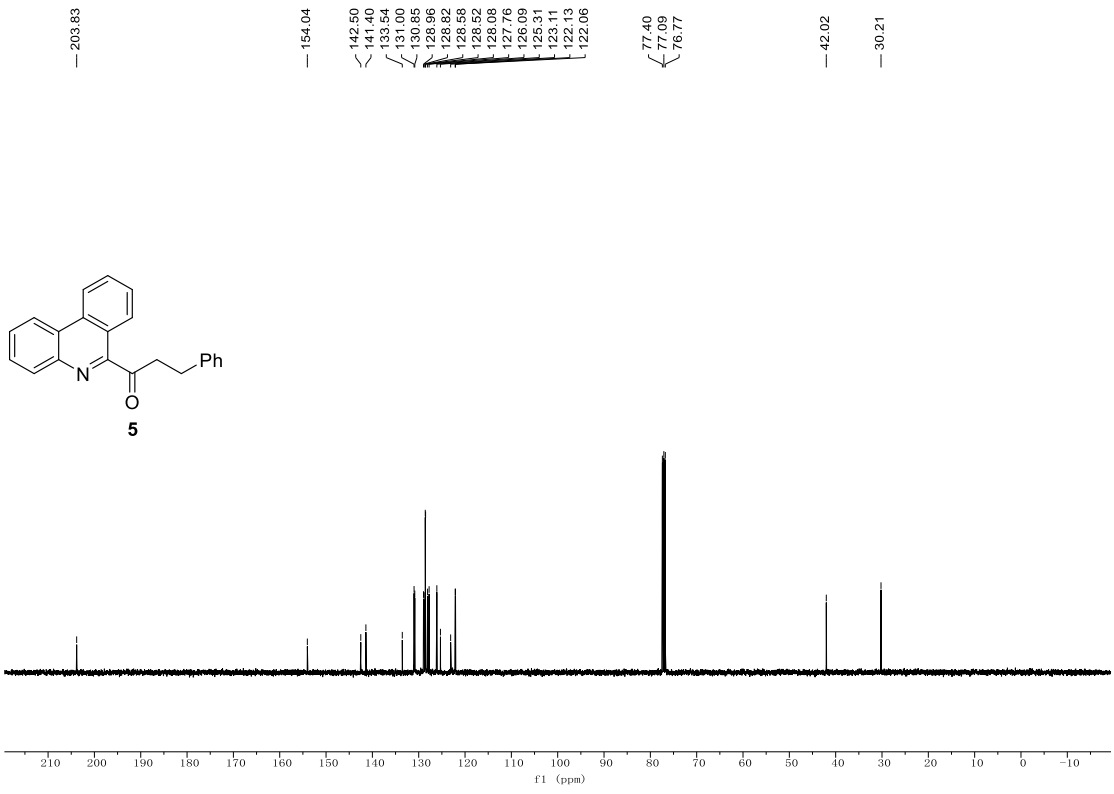
^{1}H NMR (400 MHz, CDCl3), ^{13}C NMR (100 MHz, CDCl3) spectra of product 4m



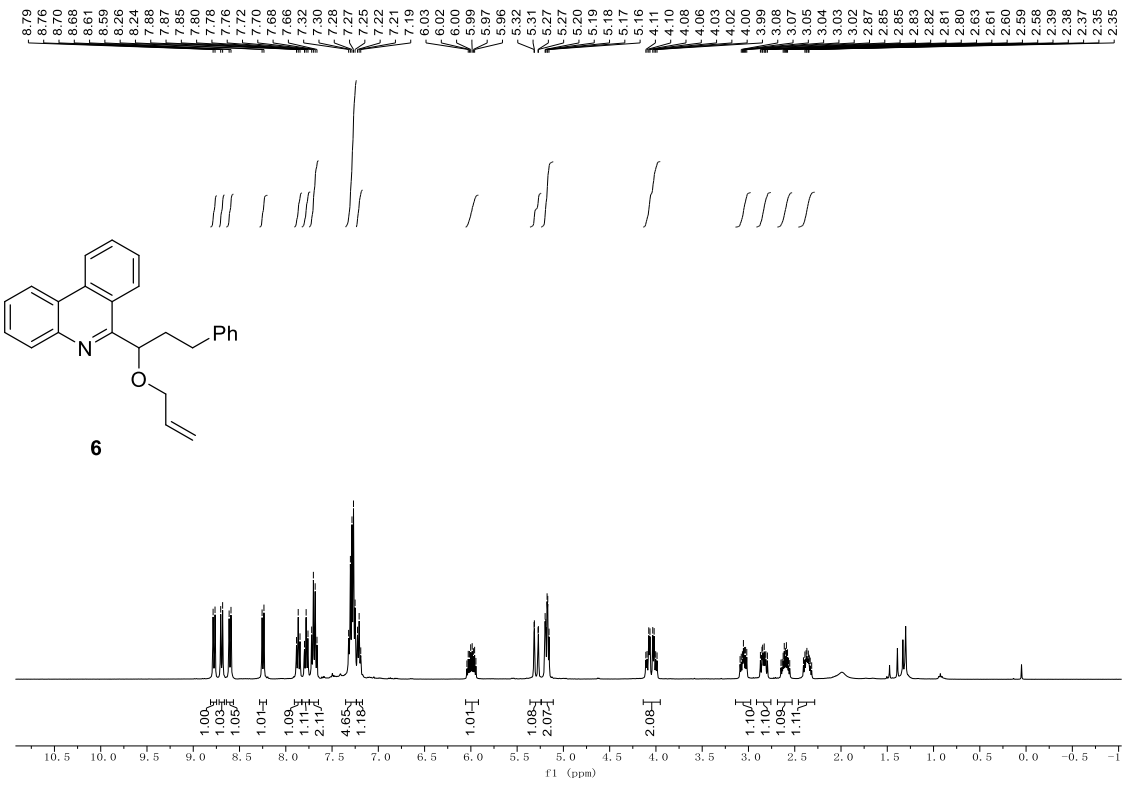


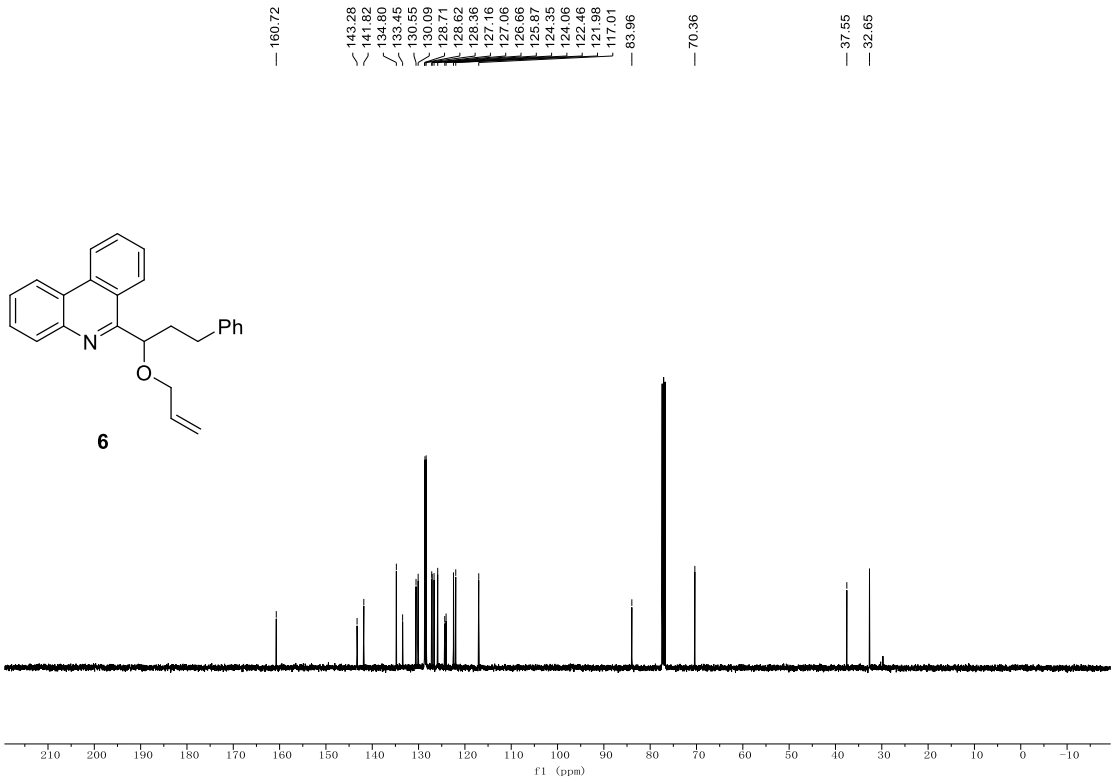
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 5



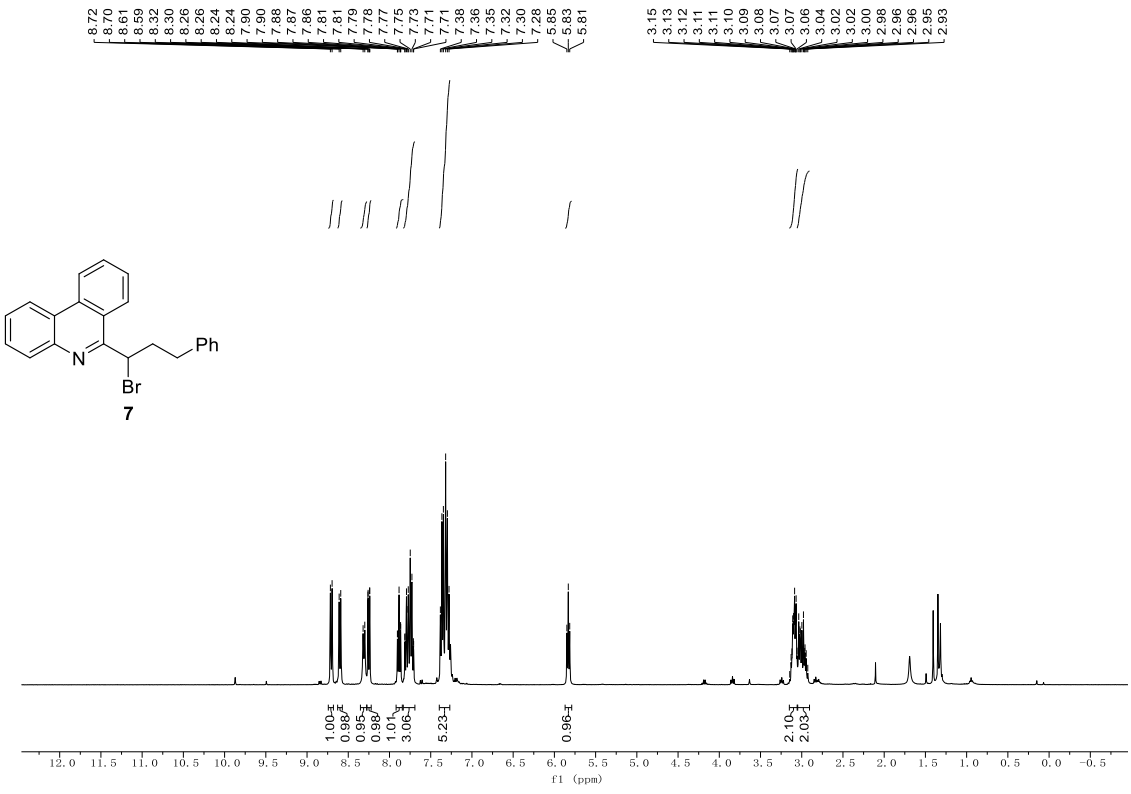


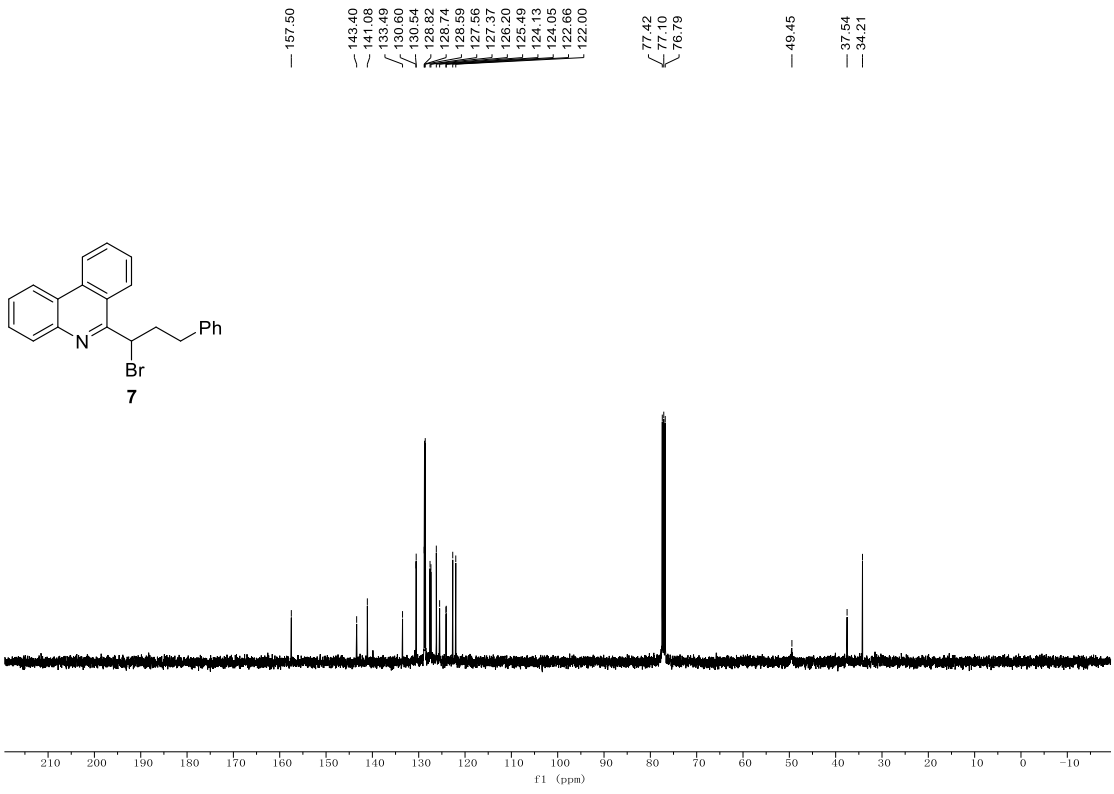
^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 6



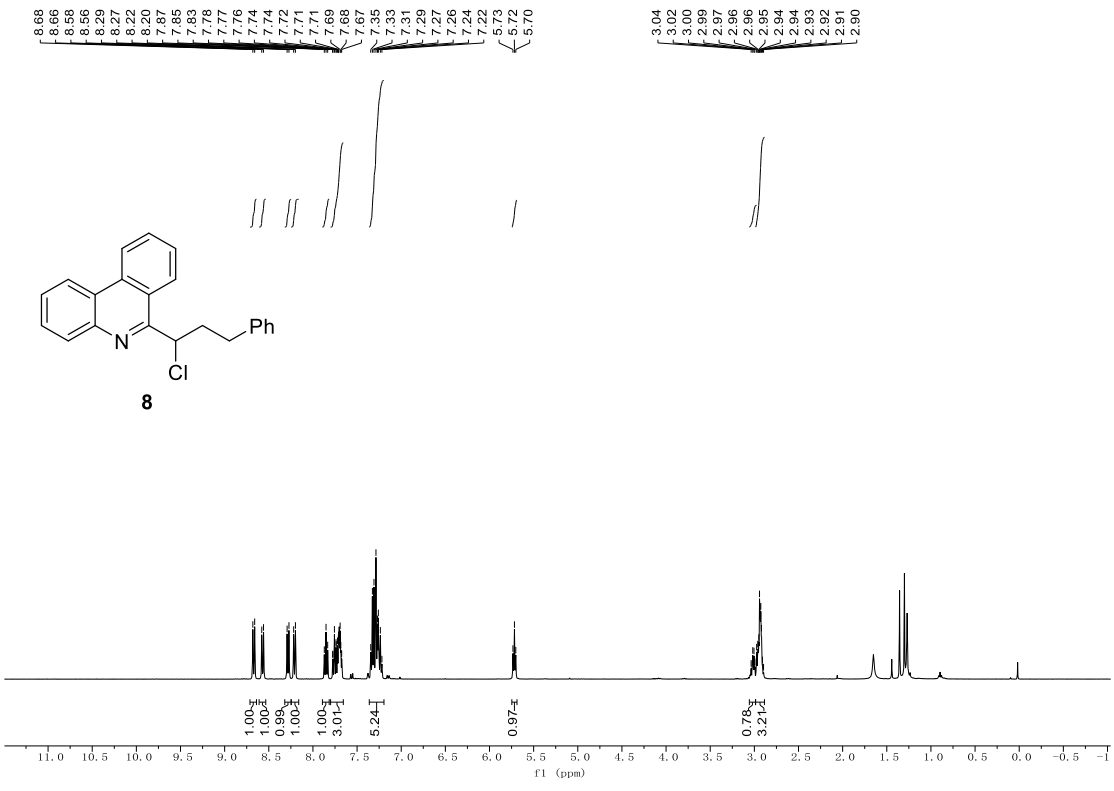


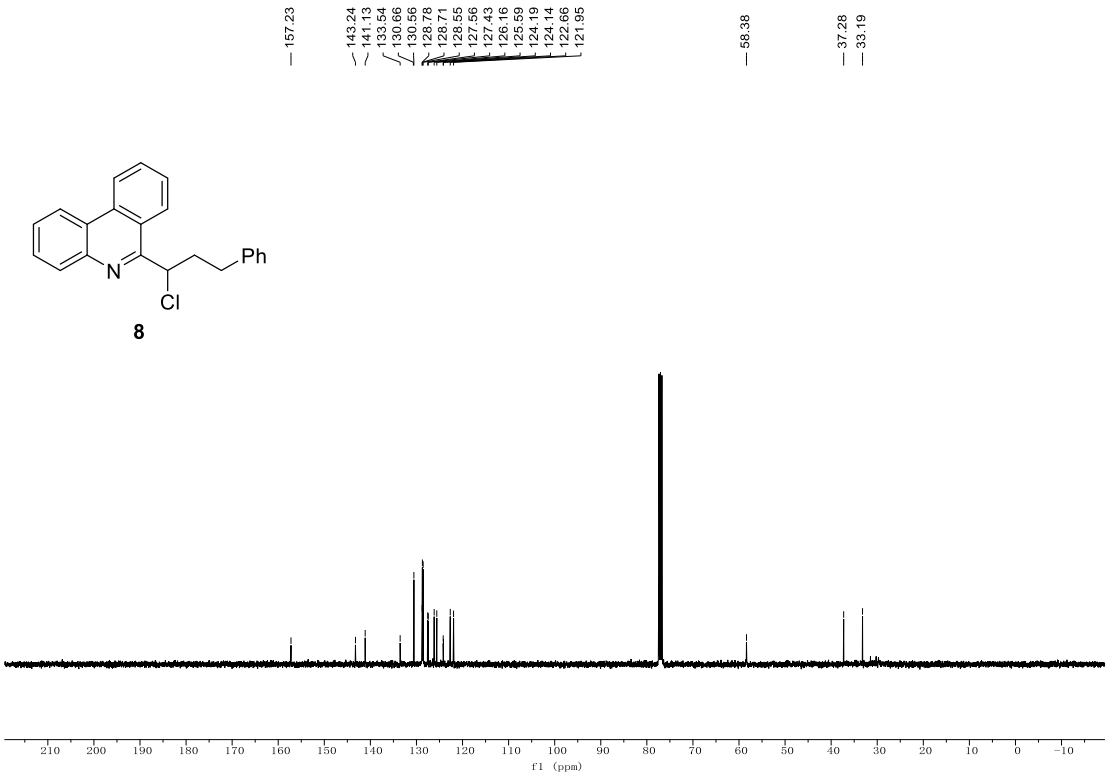
[1] H NMR (400 MHz, $CDCl_3$), [13]C NMR (100 MHz, $CDCl_3$) spectra of product 7





^{1}H NMR (400 MHz, $CDCl_3$), ^{13}C NMR (100 MHz, $CDCl_3$) spectra of product 8

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f1 (ppm)