

**Decatungstate-photocatalyzed Tandem  
Acylation/Cyclization/Self-hydrogenation of Isocyanides  
with Aldehydes to Hydroxyalkylated *N*-Heteroarenes via  
Multiple Hydrogen Atom Transfer**

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## 1. General Information

Unless otherwise noted, all reagents and solvents were obtained from commercial suppliers and used without further purification. GC yield was detected by Agilent GC-MS 8890/5977B. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel.  $^1\text{H}$  NMR spectra were recorded at 500 MHz and  $^{13}\text{C}$  NMR spectra were recorded at 125 MHz by using a Bruker Avance 500 spectrometer.  $^{19}\text{F}$  NMR data were collected at 471 MHz with complete proton decoupling. Chemical shifts were calibrated using residual undeuterated solvent as an internal reference ( $^1\text{H}$  NMR:  $\text{CDCl}_3$  7.26 ppm,  $^{13}\text{C}$  NMR:  $\text{CDCl}_3$  77.16 ppm), the chemical shifts ( $\delta$ ) were expressed in ppm and J values were given in Hz. The following abbreviations were used to describe peak splitting patterns when appropriate: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, br = broad. Mass spectra were performed on a spectrometer operating on ESI-TOF. UV-vis spectra were recorded using a Shimadzu UV-2600 spectrophotometer. The crude products were purified by HPLC (LaboACE LC-5060, Japan Analytical Industry Co., Ltd., Japan) equipped with Jaigel 2.5 HR columns with dichloromethane as the eluent.

### Photographic depiction of the reaction setup:

Manufacturer: Beijing Rogertech Ltd.

Model: 2A458520-395nm

Value: 5836.430  $\mu\text{W}/\text{cm}^2/\text{nm}$

Energy peak wavelength: 395 nm

Peak width at half-height: 22.1 nm

Material of the irradiation vessel: Schlenk flask

Not use any filters

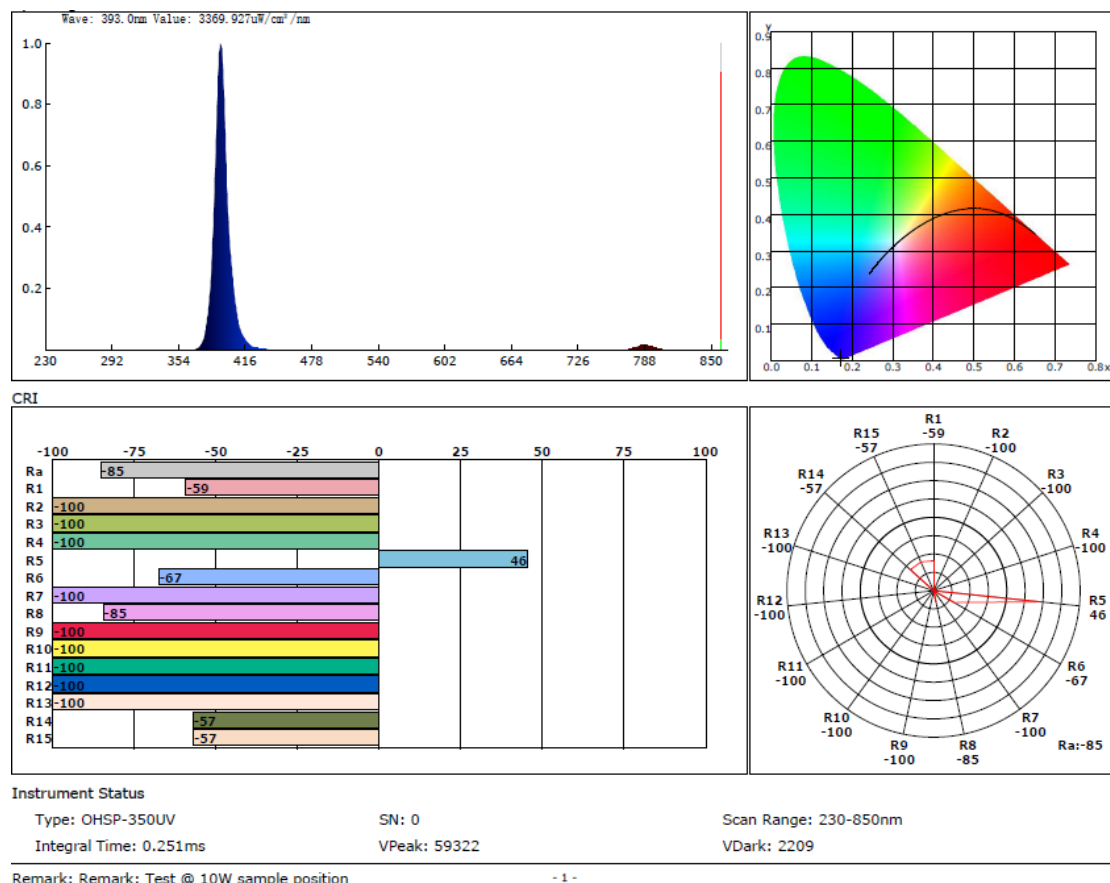
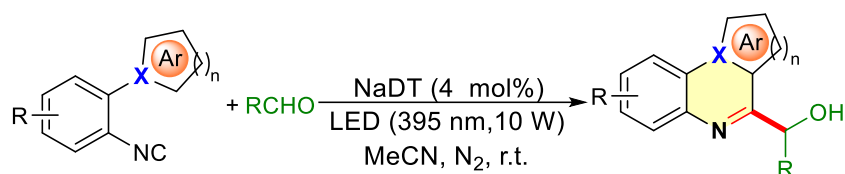


Figure S1 LED spectrum test report

## 2. Experimental Section

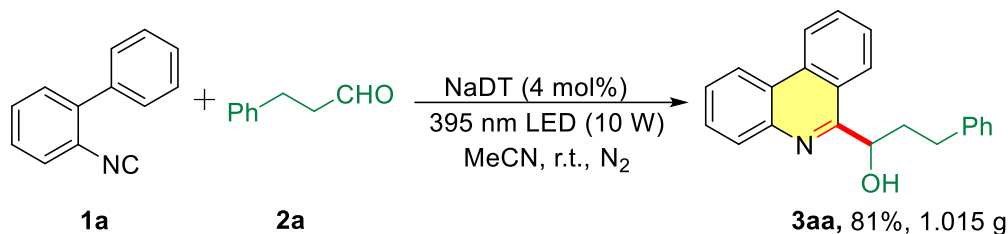
### 2.1 General Experimental Procedures for Compounds 3



To a 10 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1** (0.2 mmol), aldehyde **2** (0.2 mmol), NaDT (4 mmol%) and MeCN (2.0 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature for 24 h. The reaction progress was monitored by thin-layer chromatography analysis. After completion of the reaction, the mixture was

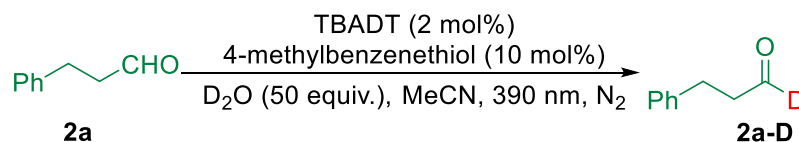
vacuum filtration and the filtrate was reduced pressure evaporation. The residue was purified by silica gel chromatography (PE/EA = 10:1) to afford product **3**.

## 2.2 Large Scale Synthesis of **3aa**

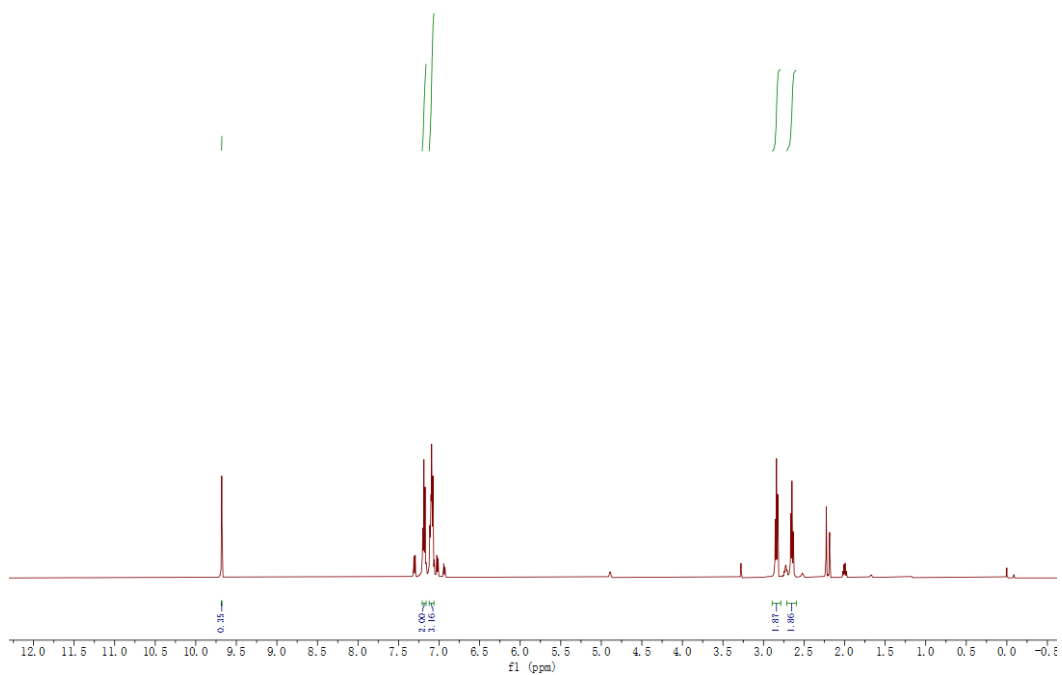


To a solution of 2-isocyanobiphenyl **1a** (4 mmol), aldehyde **2a** (4 mmol), NaDT (4 mol%) in MeCN (30 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. After completion of the reaction, the mixture was vacuum filtration, and the filtrate was reduced pressure evaporation. The residue was purified by HPLC to give 81% yield of **3aa** (1.015 g).

## 2.3 Preparation of deuterated formyl C-H bonds

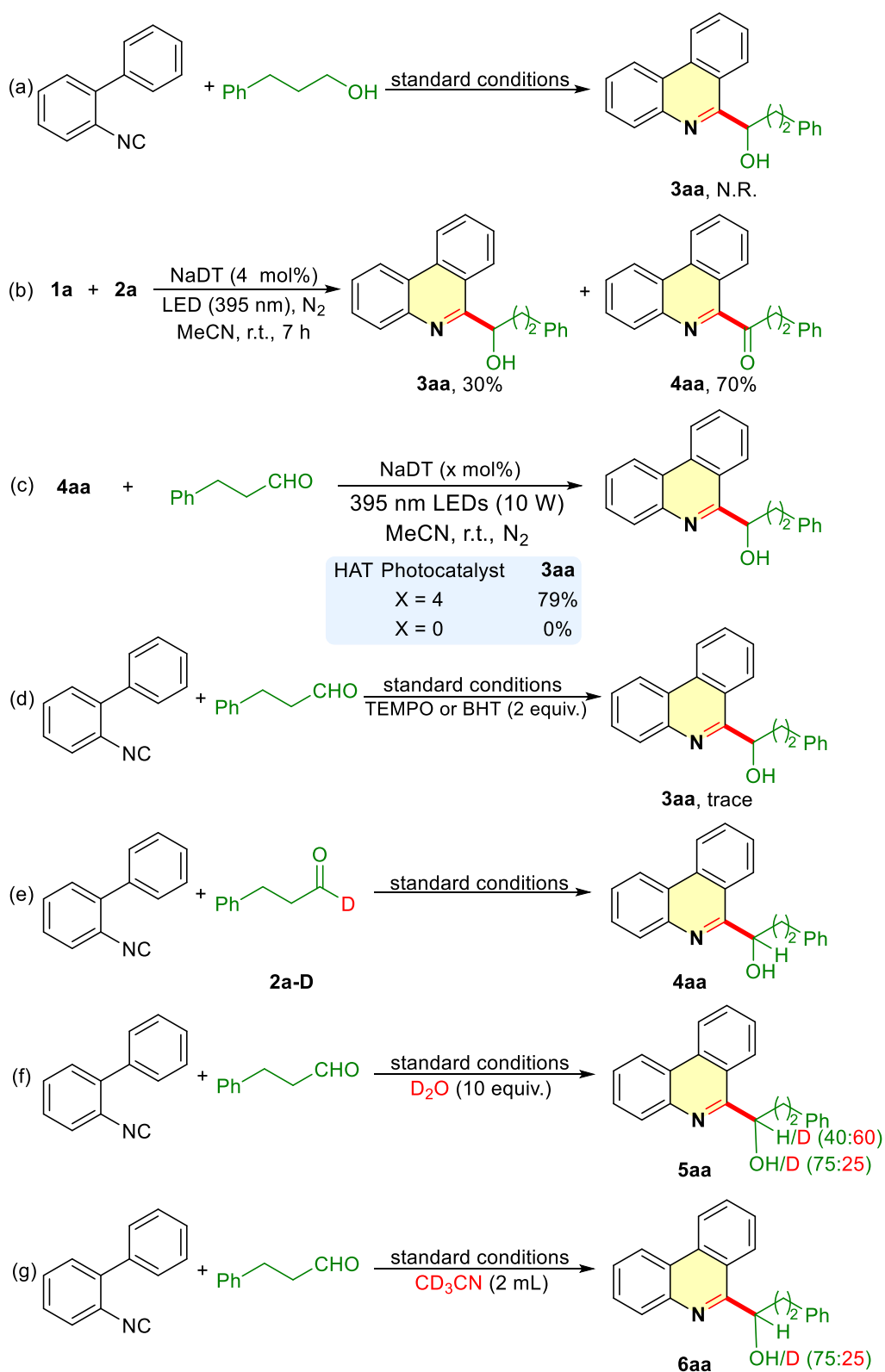


Deuterated aldehyde was prepared according to the previous report<sup>1</sup>. 3-phenylpropanal (3 mmol), TBADT (199.2 mg, 2 mol%), 4-methylbenzenethiol (37.2 mg, 10 mol%), D<sub>2</sub>O (2.7 mL, 50.0 equiv.) and CH<sub>3</sub>CN (3 mL, 1.0 M) were added to a 25 mL high borosilicate glass tube equipped with a stir bar. The reaction mixture was degassed *via* vacuum evacuation and backfilled with nitrogen for three times, irradiated with 390 nm lamp for 20 h. The deuterium incorporation was determined by the analysis of the <sup>1</sup>HNMR spectra. The reaction was quenched with water and extracted with ethyl acetate. The organic layer was washed with brine and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel with eluting (ethyl acetate/petroleum ether) to give the target product **2a-D**.



**Figure S2** <sup>1</sup>H NMR spectrum of **2a-D**

## 2.4 Control Experiments



(a) Under the standard conditions, to a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1a** (0.2 mmol), phenylpropanol (0.2 mmol), NaDT (4 mol%) and MeCN (2.0 mL). The resulting

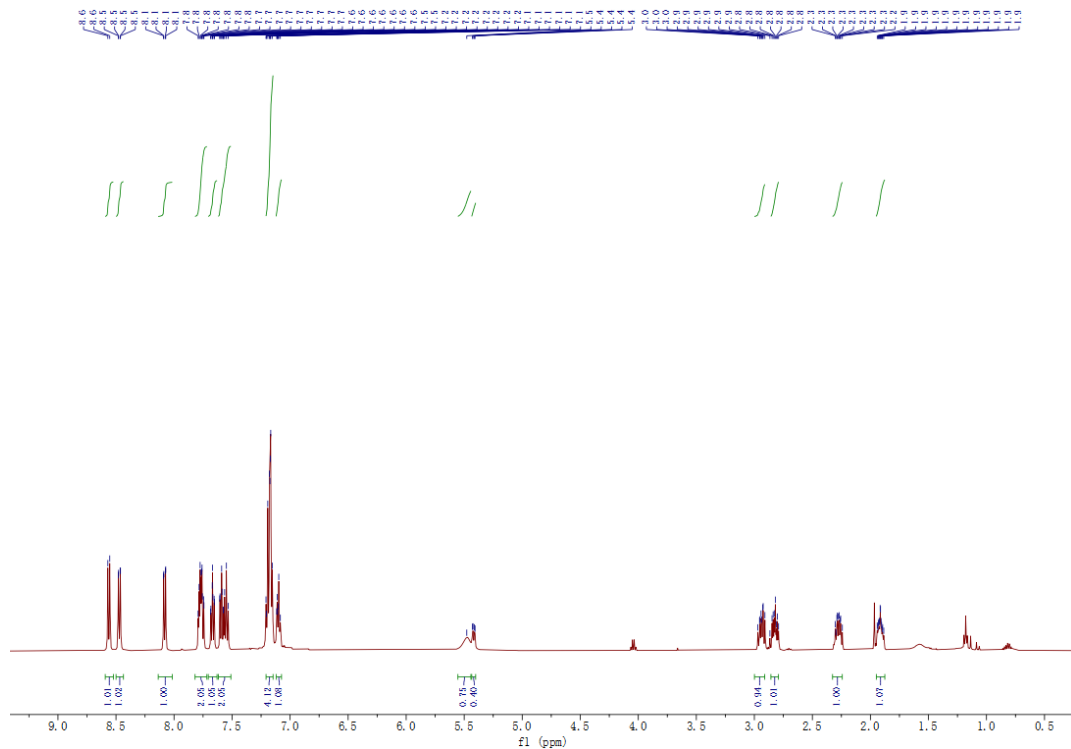
mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. The reaction mixture was analyzed by GC-MS and no desired product was detected.

- (b) Under the standard conditions, to a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1a** (0.2 mmol), **2a** (0.2 mmol), NaDT (4 mol%) and MeCN (2.0 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. After about 7 hours, the reaction mixture was analyzed by GC-MS and **3aa** (30% yield) and carbonylation product **4aa** (70% yield) were detected.
- (c) The intermediate **4aa** (0.2 mmol), NaDT (4 mol% or 0 mol%), and **2a** (0.2 mmol) were added to 2 mL MeCN. The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. The reaction mixture was analyzed by GC-MS, a 79% yield of **3aa** was detected in the presence of NaDT and no reaction was detected in the absence of NaDT.
- (d) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1a** (0.2 mmol), aldehyde **2a** (0.2 mmol), NaDT (4 mol%), TEMPO (0.4 mmol) or BHT (0.4 mmol) and MeCN (2.0 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. The reaction mixture was analyzed by GC-MS and a trace amount of desired products was detected.
- (e) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1a** (0.2 mmol), deuterated aldehyde **2a-D** (0.2 mmol), NaDT (4 mol%), and MeCN (2.0 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10



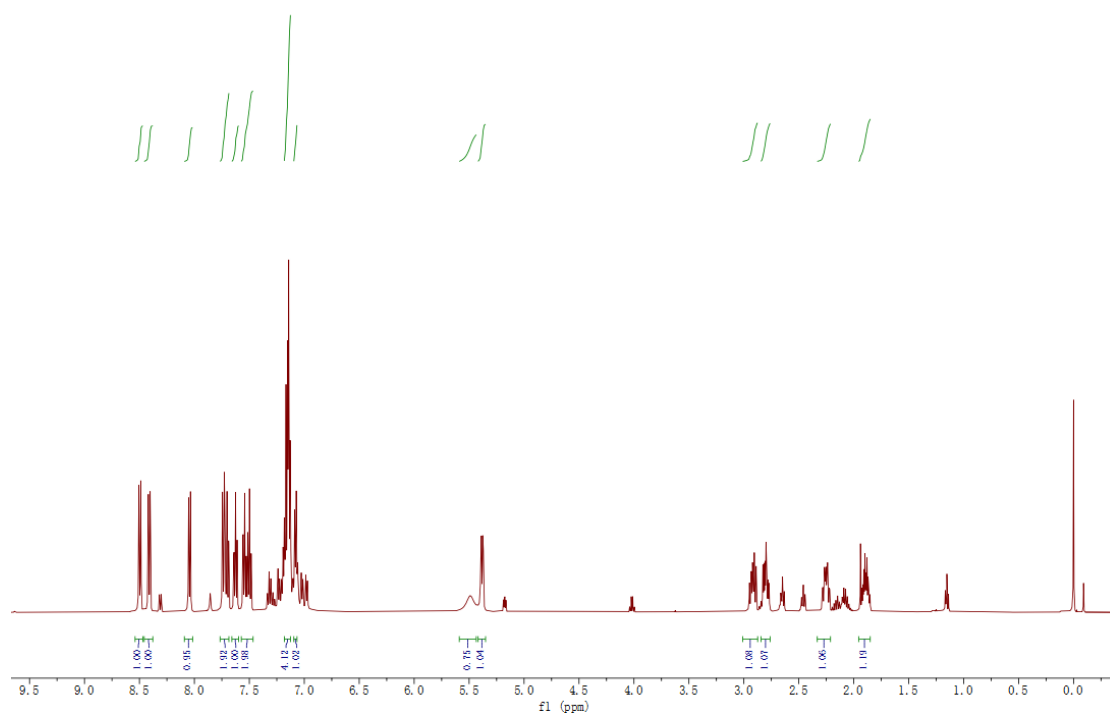


target product. The deuterium incorporation was determined by the analysis of the  $^1\text{H}$  NMR spectra and 60% of  $\alpha\text{-H}$  was deuterated and 25% of deuterium atoms were incorporated into the hydroxyl group of **5aa**.



**Figure S4**  $^1\text{H}$  NMR spectrum of **5aa**

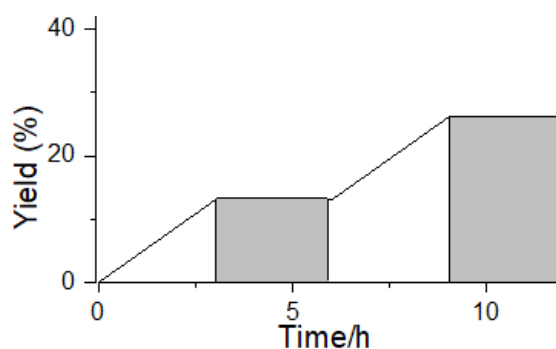
- (g) To a 10.0 mL Schlenk flask equipped with a magnetic stirring bar were added 2-isocyanobiphenyl **1a** (0.2 mmol), aldehyde **2a** (0.2 mmol), NaDT (4 mol%) and  $\text{CD}_3\text{CN}$  (2.0 mL). The resulting mixture was charged with nitrogen before light irradiation. Then the reaction mixture was stirred and irradiated by 10 W purple LEDs (395 nm) at ambient temperature. The organic layer was washed with brine and dried over anhydrous  $\text{Na}_2\text{SO}_4$ , filtered and concentrated under reduced pressure. The crude residue was subjected to flash column chromatography on silica gel eluting with ethyl acetate/petroleum ether to give the target product. The deuterium incorporation was determined by the analysis of the  $^1\text{H}$  NMR spectra and 25% of deuterium atoms were incorporated into the hydroxyl group of **6aa**.



**Figure S5**  $^1\text{H}$  NMR spectrum of **6aa**

### 2.5 Effect of Visible Light Irradiation

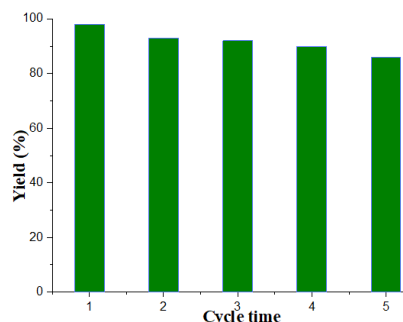
The reaction between **1a** (0.2 mmol), **2a** (0.2 mmol) and NaDT (4 mol%) in MeCN was conducted under the standard conditions. The mixture was subjected to sequential periods of stirring under visible light irradiation (10 W 395 nm LED) under a nitrogen atmosphere at room temperature with 3 hrs and followed by stirring in the absence of light with 3 hrs. At each time point, one reaction system was suspended and the yield was detected by GC.



**Figure S6** Visible light irradiation on/off experiments

### 2.6 Reusability and Stability of NaDT

The reusability and stability of NaDT was tested: In a typical procedure, the mixture of **1a** (0.2 mmol), **2a** (0.2 mmol), NaDT (4 mol%) and MeCN (2 mL) irradiated with a 10 W purple LEDs (395 nm) under a N<sub>2</sub> atmosphere at room temperature. After completion of the reaction, the photocatalyst was separated by centrifugation, washed twice with MeCN and used for next run. The reaction liquid was analyzed by GC-MS to detect the yield of **3aa**.



**Figure S7** Reusability and stability of photocatalyst

## 2.7 Calculation of Apparent Quantum Yield

$$E_{\text{photon}} = \frac{hc}{\lambda_{\text{inc}}(395 \text{ nm})} = \frac{6.63 \times 10^{-34} \text{ J}\cdot\text{s} \cdot 3 \times 10^8 \text{ m}\cdot\text{s}^{-1}}{395 \times 10^{-9} \text{ m}} = 5 \times 10^{-19} \text{ J}$$

$$E_{\text{total}} = PSt = 17.47 \times 10^{-3} \text{ W}\cdot\text{cm}^{-2} \cdot 10.63 \text{ cm}^2 \cdot 24 \cdot 3600 \text{ s} = 1.6 \times 10^4 \text{ J}$$

$$\text{Number of Incident Photons} = \frac{E_{\text{total}}}{E_{\text{photon}}} = \frac{1.6 \times 10^4 \text{ J}}{5 \times 10^{-19} \text{ J}} = 3.2 \times 10^{22} = 53 \text{ mmol}$$

$$\text{A.Q.Y}(\%) = \frac{\text{Number of Product}}{\text{Number of Incident Photons}} = \frac{0.188 \text{ mmol}}{53 \text{ mmol}} = 0.4 \% < 1$$

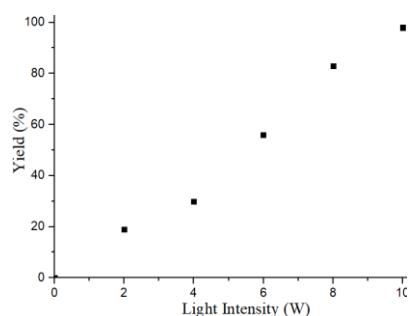
Where  $h$  (J·s) is Planck's constant,  $c$  (m·s<sup>-1</sup>) is the speed of light and  $\lambda_{\text{inc}}$  (m) is the wavelength of the incident light.  $P$  (W·cm<sup>-2</sup>) is the power density of the incident light,  $S$  (cm<sup>2</sup>) is the irradiation area and  $t$  (s) is the photoreaction time.

## 2.8 Dependent Relationship of Product Yields on Light Intensity

The reaction between **1a** (0.2 mmol), **2a** (0.2 mmol) and NaDT (4 mol%) in MeCN (2 mL) was conducted under the standard conditions. The mixture was subjected to

light irradiation (2 W, 4 W, 6 W, 8 W, 10 W, respectively) under a nitrogen atmosphere at room temperature. After reaction, the reaction system was suspended and the yield was detected by GC-MS. A linear dependence of the product yield on the light intensity was obtained, which could confirm that this was a photocatalytic reaction.

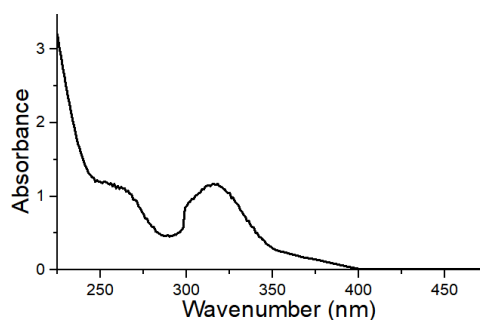
LED power	2 W	4 W	6 W	8 W	10 W
Yields of <b>3aa</b>	19 %	30%	56%	83%	98%



**Figure S8** Dependence of product yield on light intensity

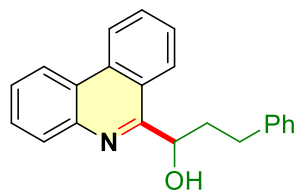
## 2.9 UV/Vis Absorption Spectroscopy Analysis

The UV/Vis absorption spectra of NaDT were recorded in 1 cm path quartz cuvettes by using a Shimadzu UV-2600 spectrophotometer. The obtained bands in UV/vis absorption spectra were shown in Figure S9.

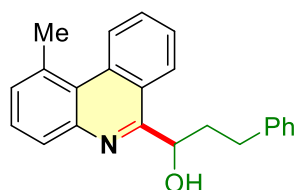


**Figure S9** UV-vis spectra of NaDT ( $5 \times 10^{-6}$  M) in MeCN

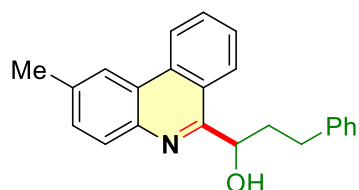
### 3. Characterization Data of Products



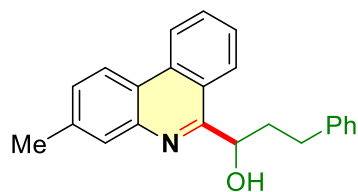
**1-(phenanthridin-6-yl)-3-phenylpropan-1-ol (3aa):** 94%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.53 (d,  $J = 8.3$  Hz, 1H), 8.44 (dd,  $J = 8.1, 1.3$  Hz, 1H), 8.07 (dd,  $J = 8.2, 1.3$  Hz, 1H), 7.77 – 7.71 (m, 2H), 7.67 – 7.62 (m, 1H), 7.58 – 7.50 (m, 2H), 7.19 – 7.13 (m, 4H), 7.11 – 7.07 (m, 1H), 5.40 (dd,  $J = 8.7, 2.6$  Hz, 1H), 2.96 – 2.90 (m, 1H), 2.84 – 2.78 (m, 1H), 2.30 – 2.23 (m, 1H), 1.94 – 1.87 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.1, 142.1, 142.0, 133.4, 131.0, 129.5, 129.0, 128.8, 128.5, 127.5, 127.1, 126.0, 125.1, 124.2, 123.1, 122.8, 122.2, 68.9, 40.8, 32.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{22}\text{H}_{20}\text{NO}$   $[\text{M}+\text{H}]^+$  314.1539, found 314.1540.



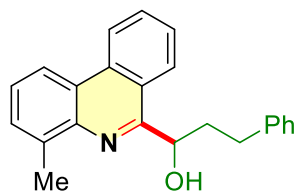
**1-(1-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3ba):** 83%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.79 (d,  $J = 8.6$  Hz, 1H), 7.97 (d,  $J = 8.1$  Hz, 1H), 7.80 (d,  $J = 8.2$  Hz, 1H), 7.76 – 7.69 (m, 1H), 7.57 – 7.51 (m, 2H), 7.40 (d,  $J = 7.3$  Hz, 1H), 7.19 – 7.13 (m, 4H), 7.10 – 7.07 (m, 1H), 5.58 (s, 1H), 5.41 (d,  $J = 8.5$  Hz, 1H), 3.00 (s, 3H), 2.89 (s, 1H), 2.95 – 2.89 (m, 1H), 2.82 – 2.76 (m, 1H), 2.30 – 2.24 (m, 1H), 1.93 – 1.86 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.4, 143.6, 142.0, 135.2, 134.7, 131.4, 130.1, 128.8, 128.5, 128.5, 128.1, 127.3, 126.7, 125.9, 125.0, 124.1, 123.9, 68.7, 40.7, 32.0, 26.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  328.1696, found 328.1696.



**1-(2-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3ca):** 85%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.51 (d,  $J = 8.3$  Hz, 1H), 8.21 (s, 1H), 7.94 (d,  $J = 8.3$  Hz, 1H), 7.79 – 7.66 (m, 2H), 7.55 – 7.41 (m, 2H), 7.21 – 7.14 (m, 4H), 7.11 – 7.07 (m, 1H), 5.51 (s, 1H), 5.38 (d,  $J = 8.4$  Hz, 1H), 2.95 – 2.89 (m, 1H), 2.83 – 2.77 (m, 1H), 2.53 (s, 3H), 2.29 – 2.23 (m, 1H), 1.93 – 1.86 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  160.0, 142.1, 140.4, 137.0, 133.1, 130.7, 130.7, 129.2, 128.8, 128.5, 127.3, 125.9, 125.0, 124.1, 123.2, 122.8, 121.8, 68.9, 40.8, 32.1, 22.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  328.1696, found 328.1695.

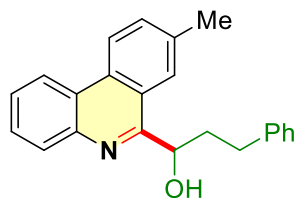


**1-(3-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3da):** 91%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.46 (d,  $J = 8.3$  Hz, 1H), 8.29 (d,  $J = 8.4$  Hz, 1H), 7.88 – 7.81 (m, 1H), 7.77 – 7.64 (m, 2H), 7.73 – 7.67 (m, 1H), 7.37 (dd,  $J = 8.4, 1.9$  Hz, 1H), 7.22 – 7.12 (m, 4H), 7.10 – 7.04 (m, 1H), 5.53 (s, 1H), 5.37 (dd,  $J = 8.6, 2.6$  Hz, 1H), 2.95 – 2.89 (m, 1H), 2.81 – 2.81 (m, 1H), 2.49 (s, 3H), 2.28 – 2.22 (m, 1H), 1.92 – 1.84 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.0, 142.2, 142.0, 139.2, 133.4, 130.8, 129.1, 128.8, 128.7, 128.5, 127.0, 125.9, 125.0, 122.8, 122.6, 122.0, 121.9, 68.9, 40.8, 32.1, 21.6; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  328.1696, found 328.1693.

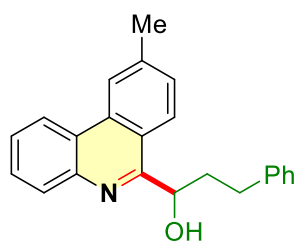


**1-(4-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3ea):** 89%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.43 (d,  $J = 8.4$  Hz, 1H), 8.21 (d,  $J = 8.1$  Hz, 1H), 7.69 (d,  $J = 8.2$  Hz, 1H), 7.63 (t,  $J = 7.8$  Hz, 1H), 7.47 – 7.42 (m, 2H), 7.38 (t,  $J = 7.7$  Hz, 1H), 7.16 – 7.10 (m, 4H), 7.05 (t,  $J = 7.0$  Hz, 1H), 5.65 (s, 1H), 5.38 – 5.29 (m, 1H), 2.93 – 2.87 (m, 1H), 2.74 (s, 3H), 2.67 – 2.57 (m, 1H), 2.28 – 2.21 (m, 1H), 1.88 – 1.80 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  159.5, 142.0, 140.5, 137.0, 133.6, 130.7, 129.7,

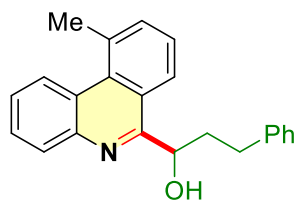
128.7, 128.6, 128.4, 128.3, 127.2, 126.6, 125.9, 124.9, 123.0, 120.0, 77.4, 77.2, 76.9, 69.0, 40.8, 32.0, 18.5; HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{22}NO$   $[M+H]^+$  328.1696, found 328.1698.



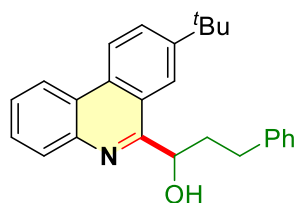
**1-(8-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3fa):** 88%, yellow oil.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.39 (d,  $J = 8.3$  Hz, 2H), 8.03 (dd,  $J = 8.3, 1.4$  Hz, 1H), 7.62 – 7.59 (m, 1H), 7.55 – 7.52 (m, 2H), 7.38 (s, 1H), 7.25 – 7.18 (m, 4H), 7.15 – 7.11 (m, 1H), 5.47 (s, 1H), 5.33 (dd,  $J = 8.7, 2.4$  Hz, 1H), 2.99 – 2.93 (m, 1H), 2.84 – 2.79 (m, 1H), 2.39 (s, 3H), 2.27 – 2.22 (m, 1H), 1.92 – 1.85 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  160.8, 142.1, 141.9, 137.5, 132.6, 131.2, 129.4, 129.0, 128.5, 128.5, 127.0, 126.0, 124.6, 124.3, 123.2, 122.7, 122.0, 68.5, 40.8, 32.1, 21.9; HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{22}NO$   $[M+H]^+$  328.1696, found 328.1696.



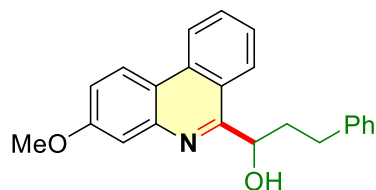
**1-(9-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3ga):** 87%, yellow oil.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.45 (d,  $J = 8.1$  Hz, 1H), 8.33 (s, 1H), 8.05 (d,  $J = 8.1$  Hz, 1H), 7.65 (dd,  $J = 11.7, 8.0$  Hz, 2H), 7.56 (t,  $J = 7.6$  Hz, 1H), 7.36 (dd,  $J = 8.3, 1.7$  Hz, 1H), 7.21 – 7.15 (m, 4H), 7.11 (d,  $J = 7.3$  Hz, 1H), 5.53 (s, 1H), 5.38 (dd,  $J = 8.7, 2.7$  Hz, 1H), 2.96 – 2.90 (m, 1H), 2.83 – 2.77 (m, 1H), 2.55 (s, 3H), 2.29 – 2.22 (m, 1H), 1.94 – 1.87 (m, 1H).  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  161.0, 142.3, 142.1, 141.5, 133.6, 129.5, 129.2, 128.9, 128.8, 128.5, 126.9, 126.0, 125.0, 124.1, 122.5, 122.2, 121.2, 68.9, 40.9, 32.1, 22.4; HRMS (ESI)  $m/z$  calcd for  $C_{23}H_{22}NO$   $[M+H]^+$  328.1696, found 328.1697.



**1-(10-methylphenanthridin-6-yl)-3-phenylpropan-1-ol (3ha):** 83%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.74 (d,  $J = 8.5$  Hz, 1H), 8.13 (d,  $J = 8.0$  Hz, 1H), 7.73 – 7.66 (m, 2H), 7.62 – 7.57 (m, 2H), 7.46 (t,  $J = 7.7$  Hz, 1H), 7.19 – 7.15 (m, 4H), 7.10 (d,  $J = 7.2$  Hz, 1H), 5.61 (s, 1H), 5.42 (dd,  $J = 8.5, 2.5$  Hz, 1H), 3.06 (s, 3H), 2.96 – 2.90 (m, 1H), 2.84 – 2.78 (m, 1H), 2.31 – 2.24 (m, 1H), 1.94 – 1.86 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 143.2, 142.1, 136.1, 135.2, 132.9, 129.9, 128.8, 128.5, 128.3, 126.9, 126.8, 126.3, 125.9, 125.7, 124.6, 123.6, 69.0, 40.8, 32.1, 27.1; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{23}\text{H}_{22}\text{NO}$   $[\text{M}+\text{H}]^+$  328.1696, found 328.1694.

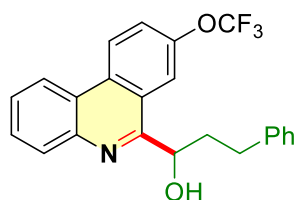


**1-(8-(tert-butyl)phenanthridin-6-yl)-3-phenylpropan-1-ol (3ia):** 93%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.42 (dd,  $J = 19.9, 8.3$  Hz, 2H), 8.10 – 8.00 (m, 1H), 7.80 (dd,  $J = 8.6, 2.0$  Hz, 1H), 7.68 (d,  $J = 1.8$  Hz, 1H), 7.60 (t,  $J = 7.4$  Hz, 1H), 7.57 – 7.46 (m, 1H), 7.20 (d,  $J = 4.3$  Hz, 4H), 7.10 (h,  $J = 4.1$  Hz, 1H), 5.55 (s, 1H), 5.39 (dd,  $J = 9.3, 2.4$  Hz, 1H), 3.03 – 2.97 (m, 1H), 2.83 – 2.78 (m, 1H), 2.28 – 2.21 (m, 1H), 1.96 – 1.84 (m, 1H), 1.26 (s, 9H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.4, 150.6, 141.9, 141.7, 131.1, 129.3, 129.2, 128.9, 128.6, 128.6, 127.0, 126.0, 124.2, 122.9, 122.6, 122.0, 120.7, 68.3, 40.9, 35.1, 32.1, 31.3; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{26}\text{H}_{28}\text{NO}$   $[\text{M}+\text{H}]^+$  370.2165, found 370.2168.

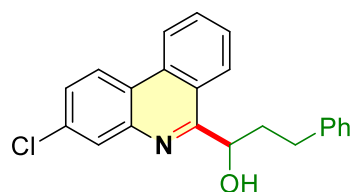




**1-(3-methoxyphenanthridin-6-yl)-3-phenylpropan-1-ol (3ja):** 84%, yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.40 (d, *J* = 8.2 Hz, 1H), 8.30 (d, *J* = 9.0 Hz, 1H), 7.75 – 7.65 (m, 2H), 7.49 – 7.41 (m, 2H), 7.20 – 7.14 (m, 5H), 7.10 – 7.07 (m, 1H), 5.45 (s, 1H), 5.38 (dd, *J* = 8.6, 2.6 Hz, 1H), 3.90 (s, 3H), 2.95 – 2.89 (m, 1H), 2.83 – 2.78 (m, 1H), 2.29 – 2.22 (m, 1H), 1.95 – 1.89 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 161.6, 160.3, 143.8, 142.0, 133.6, 130.9, 128.8, 128.5, 126.4, 126.0, 125.1, 123.4, 122.3, 122.1, 118.2, 118.0, 109.4, 68.9, 55.7, 40.9, 32.1; HRMS (ESI) *m/z* calcd for C<sub>23</sub>H<sub>22</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 344.1645, found 344.1644.

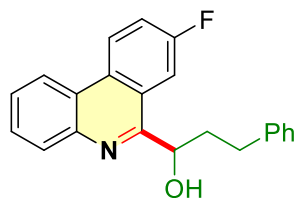


**3-phenyl-1-(8-(trifluoromethoxy)phenanthridin-6-yl)propan-1-ol (3ka):** 95%, yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.57 (d, *J* = 9.1 Hz, 1H), 8.41 (dd, *J* = 8.3, 1.4 Hz, 1H), 8.08 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.70 – 7.67 (m, 1H), 7.62 – 7.59 (m, 2H), 7.50 (d, *J* = 2.4 Hz, 1H), 7.23 – 7.14 (m, 4H), 7.13 – 7.08 (m, 1H), 5.30 (dd, *J* = 15.5, 8.2 Hz, 2H), 2.98 – 2.91 (m, 1H), 2.86 – 2.80 (m, 1H), 2.26 – 2.19 (m, 1H), 1.94 – 1.86 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 160.6, 147.8, 147.8, 142.2, 141.6, 131.9, 129.7, 129.5, 128.8, 128.6, 127.7, 126.1, 125.2, 124.5, 123.9, 123.5, 122.2, 120.6 (*J* = 258.3 Hz), 116.6, 68.7, 40.8, 32.0; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -57.79; HRMS (ESI) *m/z* calcd for C<sub>23</sub>H<sub>19</sub>F<sub>3</sub>NO<sub>2</sub> [M+H]<sup>+</sup> 398.1362, found 398.1360.

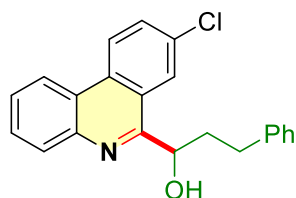


**1-(3-chlorophenanthridin-6-yl)-3-phenylpropan-1-ol (3la):** 89%, yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.43 (d, *J* = 8.3 Hz, 1H), 8.31 (d, *J* = 8.8 Hz, 1H), 8.01 (d, *J* = 2.3 Hz, 1H), 7.73 (t, *J* = 7.9 Hz, 2H), 7.55 – 7.47 (m, 2H), 7.20 – 7.13 (m, 4H), 7.11 – 7.07 (m, 1H), 5.38 – 5.35 (m, 1H), 5.29 (d, *J* = 6.7 Hz, 1H), 2.94 – 2.88 (m, 1H), 2.83 – 2.77 (m, 1H), 2.27 – 2.22 (m, 1H), 1.91 – 1.84 (m, 1H); <sup>13</sup>C NMR (125

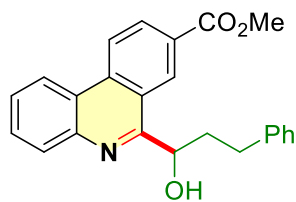
MHz, CDCl<sub>3</sub>)  $\delta$  162.6, 142.8, 141.8, 134.6, 132.9, 131.3, 128.8, 128.7, 128.5, 127.8, 127.6, 126.0, 125.2, 123.6, 123.0, 122.7, 122.7, 68.9, 40.8, 32.0; HRMS (ESI)  $m/z$  calcd for C<sub>22</sub>H<sub>19</sub>ClNO [M+H]<sup>+</sup> 348.1150, found 348.1153.



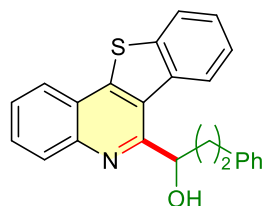
**1-(8-fluorophenanthridin-6-yl)-3-phenylpropan-1-ol (3ma):** 91%, yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.51 (dd,  $J = 9.1, 5.3$  Hz, 1H), 8.37 (dd,  $J = 8.0, 1.3$  Hz, 1H), 8.06 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.69 – 7.62 (m, 1H), 7.59 – 7.56 (m, 1H), 7.50 – 7.46 (m, 1H), 7.32 (dd,  $J = 9.6, 2.5$  Hz, 1H), 7.21 – 7.15 (m, 4H), 7.13 – 7.08 (m, 1H), 5.35 (s, 1H), 5.26 (dd,  $J = 8.7, 2.5$  Hz, 1H), 2.95 – 2.89 (m, 1H), 2.85 – 2.79 (m, 1H), 2.26 – 2.19 (m, 1H), 1.93 – 1.86 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  160.9 ( $J = 237.5$  Hz), 141.7, 130.0, 130.0, 129.6, 128.9, 128.8, 128.6, 127.5, 126.1, 125.5 ( $J = 12.5$  Hz), 124.3 ( $J = 12.5$  Hz), 123.8, 122.0, 120.2 ( $J = 25$  Hz), 109.9 ( $J = 12.5$  Hz), 68.9, 40.6, 32.0; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>)  $\delta$  -110.96; HRMS (ESI)  $m/z$  calcd for C<sub>22</sub>H<sub>19</sub>FNO [M+H]<sup>+</sup> 332.1445, found 332.1443.



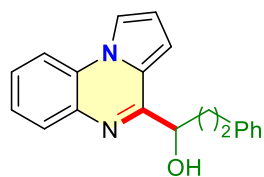
**1-(8-chlorophenanthridin-6-yl)-3-phenylpropan-1-ol (3na):** 86%, yellow oil. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta$  8.43 (d,  $J = 8.8$  Hz, 1H), 8.36 (d,  $J = 8.1$  Hz, 1H), 8.04 (d,  $J = 8.1$  Hz, 1H), 7.70 – 7.60 (m, 3H), 7.60 – 7.54 (m, 1H), 7.23 – 7.15 (m, 4H), 7.14 – 7.10 (m, 1H), 5.42 – 5.22 (m, 2H), 2.96 – 2.90 (m, 1H), 2.84 – 2.79 (m, 1H), 2.26 – 2.19 (m, 1H), 1.92 – 1.85 (m, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta$  160.2, 142.1, 141.7, 133.5, 131.7, 131.5, 129.7, 129.3, 128.8, 128.6, 127.5, 126.1, 124.6, 124.5, 124.0, 123.6, 122.1, 68.7, 40.7, 31.9; HRMS (ESI)  $m/z$  calcd for C<sub>22</sub>H<sub>19</sub>ClNO [M+H]<sup>+</sup> 348.1150, found 348.1152.



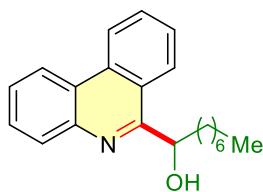
**Methyl 6-(1-hydroxy-3-phenylpropyl)phenanthridine-8-carboxylate (3oa):** 85%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.62 – 8.54 (m, 2H), 8.46 (dd,  $J = 8.2, 1.3$  Hz, 1H), 8.35 (dd,  $J = 8.6, 1.7$  Hz, 1H), 8.08 (dd,  $J = 8.1, 1.3$  Hz, 1H), 7.73 – 7.70 (m, 1H), 7.63 – 7.59 (m, 1H), 7.19 – 7.14 (m, 4H), 7.11 – 7.07 (m, 1H), 5.51 – 5.43 (m, 1H), 5.36 (d,  $J = 6.1$  Hz, 1H), 3.94 (s, 3H), 2.99 – 2.93 (m, 1H), 2.80 – 2.75 (m, 1H), 2.35 – 2.28 (m, 1H), 1.97 – 1.90 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  166.3, 161.7, 143.0, 141.8, 136.3, 130.8, 130.2, 129.7, 128.9, 128.7, 128.5, 127.5, 127.3, 125.9, 123.6, 123.2, 122.8, 122.7, 68.9, 52.7, 40.8, 31.8; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{22}\text{NO}_3$   $[\text{M}+\text{H}]^+$  372.1594, found 372.1591.



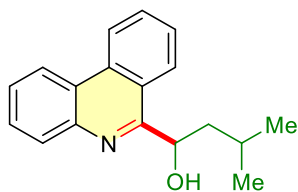
**1-(6a,11a-dihydrobenzo[4,5]thieno[3,2-c]quinolin-6-yl)-3-phenylpropan-1-ol (3pa):** 89%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.08 (d,  $J = 8.3$  Hz, 1H), 7.98 (d,  $J = 8.1$  Hz, 1H), 7.83 (d,  $J = 8.1$  Hz, 1H), 7.68 – 7.63 (m, 1H), 7.51 (t,  $J = 7.5$  Hz, 1H), 7.41 (d,  $J = 8.3$  Hz, 1H), 7.35 (t,  $J = 7.6$  Hz, 1H), 7.28 – 7.22 (m, 4H), 7.20 – 7.16 (m, 2H), 5.75 (s, 1H), 5.47 (dd,  $J = 9.9, 2.2$  Hz, 1H), 3.14 – 3.08 (m, 1H), 2.94 – 2.88 (m, 1H), 2.26 – 2.18 (m, 1H), 1.81 – 1.74 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.4, 148.0, 142.7, 141.7, 138.9, 134.4, 129.8, 129.3, 129.3, 128.6, 127.0, 126.3, 126.2, 125.7, 125.2, 124.9, 124.0, 123.7, 123.1, 77.4, 77.2, 76.9, 69.5, 39.3, 32.2; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{24}\text{H}_{20}\text{NOS}$   $[\text{M}+\text{H}]^+$  370.1260, found 370.1263.



**3-phenyl-1-(pyrrolo[1,2-a]quinoxalin-4-yl)propan-1-ol (3qa):** 80%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  7.90 – 7.78 (m, 2H), 7.74 (d,  $J = 8.4$  Hz, 1H), 7.42 (t,  $J = 7.7$  Hz, 1H), 7.35 (t,  $J = 7.8$  Hz, 1H), 7.19 – 7.13 (m, 4H), 7.08 (t,  $J = 7.5$  Hz, 1H), 6.74 (d,  $J = 3.5$  Hz, 1H), 6.62 (d,  $J = 3.4$  Hz, 1H), 4.97 (d,  $J = 8.2$  Hz, 1H), 4.95 – 4.78 (m, 1H), 2.89 – 2.83 (m, 1H), 2.79 – 2.73 (m, 1H), 2.32 – 2.25 (m, 1H), 2.03 – 1.97 (m, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.7, 141.9, 134.4, 129.5, 128.7, 128.4, 127.7, 127.6, 125.9, 125.4, 123.5, 114.8, 114.0, 113.9, 106.3, 77.4, 77.2, 76.9, 69.4, 39.6, 31.6; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{20}\text{H}_{19}\text{N}_2\text{O}$   $[\text{M}+\text{H}]^+$  303.1492, found 303.1491.

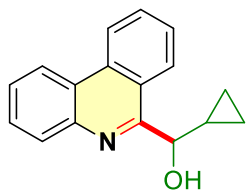


**1-(phenanthridin-6-yl)octan-1-ol (3ab):** 87%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.66 (d,  $J = 8.1$  Hz, 1H), 8.56 (dd,  $J = 8.1, 1.4$  Hz, 1H), 8.15 (dd,  $J = 8.1, 1.4$  Hz, 1H), 8.11 (dd,  $J = 8.3, 1.1$  Hz, 1H), 7.88 – 7.85 (m, 1H), 7.78 – 7.64 (m, 3H), 5.62 – 5.34 (m, 2H), 2.08 – 2.04 (m, 1H), 1.72 – 1.64 (m, 2H), 1.57 – 1.51 (m, 1H), 1.32 – 1.24 (m, 8H), 0.86 (d,  $J = 6.7$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  161.6, 142.2, 133.4, 130.9, 129.6, 129.0, 127.5, 127.1, 125.3, 124.2, 123.3, 122.9, 122.2, 69.9, 39.2, 32.0, 29.7, 29.4, 25.9, 22.8, 14.2; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{21}\text{H}_{26}\text{NO}$   $[\text{M}+\text{H}]^+$  308.2009, found 308.2010.

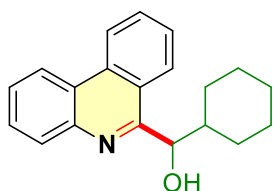


**4-methyl-1-(phenanthridin-6-yl)pentan-1-ol (3ac):** 84%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.67 (d,  $J = 8.3$  Hz, 1H), 8.56 (dd,  $J = 8.2, 1.4$  Hz, 1H), 8.15 (dd,  $J = 8.1, 1.4$  Hz, 1H), 8.08 (d,  $J = 8.2$  Hz, 1H), 7.87 (m, 1H), 7.73 (m, 2H), 7.67 (m, 1H), 5.57 (dd,  $J = 10.4, 2.1$  Hz, 1H), 5.44 (s, 1H), 2.26 (m, 1H), 1.76 (m, 2H), 1.24 (d,  $J = 6.6$  Hz, 3H), 0.96 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  162.0, 142.3, 133.5, 130.9, 129.5, 129.0, 127.5, 127.1, 125.2, 124.2, 123.2, 122.9, 122.2, 77.4, 77.2,

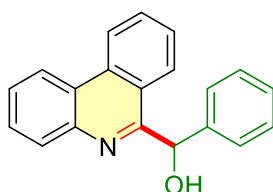
76.9, 68.3, 48.7, 25.6, 24.1; HRMS (ESI)  $m/z$  calcd for  $C_{18}H_{20}NO$   $[M+H]^+$  266.1539, found 266.1540.



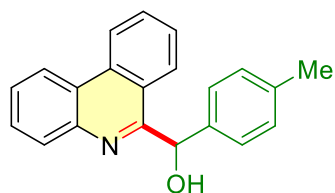
**Cyclopropyl(phenanthridin-6-yl)methanol (3ad):** 88%, yellow oil.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.64 (d,  $J = 8.3$  Hz, 1H), 8.54 (dd,  $J = 8.2, 1.4$  Hz, 1H), 8.26 (dd,  $J = 8.3, 1.2$  Hz, 1H), 8.14 – 8.12 (m, 1H), 7.87 – 7.84 (m, 1H), 7.75 – 7.70 (m, 2H), 7.67 – 7.64 (m, 1H), 5.53 – 5.47 (m, 1H), 5.38 (d,  $J = 6.2$  Hz, 1H), 1.42 – 1.31 (m, 1H), 0.85 – 0.76 (m, 1H), 0.61 – 0.51 (m, 2H), 0.37 – 0.27 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  161.1, 142.2, 133.4, 130.9, 129.6, 128.9, 127.4, 127.0, 125.7, 124.2, 123.5, 122.8, 122.2, 77.4, 77.2, 76.9, 69.0, 17.8, 2.7; HRMS (ESI)  $m/z$  calcd for  $C_{17}H_{16}NO$   $[M+H]^+$  250.1226, found 250.1224.



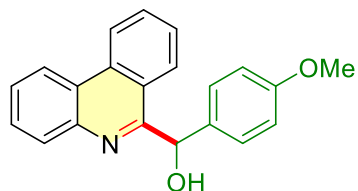
**Cyclohexyl(phenanthridin-6-yl)methanol (3ae):** 85%, yellow oil.  $^1H$  NMR (500 MHz,  $CDCl_3$ )  $\delta$  8.62 (d,  $J = 8.3$  Hz, 1H), 8.53 (dd,  $J = 8.3, 1.4$  Hz, 1H), 8.13 (m, 2H), 7.84 (m, 1H), 7.71 (m, 2H), 7.64 (m, 1H), 5.38 (d,  $J = 7.4$  Hz, 2H), 1.93 (m, 2H), 1.84 (m, 1H), 1.78 – 1.70 (m, 1H), 1.64 – 1.56 (m, 2H), 1.33 – 1.25 (m, 2H), 1.17 (m, 1H), 1.10 – 1.02 (m, 1H), 0.95 (m, 1H);  $^{13}C$  NMR (125 MHz,  $CDCl_3$ )  $\delta$  160.6, 142.0, 133.2, 130.8, 130.0, 129.6, 128.9, 127.4, 127.0, 125.4, 124.0, 123.5, 122.8, 122.1, 73.7, 44.9, 31.2, 26.9, 25.2; HRMS (ESI)  $m/z$  calcd for  $C_{20}H_{22}NO$   $[M+H]^+$  292.1696, found 292.1693.



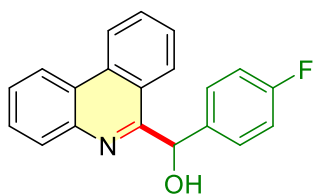
**Phenanthridin-6-yl(phenyl)methanol (3af)<sup>2</sup>:** 77%, light yellow solid. mp:169-170°  
<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.55 (d, *J* = 8.3 Hz, 1H), 8.50 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.19 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.74 – 7.67 (m, 2H), 7.65 – 7.62 (m, 1H), 7.47 (t, *J* = 7.6 Hz, 1H), 7.32 – 7.30 (m, 2H), 7.23 – 7.14 (m, 3H), 6.51 (s, 1H), 6.32 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.1, 143.1, 141.9, 133.5, 131.0, 129.8, 129.1, 129.0, 128.2, 128.0, 127.6, 127.4, 126.1, 124.6, 123.5, 122.7, 122.3, 72.9.



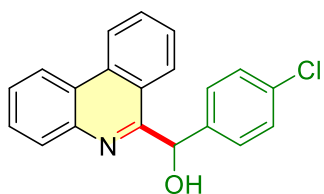
**Phenanthridin-6-yl(p-tolyl)methanol (3ag)<sup>2</sup>:** 83%, yellow solid. mp:164-165°, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.58 – 8.47 (m, 2H), 8.18 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.98 – 7.92 (m, 1H), 7.74 – 7.68 (m, 2H), 7.65-7.62 (m, 1H), 7.48-7.45 (m, 1H), 7.19 (d, *J* = 7.7 Hz, 2H), 7.01 (d, *J* = 7.9 Hz, 2H), 6.46 (s, 3H), 6.30 (s, 3H), 2.20 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.3, 141.9, 140.2, 137.9, 133.5, 130.9, 129.8, 129.6, 129.1, 127.9, 127.5, 127.4, 126.2, 124.6, 123.6, 122.7, 122.3, 72.6, 21.3.



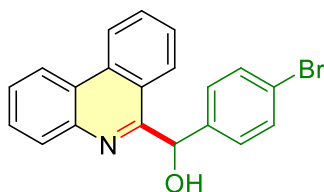
**(4-methoxyphenyl)(phenanthridin-6-yl)methanol (3ah)<sup>2</sup>:** 80%, light yellow solid. mp:165-166°, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.62 (d, *J* = 8.3 Hz, 1H), 8.57 (d, *J* = 8.1 Hz, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.83 – 7.76 (m, 2H), 7.74 – 7.69 (m, 1H), 7.57 – 7.50 (m, 1H), 7.30 (d, *J* = 8.3 Hz, 2H), 6.81 (d, *J* = 8.3 Hz, 2H), 6.55 (s, 1H), 6.37 (s, 1H), 3.74 (s, 3H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 159.4, 159.3, 141.9, 135.5, 133.5, 130.9, 129.7, 129.2, 129.1, 127.5, 127.4, 126.2, 124.6, 123.5, 122.7, 122.3, 114.3, 72.3, 55.3.



**(4-fluorophenyl)(phenanthridin-6-yl)methanol (3ai)**<sup>2</sup>: 81%, yellow solid. mp:170-171°, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.64 (d, *J* = 8.2 Hz, 1H), 8.58 (dd, *J* = 8.2, 1.4 Hz, 1H), 8.26 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.96 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.82 – 7.78 (m, 2H), 7.74 – 7.71 (m, 1H), 7.37 – 7.34 (m, 1H), 7.39 – 7.33 (m, 2H), 7.04 – 6.93 (m, 2H), 6.59 (s, 1H), 6.39 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 162.5 (*J* = 250 Hz), 158.8, 153.7, 141.8, 139.0, 139.0, 133.6, 131.0, 129.8, 129.7, 129.5 (*J* = 12.5 Hz), 127.6, 127.6, 126.0, 124.6, 123.4, 122.8, 122.3, 115.9 (*J* = 12.5 Hz), 72.1; <sup>19</sup>F NMR (471 MHz, CDCl<sub>3</sub>) δ -114.07.

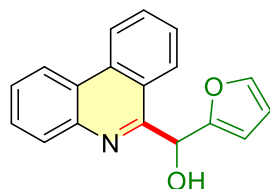


**(4-chlorophenyl)(phenanthridin-6-yl)methanol (3aj)**<sup>2</sup>: 76%, light yellow solid. mp:169-170°, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.50 (d, *J* = 8.2 Hz, 1H), 8.18 (d, *J* = 8.1 Hz, 1H), 7.87 (d, *J* = 8.3 Hz, 1H), 7.73 (t, *J* = 7.6 Hz, 2H), 7.65 (t, *J* = 7.6 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 8.2 Hz, 2H), 7.17 (d, *J* = 7.9 Hz, 2H), 6.52 (s, 1H), 6.29 (s, 1H); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>) δ 158.6, 141.8, 141.6, 134.0, 133.6, 131.1, 129.7, 129.4, 129.2, 129.1, 127.6, 127.6, 125.9, 124.6, 123.3, 122.8, 122.3, 72.1.



**(4-bromophenyl)(phenanthridin-6-yl)methanol (3ak)**<sup>2</sup>: 74%, light yellow solid. mp:167-168°, <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>) δ 8.56 (d, *J* = 8.3 Hz, 1H), 8.51 (dd, *J* = 8.2, 1.3 Hz, 1H), 8.18 (dd, *J* = 8.1, 1.3 Hz, 1H), 7.88 (d, *J* = 8.3 Hz, 1H), 7.76 – 7.71

(m, 2H), 7.65 (ddd,  $J = 8.4, 7.0, 1.4$  Hz, 1H), 7.51 – 7.47 (m, 1H), 7.35 – 7.31 (m, 2H), 7.20 – 7.17 (m, 2H), 6.50 (s, 1H), 6.28 (s, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  158.5, 142.1, 141.8, 133.6, 132.1, 131.1, 129.8, 129.7, 129.2, 127.7, 127.6, 125.9, 124.6, 123.3, 122.8, 122.3, 122.2, 72.2.



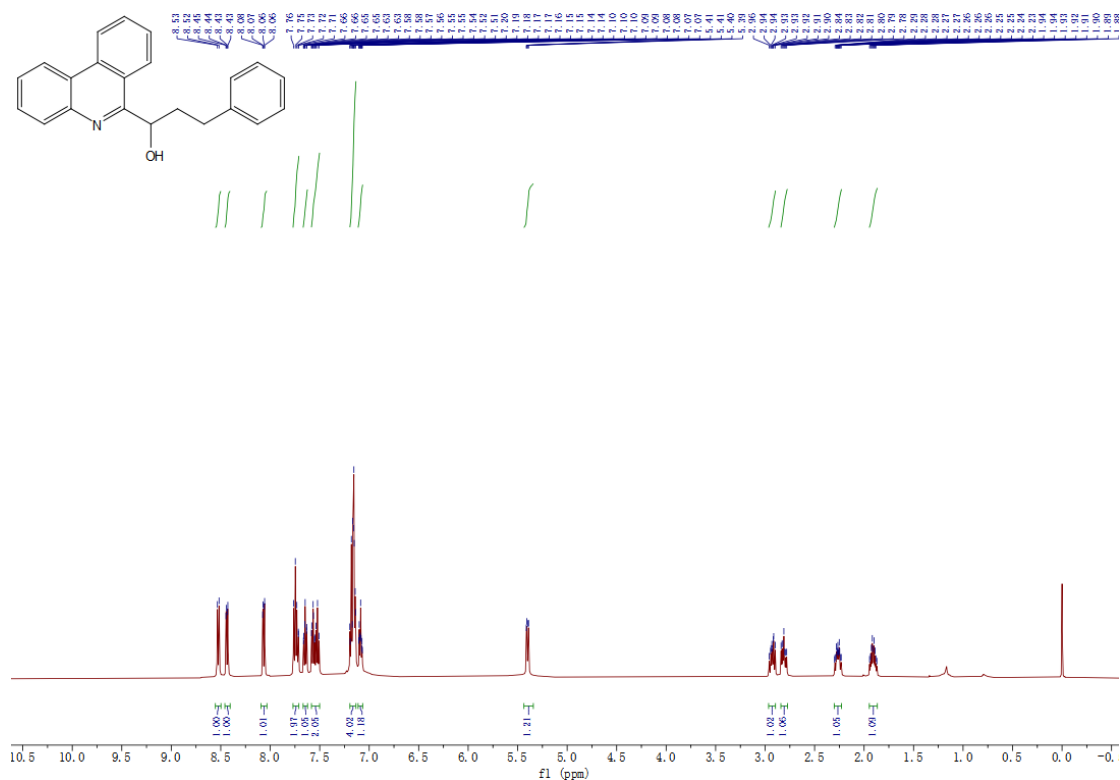
**Furan-2-yl(phenanthridin-6-yl)methanol (3al):** 89%, yellow oil.  $^1\text{H}$  NMR (500 MHz,  $\text{CDCl}_3$ )  $\delta$  8.64 (d,  $J = 8.3$  Hz, 1H), 8.57 (dd,  $J = 8.2, 1.4$  Hz, 1H), 8.23 (dd,  $J = 8.1, 1.4$  Hz, 1H), 8.06 (dd,  $J = 8.3, 1.2$  Hz, 1H), 7.84 – 7.76 (m, 2H), 7.73 – 7.69 (m, 1H), 7.63 – 7.59 (m, 1H), 7.33 (d,  $J = 1.7$  Hz, 1H), 6.49 (s, 1H), 6.43 (s, 1H), 6.29 (dd,  $J = 3.3, 1.8$  Hz, 1H), 6.19 (d,  $J = 3.3$  Hz, 1H);  $^{13}\text{C}$  NMR (125 MHz,  $\text{CDCl}_3$ )  $\delta$  156.6, 155.5, 142.6, 141.9, 133.5, 131.1, 129.8, 129.1, 127.6, 127.6, 125.6, 124.7, 123.6, 122.7, 122.3, 110.6, 108.2, 66.0; HRMS (ESI)  $m/z$  calcd for  $\text{C}_{18}\text{H}_{14}\text{NO}_2$   $[\text{M}+\text{H}]^+$  276.1019, found 276.1020.

#### 4. Reference

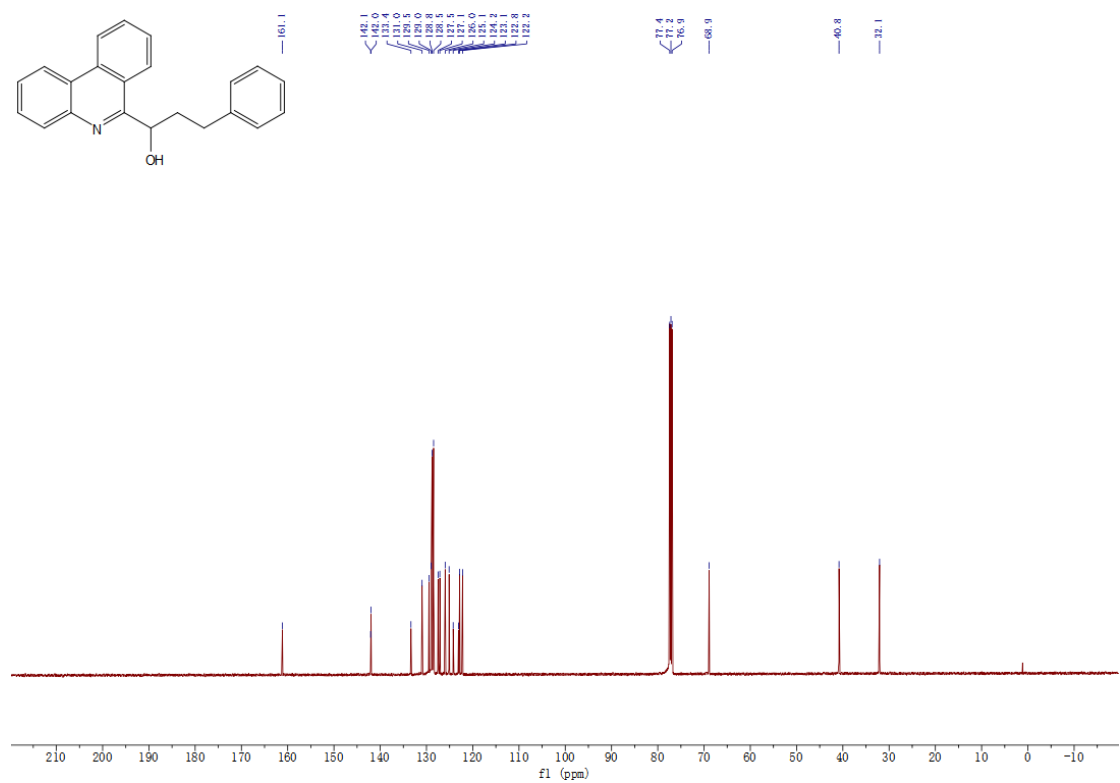
1. J. Xu, L. Liu, Z.-C. Yan, Y. Liu, L. Qin, N. Deng and H.-J. Xu, *Green Chem.*, 2023, **25**, 2268.
2. W. Shi, F. Ma, P. Li, L. Wang and T. Miao, *J. Org. Chem.*, 2020, **85**, 13808.



## 5. $^1\text{H}$ , $^{13}\text{C}$ and $^{19}\text{F}$ NMR Spectra of Products



$^1\text{H}$  NMR of compound **3aa**

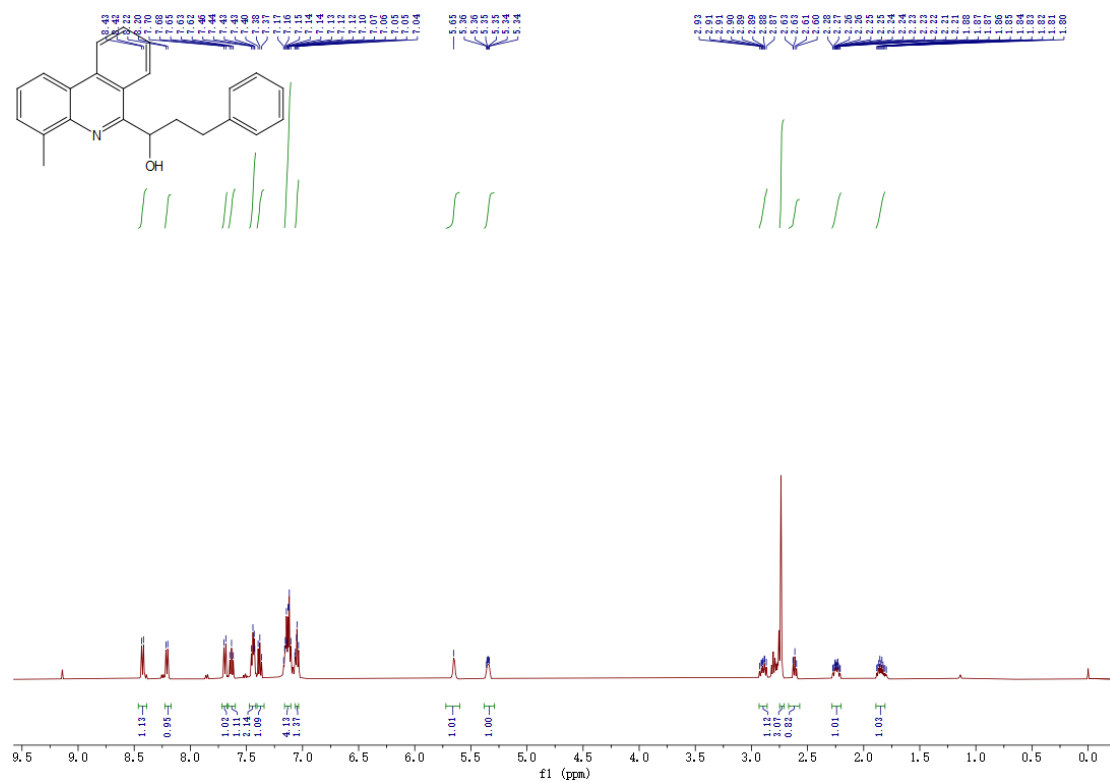


$^{13}\text{C}$  NMR of compound **3aa**

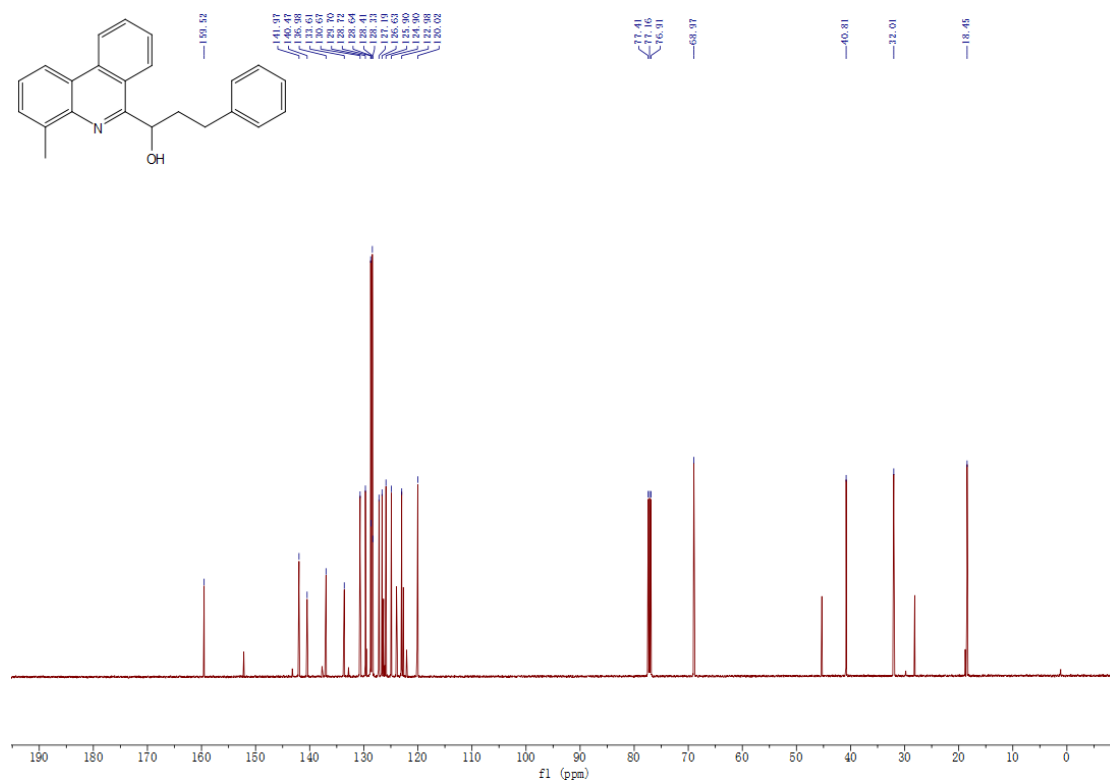




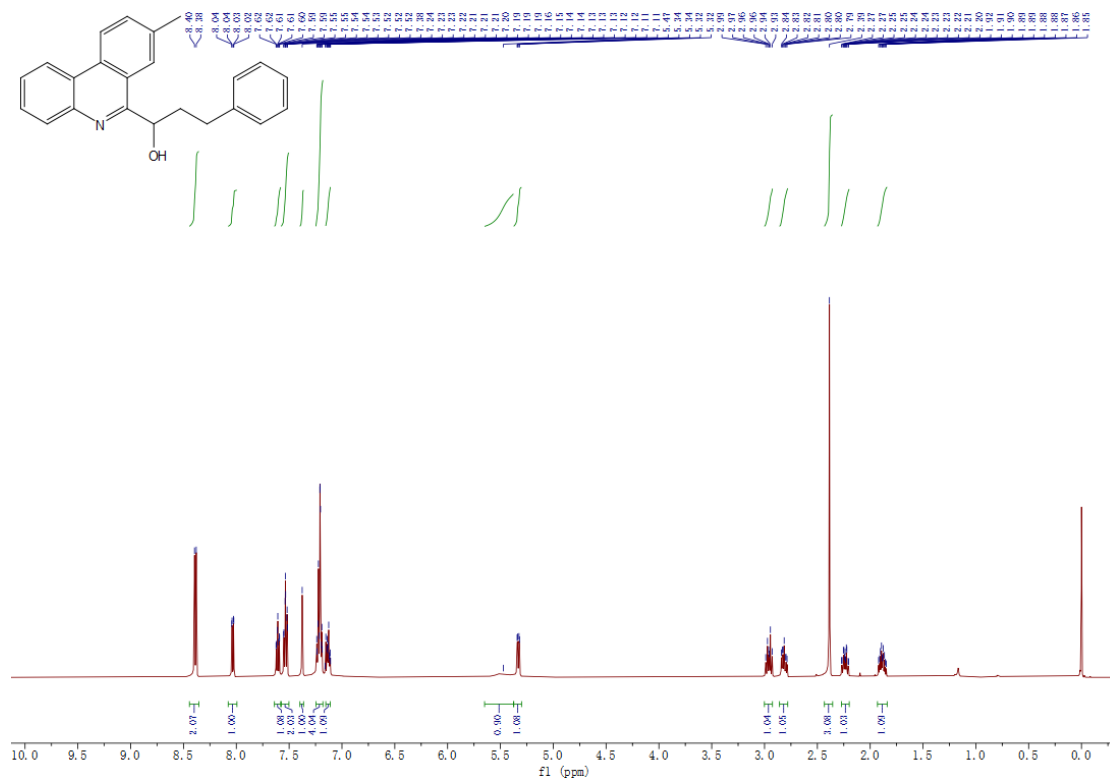




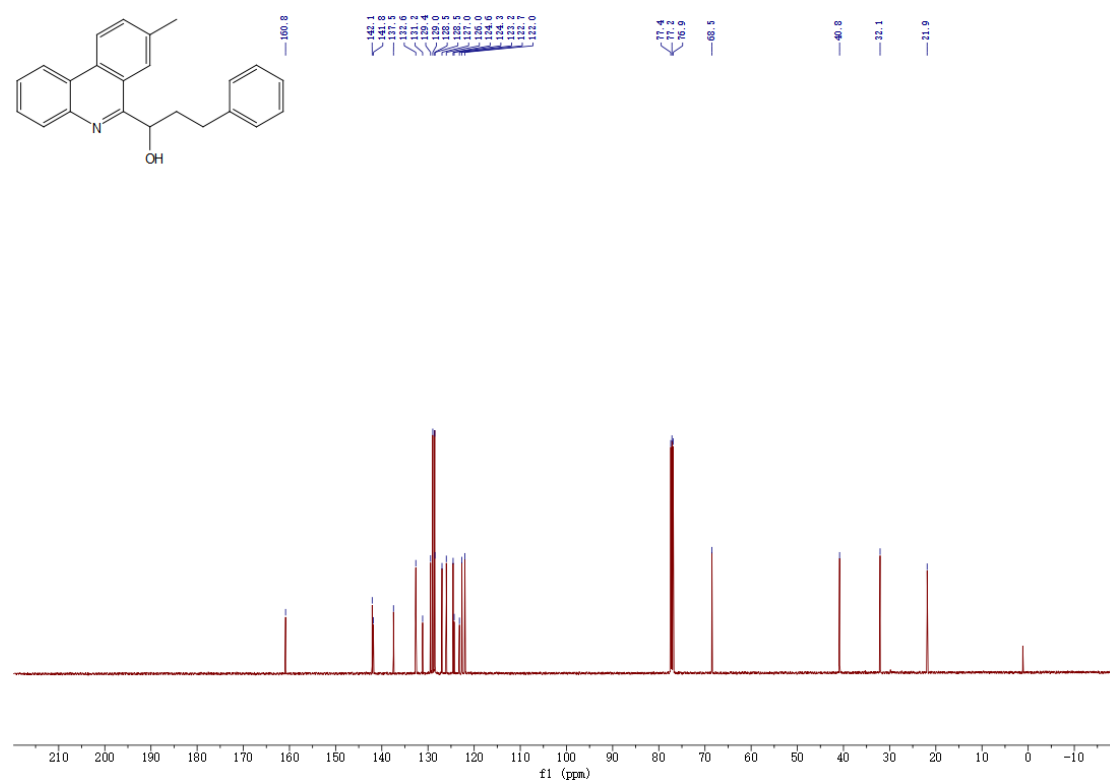
**<sup>1</sup>H NMR of compound 3ea**



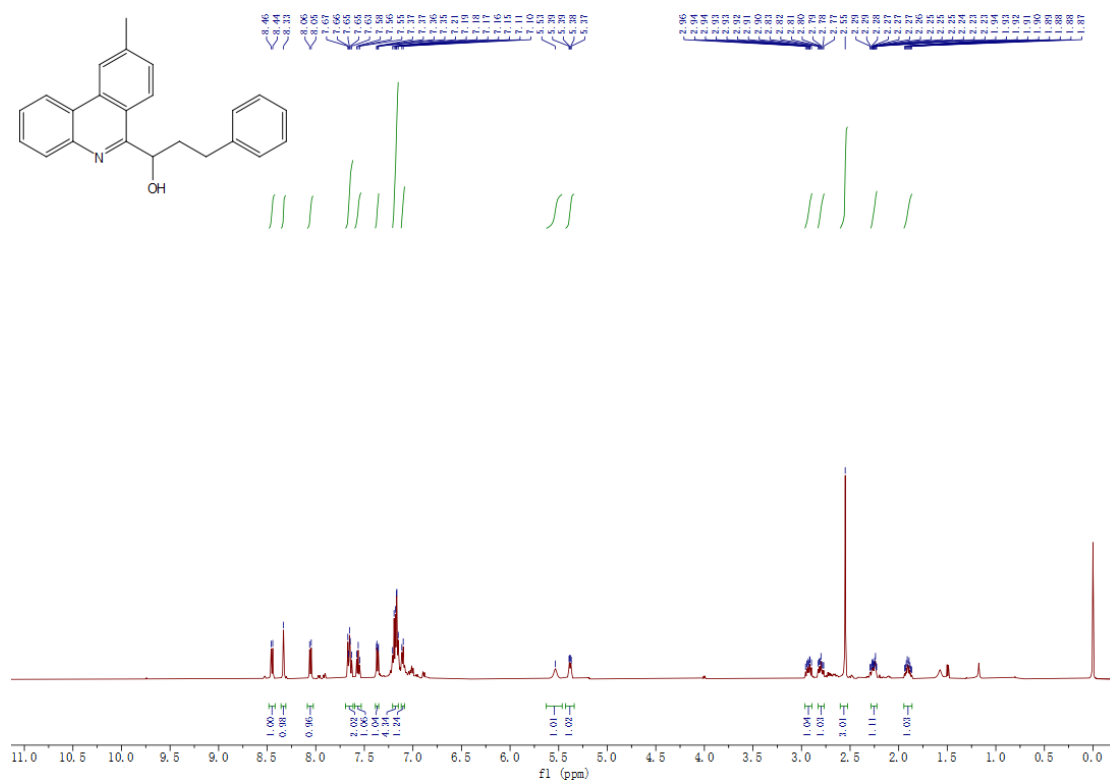
**<sup>13</sup>C NMR of compound 3ea**



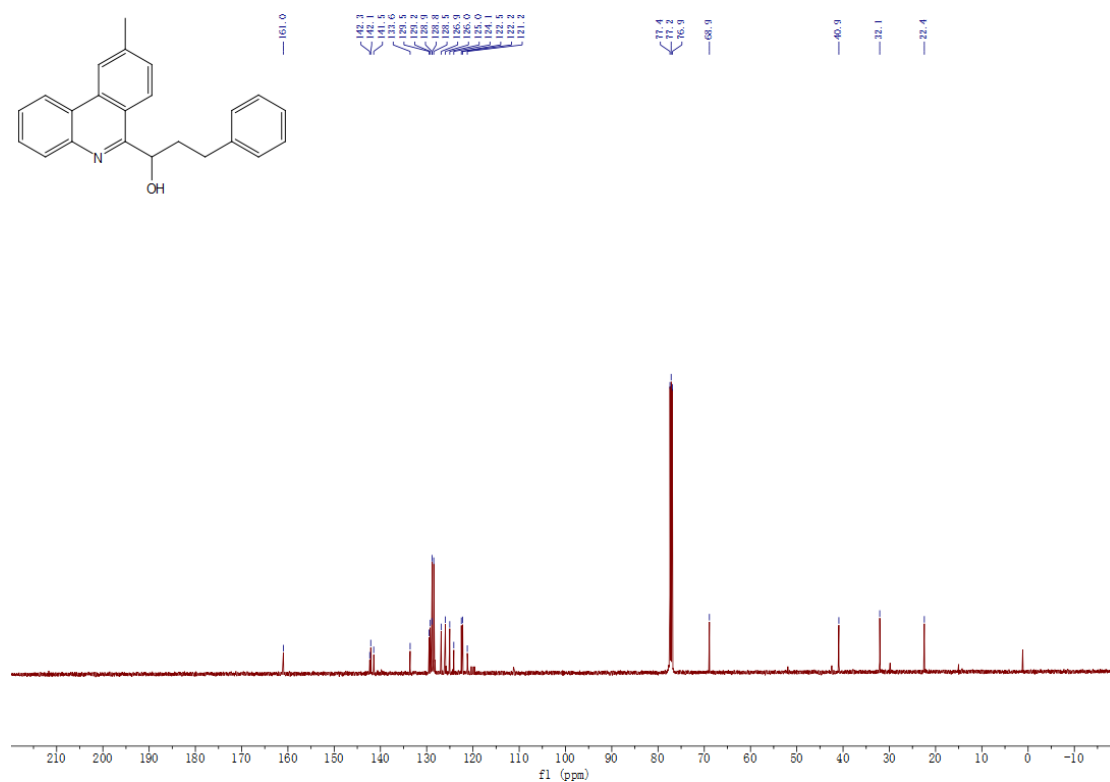
**<sup>1</sup>H NMR of compound 3fa**



**<sup>13</sup>C NMR of compound 3fa**



**<sup>1</sup>H NMR of compound 3ga**

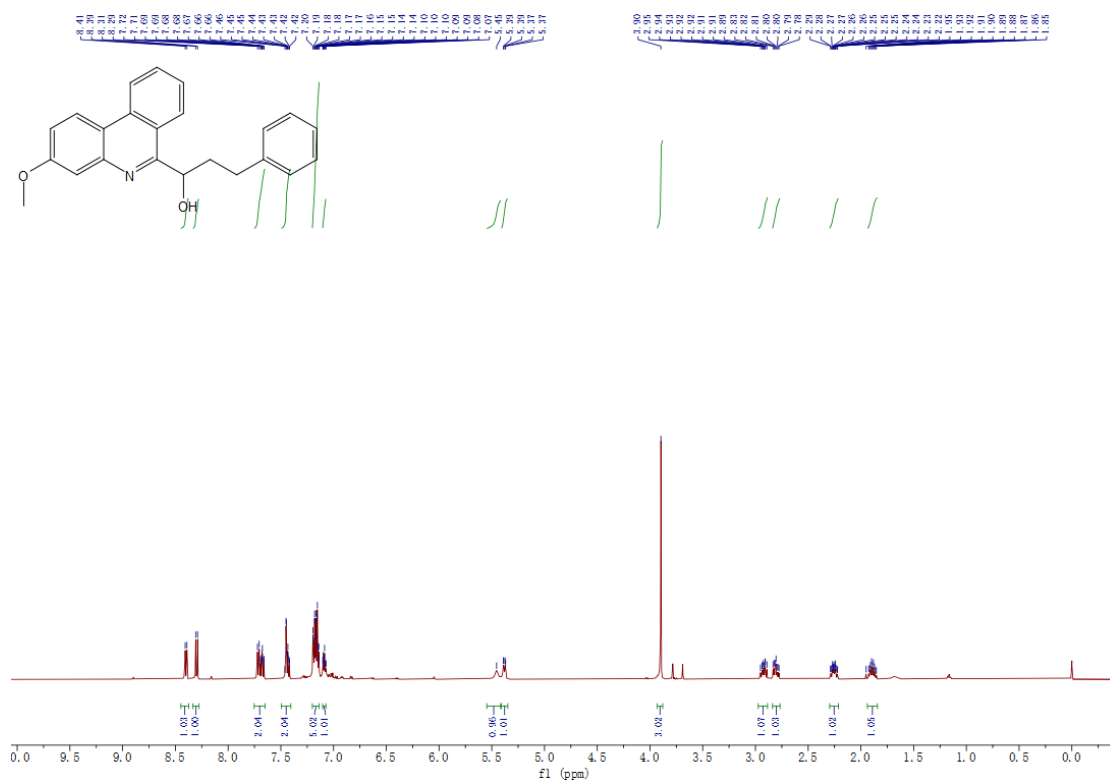


**<sup>13</sup>C NMR of compound 3ga**

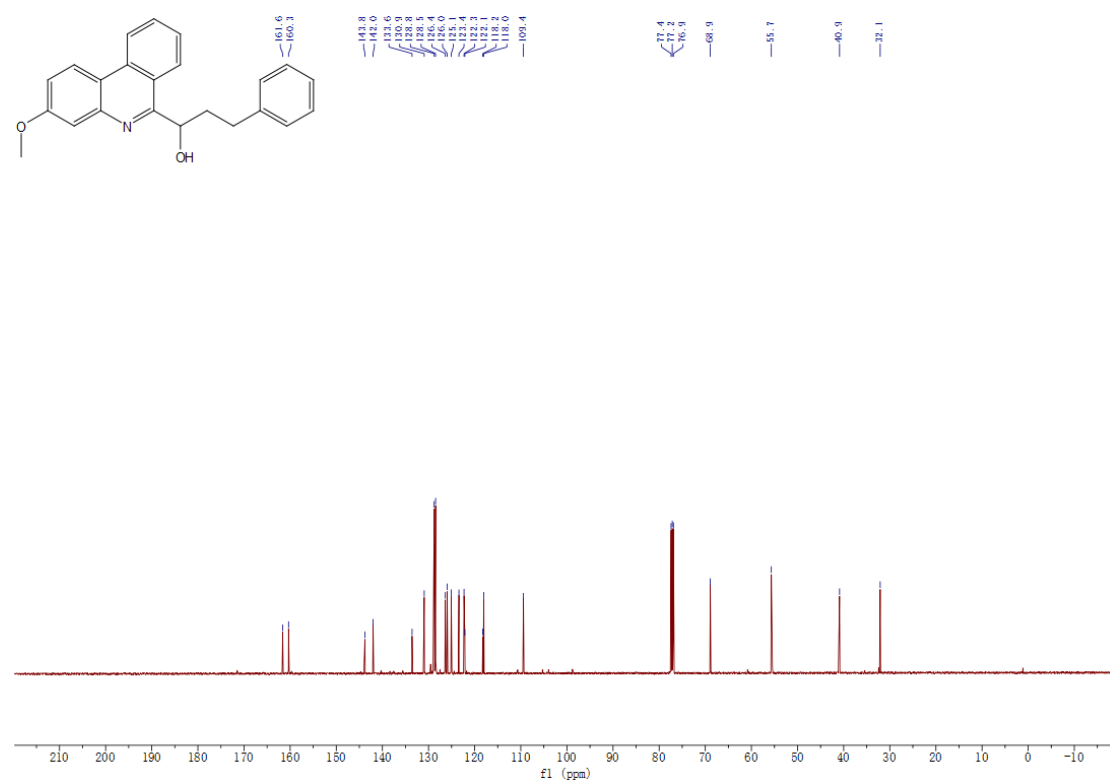




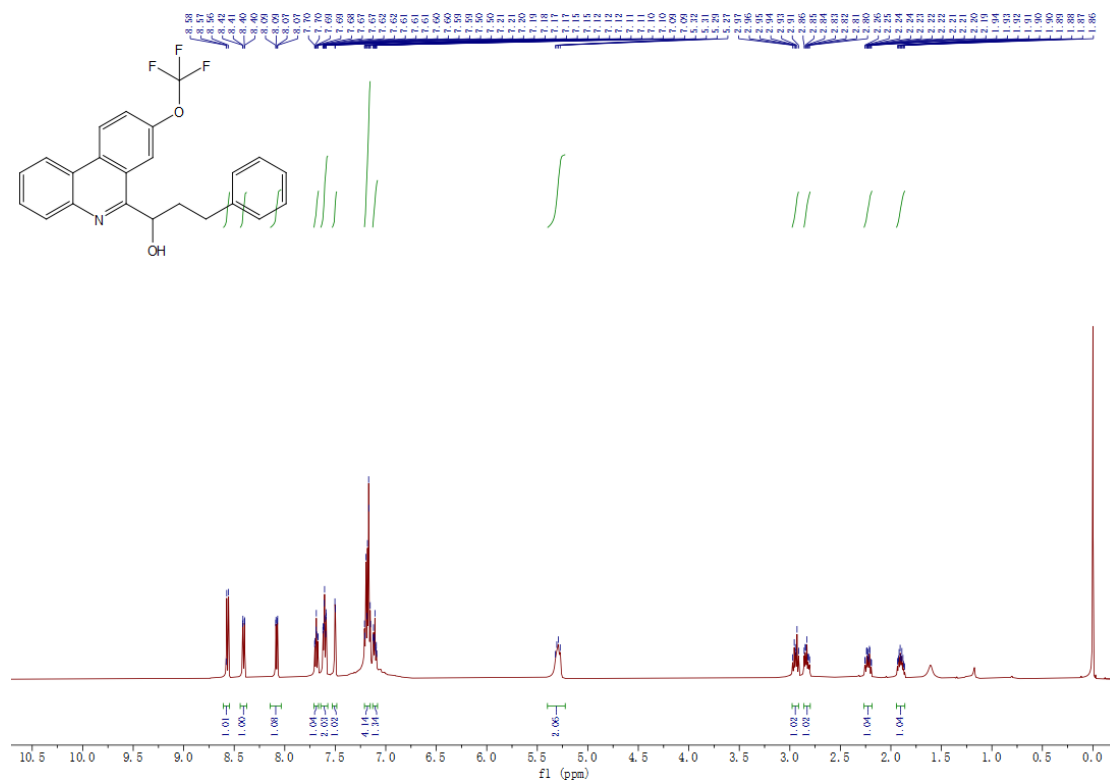




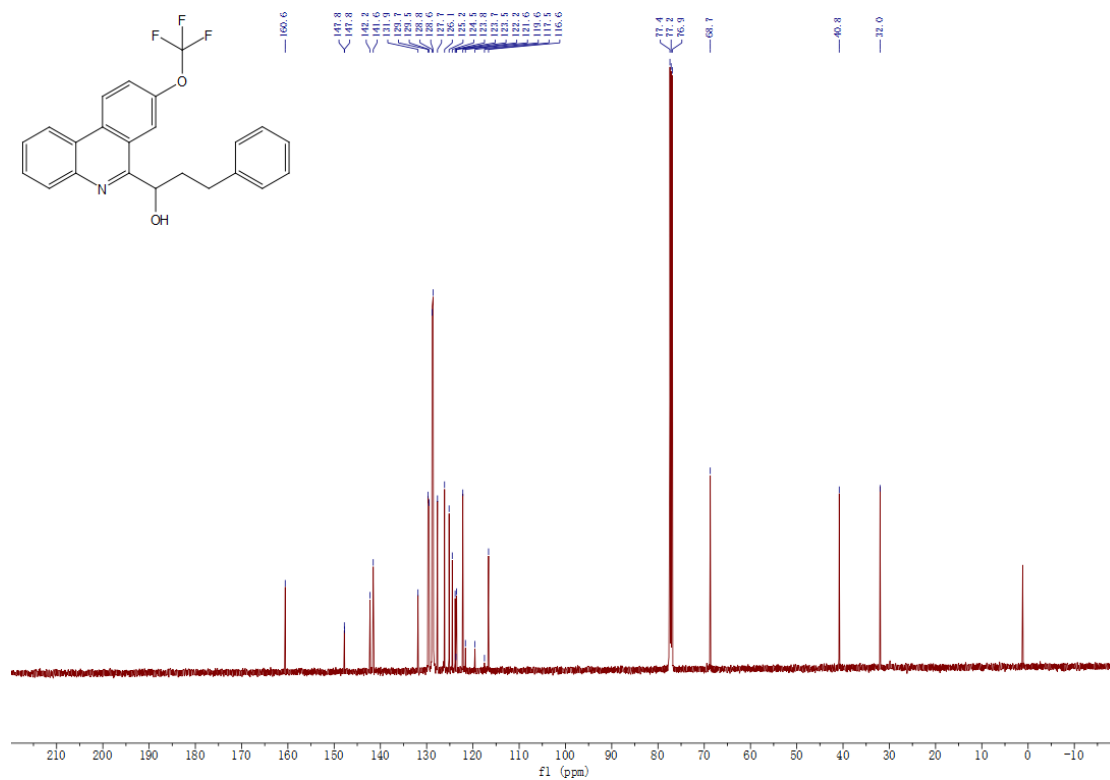
**<sup>1</sup>H NMR of compound 3ja**



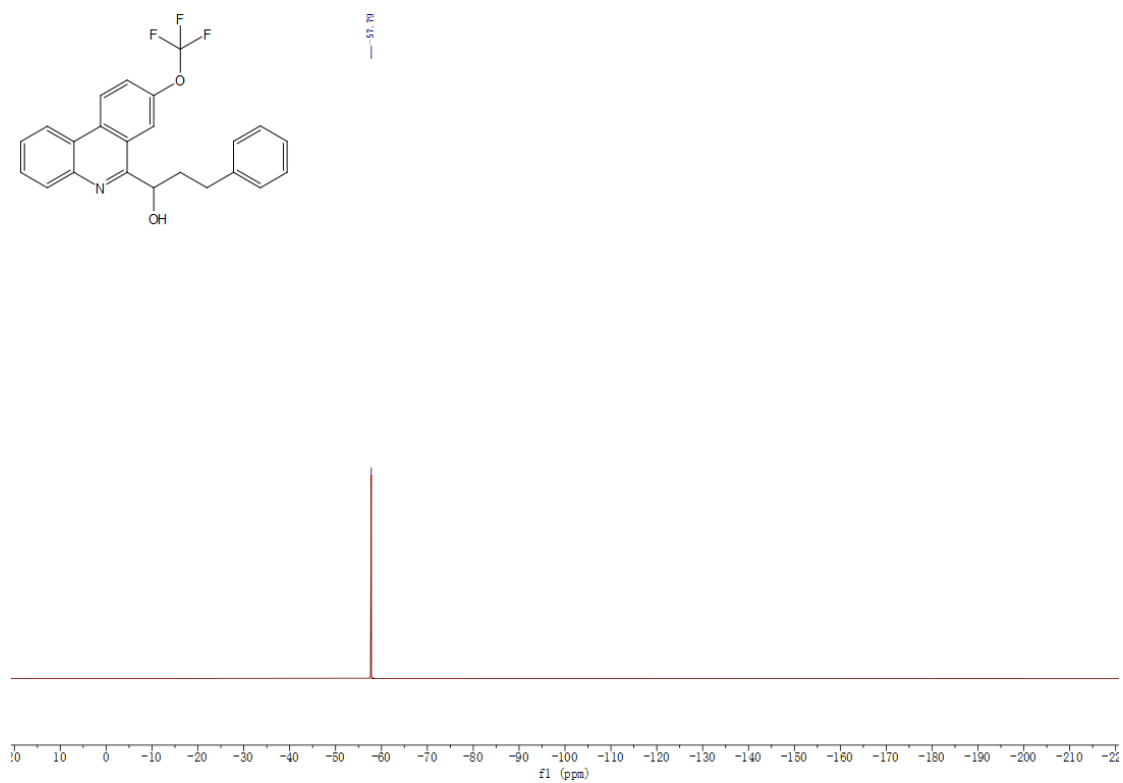
**<sup>13</sup>C NMR of compound 3ja**



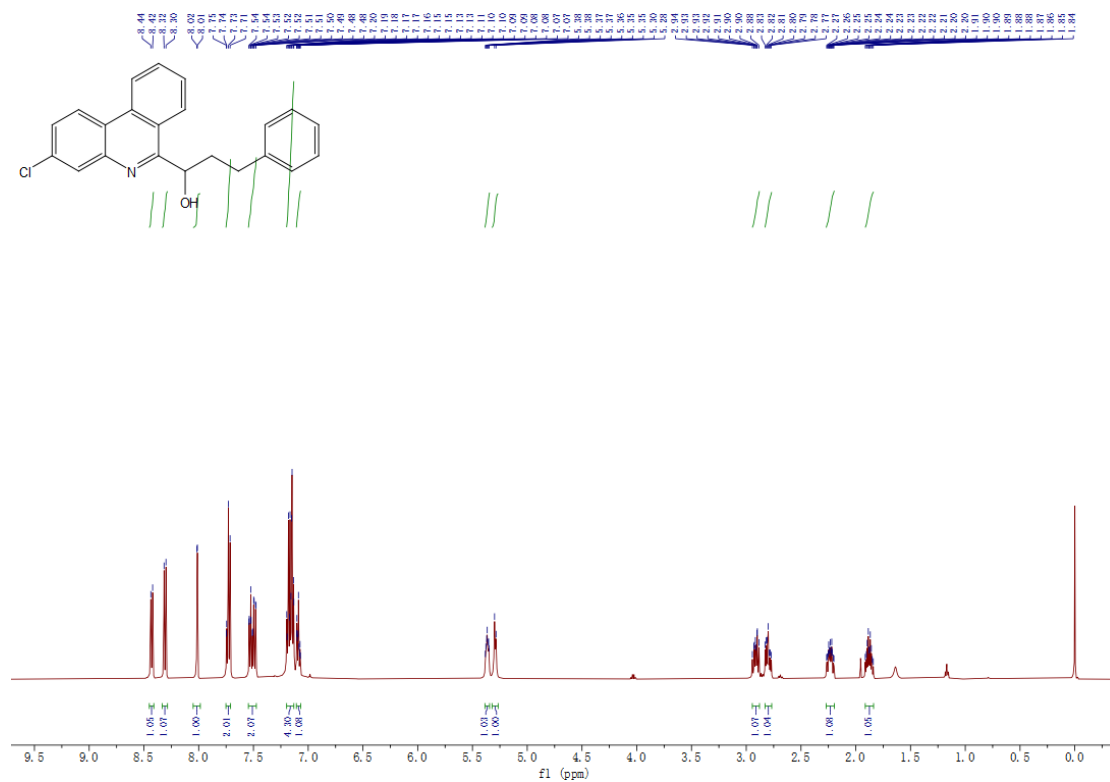
<sup>1</sup>H NMR of compound **3ka**



<sup>13</sup>C NMR of compound **3ka**

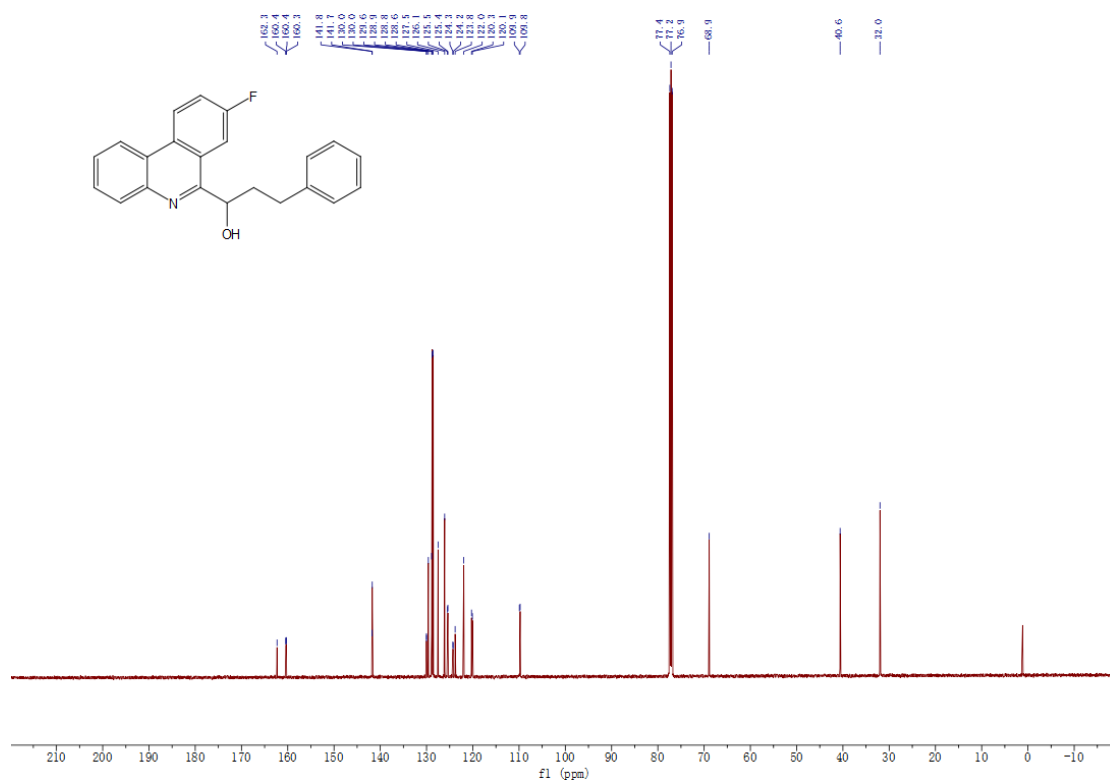


$^{19}\text{F}$  NMR of compound **3ka**

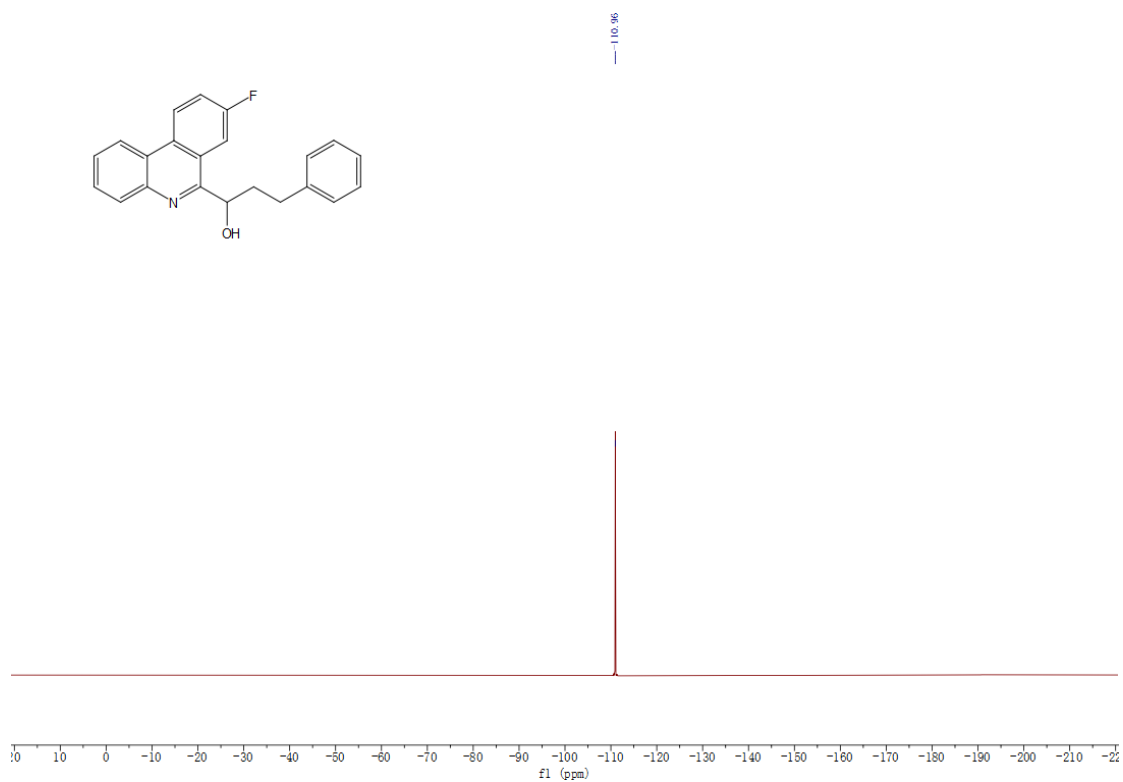


$^1\text{H}$  NMR of compound **3la**

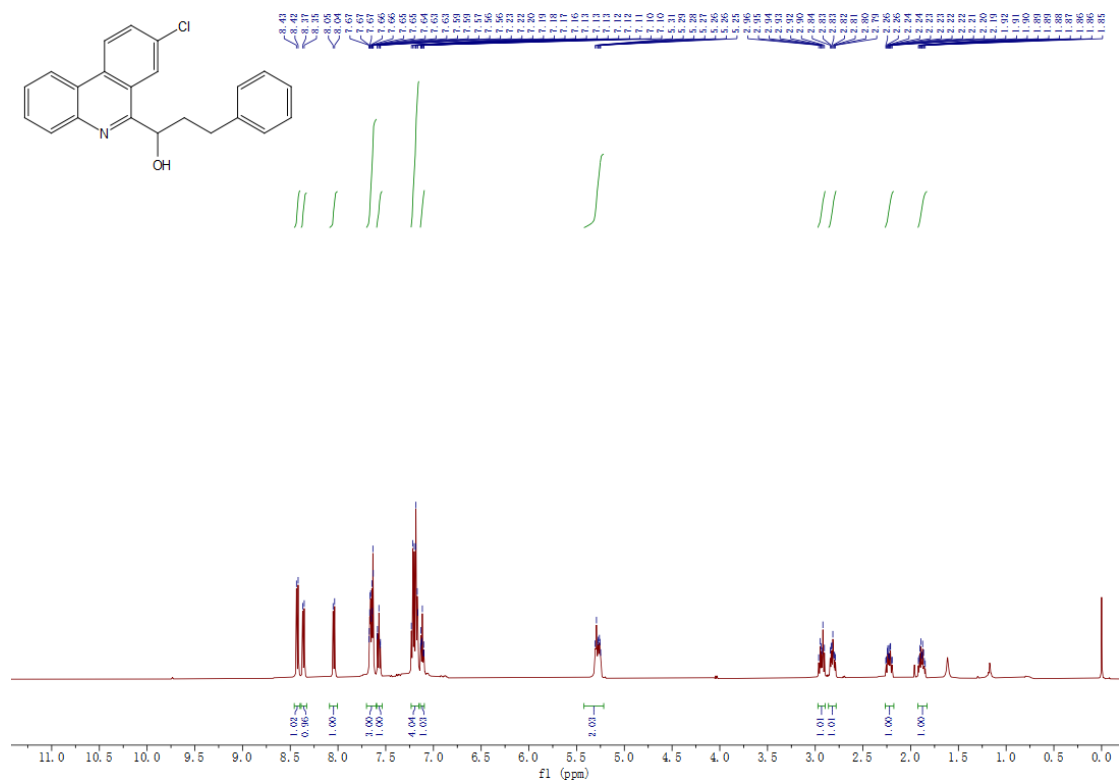




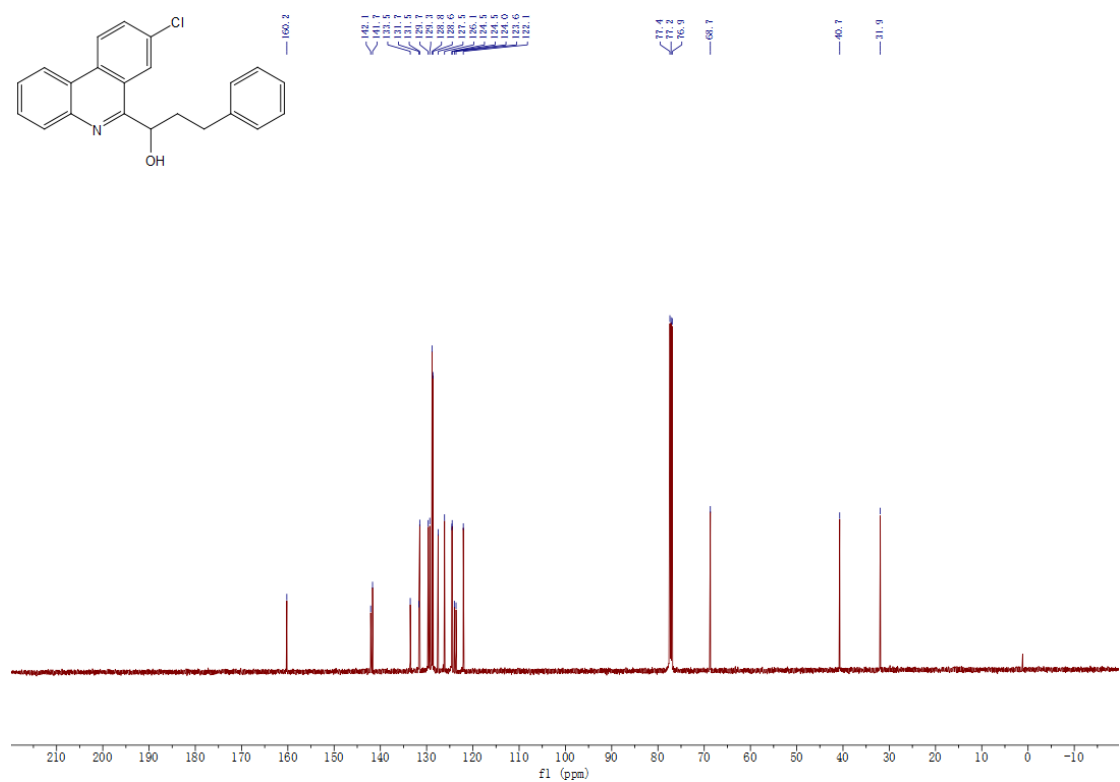
<sup>13</sup>C NMR of compound **3ma**



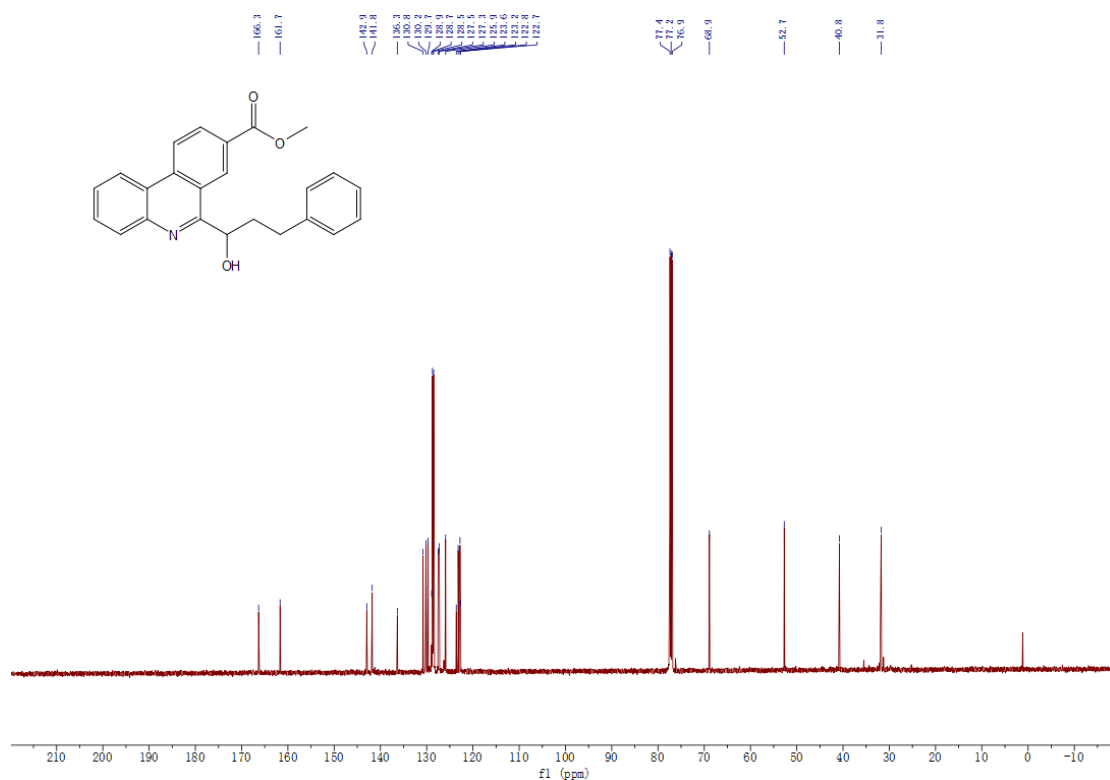
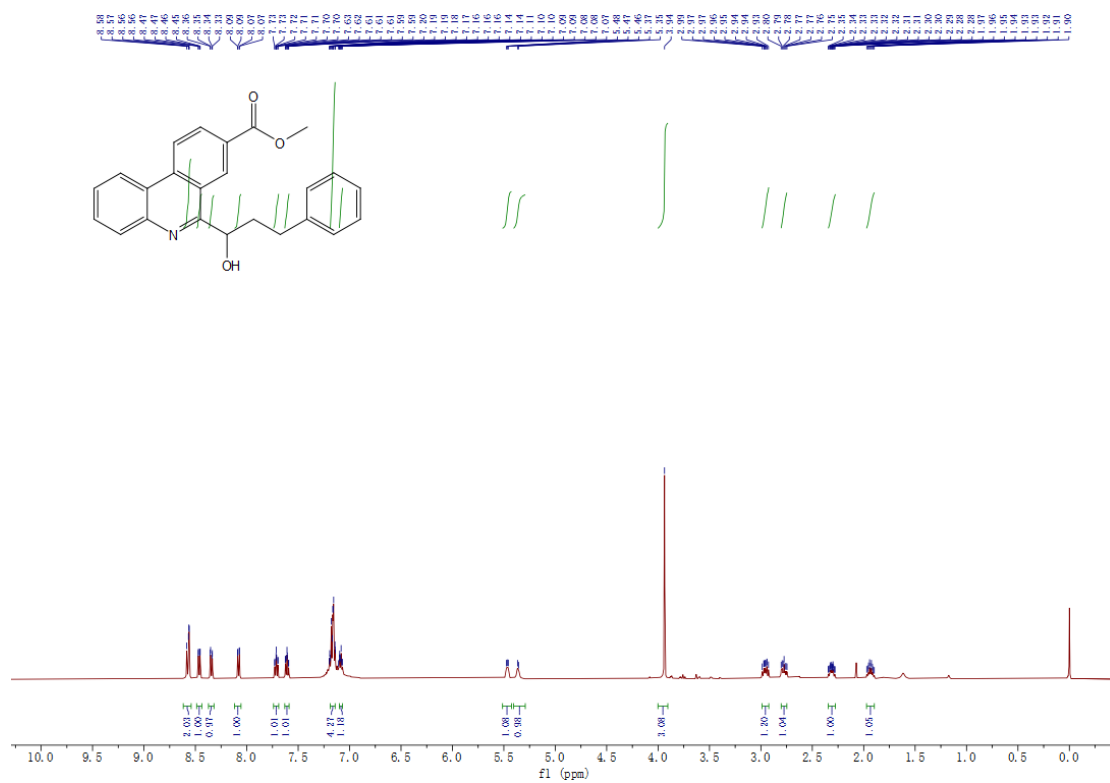
<sup>19</sup>F NMR of compound **3ma**



<sup>1</sup>H NMR of compound 3na



<sup>13</sup>C NMR of compound 3na

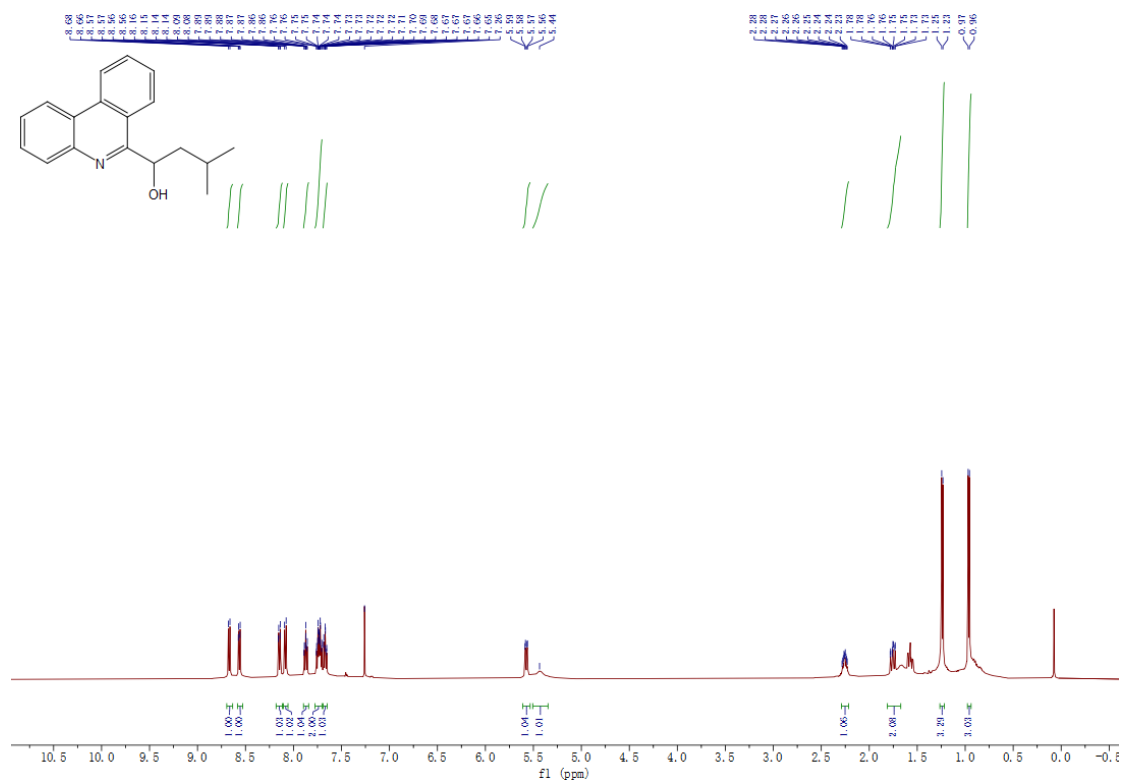




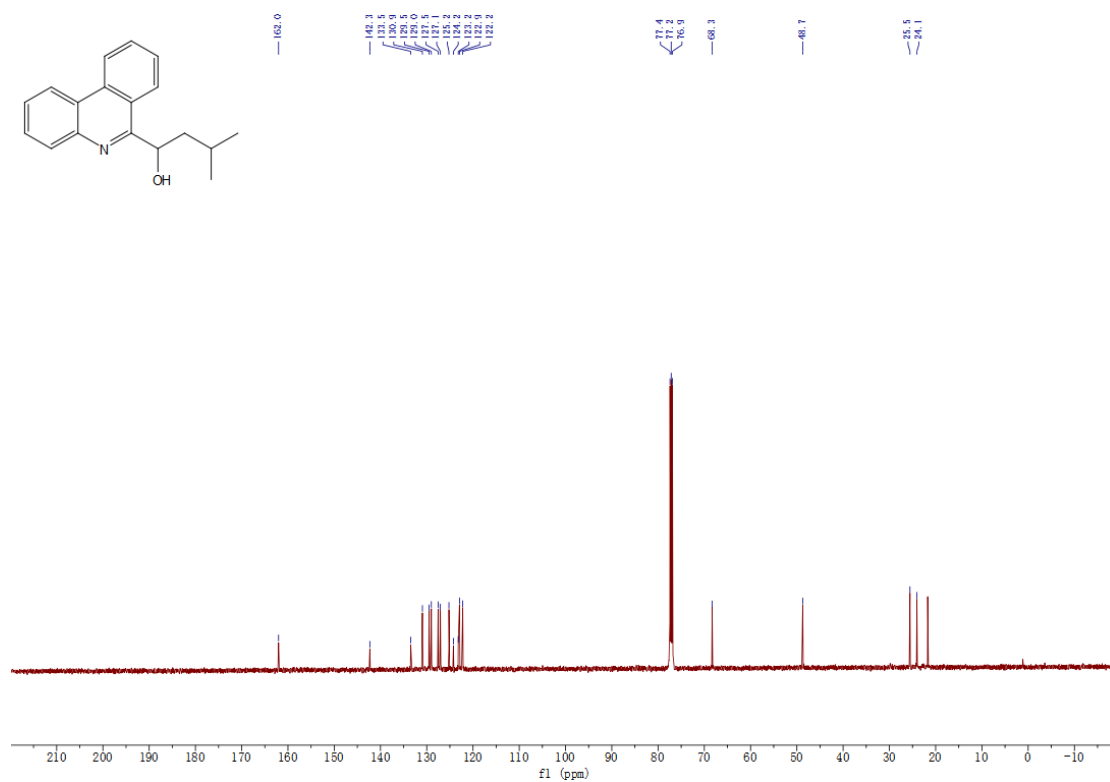








**<sup>1</sup>H NMR of compound 3ac**



**<sup>13</sup>C NMR of compound 3ac**





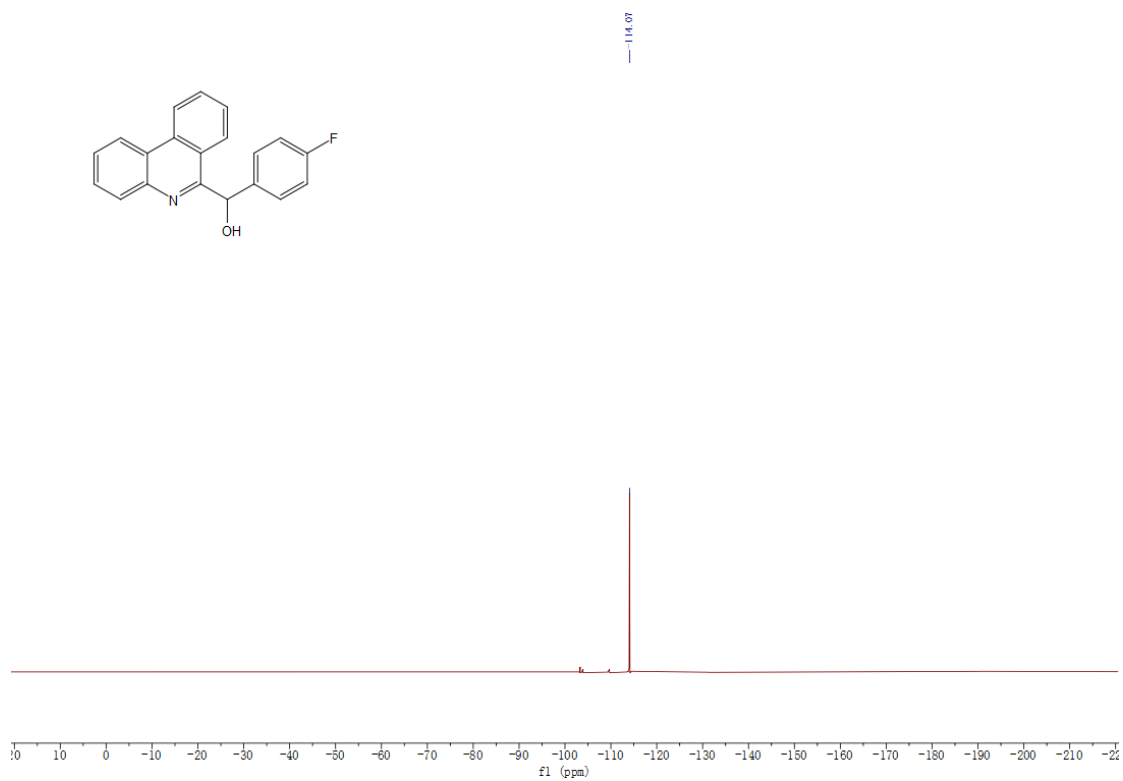




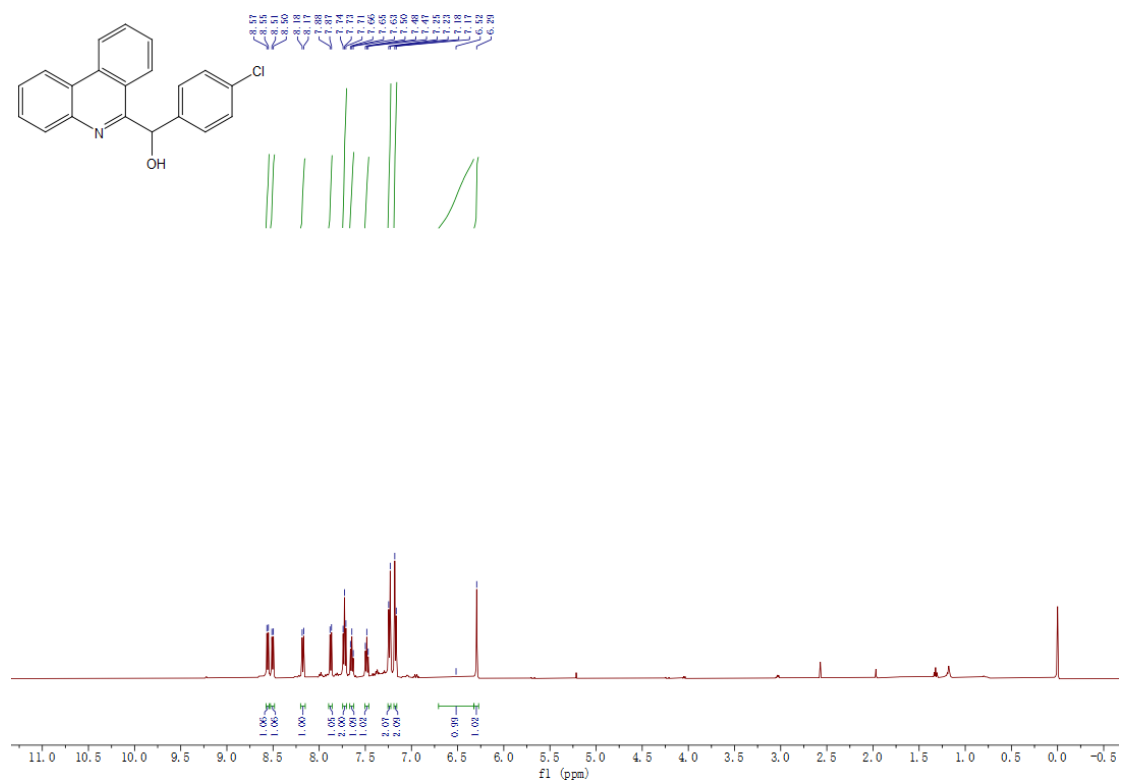








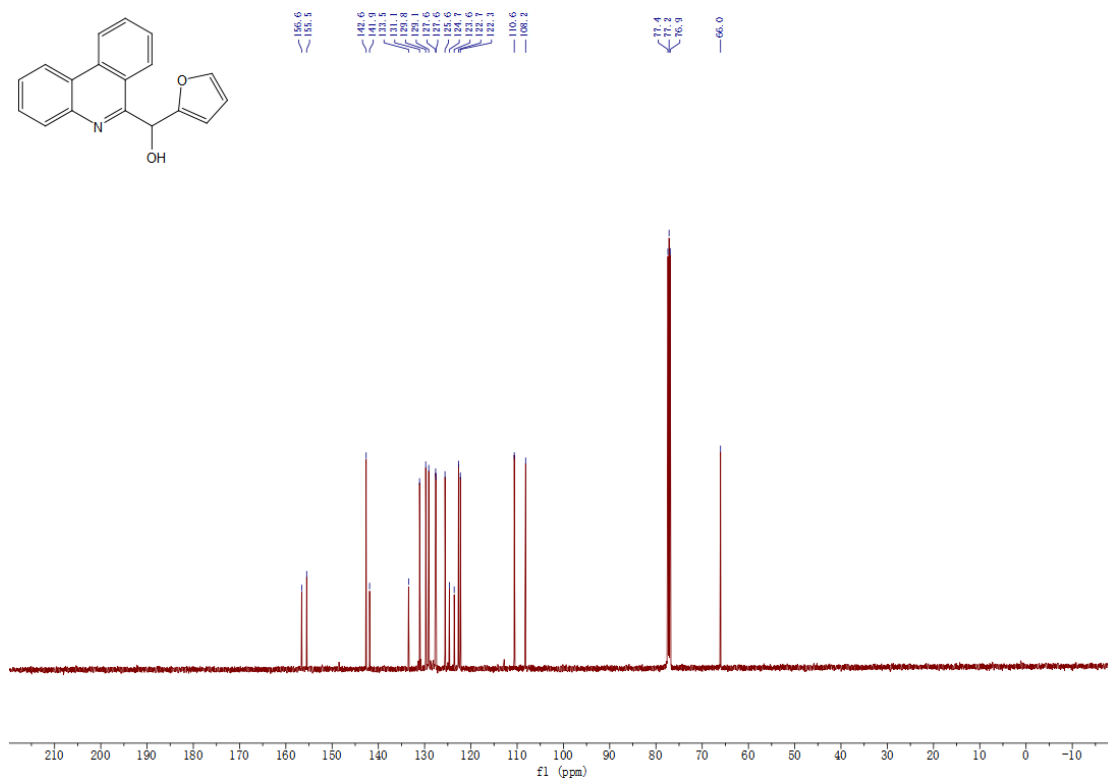
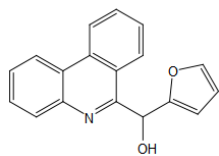
<sup>19</sup>F NMR of compound **3ai**



<sup>1</sup>H NMR of compound **3aj**







$^{13}\text{C}$  NMR of compound **3al**