Supporting Information

Selective C(sp^3)–H activation of simple alkanes: visible light-induced metal-free synthesis of phenanthridines with H_2O_2 as sustainable oxidants

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1. General Information

Materials and methods:

Isocyanides were prepared according to published literature procedures.[1] Other chemicals were used as received from commercial sources without special purification. CH_3CN used for reaction was distilled. Purple LED blocky lights (30 W, 395 nm) were purchased from Taiwan Epileds Technologies and assembled by Shenzhen Xinxingyuan Photoelectric Technology. Reactions were performed with rigorous exclusion of air. The reaction temperature was controlled using water baths. Reactions were monitored by thin-layer chromatography (TLC) on 2.5×5 cm HSGF254 plates. Chromatographic purification of products was accomplished by column chromatography using silica gel. Yield was determined by ^{1}H-NMR based on an internal standard of dibromomethane.

Instrumentation

^{1}H and ^{13}C NMR spectra were recorded at ambient temperature on Bruker Avance II 400 or Bruker Avance III 500 MHz instruments. NMR experiments are reported in δ units, parts per million (ppm), and were referenced to $CDCl_3$ (δ 7.26 or 77.0 ppm) as the internal standard. The multiplicity was described by s (singlet), d (doublet), t (triplet), q (quintet) and m (multiplet). The coupling constants *J* are given in Hz. ^{13}C NMR δ 29.6 was attributed to grease; ^{1}H NMR δ 1.25ppm, 0.80 ppm, and ^{13}C NMR δ 14.08, 22.64, 31.88 were attributed to high boiling component from n-hexane; ^{1}H NMR δ 1.56ppm was attributed to water from the wet air in Dalian (H.E. Gottlieb, *et al.*, *J. Org. Chem.* **62**, 7512-7515 (1997)). High-resolution mass spectra were obtained using an LCMS-IT/TOF (Shimadzu. Japan) Mass Spectrometer with electrospray ionization (ESI) probe operating in positive ion mode. Uv-vis spectra were measured on a HP 8453 spectrometer. The fluorescence spectra were measured with Edinburgh Analytical Instruments FLS 920.

General procedure:

A 10mL quartz photoreaction tube was charged with 2-phenyl phenyl isocyanide (0.15 mmol), cyclohexane (1.5 mmol), 2,4,5,6-Tetra-9H-carbazol-9-yl-1,3-benzenedicarbonitrile (4CzIPN, 1 mol%), *N,N*-Diisopropylethylamine (0.015 mmol), H_2O_2 (0.45 mmol) and CH_3CN (1.5 mL). The reaction tube was capped with a greased two-way septum cock. The resulting mixture was then cooled to -78 °C, degassed and backfilled with N_2 five times. The tube was placed ~2 cm away from a 30 W 395 nm LED light with circulating water to keep the reaction at room temperature and kept stirring for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

General Procedure for Phenanthridinylation of Gaseous Alkanes.

A 10mL quartz photoreaction tube was charged with 2-phenyl phenyl isocyanide (0.15 mmol), 4CzIPN (1 mol%), *N,N*-Diisopropylethylamine (0.015 mmol), H_2O_2 (0.45 mmol) and CH_3CN (1.5 mL). The reaction tube was sealed with a greased three-way septum cock. The reaction mixture was degassed by gaseous alkane for five times and kept at ambient pressure all the time. The tube was placed ~2 cm away from a 30 W 395 nm LED light with circulating water to keep the reaction at room temperature and kept stirring for 48 h. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give the desired product.

Gram-scale synthesis

A 100 mL quartz photoreaction tube was charged with 2-phenyl phenyl isocyanide (5.6 mmol, 1 g), cyclohexane (56 mmol, 6.03 mL), 4CzIPN (1 mol%, 55.8 mg), *N*,*N*-Diisopropylethylamine (0.56 mmol, 1.84 mL), H_2O_2 (16.8 mmol, 1.79 mL) and CH_3CN (56 mL). The resulting mixture was then cooled to -78 °C, degassed and backfilled with N_2 five times. The tube was placed ~5 cm away from six 30 W 395 nm LED lights and kept stirring for 108 h. As shown in Figure S1, six LED lights

were circled for irradiating the reaction. For maintaining the room temperature, the rubber tube was immersed in the water and connected to the circulating condensing pump. After completion of the reaction (monitored by TLC), the mixture was concentrated in vacuum and the residue was purified by column chromatography on silica gel with petroleum ether-ethyl acetate of 50:1 as eluent to give 1.24 g the desired product.

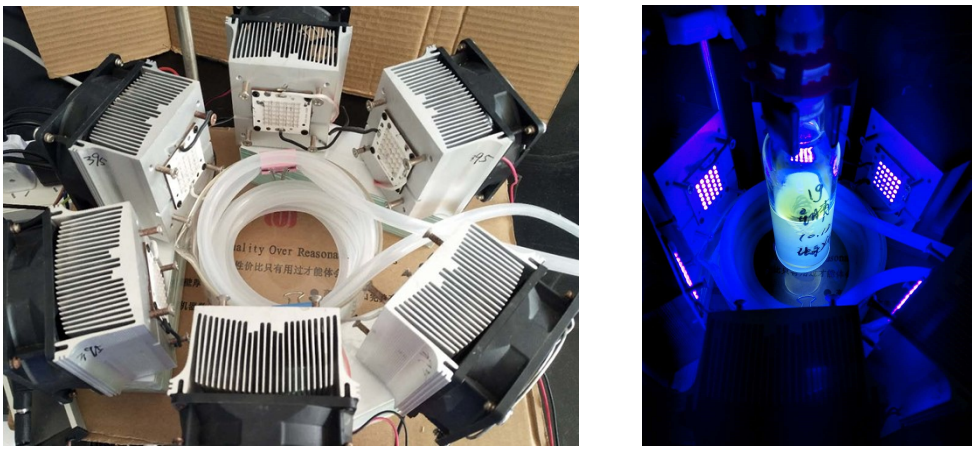


Figure S1. The reactive installation of gram-scale synthesis.

2. Free radical capture experiments

A 10 mL quartz photoreaction tube was charged with 2-phenyl phenyl isocyanide (0.1 mmol), cyclohexane (1 mmol), 4CzIPN (1 mol%), *N*, *N*-Diisopropylethylamine (0.01 mmol), H_2O_2 (0.3 mmol), TEMPO (0.3 mmol) and CH_3CN (1 mL). The resulting mixture was then cooled to -78 °C, degassed and backfilled with N_2 five times. The tube was placed ~2 cm away from a 30 W 395 nm LED light and kept stirring for 10 h. The product of **3a** was not detected and 1-(cyclohexyloxy)-2,2,6,6-tetramethylpiperidine was confirmed by GC-MS and HRMS (Figure S2-S4).

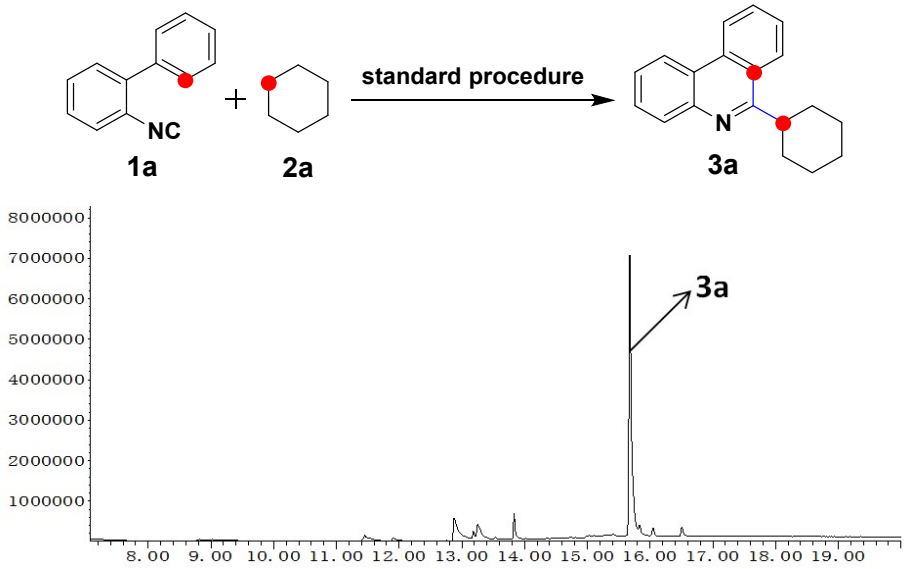


Figure S2 GC-MS date of the standard reaction (residual time of **3a**: 15.689 min).

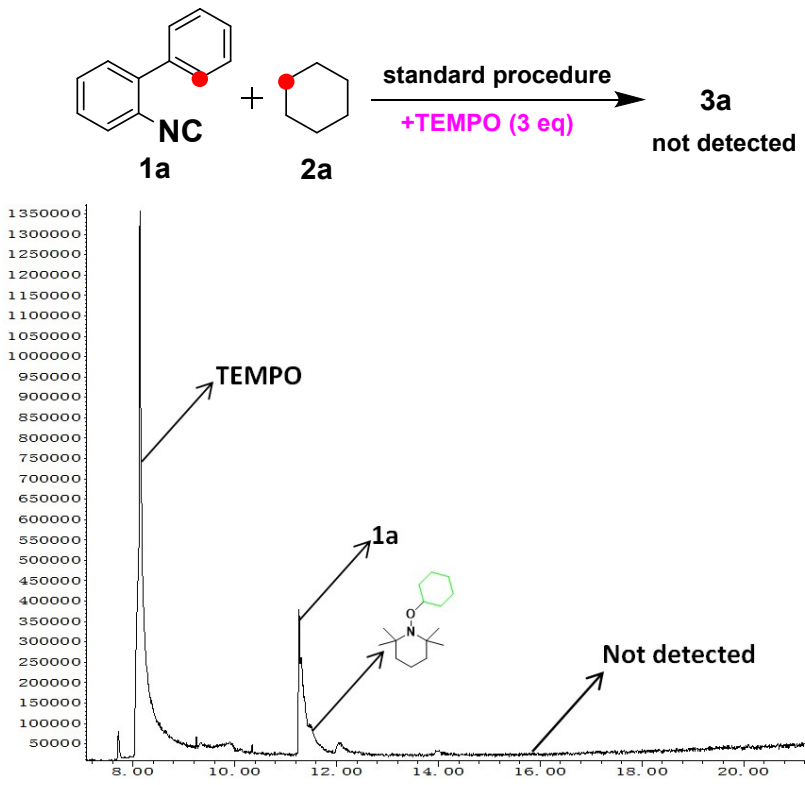


Figure S3 GC-MS date of free radical capture results, **3a** was not detected.

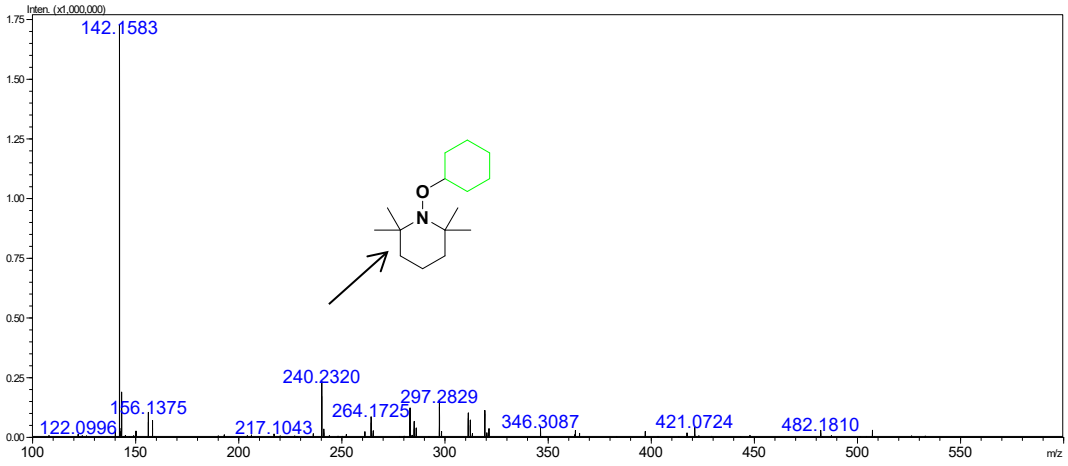
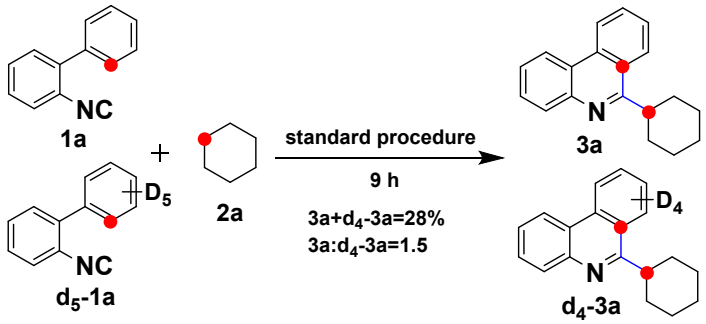


Figure S4 HRMS spectra of free radical capture results

3. KIE studies of isocyanide and cyclohexane

In a sealed tube, the mixture of **1a** (0.1 mmol) and **d_5-1a** (0.1 mmol) was treated by standard procedures and irradiated for 9 h. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3a** and **d_4-3a**. The mixture was analyzed using ^{1}H NMR spectrometer with dibromomethane as the internal standard. As shown in Figure S5, the ratio of **3a** and **d_4-3a** is nearly 1.5:1.



Scheme S1 KIE experiment of **1a** and **d_5-1a**

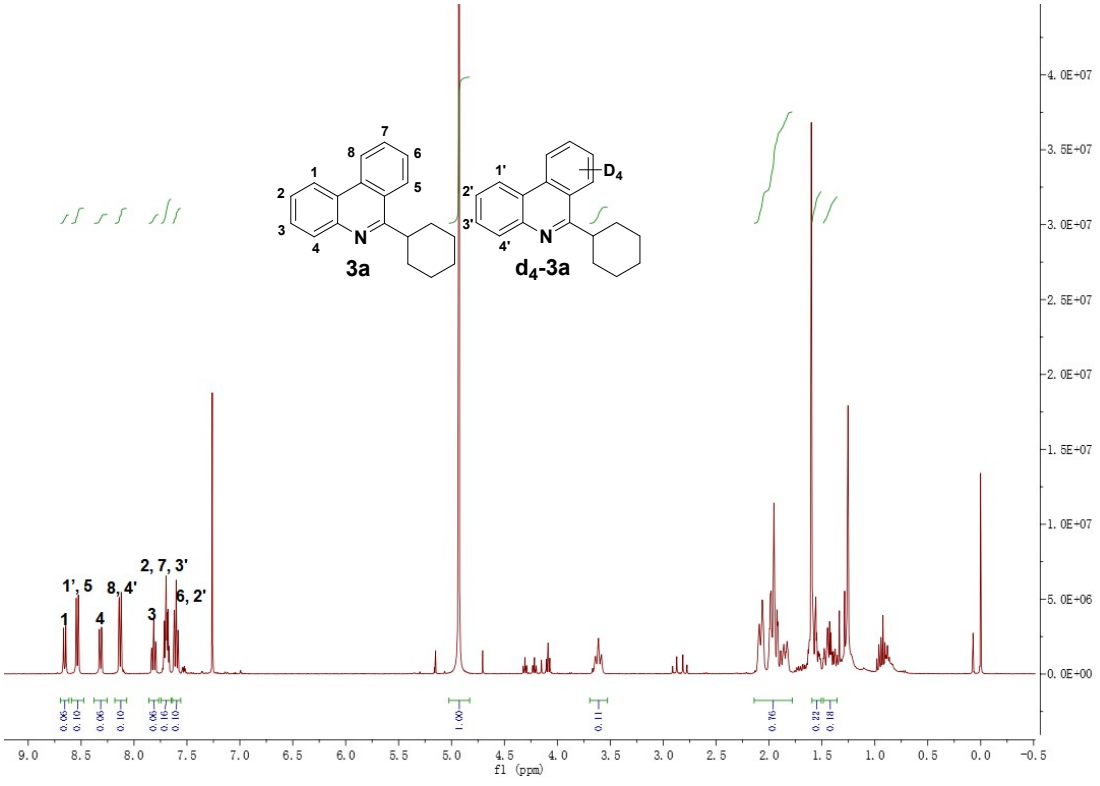
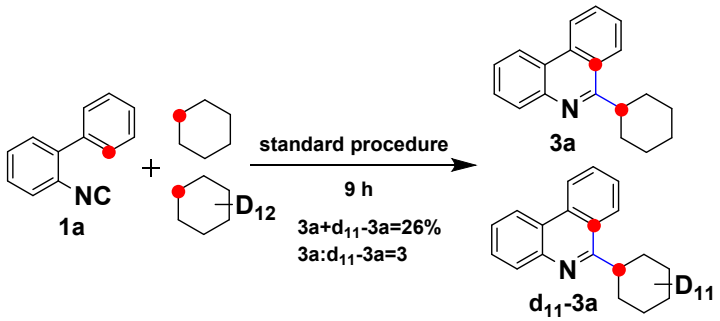


Figure S5 The ^{1}H NMR spectrum of the KIE results with **3a** and **d_4-3a**

In a sealed tube, the mixture of **1a** (0.1 mmol), **cyclohexane/d_{12}-cyclohexane**

(1:1, 2 mmol) was treated by standard condition for 9 h. The mixture was concentrated in vacuum and the residue was purified by flash column chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3a** and **d_{11}-3a**. The mixture was analyzed using ^{1}H NMR spectrometer with dibromomethane as the internal standard. As shown in Figure S6, the ratio of **3a** and **d_{11}-3a** is nearly 3.



Scheme S2 KIE experiment of **cyclohexane** and **d_{12}-cyclohexane**

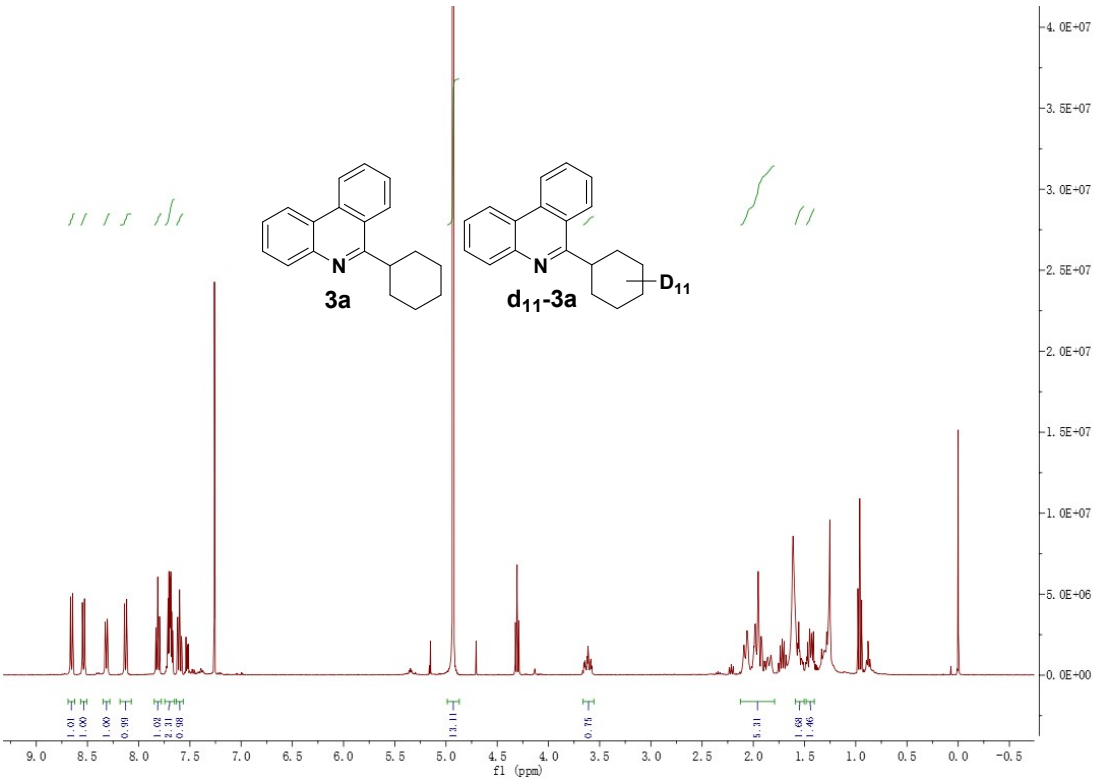
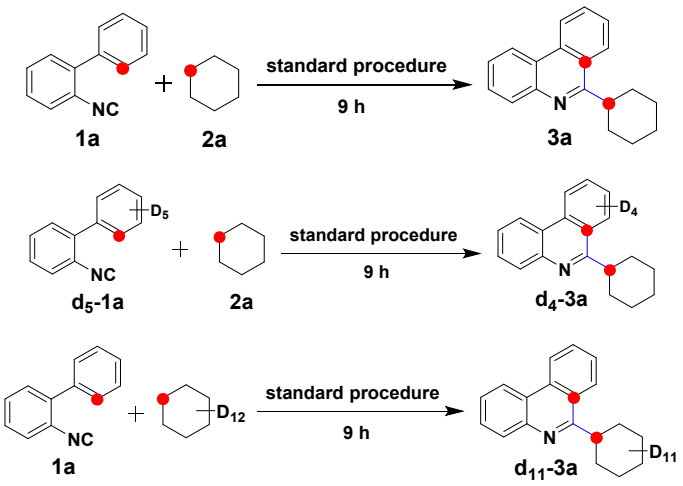


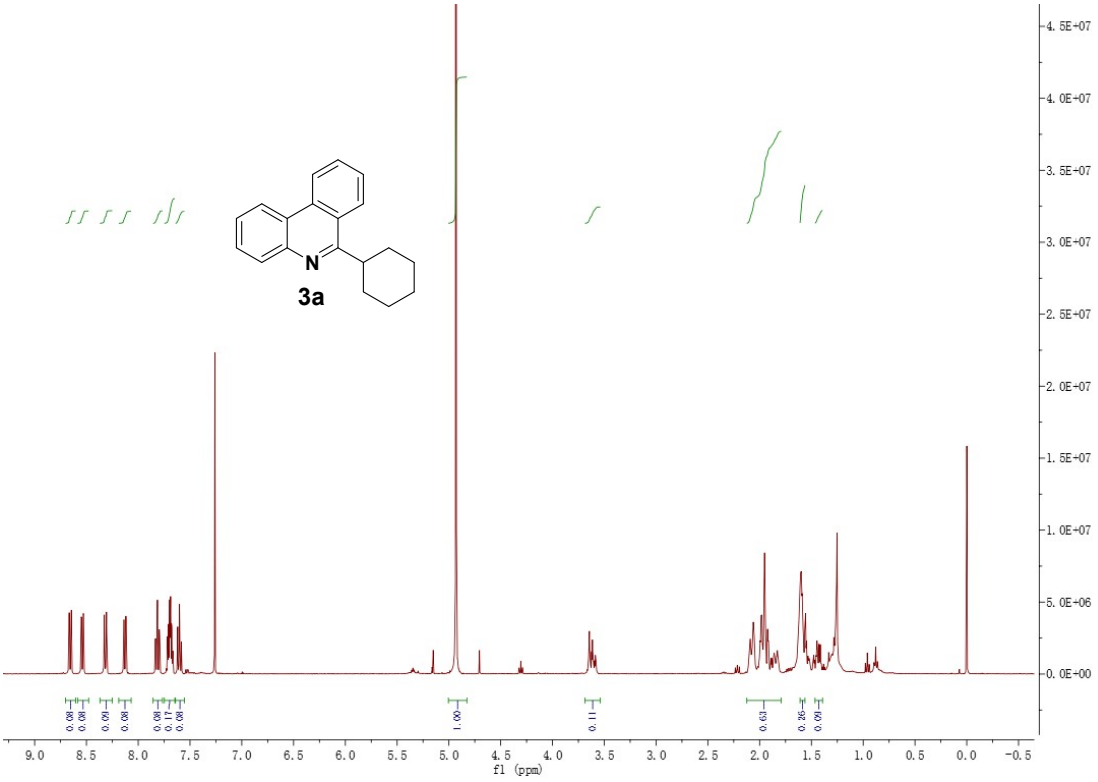
Figure S6 The ^{1}H NMR spectrum of the KIE results with **3a** and **d_{11}-3a**

In three sealed tubes, **1a** (0.1 mmol)/**cyclohexane** (1 mmol), **d_5-1a** (0.1 mmol)/**cyclohexane** (1 mmol) and **1a** (0.1 mmol)/**d_{12}-cyclohexane** (1 mmol) were respectively treated by standard procedures and irradiated for 9 h. These mixtures were concentrated in vacuum and the residue was purified by flash column

chromatography on silica gel with petroleum ether-ethyl acetate as eluent to give product **3a**, **d_4-3a** and **d_{11}-3a**. As shown in Figure S7, the yields were analyzed using ^{1}H NMR spectrometer with CH_2Br_2 as the internal standard. the ratio of **3a** and **d_4-3a** is nearly 1.0 while **3a** and **d_{11}-3a** is nearly 1.9.



Scheme S3 KIE experiments of isocyanide and cyclohexane



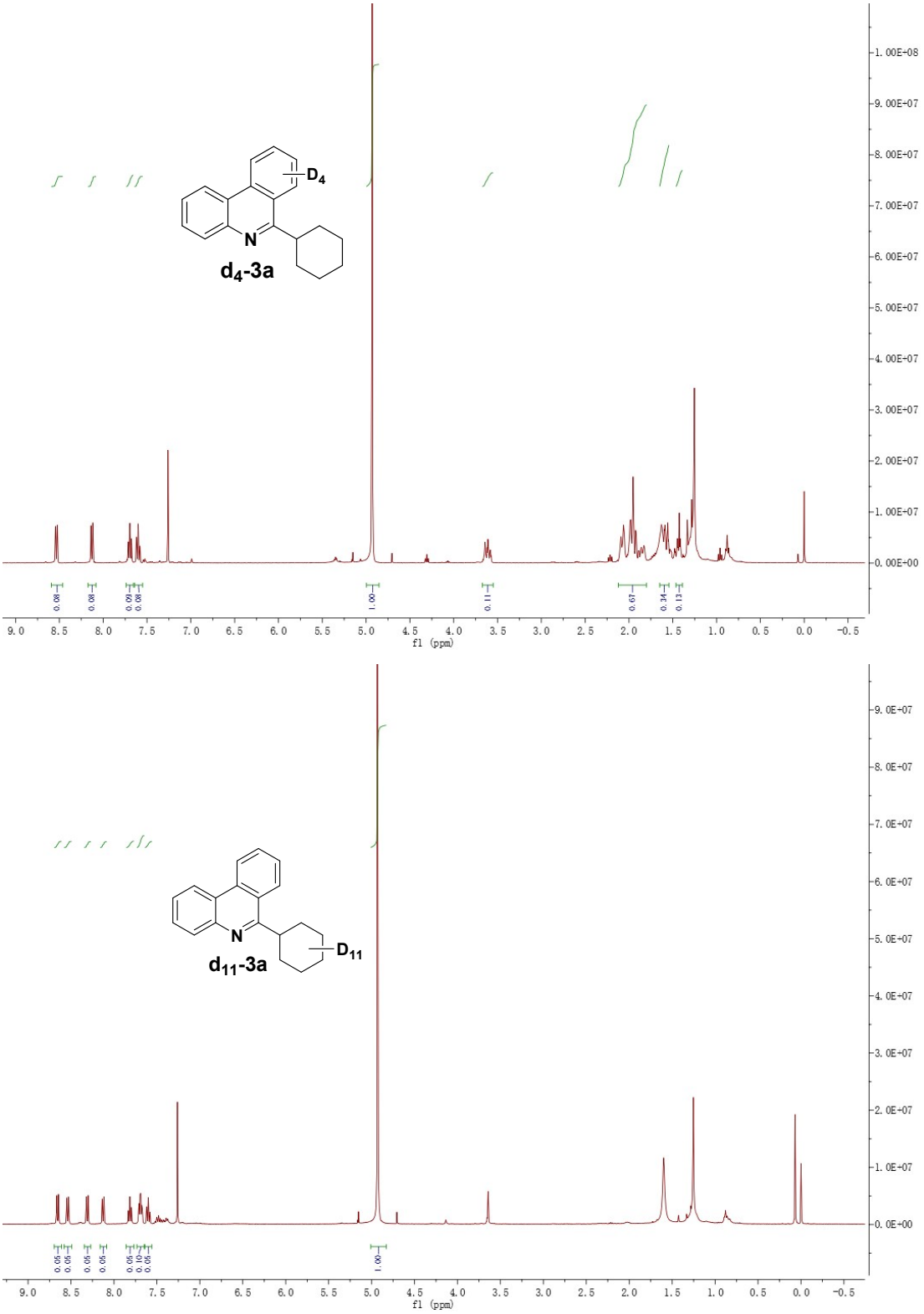


Figure S7 The ^{1}H NMR spectra of the KIE results of **3a, d_4-3a** and **d_{11}-3a**.

4. Determination of light intensity

Determination of the light intensity at 405 nm:

The photon flux was determined by standard ferrioxalate actinometry. [2][3] A 0.006 M solution of ferrioxalate was prepared by dissolving 88.4 mg of potassium ferrioxalate hydrate in 30 mL of 0.05 M H_2SO_4. A buffered solution of phenanthroline was prepared by dissolving 50 mg of phenanthroline and 11.25 g of sodium acetate in 50 mL of 0.5 M H_2SO_4. Both solutions were stored in the dark. To determine the photon flux, 2.0 mL of the ferrioxalate solution was placed in a sealed tube and irradiated for 30.0 seconds with a commercial 405 nm laser. After irradiation, 0.35 mL of the phenanthroline solution was added to the tube. The solution was then allowed to rest for 1 h to allow the ferrous ions to completely coordinate to the phenanthroline. The absorbance of the solution was measured at 510 nm. A non-irradiated sample was also prepared and the absorbance at 510 nm measured. Conversion was calculated using eq 1.

$$\text{mol Fe}^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} \quad (1)$$

Where V is the total volume (0.00235 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions, l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L $mol^{-1}cm^{-1}$). [1] The photon flux can be calculated using eq 2.

$$\text{photon flux} = \frac{\text{mol Fe}^{2+}}{\Phi \cdot t \cdot f} \quad (2)$$

Where Φ is the quantum yield for the ferrioxalate actinometer (1.13 for a 0.006 M solution at λ =405 nm), [1] t is the time (30.0 s), and f is the fraction of light absorbed at λ = 405 nm (0.92607, *vide infra*). The photon flux was calculated to be 4.52×10^{-9} einstein s^{-1}.

Sample calculation:

$$\text{mol Fe}^{2+} = \frac{0.00235\,\text{L}\cdot 0.6721}{1.000\,\text{cm}\cdot 11100\,\text{L mol}^{-1}\,\text{cm}^{-1}} = 1.42\times10^{-7}\ \text{mol}$$

$$\text{photon flux} = \frac{1.42\times10^{-7}\ \text{mol}}{1.13\cdot 30\,\text{s}\cdot 0.92607} = 4.52\times10^{-9}\ \text{einstein s}^{-1}$$

Determination of fraction of light absorbed at 405 nm for the ferrioxalate solution:

The absorbance of the above ferrioxalate solution and 4CzIPN solution at 405 nm was measured to be 1.13115 and 3.67815 (Figure S8 and S9). The fraction of light absorbed (f) by the solution was calculated using eq 3, where A is the measured absorbance at 405 nm.

$$f = 1 - 10^{-A} \qquad (3)$$

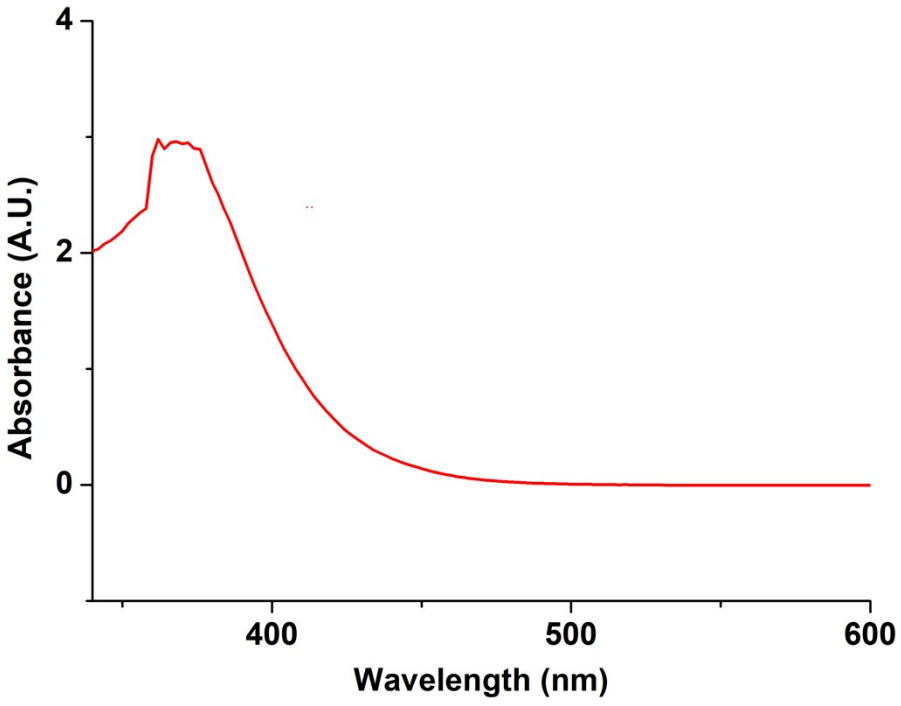


Figure S8 Absorbance of the ferrioxalate actinometer solution.

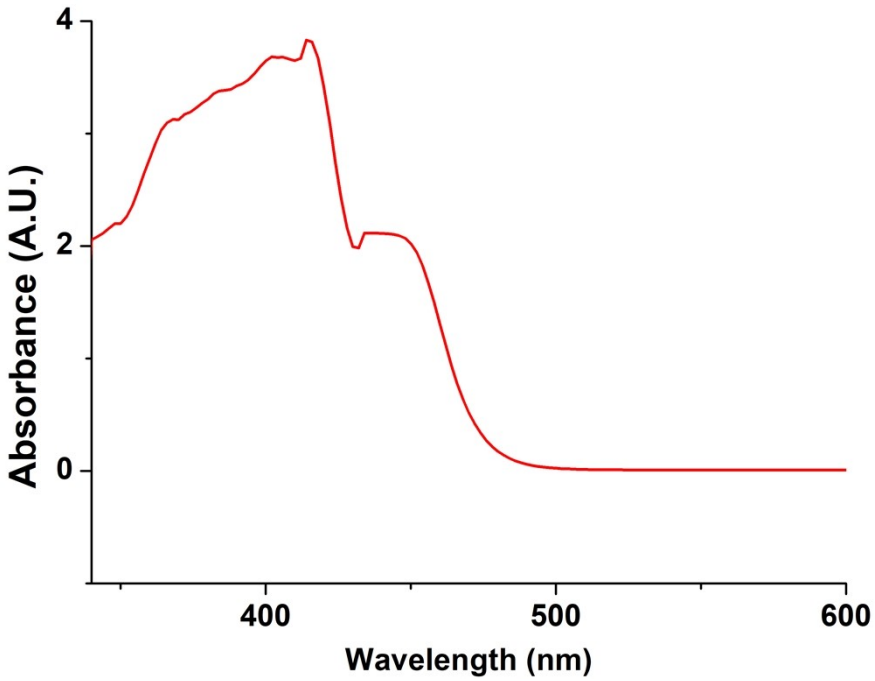
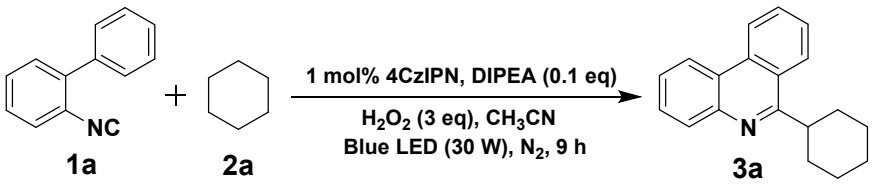


Figure S9 Absorbance of 4CzIPN solution (1% in CH_3CN).

5. Determination of quantum yield



A 10 mL quartz photoreaction tube was charged with isocyanide (0.1 mmol, 1 equiv.), cyclohexane (1 mmol, 10 equiv.), 4CzIPN (0.0013 mmol, 1 mol%), DIPEA (0.01 mmol, 0.1 equiv.), H_2O_2 (0.3 mmol, 3 equiv.) and 1.0 mL CH_3CN (0.1 M) under nitrogen atmosphere. The tube was placed ~2 cm away from 405 nm laser and kept stirring for 32400 s (9 h). After irradiation, the product was purified by column chromatography on silica gel. The yield was determined by ^1H NMR based on a dibromomethane standard. The quantum yield was determined using eq 4.

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot \text{t} \cdot \text{f}} \tag{4}$$

18 mg (0.1 mmol) isocyanide, 108 μL (1 mmol) cyclohexane, 1 mg (0.0013 mmol) 4CzIPN, 1.7 μL (0.01 mmol) DIPEA, 32 μL (0.3 mmol) H_2O_2, 1.0 mL (0.1 M) CH_3CN after 32400 s yielded 4.8% of **3a**. Φ(4.8%) = 0.033.

Sample quantum yield calculation:

$$\Phi = \frac{4.8 \times 10^{-6}\ \text{mol}}{4.52 \times 10^{-9}\ \text{einstein s}^{-1} \cdot 32400\ \text{s} \cdot 1} = 0.033$$

6. Fluorescence quenching of 4CzIPN

The collection of emission spectra (λ_{ex} = 405nm) for the fluorescence quenching measurements were carried out at room temperature in air using quartz cuvettes. The concentration of 4CzIPN in CH_3CN was 1.0×10^{-4} M. The solutions of DIPEA, H_2O_2 and cyclohexane (1 M in CH_3CN) were prepared and used as quenchers.

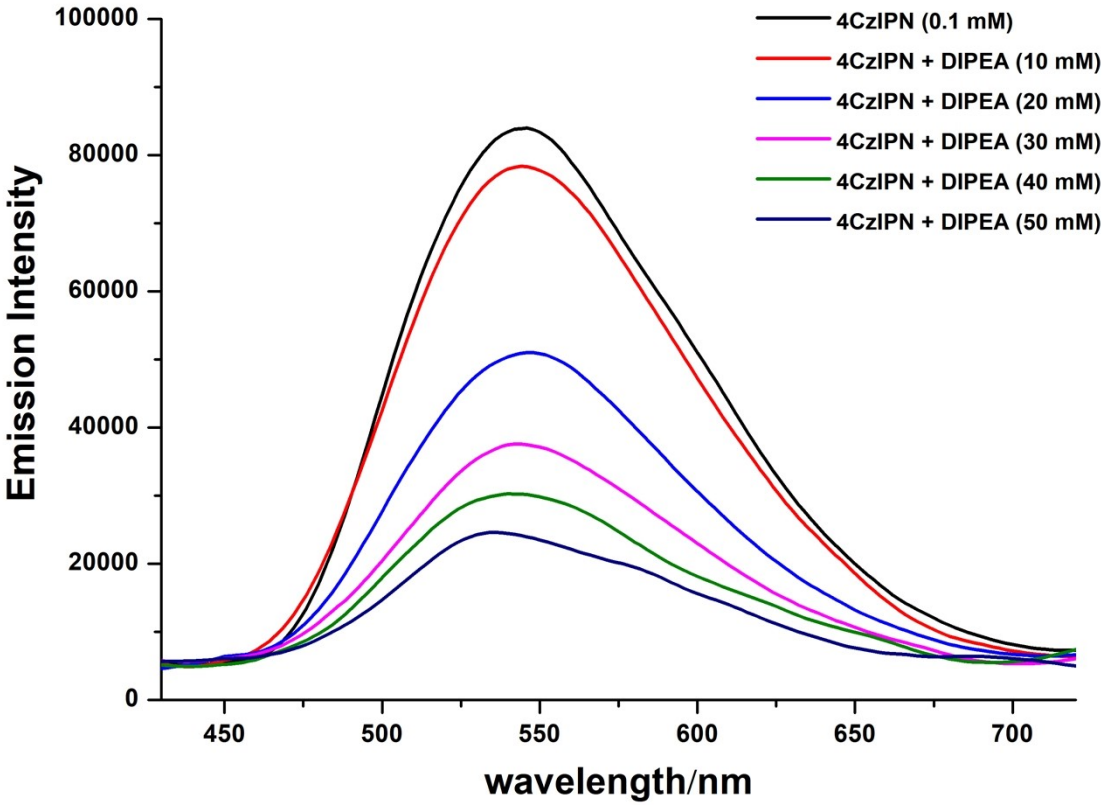


Figure S10 Fluorescence quenching spectra of 4CzIPN with DIPEA, λ_{ex} = 405 nm. Obvious quenching was observed.

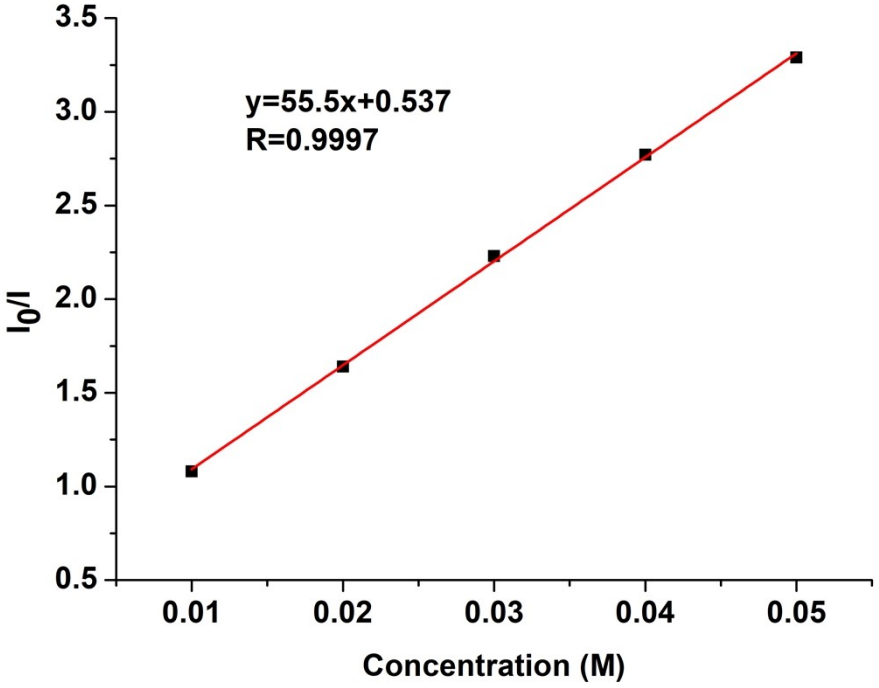


Figure S11 The corresponding Stern–Volmer curve for the fluorescence quenching of 4CzIPN, λ_{em} = 548 nm.

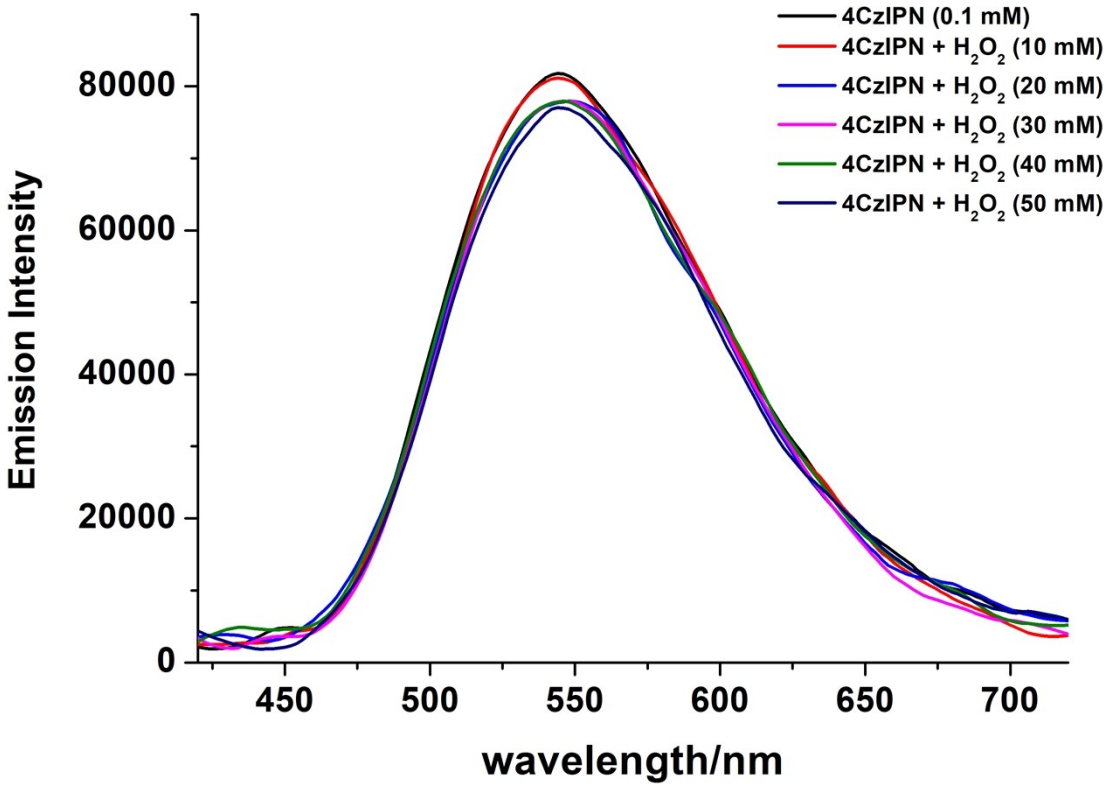


Figure S12 Fluorescence quenching spectra of 4CzIPN with H_2O_2, λ_{ex} = 405 nm. No obvious quenching was observed.

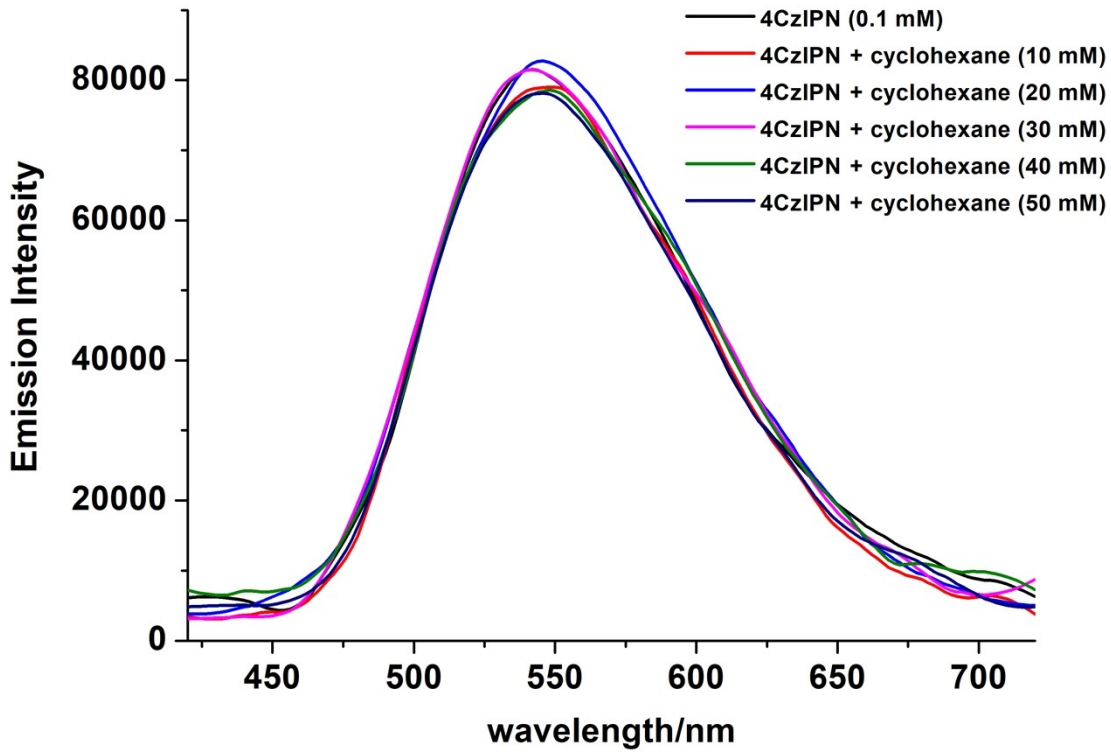
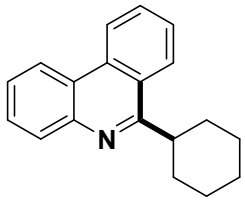


Figure S13 Fluorescence quenching spectra of 4CzIPN with cyclohexane, λex = 405 nm. No obvious quenching was observed.

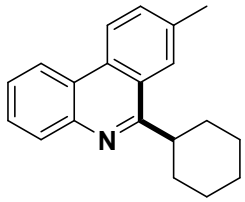
7. Characterization data for the products

6-cyclohexylphenanthridine (3a)



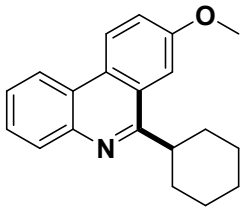
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3a** (34.9 mg, 89% yield) as yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.4 Hz, 1H), 8.54 (d, *J* = 8.0 Hz, 1H), 8.32 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.87-7.76 (m, 1H), 7.76-7.65 (m, 2H), 7.64-7.55 (m, 1H), 3.74-3.53 (m, 1H), 2.19-1.80 (m, 7H), 1.68-1.52 (m, 2H), 1.52-1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.23, 143.82, 132.94, 129.87, 129.85, 128.32, 127.00, 126.06, 125.55, 124.66, 123.28, 122.51, 121.76, 41.93, 32.25, 26.83, 26.28.
HRMS (ESI, m/z): Calculated for $C_{19}H_{20}N$ $[M+H]^+$ 262.1590, found 262.1587

6-cyclohexyl-8-methylphenanthridine (3b)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3b** (35.9 mg, 87% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57-8.45 (m, 2H), 8.13 (d, *J* = 6.8 Hz, 1H), 8.07 (s, 1H), 7.72-7.53 (m, 3H), 3.68-3.51 (m, 1H), 2.63 (s, 3H), 2.14-1.81 (m, 7H), 1.68-1.53 (m, 2H), 1.52-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.96, 143.54, 136.83, 131.57, 130.81, 129.82, 127.87, 125.98, 125.02, 124.83, 123.39, 122.45, 121.59, 41.79, 32.26, 26.86, 26.31, 21.95.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1744

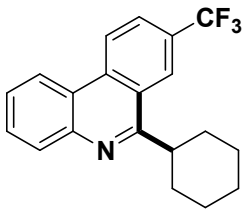
6-cyclohexyl-8-methoxyphenanthridine (3c)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3c** (36.2 mg, 83% yield) as yellow solid.

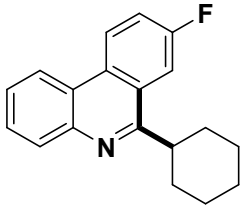
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 9.2 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 7.69-7.52 (m, 3H), 7.44 (dd, *J* = 9.2, 2.4 Hz, 1H), 4.00 (s, 3H), 3.59-3.45 (m, 1H), 2.18-1.79 (m, 7H), 1.65-1.51 (m, 2H), 1.50-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.35, 158.48, 142.98, 129.83, 127.37, 127.26, 126.16, 125.97, 124.22, 123.38, 121.28, 119.63, 106.55, 55.49, 42.11, 32.10, 26.86, 26.29.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}NO$ $[M+H]^+$ 292.1696, found 292.1693

6-cyclohexyl-8-(trifluoromethyl)phenanthridine (3d)



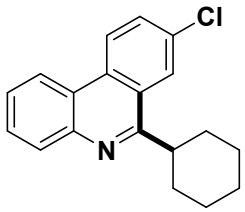
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3d** (44.4 mg, 90% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.8 Hz, 1H), 8.63-8.44 (m, 2H), 8.17 (d, *J* = 8.4, 1H), 7.99 (d, *J* = 8.8, 1H), 7.85-7.71 (m, 1H), 7.69-7.56 (m, 1H), 3.71-3.47 (m, 1H), 2.20-1.79 (m, 7H), 1.72-1.51 (m, 2H), 1.50-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.06, 144.49, 135.21, 130.12, 129.55, 128.77 (q J_{CF} = 32.5 Hz), 126.66, 125.71 (q J_{CF} = 3.1 Hz), 124.16 (q J_{CF} = 270.6 Hz), 123.97, 123.64, 122.92 (q J_{CF} = 4.3 Hz), 122.32, 122.14, 41.89, 32.32, 26.68, 26.19.
HRMS (ESI, m/z): Calculated for $C_{20}H_{19}F_3N$ $[M+H]^+$ 330.1464, found 330.1462

6-cyclohexyl-8-fluorophenanthridine (3e)



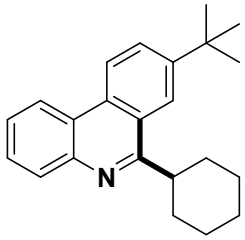
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3e** (34.3 mg, 82% yield) as light yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.59 (m, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 10.4, 1H), 7.73-7.65 (m, 1H), 7.64-7.47 (m, 2H), 3.46 (m, 1H), 2.10-1.79 (m, 7H), 1.65-1.51 (m, 2H), 1.49-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.34, 161.41 (d J_{CF} = 245.7 Hz), 143.47, 130.01, 129.59 (d J_{CF} = 1.8 Hz), 128.22, 126.46, 125.98 (d J_{CF} = 7.8 Hz), 125.01 (d J_{CF} = 8.3 Hz), 122.84, 121.51, 118.94 (d J_{CF} = 23.5 Hz), 110.21 (d J_{CF} = 21.4 Hz), 42.11, 32.13, 26.75, 26.22.
HRMS (ESI, m/z): Calculated for $C_{19}H_{19}FN$ $[M+H]^+$ 280.1496, found 280.1496

6-cyclohexyl-8-chlorophenanthridine (3f)



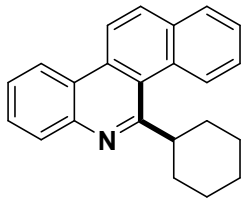
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3f** (37.6 mg, 85% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, *J* = 8.8 Hz, 1H), 8.47 (d, *J* = 8.4 Hz, 1H), 8.25 (d, *J* = 2.0 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.85-7.67 (m, 2H), 7.66-7.56 (m, 1H), 3.60-3.41 (m, 1H), 2.15-1.78 (m, 7H), 1.64-1.52 (m, 2H), 1.49-1.36 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.20, 142.79, 132.06, 130.42, 129.41, 129.05, 127.69, 125.52, 124.70, 123.96, 123.36, 121.69, 120.66, 40.91, 31.23, 25.74, 25.22.
HRMS (ESI, m/z): Calculated for $C_{19}H_{19}ClN$ $[M+H]^+$ 296.1201, found 296.1201

6-cyclohexyl-8-tert-butyl-phenanthridine (3g)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3g** (34.7 mg, 73% yield) as brown solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (d, *J* = 8.8 Hz, 1H), 8.51 (d, *J* = 8.4 Hz, 1H), 8.28 (s, 1H), 8.12 (d, *J* = 8.0 Hz, 1H), 7.90 (d, *J* = 8.4 Hz, 1H), 7.67 (t, *J* = 7.2 Hz, 1H), 7.58 (t, *J* = 8.0 Hz, 1H), 3.69-3.54 (m, 1H), 2.14-1.83 (m, 7H), 1.66-1.54 (m, 3H), 1.49 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.26, 148.88, 142.64, 129.77, 128.80, 127.17, 126.91, 124.98, 123.51, 122.33, 121.35, 120.65, 120.01, 41.17, 34.06, 31.26, 30.32, 25.88, 25.32.
HRMS (ESI, m/z): Calculated for $C_{23}H_{28}N$ $[M+H]^+$ 318.2216, found 318.2213

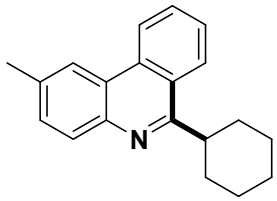
5-cyclohexyl benzo[i]phenanthridine (3h)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3h** (28.5 mg, 61% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.8 Hz, 1H), 8.61-8.50 (m, 2H), 8.18 (d, *J* = 8.4 Hz, 1H), 8.11 (d, *J* = 8.8 Hz, 1H), 8.02 (d, *J* = 7.6 Hz, 1H), 7.81-7.57 (m, 4H), 4.10-3.85 (m, 1H), 2.29-1.79 (m, 7H), 1.59-1.40 (m, 3H). ^{13}C NMR (100 MHz,

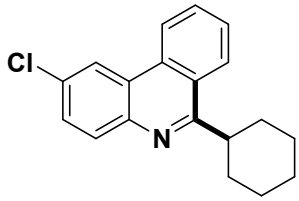
$CDCl_3$) δ 164.61, 144.29, 133.44, 133.29, 131.25, 130.02, 129.15, 128.73, 128.60, 127.41, 126.50, 126.25, 125.83, 122.80, 122.38, 122.06, 120.25, 45.72, 33.43, 26.76, 26.21.
HRMS (ESI, m/z): Calculated for $C_{23}H_{22}N$ $[M+H]^+$ 312.1747, found 312.1751

6-cyclohexyl-2-methylphenanthridine (3i)



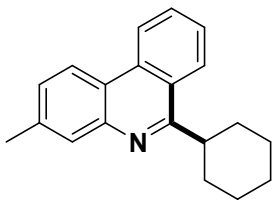
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3i** (35.9 mg, 87% yield) as white solid.
^1H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 1.6 Hz, 1H), 8.29 (s, 1H), 8.03 (d, *J* = 8.0 Hz, 1H), 7.84-7.73 (m, 1H), 7.72-7.60 (m, 1H), 7.53 (d, *J* = 8.4, 1H), 3.70-3.50 (m, 1H), 2.61 (s, 3H), 2.16-1.77 (m, 7H), 1.65-1.51 (m, 2H), 1.49-1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.23, 142.13, 135.79, 132.74, 130.02, 129.65, 129.61, 126.85, 125.54, 124.74, 123.09, 122.49, 121.42, 41.86, 32.26, 26.87, 26.30, 21.89.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1746

6-cyclohexyl-2-chlorophenanthridine (3j)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3j** (34.5 mg, 78% yield) as white solid.
^1H NMR (400 MHz, $CDCl_3$) δ 8.55 (d, *J* = 8.0 Hz, 1H), 8.48 (d, *J* = 2.0 Hz, 1H), 8.31 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.8 Hz, 1H), 7.87-7.78 (m, 1H), 7.76-7.67 (m, 1H), 7.63 (d, *J* = 8.4, 1H), 3.68-3.50 (m, 1H), 2.14-1.78 (m, 7H), 1.65-1.49 (m, 2H), 1.48-1.35 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.65, 142.32, 132.03, 131.89, 131.42, 130.22, 128.84, 127.75, 125.71, 124.85, 124.45, 122.62, 121.50, 42.00, 32.27, 26.84, 26.31.
HRMS (ESI, m/z): Calculated for $C_{19}H_{19}ClN$ $[M+H]^+$ 296.1201, found 296.1201

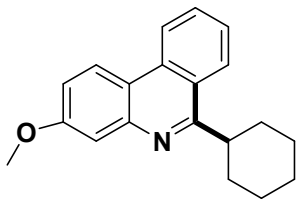
6-cyclohexyl-3-methylphenanthridine (3k)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1)

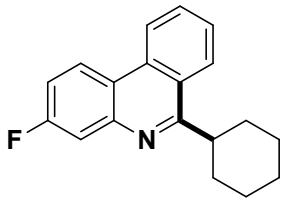
give **3k** (33.0 mg, 80% yield) as yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.61 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 8.4 Hz, 1H), 8.29 (d, *J* = 8.4 Hz, 1H), 7.94 (s, 1H), 7.84-7.74 (m, 1H), 7.70-7.60 (m, 1H), 7.43 (d, *J* = 8.4, 1H), 3.66-3.53 (m, 1H), 2.58 (s, 3H), 2.11-1.80 (m, 7H), 1.60-1.53 (m, 2H), 1.48-1.39 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.38, 143.98, 138.51, 133.10, 129.87, 129.53, 127.83, 126.59, 125.62, 124.44, 122.41, 121.64, 120.99, 41.94, 32.33, 26.90, 26.34, 21.45.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1743

6-cyclohexyl-3-methoxyphenanthridine (3l)



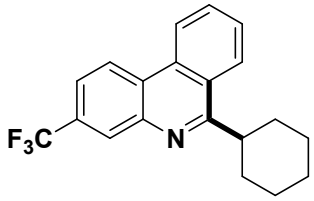
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3l** (39.3 mg, 90% yield) as yellow solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.54 (d, *J* = 8.4 Hz, 1H), 8.42 (d, *J* = 9.2 Hz, 1H), 8.28 (d, *J* = 8.4 Hz, 1H), 7.82-7.73 (m, 1H), 7.65-7.57 (m, 1H), 7.54 (d, *J* = 2.4 Hz, 1H), 7.25-7.19 (m, 1H), 4.00 (s, 3H), 3.66-3.56 (m, 1H), 2.12-1.80 (m, 7H), 1.61-1.54 (m, 2H), 1.49-1.40 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.95, 159.98, 145.53, 133.24, 130.01, 125.98, 125.66, 123.81, 123.07, 122.10, 117.38, 117.26, 109.69, 55.59, 42.01, 32.36, 26.90, 26.31.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}NO$ $[M+H]^+$ 292.1696, found 292.1696

6-cyclohexyl-3-fluorophenanthridine (3m)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3m** (32.2 mg, 77% yield) as yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (d, *J* = 8.4 Hz, 1H), 8.52-8.44 (m, 1H), 8.30 (d, *J* = 8.4 Hz, 1H), 7.86-7.73 (m, 2H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.41-7.29 (m, 1H), 3.70-3.49 (m, 1H), 2.16-1.77 (m, 7H), 1.63-1.49 (m, 2H), 1.49-1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.78, 162.62 (d J_{CF} = 245.6 Hz), 145.22 (d J_{CF} = 11.8 Hz), 132.80, 130.30, 126.91, 125.77, 124.29, 123.71 (d J_{CF} = 9.6 Hz), 122.38, 120.03 (d J_{CF} = 1.9 Hz), 115.06 (d J_{CF} = 23.5 Hz), 114.39 (d J_{CF} = 20.1 Hz), 42.04, 32.29, 26.84, 26.31.
HRMS (ESI, m/z): Calculated for $C_{19}H_{19}FN$ $[M+H]^+$ 280.1496, found 280.1497

6-cyclohexyl-3-trifluoromethylphenanthridine (3n)

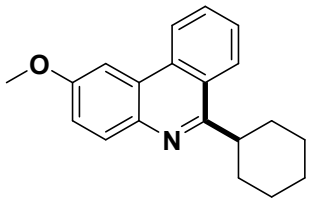


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3n** (37.0 mg, 75% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71-8.58 (m, 2H), 8.43 (s, 1H), 8.35 (d, J = 8.0 Hz, 1H), 7.87 (t, J = 7.6 Hz, 1H), 7.82-7.73 (m, 2H), 3.70-3.55 (m, 1H), 2.13-1.80 (m, 7H), 1.63-1.52 (m, 2H), 1.50-1.36 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.97, 143.22, 132.21, 130.50, 130.19 (q J_{CF} = 32.4 Hz), 128.28, 127.48 (q J_{CF} = 4.1 Hz), 125.84, 125.71, 125.33, 124.28 (q J_{CF} = 270.4 Hz), 122.97, 122.86, 121.97 (q J_{CF} = 3.3 Hz), 42.06, 32.29, 26.81, 26.28.

HRMS (ESI, m/z): Calculated for $C_{20}H_{19}F_3N$ $[M+H]^+$ 330.1464, found 330.1460

6-cyclohexyl-2-methoxyphenanthridine (3o)

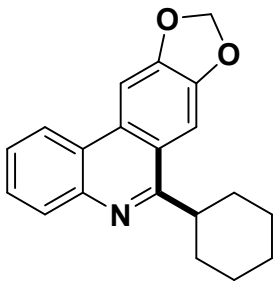


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3o** (35.4 mg, 81% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (d, J = 8.0 Hz, 1H), 8.30 (d, J = 8.4 Hz, 1H), 8.06 (d, J = 10.0 Hz, 1H), 7.88 (d, J = 2.8 Hz, 1H), 7.83-7.74 (m, 1H), 7.73-7.60 (m, 1H), 7.34 (d, J = 9.2, 1H), 4.00 (s, 3H), 3.64-3.50 (m, 1H), 2.13-1.75 (m, 7H), 1.65-1.50 (m, 2H), 1.50-1.37 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.69, 157.78, 139.13, 132.51, 131.26, 129.46, 127.06, 125.59, 124.78, 124.19, 122.40, 118.03, 102.82, 55.58, 41.73, 32.28, 26.87, 26.30.

HRMS (ESI, m/z): Calculated for $C_{20}H_{22}NO$ $[M+H]^+$ 292.1696, found 292.1697

6-cyclohexyl-[1,3]dioxolo[4,5-j]phenanthridine (3p)

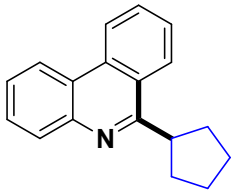


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3p** (26.5 mg, 58% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32 (d, J = 8.0 Hz, 1H), 8.09 (d, J = 8.0 Hz, 1H), 7.94 (s, 1H), 7.69–7.58 (m, 2H), 7.57–7.48 (m, 1H), 6.15 (s, 2H), 3.48-3.31 (m, 1H), 2.07–

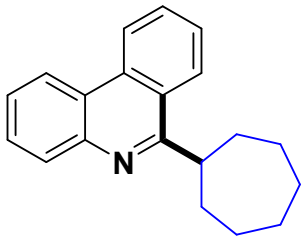
1.80 (m, 7H), 1.61–1.36 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.84, 150.33, 148.05, 130.63, 129.87, 127.74, 125.82, 123.51, 121.64, 121.27, 103.15, 101.81, 100.46, 42.43, 32.21, 26.89, 26.30.
HRMS (ESI, m/z): Calculated for $C_{20}H_{20}NO_2$ $[M+H]^+$ 306.1489, found 306.1486

6-cyclopentylphenanthridine (3q)



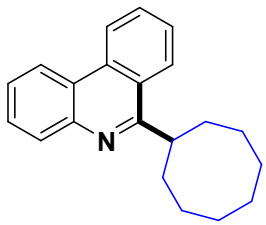
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3q** (32.3 mg, 87% yield) as yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.34 (d, *J* = 8.4 Hz, 1H), 8.13 (d, *J* = 8.4 Hz, 1H), 7.81 (t, *J* = 7.2 Hz, 1H), 7.69 (m, 2H), 7.61 (t, *J* = 7.6 Hz, 1H), 4.18-3.96 (m, 1H), 2.38-2.09 (m, 4H), 2.03-1.67 (m, 4H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.21, 143.74, 132.95, 129.96, 128.41, 127.07, 126.25, 126.14, 125.65, 123.50, 122.43, 121.84, 43.61, 32.21, 26.04.
HRMS (ESI, m/z): Calculated for $C_{18}H_{18}N$ $[M+H]^+$ 248.1434, found 248.1431

6-cycloheptylphenanthridine (3r)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3r** (33.8 mg, 82% yield) as yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.30 (d, *J* = 8.0 Hz, 1H), 8.14 (d, *J* = 6.8 Hz, 1H), 7.88-7.76 (m, 1H), 7.70 (m, 2H), 7.64-7.54 (m, 1H), 3.79 (m, 1H), 2.26-2.05 (m, 4H), 2.04-1.89 (m, 2H), 1.88-1.63 (m, 6H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 166.57, 143.74, 133.07, 129.84, 128.34, 127.01, 126.04, 125.71, 124.52, 123.25, 122.54, 121.75, 43.61, 34.10, 28.17, 27.51.
HRMS (ESI, m/z): Calculated for $C_{20}H_{22}N$ $[M+H]^+$ 276.1747, found 276.1746

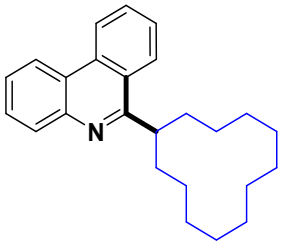
6-cyclooctylphenanthridine (3s)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1)

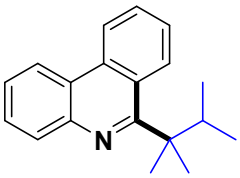
give **3s** (36.9 mg, 85% yield) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.53 (d, *J* = 8.4 Hz, 1H), 8.31 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.81 (m, 1H), 7.70 (m, 2H), 7.60 (m, 1H), 3.98-3.80 (m, 1H), 2.30-2.05 (m, 4H), 1.83 (m, 10H). ^{13}C NMR (100 MHz, CDCl3) δ 167.14, 143.70, 133.15, 129.83, 128.34, 127.00, 126.03, 125.76, 124.51, 123.22, 122.57, 121.74, 41.50, 32.56, 26.82, 26.26.
HRMS (ESI, m/z): Calculated for $C_{21}H_{24}N$ $[M+H]^+$ 290.1903, found 290.1904

6-cyclododecylphenanthridine (3t)



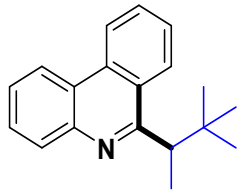
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3t** (26.9 mg, 52% yield) as white solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.2 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.35 (d, *J* = 8.2 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 7.5 Hz, 1H), 7.75-7.65 (m, 2H), 7.61 (t, *J* = 7.5 Hz, 1H), 4.04-3.84 (m, 1H), 2.13-1.91 (m, 4H), 1.65-1.23 (m, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.18, 143.85, 133.06, 129.95, 129.91, 128.38, 127.20, 126.10, 125.55, 125.49, 123.29, 122.61, 121.81, 37.01, 29.51, 24.04, 23.88, 23.48, 23.34.
HRMS (ESI, m/z): Calculated for $C_{25}H_{32}N$ $[M+H]^+$ 346.2529, found 346.2526

6-(2,3-dimethyl butane-2-yl) phenanthridine (3u)



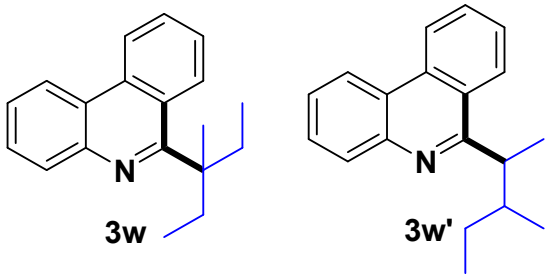
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3u** (32.0 mg, 81% yield) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (t, *J* = 8.0 Hz, 2H), 8.53 (d, *J* = 8.0, 1H), 8.14 (d, *J* = 8.0, 1H), 7.78 (t, *J* = 8.0 Hz, 1H), 7.71 (t, *J* = 7.2 Hz, 1H), 7.66-7.56 (m, 2H), 3.00-2.88 (m, 1H), 1.65 (s, 6H), 0.87 (d, *J* = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.70, 142.82, 134.01, 130.41, 129.22, 128.31, 127.85, 126.39, 125.88, 124.70, 123.29, 123.03, 121.59, 47.09, 35.53, 25.16, 18.22.
HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1747

6-(2,2-dimethyl butane-3-yl) phenanthridine (3v)



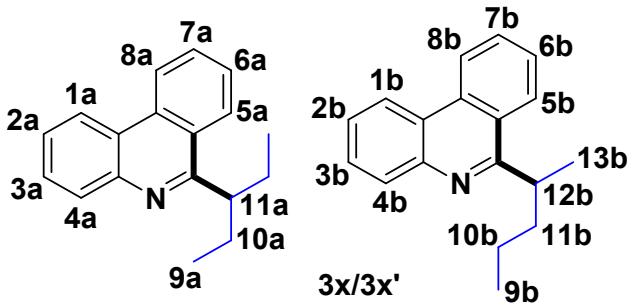
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3v** (22.9 mg, 58% yield) as yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.42 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.0 Hz, 1H), 7.81 (t, *J* = 7.6 Hz, 1H), 7.76-7.65 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 3.92-3.72 (m, 1H), 1.48 (d, *J* = 6.8 Hz, 3H), 1.05 (s, 9H).
^{13}C NMR (100 MHz, $CDCl_3$) δ 163.98, 142.48, 131.67, 129.07, 128.67, 127.24, 125.81, 125.34, 125.24, 125.04, 122.03, 121.44, 120.73, 42.37, 34.17, 27.33, 14.86.
HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1744

6-(3-methyl pentane-3-yl) phenanthridine (3w)
6-(3-methyl pentane-2-yl) phenanthridine (3w')



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 200: 1 and 50:1) give **3w** and **3w'** (18.5 mg and 10.3 mg, 73% yield) as yellowish oil.
3w ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73-8.62 (m, 2H), 8.54 (d, *J* = 8.4 Hz, 1H), 8.15 (d, *J* = 8.0 Hz, 1H), 7.82-7.74 (m, 1H), 7.73-7.67 (m, 1H), 7.67-7.58 (m, 2H), 2.49-2.34 (m, 2H), 2.07-1.92 (m, 2H), 1.67 (s, 3H), 0.72 (t, *J* = 7.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.61, 143.00, 133.58, 130.44, 129.27, 128.24, 127.08, 126.37, 126.18, 125.34, 123.23, 122.94, 121.60, 48.02, 34.36, 25.89, 9.24.
HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1747
3w' (a mixture of two diastereoisomeric products) ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.14 (d, *J* = 8.0 Hz, 1H), 7.86-7.77 (m, 1H), 7.75-7.65 (m, 2H), 7.65-7.56 (m, 1H), 3.83-3.62 (m, 1H), 2.27-2.10 (m, 1H), 1.80-1.67 (m, 1H), 1.44 (t, *J* = 6.8 Hz, 3H), 1.29-1.22 (m, 1H), 0.99-0.84 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.74, 165.46, 143.79, 143.75, 133.02, 133.00, 129.99, 129.92, 129.87, 128.38, 128.36, 127.07, 126.11, 126.10, 125.80, 125.70, 125.56, 125.34, 123.24, 123.23, 122.60, 122.58, 121.82, 121.81, 41.76, 40.91, 39.19, 39.12, 28.57, 25.44, 17.98, 16.80, 15.47, 15.34, 11.96, 11.24.
HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1745

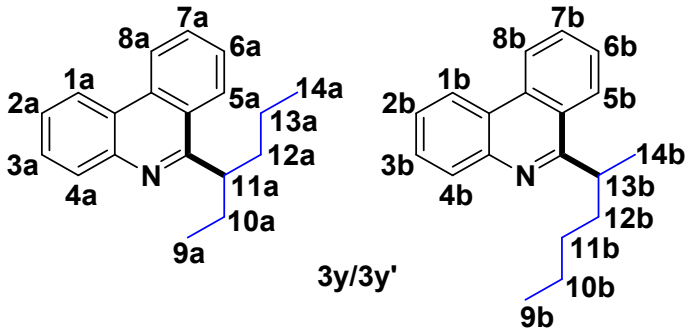
6-(pentane-3-yl) phenanthridine (3x)
6-(pentane-2-yl) phenanthridine (3x')



3x/3x'

Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3x** and **3x'** (24.7 mg, 66% yield) as brown oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, J = 8.0 Hz, H_{1a}, H_{1b}), 8.61-8.49 (m, H_{5a}, H_{5b}), 8.40-8.28 (m, H_{4a}, H_{4b}), 8.14 (d, J = 8.0 Hz, H_{8a}, H_{8b}), 7.83 (t, J = 7.2 Hz, H_{3a}, H_{3b}), 7.77-7.65 (m, H_{2a}, H_{2b}, H_{7a}, H_{7b}), 7.61 (t, J = 7.6 Hz, H_{6a}, H_{6b}), 3.93-3.80 (m, H_{12b}), 3.66-3.54 (m, H_{11a}), 2.18-2.03 (m, H_{11b}), 1.95-1.56 (m, H_{10a}, H_{10b}), 1.48 (d, J = 6.8 Hz, H_{13b}), 0.98-0.81 (m, H_{9a} H_{9b}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.68, 164.74, 143.92, 143.86, 133.02, 132.85, 129.97, 129.94, 129.92, 128.41, 128.38, 127.13, 127.08, 126.31, 126.15, 126.11, 125.78, 125.64, 125.17, 123.32, 123.19, 122.60, 122.52, 121.84, 38.57, 36.34, 27.67, 21.06, 20.10, 14.38, 12.44.
HRMS (ESI, m/z): Calculated for $C_{18}H_{20}N$ $[M+H]^+$ 250.1590, found 250.1588

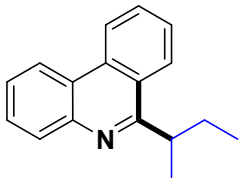
6-(hexan-2-yl) phenanthridine (3y)
6-(hexan-3-yl) phenanthridine (3y')



3y/3y'

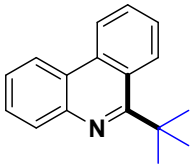
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3y** and **3y'** (26.4 mg, 67% yield) as brown oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75-8.46 (m, H_{1a}, H_{1b}, H_{5a}, H_{5b}), 8.43-8.24 (m, H_{4a}, H_{4b}), 8.15 (d, J = 8.0 Hz, H_{8a}, H_{8b}), 7.95-7.49 (m, H_{2a}, H_{2b}, H_{3a}, H_{3b}, H_{6a}, H_{6b}, H_{7a}, H_{7b}), 3.91-3.76 (m, H_{13b}), 3.75-3.59 (m, H_{11a}), 2.21-1.99 (m, H_{12a}, H_{12b}), 1.94-1.66 (m, H_{10a}, H_{10b}, H_{12a}), 1.49 (d, J = 6.8 Hz, H_{14b}), 1.41-1.17 (m, H_{10b}, H_{11b}, H_{13a}), 0.98-0.75 (m, H_{9a}, H_{9b}, H_{14a}). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.70, 164.98, 143.94, 143.87, 133.02, 132.85, 129.96, 129.94, 128.41, 128.38, 127.14, 127.09, 126.23, 126.15, 126.10, 125.73, 125.64, 125.18, 123.32, 123.19, 122.60, 122.54, 121.85, 37.20, 36.62, 36.07, 30.21, 28.05, 22.99, 21.07, 20.17, 14.46, 14.17, 12.49.
HRMS (ESI, m/z): Calculated for $C_{19}H_{22}N$ $[M+H]^+$ 264.1747, found 264.1746

6-(butane-2-yl) phenanthridine (3z)



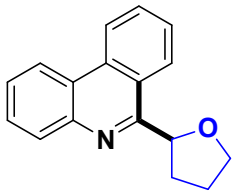
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3z** (15.9 mg, 45% yield) as yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.33 (d, *J* = 8.4 Hz, 1H), 8.16 (d, *J* = 7.6 Hz, 1H), 7.87-7.78 (m, 1H), 7.75-7.66 (m, 2H), 7.65-7.56 (m, 1H), 3.84-3.70 (m, 1H), 2.24-2.09 (m, 1H), 1.92-1.78 (m, 1H), 1.49 (d, *J* = 6.8 Hz, 3H), 0.98 (t, *J* = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.47, 143.86, 133.02, 129.94, 129.93, 128.39, 127.10, 126.14, 125.67, 125.27, 123.32, 122.58, 121.83, 38.33, 29.18, 19.79, 12.47.
HRMS (ESI, m/z): Calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1434, found 236.1433

6-(iso-butane-2-yl) phenanthridine (3aa)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 100: 1) give **3aa** (18.3 mg, 52% yield) as colorless oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.53 (d, *J* = 8.1 Hz, 1H), 8.12 (d, *J* = 8.1 Hz, 1H), 7.79 (t, *J* = 7.6 Hz, 1H), 7.73-7.57 (m, 3H), 1.73 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.67, 142.96, 134.02, 130.27, 129.26, 128.37, 128.27, 126.45, 125.94, 124.33, 123.43, 122.98, 121.61, 40.20, 31.20.
HRMS (ESI, m/z): Calculated for $C_{17}H_{18}N$ $[M+H]^+$ 236.1434, found 236.1431

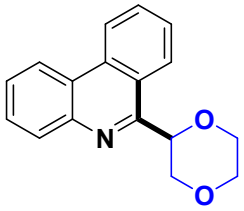
6-(tetrahydrofuran-2-yl) phenanthridine (3ab)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ab** (34.0 mg, 91% yield) as brown solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.46 (d, *J* = 8.0 Hz, 1H), 8.20 (d, *J* = 8.0 Hz, 1H), 7.83 (t, *J* = 7.6 Hz, 1H), 7.76-7.57 (m, 3H), 5.78 (t, *J* = 6.8 Hz, 1H), 4.29-3.95 (m, 2H), 2.85-2.63 (m, 1H), 2.52-2.33 (m, 1H), 2.30-2.00 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.41, 143.42, 133.41,

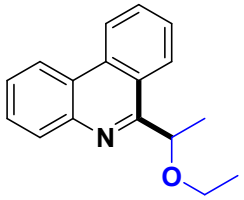
130.61, 130.39, 128.60, 127.32, 127.00, 126.65, 124.97, 124.23, 122.49, 121.99, 79.77, 69.14, 30.09, 26.12.
HRMS (ESI, m/z): Calculated for $C_{17}H_{16}NO$ $[M+H]^+$ 250.1226, found 250.1226

6-(1, 4-dioxan-2-yl) phenanthridine (3ac)



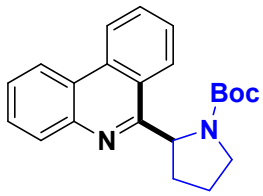
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ac** (35.0 mg, 88% yield) as yellowish solid.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 7.6 Hz, 1H), 8.44 (d, *J* = 8.0 Hz, 1H), 8.21 (d, *J* = 8.0, 1H), 7.85 (t, *J* = 6.8 Hz, 1H), 7.79-7.59 (m, 3H), 5.49 (t, *J* = 6.8 Hz, 1H), 4.38-4.24 (m, 2H), 4.21-4.05 (m, 2H), 4.00-3.85 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.14, 143.19, 133.24, 130.56, 130.54, 128.64, 127.41, 127.35, 126.07, 124.54, 124.05, 122.48, 121.90, 76.22, 70.10, 67.77, 66.59.
HRMS (ESI, m/z): Calculated for $C_{17}H_{16}NO_2$ $[M+H]^+$ 266.1176, found 266.1178

6-(Diethyl ether-2-yl) phenanthridine (3ad)



Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ad** (35.4 mg, 94% yield) as yellowish oil.
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (d, *J* = 8.4 Hz, 1H), 8.66 (d, *J* = 8.4 Hz, 1H), 8.56 (d, *J* = 8.4, 1H), 8.17 (d, *J* = 8.0, 1H), 7.83 (t, *J* = 5.6 Hz, 1H), 7.77-7.59 (m, 3H), 5.22 (q, *J* = 6.8 Hz, 1H), 3.65-3.53 (m, 1H), 3.52-3.40 (m, 1H), 1.79 (d, *J* = 6.8 Hz, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.92, 143.28, 133.51, 130.47, 130.01, 128.64, 127.04, 126.95, 126.86, 124.07, 122.44, 121.94, 81.44, 64.68, 21.56, 15.54.
HRMS (ESI, m/z): Calculated for $C_{17}H_{18}NO$ $[M+H]^+$ 252.1383, found 252.1385

***tert*-Butyl-2-(phenanthridin-6-yl)pyrrolidine-1-carboxylate (3ae)**



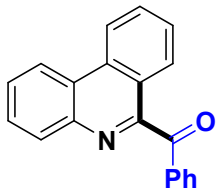
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3ae** (41.3 mg, 79% yield) as yellow solid.

The product gives two sets of NMR signals, owing to the presence of rotamers around the tertiary amide.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72-8.60 (m, 1H), 8.58-8.48 (m, 1H), 8.31-8.20 (m, 1H), 8.15-8.04 (m, 1H), 7.89-7.77 (m, 1H), 7.74-7.56 (m, 3H), 5.95-5.71 (m, 1H), 4.03-3.87 (m, 1H), 3.80-3.57 (m, 1H), 2.61-2.42 (m, 1H), 2.11-1.94 (m, 3H), 1.47 (s, 3H), 0.92 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 161.19, 160.17, 154.89, 154.73, 143.56, 143.42, 133.31, 133.08, 130.35, 130.29, 130.17, 128.61, 128.27, 127.15, 127.08, 126.50, 126.33, 125.25, 124.99, 124.04, 123.95, 123.85, 123.57, 122.68, 122.60, 121.80, 79.06, 78.79, 60.11, 59.40, 47.15, 46.99, 33.31, 32.23, 28.63, 28.03, 23.74, 23.45.

HRMS (ESI, m/z): Calculated for $C_{22}H_{24}N_2O_2Na$ $[M+Na]^+$ 371.1730, found 371.1731

Phenanthridin-6-yl(phenyl)methanone (3af)

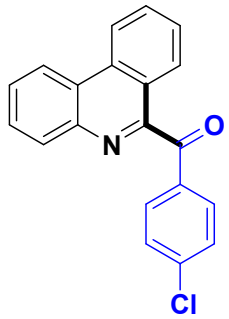


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3af** (28.5 mg, 67% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 (d, J = 8.4 Hz, 1H), 8.69-8.63 (m, 1H), 8.25-8.19 (m, 1H), 8.15 (d, J = 8.0 Hz, 1H), 8.08-8.01 (m, 2H), 7.94-7.87 (m, 1H), 7.82-7.74 (m, 2H), 7.70-7.59 (m, 2H), 7.53-7.43 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.76, 156.46, 141.64, 135.14, 132.95, 132.26, 130.23, 129.80, 129.63, 128.07, 127.55, 127.16, 126.78, 126.31, 123.45, 122.78, 121.29, 121.14.

HRMS (ESI, m/z): Calculated for $C_{20}H_{14}NO$ $[M+H]^+$ 284.1070, found 284.1072

Phenanthridin-6-yl(4-chlorophenyl)methanone (3ag)

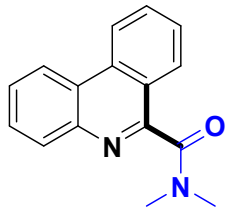


Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 10: 1) give **3ag** (28.1 mg, 59% yield) as white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, J = 8.0 Hz, 1H), 8.65 (d, J = 7.2 Hz, 1H), 8.28-8.10 (m, 2H), 8.00 (d, J = 8.0 Hz, 2H), 7.90 (t, J = 7.6 Hz, 1H), 7.84-7.72 (m, 2H), 7.68 (t, J = 7.4 Hz, 1H), 7.46 (d, J = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.45, 156.70, 142.53, 140.56, 134.59, 133.39, 132.26, 131.40, 130.67, 129.22, 128.95, 128.45, 127.95, 127.23, 124.58, 123.74, 122.40, 122.23.

HRMS (ESI, m/z): Calculated for $C_{20}H_{13}ClNO$ $[M+H]^+$ 318.0680, found 318.0684

N,N-Dimethylphenanthridine-6-carboxamide (3ah)

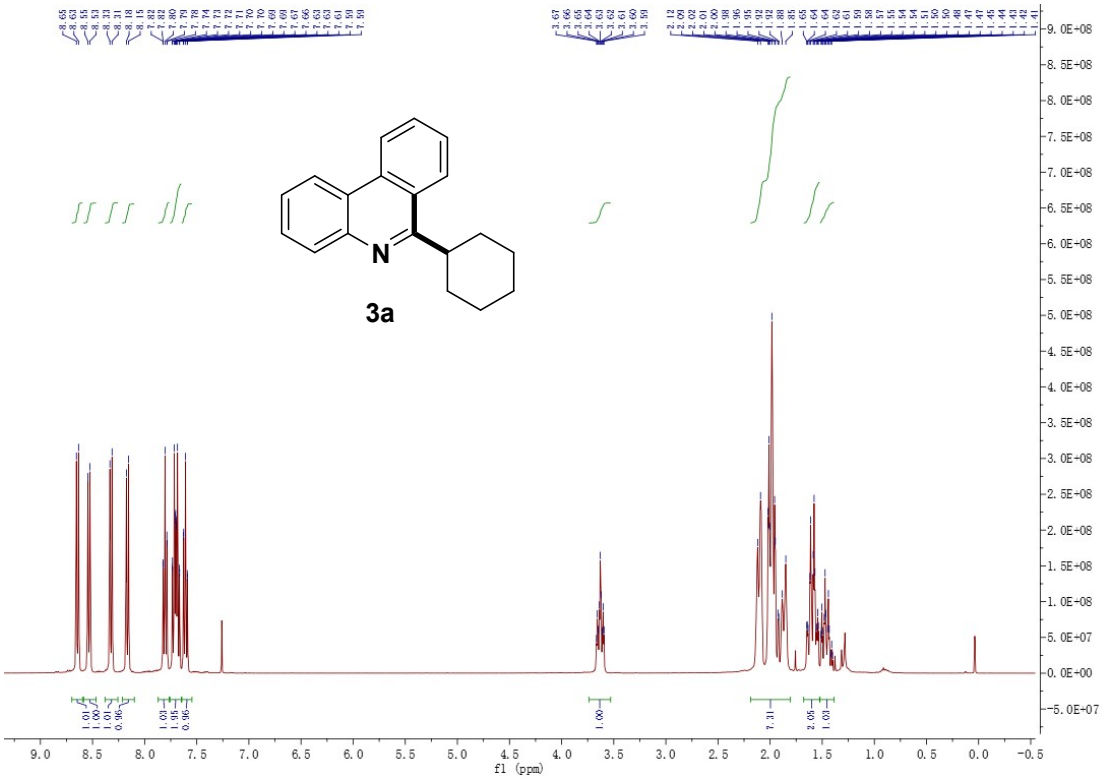


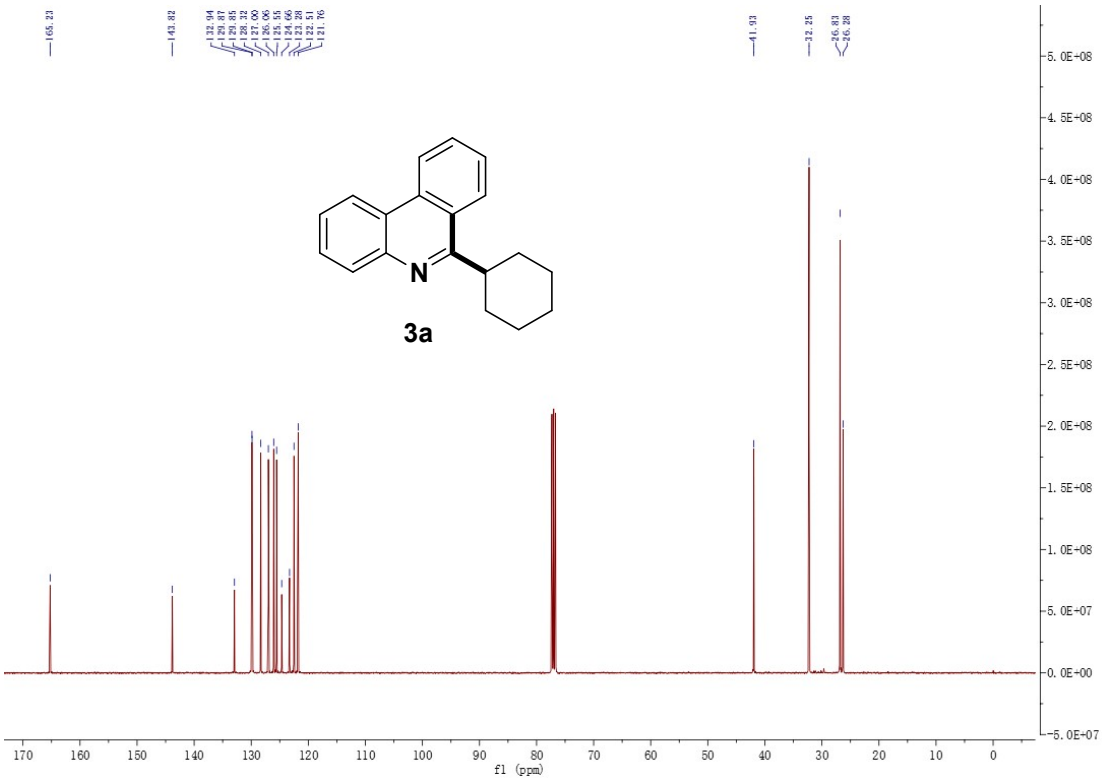
Flash column chromatography on a silica gel (petroleum ether: ethyl acetate, 5: 1) give **3ah** (15.8 mg, 42% yield) as yellowish oil.

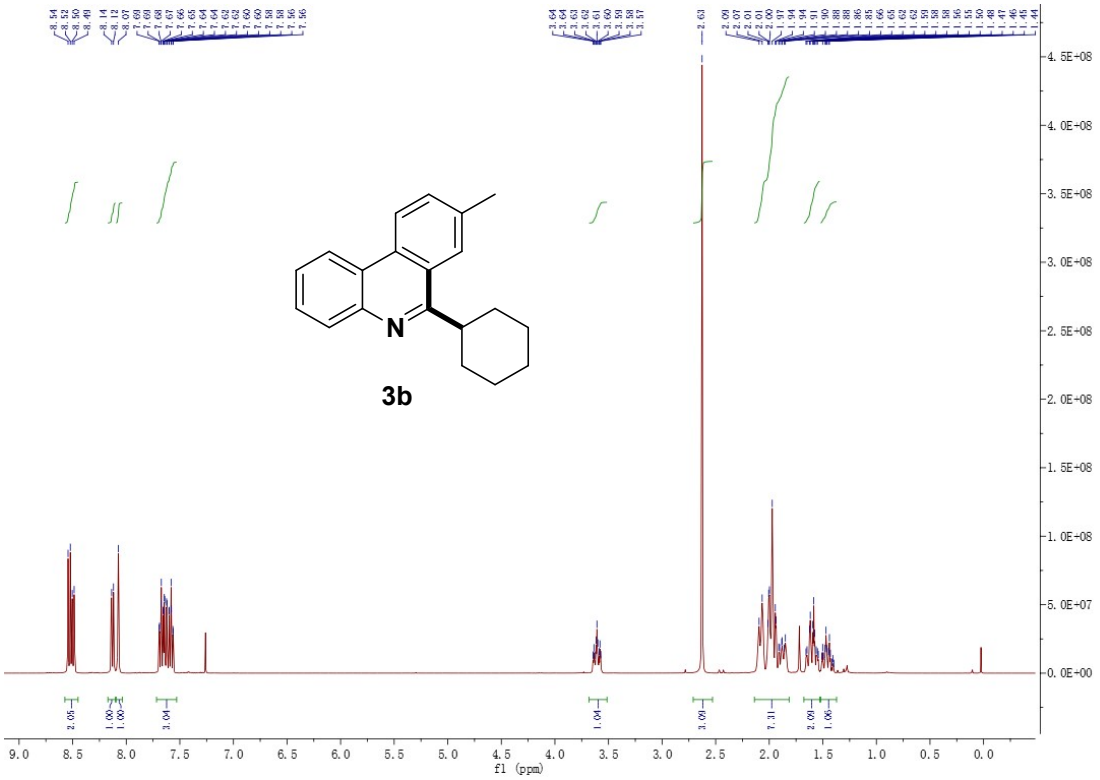
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.4 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.16 (d, *J* = 8.0 Hz, 1H), 8.04 (d, *J* = 8.0 Hz, 1H), 7.84 (t, *J* = 7.6 Hz, 1H), 7.78-7.61 (m, 3H), 3.28 (s, 3H), 2.89 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.21, 156.32, 143.06, 133.18, 131.40, 130.19, 129.04, 127.93, 127.75, 127.06, 124.07, 123.11, 122.33, 122.15, 38.33, 34.85.

HRMS (ESI, m/z): Calculated for $C_{16}H_{15}N_2O$ $[M+H]^+$ 251.1179, found 251.1174

8. Copies of ^{1}H NMR and ^{13}C NMR spectra



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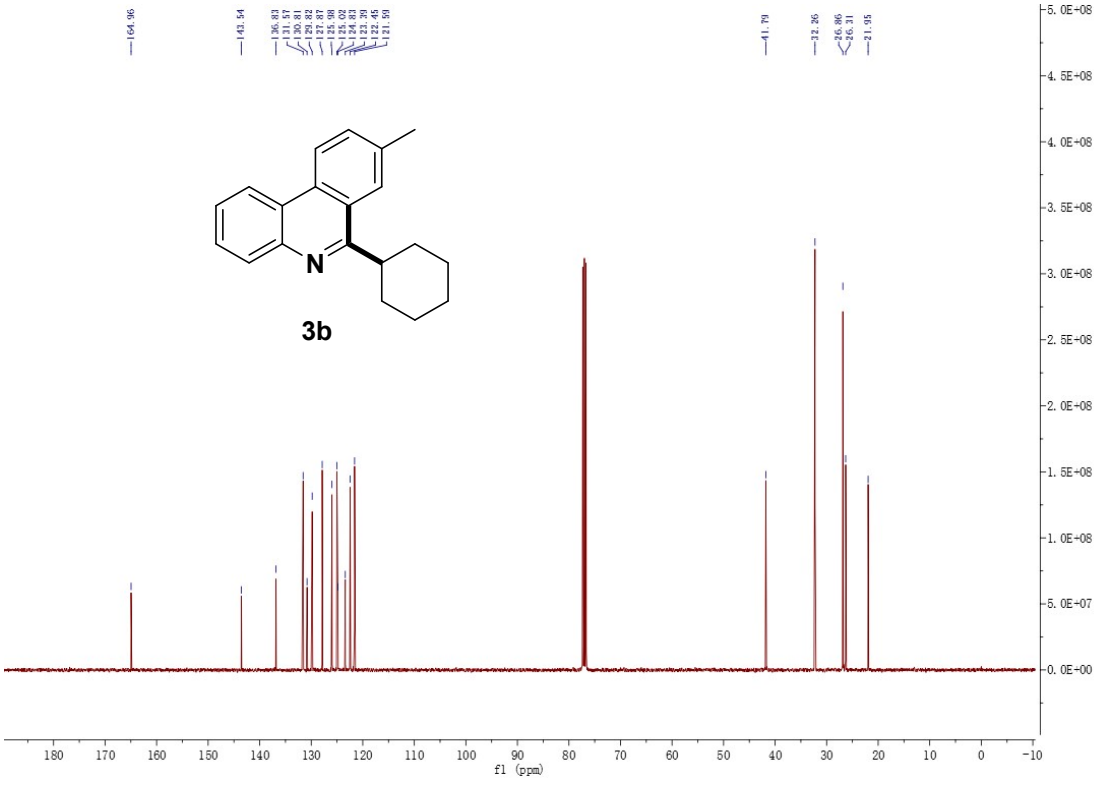
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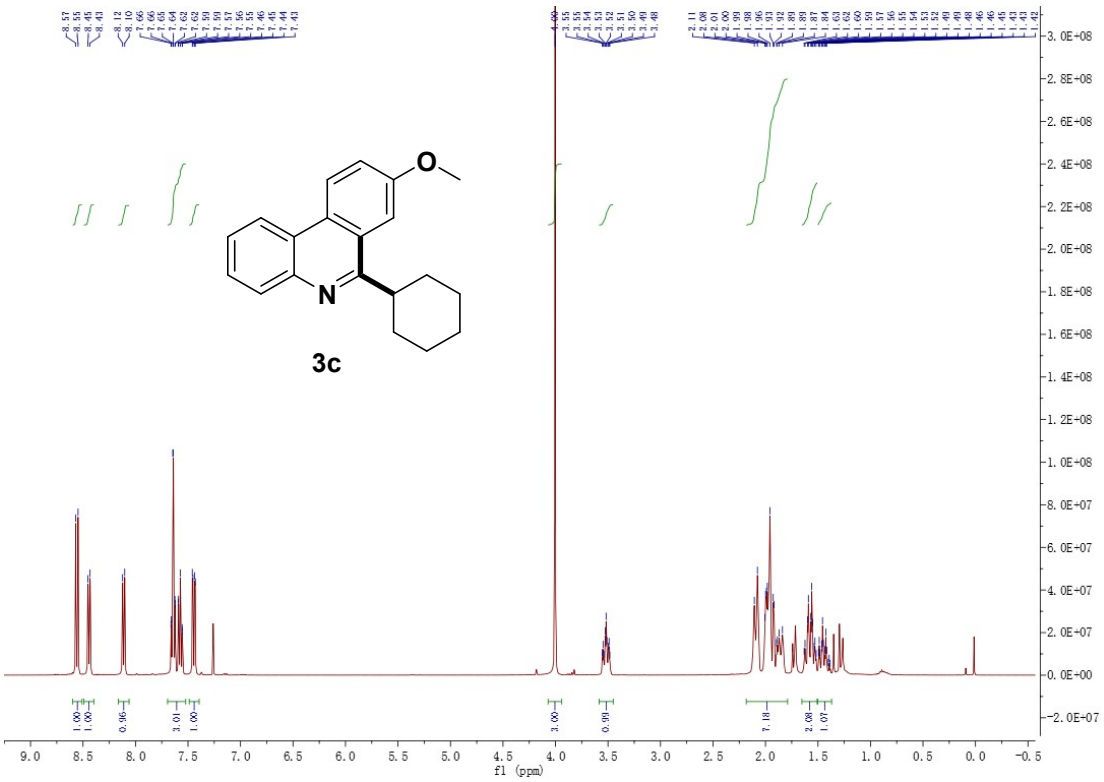
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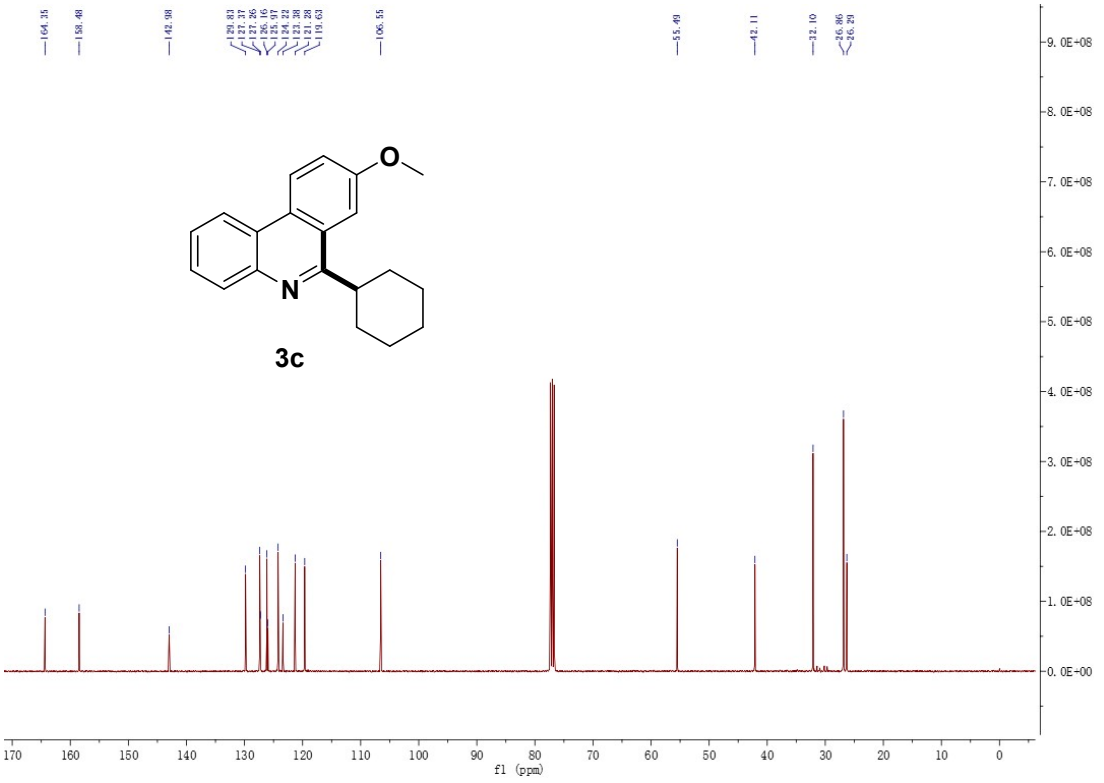
3c
fl (ppm)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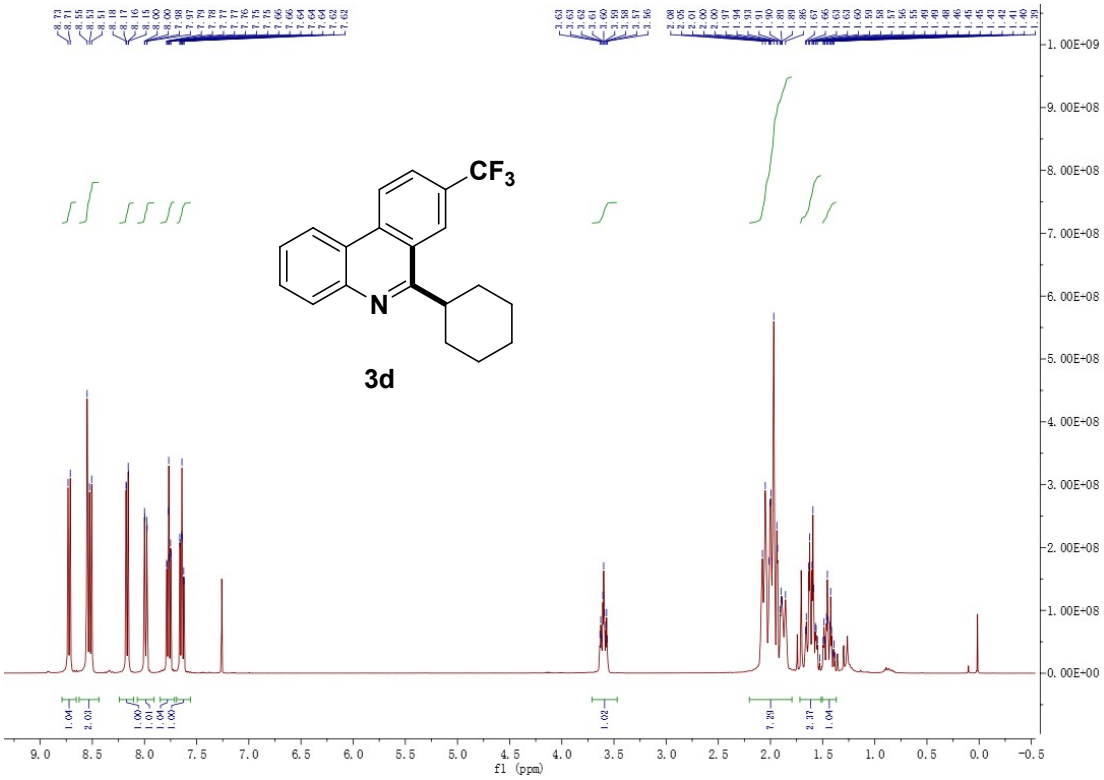
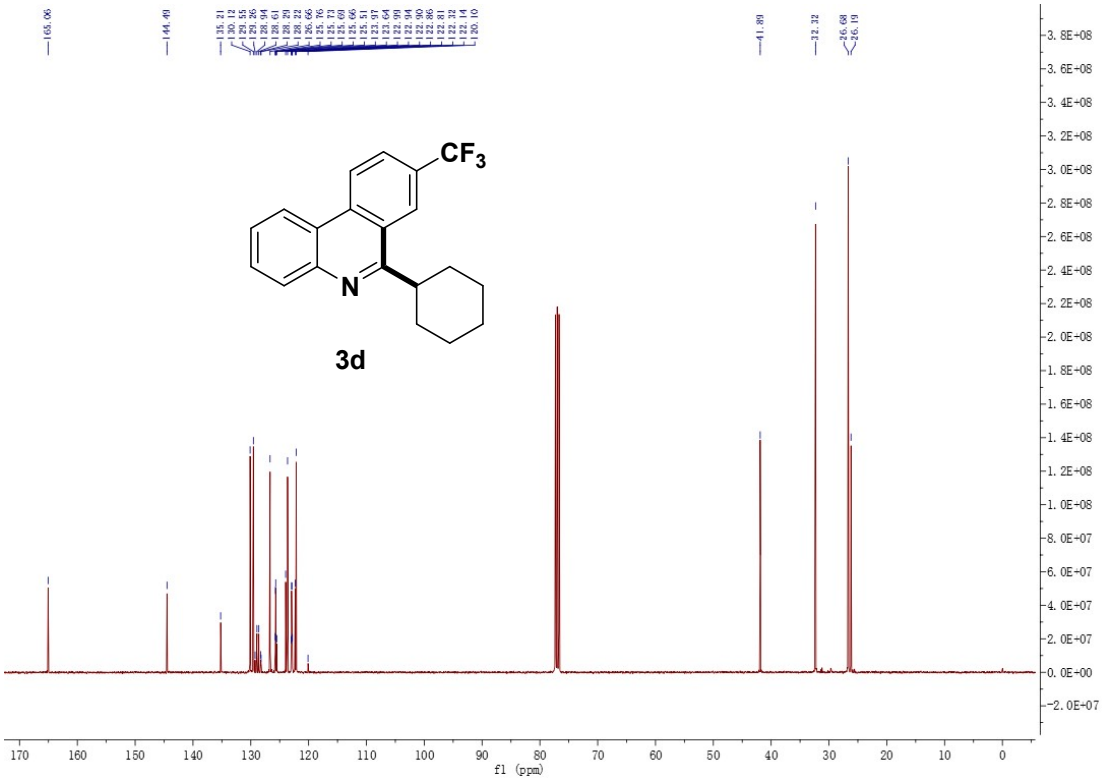
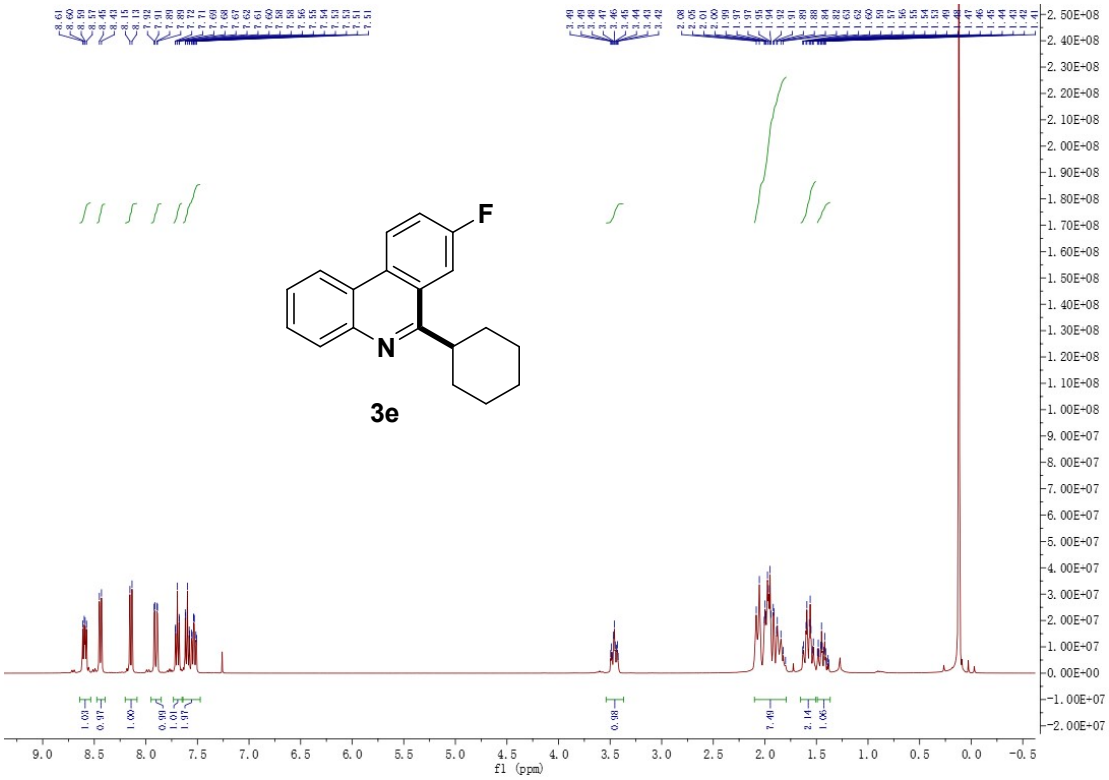
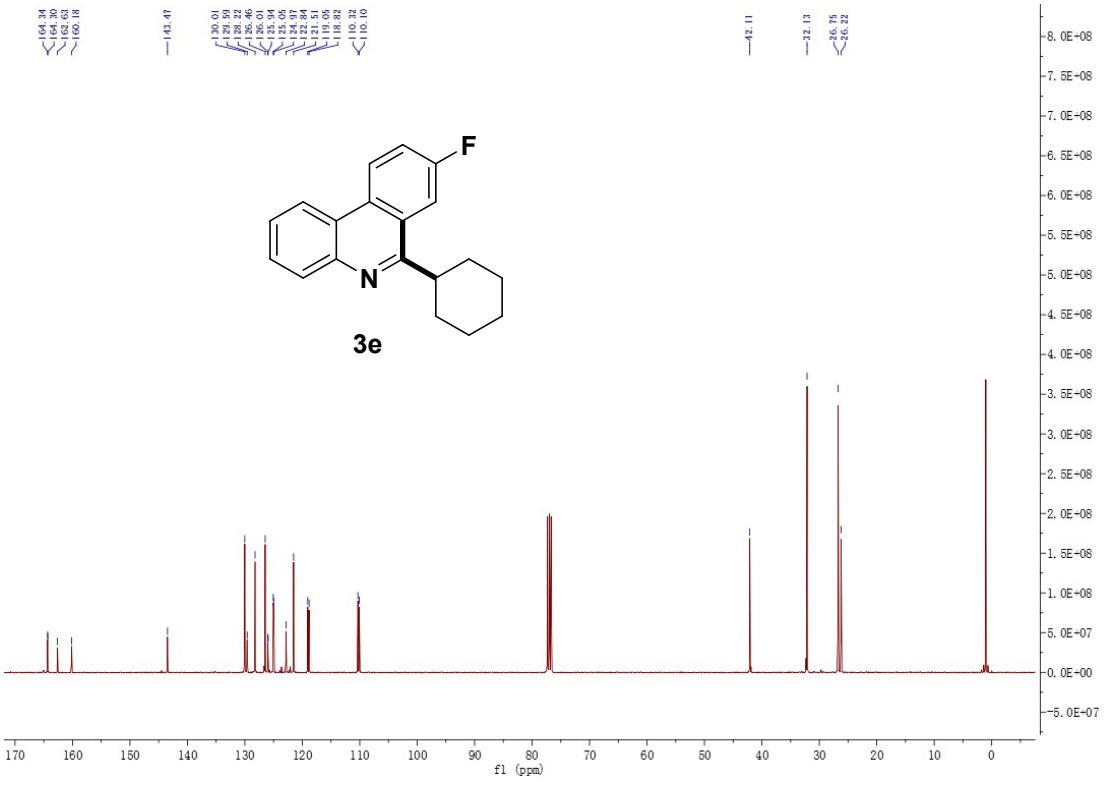
3c
fl (ppm)


CF3
N
3d
f1 (ppm)


CF3
N
3d
f1 (ppm)


F
N
3e
f1 (ppm)


F
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3e
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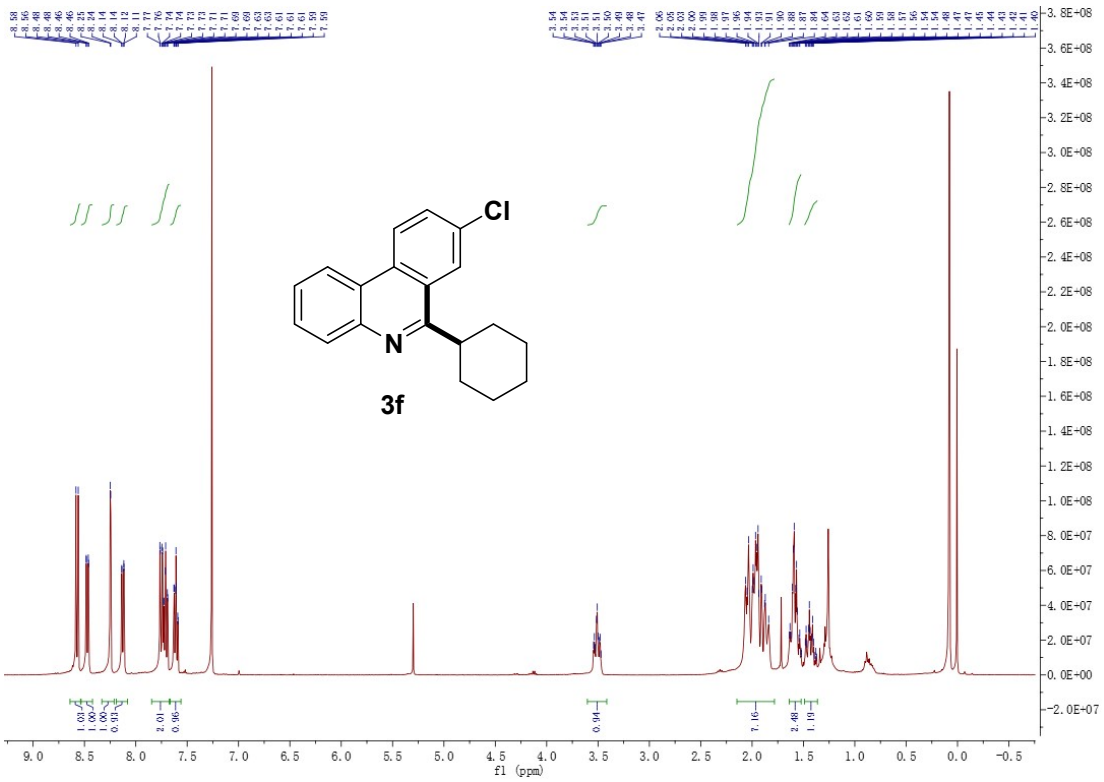
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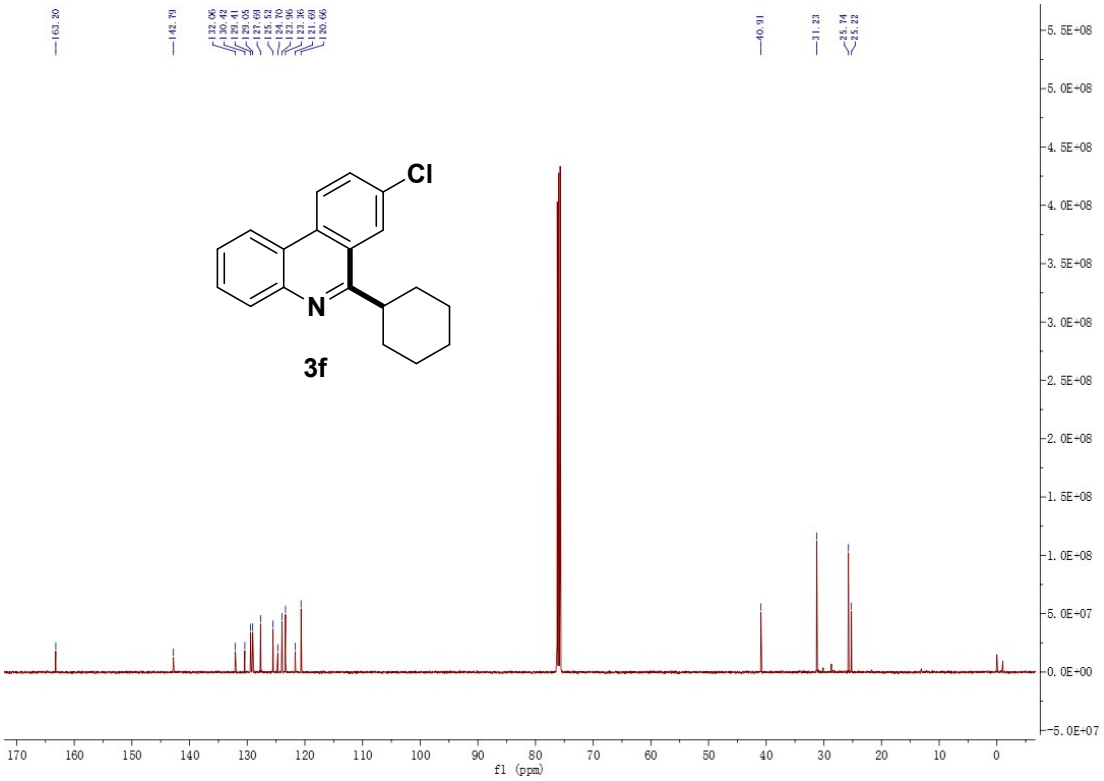
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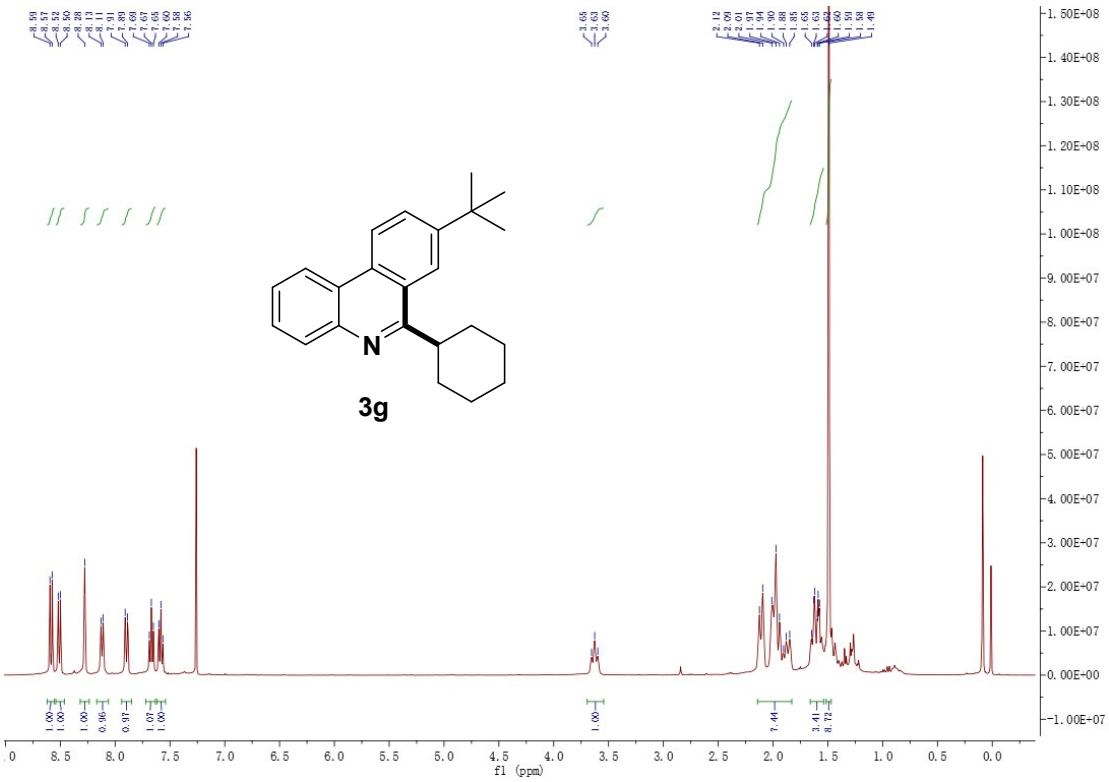
fl (ppm)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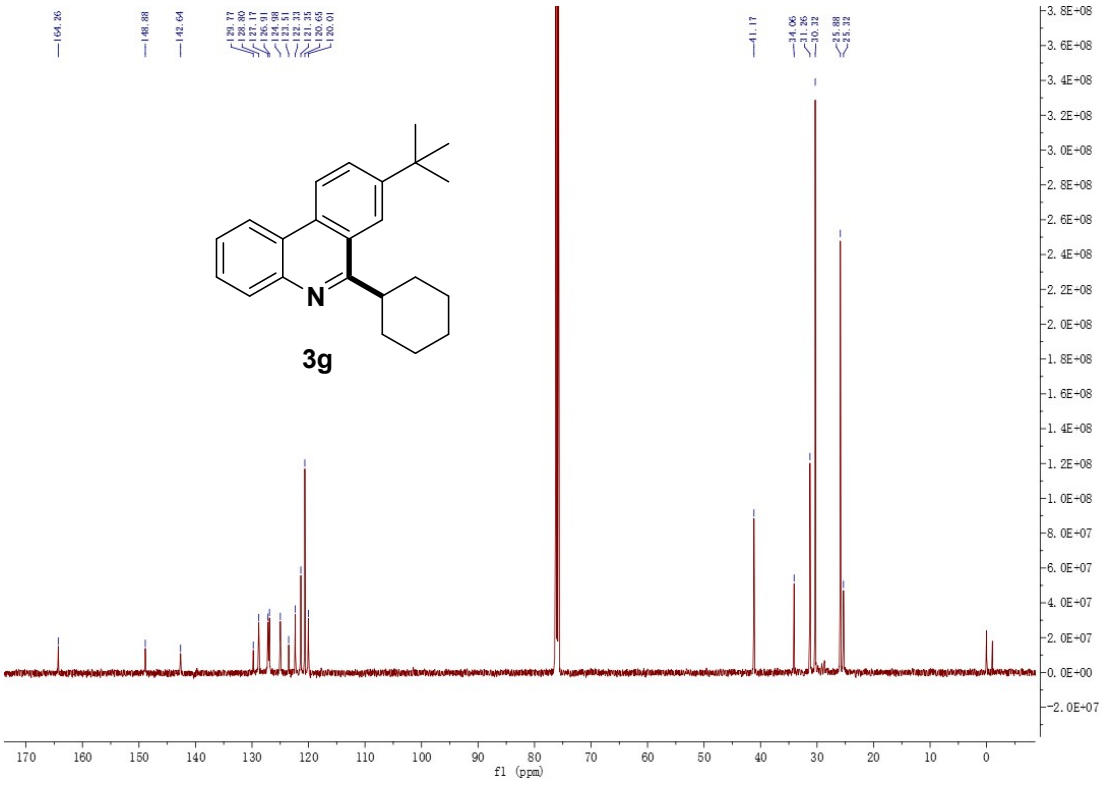
fl (ppm)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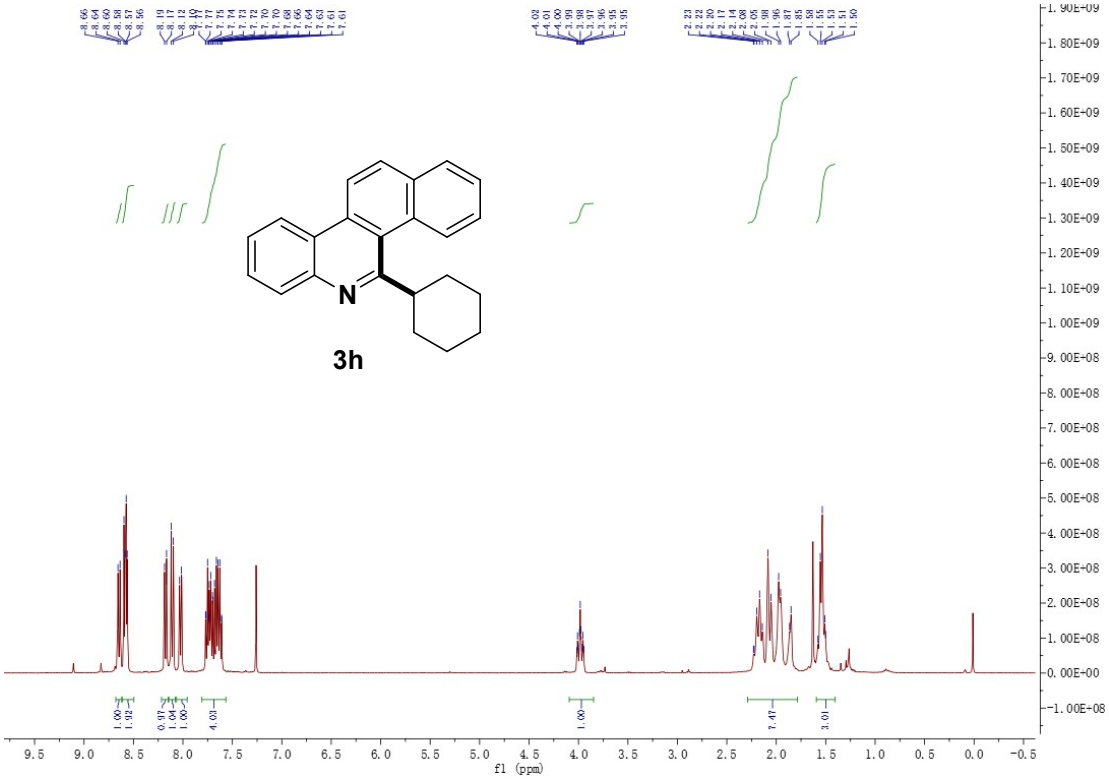
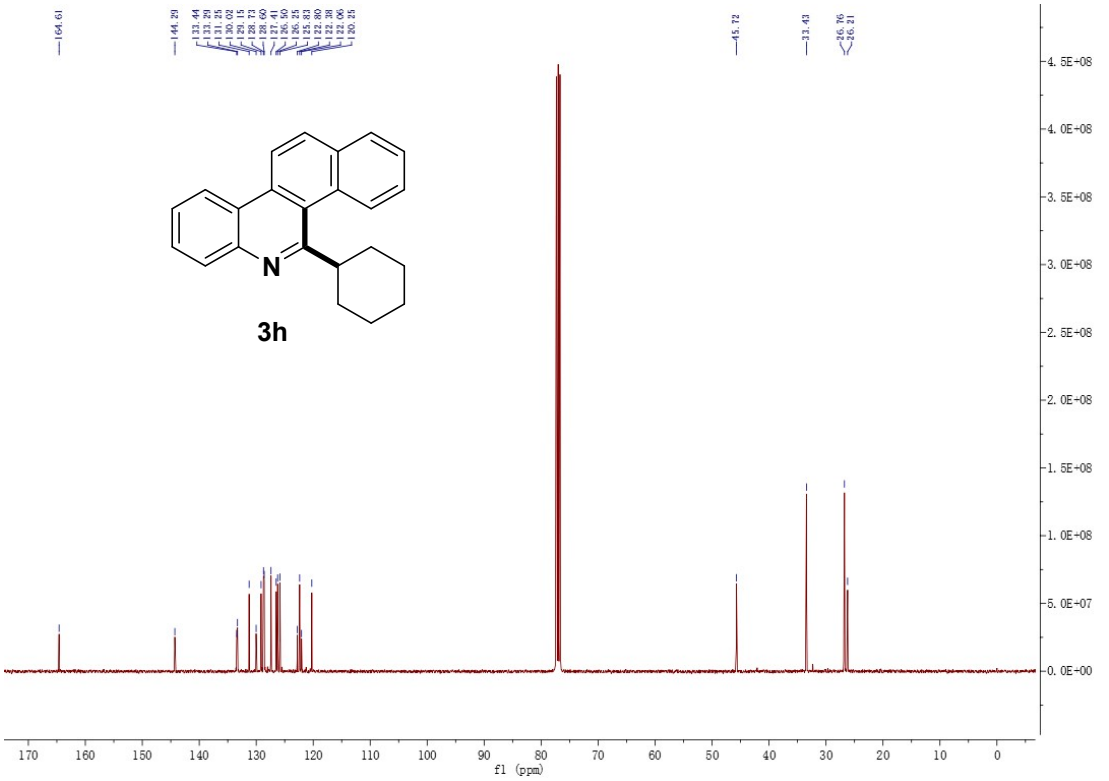
fl (ppm)


N
3h
f1 (ppm)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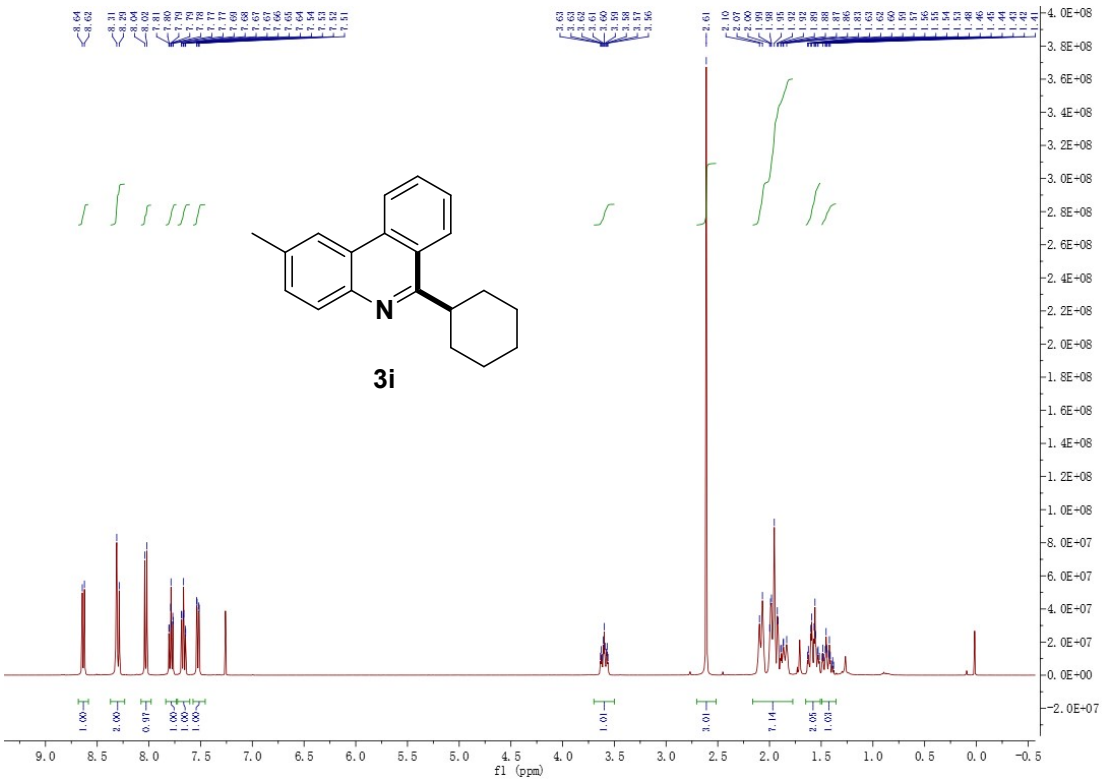
3h
f1 (ppm)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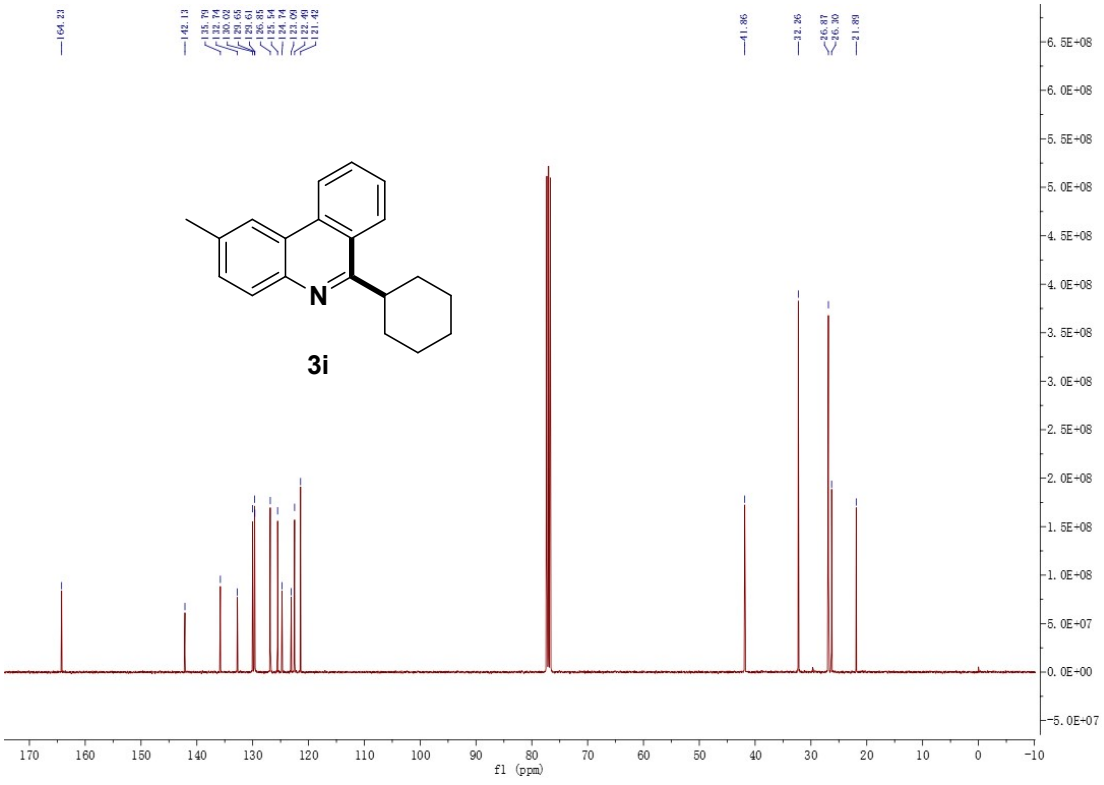
f1 (ppm)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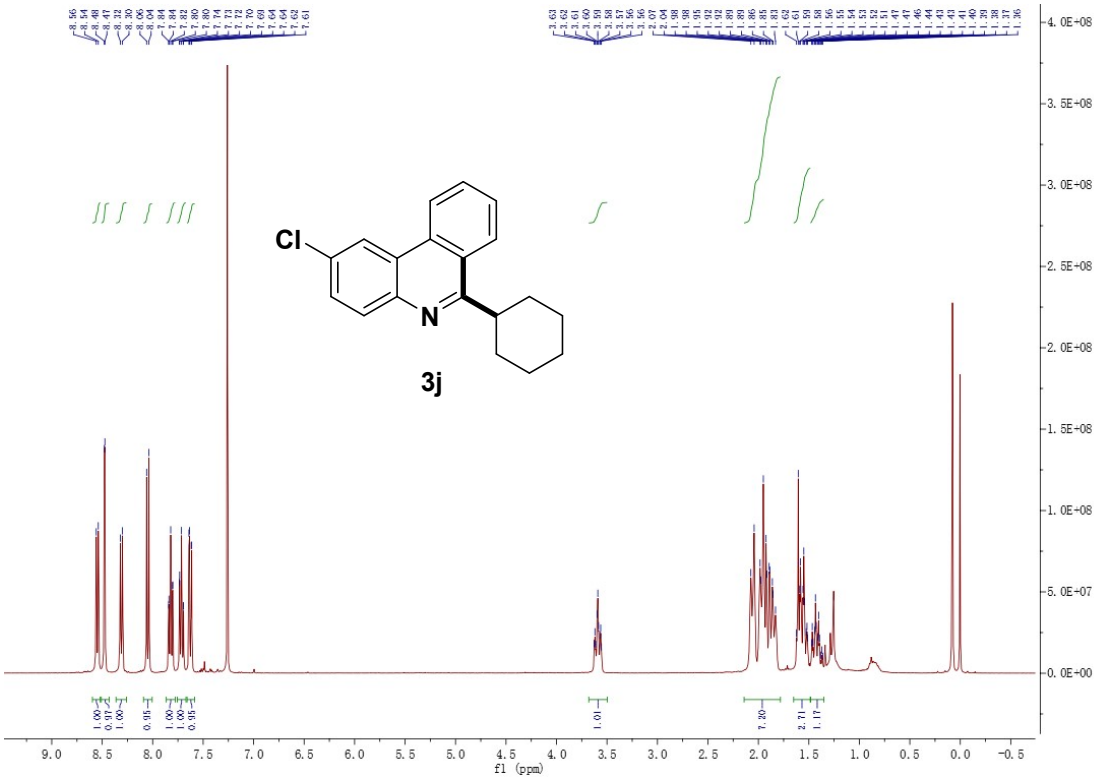
3i
f1 (ppm)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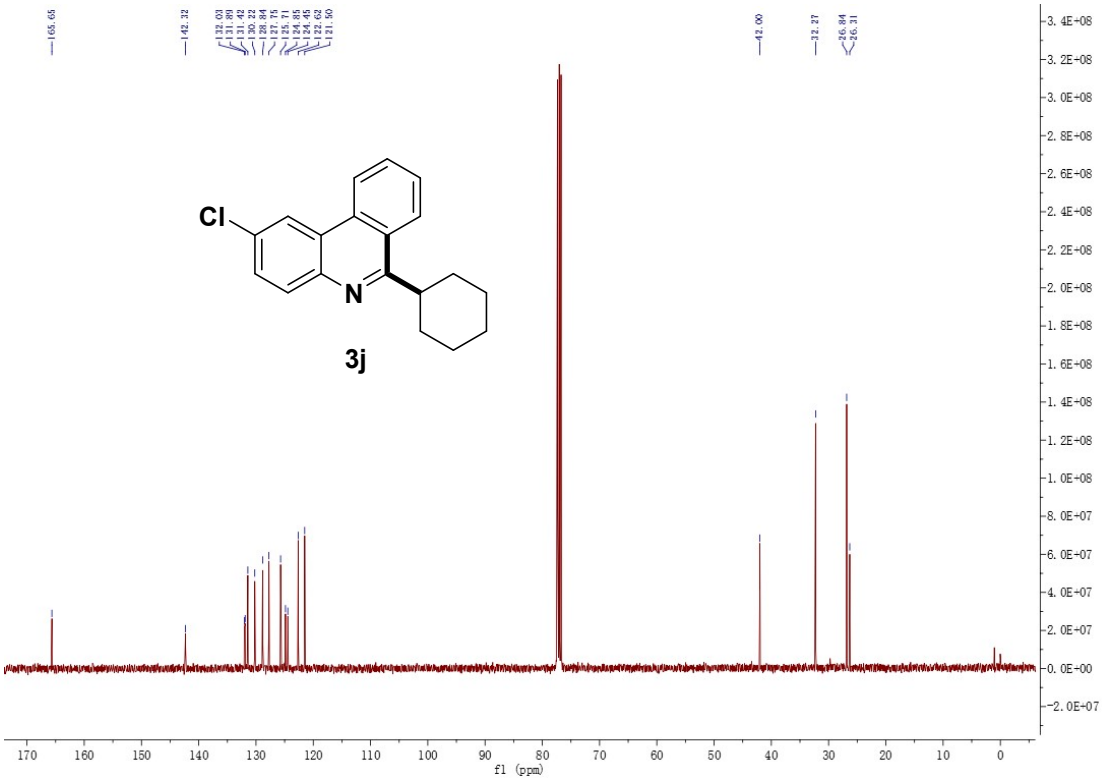
N
3j
f1 (ppm)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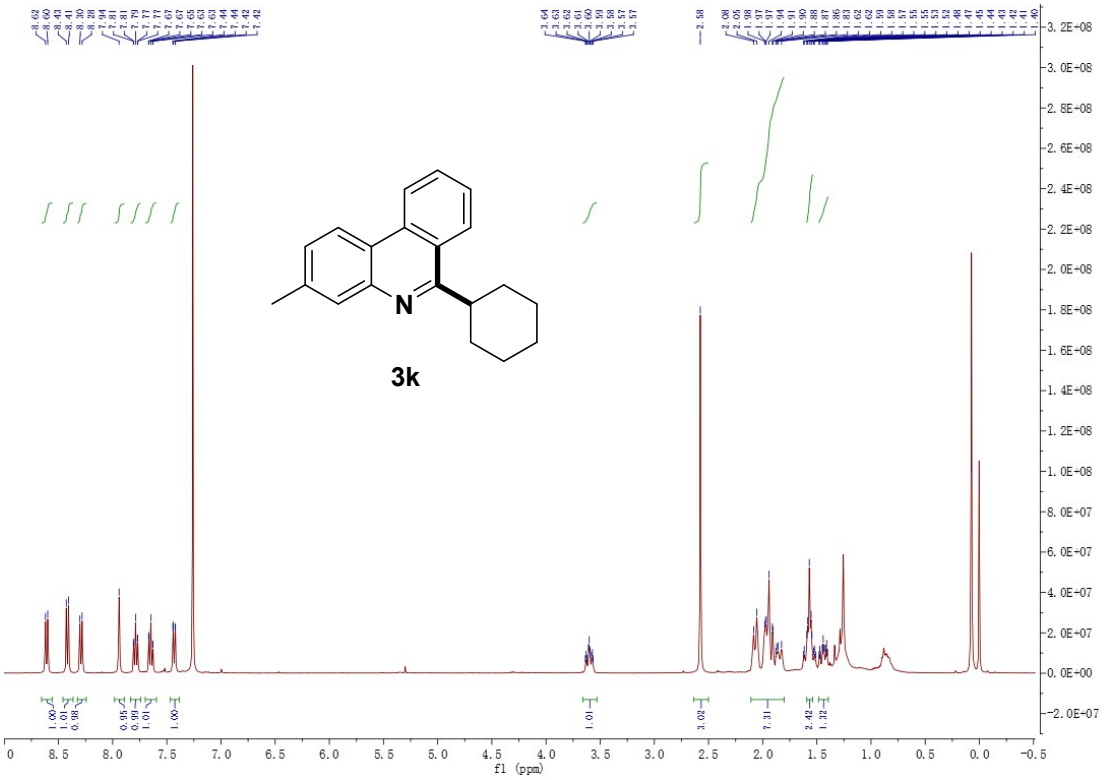
N
3j
f1 (ppm)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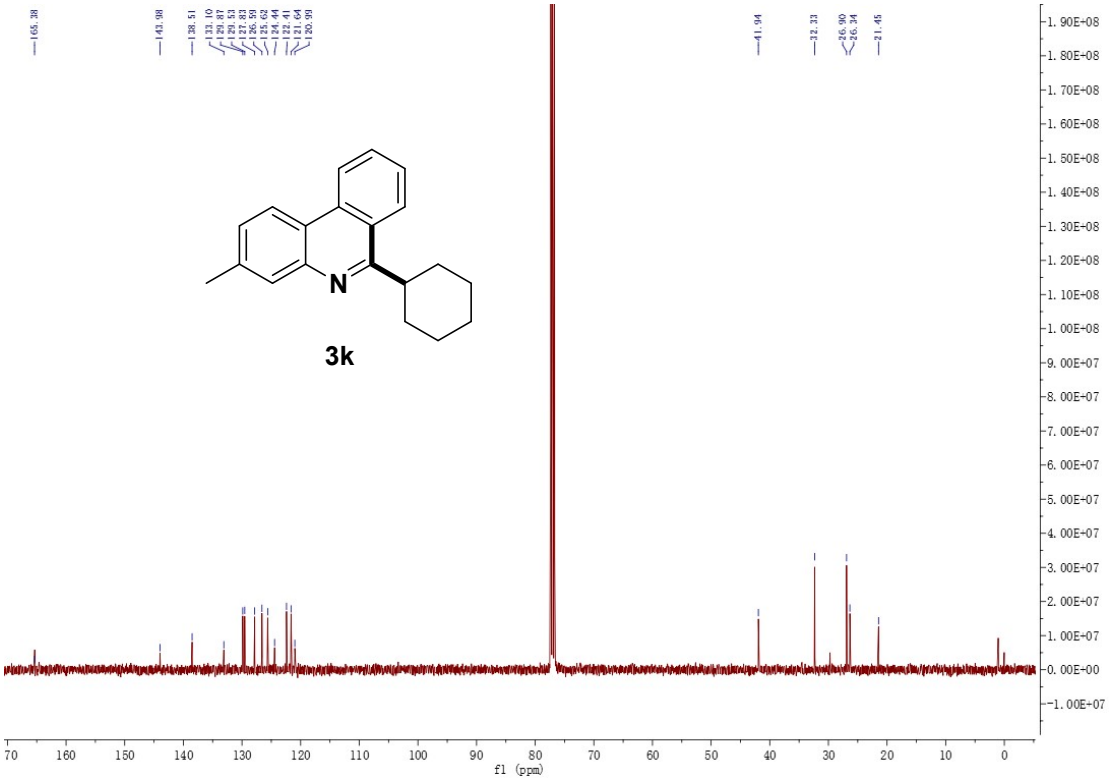
3k
fl (ppm)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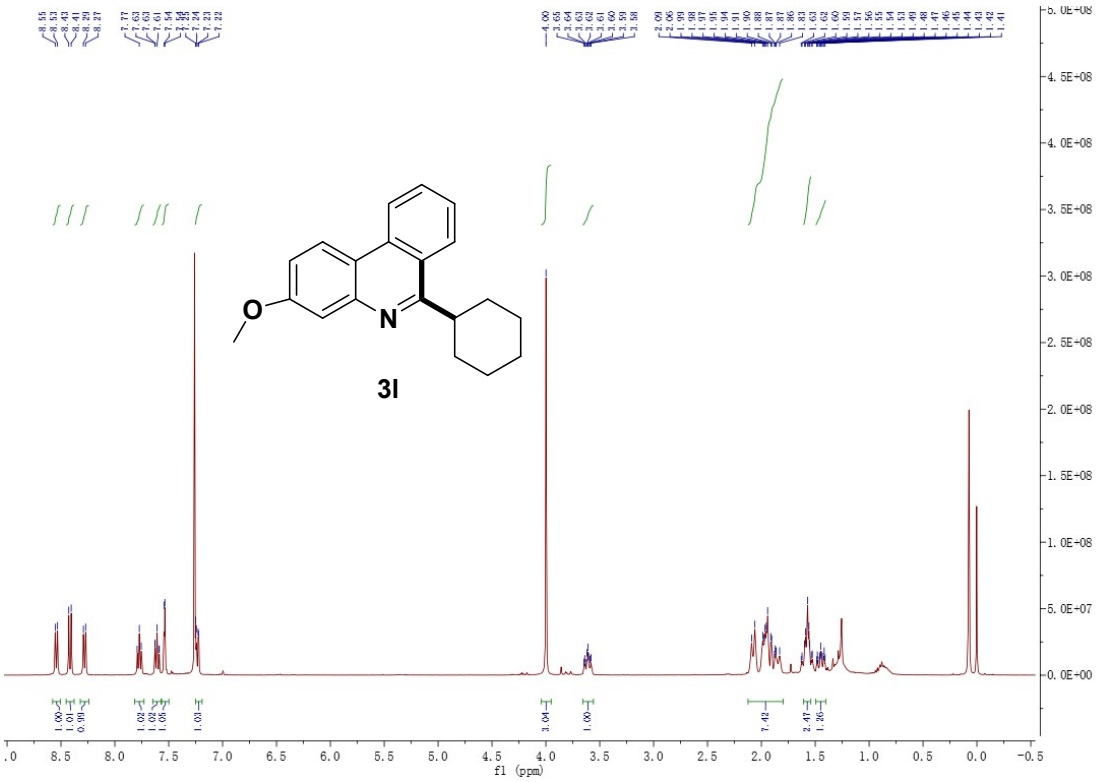
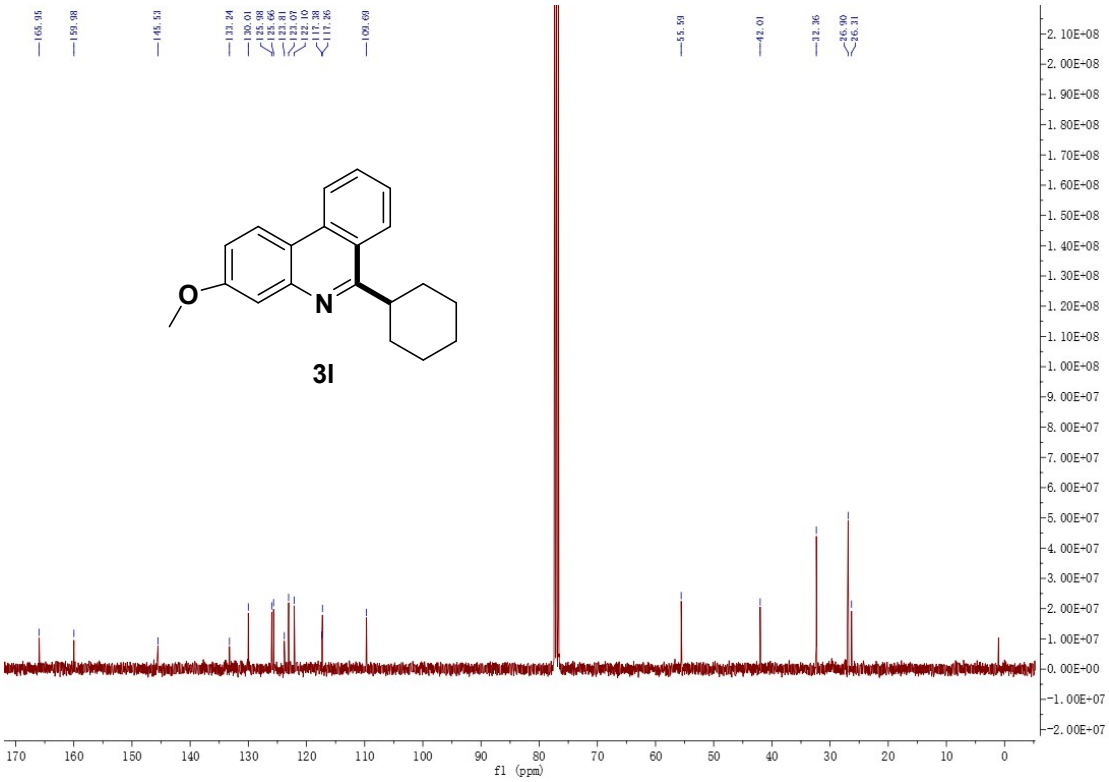
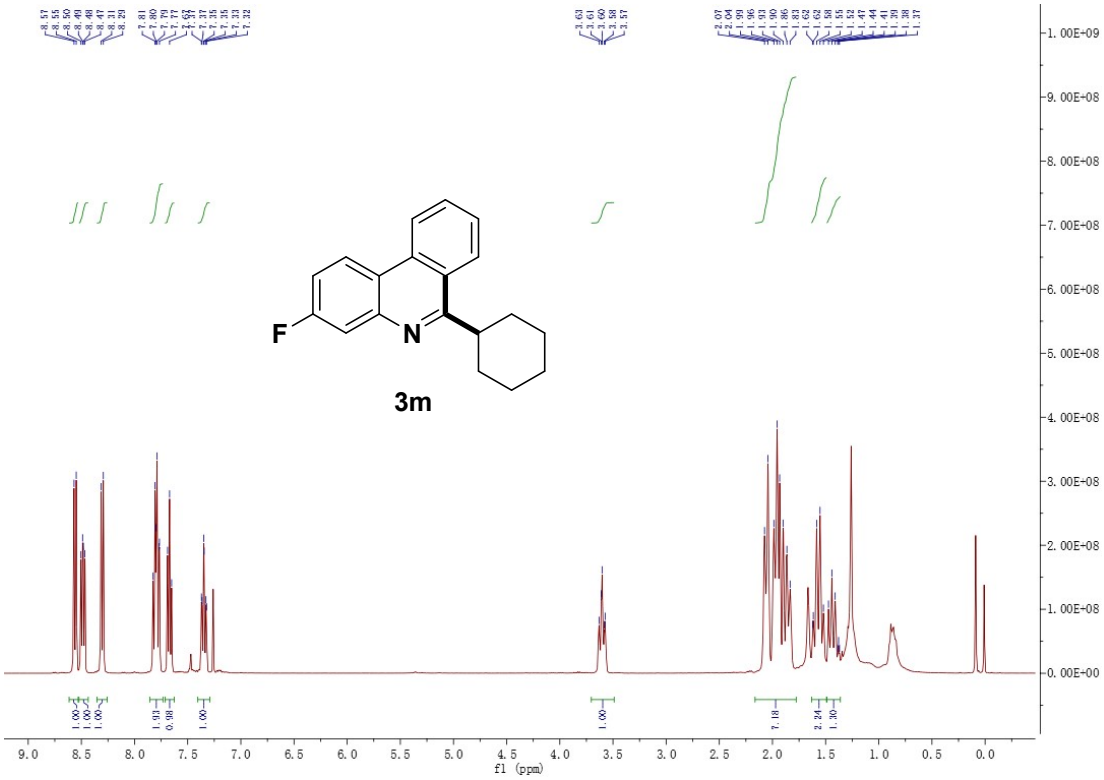
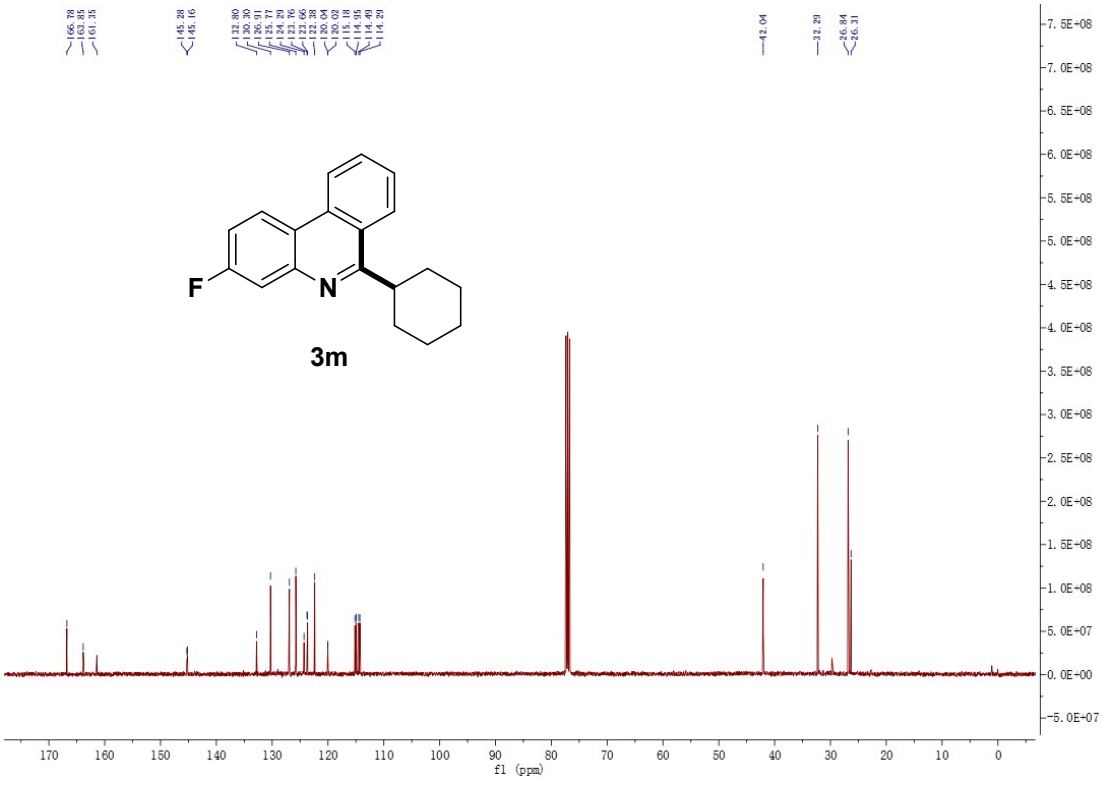
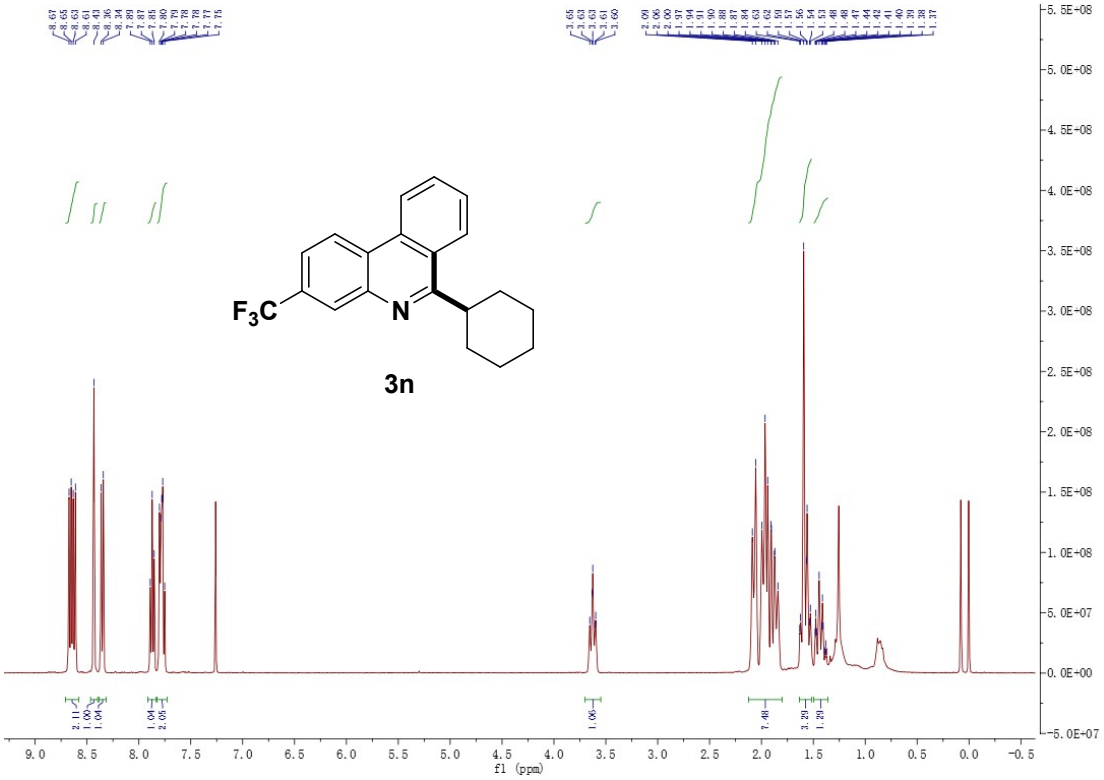
3k
fl (ppm)


O
N
3l
f1 (ppm)


O
N
3l
f1 (ppm)


F
N
3m
f1 (ppm)


F
N
3m
f1 (ppm)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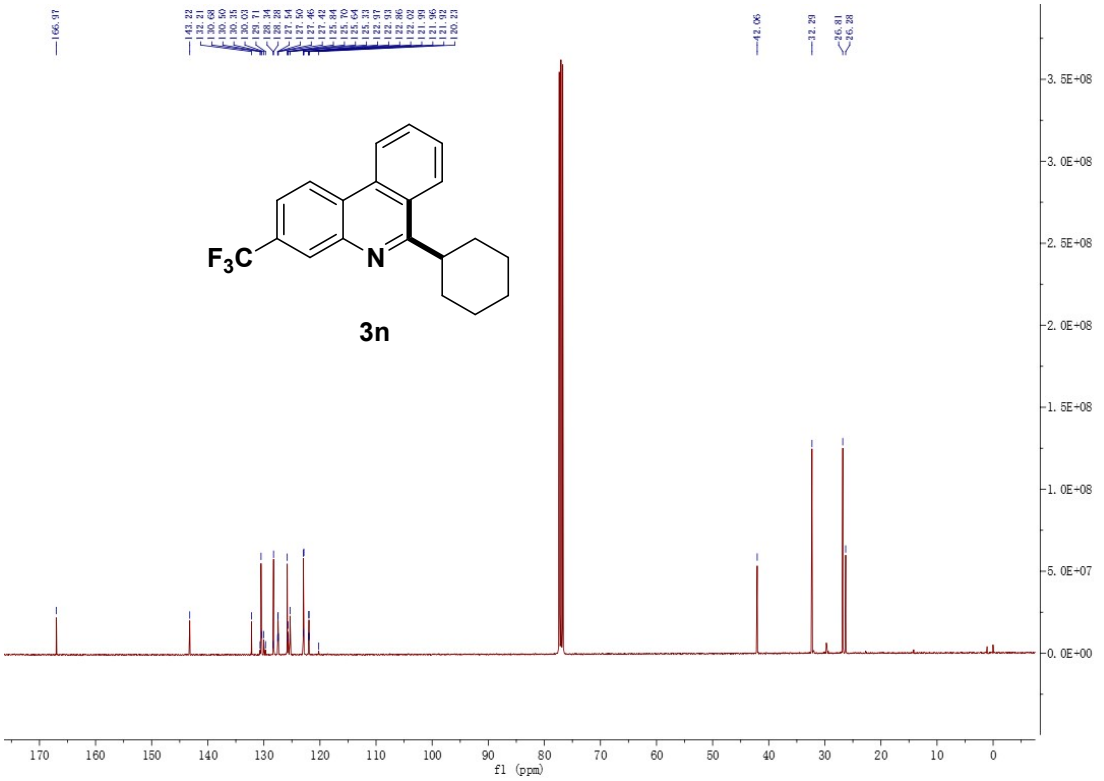
N
3n
fl (ppm)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N
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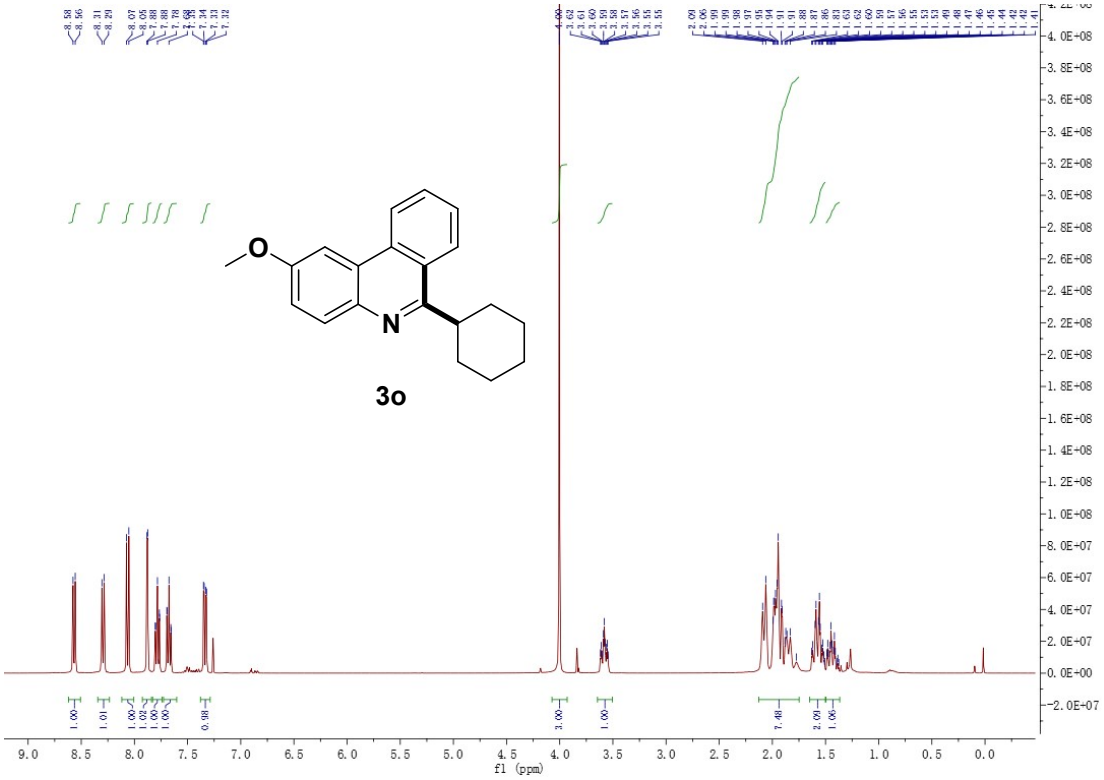
fl (ppm)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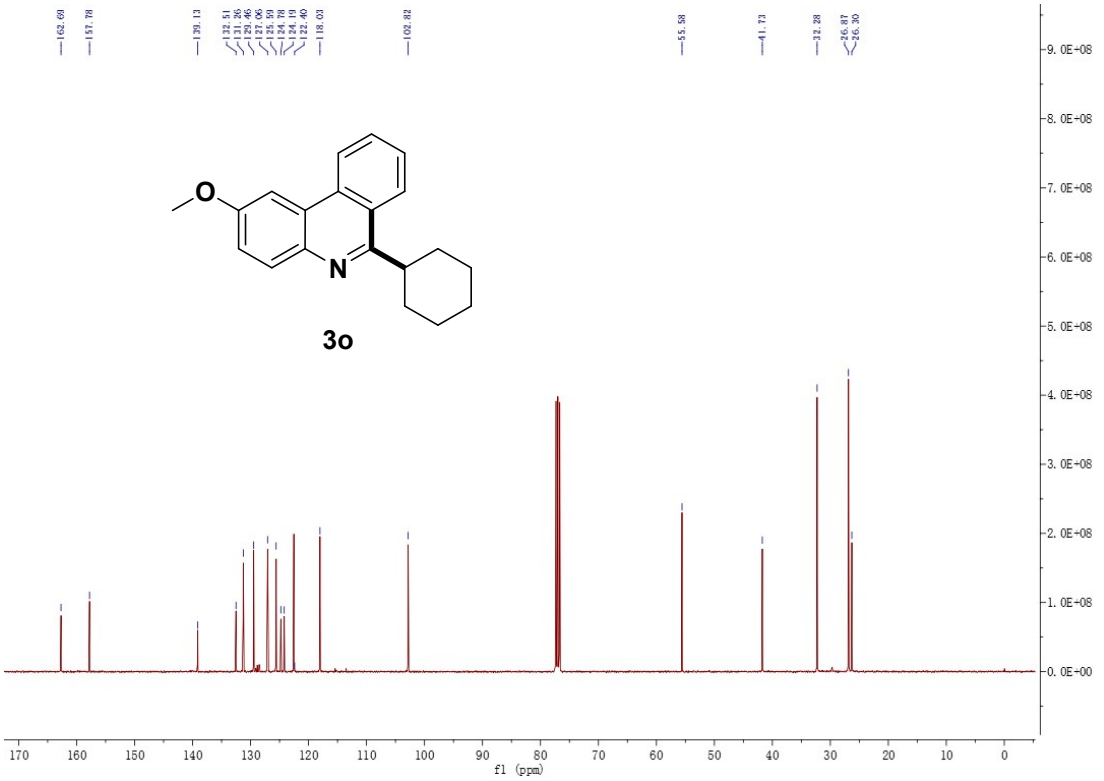
N
3o
f1 (ppm)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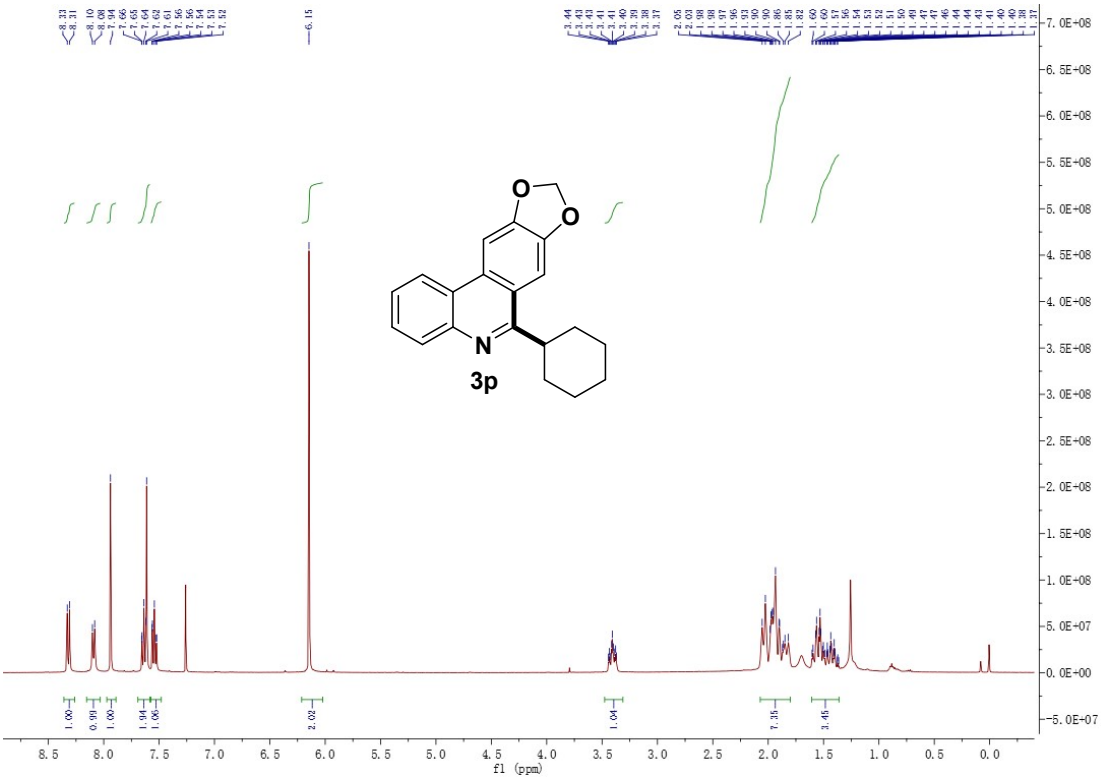
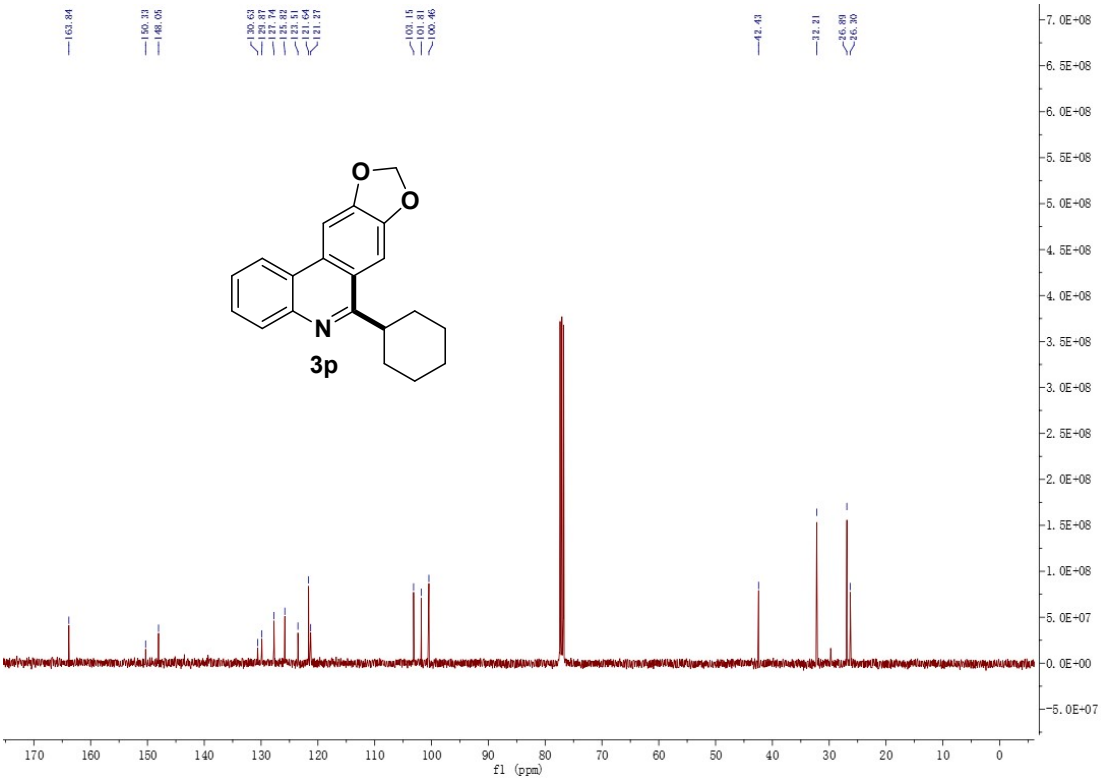
N
3o
f1 (ppm)


3p
fl (ppm)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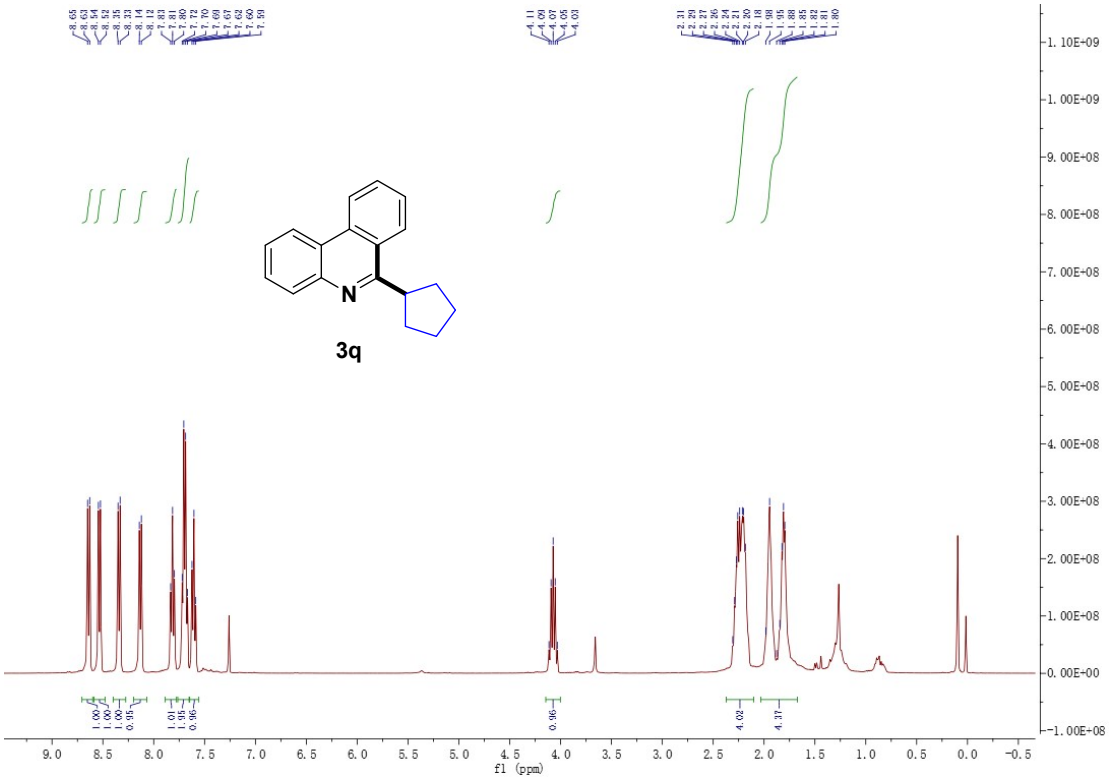
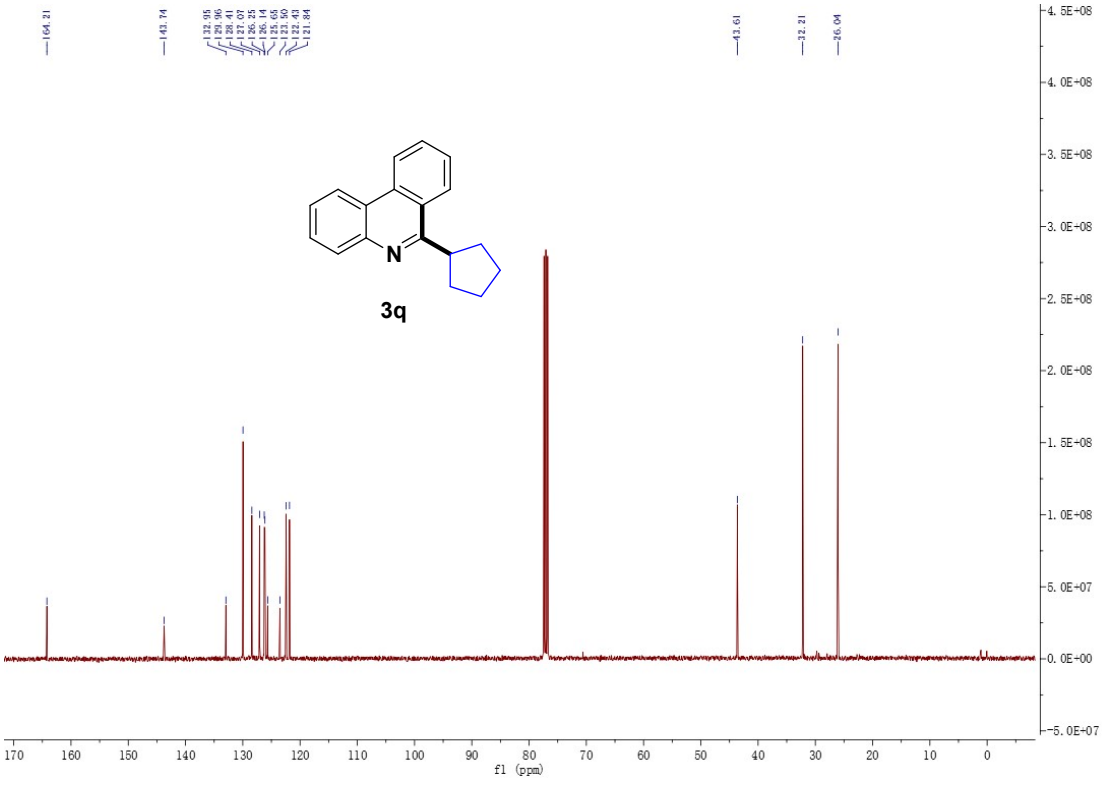
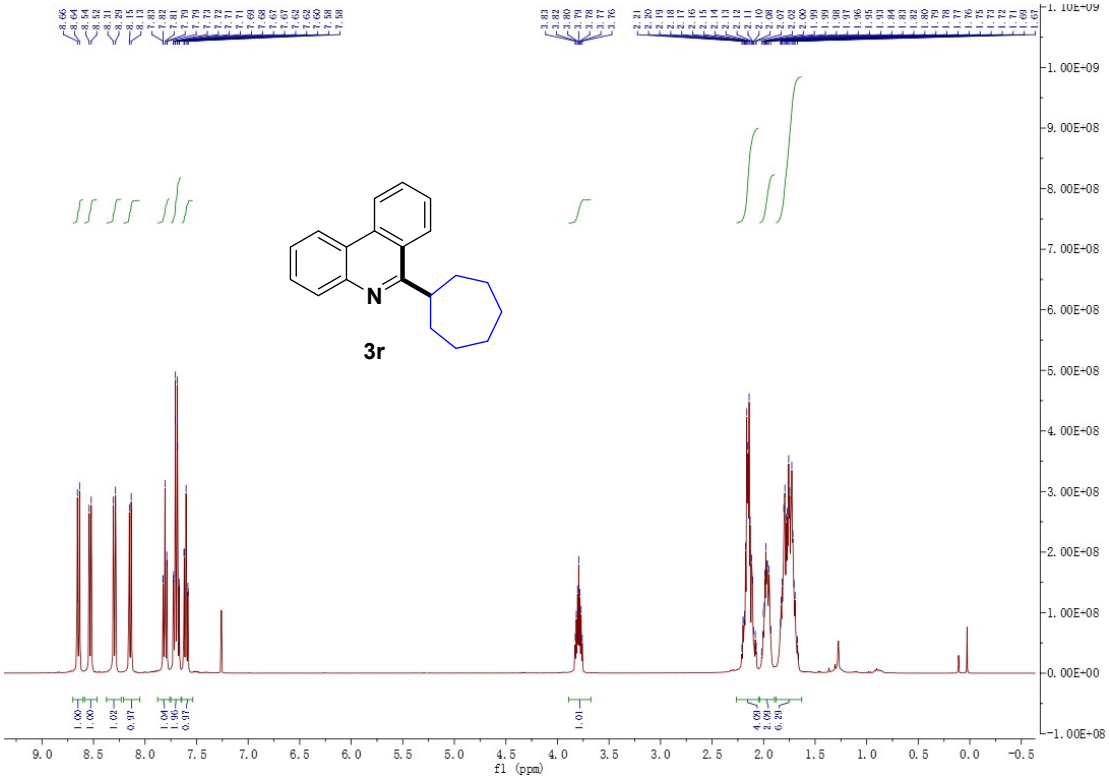
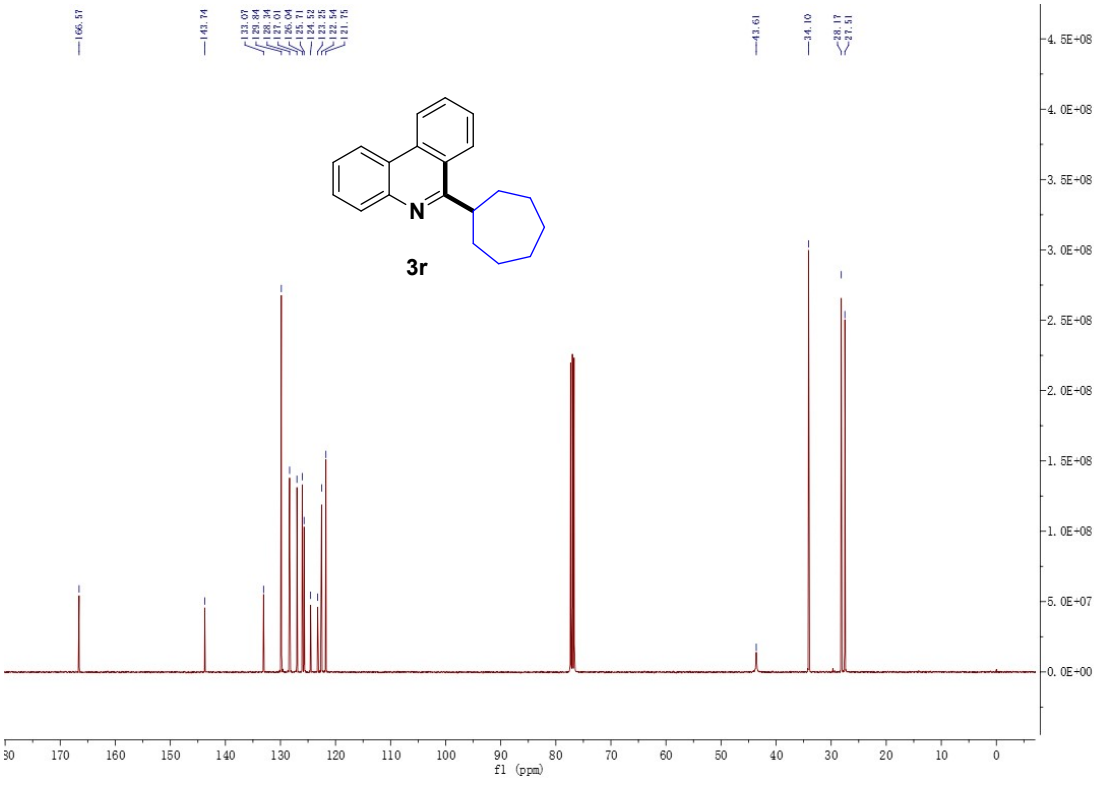
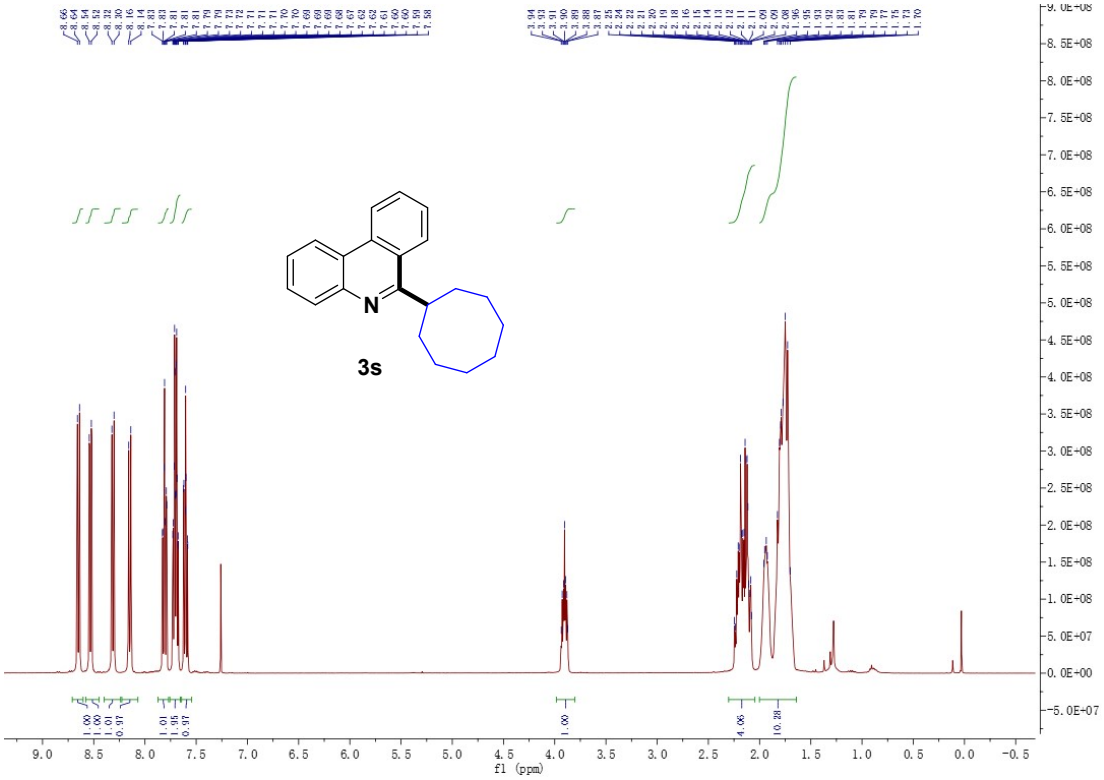
fl (ppm)

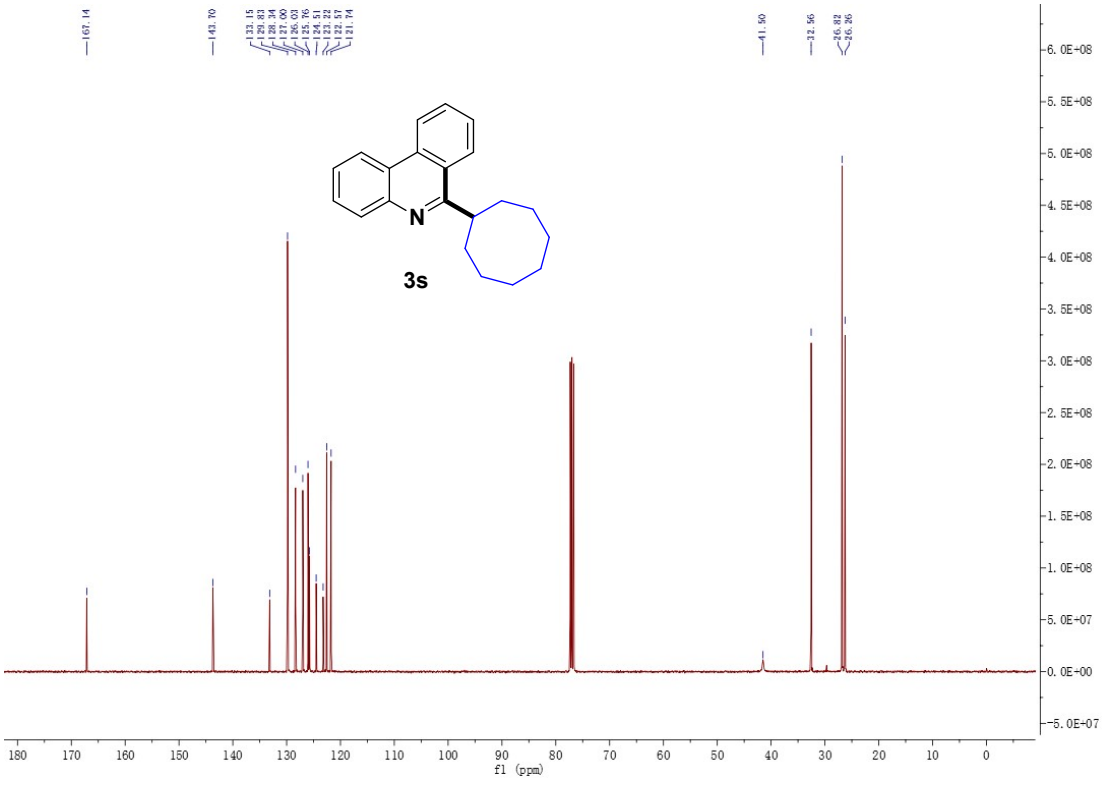

3q
f1 (ppm)

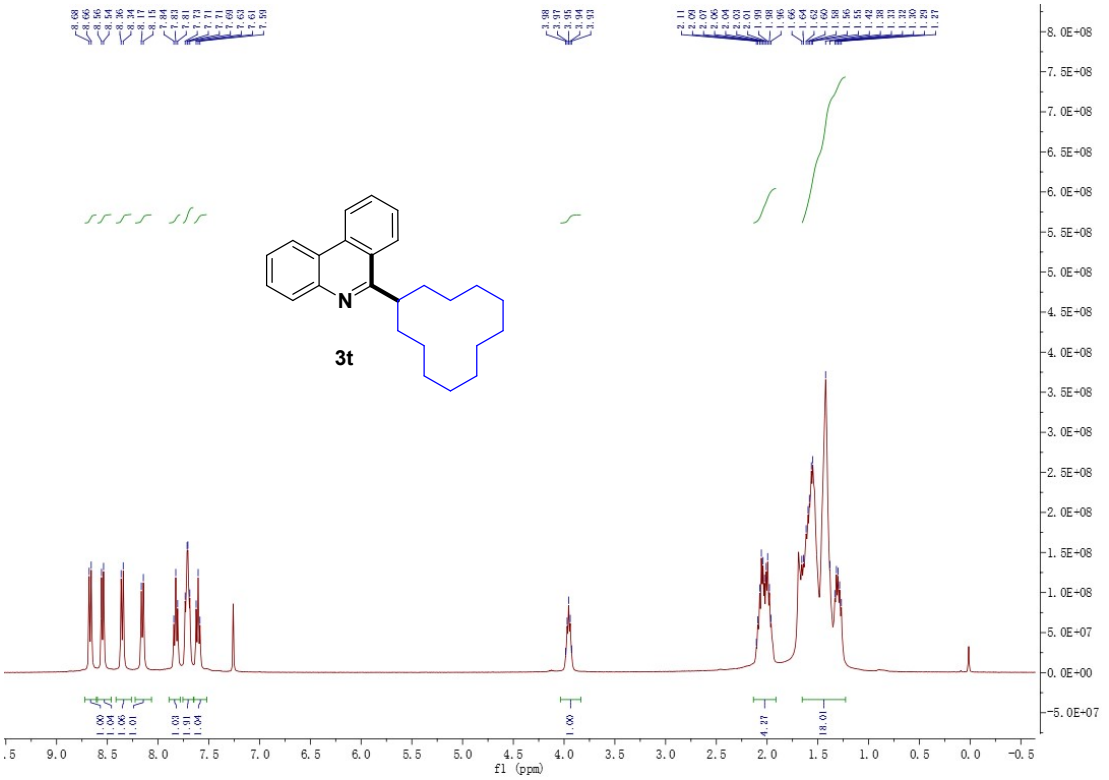

3q
f1 (ppm)

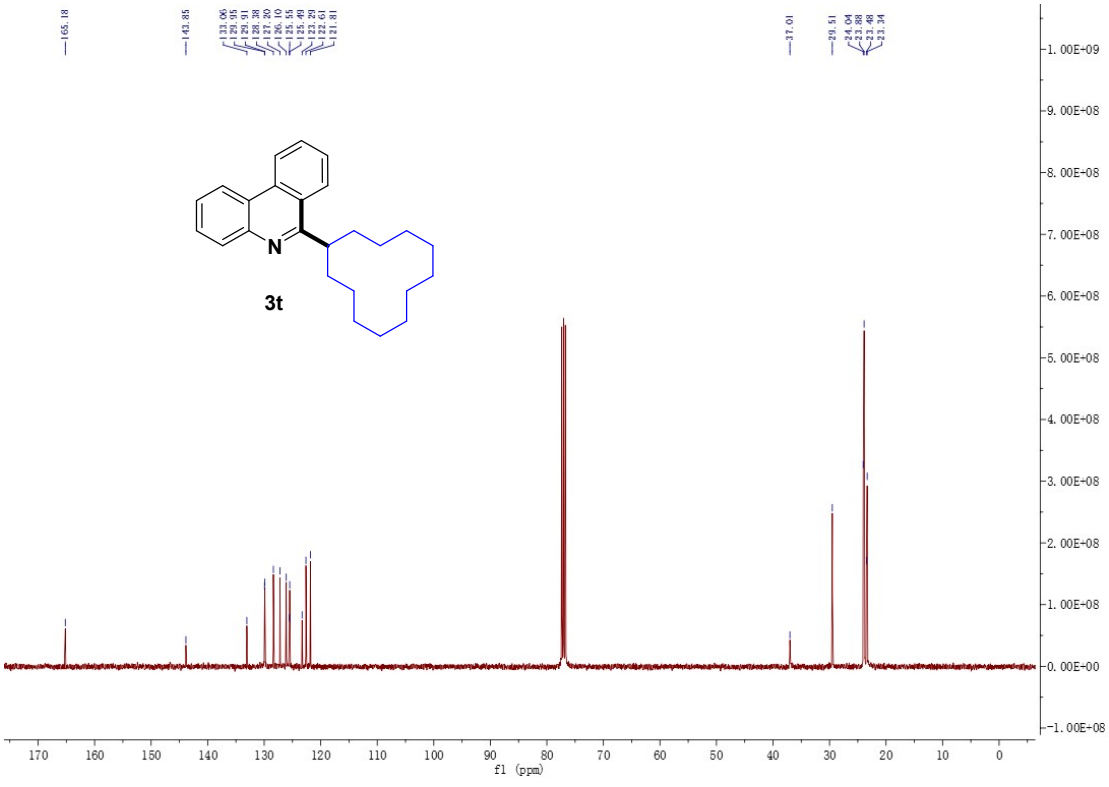

3r
fl (ppm)

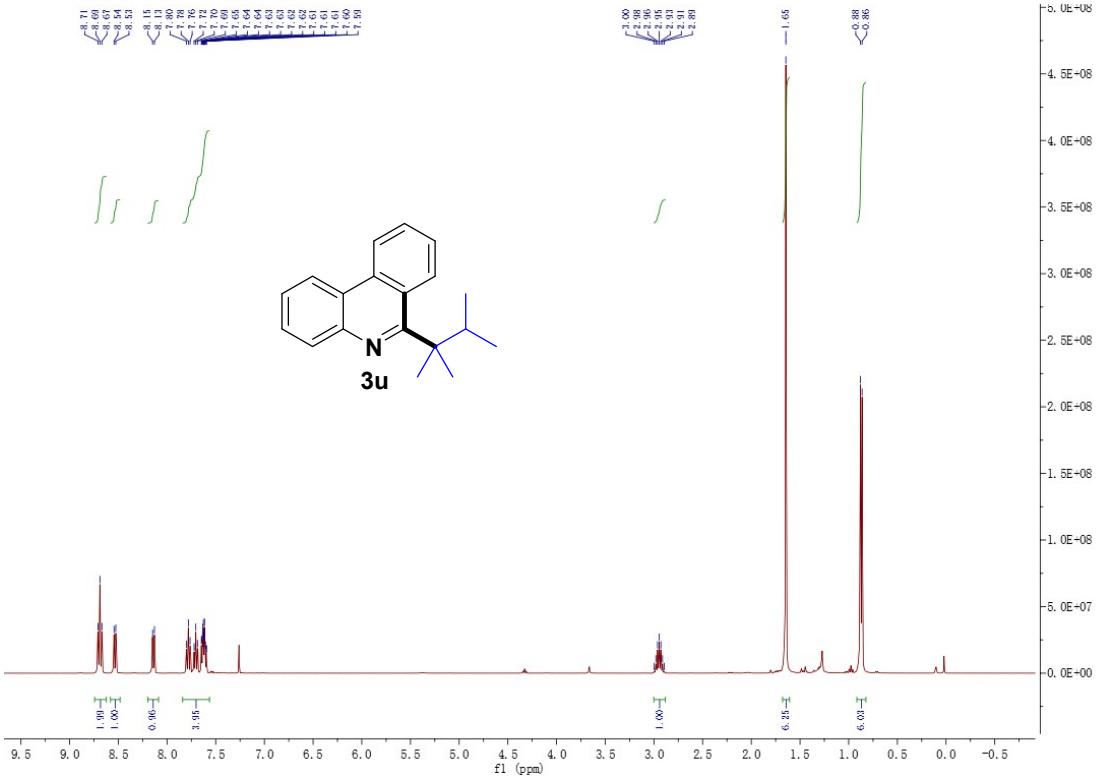

3r
fl (ppm)


3s
f1 (ppm)


3s
f1 (ppm)


3t
f1 (ppm)


3t
f1 (ppm)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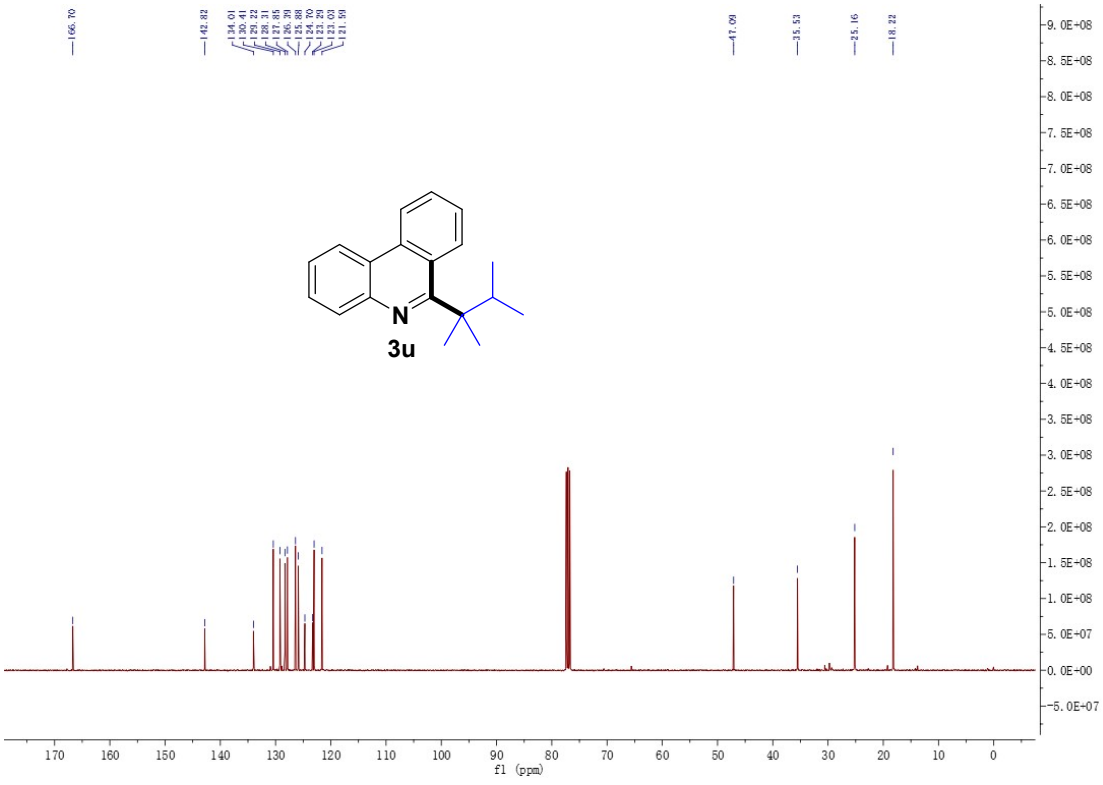
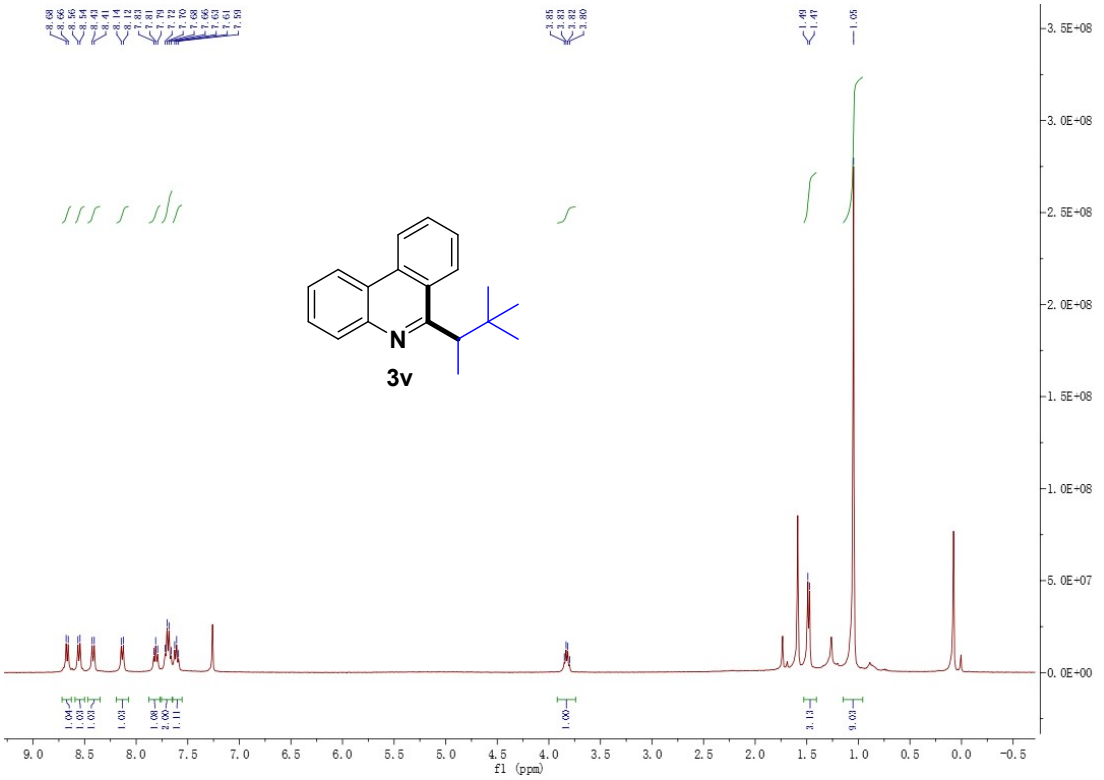
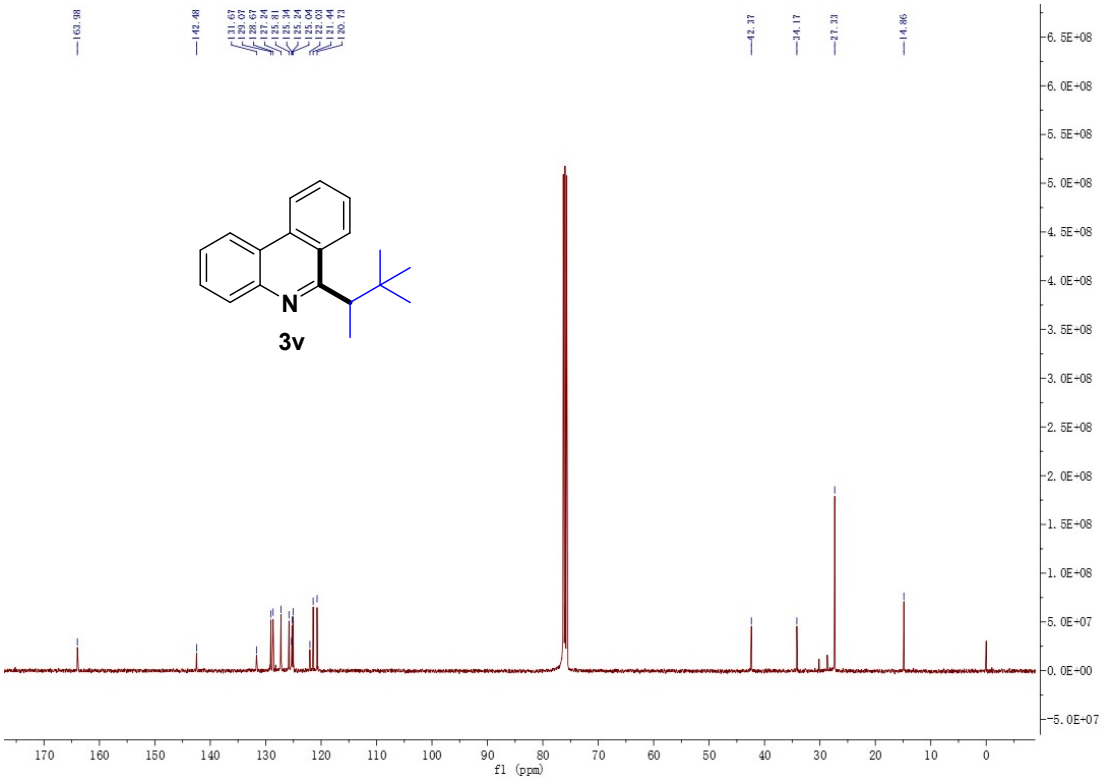

3u
f1 (ppm)


8.68
8.66
8.56
8.54
8.43
8.41
8.14
8.12
7.82
7.81
7.79
7.72
7.70
7.68
7.66
7.63
7.61
7.59
3.85
3.83
3.82
3.80
1.49
1.47
1.05
N
3v
1.04
1.03
1.03
1.03
1.08
2.00
1.11
1.00
3.13
9.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)
3.5E+08
3.0E+08
2.5E+08
2.0E+08
1.5E+08
1.0E+08
5.0E+07
0.0E+00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142.48
131.67
129.07
128.67
127.24
125.81
125.34
125.24
122.03
121.44
120.73
42.37
34.17
27.33
14.86
N
3v
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
6.5E+08
6.0E+08
5.5E+08
5.0E+08
4.5E+08
4.0E+08
3.5E+08
3.0E+08
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2.0E+08
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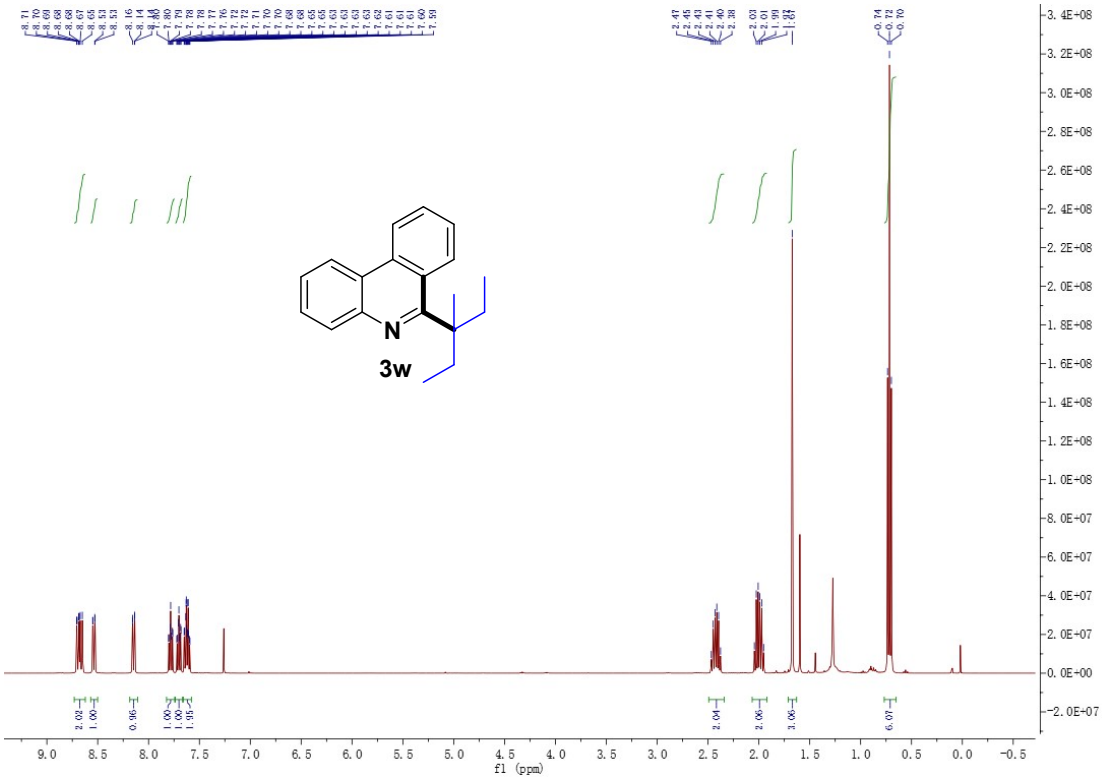
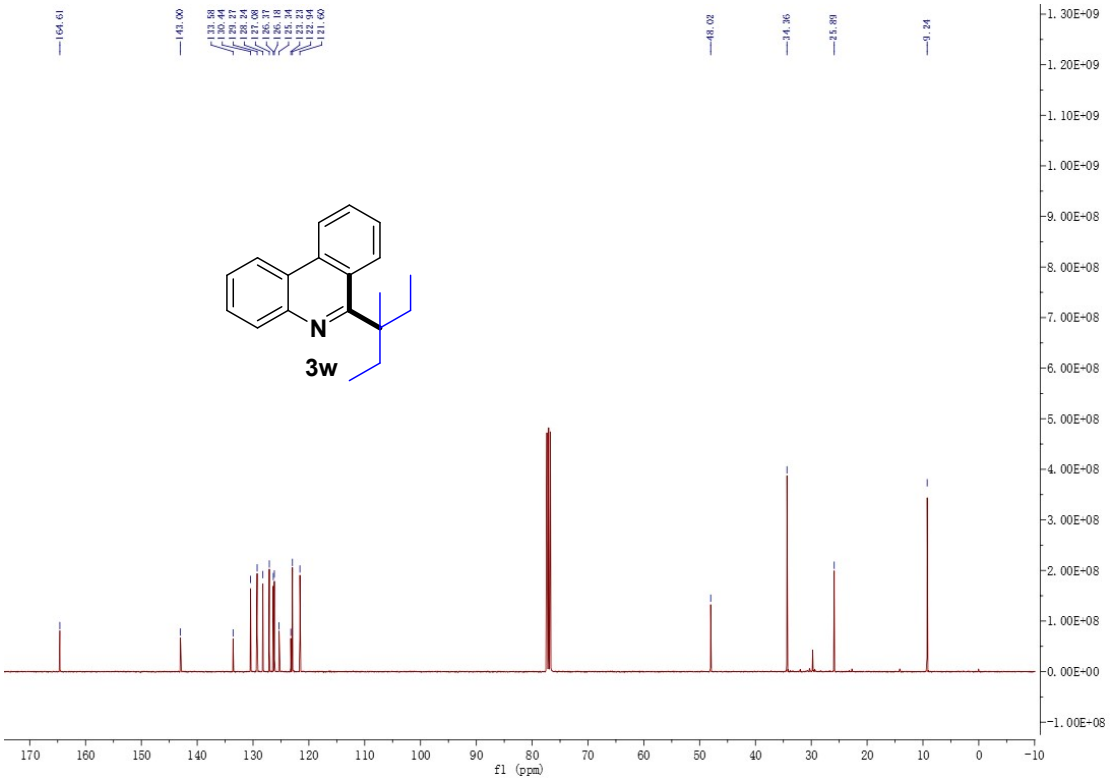
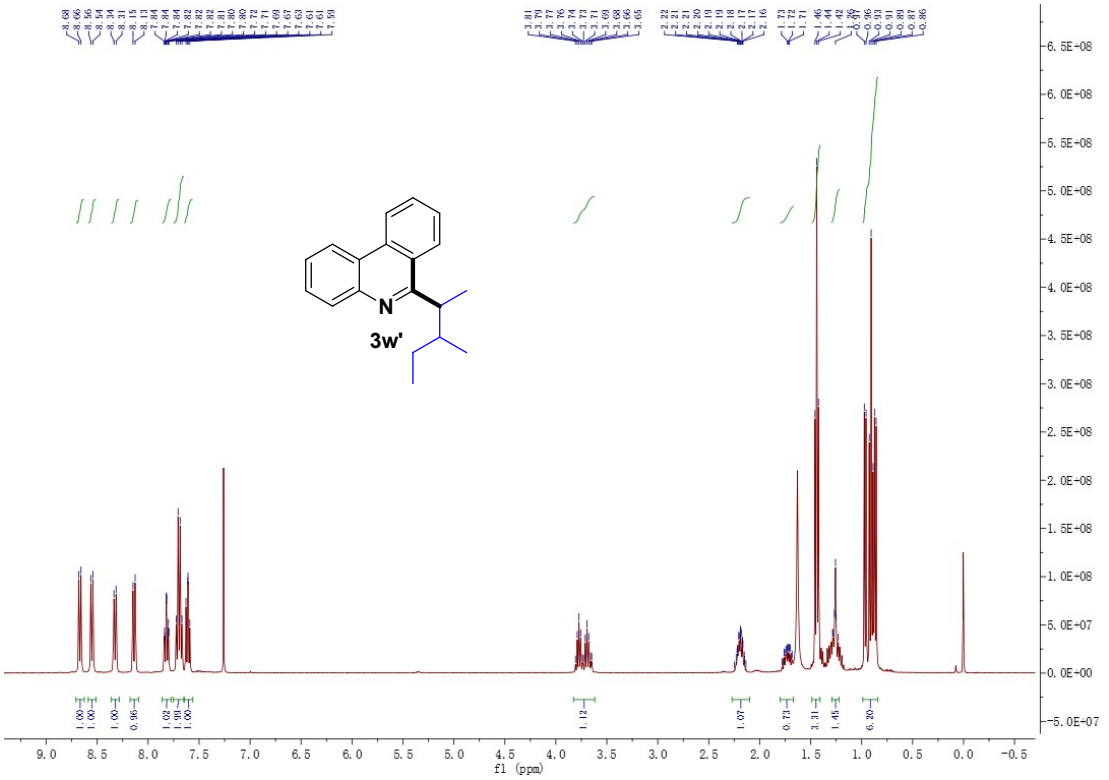
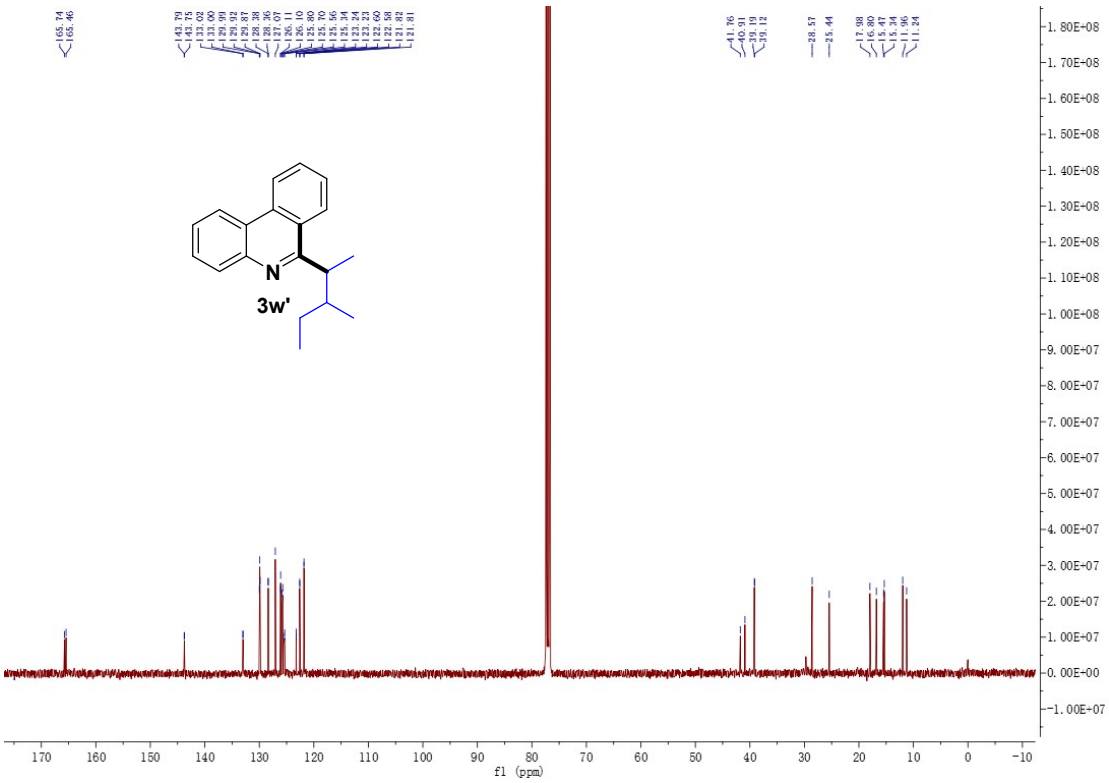
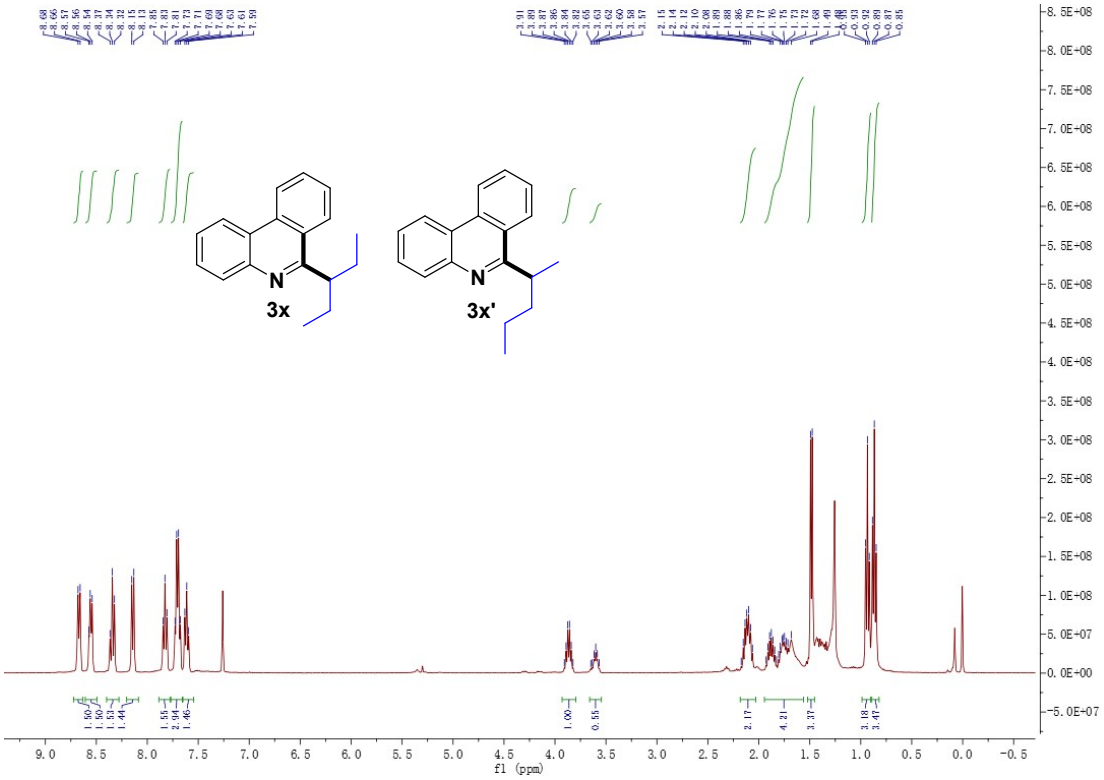
1.0E+08
5.0E+07
0.0E+00
-5.0E+07

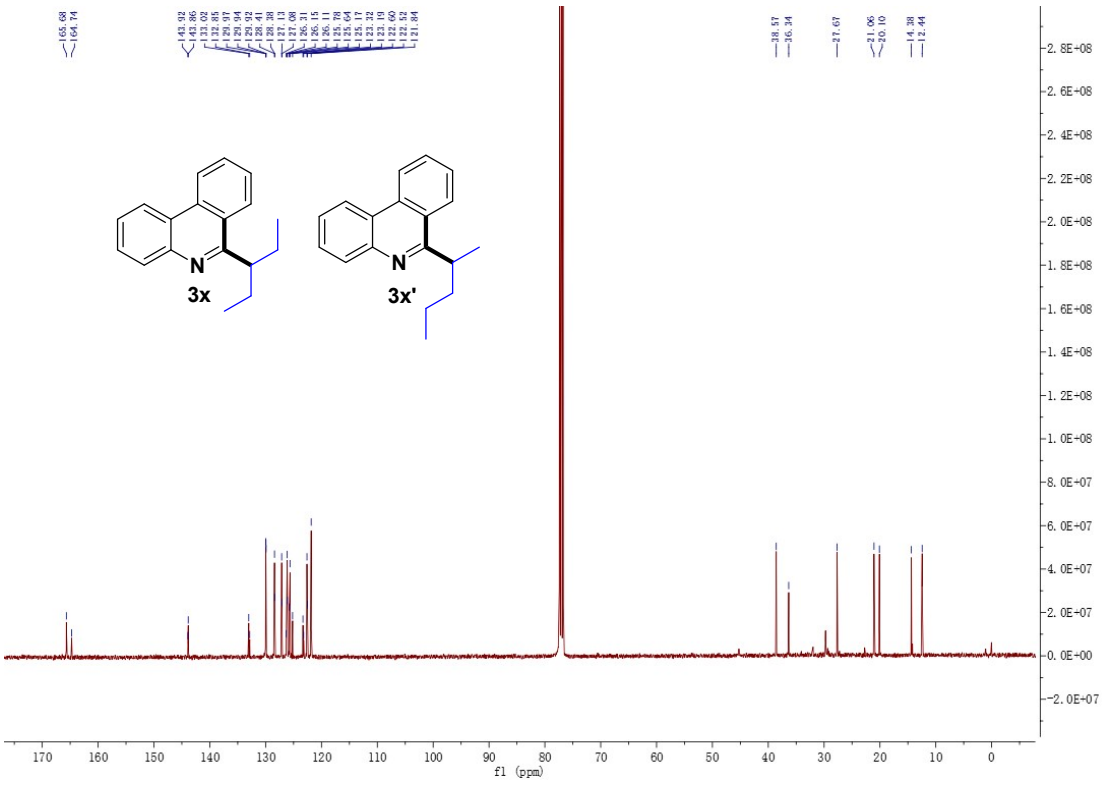

N
3w
f1 (ppm)

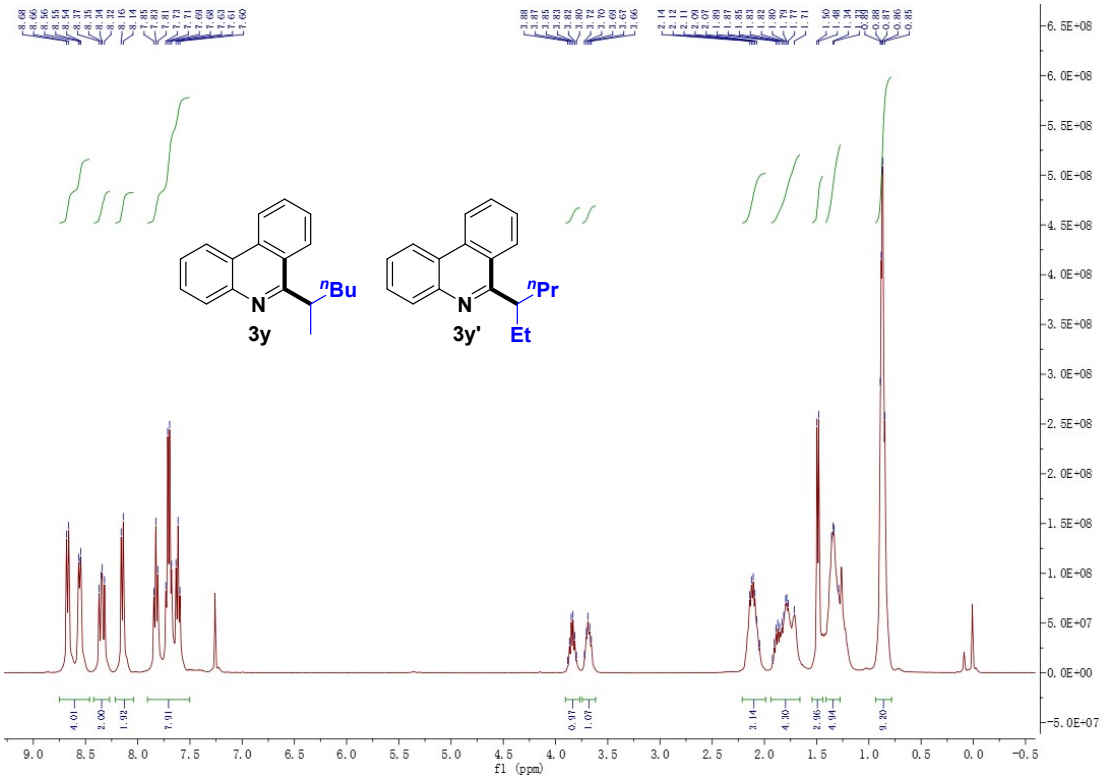

N
3w
f1 (ppm)

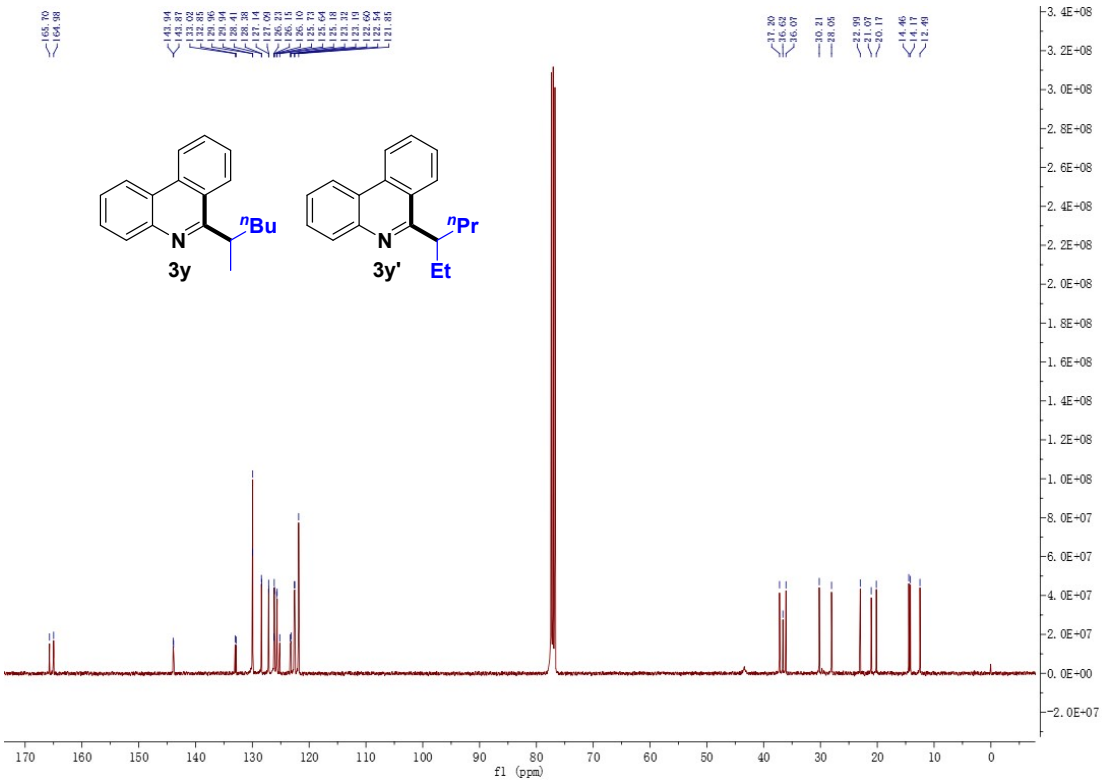

3w'
f1 (ppm)


3w'
f1 (ppm)


3x
3x'
f1 (ppm)


3x
3x'
f1 (ppm)


nBu
N
3y
nPr
N
3y'
Et
f1 (ppm)


nBu
N
3y
nPr
N
3y'
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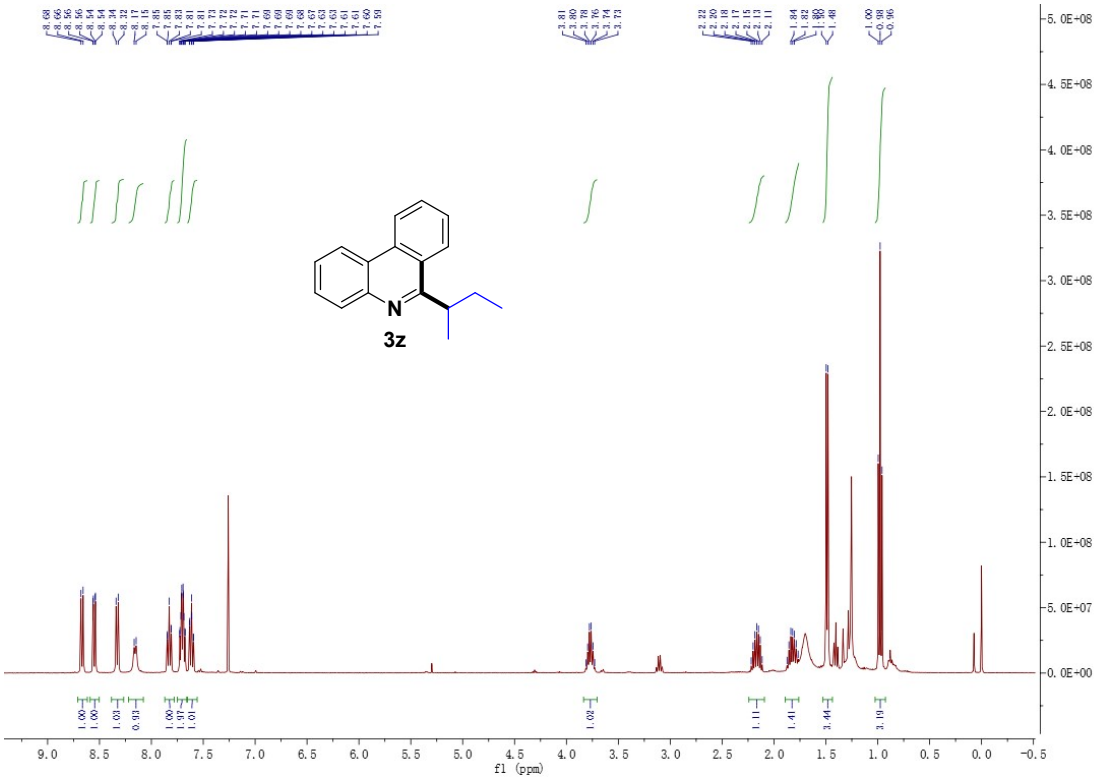
f1 (ppm)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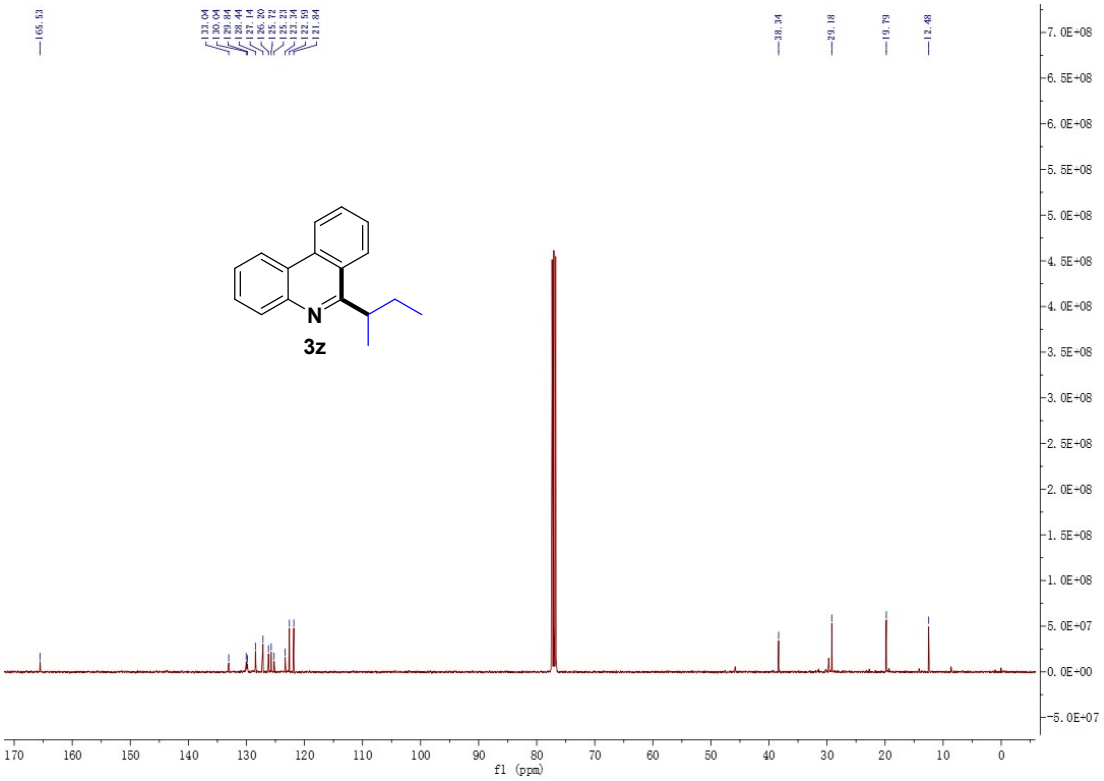
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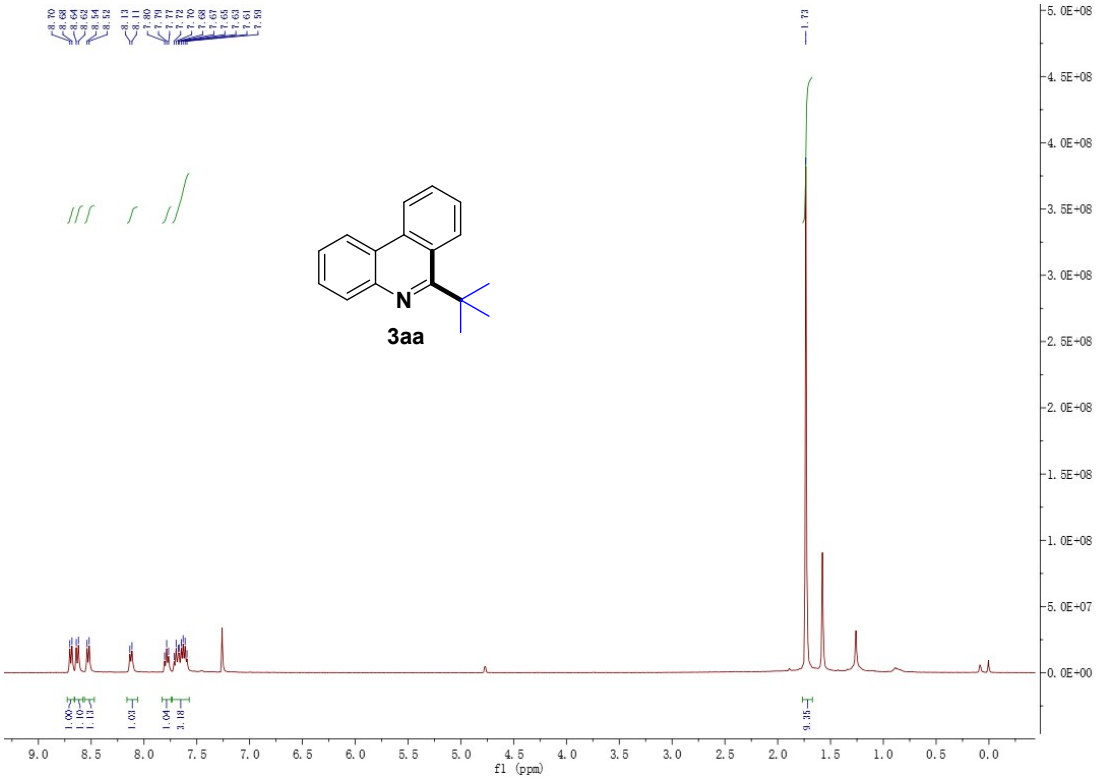
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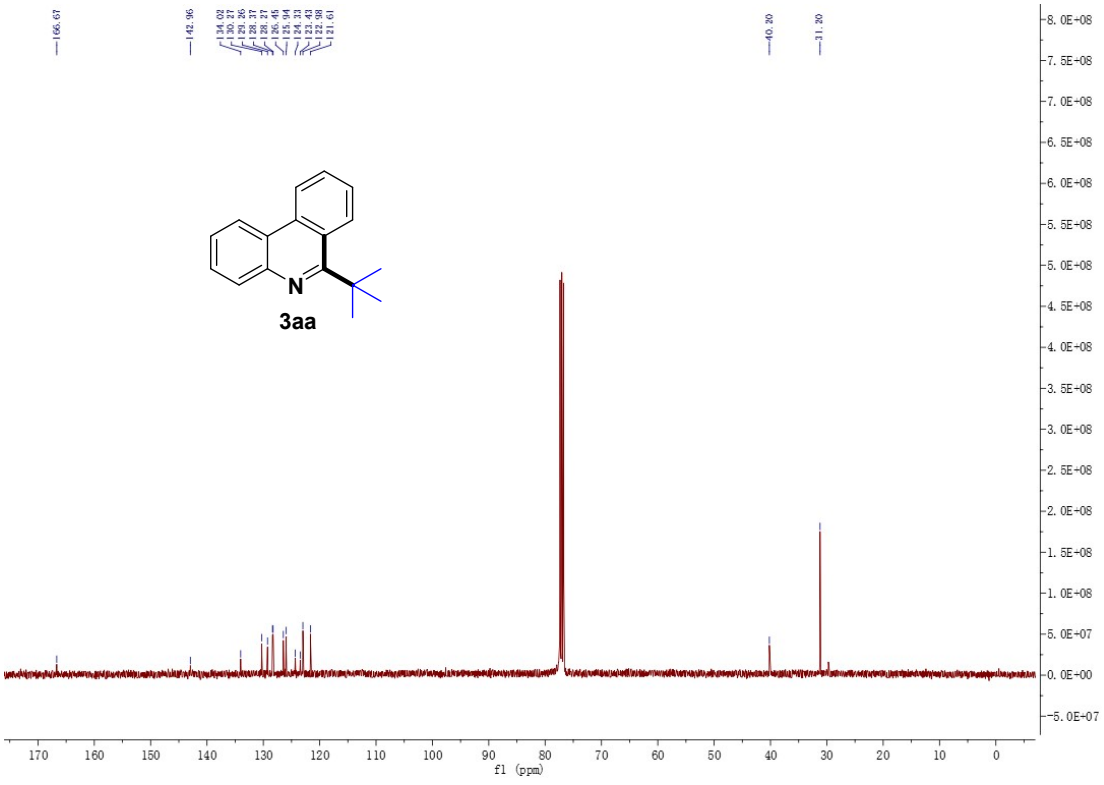
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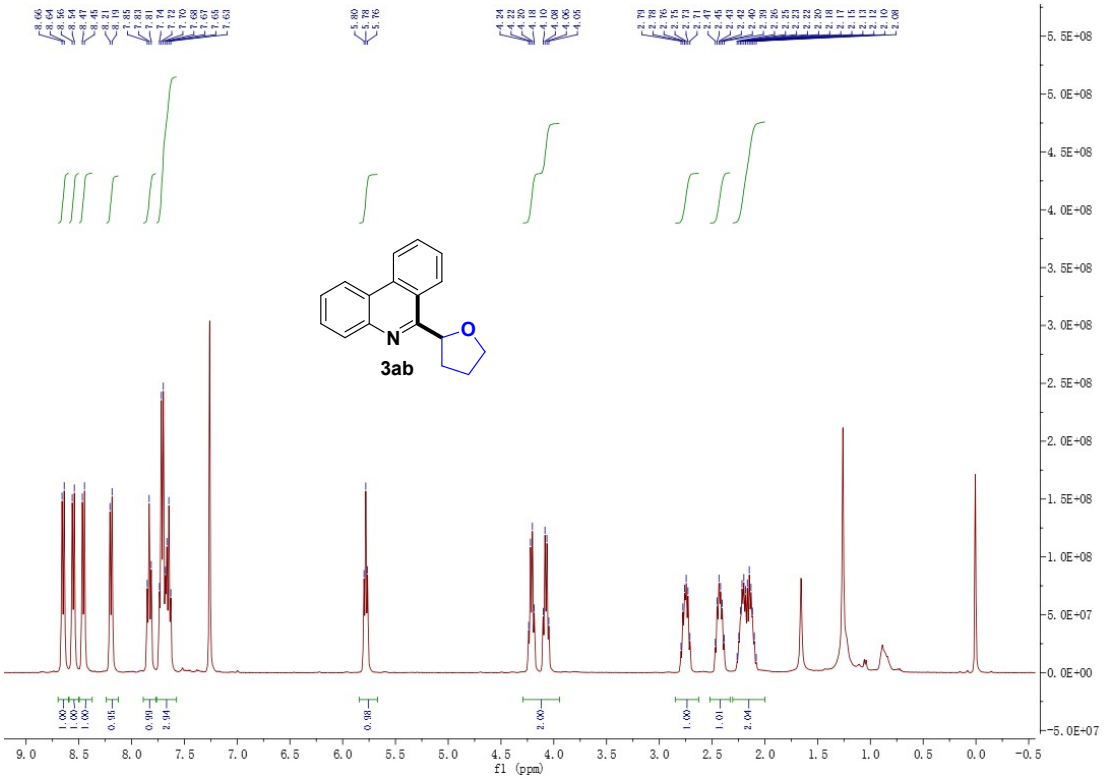
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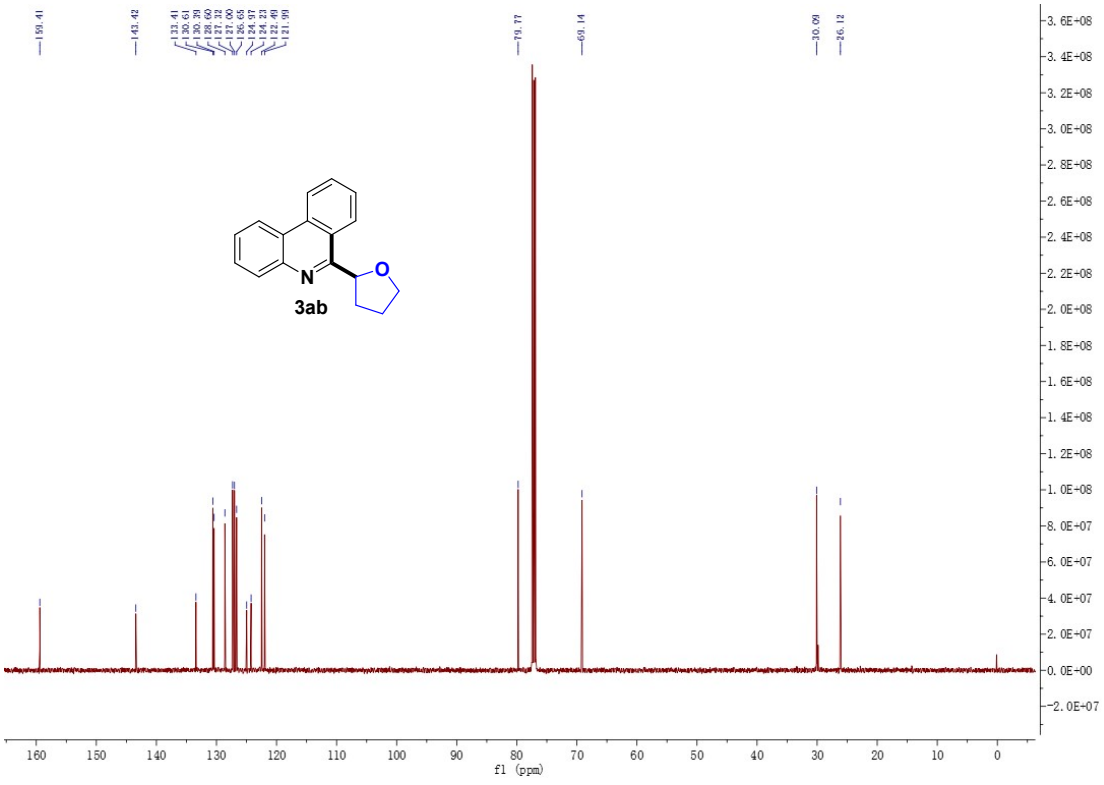
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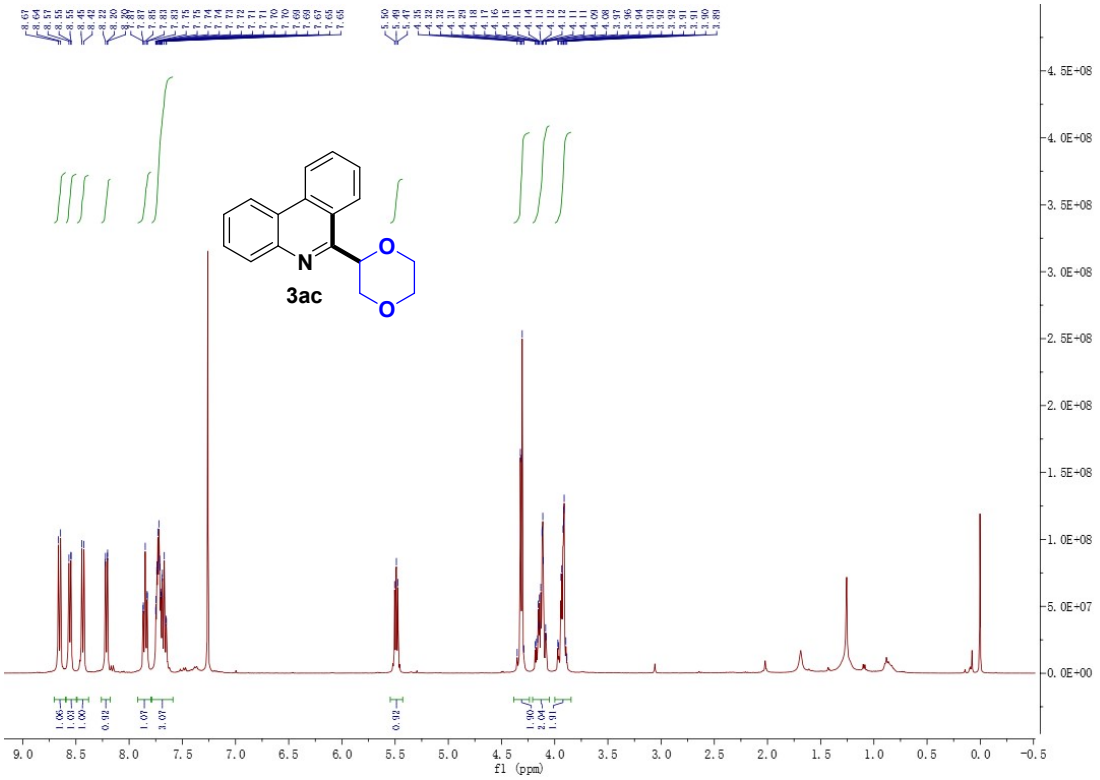
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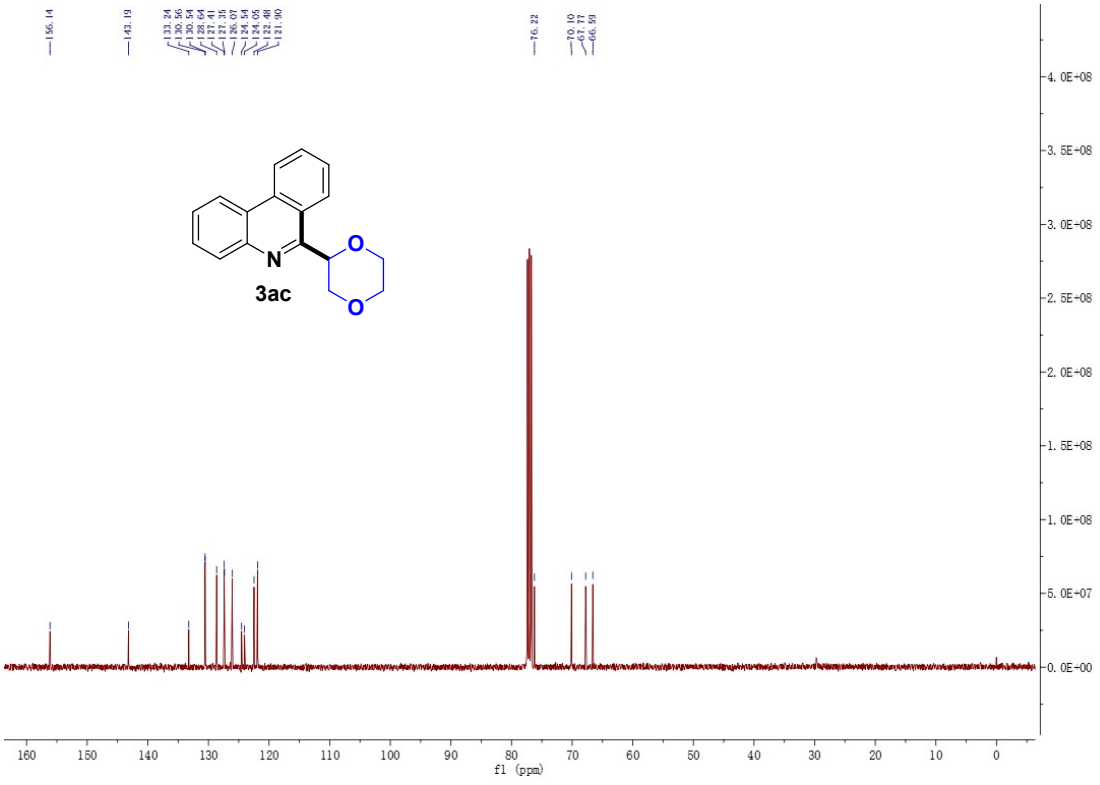
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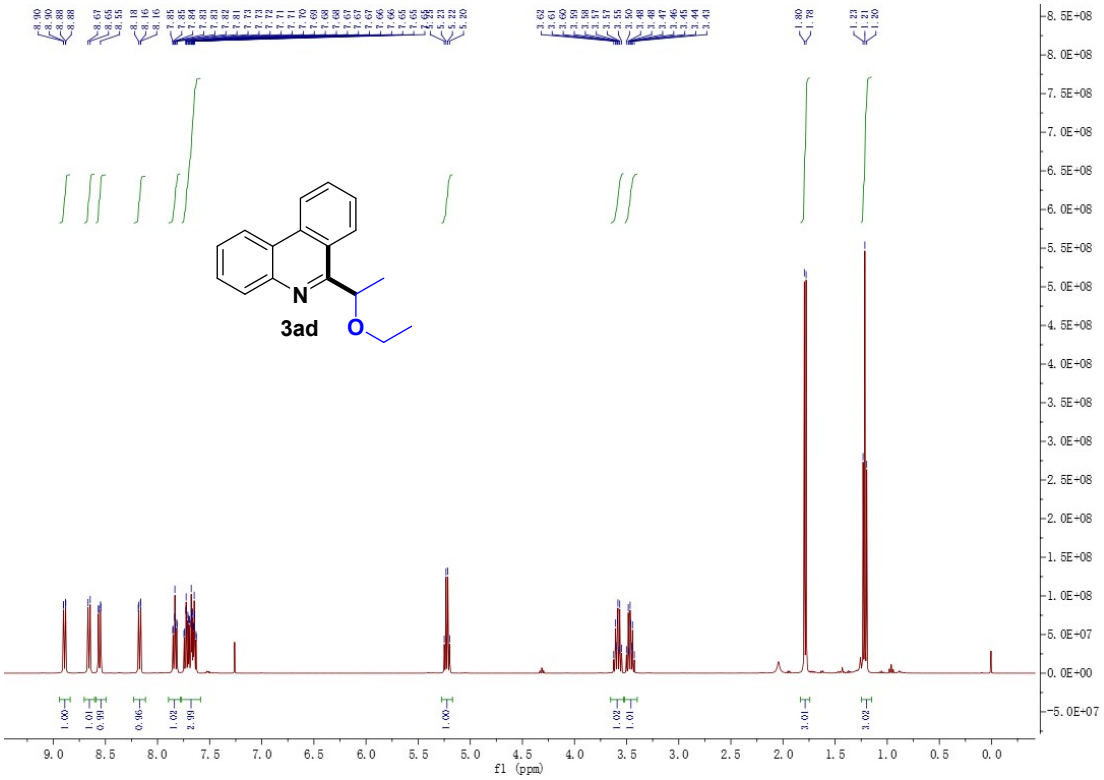
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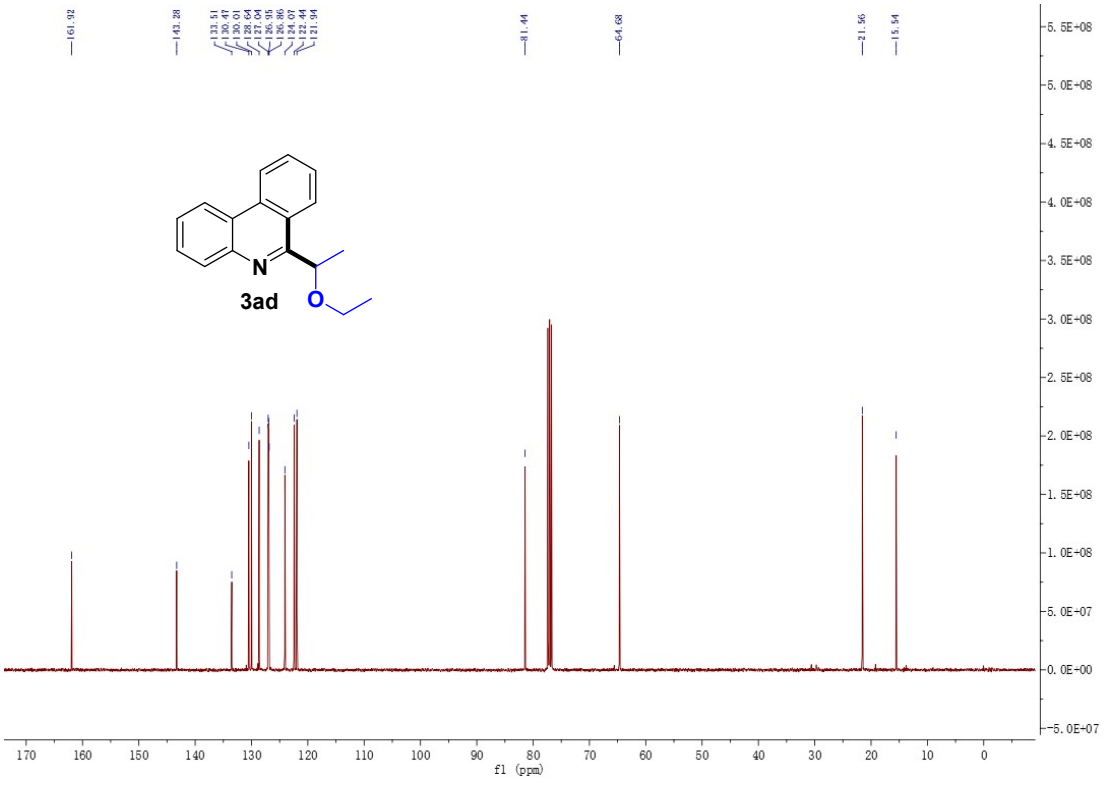
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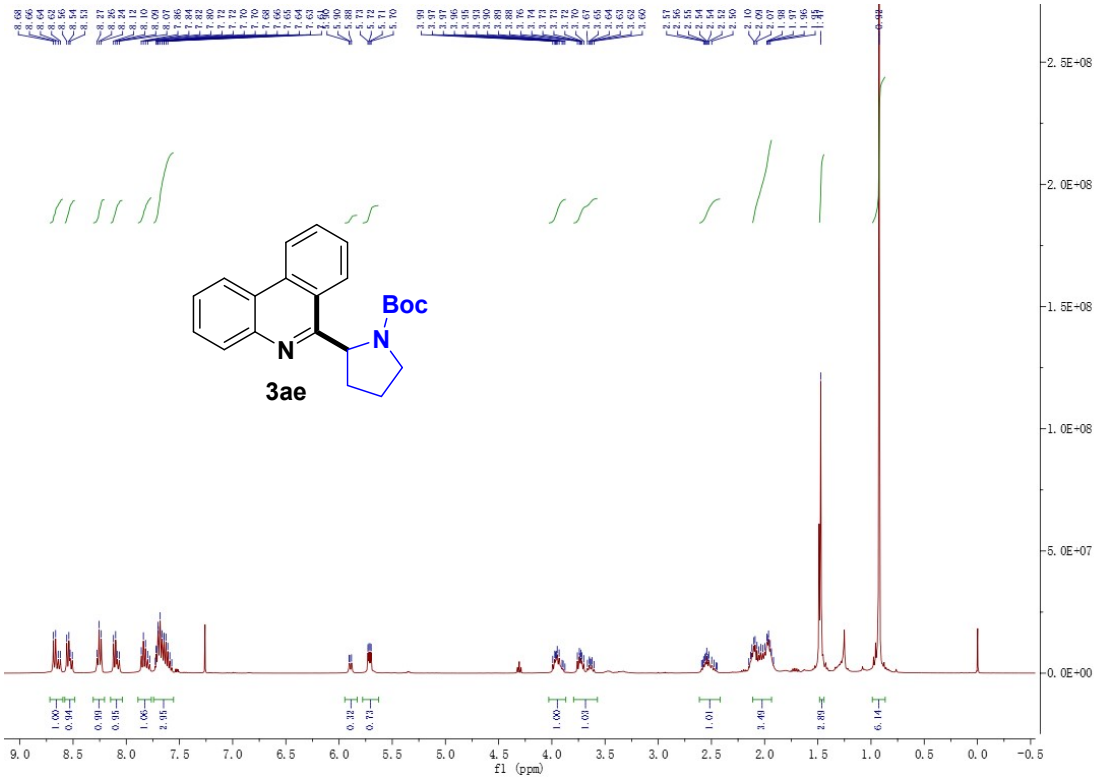
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N
3ae
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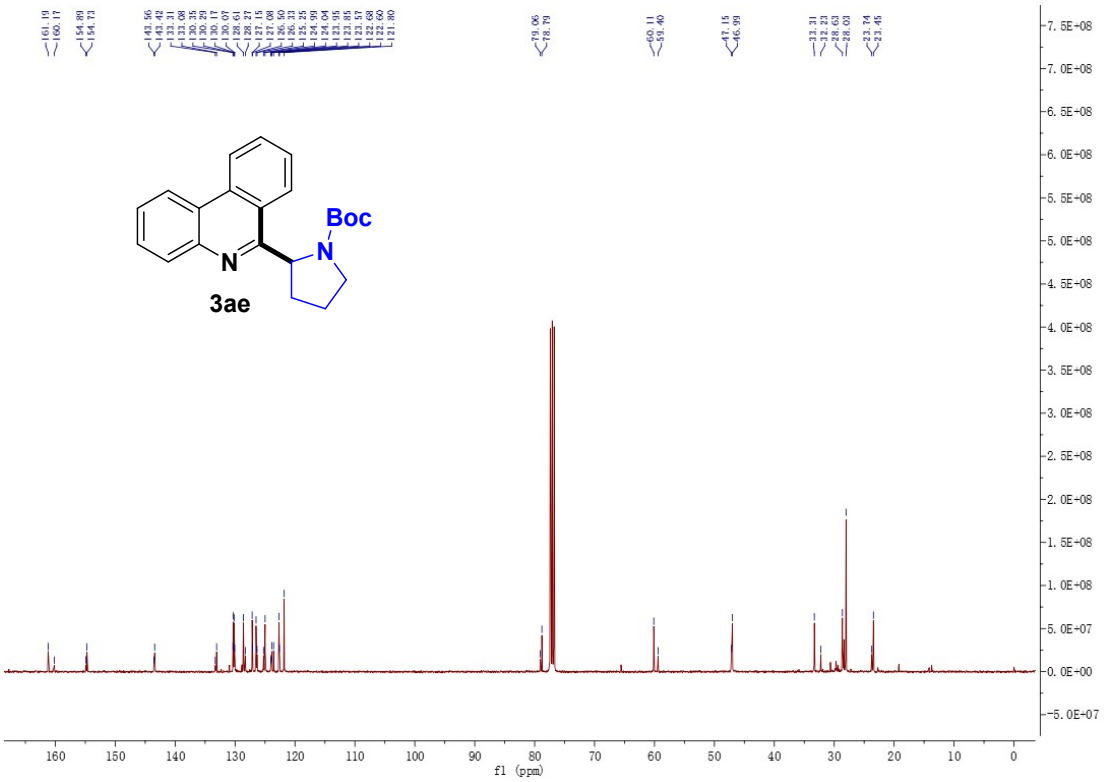
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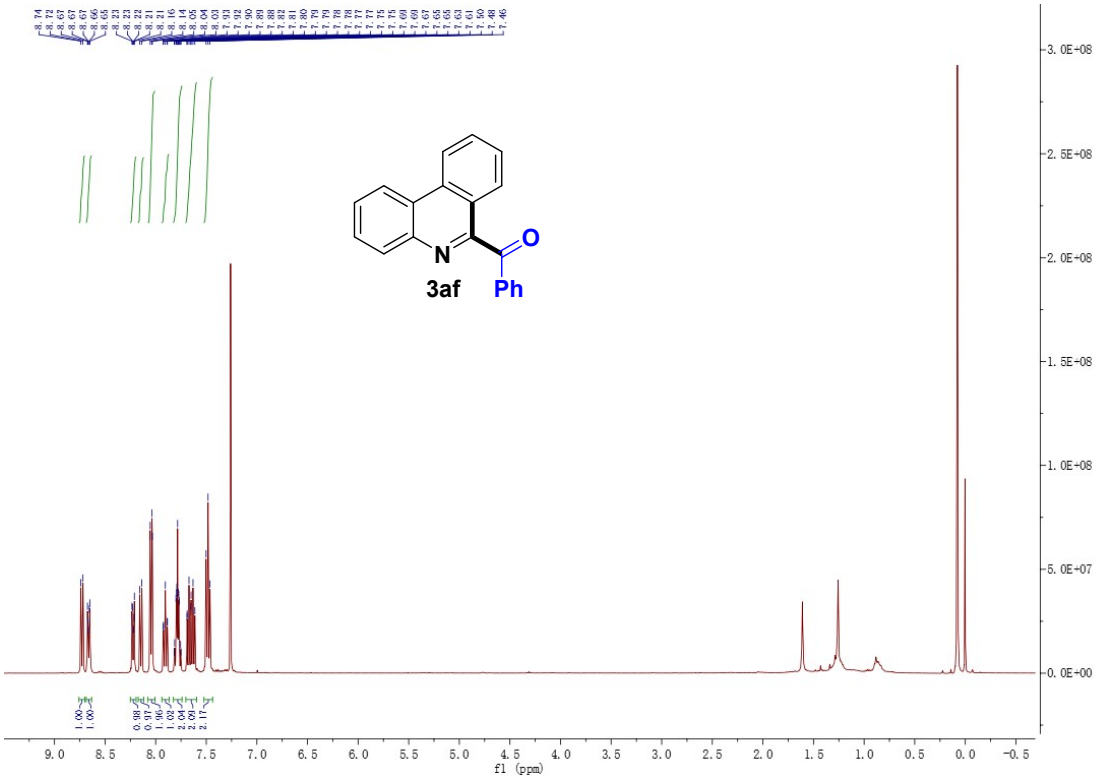
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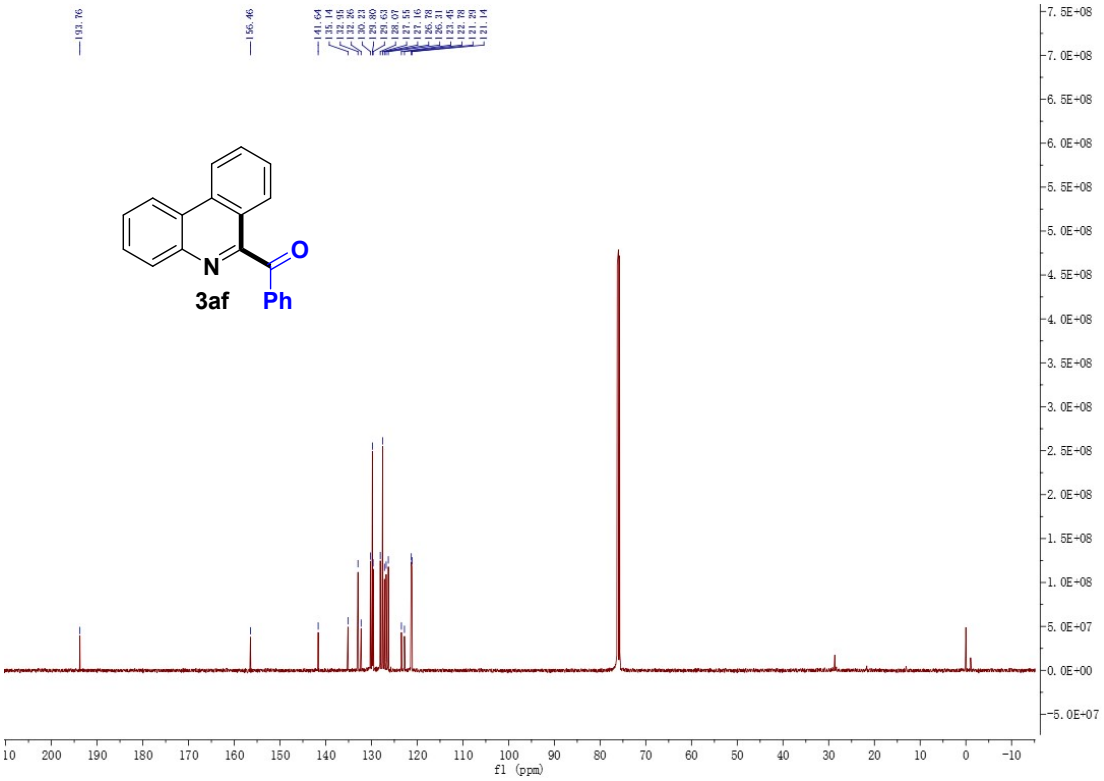
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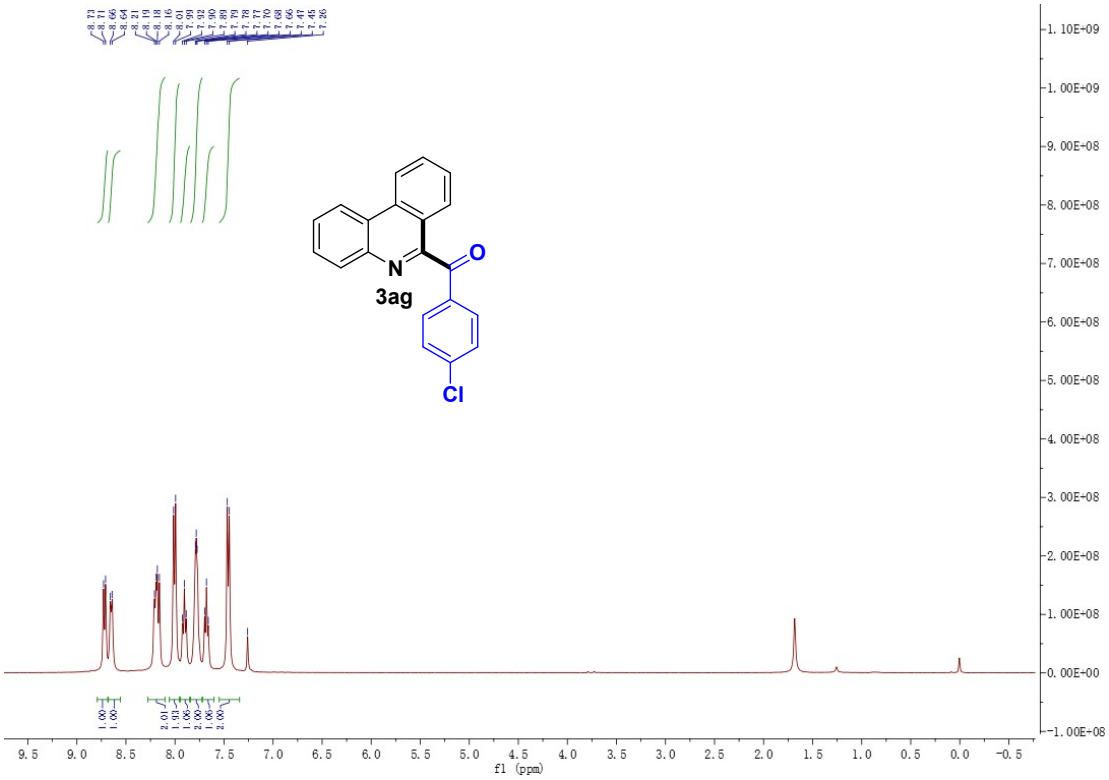
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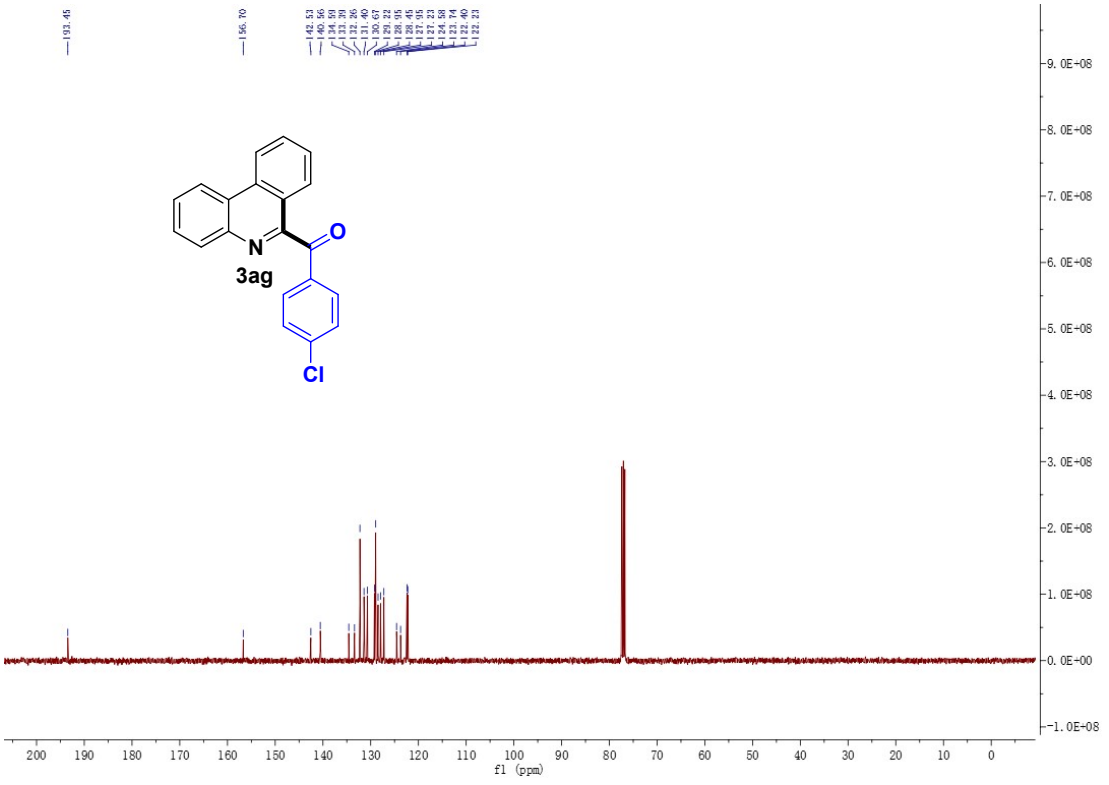
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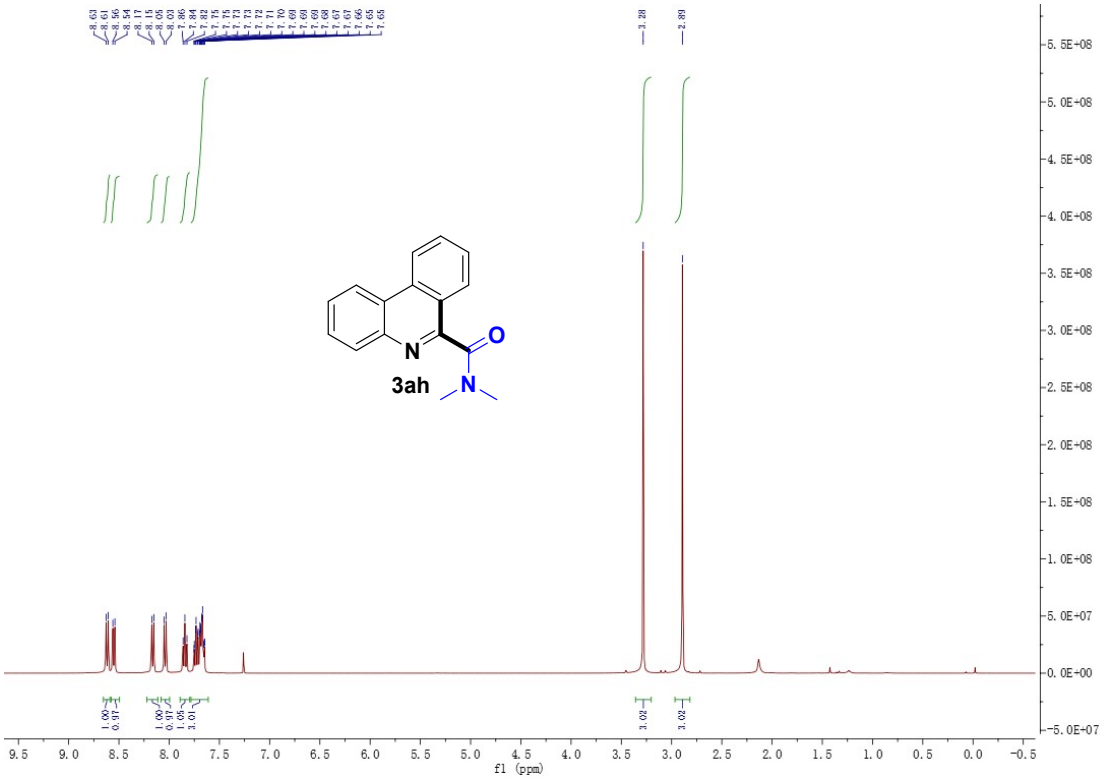

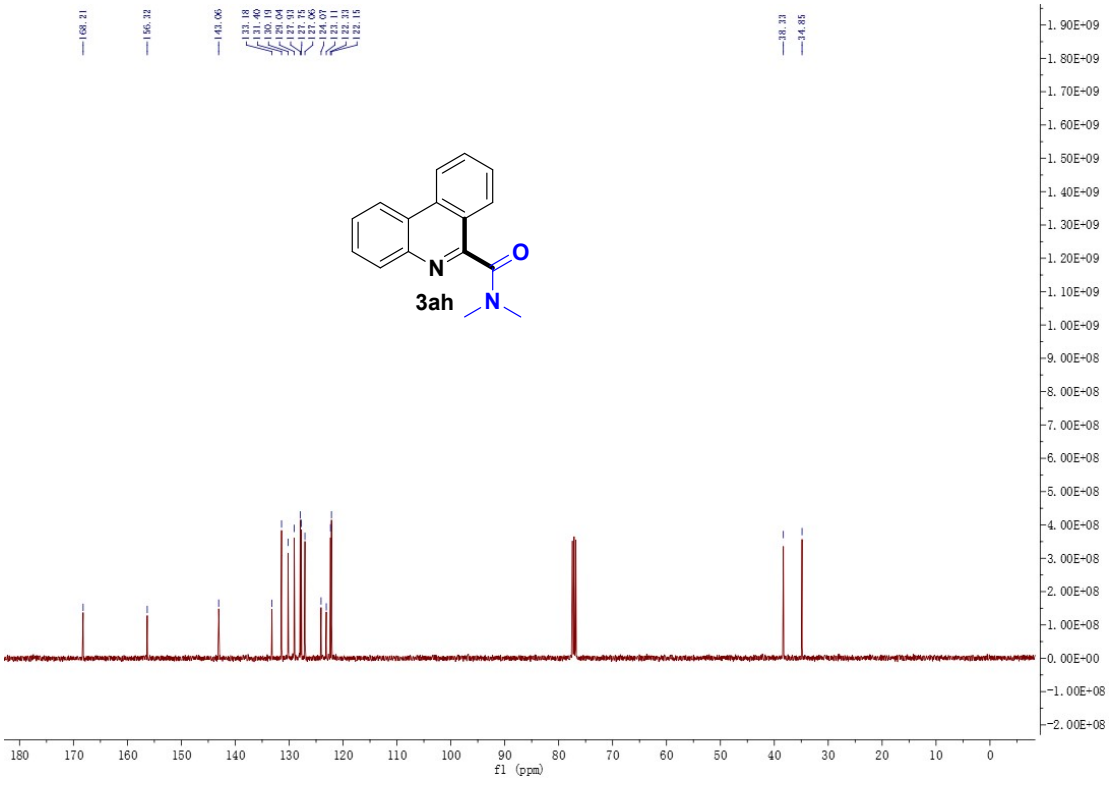

9. References

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6-(Trifluoromethyl)phenanthridines by Oxidative Cyclization of 2-Isocyanobiphenyls with CF_3SiMe_3 under Metal-Free Conditions. *Organic Letters.* 2019. DOI:10.1021/ol4022589

[2] Hatchard, C. G.; Parker, C. A. *Proc. Roy. Soc. (London)* 1956, *A235*, 518–536.

[3] a) Kuhn, H. J.; Braslavsky, S. E.; Schmidt, R. *Pure Appl. Chem.* 2004, *76*, 2105–2146. b) Monalti, M. *et. al.* Chemical Actinometry. *Handbook of Photochemistry*, 3rd Ed; Taylor & Francis Group, LLC. Boca Raton, FL, 2006, 601–616.