Synthesis of 6-Substituted Phenanthridines by Metal-free, Visible-light Induced Aerobic Oxidative Cyclization of 2-Isocyanobiphenyls with Hydrazines

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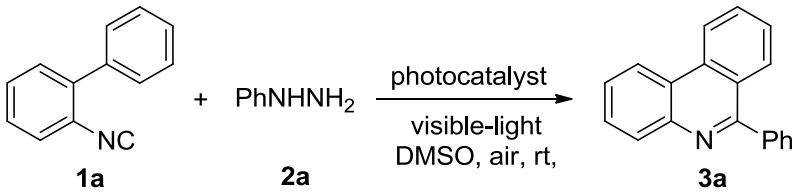
General All reactions were performed in a 10 mL microwave tube in the open air. Photoirradiation was carried out with a 5W blue LED. For chromatography, 200-300 mesh silica gel (Qingdao, China) was employed. ^{1}H NMR and ^{13}C NMR spectra were measured in $CDCl_3$ and recorded on Varian 300 or Brucker ARX 400 spectrometer. Mass spectra were obtained on Thermo Trace GC Ultra-DCQ, and HRMS were performed on Bruker Daltonics ESI-Q-TOF at Lenh Insititute of Functional Materials or Thermo MAT95XP mass spectrometer at analytical center of Sun Yat-Sen University. Compounds described in the literature were characterized by comparing their ^{1}H NMR and ^{13}C NMR to the reported values. 2-Isocyanobiphenyls **1a-i** were prepared according to our previous reported procedures.[1] Hydrazine hydrochlorides were converted into the corresponding hydrazines by using NaOH (1 M) as a base in water and extracted with ethyl acetate. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification.

General procedure to prepare 6-substituted phenanthridines: To a test tube equipped with a magnetic stir bar was charged with 2-isocyanobiphenyls **1** (0.2 mmol), hydrazines or hydrazine hydrochlorides **2** (0.6 mmol, 3 equiv), K_2CO_3 (0.6 mmol, 3equiv), eosin B (6.5 mg, 5 mol%) and 1 mL of DMSO. The solution was stirred at room temperature with the irradiation of a 5 W blue LED. After the reaction was completed, as monitored by TLC, distilled water (10 mL) was added, the resulting mixture was extracted with ethyl acetate (5 mL×3). The combined organic layers were washed with brine and dried

(Na_2SO_4). After evaporation of the solvent, the crude product was purified by flash column chromatography (SiO_2) with hexane/ethyl acetate.

Table S1 The effects of different organic dyes and light sources.[a]

Different wavelength of light sources is used and each of the photosensitizers is compared at wavelengths in which it absorbs. As shown in Table S1, the combination of eosin B and blue LED is the best choice.

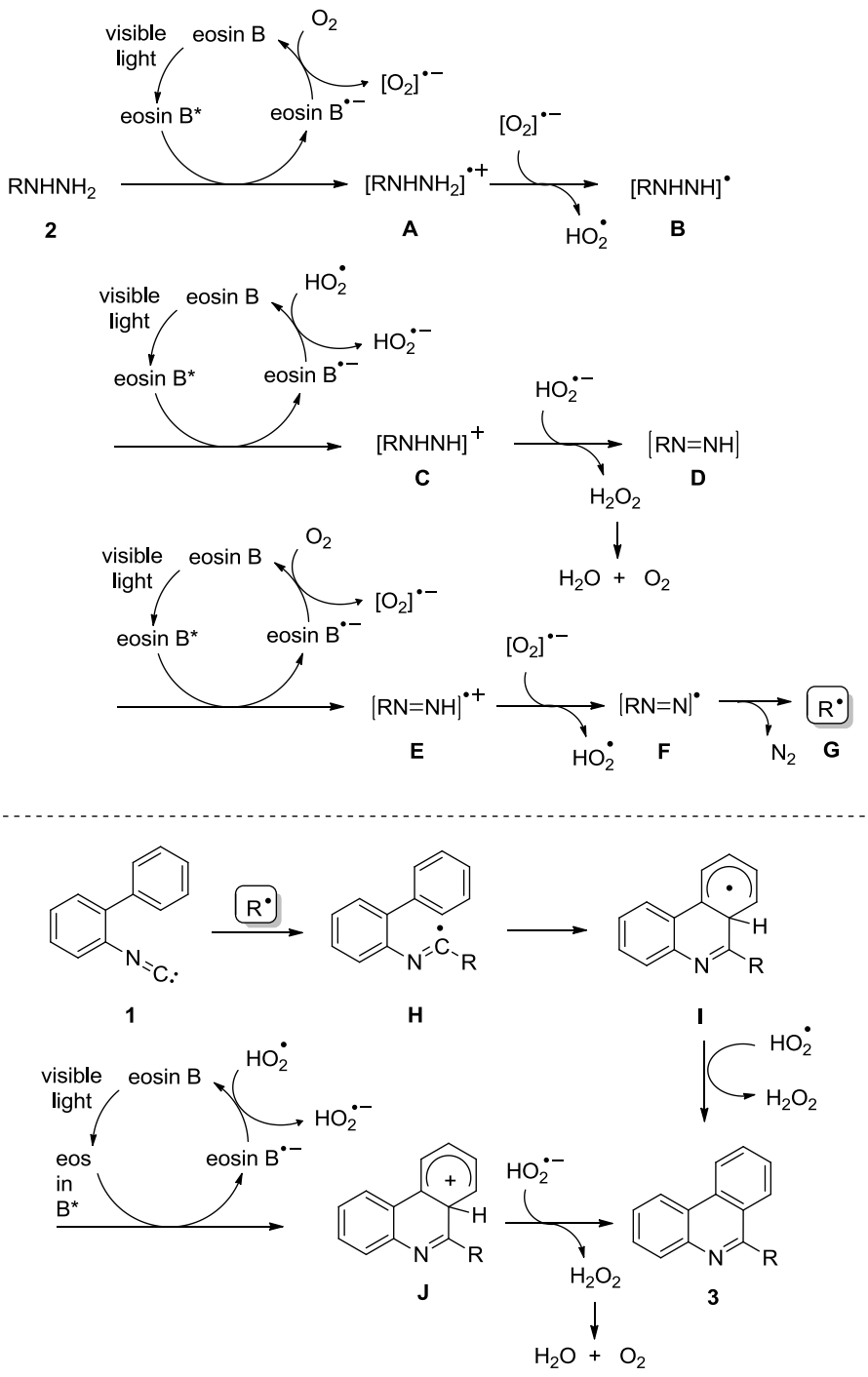


Entry	Photocatalyst	Light source	Base	Yield(%)[b]
1	eosin Y	5 WBlue LED	none	25
2	eosin B	5 W Blue LED	none	64
3	RB	5 W Blue LED	none	55
4	MB	5 W Blue LED	none	13
5	eosin Y	5 W Green LED	none	32
6	eosin B	5 W Green LED	none	60
7	RB	5 W Green LED	none	51
8	MB	5 W Green LED	none	22
9	eosin Y	24W fluorescent bulb	none	30
10	eosin B	24W fluorescent bulb	none	46
11	RB	24W fluorescent bulb	none	26
12	MB	24W fluorescent bulb	none	15

[a] All the reactions were carried out by using 2-isocyanobiphenyl **1a** (0.2 mmol), phenyl hydrazine **2a** (0.6 mmol), DMSO (1 mL), photocatalyst (5 mol%), rt in the open air. [b] Yields were determined by ^{1}HNMR analysis using CH_3NO_2 as internal standard.

Plausible reaction mechanism

A plausible reaction mechanism for the reaction is proposed in Scheme S1. Initially, photoexcitation of eosin B by visible light generates excited eosin B*, which is readily quenched by hydrazine **2** to give the cation radical **A**.[2] The generated eosin $B^{\bullet-}$ can be oxidized by oxygen to return to its original form.[3] Proton abstraction of the cation radical **A** by a superoxide radical anion gives the radical intermediate **B**. The subsequent process involving the single-electron oxidation of **B** with the aid of photoredox catalyst to



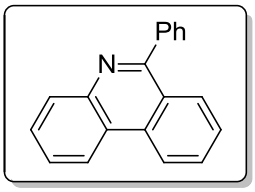
Scheme S1 Possible mechanism.

generate diazene **D**. Diazene **D** is oxidized by a similar pathway to give the radical species **G**.[4] Intermolecular addition of radical **G** to isocyanide **1**, followed by intramolecular aromatic substitution of the resulting imidoyl radical **H** to generate the

intermediate **I**.[5] One-electron oxidation of **I** by excited eosin B* forms the cation intermediated **J**, and subsequent deprotonation of **J** leads to the desired 6-substituted phenanthridines **3**. Another possible pathway is the direct oxidation of **I** by HOO• without formation of cation intermediated **J**.[6]

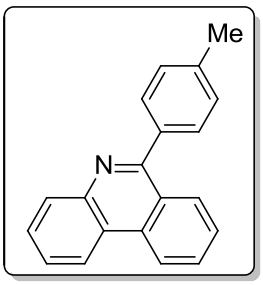
Characterization data

6-phenylphenanthridine (3a):[7]



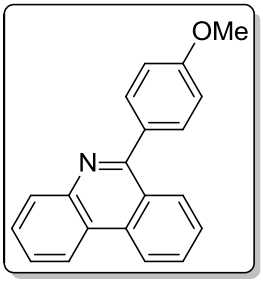
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 7.5 Hz, 1H), 8.27 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.11 (d, *J* = 8.2 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.80 – 7.72 (m, 3H), 7.71 – 7.65 (m, 1H), 7.63 – 7.59 (m, 1H), 7.58 – 7.51 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.30, 143.79, 139.79, 133.45, 130.60, 130.37, 129.77, 128.94, 128.89, 128.76, 128.48, 127.16, 126.98, 125.25, 123.77, 122.23, 121.99; EI-MS (m/z, relative intensity): 255 (M^+, 46), 254 (100), 127 (22), 113 (6).

6-(*p*-tolyl)phenanthridine (3b):[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.61 (dd, *J* = 8.2, 1.0 Hz, 1H), 8.26 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.15 (dd, *J* = 8.3, 0.5 Hz, 1H), 7.857 – 7.82 (m, 1H), 7.79 – 7.72 (m, 1H), 7.71 – 7.58 (m, 4H), 7.39 –7.37 (m, 2H), 2.49 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.35, 143.78, 138.66, 136.83, 133.47, 130.56, 130.27, 129.73, 129.14, 129.11, 129.04, 128.85, 127.11, 126.86, 123.71, 122.21, 121.97, 21.47; EI-MS (m/z, relative intensity): 269 (M^+, 65), 268 (100), 253 (9), 145 (91), 134 (25).

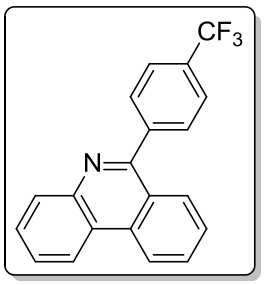
6-(4-methoxyphenyl)phenanthridine (3c):[7]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 7.7 Hz, 1H), 8.28 – 8.21 (m, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.87 – 7.81 (m, 1H), 7.76 – 7.59 (m, 5H), 7.09 (d, *J* = 8.7 Hz, 2H), 3.91 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.92, 160.13, 143.83,

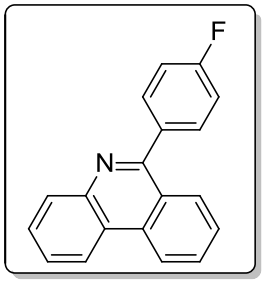
133.52, 132.23, 131.21, 130.52, 130.21, 128.98, 128.84, 127.11, 126.78, 125.35, 123.64, 122.23, 121.95, 113.90, 55.49; EI-MS (m/z, relative intensity): 285 (M^+, 15), 284 (100), 269 (13), 254 (31), 241 (55), 120 (29).

6-(4-(trifluoromethyl)phenyl)phenanthridine (3d):[8]



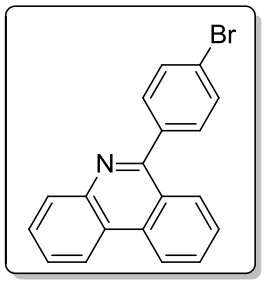
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.3 Hz, 1H), 8.62 (dd, *J* = 8.2, 1.1 Hz, 1H), 8.24 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.05 – 7.99 (m, 1H), 7.89 – 7.83 (m, 5H), 7.78 (dd, *J* = 7.5, 6.2 Hz, 1H), 7.72 (dd, *J* = 8.2, 1.3 Hz, 1H), 7.65 – 7.61 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.72, 143.65, 143.35, 133.49, 130.87, 130.81(q, *J* = 32.6 Hz), 130.40, 130.19, 129.09, 128.32, 127.41, 125.48 (q, *J* = 3.7 Hz), 124.83, 123.86, 122.42, 122.05; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.3 (s, 3F); EI-MS (m/z, relative intensity): 323 (M^+, 61), 322 (100), 302 (16), 254 (35), 126 (18).

6-(4-fluorophenyl)phenanthridine (3e):[9]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.77 (d, *J* = 8.3 Hz, 1H), 8.72 – 8.64 (m, 1H), 8.30 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.88 (m, 1H), 7.87 – 7.72 (m, 4H), 7.72 – 7.67 (m, 1H), 7.35 – 7.30 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.18 (d, *J* = 248.0 Hz), 160.17, 143.68, 135.81 (d, *J* = 3.1 Hz), 133.51, 131.64 (d, *J* = 8.4 Hz), 130.70, 130.28, 128.97, 128.64, 127.27, 127.10, 125.14, 123.75, 122.33, 122.00, 115.50 (d, *J* = 21.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ -113.2 (s, F); EI-MS (m/z, relative intensity): 273 (M^+, 58), 272 (100), 251 (13), 126 (7).

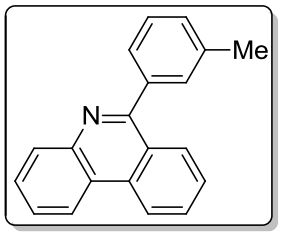
6-(4-bromophenyl)phenanthridine (3f):[10]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 7.8 Hz, 1H), 8.23 (d, *J* = 7.9 Hz, 1H), 8.06 (d, *J* = 8.2 Hz, 1H), 7.87 (dd, *J* = 11.3, 4.0 Hz, 1H), 7.80 – 7.74 (m, 1H), 7.70 (d, *J* = 8.4 Hz, 2H), 7.64 – 7.61 (m, 3H), 7.47 – 7.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.01, 143.69, 138.65, 133.49, 131.66,

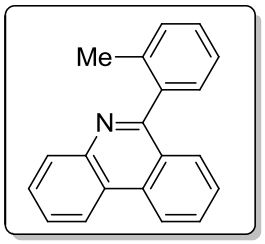
131.46, 130.77, 130.33, 129.02, 128.51, 127.32, 127.21, 124.93, 123.77, 123.19, 122.37, 122.03; EI-MS (m/z, relative intensity): 335 (^{81}Br, M^+, 58), 333 (^{79}Br, M^+, 86), 332 (91), 254 (100), 226 (9), 127 (58).

6-(*m*-tolyl)phenanthridine (3g):[7]



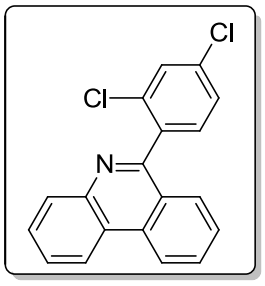
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.61 (d, *J* = 8.1 Hz, 1H), 8.26 (dd, *J* = 8.1, 0.9 Hz, 1H), 8.11 (d, *J* = 8.1 Hz, 1H), 7.89 – 7.81 (m, 1H), 7.79 – 7.73 (m, 1H), 7.72 – 7.65 (m, 1H), 7.64 – 7.59 (m, 1H), 7.57 (s, 1H), 7.51 (d, *J* = 7.6 Hz, 1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 2.48 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.55, 143.79, 139.70, 138.28, 133.42, 130.58, 130.36, 130.29, 129.49, 129.06, 128.87, 128.24, 127.13, 126.92, 126.88, 125.34, 123.76, 122.19, 121.98, 21.61; EI-MS (m/z, relative intensity): 269 (M^+, 30), 268 (100), 253 (9), 133 (26).

6-(*o*-tolyl)phenanthridine (3h):[11]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.71 (d, *J* = 8.3 Hz, 1H), 8.65 (dd, *J* = 8.1, 1.2 Hz, 1H), 8.28 (dd, *J* = 8.1, 1.2 Hz, 1H), 7.86 (ddd, *J* = 8.3, 7.1, 1.3 Hz, 1H), 7.79 (dd, *J* = 7.0, 1.3 Hz, 1H), 7.74 – 7.70 (m, 2H), 7.62 – 7.56 (m, 1H), 7.43 – 7.35 (m, 4H), 2.12 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.01, 143.65, 138.99, 136.43, 133.06, 130.81, 130.38, 130.15, 129.29, 128.92, 128.74, 128.66, 127.40, 127.06, 126.90, 125.85, 123.89, 122.17, 122.06, 19.85; EI-MS (m/z, relative intensity): 269 (M^+, 30), 268 (100), 254 (63), 134 (38).

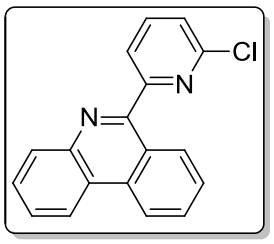
6-(2,4-dichlorophenyl)phenanthridine (3i):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.75 (d, *J* = 8.3 Hz, 1H), 8.69 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.31 – 8.24 (m, 1H), 7.95 – 7.88 (m, 1H), 7.85 – 7.74 (m, 2H), 7.72 – 7.61 (m, 3H), 7.54 – 7.48 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.36, 143.55, 137.06, 135.32, 134.28, 133.03, 131.98, 131.02, 130.33, 129.62, 129.06, 128.18,

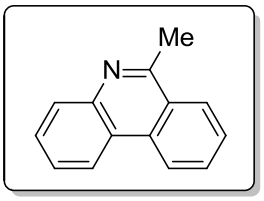
127.58, 127.55, 127.49, 125.23, 124.14, 122.31, 122.15; EI-MS (m/z, relative intensity): 327 (^{37}Cl, ^{37}Cl, M^+, 9), 326 (18), 325 (^{37}Cl, ^{35}Cl, M^+, 40), 324 (67), 323 (^{35}Cl, ^{35}Cl, M^+, 72), 322 (100), 288 (42), 251 (30), 144 (20), 26 (32); HRMS (EI) calcd. for $C_{19}H_{11}NCl_2$ $[M]^+$ 323.0263, found: 323.0256.

6-(6-chloropyridin-2-yl)phenanthridine (3j):



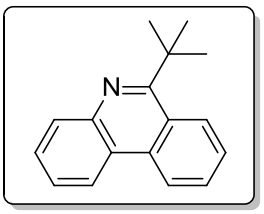
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.67 (d, *J* = 8.3 Hz, 1H), 8.60 (dd, *J* = 8.1, 1.0 Hz, 1H), 8.50 (d, *J* = 8.3 Hz, 1H), 8.23 (dd, *J* = 8.1, 1.1 Hz, 1H), 7.99 – 7.93 (m, 1H), 7.90-7.83 (m, 2H), 7.79 – 7.73 (m, 1H), 7.73 – 7.63 (m, 2H), 7.50 – 7.45 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.81, 156.66, 150.26, 143.38, 139.76, 133.63, 130.82, 130.47, 128.89, 128.61, 127.69, 127.62, 124.54, 124.37, 124.18, 123.77, 122.14, 122.11; EI-MS (m/z, relative intensity): 292(^{37}Cl, M^+, 24) 291 (36), 290 (^{35}Cl, M^+, 73), 289 (100), 253 (17) 126 (25); HRMS (EI) calcd. for $C_{18}H_{11}N_2Cl$ $[M]^+$ 290.0605, found: 290.0602.

6-methylphenanthridine (3k):[12]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (d, *J* = 8.3 Hz, 1H), 8.55 (d, *J* = 8.1 Hz, 1H), 8.23 (d, *J* = 8.2 Hz, 1H), 8.13 (d, *J* = 8.3 Hz, 1H), 7.89 – 7.84 (m, 1H), 7.78 – 7.67 (m, 2H), 7.66 – 7.61 (m, 1H), 3.07 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 158.91, 143.65, 132.53, 130.52, 129.32, 128.67, 127.33, 126.56, 126.35, 125.89, 123.78, 122.32, 121.98, 77.40, 77.08, 76.76, 23.46; EI-MS (m/z, relative intensity): 193 (M^+, 100), 178 (14), 95 (8).

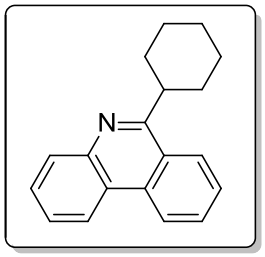
6-(*tert*-butyl)phenanthridine (3l):[13]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.2 Hz, 1H), 8.66 – 8.60 (m, 1H), 8.53 (dd, *J* = 8.2, 1.2 Hz, 1H), 8.14 (dd, *J* = 8.1, 1.0 Hz, 1H), 7.81 – 7.77 (m, 1H), 7.73 – 7.56 (m, 3H), 1.74 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.66, 142.95, 134.01, 130.28, 129.28, 128.40, 128.27, 126.47, 125.97, 124.33, 123.43, 123.00,

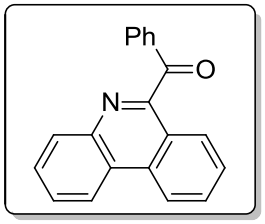
121.64, 40.23, 31.23; EI-MS (m/z, relative intensity): 235 (M^+, 45) 234 (83), 220 (72), 203 (42), 193 (100), 179 (47).

6-cyclohexylphenanthridine (3m):[14]



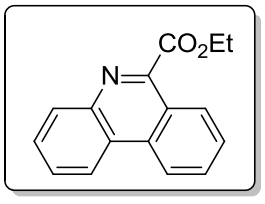
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.65 (d, *J* = 8.2 Hz, 1H), 8.54 (d, *J* = 7.9 Hz, 1H), 8.32 (d, *J* = 8.2 Hz, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 7.84 – 7.77 (m, 1H), 7.72-1.67 (m, 2H), 7.63 – 7.57 (m, 1H), 3.67 – 3.54 (m, 1H), 2.10 – 2.07 (m, 2H), 1.99 – 1.89 (m, 4H), 1.84 – 1.87 (m, 1H), 1.64 – 1.51 (m, 2H), 1.49 – 1.41 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.33, 143.86, 133.01, 129.96, 129.93, 128.42, 127.10, 126.16, 125.65, 124.73, 123.36, 122.60, 121.84, 42.00, 32.32, 26.91, 26.34; EI-MS (m/z, relative intensity): 261 (M^+, 32), 260 (57), 217 (16), 206 (100), 193 (39), 178 (10), 108 (14).

phenanthridin-6-yl(phenyl)methanone (3n):[15]



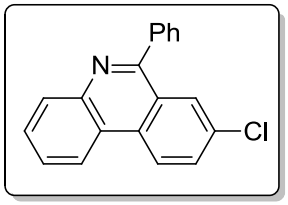
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, *J* = 8.3 Hz, 1H), 8.66 (dd, *J* = 6.7, 2.8 Hz, 1H), 8.22 (dd, *J* = 6.8, 2.7 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.04 (d, *J* = 7.8 Hz, 2H), 7.90 (t, *J* = 7.7 Hz, 1H), 7.83 – 7.73 (m, 2H), 7.67 – 7.61 (m, 2H), 7.50 – 7.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 194.81, 157.51, 142.67, 136.16, 134.01, 131.29, 130.84, 130.65, 129.13, 128.60, 128.21, 127.83, 127.36, 126.79, 124.49, 123.81, 122.34, 122.19; EI-MS (m/z, relative intensity): 283 (M^+, 49), 282 (73), 254 (100), 177 (14), 151 (15), 104 (40), 77 (54).

ethyl phenanthridine-6-carboxylate (3o):[16]



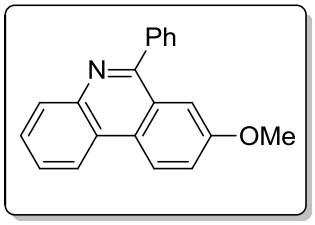
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (d, *J* = 8.3 Hz, 1H), 8.60 (d, *J* = 8.0 Hz, 1H), 8.55 (d, *J* = 8.3 Hz, 1H), 8.29 (dd, *J* = 7.8, 1.6 Hz, 1H), 7.92 – 7.87 (m, 1H), 7.79 – 7.70 (m, 3H), 4.64 (q, *J* = 7.1 Hz, 2H), 1.53 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.36, 151.17, 142.70, 133.43, 131.21, 130.97, 129.08, 128.61, 127.92, 127.34, 124.86, 123.41, 122.22, 122.07, 62.45, 14.39; EI-MS (m/z, relative intensity): 251 (M^+, 22), 207 (11), 178 (100), 151 (35).

8-chloro-6-phenylphenanthridine (3p):[7]



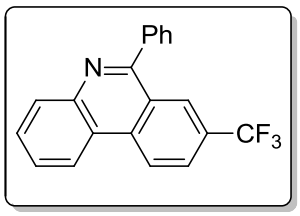
^{11}H NMR (400 MHz, $CDCl_3$) δ 8.62 (d, *J* = 8.9 Hz, 1H), 8.55 (d, *J* = 7.6 Hz, 1H), 8.24 (d, *J* = 8.1 Hz, 1H), 8.07 (d, *J* = 2.1 Hz, 1H), 7.82 – 7.76 (m, 2H), 7.75 – 7.66 (m, 3H), 7.61 – 7.55 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.19, 143.65, 139.04, 133.14, 131.87, 131.20, 130.44, 129.66, 129.24, 129.07, 128.69, 127.96, 127.43, 126.18, 124.07, 123.16, 121.87; EI-MS (m/z, relative intensity): 291 (^{37}Cl, M^+, 19), 289 (^{35}Cl, M^+, 58), 288 (100), 254 (45), 125 (26).

8-methoxy-6-phenylphenanthridine (3q):[17]



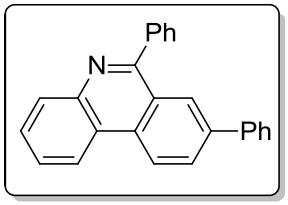
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.8 Hz, 1H), 8.54 – 8.50 (m, 1H), 8.23 (dd, *J* = 8.0, 1.3 Hz, 1H), 7.79 – 7.73 (m, 2H), 7.71 – 7.62 (m, 2H), 7.59 – 7.51 (m, 3H), 7.49 – 7.46 (m, 2H), 3.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.50, 158.46, 142.91, 139.78, 130.20, 130.18, 129.55, 128.79, 128.55, 127.93, 127.07, 123.94, 121.51, 121.10, 115.49, 114.21, 109.00, 55.47; EI-MS (m/z, relative intensity): 285 (M^+, 70), 284 (100), 254 (47), 241 (49), 121 (15).

6-phenyl-8-(trifluoromethyl)phenanthridine (3r):



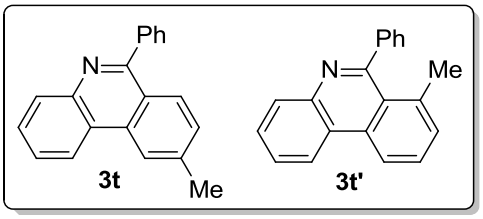
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.82 (d, *J* = 8.7 Hz, 1H), 8.64 (d, *J* = 7.8 Hz, 1H), 8.41 (s, 1H), 8.28 (dd, *J* = 8.1, 0.8 Hz, 1H), 8.05 (dd, *J* = 8.7, 1.5 Hz, 1H), 7.88 – 7.81 (m, 1H), 7.78 – 7.71 (m, 3H), 7.63 – 7.57 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.06, 144.43, 138.85, 135.68, 130.96, 130.58, 130.11, 129.72, 129.25, 129.33 (q, *J* = 33.2 Hz), 128.77, 127.57, 126.44 (q, *J* = 3.2 Hz), 126.30, 124.53, 123.42, 122.80, 122.35; ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.0 (s, 3F); EI-MS (m/z, relative intensity): 323 (M^+, 47), 322 (100), 302 (5), 253 (14), 151 (17); HRMS (EI) calcd. for $C_{20}H_{12}NF_3$ $[M]^+$ 323.0916, found: 323.0922.

6,8-diphenylphenanthridine (3s):



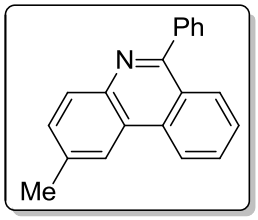
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (d, *J* = 8.6 Hz, 1H), 8.63 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.32 (d, *J* = 1.8 Hz, 1H), 8.28 (dd, *J* = 8.1, 1.1 Hz, 1H), 8.11 (dd, *J* = 8.6, 1.9 Hz, 1H), 7.82 – 7.76 (m, 3H), 7.71 (dd, *J* = 7.5, 6.3 Hz, 1H), 7.65 – 7.61 (m, 2H), 7.59 – 7.54 (m, 3H), 7.46 (d, *J* = 7.8 Hz, 2H), 7.40 (dt, *J* = 8.2, 3.7 Hz, 1H).; ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.44, 143.72, 140.26, 139.97, 139.65, 132.54, 130.32, 129.88, 129.79, 129.05, 128.93, 128.87, 128.59, 127.83, 127.41, 127.13, 126.88, 125.62, 123.62, 122.91, 122.04; EI-MS (m/z, relative intensity): 331 (M^+, 66), 330 (100), 254 (35), 164 (29); HRMS (EI) calcd. for $C_{25}H_{17}N_1$ $[M]^+$ 331.1356, found: 331.1350.

9-methyl-6-phenylphenanthridine (3t)[7] and 7-methyl-6-phenylphenanthridine (3t')[7] (1: 2 mixture of 3t and 3t'):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.60 (d, *J* = 8.2 Hz, 1H, 2H'), 8.47 (s, 1H), 8.29 – 8.18 (m, 1H, 1H'), 7.99 (d, *J* = 8.4 Hz, 1H), 7.75 – 7.70 (m, 3H, 2H'), 7.69 – 7.63 (m, 2H, 1H'), 7.58 – 7.47 (m, 3H, 4H'), 7.43 (d, *J* = 7.3 Hz, 2H'), 2.65 (s, 3H), 2.09 (s, 3H'); ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.09, 160.79, 144.59, 143.95, 142.75, 141.01, 139.91, 137.63, 134.68, 133.62, 131.39, 130.27, 130.20, 129.91, 129.75, 128.87, 128.83, 128.74, 128.70, 128.68, 128.56, 128.43, 128.15, 126.87, 126.72, 124.72, 123.85, 123.64, 123.39, 122.22, 121.96, 121.89, 120.40, 25.02, 22.31; EI-MS (m/z, relative intensity): 269 (M^+, 55), 268 (100), 254 (52), 124 (73), 92 (30).

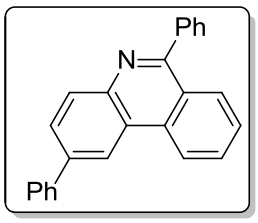
2-methyl-6-phenylphenanthridine (3u):[5a]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.69 (d, *J* = 8.3 Hz, 1H), 8.40 (s, 1H), 8.15 (d, *J* = 8.3 Hz, 1H), 8.09 (d, *J* = 8.2 Hz, 1H), 7.83 (dd, *J* = 11.3, 3.9 Hz, 1H), 7.78 – 7.69 (m, 2H), 7.62 – 7.51 (m, 5H), 2.65 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 160.34, 142.04, 139.80,

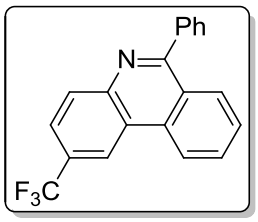
136.87, 133.20, 130.63, 130.40, 130.00, 129.78, 128.88, 128.65, 128.43, 127.00, 125.30, 123.60, 122.18, 121.59, 22.08; EI-MS (m/z, relative intensity): 269 (M^+, 69), 268 (100), 254 (53), 124 (71), 91 (30).

2,6-diphenylphenanthridine (3v):[18]



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.81 – 8.77 (m, 2H), 8.33 (d, *J* = 8.5 Hz, 1H), 8.14 (d, *J* = 8.2 Hz, 1H), 8.01 (dd, *J* = 8.5, 1.7 Hz, 1H), 7.87 – 7.75 (m, 5H), 7.64 (d, *J* = 7.7 Hz, 1H), 7.62 – 7.51 (m, 5H), 7.46 – 7.43 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.26, 143.10, 141.01, 139.79, 139.68, 133.53, 130.68, 129.80, 129.46, 129.08, 129.03, 128.83, 128.50, 128.33, 127.70, 127.64, 127.32, 125.46, 123.95, 122.25, 120.32; EI-MS (m/z, relative intensity): 331 (M^+, 69), 330 (100), 254 (45), 164 (54).

6-phenyl-2-(trifluoromethyl)phenanthridine (3w):



^{1}H NMR (400 MHz, $CDCl_3$) δ 8.89 (s, 1H), 8.73 (d, *J* = 8.3 Hz, 1H), 8.34 (d, *J* = 8.6 Hz, 1H), 8.16 (d, *J* = 8.2 Hz, 1H), 7.96 – 7.91 (m, 2H), 7.80 – 7.72 (m, 2H), 7.72 – 7.66 (m, 1H), 7.62 – 7.54 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 163.49, 145.17, 139.17, 131.31, 131.18, 129.91 (q, *J* = 36.2 Hz), 129.19, 128.72, 128.57, 128.23, 128.09, 125.48, 124.87 (q, *J* = 3.1 Hz), 123.40, 122.27, 119.88, 119.83, 119.79; ^{19}F NMR (376 MHz, $CDCl_3$) δ -62.5 (s, 3F); EI-MS (m/z, relative intensity): 323 (M^+, 52) 322 (100), 302 (9), 253 (18), 151 (17); HRMS (EI) calcd. for $C_{20}H_{12}NF_3$ $[M]^+$ 323.0916, found: 323.0918.

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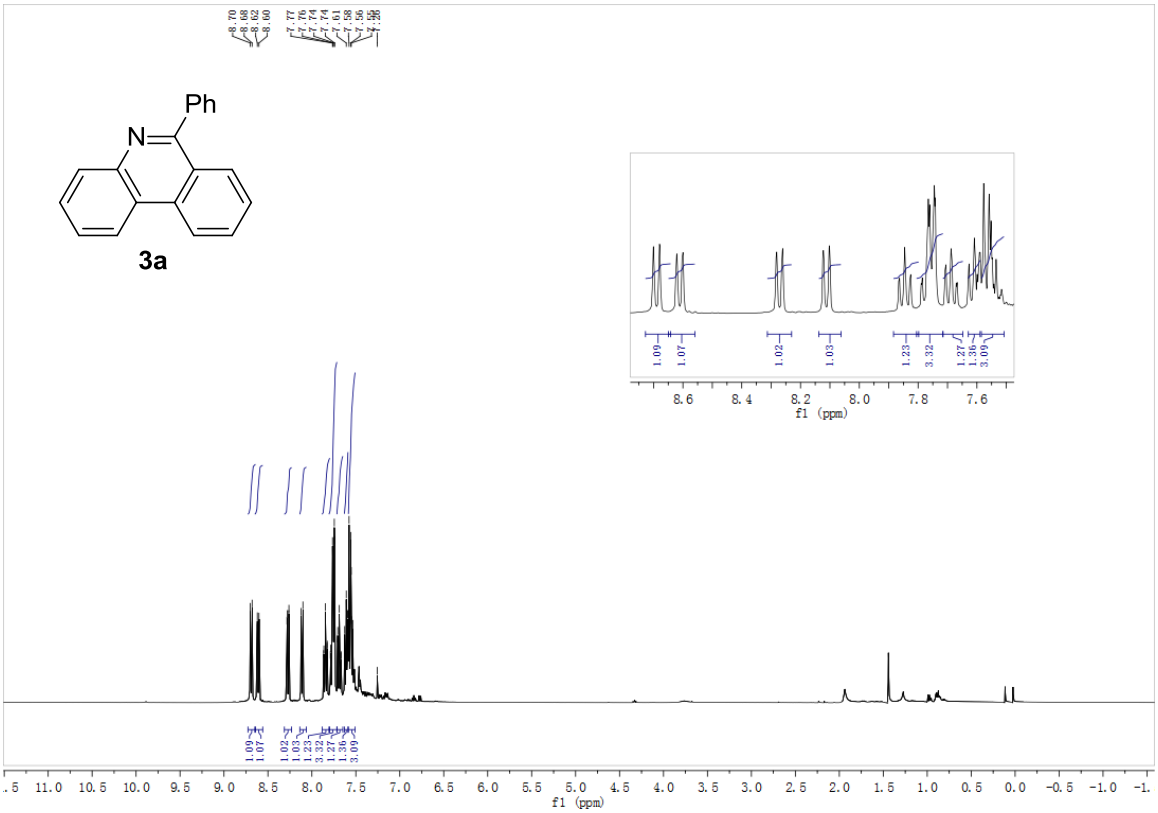
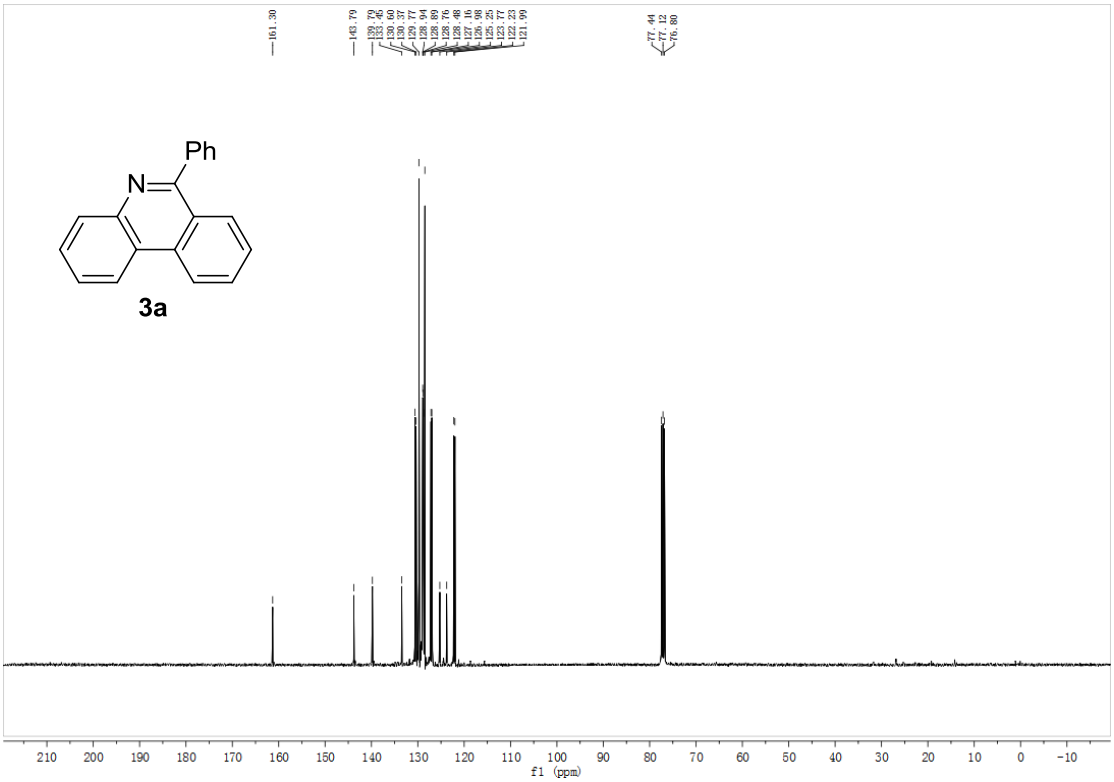
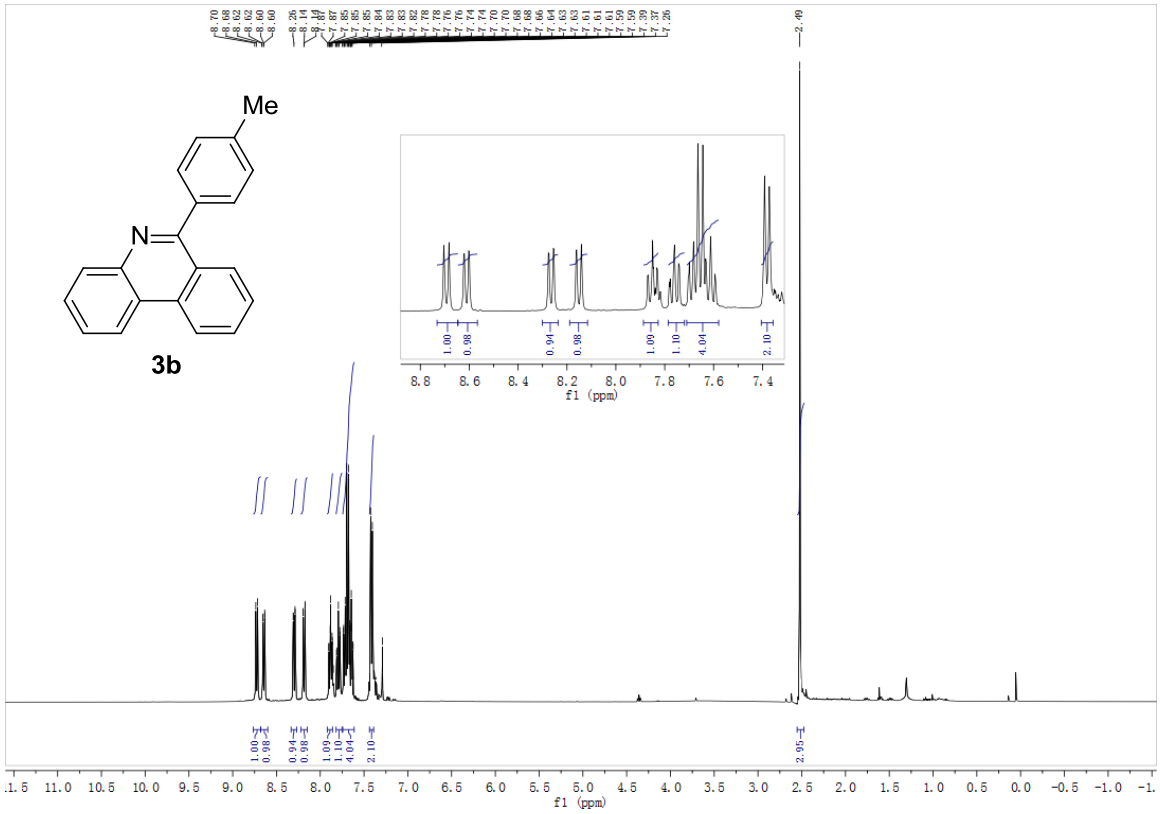
^{1}H NMR and ^{13}C NMR spectra



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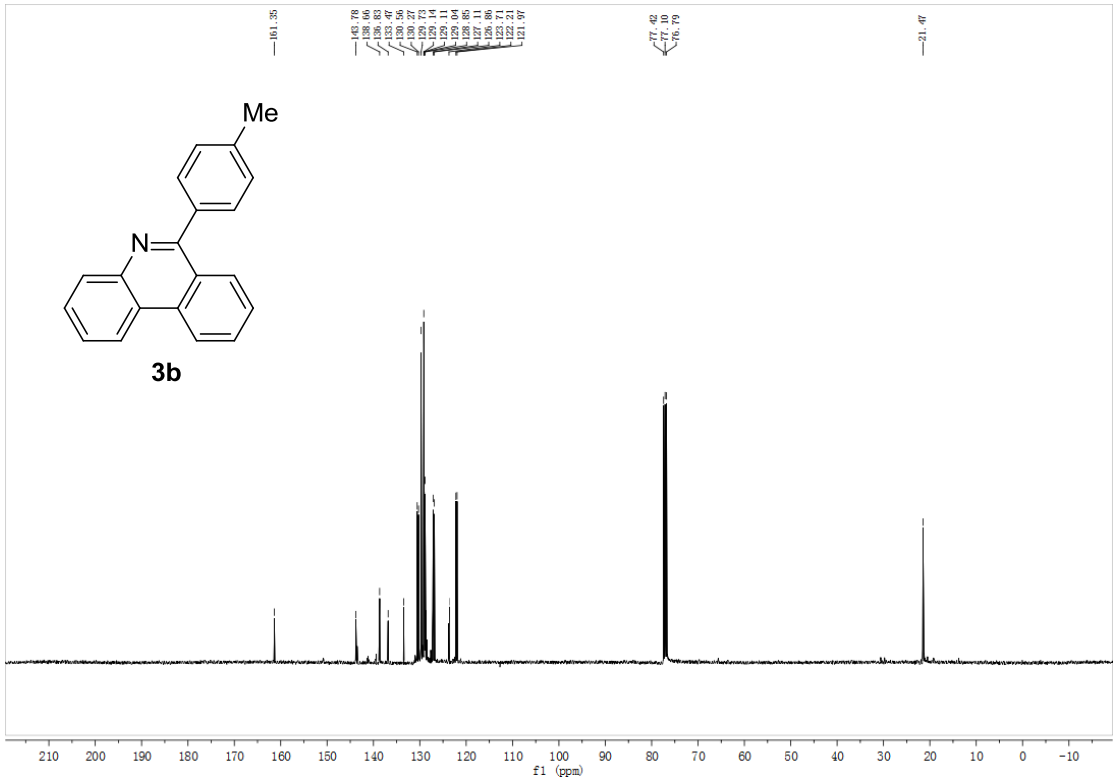
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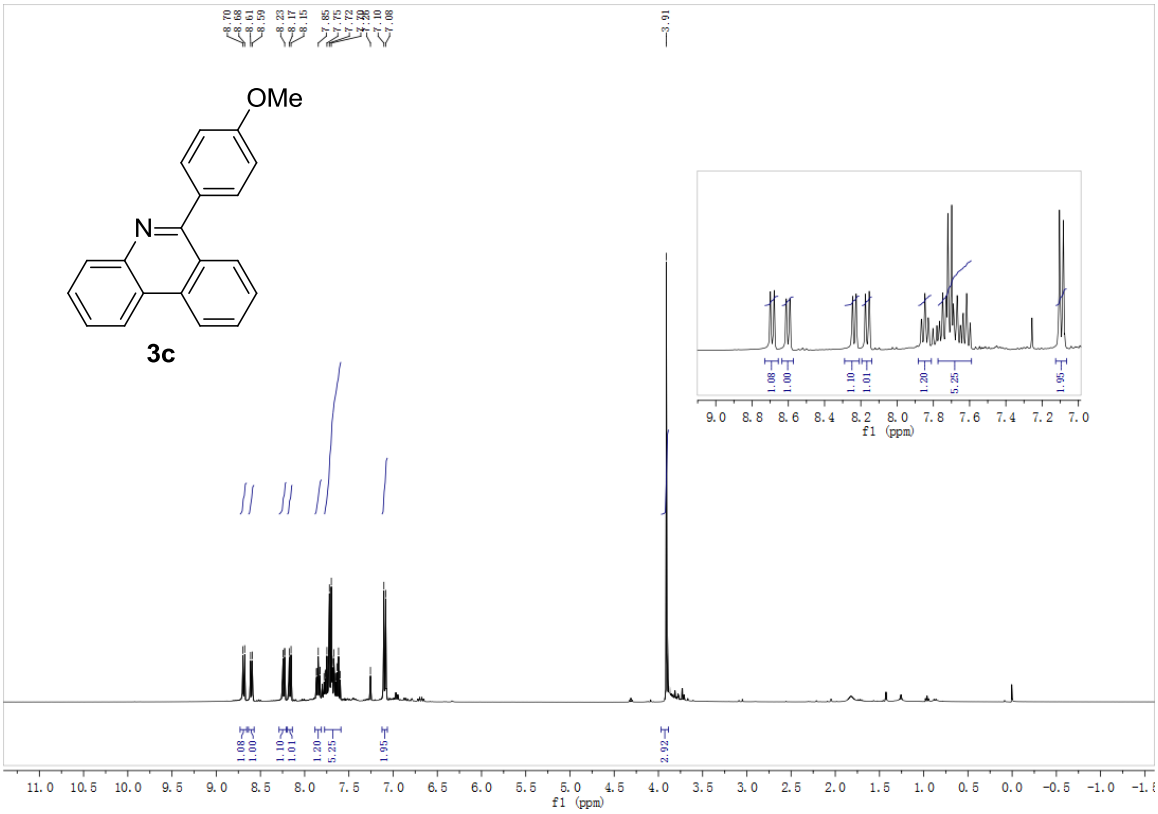
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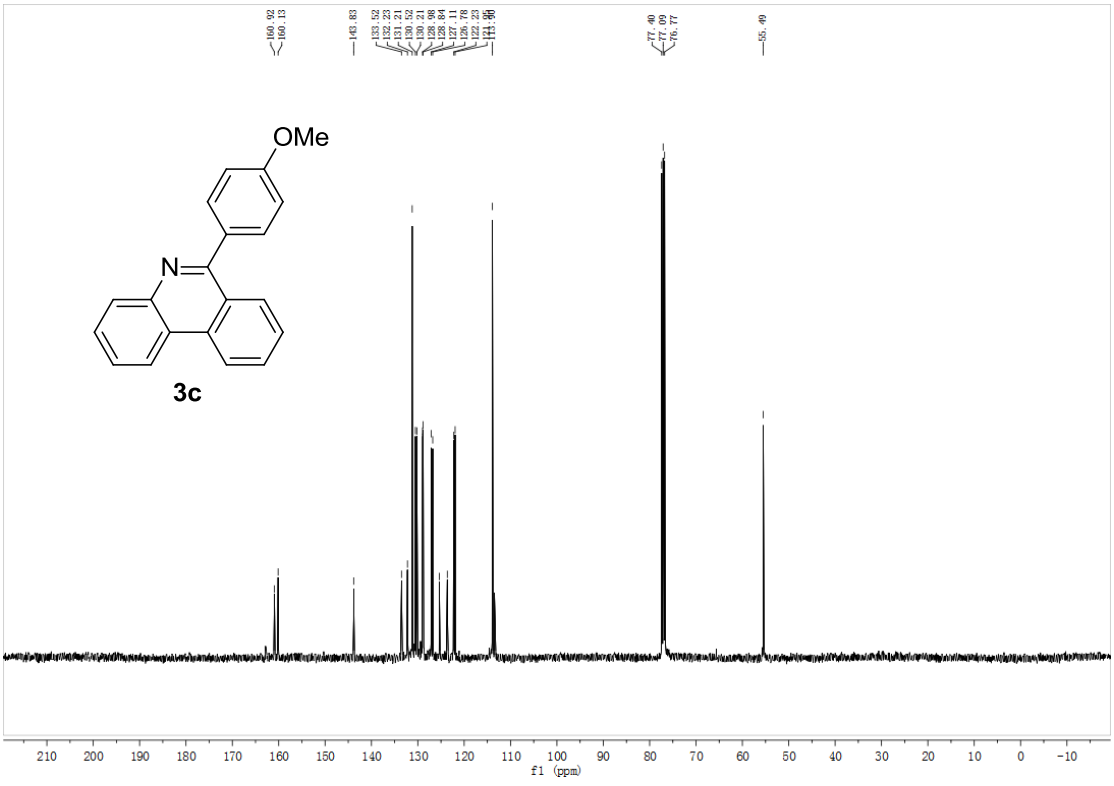
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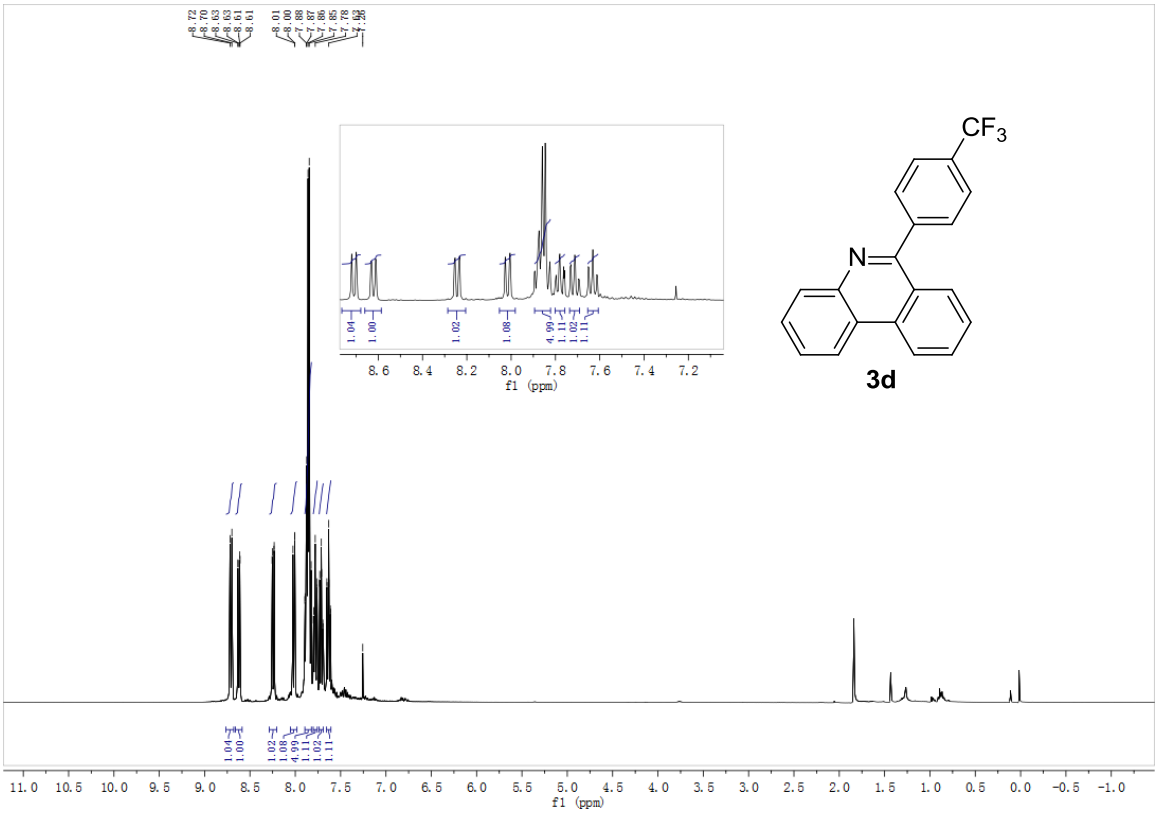
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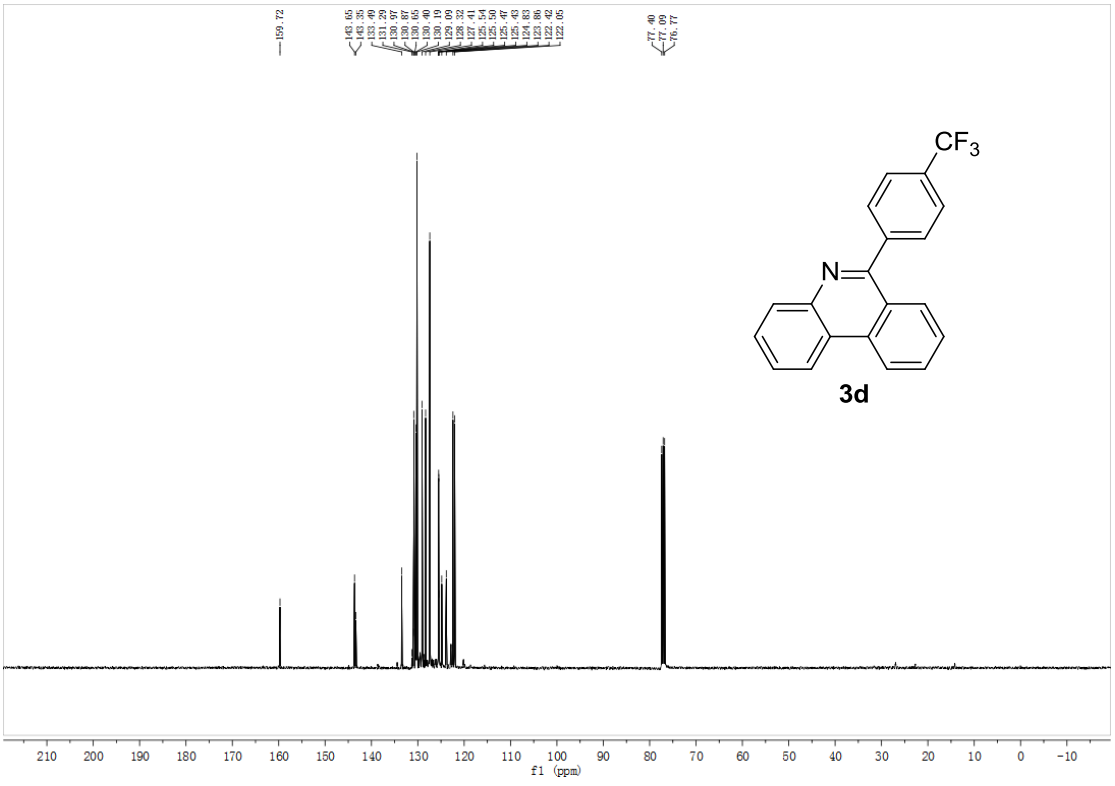
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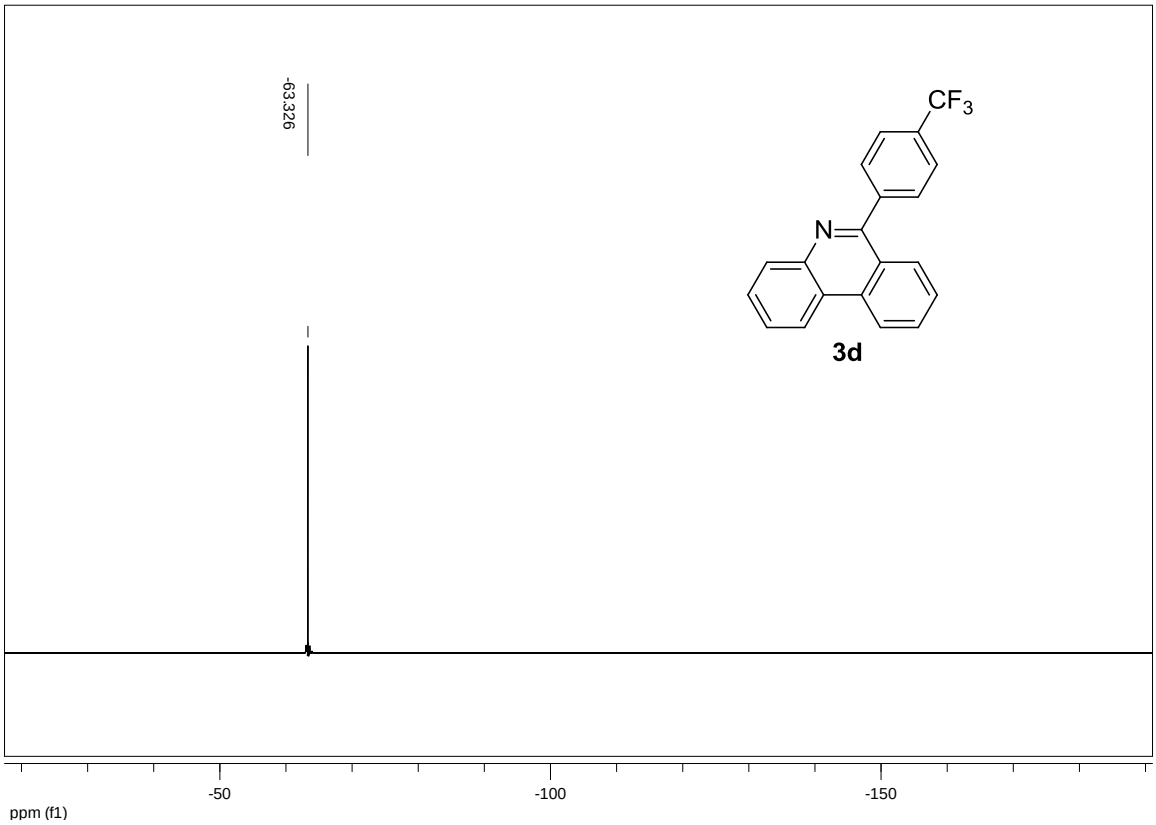
3d
f1 (ppm)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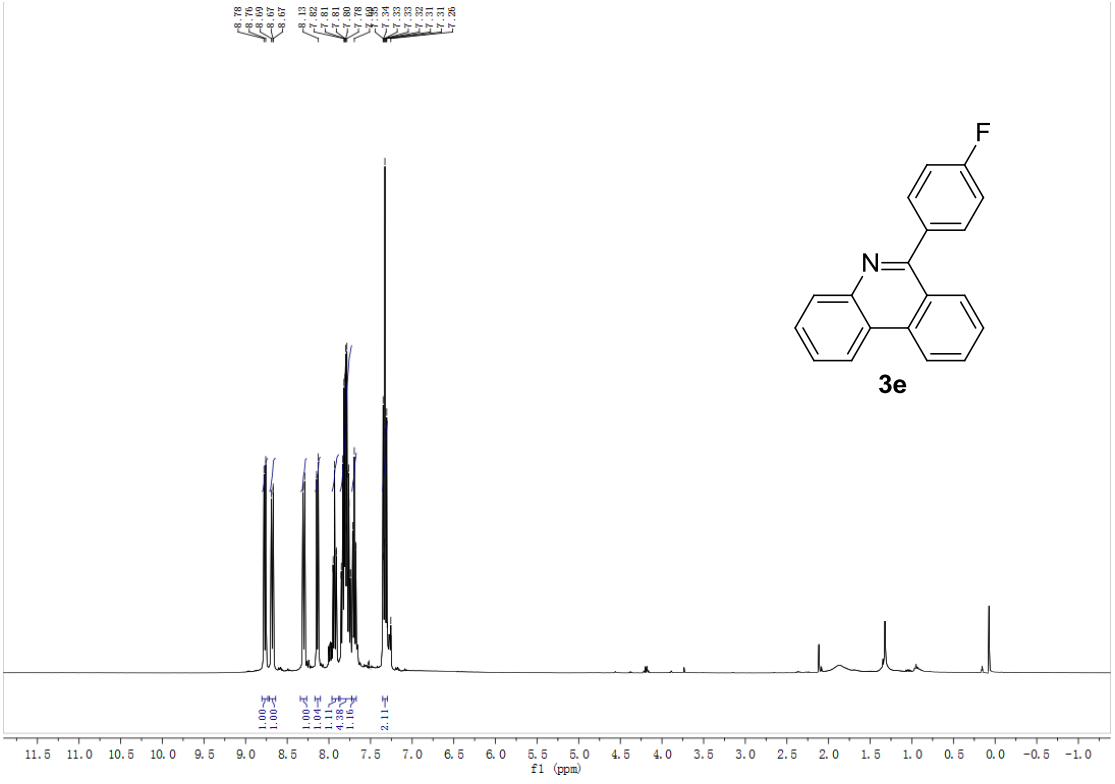
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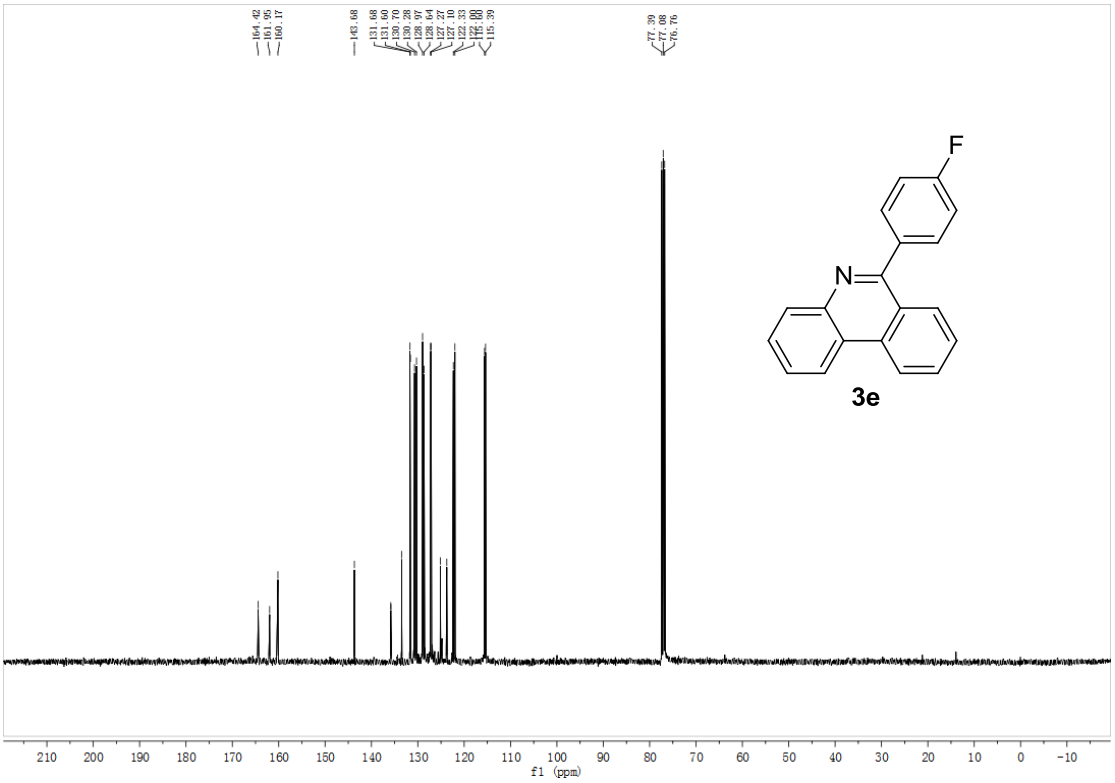
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122.33
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N
3e
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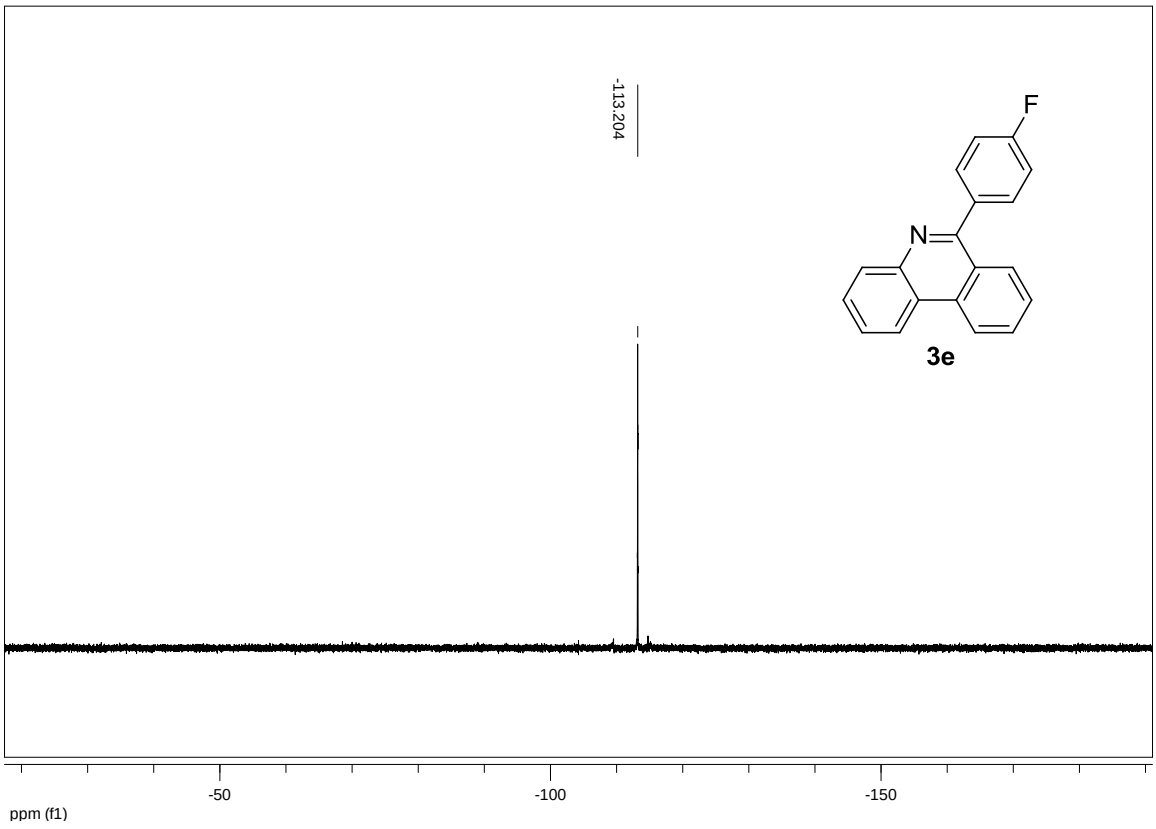
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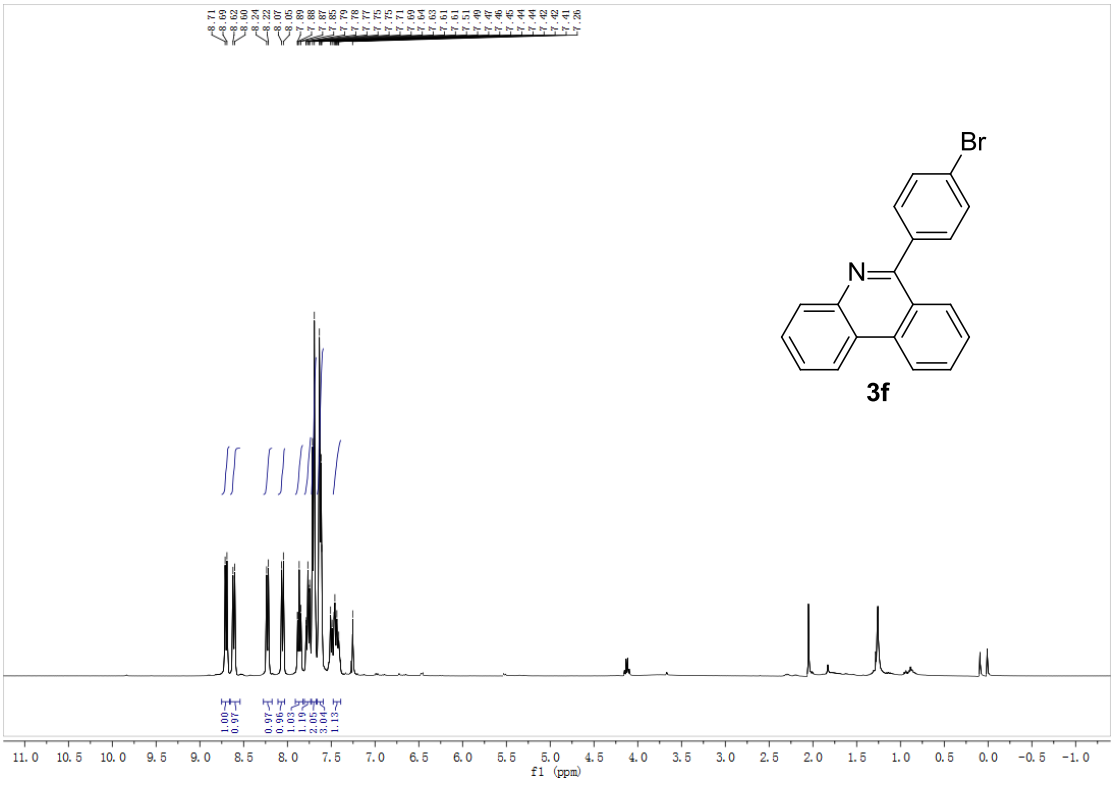
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N
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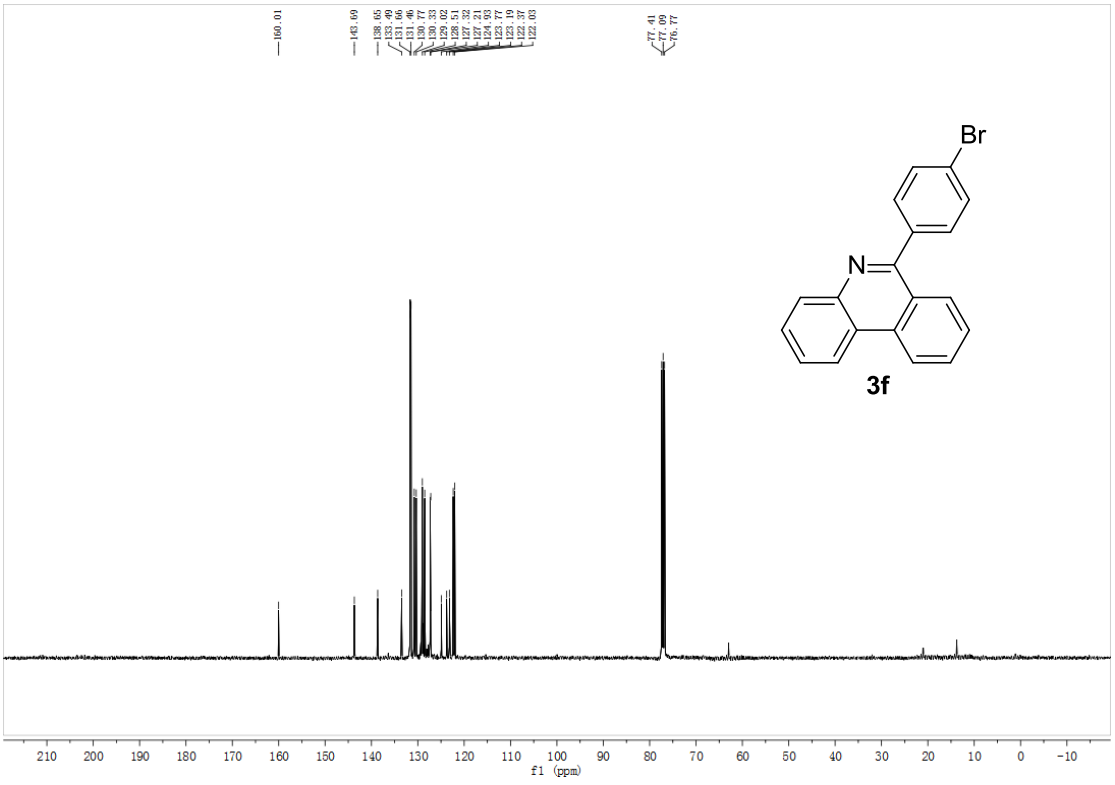
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N
3f
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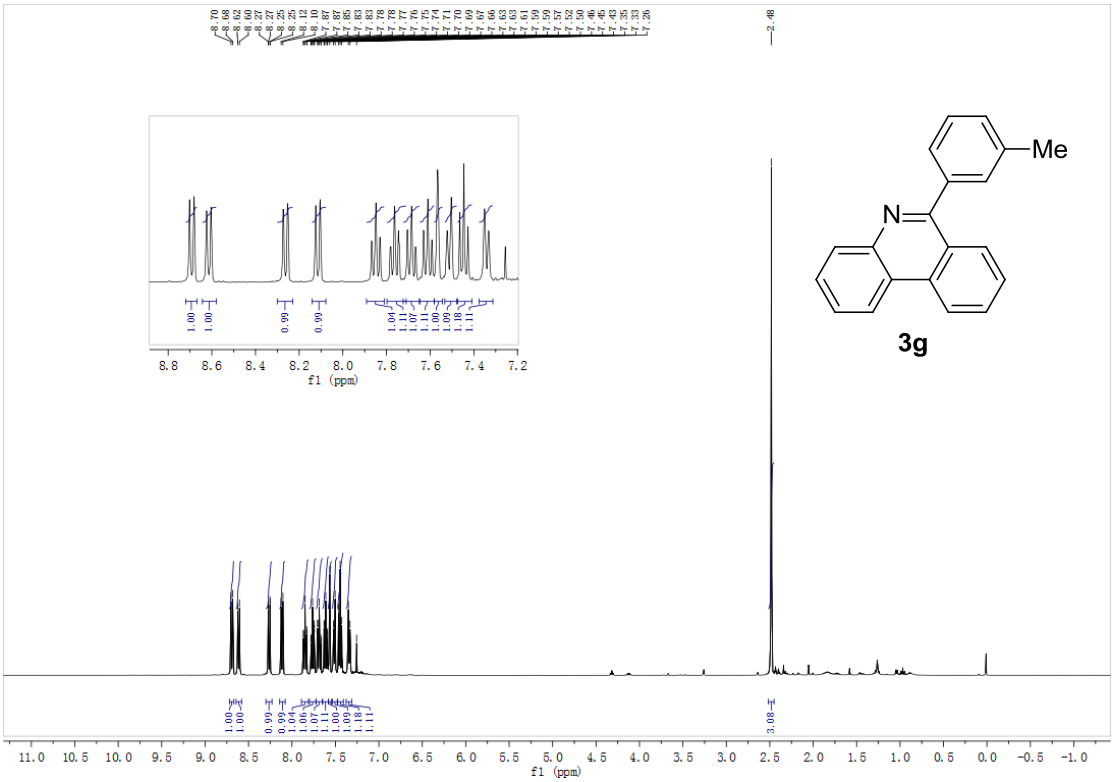
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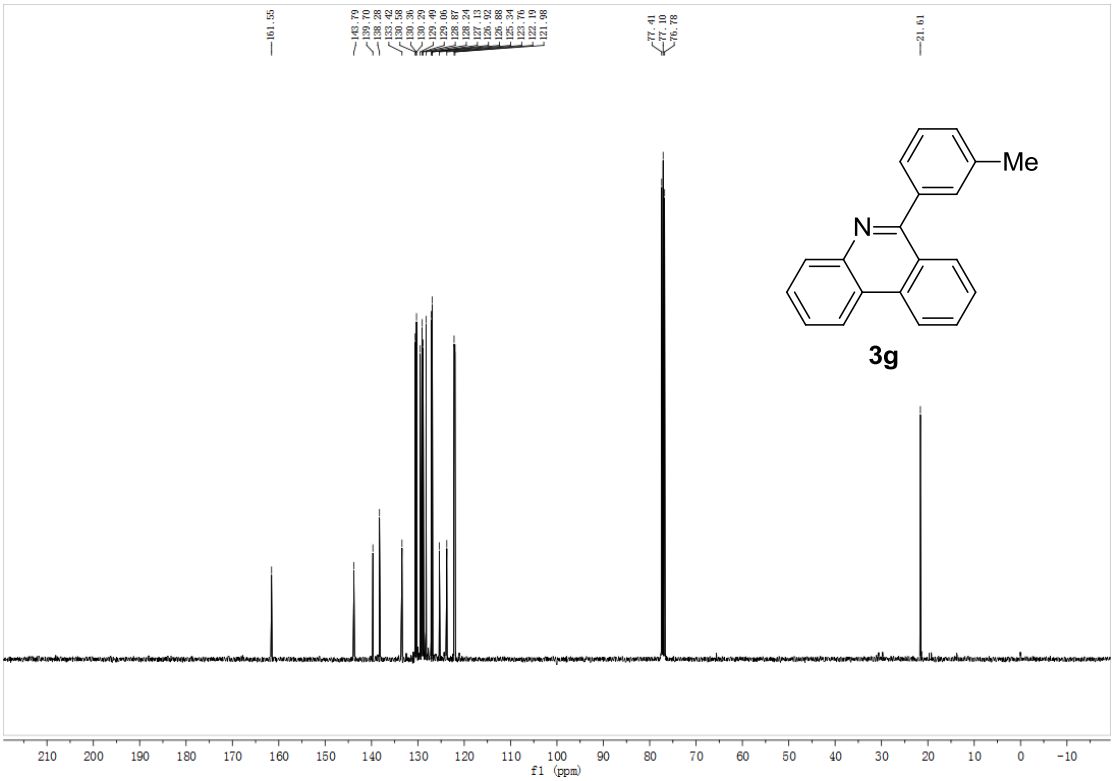
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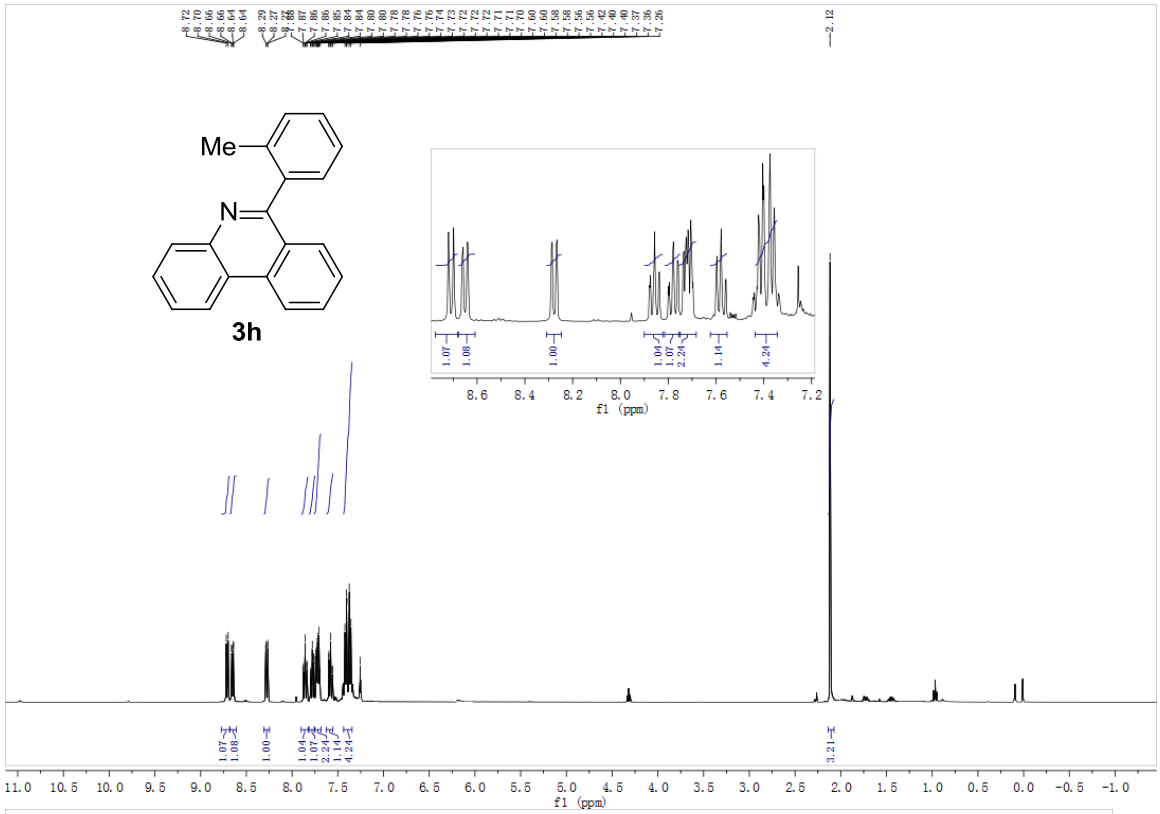
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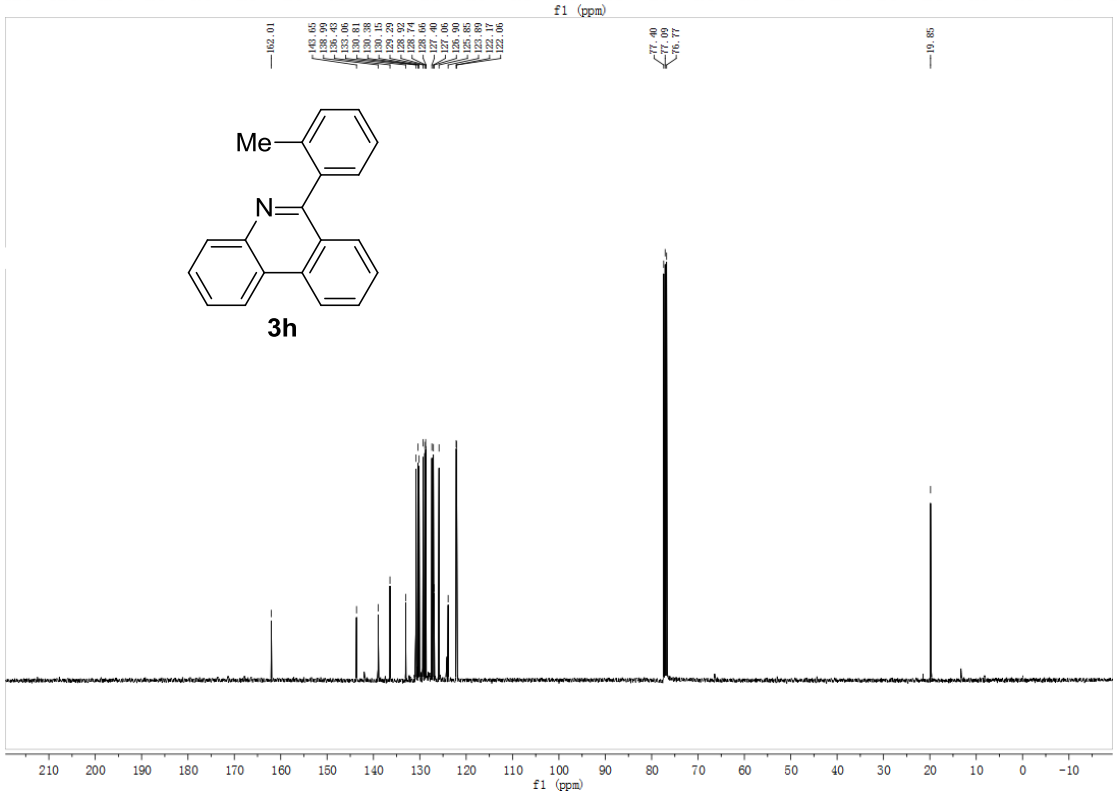
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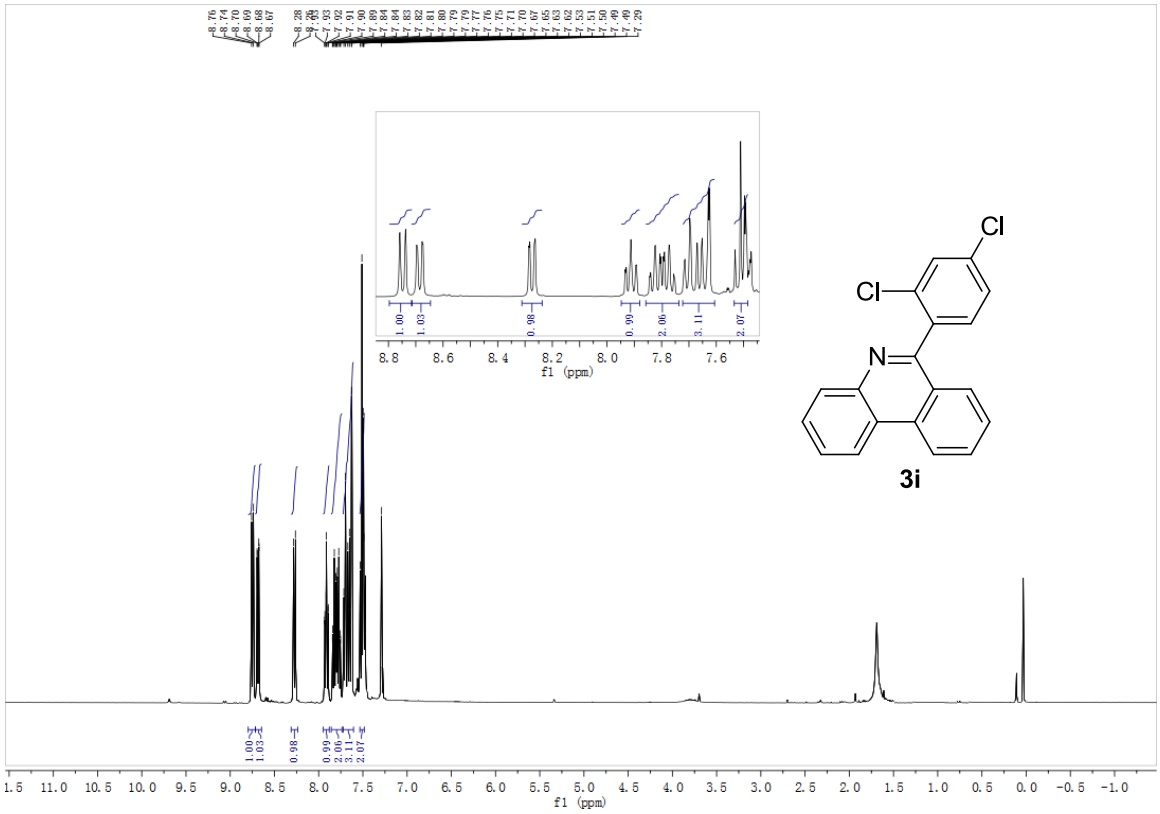
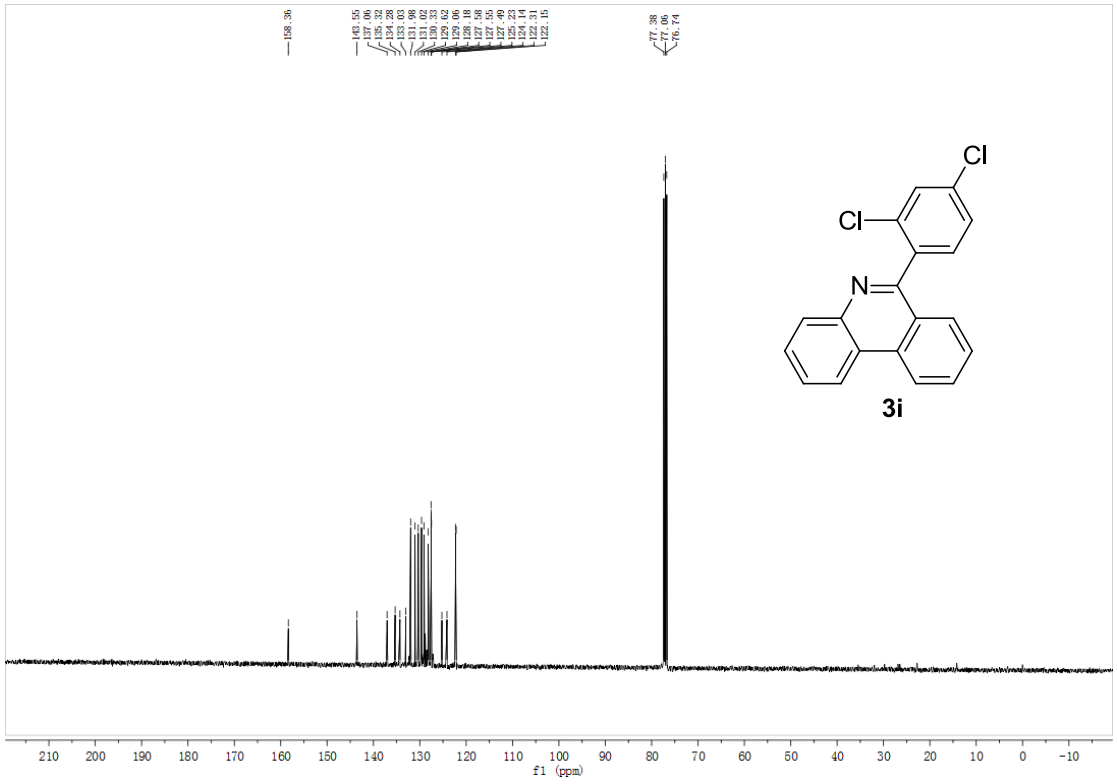
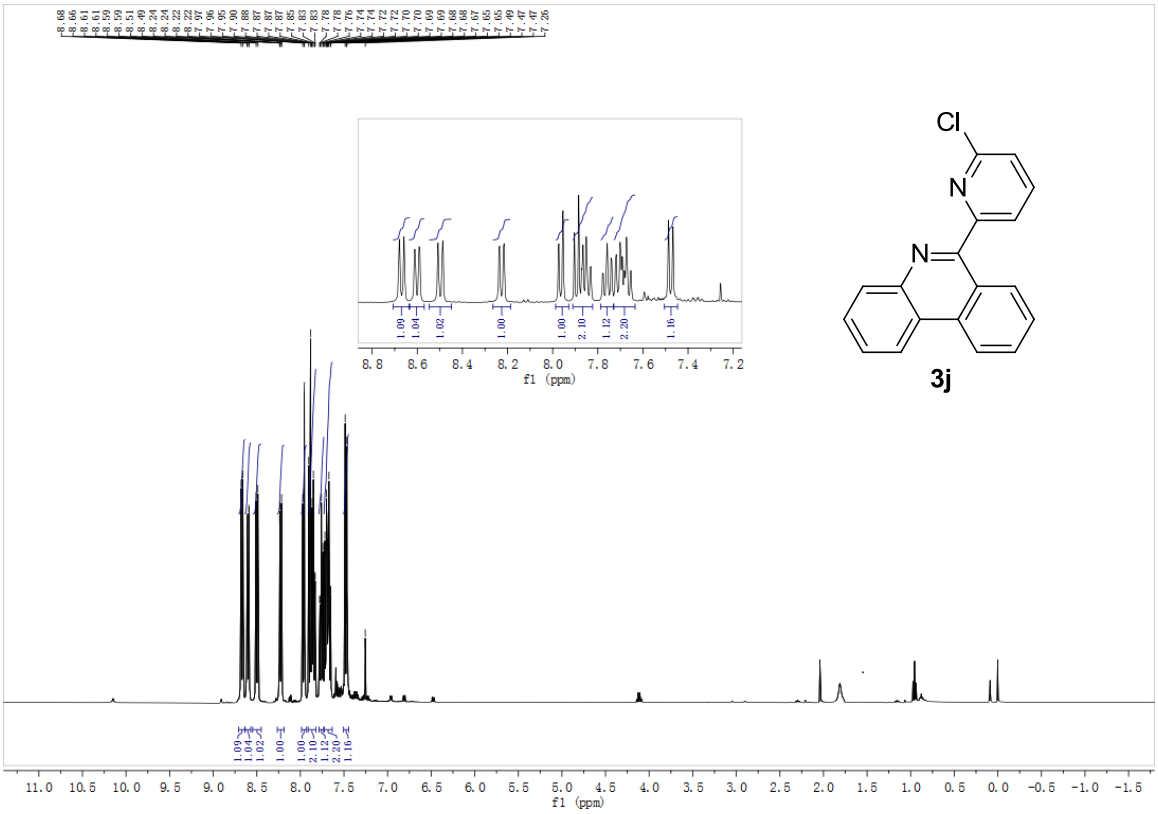
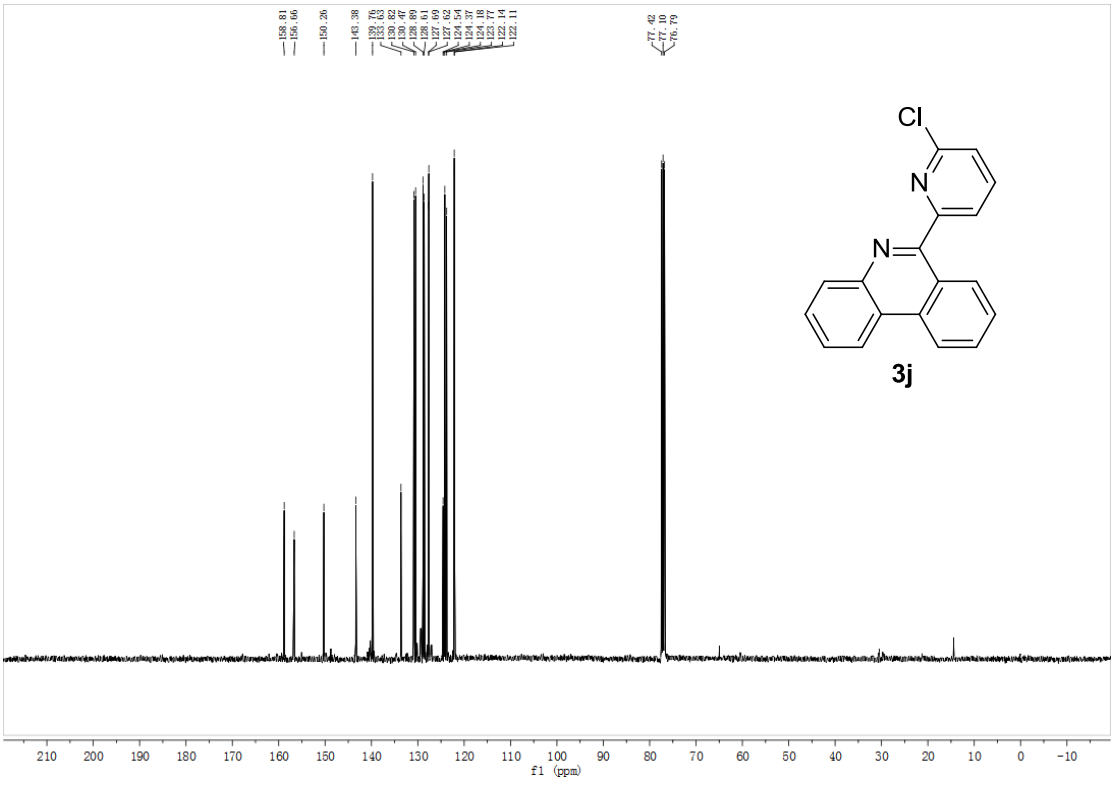
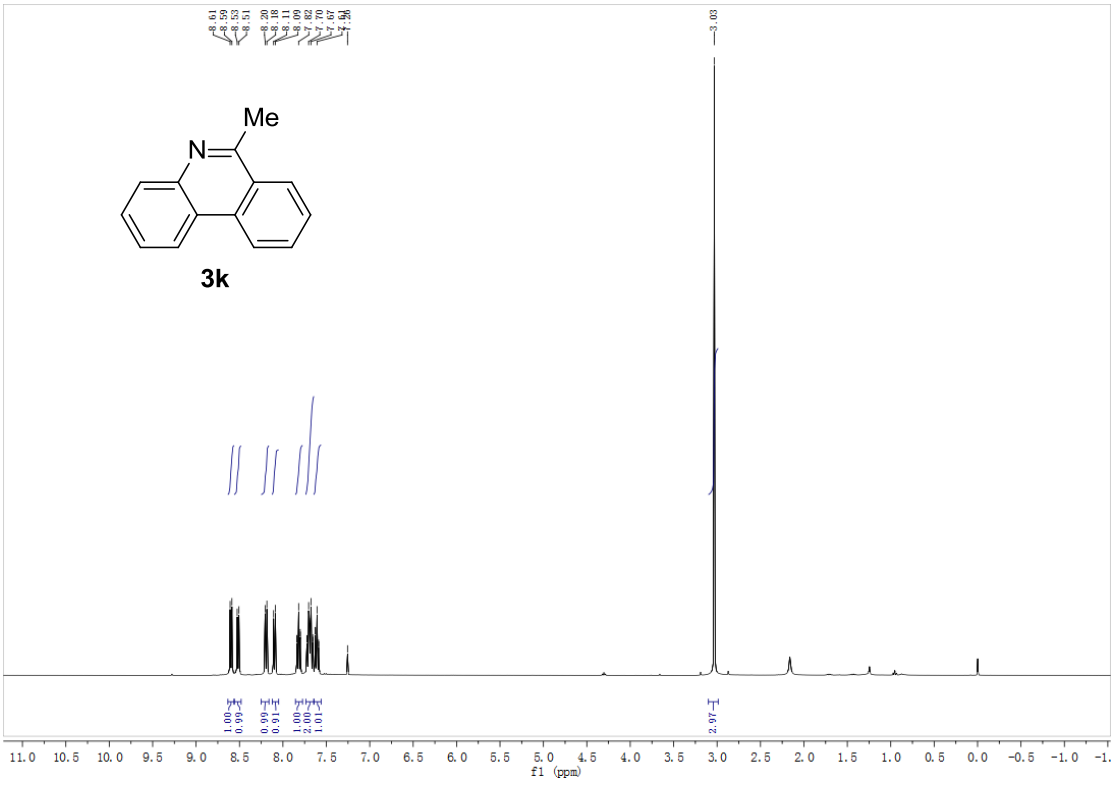
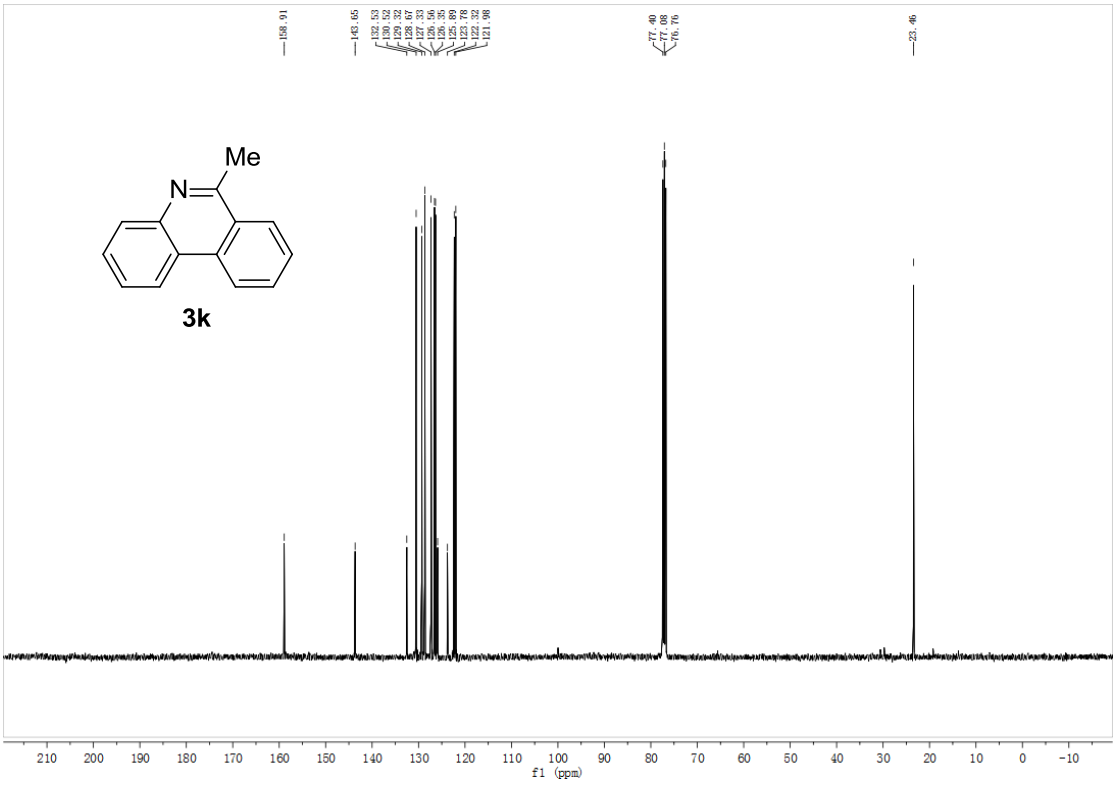

Cl
Cl
N
3i
f1 (ppm)

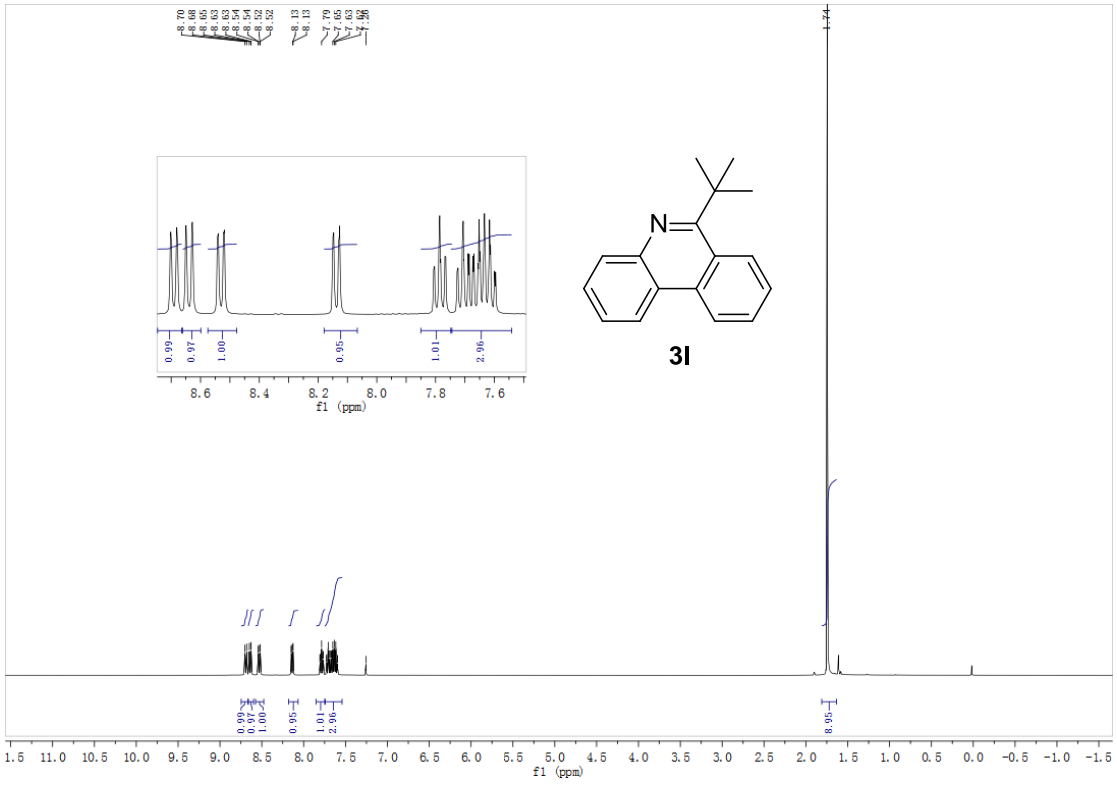

Cl
Cl
N
3i
f1 (ppm)


Cl
N
N
3j
f1 (ppm)

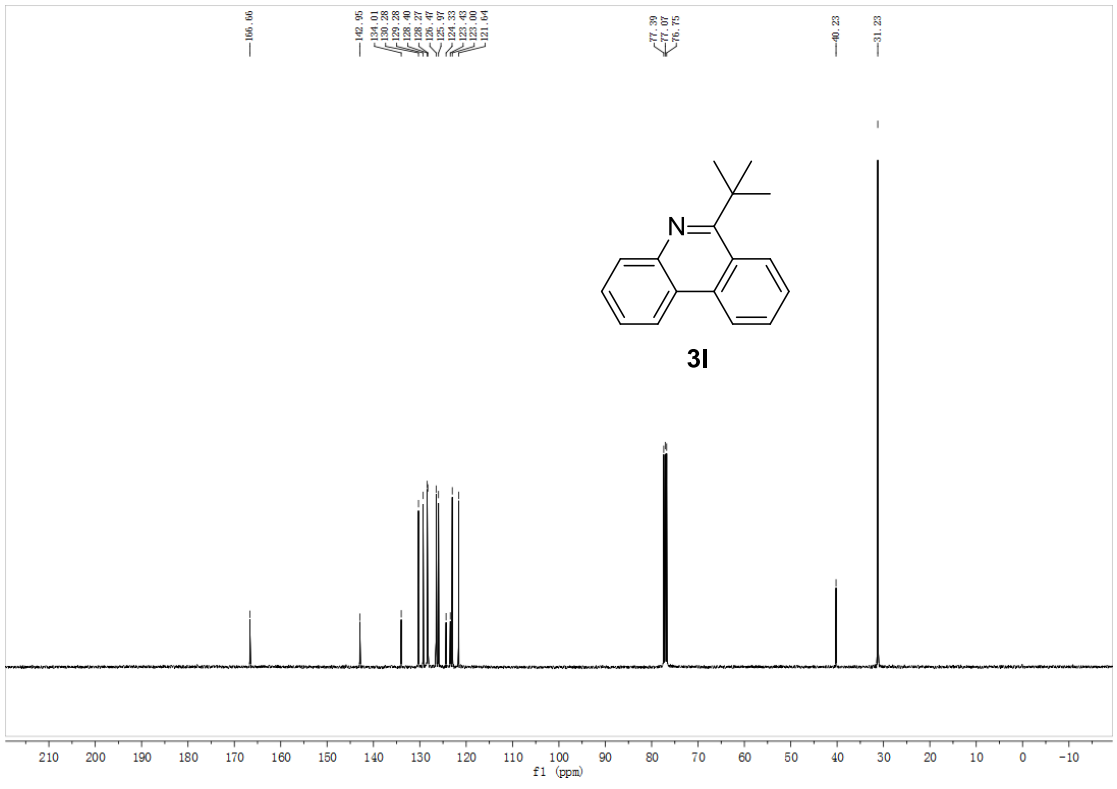

Cl
N
N
3j
f1 (ppm)


Me
N
3k
f1 (ppm)

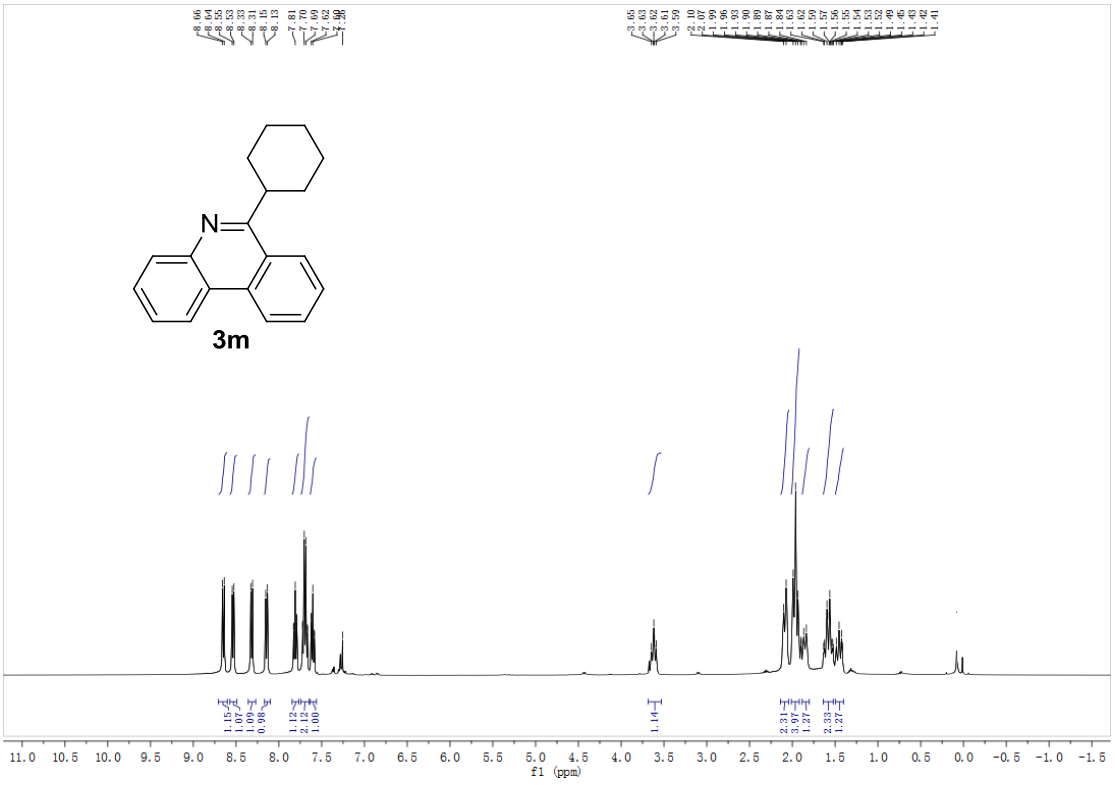

Me
N
3k
f1 (ppm)

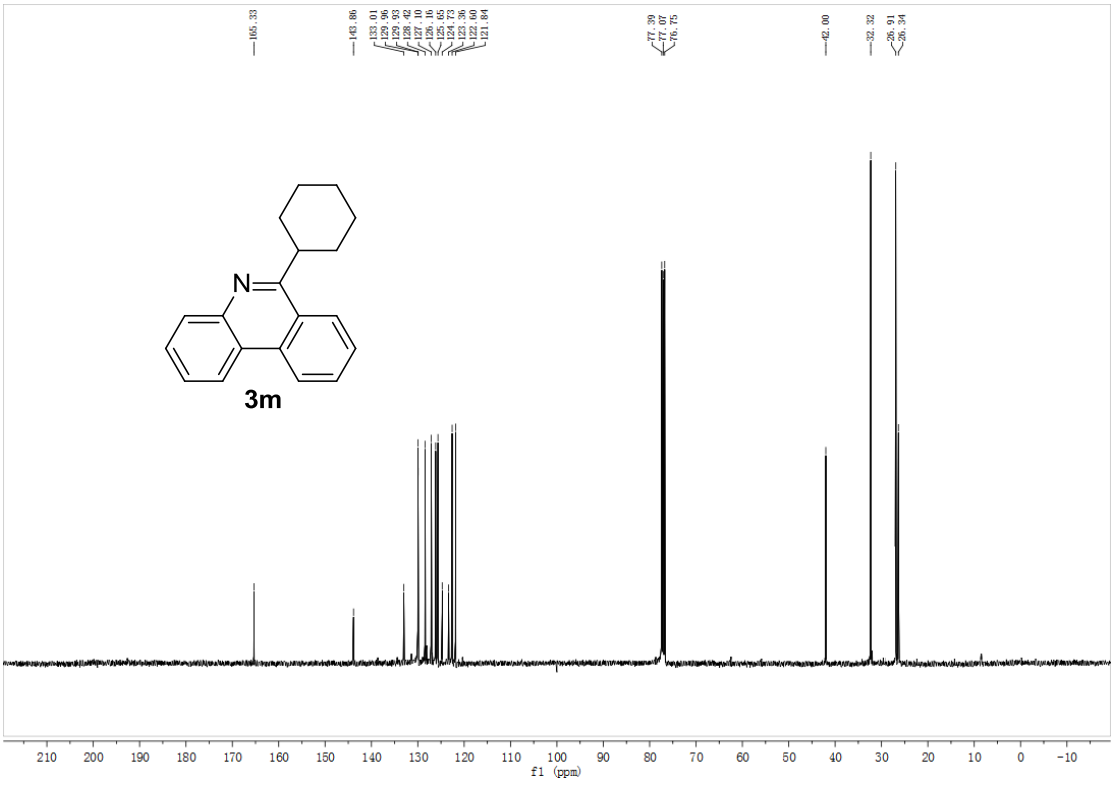

8.70
8.68
8.65
8.63
8.61
8.54
8.52
8.13
8.11
7.79
7.65
7.63
7.62
7.60
1.74
0.99
0.97
1.00
0.95
1.01
2.96
8.95
8.6
8.4
8.2
8.0
7.8
7.6
f1 (ppm)
1.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1.5
f1 (ppm)
N

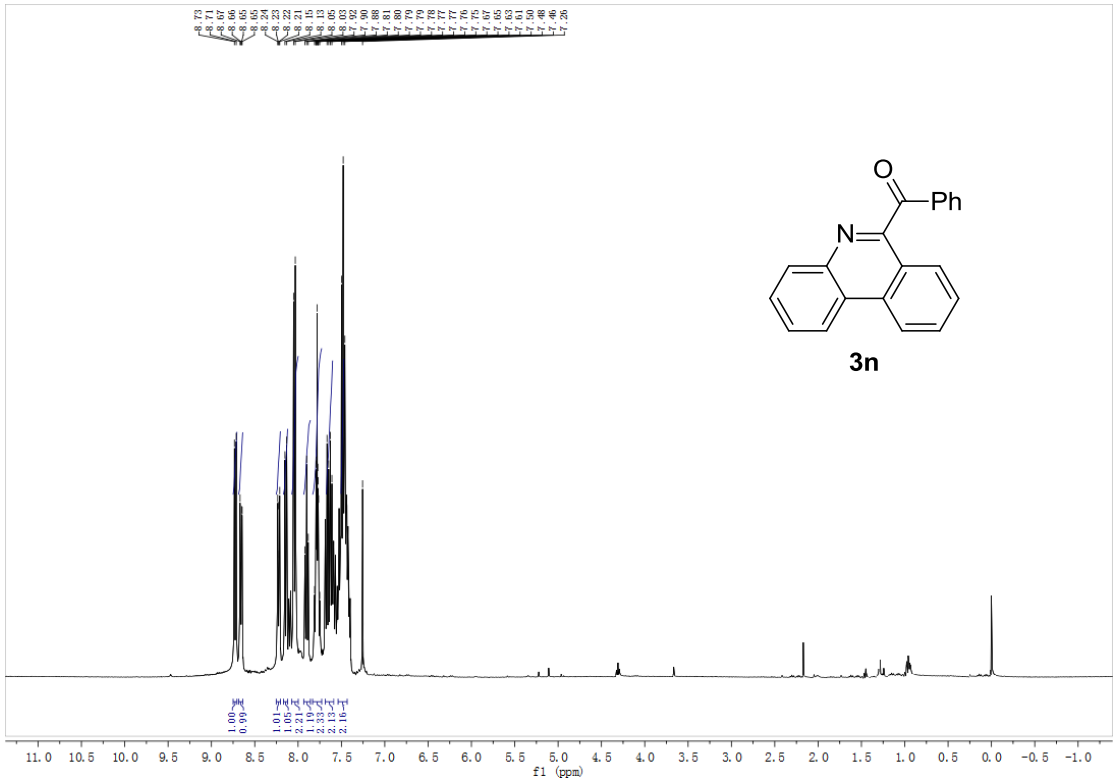
3l

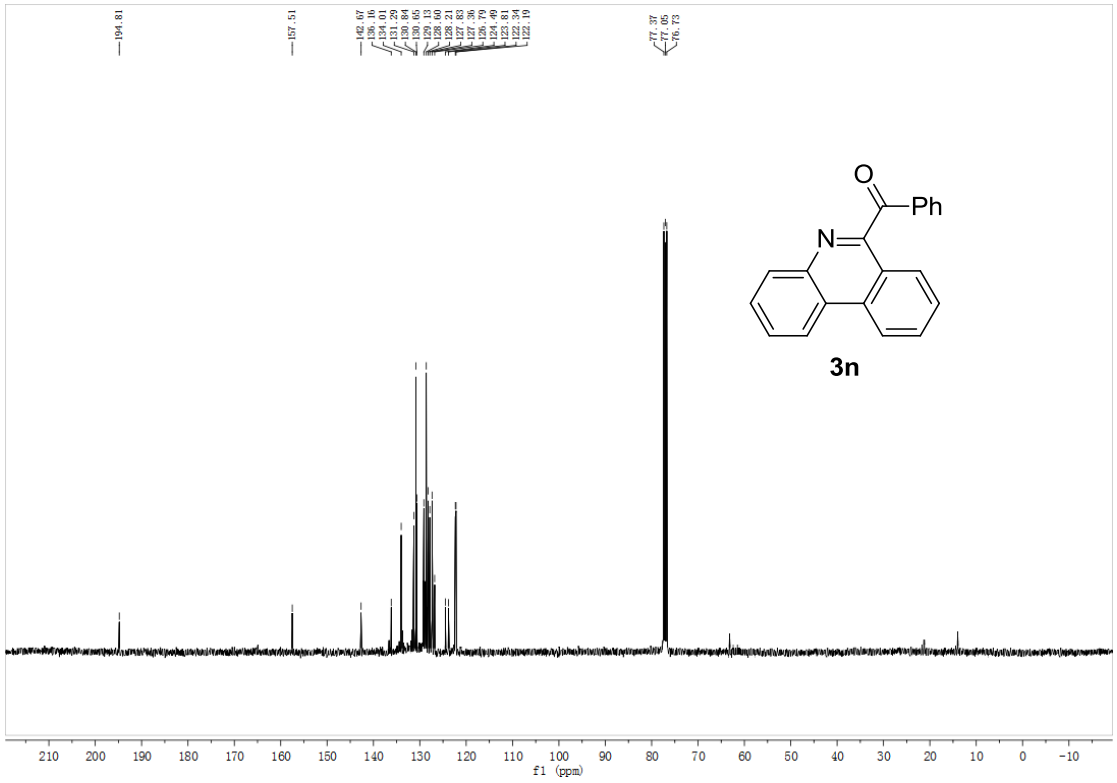

166.66
142.95
134.01
130.28
129.28
128.40
127.78
126.47
125.97
124.33
123.45
123.00
121.64
77.39
77.07
76.75
40.23
31.23
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)
N

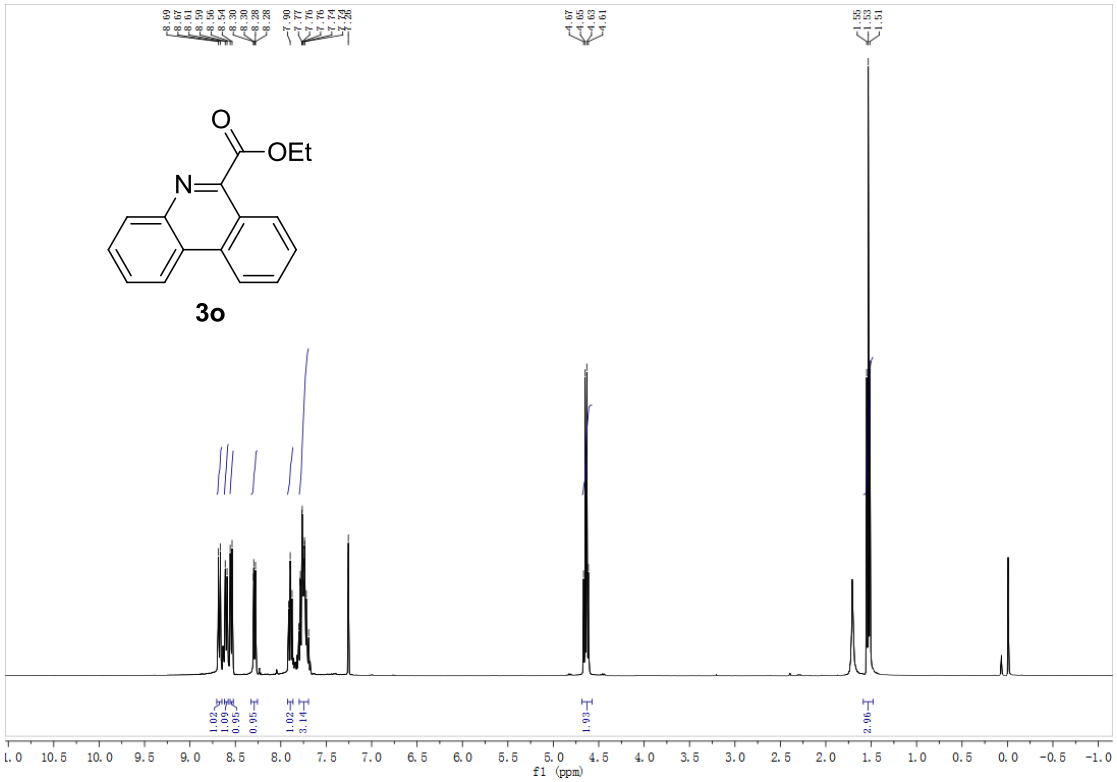
3l

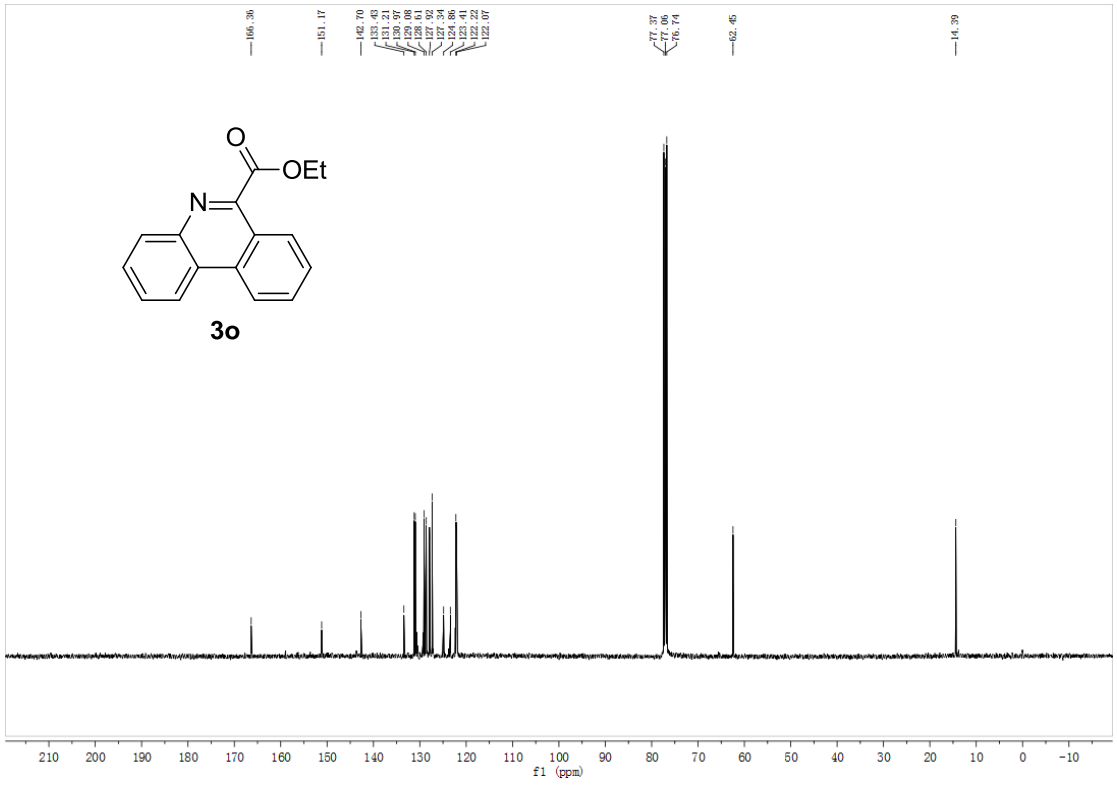

3m
f1 (ppm)

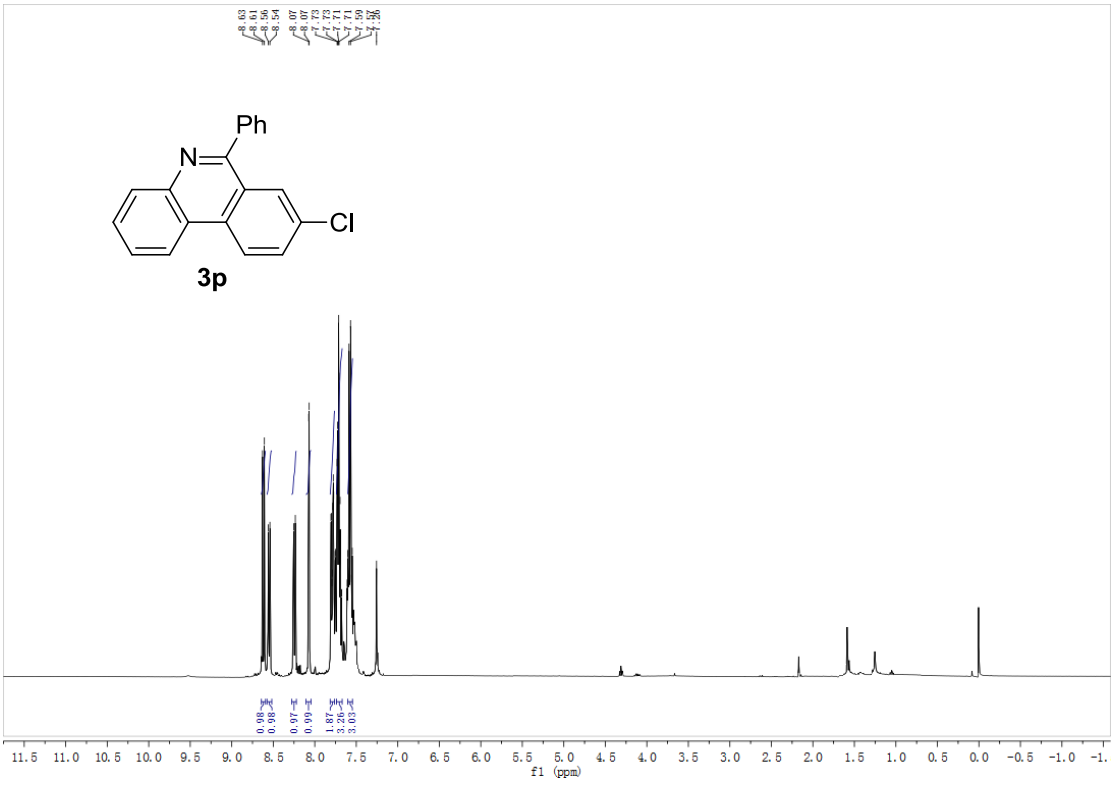

3m
f1 (ppm)

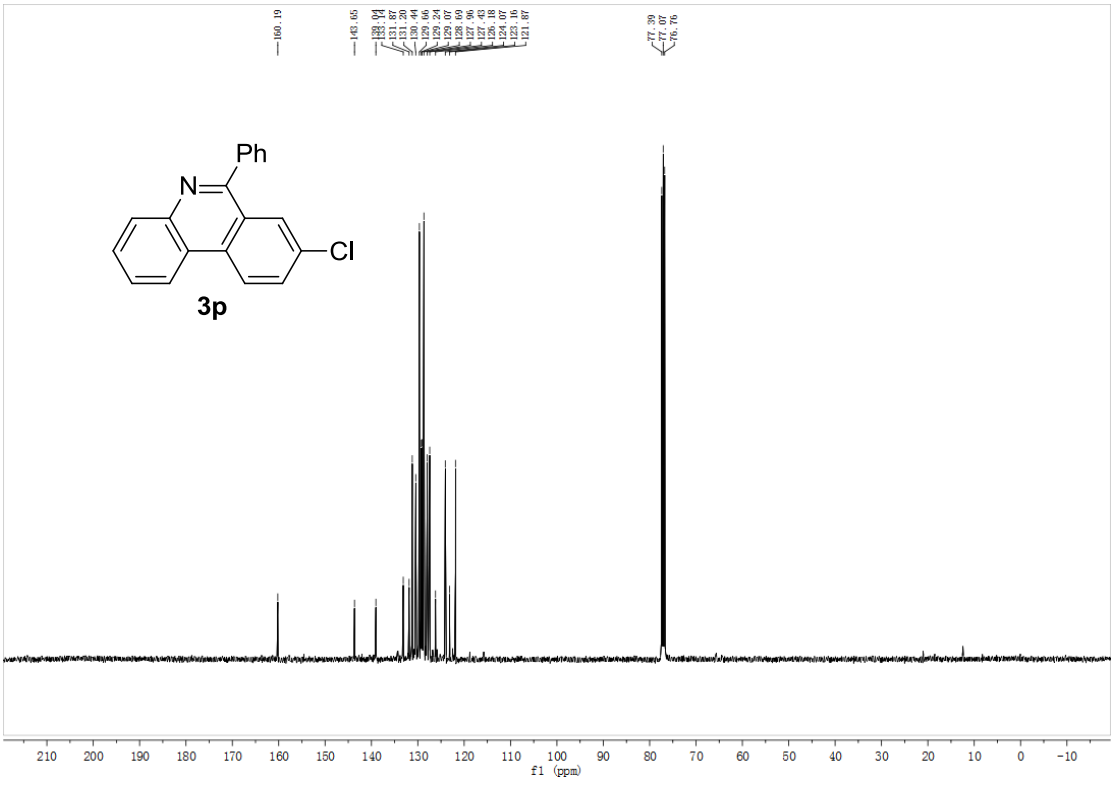

O
Ph
N
3n
f1 (ppm)

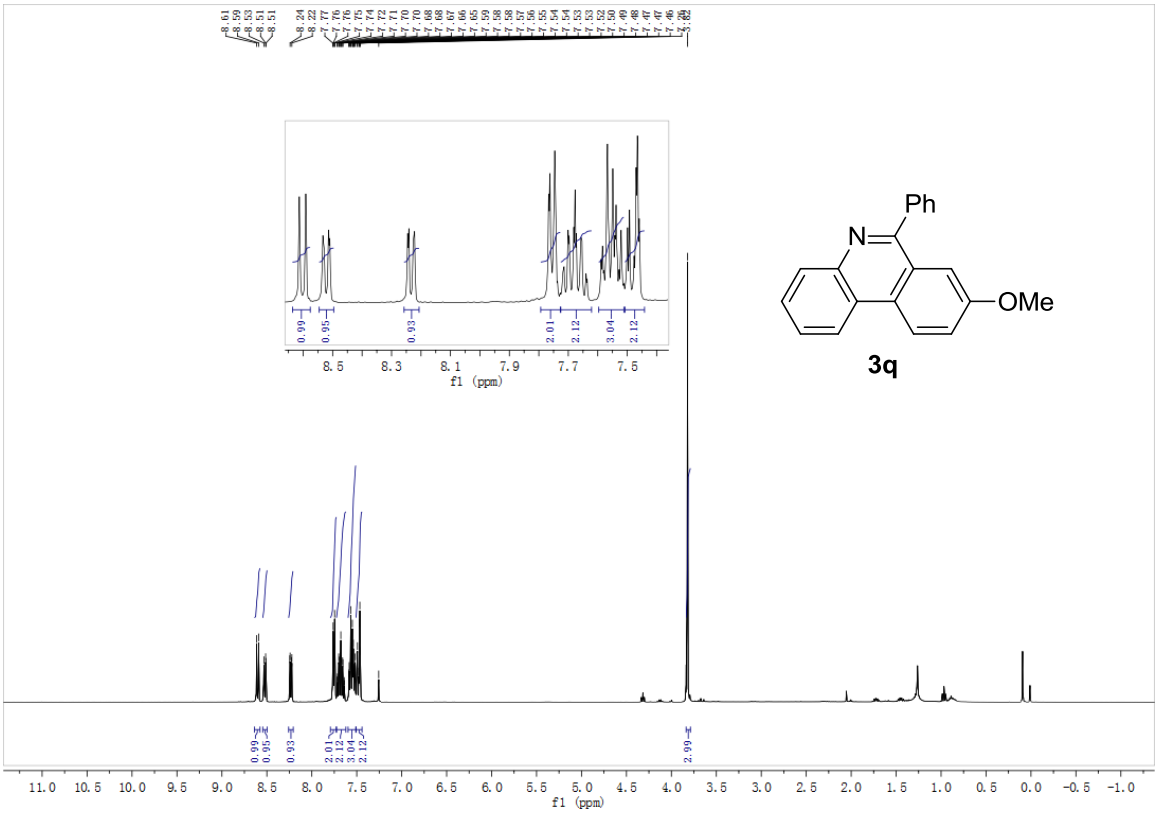

O
Ph
N
3n
f1 (ppm)

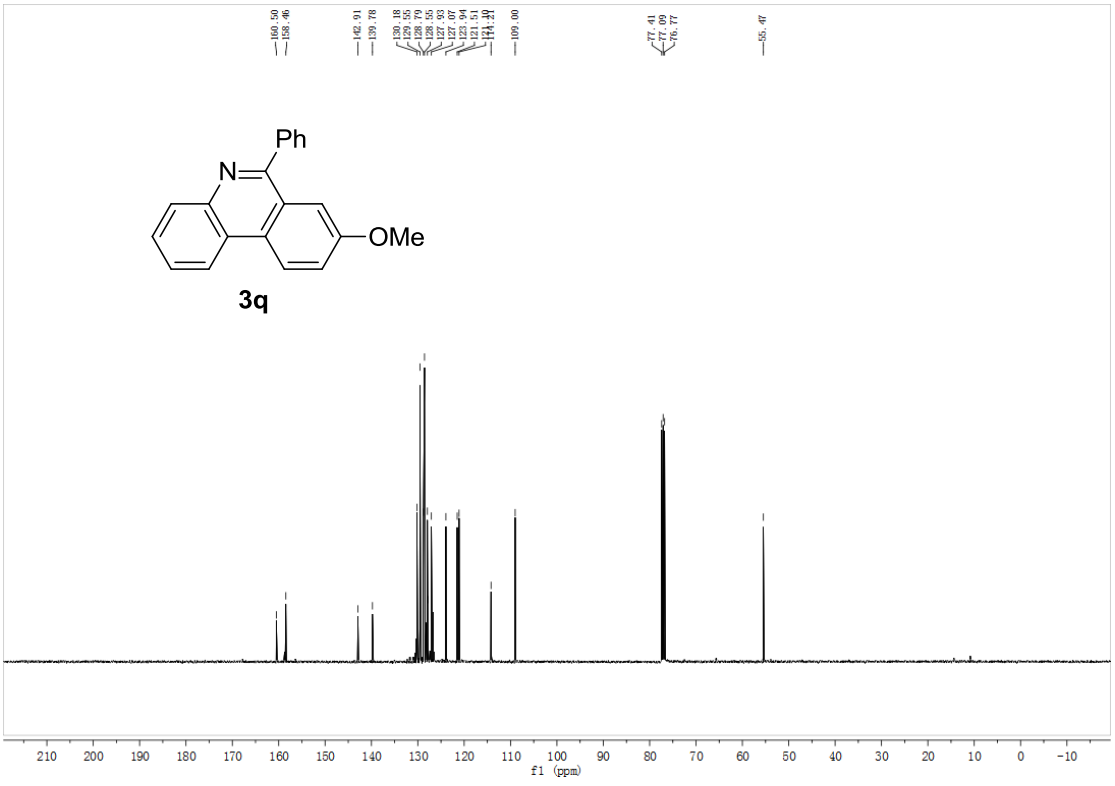

O
OEt
N
3o
f1 (ppm)

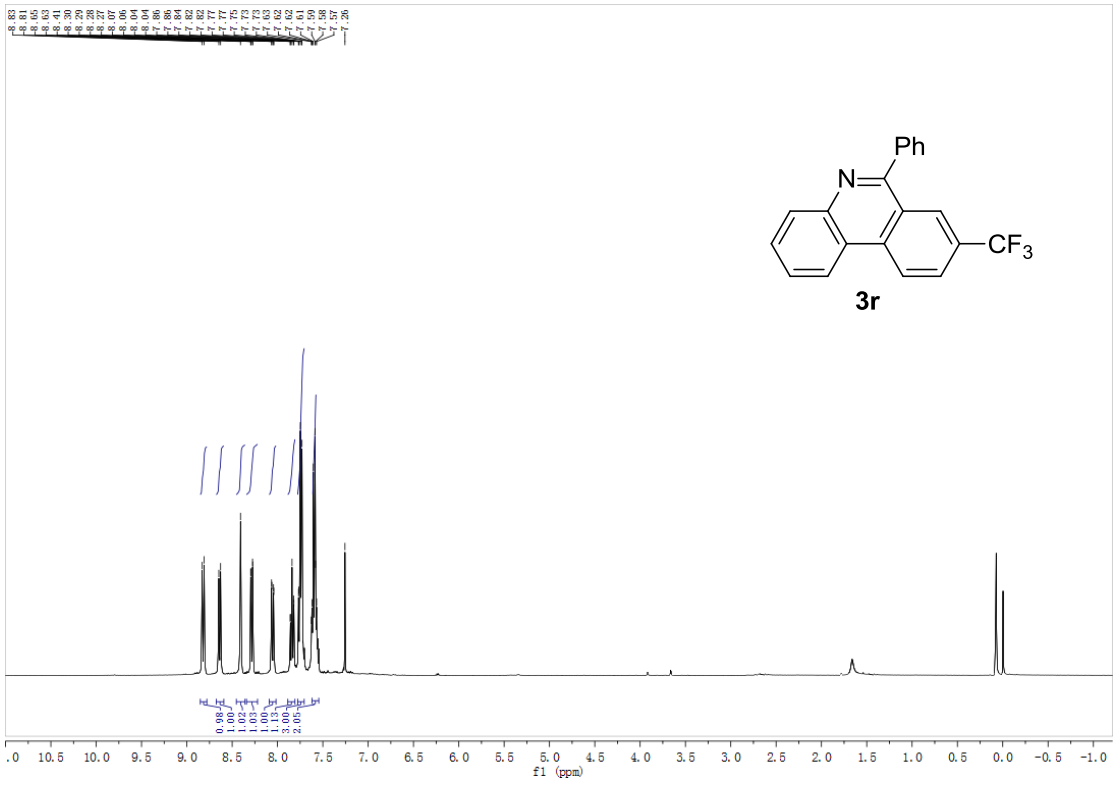

O
OEt
N
3o
f1 (ppm)

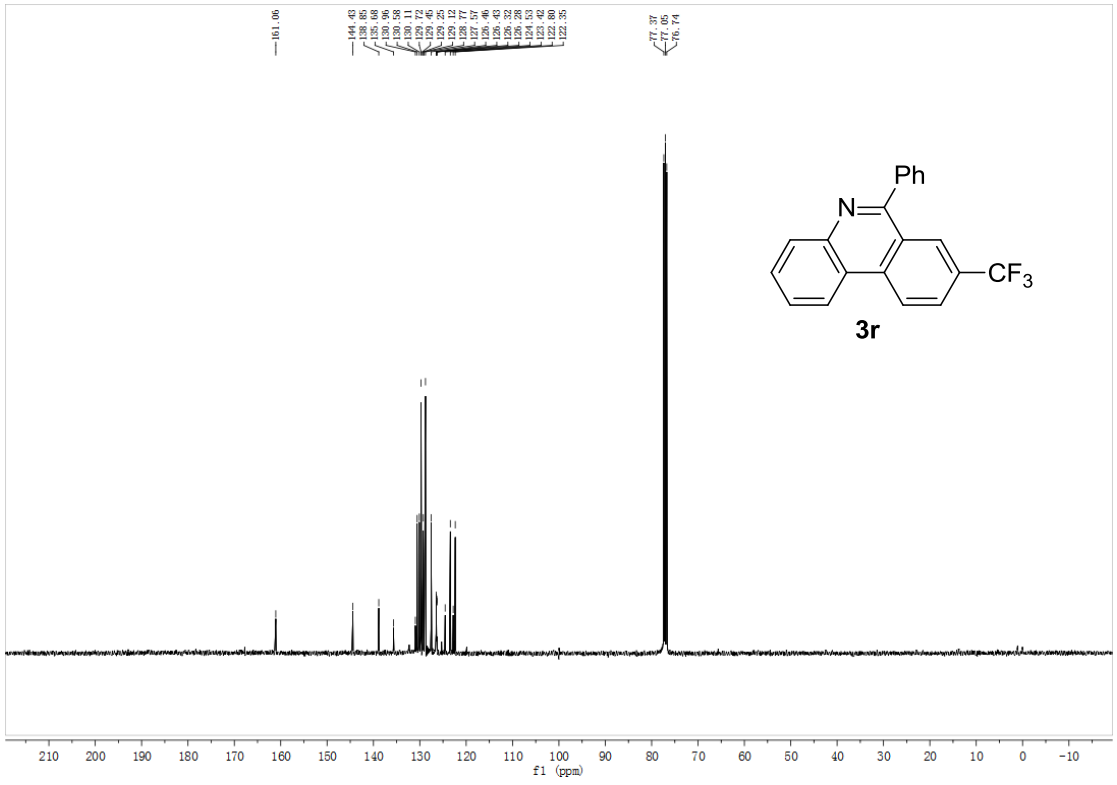

Ph
N
Cl
3p
f1 (ppm)

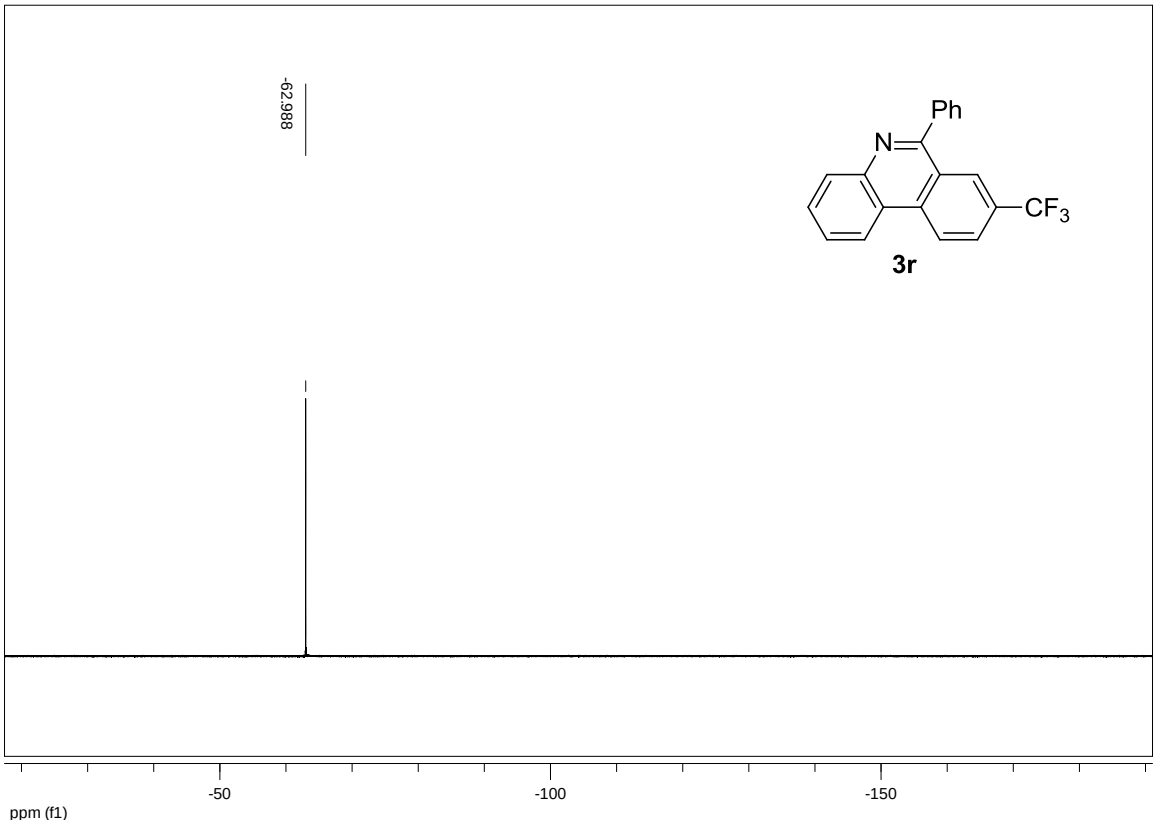

Ph
N
Cl
3p
f1 (ppm)

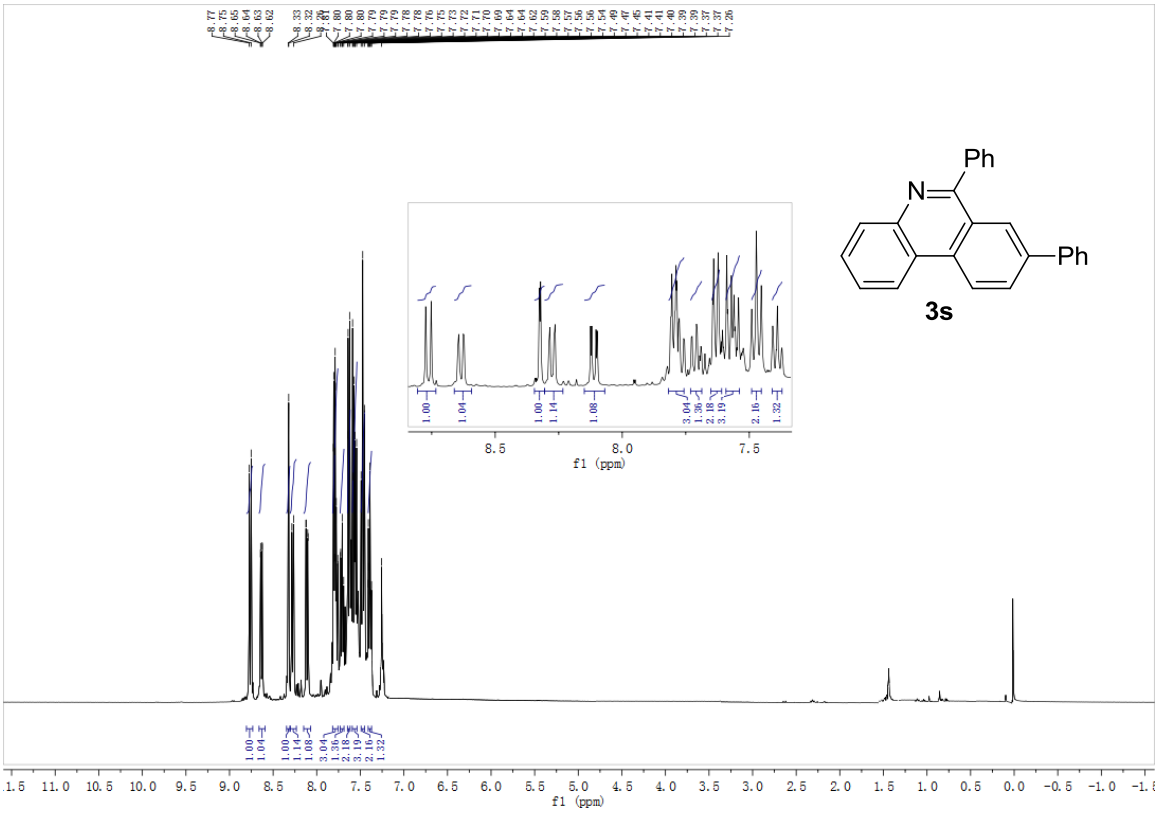

Ph
N
OMe
3q
f1 (ppm)

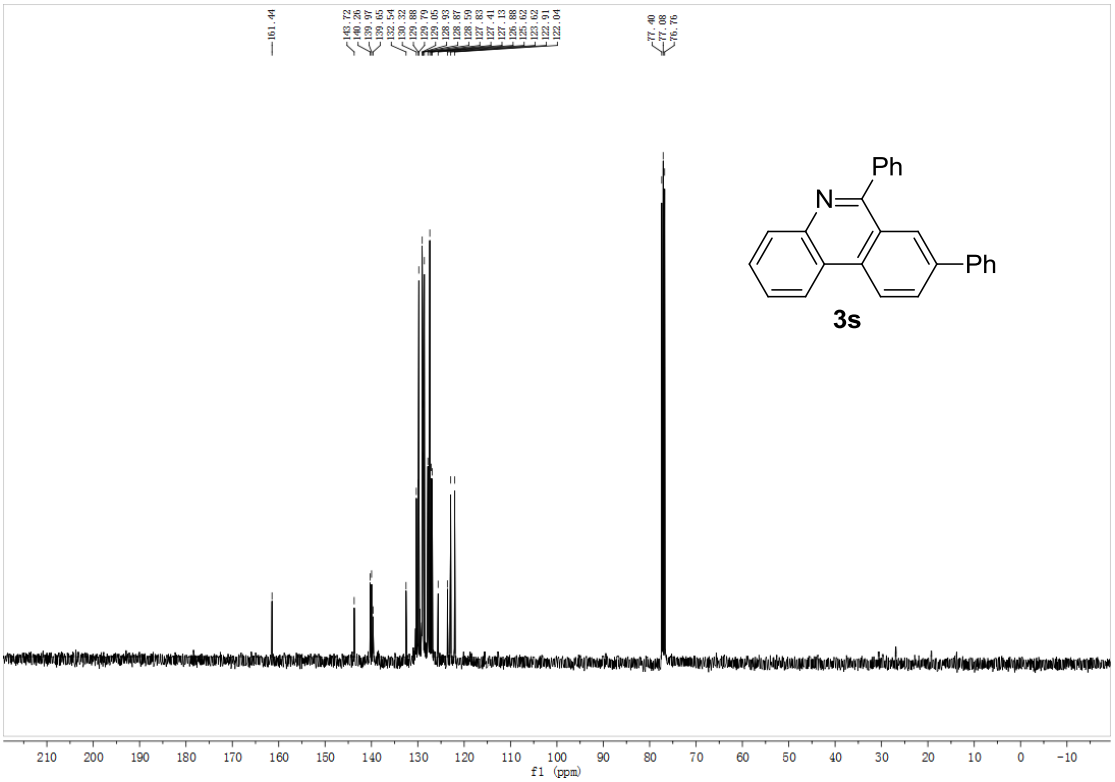

Ph
N
OMe
3q
f1 (ppm)

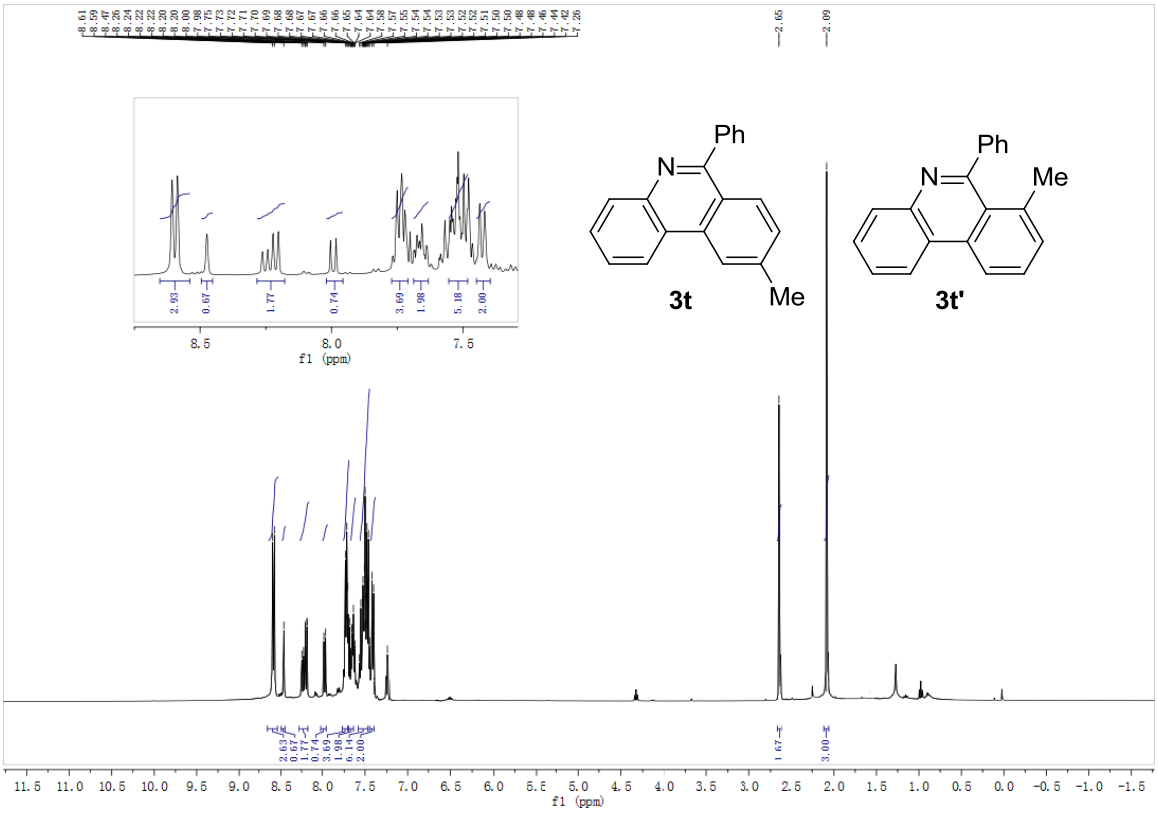

Ph
N
CF3
3r
f1 (ppm)

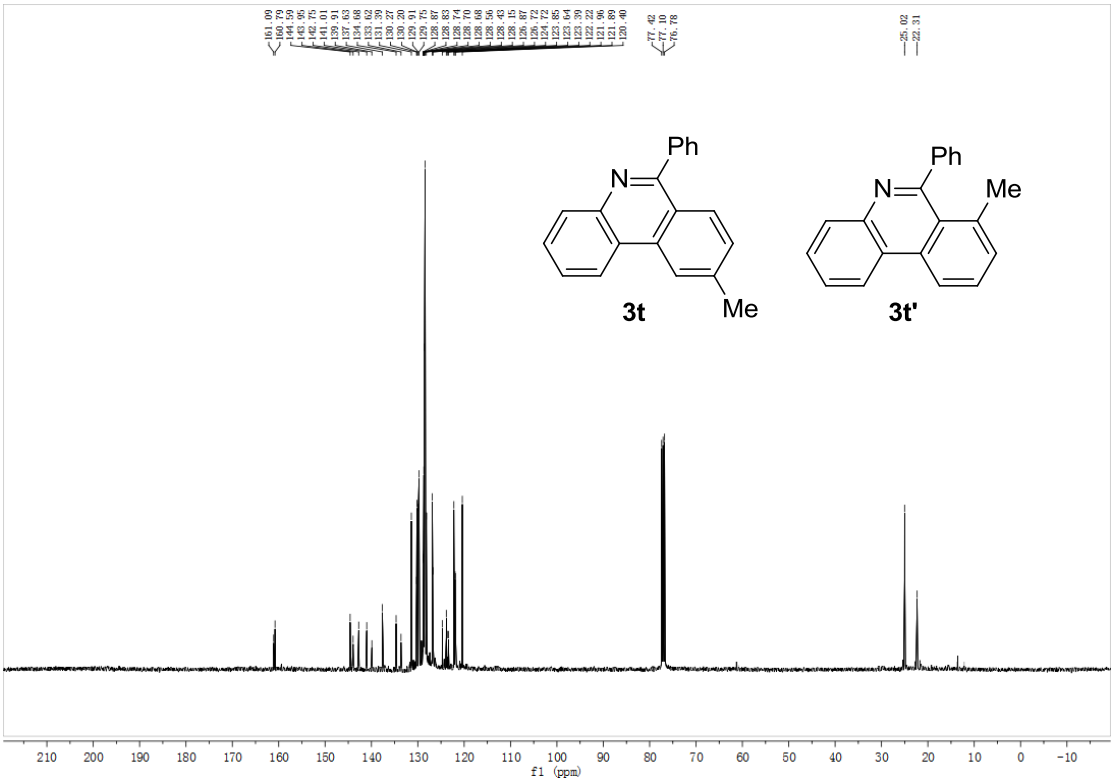

Ph
N
CF3
3r
f1 (ppm)

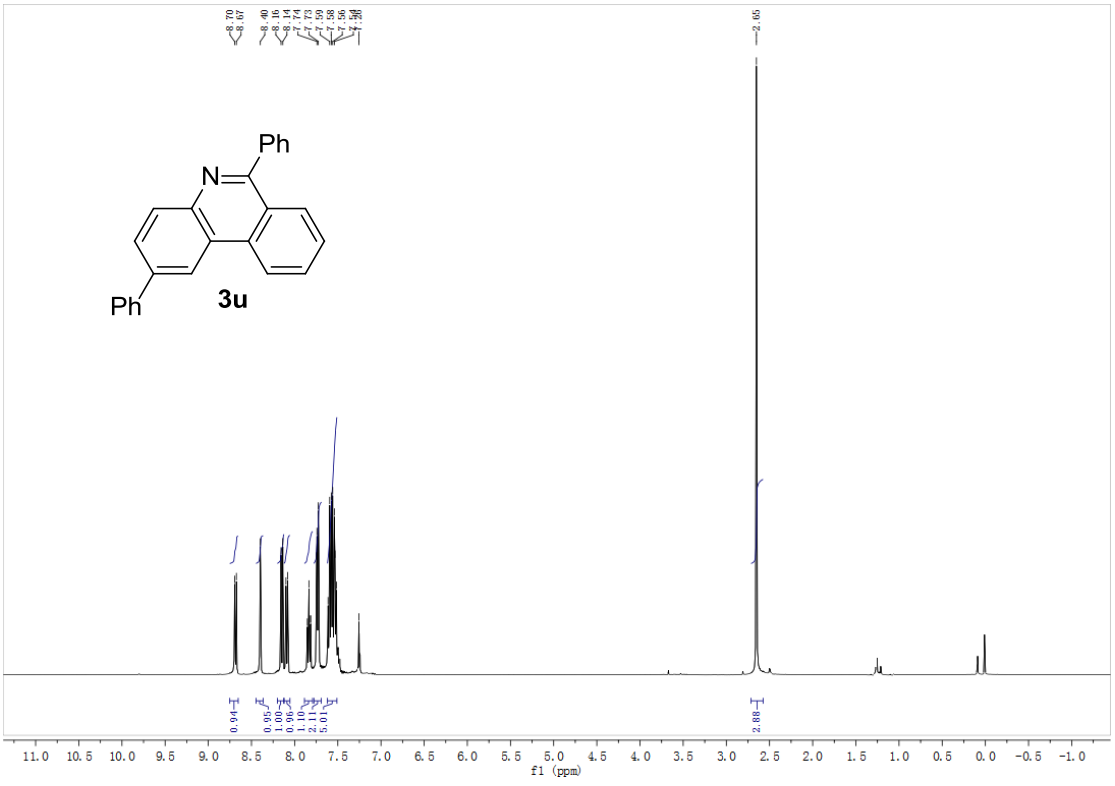

-62.988
Ph
N
CF3
3r
-50
-100
-150
ppm (f1)

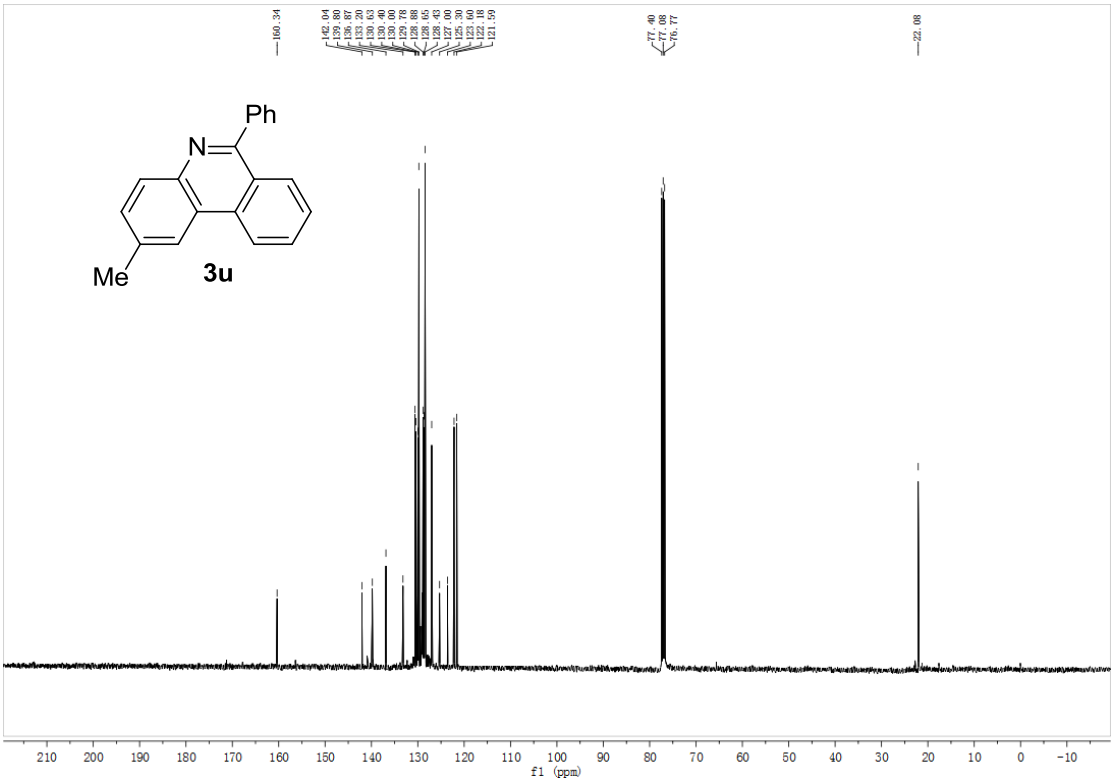

Ph
N
Ph
3s
8.5
8.0
7.5
f1 (ppm)

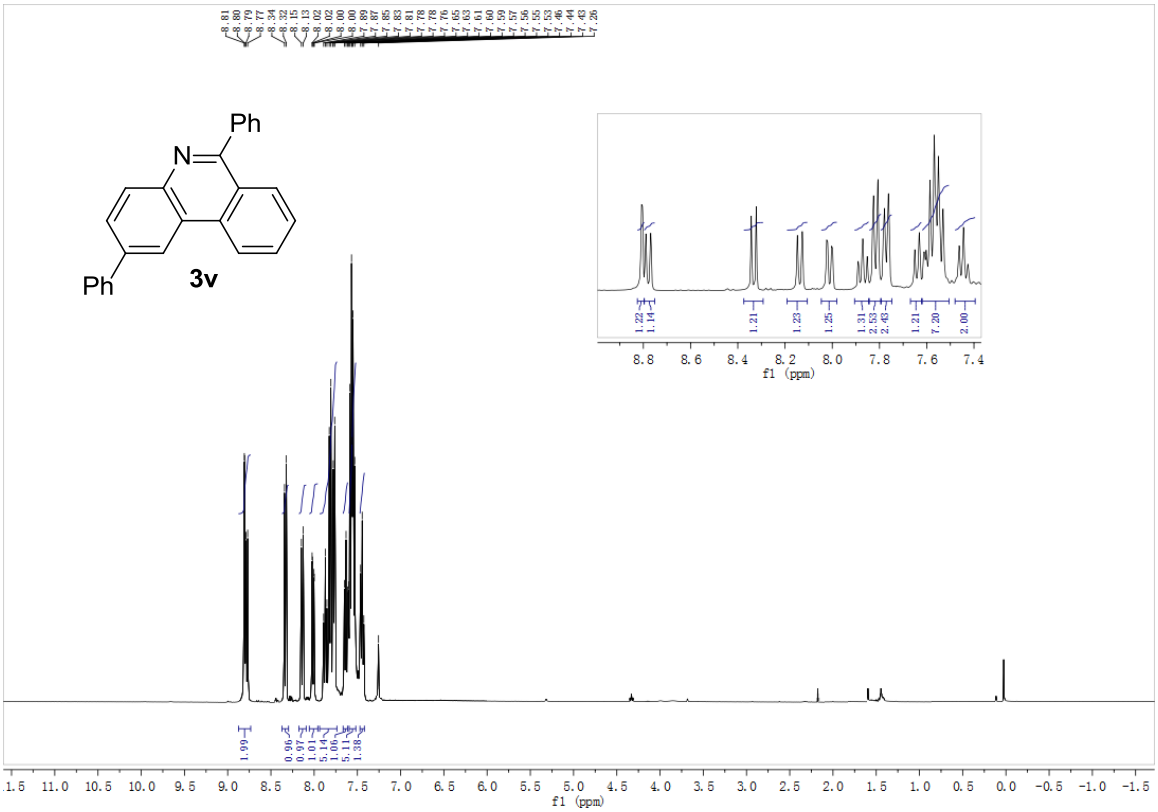

Ph
N
Ph
3s
f1 (ppm)

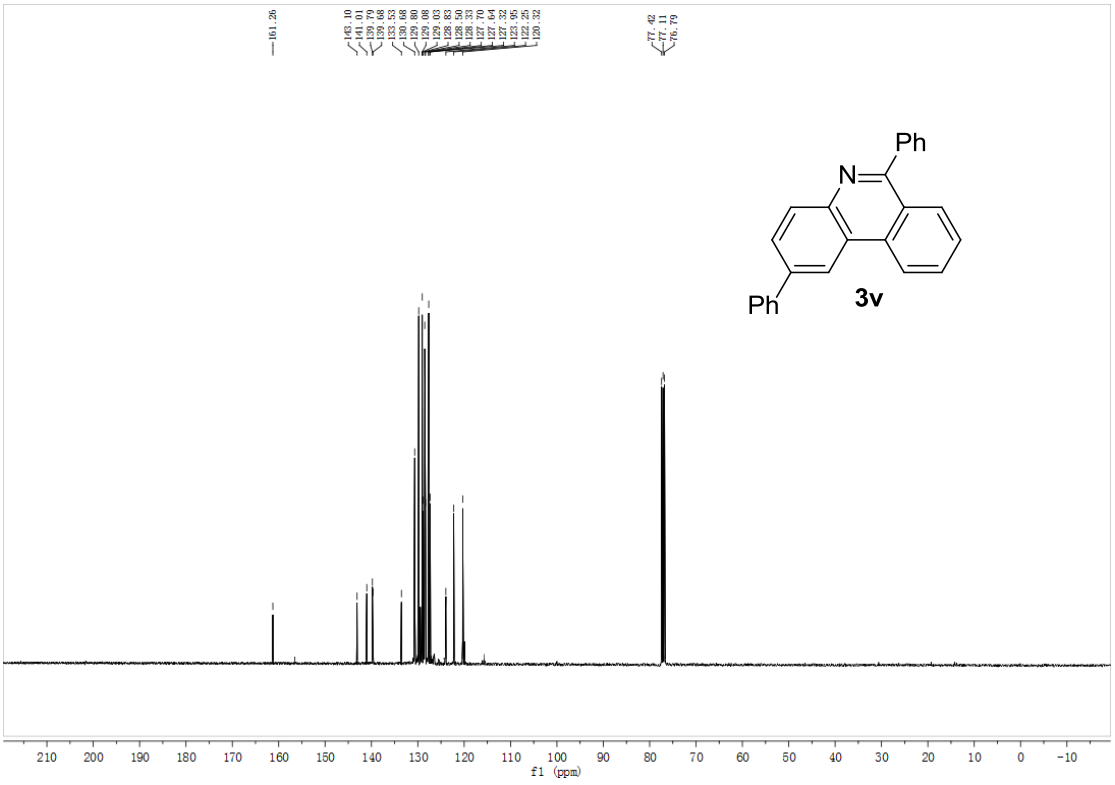

Ph
N
Me
3t
Ph
N
Me
3t'
f1 (ppm)

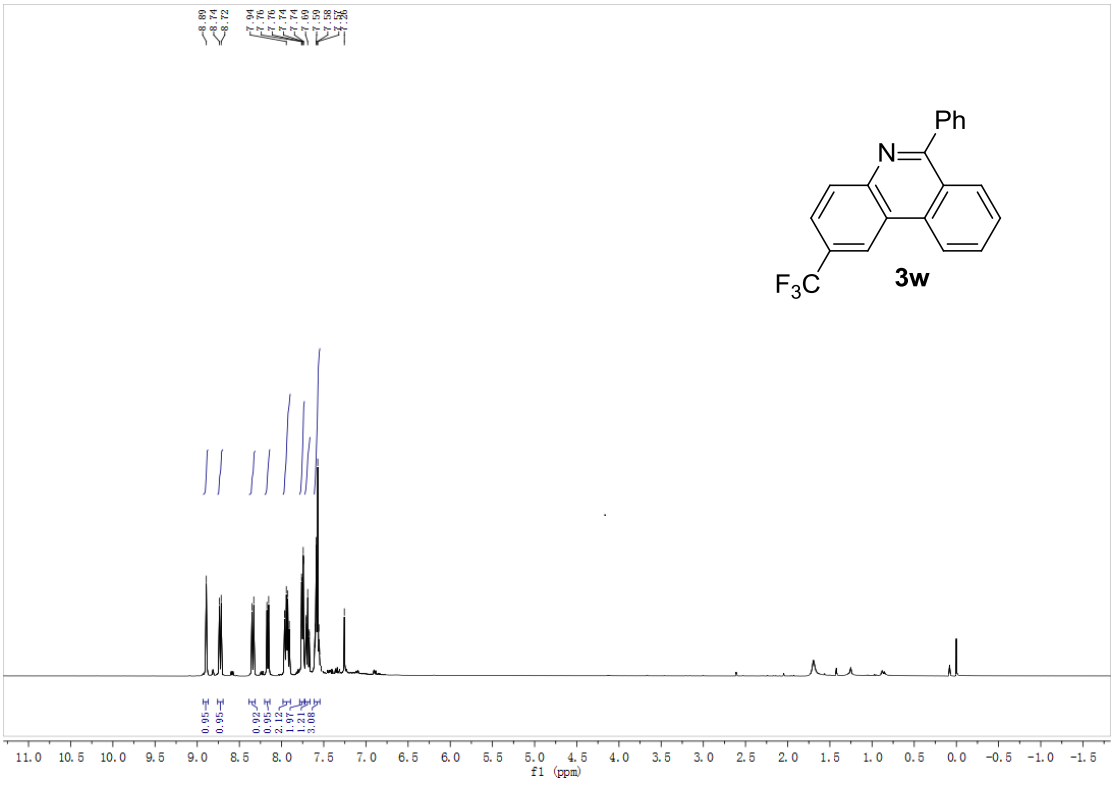

Ph
N
Me
3t
Ph
N
Me
3t'
f1 (ppm)

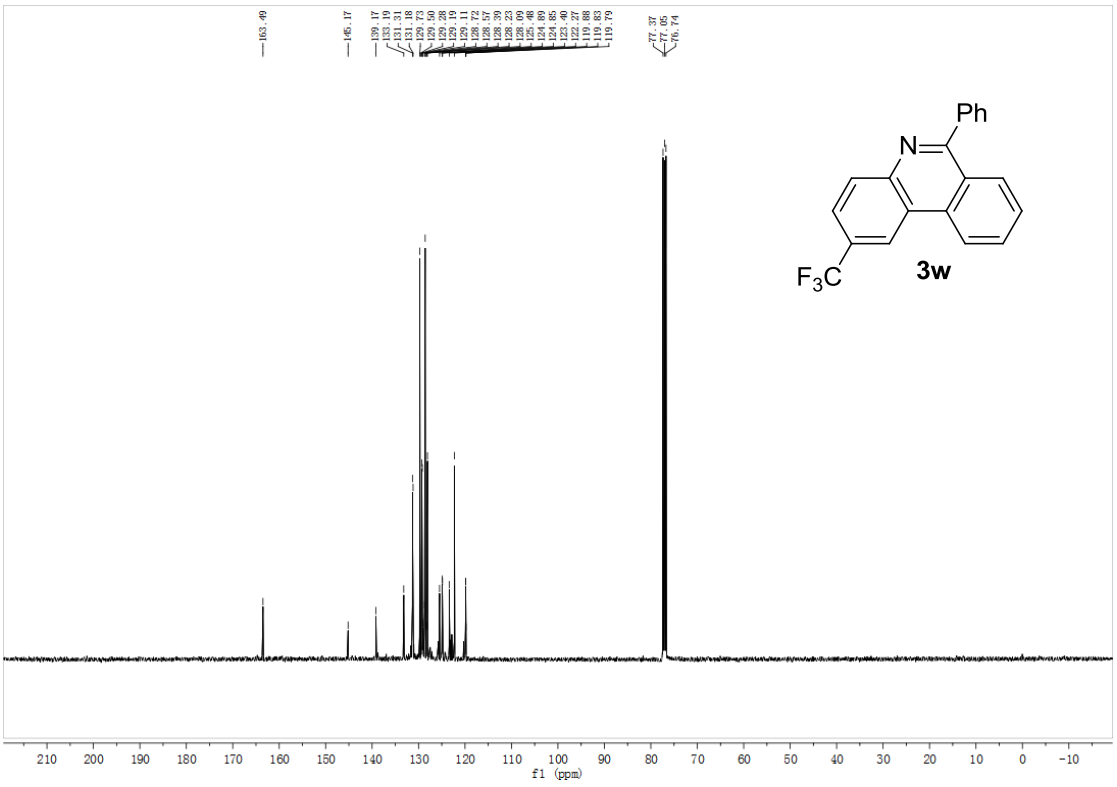

Ph
N
Ph
3u
f1 (ppm)

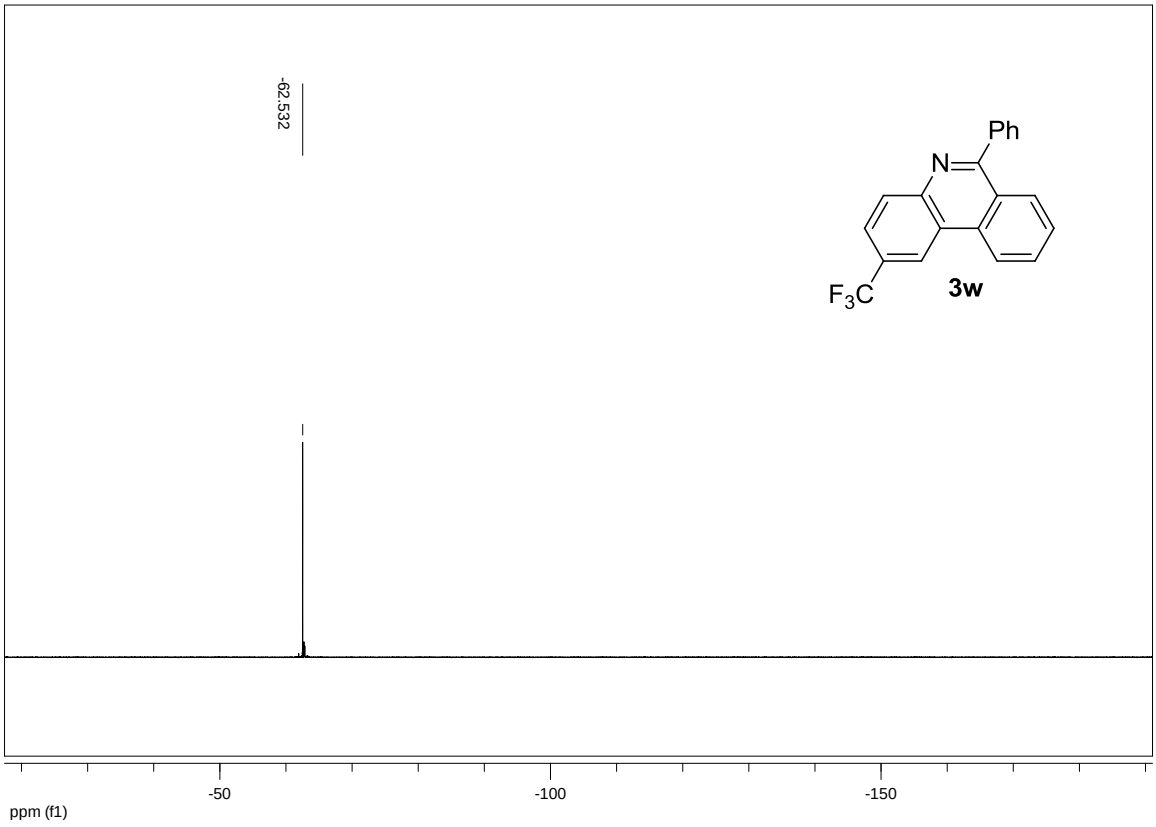

Ph
N
Me
3u
f1 (ppm)


Ph
N
Ph
3v
f1 (ppm)


161.26
148.10
141.01
139.79
139.68
133.53
130.68
129.80
129.08
129.03
128.83
128.50
128.33
127.70
127.64
127.32
125.95
122.25
120.32
77.42
77.11
76.79
Ph
N
Ph
3v
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


8.89
8.74
8.72
7.94
7.76
7.76
7.74
7.74
7.69
7.59
7.58
7.58
7.50
Ph
N
F3C
3w
0.95
0.95
0.92
0.95
2.12
1.00
1.21
3.08
11.0 10.5 10.0 9.5 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 -1.0 -1.5
f1 (ppm)


163.49
145.17
139.47
133.19
131.31
131.18
129.73
129.56
129.38
129.19
129.11
128.72
128.57
128.39
128.23
128.09
125.46
124.89
124.85
123.40
122.27
119.88
119.85
119.79
77.37
77.05
76.74
Ph
N
F3C
3w
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


-62.532
Ph
N
F3C
3w
-50
-100
-150
ppm (f1)