Electronic Supplementary Information

A photocatalyst-free method for synthesis of 6-alkyl(aryl)phenanthridines under visible light irradiation

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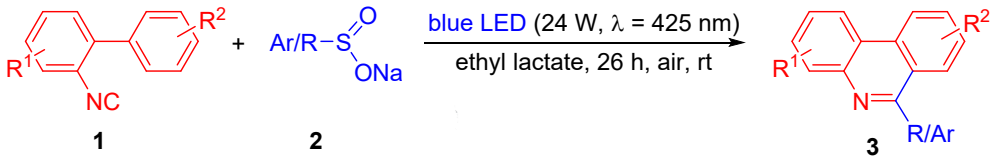
1. General Information

Unless otherwise stated, all reagents and substrates were purchased from commercial sources with the best quality and they were used without further purification. All the reactions were carried out in open vessel using oven-dried glassware. All solvents were dried over 3 Å/4 Å molecular sieves and distilled prior to use.[1] The progress of the optimization reactions were monitored by gas chromatography/isolation. The progress of the reactions were monitored by analytical thin layer chromatography on silica gel and visualization was accomplished by irradiation with short wave UV light at 254 nm, near UV 366 nm lights and by staining in an I_2 chamber. All products are known and were characterized by NMR followed by a comparison with authentic samples spectra. Chemical shifts are expressed as δ-value in parts per million (ppm) and were calibrated using the residual protonated solvent as an internal standard. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; m, multiplet and so on. The coupling constants, J, are reported in Hertz (Hz). Photochemical reactions were performed with 425 nm [Mavi blue LEDs (λ = 425 ± 5 nm), 24 W].

2. Experimental Section

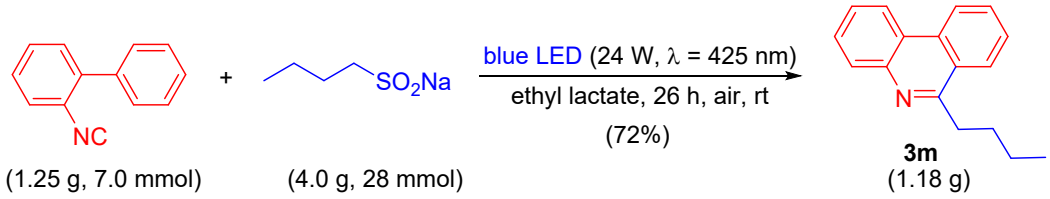
2.1. General procedure for the synthesis of 6-functionalized phenanthridines



An oven-dried glass vial equipped with a magnetic stir bar was charged with 2-isocyanobiaryl (**1**, 0.5 mmol) and sodium arylsulfinate (**2**, 2.0 mmol). To this mixture, ethyl lactate (4 mL) was added. Resultant mixture was stirred few minutes to dissolve well at ambient conditions and then with stirring irradiated through the plane bottom side of the vial using 24 W blue LEDs at a distance of 2 cm under open air atmosphere. The progress of reaction was monitored by TLC. In many cases, after reaction completion (26 h, as indicated by disappearance of precursor in TLC), the volatiles were completely removed by vacuum evaporation. Afterwards, water was added and product was extracted with ethyl acetate, dried over anhydrous sodium sulphate, filtered and concentrated. The resulting crude mixture was purified by column chromatography on silica gel using 20% ethyl acetate in hexane to provide the desired product **3**. Spectroscopic examination

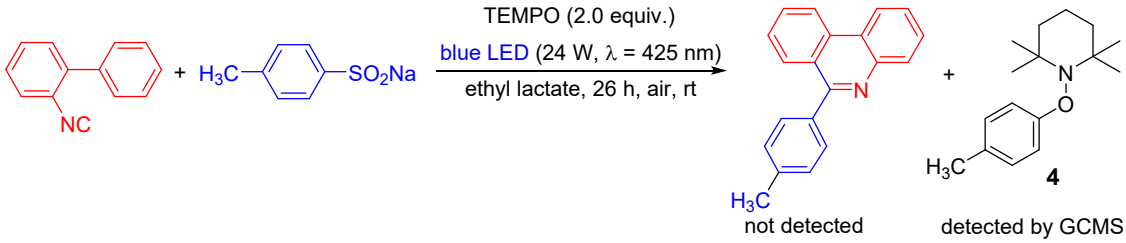
and a comparison with authentic sample spectra were used to establish the product's identity and purity (vide infra).

2.2. Large-scale synthesis of 3m



An oven-dried round bottom flask equipped with a magnetic stir bar was charged with 2-isocyano-1,1'-biphenyl (1.25g, 7.0 mmol, 1.0 equiv.) and butane-1-sulfinate (4.0g, 28.0 mmol, 4.0 equiv.). To this mixture, ethyl lactate (40 mL) was added. Resultant mixture was stirred few minutes to soluble well at ambient conditions and then with stirring irradiated through the bottom side of the flask using 24 W blue LEDs at a distance of 2 cm under open air atmosphere for 26 h. Subsequently, the volatiles were completely removed by vacuum evaporation, product was extracted with ethyl acetate, dried over anhydrous sodium sulphate, filtered and concentrated. The resulting crude mixture was purified by column chromatography on silica gel using 5% ethyl acetate in hexane to provide the desired product **3m**.

2.3. The aryl radical trapping experiment



A radical scavenger (2,2,6,6-tetramethylpiperidinoxy, TEMPO, 2.0 equiv), 2-isocyano-1,1'-biphenyl (1.0 equiv.) and sodium *p*-toluenesulfinate (4.0 equiv.) in ethyl lactate were irradiated through the plane bottom side of the vial using 24 W blue LEDs at a distance of 2 cm under open air atmosphere. After 26 h, the crude reaction mixture was passed through a silica-gen column to remove excess unreacted precursors and analyzed by GCMS and NMR (Figure S1). **2,2,6,6-Tetramethyl-1-tolyloxypiperidine:** Colorless solid (21% yield); ^{1}H NMR ($CDCl_3$) δ (ppm) 7.24-7.17 (m, 2H), 6.87-6.80 (m, 2H), 1.62-1.51 (m, 5H), 1.41-1.38 (m, 1H), 2.39 (s, 3H), 1.22

(s, 6H), 1.02 (s, 6H); ^{13}C NMR ($CDCl_3$) δ (ppm) 163.3, 129.1, 120.0, 113.8, 60.3, 39.7, 32.4, 21.4, 20.6, 17.2. GCMS (m/z): 247.

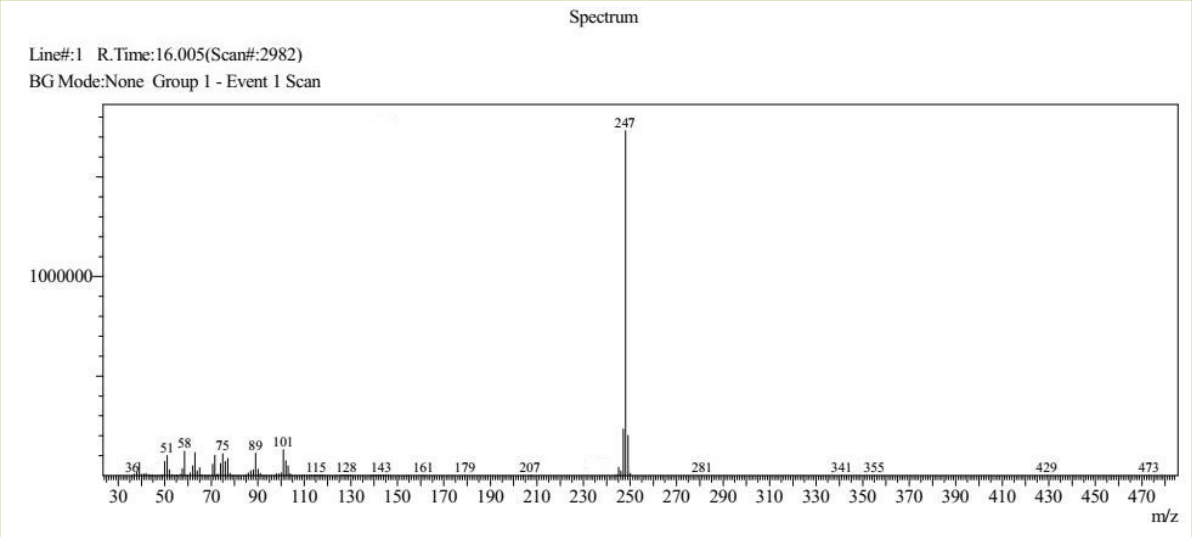


Figure S1. The GCMS analysis of tolyl-radical formed in situ was trapped by TEMPO.

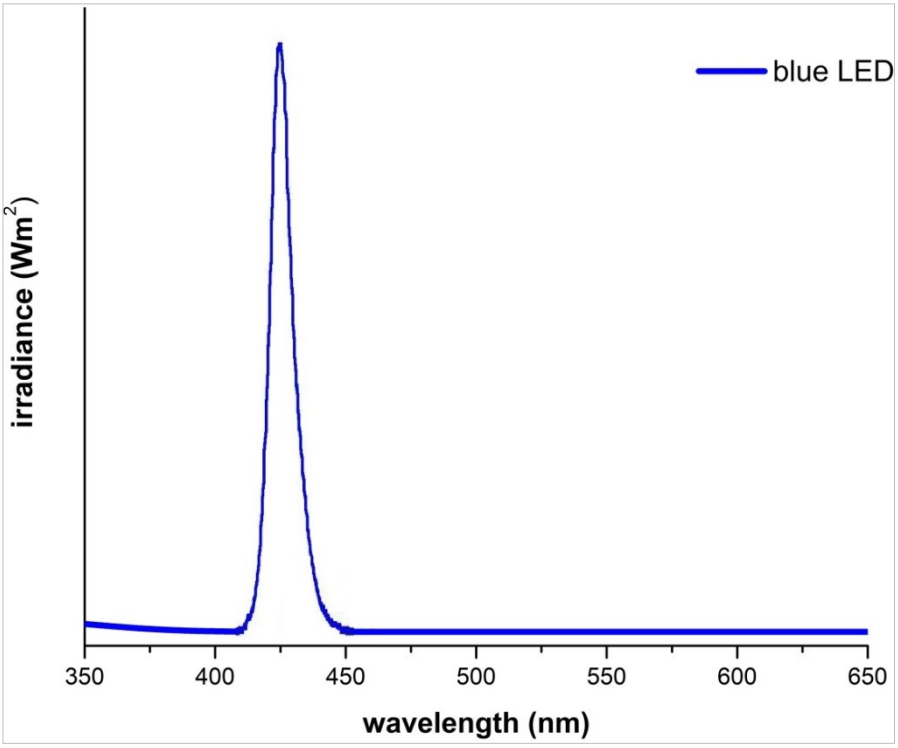


Figure S2. Emission spectra of light source

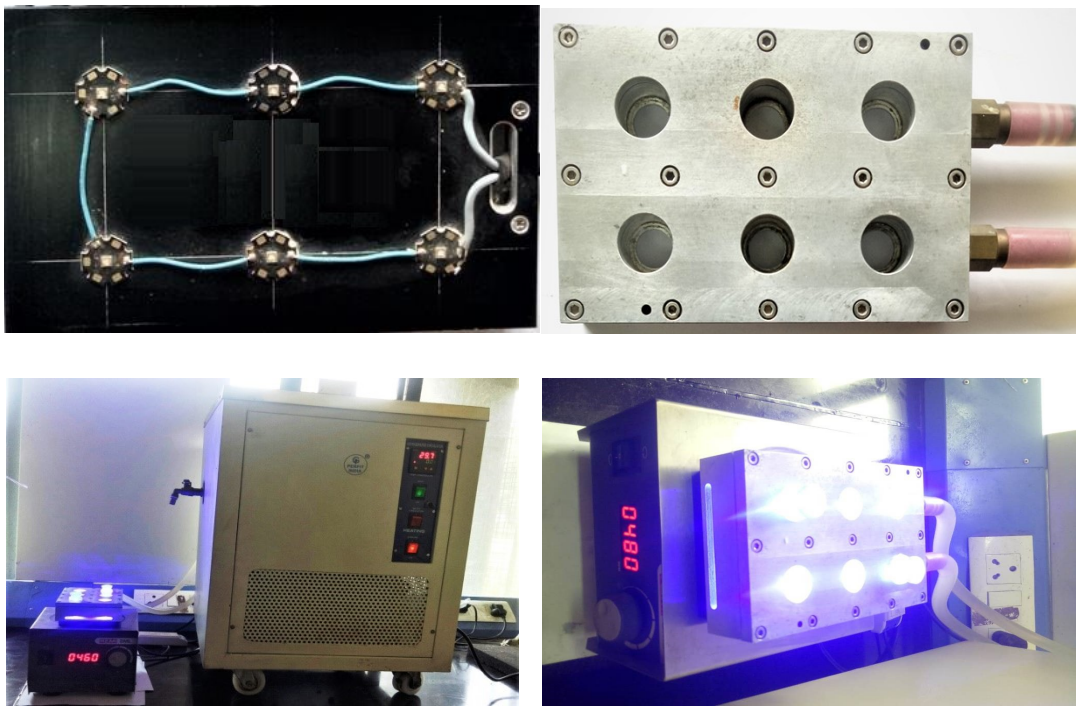
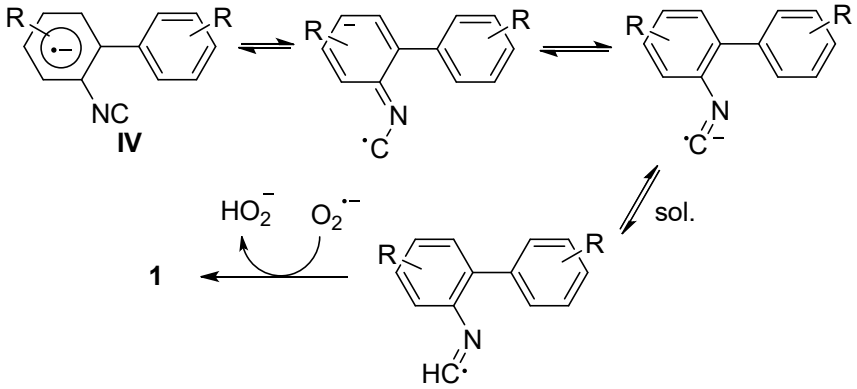
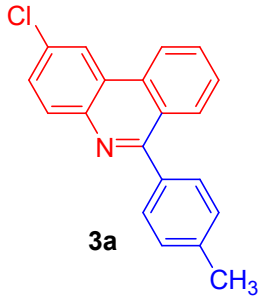


Figure S3. A few photographs of parts of a custom made photochemical reactor setup used to perform reactions described in this work. LEDs with a solid support (top, left), holding *cum* cooling unit (top, right), a picture of complete photochemical reactor setup under running conditions with turn-on blue LEDs with the cooling machine for maintaining uniform temperature (below, left) and a cross section of the setup (below, right).



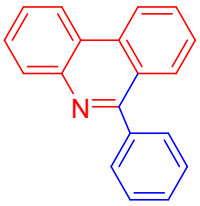
Scheme 1. The possible process through which compound 1 could have regenerated from intermediate IV.

Experimental characterization data for products



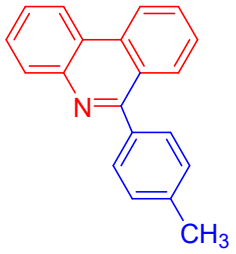
3a

2-Chloro-6-(*p*-tolyl)phenanthridine (3a):[2] Synthesized according to the general procedure described in section 2.1. Colorless solid (115 mg, 75% yield). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.58 (d, J = 7.8 Hz, 1H), 8.54 (s, 1H), 8.16 (d, J = 8.8 Hz, 2H), 7.87 (t, J = 8.0 Hz, 1H), 7.68-7.60 (m, 4H), 7.36 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.6, 142.4, 139.1, 136.7, 132.8, 132.5, 131.9, 130.8, 129.8, 129.4, 129.3, 129.2, 127.7, 125.6, 124.8, 122.4, 121.7, 21.7.



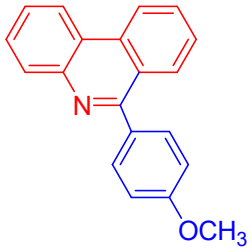
3b

6-Phenylphenantridine (3b):[2] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (78 mg, 61% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.68 (d, J = 8.4 Hz, 1H), 8.62 (d, J = 8.4 Hz, 1H), 8.25 (d, J = 8.0 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.88-7.82 (m, 1H), 7.79-7.73 (m, 3H), 7.69-7.63 (m, 1H), 7.62-7.51 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 143.6, 139.7, 133.5, 130.6, 130.3, 129.8, 129.1, 128.8, 128.7, 128.4, 127.3, 127.1, 125.4, 123.7, 122.3, 122.0.



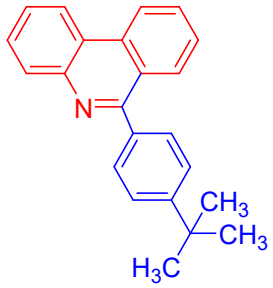
3c

6-(*p*-Tolyl)phenanthridine (3c):[2] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (85 mg, 63% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.14 (d, J = 8.0 Hz, 1H), 7.80 (t, J = 7.6 Hz, 1H), 7.75 (t, J = 7.6 Hz, 1H), 7.69-7.66 (m, 3H), 7.61 (t, J = 7.6 Hz, 1H), 7.39 (d, J = 7.6 Hz, 2H), 2.51 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.3, 143.9, 138.6, 137.0, 133.5, 130.5, 130.2, 129.7, 129.2, 129.1, 128.7, 127.2, 126.8, 125.2, 123.8, 122.3, 121.9, 21.4.



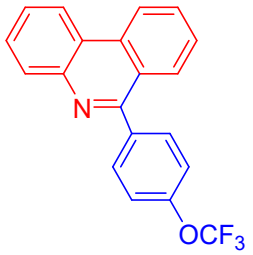
3d

6-(4-Methoxyphenyl)phenanthridine (3d):[2] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (82 mg, 57% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.68 (d, J = 8.4 Hz, 1H), 8.59 (d, J = 7.4 Hz, 1H), 8.25-8.21 (m, 1H), 8.14 (d, J = 8.4 Hz, 1H), 7.84-7.80 (m, 1H), 7.75-7.71 (m, 1H), 7.71 (dd, J = 8.4 Hz, J = 1.8, 2H), 7.66-7.60 (m, 2H), 7.10-7.07 (m, 2H), 3.91 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.8, 160.0, 143.7, 133.5, 132.3, 131.1, 130.6, 130.2, 128.9, 128.6, 127.2, 126.7, 125.4, 123.5, 122.2, 121.8, 113.7, 55.4.



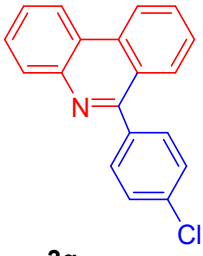
3e

6-(4-(*tert*-Butyl)phenyl)phenanthridine (3e):[3] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (95 mg, 60% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.28 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.2 Hz, 1H), 7.82 (td, J = 7.4, 0.8 Hz, 1H), 7.75 (td, J = 7.4, 1.0 Hz, 1H), 7.71-7.66 (m, 3H), 7.60 (t, J = 7.6 Hz, 3H), 1.42 (s, 9H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 151.7, 143.8, 136.7, 133.4, 130.5, 130.3, 129.3, 129.0, 128.6, 127.0, 126.6, 125.3, 125.2, 123.5, 122.1, 121.8, 34.6, 31.3.



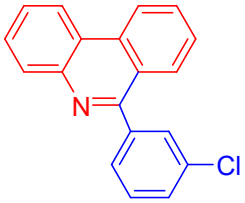
3f

6-(4-(Trifluoromethoxy)phenyl)phenanthridine (3f): Synthesized according to the general procedure described in section 2.1. Pale yellow solid (106 mg, 62% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.72 (d, J = 8.4 Hz, 1H), 8.64 (d, J = 7.4 Hz, 1H), 8.41 (d, J = 8.2 Hz, 2H), 8.21 (d, J = 7.4 Hz, 1H), 7.98 (d, J= 8.2 Hz, 1H), 7.95-7.88 (m, 3H), 7.79 (t, J = 7.2 Hz, 1H), 7.73 (t, J = 7.2 Hz, 1H), 7.65 (t, J = 7.6 Hz, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.6, 148.1, 146.1, 143.4, 133.3, 131.0, 130.8, 130.4, 129.2, 128.6, 127.9, 127.7, 127.5, 124.5, 123.8, 123.7, 122.5, 122.1.



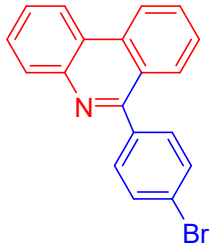
3g

6-(4-Chlorophenyl)phenanthridine (3g):[2] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (84 mg, 57% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.70 (d, J = 8.4 Hz, 1H), 8.61 (d, J = 8.0 Hz, 1H), 8.22 (d, J = 8.0 Hz, 1H), 8.07 (d, J = 8.0 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.78-7.75 (m, 1H), 7.71-7.69 (m, 3H), 7.62 (t, J = 7.6 Hz, 1H), 7.54 (d, J = 8.4 Hz, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.1, 143.6, 138.2, 134.9, 133.4, 131.1, 130.6, 130.3, 129.1, 128.7, 128.5, 127.2, 127.1, 125.1, 123.7, 122.2, 122.0.



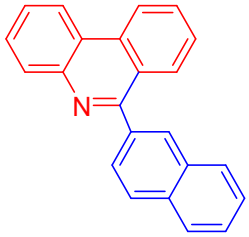
3h

6-(3-Chlorophenyl)phenanthridine (3h):[4] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (86 mg, 59% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67 (d, J = 8.4, 1H), 8.60 (dd, J = 8.0 Hz, J = 1.1, 1H), 8.23 (dd, J = 8.0 Hz, J = 1.0 Hz, 1H), 8.06 (dd, J = 8.0 Hz, J = 0.4 Hz, 1H), 7.88-7.84 (m, 1H), 7.77-7.73 (m, 2H), 7.70-7.61 (m, 3H), 7.54-7.49 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.5, 143.4, 141.1, 134.6, 133.5, 130.9, 130.3, 129.8, 129.7, 129.1, 128.8, 128.5, 127.9, 127.4, 127.2, 124.9, 123.7, 122.3, 121.8.



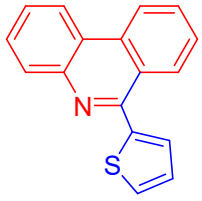
3i

6-(4-Bromophenyl)phenanthridine (3i):[4] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (93 mg, 56% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.71 (d, J = 8.4 Hz, 1H), 8.60 (dd, J = 7.8 Hz, J = 1.4, 1H), 8.23 (dd, J = 7.8 Hz, J = 1.0, 1H), 8.05 (dd, J = 7.8 Hz, J = 1.0, 1H), 7.86-7.84 (m, 1H), 7.77-7.74 (m, 1H), 7.71-7.68 (m, 3H), 7.65-7.62 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 159.8, 143.8, 138.6, 133.4, 131.6, 131.4, 130.6, 130.3, 128.7, 128.4, 127.5, 127.2, 124.8, 123.6, 123.1, 122.3, 122.1.



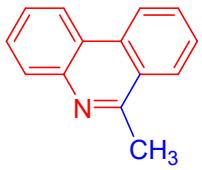
3j

6-(Naphthalen-2-yl)phenanthridine (3j):[3] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (89 mg, 58% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.72 (d, J = 8.0 Hz, 1H), 8.63 (d, J = 8.0 Hz, 1H), 8.31 (d, J = 8.4 Hz, 1H), 8.24 (s, 1H), 8.18 (d, J = 8.4 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H), 7.97-7.94 (m, 2H), 7.88-7.84 (m, 2H), 7.78 (t, J = 7.1 Hz, 1H), 7.70 (t, J = 7.0 Hz, 1H), 7.64-7.57 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.3, 143.9, 137.1, 133.6, 133.3, 133.2, 130.5, 130.4, 129.2, 129.0, 128.9, 128.5, 128.1, 127.8, 127.4, 127.1, 127.0, 126.5, 126.4, 125.3, 123.6, 122.2, 122.0.



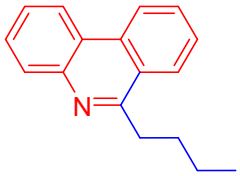
3k

6-(Thiophen-2-yl)phenanthridine (3k):[5] Synthesized according to the general procedure described in section 2.1. Yellow solid (87 mg, 66% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.68 (d, J = 8.4 Hz, 1H), 8.61-8.55 (m, 1H), 8.18 (d, J = 8.0 Hz, 1H), 7.87-7.82 (m, 1H), 7.74-7.64 (m, 5H), 7.56 (d, *J* = 4.7 Hz, 1H), 7.25-7.22 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 154.6, 143.3, 142.4, 133.2, 130.6, 130.2, 129.2, 128.8, 128.0, 127.9, 127.4, 127.1, 126.7, 124.7, 123.5, 122.3, 121.7.



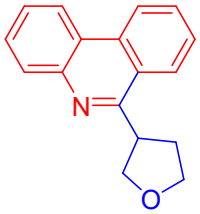
3l

6-Methylphenanthridine (3l):[7] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (67 mg, 69% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.48 (d, J = 8.0 Hz, 1H), 8.41 (d, J = 8.0 Hz, 1H), 8.08 (d, J = 8.0 Hz, 2H), 7.75-7.71 (m, 1H), 7.69-7.64 (m, 1H), 7.60-7.54 (m, 2H), 2.97 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 158.5, 143.4, 132.2, 130.2, 129.1, 128.4, 127.3, 126.3, 126.1, 125.6, 123.6, 122.1, 121.7, 23.2.



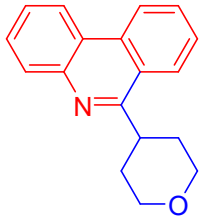
3m

6-Butylphenanthridine (3m):[7] Synthesized according to the general procedure described in section 2.1. Colorless solid (88 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66-8.60 (m, 1H), 8.55 (dd, J = 8.0 Hz, J = 1.4 Hz, 1H), 8.27-8.23 (m, 1H), 8.16-8.11 (m, 1H), 7.84-7.79 (m, 1H), 7.72-7.68 (m, 2H), 7.63-7.58 (m, 1H), 3.43-3.29 (m, 2H), 2.01-1.87 (m, 2H), 1.60-1.54 (m, 2H), 1.02 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.4, 143.8, 132.8, 130.2, 129.4, 128.5, 127.1, 126.3, 126.2, 125.1, 123.5, 122.4, 121.9, 36.2, 31.8, 23.2, 14.0.



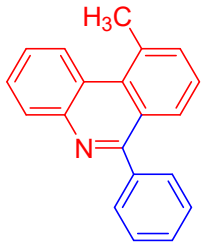
3n

6-(Tetrahydrofuran-3-yl) phenanthridine (3n):[9] Synthesized according to the general procedure described in section 2.1. Pale yellow dense liquid (90 mg, 72% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.67 (d, J = 8.4 Hz, 1H), 8.53 (d, J = 8.0 Hz, 1H), 8.27 (d, J = 8.0 Hz, 1H), 8.12 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.6 Hz, 2H), 7.64 (d, J = 7.8 Hz, 1H), 4.45-4.37 (m, 2H), 4.31 (q, J = 7.2 Hz, 1H), 4.20-4.16 (m, 1H), 4.06 (q, J = 7.2 Hz, 1H), 2.76-2.71 (m, 1H), 2.50-2.44 (m, 1H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.4, 143.5, 133.2, 130.5, 130.2, 128.7, 127.3, 126.7, 125.6, 125.5, 123.8, 122.7, 121.9, 72.5, 68.9, 43.3, 32.2.



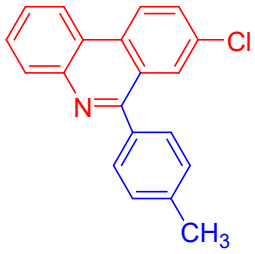
3o

6-(Tetrahydro-2H-pyran-4-yl) phenanthridine (3o):[6] Synthesized according to the general procedure described in section 2.1. Yellow solid (98 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66 (d, J = 8.4 Hz, 1H), 8.54 (d, J = 8.2 Hz, 1H), 8.32 (d, J = 8.4 Hz, 1H), 8.14 (d, J = 8.2 Hz, 1H), 7.85 (t, J = 7.6 Hz, 1H), 7.74-7.69 (m, 2H), 7.62 (t, J = 7.6 Hz, 1H), 4.21-4.18 (m, 2H), 3.91-3.84 (m, 1H), 3.76-3.71 (m, 2H), 2.40-2.32 (m, 2H), 1.99-1.95 (m, 2H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 163.2, 143.9, 133.3, 130.2, 128.6, 127.4, 126.5, 125.2, 124.6, 123.4, 122.8, 121.9, 68.4, 39.2, 32.1.



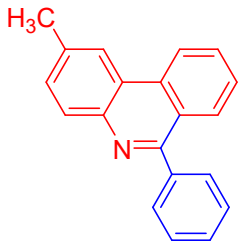
3q

1-Methy1-6-phenylphenanthridine (3q):[3] Synthesized according to the general procedure described in section 2.1. Colorless solid (57 mg, 39% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.72 (d, J = 8.4 Hz, 1H), 8.22 (d, J = 8.6 Hz, 1H), 8.13 (d, J = 8.4 Hz, 1H), 7.87-7.82 (m, 1H), 7.78-7.74 (m, 2H), 7.65-7.60 (m, 2H), 7.57-7.52 (m, 3H), 7.19 (d, J = 7.8 Hz, 1H), 2.53 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 156.1, 140.2, 135.5, 133.4, 130.6, 130.2, 129.4, 128.9, 128.6, 127.5, 127.2, 125.8, 125.2, 122.8, 114.0, 108.8, 20.8.



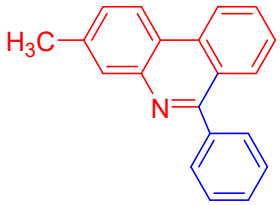
3r

8-Chloro-6-(*p*-tolyl)phenanthridine (3r):[7] Synthesized according to the general procedure described in section 2.1. Tan color solid (102 mg, 67% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.62 (d, J = 8.4 Hz, 1H), 8.58 (d, J = 8.0 Hz, 1H), 8.24 (d, J = 6.8 Hz, 1H), 8.13 (d, J = 2.2 Hz, 1H), 7.81-7.76 (m, 2H), 7.73-7.69 (m, 1H), 7.61 (d, J = 8.0 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 2.47 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.1, 143.8, 138.7, 136.1, 133.0, 131.7, 131.0, 130.3, 129.4, 129.3, 129.1, 127.8, 127.2, 126.2, 123.9, 123.0, 121.7, 21.3.



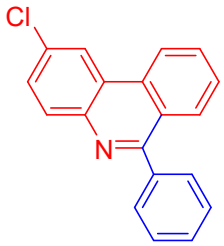
3t

2-Methyl-6-phenylphenanthridine (3t):[4] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (84 mg, 62% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66 (d, J = 8.2 Hz, 1H), 8.38 (s, 1H), 8.12 (d, J = 8.2 Hz, 1H), 8.06 (d, J = 8.4 Hz, 1H), 7.82-7.76 (m, 1H), 7.73-7.68 (m, 2H), 7.57-7.46 (m, 5H), 2.57 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 160.5, 142.1, 139.7, 136.4, 133.2, 130.7, 130.2, 130.0, 129.6, 128.8, 128.6, 128.4, 127.1, 125.2, 123.3, 122.2, 121.4, 22.3.



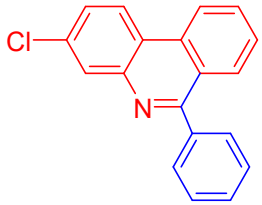
3u

3-Methyl-6-phenylphenanthridine (3u):[8] Synthesized according to the general procedure described in section 2.1. Pale yellow solid (93 mg, 69% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.66 (d, J = 8.2 Hz, 1H), 8.51 (d, J = 8.2 Hz, 1H), 8.10-8.04 (m, 2H), 7.86-7.81 (m, 1H), 7.75-7.70 (m, 2H), 7.62- 7.51 (m, 5H), 2.58 (s, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 143.8, 139.8, 139.1, 133.7, 130.5, 129.9, 129.8, 129.1, 128.7, 128.5, 128.3, 126.7, 125.0, 122.1, 121.8, 121.2, 21.5.



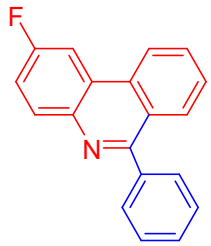
3w

2-Chloro-6-phenylphenanthridine (3w):[5] Synthesized according to the general procedure described in section 2.1. Colorless solid (108 mg, 74% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65 (d, J = 8.2 Hz, 1H), 8.60 (d, J = 3.8 Hz, 1H), 8.17 (d, J = 8.2 Hz, 1H), 8.11 (d, J = 8.4 Hz, 1H), 7.90-7.86 (m, 1H), 7.74-7.61 (m, 4H), 7.57-7.52 (m, 3H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.2, 141.8, 139.5, 133.2, 132.3, 131.7, 131.2, 130.0, 129.6, 129.2, 129.0, 128.5, 127.8, 125.4, 124.8, 122.7, 122.2.



3x

3-Chloro-6-phenylphenanthridine (3x):[2] Synthesized according to the general procedure described in section 2.1. Colorless solid (92 mg, 63% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.65 (d, J = 8.2 Hz, 1H), 8.52 (d, J = 8.2 Hz, 1H), 8.28-8.22 (m, 1H), 8.17-8.11 (m, 1H), 7.91-7.82 (m, 1H), 7.75-7.71 (m, 2H), 7.66-7.54 (m, 5H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 162.2, 144.6, 139.7, 134.5, 133.0, 130.1, 129.8, 129.6, 129.2, 128.8, 128.6, 127.5, 127.3, 125.1, 123.3, 122.4, 122.1.



3y

2-Fluoro-6-phenylphenanthridine (3y):[5] Synthesized according to the general procedure described in section 2.1. Colorless solid (100 mg, 73% yield). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 8.57 (d, J = 8.2 Hz, 1H), 8.32-8.21 (m, 2H), 8.13 (d, J = 8.2 Hz, 1H), 7.86 (t, J = 7.6 Hz, 1H), 7.72 (d, J = 7.4 Hz, 2H), 7.65 (t, J = 7.6 Hz, 1H), 7.60-7.49 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz) δ 161.4 (d, J = 244 Hz), 160.8 (d, J = 2.6 Hz), 140.5, 139.5, 133.2 (d, J = 4.2 Hz), 132.5 (d, J = 8.8 Hz), 130.8, 129.9, 129.1, 129.0, 128.6, 128.0, 125.4, 125.1 (d, J = 9.2 Hz), 122.6, 117.8 (d, J = 23.8 Hz), 107.2 (d, J = 23.2 Hz).

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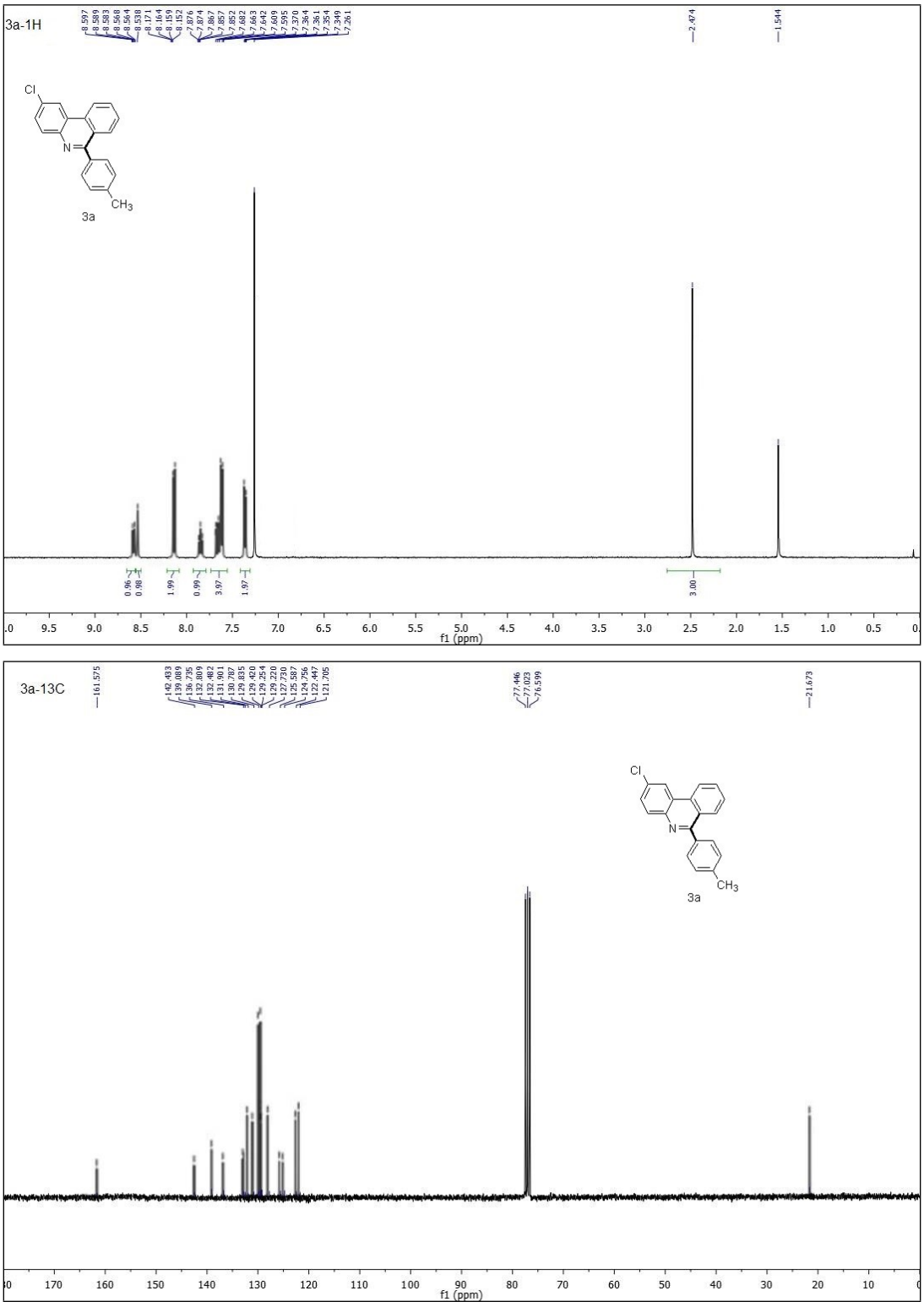

Figure S4. ^{1}H (top) and ^{13}C (bottom) spectra of 3a in $CDCl_3$.

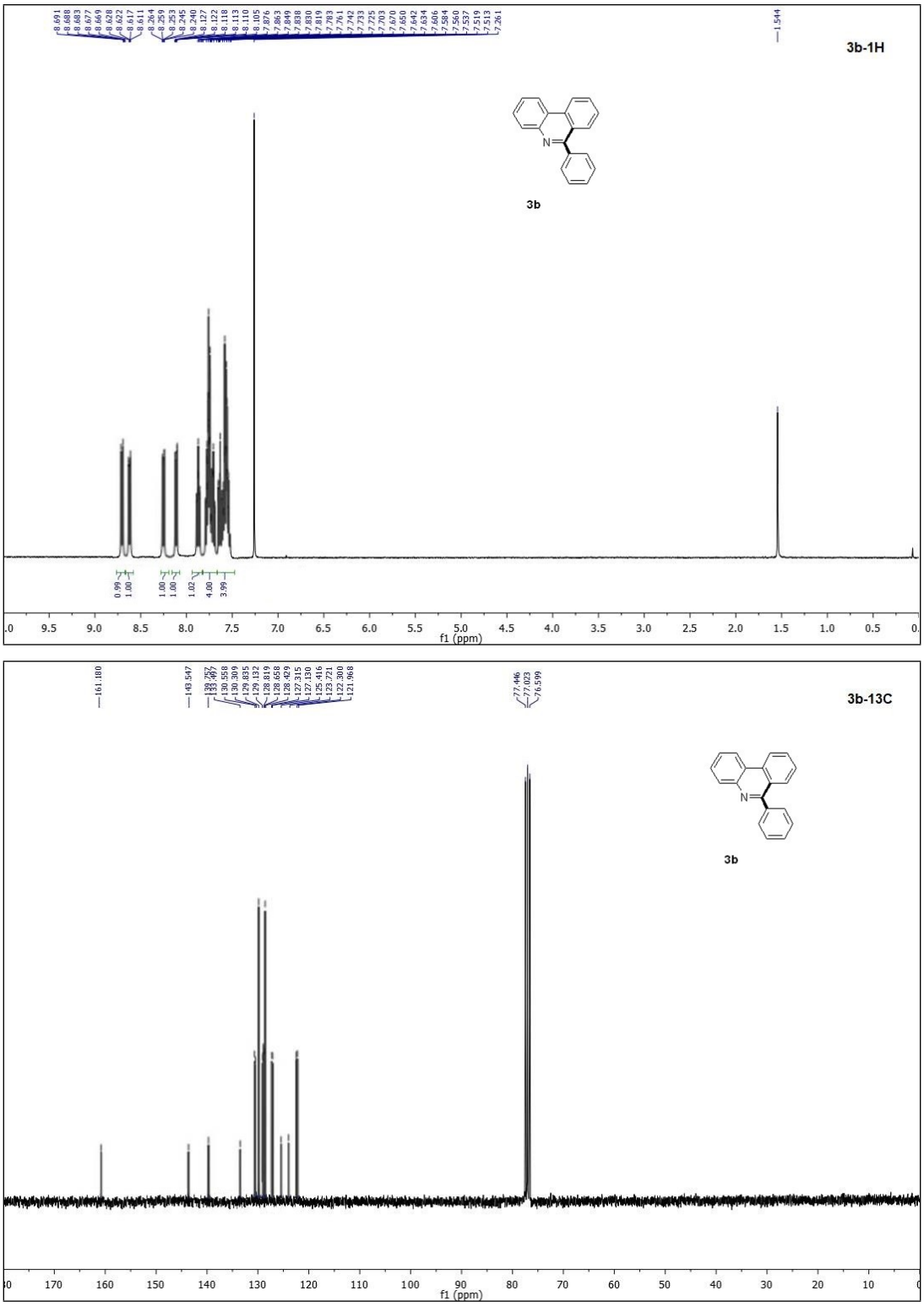

Figure S5. ^{I}H (top) and ^{13}C (bottom) spectra of 3b in $CDCl_3$.

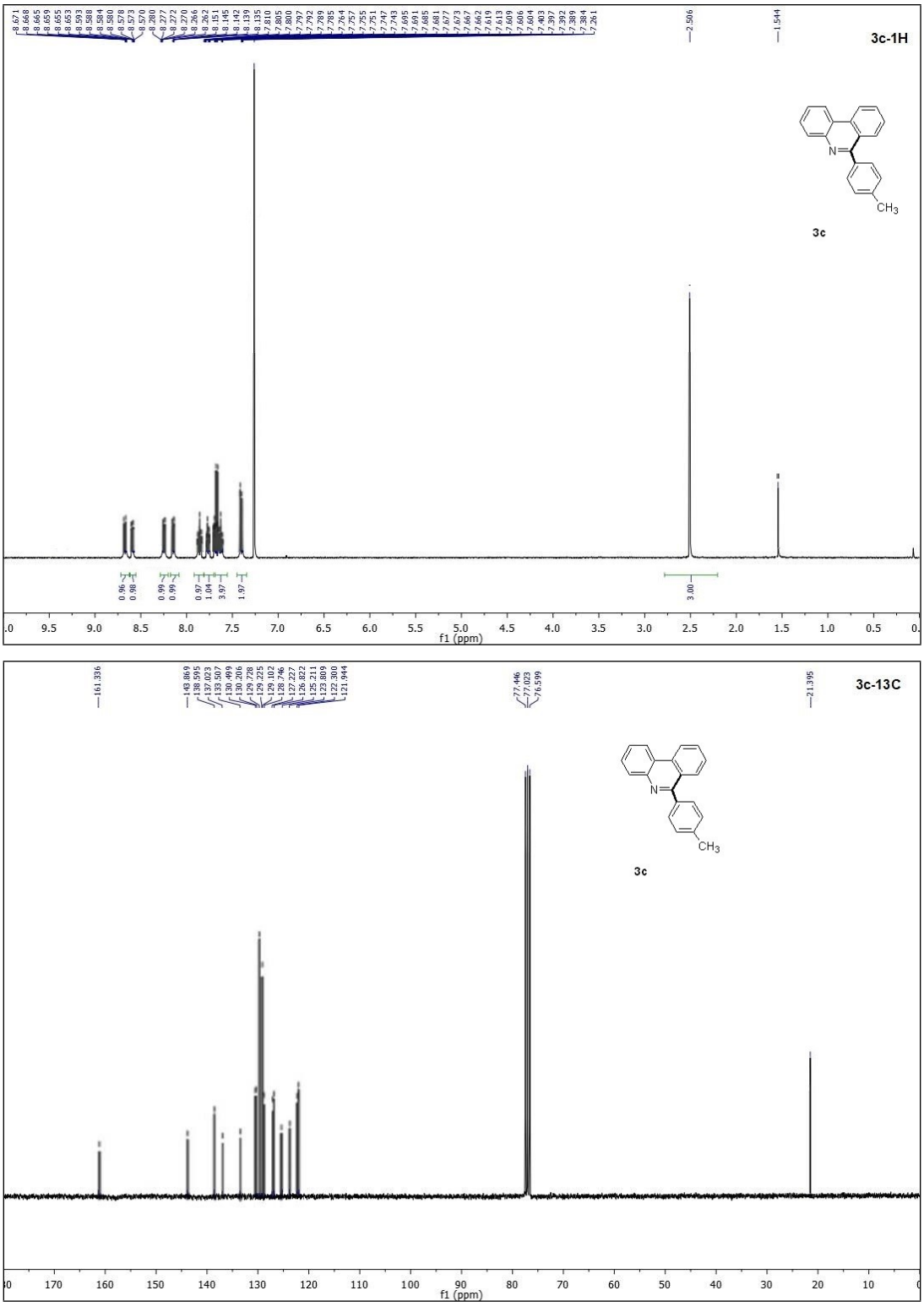

Figure S6. ^{1}H (top) and ^{13}C (bottom) spectra of 3c in $CDCl_3$.

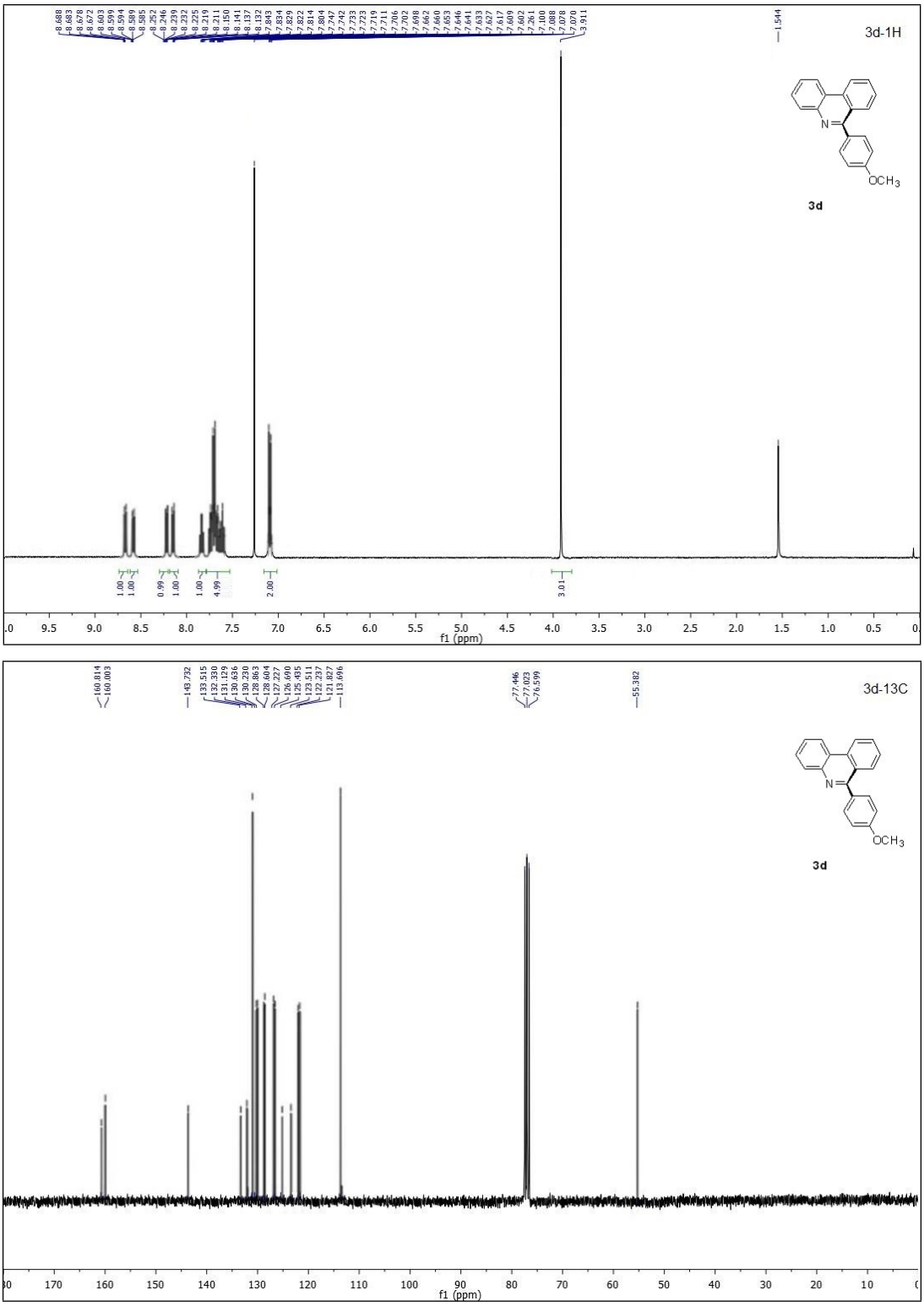

Figure S7. ^{I}H (top) and ^{13}C (bottom) spectra of 3d in $CDCl_3$.

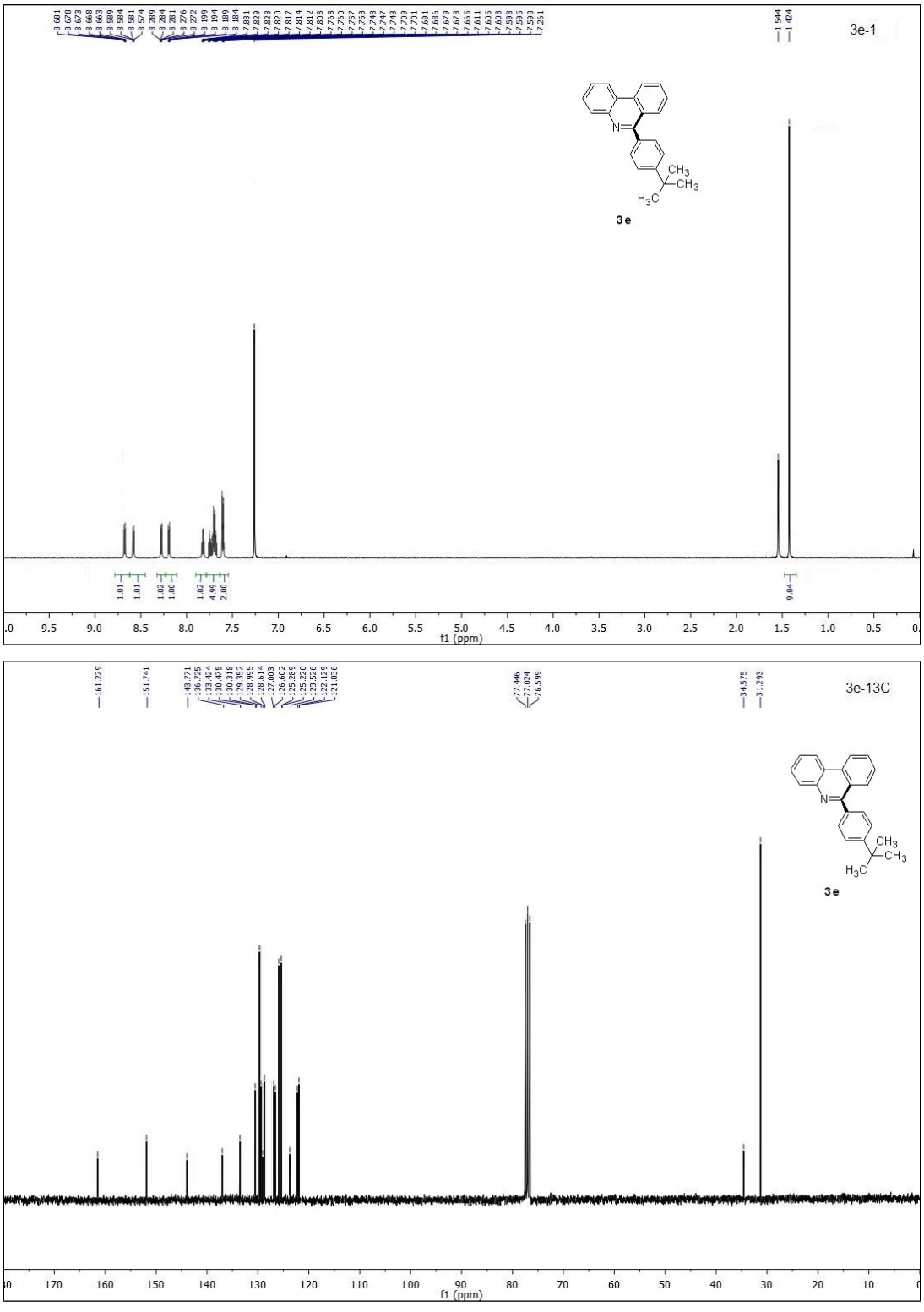

Figure S8. ^{I}H (top) and ^{13}C (bottom) spectra of 3e in $CDCl_3$.

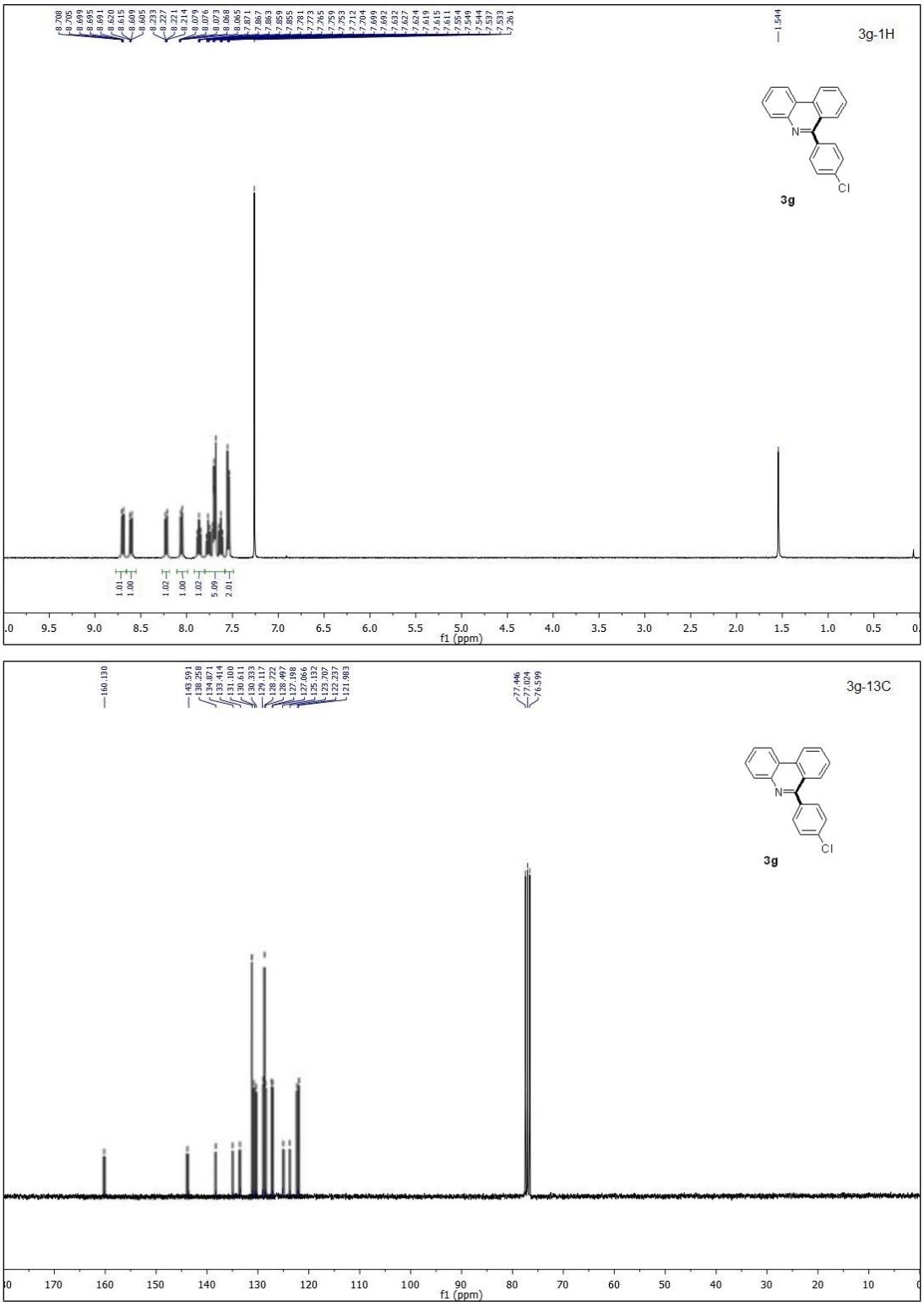

Figure S9. ^{1}H (top) and ^{13}C (bottom) spectra of 3g in $CDCl_3$.

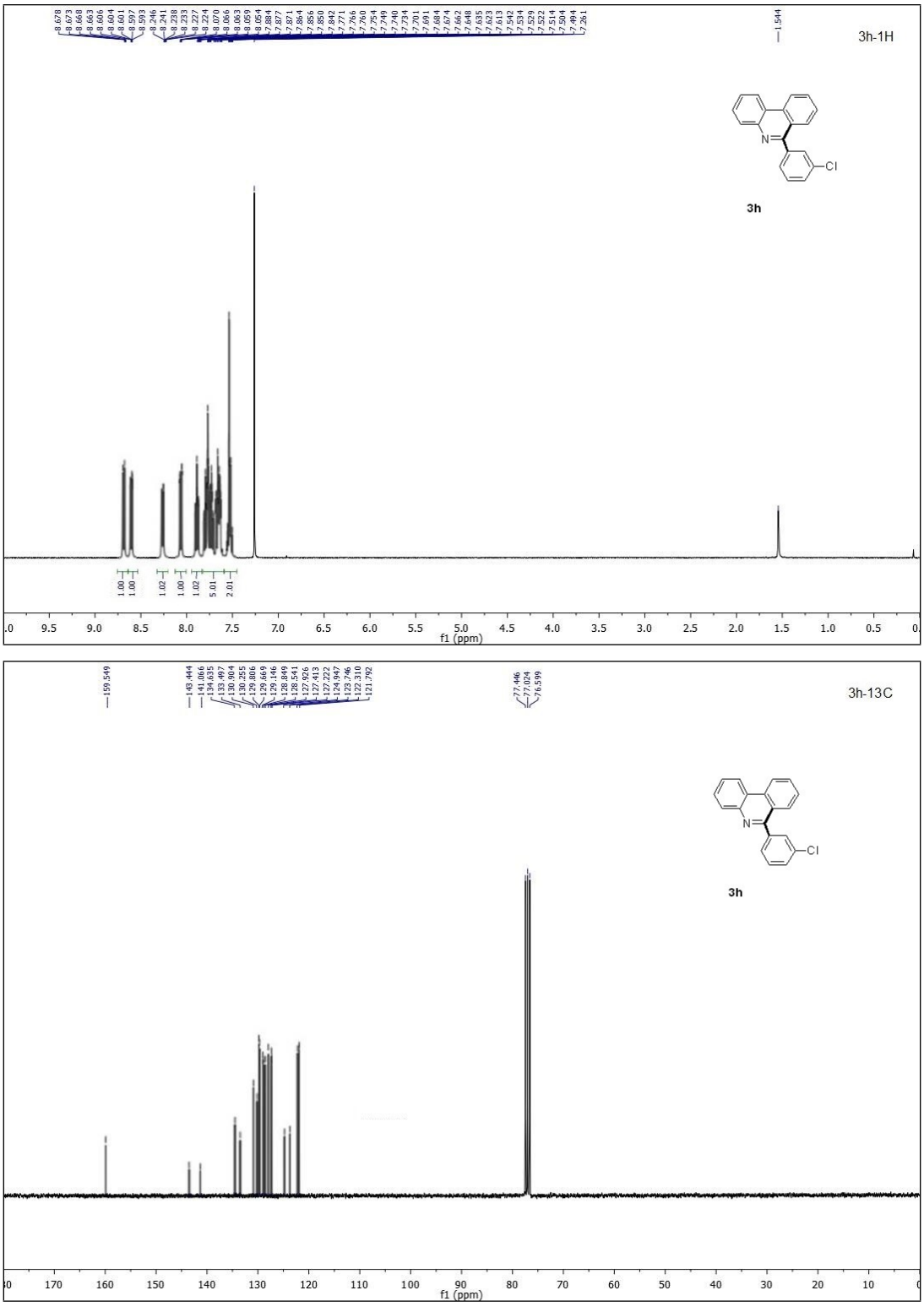

Figure S10. ^{1}H (top) and ^{13}C (bottom) spectra of 3h in $CDCl_3$.

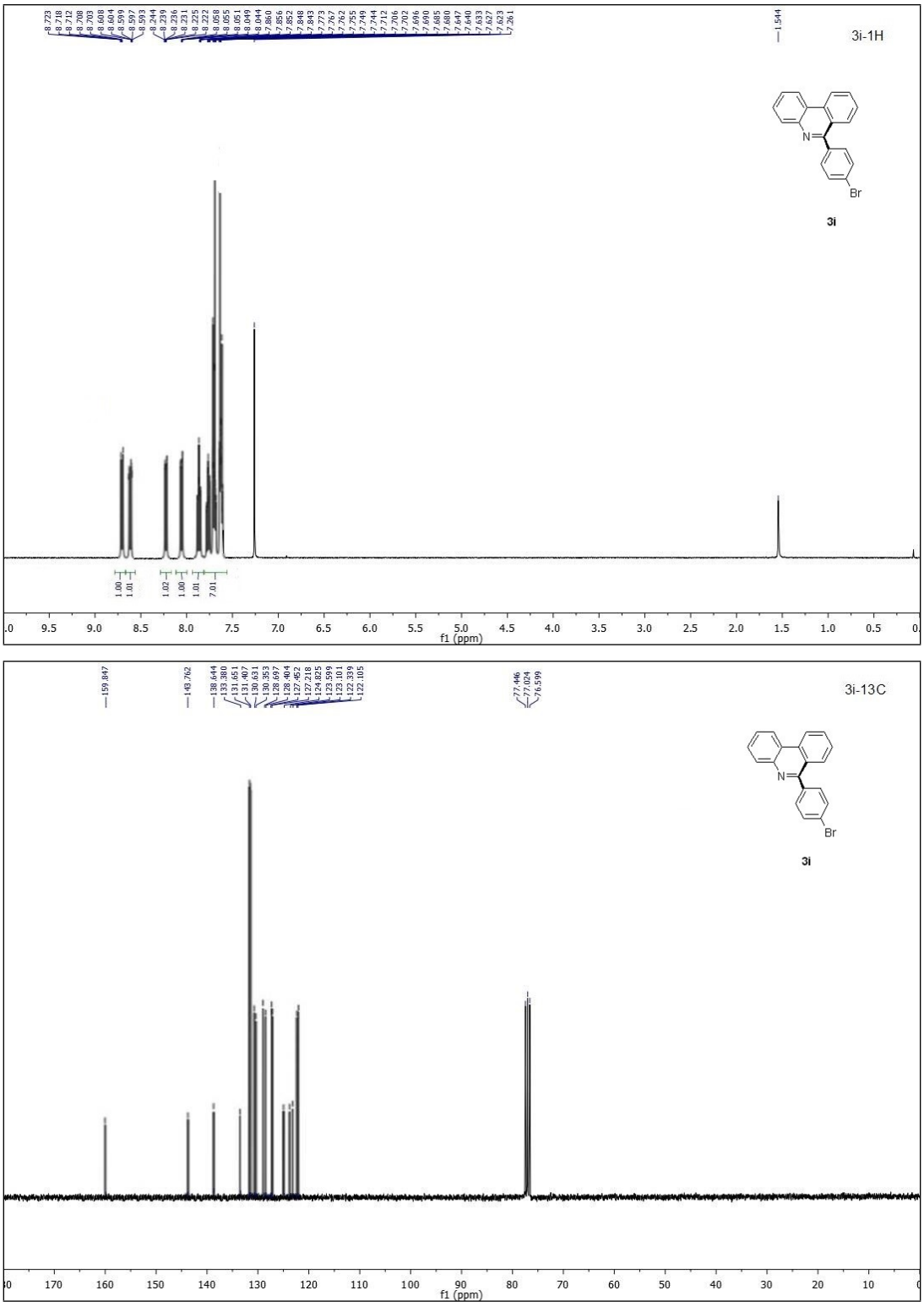

Figure S11. ^{1}H (top) and ^{13}C (bottom) spectra of 3i in $CDCl_3$.

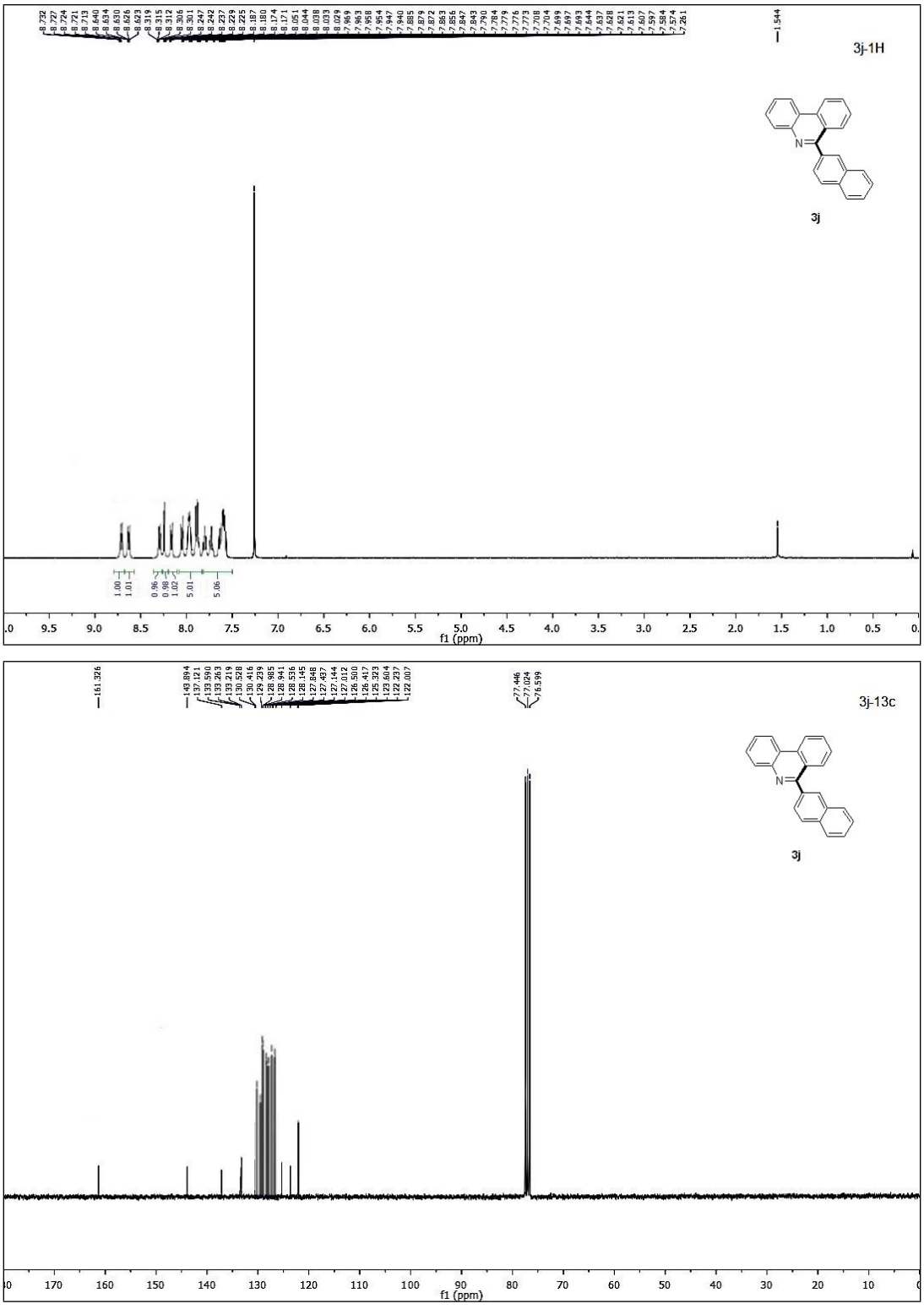

Figure S12. ^{1}H (top) and ^{13}C (bottom) spectra of 3j in $CDCl_3$.

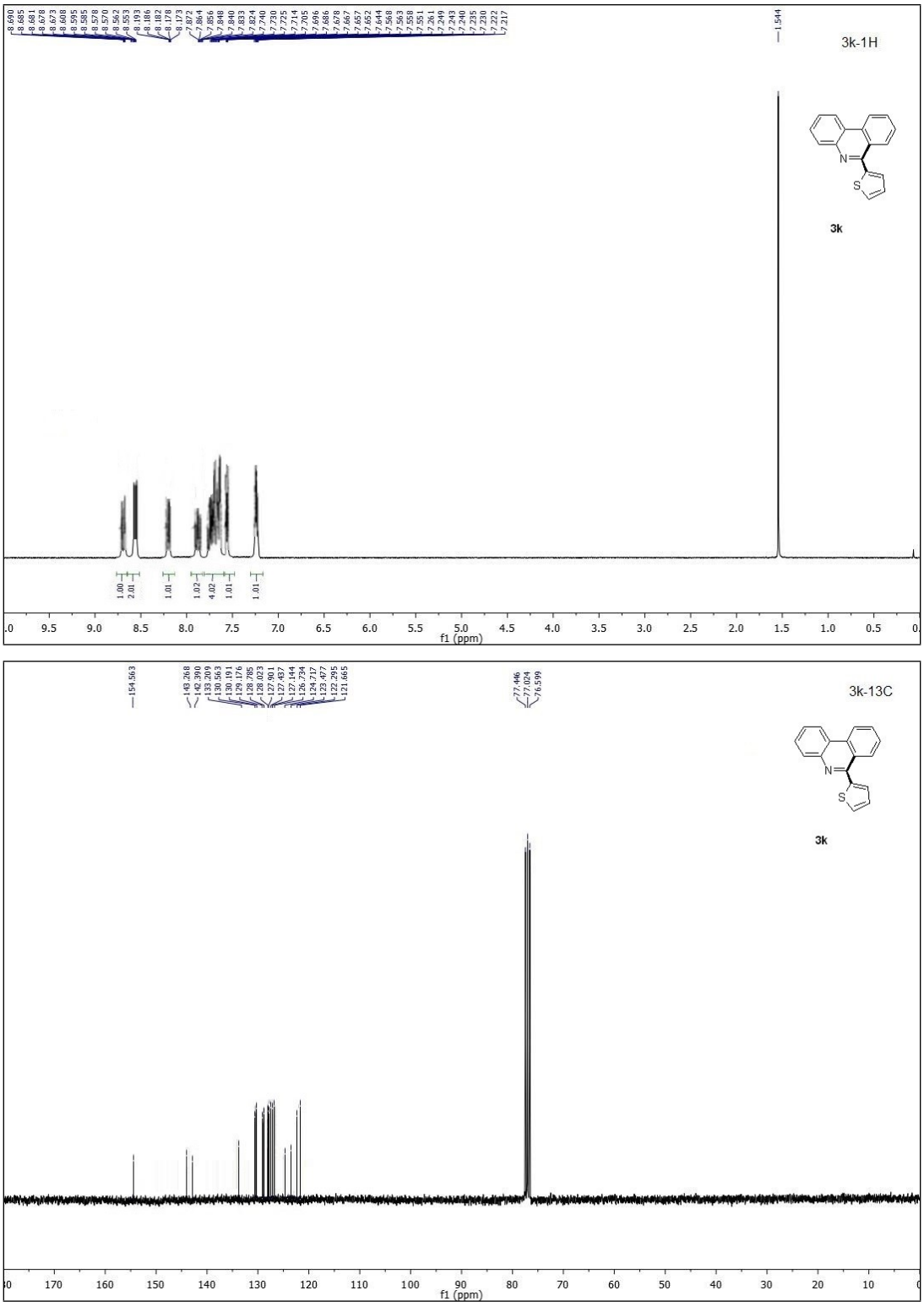

Figure S13. ^{1}H (top) and ^{13}C (bottom) spectra of 3k in $CDCl_3$.

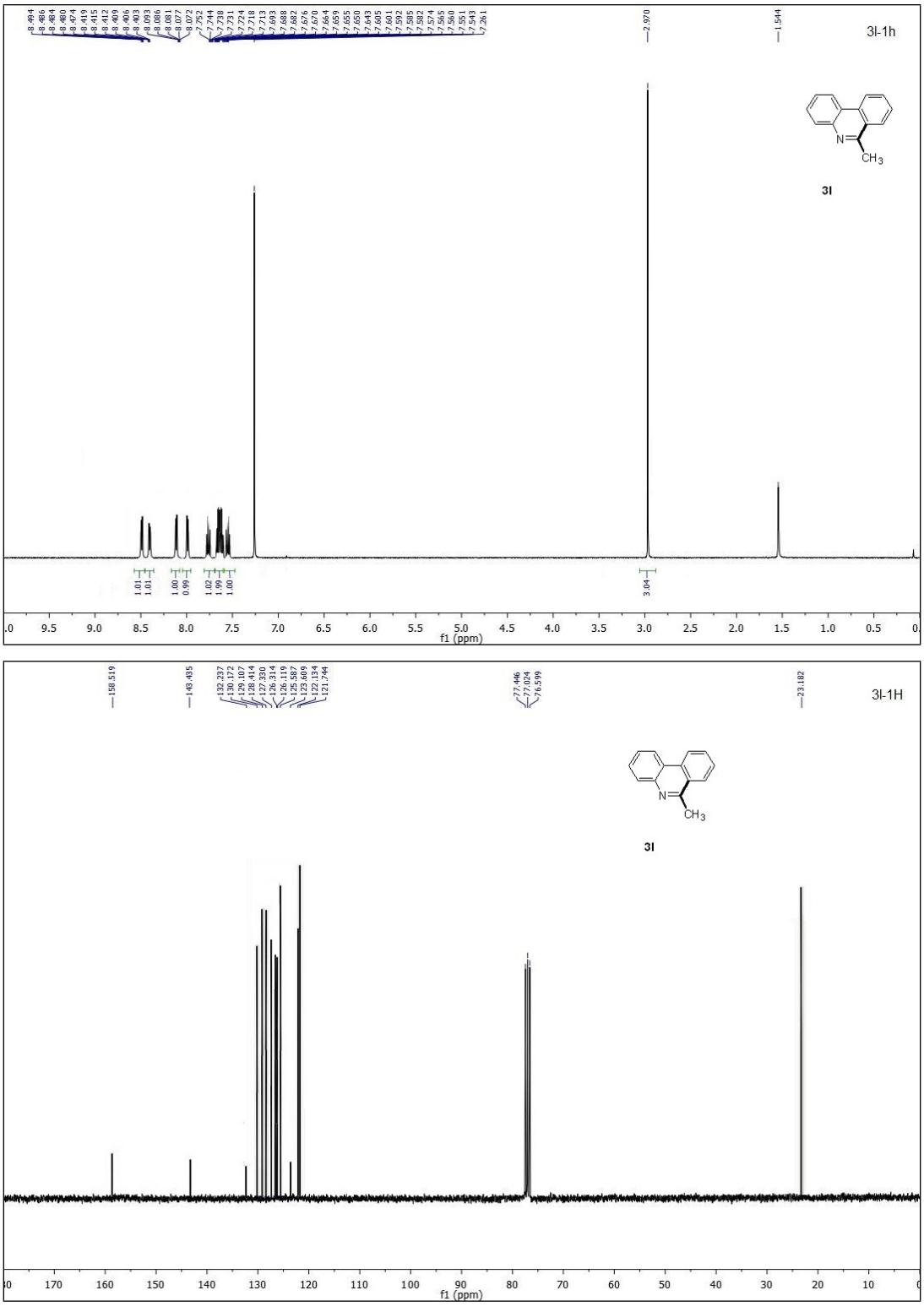

Figure S14. ^{1}H (top) and ^{13}C (bottom) spectra of 3l in $CDCl_3$.

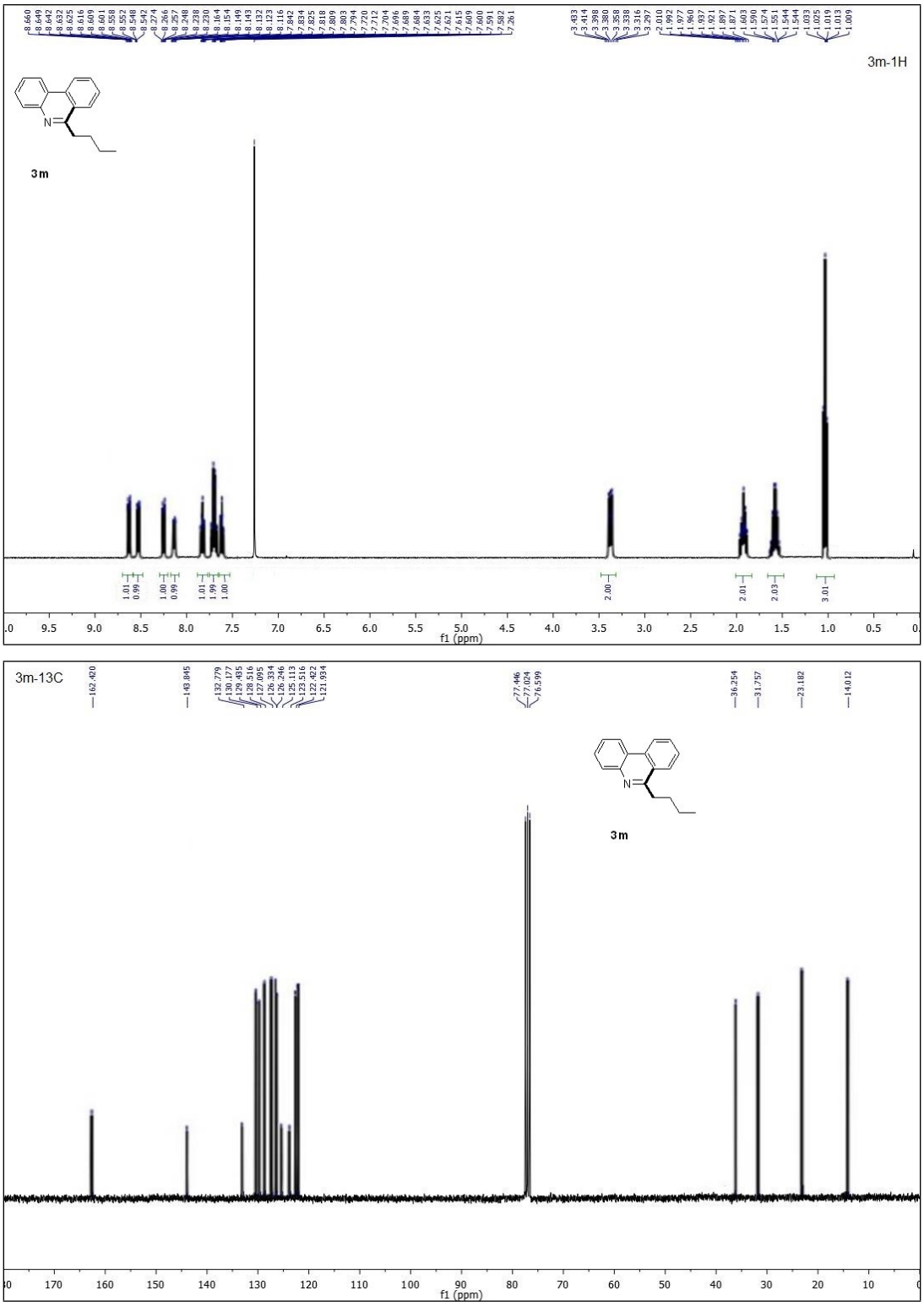

Figure S15. ^{1}H (top) and ^{13}C (bottom) spectra of 3m in $CDCl_3$.

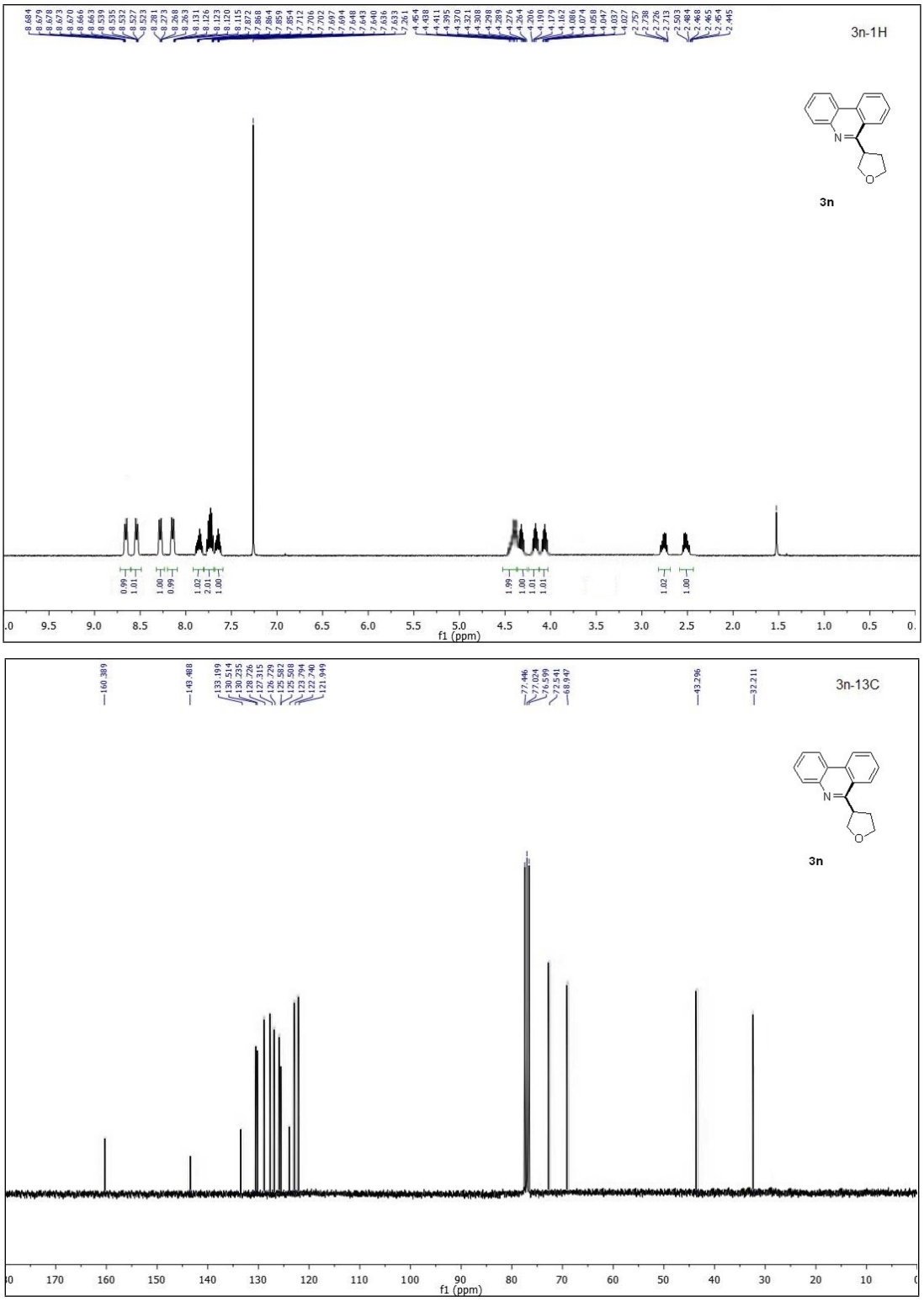

Figure S16. ^{1}H (top) and ^{13}C (bottom) spectra of 3n in $CDCl_3$.

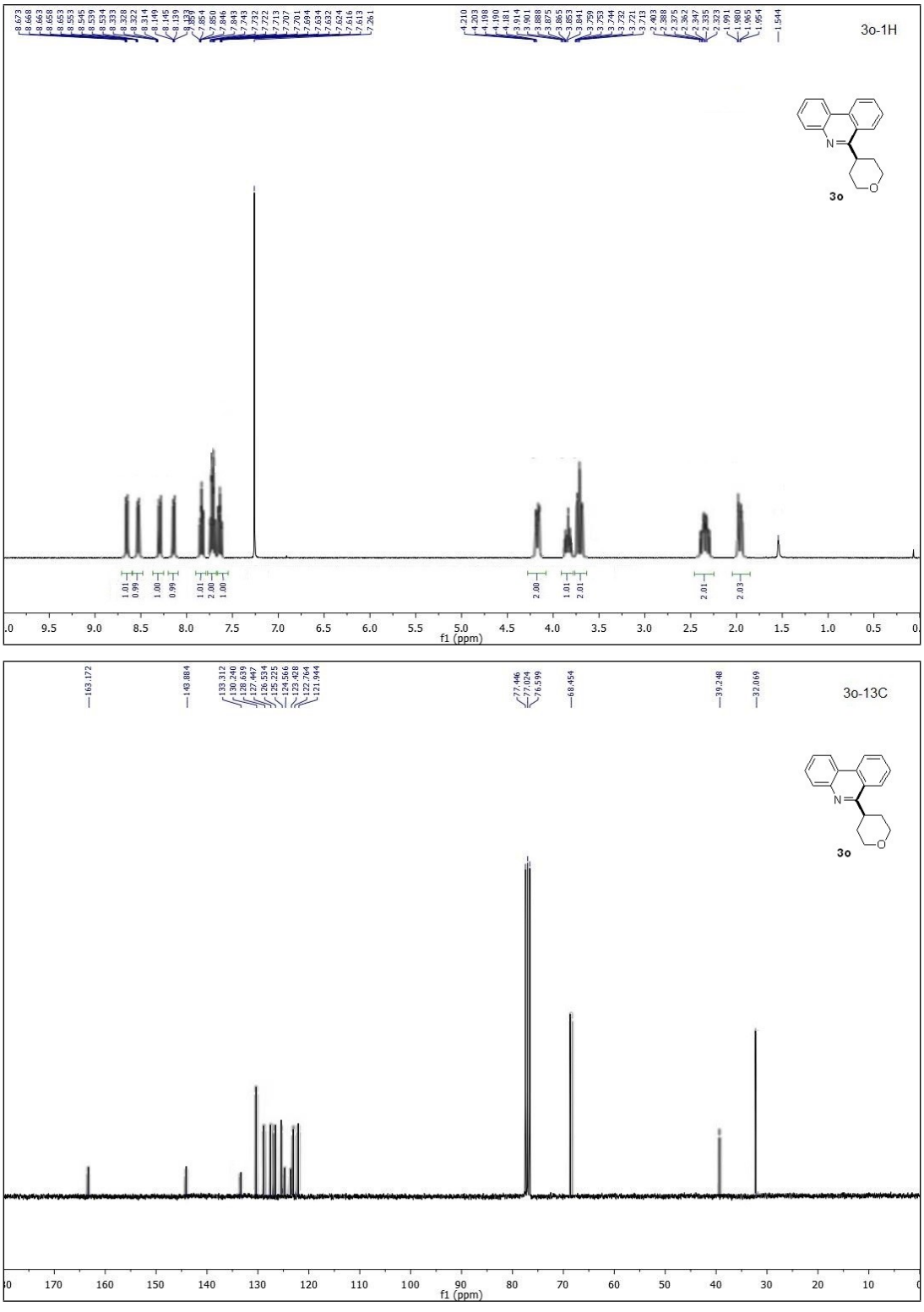

Figure S17. ^{1}H (top) and ^{13}C (bottom) spectra of 3o in $CDCl_3$.

Figure S18. ^{1}H (top) and ^{13}C (bottom) spectra of **3q** in $CDCl_3$.

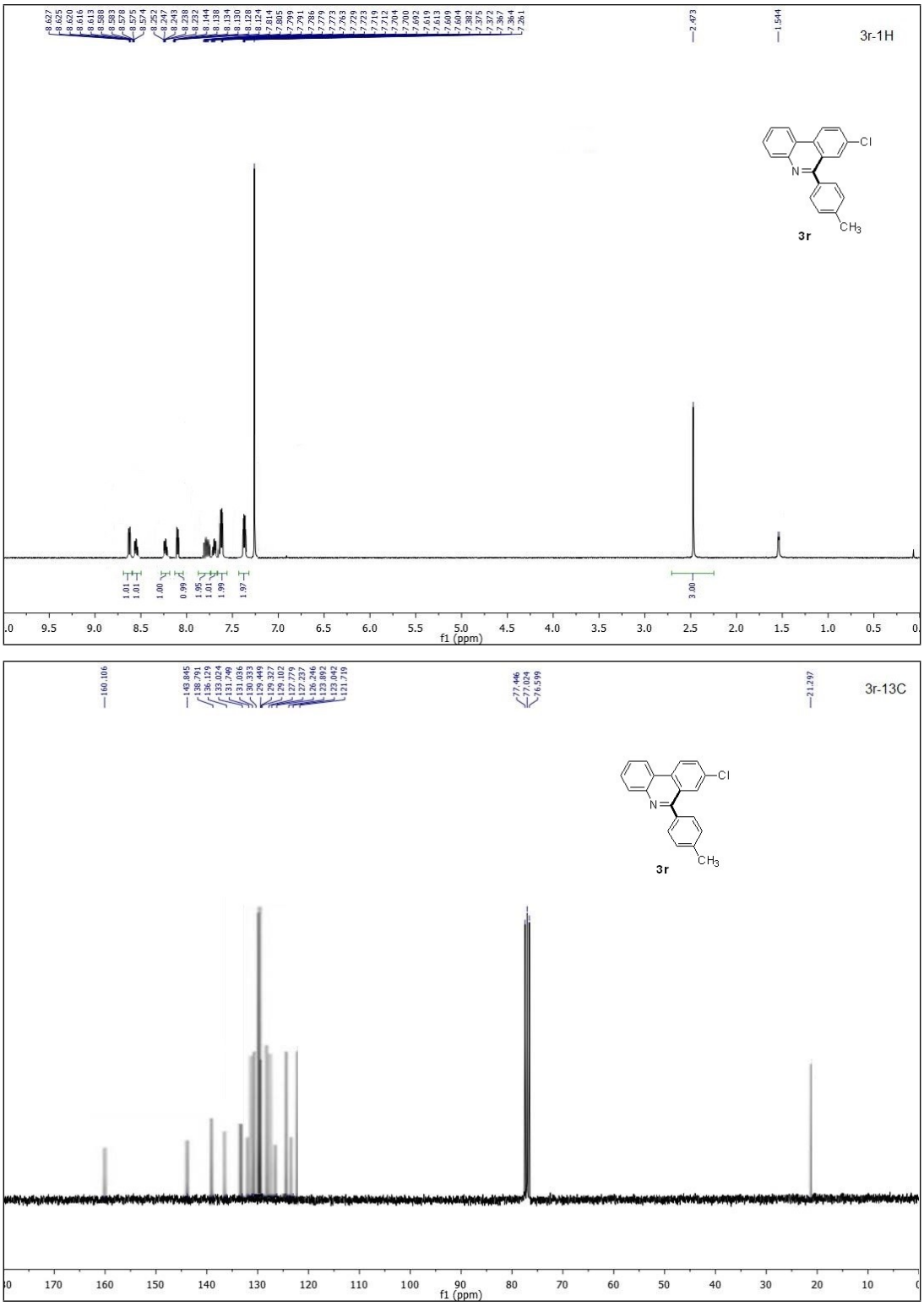

Figure S19. ^{1}H (top) and ^{13}C (bottom) spectra of **3r** in $CDCl_3$.

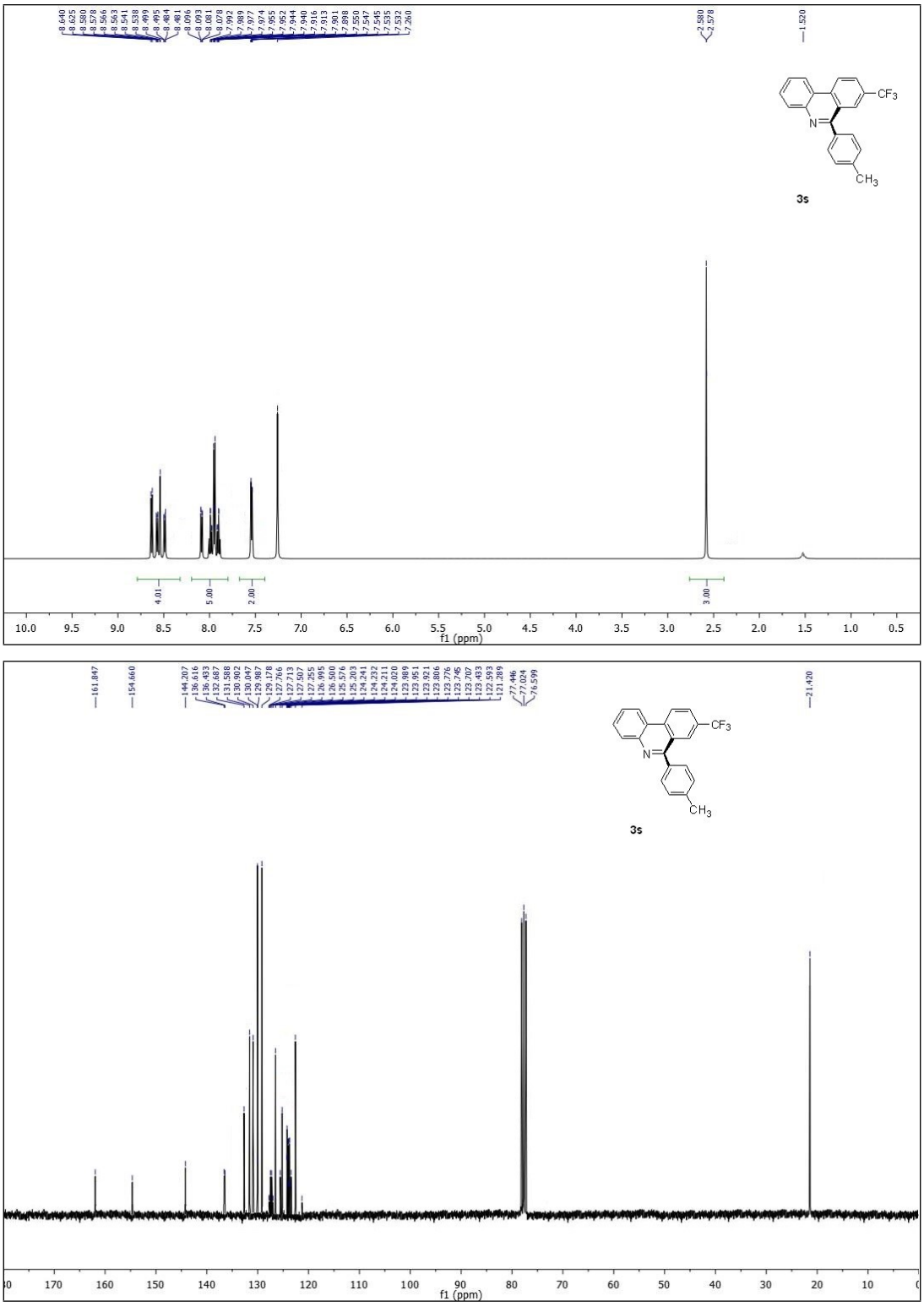

Figure S20. ^{1}H (top) and ^{13}C (bottom) spectra of **3s** in $CDCl_3$.

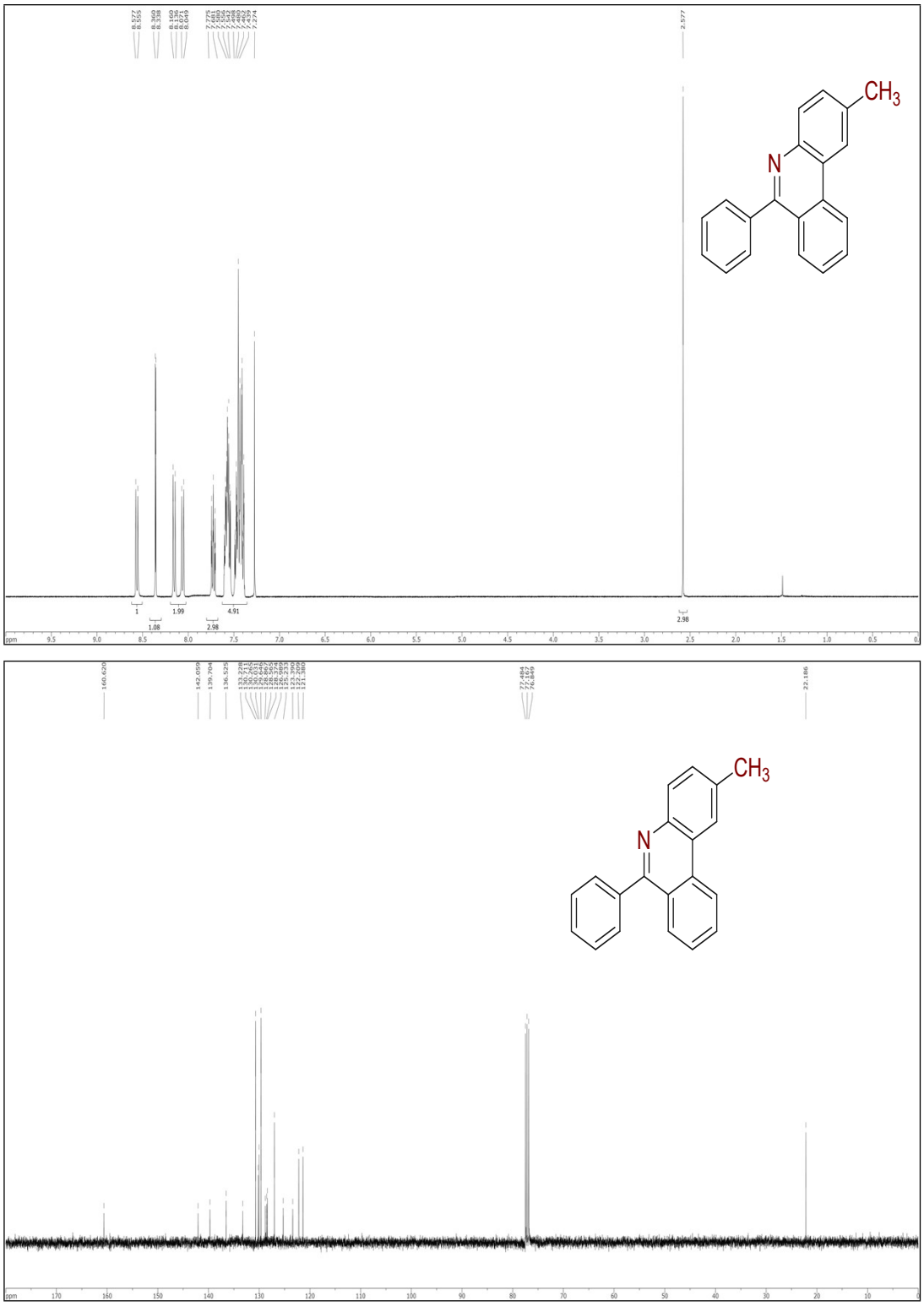

Figure S21. ^{1}H (top) and ^{13}C (bottom) spectra of 3t in $CDCl_3$.

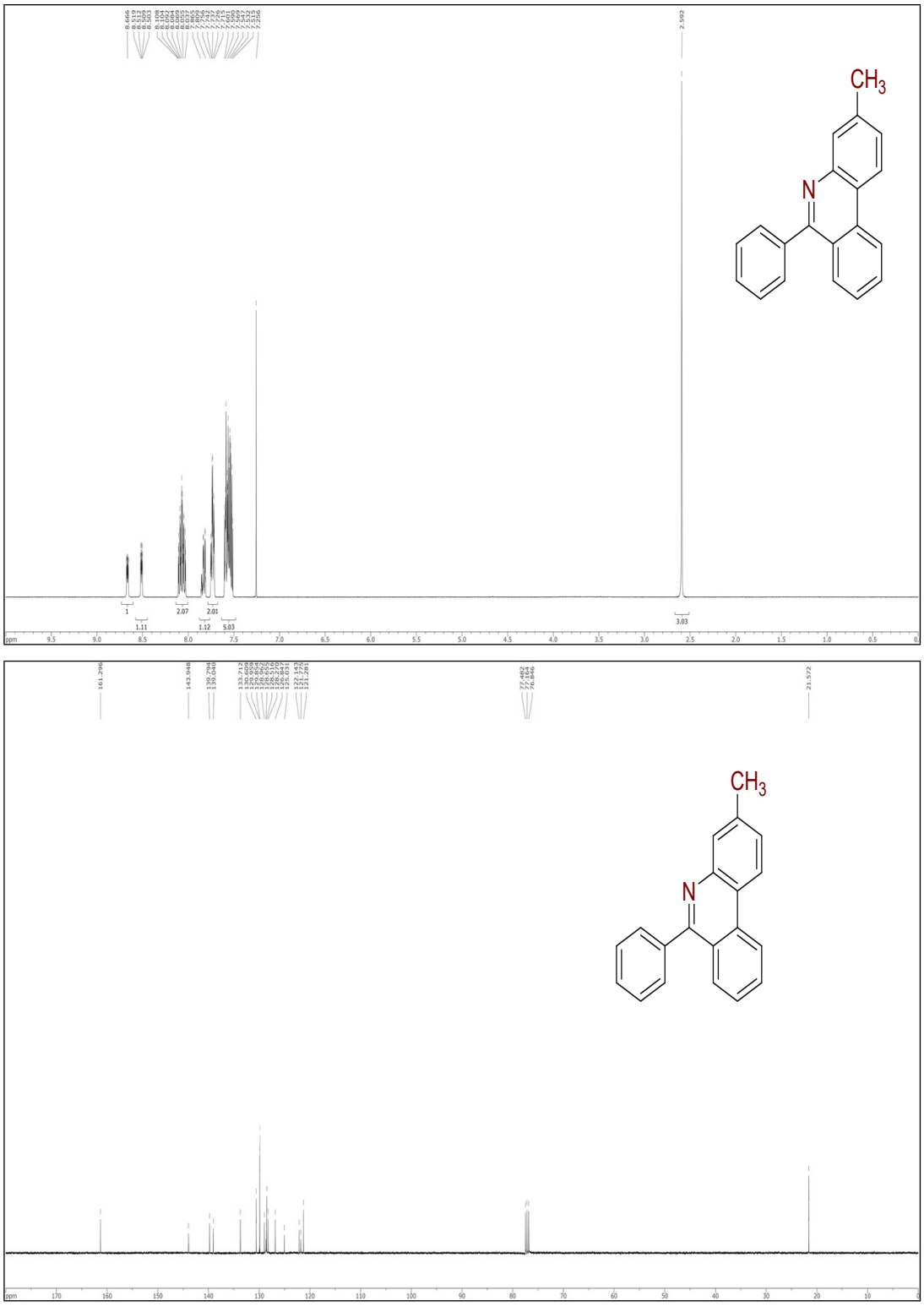

Figure S22. ^{1}H (top) and ^{13}C (bottom) spectra of 3u in $CDCl_3$.

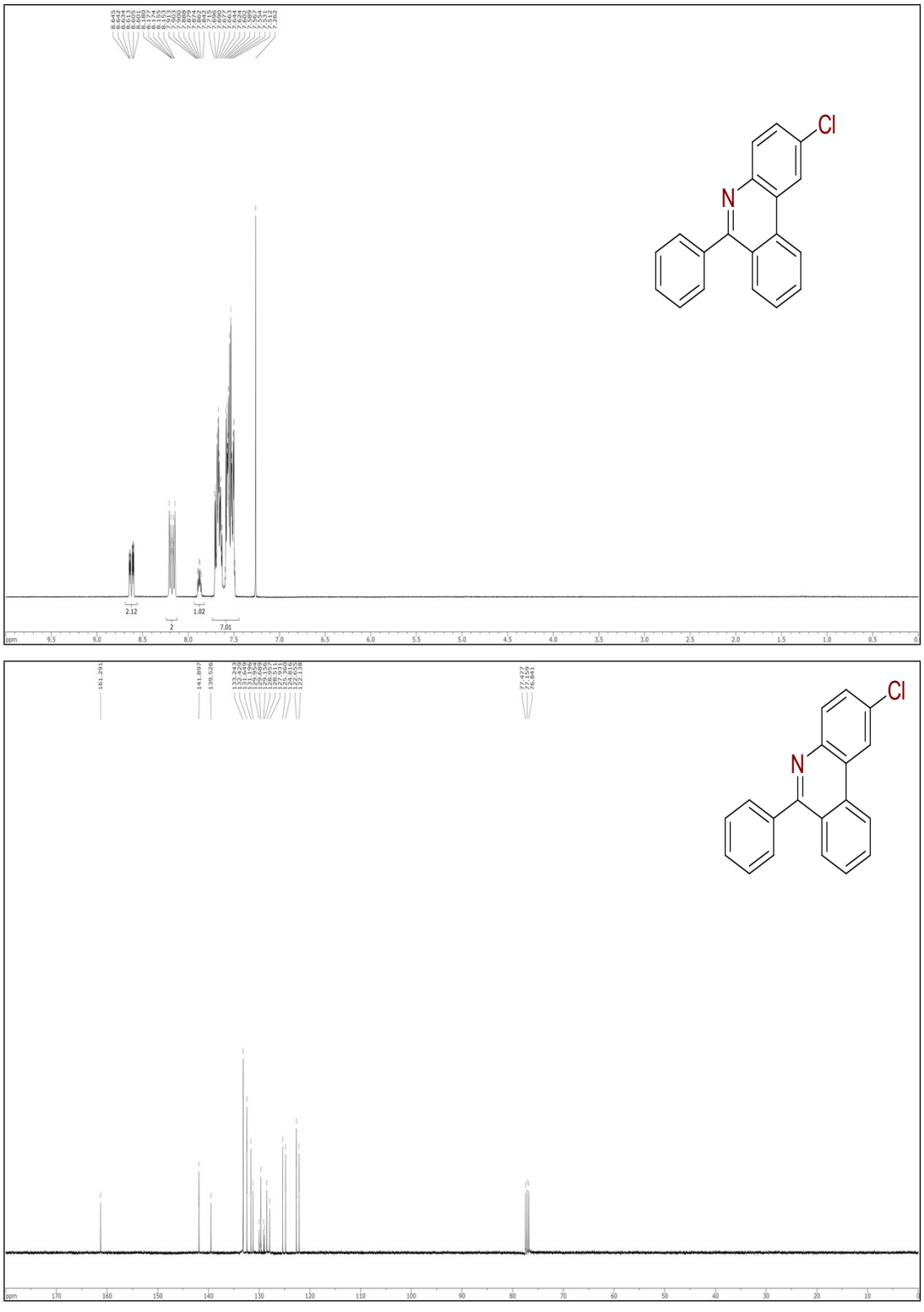

Figure S23. ^{1}H (top) and ^{13}C (bottom) spectra of 3w in $CDCl_3$.

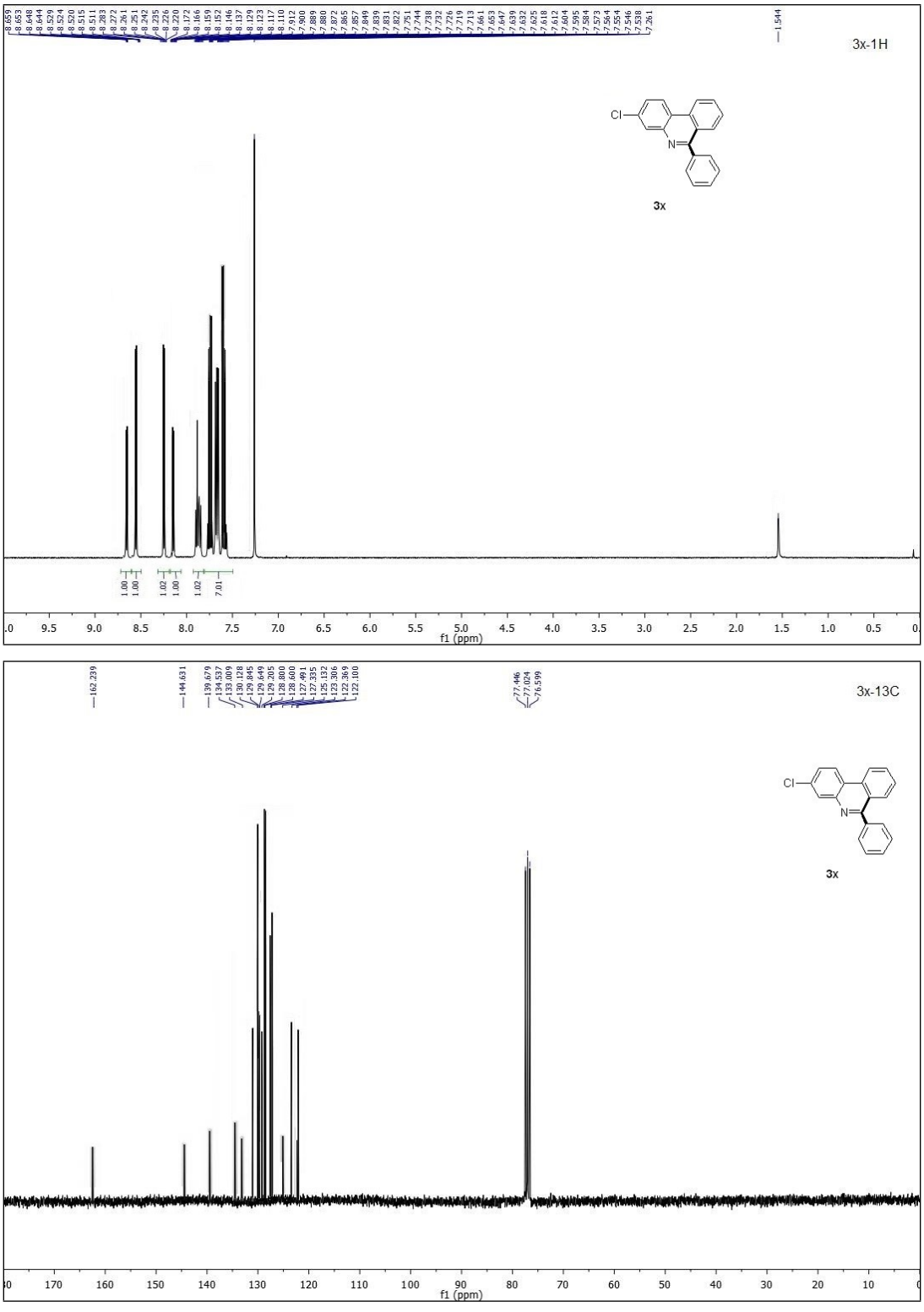

Figure S24. ^{1}H (top) and ^{13}C (bottom) spectra of 3x in $CDCl_3$.

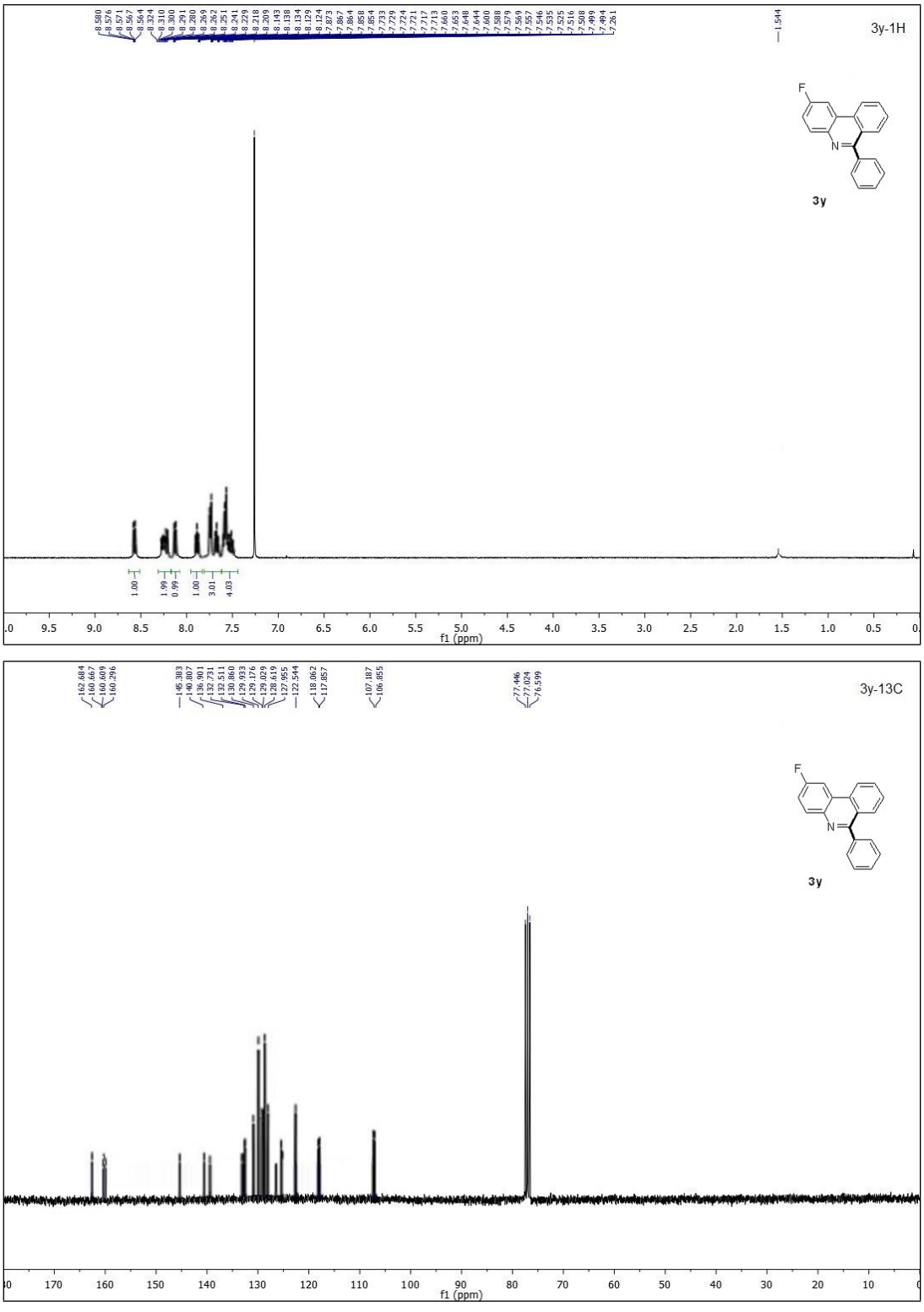

Figure S25. ^{1}H (top) and ^{13}C (bottom) spectra of 3y in $CDCl_3$.