Electronic Supplementary Material (ESI) for Green Chemistry.

Supporting Information

$K_2S_2O_8$-Induced Site-selective Phenoxazination/Phenothiazination of Electron-Rich Anilines

Zhang et al.

Contents

General information

Reagents and materials.

Unless otherwise stated, analytical grade solvents and commercially available reagents were used without further purification. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200−300 mesh silica gel in petroleum ether (bp. 60−90 ºC). Gradient flash chromatography was conducted eluting with a continuous gradient from petroleum ether to the indicated solvent, and listed as volume/volume ratio.

Characterization.

All new compounds were characterized by ^{1}H NMR, ^{13}C NMR and HRMS. The known compounds were characterized by ^{1}H NMR and ^{13}C NMR. The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 400 MHz NMR spectrometer. All chemical shifts (δ) were reported in ppm and coupling constants (*J*) in Hz. All chemical shifts were reported relative to tetramethylsilane (0 ppm for ^{1}H), $CDCl_3$ (77.16 ppm for ^{13}C) respectively. High resolution mass spectra (HRMS) were measured with a Thermo Orbitrap Elite instrument and accurate masses were reported for the molecular ion+ Hydrogen $(M+H)^+$. EPR spectra were recorded on a Bruker X-band A-200 spectrometer. UV-vis absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer. Photoluminescence (PL) spectra were processed on a Hitachi F-4600 fluorescence spectrophotometer.

Experiment procedure

General procedure:

A solution of *N,N*-Dimethylaniline (**1a**, 0.2 mmol, 24.2 mg), 10H-phenoxazine (**2a**, 0.3 mmol, 54.9 mg), $K_2S_2O_8$ (0.4 mmol, 2 equiv., 108.1 mg), in CH_3CN (3 mL) were stirred under air at room temperature for 1 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 50/1).

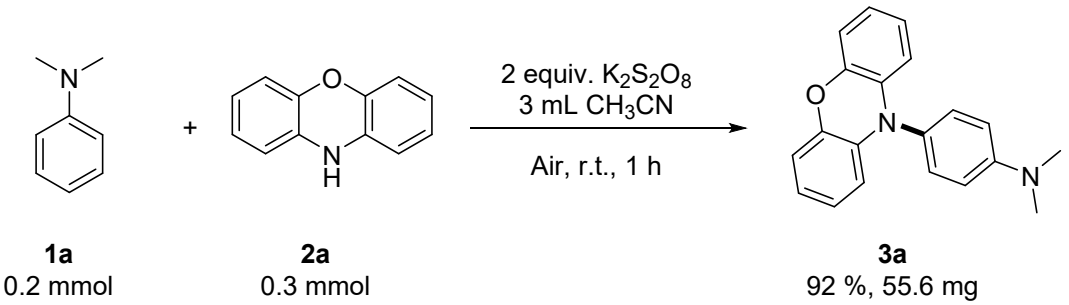


Fig. S1 General procedure synthesis experiment

General procedure for direct amination of triarylamine:

A solution of 4,4'-dimethlytriphenyamine (**4a**, 0.2 mmol, 54.6 mg), 2-Cyano-phenothiazine (**2j**, 0.3 mmol, 67.2 mg), $K_2S_2O_8$ (0.4 mmol, 2 equiv., 108.1 mg), in CH_3CN/AcOH (1.5 mL/1.5 mL) were stirred under air at room temperature for 24 h. After completion of the reaction, the solvent was removed under reduced pressure by rotary evaporation. Then, the product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 200/1).

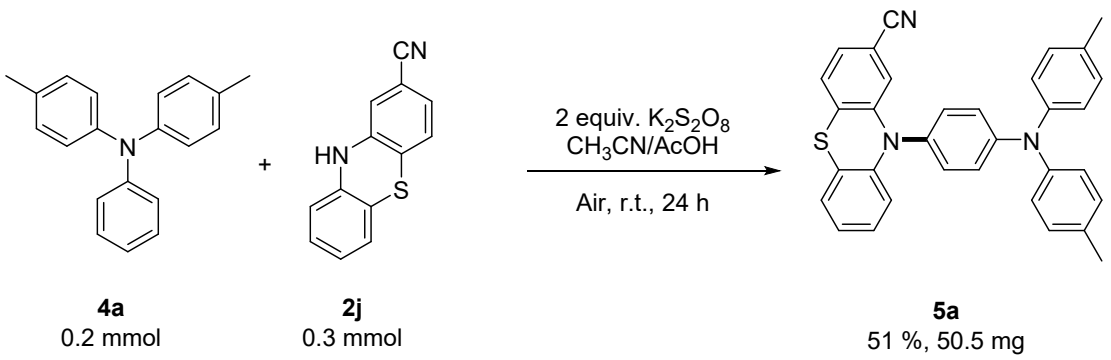


Fig. S2. General procedure for direct amination of triarylamine

Procedure for gram-scale synthesis experiment:

A solution of *N,N*-Dimethylaniline **1a** (5 mmol, 0.61 g), 10H-phenoxazine **2a** (7.5 mmol, 1.37 g), in CH_3CN (50 mL) were stirred under air at room temperature. $K_2S_2O_8$ (10 mmol, 2 equiv., 108.1 mg) was added step-by-step in 4 hours. After continuous stirring for 2 hours, the solvent was removed under reduced pressure by rotary evaporation. Then, the product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 50/1). It only afforded 51 % isolated yield because side reactions exist while mixing is not sufficient.

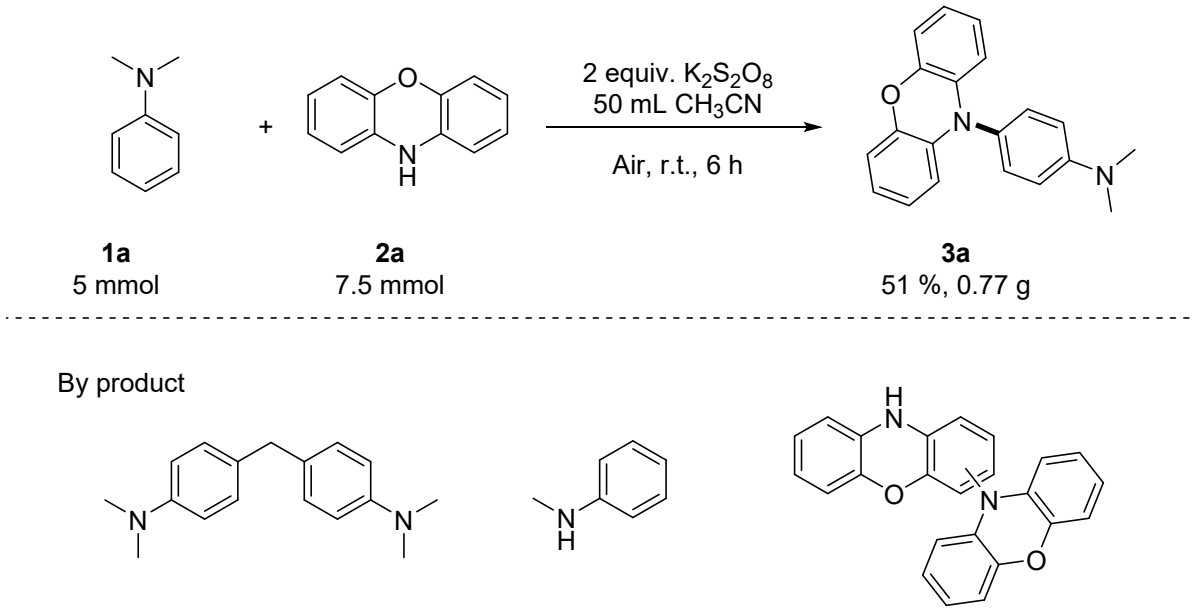


Fig. S3. The gram-scale synthesis experiment

Procedure for flow chemistry was different from direct increasing the amount of solvent and substrates. *N,N*-Dimethylaniline **1a** (5 mmol, 0.61 g), 10H-phenoxazine **2a** (7.5 mmol, 1.37 g) was dissoloved in CH_3CN (100 mL); $K_2S_2O_8$ (10 mmol, 2 equiv., 2.70 g) was dissolved in water (100 mL). Then, two solutions were mixed via a simple flow-chemistry reactor (**Fig S4, B** or **C**). The reaction finished in 1 hour, then, the solvent was removed under reduced pressure by rotary evaporation. And the product was obtained by flash column chromatography on silica gel (eluent: petroleum ether/ ethyl acetate = 50/1).

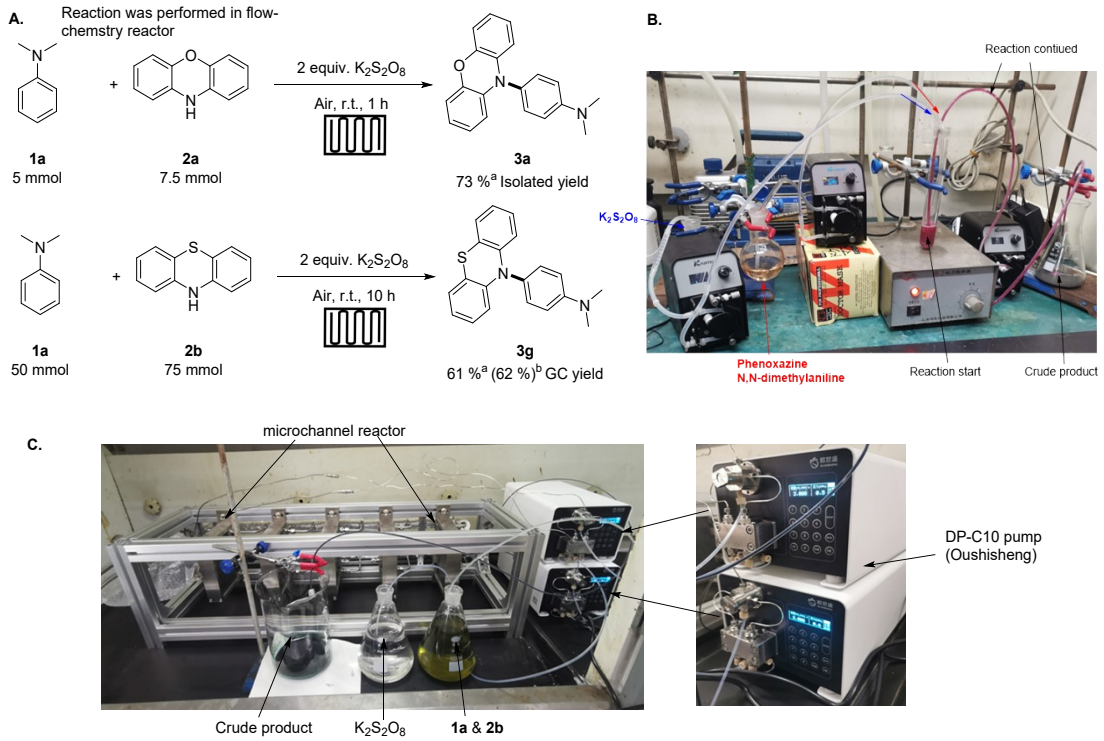


Fig. S4. The gram-scale synthesis experiment in flow-chemistry reactor. **(A)**: reactions was performed in flow- chemistry reactor; [a]: the reaction was carried in reactor B; [b]: the reaction was carried in reactor C; **(B)**:a simple flow reactor construct by 3 pumps and a tube; **(C)**: microchannel reactor equipped with 2 DP-C10 high pressure constant current infusion pumps.

Procedure for Electron Paramagnetic Resonance (EPR) experiment:

A mixture of 10H-phenoxazine **2a** (0.02 mmol, 5.5 mg), and oxidant (0.02 mmol, 5.4 mg), in MeOH (3 mL) was stirred under N_2 at room temperature for 5 min. Then, this reaction solution was taken out by capillary and was analyzed by a Bruker X-band A-200 spectrometer at room temperature. Following spectrum was then obtained (Fig.

S4. black line, g = 2.0043). After fitting, we proposed that this radical signal belongs to phenoxazine nitrogen radical (A_N= 8.0 g, A_H=3.8 g, A_H=3.8 g, A_H=3.8 g, A_H=3.8 g). (Although CH_3CN was selected as the solvent in standard condition in this paper, it did not work well in EPR experiment, multiplets could not be observed if CH_3CN was used in EPR experiment.)

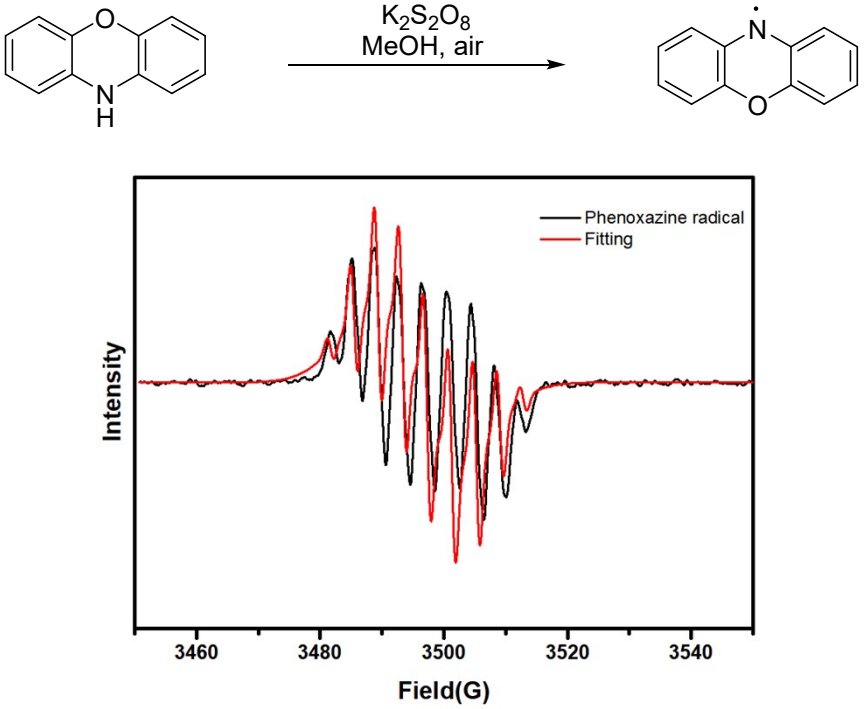


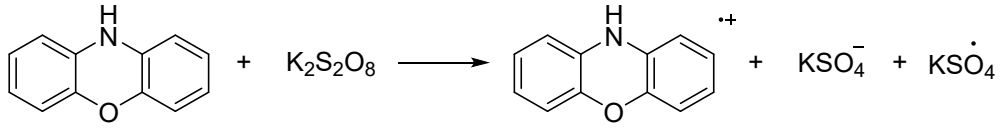
Fig. S5. Electron paramagnetic resonance (EPR) spectra of *N*-centered radical

General Computational Calculation Details

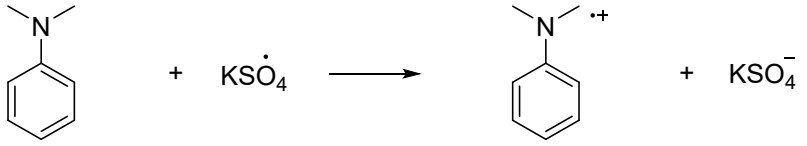
DFT calculations were performed using the M06-2x method[1] with the Gaussian09 program[2]. The 6-31G(d) basis set was used for all the elements and acetonitrile was employed as the solvent during the geometry optimization. For the integration grid in the calculations, the parameter int = ultrafine was used. Frequency calculations at the same level of theory have been performed to identify all of the stationary points as minima (zero imaginary frequencies) or transition state (one imaginary frequencies) and to provide free energies at 298.15 K. The transition states were checked through intrinsic reaction coordinate (IRC) calculations. The solvent effects were considered

during the geometry optimization with SMD model[3]. For the single point energy calculations, 6-311+G(d,p) basis set was used for all the elements. Grimme's dispersion correction[4] was used during the calculations.

The activation free energies of single electron transfer reactions (1) & (2) were calculated using the Savéant's model[5, 6] and the outer sphere Marcus-Hush model[7-9], respectively.



(1)



(2)

$$\Delta G_{\mathrm{OSET}}^{\neq} = \Delta G_0^{\neq}(1+\frac{\Delta_r G}{4\Delta G_0^{\neq}})^2 \quad (3)$$

The activation free energy of single electron transfer reaction can be calculated using the above equation (3), in which $\Delta_r G$ is the Gibbs free energy of the reaction, $\Delta G_0^{\neq}$ is the intrinsic barrier for the outer sphere electron transfer.

For reaction (2), the $\Delta G_0^{\neq}$ can be calculated by the following equation.

$$\Delta G_0^{\neq} = \frac{\lambda_0 + \lambda_i}{4} \approx \frac{\lambda_0}{4}$$

λ_i is the inner reorganization energy, which is usually expected to be small enough to be neglected. λ_0 is the solvent reorganization energy and can be calculated by the following equation.

$$\lambda_0 = (332\mathrm{kcal}\cdot\mathrm{mol}^{-1})(\frac{1}{2r_1}+\frac{1}{2r_2}-\frac{1}{r_1+r_2})(\frac{1}{\varepsilon_{\mathrm{op}}}-\frac{1}{\varepsilon})$$

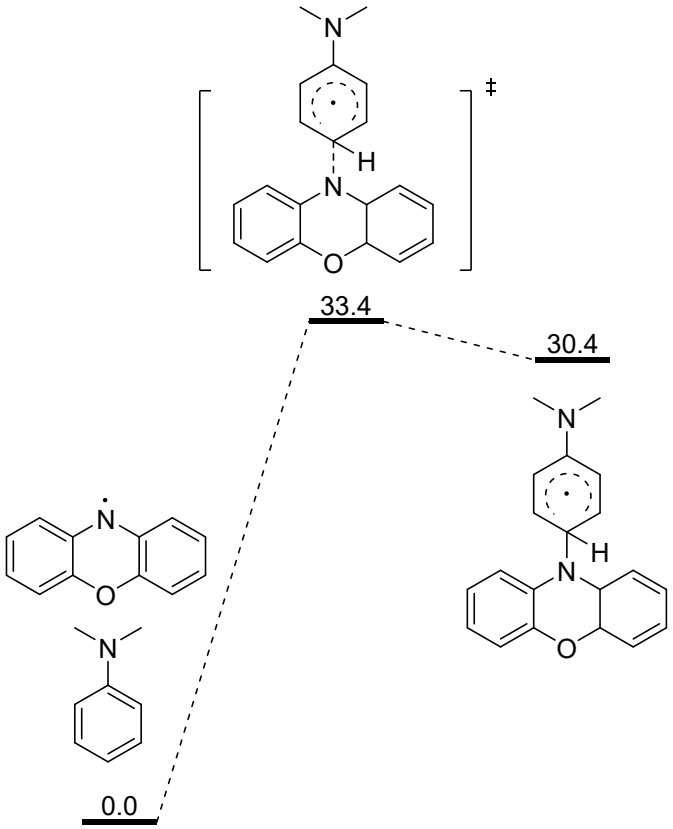
r_1 and r_2 are the radii of the molecules involved in electron transfer, $\varepsilon_{\mathrm{op}}$ is the optical dielectric constant (1.807 in this case), ε is the static dielectric constant for the acetonitrile solvent (35.688 in this case). Radii of the molecule can be estimated by assuming the molecule to be a perfect sphere, i.e. $r = (\frac{3V}{4\pi})^{1/3}$. The volume of the molecule can be calculated using the "volume" keyword in Gaussian 09.

For reaction (1), the single electron transfer and the cleavage of $K_2S_2O_8$ are concerted.

$$\Delta G_0^{\neq} = \frac{\lambda_0 + \lambda_i + \mathrm{BDFE}}{4} \approx \frac{\lambda_0 + \mathrm{BDFE}}{4}$$

BDFE is the bond dissociation free energy of $K_2S_2O_8$.

The activation free energy of reaction (1) and (2) are estimated to be 18.8 kcal·mol^{-1} and 0.5 kcal·mol^{-1}, respectively.



For the radical addition pathway as shown above, the free energy barrier was calculated to be 33.4 kcal·mol^{-1}, which meant that it was unrealizable under the room temperature.

Optical properties of 5a：

To test the optical properties of **5a**, **5a** was dissolved in solvent first, then diluted to 10^{-5} M. UV-vis absorption spectra were recorded on a Shimadzu UV-2700 spectrophotometer. UV-vis absorption spectra (Fig. S5.) showed that **5a** not only could adsorb the ultraviolet light, but also have a weak adsorption in visible light region (390-760 nm). Photoluminescence (PL) spectra were processed on a Hitachi F-4600 fluorescence spectrophotometer. PL spectra showed that **5a** could be excited by

either ultraviolet light (λ_{exc} = 300 nm, Fig. S6. red line) or visible light (λ_{exc} = 450 nm, blue light, Fig. S6. black line).

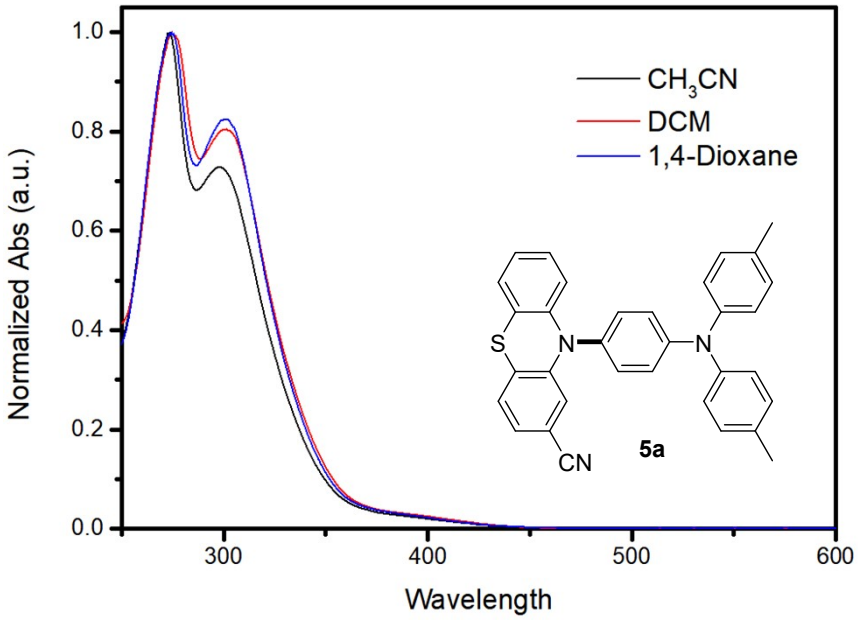


Fig. S6 UV-Vis adsorption spectra of **5a,** 10^{-5} M **5a** solution in CH_3CN, DCM, 1,4-Dioxane were test

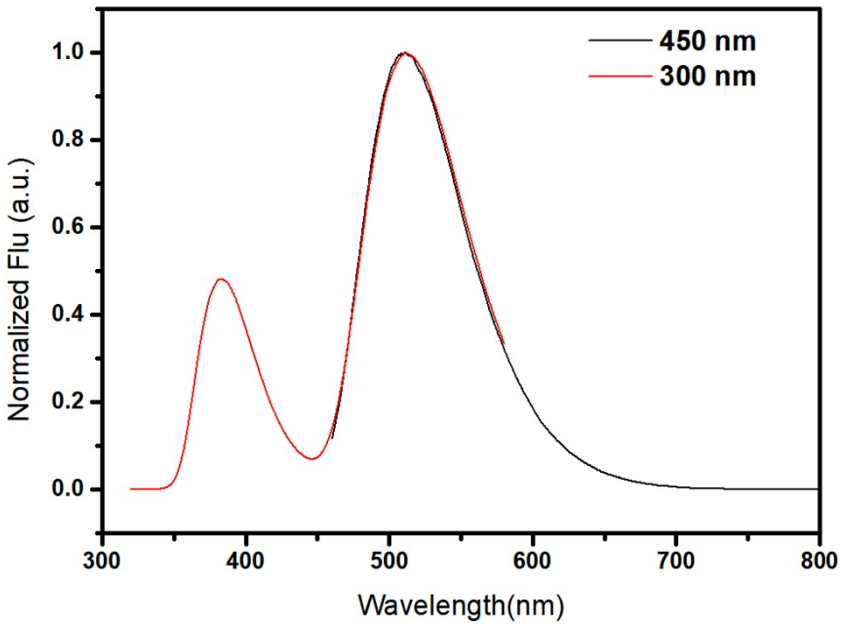


Fig. S7 Fluorescence of spectra of **5a,** 10^{-5} M **5a** was excited by 300 nm (red line) or 450 nm (black line) light in CH_3CN

Procedure for debromination:

A schlenk tube equipped with a stir bar was loaded with 6-Bromonicotinic acid ethyl

ester (0.2 mmol, 43.2 mg), photo-catalyst **5b** (0.01 mmol, 5.0 mg), Tri-n-butylamine (1 mmol, 185.4 mg) and CH_3CN (3 mL) under N_2 atmosphere. The solution was then stirred at room temperature under the irradiation of 12W blue LED lamp for 24 h. After the completion of reaction, biphenyl (15.4 mg, 0.1 mmol) was added as an internal standard, and the reaction yield was monitored by GC.

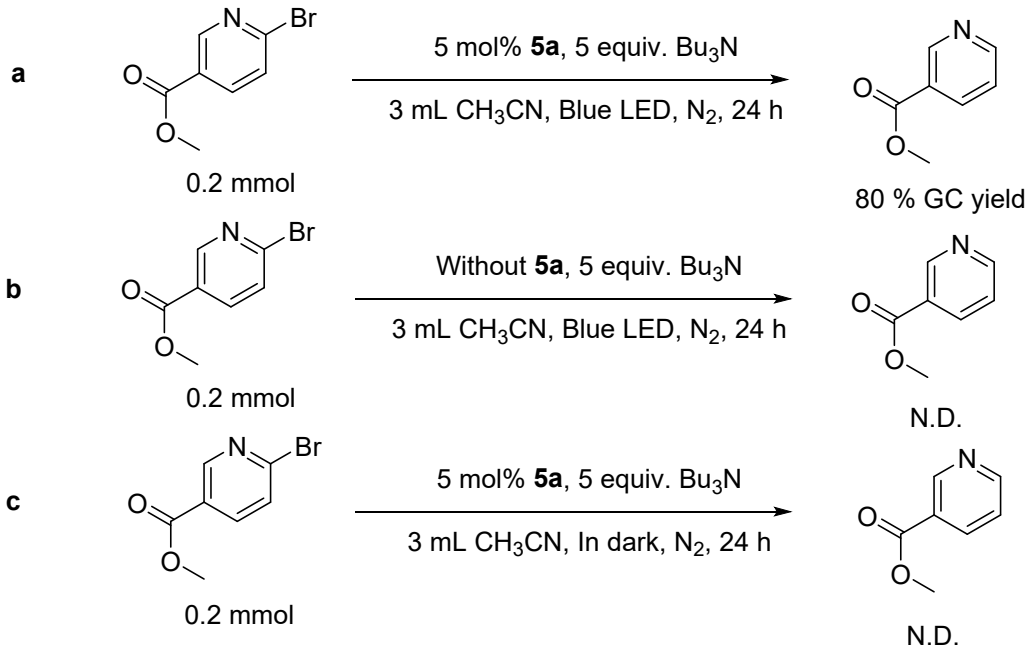
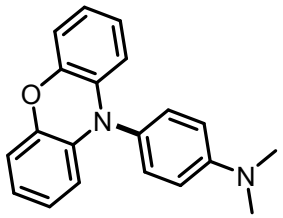


Fig. 8. Control experiments.

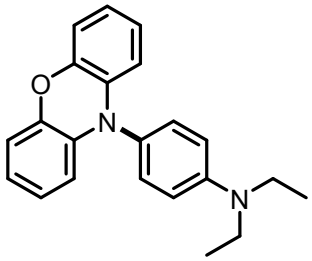
Detail descriptions for products

3a, 3g, 3h, 3i, 3j& 3k has been reported in our previous work[10], so that only NMR spectra was provided. Both NMR spectra and high resolution mass data were provided for other compounds.

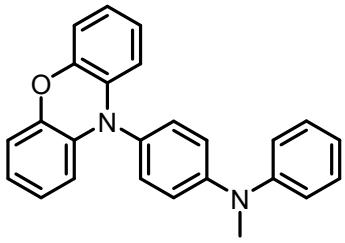


***N,N*-Dimethyl-4-(10H-phenoxazin-10-yl)aniline (3a):** white solid was obtained in 92% isolated yield.^{1}H NMR (400 MHz, Chloroform-d) δ 7.14 (d, J = 8.9 Hz, 2H), 6.85 (d, J = 8.9 Hz, 2H), 6.66 – 6.54 (m, 6H), 6.00 – 5.94 (m, 2H), 3.02 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.22, 144.14,

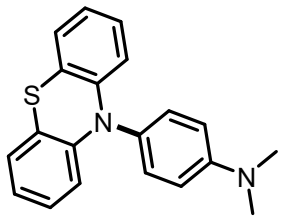
135.30, 131.21, 127.10, 123.31, 120.90, 115.25, 114.13, 113.38, 40.67.



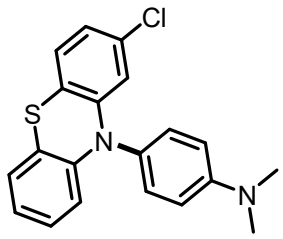
***N,N*-diethyl-4-(10H-phenoxazin-10-yl)aniline(3b):**white solid was obtained in 93% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.09 (d, *J* = 9.0 Hz, 2H), 6.79 (d, *J* = 9.0 Hz, 2H), 6.67 – 6.55 (m, 6H), 6.05 – 5.96 (m, 2H), 3.40 (q, *J* = 7.1 Hz, 4H), 1.22 (t, *J* = 7.1 Hz, 6H).^{13}C NMR (101 MHz, $CDCl_3$) δ 147.56, 144.14, 135.37, 131.32, 125.86, 123.29, 120.80, 115.19, 113.43, 113.21, 44.55, 12.71. HRMS (ESI) calculated for $C_{22}H_{23}N2O^{+}[M+H]^{+}$: 331.1805; found: 331.1804



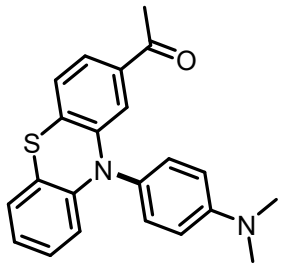
***N*-methyl-4-(10H-phenoxazin-10-yl)-*N*-phenylaniline(3e):** white solid was obtained in 88% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.24 (m, 2H), 7.15 – 7.11 (m, 2H), 7.08 – 6.93 (m, 5H), 6.62 – 6.47 (m, 6H), 5.97 – 5.86 (m, 2H), 3.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.90, 148.46, 144.09, 134.98, 131.24, 129.86, 129.69, 123.75, 123.32, 121.07, 119.16, 115.34, 113.35, 40.50. HRMS (ESI) calculated for $C_{25}H_{21}N_2O^{+}[M+H]^{+}$: 365.1648; found: 365.1647.



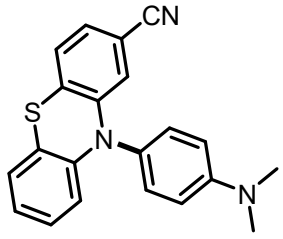
N,N-dimethyl-4-(10H-phenothiazin-10-yl)aniline (3g): white solid was obtained in 63% isolated yield.1H NMR (400 MHz, Chloroform-d) δ 7.21 (d, J = 8.9 Hz, 2H), 6.96 (d, J = 7.4 Hz, 2H), 6.87 (d, J = 8.9 Hz, 2H), 6.82 (t, J = 7.7 Hz, 2H), 6.75 (t, J = 7.3 Hz, 2H), 6.24 (d, J = 8.2 Hz, 2H), 3.03 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.07, 145.13, 131.71, 129.13, 126.91, 126.59, 122.09, 119.49, 115.77, 113.80, 40.67.



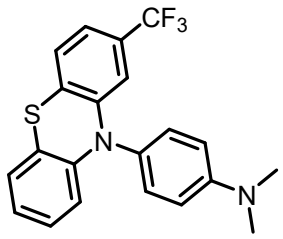
4-(2-Chloro-10H-phenothiazin-10-yl)-*N,N*-dimethylaniline (3h): white solid was obtained in 37% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 (d, *J* = 8.9 Hz, 2H), 6.95 (dd, *J* = 7.3, 1.7 Hz, 1H), 6.90 – 6.85 (m, 3H), 6.85 – 6.71 (m, 3H), 6.25 – 6.20 (m, 2H), 3.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.27, 146.33, 144.55, 132.73, 131.43, 128.39, 127.18, 127.11, 126.61, 122.59, 121.85, 119.23, 118.00, 116.12, 115.76, 40.64.



1-(10-(4-(dimethylamino)phenyl)-10H-phenothiazin-2-yl)ethan-1-one (3i): yellow solid was obtained in 61% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.19 (d, *J* = 8.9 Hz, 2H), 6.99 (d, *J* = 7.9 Hz, 1H), 6.94 – 6.86 (m, 3H), 6.85 – 6.74 (m, 3H), 6.20 (dd, *J* = 8.2, 1.4 Hz, 1H), 3.05 (s, 6H), 2.36 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.45, 150.26, 145.18, 144.55, 136.03, 131.36, 128.38, 127.38, 126.72, 126.50, 126.26, 122.44, 118.31, 116.17, 114.39, 114.04, 40.62, 26.57.

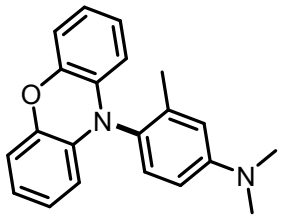


10-(4-(Dimethylamino)phenyl)-10H-phenothiazine-2-carbonitrile (3j): yellow solid was obtained in 54% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (d, *J* = 8.9 Hz, 2H), 7.00 – 6.76 (m, 7H), 6.34 (s, 1H), 6.22 (d, *J* = 8.0 Hz, 1H), 3.07 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.45, 145.63, 143.84, 131.11, 127.57, 126.77, 126.68, 126.55, 125.43, 122.96, 119.28, 117.89, 117.78, 116.24, 114.14, 110.13, 40.59.

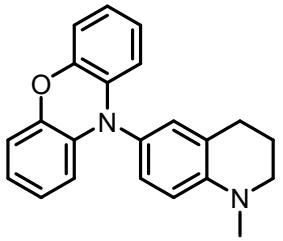


***N, N*-Dimethyl-4-(2-(trifluoromethyl)-10H-phenothiazin-10-yl)aniline(3k)**: white solid was obtained in 50 % isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.19 (d, *J* = 9.0 Hz, 2H), 7.04 – 6.76 (m, 7H), 6.43 (s, 1H), 6.21 (dd, *J* = 8.1, 1.3 Hz, 1H), 3.06 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 150.15, 145.39, 144.34, 131.18, 129.18(q, J_{C-F} = 31.0 Hz), 127.94, 127.19, 126.49, 126.44, 125.27, 124.20, 122.58, 118.53(q, J_{C-F} = 4.0 Hz), 116.05, 113.83, 111.74(q, J_{C-F} = 4.0 Hz), 40.44.

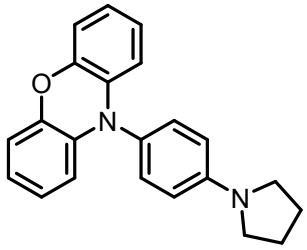
^{19}F NMR (377 MHz, $CDCl_3$) δ -62.84.



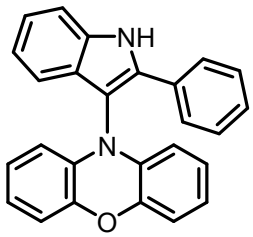
***N, N,* 3-trimethyl-4-(10H-phenoxazin-10-yl) aniline(3m)**: white solid was obtained in 63% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.11 – 7.03 (m, 1H), 6.75 – 6.52 (m, 8H), 5.89 – 5.80 (m, 2H), 3.01 (s, 6H), 2.17 (s, 3H).^{13}C NMR (101 MHz, $CDCl_3$) δ 150.51, 144.08, 139.21, 134.32, 131.29, 125.46, 123.49, 120.80, 115.23, 114.98, 112.81, 112.11, 40.68, 18.22. HRMS (ESI) calculated for $C_{21}H_{21}N2O^{+}[M+H]^{+}$: 317.1648; found: 317.1645.



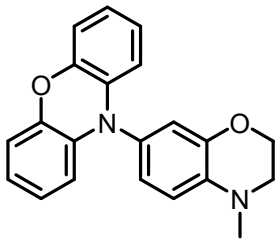
10-(1-methyl-1,2,3,4-tetrahydroquinolin-6-yl)-10H-phenoxazine(3n): white solid was obtained in 82% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.96 (dd, *J* = 8.5, 2.4 Hz, 1H), 6.86 (d, *J* = 2.3 Hz, 1H), 6.71 – 6.55 (m, 7H), 6.00 (m, 2H), 3.33 – 3.27 (m, 2H), 2.95 (s, 3H), 2.78 (t, *J* = 6.4 Hz, 2H), 2.02 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.45, 144.11, 135.33, 130.33, 128.99, 126.64, 125.11, 123.27, 120.78, 115.18, 113.44, 112.28, 51.27, 39.21, 27.93, 22.30. HRMS (ESI) calculated for $C_{22}H_{21}N_2O^{+}[M+H]^{+}$: 329.1648; found: 329.1642.



10-(4-(pyrrolidin-1-yl)phenyl)-10H-phenoxazine(3o): white solid was obtained in 83% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.12 (d, *J* = 8.7 Hz, 2H), 6.69 (d, *J* = 8.8 Hz, 2H), 6.65 – 6.54 (m, 6H), 5.97 (m, 2H), 3.34 (t, *J* = 6.5 Hz, 4H), 2.08 – 2.01 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.57, 144.12, 135.40, 131.30, 126.06, 123.29, 120.81, 115.20, 113.33, 47.80, 25.72. HRMS (ESI) calculated for $C_{22}H_{21}N2O^{+}[M+H]^{+}$: 329.1648; found: 329.1646.

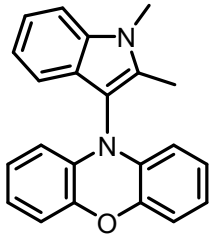


10-(2-phenyl-1H-indol-3-yl)-10H-phenoxazine(3p): pale red solid was obtained in 96% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 11.95 (s, 1H), 7.86 (d, *J* = 8.5 Hz, 2H), 7.55 (d, *J* = 8.1 Hz, 1H), 7.45 (t, *J* = 7.8 Hz, 2H), 7.36 – 7.16 (m, 3H), 7.00 (t, *J* = 7.8 Hz, 1H), 6.78-6.75 (m, 2H), 6.66-6.54 (m, 4H), 5.95 (dd, *J* = 7.9, 1.5 Hz, 2H). ^{13}C NMR (101 MHz, DMSO) δ 143.72, 135.82, 134.84, 133.23, 130.59, 129.22, 128.39, 126.07, 124.05, 122.87, 121.64, 120.17, 117.71, 115.48, 113.43, 112.39, 109.16. HRMS (ESI) calculated for $C_{26}H_{19}N_2O^{+}[M+H]^{+}$: 375.1492; found: 375.1482.

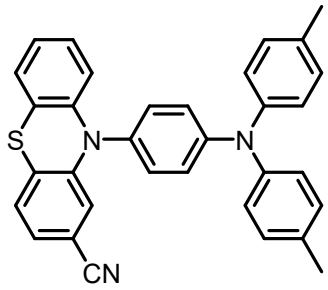


10-(4-methyl-3,4-dihydro-2H-benzo[b][1,4]oxazin-7-yl)-10H-phenoxazine(3q):white solid was obtained in 60% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 6.81 (s, 2H), 6.75 (s, 1H), 6.72 – 6.58 (m, 7H), 6.10 – 6.02 (m, 2H), 4.42 – 4.35 (m, 2H), 3.44 – 3.32 (m, 2H), 2.99 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.65, 143.93, 136.59, 134.93, 128.44, 123.18, 120.86, 117.55, 115.14, 113.57,

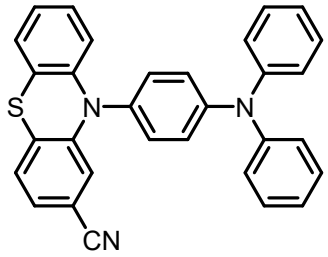
113.38, 64.95, 48.87, 38.72. HRMS (ESI) calculated for $C_{21}H_{19}N_2O_2^+[M+H]^+$: 331.1441; found: 331.1435.



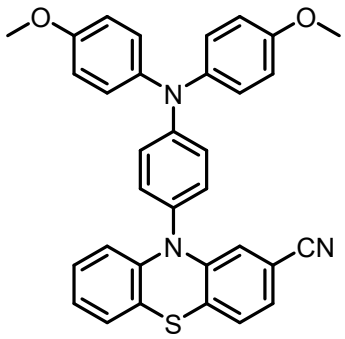
10-(1,2-dimethyl-1H-indol-3-yl)-10H-phenoxazine(3r): white solid was obtained in 33% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 (dd, *J* = 8.0, 5.1 Hz, 2H), 7.29-7.25 (m, 1H), 7.11 (t, *J* = 7.4 Hz, 1H), 6.77 – 6.56 (m, 6H), 6.04 (dd, *J* = 7.9, 1.5 Hz, 2H), 3.81 (s, 3H), 2.35 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.41, 136.32, 135.64, 134.34, 123.96, 123.56, 121.65, 121.11, 119.93, 118.14, 115.34, 113.43, 110.05, 109.27, 30.04, 9.81. HRMS (ESI) calculated for $C_{22}H_{19}N_2O^+[M+H]^+$: 327.1492; found: 327.1490.



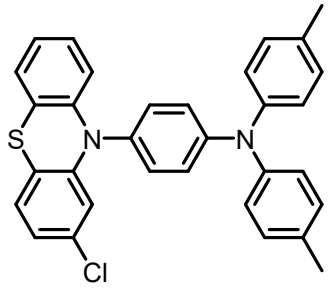
10-(4-(di-p-tolylamino)phenyl)-10H-phenothiazine-2-carbonitrile(5a): yellow solid was obtained in 51% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.14 (s, 10H), 7.09 – 7.05 (m, 2H), 7.01 – 6.94 (m, 2H), 6.92 – 6.85 (m, 2H), 6.82-6.78 (m, 1H), 6.43 (d, *J* = 1.4 Hz, 1H), 6.28 – 6.22 (m, 1H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.81, 145.18, 144.55, 143.50, 133.94, 131.11, 131.06, 130.33, 127.59, 126.94, 126.88, 126.65, 125.86, 125.66, 123.14, 122.17, 119.25, 118.10, 117.73, 116.23, 110.14, 21.04. HRMS (ESI) calculated for $C_{33}H_{26}N_3S^+[M+H]^+$: 497.1876; found: 497.1876.



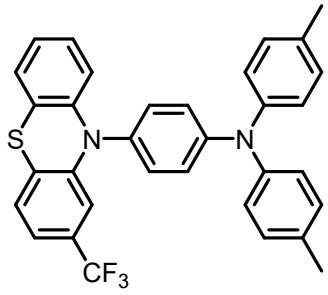
10-(4-(diphenylamino)phenyl)-10H-phenothiazine-2-carbonitrile(5b): yellow solid was obtained in 31% isolated yield ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40-7.36 (m, 4H), 7.27 – 7.10 (m, 12H), 7.09 – 6.92 (m, 3H), 6.87 (t, *J* = 7.0 Hz, 1H), 6.41 (d, *J* = 1.3 Hz, 1H), 6.22 (d, *J* = 8.2 Hz, 1H). ^{13}C NMR (101 MHz, DMSO) δ 147.76, 146.66, 144.40, 142.89, 131.82, 131.32, 129.90, 129.63, 128.00, 127.50, 126.74, 126.44, 126.22, 125.36, 124.26, 123.43, 122.96, 118.73, 117.58, 117.10, 116.30, 109.69. HRMS (ESI) calculated for $C_{31}H_{22}N_3S^+$[M+H]$^+$: 468.1534; found: 468.1525.



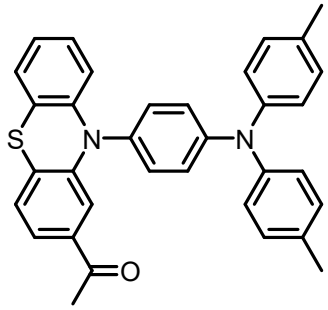
10-(4-(bis(4-methoxyphenyl)amino)phenyl)-10H-phenothiazine-2-carbonitrile(5c): yellow solid was obtained in 67% isolated yield ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.24 – 7.15 (m, 8H), 7.03-7.00 (m, 1H), 6.99 – 6.95 (m, 5H), 6.92 –6.86 (m, 3H), 6.35 (d, *J* = 1.5 Hz, 1H), 6.18 (dd, *J* = 8.2, 0.9 Hz, 1H), 3.75 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 156.59, 148.92, 144.62, 143.07, 139.33, 131.03, 129.54, 127.99, 127.50, 126.72, 126.34, 126.10, 123.36, 119.09, 118.79, 117.42, 116.99, 116.23, 115.26, 109.62, 55.37. HRMS (ESI) calculated for $C_{33}H_{26}O_2N_3S^+$[M+H]$^+$: 528.1746; found: 528.1740.



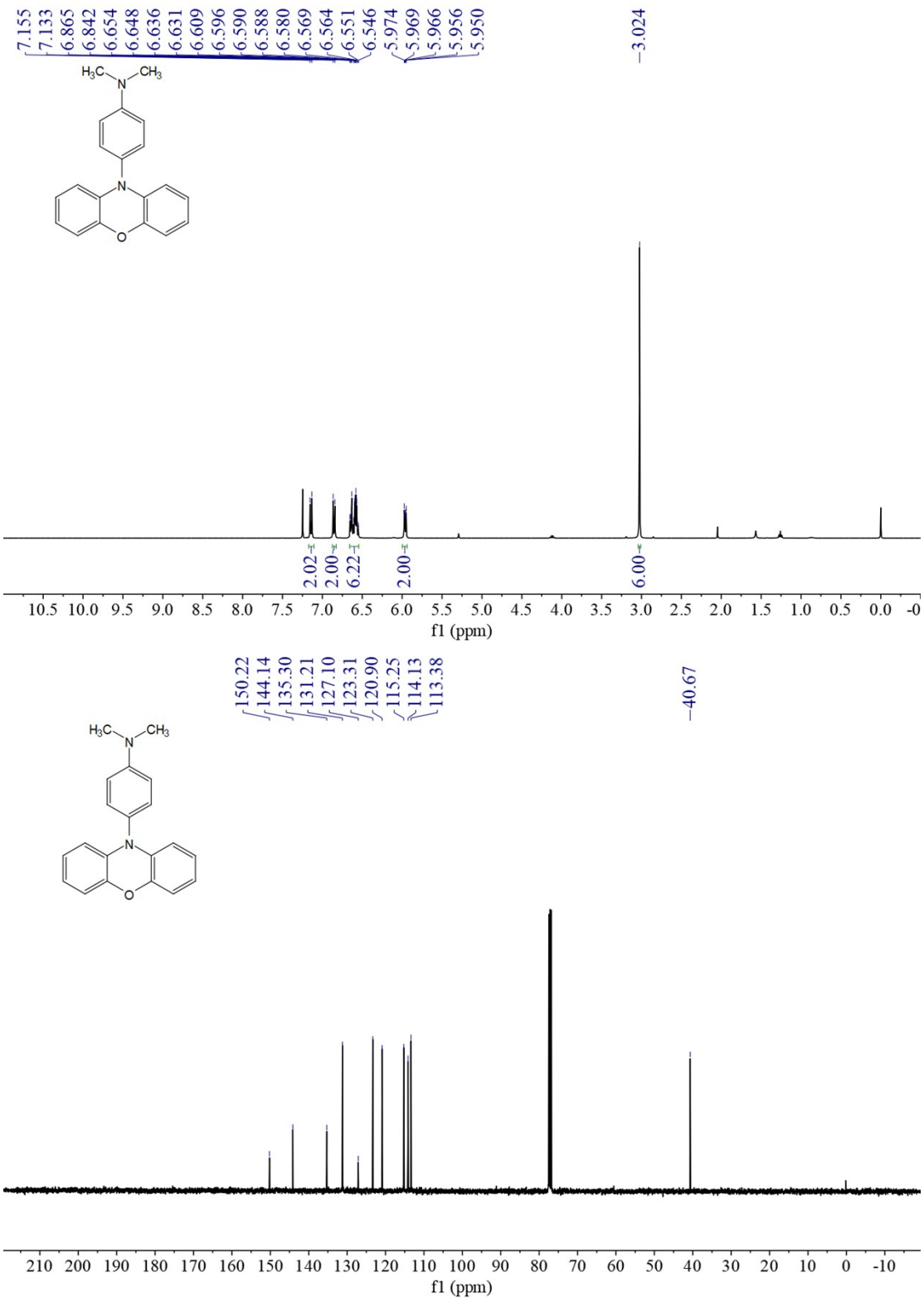
4-(2-chloro-10H-phenothiazin-10-yl)-*N*,*N*-di-p-tolylaniline(5d): white solid was obtained in 30% isolated yield. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.18 – 7.09 (m, 12H), 6.98-6.95 (m, 1H), 6.92 – 6.86 (m, 2H), 6.83 – 6.74 (m, 2H), 6.30-6.28 (m, 2H), 2.34 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.50, 145.92, 144.78, 144.19, 133.72, 132.74, 132.16, 131.38, 130.30, 127.31, 127.15, 126.74, 125.65, 122.81, 122.49, 122.08, 119.51, 118.30, 116.16, 115.84, 21.05. HRMS (ESI) calculated for $C_{32}H_{26}N_2ClS^+$[M+H]$^+$: 505.1500; found: 505.1496.

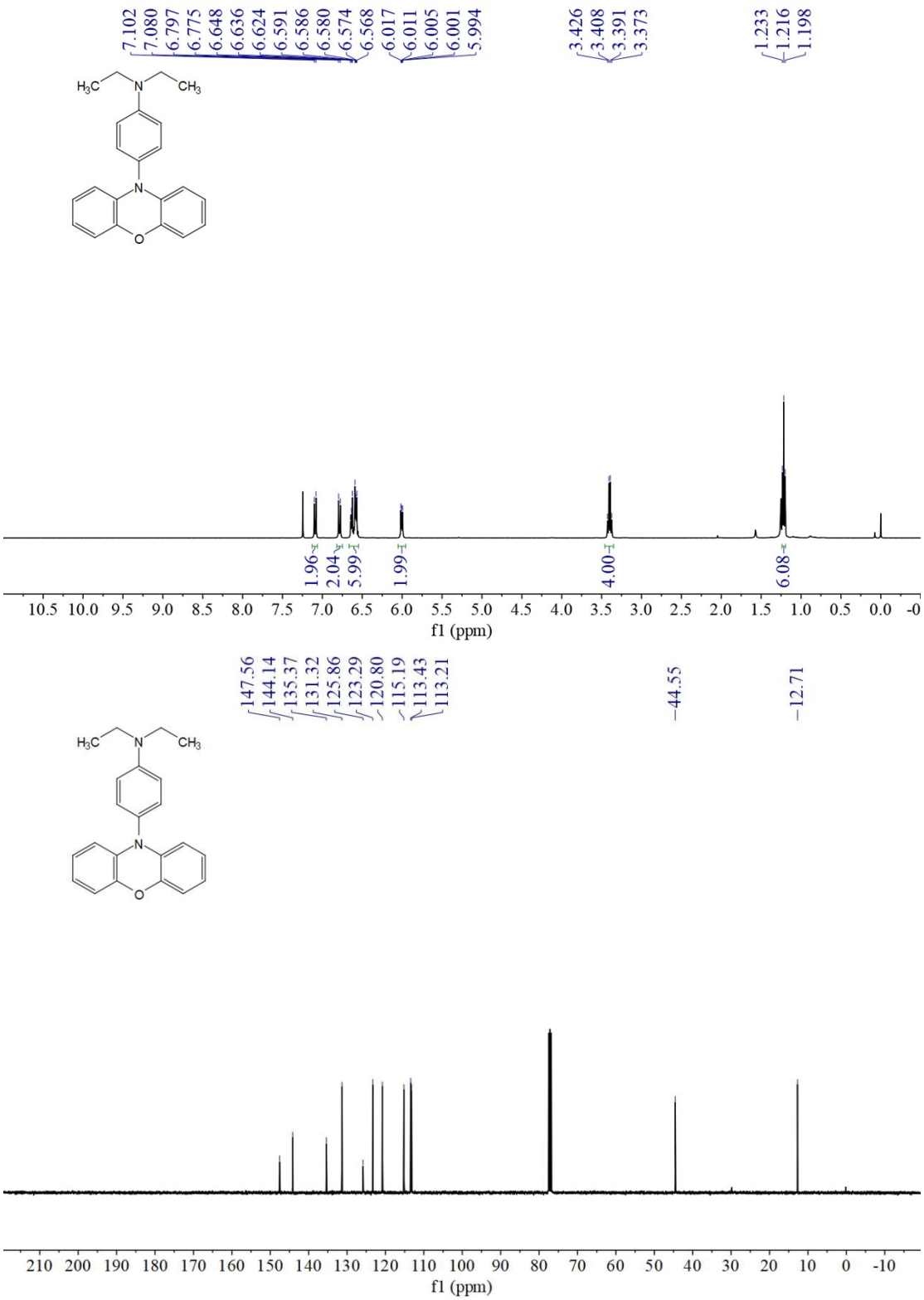


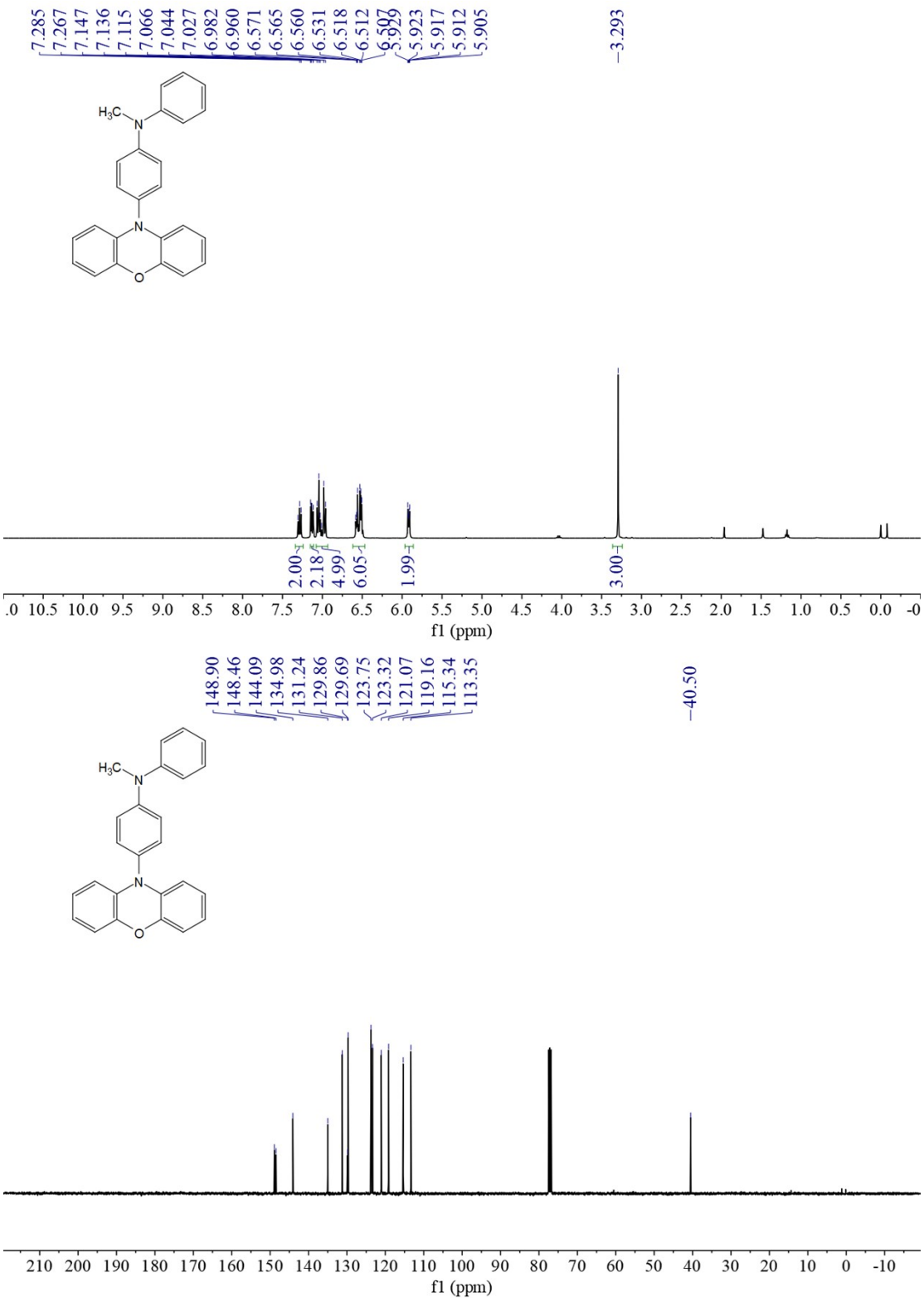
4-methyl-N-(p-tolyl)-N-(4-(2-(trifluoromethyl)-10H-phenothiazin-10-yl)phenyl)aniline(5e): white solid was obtained in 20% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.24 – 7.20 (m, 3H), 7.17-7.12 (m, 5H), 7.07-7.01 (m, 7H), 6.98 – 6.94 (m, 1H), 6.89-6.84 (m, 1H), 6.32 (d, J = 2.1 Hz, 1H), 6.24 (dd, J = 8.3, 1.3 Hz, 1H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 148.14, 144.59, 144.19, 143.10, 133.52, 131.36, 131.28, 130.40, 128.02(q, J_{C-F} = 39.0 Hz), 126.74, 125.41, 124.51, 123.33, 122.01, 119.01(q, J_{C-F} = 4.0 Hz), 117.67, 116.14, 110.88 (q, J_{C-F} = 4.0 Hz), 20.54. ^{19}F NMR (377 MHz, DMSO) δ -61.76. HRMS (ESI) calculated for $C_{32}H_{26}N_2F_3S^+$[M+H]$^+$: 539.1763; found: 539.1756.

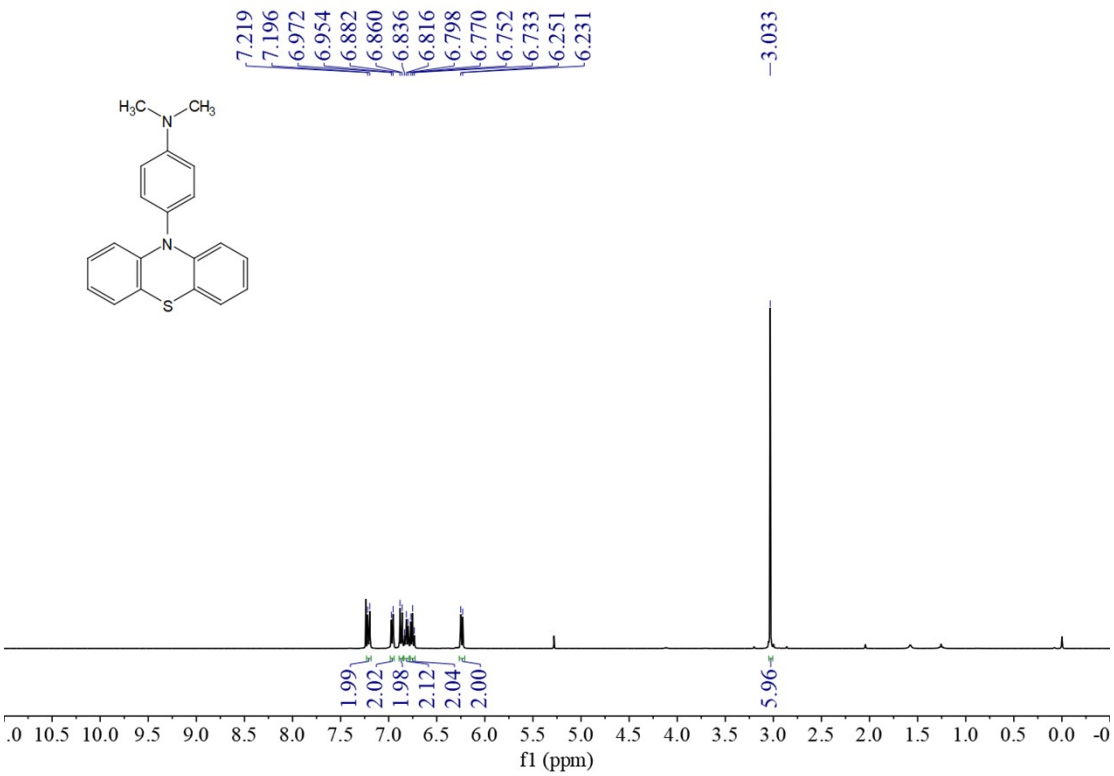


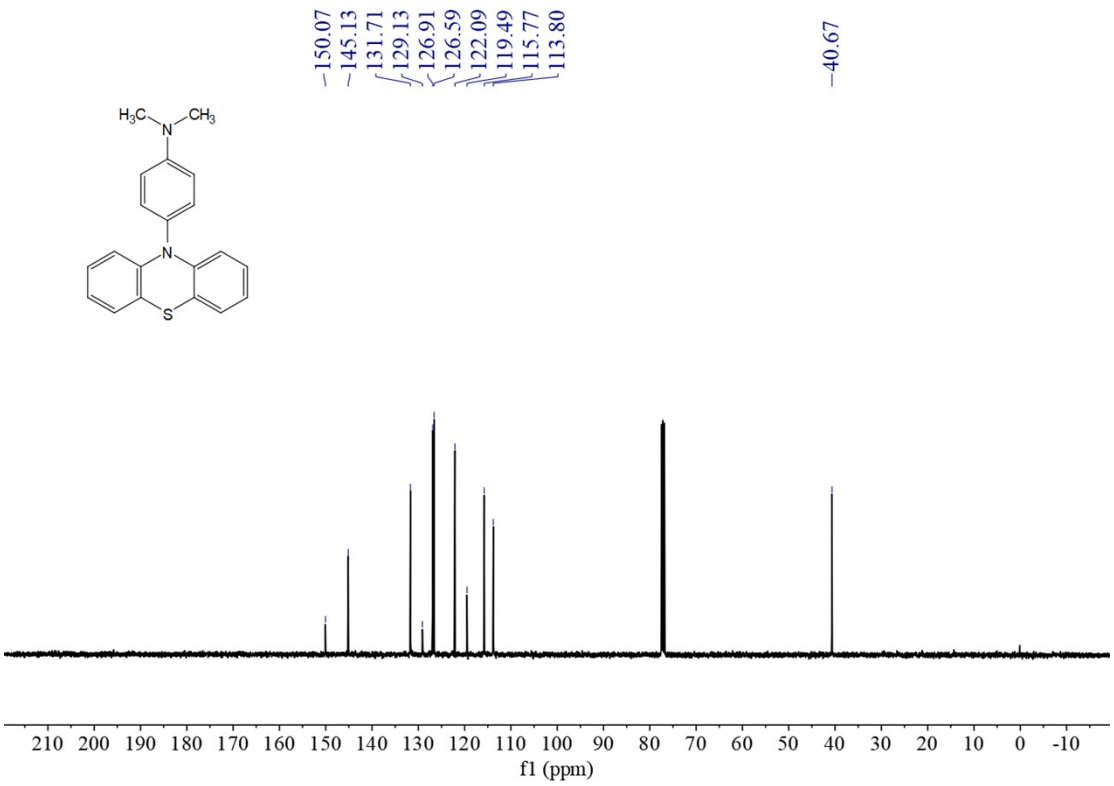
1-(10-(4-(di-p-tolylamino)phenyl)-10H-phenothiazin-2-yl)ethan-1-one(5f): yellow solid was obtained in 45% isolated yield. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (dd, J = 8.0, 1.7 Hz, 1H), 7.21 – 7.11 (m, 7H), 7.08 – 6.99 (m, 7H), 6.96 – 6.91 (m, 1H), 6.85-6.80 (m, 1H), 6.67 (d, J = 1.6 Hz, 1H), 6.22 (dd, J = 8.2, 0.9 Hz, 1H), 2.36 (s, 3H), 2.27 (s, 6H). ^{13}C NMR (101 MHz, DMSO) δ 196.67, 147.92, 144.30, 143.99, 143.25, 135.75, 133.33, 131.98, 131.33, 130.36, 127.79, 126.62, 126.49, 125.75, 125.24, 123.30, 122.87, 122.33, 117.58, 115.96, 113.52, 26.39, 20.54. HRMS (ESI) calculated for $C_{34}H_{29}ON_2S^+$[M+H]$^+$: 513.1995; found: 539.1994.

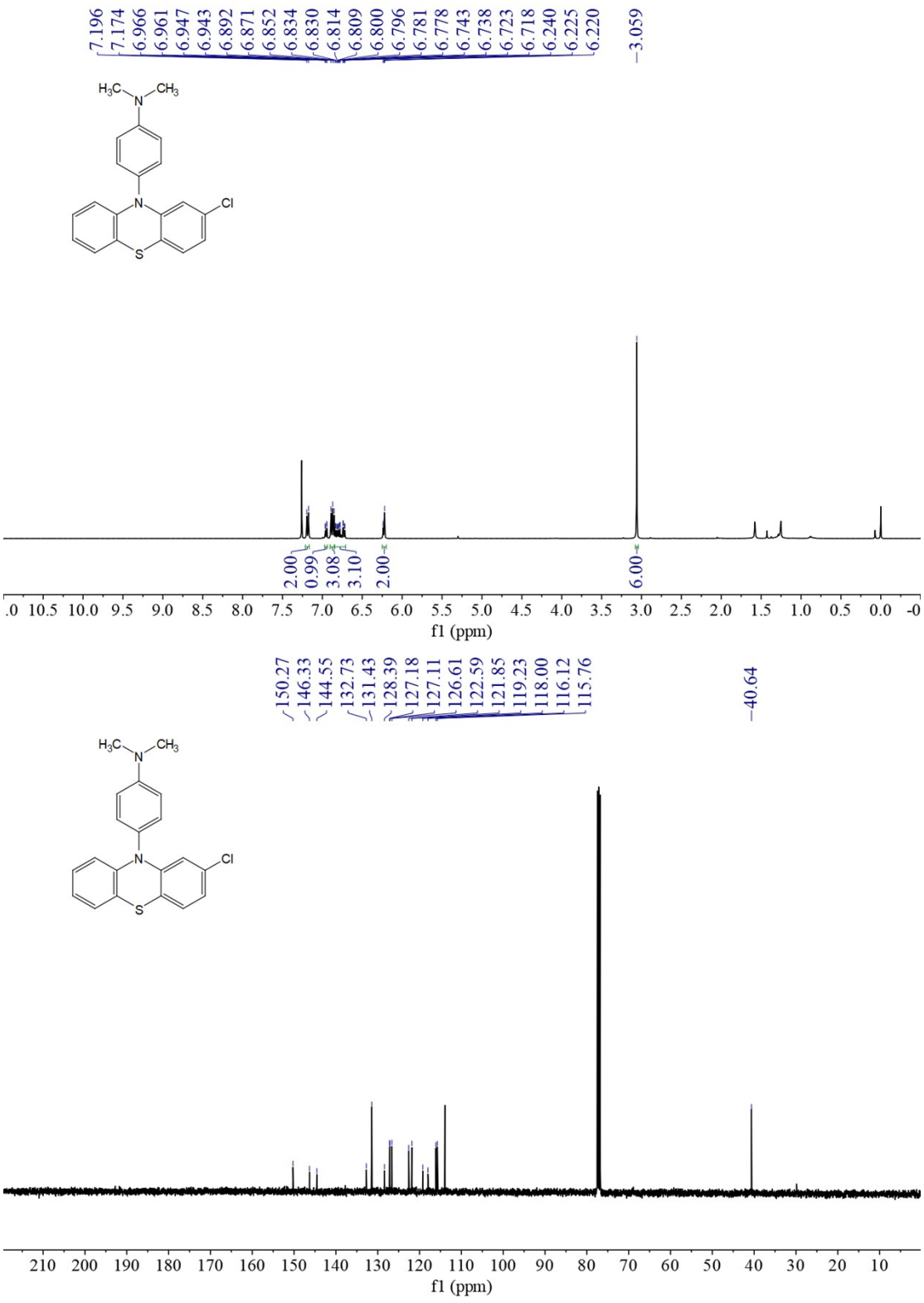

7.155
7.133
6.865
6.842
6.654
6.648
6.636
6.631
6.609
6.596
6.590
6.588
6.580
6.569
6.564
6.551
6.546
5.974
5.969
5.966
5.956
5.950
3.024
H3C
N
CH3
O
2.02
2.00
6.22
2.00
6.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
150.22
144.14
135.30
131.21
127.10
123.31
120.90
115.25
114.13
113.38
40.67
H3C
N
CH3
O
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)

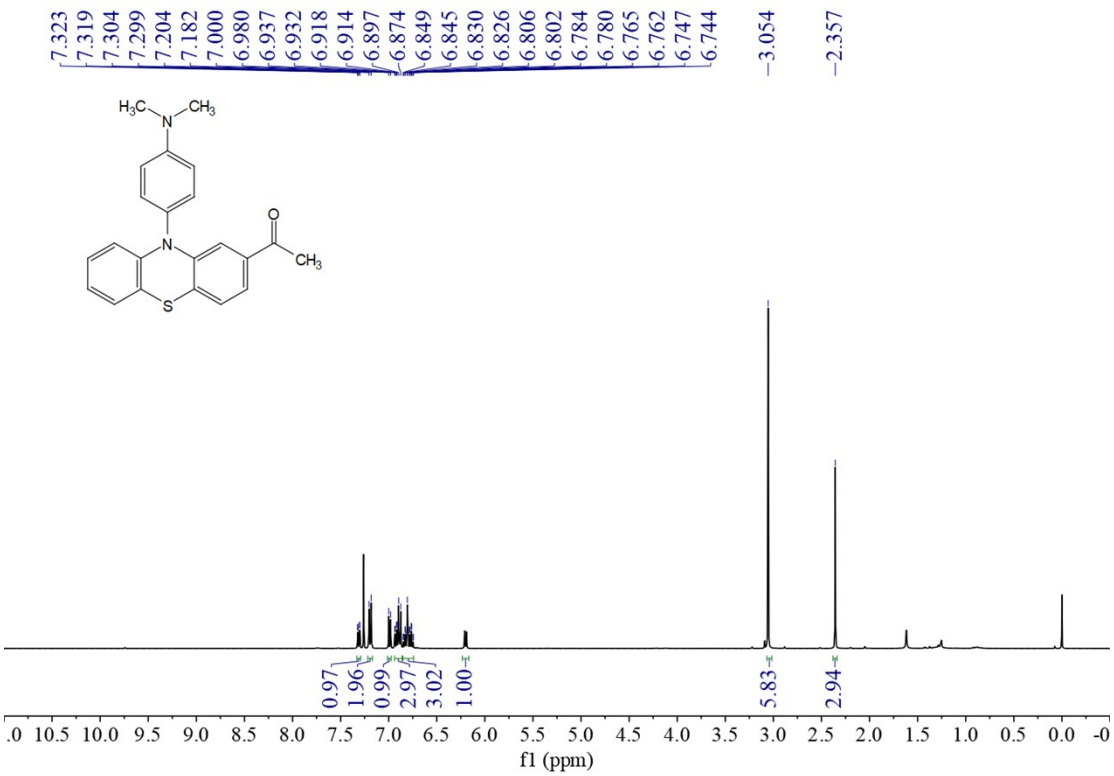

7.102
7.080
6.797
6.775
6.648
6.636
6.624
6.591
6.586
6.580
6.574
6.568
6.017
6.011
6.005
6.001
5.994
3.426
3.408
3.391
3.373
1.233
1.216
1.198
H3C
N
CH3
1.96
2.04
5.99
1.99
4.00
6.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)
147.56
144.14
135.37
131.32
125.86
123.29
120.80
115.19
113.43
113.21
44.55
12.71
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)

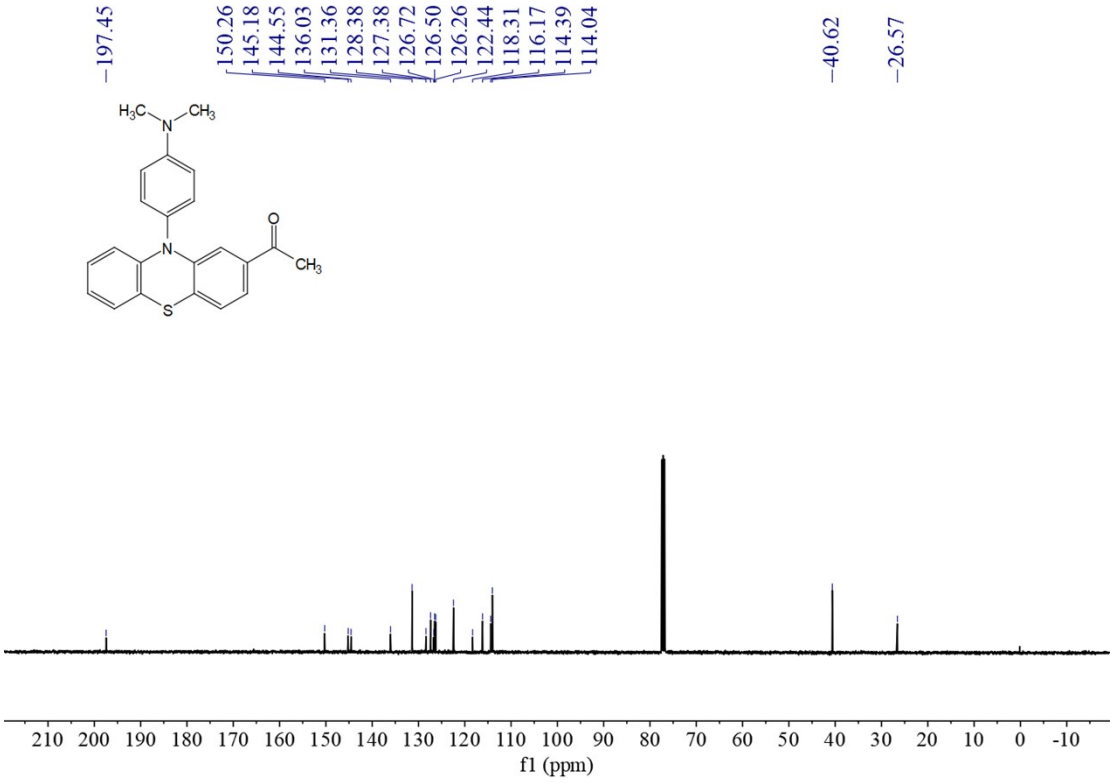

7.285
7.267
7.147
7.136
7.115
7.066
7.044
7.027
6.982
6.960
6.571
6.565
6.560
6.531
6.518
6.512
5.923
5.917
5.912
5.905
3.293
H3C
N
O
2.00
2.18
4.99
6.05
1.99
3.00
f1 (ppm)
148.90
148.46
144.09
134.98
131.24
129.86
129.69
123.75
123.32
121.07
119.16
115.34
113.35
40.50
f1 (ppm)

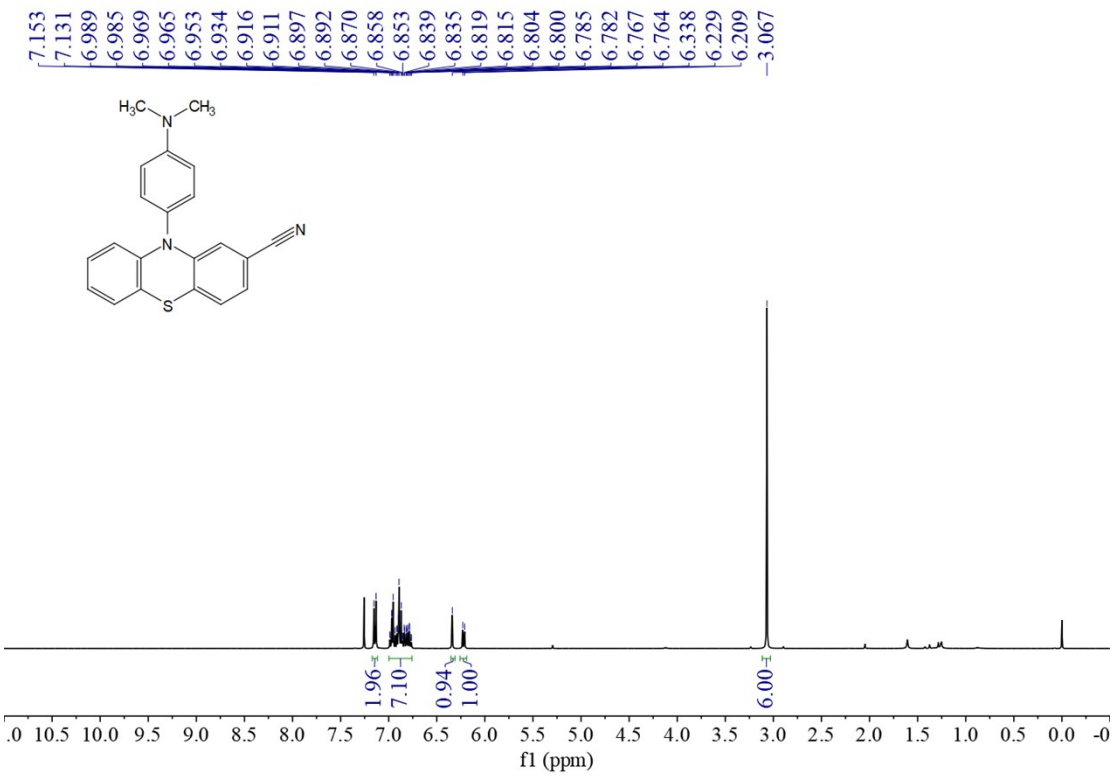

7.219
7.196
6.972
6.954
6.882
6.860
6.836
6.816
6.798
6.770
6.752
6.733
6.251
6.231
3.033
1.99
2.02
1.98
2.12
2.04
2.00
5.96
f1 (ppm)

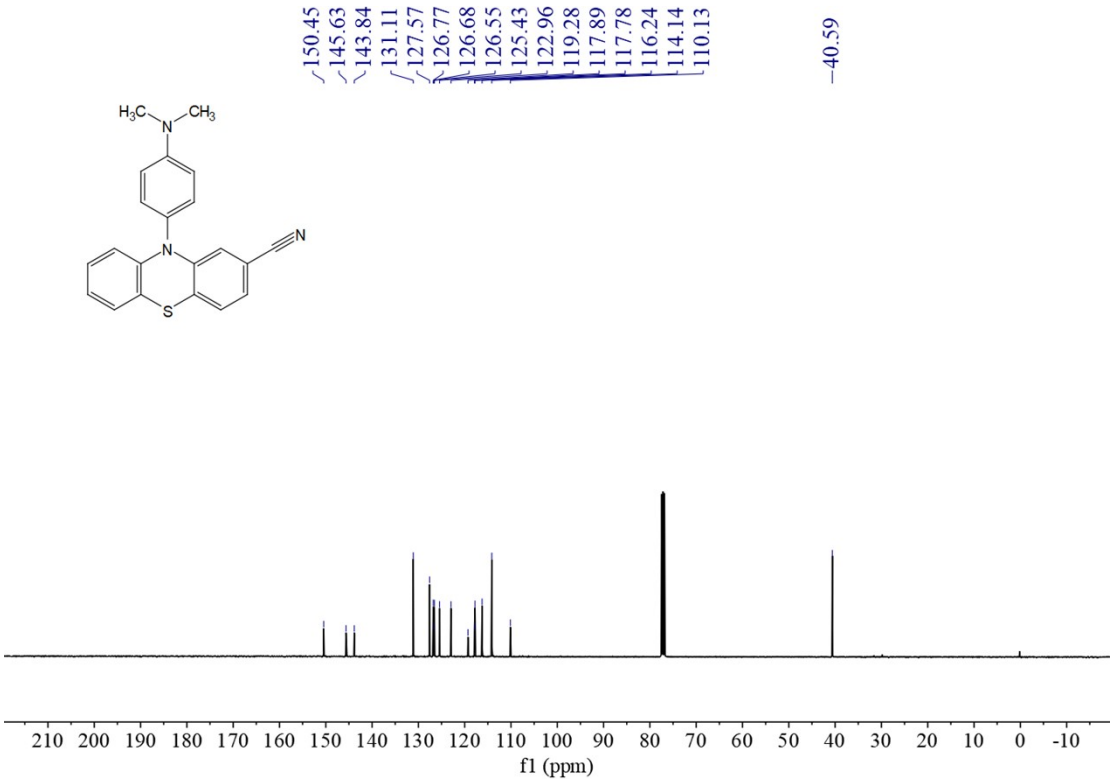

150.07
145.13
131.71
129.13
126.91
126.59
122.09
119.49
115.77
113.80
40.67
f1 (ppm)

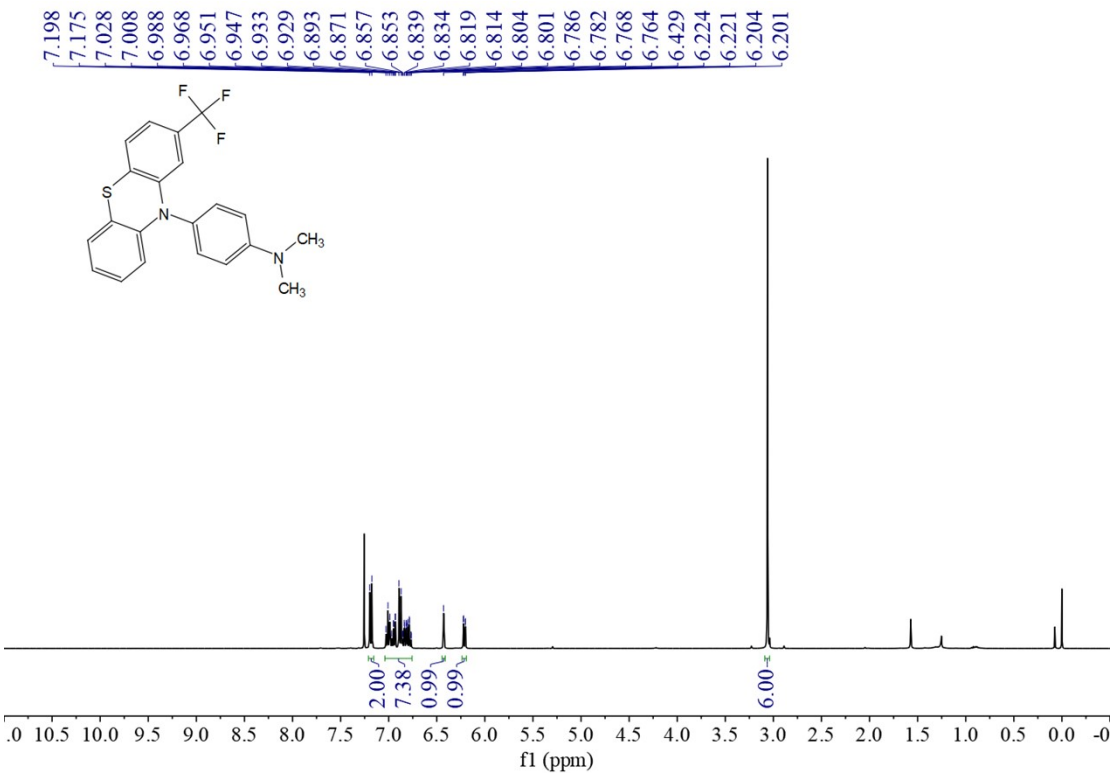

7.196
7.174
6.966
6.961
6.947
6.943
6.892
6.871
6.852
6.834
6.830
6.814
6.809
6.800
6.796
6.781
6.778
6.743
6.738
6.723
6.718
6.240
6.225
6.220
3.059
H3C
N
CH3
N
Cl
S
2.00
0.99
3.08
3.10
2.00
6.00
f1 (ppm)
150.27
146.33
144.55
132.73
131.43
128.39
127.18
127.11
126.61
122.59
121.85
119.23
118.00
116.12
115.76
40.64
f1 (ppm)

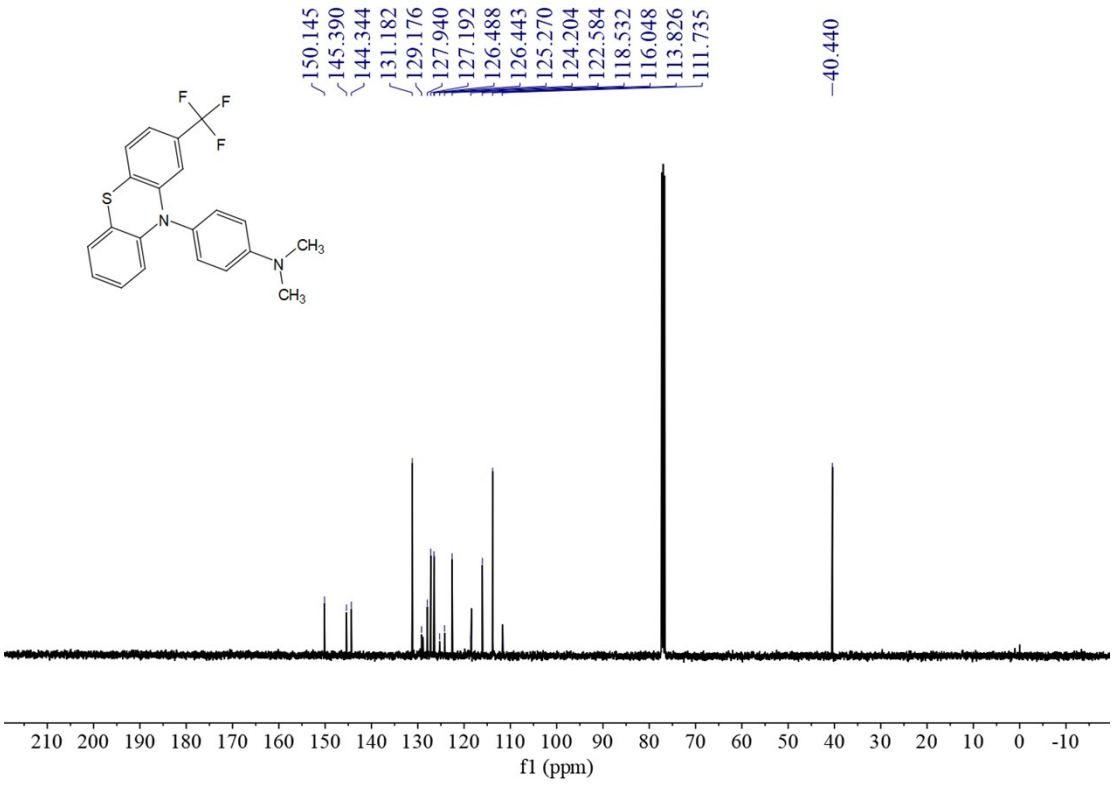

7.323
7.319
7.304
7.299
7.204
7.182
7.000
6.980
6.937
6.932
6.918
6.914
6.897
6.874
6.849
6.845
6.830
6.826
6.806
6.802
6.784
6.780
6.765
6.762
6.747
6.744
3.054
2.357
0.97
1.96
0.99
2.97
3.02
1.00
5.83
2.94
f1 (ppm)

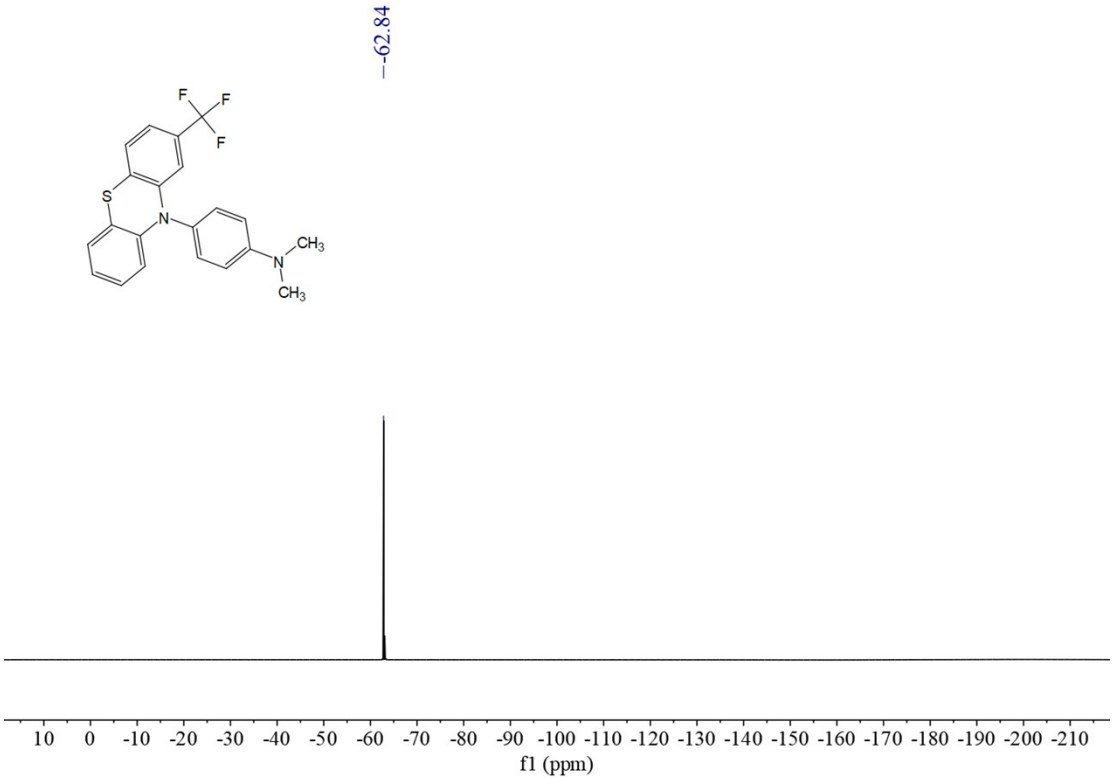

197.45
150.26
145.18
144.55
136.03
131.36
128.38
127.38
126.72
126.50
126.26
122.44
118.31
116.17
114.39
114.04
40.62
26.57
f1 (ppm)

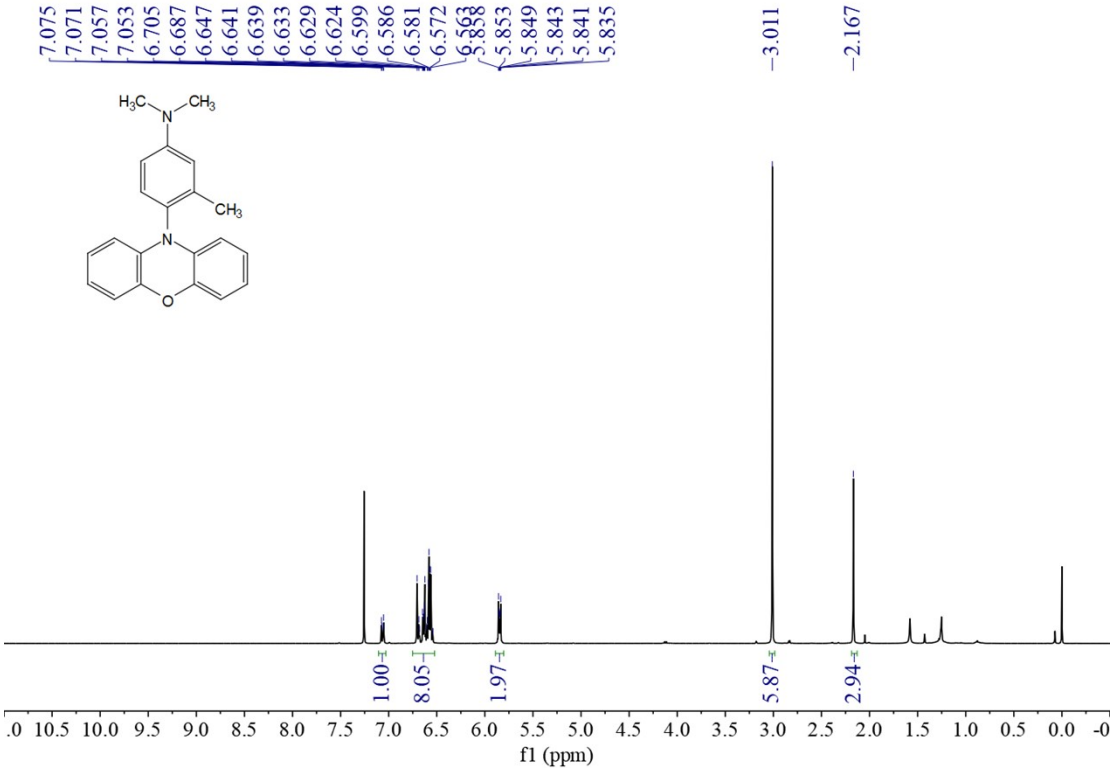

7.153
7.131
6.989
6.985
6.969
6.965
6.953
6.934
6.916
6.911
6.897
6.892
6.870
6.858
6.853
6.839
6.835
6.819
6.815
6.804
6.800
6.785
6.782
6.767
6.764
6.338
6.229
6.209
3.067
H3C
N
CH3
N
S
N
1.96
7.10
0.94
1.00
6.00
f1 (ppm)

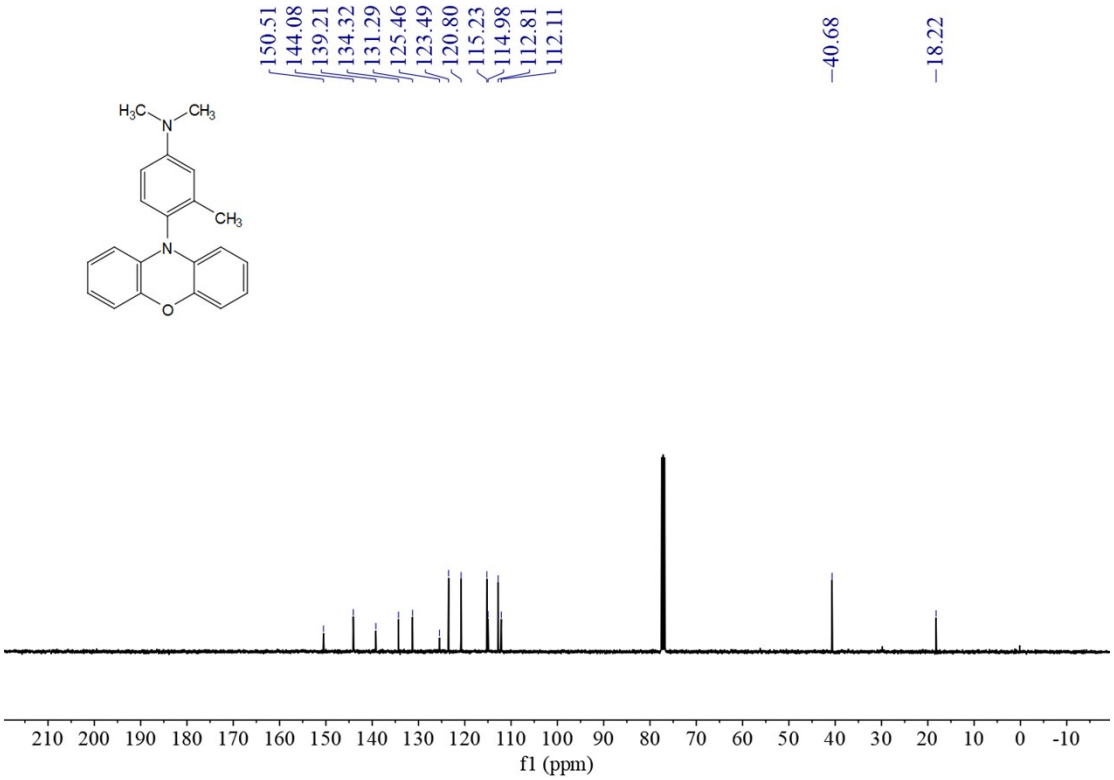

150.45
145.63
143.84
131.11
127.57
126.77
126.68
126.55
125.43
122.96
119.28
117.89
117.78
116.24
114.14
110.13
40.59
H3C
N
CH3
N
S
N
f1 (ppm)

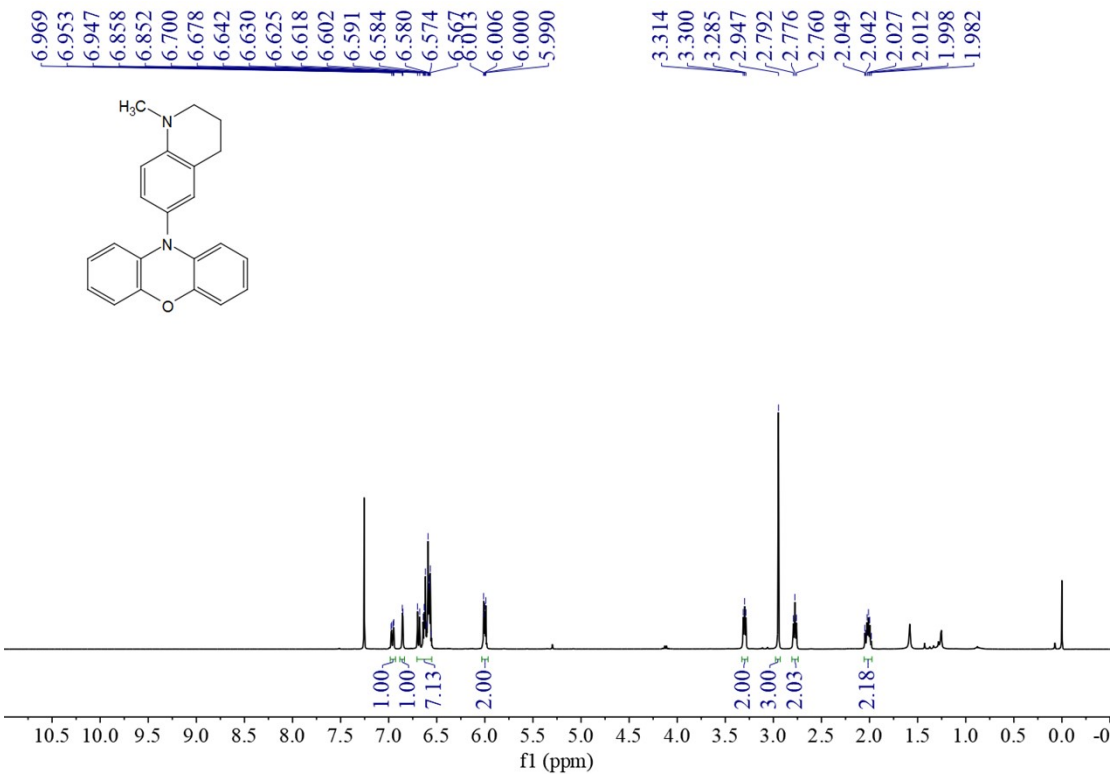

7.198
7.175
7.028
7.008
6.988
6.968
6.951
6.947
6.933
6.929
6.893
6.871
6.857
6.853
6.839
6.834
6.819
6.814
6.804
6.801
6.786
6.782
6.768
6.764
6.429
6.224
6.221
6.204
6.201
F
F
F
S
N
CH3
N
CH3
2.00
7.38
0.99
0.99
6.00
f1 (ppm)

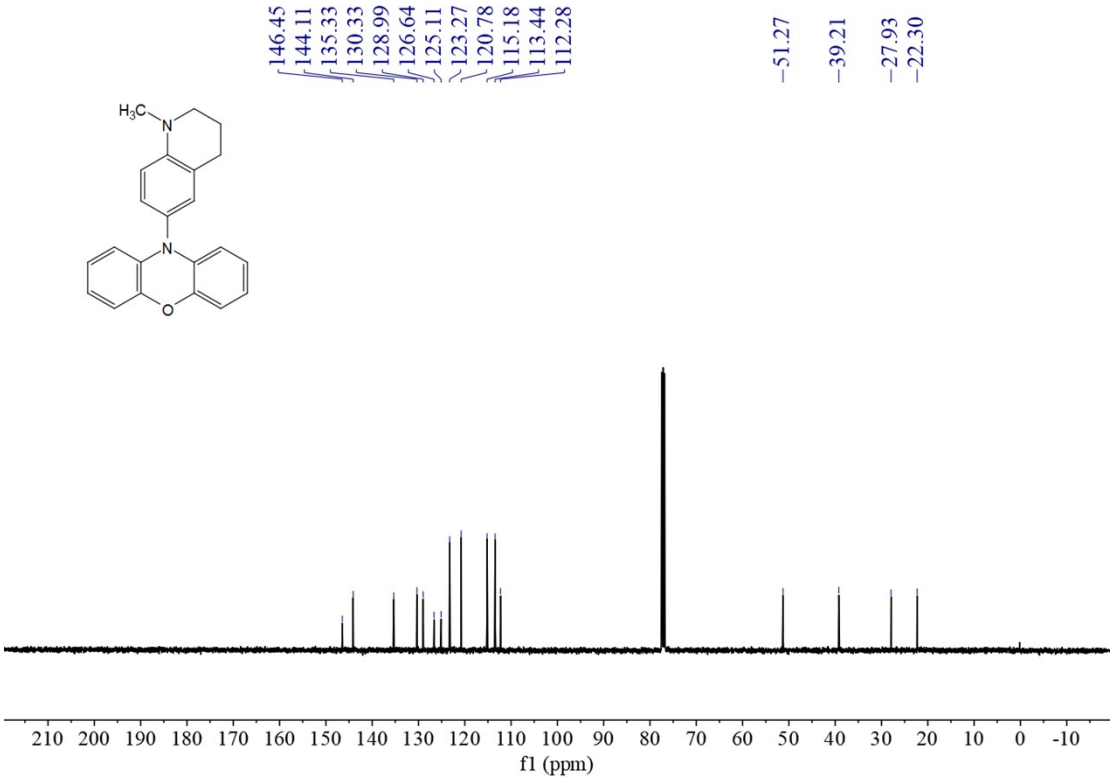

150.145
145.390
144.344
131.182
129.176
127.940
127.192
126.488
126.443
125.270
124.204
122.584
118.532
116.048
113.826
111.735
40.440
F
F
F
S
N
CH3
N
CH3
f1 (ppm)

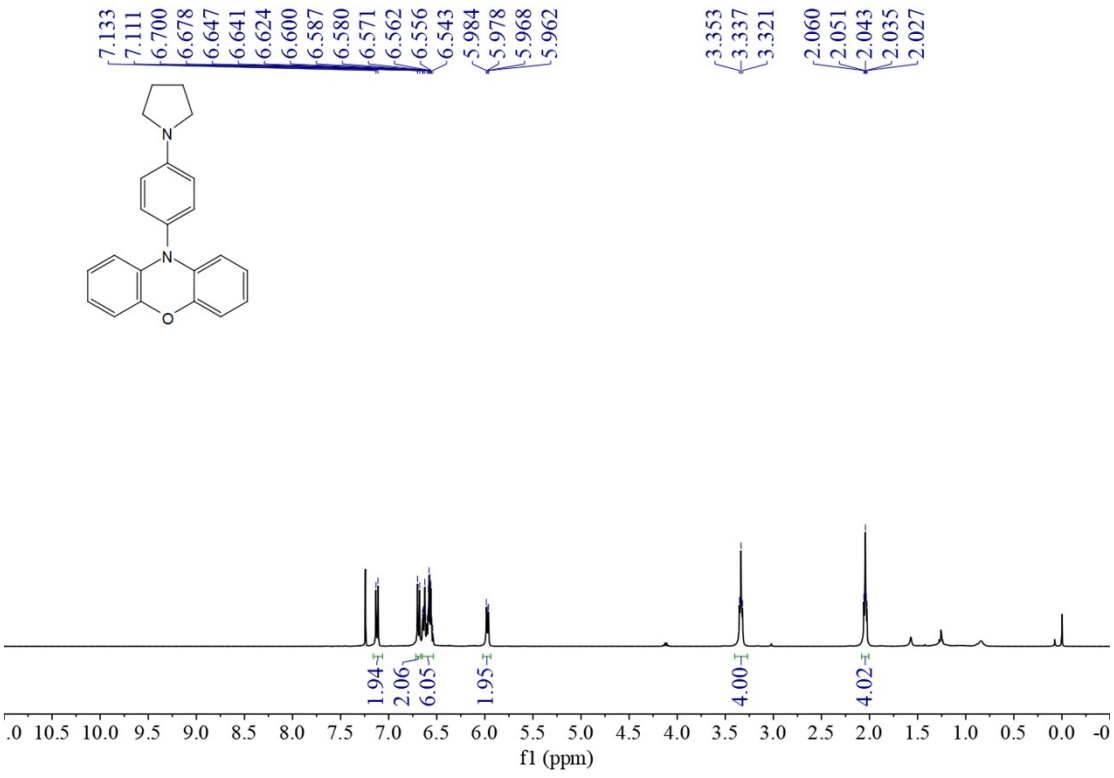

-62.84
F
F
F
S
N
N
CH3
CH3
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

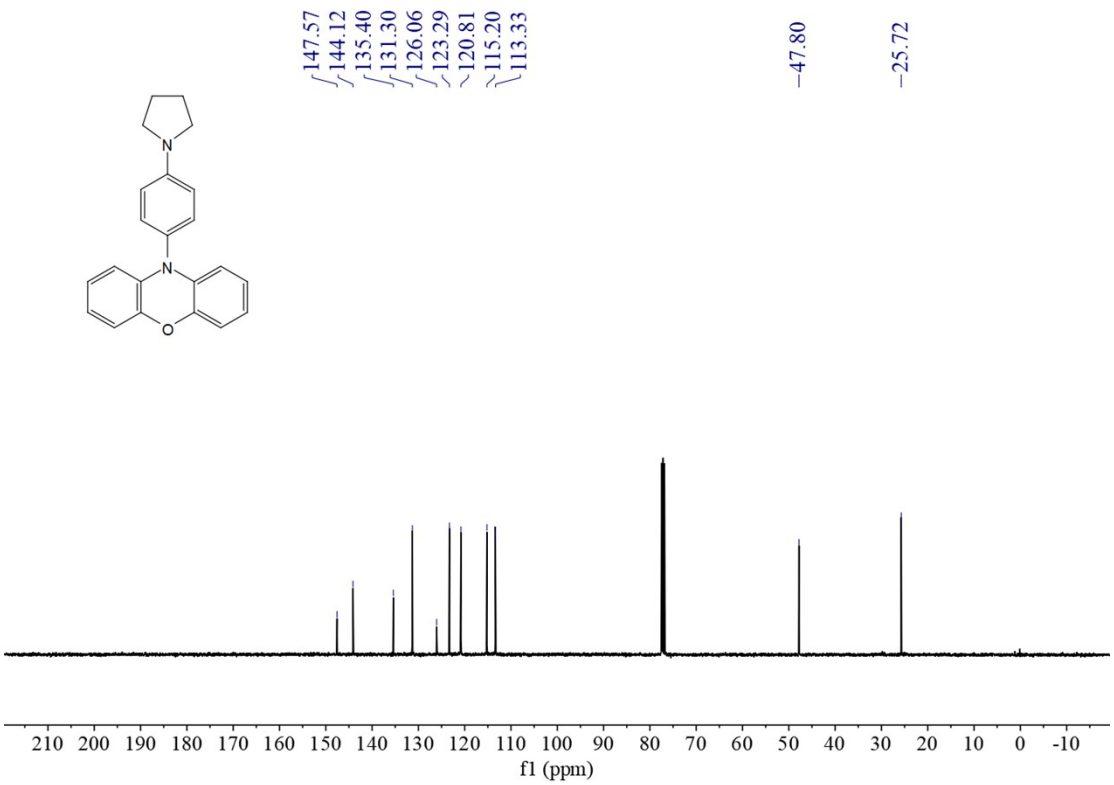

7.075
7.071
7.057
7.053
6.705
6.687
6.647
6.641
6.639
6.633
6.629
6.624
6.599
6.586
6.581
6.572
6.563
5.858
5.853
5.849
5.843
5.841
5.835
3.011
2.167
H3C
N
CH3
CH3
N
O
1.00
8.05
1.97
5.87
2.94
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

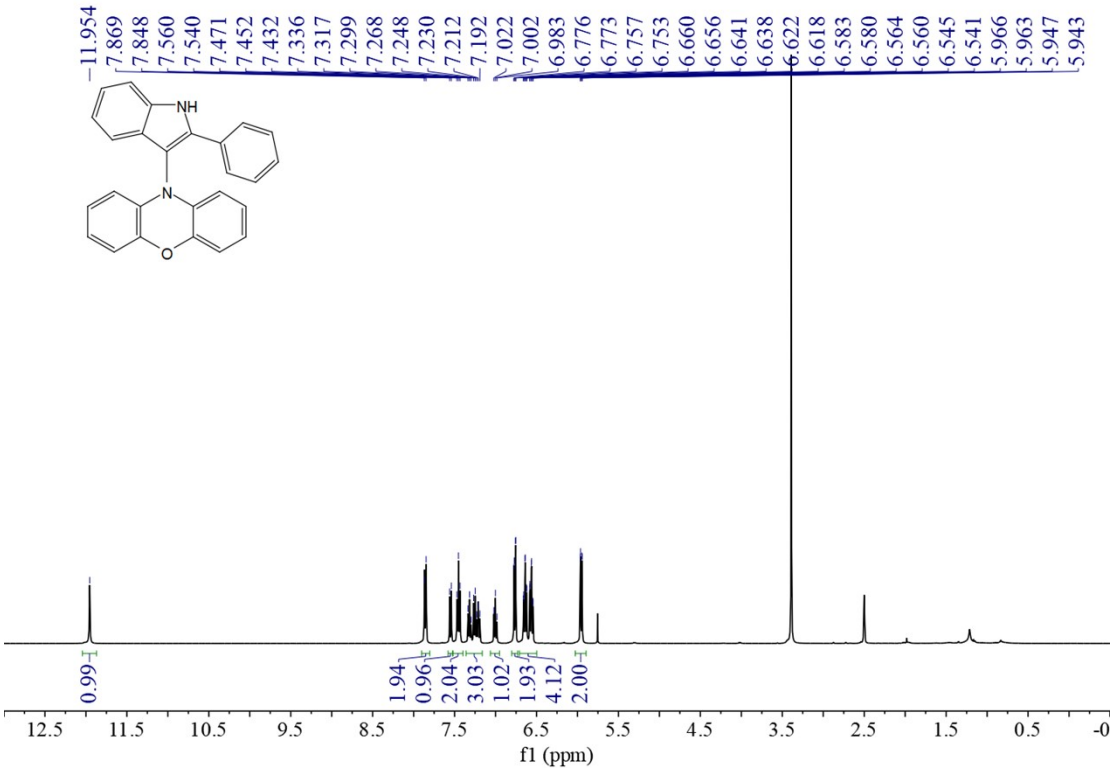

150.51
144.08
139.21
134.32
131.29
125.46
123.49
120.80
115.23
114.98
112.81
112.11
40.68
18.22
H3C
N
CH3
CH3
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

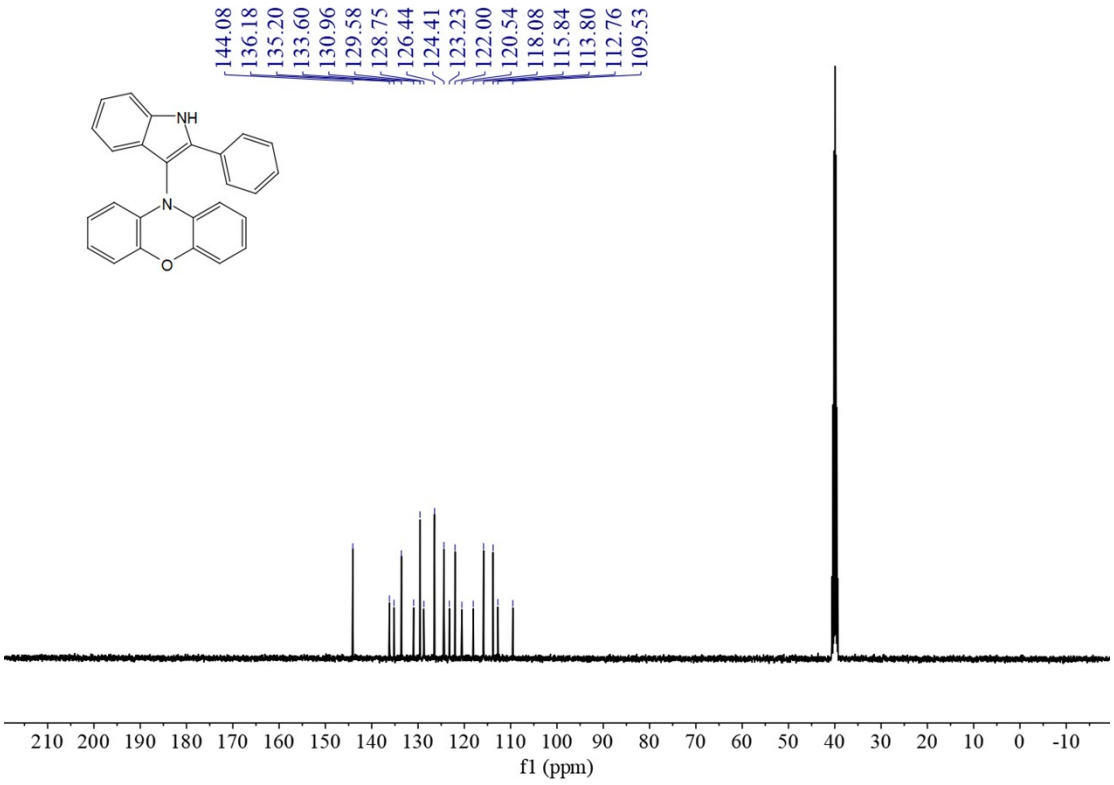

6.969
6.953
6.947
6.858
6.852
6.700
6.678
6.642
6.630
6.625
6.618
6.602
6.591
6.584
6.580
6.574
6.567
6.013
6.006
6.000
5.990
3.314
3.300
3.285
2.947
2.792
2.776
2.760
2.049
2.042
2.027
2.012
1.998
1.982
H3C
N
N
O
1.00
1.00
7.13
2.00
2.00
3.00
2.03
2.18
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

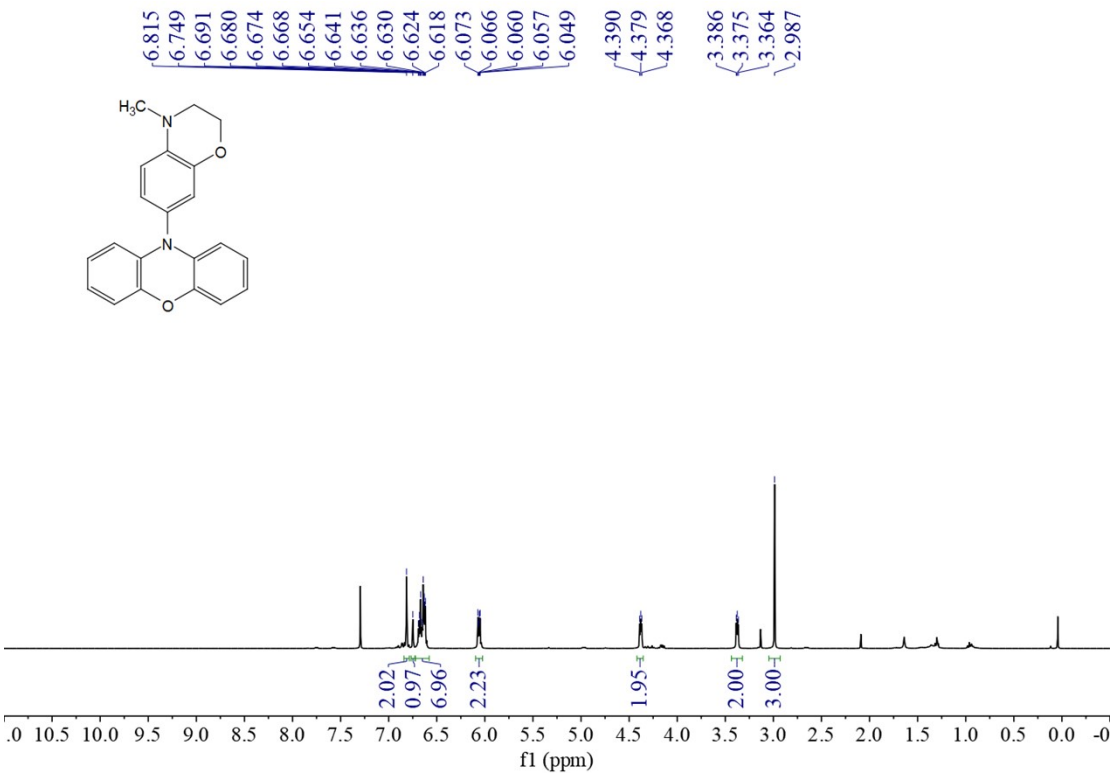

146.45
144.11
135.33
130.33
128.99
126.64
125.11
123.27
120.78
115.18
113.44
112.28
51.27
39.21
27.93
22.30
H3C
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

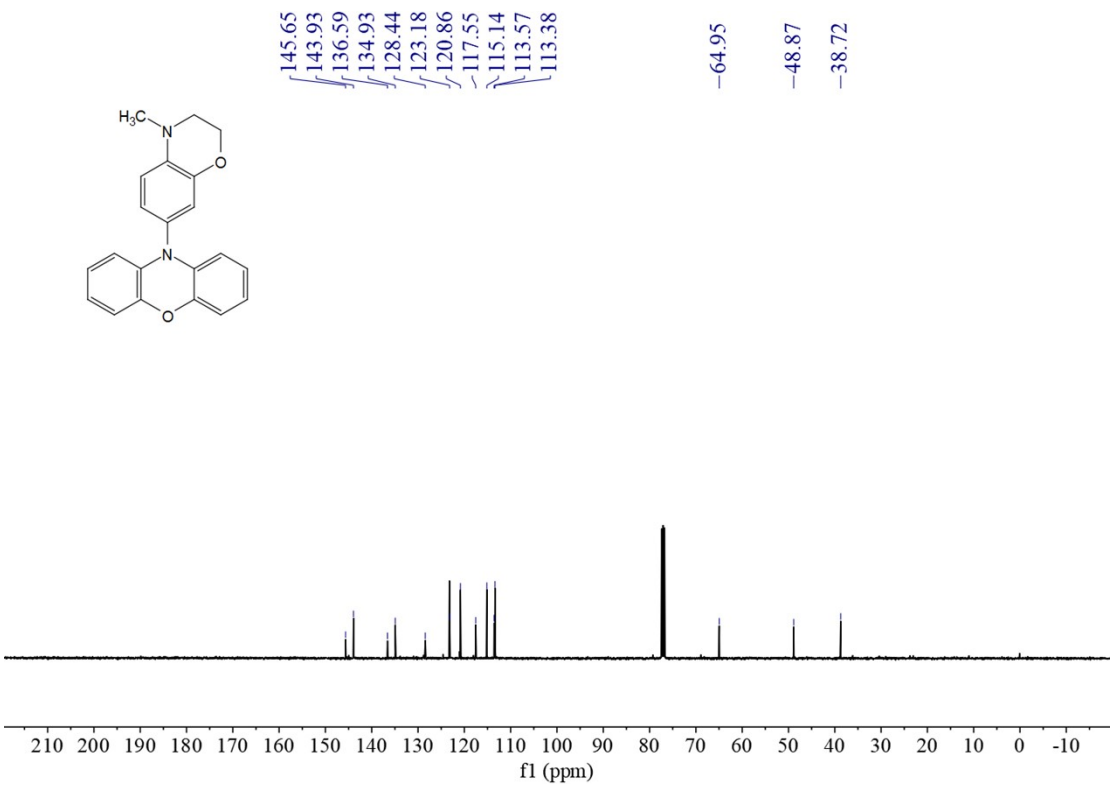

7.133
7.111
6.700
6.678
6.647
6.641
6.624
6.600
6.587
6.580
6.571
6.562
6.556
6.543
5.984
5.978
5.968
5.962
3.353
3.337
3.321
2.060
2.051
2.043
2.035
2.027
N
N
O
1.94
2.06
6.05
1.95
4.00
4.02
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

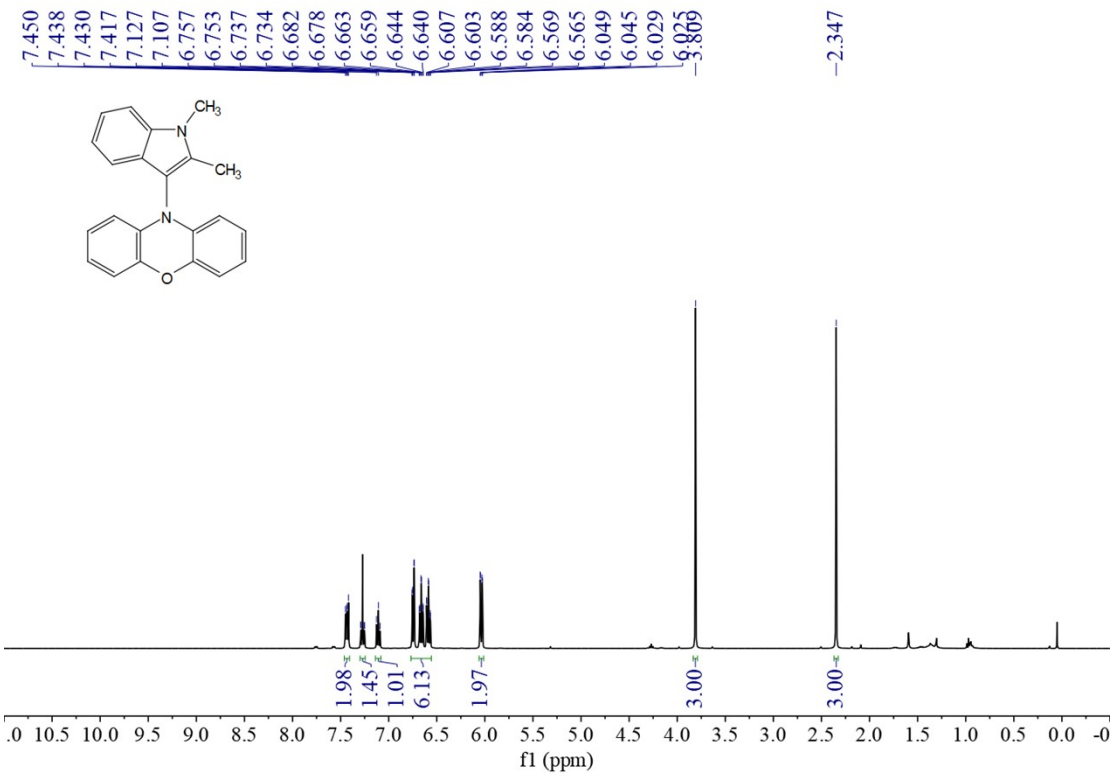

147.57
144.12
135.40
131.30
126.06
123.29
120.81
115.20
113.33
47.80
25.72
N
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

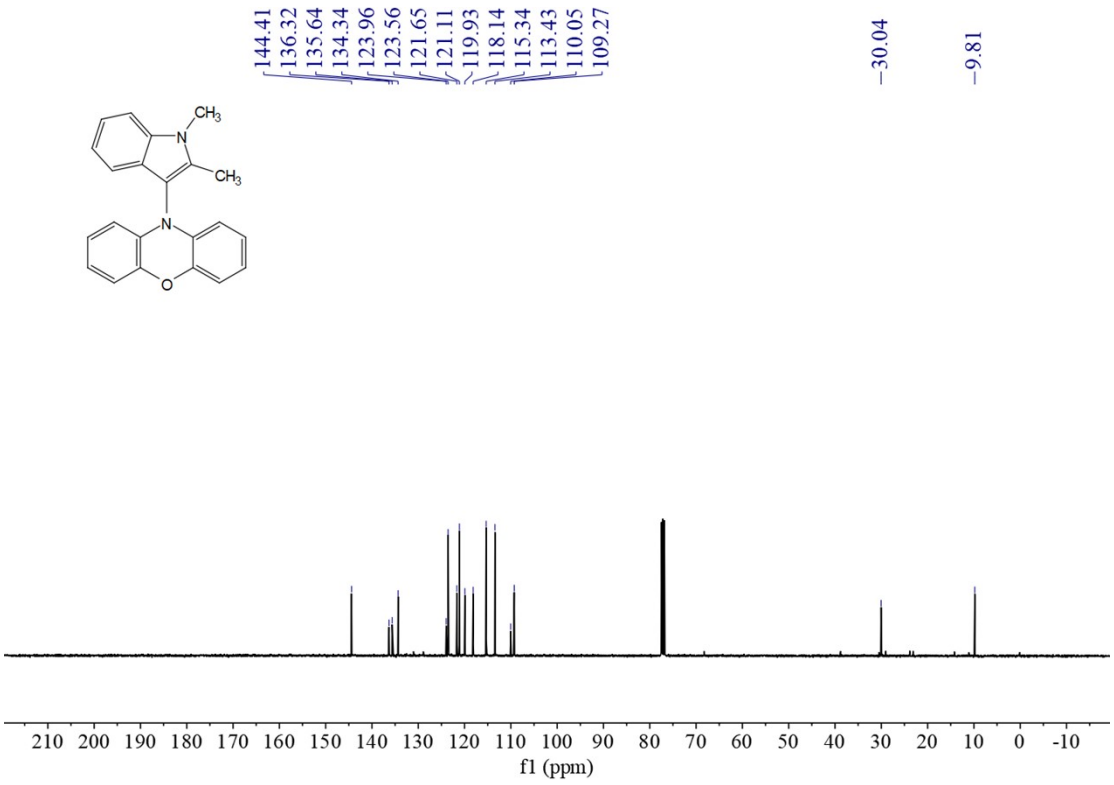

11.954
7.869
7.848
7.560
7.540
7.471
7.452
7.432
7.336
7.317
7.299
7.268
7.248
7.230
7.212
7.192
7.022
7.002
6.983
6.776
6.773
6.757
6.753
6.660
6.656
6.641
6.638
6.622
6.618
6.583
6.580
6.564
6.560
6.545
6.541
5.966
5.963
5.947
5.943
NH
N
O
0.99
1.94
0.96
2.04
3.03
1.02
1.93
4.12
2.00
12.5 11.5 10.5 9.5 8.5 7.5 6.5 5.5 4.5 3.5 2.5 1.5 0.5 -0
f1 (ppm)

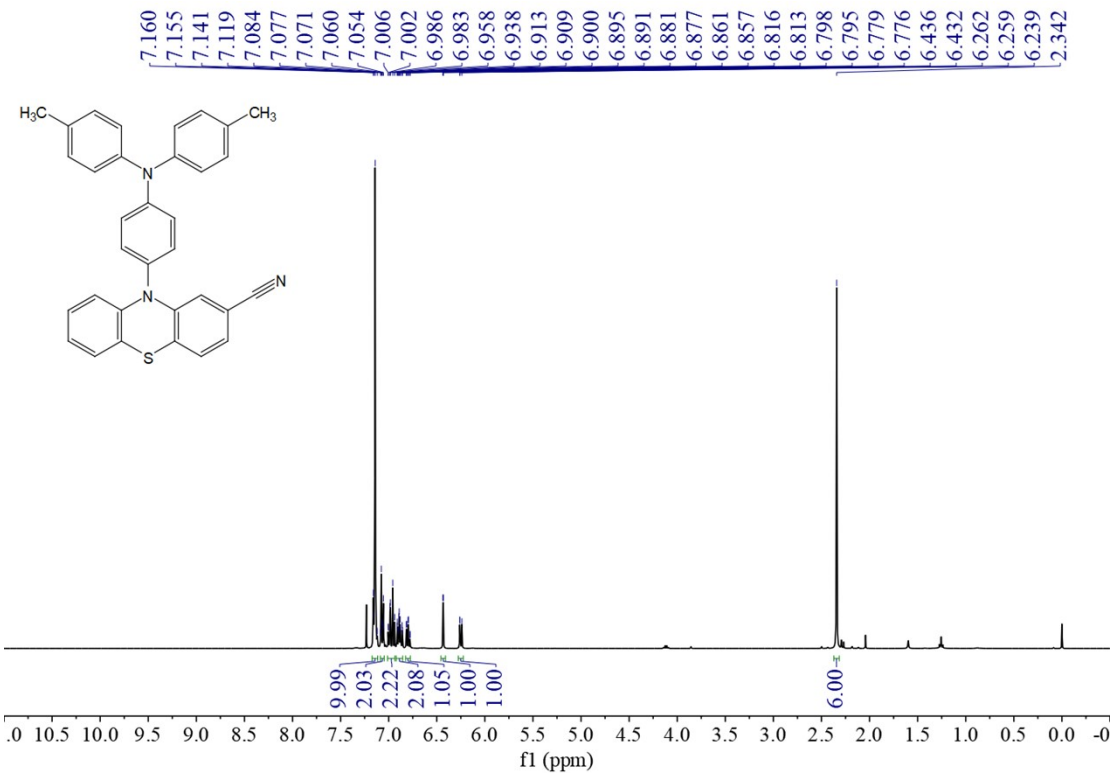

144.08
136.18
135.20
133.60
130.96
129.58
128.75
126.44
124.41
123.23
122.00
120.54
118.08
115.84
113.80
112.76
109.53
NH
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

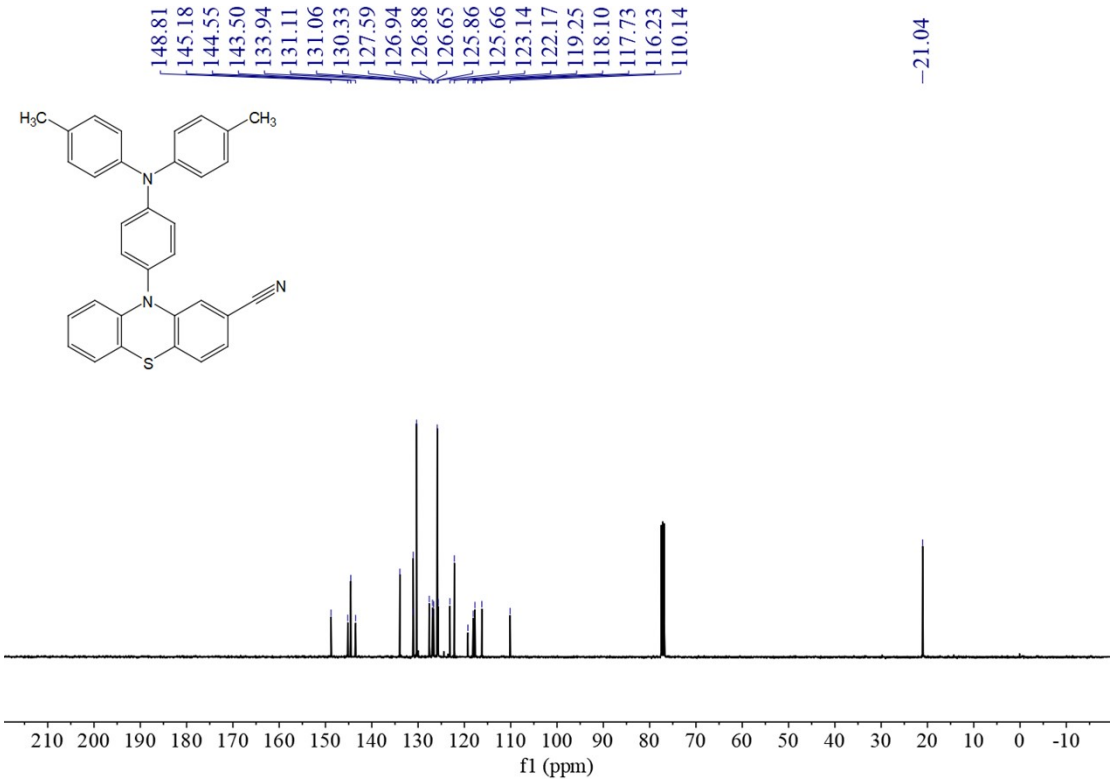

6.815
6.749
6.691
6.680
6.674
6.668
6.654
6.641
6.636
6.630
6.624
6.618
6.073
6.066
6.060
6.057
6.049
4.390
4.379
4.368
3.386
3.375
3.364
2.987
H3C
N
O
N
O
2.02
0.97
6.96
2.23
1.95
2.00
3.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

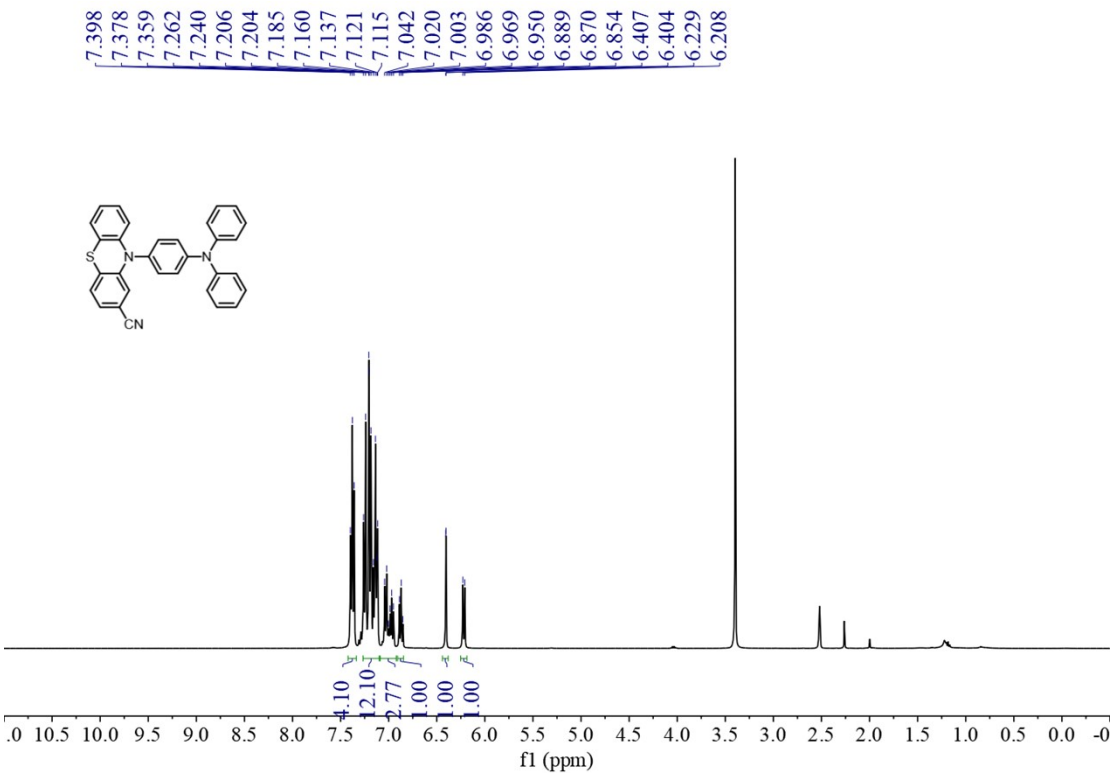

145.65
143.93
136.59
134.93
128.44
123.18
120.86
117.55
115.14
113.57
113.38
64.95
48.87
38.72
H3C
N
O
N
O
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

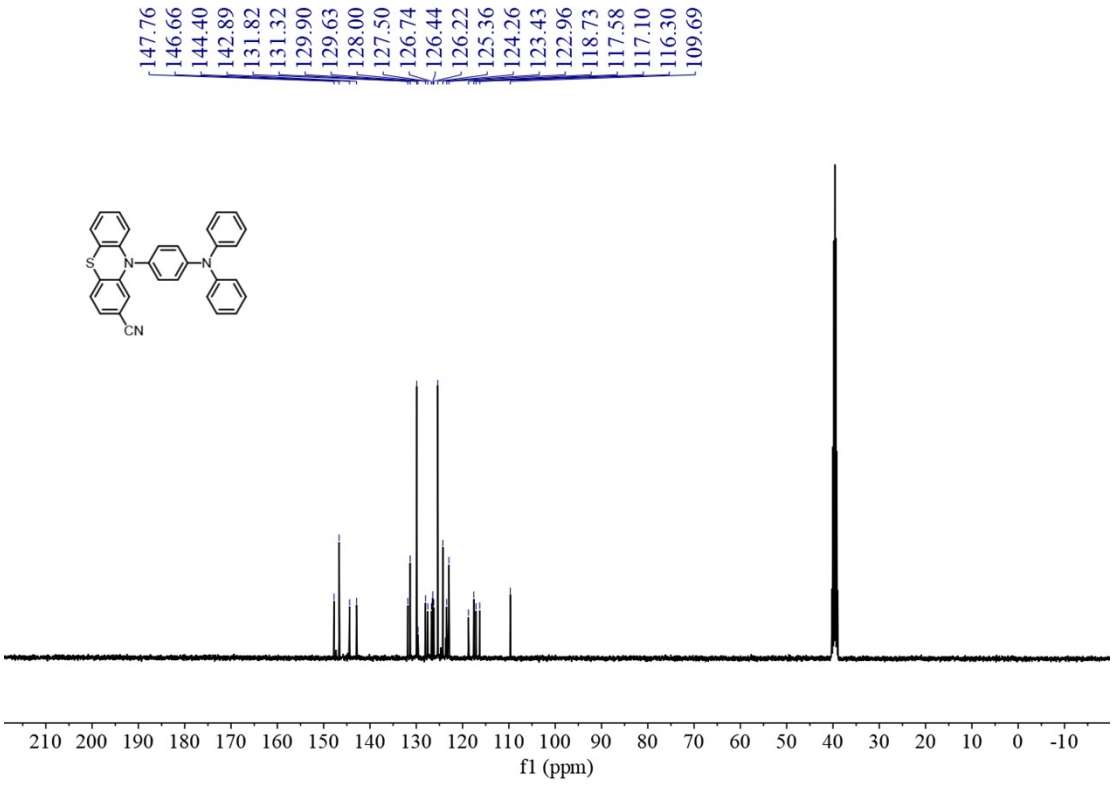

7.450
7.438
7.430
7.417
7.127
7.107
6.757
6.753
6.737
6.734
6.682
6.678
6.663
6.659
6.644
6.640
6.607
6.603
6.588
6.584
6.569
6.565
6.049
6.045
6.029
6.025
6.009
3.809
2.347
CH3
CH3
N
O
1.98
1.45
1.01
6.13
1.97
3.00
3.00
f1 (ppm)

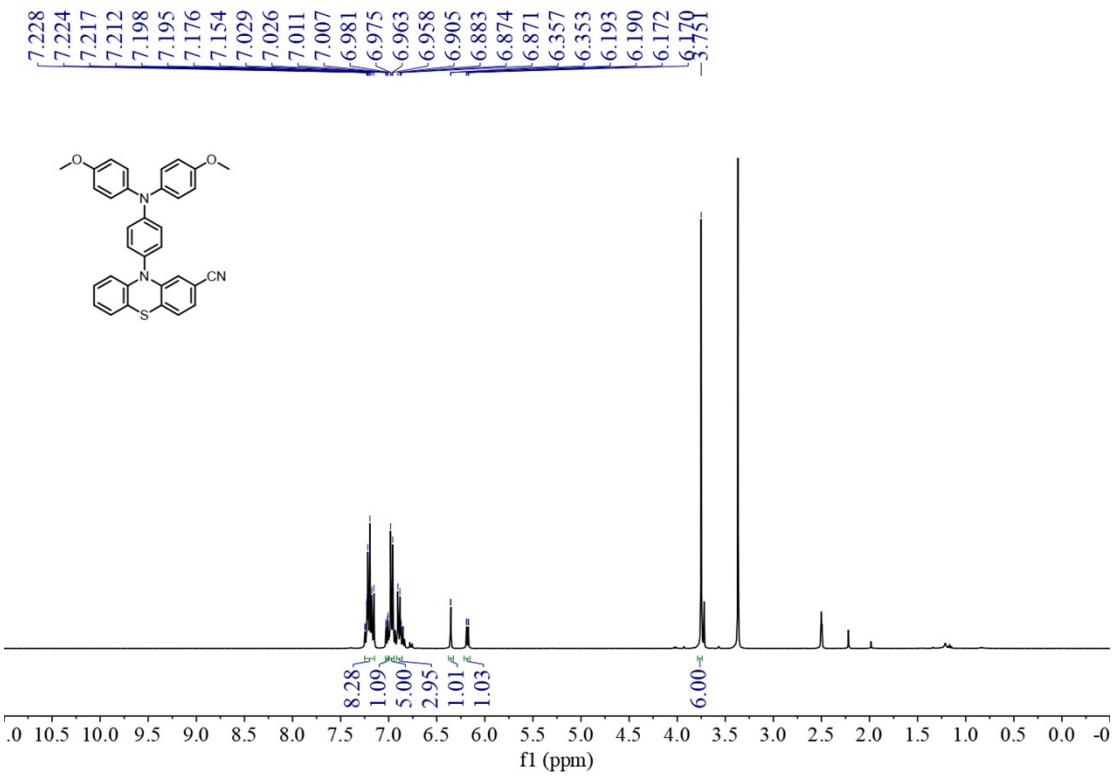

144.41
136.32
135.64
134.34
123.96
123.56
121.65
121.11
119.93
118.14
115.34
113.43
110.05
109.27
30.04
9.81
CH3
CH3
N
O
f1 (ppm)

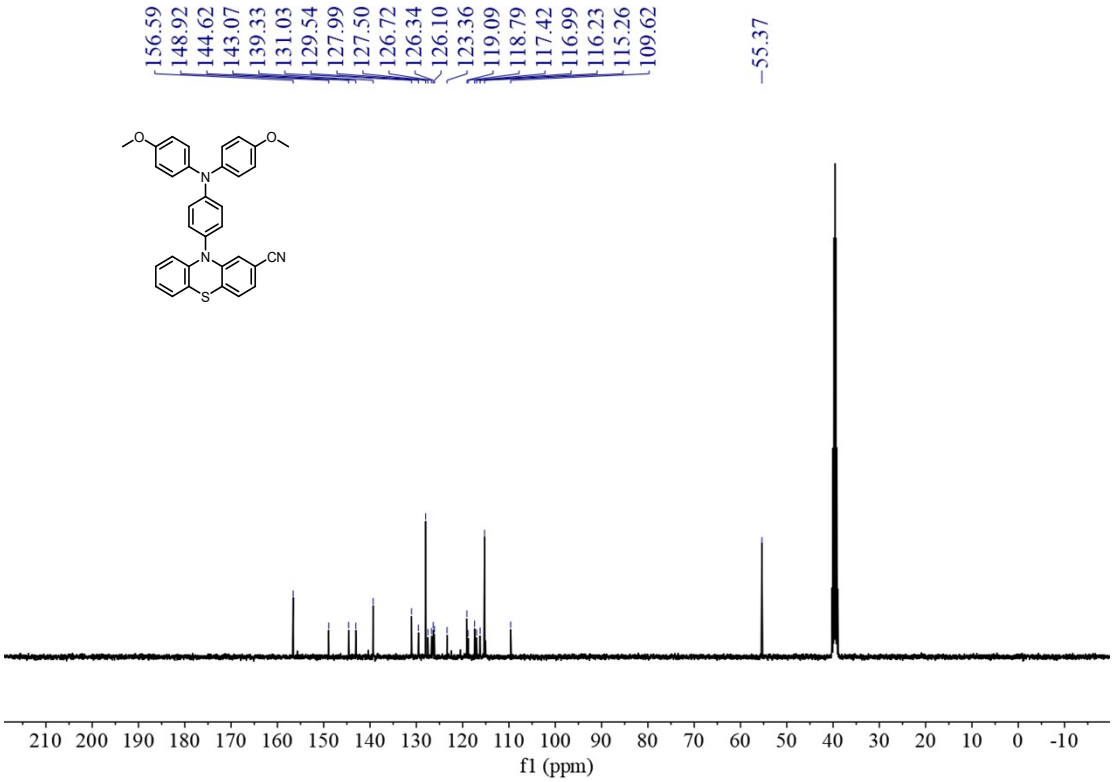

7.160
7.155
7.141
7.119
7.084
7.077
7.071
7.060
7.054
7.006
7.002
6.986
6.983
6.958
6.938
6.913
6.909
6.900
6.895
6.891
6.881
6.877
6.861
6.857
6.816
6.813
6.798
6.795
6.779
6.776
6.436
6.432
6.262
6.259
6.239
2.342
H3C
CH3
N
N
S
CN
9.99
2.03
2.22
2.08
1.05
1.00
1.00
6.00
f1 (ppm)

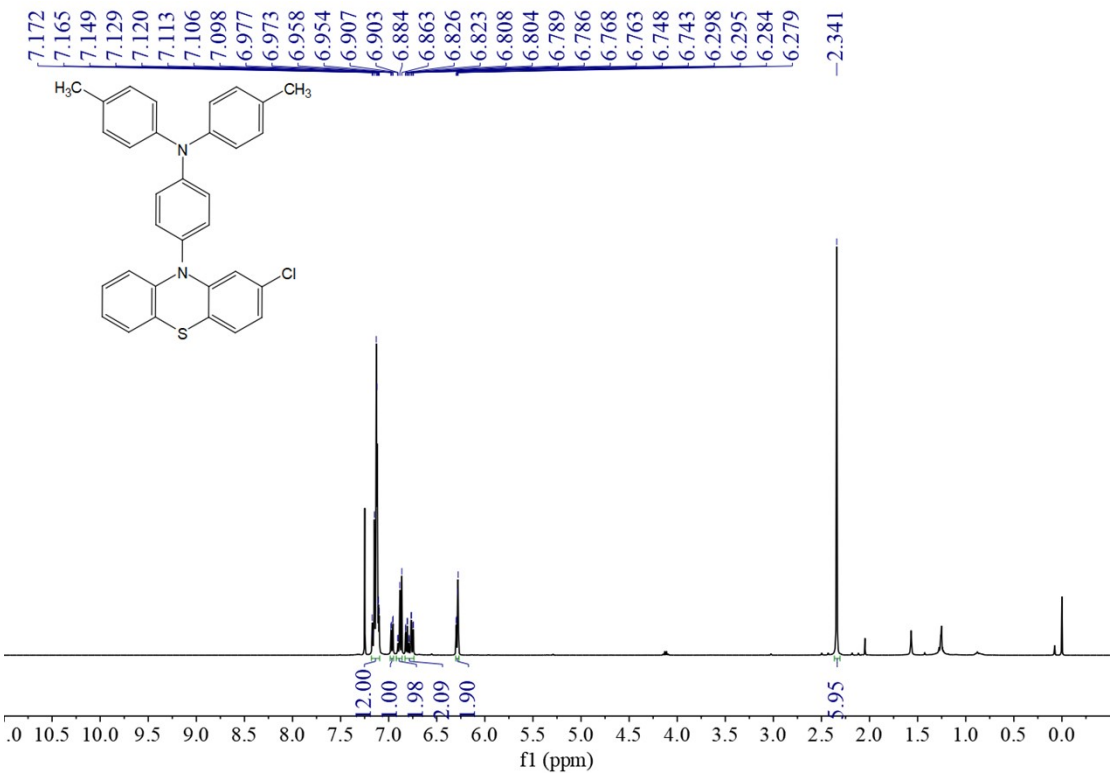

148.81
145.18
144.55
143.50
133.94
131.11
131.06
130.33
127.59
126.94
126.88
126.65
125.86
125.66
123.14
122.17
119.25
118.10
117.73
116.23
110.14
21.04
H3C
CH3
N
N
S
CN
f1 (ppm)

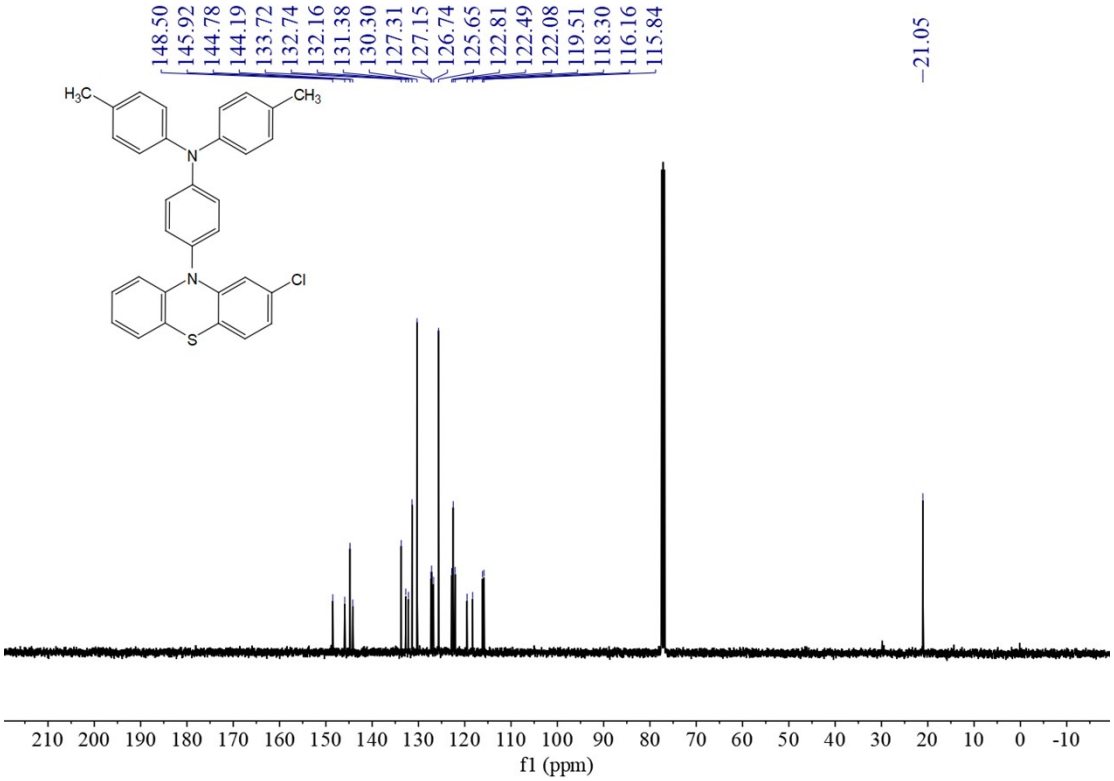

7.398
7.378
7.359
7.262
7.240
7.206
7.204
7.185
7.160
7.137
7.121
7.115
7.042
7.020
7.003
6.986
6.969
6.950
6.889
6.870
6.854
6.407
6.404
6.229
6.208
S
N
N
CN
4.10
12.10
2.77
1.00
1.00
1.00
f1 (ppm)

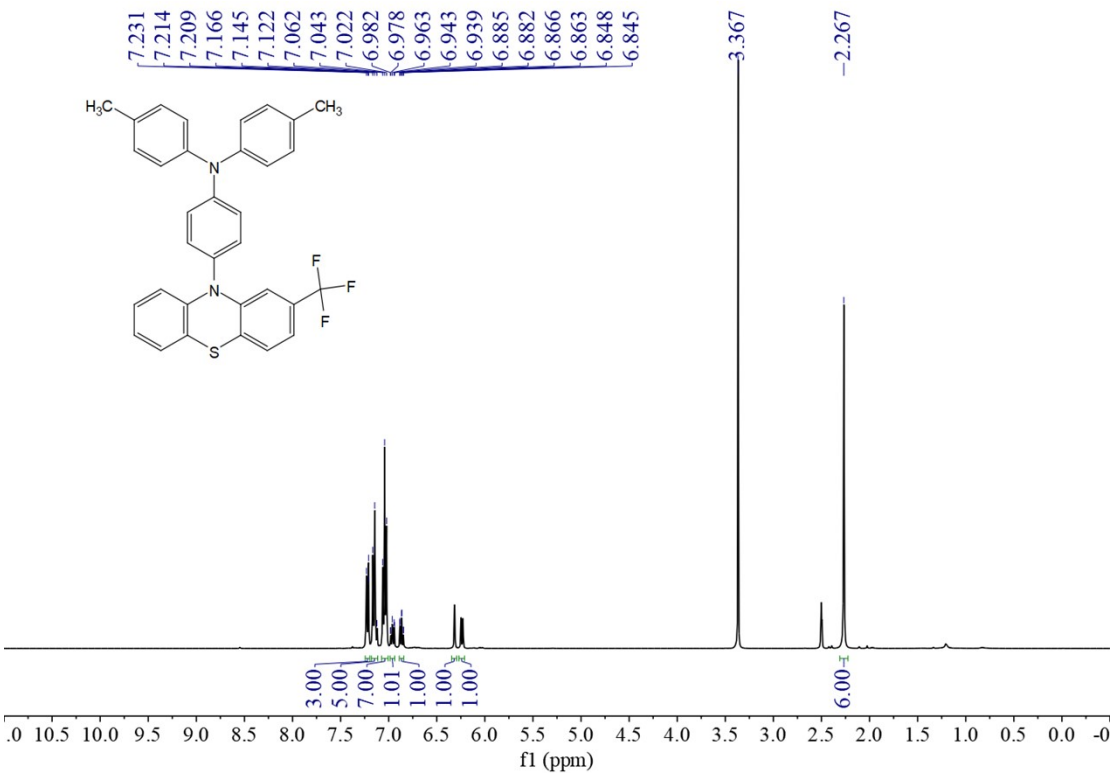

147.76
146.66
144.40
142.89
131.82
131.32
129.90
129.63
128.00
127.50
126.74
126.44
126.22
125.36
124.26
123.43
122.96
118.73
117.58
117.10
116.30
109.69
S
N
N
CN
f1 (ppm)

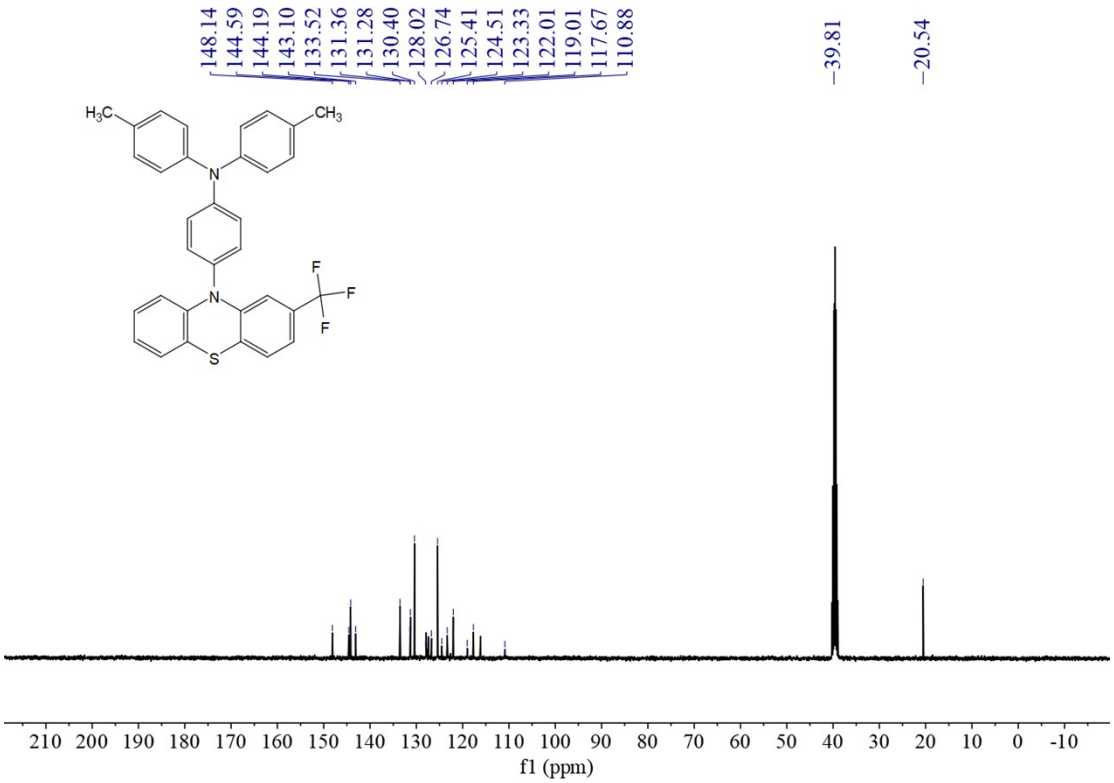

7.228
7.224
7.217
7.212
7.198
7.195
7.176
7.154
7.029
7.026
7.011
7.007
6.981
6.975
6.963
6.958
6.905
6.883
6.874
6.871
6.357
6.353
6.193
6.190
6.172
6.170
3.751
O
N
O
N
CN
S
8.28
1.09
5.00
2.95
1.01
1.03
6.00
.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

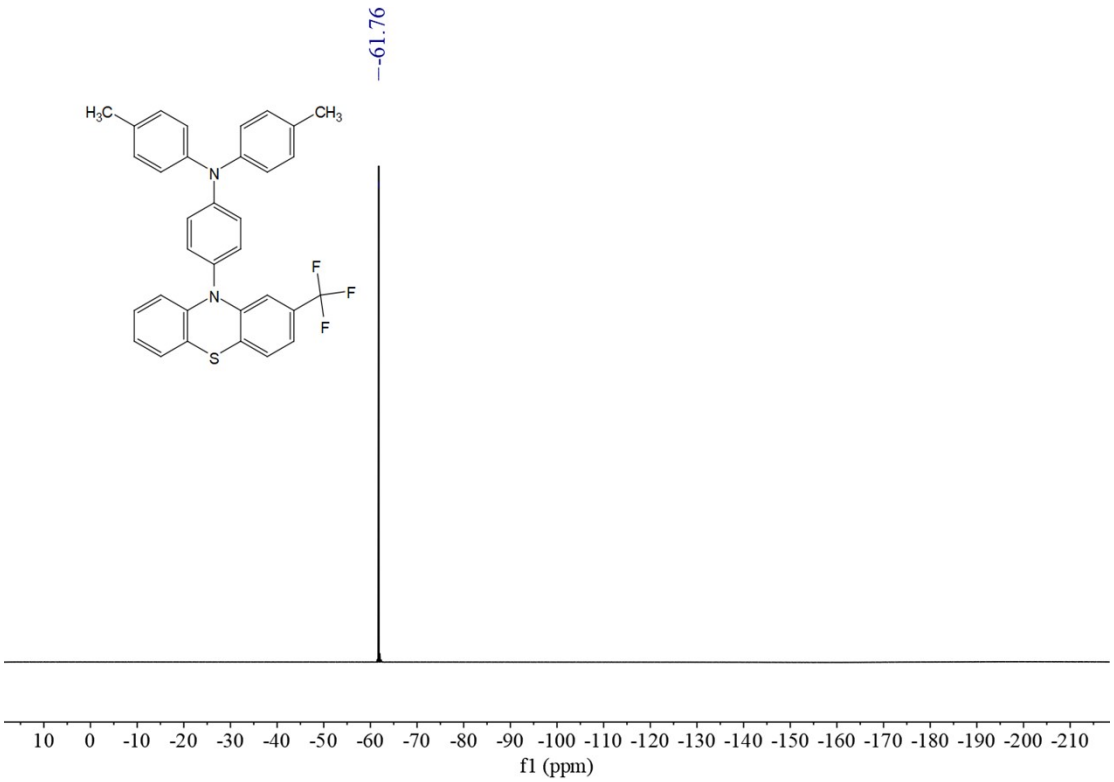

156.59
148.92
144.62
143.07
139.33
131.03
129.54
127.99
127.50
126.72
126.34
126.10
123.36
119.09
118.79
117.42
116.99
116.23
115.26
109.62
55.37
O
N
O
N
CN
S
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

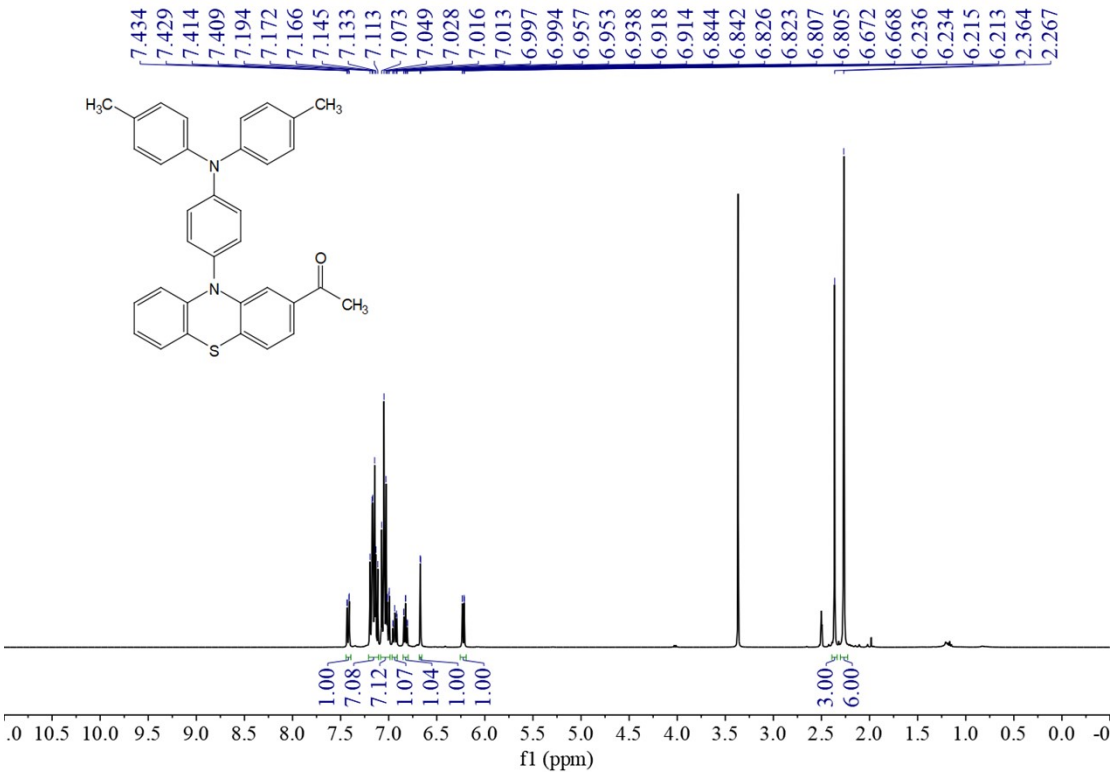

7.172
7.165
7.149
7.129
7.120
7.113
7.106
7.098
6.977
6.973
6.958
6.954
6.907
6.903
6.884
6.863
6.826
6.823
6.808
6.804
6.789
6.786
6.768
6.763
6.748
6.743
6.298
6.295
6.284
6.279
2.341
H3C
CH3
N
N
Cl
S
12.00
1.00
1.98
2.09
1.90
5.95
f1 (ppm)

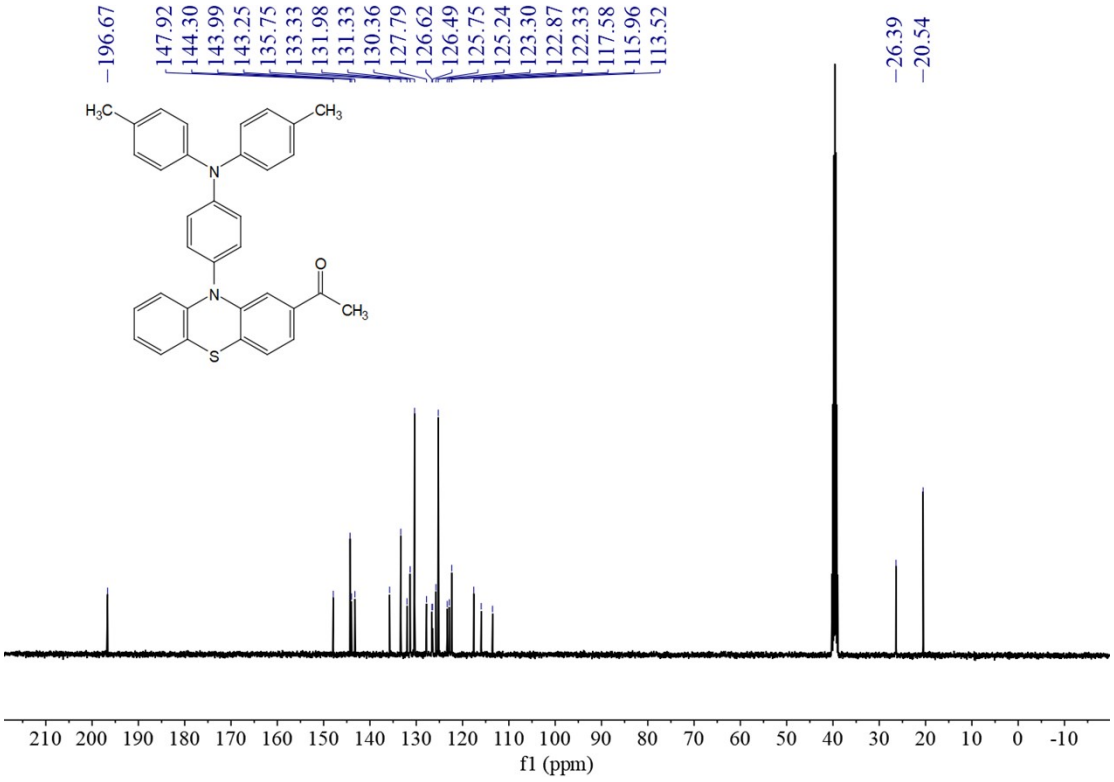

148.50
145.92
144.78
144.19
133.72
132.74
132.16
131.38
130.30
127.31
127.15
126.74
125.65
122.81
122.49
122.08
119.51
118.30
116.16
115.84
21.05
H3C
CH3
N
N
Cl
S
f1 (ppm)


7.231
7.214
7.209
7.166
7.145
7.122
7.062
7.043
7.022
6.982
6.978
6.963
6.943
6.939
6.885
6.882
6.866
6.863
6.848
6.845
3.367
2.267
H3C
CH3
N
F
F
F
S
3.00
5.00
7.00
1.01
1.00
1.00
1.00
6.00
f1 (ppm)


148.14
144.59
144.19
143.10
133.52
131.36
131.28
130.40
128.02
126.74
125.41
124.51
123.33
122.01
119.01
117.67
110.88
39.81
20.54
H3C
CH3
N
F
F
F
S
f1 (ppm)


-61.76
H3C
CH3
N
N
F
F
F
S
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


7.434
7.429
7.414
7.409
7.194
7.172
7.166
7.145
7.133
7.113
7.073
7.049
7.028
7.016
7.013
6.997
6.994
6.957
6.953
6.938
6.918
6.914
6.844
6.842
6.826
6.823
6.807
6.805
6.672
6.668
6.236
6.234
6.215
6.213
2.364
2.267
H3C
CH3
N
N
O
CH3
S
1.00
7.08
7.12
1.07
1.04
1.00
1.00
3.00
6.00
.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
f1 (ppm)



Reference：

(1) Zhao, Y.; Truhlar, D. G. *Theor. Chem. Acc.,* **2007**, *120*, 215.

(2) Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B.

Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2013.

(3) Marenich, A. V.; Cramer, C. J.; Truhlar. D. G. *J. Phys. Chem., B* **2009**, *113*, 6378.

(4) Grimme, S.; Antony, J.; Ehrlich, S. Krieg, H. *J. Chem. Phys.* **2010**, *132*, 154104.

(5) Savéant, J. M. *Acc. Chem. Res.* **1993**, *26*, 455.

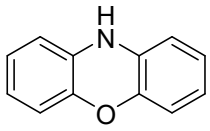
(6) Savéant, J. M. *J. Am. Chem. Soc.* **1987**, *109*, 6788.

(7) Marcus, R. A. *J. Chem. Phys.* **1956**, *24*, 966.

(8) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(9) Hush, N. S. *Trans. Faraday Soc.* **1961**, *57*, 557.

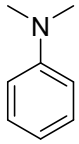
(10) K. Liu, S. Tang, T. Wu, S. Wang, M. Zou, H. Cong and A. Lei, *Nat. Commun.*, 2019, **10**, 639.



Thermal correction to Gibbs Free Energy= 0.147268
Sum of electronic and thermal Free Energies= -592.291781

C	0.64371100	0.25099900	3.58213300
C	1.37807100	0.06398200	2.41010200
C	0.72568800	-0.14283600	1.19688700
C	-0.67655200	-0.14506400	1.17477700
C	-1.40864800	0.05382500	2.33251700
C	-0.74675500	0.24596600	3.54810200
C	-0.67655200	-0.14506400	-1.17477700
C	0.72568800	-0.14283600	-1.19688700
C	1.37807100	0.06398200	-2.41010200
H	2.46450700	0.07011000	-2.42617200
C	0.64371100	0.25099900	-3.58213300
C	-0.74675500	0.24596600	-3.54810200
C	-1.40864800	0.05382500	-2.33251700
H	1.16848200	0.40278700	4.51992800
H	2.46450700	0.07011000	2.42617200
H	-2.49233000	0.04891700	2.26974400
H	-1.32189800	0.39253700	4.45617800
H	1.16848200	0.40278700	-4.51992800
H	-1.32189800	0.39253700	-4.45617800
H	-2.49233000	0.04891700	-2.26974400
N	1.41112600	-0.36767900	0.00000000
H	2.39936400	-0.13816300	0.00000000

O	-1.36261900	-0.37990600	0.00000000



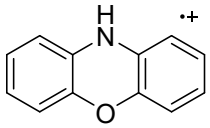
Thermal correction to Gibbs Free Energy= 0.142546
Sum of electronic and thermal Free Energies= -365.908102

C	-0.54338600	-1.20730500	-0.03552000
C	0.18724200	-0.00030200	-0.08984200
C	-0.54503200	1.20641900	-0.05113900
C	-1.93435600	1.19600800	0.01280700
C	-2.64714400	-0.00108200	0.05056100
C	-1.93285400	-1.19752500	0.02876500
H	-0.02801200	-2.16024100	-0.03955500
H	-0.03010500	2.15949200	-0.07125900
H	-2.46323000	2.14489800	0.03833600
H	-3.73094200	-0.00147100	0.10336000
H	-2.46045400	-2.14664300	0.06869800
N	1.56933700	0.00208200	-0.18925200
C	2.27647300	1.23931500	0.09030100
H	2.06300700	1.62957700	1.09676200
H	3.34883800	1.05785600	0.00966800
H	2.01386200	2.01254800	-0.63830600
C	2.28174400	-1.23765900	0.06151100
H	1.98715900	-2.00688200	-0.65862700
H	3.35063300	-1.06035300	-0.06377200
H	2.10775900	-1.63058200	1.07480300

$K_2S_2O_8$

Thermal correction to Gibbs Free Energy= -0.006197
Sum of electronic and thermal Free Energies= -2597.653138

O	0.31102800	0.98836500	0.15674100
O	-0.73846900	0.71195100	-0.76919800
S	-2.22769300	0.99401100	0.01379800
O	-2.13627400	0.22069200	1.25553600
O	-2.33295800	2.43446100	0.16007300
O	-3.06755400	0.35723200	-1.00898600
S	1.26920800	-0.38116400	0.22689600
O	1.92955500	-0.46298800	-1.08338400
O	2.18601200	0.02843700	1.29666000
O	0.37482500	-1.49678300	0.52743200
K	-2.04945200	-2.08659200	-0.15053700
K	4.31926400	0.39940800	-0.27736300



Thermal correction to Gibbs Free Energy= 0.147955
Sum of electronic and thermal Free Energies= -592.116758

C	-0.66895800	0.00001700	3.59426600
C	-1.39940400	-0.00001600	2.42617100
C	-0.71933400	-0.00001700	1.19536400
C	0.69230800	-0.00001700	1.17400800
C	1.42431300	-0.00000900	2.35823100
C	0.74038100	0.00001000	3.56109800
C	0.69230800	-0.00001700	-1.17400800
C	-0.71933400	-0.00001700	-1.19536400
C	-1.39940400	-0.00001600	-2.42617100
H	-2.48483600	-0.00005500	-2.42634100
C	-0.66895800	0.00001700	-3.59426600
C	0.74038100	0.00001000	-3.56109800
C	1.42431300	-0.00000900	-2.35823100
H	-1.18348300	0.00003300	4.54855400
H	-2.48483600	-0.00005500	2.42634100
H	2.50757400	-0.00001800	2.30917600
H	1.29857300	0.00004200	4.49073000
H	-1.18348300	0.00003300	-4.54855400
H	1.29857300	0.00004200	-4.49073000
H	2.50757400	-0.00001800	-2.30917600
N	-1.38026400	-0.00001100	0.00000000
H	-2.40119000	0.00027000	0.00000000
O	1.36946300	0.00002500	0.00000000

KSO_4^-

Thermal correction to Gibbs Free Energy= -0.015101
Sum of electronic and thermal Free Energies= -1298.996802

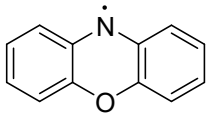
O	0.01025900	-0.01452700	1.21704800
S	-0.90006700	0.00002700	0.00012300
O	-1.76031500	-1.21630400	-0.00077700
O	-1.72114100	1.24388500	0.00056400
O	0.00986800	-0.01317600	-1.21678600
K	2.21535300	0.00002900	-0.00012400

$KSO_4^{\cdot}$

Thermal correction to Gibbs Free Energy= -0.017030

Sum of electronic and thermal Free Energies= -1298.800332

O	-0.29437800	0.82918000	1.07807700
S	-0.92132700	-0.06617400	-0.00040400
O	-2.37068500	-0.09447700	0.02667100
O	-0.33241400	0.84084600	-1.09086100
O	-0.24428600	-1.36988500	-0.01896100
K	2.14080700	-0.03087000	0.00247700



Thermal correction to Gibbs Free Energy= 0.135013

Sum of electronic and thermal Free Energies= -591.676992

C	3.58444100	-0.69287600	0.00000000
C	2.40252700	-1.40688800	0.00000000
C	1.15282500	-0.74442600	0.00000000
C	1.16800700	0.67190600	0.00000000
C	2.35455200	1.39657900	0.00000000
C	3.56270900	0.71199900	0.00000000
C	-1.16800700	0.67190600	0.00000000
C	-1.15282500	-0.74442600	0.00000000
C	-2.40252700	-1.40688800	0.00000000
H	-2.39328600	-2.49252300	0.00000000
C	-3.58444100	-0.69287600	0.00000000
C	-3.56270900	0.71199900	0.00000000
C	-2.35455200	1.39657900	0.00000000
H	4.53428800	-1.21730800	0.00000000
H	2.39328600	-2.49252300	0.00000000
H	2.31053700	2.48081200	0.00000000
H	4.49326000	1.26972100	0.00000000
H	-4.53428800	-1.21730800	0.00000000
H	-4.49326000	1.26972100	0.00000000
H	-2.31053700	2.48081200	0.00000000
N	0.00000000	-1.47116100	0.00000000
O	0.00000000	1.37264800	0.00000000

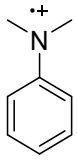
$KHSO_4$

Thermal correction to Gibbs Free Energy= -0.004443

Sum of electronic and thermal Free Energies= -1299.465344

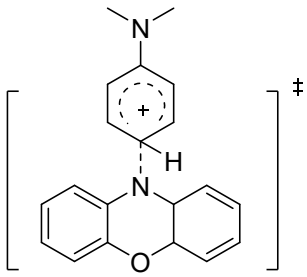
O	-0.00794100	0.11693100	-1.22219600
S	-0.84925200	0.12494800	-0.01077700
O	-1.94059100	1.09331300	0.00426700
O	-1.54605200	-1.34807800	-0.07753900
O	-0.01762700	0.12120100	1.21387300

K	2.31073600	-0.02460700	0.01028200
H	-2.21827400	-1.39858600	0.62982800



Thermal correction to Gibbs Free Energy= 0.143025
Sum of electronic and thermal Free Energies= -365.724450

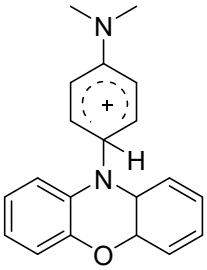
C	-0.54416900	-1.23198200	0.01623600
C	0.18027000	-0.00000100	-0.00007100
C	-0.54418100	1.23198200	-0.01639800
C	-1.92011300	1.21723000	-0.01742600
C	-2.61856700	-0.00000200	0.00009000
C	-1.92010600	-1.21722700	0.01744400
H	-0.01582400	-2.17637900	0.03639000
H	-0.01581300	2.17636300	-0.03674700
H	-2.46543600	2.15420600	-0.03333200
H	-3.70329300	-0.00000800	0.00020900
H	-2.46542200	-2.15420700	0.03333500
N	1.52966700	0.00000500	0.00001700
C	2.27957100	1.25569600	0.03220600
H	1.99043600	1.83634300	0.91160200
H	3.34116200	1.02909800	0.08052200
H	2.07065800	1.83395700	-0.87225300
C	2.27956700	-1.25569700	-0.03212200
H	1.99052300	-1.83632400	-0.91156200
H	3.34116300	-1.02910200	-0.08033900
H	2.07055100	-1.83396900	0.87230600



Thermal correction to Gibbs Free Energy= 0.304671
Sum of electronic and thermal Free Energies= -957.390613

C	-2.00517400	-1.07561700	2.00329800
C	-0.98182900	-0.14744700	2.01494600
C	0.12558600	-0.28690000	1.14474300
C	0.15696500	-1.41343500	0.28096300
C	-0.88851100	-2.32964000	0.24366100

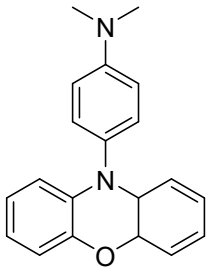
C	-1.97329700	-2.14304500	1.09182900
C	2.35446500	-0.88808700	-0.29677500
C	2.30207100	0.25004300	0.51842100
C	3.47445600	0.99310400	0.71177600
H	3.42404900	1.87615300	1.34195400
C	4.65750300	0.60011400	0.10635000
C	4.68418000	-0.53971100	-0.70821800
C	3.53421400	-1.29139400	-0.91255800
H	-2.84360300	-0.96904800	2.68306500
H	-0.98646300	0.69731700	2.69586300
H	-0.83121400	-3.17169900	-0.43780700
H	-2.79197100	-2.85585000	1.06780400
H	5.56314100	1.17630000	0.26227400
H	5.61060600	-0.84452800	-1.18367800
H	3.53129900	-2.17925600	-1.53602800
N	1.10398900	0.67263100	1.11429200
O	1.23304300	-1.64091400	-0.50696100
C	0.29820800	1.34064200	-1.37484300
C	-0.72968400	2.58694400	0.45931200
C	-0.87682400	0.70185100	-1.62456600
H	1.15424600	1.16497400	-2.01940300
C	-1.92214000	1.98140600	0.22047600
H	-0.65836000	3.36239800	1.21522200
C	-2.01077300	0.91421300	-0.75394000
H	-0.96627300	0.04062100	-2.47714700
H	-2.80746100	2.29430500	0.75907500
N	-3.09983700	0.16126100	-0.85172800
C	-3.22550200	-0.84447700	-1.90900700
H	-2.34431500	-1.48827100	-1.92731000
H	-4.10082300	-1.45738700	-1.70201800
H	-3.34536800	-0.36165900	-2.88402500
C	-4.28499600	0.42568600	-0.03240700
H	-4.83252300	1.28983000	-0.42275800
H	-4.92903000	-0.45147900	-0.06268000
H	-4.00010600	0.61118500	1.00301900
C	0.46012500	2.13825300	-0.19647700
H	1.36651100	2.72114200	-0.07957800



Thermal correction to Gibbs Free Energy= 0.304998
Sum of electronic and thermal Free Energies= -957.414123

C	-0.21241200	3.33607900	0.64809600
C	0.03651000	1.98327200	0.40220000
C	-0.99821500	1.13928700	0.00028000
C	-2.28905400	1.67688700	-0.11745000
C	-2.54410800	3.01037700	0.14655300
C	-1.49518100	3.85327000	0.52085600
C	-3.22237300	-0.45925100	-0.23847800
C	-1.95616700	-1.05528600	-0.12466900
C	-1.89302600	-2.42056600	0.15562200
H	-0.93619100	-2.91402300	0.28454300
C	-3.06543600	-3.17143500	0.27729300
C	-4.30929100	-2.56734600	0.14973600
C	-4.38489300	-1.19501000	-0.09784700
H	0.61060800	3.97666000	0.94742600
H	1.04101300	1.59580300	0.52704500
H	-3.56069500	3.37549900	0.04172300
H	-1.69018600	4.90254900	0.71485000
H	-2.99003400	-4.23421900	0.48260400
H	-5.21985600	-3.14874300	0.24715300
H	-5.33708600	-0.68440900	-0.19967800
N	-0.83317300	-0.22451000	-0.31310600
O	-3.33250000	0.88135600	-0.53708700
C	1.35193400	-0.11778900	-1.42263400
C	1.18695100	-1.00690000	0.90797800
C	2.68060700	0.00502900	-1.28525000
H	0.85787700	0.21067400	-2.33291900
C	2.51488300	-0.88233200	1.05279300
H	0.56814400	-1.30378300	1.75120500
C	3.34054400	-0.44600200	-0.06672700
H	3.26757700	0.43930200	-2.08379000
H	2.97646900	-1.05983600	2.01571200
N	4.64587000	-0.42607400	0.03008700
C	5.48183000	0.13531900	-1.04240900
H	5.18475200	1.16531800	-1.24650500
H	6.51713200	0.12405100	-0.71143700

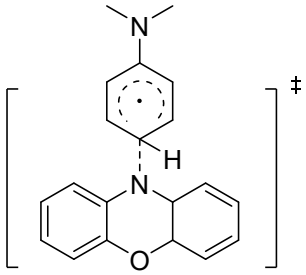
H	5.38278700	-0.46773400	-1.94786000
C	5.34385500	-0.93136800	1.22108000
H	4.87831100	-1.85310500	1.56763100
H	6.37553700	-1.14055300	0.94589000
H	5.32329700	-0.17764000	2.01312300
C	0.49383900	-0.80148400	-0.40490300
H	0.35686800	-1.81106400	-0.83161800



Thermal correction to Gibbs Free Energy= 0.289007
Sum of electronic and thermal Free Energies= -957.012035

C	1.53813800	3.64363900	0.01564100
C	0.82062200	2.44530600	0.00990800
C	1.48272300	1.21647900	0.00536000
C	2.88830800	1.22213300	0.00770800
C	3.60021500	2.40854400	0.01323900
C	2.92654400	3.63260900	0.01714800
C	2.94158800	-1.14081500	-0.00316700
C	1.53706900	-1.19846000	-0.00676100
C	0.93098600	-2.45578500	-0.01641000
H	-0.15147700	-2.51990400	-0.02003900
C	1.70181700	-3.62061300	-0.02116000
C	3.08827700	-3.54710500	-0.01671000
C	3.70624200	-2.29399500	-0.00799300
H	0.99549000	4.58350300	0.01902700
H	-0.26368800	2.46068400	0.00890900
H	4.68450200	2.35625100	0.01474900
H	3.49070600	4.55907800	0.02152400
H	1.20209700	-4.58398400	-0.02838800
H	3.69349400	-4.44732200	-0.02012200
H	4.78710200	-2.19319500	-0.00467800
N	0.80123500	-0.00698300	-0.00066000
O	3.62073900	0.05659900	0.00548000
C	-0.62679100	-0.03940400	-0.00158800
C	-1.33424700	-0.08081000	1.19905000
C	-1.33477400	-0.02195200	-1.20269300
C	-2.72204900	-0.10980600	1.20712000
H	-0.78756900	-0.08535300	2.13837500

C	-2.72249900	-0.04773900	-1.21136200
H	-0.78845700	0.01809300	-2.14140400
C	-3.45467000	-0.10377900	-0.00256800
H	-3.23659400	-0.13327000	2.15979400
H	-3.23799800	-0.02517900	-2.16366000
N	-4.82985500	-0.15638200	-0.00506400
C	-5.54320800	-0.01013800	1.25031800
H	-5.34398700	0.95568100	1.73701900
H	-6.61358700	-0.08752500	1.05827700
H	-5.26984900	-0.80814700	1.94827500
C	-5.54168900	0.11702300	-1.24046200
H	-5.30442600	-0.63109200	-2.00407300
H	-6.61360100	0.07029600	-1.04758000
H	-5.30335100	1.11015300	-1.64748200

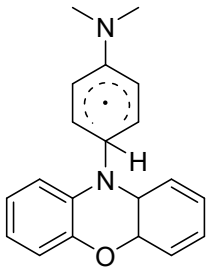


Thermal correction to Gibbs Free Energy= 0.299633

Sum of electronic and thermal Free Energies= -957.531756

C	1.64160100	1.94492100	1.79281300
C	0.73193300	0.90496500	1.97184100
C	-0.30151400	0.68365200	1.05430500
C	-0.42447300	1.57934400	-0.02116000
C	0.46972100	2.62560200	-0.20764600
C	1.51904400	2.79647400	0.69497100
C	-2.49947800	0.64515000	-0.55683100
C	-2.36437400	-0.26928200	0.49873500
C	-3.46633700	-1.07008700	0.81611200
H	-3.36389700	-1.77778900	1.63441300
C	-4.65822000	-0.96635800	0.10286400
C	-4.76895500	-0.04634400	-0.93948100
C	-3.68686300	0.76954000	-1.26655200
H	2.44378500	2.08960800	2.50966000
H	0.81257100	0.23130200	2.81917000
H	0.33484100	3.28813900	-1.05701000
H	2.22595800	3.60676200	0.54750400
H	-5.49948400	-1.60095400	0.36278100
H	-5.69557500	0.04292900	-1.49730200
H	-3.74444100	1.49603500	-2.07118100

N	-1.14301900	-0.43557100	1.18493900
O	-1.45041400	1.45265900	-0.92439000
C	-0.06113300	-1.51526100	-0.97703900
C	0.87643600	-2.16123000	1.17622100
C	1.16469900	-1.05572700	-1.37662500
H	-0.88898100	-1.51064100	-1.68055700
C	2.10962700	-1.73457700	0.76859800
H	0.76938200	-2.65243100	2.13898000
C	2.28770000	-1.08920900	-0.49464800
H	1.28890000	-0.69431200	-2.39154100
H	2.96654800	-1.89960600	1.41266800
N	3.48680000	-0.55160200	-0.85220700
C	3.63023500	0.11956000	-2.13250600
H	2.91374100	0.94485500	-2.22526700
H	4.63832000	0.52447700	-2.20959600
H	3.47094200	-0.57231100	-2.96761000
C	4.60871800	-0.58877700	0.07016600
H	4.92135600	-1.61818200	0.28023500
H	5.45008200	-0.05708300	-0.37277700
H	4.35204900	-0.10436300	1.01991000
C	-0.31468900	-1.88858100	0.39934600
H	-1.16131700	-2.55014600	0.57260900



Thermal correction to Gibbs Free Energy= 0.300656

Sum of electronic and thermal Free Energies= -957.537626

C	0.38857700	3.08615600	0.59953800
C	0.39560600	1.71216200	0.34522400
C	-0.77941500	1.05673100	-0.03478700
C	-1.95693300	1.81960900	-0.11584100
C	-1.97298200	3.17515200	0.15908400
C	-0.78576100	3.82290400	0.50730300
C	-3.26239600	-0.10959100	-0.19308400
C	-2.11571900	-0.91818000	-0.11242100
C	-2.29252000	-2.27029200	0.19474600
H	-1.43492900	-2.92461900	0.30375200
C	-3.57573900	-2.79575300	0.37092800
C	-4.69623000	-1.98070700	0.27496700

C	-4.53239100	-0.61981700	0.00404500
H	1.31825600	3.57243800	0.87818800
H	1.32008900	1.15729800	0.44098200
H	-2.91422400	3.70976000	0.07901500
H	-0.78956900	4.88917800	0.70742300
H	-3.68452100	-3.85215800	0.59488000
H	-5.69197200	-2.38800000	0.41435100
H	-5.38031600	0.05330100	-0.07394600
N	-0.87183900	-0.31031700	-0.34746900
O	-3.13561600	1.22436300	-0.51645200
C	1.25829300	-0.55488100	-1.56887400
C	1.04715500	-1.46969000	0.73402700
C	2.58872600	-0.38174000	-1.35601100
H	0.81736900	-0.27295600	-2.52094900
C	2.37765500	-1.26191800	0.91599200
H	0.44662300	-1.87030800	1.54686200
C	3.21768900	-0.72447200	-0.11456700
H	3.18437100	0.04717300	-2.15488600
H	2.80975600	-1.50663500	1.88073600
N	4.56772400	-0.55949700	0.07625100
C	5.35628500	0.12976200	-0.92950200
H	5.03448100	1.17178400	-1.06414600
H	6.40204800	0.12483600	-0.62265300
H	5.28501800	-0.38047800	-1.89507700
C	5.12838200	-0.71220900	1.40747800
H	4.96300200	-1.72529200	1.78788800
H	6.20379200	-0.54191500	1.35957400
H	4.69301900	0.00059700	2.12122100
C	0.33187400	-1.15270100	-0.54995000
H	-0.08949300	-2.07335300	-0.98284400