*Electronic Supplementary Information*

# Phenothiazine Derivatives as Organic Sensitizers for Highly Efficient Dye-sensitized Solar Cells

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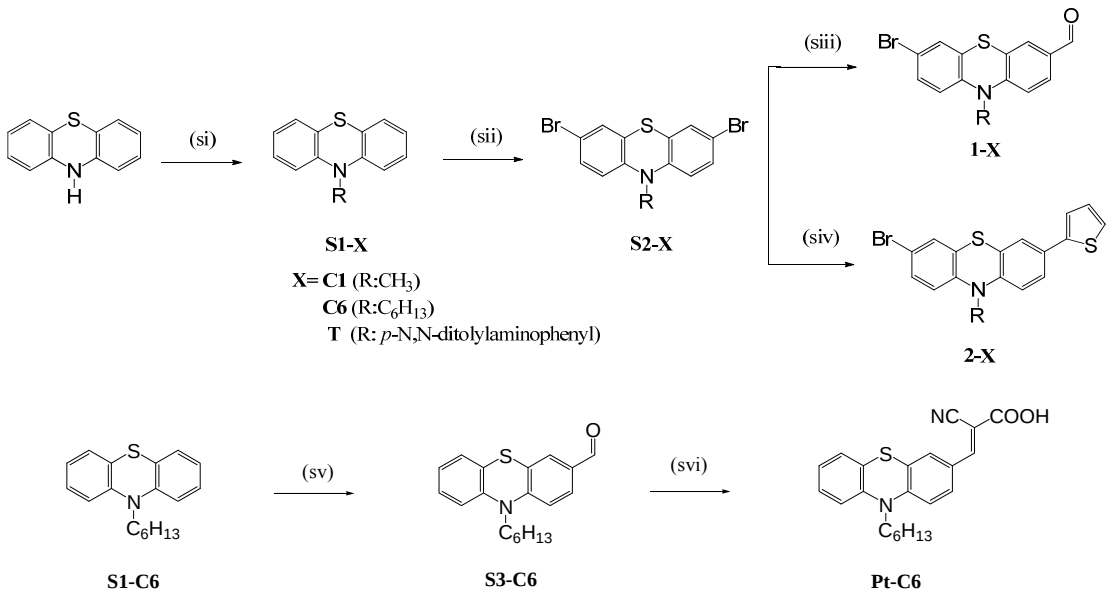
Contents

## 1. Experimental (1-X, 2-X, Pt-C6)

General Information

All reactions and manipulations were carried out under a nitrogen atmosphere. Solvents were distilled freshly according to standard procedures. $^{1}H$ and $^{13}C$ NMR spectra were recorded on Brucker (AV 400/AV 500 MHz) spectrometer in $CDCl_3$, and DMSO-$d_6$ as a solvent. Chemical shifts are reported in scale downfield from the peak for tetramethylsilane. Absorption spectra were recorded on a Jasco-550 spectrophotometer. Emission spectra obtained from a Hitachi F-4500 spectrofluorimeter. The emission spectra in solution were measured in spectral grade solvent by a 90° angle detection. The redox potentials were measured by using cyclic voltammetry on CHI 620 analyzer. All measurements were carried out in THF solutions containing 0.1 M tetrabutylammonium hexaflourophosphate ($TBAPF_6$) as supporting electrolyte at ambient condition after purging 10 minutes with $N_2$. The conventional three electrode configuration was employed, which consists of a glassy carbon working electrode, a platinum counter electrode, and a $Ag/Ag^+$ reference electrode calibrated with ferrocene/ferrocenium ($Fc/Fc^+$) as an internal reference. Mass spectra were recorded on a VG70-250S mass spectrometer. The cell parameters were obtained under an incident light with intensity 100 $mW{\cdot}cm^{-2}$ measured by a thermopile probe (Oriel 71964), which was generated by a 300 W (Oriel Class A Solar Simulator 91160A-1000, Newport) passing through a AM 1.5 filter (Oriel 74110). The light intensity was further calibrated by an Oriel reference solar cell (Oriel 91150) and adjusted to be 1.0 sun. The monochromatic quantum efficiency was recorded through a monochromator (Oriel 74100) at short circuit condition. Electrochemical impedance spectra of DSSCs were recorded by an Impedance/ Gain-Phase analyzer (SI 1260, Solartron).

The chemicals, i.e., phenothiazine, iodomethane, 1-bromohexane, n-butyllithium (1.6 M in hexane), trans-dichlorobis(triphenylphosphine) palladium (II) ($PdCl_2(PPh_3)_2$), N,N-dimethylformamide, palladium(II) acetate ($Pd(OAc)_2$), 1,1'-bis-(diphenylphosphanyl)ferrocene (dppf), N-bromosuccinimide (NBS), phosphoryl chloride ($POCl_3$), cyanoacetic acid, ammonium acetate, and acetic acid. All chemicals were purchased from ACROS, Alfa, Merck, Lancaster, TCI, Showa, Sigma-Aldrich, separately. Chromatographic separations were carried out by using silica gel from Merk, Kieselgel si 60 (40 - 63 μm).




**Scheme S1.** Synthetic routes of **1-X**, **2-X**, and **Pt-C6**. Reagents and conditions: (si) (a) KO$^t$Bu, $CH_3I$ (or $C_6H_{13}Br$), THF, 0~25 °C, or (b) NaO$^t$Bu, dppf, $Pd(OAc)_2$, toluene, 90 °C. (sii) NBS, dichloromethane, 0 °C; (siii) *n*-BuLi, DMF, THF, -78 °C; (siv) $PdCl_2(PPh_3)_2$, 2-(tributyl-stannyl)thiophene, DMF, 90°C. (sv) $POCl_3$, DMF, 90°C. (svi) cyanoacetic acid, $NH_4OAc$, AcOH, 90~100 °C.

**N-Methylphenothiazine (S1-C1)**

A mixture of compound phenothiazine (3.00 g, 15.0 mmol) and potassium *tert*-butoxide (2.53 g, 22.6 mmol) in dry THF (30 mL) was placed in a three-necked flask and was stirred in an ice bath for 20 minutes under a nitrogen atmosphere. To it was added $CH_3I$ (1.87 mL, 30.1 mmol), then the mixture was stirred overnight. The reaction was quenched by adding deionized water, and the mixture was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with hexane. White solid of **S1-C1** was obtained in 90% yield (2.91 g, 12.3 mmol). Spectroscopic data of **S1-C1**: $\delta_H$ (500 MHz, $CDCl_3$) 7.17-7.21 (m, 4H), 6.92 (t, 2H, $J$ = 7.4 Hz), 6.81 (d, 2H, $J$ = 8.0 Hz), 3.38 (s, 3H**)**; $\delta_C$ NMR (125 MHz, $CDCl_3$) 145.7, 127.4, 127.1, 123.3, 122.4, 114.0, 35.2; *m/z* (EI) 213.0612 ($M^+$, $C_{13}H_{11}NS$ requires 213.0612).

**N-Hexylphenothiazine (S1-C6)**

Compound **S1-C6** was synthesized according to the same procedure as that of **S1-C1**, gave colourless liquid of **S1-C6** in 80% yield. $\delta_H$ (500 MHz, $CDCl_3$) 7.04-7.08 (m, 4H), 6.83 (t, 2H, $J$ = 6.1 Hz), 6.77 (d, 2H, $J$ = 7.9 Hz), 3.73 (t, 2H, $J$ = 7.2 Hz),

1.69-1.75 (m, 2H), 1.32-1.38 (m, 2H), 1.21-1.25 (m, 4H), 0.84 (t, 3H, $J$ = 6.9 Hz); $\delta_C$ NMR (125 MHz, $CDCl_3$) 145.2, 127.2, 127.0, 124.8, 122.1, 115.2, 47.2, 31.3, 26.7, 26.5, 22.5, 13.9; *m/z* (EI) 283.1392 ($M^+$, $C_{18}H_{21}NS$ requires 283.1395).

**N-(*p*-N,N-ditolylaminophenyl)phenothiazine (S1-T)**

A mixture of phenothiazine (3.00 g, 15.0 mmol), $Pd(OAc)_2$ (170 mg, 0.75 mmol), dppf (420 mg, 0.75 mmol), N-(4-bromophenyl)-4-methyl-N-*p*-tolylbenzenamine (2.00 g, 9.13 mmol), and sodium *tert*-butoxide (5.30 g, 15.0 mmol) in dry toluene was placed in a three-necked flask under a nitrogen atmosphere and was stirred at 90 °C for 15 h. After cooling, the reaction was quenched by adding water, and extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and was concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/9). White solid of **S1-T** was obtained in 79% yield (5.62 g, 11.95 mmol). Spectroscpoic data of **S1-T**: $\delta_H$ (500 MHz, $CDCl_3$) 7.10-7.15 (m, 12H), 6.93 (dd, 2H, $J$ = 1.6, 7.6 Hz), 6.80-6.84 (m, 2H), 6.71-6.74 (m, 2H), 6.28 (d, 2H, $J$ = 1.0 Hz), 2.29 (s, 6H); $\delta_C$ (125 MHz, $CDCl_3$) 148.0, 144.8, 144.5, 133.2, 133.1, 131.4, 130.0, 126.7, 126.5, 125.2, 122.7, 122.2, 119.8, 115.7, 20.8; *m/z* (EI) 470.1824 ($M^+$, $C_{32}H_{26}N_2S$ requires 470.1817).

**3,7-Dibromo-N-methylphenothiazine (S2-C1)**

To a solution of **S1-C1** (10.0 g, 46.9 mmol) in dichloromethane at 0°C was added NBS (20.9 g, 117 mmol) in three portions. The mixture was stirred with a magnetic bar for 8 hours at room temperture, then was quenched by adding water, then was extracted with dichloromethane. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/5). White solid of **S2-C1** was obtained in 85% yield (14.7 g, 39.85 mmol). Spectroscopic data of **S2-C1**: $\delta_H$ (400 MHz, $CDCl_3$) 7.22 (d, 1H, $J$ = 2.1 Hz), 7.20 (d, 1H, $J$ = 2.1 Hz), 7.17 (d, 2H, $J$ = 2.1 Hz), 6.57 (d, 2H, $J$ = 8.6 Hz) 3.24 (s, 3H**)**; $\delta_C$ (100 MHz, $CDCl_3$)：$\delta$ 144.5, 130.2, 129.3, 124.7, 115.2, 114.9, 35.3; *m/z* (FAB) 368.8830 ($M^+$, $C_{13}H_9NSBr_2$ requires 368.8822).

**3,7-Dibromo-N-hexylphenothiazine (S2-C6)**

Compound **S2-C6** was synthesized according to the same procedure as that of **S2-C1**, gave yellow solid of **S2-C6** in 81% yield. $\delta_H$ (400 MHz, $CDCl_3$) 7.15-7.20 (d, 4H), 6.62 (d, 2H, $J$ = 8.6 Hz), 3.69 (t, 2H, $J$ = 7.0 Hz), 1.73-1.68 (m, 2H), 1.39-1.32 (m, 2H), 1.27-1.24 (m, 4H), 0.85(t, 3H, $J$ = 6.6 Hz); $\delta_C$ (100 MHz, $CDCl_3$) 144.0, 130.0,

129.6, 126.3, 116.5, 114.6, 47.5, 31.3, 26.5, 26.4, 22.5, 13.9; *m/z* (FAB) 438.9613 ($M^+$, $C_{18}H_{19}NSBr_2$ requires 438.9605).

**3,7-Dibromo-N-(*p*-N,N-ditolylaminophenyl)phenothiazine (S2-T)**

Compound **S2-T** was synthesized according to the same procedure as that of **S2-C1**, gave white solid of **S2-T** in 72% yield. $\delta_H$ (400 MHz, $CDCl_3$) 7.04-7.14 (m, 14H), 6.92 (dd, 2H, *J* = 2.0, 8.8 Hz), 6.11 (d, 2H, *J* = 8.9 Hz), 2.33 (s, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 148.5, 144.6, 143.5, 133.7, 131.9, 131.0, 130.2, 129.7, 128.7, 125.5, 122.4, 122.0, 117.0, 114.4, 20.9; *m/z* (FAB) 626.0024 ($M^+$, $C_{32}H_{24}N_2SBr_2$ requires 626.0027).

**7-Bromo-N-methylphenothiazine-3-carbaldehyde (1-C1)**

To a solution of **S2-C1** (3.0 g, 8.08 mmol) in THF at -78 °C was added dropwise n-BuLi (6.6 mL, 10.51 mmol, 1.6 M in hexane). The mixture was stirred for 1 h, then to it was added DMF (0.8 mL, 10.51 mmol). The reaction was stirred with a magnetic bar for 6 h, then was quenched by adding water, then was extracted with ethyl acetate. The organic layer was dried over anhydrous $MgSO_4$ and concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/5). Yellow solid of **1-C1** was obtained in 70% yield (1.81 g, 5.68 mmol). Spectroscopic data of **1-C1**: $\delta_H$ (400 MHz, $CDCl_3$) 9.79 (s, 1H), 7.64 (dd, 1H, *J* = 1.3, 8.4 Hz), 7.55 (d, 1H, *J* = 1.3 Hz), 7.24 (dd, 1H, *J* = 1.9, 9.4), 7.19 (d, 1H, *J* = 2.0 Hz), 6.83 (d, 1H, *J* = 8.36 Hz), 6.64 (d, 1H, *J* = 8.6 Hz), 3.37 (s, 3H); $\delta_C$ (100 MHz, $CDCl_3$) 189.9, 150.5, 143.2, 131.3, 130.6, 130.3, 129.4, 127.9, 124.7, 123.2, 115.9, 115.8, 113.8, 35.8; *m/z* (EI) 318.9670 ($M^+$, $C_{14}H_{10}ONSBr$ requires 318.9666).

**7-Bromo-10-hexylphenothiazine-3-carbaldehyde (1-C6)**

Compound **1-C6** was synthesized according to a similar procedure as that of **1-C1**, gave yellow liquid of **1-C6** in 68% yield. $\delta_H$ (400 MHz, $CDCl_3$) 9.78 (s, 1H), 7.63 (dd, 1H, *J* = 1.8, 8.4), 7.55 (d, 1H, *J* = 1.8 Hz), 7.23 (dd, 1H, *J* = 2.2, 8.6), 7.20 (d, 1H, *J* = 2.2 Hz), 6.88 (d, 1H, *J* = 8.4 Hz), 6.70 (d, 1H, *J* = 8.6 Hz), 3.83 (t, 2H, *J* = 7.2 Hz), 1.73-1.80 (m, 2H), 1.42-1.45 (m, 2H), 1.25-1.32 (m, 4H), 0.89 (t, 3H, *J* = 2.52 Hz); $\delta_C$ (100 MHz, $CDCl_3$) 189.9, 150.3, 142.6, 131.3, 130.3, 130.2, 129.8, 128.4, 126.1, 124.4, 117.1, 115.8, 115.0, 48.1, 31.3, 26.6, 26.4, 22.6, 14.0; *m/z* (FAB) 390.0527 ($(M+H)^+$, $C_{19}H_{21}ONSBr$ requires 390.0527).

**7-Bromo-N-(*p*-N,N-ditolylaminophenyl)phenothiazine-3-carbaldehyde (1-T)**

Compound **1-T** was synthesized according to the same procedure as that of **1-C1**,

gave yellow solid of **1-T** in 55% yield. $\delta_H$ (400 MHz, $CDCl_3$) 9.70 (s, 1H), 7.42 (d, 1H, $J$ = 1.7 Hz), 7.33 (dd, 1H, $J$ = 1.8, 8.6 Hz), 7.05-7.16 (m, 13H), 6.94 (dd, 1H, $J$ = 2.2, 8.9 Hz), 6.30 (d, 1H, $J$ = 8.6 Hz), 6.11 (d, 1H, $J$ = 8.8 Hz), 2.34 (s, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 189.6, 149.1, 148.8, 144.4, 142.2, 133.9, 131.1, 131.0, 130.7, 130.2, 130.1, 129.7, 128.7, 127.5, 125.6, 122.1, 121.2, 119.3, 117.7, 115.6, 115.2, 20.9; *m/z* (FAB) 577.0949 ($(M+H)^+$, $C_{33}H_{26}ON_2SBr$ requires 577.0949).

**3-Bromo-N-hexyl-7-(thiophen-2-yl)phenothiazine (2-C6)**

To a three-necked flask containing a mixture of **S2-C6** (2.00 g, 4.56 mmol), $PdCl_2(PPh_3)_2$ (96 mg, 0.14 mmol), 2-tributylstannylthiophene (1.8 mL, 5.5 mmol) was added DMF (20 mL). The reaction mixture was stirred at 90 °C for 12 h. After cooling, the reaction was quenched by adding MeOH and $KF_{(aq)}$ (saturated 15 mL). The mixture was extracted with $CH_2Cl_2$ and the organic layer was dried over anhydrous $MgSO_4$. Evaporation under reduced pressure to give the crude product, which was purified by silica gel column chromatograph eluted with hexane. Yellow-green liquid of **2-C6** was obtained in 60% yield (1.22 g, 2.74 mmol). $\delta_H$ (400 MHz, $CDCl_3$) 7.37-7.41 (m, 2H), 7.21-7.26 (m, 4H), 7.06-7.08 (m, 1H), 6.84 (d, 1H, $J$ = 8.0 Hz), 6.70-6.72 (m, 1H), 3.82 (t, 2H, $J$ = 7.2 Hz), 1.76-1.84 (m, 2H), 1.41-1.48 (m, 2H), 1.30-1.33 (m, 4H), 0.90 (t, 3H, $J$ = 6.8 Hz); $\delta_C$ NMR (100 MHz, $CDCl_3$) 144.1, 143.3, 129.9, 129.6, 129.2, 128.0, 126.5, 125.1, 124.7, 124.6, 124.2, 122.4, 116.5, 115.6, 114.5, 47.6, 31.4, 26.7, 26.5, 22.6, 14.0; *m/z* (FAB) 444.0455 ($(M+H)^+$, $C_{22}H_{23}NS_2Br$ requires 444.0455).

**3-Bromo-7-(thiophen-2-yl)-N-(*p*-N,N-ditolylaminophenyl)phenothiazine (2-T)**

Compound **2-T** was synthesized according to the same procedure as that of **2-C6**, gave orange solid of **2-T** in 75% yield. $\delta_H$ (400 MHz, $CDCl_3$) 7.06-7.17 (m, 17H), 6.99 (t, 1H, $J$ = 4.4 Hz), 6.92 (dd, 1H, $J$ = 2.0, 8.8 Hz), 6.24 (d, 1H, $J$ = 8.6 Hz), 6.12 (d, 1H, $J$ = 8.8 Hz), 2.33 (s, 6H); $\delta_C$ (100 MHz, $CDCl_3$) 148.4, 144.6, 143.4, 143.3, 143.2, 133.6, 132.2, 131.1, 130.1, 129.5, 129.0, 128.6, 127.9, 125.4, 124.7, 124.0, 123.8, 122.5, 122.1, 121.4, 119.4, 116.9, 116.0, 114.2, 20.9; *m/z* (FAB) 631.0877 ($(M+H)^+$, $C_{36}H_{28}N_2S_2Br$ requires 631.0877).

**N-Hexylphenothiazine-3-carbaldehyde (S3-C6)**

To a three-necked flask containing a mixture of $POCl_3$ (1.26 mL, 8.47 mmol) and DMF (3.27 mL, 8.47 mmol) was added dropwise **S1-C6** (2.0 g, 7.06 mmol) in DMF (50 mL) with dropwise in an ice bath with stirring. After the addition was completed, the reaction mixture was warmed up to 90 °C for 12 h. After cooling, the mixture was extracted with $CH_2Cl_2$, the organic layer was dried over anhydrous $MgSO_4$.

Evaporation under reduced pressure to give the crude product, which was purified by silica gel column chromatograph eluted with dichloromethane/hexane (1/1). Yellow liquid of **S3-C6** was obtained in 79.1 % yield (1.85 g, 5.58 mmol). $\delta_H$ (400 MHz, $CDCl_3$) 9.78 (s, 1H), 7.62 (dd, 1H, $J$ = 1.9, 8.4 Hz), 7.56 (d, 1H, $J$ = 1.8 Hz), 7.13-7.17 (m, 1H), 7.09 (dd, 1H, $J$ = 1.3, 7.6 Hz), 6.95 (t, 1H, $J$ = 7.5 Hz), 6.86-6.89 (m, 2H), 3.87 (t, 2H, $J$ = 7.2 Hz), 1.76-1.83 (m, 2H), 1.39-1.46 (m, 2H), 1.29-1.31 (m, 4H), 0.87 (t, 3H, $J$ = 7.0 Hz); $\delta_C$ (100 MHz, $CDCl_3$) 189.9, 150.7, 143.4, 131.0, 130.0, 128.3, 127.5, 125.0, 123.7, 123.5, 115.9, 114.7, 48.0, 31.3, 26.7, 26.5, 22.5, 13.9; *m/z* (FAB) 311.1341 ($M^+$, $C_{19}H_{21}NOS$ requires 311.1344).

**(*E*)-2-Cyano-3-(N-hexylphenothiazin-7-yl)acrylic acid (Pt-C6)**

A mixture of **S3-C6** (1.00 g, 3.21 mmol), cyanoacetic acid (355 mg, 4.17 mmol), and ammonium acetate (74 mg, 0.96 mmol) were placed in a three-necked flask in acetic acid under a nitrogen atmosphere with heating 100 °C for 12 h. After cooling, the reaction was quenched by adding water, and extracted with $CH_2Cl_2$. The organic layer was dried over anhydrous $MgSO_4$, and concentrated under reduced pressure to give the crude product. The product was purified by silica gel column chromatograph eluted with $CH_2Cl_2$/acetic acid (19/1). The deeply red solid was isolated in 70% yield (770 mg, 1.28 mmol), mp: 154~156 °C. Spectroscopic data of **Pt-C6**: $\delta_H$ (400 MHz, DMSO-$d_6$) 8.14 (s, 1H), 7.90 (d, 1H, $J$ = 8.7 Hz), 7.79 (d, 1H, $J$ = 1.7 Hz), 7.22 (t, 1H, $J$ = 8.0 Hz), 7.13-7.16 (m, 2H), 7.06 ( d, 1H, $J$ = 8.2 Hz), 6.99 (t, 1H, $J$ = 7.4 Hz), 3.92 (t, 2H, $J$ = 7.2 Hz), 1.63-1.70 (m, 2H), 1.34-1.39 (m, 2H), 1.22-1.24 (m, 4H), 0.81 (t, 3H, $J$ = 6.8 Hz); $\delta_C$ (100 MHz, DMSO-$d_6$) 163.8, 152.2, 148.8, 142.7, 131.5, 129.0, 128.0, 127.3, 125.6, 123.6, 123.2, 122.1, 116.9, 116.4, 115.6, 100.0, 46.9, 30.7, 26.0, 25.7, 22.0, 13.8; *m/z* (FAB) 378.1400 ($M^+$, $C_{22}H_{22}N_2O_2S$ requires 378.1402).

## 2. $^{1}$H and $^{13}$C NMR spectra

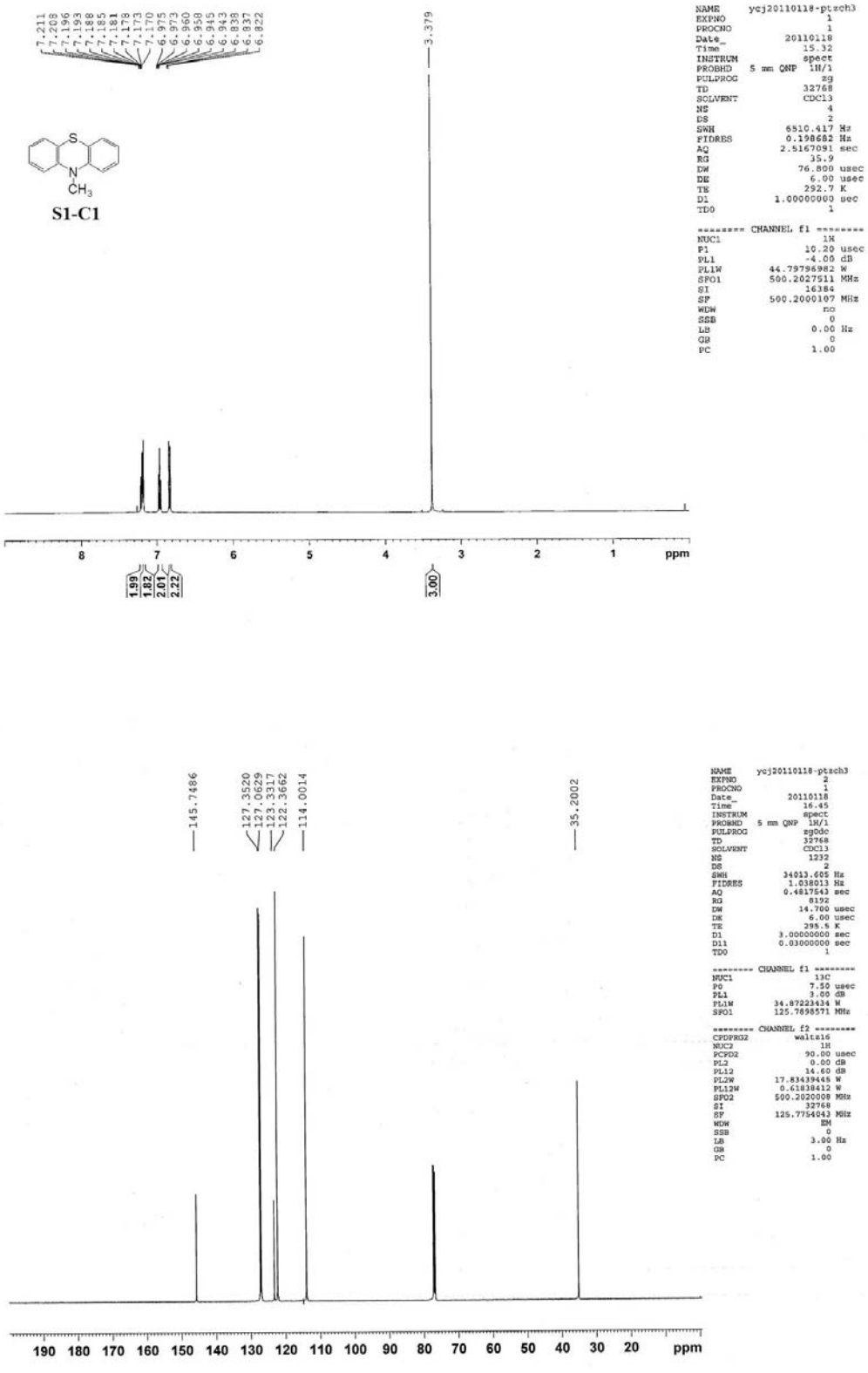



**Figure S1:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **S1-C1** in $CDCl_3$.

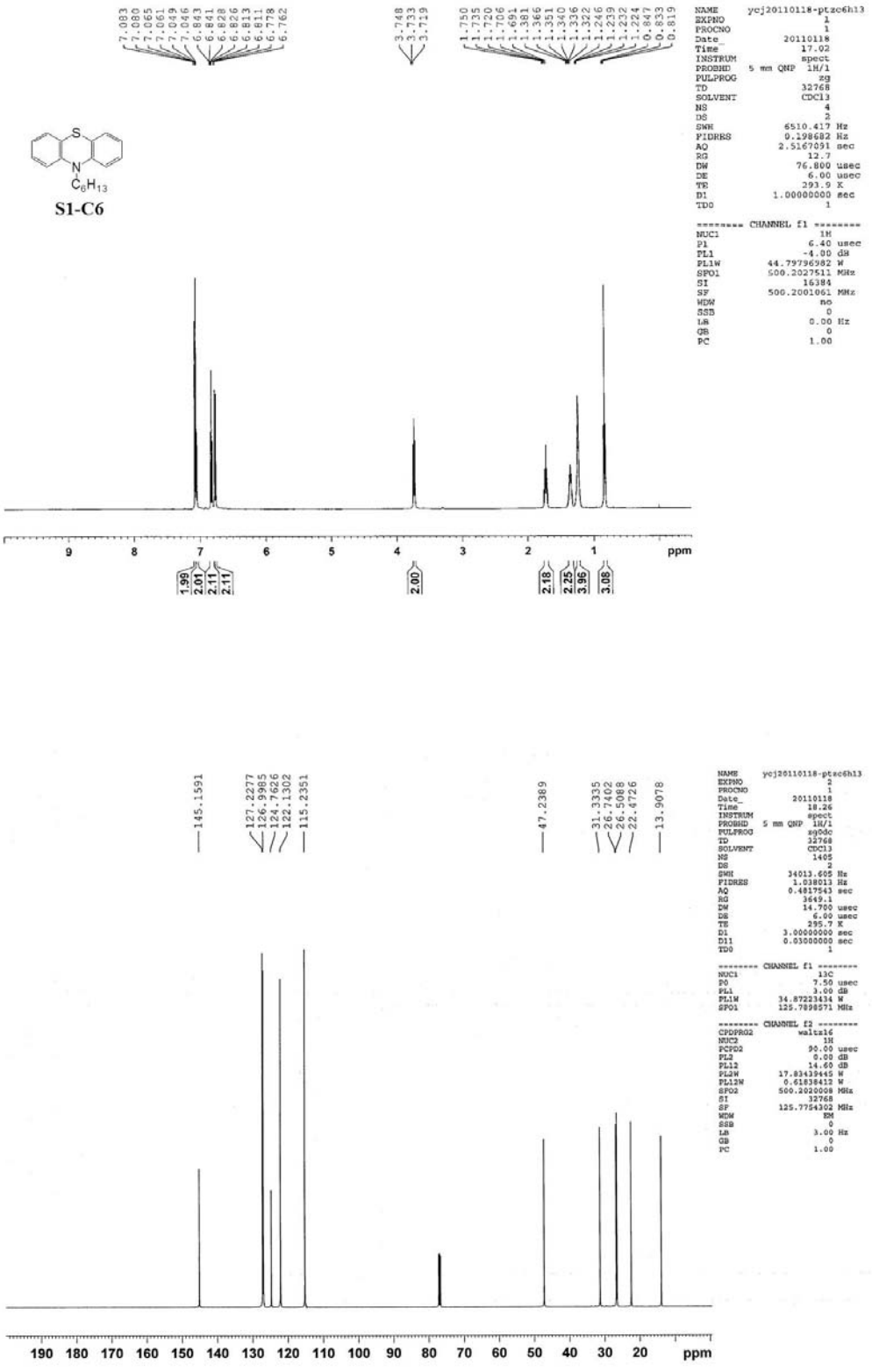



**Figure S2:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **S1-C6** in $CDCl_3$.

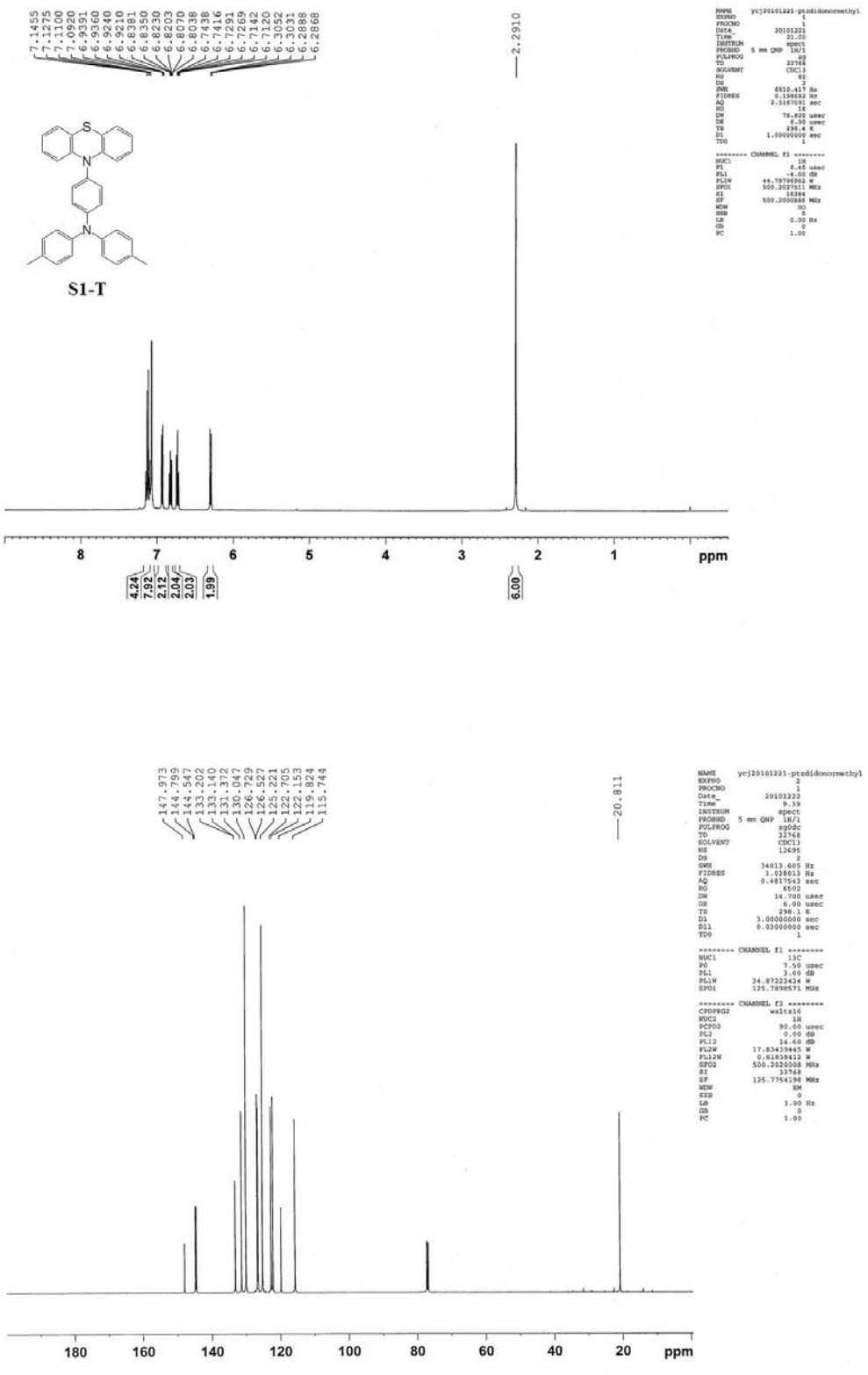



**Figure S3:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **S1-T** in $CDCl_3$.

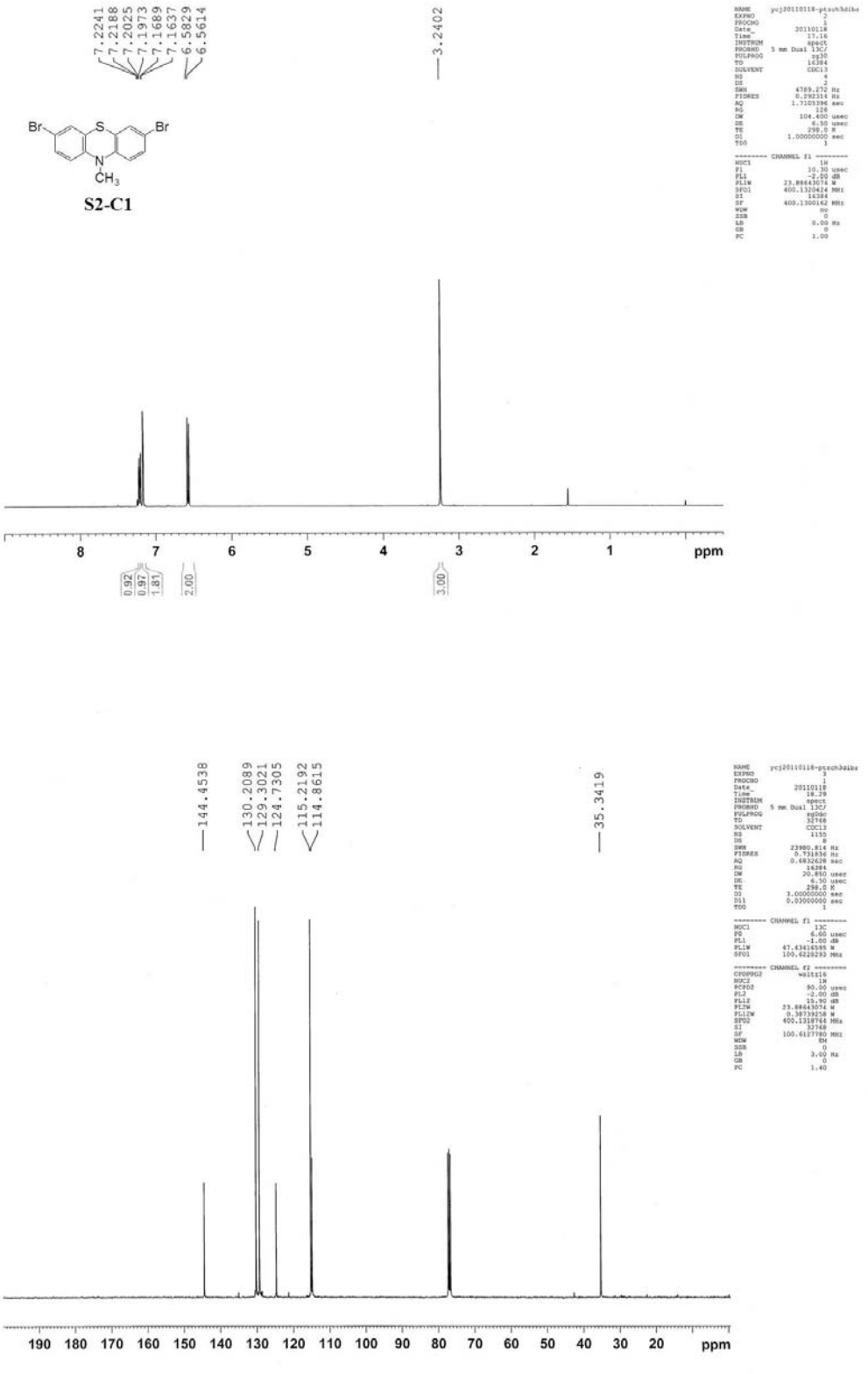



**Figure S4:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **S2-C1** in $CDCl_3$.

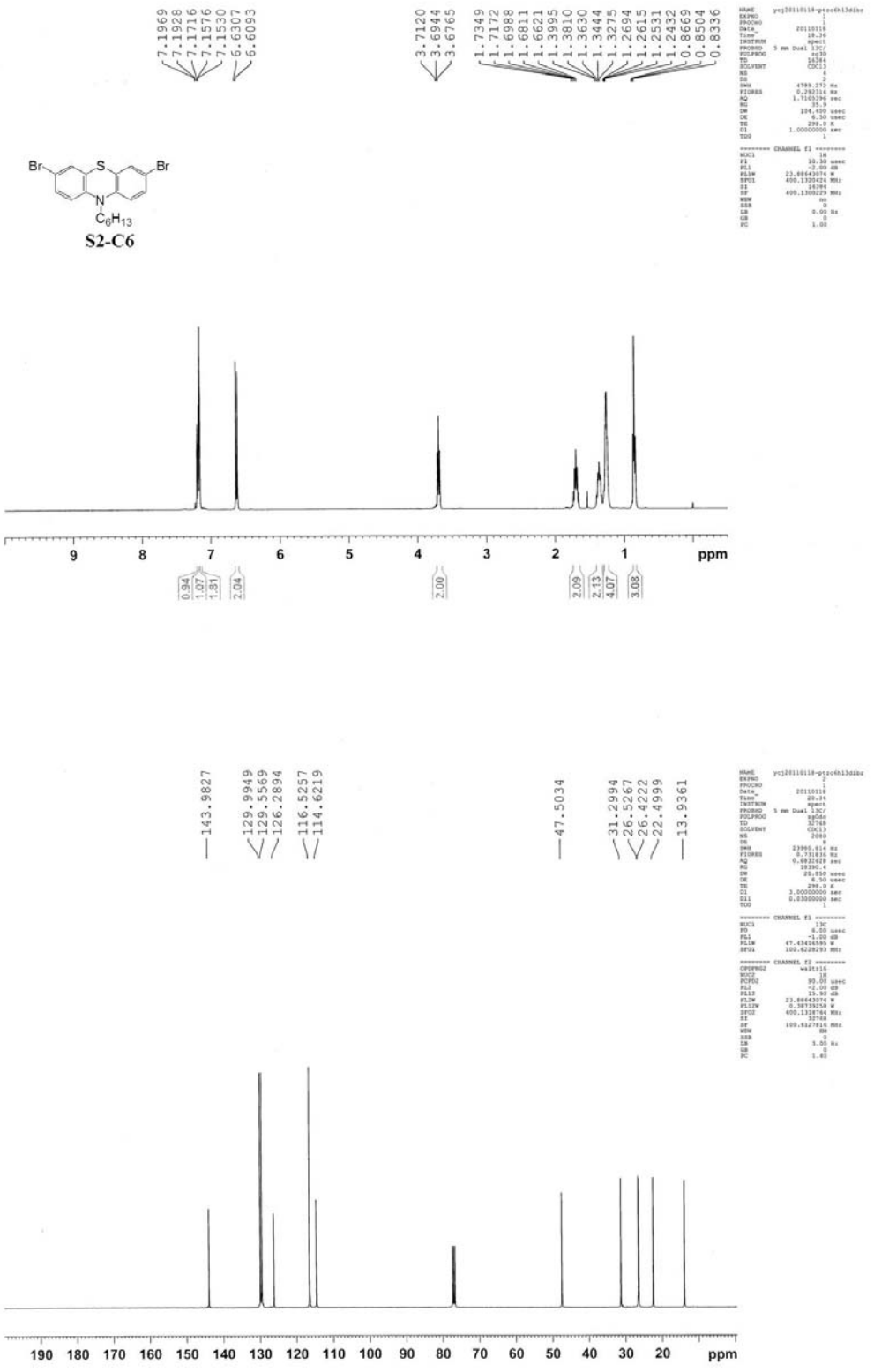



**Figure S5:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **S2-C6** in $CDCl_3$.

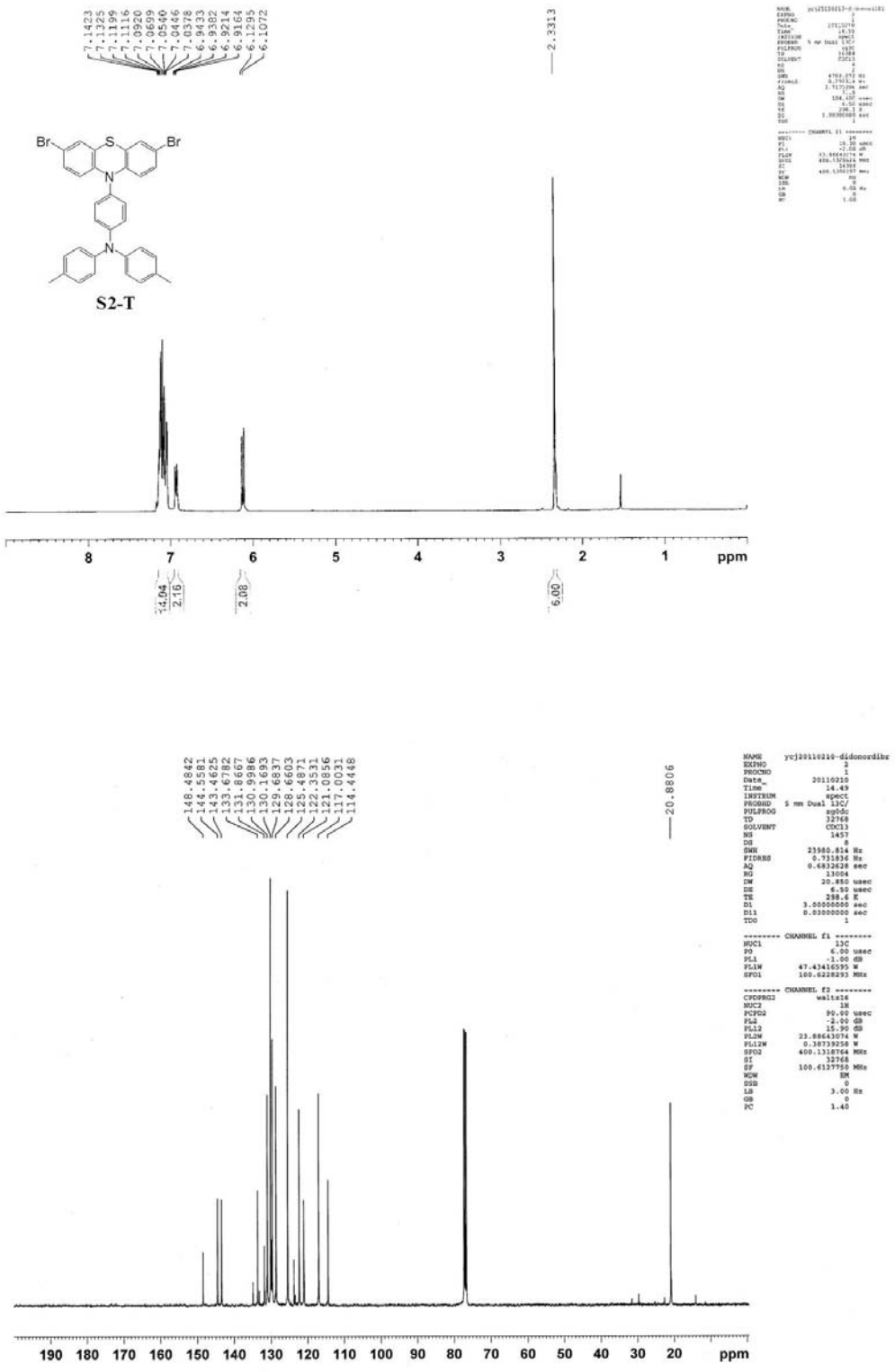



**Figure S6:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **S2-T** in $CDCl_3$.

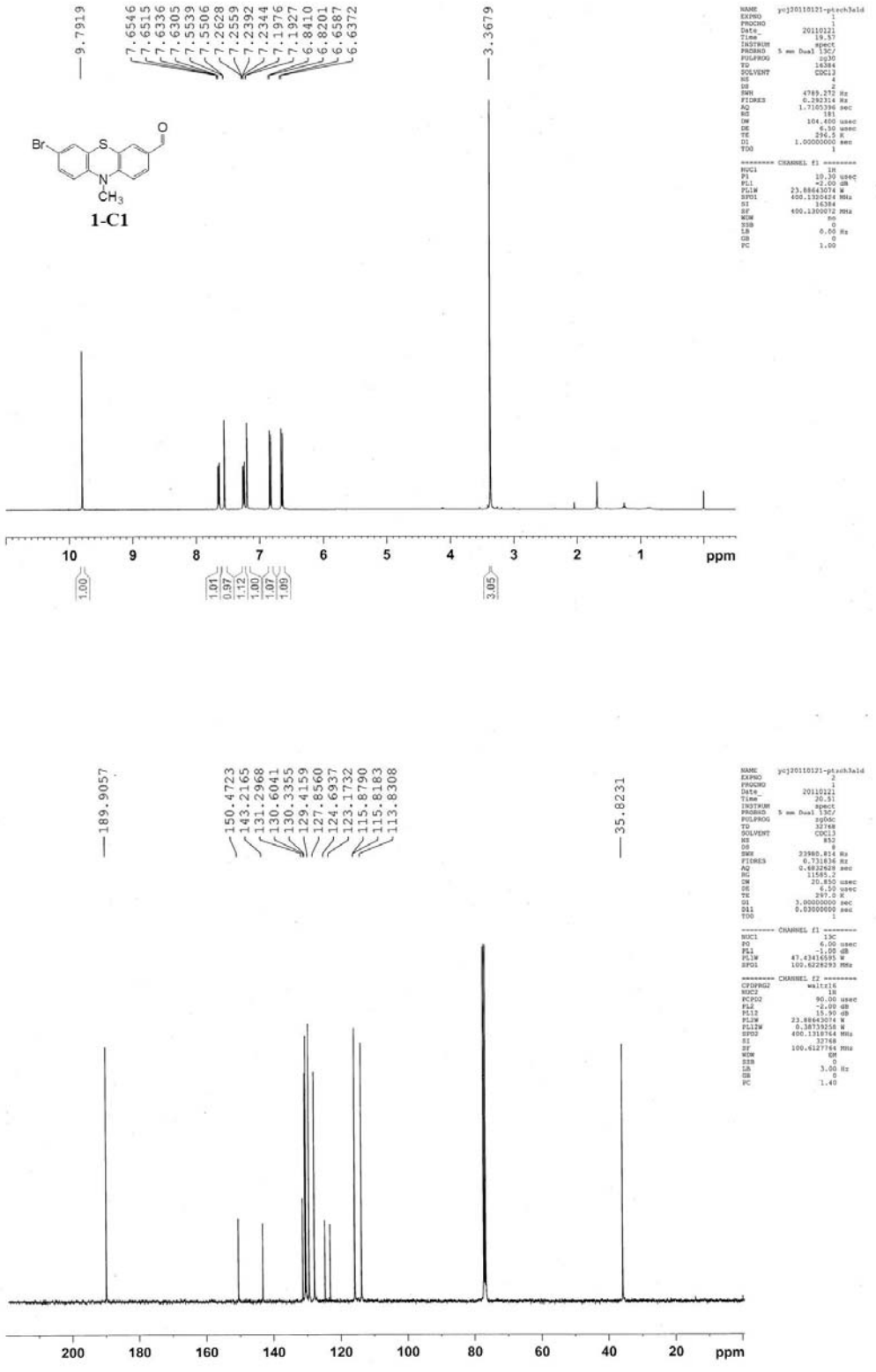



**Figure S7:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **1-C1** in $CDCl_3$.

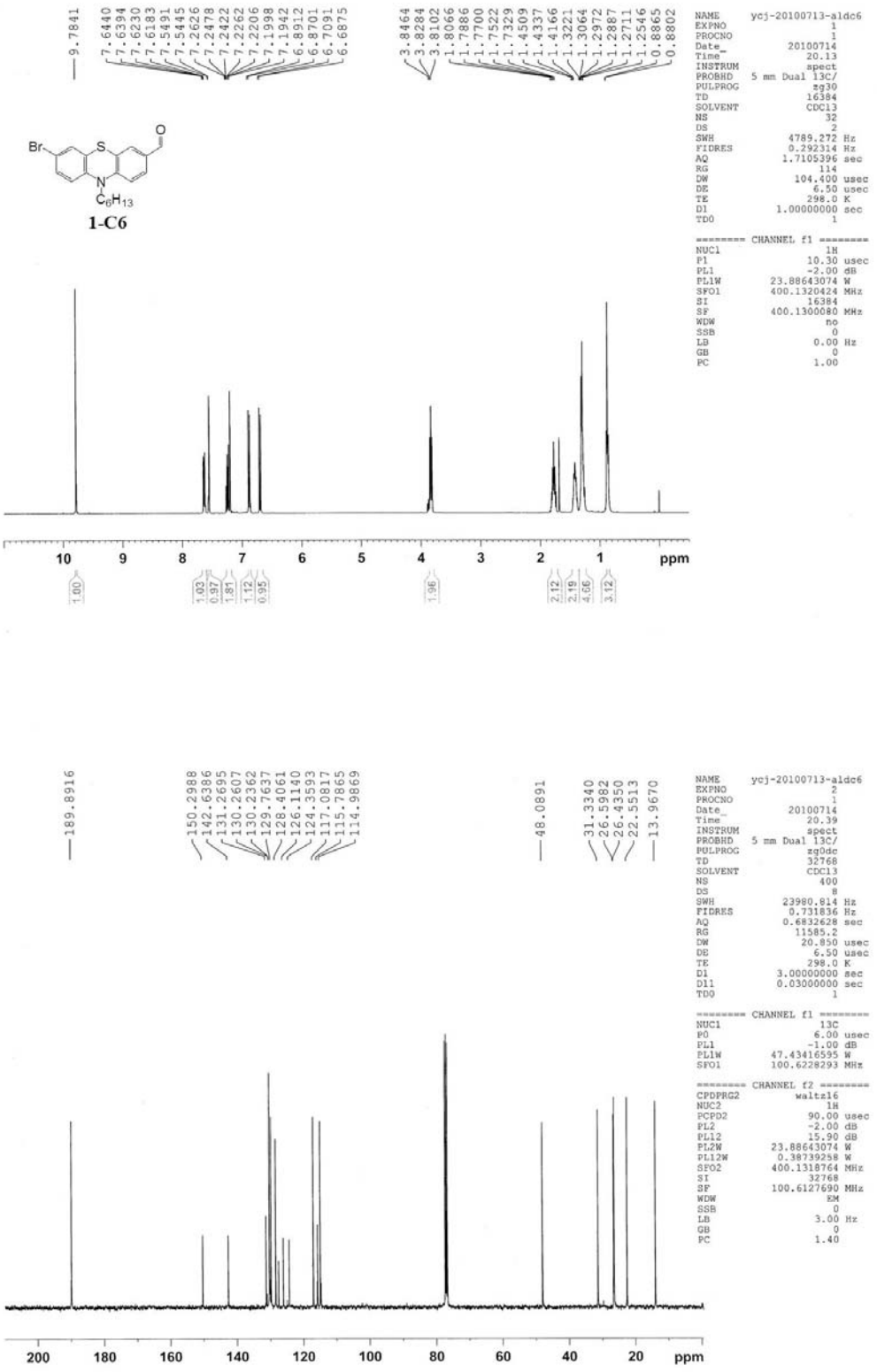



**Figure S8:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **1-C6** in $CDCl_3$.

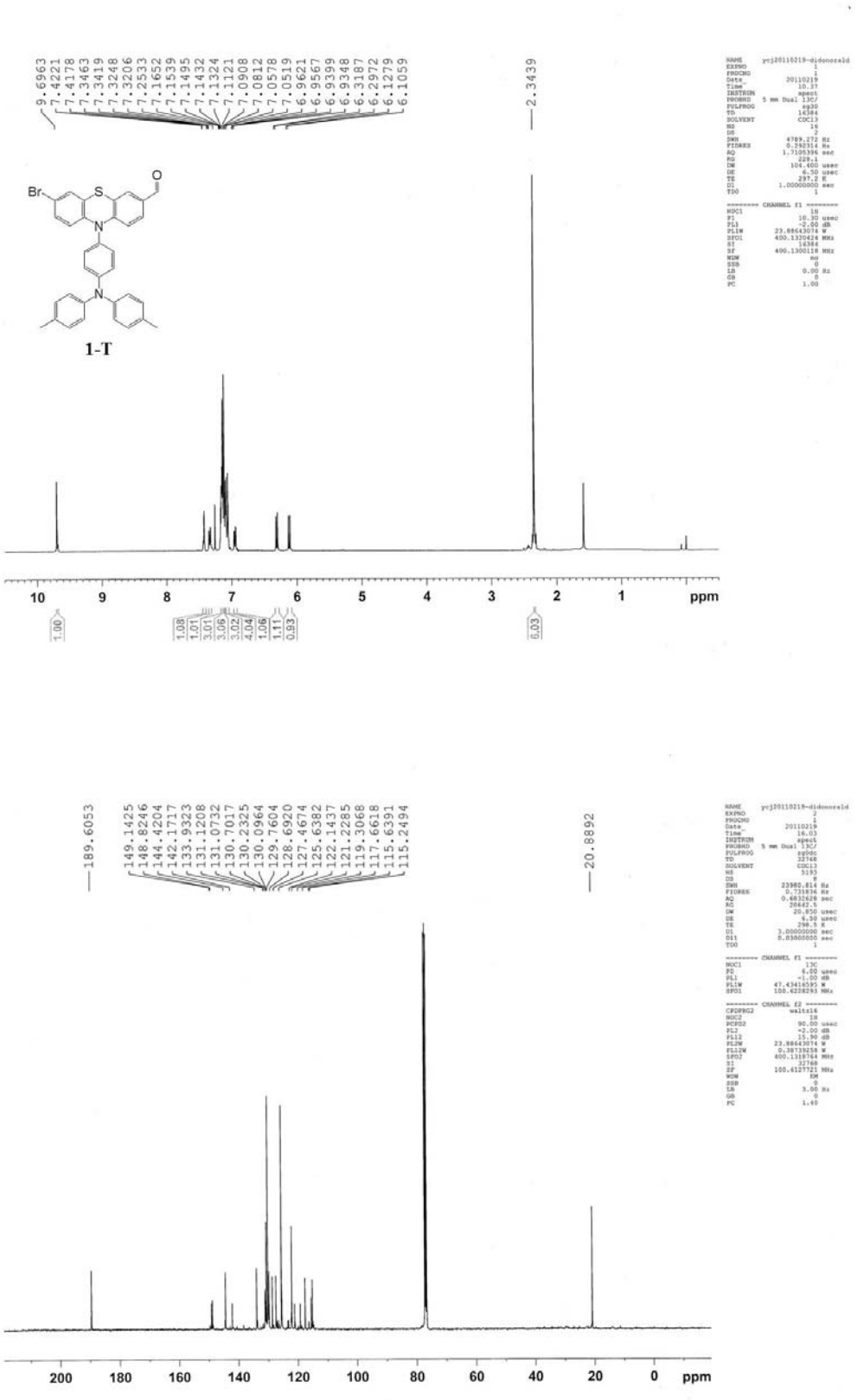



**Figure S9:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **1-T** in $CDCl_3$.

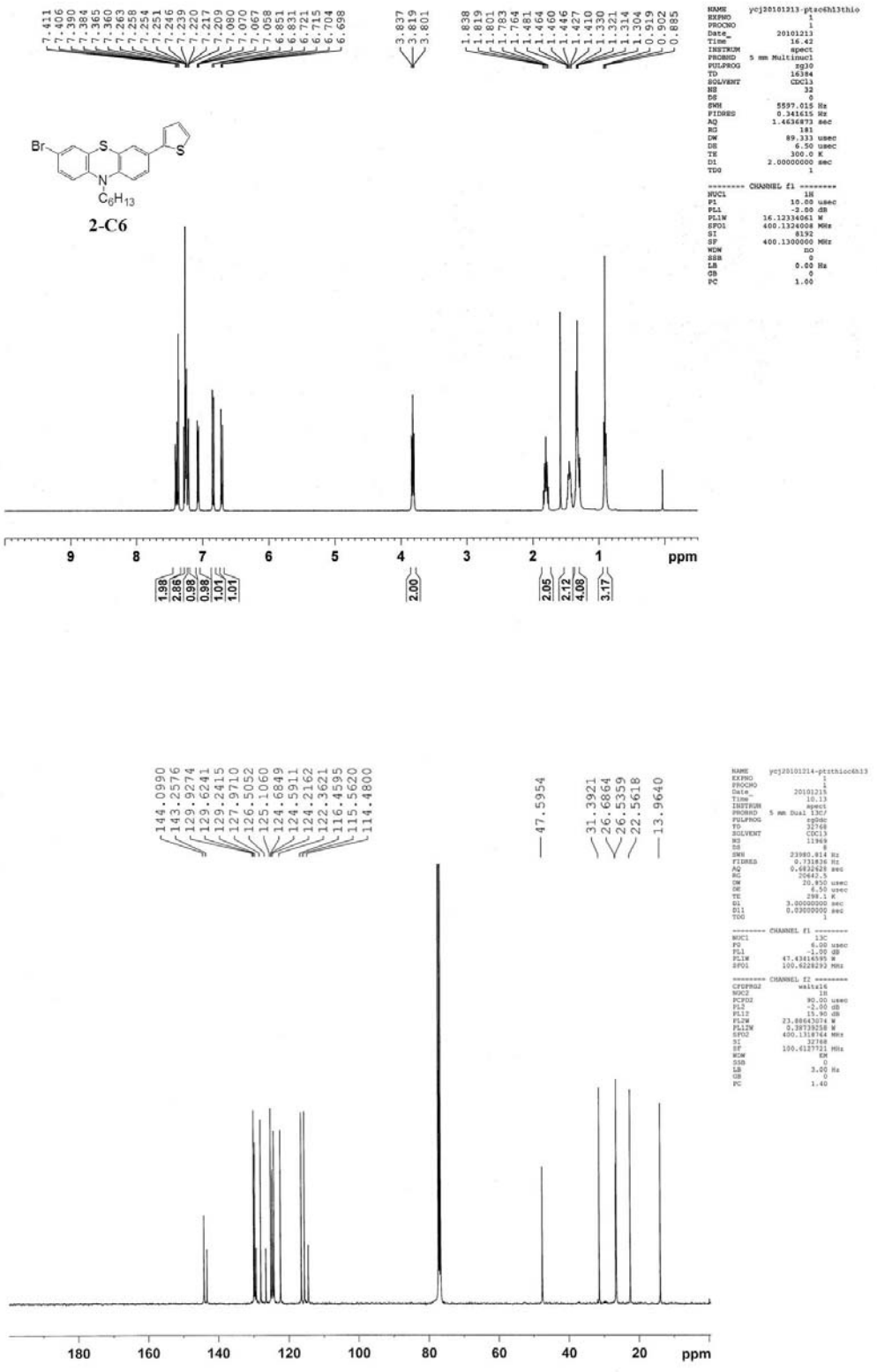



**Figure S10:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **2-C6** in $CDCl_3$.

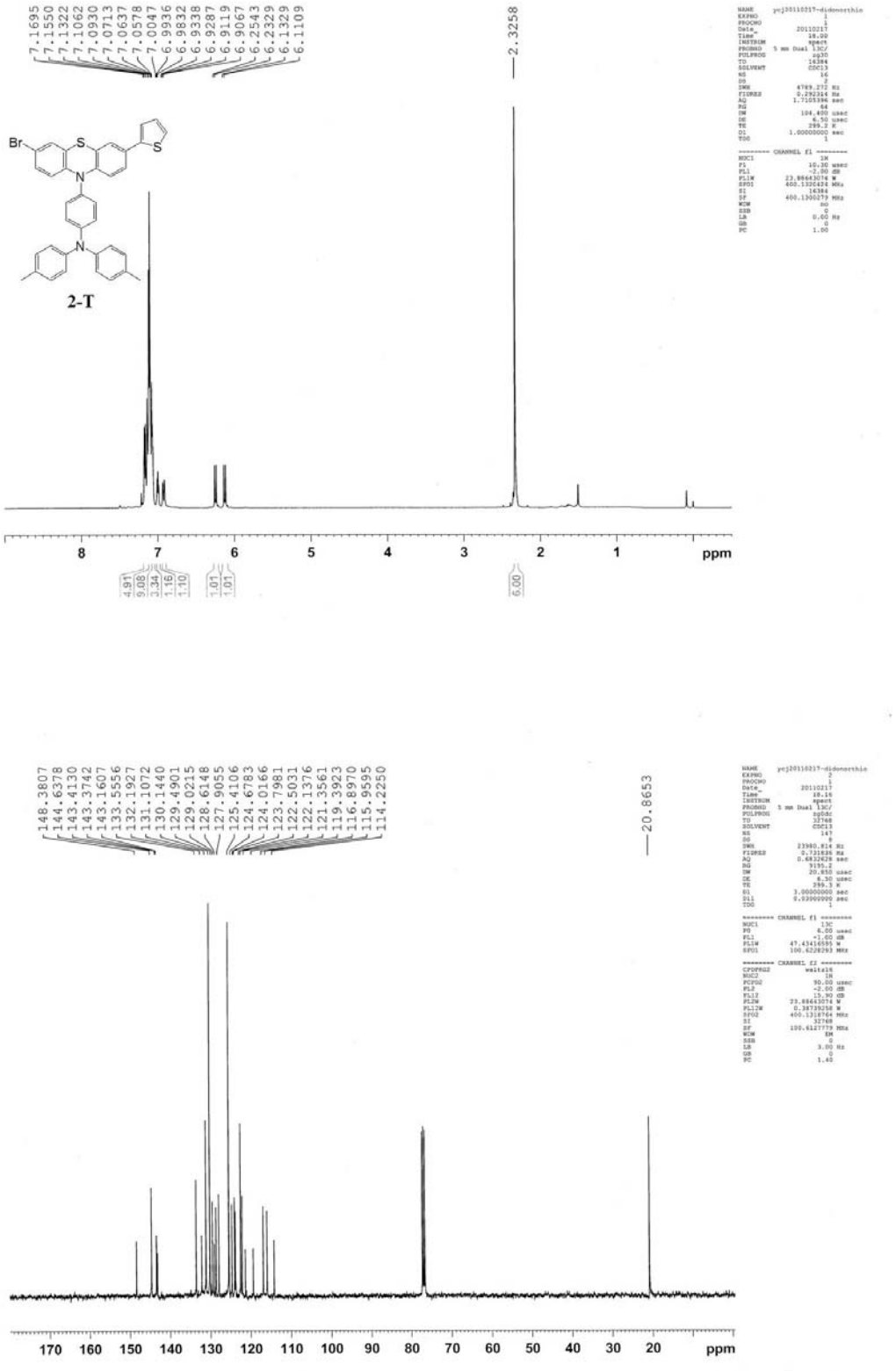



**Figure S11:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **2-T** in $CDCl_3$.

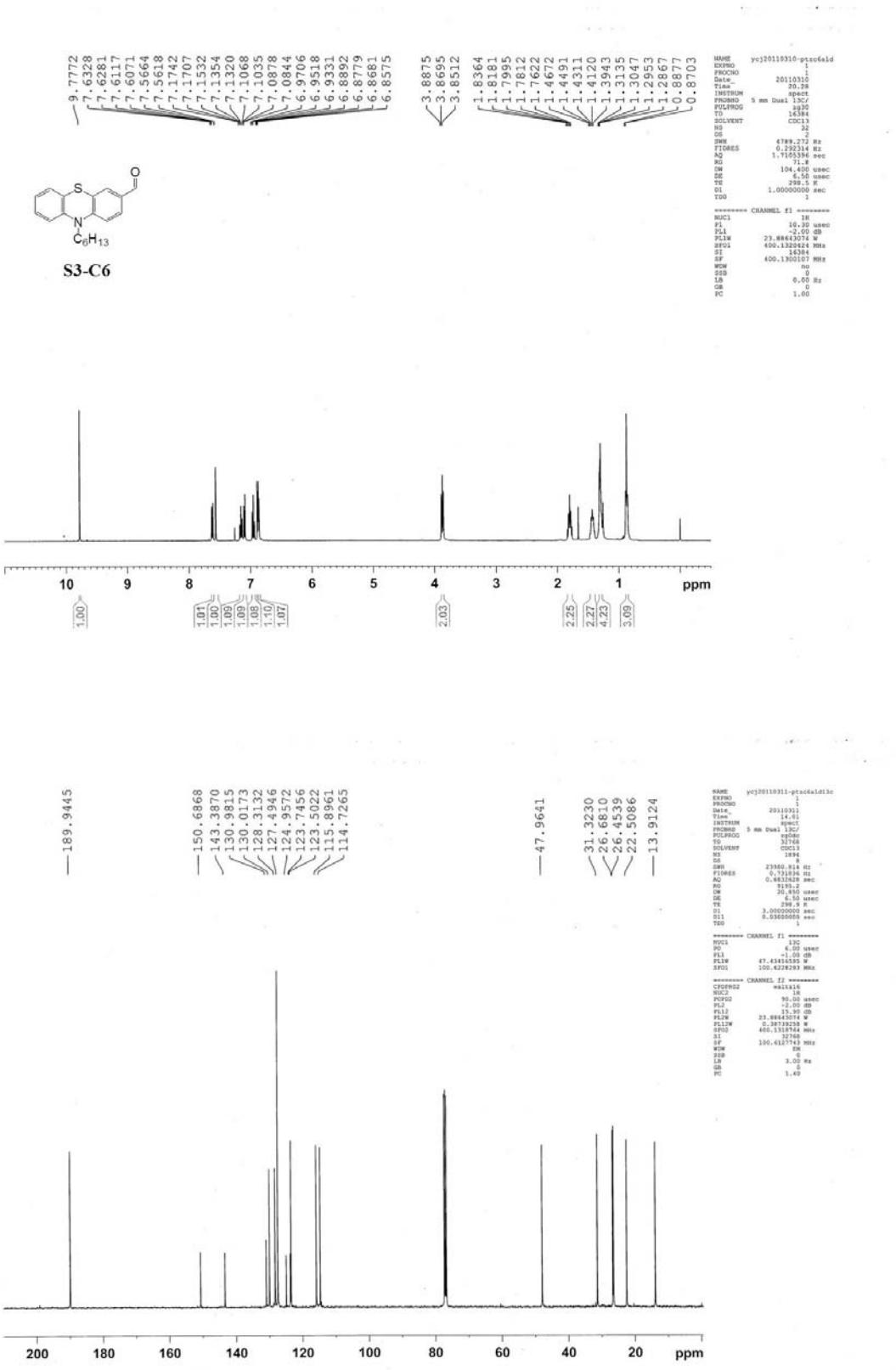



**Figure S12:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **S3-C6** in $CDCl_3$.

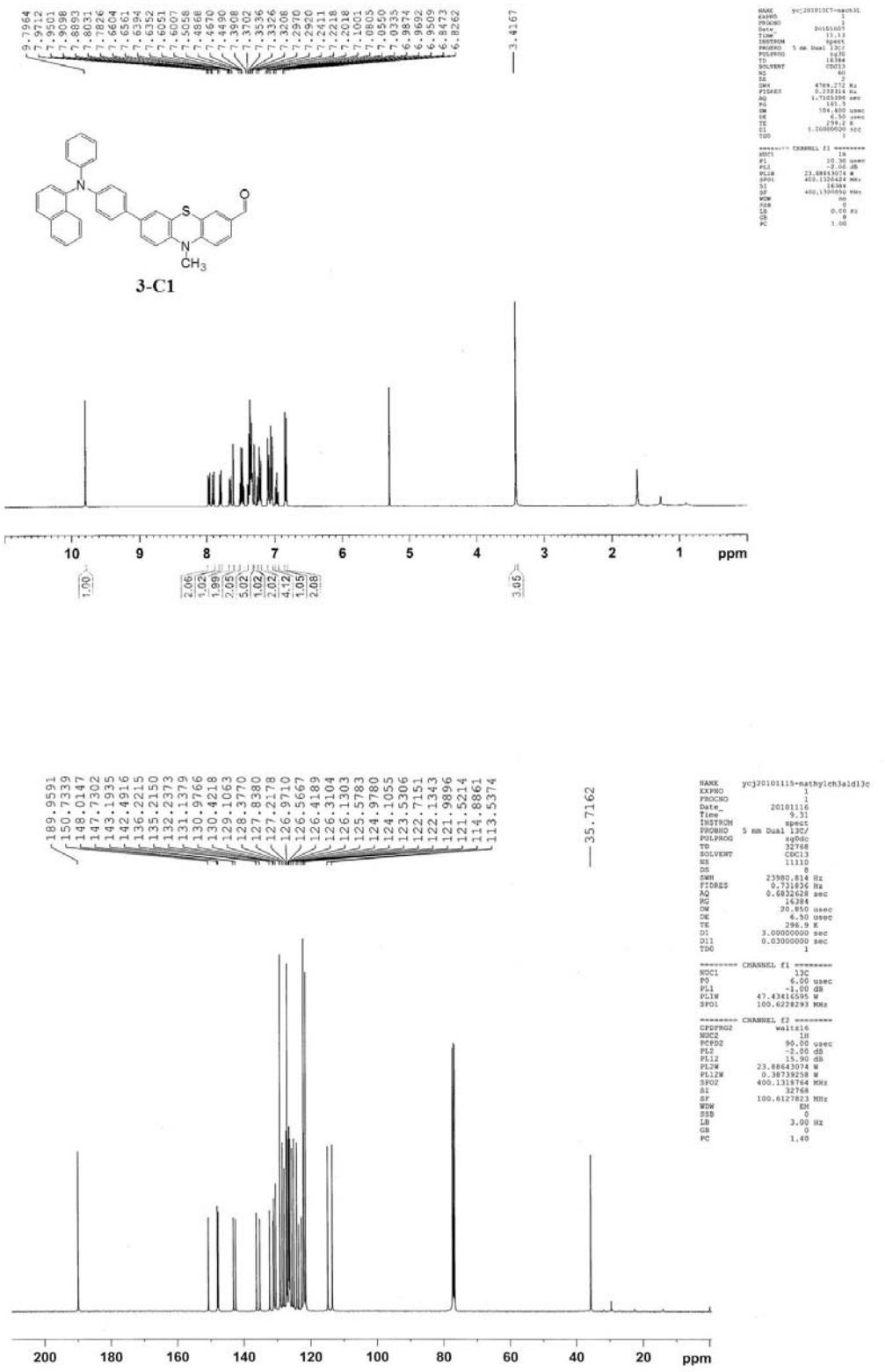



**Figure S13:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **3-C1** in $CDCl_3$.

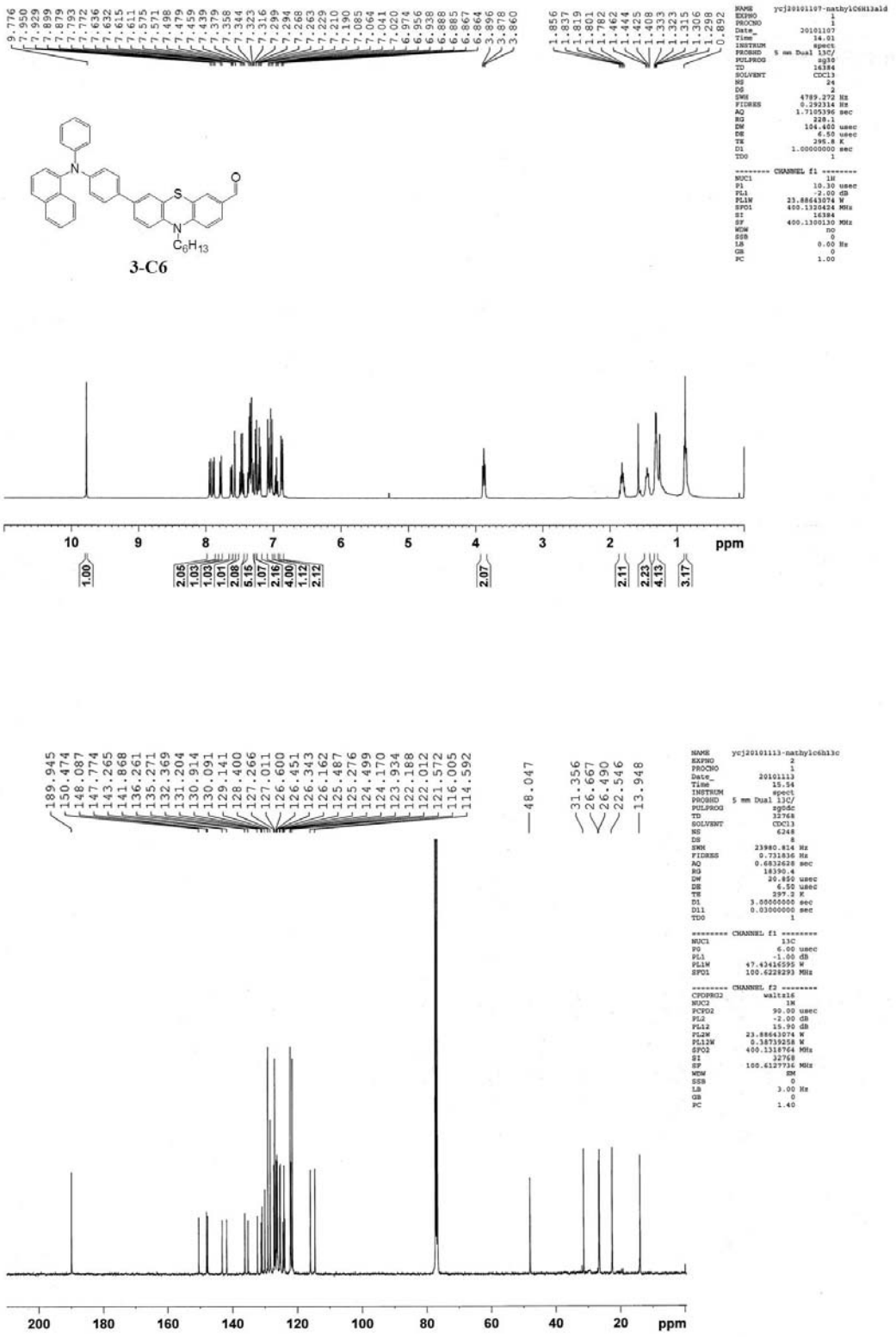



**Figure S14:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **3-C6** in $CDCl_3$.

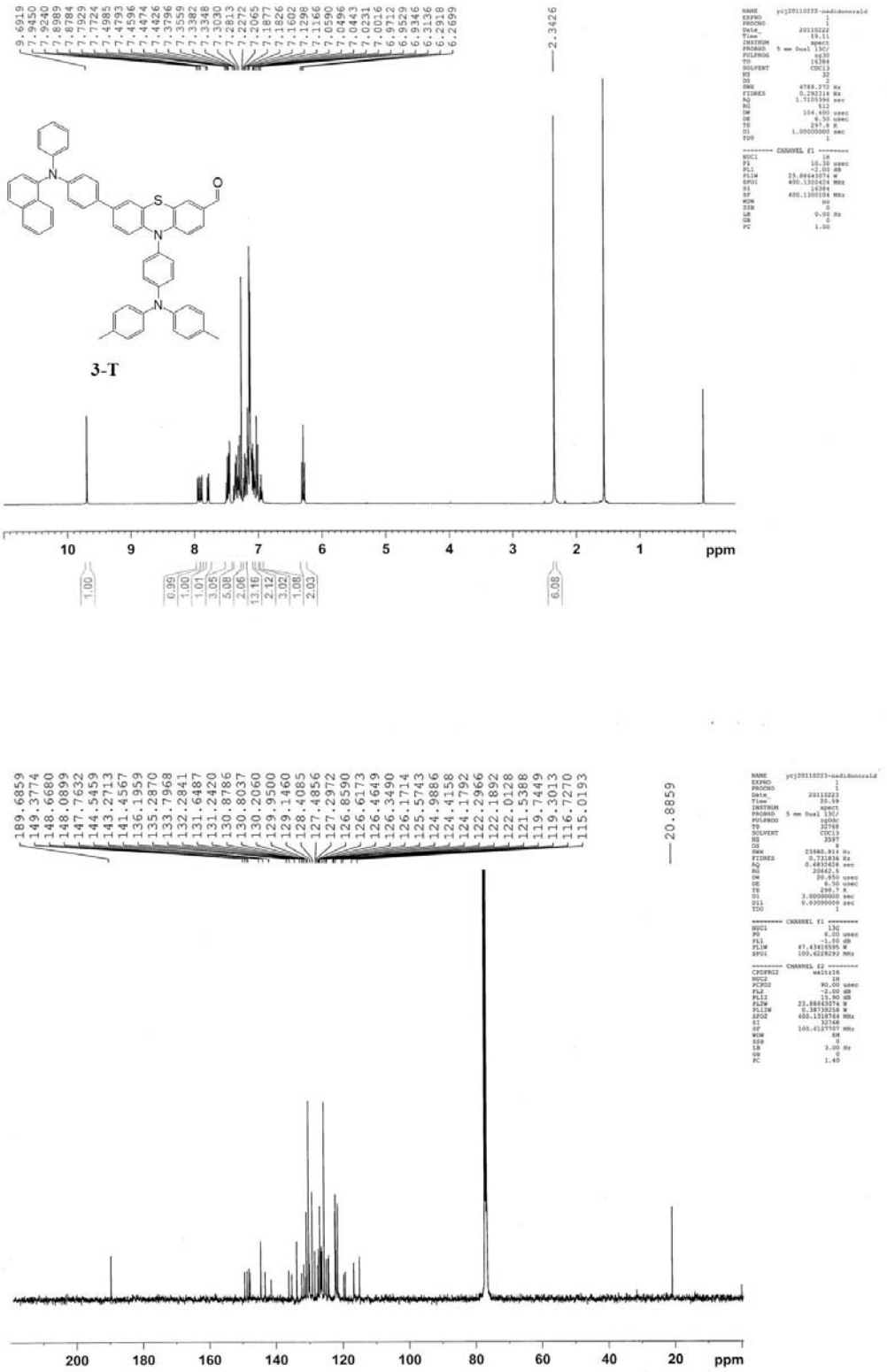



**Figure S15:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **3-T** in $CDCl_3$.

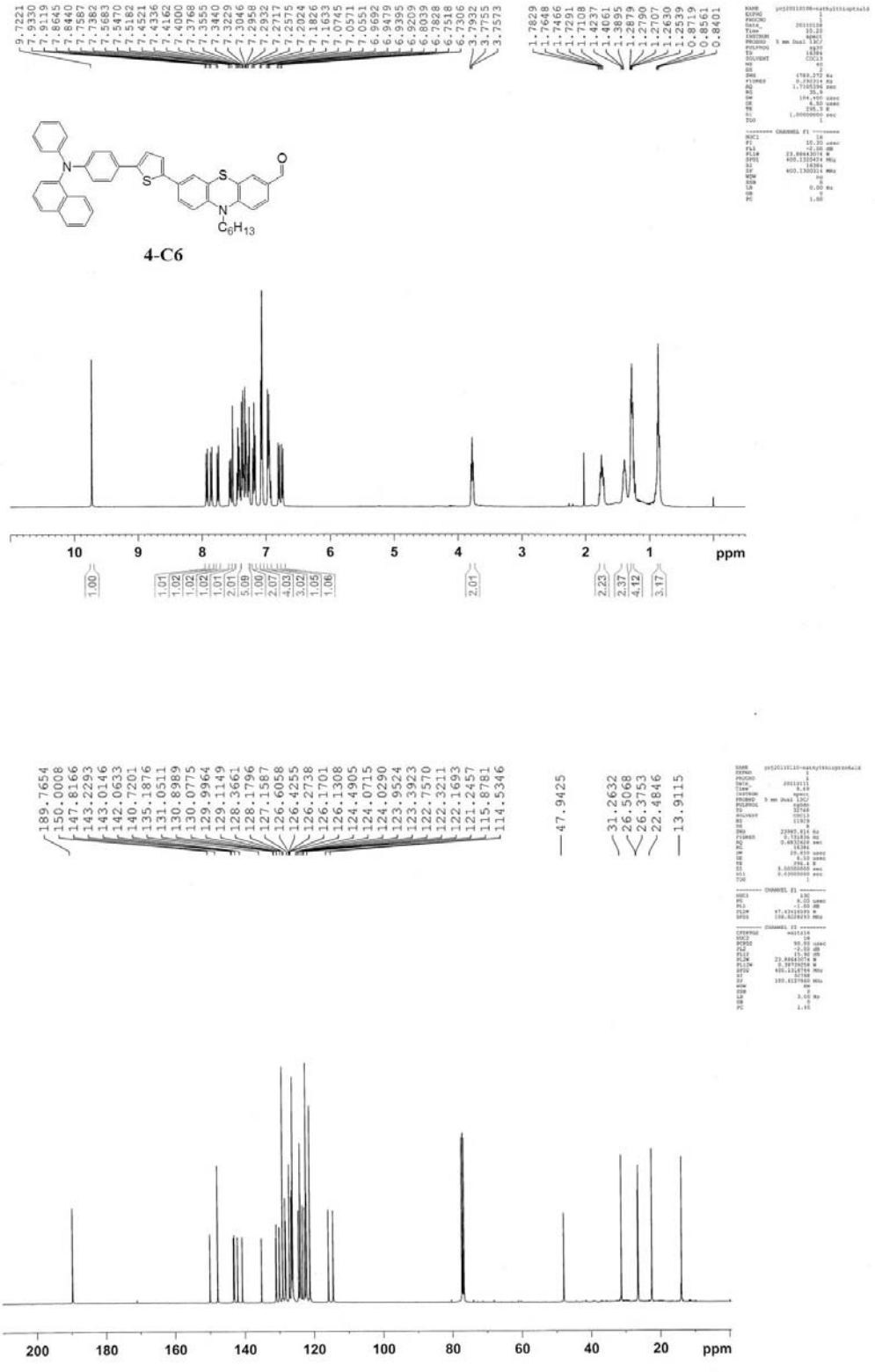



**Figure S16:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **4-C6** in $CDCl_3$.

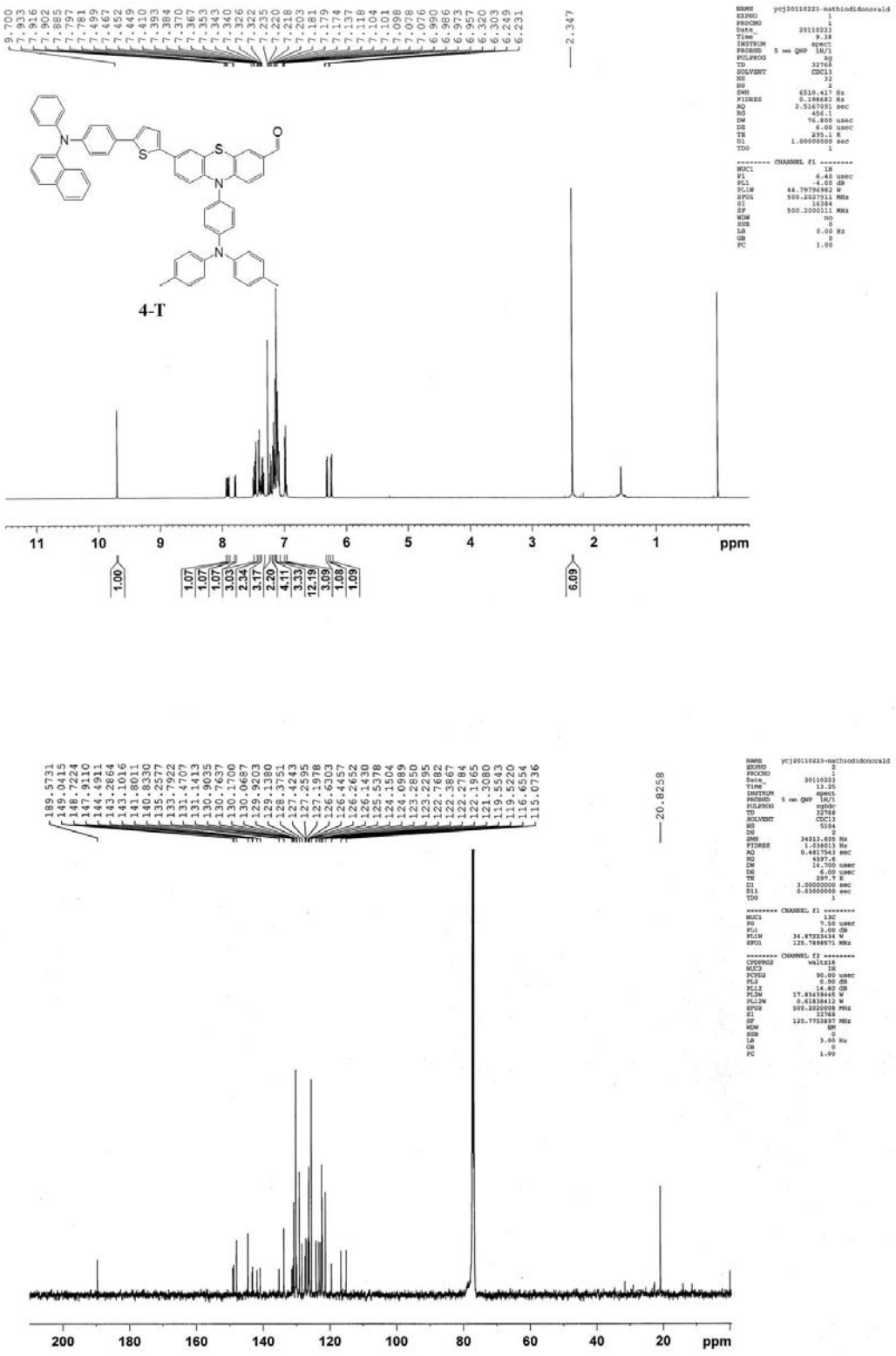



**Figure S17:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **4-T** in $CDCl_3$.

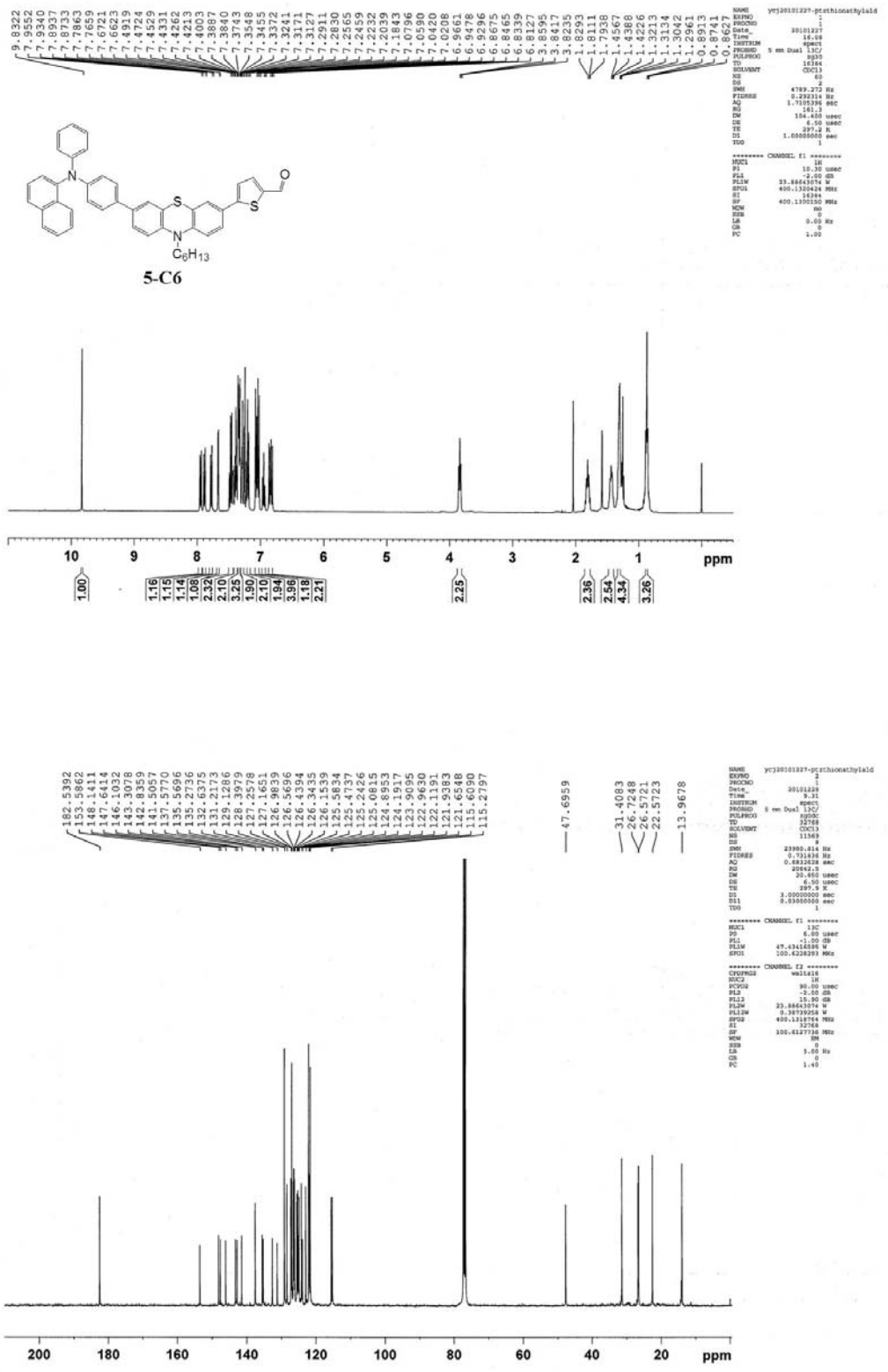



**Figure S18:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **5-C6** in $CDCl_3$.

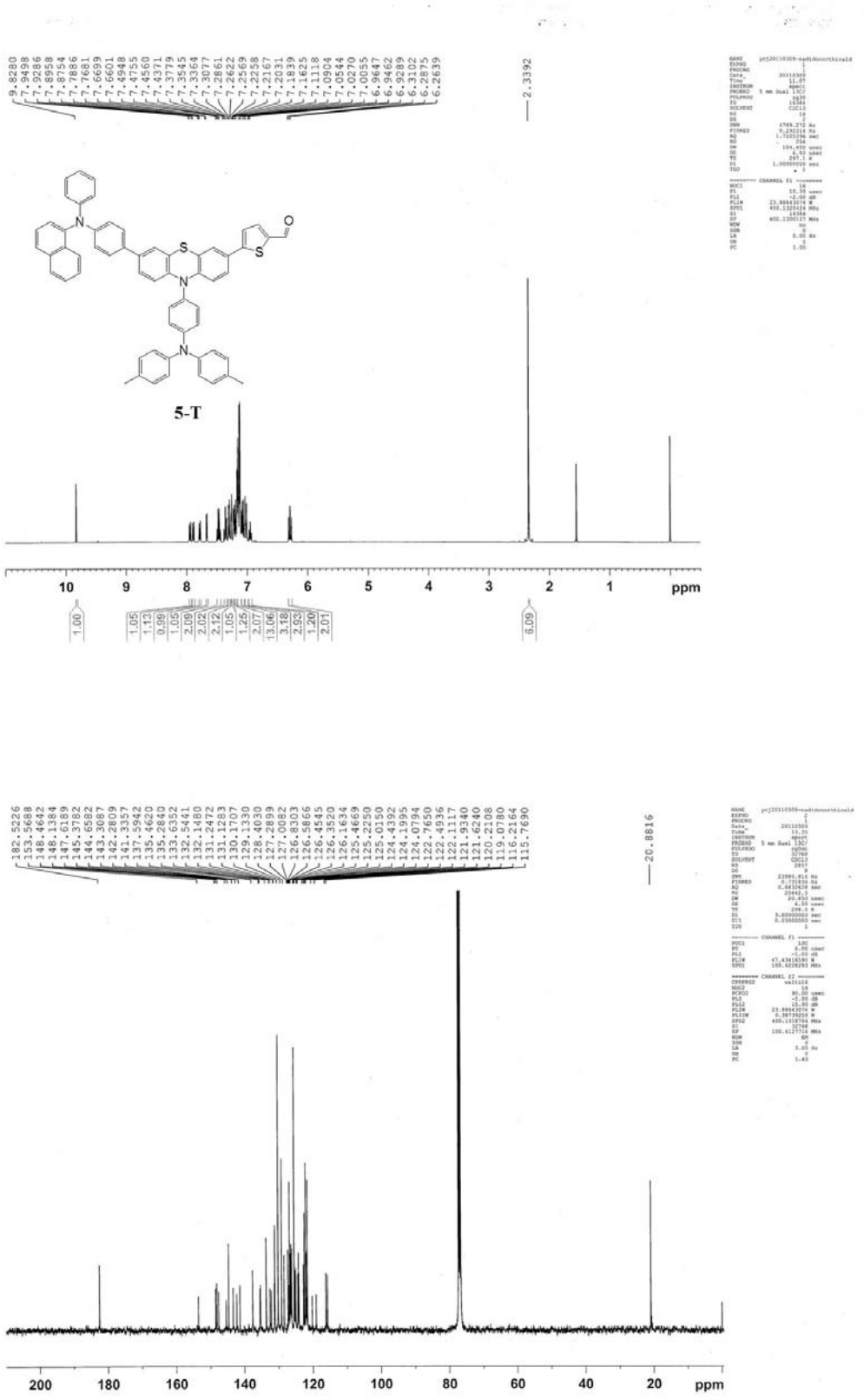



**Figure S19:** $^{1}H$ NMR (upper) and $^{13}C$ NMR (lower) spectra of **5-T** in $CDCl_3$.

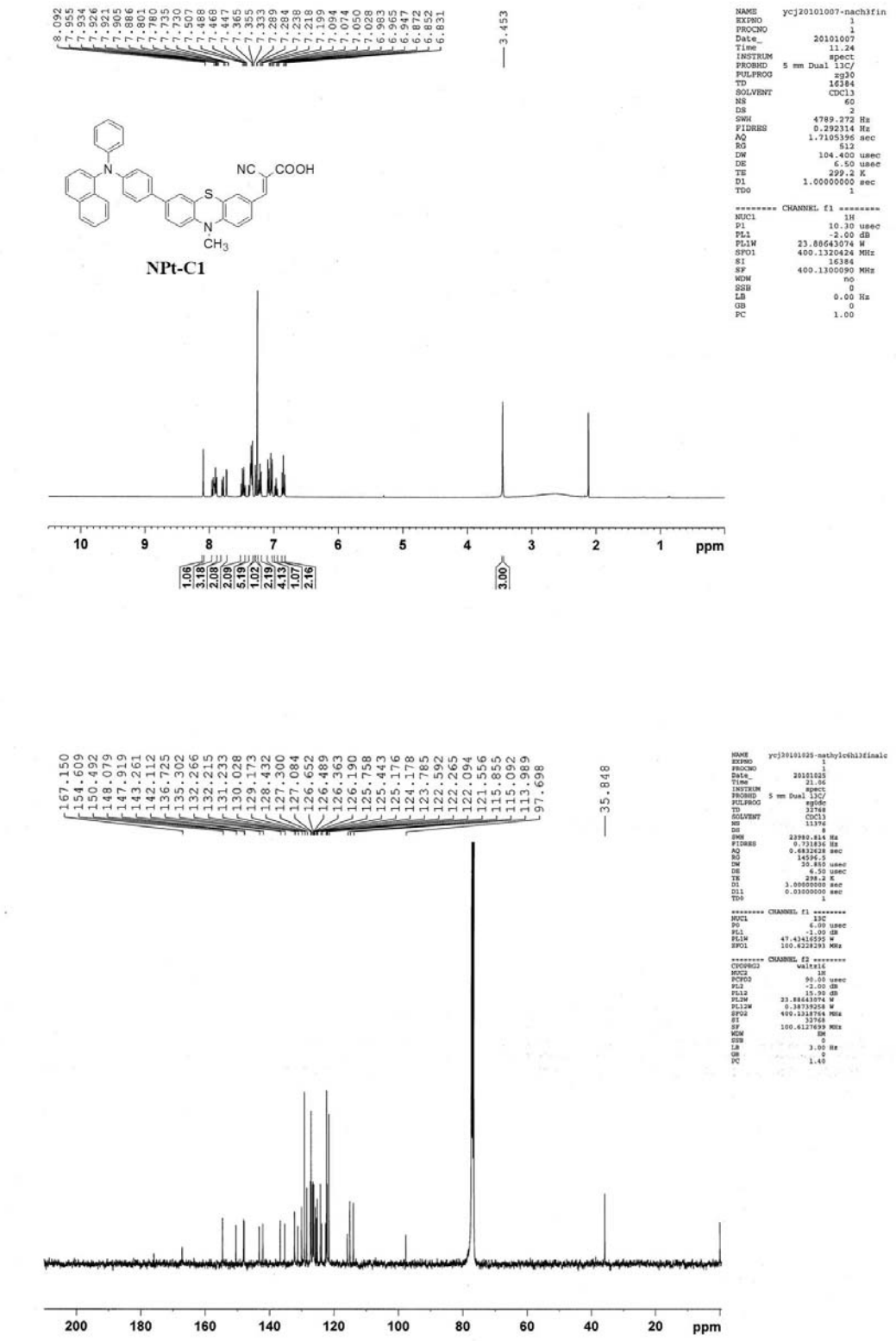



**Figure S20:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NPt-C1** in $CDCl_3$.

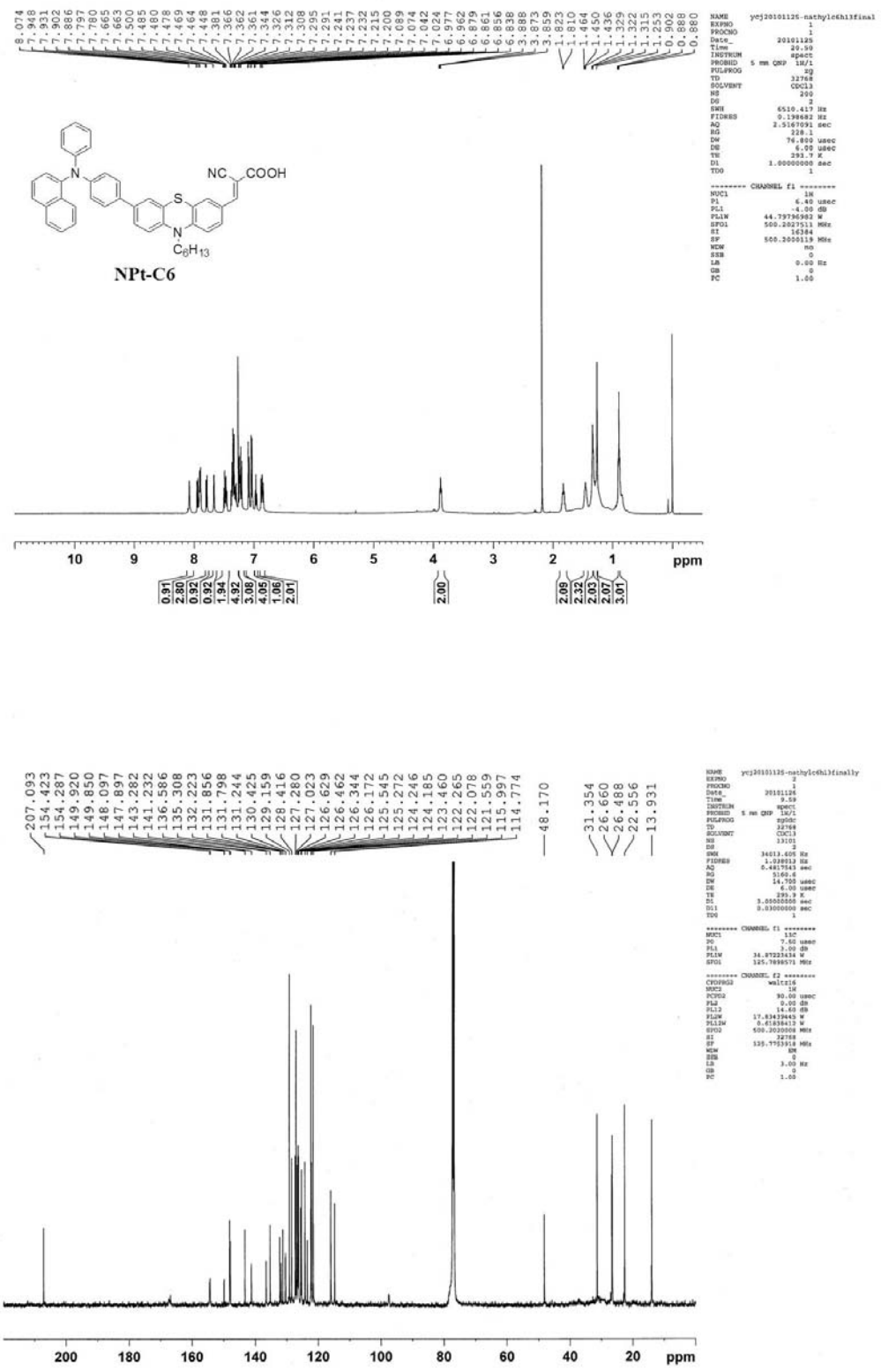



**Figure S21:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NPt-C6** in $CDCl_3$.

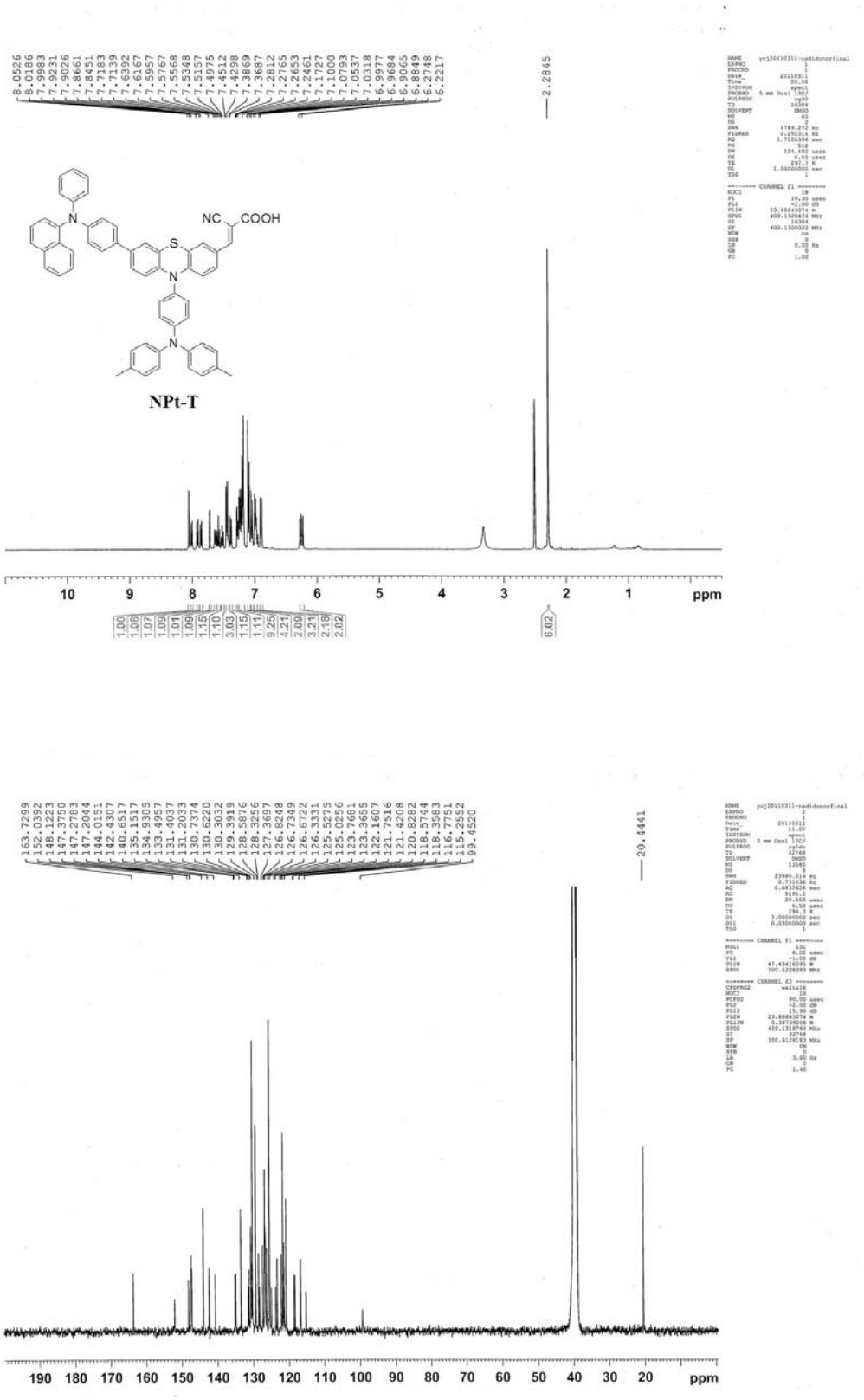



**Figure S22:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NPt-T** in DMSO-$d_6$.

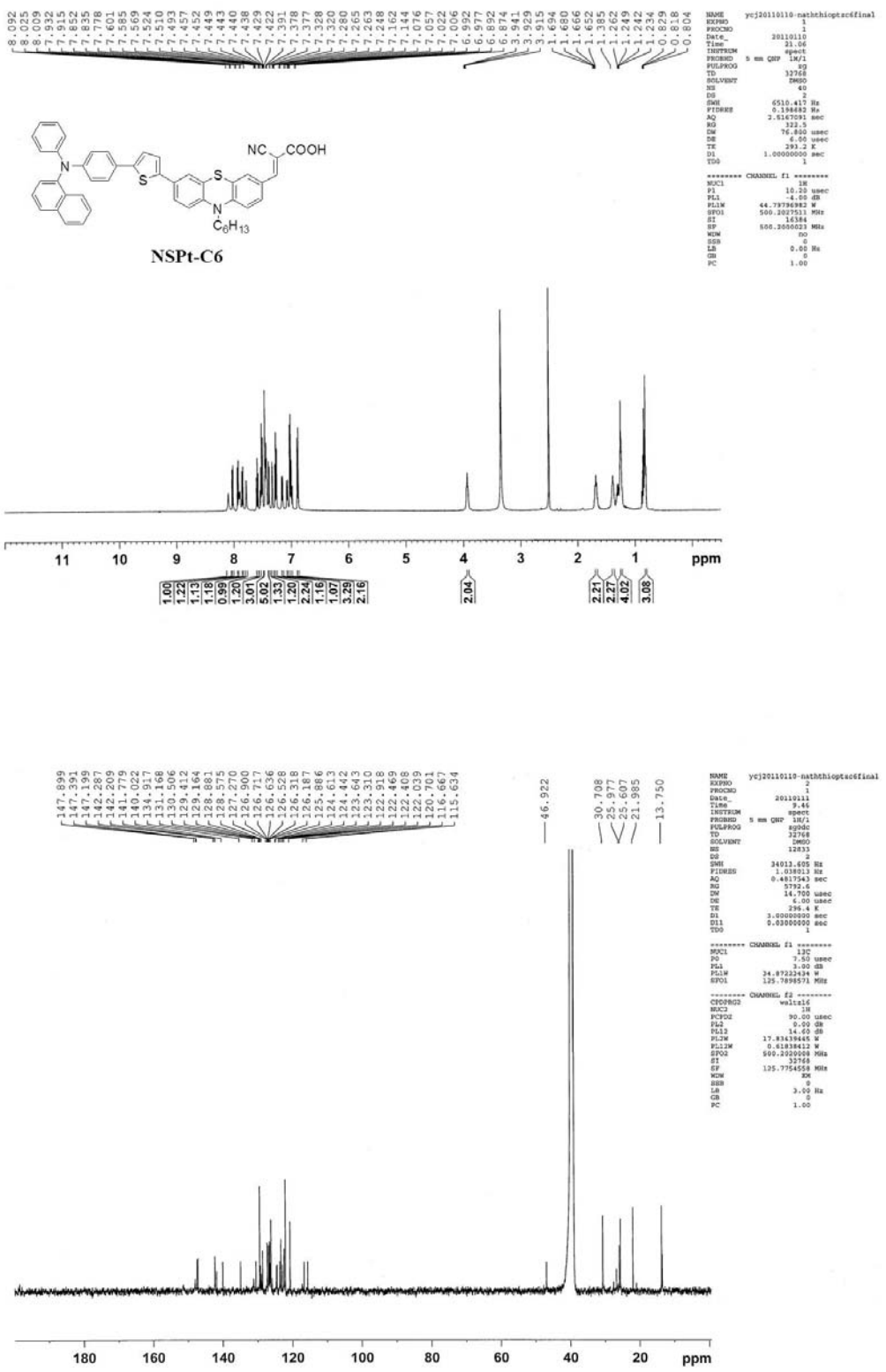



**Figure S23:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NSPt-C6** in DMSO-$d_6$.

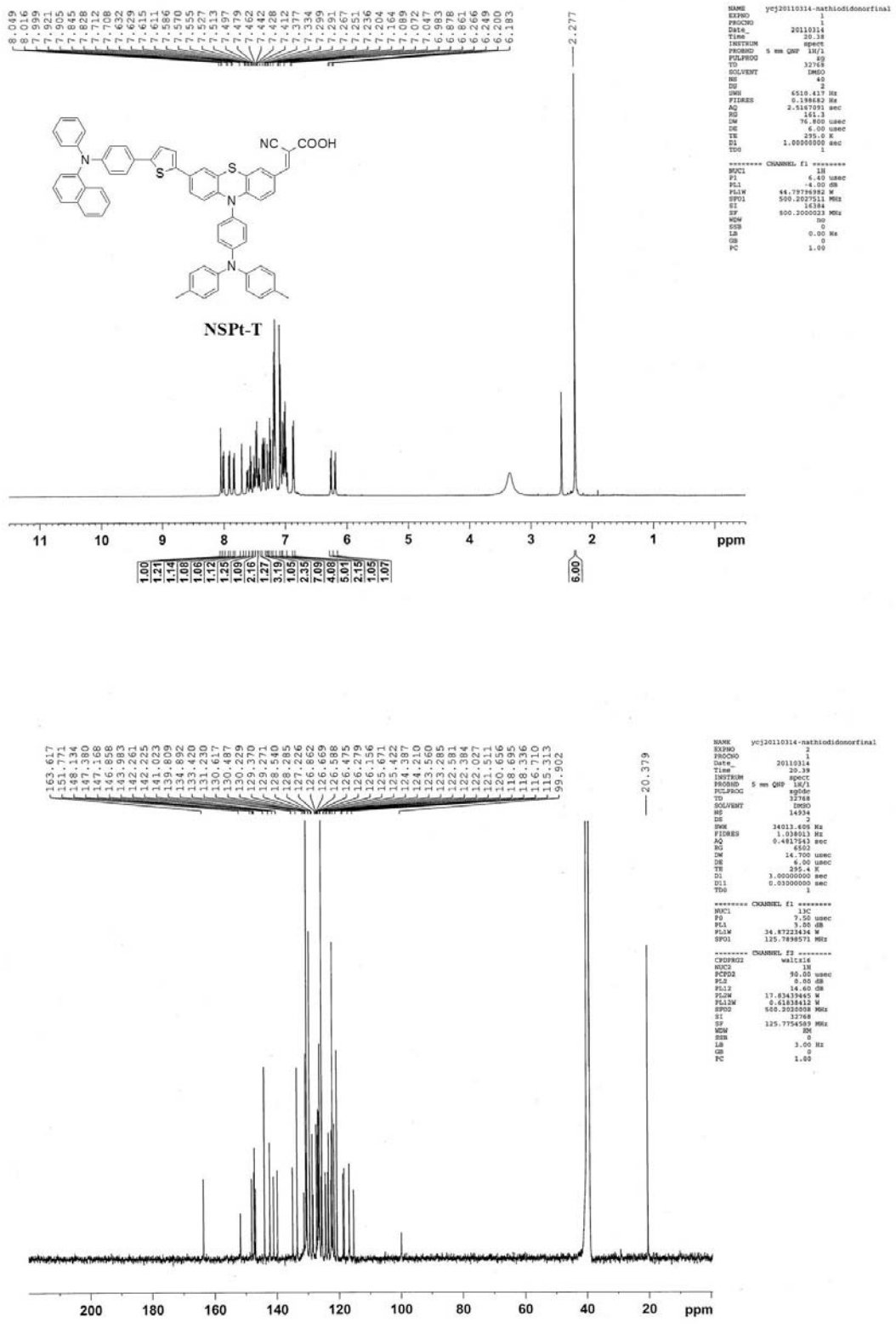



**Figure S24:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NSPt-T** in DMSO-$d_6$.

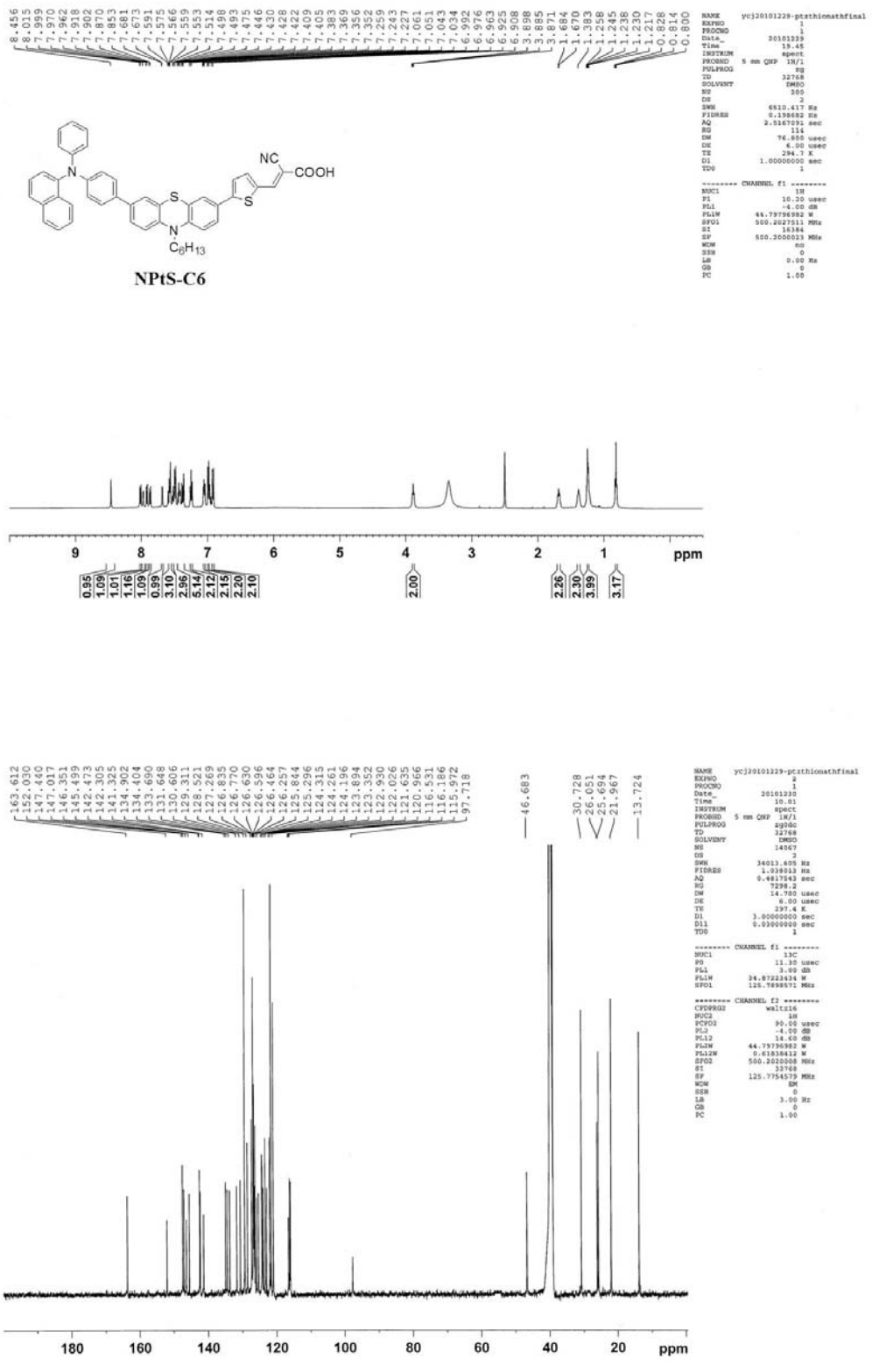



**Figure S25:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NPtS-C6** in DMSO-$d_6$.

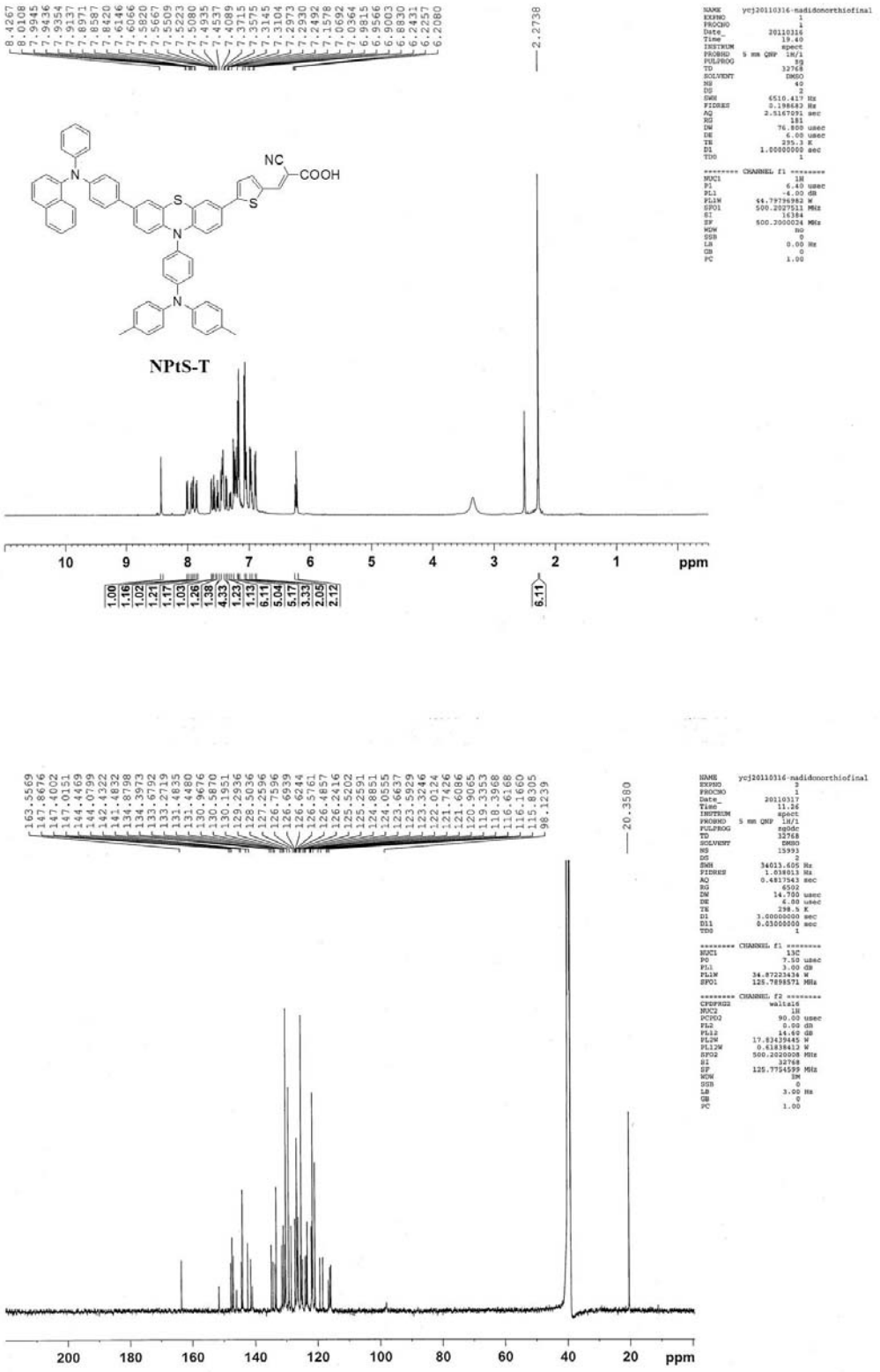



**Figure S26:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **NPtS-T** in DMSO-$d_6$.

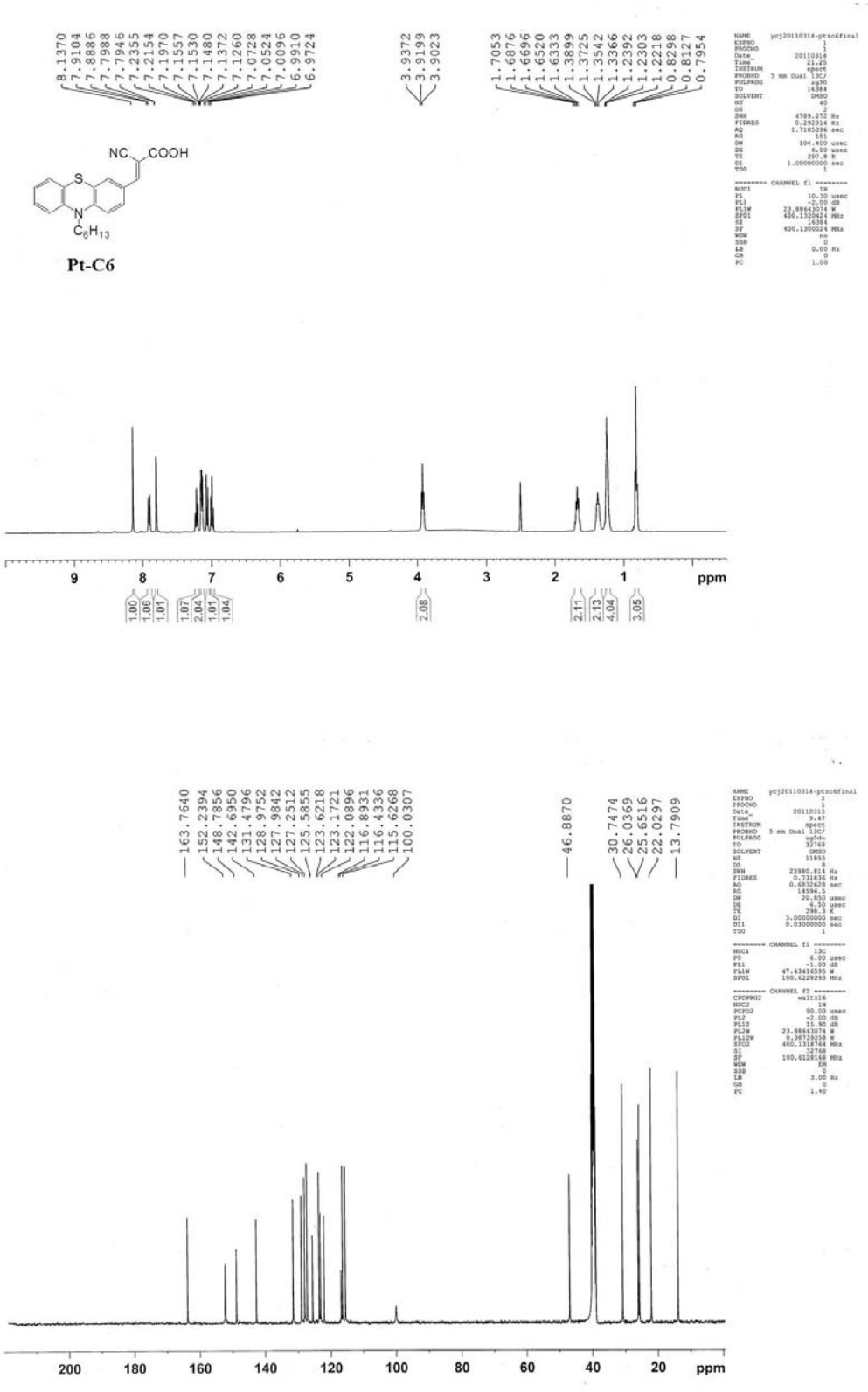



**Figure S27:** $^{1}$H NMR (upper) and $^{13}$C NMR (lower) spectra of **Pt-C6** in DMSO-$d_6$.

## 3. Theoretical calculation

**Table S1.** Calculated Low-Lying Transition for dyes.

| dye | state | excitation[a] | $\lambda_{cal}$ (eV, nm) | $f^b$ B3LYP/631G* | HOMO/LUMO |
|---|---|---|---|---|---|
| NPt-C1 | S1 | 97.37% H→L | 2.36(526) | 0.1730 | -4.99/ -2.36 |
| | S2 | 93.04% H-1→L | 2.73(454) | 0.1432 | |
| | S3 | 94.63% H→L+2 | 3.20(387) | 0.1323 | |
| NPt-C6 | S1 | 97.45% H→L | 2.37(523) | 0.1409 | -4.99/ -2.34 |
| | S2 | 93.18% H-1→L | 2.73(453) | 0.1671 | |
| | S3 | 94.90% H→L+1 | 3.26 (380) | 0.1467 | |
| NPtS-C6 | S1 | 97.20% H→L | 2.16(574) | 0.2144 | -4.98/ -2.58 |
| | S2 | 95.64% H-1→L | 2.50(496) | 0.2132 | |
| | S3 | 46.41% H→L+1 | 3.18(389) | 0.7136 | |
| NSPt-C6 | S1 | 96.86% H→L | 2.27(546) | 0.2045 | -4.90/ -2.38 |
| | S2 | 90.70% H-1→L | 2.66(465) | 0.2751 | |
| | S3 | 86.95% H→L+1 | 3.02(410) | 0.9453 | |
| NPt-T | S1 | 96.27% H→L | 2.37(523) | 0.2928 | -4.88/ -2.22 |
| | S2 | 85.00% H-1→L | 2.71(456) | 0.0263 | |
| | S3 | 86.50% H-2→L | 2.73(454) | 0.0807 | |
| NPtS-T | S1 | 97.43% H→L | 2.10(591) | 0.3567 | -4.85/ -2.50 |
| | S2 | 96.49% H-1→L | 2.38(520) | 0.0199 | |
| | S3 | 93.68% H-2→L | 2.46(502) | 0.1067 | |
| NSPt-T | S1 | 95.62% H→L | 2.29(541) | 0.4024 | -4.82/ -2.27 |
| | S2 | 90.29% H-1→L | 2.65(467) | 0.1784 | |
| | S3 | 85.65% H→L+1 | 3.03(409) | 0.8801 | |
| Pt-C6 | S1 | 95.27% H→L | 2.71(457) | 0.2340 | -5.47/-2.38 |
| | S2 | 88.73% H-1→L | 3.55(349) | 0.2513 | |
| | S3 | 85.21% H→L+1 | 3.95(313) | 0.1333 | |

[a]H=HOMO, L=LUMO, H+1=HOMO+1, L+1=LUMO+1, and L+2=LUMO+2. [b]Oscillator strengths.

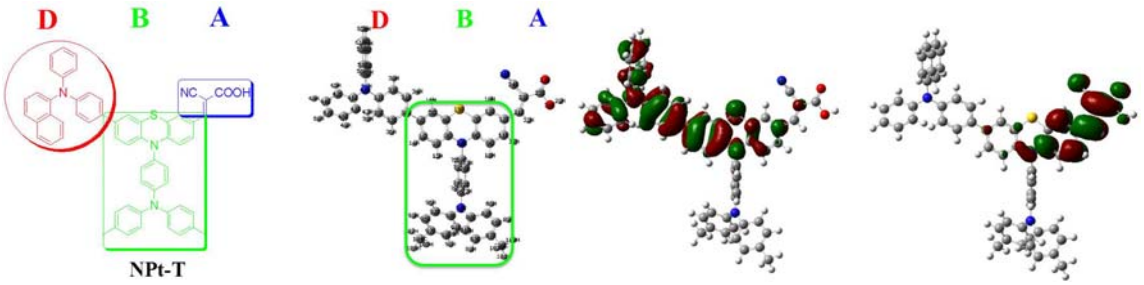



**Table S2.** Difference of Mulliken charges between ground state ($S_0$) and excited state ($S_1$), estimated by time dependent DFT/B3LYP model.

| dye | D | B | A |
|---|---|---|---|
| NPt-C1 | 0.65223 | -0.06764 | -0.47078 |
| NPt-C6 | 0.62360 | -0.02970 | -0.59360 |
| NPtS-C6 | 0.51426 | -0.05201 | -0.46225 |
| NSPt-C6 | 0.51879 | 0.06783 | -0.58662 |
| NPt-T | 0.63867 | -0.26813 | -0.61879 |
| NPtS-T | 0.52753 | -0.04825 | -0.47938 |
| NSPt-T | 0.55140 | 0.04979 | -0.61187 |
| Pt-C6 | | 0.54922 | -0.54922 |

Difference of Mulliken charge between ground state and excited state.

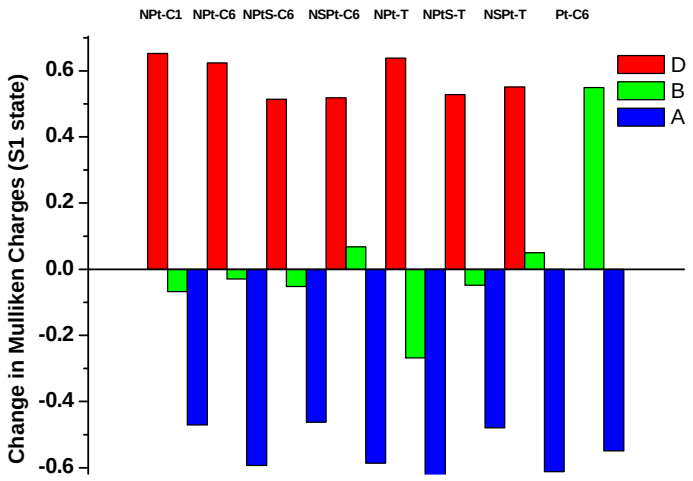
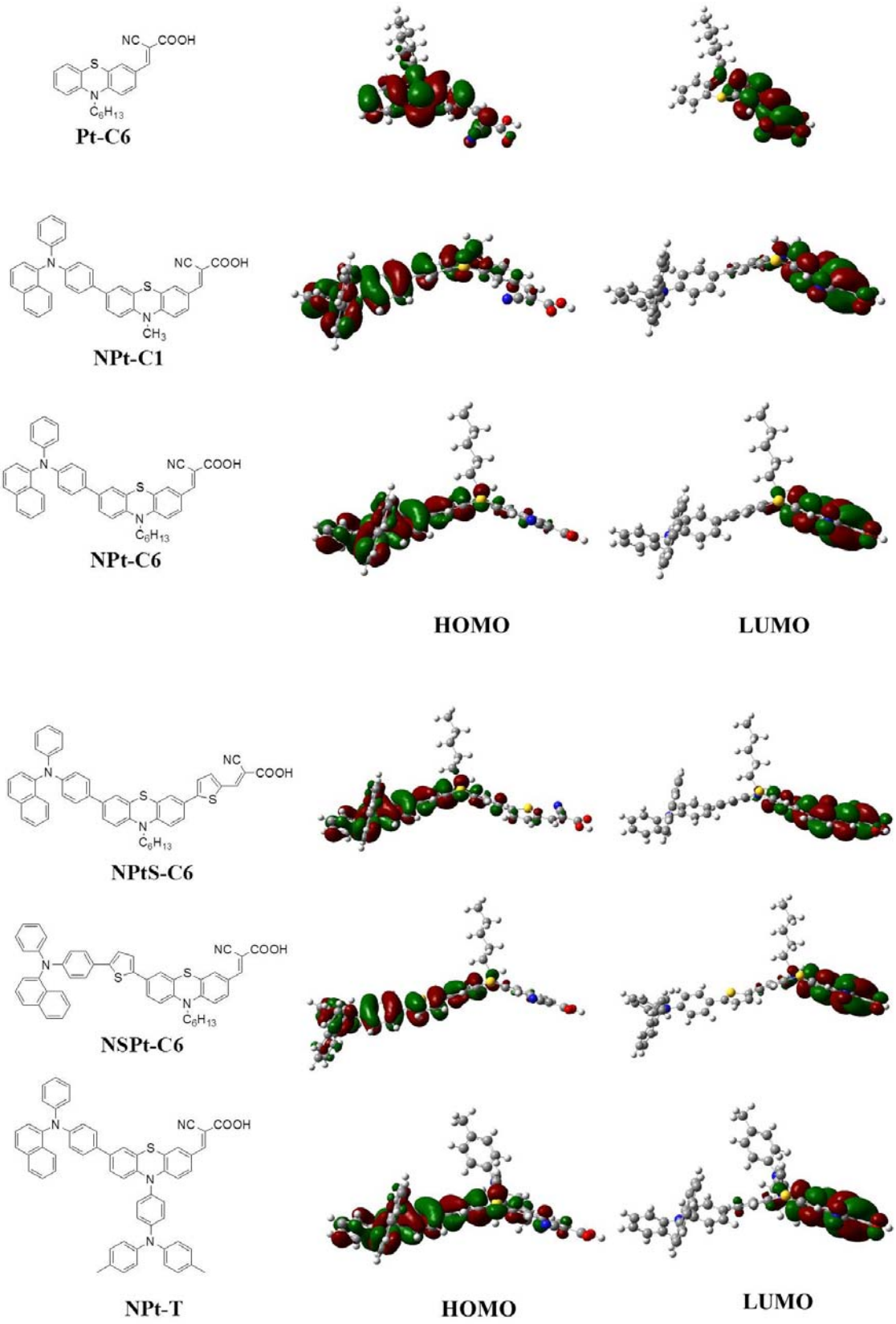



**Figure S28.** Bar-chart plots foe the difference of Mulliken charge listed in Table S2.


Pt-C6
NPt-C1
NPt-C6
HOMO
LUMO
NPtS-C6
NSPt-C6
NPt-T
HOMO
LUMO

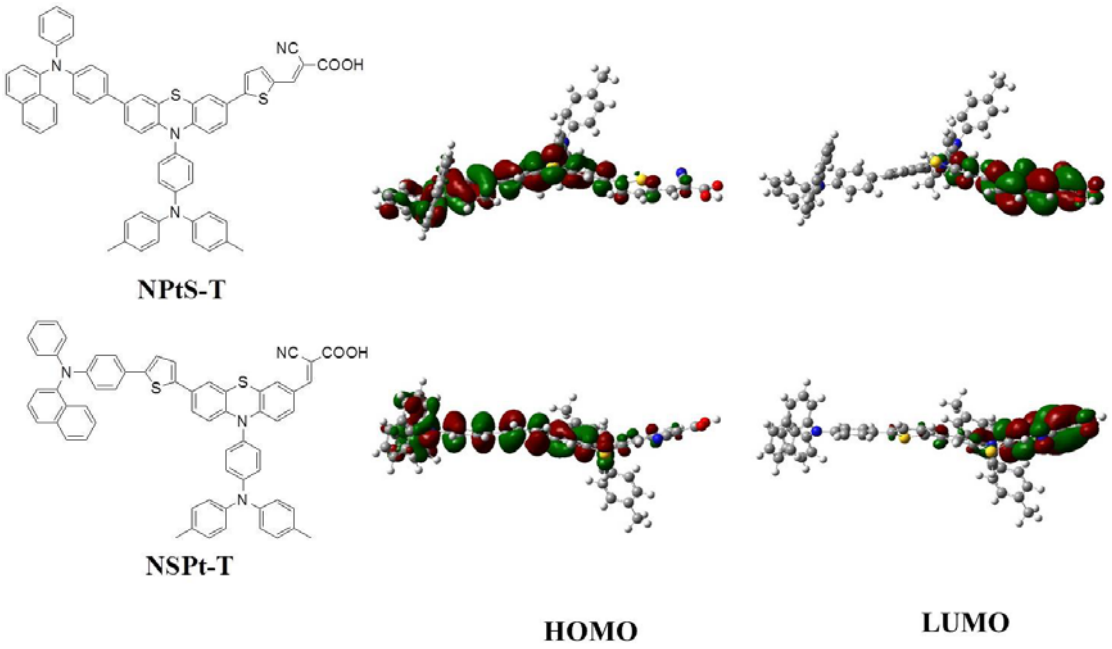



**Figure S29.** Computed HOMO and LUMO orbitals of **Phenothiazine**-series compounds.

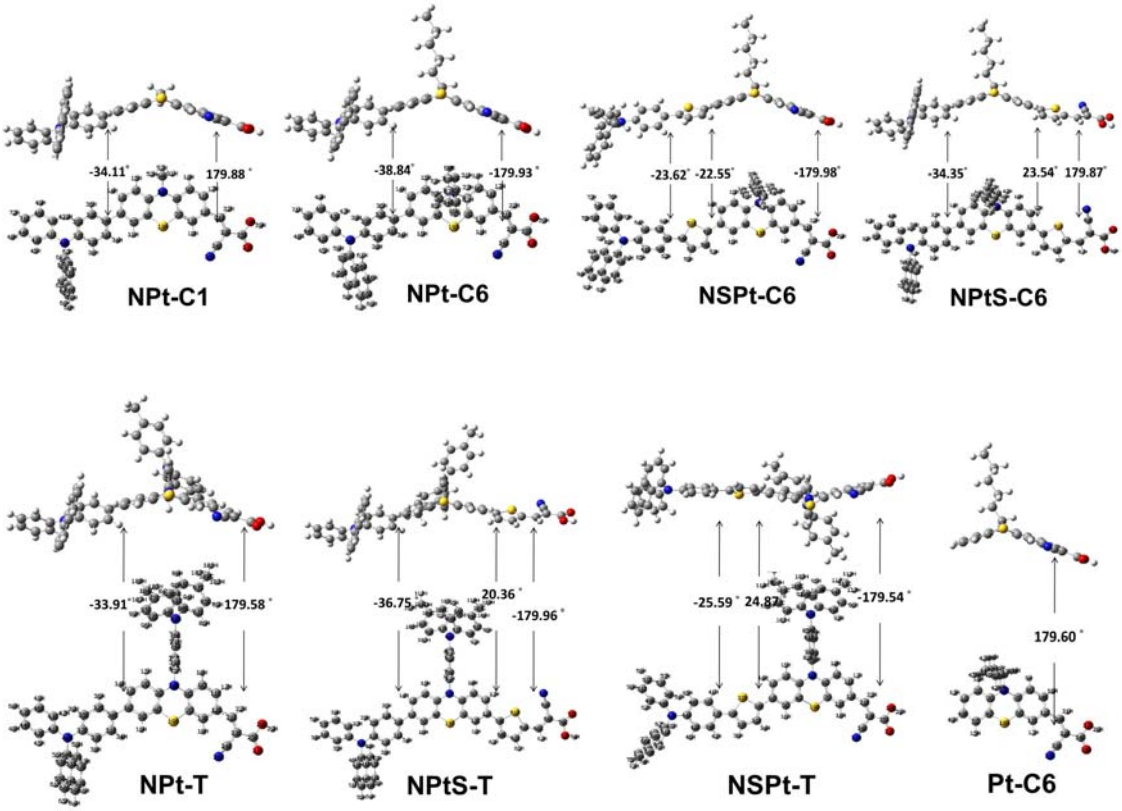



**Figure S30.** Computed dihedral angles of **Phenothiazine**-series.

## 4. Loading amount

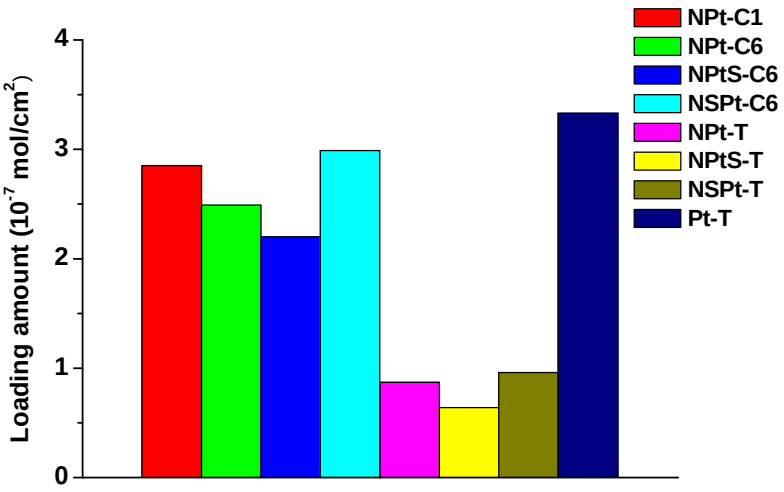



**Figure S31**. Loading amount of organic dyes on $TiO_2$ film.

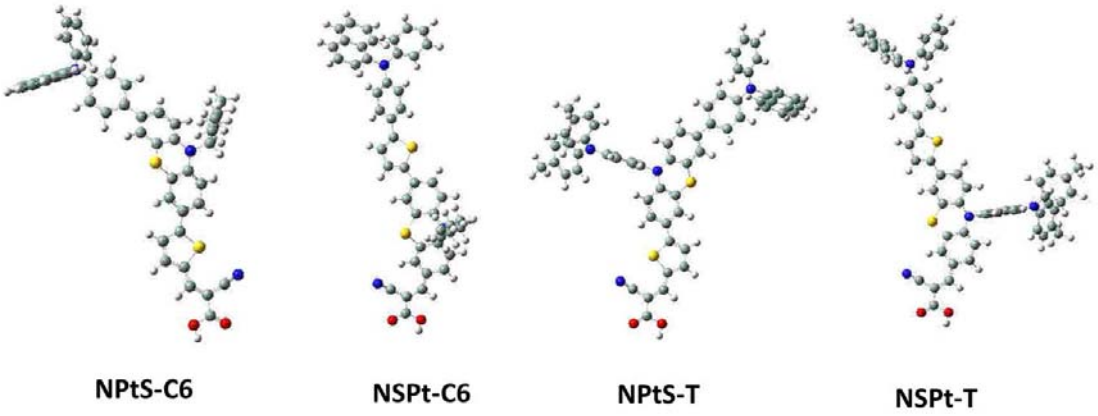



**Figure S32.** Imaged molecular volume of **Phenothiazine**-series dyes on $TiO_2$.

## 5. HOMO-LUMO level

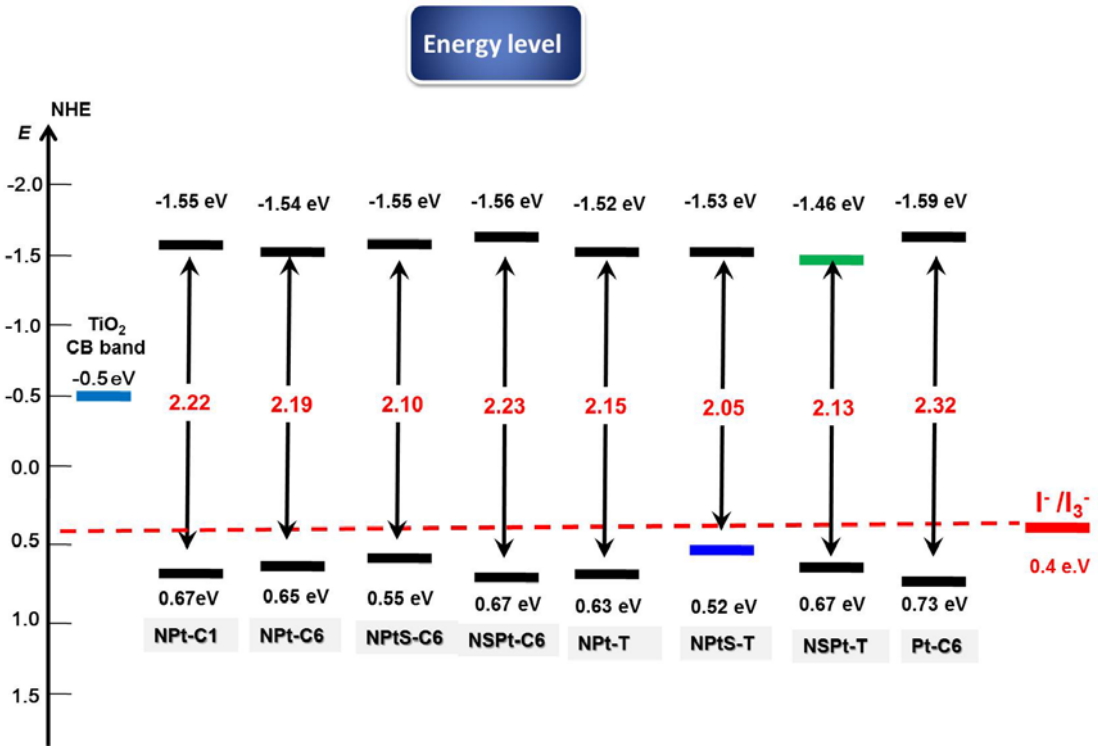



**Figure S33.** HOMO - LUMO energy levels of **Phenothiazine**-series.

## 6. EIS spectra

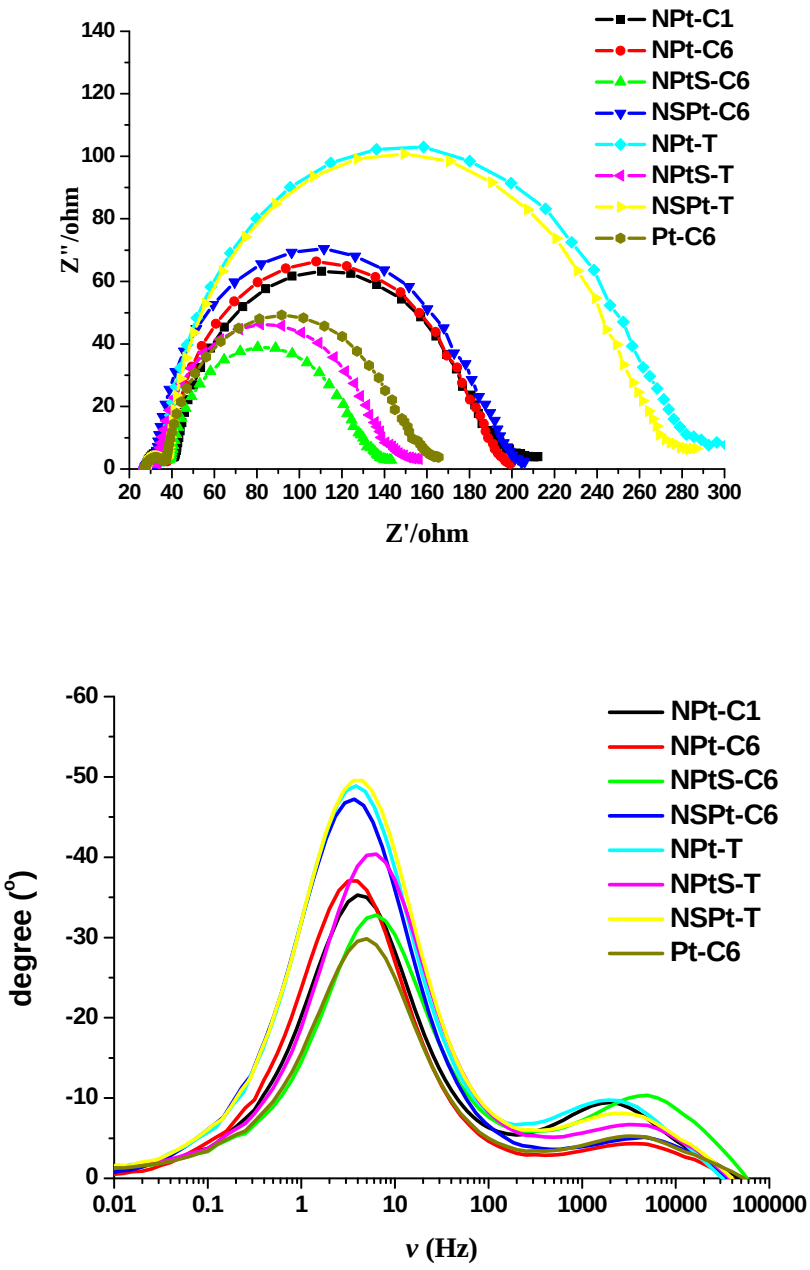



**Figure S34.** Impedance spectra of **PSP**-series organic dyes at -0.73 V bais in the dark. (upper) Nyquist plots; (lower) Bode phase plots.

## 7. *J-V* curves

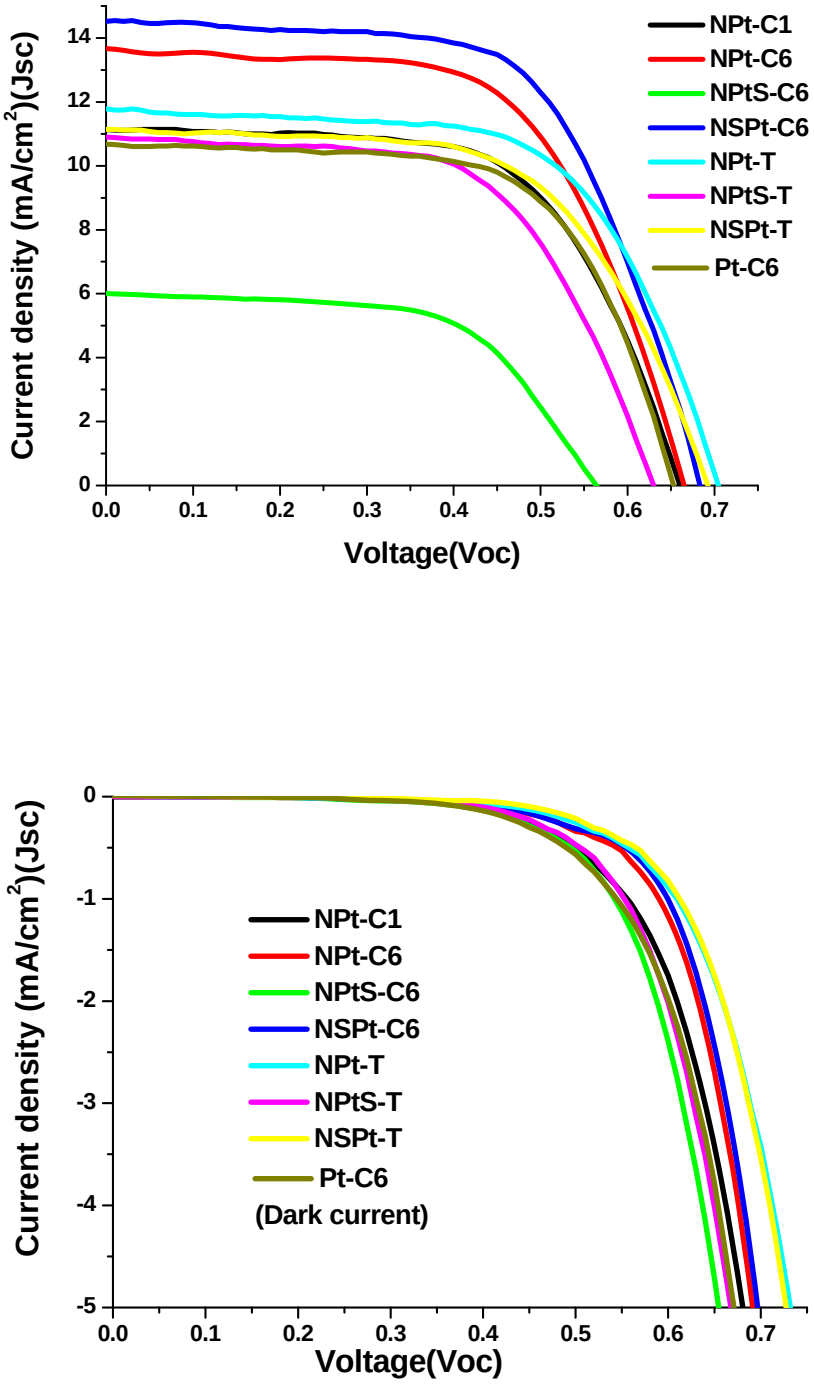



**Figure S35.** *J*-V curves of the DSSC devices made with the dyes. The plots in the upper were measured under the light intensity of 1.0 sun. And the plots in the bottom were taken in the dark.

## 8. CDCA influence

**TABLE S3: Photovoltaic Parameters of Devices made NPtS-C6 and Pt-C6 with and without CDCA.**

| Dye[a] | CDCA (mM) | $J_{sc}$(mA·cm$^{-2}$) | $V_{oc}$ (V) | FF | $\eta^b$ (%) |
|---|---|---|---|---|---|
| **NPtS-C6** | **0** | 5.99 | 0.57 | 0.60 | 2.04 |
| | **10** | 6.20 | 0.59 | 0.61 | 2.22 |
| **Pt-C6** | **0** | 10.73 | 0.65 | 0.64 | 4.49 |
| | **10** | 11.90 | 0.69 | 0.60 | 4.92 |

$J_{sc}$: short-circuit photocurrent density; $V_{oc}$: open-circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

[a] Concentration of dye is 3 × 10$^{-4}$ M in THF. [b] Performance of DSSC measured in a 0.25 cm$^2$ working area on an FTO (8Ω/square) substrate under AM 1.5 condition.

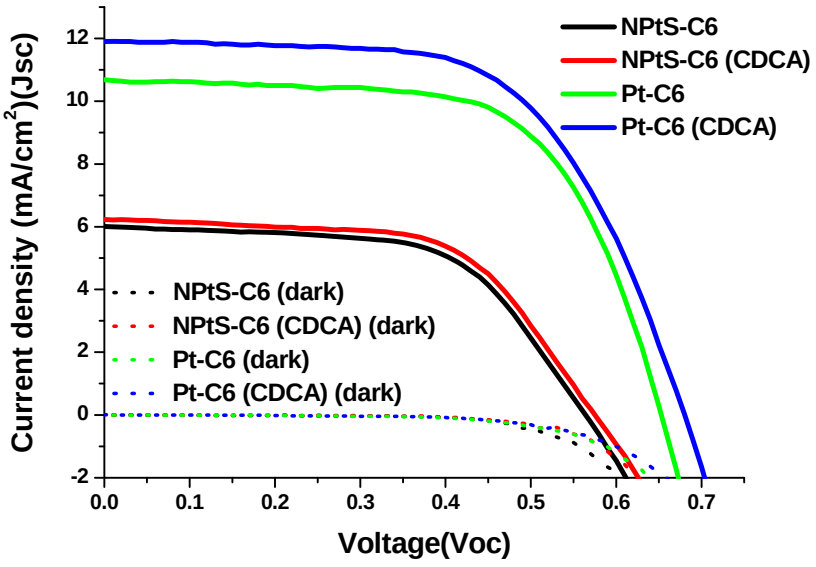



**Figure S36.** *J*-V curves of the DSSC devices made with the dyes. The plots in the upper were measured under the light intensity of 1.0 sun. And the plots in the bottom were taken in the dark.

**TABLE S4: Photovoltaic Parameters of Devices made NPt-C6 and NPt-T with and without CDCA.**

| Dye[a] | CDCA (mM) | $J_{sc}$(mA·cm$^{-2}$) | $V_{oc}$ (V) | FF | $\eta^b$ (%) |
|---|---|---|---|---|---|
| **NPt-C6** | **0** | 13.66 | 0.67 | 0.61 | 5.60 |
| | **10** | 11.47 | 0.72 | 0.61 | 5.08 |
| **NPt-T** | **0** | 11.65 | 0.71 | 0.63 | 5.22 |
| | **10** | 10.73 | 0.74 | 0.62 | 4.91 |

$J_{sc}$: short-circuit photocurrent density; $V_{oc}$: open-circuit photovoltage; FF: fill factor; η: total power conversion efficiency.

[a] Concentration of dye is 3 × 10$^{-4}$ M in THF. [b] Performance of DSSC measured in a 0.25 cm$^2$ working area on an FTO (8Ω/square) substrate under AM 1.5 condition.

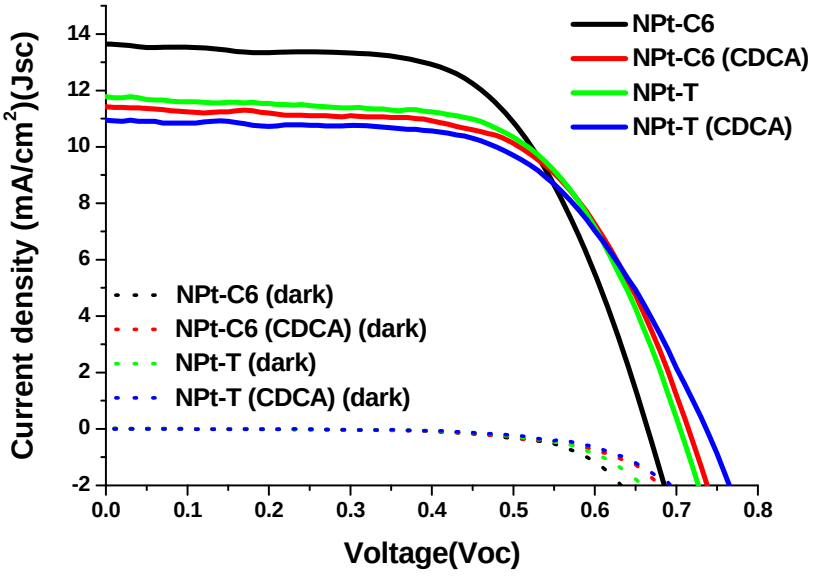



**Figure S37.** *J*-V curves of the DSSC devices made with the dyes. The plots in the upper were measured under the light intensity of 1.0 sun. And the plots in the bottom were taken in the dark.

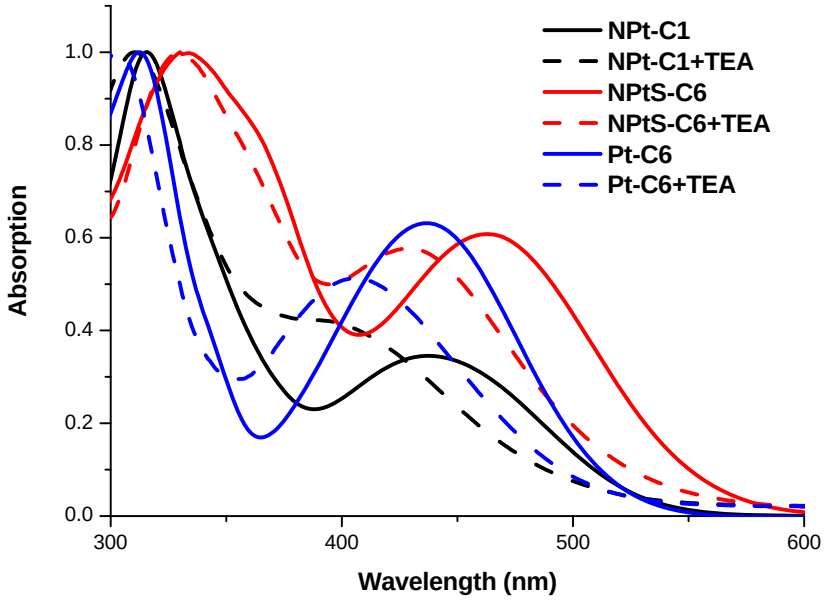



**Figure S38. Comparisons between the absorption spectra of compounds NPt-C1 (black lines), NPtS-C6 (red lines), and Pt-C6 (blue lines) in THF before (solid lines) and after (dash lines) the addition of triethylamine. Apparent blue shifts are observed upon the addition of base.**