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Trend breaking substitution pattern of phenothiazine with acceptors as a rational design platform for blue emitters

Sunil Kumar[a], Meenu Singh[b], Jwo-Huei Jou[b*], Subrata Ghosh[a*]

[a]School of Basic Sciences, Indian Institute of Technology Mandi, Himachal Pradesh- 175001, India. *E-mail: subrata@iitmandi.ac.in.

[b]Department of Material Science and Engineering, National Tsing Hua University, Hsinchu 30013, Taiwan

General: ^1H and ^{13}C and DEPT-135 NMR spectra were recorded on Jeol ECX NMR spectrometer. FT-IR spectra were recorded on a Carry-660 spectrophotometer. HRMS-ESI spectra were recorded on Bruker Maxis Impact HD instrument. UV–vis and fluorescence spectra were recorded on Simadzu UV-2450 and Cary Eclipse spectrophotometer respectively with 5/5 slit widths. All the spectral studies were performed at 5 micromolar concentration. Solvents and chemicals were purchased from commercial resources and used without further purification. Spectroscopic grade solvents were used for photophysical studies. Melting points (mp) were recorded using Stuart Melting point instrument. Thermogravimetric analysis (TGA) was recorded on a Perkin Elmer Pyris 1 and NETZSCH STA449 F1 *JUPITER* instrument under nitrogen atmosphere at a heating rate of 10 °C/min. The temperature of degradation (T_d) was correlated to a 5% weight loss. Cyclic voltammetry (CV) was carried out in nitrogen-purged dichloromethane (oxidation scan) at room temperature on Metrohm Autolab electrochemical workstation. Tetrabutylammonium hexafluorophosphate ($TBAPF_6$) (0.1 M) was used as the supporting electrolyte. The conventional three-electrode configuration consists of a platinum disc working electrode, a platinum wire auxiliary electrode, and Ag/AgCl as reference electrode with ferrocenium–ferrocene (Fc^+/Fc) as the external standard. Cyclic voltammograms were obtained at scan rate of 100 mV s^{-1} in dichloromethane solutions. Diffraction studies were performed on Agilent Technologies X-ray diffractometer..

OLED device fabrication: All the devices were fabricated on a 125 nm thick ITO coated glass substrate. The substrate was cleaned in detergent and de-ionized water, ultrasonic bathed with acetone, isopropanol, and dried in a UV-ozone slot for 10 mins.

The fabrication process initially involved the spin coating of an aqueous solution of poly(3,4-ethylene-dioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS) at 4000 rpm for 20 sec to form a 35 nm hole injection layer on pre-cleaned ITO anode. Before depositing the following emissive layer (EML), the solution was prepared by dissolving the host α-NPD and guest molecules in tetrahydrofuran at 40^0C for 0.5 h with stirring. The resulting EML solutions were deposited by spin-coating at 2500 rpm for 20 sec under nitrogen. The electron-transporting layer 32 nm of 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi), electron injection layer 1 nm of LiF, and 100 nm layer of Al as a cathode were deposited by using thermal deposition method in high vacuum of 10^{-4} torr at respective rates of 0.3, 0.1 and 10 Ås^{-1}.

The current density-voltage and luminance (J-V-L) characteristics of the resultant devices were measured through a Keithley 2400 electrometer by using Minolta CS-100A luminance-meter, while spectrum and CIE color chromatic coordinates were measured by using PR-655 spectroradiometer. The emission area of devices were 25mm^2, and luminance in forward direction was measured.

Computational Details: The ground state (S0) and lowest singlet excited state (S1) geometries were optimized at B3LYP/6-31G(d,p) level. The optimized geometries are in good agreement with the experimental outcomes. The absorption transition were calculated using TD-DFT level of theory on same level. The natural transitions orbitals for the first absorption transitions obtained from TD-DFT studies were also calculated in a similar manner.

Detailed synthetic procedures and Characterization

*10-(4-methoxyphenyl)-10H-phenothiazine (2a)***:** A suspension of phenothiazine (5 mmol), 4-iodoanisole (6 mm), potassium carbonate (10 mmol) and copper powder (5 mmol) was refluxed in triethylene glycol dimethyl ether (20 ml) at 190°C for 12 h under inert atmosphere.[1]After the completion of reaction, reaction mixture was added in ice cold water and precipitates were collected. Precipitates were then dissolved in ethyl acetate, dried over anhydrous Na_2SO_4. Pure product was obtained using column chromatography purification (Hexane as eluent, yield: 70%). mp = 173-176 °C. FT-IR (cm^{-1}): 3064.2, 2955.5, 2929.2, 1607, 1570.2, 1510, 1460.1, 1440.9, 1305.2, 1242.6, 1023.3, 832.5, 745.7. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 7.31-7.29 (m, 2H), 7.11-7.09 (m, 2H), 6.99 (dd, J = 7.22 Hz, 1.72 Hz, 2H), 6.84-6.76 (m, 4H), 6.19 (dd, J = 8.25 Hz, 1.25 Hz, 2H), 3.89 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 159.18, 144.61, 133.21, 132.23, 126.78, 126.57, 122.2, 119.57, 115.83, 115.58, 55.49. HRMS (m/z): $C_{19}H_{15}NOS$, Calculated = 305.0874, found= 305.0874 (M^+).

10-(4-methoxyphenyl)-10H-phenothiazine-3-carbaldehyde ***(2b)*****.** To the DMF solution of compound **2a** (1.180g, 1eq) was added phosphorous oxychloride (3eq) at 0°C and reaction mixture was stirred at same temperature for 30 min. After that reaction mixture was heated at 90°C for 12 h. The reaction mixture was quenched with ice and the formed yellow precipitates were collected. Pure product was collected after column chromatography purification using ethyl acetate: hexane (15: 85) as eluent (yield: 72%). mp = 162-165 °C FT-IR (cm^{-1}): 3068.9, 2923.1, 2741.7, 1677, 1606.2, 1572.2, 1508.3, 1462.8, 1440.5, 1311.1, 1287.2, 1244.4, 1201.08, 1166.9, 1027.7, 879.7, 830.3, 746.5. ^{1}H-NMR (500 MHz, $CDCl_3$): δ 9.69 (s, 1H), 7.45 (d, J = 2.05

Hz, 1H), 7.29-7.26 (m, 3H), 7.14-7.13 (m, 2H), 6.95 (m, 1H), 6.84 (q, J = 3.45 Hz, 2H), 6.20-6.15 (m, 2H), 3.91 (s, 3H). ^{13}C-NMR (125 MHz, $CDCl_3$): δ 189.73, 159.61, 149.53, 142.84, 132.2, 131.6, 130.85, 129.92, 127.46, 127.10, 126.63, 123.55, 119.9, 118.9, 116.39, 116.22, 114.96, 55.57. HRMS (m/z): $C_{20}H_{15}NO_2S$, Calculated = 333.0823, found= 334.0897 (M+H).

10H-phenothiazine-3-carbaldehyde **(3a)**. To the acetic acid (20 ml) solution of phenothiazine (5 mmol) was added 1,3,5,7-Tetraazatricyclo[3.3.1.13,7]decane (5.2 mmol) and reaction mixture was refluxed at 110 ^{o}C for 6 hours. After the completion of reaction as indicated by the formation of polar spot in TLC reaction mixture was poured on ice in 1000 ml beaker and quenched further with concentrated sodium bicarbonate solution. After that reaction mixture was extracted with ethyl acetate and dried over sodium sulphate. Organic layer was then concentrated under reduced pressure. The required compound **3a** was obtained by purifying crude product using column chromatography in ethylacetate (2): hexane (8) eluent. The pure product was obtained as yellowish brown powder (yield: 58%). mp = 188-190 ^{o}C FT-IR (cm^{-1}): 1668, 1505, 1469, 1199. ^{1}H NMR (500 MHz, $CDCl_3$): δ 9.71 (s, 1H), 7.47-7.43 (m, 2H), 7.01-6.97 (m, 2H), 6.94-6.84 (m, 1H), 6.56-6.52 (m, 2H), 6.16 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): 189.7, 146.7, 139.1, 131.5, 130.4, 128.0, 127.6, 126.8, 123.8, 118.9, 117.5, 114.9, 113.9. HRMS (m/z): calculated = $C_{13}H_9NOS$, 227.04048, found = 227.0405 (M^+).

10-(4,6-dimethoxy-1,3,5-triazin-2-yl)-10H-phenothiazine-3-carbaldehyde **(3b).** To the tetrahydrofuran (5ml) solution of **3a** (0.5 mmol) was added potassium tert. butoxide (0.55 mmol) at 0 °C and reaction mixture was stirred at same temperature for 15 min followed by the addition of 2-chloro-4,6-dimethoxy-1,3,5-triazine (0.52 mmol). The reaction mixture was brought to room temperature and stirred for 6 hours at 50°C. After the completion of reaction, the reaction mixture was quenche by water, extracted with ethylacetate (20ml) and washed with water (3 X 10ml). Then the organic layer was dried over sodium sulphate and concentrated under vacuum. The pure product was obtained using column chromatography in ethylacetate (1): hexane (9) as eluent (yield: 55%). mp = 97-100 °C. FT-IR (cm^{-1}): 3329, 3163, 3055, 1670, 1599, 1565.1, 1469.2, 1362, 1306, 1197, 968, 816, 747. ^1H NMR (500 MHz, $CDCl_3$): δ 9.9 (s, 1H), 7.86 (d, J = 2.1Hz 1H), 7.83 (dd, J_1 = 8.25Hz; J_2 = 1.4Hz, 1H), 7.78 (dd, J_1 = 8.25Hz; J_2 = 1.4Hz, 1H), 7.79 - 7.77 (m, 1H), 7.37 (dd, J_1 = 8.25Hz; J_2 = 1.4Hz,, 1H), 7.32 – 7.28 (m, 1H), 7,19 – 7.18 (m, 1H), 3.82 (s, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): 190.5, 172.4, 166.5, 143.8, 137.5, 134.5, 134.3, 131.9, 129.3, 128.5, 127.9, 127.3, 126.9, 126.7, 55.023. HRMS (m/z): $C_{18}H_{14}N_4O_3S$ calculated = 366.07866, found = 367.0858 (M+H).

General Procedure for the synthesis of 2 and 3.

A mixture of corresponding aldehyde (1 mmol), 9,10-phenanthrenequinone (1 mmol), aniline (1.2 mmol) and ammonium acetate (10 mmol) was refluxed in acetic acid (15 mL) under nitrogen atmosphere. After 6h, reaction mixture was quenced with addition of water and extracted in ethyl acetate. The organic layer was then washed with water (2X25 ml) and dried over sodium sulphate. The pure product was obtained using column chromatography in ethylacetate (2.5): hexane (7.5) as eluent [yields: **2** = 65% (mp = 304 ^oC), **3** = 53% (mp = 112-115 ^oC)].

Compound 2: FT-IR (cm^{-1}): 3050.2, 2960.2, 1606.2, 1576.6, 1509.2, 1446.3, 1310.9, 1239.2, 1104.4, 1032.7, 914.2, 842.5, 813.4, 745.5, 720.2, 694.8. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.85 (d, 1H, J = 7.55 Hz), 8.74 (d, 1H, J = 8.2 Hz), 8.68 (d, 1H, J = 8.2 Hz), 7.73(t, 1H, J = 7.5 Hz), 7.65-7.59 (m, 4H), 7.50-7.46 (m, 3H), 7.32-7.30 (m, 1H), 7.29-7.23 (m, 3H), 7.25-7.08 (m, 3H), 6.95-6.82 (m, 2H), 6.11 (d, 1H, J = 7.5 Hz), 5.99 (d, 1H, J = 8.9Hz), 3.88(s, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 159.2, 149.8, 144.8, 143.8, 138.7, 137.2, 132.8, 132.0, 130.2, 129.8, 129, 128.1, 128, 127.5, 127.3, 127.1, 126.8, 126.5, 126.1, 125.5, 124.6, 124.3, 124, 123, 122.9, 122.6, 122.5, 120.0, 119.4, 119.2, 115.9, 115.7, 114.8, 55.5. HRMS (m/z): $C_{40}H_{27}N_3OS$ calculated = 597.1874, Found = 597.1869 (M^+)

Compound 3: FT-IR (cm^{-1}): 3289.7, 3261.7, 3189, 3129.9, 3054.6, 2926.8, 2850.4, 1660.1, 1536.5, 1544.6, 1485.1, 1437.2, 1365.3, 1317.6, 1257.6, 1178.2, 1078.5, 1010.8, 962.9, 911.1, 847.4, 815.8, 751.8, 692.2. ^1H NMR ($CDCl_3$, 500 MHz): δ 8.85 (d, 1H, J = 7.5 Hz), 8.76 (d, 1H, J = 8.2 HZ), 8.71 (d, 1H, J = 8.2 Hz), 7.80 (d, 1H, J = 2.05 Hz), 7.74 (t, 1H, J = 7.2 Hz), 7.71-7.57 (m, 5H), 7.56-7.46 (m, 4H), 7.43-7.37 (m, 2H), 7.37-7.25 (m, 5H), 7.21 (t, 1H, J = 7.5 Hz), 7.17 (d, 1H, J = 8.2 Hz), 7.10 (t, 1H, J = 7.5 Hz), 3.83 (s, 6H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 172.3, 166.5, 149.3, 138.6, 138.5, 138, 137.4, 133.3, 132.4, 130.2, 129.9, 129.3, 129, 128.9, 128.7, 128.6, 128.3, 127.8, 127.3, 127, 126.7, 126.6, 126.4, 126.3, 125.7, 125.7, 125.0, 124.2, 124.1, 123.1, 122.9, 122.6, 120.8, 119.7, 54.9. HRMS (m/z): $C_{38}H_{26}N_6O_2S$ Calculated = 630.1837, Found = 631.0858 (M+H).

Photophysical Data

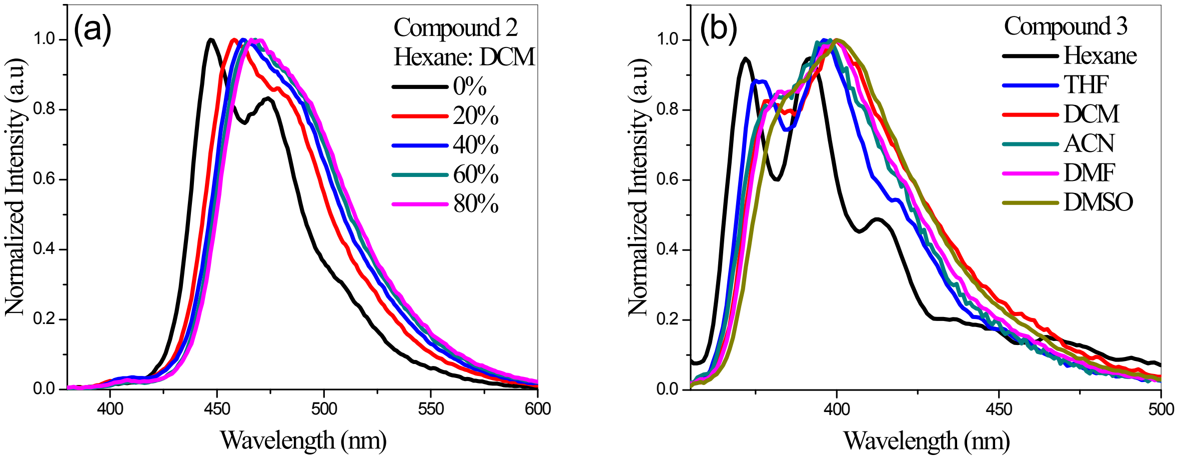

Fig. S1 (a) Solvatochromic emission behavior of compound **2** in Hexane: DCM mixture and (b) Solvatochromic emission behavior of compound **3** in different solvents.

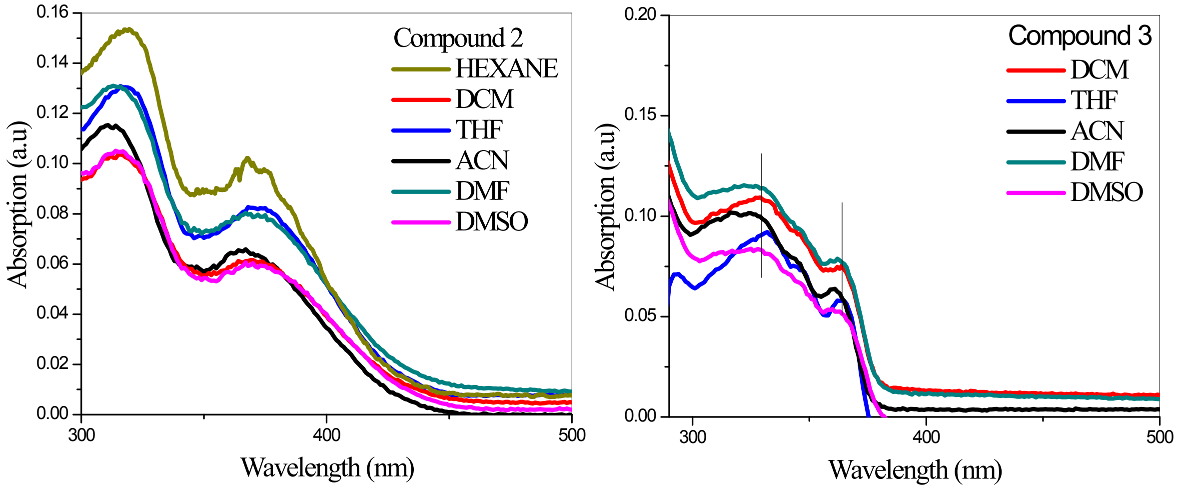

Fig. S2: Solvatochromic UV-vis absorption behavior of **2** and **3** in different solvents.

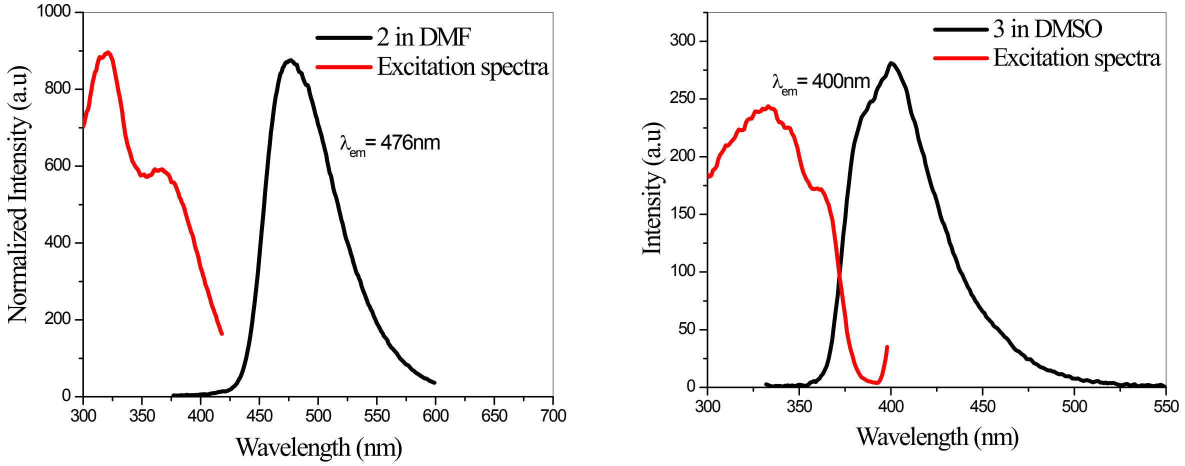

Fig. S3 Excitation spectra recorded for compounds **2** and **3.**

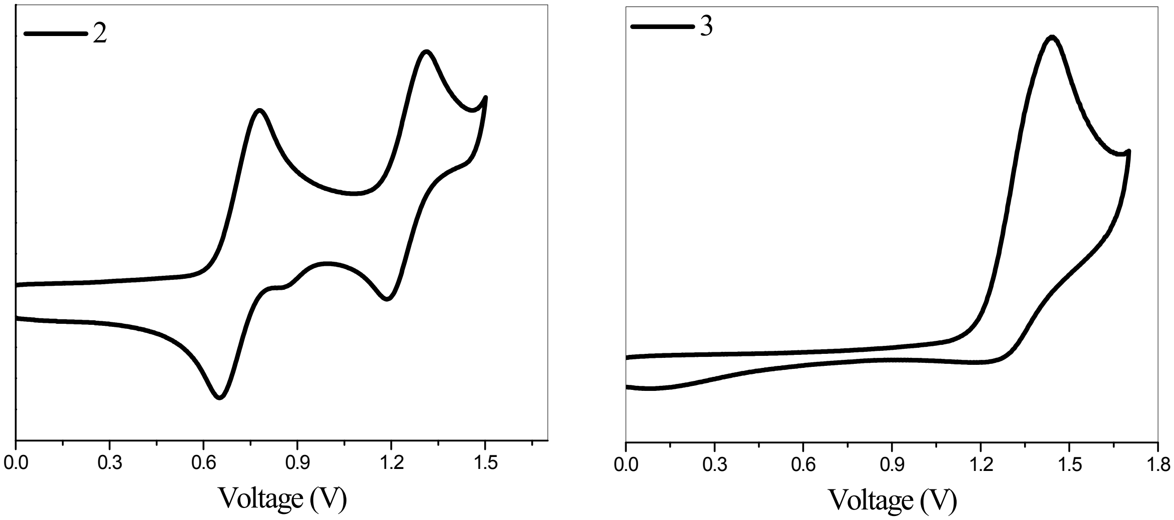

Fig. S4 Cyclic voltammograms for compound **2** and **3.**

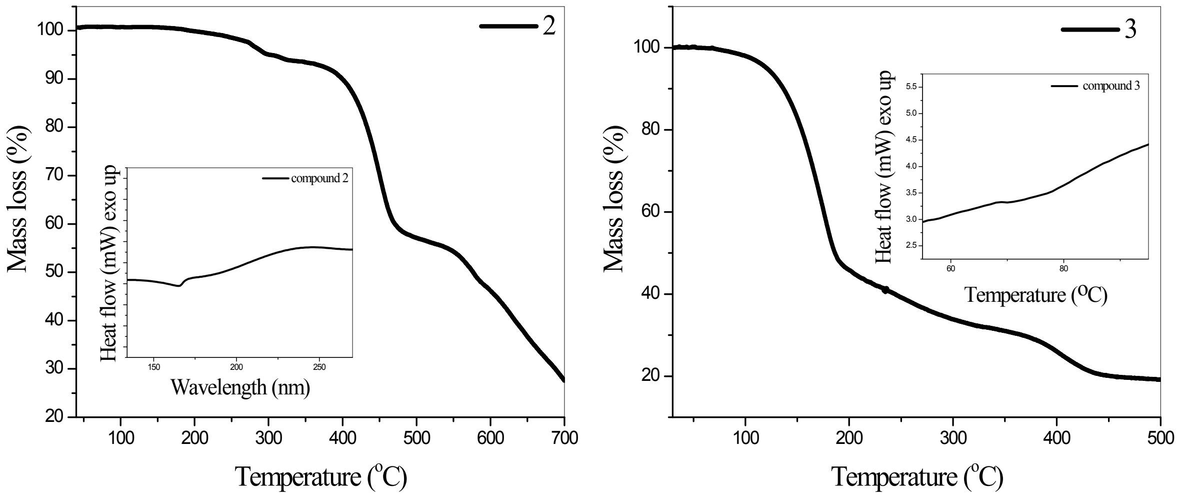

Fig. S5 TGA (Thermogravimetric analysis) graphs for compound **2** and **3.** (inset: DSC traces showing glass transition)

Single crystal X-Ray Diffraction data analysis

Empirical formula	$C_{40}H_{27}N_3OS$
Formula weight	597.71
Temperature/K	150.00(10)
Crystal system	triclinic
Space group	P-1
a/Å	10.1788(5)
b/Å	12.4494(7)
c/Å	12.8652(6)
α/°	67.749(5)
β/°	85.414(4)
γ/°	78.057(5)
Volume/$Å^3$	1476.21(14)
Z	2

ρ_{calc}mg/mm^3	1.345
m/mm^{-1}	0.149
F(000)	624.0
Crystal size/mm^3	0.1822 × 0.1441 × 0.0934
2Θ range for data collection	3.94 to 56.48°
Index ranges	$-13 \le h \le 13$, $-10 \le k \le 16$, $-14 \le l \le 16$
Reflections collected	8582
Independent reflections	6383[R(int) = 0.0142]
Goodness-of-fit on F^2	1.090
Final R indexes [I>=2σ (I)]	$R_1 = 0.0662$, $wR_2 = 0.1728$
Final R indexes [all data]	$R_1 = 0.0758$, $wR_2 = 0.1810$

Table S1: Crystal data and structure refinement for Compound **2.**

Empirical formula	$C_{38}H_{26}N_6O_2S$
Formula weight	Exact Mass: 631.08
Temperature/K	293(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	14.3280(9)
b/Å	15.8222(8)
c/Å	16.5190(10)
α/°	90.00
β/°	93.784(5)
γ/°	90.00
Volume/Å^3	3736.7(4)
Z	4
ρ_{calc}mg/mm^3	1.313

m/mm^{-1}	0.141
F(000)	1552.0
Crystal size/mm^3	0.2914 × 0.2198 × 0.1218
2Θ range for data collection	3.56 to 56.86°
Index ranges	$-13 \leq h \leq 17$, $-20 \leq k \leq 17$, $-22 \leq l \leq 9$
Reflections collected	12742
Independent reflections	8080[R(int) = 0.0286]
Data/restraints/parameters	8080/0/460
Goodness-of-fit on F^2	1.038
Final R indexes [I>=2σ (I)]	$R_1 = 0.0855$, $wR_2 = 0.2458$
Final R indexes [all data]	$R_1 = 0.1289$, $wR_2 = 0.2836$

Table S2: Crystal data and structure refinement for Compound **3.**

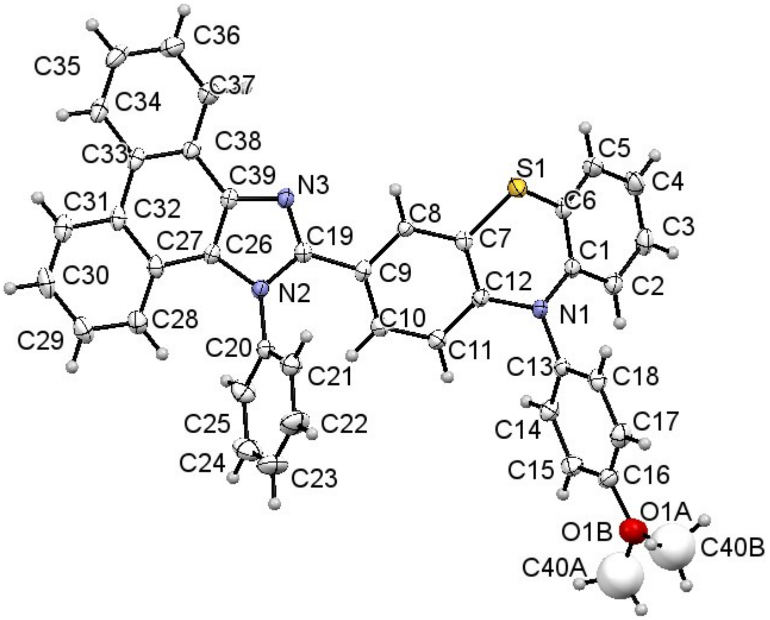

Fig. S6 ORTEP diagram for crystal structure of compound **2.**

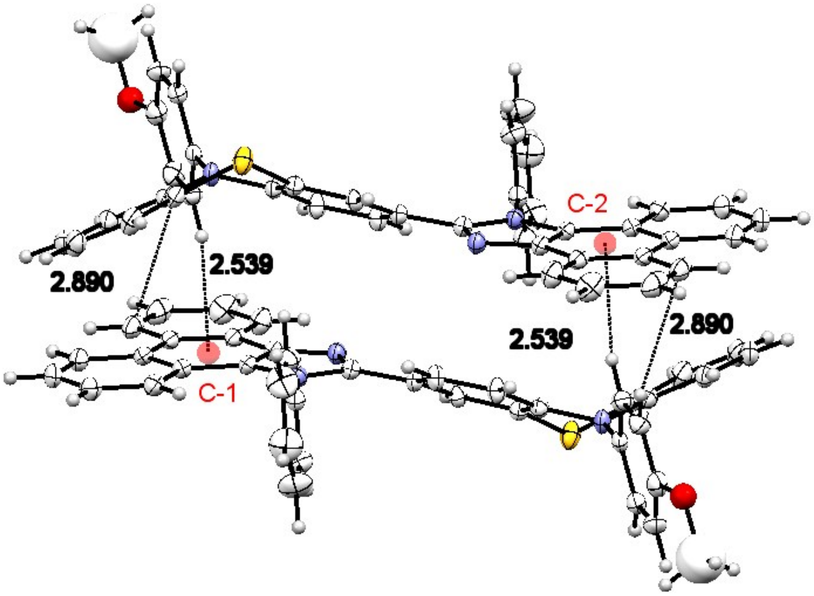

Fig. S7 Existed short range interactions of compound **2** with the neighboring molecule.

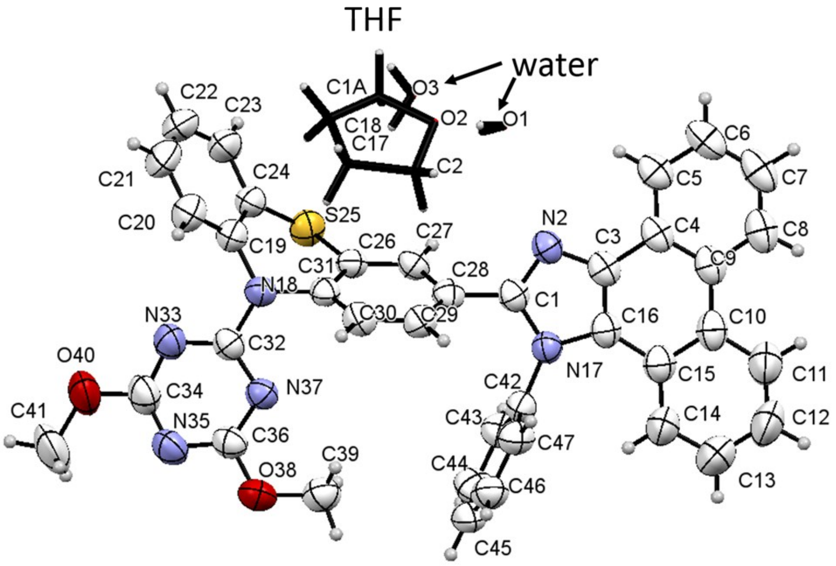

Fig. S8 ORTEP diagram for crystal structure of compound **3** (crystal structure contained tetrahydrofuran (THF) and water molecules).

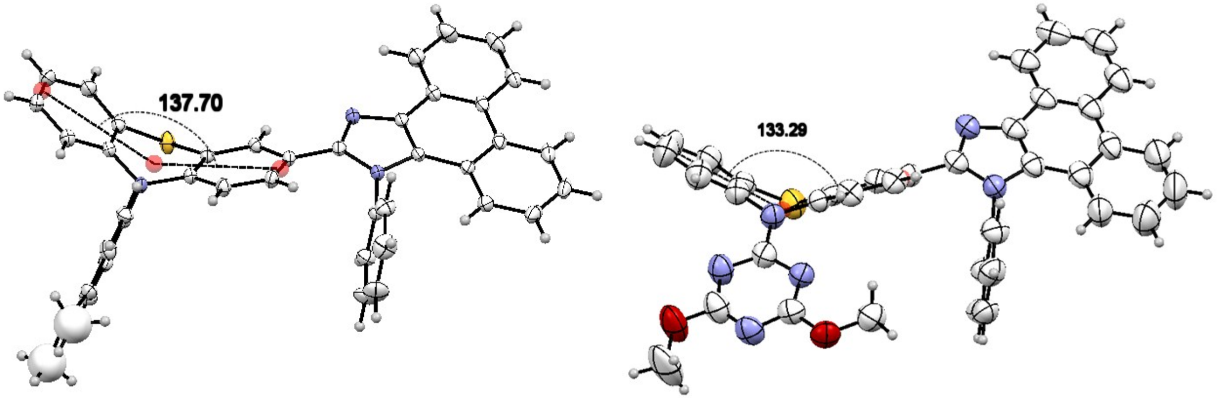

Fig. S9 ORTEP diagram showing butterfly angle (137.7°and 133.2°) and dihedral angle (-154.8**°** and -125.9°) for **2** and **3.**

Theoretical Analysis

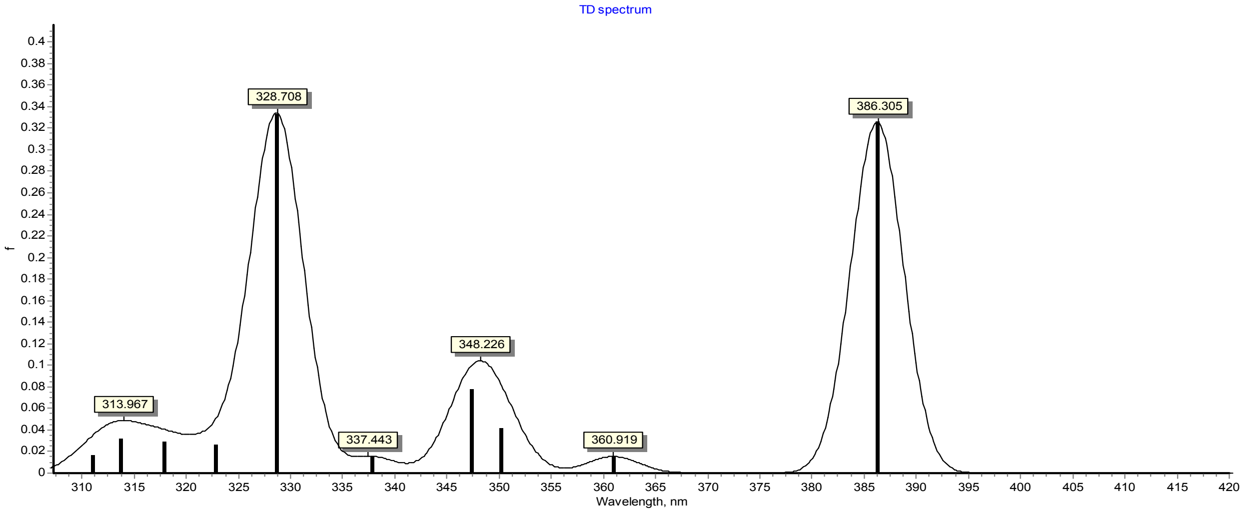

Fig. S10 TD-DFT calculated UV-vis transitions profile for compound **2.**

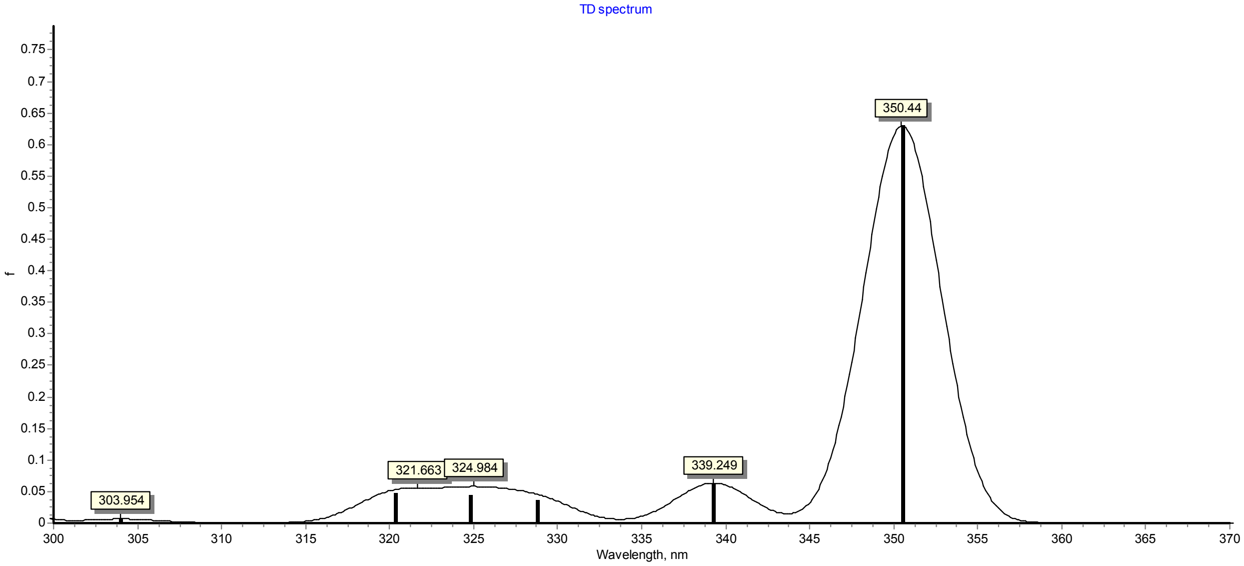

Fig. S11 TD-DFT calculated UV-vis transitions profile for compound **3.**

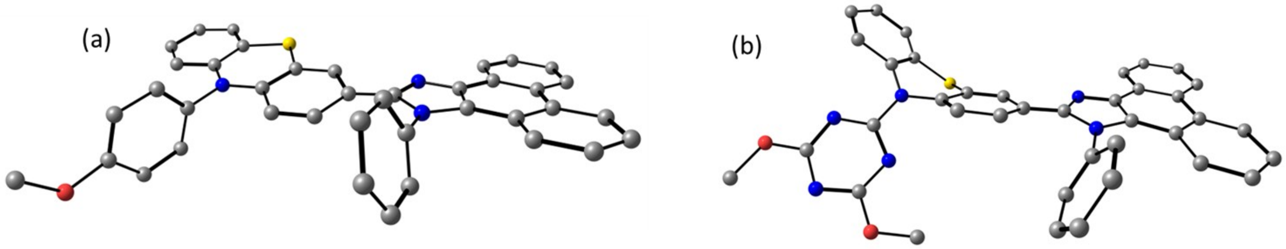

Fig. S12 DFT calculated optimized geometries for first excited state for compound **2** (a) and **3** (b).

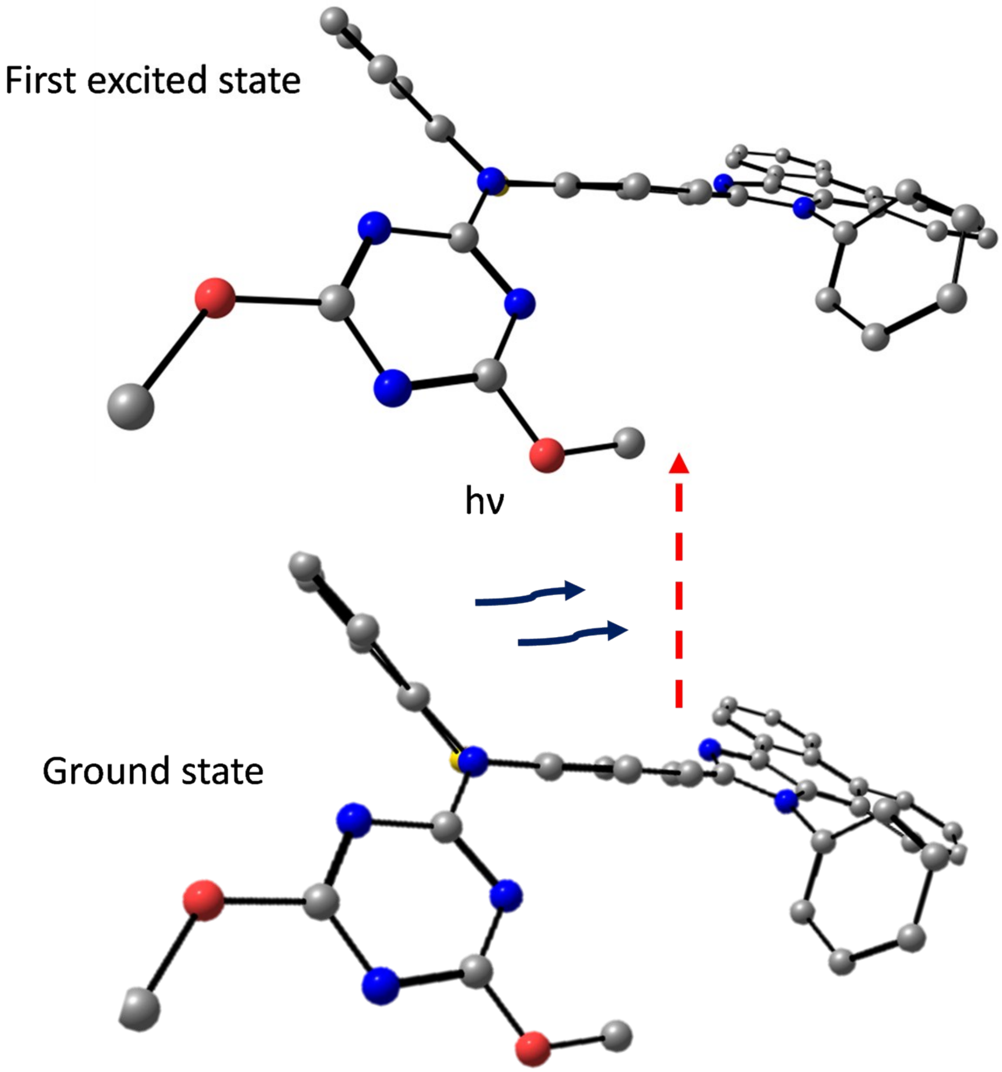

Fig. S13 Geometrical changes occurred on excitaion from ground state to excited state in compound **3**.

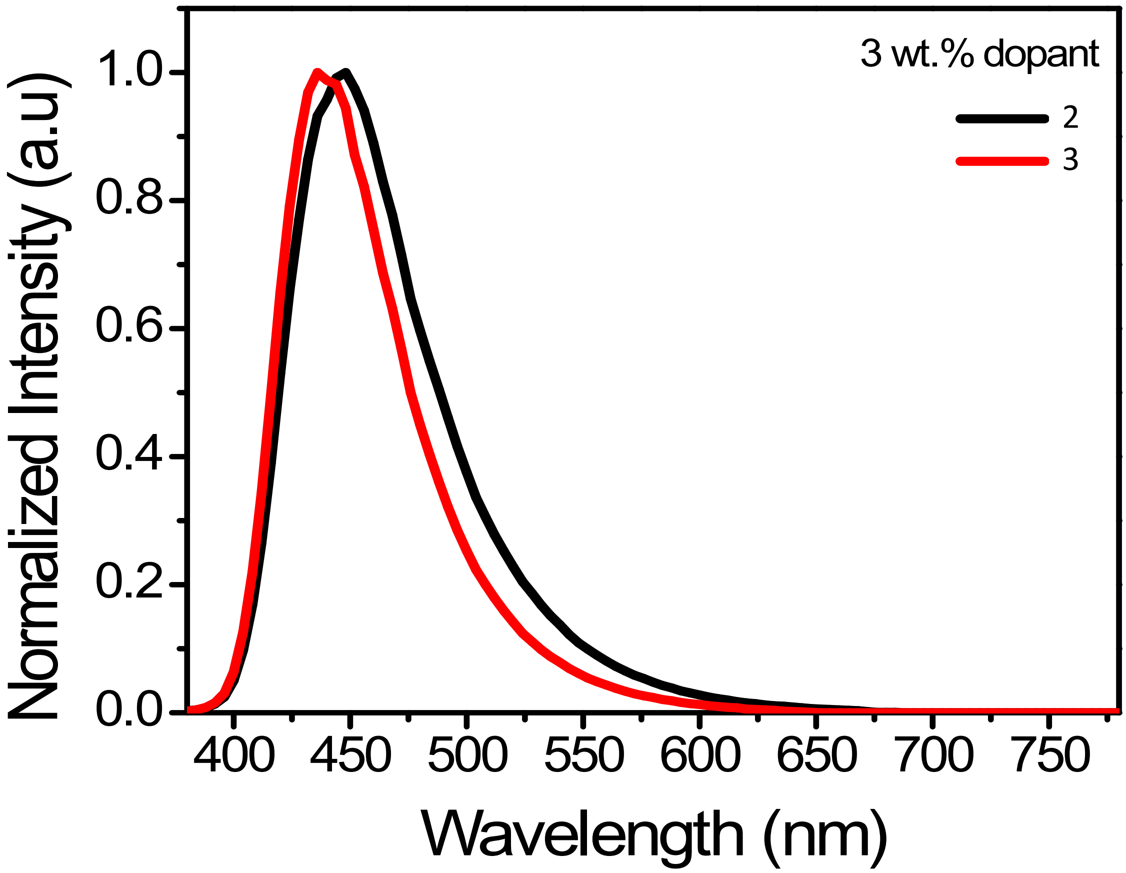

Fig. S14 Electroluminescence spectar for devices using dopants 2 and 3 (3 wt%) in host matrix.

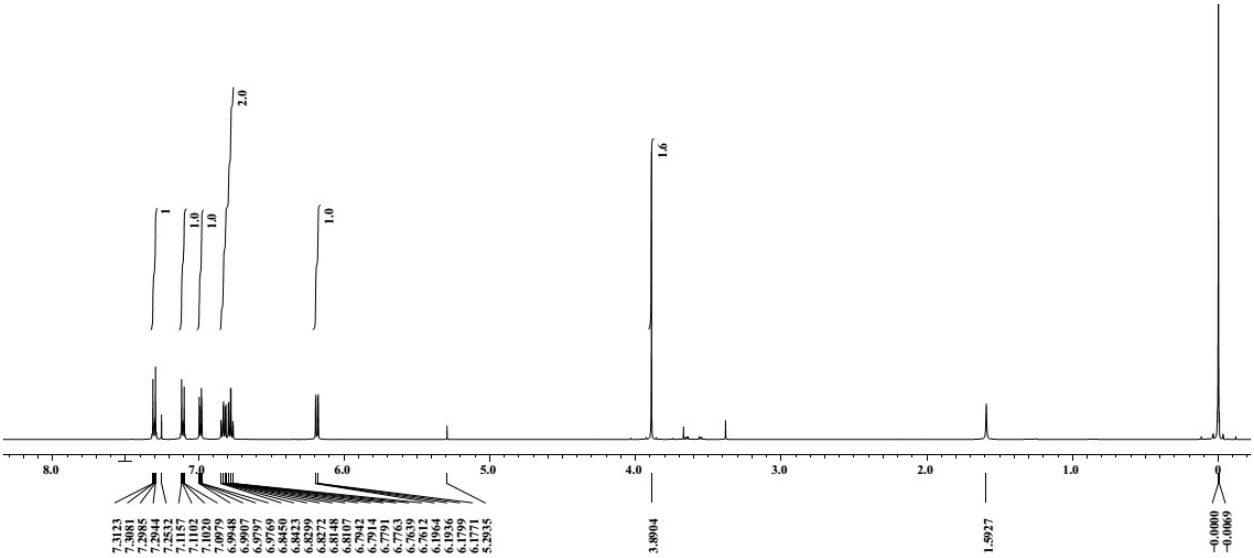

Fig. S15 ^{1}H-NMR for **1a.**

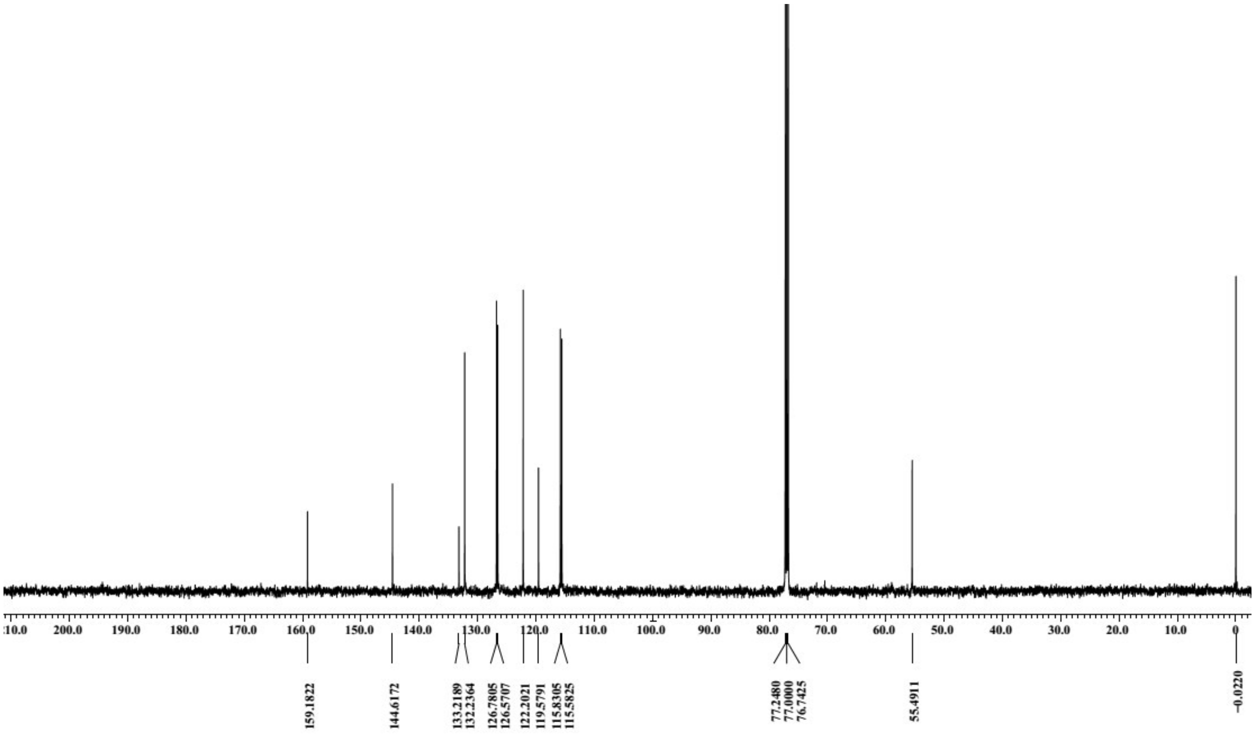

Fig. S16 ^{13}C-NMR for **2a.**

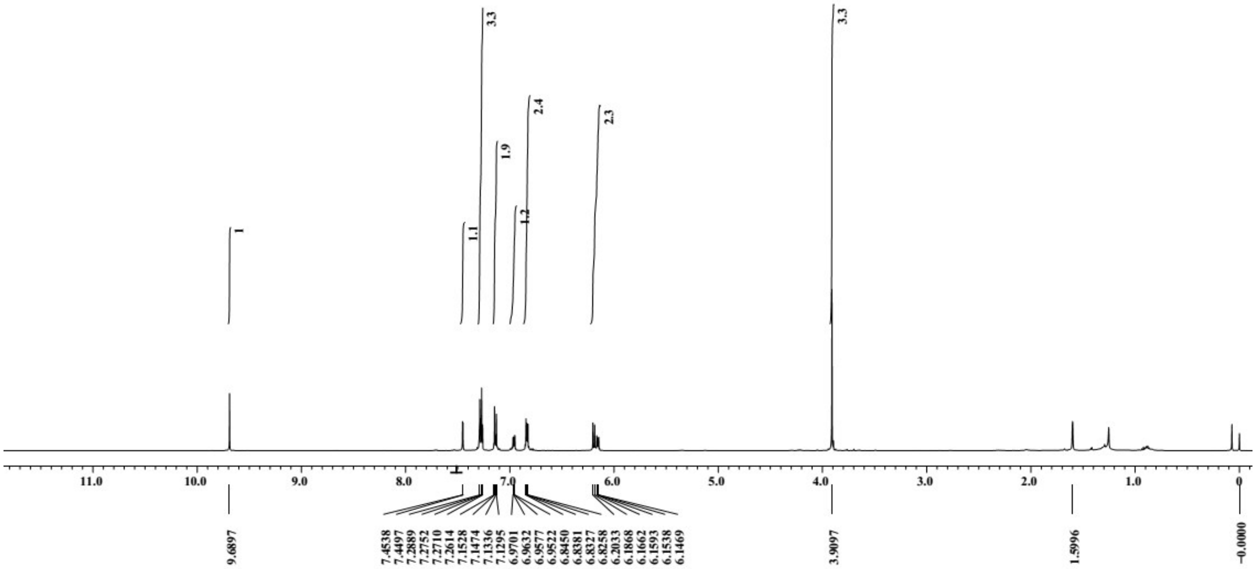

Fig. S17 ^{1}H-NMR for **2b.**

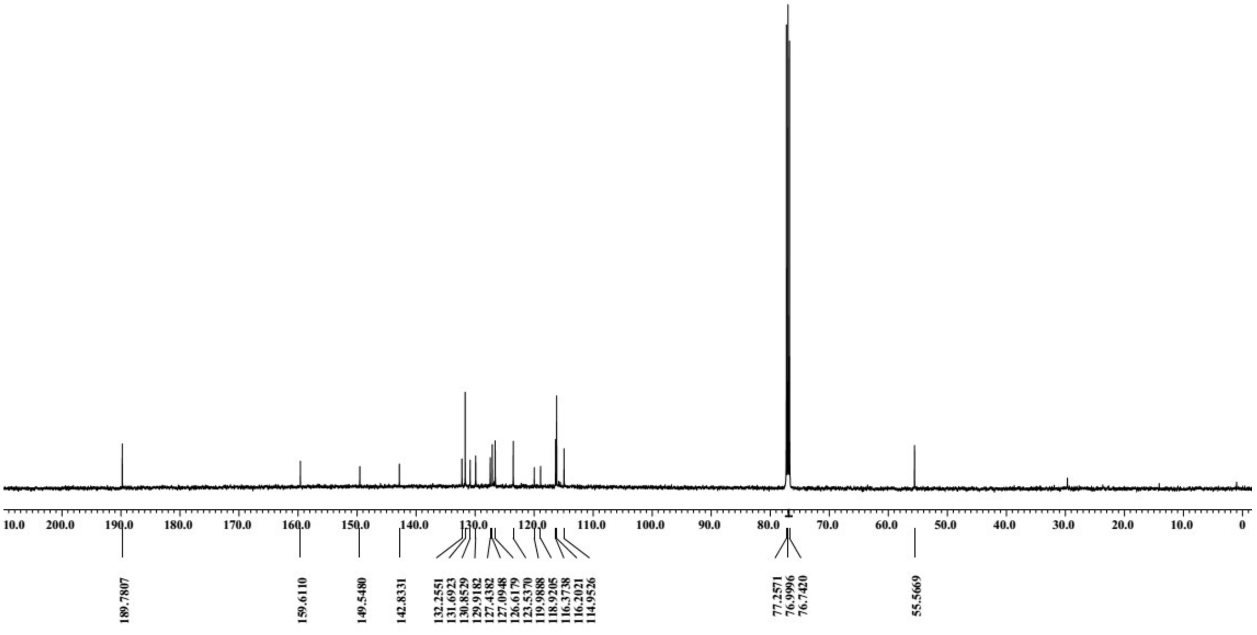

Fig. S18 ^{13}C-NMR for **2b.**

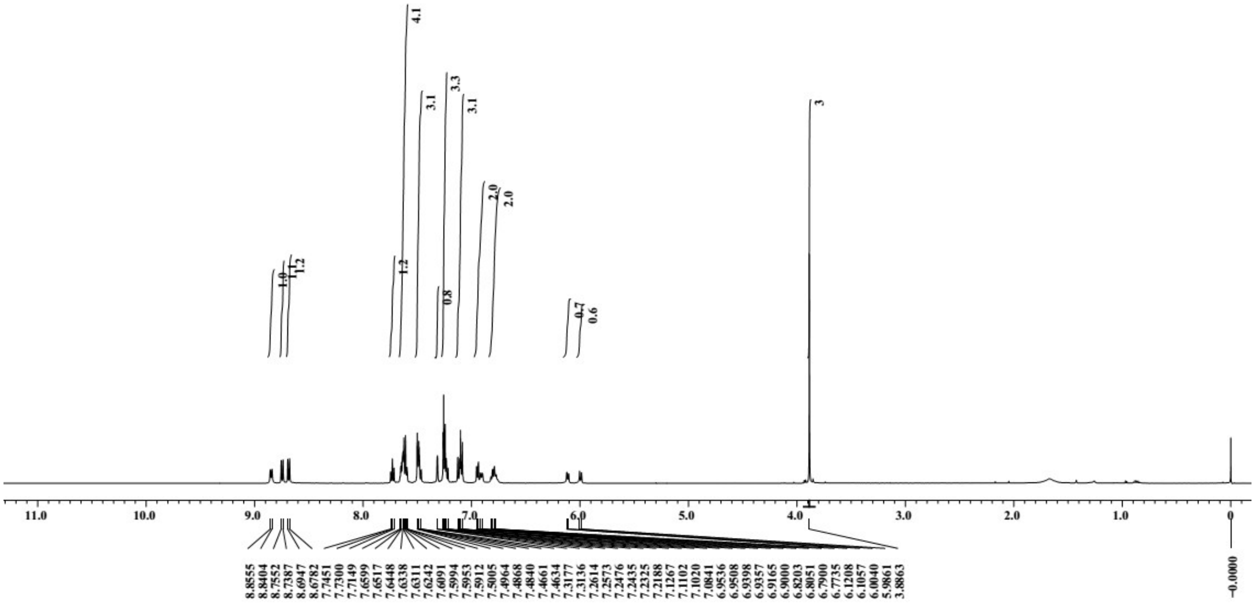

Fig. S19 ^{1}H-NMR for **2.**

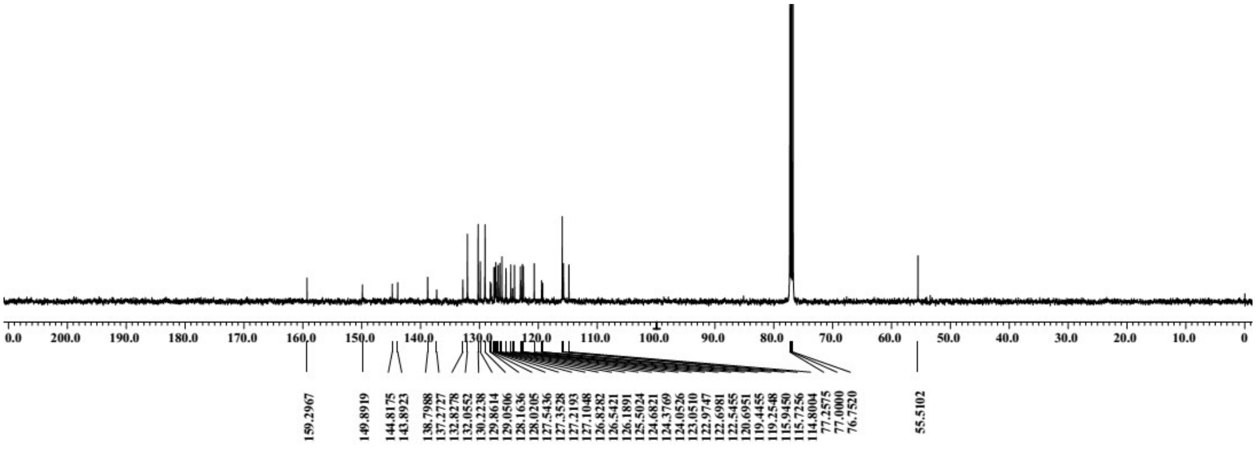

Fig. S20 ^{13}C-NMR for **2.**

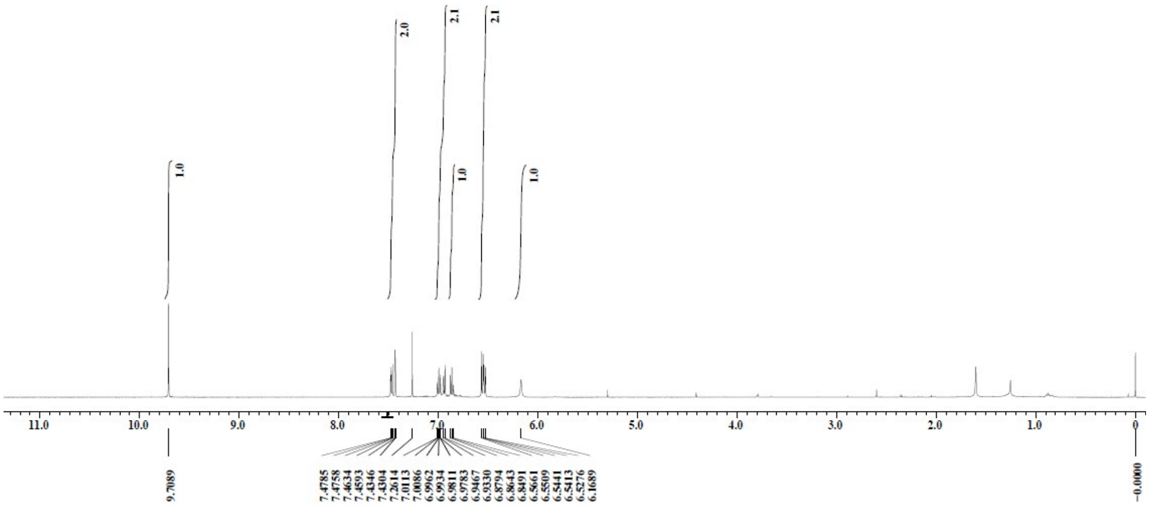

Fig. S21 ^{1}H-NMR for **3a.**

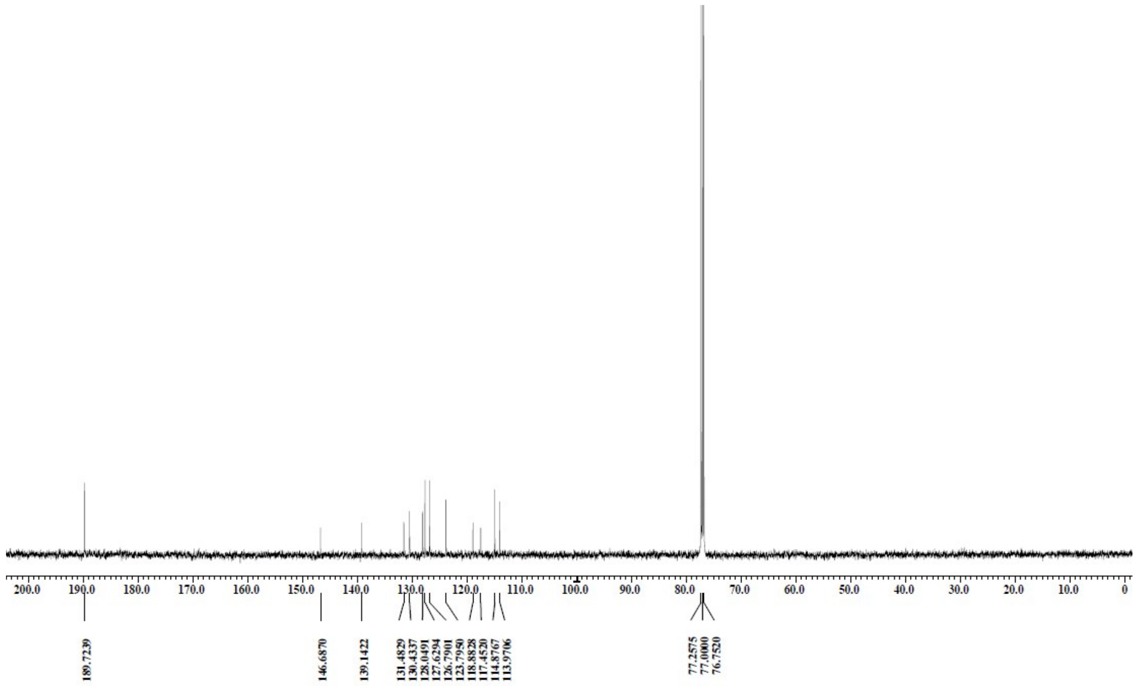

Fig. S22 ^{13}C-NMR for **3a.**

^{13}H-NMR

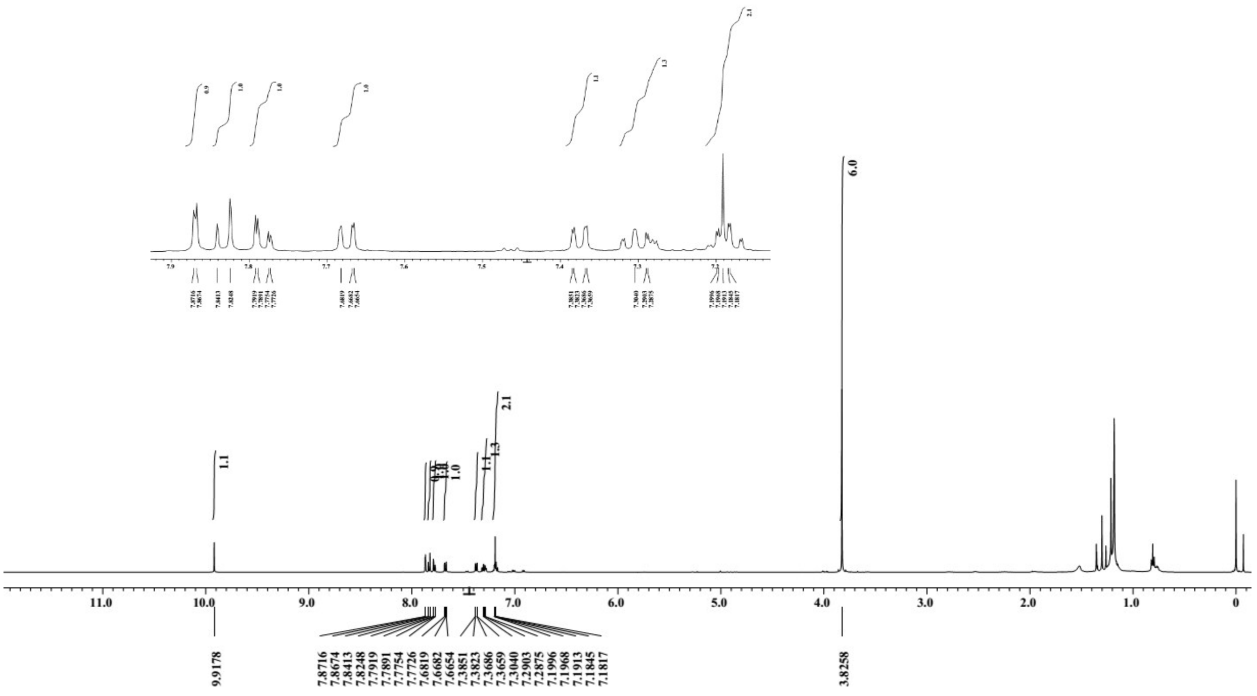

Fig. S23 ^{1}H-NMR for **3b.**

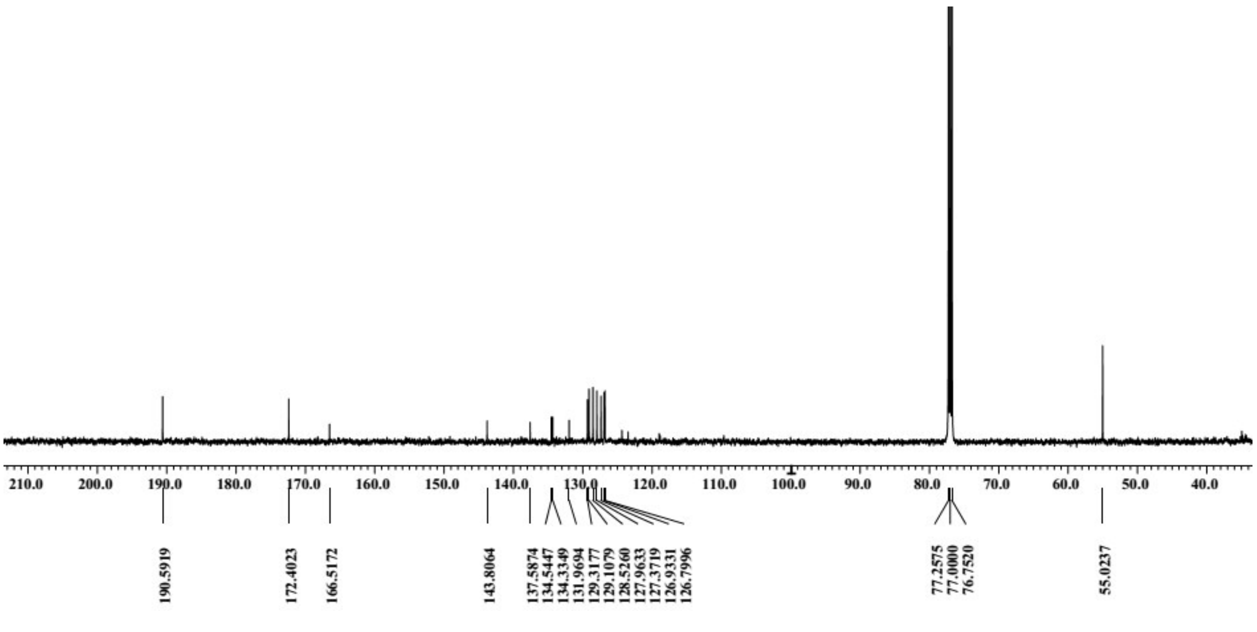

Fig. S24 ^{13}C-NMR for **3b.**

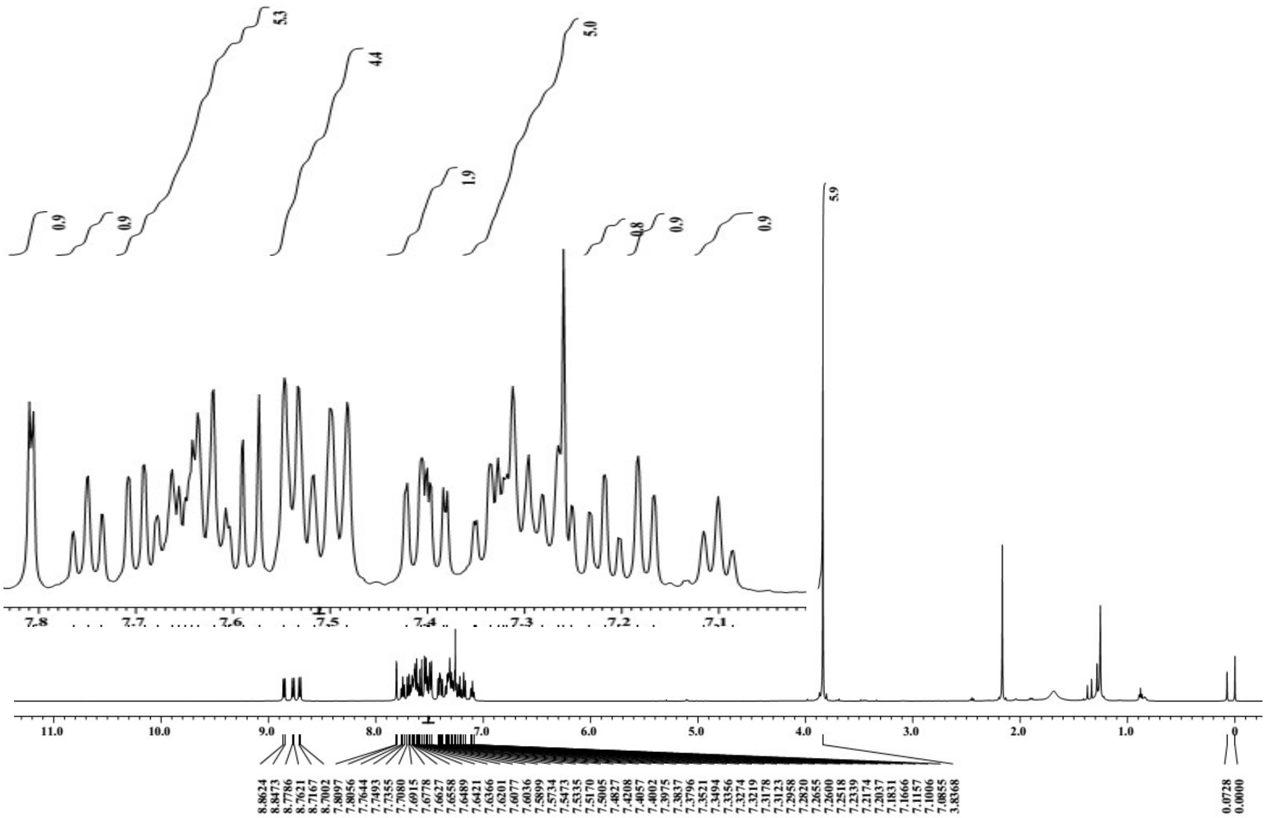

Fig. S25 ¹H-NMR for **3.**

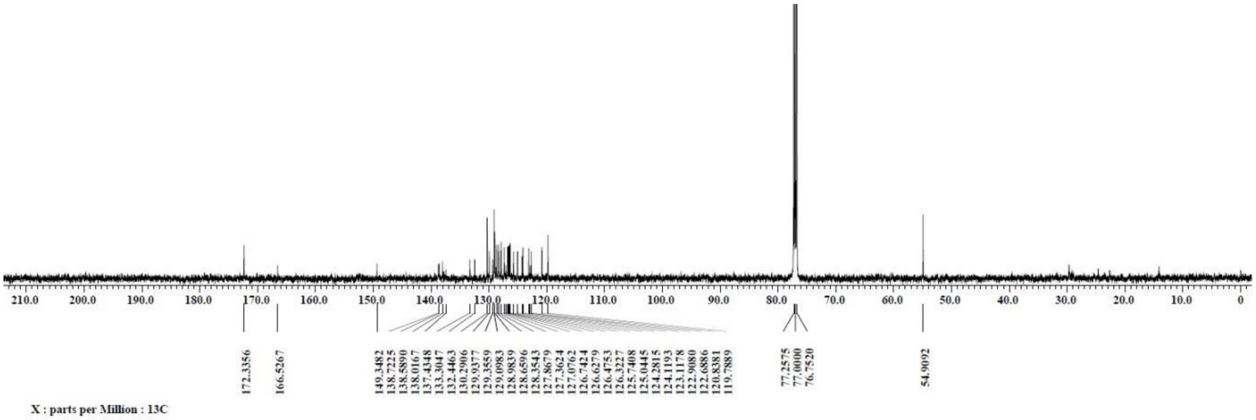

Fig. S26 ¹³C-NMR for **3.**

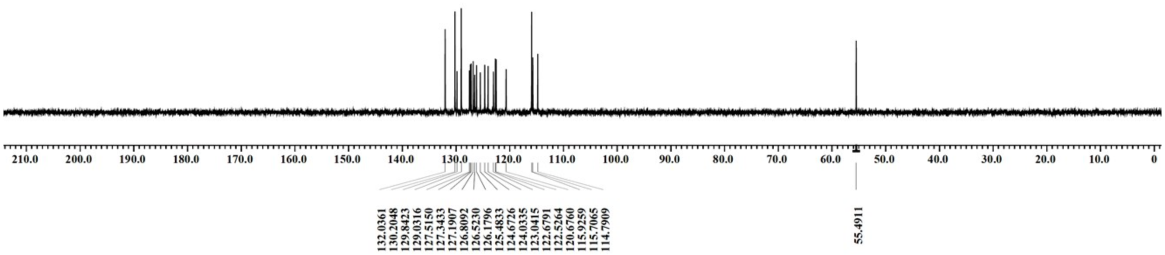

Fig. S27 DEPT-135 NMR for **2.**

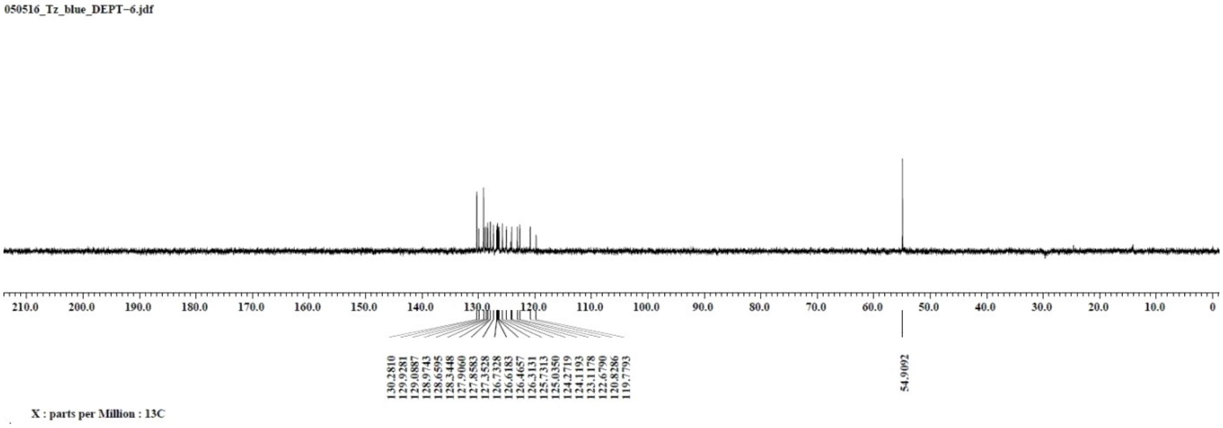

Fig. S28 DEPT-135 NMR for **3.**