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Design and Synthesis of Some Imidazolyl Derivatives: Photophysical Studies and Application in the Detection of Anions

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Supplementary Material

General: Tetrabutylammonium salts of different anions were purchased from Sigma-Aldrich Chemical Co. Pvt. Ltd. stored in a desiccator under vacuum containing self indicating silica, and used without any further purification. Solvents were purified prior to use. Spectroscopic grade solvents were used for titration studies. UV-vis absorption spectra were recorded on a Shimadzu 1700 spectrophotometer using a quartz cuvette (path length = 1cm). Infrared (IR) spectra were recorded in potassium bromide (KBr) on a FT-IR Perkin Elmer Spectrophotometer. ^{1}H NMR spectra (chemical shifts in δ ppm) were recorded on a JEOL AL 300 FT-NMR (300 MHz) spectrometer, using tetramethylsilane (TMS) as internal standard. Fluorescence spectra were recorded on Varian eclipse Carry spectrofluorometer using a quartz cuvette (path length = 1 cm) at 500 PMT voltage and slit width 5nm/5nm. All the spectroscopic experiments were carried out at room temperature. The stock solution of **DCPPI** ($1x10^{-3}$ M) were prepared in MeCN and diluted to obtain 5 ìM and 1.5 ìM solution for the absorption and fluorescence measurements, respectively. The stock solutions of different anions ($1x10^{-1}$ M) were prepared by dissolving their tetrabutylammonium salt in MeCN. The anion interaction studies were performed by the addition of 10 Equiv. of $1x10^{-1}$ M of different anions. The absorption and fluorescence titration experiment were performed by the gradual increase of concentration of F^-, CN^-, AcO^- (c =$1x10^{-3}$). The UV-vis and fluorescence measurements of DCPPI were also performed in aqueous medium, by preparing 5 ìM and 1 ìM solution respectively in H_2O-MeCN (50%). For these studies the stock solutions of different anions ($1x10^{-1}$ M) were prepared by dissolving their sodium salt in H_2O. The anion interaction and interference studies were performed by the addition of 20 and 40 Equiv. of $1x10^{-1}$ M of different anions respectively. Similarly for DCPPIA the stock solution ($1x10^{-3}$ M) were prepared in MeCN and diluted by mixing appropriate amount of solution to obtained 10 ìM and 0.4 ìM solutions in MeCN for physico-chemical studies respectively. The anion interaction studies were performed by the addition of 40 Equiv of $1x10^{-1}$ M of different anions. The absorption and fluorescence titration experiment were performed by gradual increasing concentration of F^-, CN^-, AcO^- (c =$1x10^{-3}$ M). ^{1}H NMR titration studies were performed in DMSO-d_6 by increasing the concentration of F^- and CN^- anions to a solution of **DCPPI** (c = 2.1 x 10^{-2} M in DMSO-d_6).

The absorption and fluorescence experimental data were utilized to calculate association constants by Benesi-Hildebrand method[18] (B-H method) employing equations (1) and (2) for 1:1 and 2:1 stoichiometries.

$$1/(I - I_o) = 1/(I - I_f) + 1/K(I - I_f)[M] \quad \textbf{(1)}$$

$$1 / (I - I_o) = 1 / (I - I_f) + 1 / K (I - I_f) [M]^{1/2} \quad \textbf{(2)}$$

Where K is the association constant, I is the absorbance/fluorescence intensity of the free probe **DCPPI**, I is the

observed absorbance/fluorescence intensity of the **DCPPI-A**$^-$complex, and I_f is the absorbance/fluorescence intensity at saturation level. The quantum yields were estimated with respect to the quinine sulfate as standard in 0.1M H_2SO_4 solution by secondary methods,[1h]using equation (3).

$$Q = Q_R . I/I_R . OD_R/OD . n^2/n^2_R \quad \textbf{(3)}$$

Where Q is the quantum yield, *I* is the integrated intensity, OD is the optical density, and n is the refractive index. The subscript R refers to the reference fluorophore of known quantum yield.

The limit of detection (LOD) was estimated by using equation (4).

$$LOD = 3\sigma/m \quad \textbf{(4)}$$

Where, σ stands for the standard deviation of blank solution of **DCPPI** and m stands for calibration sensitivity toward F^- and CN^- ions in MeCN solution of **DCPPI**.

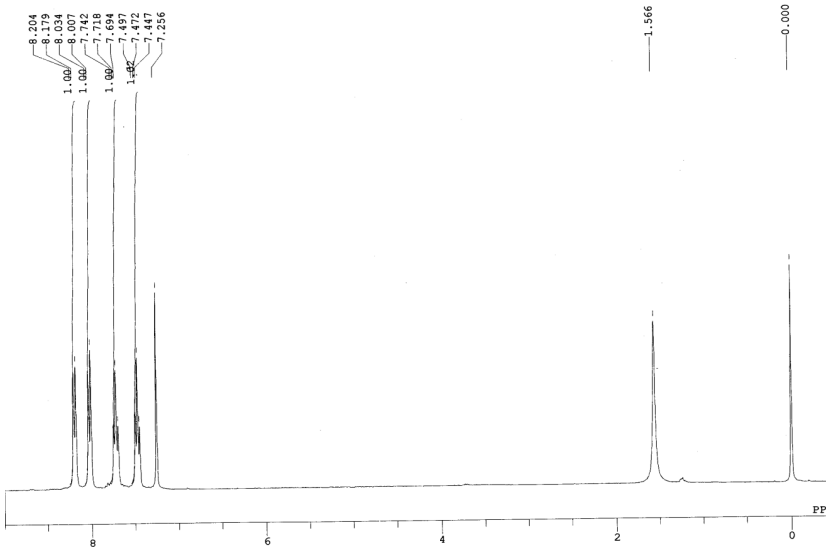


Fig. (S1). ^{1}H NMR spectrum of **2** in $CDCl_3$.

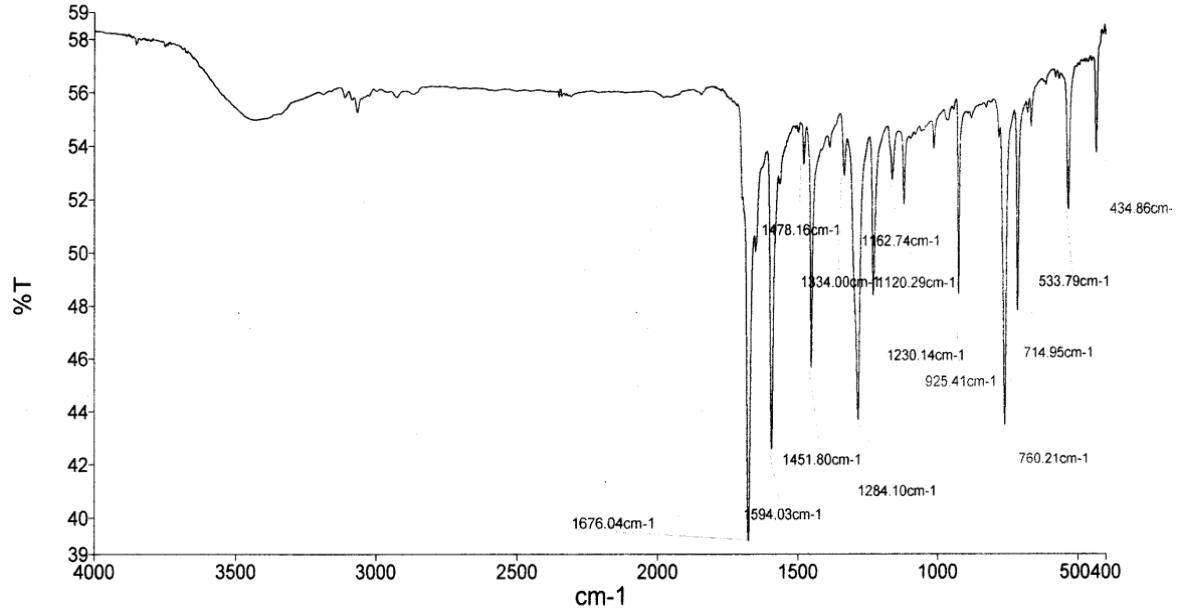


Fig. (S2). FT-IR spectrum of 3 **2**.

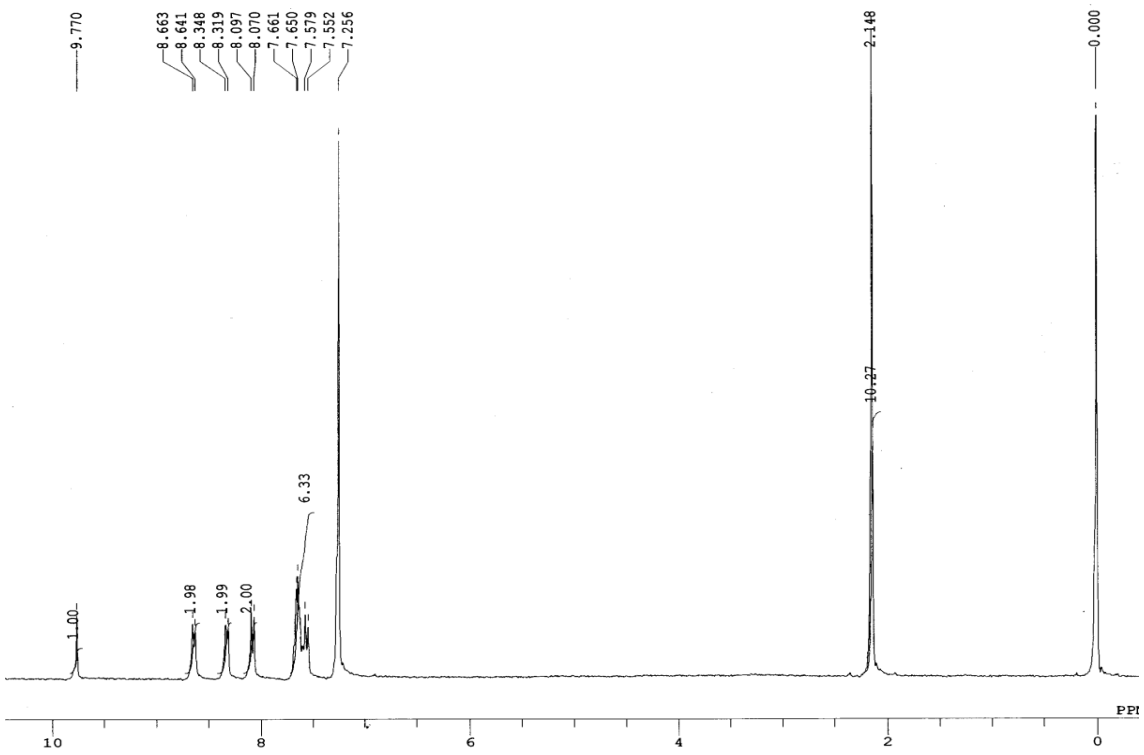


Fig. (S3). ^{1}H NMR spectrum of 3 in $CDCl_3$.

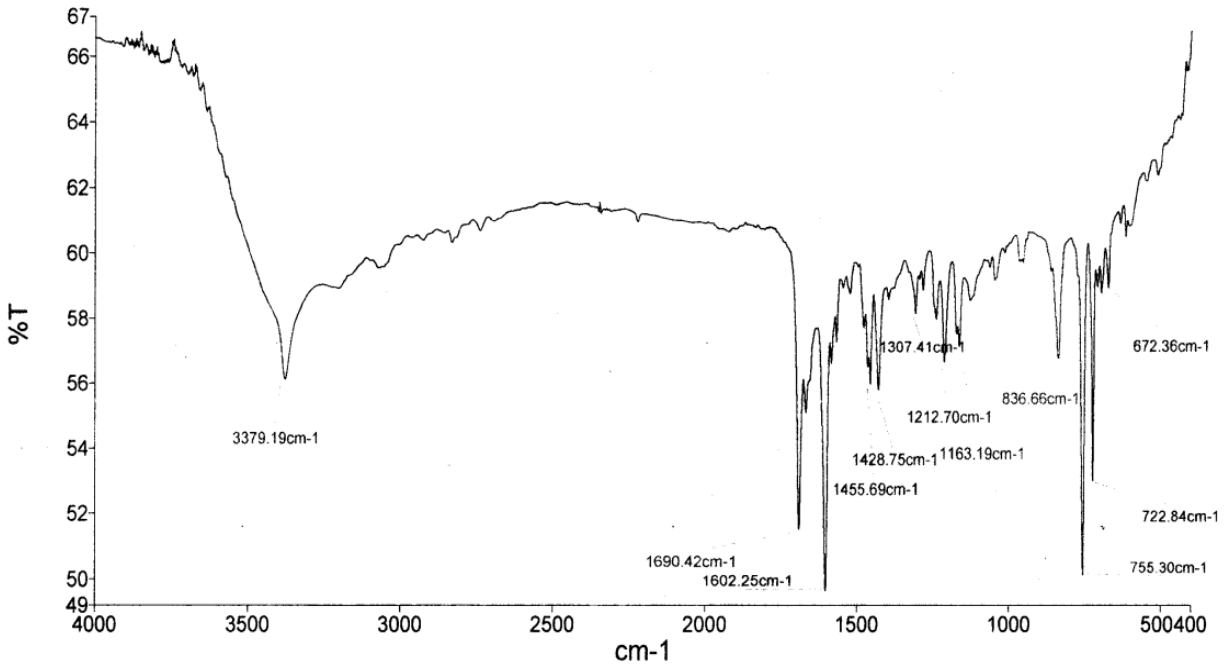


Fig. (S4). FT-IR spectrum of **3**.

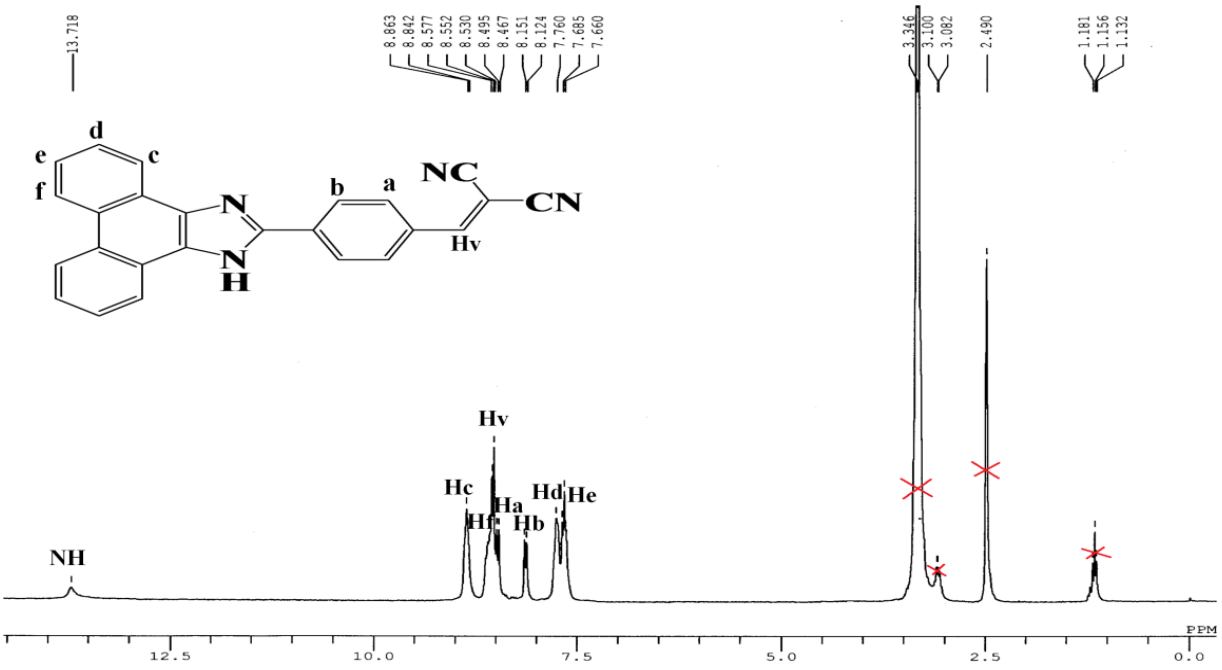


Fig. (S5). [1]H NMR spectrum of **DCPPI** in DMSO-d_6.

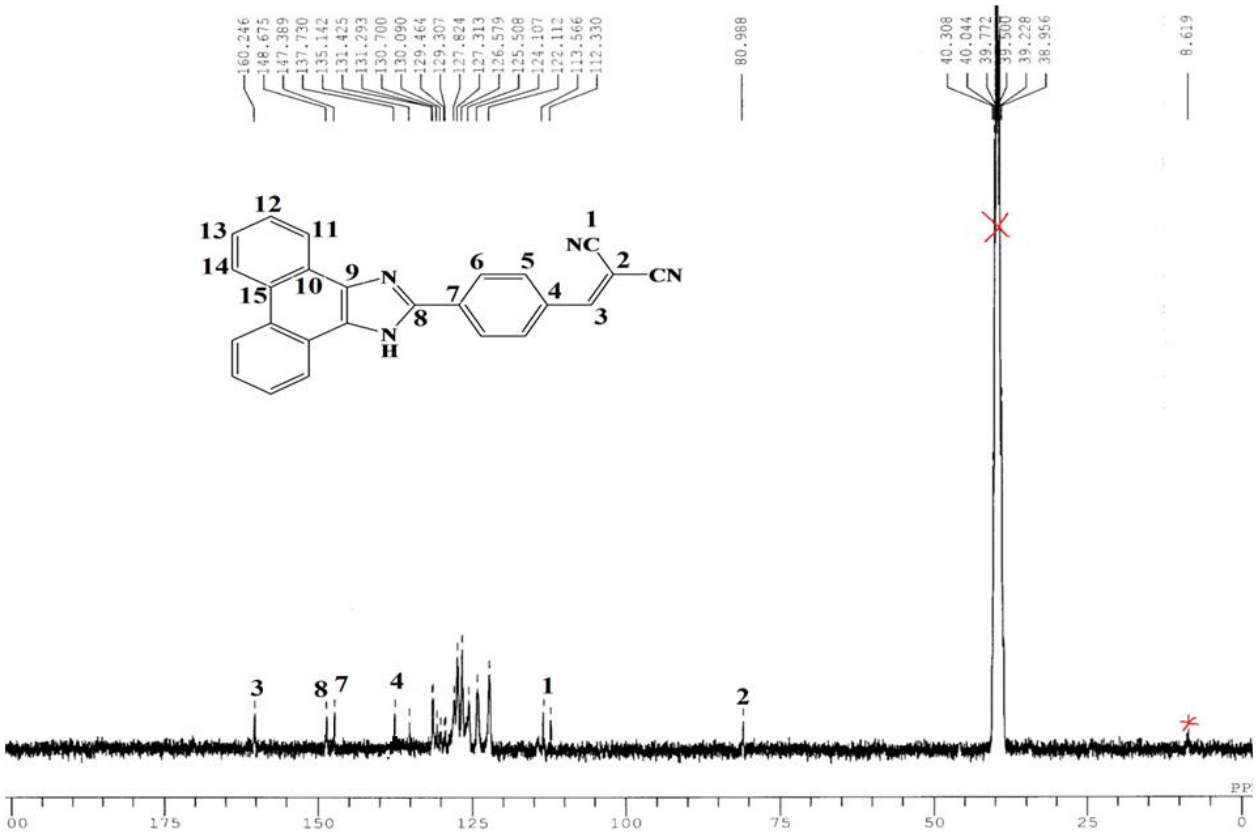


Fig. (S6). [13]C NMR spectrum of **DCPPI** in DMSO-d_6.

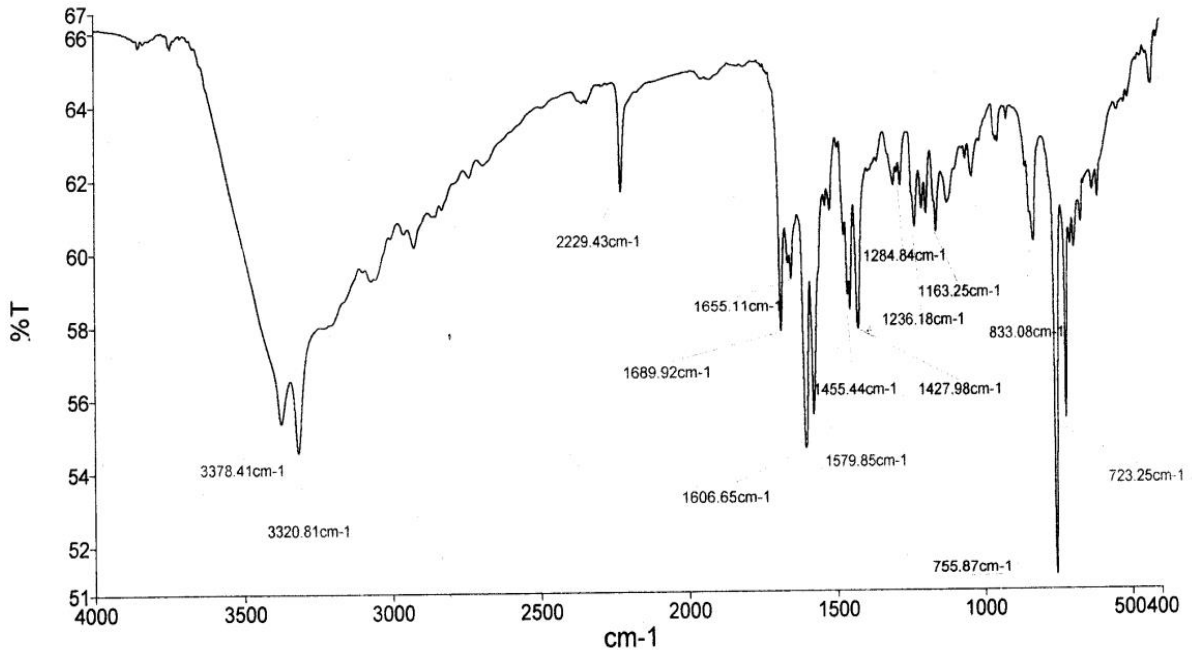


Fig. (S7). FT-IR spectrum of **DCPPI**.

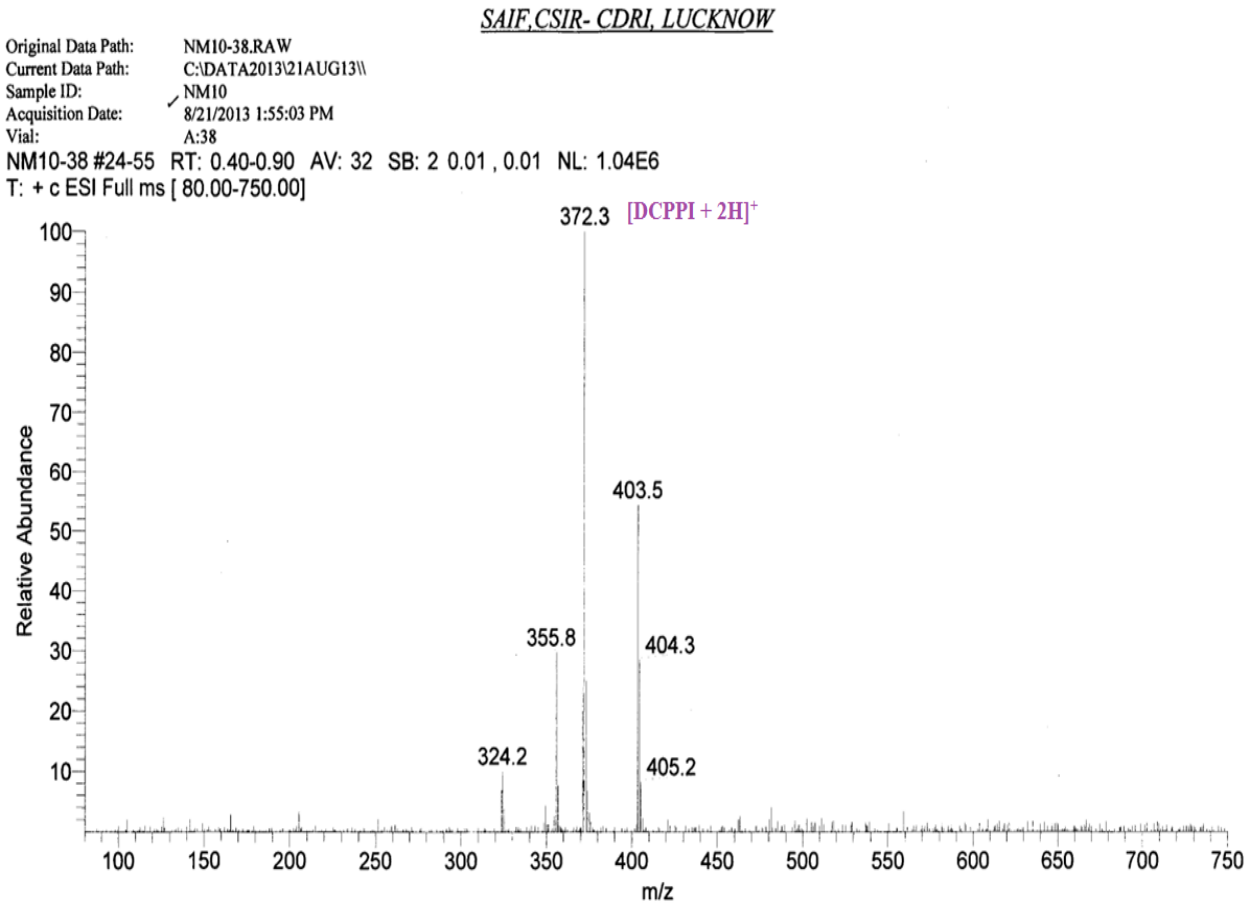


Fig. (S8). ESI-MS spectrum of **DCPPI**.

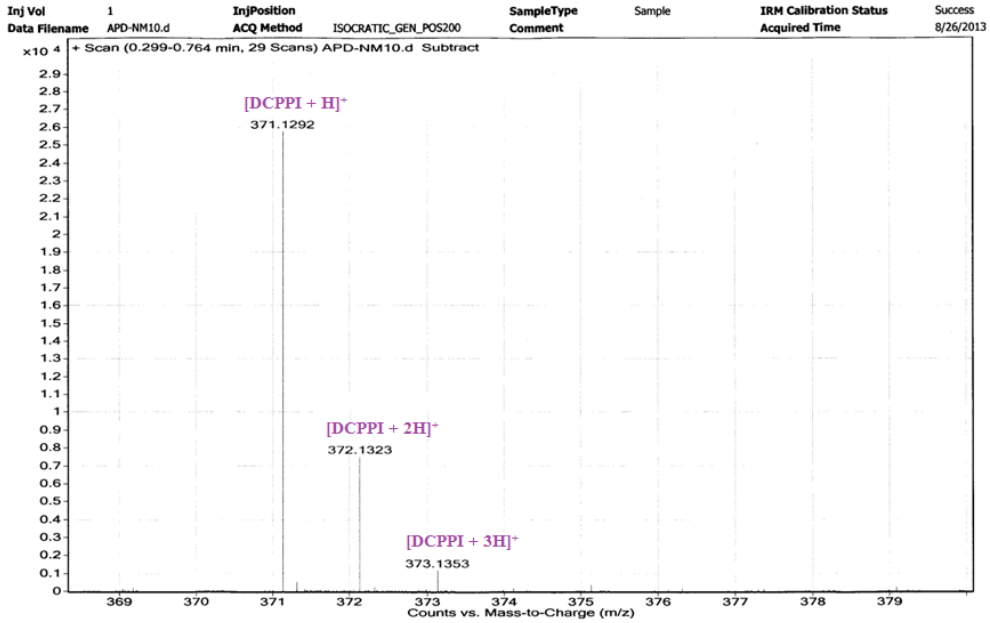


Fig. (S8a). HRMS spectrum of **DCPPI**.

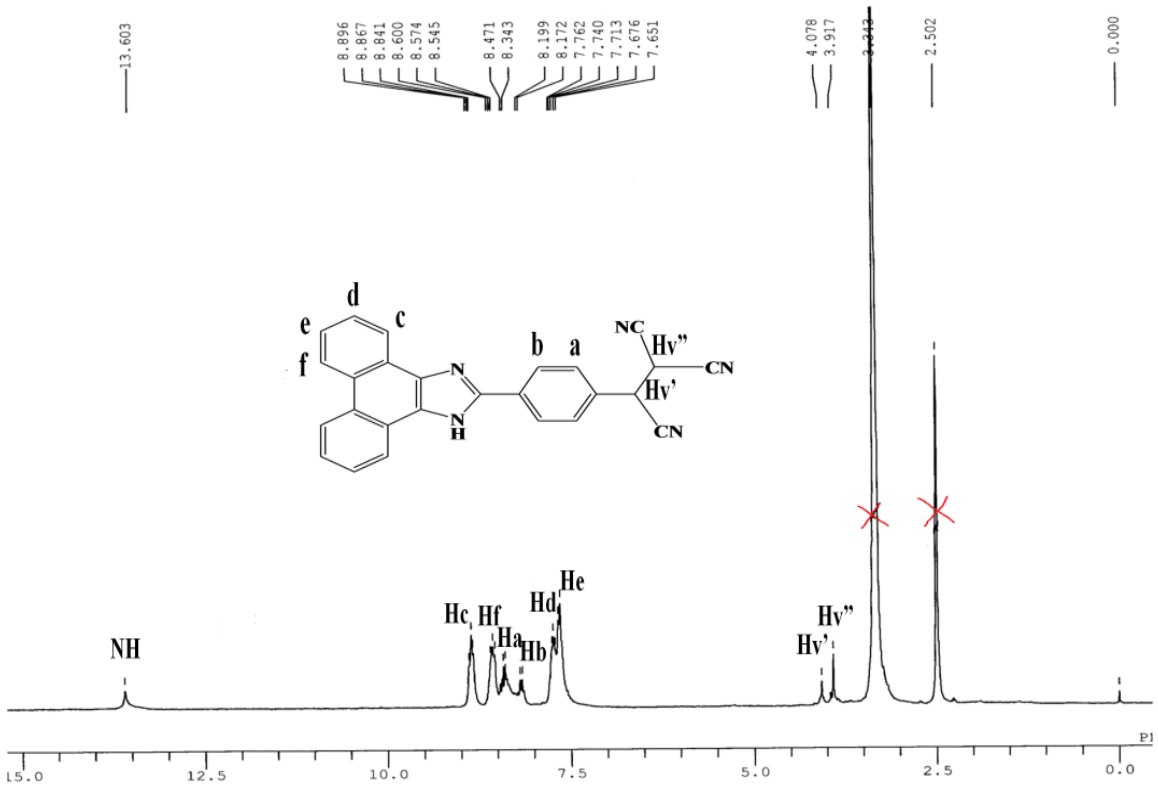


Fig. (S9). ^{1}H NMR spectrum of **DCPPIA** in DMSO-d_6.

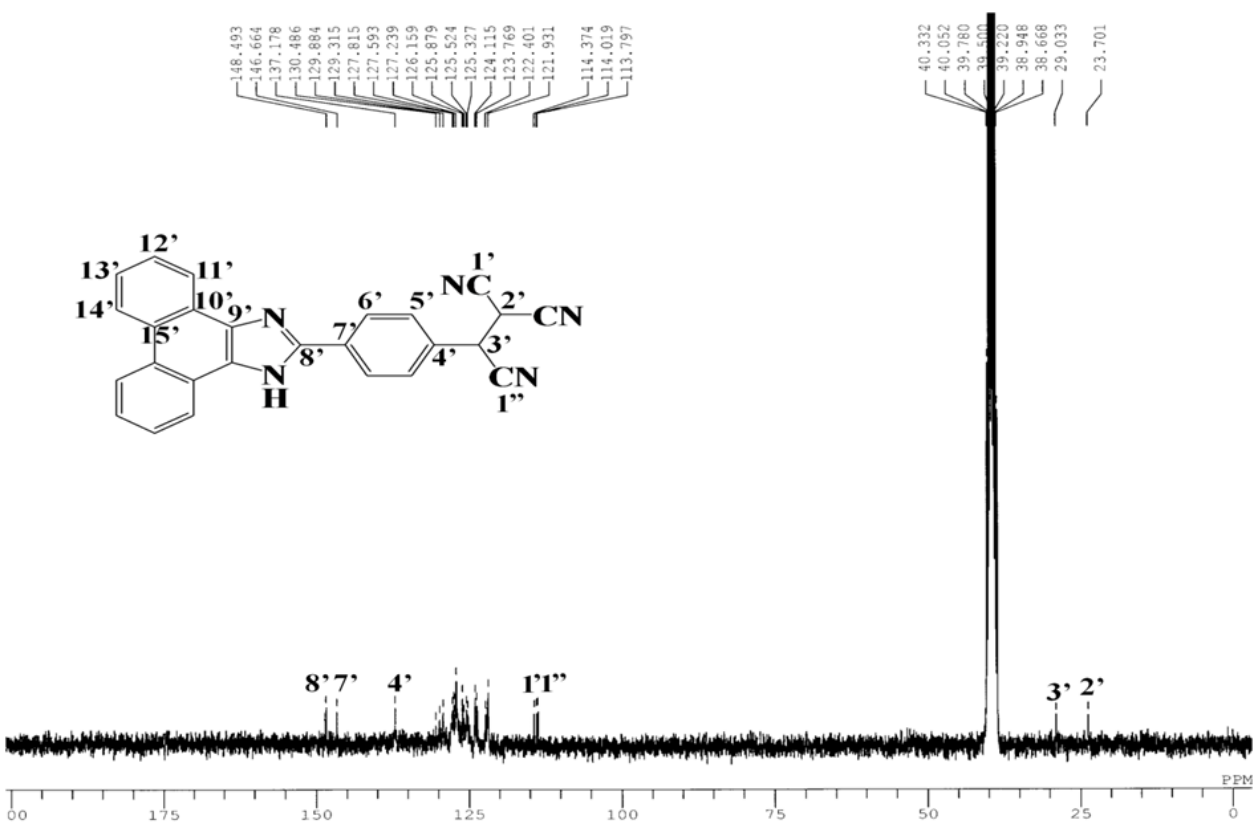


Fig. (S10). ^{13}C NMR spectrum of **DCPPIA** in DMSO-d_6.

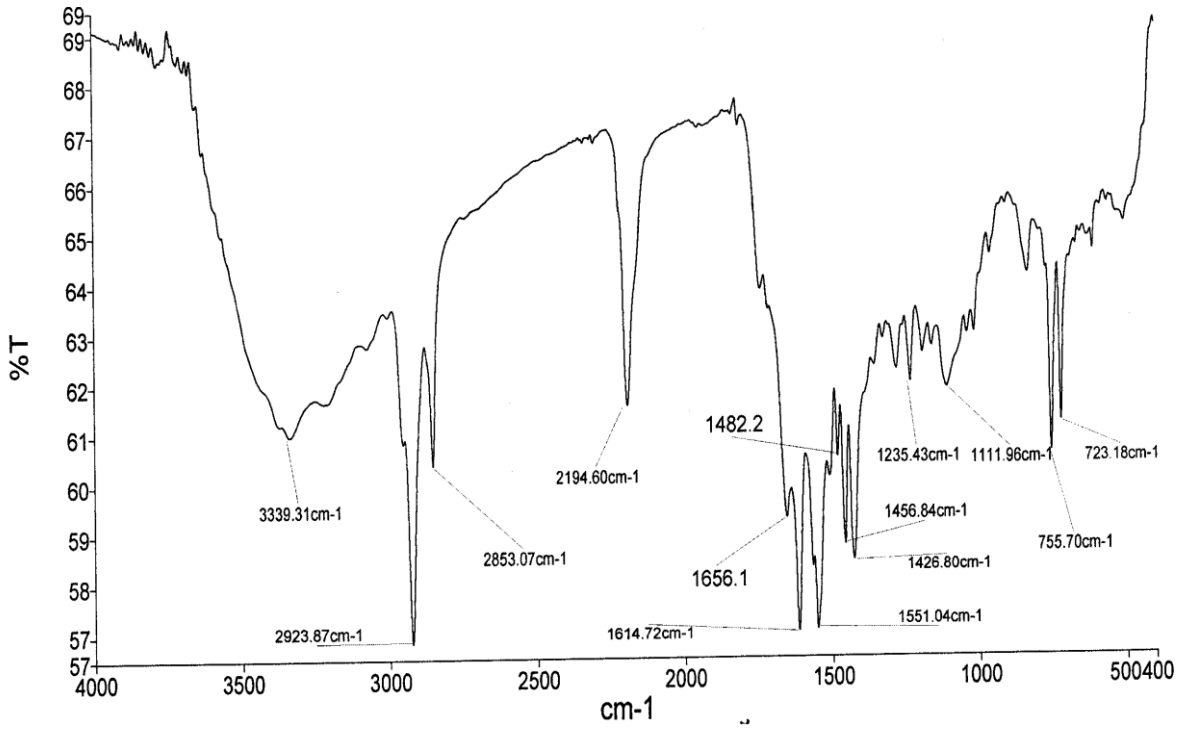


Fig. (S11). FT-IR spectrum of **DCPPIA**.

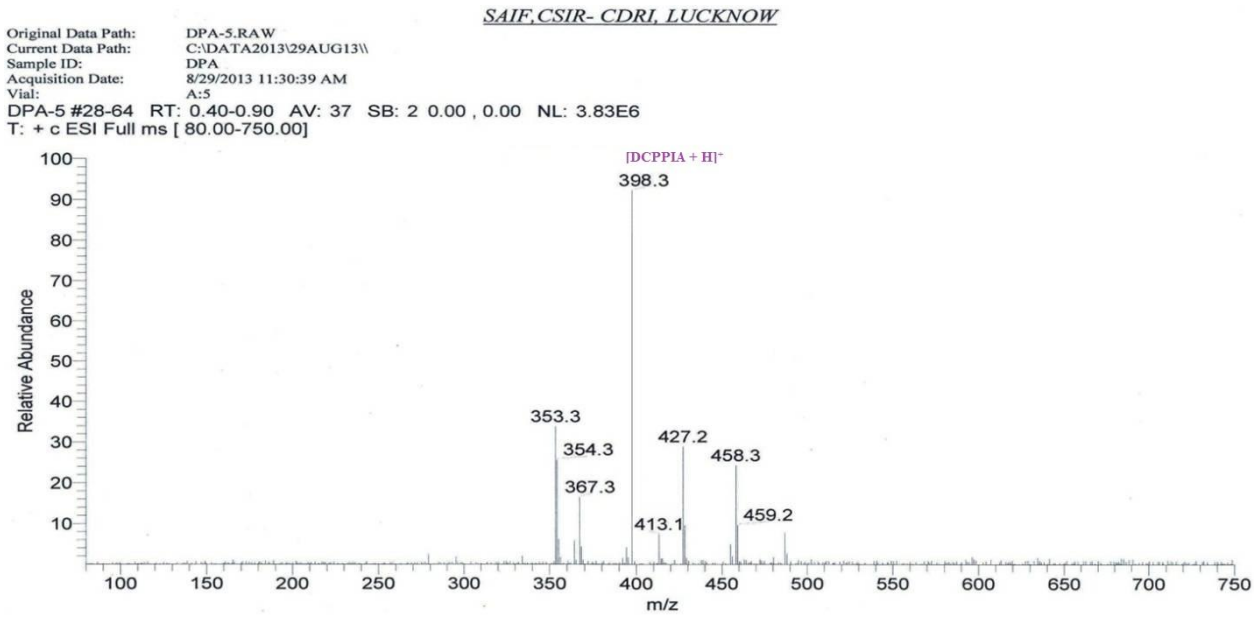


Fig. (S12). ESI-MS spectrum of **DCPPIA**.

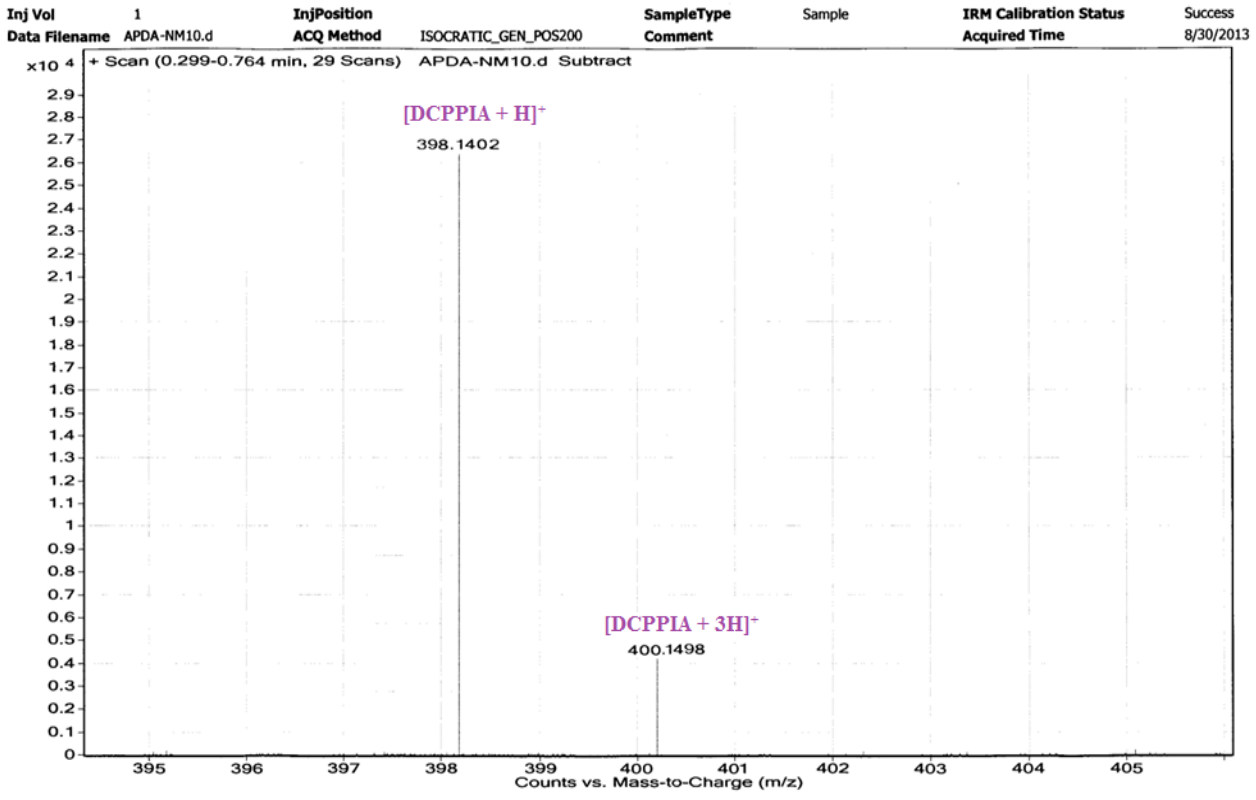


Fig. (S12a). HRMS spectrum of **DCPPIA.**

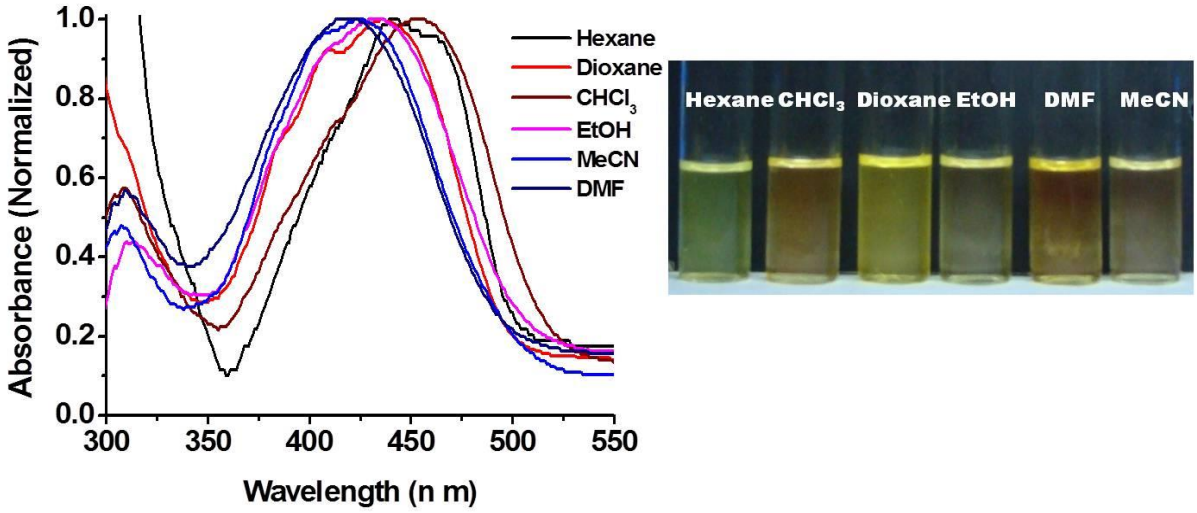
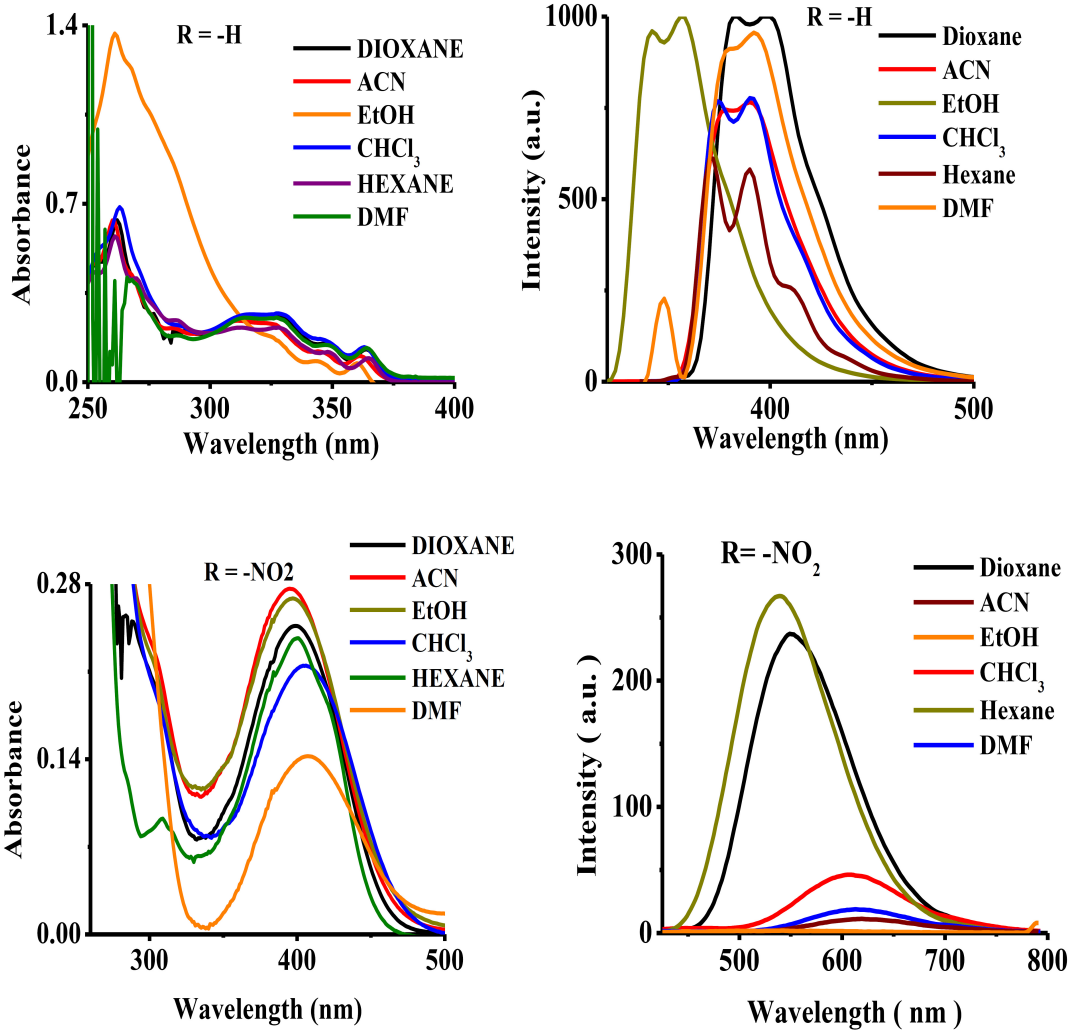


Fig. (S13). Normalized UV-Vis absorption spectra of **DCPPI** in solvents of different polarities. Inset: Photograph of **DCPPI** in solvents of different polarities.



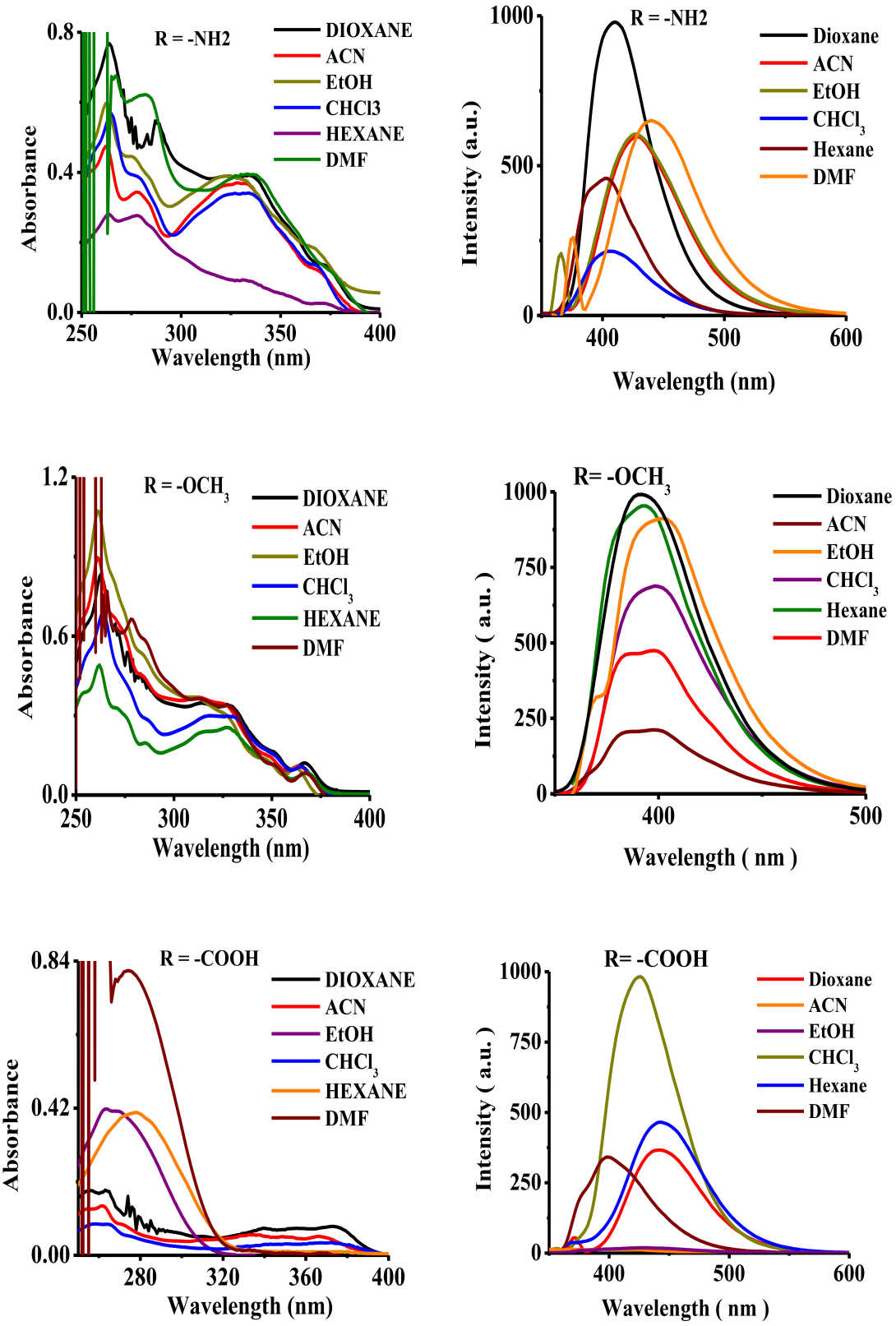


Fig. (S13a). Absorption and emission spectra of derivatives (R1 = H, NO_2, NH_2, OCH3, COOH) in different solvents.

Table S1. Optical properties of derivatives in different solvents.

Medium	λ_{max} (nm)	λ_{em} (nm)	Stoke's Shift (Δ h) (cm^{-1})	Molar absoptivity ε ($M\text{-}1cm^{-1}$)	Quantum yield ϕ	Derivatives (R)
Dioxane	364	384	1430.861	12800	0.565	H
	399	548	6814.481	24600	0.141	NO^2
	373	424	3224.746	8260	0.986	COOH
	367	398	2122.328	12100	0.576	OCH^3
	334	410	5549.876	39200	0.197	NH^2
	436	556	4950.894	38,400	0.144	**DCPPI**
ACN	361	390	2059.805	10200	0.464	H
	395	618	9135.226	27600	0.006	NO^2
	335	442	7226.312	5800	0.707	COOH
	363	398	2422.581	10900	0.422	OCH^3
	332	428	6755.996	36800	0.138	NH^2
	427	614	7132.559	29,900	0.168	**DCPPI**
EtOH	342	356	1149.878	7400	0.829	H
	397	542	6738.732	26800	0.001	NO^2
	263	398	12897.19	42700	0.062	COOH
	362	393	2179.017	10100	0.624	OCH^3
	328	428	7123.319	38600	0.142	NH^2
	433	616	6860.411	29,600	0.018	**DCPPI**
CHCl3	363	390	1907.184	13700	0.394	H
	406	606	8128.892	21400	0.025	NO^2
	375	442	4042.232	3400	0.996	COOH
	365	398	2271.632	10600	0.337	OCH^3
	334	406	5309.578	34100	0.054	NH^2
	439	585	5685.205	28,600	0.129	**DCPPI**
Hexane	365	388	1624.064	9400	0.342	H
	401	538	6350.295	23600	0.113	NO^2
	278	394	10590.51	40700	0.004	COOH
	368	398	2048.285	8400	0.180	OCH^3
	278	404	11218.75	27600	0.119	NH^2
	442	526	3613.424	13,800	0.118	**DCPPI**
DMF	364	392	1962.323	13400	0.531	H
	407	612	8230.155	14200	0.015	NO^2
	273	323	5670.284	81000	0.003	COOH
	367	402	2372.335	8200	0.877	OCH^3
	336	440	7034.632	39400	0.170	NH^2
	434	619	6886.584	2500	0.043	**DCPPI**

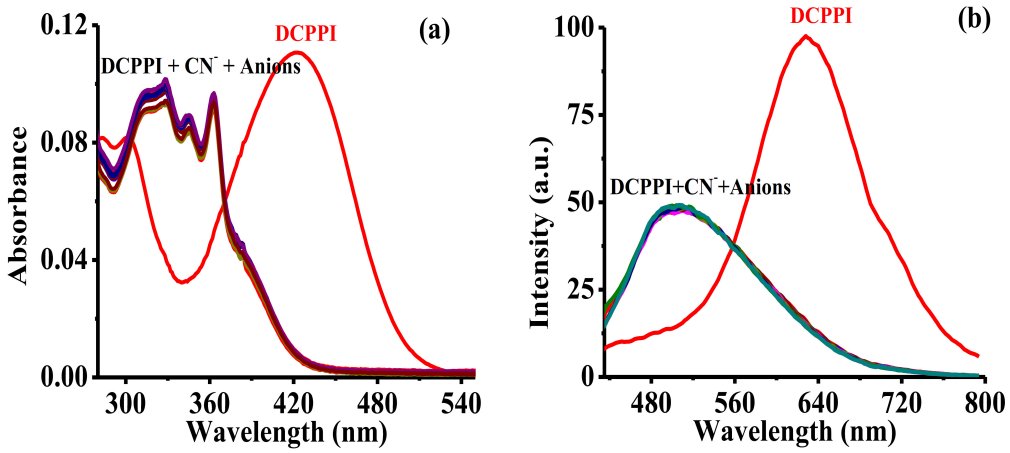


Fig. (S14). (**a**) Absorption (5 µM) (**b**) Emission spectra (1 µM) of interference study of **DCPPI + CN-** upon addition of different anions (40 Equiv) in H_2O-MeCN (50 %).

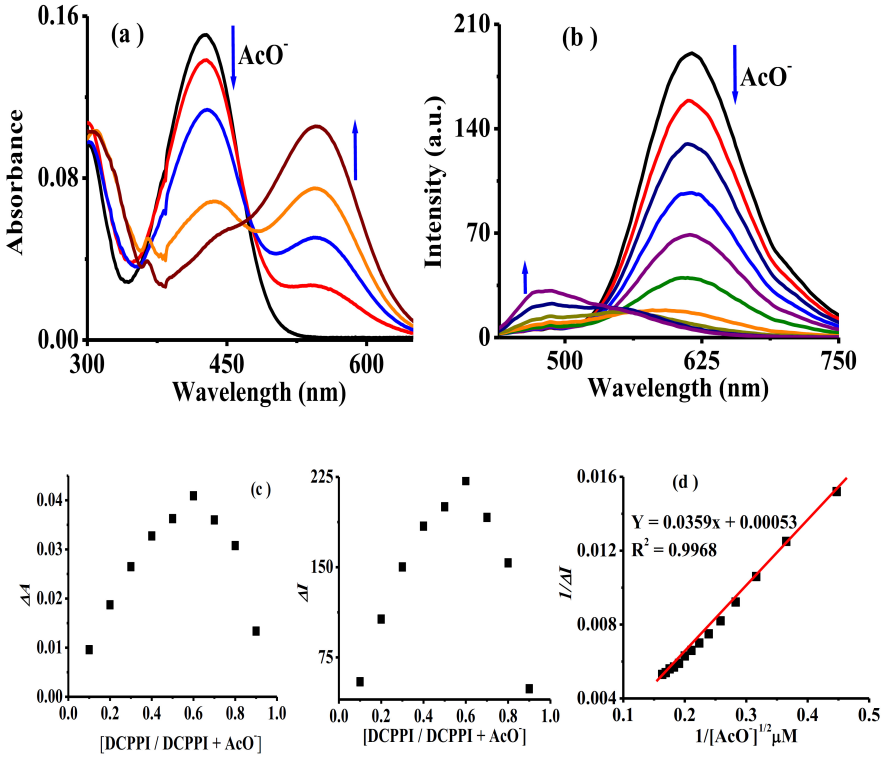


Fig. (S15). (**a**) UV-vis absorption (5µM) and (**b**) Emission titration spectra (1.5µM) of DCPPI upon addition of 0-7 Equiv and 38 Equiv of AcO- anions in MeCN. (**c**) Job's plot obtained from absorption and emission spectral data. (**d**) Benesi-Hildebrand plot.

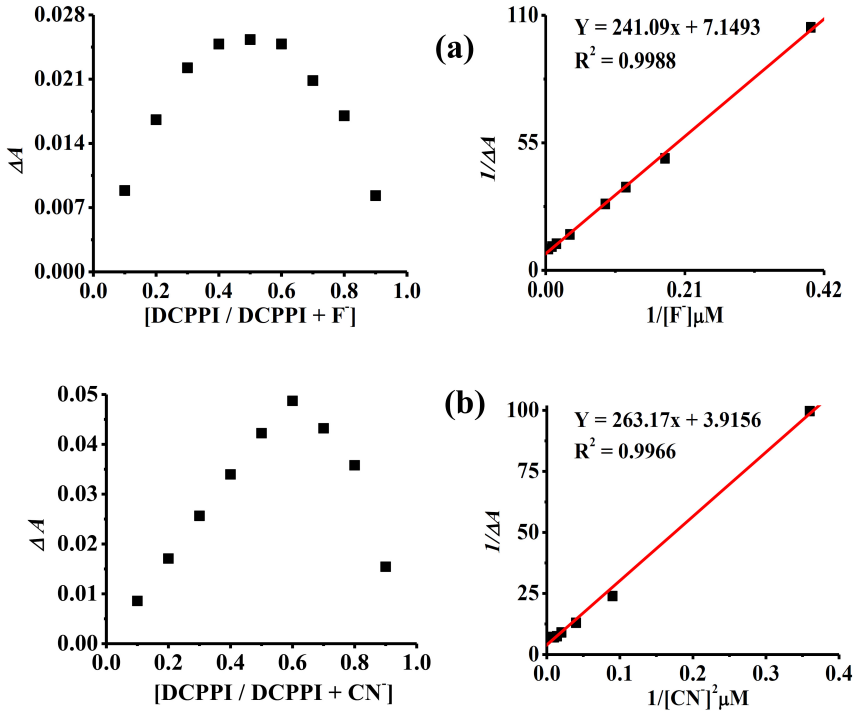


Fig. (S16). Job's plot and Benesi-Hildebrand plots obtained from absorption(5µM) titration spectra of **DCPPI** upon addition of (**a**) 0-9 Equiv. of F- anions and (**b**) 0-5 Equiv. of CN- in MeCN.

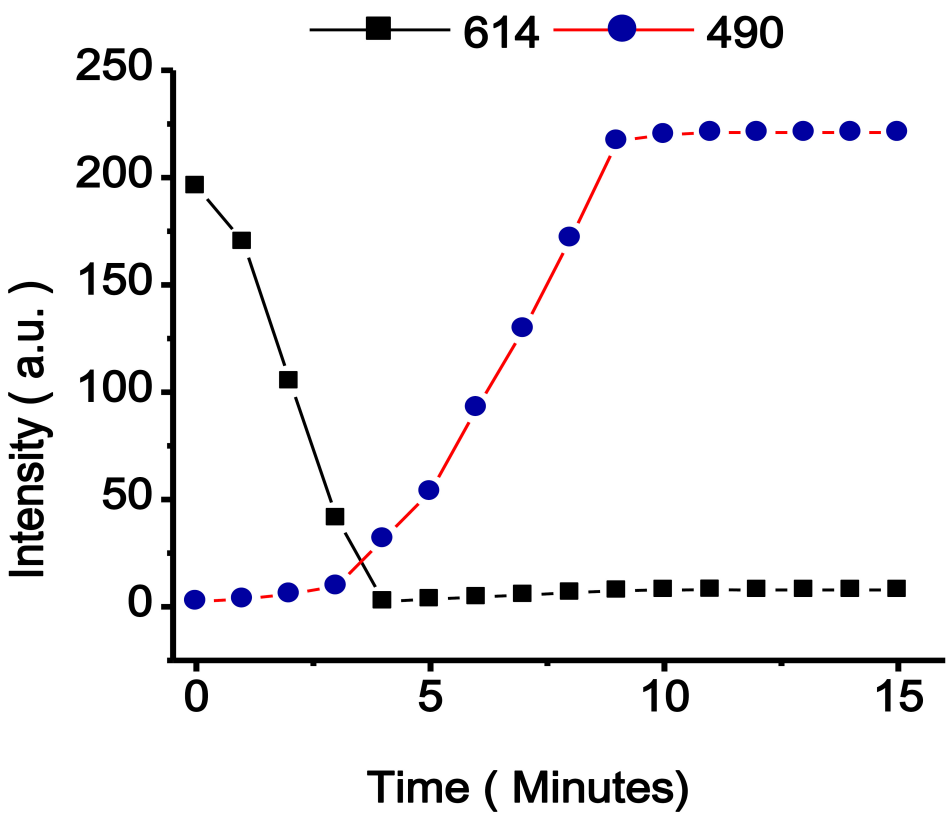


Fig. (S17). A time versus intensity reaction kinetics plot for **DCPPI** upon interaction with CN- (20 Equiv) in MeCN.

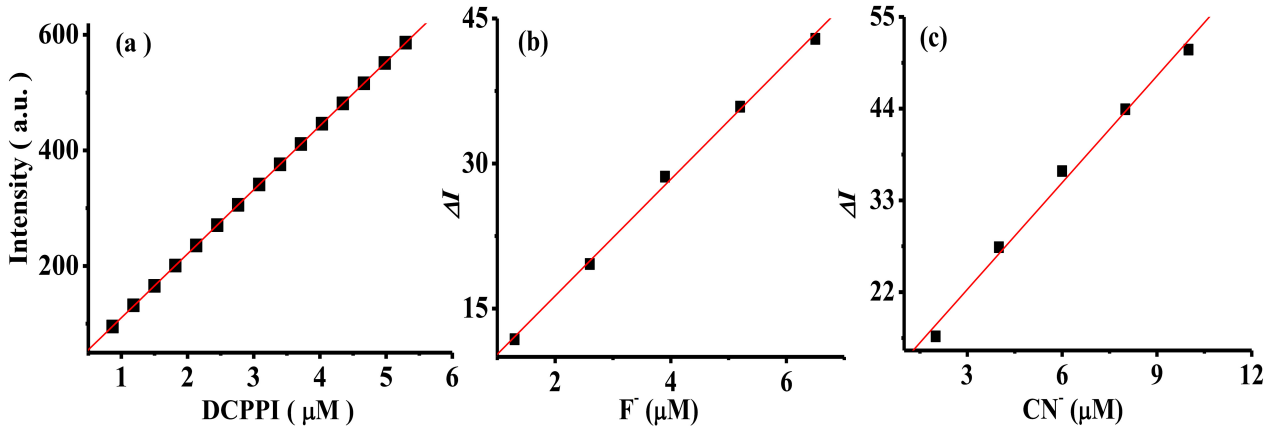


Fig. (S18). (**a**) Calibration curve for DCPPI (**b**) Calibration sensitivity curve (m) for DCPPI with respect to F- and (**c**) CN- ions (where DI shows the change in emission intensity of **DCPPI** upon addition of F- and CN- respectively.

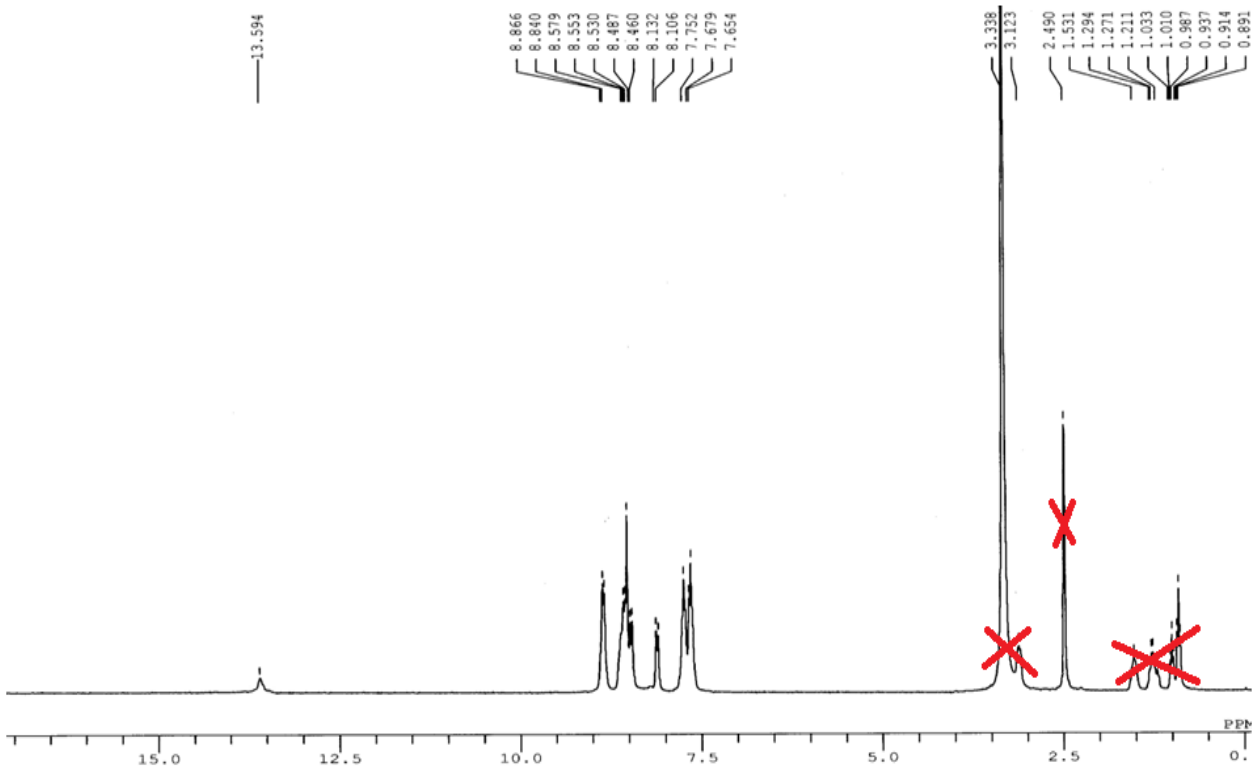


Fig. (S19). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.25 Equiv of F- in DMSO-d_6.

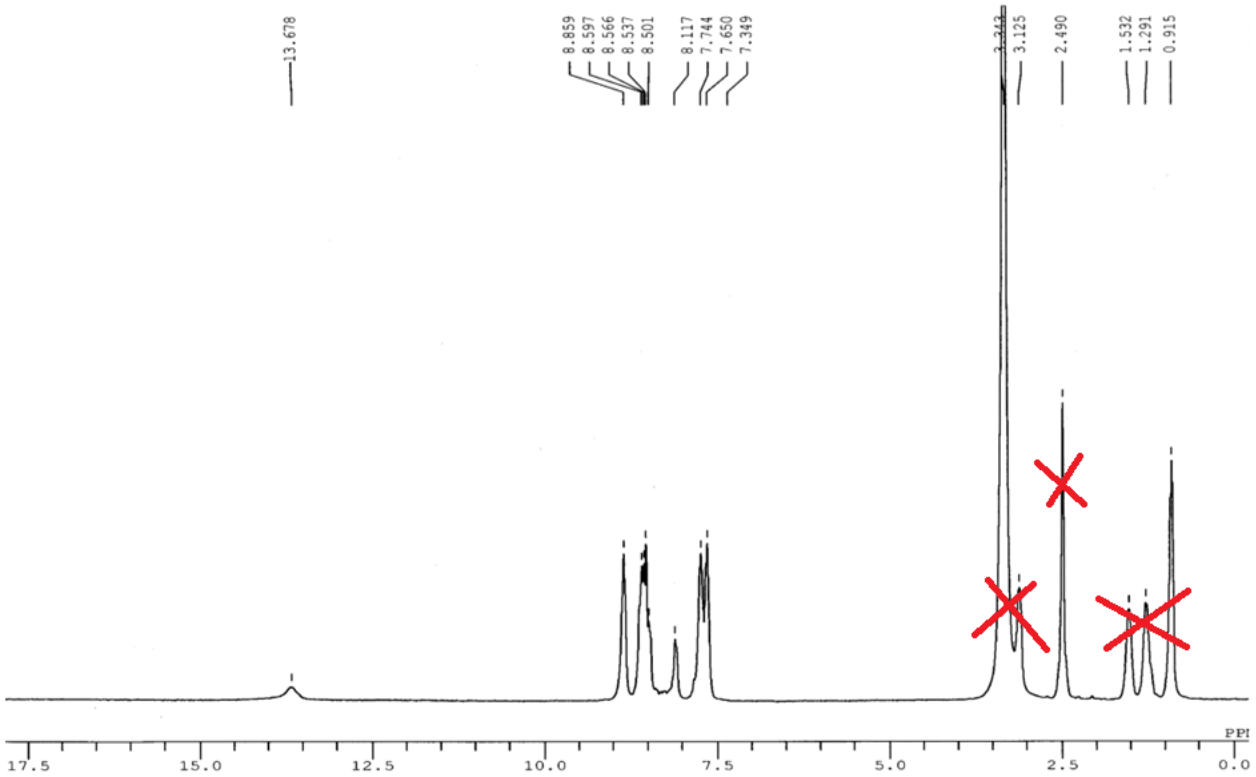


Fig. (S20). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.50 Equiv of F- in DMSO-d_6.

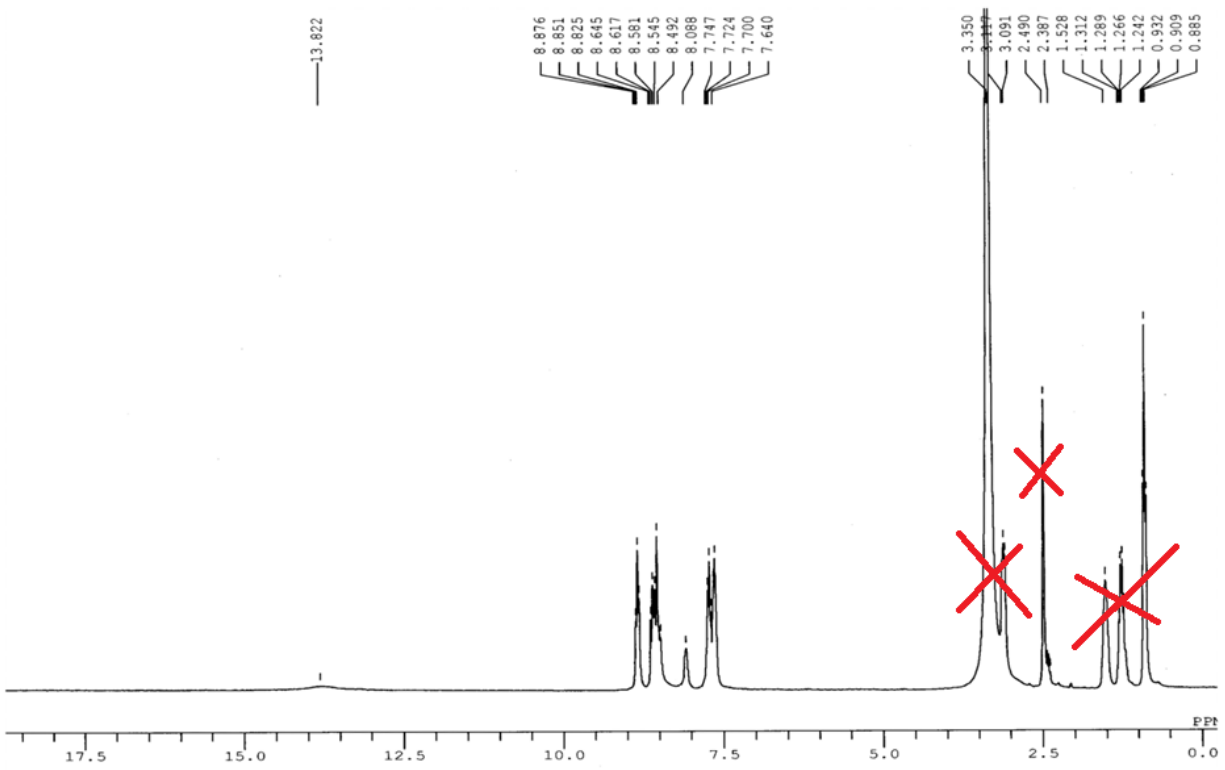


Fig. (S21). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.75 Equiv of F- in DMSO-d_6.

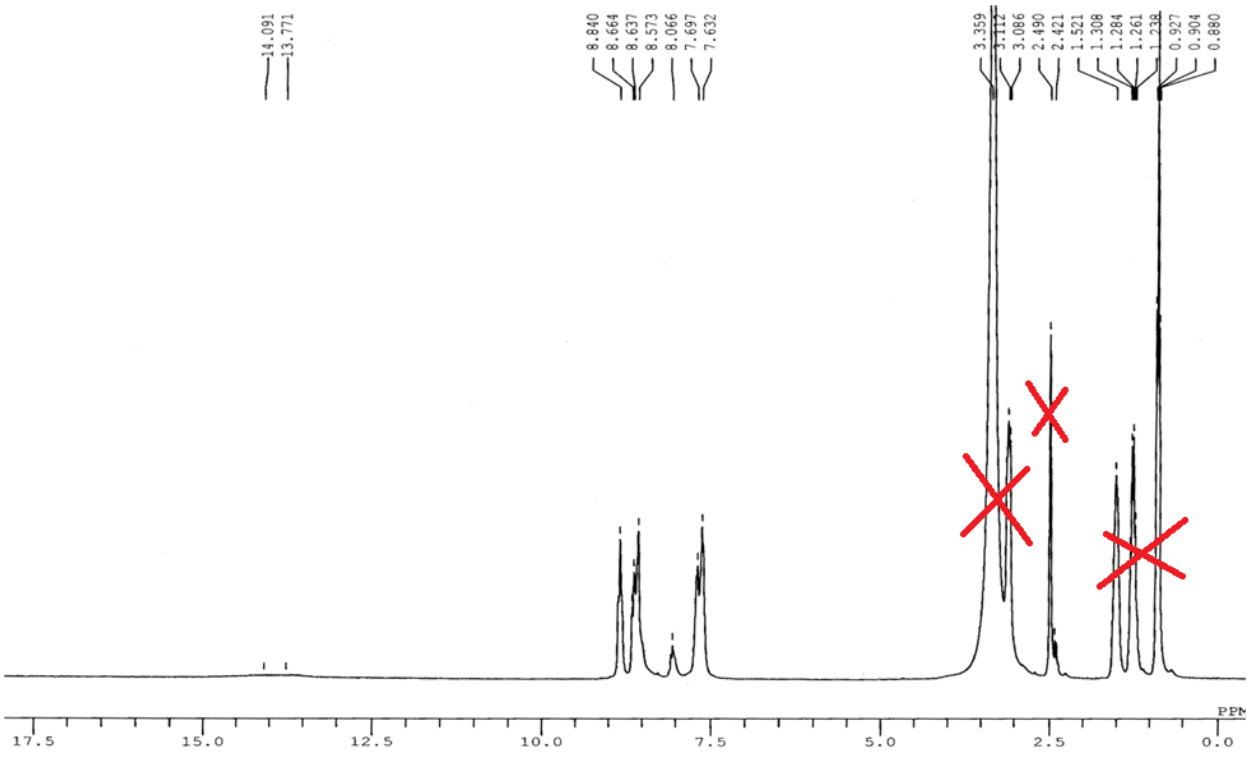


Fig. (S22). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.25 Equiv of CN- in DMSO-d_6.

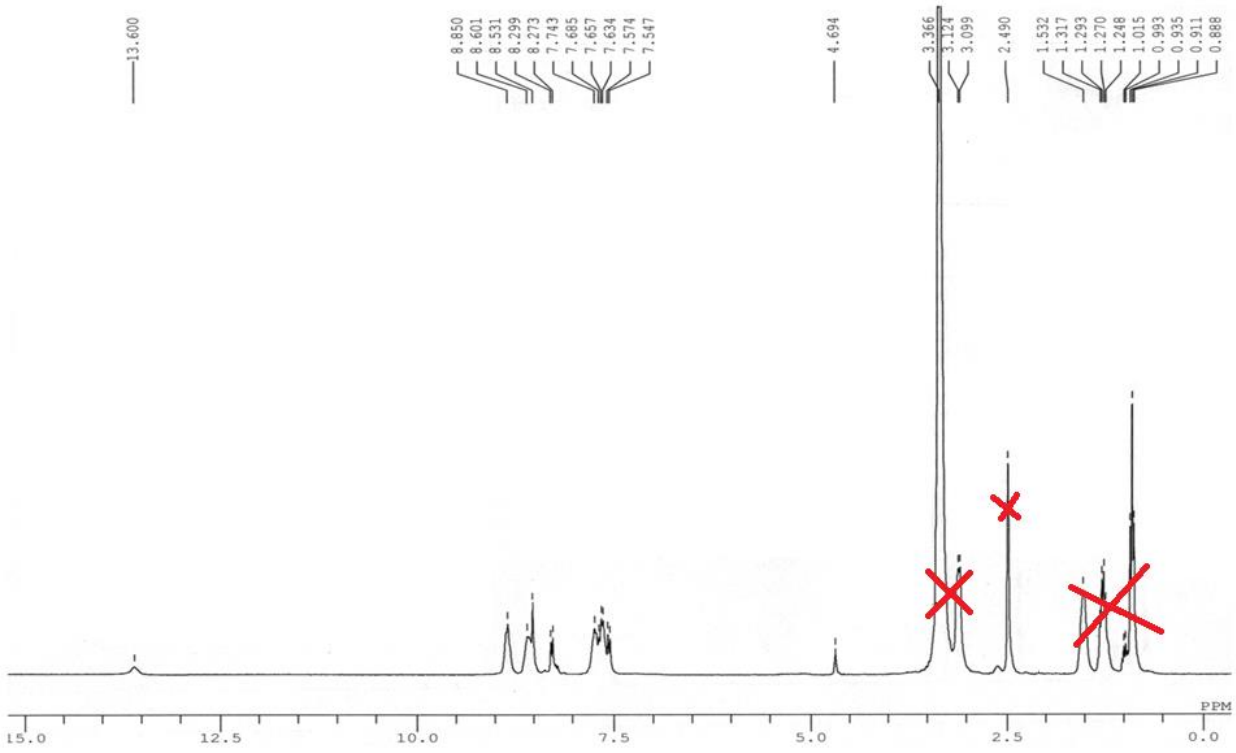


Fig. (S23). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.50 Equiv of CN- in DMSO-d_6.

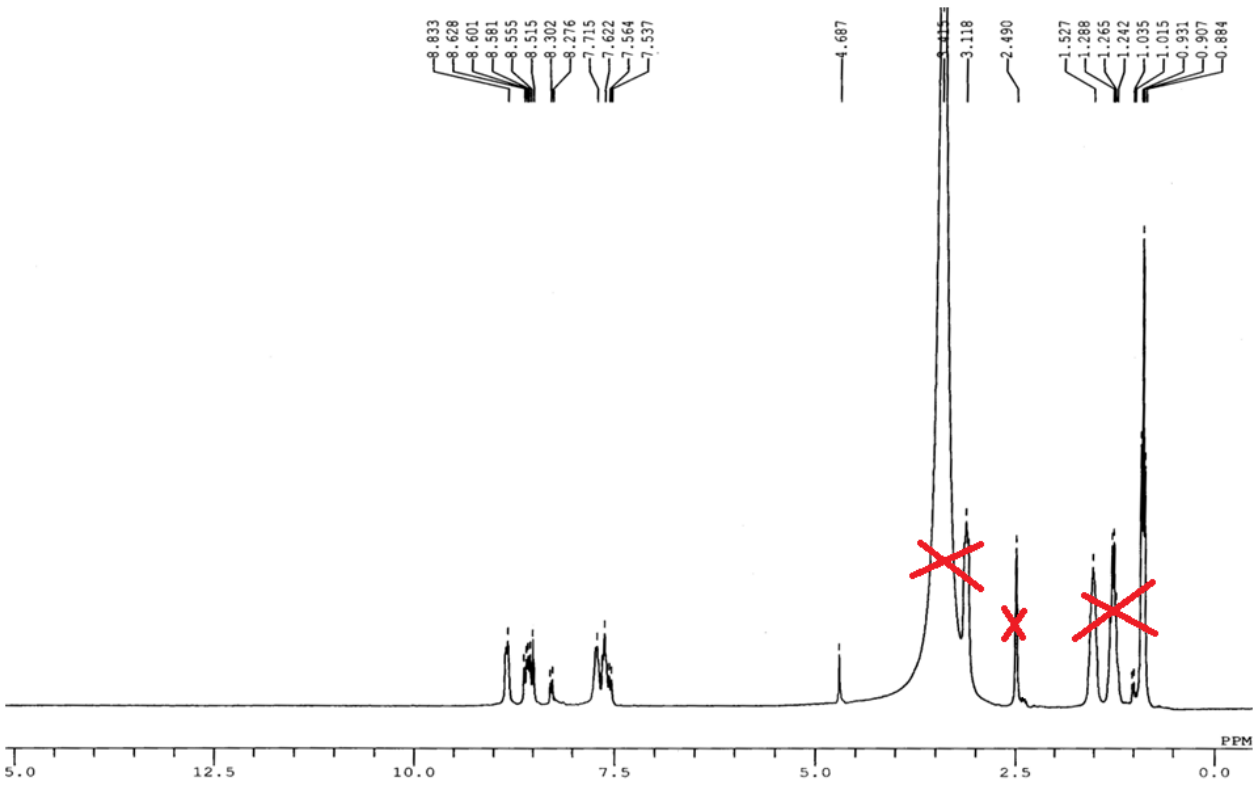


Fig. (S24). ^{1}H NMR spectrum of **DCPPI** upon addition of 0.75 Equiv of CN- in DMSO-d_6.

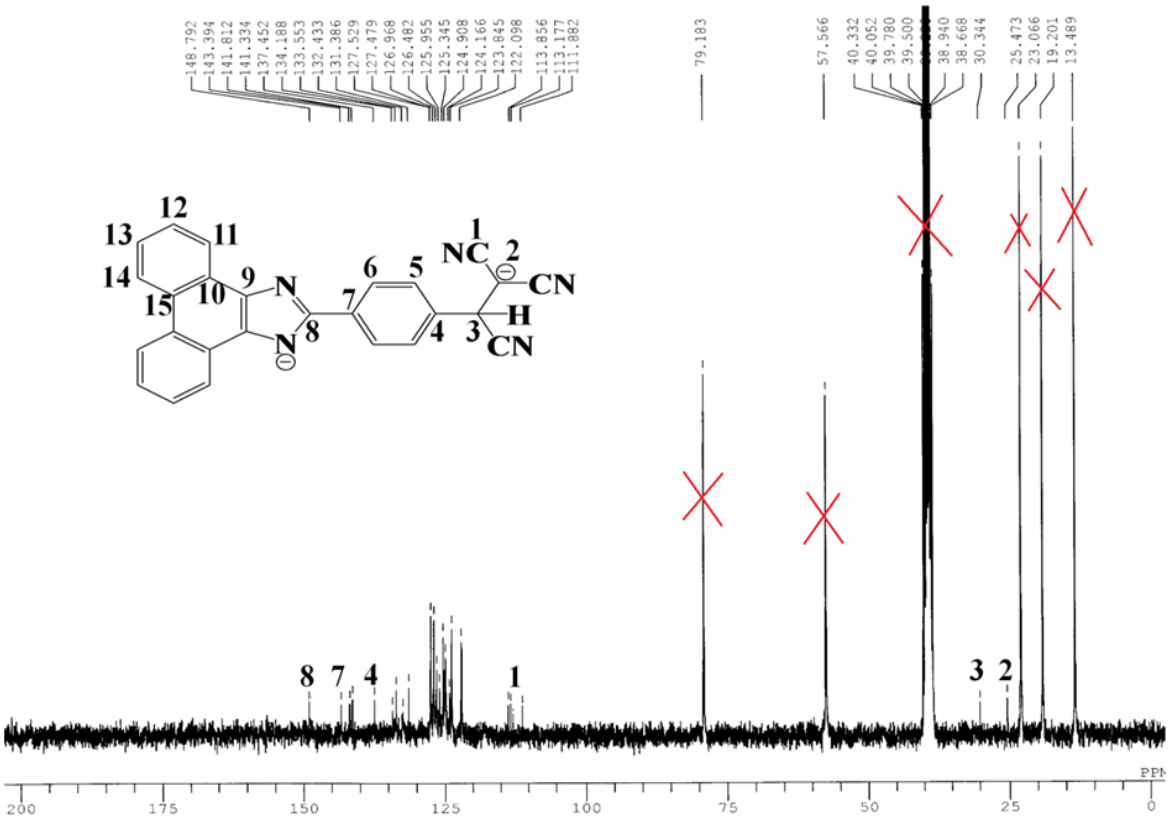


Fig. (S25). ^{13}C NMR spectrum of **DCPPI** upon addition of 1.5 Equiv of CN- in DMSO-d_6