

Synthesis and Characterization of Fluorene Based Organic Dyes and its Application in Dye Sensitized Solar Cells

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By

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INDIA
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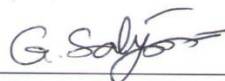
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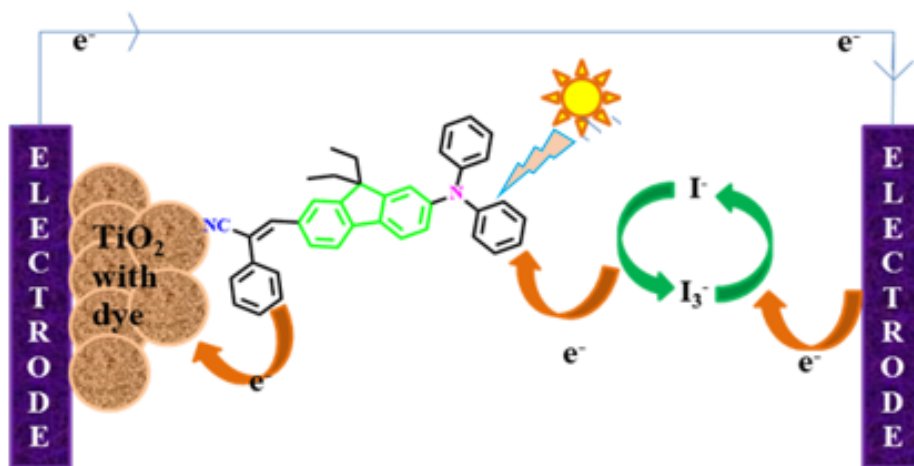
Finally, I express respect to my parents and beautiful sisters Jasmine, Avreen for their love and encouragement for pursuing my dream.

Amreen Kaur Bains

Dedicated
To
Waheguru ji, My Parents and Sisters.

ABSTRACT

Synthesis of novel metal-free fluorene and imidazole pyridine π -spacer based organic dye with –CN (cyano), –C=O (carboxyl), –NO₂ (nitro) as acceptors (anchoring group) and diphenylamine as electron donor part for dye-sensitized solar cells. Time dependent density functional theory (TDDFT) theoretical investigation was carried out to explain the characteristic feature of the dye, photophysical property (UV-Vis absorption) and electrochemical property (Cyclic Voltammetry) was done as an evidence to check the influence of electron donor, electron acceptor part on dye and these calculation shows that these dyes could prove to be efficient in solar cell.



Working scheme of organic dyes in DSSC

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“Synthesis and Characterization of Flourene Based Organic Dyes and its Application in Dye Sensitized Solar Cells”

1. INTRODUCTION:

The increasing world-wide demand for energy and rapidly depleting fossil fuel energy sources has encouraged to research on the objective as to explore and develop renewable and environmentally friendly energy sources, as energy crisis will be the major problem to be faced by humanity with the increasing energy demands. For this perspective, Dye Sensitized Solar Cells (DSSCs) is emerging as an important tool in alternative to the other silicon based solar cells as to convert sunlight directly into electricity^[1], owing to their striking features such as easy and low fabrication cost with high efficiency^[2], and the growing interest for the construction of the metal-free organic dyes which has a potential to act as a sensitizer with nano-crystalline TiO₂ having a donor part, acceptor part and π -bridge part in high conjugation.

Organic dyes have gained much attention since their invention by O'Regan and Grätzel in 1991^[2] and have become one of major competitors among other photovoltaic devices. On a whole solar cells are usually divided into different categories of generations. The first generation solar cells which consist of silicon or germanium based solar cells are mainly expensive possesses low efficiency and costly. The second generation solar cells are less expensive but on the other hand are less effective towards generating high efficiency conversion.

In the case with the working of the first and second generation solar cells the efficiency limit is observed with the formation of the electron-hole pair and in this all the photon energy in the energy gap is lost as heat^[4]. As to overcome this limit which is known as Shockley-Queisser limit. Then third generation solar cell devices came into picture. This generation cells were constructed as to act as the cheapest option for the production of energy. DSSCs are considered to be between second and third generation type solar cells.

The main difference between other generation solar cells and the third generation solar cells is that it is the type of technology which utilizes the nano-scale property of device.

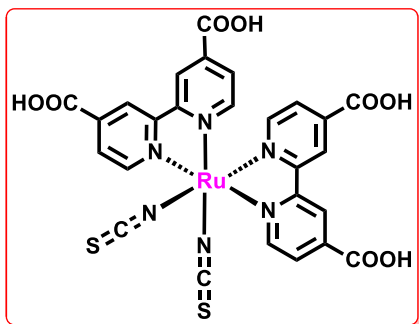
For the construction of the dyes there are few essential characteristic features it should fulfill ^[4]:

- 1) Dye on a whole should be able to possess three main components such as donor part, π -bridge part and the acceptor part.
- 2) The photosensitizer should have an acceptor or anchoring substituent such as -COOH, -H₂PO₃, -SO₃H, -CN, -NO₂ etc as to bind to the semiconductor surface.
- 3) The absorption spectrum of the dye should be able to cover visible as well as near infrared region (NIR).
- 4) The excited state level of the conduction band edge of n-type semiconductor should be lower than that of the photosensitizer so that an efficient electron transfer can take place between the conduction band of the semiconductor and the excited state level.
- 5) The metal-free organic dye moiety should be stable electrochemically, thermally and photochemically.
- 6) Aggregation of the dye on semiconductor surface should not occur.

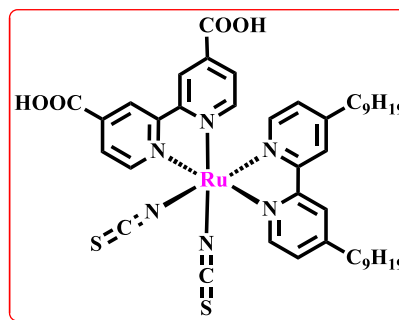
Based on the above conditions various metal free organic dyes have been able to synthesis in the past few decades.

In earlier times, before the establishment of the metal-free organic dyes, metal based dyes were used as photovoltaic for the conversion with effective efficiency. The light absorption observed in the metal based dyes is due to metal ligand charge transfer (MLCT) process. In this, central metal plays an important which takes controls of all the properties observed by a particular dye. The photochemical and electrochemical property can be tuned by using different substituent's on ligand. Firstly, a series of Ru complexes were developed which was the main breakthrough in the photovoltaic series as in year 1991 O'Regan and Gratzel were able to achieve 7.1-7.9% solar cell efficiency ^[2]. In next

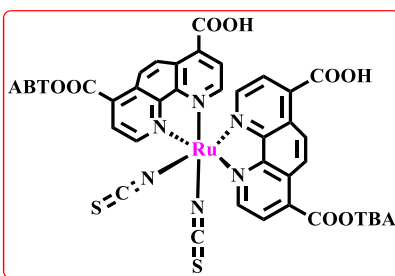
few years, improved efficiency was observed with tuning the substituent effect and absorption factor.



Efficiency: 10%^[5]



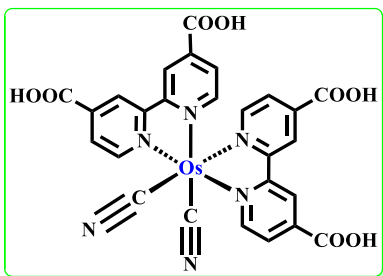
7%^[6]



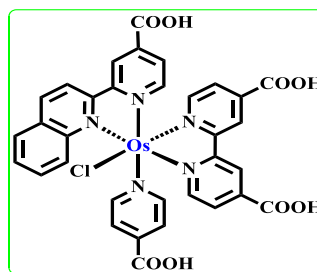
7.7%^[7]

Figure 1: Ru-Complex Photosensitizers.

In later years, subsequent dyes were developed with other metal ions such as, Os, Re, Fe, Pt, and Cu.



(a)^[8]



(b)^[8]

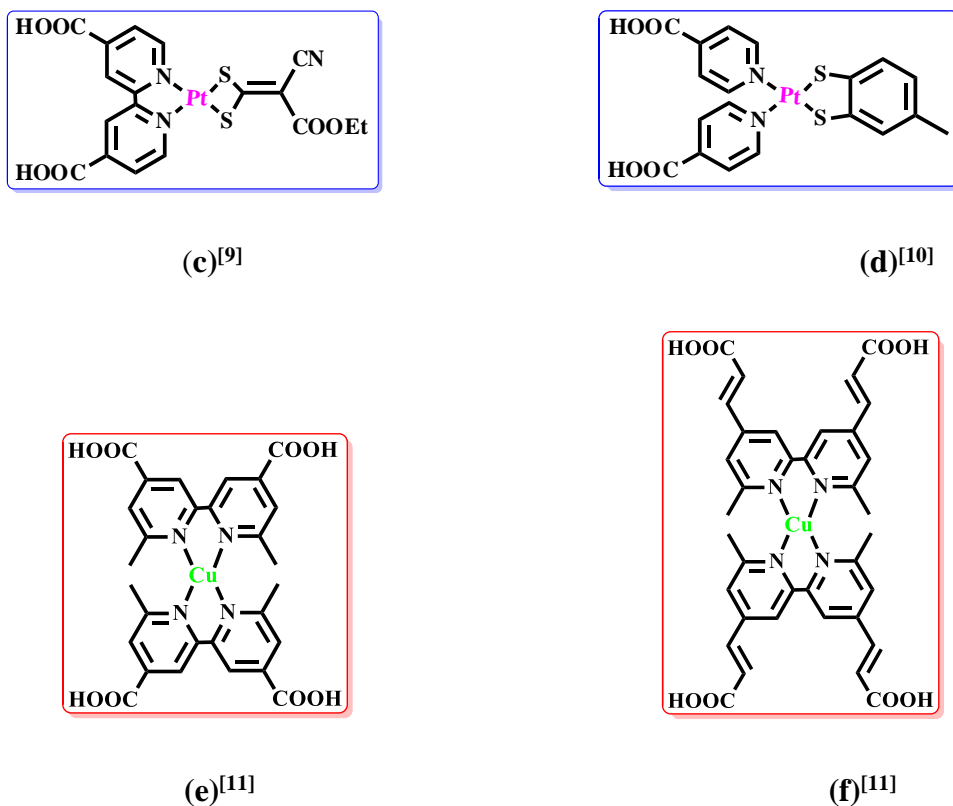
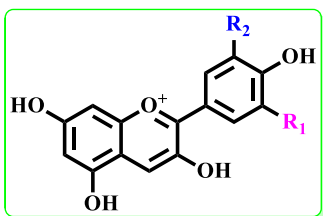


Figure 2: Structure of various metal-based dyes.

Lewis and co-workers focused on development of Os metal based dye. Later metal complexes with Os as central metal were formed by various other group members. 10-11% efficiency was observed by Ferrere and co-workers which forms Fe(II) complexes for DSSCs. Photovoltaic behavior of the Pt(II) based square planar sensitizers has also been seen by Sugihara and co-workers having overall efficiency of 3%.

Other than the metal based sensitizers there have been natural dyes^[12] which can be extracted from nature and have been quite useful due to their easy extraction, low cost, and because of their environment friendly nature. Only anthocyanin which is the member of the flavonoid group lies in different range of colors and thus can be considered as organic photosensitizer. It shows the maximum absorption in the range of 510 to 548 nm.



Flavanoid based natural dyes

	R ₁	R ₂
Pelargonodin	H	H
Cyanidin	OH	H
Peonidin	CH ₃	H
Delphinidin	OH	OH
Peturidin	OCH ₃	OH
Malvidin	OCH ₃	OCH ₃

The side substituent chain length affects the performance of dye. Longer length efficiency reduced due to steric hindrance. As the interaction of the acceptor part is less with TiO₂ results in low efficiency.

ORGANIC DYES:

Organic dyes can be used as an alternate source of photovoltaic to Ru complexes and are at advantage because it does not consist of noble metal such as there is no limited source of formation of dye.

The most widely used sensitizers in conventional DSSCs are ruthenium metal based dyes but despite their superiority there have been a great progress in the development of the novel metal free organic dye. Ruthenium based dyes have limited large scale advantage thus the construction of this organic dyes of higher efficiency have been a attractive area of research due to various flexible reasons such as firstly, the variety in the molecular structures provides possibility to various molecular designs such as it can be constructed on the basis of three main parts which are acceptor part, π -bridge part and donor part such that by alternating this and by introduction of different substituent's, we can have a easy control over the extent of conjugation and absorption spectra .Secondly, organic dyes have sufficient price to performance ratio as there is no concern about the limitation of the resources because it does not consist of noble metal such as ruthenium due to this it is cost efficient^[3]. Thirdly, due to the presence of high conjugation these hybrid organic dyes have high absorption coefficient (which is due to intra-molecular σ to σ^* transition)

than metal dyes and thus absorbs large amount of light which results in larger light harvesting property.

Correspondingly, the other advantages of metal free organic dyes are that it is more efficient than standard silicon-solar panels and can be easily made from abundant, and stable source material. So far hundreds of organic dyes have been made and have shown good efficiency.

The common characteristics of the organic dye can be depicted here as follows:

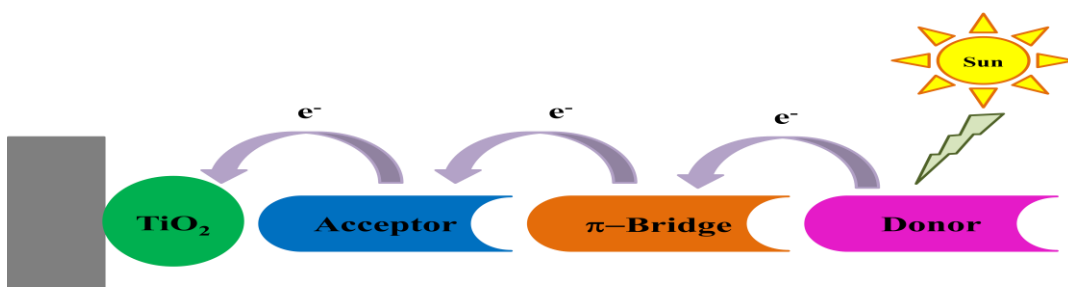


Figure 3: Schematic of D- π -A structure for metal-free dye.

THE ROLE OF THREE COMPONENTS IN DSSCs:

The construction of the organic dye is composition of 3 components such as:

- 1) **Electron-Donor part:** This part when exposed to sunlight initiates the transfer of the electron by the excitation of the dye. The various type of the electron donor part that can be used are: triphenylamine, diphenylamine, coumarin, indomine, carbazole etc.
- 2) **π -bridging part:** This part helps initiate the conjugation in the ring which causes the increase in the absorption coefficient compound which leads to efficient light-harvesting properties. The various types of the π -bridging part are flourene, azacarboline, oxindole and imidazole etc.
- 3) **Electron-acceptor part:** This part gets attached to the TiO₂ semiconductor plated electrode and initiates the transfer of the electron which is first originated from electron

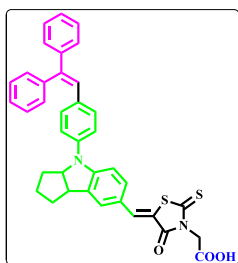
donor part and is then through the Π -bridging part to electron acceptor part to the TiO_2 semiconductor. The various types of the electron acceptor part that can be used are: barbituric acid, cyano, carboxyl, nitro and hydroxamate etc.

The dye constructed with above components will constitute of varying absorption spectra, different Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) levels and the performance of DSSCs with these sensitizers can be governed and will be different for different light absorbers. By changing one of the components we can optimize the sensitizer performance. There have been many examples in which by varying different electron donor groups an electron acceptor groups we can vary efficiency. As dye can be seen in visible region and more the absorption spectra is red shift this will attribute to the shift of HOMO to higher energy level rather than decrease in LUMO energy level^[4].

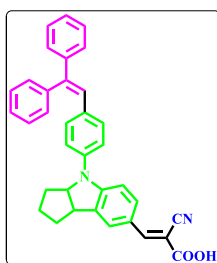
Different components play important role in the construction of an organic dye, such as donor components widely used are Triphenylamine, diphenylamine, carbazole, phenthiazole, coumarin, indoline, and other substituted hydrocarbons.

2. LITERATURE STUDIES OF THE ORGANIC DYES IN HISTORY AND THEIR CORRESPONDING EFFICIENCY WITH DIFFERENT ELECTRON DONOR AND ELECTRON ACCEPTOR GROUPS:

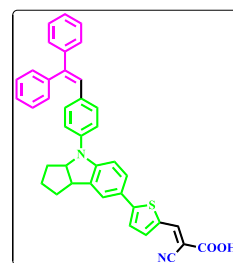
1) INDOLINE DYE:



(a)^[13]



(b)^[14]

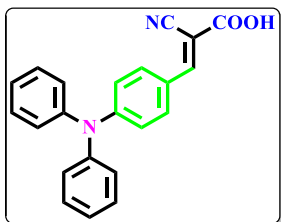


(c)^[14]

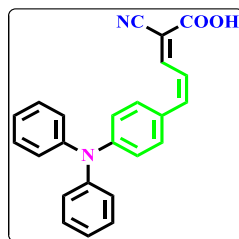
(a) is possesses efficiency of 6.1% while comparing the efficiency of (b) and (c) the introduction of thiophene increases the efficiency from 2.6% to 3.8% this can be

conclude that with more π -bridge part the extent of conjugation increases resulting in increased absorption.

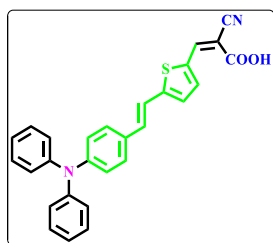
2) TRIARYLAMINE DYE:



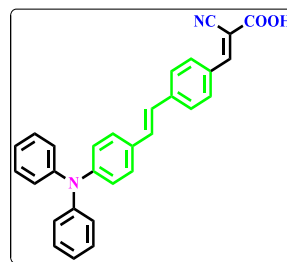
(a)^[15]



(b)^[16]



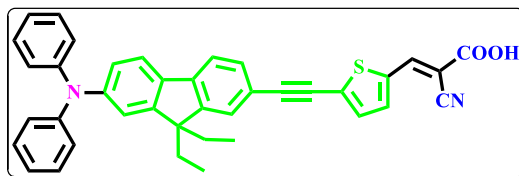
(c)^[16]



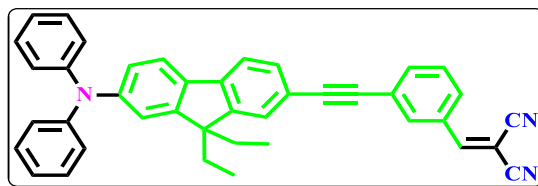
(d)^[17]

The overall DSSC efficiency of the above dyes are (a) with 3.3 %, (b) with 5.3 %, (c) with 5.1%, and (d) with 5.3%.

3) FLOURENE BASED ORGANIC DYES:



(a) 3 % (efficiency)^[18]



(b) 0.61 % (efficiency)^[18]

Organic-dye photosensitizers used in DSSC must have an anchoring group (e.g.-COOH,-CN,-NO₂) to be absorbed onto the semiconductor surface with large electronic coupling. The absorption of the dye could be red-shifted by expansion of conjugation in the dyes and the introduction of the electron withdrawing and donating substituent into the dye framework, such substituent can shift the levels of the dye HOMO and their LUMO. The potential levels of the HOMO and LUMO must be matched to the conduction band level of the semiconductor electrode and to the iodine redox potential. To accept electrons, the HOMO level must be more positive than the iodine redox potential, and to inject electrons, the LUMO level must be more negative than the conduction band of the semiconductor^[20]

In the present scenario both at national and international level the scientific community has turned their attention to develop organic dyes for efficient solar energy harvesting by tuning the different sections (donor part, acceptor part, the conjugated π chain (D- π -A) and anchoring moiety) of general molecular structure of the dye.^[21, 22] To date 12.5% is the highest efficiency reported for organic dyes in DSSC. In spite of these developments, there is a demand for developing highly efficient and durable dye. With this perspective, we plan to design and develop a series of novel metal-free dyes with higher photovoltaic performance in DSSCs.

WORKING OUTLINE OF DSSC:

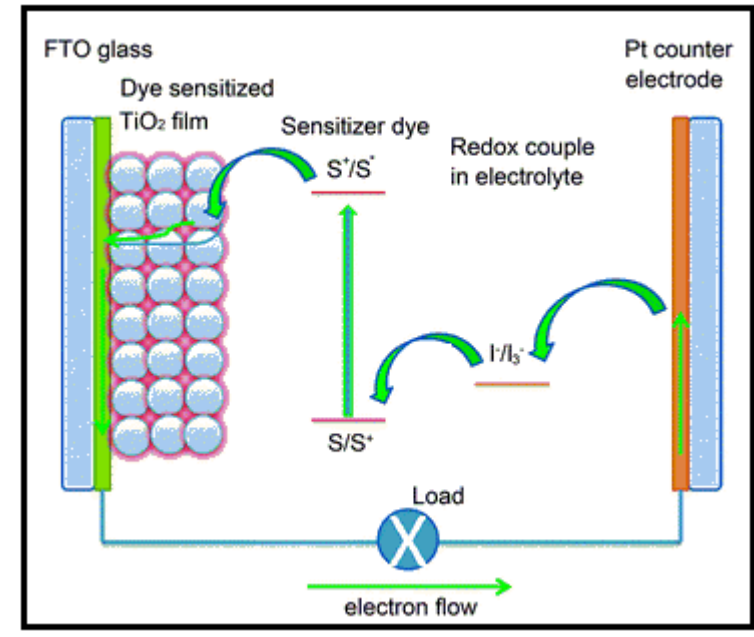
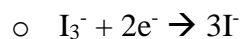


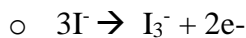
Figure 4: Working principle of dye in DSSC.

STEPS INVOLVED:

- When incident light falls on the surface of dye then it results in the excitation of dye which in return transferring of electrons from valance band to conduction band.
 - $S \rightarrow S^*$ (S^* - Excited state of dye)
 - $S^* \rightarrow S^+ + e^-$
- The excited electrons in the conduction band of the dye transfers electron to the conduction band of the semiconductor TiO_2 .
- Thus now electron is transferred to the transparent electrode which later causes the electron to be passed through the circuit generating electricity.
- At another electrode the electron is taken up by oxidised species and is reduced (species is mainly electrolyte).



- Now this reduced species gives its electron to the dye (S^+) and thus causes the regeneration of dyes.



Summary of the dyes for DSSCs:

Till now hundreds of dyes have been made, here is the brief explanation about the construction of the dye and how to design a dye as to get an improved efficiency and dye performance.

- 1) For effective construction of dye three components are required such as electron donor, electron acceptor, and conjugated bridge part which helps us tailor the construction of appropriate dye.
- 2) By changing the substituent effect on the dye we can increase the HOMO energy level rather than decreasing LUMO and thus a dye can be red shifted and becoming compatible as to show good efficiency.
- 3) Various types of organic dyes can be prepared with enormous versatility with high conjugation and successful performance.
- 4) Stronger anchoring groups in dye and helps it to have longer stability, prevent dye degradation and helps the dye to be stable at elevated temperature.

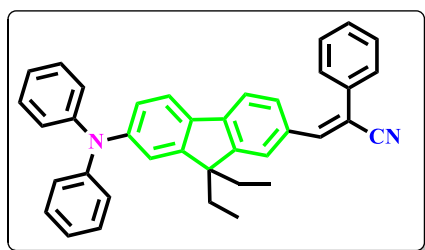
3. RESULTS AND DISCUSSION:

During the past one decade there has been a revolution in the development of new kind of organic dye with improved performance and efficiency. There have been several reports on the type of electron donor and acceptor parts attached as a substituent which drove us to construct novel organic dye in subsequent steps achieving moderate to good yield at every step.

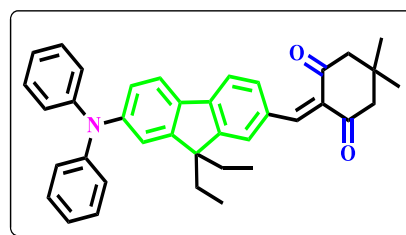
In our investigation for synthesizing dyes, initially we started with commercially available starting material fluorene, Firstly bromination was performed at two of the positions of fluorene followed by ethylation which produces compound **(1b)** in fairly good yield and for the synthesis of compound **(1c)** Heck reaction was carried out which yielded product with one side N-arylation, and further formylation reaction was performed with n-buli in THF and DMF in which DMF acts as formyl source for required aldehyde **(1d)**. For the final step of synthesizing our dyes, we performed Knoevenagel condensation reaction with benzyl cyanide and dimadone which results in the dye **D1** and **D2**(Scheme 1).

For the synthesis of dye **D3**, initially we performed formylation reaction on triphenylamine to obtain formylated compound **(2a)** and then Groebke reaction was performed with **(2a)** aldehyde, cyclohexyl isocyanide and 5-nitropyridin-2-amine under hot conditions at 160°C yielded dye **D3**(Scheme 2).

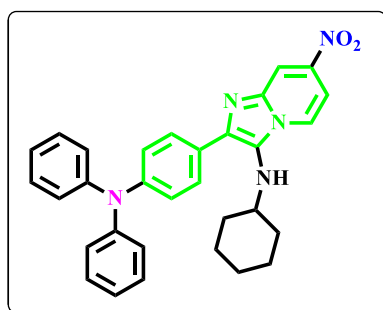
The structure of the organic dye is as follows:



(D1)



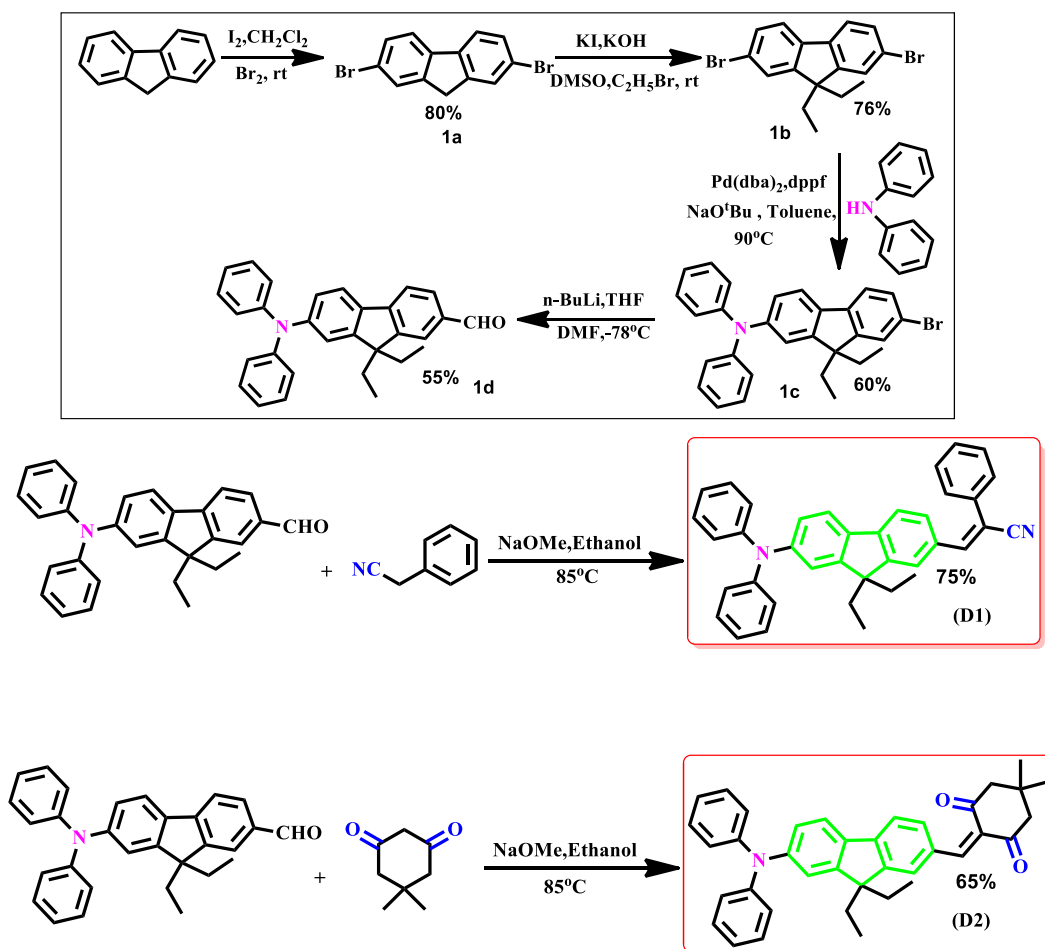
(D2)



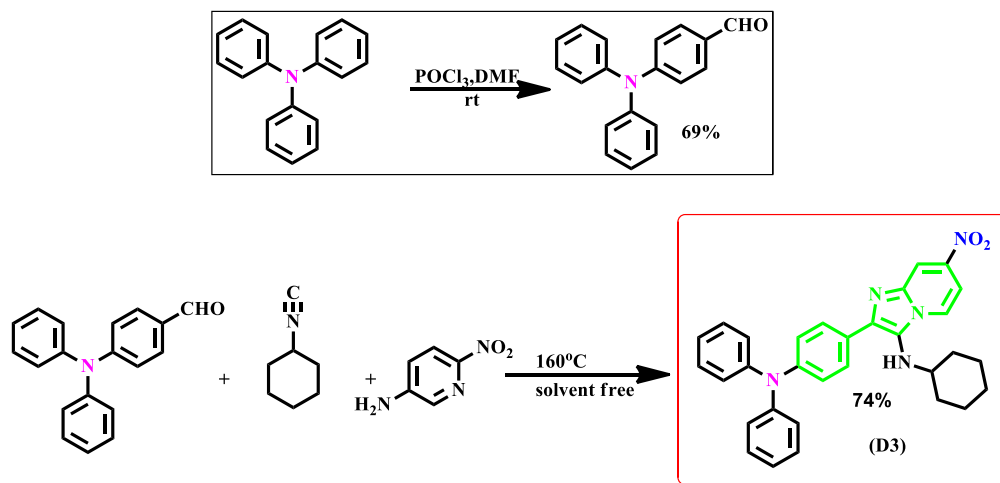
(D3)

These above three dyes were made with dialkylamine as the electron donor part, with different electron acceptor parts such as $-\text{CN}$, $-\text{NO}_2$, $-\text{C}=\text{O}$.

3.1 OUTLINE SCHEME FOR THE PREPERATION OF ORGANIC DYE:



Scheme 1: Synthesis of organic dye (D1) and (D2).

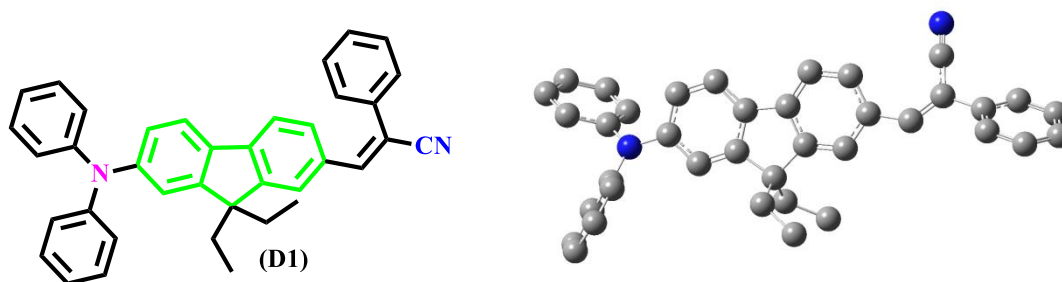


Scheme 2: Synthesis of organic dye (D3).

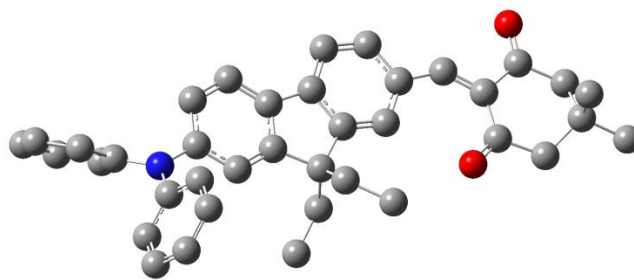
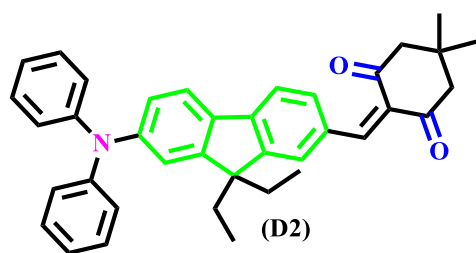
3.2 MOLECULAR ORBITAL CALCULATIONS:

TD-DFT (Time Dependent Density Functional Theory) helps in explaining the electronic and geometrical properties of the synthesized dye using the Gaussian 05 program package. The optimized structure of the dye **D1-D3** is shown in **figure 5**. The calculations are done by using B3LYP/6-31G (d) level for geometry optimizations in the ground state. B3LYP is a hybrid function which is modified from the three-parameter exchange-correlation functional of Becke, while the gradient-corrected exchange and correlation functions are determined according to Becke and Lee *et al.*

1) D1



2) D2



3) D3

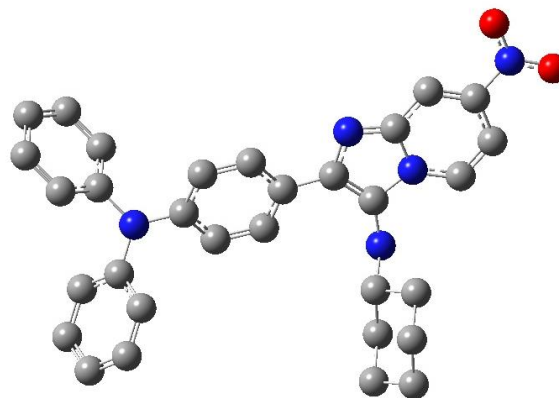
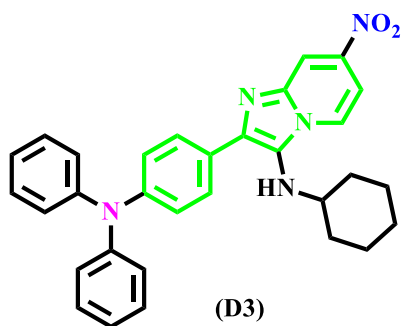
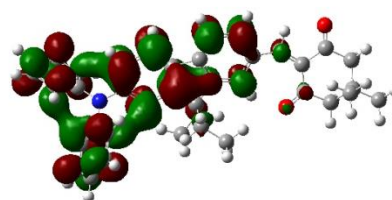
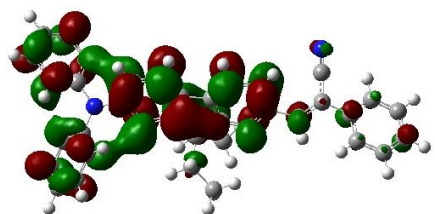


Figure 5: Optimized structure of D1, D2 and D3.

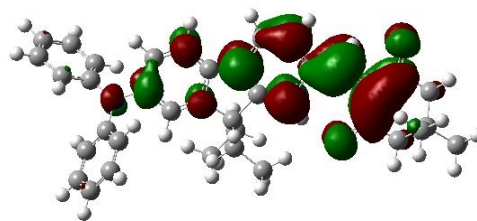
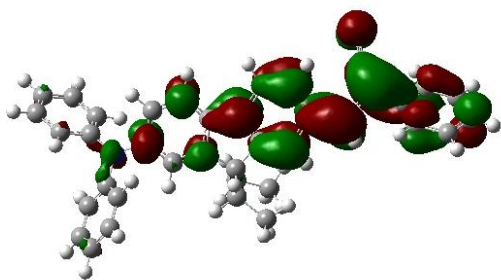
D1

D2

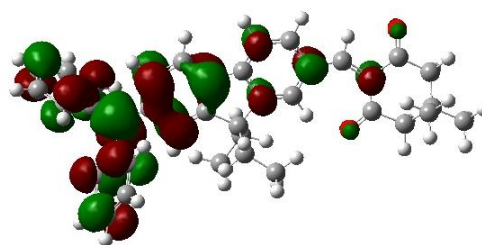
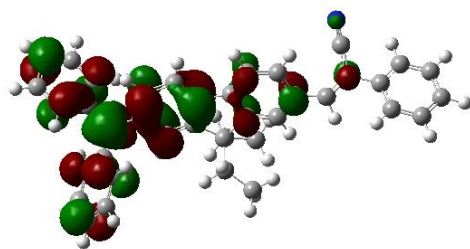
LUMO+1



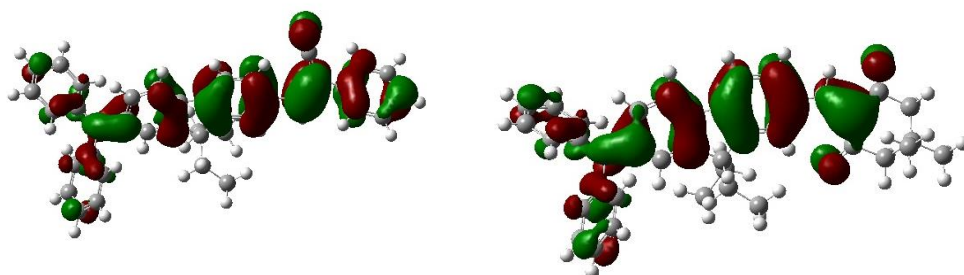
LUMO



HOMO

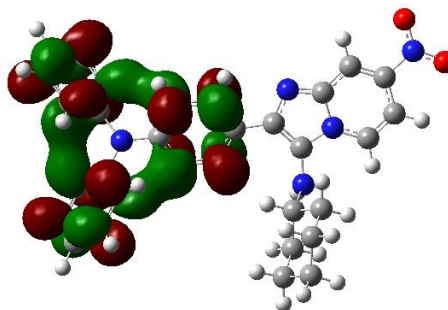


HOMO-1

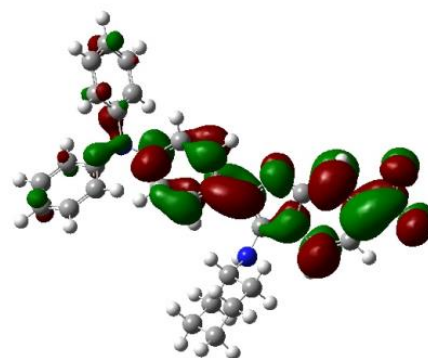


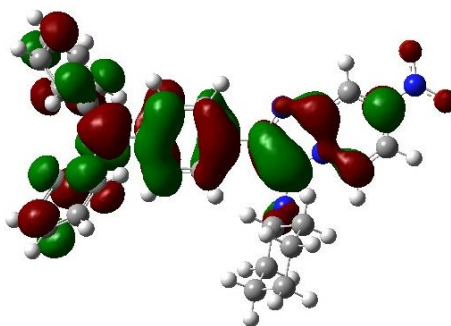
(D3)

LUMO+1

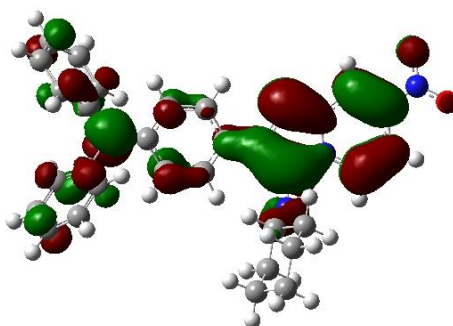


LUMO





HOMO



HOMO-1

Figure 6: Computational electron density distribution in HOMO and LUMO orbital of **D1**, **D2** and **D3**.

3.3 ANALYSIS OF THE ELECTRON DENSITY DISTRIBUTION IN HOMO AND LUMO:

- 1) The frontier MOs of dye **D1**, **D2** and **D3** reveal that in case of **D1** and **D2** the HOMO-LUMO excitation moves the electron density from the electron donor part of organic dye such as diphenylamine to the electron acceptor part such as $-\text{CN}$, $-\text{C}=\text{O}$. Similar distribution of electron density was observed in **D3** from electron donor diphenylamine to the acceptor $-\text{NO}_2$.
- 2) On comparing the electron density distribution in the frontier MOs of **D1-D3** at the ground state (HOMO) considering **D1** and **D2** there is equal distribution of the electron density observed in both i.e over the diphenylamine moiety and fluorene bridge, while in case of **D3** electron density is homogeneously distributed.

3). While going from HOMO TO LUMO a little amount of electron density is shifted from diphenylamine moiety , flourene bridge to flourene bridge and electron acceptor/anchoring moiety such as $-CN$ and $-C=O$. However in HOMO-1 the electron density is uniformly distributed on **D1, D2 and D3**.

Furthermore, the location of the LUMO at the side of the TiO_2 surface and the HOMO at the opposite end of the molecule makes the electron injection into the semiconductor easier and prevents back regeneration of the dye with injected electrons. Highest occupied molecular orbital (HOMO), lowest unoccupied molecular orbital (LUMO) are calculated to find ΔE (Energy gap) as given in **Table 1**.

Dyes	B3LYP/6-31G(d) (eV)			Oscillator Strength (<i>f</i>)
	HOMO	LUMO	Energy gap (LUMO-HOMO)	
D1	-5.0504	-1.7758	3.2746	0.711
D2	-5.01070	-2.2648	2.7459	0.6075
D3	-5.04716	-2.4982	2.548	0.1203

Table 1: HOMO LUMO energy calculated by DFT method (eV).

Dye	Excited State	Oscillator Strength (<i>f</i>)	Excitation energy ΔE (eV)	Excitation energy ΔE (nm)	Composition H=HOMO, L=LUMO	μ_g (debye)
D1	1	0.7110	2.8713	431.81	0.70368×(H→L)	4.8137
	2	0.6106	3.8407	322.82	0.51730×(H-2→L)	
	3	0.2022	3.8774	319.76	0.42189×(H-1→L)+	
D2	1	0.6075	2.4841	499.12	0.70546×(H→L)	
	2	0.0001	2.9983	413.52	0.68580×(H-1→L)+	

	3	0.0055	3.3783	367.00	0.67729×(H-2→L)	2.7356
D3	1	0.1203	2.2661	547.13	0.70539×(H→L)	7.7144
	2	0.3213	3.3153	373.98	0.66511×(H-1→L)	

Table 2: Excitation energies (eV, nm), Oscillator strengths (*f*), Dipole moment of the dyes calculated by TD-DFT of dye **D1-D3**.

LIGHT HARVESTING EFFICIENCY (LHE) OF DYES AND ITS CORRESPONDING OSCILLATOR STRENGTH (*f*):

Light harvesting efficient (LHE) is one of the important factors which suggest the proper working of dye as it indicated the efficiency of dye. The light harvesting efficiency (LHE) is defined as the efficiency of the dye in response to the light. Increased light harvesting efficiency will increase the response of dye towards light. This can be calculated with the help of the oscillator strength as shown in **equation (1)**. This factor can be calculated directly by **TD-DFT** method. The calculated LHE have been shown in **table 3**.

$$\text{LHE} = 1 - 10^{-f} \quad \text{----- (1)}$$

Dyes	Gas phase		
	Excitation energy ΔE (eV)	λ_{max} (nm)	LHE
D1	2.87	431.81	0.805
D2	2.48	499.12	0.753
D3	2.26	547.13	0.246

Table 3: Light Harvesting Efficiency (LHE) of **D1-D3**

3.4 PHOTOPHYSICAL PROPERTIES:

The optical spectra of the dyes recorded in dichloromethane (DCM) are displayed in **Fig.7**. All the three organic dyes exhibit an intense absorption in the region lying between 321 and 492 nm

due to the combination of the electronic transitions which has been originated from $\pi \rightarrow \pi^*$ transition and intramolecular charge excitation.

The UV-Vis absorption spectrum for the three dye was taken in DCM and the λ_{max} are listed in the **table 4**. The absorption spectrum of dye **D1** in DCM has absorption band around 372 and 492nm . The absorption peak $\pi \rightarrow \pi^*$ electron transition of the conjugated molecule is around 372 nm; and the absorption peaks can be assigned to an intramolecular charge transfer at 492nm between the triphenylamine-based donor and the cyano acceptor moiety, providing efficient charge-separation at the excited state. On the similar note absorption peak of dye **D2** for $\pi \rightarrow \pi^*$ electron transition of the conjugated molecule is 321 nm ; and the absorption peaks at around 406 nm due to the intramolecular charge transfer between electron donor and acceptor part and **D3** have $\pi \rightarrow \pi^*$ transition at 380 nm and intramolecular charge transfer at 426nm.

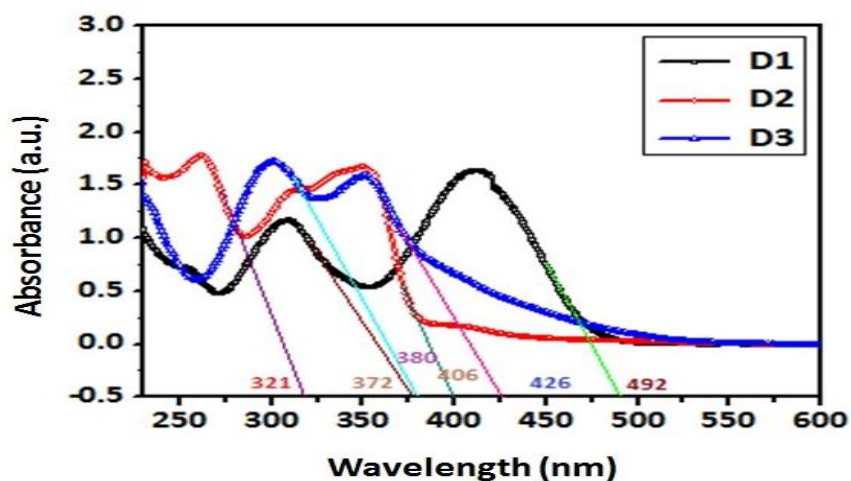


Figure 7: Absorption spectra of **Dyes** in DCM

Dyes	$\lambda_{\text{abs}}(\text{nm})$ in DCM
D1	372,492
D2	321,406
D3	380,426

Table 4: Absorption spectrum (λ_{abs}) of **D1-D3**.

3.5 ELECTROCHEMICAL PROPERTY:

Cyclic voltammetry (CV) helps us investigate the electrochemical properties of dyes and was done in dichloromethane solution containing 0.1M tetrabutylammonium iodide as the electrolyte as shown in **figure 8** . It helps to predict the possibility of the electron transfer from the excited level of the dye to the conductive band of TiO₂ and later which causes the regeneration of the dyes. The electrochemical data calculated have been listed in **Table 5**. The excited-state oxidation potentials was obtained from the first oxidation potential E_{ox} (vs. NHE) measured by cyclic voltammetry, Ag/AgCl/KCl redox couple was used as an internal potential reference.

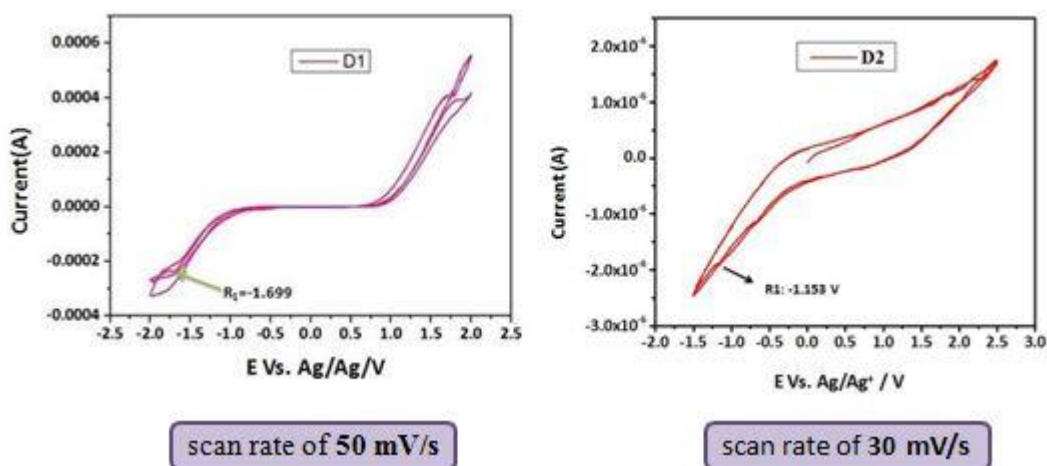


Figure 8: Cyclic voltammograms recorded at a scan rate of 50 mV/s in a 0.1 M tetrabutylammonium iodide solution in two electrode electrochemical cells with (a) D1 in DCM/FTO plates as both electrodes at a scan rate of 50 mV/s, (b) D2 in DCM/FTO plates as both electrodes at a scan rate of 30 mV/s, Ag/AgCl/KCl as reference electrode and a Pt rod as the auxiliary electrode.

The potential of reference electrode (Ag/Ag⁺) was +0.197 V (versus 4 NHE). The CV curve of **D1** show the first reduction peak marked as R₁ at -1.699 (versus Ag/Ag⁺) in their cathodic

branches respectively and the first reduction peak of **D2** is -1.153 V. The reduction potential (versus NHE) corresponds to the LUMO of the electroactive dyes.

Dyes	LUMO from CV		Absorbance from UV-Vis		HOMO	
	w.r.t. NHE (V)	w.r.t. vacuum (eV)	in nm	in eV	in eV	in V(w.r.t. NHE)
D1	-1.502	2.998	492	2.52	5.518	1.018
D2	-0.956	3.544	406	3.08	6.624	2.124

Table 5: Electrochemical data of **D1** and **D2**.

Therefore, the reduction potential of **D1** (Vs NHE) is $(ER) = (-1.699 + 0.197) V = -1.502 V$, the reduction potential of **D2** (Vs NHE) is $(ER) = (-1.153 + 0.197) V = -0.956 V$, A potential of 0 V (versus NHE) corresponds to 4.5 eV (w.r.t. vacuum level). Hence, LUMO of **D1** and **D2** calculated is 2.998 and 3.544 eV respectively. As in case of **D3** CV deformed curve was observed.

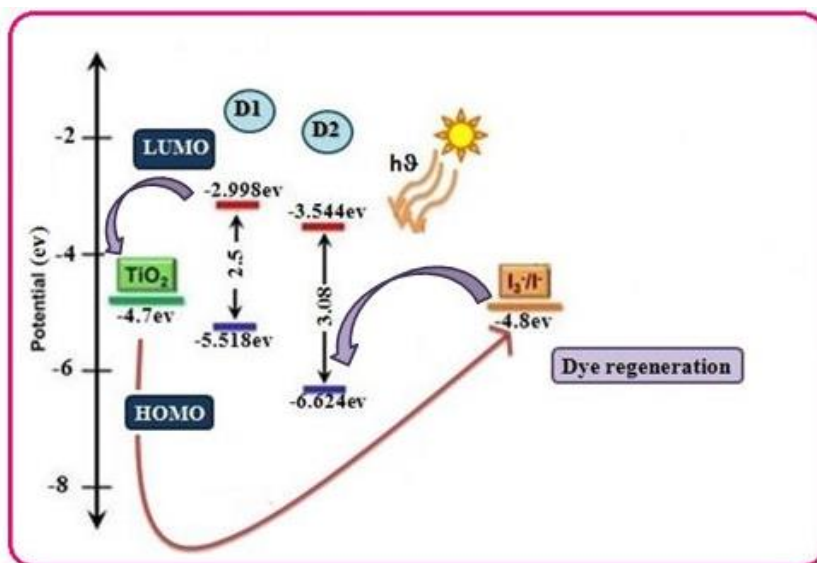


Figure 9: Electrochemical interpretation.

4. CONCLUSION:

1) In summary we have developed a very simple and novel organic dyes with diarylamine as the electron donor part, with different electron acceptor/anchoring parts having fluorene and imidazole pyridine as π -bridging moiety and $-\text{CN}$, $-\text{C}=\text{O}$, and $-\text{NO}_2$ as electron acceptor part which are hoped to show the promising results in future due to their low cost, high extent of absorption.

2) The synthesised dye has been characterized by:

1) TD-DFT (features extracted are excitation energy, photoabsorbtion spectra, light harvesting efficiency)

2) UV-Vis absorption

3) Cyclic Voltammetry (CV)

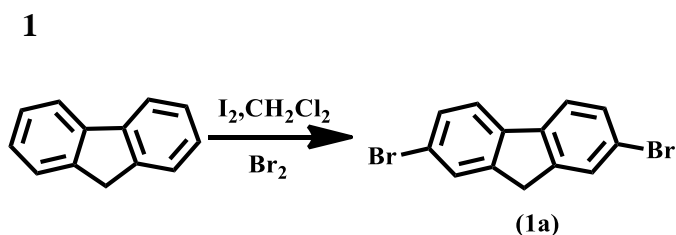
These calculation shows that these dyes could prove to be efficient in solar cell.

5. EXPERIMENTAL SECTION:

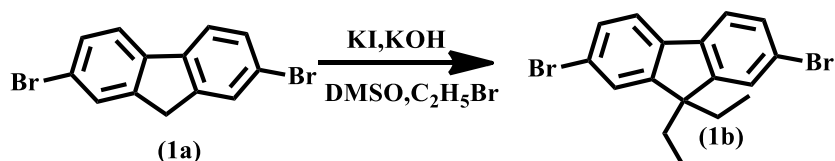
General information: For the experiments, all starting material and reagents are purchased from standard commercial sources or were prepared in the laboratory. All the glass wares were cleaned with soap water followed by acetone and dried in hot air oven at $100\text{ }^\circ\text{C}$ for 2h. Solvents were distilled prior to use; petroleum ether with a boiling point range $40\text{-}60\text{ }^\circ\text{C}$ was used. IR spectra were recorded on the Bruker Tensor 37 (FTIR) spectrophotometer. ^1H NMR Spectra were recorded on Bruker Avance 400 (400 MHz) spectrometer at 295K in CDCl_3 ; Chemical shifts value (δ ppm) and coupling constants (Hz) are reported in standard fashion with reference to either tetramethylsilane (TMS) ($\delta\text{-H} = 0.00$ ppm) or CHCl_3 ($\delta\text{-H} = 7.26$ ppm). ^{13}C NMR spectra were recorded on Bruker Avance 400 (100 MHz) spectrometer at 298K in CDCl_3 ; chemical shifts (δ ppm) are reported relative to CHCl_3 [$(\delta\text{-C}=77.00$ ppm) central line of triplet]. In ^{13}C NMR the nature of carbons (C, CH, CH_2 , and CH_3) was determined by recording the DEPT- 135 spectra. In ^1H NMR, the following abbreviations were used throughout the thesis; =

singlet, d = doublet, t = triplet, q = quartet, qui = quintet, m = multiplet and br.s = broad singlet. The assignment of the signals was confirmed by ^1H , ^{13}C and DEPT spectra. Reactions were monitored by TLC on silica gel (254 mesh) using a combination of petroleum ether and ethyl acetate as eluents.

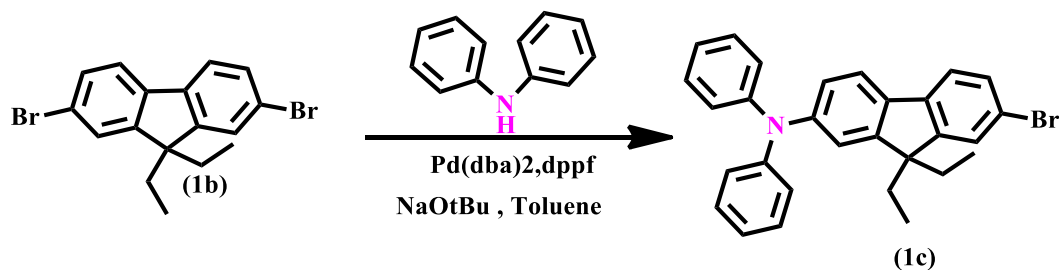
Preparation of starting material :



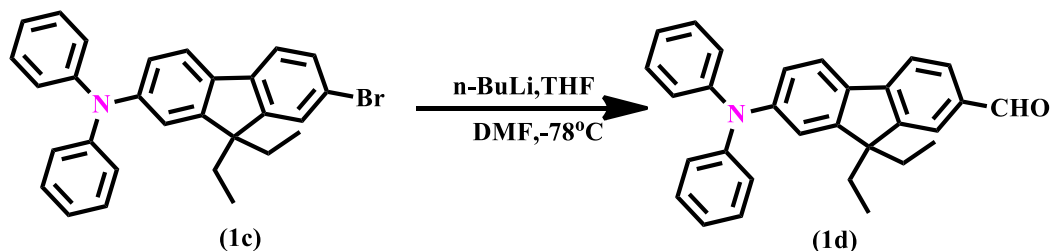
Synthesis of 2,7-dibromo-9H-fluorene (1a) : (5.376g,0.0323mol) of fluorene was taken to it iodine(98mg,0.0069mmol) and methylene chloride (37ml) was taken and was stirred vigorously . to this stirred solution bromine(3.7ml,0.06mol) was added drop wise at room temperature over a period of 30 minutes . After which saturated solution of sodium thiosulphate was added and the mixture became colourless. Water (37ml) was added and methylene chloride was distilled off. The obtained product was filtered and dried. Yield : (80%) 4g.



Synthesis of 2,7-dibromo-9,9-diethyl-9H-fluorene (1b) : To **1a**(4g,0.0123mol) powdered potassium hydroxide(3.37g,0.0602mol), potassium iodide(0.2044g) and DMSO(10ml) was added at 10°C, then ethyl bromide(3.5mg,0.0321mol)was added drop wise for 30 minute and was allowed to stir at room temperature overnight. The mixture turned red to light purple in colour. Then after stirring the mixture it was poured into water. DMSO was removed and treatment was done with charcoal and recrystallised from hexane .Yield:2.8 g (76%)

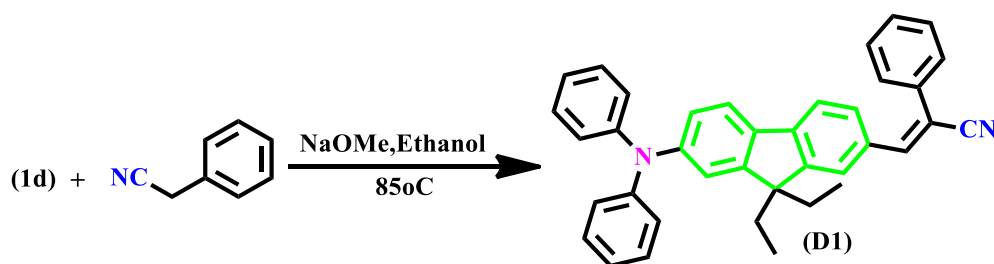


Synthesis of 7-bromo-9,9-diethyl-N,N-diphenyl-9H-fluoren-2-amine (1c) : To **1b** (2.5g, 1eq) diphenylamine (600mg, 0.66 eq) was added and was put to high vacuum. Then dried sodium *t*-butoxide (520mg, 1eq), Pd(dba)₂ (40mg, 0.0133eq), 1,2-bis(diphenylphosphino)ferrocene (dppf) (40mg, 0.0133 eq) was added to the flask containing above dried starting material and toluene (10ml) was added to it. The whole reaction mixture was heated at 90°C for 24 h. After completion of the reaction toluene was removed by evaporation and the crude left behind was treated with water and methylene chloride. Organic layer was dried over sodium sulphate and solvent was evaporated. Purified by column chromatography using hexane as elutant. Yield: 60% colourless solid.



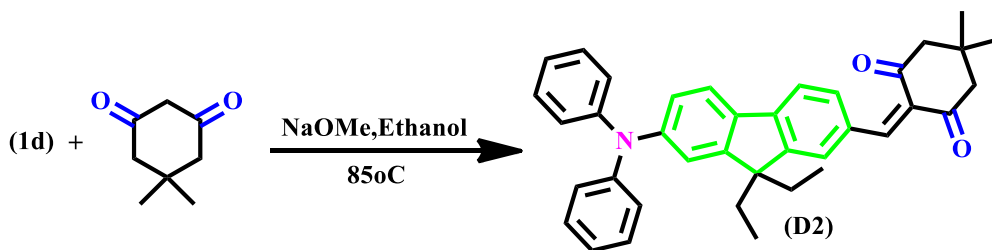
Synthesis of 7-(diphenylamino)-9,9-diethyl-9H-fluorene-2-carbaldehyde (1d) : A stirred solution of **1c** (500mg, 5 mmol) in tetrahydrofuran (1 mL) was cooled to -74 °C. A hexane solution of *n*-butyl lithium (1.6 M, 1.5 mL, 6 mmol) was added to it with vigorous stirring over 1 hr. After the addition was over, the resulting mixture was stirred for another 1 h at this temperature and 2 mL dimethylformaldehyde (DMF) added through the syringe. The final

reaction mixture was allowed to be stirred for next 1 hour and allowed to attain room temperature and stirred for next 30 minute. It was quenched by adding dilute hydrochloric acid (5 mL) and extracted with methylene chloride .The combined yellow organic extract was dried over sodium sulphate Na_2SO_4 and evaporated to dryness. The crude yellow solid thus obtained was purified by column chromatography using silica gel as stationary phase and hexane/ethyl acetate (1:0.05) mixture as eluant. Green solid. Yield: 50%.



Synthesis of 3-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)-2-phenylacrylonitrile (D1) :

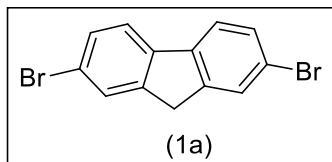
To a solution of (20mg, 1eq) **1d** in ethanol (0.5ml) phenyl nitrile was added and was stirred for 15 minutes . After which sodium methoxide (10mmol) solution in ethanol was added to it and was stirred at room temperature for 1 hr. After which it was refluxed at 85°C and was continuously monitored with TLC . After completion of the reaction to it little HCl was added and work up was done with ethyl acetate and water and organic layer was collected on Na_2SO_4 . Solvent was removed and was purified by column chromatography using silica gel as stationary phase and hexane/ethyl acetate (1:0.05) mixture as eluent. Yellow compound . Yield: 75%.



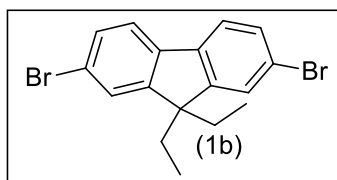
Synthesis of 2-((7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)methylene)-5,5-

dimethylcyclohexane 1,3 dione (1f) : To a solution of (20mg) **1d** in ethanol (0.5ml) dimadone was added and was stirred for 15 minutes . After which sodium methoxide (10mmol) solution in ethanol was added to it and was stirred at room temperature for 1 hr. After which it was refluxed at 85°C and was continuously monitored with TLC . After completion of the reaction to it little

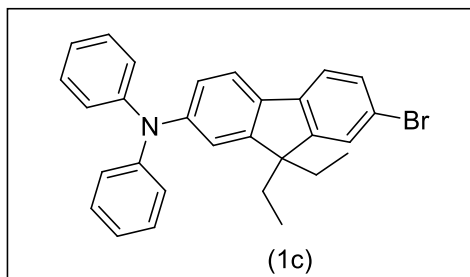
SPECTRAL DATA:



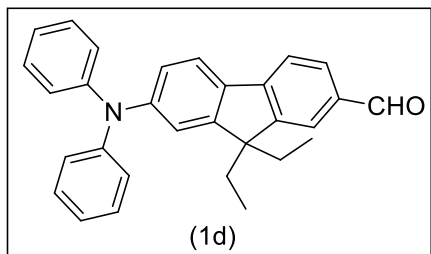
2,7-dibromo-9H-fluorene(1a): White solid (80%) ; ^1H NMR (CDCl_3 , 400 MHz) : $\delta_{\text{H}} = 7.67$ (s, 2H), 7.62-7.60 (m, 2H), 7.52-7.50 (d, $J = 8.3$ Hz, 2H), 3.87 (s, 2H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta_{\text{C}} = 144.77, 139.66, 130.12, 128.28, 121.18, 120.91, 36.53$.



2,7-dibromo-9,9-diethyl-9H-fluorene (1b) : White crystal (70%) ; ^1H NMR (CDCl_3 , 400 MHz,) : $\delta_{\text{H}} = 7.55$ -7.53 (m, 2H) ,7.48-7.40 (d, $J = 1.5$ Hz, 2H), 2.03-1.98 (q, $J = 7.3$ Hz, 4H), 0.34-0.31 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta_{\text{C}} = 152.04, 139.52, 130.52, 126.56, 121.78, 121.40, 57.04, 32.92, 8.70$.

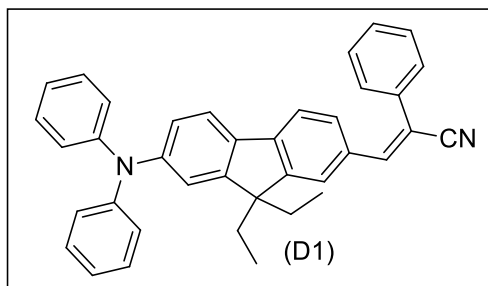


7-bromo-9,9-diethyl-N,N-diphenyl-9H-fluorene-2-amine (1c) : White crystal(60%) ; ^1H NMR (CDCl_3 , 400 MHz): $\delta_{\text{H}} = 7.52$ -7.50 (d, $J = 7.8$ Hz, 1H), 7.46-7.40 (m, 3H), 7.26-7.22 (m, 3H), .12-7.07 (m, 5H), 7.03-6.98 (m, 3H), 1.94-1.85 (m, 4H), 0.37-0.33 (t, $J = 7.3$ Hz, 6H); ^{13}C NMR (CDCl_3 , 100 MHz): $\delta_{\text{C}} = 152.08, 150.88, 147.87, 147.57, 140.32, 135.39, 129.93, 126.03, 123.90, 123.51, 122.61, 120.41, 120.34, 120.11, 119.05, 56.31, 32.53, 8.48$.



7-(diphenylamino)-9,9-diethyl-9H-fluorene-2-carbaldehyde (1d) : Green crystal (50%);

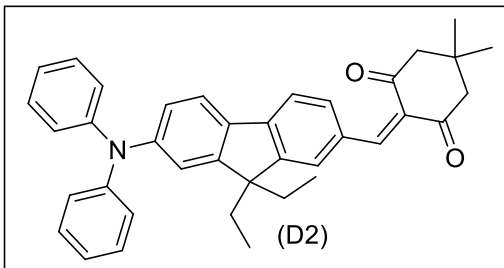
$^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta_{\text{H}} = 10.02$ (s, 1H), 7.83-7.82 (m, 2H), 7.73-7.71 (d, 1H, $J = 8.3$ Hz), 7.63-7.61 (d, $J = 8.3$ Hz, 1H), 7.30-7.25 (m, 4H), 2.02-1.63 (m, 4H), 0.36-0.32 (t, $J = 7.3$ Hz, 6H); $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz): $\delta_{\text{C}} = 191.92, 152.52, 150.18, 148.59, 147.56, 147.30, 134.00, 128.97, 124.09, 122.79, 122.53, 121.34, 118.74, 117.81, 55.81, 32.11, 8.15$.



3-(7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)-2-phenylacrylonitrile (D1) : Yellow

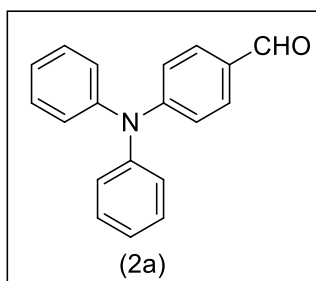
Solid (75%); M.pt: 158-160 °C; IR (MIR-ATR, 4000-600 cm^{-1}): $\nu_{\text{max}} = 2918.84, 2850.24, 2209.76, 1588.87, 1465.49, 1280.13, 754.93, 696.61\text{cm}^{-1}$. $^1\text{H NMR}$ (CDCl_3 , 400 MHz): $\delta_{\text{H}} = 7.92$ (s, 1H), 7.85-7.82 (dd, $J = 8.1\text{Hz}$, 1H), 7.71-7.67 (m, 3H), 7.61-7.59 (t, $J = 3.9$ Hz, 2H), 7.50-7.36 (m, 5H), 7.29-7.23 (m, 6H), 7.14-7.10 (m, 6H), 7.05-7.02 (t, $J = 7.1$ Hz, 4H), 2.05-1.89 (m, 4H), 0.42-0.30 (t, $J = 7.36$ Hz, 6H); $^{13}\text{CNMR}$ (CDCl_3 , 100 MHz) $\delta_{\text{C}} = 152.40, 150.53, 148.25, 147.83, 144.15, 143.01, 135.28, 129.29, 129.04, 128.86, 125.92, 124.24, 123.36, 123.20, 122.90, 121.10, 119.35, 118.70, 109.60, 56.25, 32.56, 8.60$.

HR-MS (ESI⁺) m/z calcd for $[\text{C}_{38}\text{H}_{32}\text{N}_2]^+ = [\text{M} + \text{Na}^+]$: 539.2458; found: 539.2449.

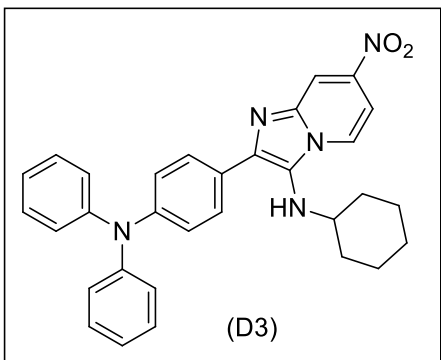


**2-((7-(diphenylamino)-9,9-diethyl-9H-fluoren-2-yl)methylene)-5,5-dimethylcyclohexane
1,3 dione (D2) :**

Red Solid(65%) ; M.pt: 145 °C; IR (MIR-ATR, 4000-600 cm⁻¹): ν_{\max} = 3034.75, 2960.70, 1719.40, 1592.7, 1466.46, 1372.07, 1266.49, 736.21, 698.50cm⁻¹. ¹H NMR (CDCl₃, 400 MHz): δ_{H} = 7.52-7.49 (dd, J_a = 8.4 & J_b = 2.6, 2H), 7.26-7.22 (m, 5H), 7.11-7.07 (m, 5H), 5.63 (s, 1H), 2.46-2.35 (m, 4H), 1.84-1.78 (q, J = 7.3 Hz, 4H), 1.27-1.12 (t, 6H), 0.36-0.32 (t, J = 7 Hz, 6H) HR-MS (ESI⁺) m/z calcd for [C₃₈H₃₇NO₂]⁺ = [M+H⁺] : 540.2892; found: 539.2823.



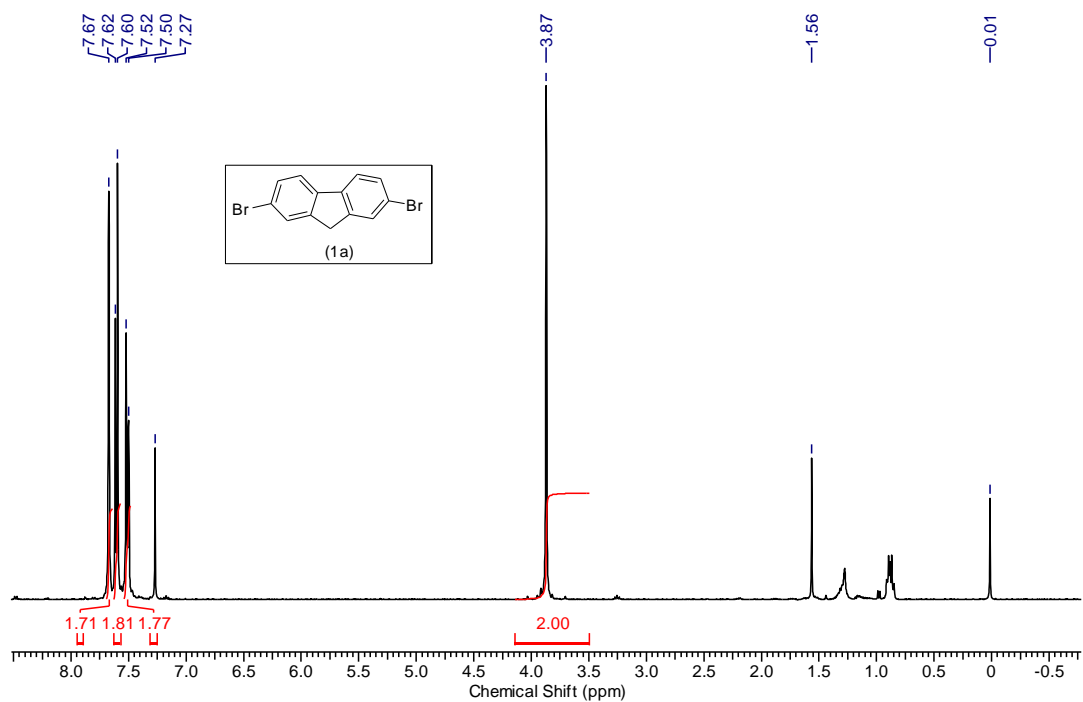
4-(diphenylamino)benzaldehyde (2a): Yellow Solid (76%); ¹H NMR (CDCl₃, 400 MHz): δ_{H} = 9.80 (s, 1H), 7.69–7.66 (d, J = 8.8Hz, 2H), 7.36-7.32 (t, 4H), 7.18-7.15 (m, 6H), 7.03-7.00 (d, J = 8.8 Hz, 2H)



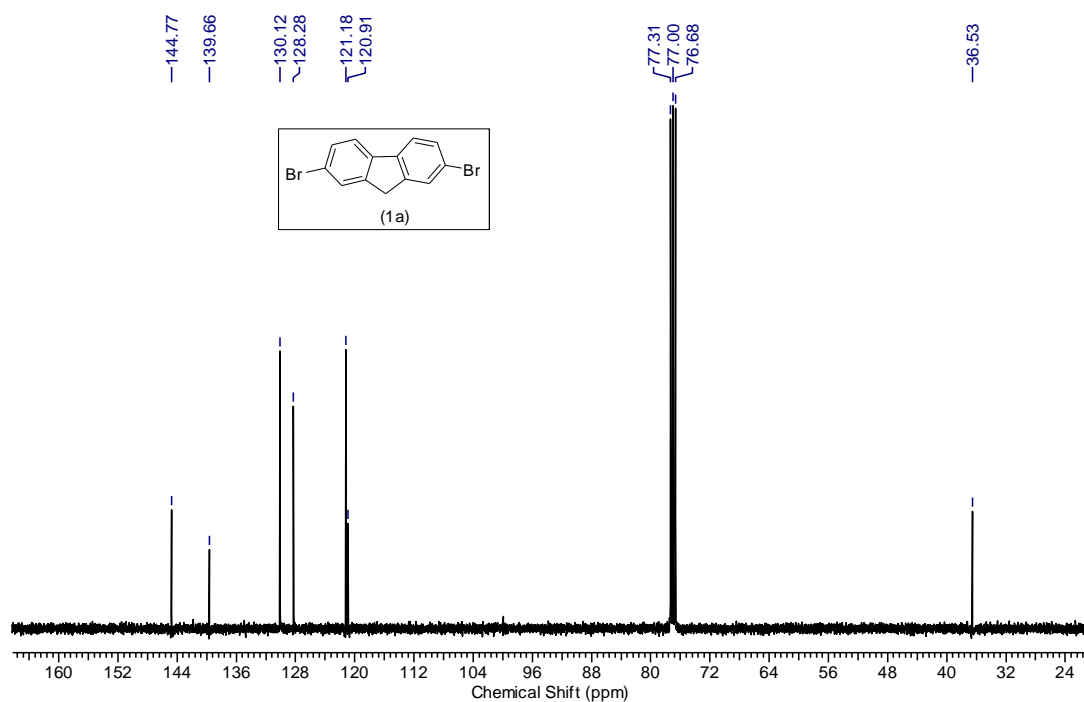
N-cyclohexyl-2-(4-(diphenylamino)phenyl)-7-nitroimidazo[1,2-a]pyridin-3-amine(D3) : Red Solid(67%); M.pt: 160 °C; IR(MIR-ATR, 4000-600 cm⁻¹): ν_{\max} = 3343.19, 2926.66, 2852.68, 1590.61, 1490.40, 1317.50, 1179.64, 750.87, 696.96cm⁻¹; ¹H NMR (CDCl₃, 400 MHz): δ_{H} = 9.23–9.22 (d, J = 2 Hz, 1H), 7.93-7.88 (m, 3H), 7.55-7.53 (d, J = 9.8Hz, 1H), 7.32-7.27 (m, 6H), 7.18-7.16 (dd, J_a = 8.1 & J_b = 2.2 Hz, 6H), 7.09-7.06 (m, 2H), 3.16-3.07 (m, 2H), 1.82-1.6 (m, 4H), 1.34-1.20 (m, 6H); ¹³CNMR (CDCl₃,100 MHz): δ_{C} = 147.99, 147.40, 141.30, 140.19, 136.79, 129.39, 127.39, 127.93, 126.68, 126.15, 124.89, 123.39, 122.83, 117.94, 116.56, 57.20, 34.12, 25.59, 24.76.

HR-MS (ESI⁺) m/z calcd for [C₃₁H₂₉N₅O₂]⁺ = [M+H⁺] : 504.2394 ; found: 504.2385.

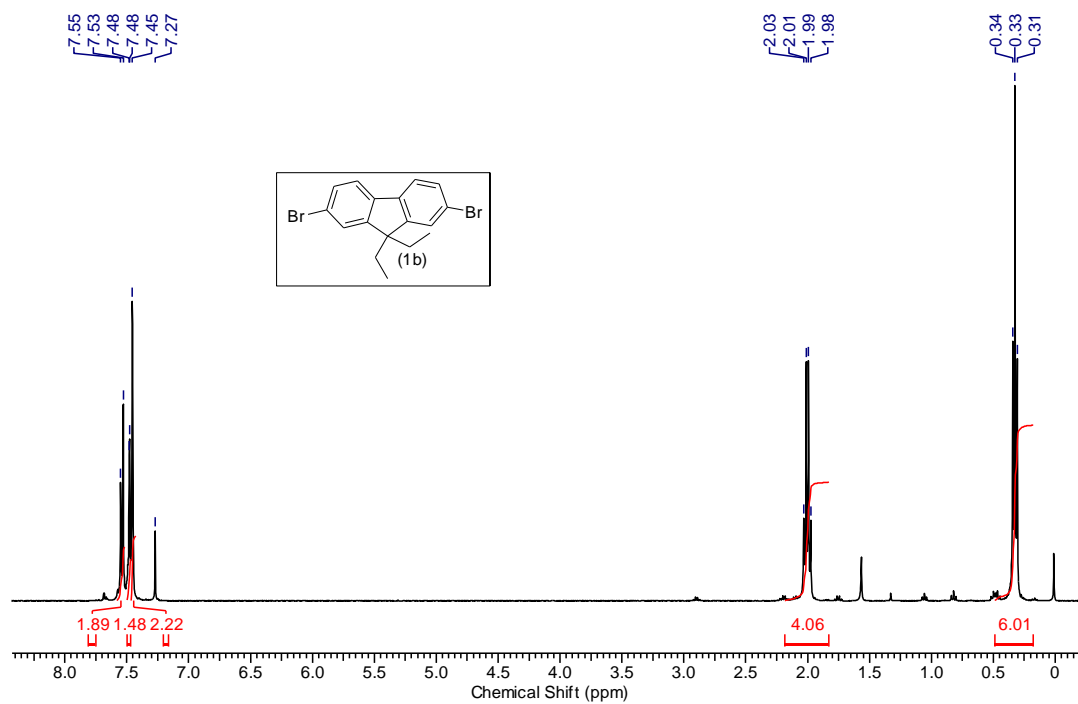
SPECTRAL GRAPH:



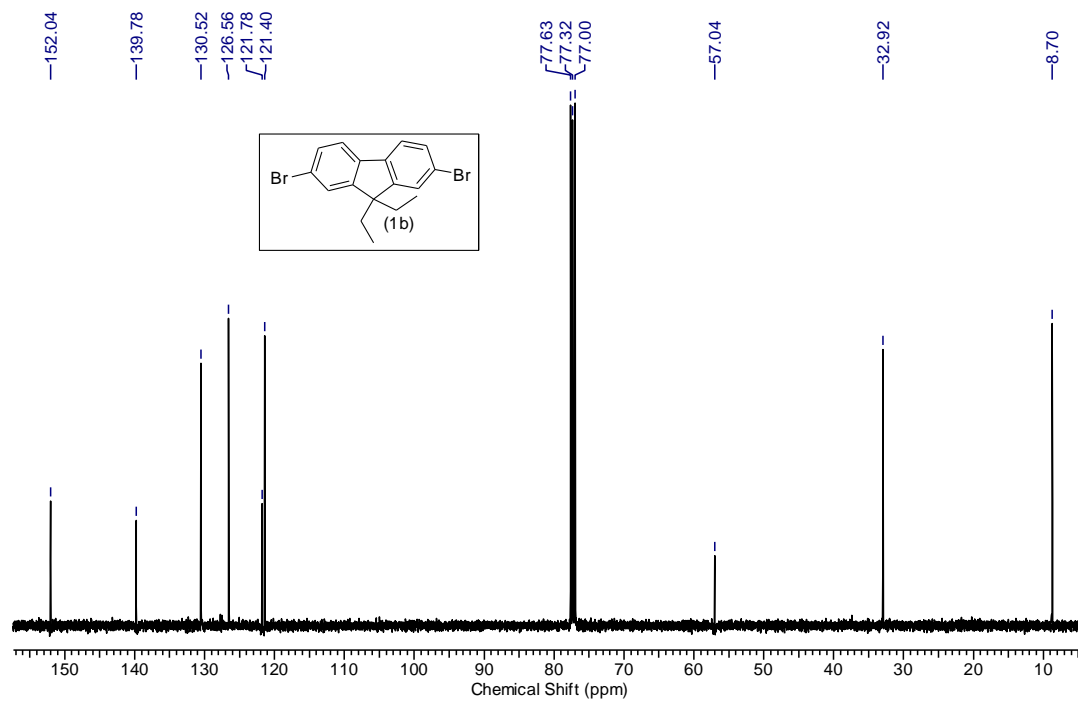
^1H (400 MHz) spectrum of 1a in CDCl_3



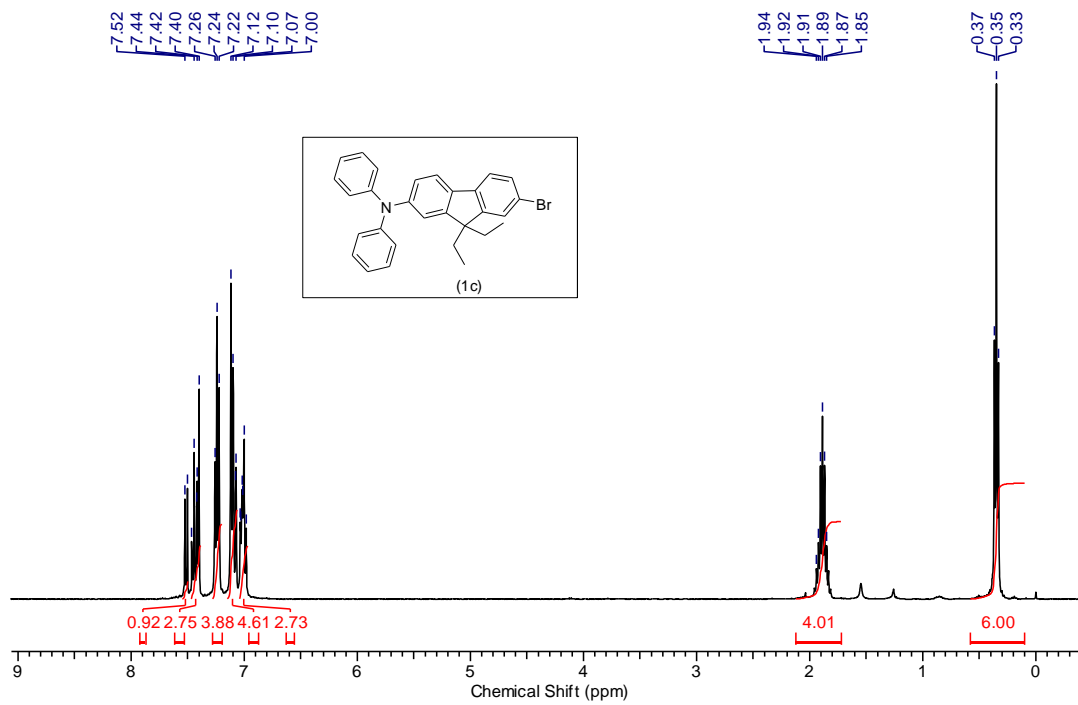
^{13}C (100 MHz) spectrum of 1a in CDCl_3



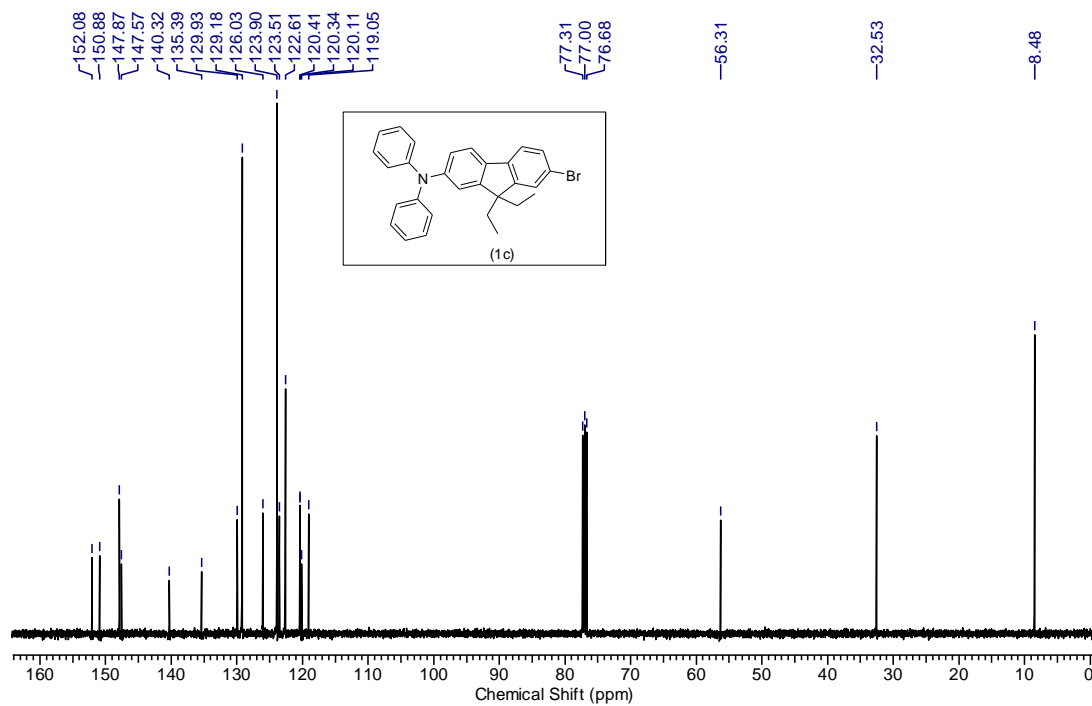
^1H (400 MHz) spectrum of 1b in CDCl_3



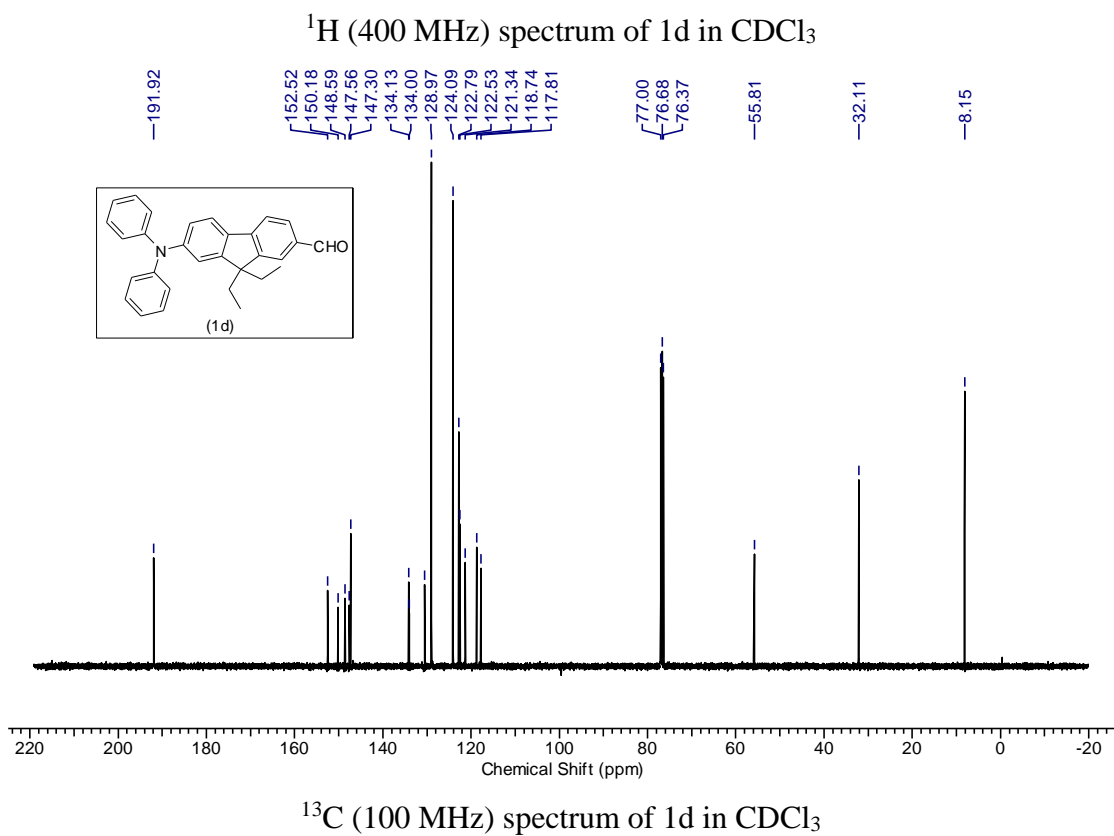
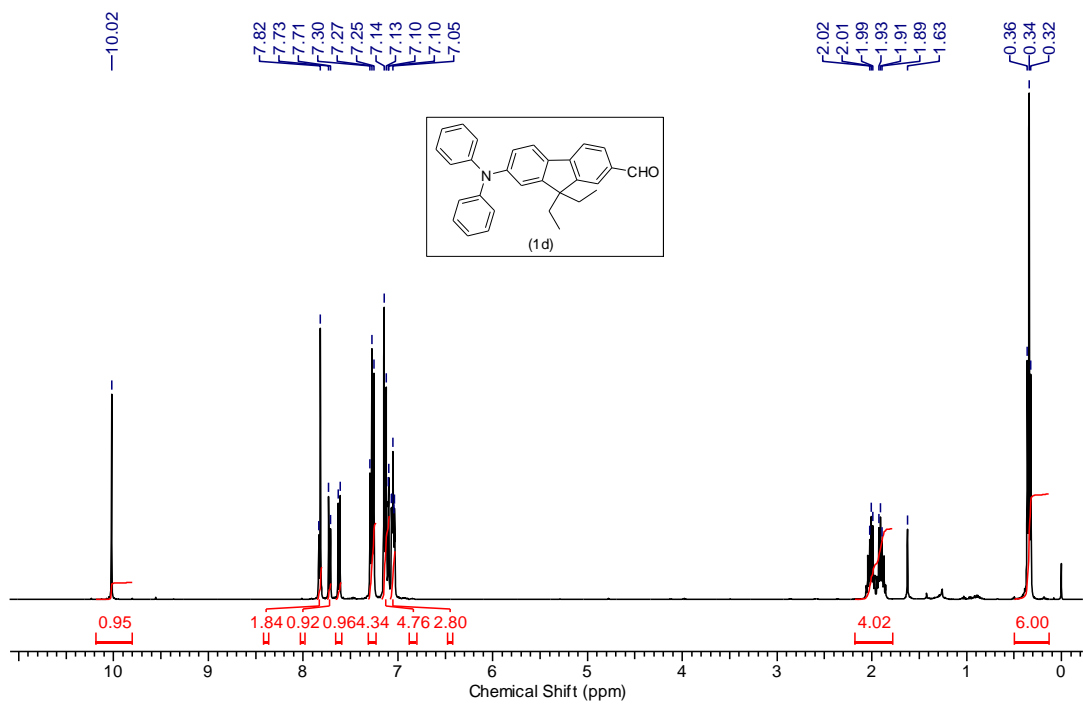
^{13}C (100 MHz) spectrum of 1b in CDCl_3

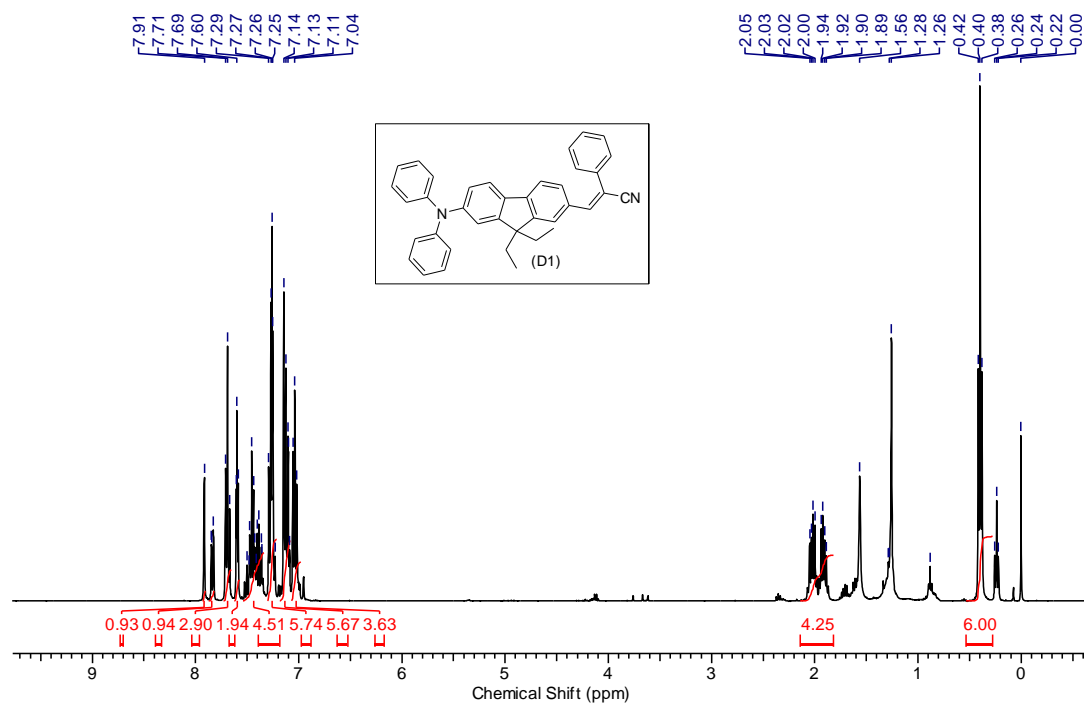


^1H (400 MHz) spectrum of 1c in CDCl_3

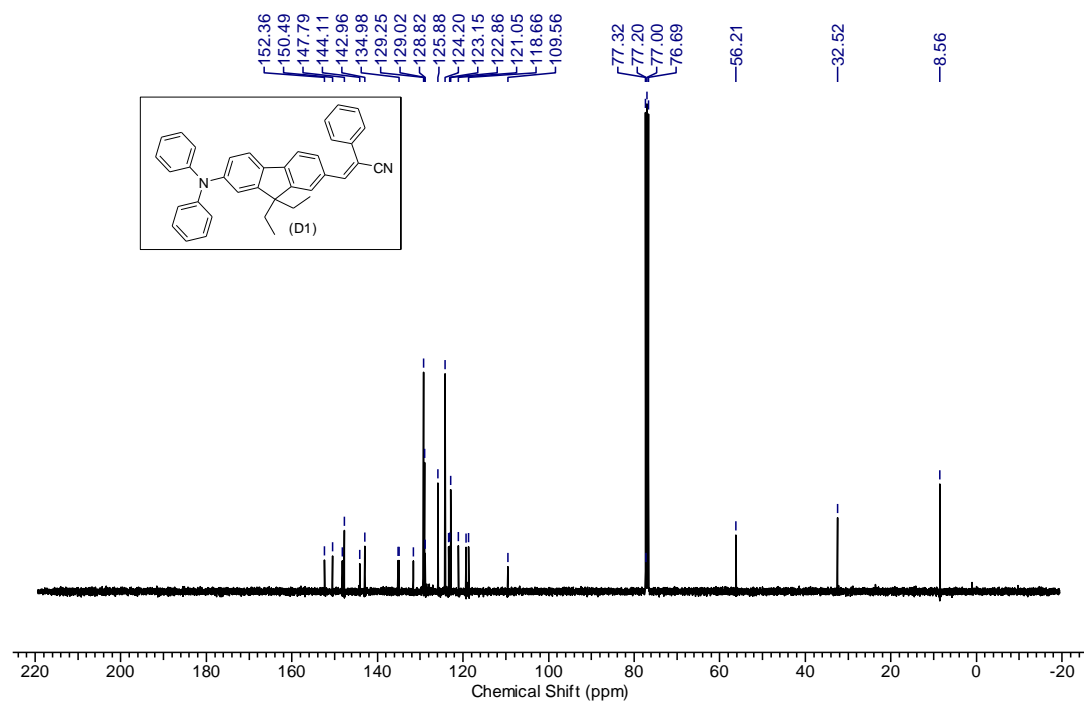


^{13}C (100 MHz) spectrum of 1c in CDCl_3

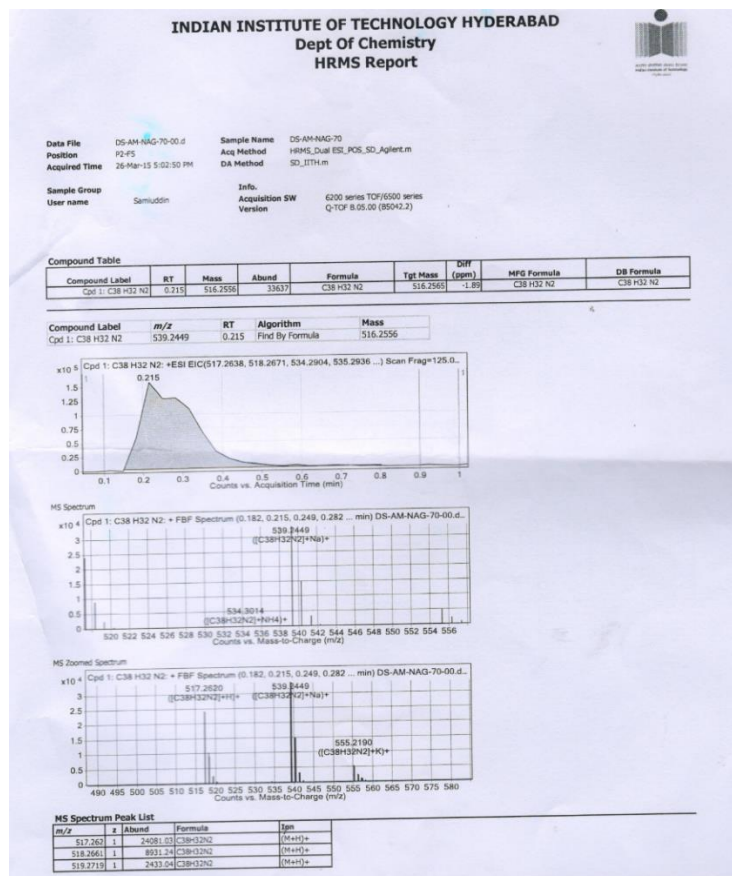




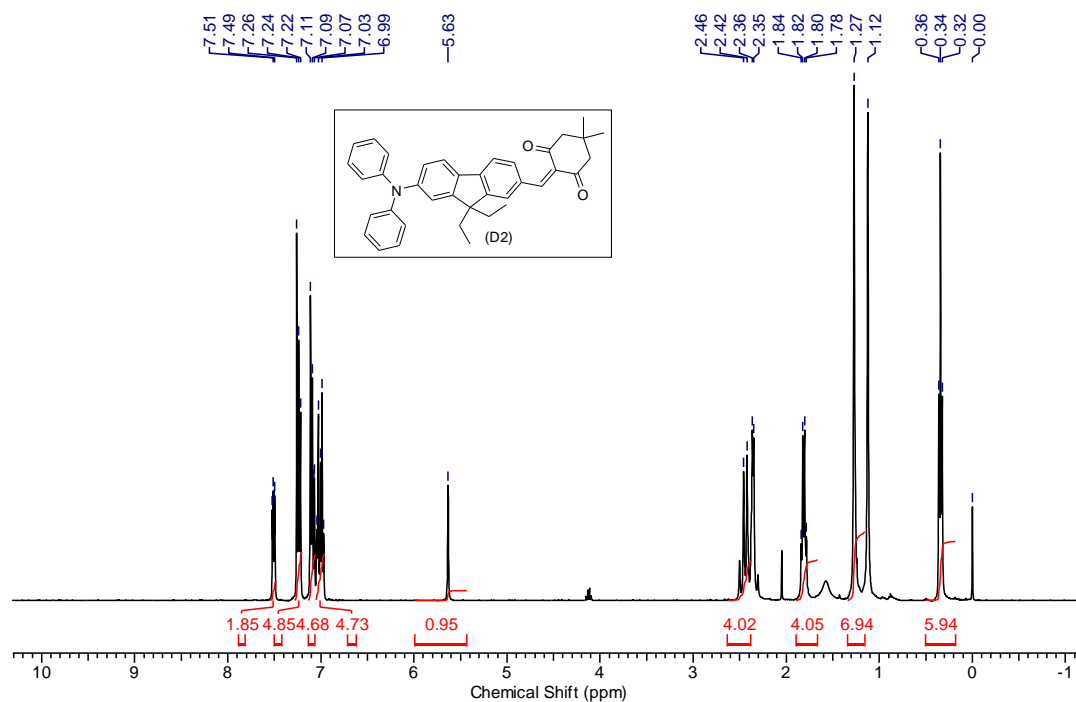
¹H (400 MHz) spectrum of D1 in CDCl₃



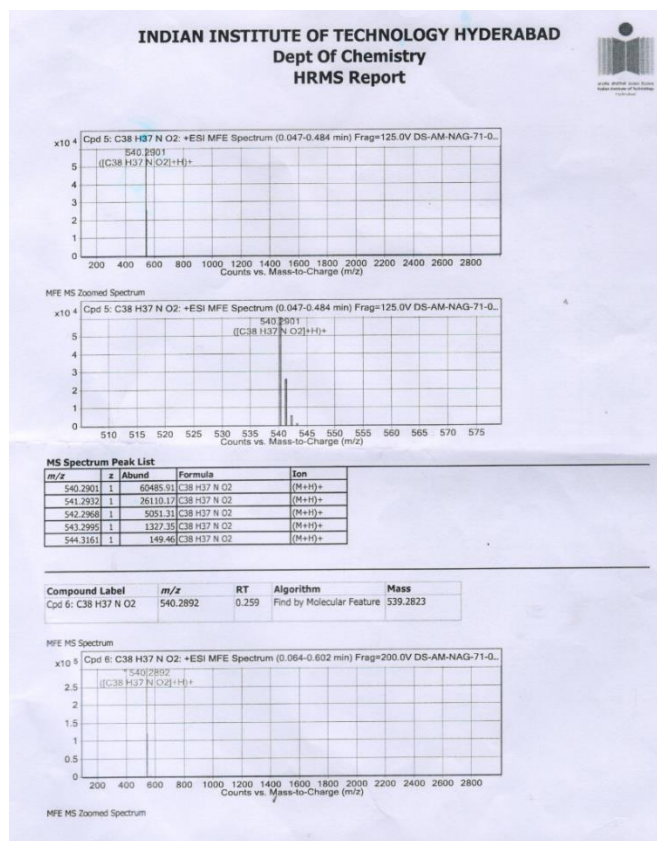
¹³C (100 MHz) spectrum of D1 in CDCl₃



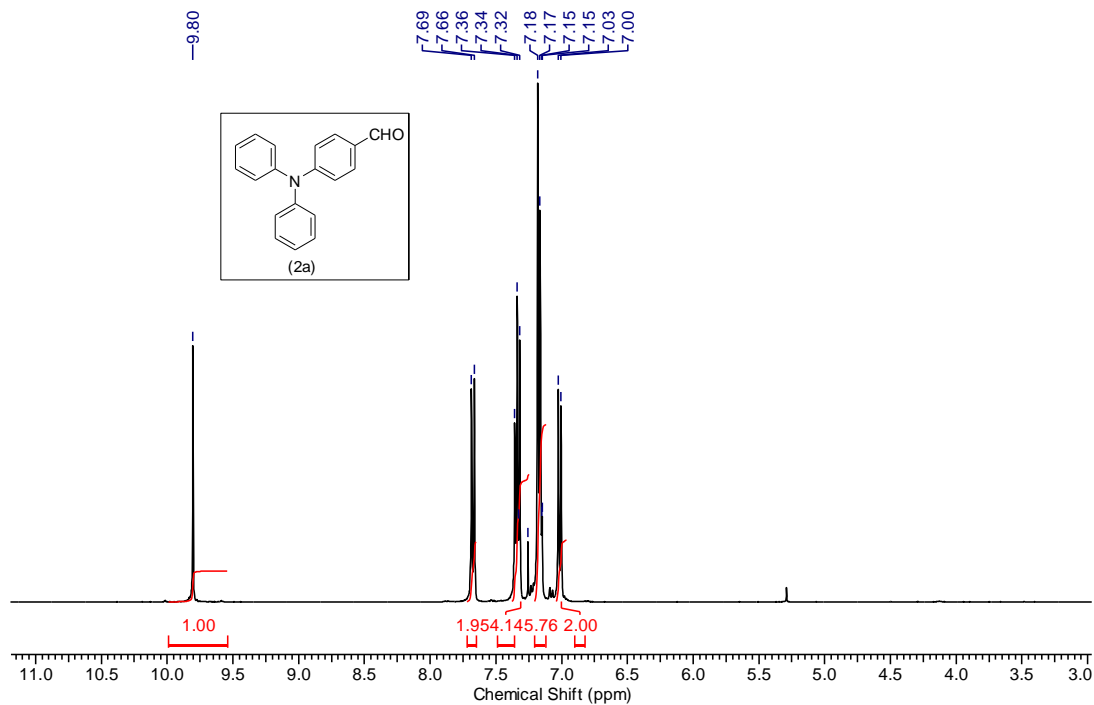
Mass spectrum of D1.

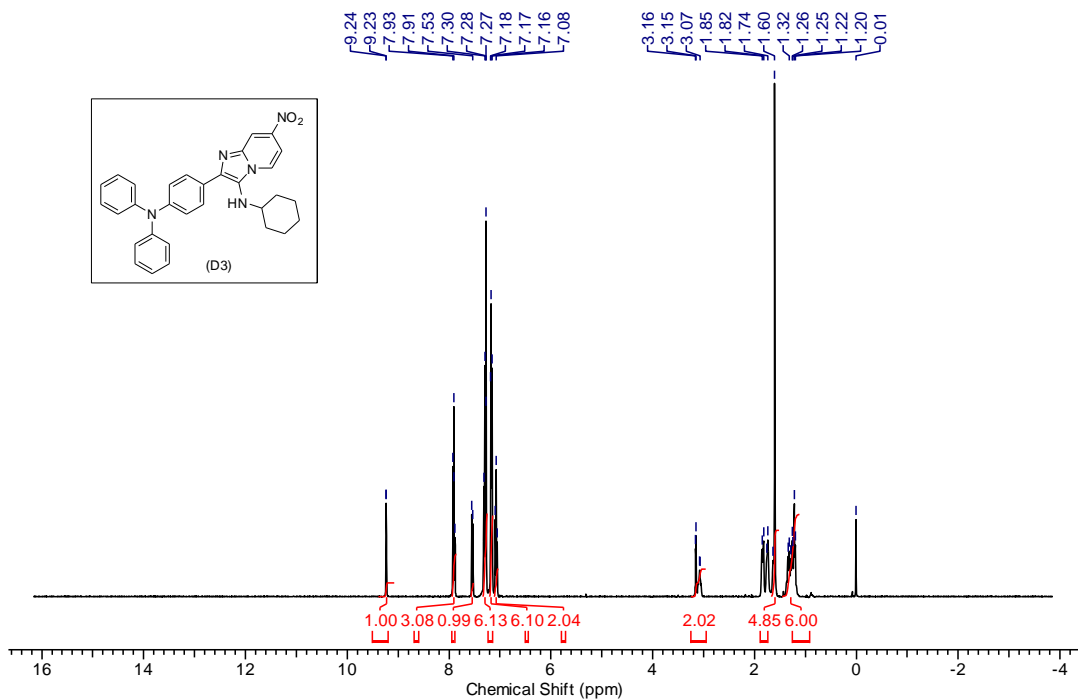


^1H (400 MHz) spectrum of D2 in CDCl_3

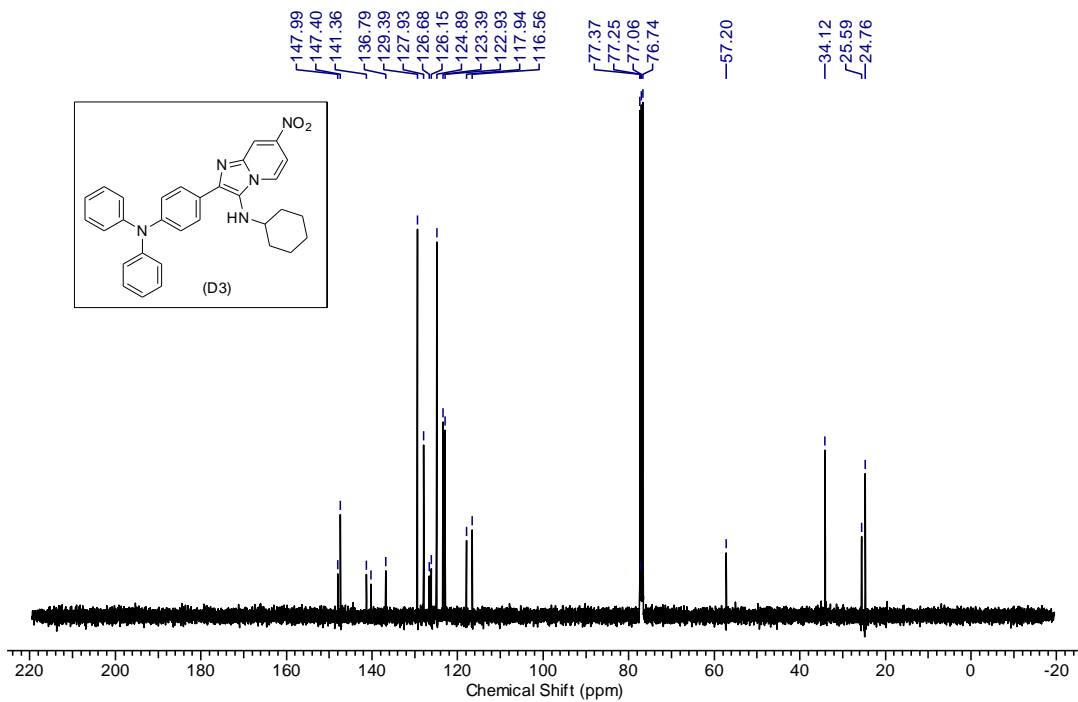


Mass spectrum of D2.

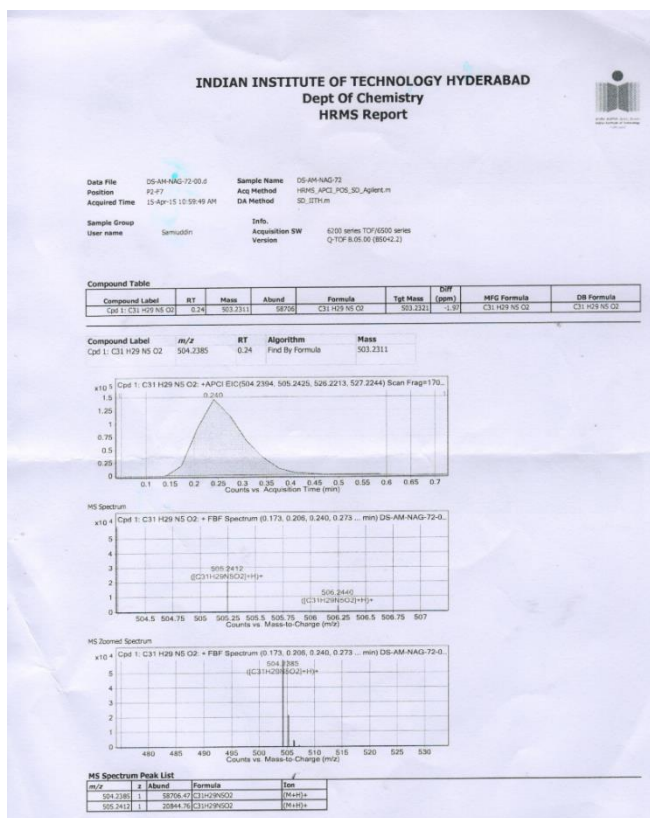




¹H (400 MHz) spectrum of D3 in CDCl₃



¹³C (100 MHz) spectrum of D3 in CDCl₃



Mass spectrum of D3

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