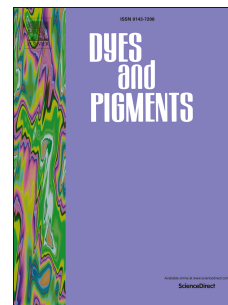


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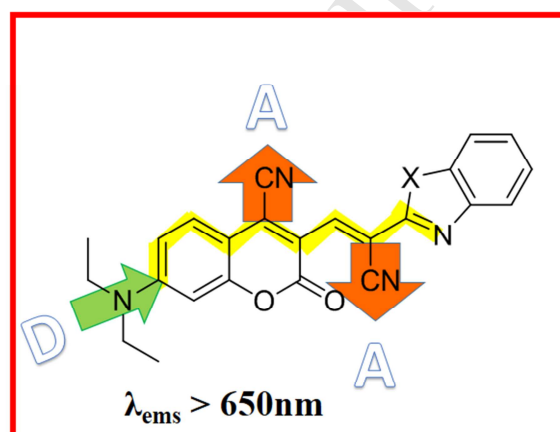
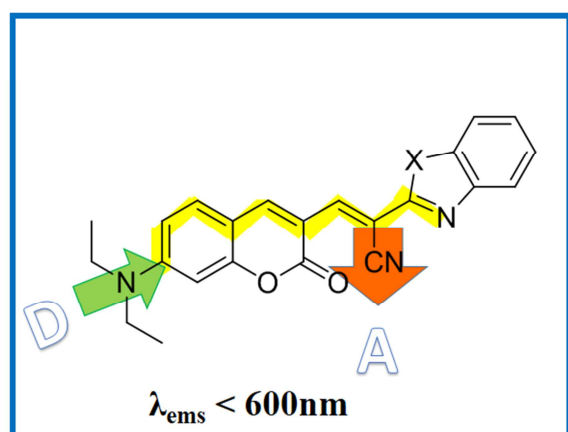
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Graphical abstract



Synthesis and combined experimental and computational investigations on spectroscopic and photophysical properties of red emitting 3-styryl coumarins

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Abstract

The coumarin derivatives are though highly fluorescent, lack in the absorption and emission in the red region. Modifying them to red emission included the strategy of formylation of 7-(N,N-diethyl amino) coumarin by Vilsmeier-Haak reaction followed by oxidative cyanation. The aldehyde synthesized was reacted with cyanomethyl benzoxazole/benzothiazole to give target compounds. All the compounds were characterised by spectral analysis. The cyanated molecules are found to be red shifted in absorption and emission by 90 to 100 nm. There was an increase in the quantum yield by about 10 times. The solvent polarity plots revealed the charge transfer process in the synthesized molecules and higher excited state to ground state dipole moment ratio. Density functional theory computations were performed to understand the nature of transitions involved in absorption and emission process.

Keywords

4-Cyano coumarin, styryl, DFT, TD-DFT, red emitting dyes

Introduction:

The dyes with red emission are employed in the area of OLED [1–4], protein tracking [5], multicolor imaging [6], far-field optical nanoscopy [7,8]. The red emitting dyes are attractive in OLEDs to complement their blue [9,10] and green [11,12] dye counterparts in the fabrication of displays. In biological applications red emitting dyes stand high and apart due to their ability to produce emission signals discrete from the autofluorescence [13–15] of biomolecules (195-600 nm), low energy excitation, emission in biological window [16,17]. The coumarin molecules with red emission are rarely synthesized and studied. Considering the structure of the coumarin the

absorption and emission can be enhanced by placing 1) Electron donor at 7-position [18,19] 2) electron withdrawing group at 3 and 4 position [20,21] and 3) extension of conjugation [18,22].

This strategy ensures there is enough charge transfer in the coumarin molecule to push the absorption and emission in the red region. Synthesis of styryl dyes is well documented in the literature and has an easier protocol [23–26].

In the current study we have synthesized three 4-cyano 3-styryl coumarins (**Figure 1**) and their photophysical properties were studied with respect to various solvent polarity parameters. The photophysical properties were computed with DFT and TD-DFT to have an insight into their photophysical behaviour.

Methods

All commercial reagents were procured from SD Fine Chemicals (Mumbai) and were used without further purification. Laboratory reagent grade solvents were purchased from Rankem, Mumbai. The reactions were monitored by TLC using on 0.25 mm E-Merck silica gel 60 F_{254} precoated plates, which were visualized with UV light (254 nm and 344 nm). ^1H NMR and ^{13}C NMR spectra were recorded on Agilent 500MHz NMR. Mass spectra were recorded on FINNIGAN LCQ ADVANTAGE MAX instrument from Thermo Electron Corporation (USA). The absorption spectra of the compounds were recorded on a Perkin Elmer Lambda 25 UV-Visible spectrophotometer; emission spectra were recorded on Varian Inc. Cary Eclipse spectrofluorometer. The ground state (S_0) geometry of the compound **6-9** was optimized in the gas phase using Density Functional Theory (DFT) [27]. The popular hybrid functional B3LYP was used, which combines Becke's three parameter exchange functional (B3)[28] with the nonlocal correlation functional by Lee, Yang, and Parr (LYP) [29]. All the atoms were treated with 6-31 G(d) basis set, which deems to be sufficient for the molecules involved. The validity of the structures as local minima on potential energy surface was verified with vibrational analysis and was confirmed that they are with no imaginary frequencies. TD-DFT (Time Dependent Density Functional Theory) with same hybrid functional and basis set was used to estimate vertical excitation and their oscillator strength. The lowest singlet excited state (S_1) was relaxed using TD-DFT to get optimised geometry of the excited state. Emissions were obtained by calculating vertical excitations of excited state geometry at ground state. Frequency computations were also carried out on the optimized geometry of the low-lying vibronically relaxed first excited state of

conformers. Computations in solvents were carried out using the Polarizable Continuum Model (PCM). Gaussian 09 program [30] was used for all the quantum mechanical computations.

Synthesis

Figure 1 Synthesis of 4-Cyano coumarin 3-styryls (Compound 6-9)

The compound **3** was prepared by cyclisation of 5-(diethylamino)-2-hydroxybenzaldehyde with diethyl malonate in presence of piperidine and ethanol followed by decarboxylation with conc. HCl and glacial acetic acid using the reported procedure [31]. Compound **3** was subjected to Vilsmeier-Haack reaction using DMF/POCl₃ to give 7-(diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (**4**) according to the procedure has been described by Wu *et al.* [32]

Synthesis of 7-(diethylamino)-3-formyl-2-oxo-2*H*-chromene-4-carbonitrile (**5**)

7-(Diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde (**4**) (1.5 g, 6.9 mmol) was dissolved in DMF (10 mL) and mixture was cooled to 5°C in ice bath. A solution of sodium cyanide (0.374, 7.6mmol) in water (4 mL) was added drop wise to the cooled mixture. The reaction mixture turns pale yellow from yellow. The reaction mixture was stirred and allowed to attain room temperature (~27°C) over a period of 1.5 h. It was cooled to 0°C and bromine liquid (0.548 mL, 10.3mmol) was added to it dropwise. The solution turns red-brown. The solid separated after 30 min. was then filtered and dried under vacuum to give brown colored product (0.98 g).

¹HNMR (CDCl₃, 500MHz, δ ppm): 1.25-1.30 (t, *J*= 7.2 Hz, 6H), 3.50-3.54 (q, *J*= 7.2 Hz, 4H), 6.48-6.49 (d, *J*= 2.5 Hz, 1H), 6.74-6.76 (dd, *J*= 2.5 & 7.5 Hz, 1H), 7.76-7.78 (d, *J*= 9.3 Hz, 1H), 10.16 (s, 1H)

¹³CNMR (CDCl₃, 125 MHz, δ ppm): 12.5, 46.5, 97.4, 107.9, 111.6, 112.8, 114.3, 125.3, 130.3, 154.1, 158.0, 160.0, 185.5

HRMS: 271.1087 (M+H⁺) (Calculated for C₁₅H₁₅N₂O₃ : 271.1083)

General procedure for synthesis of styryl derivatives of **4** and **5**

2-(Benzo[d]azol-2-yl)acetonitrile (1.2 mmol) was dissolved in ethanol (10 mL) and the reaction mixture was cooled to 5°C and 7-(diethylamino)-3-formyl-2-oxo-2*H*-chromene-4-carbonitrile **5** or 7-(diethylamino)-2-oxo-2*H*-chromene-3-carbaldehyde **4** (1.2 mmol) was added to it in a single portion, piperidine (0.1 mL) was added to it. The mixture was stirred at 5°C for an hour and allowed to attain room temperature (~26°C). The reaction was monitored by TLC and was completed in 12 h. The reaction mass was then poured to ice-water (25 mL) and extracted with chloroform. The organic layer was washed with water and brine, dried with sodium sulphate and evaporated under reduced pressure to give the styryl derivative.

2-(Benzo[d]oxazol-2-yl)-3-(7-(diethylamino)-2-oxo-2*H*-chromen-3-yl)acrylonitrile (6)

¹HNMR (CDCl₃, 500MHz, δ ppm): 1.19-1.21 (t, *J* = 7.5 Hz, 6H), 3.39-3.344 (q, *J* = 7.5 Hz, 4H), 6.42 (s, 1H), 6.59-6.60 (d, *J* = 5 Hz, 1H), 7.29-7.31 (m, 2H), 7.36-7.38 (d, *J* = 10 Hz, 1H), 7.46-7.49 (t, *J* = 5 Hz, 1H), 7.70-7.72 (t, *J* = 5 Hz, 1H), 8.54 (s, 1H), 8.88 (s, 1H).

¹³CNMR (CDCl₃, 125 MHz, δ ppm): 12.4, 45.5, 96.2, 97.5, 109.1, 110.5, 110.6, 112.0, 115.9, 120.5, 125.0, 125.9, 131.8, 141.7, 143.0, 150.7, 153.0, 157.6, 159.5, 161.1.

HRMS: 386.1470 (M+H⁺) (Calculated for C₂₃H₂₀N₃O₃: 386.1460)

2-(Benzo[d]thiazol-2-yl)-3-(7-(diethylamino)-2-oxo-2*H*-chromen-3-yl)acrylonitrile (7)

¹HNMR (CDCl₃, 500MHz, δ ppm): 1.24-1.28 (t, *J* = 7.2 Hz 6H), 3.45-3.50 (q, *J* = 7.2 Hz 4H), 6.49-6.50 (d, *J* = 5 Hz), 6.64-6.67 (q, *J* = 5 Hz, 1H), 7.40-7.50 (m, 3H), 7.87-7.88 (d, *J* = 5 Hz, 1H), 8.07-8.09 (d, *J* = 10 Hz, 1H), 8.40 (s, 1H), 8.90 (s, 1H)

¹³CNMR (CDCl₃, 125 MHz, δ ppm): 12.5, 45.4, 97.4, 103.5, 109.0, 110.3, 112.3, 116.8, 121.5, 123.7, 125.9, 126.7, 131.6, 134.7, 140.4, 142.7, 152.8, 153.7, 157.4, 161.2, 163.4.

HRMS: 402.1255 (M+H) (Calculated for C₂₃H₂₀N₃O₂S: 402.1276)

3-(2-(Benzo[d]oxazol-2-yl)-2-cyanovinyl)-7-(diethylamino)-2-oxo-2*H*-chromene-4-carbonitrile (8)

¹HNMR (CDCl₃, 500MHz, δ ppm): 1.28-1.30 (t, J = 7.2 Hz, 6H), 3.50-3.54 (q, J = 7.2 Hz, 4H), 6.59-6.60 (d, J = 2.3 Hz, 1H), 6.72-6.74 (dd, J = 2.2 & 5 Hz, 1H), 7.40-7.42 (dd, 2.5 & 3.5 Hz, 2H), 8.33-8.34 (d, J = 9.2 Hz, 1H), 11.79 (s, 1H).

¹³CNMR (CDCl₃, 125 MHz, δ ppm): 12.6, 45.5, 97.6, 104.8, 108.3, 109.6, 111.3, 113.9, 125.53, 126.3, 127.7, 140.6, 148.7, 149.6, 153.8, 154.6, 159.8, 160.4, 165.9

HRMS: 427.1384 (M+OH[•]) (Calculated for C₂₄H₁₉N₄O₄: 427.1406)

3-(2-(Benzo[d]thiazol-2-yl)-2-cyanovinyl)-7-(diethylamino)-2-oxo-2H-chromene-4-carbonitrile (9)

¹HNMR (CDCl₃, 500MHz, δ ppm): 1.24-1.30 (t, J = 7.3 Hz, 6H), 3.50-3.54 (q, J = 7.3 Hz, 4H), 6.65-6.67 (d, J = 10 Hz, 1H), 6.72-6.74 (d, J = 10 Hz, 1H), 7.45-7.46 (m, 1H), 7.54-7.56 (m, 1H), 7.92-7.94 (d, J = 10 Hz, 1H), 8.04-8.05 (d, J = 5 Hz, 1H), 8.35-8.37 (m, 1H) 12.26 (s, 1H)

¹³CNMR (CDCl₃, 125 MHz, δ ppm): 12.5, 45.7, 97.6, 104.5, 110.7, 116.5, 121.7, 122.8, 126.6, 127.2, 134.3, 140.3, 153.3, 155.3, 159.5, 164.6, 166.3.

HRMS: 443.1178 (M+H⁺) (Calculated for C₂₄H₁₉N₄O₂S: 443.1149)

Results and discussion

Photophysical study

The compounds synthesized were studied for their absorption characteristics in solvents of different polarity. The compounds without 4-cyano group i.e. compound **6** and **7** absorbed in the region of 500 nm to 529 nm (**Table 1**) in various solvents. There is very little effect of presence of benzoxazole or benzothiazole acceptors on absorption property as the compounds **6** and **7** absorb at 500 nm and 501 nm in toluene respectively. However the compound **7** was expected to be red shifted as compared to the compound **6** due to presence of benzothiazole acceptor. Absorption maxima for the compounds **6** and **7** are sensitive to the solvent polarity and show a clear trend of positive solvatochromism. The molar extinction coefficient ranges 25795 and 53900 L mol⁻¹ cm⁻¹. The polar solvents have consistently shown lower molar extinction coefficient value whereas the chlorinated solvent dichloromethane shows highest value (**Table 1**)

The 4-cyanated styryl compounds (**8** and **9**) absorbed at lower energy by 215 cm^{-1} to 3279 cm^{-1} around as compared to their non-cyanated counterparts. The compounds **7** and **8** show single peaks in the absorption spectrum which mainly consists of the absorption arising from a single chromophoric unit. It consists of the donor (7-(N,N-diethylamino)-coumarin)-acceptor (cyanomethyl benzoxazole/benzothiazole unit) system whereas the compounds **8** and **9** show two peaks in the absorption spectrum originating from the dual chromophoric units, the additional chromophoric unit consisting of (N,N-diethylamino)-coumarin-acceptor (cyano) system. The longer and shorter wavelength absorptions are predominant in non-polar and polar solvents respectively.

Compared to absorption the emission is more sensitive to the solvent polarity and shows a positive solvatochromism in the compounds **8** and **9**. In toluene, compound **8** and **9** emit at 634 nm and 637 nm, whereas in ethanol they emit at 692 nm and 700 nm respectively (**Table 1**). The 4-cyanated compounds (**8** and **9**) are found to be non-fluorescent in polar aprotic solvents, this may be due to the interaction of more polar cyano coumarin styryl molecules **8** and **9** with polar solvents at the excited state. In the case of the non-cyanated compounds **6** and **7**, they show highest intensity of fluorescence emission in DMF and DMSO and there is no quenching of fluorescence like cyanated molecules. However there is a clear red shift is seen in the absorption and emission of the cyanated molecules (**8** and **9**), Stokes shifts are lower than those of non-cyanated molecules (**6** and **7**). The presence of 4-cyano group is responsible for the decrease in Stokes shift by interacting with the solvent at excited state.

However the Stokes shifts are lower for compounds **8** and **9** as compared to the compounds **6** and **7** in all the solvents, the quantum yields have improved many folds. This may be attributed to the restriction of conformations around the styryl double bond. There is about a 10 fold increase in the quantum yield, when compared to the non-cyanated compounds **6** and **7**. Only exception is compounds **6** and **8** which are benzoxazole derivatives in methanol and ethanol show a reverse trend. This observation can be attributed to the better hydrogen bonding ability of the benzoxazole oxygen with the protic solvents. The compounds **6** and **7** tend to show a lower quantum yield in non-polar solvents and the trend is reversed in their 4-cyano derivatives (compound **8** and **9**)

Table 1 Photophysical Data of compound **6-9**

To understand the nature of the transitions and to have more insights into the photophysical properties of the dyes studied, quantum chemical computations were performed. The excitation energies and their oscillator strengths are tabulated in **Table 1**. The red shift induced by introducing –CN group at 4-position is also well predicted by TD-DFT computations. The predicted values for compound **6** and **7** lies between 466 nm to 480 nm in all the solvents. There is a difference of 18-50 nm in all the computations with experimental measurements. The red shift in absorption with increase in the polarity is predicted but is not consistent with experiments. There is a decrease in the oscillator strength value when 4-position is substituted by –CN group.

To understand the red shift induced by the introduction of the –CN group at 4-position, energy of frontier molecular orbitals were plotted against the solvents (**Figure 2**).

Figure 2 Lowering of LUMO in compound **8** and **9** as compared to compound **6** and **7**

It is clear from the energy profile diagram given in **Figure** that there is a lowering of both HOMO and LUMO energies after substitution by –CN group. But the extent of lowering of energy in LUMO is more as compared to HOMO. This lead to decrease in band gap between HOMO and LUMO, which is part of important transition due to absorption.

The emission calculated by considering ground state energy at excited state geometry gives overestimated energies of de-excitations and are given in **Table 1**. These values also predict a red shifted emission shown by the compounds **8** and **9** when compared to the compounds **6** and **7** respectively. The percent deviation of the calculated values of de-excitation energies from the experimental ones ranges from 2.4 to 11.4%

Solvent polarity function plots

The solvatochromic behaviour of the molecules **6-9** was studied with the help of Lippert [33], Weller[34] and Rettig's [34] plots. Lippert's plot is the plot of stokes shift in cm^{-1} vs orientation polarizability. The Lippert function is constituted of the polarity function $f(\epsilon)$ and polarizability function $f(\eta)$. The Wellers and Rettigs plots were also screened for the linearity, which are the plots of emission wave numbers of emission versus the respective polarity functions. For convenience the solvents were chosen which do not have specific interaction with the solute. The

polar solvents were not used to plot these functions. There is very less correlation was found in the Lippert plot, however the constituent function $f(\eta)$ (polarizability function) shows very good correlation. It is clear from these plots that the solvatochromic behaviour of these molecules is polarizability dependent and independent of polarity parameter defined by $f(\epsilon)$.

The Weller and Rettig plots show good linear behaviour and is indicative of CT (Charge transfer) at excited state in these molecules. In the charge transfer process, though absorption spectrum is not solvent polarity dependent but the emission is highly sensitive to the solvent. As there is change in the polarity of the solute at excited state the solvent polarity has greater effect on the emission properties. The solvent polarity function plots are given in supporting information.

The deviations from the above plots observed in the case of alcohols may be attributed to the specific solvent effects arising from specific solute-solvent interactions (hydrogen bonding, etc.). The carbonyl Oxygen ($>C=O$) and the lactone Oxygen ($-O-$) are the sources of hydrogen bonding sites in these molecules.

Oscillator strength and transition dipole moment of the dyes

In addition to this the dipole moments between the excited and ground states the charge transfer character of the fluorophore can be understood from the oscillator strength (f) (**Table 1**) and transition dipole moment of the dyes (M_a). The effective number of electrons transition from the ground to excited state is usually described by the oscillator strength, which provides the absorption area in the electronic spectrum. The oscillator strength (f) can be calculated using the following Equation 1 [35].

$$f = 4.32 \times 10^{-9} \int \epsilon(\bar{\nu}) d\bar{\nu} \quad \text{Equation 1}$$

Where ϵ is the extinction coefficient ($L \text{ mol}^{-1} \text{ cm}^{-1}$), and $\bar{\nu}$ represents the numerical value of wavenumber (cm^{-1}).

Transition dipole moments for absorption (M_a) which is a measure of the probability of radiative transitions have been calculated for the dyes different solvent environments using the equation 6 [36].

$$M_a^2 = \frac{f}{4.72 \times 10^{-7} \times \bar{\nu}} \quad \text{Equation 2}$$

The values of oscillator strength (f) and transition dipole moment (M_a) for compound **6-9** for each solvent is given in **Table 2**.

Table 2 Transition dipole moments (M_a) obtained from absorption properties of compound **6-9** in various solvents.

The transition dipole moments obtained for the 4-CN substituted compounds **8** and **9** shows a decline in value as compared to the non-cyanated counterpart compound **6** and **7**. The molar extinction co-efficients (ϵ) and apparently the transition dipole moments (M_a) are lower for cyano compounds **8** and **9**.

Dipole Moment Ratio

The compounds **6-9** responds well to the solvent polarity functions (ϵ , n), the similar equations are introduced by Bilot-Kawski [37], Bakhshiev [38] and Liptay [39] for the estimation of ratio of excited state dipole moment and ground state dipole moment i.e. $\frac{\mu_e}{\mu_g}$. The dipole moments calculated with the above equations is given in **Table 3**.

Table 3 Dipole moment ratio of compound **6-9** by various methods

The compounds **6** and **7** has $\frac{\mu_e}{\mu_g}$ ratio less than unity and implies that the excited state is less polar for these molecules, on the contrary their 4-cyanated analogues has $\frac{\mu_e}{\mu_g}$ ratio more than unity and suggests the more polar excited state. This leads to a positive solvatochromism. The Bilot-Kawski equation has consistently estimated lower $\frac{\mu_e}{\mu_g}$ ratio as compared to the Bakhshiev and Liptay equations.

Excited State Geometry

The styryl molecules **6-8** are observed to have a twist in dihedral angle at ground state which takes the withdrawing groups out of plane **Figure 3**. This dihedral angle is important to understand the

charge transfer from the donor part to acceptor. Lower the twist from planarity more the overlap of molecular orbitals and in result more the charge transfer.

Figure 3 Twist of dihedral angle and the atoms involved in dihedral angle in compound **6-9**

The dihedral angles from the optimized structures at the ground and excited states for all the four molecules in various solvents are given in **Table 4**.

Table 4 Dihedral angles calculated with B3LYP/6-31G(d) method and various solvents for compound **6-9**

The dihedral angles optimized at the ground state (GS) and excited state (ES) suggests that there is an increase in planarity at the excited state. The extent of attaining planarity is solvent dependent in case of compound **6** and **7**, whereas there is very less solvent dependence in compound **8** and **9**. The change in dihedral angle from GS to ES is higher for 4-cyanated compounds (**8** and **9**) as compared to compound **6** and **7**.

Molecular orbitals

The molecular orbital shapes and density illustrations can throw some light on how the donor-acceptor relationship is established in a molecule. The MOs involved in excitation and de-excitation (emission) are HOMO and LUMO for all the molecules. The FMO diagrams show that the $-NEt_2$ group constitutes the major density in HOMO for molecules **6-9**. In the case LUMOs of the molecules **6** and **7** the electron density is located on the styryl double bond and around, whereas in LUMOs of the molecules **8** and **9** the electron density is clearly located on 4-cyano substitution. This suggests the role of $-CN$ group as an efficient acceptor and helps in lowering the energy of LUMO in molecule **8** and **9**.

Conclusion

In conclusion, the styryl compound **8** and **9** from 7-(diethylamino)-3-formyl-2-oxo-2*H*-chromene-4-carbonitrile (**5**) were synthesized and their photophysical properties were compared with the compound **6** and **7**. All the compounds synthesized were confirmed by NMR spectral analysis and HRMS. The photophysical study revealed that there is not only a red shift imparted by the introduction of cyano group at the 4-position but there is a many fold increase in the quantum

yields of these molecules. The study of charge transfer characteristics of the dyes by various solvent polarity parameter plots shows the evidence of charge transfer at excited state. The DFT computations of the dyes also supports the red shift induced by –CN group at 4-position. The geometrical change occurring at the excited state (i.e. the decrease in dihedral angle which brings the donor and acceptor in a single plane.) also supports the charge transfer at excited state. The dipole moment ratios calculated with different solvent polarity parameter plots suggests more polar excited states for the compound **8** and **9**. The molecules **8** and **9** can be used as a basic structures to the dyes or probes requiring emission in red region and moderate quantum yields.

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Synthesis and combined experimental and computational investigations on spectroscopic and photophysical properties of red emitting 3-styryl coumarins

Abhinav B. Tathe, Vinod D. Gupta, Nagaiyan Sekar *

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Table 1 Photophysical Data of compound **6-9**

Solvent	Experimental					Theoretical*				
	λ_{abs} (nm)	E (L mol ⁻¹ cm ⁻¹)	<i>f</i>	λ_{em} (nm)	Stokes Shift (cm ⁻¹)	Φ	Vertical Excitation (nm)	<i>f</i>	Emission (nm)	
6	Acetonitrile	510	37345	0.672	585	2514	0.0071	471	1.6364	526
	Dichloromethane	511	53900	0.552	576	2208	0.0066	473	1.6464	532
	1,4-dioxane	497	30415	0.464	560	2264	0.0097	466	1.6177	534
	N,N-dimethylformamide	529	40810	0.697	594	2069	0.0307	475	1.6582	532
	Dimethylsulphoxide	519	36575	0.800	589	2290	0.0263	474	1.6561	531
	Ethyl acetate	506	33880	0.552	570	2219	0.0068	470	1.6122	530
	Ethanol	516	32340	0.509	584	2257	0.0158	472	1.6391	528
	Methanol	509	25795	0.413	584	2523	0.0157	470	1.6317	526
	Toluene	500	34265	0.586	560	2143	0.0061	469	1.6360	537
7	Acetonitrile	506	27669	0.528	596	2984	0.0027	476	1.6404	530
	Dichloromethane	509	42350	0.582	580	2405	0.0033	477	1.6499	536
	1,4-dioxane	498	38656	0.726	570	2536	0.0043	470	1.6247	535
	N,N-dimethylformamide	528	40425	0.715	605	2410	0.0122	480	1.6628	534
	Dimethylsulphoxide	525	35288	0.659	613	2734	0.0104	479	1.6612	535
	Ethyl acetate	504	31647	0.582	576	2480	0.0035	474	1.6617	533
	Ethanol	511	30596	0.541	594	2734	0.0048	477	1.6426	532
	Methanol	512	40810	0.785	598	2809	0.0061	475	1.6354	530
	Toluene	501	31679	0.583	567	2323	0.0036	473	1.6426	539
8	Acetonitrile	602	12952	0.178	676	1818	0.0658	546	1.3212	620
	Dichloromethane	611	17672	0.289	666	1352	0.1048	548	1.3281	625
	1,4-dioxane	563	15908	0.208	641	2161	0.0328	537	1.2923	617
	N,N-dimethylformamide	594	10819	0.191	--	--	--	551	1.3435	--
	Dimethylsulphoxide	585	9307	0.137	--	--	--	551	1.3413	--
	Ethyl acetate	573	19366	0.289	658	2254	0.0434	547	1.3142	620
	Ethanol	607	12628	0.180	700	2189	0.0144	547	1.3236	621
	Methanol	599	10665	0.129	695	2306	0.0121	545	1.3164	619
	Toluene	561	13079	0.164	634	2052	0.1011	541	1.3111	622
9	Acetonitrile	597	28840	0.315	679	2023	0.0336	549	1.3432	621
	Dichloromethane	611	28298	0.187	666	1352	0.1034	549	1.3431	626
	1,4-dioxane	561	23174	0.199	647	2369	0.0371	538	1.3067	616
	N,N-dimethylformamide	525	27516	0.168	--	--	--	554	1.3658	--
	Dimethylsulphoxide	531	22067	0.123	--	--	--	553	1.3637	--
	Ethyl acetate	568	21991	0.187	664	2545	0.0676	542	1.3502	620
	Ethanol	602	30246	0.340	692	2160	0.0213	549	1.3455	622
	Methanol	591	27720	0.353	701	2655	0.0157	548	1.3381	620
	Toluene	560	28755	0.263	637	2159	0.0969	542	1.3253	622
*TD-B3LYP/6-31G(d)										

Table 2 Transition dipole moments (M_a) obtained from absorption properties of compound **6-9** in various solvents.

	Compound 6	Compound 7	Compound 8	Compound 9
Acetonitrile	8.92	7.94	5.01	6.64
Dichloromethane	8.09	8.35	6.43	5.17
Dioxane	7.42	9.19	5.24	5.11
DMF	9.09	9.41	5.15	4.54
DMSO	9.74	8.95	4.33	3.91
Ethyl acetate	8.09	8.30	6.23	4.99
Ethanol	7.77	8.09	5.06	6.92
Methanol	7.00	9.67	4.25	6.99
Toluene	8.33	8.26	4.64	5.87

Table 3 Dipole moment ratio of compound **6-9** by various methods.

	6	8	7	9
Bilot-Kawski	0.852	1.036	0.715	1.029
Bakhshiev	0.844	1.039	0.699	1.031
Liptay	0.823	1.027	0.682	1.014

Table 4 Dihedral angles calculated with B3LYP/6-31G(d) method and various solvents for compound **6-9**.

	6			7			8			9		
	GS	ES	Δ°	GS	ES	Δ°	GS	ES	Δ°	GS	ES	Δ°
Acetonitrile	21.5	17.8	3.6	21.4	18.9	2.6	26.6	17.5	9.1	25.1	17.9	7.2
Dichloromethane	22.3	17.6	4.7	22.4	19.0	3.4	27.3	17.7	9.6	27.4	18.2	9.2
Dioxane	24.0	17.6	6.4	23.7	18.7	5.1	29.3	21.0	8.3	29.3	19.5	9.8
DMF	21.5	17.9	3.6	21.4	18.9	2.5	26.6	17.5	9.1	25.1	17.9	7.2
DMSO	21.4	17.9	3.4	21.2	18.9	2.3	26.5	17.5	9.1	25.0	17.8	7.2
Ethyl acetate	21.9	17.8	4.1	22.7	19.0	3.7	27.7	18.9	8.8	27.9	18.4	9.4
Ethanol	21.7	17.8	3.9	21.7	18.9	2.8	26.7	17.5	9.2	25.2	17.9	7.3
Methanol	21.5	17.9	3.6	21.5	18.9	2.6	26.6	17.5	9.2	25.1	17.9	7.2
Toluene	23.8	17.6	6.3	23.6	18.7	4.9	29.1	20.9	8.2	29.1	19.4	9.8

All the angles expressed in $^\circ$

Synthesis and combined experimental and computational investigations on spectroscopic and photophysical properties of red emitting 3-styryl coumarins

Abhinav B. Tathe, Vinod D. Gupta, Nagaiyan Sekar *

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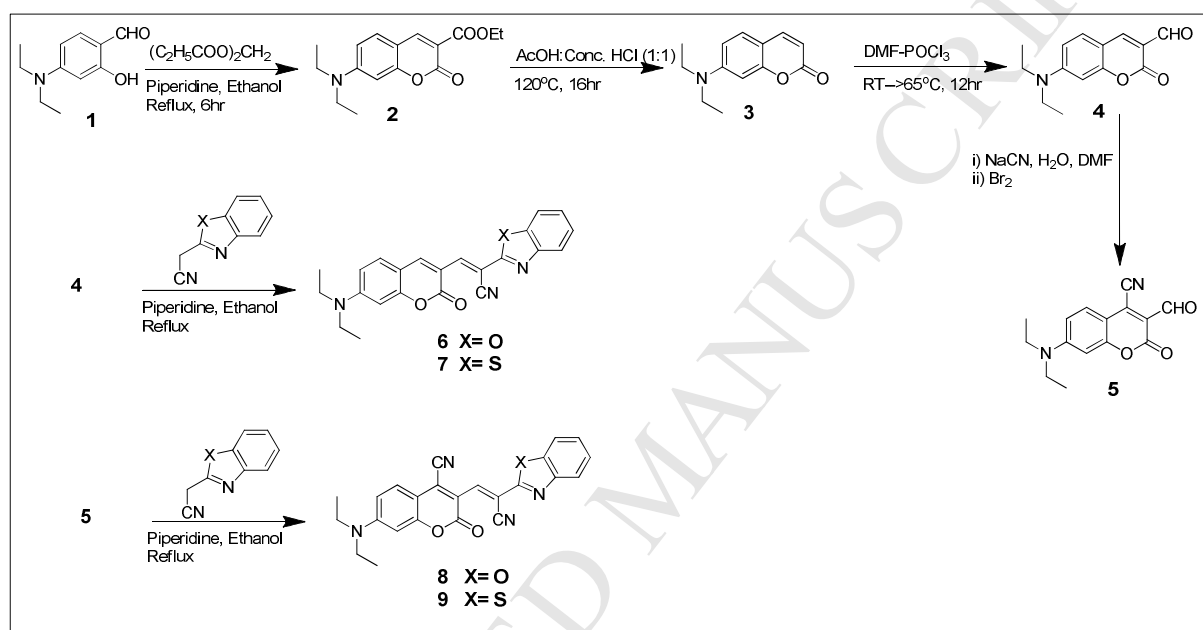


Figure 1 Synthesis of 4-Cyano coumarin 3-styryls (Compound 6-9)

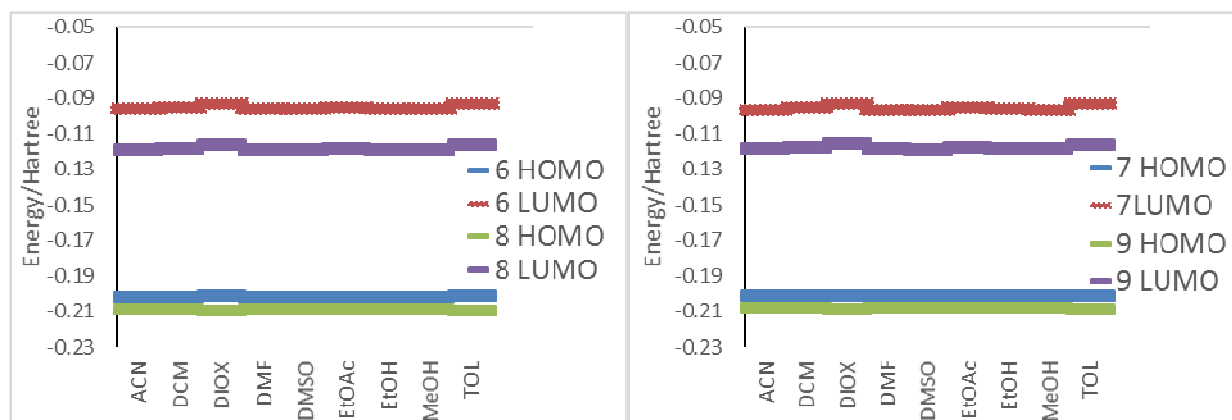


Figure 2 Lowering of LUMO in compound 8 and 9 as compared to compound 6 and 7

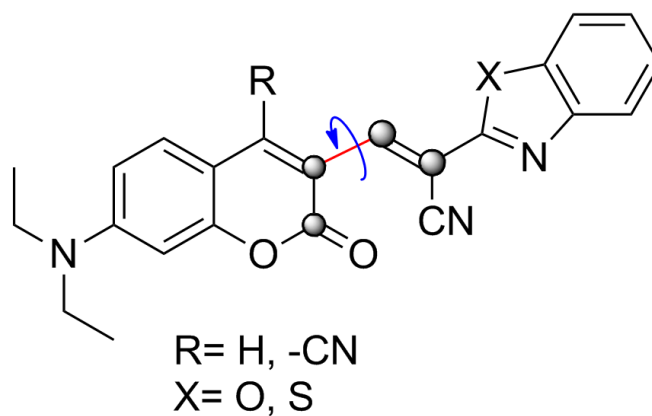


Figure 3 Twist of dihedral angle and the atoms involved in dihedral angle in compound **6-9**

Highlights of Manuscript

1. Synthesis of novel red emitting coumarins.
2. DFT studies on the 4-cyano 3-styryl coumarins .
3. Photophysical and spectroscopic studies of 4-cyano 3-styryl coumarins.

Supporting Information

Synthesis and combined experimental and computational investigations on spectroscopic and photophysical properties of red emitting 3-styryl coumarins

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Figure 18 HRMS of compound **8**

Figure 19 HRMS of compound **9**

Table 1 Absorption properties of compound 6

	$\lambda^{\max}$	FWHM	$\varepsilon^{\max}$	IAC $\times 10^8$	f	σ $\times 10^{-19}$	M_a
Acetonitrile	506	98	27669	1.56	0.672	1.05	8.92
Dichloromethane	509	92	42350	1.28	0.552	1.62	8.09
Dioxane	498	85	38656	1.07	0.464	1.48	7.42
DMF	528	93	40425	1.61	0.697	1.54	9.09
DMSO	525	118	35288	1.85	0.800	1.35	9.74
Ethyl acetate	504	90	31647	1.28	0.552	1.21	8.09
Ethanol	511	89	30596	1.18	0.509	1.17	7.77
Methanol	512	84	40810	0.96	0.413	1.56	7.00
Toluene	501	89	31679	1.36	0.586	1.21	8.33

Table 2 Absorption properties of compound 7

	$\lambda^{\max}$	FWHM	$\varepsilon^{\max}$	IAC $\times 10^8$	f	σ $\times 10^{-19}$	M_a
Acetonitrile	510	107	37345	1.22	0.528	1.43	7.94
Dichloromethane	511	98	53900	1.35	0.582	2.06	8.35
Dioxane	497	103	30415	1.68	0.726	1.16	9.19
DMF	529	96	40810	1.65	0.715	1.56	9.41
DMSO	519	110	36575	1.53	0.659	1.40	8.95
Ethyl acetate	506	99	33880	1.35	0.582	1.29	8.30
Ethanol	516	99	32340	1.25	0.541	1.24	8.09
Methanol	509	101	25795	1.82	0.785	0.99	9.67
Toluene	500	98	34265	1.35	0.583	1.31	8.26

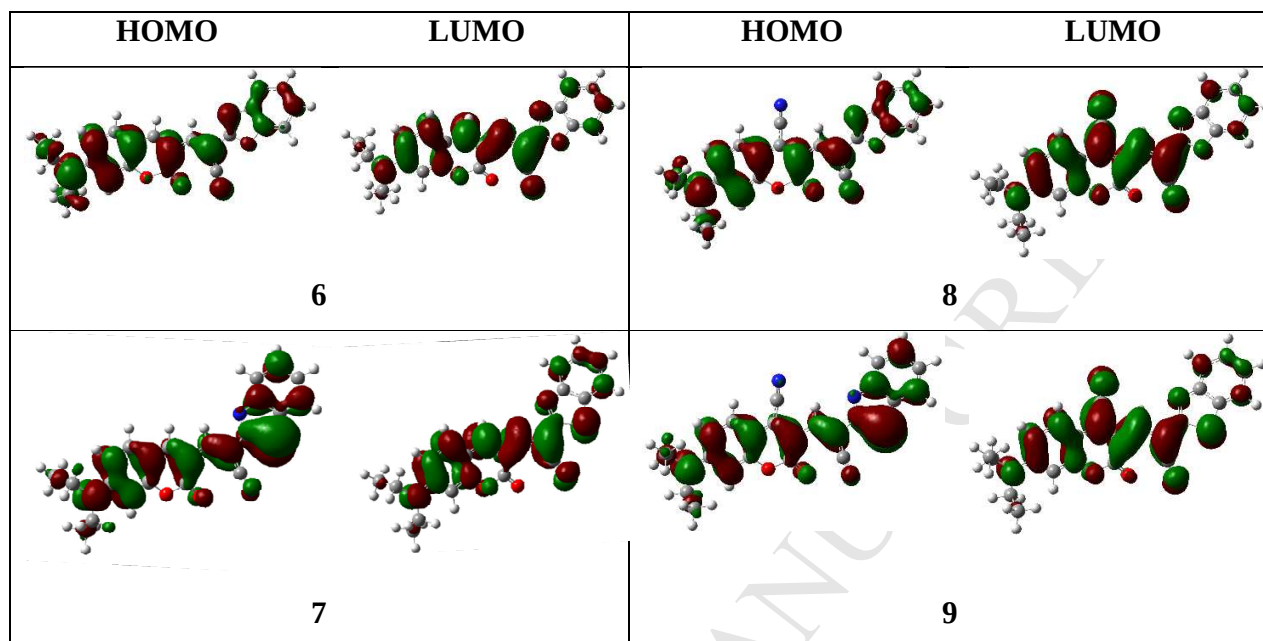
Table 3 Absorption properties of compound **8**

	$\lambda^{\max}$	FWHM	$\epsilon^{\max}$	IAC $\times 10^8$	f	σ $\times 10^{-19}$	M_a
Acetonitrile	602	110	12952	0.41	0.178	0.49	5.01
Dichloromethane	611	102	17672	0.67	0.289	0.68	6.43
Dioxane	563	109	15908	0.48	0.208	0.61	5.24
DMF	594	249	10819	0.44	0.191	0.42	5.15
DMSO	585	114	9307	0.32	0.137	0.36	4.33
Ethyl acetate	573	100	19366	0.67	0.289	0.74	6.23
Ethanol	607	113	12628	0.47	0.180	0.48	5.06
Methanol	599	91	10665	0.30	0.129	0.41	4.25
Toluene	561	102	13079	0.38	0.164	0.50	4.64

Table 4 Absorption properties of compound **9**

	$\lambda^{\max}$	FWHM	$\epsilon^{\max}$	IAC $\times 10^8$	f	σ $\times 10^{-19}$	M_a
Acetonitrile	597	112	28840	0.73	0.315	1.10	6.64
Dichloromethane	611	101	28298	0.43	0.187	1.08	5.17
Dioxane	561	108	23174	0.46	0.199	0.89	5.11
DMF	525	126	27516	0.39	0.168	1.05	4.54
DMSO	531	110	22067	0.28	0.123	0.84	3.91
Ethyl acetate	568	114	21991	0.43	0.187	0.84	4.99
Ethanol	602	116	30246	0.79	0.340	1.15	6.92
Methanol	591	123	27720	0.82	0.353	1.05	6.99
Toluene	560	120	28755	0.61	0.263	1.09	5.87

Table 5 FMO diagrams for compound **6-9** calculated with B3LYP/6-31G(d) method in acetonitrile (iso= 0.002)



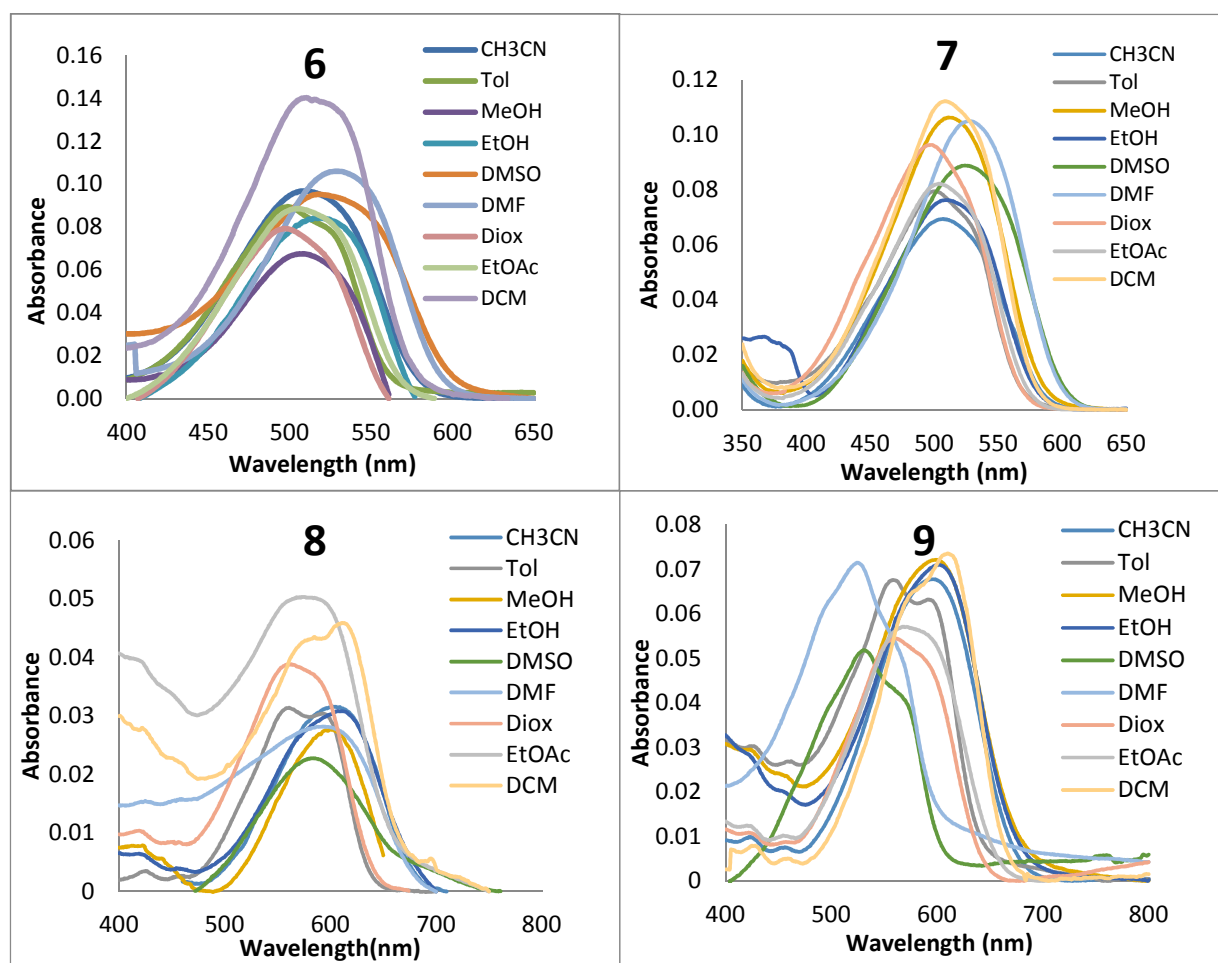


Figure 1 Absorption spectrum of the compound 6-9 in various solvents

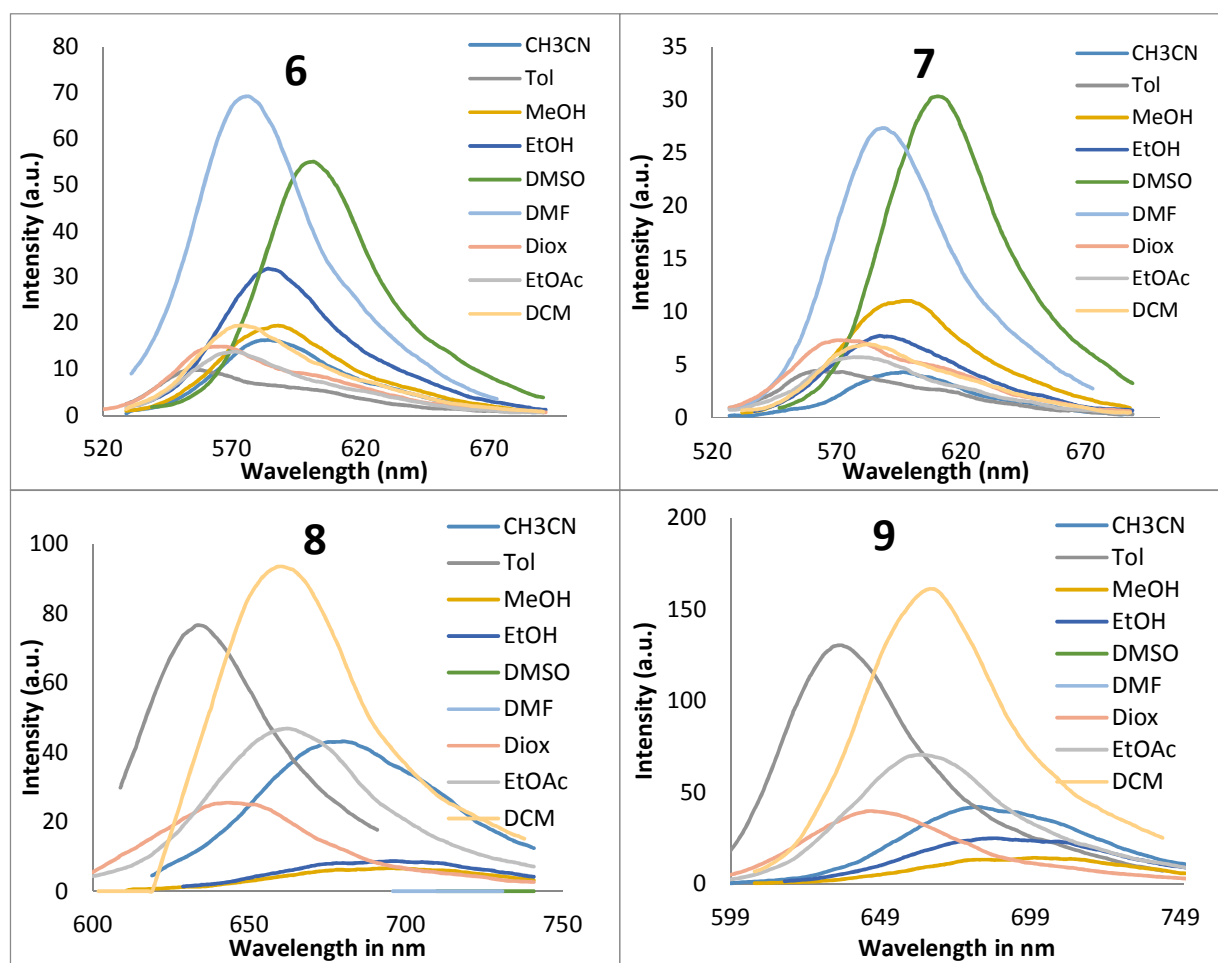


Figure 2 Emission spectrum of the compound 6-9 in various solvents

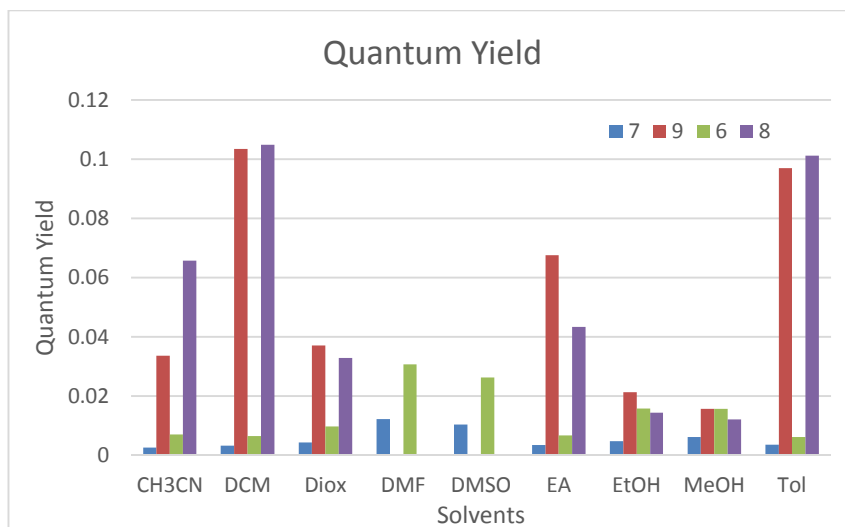


Figure 3 Quantum yield of compound 6-9 in various solvents

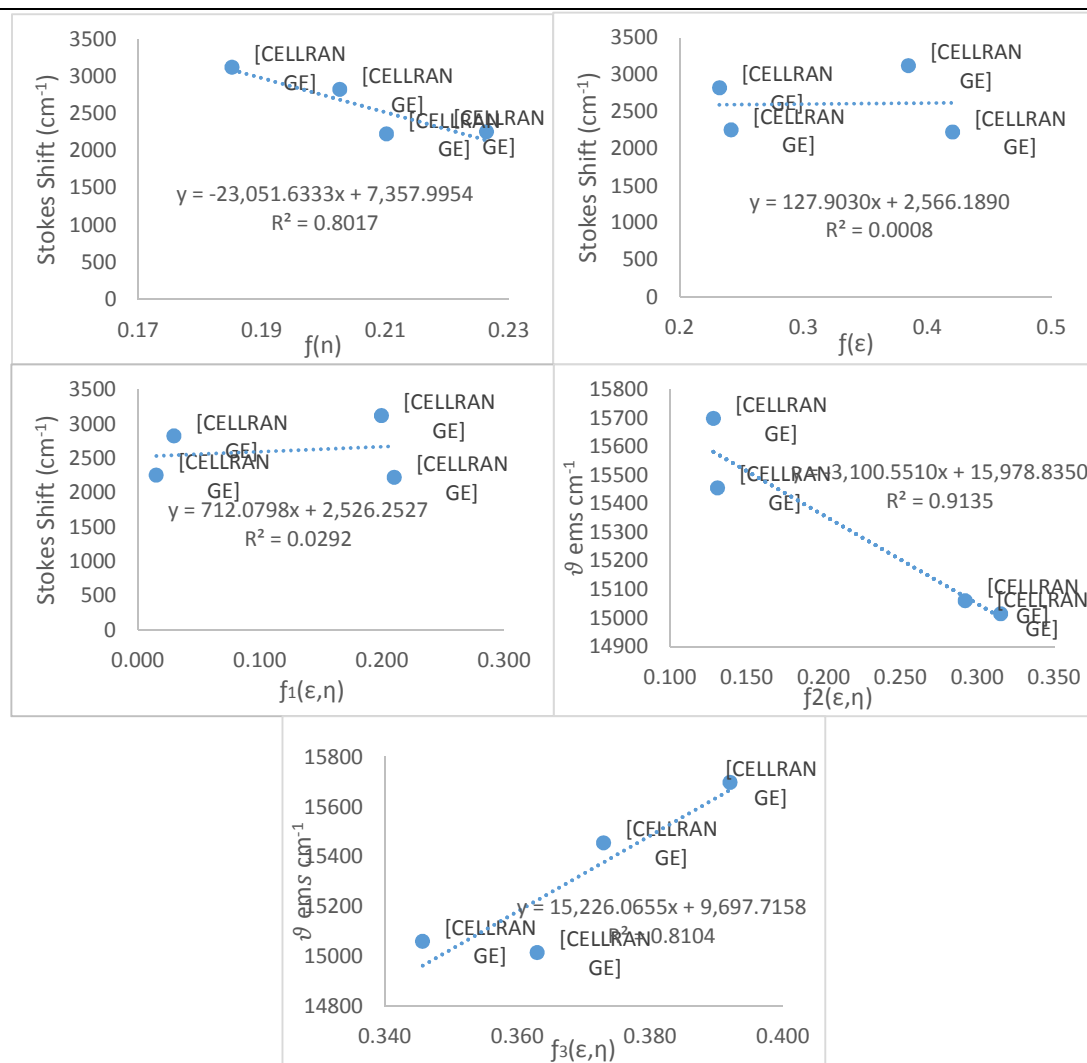
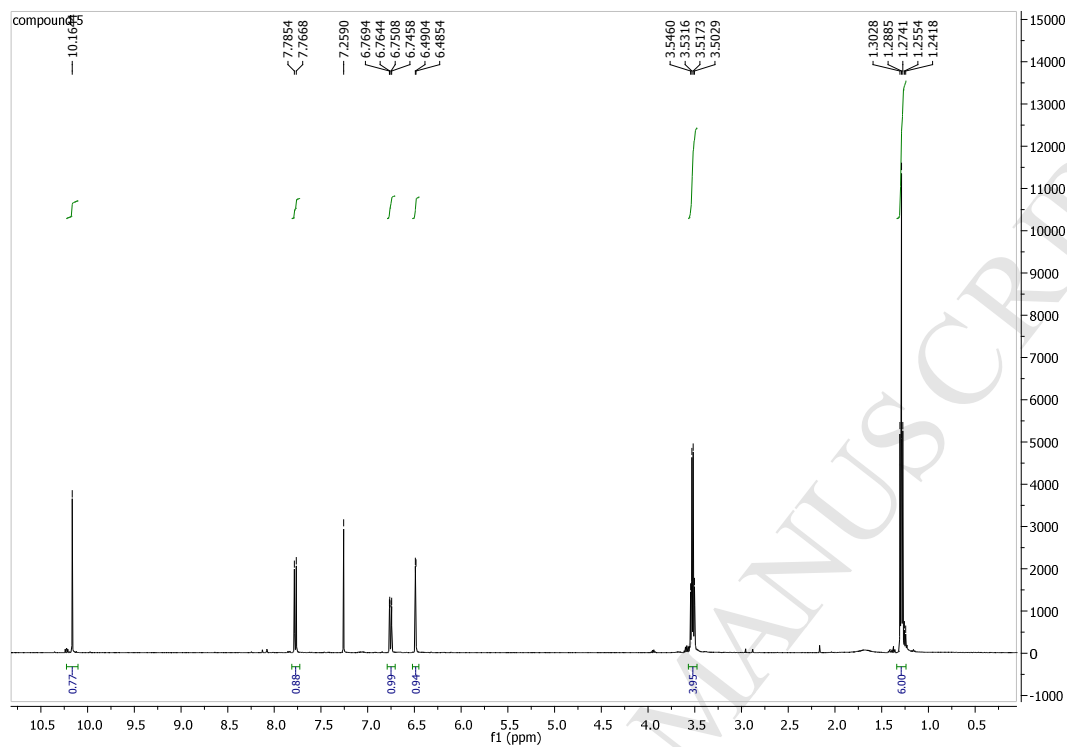
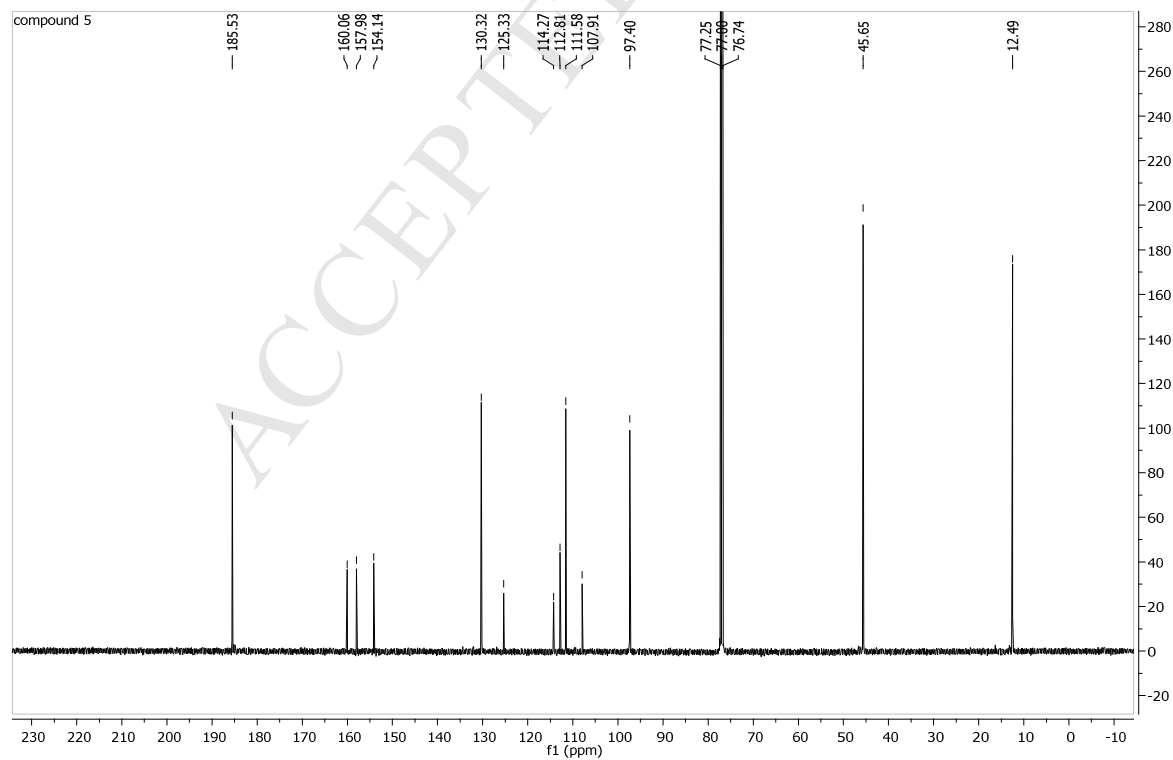


Figure 4 Solvent polarity function plots of Compound 6

NMR Spectra**Figure 5** ¹H NMR spectrum of compound 5**Figure 6** ¹³C NMR spectrum of compound 5

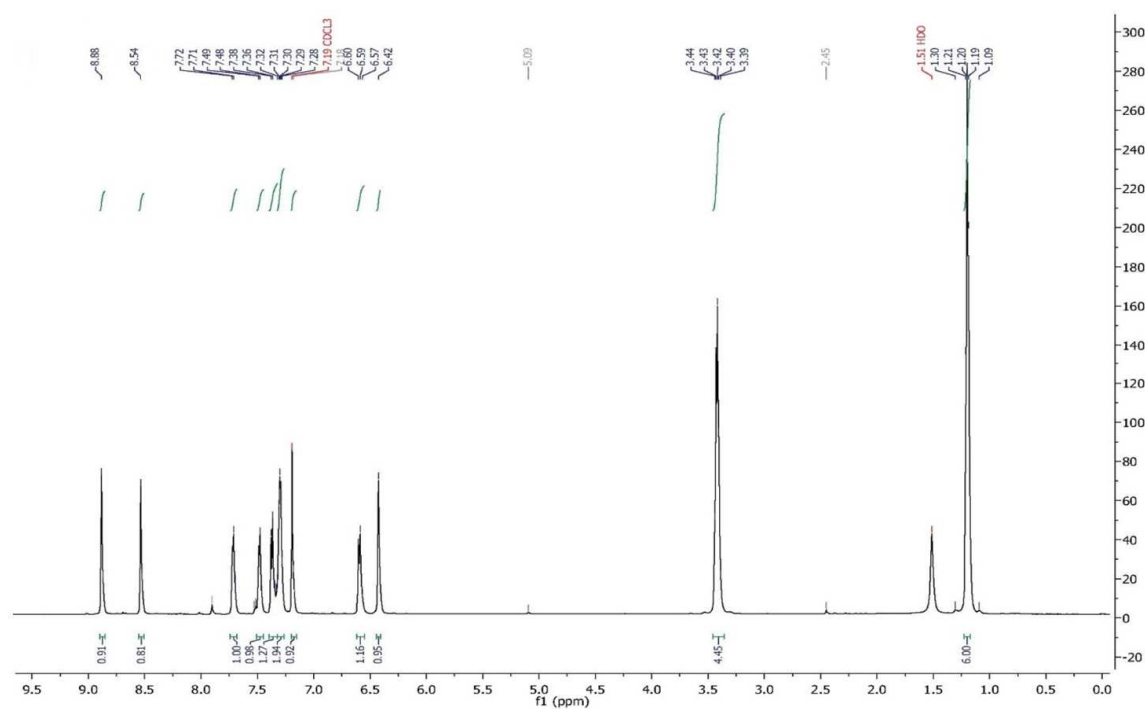


Figure 7 ^1H NMR spectrum of compound 6

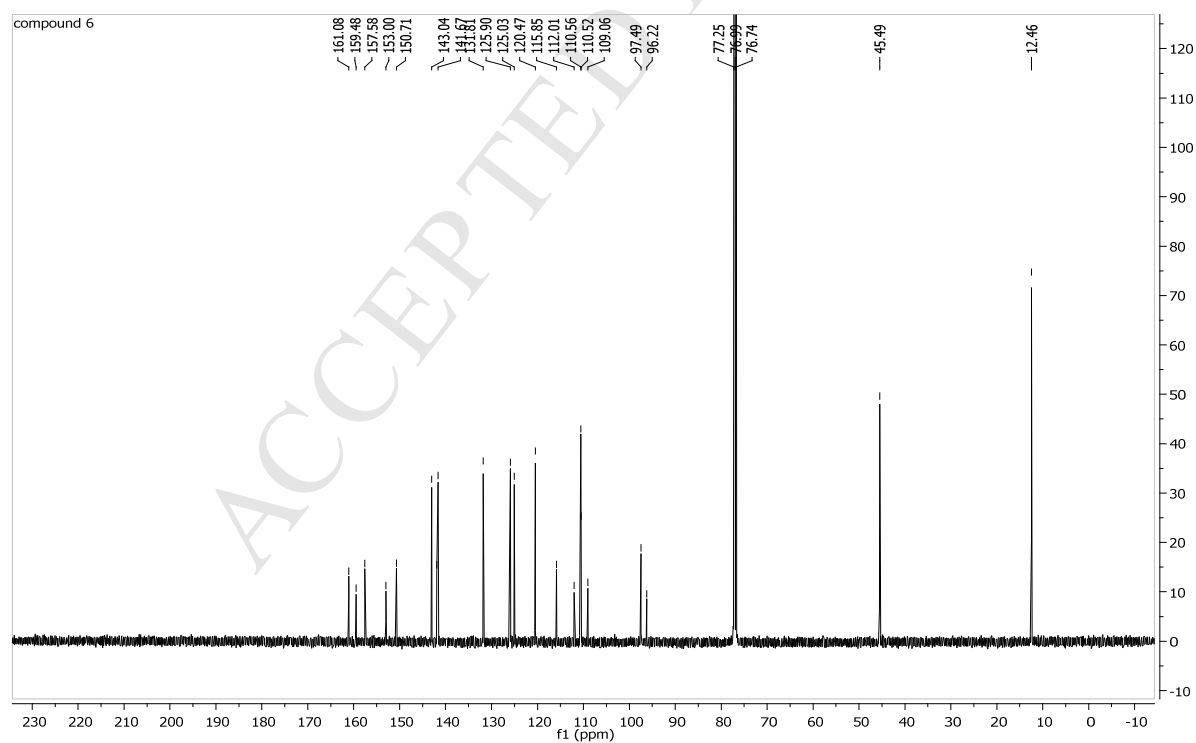


Figure 8 ^{13}C NMR spectrum of compound 6

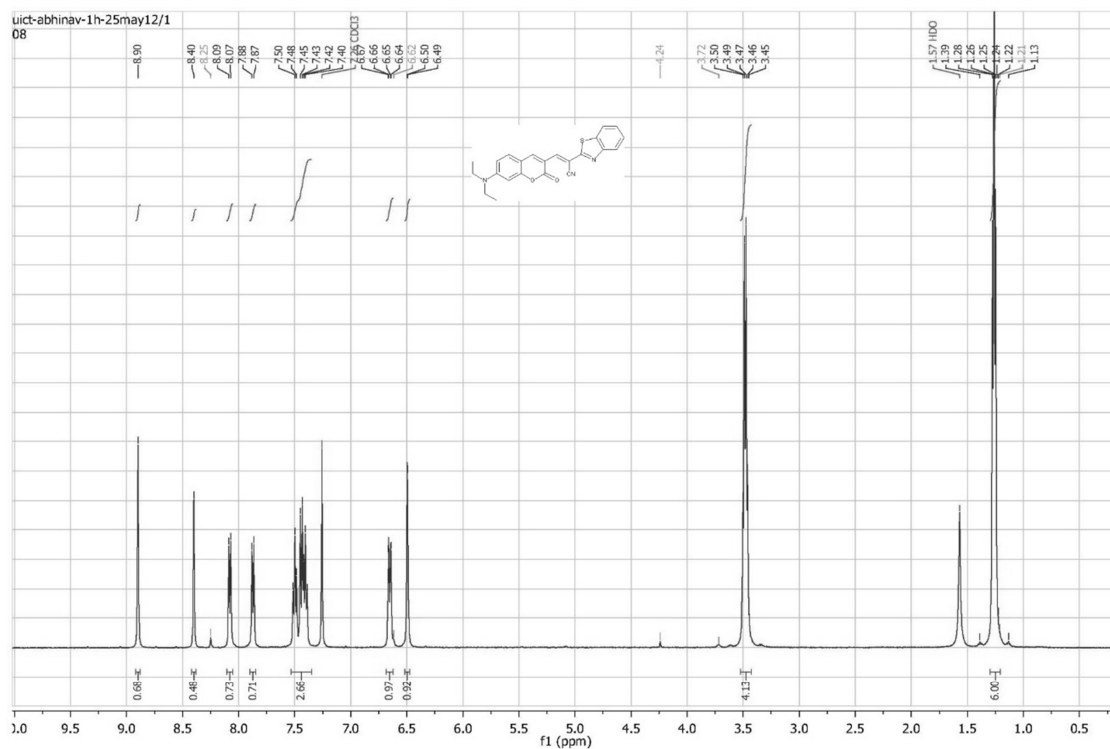


Figure 9 ^1H NMR spectrum of compound 7

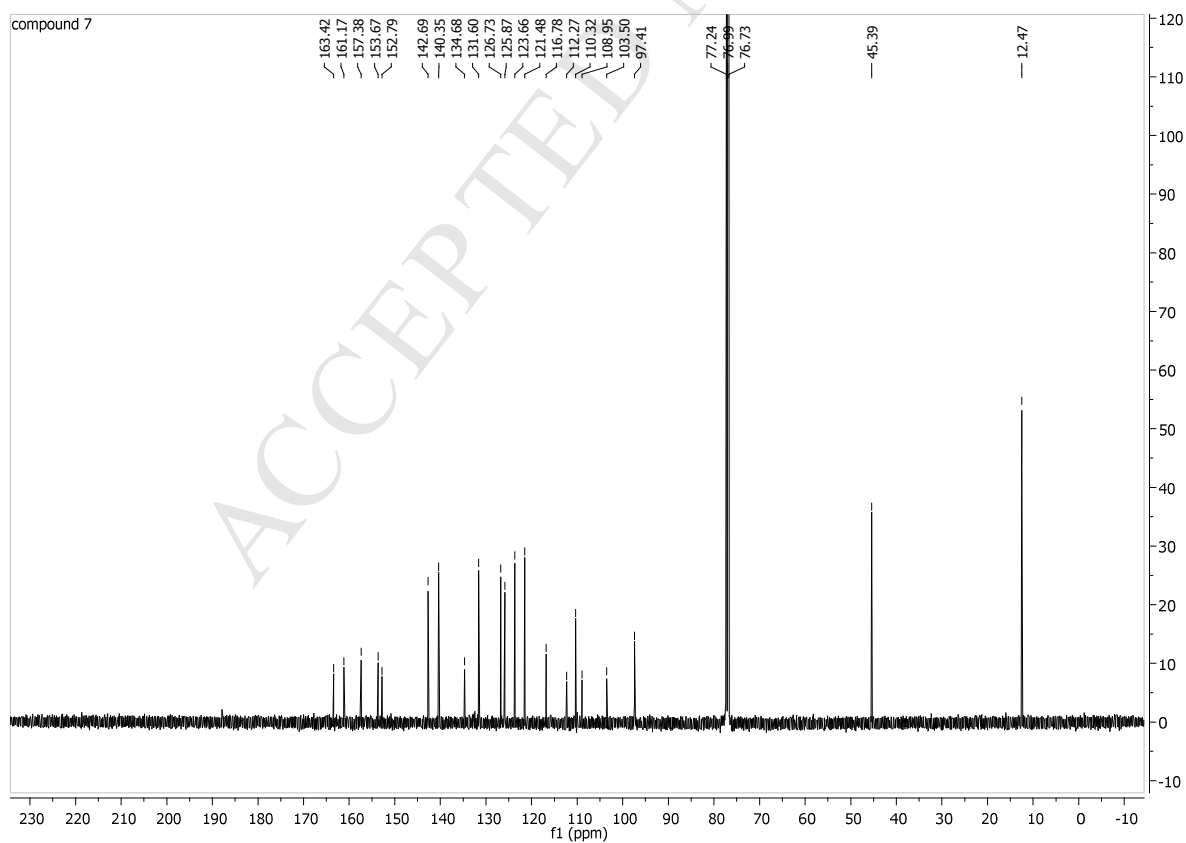


Figure 10 ^{13}C NMR spectrum of compound 7

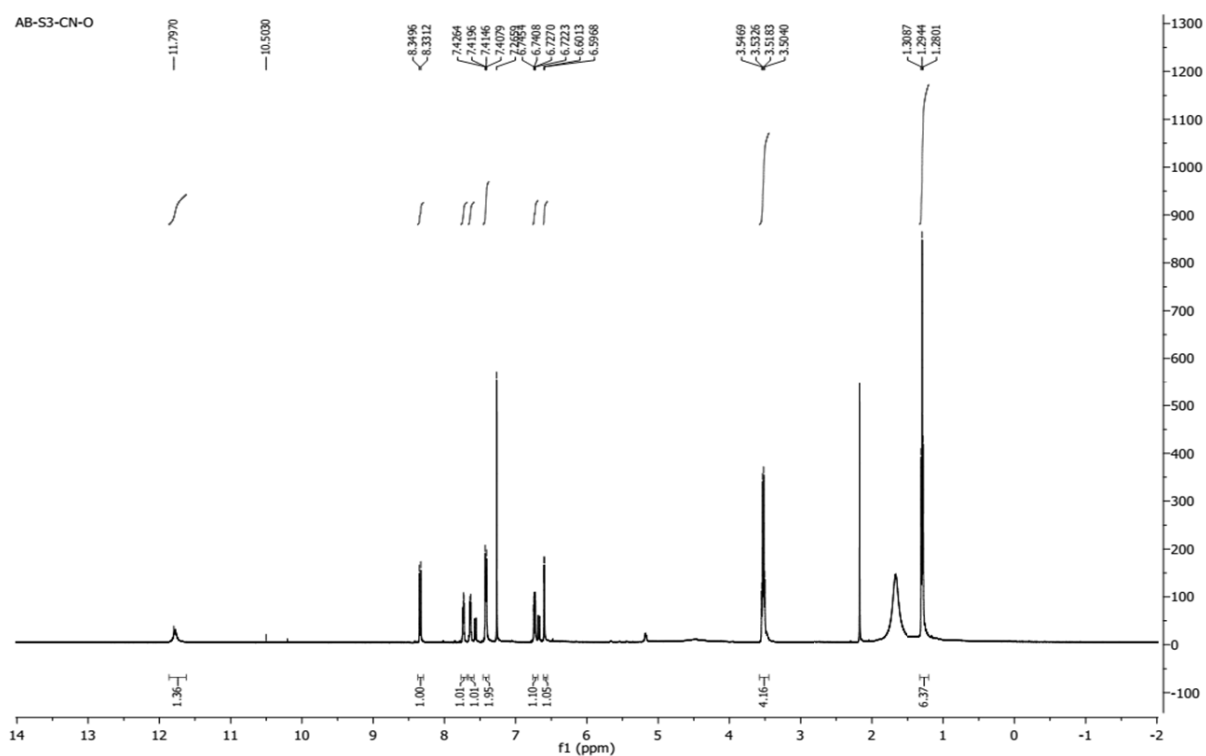


Figure 11 ¹H NMR spectrum of compound 8

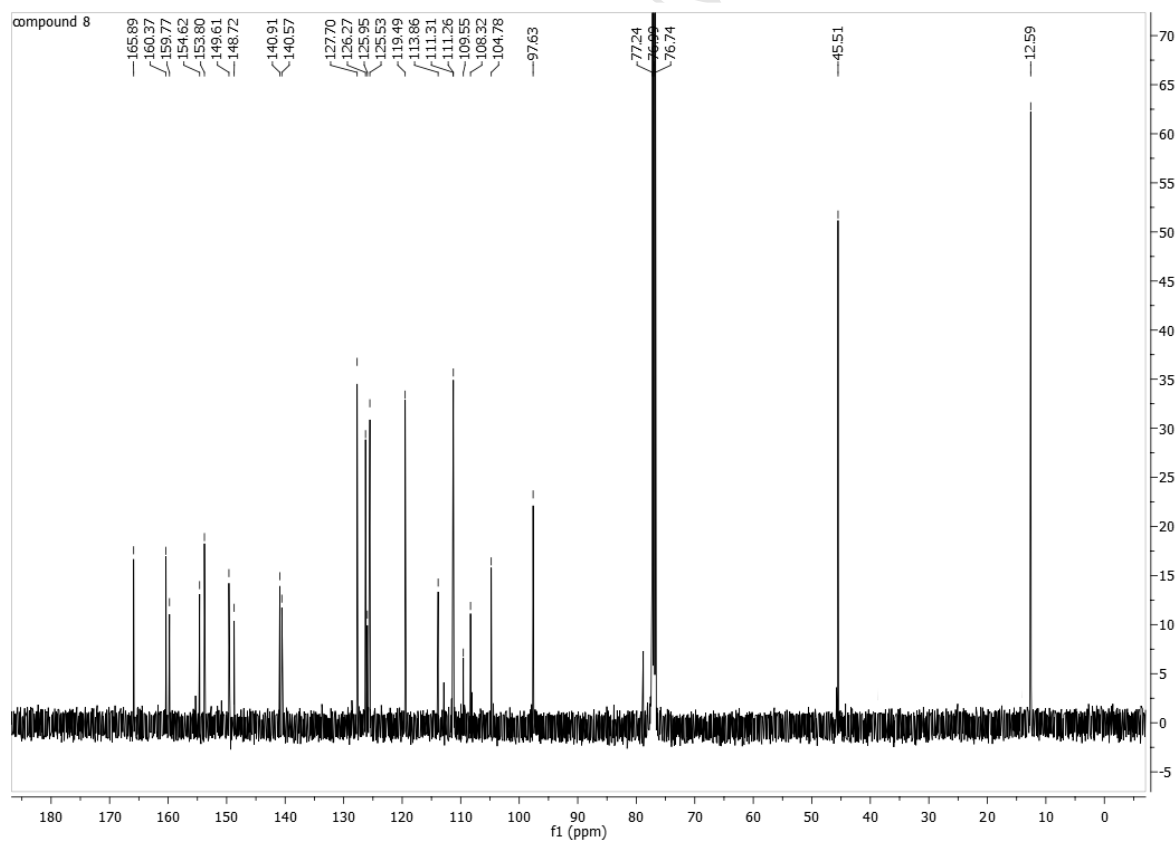


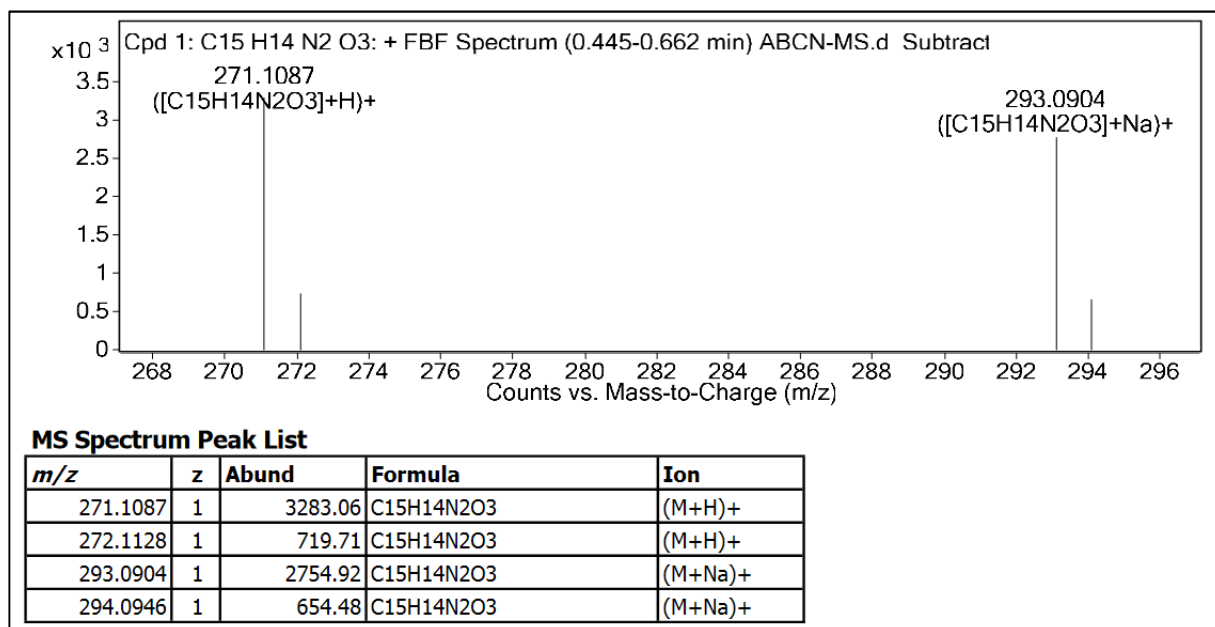
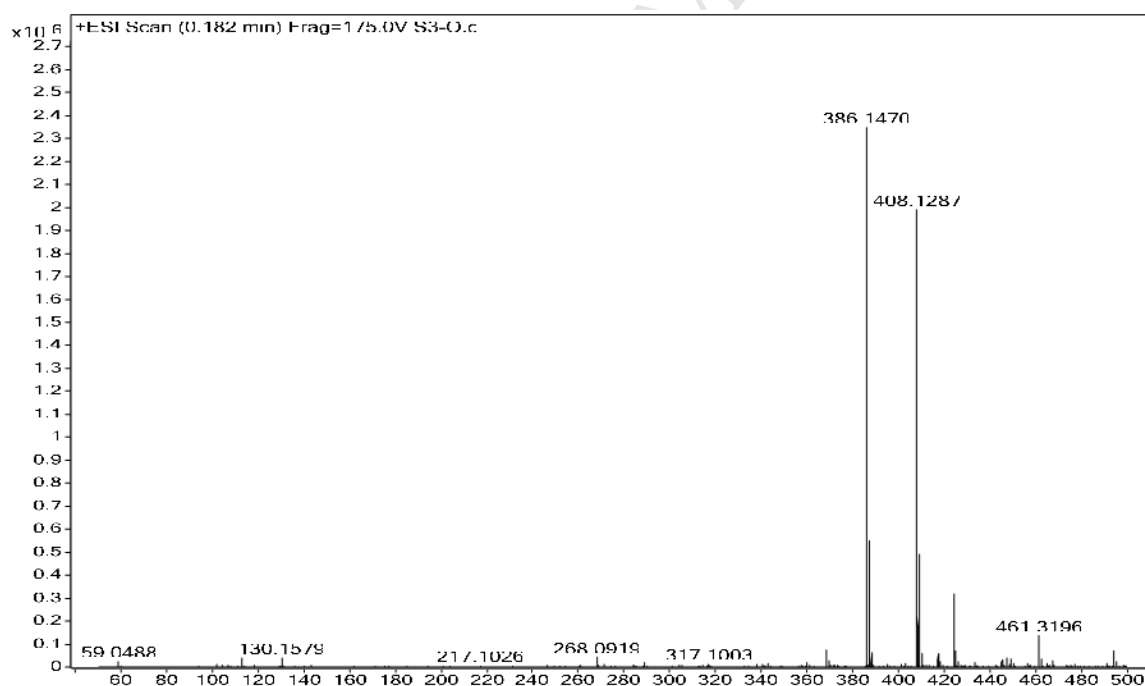
Figure 12 ¹³C NMR spectrum of compound 8

compound 9

166.31
164.64
159.47
155.32
153.34
145.67
140.27
134.28
127.62
127.19
126.63
126.01
122.78
121.65
116.55
111.12
110.73
104.54
97.64
77.39
77.24
76.98
76.73
45.67
12.52

f1 (ppm)

Figure 14 ^{13}C NMR spectrum of compound **9**

HRMS**Figure 15** HRMS of compound 5**Figure 16** HRMS of compound 6

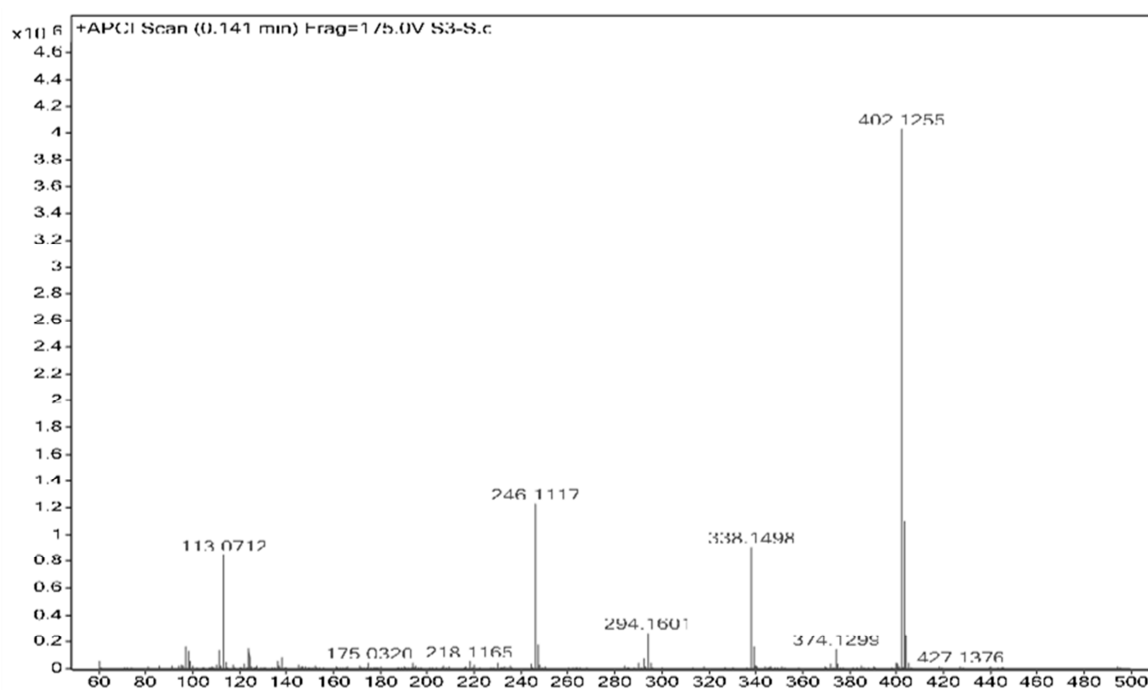


Figure 17 HRMS of compound 7

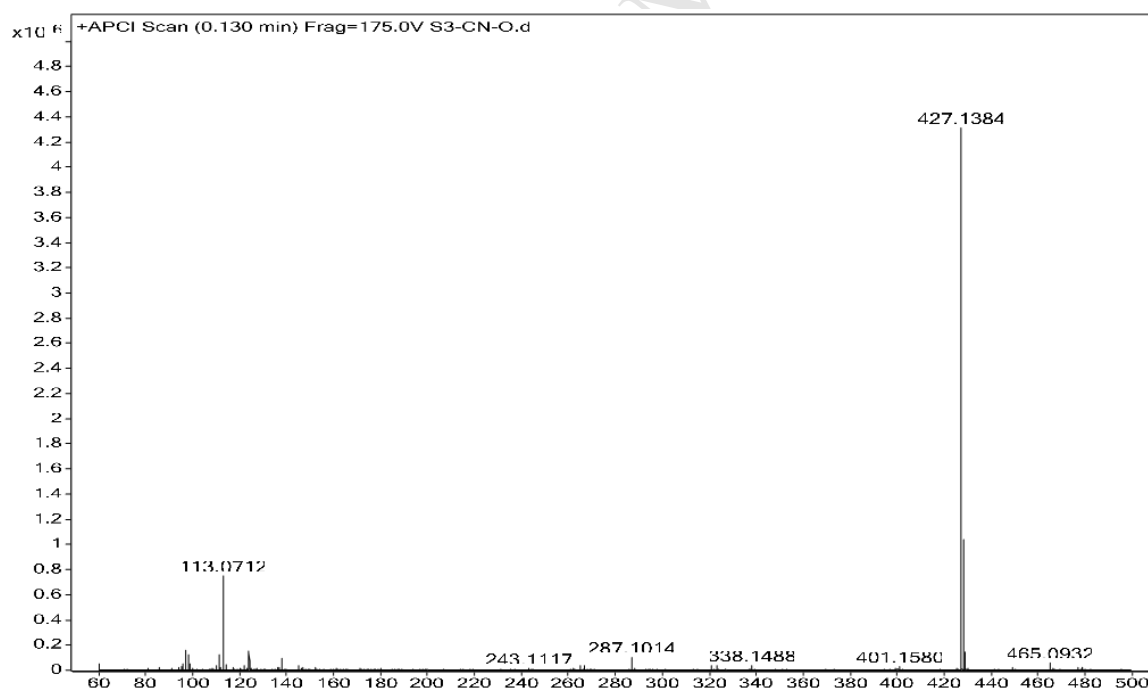


Figure 18 HRMS of compound 8

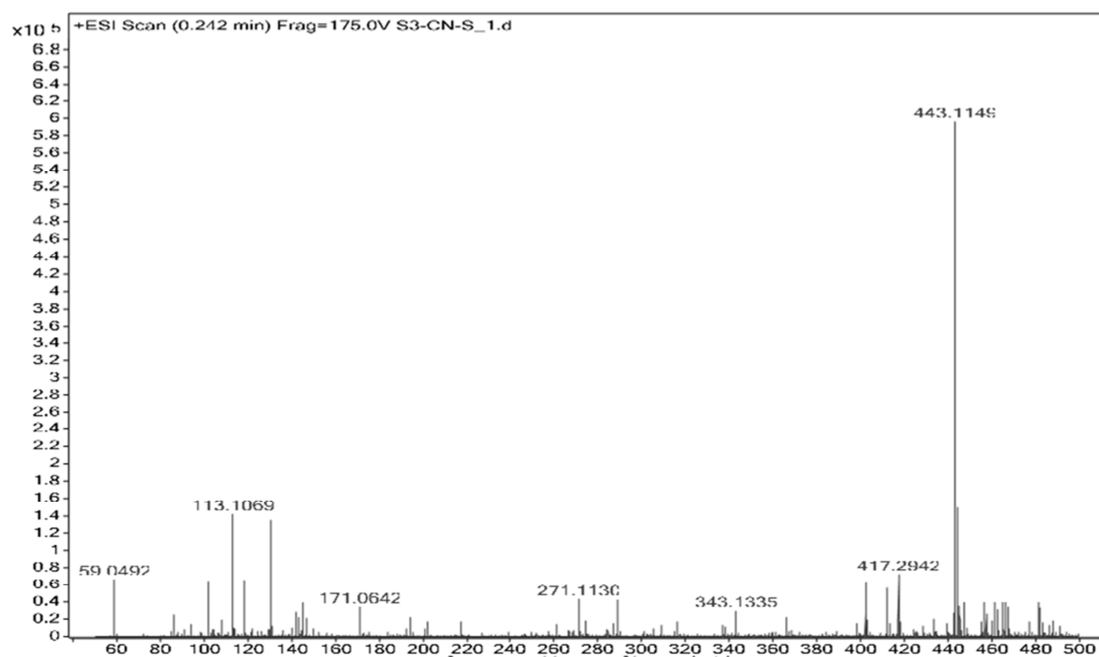


Figure 19 HRMS of compound **9**