

# Investigation on Photoluminescence Behaviour of 2, 3-Diphenylquinoxalin-6-Vinyl Benzaldehyde

R Padma, M Sathiya, S Guhanathan\*

*PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore, TN, India.*

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\*Corresponding author: Guhanathan S, PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore-632 002, TN, India, E-mail: [sai\\_gugan@yahoo.com](mailto:sai_gugan@yahoo.com)

## Abstract

Poly (p-phenylene vinylene) is one of the most important classes of conjugated polymers, with a wide range of applications, such as light-emitting diodes, optoelectronic devices etc. Electroluminescence from OLEDs arises from the radioactive decay of excitation generated by the recombination of electrons and holes injection from two opposite electrodes into the emissive polymer layer. Quinoxaline is a useful n-type building block with high electron affinity and good thermal stability. It has been successfully incorporating small molecules to find utility as electron transport materials in multilayer OLEDs based on PPV. Hence, vinyl benzaldehyde containing quinoxaline derivatives was synthesized using 6-methyl-2, 3-diphenylquinoxaline with terephthalaldehyde via Wittig reaction. The structures of synthesised compounds were confirmed by FT-IR, <sup>1</sup>H, <sup>13</sup>C, <sup>31</sup>P-NMR, and MASS spectral data. The result of photoluminescence studies showed that vinyl benzaldehyde capped quinoxaline exhibited green emission maxima at shorter wavelengths of 454nm.

**Keywords:** Quinoxaline Derivatives; Photoluminescence; Spectral Studies; Wittig Reaction

## Introduction

A polymer that can be used as light-emission material must have two basic characteristics: electrical conductivity (semi conductive polymer) and high Photoluminescence (PL) efficiency. Electroluminescence (EL), an electrically driven radioactive emission process, is a phenomenon that exists in a wide range of conventional semiconductors, and organic EL was first reported and extensively studied during 1960s [1, 2]. Electroluminescence (EL) from OLEDs arises from the radioactive decay of excitations generated by the recombination of electrons and holes injected from two opposite electrodes into the emissive polymeric layer. Balanced rates of injection and transport of both electrons and holes are essential to achieving high External Quantum Efficiency (EQE) in an OLED. However, most emissive conjugated polymers such as PPVs have much higher hole mobility than electron mobility and low electron affinities, causing an imbalance in charge injection and transport results in poor EQEs from single-layer OLEDs.[3-9] Quinoxaline is a useful n-type building block with high electron affinity and good thermal stability. It has

been successfully incorporated in small molecules and polymers for use as electron-transport materials in multilayer OLEDs based on PPV.[10-13] Furthermore, quinoxaline possess an excellent  $\pi$ -deficient aromatic heterocycle, capable as electron withdrawing portion in push-pull structures for Intermolecular Charge Transfer (ICT) such important ICT along the backbone of the molecule can induce luminescence properties.[14]

In this work, we describe the preparation of new electron-accepting  $\pi$ -conjugated 2, 3-disubstituted quinoxaline capped vinyl benzaldehyde compound via Wittig reaction in hope of combining both excellent electron-affinitive and light-emitting properties into the compound.

## Results and discussion

The Vinyl Benzaldehyde capped quinoxaline derivatives (VB-QUI) have been prepared in four stages similar to our earlier report. [15-17] initially, 6-methyl-2, 3-diphenylquinoxaline was synthesized from benzil and 4-methyl-o-phenylenediamine. For the conversion of methyl to bromomethyl, NBS has been used as a brominating agent via free radical mechanism. Based on Wittig reaction, bromomethyl group is converted to phosphonium salt. The target moiety (VB-QUI) was achieved while reacting phosphonium salt with terephthalaldehyde. The formations of various compounds were characterized by UV, FT-IR, <sup>1</sup>H, <sup>31</sup>P NMR. The optical properties including absorption and luminescence of VB-QUI were measured with UV-Vis and Photoluminescence spectral studies.

The UV spectral details of 6-methyl-2, 3-diphenylquinoxaline have been listed as follows, the n- $\pi^*$  and  $\pi$ - $\pi^*$  transitions were observed at -347.50nm and 248.50nm implies the C=N, and C=C in the 6-methyl-2, 3-diphenylquinoxaline moiety. The MASS spectrum of 6-methyl-2, 3-diphenylquinoxaline notified that the observed molecular ion peak at 297.21 suits well with the theoretical value.

FTIR spectra of bromomethylated quinoxaline derivative justify the peak at 686.66 for C-Br functional group. <sup>1</sup>H-NMR the

signal at 4.7 $\delta$  confirmed the bromomethylation occurred in the methyl group of quinoxaline derivatives.

$^1\text{H}$  NMR spectra of phosphonium ylide compound justifies the signal shifted from 4.7  $\delta$  to 2.7  $\delta$  (ppm). The aromatic ring protons signal was appeared at 7.2-7.9 $\delta$ . The signals at 25.60  $\delta$  have been noticed in  $^{31}\text{P}$  NMR for the presence of phosphorous in the ylide compound.

Similarly, FTIR spectra of VB-QUI the carbonyl (aldehyde) stretching band have identified near 1689.09  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra of VB-QUI shows that 7.2-7.9  $\delta$  and 8.1- 9.9 $\delta$  for quinoxaline ring protons and phenylene proton respectively. The vinylene proton and aldehyde proton have appeared at 6.9 $\delta$ , and 10.0  $\delta$ . The  $\lambda_{\text{max}}$  was observed from UV spectrum at 250nm indicated  $\pi$ - $\pi^*$  transition and 348nm suggested for n- $\pi^*$  transition in VB-QUI. The MASS spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde clearly pointed out that the molecular ion peak identical to the theoretical value of 413.2.

### Photo luminescent properties

The uv-vis absorption and Photoluminescence spectra of the VB-QUI compound in the ethanol solution have been taken to know about the luminescence behavior of VB-QUI. The uv-vis absorption spectra of the solution exhibited the band around 200-250nm may be due to the  $\pi$ - $\pi^*$  electronic transition associated with the  $\pi$ -conjugation in the compound. In the PL spectra excitation at 348nm exhibits a bluish-green emission approximately around 454nm.

### Conclusions

The vinyl benzaldehyde capped quinoxaline derivative was synthesised through Wittig reaction using Phosphonium salt and terephthalaldehyde. The resulting compound was characterised by FTIR,  $^1\text{H}$ ,  $^{13}\text{C}$ ,  $^{31}\text{P}$  NMR. Photo luminescent property of the synthesized vinyl benzaldehyde capped quinoxaline derivative was investigated using UV-Vis and fluorescent spectrometer. The VB-QUI compound found to have the photoluminescence with bluish-green emission at 454nm.

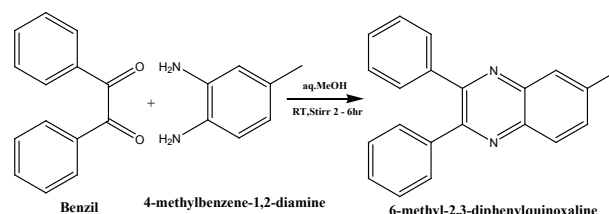
### Experimental Materials

All the chemicals were obtained from Avra chemicals, Hyderabad, India and were used as supplied. Solvents used were purified and dried according to the standard procedure.

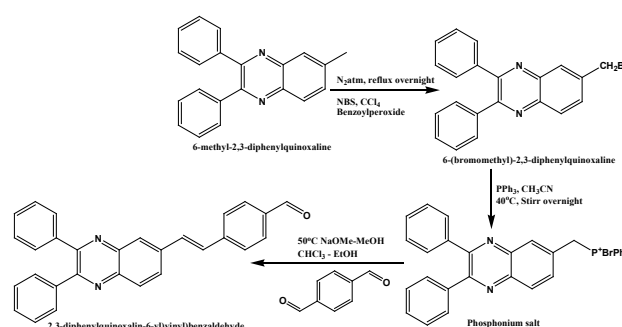
### Characterization Methods

The UV-Visible spectra were recorded on an Alpha-Bruker UV spectrophotometer equipped in the range between 200-800nm. Room temperature FTIR spectra were recorded as KBr pellet with an Alpha-Bruker FTIR spectrophotometer in the range of 4000-400 $\text{cm}^{-1}$ . Nuclear magnetic resonance spectra with different core viz.,  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR and  $^{31}\text{P}$  NMR were recorded in either DMSO- $d_6$  or  $\text{CDCl}_3$  on Bruker ADVANCE III 500MHz spectrometer.

The fluorescence spectra of the synthesised compound in ethanol were recorded on fluorescence spectrophotometer, FP-8500, JASCO. Mass spectroscopy was recorded on ES-FIGIEAN ionization mass spectrometer.



Scheme1: Synthesis of 6-methyl-2, 3-diphenylquinoxaline



Scheme2: Synthesis of vinyl benzaldehyde capped quinoxaline derivative

### Synthesis of 6-methyl-2,3-diphenylquinoxaline

The 2mmol of benzil was dissolved in 3ml of methanol and was made homogeneous by vigorous stirring at room temperature. To this 2mmol of 4-methylbenzene-1, 2-diamine was added in the form of powder. The progress of the reaction was monitored by TLC. The solvent methanol was evaporated under reduced pressure the solid product thus formed was recrystallized from

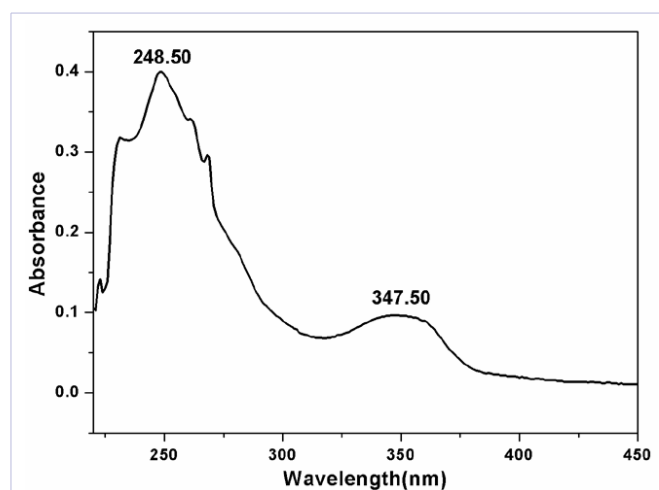


Figure 1: UV spectrum of 6-methyl-2, 3-diphenylquinoxaline.  
Stage 1: 6-methyl-2, 3-diphenylquinoxaline.

ethanol. UV ( $\lambda_{max}$ , nm): 248.50, 347.50, FTIR (KBr,  $cm^{-1}$ ): 3045.0 (C-H, st), 1566.5 (C=N, st), 1330.0 (C-N, st) 771.53 (C-H, b).  $^1H$  NMR ( $CDCl_3$ , ppm): 2.6  $\delta$  (3H, s), 7.9  $\delta$  (1H, d) 8.0  $\delta$  (2H, s) 7.5  $\delta$  (4H, m) 7.3  $\delta$  (4H, m) 7.2  $\delta$  (2H, m) Mass (m/z): Calculated M.W 296.38, Observed M.W 297.21( $M^+$ ).

### Synthesis of 6-bromomethyl-2,3-diphenylquinoxaline

To 0.2964g (0.01mol) of 6-methyl-2,3-diphenylquinoxaline 0.1780g (0.01mol) N-bromosuccinimide in 30ml of  $CCl_4$  containing 0.08g (0.0003mol) benzoyl peroxide as radical initiator were refluxed overnight. After the completion of reaction, the solid by-product was removed by filtration. Further, the filtrate was washed with  $CCl_4$  and the solvent was evaporated to get reddish-yellow solid product. FT-IR (KBr,  $cm^{-1}$ ): 2927.94 (C-H, st), 1616.36 (C=N, st) 1427.32 (C=C, st) 1336.67 (C-N, st) 686.66 (C-Br, st).  $^1H$ -NMR (DMSO, ppm): 4.7  $\delta$  (2H, s) 8.1  $\delta$  (2H, m) 7.8  $\delta$  (1H, m) 7.5  $\delta$  (4H, m) 7.3  $\delta$  (4H, m) 6.8  $\delta$  (2H, m).  $^{13}C$ -NMR (DMSO, ppm): 32.04 $\delta$ , 125.07-154.13 $\delta$ . Mass (m/z): Calculated M.W 375.287, Observed M.W 378.087( $M+2$ ).

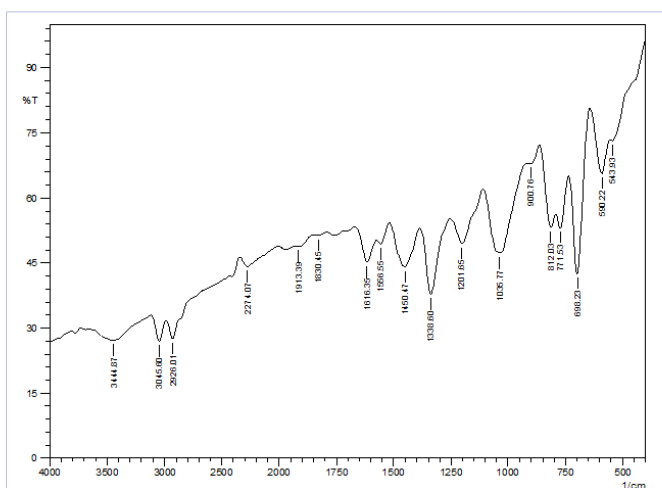


Figure 2: FTIR spectrum of 6-methyl-2, 3-diphenylquinoxaline.

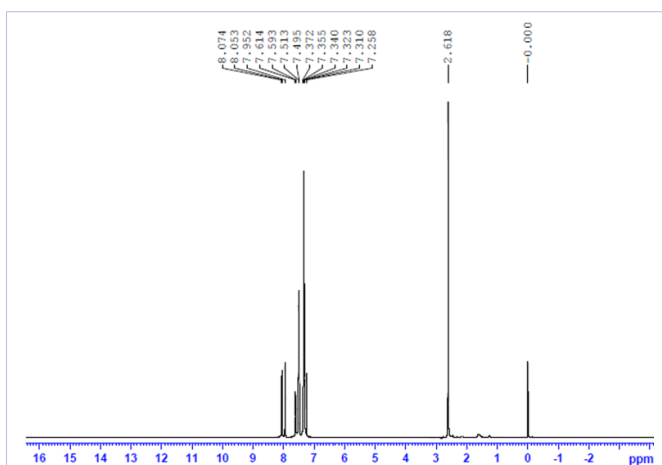


Figure 3:  $^1H$  NMR spectrum of 6-methyl-2, 3-diphenylquinoxaline.

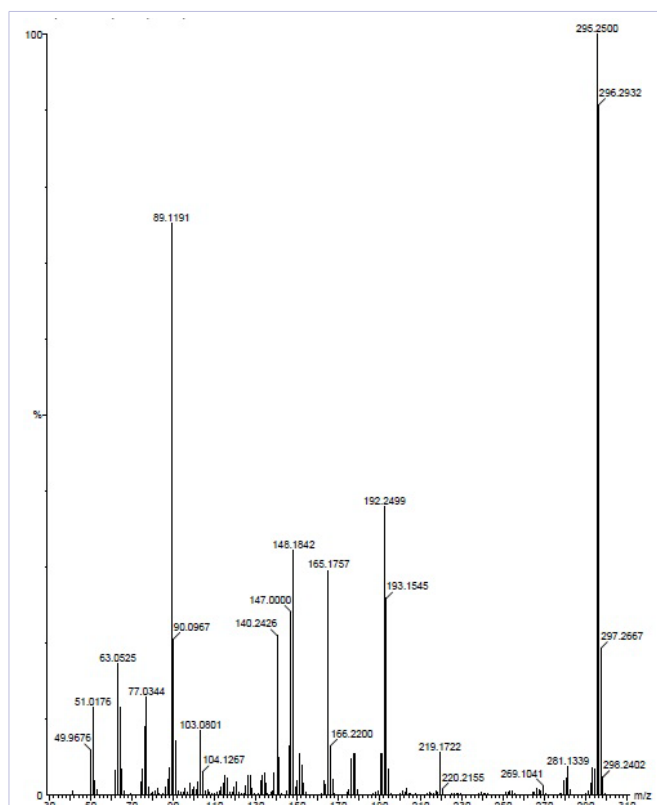


Figure 4: MASS spectrum of 6-methyl-2, 3-diphenylquinoxaline.

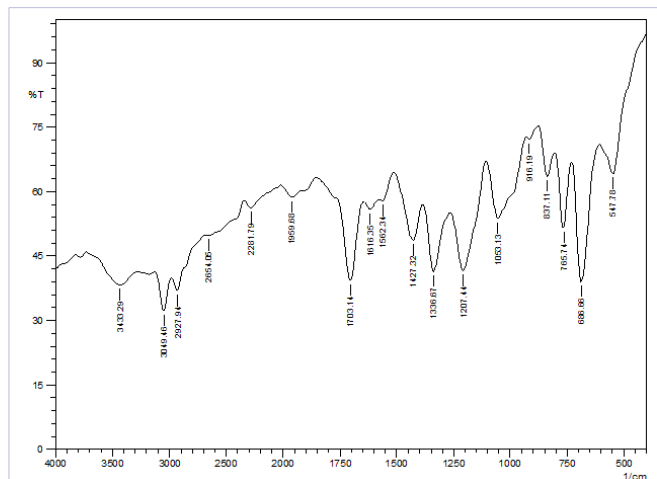


Figure 5: FTIR spectrum of 6-bromomethyl-2, 3-diphenylquinoxaline Stage 2: 6-bromomethyl-2, 3-diphenylquinoxaline

### Synthesis of 6-triphenylphosphonium-bromomethyl-2,3-diphenylquinoxaline

6-bromomethyl-2, 3-diphenylquinoxaline (0.38g, 1mmol) and triphenylphosphine (0.26g, 1mmol) were dissolved together in acetonitrile (20ml). The solution was stirred overnight at 40°C. The resulting precipitate was recrystallized from toluene-methanol mixture (2:1) to yield phosphonium ylide compound.

<sup>1</sup>H-NMR (DMSO, ppm): 2.7δ (2H, s), 7.2 – 7.9 δ aromatic protons.  
<sup>31</sup>P-NMR (DMSO, ppm): 25.60 δ (1P, s).

### Synthesis of vinyl benzaldehyde capped quinoxaline derivative

The phosphonium salt (0.64g, 1mmol) and terephthalaldehyde (0.135g, 1mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12ml, 3+1 v/v) under N<sub>2</sub> atmosphere. Further, stoichiometric amount of sodium methoxide (25wt % in methanol, 1.3ml, 5.6mmol) was added and the resulting solution was stirred at 50° C overnight. The product was washed with methanol and reprecipitated from dichloromethane-methanol (1:1) followed by dissolving in acetonitrile – chloroform mixture (1:1) and dried under vacuum to yield 80 % of yellow colour solid product (M.Pt: 110° C) as

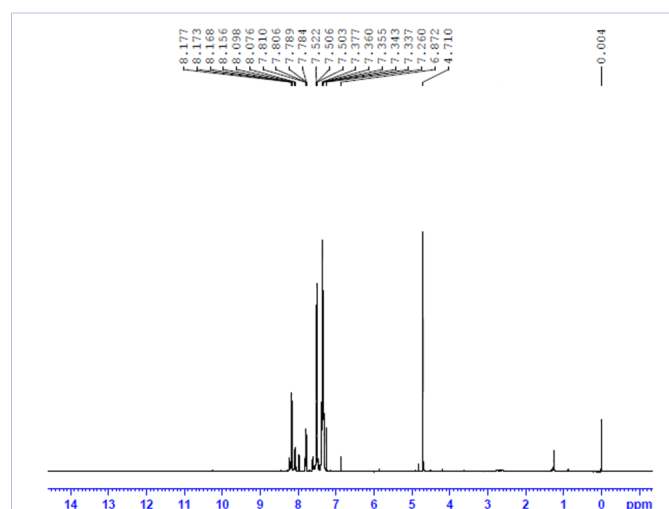


Figure 6: <sup>1</sup>H NMR spectrum of 6-bromomethyl-2, 3-diphenylquinoxaline

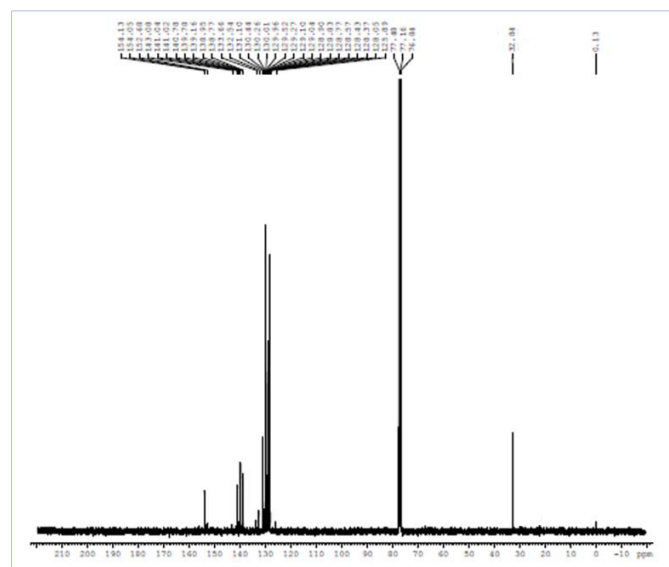


Figure 7: <sup>13</sup>C NMR spectrum of 6-bromomethyl-2, 3-diphenylquinoxaline

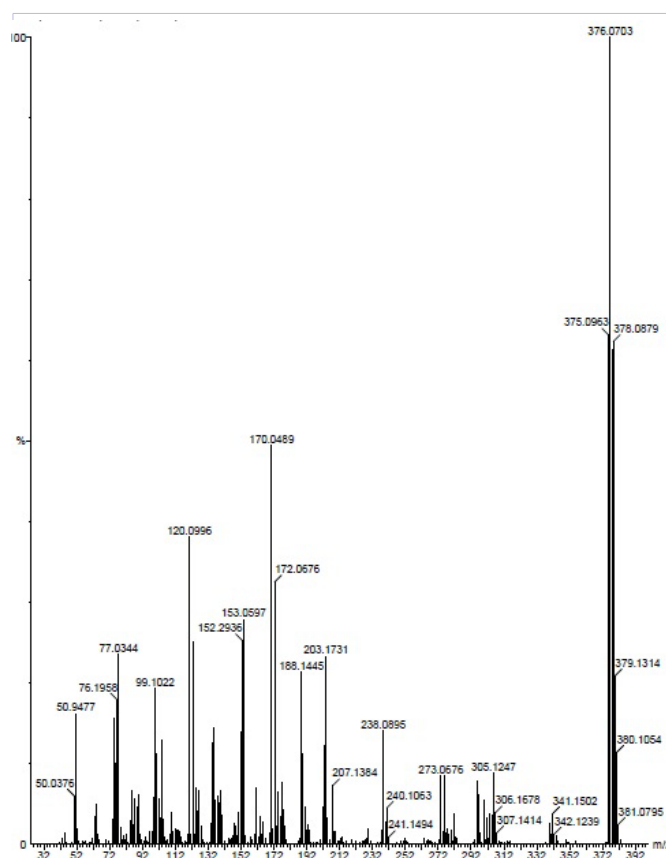


Figure 8: MASS spectrum of 6-bromomethyl-2, 3-diphenylquinoxaline

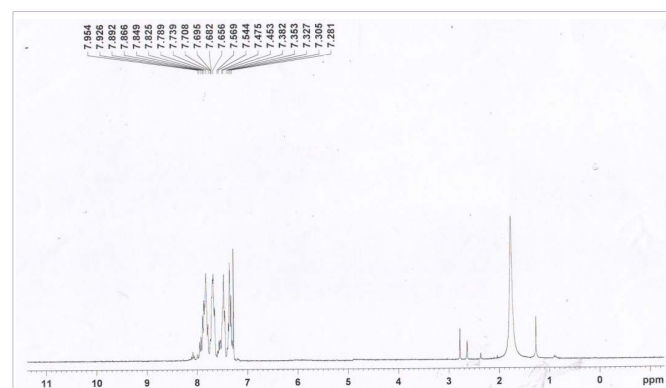


Figure 9: <sup>1</sup>H NMR spectrum of 6-triphenylphosphonium-bromomethyl-2, 3-diphenylquinoxaline.  
Stage 3: 6-triphenylphosphonium-bromomethyl-2, 3-diphenylquinoxaline

vinyl benzaldehyde capped quinoxaline derivative. UV( $\lambda_{max}$ , nm): 260.03nm ( $\pi$ - $\pi^*$ ), 348.03nm ( $n$ - $\pi^*$ ); FT-IR (KBr, cm<sup>-1</sup>): 2918.34 (C-H, st), 1689.09 (C=O, st), 1 (C=N, st), 1429.01 (C=C), 1347.75 (C-N, st); <sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 10.0 δ(1H, s), 9.9 δ(2H, m) 8.1 δ(1H, m) 7.9 δ(2H, m) 7.7 δ(2H, m) 7.5 δ(4H, m) 7.3 δ(2H, m) 7.2 δ(2H, m) 6.9 δ(2H, m); <sup>13</sup>C-NMR (CDCl<sub>3</sub>, ppm): 191.0δ, 127.29-154.10 δ; Mass(m/z): Calculated M.W 412.48, Observed M.W 413.2(M+1); PL : 454nm Emission

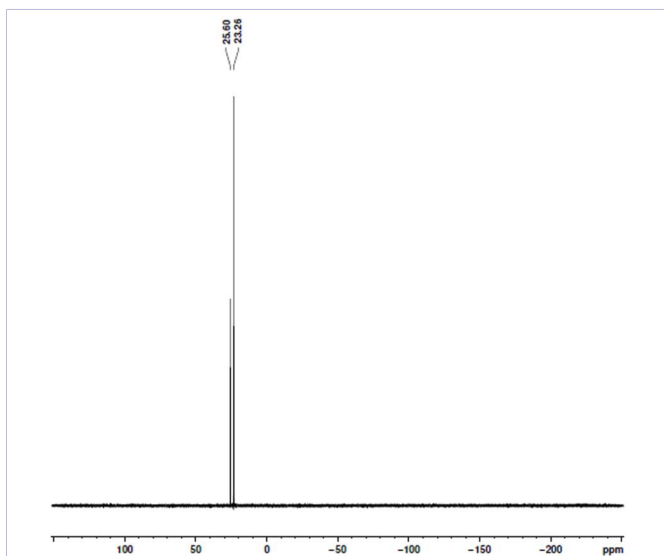


Figure 10: <sup>31</sup>P NMR spectrum of 6-triphenylphosphonium-bromomethyl-2, 3-diphenylquinoxaline

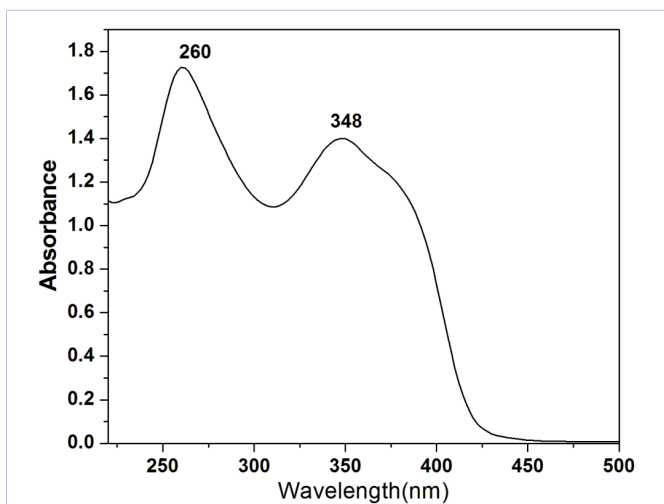


Figure 11: UV spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde  
Stage 4: 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

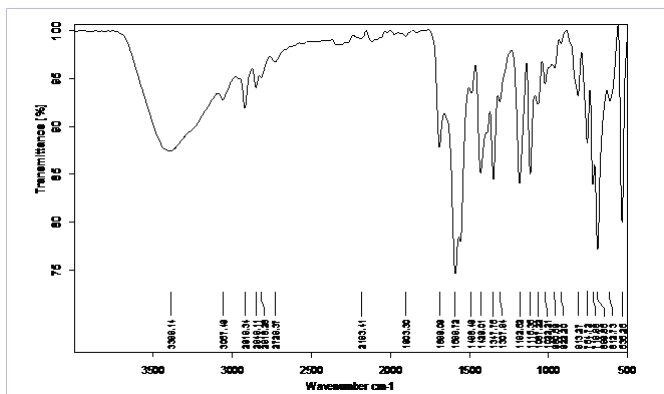


Figure 12: FTIR spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

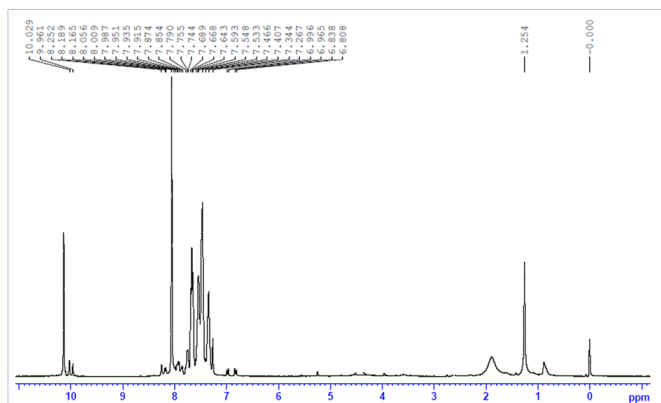


Figure 13: <sup>1</sup>H NMR spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

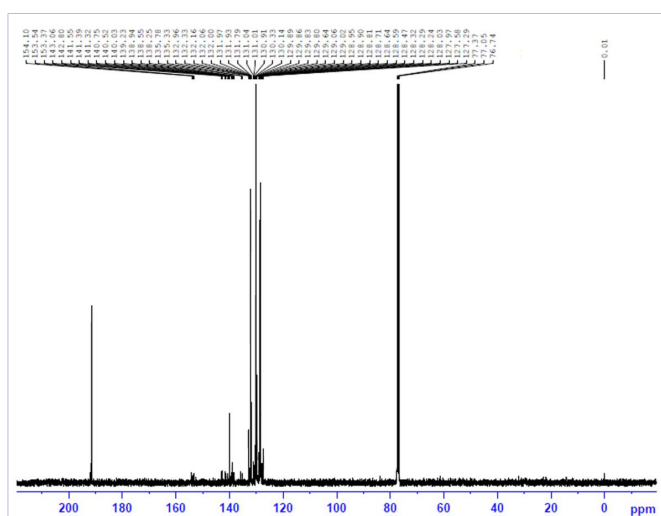


Figure 14: <sup>13</sup>C NMR spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

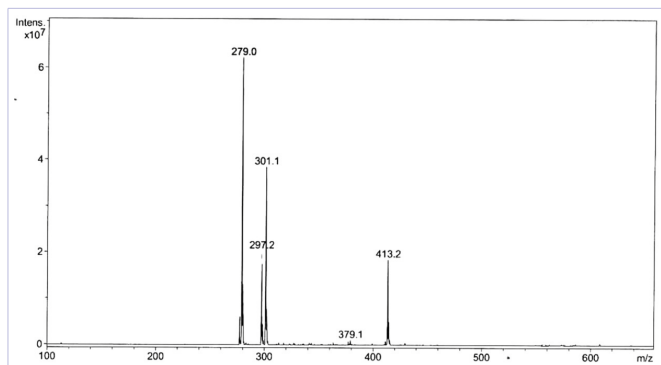


Figure 15: MASS spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

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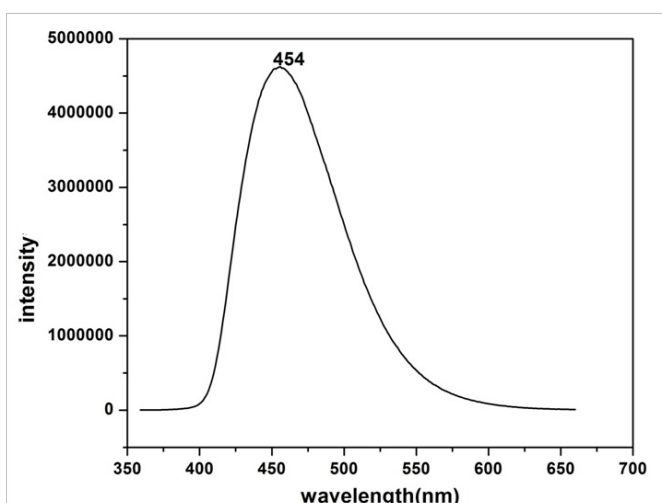


Figure 16: PL spectrum of 2, 3-diphenylquinoxalin-6-vinyl benzaldehyde

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