WORLD JOURNAL OF PHARMACEUTICAL RESEARCH
SJIF Impact Factor 8.074
Volume 7, Issue 8, 219-233. Conference Article ISSN 2277–7105

# A DONOR-ACCEPTOR MOLECULE OF VINYL BENZALDEHYDE CONTAINING QUINOXALINE DERIVATIVES FOR PHOTOLUMINESCENCE AND ANTI-BACTERIAL APPLICATIONS

**R. Padma and S. Guhanathan***

PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore-632 002, TN, India.

Article Received on
05 March 2018,
Revised on 25 March 2018,
Accepted on 15 April 2018
DOI: 10.20959/wjpr20188-11012

***Corresponding Author**
**S. Guhanathan**
PG & Research Department of Chemistry, Muthurangam Government Arts College (Autonomous), Vellore-632 002, TN, India.

## ABSTRACT

Fluorescent polymers, which are very interesting because of their potential applications in new display technology. Conjugated molecules are particularlay known as electroluminescence (EL) and photoluminescence (PL) materials. Quinoxaline finds many pharmacological activities and electron transport properties. The quinoxaline moiety, which contains electron-withdrawing nitrogen atoms is highly electron deficient and thus serves as an efficient electron acceptor. The present study involves to synthesis vinyl benzaldehyde containing quinoxaline derivatives by Wittig route. Quinoxaline containing segments were publicized to be promising acceptors when combined with vinyl benzaldehyde forming small conjugated donor-acceptor molecule. The synthesised compounds were characterised by FT-IR, $^{1}H$, $^{13}C$, $^{31}P$-NMR and Mass. The result of Fluorescent spectral investigation reveals that vinyl benzaldehyde containing quinoxaline derivatives exhibited photoluminescence nature with bluish-green emission maxima at shorter wavelengths of 455nm. Vinyl benzaldehyde containing quinoxaline derivatives were subjected to antibacterial screening against gram positive and gram negative bacteria. The results of anti-bacterial testing revealed that vinyl benzaldehyde containing quinoxaline derivatives showed considerable activity, obtained in terms of MIC, against all the strains used as compared to standard Ampicillin.

**KEYWORDS:** Wittig reaction, quinoxaline derivatives, photoluminescence, spectral studies, anti-baterial activity.

## INTRODUCTION

The various compounds containing Quinoxaline nucleus has been reported to have various pharmacological activities as anti-microbial[1-2] anti-inflammatory[3-4], anticancer[5] and anti-HIV.[6] They have also found applications in organic semiconductors,[7] dyes,[8] electroluminescent materials.[9]

The discovery of electroluminescence in poly (*p*phenylenevinylene) (PPV) in 1990[10] created a new domain in polymeric material applications. Since then, enormous progress has been made in the macromolecular engineering of the π-conjugated polymers and in their uses as active materials in polymeric light-emitting diodes (PLEDs).[11-12]

For the most of conjugated polymers, the barrier of electron injection is much higher than that of hole injection. To improve efficiency of PLEDs, it is necessary to balance the rate of injection of electrons and holes from opposite electrodes into the device.[13] Therefore, many high electron affinity substituents such as quinoxaline[14], oxadiazole[15], triazole[16] and quinoline[17] have been introduced.

The insertion of electron transporting moietie of quinoxaline derivative in the conjugated backbone is another well known technique to improve the electron affinity of a light emitting polymer.

Hence, In this paper, our interest towards synthesis, photophysical and electrochemical aspects of a new conjugated vinyl benzaldehyde containing quinoxaline derivatives via Wittig reaction in hope of combining both electron-affinity and light-emitting properties.

## Experimental section

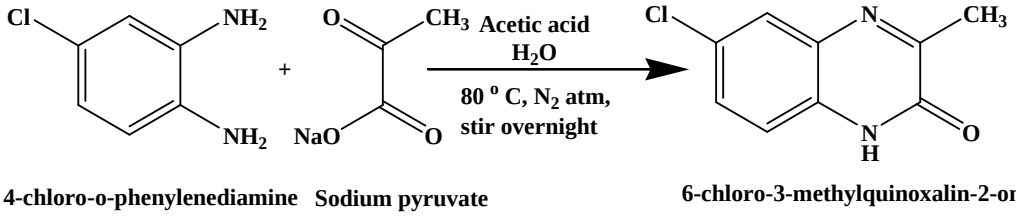
### Materials

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.

### Characterisation Methods

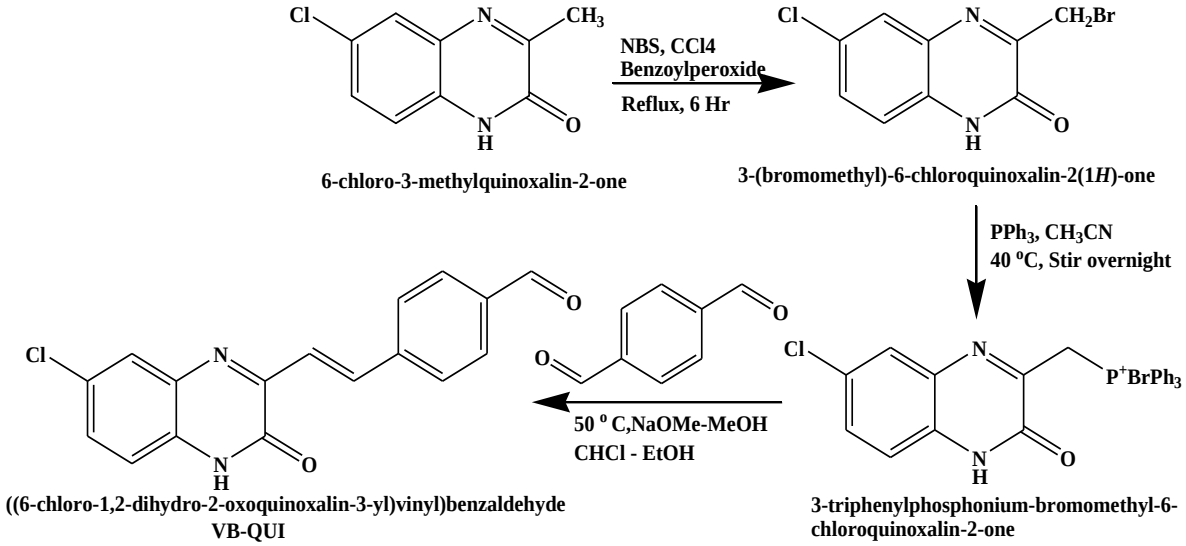
The UV-Visible spectra were recorded on an Alpha-Bruker UV spectrophotometer equipped in the range between 200-800nm. Room temperature FTIR spectra were recorded as KBr pellet with an Alpha-Bruker FTIR spectrophotometer in the range of 4000-400cm$^{-1}$. Nuclear magnetic resonance spectra with different core viz., $^{1}$H NMR, $^{13}$C NMR and $^{31}$P NMR were recorded in either DMSO-$d_6$ or $CDCl_3$ 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.




4-chloro-o-phenylenediamine Sodium pyruvate 6-chloro-3-methylquinoxalin-2-one

**Scheme 1: Synthesis of 6-chloro-3-methylquinoxalin-2-one.**




6-chloro-3-methylquinoxalin-2-one

3-(bromomethyl)-6-chloroquinoxalin-2(1*H*)-one

((6-chloro-1,2-dihydro-2-oxoquinoxalin-3-yl)vinyl)benzaldehyde VB-QUI

3-triphenylphosphonium-bromomethyl-6-chloroquinoxalin-2-one

**Scheme 2. Synthesis of Vinyl benzaldehyde capped quinoxaline derivatives.**

**Synthesis of 6-chloro-3-methylquinoxalin-2-one**

The 4-chloro-o-phenylenediamine (5.2725g, 37.0 mmol) in acetic acid (150ml), water (200ml), the formed solution mixture was heated upto 80$^{o}$C under nitrogen atmosphere. To this mixture the sodium pyruvate (4.089g, 37.0 mmol) was added over a period of 20 minutes with constant stirring. TLC were used to monitor the progress of the reaction until the formation of the product. The solvent was evaporated under reduced pressure. The crude product was purified by silica gel column chromatography using Hexane:Ethylacetate (9:1) as eluent, affording sandal solid. m.p. 230 - 232˚C, (Fig. 1) UV(λmax, nm): 239(π–π*), 321(n-π*)**;** (Fig. 2) FTIR (KBr, cm$^{-1}$): 3367(N-H, st), 2811(C-H, st), 1660(C=O, st), 1557(C=N, st) 1415(C=C, st), 1285(C-N, st), 1014(C-Cl, st); (Fig. 3) $^{1}$H NMR(CDCl3, 300MHz), d(ppm): 2.62(3H,s), 10.44(1H,s), 7.15–7.86(3H, m); (Fig. 4) Mass(m/z): Calculated M.W 194.02, Observed M.W 194.2(M$^{+}$).

**Synthesis of 3-bromomethyl-6-chloroquinoxalin-2-one**

A mixture of 6-chloro-3-methylquinoxalin-2-one (0.1946g, 1mmol), *N*-bromosuccinimide (0.1780g, 1mmol) were dissolved in 30ml of $CCl_4$ along with the initiator benzoyl peroxide (0.08g, 0.0003mol). The resulting reaction mixture was refluxed for 6 hours. The solid by product in the reaction mixture was removed by filtration, the filtrate was washed with $CCl_4$. The solvent was evaporated to get 3-bromomethyl-6-chloroquinoxalin-2-one as dark maroon crystals. m.p. 71 - 73˚C ( Fig. 5) FT-IR (KBr, $cm^{-1}$): 2926 (C-H, st), 3422 (N-H, st) 1698 (C=O, st) 1589 (C=N, st) 1421 (C=C, st) 1292 (C-N, st) 926 (C-Cl, st) 797 (C-Br, st) ( Fig. 6) $^1$H-NMR (DMSO, ppm): 4.71 δ(2H, s) 8.18 δ (1H, s) 7.50 δ (1H, d) 7.41 δ (2H, m) (Fig. 2).

**Synthesis of 3-triphenylphosphonium-bromomethyl-6-chloroquinoxalin-2-one**

1mmol (0.2734g) of 3-bromomethyl-6-chloroquinoxalin-2-one and 1mmol (0.2623g) of triphenylphosphine were dissolved in 20ml of acetonitrile with constant stirring for 12 hours at 40˚C. Then, the reaction mixture was filtered, and the solvent was evaporated through distillation to get brown waxy phosphonium ylide compound**.** ( Fig. 7) FT-IR (KBr, cm-1): 2926, (C-H, st), 3383 (N-H, st), 1718 (C=O, st), 1540 (C=N, st), 1431 (C=C, st) 1341 (C-N, st), 1103 (C-Cl, st) 757 (C-Br, st), 677 (C-P, st), 540 (P-Br, st) ( Fig. 8) $^1$H-NMR (DMSO, ppm): 2.67δ (2H, s), 8.11 δ (1H, s), 7.52-7.64δ (3H, m), 6.98-7.25 δ (15H, m) (Fig. 9) $^{31}$P-NMR (DMSO, ppm): 25.53δ (1P, s).

**Synthesis of 6-Chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde**

The vinyl benzaldehyde capped quinoxaline derivative were prepared from the corresponding phosphonium salt using the well-known Wittig reaction.[18] The phosphonium salt (0.535g, 1mmol) and terephthaldicarboxaldehyde (0.135g, 1mmol) were dissolved in a mixture of absolute ethanol and dry chloroform (12ml, 3+1 v/v) under $N_2$ atmosphere. Then, a predetermined amount of sodium methoxide (25wt% in methanol, 1.3ml, 5.6mmol) was added and the resulting solution was stirred at 50$^o$C overnight. Precipitation in methanol gave precipitate, which was reprecipitated from dichloromethane-methanol. Formed compound was purified by dissolving in acetonitrile and chloroform. (yield; 80%, m.p. ˚C) ( Fig. 10) FT-IR (KBr, cm-1): 2921(C-H, st), 3401 (N-H, st), 1693 (C=O, st), 1549 (C=N, st), 1424(C=C, st), 1307 (C-N, st**),** 1023 (C-Cl, st) **(** Fig. 11) $^1$H-NMR ($CDCl_3$, ppm): 10.03δ (1H, s) 9.98δ (1H, s) 4.19-4.20δ (1H, d) 4.15-4.17 δ(1H, d) 7.64-7.69δ(2H, m) 7.83-7.90δ(2H, m) 7.45-7.49 δ(2H,m) 7.55-7.57 δ(1H, m) ( Fig. 12) $^{13}$C-NMR ($CDCl_3$, ppm): 126.40 and 132.0 δ (vinyl carbons), 191.86 and 145.58 δ (C=O), 129.54, 127.29, 136.20,

131.89, 139.06, 128.36, 128.48 and 136.20 δ (Aromatic ring carbons) (Fig. 13) Mass(m/z): Calculated M.W 310.1, Observed M.W 312.2(M+2) ( Fig. 14) UV (nm) : 238nm (π-π*) 363nm (n- π*) (Fig. 15) PL : 455nm Emission.

## RESULTS AND DISCUSSION

The vinyl benzaldehyde containing quinoxaline derivatives (VB-QUI) have been prepared similar to our earlier report[19-21] Initially 6-chloro-3-methylquinoxalin-2-one was synthesized from sodium pyruvate and 4-chloro-o-phenylenediamine. For conversion of methyl to bromomethyl NBS used as a brominating agent via free radical mechanism. Based on Wittig reaction bromomethyl group is converted to phosphonium salt. The final olefination is achieved with phosphonium salt and terephthaldehyde. The structures of the products were characterized by UV, FT-IR, $^{1}H$, $^{31}P$ NMR. The optical properties including absorption and luminescence of these VB-QUI were measured with UV-Vis and PL systems.

Fig. 1 summarised the UV spectral details of 6-chloro-3-methylquinoxalin-2-one. From the fig the n-π* and π-π* transitions were observed at 321nm and 239nm respectively., which implies the C=N, C=O, and C=C in the compound. Fig. 4 shows the mass spectrum of quinoxaline derivatives from the spectra molecular ion peak observed at 194.2 this value agreed well with the theoretical value.

Fig.5 and fig.6 showed the FTIR and 1H NMR spectra of bromomethylated quinoxaline derivative from the FTIR spectrum the peak at 797 for C-Br functional group. From the $^{1}H$-NMR the bromomethyl proton signal appeared deshielded region at 4.7 δ confirmed the bromination of quinoxaline derivatives.

The phosphonium ylide compound has been confirmed from the $^{1}H$ NMR spectra (Fig. 7) the signal at 2.6 δ (ppm) corresponds to methyl protons, the aromatic ring protons signal appeared at 6.98-7.25 δ . Fig. 9 depicts the $^{31}P$ NMR the single peak at 25.60 δ supports the single phosphorous present in the ylide compound.

The vinyl benzaldehyde containing quinoxaline derivative has been obtained from phosphonium salt. Fig. 10 summarised FTIR spectrum of VB-QUI. It displays week transmittance peak at 2921 $cm^{-1}$for C-H stretching frequency. The peak at 3401$cm^{-1}$ due to N-H stretching and peak at 1549$cm^{-1}$, 1693 $cm^{-1}$, 1424$cm^{-1}$ for C=N, C=O, C=C stretching frequency. The C-N stretching frequency appeared at 1307$cm^{-1}$ The $^{1}H$ NMR spectrum of

VB-QUI compound have shown in Fig. 11. A singlet peak at 10.03δ ppm, 1H indicated the aldehyde proton (–CHO). A singlet at 9.98 δ ppm, 1H assigned to N-H proton. A double doublet peak observed at 4.15 – 4.20 δ ppm, 2H, pointed out vinyl protons. Multiplet peak appears at 7.64 – 7.90 δ ppm, 4H, assigned to aromatic protons in benzaldehyde ring. Multiplet peaks appeared at 7.45 – 7.57 δ ppm, 3H, signifies aromatic protons in quinoxaline ring moiety. Fig. 12 show the $^{13}C$ NMR spectrum of VB-QUI compound. The signals at 191.86 and 145.58 δ ppm, were associated with carbonyl carbon in benzaldehyde and quinoxaline ring moiety. The peak at 132.00 and 126.40 δ ppm, assigned to vinyl carbons. The signal appears at 129.54, 127.29, 136.20, 131.89, 139.06, 128.36, 128.48 and 136.20 δ ppm were related to aromatic carbons in the compound. Fig. 14. summarised the UV spectrum of VB-QUI compound. From the Figure $\lambda_{max}$was observed at 238 nm which implies π-π* transition and 363nm due to n-π* transition. The molecular weight was found from the GC-MASS spectrum shown in Fig 13. The molecular ion peak was observed at 312.2(M+2) found to be agreed well with the theoretical value.

**Photoluminescent properties**

Fig. 15 displays PL spectra of VB-QUI compound in the ethanol solution. In the PL spectra the compound showed a strong bluish green emission approximately 455nm.

**Anti-bacterial activity**

The anti-bacterial activity of the synthesised vinyl benzaldehyde substituted quinoxaline was evaluated using two-Gram positive (*Bacillus substilis and Staphylococccus aureus*) and two-Gram negative (*Escherichia coli and Pseudomonas auroginosa*) bacteria. Ampicilin is used as positive control. The MIC values of the compound were determined by broth dilution method.[21] Among the tested micro-organism the phosphonim ylide compound exhibited the best antibacterial activity than vinyl benzaldehyde capped quinoxaline derivatives.

**Table 2: MIC (Minimum inhibitory concentration) values of phosphonium ylide and VB-QUI compound.**

| **Compound** | ***Bacillus substilis* (MTCC 441)** | ***Staphylococccus aureus* (MTCC 6908)** | ***Escherichia Coli* (MTCC 406)** | ***Pseudomonas auroginosa* (MTCC 2453)** |
|---|---|---|---|---|
| **Phosphonium ylide** | **0.12mg** | **0.12mg** | **0.12mg** | **0.12mg** |
| **Vinyl benzaldehyde containing quinoxaline derivatives** | 0.25mg | 0.25mg | 0.25mg | 0.25mg |
| **Ampicilin** | 0.12mg | 0.12mg | 0.12mg | 0.12mg |

**Stage I - 6-chloro-3-methylquinoxalin-2-one**

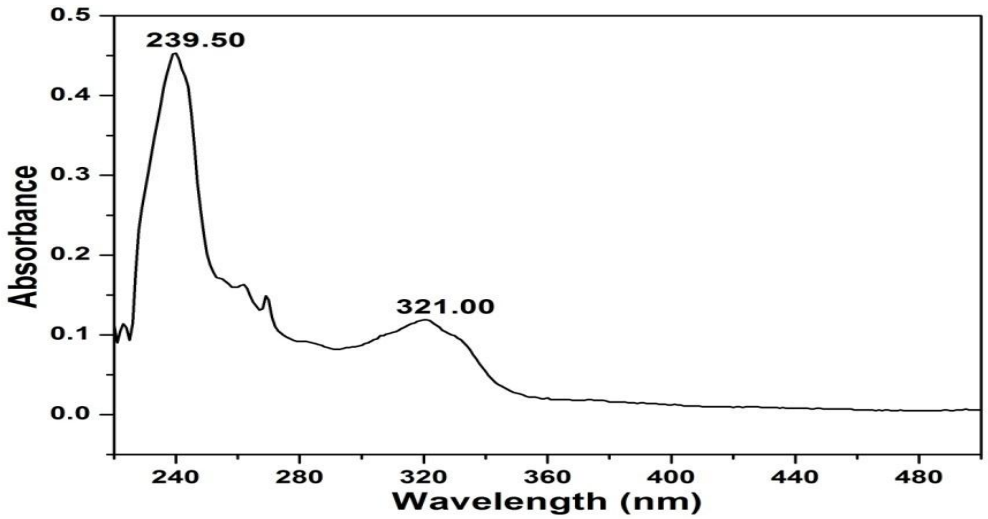



**Figure 1: UV spectrum of 6-chloro-3-methylquinoxalin-2-one.**

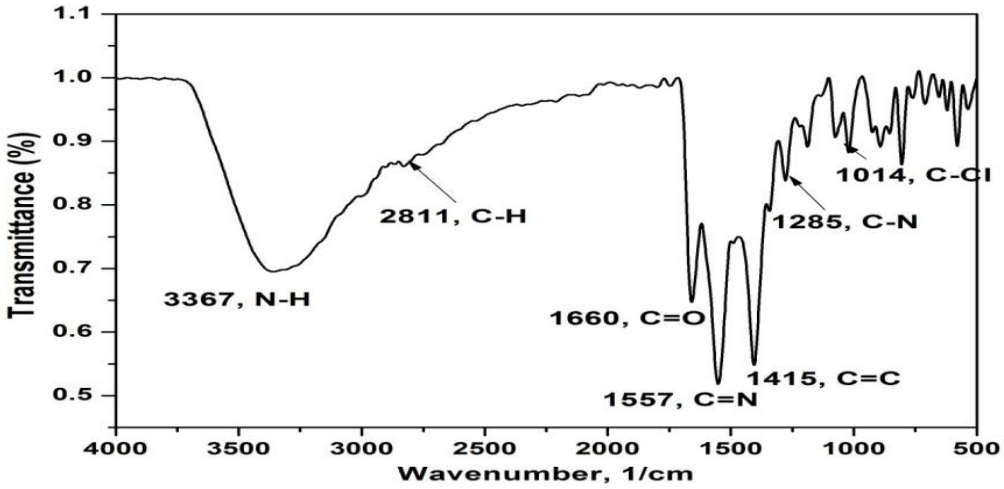



**Figure 2: FTIR spectrum of compound 6-chloro-3-methylquinoxalin-2-one.**

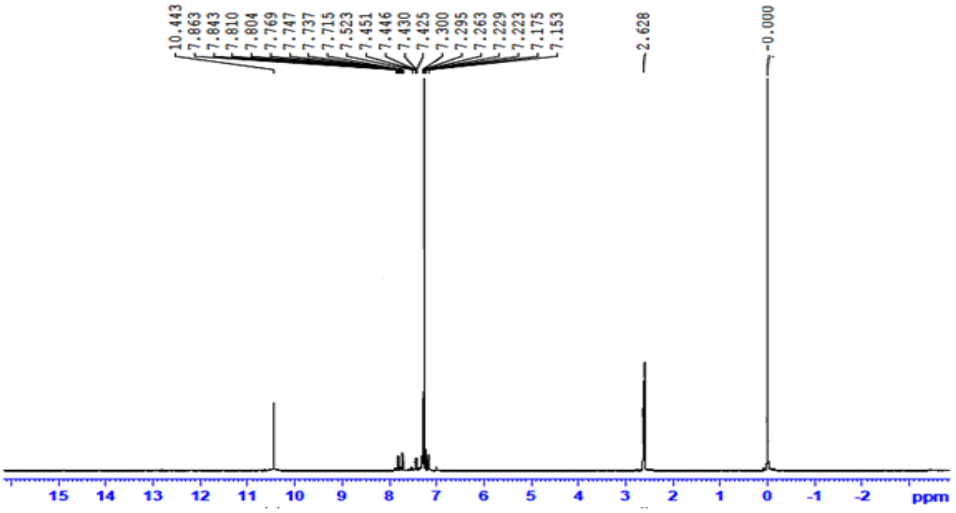



**Figure 3: $^{1}$H NMR spectrum of 6-chloro-3-methylquinoxalin-2-one.**

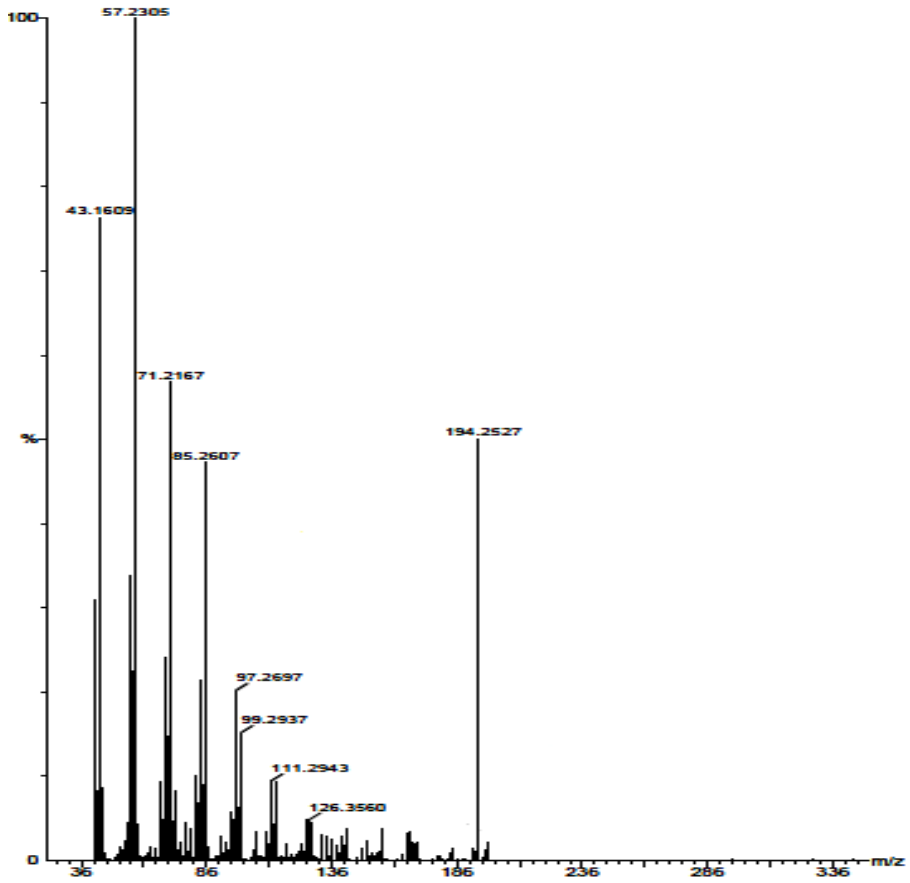



**Figure 4: mass spectrum of 6-chloro-3-methylquinoxalin-2-one.**

**Stage II – 3-bromomethyl-6-chloroquinoxalin-2-one.**

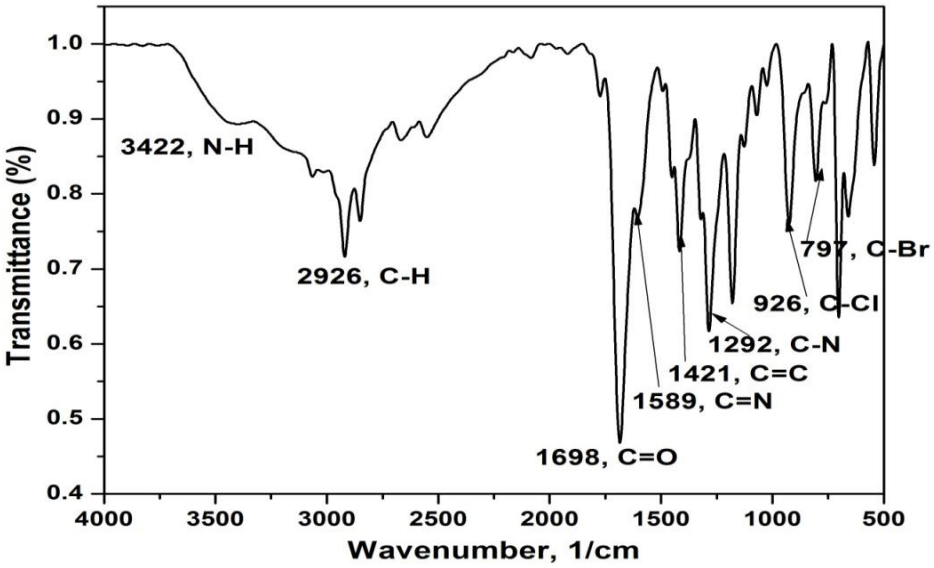



**Figure 5: FTIR spectrum of 3-bromomethyl-6-chloroquinoxalin-2-one.**

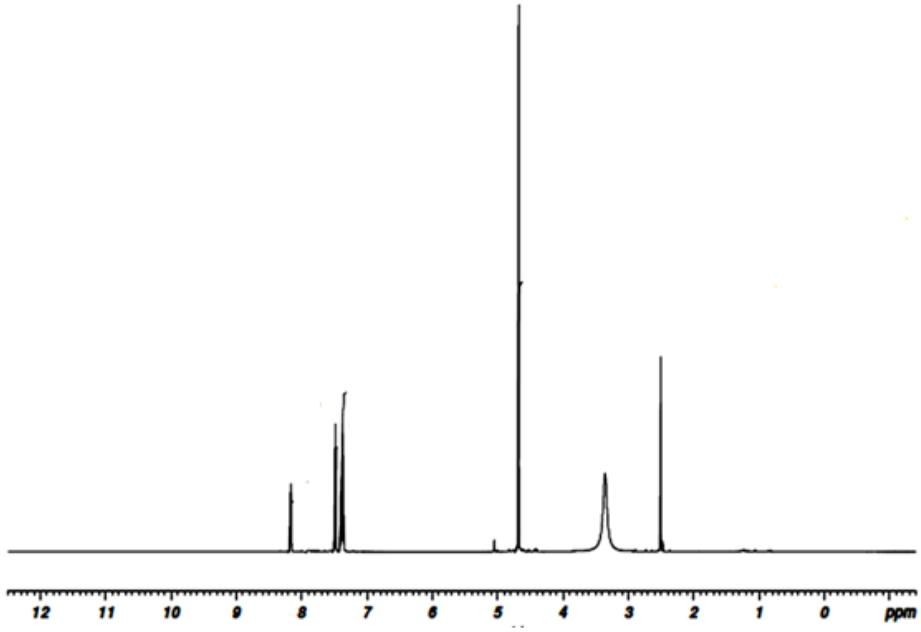



**Figure 6: $^{1}$H NMR spectrum of 3-bromomethyl-6-chloroquinoxalin-2-one.**

**Stage III- 3-triphenylphosphonium-bromomethyl-6-chloroquinoxalin-2-one.**

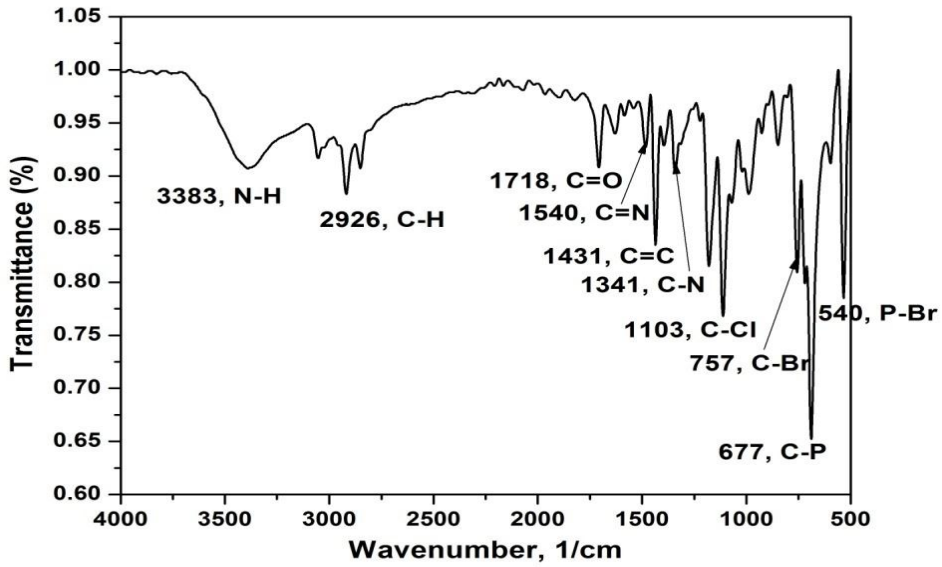



**Figure 7: FTIR spectrum of 3-triphenylphosphonium-bromomethyl-6-chloroquinoxalin-2-one.**

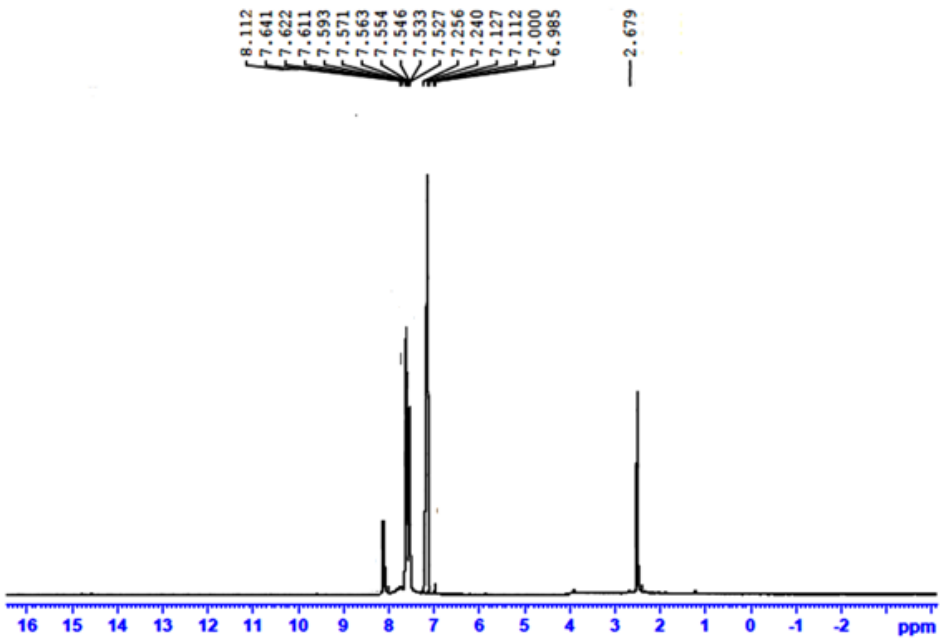



**Figure 8: $^{1}H$ NMR spectrum of 3-triphenylphosphonium-bromomethyl-6-chloroquinoxalin-2-one.**

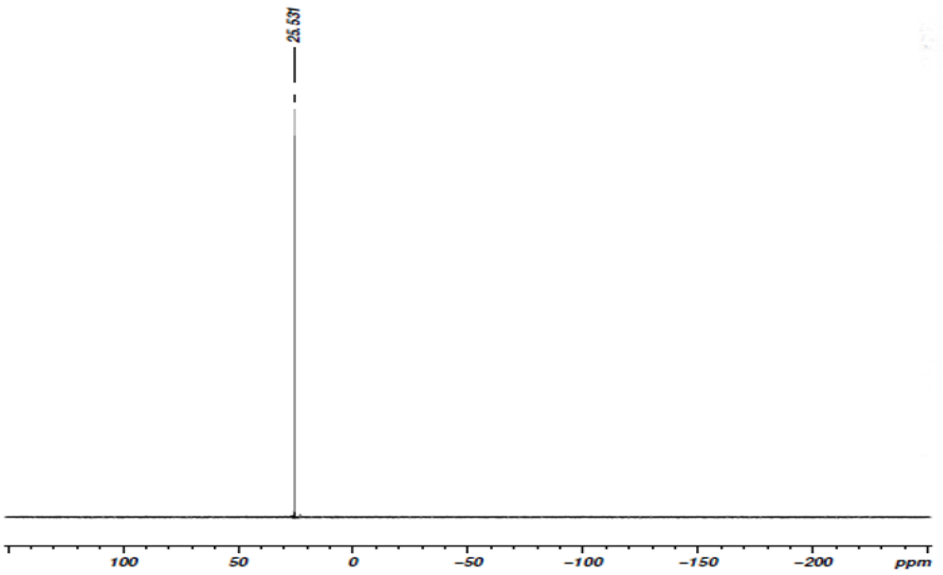



**Figure 9: $^{31}P$ NMR spectrum of 3-triphenylphosphonium-bomomethyl-6-chloroquinoxalin-2-one.**

**Stage IV – 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde**

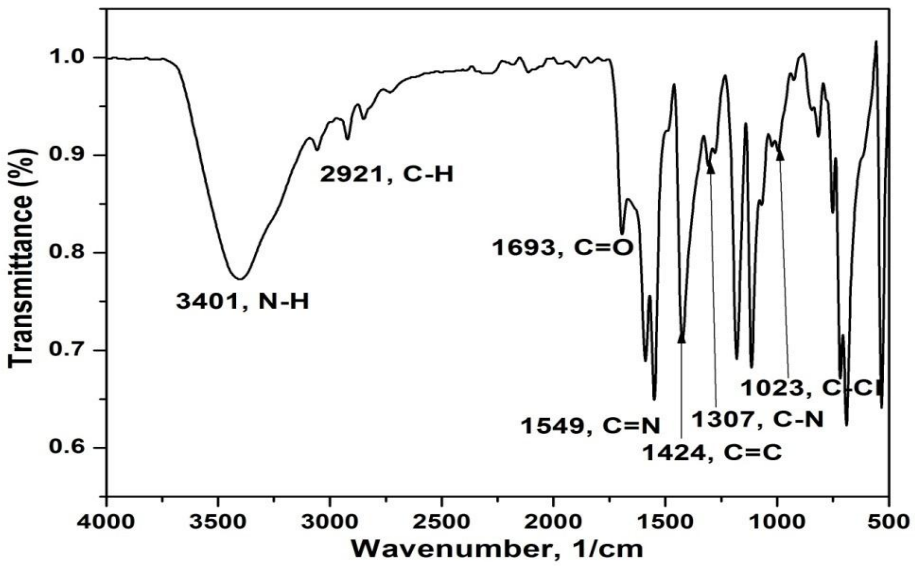



**Figure 10: FTIR spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

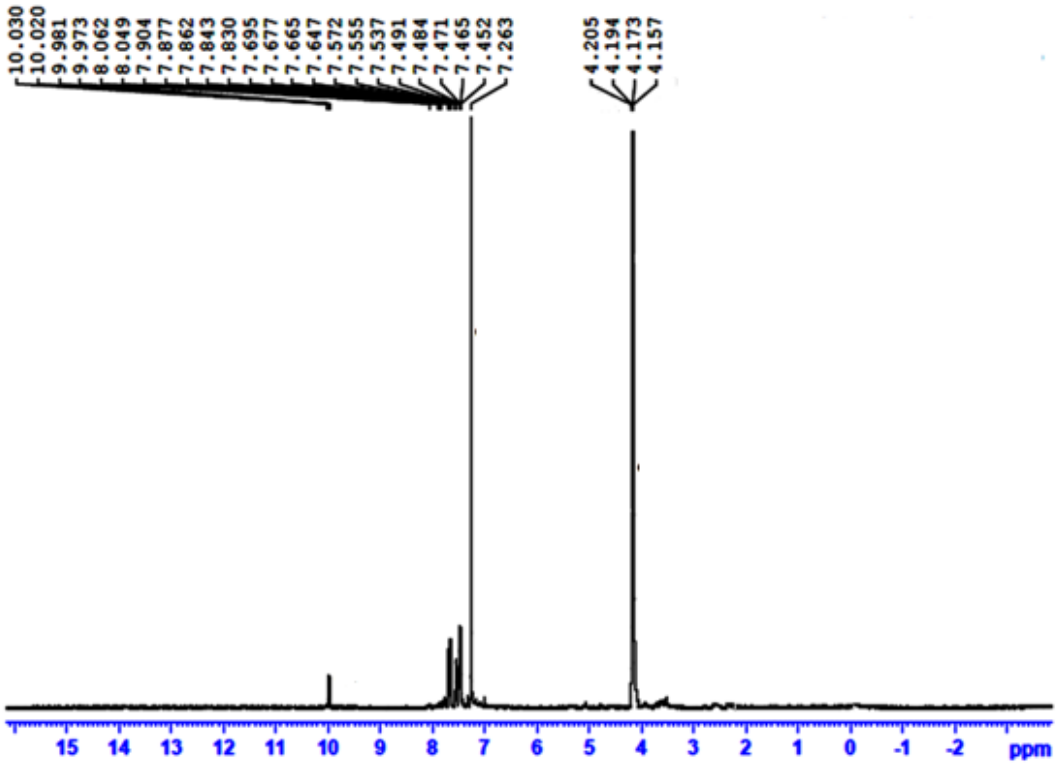



**Figure 11: $^{1}$H NMR spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

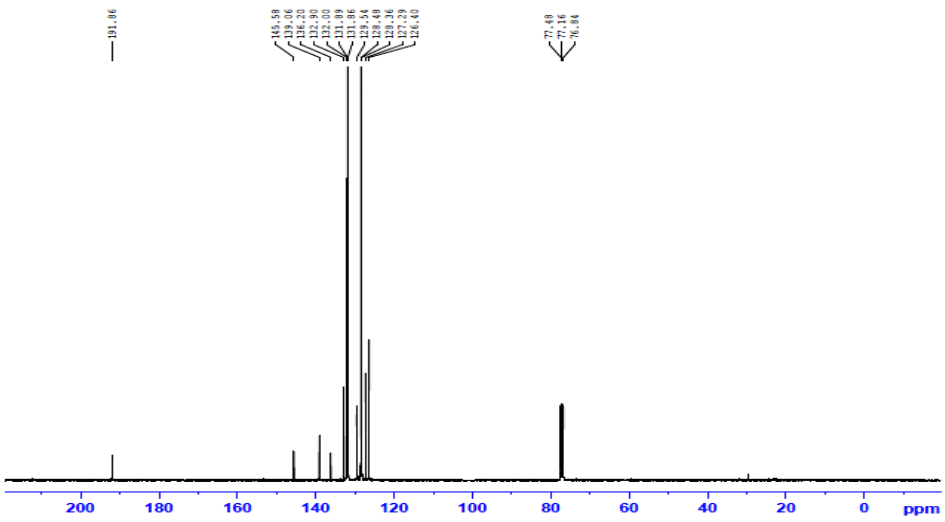



**Figure 12: $^{13}C$ NMR spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

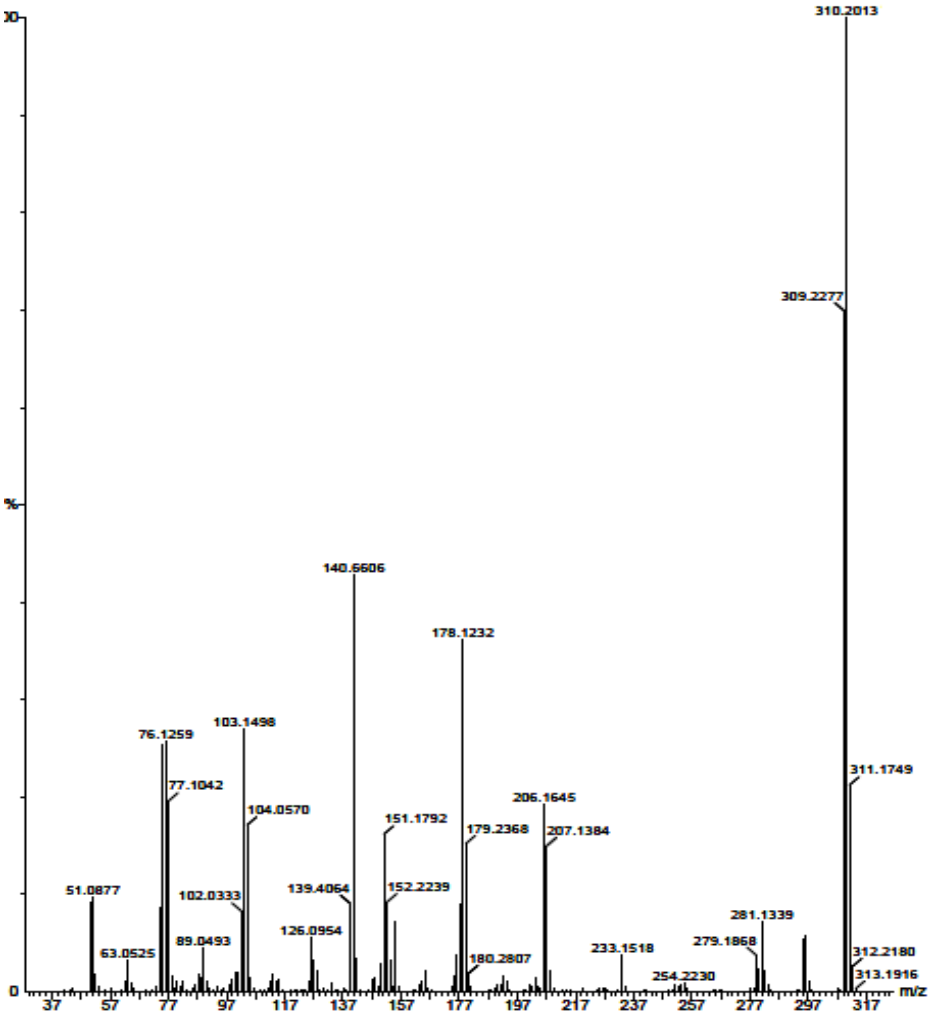



**Figure 13: GC-Mass spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

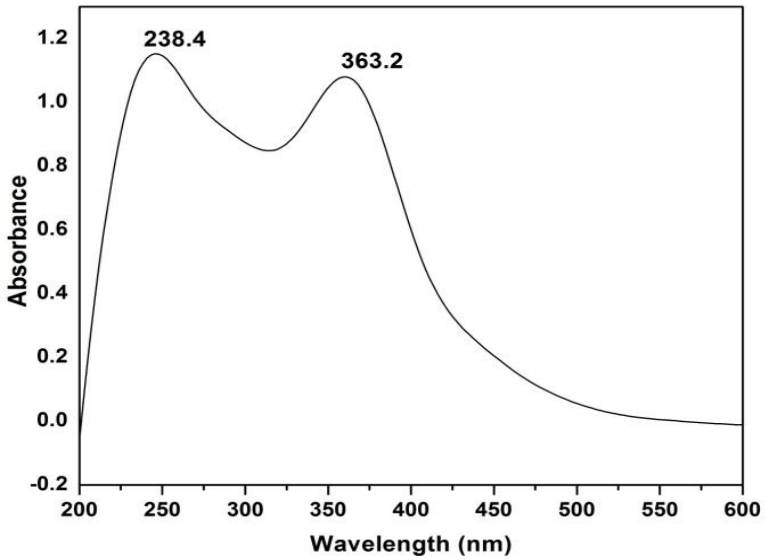



**Figure 14: UV spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

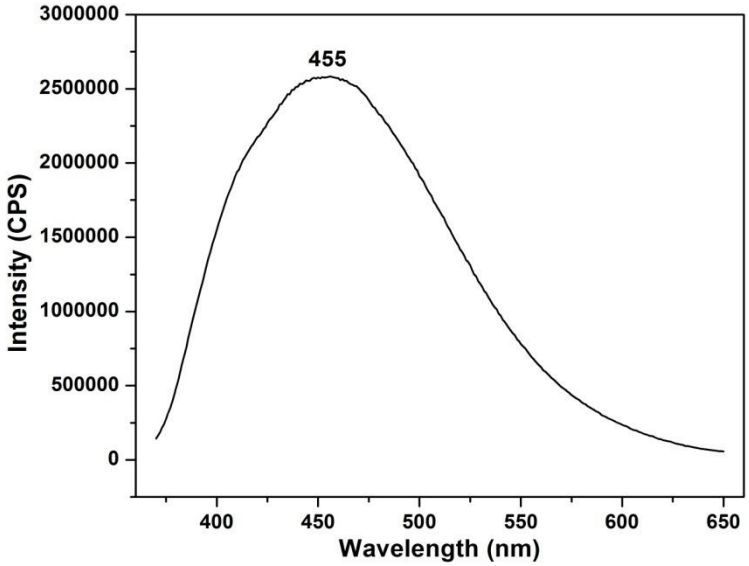



**Figure 15: PL spectrum of 6-chloro-1,2-dihydro-2-oxoquinoxalin-3-vinyl benzaldehyde.**

## CONCLUSIONS

The vinyl benzaldehyde capped quinoxaline derivative compound was synthesised through Wittig reaction using Phosphonium salt and terephthaldehyde. The resulting compound was characterised by UV, FTIR, $^{1}H$, $^{13}C$, $^{31}P$ NMR and GC-MASS spectral studies. The vinyl benzaldehyde introduced into the quinoxaline derivatives in the conjugation unit showed strong bluish green emission at 455nm in the Photoluminescene spectra. Anti-bacterial activities of the synthesised compound were studied using Gram positive and Gram negative bacteria. In comparison with positive control ampicillin, the phosphonium ylide compound

show relatively good anti-bacterial activity against tested micro-organism than vinyl benzaldehyde containing quinoxaline derivatives.

**ACKNOWLEDGEMENT**

We gratefully acknowledge Muthurangam Govt Arts College (Autonomous) for providing laboratory facilities. We thank SIF-VIT and SAIF-IIT madras for recording spectral data.

**REFERENCES**

1. Badar MZA, Mahgoub SA, Latif FFA, Fahmy AM, Moustafa OS, J. Indian Chem. Soc., 1990; 67: 216.
2. Kim BY, Kim YH, Park JY, Kim SK, Synthesis and biological activity of new quinoxaline antibiotics of echinomycin analogues. Bioorg. Med. Chem. Lett., 2004; 74: 541-544.
3. Kozminykh VO, Igidov NM, Andreichikov Yu S, Semenova ZN, Kolla VE and Drovosekova LP, Pharm. Chem. J., 1990; 1665.
4. Andreichikov Yu S, Nekrasov DD, Pitirimova SG, Zaks AS, Korsheninnikova MI, Plaksina PN, Semenova ZN, Kopeikin VA, Pharm. Chem. J., 1990; 1665.
5. Hezeldine ST, Polin L, Kushner J, Paluch J, White K, Edelsteit M, Palomino E, Corbelt T H, Horwitz JP, J. med. Chem., 2000; 44: 1758.
6. Loriga M, Piras S, Sanna P, Paglietti G, Quinoxaline chemistry. 2-[aminobenzoates]- and 2-[aminobenzoylglutamate]-quinoxalines as classical antifolate agents. Synthesis and evaluation of in vitro anticancer, anti-HIV and antifungal activity. Farmaco, 1997; 52: 157-66.
7. Dailey S, Feast JW, Peace RJ, Till IC, Sage S and Wood EL, Synthesis and device characterization of side chain polymer electron transport materials for organic semiconductor applications. J. Mater. Chem. 2001; 11: 2238-2243.
8. Sonawane ND and Rangnekar DW, Synthesis and application of 2-styryl-6,7-dichlorothiazolo[4,5-b]-quinoxaline based fluorescent dyes. J. Heterocycl. Chem., 2002; 39**:** 303-308
9. Sakata G, Makino K, Yoshihisa kurasawa, Recent progress in the Quinoline Chemistry. Synthesis and Biological Activity. Heterocycles, 1988; 27: 2481-2515.
10. Burroughes JH, Bradley DDC, Brown AR, Marks RN, Mackay K, Friend RH, Burns PL., Holmes AB: Light-emitting diodes based on conjugated polymers. Nature, 1990; 347: 539–541.

11. Kim CG, Koo MS, Choi SH, Lee DH, Park DK. Enhanced performance in polymer light-emitting diodes (PLEDs) by using water soluble conjugation polymer. Bulletin of the Korean Chemical Society, 2012; 33: 3087–3090.
12. Teichler A, Shu Z, Wild A, Bader C, Nowotny J, Kirchner G, Harkema S, Perelaer J, Schubert US: Inkjet printing of chemically tailored light-emitting polymers. European Polymer Journal, 2013; 49: 2186–2195.
13. Greenham NC, Moratti SC, Bradley DDC, Friend RH, Holmes AB, Kraft **A,** Nature, 1993: 28: 365
14. Cui Y, Zhang X, Jenekhe SA, Thiophene-Linked Polyphenylquinoxaline: A New Electron Transport Conjugated Polymer for Electroluminescent Devices. Macromolecules, 1999; 32(11): 3824-3826.
15. Huang W, Meng H, Yu W-L, Gao J, Heeger AJ, A New Blue Light-Emitting Polymer Containing Substituted Thiophene and an Arylene-1,3,4-oxadiazole Moiety. Adv. Mater., 1998; 10(8): 593-596
16. Strukelj MJ, Timothy MM, Fotis P, Sehwan S, Effects of Polymeric Electron Transporters and the structure of poly(p-phenylenevinylene)on the performance of Light-Emitting Diodes, J. Am. Chem. SOC., 1995; 117: 11976-11983.
17. Jenekhe SA, Zhang X, Chen XL. Choong VE, Gao Y, Hsieh BR, Finite Siza Effects on Electroluminescence of Nanoscale Semiconducting Polymer Heterojunctions, Chem. Mater., 1998; 9(2): 409-412.
18. Karpagam S, Guhanathan S, Sakthivel P, Enhancement of Processability, Stability and Photoluminescence Performance of Poly(p-phenylene vinylene) Containing Diazine Heterocycle Unit, Fibers and polymers., 2012; 13: 1105-1112.
19. Karpagam S, Guhanathan S, Emitting oligomer containing quinolone group; synthesis and photophysical properties of conjugated oligomer obtained by Wittig reaction, Journal of Luminescence., 2014; 145: 752-759.
20. Karpagam S, Guhanathan S, Sakthivel P, Applications of Wittig Reactions in Dibenzo 18-Crown-6-Ether Substituted Phenylenevinylene Oligomer – Synthesis, Photo luminescent, and Dielectric properties, Journal of Applied Polymer Science, 2011; 120: 960-967.
21. Padma R, Guhanathan S, Synthesis, Characterisation and Antibacterial activity of 2,3-Difurylquinoxalin-6-Vinyl Benzaldehyde, Der Chemica Sinica, 2016; 7(4): 63-69.