

“Synthesis and Study of Schiff base Ligands”

Dr. A. Xavier¹, N. Srividhya²

(Chemistry, The Madura College, / Madurai Kamaraj University, India)
(Chemistry, PSNA College of Engineering and Technology / Anna University, India)

Abstract: The new Schiff bases are synthesis from various and aldehyde and amine under magnetic stirrer method. The synthesized Schiff base were characterized by spectral techniques (UV-Spectra & IR-Spectra). And the Schiff base are yellow colour solid and having sharp melting point and insoluble in organic solvents.

Keywords: New Schiff bases, sharp melting point, yellow solid colour

I. Introduction

Inorganic elements play crucial role in biological and biological medical processes, and it is evident that many organic compounds used in medicine do not have a purely organic mode of action, some are activated or bio transformed by metal ions metabolism. Many drugs possess modified toxicological and pharmacological properties in the form of metal complex and probably Schiff bases are versatile C=N (Imine) containing compounds possessing broad spectrum of biological activity and incorporation of metals in form of complexes showed some degree of antibacterial, antifungal, antitumor and anti-inflammatory activity.[1]

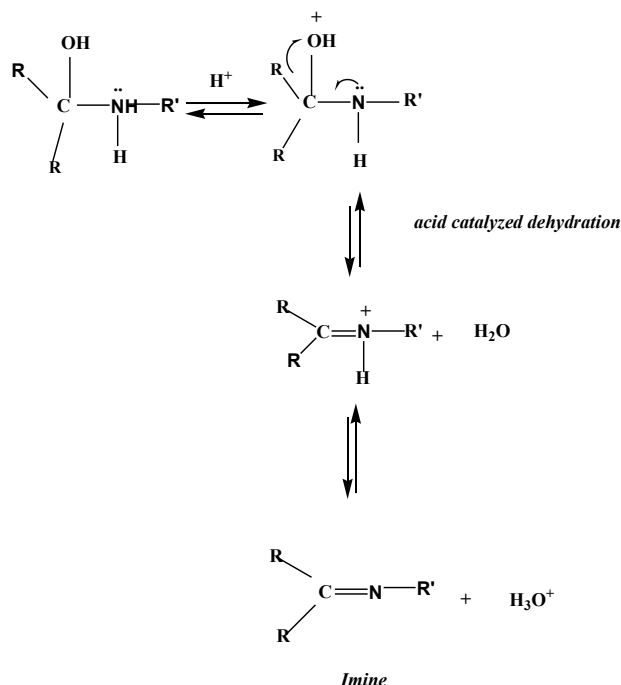
Schiff base are the compound containing azomethine group (-HC=N-). They are condensation products of ketones (or) aldehydes (aldehyde and ketones) with primary amines and were first reported by Hugo Schiff in 1864.[2] Formation of Schiff base generally takes place under acids or base catalysis or with heat. The common Schiff base are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids. Schiff base are used as intermediates for the synthesis of amino acids or as ligands for Preparation of metal complexes having a series of different structures.

A Schiff base behaves as a Flexi-dentate ligand and commonly co-ordinates through the O atom of the de -pronated phenolic group and the N atom of azomethine group.[3] In Schiff base azomethane nitrogen and other donor atoms like oxygen play a vital role in co-ordination chemistry. Hence an attempt is made to study the interaction of reduced Schiff base with transition of metals of biological interest and to investigate the co-ordination chemistry of such interactions. In the present work we described the synthesis and characterization of reduced Schiff base and its metal complexes.[4] Moreover antibacterial and analgesic activity of reduced Schiff base metal complexes is also evaluated and compared with the standards.[5]

Aromatic aldehydes especially with an effective conjugation system, form stable Schiff bases, where as those aliphatic aldehydes are unstable and readily polymerize. [6] Schiff base ligands with aldehydes are formed more readily than with ketone (carbonyl carbon). Schiff bases have very flexible and different structures. A wide range of Schiff base compounds and their behavior studied because these compounds have very flexible and diverse structure[7] Schiff bases are generally are bi, tri, or tetra-dentate chelate ligands and form very stable complexes with metal ions. Their chemical and physical properties in various field such as preparative uses, identification, or protection and determination of aldehyde or ketones, purification of carbonyl and amino compounds or production of these compounds in complex or sensitive reactions have studied by various workers [8,9]

Schiff base ligands have significant importance in chemistry, especially in the development of Schiff base complexes, because Schiff base complexes are potentially capable of forming stable complexes with metal ions. Many Schiff base complexes show excellent catalytic activity in various reaction at high temperature and in the presence of moisture. Over the past few years, there have been many report on their applications in homogeneous and heterogeneous catalysis, hence the need for a review article highlighting the catalytic activity of Schiff base complexes.

Metal complexes [Co(II), Cu(II) and Zn(II) ions] of Schiff base having played a central role in the development of co-ordination chemistry. Transition metal complexes have attracted curiosity due to DNA binding and cleavage properties under physiological conditions. Applications of metal complexes as chemical nucleases are the focus of current research. It has been demonstrated that in-organic complexes as chemical nucleases are the focus of current research. It has been demonstrated that inorganic complexes can be used in foot printing studies as sequence specific DNA binding agents, as diagnostic agents in medicinal applications and for genomic research.



The mechanism of Schiff base formation is another variation on the theme of nucleophile addition to the carbonyl group. In this case, the nucleophile is the amine. In the first part of the mechanism, the amine reacts with the aldehyde or ketone to give an unstable addition compound called carbinolamine. The carbinolamine loses water by either acid or base catalyzed pathways. Since the carbinolamine is an alcohol, it undergoes acid catalyzed dehydration.

Iminium salt ($R_2C=N^+R_2$) at the other extremes are very rapidly hydrolyzed by water and have to be prepared under rigorously anhydrous conditions. The facility of iminium salt hydrolysis has been put to use in a synthesis of secondary amines from primary amines which involves conversion into the aldimine ($R_1CH=NR_2$) and then by alkylation in to the iminium salt [$R_1CH=N^+R_2(R_3)X^-$] followed by hydrolysis to give the secondary amines (R_2NHR_3). Because of the involvement of Schiff base hydrolysis in a number of enzyme mediated processes, the detailed mechanism of hydrolytic cleavage of carbon-nitrogen double bonds have been the subject of close scrutiny both under in vivo and under in vitro conditions¹². Imines hydrolysis is also a key step in the Sommelet, Stephen, Sonn-Muller and Gattermann aldehyde synthesis.

1.1 Biological Importance of Schiff bases

Schiff bases have a large number of synthetic uses in organic chemistry. Acylation of Schiff bases by acid anhydrides, acid chlorides and acyl cyanides is initiated by attack at the nitrogen atom and leads to net addition of the acylation agent to the carbon-nitrogen double bond. Reactions of this type have been put to good use in natural product synthesis.[12] Schiff bases appear to be an important intermediate in a number of enzymatic reactions involving interaction of an enzyme with an amino or a carbonyl group of the substrate. One of the most important types of catalytic mechanism is the biochemical process which involves the condensation of a primary amine in an enzyme usually that of a lysine residue, with a carbonyl group of the substrate to form an imine or Schiff base.

Stereo chemical investigation carried out with the aid of molecular model showed that Schiff base formed between methylglyoxal and the amino group of the lysine side chains of proteins can bent back in such a way towards the N atom of peptide groups that a charge transfer can occur between these groups and oxygen atoms of the Schiff bases[13]. In this respect pyridoxal Schiff bases derived from pyridoxal and amino acids have been prepared and studied from the biological point of view.

Several studies have revealed that by condensation of salicylaldehyde with different heterocyclic compound and their[14,15] derivative with potent antibacterial and antifungal activity obtained. Osman prepared thiazidazole derivative compound of salicylaldehyde which were found to be highly potent antibacterial against *Bacillus cereus* and antifungal against *Aspergillus niger*. Several compound incorporating piperazinyl guanidine. When condensed with Salicylaldehyde were found to exhibit cardiovascular and vasodepressive antimicrobial activity.

II. Materials And Methods

2.1 Solvent Purification Methods

The solvent were purified by the reported procedures used in the synthesis of ligand and preparation of complexes and in various physical and chemical techniques.

2.2 Ethanol

Commercial ethanol was distilled from suspended impurities. To this anhydrous calcium oxide was added and refluxed for about 2 hours, distilled at 78°C and collected in a receiver fitted with a calcium chloride guard tube.

2.3 Acetone

Acetone was heated under reflux with sufficient quantity of potassium permanganate until the violet colour persists. It was then dried carbonate or anhydrous copper sulphate, filtered and fractionated was taken to exclude moisture.

2.4 Dimethylsulphoxide

This process consists in placing liquid DMSO with low water content in contact with an ion exchange resin in $-\text{SO}_3\text{H}$ form, and then separating the liquid from the resin. The DMSO thus obtained has a content of iron cation tracer element of less than or equal to 1 ppb and a content of a Na cation tracer element of less than or equal to 2 ppb.

2.5 Determination of Melting Point

Minimum amount of the substance was taken in a cleaned dry mortar with pestle. It was powdered well and taken in a small capillary tube with one end fused. A thermometer was kept in a sulphuric acid bath along with the stirrer. The capillary tube was mad to add here the thermometer, such that substance containing portion was nearer to the bulb of the thermometer and is heated slowly with constant stirring. The temperature at which the substance begins to melt was recorded.

2.6 Solubility Measurement

The individual components of the complex were having different solubility in different solvent. A little amount of the complex was taken in a test tube and dissolved in a series of solvent. The experiments were carried out with solvent like water, ethanol, acetone, benzene, dichloromethane dimethylsulphoxide and chloroform. In each case the solubility of the molecular complexes were recorded.

2.7 Techniques

Perkin-Elmer 783 FTIR spectrophotometer was used to record the IR spectra of the ligand in the range of $400\text{-}4000\text{cm}^{-1}$. The Ultraviolet-visible were recorded by using a Shimadzu in the range of $200\text{-}1100\text{nm}$.

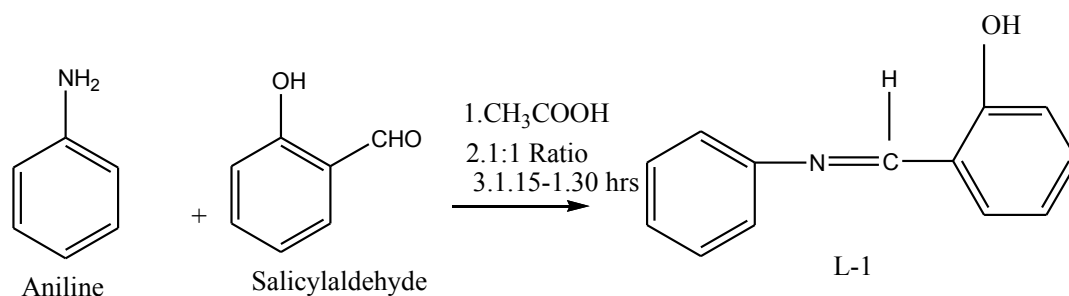
III. Experimental Work

All reagents and chemicals as well as solvents were purchased from pure Sigma products.

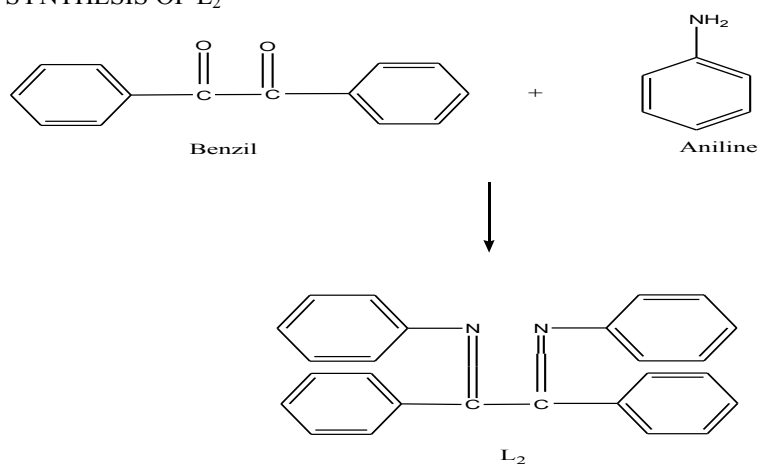
3.1 Synthesis of Ligand

The Aromatic aldehyde/substituted aldehyde in ethanol (20 mmol) are mixed with 20mmol of Amine/substituted amine, and the mixture is stirred for 1-2 hours for the magnetic stirrer method.

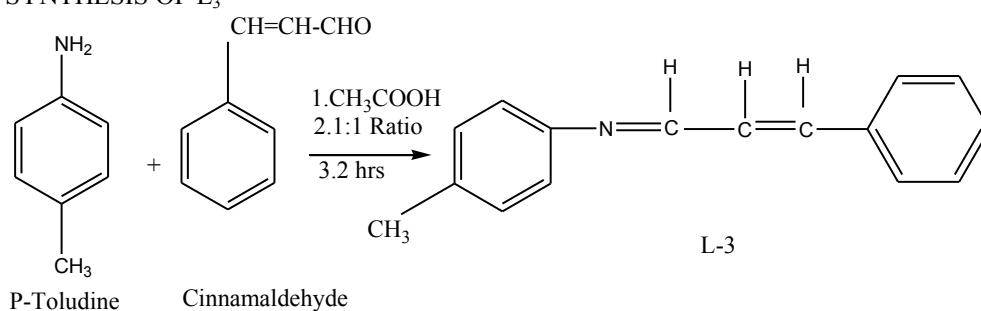
SYNTHESIS OF L₁



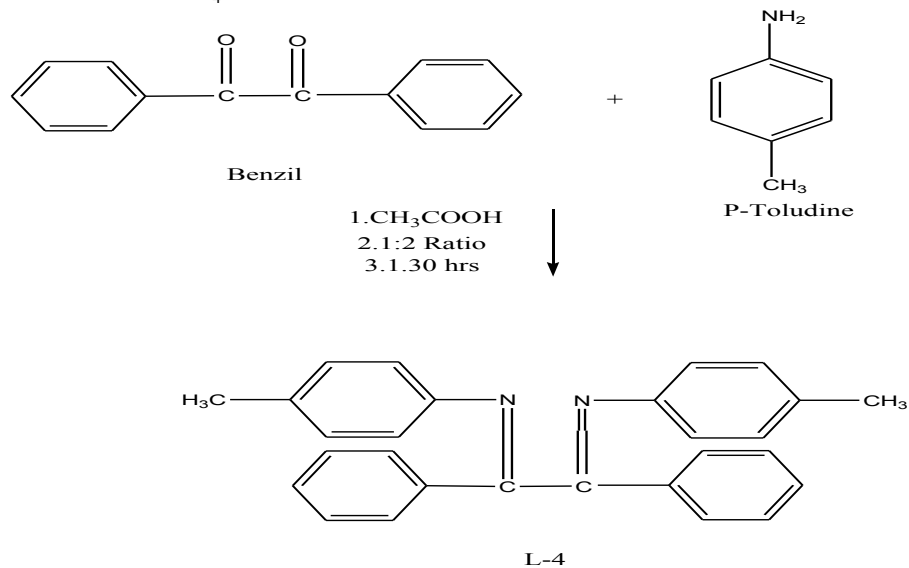
SYNTHESIS OF L₂



SYNTHESIS OF L₃



SYNTHESIS OF L₄



IV. Result And Discussion

The ligands are yellow colour solid and they are insoluble in organic solvents and the ligands having sharp melting point and IR spectral & UV spectral are given below tables.

Table-1

S.No	Schiff base	Ratio of reactants	Time(hrs)	Colour	Melting Point
1.	Salicylaldimine	1:1	1.15-1.30	Yellow	215
2.	Benzilimine	1:2	1.45	Pal yellow	142
3.	P-Toludine cinnamaldimine	1:1	2.00	Yellow	165
4.	P-Toludine benzilimine	1:2	1.30	Yellow	185

3.1 Spectral Characterization

3.1.1 FT-IR Spectra

When the infrared light is passed through a sample of organic compound, some of the frequencies absorbed and the absorbed or transmitted is plotted against frequency, the result is infrared spectrum the excitation of molecular vibration and rotation gives rise to absorption in the infrared region of the spectrum.

All the ligands are stable and have sharp melting point that indicate the purity of the ligands. The IR of each ligand confirms the formation of Imines bond (-C=N-H) and the absences of carbonyl bond (C=O). Actual band at 1643-1530 cm^{-1} is assigned to stretching vibration of the imines group at (-C=N-H). All the ligands displayed a band at 1290-1292 cm^{-1} but in the L₂ has the value is 1138 cm^{-1} which is assigned to $\nu(\text{C-O})$ stretching vibration. In the V(C-OH) band are absorbed in the range 1321-1371 cm^{-1} In the L₂ has slight higher value 1498 cm^{-1} but actual value is 1410-1310 cm^{-1} .

The IR spectra of Schiff base under study are shown the table-2 and figure of IR data. A strong to medium intensities bands are assigned to the carbon nitrogen double bond .i.e.(C=N) with the stretching frequency range between 1620-1587 cm^{-1} .

In the Aromatic C-H band has the region 3037-3047 cm^{-1} but in the L₃ has slight higher the value is 2546 cm^{-1} .

Table-2

S.No	Nomenclature	IR-band (C=N) cm^{-1}	IR -band (Ar-C-H) cm^{-1}	IR-band (C-OH) cm^{-1}
1.	Salicylaldimine	1620	3037	1381
2.	Benzilimine	1587	3049	1498
3.	P-Toludine Cinnamaldehyde	1614	2546	1371
4.	P-Toludine benzilimine	1620	3037	1321

3.1.2 UV-Spectra:

The UV- spectra of Schiff base under study for the ligands are shown figure of UV-spectra. In the UV spectra of all Schiff bases are dissolved in the DMSO solution. And gives the UV-data are shown in the following table-3.

1. The lower wavelength for the Schiff bases has a range between 260nm to 290nm. These values assigned to $n-\pi^*$ transition Schiffbase (C=N) and aromatic nature of Schiff bases. These have the molar extinction coefficient values is <100.

2. The longer wavelength for the table-3 gives the range between 337nm to 347nm.And E_{max} are greater to the $\pi-\pi^*$ transition and >10000 are given the values of the Following table-3.

Table-3

S.No	Nomenclature	UV-band (C=N)nm	UV-bands($\pi-\pi^*$)
1.	Salicylaldimine	260.80	341.40
2.	Benzilimine	262.60	341.40
3.	P-Toludine Cinnamaldehyde	291.20	337.60
4.	P-Toludine benzilimine	260.20	347.20

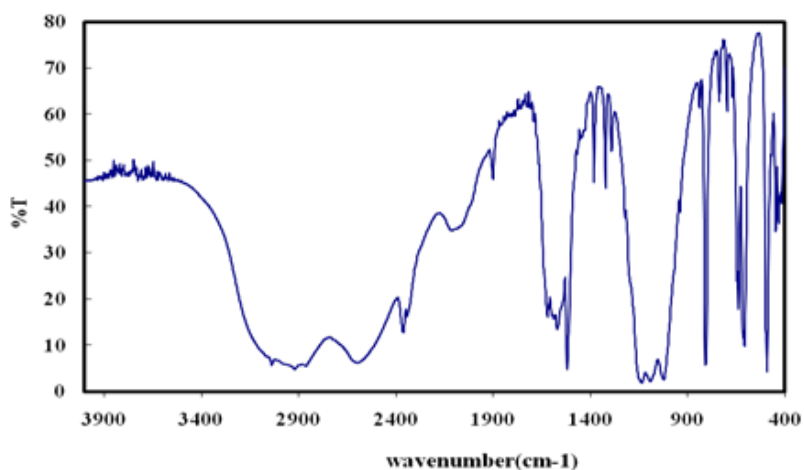
V. Conclusion

The new Schiff bases are synthesis from various aldehyde and amine under magnetic stirrer method .The synthesized Schiff base were characterized by spectral techniques (UV-Spectra & IR-Spectra). And the Schiff base are solid and having sharp melting point.

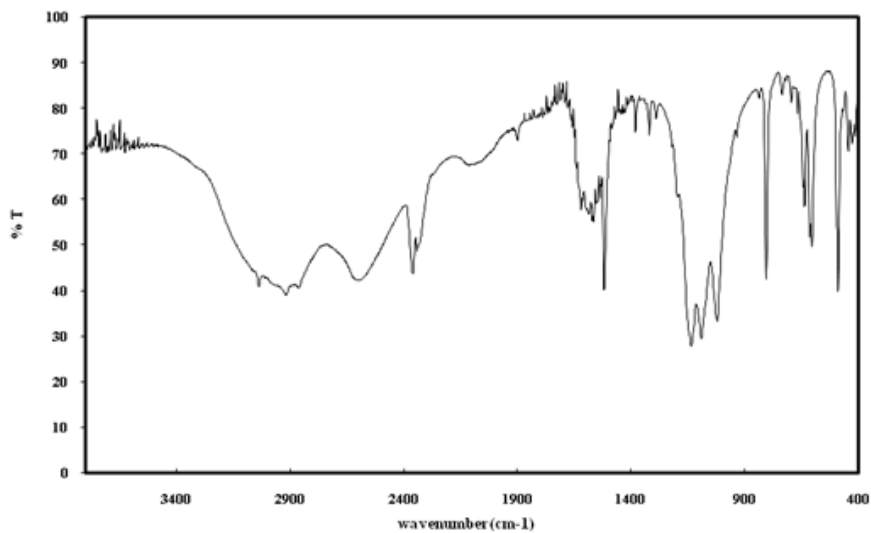
Table-4

S.No	Nomenclature	Yield(g)	Time (hrs.)
1.	Salicyladimine	1.24	1.30
2.	Benzimine	1.68	1.45
3.	P-Toudine cinnamaldimine	1.05	2.00
4.	P-Toludine benzilimine	1.47	1.30

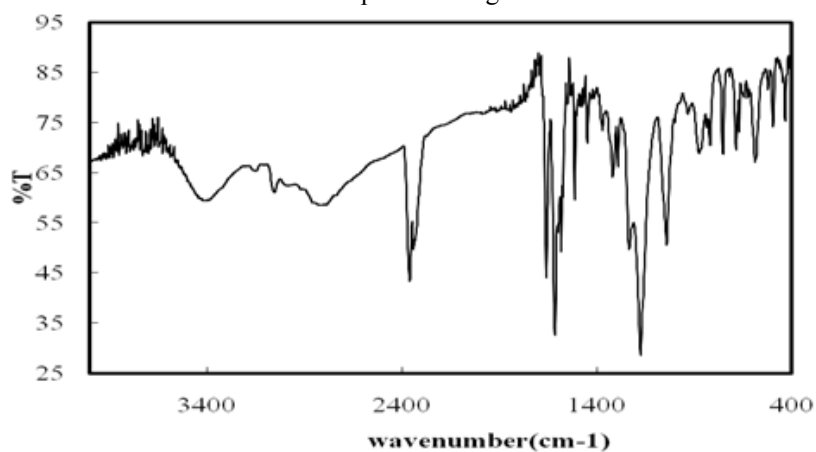
FT-IR Spectra for ligand 1



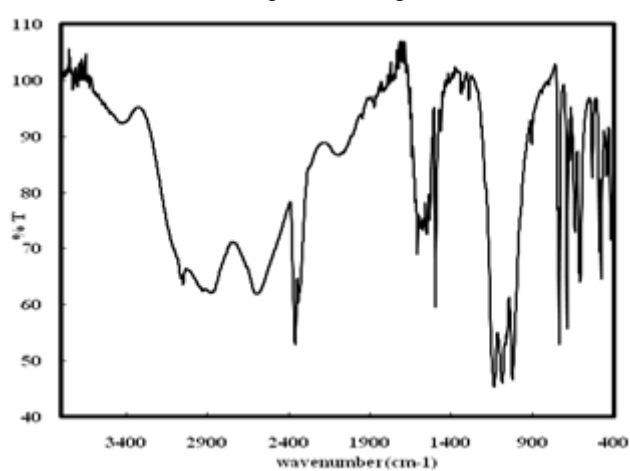
FT-IR Spectra for ligand 2



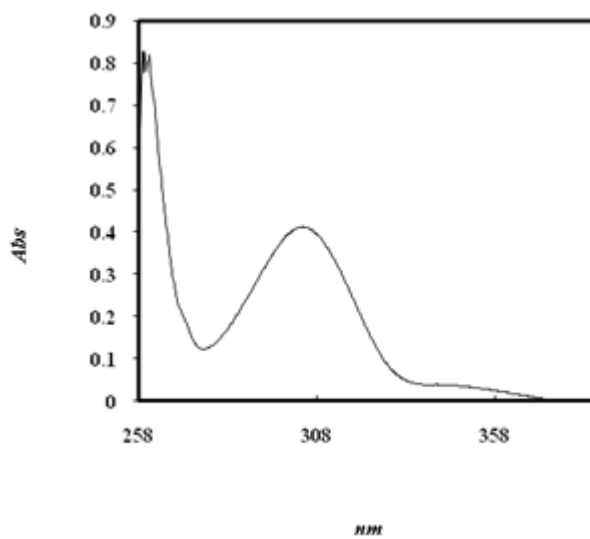
FT-IR Spectra for ligand 3



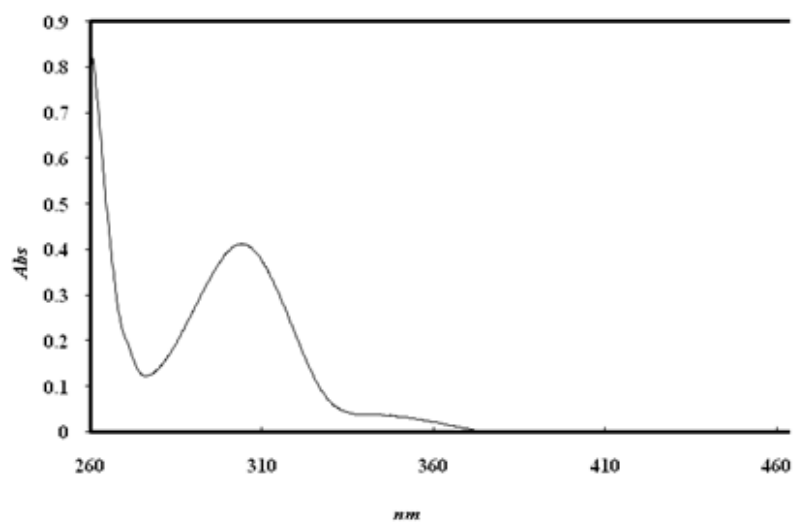
FT-IR Spectra for ligand 4



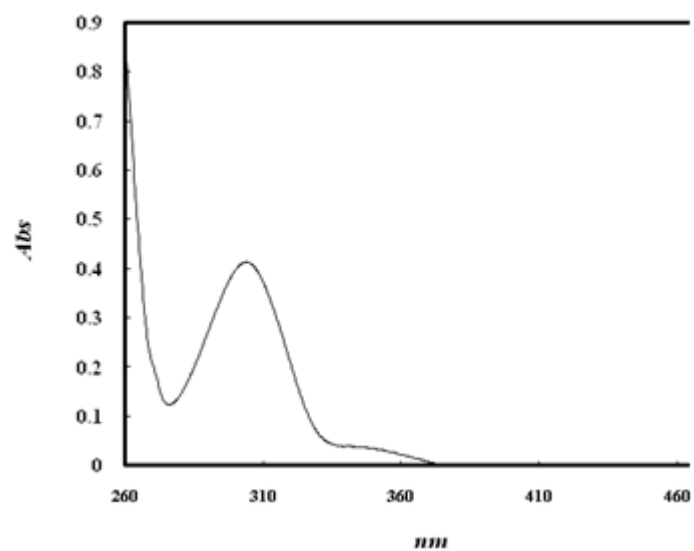
UV-Visible spectra for Ligand-1



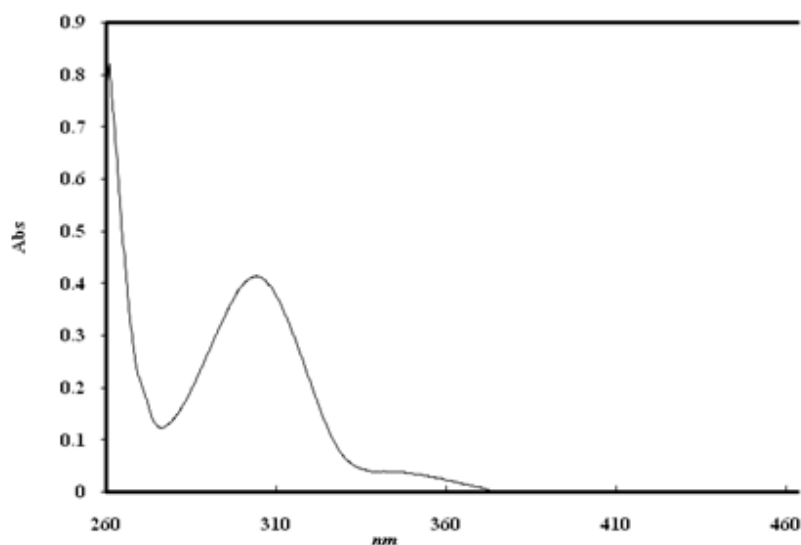
UV-Visible spectra for Ligand-2



UV-Visible spectra for Ligand-3



UV-Visible spectra for Ligand-4



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