STUDIES ON ORGANOMETALLIC CHEMISTRY OF RUTHENIUM

A DISSERTATION

Submitted in partial fulfillment of the requirements for the award of the degree of

MASTER OF TECHNOLOGY

in

ADVANCED CHEMICAL ANALYSIS

By

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to

my family and friends

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CERTIFICATE

This is to certify that the thesis entitled "STUDIES ON ORGANOMETALLIC CHEMISTRY OF RUTHENIUM" submitted by Ramakant Sahu who got his name registered on July 2005 for the award of M. Tech. degree in Advanced Chemical Analysis of Indian Institute of Technology Roorkee, is absolutely based upon his own work under my supervision and that neither this thesis nor any part of it has been submitted for any degree/diploma or any other academic award anywhere before.

Date: 29/6/07

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Preface

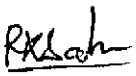
Preface

The work embodied in this thesis entitled ***"Studies on Organometallic Chemistry of Ruthenium"*** *was initiated in August, 2006.*

The thesis consists of two chapters. The synthesis, characterization and structure determination of isoindole derivatives and their reactivities with $Ru(PPh_3)_3Cl_2$ *are described in Chapter I. In Chapter II synthesis and characterization of a novel organometallic ruthenium nitrosyl complex is reported and the possibility of photolability of this complex is also explored.*

All the ligands and complexes described in this thesis were characterized by elemental analysis followed by spectral analysis. The structures of the two ligands were determined by three dimensional X-ray crystallography.

In keeping with the general practice of reporting scientific observations, due acknowledgement has been made of the findings of other investigators. I must take the responsibility of any unintentional oversights and errors which might have crept in.



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Acknowledgement

Acknowledgement

It was good fortune that I got the opportunity to pursue my M. Tech. studies under the guidance of Dr. Kaushik Ghosh. With due respect to his valuable scientific advice, constructive criticism and elegant personality I take this opportunity to express my deepest gratitude to my mentor for his encouragement and stimulating guidance throughout my M. Tech. programme here.

I express my sincere regards to the head of the department Professor Ravi Bhushan, Dr. R. K. Dutta coordinator of the M. Tech. programme and other faculty members.

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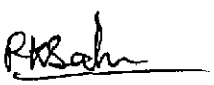
I specially thanks to Neeraj Naithani, Sridharan Srinath, Sanjay Maurya and Pankaj Choubey for their help and inspiration.

I wish to thank to all my family members and relatives for giving me close association as well as constant inspiration.

Financial support of the Ministry of Human Resources, Government of India is gratefully acknowledged. Lastly I am thankful to my institute (IIT Roorkee) for all the infrastructural facilities.



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Synthesis, Characterization and Structure Determination of Isoindole Derivatives and their Reactivities with $Ru(PPh_3)_3Cl_2$

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Synthesis, Characterization and Structure Determination of Isoindole Derivatives and their Reactivities with $Ru(PPh_3)_3Cl_2$

Abstract

Reaction of pthaladehyde with primary amine in ethanol gave rise to isoindole derivative. Two derivatives namely 4-methyl-N-(2-*p*-tolylisoindolin-1-ylidene)benzenamine (L_1) and 4-methoxy-N-(2-(4-methoxyphenyl)isoindolin-1-ylidene)benzenamine (L_2) were structurally characterized X-ray diffraction and by elemental analysis, UV-VIS and IR studies. Crystal data of L_1 are as follows: crystal system, orthorhombic; space group *Pna21*; a=19.0212Å, b=12.7684Å, c=7.1666 Å, $\alpha=\beta=\gamma=90^0$; V= 1740.6Å^3; Z=4; R1=10.6%; wR2=15.98%. Crystal data of L_2 are as follows: crystal system, monoclinic; space group *P-1*; a=5.1956 Å, b=13.1475 Å, c=13.4222 Å, $\alpha=107.855^0$, $\beta=98.780^0$, $\gamma=95.820^0$; V=916.859 Å^3; Z=2; R1=6.79%; wR2=29.97%. L_1 and L_2 result an orthometallated ruthenium complex when they react with $Ru(PPh_3)_3Cl_2$. The resultant organometallic ruthenium complexes were characterized by elemental analysis, UV-VIS, IR and ^{1}H NMR studies.

1. INTRODUCTION AND LITERATURE REVIEW

The chemistry of ruthenium has been receiving considerable current attention largely because of the interesting redox, photophysical, photochemical and biological properties exhibited by its complexes.[1] In general, the nature of metal ions, its oxidation state, the types and the number of bound ligands can all exert a critical influence on the activity of a metal complex. Because of the wide spectrum of coordination numbers, coordination geometries, thermodynamic and kinetic preferences for ligand atoms, and in some cases redox active metal complexes, offer novel mechanism of action which is unavailable to organic compounds. Ruthenium compounds are well-suited for medicinal applications also. They have been investigated as immunosuppressants, nitric oxide scavengers, antimicrobial agents, and antimalarials.[2] Electron transfer reaction in metalloproteins were extensively studied by Harry Gray and his coworkers.[3]

1.1 Ruthenium Complex as Antimalarial:

Sanchez-Delgado *et al.* synthesized[4] a novel chloroquine complex of ruthenium metal (Figure 1). They tested the antimalarial potential of the complex *in vitro* and *in vivo* and reported that the incorporation of the ruthenium complex produced an enhancement of the efficacy of chloroquine. They also mentioned that the no sign of acute toxicity was observed in experimental animals after a prolonged period of time. They found that the complex $[RuCl_2(CQ)]_2$ (CQ = Chloroquine) was also found to be considerably more active than chloroquine diphosphate in *in vitro* tests against chloroquine-resistant strains of *P. falciparum*.

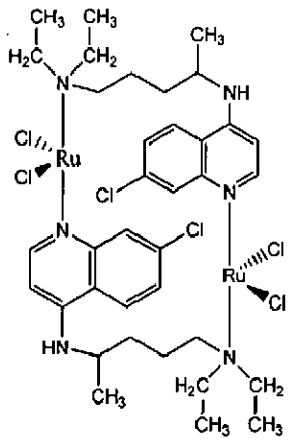


Figure 1: **$[RuCl_2(CQ)]_2$**

1.2 Ruthenium Schiff-base Complexes:

In recent years, the use of metal Schiff base complexes to catalyse organic reactions has received much attention.[5] Ruthenium Schiff base complexes, particularly those containing nitrogen and oxygen as donor atoms, were found to be very efficient catalysts in the oxidation of alcohols and alkenes.[6]

1.3 Introduction to Organometallic Complex:

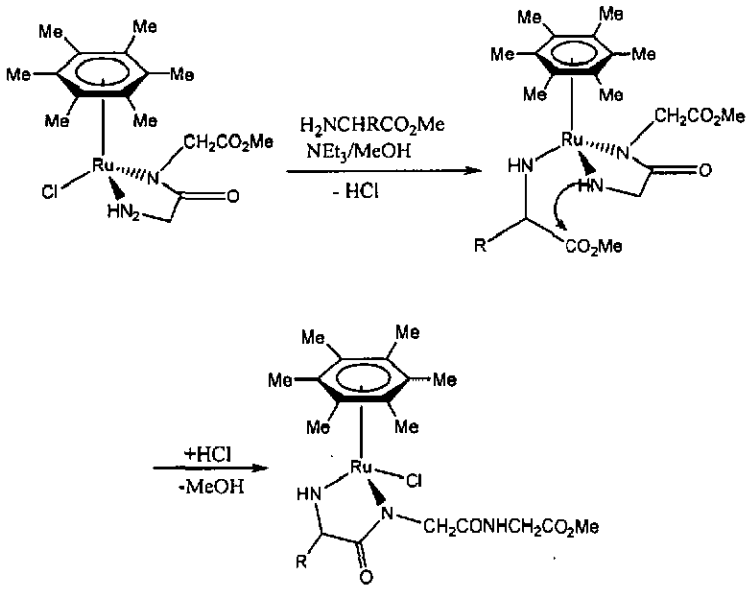
The complexes which have at least one direct metal-carbon bond are known as the organometallic complexes. Natural biomolecules with metal-carbon bonds have been shown to exist;[7] a well established example is methylcobalamin (methyl-B_{12}), which contains a distinct Co-CH_3 bond. It acts as a methylating agent in many important biochemical reactions. Recently, enzymes with metal carbon bonds have also been discovered,[8] *e.g.* NiFe hydrogenase. Ruthenium chemistry especially organometallic chemistry of ruthenium is an important area of modern research.[9]

[1.3.1] Ruthenium in Bioorganometallic Chemistry:

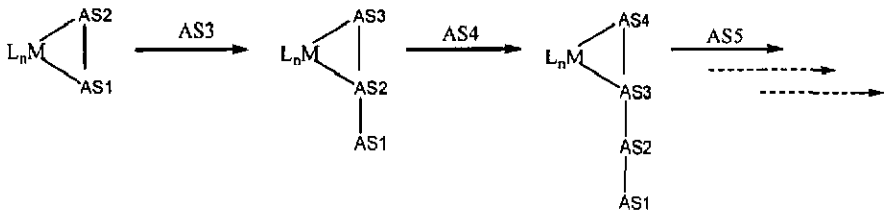
Fish *et al.* in his review entitled "Bioorganometallic Chemistry: Structural Diversity of Organometallic Complexes with Bioligands and Molecular Recognition Studies of Several Supramolecular Hosts with Biomolecules, Alkali-Metal Ions, and Organometallic Pharmaceuticals" metioned[10] that bioorganometallic chemistry is now establishing itself as an important branch of the chemistry.

Severin *et al.* have reported[11] half-sandwich complexes of ruthenium ("piano-stool" complex). These complexes have been used as a catalyst to develop a sequence-specific peptide synthesis, where the linking of the peptide bond requires neither activating reagents nor protecting groups. They reported the reaction where N, N'–coordinated peptides undergo selective chain lengthening at the N–terminus by reaction with α–amino acid esters. The resulting peptide ester can then be cleaved from the metal complex without racemization. Scheme 1 shows the reaction mechanism. This template–directed condensation proceeds through nucleophilic attack of an amino anion on the carbonyl group of the η^1–N–coordinated amino acid ester. In principle, the mechanism shown in Scheme 2 permits further chain–lengthening as desired with repeated addition of α–amino acid esters the coordinated peptide is successively lengthened at the N–terminus.[12] The half–sandwich

complex acts here solely as a catalyst.



Scheme 1: Sequence specific peptide synthesis at chiral half–sandwich complexes of ruthnium



Scheme: 2 Metal–catalyzed construction of peptides by successive reaction of α amino acid esters with coordinated peptide complexes.

[1.3.2] Ruthenium Organometallic Complexes in Catalysis: Grubbs's Catalyst:

Olefin metathesis is fundamental chemical reaction involving the rearrangement of carbon–carbon double bonds, and can be used to couple, cleave, ring–close, ring–open, or polymerize olefinic molecules and thus the olefin metathesis has led scientists to discover new disconnections in organic synthesis, paving the way for new advances in drug discovery, polymer chemistry, and natural product synthesis. The widely accepted view that olefinic metathesis revolutionized the different fields of synthetic chemistry led to the awarding of the 2005 Noble Prize in Chemistry to Robert H. Grubbs, Yves Chauvin, and Richard R. Schrock "for the development of the metathesis method in organic synthesis".

Dr. Grubbs provided synthetic chemists with active catalysts that could be handled in air and

were tolerant of various functional groups, such as esters, amides, ketones, aldehydes, and even protic functionalities like alcohols, water and acids.[13]

The Grubbs catalysts are based on a ruthenium atom surrounded by five ligands:

- Two neutral electron - donating entities (e.g., trialkylphosphines, N–heterocyclic carbenes)
- Two mono–anionic groups (e.g., halides)
- One alkylidene moiety (e.g., unsubsitituted and substituted methylidenes)

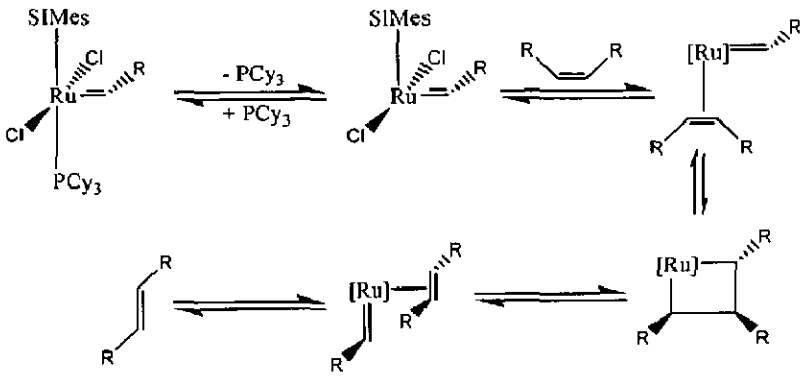
These catalysts are divided into two categories based on the nature of the neutral ligands:

1. **First–Generation Grubbs catalysts:** These were discovered first, and are represented by the general formula $L_2 X_2 Ru = CHR$ (where L is is a phosphine ligand).
2. **Second–Generation Grubbs Catalysts:** These were discovered subsequently and their general formula is (L) (L') X_2 Ru = CHR (where L is phosphine ligand and L' a saturated N–heterocyclic carbene or NHC ligand) (Figure 2).

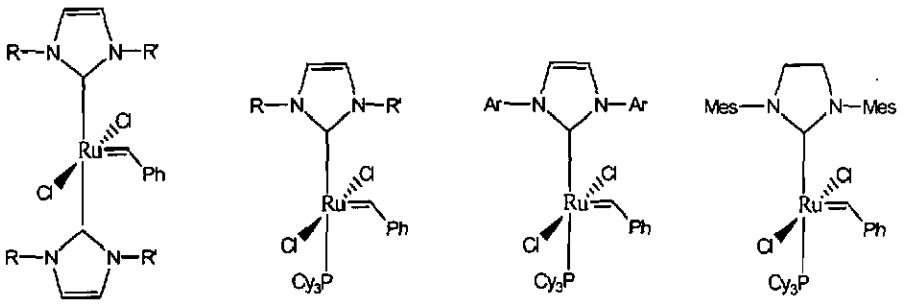
First - Generation Grubbs Catalyst

Second - Generation Grubbs Catalyst

Figure 2: Most commonly used first – and second – generation Grubbs catalyst



Scheme 3: Mechanism of the metathesis of a symmetrical cis olefin to its trans isomer.



R and R' are achiral or chiral alkyl groups such as i-Pr, Cy, or CHMePh; Ar = Aryl; Mes = Mesityl

Increasing metathesis Activity

Diver *et al.* mentioned[14] in his review that the use of the Grubbs' family of ruthenium carbene catalysts have revolutionized alkene metathesis.

Grubbs and coworkers reported[15] a ring-closing metathesis by using the second-generation Grubbs catalyst (Figure 3).

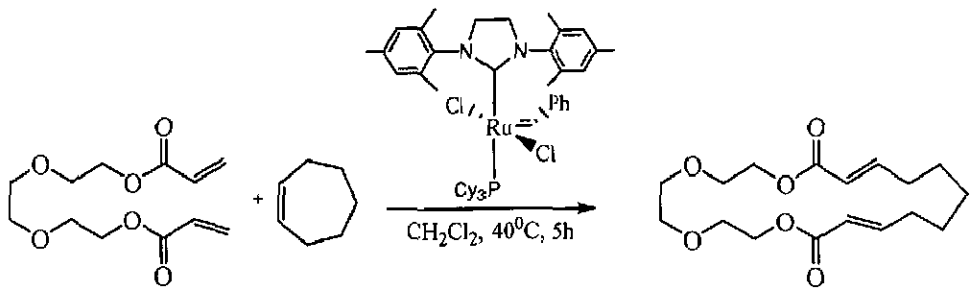


Figure 3: Ring closing metathesis

Kingsbury *et al.* reported[16] that the Ru based metathesis catalyst is recyclable. They recovered $PCy_3Cl_2Ru(=CH\text{-}o\text{-}OMe_2C_6H_4)$ in 87% purified yield after 4 days in refluxing CH_2Cl_2 and they used this catalyst for three additional rounds of the metathesis reaction (Figure 4).

This result attests to the stability of the complex. They further stated that an inert atmosphere is not required to prevent decomposition of the catalyst and in the solid state; this complex is stable indefinitely in air. Furthermore, after one week in undistilled organic solvents in the presence of water, alcohol, and/or dilute acid (0.01 M HCl), no signs of decomposition (<2%) are evident. They observed that $PCy_3Cl_2Ru(=CH\text{-}o\text{-}OMe_2C_6H_4)$ is

exceptionally robust and can be purified to homogeneity as a dark brown crystalline solid by simple silica gel column chromatography.

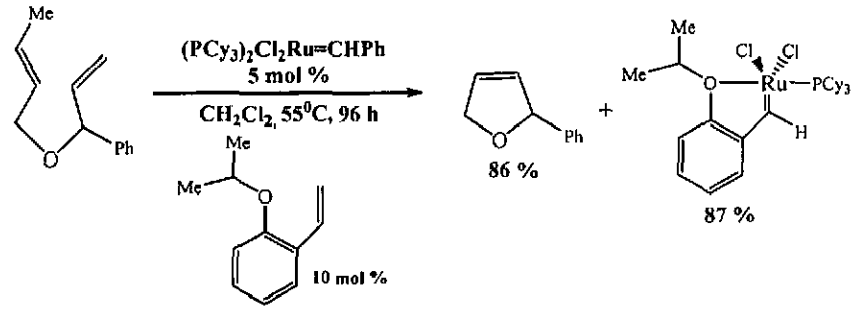


Figure 4: Recovery of the Grubbs catalyst

[1.3.3] Ru-CO Organometallic Complex as the Rapid Source of CO:

Johnson *et* al. have shown[17] that ruthenium carbonyl complexes, *e.g.* $[Ru(CO)_3Cl(glycinate)]$ (Figure 5), have the tendency to serve as rapid source of CO *in vivo*, due to which they could suppress organ graft rejection and protect tissues from ischemic injury. They also reported that blood platelet aggregation is partially inhibited by $[Ru(CO)_3Cl(glycinate)]$.

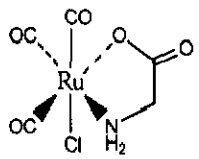


Figure 5: $[Ru(CO)_3Cl(glycinate)]$

[1.3.4] Ruthenium Organometallic Complexes as Anti Cancer Agents:

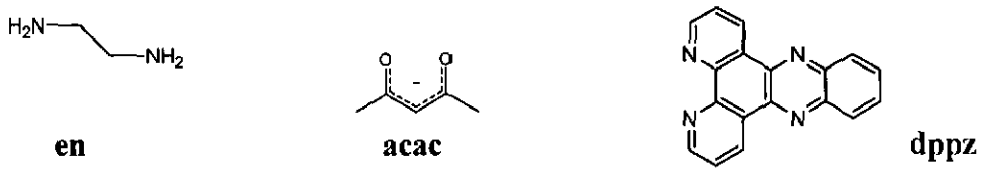
Sadler and coworkers reported[18] in his review that organometallic chemistry of ruthenium has a lot of contribution in cancer therapy. In particular, organometallic complexes, *i.e.* complexes with at least one direct metal-carbon bond, have the large diversity of structure and bonding modes (*e.g.* π-coordination, M-C multiple bonds) that are unique to them due to which they offer much potential for exploration as anticancer agents.

Sadler and coworkers found that Ru(II) aminophosphine complexes are cytotoxic to cancer cells but they bear poor aqueous solubility and also are difficult to isolate and purify in large quantities. Aqueous solubility is very important for any drug to be pharmaceutically useful. On an investigation, they found that "half-sandwich" Ru(II) mono-arene complexes often

possess good aqueous solubility and the arene ligand is relatively inert towards displacement under physiological conditions.

A typical structure of a half-sandwich "piano-stool" [(η^6-arene)Ru(X)(Y)(Z)] complex is shown in Figure 6.

Figure 6: Structure of [(η^6 arene)Ru(X)(Y)(Z)] complex

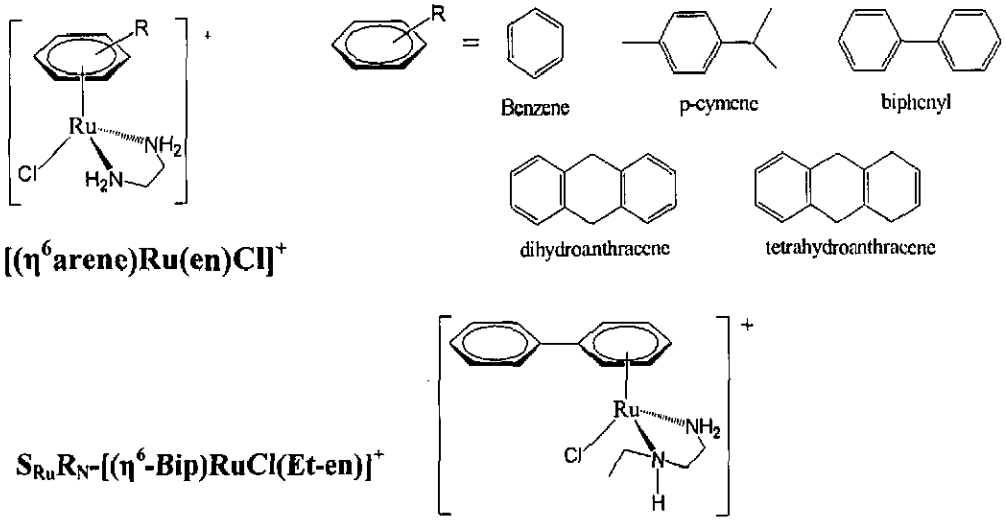


en **acac** **dppz**

Examples of L

Figure 7: Typical structure of Ru(II) half-sandwich complexes and examples of chelating ligands (L)

Authors reported that the complexes [(η^6-arene)Ru(en)Cl]$^+$ (Figure 8) exhibited the reproducible cytotoxicity against human ovarian cells. Activity appeared to increase to with the size of the coordinated arene.



[(η^6arene)Ru(en)Cl]$^+$

$S_{Ru}R_N$-[(η^6-Bip)RuCl(Et-en)]$^+$

Figure 8: Examples of mono-nuclear Ru(II) arene complex.

[1.3.5] Biocatalysis by Ru(II) Arene Complexes :

Along with the anticancer potential of the Ru(II) arene complexes, Sadler and coworkers reported[18] an interesting feature of these complexes that they can act as the biocatalyst. These complexes form stable hydride complexes in aqueous solution with formate as the hydride donor:

$$[(\eta^6\text{-}C_6Me_6)Ru(bpy)(H_2O)]^{2+} + HCO_2^- \longrightarrow [(\eta^6\text{-}C_6Me_6)Ru(bpy)(H)]^+ + CO_2$$

(bpy = 2,2'-bipyridine)

They reported that complexes such as $[(\eta^6\text{-}C_6Me_6)Ru(en)(H_2O)]^{2+}$ (en = ethylenediamine) have the potential to catalyse regioselective reduction of NAD^+ under biological conditions. These reductions occur through the hydride complex formation *i.e.* $[(\eta^6\text{-}C_6Me_6)Ru(en)(H)]^+$. However, such reactions are slow but the further research in this field is underway.

[1.3.6] Ruthenium Organometallics as Antimicrobial Agents:

Allardyce *et al.* prepared[19] some organometallic ruthenium complexes according to the following scheme (Figure 9) and reported that the product showed varying degrees of anti-microbial activity and suggested that the pta (pta : 1,3,5-triaza-7-phosphatricyclo[3.3.1.1]decane) ligand plays a role in cytotoxicity. They mentioned that the pta group could facilitate the ability of a compound to cross a cell membrane.

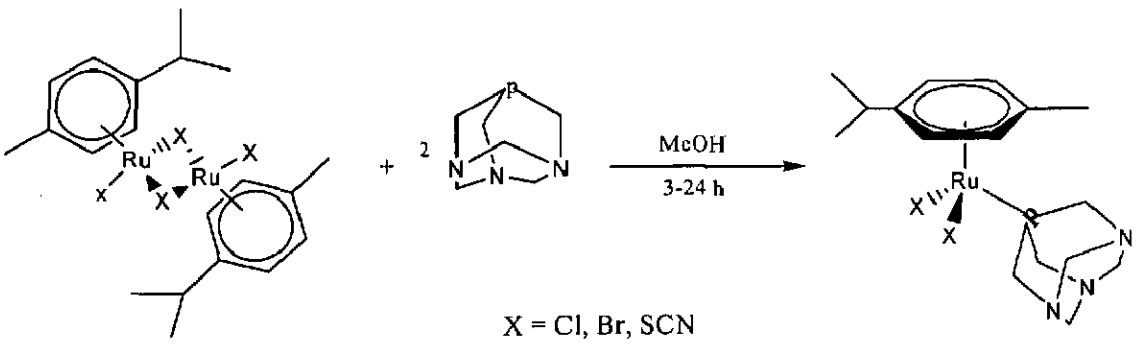


Figure 9: Synthesis of Antimicrobial Compounds

They also reported that the following complex exhibited the activity against polio virus.

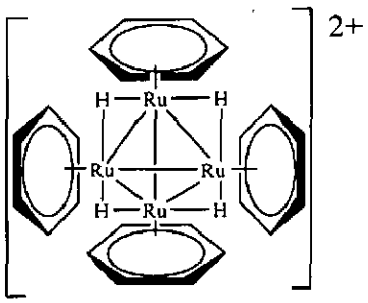
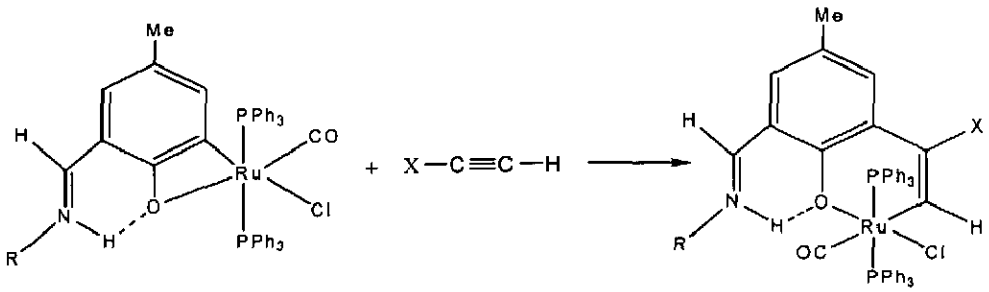


Figure 10: Ruthenium organometallic complex having anti polio activity

[1.3.7] Alkyne Insertion into Ru-C Bond: A Versatile Tool for Organometallic and Organic Synthesis:

[a] Metallacycle expansion:

Ghosh *et al.* provided[20] the new family of ruthenium organometallic compound by the regiospecific alkyne insertion into ruthenium-carbon bond (*i.e.* metallacycle expansion). They are the first to report the insertion of unsubstituted alkyne to Ru-C bond. They expanded the four-membered metallacyle to six membered (Figure 11). The net outcome of this type of reactions is the formation of new metal-carbon, carbon-carbon, and/or carbon-nonmetal bonds. This makes alkyne insertion a potentially versatile tool for organometallic and organic synthesis.



R=Alkyl or Aryl, X= H, Ph, CH_2OH

Figure 11: Alkyne insertion to the Ru-C bond

[b] Cumulene formation and bis-insertion:[21]

Bruce *et al.* reported the synthesis of cummulene and bis insertion reaction.

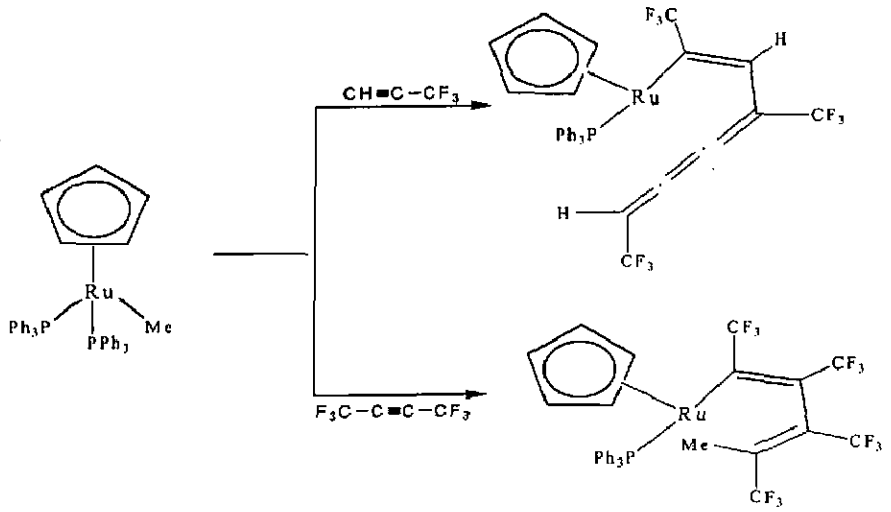


Figure 12: Cumulene formation

[c] η^5- cyclopentadienyl formation:

Lutsenko *et al.* reported[22] the coupling reaction of a π-allyl ligand with an alkyne molecule to give a cyclopentadienyl ring (Figure 13).

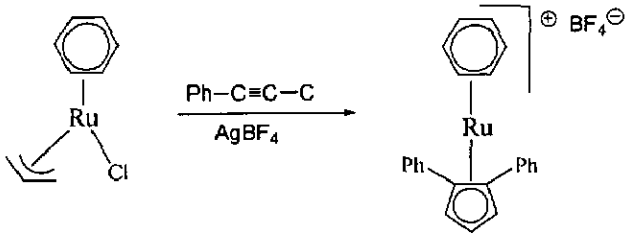
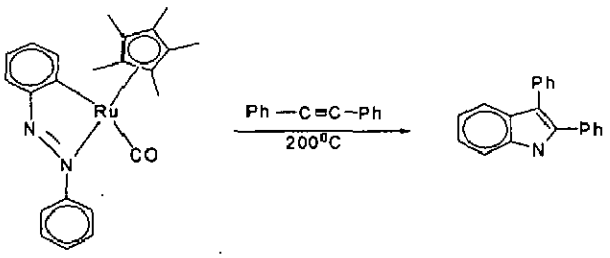


Figure 13: η^5- Cyclopentadienyl formation

[d] Indole synthesis:

Garn *et al.* reported[23] a very important method of indole synthesis through alkyne insertion into Ru-C bond of an organometallic ruthenium complex (Figure 14).

Figure 14: Indole synthesis through alkyne insertion



[e] Alkyne insertion:

Ferstl *et al.* reported[24] the alkyne insertion to Ru-C bond followed by the reductive elimination to produce the heterocyclic compound under extremely mild conditions (Figure 15)

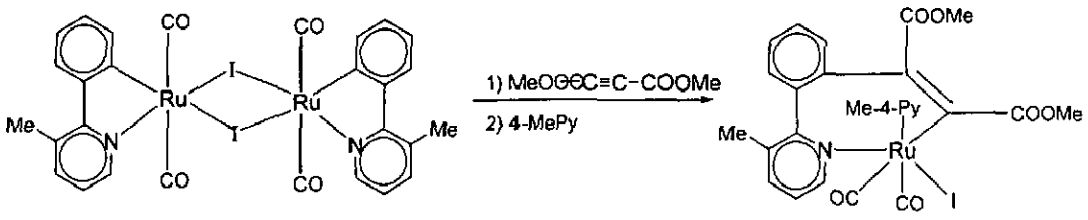


Figure 15: Alkyne insertion

Hence chemistry as well as organometallic chemistry of ruthenium are growing fields of chemical research with applications to organic, organometallic, inorganic and biological chemistry.

Chakravorty and coworkers worked with following ligand,[25] (Figure 16) 4-methyl-2,6-diformylphenol.

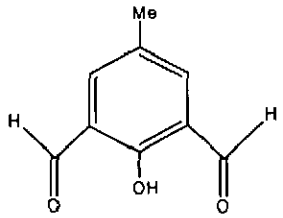


Figure 16: 4-methyl-2,6-diformylphenol

This ligand reacts with $[Ru(PPh_3)_3Cl_2]$ and gives an organometallic complex shown in Figure 17.[25]

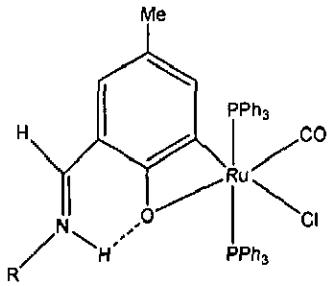
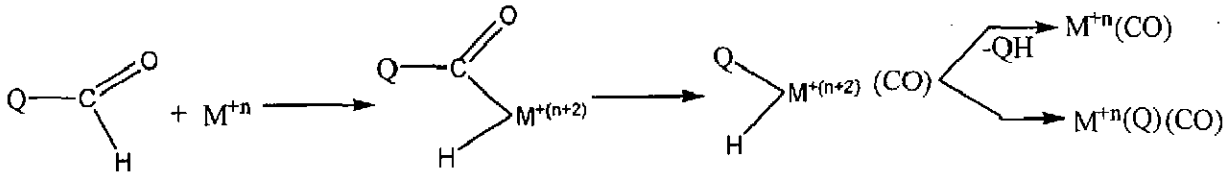


Figure 17: Ru(p-MeC$_6$H$_4$L)(CO)(PPh$_3$)$_2$Cl

Decarbonylative orthometallation leads to the formation of a sigma aryl ruthenium complex with zwitterionic iminium phenolato motif. There is a phenolic group in between two aldehyde groups in the above ligand. The mechanism of formation of the ruthenium complex has been described as shown in Scheme 4.[26]

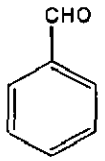


Q = alkyl or aryl

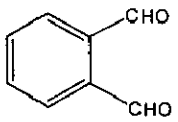
Scheme 4: Mechanism of decarbonylative orthometallation process

The above predicted mechanism has been supported by the formation of retrodecarbonylation reaction of the σ-aryl complex with isocyanide.[27] Rhodium derivative of the same ligand system (Schiff bases of 4-methyl-2,6-diformylphenol) gave rise to a new family of acyl rhodium organometallic complexes.[28] So the acyl intermediate was stabilized in those complexes. Moreover, Panda *et al.* also reported[29] that acyl ruthenium organometallic complex could also be formed by CO insertion in the Ru-C bond of $Ru(p\text{-}MeC_6H_4L)(CO)(PPh_3)_2Cl$ (Figure 17).

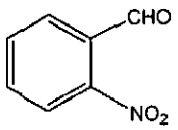
Herein we took the following ligands (shown in Figure 18) and studied their reactivities with $Ru(PPh_3)_3Cl_2$.



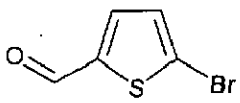
benzaldehyde



Pthalaldehyde



o-nitrobenzaldehyde



5-bromothiophene-2-carbaldehyde

Figure 18: Ligands used to study their reactivities with $Ru(PPh_3)_3Cl_2$

Synthesis & characterization of ligands and their interaction with $[Ru(PPh_3)_3Cl_2]$ will be described in this thesis.

2. EXPERIMENTAL:

[2.1] Materials:

S. No.	Chemical	Grade	Make
1.	Pthalaldehyde	AR	SRL
2.	p-toluidine	GR	Loba Chemie
3.	p-anisidine	LR	Himedia
4.	p-chloroaniline	LR	Thomas Baker
5.	Ruthenium trichloride trihydrate	Pure	SRL
6.	Triphenylphosphine	Pure	SRL
7.	2-nitrobenzaldehyde	AR	SRL
8.	Methanol	AR	sdfine
9.	Ethanol	AR	Changshu Yanguan
10.	Dichloromethane	AR	Rankem
11.	Acetonitrile	AR	Rankem
12.	Chloroform	LR	Sdfine
13.	Ethylamine	LR	Rankem
14.	5-bromothiophene-2-carbaldehyde	AR	Acros

[2.2] Synthesis:

[2.2.1] 4-methyl-N-(2-*p*-tolylisoindolin-1-ylidene)benzenamine (L_1):

This Schiff base ligand was prepared by refluxing 0.335g (2.5 mmol) of pthalaldehyde and 0.546g (5.1 mmol) of *p*-toluidine They were refluxed for 1.5 h using 50 mL of methanol as solvent. After refluxing the solvent was evaporated in vacuo, on evaporation yellow-orange product obtained which was washed with little amount of methanol and dried. The product was recrystalized in DCM : ACN (3:1). Very good crystals obtained which was used for the

further reaction. After crystallization the yield was 70 %. Its melting point was found to be 150^0C.

[2.2.2] 4-methoxy-N-(2-(4-methoxyphenyl)isoindolin-1-ylidene)benzenamine (L_2):

For the synthesis of this Schiff base ligand, 0.335g (2.5 mmol) of pthalaldehyde was mixed with 0.628g (5.1 mmol) of *p*-anisidine and refluxed for 1.5 h in 50 mL of methanol. After refluxing the reaction mixture was concentrated to about 5.0 mL in vacuo, yellow-orange product precipitated which was filtered and washed with little amount of methanol and dried. The product was recrystallized in DCM : ACN(3:1). Very good diffraction quality crystals were obtained. These crystals were used for the reaction with $[Ru(PPh_3)_3Cl_2]$. 74 % yield was recorded after crystallization. Its melting point was 154^0C.

[2.2.3] 4-chloro-N-(2-(4-chlorophenyl)isoindolin-1-ylidene)benzenamine (L_3):

It was synthesized by refluxing 0.651g (5.1 mmol) of *p*-chloroaniline with 0.335g (2.5 mmol) of pthalaldehyde in 50 mL of methanol. The yellow precipitate appeared after about 1.5 h which was filtered and washed with little amount of methanol and dried. The product was recrystallized in DCM : ACN (3:1). Needle like crystals obtained which were used for the ruthenium organometallic complex formation. After crystallization the yield was found to be 80 %. Its melting point was recorded as 156^0C.

[2.2.4] $[Ru(PPh_3)_3Cl_2]$:

The synthesis of this complex was described by the Stephenson *et al.*[30] Ruthenium trichloride trihydrate 0.2g was dissolved in 50 mL methanol and 1.2g of triphenylphosphine added and shaked vigorously. The reaction mixture was refluxed for ca. 1.5 h. The resulting reddish-brown crystals of the complex were washed well with methanol and ether and dried in vaccuo. The yield was 75%.

[2.2.5] $[Ru(PPh_3)_2L_nCOCl]$ (n=1,2,3):

All the complexes were synthesized in a similar way, one of which is described here:

[2.2.6] $[Ru(PPh_3)_2L_1COCl]$ (Complex 1):

For the synthesis of this complex, 0.083g (0.24 mmol) of ligand L_1 was added in a suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 50 mL hot ethanol. The reaction mixture was refluxed for 4.0 – 4.5 h and then the solvent was evaporated in vacuo. A dark

brown solid was obtained which was filtered and washed thoroughly with cold ethanol. The yield obtained was 53 %.

[2.2.7] In situ Reaction of pthalaldehyde and $Ru(PPh_3)_3Cl_2$ in presence of *p*-toluidine:

For this reaction 0.032g (0.24 mmol) of pthalaldehyde and 0.028g (0.26 mmol) of *p*-toluidine were refluxed for 1.5 h in 40 mL ethanol then a suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 30 mL hot ethanol was added to the reaction mixture and refluxed for ca 4 h. The solvent was evaporated in vacuo. A dark brown solid was obtained which was filtered and washed thoroughly with cold ethanol.

[2.2.8] In situ Reaction of pthalaldehyde and $Ru(PPh_3)_3Cl_2$ in presence of ethyl amine:

0.032g (0.24 mmol) of pthalaldehyde and 0.012g (0.26 mmol) of ethyl amine were refluxed for 1.5 h in 40 mL ethanol then a suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 30 mL hot ethanol was added to the reaction mixture and refluxed for ca 4 h. The solvent was evaporated in vacuo. A dark brown solid was obtained which was filtered and washed thoroughly with cold ethanol.

[2.2.9] Reaction of $Ru(PPh_3)_3Cl_2$ with 2-nitrobenzaldehyde:

For this reaction 0.036g (0.24 mmol) of 2-nitrobenzaldehyde was added in a suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 50 mL hot ethanol. The reaction mixture was refluxed for 4.0 – 4.5 h and then the solvent was evaporated in vacuo. A dark green solid obtained which was washed thoroughly with cold ethanol.

[2.2.10] Reaction of $Ru(PPh_3)_3Cl_2$ with pthalaldehyde:

In a suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 50 mL hot ethanol, 0.032g (0.24 mmol) of pthalaldehyde was added and the reaction mixture was refluxed for 4.0–4.5h. The solvent was evaporated in vacuo. A brown solid obtained which was washed thoroughly with cold ethanol.

[2.2.11] Reaction of $Ru(PPh_3)_3Cl_2$ with 5-bromo-2-thiophenecarboxaldehyde:

A suspension of 0.192g (0.20 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 50 mL hot ethanol was added 0.046g (0.24 mmol) of 5-bromo-2-thiophenecarboxaldehyde and the reaction mixture was refluxed for 4.0–4.5 h. The solvent was evaporated in vacuo. A reddish-brown solid obtained which was washed thoroughly with cold ethanol.

[2.3] Physical Masurements:

[2.3.1] IR Spectroscopy:

Infrared spectroscopy offers the possibility to measure different types of interatomic bonc vibrations at different frequencies. Each functional group has its characteristic band. The analysis of IR spaectra shows what types of bonds are present in the sample. Thus it helps ir the elucidation of structural features and the presence of function groups.

Nexus Thermo Nicolet FT-IR is used to record IR spectra. IR spectra of all the compounds were recorded as KBr disc in 4000-400 cm^{-1} range.

[2.3.2] NMR Spectroscopy:

Bruker 400MHz Ultra Shield TM spectrometer is used to record the NMR spectra. Nuclear magnetic resonance spectroscopy analyzes certain atomic nuclei to determine different local environments of hydrogen, carbon, or other atoms in the molecule. Studying the molecules by NMR spectroscopy enables us to record differences in the magnetic properties of the various nuclei. With the help of NMR different environments present in the molecule, and which atoms are present in the neighboring group can be determined.

[2.3.3] UV-VIS Spectroscopy:

Analytik Jena is used to record UV-VIS spectra. UV-VIS spectra are based on the electronic transitions in the ligand and d-d transitions in the metal complexes. The strength o electronic transition lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules.

[2.3.4] Elemental analysis (C, H, N, S analysis):

The C, H, N, S contents of the samples were determined with the help of Elementar VarioEL III Elemental Analyser.

[2.3.5] Melting point apparatus:

Melting of the compounds were recorded with Perfit Melting Point Apparatus.

[2.3.6] Crystallography:

[2.3.6.1] X-ray data on single crystal of 4-methyl-N-(2-p-tolylisoindolin-1-ylidene)benzenamine (L_1) were collected using graphite monochromated Mo Kα radiation (λ = 0.71073Å), employing the ω–2θ scan technique. Crystal data are given in Table 1. The unit cell parameters were determined from 25 reflections measured by random search routine and indexed by the method of short vectors followed by least-squares refinement. The intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct method and refined by full-matrix least squares on F^2. The nonhydrogen atoms were refined anisotropically and the hydrogen atoms were introduced using the appropriate riding model.

[2.3.6.2] X-ray intensity data on single crystal of 4-methoxy-N-(2-(4-methoxyphenyl)isoindolin-1-ylidene)benzenamine (L_2) were collected on Kappa Apex Bruker with CCD area detector diffractometer using Mo Kα radiation (λ = 0.71073Å). The collection method involved ω-2θ scans. Crystal data is given in Table 1. The unit cell parameters were determined from 20 reflections measured by random search method and indexed by the method of short vectors followed by least squares refinement. The intensity data were corrected for Lorentz, polarization and absorption effects. The structure was solved by direct method using SHELXS (Sheldrick, 1986). Non hydrogen atoms were refined isotropically followed by anisotropic refinement by full matrix least-squares calculations based on F^2 using SHELXL (Sheldrick, 1997). Hydrogen atoms were first located in the Fourier difference map then positioned geometrically and allowed to ride on their respective parent atoms. Diagram was generated using ORTEP 3.

3. RESULTS AND DISCUSSION:

Pthalaldehyde reacts with primary amine giving rise to pthalimidine and 6- and N-substituted pthalimidine.[31] But we never isolated any pthalimidune or its derivative. However in our synthesis we tried to isolate mono- and di-Schiff bases (see Figure 19) of pthaladehyde with no success.

mono-Schiff base ***di-Schiff base***

Figure 19: mono- and di-Schiff base of pthalaldehyde

But we ended up with a different compound which is an isoindole derivative (Figure 20) only when one equivalent of pthaladehyde reacted with two equivalents of primary amine.

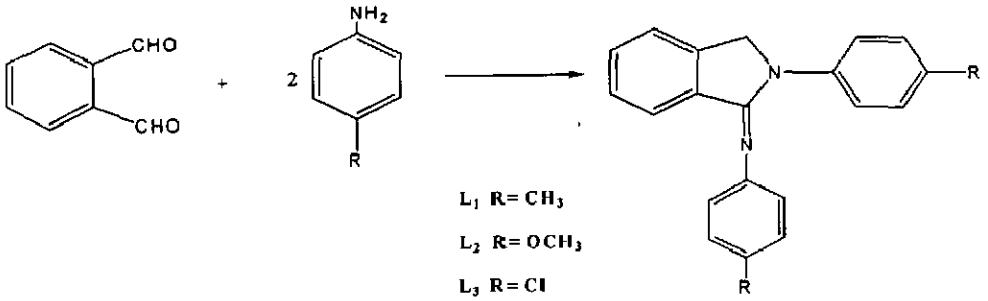


Figure 20: Synthesis of isoindole derivatives

Reaction of one equivalent of phthalaldehyde and one equivalent of primary amine didn't give any isolable product. To confirm our result we recrystallized the resultant compound and did the X-ray crystallographic study. We got the diffraction quality crystals of two compounds *i.e.* 4-methyl-N-(2-p-tolylisoindolin-1-ylidene)benzenamine (L_1) and 4-methoxy-N-(2-(4-methoxyphenyl)isoindolin-1-ylidene)benzenamine (L_2). The crystal structures of these two are shown in Figure 21 and Figure 22. Crystal data of 4-methyl-N-(2-p-tolylisoindolin-1-ylidene)benzenamine , and 4-methoxy-N-(2-(4-methoxyphenyl)isoindolin-1-ylidene)benzenamine and detail of the X-ray diffraction experiment are reported in Table 1. Selected bond distances and bond angles are reported in Table 2 and Table 3.

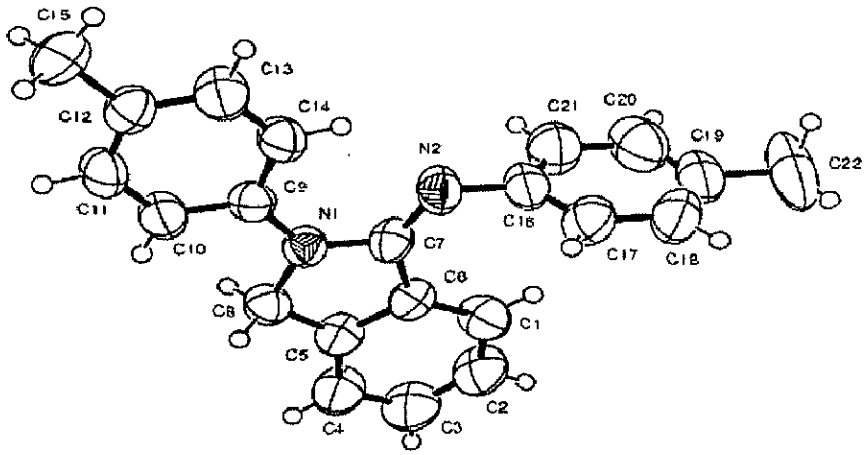


Figure 21: ORTEP plot and atom-labeling scheme for L_1

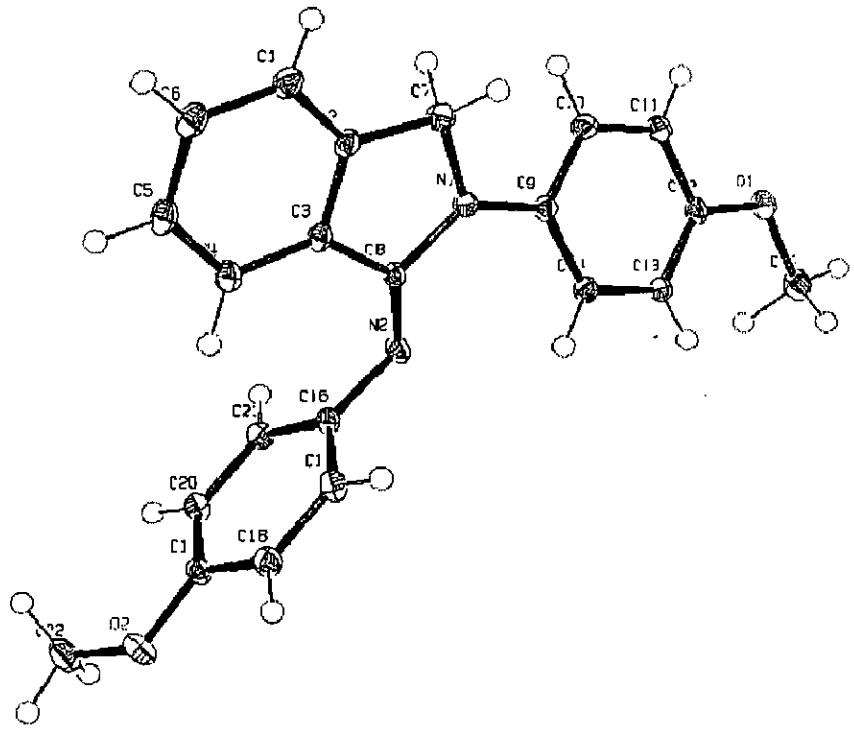


Figure 22: ORTEP plot and atom-labeling scheme for L_2

Table 1: Crystallographic and structure refinement data for L_1 & L_2

Parameters	L_1	L_2
Chemical formula	C_{22} H_{20} N_2	C_{22} H_{20} N_2 O_2
Diffractometer model	Kappa Apex Bruker	Kappa Apex Bruker
Formula weight	312.40	344.42
Crystal color	Yellow	Yellow
Crystal size (mm^3)	0.30 x 0.20 x 0.20	0.1x 0.1x 0.1
Temperature (K)	293(2)	293(2)
λ (Å)	0.71073	0.71073
Crystal system	Orthorhombic	Triclinic
Space group	*Pna21*	*P -1*
Unit cell dimensions		
a (Å)	19.0212(13)	5.1956(4)
b (Å)	12.7684(8)	13.1475(11)
c (Å)	7.1666(5)	13.4222(11)
α (^{0})	90	107.855(5)
β (^{0})	90	98.780(5)
γ (^{0})	90	95.820(5)
volume ($Å^3$)	1740.6(2)	916.859(3)
Z	4	2
μ (mm^{-1}) / F(000)	0.070 / 664	0.09 / 364.0
θ for data collection (^{0})	1.92 - 29.85	
Limiting indices	-25<=h<=26, -11<=k<=17, -9<=l<=8	-8 =< h =< 8, -21 =< k =< 20, -21 =< l =< 21,
Goodness of fitness on F^2	1.016	1.317
Reflections collected/ unique	12447 / 4487	16335/6703
Data/ restraints/parameters	4487 / 1 / 218	6703/0/315
Final R_1, wR_2 indices	0.0490, 0.1312	0.0679, 0.2997
R_1, wR_2 (all data)	0.1061, 0.1598	0.1089, 0.2997
Computer programs used		
structure solution		SHELXS-86 (Sheldrick, 1986)
structure refinement	SHELX	SHELXL-97 (Sheldrick, 1997)

Table 2: Selected bond distances and bond angles for L_1:

	Bond distances		
C(7)-N(2)	1.276(2)	C(6)-C(7)	1.491(2)
C(7)-N(1)	1.3874(19)	C(16)-N(2)	1.410(2)
C(8)-N(1)	1.460(2)	C(5)-C(8)	1.487(2)
C(9)-N(1)	1.4104(19)	C(5)-C(6)	1.376(2)
	Bond angles		
C(7)-N(1)-C(9)	128.57(13)	C(6)-C(5)-C(8)	110.21(14)
N(2)-C(7)-C(6)	131.66(15)	N(2)-C(7)-N(1)	122.47(14)
N(1)-C(7)-C(6)	105.88(14)	N(1)-C(8)-C(5)	103.14(13)
C(7)-N(1)-C(8)	112.20(12)	C(7)-N(2)-C(16)	121.22(14)
C(5)-C(6)-C(7)	108.52(14)	C(9)-N(1)-C(8)	119.21(12)

Table 3: Selected Bond distances and bond angles for L_2:

	Bond distances		
N2 - C8	1.2827 (0.0021)	C8 - C3	1.4851 (0.0020)
C8 - N1	1.3946 (0.0020)	N2 - C16	1.4090 (0.0021)
C7 - N1	1.4569 (0.0021)	C2 - C7	1.4922 (0.0022)
C9 - N1	1.4072 (0.0019)	C2 - C3	1.3851 (0.0024)
	Bond angles		
C7 - N1 - C8	112.25 (0.12)	C2 - C7 - N1	103.12 (0.13)
N1 - C8 - N2	122.10 (0.13)	C7 - N1 - C9	120.33 (0.13)
C3 - C8 - N2	131.99 (0.14)	C8 - N1 - C9	127.06 (0.14)
C3 - C8 - N1	105.81 (0.13)	C8 - N2 - C16	120.46 (0.13)
C2-C3-C7	109.81 (0.14)	C2-C3-C8	108.72 (0.13)

In the crystal structure of the ligand L_1 three benzene rings shows the C-C bond distances in the range 1.319 Å – 1.383 Å which is consistent with the standard C-C bond length in benzene. C8-N1 and C7-N1 distances are 1.460 Å and 1.3874 Å. However C7-N2 bond distance is 1.276 Å which lies in the range of C=C and also this distance is lesser as compared to C7-N1 which shows the presence of double bond. C5-C6 bond distance is 1.376 Å which lies in C=C double bond range however C8-C5 bond distance is 1.487 Å which higher as compared to C5-C6 distance and also this distance is near to C-C single

bond distance which shows that single bond is present between C8-C5 .Bond angle of N1-C8-C5 is 103.14^0 which shows that it is sp^3 hybridized.

The similar observations were found in the crystal structure of ligand L_2. Hence these X-ray crystal structure solutions confirm the formation of molecule shown in Figure 20.

These compounds have $\nu_{C=N}$ in the range 1648-1638 cm^{-1} which is in good agreement with literature (see Table 4 and Figure 23).

Table 4: Selected IR spectral data:

Compound	$\nu_{C=N}$ (cm^{-1})	$\nu_{C=O}$ (cm^{-1})
L_1	1638	--------
L_2	1648	--------
L_3	1646	--------
$Ru(PPh_3)_2L_1Cl$	------	1958
$Ru(PPh_3)_2L_2Cl$	------	1951
$Ru(PPh_3)_2L_3Cl$	------	1959

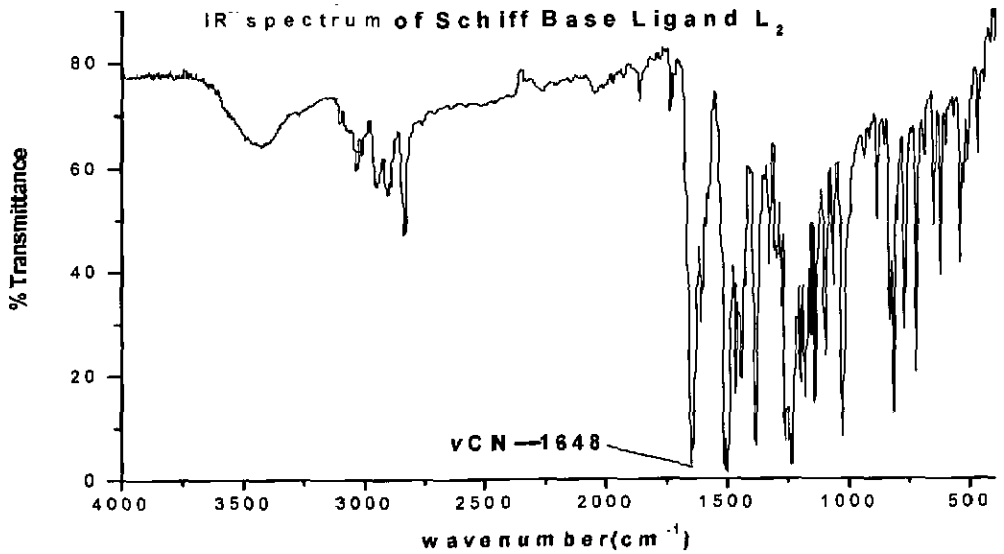


Figure 23: Representative IR spectrum of the Ligand (L_2)

These compounds have one peak around 300 nm in the UV-VIS spectra, which is most probably due to $n \rightarrow \pi^*$ or $\pi \rightarrow \pi^*$ transition another peak around 245 nm is due $\pi \rightarrow \pi^*$ transition of the benzene ring attached to the isoindole ring through nitrogen (see Table 5 and Figure 24).

Table 5: Electronic spectral data of ligands in chloroform at 298 K:

Compound	λ, nm (ε^a $_M^{-1}$ cm^{-1})
L_1	294 (5773), 245 (12123)
L_2	303 (6512), 245 (14081)
L_3	298 (6406), 247 (12512)

[c]Extinction coefficient

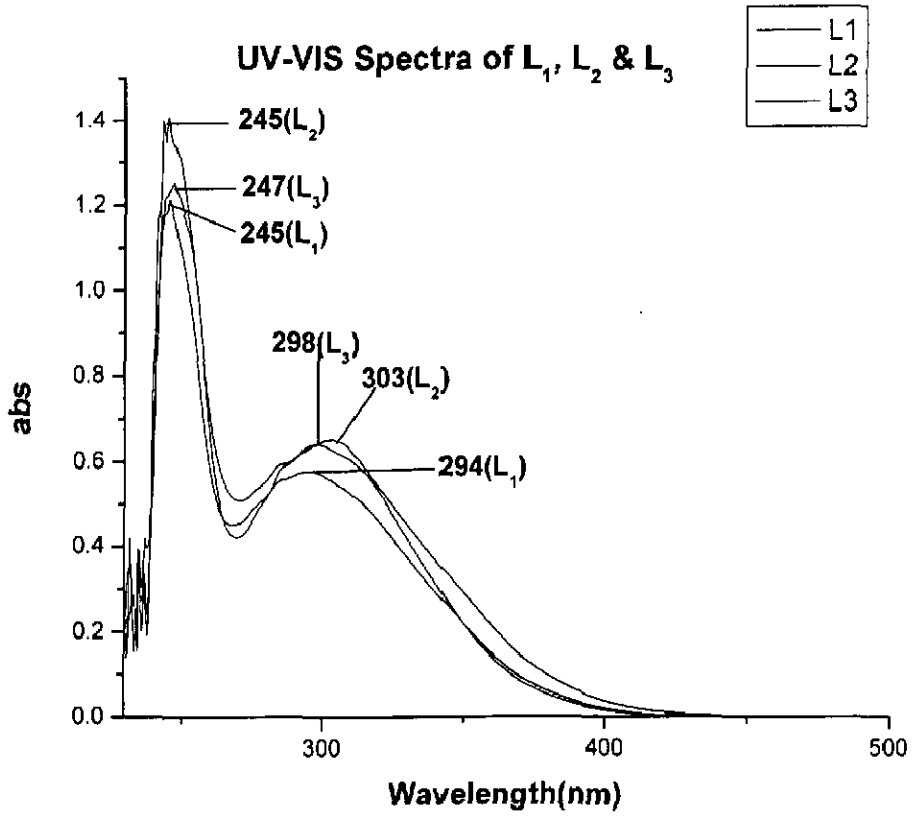


Figure 24: UV-VIS spectra of ligands L_1, L_2 and L_3

Reaction of $Ru(PPh_3)_3Cl_2$ with this isoindole derivative gave rise to a dark brown colored diamagnetic ruthenium complex (Figure 25). In $Ru(PPh_3)_3Cl_2$ complex one PPh_3 group is dissociable and ruthenium undergoes oxidative addition of the aldehydic bond to the metal produced by the hydrolysis of C=N bond of the ligand followed by CO extrusion and reductive proton elimination.[9]

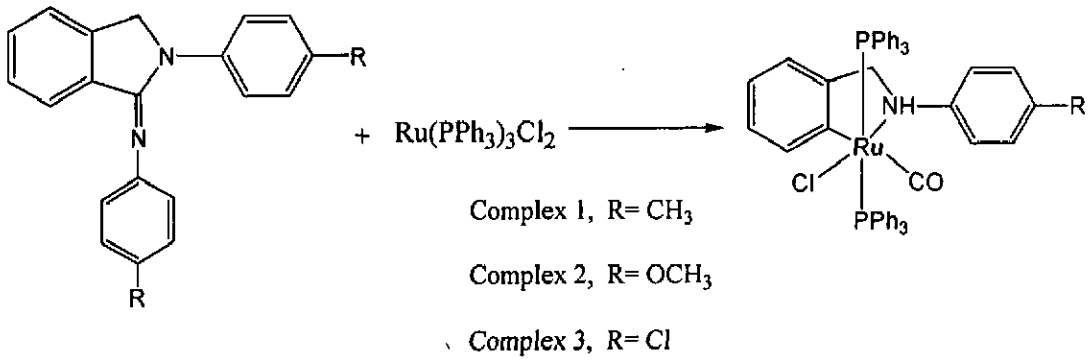


Figure 25: Interaction of isoindole derivative ligands with $[Ru(PPh_3)_3Cl_2]$

This family of complexes showed a stretching frequency ~ 1950 cm^{-1} which was characterized as ruthenium ligated carbonyl stretching frequency (see Table 4 and Figure 26).[27]

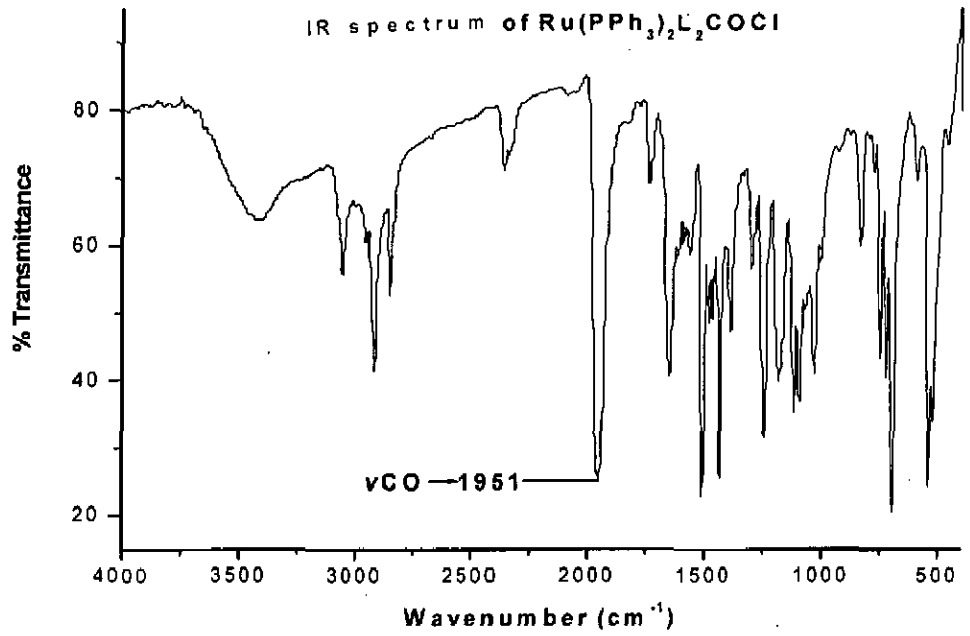


Figure 26: Representative IR spectrum of $Ru(PPh_3)_2L_2COCl$

In the NMR of these complexes (see Table 6 and Figure 27) 5H appeared in the range 2.11 - 2.24 ppm and 6H appeared in the range 7.62-7.89 ppm which has the good match with literature. The —OCH_3 proton in the complex $Ru(PPh_3)_2L_2COCl$ appeared at 3.78 ppm and —CH_3 in complex $Ru(PPh_3)_2L_1COCl$ appeared at 2.24 ppm which is consistent with literature.[26] The aromatic protons of phosphine appear in the range 7.23-7.66 ppm,[26] in these complexes aromatic PPh_3 protons appear in the range 7.33-7.50 ppm.

Table 6: ^1H spectral data NMR data (δ ppm) of $Ru(PPH_3)_2LCOCl$ in $CDCl_3$

Compound	5-H	6-H	11-H	Other protons
$Ru(PPh_3)_2L_1COCl$	2.24	7.62	2.24	7.39 - 7.41and 7.46-7.48 (arom. PPh_3) and 7.57-7.59 (arom. Benzene)
$Ru(PPh_3)_2L_2COCl$	2.11	7.87	3.78	7.33 - 7.41 and 7.44- 7.50 (arom. PPh_3) and 7.60-7.68 (arom. Benzene)
$Ru(PPh_3)_2L_3COCl$	2.16	7.89	---	7.30 - 7.35 and 7.39-7.48 (arom. PPh_3) and 7.58-7.62 (arom. Benzene)

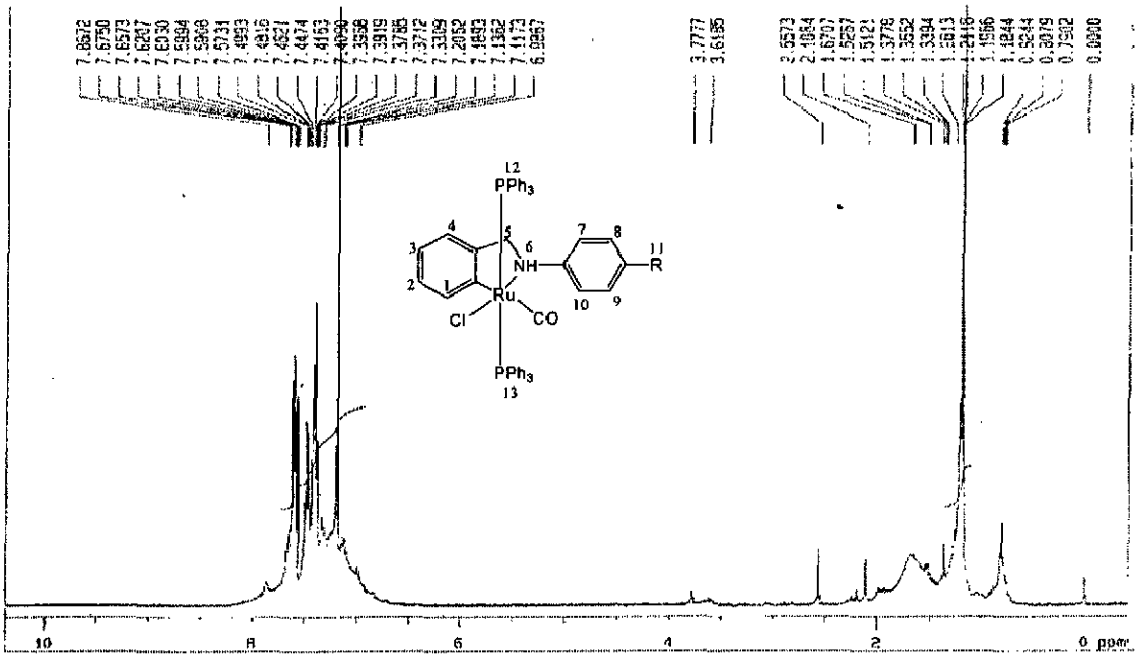


Figure 27: Representative ^1H NMR spectrum of $Ru(PPh_3)_2L_2COCl$

C, H, N contents of ligands and complexes determined experimentally are in good agreement with the calculated value (see Table 7)

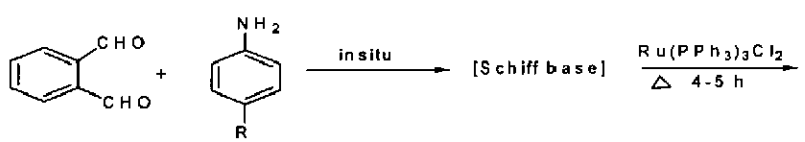
Table 7: C, H, N analytical data for the ligands and complexes synthesized:

Compound	Elemental Analysis[a] (%)		
	C	H	N
L_1	84.58(85.07)	6.45 (6.29)	8.97(8.91)
L2	75.45(74.93)	5.70(5.91)	8.80(9.05)
L3	68.00(68.64)	3.99(3.21)	7.93(6.95)
$Ru(PPh_3)_2L_1Cl$	69.11(68.26)	5.12(4.83)	1.58(2.47)
$Ru(PPh_3)_2L_2Cl$	67.88(68.76)	5.03(4.27)	1.55(1.74)
$Ru(PPh_3)_2L_3Cl$	66.23(68.05)	4.67(4.01)	1.54(1.71)

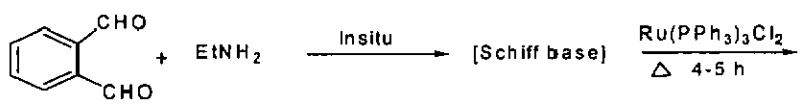
[a]Calculated values are in paraentheses

These family of complexes showed $\nu_{C\equiv O}$ band, this unprecedented observation prompted us to check the reactivity of Schiff base with some other type of Schiff base as well as *o*-substituted benzaldehyde with $Ru(PPh_3)_3Cl_2$.

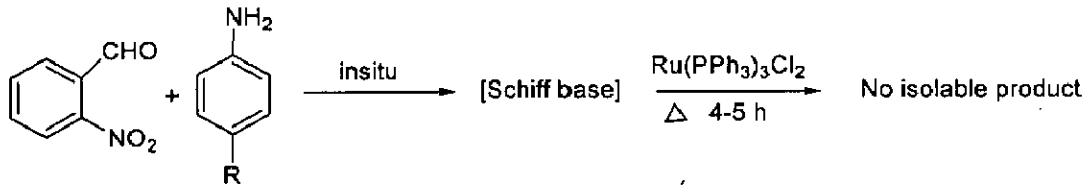
Chakravorty and coworkers reported[25] that the mono- as well as di-Schiff base of 4-methyl-2,6-diformylphenol gives *ortho*- metallated σ-aryl ruthenium complex with Ru-CO bond in presence of air. In the context to understand the mode of interaction of $Ru(PPh_3)_3Cl_2$, we studied the following reactions also:

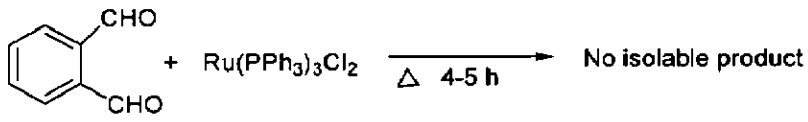


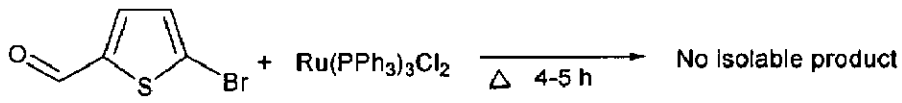
Compound with $\nu_{C\equiv O}$ in [Ru]-CO moiety



Compound with $\nu_{C\equiv O}$ in [Ru]-CO moiety







In most cases we ended up with some oily precipitate. Recrystallization in different solvents didn't give isolable product.

4. CONCLUSION:

The main finding of this work will now be summarized:

1. The phenol group in between the two aldehyde groups is very important for the synthesis and characterization of the mono as well as di-Schiff bases. However in phthalaldehde isolation of mono or di-Schiff base lead to the formation of isoinole derivative.
2. Phthalaldehyde reacts with primary amine giving rise to isoindole derivative when reacted in 1:2 ratio however 1:1 gave no isolable product. *In situ* generation of the mono Schiff base product gave free C≡O stretching frequency but not isolable product for further study.
3. Crystal structures of two isoindole derivatives show reproducibility of the synthetic procdure and orientation of the different bonds in the molecule.
4. Reactivity of the isoindole derivative with $Ru(PPh_3)_3Cl_2$ gives decarbonylation in presence of air which is consistent with the results reported in the literature.

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CHAPTER II

Synthesis and Characterization of Novel Organometallic Ruthenium Nitrosyl Complex

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Synthesis and Characterization of Novel Organometallic Ruthenium Nitrosyl Complex

Abstract

Organometallic ruthenium complex $Ru(PPh_3)_2LCl$ (L=2-(benzylideneamino)phenol) reacts with nitric oxide (*in situ* generated by an acidic solution of $NaNO_2$ in water) to give $Ru(PPh_3)_2LNO$. The resultant complex was characterized by elemental analysis, UV-VIS, IR and ^1H NMR studies. The parent complex was paramagnetic with ruthenium in +3 oxidation state but the resultant complex was diamagnetic showing ^1H NMR spectra. Reductive nitrosylation and $\{Ru\text{-}NO\}^6$ (Enemark and Feltham notation) formation is proposed in this study. Stability of the original complex was checked by UV radiation, however, the resultant nitrosyl complex undergoes decomposition most probably due the photolability of the coordinated NO.

1. INTRODUCTION AND LITERATURE REVIEW

There has been a substantial interest in nitric oxide research in recent years. Nobel prize was given to three researchers (Dr. Furchgott, Dr. Ignarro and Dr. Murad) for their valuable contributions in nitric oxide research. Nitric oxide is gaseous molecule which acts as a biological messenger and participates in several important biological functions including control of blood pressure, neurotransmission, and inhibition of tumor growth. Metal nitrosyl complexes that release NO upon illumination of light (photolabile) is of great interest because such compounds can deliver NO to biological targets on demand,[1] and such species could be used as antitumor agents in photodynamic therapy (PDT).[2] This photolability has lot of applications in photodynamic therapy and in recent years the synthesis and application of this type of complex got immense significance. Although a huge number of metal nitrosyls are reported in the literature, very few of them release NO upon illumination.[3] Smith and Otis reported that brief exposure to NO donors cause a long term increase in the spontaneous firing rate of Purkinje neurons.[4] Interaction of nitric oxide with organometallic ruthenium complexes some times lead to ligand nitration rather than metal nitrosyl complex formation.[5]

[1.1] Organometallic Ruthenium Nitrosyls:

Hubbard *et al.* reported[6] the synthesis of $Cp^*Ru(NO)(CH_2Cl)_2$ ($Cp^* = C_5Me_5$) complex which reacts smoothly to extrude ethylene and regenerate the parent $Cp^*Ru(NO)Cl_2$ complex. Authors studied the photolysis of $Cp^*Ru(NO)(CH_2Cl)_2$ in C_6D_6, at 20^0C resulting in the formation of $Cp^*Ru(NO)Cl_2$, and ethylene (Figure 1). The elimination of ethylene occurs via an intramolecular coupling of CH_2 groups with concomitant formation of the dichloro starting material. Photolysis of $Cp^*Ru(NO)(CH_2Cl)_2$ in $CDCl_3$ or hexane also produces ethylene and $Cp^*Ru(NO)Cl_2$ with similar ease.

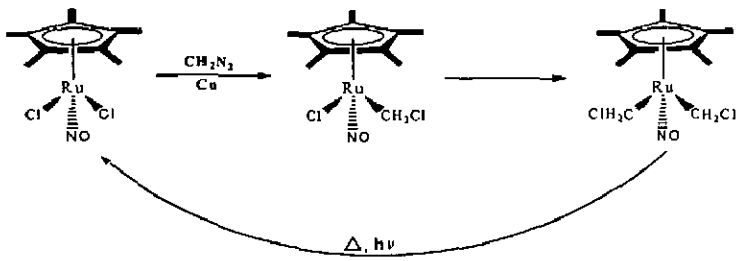
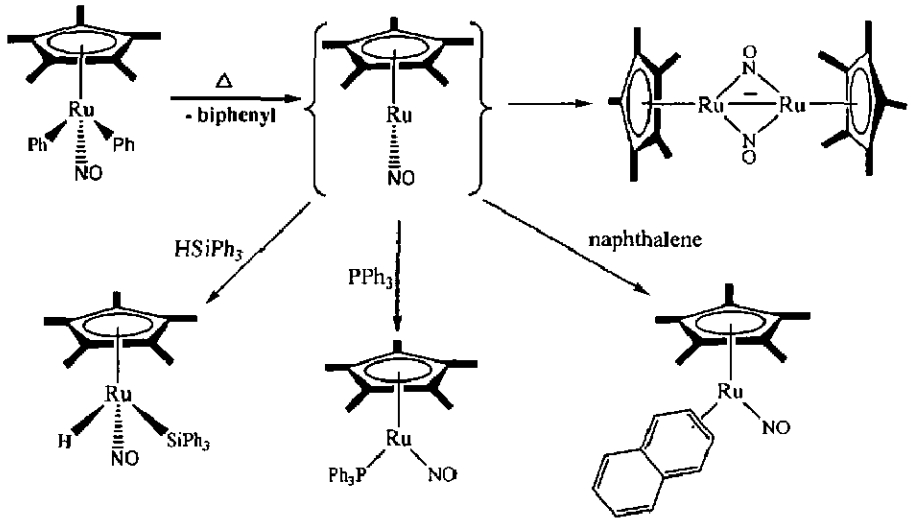


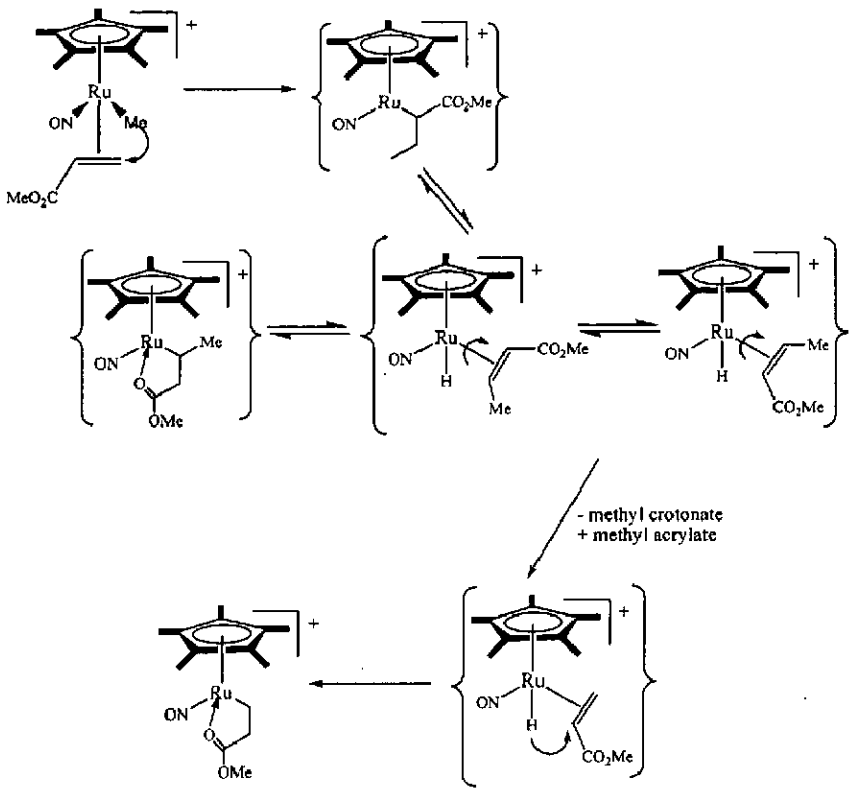
Figure 1: Photolysis of $Cp^*Ru(NO)(CH_2Cl)_2$

Tagge *et al.* reported[7] the thermally induced reductive elimination of biphenyl from the coordination sphere of Cp*Ru-(NO)Ph_2 results in the generation of the 16e transient species Cp*Ru(NO) which subsequently dimerizes to [Cp*Ru(μ-NO)]$_2$. They detected the intermediate Cp*Ru(NO)-(η^2-C_6H_6) complex by careful monitoring of the reaction in aromatic solvents by ^{1}H NMR spectroscopy. Addition of naphthalene to solutions of the intermediate complex results in displacement of benzene and formation of Cp*Ru(NO)(η^2-naphthalene). The bound arenes reversibly dissociate from the coordination sphere of the metal, thereby generating Cp*Ru(NO), which can be trapped with phosphines and oxidatively adds the siliconhydrogen bond of Ph_3SiH or a carbon-hydrogen bond of CH_2Cl_2 (Scheme 1) but they did not study its photolability.



Scheme 1: Thermally induced reductive elimination of biphenyl and addition of $HSiPh_3$, PPh_3 and naphthalene to the intermediate

Hauptman *et al.* synthesized[8] several Ru-NO organometallic complexes and reported that these complexes easily undergo protonolysis upon addition of suitable acids (Scheme 2) but they did not study the photolability of these complxes.



Scheme 2: Protonolysis of Ru-NO organometallic complexes

[1.2] Photolabile Ruthenium Nitrosyls:

Patra *et al.* reported[9] in one of his articles that nitric oxide reacts with metal centre and produces metal-nitrosyls. In some complexes, the NO group is photolabile. They synthesized a nitrosyl complex $[Ru(PaPy_3)(NO)](BF_4)_2$ [$PaPy_3H$ = *N*, *N*'-bis(2 pyridylmethyl)amine-*N*-ethyl-2-pyridine-2-carboxamide, H is the dissociable carboxamide proton] by passing purified NO gas to the hot methanolic solution of the chloro derivative of the same complex *i.e.* $[Ru(PaPy_3)(Cl)](BF_4)$ (Figure 2). They further reported that on exposure of low intensity UV light in aqueous medium, complex $[Ru(PaPy_3)(NO)](BF_4)_2$ loses NO and forms $[Ru(PaPy_3)(H_2O)]^{2+}$. This reaction can be conveniently used to transfer NO to proteins such as myoglobin and cytochrome *c* oxidase. The NO transfer reaction is clean and occurs upon short exposure to light.

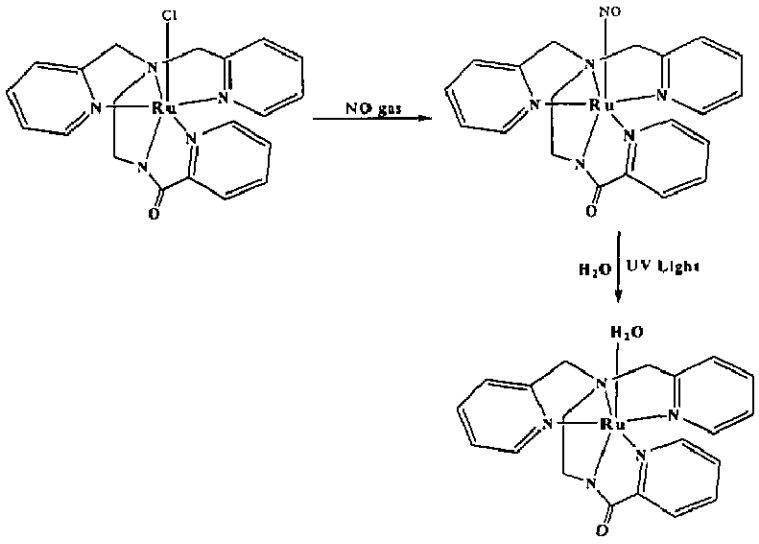
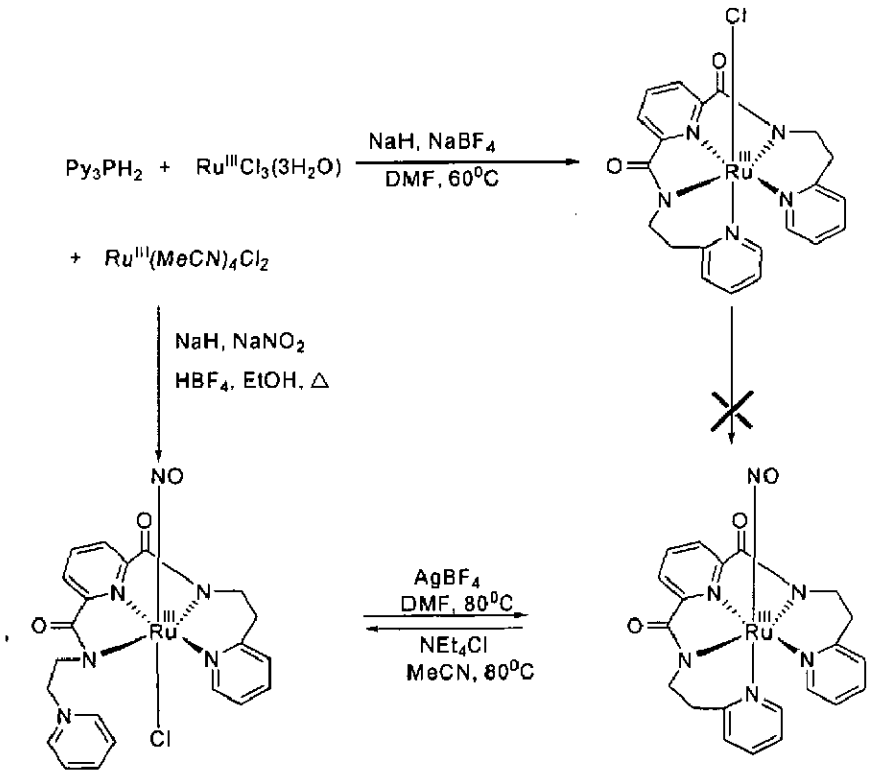


Figure 2: Synthesis and photolysis of cation of $[Ru(PaPy_3)(NO)](BF_4)_2$

Rose *et al.* synthesized[10] a set of $\{RuNO\}^6$ nitrosyls (Scheme 3) and studied their photolability. They found that the efficiency of NO release increases in the presence of negatively charged ligands (like chloride) trans to the bound NO.



Scheme 3: Synthesis of $\{RuNO\}^6$ nitrosyl

Mascharak and coworkers synthesized four ruthenium nitrosyl complexes.[5] They found that the ligand *trans* to bound NO has significant effect on the electronic and NO releasing properties of these complexes. Authors further reported that the change in the in-plane ligand strength also has effects on the rate of NO release. The extension of conjugation on the in-plane ligand frame produced the red shift in UV-VIS spectroscopy. From the above results they concluded that the extent of NO release (photolability) and their wavelength dependence can be modulated by changes of either the in-plane or the axial ligand (*trans* to bound NO) field strength.

Mascharak and coworkers synthesized[5,9,10] several ruthenium nitrosyl complexes and studied their photolability by illuminating and recording the repetitive UV-VIS spectra of the solution of those complexes. To the best of our knowledge we did not find even a single example of organometallic photolabile ruthenium nitrosyl complex in the literature. So we started the work in the field of ruthenium nitrosyl complex with the idea to prepare an organometallic photolabile ruthenium nitrosyl complex. Herein we report the synthesis and characterization of an organometallic ruthenium nitrosyl complex and the effect of UV light on its solution shown in Figure 3.

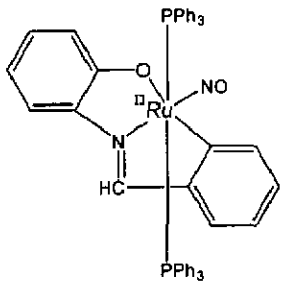


Figure 3: Organometallic ruthenium nitrosyl complex

2. EXPERIMENTAL:

2.1 Materials:

S. No.	Chemical	Grade	Make
1.	2-aminophenol	GR	Loba Chemie
2.	Benzaldehyde	LR	Rankem
3.	Sodium Nitrite	LR	Rankem
4.	Hydrochloric acid	AR	Rankem
5.	Methanol	AR	sdfine
6.	Ethanol	AR	Changshu Yanguan
7.	Dichloromethane	AR	Rankem
8.	Acetonitrile	AR	Rankem
9.	Chloroform	LR	sdfine

2.2 Synthesis:

[2.2.1] 2-(benzylideneamino)phenol (L):

Preparation of this ligand is described by Chakravorty *et al.*[11]

This ligand was prepared by refluxing 0.224g (2.05 mmoles) of 2-aminophenol with 0.214g (2.0 mmoles) of benzaldehyde in 40 mL ethanol for 1.5 h. The ligand was collected as the yellow solid after evaporating the solvent in vaccuo. This ligand was used without purification for the reaction with $[Ru(PPh_3)_3Cl_2]$. 90 % yield was recorded.

[2.2.2] $[Ru(PPh_3)_2LCl]$:

Preparation of this complex is described by the Chakravorty *et al.*[11]

In suspension of 0.960g (0.10 mmol) of $[Ru(PPh_3)_3Cl_2]$ in 30 mL ethanol, 0.030 g (0.15 mmol) of ligand L was added and refluxed for ca. 1.0 h. The reaction mixture is filtered after cooling and washed with ethanol 3-4 times; purple crystalline solid was obtained which was used without purification for the further reaction. Yield was 60 %.

[2.2.3] $[Ru(PPh_3)_2LNO]$:

A violet solution was prepared by dissolving 0.043g (0.05 mmol) of $[Ru(PPh_3)_2LCl]$ in 10 mL of dichloromethane in a vial. 3.0 mL distilled water was poured over the dichloromethane layer then in the aqueous layer 1-2 drops of concentrated hydrochloric acid were added. In the aqueous layer crystals of sodium nitrite were added, only few crystals were added at time and the process was repeated for ten times after every 30-40 seconds. The violet solution turned orange-red within a few minutes. The aqueous layer was pipetted out immediately and carefully. The solvent was evaporated under reduced pressure. The solid orange-red mass was collected. Yield was (94%).

[2.3] Physical Masurements:

[2.3.1] IR Spectroscopy:

Infrared spectroscopy offers the possibility to measure different types of interatomic bond vibrations at different frequencies. Each functional group has its characteristic band. The analysis of IR spectra shows what types of bonds are present in the sample. Thus it helps in the elucidation of structural features and the presence of function groups.

Nexus Thermo Nicolet FT-IR is used to record IR spectra. IR spectra of all the compounds were recorded as KBr disc in 4000-400 cm^{-1} range.

[2.3.2] NMR Spectroscopy:

Bruker 400MHz Ultra Shield TM spectrometer is used to record the NMR spectra.

Nuclear magnetic resonance spectroscopy analyzes certain atomic nuclei to determine different local environments of hydrogen, carbon, or other atoms in the molecule. Studying the molecules by NMR spectroscopy enables us to record differences in the magnetic properties of the various nuclei. With the help of NMR different environments present in the molecule, and which atoms are present in the neighboring group can be determined.

[2.3.3] UV-VIS Spectroscopy:

Varian Carry 100 is used to record UV-VIS spectra. UV-VIS spectra are based on the electronic transitions in the ligand and d-d transitions in the metal complexes. The strength of electronic transition lies in its ability to measure the extent of multiple bond or aromatic conjugation within molecules.

[2.3.4] Elemental analysis (C, H, N, S analysis):

The C, H, N content of the samples was determined with the help of Elementar, VarioEL III Elemental Analyser.

3. RESULTS AND DISCUSSION:

Organometallic Ru^{III} complex $Ru(PPh_3)_2LCl$ (Figure 4) was prepared by the reported procedure,[11] and characterized by IR and UV-VIS spectra.

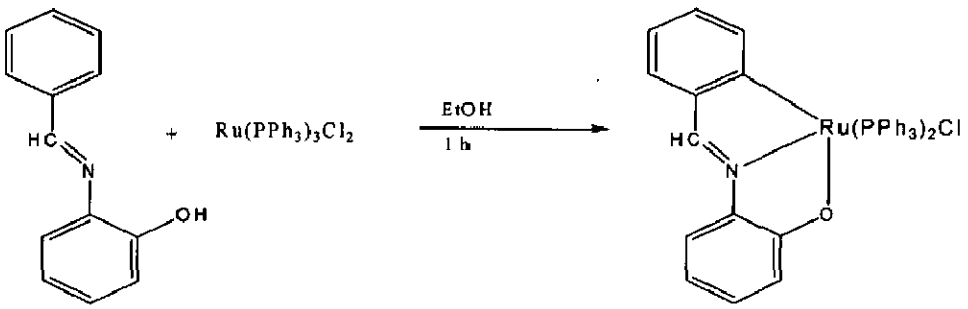


Figure 4: Synthesis of $Ru(PPh_3)_2LCl$

In the ligand, the OH stretching frequency appeared at 3305 cm^{-1} and 3375 cm^{-1} as two sharp peaks (see Table 1 and Figure 5). Most probably the OH group of ligand appeared at 3375 cm^{-1} and the peak at 3305 cm^{-1} may be due to the unreacted *o*-aminophenol. In the ligand C=N stretching frequency appeared at 1622 cm^{-1}.

Table 1: Selected IR spectral data:

Compound	$\nu_{C=N}$ (cm^{-1})	$\nu_{N=O}$ (cm^{-1})	ν_{OH} (cm^{-1})
L	1622	---	3375
$Ru(PPh_3)_2LCl$	1585	---	----
$Ru(PPh_3)_2LNO$	1587	1863	----

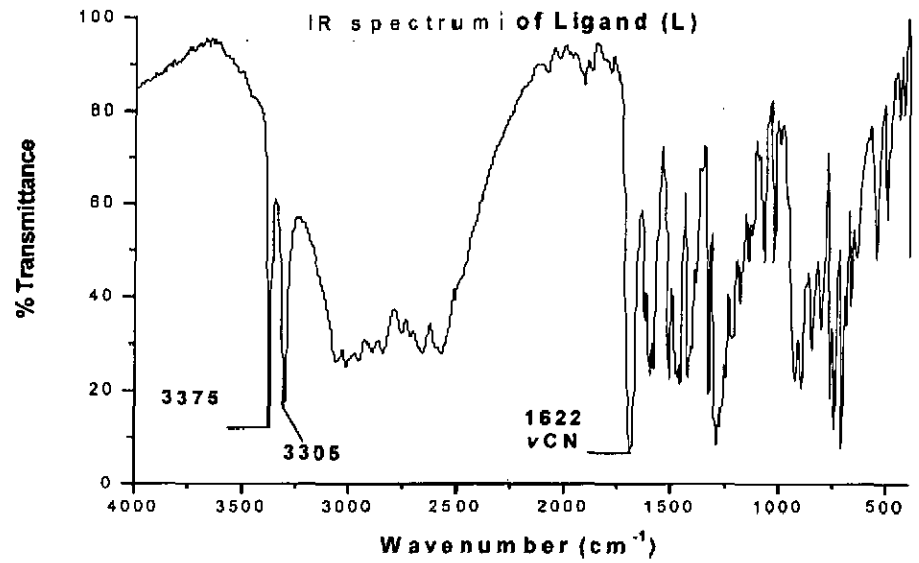


Figure 5: IR spectrum of ligand (L)

Ligand showed three bands in the UV-VIS spectra at 343 nm, 281nm and 228nm (see Table 2 and Figure 6). The band at 343 nm is most probably due to n→π* or π→π* transition. 281 nm band could be due to π→π* transition in *o*-substituted benzene ring and 228 nm band could most probably be due to π→π* in another benzene ring.

Table 2: Electronic spectral data of ligand and complexes

Compound	**λ, nm ($\varepsilon^c{}_M{}^{-1}$ cm^{-1})**
L	343 (1133), 284 (3541), 228 (11008)
$Ru(PPh_3)_2LCl$	559 (5740), 471 (4920),
$Ru(PPh_3)_2LNO$	415 (410), 265(1160)

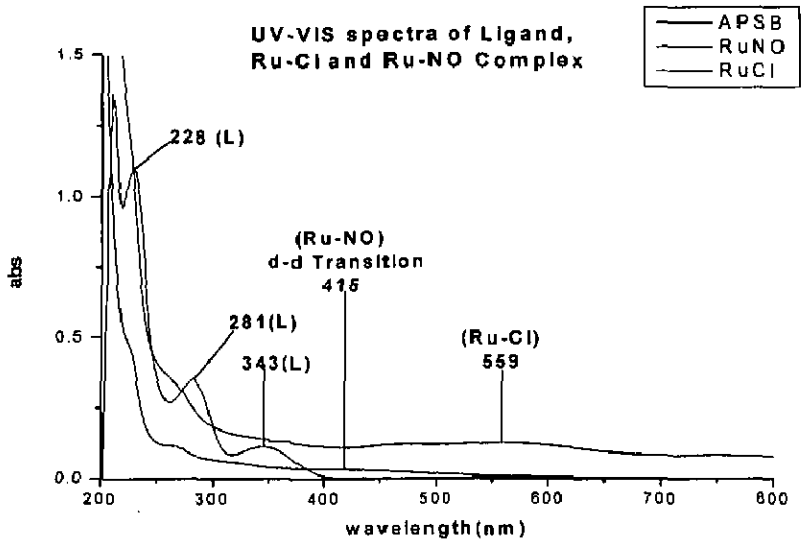


Figure 6: UV-VIS spectra of ligand (L), $Ru(PPh_3)_2LCl$ and $Ru(PPh_3)_2LNO$

$Ru(PPh_3)_2LCl$ absorbs moderately strongly in the visible region, with charge transfer bands in the region 400-700 nm (see Table 2 and Figure 6) .[11]

In the study of reactivity of the original complex ($Ru(PPh_3)_2LCl$) with $NaNO_2$ in the acidic media we got some interesting results. Retention of metal-carbon bond in course of nitration of ligand is sparse in literature. $NaNO_2$ in acidic medium produces NO,[12] a very reactive species, could react with metal centre or any other ligand cite which is electron reach (formation of reactive species NO_2^+ in air).[5] Here NO reacted with metal centre in a reductive nitrosylation fashion and diamagnetic organometallic ruthenium nitrosyl complex is formed (Figure 7) from the parent paramagnetic species.

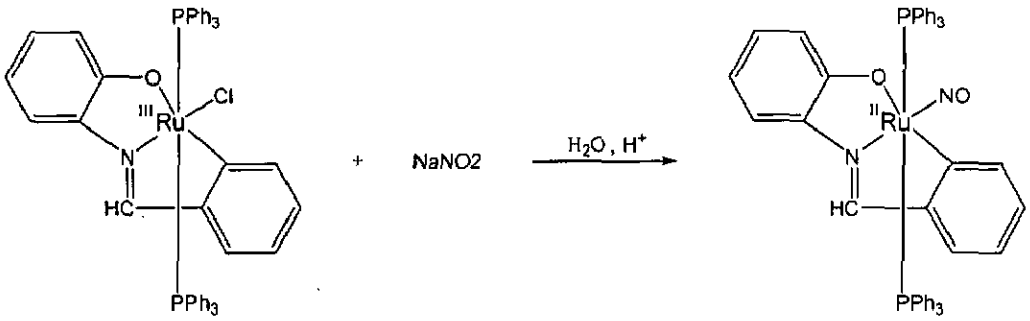


Figure 7: Synthesis of $Ru(PPh_3)_2LNO$

This complex was characterized by the IR, UV-VIS and NMR spectra. Ruthenium nitrosyl complexes exhibit ν_{NO} in the range[5a] 1830-1870 cm^{-1} indicating the {Ru-NO}^{6} [13] configuration. This compound shows ν_{NO} at 1863 cm^{-1} which is consistent with the literature. The OH stretching frequency present in the ligand are absent in complex $Ru(PPh_3)_2LCl$ and $Ru(PPh_3)_2LNO$ as expected (see Table 1 and Figure 8). The C=N stretching frequency in both the complexes ($Ru(PPh_3)_2LCl$ and $Ru(PPh_3)_2LNO$) display a significant shift (~ 50 cm^{-1}) to lower frequency compared with the free ligand which is due to the coordination of the azomethine function to the metal atom.[14]

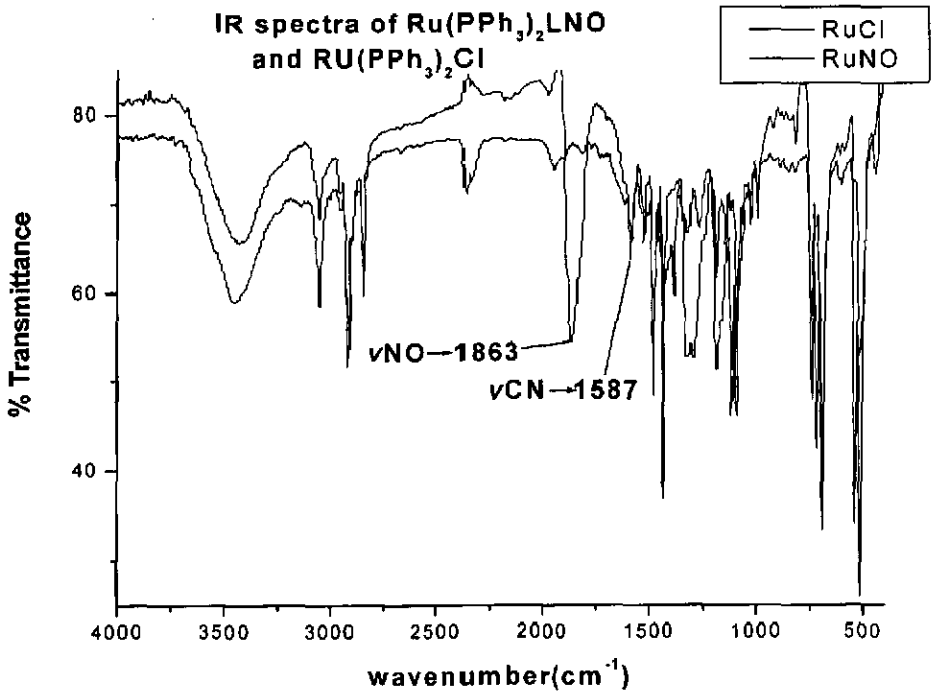


Figure 8: IR spectra of $Ru(PPh_3)_2LCl$ and $Ru(PPh_3)_2LNO$

In the UV-VIS spectra of the Ru-NO complex, d→d transition appeared at 419 nm with the ε value 410 $M^{-1}cm^{-1}$ (see Table 2 and Figure 6).

This compound shows NMR (see Table 3 and Figure 9) which shows that the original paramagnetic nature of the compound is lost and diamagnetic species has been formed. P. Ghosh has reported[15] that the —CH=N proton appears in the range 7.26 – 8.82 ppm, in the case of this complex —CH=N proton appeared at 7.92 ppm. The aromatic region of the NMR spectra clearly shows the presence of aromatic protons. The aromatic protons of

phosphine appear in the region 7.23 – 7.66 ppm.[15] In this complex these protons appeared in the region 7.39-7.51 and 7.55- 7.60. Other aromatic benzene protons appeared in the region 7.26- 7.37 and 7.65-7.69.

Table 3: ^{1}H NMR spectral data (δ ppm) of Ru(PPh$_3$)$_2$LNO in CDCl$_3$

Compound	CH=N	Other protons
Ru(PPh$_3$)$_2$LNO	7.92	7.39-7.51 and 7.55- 7.60 (aromatic PPh$_3$),.7.26- 7.37 and 7.65-7.69 benzene aromatic protons.

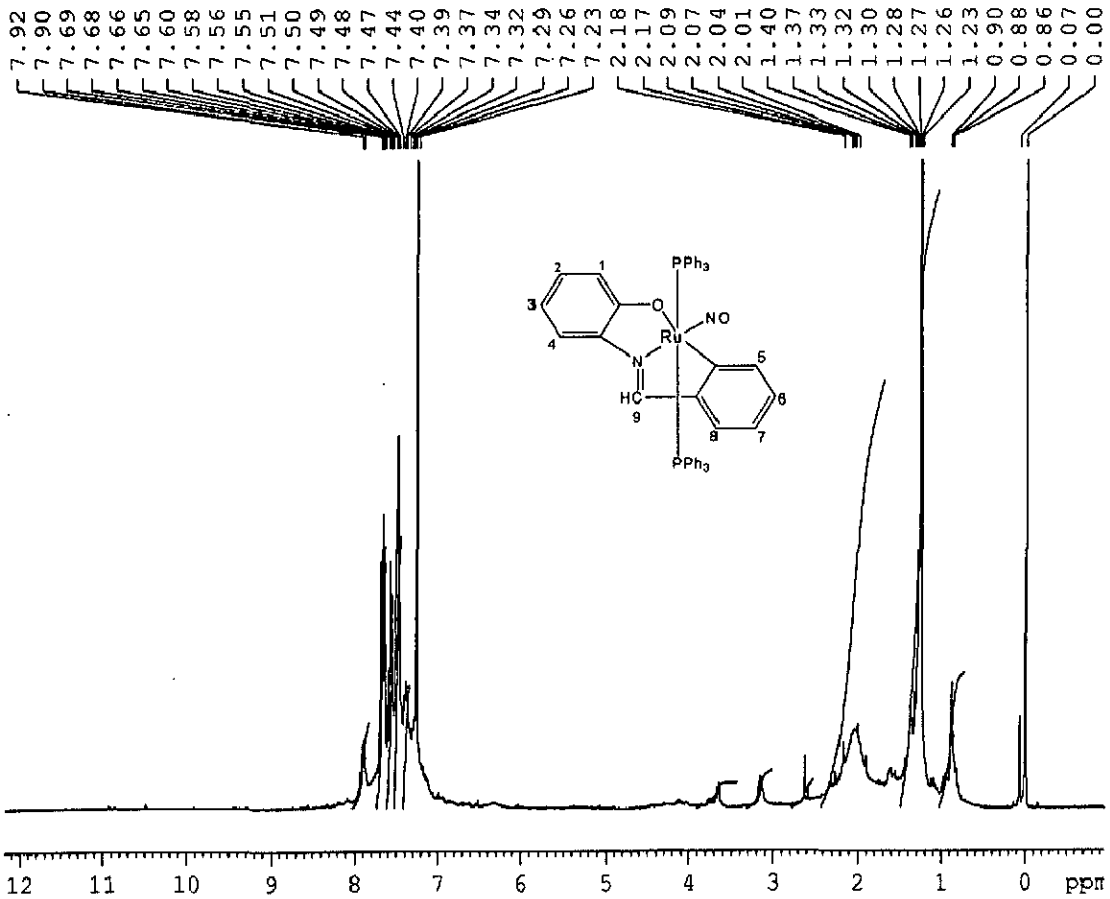


Figure 9: ^{1}H NMR spectrum of Ru(PPh$_3$)$_2$LNO complex

C, H, N contents of ligand and complexes determined experimentally are in good agreement with the calculated value (see Table 4)

Table 4: C, H, N analytical data:

Compound	Elemental Analysis[a] (%)		
	C	H	N
L	79.16(78.98)	5.62(5.39)	7.18(7.30)
$Ru(PPh_3)_2LCl$	68.73(68.26)	4.59(4.10)	1.64(1.97)
$Ru(PPh_3)_2LNO$	69.17(68.99)	4.62(4.29)	3.29(3.45)

[a] Calculated values are in parenthesis

This type of complexes shows photolability of coordinated NO. The photolability of our complex was examined following the procedure reported by Patra *et al.*[2c, 3, 9, 10] Figure 10 shows that the original compound doesn't undergo decomposition under UV radiation.

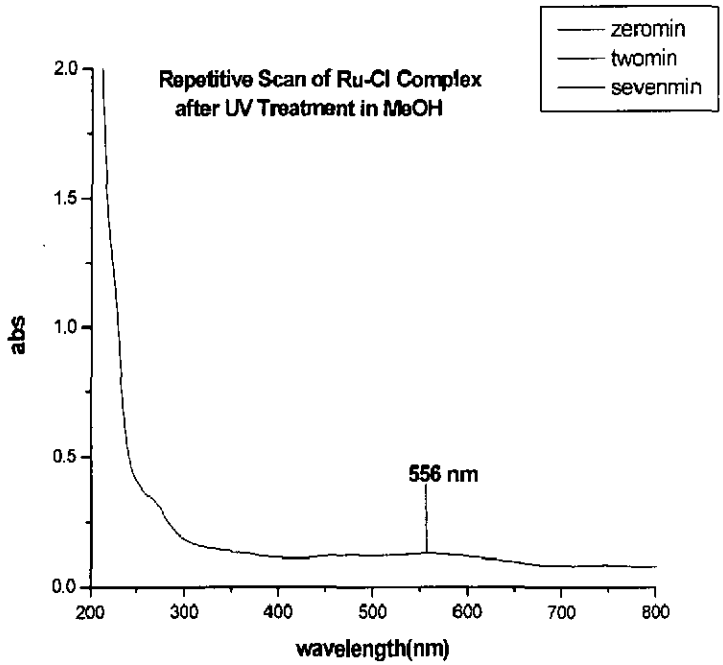


Figure10: Repetitive scan of $Ru(PPh_3)_2LCl$ after UV treatment in CH_3OH

Moreover, there is no change in UV-VIS spectra of the nitrosyl complex in exposure to visible light for two weeks and this complex is stable in CH_3OH for a long period of two months. However illumination of UV light to the complex in presence and absence of Cl^- ion clearly shows the decomposition of the nitrosyl complex. Illumination in presence of Cl^- ion is shown in Figure 11. There is an increase in absorption around 575 nm wavelengths and there is decrease in absorption around 259 nm and 294 nm wavelengths. Isosbestic points (at 442 nm) noted in the absorption spectra of the solution undergoing photolysis in presence of Cl^- (Figure 11) confirm clean conversion of Ru-NO to original Ru-Cl complex because Ru-Cl complex has moderate charge transfer band in the region 400 -700 nm.[11] We were unable to trap the NO through heme binding protein or any thiol. However this result is enough to prove the possibility of photolability of the coordinated Ru-NO complex.

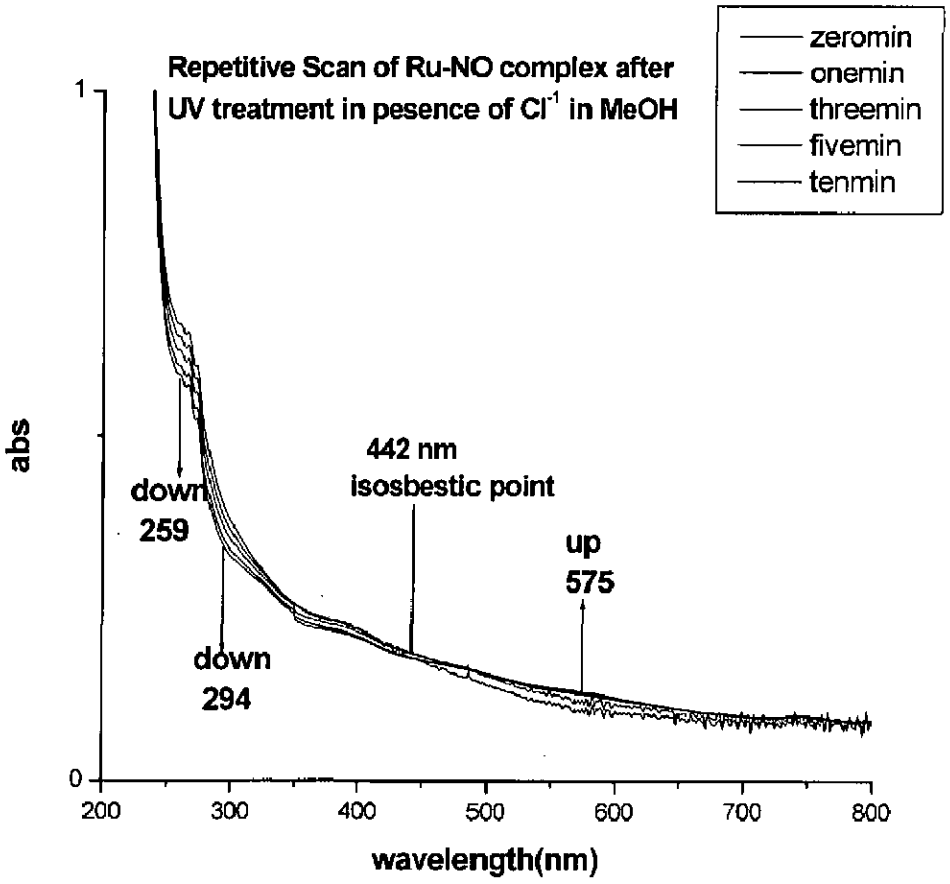


Figure 11: Repetitive scan of $Ru(PPh_3)_2LNO$ after UV treatment in presence of Cl^- in CH_3OH

4. CONCLUSION:

The main finding of this work will now be summarized:

1. We prepared a novel organometallic ruthenium nitrosyl complex. Ruthenium (III) organometallic complex has been converted to diamagnetic ruthenium complex showing clear NMR.
2. *In situ* generation of NO reacted at the metal center. Ligand nitration was not observed.
3. Metal ligated NO was photolabile.

5. REFERENCES:

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3. (a) Patra, A. K.; Rose, M. J.; Murphy, K. A.; Olmstead, M. M.; Pradip K. Mascharak, P. K. *Inorg. Chem.* **2004**, *43*, 4487-4495. (b) Patra, A.; Rose, M. J.; Olmstead, M. M.; Mascharak, P. K. *J. Am. Chem. Soc.* **2004**, *126*, 4780-4781.

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Enemark, J. H.; Feltham, R. D. *Coord. Chem. Rev.* **1974**, *13*, 339.

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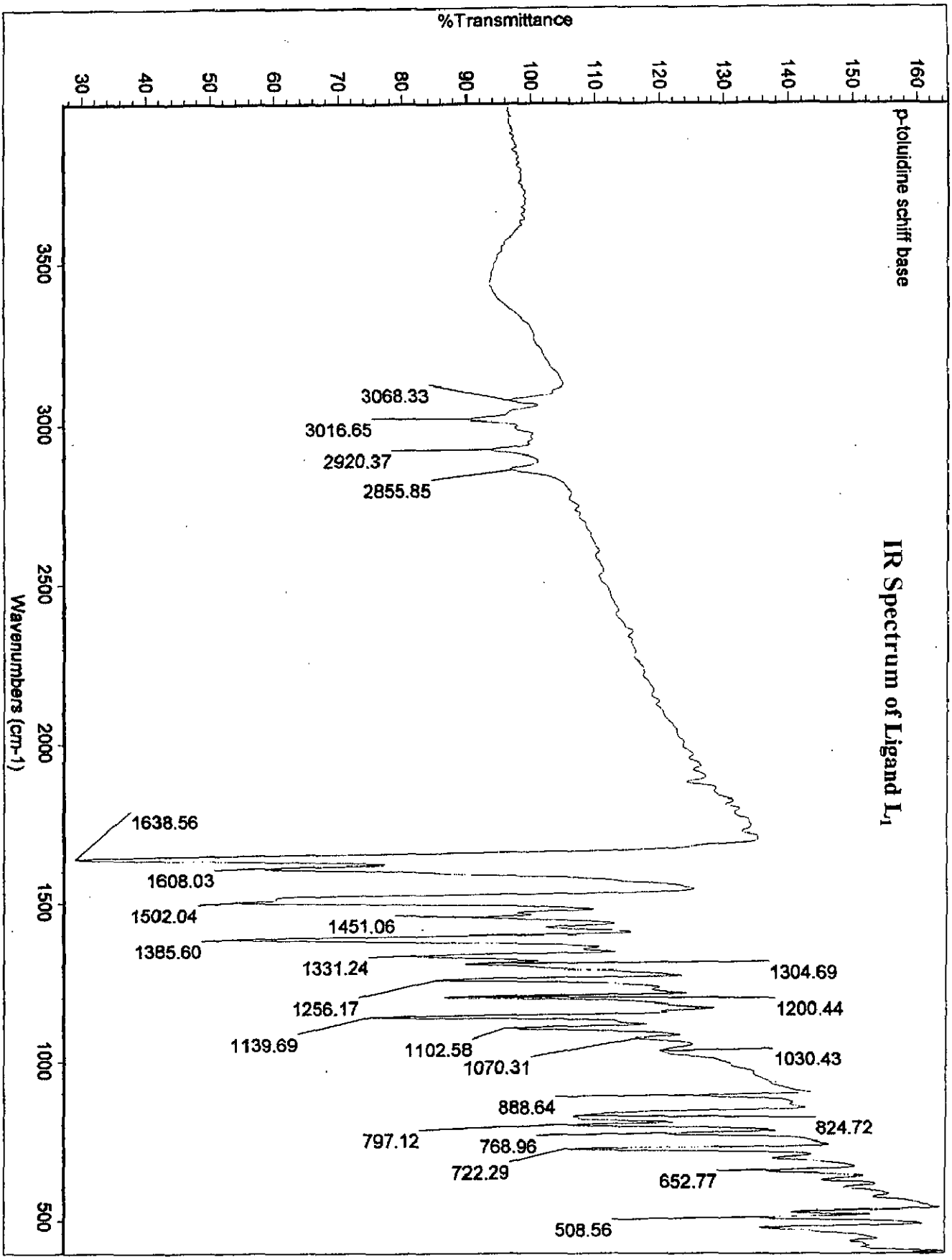
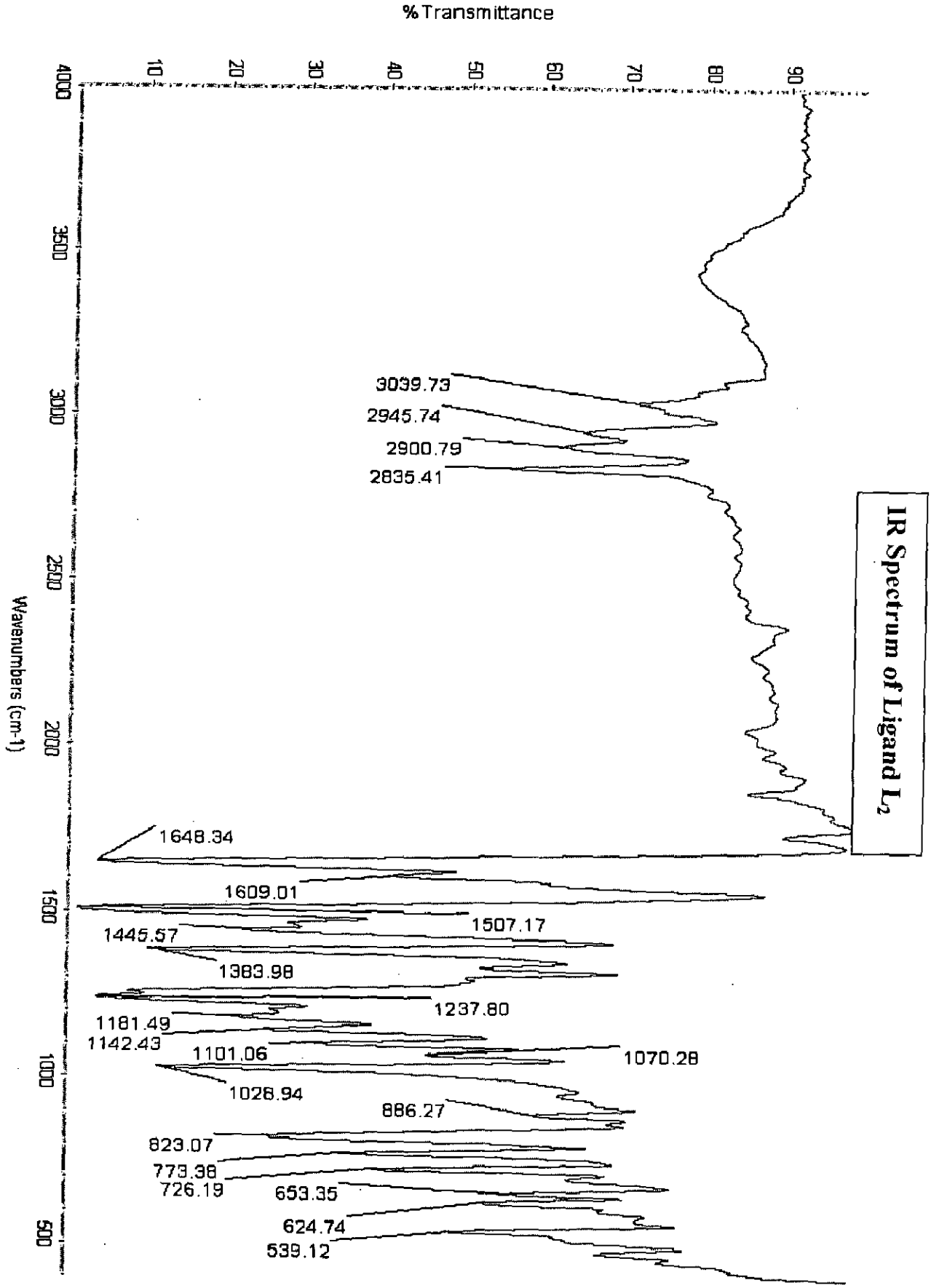
Appendices



IR Spectrum of Ligand L_1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3500
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500
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2945.74
2900.79
2835.41
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1445.57
1383.98
1237.80
1181.49
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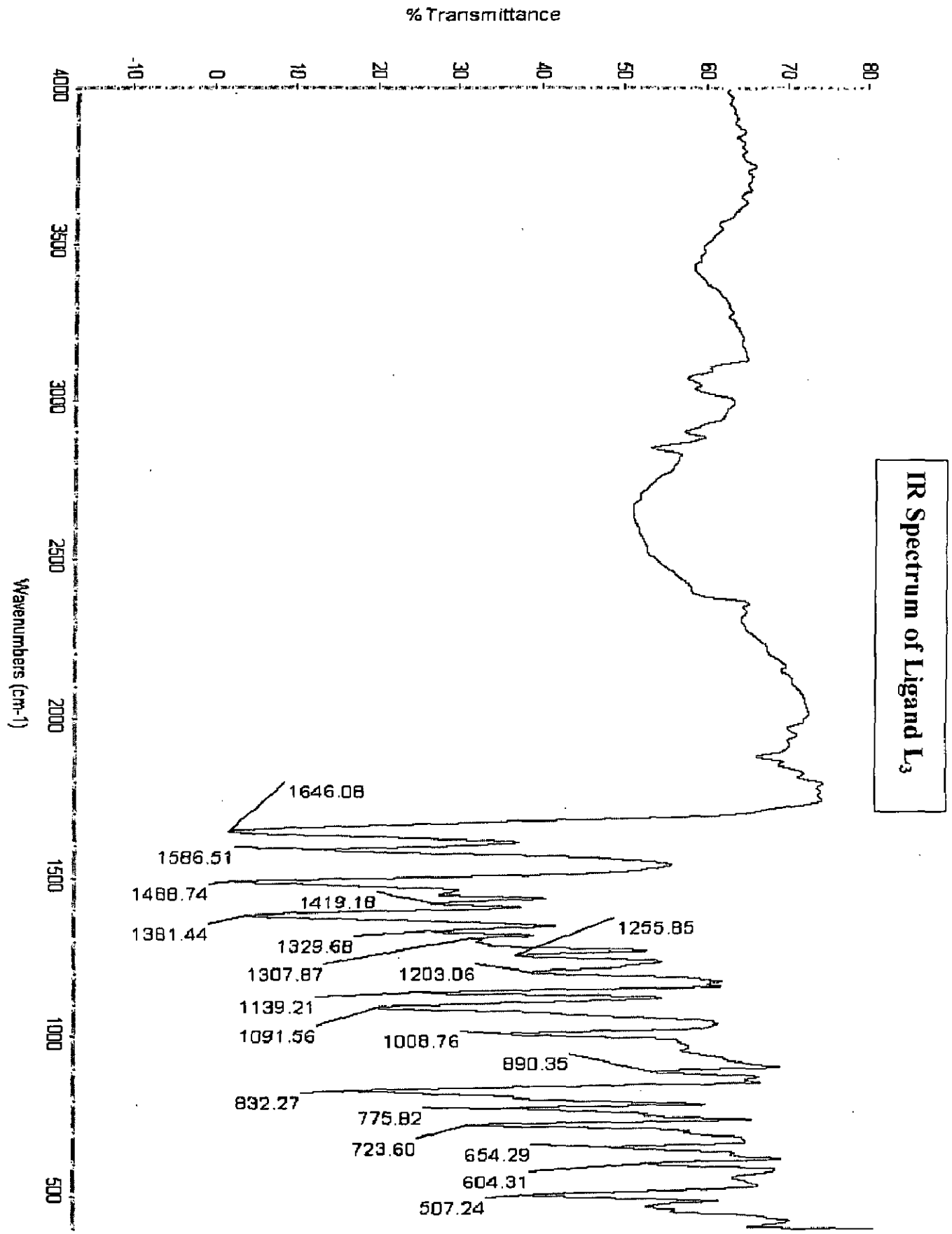

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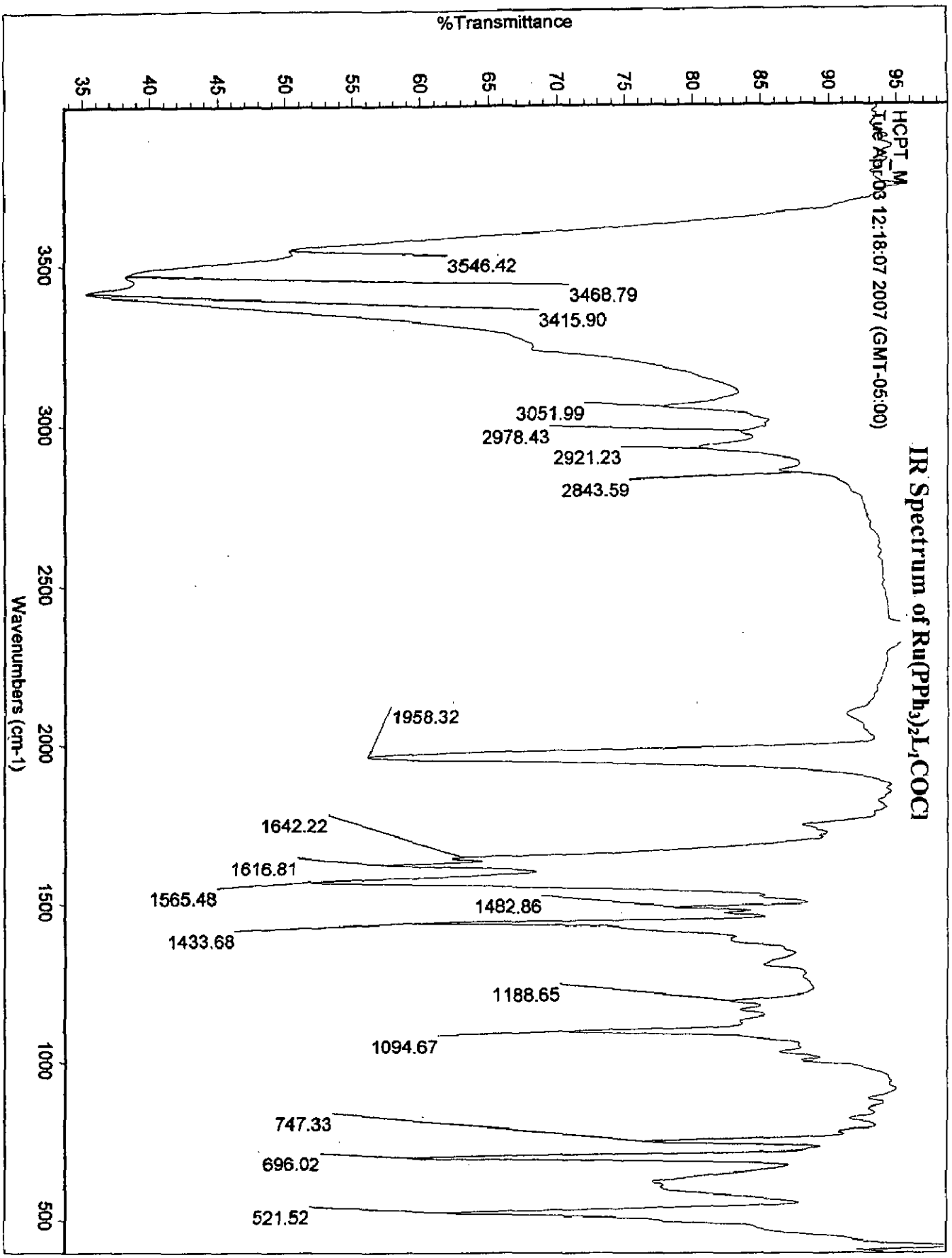
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1958.32
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1433.68
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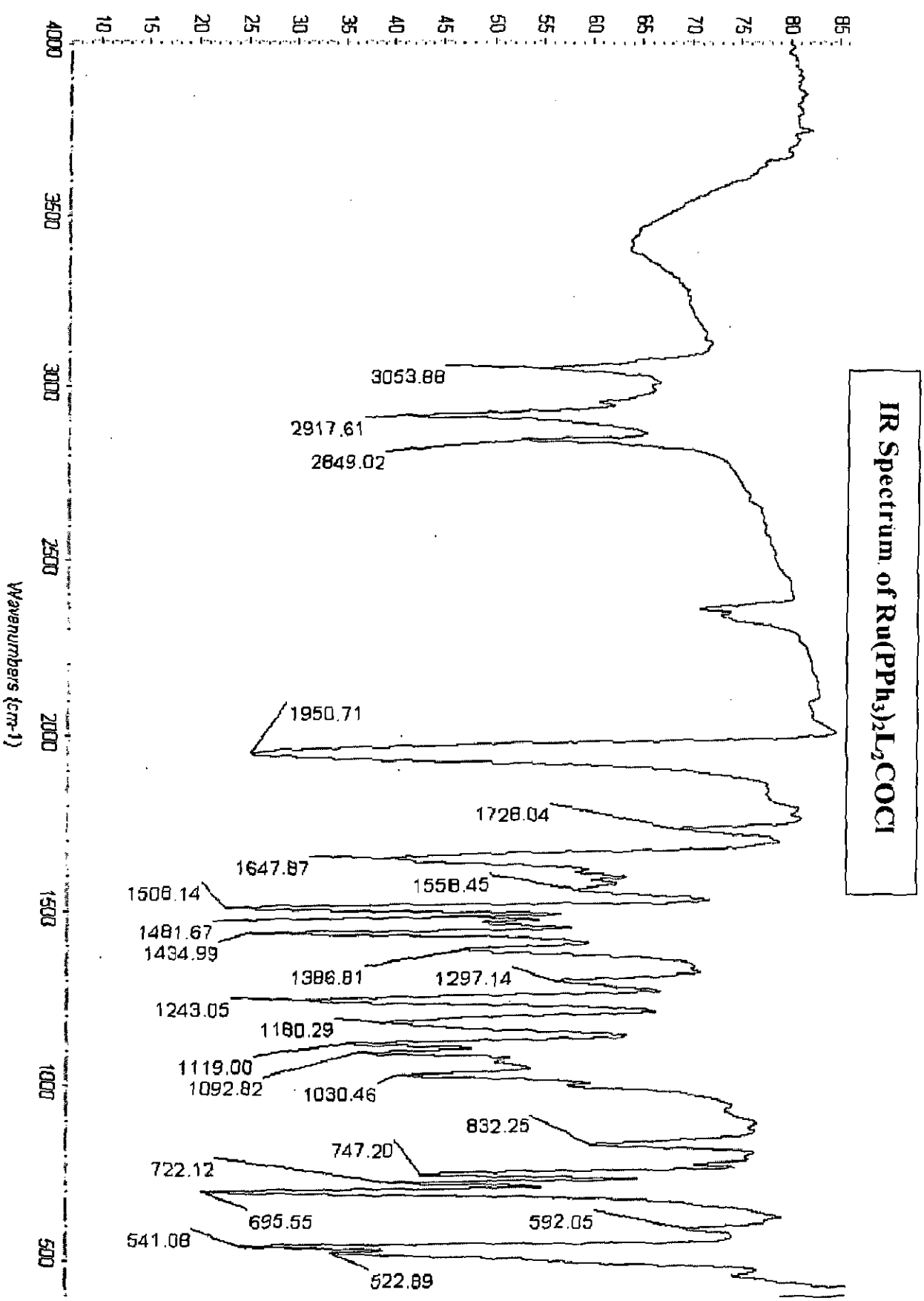
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1243.05
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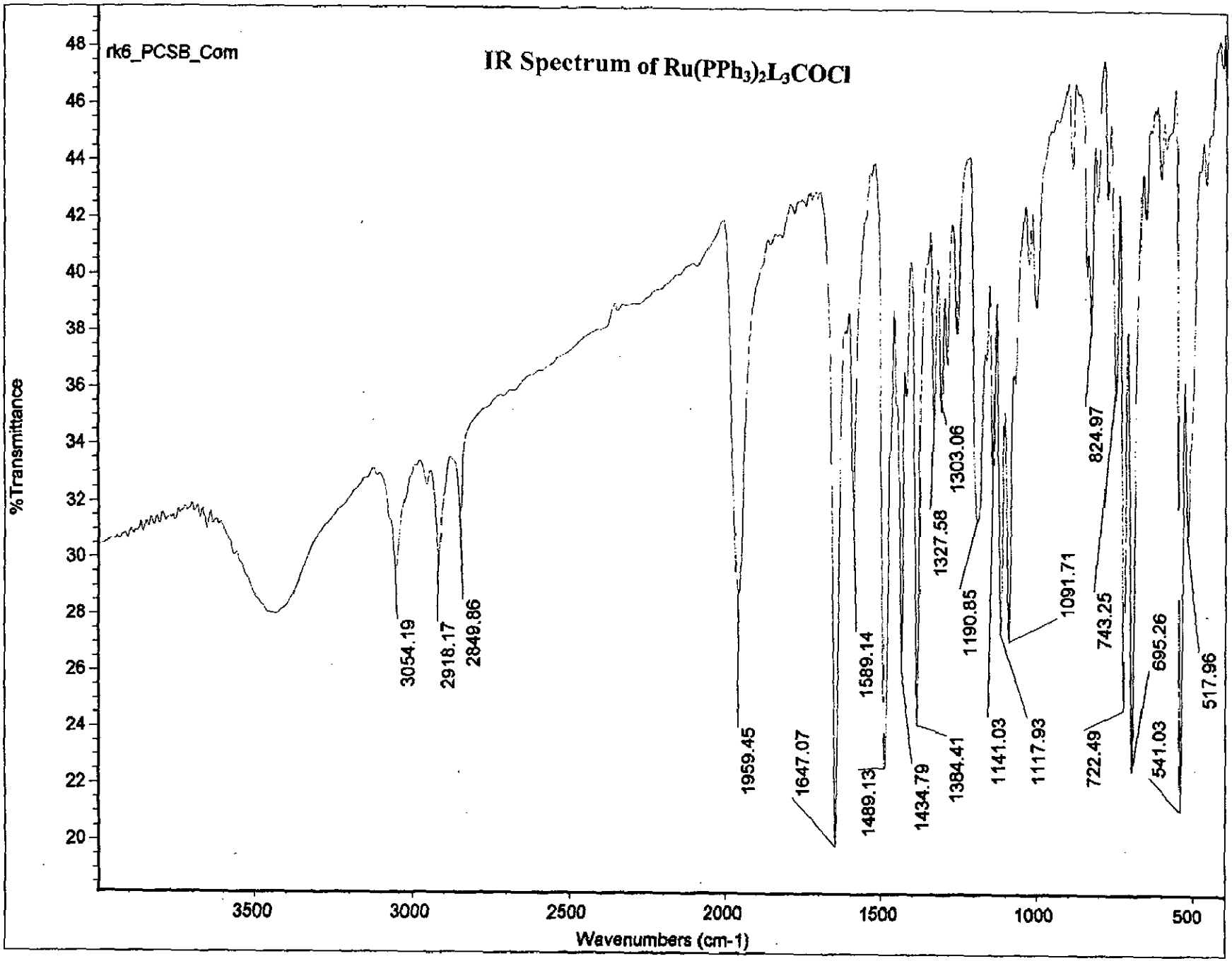
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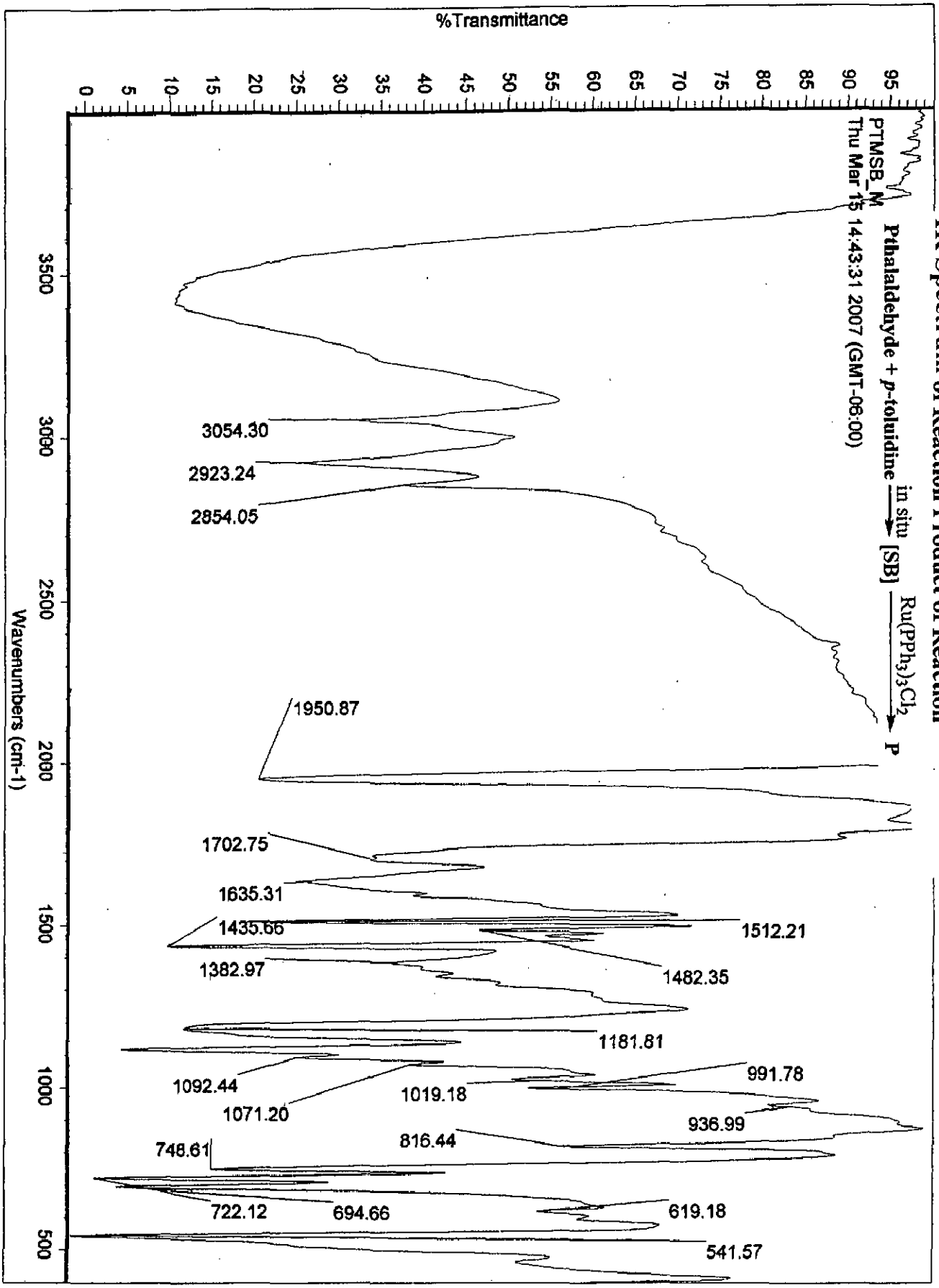

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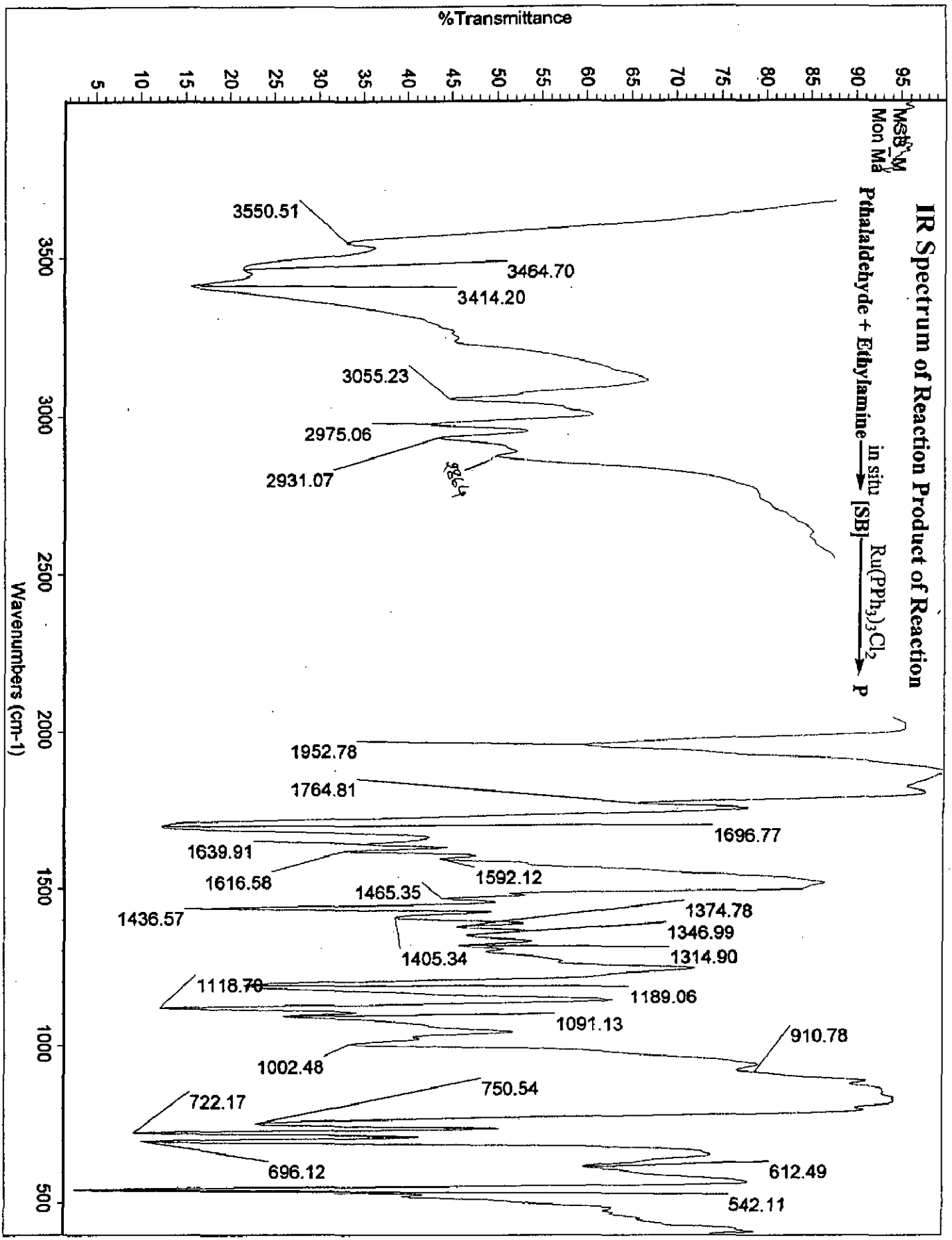

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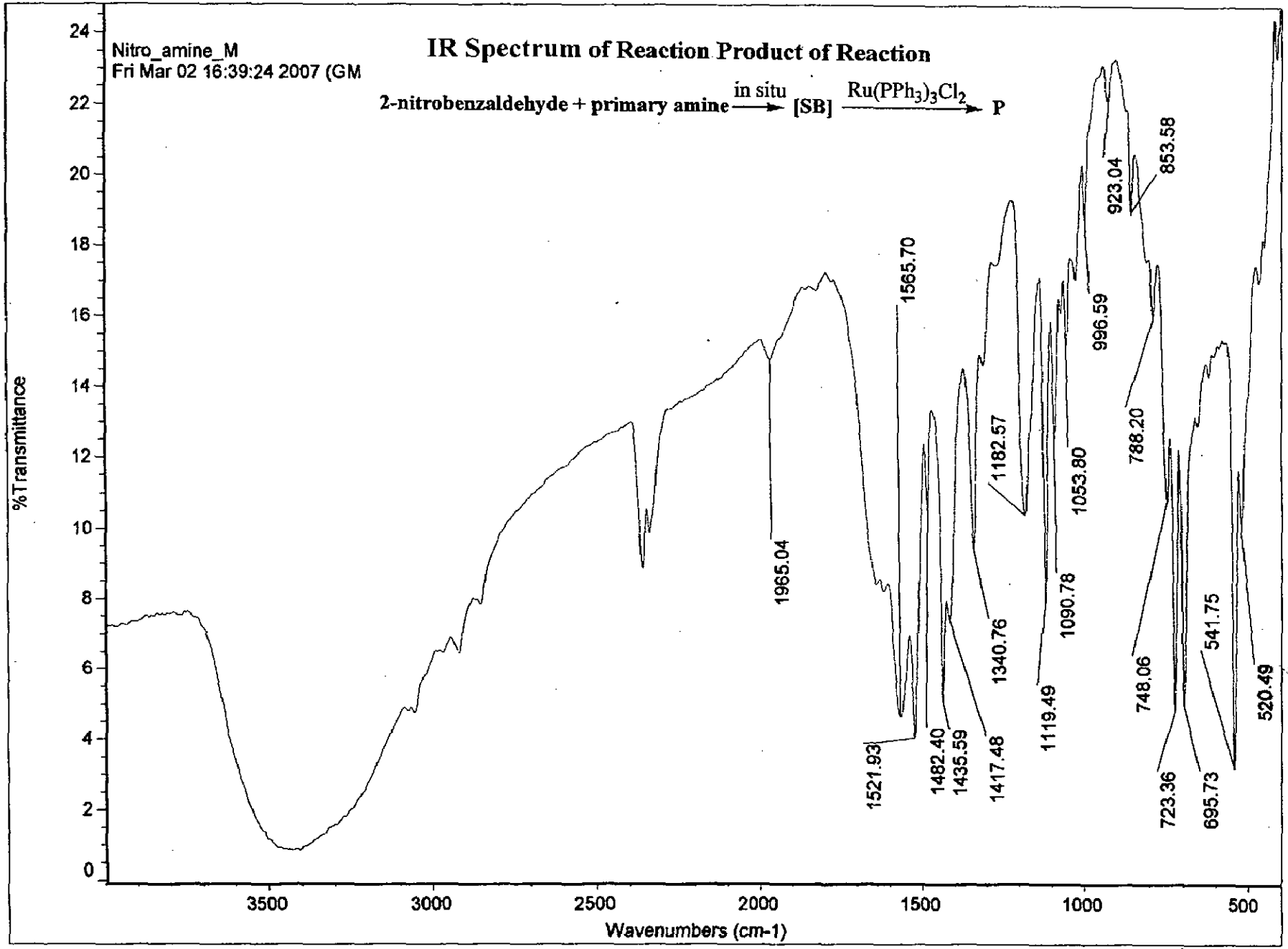
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IR Spectrum of Reaction Product of Reaction
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6
8
10
12
14
16
18
20
22
24
1965.04
1565.70
1521.93
1482.40
1435.59
1417.48
1340.76
1182.57
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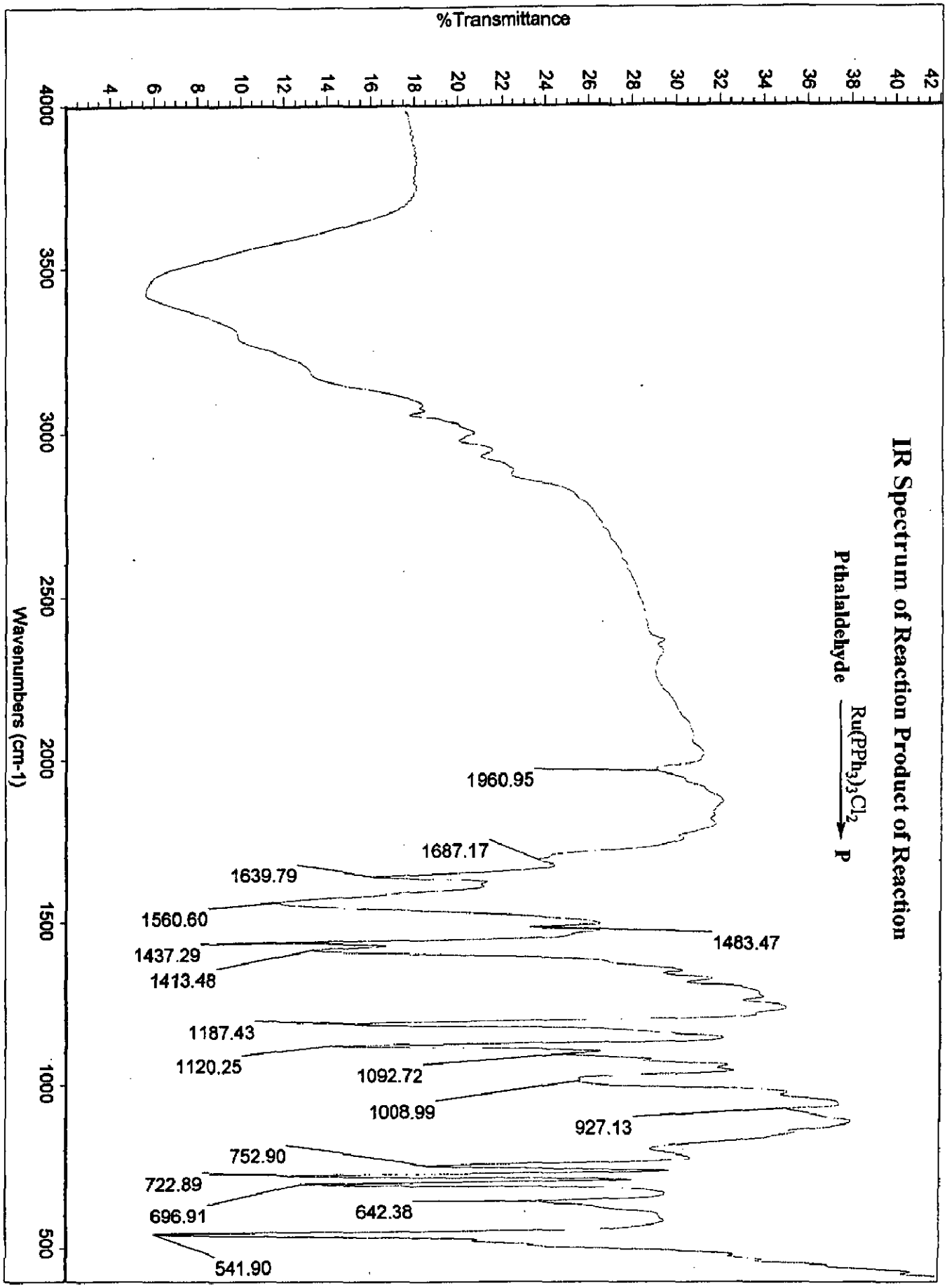
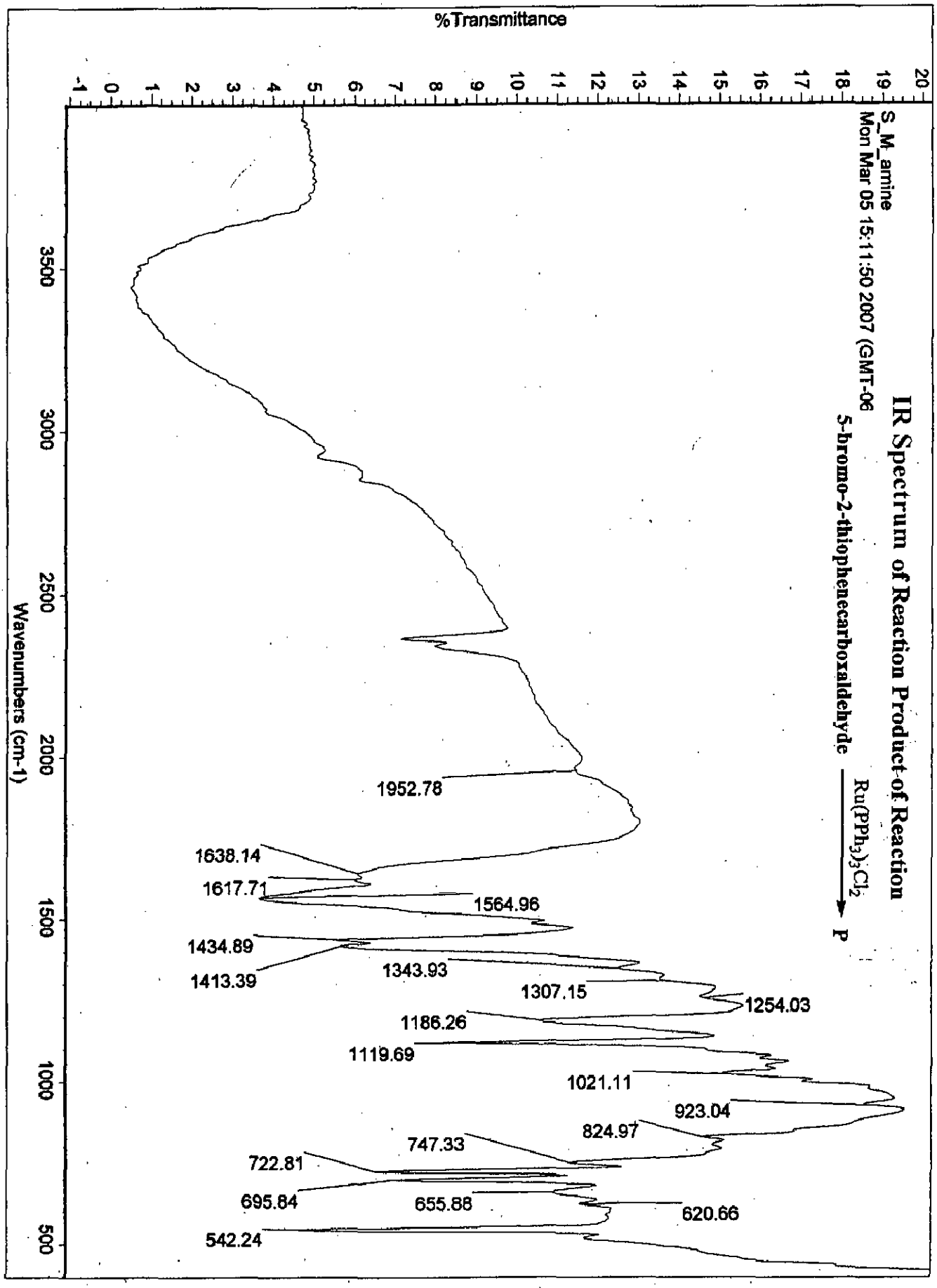


IR Spectrum of Reaction Product of Reaction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P
IR Spectrum of Reaction Product of Reaction
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1343.93
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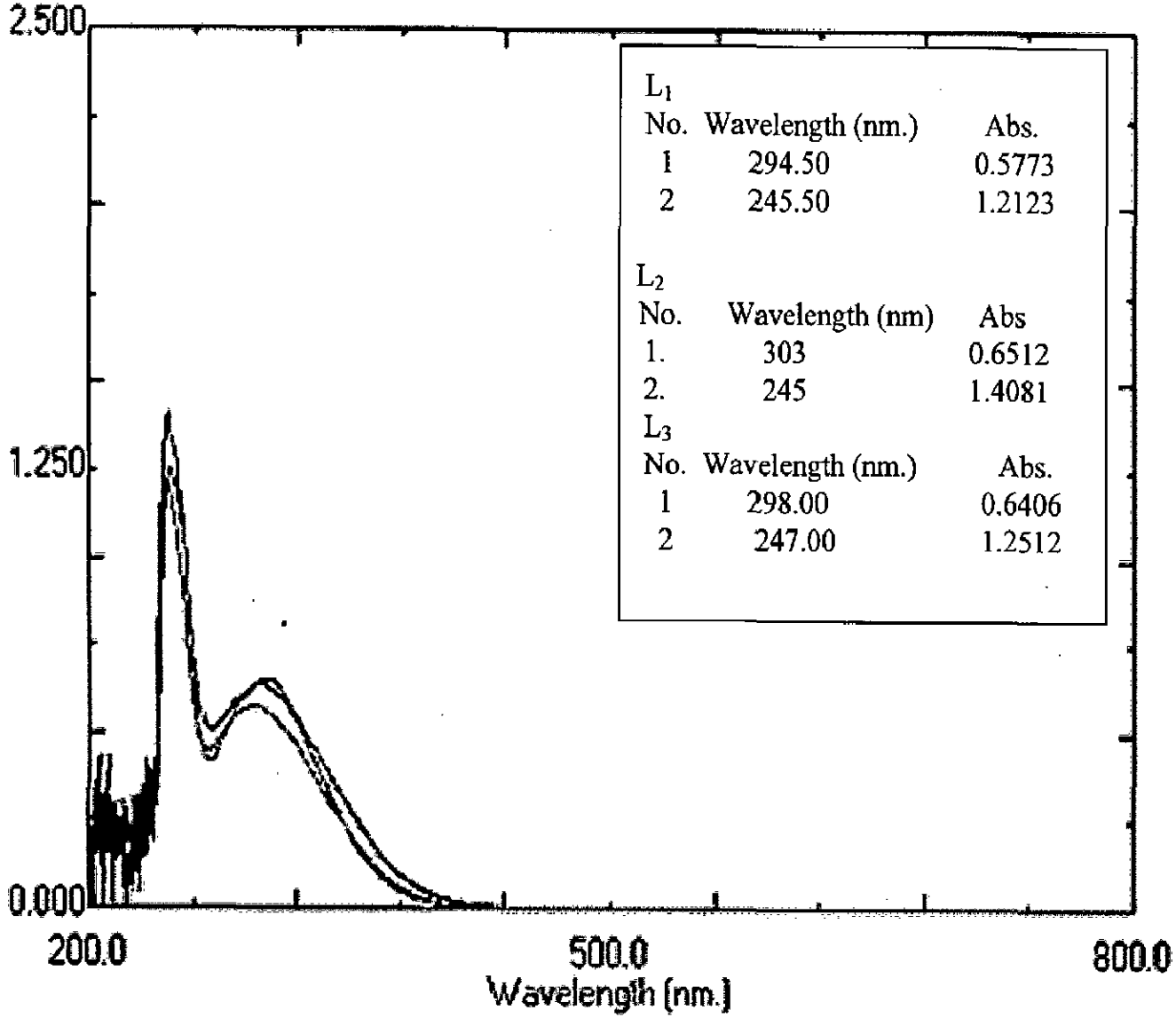
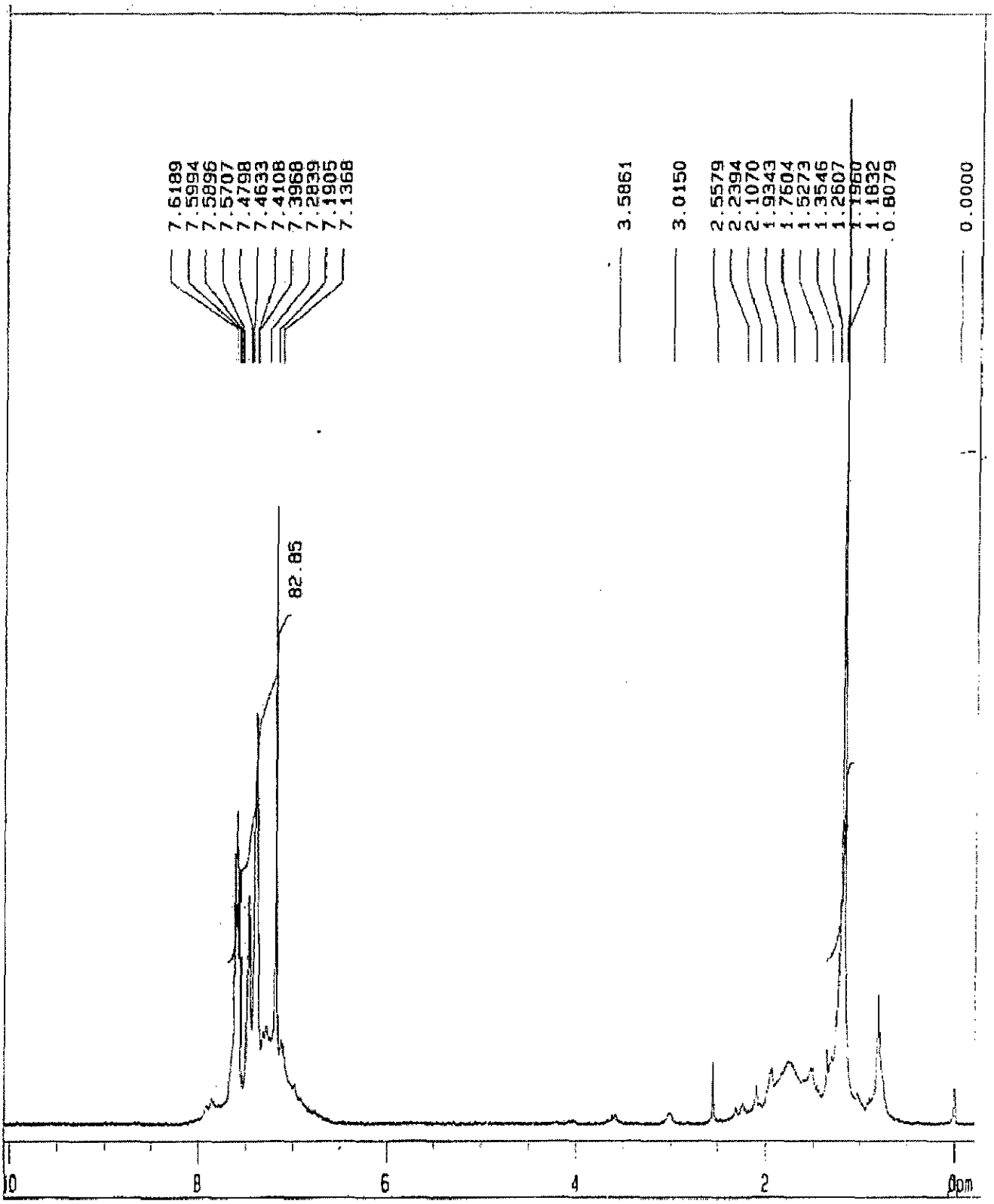


UV-VIS Spectra of Ligands L_1, L_2, and L_3

^{1}H NMR spectrum of $Ru(PPh_3)_2L_1COCl$



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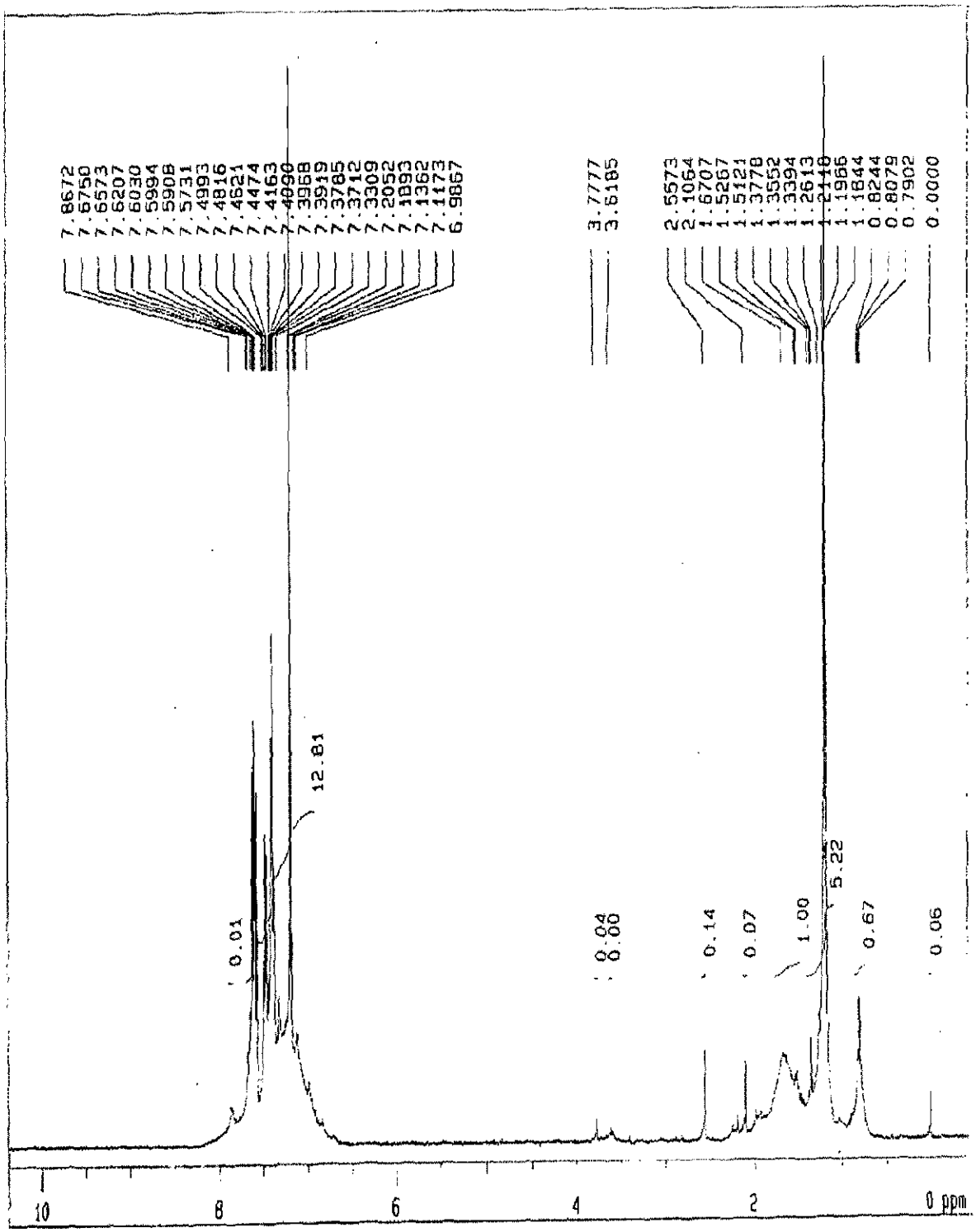

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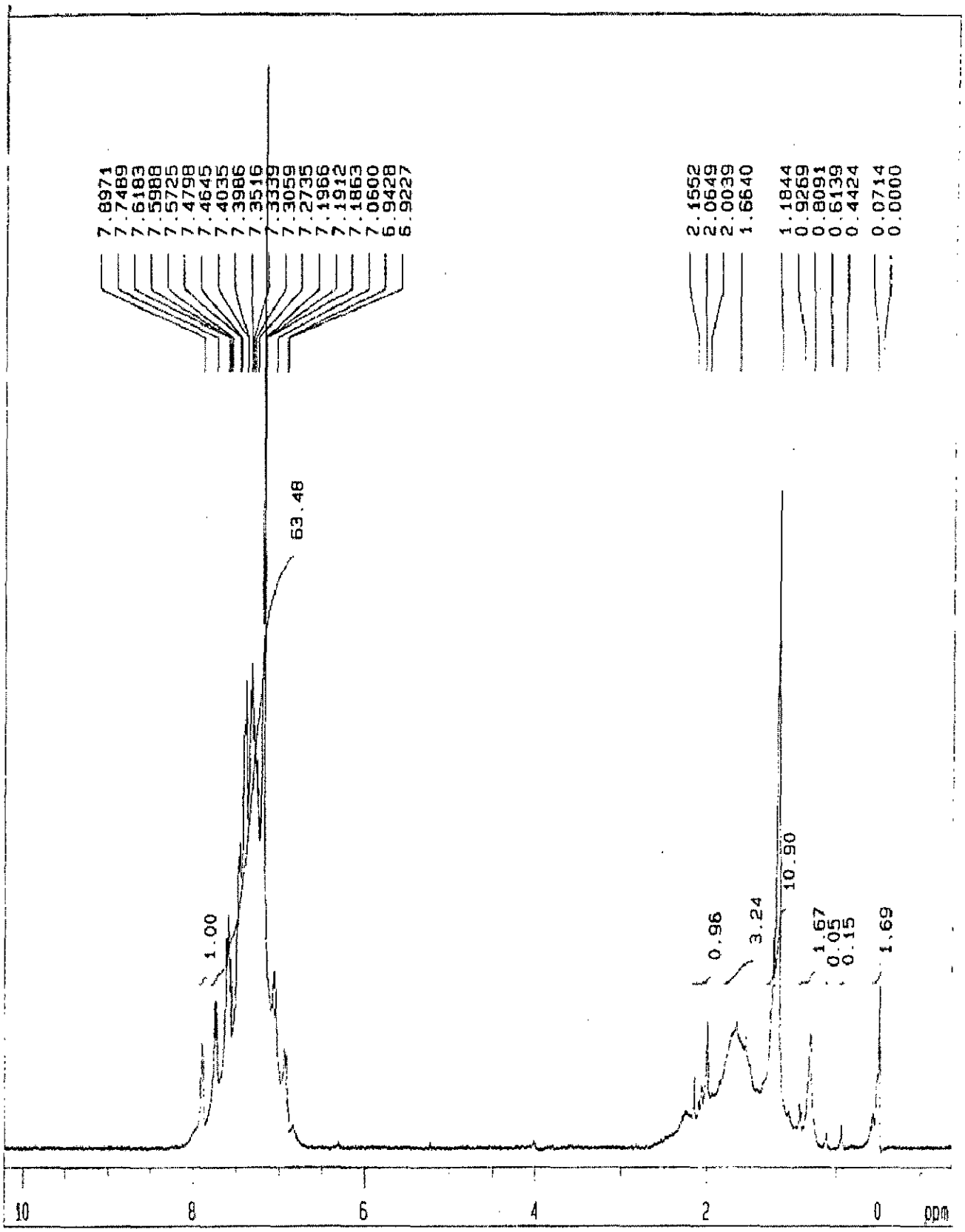
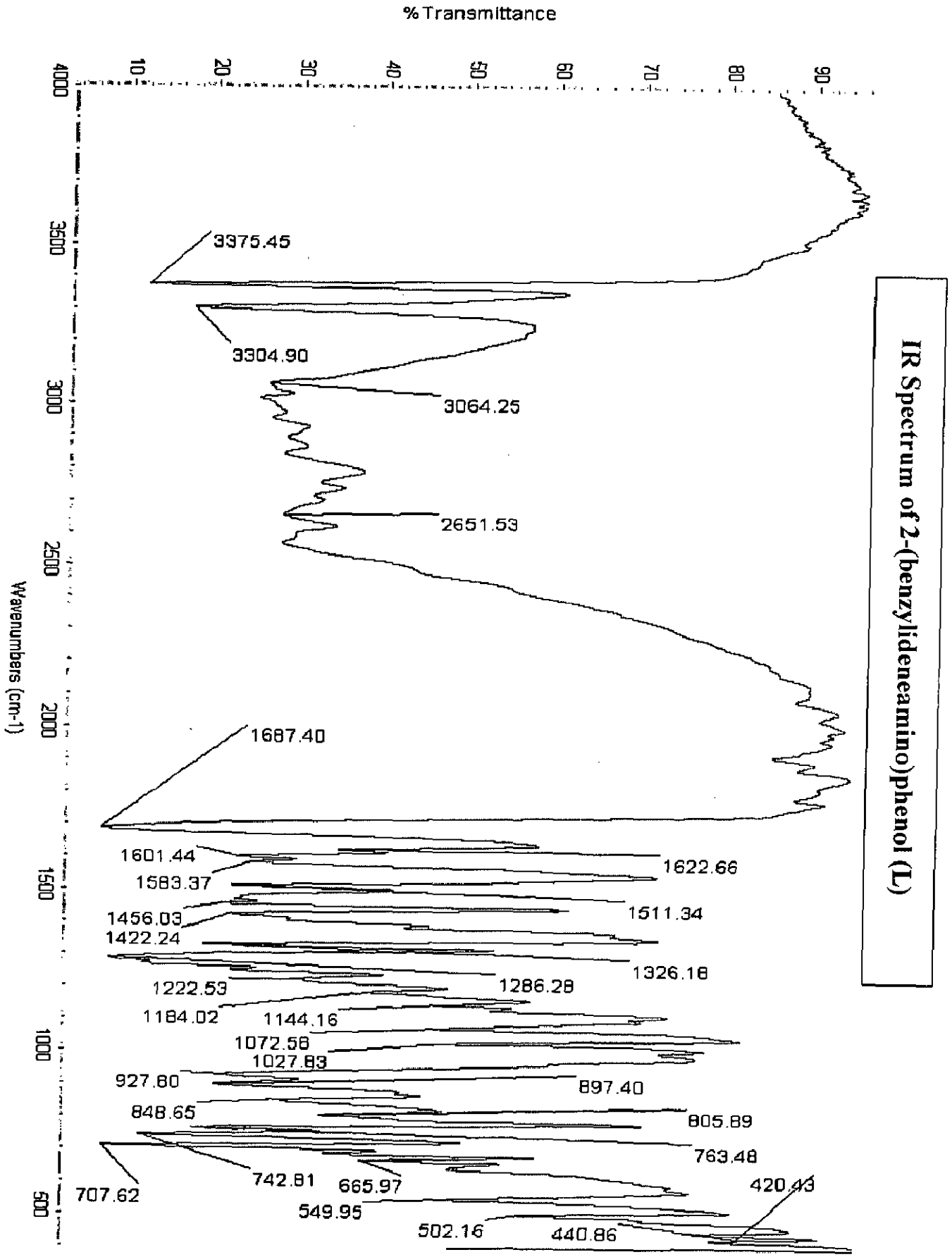
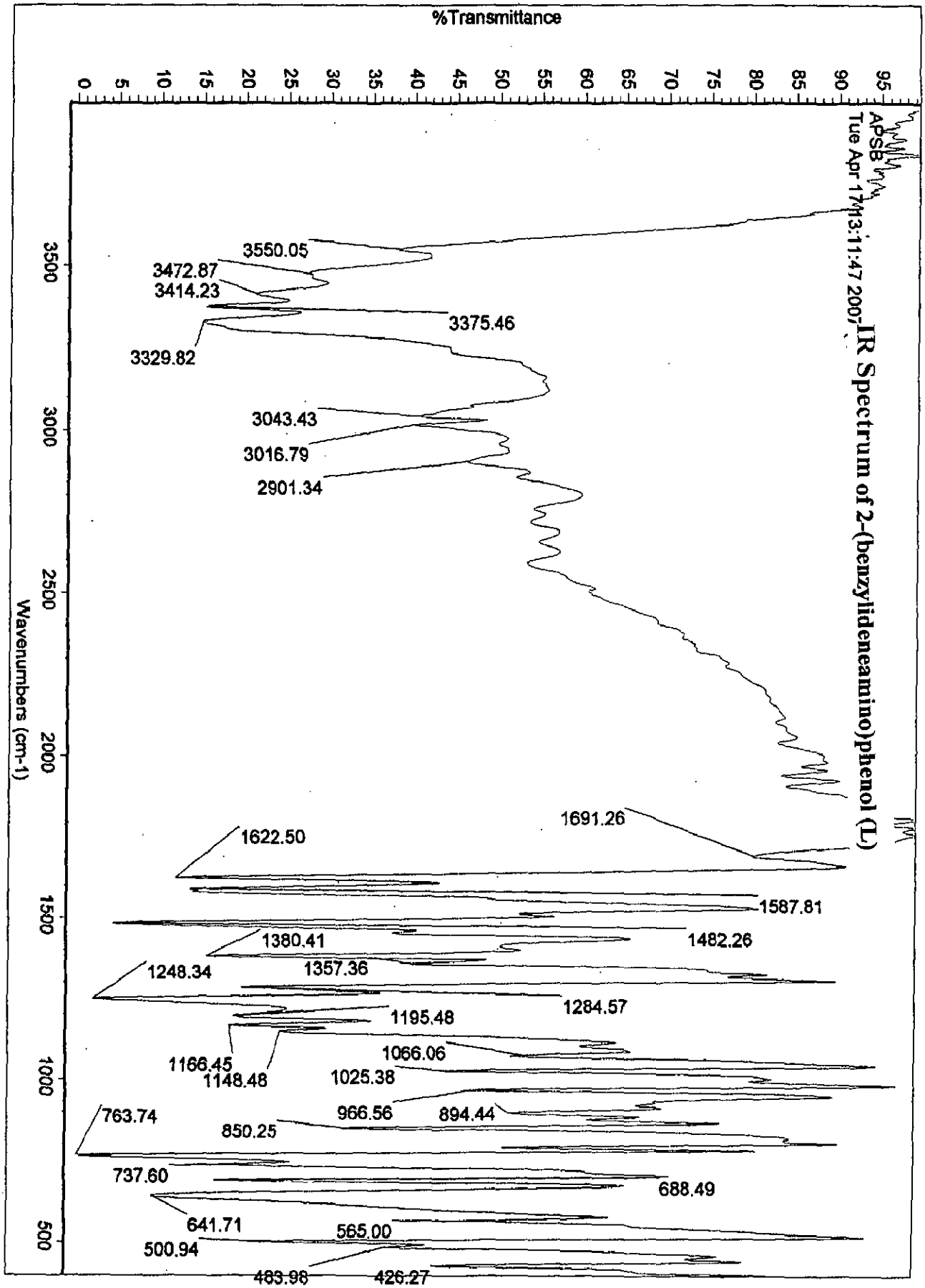




IR Spectrum of 2-(benzylideneamino)phenol (L)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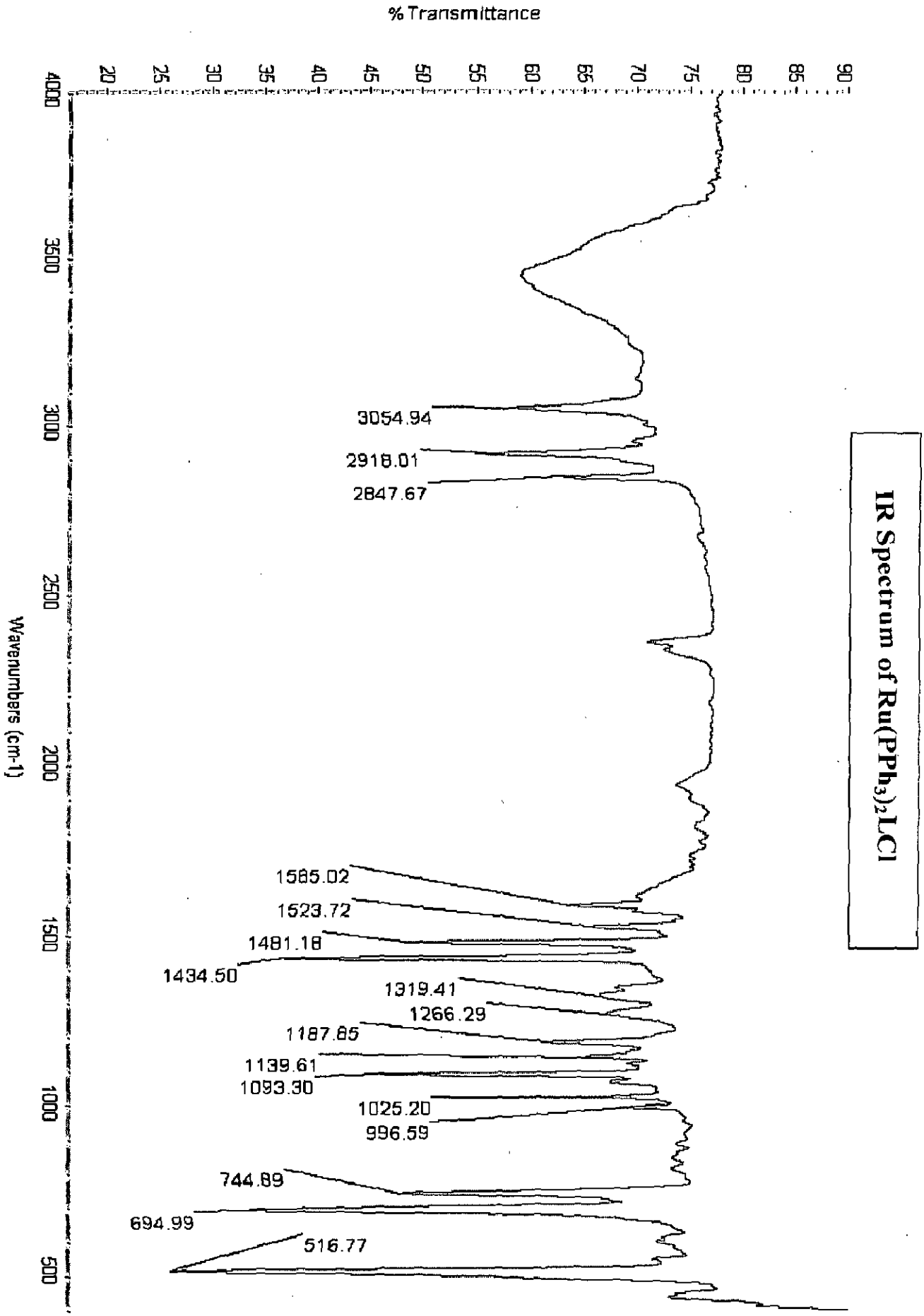

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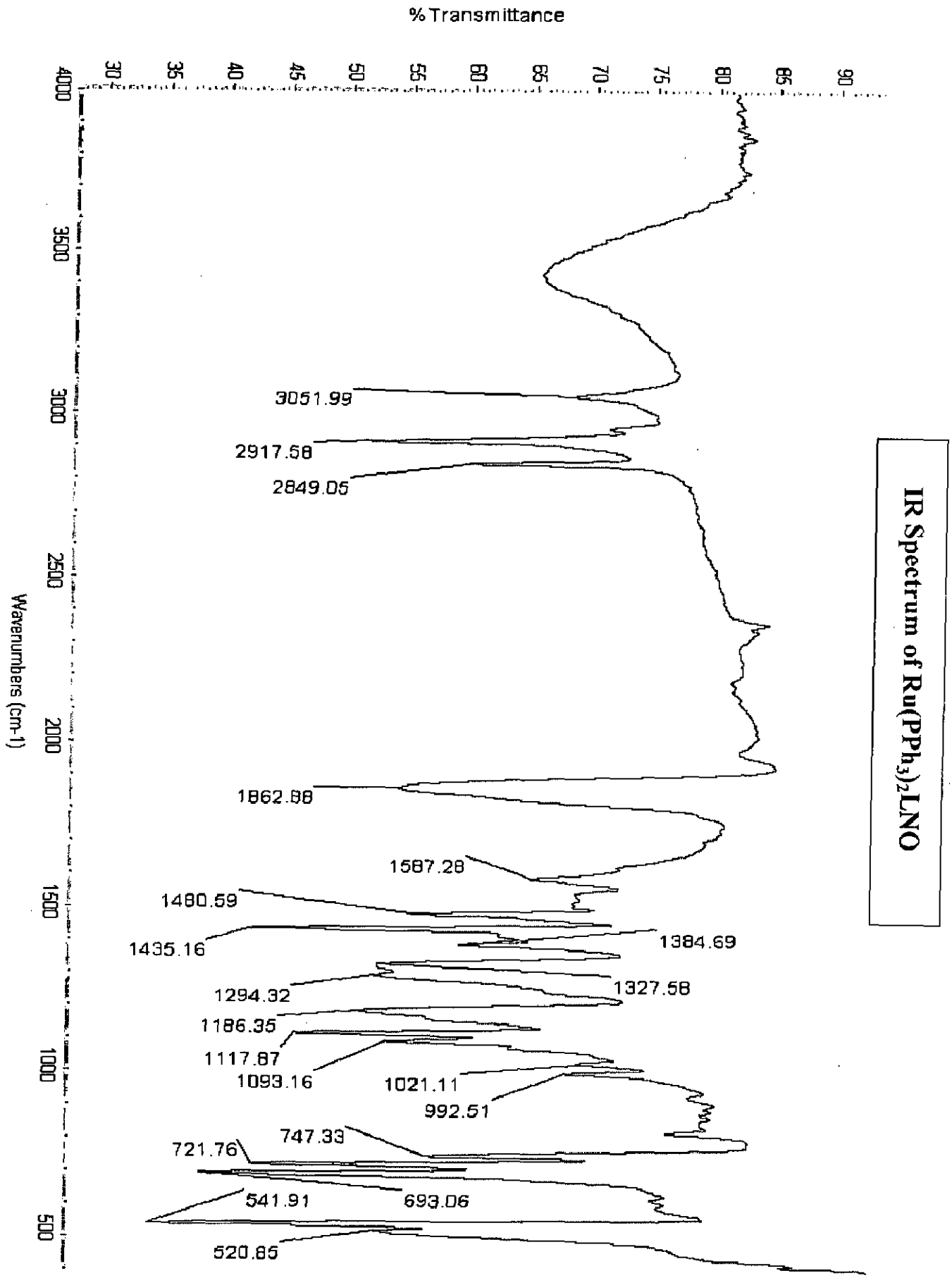

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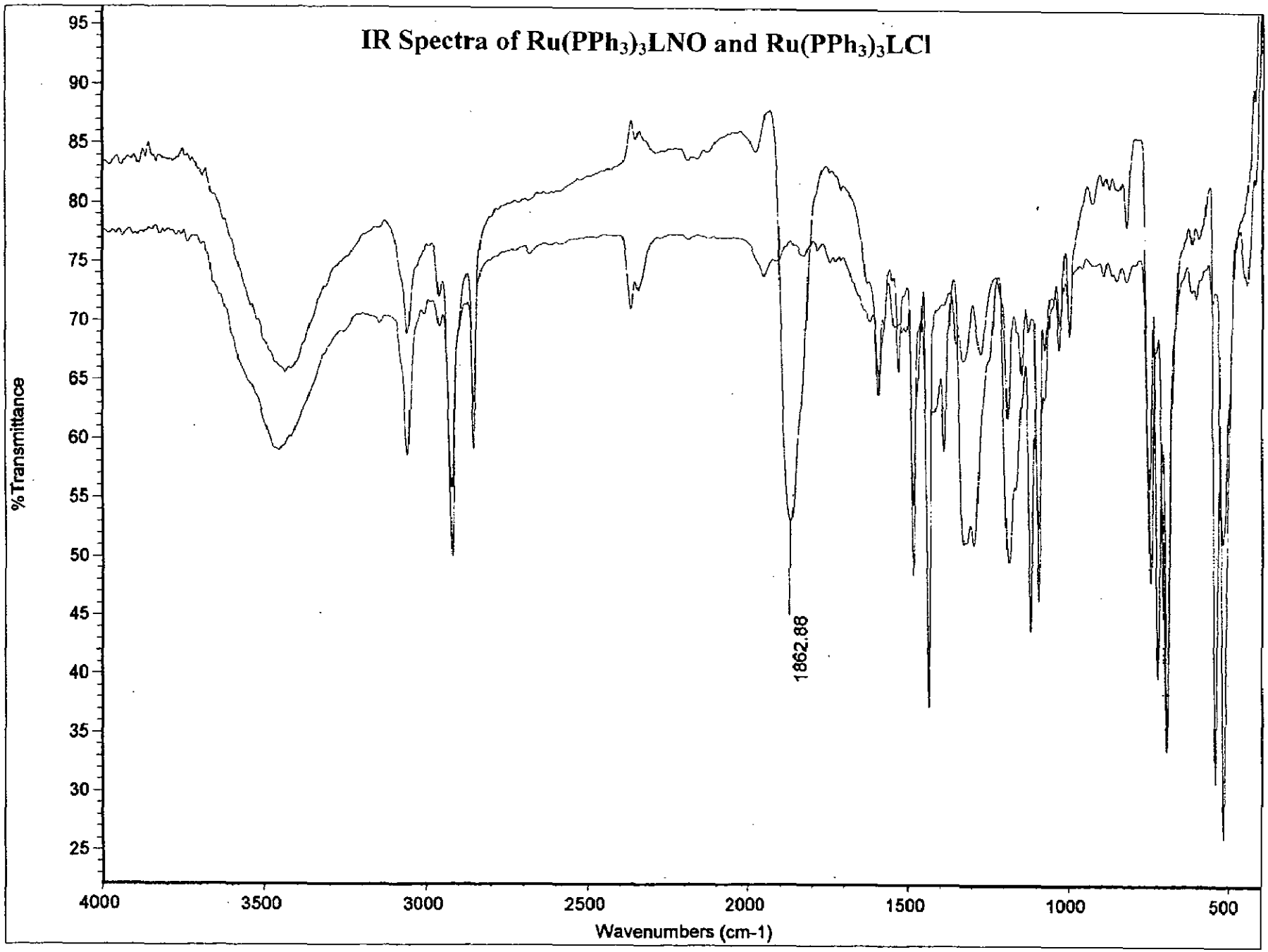
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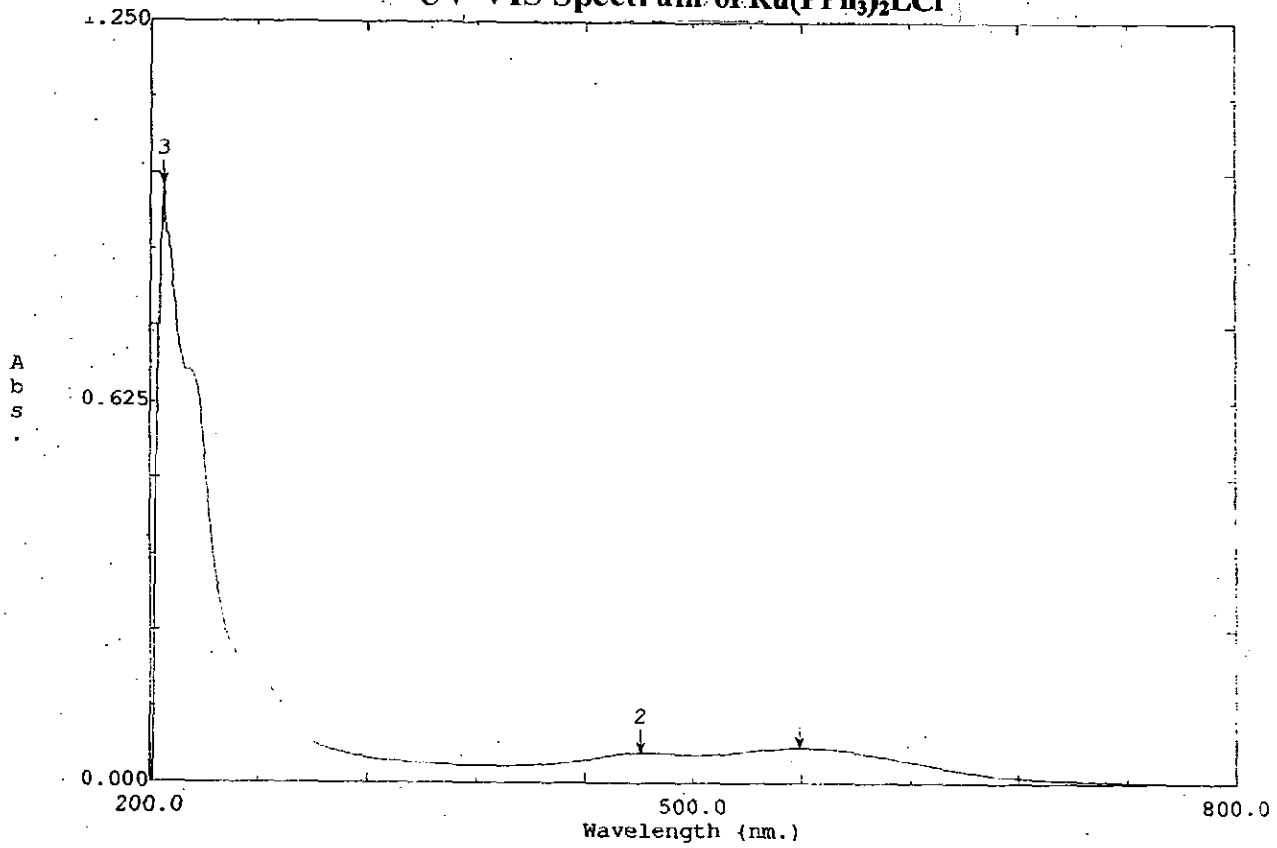
Wavenumbers (cm-1)

UV-VIS Spectrum of $Ru(PPh_3)_2LCl$



Peak Pick

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solvent MeOH

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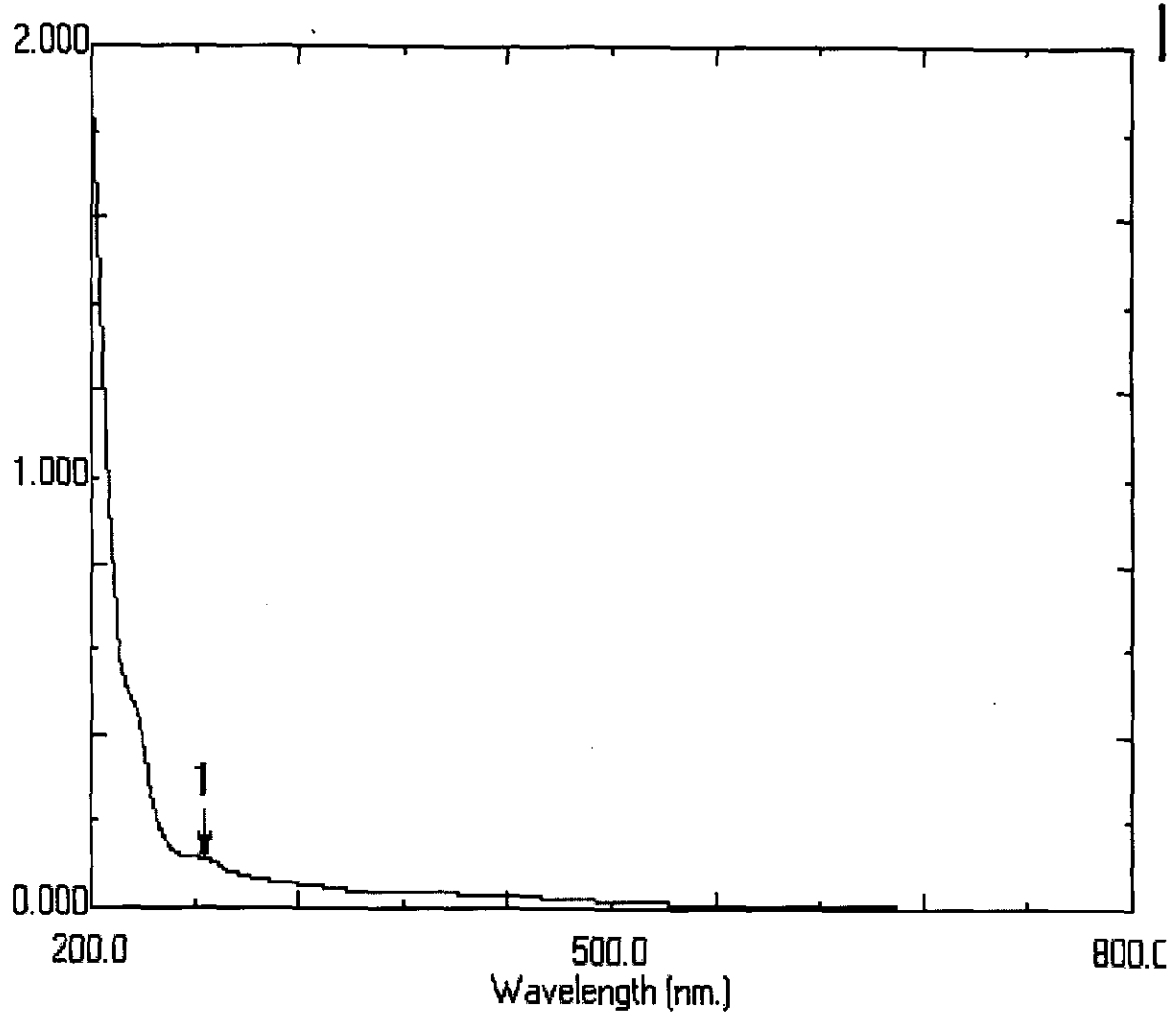

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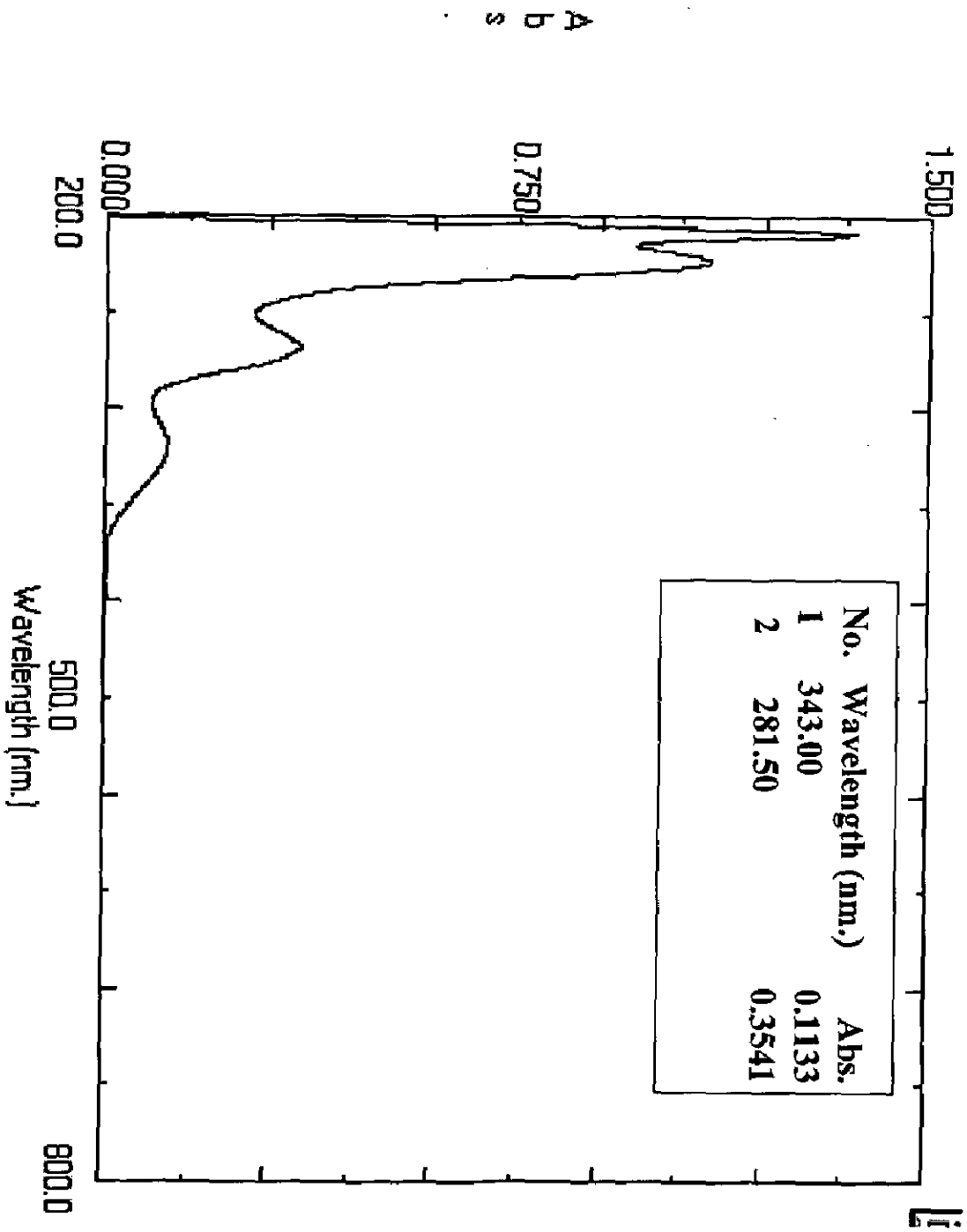

UV-VIS Spectrum of 2-(benzylideneamino)phenol (L)

^{1}H NMR spectrum of $Ru(PPh_3)_2LNO$