EGE UNIVERSTY GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

(MASTER OF SCIENCE THESIS)

THE PREPARATION OF SCHIFF BASES AND THEİR COMPLEXES FROM NATURALLY AMINO ACIDS

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BORNOVA-İZMİR

Sayın Sibel Şen tarafından yüksek lisans tezi olarak sunulan ‘’Doğal Amino Asitlerden Schiff bazları ve metal komplekslerinin hazırlanması’’ başlıklı çalışma E.Ü lisansüstü eğitim ve öğretim yönetmeliği ile E.Ü.Fen Bilimleri Enstitüsü Eğitim ve Öğretim Yönergesi’nin ilgili hükümleri uyarınca tarafımızdan değerlendirilerek savunmaya değer bulunmuş ve ………….. Tarihinde yapılan tez savunma sınavında aday oybirliği/oyçokluğu ile başarılı bulunmuştur.

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ÖZET

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Tez yöneticisi: Prof. Dr. Demet Astlety

Temmuz 2009, 111 Sayfa

2,3-dihidroksibenzaldehit, 2-hidroksi-3-bütoksibenzaldehit, o-Vanilin ile üç farklı amino asit (L İzolösin, L Tersiyerlösin, L Valin) kullanılarak üç dişli Schiff bazları sentezlendi. Bu ligandların Ni(II), Cu(II) gibi metal iyonları ile oluşturdukları kompleksler incelendi. Ürünlerin yapıları spektroskopik analizler (IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR) ve elementel analiz sonuçları ile karakterize edildi.

Anahtar Kelimeler: Schiff bazı, Metal Kompleksleri, 2,3-Dihidroksibenzaldehit, 2-hidroksi- 3-bütoksibenzaldehit, o-Vanilin , amino asit.

ABSTRACT

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Tridentate Schiff base ligands were synthesized from 2,3-dihydroxybenzaldehyde, 2-hydroxy-3butoxybeznaldehyde, o-Vanillin and three different amino acids (L tert-leucine, L iso-leucine, L valine). Metal complexes of the Schiff bases with Ni(II), Cu(II) metal ions were prepared. The products were characterized by spectroscopic methods (IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR, TGA) and elemental analysis.

Key words: Schiff base, metal complexes, 2,3-dihydroxybenzaldehyde
2-hydroxy-3butoxybeznaldehyde, o-Vanillin.

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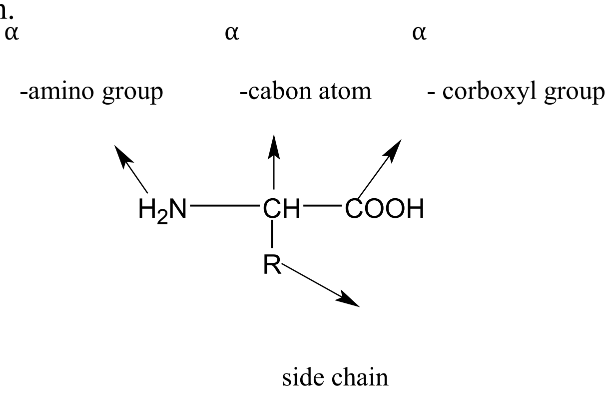
ABBREVIATIONS

DNA	Deoxyribonucleic Acid
NMR	Nuclear Magnetic Resonance
IR	Infrared
FT-IR	Fourier Transformation Infrared
UV	Ultraviolet
T.L.C	Thin Layer Chromatography
NaOH	Sodium hydroxide
KBr	potassium hydroxide
TGA	Thermo gravimetric analysis
s	singlet
m	multiplet
b	broad
d	doublet
t	triplet

1. Introduction

1.1 Amino acids

Proteins are the most abundant organic molecules in animals, playing important rules in all aspects of cell structure and function. Proteins are biopolymers of α-amino acids, and the physical and chemical properties of a protein are determined by its constituent amino acids (Wade, 1987). The term amino acids might mean any molecule both an amino group and any type of acid group; however, the term is almost always used to refer an α-amino acetic acid. Each amino acid consists of an α-carbon atom which is attached; a hydrogen atom, an amino group, a carboxyl group, an R (side chain) group. The various alpha amino acids differ in which side chain (R group) is attached to their alpha carbon. They can vary in size from just a hydrogen atom in glycine through a methyl group in alanine to a large heterocyclic group in tryptophan.



Scheme 1.1

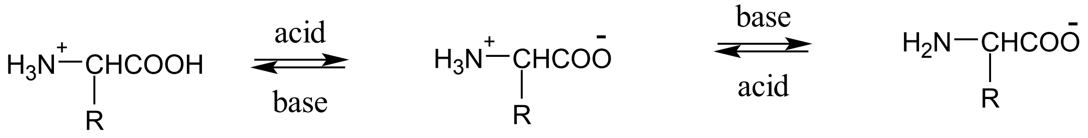
The 20 amino acids that are major components of peptides and proteins are often called standard amino acids (Weininger and Stermitz, 1984). Humans can produce 10 of 20 amino acids. The others must be supplied in the food. Failure to obtain enough of even 1 of the 10 essential amino acids, those that we cannot make, result in degradation of the body's proteins to obtain the one amino acid that is needed. Unlike fat and starch, the human body does not store excess amino acids for later use. The amino acids must be in the food every day. The 10 amino acids that we can produce are; alanine-asparagine-aspartic acid-cysteine-glutamic acid-glutamine-glycine-proline-serine-tyrosine.The essential amino acids are arginine (required for young but not adults), histidine, isoleucine,phenylalanine, leucine, lysine, methionine, threonine, trypyophn, and valine. These amino acids are required for the diet. Plants must be able to make all the amino acids. Humans do not have all the enzymes required for the biosynthesis of all of the amino acid.

1.1.1 Properties of amino acids

Amino acids have high melting points, usually decomposing above 200 C^0. They have good solubility in water and low solubility in nonpolar solvents (Ege, 1984). Amino acids have much larger dipole moments (μ) than simple amines or simple acids.

Amino acids are less acidic than most carboxylic acids and less basic than most amines. In fact, the acidic part of amino acid molecule is the NH_3^+ group, not a COOH group. The basic part is the COO^- group, and not a free NH_2 group.

Amino acids contain both an acidic carboxyl (-COOH) and a basic amino ($-NH_2$) group. Carboxylic acids are strong enough to protonate most amines, and the amino acid undergoes an internal acid-base reaction. The carboxyl group loses a proton to become a carboxylate ion, and the amino group is protonated to give an ammonium ion. The overall structure has a net charge of zero, but there is positive charge on nitrogen and negative charge spread over the oxygen's of carboxylate group. This structure is called a dipolar ion or zwitterion. We have seen that an amino acids bears a negative charge in basic solution (high pH), and a positive charge in acidic solution (low pH). There must be an intermediate pH where the amino acid evenly balanced between the two forms, as the dipolar zwitterion with a net charge of zero. This pH is called the isoelectric point or isoelectronic pH (Wade, 1987).



$$H_3\overset{+}{N}-\underset{R}{\underset{|}{C}}HCOOH \underset{base}{\overset{acid}{\rightleftharpoons}} H_3\overset{+}{N}-\underset{R}{\underset{|}{C}}HCO\overset{-}{O} \underset{acid}{\overset{base}{\rightleftharpoons}} H_2N-\underset{R}{\underset{|}{C}}HCO\overset{-}{O}$$

cation predominant form in acid

zwitterion predominant form at the isoelectric point

anion predominant form in base

Scheme 1.2

A tetrahedral carbon atom with 4 distinct constituent is said to be chiral. The one amino acid not exhibiting chirality is glycine since its R-group is a hydrogen atom. Chirality describes the handedness of a molecule that is observable by the ability of a molecule to rotate the plane of polarized light either to right (dextrorotatory) or to the left (levorotatory). All of amino acids in proteins exhibit the same absolute steric configuration as L-glyceraldehyde. Therefore, they are all L-α-amino acids. D-amino acids are often found in polypeptide antibiotics.

1.1.2 Essential amino acids

1.1.2.1 Histidine:

Histidine, an essential amino acid, has as a positively charged imidazole functional group. The imidazole makes it a common participant in enzyme catalyzed reactions. The unprotonated imidazole is nucleophilic and can serve as a general base, while the protonated form can serve as a general acid. The residue can also serve a role in stabilizing the folded structures of proteins. Histidine is given in scheme 1.3.

1.1.2.2 Arginine:

Arginine, an essential amino acid, has a positively charged guanidino group. Arginine is well designed to bind the phosphate anion, and is often found in the active centers of proteins that bind phosphorylated substrates. As a cation, arginine, as well as lysine, plays a role in maintaining the overall charge balance of a protein. Arginine also plays an important role in nitrogen metabolism. In the urea cycle, the enzyme arginase cleaves (hydrolyzes) the guanidinium group to yield urea and the L-amino acid ornithine. Ornithine is lysine with one fewer methylene groups in the side chain. L-ornithine is not normally found in proteins. Arginine is given in scheme 1.3.

1.1.2.3 İsoleucine:

Isoleucine, an essential amino acid, is one of the three amino acids having branched hydrocarbon side chains. It is usually interchangeable with leucine and occasionally with valine in proteins. The side chains of these amino acids are not reactive and therefore not involved in any covalent chemistry in enzyme active centers. However, these residues are critically important for ligand binding to proteins, and play central roles in protein stability. Note also that the β carbon of isoleucine is optically active, just as the β carbon of threonine. These two amino acids, isoleucine and threonine, have in common the fact that they have two chiral centers. İsoleucne is given in scheme 1.3.

1.1.2.4 Lysine:

Lysine, an essential amino acid, has a positively charged ε-amino group (a primary amine) Lysine is basically alanine with a propylamine substituent on the β-carbon. Lysine is given in scheme 1.3.

The ε-amino group has a significantly higher pK_a (about 10.5 in polypeptides) than does the α-amino group. The amino group is highly reactive and often participates in reactions at the active centers of enzymes. Proteins only have one α amino group, but numerous ε amino groups. However, the higher pK_a renders the lysyl side chains effectively less nucleophilic. Specific environmental effects in enzyme active centers can lower the pKa of the lysyl side chain such that it becomes reactive. Note that the side chain has three methylene groups, so that even though the terminal amino group will be charged under physiological conditions, the side chain does have significant hydrophobic character. Lysines are often found buried with only the ε-amino group exposed to solvent.

1.1.2.5 Methionine:

Methionine, an essential amino acid, is one of the two sulfur-containing amino acids. The side chain is quite hydrophobic and methionine is usually found buried within proteins. Unlike cysteine, the sulfur of methionine is not highly nucleophilic, although it will react with some electrophilic centers. It is generally not a participant in the covalent chemistry that occurs in the active centers of enzymes. Methionine is given in scheme 1.3.

1.1.2.6 Threonine:

Threonine, an essential amino acid, is a hydrophilic molecule. Threonine is another hydroxyl-containing amino acid. It differs from serine by having a methyl substituent in place of one of the hydrogens on the β carbon and it differs from valine. By replacement of a methyl substituent with a hydroxyl group. Note that both the α and β carbons of threonine are optically active. Threonine is given in scheme 1.3.

1.1.2.7 Valine:

Valine, an essential amino acid, is hydrophobic, and as expected, is usually found in the interior of proteins. Valine differs from threonine by replacement of the hydroxyl group with a methyl substituent. Valine is often referred to as one of the amino acids with hydrocarbon side chains, or as a branched chain amino acid. Valine is given in scheme 1.3.

1.1.2.8 Leucine:

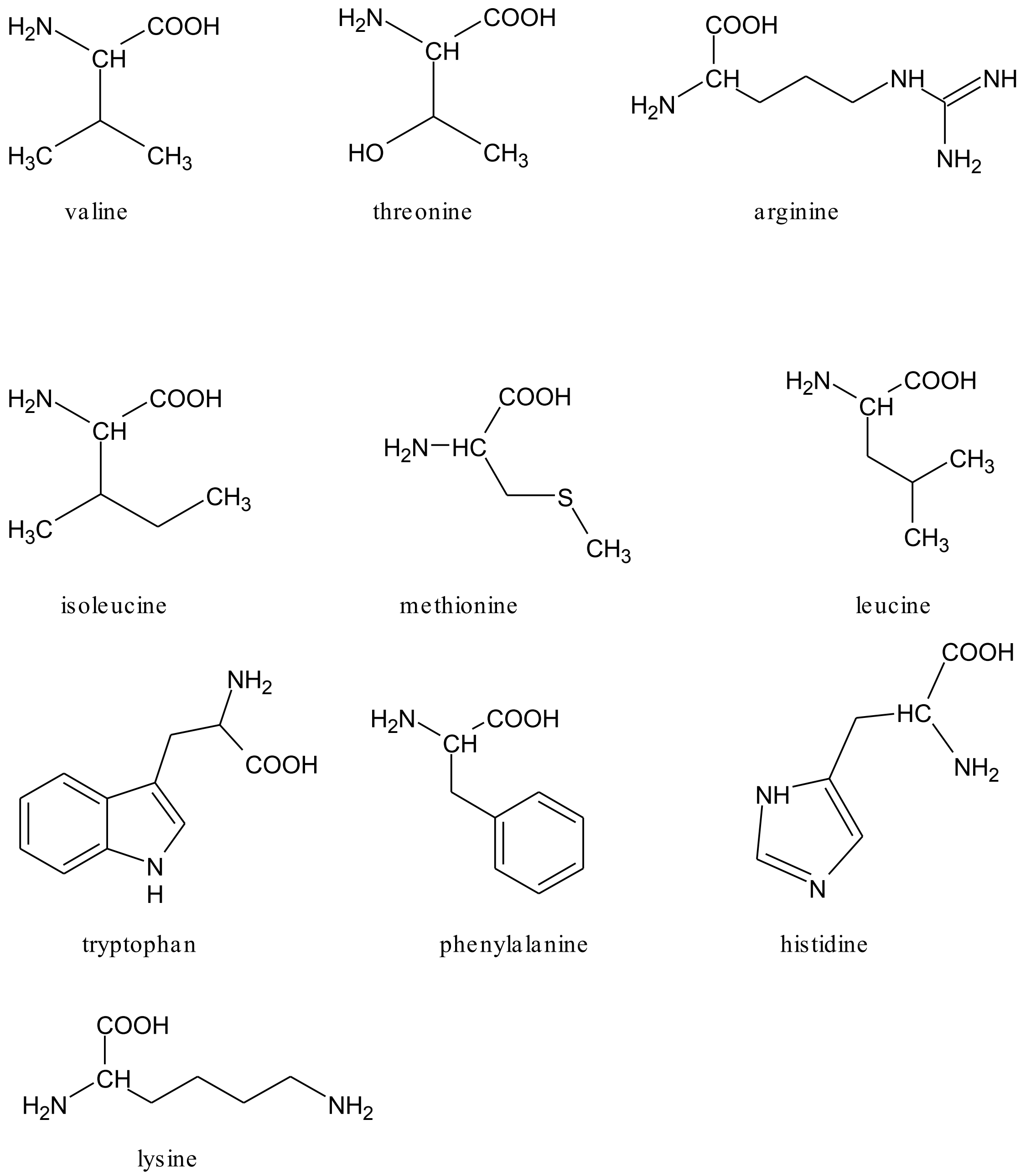
Leucine, an essential amino acid, is one of the three amino acid with a branched hydrocarbon side chain. It has one additional methylene group in its side chain compared with valine. Like valine, leucine is hydrophobic and generally buried in folded proteins. Leucine is given in scheme 1.3.

1.1.2.9 Phenylalanine:

As the name suggests, phenylalanine, an essential amino acid, is a derivative of alanine with a phenyl substituent on the β carbon. Phenylalanine is quite hydrophobic and even the free amino acid is not very soluble in water. Due to its hydrophobicity, phenylalanine is nearly always found buried within a protein. The π electrons of the phenyl ring can stack with other aromatic systems and often do within folded proteins, adding to the stability of the structure. Phenylalanine is given in scheme 1.3.

1.1.2.10 Tryptophan:

Tryptophan, an essential amino acid, is the largest of the amino acids. It is also a derivative of alanine, having an indole substituent on the β carbon. The indole functional group absorbs strongly in the near ultraviolet part of the spectrum. The indole nitrogen can hydrogen bonds donate, and as a result, tryptophan, or at least the nitrogen, is often in contact with solvent in folded proteins. Tryptophan is given in scheme 1.3.

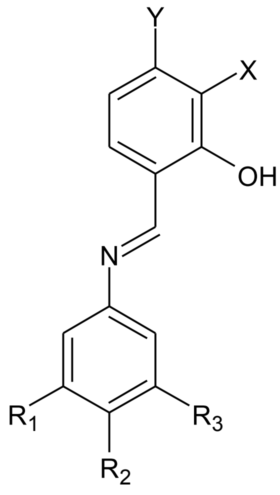

valine
threonine
arginine
isoleucine
methionine
leucine
tryptophan
phenylalanine
histidine
lysine

Scheme 1.3

1.2 Schiff bases

The condensation of primary amines with carbonyl compounds yields Schiff bases (Lv et al, 2006) imine or azomethines, which are more commonly known as Schiff bases, are used for complex formation studies. Schiff bases are characterized by the -N=CH- (imine) group which is important in elucidating the mechanism of transamination and racemisation in biological system. Due to great flexibility and diverse structural aspects, a wide range of Schiff bases was synthesis and their complication behaviors were studied. They have been synthesized from a variety of compounds, such as amino thiozoles, 2-hydroxy-1-napthalaniline, amino sugars, aromatic aldehydes, isatin, the triazole ring, thiosemicarbazides, amino asids, pyrozoline, e.t.c (Negm and Zaki, 2008).

Schiff bases have been extensively studied as they possess many interesting features, including photochromic and thermochromic properties. Proton transfer tautomeric equilibria, biological and pharmacological activities, as well as, suitability for analytical applications (Galic et al, 2008). Schiff bases have been studied extensively because of their high potential chemical permutation. Literature survey shows that Schiff bases show bacteriostaric and bacterial activity. Antibacterial, antifungal, antitumor, anticancer activity has been reported and they are also active against a wide range of organisms, e.g.,C. albicans, E.coli, s.aureus, B.polymyxa, P.viticola, etc. Many schiff bases are known to be to design medicinal compounds (Negm and Zaki, 2008). For example the ligands shown in scheme 1.3 are effective against the bacterium *b.megaterium* (Golcu et al, 2004).



X; OH, H

Y; H.OH

R_1; H, C(CH_3)

R_2; Br, OH, CH_3

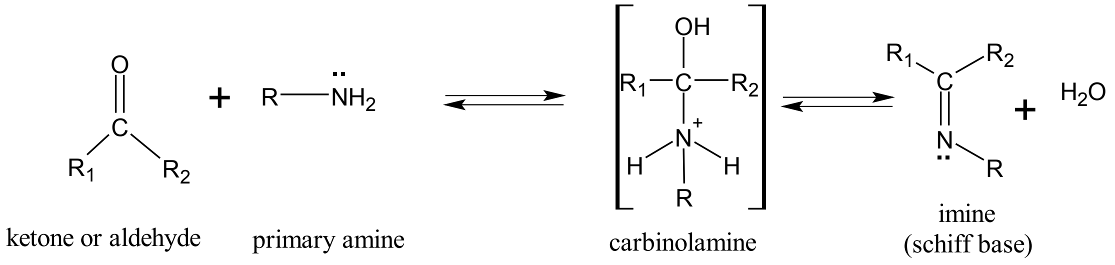
R_3; H, C(CH_3)

Antibacterial agent

Scheme 1.3

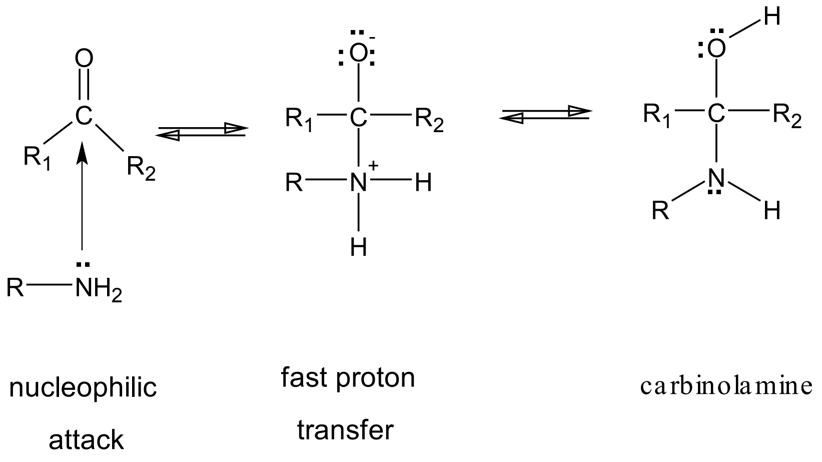
1.2.1Preparation of Schiff bases

One of the preparations of Schiff bases is; condensation reaction of primary amines with a ketone or an aldehyde. Either ammonia or a primary amine reacts with a ketone or an aldehyde, with a carbon nitrogen double bond (-C=N-) in place of carbonyl group. Like amines, imines are basic; a substituent imine is called a Schiff base. Imine formation is an example of a large class of reactions called condensation, reactions in which two (or more) organic compounds are joined with the elimination of water or another small molecule (Wade, 1987). This reaction was first discovered by Schiff (Schiff, 1864). As it is shown in the scheme 1.4 below, general formation reaction of Schiff base is demonstrated.



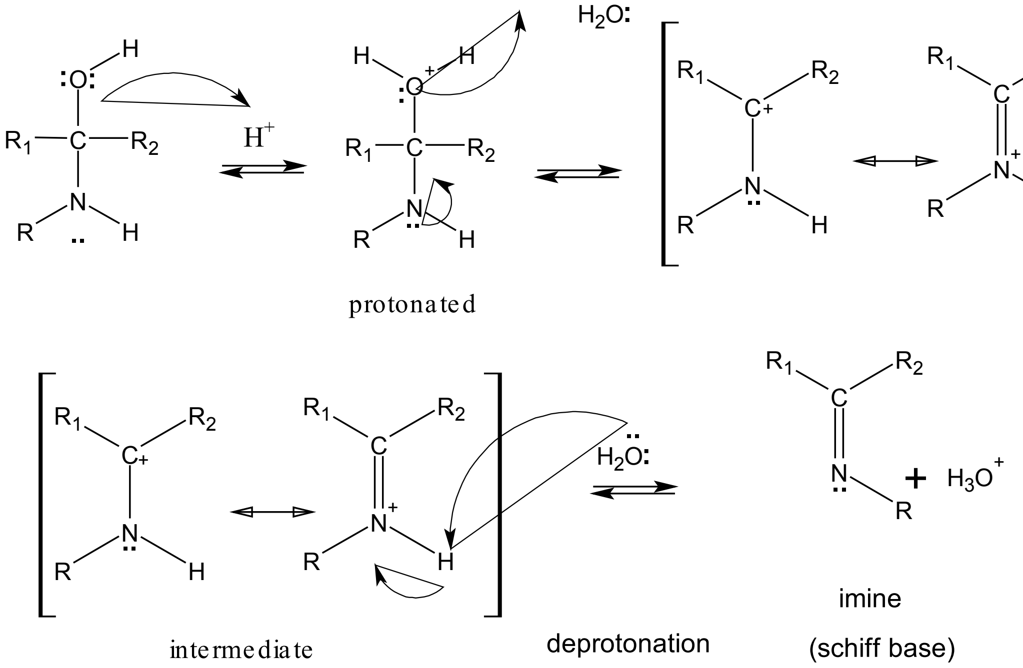
Scheme 1.4

The first step of the mechanism is attack by the nucleophilic amine on carbonyl. A rapid proton transfer result in an unstable intermediate called a carbinolamine. As the first step is shown in scheme 1.5 below.



Scheme 1.5

A carbinolamine reaction to form an imine by the loss of water and formation of a double bond: dehydration. This dehydration follows the same mechanism as the acid-catalzed dehydration of an alcohol. Protonation of the hydroxyl group converts it is a good leaving group and it leaves as water. The resulting cation is stabilized by a resonance structure with all octets filled and the positive charge on nitrogen. Loss of a proton gives the imine. As the second step is shown in scheme 1.6 below.



Scheme 1.6

The second step is acid catalyzed, so the solution must be somewhat acidic. If the solution is too acidic, however the imines become protonated and nonnucleophilic, inhibiting the first step. That is why if the solution is basic or too acidic, the reaction rate slows. The fast information of Schiff bases is in pH between 4 and 5 (Wade, 1987).

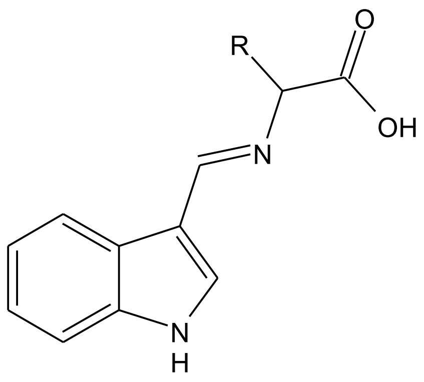
There are some other methods for preparation of imines including of reactions of nitriles with organometallic compounds (Moureau and Mignonac, 1913), reaction of carbon- nitrogen double bond compounds with organometallics (Busch and Falco, 1910), dehydrogenation of imines (Ritter, 1953), reactions of phenols and phenols ethers with nitriles (Hoesch, 1915), reaction of carbon nitrogen compounds (Mignonac, 1920) and reaction of nitroso compounds with active hydrogen compounds (Pfeiffer and Roos, 1941).

1.2.2 Schiff Bases and Metal Complexes

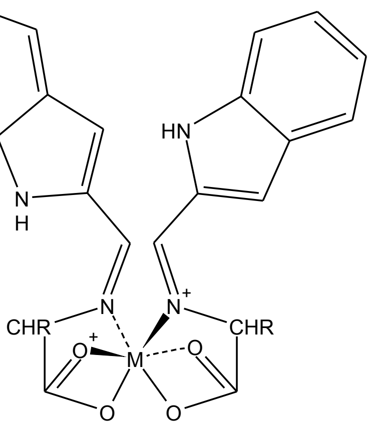
Co-ordination compounds exhibit different characteristic properties which depend on the metal ion to which they are bond, the nature of the metal as well as the type of ligand, etc. These metal complexes have found extensive applications in various fields of human interest. The nature of coordination compounds depends on the metal ion and the donor atoms as well as on the structure of the ligand and the metal ligand interaction (Negm and Zaki, 2008). A large number of Schiff base compounds are often used as a ligands in coordination chemistry by considering their metal binding ability (Nair and Joseyphus, 2007).

In recent years, it has been considerable interest in the chemistry of tridentate transition metal complexes of Schiff bases, since they are becoming increasing importance of their ability to serve as polymeric ultraviolet stabilizer, as laster dyes, and molecular switche, in logic or memory circuit. Schiff base complexes have been also employed as catalysts for many reactions and as biomolecules models in understanding the structure of biomolecule and biological process. Moreover, it is well known that some drugs have increasing activity administered as metal complexes, and their interactions with DNA have been reported. Several Schiff base complexes have also been shown to inhibit tumor growth. Furthermore tridentate Schiff base complexes are increasingly important for designing metal complexes related to synthetic and natural oxygen carries (Lv et.al., 2006). Furthermore Schiff base metal complexes have ability to reversibly bind oxygen in epoxidation reactions (Nair and Joseyphus, 2007). Due to the fact that Schiff bases offer opportunities for inducing substrate chirality tuning the metal centered electronic factor, enhancing the solubility and stability of either homogeneous or heterogeneous catalyst. Transition metal complexes of Schiff bases are important. A large number of reports are available on the chemistry and the biocidal activities of transition metal complexes containing O,N and N,S donor atoms. The transition metal complex having oxygen and nitrogen donor Schiff bases possess unusual configuration, structural ability and are sensitive to molecular environment. The environment around the metal center ’’as coordination ligands and their donor groups’’ is the key factor for metalloproteins to carry out specific physiological functions (Golcu et.al., 2004).

Recently; biologically active tridentate amino acid (Alanine, Glycine & Tyrosine) derived Schiff bases and their Co(II), Cu(II) and Ni(II) complexes shown below are reported. They have been synthesized and characterized by basis of their conductance and magnetic measurements, elemental analysis and ^{13}C-NMR, H-NMR, IR and electronic spectral data. These Schiff-bases and their complexes have been evaluated for their antibacterial activity against bacterial species such as Staphylococcus aureus, Escherichia coli, Klebsiella pneumonae, Proteus vulgqrus and Pseu.domon.as, aeru.inosa and this activity data show that the metal complexes to be more antibacterial than the Schiff-bases against one or more bacterial species (Cehohan et.al., 1997).



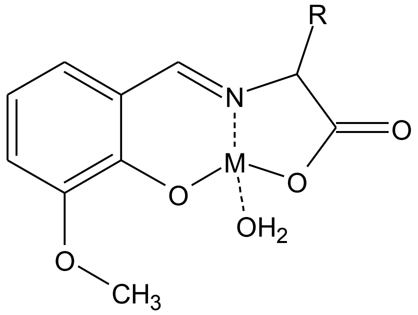
structure of schiff bases



Scheme 1.7

metal complex

Schiff base ligands derived from the condensation of salicylaldeyhde and its derivatives with various primary amines become important. These Schiff base ligands may act as a bidantate N, O- and tridentate N, O, O-donor ligand (Li et.al., 2007). In literature we can see the synthesis of metal complexes of Schiff base derived from the condensation of salicylaldeyhde and various in primary amines. The following complex is given as an example; (Kumarı and Neelakantan, 2006).

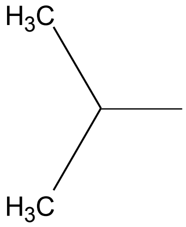


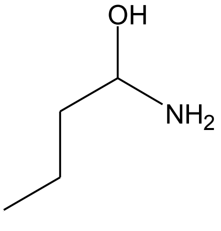
Scheme 1.8

The structure of the MAB system; M (II)=Co(II), Ni(II), Cu(II) and Zn(II),

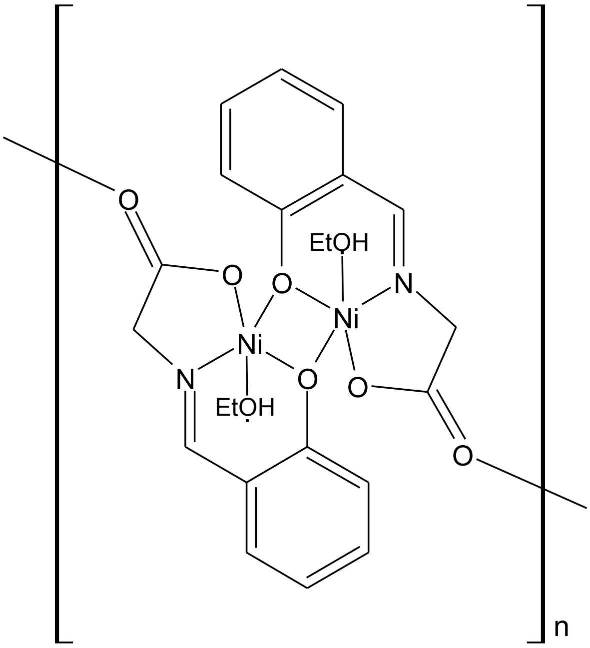
A= o –vanillin B=val and gln

R;

val; 

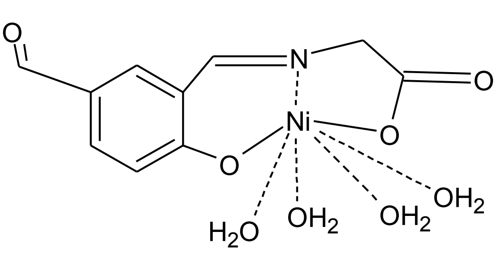
gln; 

In a recently published paper the synthesis, characterization of Ni (II) Schiff base complexes are reported. The Schiff bases derived from condensation of salicylaldehyde and Glysine. Each Ni(II) centre adopts a distorted octahedral configuration defined by one ethanol O atom, and four O atoms and one N atom from three fully deprotonated N-salicylideneglycinate (salgly) anionsA two-dimensional Ni^{II} polymer constructed through binding coordination covalent bondig is given below (Yuan et.al., 2005).



Scheme 1.9

The synthesis and structural characterization of ligand complex derived from 5 formyl-salicylaldehyde derivative have been reported. The Ni atoms was coordinated by the imine N, the phenolate O and one carboxyl O atom of the tridentate ligand Schiff base. The Octahedral geometry is completed by the three O atoms of the coordinated water molecules (Liu et.al., 2006).



Scheme 1.10

2. Materials and Methods

2.1. General techniques and materials

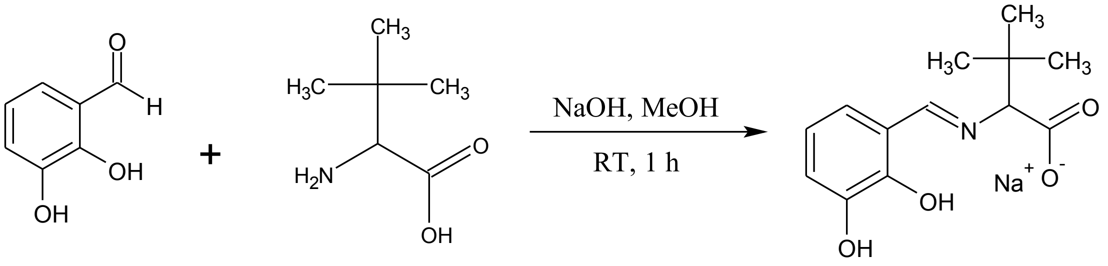
In spectroscopic studies IR spectra were recorded using a Mattson FTIR 1000. ^{1}H-NMR and ^{13}C-NMR spectra were carried out using a 400 MHz Varian NMR spectrometer. UV spectra were run using a Shimadzu UV 160 A spectrophotometer. Melting points were recorded with an electro thermal digital melting points apparatus. All solvents distilled before use.

For TLC (thin layer chromatography) silica gel F_{254} (Merck 5554) precoated plates were used and for column chromatography (CC) Silica gel 60 (Merck 7743) was used. For UV active components, the spots were observed under the UV lamp for TLC. Perkin Elmer Instrument was used For TGA (Thermal gravimetric analysis)

L-tert-leucine(Alfa Aesar), L-isoleucine(Alfa Aesar), L-valine(Alfa Aesar), $Ni(NO_3)_2.6H_2O$ (Alfa Aesar), 2,3dihydroxybenzaldehyde(Aldrich), o-vanillin(Aldrich), 3-butoxy-2-hydroxy-benzaldehyde(Aldrich), were used as received.

2.2 Experiments

2.2.1 Preparation of Schiff base of L-tert leucine and 2,3dihydroxybenzaldehyde (general procedure) (Schiff base-1)



2,3 dihydroxybenzaldehyde L-tert-leucine

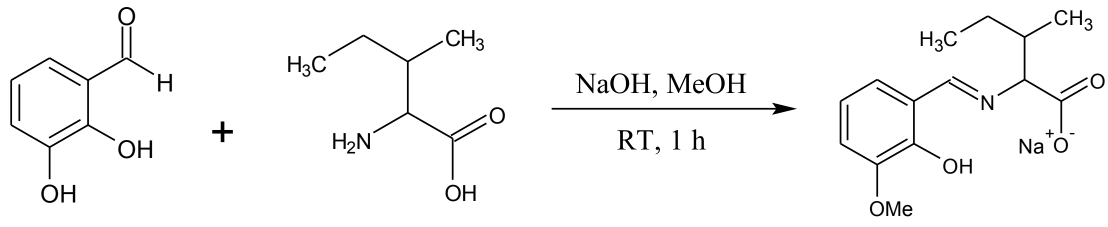
40 mg (1mmol) NaOH was dissolved in 4 ml methanol, 132.48 mg (1,01 mmol) L-tert-leucine was added in the reaction mixture and stirred. Then 151.93 mg (1,1 mmol) 2,3 dihydroxybenzaldehyde was added and stirred for 1 hour at room temperature. Solvent was removed until a small amount of solvent remained. Ether was added and crude product was filtered and washed with ether. The reaction was monitored by TLC. The eluting solvent of TLC is 3:2 ethyl acetate:methanol. The purity of the product was determined by using TLC. The TLC plate was observed under UV light.

%

The Schiff base-1 (sodium N-(2,3dihydroxybenzylidene) tertleucinate) was obtained in 95.85 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(2,3dihydroxybenzylidene)tertleucinate (Schiff base 1) are shown in figures1, 30, 12, 21 and the result of the elemental analysis is given in table 3.3.

2.2.2 Preparation of Schiff base of L-ısoleucine and 2,3dihydroxybenzaldehyde (Schiff base-2)



2,3 dihydroxybenzaldehyde L-isoleucine

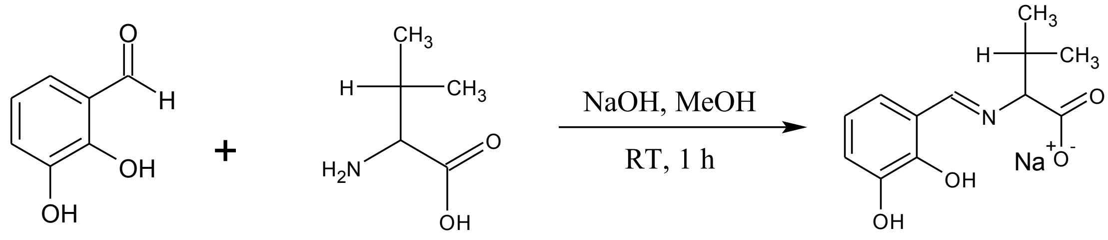
The Schiff base was synthesis according to the same procedure as described above.

40 mg (1mmol) NaOH, 132.48 mg(1.01 mmol) L-isoleucine and 151.93 mg (1,1 mmol) 2,3dihydroxybenzaldehyde w%ere used. 5 ml MeOH was used.

The Schiff base-was obtained in 94.4 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(2,3dihydroxybenzylidene)isoleucinate (Schiff base 2) are shown in figures 2, 31, 13, 22 and the result of the elemental analysis is given in table 3.3.

2.2.3 Preparation of Schiff base of L-valine and 2,3dihydroxybenzaldehyde (Schiff base-3)



2,3dihydroxybenzaldehyde L-valine

The Schiff base was synthesis according to the same procedure as described above.

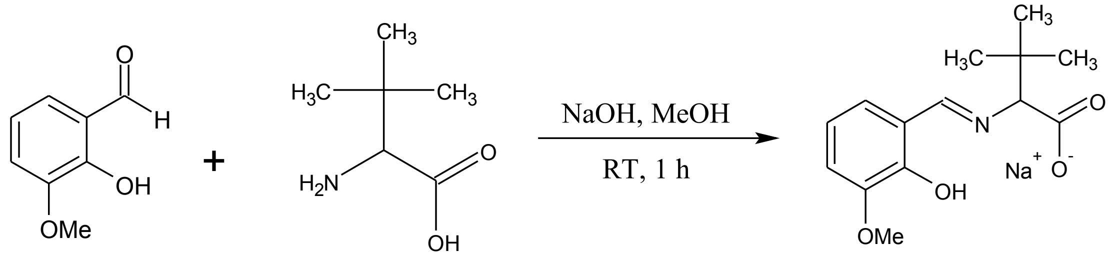
40 mg (1mmol) NaOH, 117.15 mg(1.01 mmol) L-valine and 151.93 mg (1,1 mmol) 2,3dihydroxybenzaldehyde were used. 5 ml MeOH was used.

%

The Schiff base-3 was obtained in 95 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N(2,3-dihydroxybenzylidene) valinate (Schiff base 3) are shown in figures 3, 32, 14, 23 and the result of the elemental analysis is given in table 3.3.

2.2.4 Preparation of Schiff base of L-tert-leucine and o-vanillin (Schiff base-4)



o-vanillin L-tert-leucine

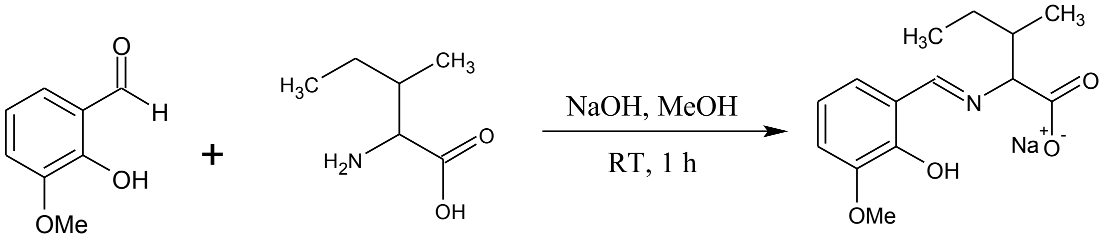
The Schiff base was synthesis according to the same procedure as described above.

40 mg (1mmol) NaOH, 132.48 mg (1, 01 mmol) L-tert-leucine and 167.365 mg (1,1mmol) o-vanillin were used, 5 ml MeOH was used.

% The Schiff base-4 was obtained in 89.26 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(2-hydroxy-3metoxy benzylidene)tertleucinate (Schiff base 4) are shown in figures 4, 33, 15, 24 and the result of the elemental analysis is given in table 3.3.

2.2.5 Preparation of Schiff base of L-ısoleucine and o-vanillin (Schiff base-5)



o-vanillin

L-ısoleucine

The Schiff base was synthesis according to the same procedure as described above.

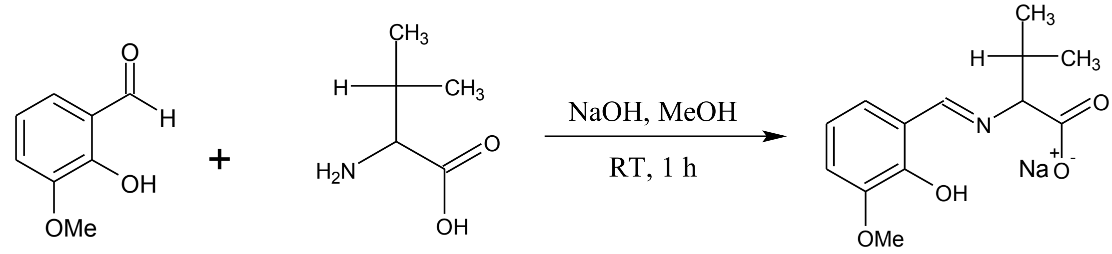
40 mg (1mmol) NaOH, 132.48 mg (1,01 mmol) L-ısoleucine and 167.365 mg (1,1mmol) o-vanillin were used, 5 ml MeOH was used.

%

The Schiff base-5 was obtained in 94.46 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(2-hydroxy-3-metoxy-benzaldehyde)isoleucinate (Schiff base 5) are shown in figures 5, 34, 16, 25 and the result of the elemental analysis is given in table 3.3.

2.2.6 Preparation of Schiff base of L-valine and o-vanillin (Schiff base-6)



o-vanillin L-valine

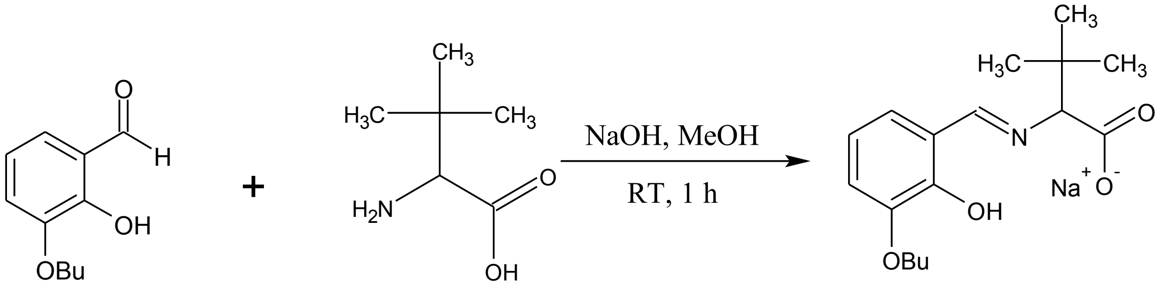
The Schiff base was synthesis according to the same procedure as described above.

40 mg (1mmol) NaOH, 117.15 mg (1,01 mmol) L-valine and 167.365 mg (1,1mmol) o-vanillin were used. 5 ml MeOH% was used.

The Schiff base-6 was obtained in 93.44 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(2-hydroxy-3metoxy benzylidene)valinate (Schiff base 6) are shown in figures 6, 35, 17, 26 and the result of the elemental analysis is given in table 3.3.

2.2.7 Preparation of Schiff base of L-tert-leucine and 3-butoxy-2-hydroxy-benzaldehyde (Schiff base-7)



3-butoxy-2-hydroxy-benzaldehyde L-tert-leucine

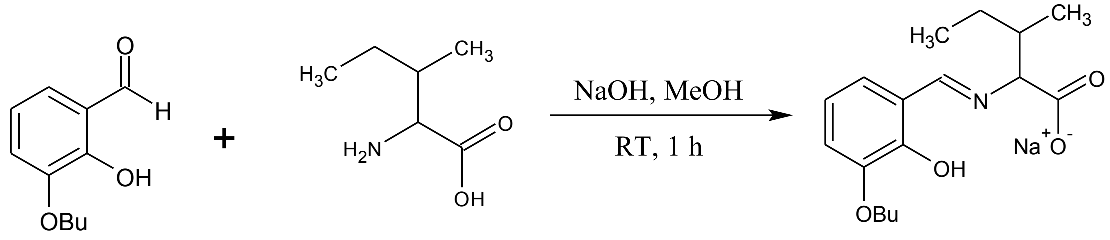
The Schiff base was synthesis according to the same procedure as described above.

23.59 mg (0.59 mmol) NaOH, 65.58 mg (0.5 mmol) L-tert-leucine and 115.2 mg (0.59 mmol) 3-butoxy-2-hydroxy-benzaldehyde % were used,5 ml MeOH was used.

The Schiff base-7 was obtained in 98.97 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(3-butoxy-2-hydroxybenzylidene)tertleucinate (Schiff base 7) are shown in figures 7, 36, 18, 27 and the result of the elemental analysis is given in table 3.3.

2.2.8 Preparation of Schiff base of L-ısoleucine and 3-butoxy-2-hydroxy-benzaldehyde (Schiff base-8)



3-butoxy-2-hydroxy-benzaldehyde L-ısoleucine

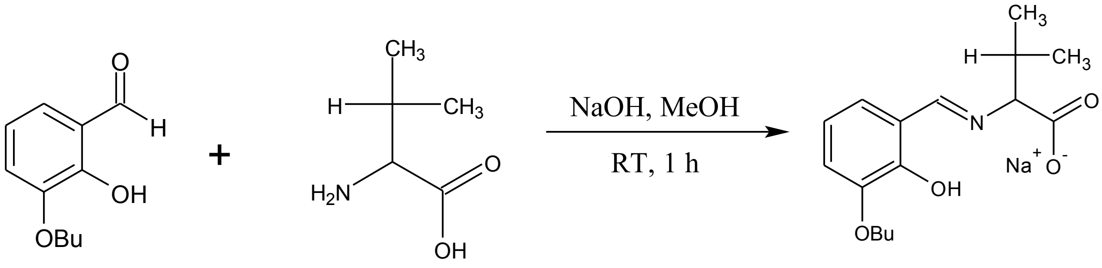
The Schiff base was synthesis according to the same procedure as described above.

23.59 mg (0.59 mmol) NaOH, 65.58 mg (0.5 mmol) L-ısoleucine and 115.2 mg (0.59 mmol) 3-butoxy-2-hydroxy-benzaldehyde were used, 5 ml MeOH was used.

The Schiff base-8 was obtained in %91.08 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(3-butoxy-2-hydroxy-benzylidene)isoleucinate (Schiff base 8) are shown in figures 8, 37, 19, 28 and the result of the elemental analysis is given in table 3.3.

2.2.9 Preparation of Schiff base of L-valine and 3-butoxy-2-hydroxy-benzaldehyde (Schiff base-9)



3-butoxy-2-hydroxy-benzaldehyde L-valine

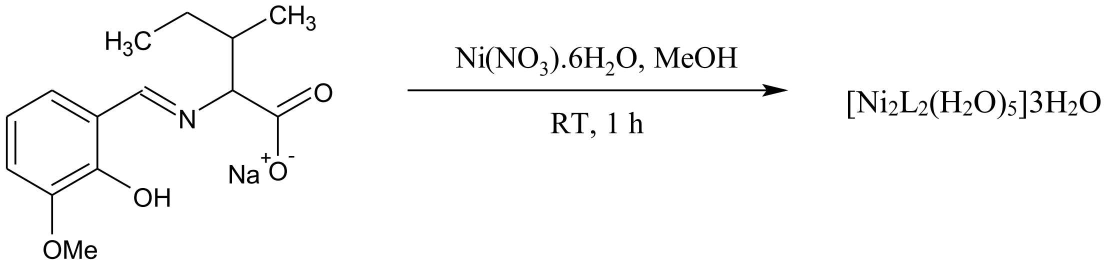
The Schiff base was synthesis according to the same procedure as described above.

23.59 mg (0.59 mmol) NaOH, 58.675 (0.5 mmol) L-valine and 115.2 mg (0.59 mmol) 3-butoxy-2-hydroxy-benzaldehyde%were used, 5 ml MeOH was used.

The Schiff base-9 was obtained in 30.33 yield.

The IR spectrum, UV-Vis spectrum, ^{1}H-NMR and ^{13}C-NMR spectrums of sodium N-(3-butoxy-2-hydroxy benzylidene)valinate (Schiff base 9) are shown in figures 9, 38, 20, 29 and the result of the elemental analysis is given in table 3.3.

2.2.10 Preparation of a Ni (II) Complex from Schiff base 5 and $Ni(NO_3)_2 6H_2O$ (general procedure) (Complex-1)

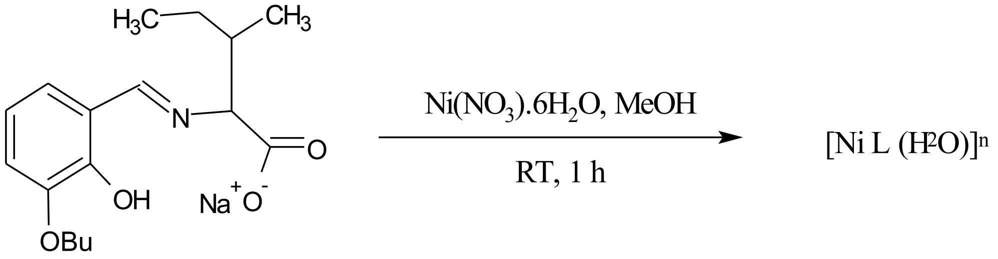


50 mg (0.17 mmol) Schiff base 5 was dissolved in 2 ml MeOH. 6.8 mg (0.17 mmol) NaOH was dissolved in 2 ml MeOH and added to Schiff base solution stirred. To the yellow solution was added. 49.4 mg (0.17mmol) $Ni(NO_3)6H_2O$ in 2 ml MeOH drop wise. The colored of the reaction mixture turned in to the pale green. Solution was stirred for a few hours in room temperature. Then the solvent was evaporated and a few of drop water was added. The solid product filtered and washed with water.

Complex 1 was obtained in % 59.9 yield.

The IR and UV-Vis spectra's of complex-1 are shown in figures 10, 39 and result of the elemental analysis is given in table 3.4.

2.2.11 Preparation of a Ni (II) Complex from Schiff base 8 and $Ni(NO_3)_2 6H_2O$ (Complex-2)



The Schiff base was synthesis according to the same procedure as described above.

25 mg(0.08 mmol) Schiff base 8, 3.199 mg(0.08 mmol) NaOH and 23,11 (0.08mmol) $Ni(NO_3).6(H_2O)$ were u%sed. 4 ml MeOH was used.

Complex 2 was obtained in 77 yield.

The IR and UV-Vis spectra's of complex-1 are shown in figures 11, 40 and result of the elemental analysis is given in table 3.4.

3. RESULTS and DISCUSSION

In this study, Schiff bases and their Ni complexes which have been expected to show biological activity were synthesized. L Tert-leucine, L iso-leucine, L valine are used as amino acids and 2,3dihydroxybenzaldehyde, o-vanillin, 2 hydroxy-3 butoxybenzaldehyde are used as aldehyde.

All Schiff bases were synthesized by condensation of equivalent amount of amino acids and aldehydes. Then the achieved Schiff bases were reacted with metal salts. Finally we obtained metal complex of Schiff bases.

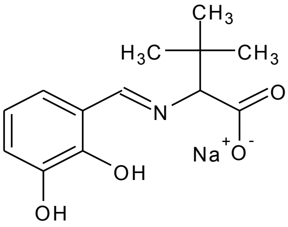
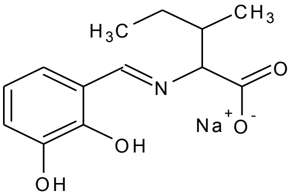
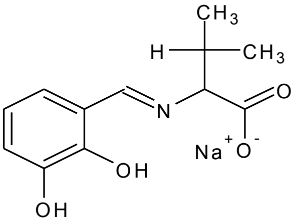
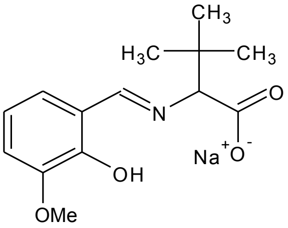
The achieved Schiff bases were soluble in general organic solvents such as MeOH, ethyl acetate. And metal complexes were not soluble in general organic solvents except MeOH. Metal complexes weren’t soluble in water too, we benefited from this case to crystallization. Schiff bases were found to be unstable to air however metal complexes were found stable to the air and light. All compounds decompose at temperature above 160 C^o.

The yields of the Schiff bases are given in table 3.1 and the yields of metal complexes are given in table 3.2. The yields of compounds are good.

The structure of products was characterized by IR, UV-Vis, ^{1}H-NMR, ^{13}C-NMR, elemental analyses and TGA. The results of elemental analyses of Schiff bases are given in table 3.3, and the result of elemental analyses of metal complexes are given in table 3.4.

The results of TGA are consistent with the elemental analysis results. Thus, there are four water molecules involved in the empirical formula of complex one and one water molecule in the empirical formula of complex 2. The TGA data of complex 1 is given figure 41 and the TGA data of complex 2 is given figure 42.

Table 3.1. The yields of Schiff bases

Schiff bases	Formula	Yield (%)
Schiff base 1		%95.85
Schiff base 2		%94.4
Schiff base 3		%95
Schiff base 4		%89.26

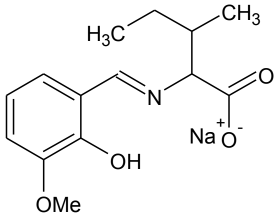
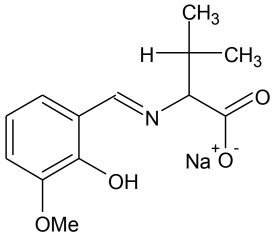
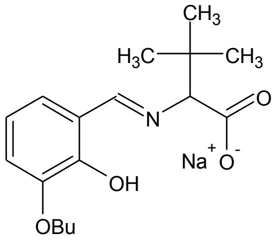
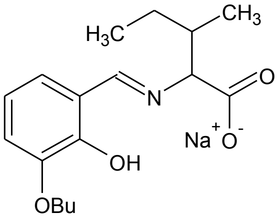
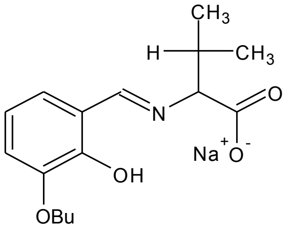
Schiff bases	Formula	Yield (%)
Schiff base 5		%94.49
Schiff base 6		%93.44
Schiff base 7		%98.87
Schiff base 8		% 91.08
Schiff base 9		%30.33

Table 3.2. The yields of Schiff bases

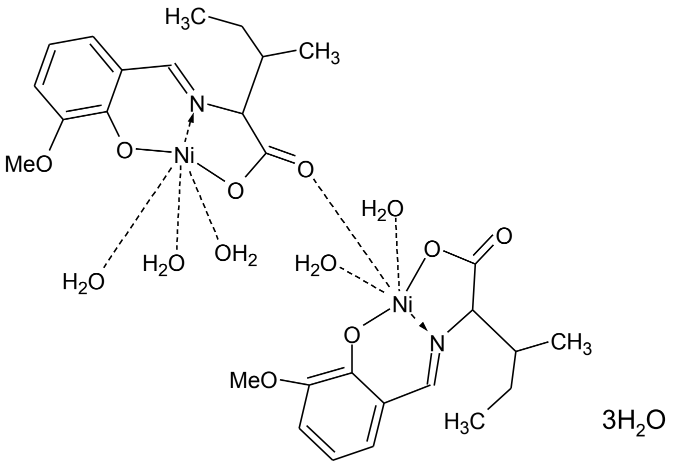
Complexes	Formula	Yield (%)
Complex 1	$[Ni_2L_2(H_2O)_5].3H_2O$	%59.9
Complex 2	$[Ni\ L(H_2O)]_n$	%77

IR results demonstrate the tridentate binding of Schiff base ligand involving azomethine nitrogen, phenolic oxygen and carboxylate oxygen atoms.

IR results showed that which groups are involved in coordination in the complex, elemental analysis demonstrated that compound of molecule and the number of water molecule which coordinated with metal atom, TGA analysis indicated that the number of coordinated water molecule. These results of analysis give an idea about structure of molecules. The molecules that have similar results with those of the compounds we have synthesized as shown above are reported in the literature. We think that the complexes that we have synthesized are of similar structure with the above said complexes of in the literature. Thus;

For complex-1; $[(Ni_2L_2 (H_2O)_5]3H_2O$

The IR spectrum of complex-1 clearly shows that there are two types of carbonate group. One of the carboxylate groups is a bridging carboxylate group. Because the IR spectrum of this complex is very similar to a recently characterized dinickel complex (Korkmaz, et.al.2009), we think that the structure of the complex-1 involves octahedral coordination geometry defined by three H_2O groups and two O atoms and one N atom from the tridentate ligand. The bridging carboxylate group forms a bridge between the 2 Ni atoms of the complex. The complex 1 is given in scheme 3.1.

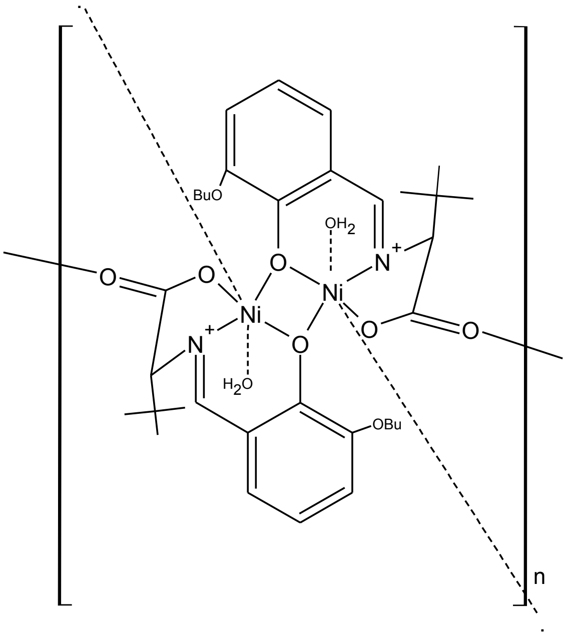


Scheme 3.1

For complex-2 $[Ni L (H_2O)]_n$

The IR spectrum of complex 2 is different to the spectrum of complex 1, but again there are bands present due to a bridging carboxylate group. We think that the structure of the complex is similar to a previously reported compound (Bıan et.al.,

2008) and has octahedral coordination geometry. In addition to one coordinated H_2O group, and two O atoms and one N atom from the ligand, there are bridging phenolate and carboxylate groups. The phenolate bridges the two nickel atoms of the dinickel unit. The bridging carboxylate groups form bridges between different dinickel units making it a polymeric structure. The structure of complex 2 is given in scheme 3.2.



Scheme 3.2

We tried to prepare a Cu(II) complex of the Schiff base 1, Schiff base 2, Schiff base 3, Schiff base 4, Schiff base 5 and Schiff base 6, but we didn’t obtained any products.

Table 3.3. The elemental analyses of Schiff bases

%

Schiff bases	Calculated ( )			Found (%)		
	C	H	N	C	H	N
Schiff base 1 (2 H_2O)	53.4	5.51	4.79	52.50	5.98	4.88
Schiff base 2 (2 H_2O)	53.4	5.51	4.79	53.89	5.96	4.90
Schiff base 3 (0.5 H_2O)	53.53	6.00	5.20	53.56	5.66	5.13
Schiff base 4 (2 H_2O)	51.85	7.31	4.32	52.32	6.27	4.39
Schiff base 5 (1 H_2O)	54.90	7.04	4.57	55.41	6.37	4.65
Schiff base 6 (2 H_2O)	53.56	6.22	4.80	54.36	6.05	4.67
Schiff base 7 (1 H_2O)	58.78	7.54	4.03	60.34	7.19	4.13
Schiff base 8 (1 H_2O)	58.78	7.54	4.03	59.87	7.00	4.06
Schiff base 9 (2 H_2O)	54.71	7.45	3.96	55.47	6.74	3.85

Table 3.4. The elemental analyses of metal complexes

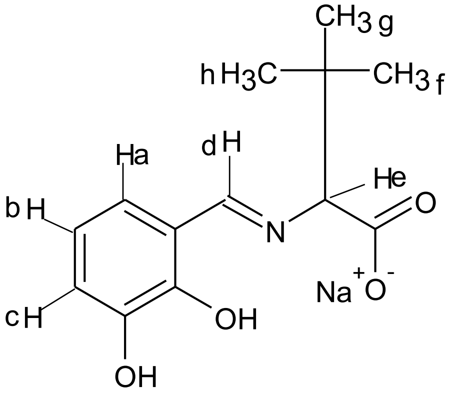
%

Complexes	Calculated ( )			Found (%)		
	C	H	N	C	H	N
Complex 1 (4H_2O)	42.67	6.39	3.55	42.43	5.64	3.90
Complex 2 (1H_2O)	53.44	6.60	3.67	52.74	6.41	3.43

3.1 ^{1}H NMR Spectroscopic Studies

The ^{1}HNMR spectra of Schiff bases 1, 2, 3, 4, 5, 6, 7, 8 and 9 are given in below.

3.1.1 Schiff Base-1

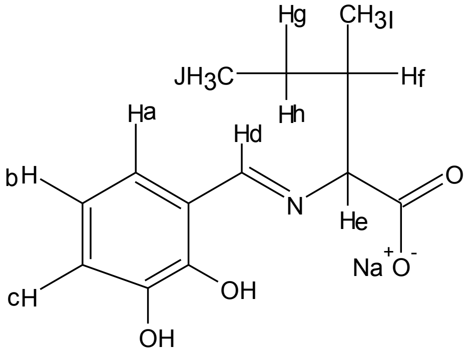


For Schiff base 1, the signals of the azomethine hydrogen (Hd) was determined as a singlet at δ 8.20 ppm. The peak of aromatic hydrogens, that is, Ha and Hc appeared at δ 6.63 ppm (m) and the signal of Hb was observed at δ 6,18 ppm as a triplet. The signals of aliphatic hydrogen, namely, He showed a singlet peak at δ 3.54 ppm (s). We would expect a singlet signal due to equivalent aliphatic hydrogens, that is, Hg, Hh, Hf. The peak was seen at δ 0.96 ppm. The ^{1}HNMR values of Schiff base-1 are given in table 3.5.

Table 3.5. ^{1}H-NMR spectral data of the Schiff base-1

H	**(ppm)**	**J(Hz)**
$H_{a,c}$	6.63	M
H_b	6.18	8 (t)
H_d	8.20	s
H_e	3.54	s
$H_{f,h,g}$	0.96	s

3.1.2 Schiff Base -2

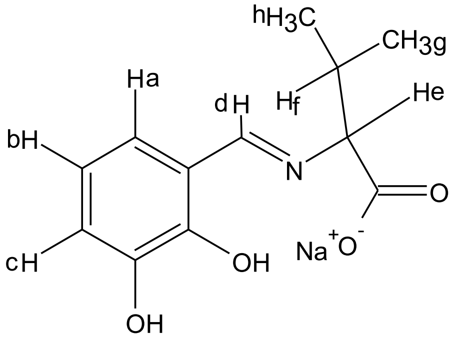


For Schiff base -2 the peak of azomethine hydrogen (Hd) was observed as a singlet at δ 8.25 ppm. The aromatic hydrogen, that is, Ha and Hc were seen at δ 6.65 ppm (m) and Hb was observed in the expected region. The signal resembling a triplet for H_b was observed at δ 6.23 ppm . The signal of He was determined at δ 3.73 ppm as a dublet. The signals of the aliphatic hydrogen, namely, Hf, Hg, Hh, were observed at δ 1.98 ppm (m), δ 1.55 ppm (s), and δ 1.08 ppm(s), respectively. The signals of Hı and Hj were seen at δ 0.86 ppm (m). The ^{1}HNMR values of Schiff base-2 are given in table 3.6.

Table 3.6. ^{1}H-NMR spectral data of the Schiff base-2

H	ppm	j (Hz)
$H_{a,c}$	6.65	M
H_b	6.23	8 (t)
H_d	8.25	s
H_e	3.73	4 (d)
$H_{f,}$	1.98	m
H_g	1.55	s
Hh	1.08	s
$H_{ı,j}$	0.86	m

3.1.3 Schiff Base -3

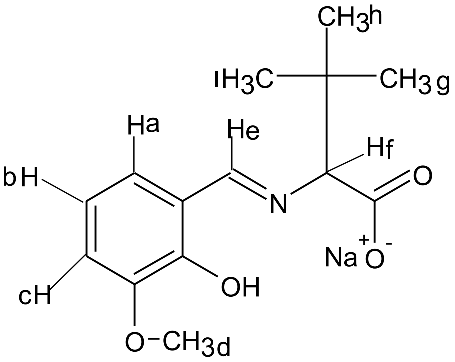


For Schiff base-3 the signals of the azomethine hydrogen (Hd) was observed as a singlet at δ 8.23 ppm (s). The aromatic hydrogens, that is, Ha and Hc were δ observed at δ 6.65 ppm (m) and the Hb was observed in the expected region. The signal resembling a triplet for H_b was observed at 6.22 ppm . The aliphatic hydrogen He was determined at 3.66 δ ppm as a doublet. The peak of the Hf was determined at δ 2.26 (m). Hh and Hg were observed in the expected region. Hh and Hg were seen at δ 0.88 ppm (d), δ 0.86 ppm (d), respectively. The ^{1}HNMR values of Schiff base-4 are given in table 3.7.

Table 3.7. ^{1}H-NMR spectral data the of Schiff base-3

H	**δ ppm**	**J (Hz)**
$H_{a,c}$	6.65	M
H_b	6.22	8 (t)
H_d	8.23	s
H_e	3.66	4.8 (d)
H_f	2.26	m
H_h	0.88	d
H_g	0.86	d

3.1.4 Schiff Base 4

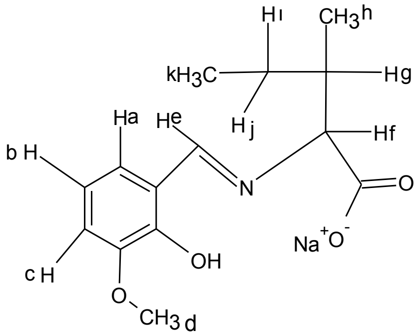


For Schiff base-4 the signals of the azomethine hydrogen (He) was determined at δ 8.22 ppm (s). The aromatic hydrogens, namely, Ha and Hc were seen at δ 6.77 ppm (m) and Hb was seen at δ 6.34 ppm as a triplet. The aliphatic hydrogen (Hf) was observed at δ 3.67 ppm (s). Hd was seen at δ 3.52 ppm (s). We would expect a singlet signal due to equivalent aliphatic hydrogens, that is, H_g, H_h $H_ı$.. the peak was seen at δ 0.95 ppm . The ^{1}HNMR values of Schiff base-4 are given in table 3.8.

Table 3.8. ^{1}H-NMR spectral data of the Schiff base-4

H	(ppm)	J(Hz)
$H_{a,c}$	6.77	m
H_b	6.34	8 (t)
H_d	3.52	s
H_e	8.22	s
H_f	3.67	s
Hg,h,ı	0.95	s

3.1.5 Schiff Base -5

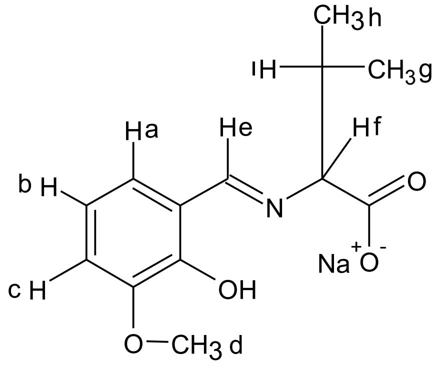


For Schiff base-5 the peak of the azomethine hydrogen (He) was observed at δ 8.24 ppm (s). The aromatic hydrogens, that is, Ha and Hc were observed at δ 6.79 ppm (m) and Hb was observed at δ 6.39 ppm a triplet peak as expected. Hd was determined at δ 3.43 ppm(s). The aliphatic hydrogen (Hf) was observed at δ 3.62 ppm (d). And the other aliphatic hydrogens, that is, Hg, Hı Hj were observed at δ 1.98 ppm (b), δ 1.51ppm (m), δ 1.50 ppm(m) respectively. The Hh and Hk were determined at δ 0.86 ppm as a multiplet. The peak of –OH was observed at δ 14.32 ppm. The ^{1}HNMR values of Schiff base-5 are given in table 3.9.

Table 3.9. ^{1}H-NMR spectral data of the Schiff base 5

H	ppm	j (Hz)
$H_{a,c}$	6.79	M
H_b	6.39	8 (t)
H_d	3.43	s
H_e	8.24	s
H_f	3.62	5 (d)
H_g	1.98	b
$H_ı$	1.51	m
H_j	1.50	m
$H_{h,k}$	0.86	m

3.1.6 Schiff Base 6

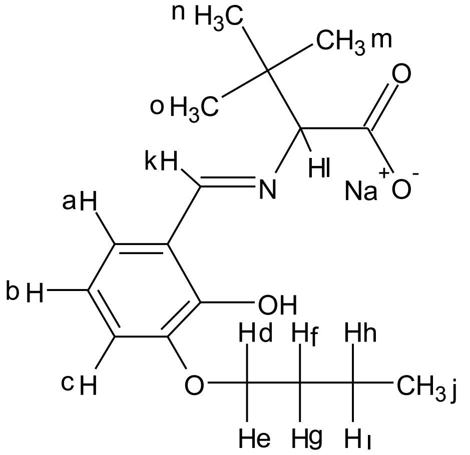


For Schiff base-6 the peak of the azomethine hydrogen (He) was determined at δ 8.25 ppm a singlet peak as expected. The aromatic hydrogens, namely, Ha and Hc were observed at δ 6.80 ppm (m) and Hb was determined in the expected region. Hb was seen at δ 6.41 ppm as a triplet. Hd was determined at δ 3.50 ppm (s). Hf was observed at δ 3.59 ppm a dublet as expected. Hı was observed at δ 2.26 ppm (m). Hh and Hg were observed at δ 0.85 ppm (d), δ 0.85 ppm (d), respectively. The ^{1}HNMR values of Schiff base-6 are given in table 3.10.

Table 3.10. ^{1}H-NMR spectral data of the Schiff base-6

H	δ ppm	j (Hz)
$H_{a,c}$	6.80	m
H_b	6.41	8 (t)
H_d	3.50	s
H_e	8.25	s
H_f	3.59	5 (d)
H_g	0.85	6.4 (d)
H_h	0.85	6.4 (d)
$H_ı$	2.26	m

3.1.7 Schiff Base 7

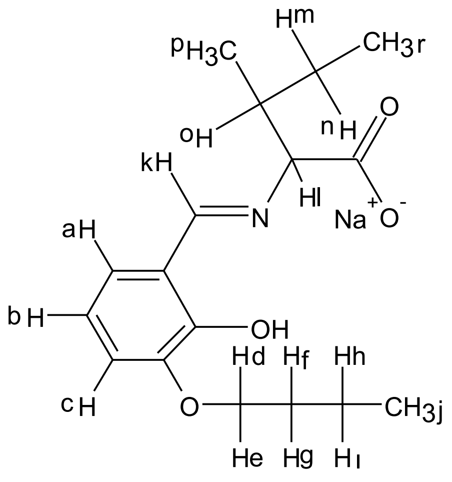


For Schiff base-7 the peak of the azomethine hydrogen (Hk) was determined at δ 8.21 ppm (s). The aromatic hydrogen Ha and Hc were observed at δ 6.79 ppm as a singlet and Hb was seen at δ 6.37 ppm a triplet peak as expected. Hl was observed at δ 3.49 ppm (s). The peak of aliphatic hydrogens, namely, Hd and He appeared at δ 3.88 ppm (m), Hf and Hg were determined at δ 1.66 ppm (m), Hh and Hı were observed at δ 1.42 ppm (m), Hj was seen at δ 0.98 ppm as a triplet. Ho, Hn, Hm were observed in the expected region. Ho, Hn, Hm were observed at δ 0.96 ppm (s). The peak of –OH was seen at δ 14.46 ppm. The ^{1}HNMR values of Schiff base-7 are given in table 3.11.

Table 3.11. ^{1}H-NMR spectral data of the Schiff base-7

H	ppm	j(Hz)
$H_{a,c}$	6.79	s
H_b	6.37	8 (t)
$H_{d,e}$	3.88	m
$H_{f,g}$	1.65	m
$H_{h,I}$	1.42	m
H_j	0.98	7 (t)
H_k	8.21	s
H_l	3.49	s
$H_{m,n,o}$	0.96	s

3.1.8 Schiff Base 8

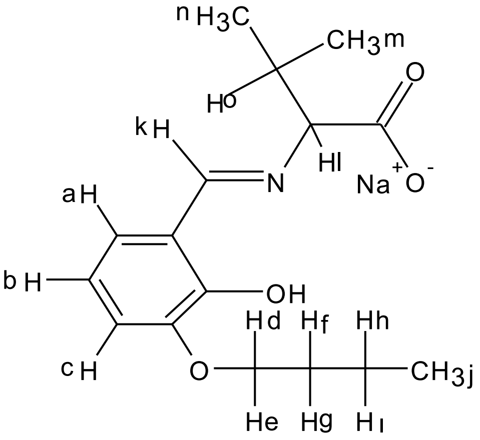


For Schiff base-8 the peak of the azomethine hydrogen (Hk) appeared at δ 8.21 ppm (s). The aromatic hydrogens, that is, Ha and Hc were observed at δ 6.80 ppm (m) and Hb was determined at δ 6.38 ppm a dublet as expected. The aliphatic hydrogens, that is, Hd and He were observed at δ 3.90 ppm (m), Hf and Hg were seen at δ 1.67 ppm (m), Hh and Hı were observed at δ 1.43 ppm (m), Hj was observed at δ 0.93 ppm a triplet peak as expected. The signal of H_l was determined at δ 3.56.ppm (s). Ho, Hn, Hm were seen at δ 1.99 ppm (b), δ 1.51 ppm (m), δ 1.07 ppm (m), respectively. Hp was observed at δ 0.85 ppm (d), Hr was observed at δ 0.85 ppm (t). the peak of –OH was determined at δ 14.44 ppm. The ^{1}HNMR values of Schiff base-8 are given in table 3.12.

Table 3.12. ^{1}H-NMR spectral data of the Schiff base-8

H	ppm	j(Hz)
$H_{a,c}$	6.80	M
H_b	6.38	8 (t)
$H_{d,e}$	3.90	m
$H_{f,g}$	1.67	m
$H_{h,ı}$	1.43	m
H_j	0.93	7 (t)
H_k	8.21	s
H_l	3.56	s
H_m	1.07	m
H_n	1.51	m
H_o	1.99	m
H_p	0.85	7 (d)
H_r	0.85	7 (t)

3.1.9 Schiff Base 9



For Schiff base-9 the peak of the azomethine hydrogen (Hk) was observed at δ 8.22 ppm (s). The aromatic hydrogens, that is, Ha and Hc were determined at δ 6.81 ppm (m) and Hb was observed at δ 6.40 ppm (t). The aliphatic hydrogens, namely, He and Hd were determined at δ 3.90 ppm (m), Hf and Hg were observed at δ 1.66 ppm(m), Hh and Hı were observed at δ 1.42 ppm (m), Hj was observed at δ 0.90 ppm a triplet peak as excepted . H_l was seen at δ 3.52 ppm (d). Ho was at δ 2.22 ppm (m). Hn and Hm were observed in the expected region Hn and Hm were determined at δ 0.85 ppm (d). The ^{1}HNMR values of Schiff base-9 are given in table 3.13.

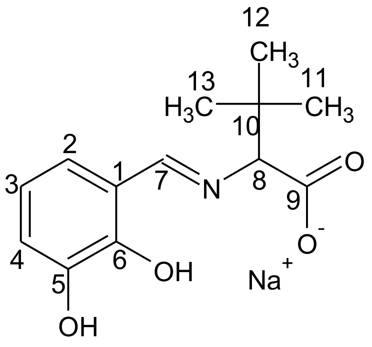
Table 3.13. ^{1}H-NMR spectral data of the Schiff base-9

δ

H	ppm	j(Hz)
$H_{a,c}$	6.81	M
H_b	6.40	8 (t)
$H_{d,e}$	3.90	m
$H_{f,g}$	1.66	m
$H_{h,I}$	1.42	m
H_j	0.90	7 (t)
H_k	8.22	s
H_l	3.52	5 (d)
$H_{m,n}$	0.85	7 (d)
H_o	2.22	m

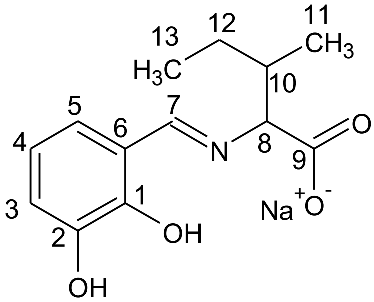
3.2 ^{13}C-NMR Spectroscopic Studies

3.2.1 Schiff Base 1



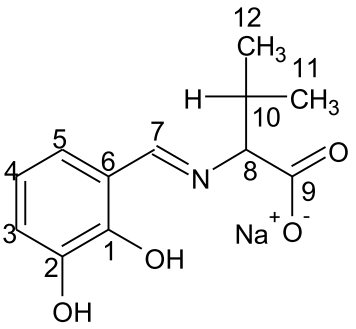
For Schiff base-1, the signal of carbonyl carbon (C_9) was observed at the highest chemical shift, at δ 171.15 ppm. Due to the effect of –OH group at C_6 and C_5, were observed at δ 165.70 ppm and δ 163.36 ppm, respectively. C_7, which is, azomethine carbon was seen at δ 149.58 ppm. The aromatic carbon (C_2), was observed at δ 122.95 ppm. Each value of C_1, C_4, and C_3, may either correspond to δ 114.62 ppm, δ 114.00 ppm, or δ 112.68. C_8, C_{10}, each one of which is, aliphatic carbon were observed at δ 77.362 ppm, δ 34.41 ppm, respectively. C_{11}, C_{12}, C_{13} were observed at δ 27.59 ppm . The ^{13}C-NMR values of Schiff base-1 are given in table 3.14.

3.2.2 Schiff Base 2



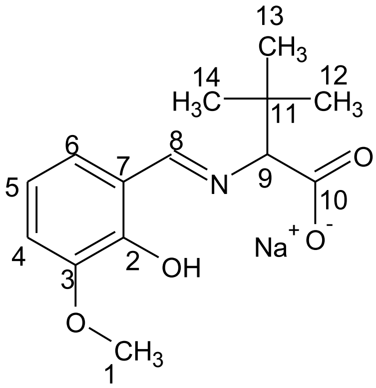
For schiff base-2, the signal of C_9, that is, carbonyl carbon, was observed at the highest chemical shift, at δ 172.02 ppm. –OH group raises electron density at C_1 and C_2 atoms. Because of this reason, C_1 and C_2 were observed at δ 164.6 ppm, δ 164.08 ppm, respectively. Azomethine carbon (C_7), was observed at δ 122.87 ppm. Each value of C_6, C_4, and C_3 may either correspond to δ 114.95 ppm, δ 114.57 ppm, δ 113.13 ppm. Aromatic carbon (C_5) was observed at δ 122.87 ppm. Aliphatic carbons; C_{10}, C_{11}, C_{12}, C_{13}, were observed at δ 38.69 ppm, δ 16.77 ppm, δ 25.10 ppm, δ 12.34 ppm, respectively. The peak of C_8 appeared at δ 72.812 ppm. The ^{13}C-NMR values of Schiff base-2 are given in table 3.15.

3.2.3 Schiff Base 3



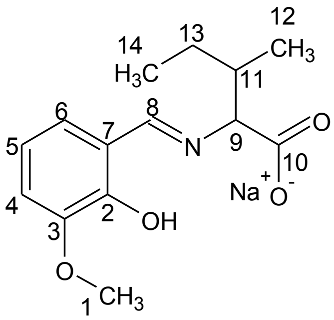
For Schiff base-3, carbonyl group carbon, that is, C_9 was observed at δ 171.98 ppm in the highest chemical region. Azomethine carbon (C_7) was observed at δ 149.48 ppm. Due to the effect of –OH group on C_1 and C_2, they were observed at δ 165.13 ppm, δ 164.12 ppm respectively. The aromatic carbon (C_5) was observed at δ 122.86. Each value of C_3, C_4, C_6 may either corresponds to δ 114.88 ppm, δ 114.4 ppm, δ 112.97 ppm. Aliphatic carbons; C_{10}, C_{11}, C_{12} were observed between δ 31.79 ppm and δ 18.32 ppm and the peak of C_8 was observed at δ 73.37 ppm. The ^{13}C-NMR values of Schiff base-3 are given in table 3.16.

3.2.4 Schiff Base 4



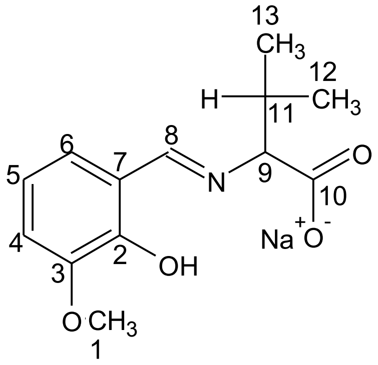
For Schiff base- 4, the peak of carbonyl group carbon, that is, C_{10} was seen at the highest chemical shift, appeared at δ 171.82 ppm.C_2 was effected by –OH group and C_{13} was effected by –OR group. Because of this reasons C_2 and C_3 were determined at δ 163.47 ppm and δ 163.14 ppm, respectively. Aromatic carbon C_6 was seen at δ 124.77 ppm and each value of C_4, C_5, C_7 may either corresponds to δ 116.21 ppm, δ 114.42 ppm, δ 113.53 ppm. Aliphatic carbon (C_9) was determined at δ 79.30 ppm and C_{12}, C_{13}, C_{14} seen at 27.68 ppm. The ^{13}C-NMR values of Schiff base-4 are given in table 3.17.

3.2.5 Schiff Base-5



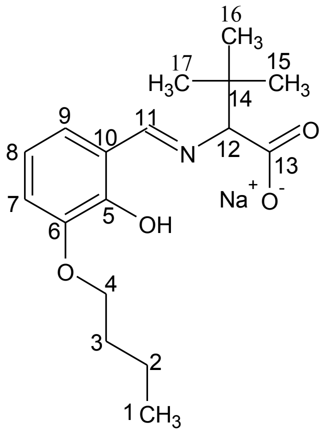
For schiff base-5 The signal of carbonyl carbon, that is, C_{10} was seen at the highest chemical shift, at 172.44 ppm. Due to effect of -OH group at C_2 and effect of –OR group at C_3, they were seen at δ 164.12 ppm, δ 162.74 ppm, respectively. Azomethine carbon; C_8 was determined at δ 151.02 ppm. Aromatic carbons namely C_4, C_5, and C_6 were observed between δ 116.58 ppm and δ 113.79 ppm. And the other aromatic carbon C_6 was seen at δ 124.71 ppm. C_9 was seen at δ 71.104 ppm and C_1 was determined at δ 56.13 ppm.C_{10}, C_{11}, C_{12}, C_{13} andC_{14} were determined between 38.45 and 12.29 ppm. The ^{13}C-NMR values of Schiff base-5 are given in table 3.18.

3.2.6 Schiff Base-6



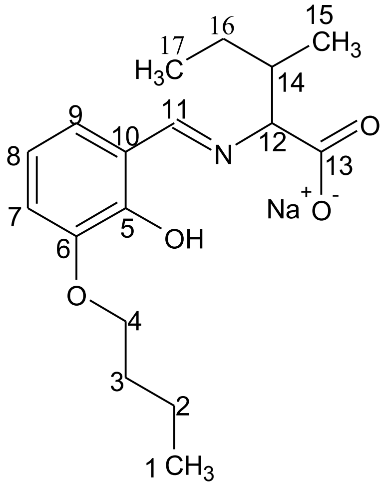
For Schiff base-6 carbonyl carbon ,that is, C_{10} was determined at δ 172.68 ppm, in the highest chemical region. Because of the effect of –OH and OR groups at C_2 and C_3 were observed at δ 164.36 ppm, δ 162.51ppm, respectively. Aromatic carbons; C_4, C_5, C_7 were observed between δ 116.60ppm and δ 113.93 ppm, and C_6 was seen at δ 124.68 ppm. C_1 was seen at δ 56.13 ppm. Aliphatic carbons; C_{11}, C_{12}, C_{13} were determined between δ 31.65 ppm and δ 18.44 ppm and C_9 was seen at δ 75.59 ppm. The ^{13}C-NMR values of Schiff base-6 are given in table 3.19.

3.2.7 Schiff Base 7



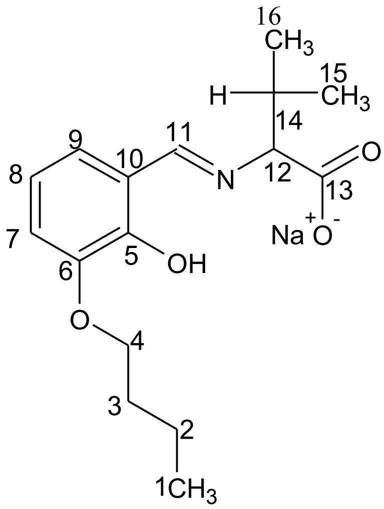
For Schiff base -7, the peak of the carbonyl carbon, namely, C_{13} was seen at δ 172.23 ppm. Aromatic carbons C_5 and C_6 were observed at δ 163.33 ppm and δ 162.88 ppm, respectively. –OH and –OR groups raise the electron density on these carbons. Because of this reason the peak of C_5 and C_6 shifted to higher chemical region. Azomethine carbon (C_{11}) was seen at δ 150.32 ppm. C_9 was seen at δ 124.82 ppm. Each value of C_7, C_8, C_{10} way either corresponds to δ 116.79 ppm, δ 116.08 ppm, δ 113.85 ppm. C_{12} and C_4 were seen at δ 79.95ppm and δ 68.46 ppm respectively. C_4, C_3, C_2, C_1 were observed between δ 14.44 ppm and δ 34.28 ppm. C_{15}, C_{16}, C_{17} were determined at the same chemical shift, at δ 16.79 ppm. The ^{13}C-NMR values of Schiff base-7 are given in table 3.20.

3.2.8 Schiff Base 8



For Schiff base-8; the highest chemical shift corresponds to carbonyl carbon, namely, C_{13}, the paek of C_{13} was determined at δ 171.79 ppm. Due to the effect of –OH and –OR groups at C_4 and C_5, they were observed at δ 163 83 ppm and δ 162.73 ppm, respectively. Azomethine carbon, that is, C_{11} was seen at δ 150.30 ppm.the peak of C_{12} and C_4 appeared at δ 75.66 ppm and δ 68.50 ppm respevtively. C_1, C_2, C_3, C_{14}, C_{15}, C_{16}, C_{17} each one of which is, aliphatic carbons were determined between δ 31.74 and δ 12.35 ppm. The ^{13}C-NMR values of Schiff base-8 are given in table 3.21.

3.2.9 Schiff Base 9



For Schiff base-9**;** the signal of carbonyl carbon, namely; C_{13} appeared at the highest chemical shift, at δ 172.43 ppm. Because of the effect of -OH and -OR groups at C_4 and C_5 were seen at higher chemical region, they determined at δ 164.08 ppm and δ 162.29 ppm respectively. Azomethine carbon, that is, C_{11} was observed at δ 150.18 ppm. Aromatic carbon (C_9) was seen at δ 124.76 ppm and each value of C_7,C_8,C_{10} may either corresponds to δ 117.08 ppm, δ 116.19 ppm, δ 114.07 ppm. C_{12} and C_4 were determined at δ 76.23 ppm and δ 68.52 ppm respectively. Aromatic carbons C_{15} and C_{16} were observed at δ 124.76 ppm. C_1, C_2, C_3, C_{14} were seen between δ 20.68 ppm and δ 14.34 ppm. The ^{13}C-NMR values of Schiff base-9 are given in table 3.22.

Table 3.14. ^{13}C-NMR spectral data of the Schiff base-1

C	Schiff base-1
C_9	171.15
C_6	165.70
C_5	163.36
C_2	122.94
C_3, C_4, C_1	114.62, 114.00, 112.68
C_8	77.36
C_{10}	34.41
C_{11}, C_{12}, C_{13}	27.59

Table 3.15. ^{13}C-NMR spectral data of the Schiff base-2

C	**Schiff base-2**
C_9	172.02
C_1	164.60
C_2	164.08
C_7	149.37
C_5	122.87
C_3, C_4, C_6	114.95, 114.57, 113.13
C_8	72.81
C_{10}	38.69
C_{12}	25.10
C_{11}	16.77
C_{13}	12.34

Table 3.16. ^{13}C-NMR spectral data of the Schiff base-3

C	Schiff base-3
C_9	171.98
C_1	165.13
C_2	164.12
C_7	149.44
C_5	122.96
C_3, C_4, C_6	114.88, 114.40, 112.97
C_8	73.34
C_{11}, C_{12}, C_{10}	31.79, 20.35, 18.23

Table 3.17. ^{13}C-NMR spectral data of the Schiff base-4

C	Schiff base-4
C_{10}	171.85
C_2	163.47
C_3	163.14
C_8	151.17
C_6	124.77
C_4, C_5, C_7	116.24, 114.42, 113.53
C_9	79.30
C_1	56.09
C_{11}	34.33
C_{12}, C_{13}, C_{14}	27.68

Table 3.18. ^{13}C-NMR spectral data of the Schiff base-5

C	Schiff base-5
C_{10}	172.44
C_2	164.11
C_3	162.74
C_8	151.02
C_6	124.71
C_4, C_5, C_7	116.58, 114.49, 113.79
C_9	75.10
C_1	56.13
C_{11}, C_{12}, C_{13}, C_4	38.45, 25.15, 16.93, 12.29

Table 3.19. ^{13}C-NMR spectral data of the Schiff base-6

C	Schiff base-6
C_{10}	172.68
C_2	164.36
C_3	162.51
C_8	150.96
C_6	124.68
C_4, C_5, C_7	116.60, 114.48, 113.93
C_9	75.59
C_1	56.13
C_{11}, C_{12}, C_{13}	31.65, 20.55, 18.44

Table 3.20. ^{13}C-NMR spectral data of the Schiff base-7

C	Schiff base-7
C_{13}	172.23
C_5	163.33
C_6	162.88
C_{11}	150.32
C_9	124.82
$C_{8,} C_{7,} C_{10}$	116.79, 116.08, 113.85
C_{12}	79.95
C_4	68.46
$C_{1,} C_{2,} C_{3,} C_{14}$	34.28, 31.68, 19.47, 14.44
$C_{15,} C_{16,} C_{17}$	27.73

Table 3.21. ^{13}C-NMR spectral data of the Schiff base-8

C	Schiff base-8
C_{13}	171.79
C_5	163.83
C_6	162.73
C_{11}	150.30
C_9	124.80
$C_{7,}C_{8,} C_{10}$	117.00, 116.19, 113.80
C_{12}	75.66
C_4	68.50
$C_{14,} C_{15,} C_{16,} C_{17,} C_{1,} C_{2,}C_3$	31.74-12.35

Table 3.22. ^{13}C-NMR spectral data of the Schiff base-9

C	Schiff base-9
C_{13}	172.43
C_5	164.08
C_6	162.29
C_{11}	150.18
C_9	124.76
C_7, C_8, C_{10}	117.08, 116.19, 114.07
C_{12}	73.23
C_4	68.52
C_{14}, C_{15}, C_{16}, C_1, C_2, C_3	31.70-14.43

3.3 IR Spectra and Mode of Bonding

The IR spectra of all compounds were carried out as KBr pellet. The selected IR spectra of ligands and its metal complex along with their tentative assignments are reported in table 3.24 the IR data is good agreement with our proposed structures.

The IR data of Schiff bases demonstrate the disappearances the peak of ν(-NH$_2$) due to amino acids and the peak of ν(-HC=O) due to aldehyde and appearance of the new band at 1590-1615 cm^{-1}, because of the azomethine group ν(C=N) , is seen .this case determinate that ν(-NH$_2$) and ν(-HC=O) groups condensate.

The free Schiff base showed characteristic azomethine, carbonyl, and hydroxyl frequencies as shown in table 3.23

For complex 1:

For ligand the strong band determined at 1604 cm^{-1} was assigned to the azomethine group vibration. In the complex this band was shifted higher frequency, 1602 cm^{-1} , suggesting that the involvement of the azomethine –N with the metal ion. For the ligand the band in 3425 cm^{-1} was assigned to υ(O-H) stretching, this band was expected to disappear in complex, as a result of proton substitution by cation coordination to oxygen but region between 3000 and 3500 cm^{-1} was complicated due to υ(OH) stretching band of water molecules. This is why the disappearance of υ(O-H) stretching band was not observed clearly. However –OH band shifted 3425 cm^{-1} to 3364 cm^{-1} this case shows the involvement of the hydroxyl group –O with the metal ion. We also obtained bands at 16433 cm^{-1} and 1384 cm^{-1} due to $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ respectively. Other characteristic peaks were observed for example; aliphatic υ(C-H) bonds were determined between 2933-2963 cm^{-1} as expected, aromatic υ(C=C) bonds were observed between 1470-1553 cm^{-1} , υ(C-O) bond was observed at 1216 cm^{-1} , aromatic υ(C-H) bond was not clear because -OH bond was very broad.

For complex 2:

The band of azomethine group was shifted lower wavenumber, from 1613 cm^{-1} to 1600 cm^{-1}. This case shows that azomethine –N was involved in the coordination of the metal in the complex. -OH bond was shifted higher frequency; from 3419 cm^{-1} to 3425 cm^{-1} . This is shows that hydroxyl group of oxygen involved with the metal ion. Other characteristic peaks observed such as; $\upsilon(COO)_{asym}$ and $\upsilon(COO)_{sym}$ were observed at 1641 cm^{-1} and 1389 cm^{-1} respectively, υ(C-O) bond was determined at 1203 cm^{-1}, υ(C-H) bonds were determined between 2871-2970 cm^{-1} as expected, aromatic υ(C=C) bonds were observed between 1464-1492 cm^{-1}

Table 3.23 IR data of Schiff base

	substituent's	Expected(cm^{-1})	Observed
Schiff base1	-OH -C=N -C=O	3600-3200 1640-1690 1630-1780	3395 1601 1635
Schiff base2	-OH -C=N -C=O	3600-3200 1640-1690 1630-1780	3388 1604 1638
Schiff base3	-OH -C=N -C=O	3600-3200 1640-1690 1630-1780	3382 1604 1639
Schiff base4	-OH -C=N -C=O	3600-3200 1640-1690 1630-1780	3430 1606 1633
Schiff base5	-OH -C=N -C=O	3600-3200 1640-1690 1630-1780	3390 1604 1632

Schiff base 6	-OH	3600-3200	3422
	-C=N	1640-1690	1604
	-C=O	1630-1780	1638
Schiff base7	-OH	3600-3200	3423
	-C=N	1640-1690	1607
	-C=O	1630-1780	1632
Schiff base8	-OH	3600-3200	3425
	-C=N	1640-1690	1613
	-C=O	1630-1780	1637
Schiff base9	-OH	3600-3200	3433
	-C=N	1640-1690	1607
	-C=O	1630-1780	1638

Table 3.24. the IR data of metal complexes

Number of the Schiff bases	Substituent	Schiff base	Ni complex
1	-C=N -C=O	1604 1632	1602 1643
2	-C=N -C=O	1613 1637	1600 1641

3.4 UV-Vis spectroscopy studies

UV-Vis spectra of all Schiff bases and Ni complexes of Schiff base ligands have been determined by using MeOH as a solvent. The bands of Schiff base and metal complexes are given in table 3.25

Table 3.25. UV-Vis spectral data of Schiff bases and metal complexes

Product	Absorbance (λ) (nm)
Schiff base 1	422, 301,223
Schiff base 2	423, 299, 223, 208
Schiff base 3	423, 299, 271, 221
Schiff base 4	417, 297, 241
Schiff base 5	418, 294, 230, 205
Schiff base 6	409, 294, 228, 204
Schiff base 7	420, 296, 230, 215
Schiff base 8	420, 295, 267, 223
Schiff base 9	405,285,238
Complex 1	377, 281, 234, 211
Complex 2	385, 269, 229

In summary, we synthesized nine Schiff bases and we attempted to prepare Ni complexes of these ligands. We obtained two Ni complexes of Schiff base ligands, but they have very different empirical formulas and structures. Thus, although mononuclear (Liu et.al., 2006), dinuclear (Rodrigues et.al.,1989) and polynuclear(Bıan et.al., 2007) complexes are known of tridentate amino acid Schiff base ligands it appears difficult to obtain a series of Ni complexes of tridentate amino acid Schiff base ligands which all have the same structure. It appears as though small changes in ligand structure or solution may favour one type of structure over another. As a result, pure products are not always easy to obtain and many times decomposition results.

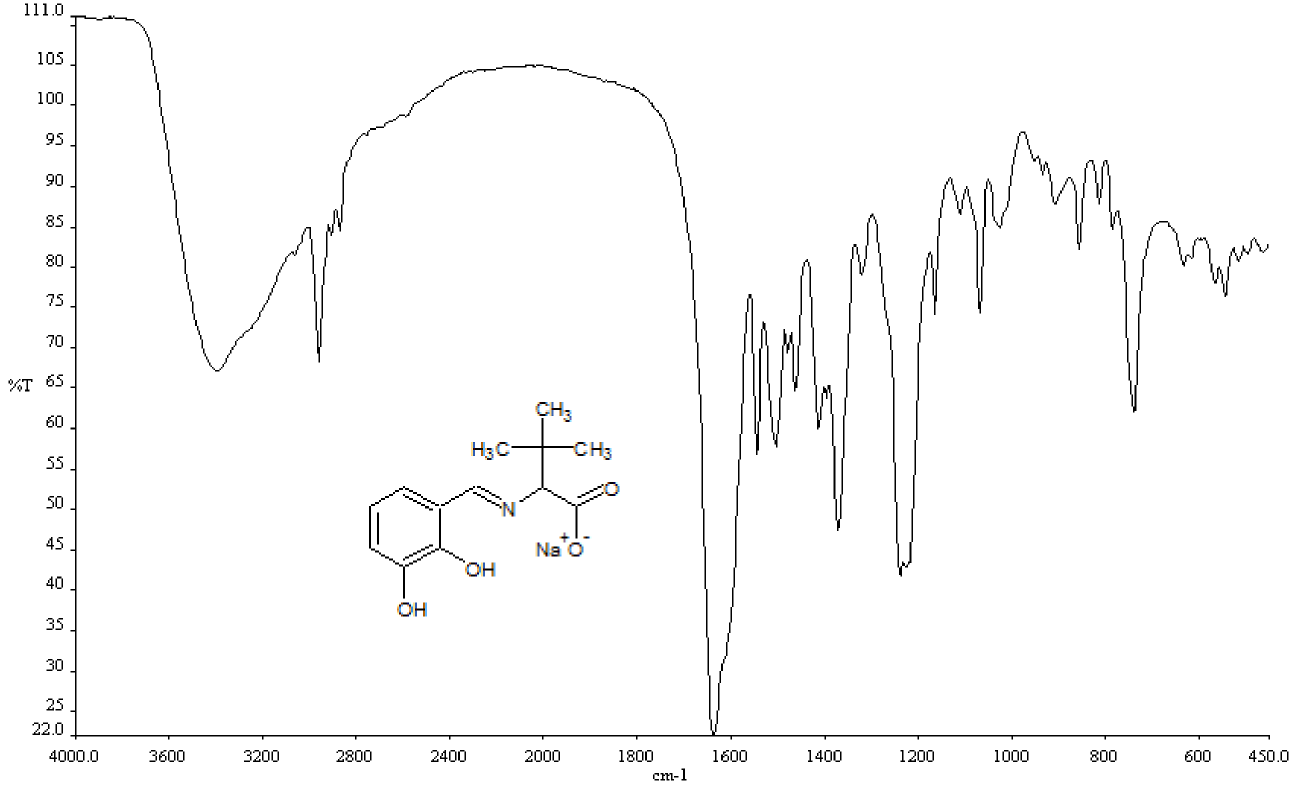


Figure -1 IR spectrum of Schiff base-1

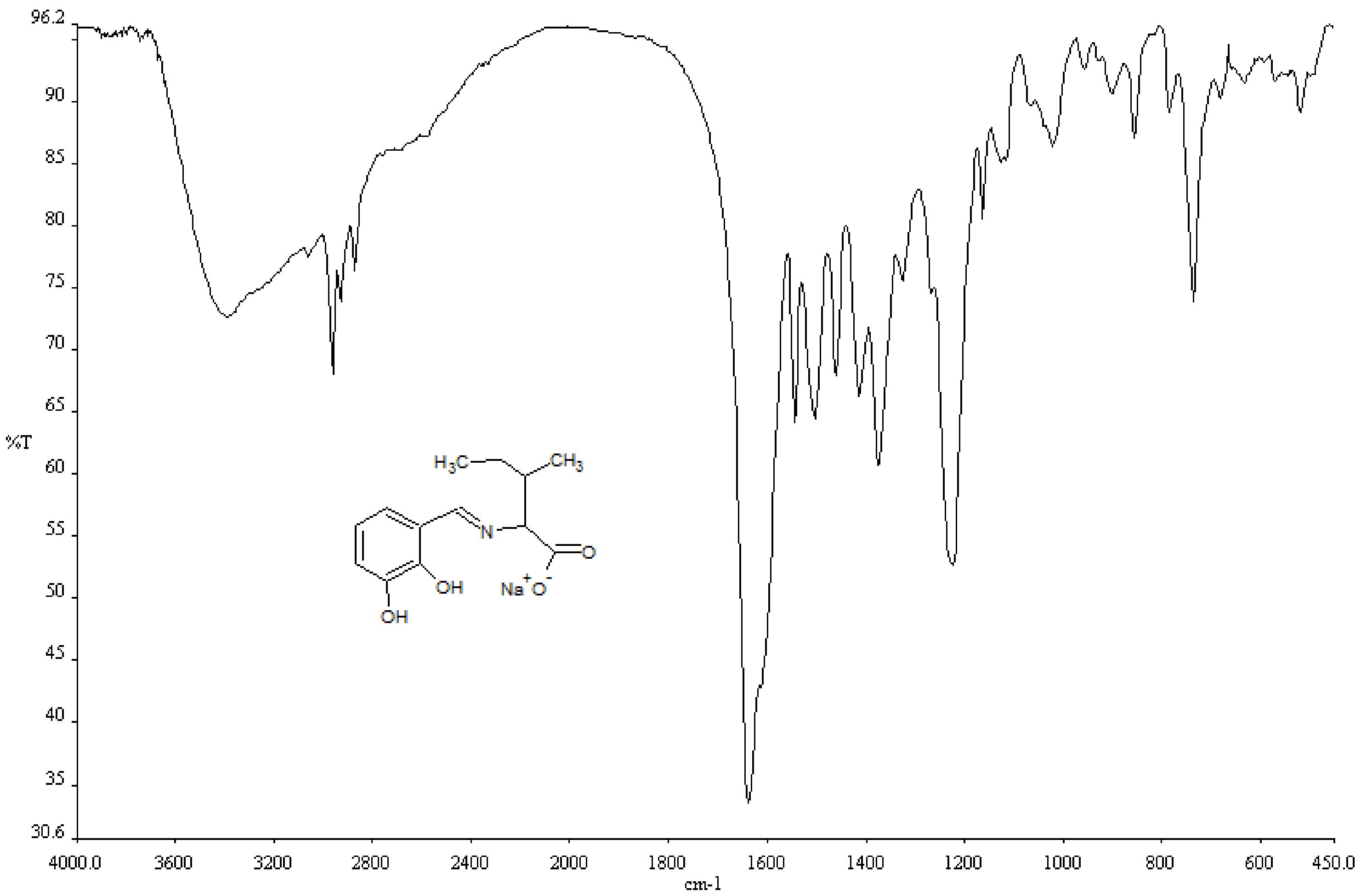


Figure -2 IR spectrum of Schiff base-2

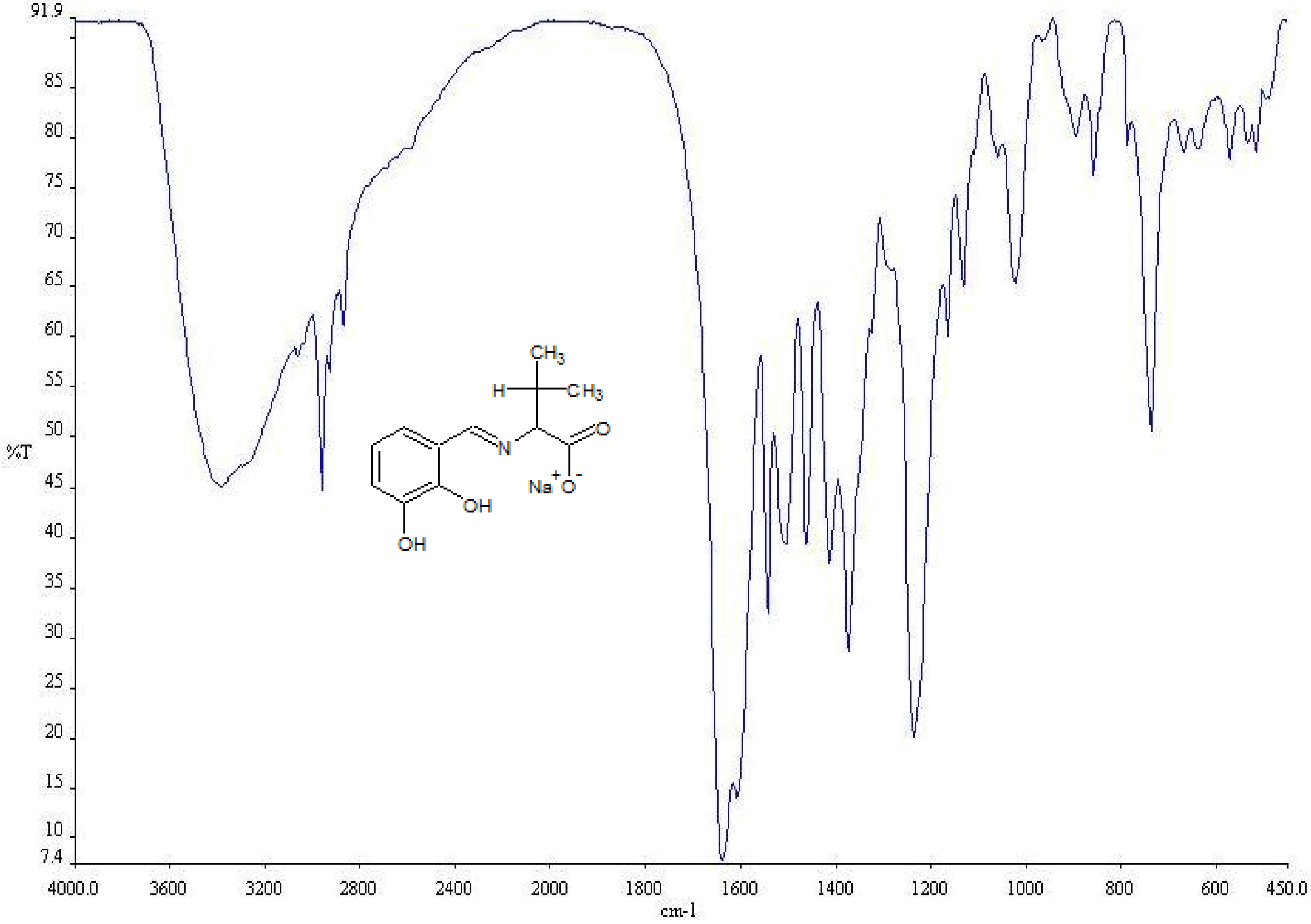


Figure-3 IR spectrum of Schiff base-3

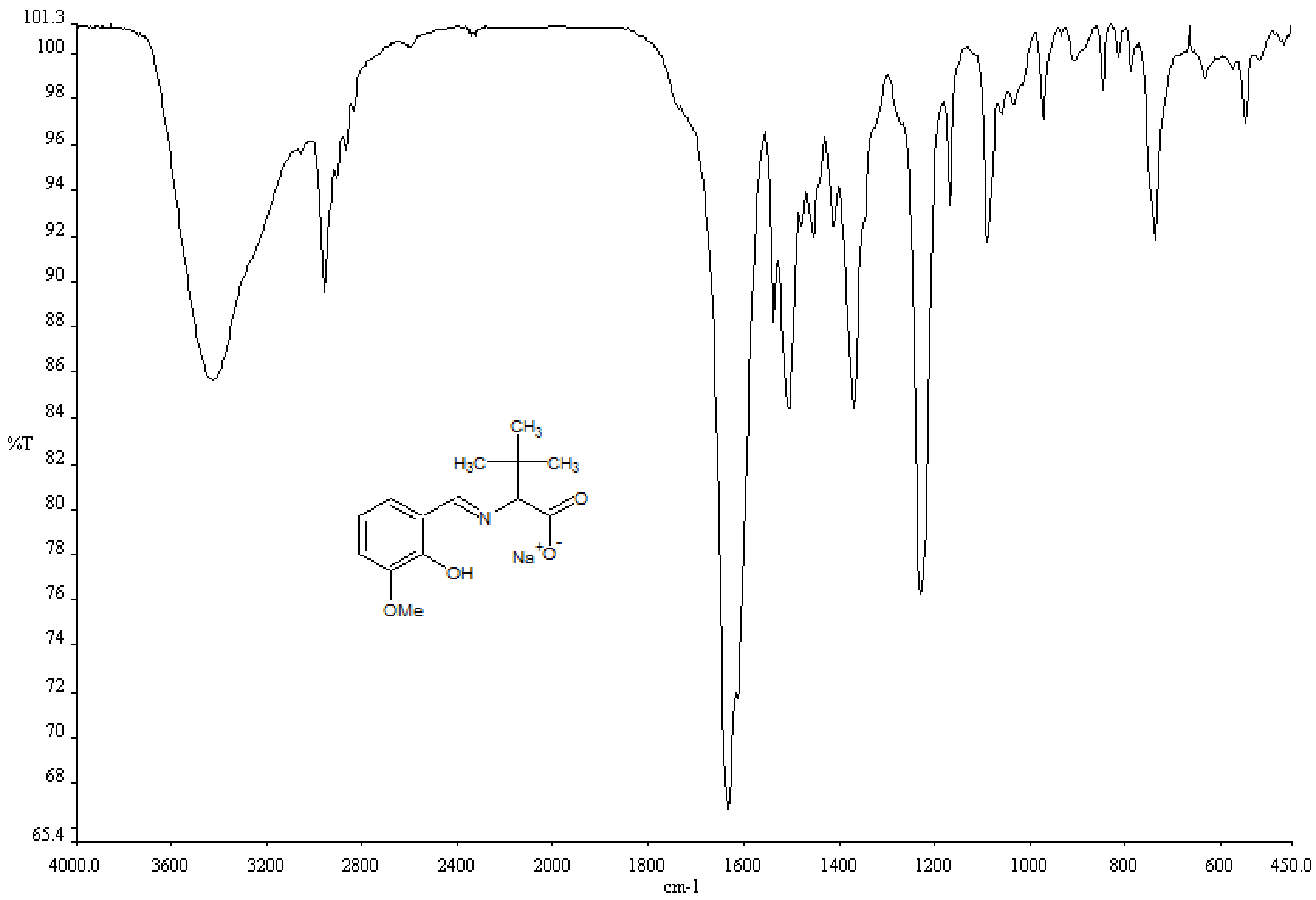


Figure-4 IR spectrum of Schiff base-4

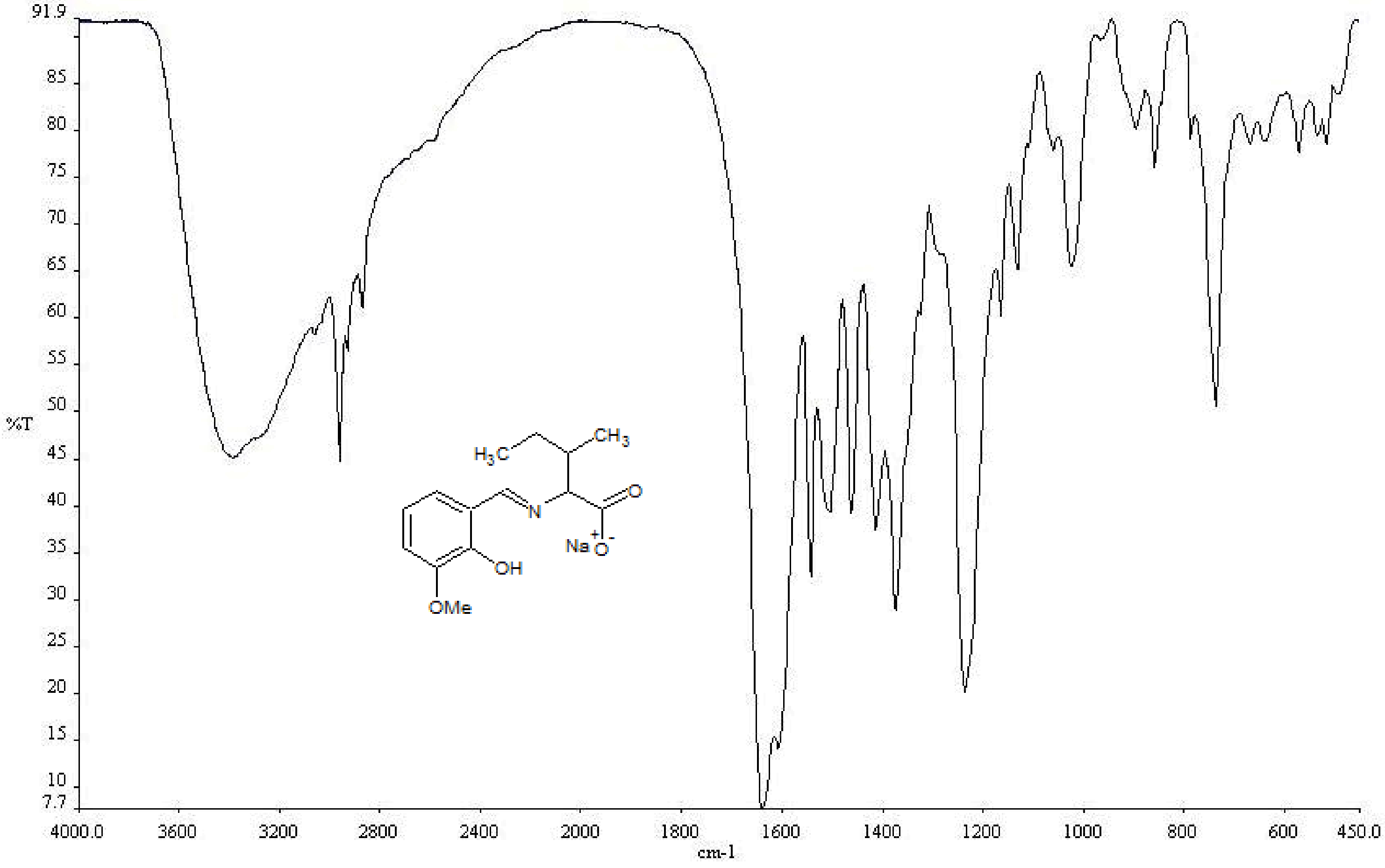


Figure-5 IR spectrum of Schiff base-5

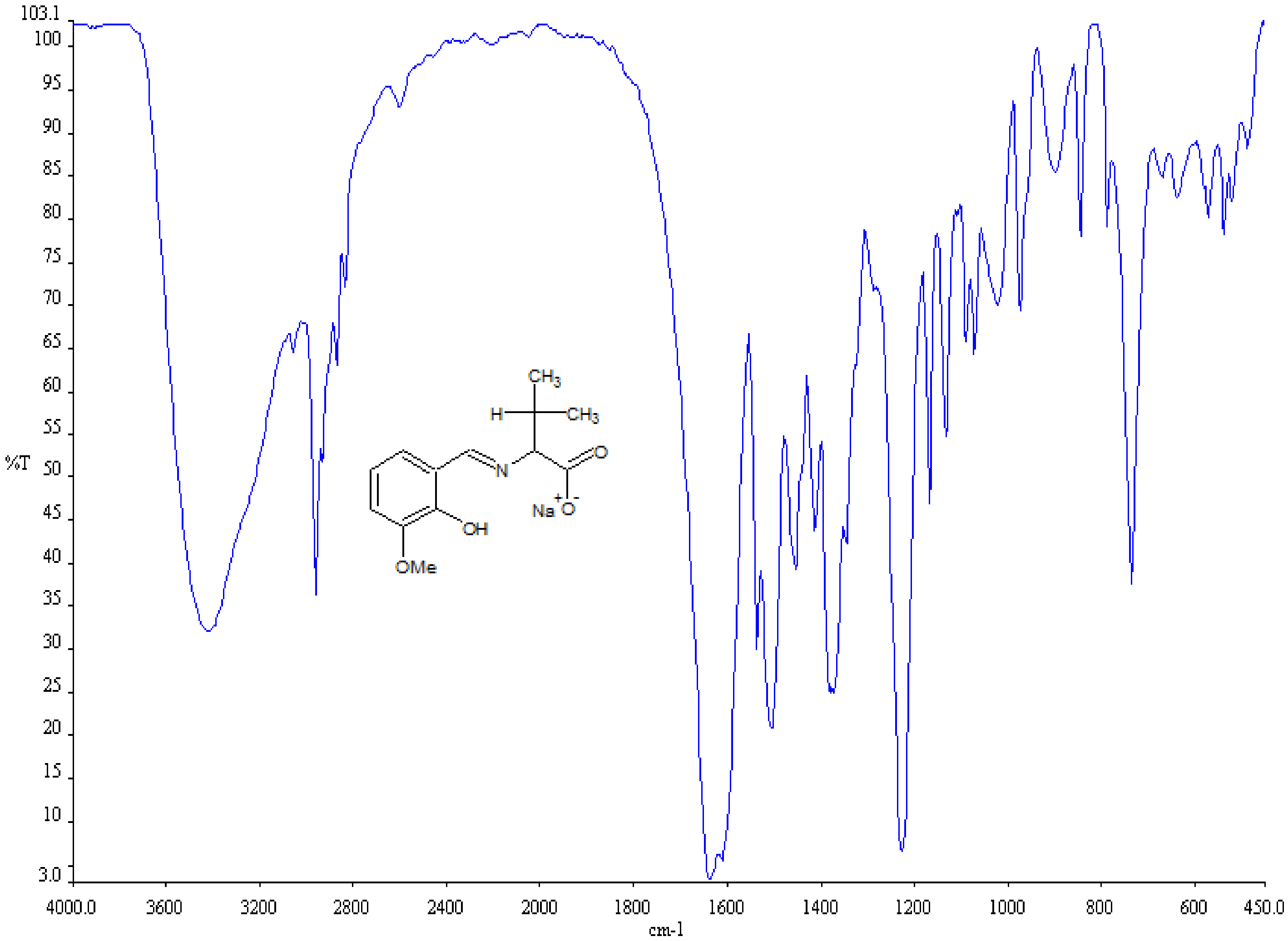


Figure-6 IR spectrum of Schiff base 6

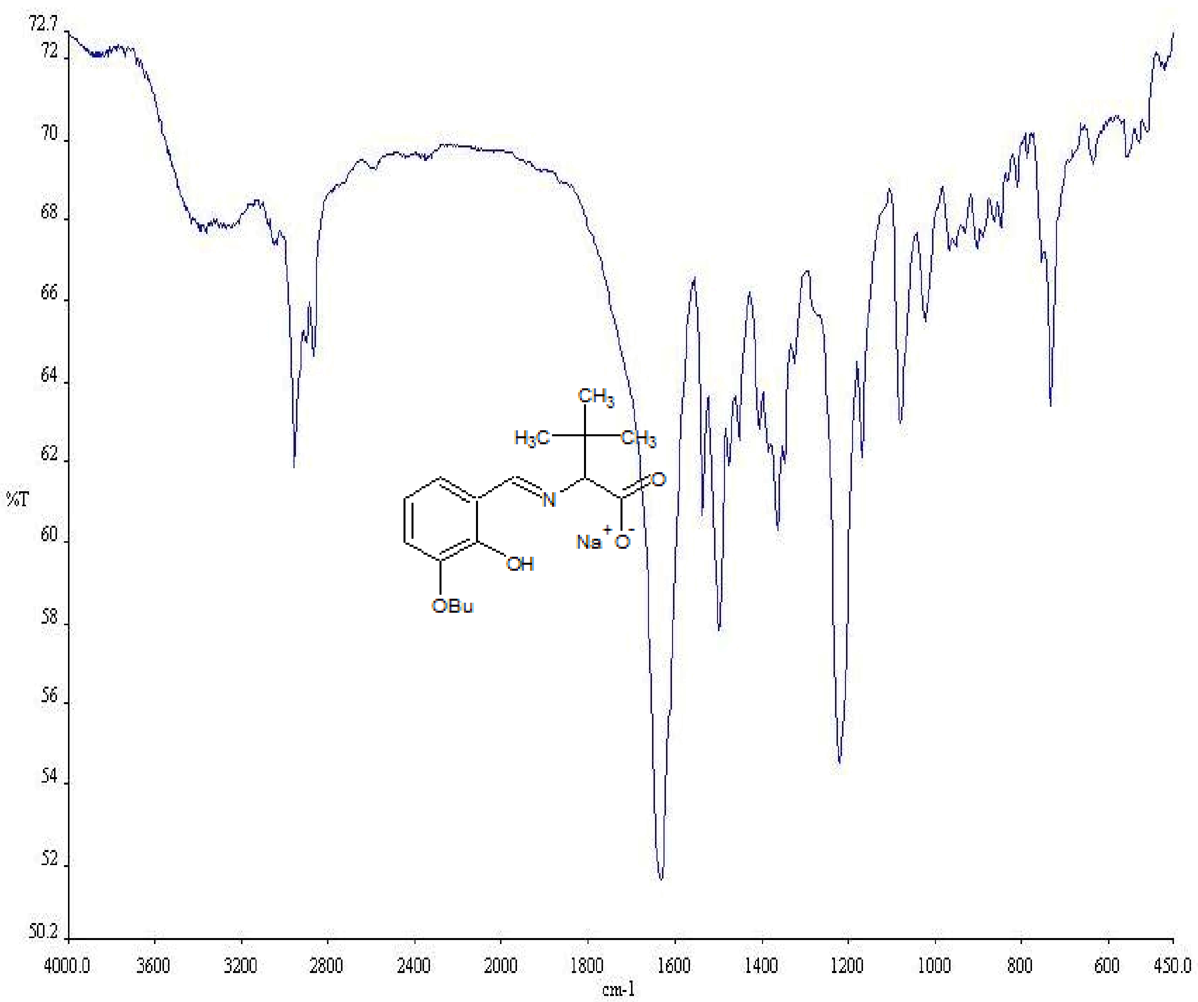


Figure-7 IR spectrum of Schiff base-7

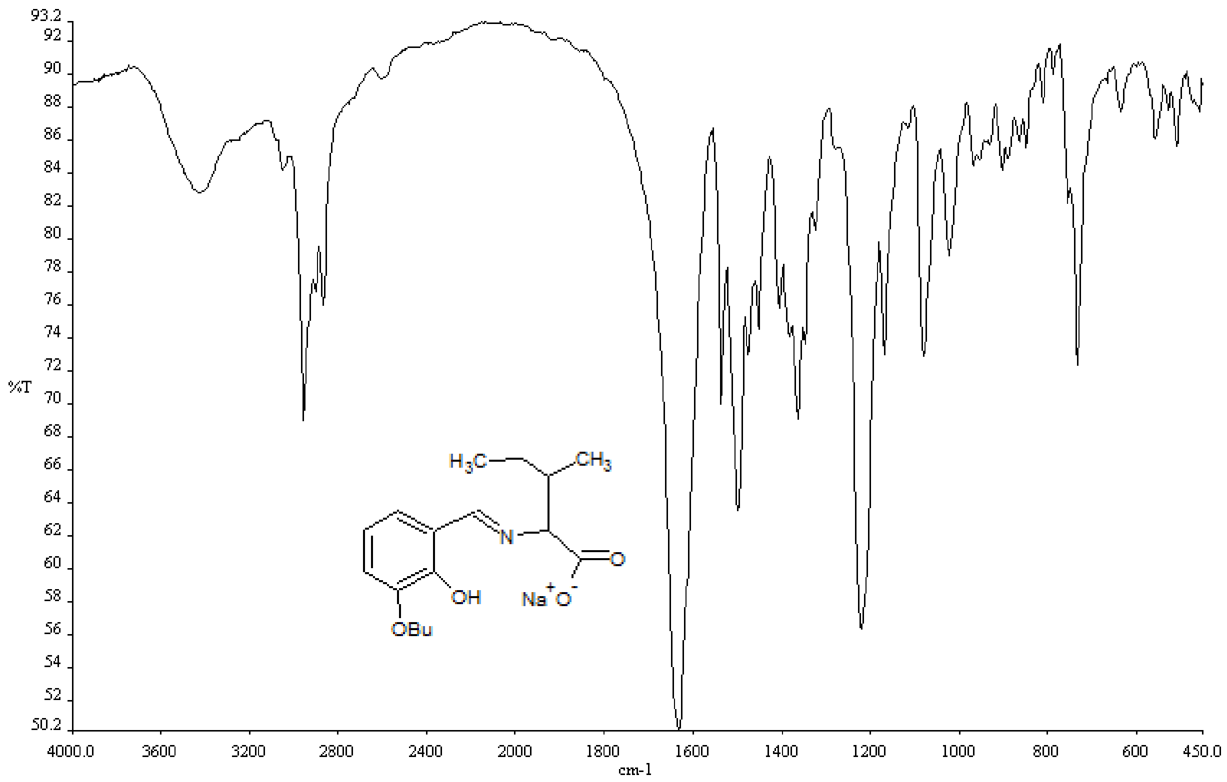


Figure-8 IR spectrum of Schiff base-8

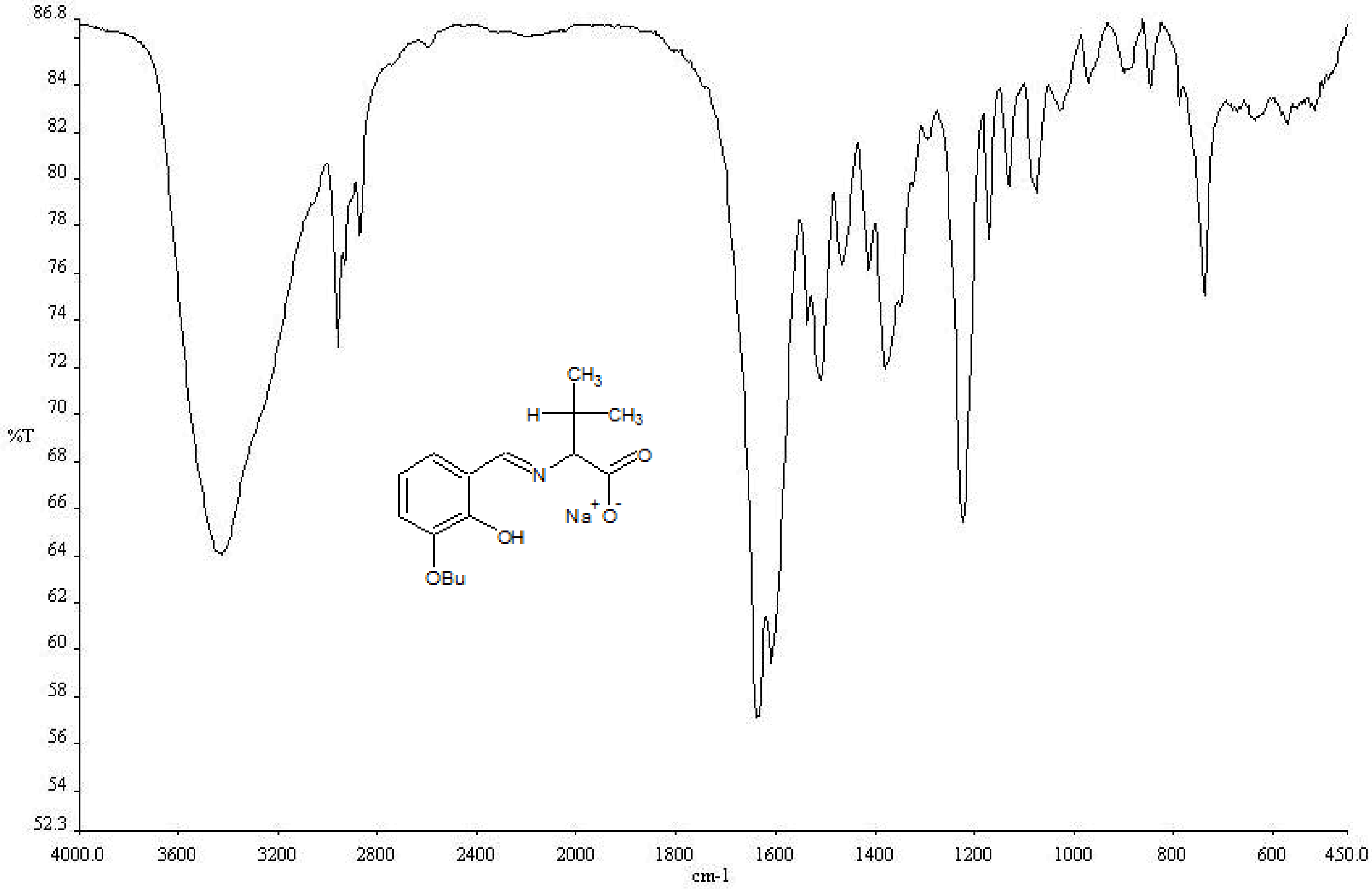


Figure-9 IR spectrum of Schiff base-9

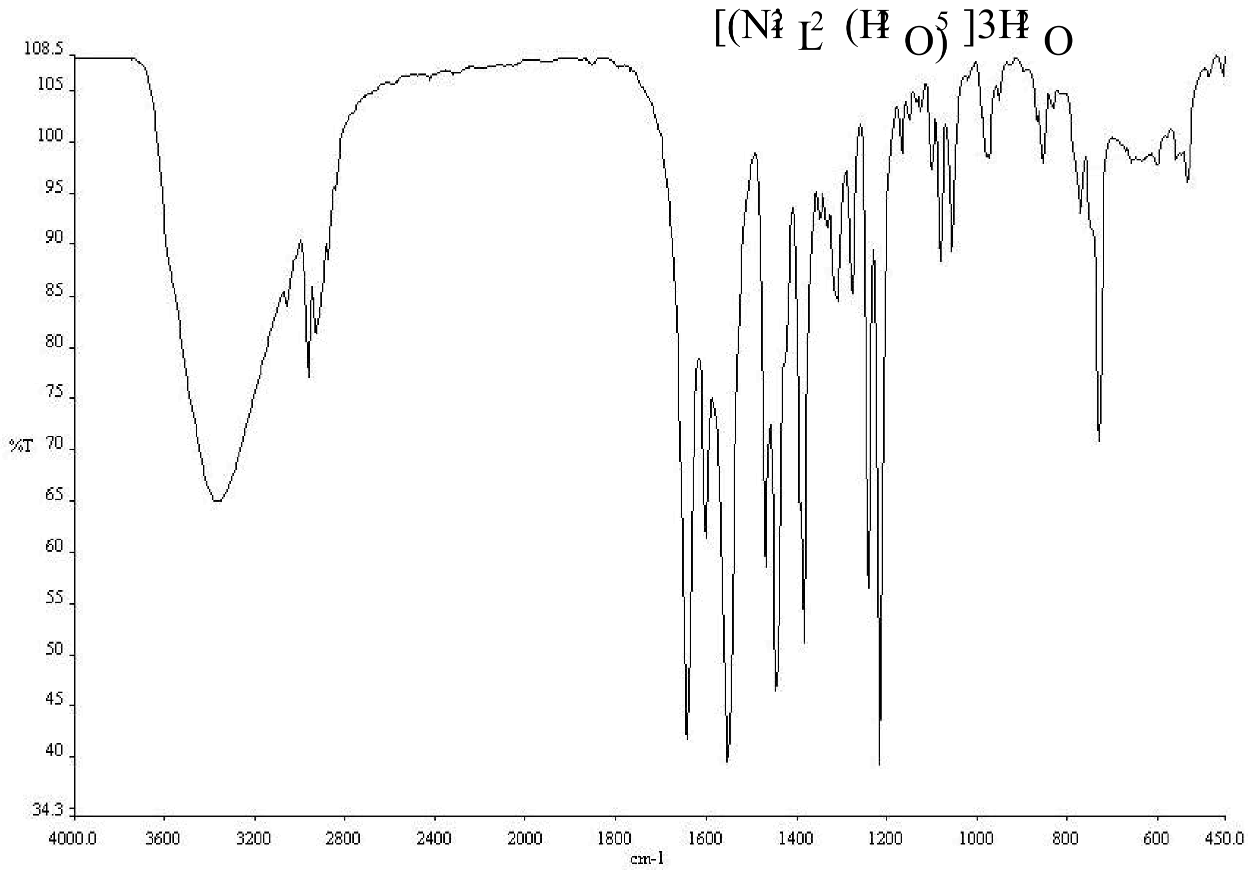


Figure-10 IR spectrum of complex-1

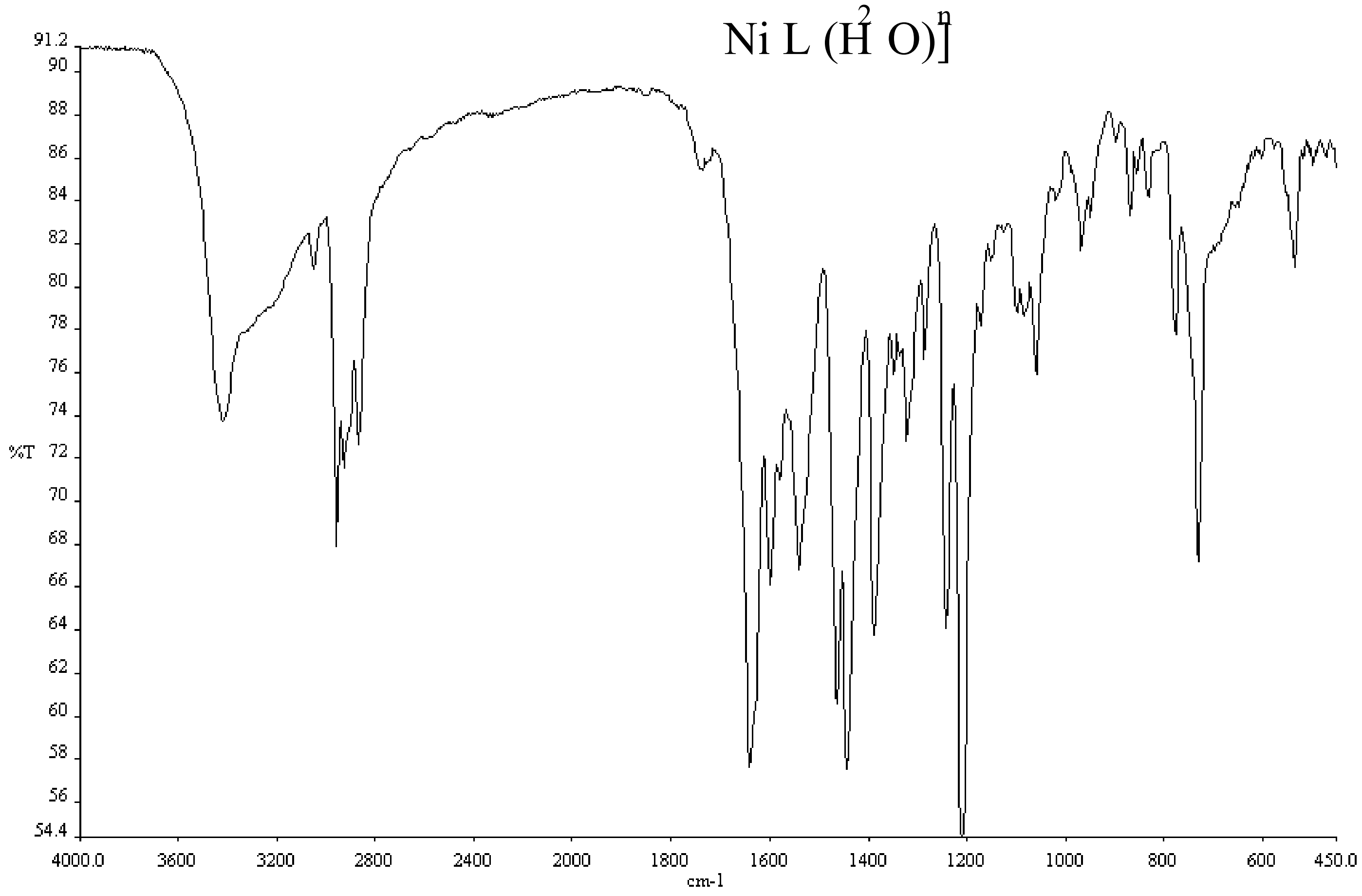


Figure-11 IR spectrum of metal complex-2

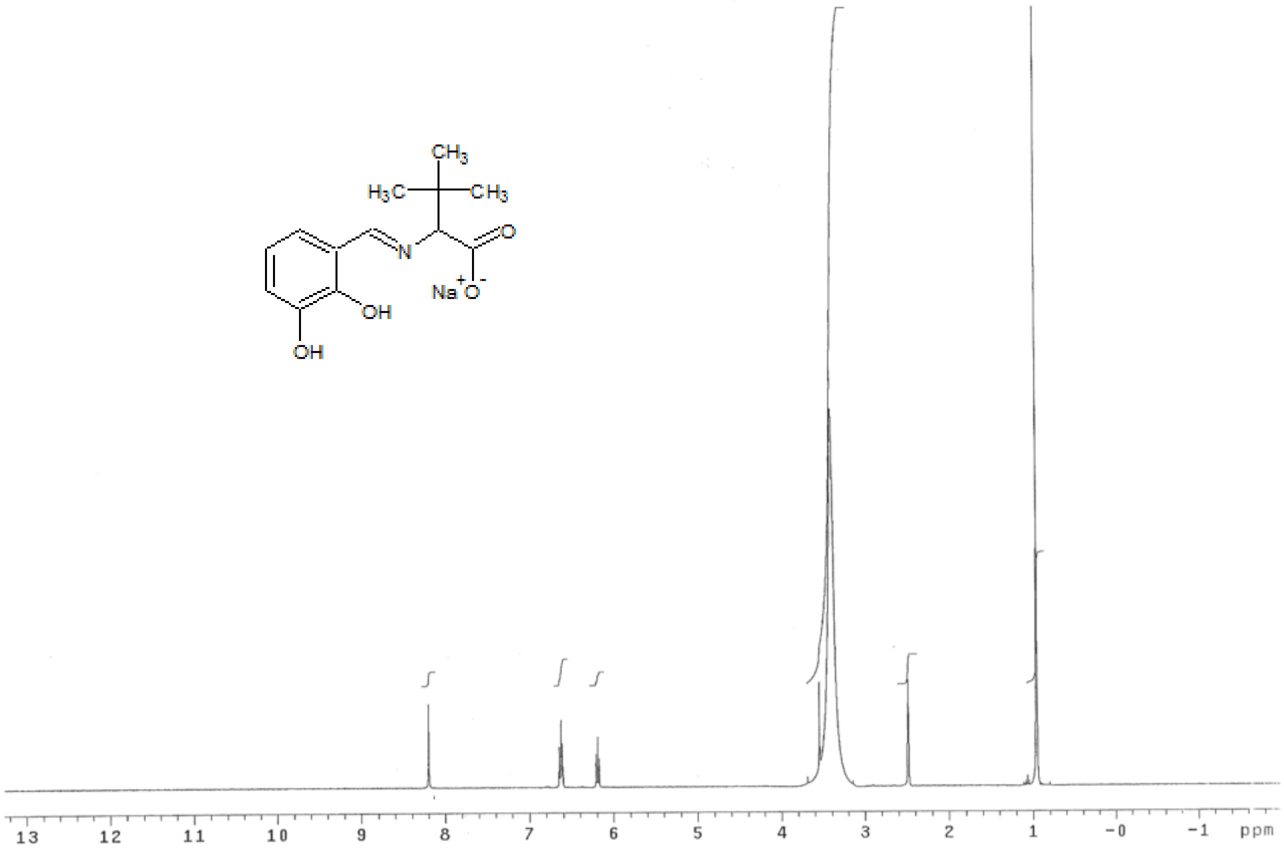


Figure-12 ^{1}H-NMR of Schiff base-1

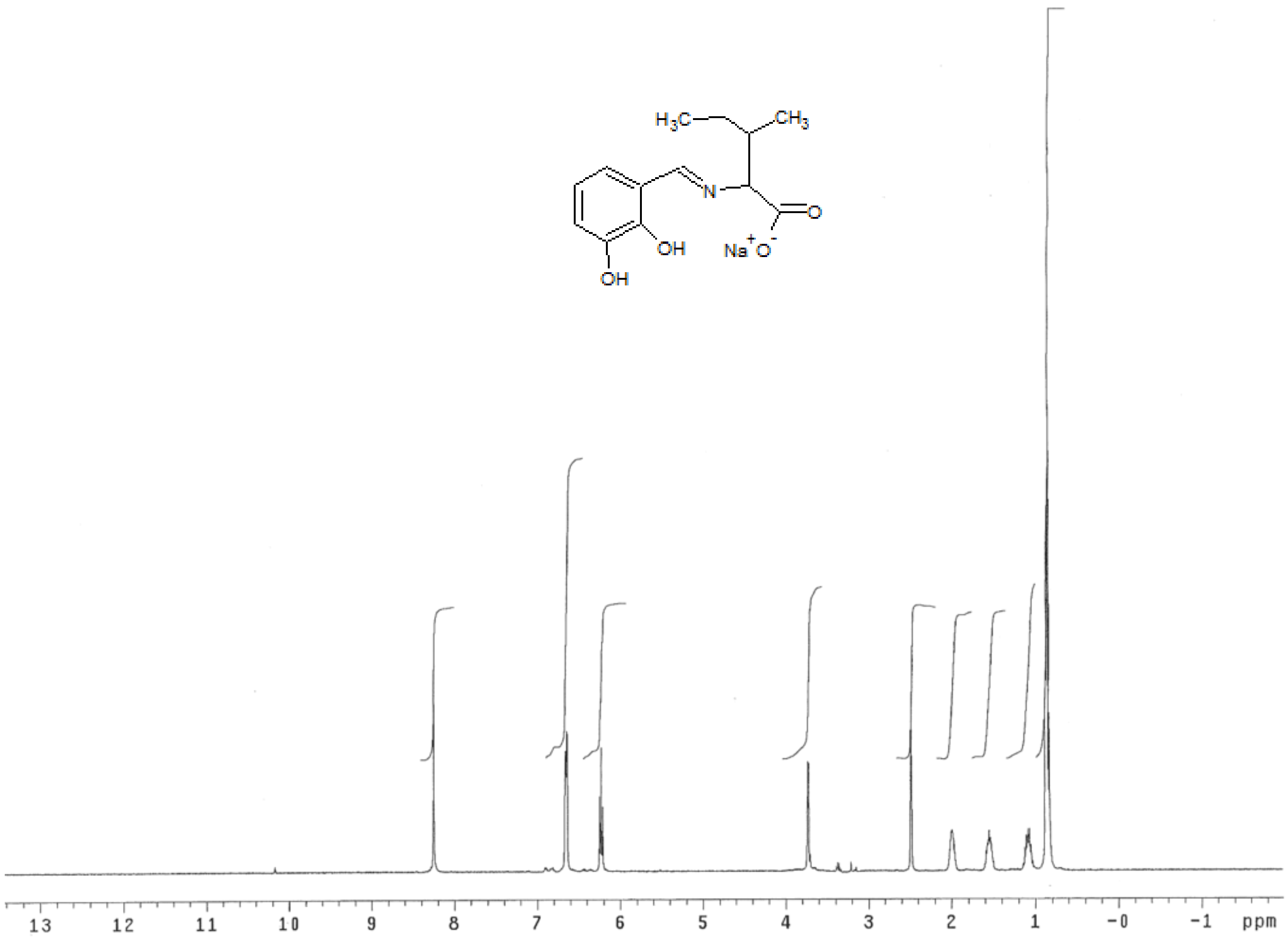


Figure-13 ^{1}H-NMR spectrum of Schiff base-2

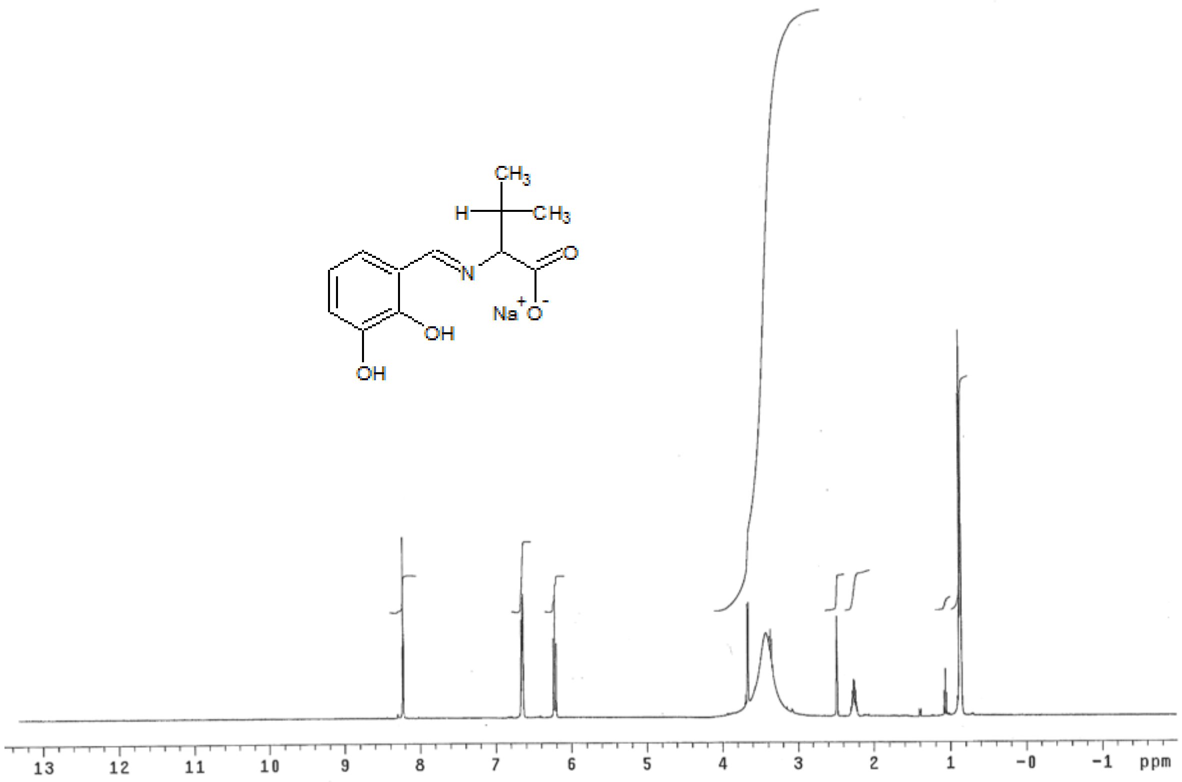


Figure-14 ^{1}H-NMR of Schiff base-3

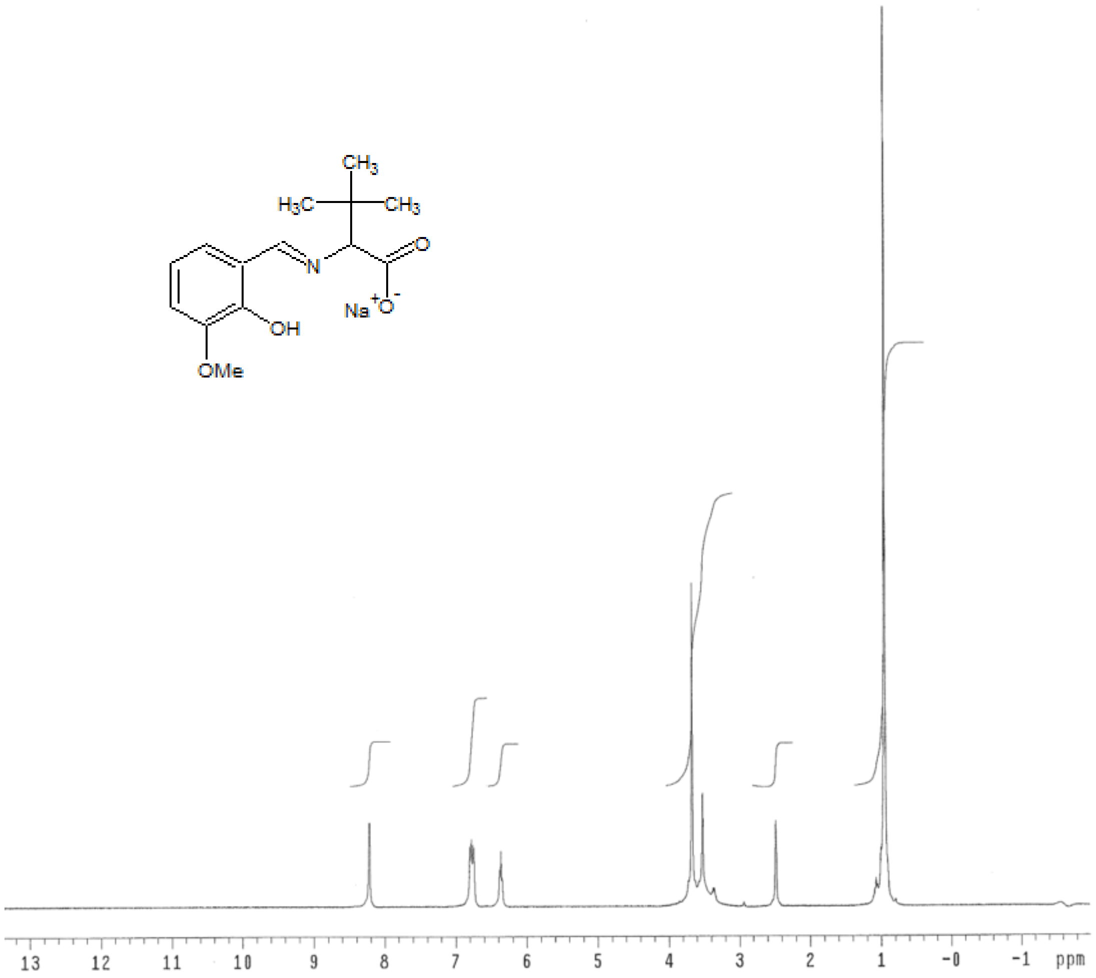


Figure-15 ^{1}H-NMR of Schiff base-4

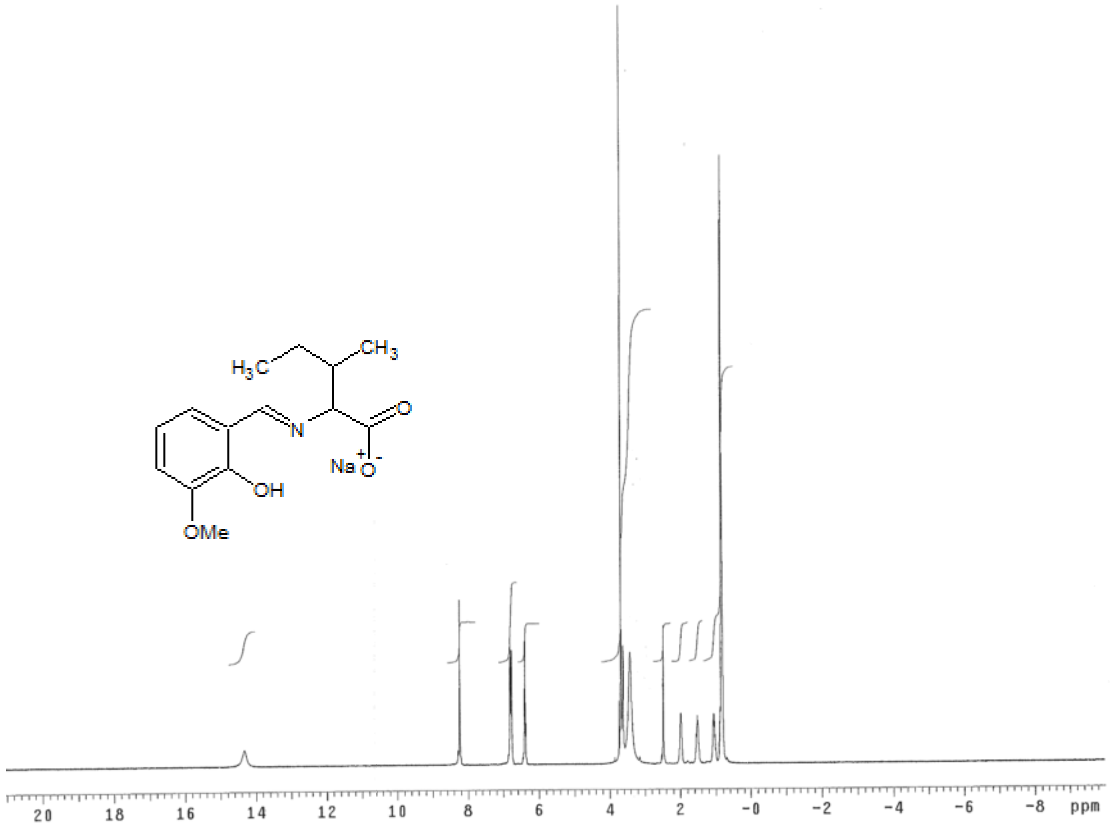


Figure -16 ^{1}H-NMR of Schiff base-5

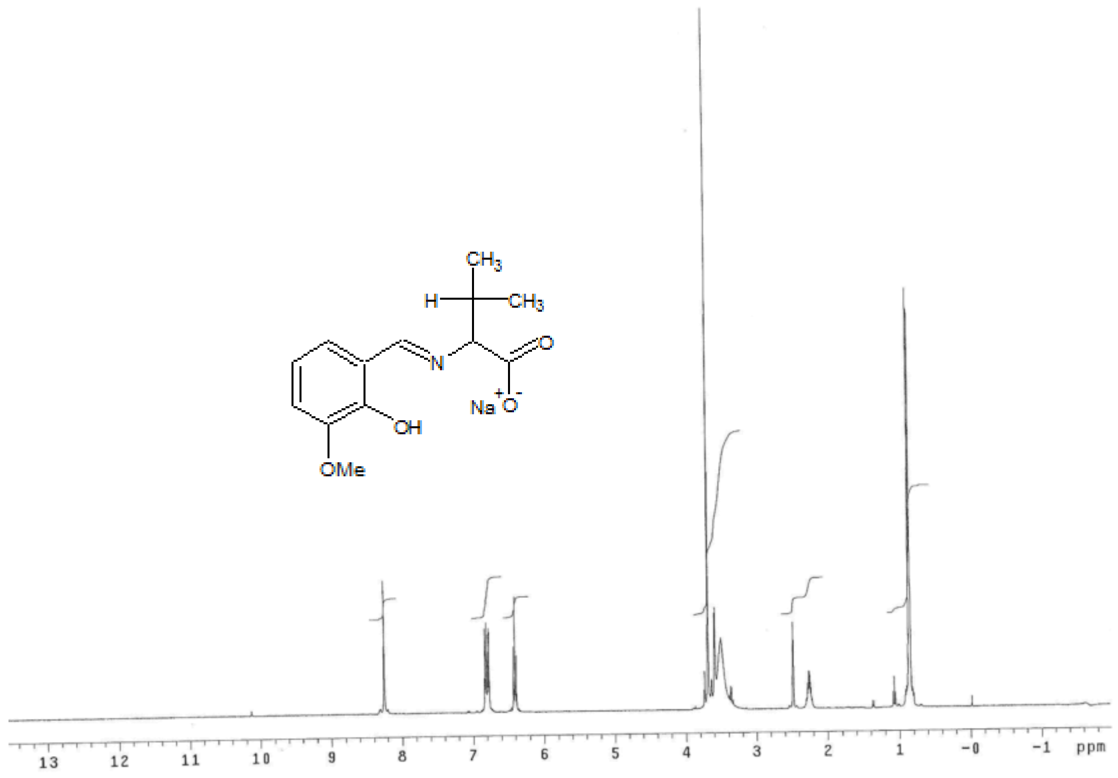


Figure-17 ^{1}H-NMR of Schiff base-6

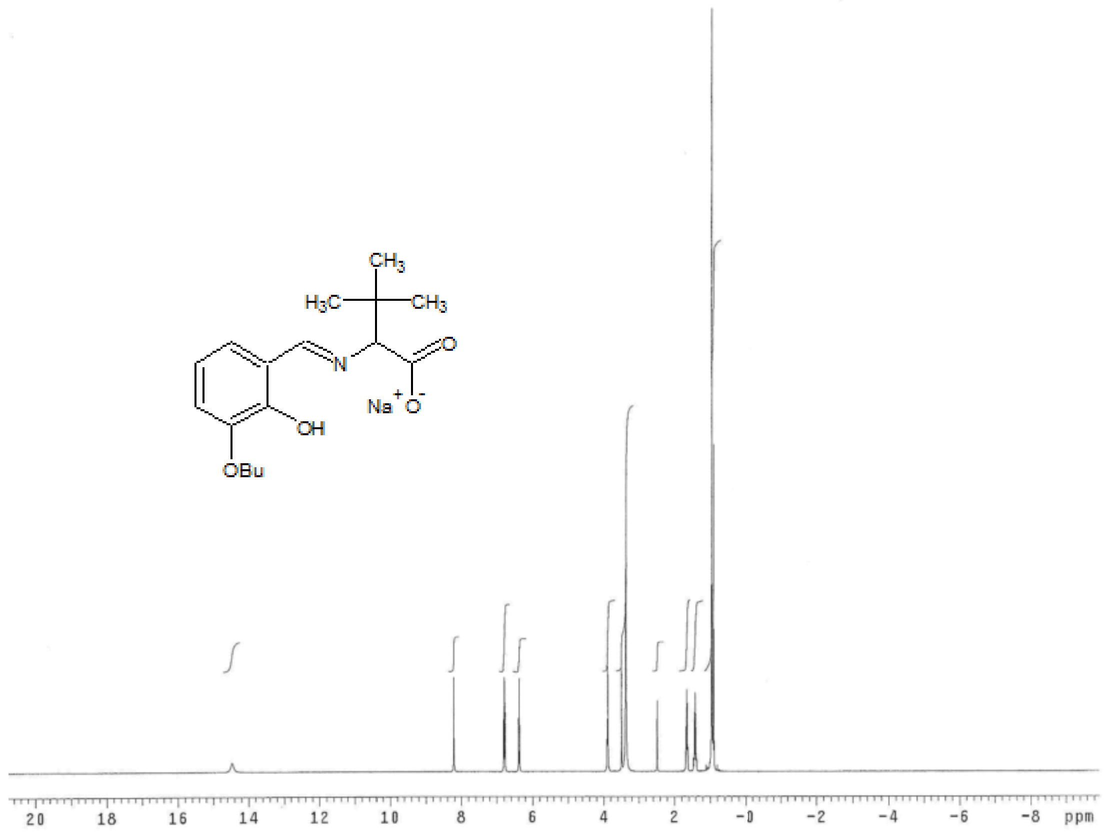


Figure-18 ^{1}H-NMR spectrum of Schiff base 7

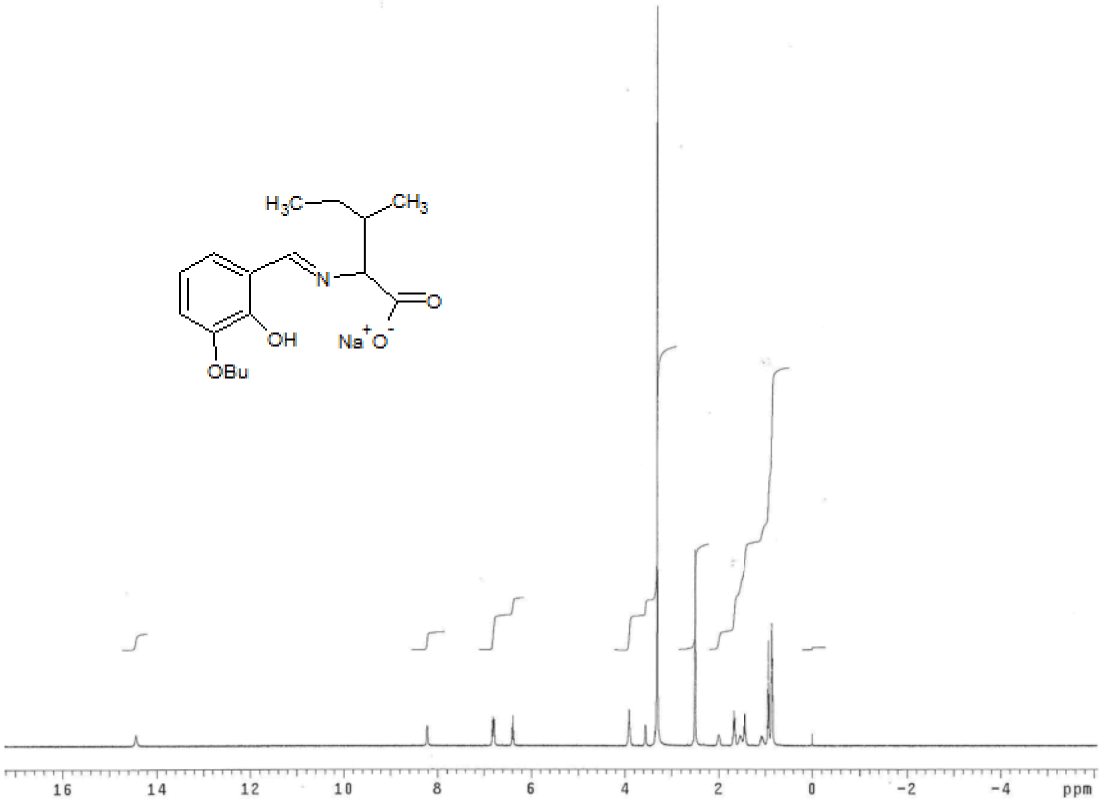


Figure-19 ^{1}H-NMR spectrum of Schiff base 8

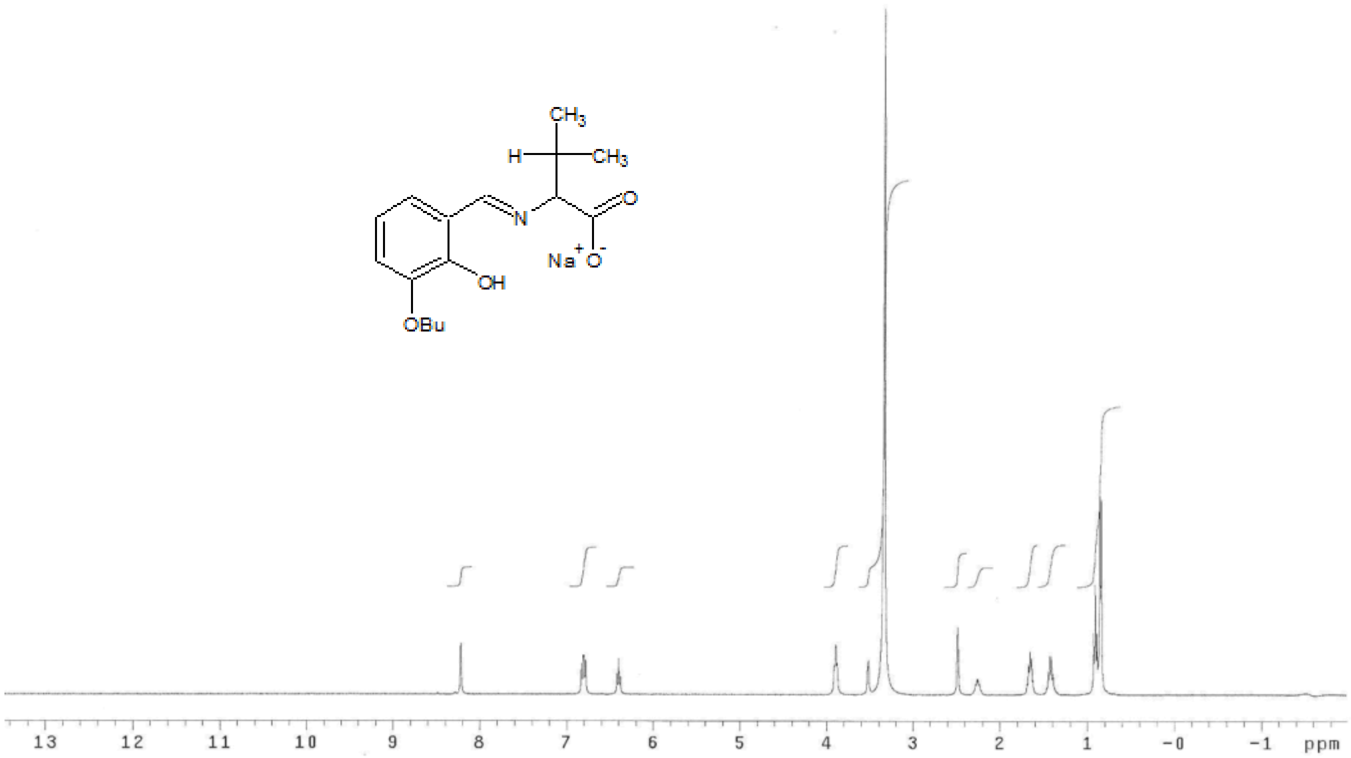


Figure-20 ^{1}H-NMR spectrum of Schiff base 9

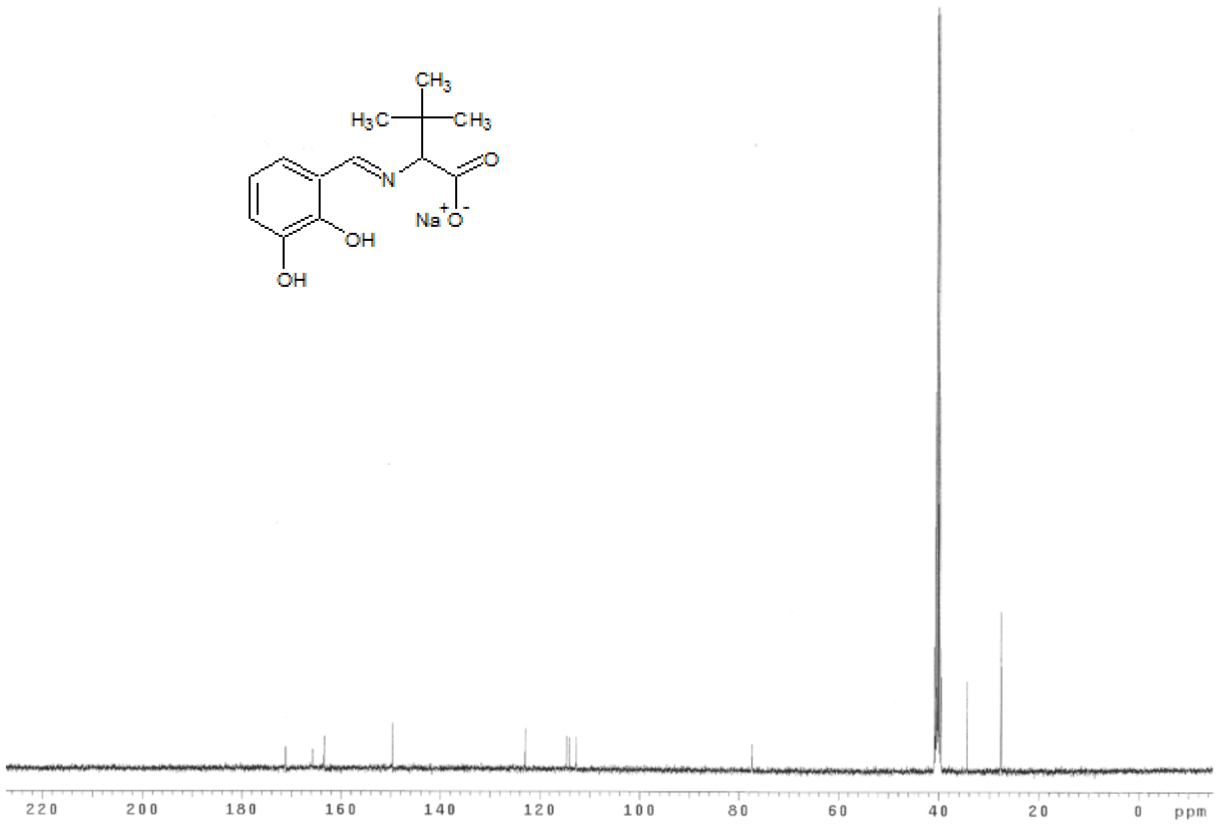


Figure-21 ^{13}C-NMR spectrum of Schiff base-1

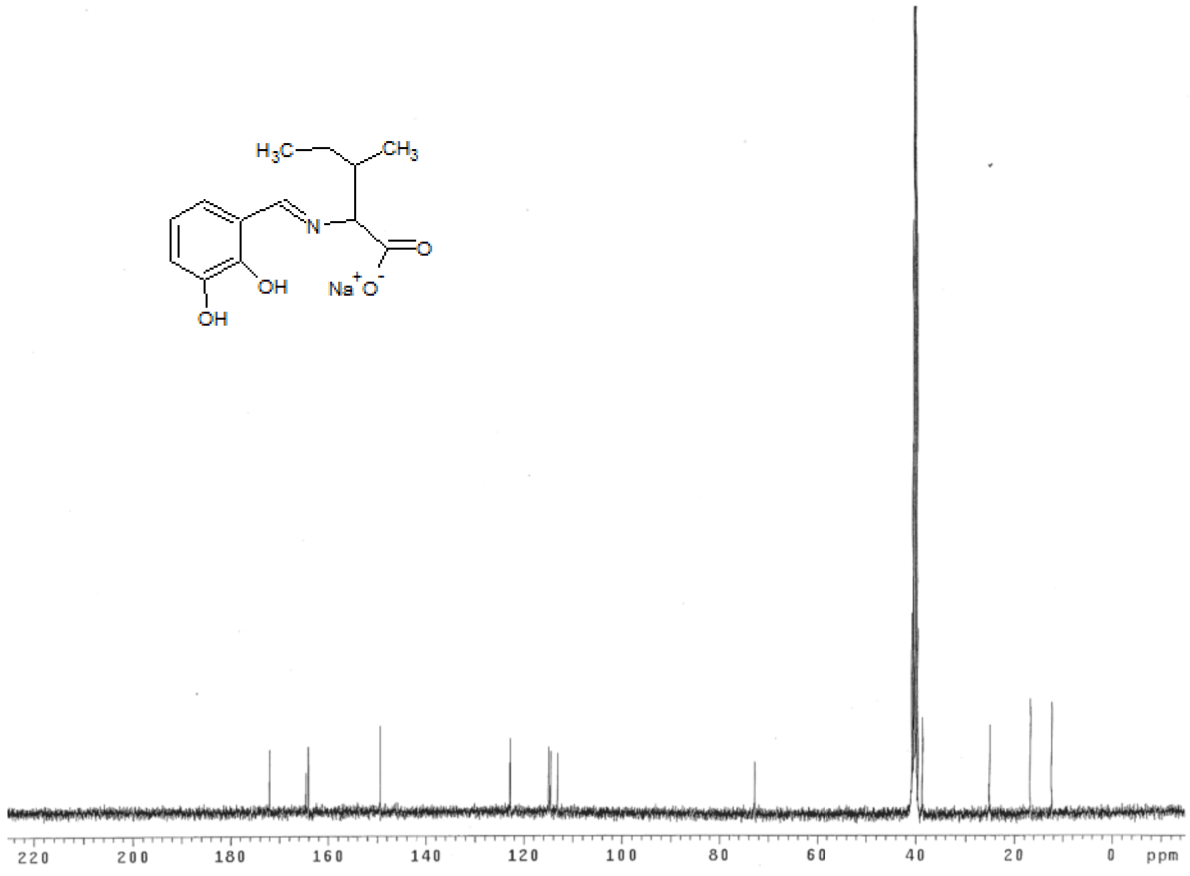


Figure-22 ^{13}C-NMR spectrum of Schiff base-2

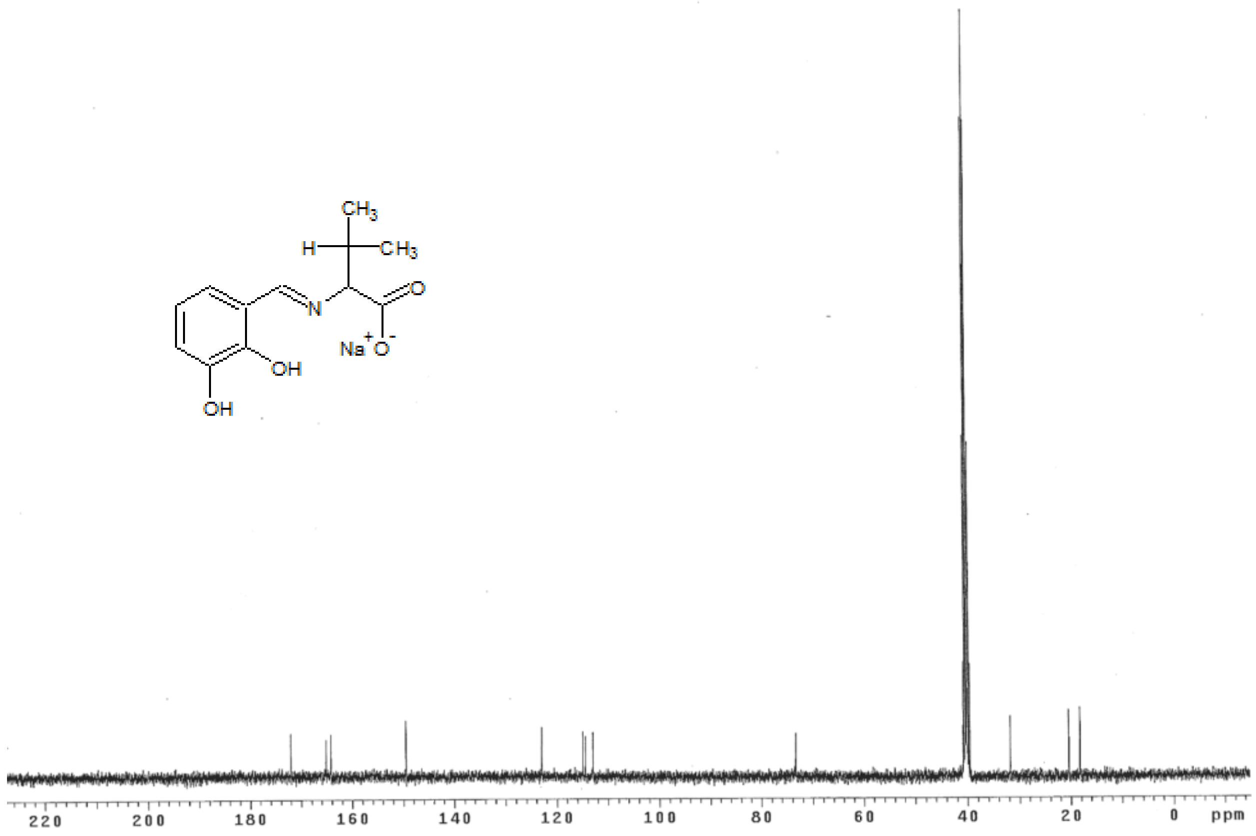


Figure-23 ^{13}C-NMR spectrum of Schiff base-3

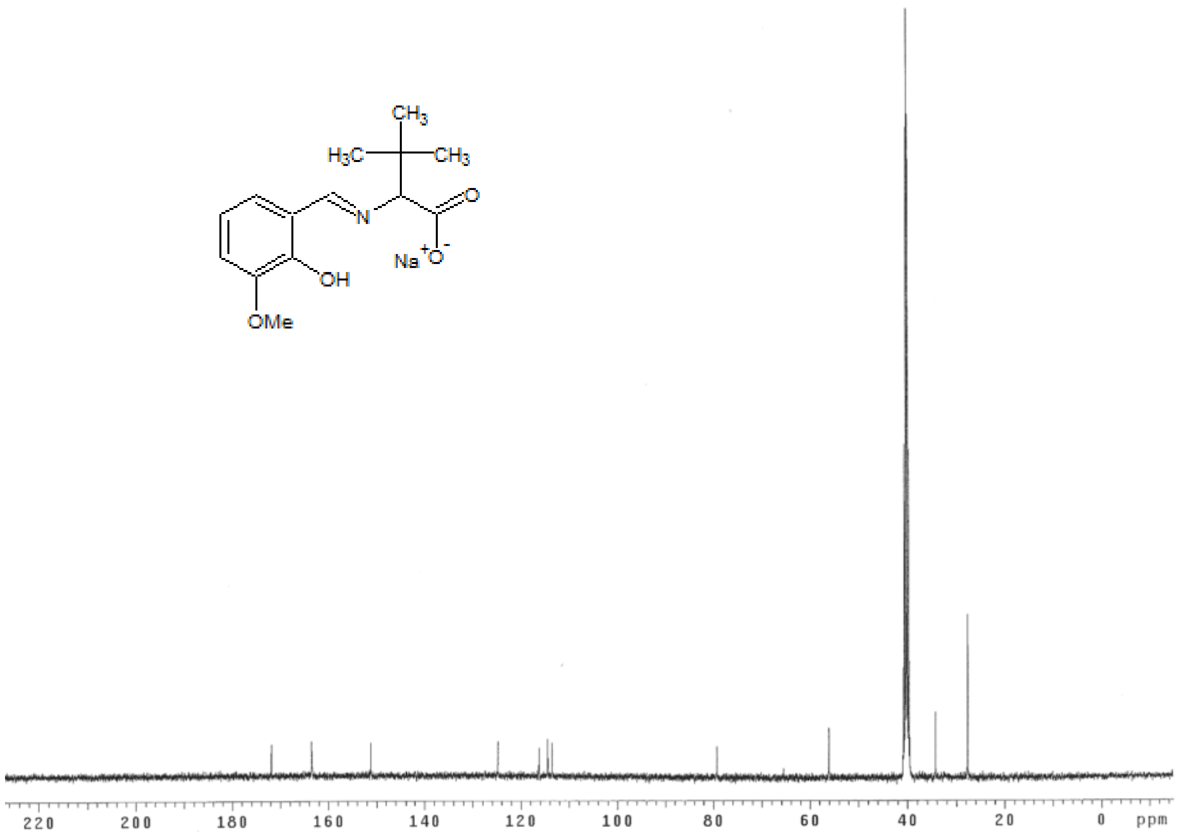


Figure-24 ^{13}C-NMR spectrum of Schiff base-4

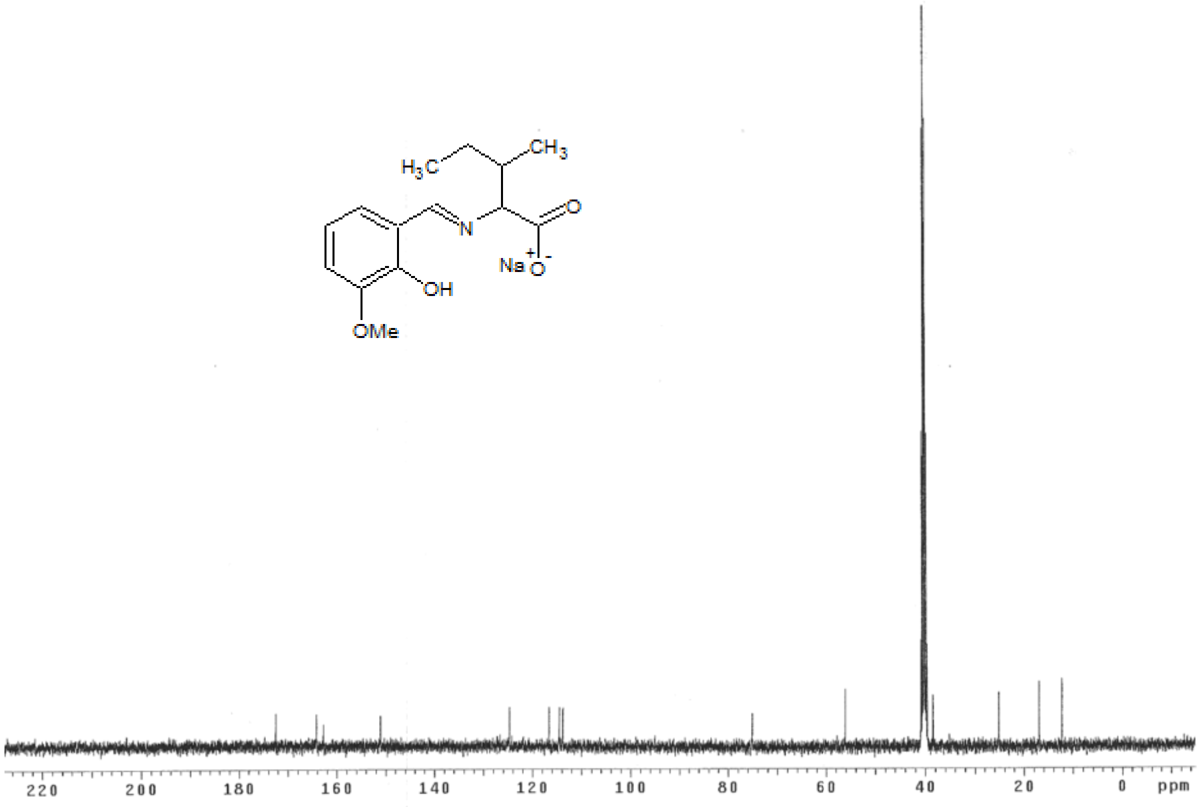


Figure-25 ^{13}C-NMR spectrum of Schiff base-5

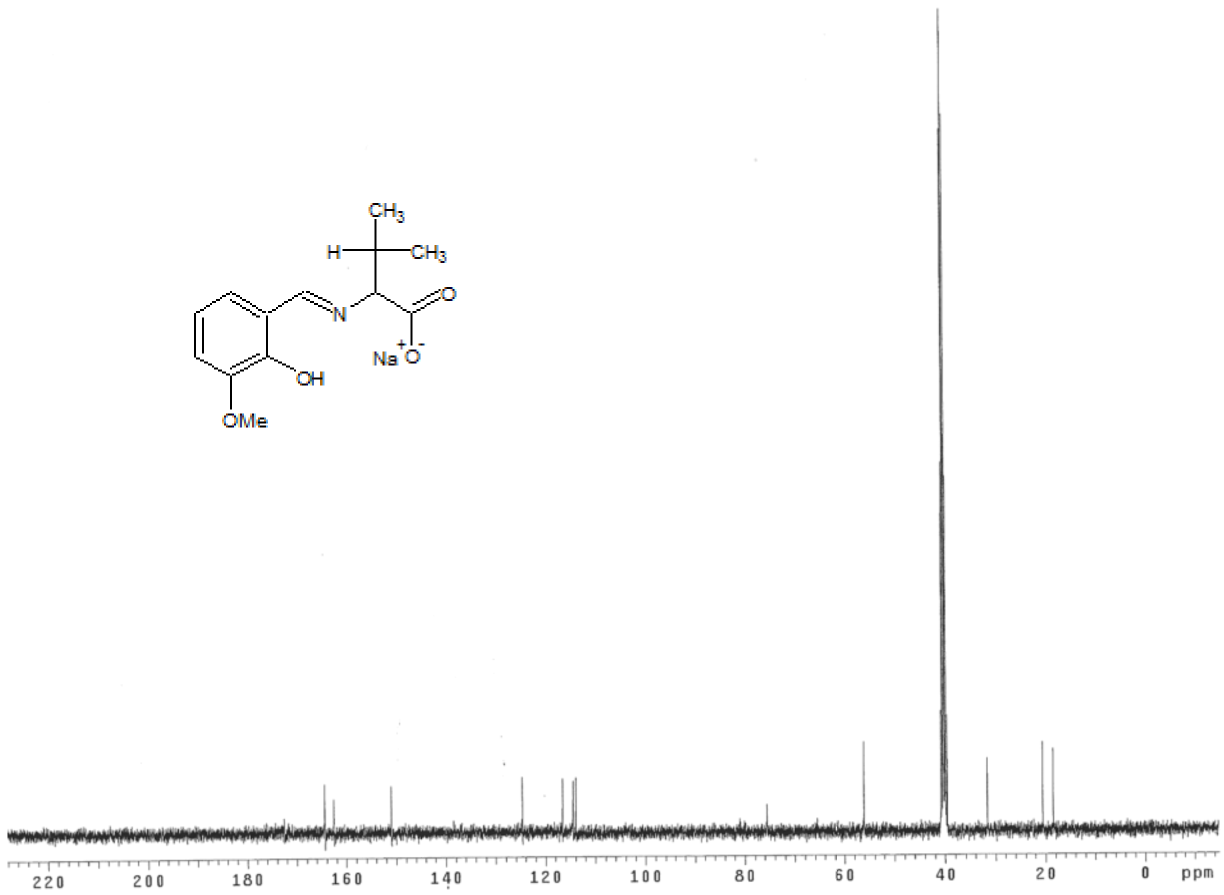


Figure-26 ^{13}C-NMR spectrum of Schiff base-6

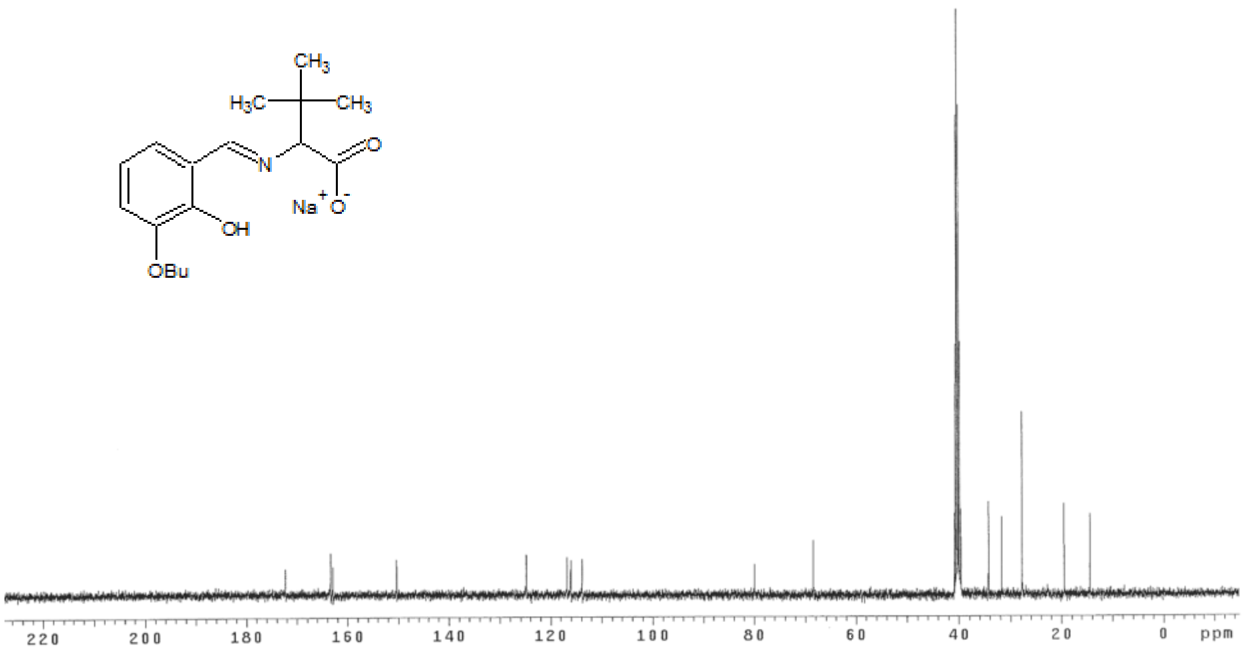


Figure-27 ^{13}C-NMR spectrum of Schiff base-7

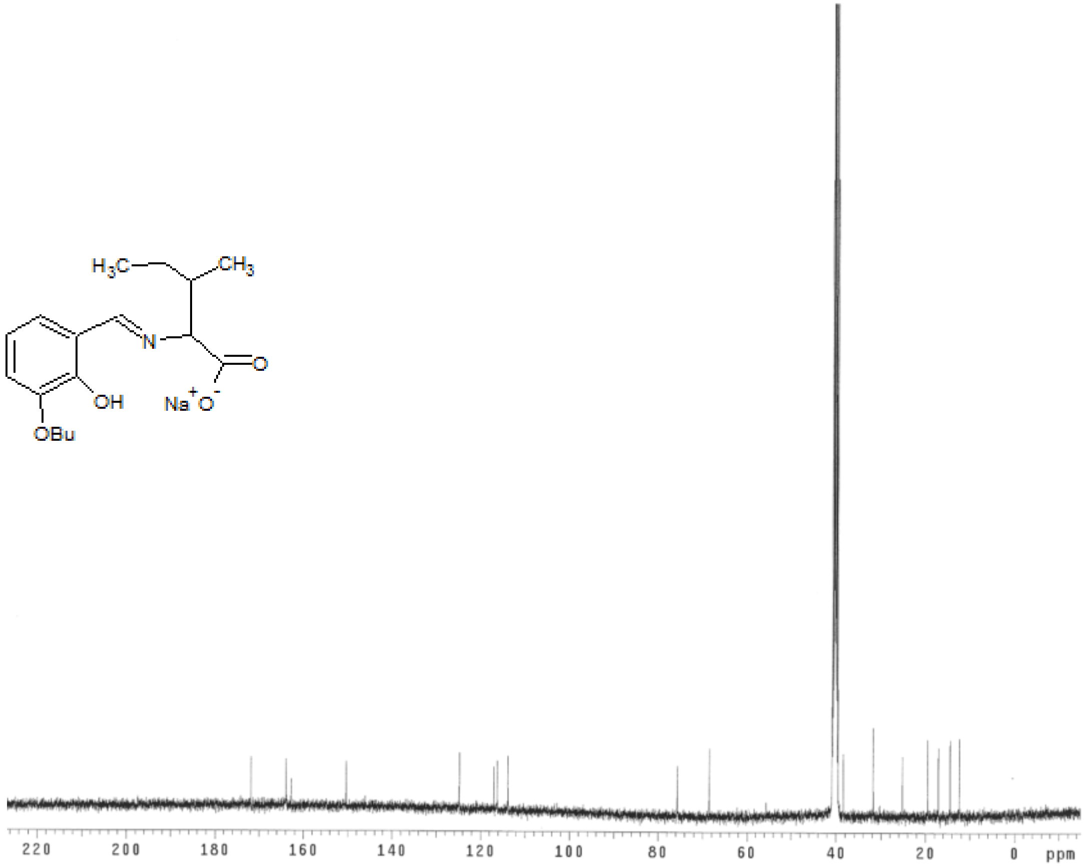


Figure-28 ^{13}C-NMR spectrum of Schiff base-8

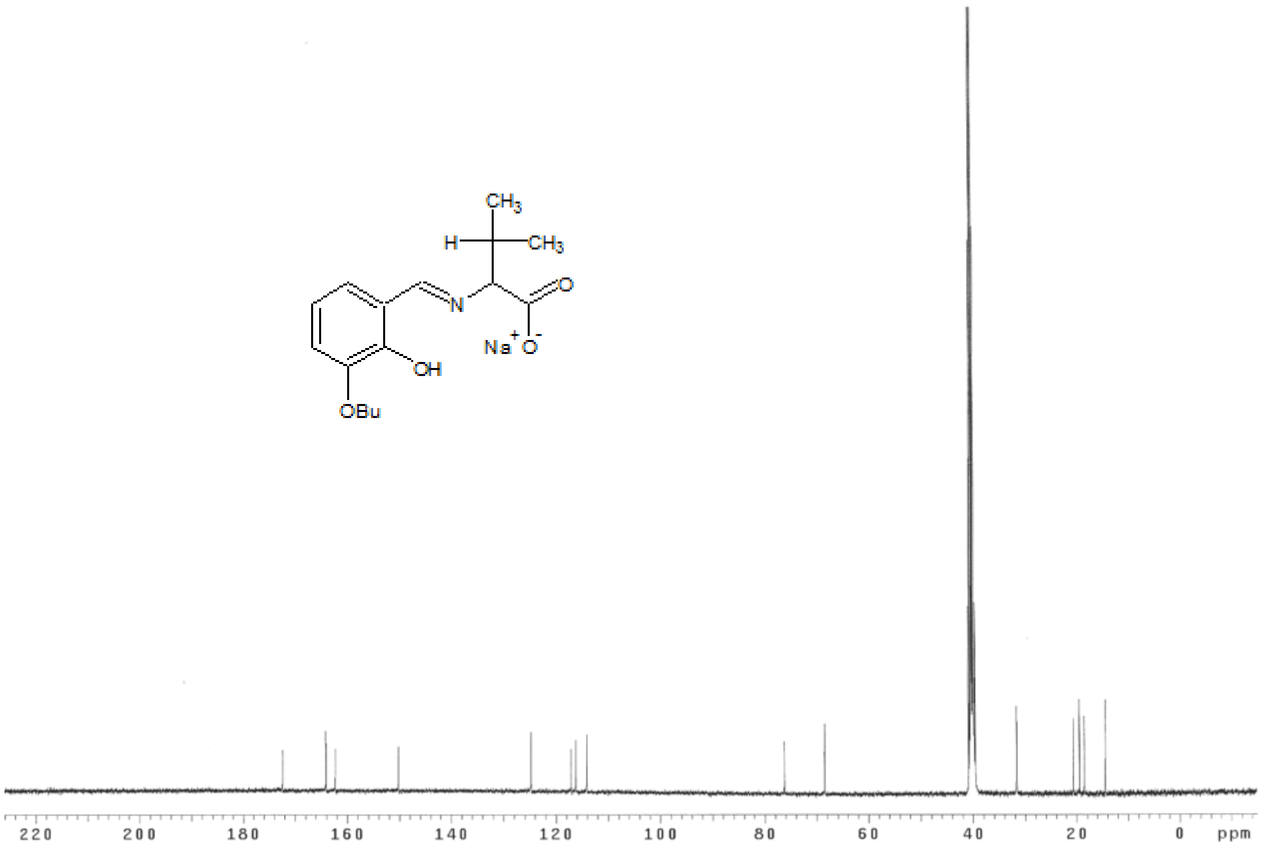


Figure-29 ^{13}C-NMR spectrum of Schiff base-9

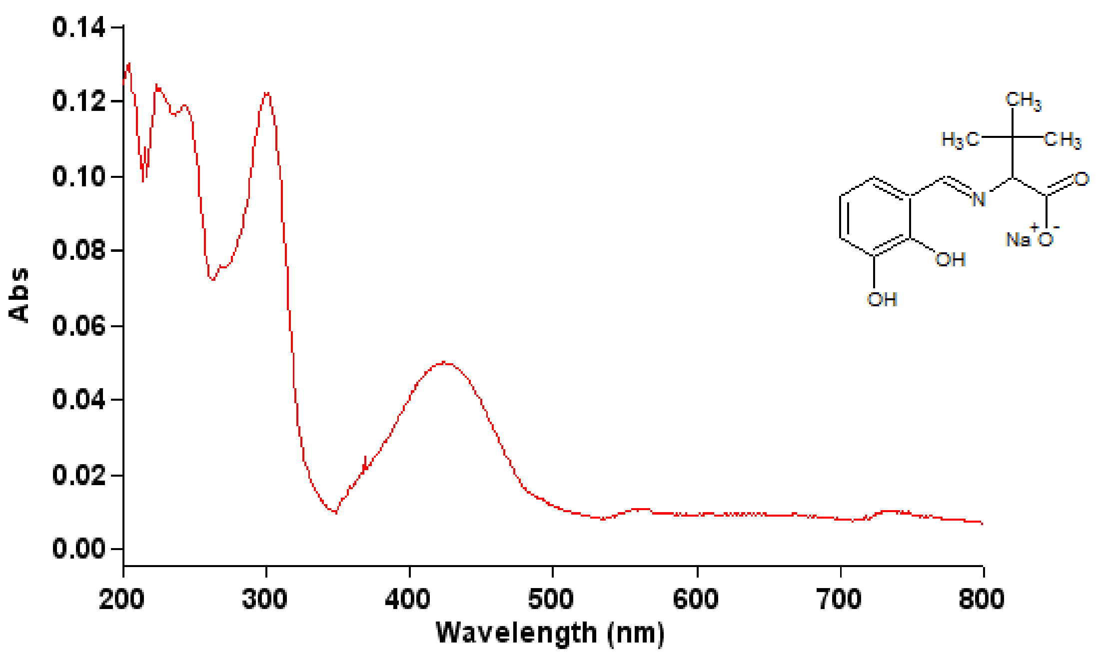


Figure-30 UV-Vis spectrum of Schiff base-1

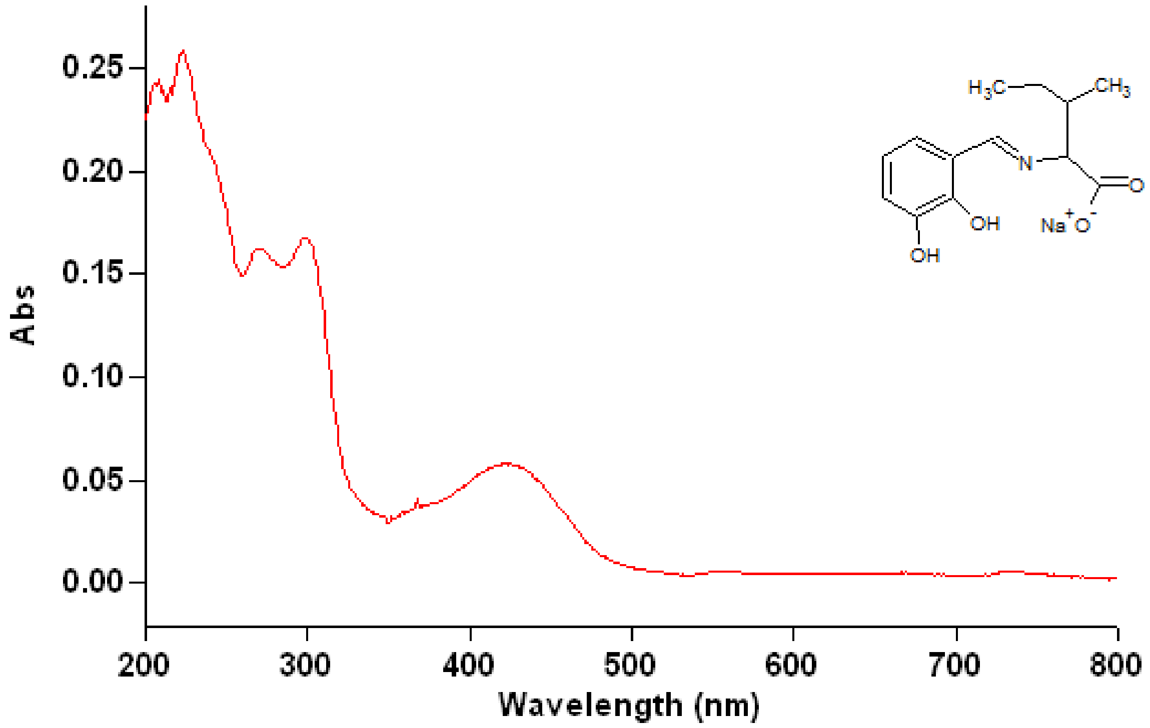


Figure-31 UV-Vis spectrum of Schiff base-2

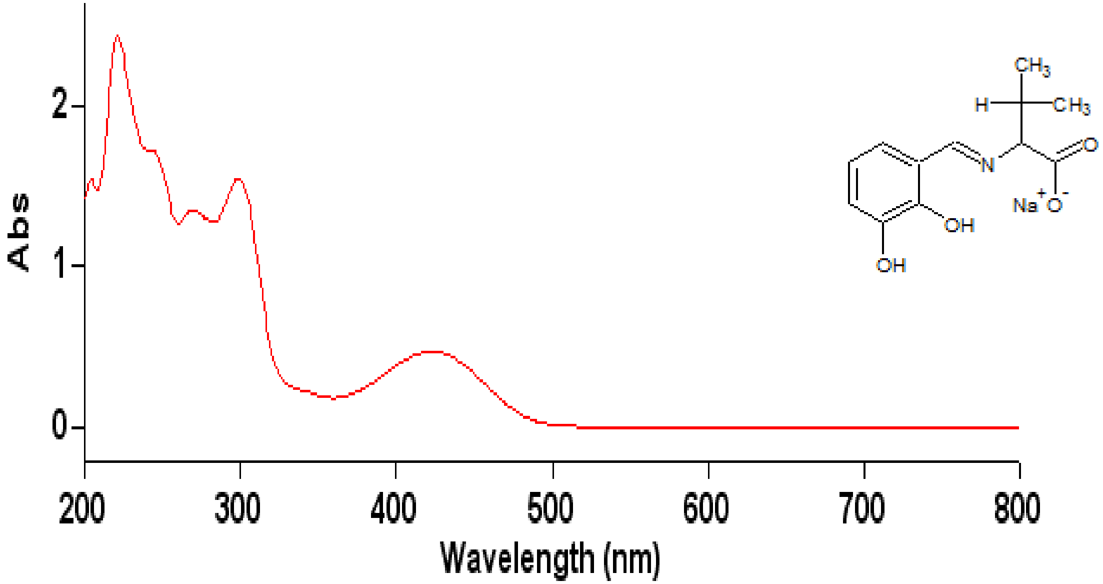


Figure-32 UV-Vis spectrum of Schiff base-3

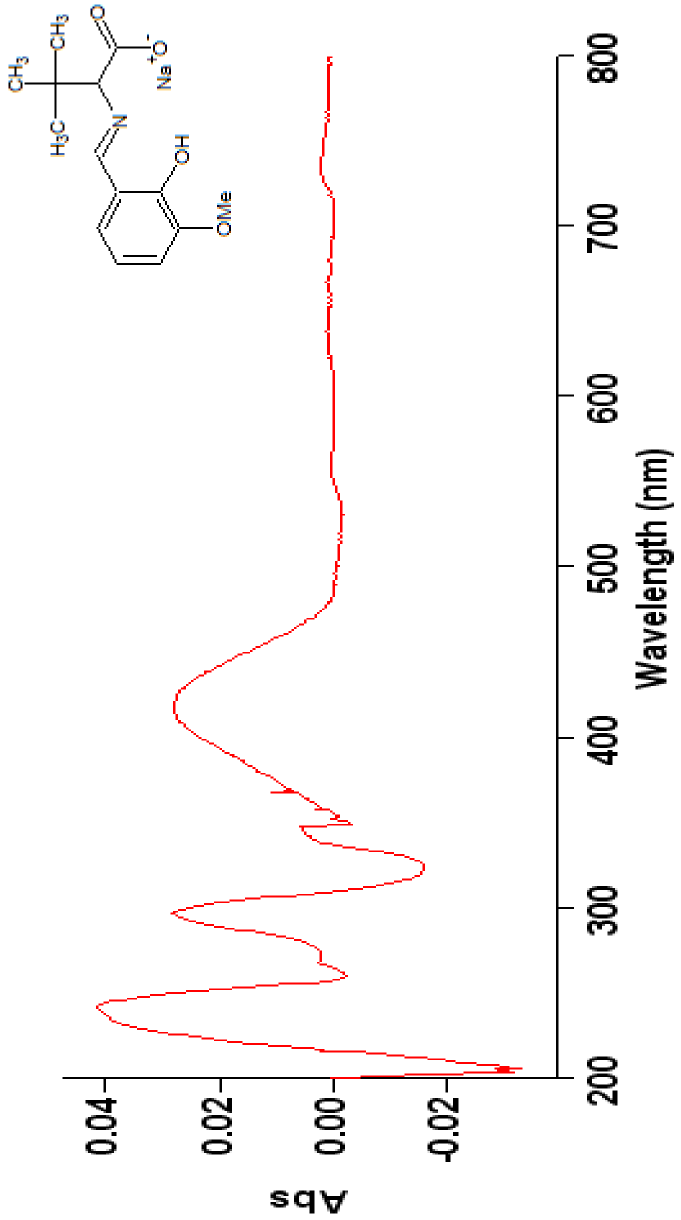
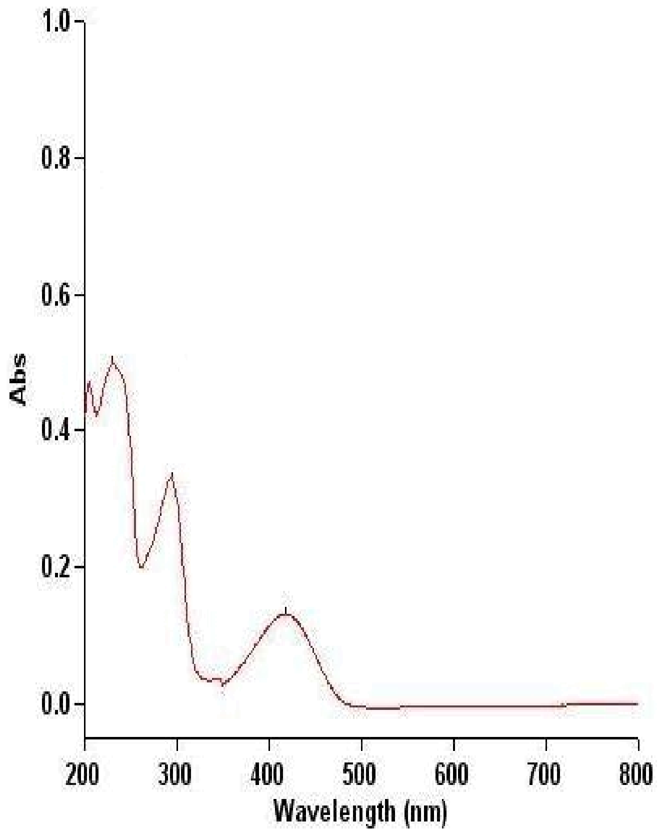


Figure-33 UV-Vis spectrum of Schiff base-4



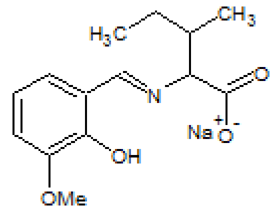


Figure-34 UV-Vis spectrum of Schiff base-5

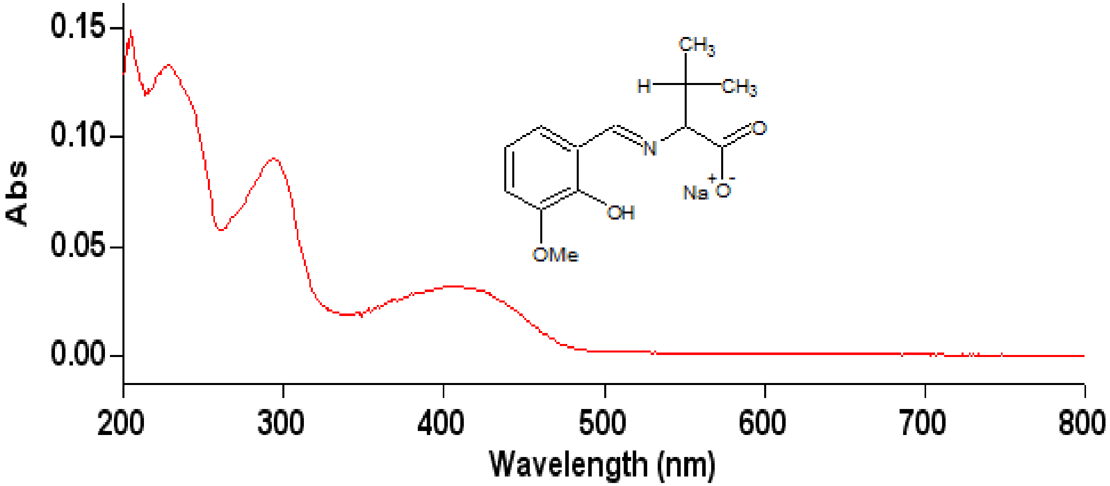


Figure-35 UV-Vis spectrum of Schiff base-6

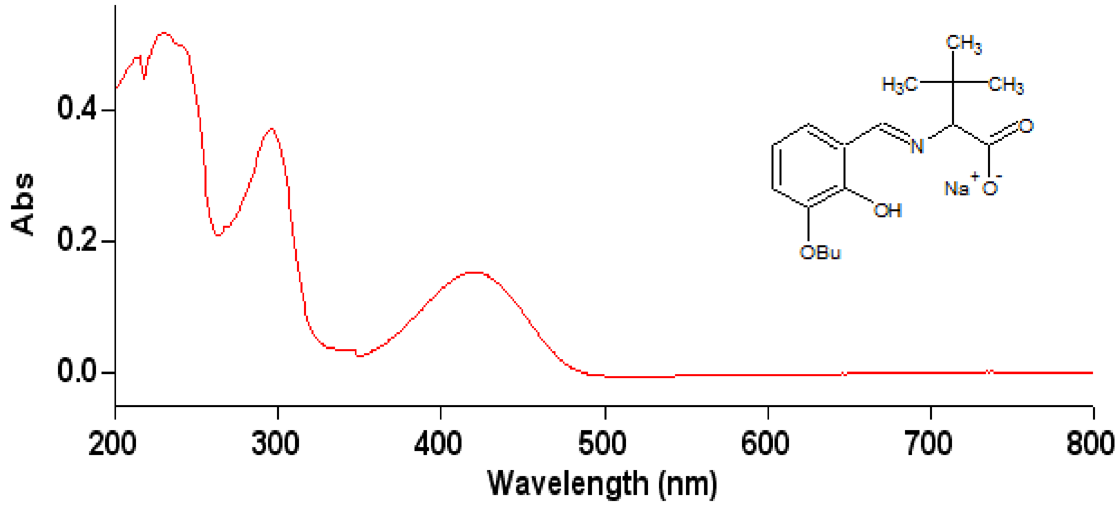


Figure-36 UV-Vis spectrum of Schiff base-7

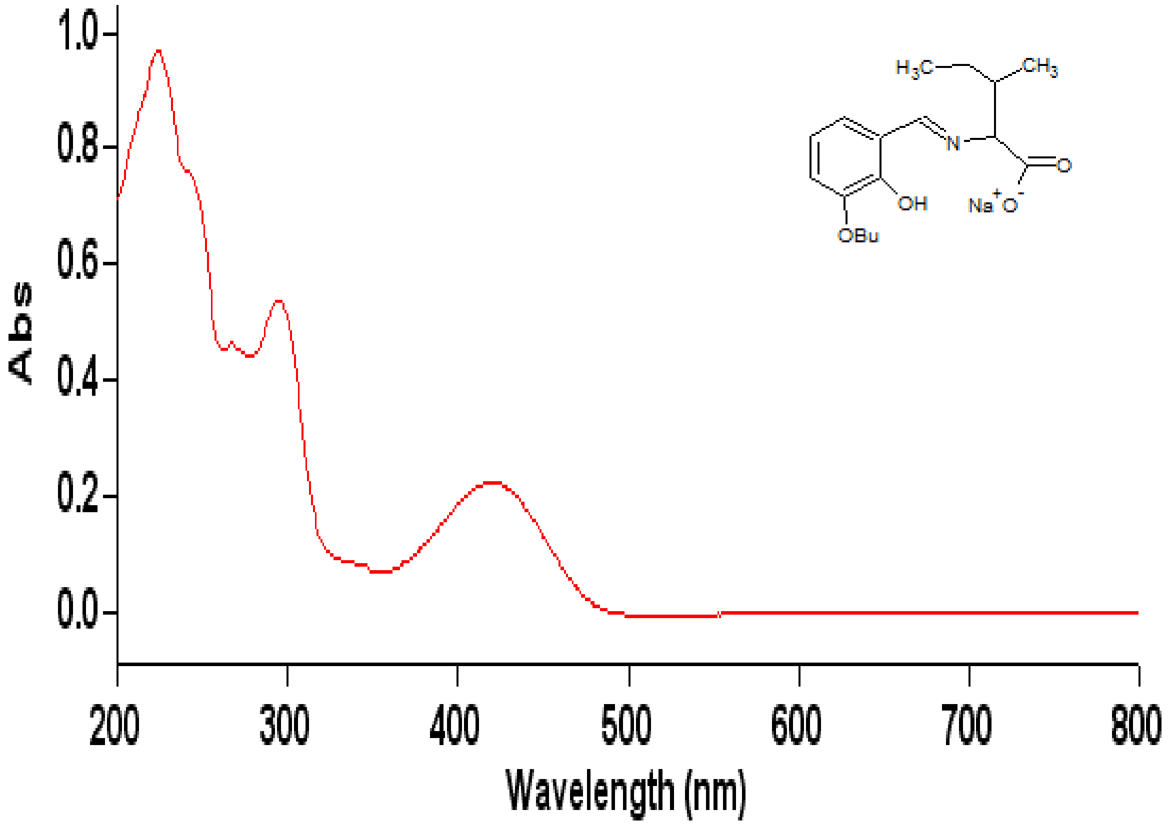
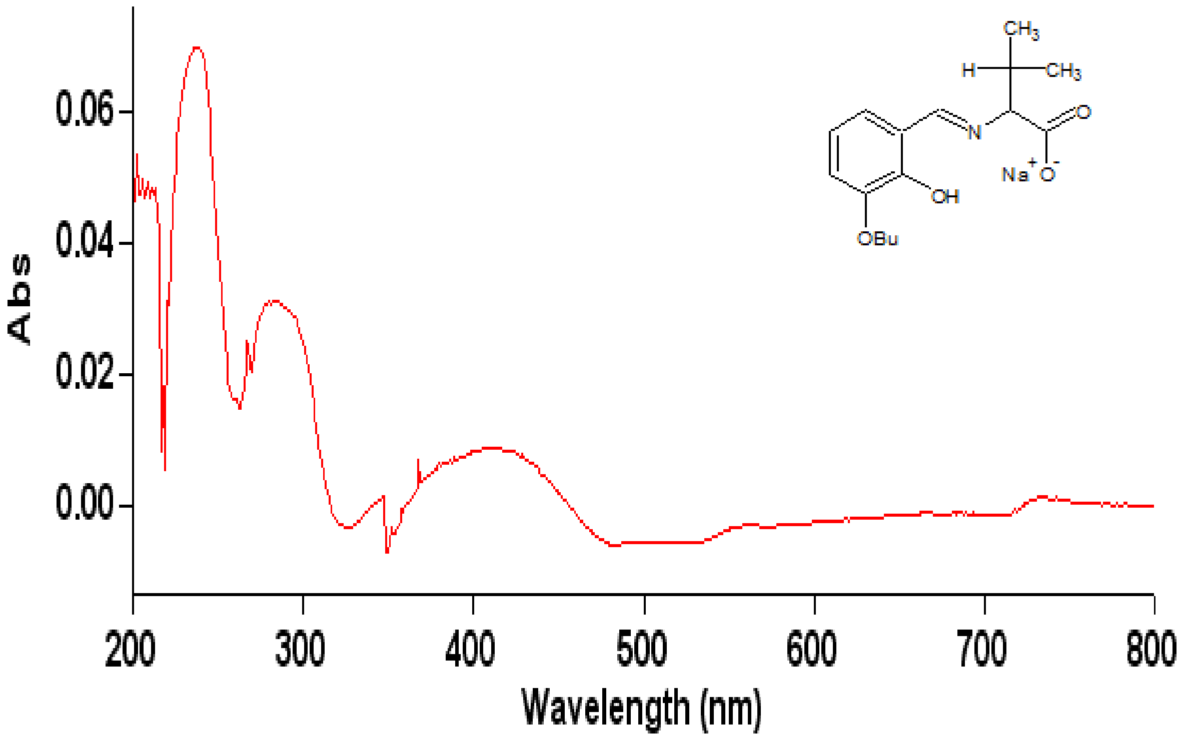


Figure-37 UV-Vis spectrum of Schiff base-8



Figure^{-38} UV^{-}Vis spectrum of Schiff ba^{se-9}

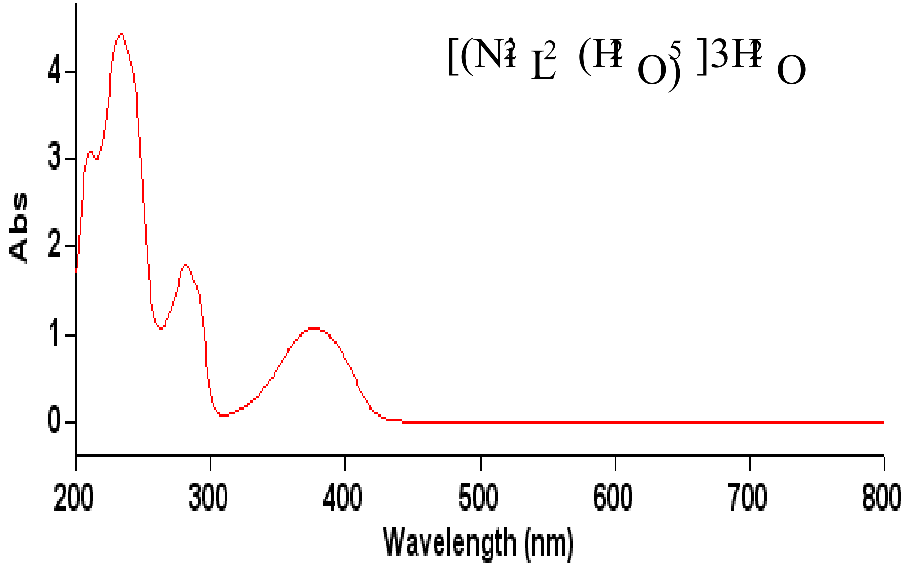


Figure-39 UV-Vis spectrum of Metal Complex-1

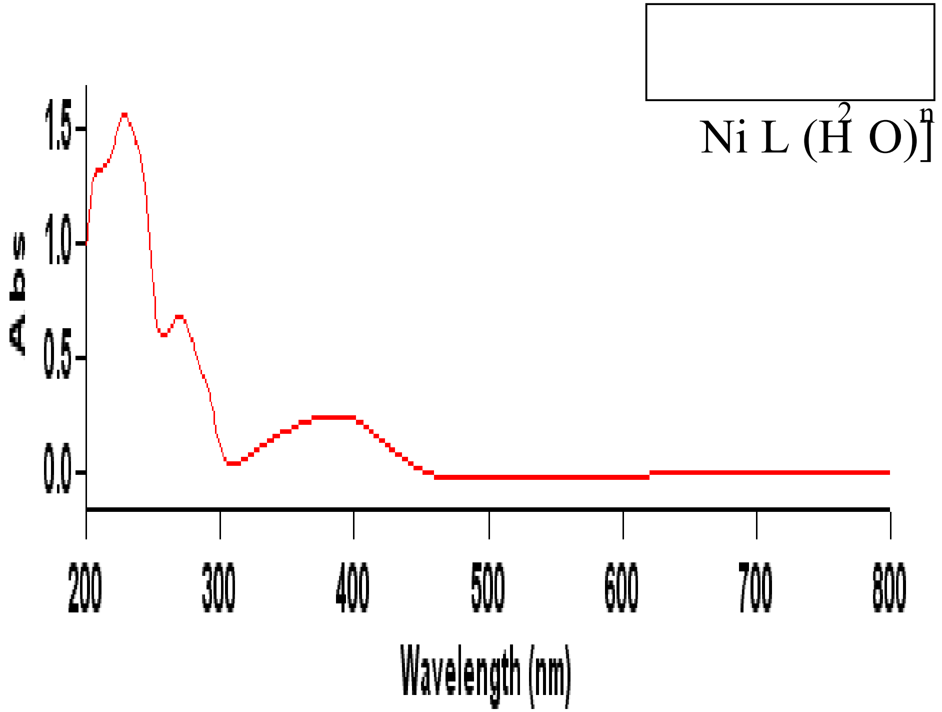


Figure-40 UV-Vis spectrum of Metal Complex-2

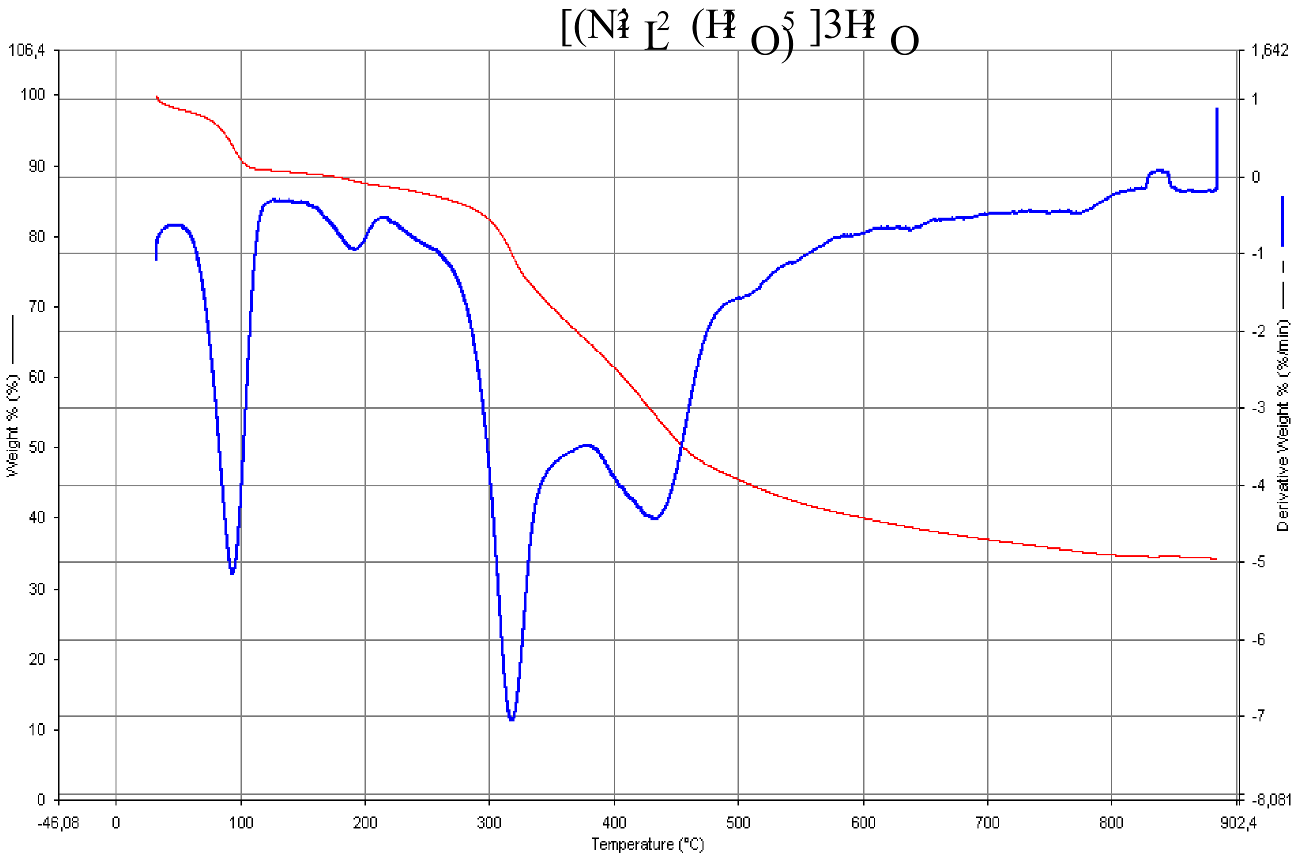


Figure-41 TGA data of Metal Complex-1

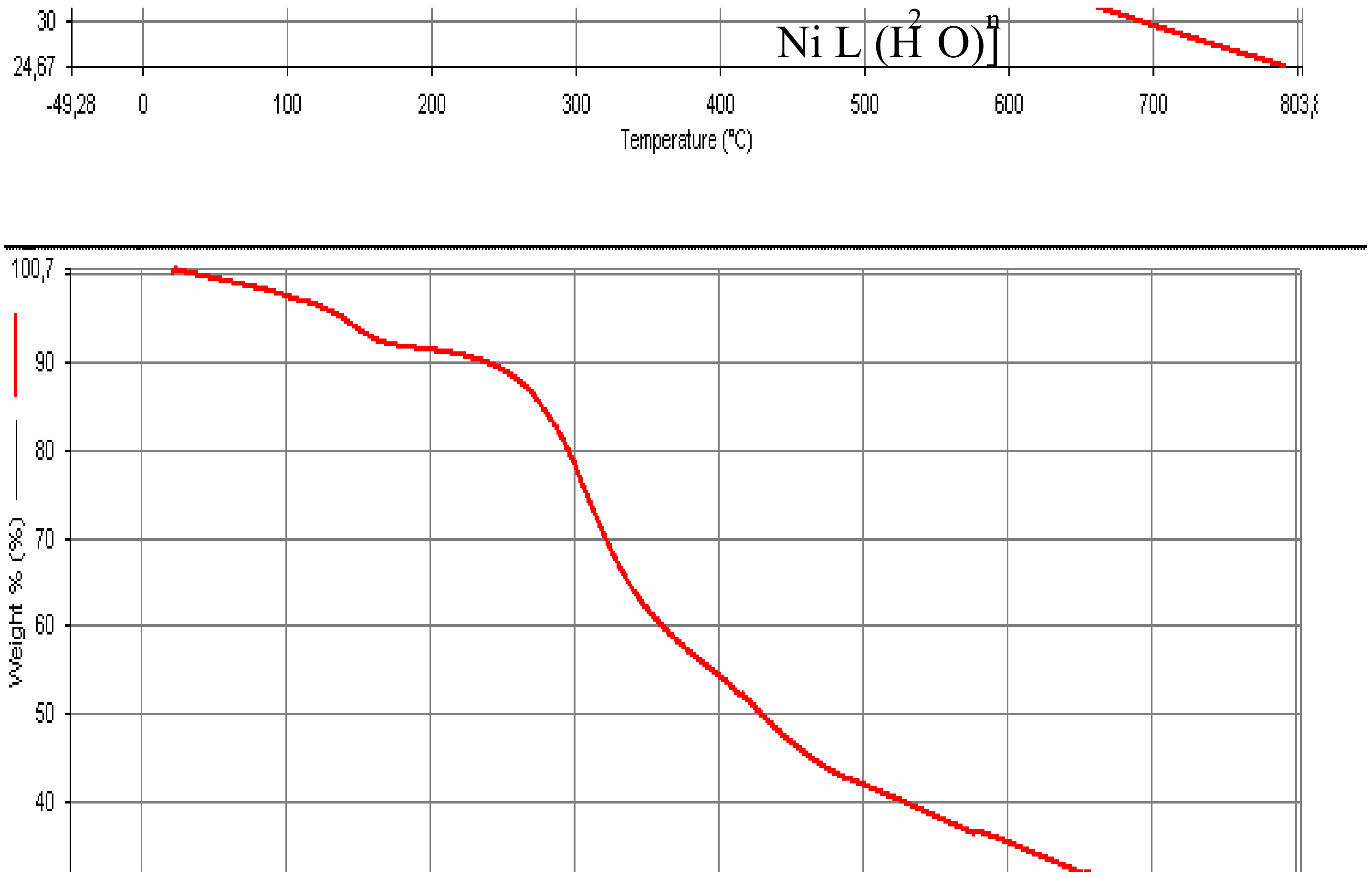


Figure-42 TGA data of Metal Complex-2

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