Republic of Iraq
Ministry of Higher education
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Al-Nahrain University
College of Science
Department of Chemistry

# Preparation of Aromatic Organic Compounds containing Hetero-atoms as Corrosion Inhibitors for Mild Steel in Acidic Solution

*A Thesis submitted to the College of Science of Al-Nahrain University in partial Fulfillment of the requirements for the Degree of Master in chemistry*

**By**

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**2014** **1435**

اقْرَأْ بِاسْمِ رَبِّكَ الَّذِي خَلَقَ * خَلَقَ الْإِنْسَانَ مِنْ عَلَقٍ * اقْرَأْ وَرَبُّكَ الْأَكْرَمُ * الَّذِي عَلَّمَ بِالْقَلَمِ * عَلَّمَ الْإِنْسَانَ مَا لَمْ يَعْلَم

صدق الله العظيم

سورة العلق(1-5)

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We, the examining committee, certify that we have read this thesis and Examined the student **Hanan Hussein Ali**, in content and that, in our opinion it is adequate as a thesis for the degree of Master of Science, in Chemistry.

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# الاهـــــــــــــــــــداء

إلى من بلغ الرسالة وأدى الأمانة .. ونصح الأمة .. إلى نبي الرحمة ونور العالمين..
سيدنا محمد صلى الله عليه وسلم

الى من أحمل اسمك بكل فخر...الى من أفتقدك منذ الصغر...الى من يرتعش قلبي لذكرك... الى
من أودعتني لله أهديك هذا البحث أبي

إلى ملاكي في الحياة .. إلى معنى الحب وإلى معنى الحنان والتفاني .. إلى بسمة الحياة وسر
الوجود إلى من كان دعائها سر نجاحي وحنانها بلسم جراحي إلى أغلى الحبايب
أمي الحبيبة

إلى سندي وقوتي وملاذي بعد الله .. إلى من آثروني على نفسهم .. إلى من علموني علم الحياة
إلى من أظهروا لي ما هو أجمل من الحياة

إخواتي

إلى من كانوا ملاذي وملجئي .. إلى من تذوقت معهم أجمل اللحظات .. إلى من سأفتقدهم ..
وأتمنى أن يفتقدوني .. إلى من جعلهم الله أخواتي بالله ..... و من أحببتهم بالله صديقاتي

سرى ورسل

إلى من يجمع بين سعادتي وحزني .. إلى من لم أعرفهم ولن يعرفوني ..إلى من أتمنى أن
أذكرهم إذا ذكروني .. إلى من أتمنى أن تبقى صورهم في عيوني

اليهم جميعا أهدي ثمرة جهدي هذا

*Hanan H. Ali*

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***Hanan H. Ali***

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# *List of Abbreviations*

| | |
|---|---|
| **FTIR** | Fourier Transform infrared |
| **$^{1}$H-NMR** | Proton Nuclear Magnetic Resonance |
| **$^{13}$C-NMR** | Carbon Nuclear Magnetic Resonance |
| **M.P.** | Melting point |
| **W** | Corrosion rate |
| **ΔM** | Mass Loss |
| **S** | Area |
| **T** | immersion period |
| **E%** | percentage inhibition efficiency |
| **θ** | degree of surface coverage |
| $K_{ads}$ | equilibrium constant of the adsorption/desorption process |
| $C$ | Inhibitor concentration (M) in the test solution. |
| $\Delta G^{o}_{ads}$ | standard free energy of adsorption |
| $E_{HOMO}$ | energy of the highest occupied molecular orbital |
| $E_{LUMO}$ | energy of the lowest unoccupied molecular orbital |
| **ΔE** | energy gap between LUMO and HOMO |
| **EtOH** | Ethanol |
| **E** | Two groups of higher priority are on opposite sides of the double bond, the bond is assigned the configuration E (from entgegen, the German word for "opposite"). |
| **Z** | Two groups of higher priority are on the same side of the double bond, the bond is assigned the configuration Z (from zusammen, the German word for "together"). |
| **PM3** | Parameterized Model Number 3 |
| **ASTM** | American Society for Testing and Materials |

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# *List of Schemes*

## Abstract

1-In this study, some organic compounds contain hetero-atoms were synthesized by several steps as following:

**First;** 4-phenylazoaniline **[1]** and 4-phenyl azophenol **[17]** were prepared in two steps:

- The treatment of a primary aromatic amine (aniline) with nitrous acid to form a diazonium salt.
- Coupling reaction of aromatic diazonium ion with activated aromatic ring (aniline, phenol).

**Second;** Organic compounds (1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-one **[2]**, (E)-3-(furan-2-yl) acrylaldehyde **[3]** were prepared by aldol condensation reaction between two molecules of an aldehyde or a ketone.

**Third;** Organic compounds **[4-11]** were prepared by reaction of 4-phenylazoaniline **[1]** in one step by a condensation reaction between the carbonyl group of aldehydes or ketone and the amino group to yield the following compounds:

**[4]**- N, N-dimethyl-4-[(E) - 4-{(E)-phenyldiazenyl} phenylimino] methyl aniline

**[5]**- (E)-N-(4-bromobenzylidene)-4-[(E)-phenyldiazenyl] aniline

**[6]**- (E)-N-(4-nitrobenzylidene)-4-[(E)-phenyldiazenyl] aniline

**[7]**- (Z)-N-(furan-2-ylmethylene)-4-[(E)-phenyldiazenyl] aniline

**[8]**- N-[(1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-ylidene]-4-[(E)-phenyldiazenyl] aniline

**[9]**- (E)-N-[(E)-3-phenylallylidene]-4-[(E)-phenyldiazenyl] aniline

**[10]**- (E)-5-[4-{(E)-phenyldiazenyl} phenylimino] pentane-1, 2, 3, 4-tetraol

**[11]**- (E)-N-[(E)-3-{furan-2-yl} allylidene]-4-[(E)-phenyldiazenyl] aniline

Organic compound (E)-4-(4-nitrobenzylideneimino) benzenthiol **[12]** was prepared in one step by a condensation reaction between carbonyl group of *p*-nitrobenzaldehyde and aromatic primary amino group of *p*-aminothiophenol.

**Fourth;** Organic compounds **[13-16]** were prepared by reaction of **(**E)-4-(4-nitrobenzylideneimino) benzenthiol **[12]** in one step by an alkylation reaction between (Ethyl Bromide, n-propyl Bromide, Benzyl Chloride or 1, 2-Dichloroethane) and thiol group to yield following compounds:

**[13]**- (E)-4-(ethylthio)-N-(4-nitrobenzylidene) aniline

**[14]**- (E)-N-(4-nitrobenzylidene)-4-(propylthio) aniline

**[15]**- (E)-4-(benzylthio)-N-(4-nitrobenzylidene) aniline

**[16]**- (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline

Organic compounds **[18-20]** were prepared by reaction of (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline **[16]** with (**(**E)-4-(4-nitrobenzylideneimino) benzenthiol **[12]**, 4-phenyl azophenol **[17]** or *p*-aminopyridine) to yield the following compounds:

**[18]**- (NE, N'E)-4, 4'-[ethane-1, 2-diylbis (sulfanediyl)] bis [N-(4-nitrobenzylidene) aniline]

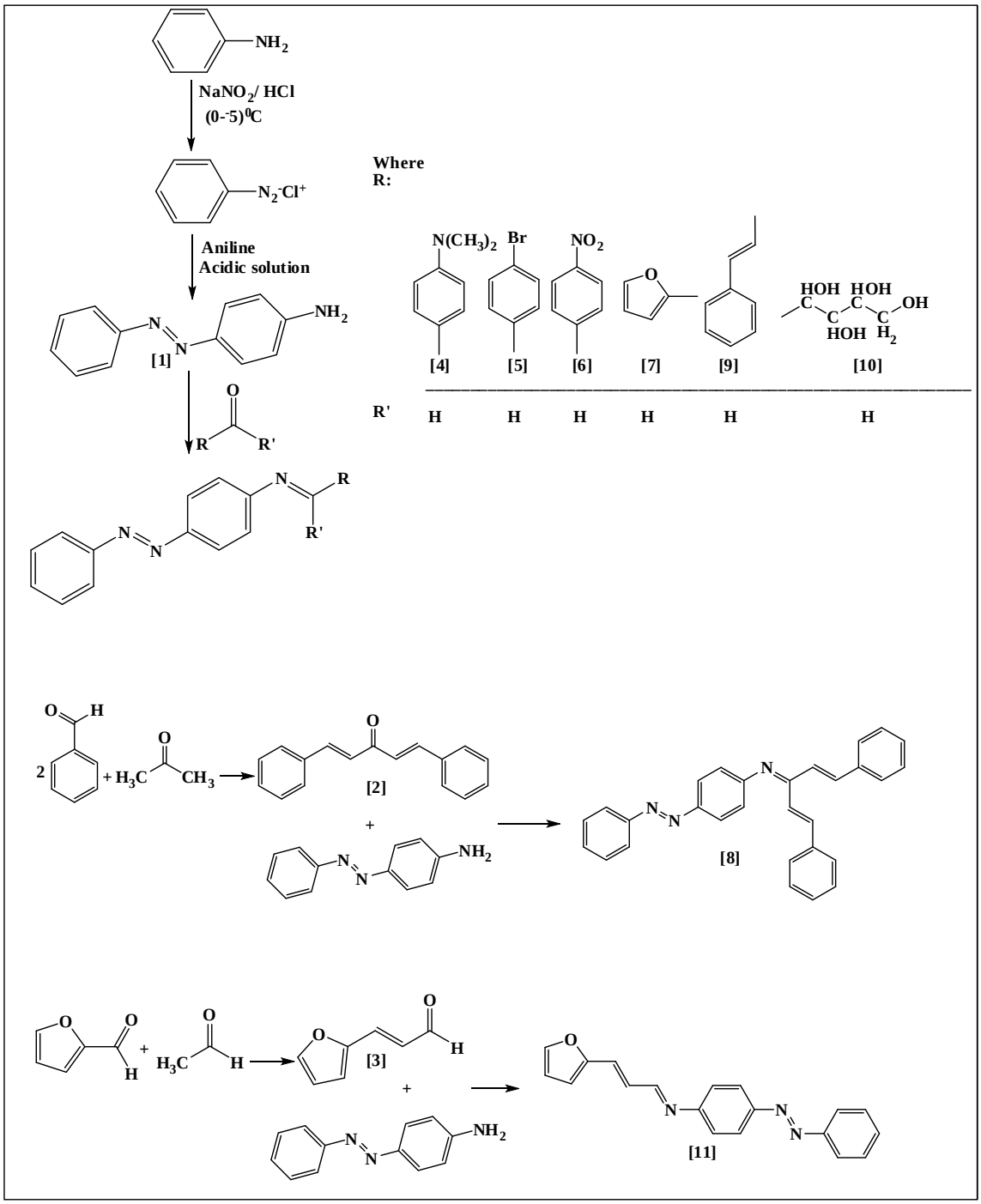
**[19]**- (E)-N-(4-nitrobenzylidene)-4-[2-{4-(Z)-phenyldiazenyl} phenoxy] ethylthio aniline

**[20]**- (E)-N-[2-{4-(4-nitrobenzylideneamino) phenylthio} ethyl] -4-amine pyridin

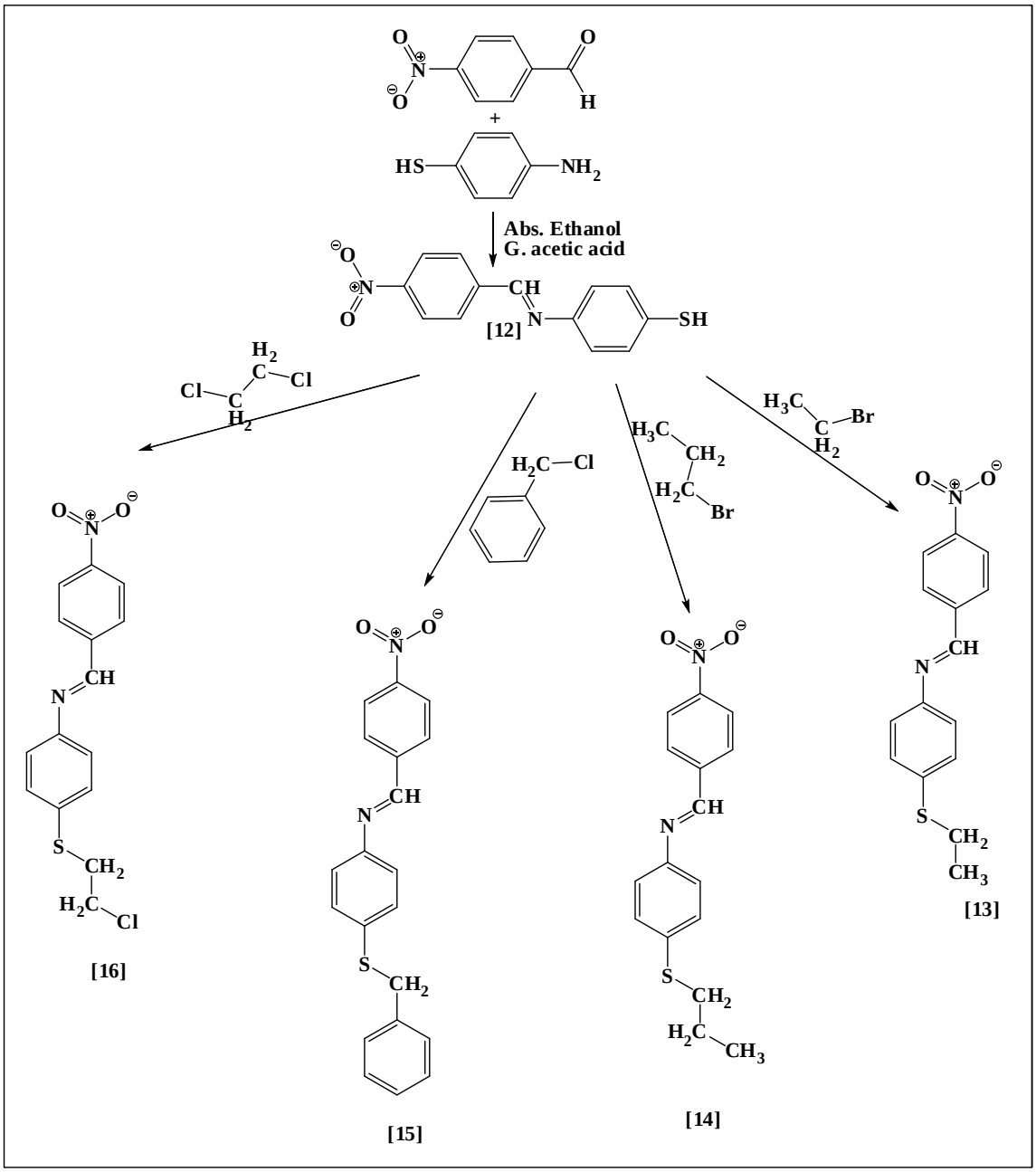
2-The prepared compounds were identified by melting points, FT-IR, UV-visb., $^{1}$H-NMR and $^{13}$C-NMR spectroscopic techniques.

3-The prepared compounds **[4-16]** and **[18-20]** were used as corrosion inhibitors for mild steel in 1M $H_2SO_4$ at 30°C. Weight loss measurement was regarded as evaluation method to test the inhibition efficiency of the above compounds.

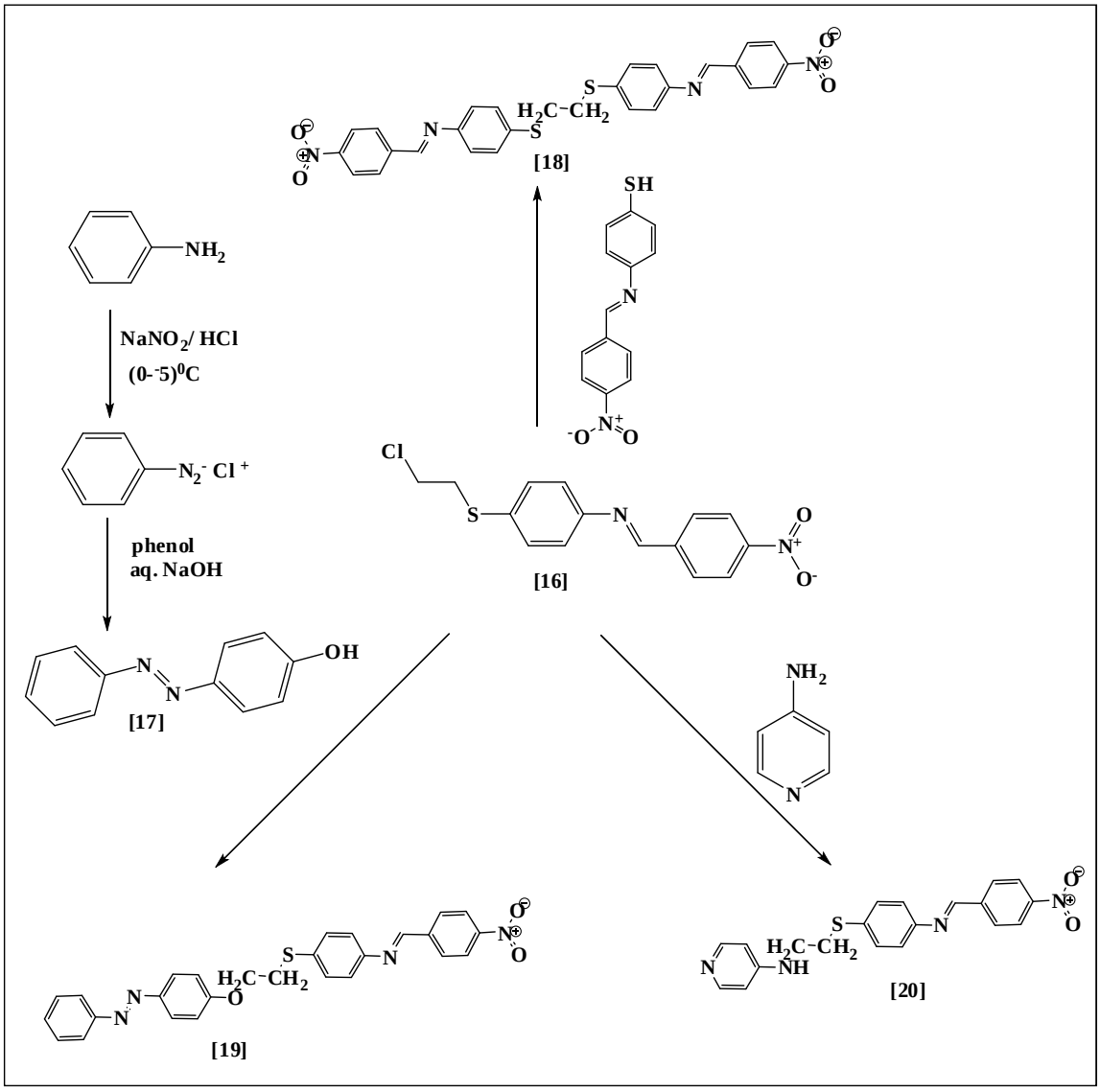
4-Semi-empirical molecular quantum calculations within the PM3 method as implemented in Hyperchem package were used to study the relationship between molecular structure and inhibition efficiency. The compound **[8]** showed lowest energy gap that gives good inhibition efficiency. Synthesis of organic compound **[1-20]** showed in these schemes




Scheme 1: The chemical steps for the synthesis of compounds **[1-11]**




Scheme 2: The chemical steps for the synthesis of compounds **[12-16]**




Scheme 3: The chemical steps for the synthesis of compounds **[17-20]**

# CHAPTER ONE

# INTRODUCTION

## 1. Introduction

### 1.1. Organic synthesis

The term synthesis means in Greek "put together". Synthetic organic chemistry is the "art" of building-up complex molecular structures of organic compounds putting together smaller easily accessible (commercially available) compounds [(1)]. Sugar, gasoline, plastics, aspirin, paper, milk, apples, meat and most of the substances important to life and life styles have one thing common: they all contain the element Carbon (C). Carbon is such a unique and important element that an entire branch of chemistry studying carbon and its compounds. Several millions of such compounds are currently known as hydrocarbons (compounds of carbon and hydrogen only) and the derivatives of hydrocarbons, (compounds containing C, H and O, N, S, P, halogen etc.) [(2)].

The first organic synthesis is the synthesis of urea performed by Wöhler in 1828 and that of acetic acid performed by Kolbe in 1845. From around 1900, a great number of synthetic efforts have been made, and more complex structure such as Camphor (Komppa 1903 and Perkin, 1904) or the complex structure of haemin ( Fisher, 1929) have been produced (see Figure 1-1) [(3)].

During the last two decades, organic chemists were able to accomplish the synthesis of entirely new types of complex, uses in drugs, flavors, nutraceuticals, and new materials. Even though the quest for the synthesis of molecules with a steadily increasing size and complexity has not found its end, [(4)] the challenge in organic synthesis today lies less in the synthesis of monstrous natural products, than in the development of efficient, selective and environmentally benign transformations. Despite the immense number of organic transformations that have been developed since the days of

Wöhler, organic synthesis is still in its early stages of development, compared to the powerful and selective synthetic tools available in nature [5].

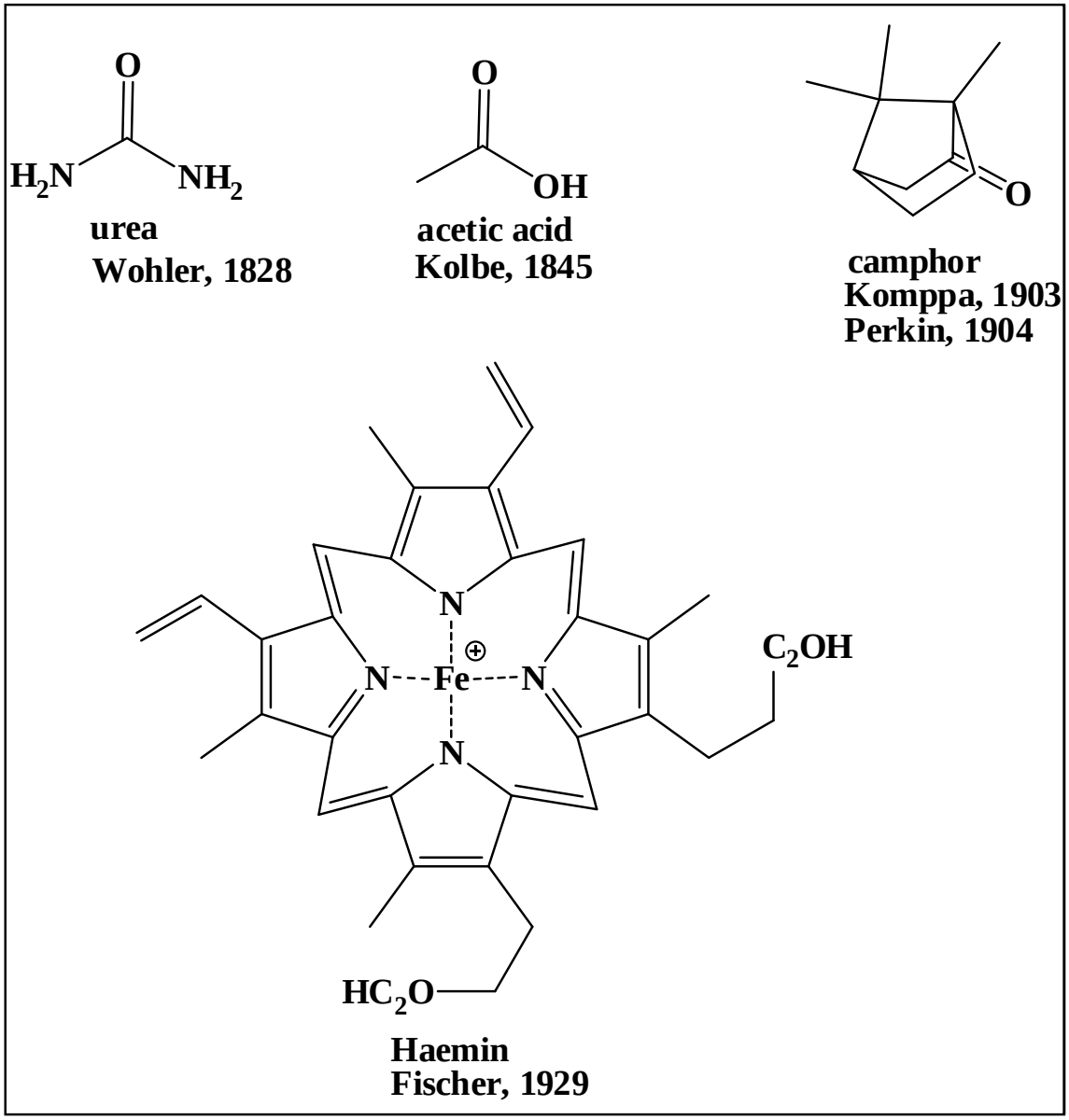



Figure 1-1: Examples of natural products synthesized in ancient times

### 1.2. Azo dyes

Azo dyes are compounds that contain azo group (-N=N-) linked to methine or aromatic $sp^2$-hybridized C-atom, colorants composed of multiple azo

groups are termed mono- , bis-, tris-, etc. of azo dyes [6]. The azo group is normally attached to two aromatic groups. The resultant dyes exist in the Trans configuration which is more stable than cis form [7]. Examples of azo dyes show in (Figure 1-2).

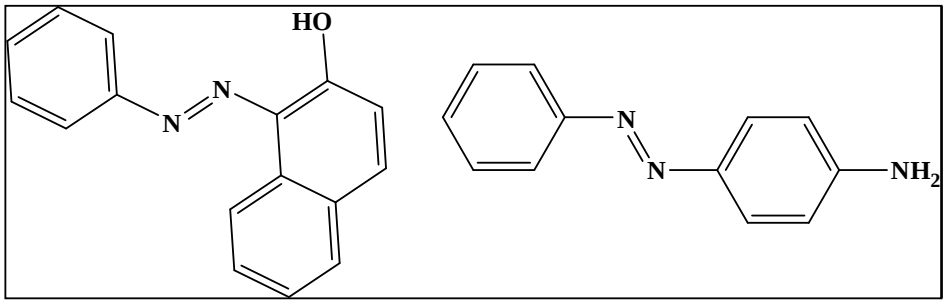



Figure 1-2: Examples of azo dyes

### 1.2.1. Preparation of azo dyes

Azo dyes are performed in two- stage reaction sequence: diazotization and azo coupling (see Figure 1-3).

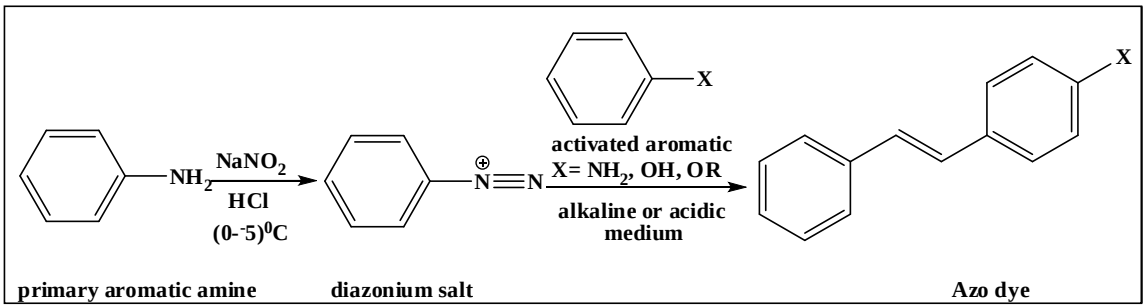



Figure 1-3: Synthesis of azo dyes

### 1.2.1. 1. Diazotization

The first stage of azo dyes synthesis involves the treatment of a primary aromatic amine ($ArNH_2$), which may be alicyclic or heterocyclic, with

nitrous acid to form a diazonium salt ($ArN_2^+Cl^-$)[8]. Nitrous acid ($HNO_2$) is a rather unstable substance that decomposes relatively easily by dissociation into oxides of nitrogen, so the reaction requires a mineral acid where the choice for many diazotizations is hydrochloric acid. This is because the presence of the chloride ion can exert a catalytic effect on the reaction under appropriate conditions thus enhancing the reaction rate [9].

A convenient and general one-step preparation of aromatic and some heterocyclic iodides in good yields includes a sequential diazotization-iodination of aromatic amines with KI, $NaNO_2$, and *p*-TsOH in acetonitrile at room temperature [10].

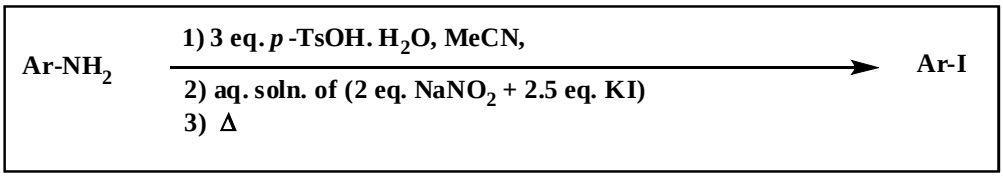



Figure 1-4: Iodination of Aromatic and Heterocyclic Compounds

A new, simple, and effective method for the diazotization of a wide range of arylamines using a polymer-supported diazotization agent in the presence of *p*-toluenesulfonic acid gives various pure arenediazonium tosylates with unusual high stabilities. As a result, these salts are useful and versatile substrates for subsequent transformations, such as halogenation and Heck-type reactions [11].

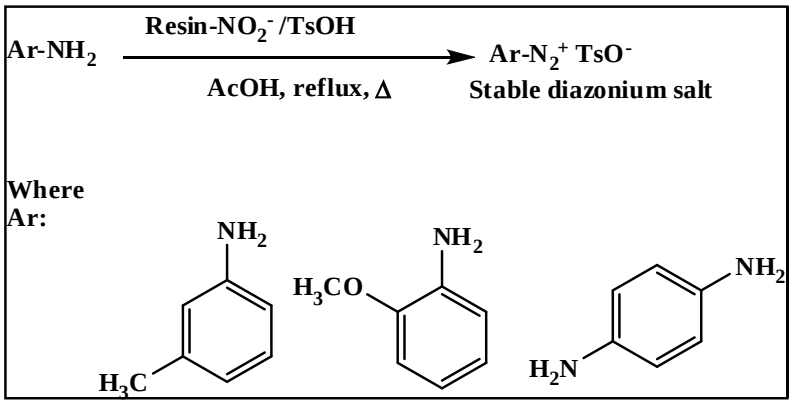



Figure 1-5: Preparation of unusually Stable and Pure Arenediazonium Tosylates

### 1.2.1. 2. Azo coupling

The second stage of azo dyes synthesis involves aromatic diazonium ion act as electrophiles in coupling reaction with activated aromatic such as aniline and phenols. Usually, the substitution occurs at the Para position; if this position is already occupied, the ortho position is favored [(12)].Also the position of coupling depends upon the nature of the condition; these in an alkaline solution, the coupling will be directed by the –OH group and in an acidic medium, the reaction will take place with respect to amino group. Electron attacking groups in the ring of the diazonium salt facilitate coupling, while the presence of electron donating groups (amino, hydroxyl etc.), especially in the Meta position of original amino or phenolic compound, also facilitates the coupling reaction. Diazonium salt with $–NO_2$ or $SO_3H$ groups, particularly in the Para position, are stronger electrophiles. Such a group facilitates coupling, because of the fact that it increases the positive charge on the nitrogen atoms. An alkyl or alkoxyl group in the Para position acts in a reverse manner. A halogen or a nitro group in the ring of

aromatic amine or phenol lowers the electron density in the ring. Hence such compounds do not undergo coupling with diazonium salt [13].

Unsymmetrical and symmetrical bis (hetaryl) azo dyes were prepared by diazotisation-coupling and oxidation reactions in moderate yields. Their absorption maxima were observed in the range of 427-631 nm, being more bathochromic than the corresponding non-hetarylazo derivatives [14].

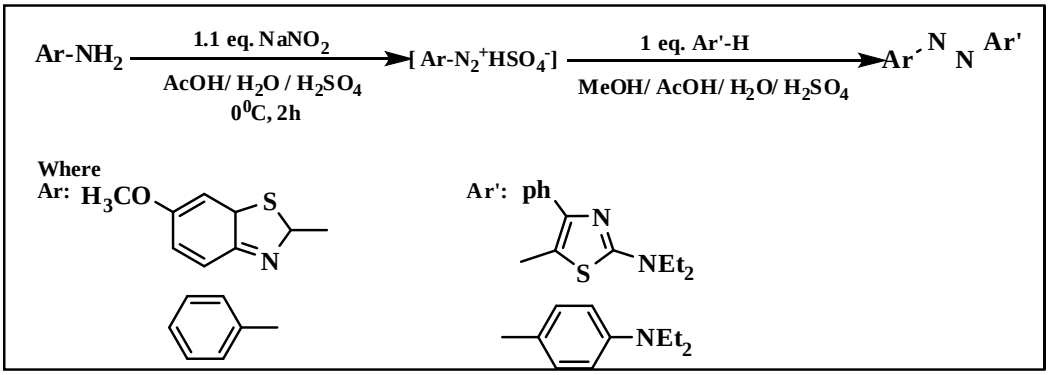



Figure 1-6: Synthesis of bis (hetaryl) azo dyes

Easily obtainable cyclic enaminones (piperidin-2-ylidenealkanones) can be transformed into substituted bicyclic pyridazinium tetrafluoroborates upon treatment with corresponding diazonium salts. The transformation can be performed either in a one-pot way or in a two-step process with the isolation of single azo-coupled enaminone as the intermediate [15].

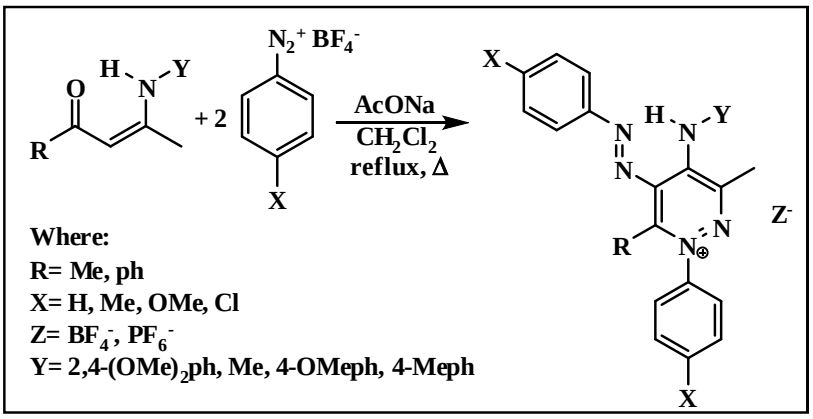



Figure 1-7: Synthesis of 1-arylpyridazinium salts

### 1. 2.2. Colour of azo dyes

Azo dyes produce colour because they selectively reflect, transmit or scatter light in the visible spectrum (see Table 1-1), contain one or more chromophoric groups (i.e., azo bonds), have a conjugated system of electrons and exhibit stability due to resonance of electrons [16]. In addition to containing this chromophoric system, azo colourants may also possess functional groups known as Auxochrome (i.e., "colour helpers"), such as carboxylic acid, sulfonic acid, amino groups and hydroxyl groups (see Figure 1-8). While these are not responsible for colour, their presence can shift the colour of a colourants and they are most often used to influence dye solubility [17].

Table 1-1: Wavelength of light absorption versus colour in organic dyes

| **Wavelength Absorbed (nm)** | **Colour Absorbed** | **Colour observed** |
|---|---|---|
| 400-435 | Violet | Yellow-green |
| 435-480 | Blue | Yellow |
| 480-490 | Green-blue | Orange |
| 490-500 | Blue-Green | Red |
| 500-560 | Green | Purple |
| 560-580 | Yellow-green | Violet |
| 580-595 | yellow | Blue |
| 595-605 | Orange | Green-blue |
| 605-700 | Red | Blue-green |

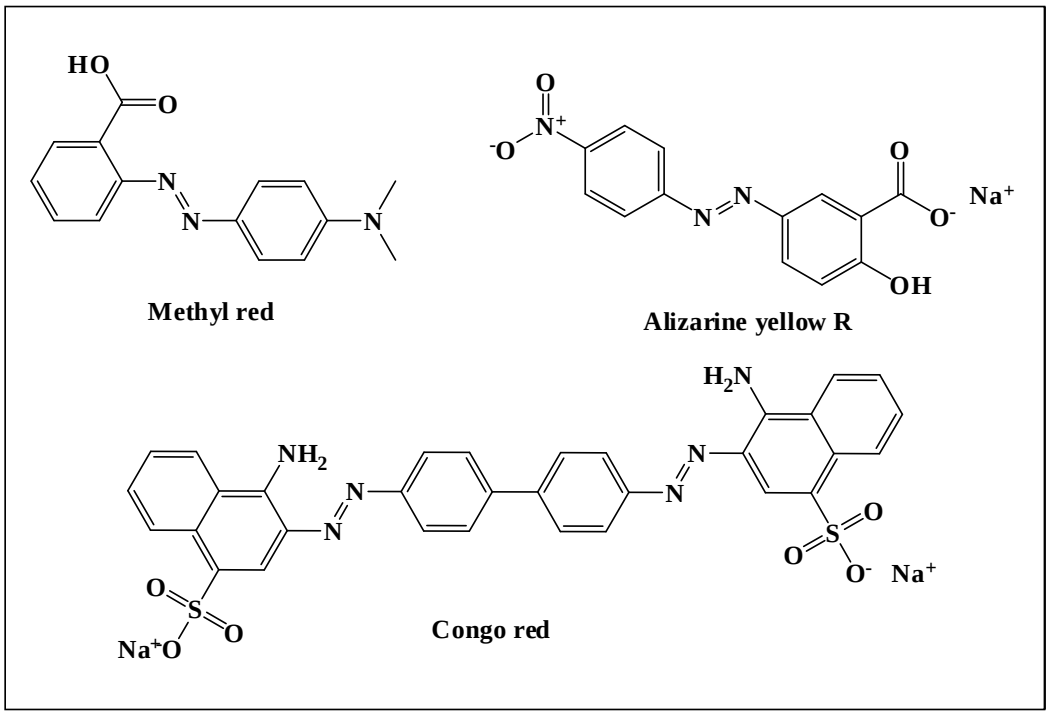



Figure 1-8: Structure of some azo dyes

### 1.2.3. Applications of azo dyes

Azo dyes are widely used in industry and daily life, where; azo dyes have been studied widely because of their excellent thermal and optical properties in applications such as optical recording medium, toner, ink-jet printing like Brilliant Blue ( see Figure 1-9), and oil-soluble light fast dyes [18].

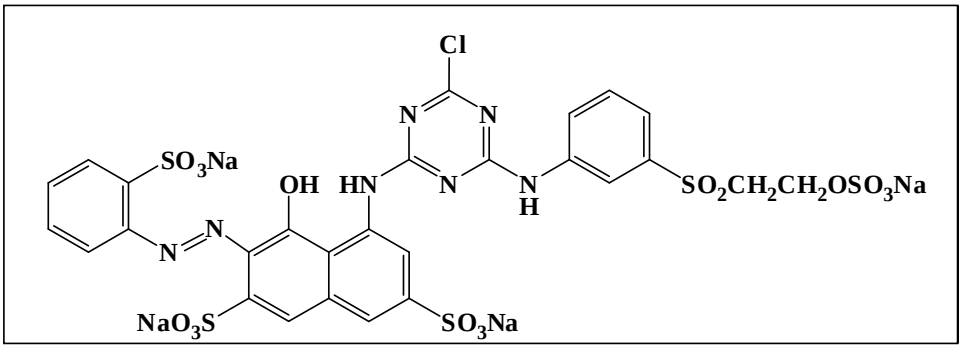


Figure 1-9: C.I reactive red (194) as inkjet dye

Different dyes used in textile industry usually have a synthetic origin and complex aromatic molecular structures which make them more stable and more difficult to be biodegraded. Due to their ease of manufacturing methodology, azo dyes accounts for almost 80% of annual production of commercial dyes all over the world [19].

Many azo pigments are non-toxic, although some, such as dinitroaniline orange, ortho-nitroaniline orange, or pigment orange 1, 2, and 5 have been found to be mutagenic [20]. Likewise, several case studies have linked azo pigments with basal cell carcinoma [21].

Azo dyes used as components in permanent hair dyes can only be decolorized by methods such as chemical bleaching using hydrogen peroxide. Flame Orange and Ruby Red are used as components in permanent hair dyes [22].

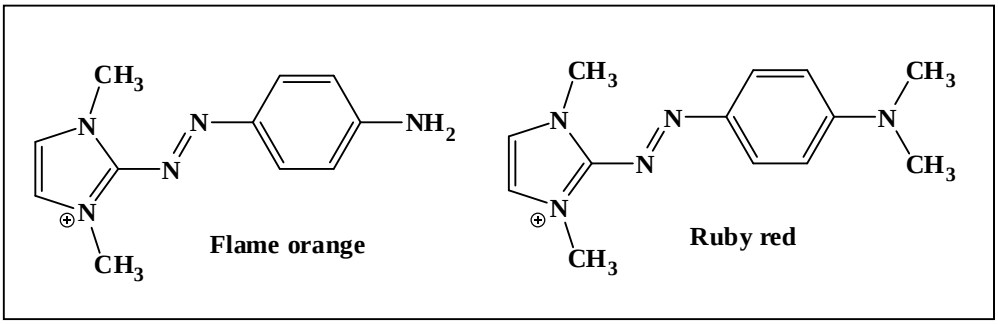



Figure 1-10: Examples of permanent hair dyes

Also, attention has been focused on the investigation of organic dyes as potential inhibitors for the metals in corrosive environment [23]. Most of the dyes consist of double bonds, hetero atoms and aromatic rings. All these functional groups present in the molecules which leads towards the dyes being considered good corrosion inhibitors azorubine dye (AZB) was used as corrosion inhibitor [24].

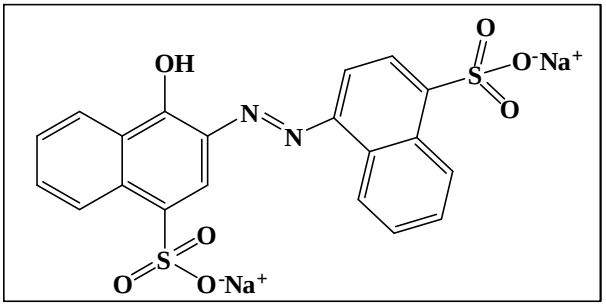



Figure 1-11: Structure of Azorubine dye (AZB)

## 1.3. Schiff bases

### 1.3.1. Synthesis of Schiff bases

Hugo Schiff was the first scientist who described Schiff bases in 1864 [25],A Schiff base (or azomethine) is a functional group that contain a carbon-nitrogen double bond with the nitrogen atom connected to an aryl or alkyl group, but not hydrogen. Schiff base are of the general formula $R_1R_2C=N-R_3$, where $R_3$ is an aryl or alkyl group that makes the Schiff base a stable imine. A Schiff base derived from aniline, where $R_3$ is a phenyl or substituted phenyl, can be called an anil [26].

The preparation of Schiff bases involves a variety of conditions and is brought about by mixing carbonyl compounds and primary amines [27] in various proportions and employing a range of solvents. The formation of Schiff bases [28] is generally favored by making use of dehydrating agents.

The acid/base catalysis or heating is employed for the synthesis of Schiff bases as their reactions are mostly reversible. The Schiff bases are formed by the reaction of amines with carbonyl compounds but it does not follow simple nucleophilic addition, but give an unstable addition compound called carbinolamine. The compound thus obtained is unstable and loses water molecule. The dehydration step during formation of Schiff base is actually

the rate determining step. The removal of product or separation of water from the reaction mixture assists the formation of product [29].

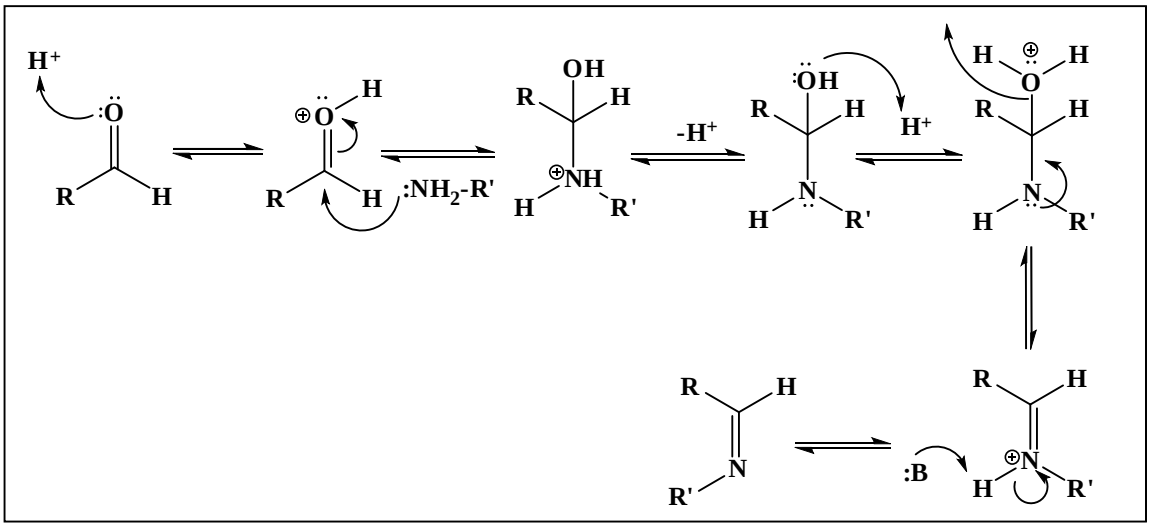


Figure 1-12: Mechanism of Schiff base

An intermolecular reductive Schiff base formation from nitroarenes and benzaldehydes to yield diarylimines is carried out in the presence of iron powder and dilute acid. This process tolerates various functional groups and often proceeds quantitatively with no need for purification [30].

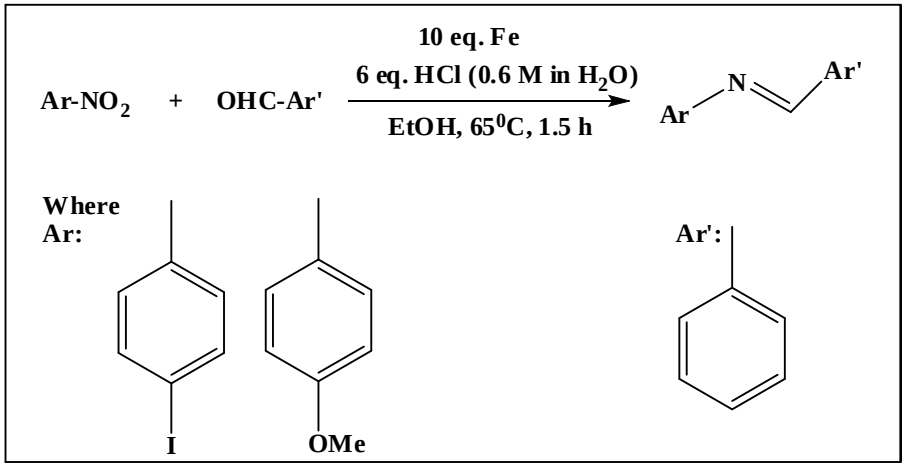



Figure 1-13: Preparation of diarylimines from nitroarenes and benzaldehyde

New Schiff bases of 1, 10-phenanthroline-2, 9-dicarboxaldehyde with sulfur-containing amines such as 2-mercaptoaniline, S-alkyl/aryl 2-aminobenzenethiol and methyl hydrazinecarbodithioate have been synthesized and characterized by spectroscopic and X-ray crystallographic techniques [31].

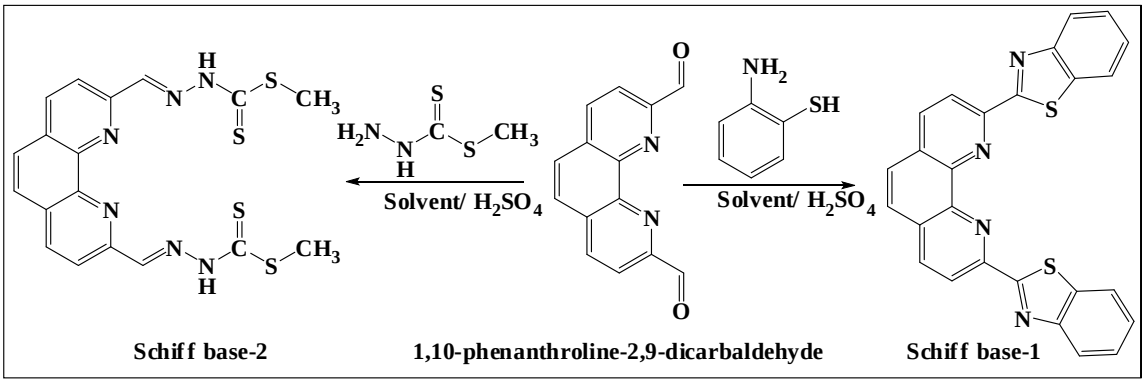



Figure 1-14: Synthesis of New Schiff Bases Formed by Condensation of 2, 9-Phenathroline-1, 10-dialdehyde with Sulfur-Containing Amines

### 1.3.2. Application of Schiff base

Schiff bases have attracted considerable attention of organic chemists due to their useful as starting material in the synthesis of important drugs, such as antibiotic, antiallergic, anticancer, antiphologistics and antitumor [32].

A series of novel Schiff's base derivatives of *N, N'*-bis (2-aminoethyl) pyridine-2, 6-dicarboxamide with different substituent showed a significant antibacterial activity [33].

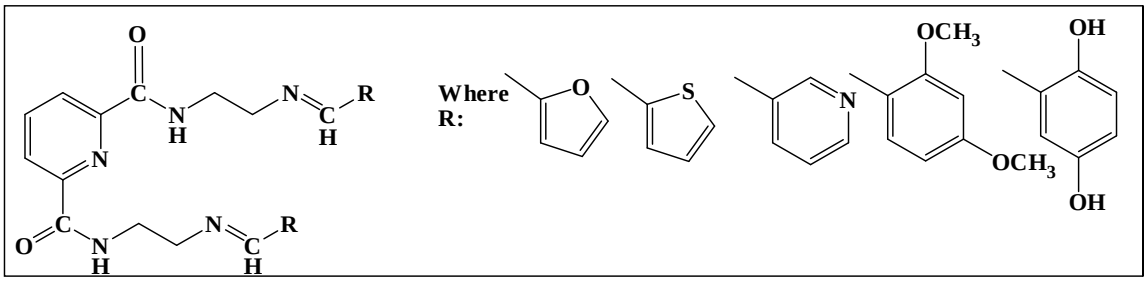



Figure 1-15: Structures of Schiff base derivatives

Moreover, Schiff bases have also attracted much attention because of their ability to act as ligands for complexation of different metal ions in various oxidation states [34], where a large number of different Schiff base ligands have been used as cation carriers in potentiometric sensors as they have shown excellent selectivity, sensitivity, and stability for specific metal ions such as Ag(II), Al(III), Co(II), Cu(II), Fe (III), Gd(III), Hg(II), Ni(II), Pb(II), Y(III), and Zn(II) [35- 40].

New type tetradentate Schiff base ligands derived from ortho phenylene diamine, salicylaldehyde and isatin where both oxygen and nitrogen donor sites. It coordinates with the metal ion in a tetradentate manner [41].

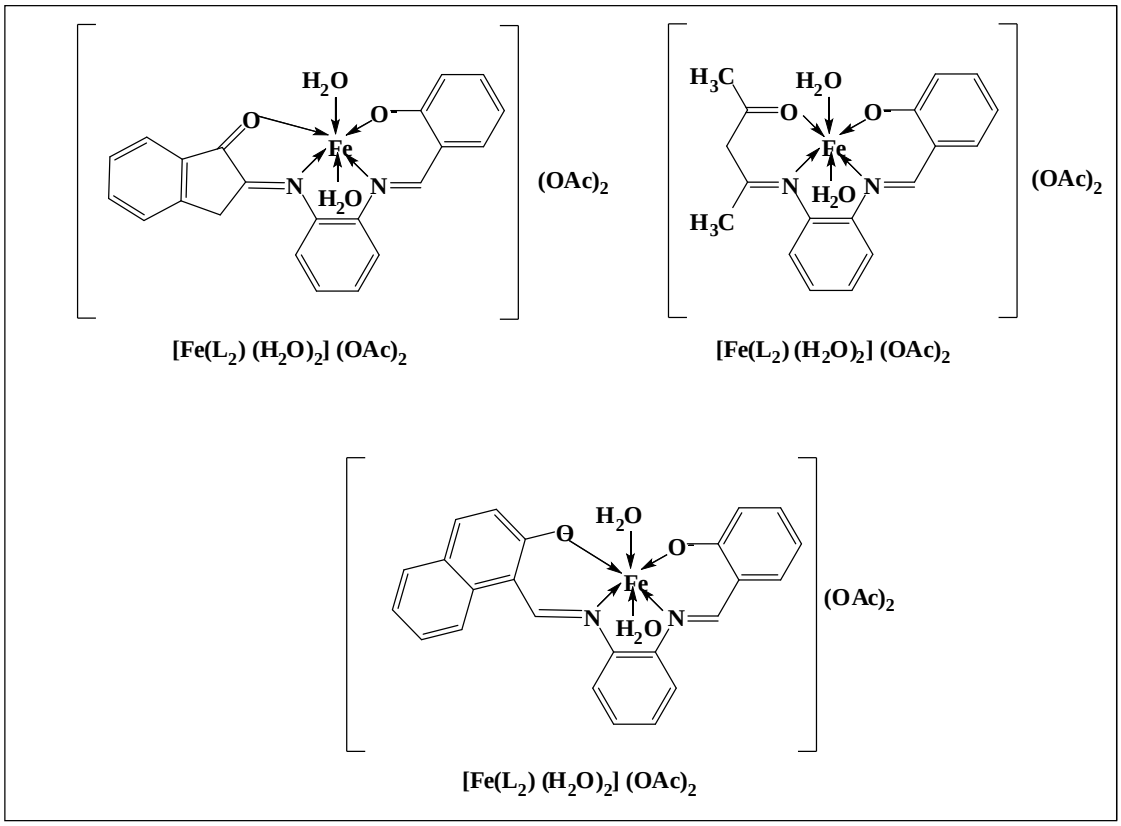



Figure 1-16: structures of Fe (III) Complexes with Schiff base Ligands

An interesting application of Schiff bases is their use as an effective corrosion inhibitor for metals and alloys, which is based on their ability to spontaneously form a monolayer on the surface to be protected .Examples of Schiff bases derivatives of 2-aminophenol as corrosion inhibitor for Al alloy[42].

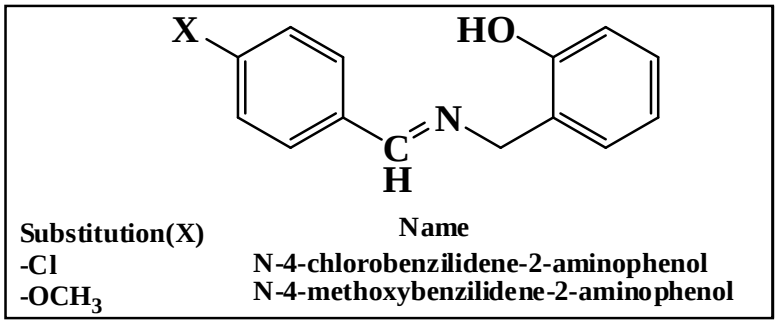



Figure 1-17: Schiff bases as corrosion inhibitor

Many commercial Schiff bases inhibitors are used for more efficiently in many cases due to the effect of C=N bond [(43)]. The principal interaction between the inhibitor and the metal surface is generally chemisorptions, physisorption or both [(44)]. The inhibitor molecule has nucleophilic center, such as oxygen, sulfur and nitrogen atoms. These atoms have free electron pairs which are readily available for sharing. Together with the electronic cloud of the benzene ring, they create multiple absorption sites for the inhibitor thus enabling stable monolayer formation [(45)].

Molecular model of Schiff base of *N*-(2-chlorobenzylidene)-4-acetylaniline (CBAA) was proposed for its corrosion inhibition towards of $St_3S$ carbon steel in acidic chloride solutions (see figure 1-18) [(46)].

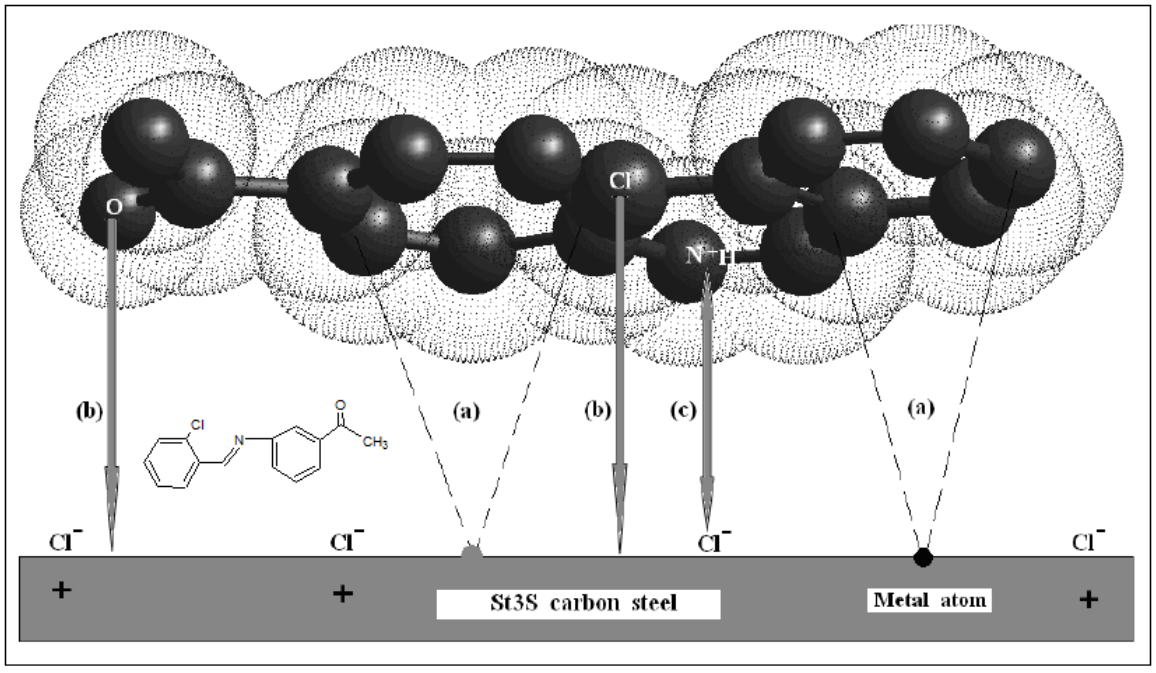



Figure 1-18: Proposal of model of protective layer of (CBAA) on $St_3S$ surface in a 1.2 M $Cl^-$ solution: (a) chemisorptions, (b) feedback bond, and (c) electrostatic interaction (physisorption)

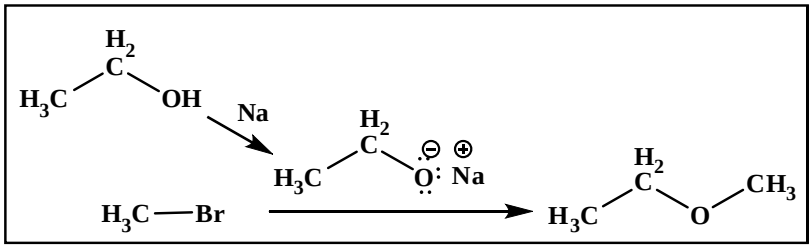
### 1.4. Alkylation reaction

Alkylation is a general term for the introduction of an alkyl group into a compound and is a more specifically known as Methylation, Ethylation, Propylation, Butylation, etc., depending upon the alkyl group inserted.

Alkylation of a phenol result in ether, while alkylation of a thiol gives a sulphide, primary and secondary amines can also be alkylated [47].

### 1.4.1. Preparation of O-alkylation

The most common general method for the synthesis of ethers is the Williamson ether synthesis [48]. Alkoxide ions are good nucleophiles and displace halide ions from alkyl halides, resulting in the formation of a new Carbon- Oxygen bond. Alkoxides are produced by treatment of alcohols with either a base or an alkali metal.




An efficient method chemoselectively converts benzyl alcohols into their methyl or ethyl ethers in the presence of aliphatic or phenolic hydroxyl groups using 2, 4, 6-trichloro-1, 3, 5-triazine (TCT) and dimethyl sulfoxide in methanol or ethanol [49].

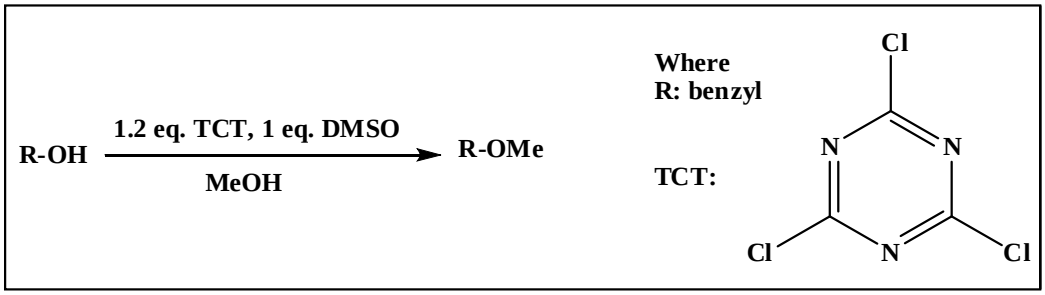
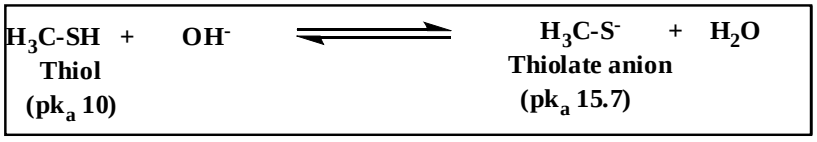



Figure 1-19: Preparation of ether

### 1.4.2. Preparation of S-alkylation [50, 51]

Thioethers can be synthesized by a pathway similar to that of the Williamson ether synthesis. A thiol is converted to the thiolate anion by reaction with sodium hydroxide.

The reaction of one equivalent of hydroxide ion with a thiol results in essentially complete conversion of the thiol into the thiolate anion (and of hydroxide ion to water).




A cobalt-catalyzed coupling of aryl halides with thiophenols and alkanethiols allows the preparation of various aryl sulfides in excellent yields under mild reaction conditions.

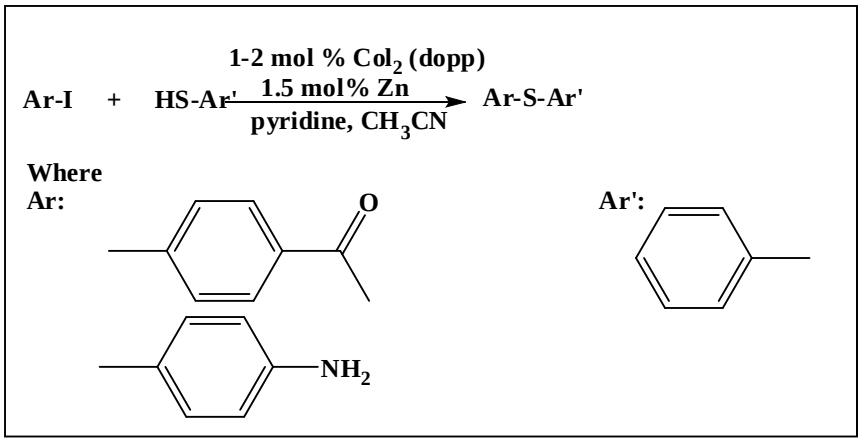



Figure 1-20: Cobalt-Catalyzed Aryl−Sulfur Bond Formation

### 1.4.3. Preparation of N-alkylation

N-alkylation of primary amines is a significant research goal because the resulting secondary amines are some of the most important partial structures of biologically active compounds and functional materials [52].

In ionic liquids 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF6]) or 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF4]), a highly regioselective N-substitution of pyrrole with alkyl halides, sulfonyl chlorides, and benzoyl chloride gave substituted pyrroles in excellent yields. Michael addition of pyrrole with electrophilic olefins was completed in a highly regioselective manner to afford *N*-alkylpyrroles [53].

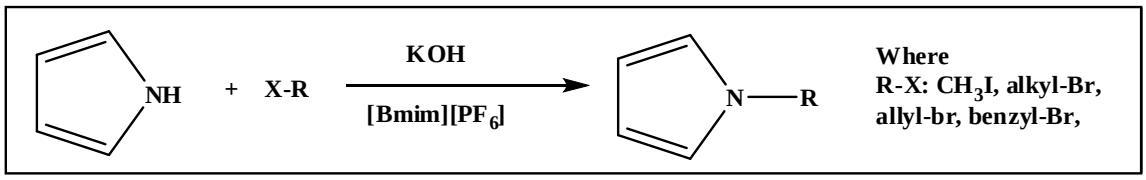



Figure 1-21: N-Substitution of pyrrole in Ionic Liquids

Reaction of 4-bromo-*NH*-1, 2, 3-triazoles with alkyl halides in the presence of $K_2CO_3$ in DMF produced the corresponding 2-substituted 4-bromo-1, 2, 3-triazoles in a regioselective process. Subsequent Suzuki cross-coupling reaction provided an efficient synthesis of 2, 4, 5-trisubstituted 1, 2, 3-triazoles, whereas hydrogenation furnished an efficient synthesis of 2, 4-disubstituted 1, 2, 3-triazoles [54].

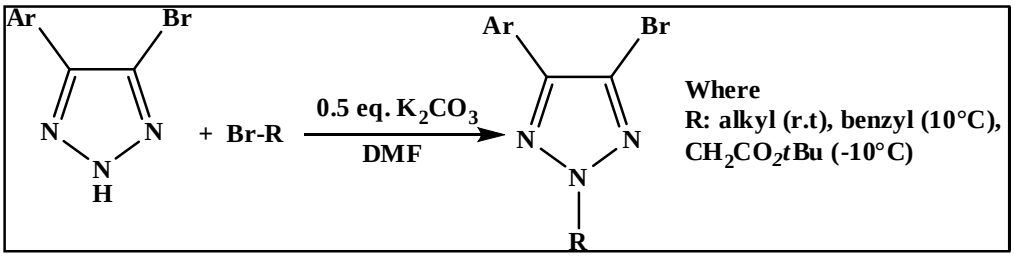



Figure 1-22: Synthesis of Poly-Substituted 1,2,3-Triazoles

A series of *N, N′*-asymmetrically substituted imidazolium iodides have been synthesized, starting from *N*-arylimidazoles and the less expensive, but less reactive, 1-chlorobutane or (3-chloropropyl)trimethoxysilane. The addition of potassium iodide and the use of 1, 2-dimethoxyethane as a solvent allowed the synthesis of multigram quantities of these salts [55].

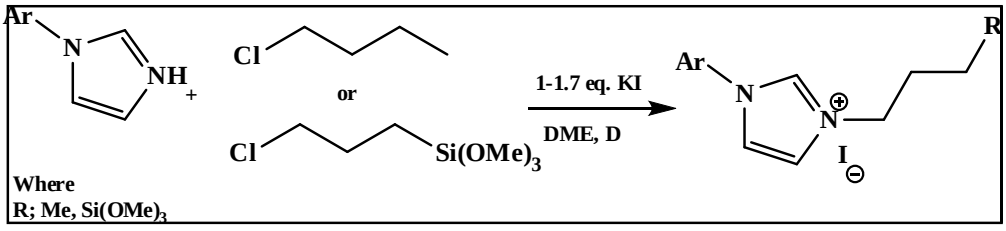



Figure 1-23: Synthesis of N-Alkyl-N'-aryl-imidazolium Iodides

## 1.5. Corrosion process

### 1.5.1. Definition of corrosion and Corrosive Environment

Corrosion is a naturally occurring phenomenon commonly defined as the deterioration of a substance (usually a metal) or its properties because of a reaction with its environment. Like other natural hazards such as earthquakes or severe weather disturbances, corrosion can cause dangerous and expensive damage to everything from automobiles, home appliances, and drinking water systems to pipelines, bridges, and public buildings [(56)].

All environments are corrosive to some degree. Following is the list of typical corrosive environments [(57)]: air and humidity, water, steam and gases (chlorine), ammonia, hydrogen sulfide, sulfur dioxide and oxides of nitrogen, fuel gases, acids, alkalis, and soils.

It may, therefore, be observed that corrosion is a potent force which destroys economy, depletes resources and causes costly and untimely failures of plants, equipment and components.

### 1.5.2. Classification of Corrosion

The differing forms of corrosion can be divided into the following eight categories based on the appearance of the corrosion damage or the mechanism of attack [(58)]:

- Uniform or general corrosion.
- Galvanic corrosion.
- Pitting corrosion.
- Crevice corrosion, including: Corrosion under tubercles or deposits, filiform corrosion and poultice corrosion.
- Erosion-Corrosion, including: cavitation erosion and fretting corrosion.
- Intergranular corrosion, including: sensitization and exfoliation.

- Dealloying.

- Environmentally assisted cracking, including: stress corrosion cracking (SCC), corrosion fatigue, and hydrogen damage (including: hydrogen embrittlement, hydrogen-induced blistering, high- temperature hydrogen attack, and hydride formation).

General corrosion is the most common form of corrosion. It is characterized by a chemical or electrochemical reaction that takes place on the expose surface. The metal becomes thinner and eventually results in perforation and failure. The general attack result from local corrosion- cell action; that is multiple anode and cathodes are operating on the metal surface at any given time. The location of anodic and cathodic areas continues to move about on the surface, resulting in uniform corrosion. Uniform corrosion can be prevented or reduced by proper materials selection, the use of coating or inhibitor, or cathodic protection. These corrosion prevention methods can be used individually or in combination [59].

### 1.5.3. Corrosion cell

The special characteristic of most corrosion processes is that the oxidation and reduction steps occur at separate locations on the metal. This is possible because metals are conductive, so the electrons can flow through the metal from the anodic to the cathodic regions. The presence of water is necessary in order to transport ions to and from the metal, but a thin film of adsorbed moisture can be sufficient. A corrosion system can be regarded as a short-circuited electrochemical cell in which the anodic process is [60]:

$$Fe_{(s)} \longrightarrow Fe^{2+}_{(aq)} + 2e^-$$

And the cathodic steps can be:

$$O_{2(g)} + 2H_2O_{(l)} + 4e^- \longrightarrow 4OH^-$$

These reactions are illustrated schematically in Figure 1-8 [61].

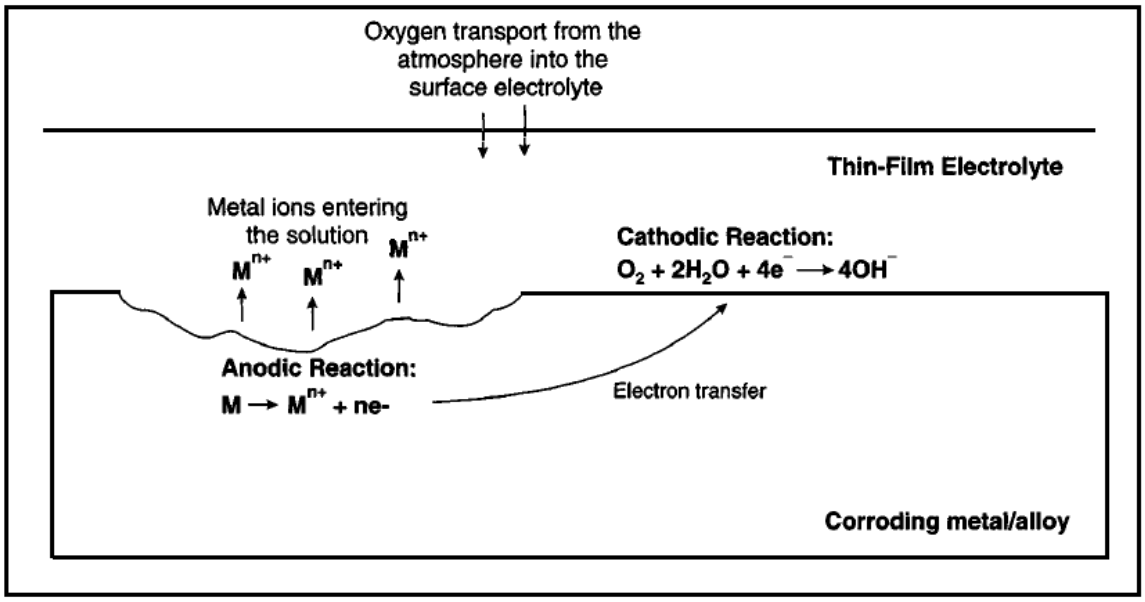



Figure 1-24: Schematic diagram of corrosion cells on metal

Corrosion often begins at anodic location where the metal is under stress. The metal ions dissolve in the moisture film and the electrons migrate to another location (cathode) where they are taken up by a depolarizer. Oxygen is the most common depolarizer; hydroxide ions react with the $Fe^{2+}$ to form the mixture of hydrous iron oxides known as rust [62].

$$Fe^{2+}_{(aq)} + 2OH^-_{(aq)} \longrightarrow Fe(OH)_{2(s)}$$

$$4Fe(OH)_{2(s)} + O_{2(g)} \longrightarrow 2Fe_2O_3.H_2O_{(s)} + 2H_2O_{(l)}$$

### 1.5.4. Corrosion Prevention [63]

Since corrosion can be defined as the undesirable reaction between metal or an alloy and its environment; therefore corrosion processes can be affected by controlling one of the reactants. In the case of corrosion inhibitors, it is environment, which is subjected to the modification by adding certain chemicals. The corrosion rate may also be reduced by other means such as adjusting the pH and temperature, removing dissolved oxygen or lowering the conductivity of the electrolyte. An inhibitor is a substance that retards or slows down the chemical reaction, thus a corrosion inhibitor is a substance which when added to an environment decrease the rate of attack by the environment on a metal. Inhibitors can be classified into the following categories: Anodic (passivators), Cathodic, Ohmic, Precipitation, Vapour phase, and Organic inhibitors.

### 1.5.5. Organic corrosion inhibitor

Corrosion inhibitor is defined as chemical substance that can reduce the corrosion rate with the present of in small concentration without changing the concentration of corroding agent in a corrosion system. Corrosion inhibitor reduces the rate of corrosion with increase the polarization behavior of anode and cathode.

Organic compounds, mainly containing oxygen, nitrogen and sulphur atoms and having multiple bonds, are recognized as effective inhibitors of the corrosion of many metals and alloys. In different media, for a given metal, the efficiency of the inhibitor depends on the stability of the formed complex and the inhibitor molecule should have centers, which are capable of forming bonds with the metal surface via an electron transfer. Generally, a

strong coordination bond causes higher inhibition efficiency, the inhibition increases in the sequence of atoms O < N< S [64].

The corrosion inhibition of carbon steel in 3% NaCl solution at 50°C with imidazoline-based inhibitors has been evaluated. The results showed a low performance of the inhibitors [65].

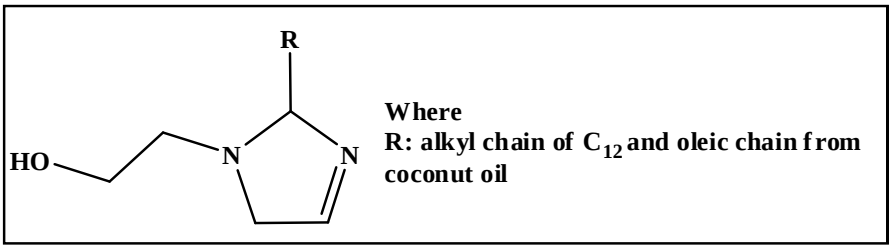



Figure 1-25: Structure of the hydroxyethyl imidazoline

A series of metal-phosphonate organic-inorganic polymeric hybrid materials are synthesized, structurally characterized, and evaluated for their anticorrosion properties for the protection of carbon steels. These materials are Zn-AMP (where AMP) amino-tris (methylenephosphonate)), Zn-HDTMP (where HDTMP) hexamethylenediamine-tetrakis (methylenephosphonate)), and Ca-PBTC (where PBTC) 2-phosphonobutane-1, 2, 4-tricarboxylate) [66].

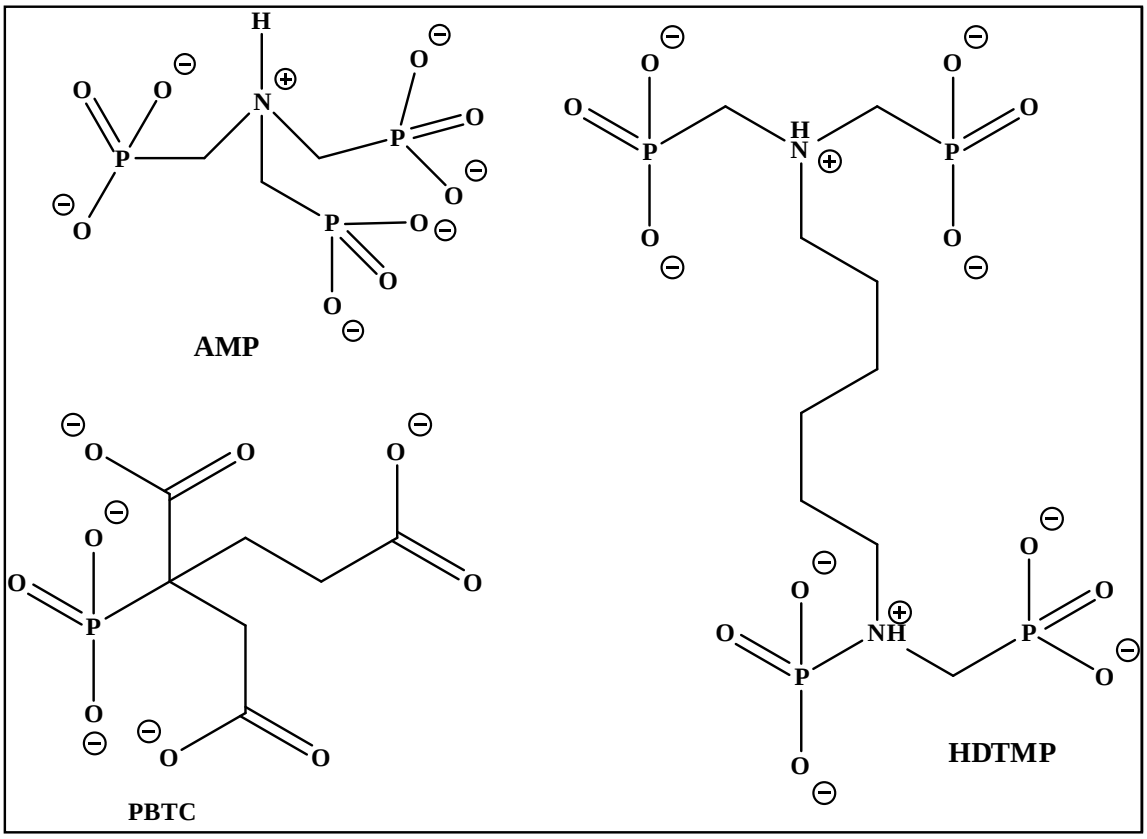



Figure 1-26: Schematic structures of the AMP, HDTMP, and PBTC corrosion inhibitors

The interesting class of inhibitors are green inhibitors because they are non-toxic and do not contain heavy metals hence they are environmentally friendly [67, 68]. It has been published that the inhibitory actions of plant extracts are due to the presence of some organic compounds such as saponins, tannin, alkaloid, steroids, glycosides and amino acids [69]. Most of these compounds have centers for π-electrons and functional groups (such as -C=C-, -OR, -OH, -COOH, $-NR_2$, $-NH_2$ and –SR), which provide electrons that facilitate the adsorption of the inhibitor on the metal surface. Also, the presence of hetero atoms such as P, O and S enhances the adsorption of the

inhibitor on the metal surface. Amino acids in the plant extracts play an important role in the inhibition mechanism [70-79].

### 1.6. Computational chemistry

Computational chemistry is the application of chemical, mathematical and computing skills to the solution of interesting chemical problems. It uses computers to generate information such as properties of molecules or simulated experimental results. Very few aspects of chemistry can be computed exactly, but almost every aspect of chemistry has been described in a qualitative or approximate quantitative computational scheme [80].

The major computational requirements are [81]:

-Molecular energies and structures.

-Geometry optimization from an empirical input.

-Energies and structures of transition states.

-Bond energies.

-Reaction energies and all thermodynamic properties.

-Molecular orbitals.

-Multipole moments.

-Atomic charges and electrostatic potential.

-Vibrational frequencies.

-IR and Raman spectra.

-NMR spectra and so on

The most important numerical techniques are ab-initio, semi-empirical and molecular mechanics. Definitions of these terms are helpful in understanding the use of computational techniques for chemistry. Semi-empirical methods use parameters derived from experimental values that simplify theoretical calculations. These methods usually do not require long computation times,

and lead to qualitative descriptions of molecular systems. In particular, the semi-empirical PM3 method makes uses of an accurate procedure to predict chemical properties, through a simplified Hartree-Fock (HF) Hamiltonian [82].

# *Aim of Work*

## Aim of work

The aim of this work is to prepare and identify some organic compounds **[4-16]** and **[18-20]** that containing hetero atoms (sulfur, oxygen and nitrogen) to act as corrosion inhibitors on mild steel surface in acidic media. Weight loss method is used to measure the inhibition efficiency of the prepared compounds. Semi-empirical molecular quantum calculations within PM3 method were used to study the relationship between molecular structures of prepared compounds and their inhibition efficiencies.

# CHAPTER TWO

# EXPERIMENTAL PART

## 2. Experimental

### 2.1. Instruments and apparatuses

1. The infra-red spectra of the prepared compounds were recoded using FTIR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium bromide (KBr) discs in the wave number range of (4000-400) $cm^{-1}$, Al-Nahrain University, department of chemistry, and Ibn Sina state company/ The Ministry of Industry located at Baghdad University, College of science for women, department of chemistry.

2. Ultraviolet spectra were recorded on SHIMADAZ U.V-visible recording spectrophotometer U.V. 1650 by using Ethanol as solvent, Al-Nahrain University, department of chemistry.

3. $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded on nuclear magnetic resonance Bruker spectrophotometer model Ultrasheild 300 $MH_Z$, using tetramethyl silane as internal standard and DMSO-$d_6$ as solvent, AL-Albait University, Amman, Jordan).

4. Melting points were determined by the open capillary method using hot stage Gallenkamp melting point apparatus and were uncorrected.

5. The elements analysis of mild steel was performed by Spectro max – Germany, 2009, State Company for Inspection and rehabilitation, Ministry of Industry and Materials.

6. Balance, Sartorius AGGOTTINGEN, Germany, BL210S.

## 2.2. Chemicals

All the chemicals used in this work were of highest purity available and they supplied without further purification. The following Table 2-1 shows the chemicals and the companies which supply themes.

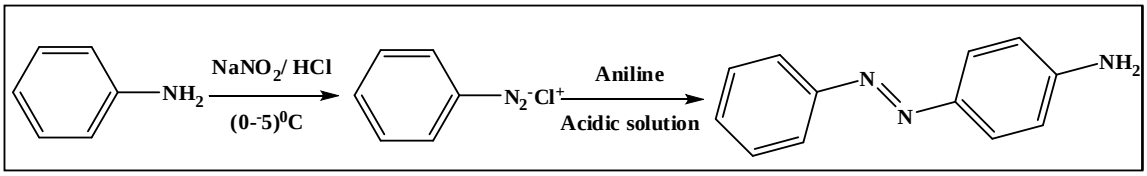
Table 2-1: Chemicals and their Manufacturers.

| Number | Chemicals | company |
|---|---|---|
| **1** | Absolute Ethanol | Scharlau |
| **2** | Acetaldehyde | Merck |
| **3** | Acetone | Fluka |
| **4** | Aniline | Himedia |
| **5** | Benzaldehyde | Riedl-Dehaen AG Seelze-Hannouer |
| **6** | Benzyl Chloride | Alpha Aesar |
| **7** | Cinnamaldehyde | Alpha Aesar |
| **8** | Diethyl ether | GCC |
| **9** | Distilled water | |
| **10** | Ethyl Bromide | Alpha Aesar |
| **11** | Ethylene Dichloride | Fluka |
| **12** | Furfural | SCRC |
| **13** | Glacial Acetic Acid | Hopkins & Williams |
| **14** | Hydrochloric Acid | Himedia |
| **15** | L-(+)-Arabinose | Merck |
| **16** | n-propyl Bromide | Alpha Aesar |
| **17** | *p*-aminothiophenol | Alpha Aesar |
| **18** | *p*-aminopyridine | Alpha Aesar |

| | | |
|---|---|---|
| **19** | *p*-bromobenzaldehyde | Merck |
| **20** | *p*-dimethylaminobenzaldehyde | Merck |
| **21** | Phenol | Fluka |
| **22** | Potassium hydroxide | Fluka |
| **23** | *p*-nitrobenzaldehyde | Alpha Aesar |
| **24** | Sodium bicarbonate | BDH |
| **25** | Sodium hydroxide | Fluka |
| **26** | Sodium nitrite | Merck |
| **27** | Sulfuric acid | Himedia |

## 2.3. Preparation methods

### 2.3.1. Preparation of 4-phenyl azoaniline [1]:




### a) Diazotization [83]

In beaker (50 mL) dissolve (2 mL, 0.02 mole) of aniline in (4 mL) distilled water and (4 mL) concentrated hydrochloric acid. Place the beaker in ice-water bath at (0 - ˉ5) °C for half hour. Add slowly sodium nitrite solution [(2 g, 0.02 mol) in (10 mL) distill water] previously cooled to 0°C. yellow solution will be obtained and keep it for the next step.

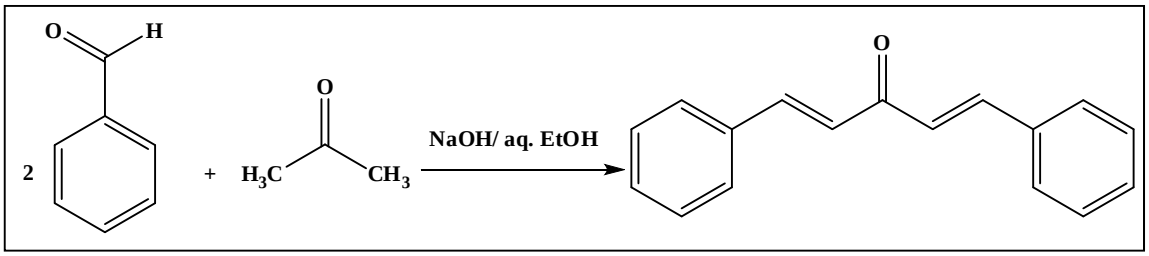
**b) Coupling [84]**

Aniline (15 mL, 0.16 mole) was added slowly to yellow solution with constant stirring, then add slowly (2.5 g) of finely powdered aniline chloride [prepared by adding (2 mL) aniline with excess (3 mL) concentration hydrochloric acid]. The result was cooled, filtered and washed with small volume of ether, then dried. After, that the mixture warmed to (40 - 45°C) in water bath for 1hr. Reaction mixture allowed to stand for 30 min., then added with stirring (15 mL) of Glacial acetic acid with equal volume of water. Allow the mixture to stand with stirring for 15min., filtered using section pump and washed with (10 mL) of water and dried. The crude product was recrystallized with $CCl_4$. The physical properties of the synthesized compound **[1]** are given in Table 2-2.

Table 2-2: Physical properties of compound **[1]**

| 4-phenyl azoaniline | |
|---|---|
| Molecular formula | $C_{12}H_{11}N_3$ |
| Colour | Orange to brown |
| Molecular weight(g/mol) | 197.24 |
| M.P., ℃ | 123-125 |
| yield% | 73 |

### 2.3.2. Preparation of (1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-one [2] [(85)]:

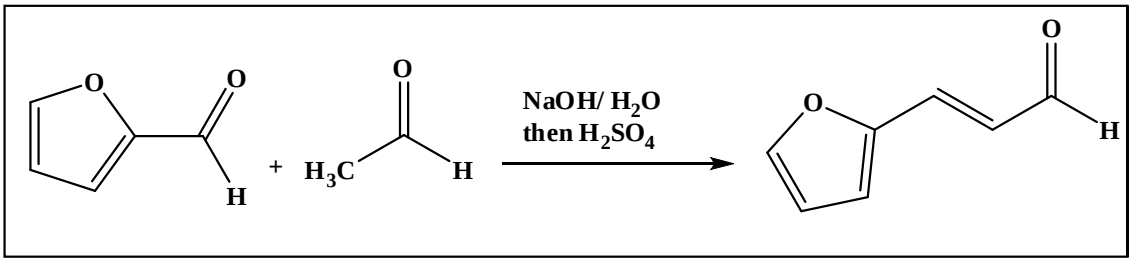



Solution of (10 g) of sodium hydroxide in (100 mL) of water and (80 mL) of ethanol was placed in water bath at about 20–25°C and stirred vigorously while one-half of a mixture of (10.18 mL, 1 mole) of Benzaldehyde and (3.67 mL, 0.5 mole) of acetone was added. In about two or three minutes a yellow cloud forms which soon becomes a precipitate. After fifteen minutes the rest of the mixed reagents were added. Additional (3 mL) of ethanol was added to the mixture. Vigorous stirring was continued for one-half hour longer, and the mush was then filtered by section pump. The product was thoroughly washed with distilled water and then dried at room temperature to constant weight with no further purification. The physical properties of the synthesized compound **[2]** are given in Table 2-3.

Table 2-3: Physical properties of compound **[2]**

| (1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-one | |
|---|---|
| Molecular formula | $C_{17}H_{14}O$ |
| Colour | Yellow |
| Molecular weight(g/mol) | 234.29 |
| M.P., ℃ | 107-110 |
| yield% | 56 |

### 2.3.3. Preparation of (E)-3-(furan-2-yl) acryl aldehyde [3] [(86)]:

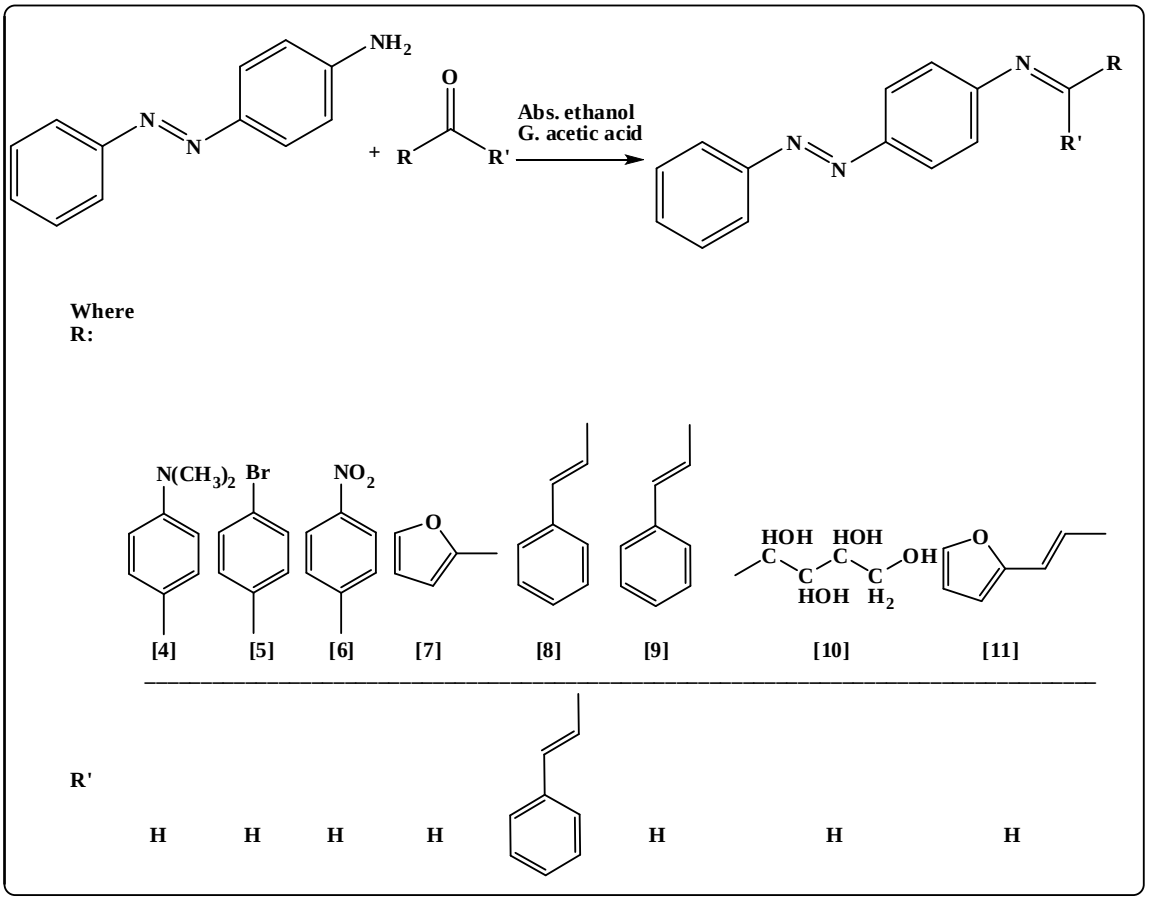



Mixed (8.4 mL, 3.8 mole) of furfural and (75 mL) of water. Then (12 mL, 8.6 mole) of acetaldehyde was added. The mixture was stirred and cooled to (10°C) and to it was added (2mL) of (33%) sodium hydroxide solution, where upon some heat were generated. Without cooling, the stirring is continued for four hours at room temperature. At the end of this time (10%) of concentrated sulfuric acid was added until the mixture was acidic. The two layers which have formed were separated. Take the bottom layer and extracted with ether. Dark red liquid was obtained. The physical properties of the synthesized compound **[3]** are given in Table 2-4.

Table 2-4: Physical properties of compound **[3]**

| (E)-3-(furan-2-yl) acryl aldehyde | |
|---|---|
| Chemical formula | $C_7H_6O_2$ |
| Colour | Dark red |
| Molecular weight(g/mol) | 122.12 |
| B.p., °C | 110 |
| yield% | 47 |

**2.3.4. Preparation of [N-substituted] (E)-4-(phenyldiazenyl) aniline [4-11] [87]:**

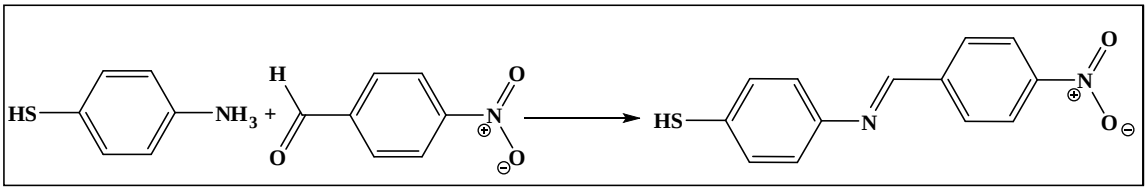



A mixture of 4-phenyl azoaniline (1.97 g, 0.01 mole), absolute ethanol (20 mL) and appropriate aromatic aldehydes or ketones (0.01 mole) and few drops glacial acetic acid was refluxed for (5-8) hours. After cooling at room temperature the precipitate was filtered and dried. The products were recrystallized from ethanol. The physical properties of the synthesized compounds **[4-11]** are given in Table 2-5.

Table 2-5: Physical properties of compounds **[4-11]**

| **Comp. Name & No.** | **Chemical formula** | **Color** | **Molecular weight (g/mol)** | **M.p., °C** | **yield %** |
|---|---|---|---|---|---|
| N, N-dimethyl-4-[(E)- 4-{(E)-phenyldiazenyl} phenylimino] methyl aniline **[4]** | $C_{21}H_{20}N_4$ | Orange | 328.41 | 148-150 | 40 |
| (E)-N-(4-bromobenzylidene)-4-((E)-phenyldiazenyl) aniline **[5]** | $C_{19}H_{14}BrN_3$ | Orange | 364.24 | 155-158 | 44 |
| (E)-N-(4-nitrobenzylidene)-4-((E)-phenyldiazenyl)aniline **[6]** | $C_{19}H_{14}N_4O_2$ | Orange | 330.34 | 157-160 | 75 |
| (Z)-N-(furan-2-ylmethylene)-4-((E)-phenyldiazenyl)aniline **[7]** | $C_{17}H_{13}N_3O$ | Brown | 275.11 | 155-157 | 66 |
| N-[(1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-ylidene]-4-[(E)-phenyldiazenyl] aniline **[8]** | $C_{29}H_{23}N_3$ | Deep yellow | 413.19 | 161-164 | 52 |
| (E)-N-[(E)-3-phenylallylidene]-4-[(E)-phenyldiazenyl] aniline **[9]** | $C_{21}H_{17}N_3$ | Brown | 311.14 | 141-144 | 47 |
| (E)-5-[4-{(E)-phenyldiazenyl} phenylimino] pentane-1, 2, 3, 4-tetraol **[10]** | $C_{17}H_{19}N_3O_4$ | Brown | 329.35 | 133-135 | 50 |
| (E)-N-[(E)-3-{furan-2-yl} allylidene]-4-[(E)-phenyldiazenyl] aniline **[11]** | $C_{19}H_{15}N_3O$ | Brown | 301.34 | 180-183 | 45 |

### 2.3.5. Preparation of (E)-4-(4-nitrobenzylideneamino) benzenethiol [12] [87]:

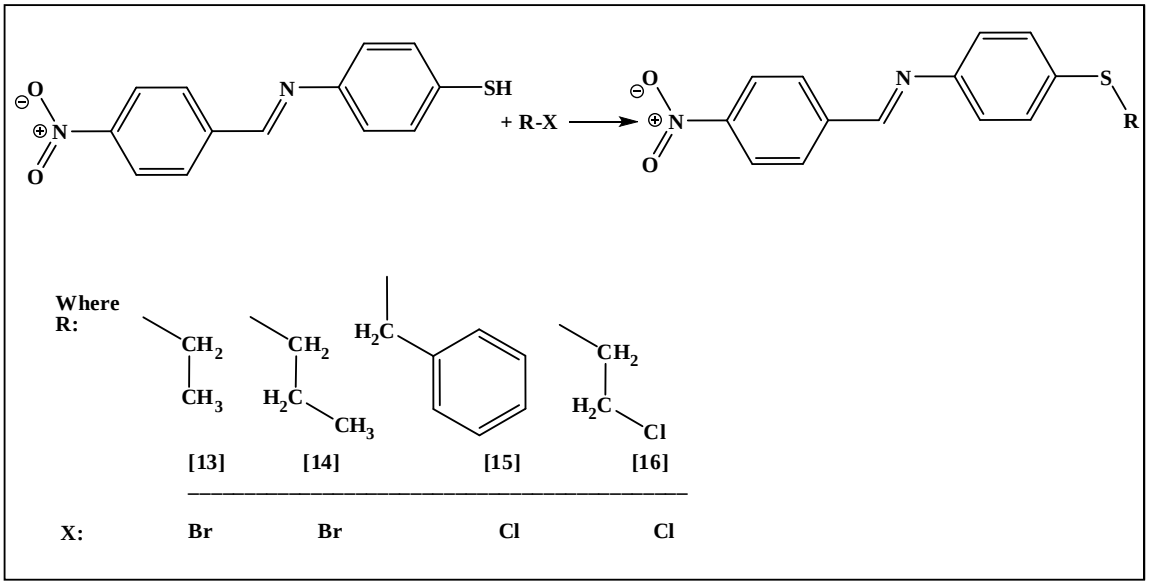


A mixture of 4-amino thiophenol (1.25 g, 0.01 mole), absolute ethanol (20 mL) and 4-nitro benzaldehyde (1.51 g, 0.01 mole) and few drops glacial acetic acid was refluxed for 5 hours. After cooling at room temperature the precipitate was filtered and dried. The products were recrystallized from ethanol. The physical properties of the synthesized compound **[12]** are given in Table 2-6.

Table 2-6: Physical properties of compound **[12]**

| (E)-4-(4-nitrobenzylideneamino)benzenethiol | |
|---|---|
| Chemical formula | $C_{13}H_{10}N_2O_2S$ |
| Colour | Orange |
| Molecular weight(g/mol) | 258.30 |
| M.p, °C | 98-100 |
| yield% | 83 |

**2.3.6. Preparation of [S-substituted] (E)-4-(4-nitrobenzylideneimino) benzenthiol [13-16]:**



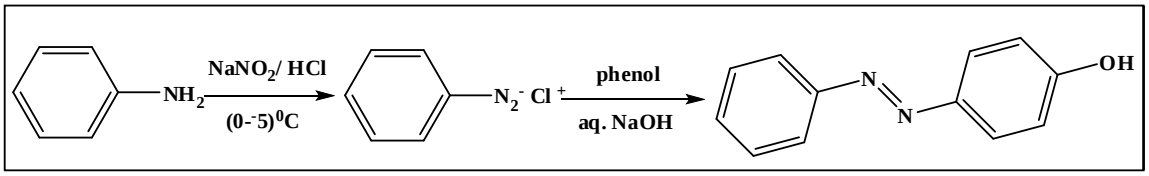

Alkyl halide (0.0025 mole) was added by small portions with stirring to a mixture of (E)-4-(4-nitrobenzylideneimino) benzenthiol (0.65 g, 0.0025 mole) with ethanolic alkali solution (0.04 g KOH in 10 mL EtOH) and then final mixture was refluxed for 2 hours. After cooling, the reaction mixture was poured into crushed ice, and the precipitate was obtained, which was filtered and then recrystallized from acetone [(84)]. In case of compound **[16]**, to a stirred solution of (100 mL) of [sodium (1 mole) in absolute ethanol (1 liter)] was added to (E)-4-(4-nitrobenzylideneimino) benzenthiol (0.0025 mole) and then drop wise 1,2-dichloroethane (0.0025 mole, 10 mL ethanol) over about one-half hour, the temperature being kept at 20-25$^{o}$C by cooling. The reaction mixture was stirred for an additional 5 hr. at room temperature, the ethanol was removed, and the residue treated with cold water. The

product was filtered and then recrystallized from acetone [88]. The physical properties for the prepared compounds **[13-16]** are given in Table 2-7.

Table 2-7: Physical properties of compounds **[13-16]**

| **Comp. Name & No.** | **Chemical formula** | **Color** | **Molecular weight (g/mol)** | **M.p., °C** | **yield %** |
|---|---|---|---|---|---|
| (E)-4-(ethylthio)-N-(4-nitrobenzylidene)aniline **[13]** | $C_{15}H_{14}N_2O_2S$ | Yellow | 286.35 | >220 | 60 |
| (E)-N-(4-nitrobenzylidene)-4-(propylthio)aniline **[14]** | $C_{16}H_{16}N_2O_2S$ | Yellow | 300.38 | 200-203 | 47 |
| **(**E)-4-(benzylthio)-N-(4-nitrobenz ylidene)aniline **[15]** | $C_{20}H_{16}N_2O_2S$ | Yellow | 340.09 | >220 | 53 |
| **(**E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene)aniline **[16]** | $C_{15}H_{13}ClN_2O_2S$ | Yellow | 320.79 | 170-173 | 62 |

### 2.3.7. Preparation of 4-phenyl azophenol [17] [89]:

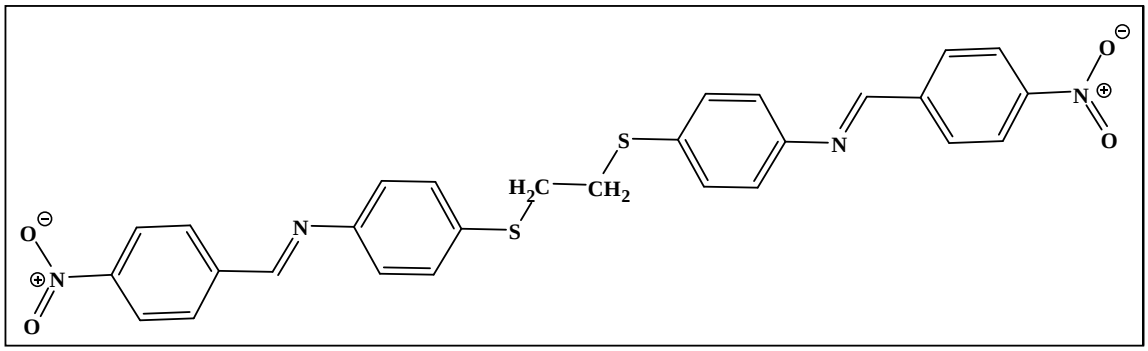



Aniline (3 mL, 0.0374 mole) was dissolved in concentrated hydrochloric acid (10.25 mL) and water (10.25 mL). Aqueous sodium nitrite [2.85 g, 0.0425 mole in water (8.75 mL)] was added to the aniline solution drop wise while stirring at 0ºC. Phenol (3.41 g, 0.0375 mole) was dissolved in a sodium hydroxide solution [3.2 mL, 0.01 mole NaOH in water (3.5 mL)], and cooled to 0°C. The aniline and sodium nitrite mixture was added drop wise to the phenolate. The yellow precipitate was formed and then filtered, dried, and recrystallized with $CCl_4$. The physical properties of the synthesized compound are given in Table 2-8.

Table 2-8: Physical properties of compound **[17]**

| 4-phenyl azophenol | |
|---|---|
| Molecular formula | $C_{12}H_{10}N_2O$ |
| Colour | Yellow |
| Molecular weight(g/mol) | 198.22 |
| M.P., °C | 148-150 |
| yield% | 85 |

**2.3.8. Preparation of (NE, N'E)-4, 4'-[ethane-1, 2-diylbis {sulfanediyl}] bis [N-{4-nitrobenzylidene} aniline] [18] [(84)]:**

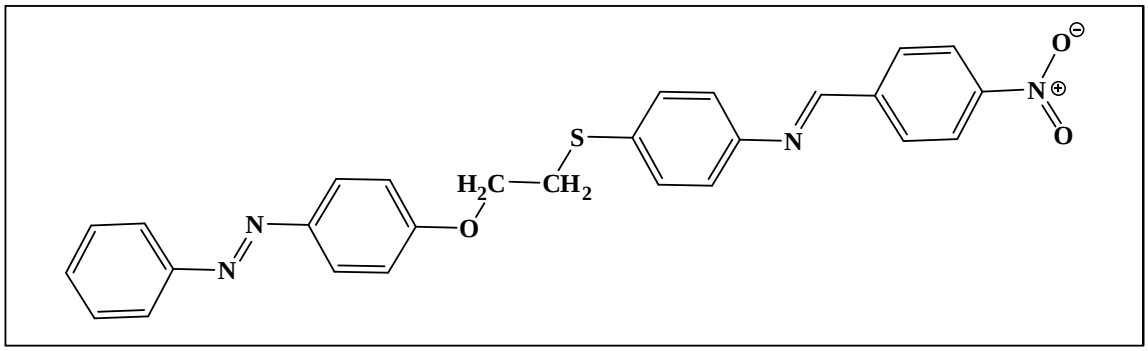


Solution of (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline (0.80 g, 0.0025 mole) was added into mixture of (0.65 g, 0.0025 mole) of (E)-4-(4-nitrobenzylideneimino) benzenthiol and ethanolic alkali solution (0.04 g KOH in 10 mL EtOH). The result was refluxed for 2 hours. After cooling, the reaction mixture was poured into crushed ice, and the precipitate was obtained, filtered and then recrystallized from acetone. The physical properties for the prepared compound **[18]** are given in Table 2-9.

Table 2-9: Physical properties of compound [18]

| (NE, N'E)-4, 4'-[ethane-1, 2-diylbis {sulfanediyl}] bis [N-{4-nitrobenzylidene} aniline] | |
|---|---|
| Chemical formula | $C_{32}H_{34}N_4S_2$ |
| Colour | Yellow |
| Molecular weight (g/mol) | 538.77 |
| M.p., °C | 200-203 |
| yield% | 64 |

**2.3.9. Preparation of (E)-N-(4-nitrobenzylidene)-4-[2-{4-(Z)-phenyldiazenyl} phenoxy] ethylthio aniline [19] [(84)]:**

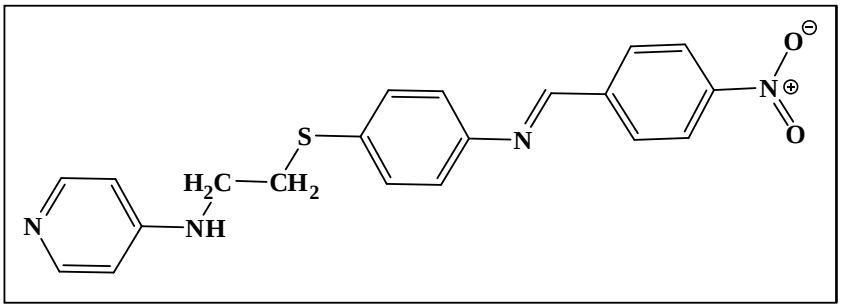


Solution of (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline (0.80 g, 0.0025 mole) was added drop wise into mixture of (0.5 g, 0.0025 mole) 4-phenyl azophenol and ethanolic alkali solution (0.04 g KOH in 10 mL EtOH) with stirring. The result was refluxed for 2 hours. After cooling, the reaction mixture was poured into crushed ice, and the precipitate was obtained, filtered and then recrystallized from acetone. The physical properties for the prepared compound **[19]** are given in Table 2-10.

Table 2-10: Physical properties of compound **[19]**

| (E)-N-(4-nitrobenzylidene)-4-[2-{4-(Z)-phenyldiazenyl} phenoxy] ethylthio aniline | |
|---|---|
| Chemical formula | $C_{27}H_{22}N_4O_3S$ |
| Colour | Yellow |
| Molecular weight (g/mol) | 482.55 |
| M.p., °C | 193-195 |
| yield% | 75 |

**2.3.10. Preparation of (E)-N-[2-{4-(4-nitrobenzylideneamino) phenylthio} ethyl] -4-amine pyridin [20] [(84)]:**



Solution of (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline (0.32 g, 0.001 mole) was slowly (about 1.5 hr) added drop wise into mixture of sodium hydrogen carbonate (0.12 g) in (1 mL) of water and (0.42 g, 0.0045 mole) of 4-aminopyridine with stirring at room temperature. The result was heated in water bath at (90-95) °C for 3 hrs. The mixture was allowed to cool, filtered and then recrystallized from ethanol. The physical properties for the prepared compound **[20]** are given in Table 2-11.

Table 2-11: Physical properties of compound **[20]**

| (E)-N-[2-{4-(4-nitrobenzylideneamino) phenylthio} ethyl] -4-amine pyridin | |
|---|---|
| Chemical formula | $C_{20}H_{18}N_4O_2S$ |
| Colour | Yellow |
| Molecular weight (g/mol) | 378.45 |
| M.p., °C | 192-195 |
| %yield | 66 |

## 2.4. Weight loss measurements

The sheet of mild steel used has the composition percentages (0.002% P, 0.288% Mn, 0.03% C, 0.0154% S, 0.0199% Cr, 0.002% Mo, 0.065% Cu, 0.0005%V and the remainder iron) which obtained by using spectro max. The mild steel sheet was mechanically press-cut into disc shape with diameter (2.5 cm). These disc shapes were polished with emery papers ranging from 110 to 410 grades to get very smooth surface. However, surface treatments of the mild steel involve degreasing in absolute ethanol and drying in acetone. The treated specimens were then stored in a moisture-free desiccator before their use in corrosion studies. Mild steel specimens were initially weighed in an electronic balance. After that the specimens was completely immersed in 250 mL beaker containing 1M sulphuric acid in the presence and absence of inhibitors. The specimens were removed after 8 hours exposure period at 30ºC, washed with water to remove any corrosion products and finally washed with acetone. Then they were dried and reweighed. Mass loss measurements were performed as ASTM method described previously [90, 91]. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in (mg $cm^{-2}$ $h^{-1}$) [91]. The corrosion rate of mild steel was determined using the relation:

$$W = \frac{\Delta m}{St} \qquad \mathbf{2.1}$$

Where (Δm) is the mass loss, (S) the area and (t) is the immersion time.

The percentage inhibition efficiency (E %) was calculated using the relationship [91] :

$$\boldsymbol{E\%} = \left(\frac{\boldsymbol{W_{corr} - W_{corr(inh)}}}{\boldsymbol{W_{corr}}}\right) \times \mathbf{100} \qquad \mathbf{2.2}$$

Where $W_{corr}$ and $W_{corr\ (inh)}$ are the corrosion rates of mild steel in absence and presence of inhibitor, respectively.

Basic information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. So that, the degree of surface coverage values ($\theta$) at different inhibitor concentrations in 1M $H_2SO_4$ was achieved from weight loss measurements [$\theta$ = E (%) /100] at 30$^o$C and tested with Langmuir isotherm relationship [92]:

$$\frac{\boldsymbol{C}}{\boldsymbol{\theta}} = \frac{\mathbf{1}}{\boldsymbol{K_{ads}}} + \boldsymbol{C} \qquad \mathbf{2.3}$$

Where $K_{ads}$ is the equilibrium constant of the adsorption/desorption process, C (M) is the inhibitor concentration in the test solution.

According to the Langmuir isotherm, $K_{ads}$ values can be calculated from the intercepts of the straight line of plotting (C/θ versus C). Kads is related to the standard free energy of adsorption, $\Delta G^o_{ads}$, with the following equation: (The value 55.5 is the molar concentration of water in the solution)

$$\boldsymbol{K_{ads}} = \frac{\mathbf{1}}{\mathbf{55.5}}\ \boldsymbol{exp}\left(\boldsymbol{-\Delta G^{\circ}_{ads}/RT}\right) \qquad \mathbf{2.4}$$

## 2.5. Theoretical calculations

Theoretical calculations were carried out using the semi-empirical calculations with PM3 method [82]. For this purpose the Hyperchem Program [93] with complete geometry optimization was used.

The purpose of these calculations is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. Some electronic properties such as energy of the highest occupied molecular orbital (EHOMO), energy of the lowest unoccupied molecular orbital (ELUMO), energy gap (ΔE) between LUMO and HOMO and Mulliken charges on the backbone atoms for prepared compounds **[4]** to **[20]** were planned to determine.

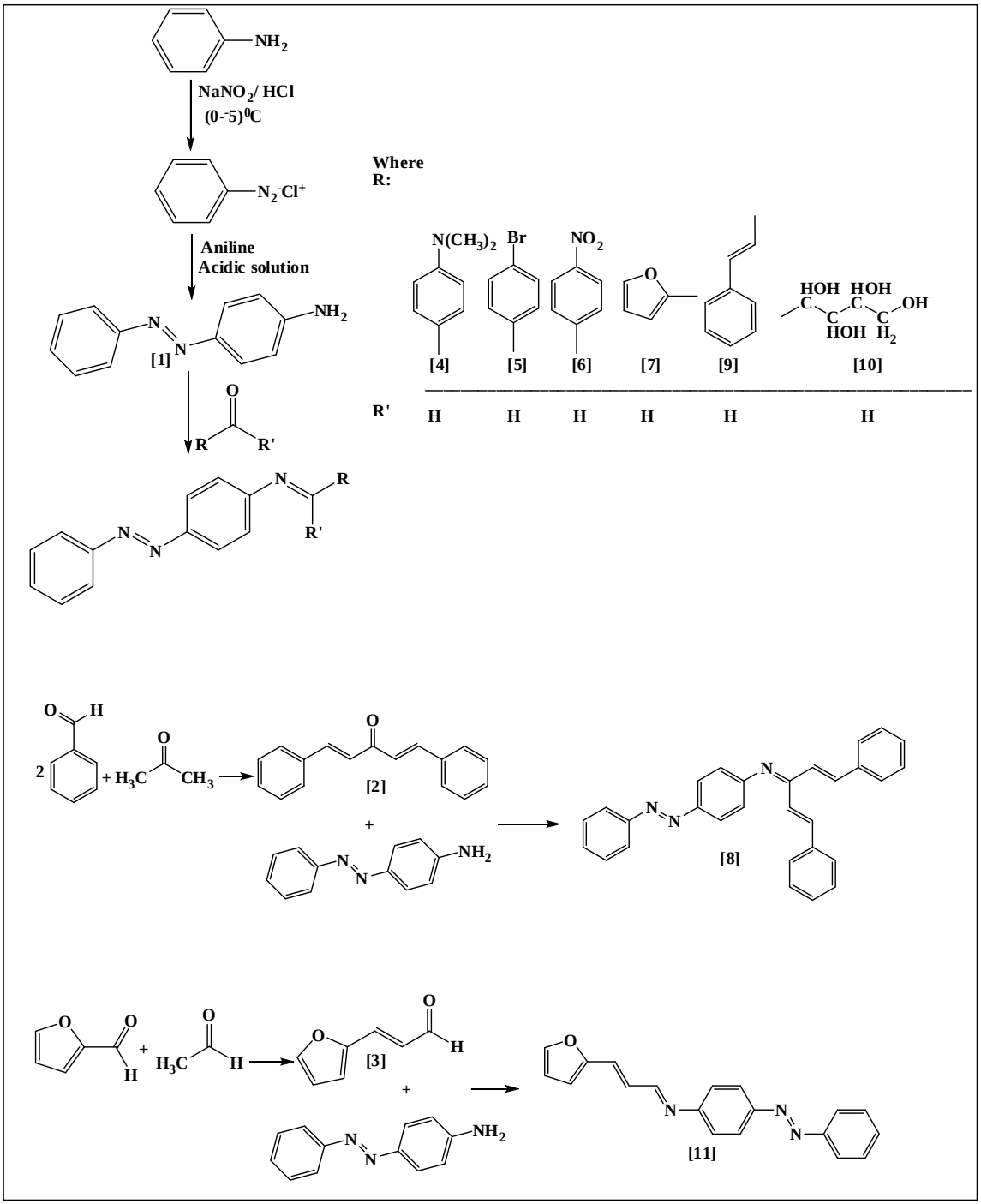
# CHAPTER THREE

# RESULT & DISCUSSION

## 3. Result & discussion

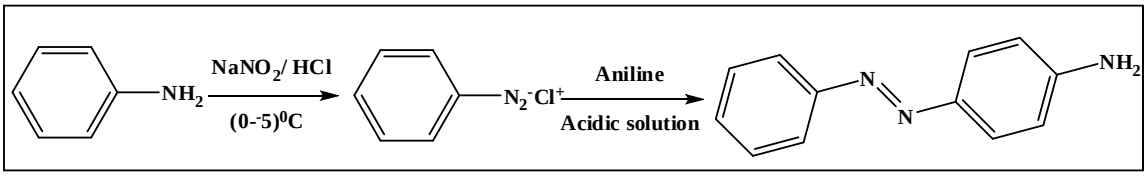
### 3.1. Synthesis of organic compounds [1-11]

First: The chemical steps for the synthesis of compounds **[1-11]** are shown in scheme 3-1

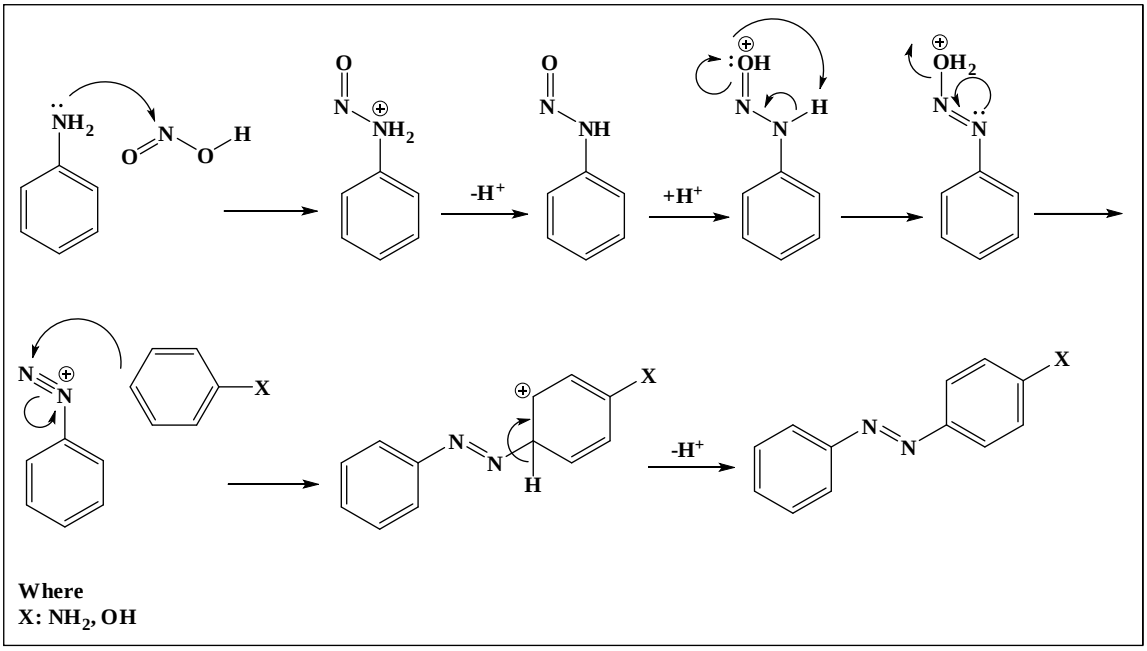



Scheme 3-1: The chemical steps for the synthesis of compounds **[1-11]**

### 3.1.1. Characterization of 4-phenyl azoaniline [1]:




The mechanism reaction for the synthesis of compound **[1]** is showed below [(94)].




The FTIR spectrum of compound **[1]** revealed a medium stretching vibration band at 1415 $cm^{-1}$ that corresponds to (N=N) bond (see Figure 3-1). In this spectrum there are three other characteristic bands at 3059$cm^{-1}$ and (3475, 3379) $cm^{-1}$ due to (C-H) aromatic and (symmetry and asymmetry) $NH_2$ stretching vibrations, respectively [(95)]. That means compound **[1]** is existing in azo form.

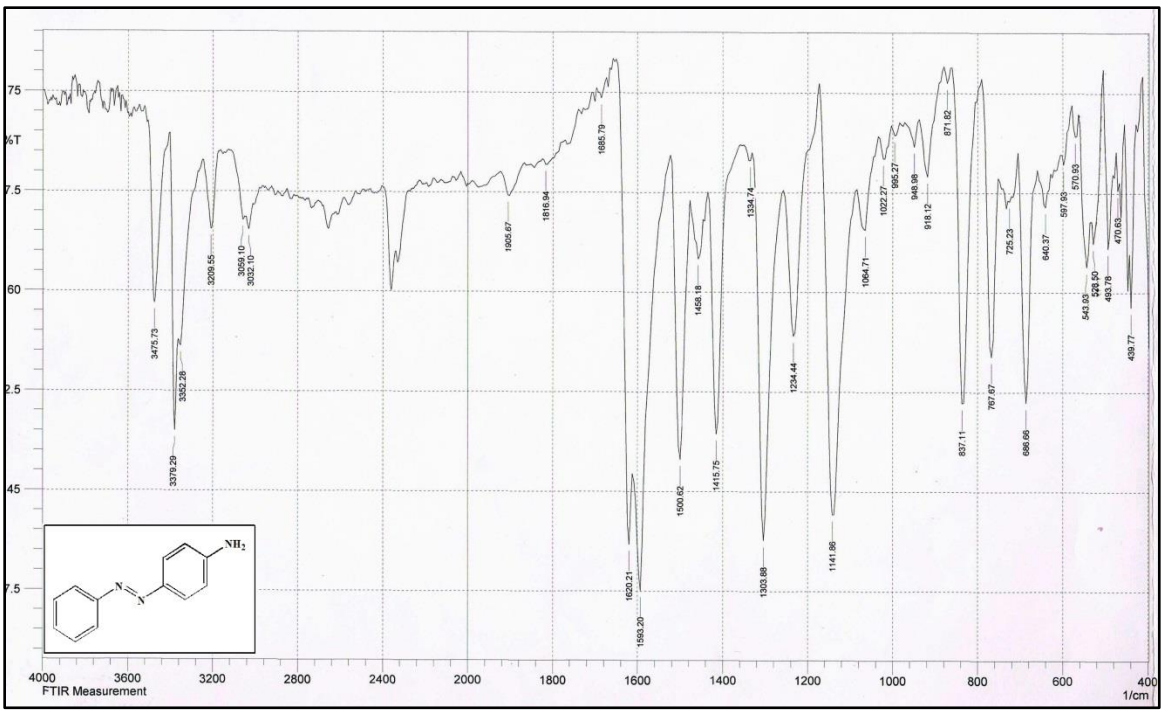
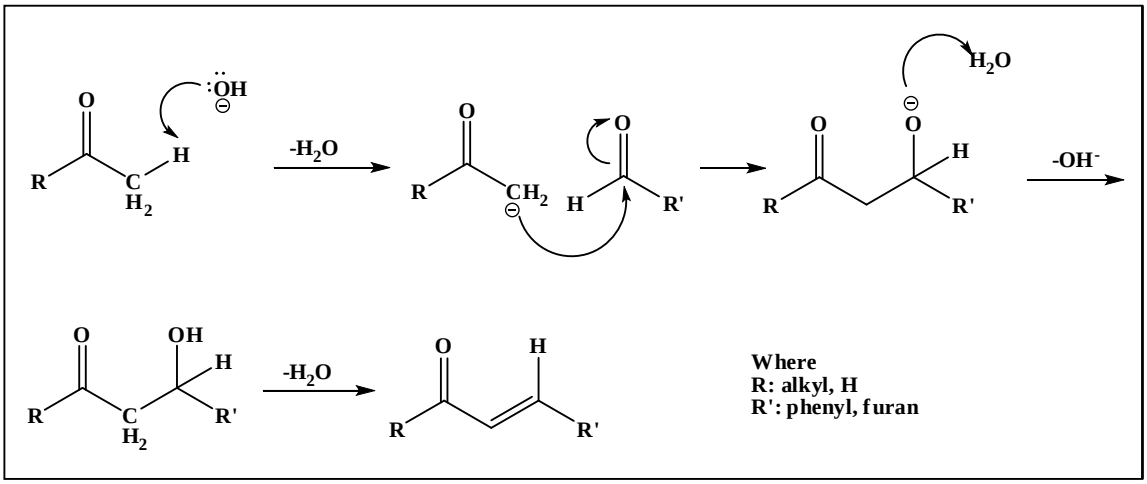



Figure 3-1: FTIR spectrum of compound **[1]**

### 3.1.2. Characterization of (1E, 4E)-1, 5-diphenylpenta-1, 4-dien-3-one & (E)-3-(furan-2-yl) acrylaldehyde [2], [3]:

These compounds were prepared by aldol condensation reaction where two molecules of an aldehyde or a ketone may combine to form a β-hydroxyaldehyde or β-hydroxyketone which is very easily dehydrated. The mechanism reaction for the synthesis of compounds **[2, 3]** was showed below [(96)].




The FTIR spectra of compounds **[2]**, **[3]** are depicted in Figures (3-2 and 3-3 respectively), and also some of their absorption bands are shown in Table 3-1.

Table 3-1: FTIR Spectral data of prepared compound **[2]**, **[3]** in $cm^{-1}$

| **Compound No.** | **Fig. No.** | **ν C-H aromatic** | **ν C=C Olfinic** | **ν C=C aromatic** | **ν C=O** | **ν C-H aldehyde** | **ν C-O** |
|---|---|---|---|---|---|---|---|
| **[2]** | 3-3 | 3051 | 1628 | 1593 | 1651 | - | - |
| **[3]** | 3-4 | 3124 | 1624 | 1546 | 1674 | 2727 | 1122 |

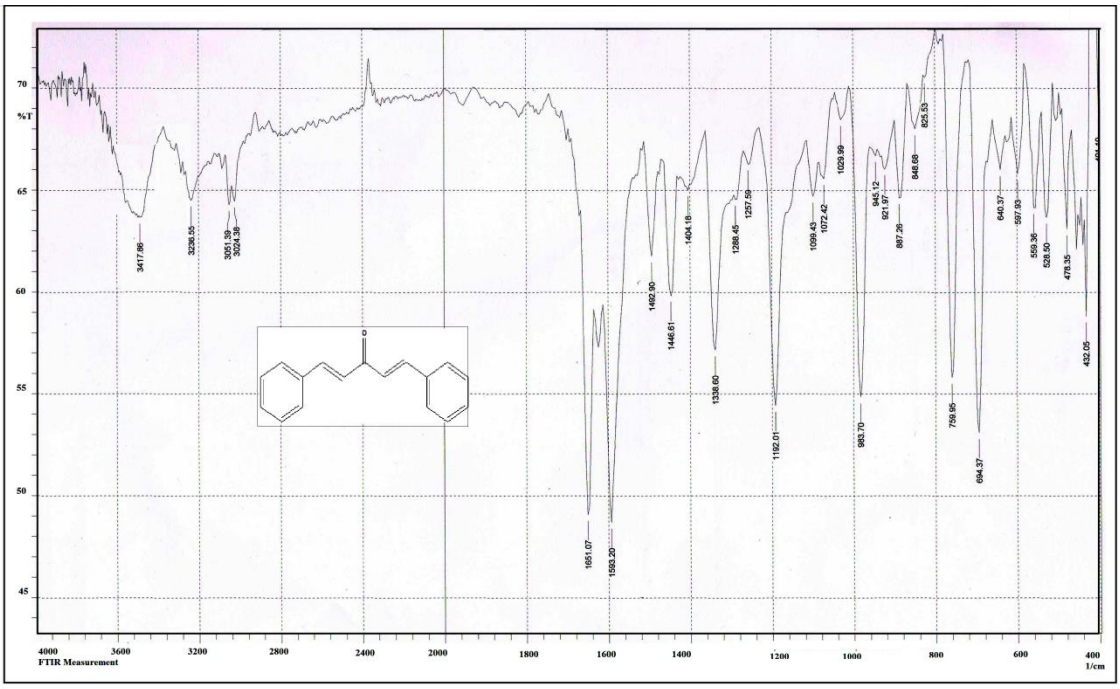



Figure3-2: FTIR Spectrum of compound **[2]**

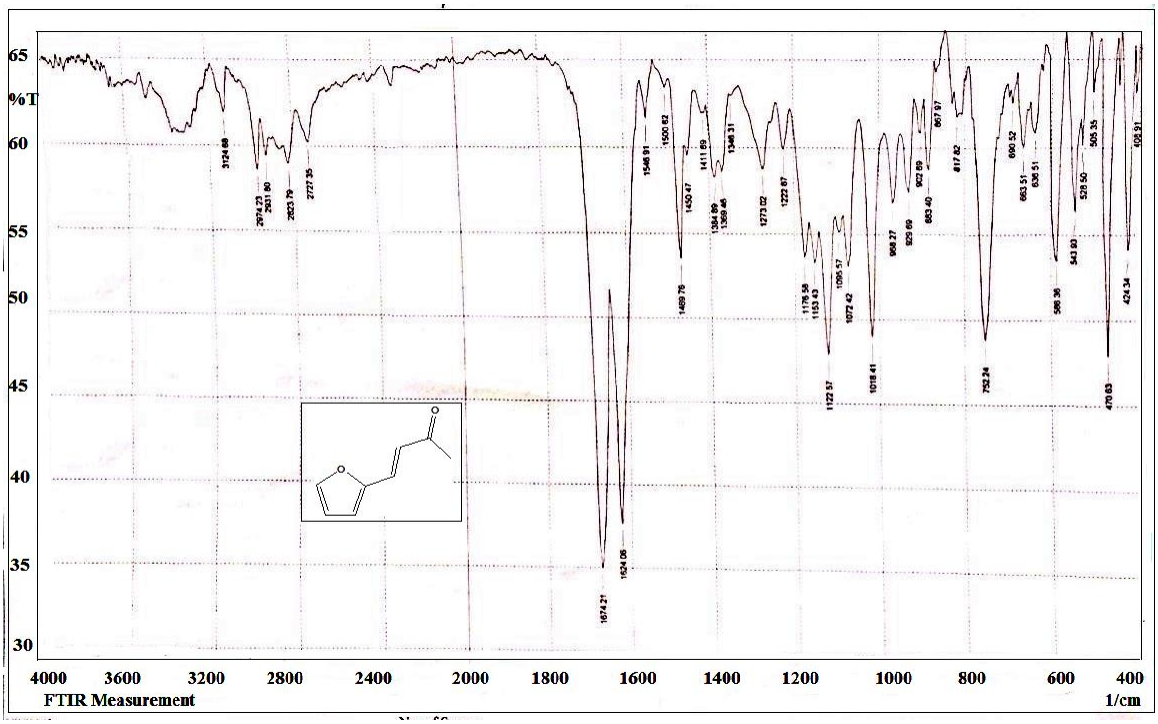



Figure 3-3: FTIR Spectrum of compound **[3]**

### 3.1.3. Characterization of N-[substituted] (E)-4-(phenyldiazenyl) aniline [4-11]:

These compounds were prepared by condensation reaction of 4-phenyl azoaniline with aldehyde or ketone in absolute ethanol.

The FTIR spectra of compounds **[4-11]** revealed disappearance of bands at (1660-1700 $cm^{-1}$) and (2700-2850 $cm^{-1}$) which belong to (C=O) and (C-H aldehyde hydrogen), respectively. In addition, appearance of absorption band of the imine (CH=N) (see table 3-2) as evidence for formation of the above compounds [97].

The FTIR spectra of compounds **[4-11]** are depicted in Figures (3-4) to (3-11) respectively, and also some of their absorption bands show in Table 3-2.

Table 3-2: FTIR Spectral data of prepared compounds **[4-11]** in $cm^{-1}$

| Compound No. | Fig. No. | ν C=N | ν N=N | ν C-H aromatic | ν C-H aliphatic | ν C=C Olfinic | C=C aromatic | ν of other bands |
|---|---|---|---|---|---|---|---|---|
| **[4]** | 3-4 | 1608 | 1435 | 3032 | 2858 | - | 1573 | C-N-C, 505 |
| **[5]** | 3-5 | 1620 | 1400 | 3043 | - | - | 1581 | C-Br, 821 |
| **[6]** | 3-6 | 1624 | 1411 | 3066 | - | - | 1577 | $-NO_2$, 1519, 1342 |
| **[7]** | 3-7 | 1643 | 1411 | 3035 | - | - | 1597 | C-O, 1238 |
| **[8]** | 3-8 | 1651 | 1408 | 3059 | 2935 | 1604 | 1523 | N-H 3360 |
| **[9]** | 3-9 | 1627 | 1438 | 3059 | 2974 | 1600 | 1573 | - |
| **[10]** | 3-10 | 1604 | 1435 | 3078 | 2933 | - | 1537 | O-H, 3342 |
| **[11]** | 3-11 | 1670 | 1411 | 3059 | 2970 | 1597 | 1504 | C-O, 1138 |

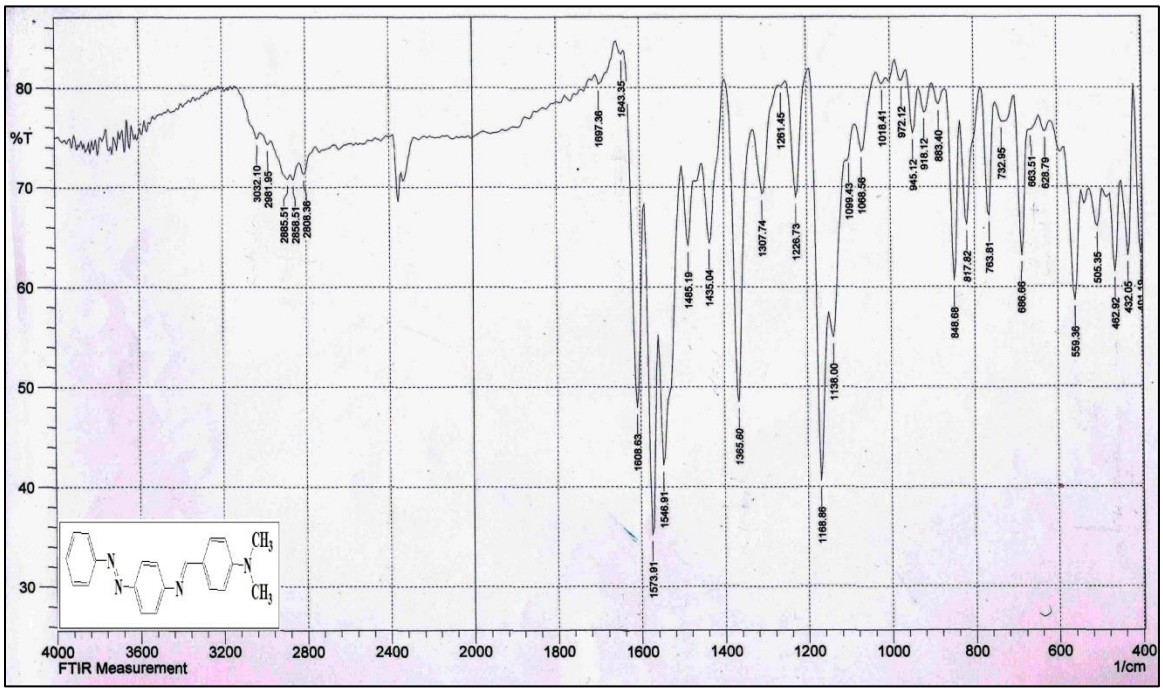



Figure 3-4: FTIR Spectrum of compound **[4]**

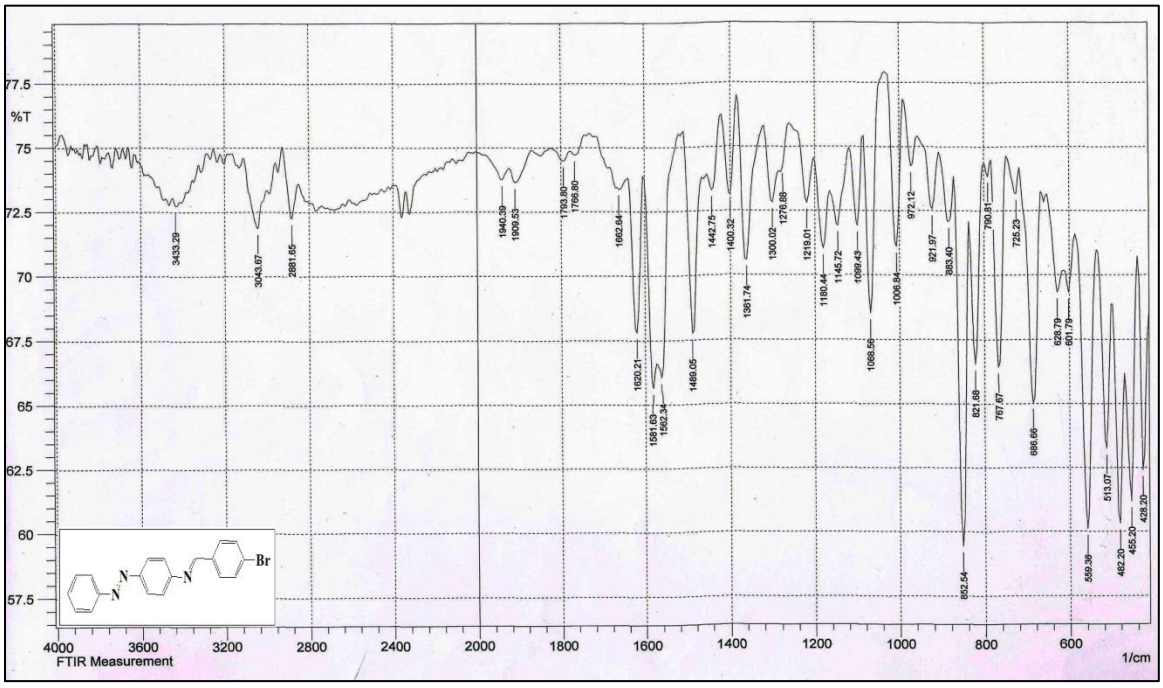



Figure 3-5: FTIR Spectrum of compound **[5]**

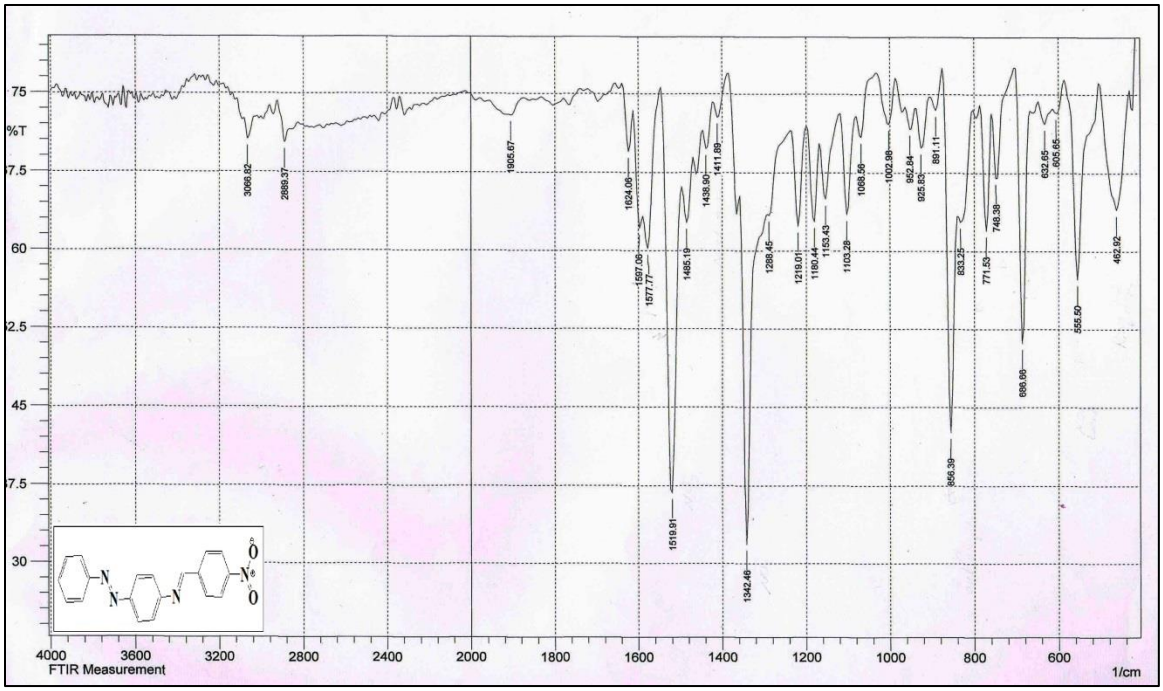



Figure 3-6: FTIR Spectrum of compound **[6]**

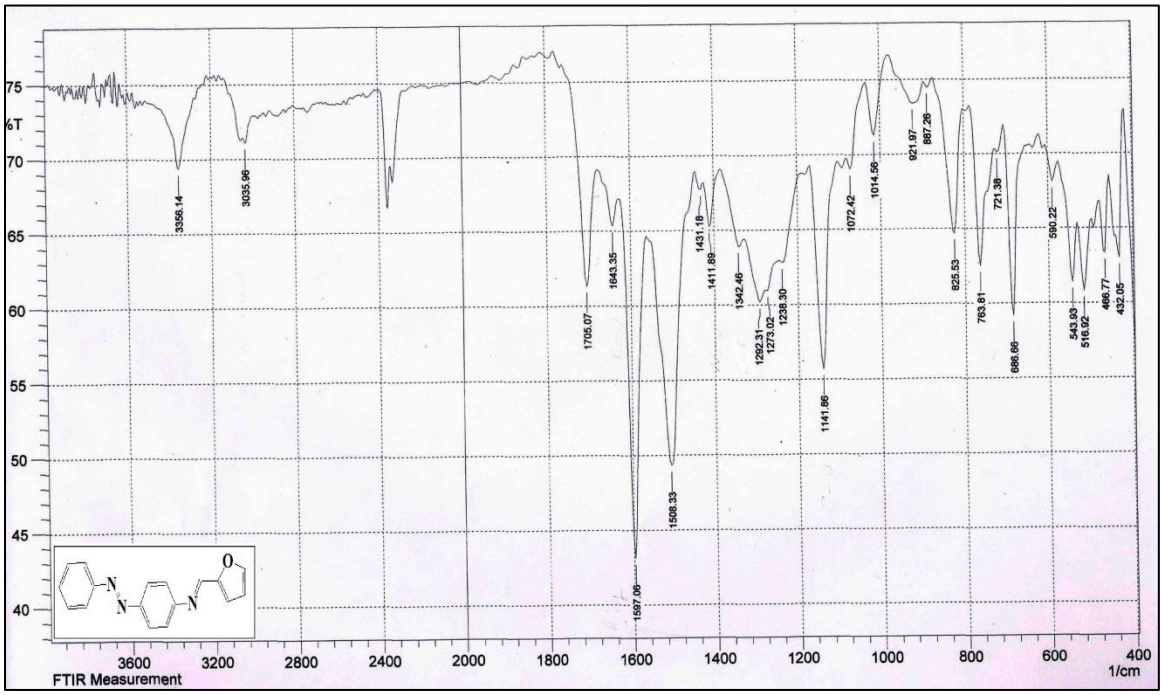



Figure 3-7: FTIR Spectrum of compound **[7]**

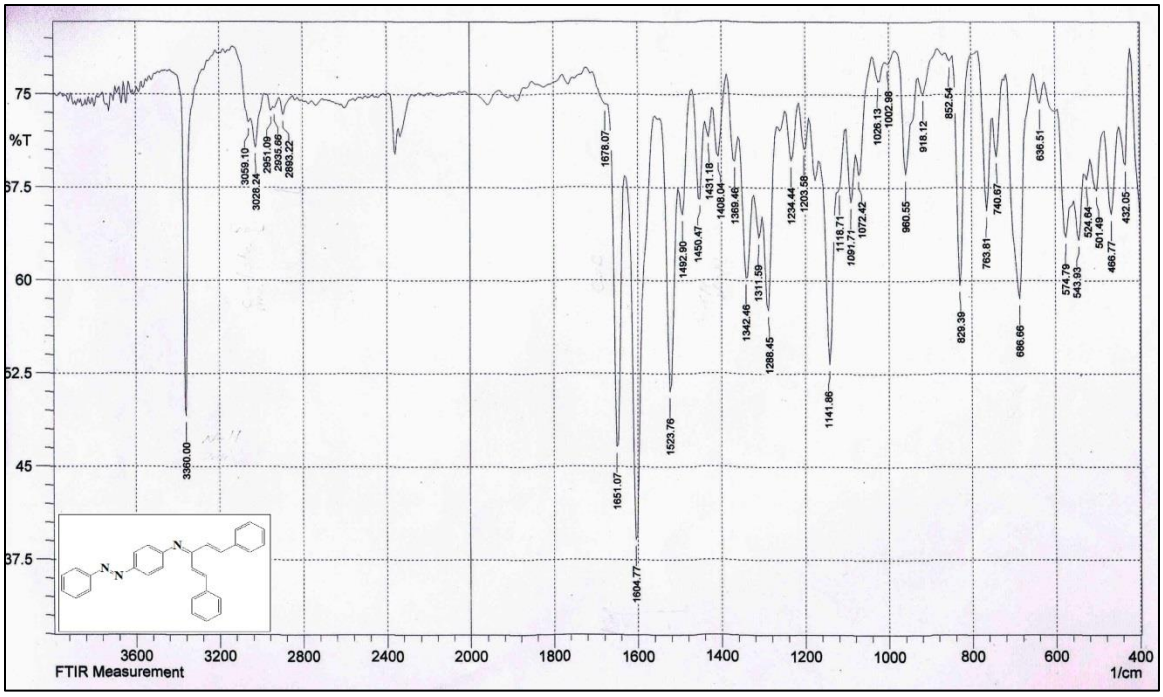



Figure 3-8: FTIR Spectrum of compound **[8]**

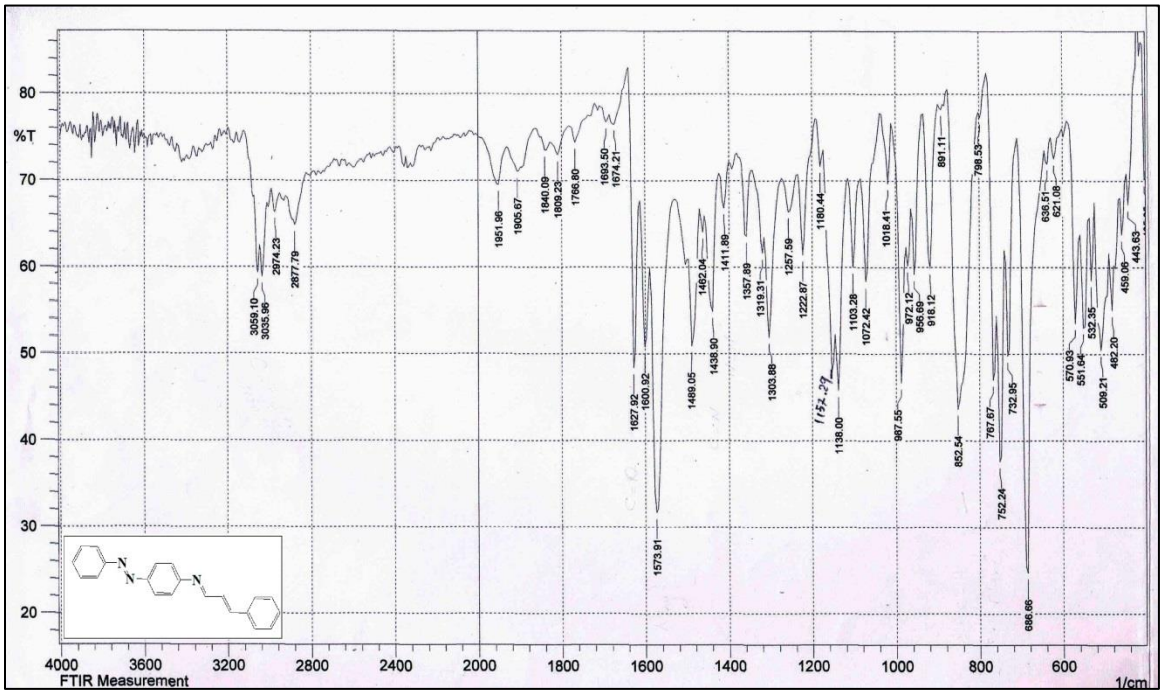



Figure 3-9: FTIR Spectrum of compound **[9]**

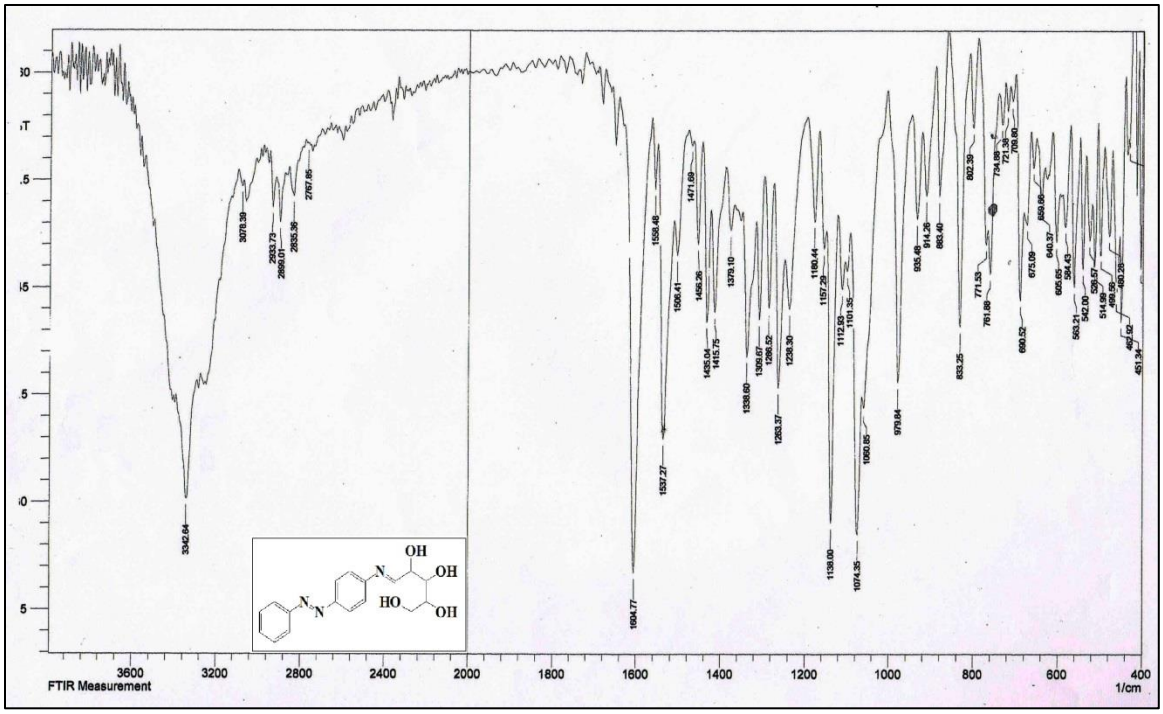



Figure 3-10: FTIR Spectrum of compound **[10]**

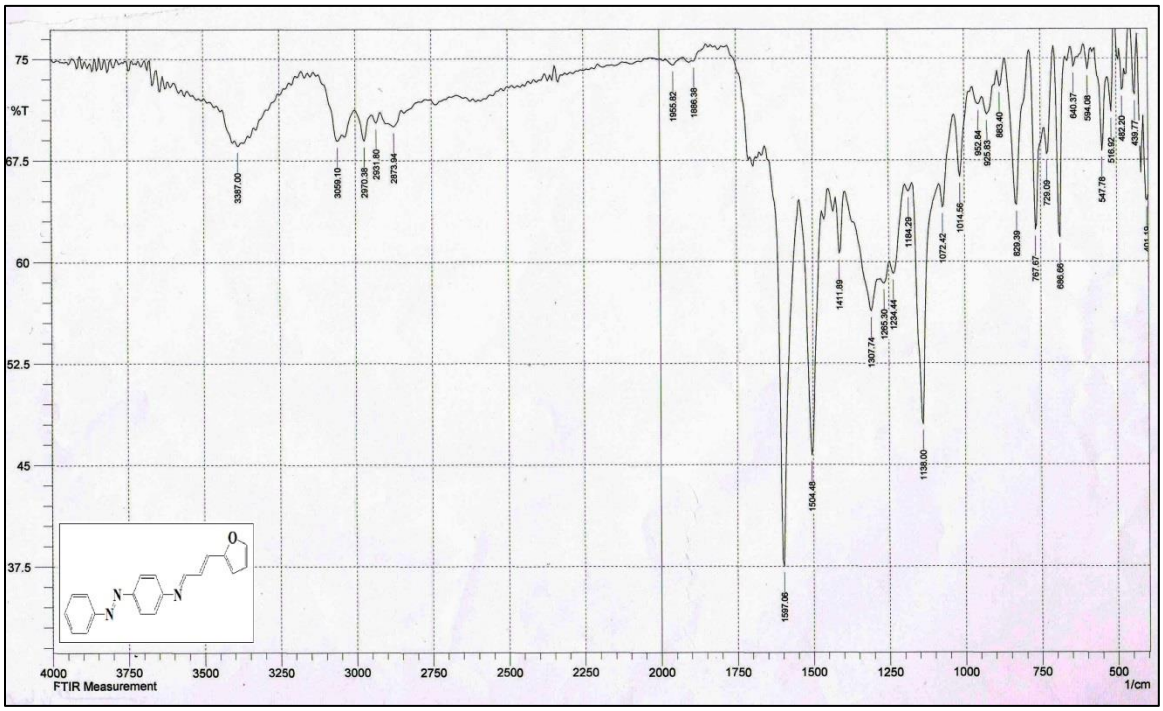
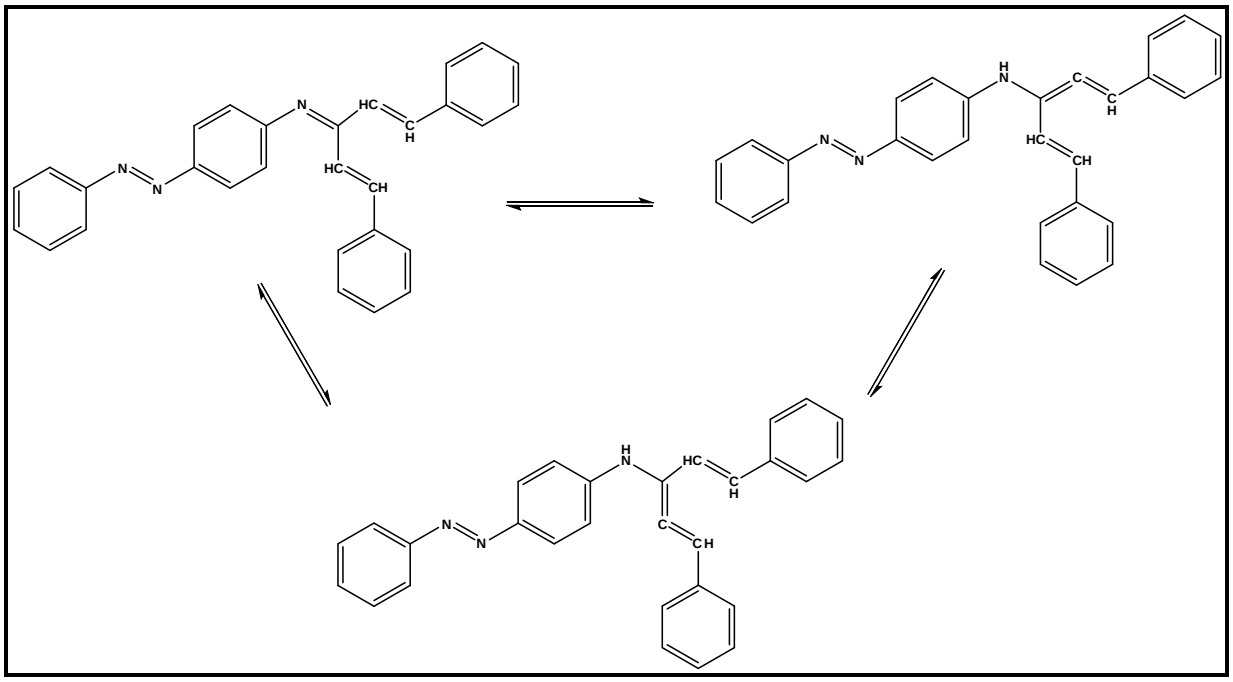



Figure 3-11: FTIR Spectrum of compound **[11]**

The FTIR spectrum of prepared compound **[8]**, which depicts in Figures (3-8), showed a tautomerism that could be occurred as below:



The appearance of absorption band of (N-H) at 3360 $cm^{-1}$ indicated the tautomerism behavior (Table 3-2).

The UV-visible spectra of the Schiff bases show two bands with maximum λ at ~370 nm and ~260 nm due to the various n→π* and π→π* transitions. The first π→π* transition is due to excitation of the π electrons of the aromatic ring, and the other n→π* transition is due to the presence of unpaired electrons in the azomethine group [(98)]. UV-visible spectra for the prepared compounds **[4-11]** in absolute ethanol are showed in Figures (3-12) to (3-19) and Table 3-3.

Table 3-3: UV-Visible Spectral data of prepared compounds **[4-11]**

| Compound No. | Fig. No. | n→π* (nm) | π→π* (nm) |
|---|---|---|---|
| **[4]** | 3-12 | 387 | 346 |
| **[5]** | 3-13 | 364 | 269 |
| **[6]** | 3-14 | 378 | 259 |
| **[7]** | 3-15 | 386 | 242 |
| **[8]** | 3-16 | 399 | 294 |
| **[9]** | 3-17 | 364 | 232 |
| **[10]** | 3-18 | 382 | 245 |
| **[11]** | 3-19 | 395 | 271 |

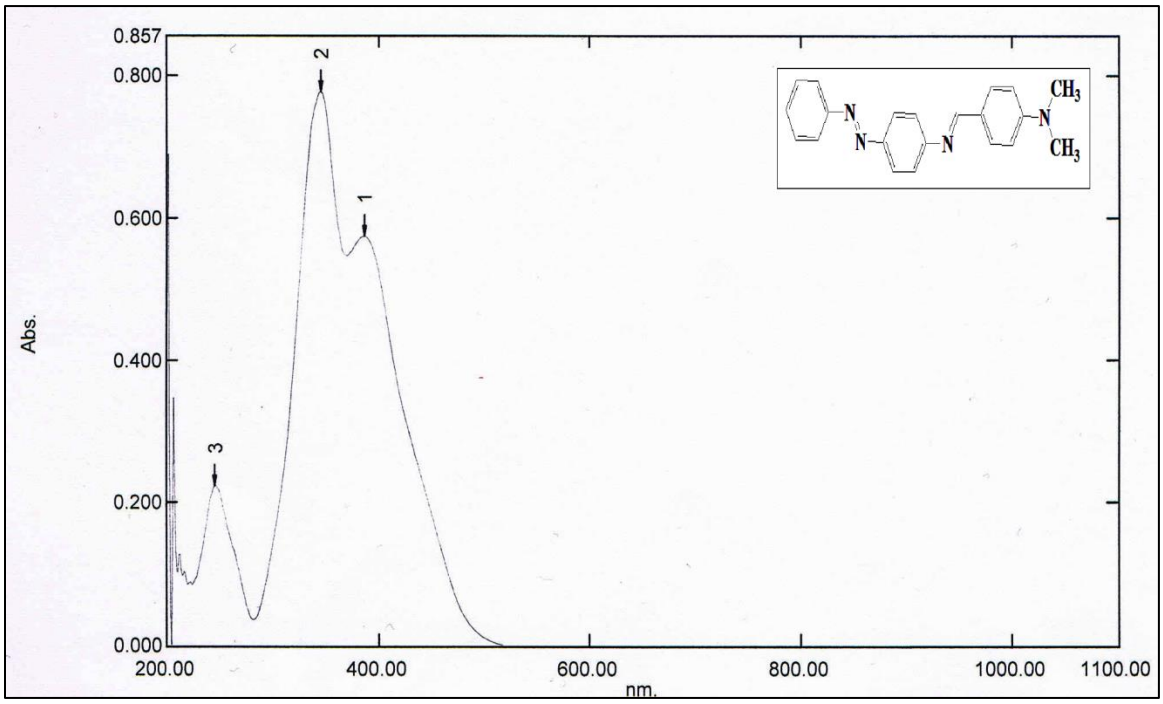



Figure 3-12: U.V. spectrum of compound **[4]**

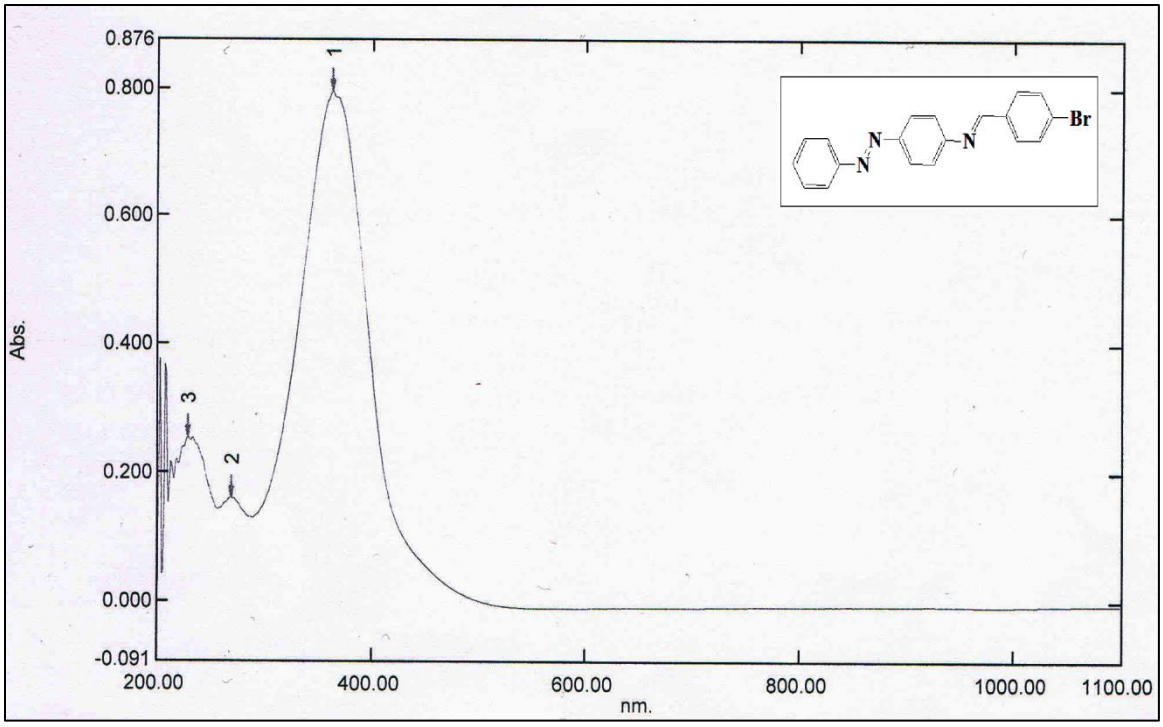



Figure 3-13: U.V. spectrum of compound **[5]**

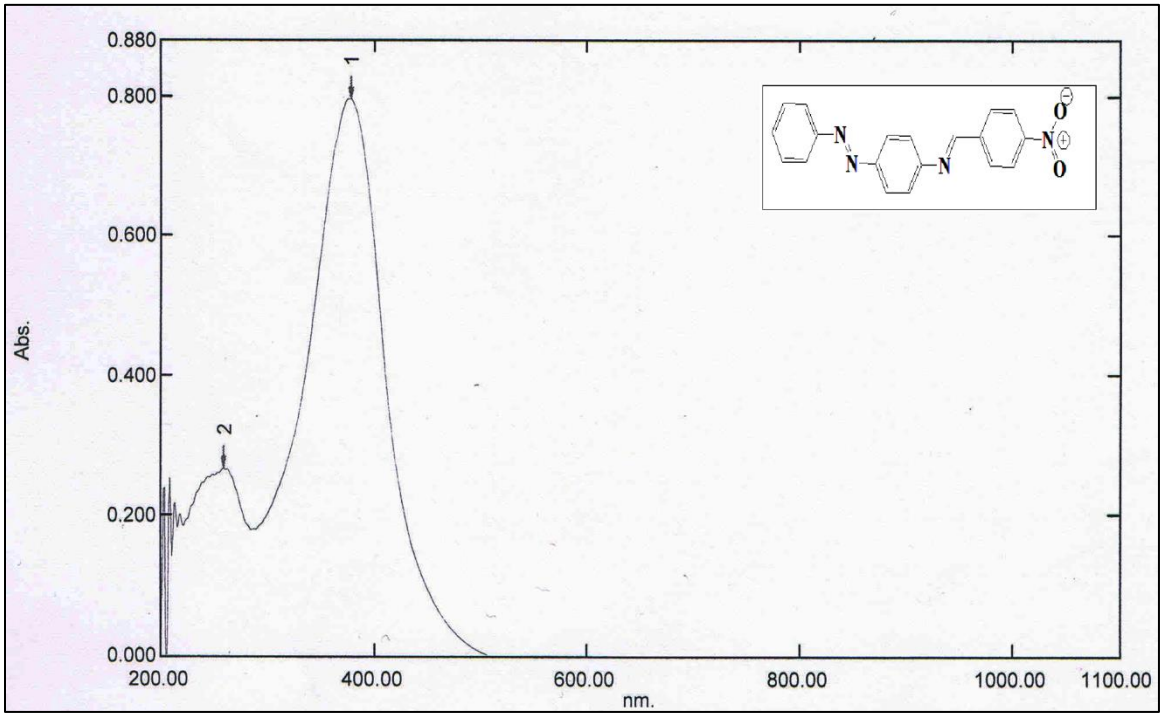



Figure 3-14: U.V. spectrum of compound **[6]**

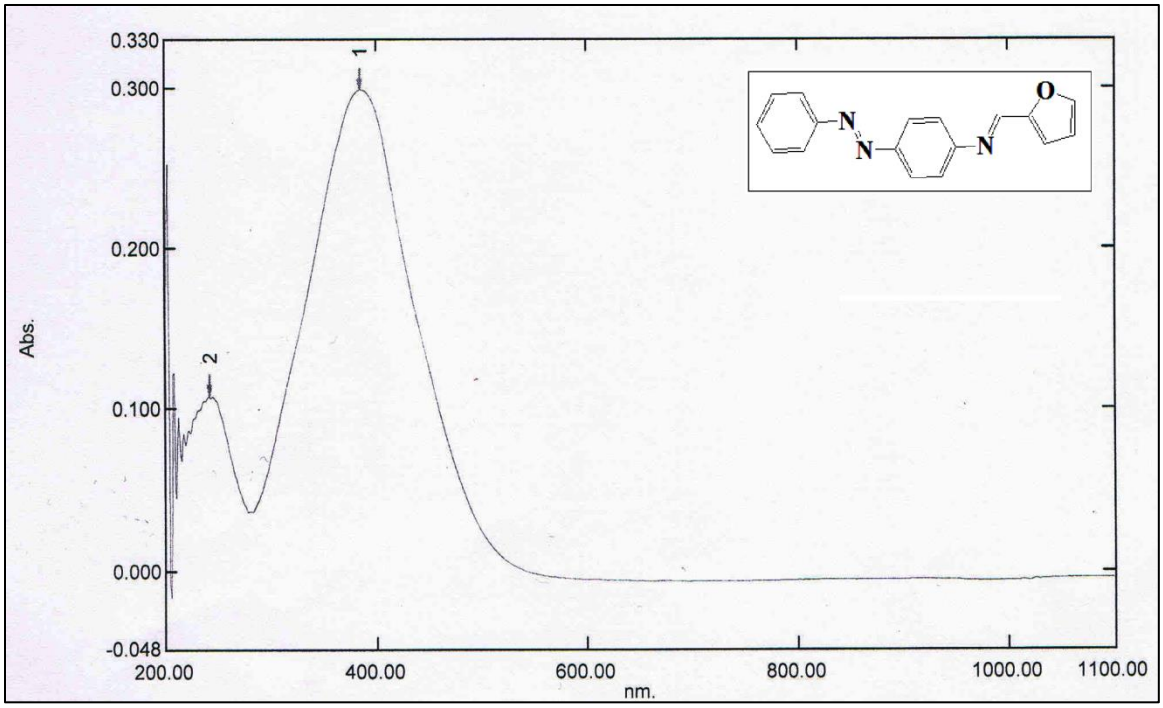



Figure 3-15: U.V. spectrum of compound **[7]**

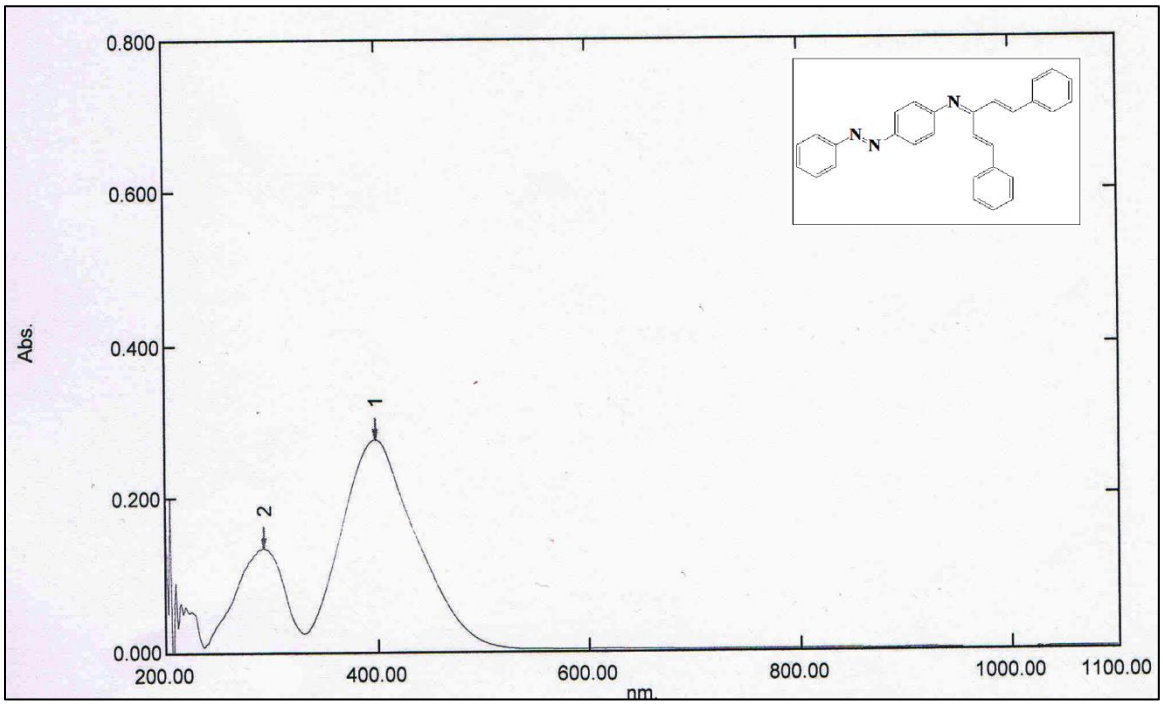



Figure 3-16: U.V. spectrum of compound **[8]**

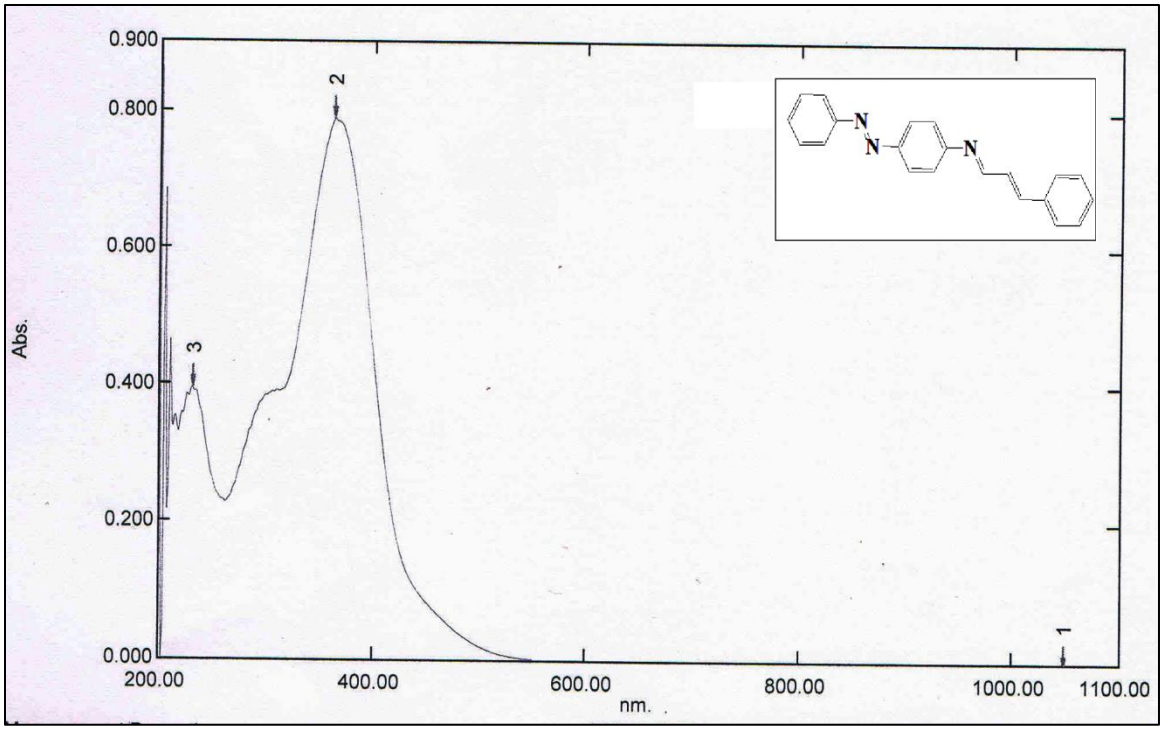



Figure 3-17: U.V. spectrum of compound **[9]**

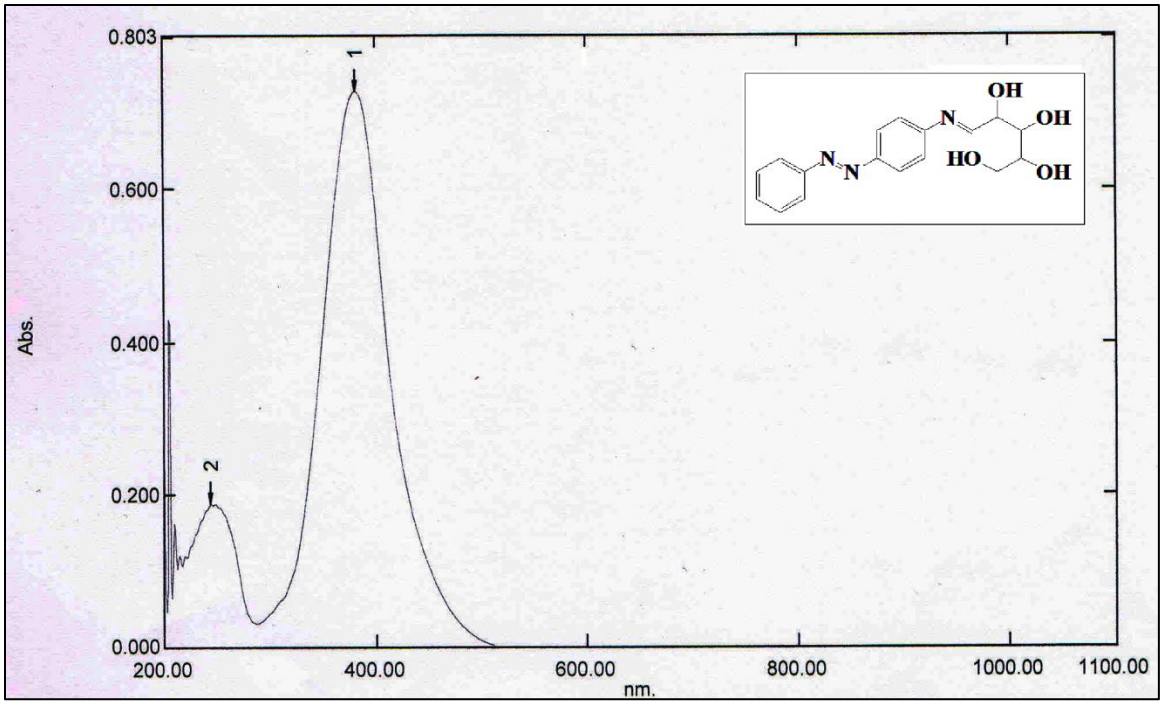



Figure 3-18: U.V. spectrum of compound **[10]**

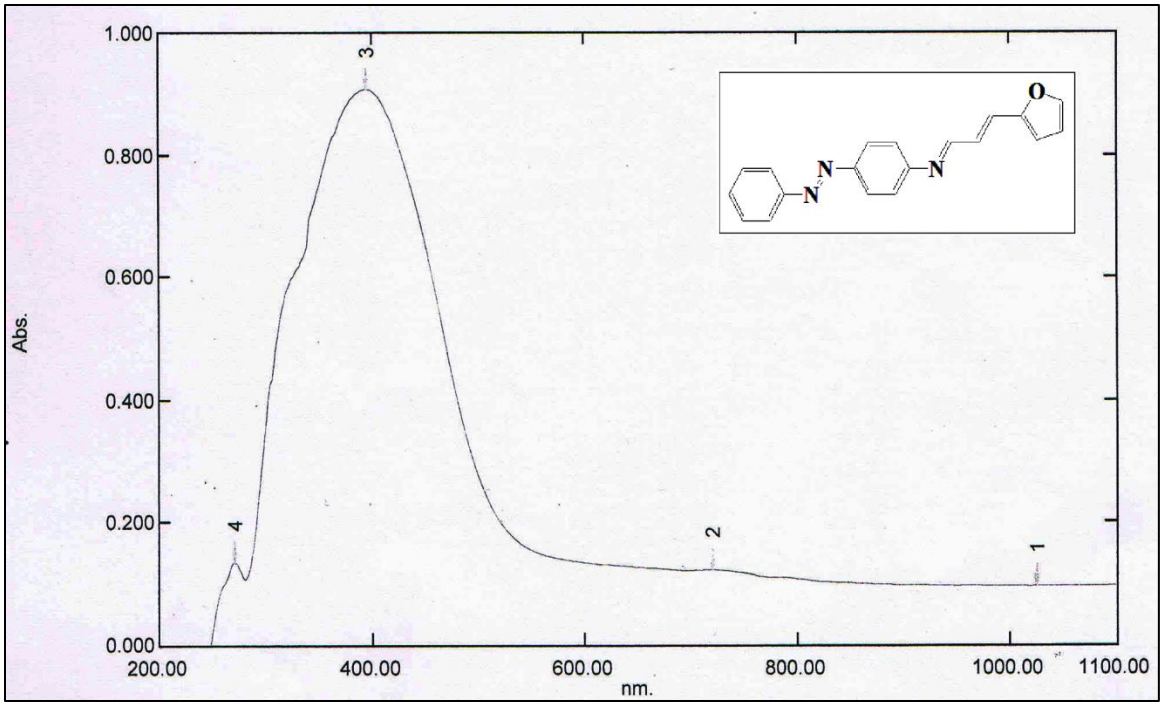



Figure 3-19: U.V. spectrum of compound **[11]**

$^{1}$H-NMR spectra of prepared compounds **[4-11]** are also used for confirming the structure of final products. Table 3-4 and Figures (3-20) to (3-24), show the following characteristic chemical shifts (ppm) in DMSO-$d_6$ as solvent. The signal at δ=2.5 ppm and δ= 3.3 ppm could be belong to DMSO-$d_6$.

Table 3-4: $^{1}$H-NMR spectral data of compounds **[4-11]** in ppm

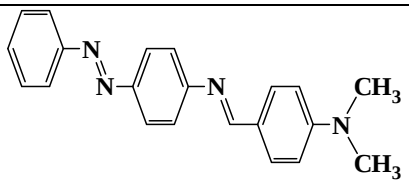
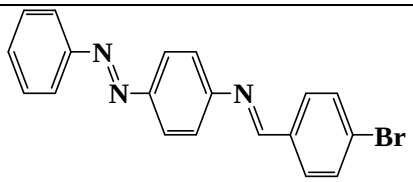
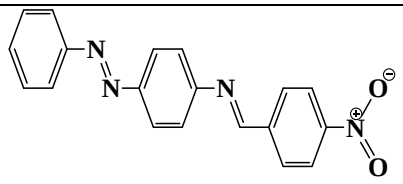
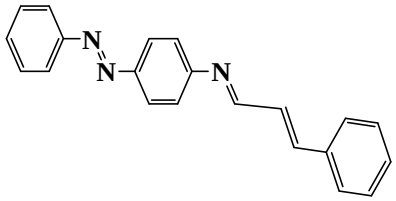
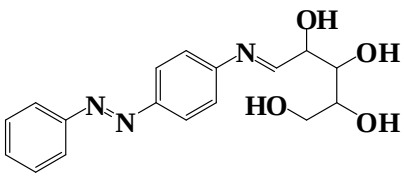
| Comp. No. | Compound structure | $^{1}$H-NMR data of ( δ-H) in ppm | Fig. No. |
|---|---|---|---|
| **[4]** |  | 3.038 [Singlet, 6H, -N-(–$CH_3$)$_2$], 6.799-6.975[doublet of doublet,4H, **ph**-N($CH_3$)$_2$], 7.382-7.602 (doublet of doublet, 4H, **ph**-N=CH-ph), 7.705-7.879(doublet of doublet, 4H, **ph**-N=N-ph), 7.951[triplet, proton in *p*-position of aromatic ring linked to (N=N)] 8.520 (Singlet, 1H, -N=CH-) | 3-20 |
| **[5]** |  | 7.476-7.573(doublet of doublet,4H, **ph**-N=CH-ph), 7.760-7.899 (doublet of doublet, 4H, **ph**-Br), 7.949-7.997 (doublet of doublet, 4H, **ph**-N=N-ph), 7.639 [triplet, proton in *p*-position of aromatic ring linked to (N=N)], 8.738 (Singlet, 1H, -N=CH-) | 3-21 |
| **[6]** |  | 7.584-7.597 (doublet of doublet, 4H, **ph**-N=CH-ph) 8.001-8.016 (doublet of doublet, 4H, **ph**-N=N-ph) 8.393-8.409 (doublet of doublet, 4H, **ph**-$NO_2$) , 7.924[triplet, proton in *p*-position of aromatic ring linked to (N=N)], 8.918(Singlet, 1H, -N=CH-) | 3-22 |
| **[9]** |  | 6.888 (doublet, 1H, -C**H**=CH-ph), 7.216 (doublet, 1H, -CH=C**H**-ph), 7.268-7.395 (doublet of doublet, 4H, **ph**-N=CH-CH), 7.707-7.729 (doublet of doublet, 4H, **ph**-CH=CH), 7.612 [triplet, proton in *p*-position of aromatic ring linked to (CH=CH)], 7.947-7.973 (doublet of doublet, 4H, **ph**-N=N), 7.488 [triplet, proton in *p*-position of aromatic ring linked to (N=N)], 8.253(Singlet, 1H, -N=CH-) | 3-23 |

Table 3-4: Continued

| Comp. No. | Compound structure | $^1$H-NMR data of ( δ-H) in ppm | Fig. No. |
|---|---|---|---|
| **[10]** |  | 3.402-3.643 [quartet, 2H, the two (-C-H) near to (N=CH)], 3.707 [quintet, 1H, (-C-H) far to (N=CH)], 3.867 (triplet, 2H, -$CH_2$), 4.475-4.920 [doublet, 3H, the three (O-H) linked to (C-H)], 5.098 [triplet, 1H, (O-H) linked to $CH_2$], 8.077(Singlet, 1H, -N=CH-) | 3-24 |

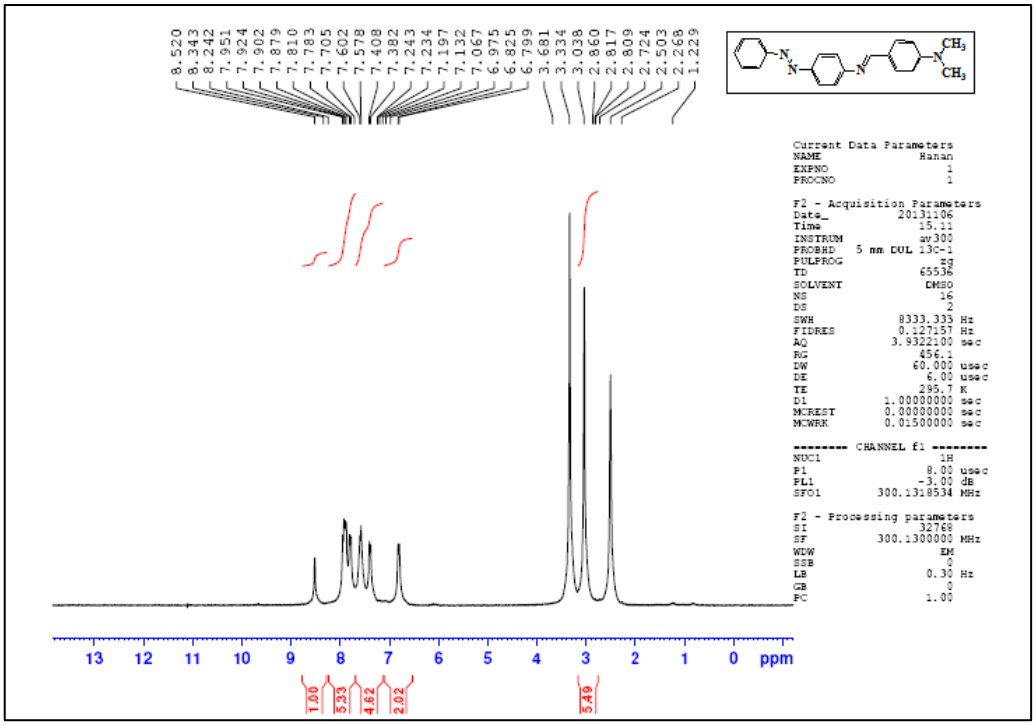



Figure 3-20:$^1$H-NMR Spectrum of compound **[4]**

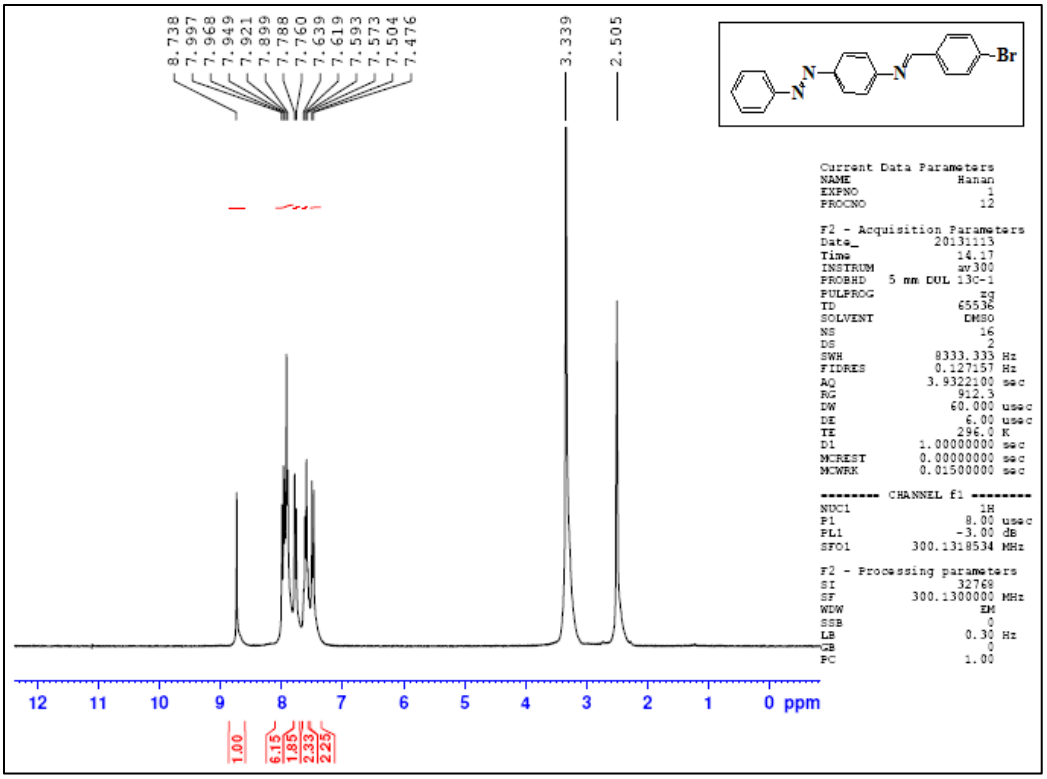



Figure 3-21: $^{1}$H-NMR Spectrum of compound **[5]**

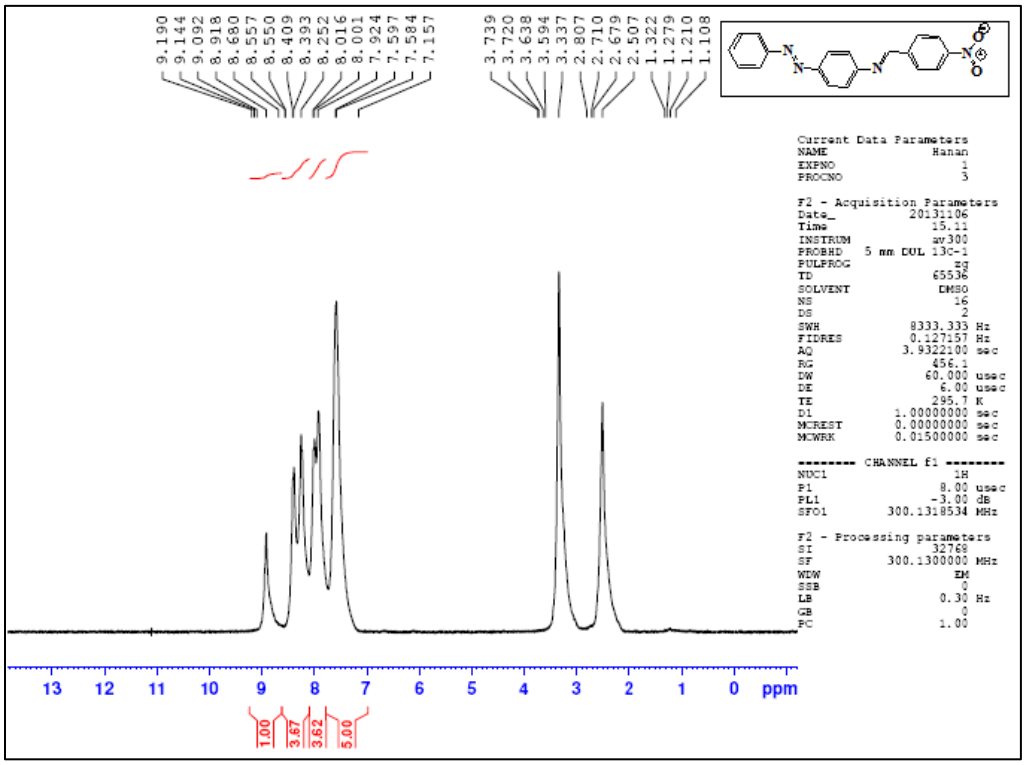



Figure 3-22: $^{1}$H-NMR Spectrum of compound **[6]**

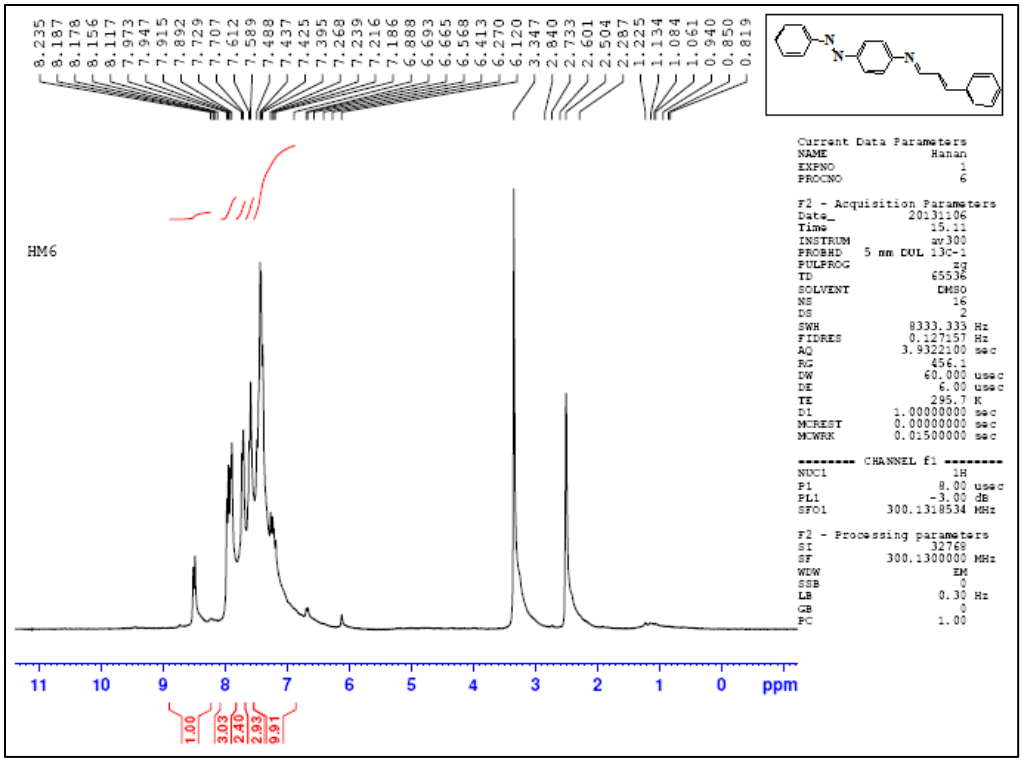



Figure 3-23: $^{1}$H-NMR Spectrum of compound **[9]**

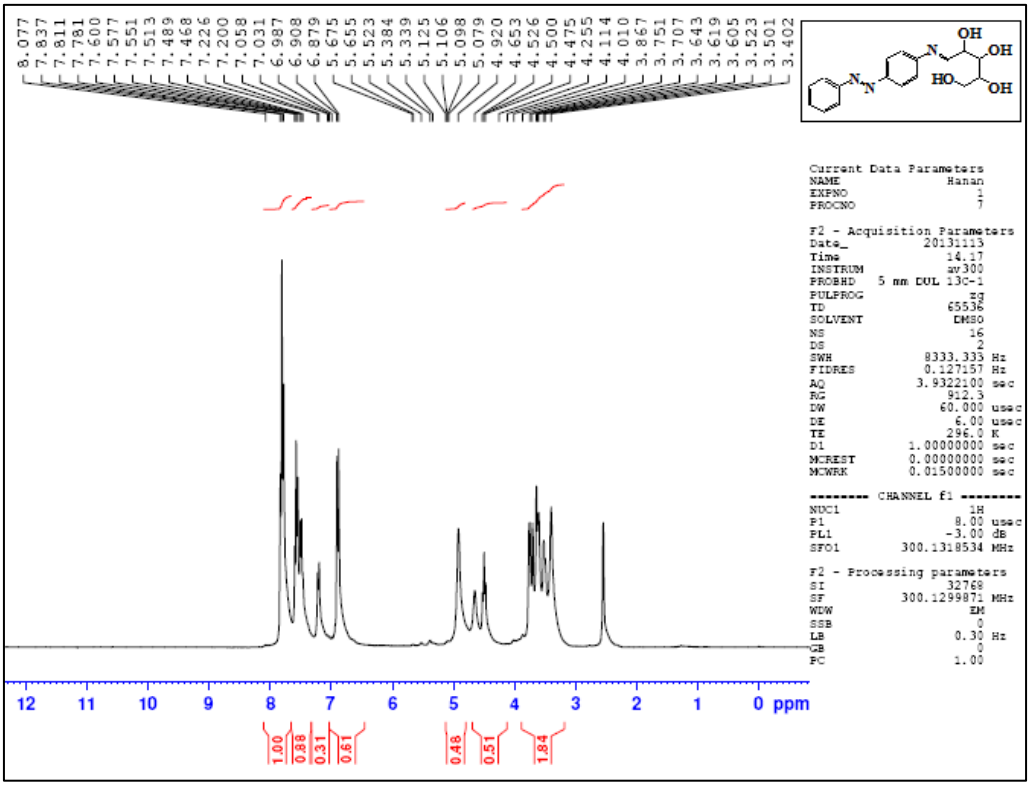



Figure 3-24: $^{1}$H-NMR Spectrum of compound **[10]**

$^{13}$C-NMR spectra were also used for characteristic of the Schiff base structures. Table 3-5 and Figures (3-25) to (3-31) are shown the characteristic chemical shifts of prepared compounds **[4-10]** in ppm, where DMSO-$d_6$ chemical shifts (as solvent) occurs at δ= 39.51 ppm.

Table 3-5: $^{13}$C-NMR spectral data of compounds **[4-10]** in ppm

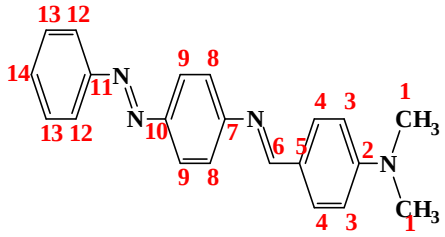
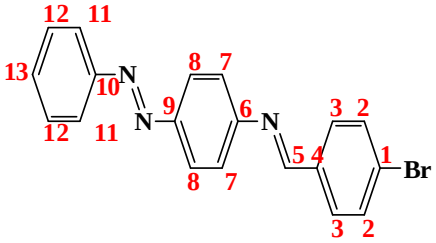
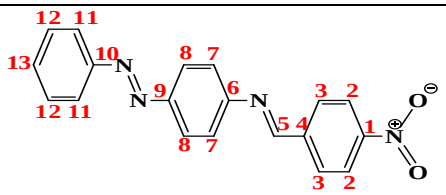
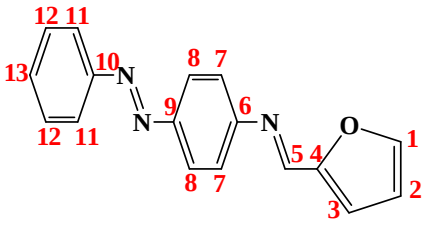
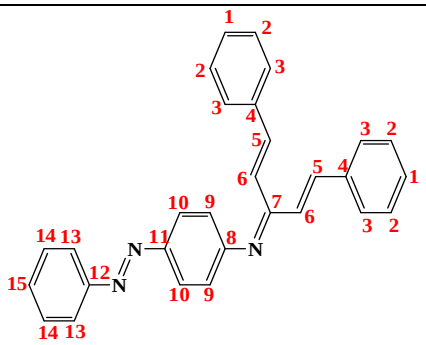
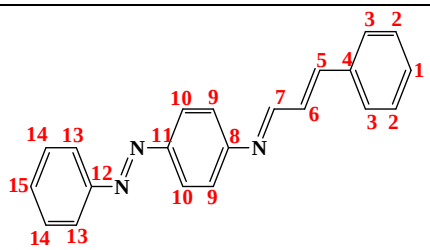
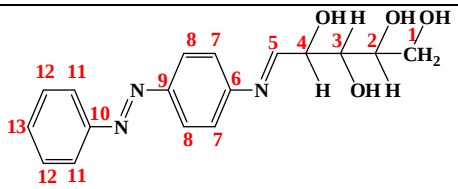
| Comp. No. | Compound structure | $^{13}$C-NMR data of ( δ-C) in ppm | Fig. No. |
|---|---|---|---|
| **[4]** |  | C1= 40.263, C2= 155.651, C3= 111.932, C4=129.913, C5= 124.355, C6=161.473, C7= 152.532, C8= 122.872, C9= 122.403, C10= 149.685, C11= 153.144, C12=123.988, C13= 131.187, C14= 131.603 | 3-25 |
| **[5]** |  | C1=122.483, C2=130.709, C3= C12=123.829, C4=131.974, C5=160.928, C6=C10=153.750, C7=C8=C11=122.150, C9=150.007, C13=129.456 | 3-26 |
| **[6]** |  | C1=C6=148.086, C2=123.057, C3=124.354, C4= 130.431, C5=155.202, C7= C8=C11=122.917, C9=C10=136.563, C12=124.570, C13=129.974 | 3-27 |

Table 3-5: Continued

| Comp. No. | Compound structure | $^{13}$C-NMR data of ( δ-C) in ppm | Fig. No. |
|---|---|---|---|
| [7] |  | C1= 129.177, C2= 112.246, C3= 117.031, C4= 129.488, C5= 139.938, C6= 121.777, C7= 112, 246, C8=C11= 122.298, C9= 145.643, C10= 122.124, C12= 124.244, C13= 129.307 | 3-28 |
| [8] |  | C1= 126.380, C2= 128.454, C3= 129.145, C4= 134.404, C5= 142.521, C6= 112.482, C7= 152.857, C8= 151.155, C9= 121.677, C10= 113.340, C11= 143.244, C12= 152.419, C13= 124.831, C14= 129.461, C15= 130.502 | 3-29 |
| [9] |  | C1= 123.854, C2= 127.756, C3= 129.443, C4= 129.087, C5= 122.462, C6= 145.457, C7= 135.313, C8= 122.651, C9= 121.955, C10= 129.864, C11= 131.307, C12= 128.237, C13= 128.980 | 3-30 |
| [10] |  | C1= 66.263, C2= 69.995, C3= 73.489, C4= 68.080, C5= 169.568, C6= 150.758, C7= C11=124.680, C8= 121.831, C9= 152.307, C10= 161.846, C12=129.205, C13= 129.747 | 3-31 |

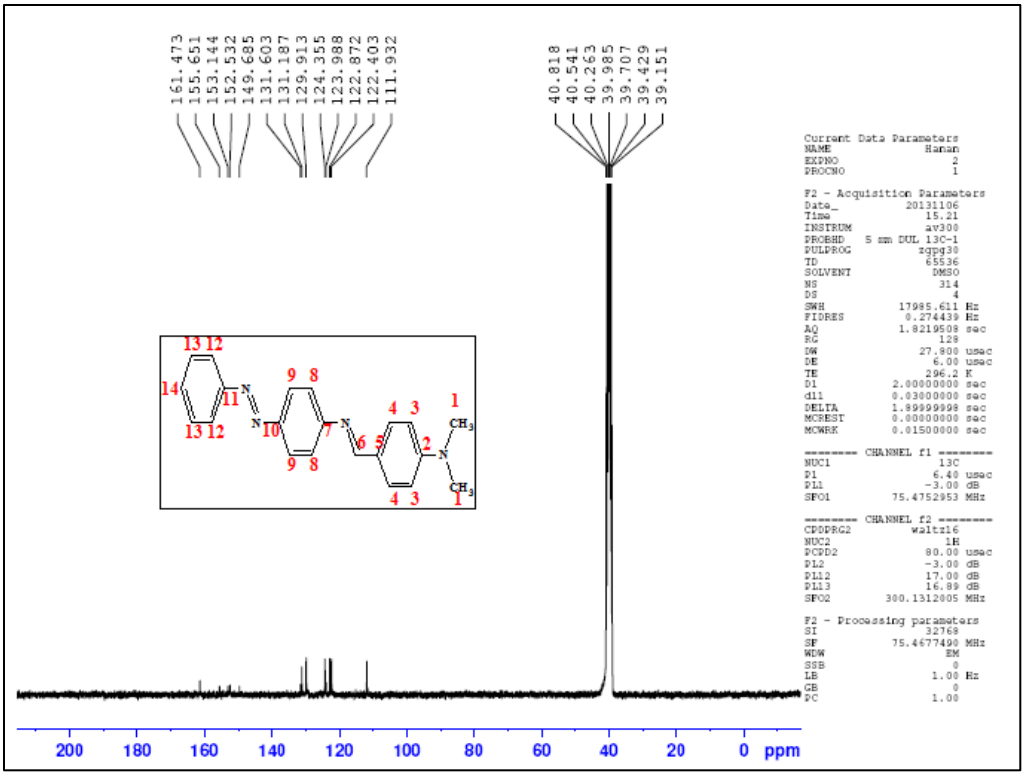



Figure 3-25: $^{13}$C-NMR Spectrum of compound **[4]**

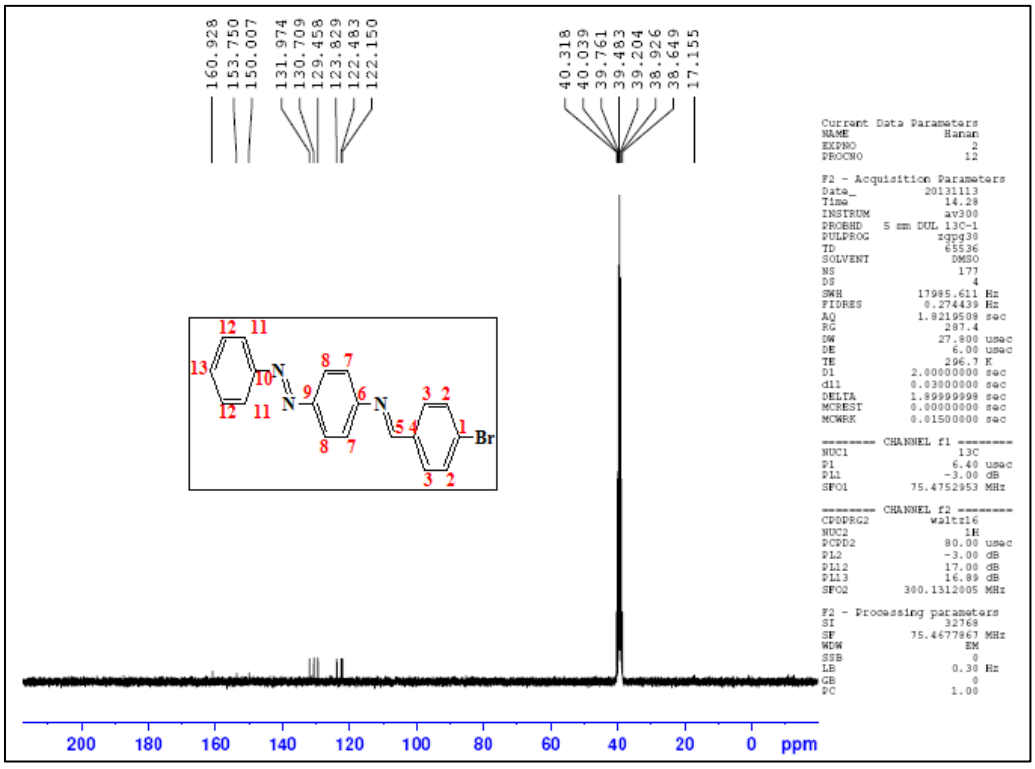



Figure 3-26: $^{13}$C-NMR Spectrum of compound **[5]**

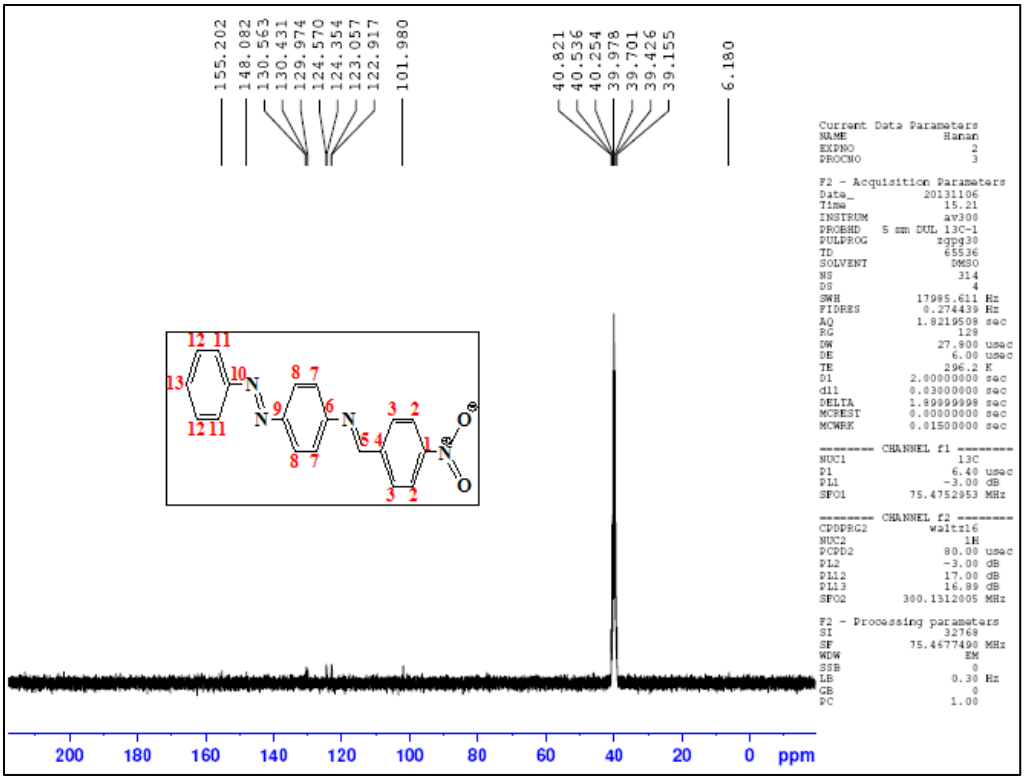



Figure 3-27: $^{13}$C-NMR Spectrum of compound **[6]**

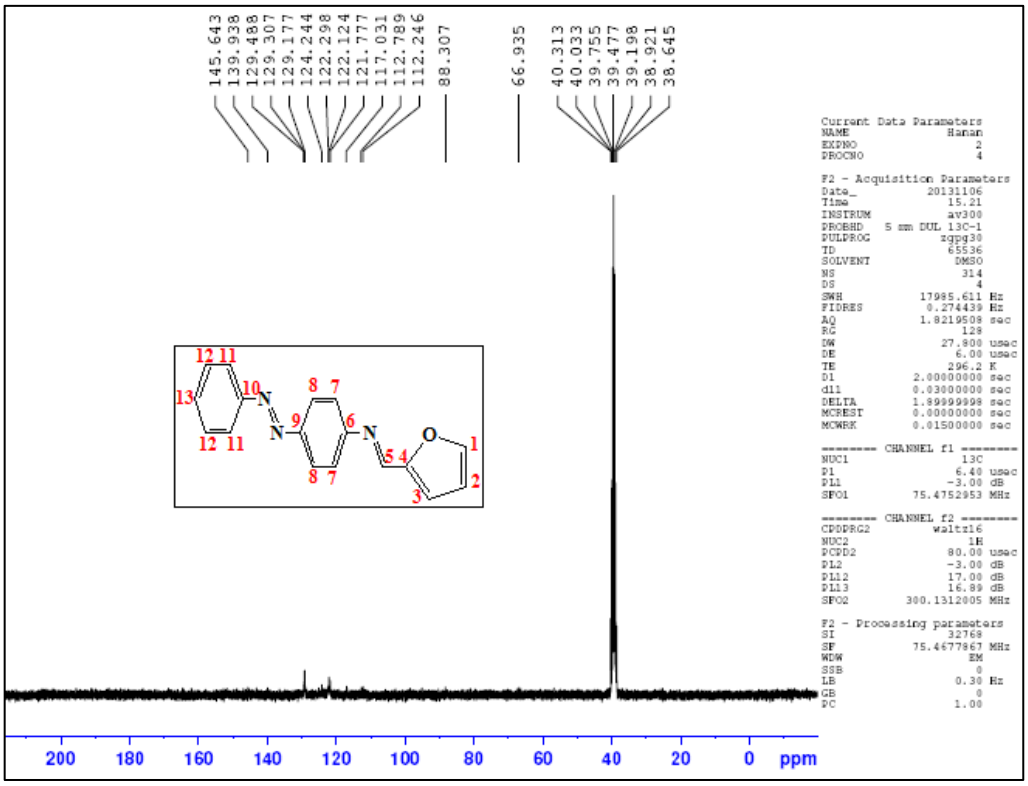



Figure 3-28: $^{13}$C-NMR Spectrum of compound **[7]**

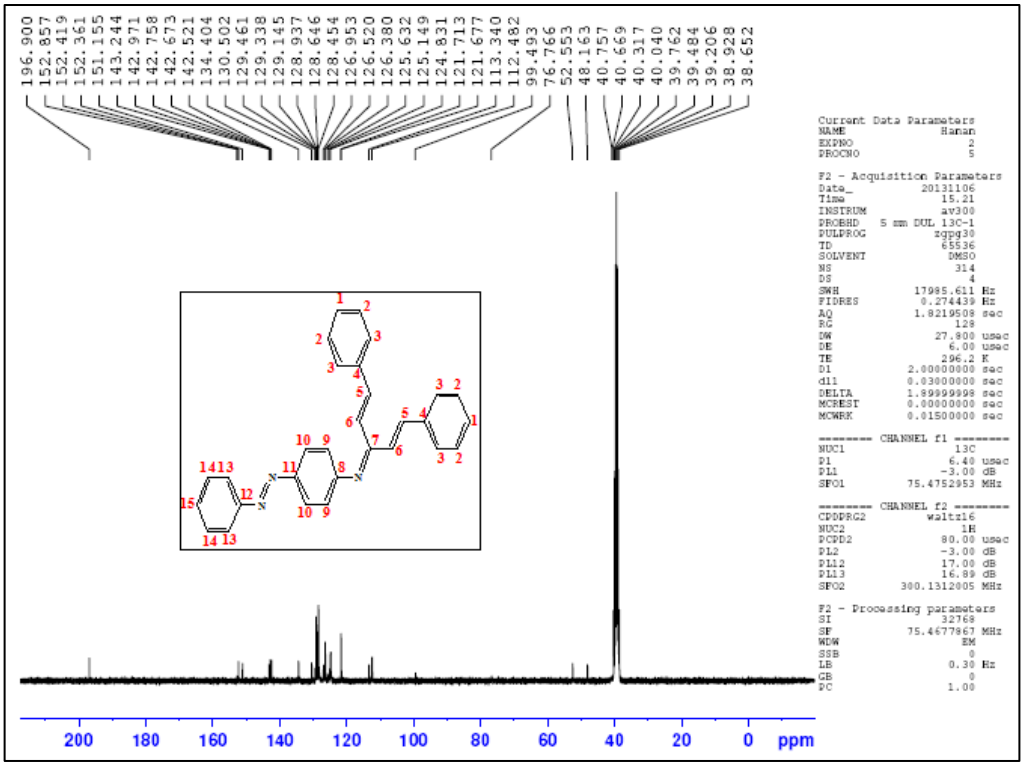



Figure 3-29: $^{13}$C-NMR Spectrum of compound **[8]**

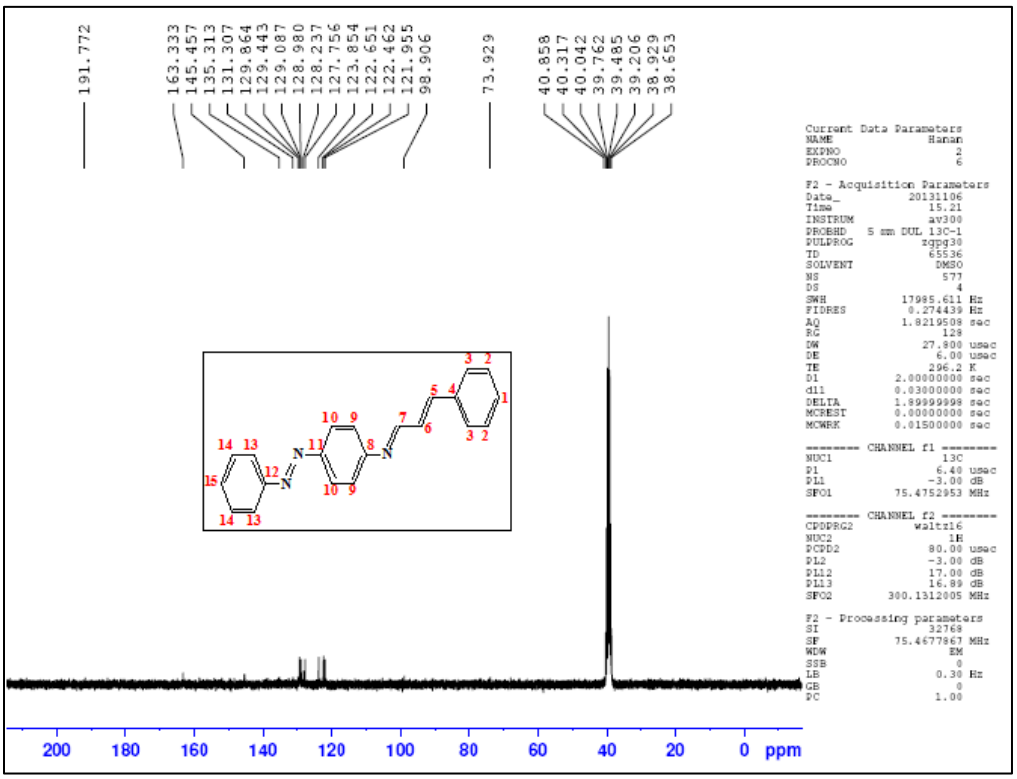



Figure 3-30: $^{13}$C-NMR Spectrum of compound **[9]**

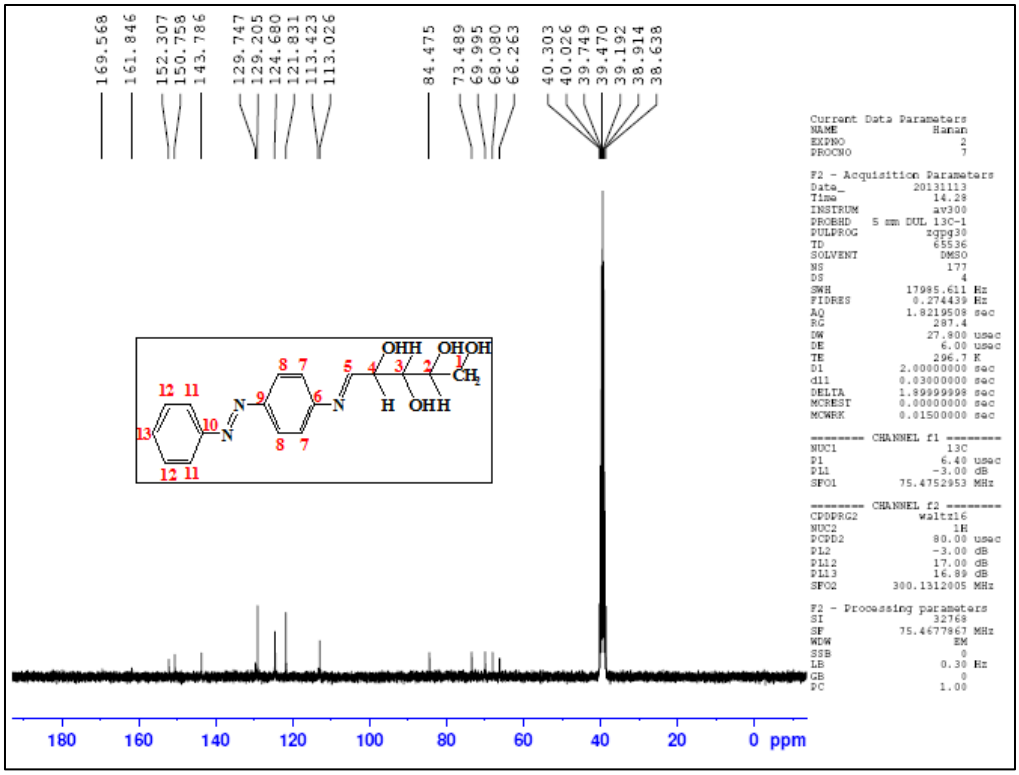
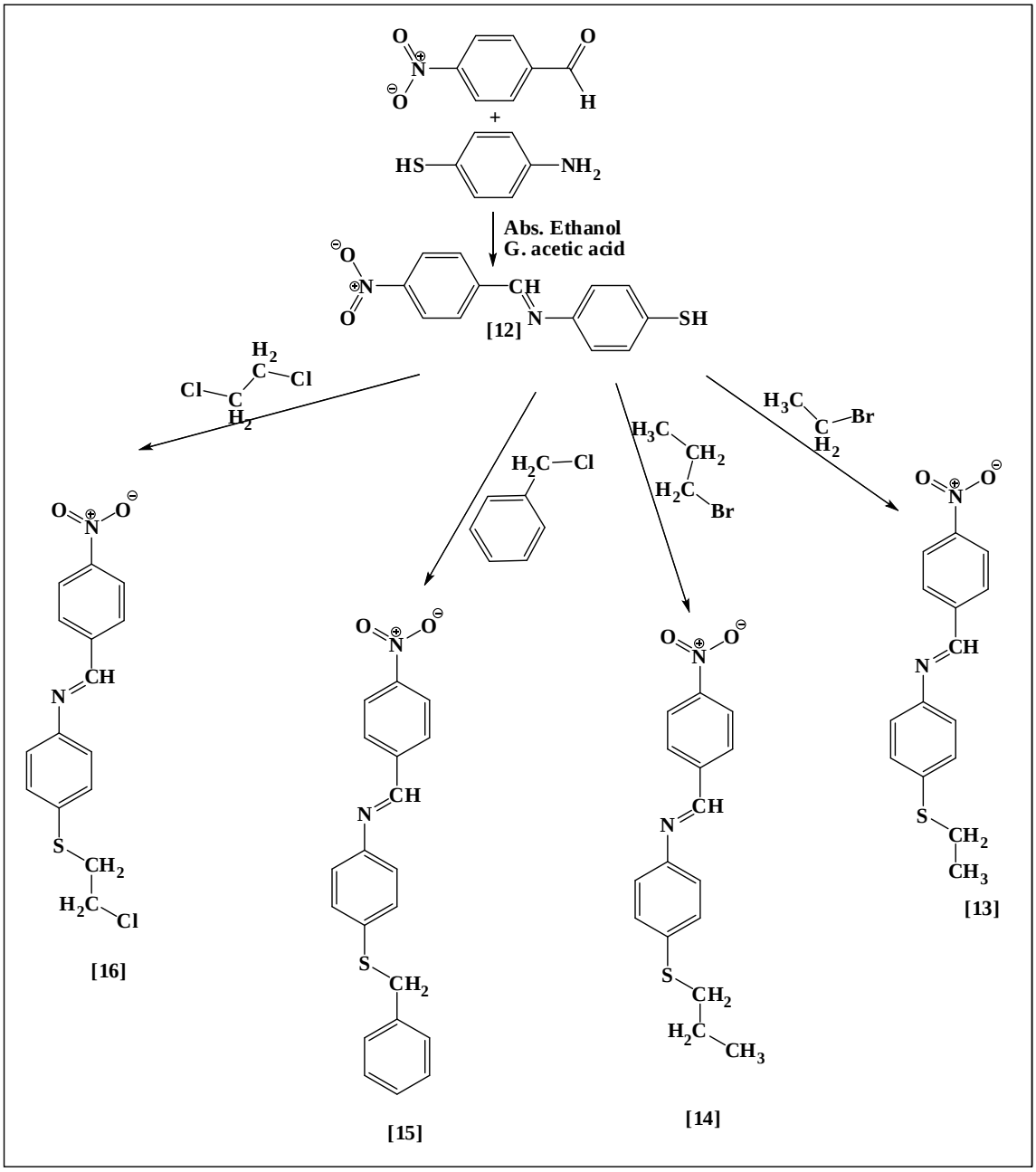



Figure 3-31: $^{13}$C-NMR Spectrum of compound **[10]**

### 3.2. Synthesis of organic compounds [12-16]

The synthesis routes for synthesis of compounds [12-16] are shown in scheme 3-2.




Scheme 3-2: The chemical steps for the synthesis of compounds **[12-16]**

### 3.2.1. Characterization of (E)-4-(4-nitrobenzylideneimino) benzenthiol [12]:

This compound was prepared from the reaction of *p*-aminothiophenol with *p*-nitrobenzaldehyde in abs. ethanol.

The FTIR spectrum of compound **[12]**, (see Figure 3-32) shows disappearance of bands at (1680- 1715 $cm^{-1}$), (2830- 2695 $cm^{-1}$), and (3400-3500 $cm^{-1}$) which due to (C=O), (C-H aldehyde) and (-$NH_2$ group), respectively, while the appearance of bands at (1624$cm^{-1}$ ) for imine bond, (2590$cm^{-1}$) for (S-H) bond, (636$cm^{-1}$) for (C-S) bond, (1516, 1346) $cm^{-1}$ for (-$NO_2$) group, (3066 $cm^{-1}$) for (C-H) aromatic and (1593 $cm^{-1}$) for (C=C).

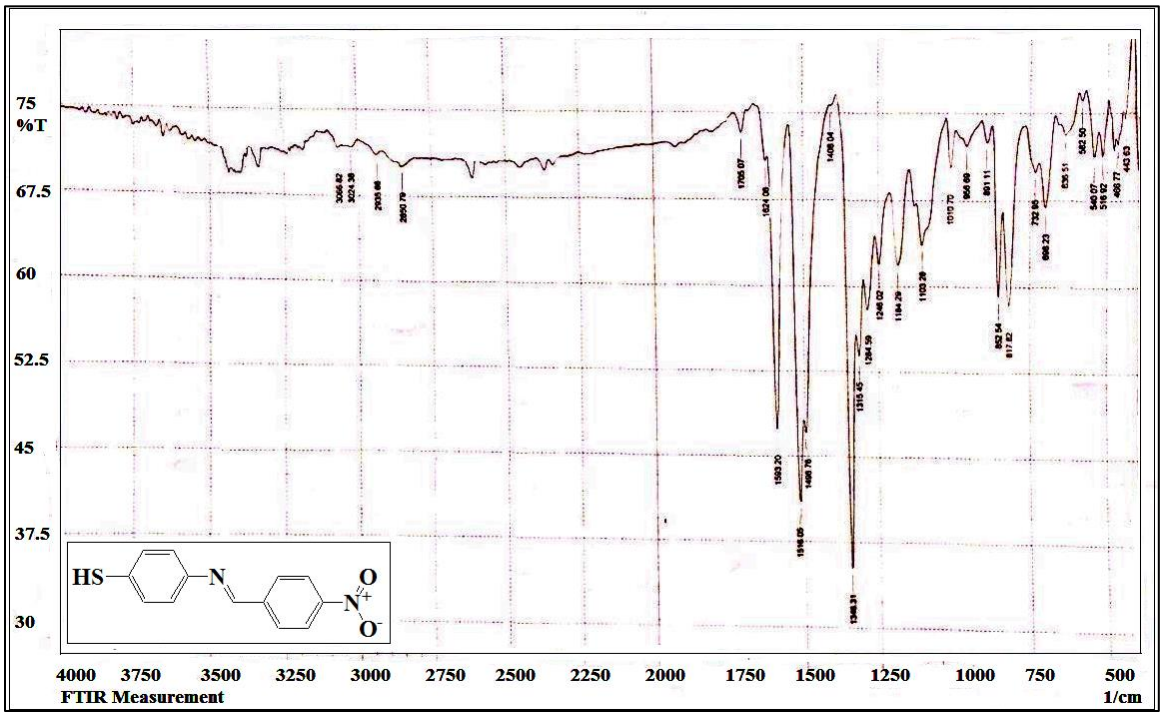



Figure 3-32: FTIR Spectrum of compound **[12]**

The UV-visible spectrum of (E)-4-(4-nitrobenzylideneimino) benzenthiol **[12]** (see Figure 3-33) in ethanol as a solvent and at room temperature shows λmax at (373, 269 nm) due to electronic transitions of (n-π*), (π-π*), respectively.

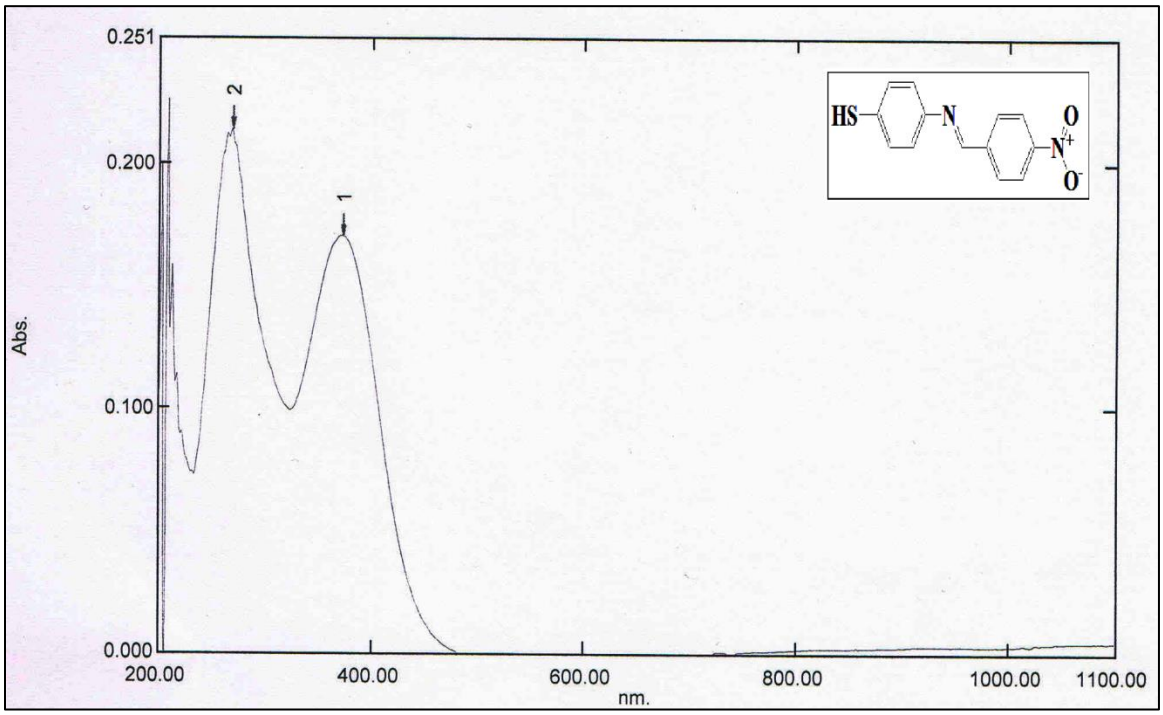



Figure 3-33: U.V. spectrum of compound **[12]**

$^{13}$C-NMR spectrum of compound **[12]**, (see Figure 3-34), shows the following characteristic chemical shifts of (C5) at δ= 159.05 ppm, while the signals appeared at the downfield region in between δ= 122.293- 149.91 ppm where attributed to aromatic carbons: δ= 122.29 ppm (C7), δ= 124.20 ppm (C2), δ= 127.90 ppm (C3), δ= 129.15 ppm (C9), δ= 130.57 ppm (C8), δ= 141.28 ppm (C4), δ= 148.80 ppm (C6) , δ= 149.91 ppm (C1).

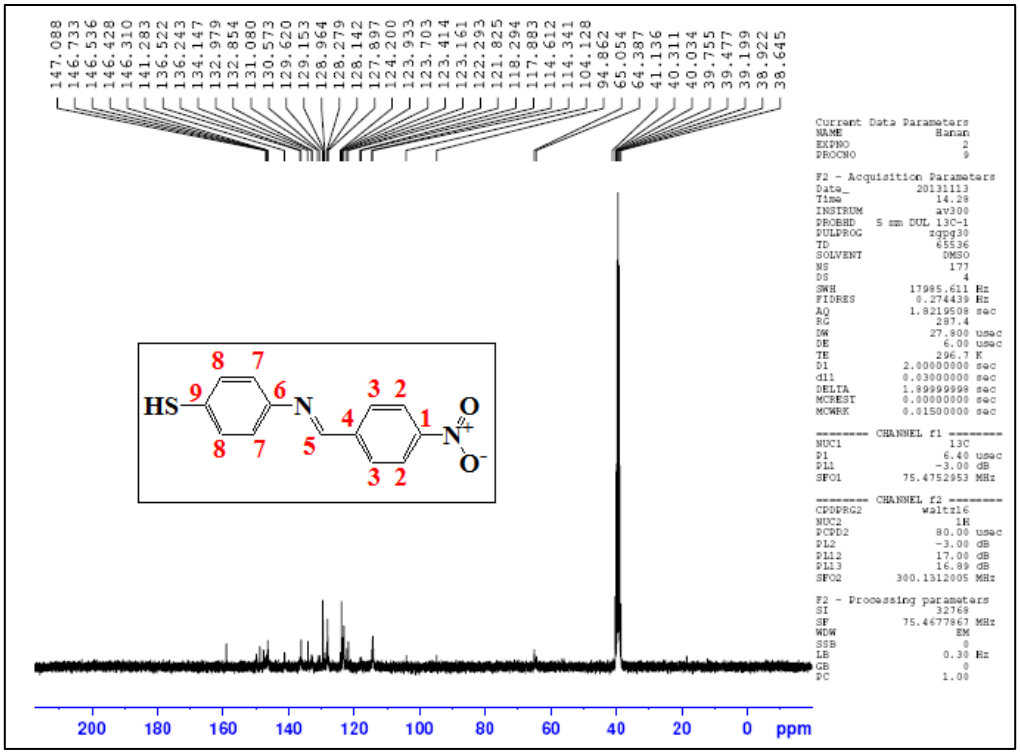
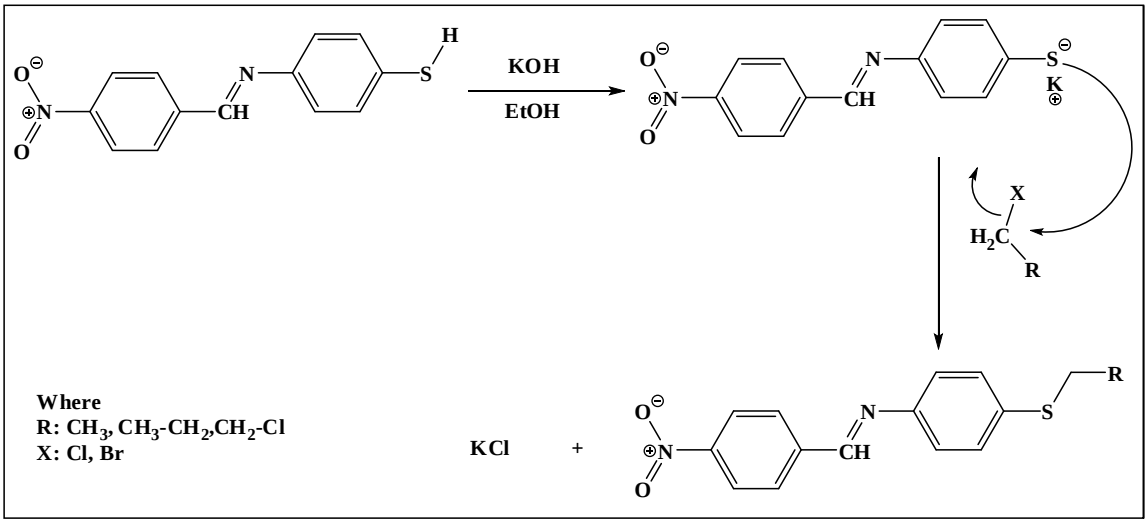



Figure 3-34: $^{13}$C-NMR spectrum of compound **[12]**

### 3.2.2. Characterization of S-[substituted] (E)-4-(4-nitrobenzylideneamino) benzenethiol [13-16]:

Compounds **[13, 14, 15** and **16]** were prepared via $SN_2$ reaction of compound **[12]** with alkyl halide in alcoholic potassium hydroxide. Mechanism of this reaction involved abstraction of proton from thiol group to form nucleophile which can be attacked carbon of alkyl halide within $SN_2$ mechanism to obtain [S-substituted] (E)-4-(4-nitrobenzylideneamino) benzenethiol **[13-16]**, mechanism of $SN_2$ reaction is shown below:




The FTIR spectra of compounds **[13-16]** in Figures (3-35) to (3-38) are shown absorption stretching band of different groups which are also listed in Table 3-6.

Table 3-6: FTIR Spectral data of prepared compounds **[13-16]** in $cm^{-1}$

| **Compound No.** | **Fig. No.** | **ν C=N** | **ν C-S** | **ν C-H aromatic** | **ν C-H aliphatic** | **ν C=C aromatic** | **ν $NO_2$** | **ν C-Cl** |
|---|---|---|---|---|---|---|---|---|
| **[13]** | 3-35 | 1624 | 636 | 3097 | 2889<br>2846 | 1597 | 1516<br>1342 | - |
| **[14]** | 3-36 | 1624 | 636 | 3097 | 2885<br>2843 | 1597 | 1516<br>1342 | - |
| **[15]** | 3-37 | 1624 | 621 | 3074 | 2885<br>2843 | 1597 | 1516<br>1342 | - |
| **[16]** | 3-38 | 1624 | 628 | 3050 | 2885<br>2839 | 1597 | 1516<br>1342 | 541 |

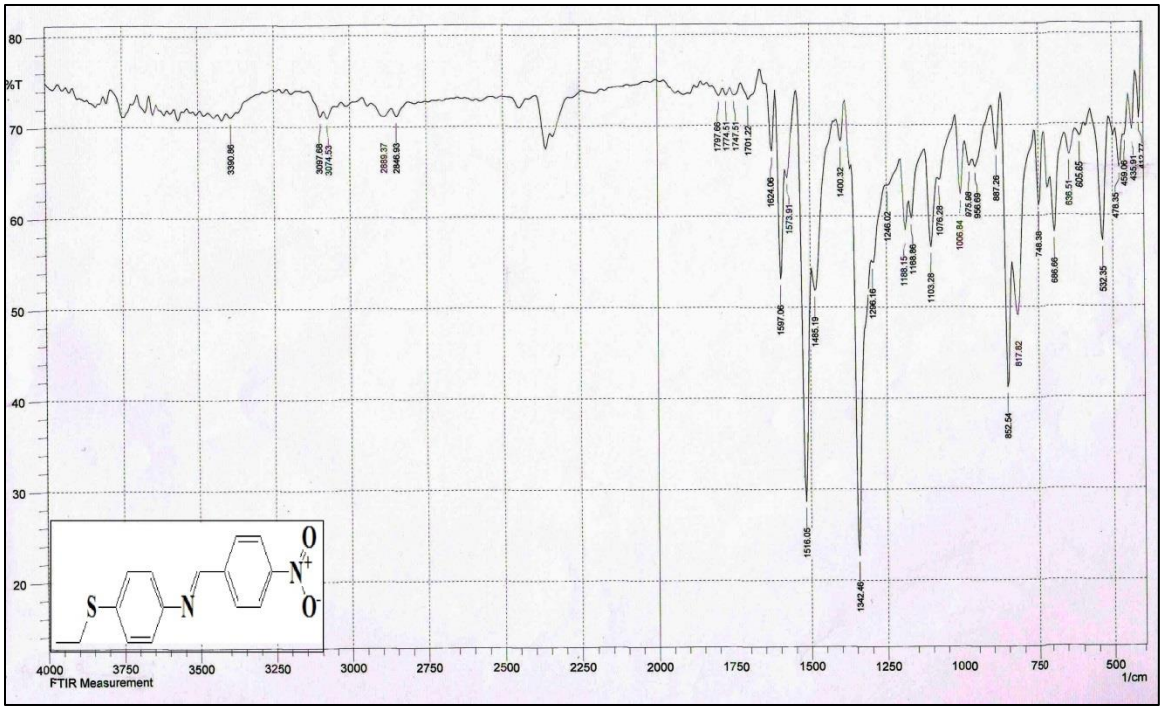



Figure 3-35: FTIR Spectrum of compounds **[13]**

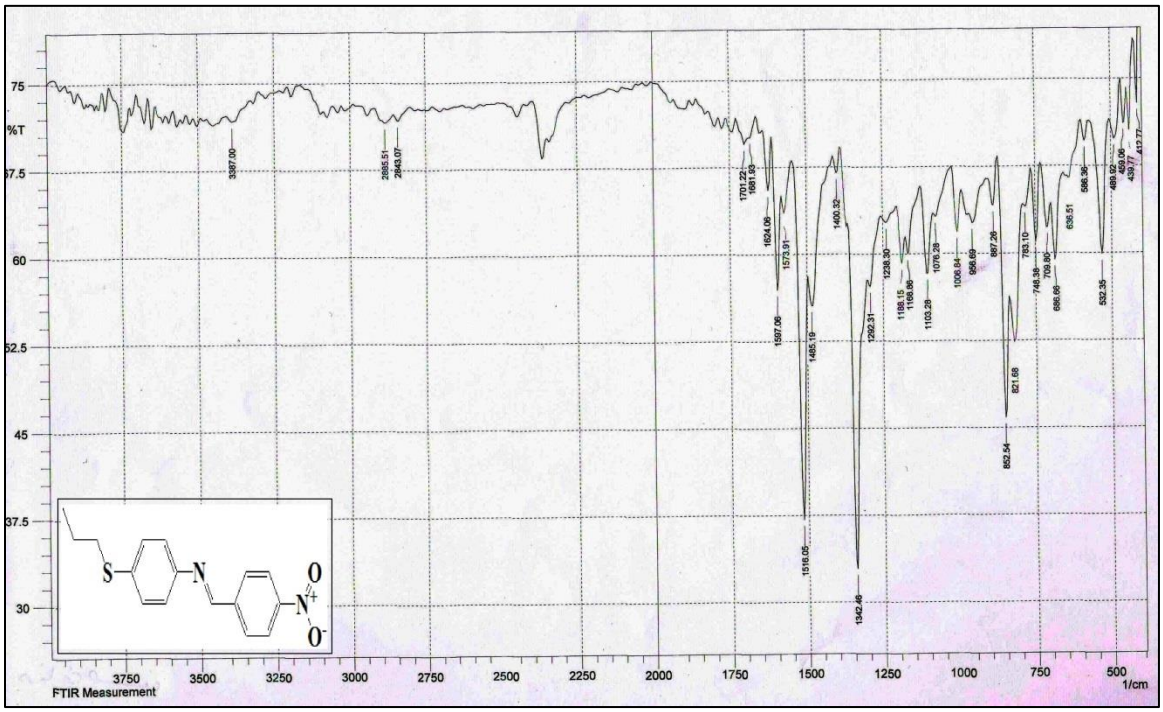



Figure 3-36: FTIR Spectrum of compounds **[14]**

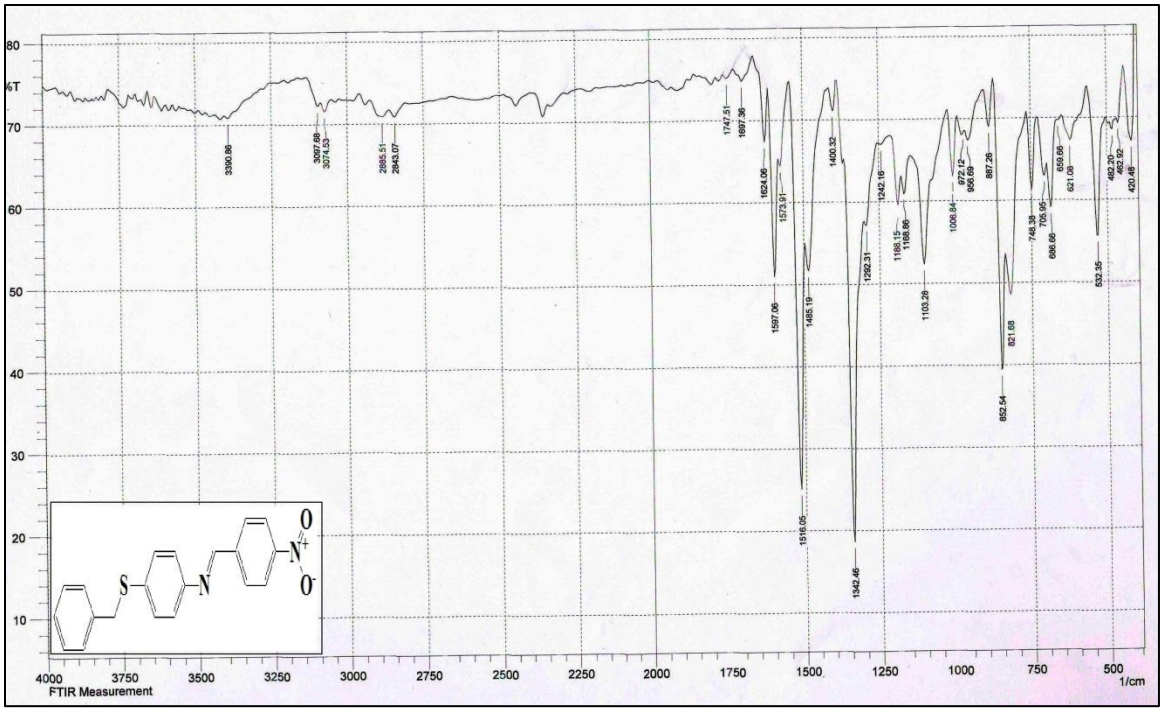



Figure 3-37: FTIR Spectrum of compounds **[15]**

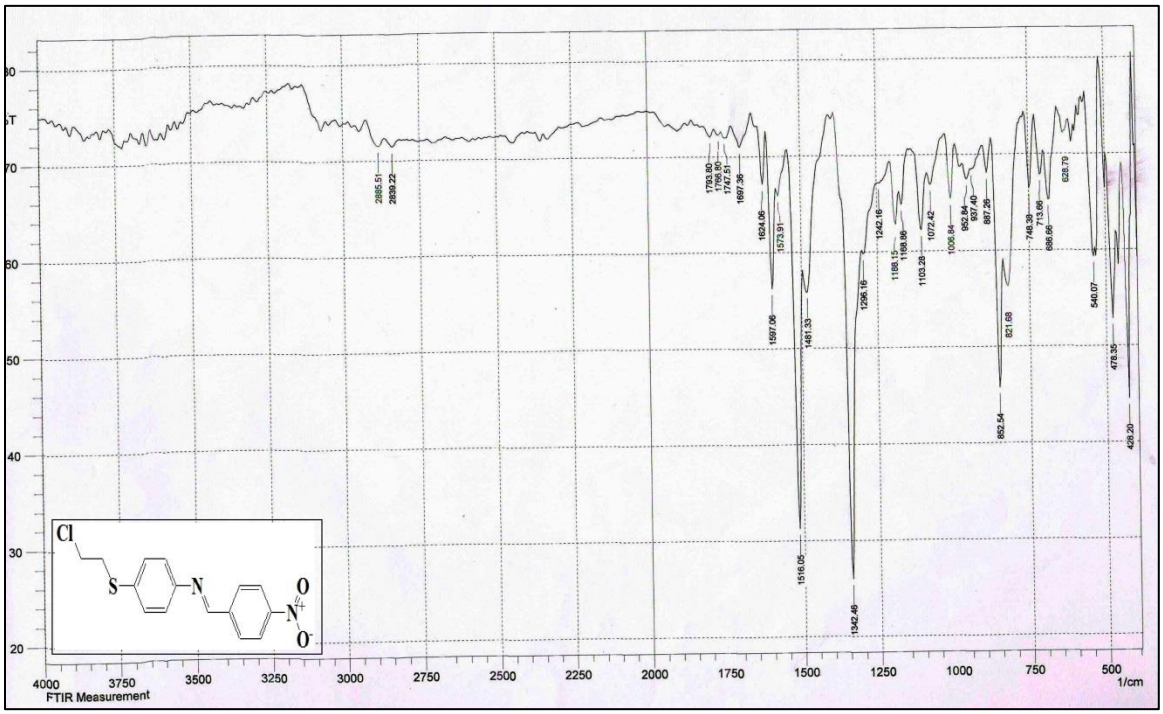



Figure 3-38: FTIR Spectrum of compounds **[16]**

The UV-visible spectra for the prepared compounds **[13-16]** are shown in Figures (3-39) to (3-42) and λmass of electronic transitions are listed in Table 3-7.

Table 3-7: UV-visible spectral data of prepared compounds **[13-16]**

| **Compound No.** | **Fig. No.** | **n→π* (nm)** | **π→π* (nm)** |
|---|---|---|---|
| **[13]** | 3-39 | 355 | 287 |
| **[14]** | 3-40 | 356 | 287 |
| **[15]** | 3-41 | 350 | 285 |
| **[16]** | 3-42 | 352 | 287 |

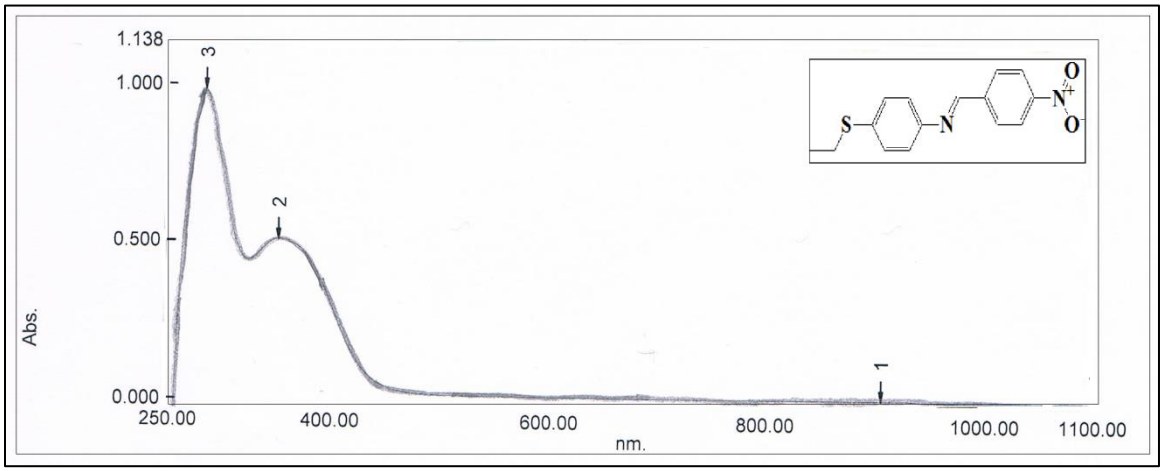



Figure 3-39: U.V. spectrum of compounds **[13]**

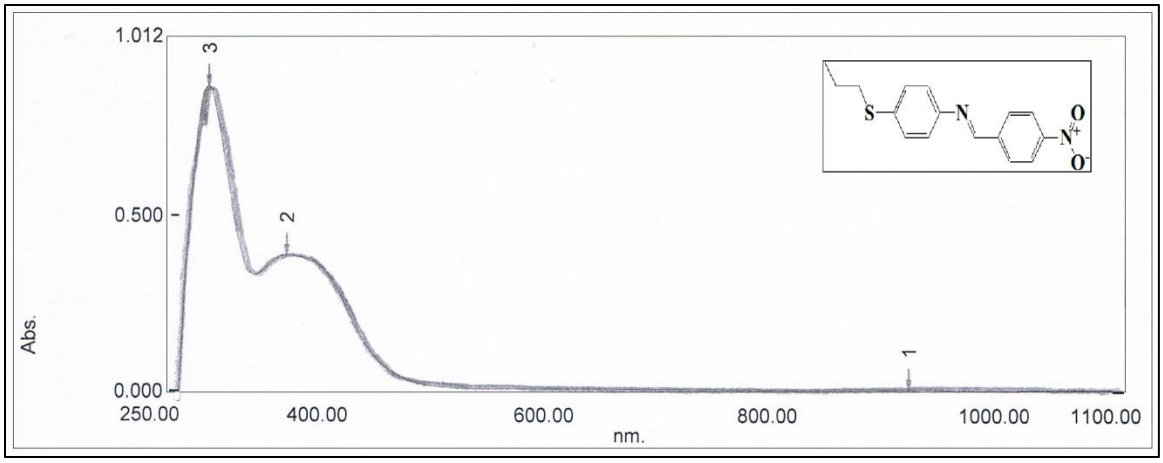



Figure 3-40: U.V. spectrum of compounds **[14]**

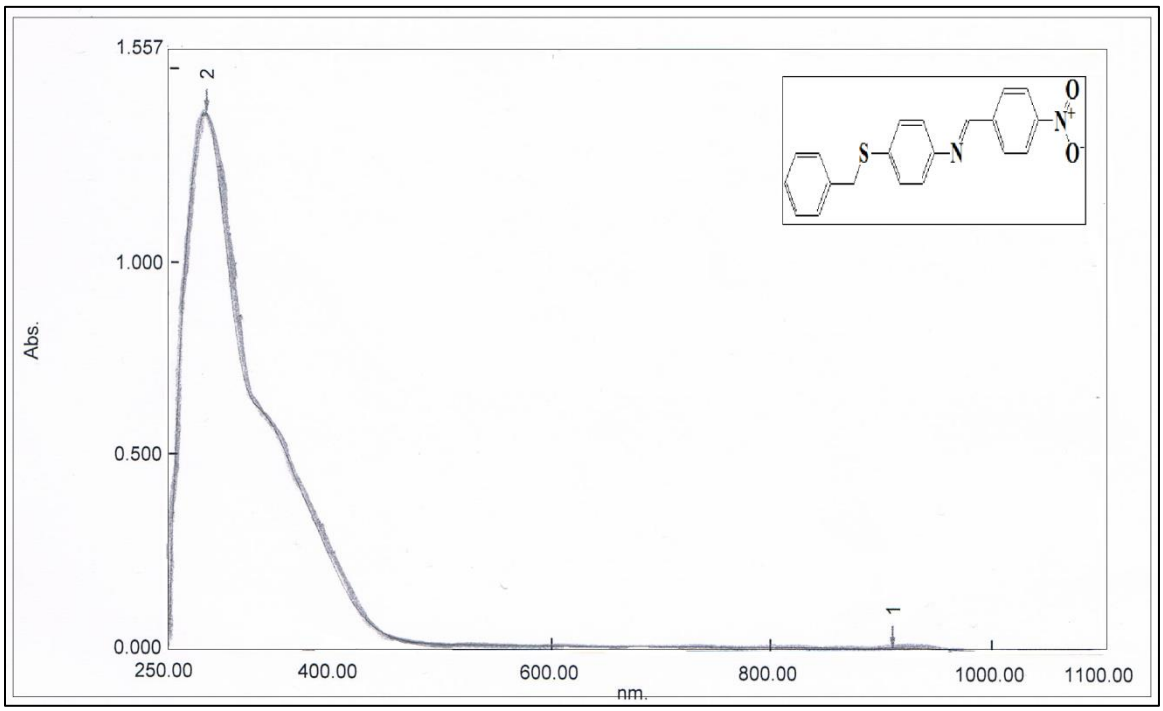



Figure 3-41: U.V. Spectrum of compounds **[15]**

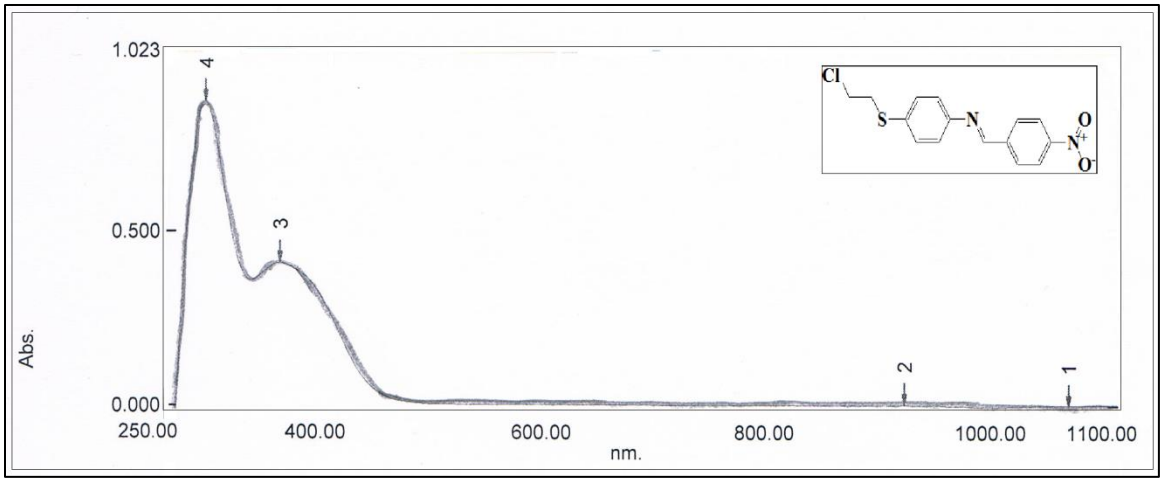
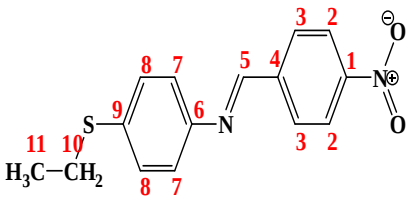
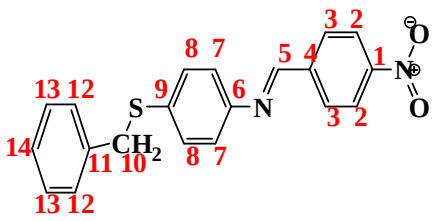



Figure 3-42: U.V. Spectrum of compounds **[16]**

$^{13}$C-NMR spectra of prepared compounds **[13]**, [**15]** are shown in Figures (3-43), (3-44) and the characteristic chemical shifts are listed in Table 3-8 (where DMSO-$d_6$ chemical shifts (as solvent) occurs at δ= 39.51 ppm).

Table 3-8: $^{13}$C-NMR spectral data of compounds **[13]**, **[16]** in ppm

| **Comp. No.** | **Compound structure** | **$^{13}$C-NMR data of ( δ-C) in ppm** | **Fig. No.** |
|---|---|---|---|
| **[13]** |  | C1, C5, C6= 142.658,<br>C2 = 124.006, C3= 128.016,<br>C4=142.658, C7= 122.530,<br>C8= 122.872, C9= 129.750,<br>C10= 38.931, C11= 24.494 | 3-43 |
| **[15]** |  | C1=150.160, C2=122.979,<br>C3=129.313, C4= 134.527,<br>C5=160.042, C6=149.386,<br>C7= 122.795, C8=129.684,<br>C9= C11=130.216 ,C10=41.343,<br>C12=C13=C14=124.519 | 3-44 |

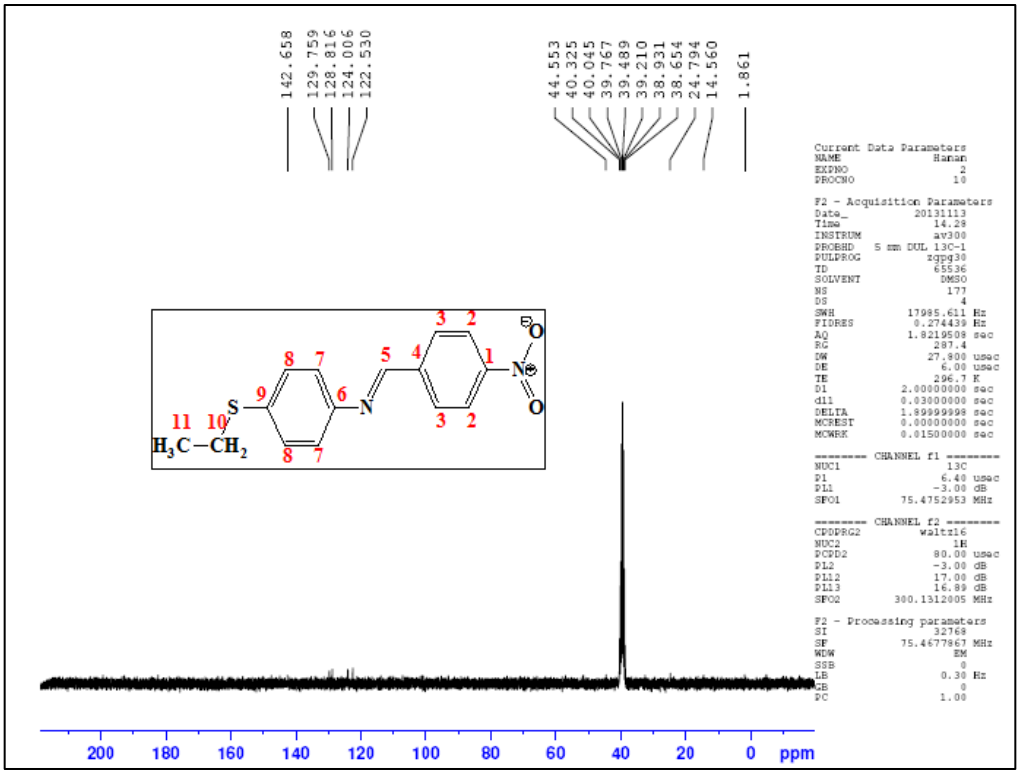



Figure 3-43: $^{13}$C-NMR spectrum of compound **[13]**

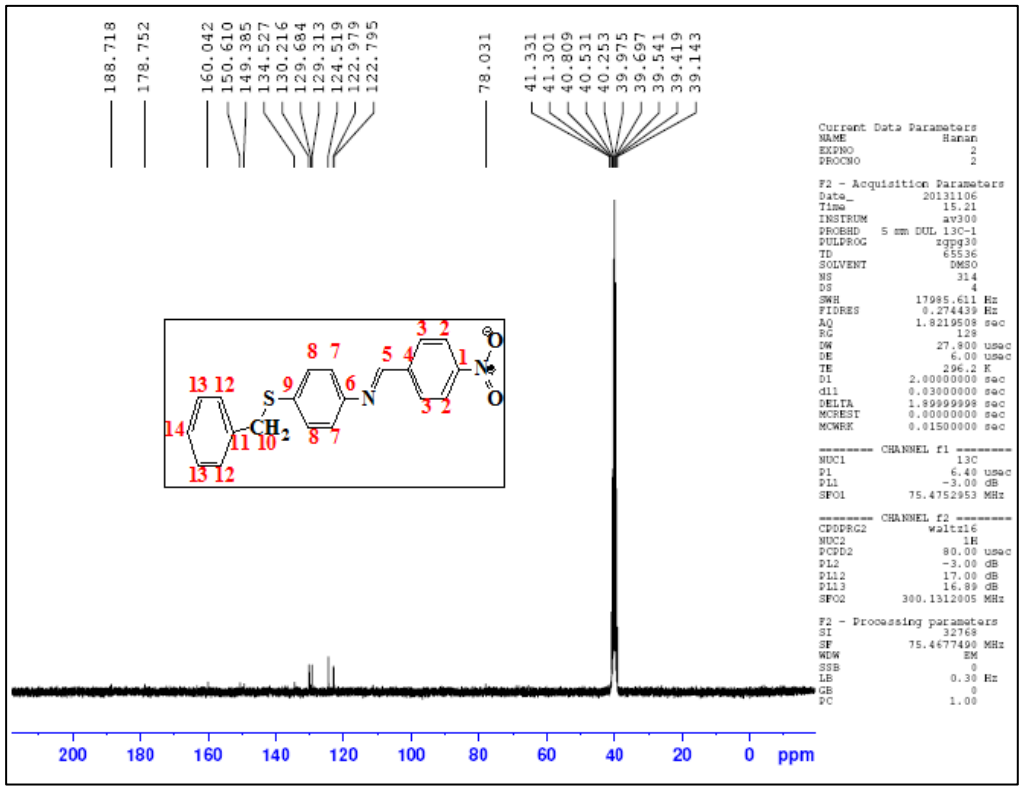
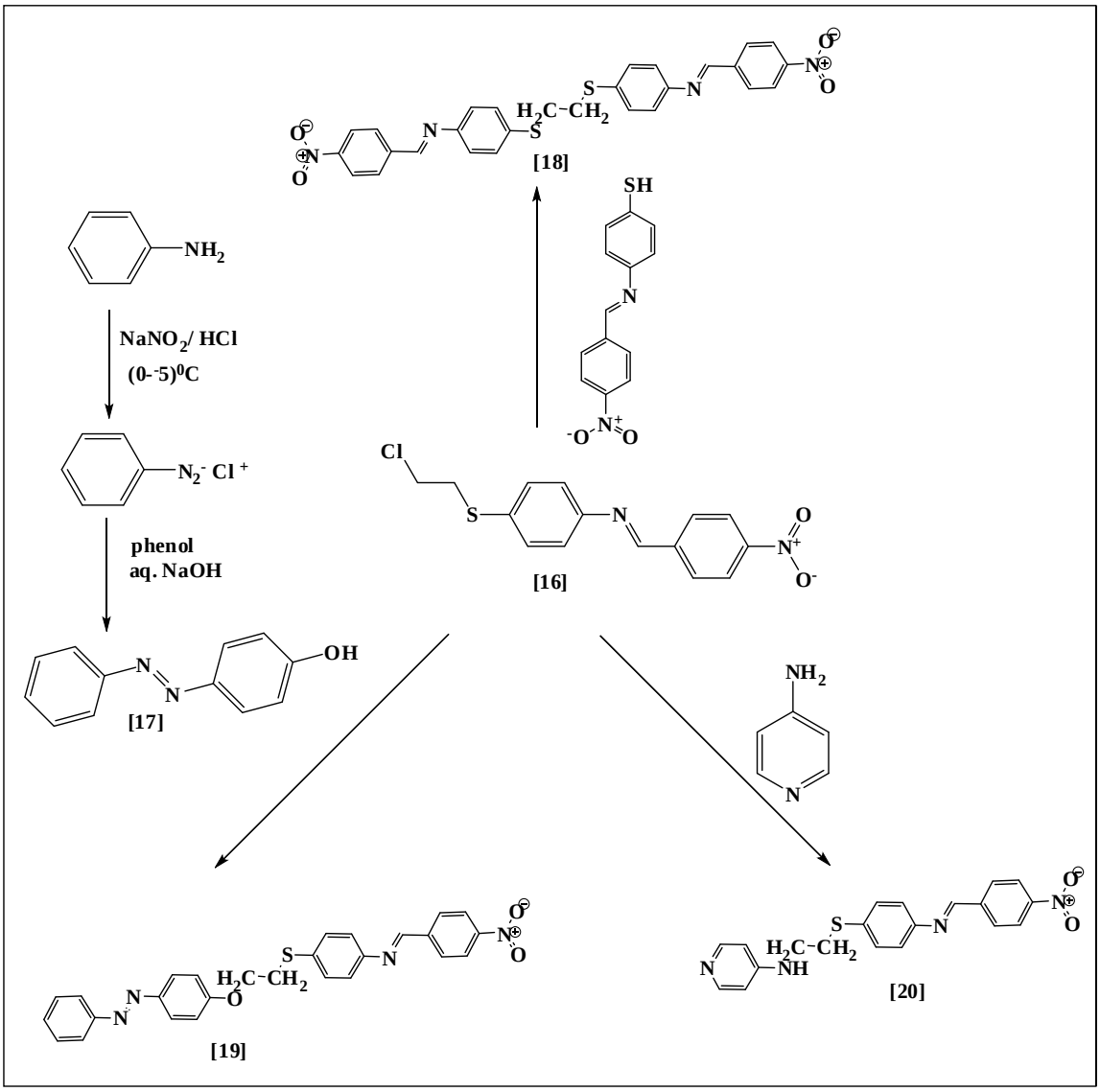



Figure 3-44: $^{13}$C-NMR spectrum of compound **[15]**

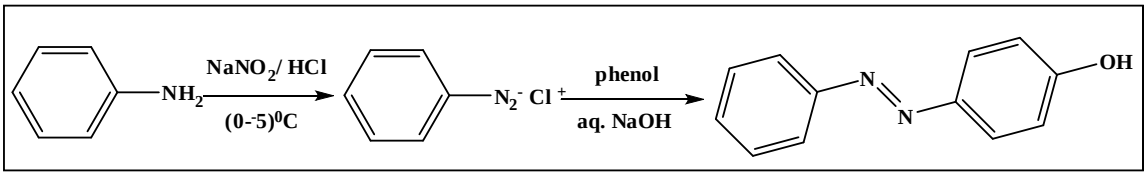
### 3.3. Synthesis of organic compounds [17-20]

The synthesis routes for synthesis of compounds [17-20] are shown in scheme 3-3.




Scheme 3-3: The chemical steps for the synthesis of compounds **[17-20]**

### 3.3.1. Characterization of 4-phenyl azophenol [17]:




The mechanism reaction for the synthesis of compound **[17]** was the same mechanism that mentioned in the preparation of the compound **[1]**.

The FTIR spectrum of compound **[17]** showed a medium stretching vibration band at 1415 $cm^{-1}$ that corresponds to (N=N) bond, band at 3363 $cm^{-1}$ that corresponds to (O-H),band at 1589 $cm^{-1}$ to (C=C), bands at 3074$cm^{-1}$ due to (C-H) aromatic stretching vibrations (Figure 3-45). That means compound **[17]** is existing in azo form.

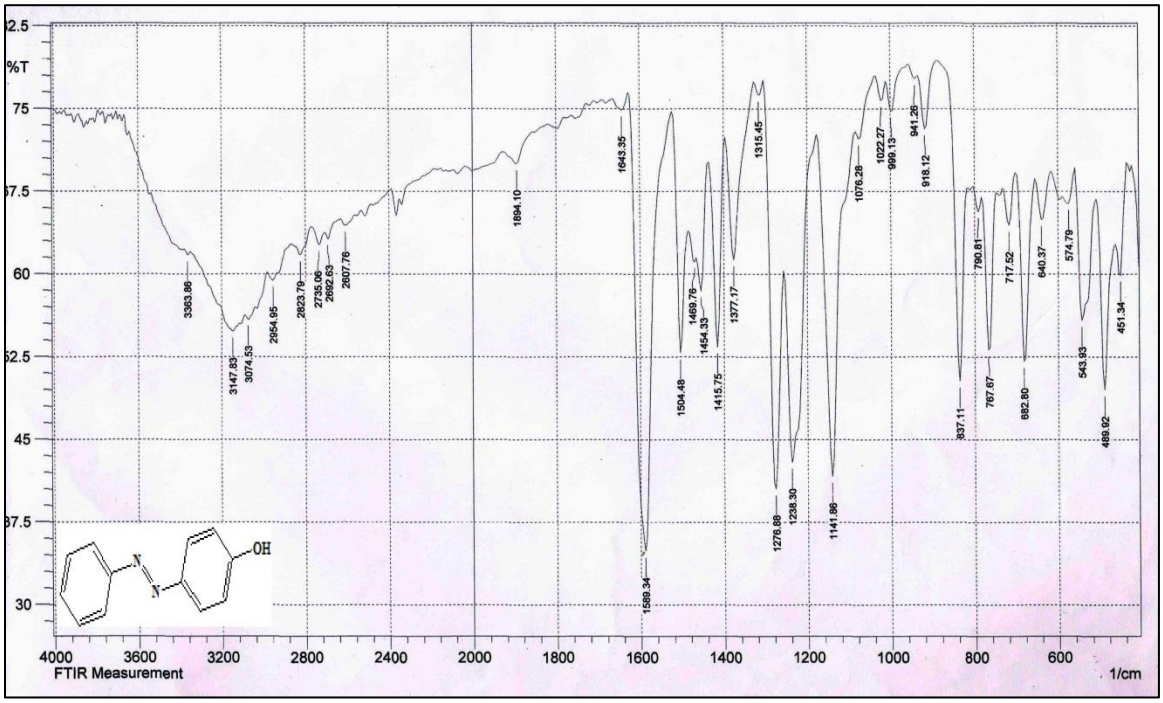
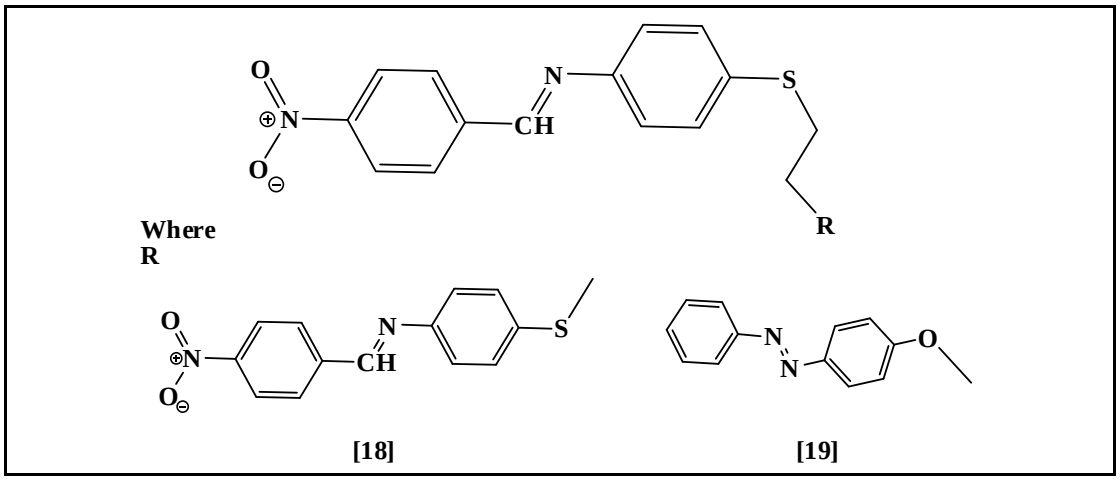
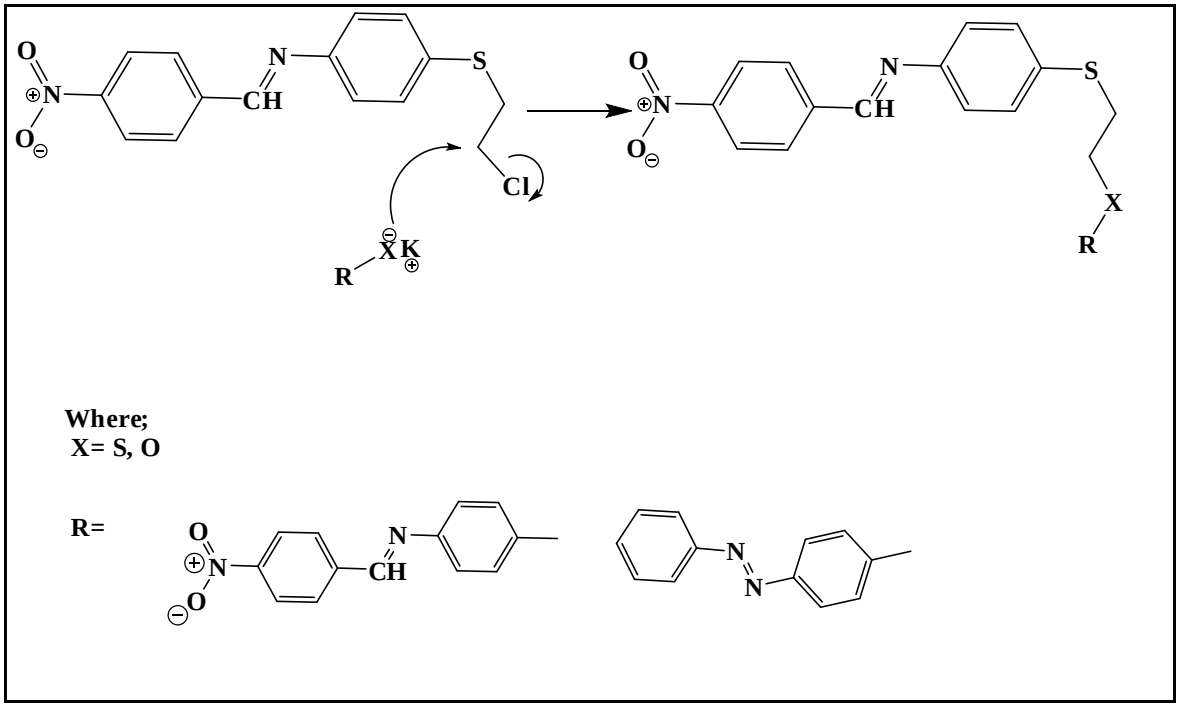



Figure 3-45: The FTIR spectrum of compound **[17]**

### 3.3.2. Characterization of C-[substituted] (E)-4-(2-chloroethylthio)-N-(4-nitrobenzylidene) aniline [18] and [19]:




The mechanism reaction for the synthesis of compound **[18, 19]** is the mechanism of $SN_2$ reaction that shown below:



The FTIR spectra of prepared compounds **[18], [19]** are shown in Figures (3-46, 3-47), where (C-Cl) disappear and absorption stretching bands of different groups which are also listed in Table 3-9.

Table 3-9: FTIR Spectral data of compounds **[18, 19]** in $cm^{-1}$

| Compound No. | Fig. No. | ν C=N | ν C-S | ν C-H aromatic | ν C-H alphatic | ν C=C | ν NO2 | Other |
|---|---|---|---|---|---|---|---|---|
| **[18]** | 3-46 | 1624 | 636 | 3050 | 2885<br>2839 | 1597 | 1516<br>1342 | - |
| **[19]** | 3-47 | 1624 | 636 | 3070 | 2947<br>2885 | 1597 | 1516<br>1342 | C-O-C<br>1238 |

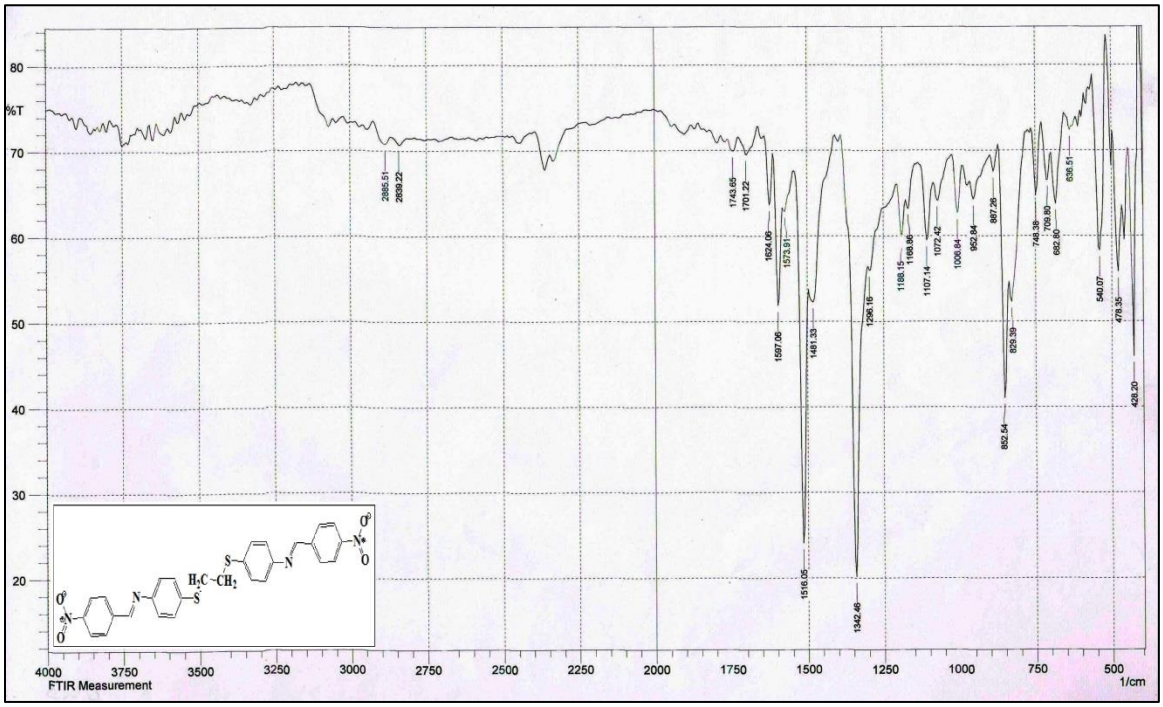



Figure 3-46: FTIR Spectrum of compounds **[18]**

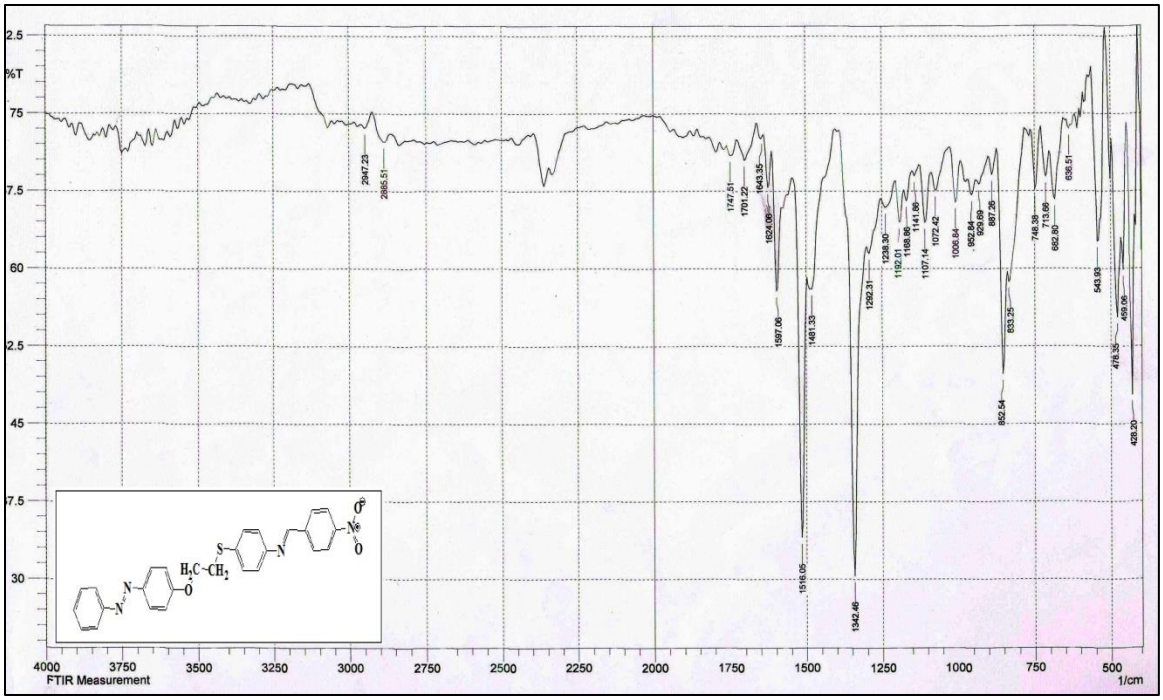



Figure 3-47: FTIR Spectrum of compounds **[19]**

The UV-visible spectra for the prepared compounds **[18], [19]** are showed in figures 3-48, 3-49 and Table 3-10.

Table 3-10: UV-visible spectral data of prepared compounds **[18, 19]**

| **Compound No.** | **Fig. No.** | **n→π* (nm)** | **π→π* (nm)** |
|---|---|---|---|
| **[18]** | 3-48 | 330 | >250 |
| **[19]** | 3-49 | 349 | 288 |

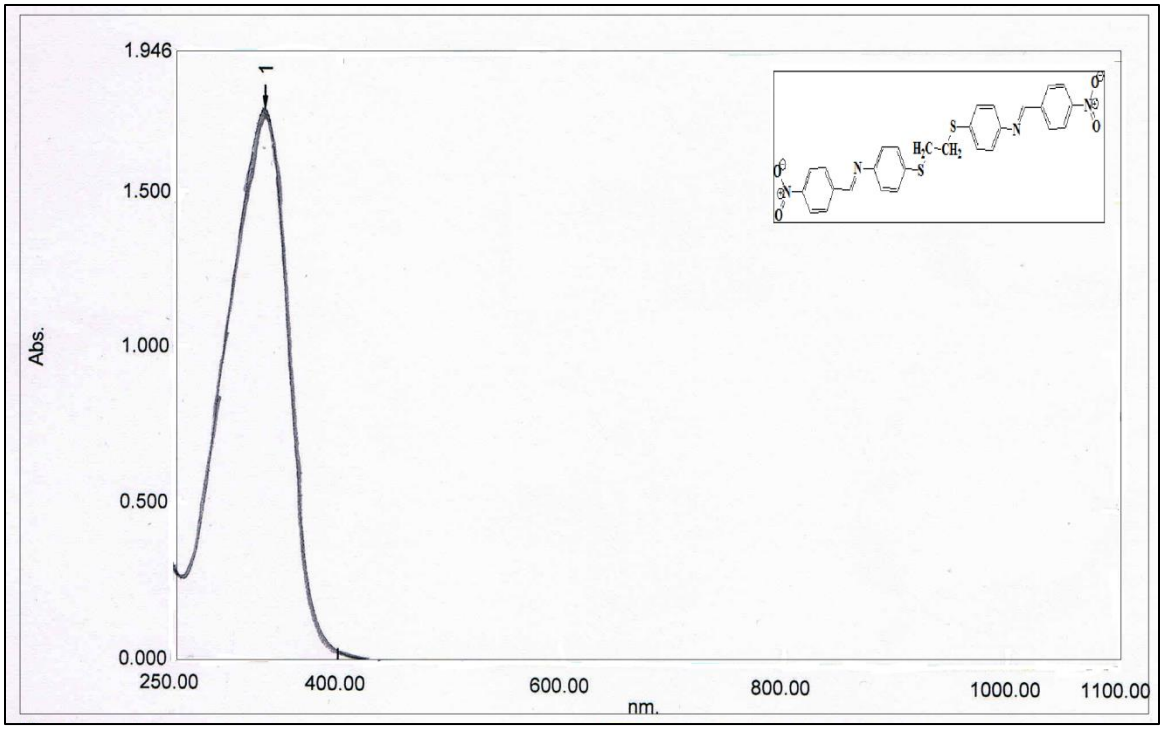



Figure 3-48: U.V. Spectrum of compounds **[18]**

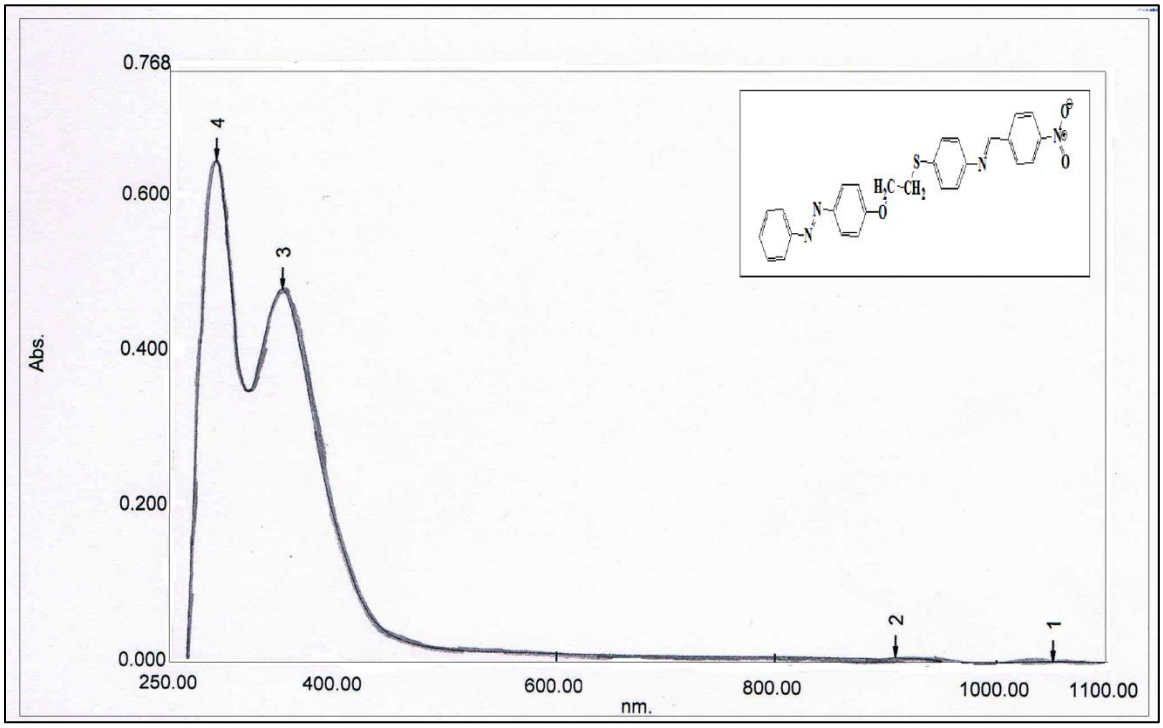



Figure 3-49: U.V. Spectrum of compounds **[19]**

$^{13}$C-NMR spectrum for the prepared compounds **[18]** is shown in Figure 3-50, and $^{13}$C-NMR spectral data of prepared compounds **[18]** in ppm as following: C1=149.061, C5=186.202, (C2, C3, C4, C6, C7, C8 and C9 within the range=122.432-242.342, C10= 55.027.

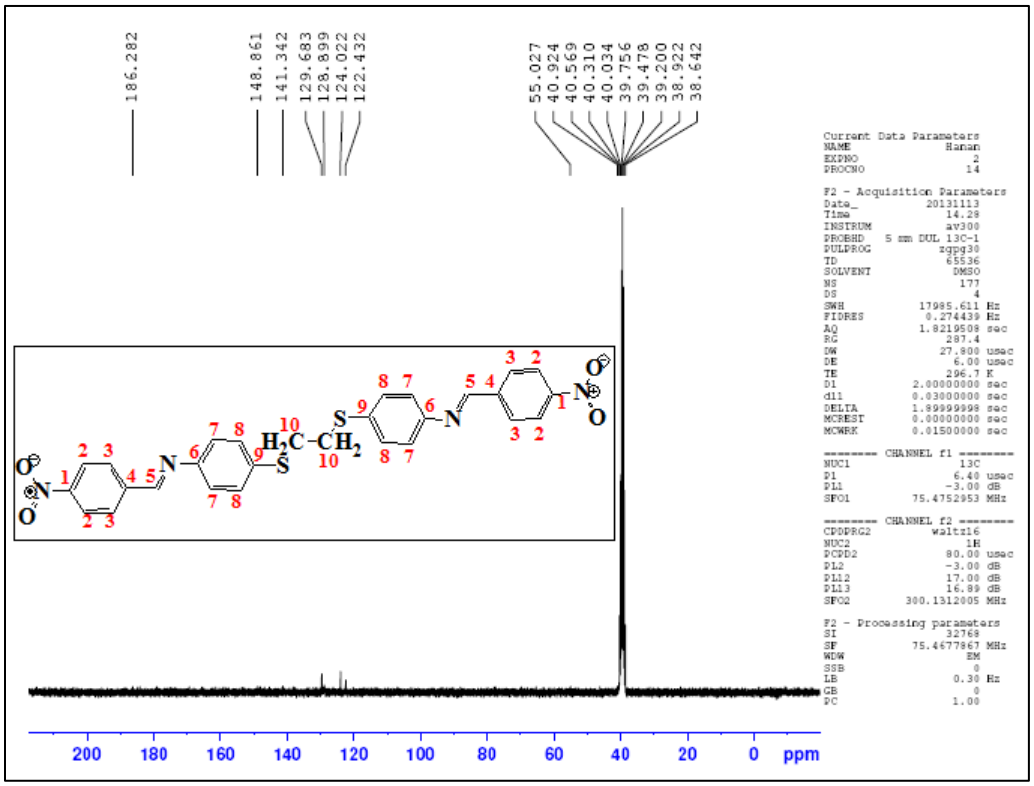
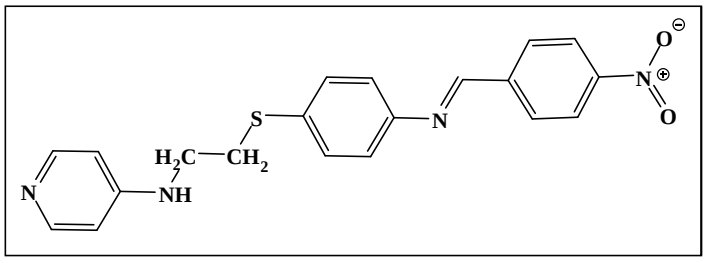



Figure 3-50: $^{13}$C-NMR spectrum of compound **[18]**

### 3.3.3. Characterization of (E)-N-(2-(4-(4-nitrobenzylideneamino) phenylthio) ethyl) pyridin-4-amine [20]:



The FTIR spectrum of prepared compound **[20]** is shown stretching vibration band at 1647 $cm^{-1}$ that corresponds to (C=N) bond. stretching vibration band at 3437 $cm^{-1}$ that corresponds to secondary (N-H) bond. Stretching vibration bands at 636 $cm^{-1}$, 3055 $cm^{-1}$, 2989 $cm^{-1}$, (1558, 1597 ) $cm^{-1}$ and (1516, 1342) $cm^{-1}$ that correspond to (C-S), (C-H) aromatic, (C-H) aliphatic, (C-N), (C=C) pyridyl ring and symmetry and asymmetry ($NO_2$) of stretching vibrations (see Figure 3-51).

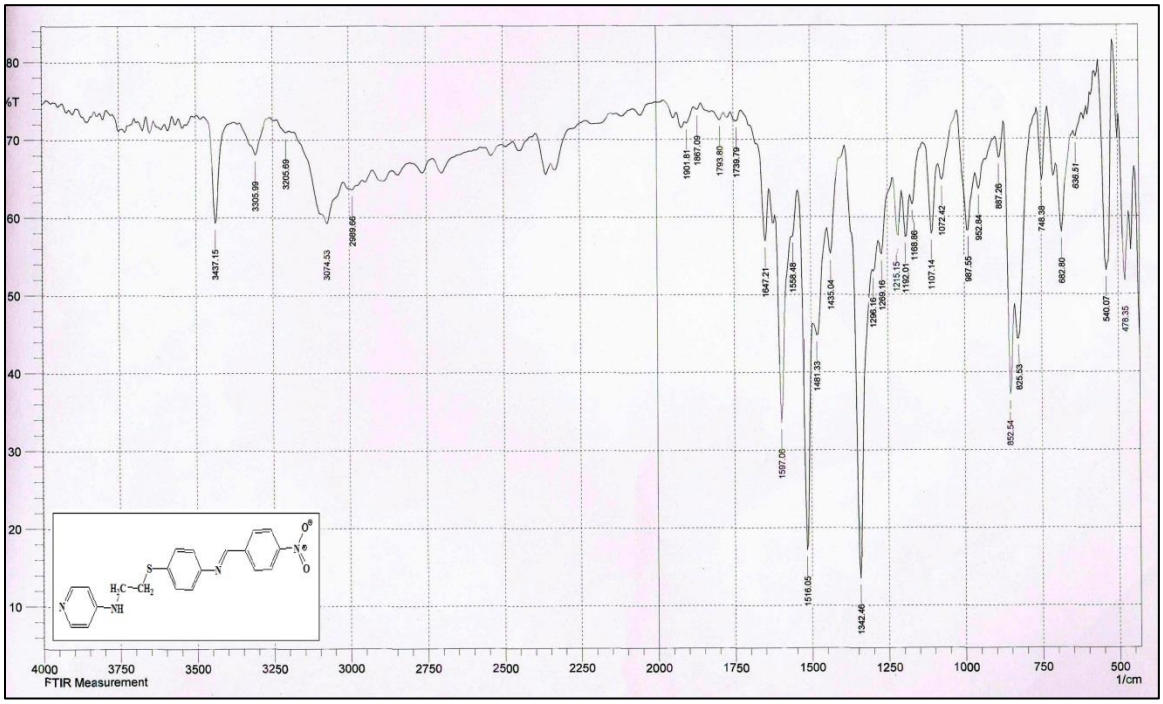



Figure 3-51: FTIR spectrum of compound **[20]**

The UV-visible spectra of Compound **[20]**, (see Figure 3-52) shows electronic transition bands with λmax at (271nm) due to π-π* transition, and n-π* at (348nm).

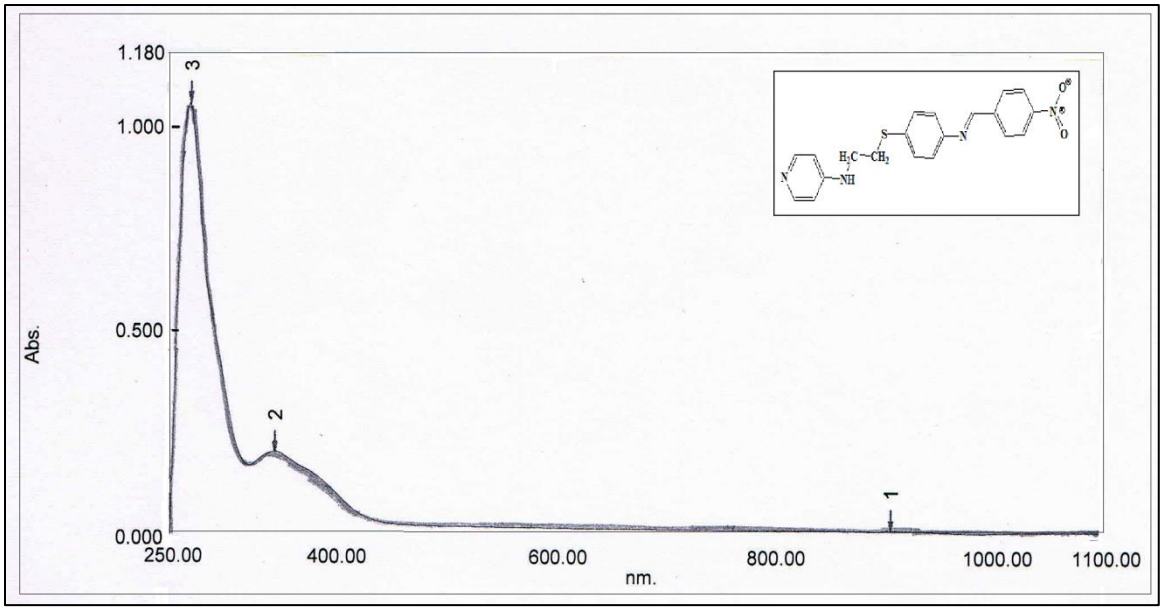



Figure 3-52: U.V. Spectrum of Compound **[20]**

### 3.4. Weight loss measurement and Theoretical calculations

#### 3.4.1. Weight loss measurement:

The prepared compounds [**4-16** and **18-20**] were used as inhibitors for the corrosion, the values of corrosion rate, surface coverage and inhibition efficiency from weight loss measurements at different concentrations of prepared compounds [**4-16** and **18-20**] after 8 hours immersion of mild steel in 1M $H_2SO_4$ at 30$^oC$ are summarized in Table (3-11) and Table (3-12), respectively.

First, the inhibition efficiency of compounds [**4-11**] as a function of concentration is shown in Figure (3-53). The results of Table (3-11) and Figure (3-53) show that as the inhibitor concentration increases, the corrosion rate decreases and therefore the inhibition efficiency increases. It can be concluded that these prepared compounds act as inhibitor through adsorption on mild steel surface and formation of a barrier layer between

iron metal and the corrosive media. The inspection of results of E (%) in Table (3-11) indicates that the protection efficiency E (%) increases with increasing the concentration of suggested inhibitors with the maximum inhibition efficiencies were achieved at $10^{-3}$ M. Thus, the comparative study reveals that order of maximum inhibition efficiency as follow: **[9]**> **[4]**> **[5]**> **[8]**> **[7]> [6]> [11]**> **[10]**. This order could be explain by the effect of molecular structure of organic inhibitors on inhibition efficiency, as well as adsorption process.

In order to confirm the adsorption of compounds [**4-11**] on mild steel surface, adsorption isotherms were studied. Adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. Thus, the degree of surface coverage values (θ), at different inhibitor concentrations in 1 M $H_2SO_4$ was evaluated from weight loss measurements (θ= E (%)/100, see Table (3-11)) at 30$^o$C and tested graphically for fitting to a suitable adsorption isotherm. The plot of parameter (C/θ) against inhibitor concentration (C) [see Figure (3-54)] yields a straight line.

The negative values of $\Delta G^o_{ads}$ as shown in Table (3-11) indicate spontaneous adsorption of **[4-11]** molecules on the mild steel surface and a strong interaction between inhibitor molecules and metal surface. The value of $\Delta G^o_{ads}$ is less than -40 kJ/mol that indicating electrostatic interaction between the charged metal surface is physical adsorption [(99)].

Table 3-11: Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption in the presence and absence of different concentrations of N-[substituted] (E)-4-(phenyldiazenyl) aniline **[4-11]** for the corrosion of mild steel in 1 M $H_2SO_4$ from weight loss measurements

| **Inhibitor concentration (M)** | **1M $H_2SO_4$** | | | | |
|---|---|---|---|---|---|
| | **ΔM(g)** | **Corrosion rate (mg $cm^{-2}$ $h^{-1}$)** | **E%** | **θ** | **$\Delta G^{o}_{ads}$ (kJ/mol)** |
| **Uninhibited** | 0.113 | 2.8790 | - | - | -36.08 ($R^2$=0.9970) |
| **[4]** | | | | | |
| 0.001 | 0.0415 | 1.0573 | 63.28 | 0.6328 | |
| 0.0005 | 0.0491 | 1.2510 | 56.55 | 0.5655 | |
| 0.0001 | 0.0575 | 1.4650 | 49.11 | 0.4911 | |
| 0.00005 | 0.0614 | 1.5643 | 45.50 | 0.4550 | |
| **[5]** | | | | | -34.90 ($R^2$=0.995) |
| 0.001 | 0.0419 | 1.0675 | 62.92 | 0.6292 | |
| 0.0005 | 0.0519 | 1.3223 | 54.07 | 0.5407 | |
| 0.0001 | 0.0563 | 1.4344 | 50.18 | 0.5018 | |
| 0.00005 | 0.0681 | 1.7350 | 39.74 | 0.3974 | |
| **[6]** | | | | | -35.08 ($R^2$=0.9980) |
| 0.001 | 0.0475 | 1.2102 | 57.96 | 0.5796 | |
| 0.0005 | 0.0542 | 1.3809 | 52.04 | 0.5204 | |
| 0.0001 | 0.0607 | 1.5465 | 46.28 | 0.4628 | |
| 0.00005 | 0.0792 | 2.0178 | 29.91 | 0.2991 | |
| **[7]** | | | | | -35.58 ($R^2$=0.9910) |
| 0.001 | 0.0443 | 1.1287 | 60.80 | 0.6080 | |
| 0.0005 | 0.0551 | 1.4038 | 51.24 | 0.5124 | |
| 0.0001 | 0.0603 | 1.5363 | 46.64 | 0.4664 | |
| 0.00005 | 0.0676 | 1.7223 | 40.18 | 0.4018 | |
| **[8]** | | | | | -38.64 ($R^2$=0.9950) |
| 0.001 | 0.0427 | 1.0879 | 62.21 | 0.6221 | |
| 0.0005 | 0.0475 | 1.2102 | 57.96 | 0.5796 | |
| 0.0001 | 0.0496 | 1.2637 | 56.11 | 0.5611 | |
| 0.00005 | 0.0564 | 1.4350 | 50.16 | 0.5016 | |
| **[9]** | | | | | -34.39 ($R^2$=0.9998) |
| 0.001 | 0.0198 | 0.5045 | 82.48 | 0.8248 | |
| 0.0005 | 0.0235 | 0.5987 | 79.20 | 0.7920 | |
| 0.0001 | 0.053 | 1.3503 | 53.10 | 0.5310 | |
| 0.00005 | 0.0688 | 1.7529 | 39.11 | 0.3911 | |

Table 3-11: To be continued

| | | | | | |
|---|---|---|---|---|---|
| **[10]** | | | | | -36.77 ($R^2$=0.9980) |
| 0.001 | 0.0691 | 1.7605 | 38.85 | 0.3885 | |
| 0.0005 | 0.0731 | 1.8624 | 35.31 | 0.3531 | |
| 0.0001 | 0.0738 | 1.8803 | 34.69 | 0.3469 | |
| 0.00005 | 0.0811 | 2.0662 | 28.23 | 0.2823 | |
| **[11]** | | | | | -37.59 ($R^2$=0.9998) |
| 0.001 | 0.0611 | 1.5567 | 45.93 | 0.4593 | |
| 0.0005 | 0.0629 | 1.6025 | 44.34 | 0.4434 | |
| 0.0001 | 0.0666 | 1.6968 | 41.06 | 0.4106 | |
| 0.00005 | 0.0741 | 1.8879 | 34.43 | 0.3443 | |

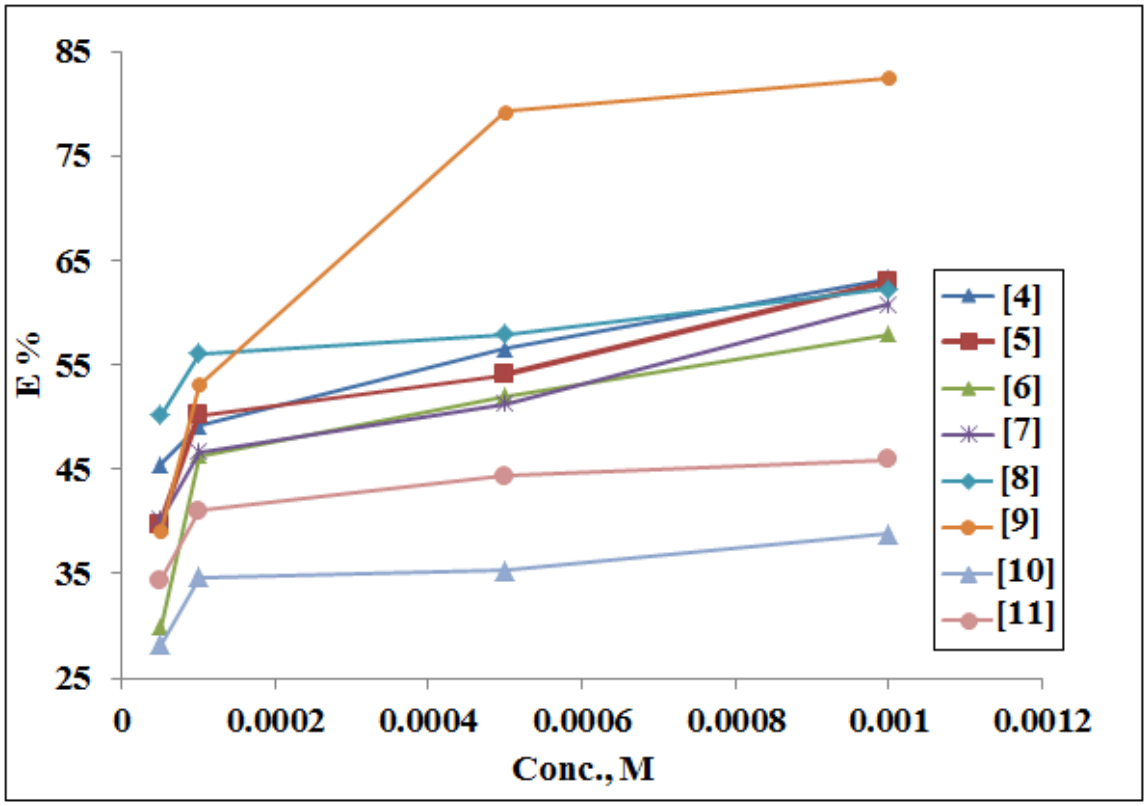



Figure 3-53: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1 M $H_2SO_4$ containing different concentrations of prepared inhibitors [**4**]-[**11**]

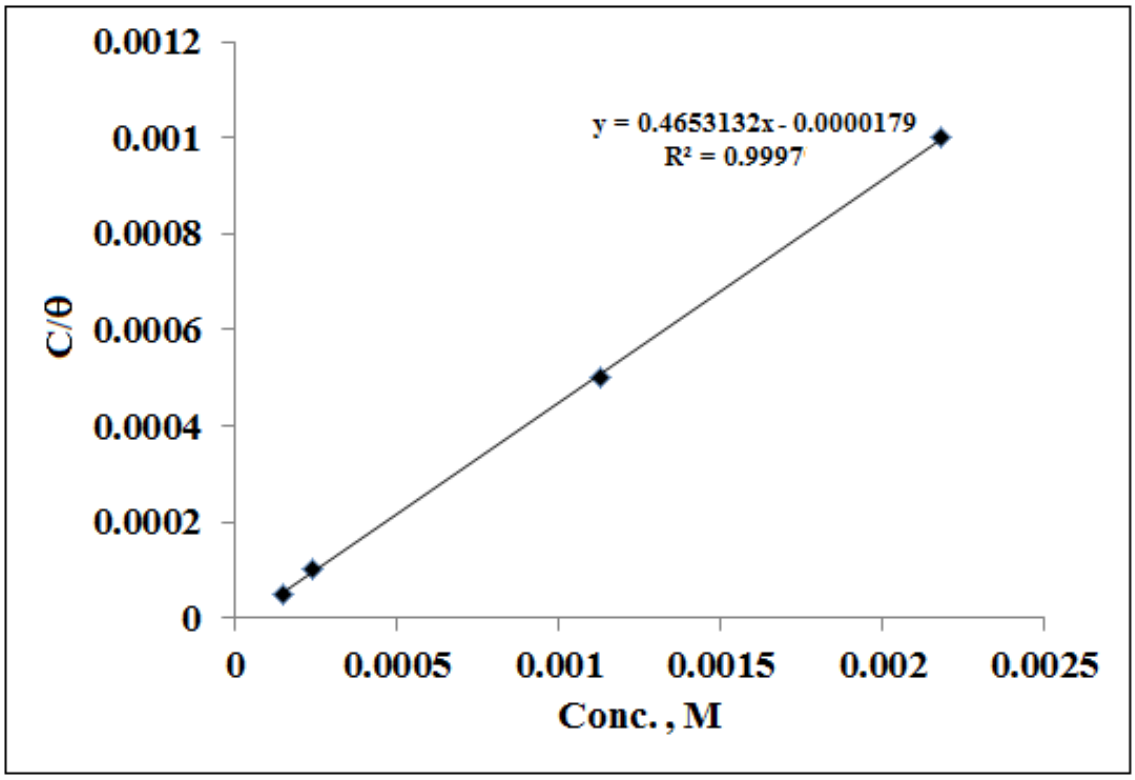



Figure 3-54: Langmuir adsorption isotherm plot for mild steel in 1M $H_2SO_4$ solution in the presence of various concentrations of inhibitor [**11**]

Second, the inhibition efficiency results of prepared compounds **[12-16]** and **[18-20]** as a function of concentration are shown in Figure (3-55). The results of Table (3-12) and Figure (3-55) are showing that as the inhibitor concentration increases, the corrosion rate decreases and therefore the inhibition efficiency increases. It can be concluded that these prepared compounds act as inhibitors through adsorption on mild steel surface and formation of a barrier layer between the metal and the corrosive media. The inspection of results of E (%) in Table (3-12) indicates that the protection efficiency E (%) increases with increasing the concentration of suggested inhibitors with the maximum inhibition efficiencies were achieved at $10^{-3}$ M. Thus, the comparative study reveals that order of maximum inhibition efficiency as follow: **[18]**> **[15]**> **[13]**> **[14]**> **[16]**> **[12]**> **[19]**> **[20]**. This

order could be explain by the effect of molecular structure of organic inhibitors on inhibition efficiency, as well as adsorption process.

In order to confirm the adsorption of compounds **[12-16]** and **[18-20]** on mild steel surface, adsorption isotherms were studied. Adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. Thus, the degree of surface coverage values (θ), at different inhibitor concentrations in 1 M $H_2SO_4$ was evaluated from weight loss measurements (θ= E (%)/100, see Table (3-12)) at 30$^{o}$C and tested graphically for fitting to a suitable adsorption isotherm. The plot of parameter (C/θ) against inhibitor concentration (C) [see Figure (3-56)] yields a straight line.

The negative values of $\Delta G^{o}_{ads}$ (as shown in Table 3-12) indicate spontaneous adsorption of **[12-16]** and **[18-20]** molecules on the mild steel surface and strong interaction between inhibitor molecules and metal surface. The value of $\Delta G^{o}_{ads}$ is less than (-40 kJ/mol); it's indicating that electrostatic interaction between the charged metal surface is physical adsorption [(99)].

Table 3-12:Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption in the presence and absence of different concentrations of compounds **[12-16]** and **[18-20]** for the corrosion of mild steel in 1M $H_2SO_4$ from weight loss measurements

| **Inhibitor concentration (M)** | **1M $H_2SO_4$** | | | | |
|---|---|---|---|---|---|
| | **ΔM(g)** | **Corrosion rate (mg $cm^{-2}$ $h^{-1}$)** | **E%** | **θ** | **$\Delta G^o_{ads}$ (kJ/mol)** |
| **Uninhibited** | 0.113 | 2.8790 | - | - | |
| **[12]** | | | | | -32.55 |
| 0.001 | 0.0301 | 0.7669 | 73.36 | 0.7336 | |
| 0.0005 | 0.0732 | 1.8650 | 35.22 | 0.3522 | $R^2$= 0.9972 |
| 0.0001 | 0.0744 | 1.8955 | 34.16 | 0.3416 | |
| 0.00005 | 0.0779 | 1.9847 | 31.06 | 0.3106 | |
| **[13]** | | | | | |
| 0.001 | 0.0275 | 0.7007 | 75.66 | 0.7566 | -32.65 |
| 0.0005 | 0.0431 | 1.0981 | 61.86 | 0.6186 | $R^2$= 0.9901 |
| 0.0001 | 0.0711 | 1.8115 | 37.08 | 0.3708 | |
| 0.00005 | 0.0715 | 1.8217 | 36.72 | 0.3672 | |
| **[14]** | | | | | -34.28 |
| 0.001 | 0.0283 | 0.7210 | 74.96 | 0.7496 | |
| 0.0005 | 0.0383 | 0.9758 | 66.11 | 0.6611 | $R^2$= 0.9965 |
| 0.0001 | 0.0451 | 1.1490 | 60.09 | 0.6009 | |
| 0.00005 | 0.0711 | 1.8115 | 37.08 | 0.3708 | |
| **[15]** | | | | | -34.65 |
| 0.001 | 0.0239 | 0.6089 | 78.85 | 0.7885 | $R^2$= 0.9992 |
| 0.0005 | 0.0295 | 0.7516 | 73.89 | 0.7389 | |
| 0.0001 | 0.0543 | 1.3834 | 51.95 | 0.5195 | |
| 0.00005 | 0.0566 | 1.4420 | 49.91 | 0.4991 | |
| **[16]** | | | | | -34.05 |
| 0.001 | 0.0290 | 0.7389 | 74.33 | 0.7433 | $R^2$= 0.9963 |
| 0.0005 | 0.0394 | 1.0038 | 65.13 | 0.6513 | |
| 0.0001 | 0.0587 | 1.4955 | 48.05 | 0.4805 | |
| 0.00005 | 0.0610 | 1.5541 | 46.02 | 0.4602 | |
| **[18]** | | | | | |
| 0.001 | 0.0206 | 0.5248 | 81.77 | 0.8177 | -34.15 |
| 0.0005 | 0.0273 | 0.6955 | 75.84 | 0.7584 | $R^2$= 0.9985 |
| 0.0001 | 0.0425 | 1.0828 | 62.39 | 0.6239 | |
| 0.00005 | 0.0746 | 1.9006 | 33.98 | 0.3398 | |

Table 3-12: Continued

| | | | | | |
|---|---|---|---|---|---|
| **[19]** | | | | | -33.53 $R^2$= 0.9972 |
| 0.001 | 0.0309 | 0.7873 | 72.65 | 0.7265 | |
| 0.0005 | 0.0334 | 0.8510 | 70.44 | 0.7044 | |
| 0.0001 | 0.0532 | 1.3554 | 52.92 | 0.5292 | |
| 0.00005 | 0.0834 | 2.1248 | 26.20 | 0.2620 | |
| **[20]** | | | | | -33.27 $R^2$= 0.9984 |
| 0.001 | 0.0355 | 0.9045 | 68.58 | 0.6858 | |
| 0.0005 | 0.0439 | 1.1185 | 61.15 | 0.6115 | |
| 0.0001 | 0.0599 | 1.5261 | 46.99 | 0.4699 | |
| 0.00005 | 0.0768 | 1.9567 | 32.04 | 0.3204 | |

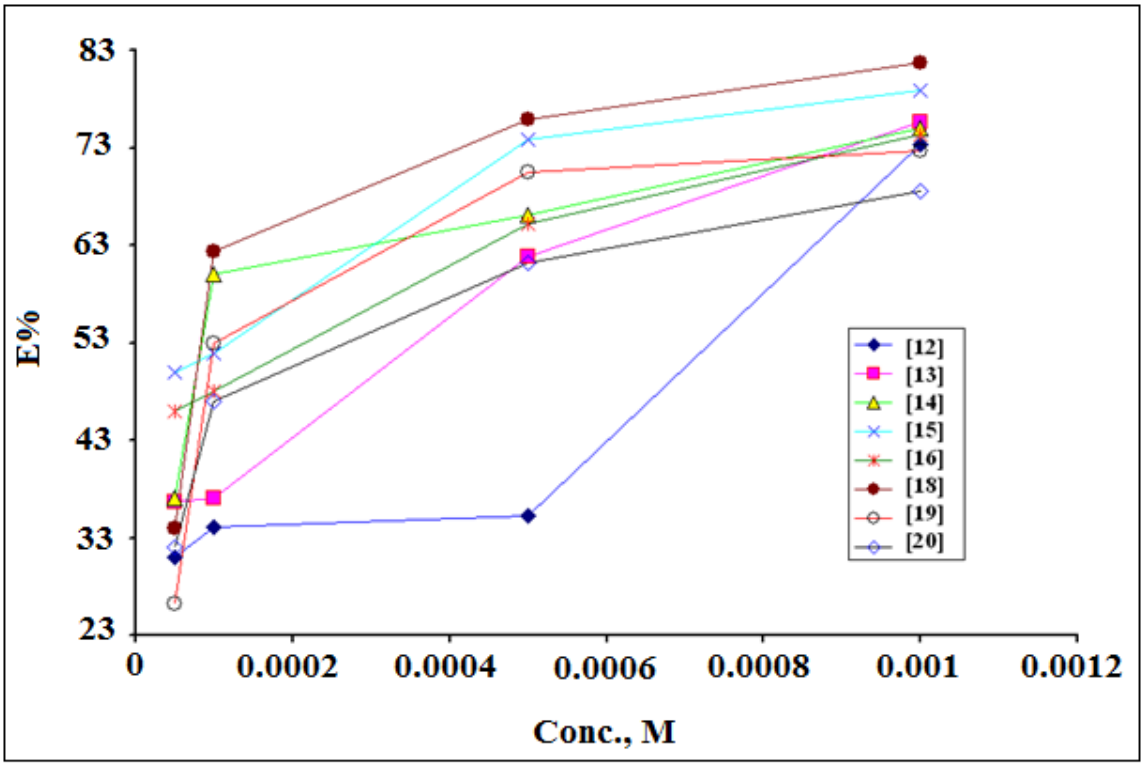



Figure3-55: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1 M $H_2SO_4$ containing different concentrations of prepared inhibitors **[12-16]** and **[18-20]**

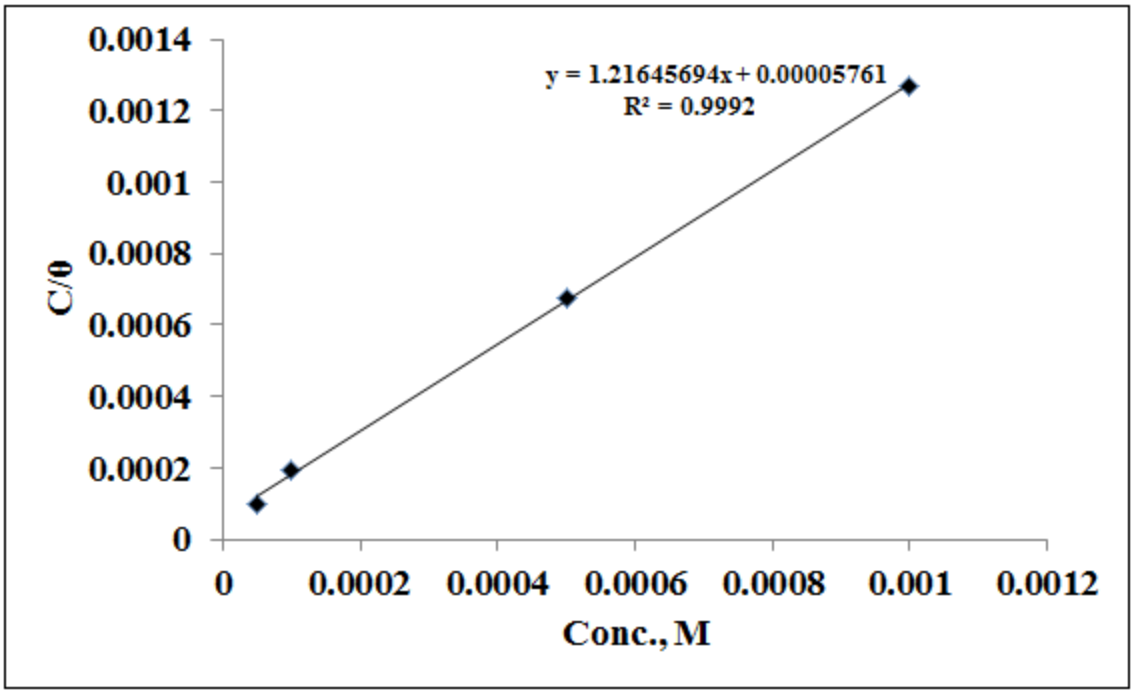



Figure 3-56: Langmuir adsorption isotherm plot for mild steel in 1M $H_2SO_4$ solution in the presence of various concentrations of inhibitor **[14]**

The anodic dissolution of iron in acidic media and the corresponding cathodic reaction has been reported as follows [(100)]:

$Fe \rightarrow Fe^{2+} + 2e^-$ (anodic reaction) (3.1)

$2H^+ + 2e^- \rightarrow H_2$ (cathodic reaction) (3.2)

As a result of these reactions, including the high solubility of the corrosion products, the metal loses weight in the solution. Corrosion inhibition of mild steel in 1 M $H_2SO_4$ by prepared compounds **[4-16]** and **[18-20]** can be explained on the basis of molecular adsorption. The compound inhibits corrosion by controlling both the anodic and cathodic reactions. In acidic solutions the prepared compounds **[4-16]** and **[18-20]** exist as protonated species. These protonated species adsorb on the cathodic sites of the mild

steel and decrease the evolution of hydrogen. The adsorption on anodic sites occurs through π-electron of aromatic ring and lone pair of electrons of nitrogen atom, which decreases anodic dissolution of mild steel [101].

## 3.4.2. Theoretical calculations

The purpose of this work is to provide information about the electron configuration of several organic inhibitors by quantum chemical calculations and to investigate the relationship between molecular structure and inhibition efficiency. All the calculations for geometry optimization were performed using the semi-empirical calculations with PM3 method. For this purpose the Hyperchem Program with complete was used. This computational method has been proven to yield satisfactory results [102, 103]. The easiest way to compare the inhibition efficiency of compounds [**4**]-[**16**] and compounds [**18**]-[**20**] is to analyze the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The calculated energies $E_{HOMO}$, $E_{LUMO}$, energy gap ($\Delta E=E_{LUMO}-E_{HOMO}$) and other indices are given in Tables 3-13 and 3-14.

Table 3-13: Calculated quantum chemical parameters of prepared compounds **[4-11]** as modeling systems by using PM3 method

| Comp. No. | HOMO (eV) | LUMO (eV) | $\Delta E^*$ (eV) | $\mu$ (Debye) | $N_{atom}$ ** | planarity |
|---|---|---|---|---|---|---|
| **[4]** | -9.0140 | -1.2485 | -7.7655 | 2.09 | -0.074 | Planar |
| **[5]** | -8.3462 | -1.0692 | -7.2769 | 1.87 | -0.054 | Planar |
| **[6]** | -9.3099 | -1.7047 | -7.6051 | 6.76 | -0.042 | Planar |
| **[7]** | -8.8004 | -1.1838 | -7.6166 | 1.58 | -0.081 | Planar |
| **[8]** | -8.5258 | -1.3765 | -7.1493 | 1.92 | -0.083 | Semi-planar |
| **[9]** | -8.7493 | -1.2083 | -7.5089 | 1.58 | -0.056 | Planar |
| **[10]** | -9.0132 | -0.9283 | -8.0849 | 3.65 | -0.046 | Semi-Planar |
| **[11]** | -8.6245 | -1.2346 | -7.3899 | 1.34 | -0.051 | Planar |

*ΔE (Energy gap) = $E_{HOMO}$-$E_{LUMO}$, ** Formal charge of N atom of imine group

Table 3-14: Calculated quantum chemical parameters of prepared compounds **[12-16]** and **[18-20]** as modeling systems by using PM3 method

| Comp. No. | HOMO (eV) | LUMO (eV) | $\Delta E^*$ (eV) | μ (D) | Formal charge** | | Planarity |
|---|---|---|---|---|---|---|---|
| | | | | | $N_{atom}$ | $S_{atom}$ | |
| **[12]** | -8.9462 | -1.6626 | -7.2836 | 5.88 | -0.024 | 0.113 | Planar |
| **[13]** | -8.7445 | -1.6110 | -7.1335 | 6.88 | -0.022 | 0.077 | Planar |
| **[14]** | -8.7838 | -1.6097 | -7.1741 | 6.87 | -0.022 | 0.081 | Semi-planar |
| **[15]** | -8.7838 | -1.6278 | -7.1560 | 6.71 | -0.023 | 0.087 | Planar |
| **[16]** | -8.9121 | -1.6701 | -7.2419 | 5.45 | -0.025 | 0.088 | Semi-planar |
| **[18]** | -8.9393 | -1.7110 | -7.2282 | 0.008 | -0.026 | 0.080 | Planar |
| **[19]** | -8.8802 | -1.6524 | -7.2277 | 6.19 | -0.027 | 0.086 | Planar |
| **[20]** | -8.94024 | -1.6992 | -7.2409 | 3.68 | -0.024 | 0.093 | planar |

*ΔE (Energy gap) = $E_{HOMO}$-$E_{LUMO}$, ** Formal charge of N atom of imine group

The energy gap (ΔE) between the HOMO and LUMO energy levels of the molecules is important factor, whereas, low absolute value of the energy gap (ΔE) gives good inhibition efficiencies [104]. The compound **[8]** showed

lowest energy gap (see Table 3-13) that in good agreement with experimental results (see Table 3-11) whereas, (E%=62.21) and also showed ($\Delta G^{o}_{ads}$=-39 kJ/mol) which is approximately chemisorption behavior [105].

Table 3-13 shows different dipole moments for suggested inhibitors [**4]-[11**]. The values of dipole moment can explain due to non-uniform distributions of positive and negative charges on the various atoms (see Figure 3-57) and concentration of negative charges on N (C=N) for all molecules (see Table 3-13). Non-uniform distribution of electronic density and planarity of molecule [106] are good factors to improve dipole–dipole interactions between organic molecules and mild steel surface.

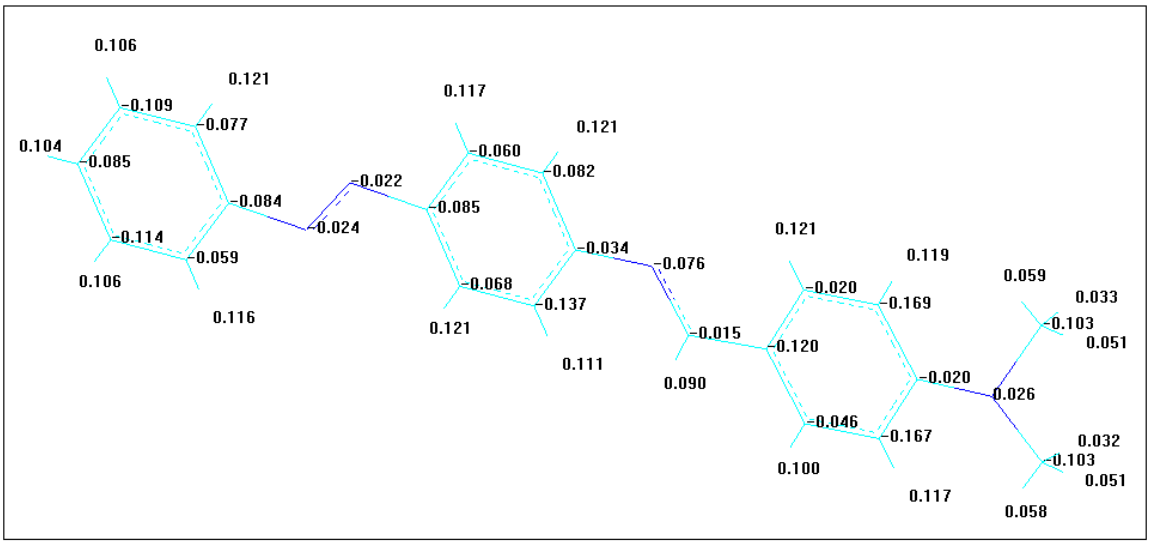



Figure 3-57: Formal charges of compound **[1]**

The compound [**13**] showed lowest energy gap (Table 3-14) that in good agreement with experimental results (see Table 3-12) whereas, (E%=76) and also showed physisorption with value $\Delta G^{o}_{ads}$=-33 kJ/mol [105].

Non-uniform distributions of positive and negative charges on the various atoms (see Figures 3-58) and concentration of negative charges on N (C=N)

and S atoms for all molecules (see Table 3-14). Non-uniform distribution of electronic density and planarity of molecule [106] are good factors to improve dipole–dipole interactions of organic molecules and mild steel surface.

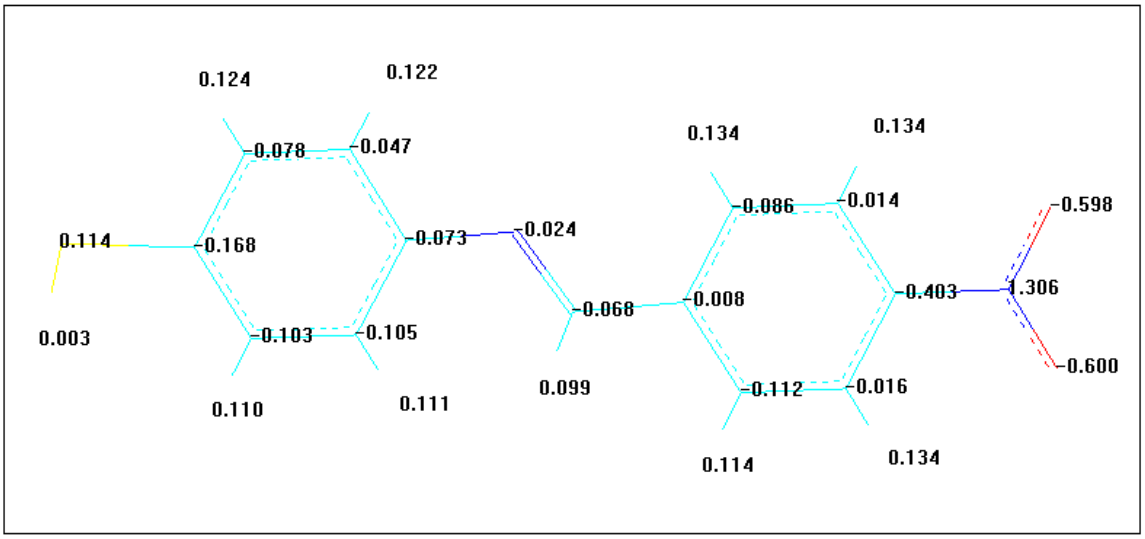



Figure 3-58: Formal charges of compound [**12**]

To the well-known of our knowledgement, the imine moiety in each compound plays important role to improve the characteristic of correction inhibitors. Therefore, planarity of molecules gave an advantage to enhance interactions between an organic inhibitor and mild steel surface. However, semi-planarity of an organic inhibitor could be useful in some cases to approach the imine moiety to the surface of iron metal. That's could be confirmed by experimental and theoretical data of present work, for the value of corrosive efficiencies, free energies adsorption and energy gap.

# *Conclusion and Future Work*

## 4. Conclusion

Different organic compounds that contain hetero-atoms (N, S, and O) were prepared as corrosion inhibitors for mild steel. The structures of prepared compounds were confirmed using spectroscopic techniques. Weight loss measurement was used to evaluate the corrosive efficiency of prepared compounds for mild steel in 1M $H_2SO_4$ solution at $30^oC$. All suggested compounds were shown good inhibition efficiency in range 40-82% and also physisorption behavior of prepared compounds were confirmed by values of free energy adsorptions. In addition, theoretical calculations were performed for prepared compounds as molecular models. These calculations gave useful information about the nature of interaction between suggested prepared compounds and iron metal.

## 5. Future Work

1. Preparation of new compounds contains heterocyclic fragments and N=N bonds.
2. Weight loss measurements are applied to study the inhibition efficiency of prepared compounds for mild steel in acidic media.
3. Theoretical calculations will be used as useful tools to investigate the relationship between molecular structure and inhibition efficiency by using semi-empirical molecular quantum calculation within the PM3 method.

# Reference

# *Reference*

## 6. Reference


1. Carey F.A., Sundberg R.J. *"Advanced Organic Chemistry. Part B: Reaction and Synthesi"*, Kluwer Academic/ Plenum publishers, New York **(2001)**.
2. Jiben R.*"A Self-Study Guide to the Principles of Organic Chemistry"*, Universal-Publishers **(2013)**.
3. Koeller, K.M.; Wong, C-H., *"Enzymes for chemical synthesis"*, Nature, 409, 232-240 **(2001)**.
4. Nicolaou, K. C.; Frederick, M. O.;Aversa, R., J. Angew. Chem. Int. Ed. 47, 7182, **(2008)**.
5. Baran, P. S.; Burns, N. Z., J. Am. Chem. Soc. 128, 3908, **(2006)**.
6. Heinrich Z.*"Color Chemistry"*, 3rd Ed., Wiley-VCH Veriag GmbH & Co. **(2003)**.
7. Klaus H.*"Industrial Dyes"*, Wiley-VCH Veriag GmbH & Co. **(2003)**.
8. Mohammad R.,Hossein E., Ali S., Zohreh G., Maryam M. M.,Fatemeh O., and Parvaneh P., Journal of the Korean Chemical Society, 56, 6 **(2012)**.
9. Robert M. C.*"Colour chemistry"*, Royal society of chemistry, UK **(2001)**.
10. Krasnokutskaya E. A., Semenischeva N. I., Filimonov V. D., Knochel P., Synthesis, 81-84 **(2007)**.

# *Reference*


11. Filimonov V. D., Trusova M., Postnikov P., Krasnokutskaya E. A., Lee Y. M., Hwang H. Y., Kim H., Chi K.-W., Org. Lett., 10, 3961-3964 **(2008)**.

12. Loebbecke S., Ferstl W., Panic S., Tuercke T., Chem. Eng. Technol. 28, 484-493 **(2005)**.

13. Sharma B.K., *"Industrial Chemistry"*, 16th Ed., Krishina-Prakashan, **(2013)**.

14. Wang M., Funabiki K., Matsui M., Dyes and Pigments, 57, 77-86 **(2003)**.

15. Frantisek J., Marketa S., Valerio B., Beilstein J. Org. Chem. 9, 1463–1471 **(2013)**.

16. Naik R D, Desai C. K., Desai K. R., Oriental J Chem., 16, 159 **(2000)**.

17. Dixit B.C., Patel H.M., Desai D.J., Dixit R.B., E-J. chem., 6(2), 315 **(2009)**.

18. Kirkan, B., Gup, R., Turk. J. Chem. 32, 9-17**(2008)**.

19. Fu Y., Viraraghavan T., Bioresour. Technol., 79, 251–262 **(2001)**.

20. Eric L. Jan S., Didier R., *"Environmental Chemistry for a Sustainable World: Vol 2: Remediation of Air and Water Pollution",* Springer **(2012)**.

21. Eva E., Heidi U., Rudolf V., Burkhard K., Michael L., Rudolf S., Wolfgang B., 216 (1): 76–80 **(2008)**.

# *Reference*


22. Pricelius S., Held C., Sollner S., Deller S., Murkovic M., Ullrich R., Hofrichter M., Cavaco-Paulo A., Macheroux P., Guebitz G.M., Enzyme and Microbial Technology 40 , 1732–1738 **(2007)**.

23. Oguzie E.E., Ebenso E.E., Pigment & Resin Technol., 35, 30 **(2006)**.

24. Sorkhabi H.A., Masoumi B., Ejbari P., Asghari E., J. Appl. Electrochem, 39, 1497**(2009)**.

25. Cimerman Z., Miljanic S. and Galic N., CroaticaChemicaActa, 73(1), 81- 95 **(2000)**.

26. Sahu R., Thakur D.S., and Kashyap P., *"Schiff base: An overview of its medicinal chemistry potential for new drug molecules"*, Int pharm sci nanotech, 5, 1757-1764 **(2012)**.

27. Vigato P. A. and Tamburini S., Coordination Chemistry Reviews, 248, 1717-2128 **(2004)**.

28. Cozzi P. G., Chemical Society Reviews, 33, 410-421 **(2004)**.

29. Borisova N. E., Reshetova M. D., Ustynyuk Y. A., Chemical Reviews, 107, 46-79 **(2007)**.

30. Korich A. L., Hughes T. S., Synlett, 2602-2604 **(2007)**.

31. Arifuzzaman Md., Mohammad R. K., Tasneem A. S., Aminul H. M., Mohamad A. A., International Journal of Organic Chemistry, 3, 81-86 **(2013)**.

32. Macho V, Kralik M, Hudec J, Cingelova J., J. Mol. Catal. A: Chem., 209, 69-73**(2004)**.

# *Reference*


33. Xia L. Z., Yi L., Hua L. C., Jun Y. H., Jun Y., Zhi P. H., Themochimica acta , 440, 51-56 **(2006)**.

34. Cozzi, P. G., Chem. Soc. Rev. 33, 410-421**(2004)**.

35. Abbaspour A., Esmaeilbeig A.R., Jarrahpour A.A., Khajeh B., Kia R., Talanta, 58, 397 **(2002)**.

36. Mahajan R.K., Kaur I., Kumar M., Sens. Actuators, B, Chem., 91, 26-31 **(2003)**.

37. Ganjali M.R., Golmohammadi M., Yousefi M., Norouzi P., Salavati-Niasari M., Javanbakht M., Anal. Sci, 19, 223-227 **(2003)**.

38. Jain A.K., Gupta V.K., Ganeshpure P.A., Raisoni J.R., Anal. Chim. Acta, 553, 177-184 **(2005)**.

39. Jeong T., Lee H.K., Jeong D.C., Jeon S., Talanta, 65, 543-548 **(2005)**.

40. Gupta V.K., Singh A.K., Mehtab S., Gupta B., Anal. Chem. Acta, 566, 5-10 **(2006)**.

41. Nagajothi A., Kiruthika A., Chitra S. and Parameswari K., Res. J. Chem. Sci., 3(2), 35-43 **(2013)**.

42. Sari N., Aytac A., Asian Journal of Chemistry, 21, 839-848 **(2009)**.

43. Li S., Chen S., Ma H., Yu R., Liu D., Corros. Sci, 41, 1273-1278 **(1999)**.

44. Ashassi-Sorkhabi H., Shabani B., Aligholipour B., and Seifzadeh D., Appl. Surf. Sci., 252, 4039-4047 **(2006)**.

45. Quan Z., and Chen S., Li Y., Corros. Sci., 43, 1071-1080**(2001)**.

# *Reference*


46. Mieczyslaw S., Joanna T., Int. J. Electrochem. Sci., 8, 8329 – 8347 **(2013)**.

47. Chetan D.M., Dinesh K.P., *"Health and Pharmaceutical Biotechnology"*, 1st Ed., laxmi publications **(2006)**.

48. William H., Christopher S., Brent L. and, Eric V., *"Organic Chemistry"*, 5th Ed., Brooks/Cole Cengage Learning **(2011)**.

49. L. Sun, Y. Guo, G. Peng, C. Li, Synthesis, 3487-3488 **(2008)**.

50. Marye A., Jones K.W., "Organic Chemistry", 3rd Ed., Jones & Bartlett Publisher Inc. **(2004)**.

51. Wong Y. C., Jayanth T. T., and Cheng C. H., Org. Lett., 8, 5613-5616 **(2006)**.

52. Takashi I., Yuki F., Tomoteru M., Sae B., Haruki T., Tomohiro M., Yasunari M. and Hironao S., Org. Biomol. Chem., 10, 293-304 **(2012)**.

53. Lea Z. G., Chen Z. C., Hu Y., Zheng Q. G., Synthesis, 1951-1954 **(2004)**.

54. Wang X.j., Sidhu K., Zhang L., Campbell S., Haddad N., Reeves D. C., Krishnamurthy D., Senanayake C. H., Org. Lett., 11, 5460-5493 **(2009)**.

55. Oertel A. M., Ritleng V., Chetcuti M. J., Synthesis, 2009, 1647-1650 **(2009)**.

56. Gerhardus H., Michiel P., Neil G., Y. Paul, and J. H. Payer, Corrosion Costs and Preventive Strategies in the United States, Supplement to Materials Performance, July 2002, Report No. FHWA - RD - 01 - 156, Federal Highway Administration, McLean, VA, **(2002)**.

# *Reference*


57. Ahmad Z., British Corrosion Journal, 31, (2), 191-197**(1996)**.

58. Davis J.R., *" Form of Corrosion: Recognation and Prevention, Corrosion: Understanding the Basics"*, Ed., ASM International, P. 99-192**(2000)**.

59. Sastri V.S., Elboujdaini M., Perumaneddi J. R., Economics of Corrosion and Wear in Canada. In: Li J., Elboujdaini M., proceedings of the international conference on Environmental Degradation of metals, metallurgical Society of Canadian Institute of Mining Vancouver,BC, Canda **(2003)**.

60. Sarmiento E., Gonzalez-Rodriguez J. G., Uruchurtu J., Sarmiento O., Menchaca M., Int. J. Electrochem. Sci., 4, 134-143**(2009)**.

61. Winston R. R., Uhlig's Corrosion Handbook, 2nd Ed., John Wiley & Sons, Inc. **(2000)**.

62. Yanyan Y., Lifen X., Yanqiang Z., Fengyun W., Int. J. Electrochem. Sci., 3, 56-66 **(2008)**.

63. Megdalena Nunez, *"Prevention of Metal Corrosion"*, Nova Science Publishers, Inc. **(2007)**.

64. Musa A. Y., Kadhum, A. A. H., Daud, A. R., Mohamad, A. B., Takriff, M. S., Kamarudin, S.K., 51, 2393–2399 **(2009)**.

65. Rivera-Grau L.M., Casales M., Regla I., Ortega-Toledo D.M., Ascencio-Gutierrez J.A., Porcayo-Calderon J., Martinez-Gomez L.,Int. J. Electrochem. Sci., 8, 2491-2503 **(2013)**.

# *Reference*


66. Konstantinos D. D., Chris M.,Panagiotis L., Ind. Eng. Chem. Res. 45, 7795-7800 **(2006)**.

67. Selles C., Benali O., Tabti B., Larabi L., Harek Y., J. Mater. Environ. Sci. 3 (1) 206-219**(2012)**.

68. Ebenso E. E., Eddy N. O., Odiongenyi A. O., Portug. Electrochim. Acta. 27(1) 13-22**(2009)**.

69. Eddy N.O., Odoemelam S.A., Odiongenyi A.O., Green Chem. Lett. Rev., 2 (2) 111-119**(2009)**.

70. Quraishi M.A., Ahamad I., Singh A.K., Shukla S.K., Lal B., Singh V., Mater. Chem.Phys. 112, 1035-1039**(2008)**.

71. Zerfaoui M., Ouddac H., Hammouti B., Kertit S., Benkaddourb M., Prog. Org. Coat., 5,134-138 **(2004)**.

72. Moretti G., Guidi F., Grion G., Corros. Sci., 46, 87- 403**(2004)**.

73. Kiani M.A., Mousavi M.F., Ghasemi S., Shamsipur M., Kazemi S.H., Corros. Sci., 50, 1035-1045**(2008)**.

74. Silva A.B., Agostinho S.M.L. Barcia O.E., Cordeiro G.G.O., D'Elia E., Corros. Sci., 48, 3668-3674**(2006)**.

75. Gao G., Liang C., Electrochim. Acta, 52, 4554-4559**(2007)**.

76. Yurt A., Bereket G., Ogretir C., J. Mol. Struct. THEOCHEM 725,215-221**(2005)**.

77. Ghasemi Z., Tizpar A., Appl. Surf. Sci., 252, 3667- 3672**(2006)**.

# *Reference*


78. Barouni K., Bazzi L., Salghi R., Mihit M., Hammouti B., Albourine A., ElIssami S., Mater. Lett. , 62, 3325-3327**(2008)**.

79. Spah M., Spah D.C., Deshwal B., Lee S., Chae Y., Park J.W., Corros. Sci., 51, 1293-1298**(2009)**.

80. Frank J.,*"Introduction to Computational Chemistry"*, 2nd Ed., John Wiley &Sons,Ltd. **(2007)**.

81. Ramachandran K. I., Deepa G., Namboori K., *"Computational Chemistry and Molecular Modeling: Principles and Applications"*, Springer-Verlag Berlin Heidelberg **(2008)**.

82. Stewart J., J. Comp. Chem., 10, 209-220**(1989)**.

83. Arun B., Bahl B. S., *"A Textbook of Organic Chemistry (for B. Sc. Students)"*, 13th Ed., S.Chand & Company Ltd. **(2006)**.

84. Vogel A. I., Tatchell A. R., Furnis B. S., Hannaford A. J. and Smith P. W. G., *"Vogel's Textbook of Practical Organic Chemistry"*,5th Ed., Prentice Hall **(1996)**.

85. Conard C. R. and Dolliver M. A., Organic Syntheses, 12, 22 **(1932)**.

86. Leuck G. J. and Cejka L., Organic Syntheses, 7, 42 **(1927)**.

87. Issa R. M., Khedr A. M. and Rizk H., Chin J., Chem. Soc., 55, 875-884 **(2008)**.

88. Kurla M., Canadian journal of chemistry, 33, 1-5 **(1955)**.

89. Lesley R., Andrea R., and Esmaeel N., Journal of under graduate Research in Bioengineering, 8,126-132 **(2008-2010)**.

# *Reference*


90. ASTM G 31 – 72, "Standard Practice for labortary Immersion Corrosion Testing of Metals", West Conshohocken, PA, ASTM **(1990)**.

91. Ajmal M., Mideen A. S., Quraishi M. A., Corros. Sci., 36, 79-84 **(1994)**.

92. Agrawal R., Namboodhiri T.K.G., Corros. Sci., 30, 37-49 **(1990)**.

93. HyperChem, version 7.5, z Hypercube, Inc.: Gainesville, FL, USA, **(2002)**.

94. Peter T., Michael G., *"The Molecular World, Alkenes and Aromatics"*, 1st Ed., Open University **(2002)**.

95. Robert M. S., Francis X. W., *"Spectrometric Identification of Organic Compounds"*, 7th Ed., Wiley **(2005)**.

96. Kalsi P. S., *"Organic Reactions Stereochemistry and Mechanism",* New Age International **(2007)**.

97. Pavia D. L., Lampman G. M. and Kriz G. S., Introduction to Spectroscopy, Brooks Cole; 3rd edition **(2000)**.

98. Raafat M. I., Abdalla M. K., Helen R., Journal of the Chinese Chemical Society, 55, 875-884 **(2008)**.

99. Umoren S. A., Obot I. B., Ebenso E.E., Obi-Egbedi N.O., Port. Electrochim. Acta, 26, 199-209 **(2008)**.

100. Amin M. A., Khaled K. F., Corros. Sci., 52**,** 1762–1770 **(2010)**.

101. Shukla S. K., Ahamad I., Quraishi M. A., Materials Letts. , 63, 819–822 (**2009)**.

# *Reference*


102. Eddy N. O., Ita B. I. and Ebenso E. E., Int. J. Electrochem. Sci., 6, 2101-2121 **(2011)**.

103. Quraishi S. M., Quraishi M. A., and Quraishi R., Open Corros. J., 2, 83-87 **(2009)**.

104. El-Naggar M. M., Corros. Sci., 49, 2226-2236 **(2007)**.

105. Bentiss F., Lebrini M., Lagren ee M., Traisnel M., Elfarouk A., Vezin H., Electrochim. Acta, 52, 6865-6872 **(2007)**.

106. Obot I. B., Obi-Egbedi N.O., Surf. Rev. Lett., 15(6), 903-910 **(2008)**.

**الخلاصه**

1-في هذه الدراسه تم تحضير بعض المركبات العضويه الحاويه على ذرات غير متجانسه من قبل العديد من الخطوات كالاتي:

اولا؛ المركبات العضوية 4-(فينيل ثنائي ازونيل) انيلين **[1]** و 4-(فنيل ثنائي ازونيل) فينول **[17]** أعدت في خطوتين:

- تفاعل الأمينات الاروماتيه الأولية (الأنيلين) مع حمض النيتروز لتكوين ملح الديازونيوم.
- اقتران أيون الديازونيوم الاروماتي مع حلقات اورماتيه الفعاله (الأنيلين، الفينول).

ثانيا ؛ المركبات العضوية 1,5- ثنائي فنيل بنتا – 1,4 – داين -3- ون **[ 2 ]** ، 3- (فيوران -2- ايل) اكريل الديهايد **[ 3 ]** حضرت بتكاثف الدولي بين جزيئين من ألديهايد أو كيتون.

ثالثا ؛ المركبات العضوية **[ 4-11]** أدناه تم تحضيرها عن طريق تفاعل **[1]** مع مجموعه الكاربونيل في الديهايدات والكيتونات و مجموعه الامين .

**[4]** -N, N –ثنائي مثيل -4- [(فنيل ثنائي ازونيل) فنيل أمينو] ميثل انيلين

**[5]**- N-(4- برومو بنزيلدين)-4- (فنيل ثنائي ازونيل) انيلين

**[6]** -N-(4- نايترو بنزيلدين)-4- (فنيل ثنائي ازونيل) انيلين

**[7]** -N-(فيوران -2- ايل ميثيليين) -4- (فنيل ثنائي ازونيل) انيلين

**[8]**- N-(5, 1- ثنائي فينل بنتا -1, 4- داين-3- يلادين) -4- (فنيل ثنائي ازونيل) انيلين

**[9]** -N-(3-فنيل الايدين)-4-(فنيل ثنائي ازونيل) انيلين

**[10]** -5-[4-(فنيل ثنائي ازونيل) فنيل أمينو] بينتاين -1, 2, 3, 4- رباعي اول

**[11]** -N- (3-فيوران-2- ايل) ألايدين-4- (فنيل ثنائي ازونيل) انيلين

مركب عضوي 4-(4-نايترو بنزيلدين أمينو) بنزين ثايول **[ 12 ]**حضر بالتكاثف بين مجموعة الكربونيل من بارا نايترو بنزل الديهايد و مجموعة الأمينية من بارا امينو فينول .

رابعا؛ المركبات العضويه **[13-16]** أدناه حضرت عن طريق **[12]** مع مجموعه الاكيليه في (اثيل برومايد, n-بروبيل برومايد, بنزل كلورايد او أثيلين ثنائي كلورايد) ومجموعة الثايول.

**[13]** -4-(أثيل ثايو)-N-(4- نايترو بنزيلدين) انيلين

**[14]** -4-(4- نايترو بنزيلدين)-4-(بروبيل ثايو) انيلين

**[15]** -4-(بنزل ثايو)-N-(4-نايترو بنزيلدين) انيلين

**[16]** -4-(2-كلورو اثيل ثايو)-N-(4-نايترو بنزيلدين) انيلين

المركبات العضويه **[18-20]** أدناه حضرت عن طريق تفاعل -4-(2-كلورو اثيل ثايو)-N-(4-نايترو بنزيلدين) انيلين **[16]** مع(4-(4-نايترو بنزيلدين أمينو) بنزين ثايول **[12]** , 4-(فنيل ثنائي ازونيل) فينول **[17]** , بارا امينو بريدين ).

**[18]** -(N,N)-4,4-[أيثان -2,1- ثنائي ايل ثنائي(سيلفان ثنائي ايل)] ثنائي[ N-(4-نايترو بنزيلدين) انيلين]

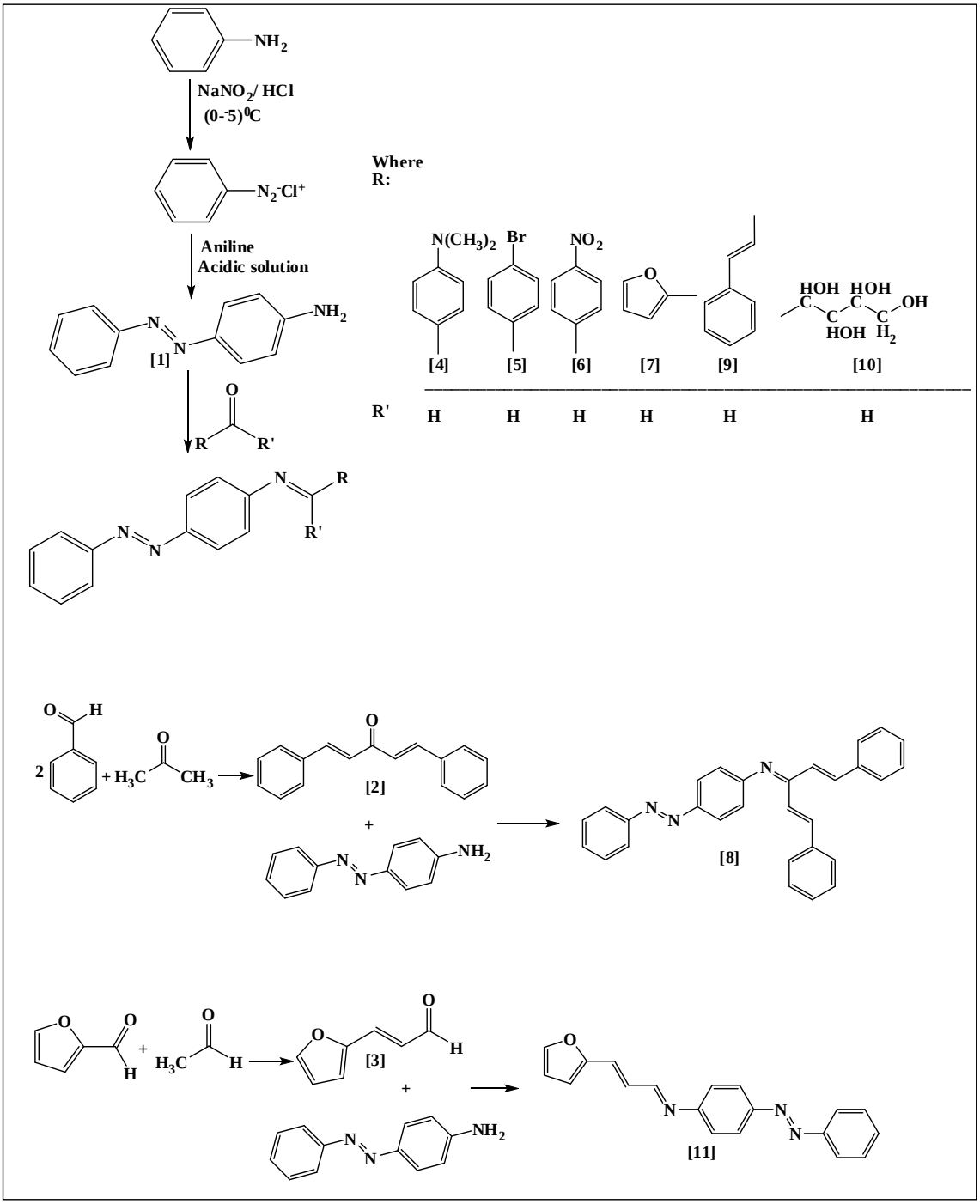
**[19]** -N-(4-نايترو بنزيلدين)-4-[2-{4-(فنيل ثنائي ازونيل) فينوكسي} أثيل ثايو] انيلين

**[20]** -N-[2-{4-(4-نايترو بنزيلدين أمينو) فنيل ثايو} أثيل] بايردين-4-امين

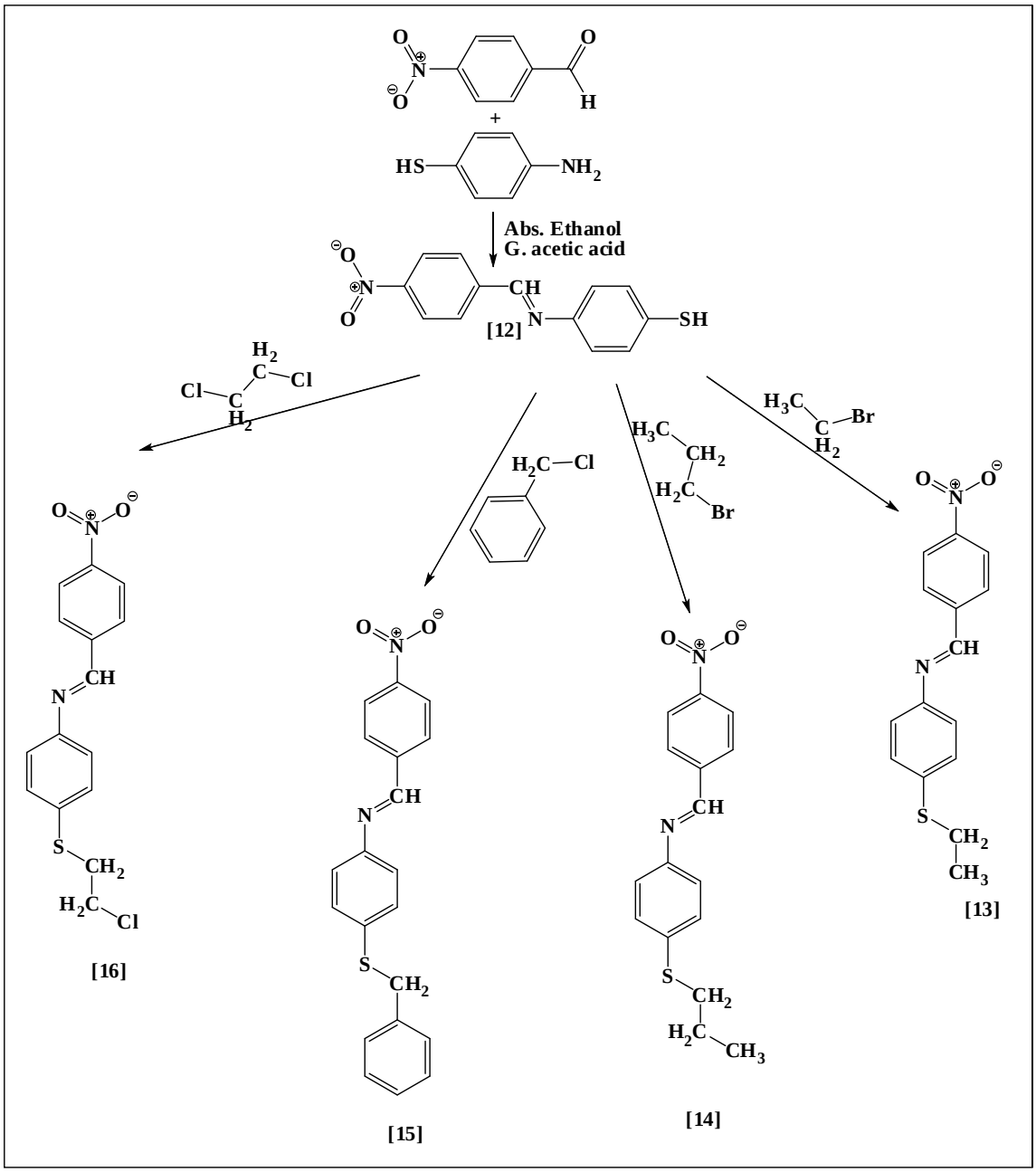
2-تشخيص المركبات اعلاه من خلال قياس درجات الانصهار , طيف الاشعه فوق الحمراء وتقنيه الاشعه المرئيه والغير المرئيه.

3- المركبات العضويه **[4-16]**و **[18-20]**تم استخدامها كمثبطات لتأكل الحديد الصلب في محلول حامض الكبريتيك بتركيز 1 مولاري وبدرجه حراره 30 مئويه. الخساره بالوزن تعتبر طريقه تقييم لأختبار كفاءه التثبيط للمركبات اعلاه.

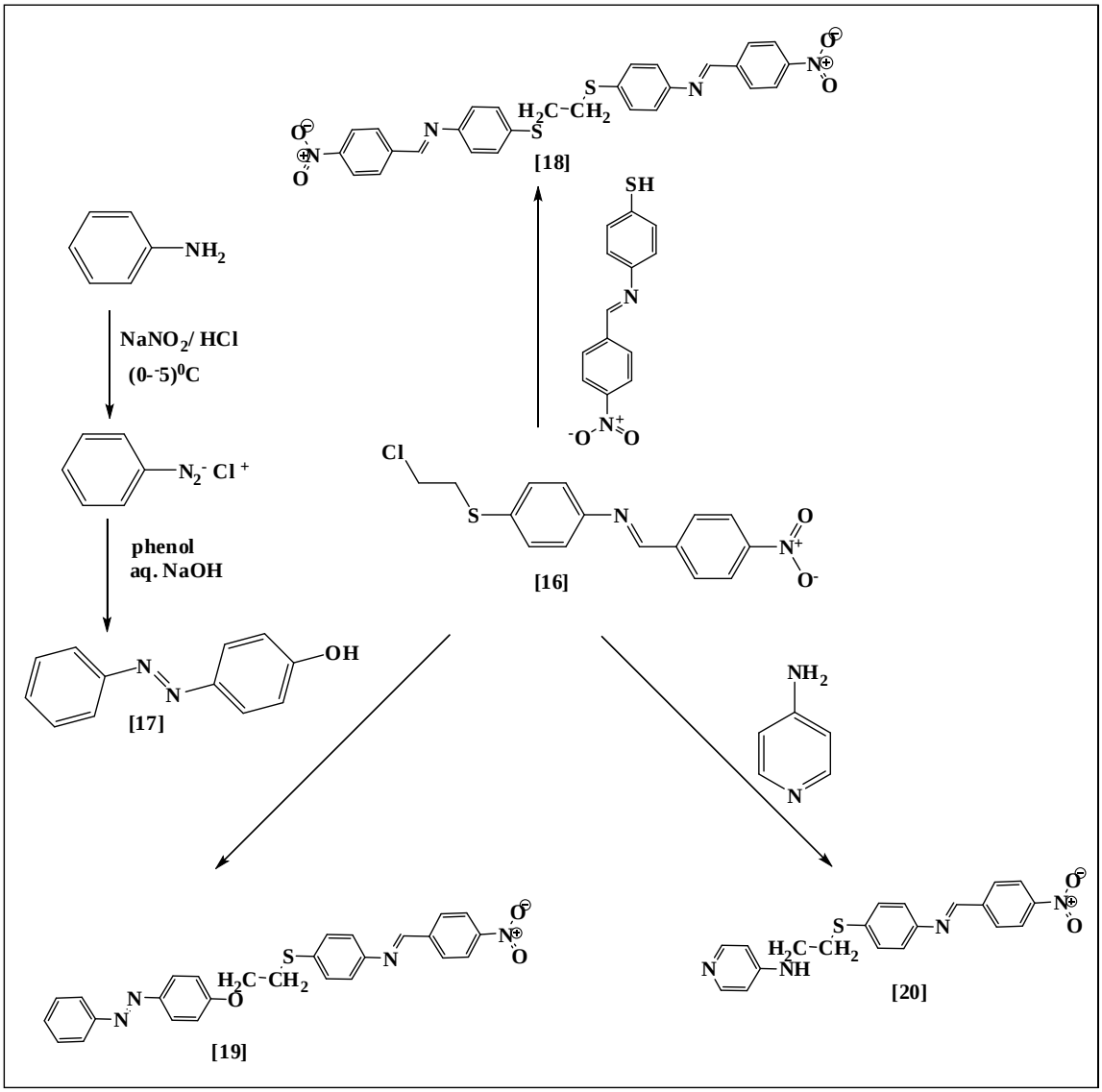
4- الحسابات النظريه تم حسابها لغرض البحث عن العلاقه بين التركيب الجزيئي وكفاءه التثبيط من خلال استعمال حسابات الميكانيك الكم التجريبيه PM3ضمن برنامج HYPERCHEM. مركب [8]أظهر أقل كفاءة الطاقة دلاله على كفاءه المثبط .الخطوات إعداد مركبات[1-20] يمكن تمثيل كما هو مبين في المخططات التالية :




المخطط 1: الخطوات الكيميائيه لتخليق المركبات **[1-11]**




المخطط 2: الخطوات الكيميائيه لتخليق المركبات **[12-16]**




المخطط 3: الخطوات الكيميائيه لتخليق المركبات **[17-20]**

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

كليه العلوم / جامعة النهرين

قسم الكيمياء

# تحضير مركبات عضوية أروماتيه تحوي على ذرات غير متجانسة لغرض استخدامها كمثبطات للتأكل لمعدن الحديد في محلول حامضي

رسالة مقدمة الى كليه العلوم – جامعه النهرين وهي جزء من متطلبات نيل
درجة الماجستير في الكيمياء

من قبل

**حنان حسين علي**

بكلوريوس 2010 (جامعة النهرين)

بأشراف

**أ. م. د.مهدي صالح شهاب**

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