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College of Science
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Synthesis and Corrosion Inhibition Study of some Heterocyclic Compounds

A Thesis

Submitted to the College of Science / Al-Nahrain University as a Partial Fulfillment of the Requirements for the Degree of Master of Science in Chemistry

By

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June 2016 Ramadan 1437

بسم الله الرحمن الرحيم

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الأهداء

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الى مقلة عيني

والدتي

الى العيون البريئة التي تنظر ألي بحب

أخي وأخواتي

الى جميع من أحب ..أهدي ثمرة جهدي

سجى صبحي

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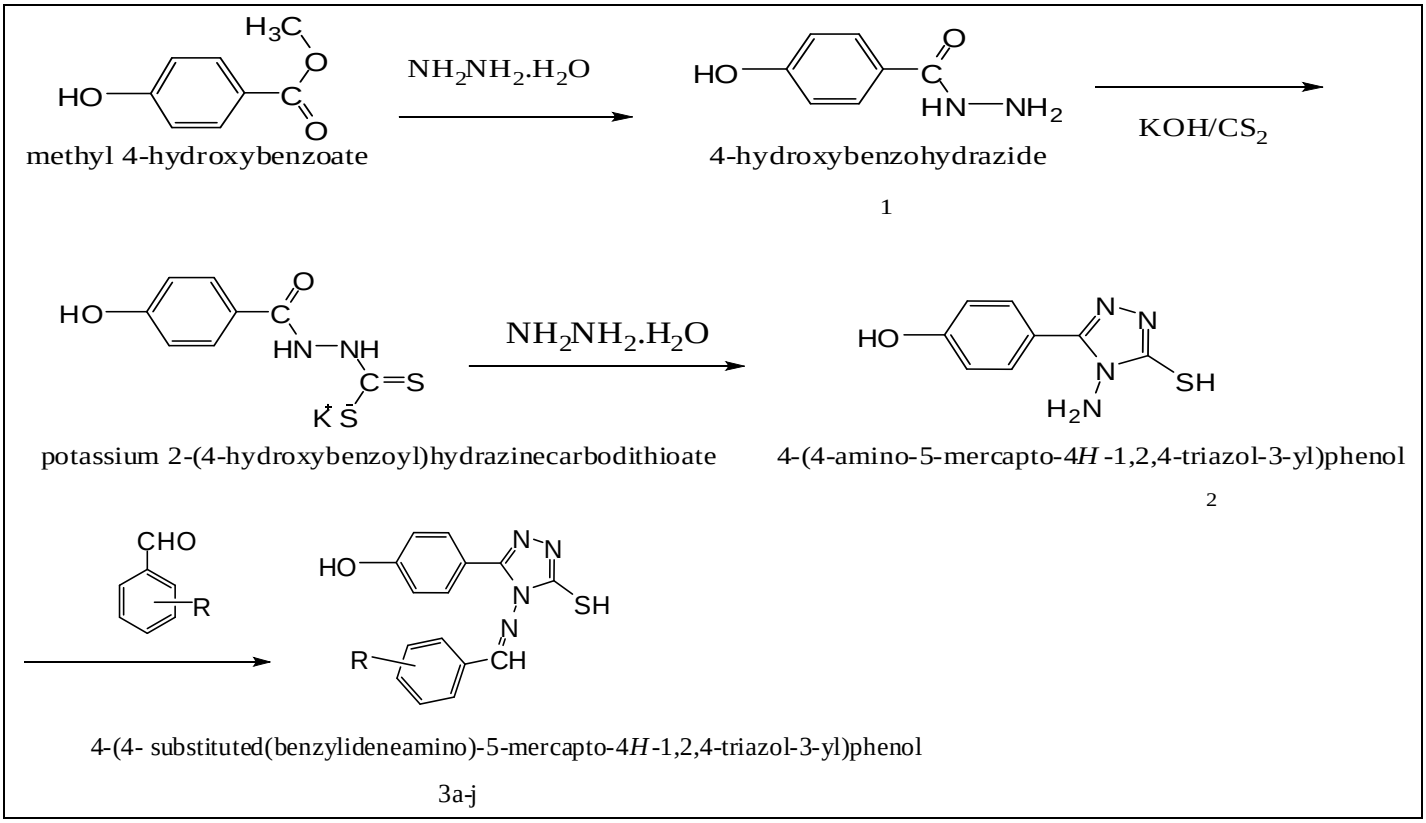
Saja subhi

Summary

New Schiff's bases with 1,2,4-triazole ring (3a-j) have been synthesized from 4-(4'-amino-5-mercapto-4H-1, 2, 4-triazol-3-yl) phenol **(2)** which is obtained from 4-hydroxybenzohydrazide **(1)** by a cyclization reaction as shown in (scheme 3-1). Infrared spectroscopy and ^{1}H NMR spectroscopy were used to characterize the structures of synthesized compounds. All the final products are indicated as thione-thiol tautomers.

The Corrosion inhibition of prepared compounds **(2)** and **(3a-j)** have been studied on mild steel in one molar sulfuric acid solution at 25 ^{o}C. Weight loss method was used to evaluate the inhibition efficiency of the above compounds. Results indicate that the inhibition efficiency IE% increases with increasing inhibitor concentration. Results indicated also that six compounds (3b, 3d, 3e, 3f, 3h, and 3j) exhibited at least 87.8 % IE with the minimum inhibition concentrations about $5*10^{-5}$ M. This excellent inhibition efficiency may attributed mostly to the presence of heteroatoms attached to benzene ring substituents derived from introduced benzaldehyde derivatives (*p*-OH, *p*-Br, o-NH_2, *p*-CH_3, *p*-OCH_3, and o-OH). High Planarity of the synthesized molecules may have been the main reason for the strong adsorption of the molecules on the metal surface.



Scheme (3-1): Synthetic pathway for compounds [1-3(a-j)], where R = H, *p*-OH, *p*- $(CH_3)_2N$, *p*-Br, *o*-NH_2), *p*-CH_3, *p*-NO_2, *p*-OCH_3, *p*-Cl, *o*-OH respectively.

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List of Abbreviations

Abbreviation	Meaning
Arom	Aromatic
Aliph	Aliphatic
ASTM	American Society for Testing and Materials
BHT	Butylated hydroxytoluene
AHPTT	4-amino-5-(2-hydroxy) phenyl-4H-1, 2, 4,-triazole-3-thiol
APTT	4-amino-5-phenyl-4H-1, 2, 4,-triazole-3-thiol
ASTT	4-amino-5-styryl-4H-1, 2, 4,-triazole-3-thiol
CNS	Central nervous system
CR	Corrosion rate
DMSO	Dimethyl sulfoxide
DPPH	2,2-diphenyl-1-picrylhydrazyl
FTIR	Fourier Transform Infrared Spectroscopy
1H-NMR	Proton Nuclear Magnetic Resonance
Inh	Inhibitor
MIC	Minimum inhibition concentration
µg	Microgram
µM	Micrometer
mL	Milliliter
m.P.	Melting point
NMR	Nuclear magnetic resonance
ppm	Part per million
SB	Schiff base
W	Corrosion Rate
ΔM	Mass Loss
S	Area
T	Immersion period
IE%	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
ΔG^0_{ads}	Standard Free Energy of Adsorption
SEM	Scanning electron micrograph

Chapter One

Introduction and Literature Review

1.1 Heterocyclic Compounds

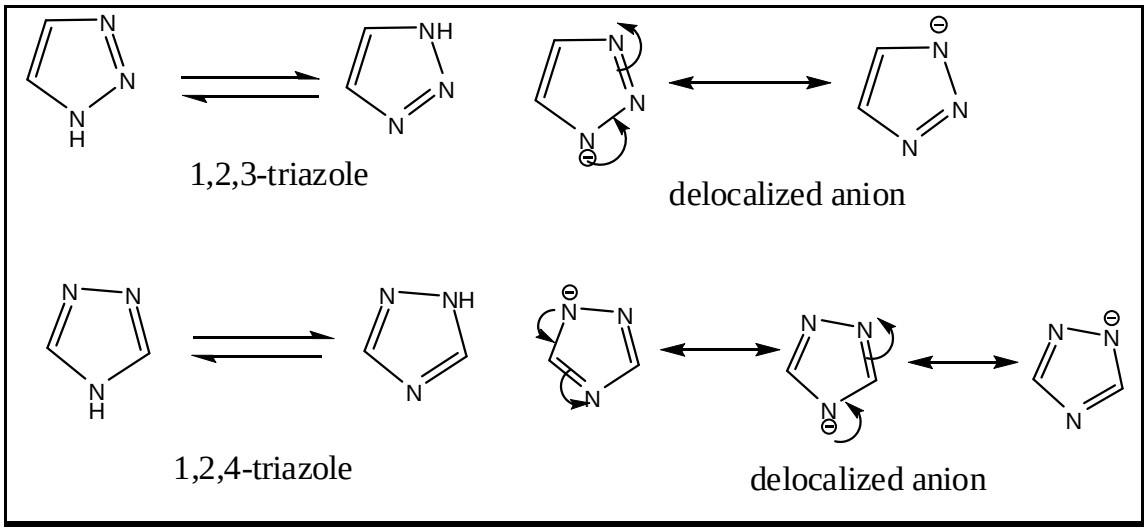
Heterocyclic chemistry is a central part of the chemical sciences and constitutes an extensive part of the modern researches that are occurring presently throughout the world. The chemistry of heterocyclic compounds is as logical as the chemistry of aliphatic or aromatic compounds. It is equally interesting for its theoretical implications, for the diversity of its synthetic procedures, and for the physiological and industrial significance of heterocyclic compounds [1]. The classification of heterocyclic compound as hetero cycloalkanes, hetero cycloalkenes, hetero annulenes and heteroaromatics allows an estimation of their stability and reactivity. In some cases, this can also be applied to inorganic heterocycles. For instance, borazine, a colorless liquid, is classified as a heteroaromatic system. Nowadays, the heterocyclic chemistry brings reagents and synthetic methods of its own usual activity in synthesis of drugs [2] pesticides [3] and detergents [4], as well as into the correlated fields such as biochemistry, polymers[5] Dyes [6], and material sciences [7].

1.2. 1, 2, 4-Triazole

Triazole, also known as pyrrodiazole is one of the classes of organic heterocyclic compounds containing a five membered diunsaturated ring structure composed of three nitrogen atoms and two carbon atoms at non-adjacent Positions. The simplest form of the triazole family is triazole itself. Triazole is a white to pale yellow crystalline solid with a weak, characteristic odor; it is soluble in water and alcohol, melts at 120 °C and boils at 260 °C. It occurs as a pair of isomeric chemical compounds 1,2,3- triazole, and 1,2,4-triazole (Figure1-1) [8]. Five-membered nitrogen heterocyclic compounds are important structural

fragments and considered including anti-inflammatory, CNS stimulants, sedatives, cardio tonic, antianxiety and antimicrobial agents, and anti-fungal activity. They are used as optical brightening agents, as antioxidants, as corrosion inhibitors and as additives with a variety of other functions. Many dye stuffs and pigments have heterocyclic. The Triazole derivative acquire a wide a range of pharmacological such as antimicrobial, analgesic, anti- Inflammatory, anticonvulsant, antineoplastic, anti-malarial, anti-viral, anti-proliferative and antimitotic activity such as fluconazole, itraconazole, voriconazole [9], and anti-cancer activities. The importance of triazole derivatives lies in the field that these have good position in heterocyclic chemistry, due to its various biological activities. Bladin, J.A.(1885) was the first science who gave the name of (triazole) to the carbon nitrogen ring system ($C_2N_3H_3$) and described triazoles' derivatives, in 1885, [10].

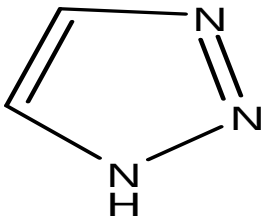
There are two isomers of triazole that differ in the relative positions of the three nitrogen atoms. Each of these has one pyrrole-like nitrogen and two pyridine-like nitrogens. Both triazoles have the possibility of tautomerism uipfand both give rise to a single anion.



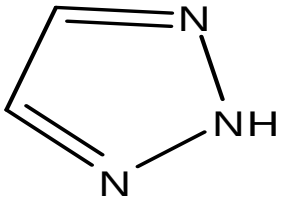
The 1, 2, 4-triazole is a ubiquitous feature of many agro chemical and pharmaceutical products and can be used as a factor in drugs such as fluconazole, terconazole, and rizatriptan alprazolam [11]. Also they found to be used as anticancer agents [12-13], antibacterial [14], antitubercular [15], and anticonvulsants [16], antiviral [17]. 1,2,3-triazole is used as antibacterial [18-20], antioxidant [21], antifungal [22], anti-leishmanial and anti-malarial drugs [23].

In literature triazole compounds are highly efficient, inward –absorbent and low poisonous. The studies on triazole derivatives are mainly interested in compounds with the triazole as the only active group, the reports of triazole compounds that contain both triazole group and other active group in the single molecule has rarely been found [24].

- **1,2,3-Triazole**

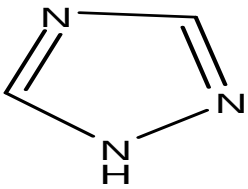


1*H*-1,2,3-Triazole

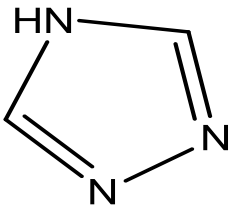


2*H*-1,2,3-Triazole

- 1,2,4-Triazole



1*H*-1,2,4-Triazole



4*H*-1,2,4-Triazole

Figure (1-1): 1,2,3 and 1,2,4-Triazole isomers.

1.3 Physical properties of 1,2,4-triazoles

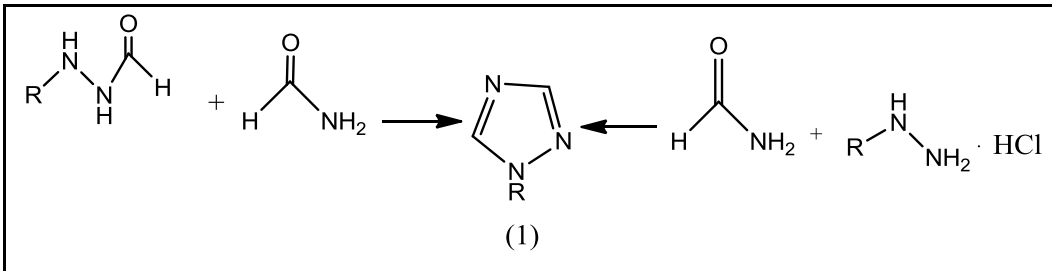
Almost 1,2,4-triazoles are solid at room temperature. They have color ranging from white to dark brown. They are generally soluble in polar solvents like ethanol, chloroform, dimethyl sulfoxide and dimethyl formamide, but insoluble in non-polar solvents like ethers, etc.1,2,4-Triazoles are soluble both in acidic and basic media due to salt formation by protonationand deprotonation, respectively [25].

1.4 Synthetic Methods of 1,2,4-Triazole

There are several methods to synthesize 1,2,4-triazole nucleus. Some of the methods have been discussed here.

1.4.1 From alkyl formohydrazine and formamide

The 1,2,4-triazole **(1)** prepared from the condensation of alkyl formohydrazine or aryl hydrazine with formamide at high temperature. This reaction has limitations from a synthetic point of view as it is low-yielding and the separation of by-products is very difficult. This reaction is helpful for the synthesis of di- and trisubstituted 1,2,4-triazoles. 1,2,4-Triazole **(1)** can also be obtained by the reaction of hydrazine hydrochloride with formamide. This reaction is usually known as Pellazari reaction [26] , as shown in scheme (1-1).



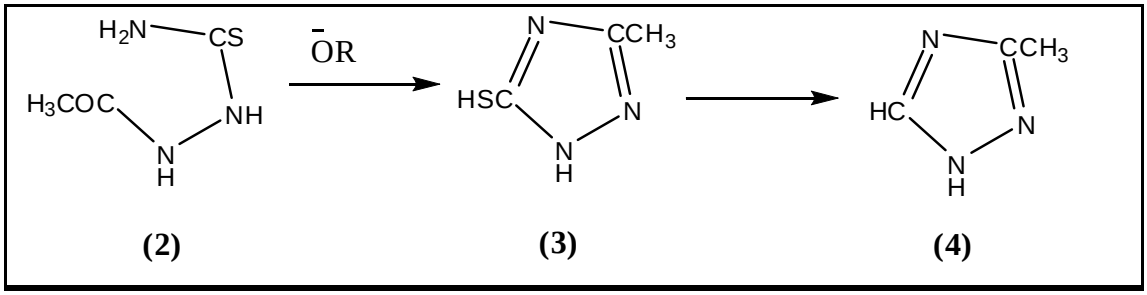
(1)

R= Methyl, phenyl, o-methylphenyl, p-methylphenyl

Scheme (1-1): Synthesis 1,2,4-triazole From alkyl formohydrazine and formamide.

1.4.2 From thiosemicarbazides

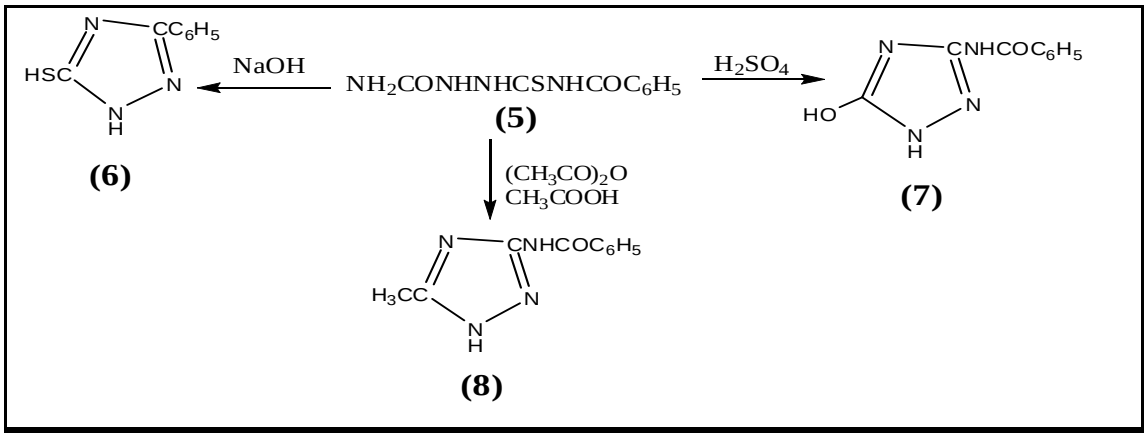
This method is generally used for the synthesis of 3 or 5 substituted 1,2,4-triazoles. Cyclization of 1-acetyl thiosemicarbazide with sodium methoxide yields 5-Thiol-3-methyl-1,2,4-triazole. The thiol group is removed upon oxidation with concentrated nitric acid solution to yield 3-methyl-1,2,4-triazole **(4)** , as shown in scheme (1-2).



(2) **(3)** **(4)**

Scheme (1-2): Synthesis of 3-methyl-1,2,4-triazole.

(Compound 5) with 20% NaOH yields 5-thiol-3-phenyl-1,2,4-triazole **(6)**, stirring of thiosemicarbazide with concentrated sulfuric acid gives 3-benzamido-5-hydroxy-1,2,4-triazole **(7)** with the elimination of hydrogen sulfide . 3-benzamido-5-methyl-1,2,4-triazole **(8)** is obtained by treating a hot mixture of acetic anhydride and acetic acid with thiosemicarbazide [27- 29] , as shown in scheme (1-3).

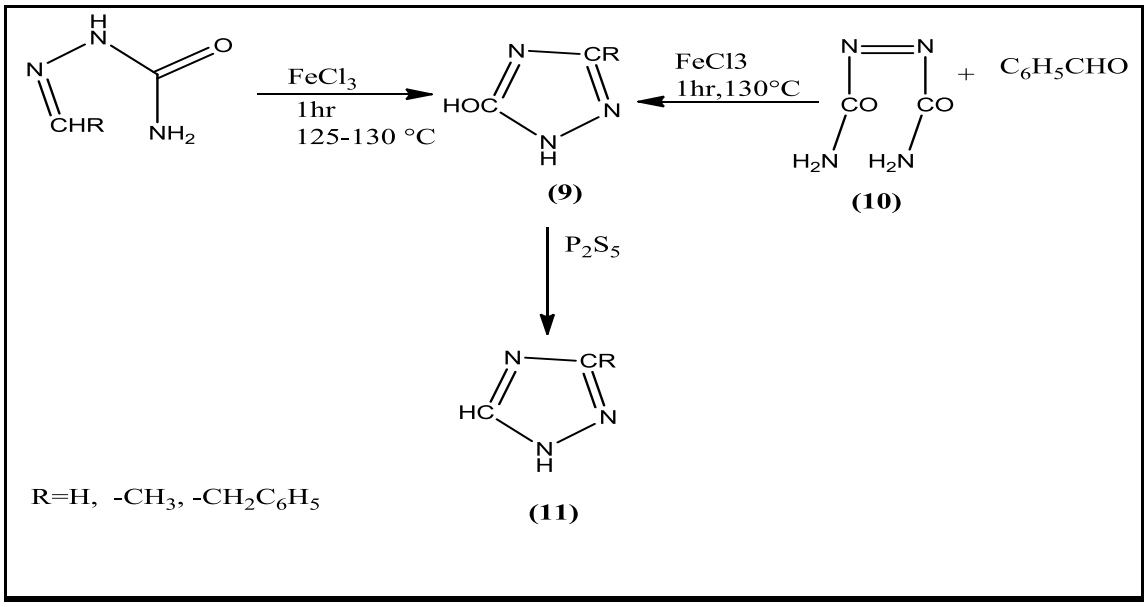


(6) **(5)** **(7)** **(8)**

Scheme (1-3): Synthesis of 3-benzamido-5-methyl-1,2,4-triazole.

1.4.3 From semicarbazones with ferric chloride

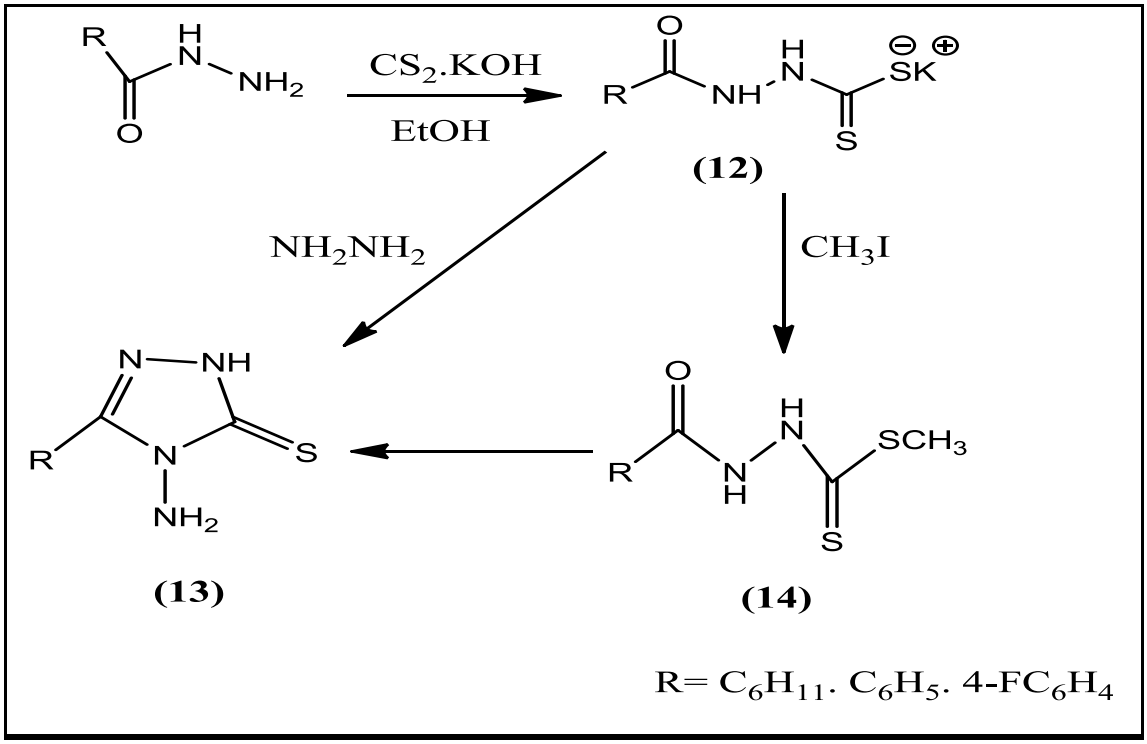
Substituted-3-hydroxy-1, 2, 4 triazole **(9)** yield from Benzalsemicarbazones on oxidation with ferric chloride. An alternate route for the synthesis of substituted 1, 2, 4-triazole **(10)** is through oxidation of benzaldehyde and azodicarbamide mixture**.** The hydroxyl group is removed from hydroxyl substituted 1, 2, 4-triazole with phosphorus pentasulphide yielding 3 or 5-substituted 1, 2,4triazoles **(11)** [30] , as shown in scheme (1-4).



Scheme (1-4): Synthesis of 3 or 5-substituted 1, 2,4triazoles.

1.4.4 From carboxylic acid hydrazides

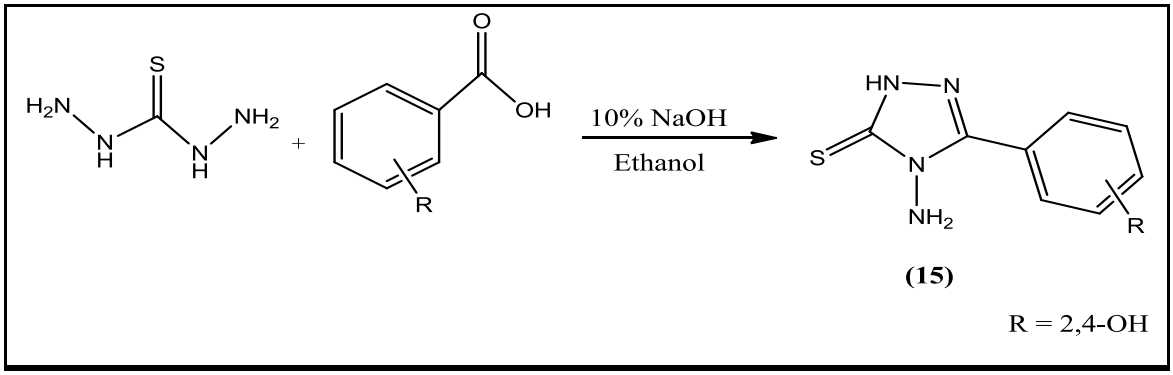
Condensation of acid hydrazides with carbon disulfide in alcoholic potassium hydroxide yields potassium salt of dithiocarbazinates **(12)**, which on refluxing with aqueous hydrazine hydrate gives 4-amino-1,2,4-triazole **(13)**. The S-substituted derivative **(14)** formed by the reaction of methyl iodide with **(12),** gives also 4- amino-1,2,4-triazoles **(13)** upon cyclization [31] , as shown in scheme (1-5).



Scheme (1-5): Synthesis of 4- amino-1,2,4-triazoles From carboxylic acid hydrazides.

1.4.5 From thiocarbohydrazide

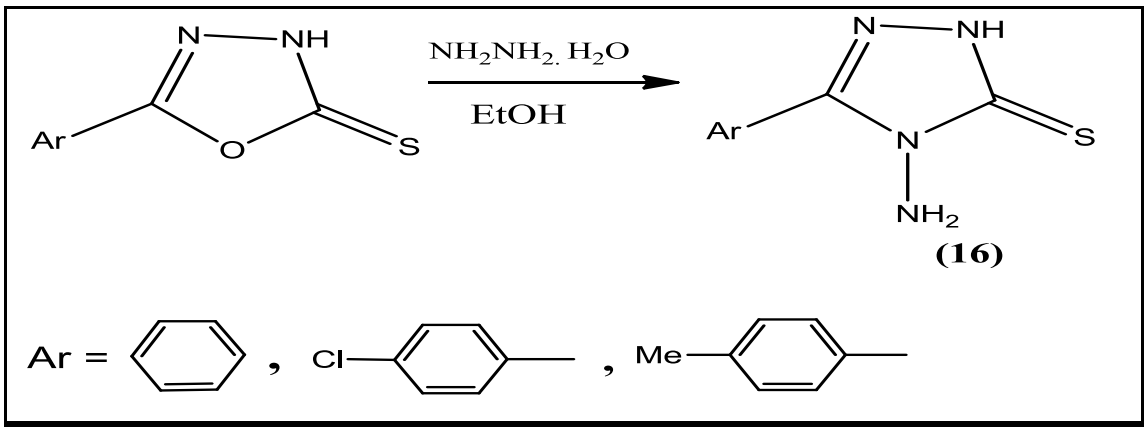
The combination of thiocarbohydrazides with aromatic carboxylic acids is usual synthetic method for the preparation of 5-aryl-4-amino-1,2,4-triazole-3-thiones **(15)** [32] , as shown in scheme (1-6).



Scheme (1-6): Synthesis of 5-aryl-4-amino-1,2,4-triazole-3-thiones.

1.4.6 From 1,3,4-oxadiazol-5-thiones

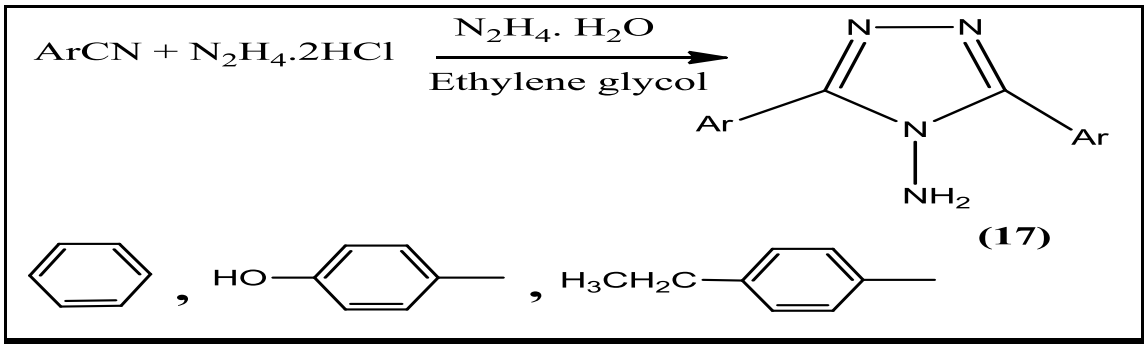
Reid, S. T., and Heindel, N. D., 1976, indicated that 2-aryl-1,3,4-oxadiazol-5-thione recyclizes to form 4-amino-1,2,4-triazole-5-thione **(16)** by refluxing in aqueous hydrazine hydrate [33] , as shown in scheme (1-7).



Scheme (1-7): Synthesis of 4-amino-1,2,4-triazole-5-thione From 1,3,4-oxadiazol-5-thiones.

1.4.7 From aromatic nitriles

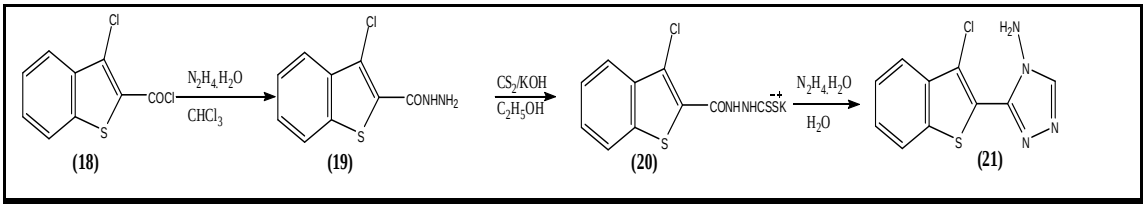
3,5-disubstituted-4-amino-(4*H*)-1,2,4-triazole **(17)** is synthesized by aromatic nitriles**,** on reaction with hydrazine dihydrochloride in the presence of hydrazine hydrate under microwave irradiation [34] , as shown in scheme (1-8).



Scheme (1-8): Synthesis of 3,5-disubstituted-4-amino-(4*H*)-1,2,4-triazole.

1.4.8 From Acid Chloride

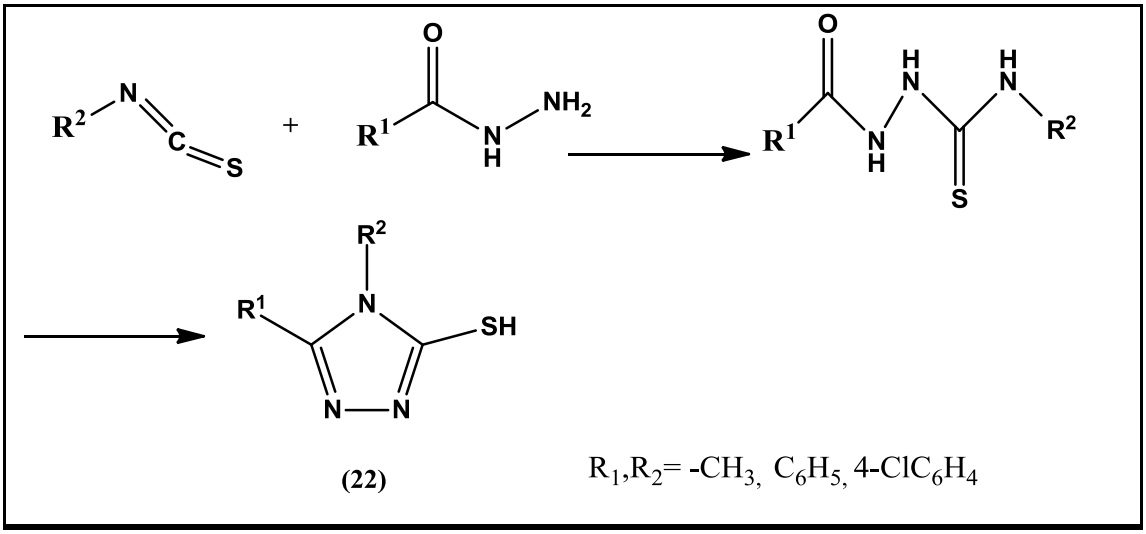
Conventional heating of 3-chloro-2-chlorocarbonylbenzo thiophene **(18)** with hydrazine hydrate afforded the corresponding hydrazide **(19)**. Potassium dithiocarbazate **(20)** was cyclized with hydrazine to afford 4-amino-5-(3-chlorobenzo[*b*]thien-2-yl)-3-mercapto-1,2,4-triazole **(21)** [35] , as shown in scheme (1-9).



Scheme (1-9): Synthesis of 4-amino-5-(3-chlorobenzo[*b*]thien-2-yl)-3-mercapto-1,2,4-triazole.

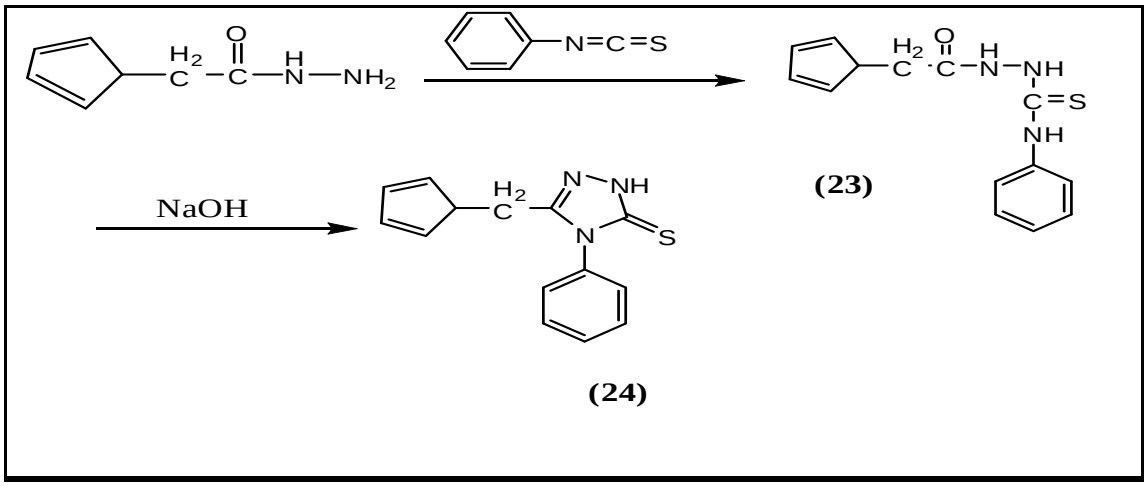
1.4.9 From isothiocyanates

Substituted thiosemicarbazides are formed by the acid hydrazides react with aromatic isothiocyanates. Thiosemicarbazides, on refluxing with dried methanol and gave substituted 1,2,4-triazoles **(22)** [36] , as shown in scheme (1-10).



Scheme (1-10): Synthesis of substituted 1,2,4-triazoles From isothiocyanates.

The phenylacetic acid hydrazide, on refluxing with phenylisothiocyanate in absolute ethanol, yields the 1-phenylacetyl-4-phenylthiosemicarbazide **(23),** which on dehydrocyclization in the presence of NaOH, affords substituted 1,2,4-triazoles **(24)** [37] , as shown in scheme (1-11).

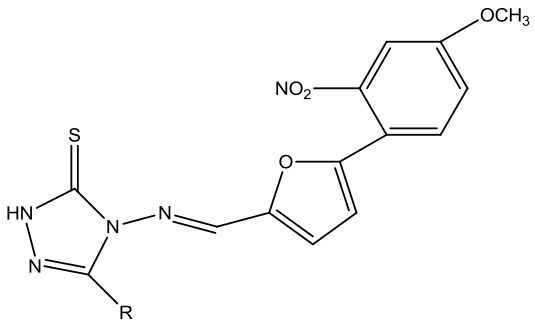


Scheme (1-11): Synthesis of substituted 1,2,4-triazoles.

1.5 Applications of triazoles

1.5.1 Anticancer activities

Organic molecules containing 1,2,4-triazole nucleus have effective anticancer activities. The Schiff base of an amino-1,2,4-triazole bearing 2,4-dichlorophenoxy group **(25)** was active against thirty-one cancer cell lines with potent in *vitro* activity at concentration less than 20 µM. The compound **(26)** was found to be active against six cancer cell lines at the concentration less than 20 µM [38].

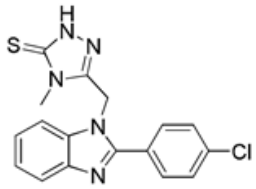


(25) R = 2,4-Cl_2 C_6H_5-OCH_2-

(26) R = H

1.5.2 Antioxidant activities

Benzimidazole derivatives containing 1,2,4-triazole nuclei have been described to possess excellent antioxidant activities using *in vitro* studies. Compounds **(27-30)** having 1,2,4-triazoles nuclei displayed excellent scavenging activities of DPPH stable free radical when compared to BHT antioxidant [39]**.**



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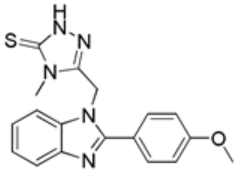

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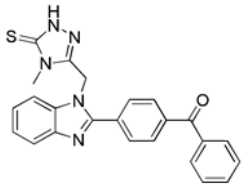

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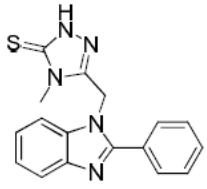
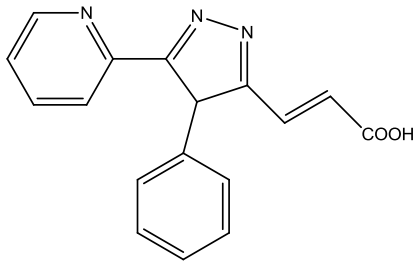


(30)

1.5.3 Anticonvulsant activities

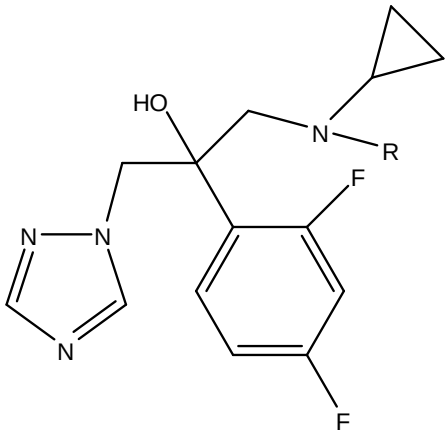
3,4-Disubstituted 1,2,4-triazole derivative of propenoic **(31)** acid displayed influence on central nervous system, as observed in the preliminary studies of behavioural test. Compound **(33)** also showed anticonvulsive activity and potent antinociceptive action [40].



(31)

1.5.4 Antifungal activities

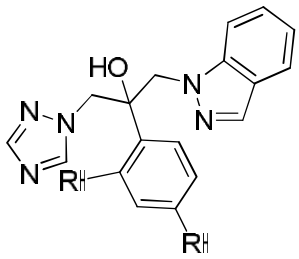
Different analogues of fluconazoles, like derivatives **(32)** and **(33)** showed excellent and broad spectrum of antifungal activities. These compounds **(32)** and **(33)** display good minimum inhibitory concentration (MIC) values less than 0.125 g/mL and were proved to be more potent than fluconazole and comparable with that of *itraconazole* [41].



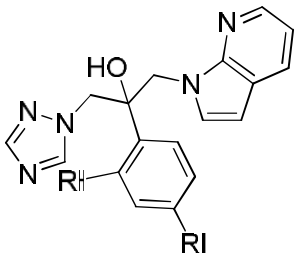
(32) R = alkyl-

(33) R = chloro- and bromobenzyl-

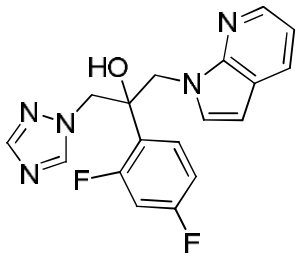
Fluconazole analogues containing aza indole and indole moieties showed excellent *in vitro* antifungal activities versus two pathogenic fungi. Compounds **(34), (35)** and **(36)** revealed excellent antifungal activities with minimum inhibitory values (MIC) 28-folds lower than that of fluconazole [42].



(34)



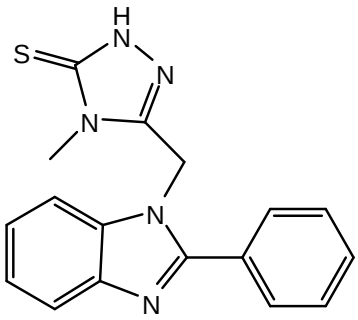
(35)



(36)

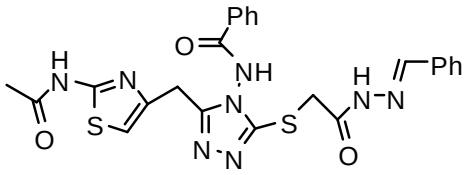
1.5.5 Antitubercular activities

Thiazolyl triazole derivatives reported great potential against mycobacterium tuberculosis H37RV strain. These derivatives have low drug resistance against these bacterial strains. In the preliminary screening, compound **(37)** showed 100 per cent inhibition at the concentration of 6.25 µg/m [43].

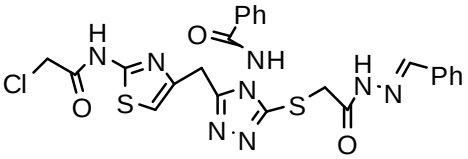


(37)

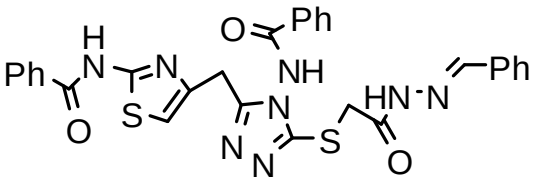
The antitubercular activity of the compound was enhanced by the derivatization at the S and N sides of the 1,2,4-triazole ring. The resulting compounds **(38-40)** showed excellent antitubercular activities in the secondary screening.



(38)



(39)



(40)

1.5.6 Triazoles as corrosion inhibitor

Inhibitors are one of the most practical methods for protection of metal against corrosion, especially in acidic media. Most of the well-known acid inhibitors are organic compounds containing nitrogen, sulphur, and oxygen atomsand inorganic compounds, such as chromate, phosphate, dichromate, nitrite, and so on. Compounds with π-electrons and functional groups containing heteroatoms which can donate lone pair electrons are found to be particularly useful as inhibitors for corrosion of metals [44]. The exiting data reveal that most organic inhibitors act by adsorption on the metal surface. This adsorption is influenced by the nature and surface charge of metal, the type of aggressive electrolyte and the chemical structure of inhibitors [45]. The compounds containing both

nitrogen and sulfur can give excellent inhibition in contrast to compounds containing only nitrogen or sulfur [46]. Triazole and triazole-type compounds containing nitrogen, sulfur, and heterocycle on the corrosion inhibition of metal in acidic media have attracted more attention because of their excellent corrosion inhibition performance. The some new triazole derivatives have been still continuously synthesized and investigated as inhibitors for corrosion ofmetals in acidic solutions.

Zhang et. al [48]. studied the corrosion inhibition of a newly synthesized oxadiazol-triazole derivative for mild steel in sulphuric solution, their results indicated that these compound was effective as corrosion inhibitor for mild steel in acid solution and its efficiency attained more than 97.6% at 298 K.

Wang et. al [49]. Also investigated the effect of some mercapto-triazole derivatives on the corrosion and hydrogen permeation of mild steel in hydrochloric acid solution and their results revealed that all the mercapto-triazole derivatives performed excellently as corrosion inhibitors. Especially, some N- and S- containing triazole derivatives are environmentally friendly corrosion inhibitors compared with some commercial acid corrosion inhibitors which are highly toxic, such as chromate and nitrite.

Three triazoles namely 4-amino-5-phenyl-4*H*-1, 2, 4,-triazole-3-thiol **(APTT)**, 4-amino-5-(2-hydroxy) phenyl-4*H*-1, 2, 4,-triazole-3-thiol, **(AHPTT)**, 4-amino-5-styryl-4*H*-1, 2, 4,-triazole-3-thiol, **(ASTT)** are investigated for their inhibition action on corrosion of mild steel in 1.0M HCl. weight loss methods were used. The choice of triazoles as corrosion inhibitors is based on the following considerations. They are conveniently synthesized in high yield from commercially available raw materials. Triazoles molecules contain four nitrogen atoms one S atom π e- and

aromatic ring through which they can easily adsorbed on metal surface and bring about inhibition. Their results revealed that all the triazoles derivatives act as mixed type inhibitors. Adsorption of the inhibitors on the mild steel surface followed Langmuir adsorption isotherm. The values of free energy of adsorption (*ΔG*°ads) indicated that adsorption of triazoles derivatives is a spontaneous process and they are adsorbed chemically as well as physically. The values of inhibition efficiency for all triazoles followed the order ASTT > AHPTT > APTT. The Styryl substituted triazole exhibited highest inhibition efficiency 95.2 % at concentration of 5.72x10-4mol L-1[50].

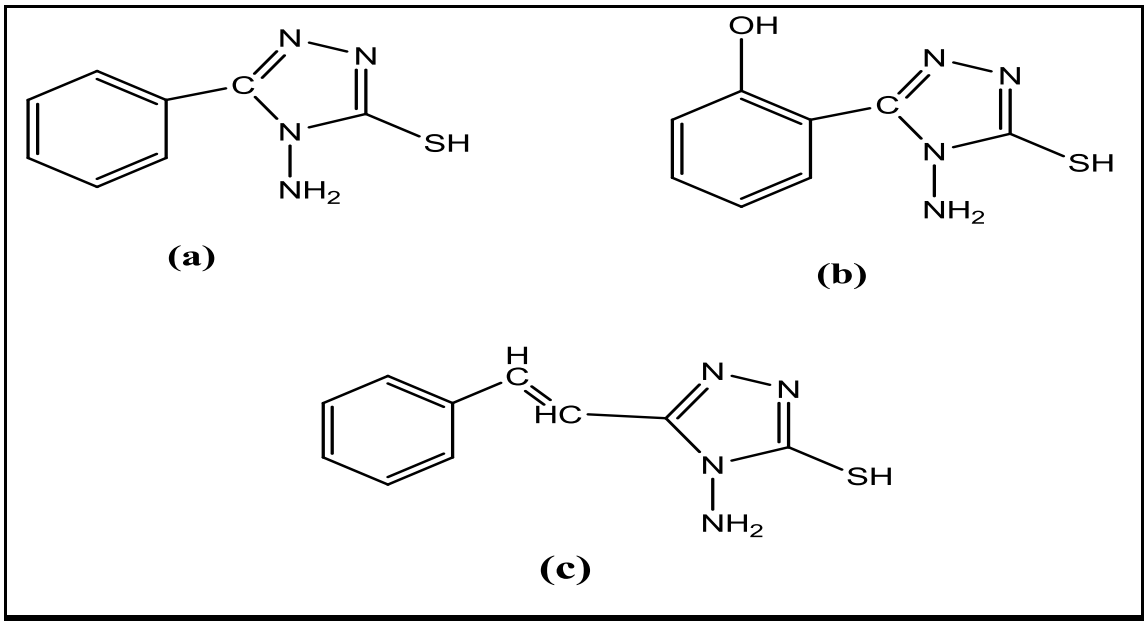


Figure (1-2). The molecular structure and IUPAC name of triazoles derivatives (a) 4-amino-5-phenyl-4*H*-1, 2, 4,-triazole-3-thiol (b) 4-amino-5-(2-hydroxy) phenyl-4*H*-1, 2, 4,-triazole-3-thiol (c) 4-amino-5-styryl-4*H*-1, 2, 4,-triazole-3-thiol

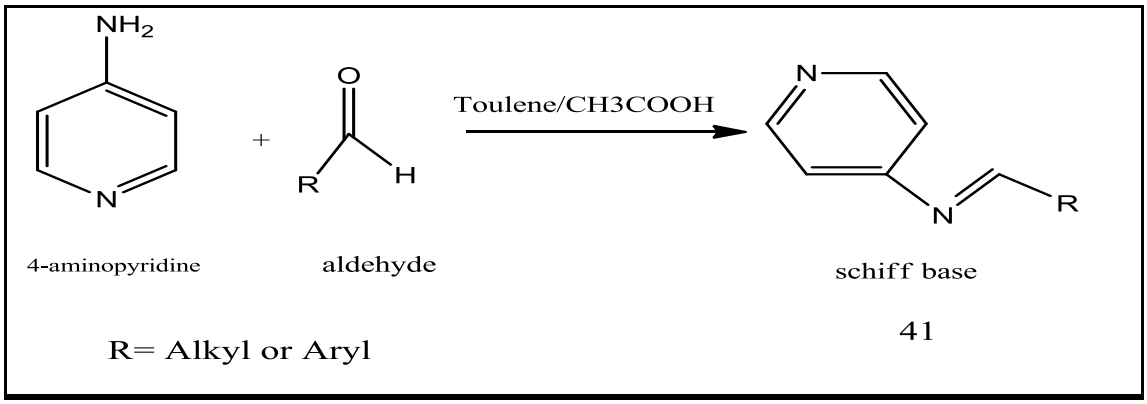
1.6 Schiff bases

The term Schiff base (SB) is used to define those Organic compounds which result from condensation of primary amines with aldehydes or ketones. The functional imine group (-C=N-) is in explaining the mechanism of transformation in biological systems and can be designated structurally as(R''R'C=NR). Schiff's bases exhibit a broad spectrum of applications as corrosion inhibitors, insecticides and pesticides. Their complexes with transition metals also have antibacterial, antiviral and antitumor activities. The Schiff bases (SB) were first prepared by H. Schiff in 1864 [51].

Nowadays many Schiff bases have been synthesized from the heterocyclic compounds. An interesting application of Schiff bases is their use as an effective corrosion inhibitor which is based on their ability to spontaneously form a monolayer on the surface to be protected. It forms complexes with transition metals which have antibacterial, antiviral and antitumor activities [52]. Several synthetic methods have been reported for the synthesis of Schiff bases in literature. However, most of them have limitations including long reaction times, need for a special catalyst, low yields, and extensive recrystallization. Therefore, the pursuance of more convenient and practical synthetic methods for preparation of these compounds still remains an active research area. Recently, the use of several catalysts, like inorganic salts and zeolites, in organic synthesis has attracted considerable attention [53]. Formation of Schiff base generally takes place under acid or base catalysis or with heat. The common Schiff bases are crystalline solids, which are feebly basic but at least some form insoluble salts with strong acids. Schiff base ligands have significant importance in chemistry; especially in the development of Schiff base complexes, because Schiff base ligands are

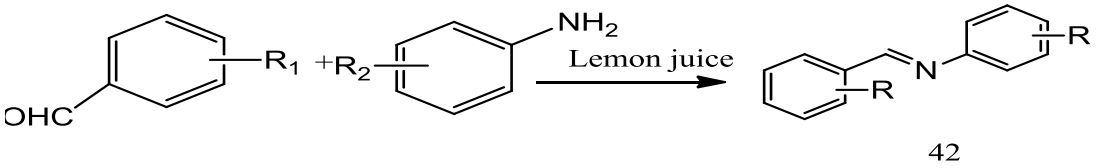
potentially capable of forming stable complexes with metal ions [54]. Many Schiff base complexes show excellent catalytic activity in various reactions at high temperature (>100 °C) and in the presence of moisture. Schiff bases have been found to possess more inhibitor efficiency than their constituent carbonyls and amines.

Sankar and Nandi synthesized Schiff bases from the 4-aminopyridine and toluene or acetic acid by using Dean Stark apparatus. After synthesis docking studies done to estimate their antitubercular effect and compared it with standard drug isoniazid. From docking studies it was concluded that compounds formed in this process were effective as anti-tubercular agent [55], as shown in scheme (1-12).



Scheme (1-12): Synthesis of Schiff bases from 4-aminopyridine

Patil and Jadhav proposed an eco-friendly method for the synthesis of Schiff bases as they used lemon juice as catalyst. This method used for the synthesis of Schiff base from the primary aromatic amines and aryl aldehydes under solvent free conditions and in non-polluting environment using lemon juice as the catalyst [56] , as shown in scheme (1-13).

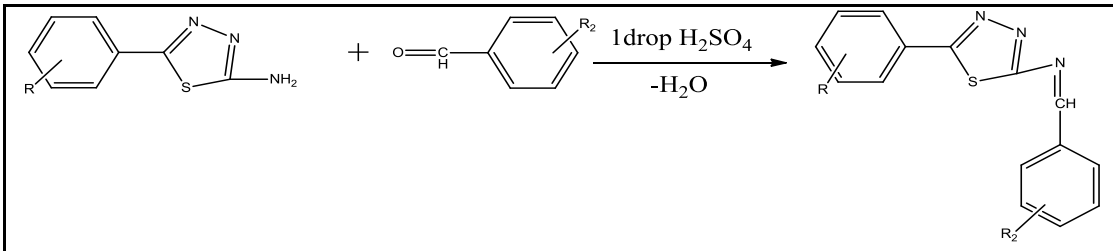


42

R= H, -CH_3, -C_6H_5, -Cl, OC_2H_5

Scheme (1-13): Synthesis of Schiff Bases using lemon juice as catalyst

Khedar and Marwani further synthesized Schiff bases derived from condensation of 2-amino-5substituted-aryl-1,3,4-thiadiazole with substituted aryl aldehydes in presence of one drop sulphuric acid. These compounds were further screened for antimicrobial activity and compounds were found quite effective as antimicrobial agent [57] , as shown in scheme (1-14).

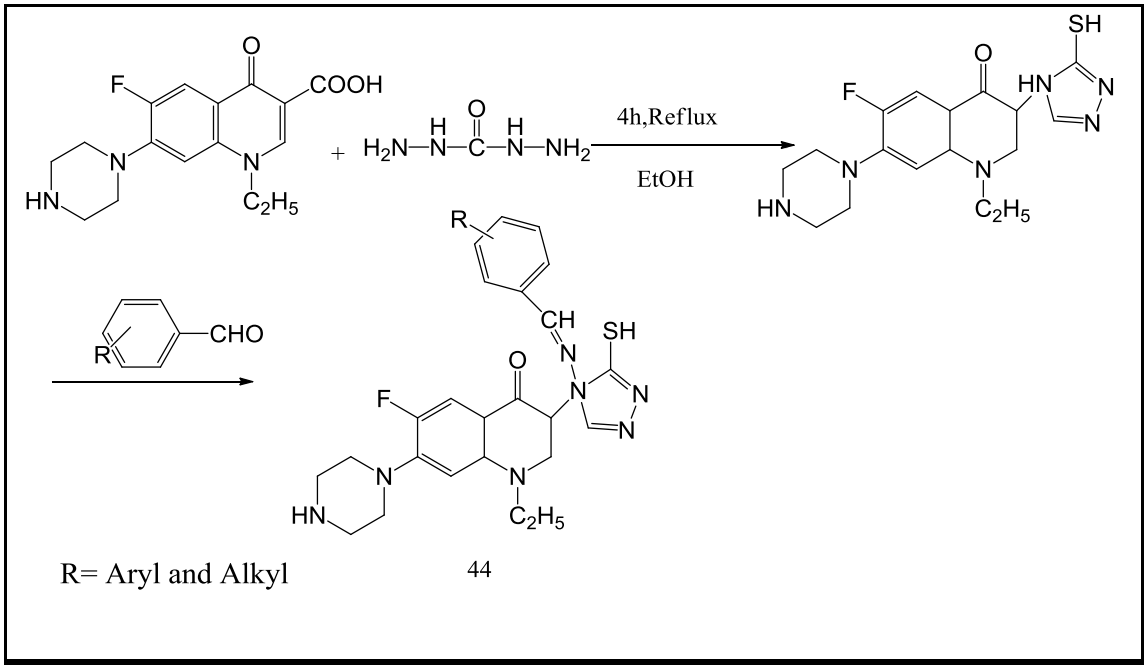


43

R_1= H, *p*-Cl R_2 = *P*-NO_2, C_6H_5N

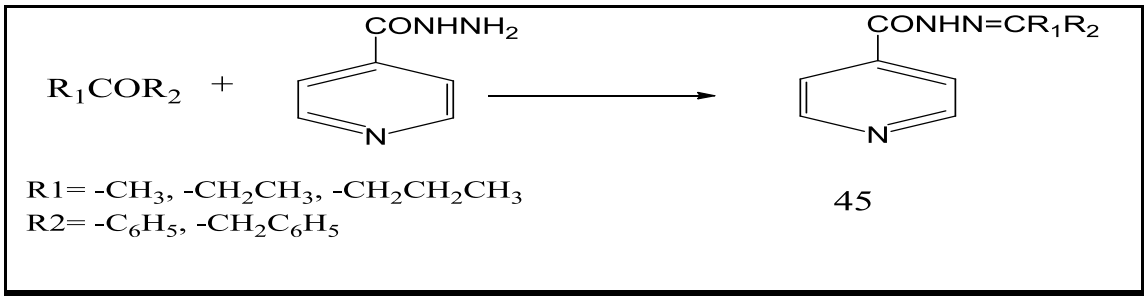
Scheme (1-14): Synthesis of 1,3,4-thiadiazole based Schiff Bases

Udupi et.al. Synthesized Schiff base derivative from the condensation of the mercapto triazole with different aromatic aldehydes. First 3-substituted-4-amino-5-mercapto-1,2,4-triazole was synthesized using hydrazine hydrate and then it was reacted with various aromatic aldehydes [58] , as shown in scheme (1-15).



Scheme (1-15): Synthesis of Schiff Bases from Mercapto triazole

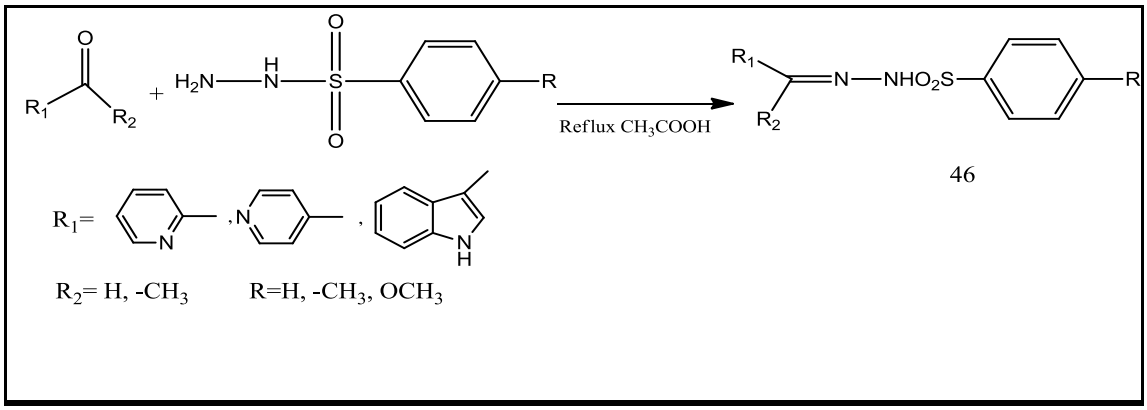
Hearn and Chen developed Schiff base derivatives from the isoniazid and carbonyl precursors, which provides increase in lipophilicity to the drug and made it more effective against tuberculosis [59] , as shown in scheme (1-16).



Scheme (1-16): Schiff base from isoniazid

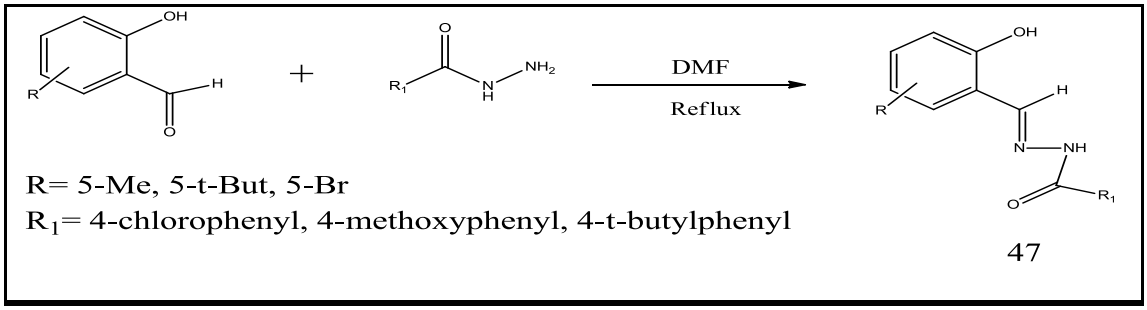
Sondhi et. al. synthesized some amidine and hydrazone derivatives and evaluated their analgesic activity. 2-Acetylpyridine and 4-acetylpyridine were condensed with sulfonylhydrazides by microwave irradiation in solid phase to give corresponding hydrazones and indole-3carboxaldehyde was condensed with sulfonylhydrazides by refluxing in acetic acid to give corresponding condensation product. Analgesic

activity evaluation was carried out using acetic acid induced writhing assay [60], as shown in scheme (1-17).



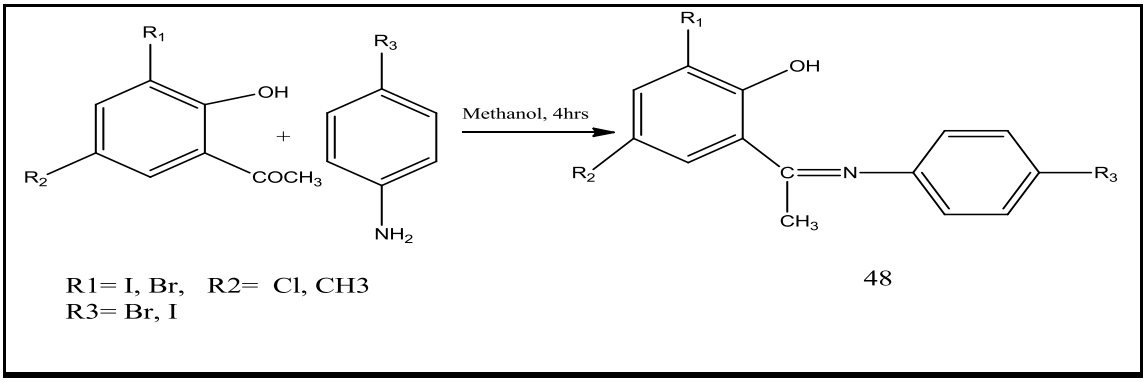
Scheme (1-17): Synthesis of Schiff Base from Sulphonylhydrazides

Melnyk et. al., synthesized acylhydrazones using dimethyl formamide as catalyst and evaluated their antimalarial activity. A library of acylhydrazone iron chelators was synthesized and evaluated for its ability to inhibit the growth of a chloroquine resistant strain of Plasmodium falciparum. Some of the new compounds were found significantly more active than desferrioxamine [61] , as shown in scheme (1-18).



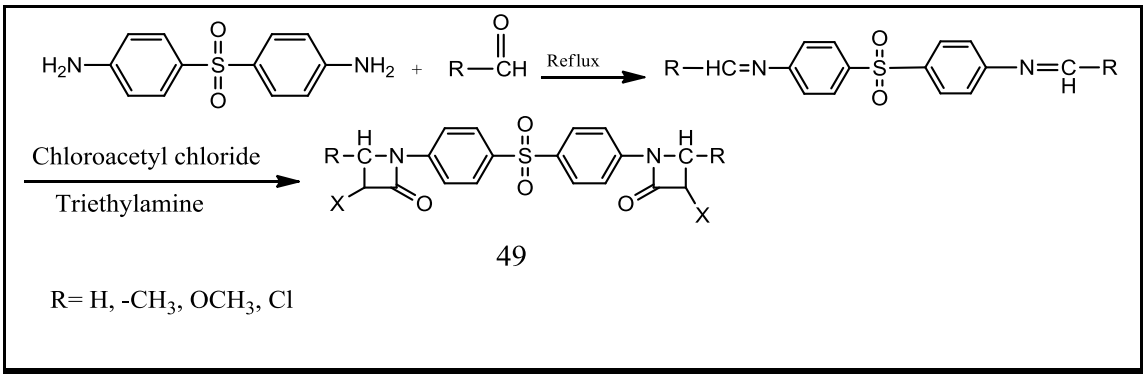
Scheme (1-18): Synthesis of acylhydrazones

Karmunge et.al., synthesized Schiff bases by refluxing the reaction mixture of 4-iodoaniline, 4chloroaniline, p-toluidine with halogen and hydroxy substituted acetophenones in presence of methanol and glacial acetic acid. After that their antimicrobial activity were evaluated by agar diffusion method and poison plate method. These compounds were found to have potent antimicrobial activity [62], as shown in scheme (1-19).



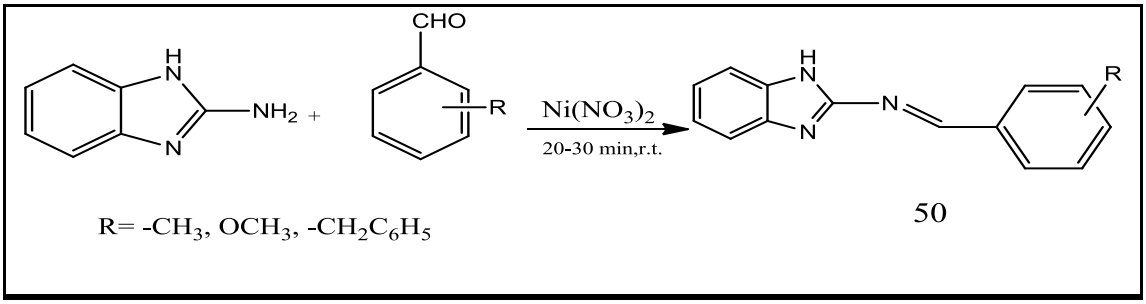
Scheme (1-19): Synthesis of Schiff bases from aniline

Wadher et.al. synthesized a series of Schiff base and 2-azetidinones of 4,4'diaminodiphenylsulphone. 4,4'-Diaminodiphenylsulphone was condensed with various aromatic or heterocyclic aldehyde in ethanol in the presence of concentrated sulphuric acid as a catalyst to yield the corresponding Schiff base. These Schiff's bases on treatment with chloroacetylchloride in the presence of triethylamine gave substituted 2-azetidinone. Out of synthesised compounds some showed potent antimicrobial activity [63], as shown in scheme (1-20).



Scheme (1-20): Synthesis of Schiff bases from 4,4' diaminodiphenylsulphone

Kalhor and Forughifar developed for the synthesis of some novel Schiff bases via the reaction of aromatic aldehydes with 2-aminobenzimidazole by using catalytic amount of $M(NO_3)_2.xH_2O$ where, M indicates metal [53], as shown in scheme (1-21).



Scheme (1-21): Synthesis of Schiff Base from 2-aminobenzimadazole

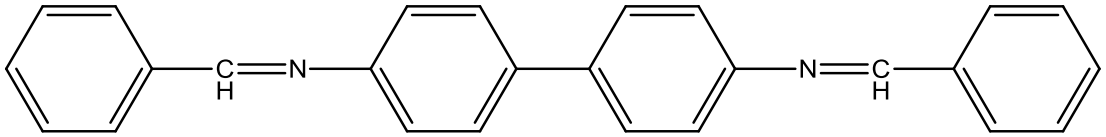
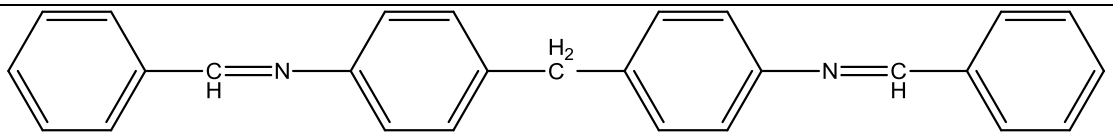
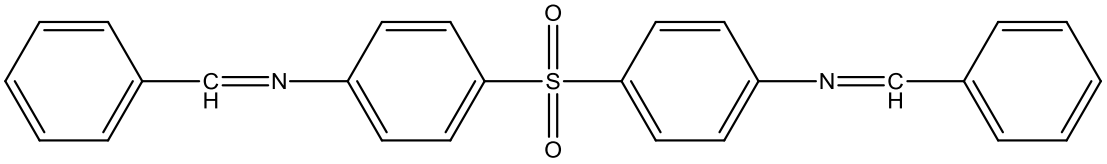
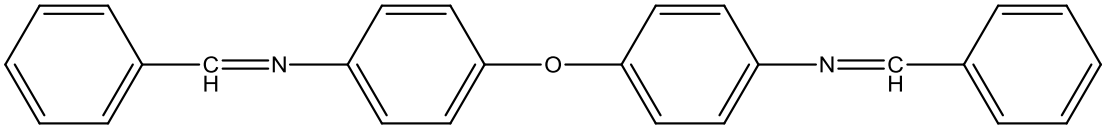
Like Triazoles Schiff's bases exhibit a broad spectrum of applications as biological activities, including antibacterial [64], antifungal [65], anti-proliferative [66], anti-malarial [67], antiviral [68], anti-inflammatory, antitubercular [69], and antipyretic properties [70].

1.6.1 Schiff bases as corrosion inhibitor [71]

Schiff bases are the condensation products of carbonyls and amines and are also called anils. Although most of the commercial formulations of inhibitors include aldehydes and amines as essential ingredients, Schiff bases have been found to possess more inhibition efficiency than their constituent carbonyls and amines. Certain authors have attributed this considerably stronger inhibition efficiency to the presence of unoccupied π-orbitals in the Schiff base molecules, which enable electron back donation from the transition metal d-orbitals and thereby stabilize the existing metal-inhibitor bond, which is not possible with the constituent amines. The review of literature reveals that despite the superlative inhibition characteristics of Schiff bases in general, this class of compounds has not been so far exploited to the extent of their high potential. Further the influence of wide range of structural variation on their inhibition efficiencies has not also been thoroughly investigated. Hence it has been thought fit to synthesis a series of Schiff bases by condensing benzaldehyde with dianilines and to study the inhibitive performance for the corrosion of mild steel in acid medium. Sulphuric

acid and hydrochloric acid are commonly used for various industrial applications such as acid pickling, descaling, in oil wells etc. Hence, the effect of dianiline Schiff bases on the corrosion rate, corrosion potential, anodic and cathodic polarization behavior of steel in 1M sulphuric acid has been investigated as it is the most commonly used electrolyte in industries for acid pickling, surface cleaning, acidizing etc. The structures of the newly synthesized dianiline Schiff bases are given in table 1.

Table **(1.1)**: Structure of the Schiff bases [71].

Name	**Structure of the Schiff bases**
DAA	 N,N¢-Bis(benzylidene)-4,4'-dianiline
MDAA	 N,N¢-Bis(benzylidene)-4-4¢-methylenedianiline
SDAA	 N,N¢-Bis(benzylidene)-4-4¢-sulphonyldianiline
ODAA	 N,N¢-Bis(benzylidene)-4-4¢-oxydianline

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1.7 Corrosion [72]

1.7.1 Introduction

Corrosion is the destructive attack of a material by reaction with its environment. The serious consequences of the corrosion process have become a problem of worldwide significance. In addition to our everyday encounters with this form of degradation, corrosion causes plant shutdowns, waste of valuable resources, loss or contamination of product,reduction in efficiency, costly maintenance, and expensive overdesign;it also risks safety and inhibits technological progress. The multidisciplinary aspect of corrosion problems combined with the distributed responsibilities associated with such problems only increase the complexity of the subject. Corrosion control is achieved by recognizing and understanding corrosion mechanisms, by using corrosion- resistant materials and designs, and by using protective systems, devices, and treatments. One of the key factors in any corrosion situation is the environment. The definition and characteristics of this variable can be quite complex. One can use thermodynamics, e.g., Pourbaix or E-pH diagrams, to evaluate the theoretical activity of a given metal or alloy provided the chemical makeup of the environment is known. But for practical situations, it is important to realize that the environment is a variable that can change with time and conditions. It is also important to realize that the environment that actually affects a metal corresponds to the microenvironmental conditions that this metal really "sees," i.e., the local environment at the surface of the metal. It is indeed the reactivity of this local environment that will determine the real corrosion damage. Thus, an experiment that investigates only the nominal environmental condition without consideration of local effects such as flow, pH cells, deposits as show in figure **(1.2)**.

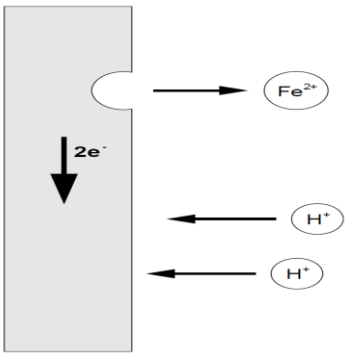


Figure (1-3): Simple models describing the electrochemical nature of corrosion processes.

cathodic reaction, which in general is much slower (cathodic control). In deaerated solutions, the cathodic reaction is

$$2H^+ + 2e- \rightarrow \quad H_2 \qquad \textbf{(1.1)}$$

This reaction proceeds rapidly in acids, but only slowly in alkaline or neutral aqueous media. The corrosion rate of iron in neutral water at room temperature, for example, is less than 5 m/year. The rate of hydrogen evolution at a specific pH depends on the presence or absence of low-hydrogen overvoltage impurities in the metal. For pure iron, the metal surface itself provides sites for H_2 evolution; hence, high-purity iron continues to corrode in acids, but at a measurably lower rate than does commercial iron. The cathodic reaction can be accelerated by the reduction of dissolved oxygen in accordance with the following reaction, a process called depolarization:

$$4H^+ + O_{2\,+}\, 4e- \rightarrow 2H_2O \qquad \textbf{(1.2)}$$

Dissolved oxygen reacts with hydrogen atoms adsorbed at random on the iron surface, independent of the presence or absence of impurities in the metal. The oxidation reaction proceeds as rapidly as oxygen reaches the

metal surface. Adding **(1.1)** and **(1.2)**, making use of the reaction $H_2O \leftrightarrow$ H OH, leads to reaction **(1.3)**,

$$2Fe + 2H_2O + O_2 \rightarrow 2Fe(OH)_2 \qquad \textbf{(1.3)}$$

Hydrous ferrous oxide ($FeO.nH_2O$) or ferrous hydroxide [$Fe(OH)_2$] composes the diffusion-barrier layer next to the iron surface through which O_2 must diffuse. The pH of a saturated $Fe(OH)_2$ solution is about 9.5, so that the surface of iron corroding in aerated pure water is always alkaline. The color of $Fe(OH)_2$, although white when the substance is pure, is normally green to greenish black because of incipient oxidation by air. At the outer surface of the oxide film, access to dissolved oxygen converts ferrous oxide to hydrous ferric oxide or ferric hydroxide, in accordance with

$$4Fe(OH)_2 + 2H_2O + O_2 \rightarrow 4\,Fe(OH)_3 \qquad \textbf{(1.4)}$$

Hydrous ferric oxide is orange to red-brown in color and makes up most of ordinary rust. It exists as nonmagnetic Fe_2O_3 (hematite) or as magnetic Fe_2O_3, the form having the greater negative free energy of formation (greater thermodynamic stability). Saturated $Fe(OH)_3$ is nearly neutral in pH. A magnetic hydrous ferrous ferrite, $Fe_3O_4.nH_2O$, often forms a black intermediate layer between hydrous Fe_2O_3 and FeO. Hence rust films normally consist of three layers of iron oxides in different states of oxidation.

1.7.2 Corrosion Inhibitors

The use of chemical inhibitors to decrease the rate of corrosion processes is quite varied. In the oil extraction and processing industries, inhibitors have always been considered to be the first line of defense against corrosion. A great number of scientific studies have been devoted

to the subject of corrosion inhibitors. However, most of what is known has grown from trial and error experiments, both in the laboratories and in the field. Rules, equations, and theories to guide inhibitor development or use are very limited. By definition, a corrosion inhibitor is a chemical substance that, when added in small concentration to an environment, effectively decreases the corrosion rate. The efficiency of an inhibitor can be expressed by a measure of this improvement:

Inhibitor efficiency (%) =100 *(CR uninhibited – CR inhibited) /CR uninhibited.

Where CR uninhibited =corrosion rate of the uninhibited system CR inhibited =corrosion rate of the inhibited system

In general, the efficiency of an inhibitor increases with an increase in inhibitor concentration (e.g., a typically good inhibitor would give 95% inhibition at a concentration of 0.008% and 90% at a concentration of 0.004%). A synergism, or cooperation, is often present between different inhibitors and the environment being controlled, and mixtures are the usual choice in commercial formulations. The scientific and technical corrosion literature has descriptions and lists of numerous chemical compounds that exhibit inhibitive properties. Of these, only very few are actually used in practice. This is partly because the desirable properties of an inhibitor usually extend beyond those simply related to metal protection. Considerations of cost, toxicity, availability, and environmental friendliness are of considerable importance.

Table **(1.2)** presents some inhibitors that have been used with success in typical corrosive environments to protect the metallic elements of industrial systems. Commercial inhibitors are available under various trade names and labels that usually provide little or no information about

their chemical composition. It is sometimes very difficult to distinguish between products from different sources because they may contain the same basic anticorrosion agent. Commercial formulations generally consist of one or more inhibitor compounds with other additives such as surfactants, film enhancers, de-emulsifiers, oxygen scavengers, and so forth. The inhibitor solvent package used can be critical in respect to the solubility/dispersibility characteristics and hence the application and performance of the products.

1.7.3 Classification of Inhibitors

Inhibitors are chemicals that react with a metallic surface, or the environment this surface is exposed to, giving the surface a certain level of protection. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Inhibitors are normally distributed from a solution or dispersion. Some are included in a protective coating formulation. Inhibitors slow corrosion processes by:

- Increasing the anodic or cathodic polarization behavior (Tafel slopes)
- Reducing the movement or diffusion of ions to the metallic surface Increasing
- Increasing the electrical resistance of the metallic surface

Table **(1.2)**: Some Corrosive Systems and the inhibitors used to protect corrosion [72].

System	Inhibitor	Metals	Concentration
	Acids		
HCl	Ethylaniline	Fe	0.5%
	MBT*	..	1%
	Pyridine + phenylhydrazine	..	0.5% + 0.5%
	Rosin amine + ethylene oxide	..	0.2%
H_2SO_4	Phenylacridine	..	0.5%
H_3PO_4	NaI	..	200 ppm
Others	Thiourea	..	1%
	Sulfonated castor oil	..	0.5–1.0%
	As_2O_3	..	0.5%
	Na_3AsO_4	..	0.5%
	Water		
Potable	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Polyphosphate	Fe, Zn, Cu, Al	5–10 ppm
	$Ca(OH)_2$	Fe, Zn, Cu	10 ppm
	Na_2SiO_3	..	10–20 ppm
Cooling	$Ca(HCO_3)_2$	Steel, cast iron	10 ppm
	Na_2CrO_4	Fe, Zn, Cu	0.1%
	$NaNO_2$	Fe	0.05%
	NaH_2PO_4	..	1%
	Morpholine	..	0.2%
Boilers	NaH_2PO_4	Fe, Zn, Cu	10 ppm
	Polyphosphate	..	10 ppm
	Morpholine	Fe	Variable
	Hydrazine	..	O_2 scavenger
	Ammonia	..	Neutralizer
	Octadecylamine	..	Variable
Engine coolants	Na_2CrO_4	Fe, Pb, Cu, Zn	0.1–1%
	$NaNO_2$	Fe	0.1–1%
	Borax	..	1%
Glycol/water	Borax + MBT*	All	1% + 0.1%
Oil field brines	Na_2SiO_3	Fe	0.01%
	Quaternaries	..	10–25 ppm
	Imidazoline	..	10–25 ppm
Seawater	Na_2SiO_3	Zn	10 ppm
	$NaNO_2$	Fe	0.5%
	$Ca(HCO_3)_2$	All	pH dependent
	$NaH_2PO_4 + NaNO_2$	Fe	10 ppm + 0.5%

*MBT = mercaptobenzotriazole.

Inhibitors have been classified differently by various authors. Some authors prefer to group inhibitors by their chemical functionality, as follows:

- Inorganic inhibitors. Usually crystalline salts such as sodium chromate, phosphate, or molybdate. Only the negative anions of these compounds are involved in reducing metal corrosion. When zinc is used instead of sodium, the zinc cation can add some beneficial effect. These zinc-added compounds are called mixed-charge inhibitors.

- Organic anionic. Sodium sulfonates, phosphonates, or mercaptobenzotriazole (MBT) are used commonly in cooling waters and antifreeze solutions.

- Organic cationic. In their concentrated forms, these are either liquids or waxlike solids. Their active portions are generally large aliphatic or aromatic compounds with positively charged amine groups.

However, by far the most popular organization scheme consists of regrouping corrosion inhibitors in a functionality scheme as follows.

- Passivating (anodic). Passivating inhibitors cause a large anodic shift of the corrosion potential, forcing the metallic surface into the passivation range. There are two types of passivating inhibitors: oxidizing anions, such as chromate, nitrite, and nitrate, that can passivate steel in the absence of oxygen and the nonoxidizing ions, such as phosphate, tungstate, and molybdate that require the presence of oxygen to passivate steel. These inhibitors are the most effective and consequently the most widely used. Chromate-based

inhibitors are the least-expensive inhibitors and were used until recently in a variety of application (e.g., recirculation-cooling systems of internal combustion engines, rectifiers, refrigeration units, and cooling towers).

- **Organic inhibtors**

Both anodic and cathodic effects are sometimes observed in the presence of organic inhibitors, but as a general rule, organic inhibitors affect the entire surface of a corroding metal when present in sufficient concentration. Organic inhibitors, usually designated as film-forming, protect the metal by forming a hydrophobic film on the metal surface. Their effectiveness depends on the chemical composition, their molecular structure, and their affinities for the metal surface. Because film formation is an adsorption process, the temperature and pressure in the system are important factors. Organic inhibitors will be adsorbed according to the ionic charge of the inhibitor and the charge on the surface. Cationic inhibitors, such as amines, or anionic inhibitors, such as sulfonates, will be adsorbed preferentially depending on whether the metal is charged negatively or positively. The strength of the adsorption bond is the dominant factor for soluble organic inhibitors. These materials build up a protective film of adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. Because the metal surface covered is proportional to the inhibitor concentrates, the concentration of the inhibitor in the medium is critical. For any specific inhibitor in any given medium there is an optimal concentration. For example, a concentration of 0.05% sodium benzoate or 0.2% sodium cinnamate is effective in water with a pH of 7.5 and containing either 17 ppm sodium chloride or 0.5% by weight of ethyl

octanol. The corrosion due to ethylene glycol cooling water systems can be controlled by the use of ethanolamine as an inhibitor.

- **Cathodic inhibitors**

Cathodic inhibitors either slow the cathodic reaction itself or selectively precipitate on cathodic areas to increase the surface impedance and limit the diffusion of reducible species to these areas. Cathodic inhibitors can provide inhibition by three different mechanisms: (1) as cathodic poisons, (2) as cathodic precipitates, and (3) as oxygen scavengers. Some cathodic inhibitors, such as compounds of arsenic and antimony, work by making the recombination and discharge of hydrogen more difficult. Other cathodic inhibitors, ions such as calcium, zinc, or magnesium, may be precipitated as oxides to form a protective layer on the metal. Oxygen scavengers help to inhibit corrosion by preventing the cathodic depolarization caused by oxygen. The most commonly used oxygen scavenger at ambient temperature is probably sodium sulfite (Na_2SO_3).

1.7.4 Precipitation inhibitors

Precipitation-inducing inhibitors are film-forming compounds that have a general action over the metal surface, blocking both anodic and Corrosion Inhibitors cathodic sites indirectly. Precipitation inhibitors are compounds that cause the formation of precipitates on the surface of the metal, thereby providing a protective film. Hard water that is high in calcium and magnesium is less corrosive than soft water because of the tendency of the salts in the hard water to precipitate on the surface of the metal and form a protective film. The most common inhibitors of this category are the silicates and the phosphates. Sodium silicate, for example, is used in many domestic water softeners to prevent the

occurrence of rust water. In aerated hot water systems, sodium silicate protects steel, copper, and brass. However, protection is not always reliable and depends heavily on pH and a saturation index that depends on water composition and temperature. Phosphates also require oxygen for effective inhibition. Silicates and phosphates do not afford the degree of protection provided by chromates and nitrites; however, they are very useful in situations where nontoxic additives are required.

1.7.5 Corrosion Inhibition Mechanism

1.7.5.1 Inhibitors for acid solutions

The corrosion of metals in acid solutions can be inhibited by a wide range of substances, such as halide ions, carbon monoxide, and many organic compounds, particularly those containing elements of Groups V and VI of the Periodic Table (i.e., nitrogen, phosphorus, arsenic, oxygen, sulfur, and selenium). Organic compounds containing multiple bonds, especially triple bonds, are effective inhibitors. The primary step in the action of inhibitors in acid solutions is generally agreed to be adsorption onto the metal surface, which is usually oxide-free in acid solutions. The adsorbed inhibitor then acts to retard the cathodic or anodic electrochemical corrosion processes. Inhibitors of corrosion in acid solution can interact with metals and affect the corrosion reaction in a number of ways, some of which may occur simultaneously. It is often not possible to assign a single general mechanism of action to an inhibitor because the mechanism may change with experimental conditions. Thus, the predominant mechanism of action of an inhibitor may vary with factors such as its concentration, the pH of the acid, the nature of the anion of the acid, the presence of other species in the solution, the extent of reaction to form secondary

inhibitors, and the nature of the metal. The mechanism of action of inhibitors with the same functional group may additionally vary with factors such as the effect of the molecular structure on the electron density of the functional group and the size of the hydrocarbon portion of the molecule.

1.7.5.2 Adsorption of corrosion inhibitors onto metals

The inhibitive efficiency is usually proportional to the fraction of the surface θ covered with adsorbed inhibitor. However, at low surface coverage ($\theta < 0.1$), the effectiveness of adsorbed inhibitor species in retarding the corrosion reactions may be greater than at high surface coverage. In other cases, adsorption of inhibitors, such as thiourea and amines, from diluted solutions, may stimulate corrosion.The information on inhibitor adsorption, derived from direct measurements and from inhibitive efficiency measurements, considered in conjunction with general knowledge of adsorption from solution, indicates that inhibitor adsorption on metals is influenced by the following main features.

1.7.5.3 Surface charge on the metal

Adsorption may be due to electrostatic attractive forces between ionic charges or dipoles on the adsorbed species and the electric charge on the metal at the metal-solution interface. In solution, the charge on a metal can be expressed by its potential with respect to the zero-charge potential. This potential relative to the zero-charge potential, often referred to as the (-potential, is more important with respect to adsorption than the potential on the hydrogen scale, and indeed the signs of these two potentials may be different. As the potential of a metallic surface becomes more positive, the adsorption of anions is favored, and as the -potential becomes more negative, the adsorption of cations is favored.

1.7.5.4 The functional group and structure of the inhibitor

Inhibitors can also bond to metal surfaces by electron transfer to the metal to form a coordinate type of link. This process is favored by the presence in the metal of vacant electron orbitals of low energy, such as occurs in the transition metals. Electron transfer from the adsorbed species is favored by the presence of relatively loosely bound electrons, such as may be found in anions, and neutral organic molecules containing lone pair electrons or -electron systems associated with multiple, especially triple, bonds or aromatic rings. The electron density at the functional group increases as the inhibitive efficiency increases in a series of related compounds.This is consistent with increasing strength of coordinate bonding due to easier electron transfer and hence greater adsorption.

1.7.5.5 Interaction of the inhibitor with water molecules

Adsorption of inhibitor molecules is often a displacement reaction involving removal of adsorbed water molecules from the surface. During adsorption of a molecule, the change in interaction energy with water molecules in passing from the dissolved to the adsorbed state forms an important part of the free energy change on adsorption. This has been shown to increase with the energy of solvation of the adsorbing species, which in turn increases with increasing size of the hydrocarbon portion of an organic molecule. Thus increasing size leads to decreasing solubility and increasing adsorbability. This is consistent with the increasing inhibitive efficiency observed at constant concentrations with increasing molecular size in a series of related compounds.

1.7.5.6 Reaction of adsorbed inhibitors

In some cases, the adsorbed corrosion inhibitor may react, usually by electrochemical reduction, to form a product that may also be inhibitive. Inhibition due to the added substance has been termed primary inhibition and that due to the reaction product, secondary inhibition. In such cases, the inhibitive efficiency may increase or decrease with time according to whether the secondary inhibition is more or less effective than the primary inhibition. Sulfoxides, for example, can be reduced to sulfides, which are more efficient inhibitors.

1.7.5.7 Effects of inhibitors on corrosion processes

In acid solutions the anodic process of corrosion is the passage of metal ions from the oxide-free metal surface into the solution, and the principal cathodic process is the discharge of hydrogen ions to produce hydrogen gas. In air-saturated acid solutions, cathodic reduction of dissolved oxygen also occurs, but for iron the rate does not become significant compared to the rate of hydrogen ion discharge until the pH exceeds a value of 3. An inhibitor may decrease the rate of the anodic process, the cathodic process, or both processes. The change in the corrosion potential on addition of the inhibitor is often a useful indication of which process is retarded. Displacement of the corrosion potential in the positive direction indicates mainly retardation of the anodic process (anodic control), whereas displacement in the negative direction indicates mainly retardation of the cathodic process (cathodic control). Little change in the corrosion potential suggests that both anodic and cathodic processes are retarded.

Aim of the Work

As previously mentioned in point 1.5.6, Heterocyclic compounds, especially triazoles, gain in recent years great importance because of their anticorrosive ability on mild steel. Therefore, Synthesis of Schiff base compounds with triazole ring and with different substituents is the main aim of this work. FTIR- and 1H NMR spectroscopic methods should be used to characterize the intended heterocyclic compounds.

These compounds are intended to be studied as corrosion inhibitors of mild steel in 1M sulfuric acid. The effect of the inhibitor concentration on corrosion inhibition has to be determined. Weight loss method as standard way should be used in this work.

Chapter Two Experimental Part

2.1 Chemicals

All of the chemicals and culture's media were obtained from various companies like: EDUCEK, Merck, Fluka, HIMEDIA, J. T. Baker, Scharlau, BDH, ALPHA CHEMIKA and Silicea. Chemicals were used without further purification the purity at least 98%.

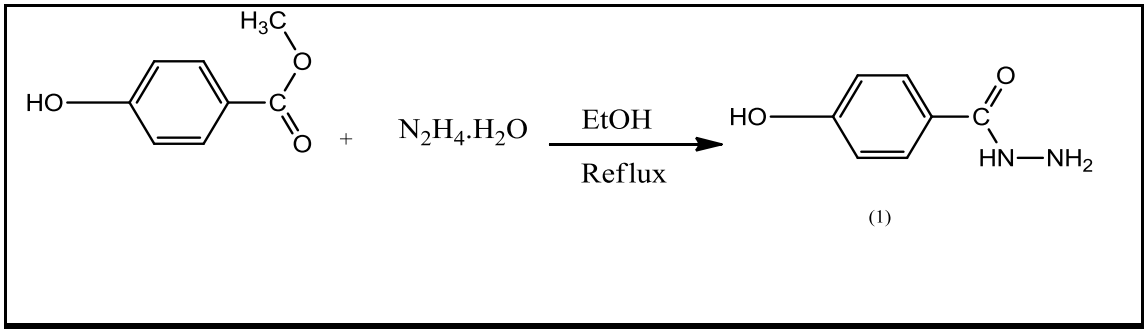
2.2. Instruments

1. Melting points were determined on electro thermal capillary apparatus, Chachan, **MLP-01, and were uncorrected.**
2. Fourier Transform Infrared Spectroscopy **(**FT-IR) spectra in the wave number range (600-4000) cm^{-1} were recorded by potassium bromide (KBr) disc on FT-IR, 8300 Shimadzu Spectrophotometer Company, (Ibn-Sena, Ministry of Industry).
3. Nuclear Magnetic Resonance spectroscopy (NMR), in the range of (0-16) ppm for ^{1}H NMR by using DMSO as solvent in NMR Spectrometer 400 MHz, Avance III 400, Bruker, Germany, (Isfahan University, Isfahan, Iran).
4. Balance, Ohaus, PA114, USA

2.3 Synthesis

2.3.1 Synthesis of 4-hydroxybenzohydrazide (1) [73]

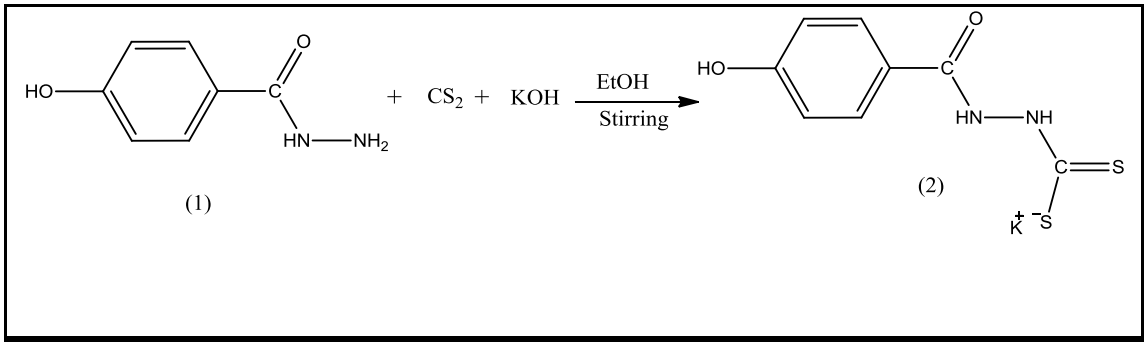
4-hydroxy methyl benzoate (0.01 mol, 1.52 g) in 25ml of ethanol is taken in a round bottom flask with hydrazine hydrate 80% (0.015 mol, 0.73 ml) and refluxed for 4 hours. The precipitate formed was filtered, dried and recrystallized from ethanol (See Table 2-1).



(1)

2.3.2. Synthesis of potassium 2-(4-hydroxybenzoyl) hydrazinecarbodithioate (2)

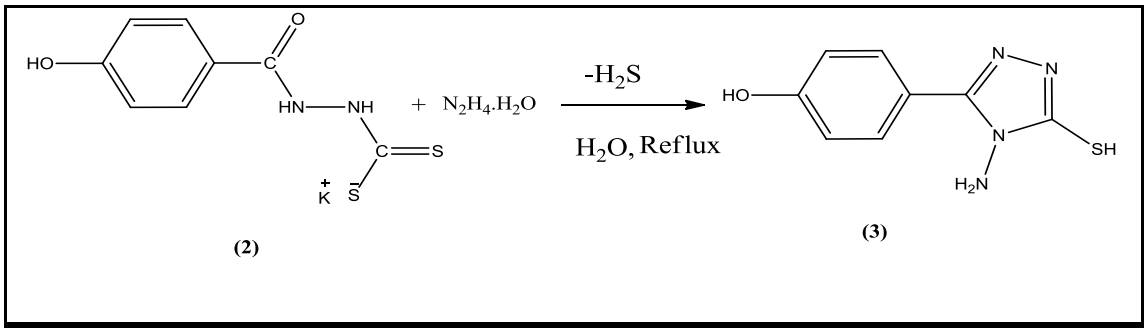
4-hydroxybenzohydrazide (0.01mol, 1.36g) was added to solution of dissolved potassium hydroxide (98%) (0.015 mol, 0.84 g) in (15 mL) of absolute ethanol. Mixture was cooled in ice bath (0-5) C^{o} with stirring. Add to this mixture (0.025 mol, 1.8 mL) carbon disulfide (99%) was added in small portions with constant stirring. The reaction mixture was left to stir continuously for 18 hrs. At room temperature. The potassium salt thus obtained was used in the next step without further purification.



(1) (2)

2.3.3. Synthesis of 4-(4-amino-5-mercapto-4H-1,2,4-triazol-3 yl)phenol (3) [73]

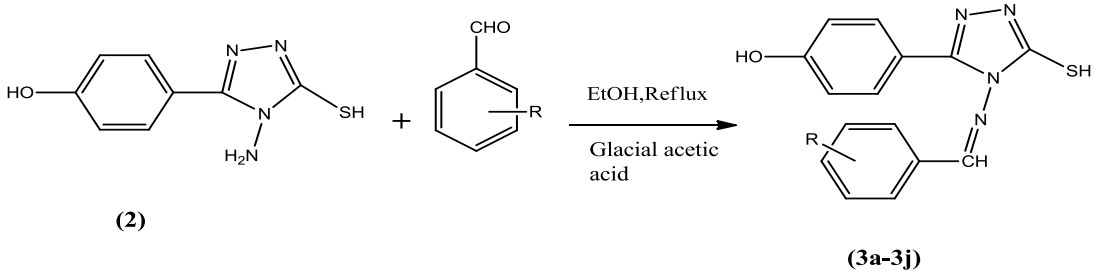
A suspension of potassium2-(4-hydroxybenzoyl) hydrazinecarbodithioate (0.01 mol, 2.6 g), hydrazine hydrate (0.02 mol, 0.97 ml) and water (40 ml) was refluxed for 8 hours. The color of the reaction mixture changed to green, hydrogen sulphide was liberated and a homogenous solution resulted. The end of the reaction was checked by (T.L.C). A white solid was precipitated by adding cold water (50 ml) and acidification with concentrated hydrochloric acid. The product was filtered, washed with cold water and recrystallized from ethanol (See Table 2-1).



(2) (3)

2.3.4 General procedure for the synthesis 4-(4-(benzylideneamino)-5-mercapto-4H-1,2,4-triazol-3-yl)phenol (3a-j) [74]

A mixture of (3) (0.01 mol, 2.1 g) and various aromatic aldehydes (0.02 mol) in (50 ml) absolute ethanol and two drops of glacial acetic acid, then refluxed for about 10 hours. Precipitate was filtered, dried and recrystallized from ethanol (See Table 2-1).



(2) **(3a-3j)**

R = H, *p*-OH, *p*- $(CH_3)_2N$, *p*-Br, *o*-NH_2, *p*-CH_3, *p*-NO_2, *p*-OCH_3, *p*-Cl, *o*-OH respectively.

Table (2-1): Physical Properties for Compounds (1-3[a-j])

No	Compound name	Chemical Formula	Molecular Weight	Color	M.P (C^o)	Yield (%)
1	4-hydroxybenzoic acid hydrazide	$C_7H_8N_2O_2$	152.06	White	264-266 dec	75
2	4-(4-amino-5-mercapto-4H 1,2,4-triazole-3-yl)phenol	$C_8H_8N_4OS$	208.04	White	298-300 dec	73
3a	4-[4-{ benzylideneamino} -5-mercapto-4H-1,2,4-triazol-3-yl]phenol	$C_{15}H_{12}N_4OS$	296.35	Pale Yellow	157-159	86
3b	4-[4-{4-hydroxy-benzylideneamino}-5-mercapto-4H-1,2,4-triazol-3-yl]phenol	$C_{15}H_{12}N_4O_2S$	312.35	White	150-153	82
3c	4-[4-{4-(dimethylamino) benzylideneamino}-5-mercapto-4H-1,2,4-triazol-3-yl]phenol	$C_{17}H_{17}N_5OS$	339.41	Red	198-200	67
3d	4-[4-{4-bromobenzylidene-amino}-5-mercapto-4H-1,2,4-triazol-3-yl]phenol	$C_{15}H_{11}BrN_4OS$	375.24	Pale Yellow	180-182	86
3e	4-(4-(2-aminobenzylidene-amino)-5-mercapto-4H-1,2,4-triazol-3-yl)phenol	$C_{15}H_{13}N_5OS$	311.36	Dark brown	200-202	63

3f	4-[5-mercapto-4-{4-methyl-benzylideneamino}-4H-1,2,4-triazol-3-yl]phenol	$C_{16}H_{14}N_4OS$	310.37	Yellow	138-140	87
3g	4-[5-mercapto4-{4-nitro-benzylideneamino}-4H-1,2,4-triazol-3-yl]phenol	$C_{15}H_{11}N_5O_3S$	341.34	Yellow	170-172	61
3h	4-[5-mercapto-4-{4-methoxybenzylideneamino}-4H-1,2,4-triazol-3-yl]phenol	$C_{16}H_{14}N_4O_2S$	326.37	Yellowish Orange	148-150	89
3i	4-[4-{4-chlorobenzylidene-amino}-5-mercapto-4H-1,2,4-triazol-3-yl]phenol	$C_{15}H_{11}ClN_4OS$	330.79	Yellow	188-190	76
3j	2-[{3-(4-hydroxyphenyl) -5-mercapto-4H-1,2,4-triazol-4-ylimino}methyl]phenol	$C_{15}H_{12}N_4O_2S$	312.35	Yellow	206-208	74

2.3.5 Weight loss measurements for the corrosion inhibition.

2.3.5.1 Requirements

- Mild steel which has the composition percentages (99.579% Fe, and the remainder is 0.002% P, 0.288%Mn, 0.03% C, 0.0154% S, 0.0199% Cr, 0.002% Mo, 0.065% Cu, 0.0005% V).
- 1M H_2SO_4
- Acetone
- Ethanol
- Distilled water
- Corrosion Inhibitors: - 4-(4-amino-5-mercapto-4H-1,2,4-triazol-3 yl) phenol **(2)** and its derivatives **(3a-3j)**.

2.3.5.2 Method

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 were suspended and completely immersed in 250 ml beaker containing 1M sulfuric acid in the presence and absence of inhibitors. The specimens were removed after 8 hours at 25 ^{o}C, washed with water, then with absolute ethanol and finally with acetone to remove any corrosion products .Then they were dried and reweighed. Weight loss measurements were performed as per ASTM method previously described [75]. Experiments were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported.

2.3.5.3 Calculation of corrosion rate (W), corrosion inhibition efficiency (IE %) and equilibrium constant of the adsorption process (K_{ads})

Weight loss allowed calculation of the mean corrosion rate in ($mg.cm^{-2}.h^{-1}$). The corrosion rate $\boldsymbol{W}$ of mild steel was determined using the relation (1):

$$\boldsymbol{W = \frac{\Delta m}{st}} \qquad (\mathbf{1})$$

Where (Δm) is the mass loss, (s) the area and (t) is the immersion period. The percentage inhibition efficiency (IE %) was calculated using the relationship (2) :

$$IE\% = \left(\frac{W_{corr} - W_{corr(inh)}}{W_{corr}}\right) \times 100 \quad (2)$$

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

the degree of surface coverage values (θ) at different inhibitor concentrations in 1M H_2SO_4 was achieved from weight loss measurements (θ = IE%/100) (see Table 3) at 25 C^o and tested with the following [76].

$$C/\theta = 1/K_{ads} + C \quad (3)$$

Where K_{ads} is the equilibrium constant of the adsorption process, C is the concentration of inhibitors, (θ) is the degree of surface coverage values.

According to the Langmuir isotherm, K_{ads} values can be calculated from the intercepts of the straight line of plotting C/θ versus C. K_{ads} is related to the standard free energy of adsorption ΔG^oads, with the following equation:

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \quad (4)$$

Where the molar concentration of water in the solution = 55.5

Chapter Three

Results and Discussion

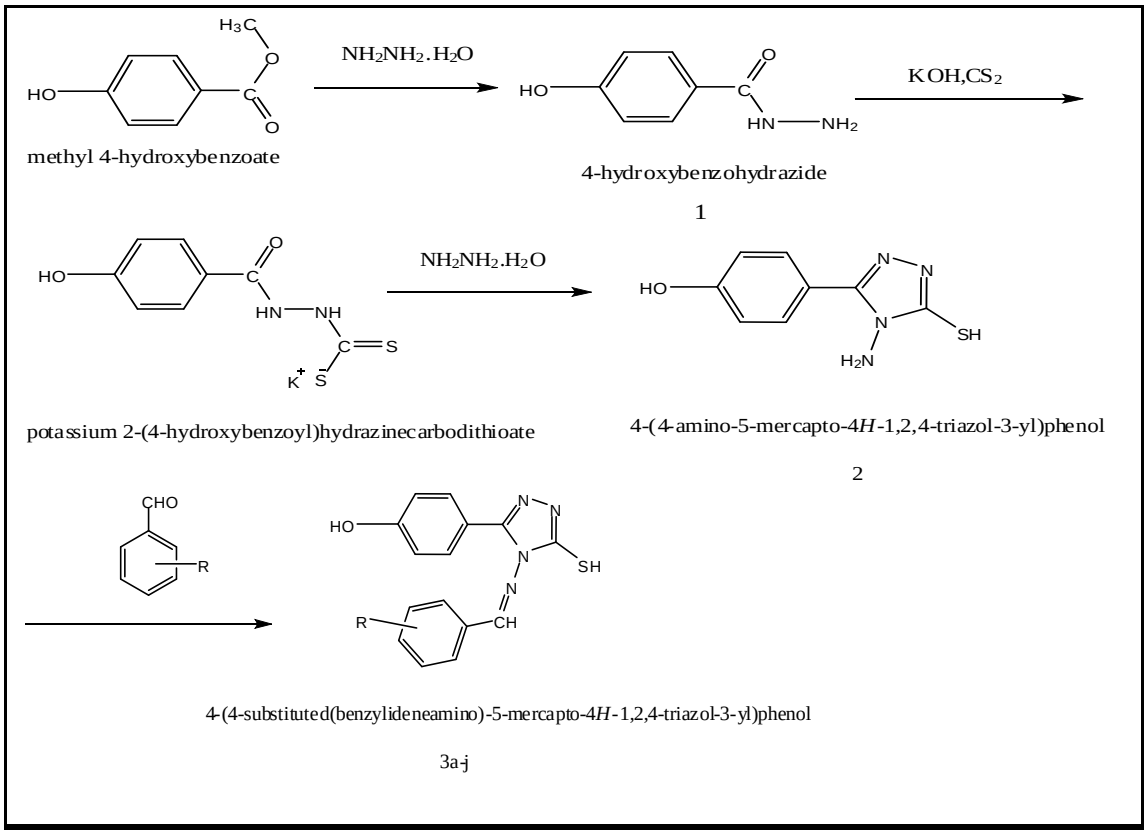
3.1 Chemistry

The technique of FT-IR, ^{1}H NMR were used to characterize the intermediates and the final products. For all NMR spectra the following notes must be taken in consideration:

Note (1): For all ^{1}H NMR spectra, signal at (2.5) ppm (DMSO-d6) and (3.3) ppm for H_2O.

Note (2): (*s = singlet, d = doublet* and *m= multiplet*).

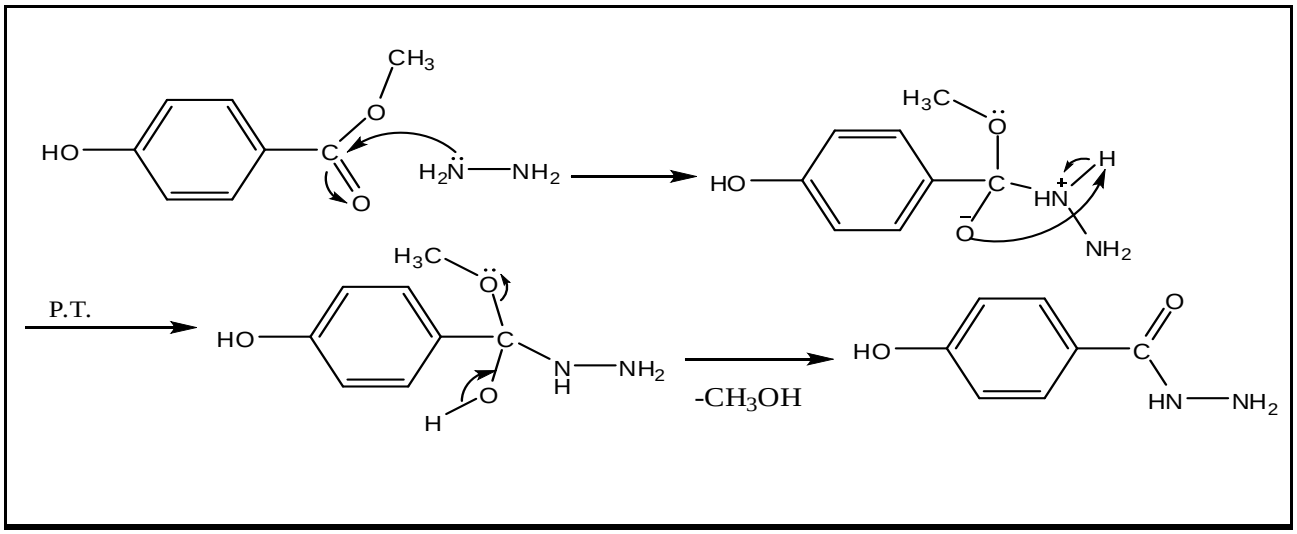
The chemical steps for the synthesis of compounds (**1-3[a-j]**) are shown in Scheme (3-1). Some physical properties for these compounds were listed in Table **(2-1)**.



Scheme (3-1): Synthetic pathway for compounds [1-3(a-j)], where (R = H, *p*-OH, *p*- $(CH_3)_2N$, *p*-Br, *o*-NH_2), *p*-CH_3, *p*-NO_2, *p*-OCH_3, *p*-Cl, *o*-OH respectively.

3.1.1 Preparation of 4-hydroxybenzohydrazide (1)

The mechanism of the reaction of 4-hydroxy methyl benzoate and hydrazine hydrate is illustrated in Scheme (3-2) [77]. The mechanism involves attacking the nucleophile hydrazine hydrate on the carbonyl carbon atom of the ester. After a proton transfer, removal of a methanol molecule leads to the imine compound.



Scheme (3-2): Mechanism of the formation of benzoic acid hydrazide (1)

The FT-IR spectrum of 4-hydroxybenzohydrazide shows two characteristic bands at 3197 cm^{-1} and 3309 cm^{-1} due to symmetrical and asymmetrical stretching vibration bands of NH_2 group and a stretching band at 3280 cm^{-1} due to hydroxyl group. In addition, Compound 1 was confirmed through the disappearance carbonyl band of ester at 1681 cm^{-1} and appearance a medium stretching vibration band at 1620 cm^{-1} belongs to carbonyl amide group as shown in (Figure 3-1&3-2) and table (3-1).

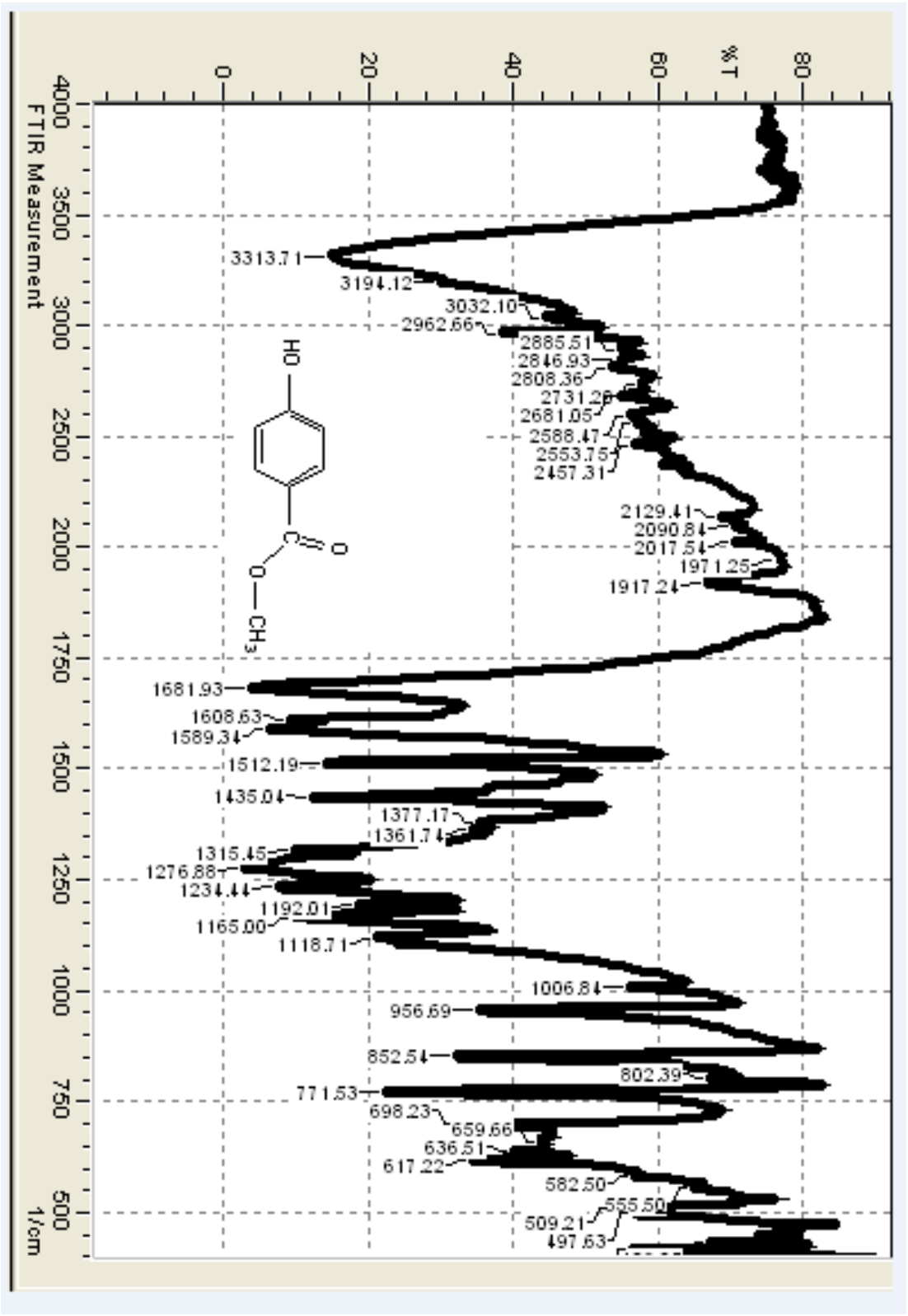


Figure (3-1): FT-IR Spectrum of methyl 4-hydroxybenzoate

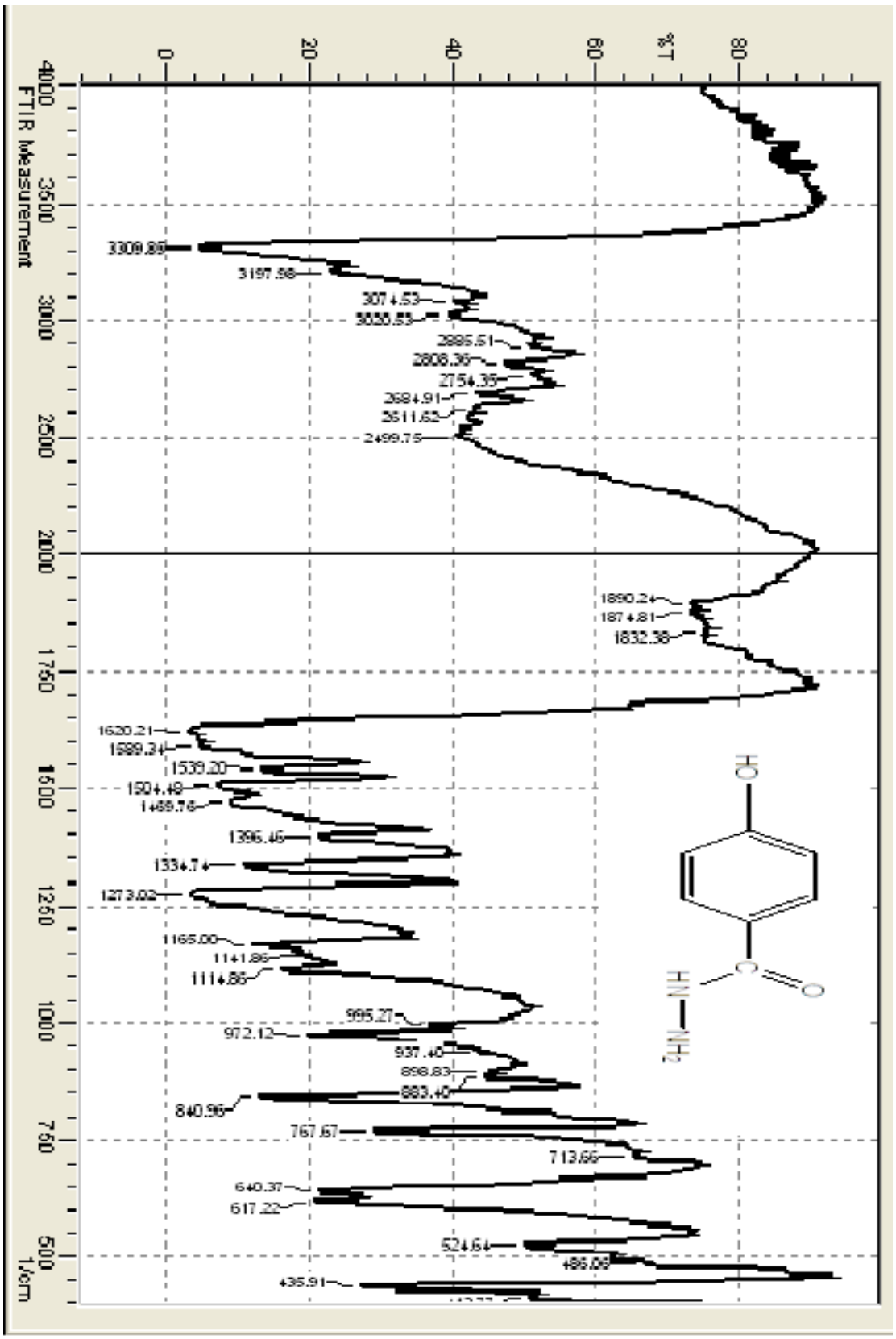
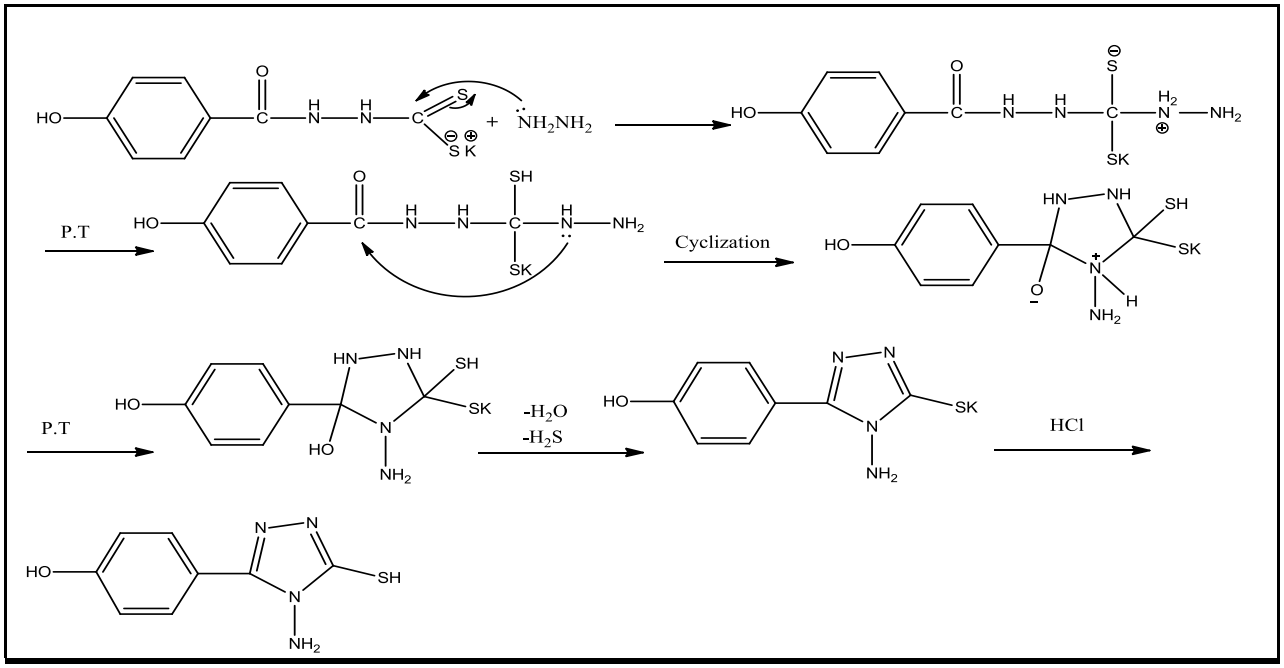


Figure (3-2): FT-IR Spectrum of 4-hydroxybenzohydrazide (1)

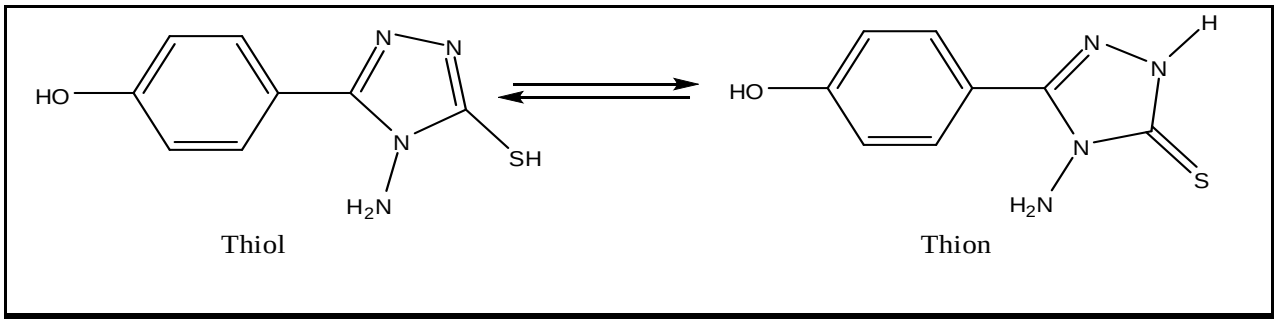
3.1.2 Preparation of 4-(4-amino-5-mercapto-*4H*-1, 2, 4-triazol-3-yl) phenol (2)

The second step of the synthesis is the preparation of the salt potassium 2-(4-hydroxybenzoyl) hydrazinecarbodithioate through the reaction of **4**-hydroxybenzohydrazide and carbon disulfide in presence of potassium hydroxide as a base. This compound is converted into triazole by the reaction with hydrazine hydrate. The addition-Elimination mechanism involves attacking of the nucleophile NH_2NH_2 on the carbonyl carbon of the resulting salt. After a proton transfer, a removal of a water molecule the neutral imine salt is formed. Attacking of the nitrogen atom on the carbon atom of the thionate group results a tetrahedral intermediate. Once more after a proton transfer and removal a H_2S, The formation of the triazole ring is completed. Acidification of the resulting triazole salt gives compound 2 [77]. As shown in scheme (3-3).



Scheme (3-3): Mechanism of 4-(4-amino-5-mercapto-*4H*-1, 2, 4-triazol-3-yl) phenol (2) formation, where P.T. = proton transfer

Compound 2 was confirmed through the disappearance of carbonyl amide group at 1624 cm^{-1} and appearance of (C=N) group of the triazole ring at 1612 cm^{-1} (figure 3-3) and table (3-1). The presence of N-C-S at 948 cm^{-1}, N-N-C at 1303 cm^{-1} bands also indicates the formation of compound **2**. FT-IR spectrum of compound 2 shows further the stretching bands (3174, 3255) cm^{-1} for the NH_2 group attached to the triazole ring and a stretching band at 3116 cm^{-1} due to OH-phenolic group. The shifting in the frequency numbers of the amino group in benzohydrazide 1 and in the traizole compound (2) is an indication for the conversion. Further bands are also detected in the IR-spectrum at 3057 cm^{-1} due to CH-aromatic, at 694 cm^{-1} due to C-S group, at 2569 cm^{-1} due to SH group. And at (1118, 1174) cm^{-1} for C=S and N-H (thion-thiol tautomerisim). Scheme **(3-3)** shows the equilibrium that exists in the compound 2 [77].



Scheme (3-4): Tautomerism of 4-amino-5-phenyl-4H-1,2,4-triazole-3-thiol (2)

The ^1H NMR spectrum (Figure 3-4) shows a singlet at 10.7ppm for the proton of hydroxyl group, 5.72 ppm for the two protons of the amino group (NH_2) attached to the aromatic ring, The aromatic protons are detected as two duplets at the both ortho positions of the benzene ring (6.88,7.86; 4H, *m*, CH- arom.).

It is not expected, that no signals are detected for the variable protons (NH and SH) in the ^1H NMR spectrum of compound **2**. This may be explained by the high tendency of the formation of hydrogen bonding of compound (2) due to presence of hydroxyl group in para postion of the

benzene ring, NH_2 group and SH or NH group of the triazole ring. This effect may lead to bring molecules strongly associated and therefore the OH and SH or NH protons were more deshielded in ^1H NMR spectrum [78].

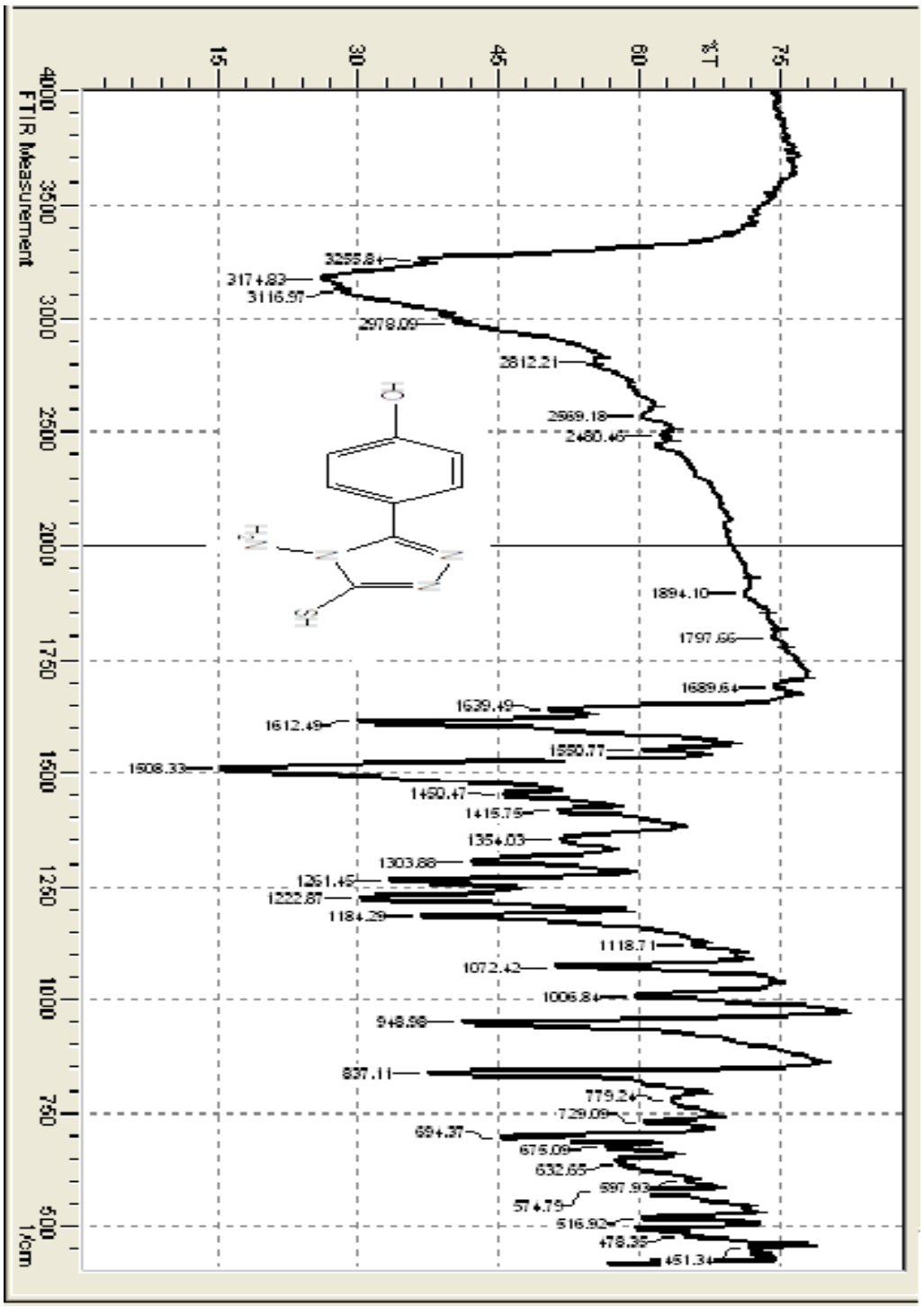


Figure (3-3): FT-IR Spectrum of 4-(4-amino-5-mercapto-*4H*-1, 2, 4-triazol-3-yl) phenol (2)

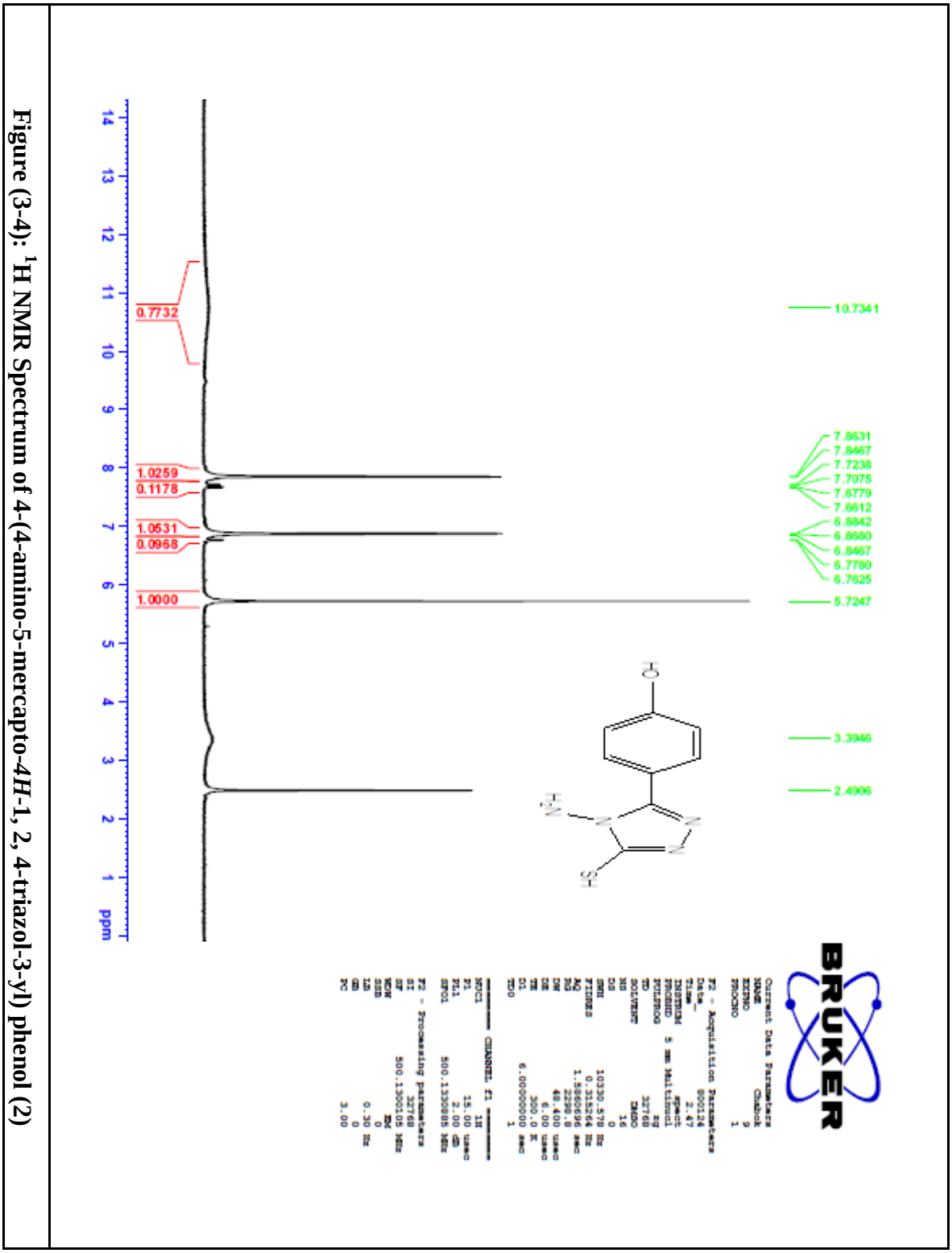
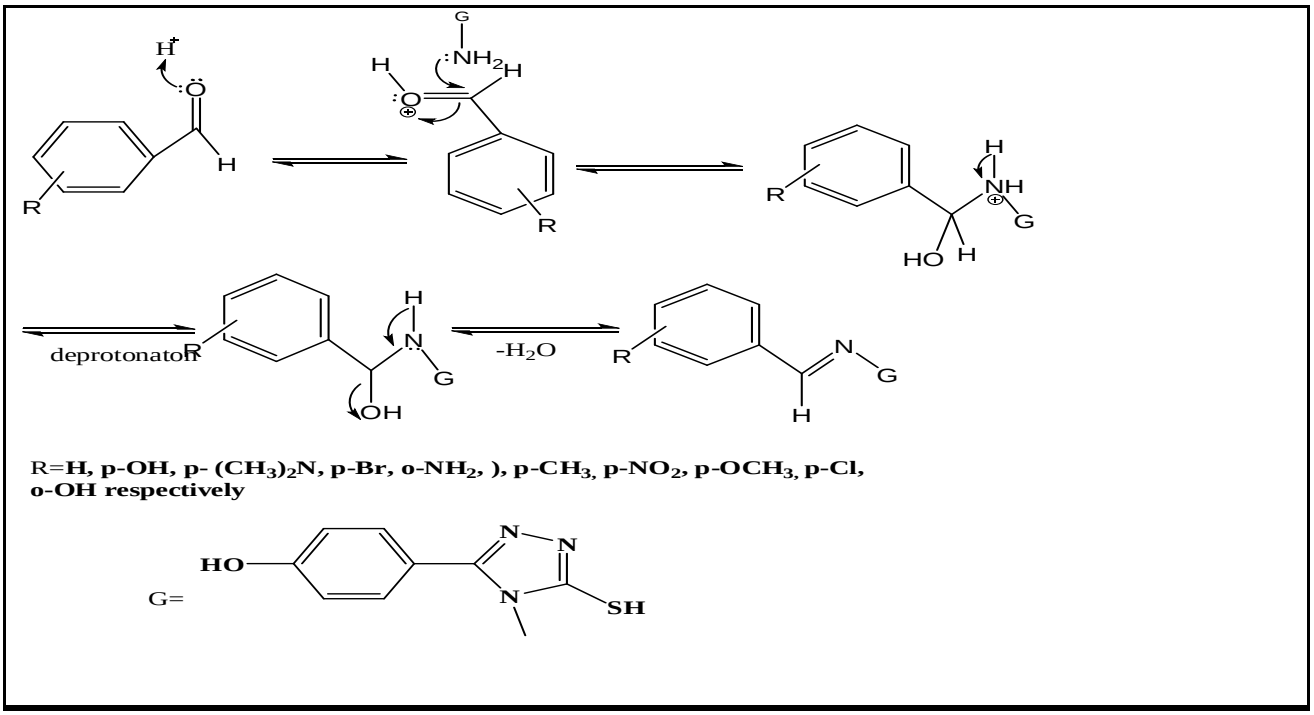


Figure (3-4): ^{1}H NMR Spectrum of 4-(4-amino-5-mercapto-4*H*-1, 2, 4-triazol-3-yl) phenol (2)

3.1.3 Synthesis and characterization of Schiff Bases 4-(4-(benzylideneamino)-5-mercapto-4H-1,2,4-triazol-3-yl)phenol (3a_j) (3)

Schiff bases (3a-j) are synthesized by the reaction of 4-(4-amino-5-mercapto-4H-1, 2, 4-triazol-3-yl) phenol with various aromatic aldehydes, in presence of acetic acid (Scheme 3-5) [77]. The Addition-Elimination mechanism involves attacking of the nucleophile R-NH_2 on the carbonyl carbon atom of the aromatic aldehyde. Firstly, a tetrahedral intermediate is formed which then gives a proton ab. The imine compound is formed after elimination of a water molecule.



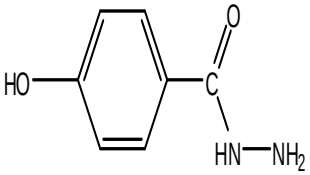
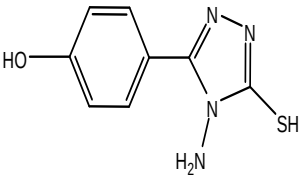
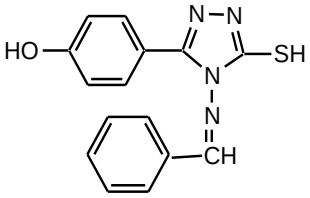
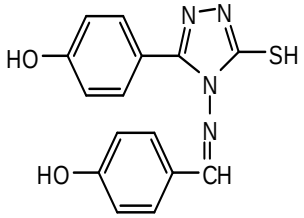
Scheme (3-5): Mechanism of Schiff's bases formation (3a-j) compounds

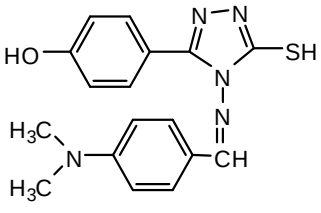
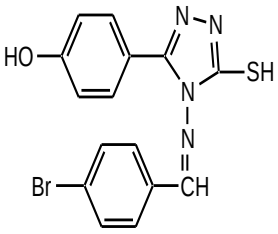
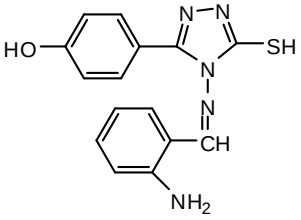
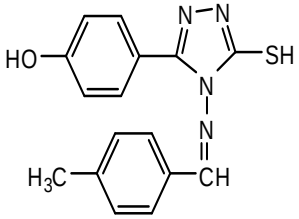
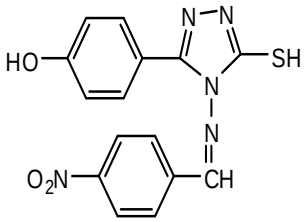
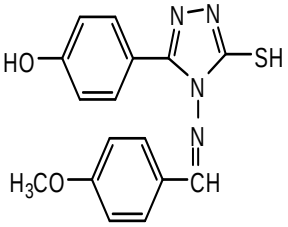
All Schiff bases were identified through their FT-IR spectra as shown in Table (3-1) and Figures [(3-5)-(3-14)], and some of them (3a-3c) by ^{1}H NMR, as shown in Table (3-2) and Figures [(3-15)-(3-17)].

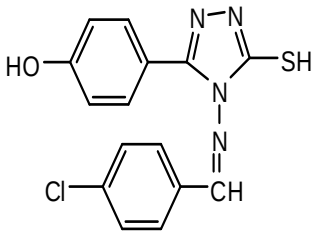
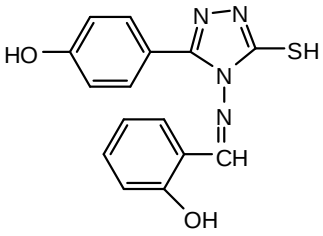
The formation of compounds (3a-3j) was indicated by the disappearance of NH_2 bands and appearance of the imine group at (1612-1624) cm^{-1}. All

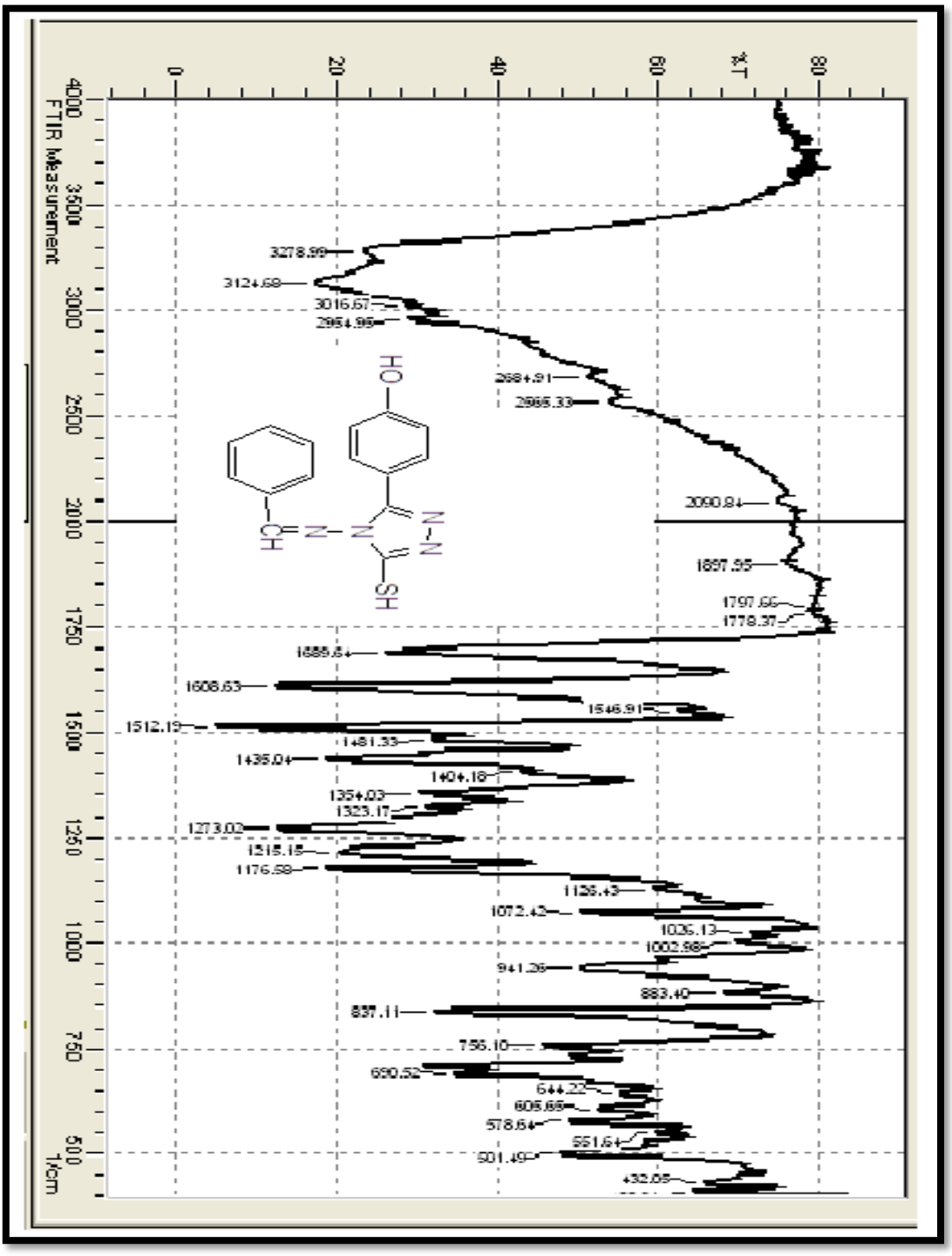
synthesized Schiff bases show stretching vibration bands at the range of (3251-3302 cm^{-1}), (3113-3197cm^{-1}), (3001-3089 cm^{-1}), (2951-2997 cm^{-1}) and at 1512 cm^{-1} for O-H phenolic, N-H (tautomer), C-H aromatic, C-H aliphatic, and for C=C bond respectively. The stretching vibration band at the range (2553-2596 cm^{-1}) is attributed to the thiol group (tautomer). The coexistence of thiol and N-H bands indicates the thione-thiol tautomerisim equilibrium (scheme 3-3). Other characteristic bands are listed in the table (3-1).

Table (3-1): FT-IR characteristic Spectral bands of compounds (1, 2 and 3a-3j).

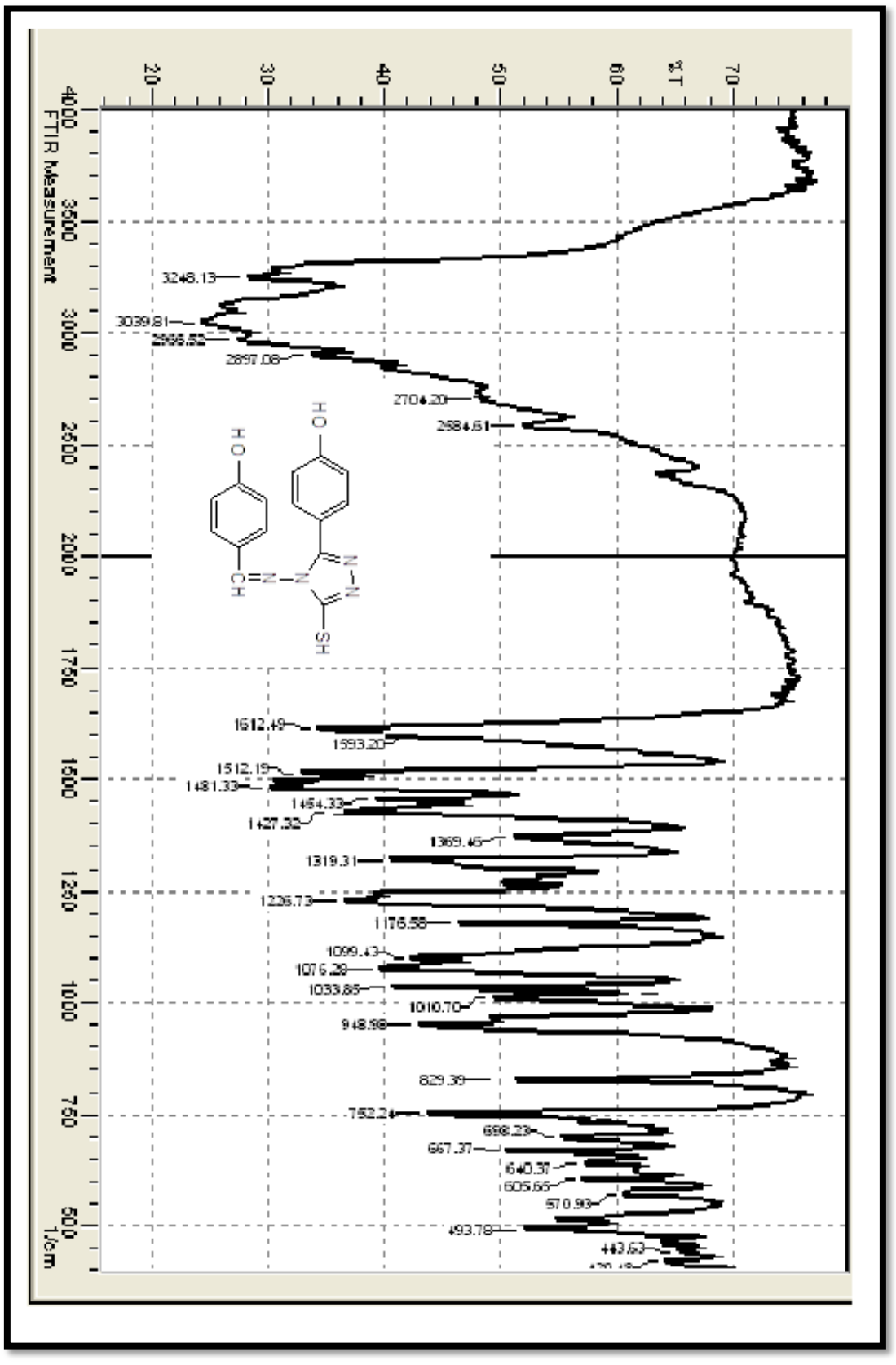
No.	Structure	Frequency numbers (cm^{-1})
1		(3309,3197) cm^{-1} for NH_2 group,3280 cm^{-1} for O-H group, 3074, 3020 cm^{-1} for CH-aromatic, 1620 cm^{-1} due to carbonyl amid group. And 1589 cm^{-1} for N-H amid group.
2		3255 cm-1 due to OH group, (3116,3174) cm^{-1} due to NH_2 group, 3057 cm-1 due to C-H-aromatic, 2569 cm^{-1} belongs to S-H group, 1612 cm^{-1} due to (C=N) group, and 694 cm-1 due to C-S group.
3a		3280 cm^{-1}due to O-H group, 3124 cm^{-1} due to N-H(tautomer), 3016 cm^{-1} due to C-H-aromatic, 2954 cm^{-1} due to C-H aliphatic, 2592 cm^{-1} due to S-H group, 1608 cm^{-1} due to C=N group, 648 cm^{-1} due to C-S group.
3b		3290 cm^{-1} for O-H bonds, (3248,3100) cm^{-1} belong to both N-H (tautomer), 3039 cm^{-1} due to C-H-aromatic, 1612 cm^{-1} due to C=N group, (2966, 2897) cm^{-1} belongs to C-H aliphatic, 2569 cm^{-1} belongs to S-H group, and 829 cm^{-1} due to para-di substituted phenyl ring.

3c		3278 cm^{-1} for OH group, 3113 cm^{-1} due to NH (tautomer), 3089 cm^{-1} due to CH-aromatic, 2584cm^{-1} for S-H group, 1604 cm^{-1} due to C=N group, (1597, 1481) cm^{-1} due to C=C aromatic, 1369 cm^{-1} due to C-H bending of (CH_3), 1172 cm^{-1} due to C-N bond, and 821 cm^{-1} due to para-disubstituted phenyl ring.
3d		3271 cm-1 for OH group, 3128 cm-1 for NH (tautomer), 3030 cm^{-1} due to CH-aromatic, 2954cm^{-1} due to C-H aliphatic, 2565cm^{-1} due to S-H, 1608 cm^{-1} due to C=N group, 690 cm^{-1} due to C-S group, 817 cm^{-1} due to para-di substituted phenyl ring, and 590 cm^{-1} due to C-Br.
3e		(3330,3197) cm^{-1} due to NH_2 group, 3257cm^{-1} for OH, 3020 cm^{-1} due to C-H-aromatic, 2908cm^{-1} due to C-H aliphatic, 2592 cm^{-1} for SH group, and1612 cm^{-1} due to C=N group.
3f		3325 cm^{-1} for OH group, 3120 cm^{-1} for NH (tautomer), 3065 cm^{-1} due to C-H-aromatic, 2954 cm^{-1} belongs to C-H aliphatic,2588cm^{-1} for S-H group, 1604 cm^{-1} due to C=N group, (1562,1512) cm^{-1} due to C=C aromatic, and 817 cm^{-1} due to para-di substituted phenyl ring.
3g		3282 cm^{-1} for OH group, 3105 cm^{-1} for NH-tautomer, 3032 cm^{-1} due to CH-aromatic, 2592 cm^{-1} belongs to SH, 1612 cm^{-1} due to C=N group, (1516, 1346) cm^{-1} due to NO_2, 829 cm^{-1} due to para-disubstituted phenyl ring, and 2974cm^{-1} due to C-H aliphatic.
3h		3124 cm^{-1} for OH, (3051, 3001) cm^{-1} due to CH-aromatic, 2947 cm^{-1} for CH aliphatic, 2588 cm^{-1} belongs to S-H group,1620 cm^{-1} due to C=N group, (1570, 1512) cm^{-1} due to C=C aromatic, 1300 cm^{-1} due to C-H bend of (CH_3), and 1165cm^{-1} due to C-O group, 752 cm^{-1} due to para-disubstituted phenyl ring

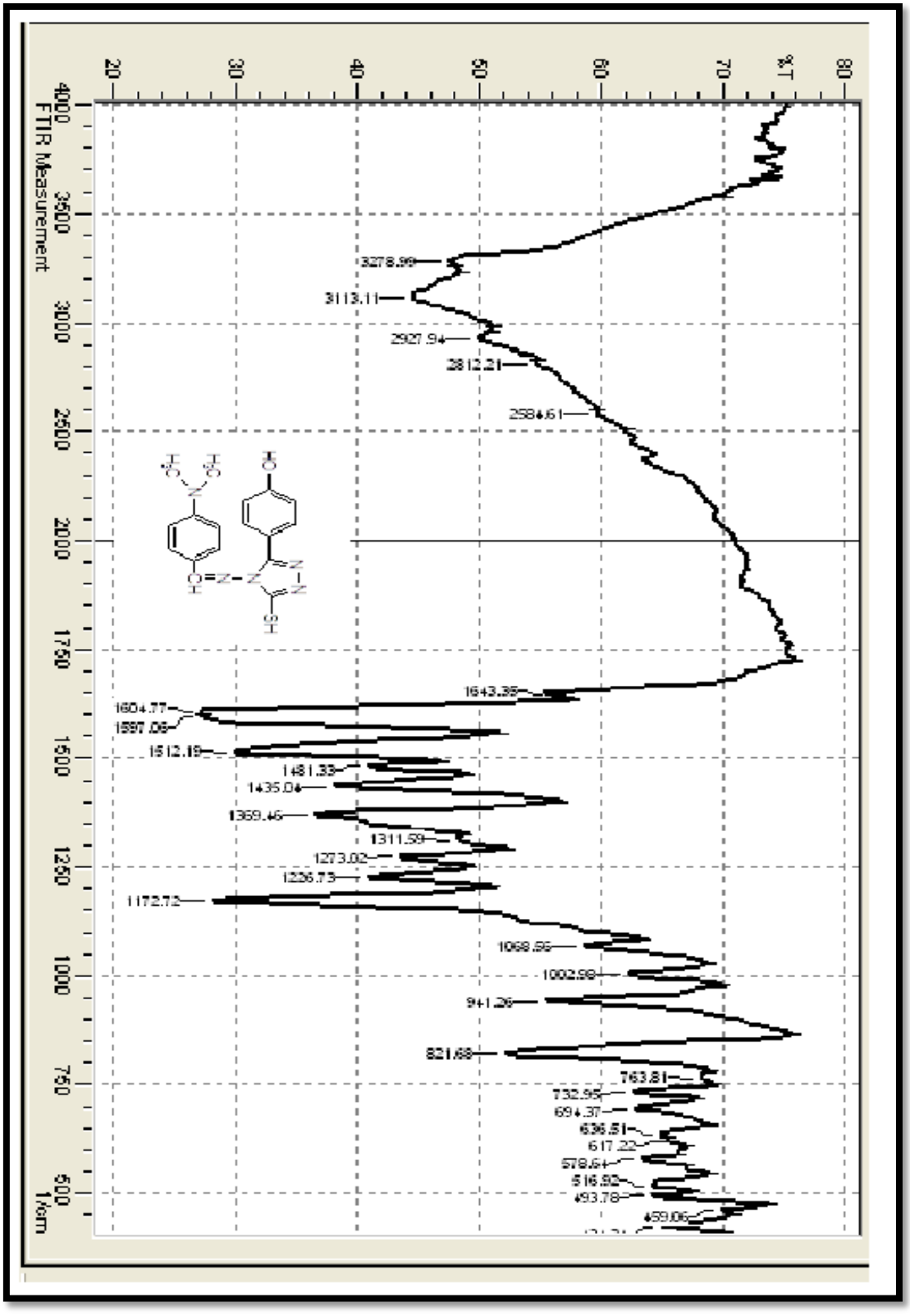
3i		3252 cm^{-1} for NH-tautomer, 3113 cm^{-1} for OH, 3051 cm^{-1} due to CH-aromatic, 2596 cm^{-1} due to S-H group,1612 cm^{-1} due to C=N group, 825 cm^{-1} for para-di substituted phenyl ring, and 497 cm^{-1} due to C-Cl.
3j		3302 cm^{-1} for OH, 3113 cm^{-1} for NH-tautomer, 3047 cm^{-1} due to CH-aromatic, 2997cm^{-1} due to C-H aliphatic, 2565 cm^{-1} belongs S-H group,1612 cm^{-1} due to C=N group.



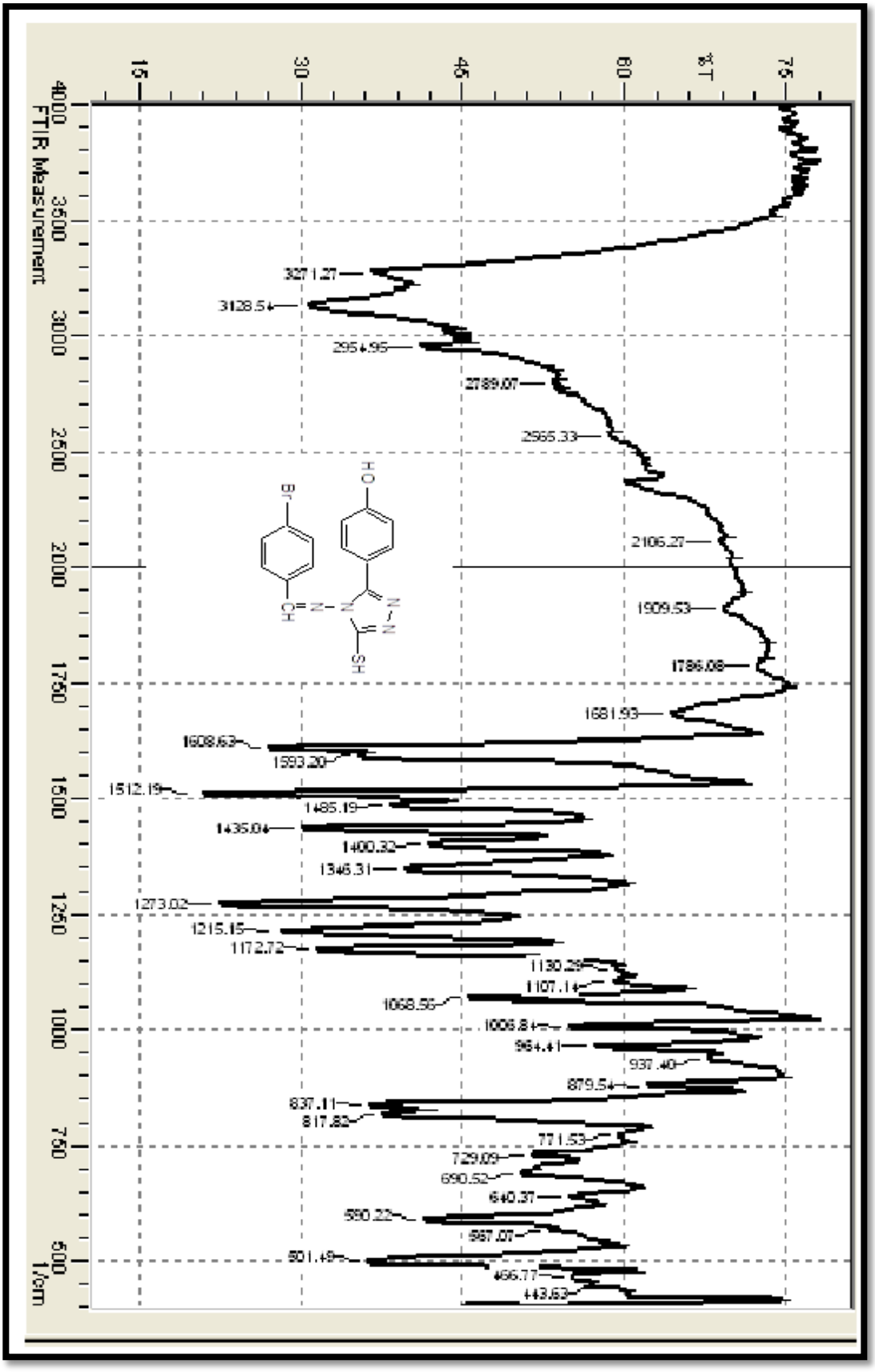
(3-5): FT-IR Spectrum of (3a).



(3-6): FT-IR Spectrum of (3b)



(3-7): FT-IR Spectrum of (3c)



(3-8): FT-IR Spectrum of (3d)

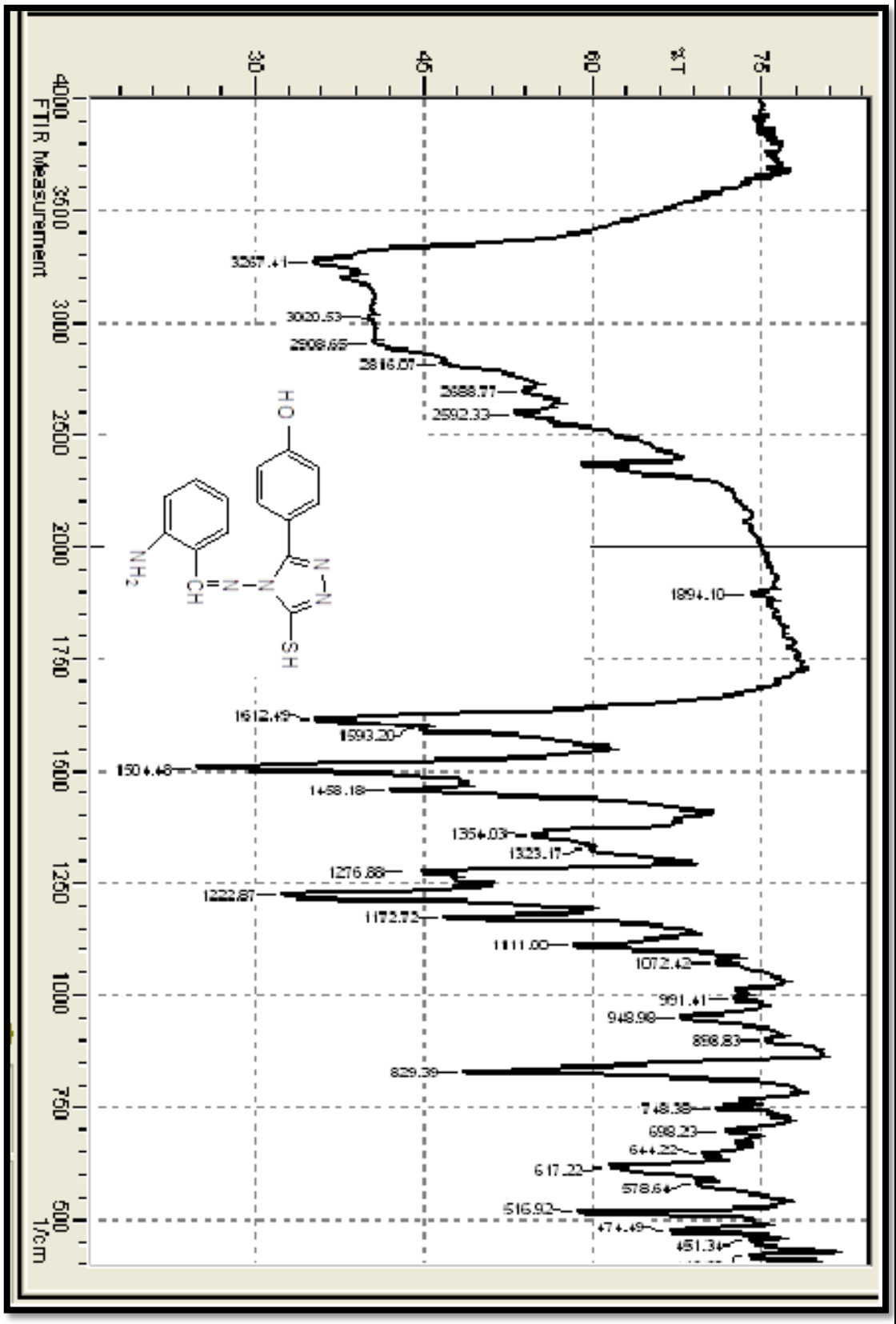
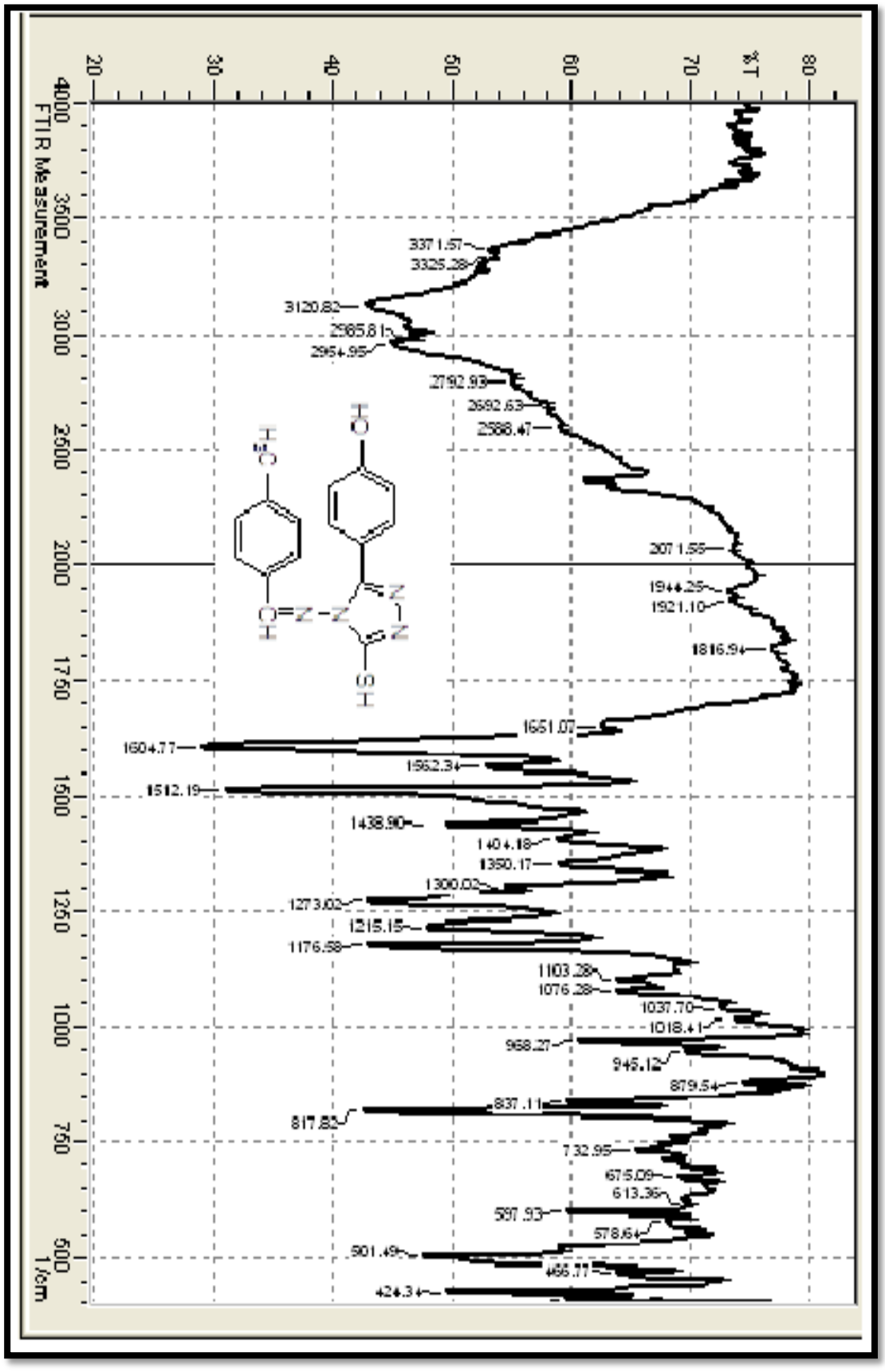


Figure (3-9): FT-IR Spectrum of (3e)



Figure(3-10): FT-IR Spectrum of (3f)

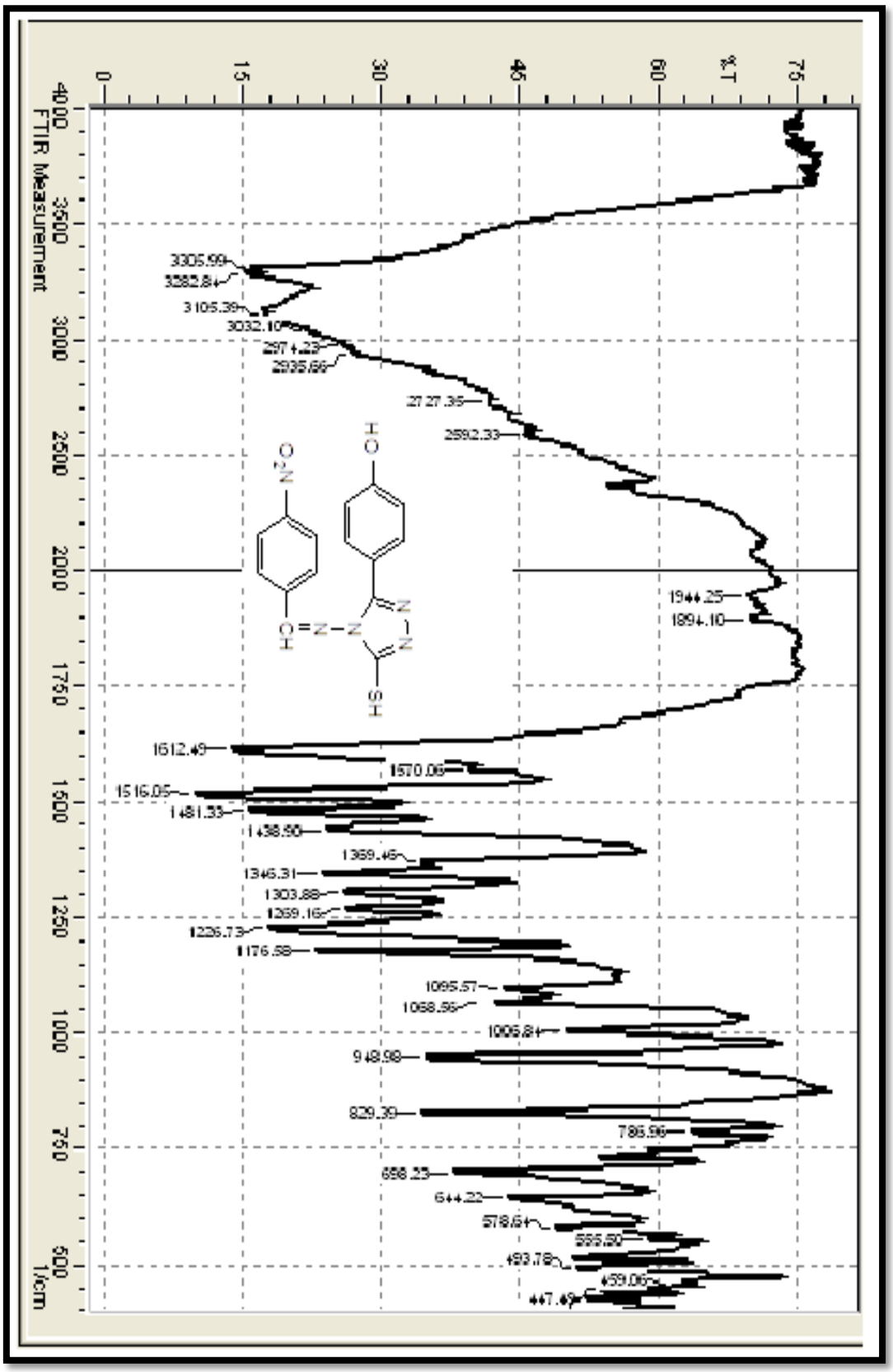


Figure (3-11): FT-IR Spectrum of (3g)

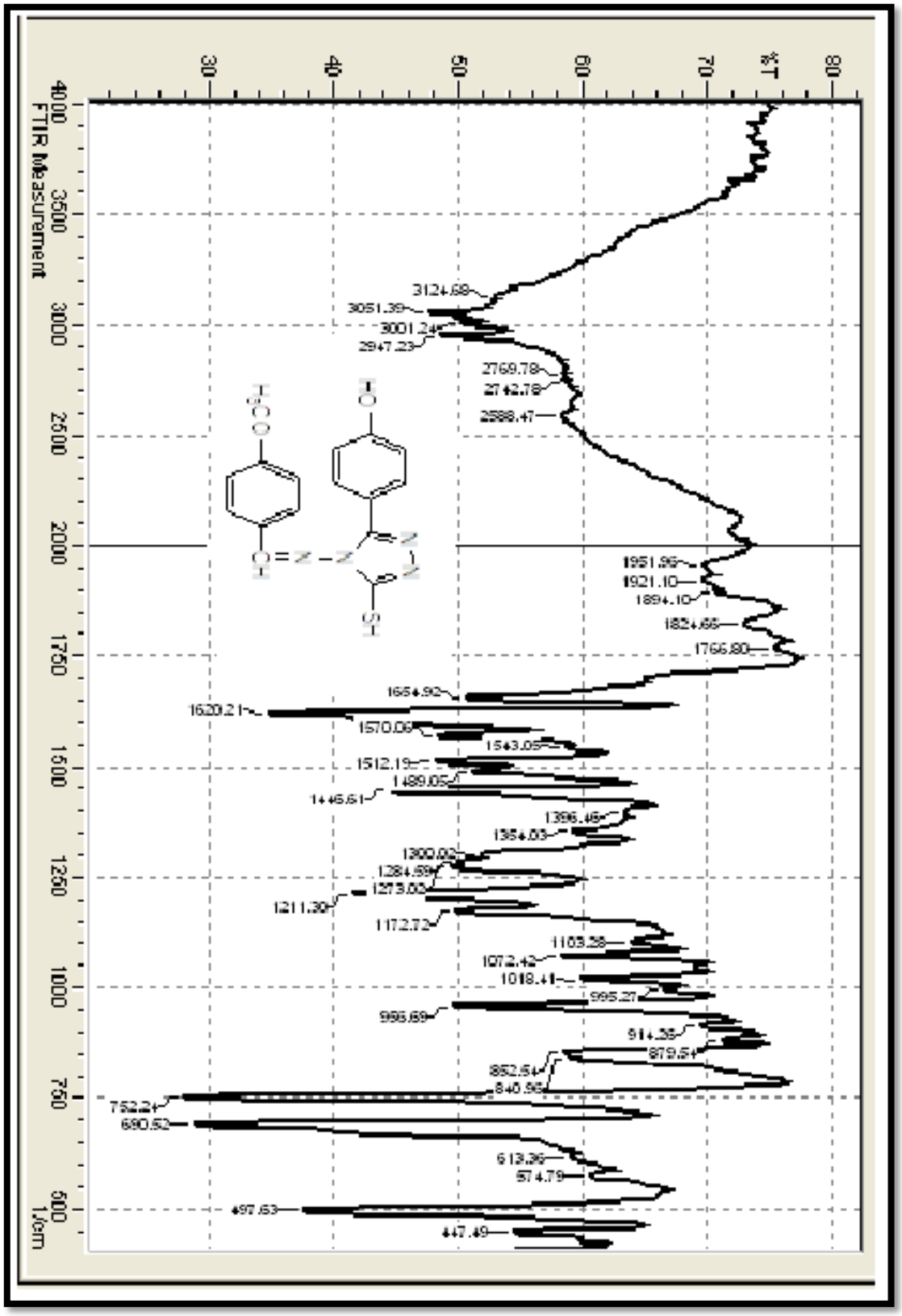


Figure (3-12): FT-IR Spectrum of (3h)

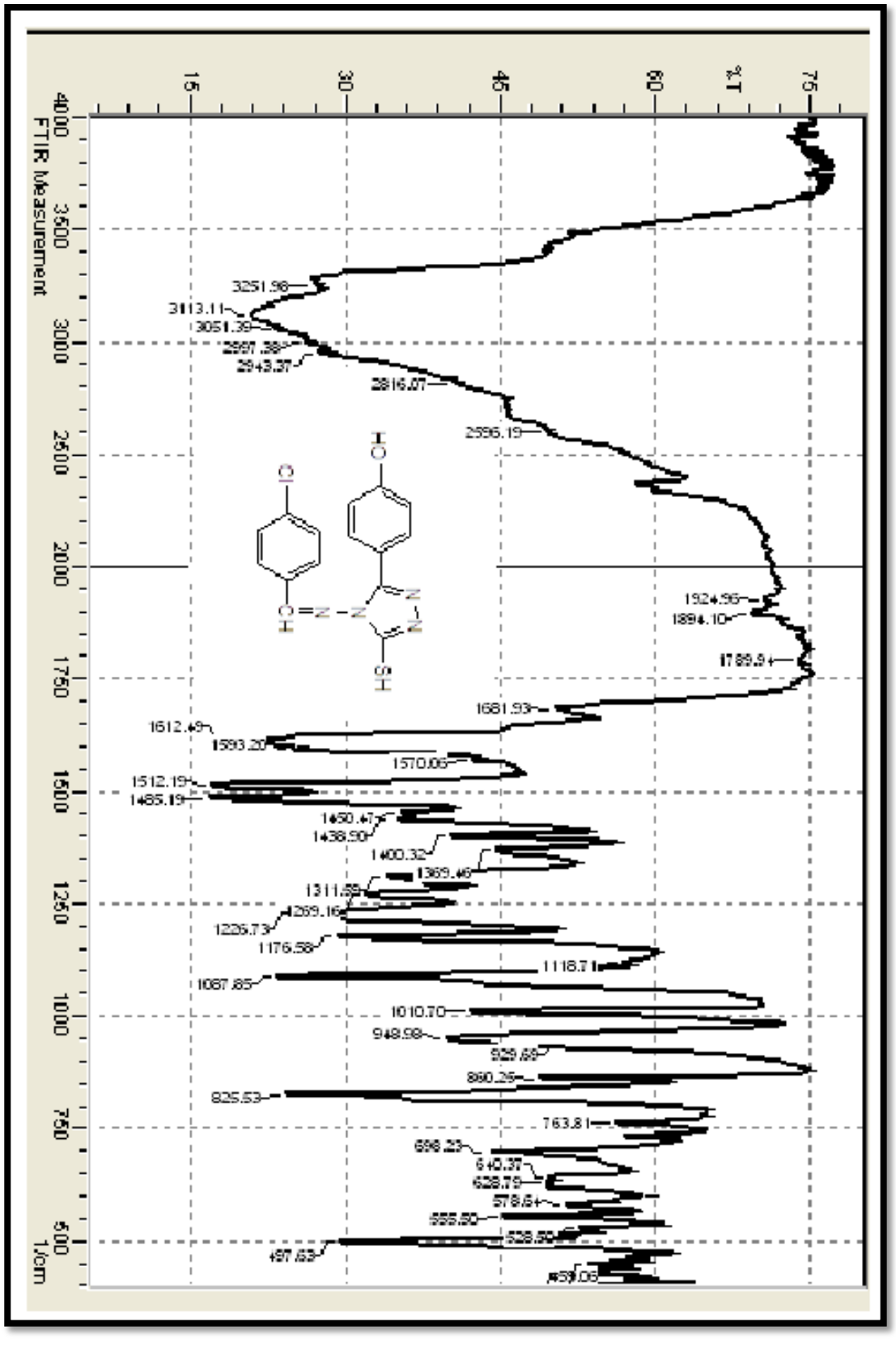


Figure (3-13): FT-IR Spectrum of (3i)

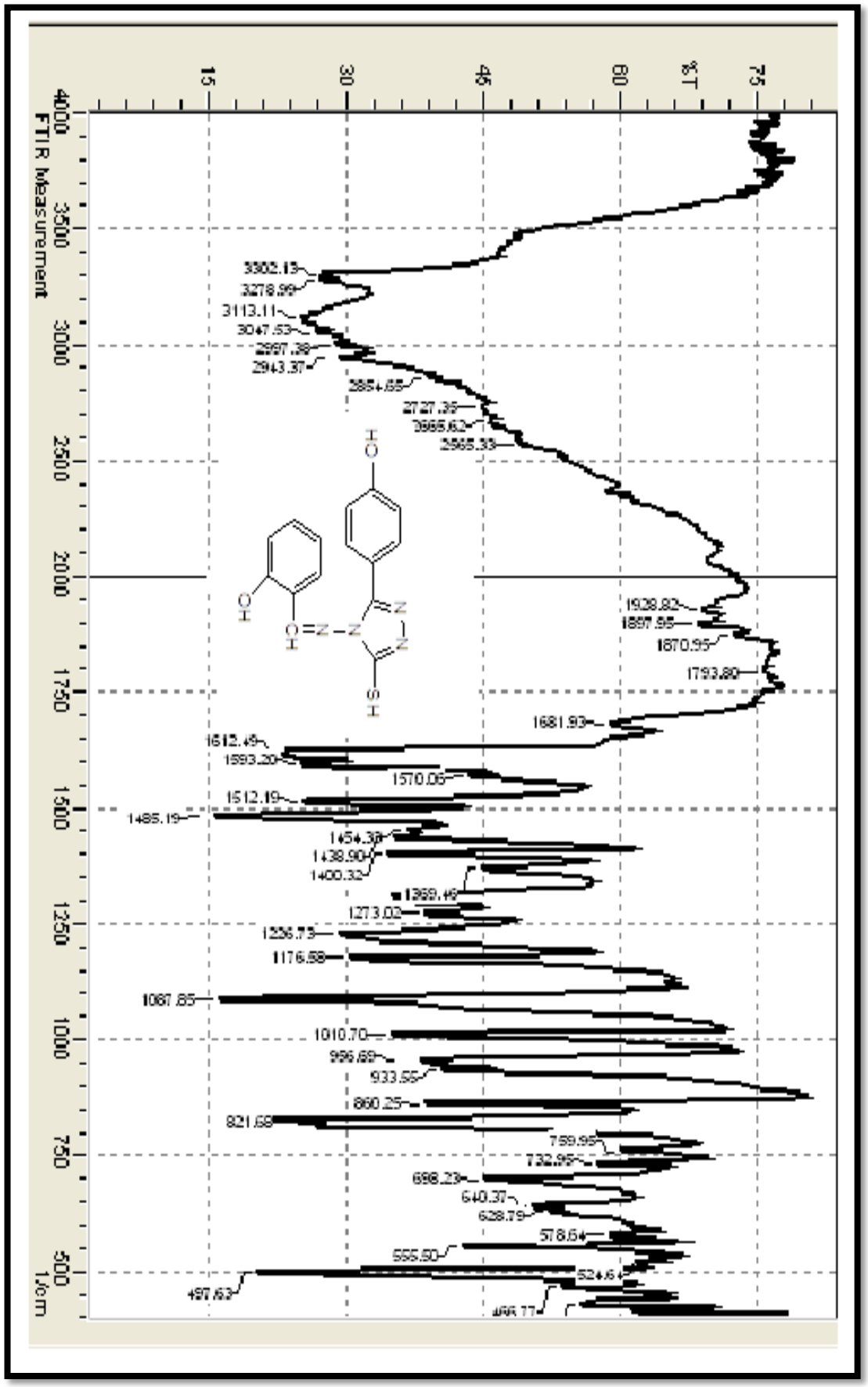
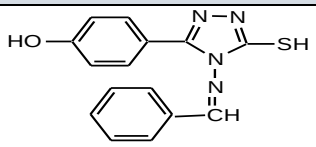
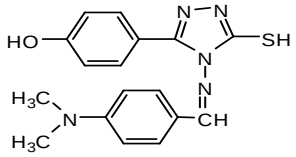
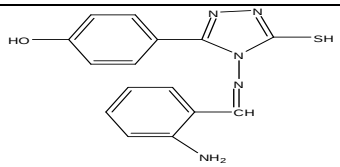


Figure (3-14): FT-IR Spectrum of (3j)

Table (3-2): ^{1}H NMR Spectroscopic detected of Prepared Schiff's Bases (3a, 3b and 3c)

No.	Structures of Compounds	^{1}H NMR Spectra (ppm)
3a		10.2 (1H, s, SH), 9.4(1H, s, OH), 8.8 (1H, s, CH=N),7.5-8 (9H, *m*, CH aromatic ring).
3b		13.92(1H, s, SH), 9.14(1H, s, OH), 8.80 (1H, s, CH=N) 6.78-8.13 (8H, *m*, CH aromatic ring), 3.15 (6H, *sex*, N $(CH_3)_2$.
3c		13.2 (1H,s, SH), 9.9(1H, s, OH), 8.5 (1H, s, CH=N), 7.9 (8H, *m*, CH aromatic ring), 6.8-5.9 (1H, s, NH2).

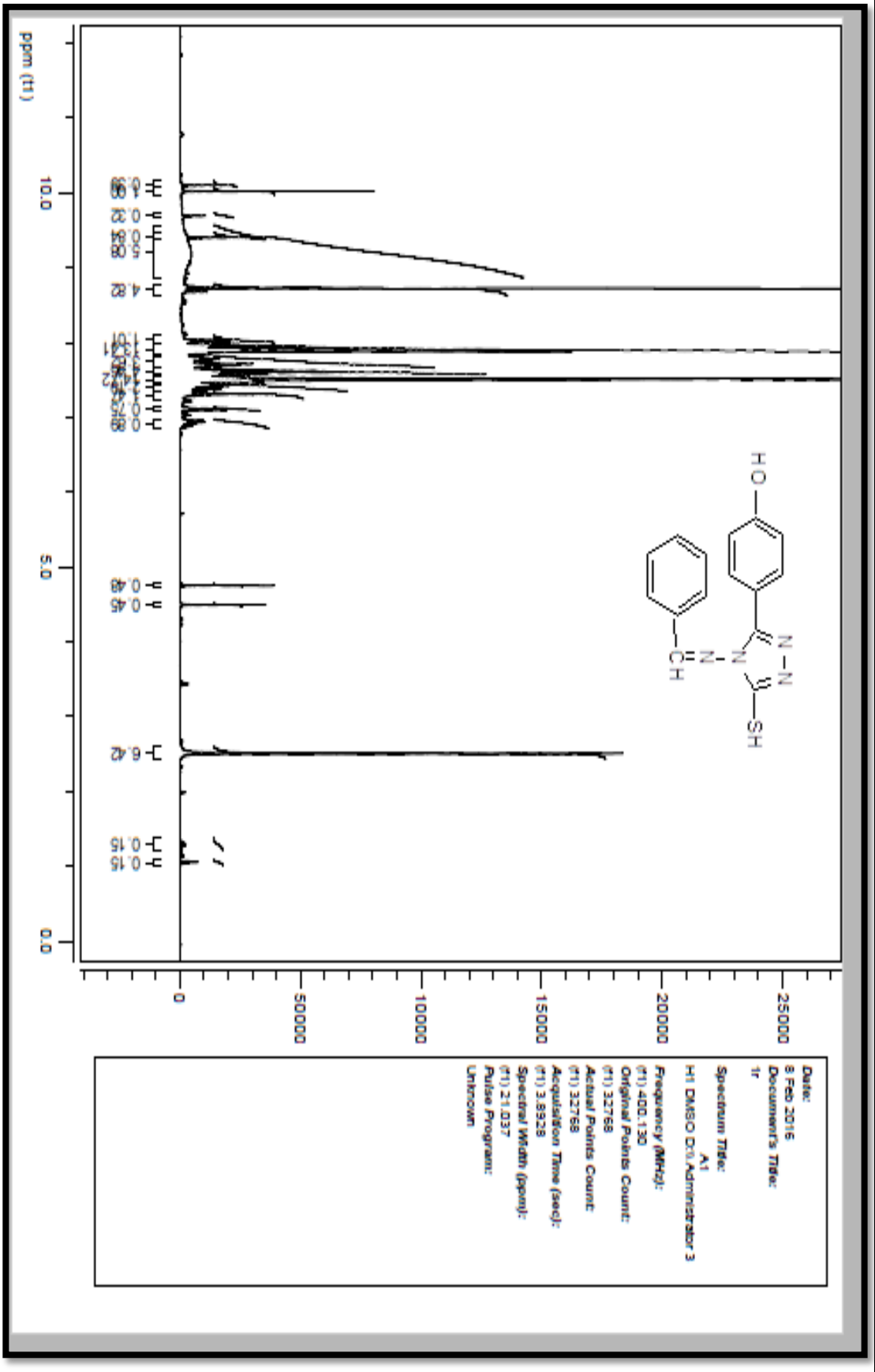


Figure (3-15): ^{1}H NMR Spectrum of (3a).

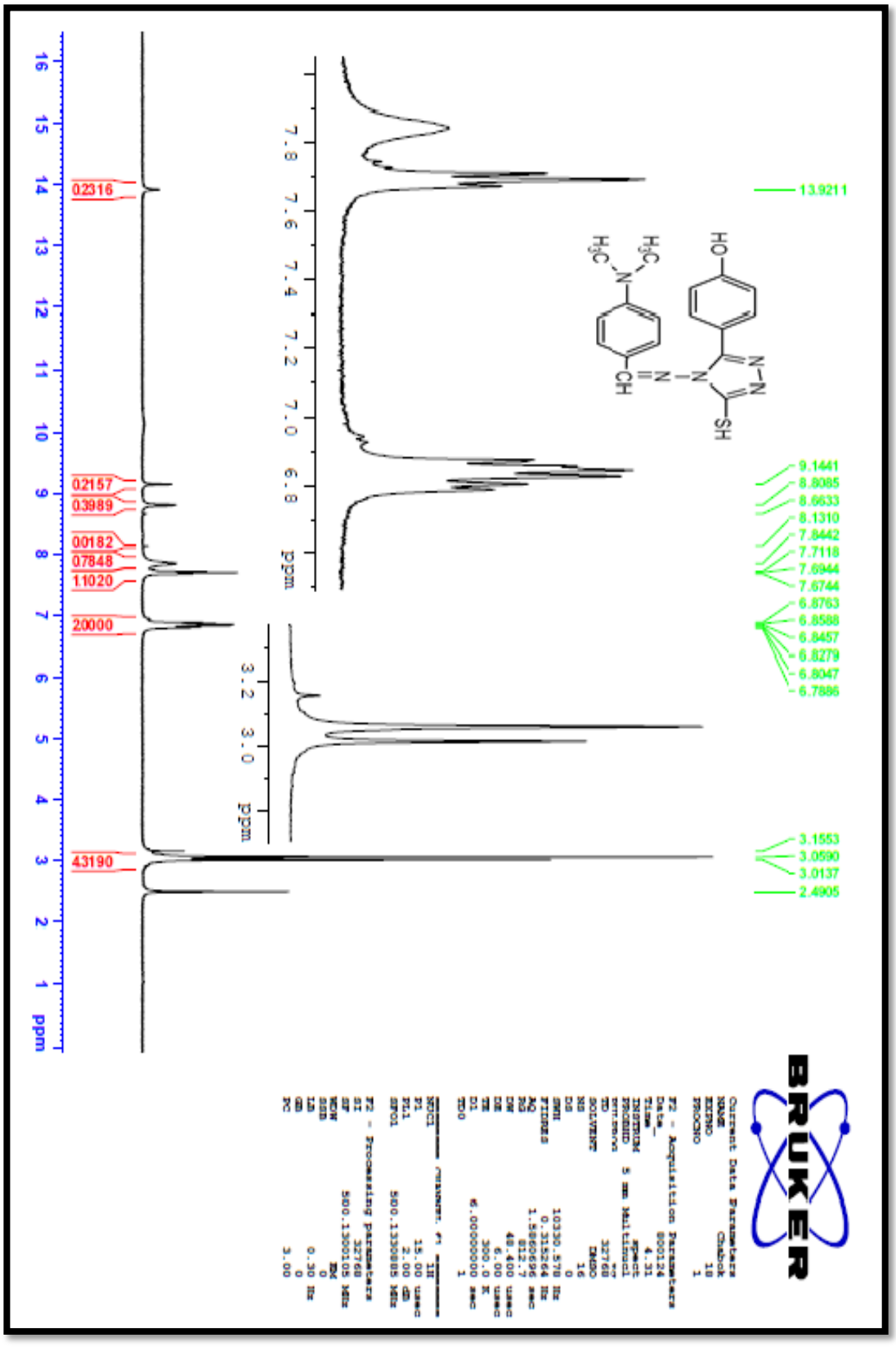


Figure (3-16): ^{1}H NMR Spectrum of (3b)

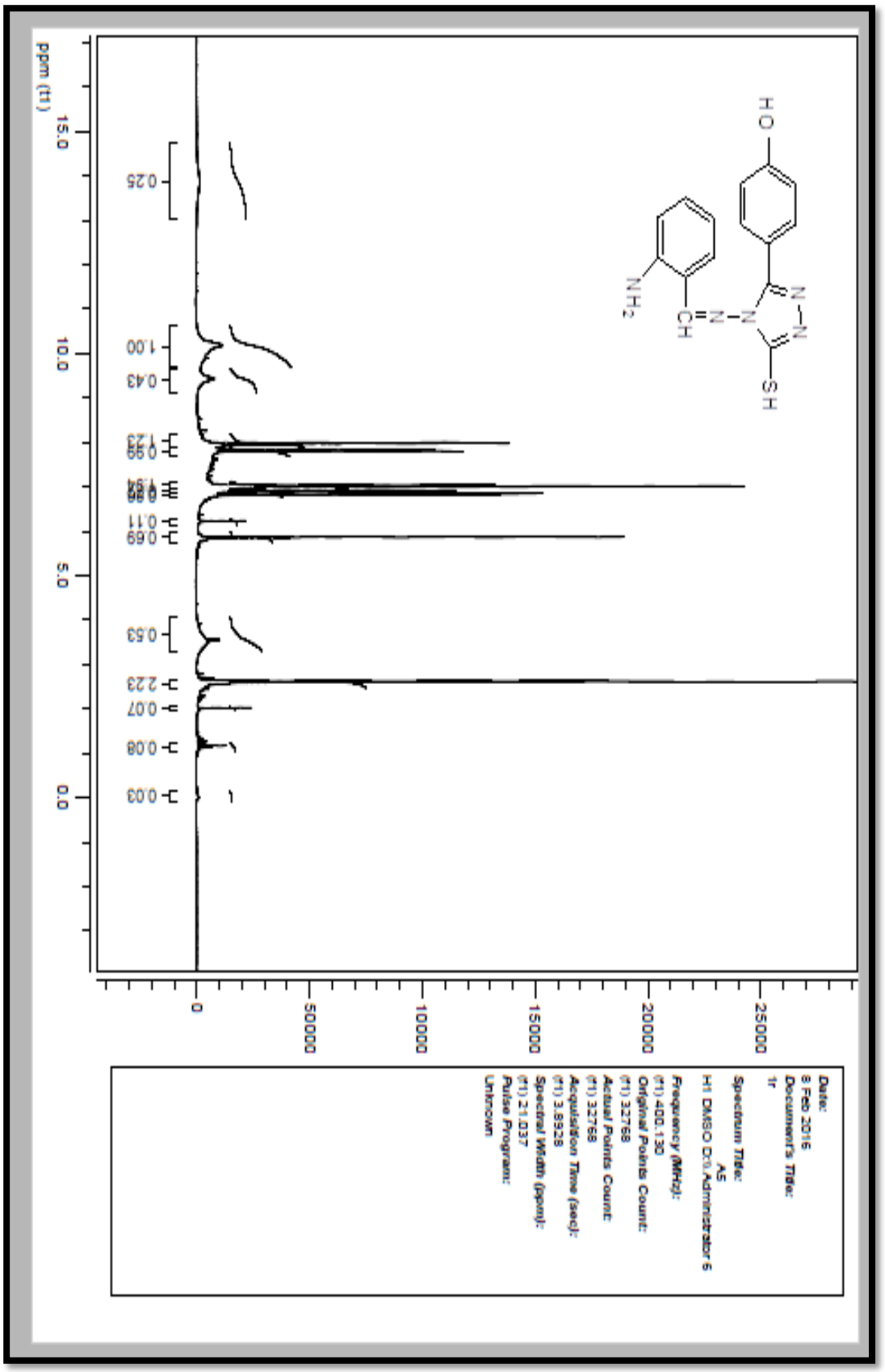


Figure (3-17): ^{1}H NMR Spectrum of (3c)

3.2 Corrosion inhibition study

The studied compounds are divided into two different groups in order to display the results more obvious. The results are illustrated in tables (3-4) and (3-5) figures (3-18), (3-19), (3-20), (3-21), (3-22) and (3-23).

The corrosion inhibition of the compounds **2** and **(3a-3j)** on mild steel was studied in 1M sulfuric acid solution. The inhibition results obtained from 8h immersion time of mild steel in 1M H_2SO_4 solution at 25 C^o with different inhibitor concentrations of compounds **2** and **(3a-3j).**

Generally, results show that as the inhibitor concentration increases, the corrosion rate decreases and therefore the inhibition efficiency increases. Corrosion inhibition results show that compounds 3b, 3d, 3e, 3f, 3h and 3j display the maximum inhibition efficiency IE % as shown in table (3-3).

Table (3-3): Synthesized compounds with the best inhibition efficiency IE % at the inhibitor concentration $5*10^{-5}$ M

Compound No.	3b	3d	3e	3F	3h	3j
Functional group ***R***	*p*-OH	*P*-Br	o-NH_2	*P*-CH_3	*P*-OCH_3	o-OH
IE %	83.66	87.58	82.58	78.43	77.12	72.55

These compounds which show the best IE % (from 72.55 % to 87.58 %) with very low inhibitor concentration $5*10^{-5}$ contain the hydroxyl, Bromo, amino, methyl, methoxy groups attached to benzene ring. All these groups except methyl group display at least one electron pair in the valence shell that can increase the electron density of the inhibitor molecule and therefore enhance the adsorption process on the metal surface. Other compounds displayed high inhibitor efficiency IE %, but they were not very effective like compounds 3c, 3d, 3e, 3f, 3H and 3j as seen in figures **(3-18), (3-19), (3-21), (3-22).** Inhibition efficiency of the

studied compounds can be explained by adsorption on mild steel surface and form a barrier layer between metal and the corrosive media [79].

In order to confirm the adsorption process of compound **2** and **(3a-3j)** on mild steel surface, adsorption isotherms were calculated. 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 = IE (%) /100, see Tables **(3-4)** and **(3-5)**] at 25 ^oC and tested graphically for fitting to a suitable adsorption isotherm. The plot of parameter (C/θ) against inhibitor concentration (C) yields a straight line Figures **(3-20)** and **(3-23)** The negative values of ΔG^o_{ads} as shown in Tables **(3-4)** and **(3-5)** indicate spontaneous adsorption of inhibitor molecules on the mild steel surface and a strong interaction between inhibitor molecules and metal surface. The value of ΔG^o_{ads} is less than -40 kJ/mole indicating electrostatic interaction between the charged metal surfaces is a physical adsorption [80].

Table (3-4): Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption for mild steel in 1M H_2SO_4 by using weight loss measurements for prepared inhibitors [2and (3a-3e)]

Inhibitor concentration (M)	1M H_2SO_4				
	ΔM (g)	Corrosion rate(mg cm^{-2} h^{-1}) W	IE %	θ	ΔG^{o}_{ads} (kJ/mol)
Blank	0.153	1.948	-	-	
2					
0.00005	0.128	1.629	16.34	0.1634	
0.0001	0.124	1.579	18.95	0.1895	-30.20
0.0005	0.105	1.337	31.37	0.3137	(R^2=0.972)
0.001	0.087	1.108	43.14	0.4314	
3a					
0.00005	0.085	1.082	44.44	0.4444	
0.0001	0.056	0.713	63.40	0.6340	-33.88
0.0005	0.007	0.089	95.42	0.9542	(R^2 =0.974)
0.001	0.006	0.076	96.08	0.9608	
3b					
0.00005	0.025	0.318	83.66	0.8366	-39.68
0.0001	0.012	0.153	92.16	0.9216	(R^2 =0.999)
0.0005	0.008	0.102	94.77	0.9477	
0.001	0.007	0.089	95.42	0.9542	
3c					
0.00005	0.102	1.298	33.33	0.3333	-37.37
0.0001	0.056	0.713	63.40	0.6340	(R^2=0.998)
0.0005	0.017	0.217	88.89	0.8889	
0.001	0.012	0.153	92.16	0.9216	
3d					
0.00005	0.019	0.242	87.58	0.8758	-34.61
0.0001	0.013	0.165	91.50	0.9150	(R^2=0.976)
0.0005	0.009	0.115	94.12	0.9412	
0.001	0.005	0.064	96.73	0.9673	

3e					
0.00005	0.019	0.242	82.58	0.8258	-39.68 (R^2 =0.999)
0.0001	0.017	0.218	88.89	0.8889	
0.0005	0.013	0.165	91.50	0.9150	
0.001	0.009	0.115	94.12	0.9412	

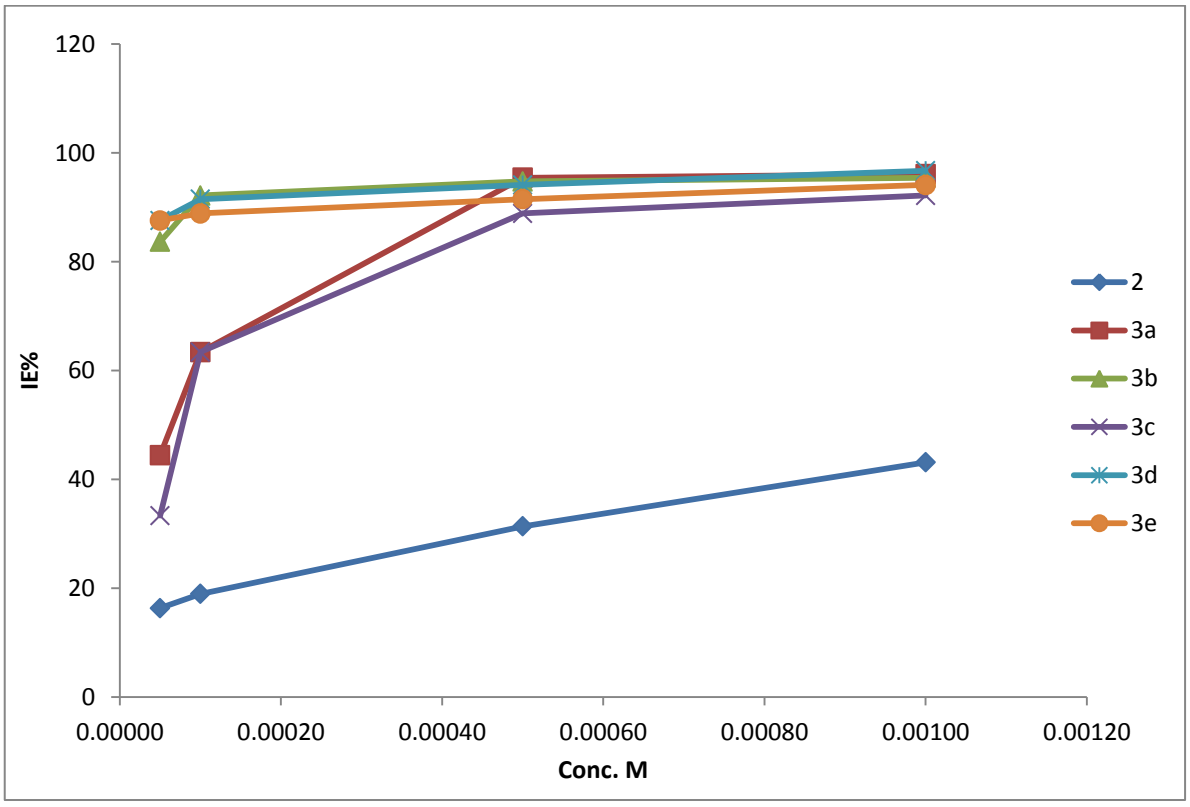


Figure (3-18): Effect of inhibitor concentration on the efficiencies of mild steel obtained at 25°C in 1M H_2SO_4 containing different concentrations of prepared inhibitors [2and (3a-3e)]

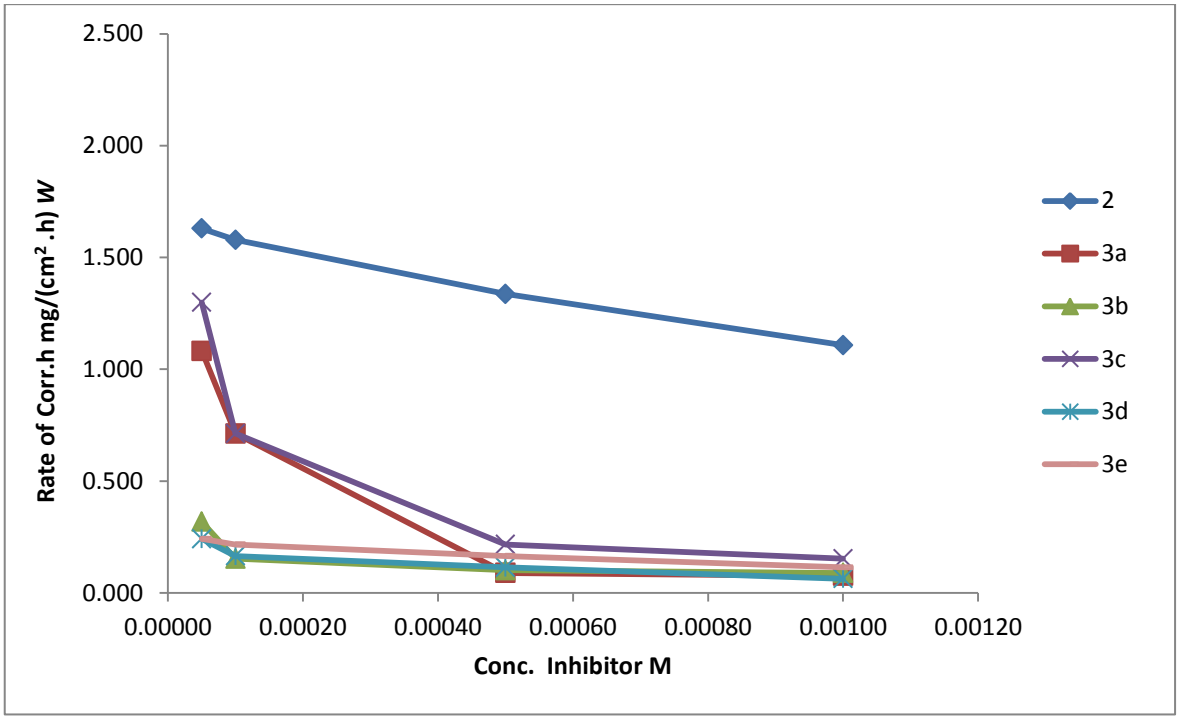


Figure (3-19): Effect of inhibitor concentrations on the rate of corrosion for mild steel 1M H_2SO_4 at 25°C for suggested inhibitors (2and (3a- 3e)].

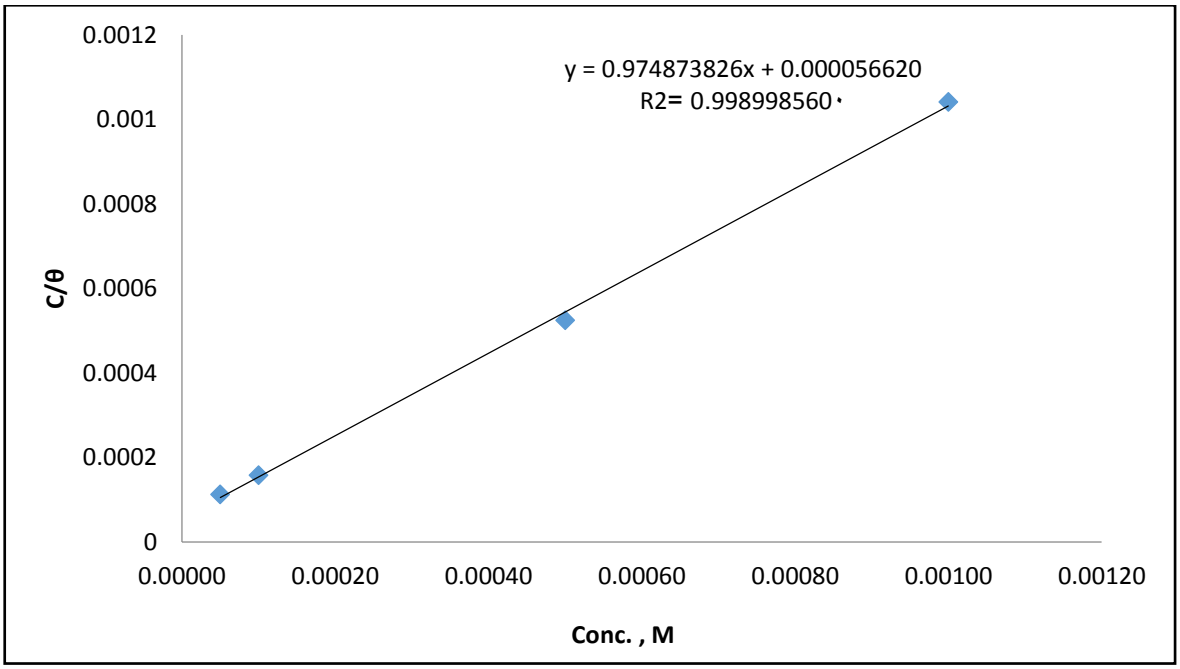


Figure (3-20): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (3a).

Table (3-5): Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption for mild steel in 1M H_2SO_4 by using weight loss measurements of compounds [2and (3f-3j)].

Inhibitor concentration (M)	1M H_2SO_4				
	ΔM (g)	Corrosion rate(mg cm^{-2} h^{-1}) *W*	IE%	θ	ΔG^{o}_{ads} (kJ/mol)
Blank	0.153	1.948	-	-	
2					
0.00005	0.128	1.629	16.34	0.1634	
0.0001	0.124	1.579	18.95	0.1895	-30.20 (R^2=0.972)
0.0005	0.105	1.337	31.37	0.3137	
0.001	0.087	1.108	43.14	0.4314	
3f					
0.00005	0.33	0.420	78.43	0.7843	
0.0001	0.021	0.267	86.27	0.8627	-35.07 (R^2=0.993)
0.0005	0.019	0.242	87.58	0.8758	
0.001	0.016	0.204	89.54	0.8954	
3g					
0.00005	0.092	1.171	39.87	0.3987	
0.0001	0.087	1.108	43.14	0.4314	-33.07 (R^2=0.999)
0.0005	0.054	0.607	64.71	0.6471	
0.001	0.034	0.433	77.78	0.7778	
3h					
0.00005	0.035	0.446	77.12	0.7712	-36.35 (R^2=0.997)
0.0001	0.028	0.356	81.70	0.8170	
0.0005	0.021	0.267	86.27	0.8627	
0.001	0.016	0.204	89.54	0.8954	
3i					
0.00005	0.062	0.789	59.49	0.5949	-35.63 (R^2 =0.997)
0.0001	0.055	0.700	64.06	0.6406	
0.0005	0.045	0.573	70.59	0.7059	

0.001	0.027	0.344	82.35	0.8235	
3j					-35.07 (R^2=0.993)
0.00005	0.042	0.535	72.55	0.7255	
0.0001	0.032	0.407	79.08	0.7908	
0.0005	0.011	0.140	92.81	0.9281	
0.001	0.009	0.115	94.12	0.9412	

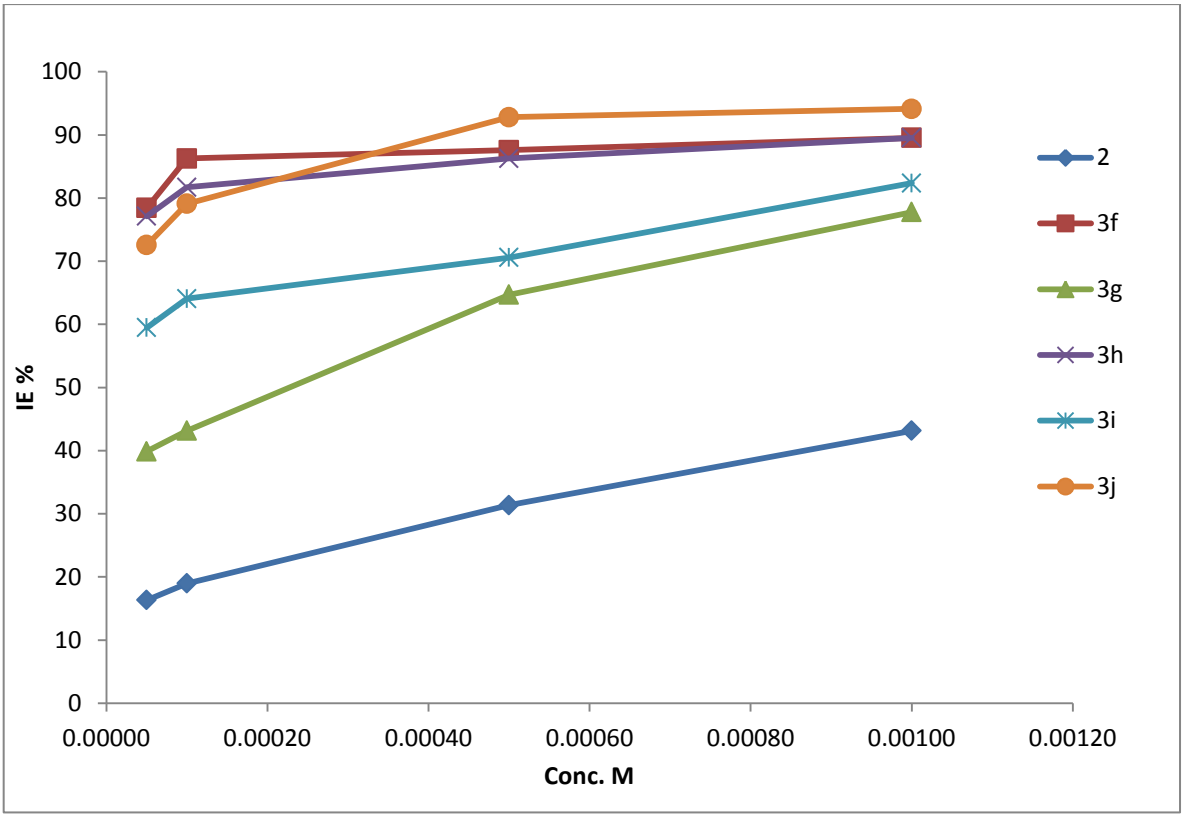


Figure (3-21): Effect of inhibitor concentration on the efficiencies of mild steel obtained at 25°C in 1 M H_2SO_4 containing different concentrations of prepared inhibitors [2 and (3f-3j].

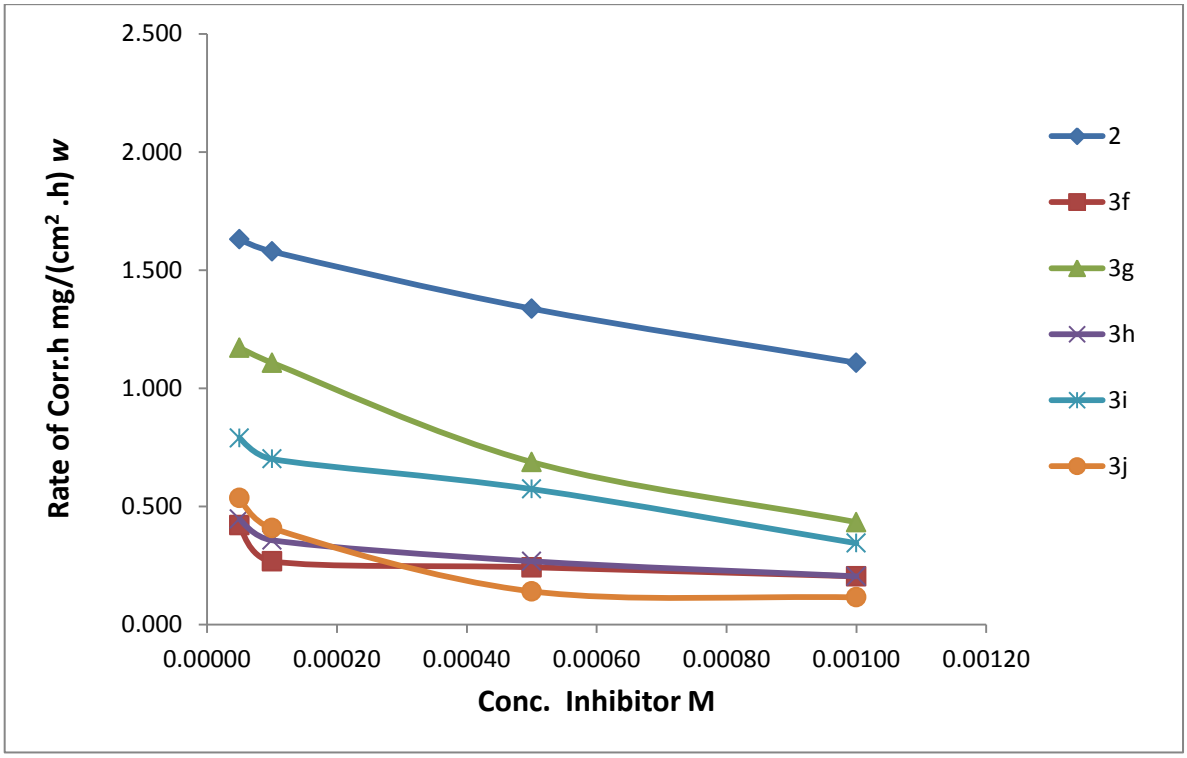


Figure (3-22): Effect of inhibitor concentrations on the rate of corrosion for mild steel 1M H_2SO_4 at 25°C for suggested inhibitors (2and (3f- 3j)].

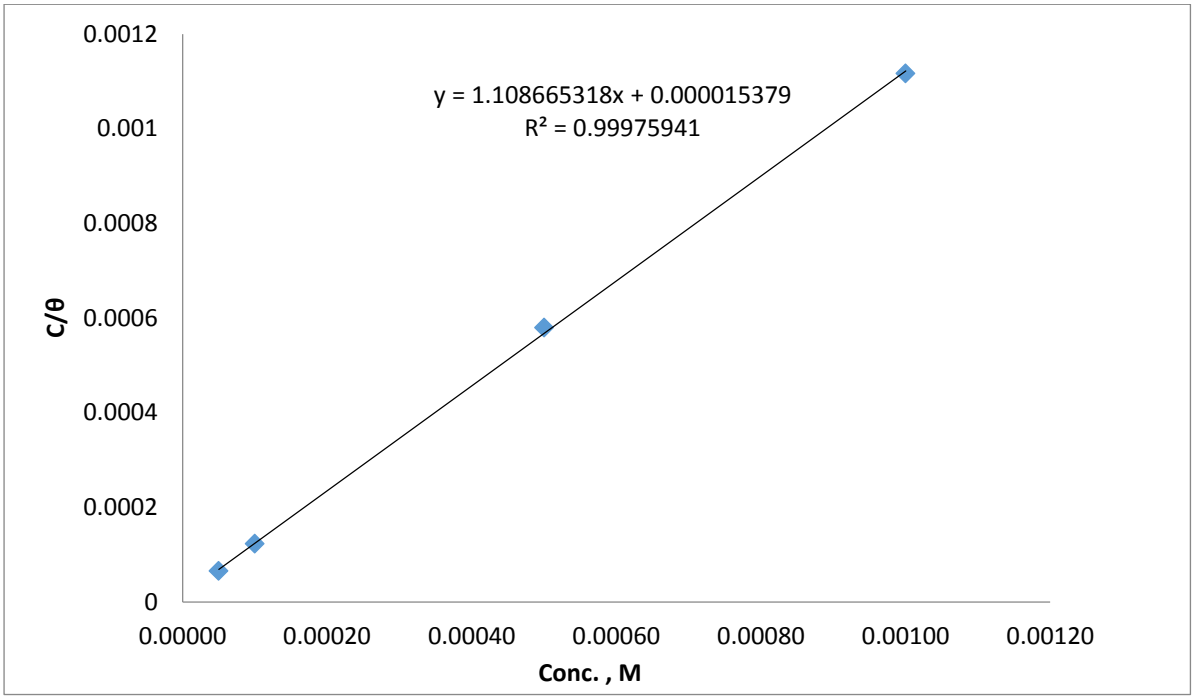


Figure (3-23): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (3h).

3.3 Conclusion

It can be concluded that most of the prepared compounds have the ability to be very effective corrosion inhibitor against mild steel, even in very low inhibitor concentration. Generally, the corrosion rates of the mild steel are gradually decrease as the inhibitor concentration increases, and therefore the inhibition efficiency IE% increases until it reaches the plateau phase. Results indicate that ring substitution in the designed compounds has a significant effect on the corrosion inhibition. Hetero atoms in the compound nucleus and as a part of substitution were indicated to have a significant role on the inhibition efficiency. Molecule planarity of the synthesized compounds may have the main driving force for the adsorption process on the metal surface.

3.4 Suggestions for Future Work

1. Synthesis of new 1,2,4-triazole-Schiff base derivatives with different aldehydes such as vanillin and furfuraldehyde and study their effects on corrosion inhibition or biological and enzymatic activities.

2. Synthesis of new heterocyclic compounds with fused ring starting from compound 3 as shown in the following scheme.

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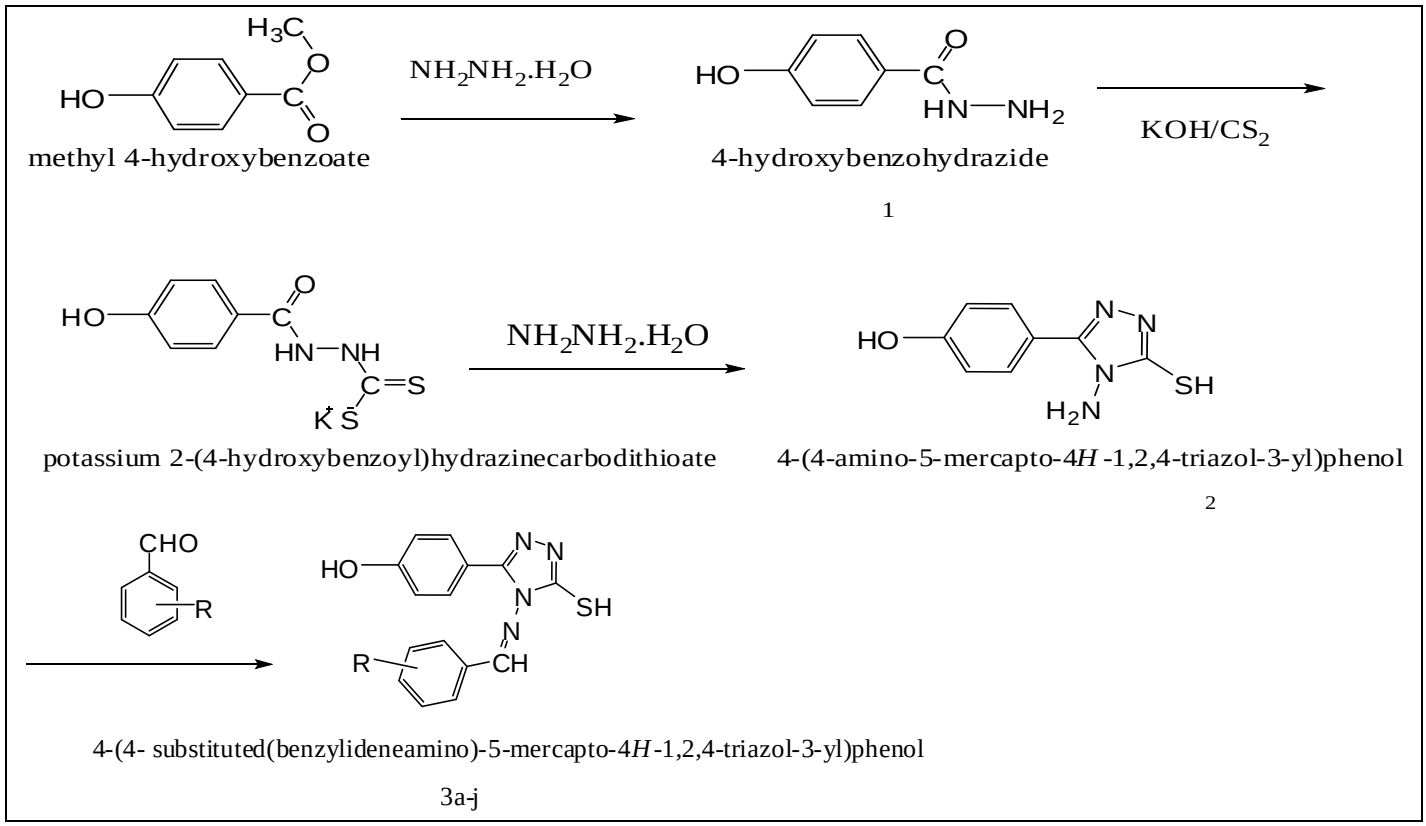
الملخص

تم تحضير قواعداشف جديدة **(3a-j)** تحتوي في تركيبها على حلقة (1,2,4- ترايزول) بدءاً من المركب (4)- (4- أمينو-5- ثايو1,2,4-4H- ترايزول-3- يل) فينول **(2)**، والمحضر بدوره من تفاعل الحولقة للمركب 4- هايدروكسي بنزوهايدرازايد **(1)**. تم تشخيص المركبات المحضرة الجديدة باستعمال طيف الأشعة تحت الحمراء FT-IR وبعض منها بطيف الرنين النووي المغناطيسي للبروتون ^{1}H NMR. اثبتت النتائج وجود حالة التوتومرزم (الثايول- ثايون).

الجزء الثاني من البحث يتضمن دراسة قابلية التثبيط للمركب (2) وللمركبات المحضرة اعلاه (3a-j) لتاكل الحديد المطاوع في محيط حامضي بتركيز واحد مولاري ودرجة حرارة 25 درجة مئوية.

استعملت طريقة نقصان الوزن لتقييم كفاءة تثبيط التأكل وقد بينت النتائج بان كفاءة التثبيط تزداد بزيادة تركيز المثبط. كما بينت النتائج ان المركبات (3b, 3d, 3e, 3f, 3h, and 3j) تمتلك طاقة تثبيط عالية تصل الى حوالي 87.8 % وبتراكيز قليلة جدا يبلغ $5*10^{-5}$ مولاري.

تعزى هذه النتائج الممتازة الى وجود مجاميع مرتبطة بحلقة البنزين المشتقة من البنزالديهايد الداخل والتي غالبا ما تكون فيها ذرات غير متجانسة، فضلا عن كون الشكل الهندسي المستوي للجزيئات المحضرة مما يسهل عملية امدصاصها على سطح المعدن.



Scheme (3-1): Synthetic pathway for compounds [1-3(a-j)], where R = H, *p*-OH, *p*- $(CH_3)_2N$, *p*-Br, *o*-NH_2), *p*-CH_3, *p*-NO_2, *p*-OCH_3, *p*-Cl, *o*-OH respectively.

جمـــــــــــــــــــهورية العراق
وزارة التعليم العالي والبحث العلمي
جامعـــــــــــــــــة النهريـــــــن
كليـــــــــــــــــة العـــــــــلوم
قـــــــــــــــــسم الكيميـــــــــاء

تحضير ودراسة تثبيط التأكل لبعض المركبات الحلقية غير المتجانسة

رسالة

مقدمة الى كلية العلوم/ جامعة النهرين
كجزء من متطلبات نيل درجة الماجستير في علوم الكيمياء

من قبل

سجى صبحي عبود

بكالوريوس علوم كيمياء / كلية العلوم للبنات / جامعة بغداد / ٢٠١٣

بإشراف

أ .م. د جواد كاظم شنين

رمضان ١٤٣٧هـ **حزيران٢٠١٦ م**