Republic of Iraq
Ministry of Higher Education
& Scientific Research
Al-Nahrain University
College of Science
Department of Chemistry

Synthesis of some N-pyridinium salt derivatives as corrosion inhibitors for mild steel in sulfuric acid

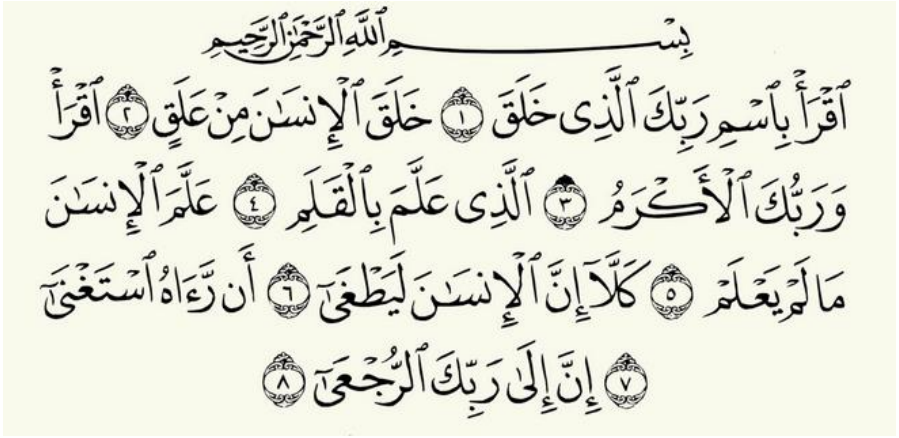
A Thesis Submitted to the College of Science of Al-Nahrain University in Partial Fulfillment of the Requirements for the Degree of Master in Chemistry

By

Ahmed Imad Jawad
B.Sc. 2014
(AL-Nahrain University)

Supervised By
Professor Dr. Mehdi S. Shihab

Jan. 2017 **Rabia-Althani 1438**



صدق الله العظيم

سورة العلق (الاية١ – ٨)

Supervisor Certification

I certify that this thesis entitled **"Synthesis of some N-pyridinium salt derivatives as corrosion inhibitors for mild steel in sulfuric acid"** was prepared by **Ahmed Imad Jawad** under my Supervision in the Department of Chemistry, College of Science, Al-Nahrain University as partial requirements for the degree of Master of Science in Chemistry.

Signature:
Name: **Dr. Mehdi S. Shihab**
Title: Professor
Address: College of Science Al-Nahrain University
Data: / / 201

In view of the available recommendation, I forward this thesis for debate by the Examining Committee.

Signature:
Professor
Dr. Emad Al-Sarraj
Head of the Department of Chemistry
College of Science
Al-Nahrain University

Committee Certification

We, the examining committee, certify that we have read this thesis entitled **"Synthesis of some N-pyridinium salt derivatives as corrosion inhibitors for mild steel in sulfuric acid"** prepared by Ahmed Imad Jawad, in content and that, in our opinion it is adequate as as thesis for the degree of Master of Science, in Chemistry.

Signature:
Name: **Dr. Ahmed A. Al-Amiery**
Scientific Degree: Professor
Date: / / 2017
(Chairman)

Signature:
Name: **Dr. Ali J. Hussein**
Scientific Degree: Assistant Professor
Date: / / 2017
(Member)

Signature:
Name: **Dr. Nasreen R. Jber**
Scientific Degree: Assistant Professor
Date: / / 2017
(Member)

Signature:
Name: **Dr. Mehdi S. Shihab**
Scientific Degree: Professor
Date: / / 2017
(Member /Supervisor)

I, hereby certify upon the decision of the examining committee.

Signature:
Name: **Dr. Hadi M. A. Abood**
Scientific Degree: Professor
Dean of the College of Science
Date: / / 2017

Dedication

To all those who lost their lives for the Sake of Science .

Ahmed I. Jawad

Acknowledgement

I am very blessed to have such a **family** that supported me and giving me all the cheer that I need to do my best

You are the most precious thing in my life.

I am very thankful and grateful to my supervisor

Prof. Dr. **Mehdi S. Shihab** first of all for his patient, continuous encouragement, advice, discussion and suggestions throughout my study.

I am very thankful to Dr. **Nasreen R. Jber**,

for being our friend and mentor in this journey for more than Six years .

To my shadows who had always been there for me

Jarjees , Yasir , Donya .

A Big thanks to all my colleague mostly for being there to support each other specially **Areej** and **Dina.**

We gratefully acknowledged the funding from the Chemistry Department in College of Science- Al-Nahrain University.

Contents

Chapter one : Introduction

Chapter two : Experimental part

Chapter three : Results & Discussion

List of Tables

List of Figures

List of Schemes

List of Abbreviations

FTIR	Fourier Transform Infrared
^{1}H-NMR	Proton Nuclear Magnetic Resonance
m.p.	Melting Point
W	Corrosion Rate
ΔM	Mass Loss
S	Area
Com.	Compound
No.	Number
T	Immersion period
E%	Percentage Inhibition Efficiency
Θ	Degree of Surface Coverage
K_{ads}	Equilibrium Constant of the Adsorption/ Desorption process
C	Inhibitor Concentration (M) in the test solution
ΔG^{0}_{ads}	Standard Free Energy of Adsorption
ASTM	American Society for Testing and Materials
Ph	Aromatic
DMSO-d6	Dimethylsluphoxide-six detrium
hr	hours
min.	minutes
M	Molarity
Sy.	symmetrical
Asy,	asymmetrical
DCM	Dichloro methane
W_o	Corrosion Rate uninhibited
W_i	Corrosion Rate inhibited

Summary

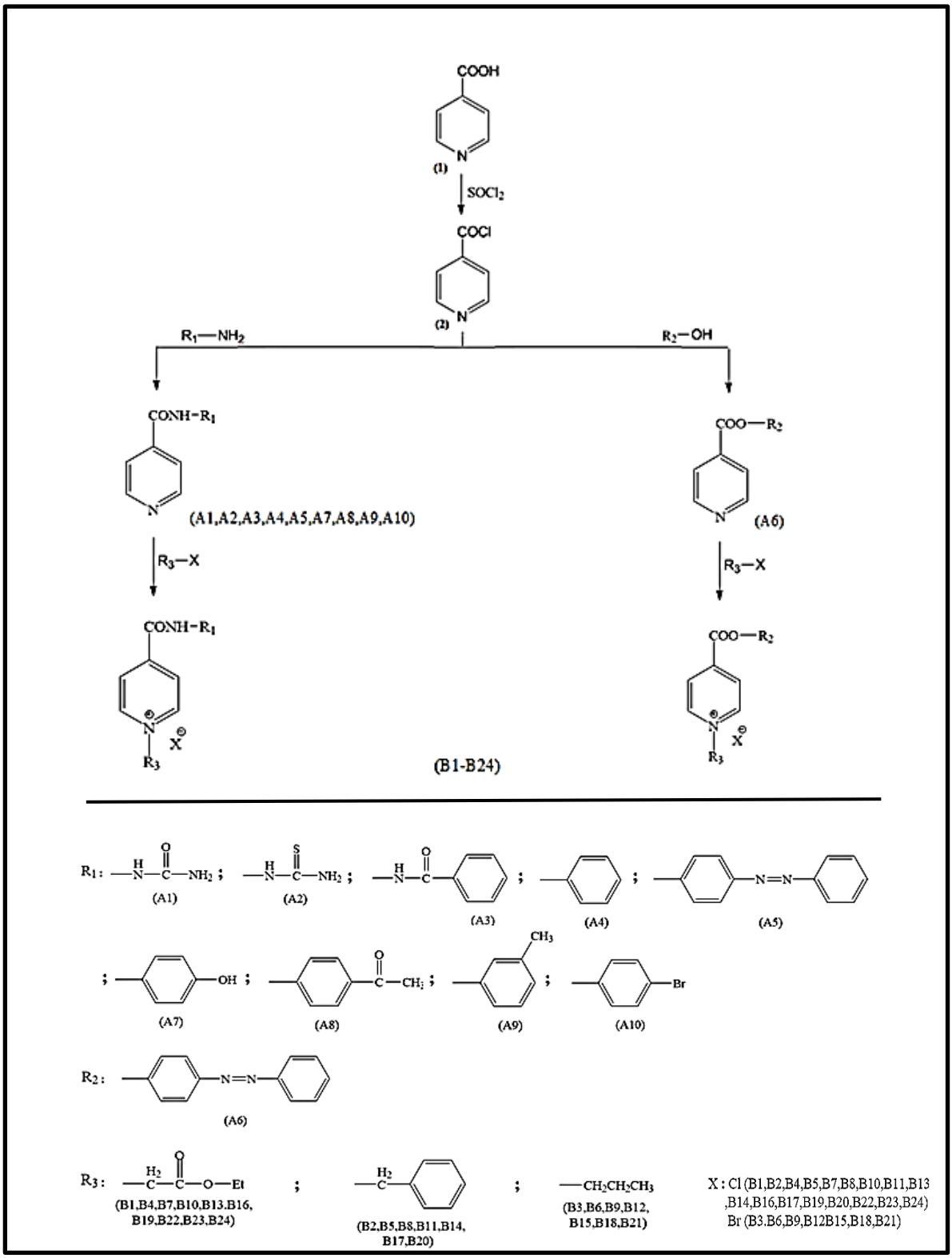
This study involves the preparations of some pyridine derivatives starting from Isonicotinic acid (1) following these steps :

First : The Synthesis of Isonicotinoyl acid chloride (2) by The reaction of Isonicotinic acid (1) and thionylchloride .

Second : The Synthesis of some amide and ester derivatives by reaction between Isonicotinoyl acid chloride (2) and substituent amine or phenol derivatives (Semicarbazide, Thiosemicarbazide, Benzohydrazide, Aniline, 4-phenylazoaniline, 4-phenylazophenol, p-Aminophenol, p-Aminoacetophenone, m-Toluidine, 4-Bromoaniline) that yielded these compounds (A1-A10) .

Third : The Synthesis of some pyridinium salt derivatives by The reaction of (A1-A10) and alkyl halides (ethyl chloroacetate,n-propyl bromide, benzyl chloride), that yielded these compounds (B1-B24) .

All The prepared structure compounds were confirmed using spectroscopic techniques (FTIR & ^{1}HNMR). Prepared compounds (B1-B24) were successfully applied as organic corrosion inhibitors for mild steel in 1M H_2SO_4 solution at 30°C by using weight loss method after 24 hours immersion. The results of weight loss measurements showed that corrosion inhibition efficiency increased by increasing the concentration of organic inhibitors for mild steel in 1M H_2SO_4 solution at 30°C.



Scheme 3-1: The chemical steps for the synthesis of compounds (B1-B24).

Chapter One

Introduction

1. Introduction

1.1. Characteristics of some pyridine derivatives

Isonicotinic acid or 4-carboxypyridine is The organic compound with the formula ($C_6H_5NO_2$). This compound was derivated from pyridine and a substituent of carboxylic group at the 4-position. Isonicotinic acid is soluble in methanol, ethanol, 1-propanol, 2-propanol, and 1,2-propanediol at (17 – 86 ^oC) [1] . The structure of isonicotinic acid has a structure of pyridine ring (see Figure 1-1) that is like benzene ring, with replacement of CH by N atom. Pyridine ring is not regular hexagonal geometry caused by the presence of the heteroatom, with short carbon – nitrogen bonds, with replacement of a hydrogen in the plane of the ring with an unshared electron pair, which is responsible for the basic properties of pyridines, and this ring has a strong permanent dipole, due to greater electronegativity of nitrogen compared with carbon [2] .

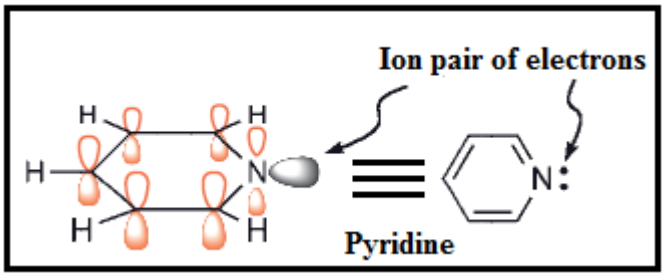


Figure 1-1: Pyridine ring.

Pyridine is nucleophilic at the nitrogen atom because the electrons pair on nitrogen atom can not be delocalized around the ring. It is weakly base, and with hydrochloric acid it forms a crystalline pyridinium hydrochloride salt by protonation reaction under mild conditions, which is the simplest being 1*H* – pyridinium formed by addition of a proton (see Figure 1-2).

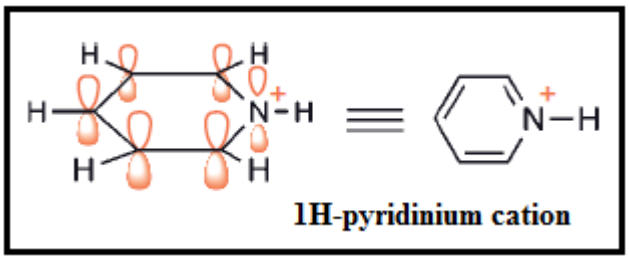
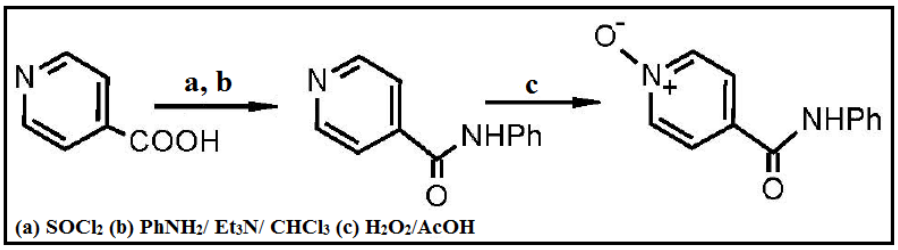


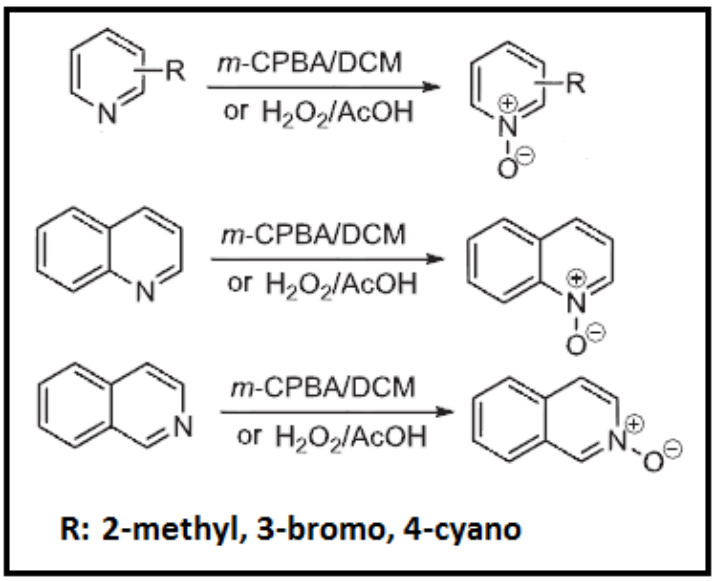
Figure 1-2: 1H-pyridinium ion

As well as pyridine, isonicotinic acid has been oxidized by oxidative agent to obtain isonicotic N-oxide through intermediate of isonicotinanilide N-oxide (see Scheme 1-1) [3] .



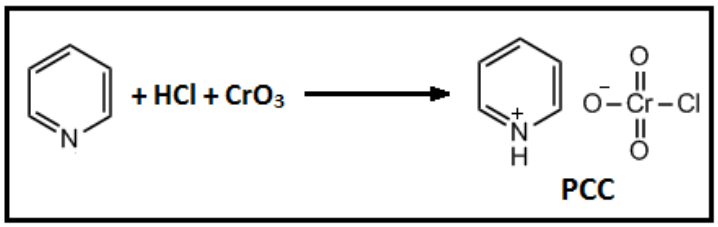
Scheme 1-1: isonicotinanilide N-oxide.

Vörös et al [4], reported that N-oxidations of different nitrogen-containing heterocyclic molecules (of different pyridine derivative, quinoline and isoquinoline) were applied using two popular oxidizing reagents (*m*-CPBA (*m*-chloroperoxybenzoic acid) in DCM or with aqueous H_2O_2 in acetic acid) (see Scheme 1-2).



Scheme 1-2 pyridine derivative

Pyridinium chlorochromate (PCC) (see Scheme 1-3) is a yellow-orange salt with the formula $[C_5H_5NH][CrO_3Cl]$. It is a good catalyst in the preparative organic reactions used primarily for oxidation of alcohols to form carbonyls [5]. PCC consists of a pyridinium cation, $[C_5H_5NH]^+$, and a tetrahedral chlorochromate anion, $[CrO_3Cl]^-$. Related salts are also known, such as 1-butylpyridinium chlorochromate, $[C_5H_5N(C_4H_9)][CrO_3Cl]$. The reagent was originally prepared via addition of pyridine into a cold solution of chromium trioxide in concentrated hydrochloric acid [6] .



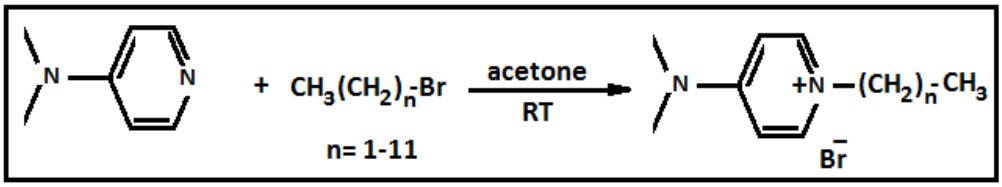
Scheme 1-3: Pyridinium chlorochromate (PCC).

Some applications of pyridinium salts derivatives:

1-Alkyl-4-(N,N-dimethylamino)pyridinium halides are a class of pyridinium salts that have found many applications such as phase-transfer catalysts in

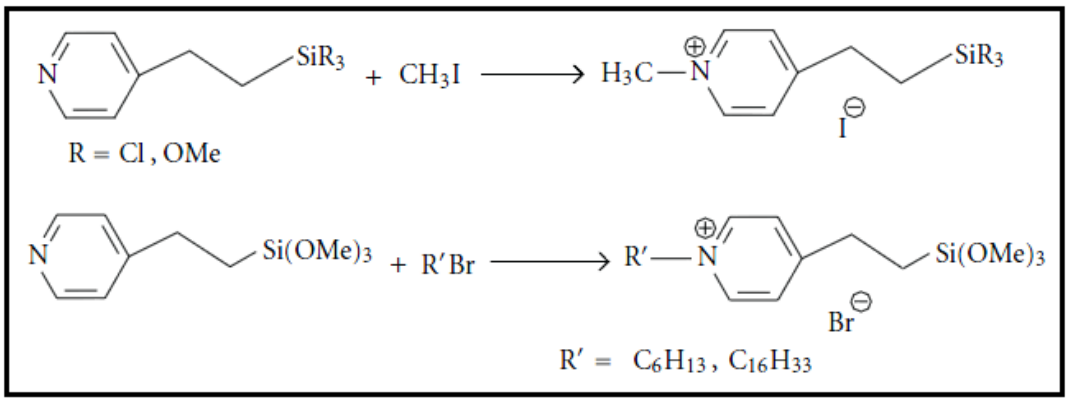
organic transformations [7], surfactants [8], liquid crystal display mediums[9], ionic crystals for second-order non-linear optics [10], ionic liquids[11] and additives for protein refolding processes [12].

Methods for the preparation of some 1-alkyl-(N,Ndimethylamino) pyridinium bromides via a quaternization reaction of the alkyl halide with 4-dimethylaminopyridine in solvents such as 2-propanol, dioxane and acetone. A homologous series of 1-alkyl-(N,N-dimethylamino)pyridinium bromides, termed compounds 1–11, was synthesized and studied for antibacterial and antifungal activity (see Scheme 1-4) [13].



Scheme 1-4: 1-Alkyl-4-(N,N-dimethylamino)pyridinium

Synthetic route to potentially biocidal silsesquioxanes functionalized by quaternary pyridinium functionalities has been developed. *N*-Alkylation reactions of the precursor compounds 4-(2-(trimethoxy silyl) ethyl)-pyridine and 4-(2-trichlorosilylethyl) pyridine with iodomethane, *n*-hexyl bromide, and *n*-hexadecyl bromide cleanly afforded the corresponding *N*-alkyl pyridinium salts (see Scheme 1-5) [14].



Scheme 1-5: *N*-alkyl pyridinium salts

A series of new bioactive polymers with pendant choline analogous group was prepared by anion exchange reaction direct at the quaternary nitrogen of the polycation. Poly(4-vinyl 2-hydroxyethylpyridinium) chloride (see Figure 1-3) was prepared in situ by simultaneous polymerization and quaternization of 4-vinyl pyridine with 2-chloroethanol that also acts as catalyst [15].

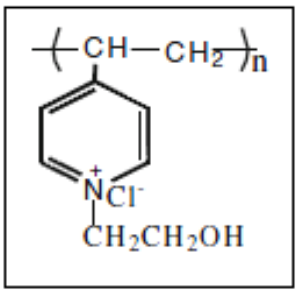
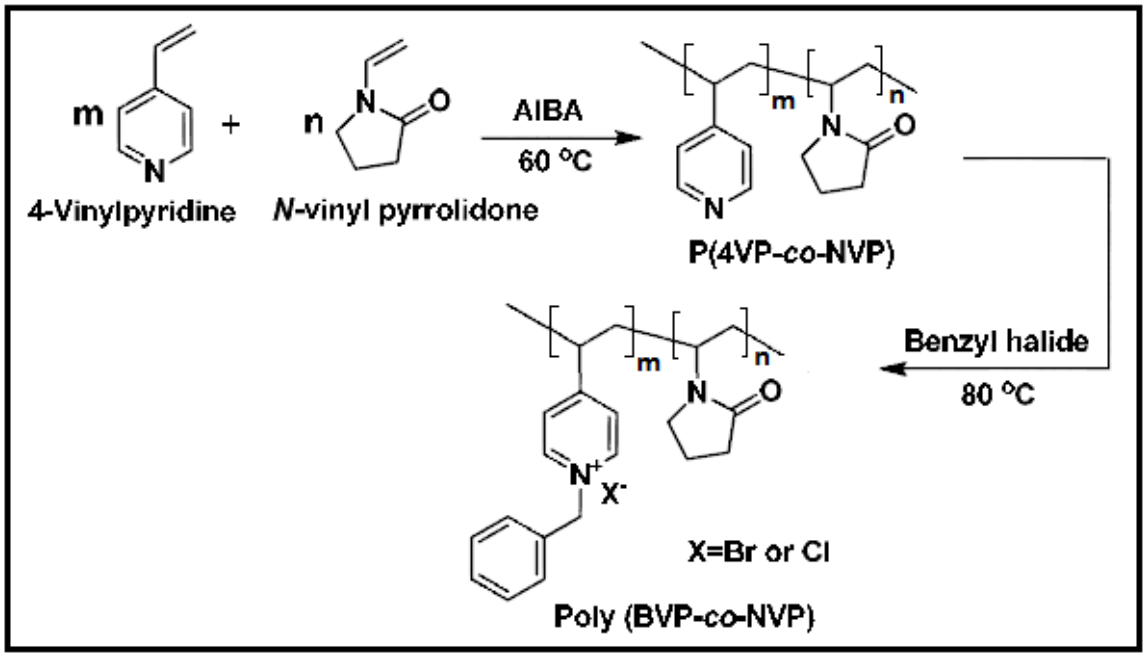


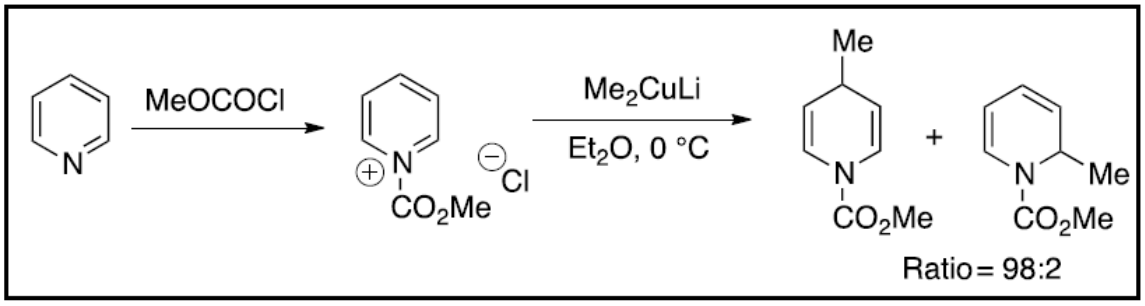
Figure 1-3: Poly(4-vinyl 2-hydroxyethyl pyridinium) chloride.

Due to the massive outbreaks of pathogen-caused diseases and the increase of drug-resistant pathogens, there is a particular interest in the development of novel disinfection agents with broad-spectrum anti-pathogenic activity. Water-soluble pyridinium-type polyvinyl pyrrolidones with different counter anions were prepared using azobisisobutyronitrile (AIBN) as initiator. The overall route of the synthesis of poly (4VP-co-NVP) and quaternization is schematically shown in Scheme(1-6) [16].



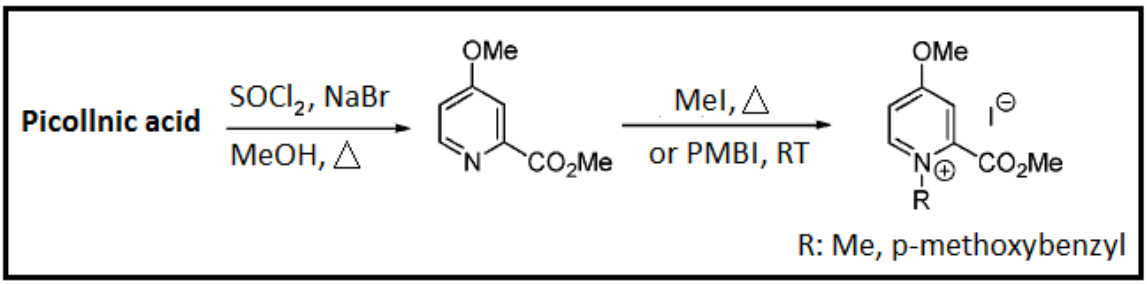
Scheme 1-6: Poly (4VP-co-NVP).

Piers et al [17], found that lithium dialkyl- and diarylcuprates demonstrated good levels of selectivity on addition to *N*-acyl pyridinium salt, generated *in situ* by the reaction of pyridine with methyl chloroformate, at the 4-position (see Scheme 1-7).



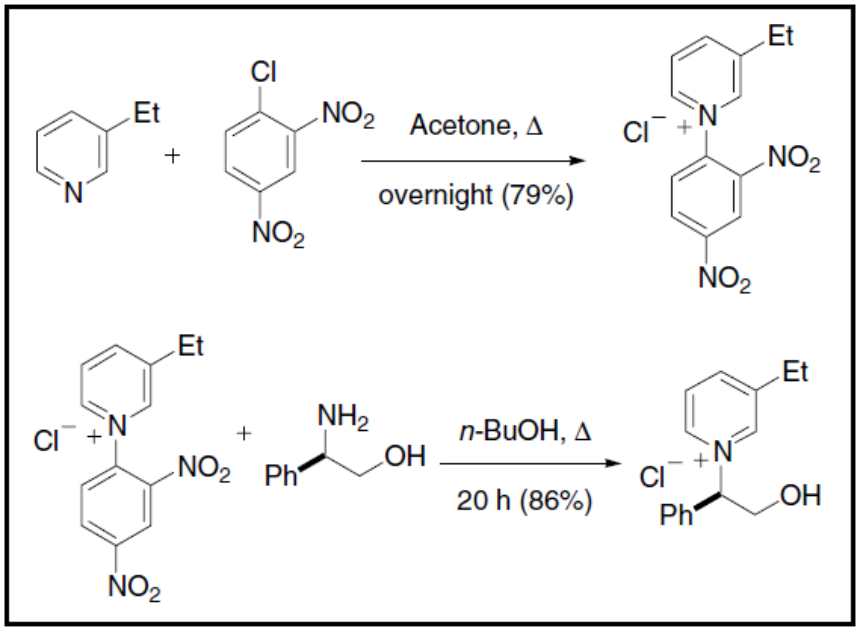
Scheme 1-7: Selectivity on addition to *N*-acyl pyridinium salt.

Donohoe et al [18], undertook an efficient, one-pot, synthesis of activated pyridine from picolinic acid (see Scheme 1-8). Subsequent N-alkylation was achieved in excellent yield to furnish pyridinium salts. The intermediate generated by the reduction of such salts can be reacted successfully with a range of different electrophiles (acids, alkyl halides, and carbonyl compounds) and the intermediate hydrolyzed in situ to provide a wide range of dihydropyridones.



Scheme 1-8: Pyridinium salts.

The Zincke reaction is an overall amine exchange process that converts *N*-(2,4-dinitrophenyl)pyridinium salts, known as Zincke salts, to *N*-aryl or *N*-alkyl pyridiniums upon treatment with the appropriate aniline or alkyl amine. Reaction of Zincke salt with (*R*)-(-)-phenylglycinol offers a practical entry to chiral 3-substituted pyridinium salt [19] (see Scheme 1-9)



Scheme 1-9: The Zincke reaction.

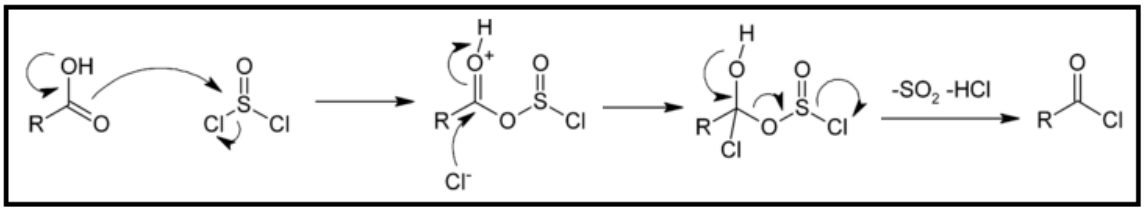
1.2.1. Acid chloride [20]

Acid chlorides are generally prepared in the same manner as alkyl chlorides, by replacing the corresponding hydroxy substituents with chlorides. Thus, carboxylic acids are treated with thionyl chloride ($SOCl_2$), phosphorus trichloride (PCl_3), or phosphorus pentachloride (PCl_5) (see Scheme 1-10).

$$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$
$$3\ RCOOH + PCl_3 \rightarrow 3\ RCOCl + H_3PO_3$$
$$RCOOH + PCl_5 \rightarrow RCOCl + POCl_3 + HCl$$

Scheme 1-10: Acid chlorides synthesis.

The reaction mechanisms involving thionyl chloride and phosphorus pentachloride are similar; the mechanism with thionyl chloride is illustrative at Scheme (1-11).

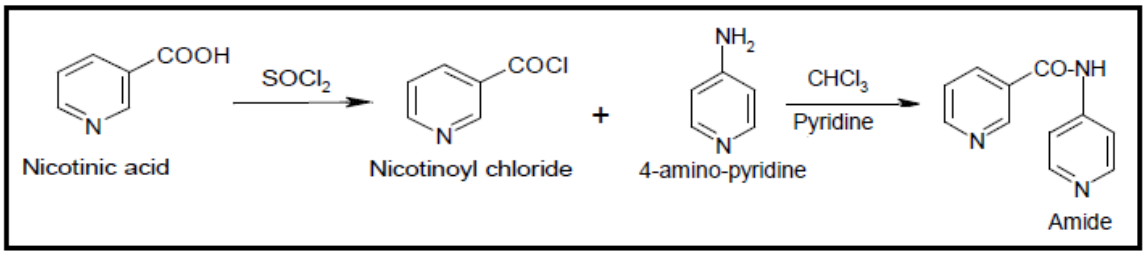


Scheme 1-11: The reaction mechanisms involving thionyl chloride.

1.2.2. Amides

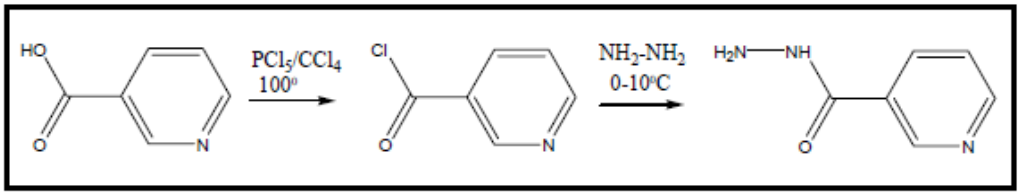
Amides are pervasive in nature and technology as structural materials. Many methods exist in amide synthesis. The simplest method for making amides is by coupling a carboxylic acid with an amine. Coupling reactions with acyl chlorides could be formed amide bond by reacting the acyl chloride with the desired amine (Aminolysis) (see Scheme 1-12). An additional base is usually required to trap the formed HCl and to avoid the conversion of the amine into its unreactive HCl salt. Couplings are usually performed in inert dry solvents, in the presence of a non-nucleophilic tertiary amine (NEt_3, iPr_2NEt (also called Hunig's base), or N-methylmorpholine) [21].

There are many substituted pyridines having simple structures and greater pharmacological importance e.g. nicotinamide, nicotinic acid, 4-Amino pyridine and isoniazid etc. Two drugs can be given simultaneously to the patient in the form of twin drugs (N-(pyridine-3-carbonyl)-Isonicotinamide) (See Scheme 1-12) in order to minimize the dose and side effects. Because of increase in lipophilicity, bioavailability is increased [22].



Scheme 1-12: N-(pyridine-3-carbonyl)-Isonicotinamide synthesis.

Ramalakshmi et al [23] , reported that nicotinic acid hydrazide was prepared by converting nicotinic acid to nicotinyl chloride using phosphorous penta chloride, then the acid chloride which on reaction with hydrazide yielded nicotinic acid hydrazide (see Scheme 1-13).

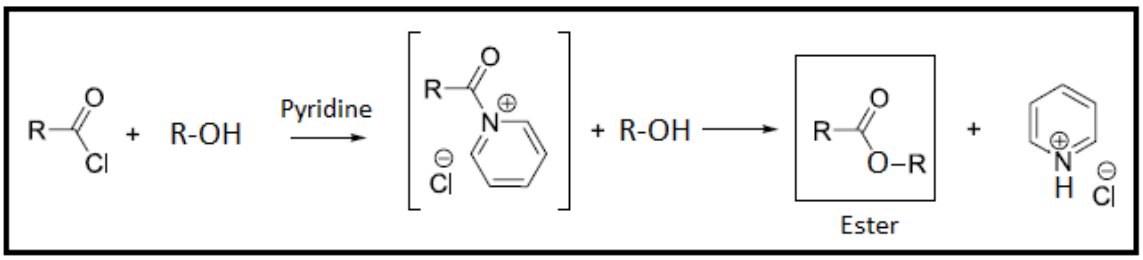


Scheme 1-13: Nicotinic acid hydrazide preparation.

1.2.3. Reactions of acid chloride with phenols

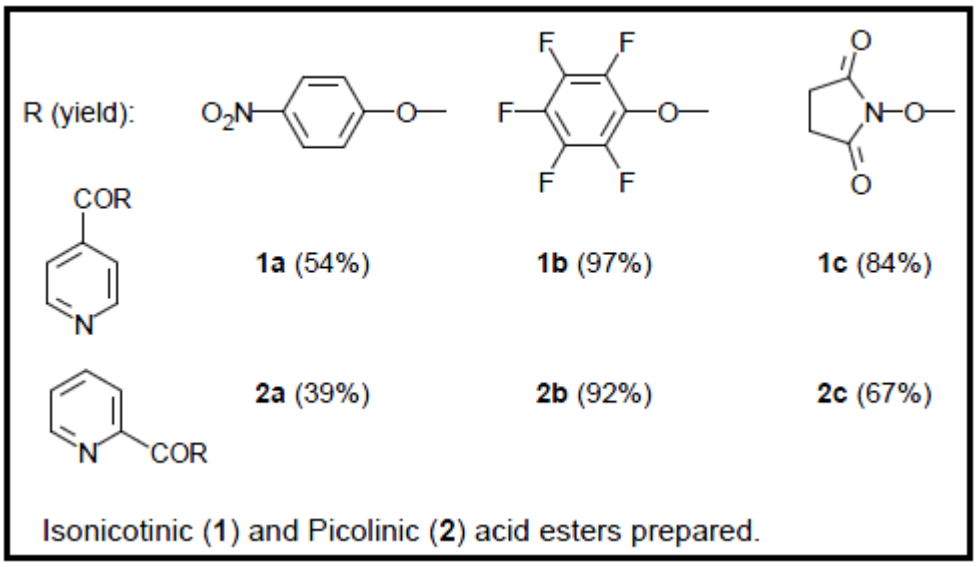
Phenols react with carboxylic acid anhydrides and acid chlorides to form esters. These reactions are quite similar to those of alcohols. The reaction of acyl chlorides with alcohols is one of the best ways to synthesize an ester. The reaction of an acyl chloride with an alcohol to form an ester occurs rapidly and does not require an acid catalyst. Pyridine is often added to the reaction mixture

to react with the HCl that forms. (Pyridine may also react with the acyl chloride to form an acylpyridinium ion, an intermediate that is even more reactive toward the nucleophile than the acyl chloride (see Scheme 1-14) [24].



Scheme 1-14: Ester preparation.

Christensen has been carried out a method for preparation of the p-nitrophenyl-, N-hydroxysuccinimidyl- and pentafluorophenyl esters of isonicotinic and picolinic acids from the corresponding acid chlorids (see Scheme 1-15) [25].

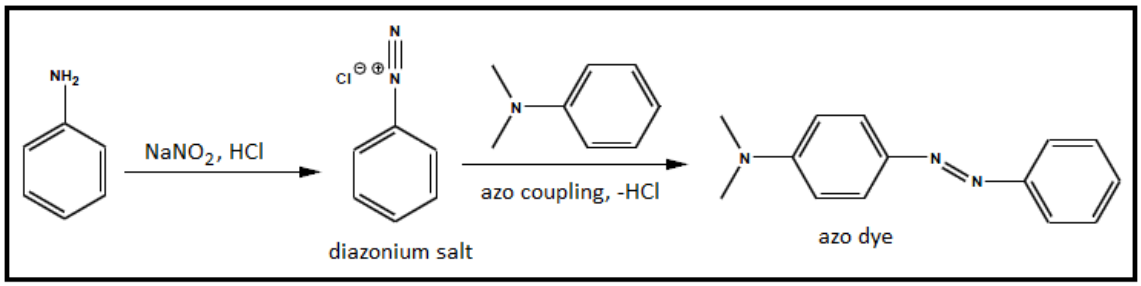


Scheme 1-15: Esters of isonicotinic and picolinic acids.

1.3. Azo compounds

Azo dyes are prepared in a two-step reaction, the first being the synthesis of an aromatic diazonium ion from an aniline derivative. The next step is coupling of the diazonium salt with electrons enrich aromatic compound (phenol,

aniline…etc.) (see Scheme 1-16). The colors of azo dyes include different shades of yellow, red, orange, brown, and blue [26].



Scheme 1-16: Azo dye preparation.

1.4. Corrosion phenomena of steel

Corrosion is an electrochemical process in which a metal reacts with its environment to form an oxide or other compound. The cell which causes this process has three essential constituents: an anode, a cathode and an electrically conducting solution. Simply, the anode is the site at which the metal is corroded; the electrolyte solution is the corrosion medium; and the cathode forms the other electrode of the cell and is not consumed in the corrosion process. Uniform corrosion or general corrosion is assumed to be most common form of corrosion and particularly responsible for most the materials loss. [27]

Mechanism of uniform corrosion includes two electrochemical reactions:

$$Fe \rightarrow Fe^{2+} + 2e^{-} \quad \text{(Reaction at anode)}$$

$$O_2 + 4H^{+} + 4e^{-} \rightarrow 2H_2O \quad \text{(Reaction at cathode)}$$

$$O_2 + 4e^{-} + 2H_2O \rightarrow 4OH^{-}$$

Formation of the rust is occurred by the reaction ferrous ions (Fe2+) with the hydroxyl ions (OH^-) to yield ferrous hydroxide $Fe(OH)_2$, this Iron(II) hydroxide is non-soluble substance and separated in the electrolytic media. $Fe(OH)_2$ usually is called a rust with a white green color of substance. Also, $Fe(OH)_2$ converted by oxidation with access of oxygen to $Fe(OH)_3$ which is known as

ferric hydroxide. Finally ferric hydroxide by oxidation could be transformed into ferric oxide Fe_2O_3 with water molecules. There are other different rust types, such as Iron(II,III) oxide (magnetite) with chemical formula Fe_3O_4, γ-Fe_3O_4 (maghemite, brown oxide) and γ-FeOOH (lepidocrocite, yellow oxide) are formed due to diversity the condition reactions in the environment. The rust formation could be explained by the mechanism that is shown in the Figure(1-4) **[28][29]**.

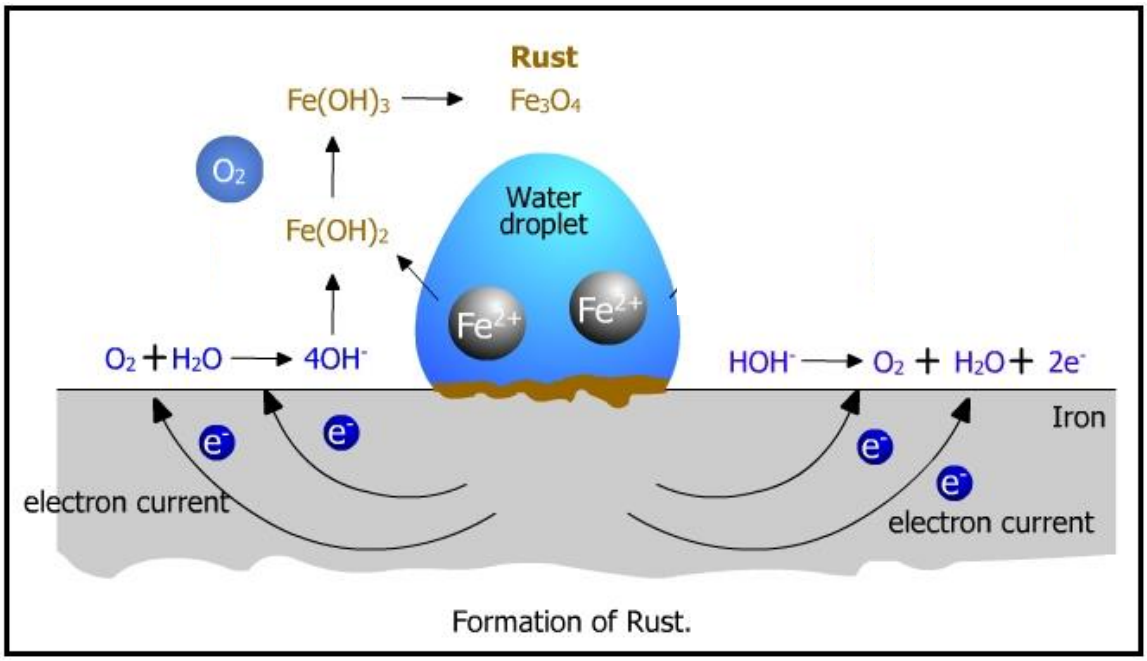


Figure 1-4 corrosion mechanism

General corrosion can be decelerated or terminated its processing on basis of the following basic treatments;

(**1**) Electrons flow can be decelerated or terminated by: (a) Metal surface coating with inert medium like different types of painting, (b) Reduce the solution conductivity that in contact with the metal by keeping it dry.

(**2**) Coating treatments can be decelerated or terminated oxygen to get to the surface.**[30]**

(**3**) High resistant metal can be prevented the electrons to flow out in the electrochemical process, that can be occurred by using sacrificial coating, cathodic protection and organic and inorganic inhibitors.

(**4**) Select a metal that is easily produced an oxide film which prevents the electrochemical reaction .[31]

1.4.1. Organic inhibitors

Organic compounds used as inhibitors, occasionally, they act as cathodic, anodic or together, as cathodic and anodic inhibitors, nevertheless, as a general rule, act through a process of surface adsorption, designated as a film- forming. Naturally the occurrence of molecules exhibiting a strong affinity for metal surfaces compounds showing good inhibition efficiency

and low environmental risk [32]. The organic inhibitors build up a protective hydrophobic film adsorbed molecules on the metal surface, which provides a barrier to the dissolution of the metal in the electrolyte. They must be soluble or dispersible in the medium surrounding the metal [33].

Example (1) The corrosion inhibition of carbon steel in saline solution at 50°C with hydroxyethyl imidazoline-type inhibitors (see Figure 1-5) has been evaluated by using electrochemical techniques. The results showed a low performance of the inhibitors. However, it was observed that inhibitors either can be adsorbed on the substrate surface or modify the solution resistivity and thereby enhanced the corrosion performance [34].

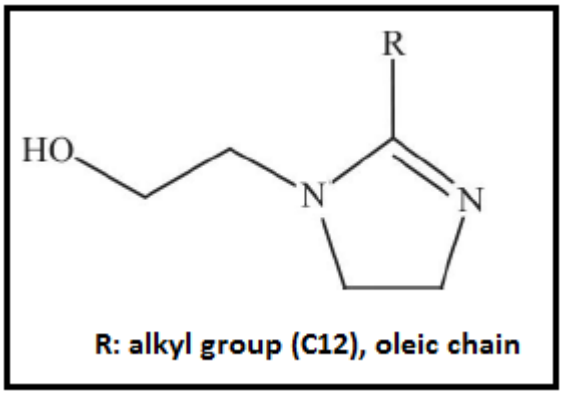


Figure 1-5 imidazoline-type inhibitors

Example (2) Corrosion inhibitory effects of new synthesized compound namely 5,5'-((1Z,1'Z)-(1,4-phenylenebis(methanylylidene))bis(azanylylidene))bis(1,3,4-thiadiazole-2-thiol) (PBB) (see Figure 1-6) on mild steel in 1.0 M HCl was investigated at different temperatures using electrochemical tests. Results showed that PBB inhibited mild steel corrosion in acid solution and indicated that the inhibition efficiencies increased with the concentration of inhibitor. Changes in impedance parameters suggested the adsorption of PBB on the mild steel surface, leading to the formation of protective films [35].

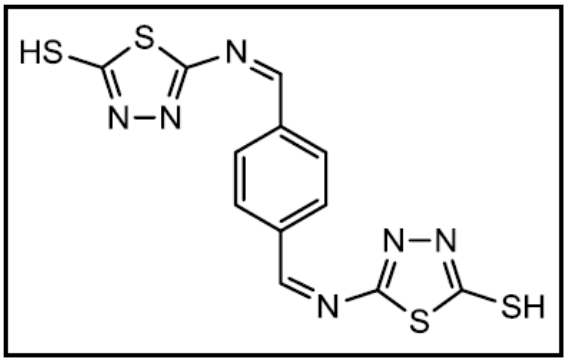


Figure 1-6 effects of new synthesized compound (PBB)

Example (3)The corrosion and inhibitor adsorption processes in mild steel pyridinium iodide derivatives (see Figure 1-7) hydrochloric acid systems was studied at different temperatures electrochemical measurements. It was found that the studied compounds exhibit a very good performance as inhibitors for mild steel corrosion in 1.5M HCl. Results show that the inhibition efficiency

increases with decreasing temperature and increasing concentration of inhibitors. A good correlation occurred between the substituent type and the inhibition efficiency [36].

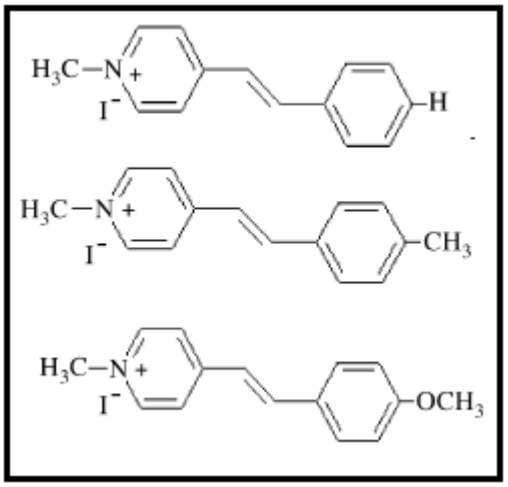


Figure 1-7 pyridinium iodide derivatives

1.5. Aim of work :

Synthesis of some new pyridinium salts derivatives as organic corrosion inhibitors on mild steel ,these compounds were finally characterized using spectroscopic techniques (FTIR & ^{1}HNMR). Weight loss method was used to evaluate the efficiency of the synthesis inhibitors.

Chapter Two

Experimental part

2- Experimental Part

2.1. Instruments and apparatuses

1- The infra-red spectra of the synthesis compounds were recorded using FTIR 8300 Fourier transform infrared spectrophotometer of SHIMADZU Company as a potassium chloride disc in the wave number wave range of (4000-400)cm-1,AL-Nahrain University, Department of Chemistry and IbnSina State Company/ the Ministry of Industry Located at Baghdad University.

2- ^{1}H-NMR spectra were recorded on nuclear magnetic resonance Bruker spectrophotometer model Ultrasheild 400 MHz using tetramethylsilane internal standard and DMSO-d6 as solvent (Isfahan University of Technology (IUT), Iran).

3- Melting point was determined by the open capillary method using hot stage Gallenkamp melting point apparatus and was uncorrected, AL-Nahrain University, Department of Chemistry.

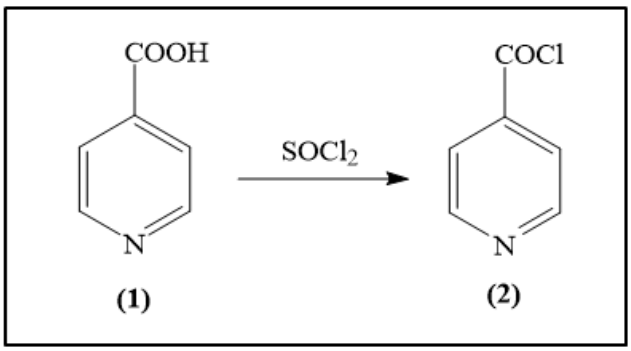
4- The element analysis of mild steel was performed by Spectro max-Germany, 2009, State Company for Inspection and Rehabilitation ,Ministry of Industry and Materials.

2.2. Chemicals

The chemicals used in this work were supplied from BDH, Fluka and Merck supplier companies.

2.3. Preparation methods

2.3.1. Synthesis of Isonicotinoyl chloride (2) [37]:

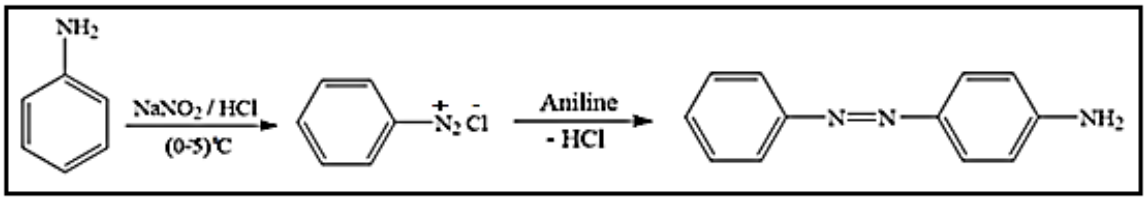


In a Round bottom flask, fitted with magnetic stirrer, a reflux condenser, is placed (1.23g, 0.01 mol) of Isonicotinic acid. The stirrer is started, and 5 ml. (8.18 g, 0.069 mol) of thionyl chloride was added. After the addition is complete, the mixture was heated with continuous stirring for 1 hour; then the excess thionyl chloride is removed by distillation. The prepared acid chloride was used freshly for the next step.

Table 2-1: Physical properties of compound (2):

Isonicotinoyl Chloride	
Molecular formula	C_6H_4NOCl
Color	Light yellow
Molecular weight(g/mole)	141.563
M.P. , ˚C	Solid
Yield%	---

2.3.2. Preparation of 4-phenylazoaniline: [38,39]



a) *Diazotization.*

In beaker (50 mL) dissolve (2 mL, 0.02 mol) of aniline in (4 mL) distilled water and (4 mL) concentrated hydrochloric acid. Place the beaker in ice water bath at (0 - 5) °C for half hour. Add slowly sodium nitrite solution [(2 g, 0.02 mol) in (10 mL) distill water] previously cooled to 0 °C. A yellow solution will be obtained and keep it for the next step.

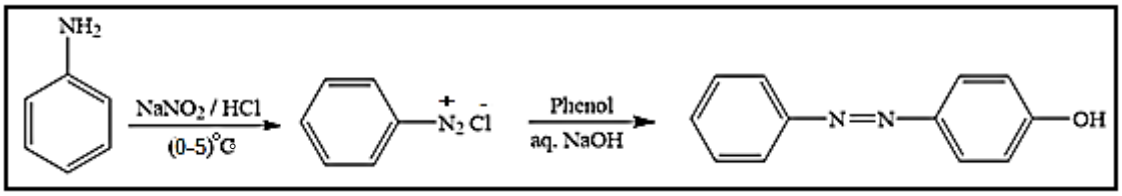
b) *Coupling reaction.*

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

Table 2-2: Physical properties of 4-phenylazoaniline:

4-phenylazoaniline	
Molecular formula	$C_{12}H_{11}N_3$
Color	Dark red
Molecular weight(g/mole)	197.24
M.P. , °C	124-126 (123 to 126 °C (lit.)) [40]
Yield%	73

2.3.3. Preparation of 4-phenylazophenol: [41]

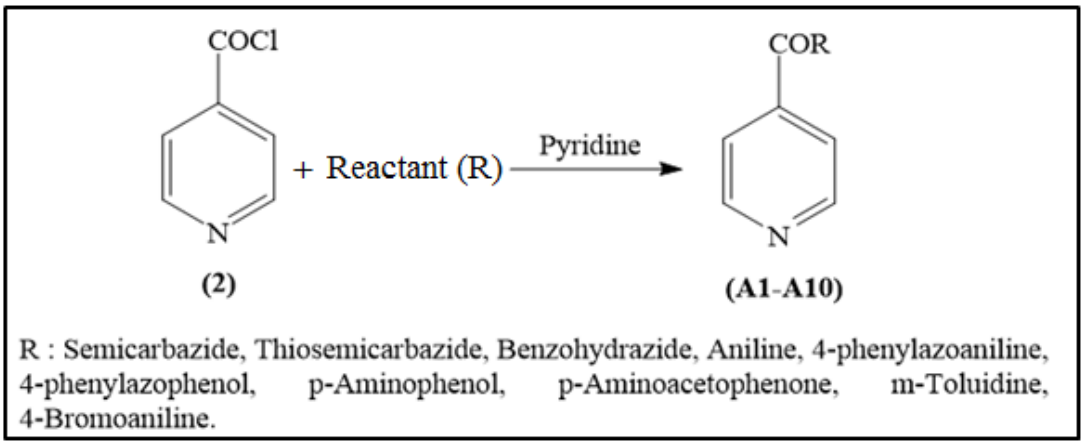


Aniline (3 mL, 0.0374 mol) was dissolved in concentrated hydrochloric acid (10.25 mL) and water (10.25 mL). Aqueous sodium nitrite [2.85 g, 0.0425 mole in water (8.75 mL)] was added to the aniline solution drop wise while stirring at 0ºC. Phenol (3.41 g, 0.0375 mole) was dissolved in a sodium hydroxide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

Table 2-3: Physical properties of 4-phenylazophenol:

4-phenylazophenol	
Molecular formula	$C_{12}H_{10}N_2O$
Color	Yellow
Molecular weight(g/mole)	198.22
M.P. , ˚C	149-151 (150-152 ℃ (lit.)) [40]
Yield%	80

2.3.4. Synthesis of Isonicotinoyl amide and Isonicotinoyl ester (A1-A10): [42]

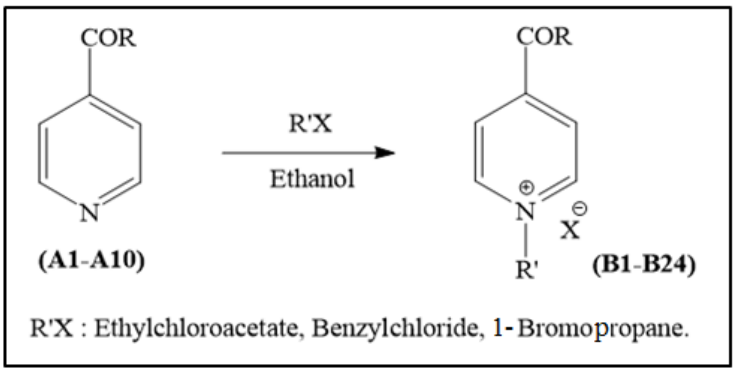


An appropriate amount of acid chloride (0.01 mol) and a proper amine (0.01 mol were added to (20 mL) pyridine. The reaction mixture was refluxed for 8 hours. The solvent was evaporated. Then (10% NaOH) in ethanol was added to the obtained product for neutralization. Finally, the crude yield was recrystallized from ethanol (A1-A10).

Table 2-4: Physical properties of compounds (A1-A10):

	Name of compound	Chemical formula	Color	M.W. (g/mol)	M.P., °C	Yield (%)
1	2-isonicotinoylhydrazinecarboxamide (A1)	$C_7H_8N_4O_2$	Brown	180.19	294 Dec	79
2	2-isonicotinoylhydrazinecarbothioamide (A2)	$C_7H_8N_4OS$	Yellow	196.11	270-273	73
3	N-benzoylisonicotinohydrazide (A3)	$C_{13}H_{11}N_3O_2$	Yellow	241.24	230-232	67
4	N-phenylisonicotinamide (A4)	$C_{12}H_{10}N_2O$	Gray	198.22	182-185	83
5	N-(4-(phenyldiazenyl)phenyl) isonicotinamide (A5)	$C_{18}H_{14}N_4O$	Dark brown	302.32	167-169	62
6	4-(phenyldiazenyl) phenyl isonicotinate (A6)	$C_{18}H_{13}N_3O_2$	Dark brown	303.31	210 Dec	69
7	N-(4-hydroxyphenyl)isonicotinamide (A7)	$\mathbf{C_{12}}H_{10}N_2O_2$	Dark brown	214.22	189-192	76
8	N-(4-acetylphenyl)isonicotinamide (A8)	$\mathbf{C_{14}}H_{12}N_2O_2$	Dark brown	240.25	256-258	60
9	N-(m-tolyl)isonicotinamide (A9)	$\mathbf{C_{13}}H_{12}N_2O$	Yellow	212.24	204-206	77
10	N-(4-bromophenyl)isonicotinamide (A10)	$\mathbf{C_{12}}H_9BrN_2O$	Brown	277.11	282-285	79

2.3.5. Synthesis of Pyridinium salts (B1-B24): [43]



A mixture of (0.01 mol) isonicotinoyl amide or ester and (0.01 mol) of a proper alkyl halide (ethyl chloroacetate, n-propyl bromide, benzyl chloride) in 10 mL of ethanol was allowed to stand overnight at room temperature. The mixture was then heated at the reflux temperature for 24 hours. Then the product was filtered, washed with ethanol and dried (B1-B24).

Table 2-5: Physical properties of compounds (B1-B24):

	Name of compound	Chemical formula	Color	M.W. (g/mol)	M.P. °C	Yield (%)
1	4-(2-carbamoylhydrazinecarbonyl)-1-(2-ethoxy-2-oxoethyl)pyridinium chloride (B1)	$C_{11}H_{15}ClN_4O_4$	Pale yellow	302.71	280 Dec.	79
2	1-benzyl-4-[(2-carbamoylhydrazinyl)carbonyl] pyridinium chloride (B2)	$C_{14}H_{15}ClN_4O_2$	Pale white	306.74	>310	74
3	4-[(2-carbamoylhydrazinyl)carbonyl]-1-propylpyridinium bromide (B3)	$C_{10}H_{15}BrN_4O_2$	Orange	303.15	270-273	77
4	4-[(2-carbamothioylhydrazinyl)carbonyl]-1-(2-ethoxy-2-oxoethyl)pyridinium chloride (B4)	$C_{11}H_{15}ClN_4O_3S$	Yellow	318.77	270 Dec.	78
5	1-benzyl-4-[(2-arbamothioylhydrazinyl) carbonyl] pyridinium chloride (B5)	$C_{14}H_{15}ClN_4OS$	White	322.81	>310	71
6	4-[(2-carbamothioylhydrazinyl)carbonyl]-1-propylpyridinium bromide (B6)	$C_{10}H_{15}BrN_4OS$	Yellow	319.22	>310	73
7	4-[(2-benzoylhydrazinyl)carbonyl]-1-(2-ethoxyprop-2-en-1-yl)pyridinium chloride (B7)	$C_{18}H_{20}ClN_3O_3$	Pale Yellow	361.82	221-223	70
8	4-[(2-benzoylhydrazinyl)carbonyl]-1-benzylpyridinium chloride (B8)	$C_{20}H_{18}ClN_3O_2$	Pale white	367.82	>310	81
9	4-[(2-benzoylhydrazinyl)carbonyl]-1-propylpyridinium bromide (B9)	$C_{16}H_{18}BrN_3O_2$	Pale yellow	364.23	>310	76
10	1-(2-ethoxy-2-oxoethyl)-4-(phenylcarbamoyl) pyridinium chloride (B10)	$C_{16}H_{17}ClN_2O_3$	Brown	320.77	>310	66
11	1-benzyl-4-(phenylcarbamoyl) pyridinium chloride (B11)	$C_{19}H_{17}ClN_2O$	Brown	324.80	>310	83
12	4-(phenylcarbamoyl)-1-propyl pyridinium bromide (B12)	$C_{15}H_{17}BrN_2O$	Brown	321.21	>310	70
13	1-(2-ethoxy-2-oxoethyl)-4-((4-(phenyldiazenyl)	$C_{22}H_{21}ClN_4O_3$	Dark	424.88	>310	78

	phenyl)carbamoyl)pyridinium chloride (B13)		brown			
14	1-benzyl-4-((4-(phenyldiazenyl)phenyl) carbamoyl)pyridinium chloride (B14)	$C_{25}H_{21}ClN_4O$	Dark brown	428.91	>310	68
15	4-((4-(phenyldiazenyl)phenyl)carbamoyl)-1-propylpyridinium bromide (B15)	$C_{21}H_{21}BrN_4O$	Dark brown	425.32	>310	80
16	1-(2-ethoxy-2-oxoethyl)-4-((4-(phenyldiazenyl) phenoxy)carbonyl)pyridinium chloride (B16)	$C_{22}H_{20}ClN_3O_4$	Dark brown	425.86	>310	80
17	1-benzyl-4-((4-(phenyldiazenyl)phenoxy) carbonyl)pyridinium chloride (B17)	$C_{25}H_{20}ClN_3O_2$	Brown	429.89	>310	71
18	4-((4-(phenyldiazenyl)phenoxy)carbonyl)-1-propyl pyridinium bromide (B18)	$C_{21}H_{20}BrN_3O_2$	Deep brown	426.30	>310	77
19	1-(2-ethoxy-2-oxoethyl)-4-[(4-hydroxyphenyl) carbamoyl]pyridinium chloride (B19)	$C_{16}H_{17}ClN_2O_4$	Dark brown	336.77	>310	78
20	1-benzyl-4-[(4-hydroxyphenyl)carbamoyl] pyridinium chloride (B20)	$C_{19}H_{17}ClN_2O_2$	Dark brown	340.80	>310	75
21	4-[(4-hydroxyphenyl)carbamoyl]-1-propyl pyridinium bromide (B21)	$C_{15}H_{17}BrN_2O_2$	Dark brown	337.21	>310	68
22	4-[(4-acetylphenyl)carbamoyl]-1-(2-ethoxy-2-oxoethyl)pyridinium chloride (B22)	$C_{18}H_{19}ClN_2O_4$	Brown	362.80	>310	79
23	1-(2-ethoxy-2-oxoethyl)-4-[(3-methylphenyl) carbamoyl]pyridinium chloride (B23)	$C_{17}H_{19}ClN_2O_3$	Pale white	334.79	>310	84
24	4-[(4-bromophenyl)carbamoyl]-1-(2-ethoxy-2-oxoethyl)pyridinium chloride (B24)	$C_{16}H_{16}BrClN_2O_3$	Yellow	399.66	290-292	81

2.4. Weight loss measurements

Weight loss measurements is a good way of measuring the corrosion rate of a metal by exposing the sample to the test medium (e.g. acidic media) and measure the loss of weight of the material as a function of time. Although these tests are simple, there is no simple way to extrapolate the results to predict the lifetime of the system under investigation. The sheet of mild steel used has the composition percentages (0.002% P, 0.288% Mn, 0.03% C, 0.0154% S, 0.0199% Cr, 0.002% Mo, 0.065% Cu, and 0.0005% V) and the remainder iron. The mild steel sheet was mechanically press-cut into disc shape with diameter (2.5 cm) **[44]**. These disc shapes were polished with emery paper of 300, 500, 700, 1000 grits successively to achieve a smooth mild steel surface. The polished surface was cleaned thoroughly with distillated water and acetone to expose the micro structure, remove polishing residuals and possible grease. 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 aqueous solution of 1M sulphuric acid in the presence and absence of inhibitors in different concentration (0.0005, 0.001, 0.005and 0.01)M for 24 hrs at 30ºC. The specimens were removed after 24 hrs exposure period, washed with water to remove any corrosion products and finally washed with acetone. Then they were dried and reweighed. The weight loss measurements were taken using the procedures and precautions described elsewhere [45-46]. Weight loss allowed calculation of the mean corrosion rate in (mg cm^{-2} h^{-1}). The corrosion rate of mild steel was determined using the relation (2.1) [47]:

$$W=\Delta m/St \quad \text{..... (2.1)}$$

where W is corrosion rate of mild steel, (Δm) is the mass loss in mg unit, (S) is the area (cm^2) and (t) is the immersion period (hours).

Duplicate experiments were performed in each case and the mean values reported. The percentage inhibition efficiency (% IE) was calculated using the following equation (2.2) [48]:

$$\% IE = (1- W_i/ W_o) \times 100 \quad \text{..... (2.2)}$$

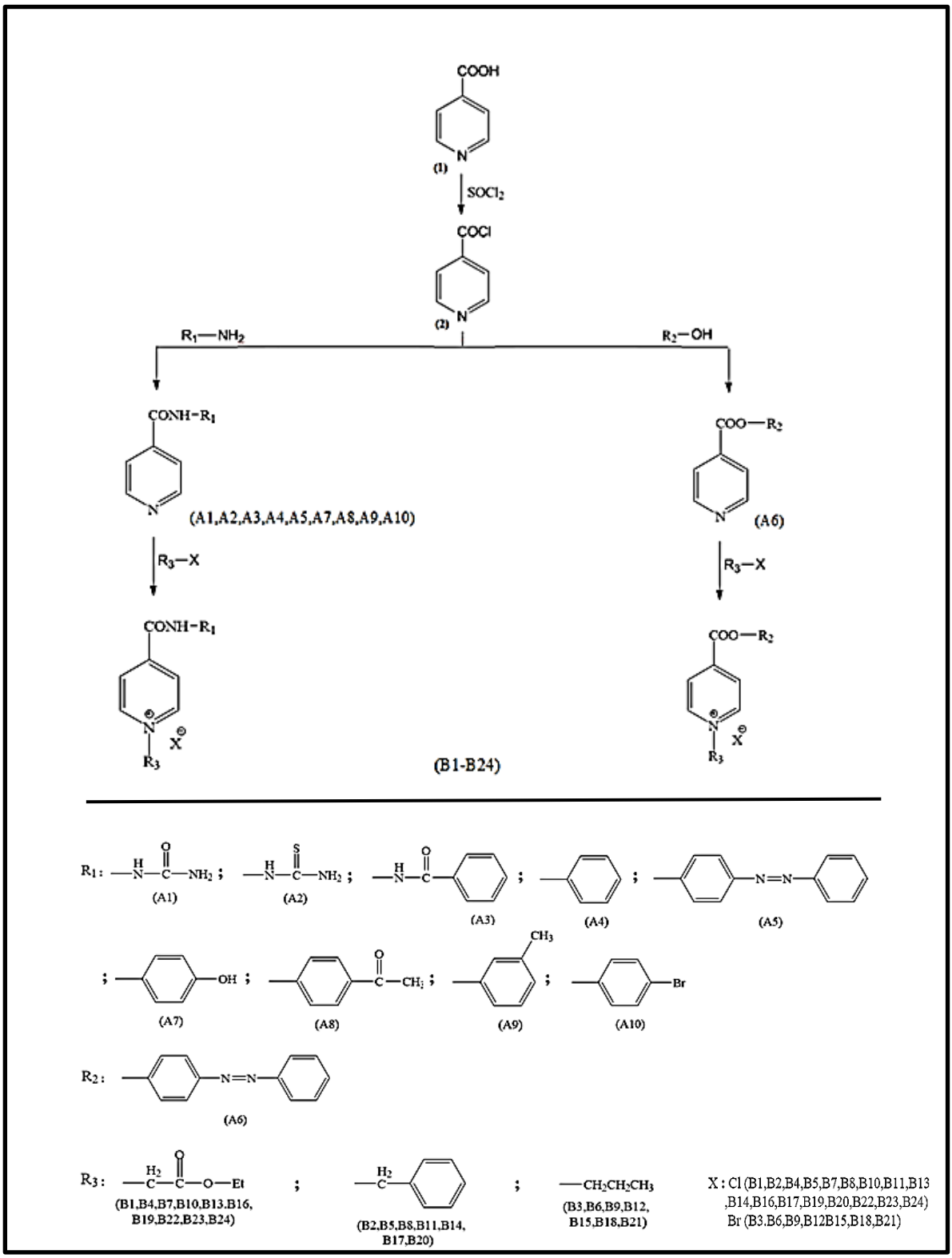
where W_o and W_i are the weight loss in uninhibited and inhibited corroding solutions, respectively.

Chapter Three

Results and Discussion

3- Results and Discussion

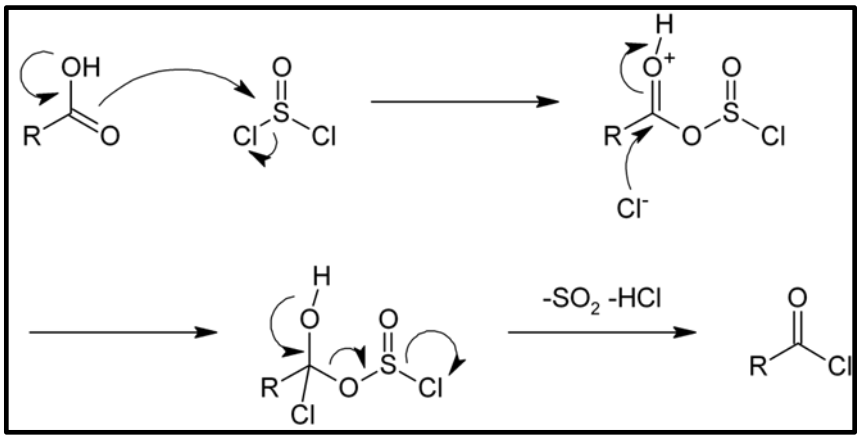
3.1. Synthesis of Pyridinium salts derivatives (B1-B24) : The chemical steps for the synthesis of compounds (B1-B24) are shown in Scheme 3-1.



Scheme 3-1: The chemical steps for the synthesis of compounds (B1-B24).

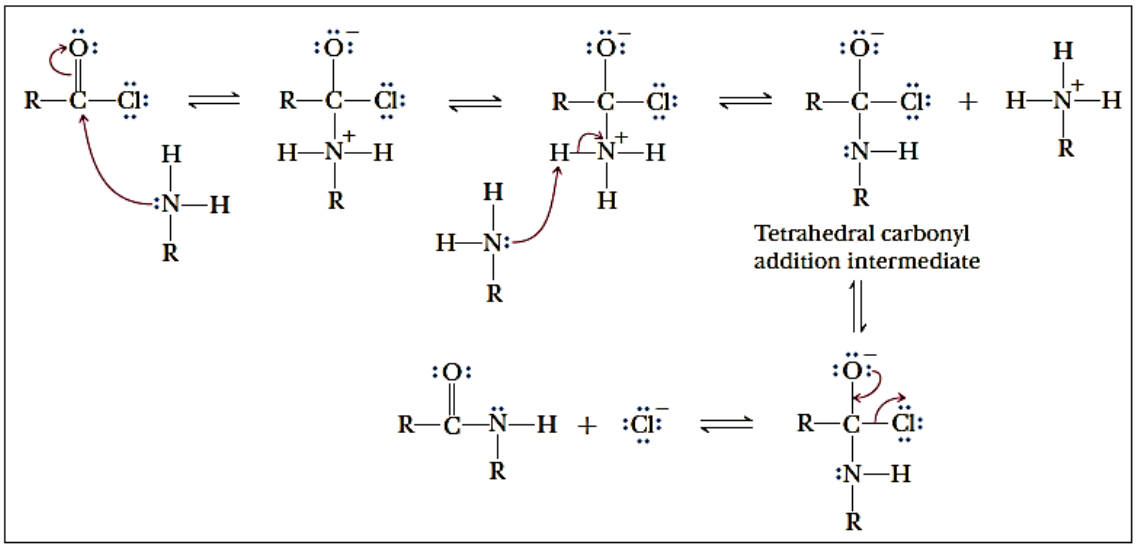
The reactions above are included new pyridinium salt derivatives(B1-B24) through usual preparation methodes by converting isonicotinic acid (1) into isonicotinoyl chloride (2), and followed to prepare some amide and ester derivatives (A1-A10). Finelly, pyridinium salt derivatives (B1-B24) were synthesized by reaction ester and amide derivatives (A1-A10) with an alkyl halide (ethyl chloroacetate, benzyl chloride and n-propyl bromide).

The mechanism reaction of preparation of isonicotinoyl chloride (2) is shown in Scheme (3-2), as a general mechanism. [49]



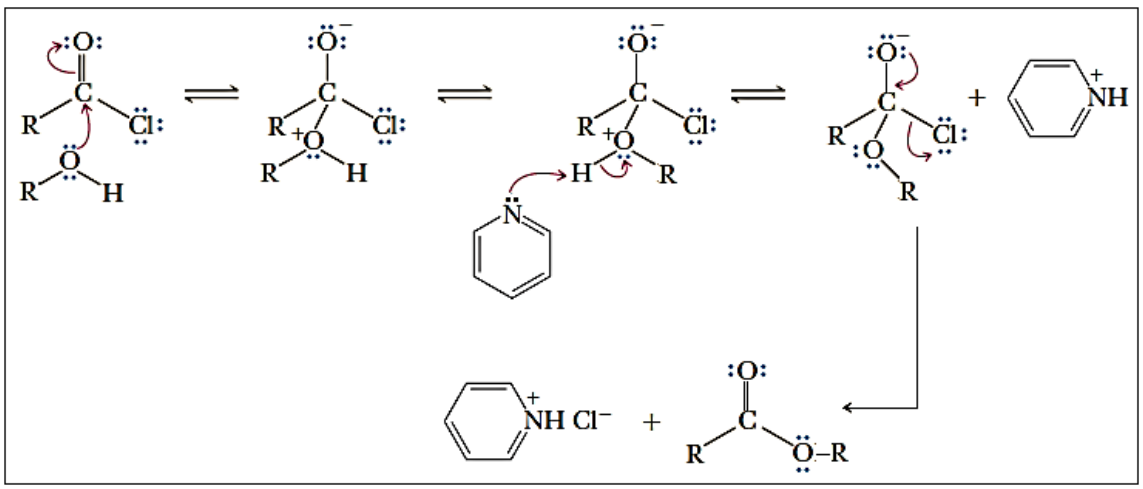
Scheme (3-2): The general mechanism of preparation an acid chloride.

The mechanism reaction for the preparation of amide derivatives is shown in scheme (3-3), as a general mechanism. [49]



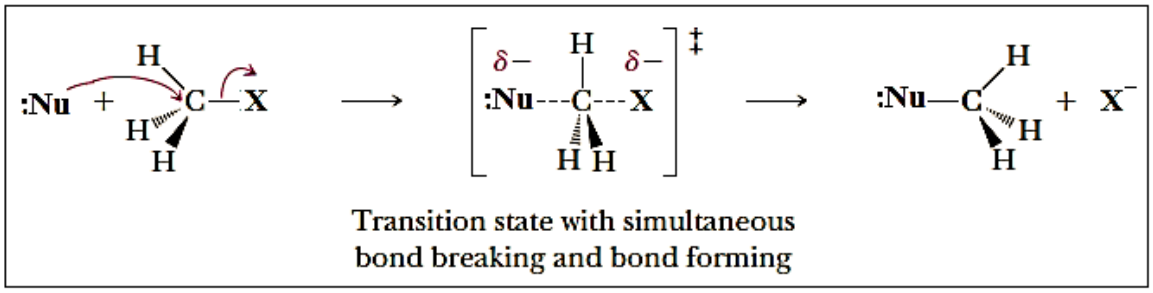
Scheme (3-3): The general mechanism of preparation of an amide derivative.

In cases in which resulting ester is sensitive to acid, the reaction can be carried out in the presence of a tertiary amine to neutralize the HCl as it is formed. The amines most commonly used for this purpose are pyridine and triethylamine. The mechanism reaction for the preparation of ester derivatives is shown in scheme (3-4), as a general mechanism. [49]



Scheme (3-4): The general mechanism of preparation of an ester derivative.

The reaction for the preparation of pyridinium salts derivatives can be followed SN_2 mechanism, as shown in scheme (3-5). [49]



Scheme (3-5): The general mechanism of preparation of SN2 mechanism.

3.2. FT-IR spectrum of synthesis compounds.

3.2.1. Characterization of amide and ester derivatives of isonicotinic acid (A1-A10).

Generally, the characterastic stretching bonds of FTIR spectra for amide and ester derivatives of isonicotinic acid (A1-A10) are (C=O) bonds. The stretching (C=O) bonds of the compounds (A1-A10) within the range (1690-1630 cm^{-1}) for amides and (1750-1720 cm^{-1}) for esters, that's comparing with the stretching (C=O) bond of the compound (1) at 1716 cm^{-1} (see Fig. 3-1). Besides, others characterastic stretching bonds, as (C-H) aromatic bond at (3100-3000 cm^{-1}) and azo (N=N) bond that exhibits absorptions at (1505-1550 cm^{-1}). As well as, characterastic stretching bond of (N-H) amide which appears at (3100-3500 cm^{-1}) [50]. Figures (3-2) to (3-11) represent the FTIR spectra for amide and ester derivatives of isonicotinic acid (A1-A10), respectively. Table (3-1) shows the spectral data of FTIR of compounds (A1-A10).

Table 3-1: IR spectral data of prepared compounds (A1-A10) in cm^{-1}.

Comp. No.	ν C-H aromatic	ν C-H aliphatic	ν C=C aromatic	ν C=O	ν N-H amide	ν N=N	Others
(1)	3051	-	1616	1716 acid	-	-	3105 (O-H)
A1	3097	-	1604	1693($CONH_2$) 1666(CONH)	3356 3163	-	-
A2	3047	-	1608	1681	3151	-	-
A3	3062	-	1604	1685	3406	-	-
A4	3043	-	1600	1658	3340	-	-
A5	3056	-	1597	1685	3356	1504	-
A6	3078	-	1600	1724	-	1546	-
A7	3078	-	1600	1651	3348	-	3348 (O-H)
A8	3043	-	1593	1676 1642	3356	-	-
A9	3059	2962 2846	1600	1678	3417	-	-
A10	3082	-	1593	1681	3309	-	520 (C-Br)

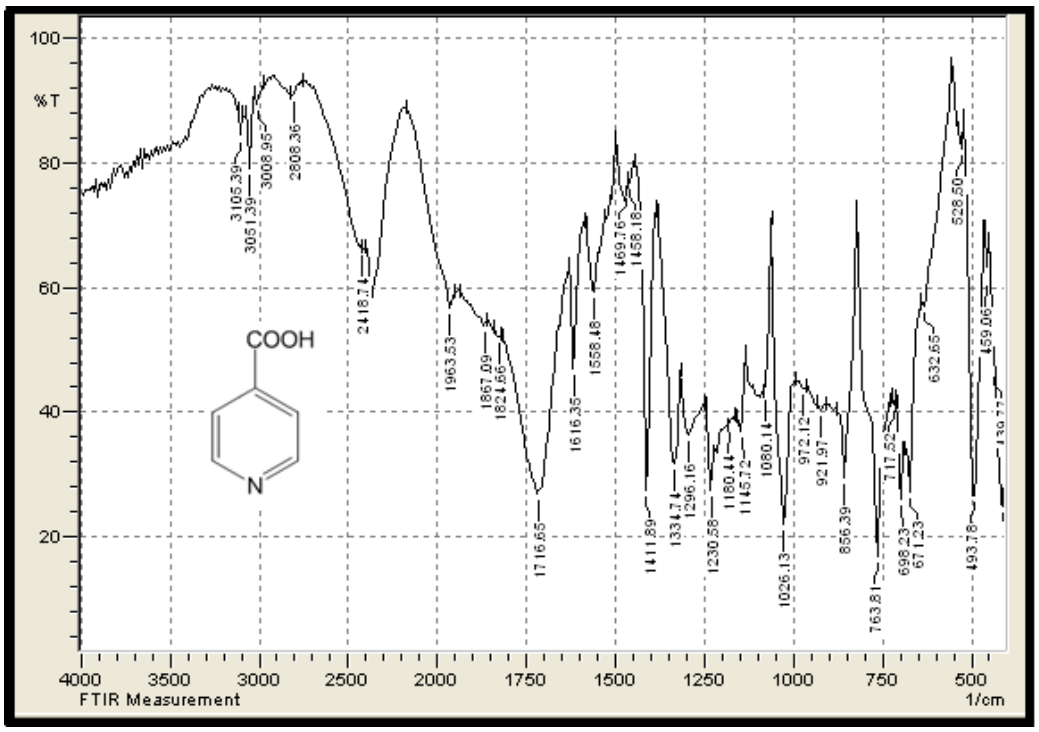


Fig 3-1: FTIR Spectrum of compound (1).

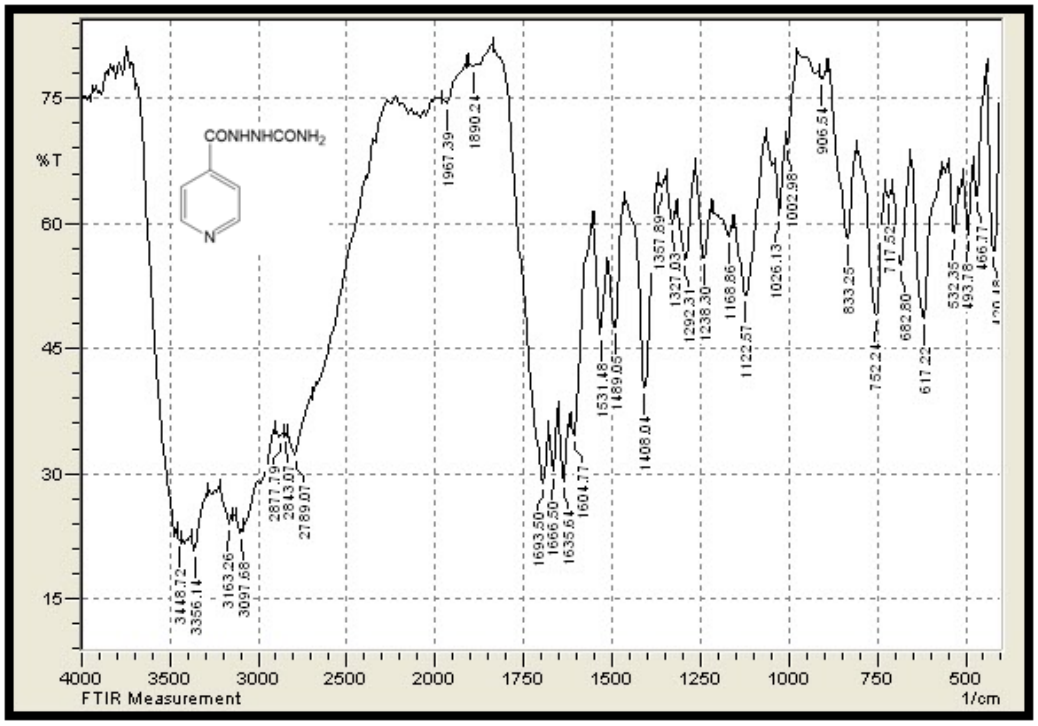


Fig 3-2: FTIR Spectrum of compound (A1).

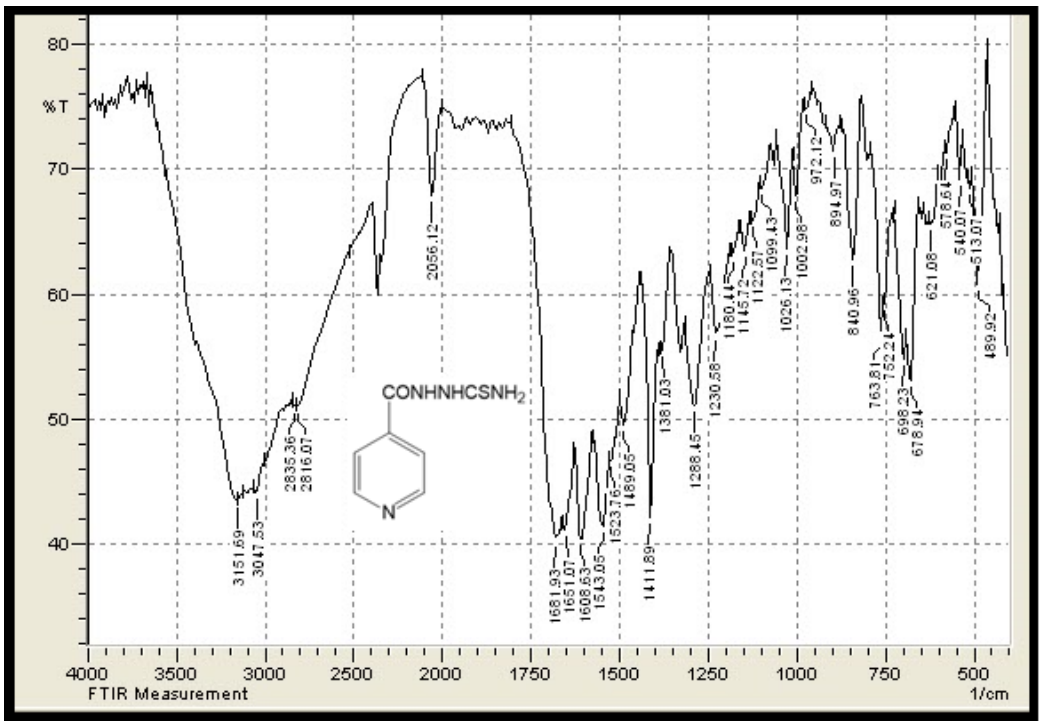


Fig 3-3: FTIR Spectrum of compound (A2).

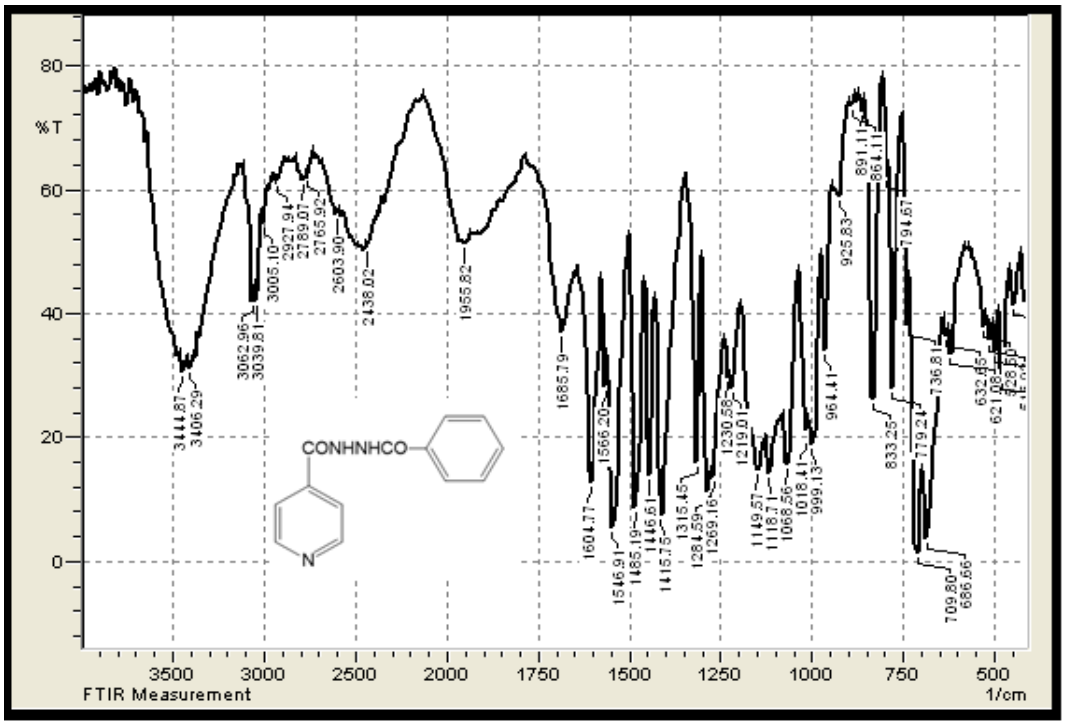


Fig 3-4: FTIR Spectrum of compound (A3).

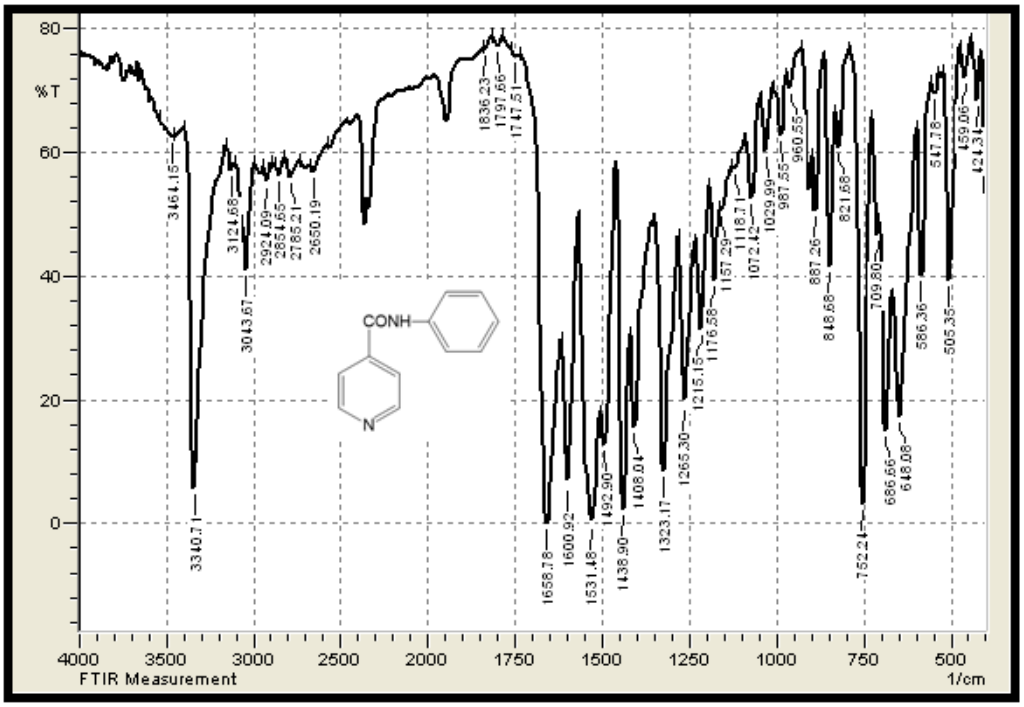


Fig 3-5: FTIR Spectrum of compound (A4).

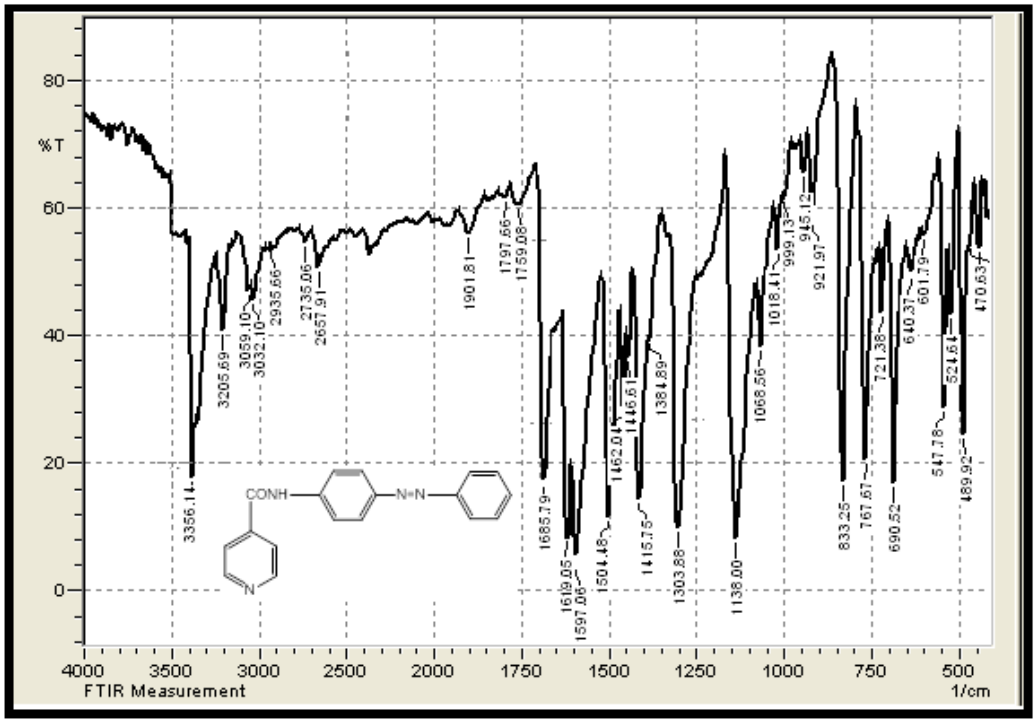


Fig 3-6: FTIR Spectrum of compound (A5).

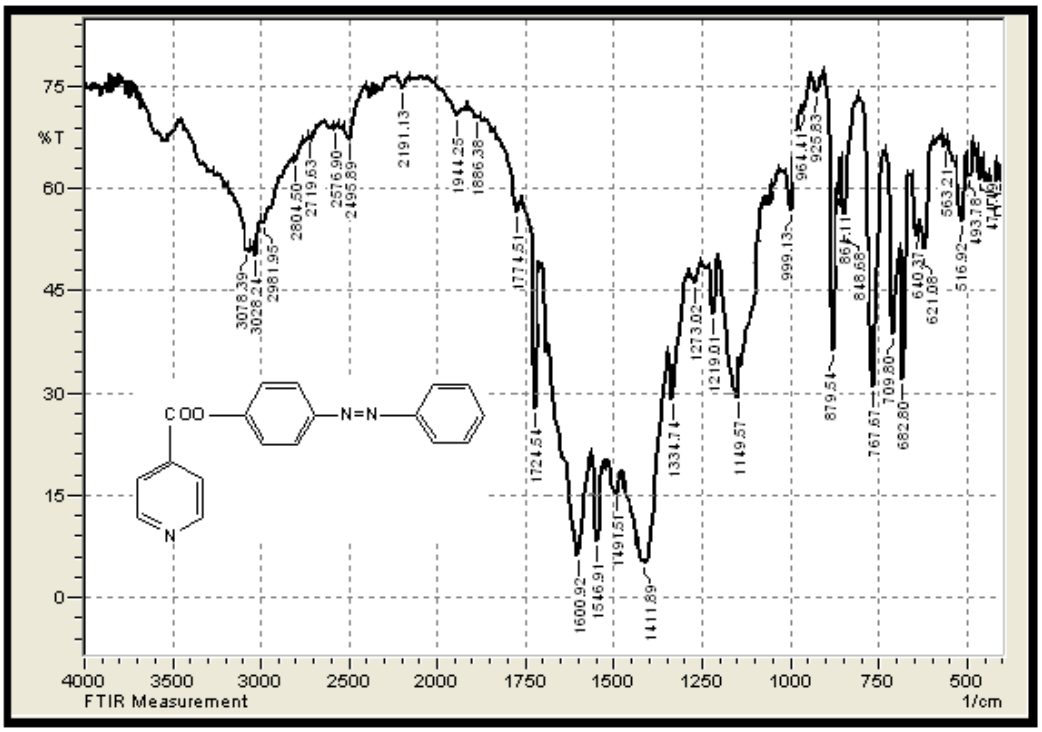


Fig 3-7: FTIR Spectrum of compound (A6).

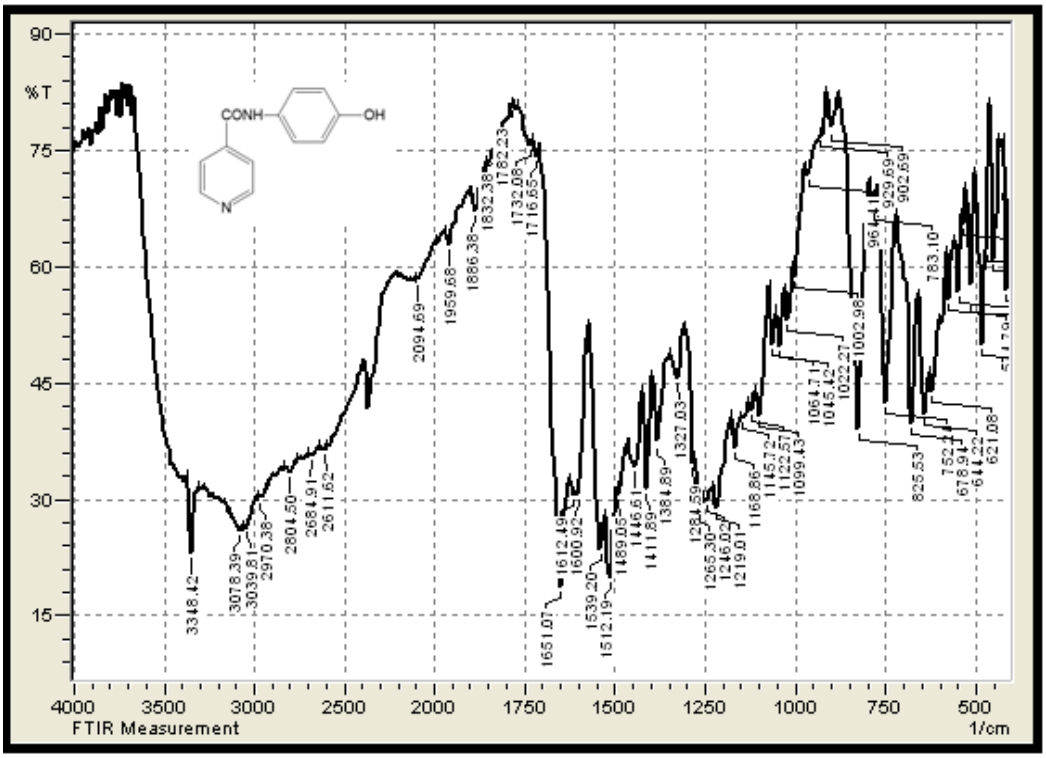


Fig 3-8: FTIR Spectrum of compound (A7).

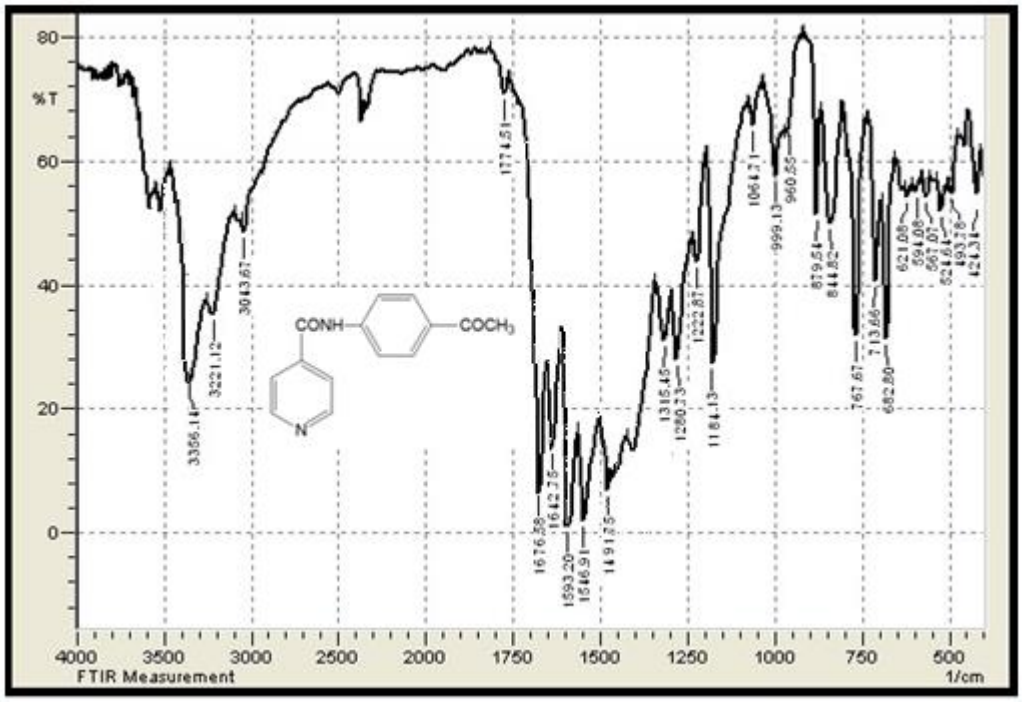


Fig 3-9: FTIR Spectrum of compound (A8).

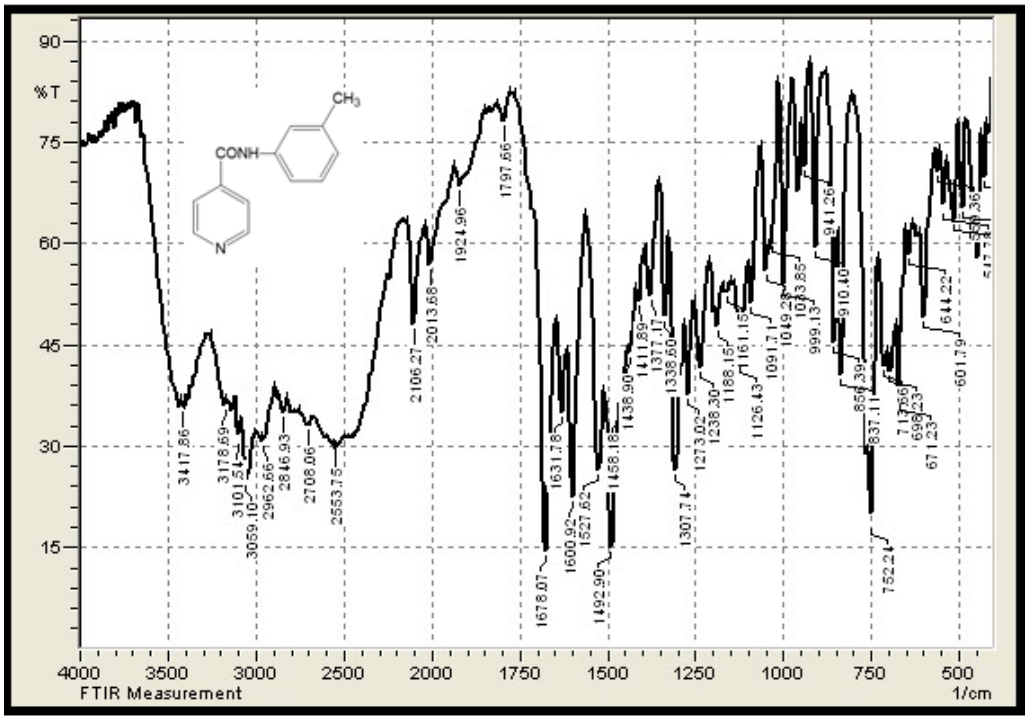


Fig 3-10: FTIR Spectrum of compound (A9).

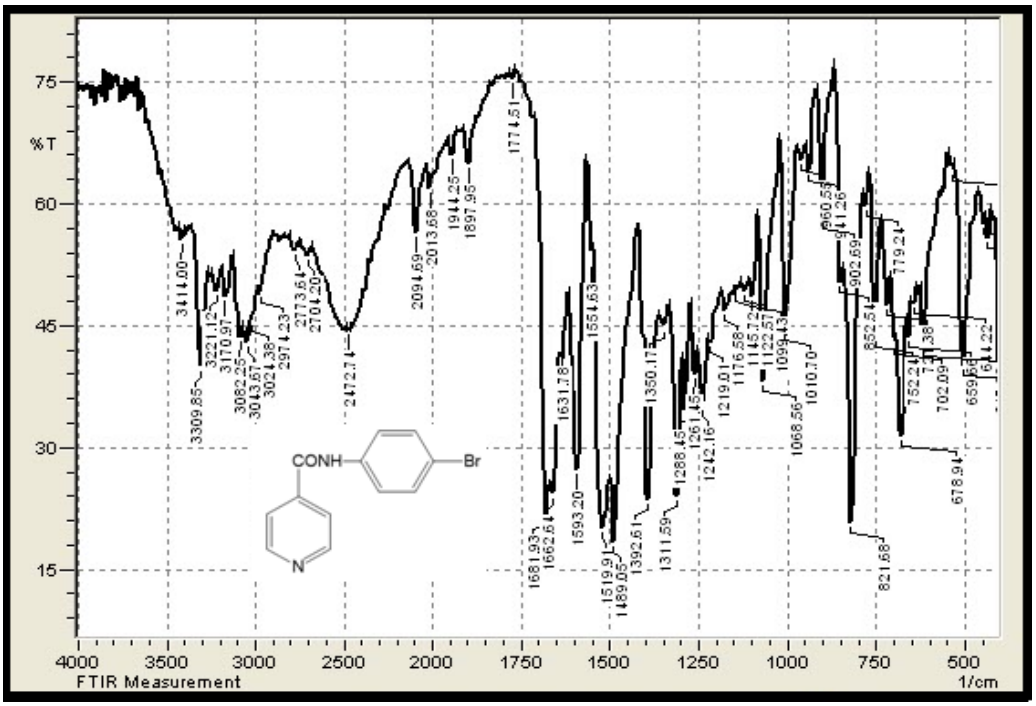


Fig 3-11: FTIR Spectrum of compound (A10).

3.2.2. Characterization of pyridinium salt derivatives (B1-B24).

The characterastic stretching bonds of FTIR spectra for pyridinium salt derivatives (B1-B24) are different stretching bonds of N-alkylation of pyridine ring by some alkyl halides (ethyl chloroacetate, benzyl chloride and n-propyl bromide). These alkyl chains reveal stretching aliphatic (C-H) bonds appear at (2850-3000 cm^{-1}) and stretching ester (C=O) bond at (1730-1750 cm^{-1}) [50]. Figures (3-12) to (3-35) represent the FTIR spectra for pyridinium salt derivatives (B1-B24), respectively. Table (3-2) shows the spectral data of FTIR of compounds (B1-B24).

Table 3-2: IR spectral data of prepared compounds (B1-B24) in cm^{-1}.

Comp. No.	ν C-H Aromatic	ν C-H aliphatic	ν C=C Aromatic	ν C=O	ν N-H	ν N=N
B1	3051	2947	1570	1743 ester 1643 amide	3120 3406	-
B2	3039	2924 2873	1635	1716 amide 1635 amide	3433 3116	-
B3	3047	2958 2850	1635	1697 amide 1635 amide	3406 3448	-
B4	3062	2981 2854	1643	1743 ester 1643 amide	3444 3132	-
B5	3055	2974 2858	1639	1685 amide	3398 3116	-
B6	3051	2974 2881	1616	1639 amide	3159 3417	-
B7	3055	2981 2870	1604	1735 ester 1647 amide	3398 3255	-
B8	3010	2978 2893	1627	1678 amide 1651 amide	3433 3244	-
B9	3051	2931 2877	1600	1681 amide 1639 amide	3410 3363	-
B10	3032	2997 2858	1600	1751ester 1670 amide	3410	-
B11	3039	2927 2839	1600	1674 amide	3433	-
B12	3043	2935 2870	1600	1674 amide	3414	-
B13	3043	2908 2866	1604	1735 ester 1604 amide	3406	1519
B14	3055	2931 2877	1627	1639 amide	3433	1570
B15	3055	2962 2873	1600	1627 amide	3410	1512
B16	3062	2985 2939	1600	1743 ester	-	1508

B17	3059	2935 2870	1604	1732 ester	-	1508
B18	3059	2924 2854	1600	1732 ester	-	1516
B19	3047	2927 2877	1600	1743 ester 1666 amide	3383	-
B20	3051	2981 2893	1612	1666 amide	3232	-
B21	3059	2931 2877	1608	1666 amide	3275	-
B22	3051	2978 2931	1635	1735 ester 1635 amide	3360	-
B23	3055	2924 2854	1608	1735 ester 1678 amide	3402	-
B24	3082	2978 2858	1600	1739 ester 1681 amide	3429	-

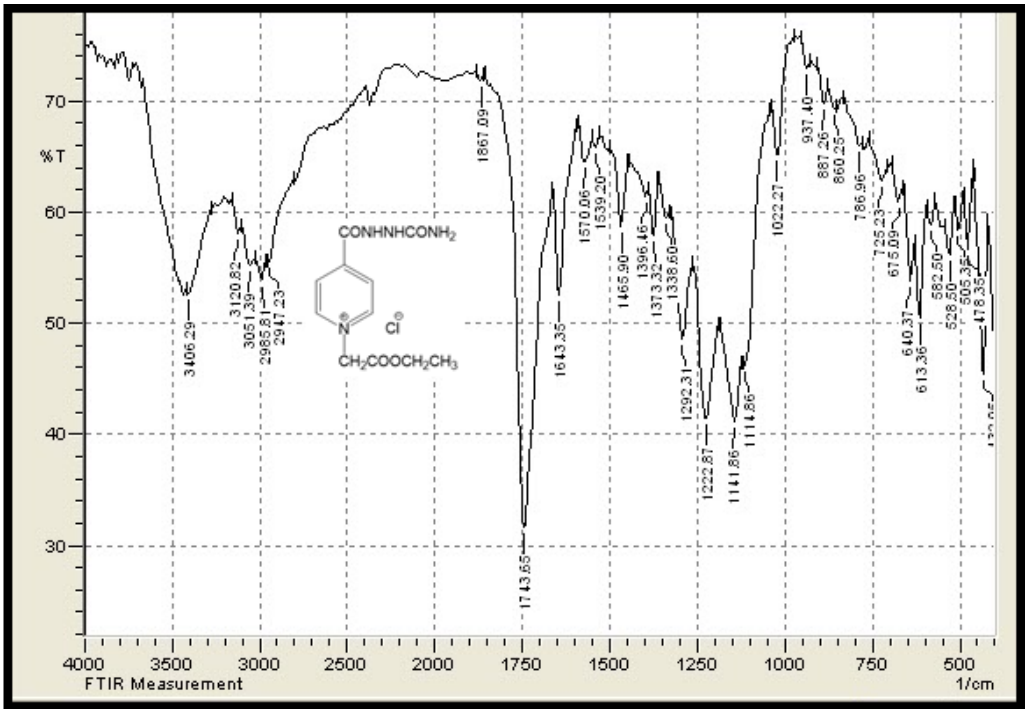


Fig 3-12: FTIR Spectrum of compound (B1).

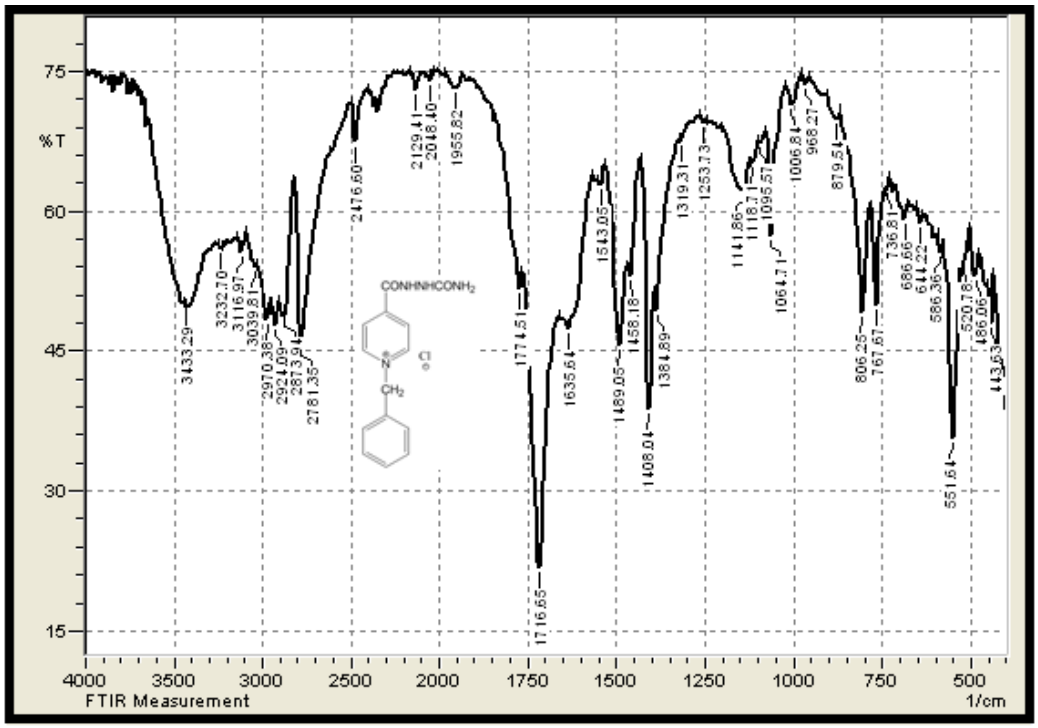


Fig 3-13: FTIR Spectrum of compound (B2).

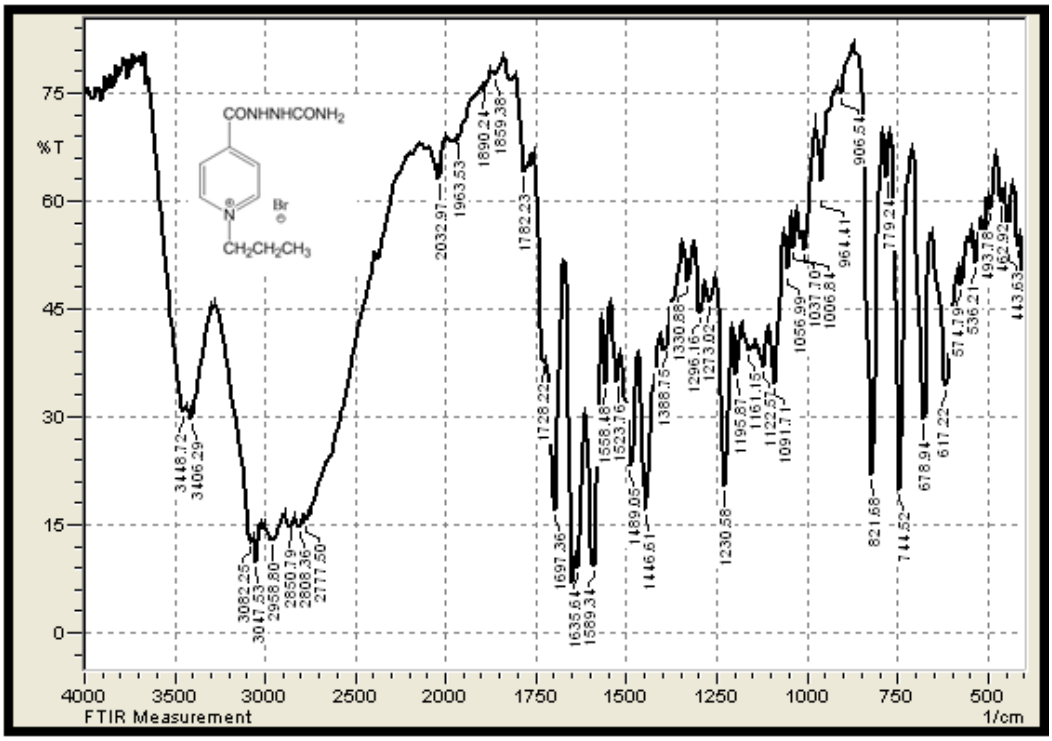


Fig 3-14: FTIR Spectrum of compound (B3).

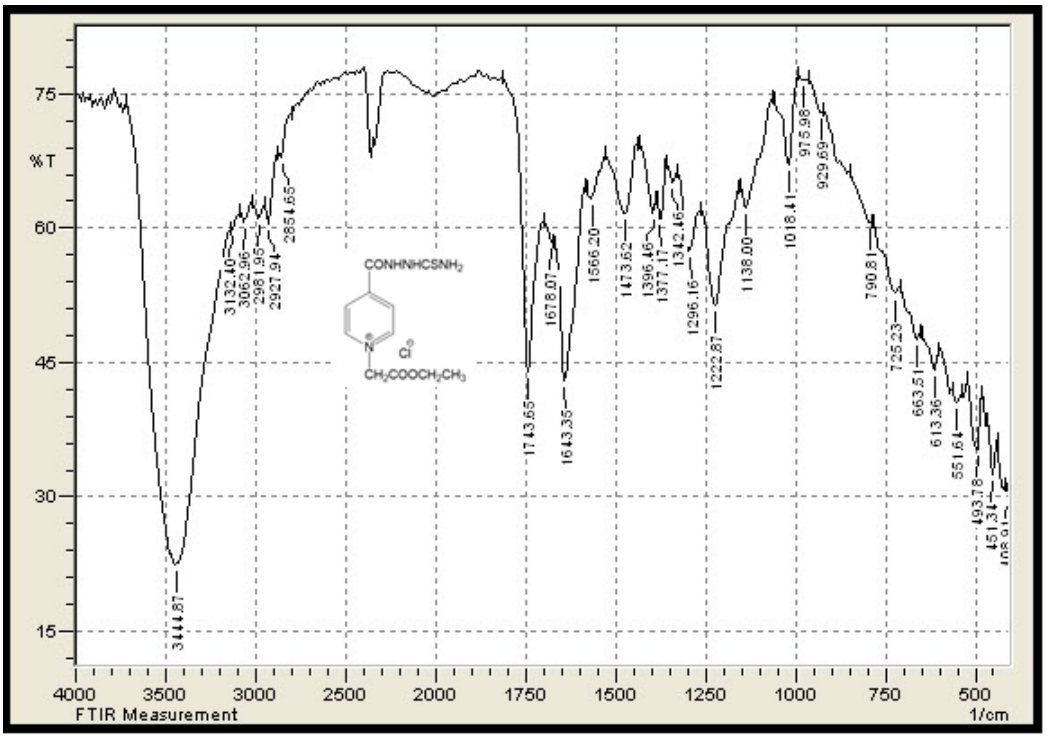


Fig 3-15: FTIR Spectrum of compound (B4).

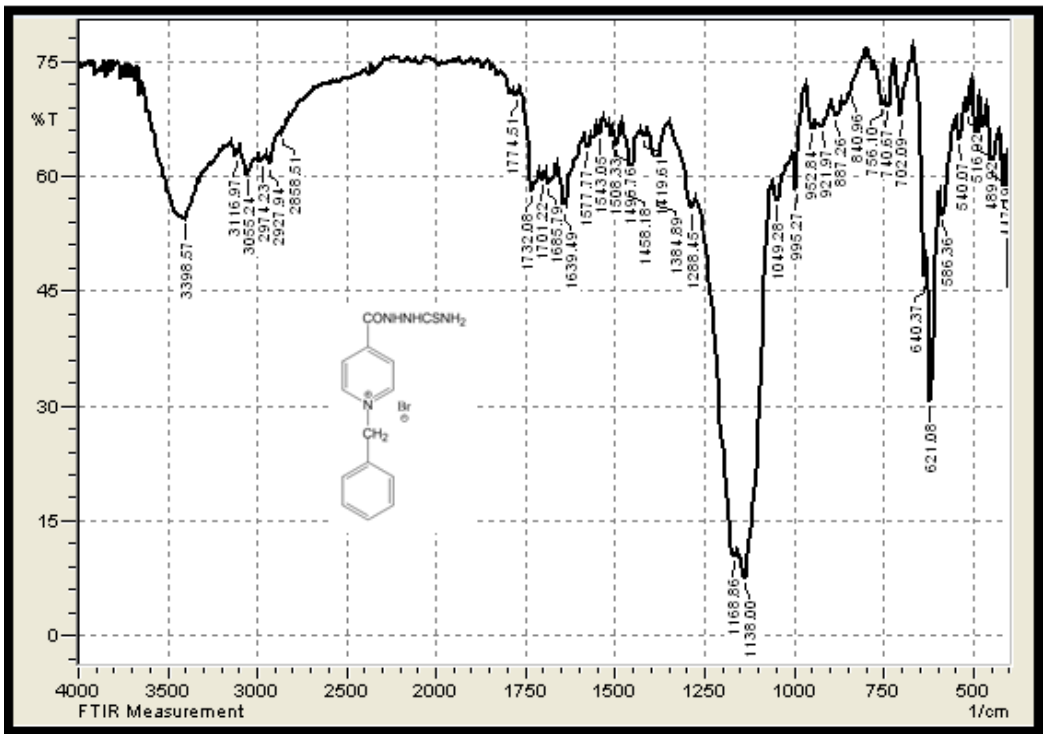


Fig 3-16: FTIR Spectrum of compound (B5).

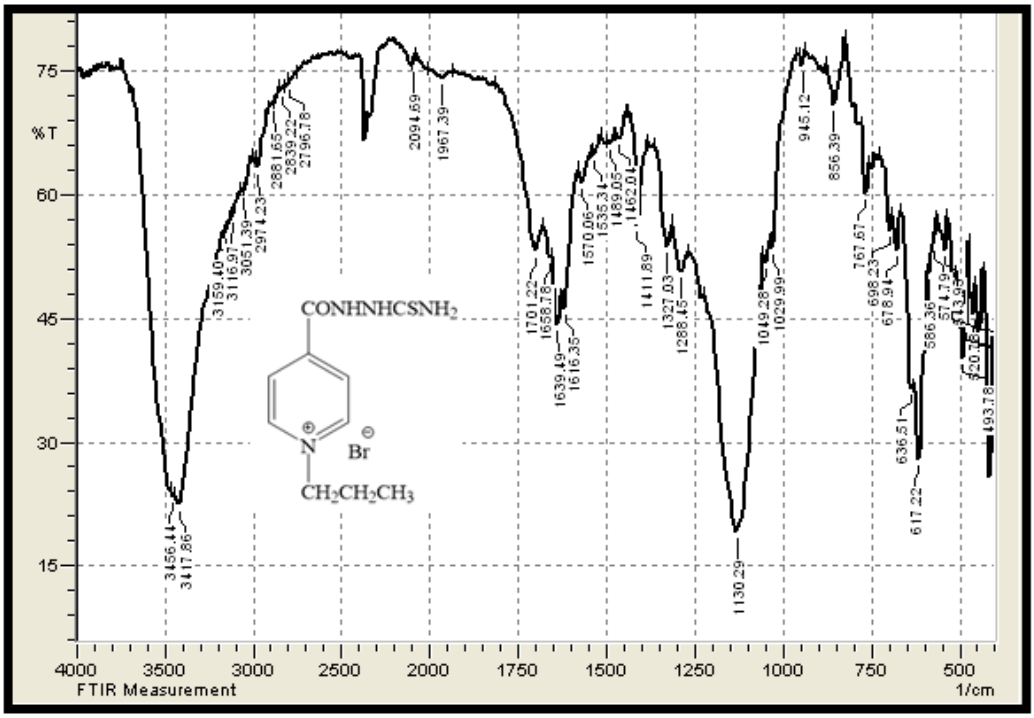


Fig 3-17: FTIR Spectrum of compound (B6).

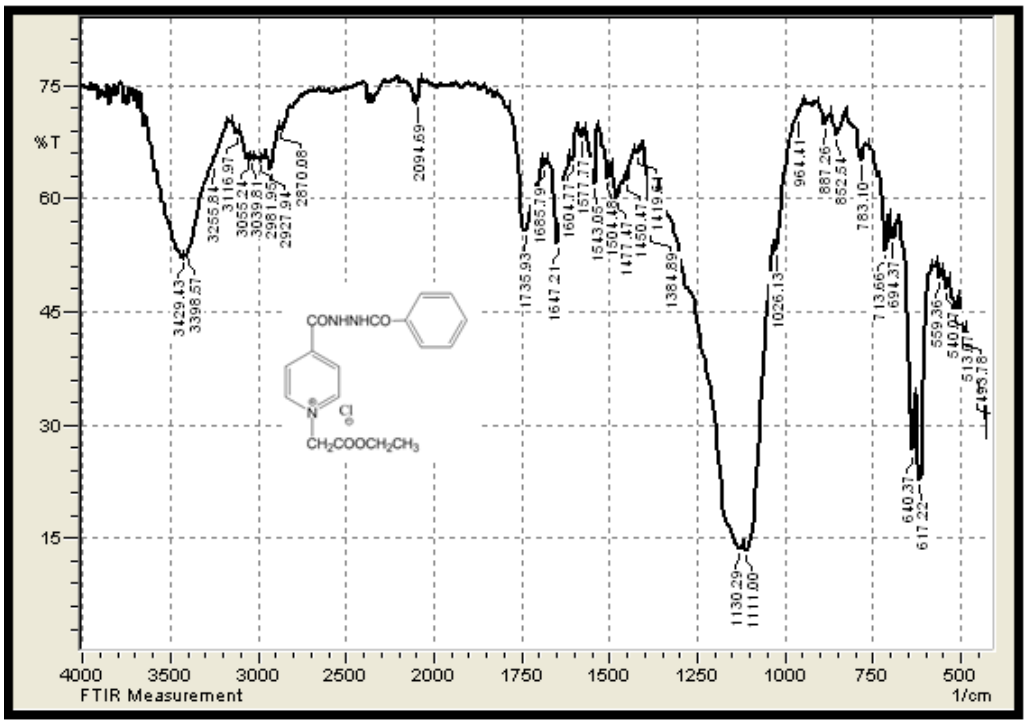


Fig 3-18: FTIR Spectrum of compound (B7).

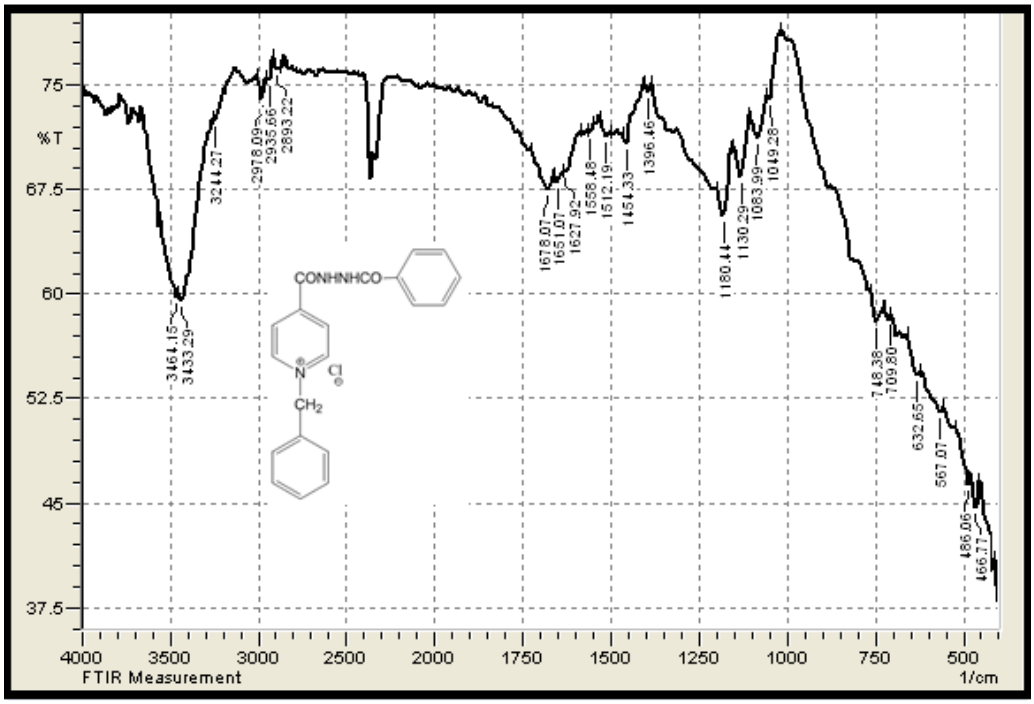


Fig 3-19: FTIR Spectrum of compound (B8).

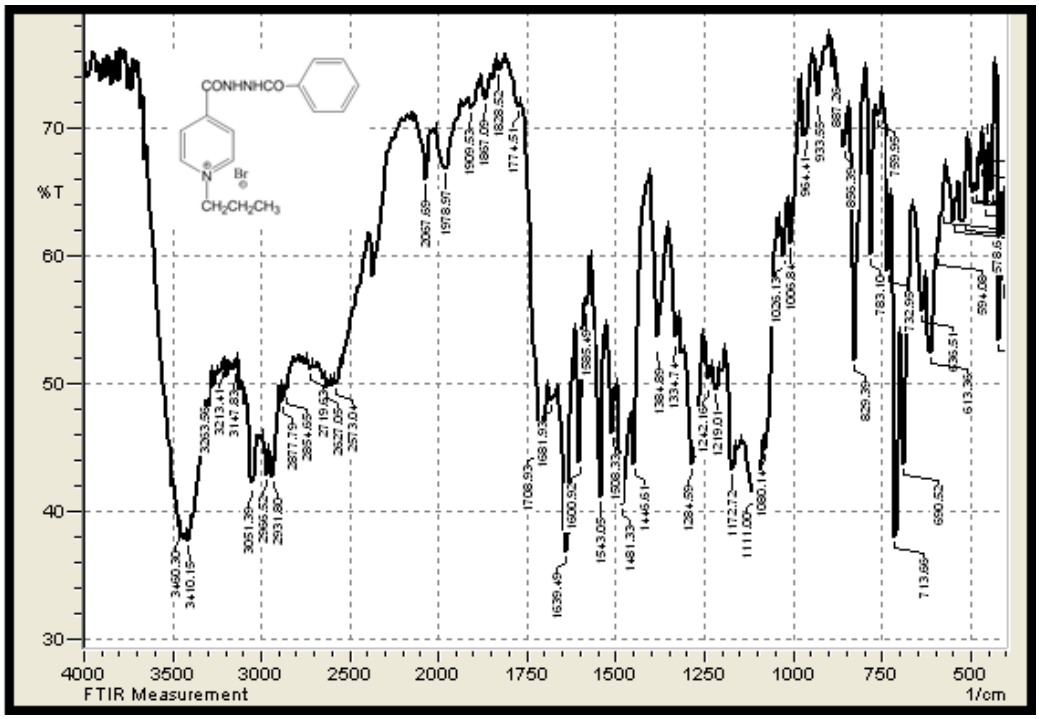


Fig 3-20: FTIR Spectrum of compound (B9).

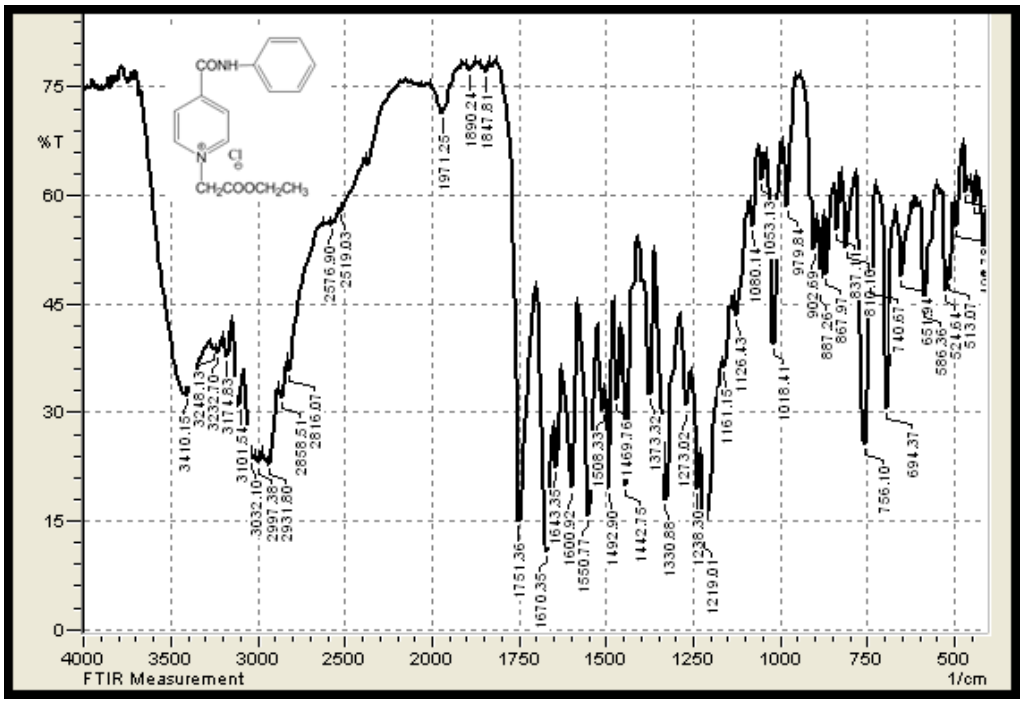


Fig 3-21: FTIR Spectrum of compound (B10).

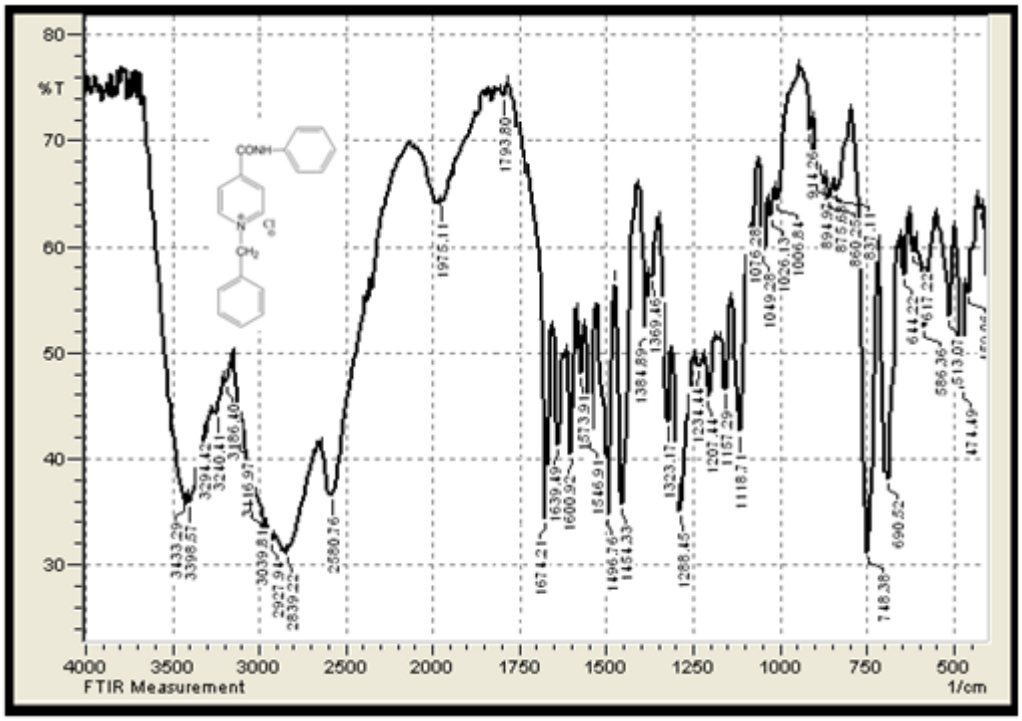


Fig 3-22: FTIR Spectrum of compound (B11).

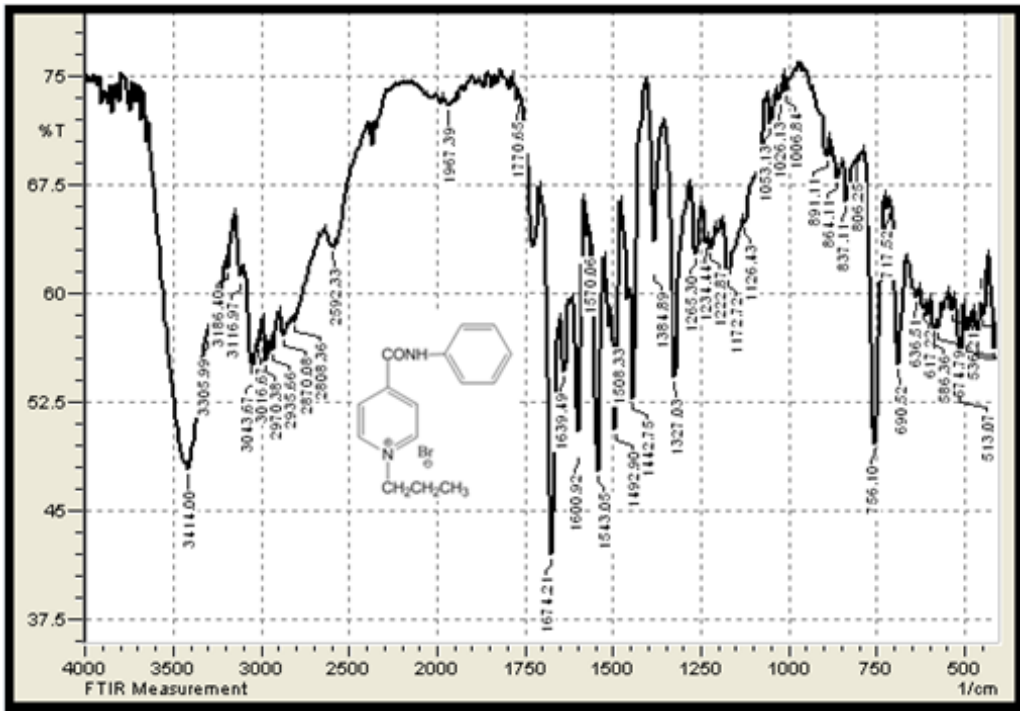


Fig 3-23: FTIR Spectrum of compound (B12).

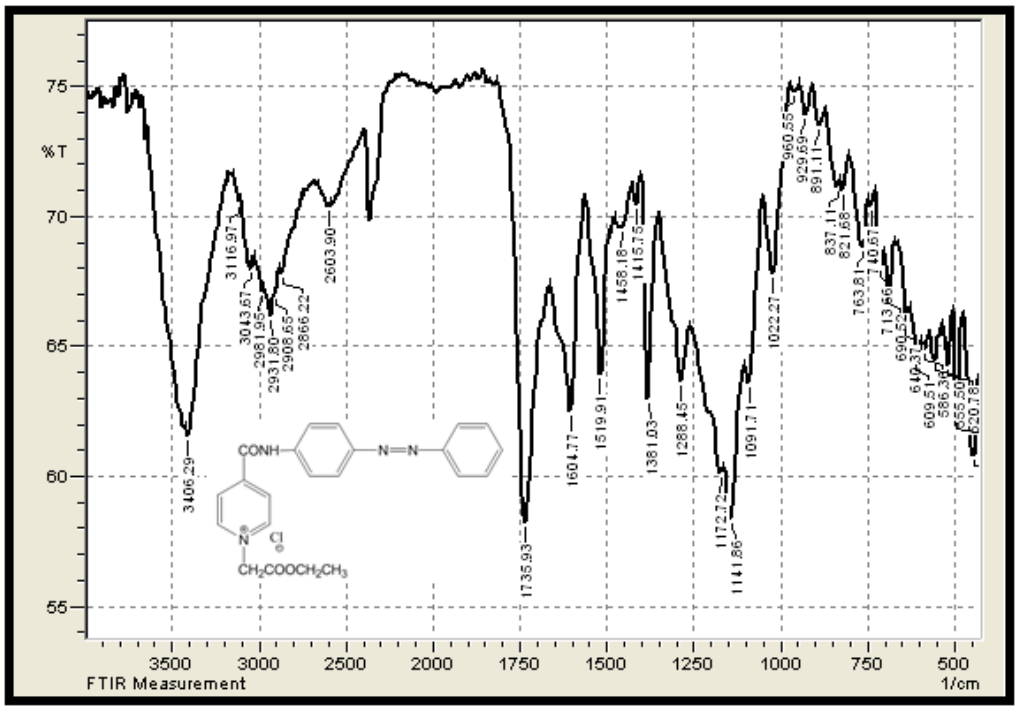


Fig 3-24: FTIR Spectrum of compound (B13).

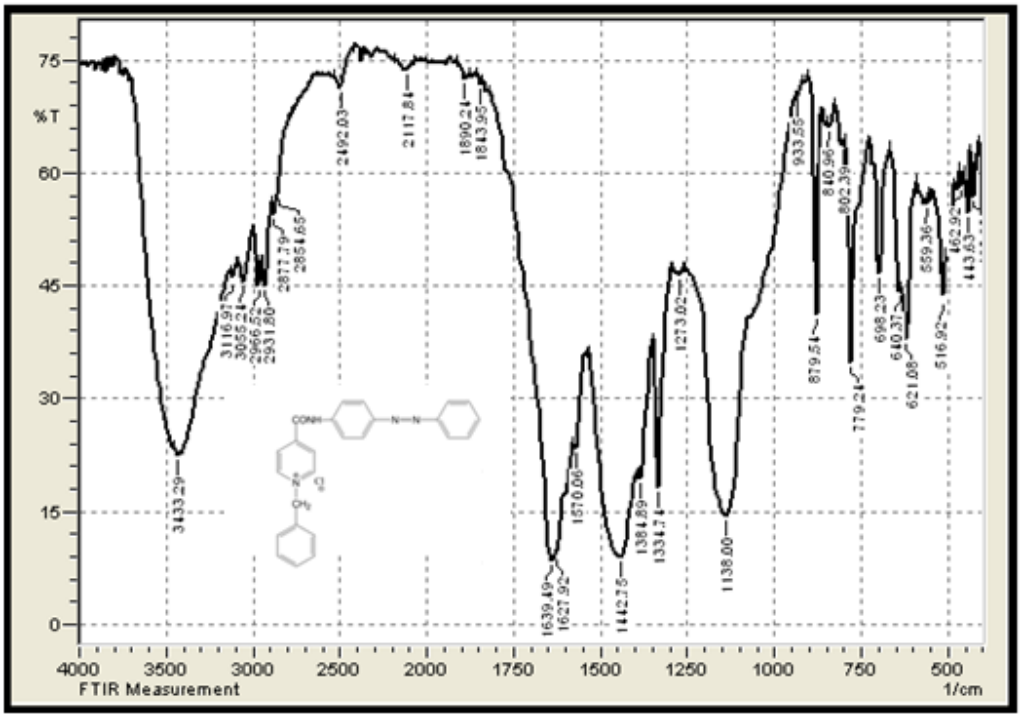


Fig 3-25: FTIR Spectrum of compound (B14).

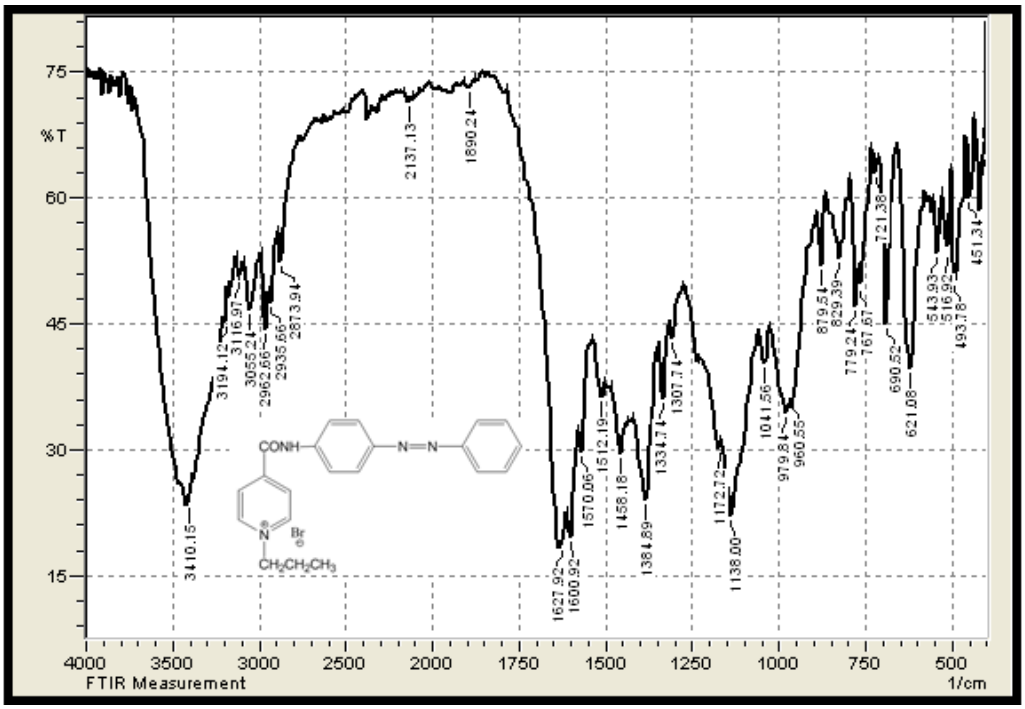


Fig 3-26: FTIR Spectrum of compound (B15).

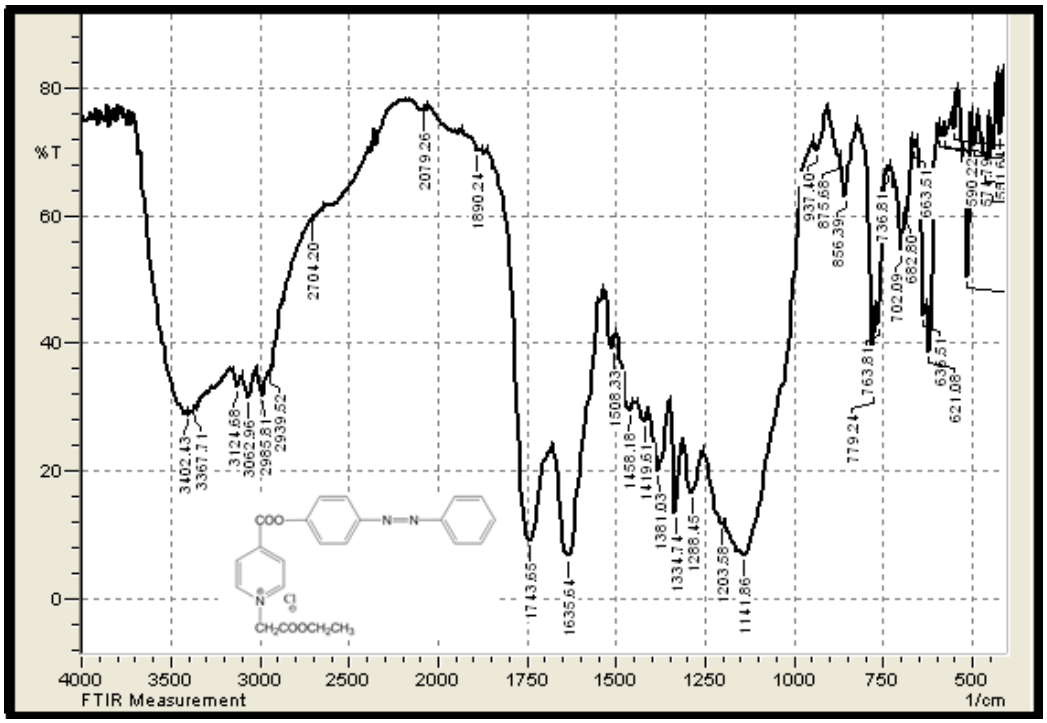


Fig 3-27: FTIR Spectrum of compound (B16).

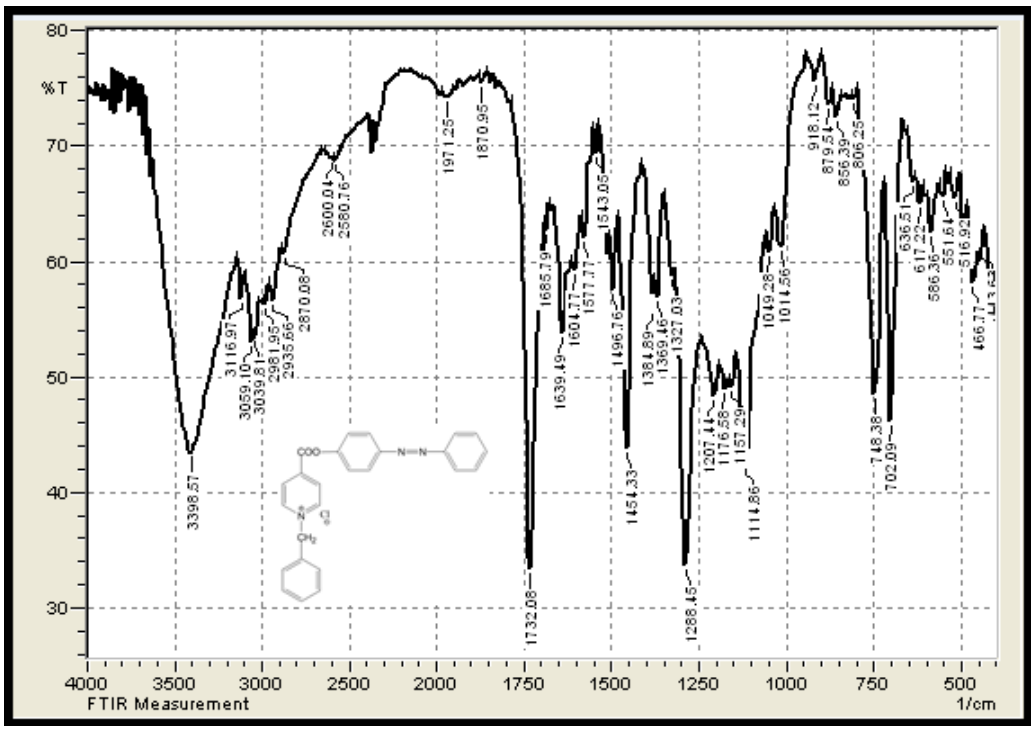


Fig 3-28: FTIR Spectrum of compound (B17).

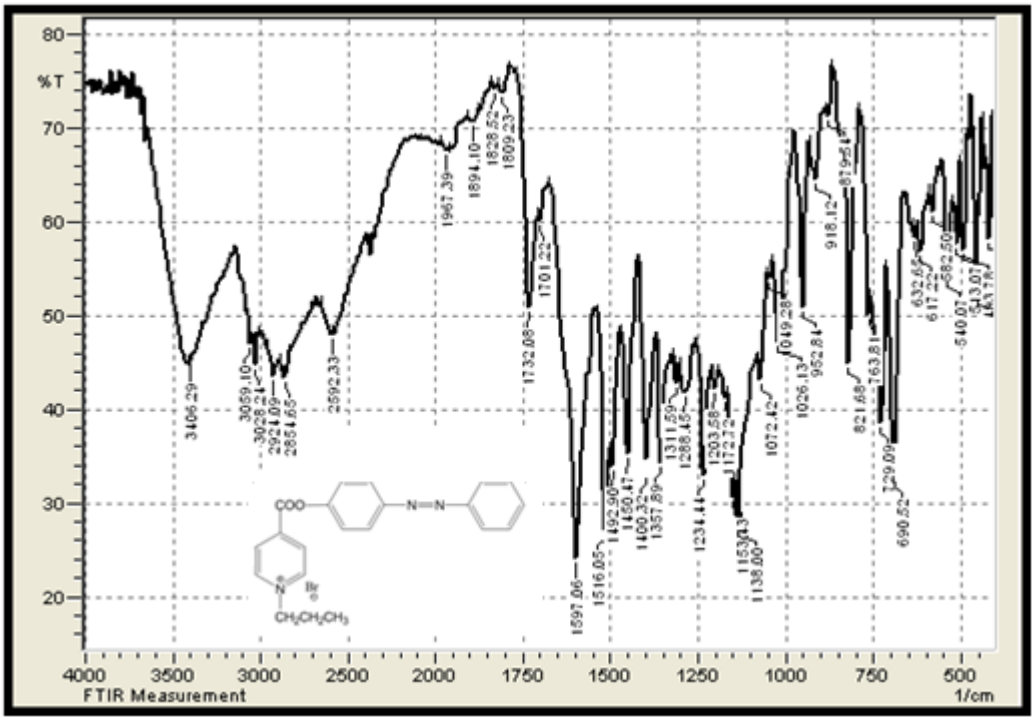


Fig 3-29: FTIR Spectrum of compound (B18).

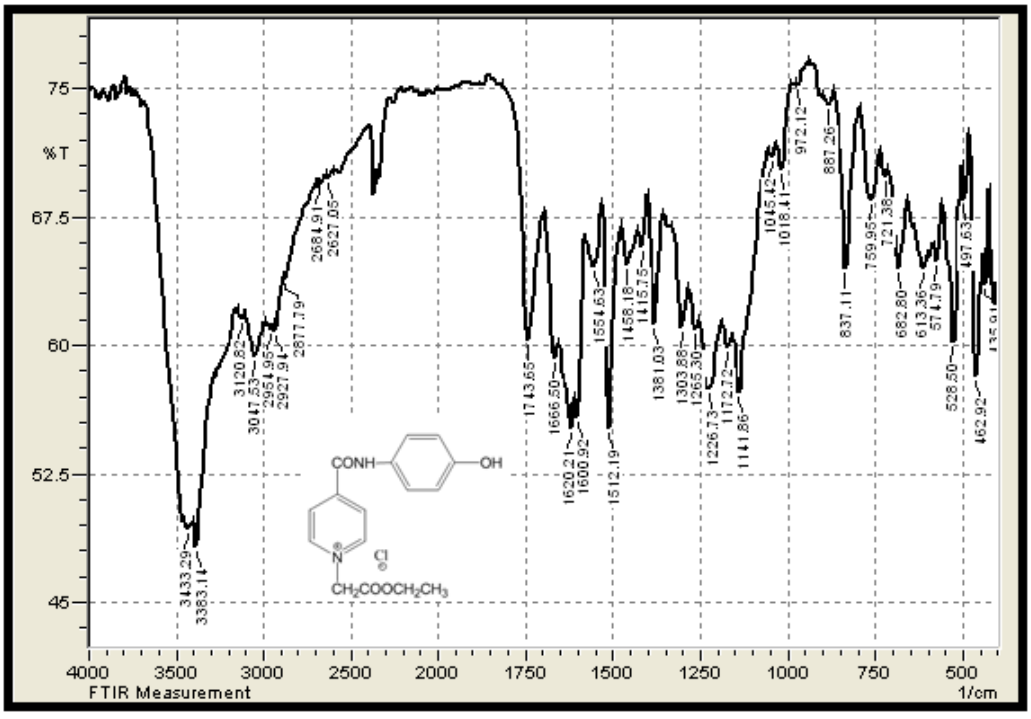


Fig 3-30: FTIR Spectrum of compound (B19).

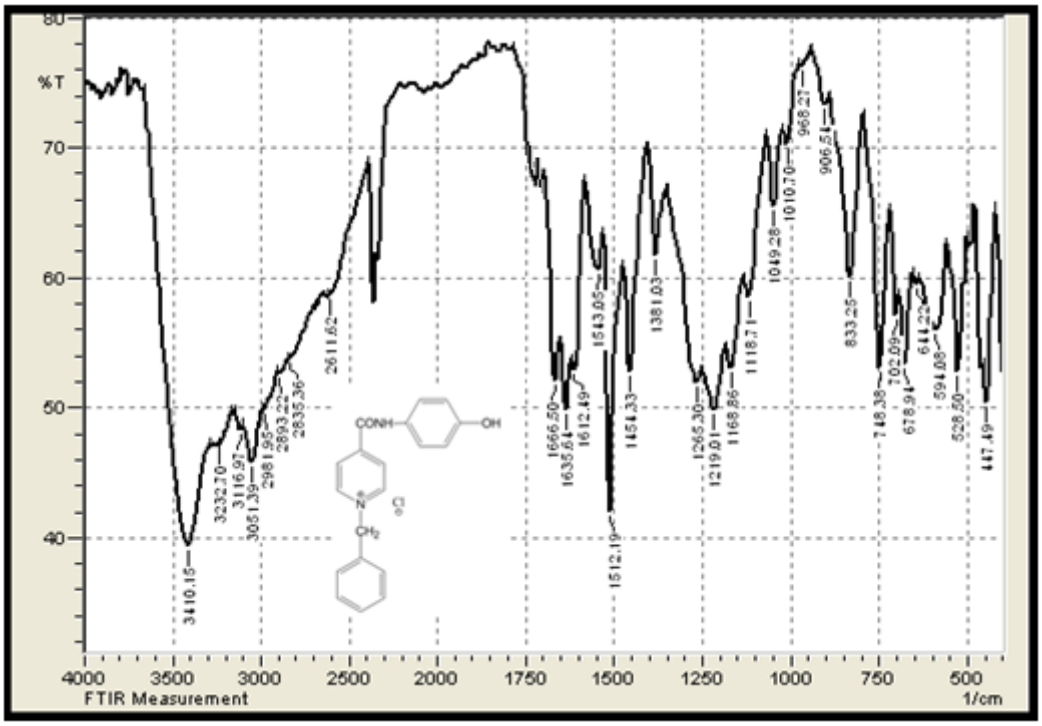


Fig 3-31: FTIR Spectrum of compound (B20).

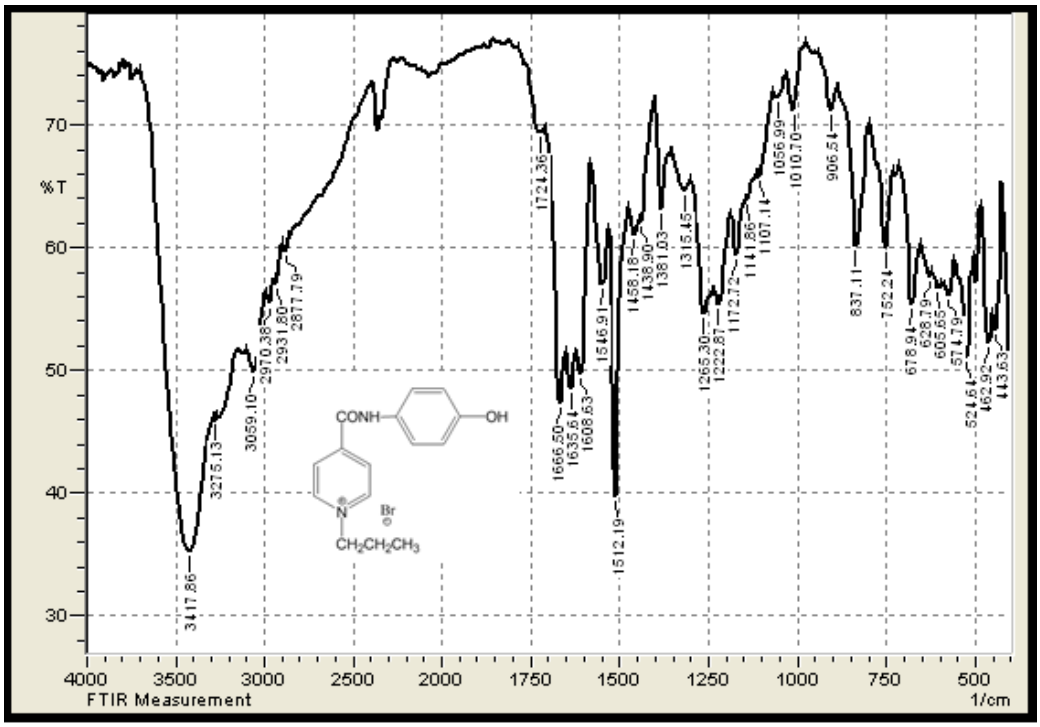


Fig 3-32: FTIR Spectrum of compound (B21).

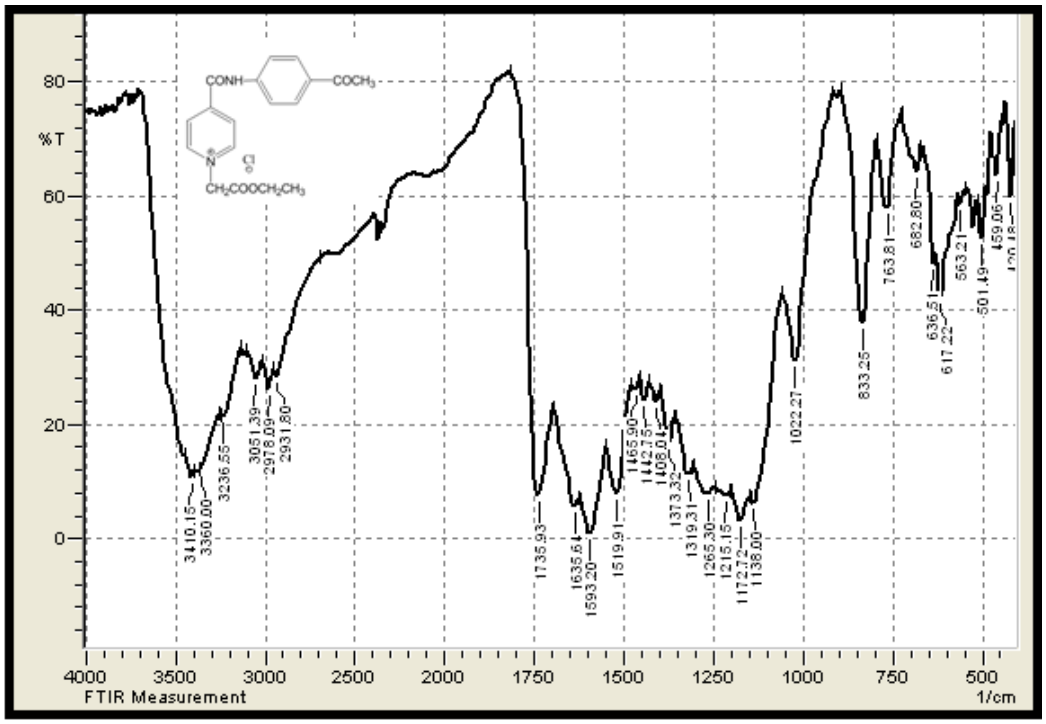


Fig 3-33: FTIR Spectrum of compound (B22).

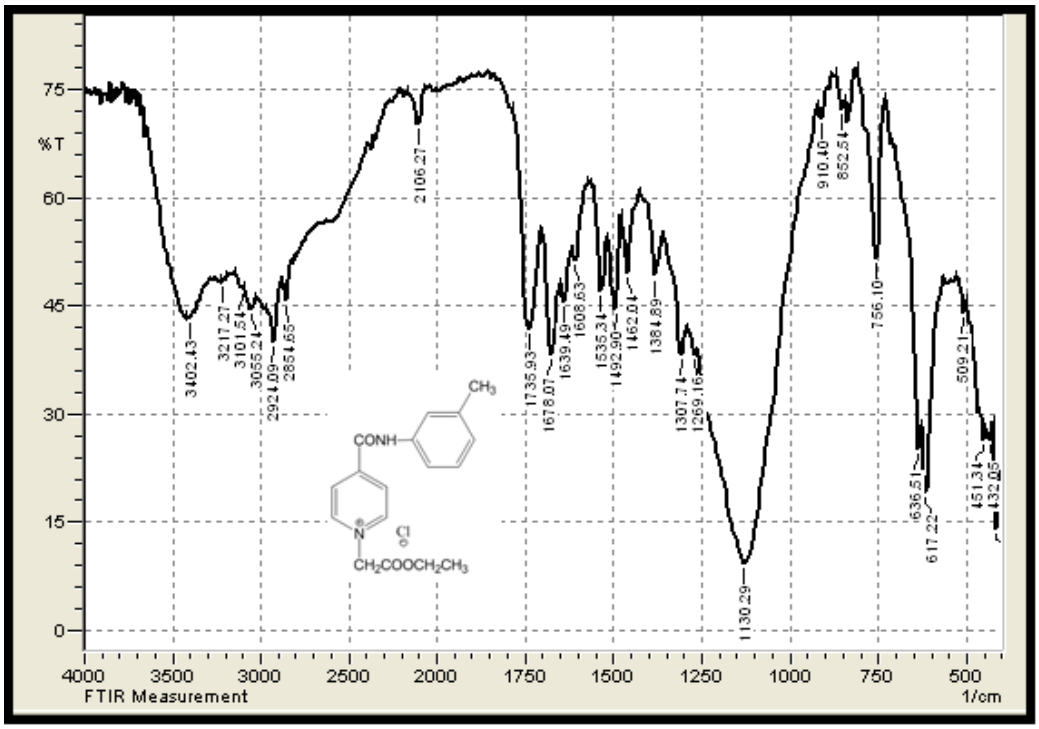


Fig 3-34: FTIR Spectrum of compound (B23).

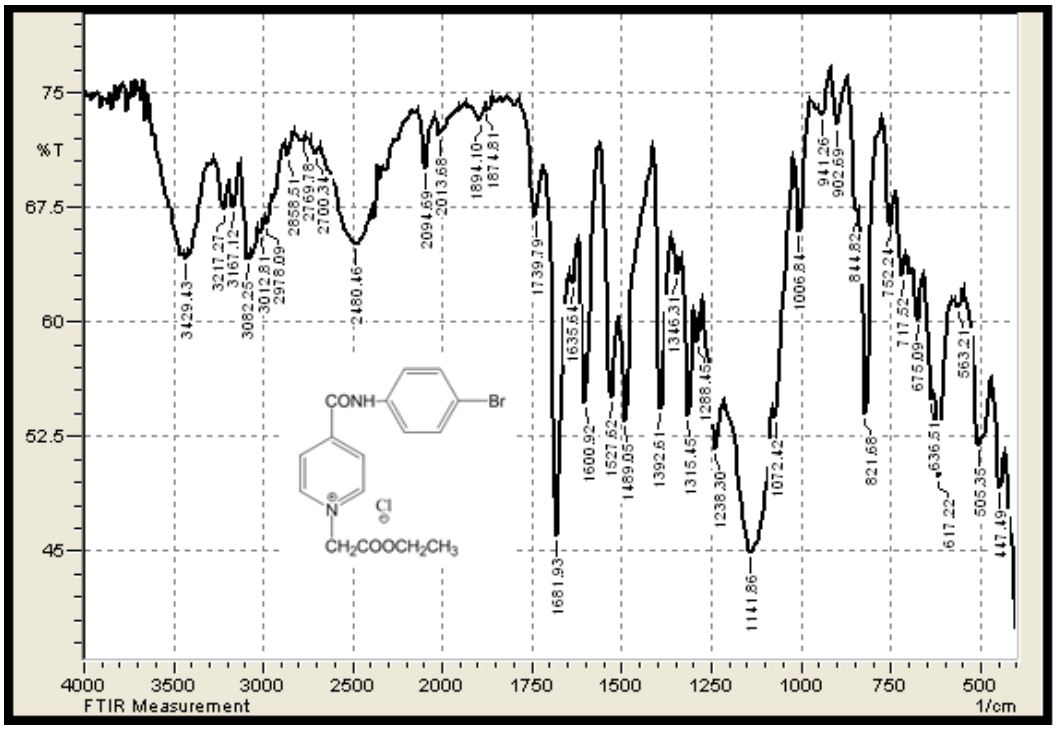
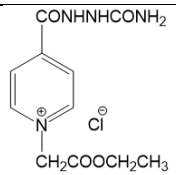
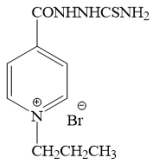
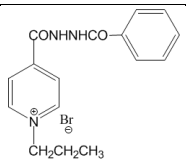
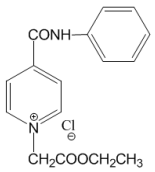
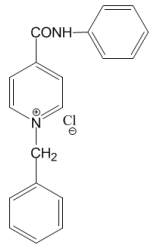
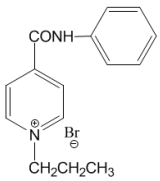
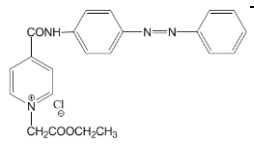


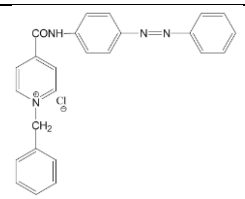
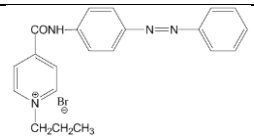
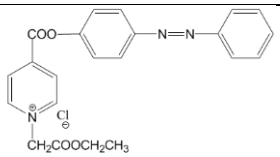
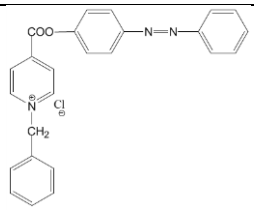
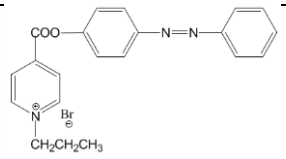
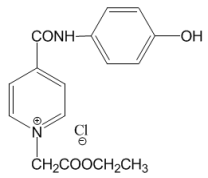
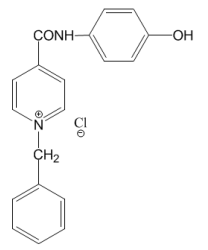
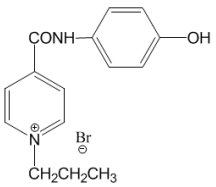
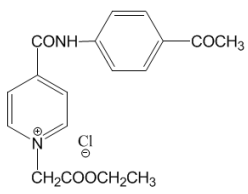
Fig 3-35: FTIR Spectrum of compound (B24).

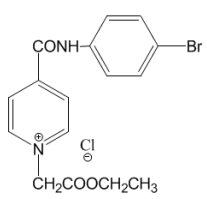
3.3. ^{1}H-NMR spectrum of a number of final prepared compounds.

The ^{1}H-NMR spectra of pyridinium salt derivatives (B1, B3, B6, B9-B20, B22 and B24) were confirmed their structures by appearing aliphatic hydrogen (C-H) in differernt chemical shift positions [51]. In pyridinium salt derivative (B1), ^{1}H-NMR spectrum (DMSO-d6), δ, ppm: 8.6-9.3 (3H, s, NH, amide), 8.4-9.1 (4H, m, Py-H), 5.7 (2H, s, -CH_2-N^+-), 3.8 (2H, m, -CH_2-O-), 1.3 (3H, t, CH_3-), as showing in Figure 3-36. The Figures (3-36) to (3-51) and Table 3-3 are predicted ^{1}H-NMR spectral data for a number of final pyridinium salt derivatives (B1, B3, B6, B9-B20, B22 and B24), respectively.

Table 3-3: ^{1}H-NMR spectral data of prepared compounds in ppm.

Comp.	Structure	^{1}H-NMR spectral data, ppm(δ)
B1		8.6-9.3 (4H,d, NH, amide), 8.4-9.1 (4H, m, Py-H), 5.7 (2H, s, -CH_2-N^+-), 3.8 (2H, q, -CH_2-O-), 1.3 (3H, t, CH_3-)
B3		8.9-9.1 (4H, d, NH, amide), 8.1-8.3 (4H, m, Py-H), 4.7 (2H, t, -CH_2-N^+-),$^+$-), 1.3 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B6		8.7-9.4 (4H, d, NH, amide), 8.1-8.8 (4H, m, Py-H), 4.6 (2H, t, -CH_2-N^+-), 1.9 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B9		8.8-9.4 (2H, d, NH, amide), 8.1-8.8 (4H, m, Py-H), 7.4-7.9 (5H, m, aromatic-H), 4.6 (2H, t, -CH_2-N^+-), 1.9 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B10		9.4 (1H, s, NH, amide), 8.0-8.8(4H, m, Py-H), 7.2-7.9 (5H, m, aromatic-H), 4.4 (2H, s, -CH_2-N^+-), 3.4 (2H, q, -CH_2-O-), 0.9(3H, t, CH_3-),
B11		9.4 (1H, s, NH, amide), 7.8-8.8 (4H, m, Py-H), 7.2-8.0 (10H, m, aromatic-H), 6.1(2H, s, -CH_2-N^+-)
B12		9.4(1H, s, NH, amide), 8.0-8.5(4H, m, Py-H), 7.2-8.0 6.4-7.8 (5H, m, aromatic-H), 4.8 (2H, t, -CH_2-N^+-), 1.3 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B13		9.2 (1H, s, NH, amide), 7.7-9.0 (4H, m, Py-H), 6.8-8.0 (9H, d, aromatic-H), 4.5 (2H, s, -CH_2-N^+-), 3.8 (2H, m, -CH_2-O-), 1.1 (3H, t, CH_3-)

B14		9.4 (1H, s, NH, amide), 7.8-8.8 (4H, m, Py-H), 6.8-7.7 (14H, d, aromatic-H),6.0 (2H, s, -CH_2-N^+-)
B15		9.0 (1H, s, NH, amide), 7.8-8.3 (4H, m, Py-H), 6.8-7.7 (9H, d, aromatic-H), 4.3 (2H, t, -CH_2-N^+-), 1.3 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B16		8.0-9.0 (4H, m, Py-H), 6.8-7.9 (9H, d, aromatic-H), 4.5 (2H, s, -CH_2-N^+-), 3.9 (2H, m, -CH_2-O-), 1.1 (3H, t, CH_3-),
B17		7.8-8.8 (4H, m, Py-H), 7.2-7.7 (10H, m, aromatic-H), 6.1 (2H, s, -CH_2-N^+-)
B18		7.8-8.3 (4H, m, Py-H), 6.8-7.7 (9H, d, aromatic-H), 4.6 (2H, t, -CH_2-N^+-), 1.3 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B19		11.1 (1H, s, O-H), 9.5 (1H, s, NH, amide), 8.0-9.0 (4H, m, Py-H), 6.8-7.9 (4H, d, aromatic-H), 4.6 (2H, s, -CH_2-N^+-), 3.9 (2H, m, -CH_2-O-), 1.1 (3H, t, CH_3-),
B20		11.1 (1H, s, O-H), 9.4 (1H, s, NH, amide), 7.8-8.8 (4H, m, Py-H), 7.2-7.7 (9H, d, aromatic-H), 6.0 (2H, s, -CH_2-N^+-)
B21		11.1 (1H, s, O-H), 9.0 (1H, s, NH, amide), 7.8-8.3 (4H, m, Py-H), 6.8-7.7 (4H, d, aromatic-H), 4.6 (2H, t, -CH_2-N^+-), 1.3 (2H, m, -CH_2-), 0.9 (3H, t, CH_3-)
B22		9.5 (1H, s, NH, amide), 8.0-9.0 (4H, m, Py-H), 6.8-7.9 (4H, d, aromatic-H), 4.6 (2H, s, -CH_2-N^+-), 3.9 (2H, m, -CH_2-O-), 2.5 (3H, s, -$COCH_3$), 1.1 (3H, t, CH_3-)

B24		9.4 (1H, s, NH, amide), 8.1-8.6 (4H, m, Py-H), 7.5-7.9 (4H, d, aromatic-H), 4.5 (2H, s, -CH_2-N^+-), 3.9 (2H, m, -CH_2-O-), 1.1 (3H, t, CH_3-)

s: singlet, d: doublet, t: triplet, m: multiplet

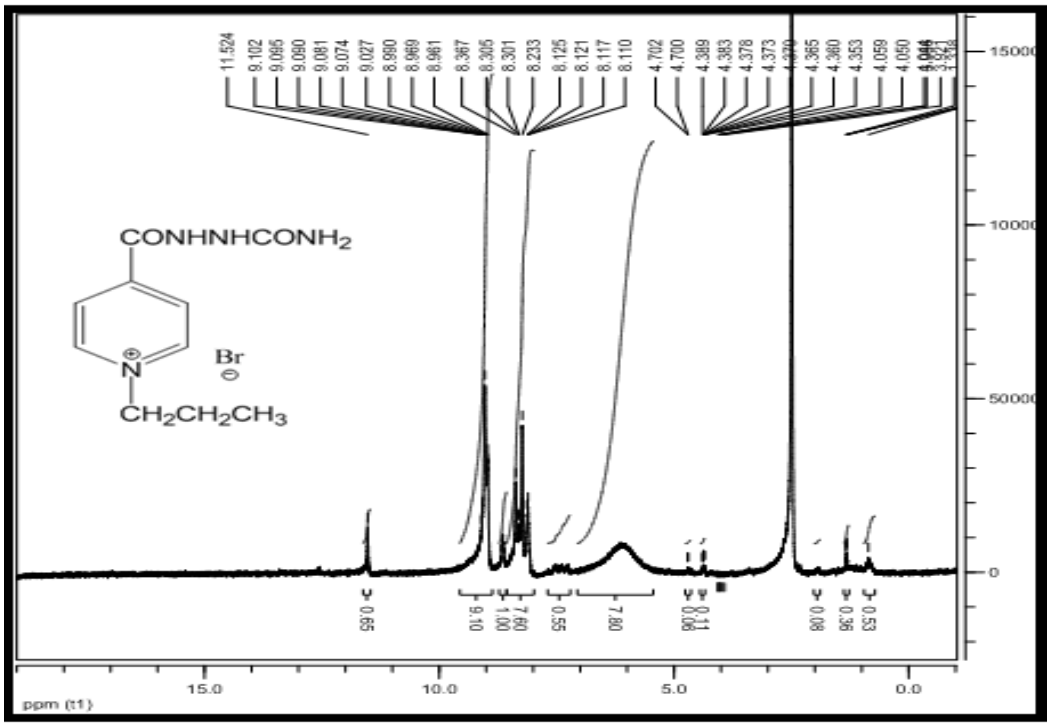


Fig. 3-36: ^{1}H-NMR spectrum of compound (B3)

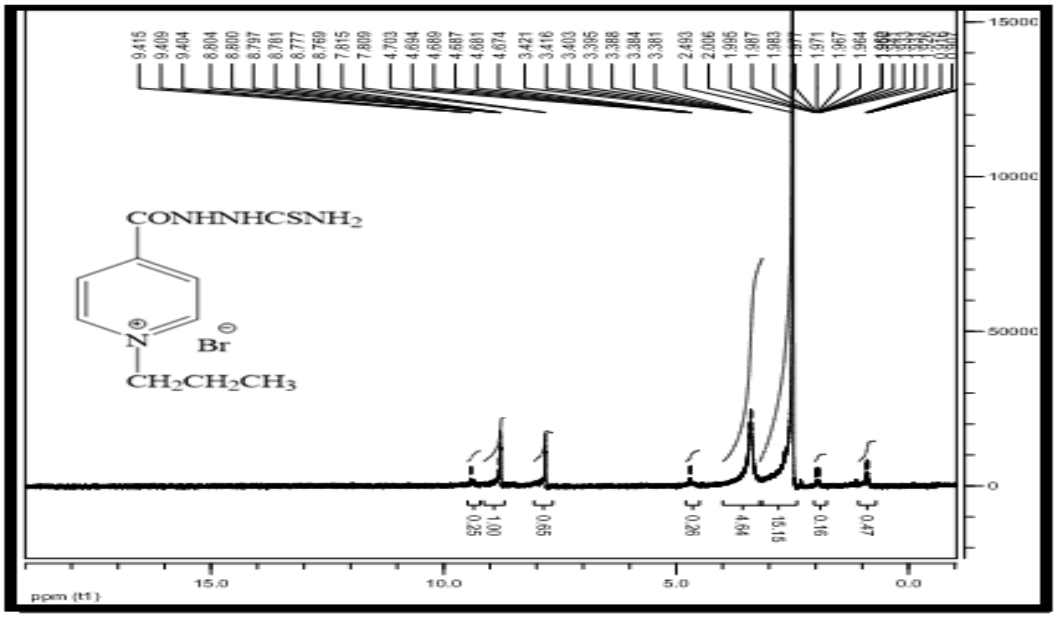


Fig. 3-37: ^{1}H-NMR spectrum of compound (B6)

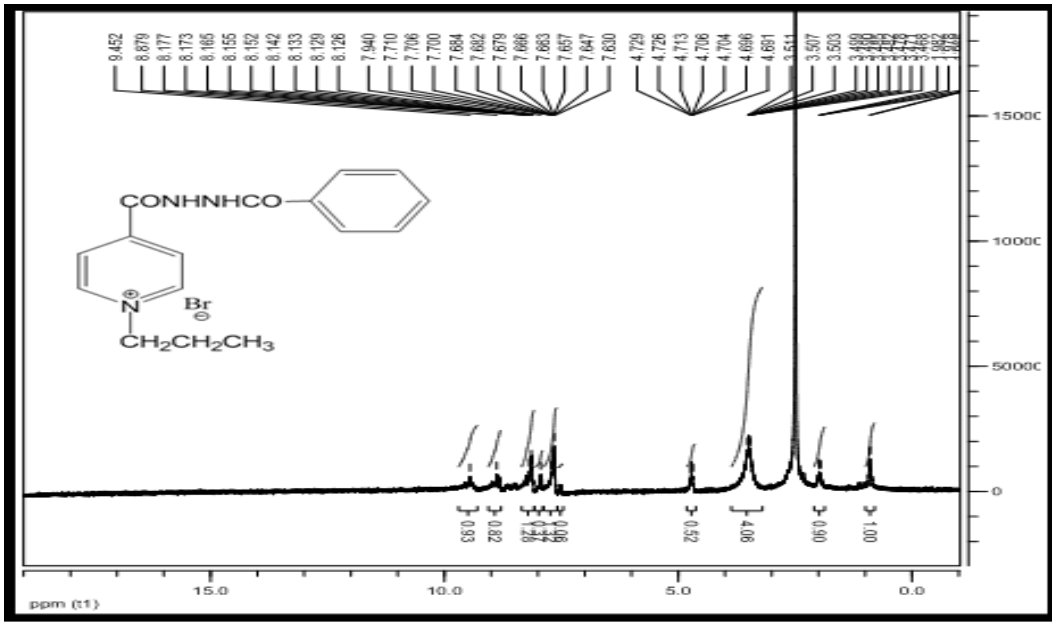


Fig. 3-38: ^{1}H-NMR spectrum of compound (B9)

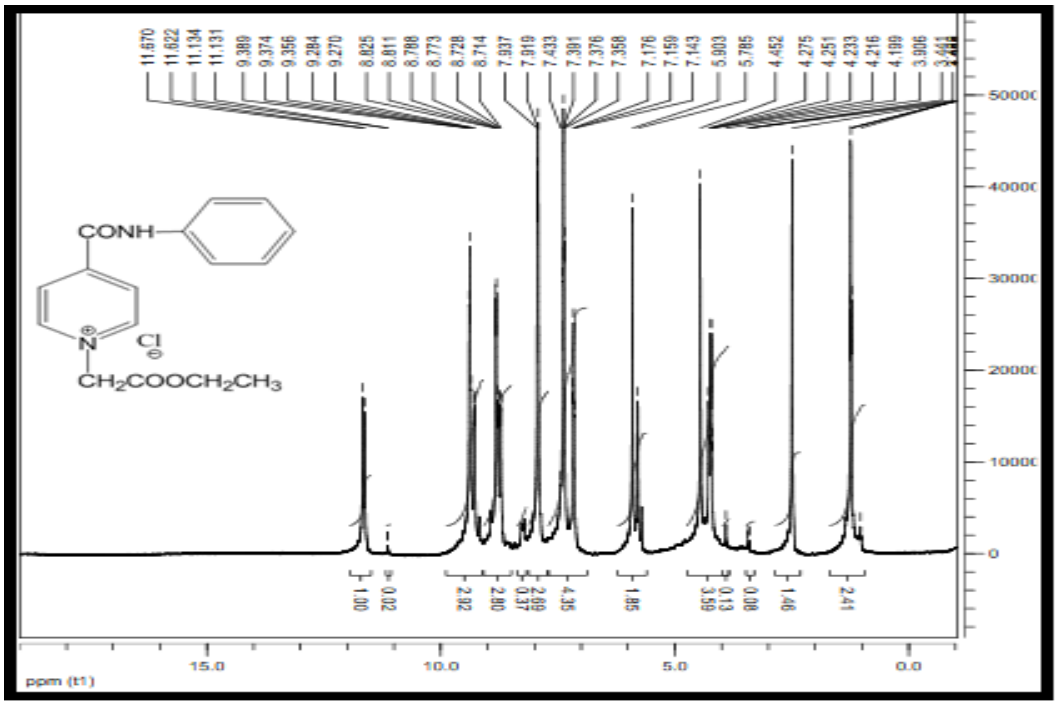


Fig. 3-39: ^{1}H-NMR spectrum of compound (B10)

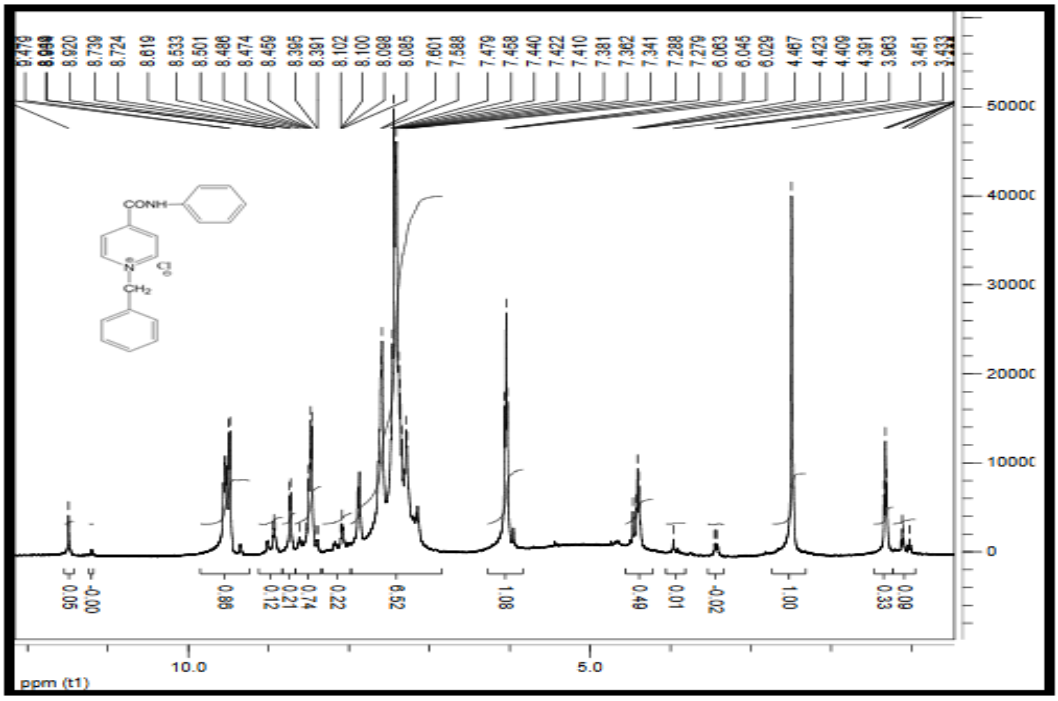


Fig. 3-40: ^{1}H-NMR spectrum of compound (B11)

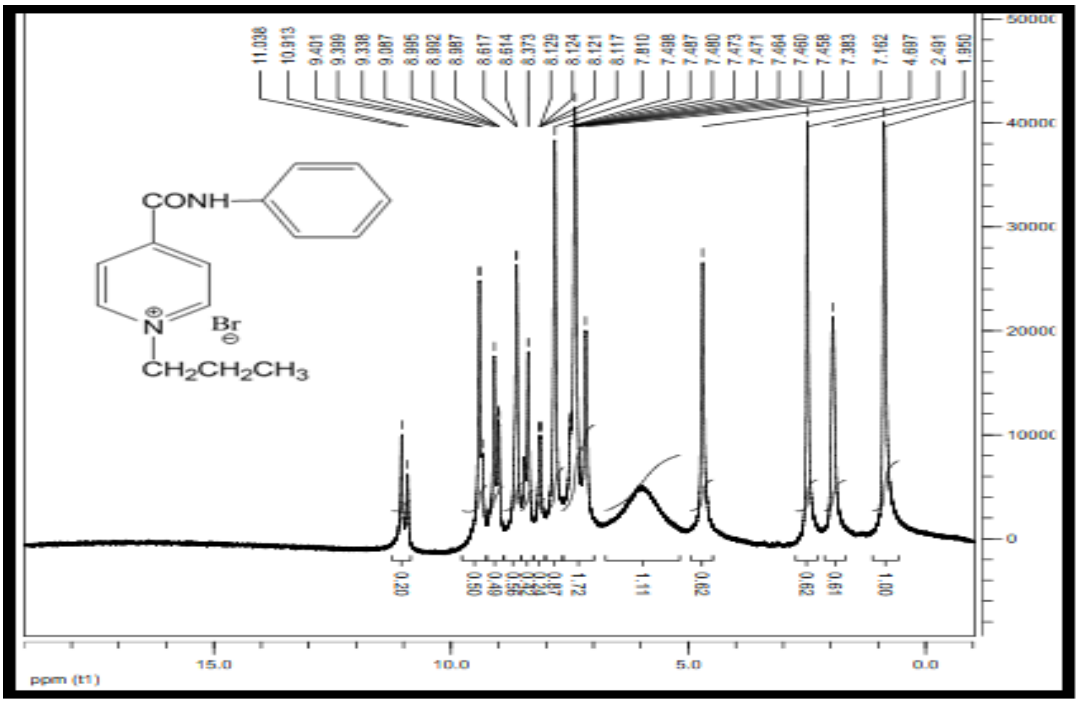


Fig. 3-41: ^{1}H-NMR spectrum of compound (B12)

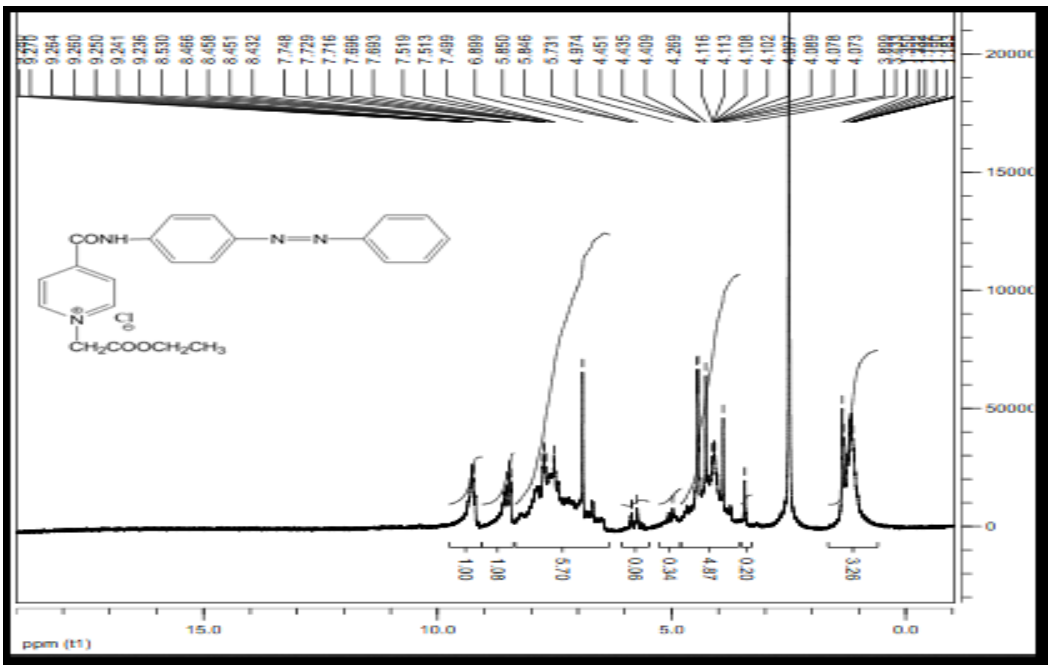


Fig. 3-42: ^{1}H-NMR spectrum of compound (B13)

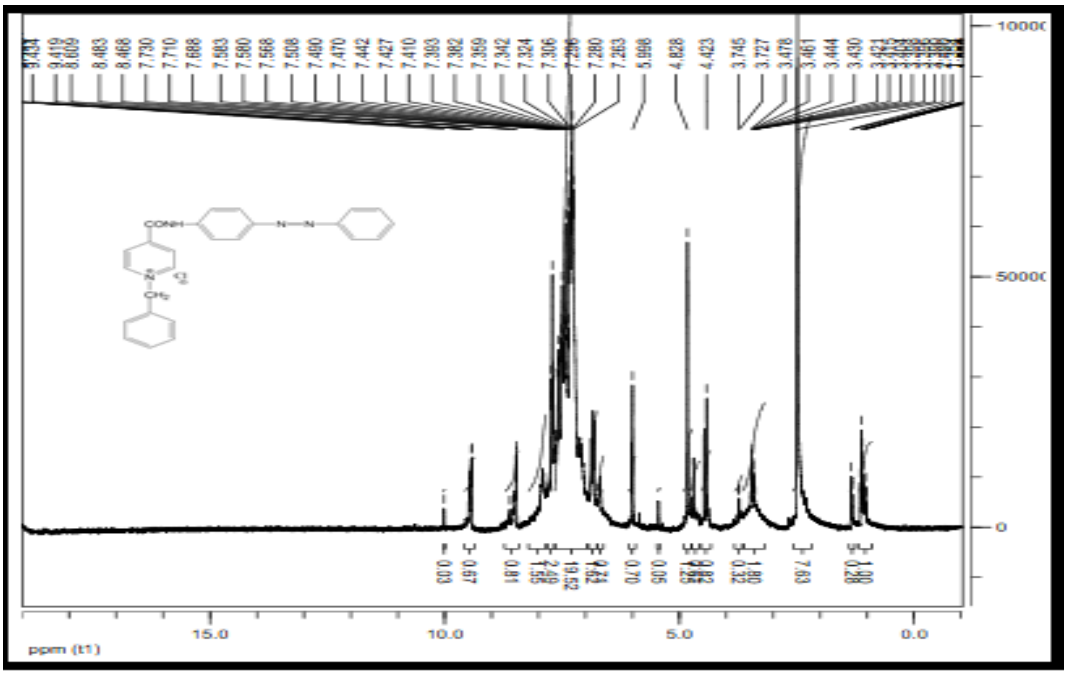


Fig. 3-43: ^{1}H-NMR spectrum of compound (B14)

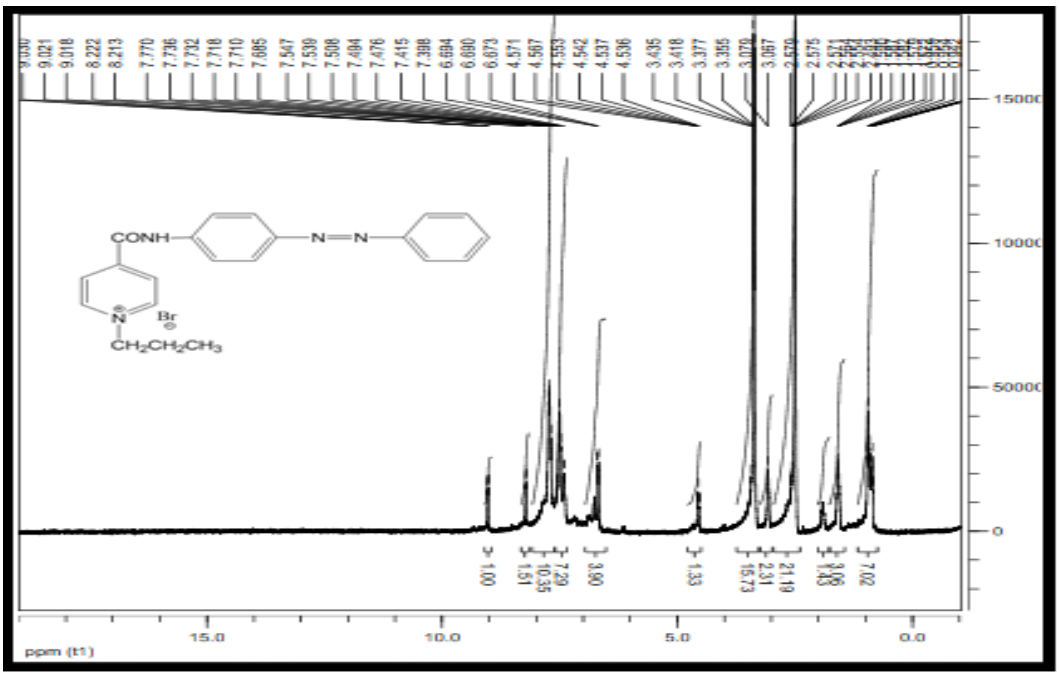


Fig. 3-44: ^{1}H-NMR spectrum of compound (B15)

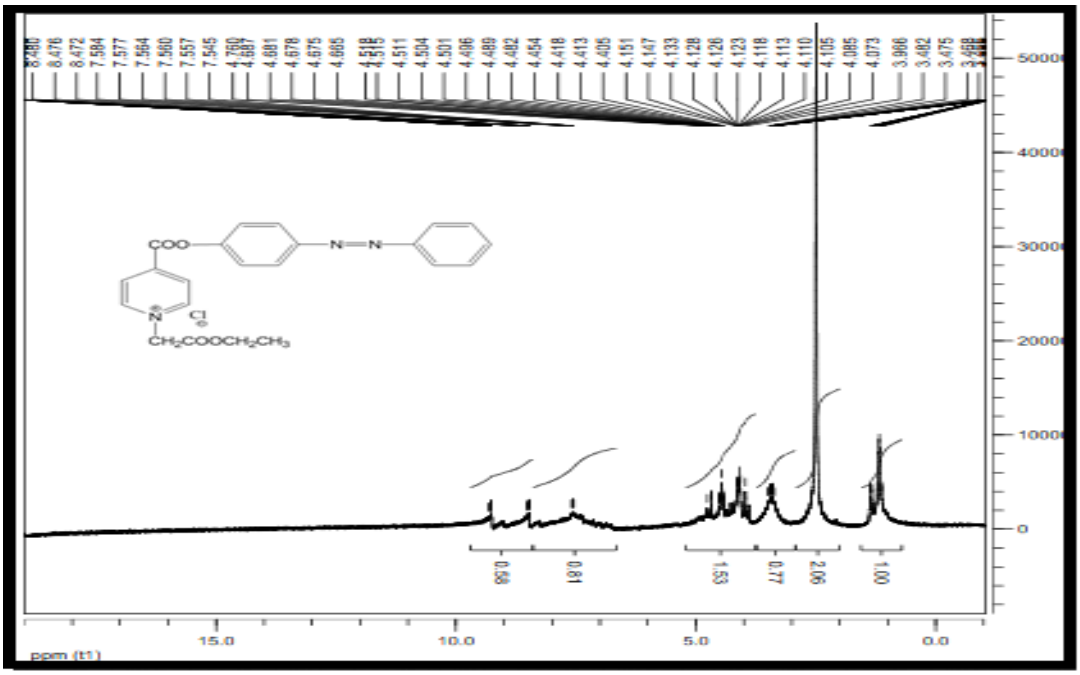


Fig. 3-45: ^{1}H-NMR spectrum of compound (B16)

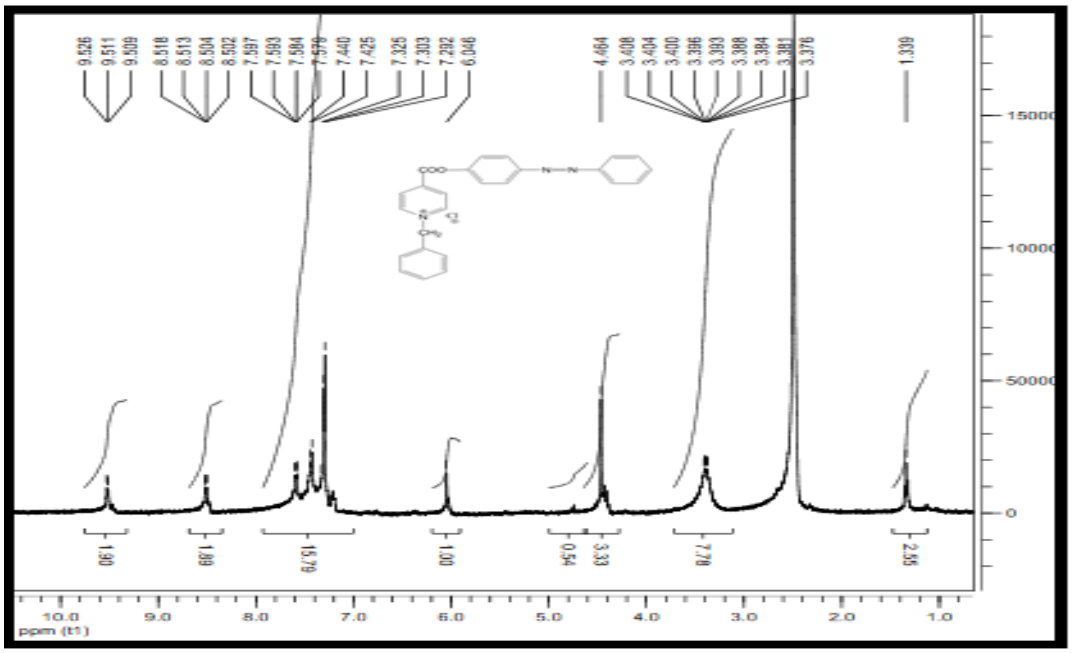


Fig. 3-46: ^{1}H-NMR spectrum of compound (B17)

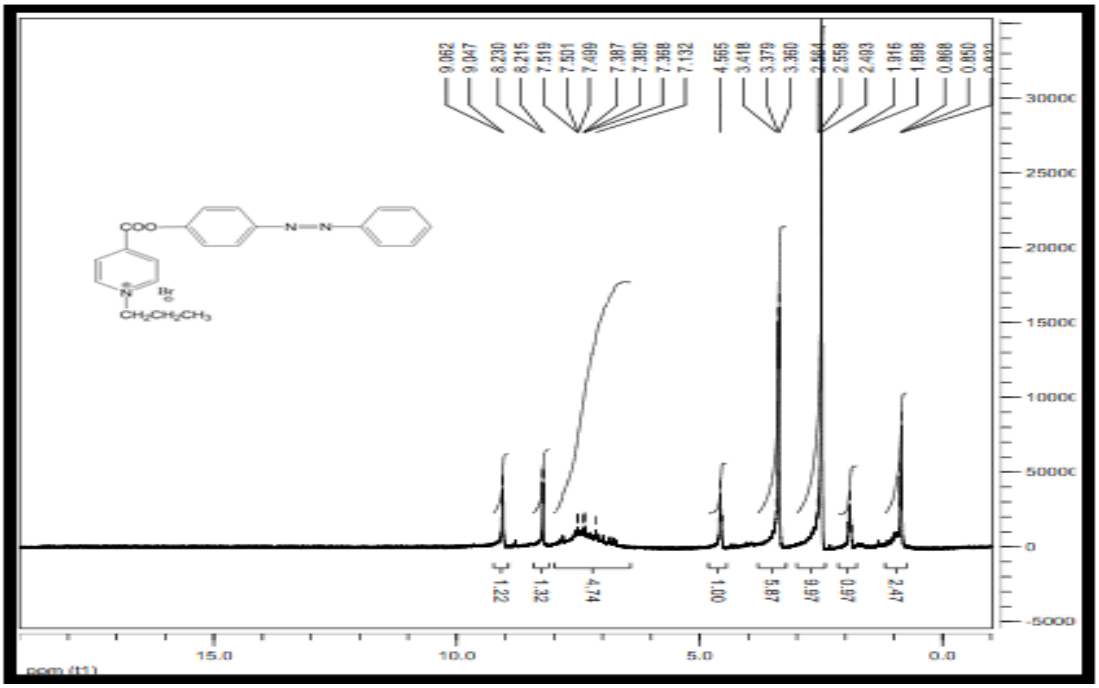


Fig. 3-47: ^{1}H-NMR spectrum of compound (B18)

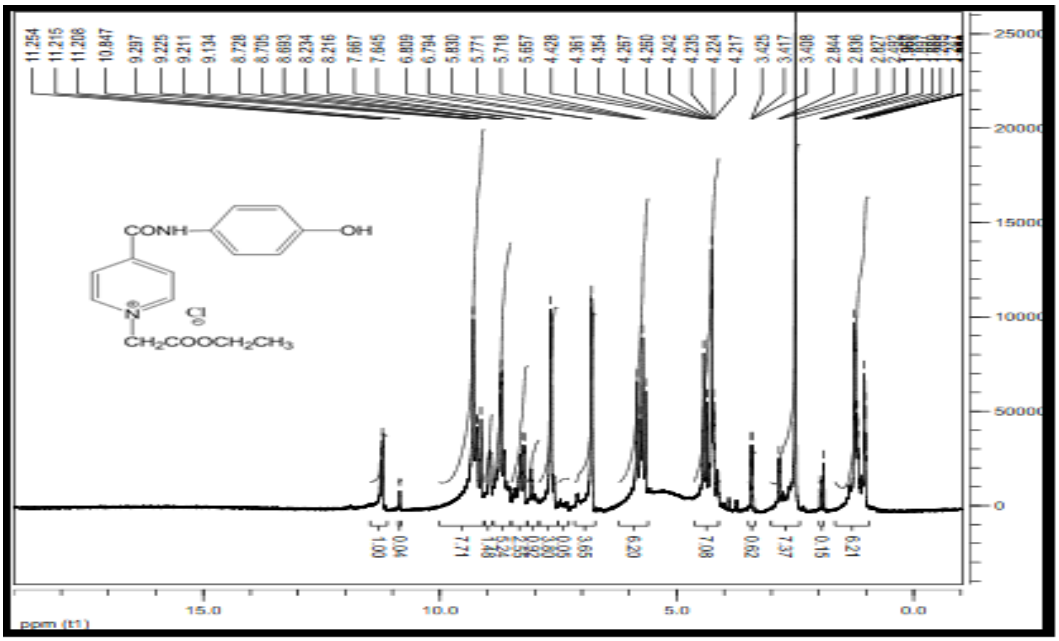


Fig. 3-48: ^{1}H-NMR spectrum of compound (B19)

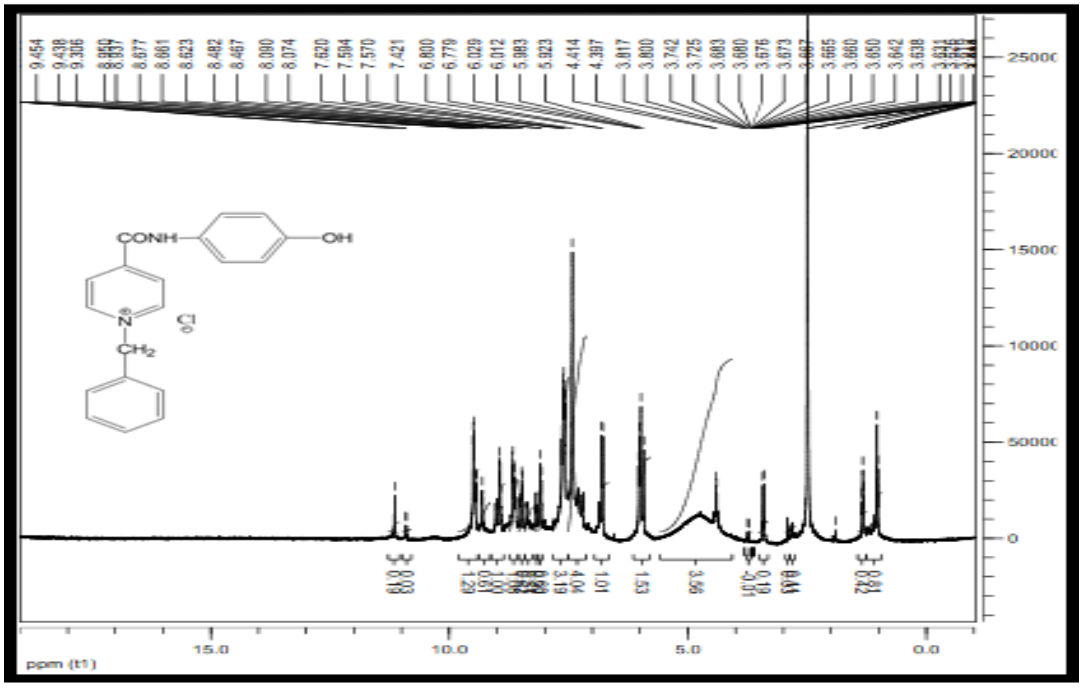


Fig. 3-49: ^{1}H-NMR spectrum of compound (B20)

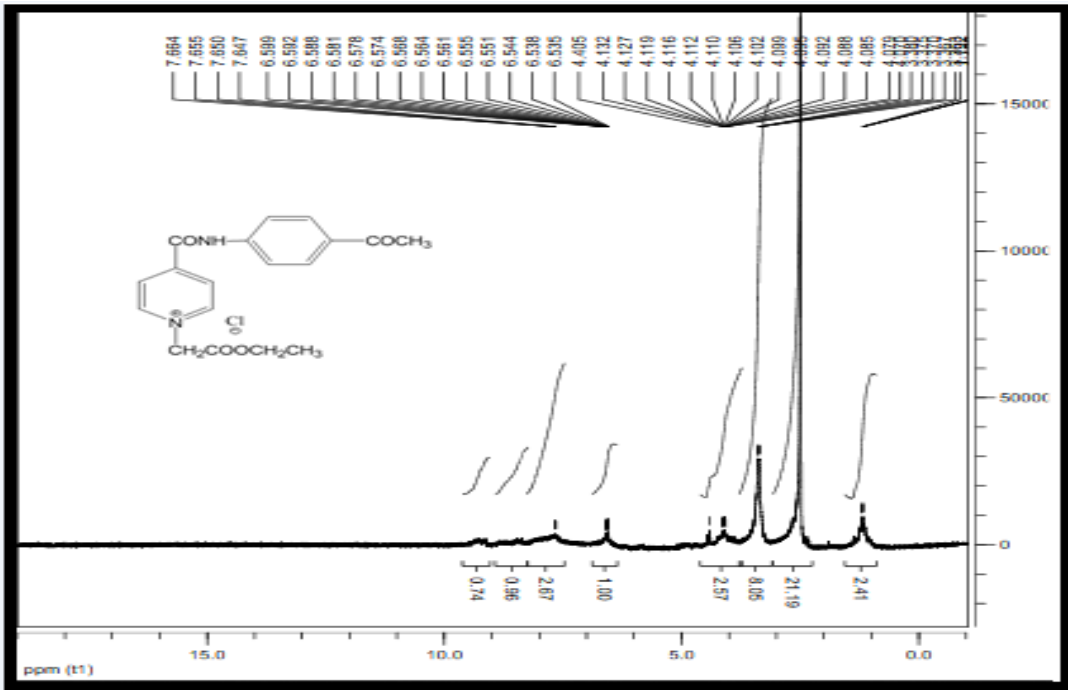


Fig.3-50: ^{1}H-NMR spectrum of compound (B22)

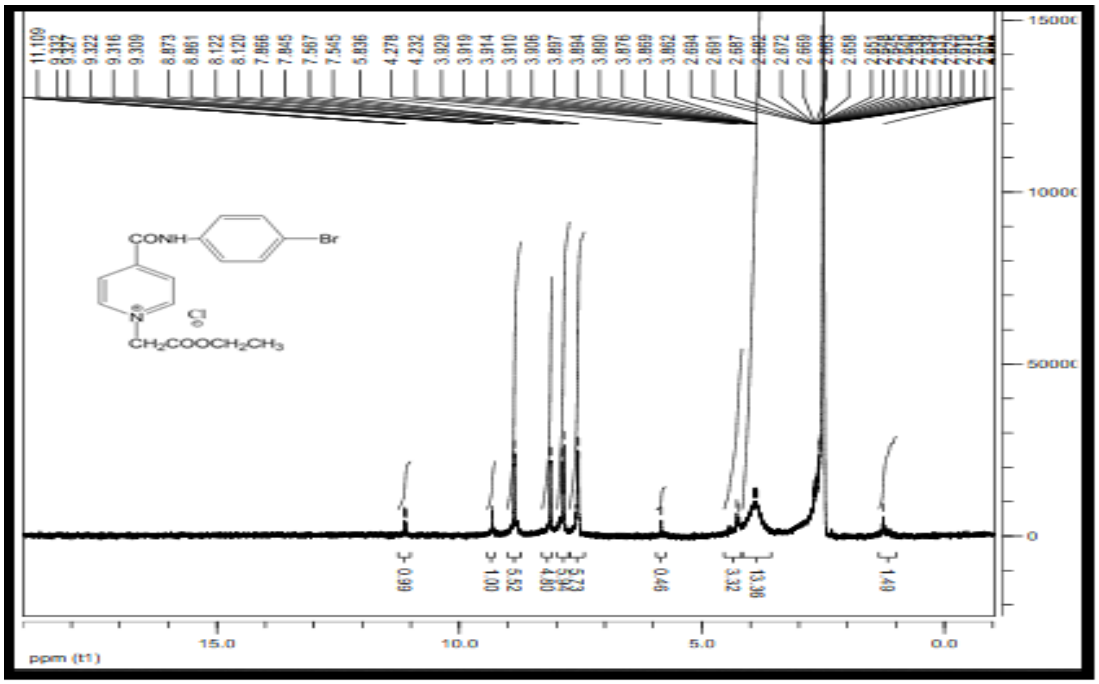


Fig.3-51: ^{1}H-NMR spectrum of compound (B24)

3.4. Weight loss method

The results of corrosion rate and inhibition efficiency that obtained from weight loss measurements at different concentrations of suggested inhibitors (B1-B24) after 24 hours immersion at 30^{o}C are depicted in Figures (3-52, 3-53, 3-54) and summarized in Table 3-4. These values indicate that the mild steel corrosion is reduced by the presence of suggested inhibitors in 1M H_2SO_4 at all concentrations that used in the present study. However, there is remarkable decreasing in the weight of mild steel specimen after 24 hours without using an inhibitor. This effect could be explain by adsorption of organic compounds on the mild steel surface which makes impediment towards corrosion environment.

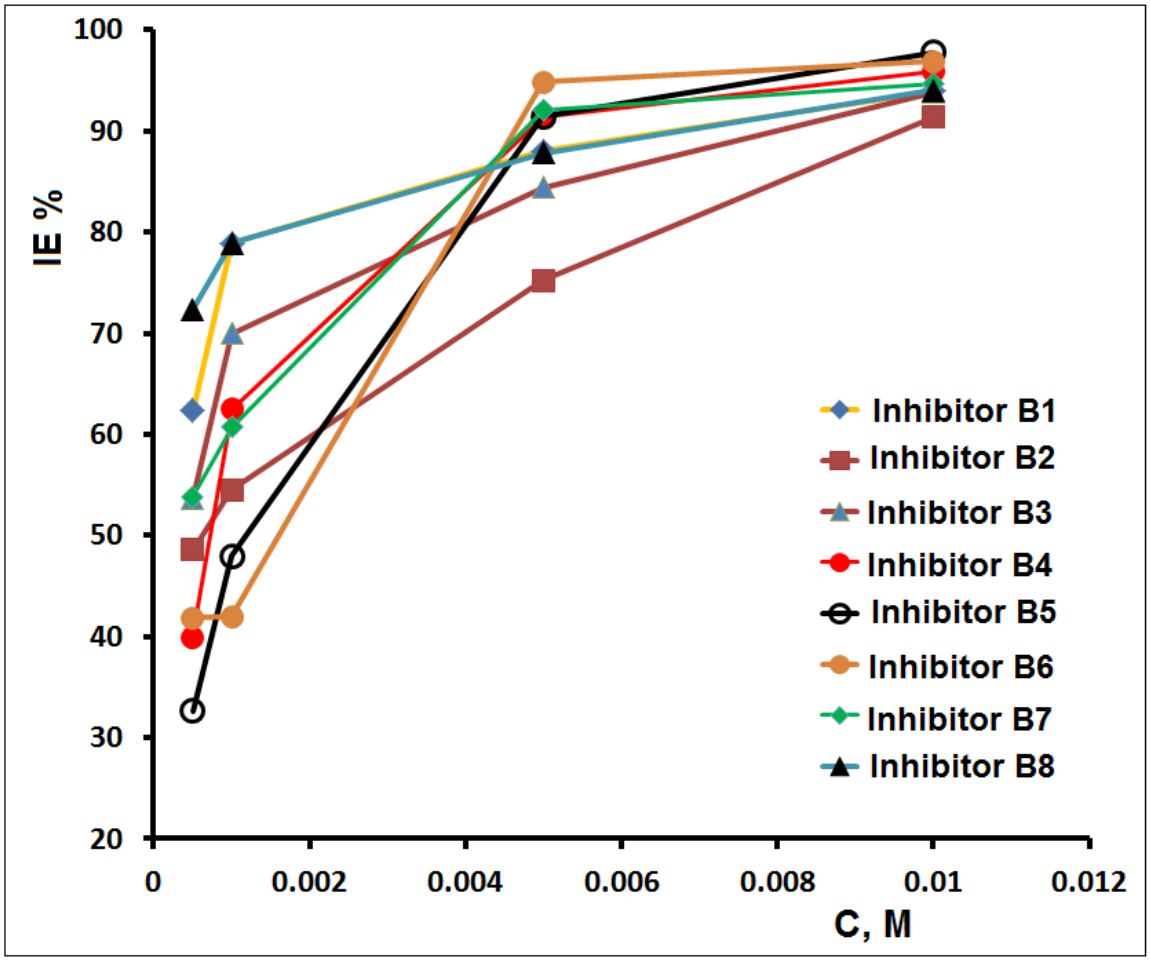


Figure 3-52: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1M H_2SO_4 containing different concentrations of suggested inhibitors (B1-B8) after 24 hours immersion.

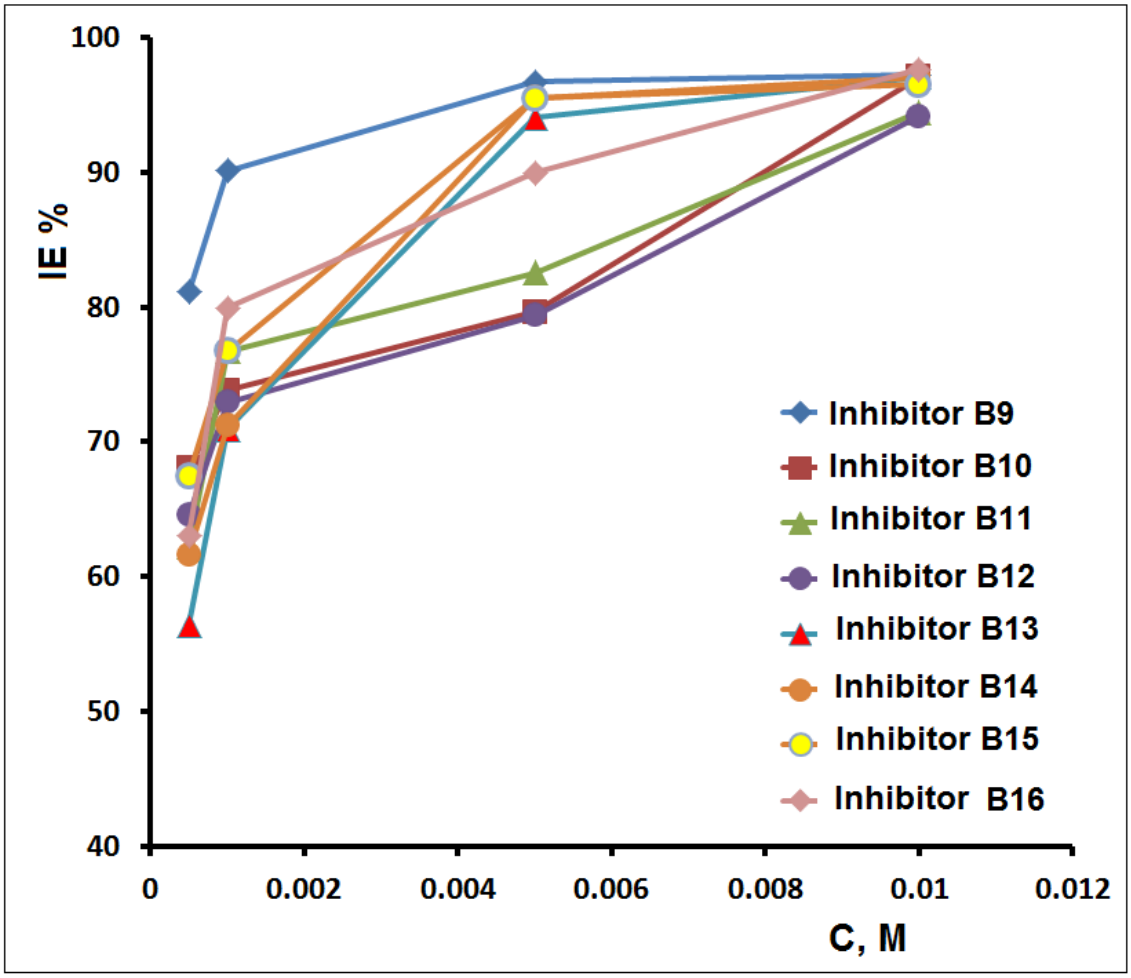


Figure 3-53: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1M H_2SO_4 containing different concentrations of suggested inhibitors (B9-B16) after 24 hours immersion.

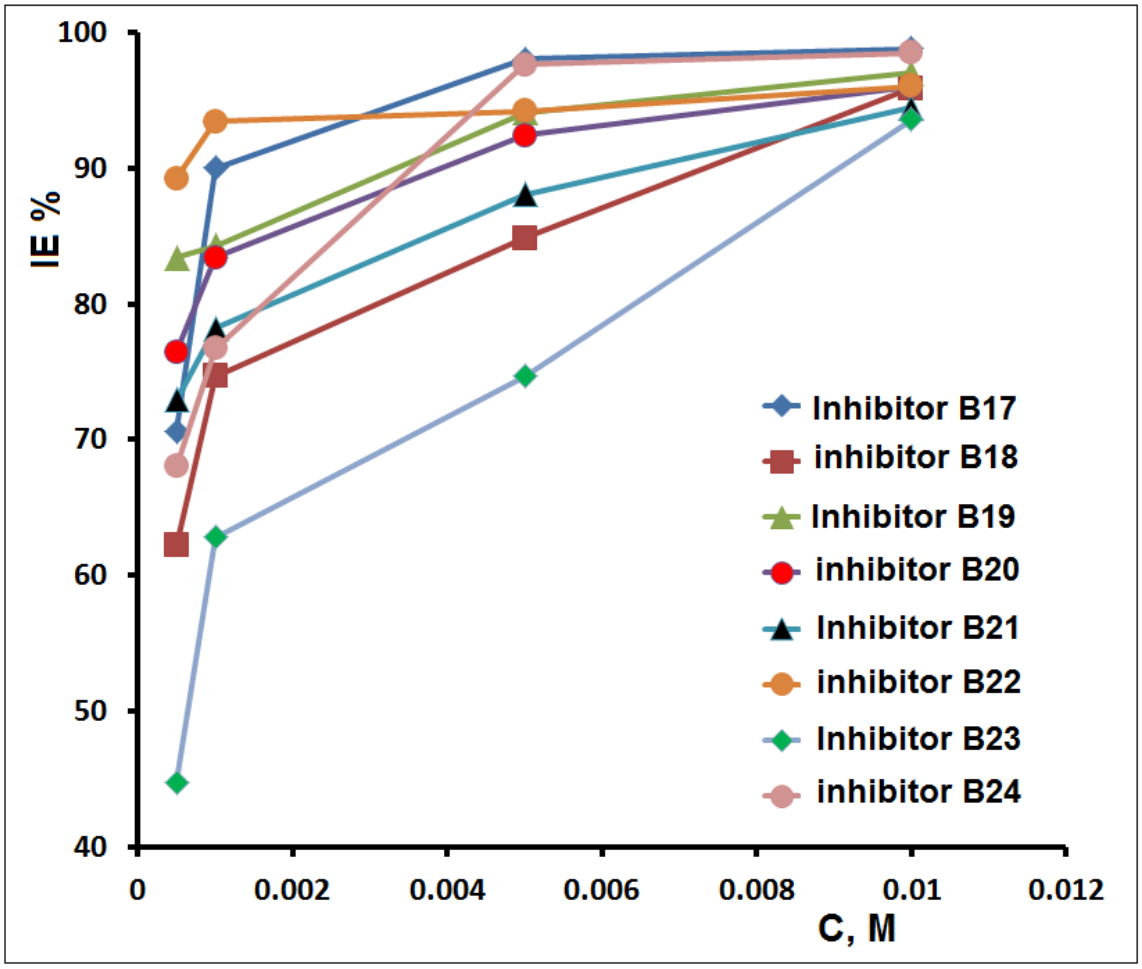


Figure 3-54: Effect of inhibitor concentration on the efficiencies of mild steel obtained at 30°C in 1M H_2SO_4 containing different concentrations of suggested inhibitors (B17-B24) after 24 hours immersion.

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.

Concentration (M)	Corrosion rate ($mg.cm^{-2}.h^{-1}$)	IE%	θ	$\Delta G°_{ads}$ ($kJ.mol^{-1}$)
Blank	0.344	-	-	-
(B1)				
5×10^{-4}	0.0991	62.35	0.6235	-31.06 (R^2=0.999)
1×10^{-3}	0.0727	78.86	0.7886	
5×10^{-3}	0.0413	87.99	0.8799	
1×10^{-2}	0.0207	93.98	0.9398	
(B2)				
5×10^{-4}	0.1769	48.57	0.4857	-28.04 (R^2=0.991)
1×10^{-3}	0.1564	54.53	0.5453	
5×10^{-3}	0.0853	75.20	0.7520	
1×10^{-2}	0.0298	91.33	0.9133	
(B3)				-29.34 (R^2=0.998)
5×10^{-4}	0.1594	53.66	0.5366	
1×10^{-3}	0.1046	69.95	0.6995	
5×10^{-3}	0.0541	84.42	0.8442	
1×10^{-2}	0.0212	93.83	0.9383	
(B4)				
5×10^{-4}	0.2090	39.92	0.3992	-28.46 (R^2=0.999)
1×10^{-3}	0.1290	62.50	0.6250	
5×10^{-3}	0.0283	91.44	0.9144	
1×10^{-2}	0.0140	95.93	0.9593	
(B5)				
5×10^{-4}	0.2317	32.64	0.3264	-27.32 (R^2=0.999)
1×10^{-3}	0.1789	47.99	0.4799	
5×10^{-3}	0.0295	91.42	0.9142	
1×10^{-2}	0.0076	97.79	0.9779	
(B6)				
5×10^{-4}	0.2000	41.86	0.4186	-27.53 (R^2=0.991)
1×10^{-3}	0.1995	42.00	0.4200	
5×10^{-3}	0.0177	94.85	0.9485	
1×10^{-2}	0.0107	96.88	0.9688	
(B7)				
5×10^{-4}	0.1590	53.77	0.5377	-29.23 (R^2=0.999)
1×10^{-3}	0.1350	60.75	0.6075	
5×10^{-3}	0.0271	92.12	0.9212	
1×10^{-2}	0.0184	94.65	0.9465	
(B8)				
5×10^{-4}	0.0941	72.35	0.7235	-31.03 (R^2=0.999)
1×10^{-3}	0.0713	78.86	0.7886	
5×10^{-3}	0.0420	87.79	0.8779	
1×10^{-2}	0.0205	94.04	0.9404	
(B9)				
5×10^{-4}	0.0650	81.10	08110	-32.79 (R^2=0.999)
1×10^{-3}	0.0339	90.14	0.9014	

5×10^{-3}	0.0113	96.71	0.9671	
1×10^{-2}	0.0095	97.23	0.9723	
(B10)				
5×10^{-4}	0.1100	68.02	0.6802	-29.39 (R^2=0.988)
1×10^{-3}	0.0900	73.83	0.7383	
5×10^{-3}	0.0700	79.65	0.7965	
1×10^{-2}	0.0100	97.09	0.9709	
(B11)				
5×10^{-4}	0.1300	62.20	0.6220	-29.84 (R^2=0.995)
1×10^{-3}	0.0800	76.74	0.7674	
5×10^{-3}	0.0600	82.55	0.8255	
1×10^{-2}	0.0190	94.47	0.9447	
(B12)				
5×10^{-4}	0.1220	64.53	0.6453	-29.50 (R^2=0.991)
1×10^{-3}	0.0930	72.96	0.7296	
5×10^{-3}	0.0710	79.36	0.7936	
1×10^{-2}	0.0200	94.18	0.9418	
(B13)				
5×10^{-4}	0.1500	56.39	0.5639	-29.87 (R^2=0.999)
1×10^{-3}	0.1000	70.93	0.7093	
5×10^{-3}	0.0200	94.09	0.9409	
1×10^{-2}	0.0100	97.09	0.9709	
(B14)				
5×10^{-4}	0.1320	61.62	0.6162	-30.68 (R^2=0.999)
1×10^{-3}	0.0990	71.22	0.7122	
5×10^{-3}	0.0152	95.58	0.9558	
1×10^{-2}	0.0100	97.09	0.9709	
(B15)				
5×10^{-4}	0.1120	67.44	0.6744	-30.97 (R^2=0.999)
1×10^{-3}	0.080	76.74	0.7674	
5×10^{-3}	0.0170	95.50	0.9550	
1×10^{-2}	0.0119	96.54	0.9654	
(B16)				
5×10^{-4}	0.1270	63.08	0.6308	-30.30 (R^2=0.998)
1×10^{-3}	0.0690	79.94	0.7994	
5×10^{-3}	0.0350	89.98	0.8998	
1×10^{-2}	0.0080	97.67	0.9767	
(B17)				
5×10^{-4}	0.1010	70.63	0.7063	-32.20 (R^2=0.999)
1×10^{-3}	0.0340	90.01	0.9001	
5×10^{-3}	0.0067	98.05	0.9805	
1×10^{-2}	0.0040	98.83	0.9883	
(B18)				
5×10^{-4}	0.1300	62.20	0.6220	-29.77 (R^2=0.996)
1×10^{-3}	0.0870	74.70	0.7470	

5×10^{-3}	0.0520	84.88	0.8488	
1×10^{-2}	0.0140	95.93	0.9593	
(B19)				
5×10^{-4}	0.0570	83.43	0.8343	-32.37 (R^2=0.999)
1×10^{-3}	0.0540	84.30	0.8430	
5×10^{-3}	0.0202	94.12	0.9412	
1×10^{-2}	0.0102	97.03	0.9703	
(B20)				
5×10^{-4}	0.0810	76.45	0.7645	-31.84 (R^2=0.999)
1×10^{-3}	0.0570	83.43	0.8343	
5×10^{-3}	0.0260	92.44	0.9244	
1×10^{-2}	0.0136	96.04	0.9604	
(B21)				
5×10^{-4}	0.0930	72.96	0.7296	-30.96 (R^2=0.999)
1×10^{-3}	0.0750	78.19	0.7819	
5×10^{-3}	0.0410	88.08	0.8808	
1×10^{-2}	0.0190	94.47	0.9447	
(B22)				
5×10^{-4}	0.0370	89.24	0.8924	-34.91 (R^2=0.999)
1×10^{-3}	0.0224	93.48	0.9348	
5×10^{-3}	0.0199	94.21	0.9421	
1×10^{-2}	0.0135	96.07	0.9607	
(B23)				
5×10^{-4}	0.1900	44.76	0.4476	-28.10 (R^2=0.986)
1×10^{-3}	0.1280	62.79	0.6279	
5×10^{-3}	0.0870	74.70	0.7470	
1×10^{-2}	0.0220	93.60	0.9360	
(B24)				
5×10^{-4}	0.1100	68.02	0.6802	-30.92 (R^2=0.999)
1×10^{-3}	0.0800	76.74	0.7674	
5×10^{-3}	0.0080	97.67	0.9767	
1×10^{-2}	0.0050	98.54	0.9854	

Information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. So that, the degree of surface coverage values (θ) at different inhibitor concentrations in 1M H_2SO_4 was achieved from weight loss measurements (θ = E (%)/100) (see Table 3-4) at 30°C and tested with Langmuir isotherm relationship [52]:

$$C/\theta = 1/K_{ads} + C \qquad \ldots\ldots\ldots\ldots\ldots (3.1)$$

where K_{ads} is the equilibrium constant of the adsorption process.

According to the Langmuir isotherm, K_{ads} values can be calculated from the intercepts of the straight line of plotting C/θ versus C (see Fig. 3-55). K_{ads} is related to the standard free energy of adsorption,ΔG^{o}_{ads}, as in equation[52]: (The value 55.5 is the molar concentration of water in the solution in M)

$$K_{ads} = \frac{1}{55.5} exp\left(\frac{-\Delta G^{\circ}_{ads}}{RT}\right) \qquad \ldots\ldots\ldots.. (3.2)$$

from Table(3-4), the values of standard free energy of adsorption are negative which indicate that the processes of adsorption of all suggested inhibitors (B1-B24) were spontaneous processes on the mild steel surface after 24 h immersion at 30°C and that's given sense for remarkable interaction between suggested inhibitors and metal surface. Adsorbed molecule moves closer to the surface of metal making electrons start to overlap with that of the surface atoms which causes physisorption for suggested inhibitors [53].

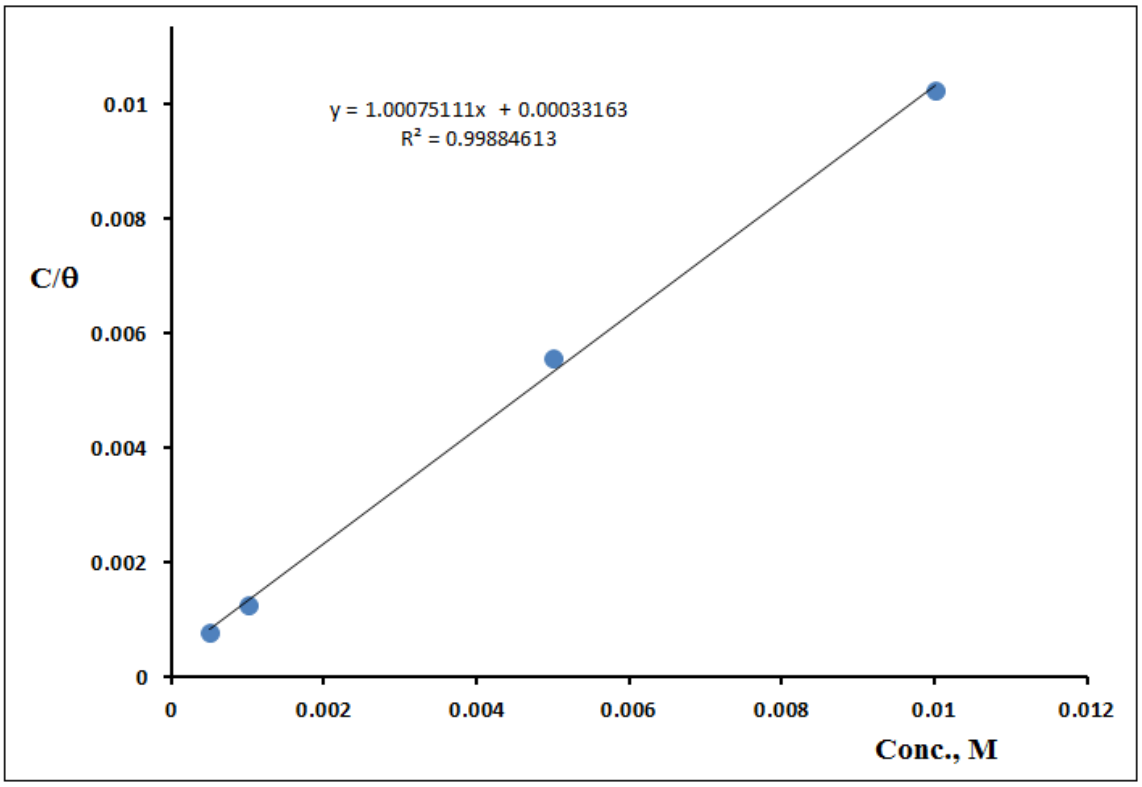


Figure 3-55: Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (B5).

The mechanism corrosion inhibition[54] depends on the formation of mono protective layer on the metal surface. The protective nature of the surface layer depends on many factors: interaction between inhibitors and substrate, incorporation of the inhibitor in the surface layer, chemical reactions, electrode potentials, concentration of the inhibitor, temperature and properties of the corresponding surface, etc. The first stage in the action mechanism of the corrosion inhibitor in aggressive media is adsorption of the surfactant molecules onto the metal surface. The adsorption process is influenced by the nature and the surface charge of the metal, the chemical structure of the organic inhibitor, and the nature of the aggressive electrolyte. Adsorption of the surfactant molecules on the metal surface can be expressed according to the following equation:

$$\text{Inhibitor}_{(sol.)} + nH_2O_{(ads.)} \longrightarrow \text{Inhibitor}_{(ads.)} + nH_2O_{(sol.)}$$

Where n is the number of water molecules removed from the metal surface for each molecule of surfactant adsorbed. Adsorption of the surfactant molecules occurs because the interaction energy between the organic molecules and the metal surface is higher than that between water molecules and the metal surface. So the inhibition effect by organic inhibitors is attributed to the adsorption of the surfactant molecules via their functional groups onto the metal surface. The adsorption rate is usually rapid and hence the reactive metal is shielded from the aggressive environment. Higher molecular size and high electron density on the adsorption centers may be responsible for high corrosion efficiency. Figure (3-56) shows proposed adsorption model of the one molecule of suggested inhibitor (**B11**) on the iron metal surface.

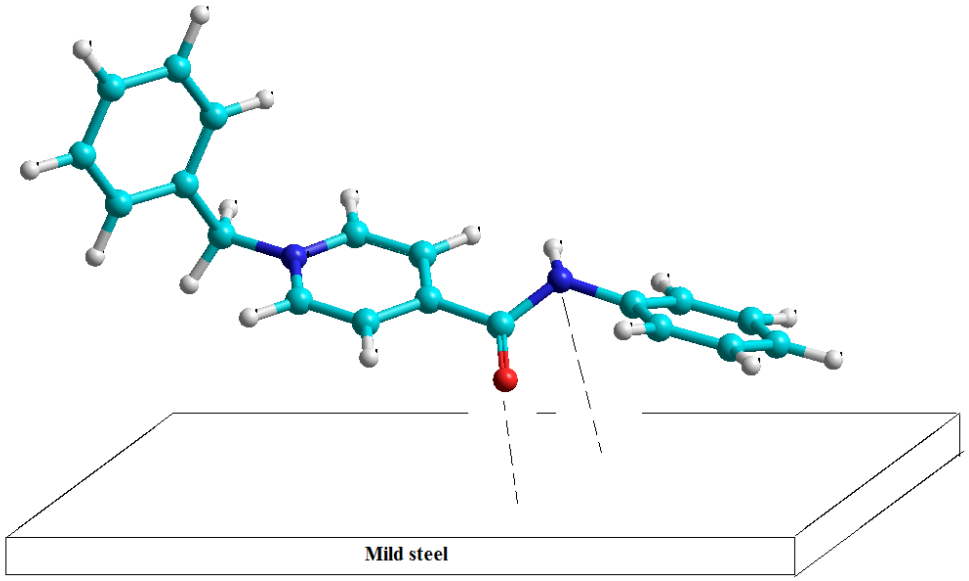


Figure 3-56. Representation model for adsorption process of organic molecule (B11) on steel surface.

3.5.CONCLUSION

The prepared and identified new pyridinium salt derivatives (B1-B24) were used successfully as corrosion inhibitors on the mild steel surface in 1M H_2SO_4 solution at 30^oC. The results of inhibitive efficiency (E%) showed interesting inhibitive effects of suggested inhibitors. The values ΔG of adsorption revealed physisorption effect for (B1-B24) and provided useful information to explain the interaction between the surface of metal and the organic molecules.

3.6. Future work :

Preparation of some new Pyridinium salt schiff base derivatives and appling them as corrosion inhibitors for mild steel in acidic media.

References

References:

1. C. Ying Song, H. Ding, J. Hong Zhao, J. She Wang and L. Cheng Wang, "*Chem. Eng. Data", 54* (3), 1120–1122, 2009.
2. R. M. Acheson," An Introduction to the Chemistry of Heterocyclic Compounds Wiley"; Second Edition edition, 1967.
3. Epsztajn J.,Bieniek A., Ptotka M. W. and Suwald K., "*Tetrahedron*," *45*, 7469, 1989.
4. A. Vörös, G. Timári, Z. Baán, P. Mizsey and Z. Finta, "*Periodica Polytechnica Chemical Engineering",* 58, 195-205, 2014.
5. *Piancatelli, G. and Luzzio, F. A., "Pyridinium Chlorochromate, e-EROS encyclopedia of reagents for organic synthesis. John Wiley & Sons", 2007.*
6. *Corey, E. J.; Suggs, J. W. ,"Pyridinium Chlorochromate. An Efficient Reagent for Oxidation of Primary and Secondary Alcohols to Carbonyl Compounds". Tetrahedron Lett. 16 (31): 2647–2650, 1975.*
7. Kupetis, G. K., Saduikis, G., Nivinskiene, O. and Eicher-Lorka, O., "*Monatsh Chem"*, 133, 313–321, 2002.
8. Gama, Y., Suzuki, H. and Narasaki, H. "*Japanese patent",* JP 56139463, 1981.
9. Ezaki, S. and Kokeguchi, N., "*Japanese patent",* JP 2006171518, 2006.
10. *Anwar, Kosuge, H., Okada, S., Oikawa, H. and Nakanishi, H. , "Japanese Journal of Applied Physics", 40 (Part 1, No. 6A), 4213–4216.*
11. *Muldoon, M., Brennecke, J. F. Maginn, E. J., Scriven, E. F. V., McAteer, C. H. and Murugan, R. ,"US patent",7687513, B1 20100330, 2010.*
12. *amamoto, E., Yamaguchi, S. and Nagamune, T. ,"Appl Biochem Biotechnol", 164, 957–967,2011.*
13. M. Sundararaman, R. R. Kumar, P. Venkatesan and A. Ilangovan, "*Journal of Medical Microbiology"*, 62, 241–248, 2013.
14. N. Kostenko, J. Gottfriedsen, L. Hilfert and F. T. Edelmann, "*International Journal of Polymer Science* ", 1-10, 2012.

15. S. K. Sharma , G. S. Chauhan, R. Gupta, J. H. Ahn, *J. Mater. "Sci: Mater. Med".*, 21, 717–724,2010 .
16. Y. Xue and H. Xiao, *"Polymers"*, 7, 2290–2303,2015.
17. Piers, E. and Soucy, "M. *Can. J. Chem"., 52*, 3563, 1974.
18. T. J. Donohoe, D. J. Johnson,L. H. Mace,M.J. Bamford and O. Ichihara, "*Organic Letters"*, 7(3), 435-437,2005 .
19. Wong, Y.-S., Marazano, C., Gnecco, D., Génisson, Y., Chiaroni, A.and Das, B. C., "*J.Org. Chem."*, 62, 729-733,1997.
20. *Clayden J., "Organic chemistry. Oxford: Oxford University Press. pp."276–296,2001.*
21. *Montalbetti C. A. G. N. and F. Virginie, "Tetrahedron" ,61 (46), 10827–10852,2005.*
22. R. Babbar and D. P. Pathak, "*Der Pharma Chemica"*, 5(4):147-152,2013 .
23. N. Ramalakshmi, S. Deepa, K. Sumanth Srinivas, A. Puratchikody and S. Arunkumar, "*Rasayan journal Chem*.", 2(2), 393-396,2009 .
24. T. W. G. Solomons and C. B. Fryhle, "Organic Chemistry" ,10th ed., John Wiley & Sons,2010.
25. J. B. Christensen, "*Molecules", 6*, 47-51,2001.
26. Gung B.W. and Taylor R.T., "*J. Chem. Ed."*, 81, 1630,2004.
27. P. A. Schweitzer, "Fundamentals of corrosion-Mechanisms", Causes and Preventative Methods. Taylor and Francis Group, LLC 2010.
28. E. Ramsden, "Key Science – Chemistry", Nelson Thornes; 2nd edition, 2002.
29. Grafen, H.; Horn, E.; Schlecker, H.; Schindler, H., "Corrosion. Ullmann's Encyclopedia of Industrial Chemistry.Wiley-VCH", 2000.
30. "Rust Removal using Electrolysis". antique-engines.com. Retrieved April 1, 2015.
31. Matcor, Inc. "Cathodic Protection Systems - Matcor, Inc.", Retrieved , 2017.
32. A. S. Yaro, A. A. Khadom and R. K. Wael, *Alexandria Engineering Journal*, 52(1), 129-135, 2013.

33. M. N. El-Haddad," *International Journal of Biological Macromolecules",* 55, 142-149, 2013.
34. L. M. Rivera-Grau, M. Casales, I. Regla, D.M. Ortega-Toledo, J. A. Ascencio-Gutierrez, J. Porcayo-Calderon and L. Martinez-Gomez, "*Int. J. Electrochem. Sci.",* 8 ,2491 – 2503,2013.
35. A. A. Al-Amiery, A. H. Kadhum, A. M. Alobaidy, A. Mohamad and P. Soh Hoon, "*Materials"* , *7*, 662-672, 2014.
36. E. A. Noor, A. H. Al-Moubaraki, "*Materials Chemistry and Physics",* 110 ,145–154,2008.
37. Wolffenstein and Hartwich, Ber., 48, 2043 ,1915.
38. Conard C. R. and Dolliver M. A., Organic Syntheses, 12, 22, 1932.
39. Lesley R., Andrea R., and Esmaeel N., "Journal of under graduate Research in Bioengineering", 8,126-132 ,2008-2010 .
40. Sigma-Aldrich Corporation, Milwaukee, Wisconsin : Sigma-Aldrich, 2011.
41. SRINIVASAN, V. and G. RAMACHANDER., "J. sci. Ind. "(kes India), 20c,351 ,1961.
42. R. Mozingo, "Org. Syntheses", Coll. Vol. 3, 687,1955 .
43. Vogel A. I., Tatchell A. R., Furnis B. S., Hannaford A. J. and Smith P. W. G., "Vogel's Textbook of Practical Organic Chemistry",5th Ed., Prentice Hall ,1996 .
44. ASTM G 31 – 72, "Standard Practice for labortary Immersion Corrosion Testing of Metals", West Conshohocken, PA, ASTM ,1990 .
45. X. Chen, C. Chen, H. Xiao, F. Cheng, G. Zhang and G. Yi, "Corrosion behavior of carbon nanotubes–Ni composite coating", J. Surf. & Coating Tech., 191,351-356, 2015.
46. B. Jabeera, S. Shibli and T. Anirudhan, "Synergistic inhibitive effect of tartarate and tungstate in preventing steel corrosion in aqueous media", Surf. Sci., 252,3520-3524, 2006.

47. E. Noor, A. Al-Moubaraki, "Corrosion Behavior of Mild Steel in Hydrochloric Acid Solutions", Int. J. Electrochem. Sci., 3,806 – 818, 2008.
48. I. Akpan and N. Offiong, "Inhibition of Mild Steel Corrosion in Hydrochloric Acid Solution by Ciprofloxacin Drug", International Journal of Corrosion, 1-5, 2013.
49. William H. Brown, Christopher S. Foote, Brent L. Iverson, Eric Anslyn, Organic Chemistry, 6th Edition, Brooks Cole ,2011 .
50. John Coates, , pp. John Wiley & Sons Ltd, Chichester, "Interpretation of Infrared Spectra, A Practical Approach, in Encyclopedia of Analytical Chemistry, R.A. Meyers (Ed.)",10815–10837, 2000.
51. Robert M. Silverstein, Francis X. Webster, "Spectrometric Identification of Organic Compounds", Wiley; 7th edition , 2005 .
52. Sudhish K. Shukla, Eno E. Ebenso, "Int. J. Electrochem. Sci.", 6 ,3277 – 3291, 2011.
53. E. Kamis, F. Bellucci, R. M. Latanision, E. S. H. El-Ashry, "Corrosion 47, 677.F. Bentiss, M. Lebrini, M. Lagrenée, Corros. Sci." 47, 2915–2931, 2005.
54. M. A. Malik, M. A. Hashim, F. Nabi, S. A. AL-Thabaiti, Z. Khan, "Anti-corrosion ability of surfactants: A review, Int. J. Electrochem. Sci.", 6 ,1927 – 1948, 2011 .

الخلاصة

تتضمن هذه الدراسة تحضير مشتقات املاح البريدين ابتداء من حامض الايزونيكوتين تبعا لهذه الخطوات

اولا : تحضير كلوريد الايزونيكوتين (2) عبر تفاعل حامض الايزونيكوتين(1) مع كلوريد الثايونيل

ثانيا : تحضير بعض مشتقات الامايدات والايسترات عبر تفاعل كلوريد الايزونيكوتين (2) مع مشتقات الامين والفينول المعوض(Semicarbazide, Thiosemicarbazide, Benzohydrazide, Aniline, 4-phenylazoaniline, 4-phenylazophenol, p-Aminophenol, p-Aminoacetophenone, m-Toluidine, 4-Bromoaniline)

تم تحضير المركبات (A1-A10)

ثالثا : تحضير بعض مشتقات املاح البريدين عبر تفاعل مشتقات الامايد والايستر المحضرة في الخطوة السابقة مع هاليد الكيل(ethyl chloroacetate, n-propyl bromide, benzyl chloride).

تم تحضير المركبات (B1-B24)

تم تشخيص المركبات المحضرة باستخدام التقنيات الطيفية (^{1}HNMR & FTIR)

المركبات العضوية (B1-B24) تم استخدامها بنجاح كمثبطات لتأكل الحديد المعتدل في محلول مائي لحامض الكبريتيك بتركيز 1 مولاري ولمدة 24 ساعة في درجة حرارة 30 درجة مئوية وتم استخدام طريقة قياس فقدان الوزن لاختبار كفائة تثبيط المركبات .

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

كليه العلوم /جامعة النهرين

قسم الكيمياء

تحضير بعض مشتقات املاح البريدين كمضادات لتأكل الفولاذ الطري في حامض الكبريتيك

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

من قبل

أحمد عماد جواد

بكلوريوس 2014 (جامعة النهرين)

بأشراف

أ. د.مهدي صالح شهاب

1438ربيع الثاني

2017 كانون الثاني