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

Synthesis and Identification of Heterocyclic Compounds as Corrosion Inhibitors in Acidic Media

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

By

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1439 **2018**

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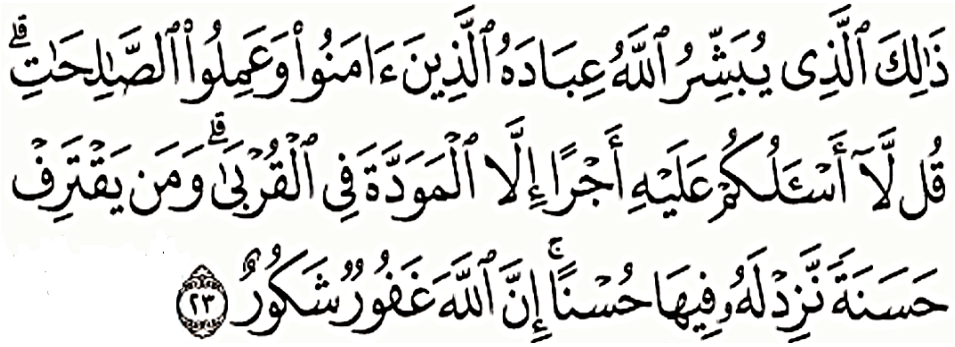
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DEDICATION

TO A PRECIOUS, KIND AND STRONG WOMAN...

MY MOTHER

TO MY BELOVED FATHER.....

TO MY LOVE OF MY LIFETIME THE ONE & ONLY ....

MY WIFE...

TO THE SOURCE OF MY HAPPINESS ... MY KIDS

TO MY DEAR SIBLINGS

ACKNOWLEDGMENT

*First of all I thank **GOD** who gives me patience and power to continue ….*

*Secondly, I would like to express my sincere thanks and deep gratitude to my supervisor **Prof. Dr. Mehdi S. Shihab** for his helpful efforts and advices, continuous encouragement, discussion , suggestions during my work.*

*Great gratitude to **staff** and **head** of Department of Chemistry, College of Science , Al- Nahrain University for assistance in providing the research facilities.*

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Aqeel. F. Mutlag

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FTIR	Fourier Transform Infrared
^{1}H-NMR	Proton Nuclear Magnetic Resonance
^{13}C-NMR	^{13}Carbon Nuclear Magnetic Resonance
ASTM	American Society for Testing and Materials
Asy.	Asymmetrical
C	Inhibitor Concentration (M) in the test solution
DMSO-d6	Dimethylsulphoxide-six detrium
E%	Percentage Inhibition Efficiency
Hr	Hours
K_{ads}	Equilibrium Constant of the Adsorption/ Desorption process
M	Molary
m.p.	Melting Point
Ph	Aromatic
S	Area
Sy.	Symmetrical
T	Immersion period
W	Corrosion Rate
ΔG^{0}_{ads}	Standard Free Energy of Adsorption
ΔM	Mass Loss
Θ	Degree of Surface Coverage

Summary:

In this study, Heterocyclic Compounds were synthesized by several steps as following:

First step: the 1-[4-(5-Bromo-pentyloxy)-phenyl]-ethanone **(B1)** was synthesized by treatment of 4-hydroxyacetophenon (A) with 1,5-dibromo pentane in presence of anhydrous potassium carbonate and acetone.

Second step: the 2-(4-Acetyl-phenoxy)-1-(4-bromo-phenyl)-ethanone **(B2)** was synthesized by treatment of 4-hydroxyacetophenon (A) with of 4-bromolphenacylbromide in presence of anhydrous potassium carbonate and acetone.

Third step: Chalcon derivatives (C1-C6) were synthesized by aldol-condensation between (B1, B2) compounds with various aldehydes

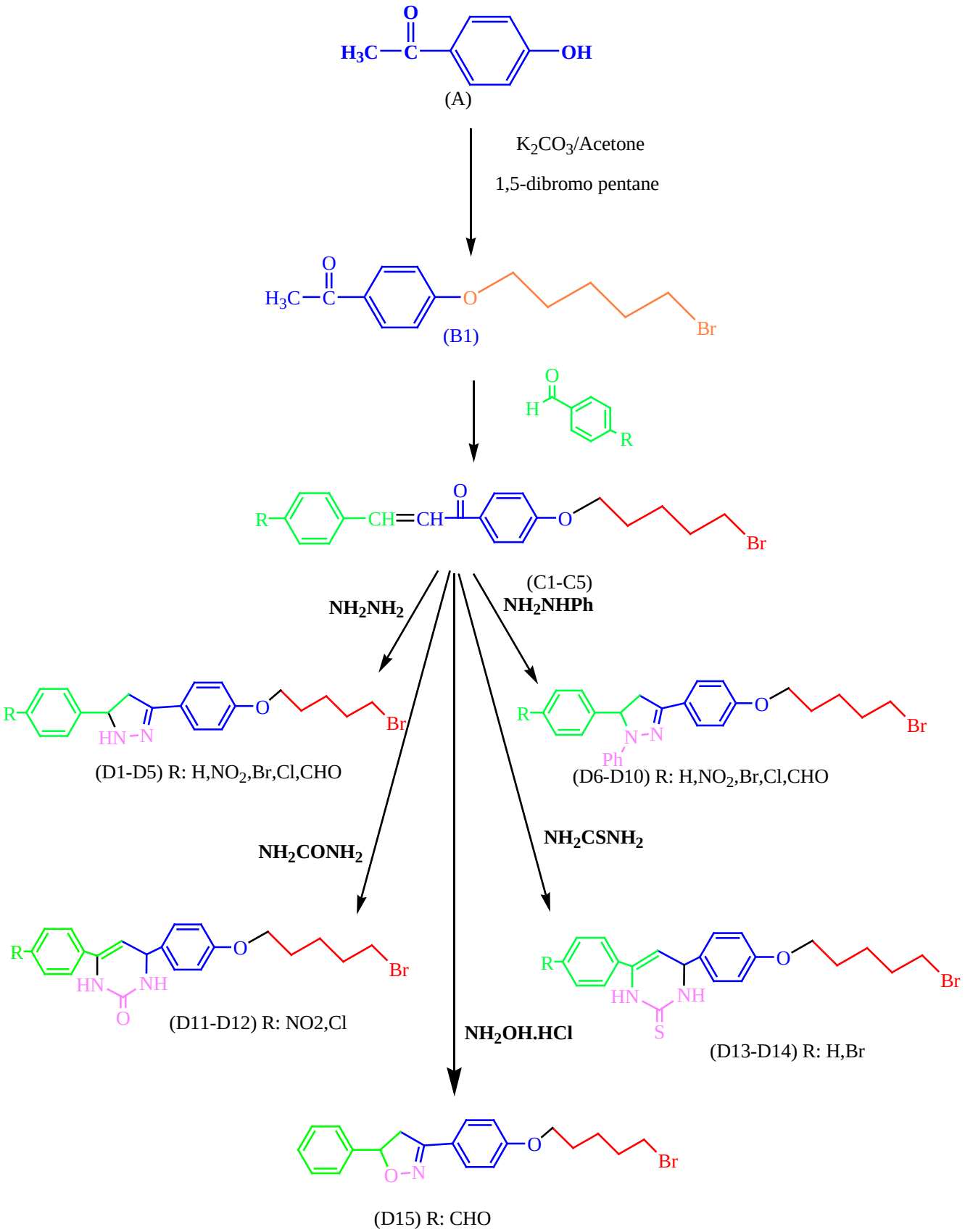
Fourth step: pyrazole derivatives (D1-D10) and (D16- D17) compounds were synthesized by reaction of Chalcon derivatives (C1-C6) with appropriate hydrazine (hydrazine hydrate, phenyl hydrazine).

Fifth step: pyrimidine derivatives (D11-D14) and (D18- D19) compounds were synthesized by reaction of Chalcon derivatives (C1-C6) with appropriate (urea, Thiourea).

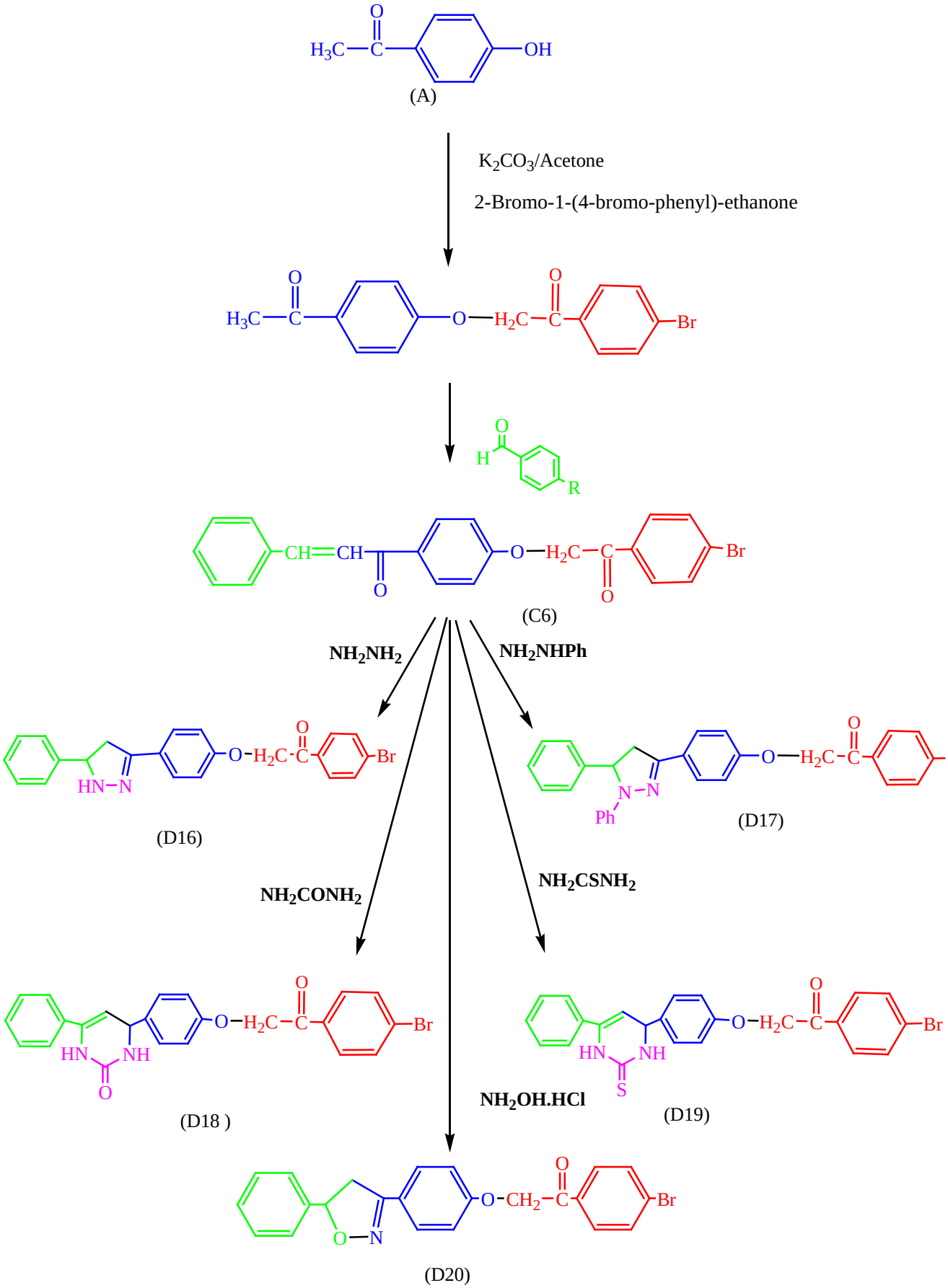
Sixth step: isoxazol derivatives (D15) and (D20) compounds were synthesized by reaction of Chalcon derivatives (C5) and (C6) with Hydroxylamine-hydrochloric.

The prepared compounds were characterized by using FT-IR, ^{1}H-NMR, ^{13}C-NMR spectroscopic techniques, CHNO-S element analysis techniques and melting point device for some of them.

The prepared compounds **(D1-D20)** were used as corrosion inhibitors for mild steel in 1M H_2SO_4 at 30°C for 24 h. Weight loss measurement was regarded as evaluation method to test the inhibition efficiency of the above compounds. Gibbs free energy values are calculated for the adsorption was obtained useful information to predict the interaction between organic compounds molecules and the metal surface as corrosion inhibitors for the metal surface.



Scheme1: The chemical steps for the synthesis of compounds **(D1-D15)**



Scheme2: The chemical steps for the synthesis of compounds **(D16-D20)**

Chapter One

Introduction and Literature Review

1. Introduction

Piceol (**4-Hydroxyacetophenone**) is a phenolic compound found in the needles and in mycorrhizal roots of Norway spruces,[1] it has chemical formula $C_8H_8O_2$ as shown in Fig. 1-1.

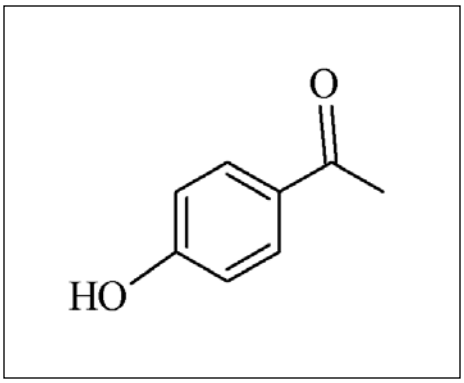
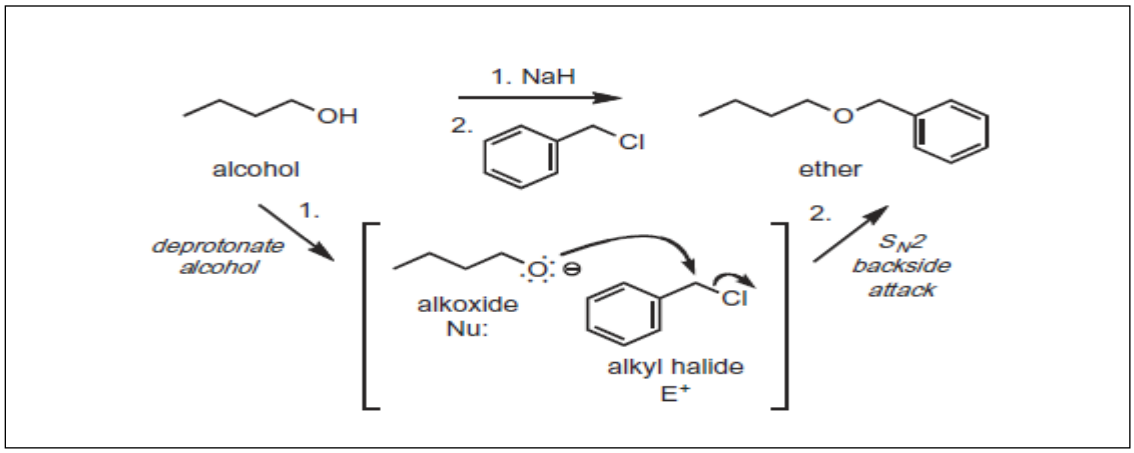


Figure 1-1: Chemical structure of piceol.

It seems a useful starting material for beginning the organic synthesis steps to yield precursors or complicated molecules. In addition to the aromatic ring, there are two functional groups (HO- and Me-CO-) and could be used to complete chemical synthesis of complex organic molecules.

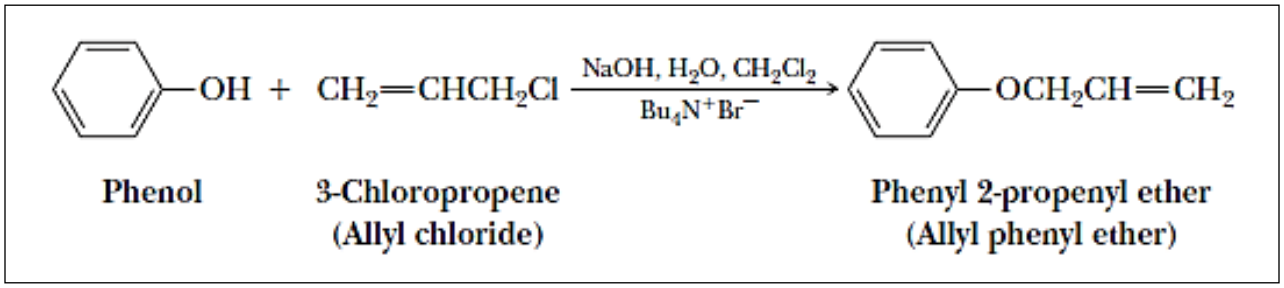
1.1. O-Alkylation

The O-alkylated product is similar to the reaction seen in Williamson ether synthesis [2], involves nucleophilic displacement of a halide ion or other good leaving group by an alkoxide ion (scheme 1-1).



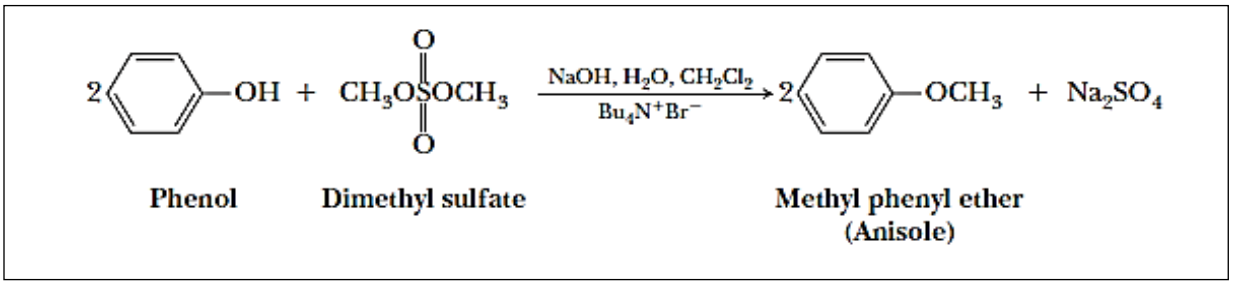
Scheme 1-1: Williamson ether synthesis

Williamson ether synthesis as Alkyl-aryl ethers [2] can be prepared from a phenoxide salt and an alkyl halide (the Williamson synthesis). Phenols are weak acids (pk_a = 9.95) and react with strong bases, such as NaOH, to form water soluble salts. Eventually, The $Bu_4N^+Br^-$ is used to facilitate reaction between the polar phenoxide salt and the hydrophobic alkyl halide in the mixed solvent (**Scheme 1-2**).



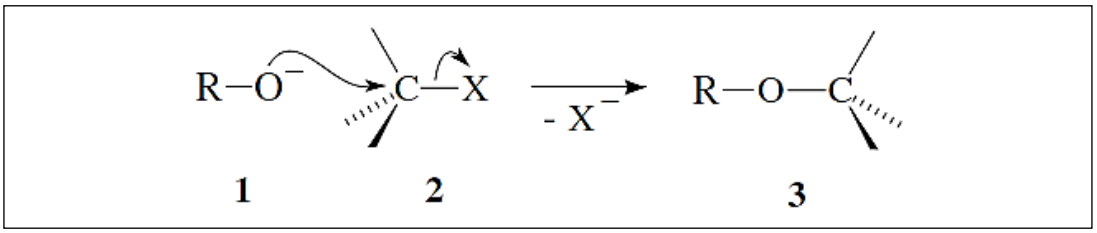
Scheme 1-2: Alkyl-aryl ether

The synthesis of anisole illustrates the use of dimethyl sulfate as a methylating agent (**Scheme 1-3**).



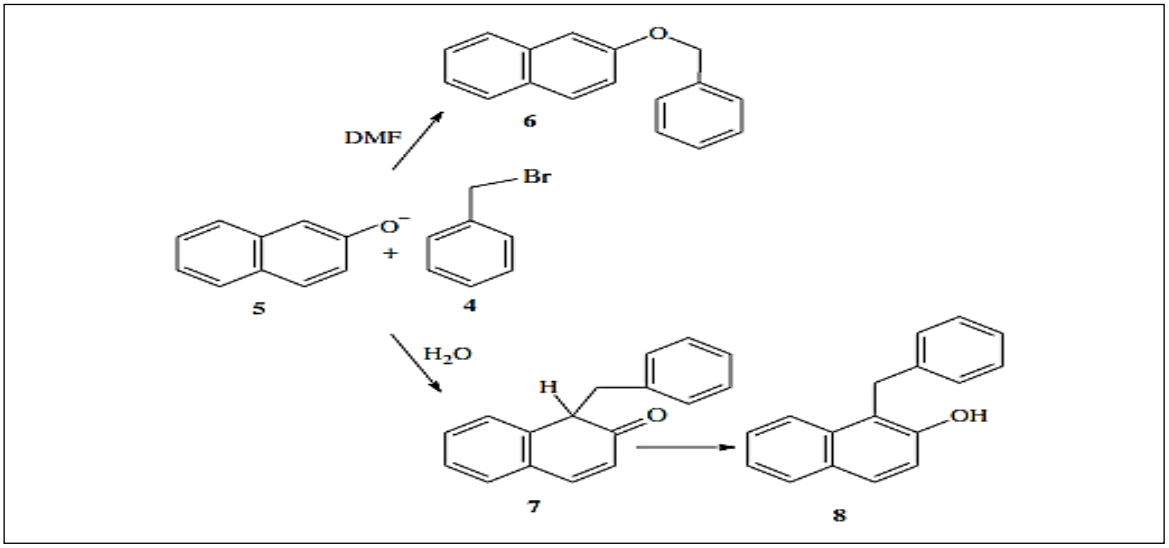
Scheme 1-3: Methyl phenyl ether

In most cases the alkoxide or phenoxide **1** reacts with the alkyl halide **2** by a bimolecular nucleophilic substitution mechanism (**Scheme 1-4**):



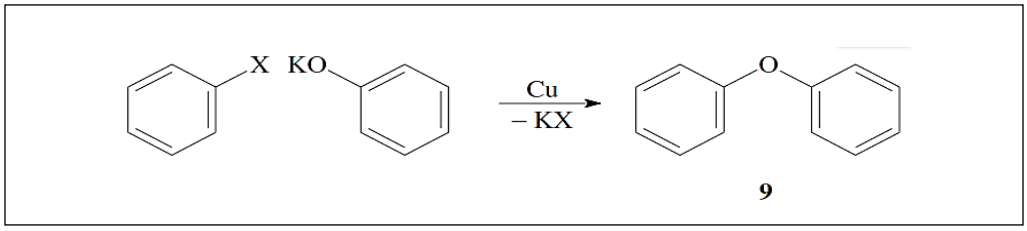
Scheme 1-4: S_N2 Mechanism

With secondary and tertiary alkyl halides an E2-elimination is often observed as a side-reaction. As the alkyl halide reactant an iodide is most often employed, since alkyl iodides are more reactive than the corresponding bromides or chlorides. With phenoxides as nucleophiles a C-alkylation can take place as a competing reaction. The ratio of O-alkylation versus C-alkylation strongly depends on the solvent used. For example reaction of benzylbromide **4** with β-naphth-oxide **5** in N,N-dimethylformamide as solvent yields almost exclusively the β-naphthyl benzyl ether **6**, while the reaction in water as solvent leads *via* intermediate **7** to formation of the C-benzylated product 1-benzyl-2-naphthol **8** as the major product [3] **(scheme 1-5)**.



Scheme 1-5: O-alkylation versus C-alkylation strongly depends on the solvent.

A variant for the synthesis of diaryl ethers—e.g. diphenyl ether **9**, where an aryl halide and a phenoxide are reacted in the presence of copper or a copper-(I) salt, is called the Ullmann ether synthesis [4] (**Scheme 1-6**).



Scheme 1-6: Synthesis of diaryl ethers.

1.2. Chalcone synthesis

The term "chalcone" is a generic term used to describe compounds with the 1,3-diphenylprop-2-en-1-one framework (Figure 1-2).

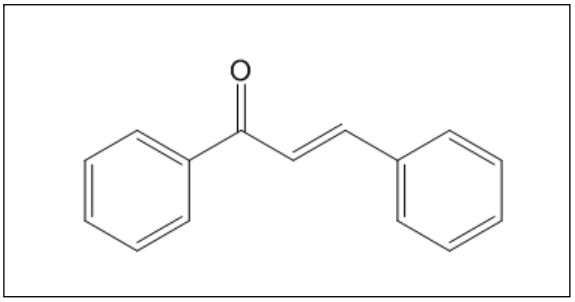


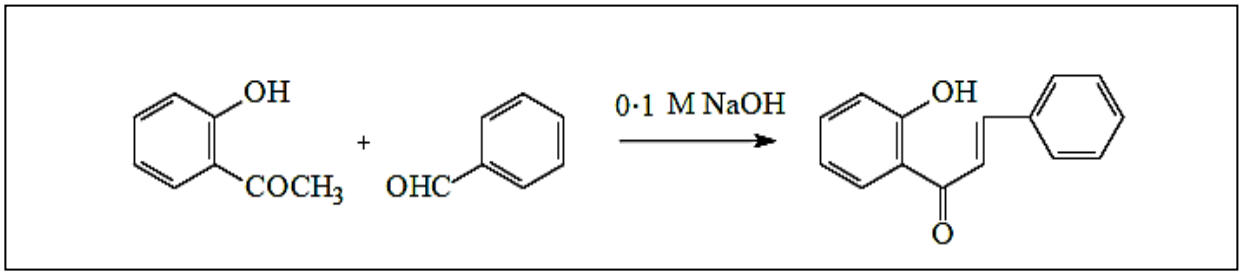
Figure 1-2: 1,3-diphenylprop-2-en-1-one

Chalcones can be prepared by two condensation reactions namely [5,6]:

1. Claisen Schmidt condensation
2. Aldol condensation

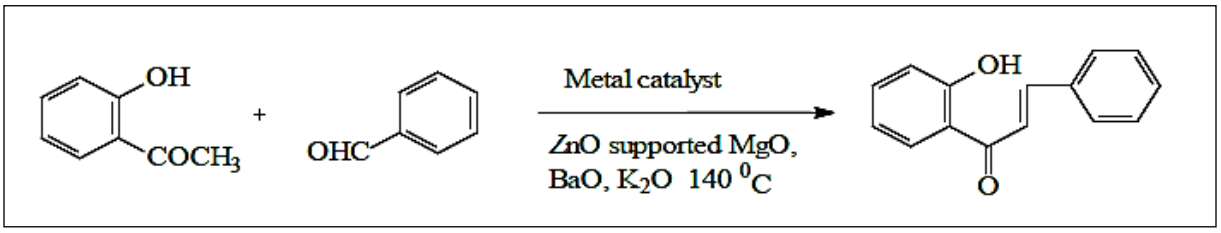
Both of these reaction results in the condensation of aromatic aldehyde or ketone with an aliphatic ketone or aldehyde to give a condensed product known as chalcone. Chalcones can be obtained by the acid or base catalyzed aldol condensation of acetophenones with aromatic aldehydes, like

2'-hydroxyacetophenone react with benzaldehyde in the presence of 0.1 M NaOH to give the chalcone [7] (**Scheme 1-7**).



Scheme 1-7: Chalcone synthesis by base

Liquid phase Claisen–Schmidt condensation between 2'-hydroxy acetophenone and benzaldehyde was carried out over a zinc oxide supported metal oxide catalyst under solvent free conditions to form 2'-hydroxychalcone [8] (s**cheme 1-8)**.



Scheme 1-8: Liquid phase Claisen–Schmidt condensation

Bandgar *et al.* [9] synthesized some β-chlorovinylchalcones by Claisen-Schmidt condensation reaction (Figure 1-3) and the compounds were screened for their antimicrobial activity.

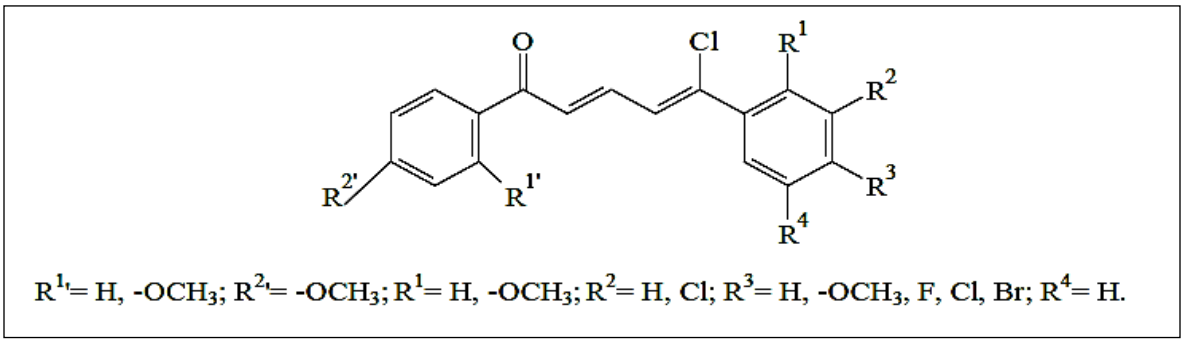
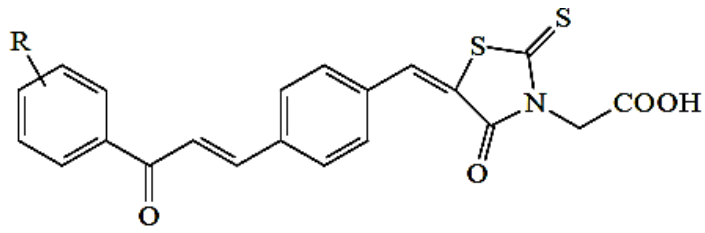


Figure 1-3: Synthesized some β-chlorovinylchalcones

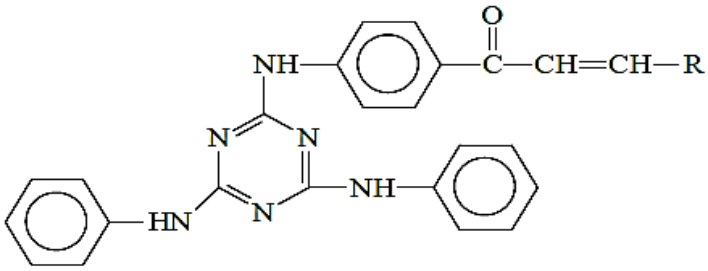
Chen *et al*.[10] synthesized some new chalcones having a rhodanine-3-acetic acid moiety (Figure 1-4).



R= 4-CH_3, 2,4-$(CH_3)_2$, 3-OCH_3, 4-OCH_3, H, 2-F, 4-F, 2-Cl, 3-Cl, 4-Cl, 2,4-$(Cl)_2$, 2-Br, 3-Br,

Figure 1-4: Synthesized some new chalcones having a rhodanine-3-acetic acid

Some novel S-triazine based chalcones and their derivatives were prepared [11] (Figure 1-5) by the reaction of 2,4-bis-(phenylamino)-6-(4'-acetylphenylamino)-s-triazine with different aldehydes to form chalcones . These chalcones were screened for their antibacterial activity by using the disc diffusion method, TLC- bioautographic and microdilution methods against a panel of Gram-positive and Gram-negative, using streptomycin and ampicillin as standards.



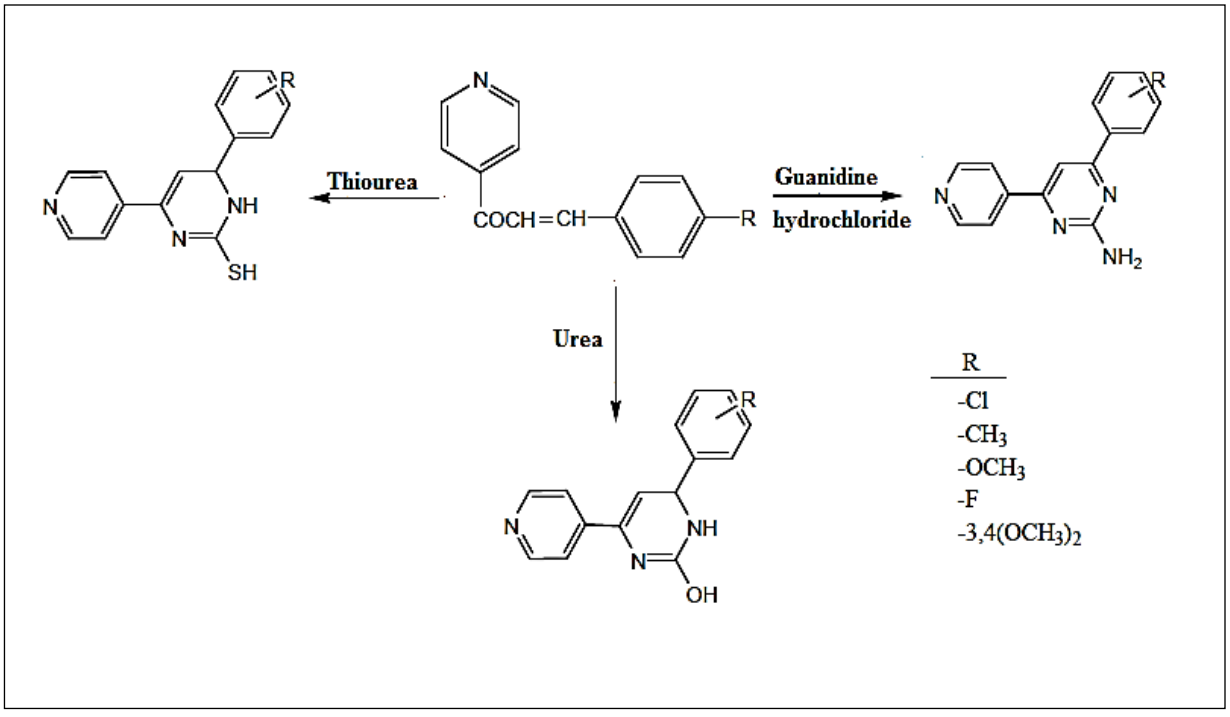
R= 4-nitrophenyl, 4-chlorophenyl, 2-furanyl, 2-thienyl, 2-methoxyphenyl

Figure 1-5: Some novel S-triazine based chalcones

1.3. Ring closure reactions of chalcones

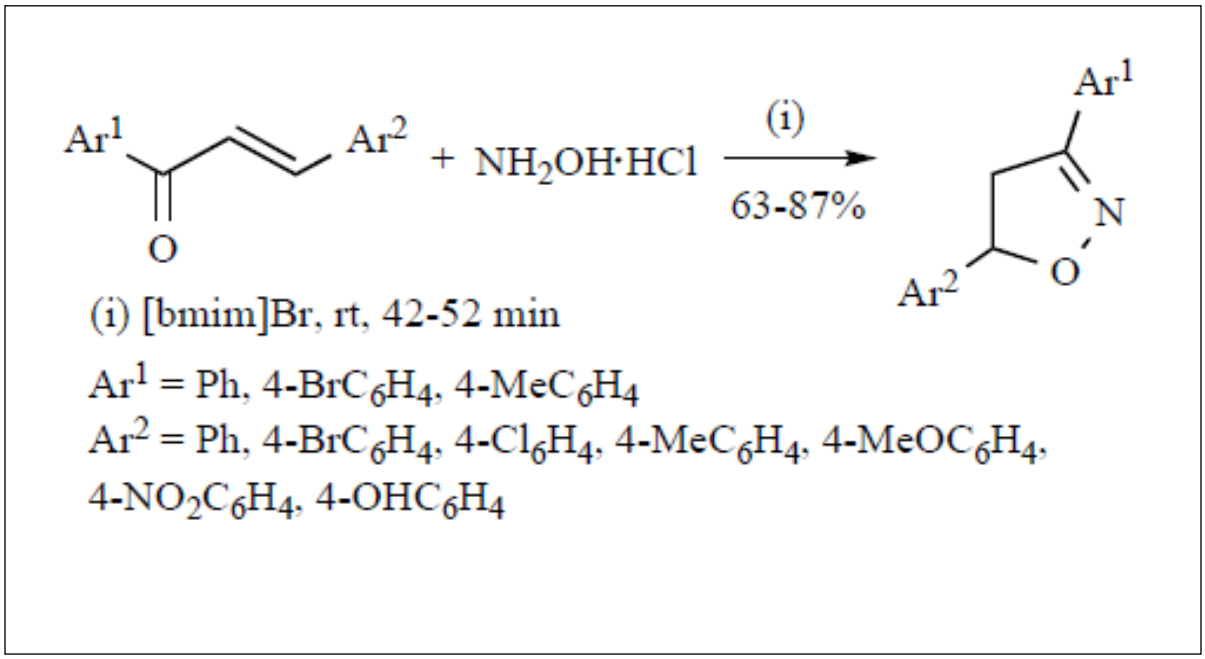
One of the important class of reactions of chalcones are the ring closure reactions with hydrazine, phenylhydrazine, guanidine, urea etc. producing heterocyclic derivatives of chalcones. Both chalcones and their heterocyclic derivatives have a number of pharmacological activities such as antiinflammatory, antimicrobial, antifungal, antibacterial, antioxidant, cytotoxic, antitumor, anticancer, antimitotic, antileishmanial, anti-malarial, antitubercular, antiviral, and so on [12].

An attempt has been made to synthesize chalcones by the reaction of 4-acetylpyridine with various aromatic and heteroaromatic aldehydes (**Scheme 1-9**). Further, chalcones derivatives were cyclized to pyrimidine analogs by using thiourea, urea and guanidine hydrochloride [13].



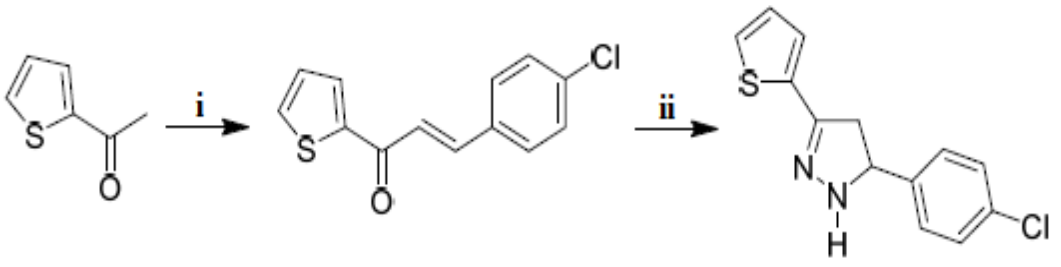
Scheme 1-9: Chalcones derivatives

Few examples of 3,5-diaryl-2-isoxazolines were obtained when chloro-substituted chalcones reacts with hydroxylamine hydrochloride in refluxing DMF containing piperidine [14]. An ecofriendly reaction occurs efficiently in the presence of the ionic liquid butylmethylimidazolium bromide ([bmim]Br), acting as solvent and catalyst [15] (**scheme 1-10**).



Scheme 1-10: 3,5-diaryl-2-isoxazolines

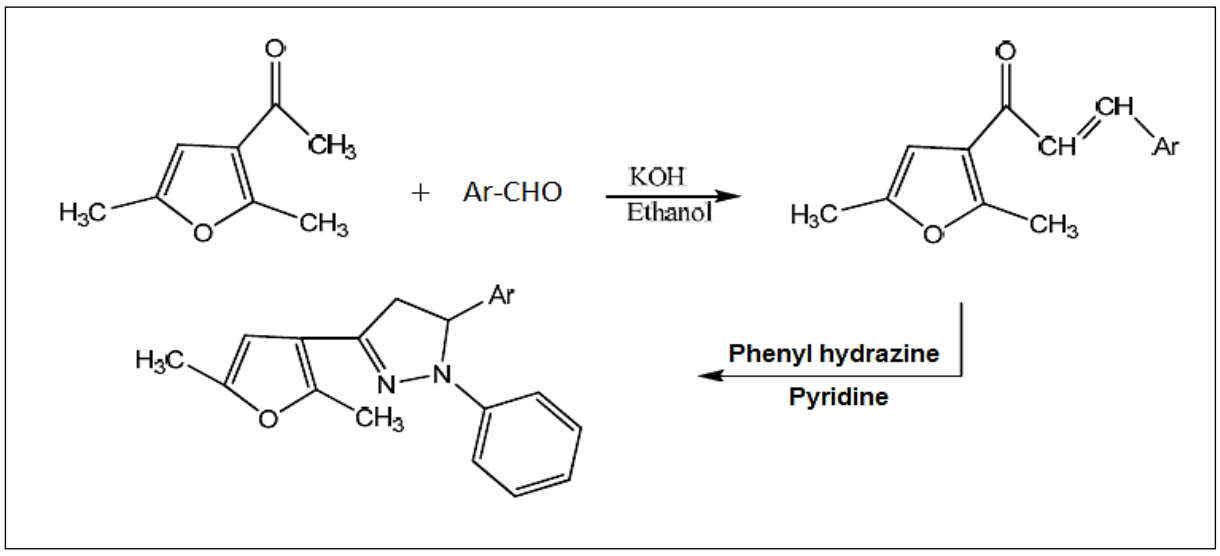
The synthesis of new pyrazoline derivatives were carried out. In the initial step, 1-(2-thienyl)-3-(4-chlorophenyl)-2-propen-1-one was synthesized via the base-catalyzed Claisen-Schmidt condensation of 2-acetylthiophene with 4-chlorobenzaldehyde. The ring closure reaction of the chalcone with hydrazine hydrate afforded 5-(4-chlorophenyl)-3-(2-thienyl)-2-pyrazoline [16] **(scheme 1-11)**.



(i) 4-Chlorobenzaldehyde, 10% aqueous sodium hydroxide solution, ethanol, rt, 6–8 h
(ii) 80% hydrazine hydrate, ethanol, reflux, 5 h

Scheme 1-11: The ring closure reaction of the chalcone with hydrazine hydrate

Sridhar and Rajendraprasad [17] synthesized some new 2-pyrazolines and studied their analgesic activity. Pyrazolines were synthesized in a two step process. In first step, 3-acetyl-2,5-dimethylfuran and appropriate aldehydes were reacted in the presence of ethanol and aqueous KOH to afford 1-(2`,5`-dimethyl-3`-foryl)-3-(aryl)-2-propen-1-one. Then these compounds were condensed with phenyl hydrazine in the presence of pyridine in refluxing ethanol to prepare 1-phenyl-3-(2`,5`-dimethyl-3`-foryl)-3-(aryl)-2-pyrazoline (**scheme 1-12**).



Scheme 1-12: New 2-pyrazolines

1.4. Corrosion phenomena

The word corrosion stands for material or metal deterioration or surface damage in an aggressive environment. Corrosion is a chemical or electrochemical oxidation process, in which the metal transfers electrons to the environment and undergoes a valence change from zero to a positive value. The environment may be a liquid, gas or hybrid soil-liquid. These environments are called electrolytes since they have their own conductivity for electron transfer. Corrosion and its control mean the corrosion process and the measures taken to control or keep in check the corrosion process or referred to as corrosion, prevention and protection [18]. The corrosion process which can be chemical in nature or electrochemical due to a current flow, requires at least two reactions that must occur in a particular corrosive environment. These reactions are classified as anodic and cathodic reactions and are defined below for a metal *M* immersed in sulfuric acid solution as an example. Hence, metal oxidation occurs through an anodic reaction and reduction is through a

$$M \rightarrow M^{+z} + ze^{-} \qquad (Anodic \equiv Oxidation)$$

$$zH^{+} + zSO_4^{-} + ze^{-} \rightarrow \frac{z}{2}H_2SO_4 \qquad (Cathodic \equiv Reduction)$$

$$M + zH^{+} + zSO_4^{-} \rightarrow M^{+z} + \frac{z}{2}H_2SO_4 \qquad (Overall \equiv Redox)$$

where M = Metal; M^{+z} = Metal cation; H^{+} = Hydrogen cation; SO_4^{-} = Sulfate anion; Z = Valence or oxidation state

Scheme 1-13: Reaction of a metal immersed in sulfuric acid solution.

The forms of corrosion have been identified based on the apparent morphology of corrosion, the basic factor influencing the mechanism of corrosion in each form. Thus, the six forms of corrosion are as given in Table 1.1[19].

Table1-1: Morphological Classification of Corrosion

1.General corrosion	Uniform,quasi-unform,and nonuniform corrosion galvanic corrosion
2.Localized corrosion	Pitting corrosion, crevice corrosion, filiform corrosion
3.Metallurgically influenced corrosion	Intergranular corrosion ,sensitization , exfoliation , dealloying
4.Microbiological corrosion	
5.Mechanically assisted corrosion	Wear corrosion, erosion corrosion, corrosion fatigue
6.Environmentally induced cracking	Stress- corrosion cracking ,hydrogen damage, embrittlement ,hydrogen-induced cracking , high temperature hydrogen attack , hot-cracking , solid metal-induced embrittlement

General corrosion can be even or uneven and is the most common form of corrosion. It is characterized by a chemical or electrochemical reaction that takes place on the exposed surface. The metal becomes thinner and eventually results in perforation and failure. General corrosion accounts for the greatest loss of metal on a tonnage basis. This mode of corrosion does not present a great threat from a technical standpoint since the life of the equipment can be estimated from the corrosion rates obtained from immersion of the sample material in the medium of interest. The corrosion rate data may then be used in the design of the equipment. General corrosion can be prevented or reduced by the proper choice of materials or by use of corrosion inhibitors or cathodic protection [19]. A corrosion inhibitor is a chemical substance that, upon addition to a corrosive environment, results in reduction of corrosion rate to an acceptable level. Organic inhibitors generally have heteroatoms. O, N, and S

are found to have higher basicity and electron density and thus act as corrosion inhibitor [20,21]. It is generally agreed that corrosion inhibition is due to the adsorption of the inhibitor molecule at the metal–solution interface, which is accompanied by a change in potential difference between the metal electrode and the solution due to the non-uniform distribution of electric charges at the interface. In acid media, nitrogen-base materials and their derivatives, sulphur-containing compounds, aldehydes, thioaldehydes, acetylenic compounds, and various alkaloids, for example, papaverine, strychnine, quinine, and nicotine are used as inhibitors [22]. Important parameters considered for inhibitors are, solubility of inhibitor in corrosive medium, compatibility of inhibitor in corroding system, stability of inhibitor by varying pH and temperature, inhibitor cost, environmental friendliness and corrosion inhibition efficiency [23]. The organic compounds as corrosion inhibitors for aluminum and its alloys in alkaline and chloride-containing solutions published over the last two decades [24] (Figure 1-6).

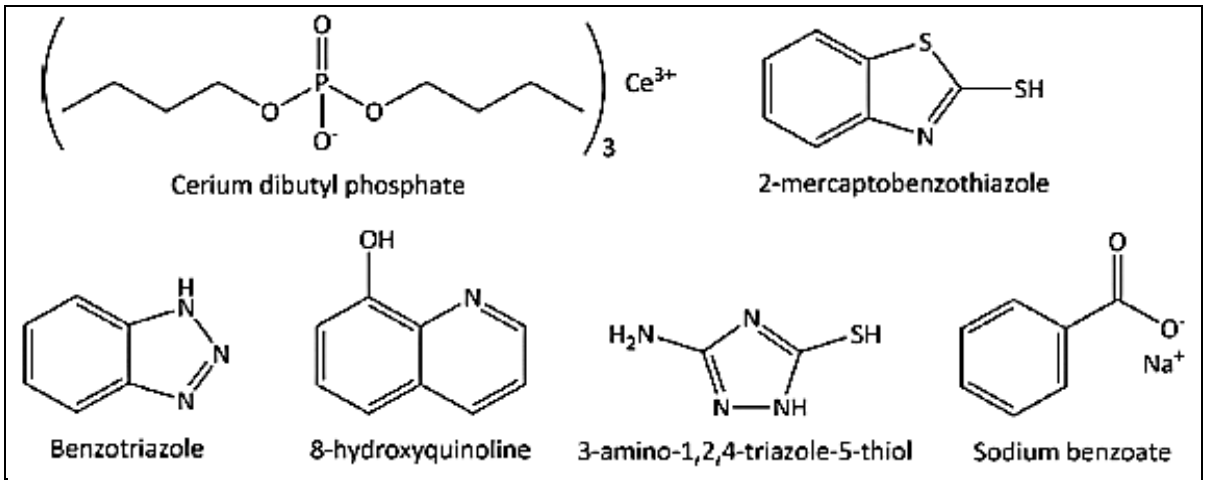


Figure 1-6: The most tested organic compounds as corrosion inhibitors for aluminum and aluminum alloys in both alkaline and chloride-containing solutions

The inhibition performance of thiocarbanilide on the electrochemical corrosion behavior of high carbon steel in 1 M H_2SO_4 and HCl acid solutions was studied through weight loss method and potentiodynamic polarization test. Data obtained showed that the organic compound performed effectively in acid solutions at all concentrations with an average thiocarbanilide inhibition efficiency above 70% in H_2SO_4 acid and 80% in HCl acid from weight loss and potentiodynamic polarization test respectively [25] (Figure 1-7).

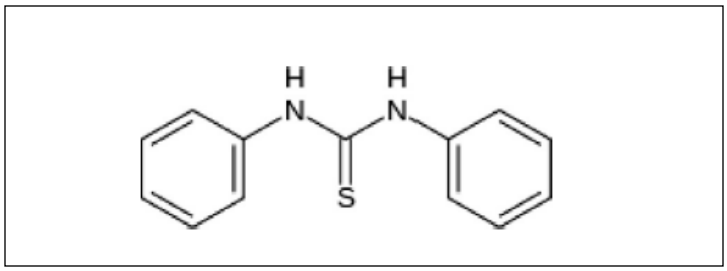


Figure 1-7: Chemical structure of thiocarbanilide

The inhibiting effect of some thiophene derivatives in 1 M HCl on the corrosion of carbon steel was studied by electrochemical techniques. The results show that the inhibition efficiency increased with increase in inhibitor concentration and decreases with raising temperature. The obtained results indicated that the investigated compounds are physically adsorbed on the carbon steel surface. Potentiodynamic polarization studies showed that these compounds are mixed-type inhibitors and the results obtained from the different techniques are in good agreement [26].

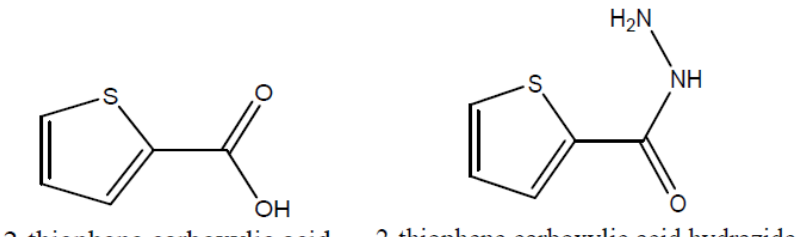
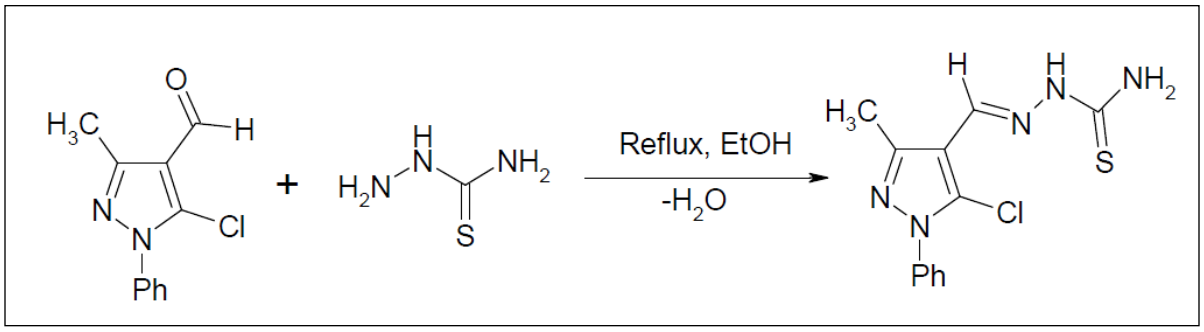


Figure 1-8: Thiophene derivatives

5-Chloro-1-Phenyl-3-methyle Pyrazolo-4-methinethiosemicarbazone was prepared and investigated as corrosion inhibitors for carbon steel in HCl by chemical and electrochemical method. It has been observed that corrosion rate decreases and inhibition efficiencies and surface coverage degree increases with increasing in inhibitor concentration and temperature [28] (**scheme1-15**).



Scheme1-14: 5-Chloro-1-Phenyl-3-methylepyrazolo-4-methinethio semicarbazone

The effect of Keto-enol derivatives namely (Z)-3-hydroxy-1-(pyridin-2-yl)but-2-en-1-one (KE-1) and (Z)-1-(1,5-dimethyl-1H-pyrazol-3-yl)-3-hydroxy-3-(pyridin-2-yl)prop-2-en-1-one (KE-2) on the inhibition of carbon steel (CS) corrosion in 1 M HCl has been studied using electrochemical techniques. Weight loss measurements indicate that these compounds reduce the corrosion rate of carbon steel in acidic solution and the inhibition effect increases with the inhibitors concentration but decreases with temperature [29]

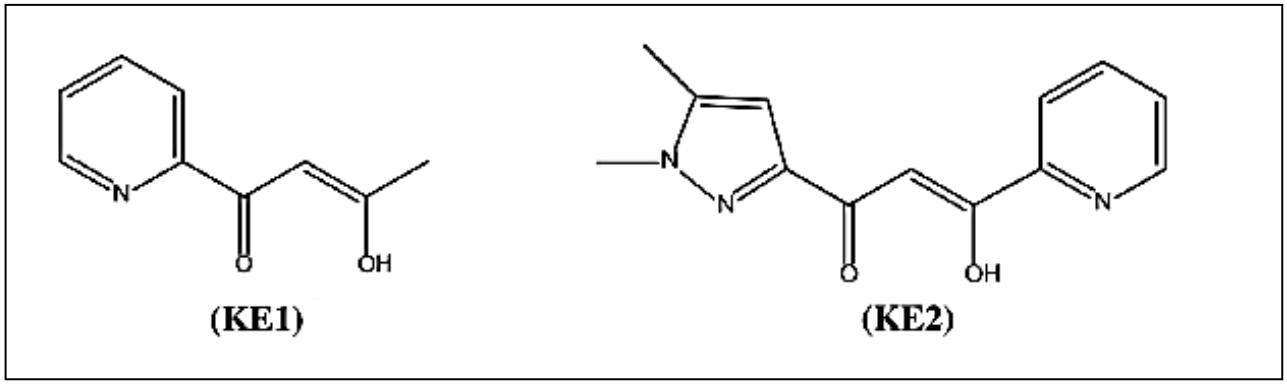
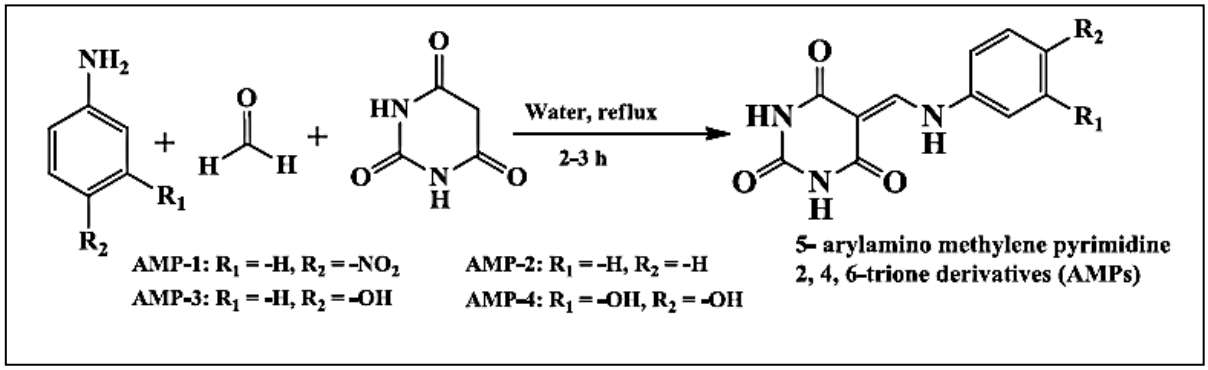


Figure 1-9:: Keto-enol derivatives(KE-1) and(KE-2)

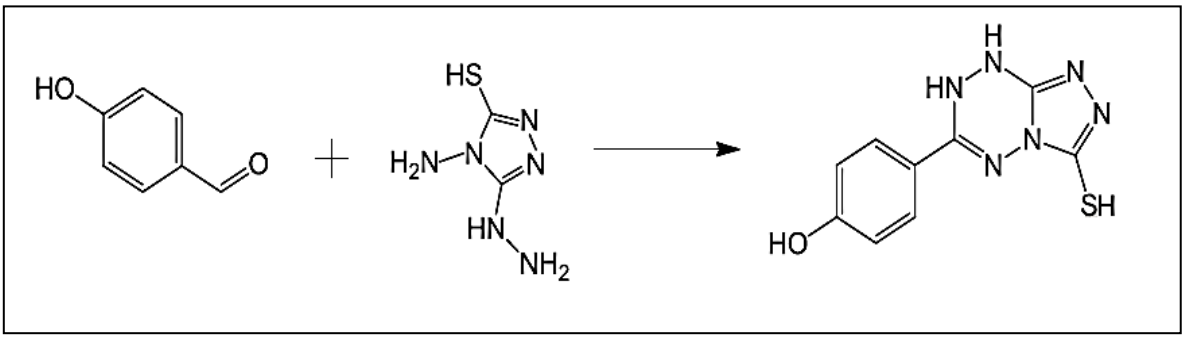
The effect of electron withdrawing nitro (–NO_2) and electron releasing hydroxyl (–OH) groups on corrosion inhibition potentials of 5-arylaminomethylenepyrimidine-2,4,6-trione (AMP) had been studied. Four AMPs tagged AMP-1, AMP-2, AMP-3 and AMP-4 were studied for their ability to inhibit mild steel corrosion in 1 M HCl using experimental and theoretical methods. Gravimetric results showed that inhibition efficiency of the studied inhibitors increases with increasing concentration. The results further revealed that that electron withdrawing nitro (–NO2) group decreases the inhibition efficiency of AMP, while electron donating hydroxyl (–OH) group increases the inhibition efficiency of AMP [30] (**scheme1-16**)..



Scheme1-15: 5-arylaminomethylenepyrimidine-2,4,6-trione

The synthesis and characterization of a novel organic corrosion inhibitor (4-(3-mercapto-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-b][1,2,4,5]tetrazin-6-yl)phenol), for mild steel in 1M hydrochloric acid (HCl) has been successfully reported for the first time. The inhibitor evaluated as corrosion inhibitor for mild steel in 1M of Hydrochloric acid solution using electrochemical measurement techniques. Changes in the electrochemical parameters suggested an adsorption of the inhibitor onto the mild steel surface, leading to the formation of protective films. The results show that the inhibition efficiencies increased with increasing the concentrations of the inhibitors and decreased

with increasing temperature. The maximum inhibition efficiency up to 67 % at the maximum concentration 0.5 mM. This shows that those inhibitors are effective in helping to reduce and slowing down the corrosion process that occurs to mild steel with a hydrochloric acid solution by providing an organic inhibitor for the mild steel that can be weakened by increasing the temperature[31] (**scheme1-17**)...



Scheme1-16: (4-(3-mercapto-5,6,7,8-tetrahydro-[1,2,4]triazolo[4,3-b][1,2,4,5] tetrazin-6-yl) phenol)

Six pyrazole and pyrazolone derivatives namely: 3-amino-1-phenyl-5-pyrazolone (1), 3-amino-1-(2,4-dinitrophenyl)-5-pyrazolone (2), 1H-pyrazole-3,5-diamine-4-(2-phenyldiazenyl) (3), 1-phenyl pyrazole-3, 5-diamine, 4-[2-(4-methylphenyl) diazenyl] (4), 1H-pyrazole-3,5-diamine, 4-[2-(4-methylphenyl) diazenyl] (5), 5-amino-1,3–diphenyl-1H-pyrazolecarbonitrile (6) were synthesized and evaluated as corrosion inhibitors for copper alloy dissolution in basic medium. Corrosion inhibition evaluation was performed using weight loss, polarization and electrochemical impedance measurements. The results showed that the prepared compounds have high efficiency as corrosion inhibitors for dissolution prevention of copper in NH4OH solution at pH of 9 [32].

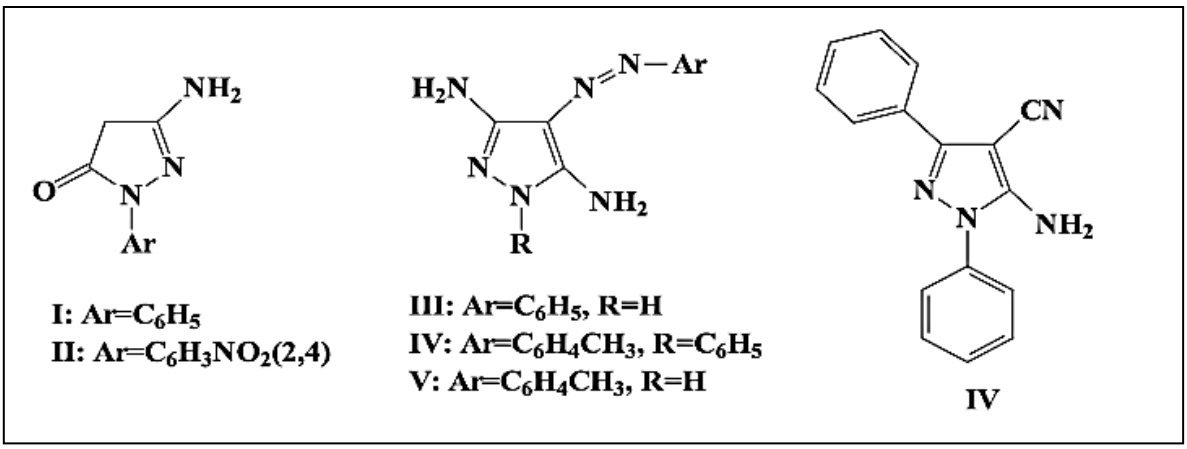


Figure 1-10: pyrazolone derivatives

The influence of azo compound 2,4-dihydroxy-5-((5-mercapto-1H-1,2,4-triazol-3-yl)diazenyl)benzaldehyde) on the carbon steel corrosion in 1 M HCl was investigated using electrochemical tests. The protection efficiency improves with raising the concentration of inhibitor, but lesser with temperature rose. The inhibitor was adsorbed on the metal surface following Langmuir's adsorption isotherm. The electrochemical results showed that the investigated compound doing as mixed-kind inhibitor. The inhibition mechanism was debated in the light of the chemical structure of the investigated compound [33]..

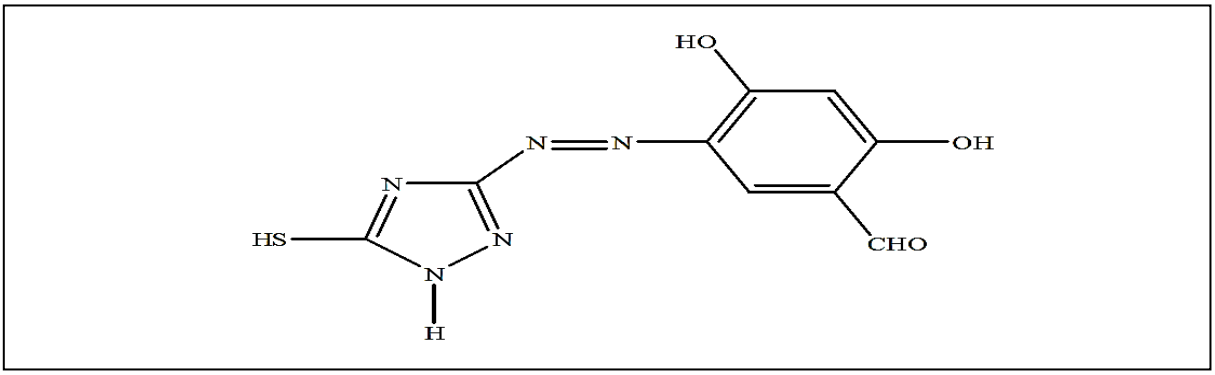


Figure 1-11: 2,4-dihydroxy-5-((5-mercapto-1H-1,2,4-triazol-3-yl)diazenyl)benzaldehyde)

The inhibition performance and mechanism of N^1,N^1,N^3,N^3-tetrakis((3,5-dimethyl-1Hpyrazol- 1-yl)methyl)propane-1,3-diamine (BF2) and N^1,N^1,N^2,N^2-tetrakis((3,5-dimethyl-1H-pyrazol-1-yl)methyl) benzene-1,2-diamine (BF4) for the corrosion of mild steel in 1.0 M HCl were investigated using weight loss method and electrochemical measurements. The results show that both tetrakis pyrazole derivatives act as good inhibitors, and inhibition efficiency follows the order: BF4 > BF2. Two tetrakis pyrazole derivatives are mixed type inhibitors exhibiting predominantly cathodic behavior [34]..

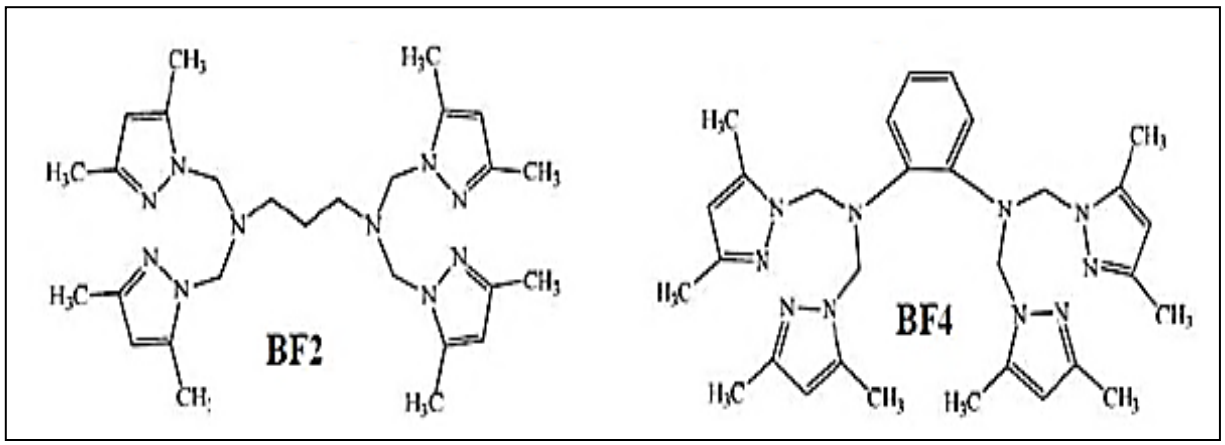


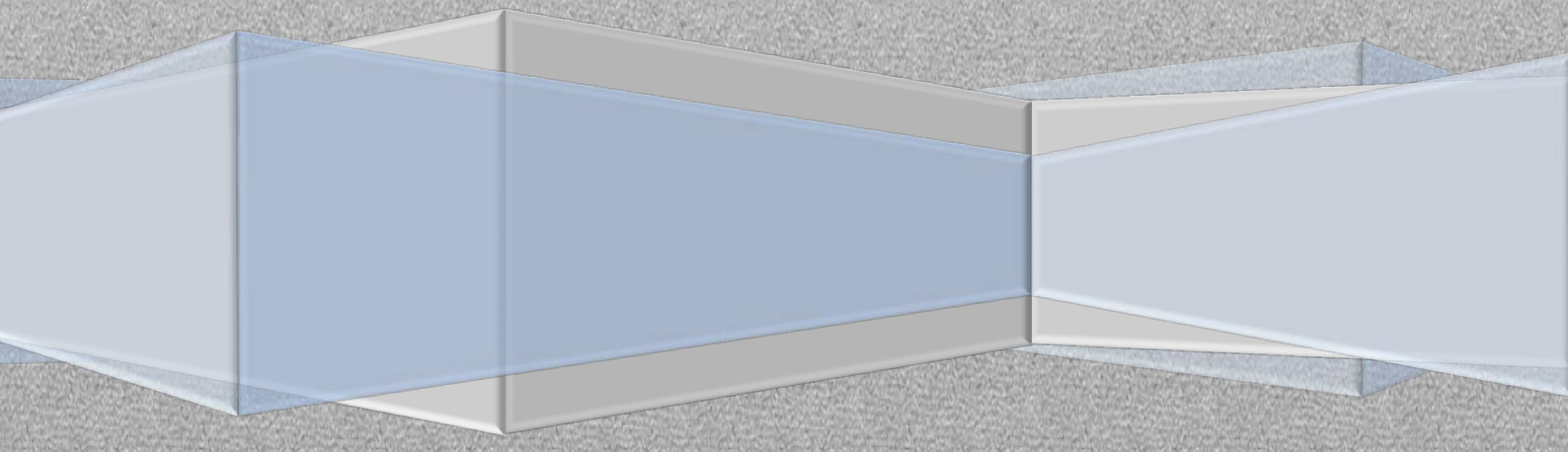
Figure 1-12: pyrazole derivatives (BF2) and (BF4)

Aim of work:

The aim of this work is mainly involving preparation of some heterocyclic compounds derivatives (pyrazole, pyrimidine and isoxazol). The preparation methods use chemical procedures to achieve the final product. These heterocyclic compounds derivatives can be tested as corrosion inhibitors on mild steel surface in 1M H_2SO_4 by using weight loss method in order to evaluate the inhibition efficiency.

Chapter Two

Experimental Part



2- Experimental

2.1. Instrument:

1- Melting points were recorded on a hot stage Gallen Kamp (United Kingdom) melting point apparatus and were uncorrected.

2- Balance, Ohaus, PA 114, USA.

3- FT-IR spectra of the compounds were recorded using Fourier Transform infrared Shimadzu FTIR-8300 infrared spectrophotometer, Japan (SHIMADZU) company as KBr discs in the wave number range of (4000-400) cm^{-1}, at Al-Nahrain University College of Science Department of Chemistry and Ibn Sina state company/ the Ministry of Industry Located at Science Department of Chemistry, College of Science for Women ,Baghdad University.

4- ^{1}H-NMR spectra and ^{13}C-NMR spectra were recorded using nuclear magnetic resonance Bruker advance spectrophotometer 100 MH_Z, using tetramethyl silane as internal standard and DMSO-d_6 as solvent (Sanati Sharif University of Technology , Iran , Tehran)

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

2.2. Chemicals

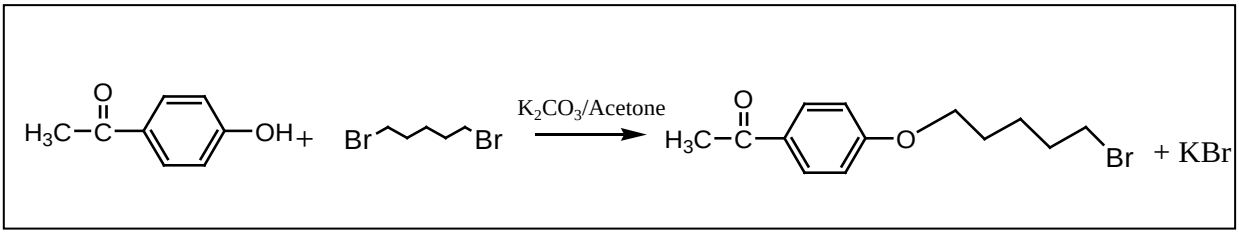
All the chemicals used in the research having highest purity available and they used without further purification. The Table (2-1) shows the listed chemical Materials that used in this research and the companies which provided them .

Table 2-1: chemicals and their Manufacturers.

NO	Chemicals	Source	purity
1	Acetone	Fluka	99%
2	1,5-dibromo pentane	Fluka	99%
3	3-bromo-Benzaldehyde	BDH	98%
4	4-Bromolphenacylbromide	Fluka	98%
5	4-chloro-Benzaldehyde	Alpha chemika	98%
6	4-hydroxyacetophenon	BDH	99%
7	Absolute ethanol	Sigma-Aldrich	99%
8	anhydrous potassium carbonate	BDH	99%
9	Benzaldehyde	Himedia	99%
10	Diethyl Ether	GCC	99%
11	Hydrazine hydrate	Himedia	80%
12	Hydrochloric Acid	Himedia	-
13	Hydroxylamine-hydrochlorid	Fluka	99%
14	Phenyl hydrazine	Himedia	80%
15	p-nitro benzaldehyde	Alpha Aeser	98%
16	Soduim hydroxide	Merck	98%
17	Sulfuric Acid	Himedia	98%
18	Terephthaldehyde	BDH	99%
19	Thiourea	Fluka	99%
20	Urea	Fluka	99%

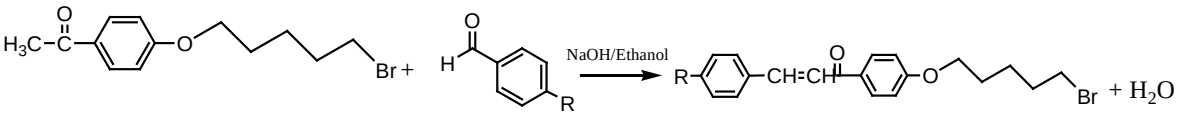
2.3. Preparation Methods of compounds

2.3.1. Preparation 0f 1-[4-(5-Bromo-pentyloxy)-phenyl]-ethanone (B1)



The mixture of 4-hydroxyacytophenon (2.7 g , 0.02 mol) and anhydrous potassium carbonate (2.8 g ,0.02 mol) and 1,5-dibromo pentane (4.6 g , 2.7 mL ,0.02 mol) and 20ml of dry acetone was heated under reflux for 48 hrs . The obtained product was filtered then dried. The filtered product was recrystallized with ethanol to give desired compound as a White solid [35]. The physical properties of synthesized compound (B1) molecular formula $C_{13}H_{17}O_2Br$, color white, molecular weight 285.181 g/mol, M.P.,℃ 43-45 and yield 80% .

2.3.2. Preparation 0f 1-[4-(5-Bromo-pentyloxy)- substituted phenyl]-3-phenyl-propan-1-one(C1-C5)



R: H,NO_2,Br,Cl,CHO

The solution of sodium hydroxide(0.55 g) in water (20 mL) and ethanol (10 mL) was stirred. Immerse the flask in cold water bath of crushed ice, then added 1-[4-(5-Bromo-pentyloxy)-phenyl]-ethanone (2.85g, 0.01 mol) with various aldehyde (0.01 mol). The temperature of the mixture operated at

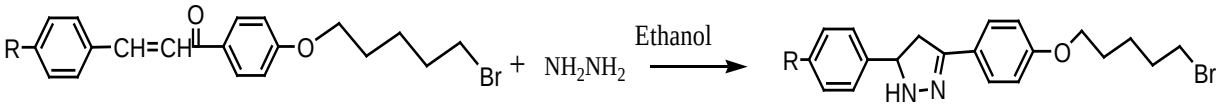
0℃ until increased to room temperature after stirring 3hrs the mixture became so thick. The reaction mixture was left in refrigerator overnight. The obtained product was filtered then dried the crude chalcon recrystallized with ethanol to give compound as a yellow solid [36].

The physical properties of synthesized compounds (C1-C5) are shown in Table (2-3).

Table 2-2: physical properties of compounds (C1-C5)

Comp. name and no.		Molecular formula	Color	M.W g/mol	M.P.,℃	Yield %
C1	1-[4-(5-Bromo-pentyloxy)-phenyl]-3-phenyl-propan-1-one	$C_{20}H_{21}O_2Br$	White	373.29	54-56	70%
C2	1-[4-(5-Bromo-pentyloxy) -phenyl]-3-(4-nitro-phenyl)-propan-1-one	$C_{20}H_{20}NO_4Br$	Yellow	419.295	290-293	87%
C3	1-[4-(5-Bromo-pentyloxy)-phenyl]-3-(4-chloro-phenyl)-propan-1-one	$C_{20}H_{20}O_2BrCl$	Yellow	407.734	140-142	75%
C4	1-[4-(5-Bromo-pentyloxy)-phenyl]-3-(3-bromo-phenyl)-propan-1-one	$C_{20}H_{20}O_2Br_2$	Yellow	452.186	133-135	78%
C5	4-{3-[4-(5-Bromo-pentyloxy)-phenyl]-3-oxo-propyl}-benzaldehyde	$C_{21}H_{21}O_3Br$	Yellow	401.3	124-126	75%

2.3.3. Preparation 0f 3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(4- substituted -phenyl)-4,5-dihydro-1H-pyrazole (D1-D5).



R: H, NO2, Br,Cl,CHO

A solution the mixture of 1-[4-(5-Bromo-pentyloxy)-phenyl]-3-phenyl-propan-1-one (0.01 mol) and hydrazine hydrate (0.32g, 0.32 mL, 0.01 mol) with ethanol was heated under reflux for 24 hrs . The resulting product poured into ice cold water filtered, washed with water and recrystallized with ethanol [37].

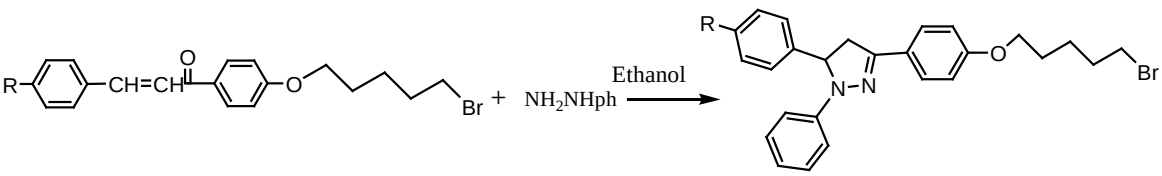
The physical properties of prepared compounds (D1-D5) are given in Table (2-4).

Table 2-3: physical properties of compounds (D1-D5)

Comp. name and no.		Molecular formula	Color	M.W g/mol	M.P.,℃	Yield %
D1	3-[4-(5-Bromo-pentyloxy) - phenyl]-5-phenyl-4,5-dihydro-1H-pyrazole	$C_{20}H_{21}N_2OBr$	Brown	385.304	230 dce.	80%
D2	3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(4-chloro-phenyl)-4,5-dihydro-1H-pyrazole	$C_{20}H_{20}O_2BrCl$	Yellow	419.748	150-152	68%

D3	3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(4-nitro-phenyl)-4,5-dihydro-1H-pyrazole	$C_{20}H_{20}N_4O_3Br$	Reddish Brown	430.301	290-292	77%
D4	3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(3-bromo-phenyl)-4,5-dihydro-1H-pyrazole	$C_{20}H_{20}O_2Br_2$	Yellow	436.186	Gam	85%
D5	4-{3-[4-(5-Bromo-pentyloxy)-phenyl]-5-{4-[5-(4-Bromo-3,4-dihydro-2H-pyrazol-3-yl}-benzaldehyde	$C_{21}H_{21}O_3Br$	Yellow	413.31	298-300	80%

2.3.4. Preparation 0f 3-[4-(5-Bromo-pentyloxy)-phenyl] -5-(substituted -phenyl)-1-phenyl-4,5-dihydro-1H-pyrazole



R: H, NO2, Br , Cl ,CHO

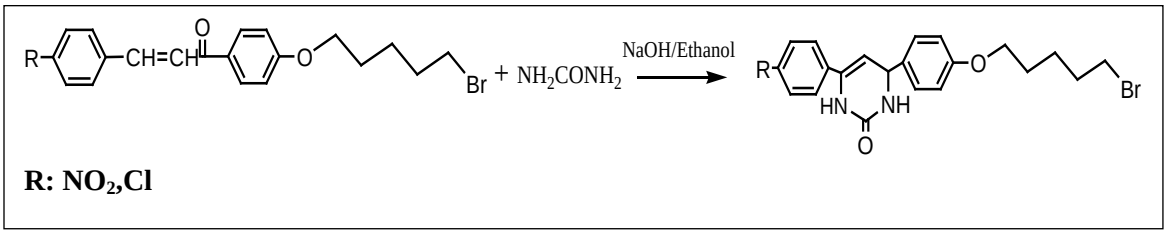
The mixture of 1-[4-(5-Bromo-pentyloxy)-phenyl]-3-phenyl-propan-1-one (0.01 mol) and phenyl hydrazine (1.08g, 0.99mL, 0.01 mol) in absolute ethanol (50mL). Was heated under reflux for 24 hrs, and then poured into ice cold water. The obtained product was filtered, washed with distilled water and recrystallized with ethanol [37].

The physical properties of prepared compounds (D6-D10) are given in Table (2-5).

Table 2-4: physical properties of compounds (D6-D10)

Comp. name and no.		Molecular formula	Color	M.W g/mol	M.P.,℃	Yield %
D6	3-[4-(5-Bromo-pentyloxy)-phenyl]-1,5-diphenyl-4,5-dihydro-1H-pyrazole	$C_{26}H_{25}N_2OBr$	Light Brown	461.401	240 dec.	72%
D7	3-[4-(5-Bromo-pentyloxy)-phenyl] -5-(4-chloro-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazole	$C_{26}H_{24}N_3O_3Br$	Deep Brown	507.407	250 dec.	69%
D8	3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(3-bromo-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazole	$C_{20}H_{20}N_2OBrCl$	Light Brown	495.846	300-302	60%
D9	3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(3-bromo-phenyl)-1-phenyl-4,5-dihydro-1H-pyrazole	$C_{20}H_{20}N_2OBr_2$	Deep Brown	540.297	120-122	76%
D10	4-{5-[4-(5-Bromo-pentyloxy)-phenyl]-2-phenyl-3,4-dihydro-2H-pyrazol-3-yl}-benzaldehyde	$C_{21}H_{21}N_2O_2Br$	Light Brown	489.412	298 dec.	65%

2.3.5. Preparation 4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(substituted-phenyl)-1H-pyrimidin-2-one (D11-D12)



R: NO_2,Cl

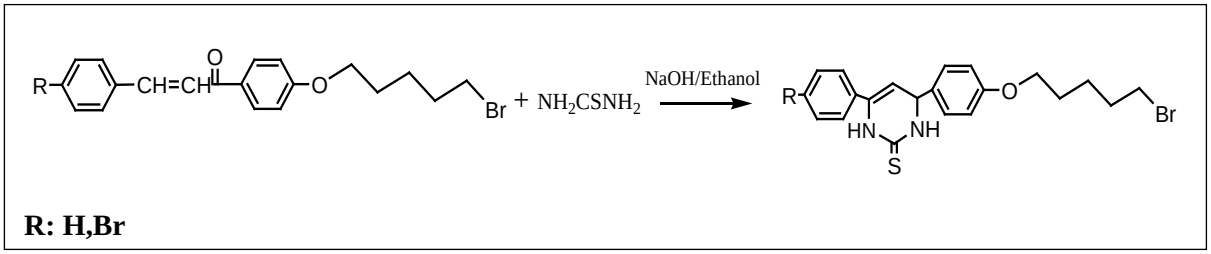
The mixture of 1-[4-(5-Bromo-pentyloxy)- substituted phenyl]-3-phenyl-propan-1-one (0.01mol) in absolute ethanol (50 ml) , urea (0.6g ,0.01 mol) and aqueous sodium hydroxide (10 ml, 0.40 g, 0.01mol) was heated under reflux overnight .The resulting mixture was poured into ice cold water and the obtained product was filtered and crystallized from ethanol [38].

The physical properties of prepared compounds (D11-D12) are given in Table (2-6)

Table 2-5: physical properties of compound(D11-D12)

Comp. name and no.		Molecular formula	Color	M.W g/mol	M.P.,℃	Yield %
D11	4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(4-chloro-phenyl)-1H-pyrimidin-2-one	$C_{21}H_{20}N_2O_2BrCl$	Dark Brown	447.759	Gum	64%
D12	4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(4-nitro-phenyl)-1H-pyrimidin-2-one	$C_{21}H_{20}N_3O_4Br$	Reddish Brown	458.312	270-272	81%

2.3.6. Preparation 4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(substituted-phenyl)-1H-pyrimidin-2-one



R: H,Br

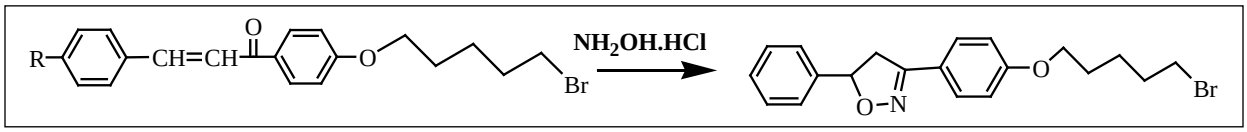
The mixture of 1-[4-(5-Bromo-pentyloxy)- substituted phenyl]-3-phenyl-propan-1-one (0.01mol) in absolute ethanol (50 ml) , thiourea (0.7g ,0.01 mol) and aqueous sodium hydroxide (10 ml, 0.40 g, 0.01 mol) was heated under reflux overnight then. The mixture was poured into ice cold water. The obtained product was filtered , washed and recrystallized from ethanol [38].

The physical properties of prepared compounds (D13-D14) are given in Table (2-7)

Table 2-6: physical properties of compound (D13-D14)

Comp. name and no.		Molecular formula	Color	M.W g/mol	M.P.,℃	Yield%
D13	4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(3-bromo-phenyl)-1H-pyrimidine-2-thione	$C_{21}H_{20}N_2OSBr_2$	Yellow	508.277	282-284	74%
D14	4-[4-(5-Bromo-pentyloxy)-phenyl]-6-phenyl-1H-pyrimidine-2-thione	$C_{21}H_{21}N_2OSBr$	Yellow	429.381	Gum	60%

2.3.7. Preparation 3-[4-(5-Bromo-pentyloxy)-phenyl]-5-phenyl-isoxazole (D15)

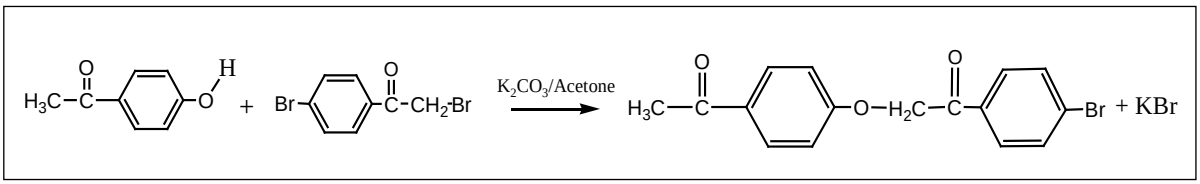


A mixture of chalcone (0.01mol), hydroxylamine hydrochloride (0.7g, 0.01mol) and sodium hydroxide solution (0.25gm in 15mL of water) in ethanol (30mL) was refluxed for 6hrs. The mixture was evaporated under vacuum and poured into ice water. The precipitate obtained was filtered, washed and recrystallized from ethanol [39]

The physical properties of prepared compound (D15) are given molecular formula $C_{20}H_{20}NO_2Br$, color yellow light, M.W 386.288 g/mol, M.P.,℃ 250 dec and yield 67%

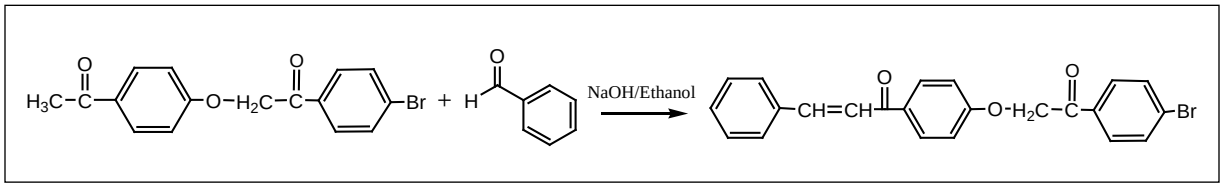
2.4. Preparation Methods of compounds (D16-D20)

2.4.1. Preparation 0f 2-(4-Acetyl-phenoxy)-1-(4-bromo-phenyl)-ethanone.(B2).



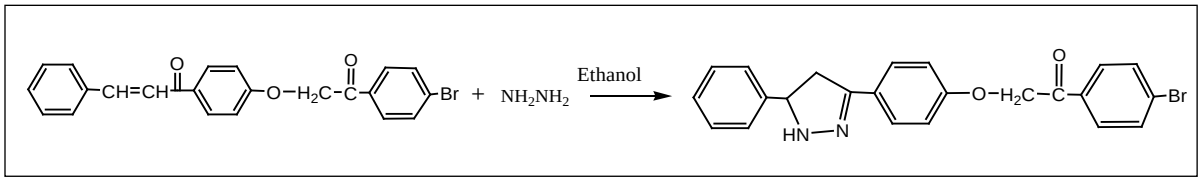
The mixture of 4-hydroxyacetophenon (2.7 g ,0.02 mol) and anhydrous potassium carbonate (2.8 g ,0.02 mol) 4-bromolphenacylbromide(5.55 g ,0.02 mol) and dry acetone(50 ml) , was heated under reflux for 24 hrs . The obtained product filtered then dried. The filtered product recrystallized from ethanol to give desired compound as a Brown solid [35]. The physical property of synthesized compound (B2) was shown molecular formula $C_{16}H_{13}0_3Br$, color reddish brown, molecular weight 333.181 g/mol , M.P.,℃ 142-144, yield %84

2.4.2. Preparation 0f 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one (C6) .



A solution of sodium hydroxide (0.5 g) were added in (20 mL) water and (10 mL) ethanol was stirred. Immersed the flask in cold water bath of crushed ice after that added 2-(4-Acetyl-phenoxy)-1-(4-bromo-phenyl)-ethanone (1.66 g, 0.005 mol) and Benzaldehyde (0.005 mol) was added. The temperature of the mixture operated at 0℃ until increased to room temperature after 3hrs the mixture became so thick. The reaction mixture was left in refrigerator overnight. The obtained product was filtered then dried the crude chalcon recrystallized with ethanol to give compound as a yellow solid [36]. The physical properties of synthesized compound (C6) is shown molecular formula $C_{23}H_{17}O_3Br$, color yellow, molecular weight 421.29 g/mol , M.P.,℃ 118-120, Yield %84

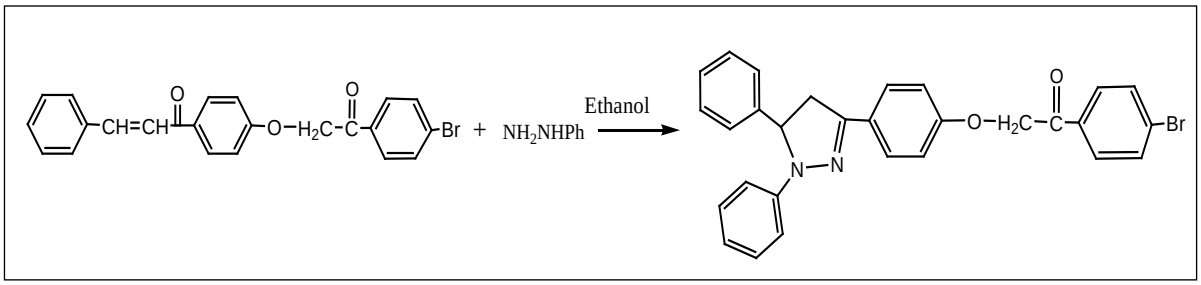
2.4.3. Preparation 0f 1-(4-Bromo-phenyl)-2-[4-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-phenoxy]-ethanone (D16)



A solution of 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one (4.2g, 0.01 mol) , hydrazine hydrate (0.32g, 0.32 mL, 0.01 mol) in absolute ethanol (50mL), was reflexed overnight and the product poured into ice cold water, filtered , washed with water and recrystallized with ethanol [37].

The physical properties of prepared compound (D16) is shown molecular formula $C_{23}H_{17}O_2N_2Br$, color brown, molecular weight 433.304 g/mol , M.P.,℃ 140-142, yield 70%

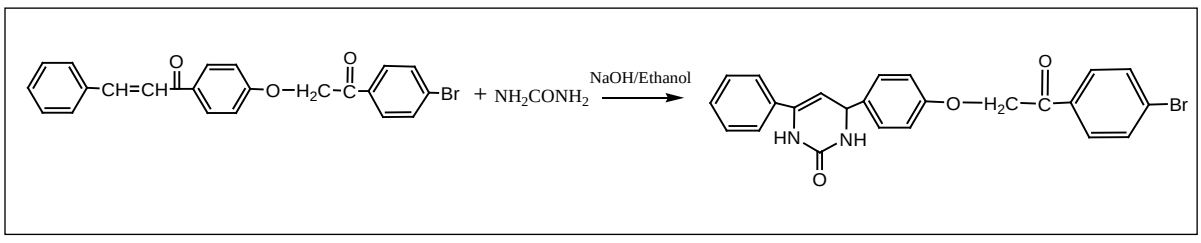
2.4.4. Preparation 0f 1-(4-Bromo-phenyl)-2-[4-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-phenoxy]-ethanone (D17)



A solution of 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one (4.2g, 0.01 mol) , phenyl hydrazine (1.08g,0.99mL, 0.01 mol) in absolute ethanol (50mL). The reaction mixture was reflexed overnight and the product poured into ice cold water, filtered , washed and recrystallized with ethanol [37].

The physical properties of prepared compound (D17) is shown molecular formula $C_{29}H_{21}O_2N_2Br$, color Brown, molecular weight 509.402 g/mol , M.P.,℃ 150 dec, yield 66%

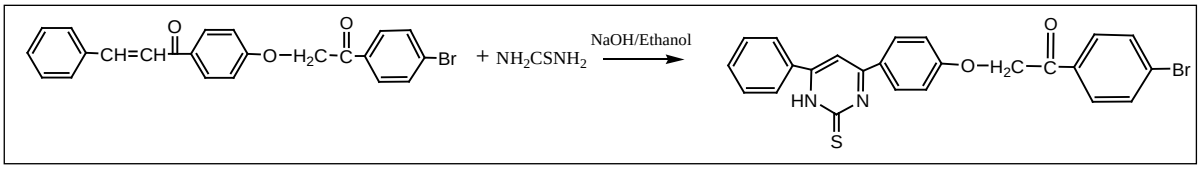
2.4.5. Preparation 4-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-6-phenyl-3,4-dihydro-1H-pyrimidin-2-one(D18)



A mixture solution 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one(4.2g, 0.01mol) in absolute ethanol (50 ml) was stirred then added urea (0.6g , 0.01 mol) and aqueous sodium hydroxide (10 ml, 0.40 g, 0,01 mol) were added. The reaction mixture was heated under reflux overnight then poured into ice cold water. The obtained product was filtered, washed with water and crystallized from ethanol. [38]

The physical properties of prepared compounds (D18) is shown molecular formula $C_{24}H_{19}O_3N_2B$, color Brown, molecular weight 463.331 g/mol , M.P.,℃ 110-112, yield 74%

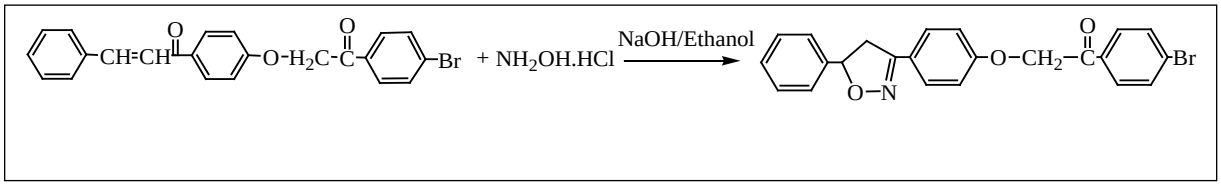
2.4.6. Preparation 1-(4-Bromo-phenyl)-2-[4-(6-phenyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidin-4-yl)-phenoxy]-ethanone(D19)



A mixture solution 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one(4.2g, 0.01mol) in absolute ethanol (50 ml) was stirred then added thiourea (0.7g, 0.01 mol) and aqueous sodium hydroxide (10 ml, 0.40 g, 0,01 mol) were added. The reaction mixture was heated under reflux overnight then poured into ice cold water. The obtained product was filtered, washed with water and crystallized from ethanol [38].

The physical properties of prepared compound (D19) is shown molecular formula $C_{24}H_{19}0_2SN_2Br$, color Brown, molecular weight 479.397 g/mol , M.P.,℃ 112-114, yield 77%

2.4.7. Preparation 1-(4-Bromo-phenyl)-2-[4-(5-phenyl-4,5-dihydro-isoxazol-3-yl)-phenoxy]-ethanone (D20)



A mixture of chalcone (1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one) (4.2g, 0.01mol), hydroxylamine hydrochloride (0.7gm,0.01mol) and sodium hydroxide solution (0.25gm NaOH in 15mL of water) in ethanol (30mL) was refluxed for 6hrs . The mixture was concentrated under vacuum and poured into ice water. The precipitate obtained was filtered, washed and recrystallized from ethanol [39].

The physical properties of prepared compound (D20) is shown molecular formula $C_{20}H_{20}NO_2Br$, color yellow, molecular weight 434.289 g/mol , M.P.,℃ Gum, yield 72%

2.5. Preparation of aggressive solution:

Aggressive solution of 1M H_2SO_4 was prepared by dilution of analytical grade 98% H_2SO_4 with distilled water. Inhibitor concentrations of ($1x10^{-2}$, $5x10^{-3}$, $1x10^{-3}$ and $5x10^{-4}$)M were prepared in 1M H_2SO_4 solution at 30^oC

2.6. Weight loss measurements:

Weight loss measurements is considered one of oldest method of measuring the corrosion rate of a metal during the exposing the sample to corrosive medium (e.g. acidic media), then measure the loss of weight of the metal as function of immersed time. Mild steel samples used have the composition percentages (0.0005% V , 0.002% P, 0.002% Mo, 0.0154% S, 0.0199% Cr, 0.03% C, 0.065% Cu, 0.288% Mn,) and balanced with iron. The mild steel samples have a diameter of (2.5 cm). These samples were polished with emery paper (1000, 1500, 2500 and 4000) grades in order to get rid of rust and get a smooth surface. Then they washed with distilled water, alcohol, and finally acetone. The treated specimen was 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 well-steady and completely immersed in 250 ml beaker containing 1M sulfuric acid in the presence and absence of inhibitors for 24 hrs. The specimens were removed after 24 hours exposure period at 30^{o}C, washed with water to remove any corrosion products and finally washed with acetone. Then they were dried and reweighed. Mass loss measurements were performed as by ASTM method described previously [40, 41]. The tests were performed in duplicate to guarantee the reliability of the results and the mean value of the weight loss is reported. Weight loss allowed calculation of the mean corrosion rate in (mg.cm^{-2} .h^{-1}). The corrosion rate of mild steel was determined using the relation (2.1) [42]:

$$W = \frac{\Delta m}{St} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2.1)$$

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

The percentage inhibition efficiency (E %) was calculated using the relationship (2.2) [43]:

$$E\% = \frac{W_{Corr} - W_{corr(inh)}}{W_{corr}} x100 \ldots\ldots\ldots\ldots\ldots (2.2)$$

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

Basic information can be provided from the adsorption isotherms to explain the interaction between the organic compounds and metal surfaces. So that, the degree of surface coverage values (θ) at different inhibitor concentrations in 1M H_2SO_4 was achieved from weight loss measurements (θ = E (%)/100) at 30°C and tested with Langmuir isotherm relationship (2.3) [44]:

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.3)$$

Where C is concentration in M, 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). K_{ads} is related to the standard free energy of adsorption, ΔG^{o}_{ads}, with the following equation (2.4): (The value 55.5 is the molar concentration of water in the solution in1 M) [45].

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G_{ads}}{RT}\right) \ldots\ldots\ldots\ldots\ldots\ldots\ldots (2.4)$$

Where R is the gas constant (8.314J/mol) and T is the temperature at kelvin.

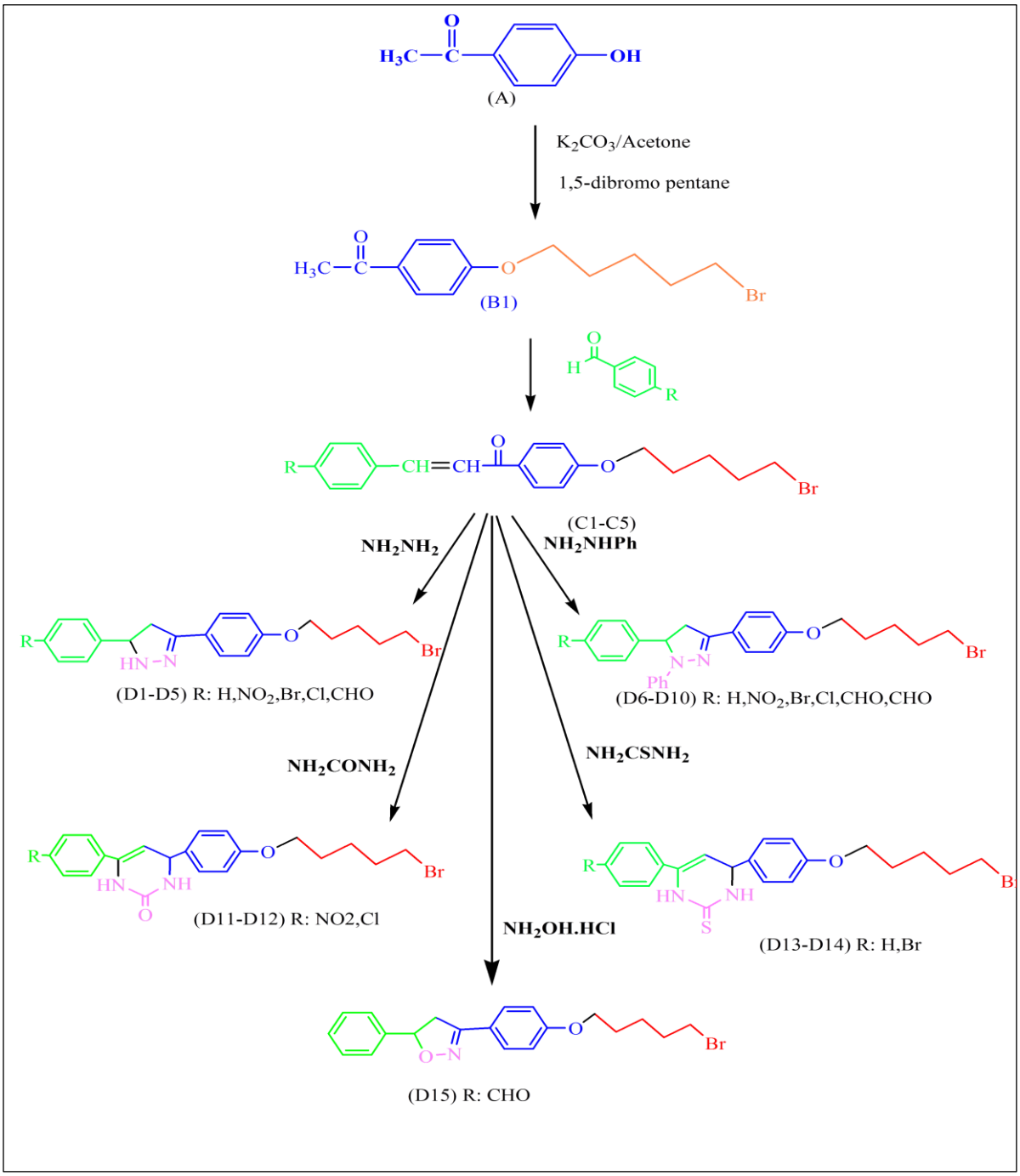
Chapter Three

Results and Discussion

Chapter Three
Results & discussion

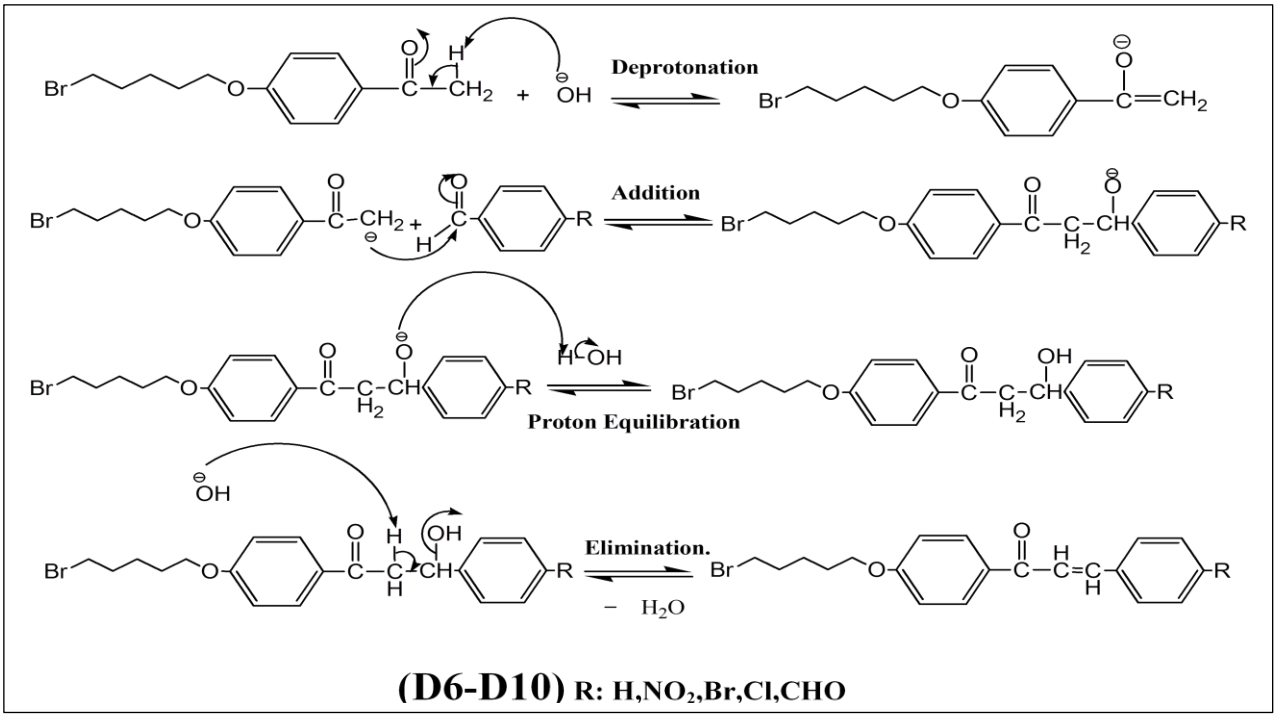
3.1. Synthesis of compounds (D1-D15):

The chemical steps for the synthesis of compounds **(D1-D15)** are shown in scheme (3-1)



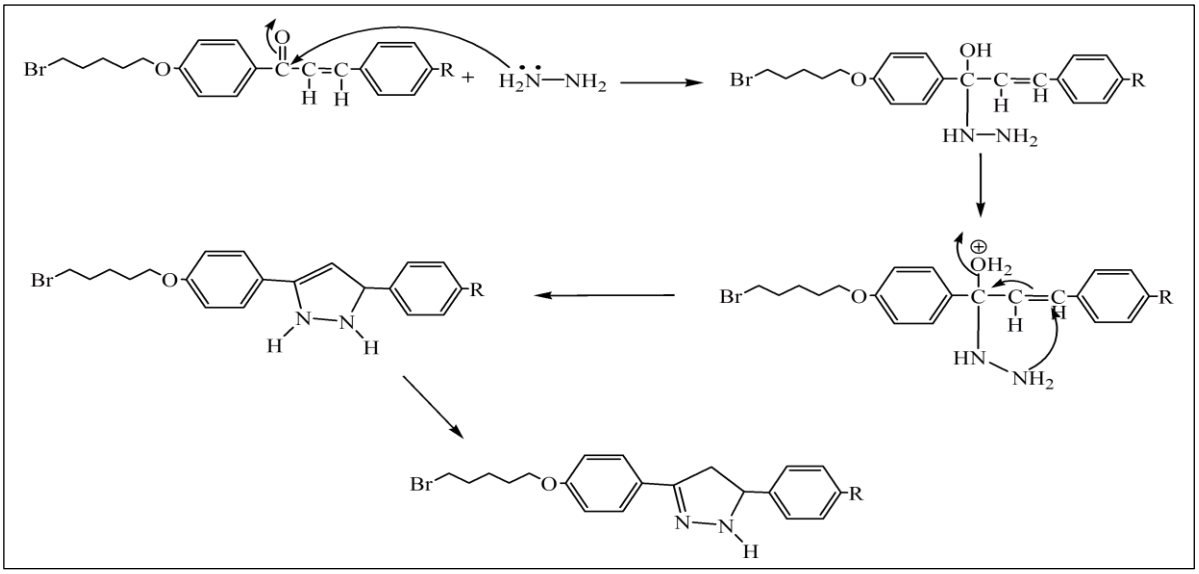
Scheme (3-1): The chemical steps for the synthesis of compounds (D1-D15)

The reaction mechanism for the synthesis of chalcone derivatives (C1-C6) was showed in scheme (3-2),[47]



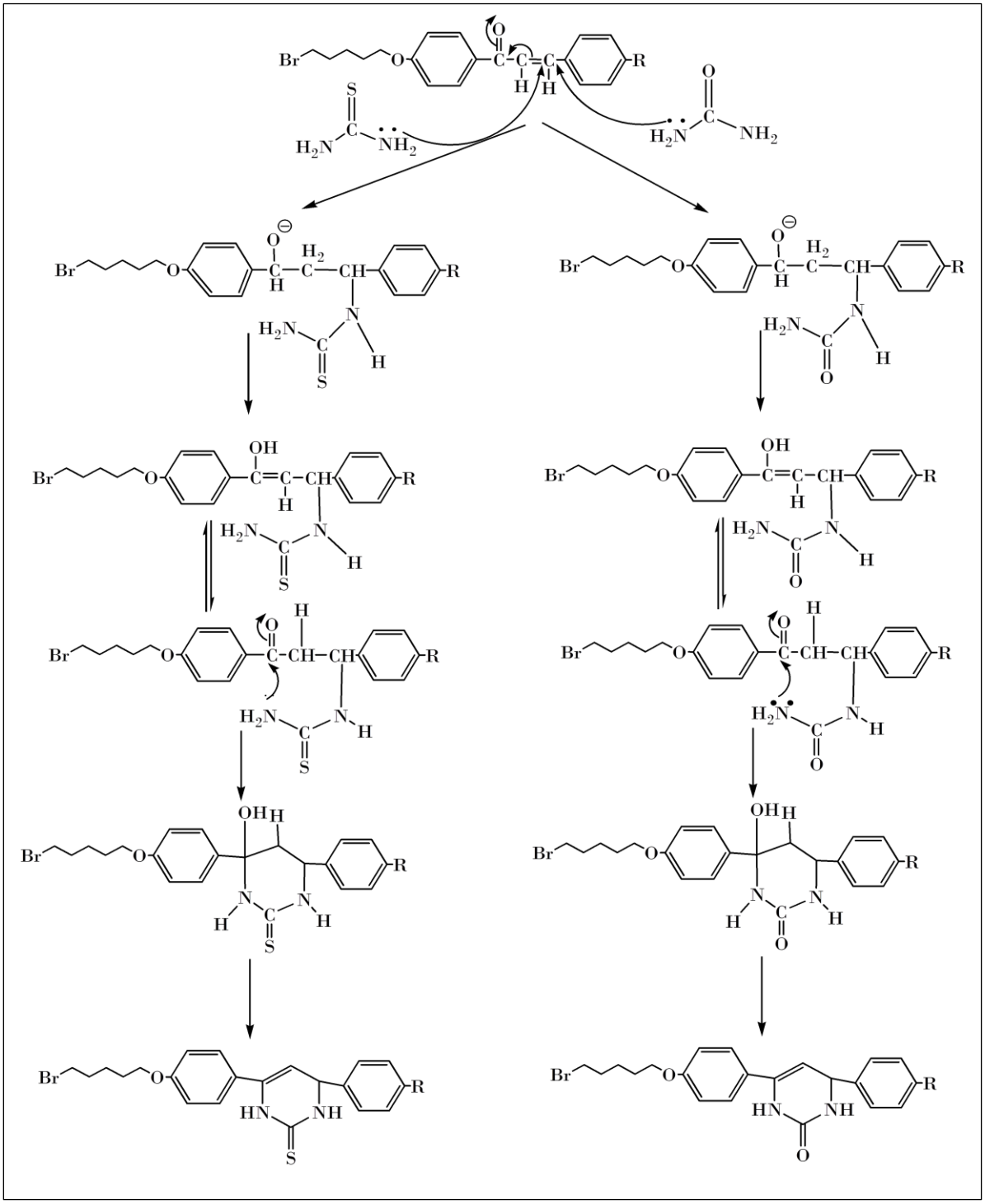
Scheme (3-2): The reaction mechanism for the synthesis of chalcone derivatives (C1-C6)

The reaction mechanism for the synthesis of pyrazole derivatives (D1-D10) and (D16- D17) are Shown in scheme (3-3),[48]



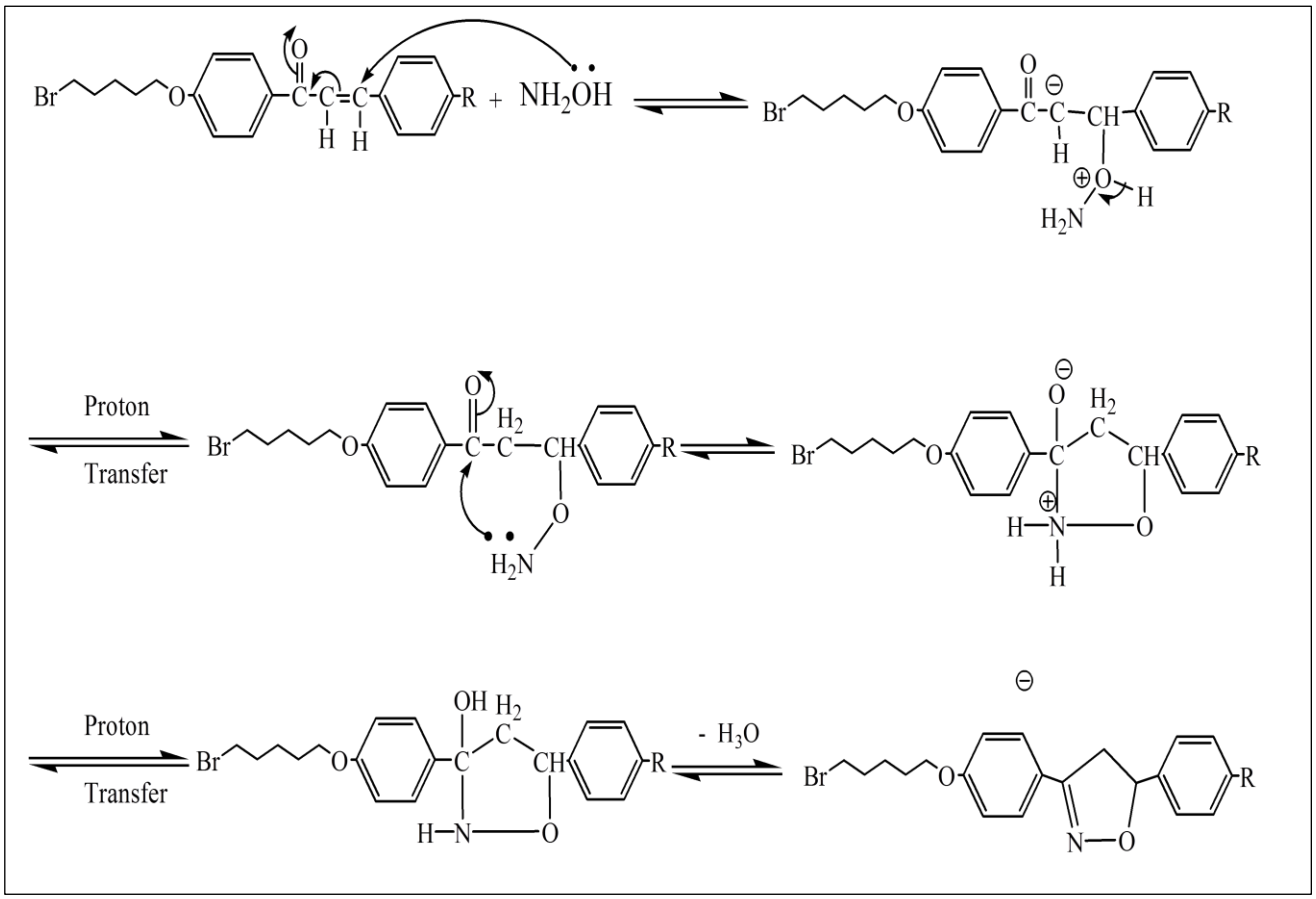
Scheme (3-3): The reaction mechanism for the synthesis of pyrazole derivatives (D1-D10) and (D16- D17)

The reaction mechanism for the synthesis of pyrimidine derivatives (D11-D14) and (D18-D19) are shown in scheme (3-4). [49]



Scheme (3-4): The reaction mechanism for the synthesis of pyrimidine derivatives (D11-D14) and (D18-D19)

The reaction mechanism for the synthesis of isoxazole derivatives (D15) are shown in scheme (3-5). [39]



Scheme (3-5): The reaction mechanism for the synthesis of isoxazole derivatives (D15) and (D20)

3.2 The FT-IR spectra & ^{1}H-NMR data of prepared compounds (D1-D15)

3.2.1Characterization of 1-[4-(5-Bromo-pentyloxy)-phenyl]-ethanone (B1)

The FT-IR spectrum of compound (B1), as shown in Figure (3-1) has important characteristic identification by showing stretching vibration bands that corresponding to (C=O) bond at (1678 cm^{-1}) and (C–O) bond at (1250 cm^{-1}) . Stretching vibration band at (2873, 2947 cm^{-1}) that related to (C-H) bonds of aliphatic and (1600 cm^{-1}) to (C=C) aromatic stretching vibrations bond.

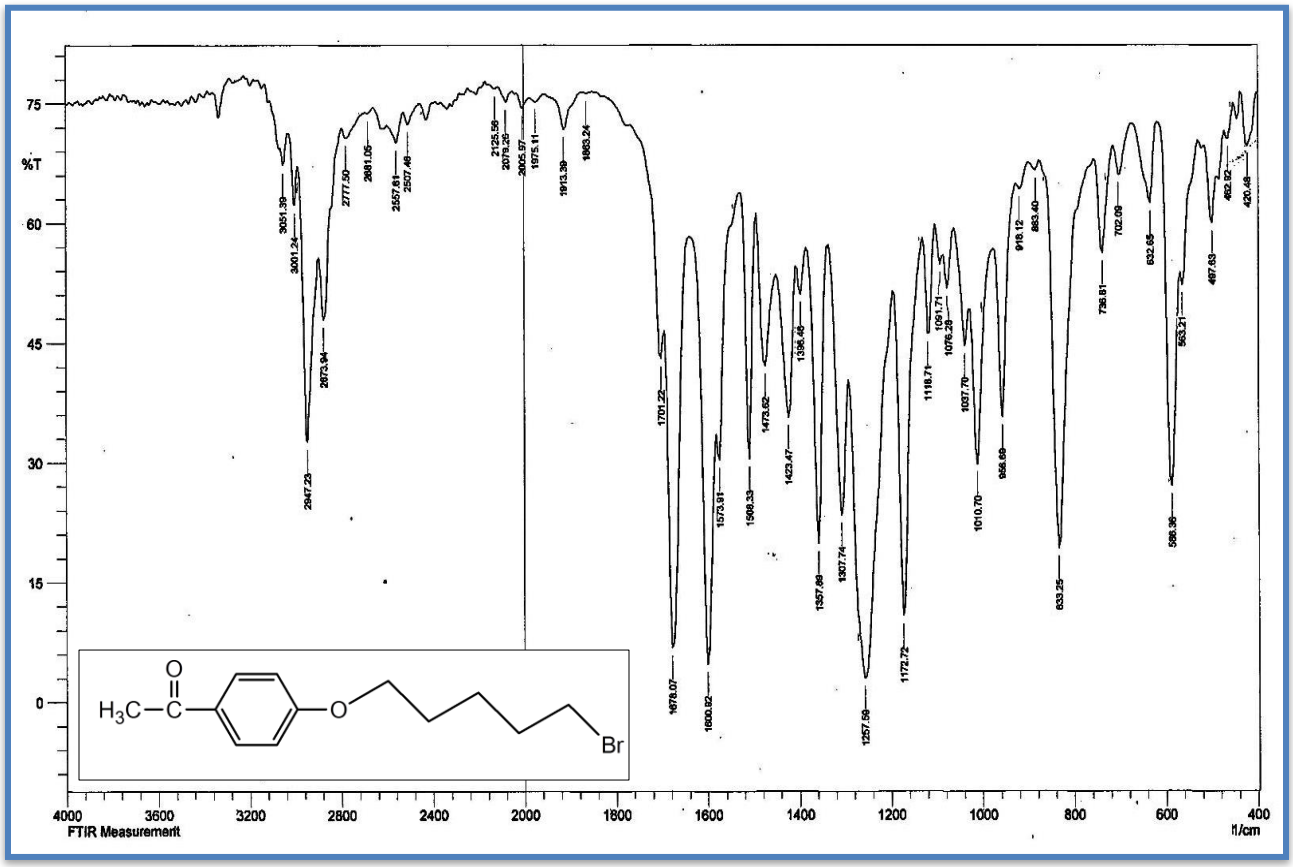


Figure (3-1): FT-IR spectrum of compound **(B1)**

3.2.2. Characterization of 1-[4-(5-Bromo-pentyloxy)- substituted phenyl]-3-phenyl-propan-1-one

The α,β unsaturated compounds (C1 –C5) were prepared according to crossed Aldol condensation reaction. The FTIR spectra of compounds (C1) to (C5) have important characteristic identification by appearing vibration band that corresponds to (C=O) (1658 cm^{-1}) which is less than normal stretching vibration bands in (B1) for carbonyl group of acetyl group and access shift in the carbonyl value because extend the conjugated system [50]. Figure (3-2 to 3-6) and Table (3-1) show the interesting stretching vibration bands for The α,β-unsaturated compounds (C1 –C5) .

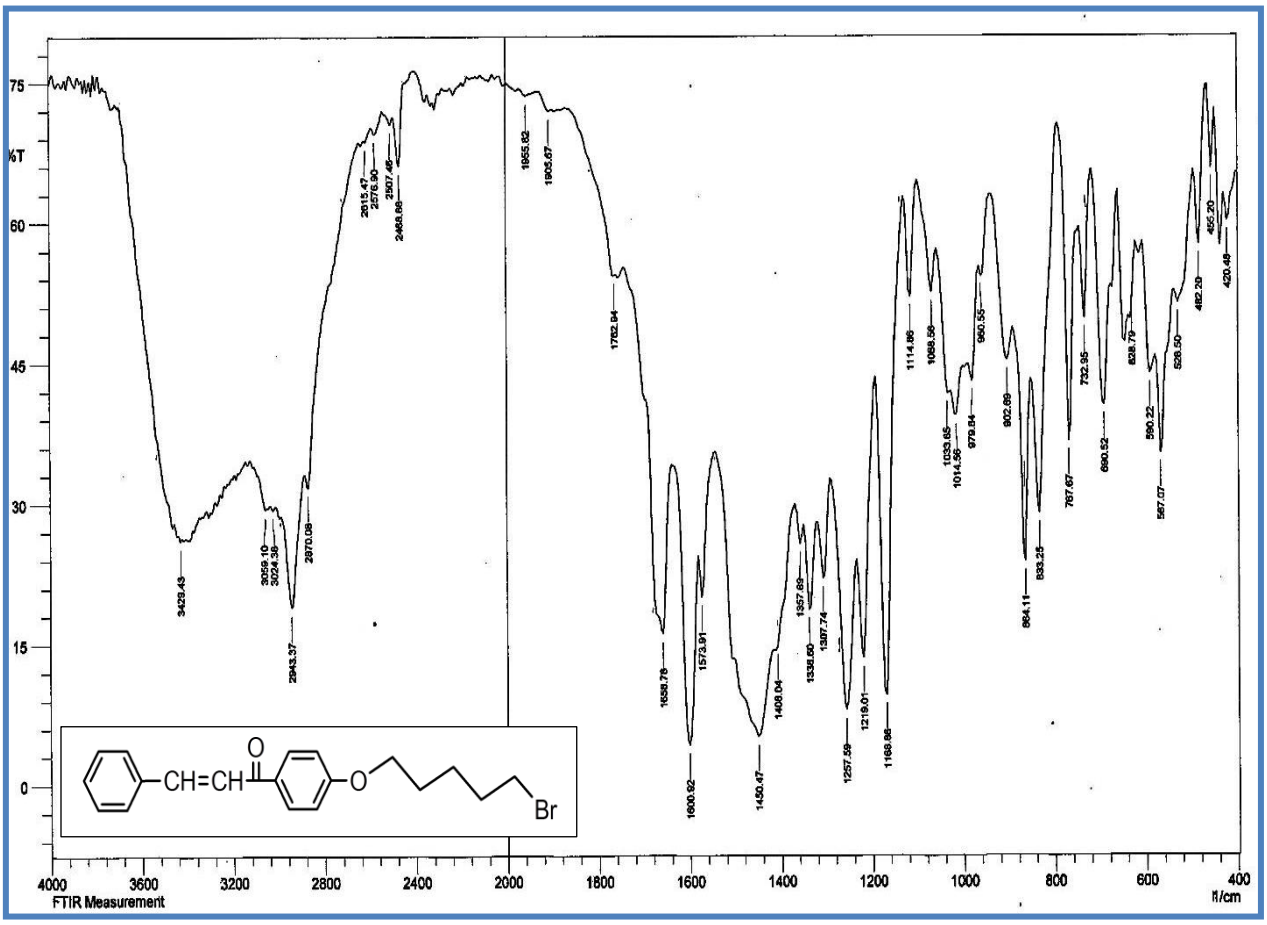


Figure (3-2): FT-IR spectrum of compound **(C1)**

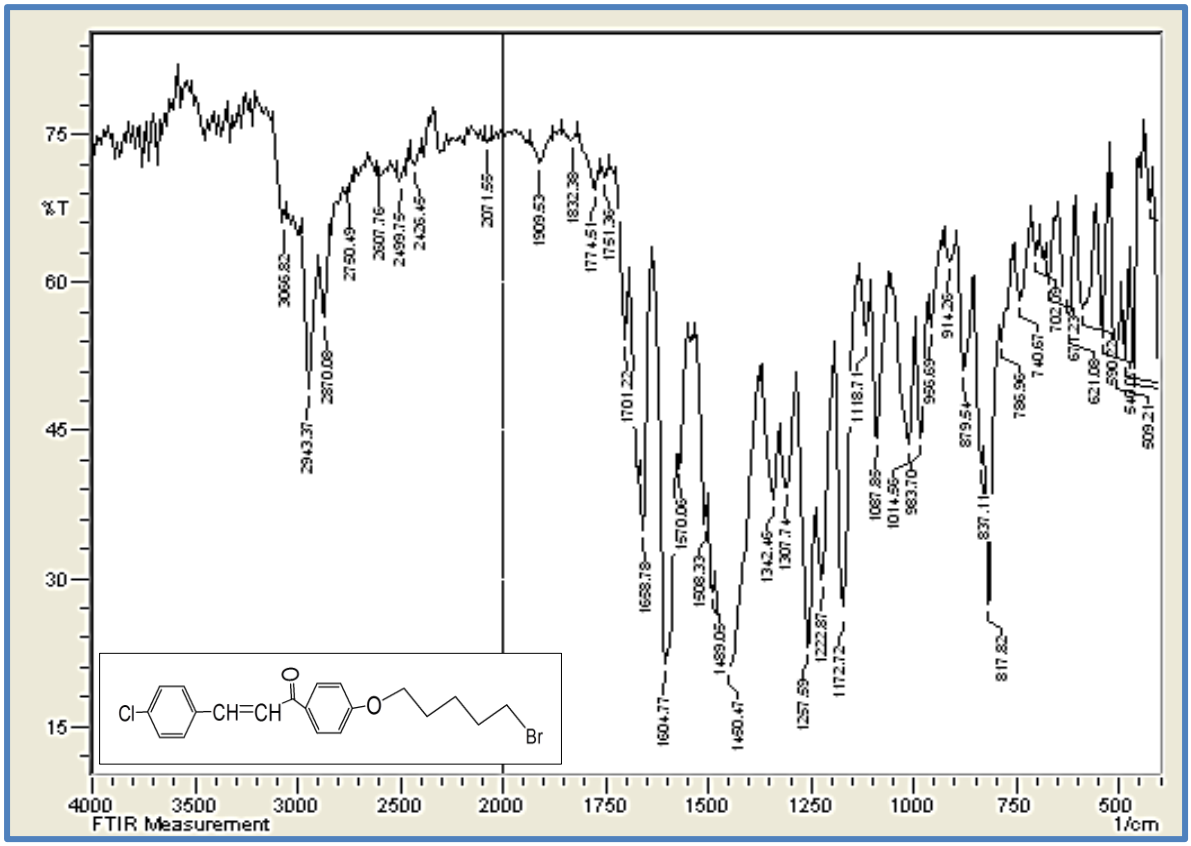


Figure (3-3): FT-IR spectrum of compound **(C2)**

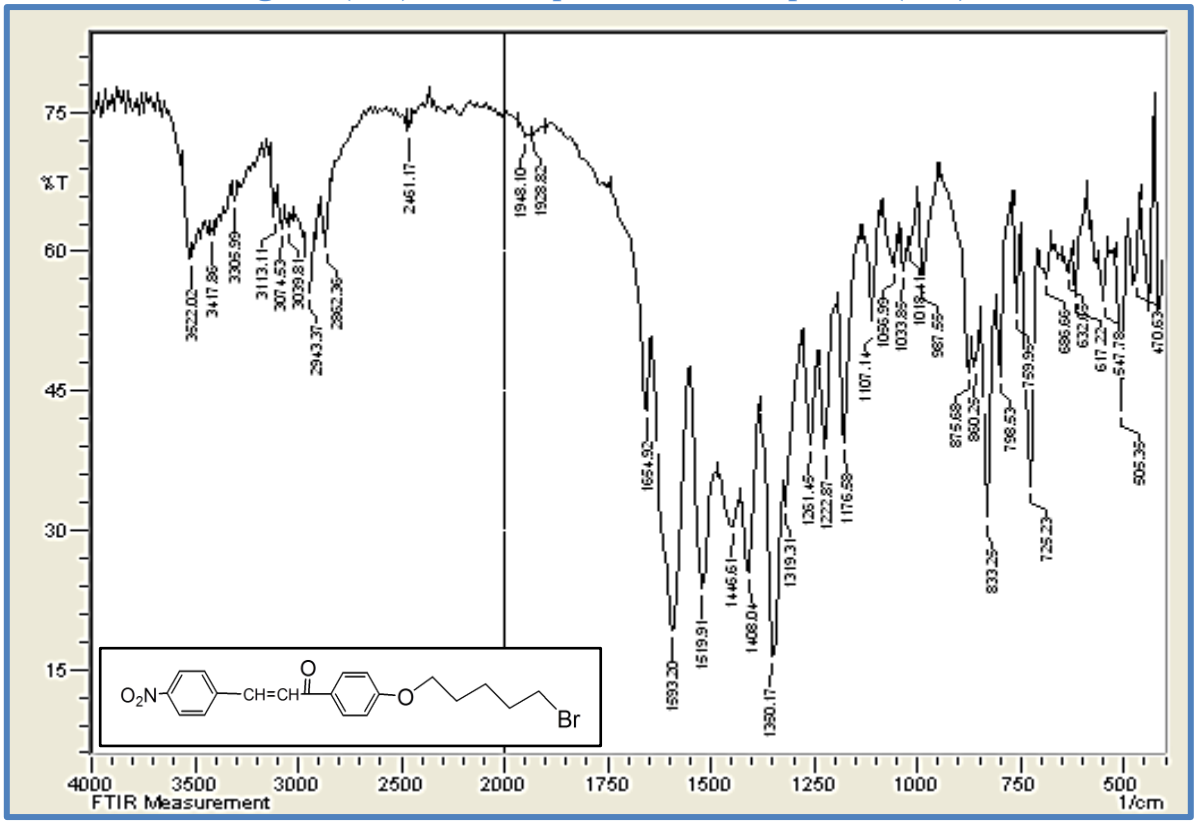


Figure (3-4): FT-IR spectrum of compound **(C3)**

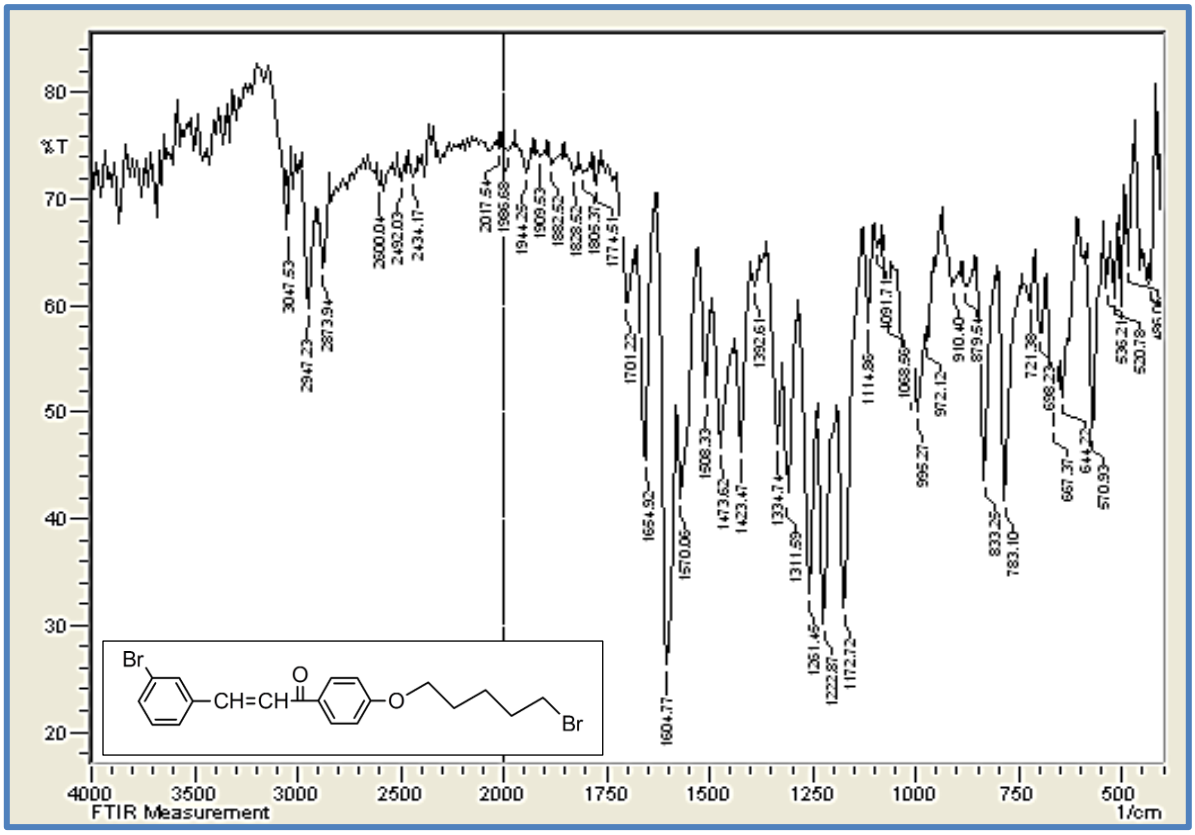


Figure (3-5): FT-IR spectrum of compound **(C4)**

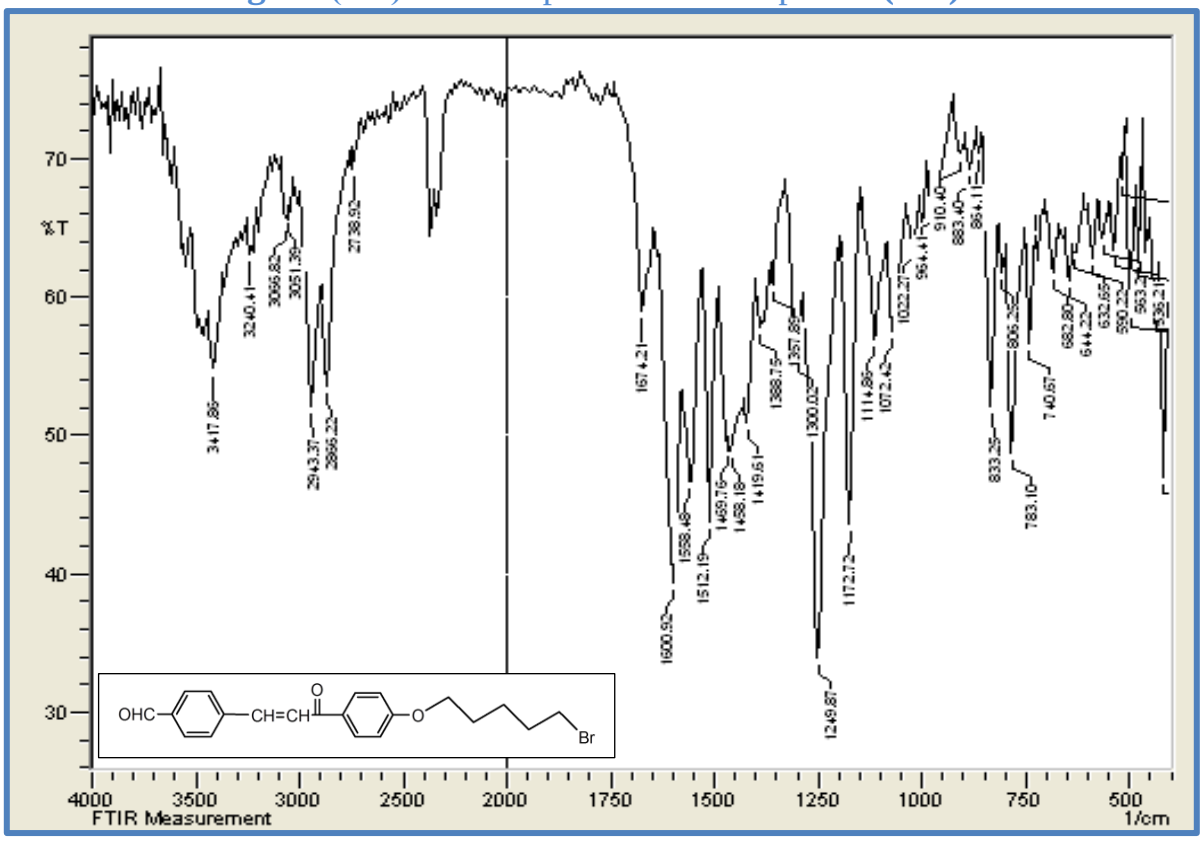


Figure (3-6): FT-IR spectrum of compound **(C5)**

Table 3-1: FT-IR Spectral data of prepared compounds **(C1 – C5)** in cm^{-1}

Comp No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Olefinic	ν C=C Aromatic	ν C=O	ν C-O
C1	3-2	3059	2943	1600	1573	1658	1257
C2	3-3	3066	2943	1604	1570	1658	1257
C3	3-4	3039	2943	1593	1519	1654	1226
C4	3-5	3047	2947	1604	1570	1654	1226
C5	3-6	3066	2943	1600	1566	1654	1257

3.2.3.1. Characterization 0f 3-[4-(5-Bromo-pentyloxy)-phenyl]-5-(4- substituted -phenyl)-4,5-dihydro-1H-pyrazole (D1-D10)

The compounds (D1 – D10) were prepared through cyclization reaction by used hydrazine hydrate and phenyl hydrazine. The FTIR spectra of compounds (D1 – D10) showed a medium stretching vibration band at (>1630 cm^{-1}) belong to (C=N) bond. The compounds (D1 – D10) also have important bands at (3025 cm^{-1}) due to (C- H) aromatic and at (3400 cm^{-1}) due to group stretching vibration band (N-H). The stretching bands of (C=O) group was disappeared in the FT-IR spectra of compounds (D1 – D10) this was good evidence to formation these compounds [50] (Figures (3-7) – (3-16) & Table (3-2)) showed the characteristic stretching vibration bands for the pyrazole compounds (D1 – D10) respectively.

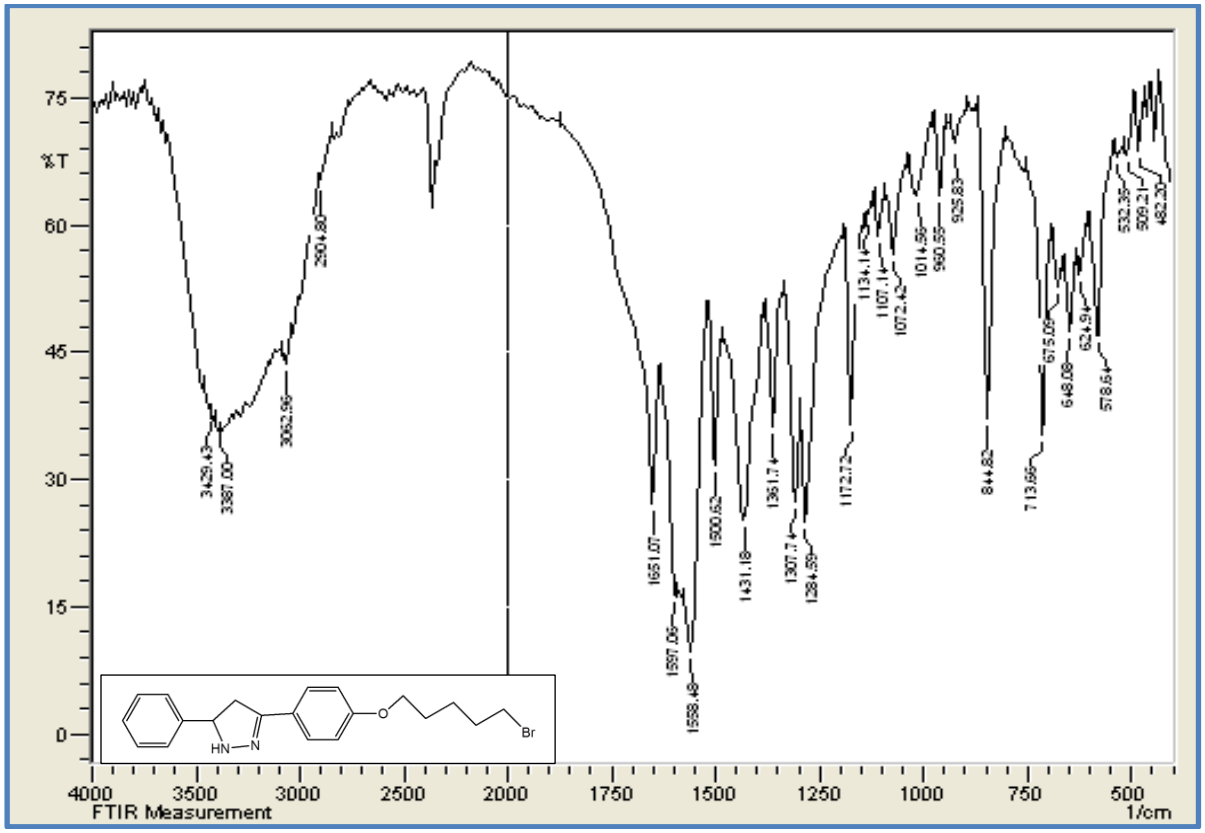


Figure (3-7): FT-IR spectrum of compound **(D1)**

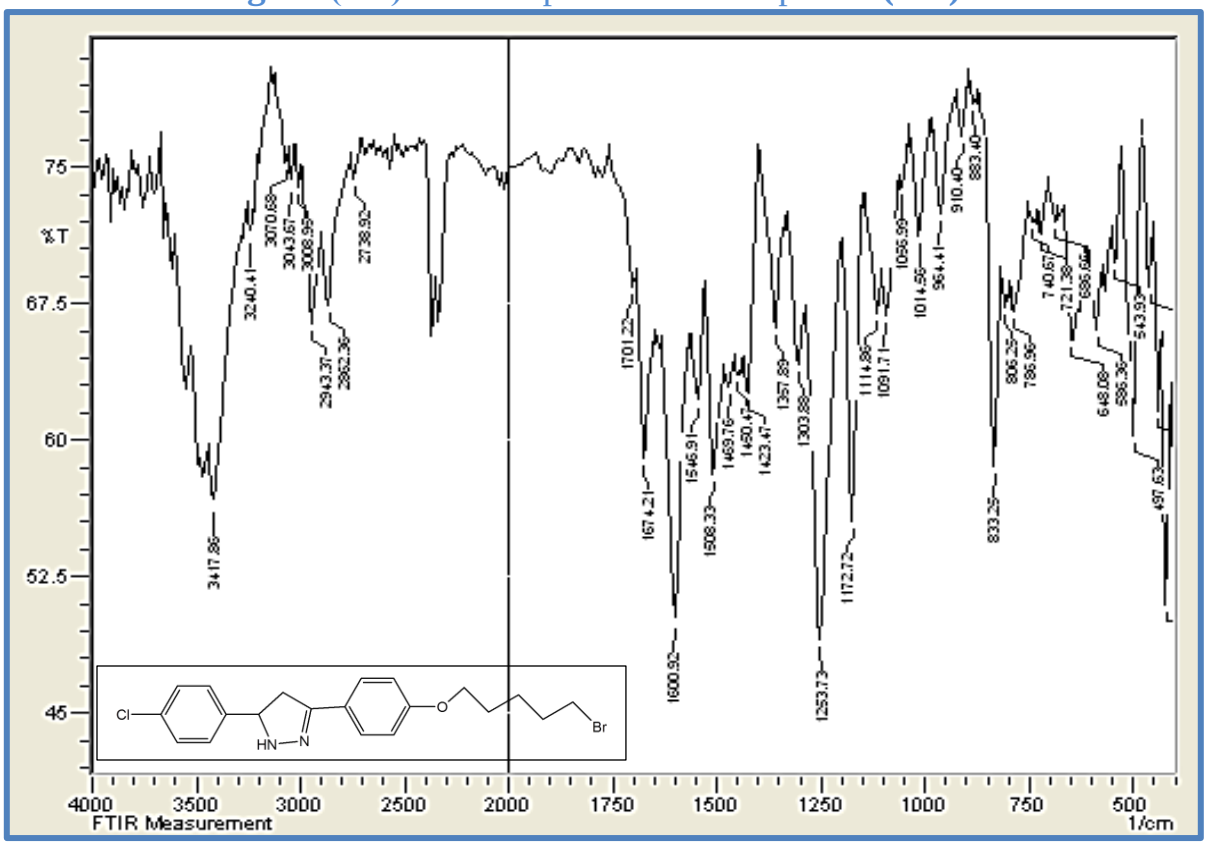


Figure (3-8): FT-IR spectrum of compound **(D2)**

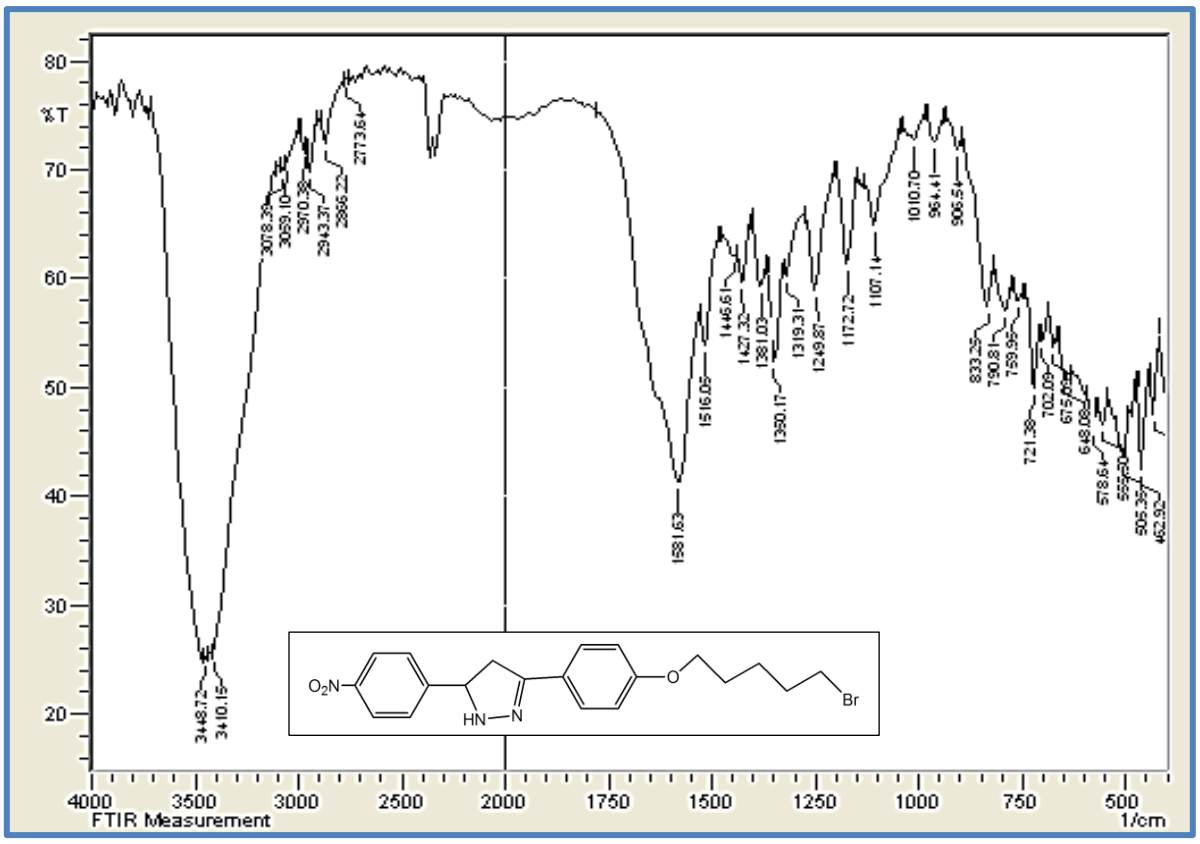


Figure (3-9): FT-IR spectrum of compound (D3)

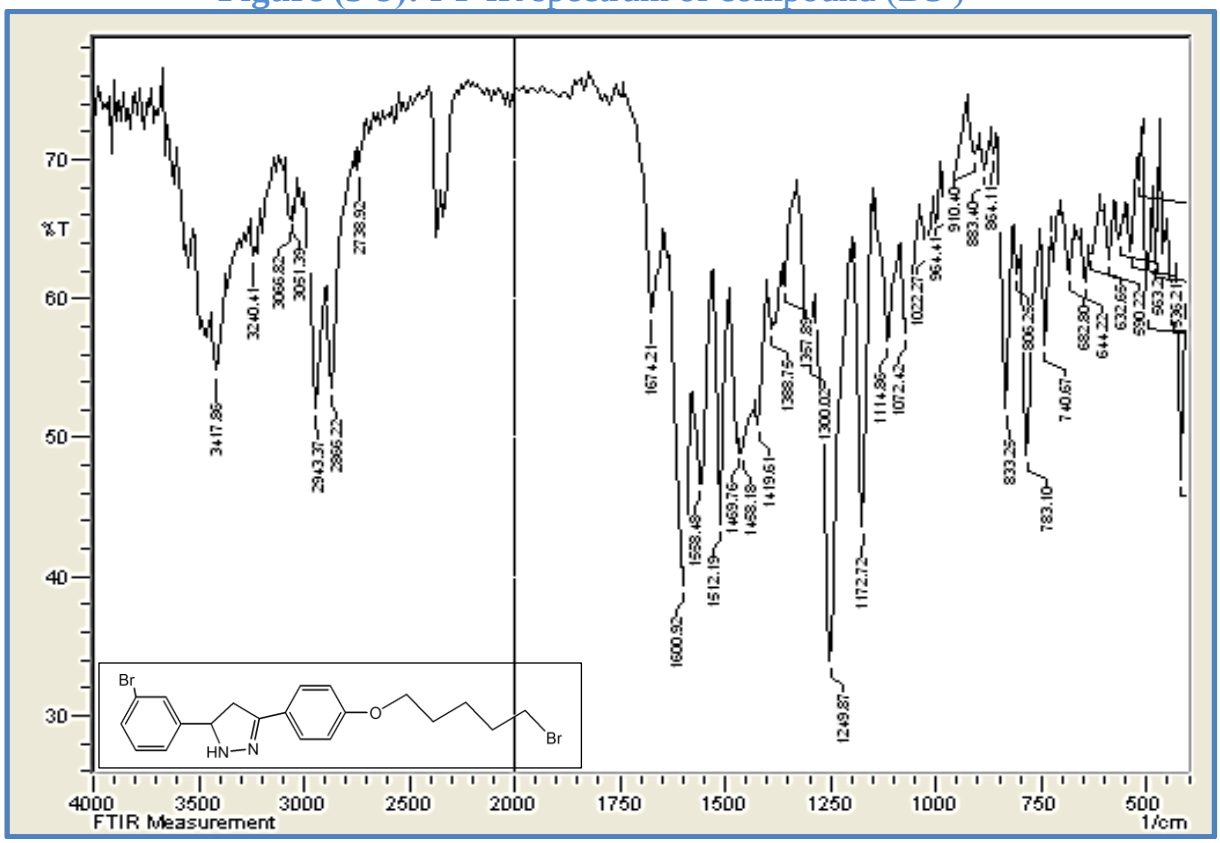


Figure (3-10): FT-IR spectrum of compound (D4)

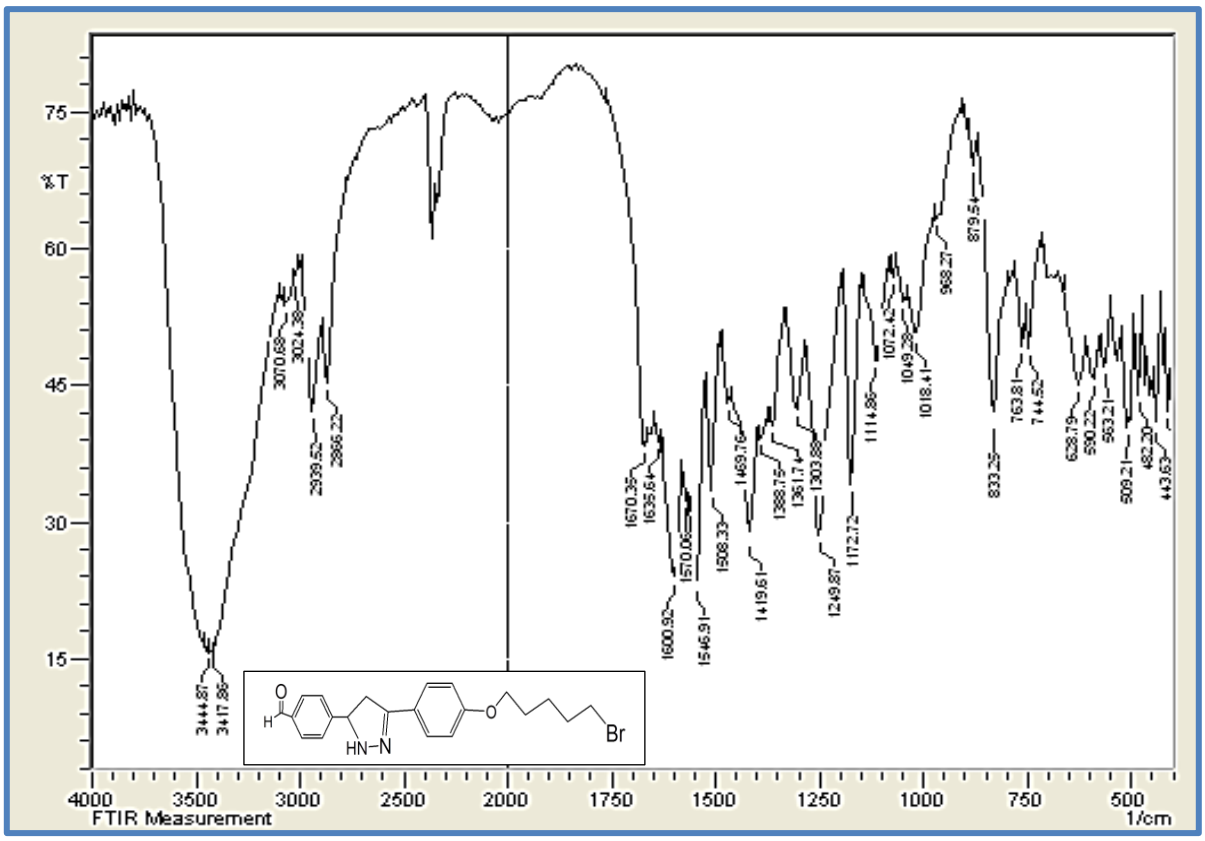


Figure (3-11): FT-IR spectrum of compound (D5)

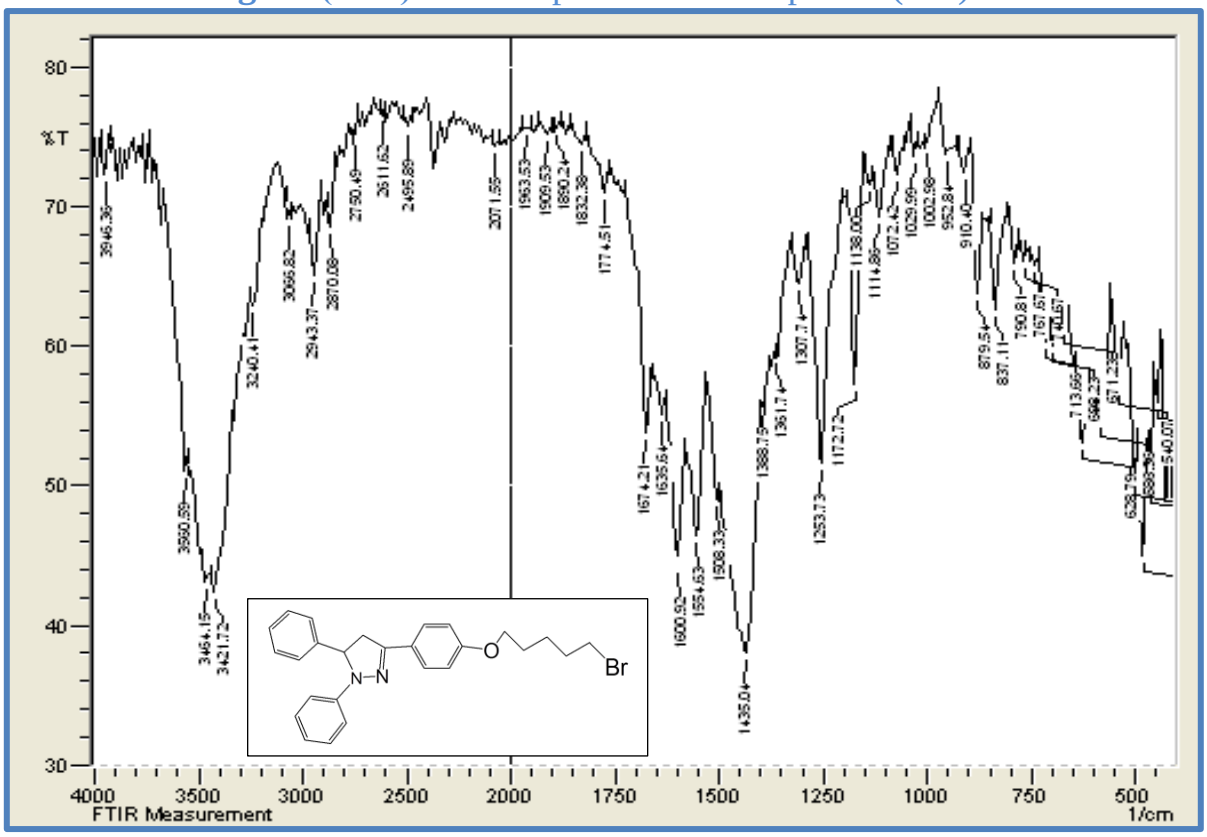


Figure (3-12): FT-IR spectrum of compound (D6)

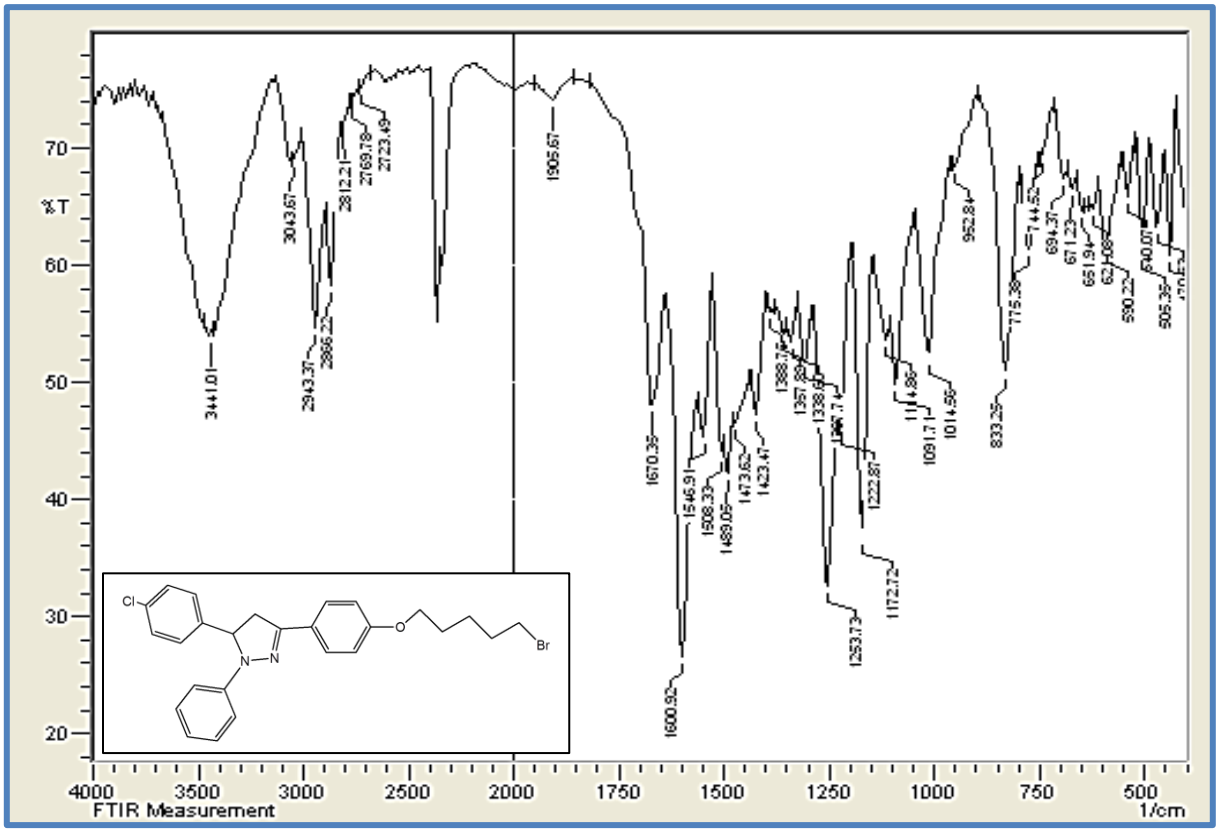


Figure (3-13): FT-IR spectrum of compound (D7)

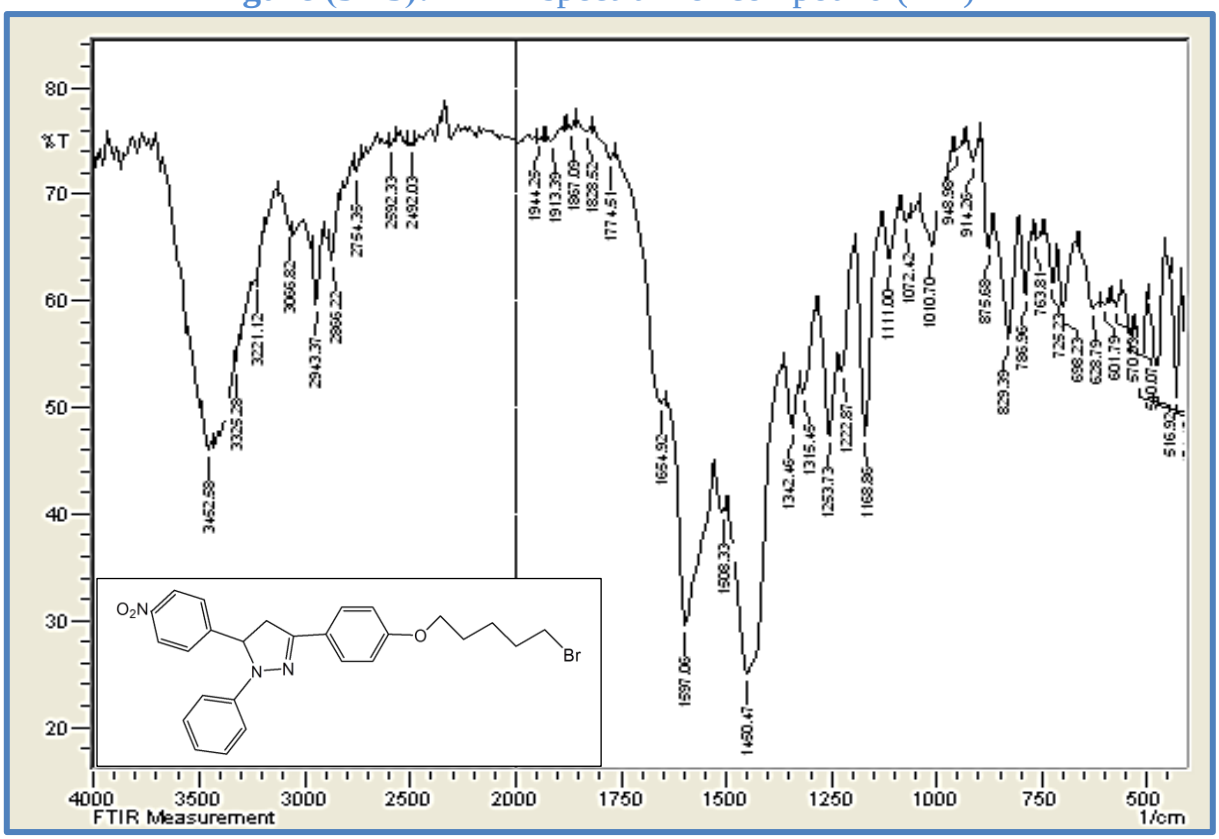


Figure (3-14): FT-IR spectrum of compound (D8)

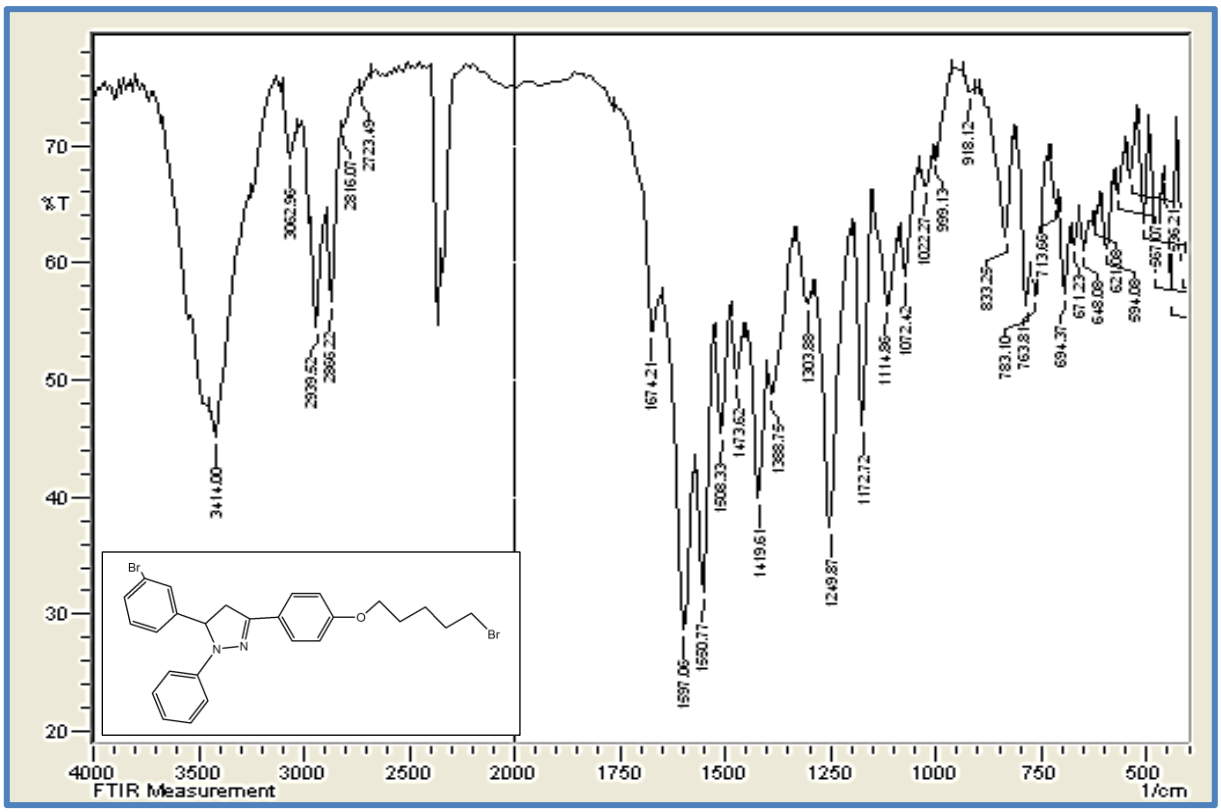


Figure (3-15): FT-IR spectrum of compound (D9)

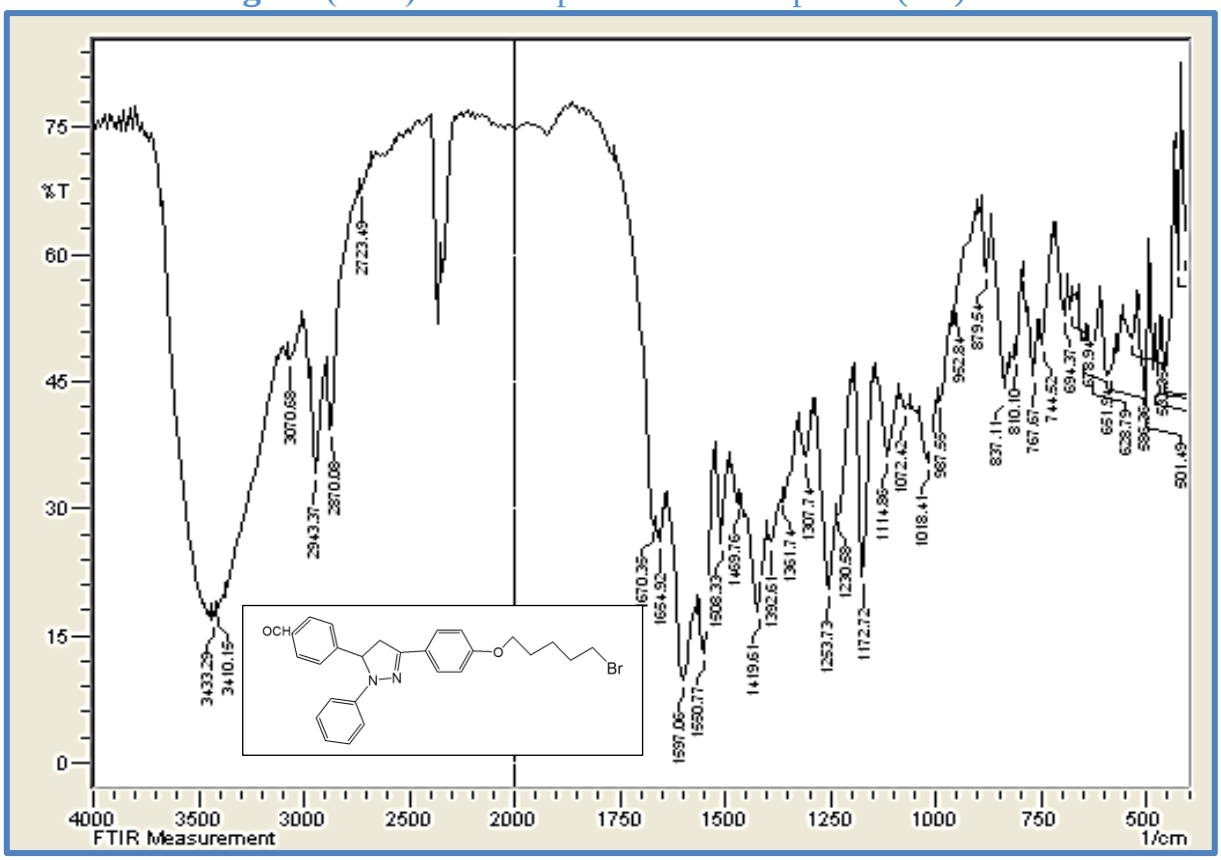


Figure (3-16): FT-IR spectrum of compound (D10)

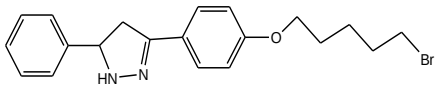
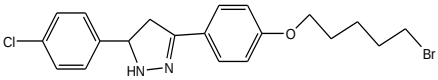
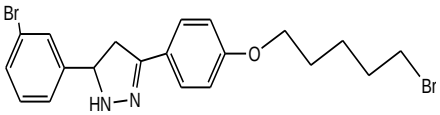
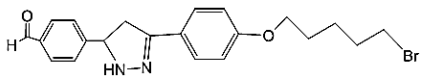
Table 3-2: FTIR Spectral data of prepared compounds **(D1 – D10)** in cm^{-1}

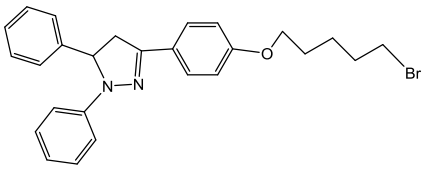
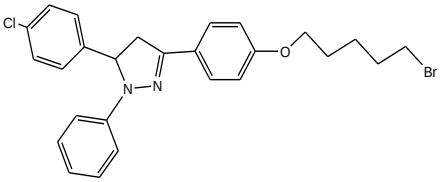
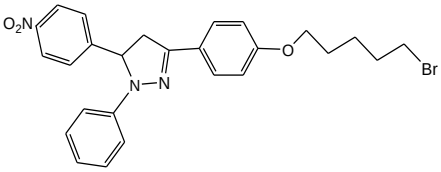
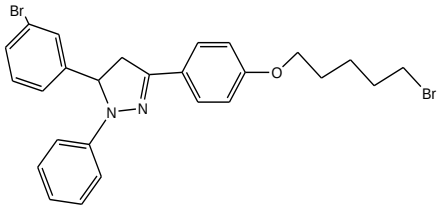
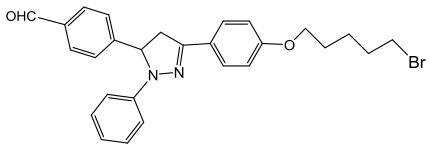
Compound No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Aromatic	ν C=N	ν N-H	ν C-O
D1	3-7	3062	2912	1597	1651	3390	1284
D2	3-8	3070	2943	1600	1674	3417	1253
D3	3-9	3078	2943	1581	1655	3410	1249
D4	3-10	3051	2943	1600	1674	3417	1249
D5	3-11	3024	2939	1600	1654	3417	1249
D5	ν C=O (HCO-1670)						
D6	3-12	3024	2943	1600	1674	3387	1253
D7	3-13	3043	2943	1600	1670	3441	1253
D8	3-14	3066	2943	1597	1654	3452	1253
D9	3-15	3062	2939	1597	1674	3414	1249
D10	3-16	3070	2943	1597	1654	3410	1253
D10	ν C=O (HCO-1670)						

3.2.3.2. ^{1}H-NMR spectra of compounds (D1-D10)

^{1}H-NMR spectra of prepared organic compounds containing heteroatoms (**D1-D20)** are also used to confirm the structure of final products **(D1-D20)**. The Figures and tables ((3-3), (3-5), (3-7), (3-9) and (3-11) showed the characteristic chemical shifts (ppm, δ) for the compounds **(D1-D10)** in DMSO-d_6 as a solvent. The signals appeared at about δ= 1.3 to δ=4.5 ppm for (C-H) bond of alkyl group which connected to O atom from one side and to bromine atom at another side in compounds **(D1-D10)** and. The signal at δ=2.5 ppm belongs to DMSO-d_6 and the signal at δ=3.5 ppm for the moisture [50]

Table 3-3: ^{1}H-NMR data of compounds (D1-D10) in ppm, δ

Comp No.	Compound structure	^{1}H-NMR data of (δ-H) in ppm	Fig. No.
D1		8.5 (1H, d, NH); 6.4-7.6 (9H, d, C-H aromatic); 4.4 (2H, t, CH_2-O); 4.1(2H, t, CH_2-Br); 1.2-2.2(6H ,m, CH_2-CH_2-CH_2); 4.2(1H, m, C-H, pyrazoline ring); 2.3 (2H, d, C-H, pyrazoline ring).	3-17
D2		8.5 (1H, d , NH); 6.8-7.8 (8H, d, C-H aromatic); 4.5 (2H, t, CH_2-O); 3.9(2H, t, CH_2-Br); 1.0-2.2(6H,m, CH_2-CH_2-CH_2); 4.2(1H ,m, C-H, pyrazoline ring); 2.3 (2H,d, C-H, pyrazoline ring).	3-18
D4		8.5 (1H, d, NH); 6.7-8.0 (8H,d, C-H aromatic); 4.1 (2H ,t, CH_2-O); 3.9(2H,t. CH_2-Br); 1.0-1.7(6H,m, CH_2-CH_2-CH_2); 4.2(1H,m, C-H, pyrazoline ring); 2.3 (2H,d, C-H, pyrazoline ring).	3-19
D5		8.5 (1H, d, NH); 6.7-7.7 (8H,d, C-H aromatic); 4.1 (2H,t. CH_2-O); 3.9(2H,t, CH_2-Br); 1.0-1.6 (6H,m. CH_2-CH_2-CH_2); 4.2(1H,m, C-H, pyrazoline ring); 2.3 (2H, C-H, pyrazoline ring).	3-20

D6		6.7-7.8 (14H,d, C-H aromatic); 4.1 (2H,t, CH_2-O); 3.9(2H,t, CH_2-Br); 1.0-1.6 (6H,m, CH_2-CH_2-CH_2); 4.0(1H,t, C-H, pyrazoline ring); 2.3 (2H,d, C-H, pyrazoline ring).	3-21
D7		6.7-7.9 (13H,d, C-H romatic); 4.4 (2H,t, CH_2-O); 3.8(2H,t, CH_2-Br); 1.0-1.7 (6H,m, CH_2-CH_2-CH_2); 4.0(1H, C-H, pyrazoline ring); 2.1 (2H, C-H, pyrazoline ring).	3-22
D8		6.7-7.9 (13H,d, C-H romatic); 4.4 (2H,t, CH_2-O); 3.8(2H,t, CH_2-Br); 1.0-1.7 (6H,m, CH_2-CH_2-CH_2); 4.0(1H,t, C-H, pyrazoline ring); 2.1 (2H,d, C-H, pyrazoline ring).	3-23
D9		6.7-7.9 (13H, C-H romatic); 4.4 (2H, CH_2-O); 3.8(2H, CH_2-Br); 1.0-1.7 (6H, CH_2-CH_2-CH_2); 4.1(1H, C-H, pyrazoline ring); 2.1 (2H, C-H, pyrazoline ring).	3-24
D10		6.6-7.8 (13H, C-H romatic); 4.4 (2H, CH_2-O); 3.8(2H, CH_2-Br); 1.0-1.7 (6H, CH_2-CH_2-CH_2); 4.0(1H, C-H, pyrazoline ring); 2.1 (2H, C-H, pyrazoline ring).	3-25

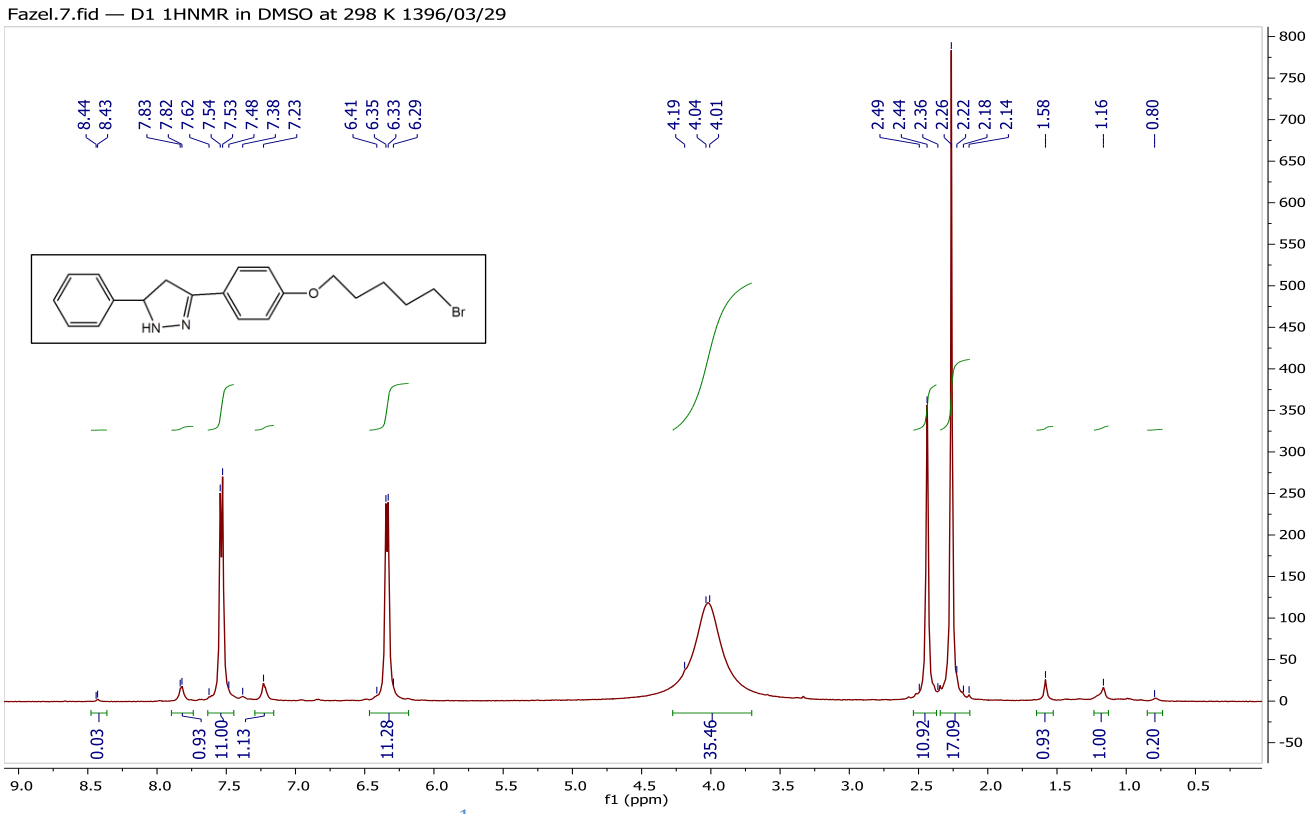


Figure (3-17): ^{1}H-NMR spectrum of compound (D1)

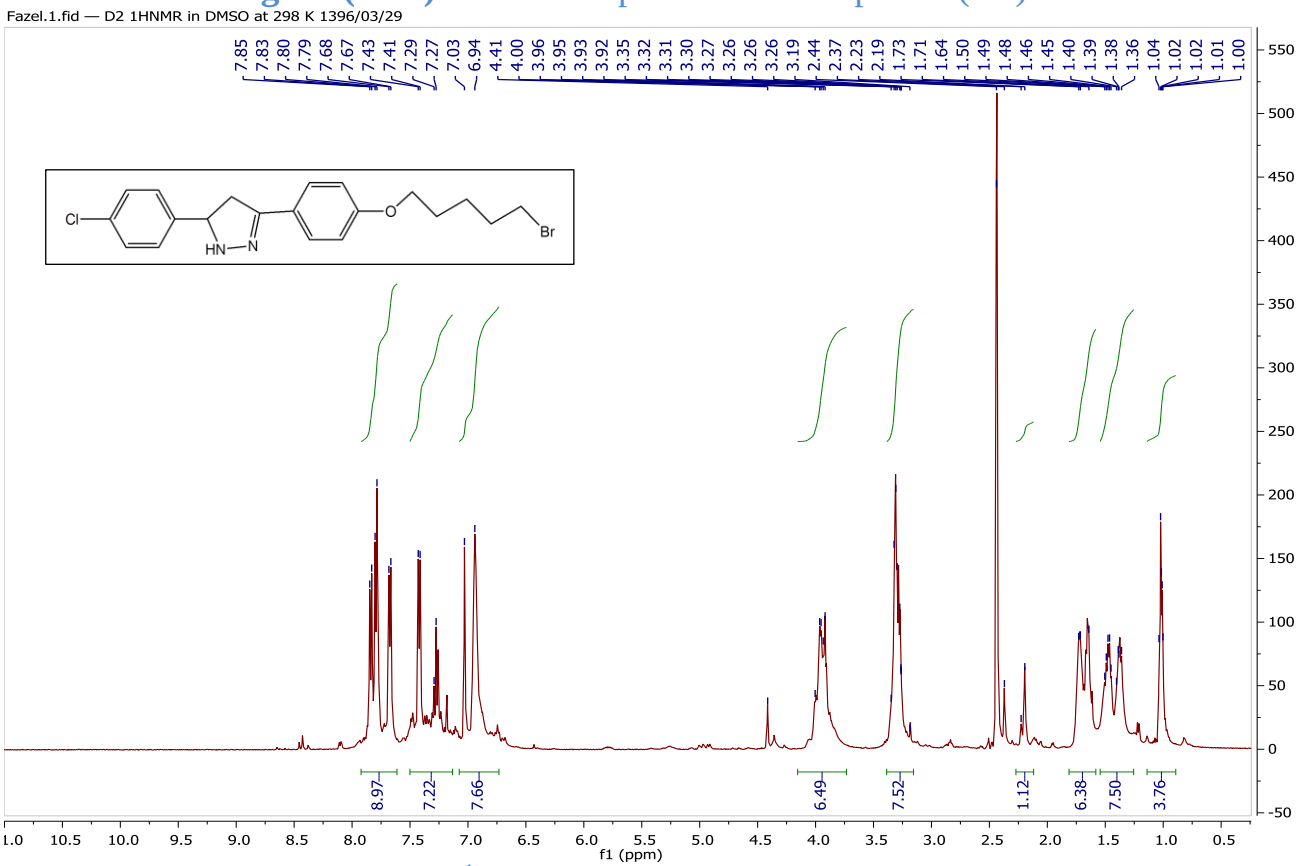


Figure (3-18): ^{1}H-NMR spectrum of compound (D2)

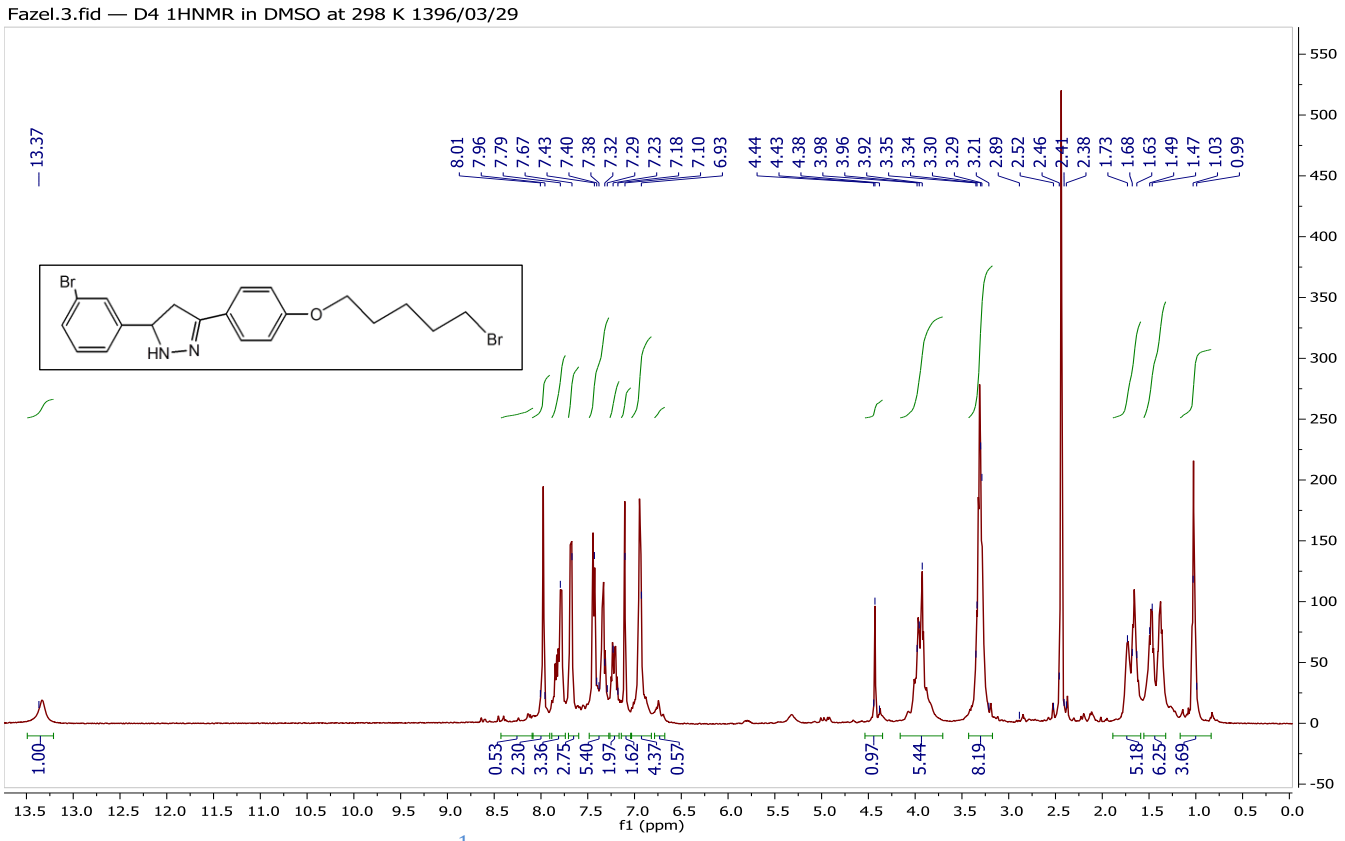


Figure (3-19): ^{1}H-NMR spectrum of compound (D4)

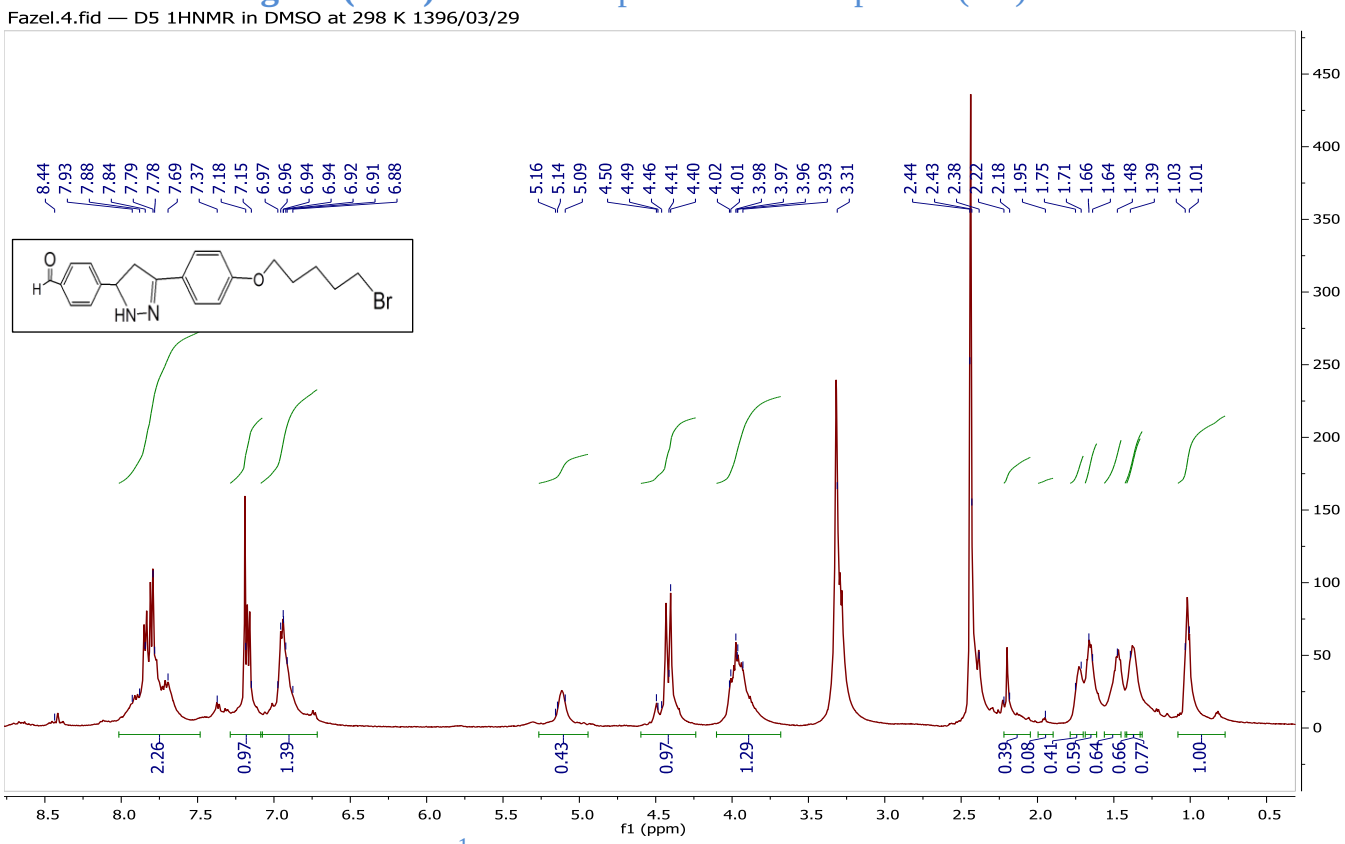


Figure (3-20): ^{1}H-NMR spectrum of compound (D5)

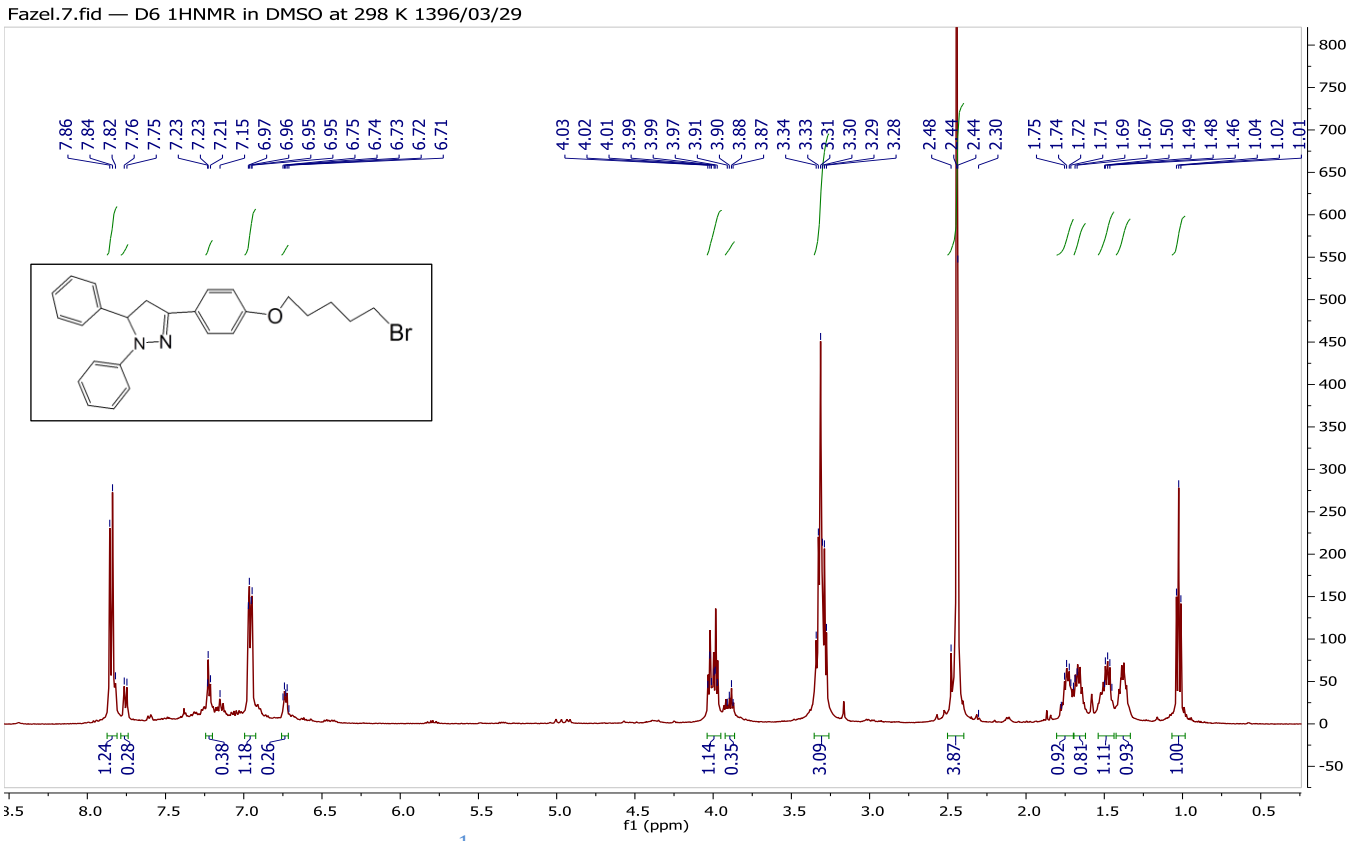


Figure (3-21): ^{1}H-NMR spectrum of compound (D6)

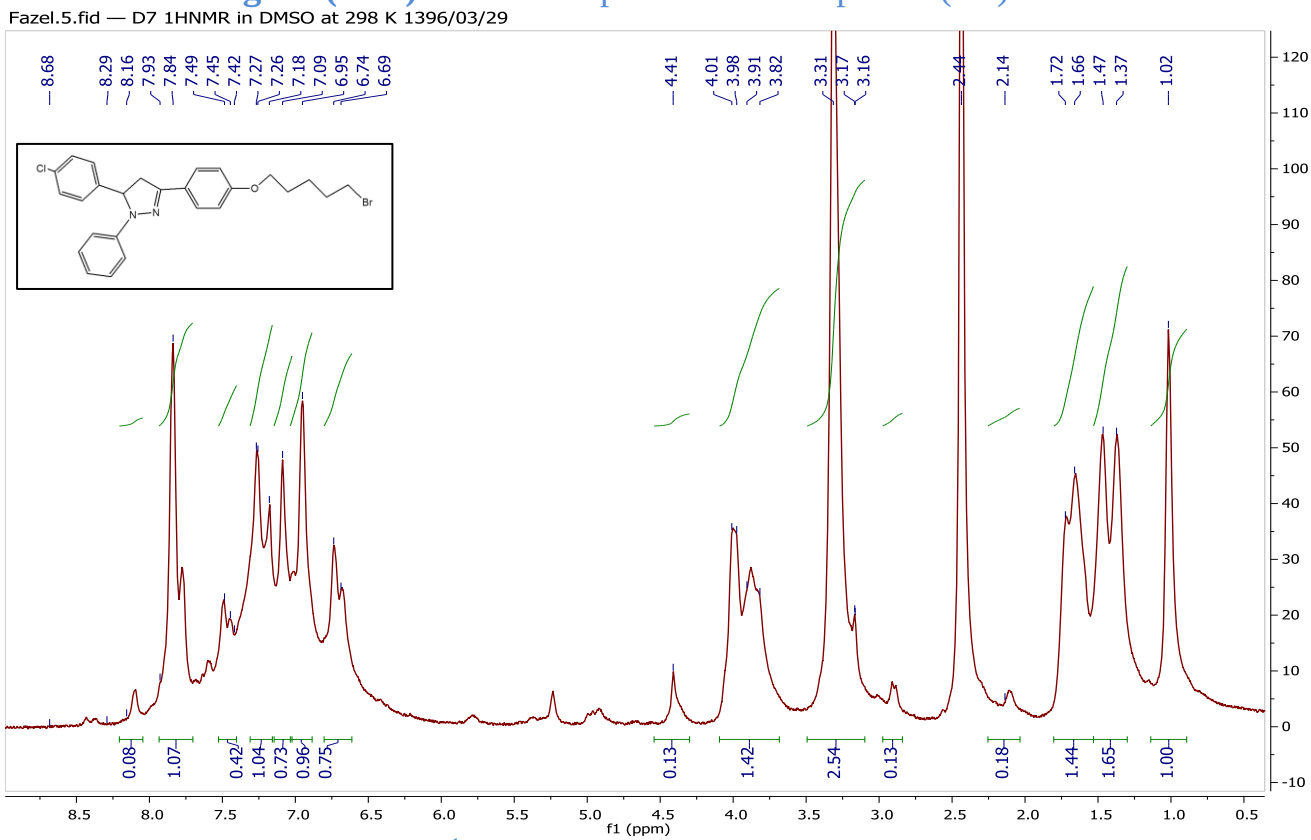


Figure (3-22): ^{1}H-NMR spectrum of compound (D7)

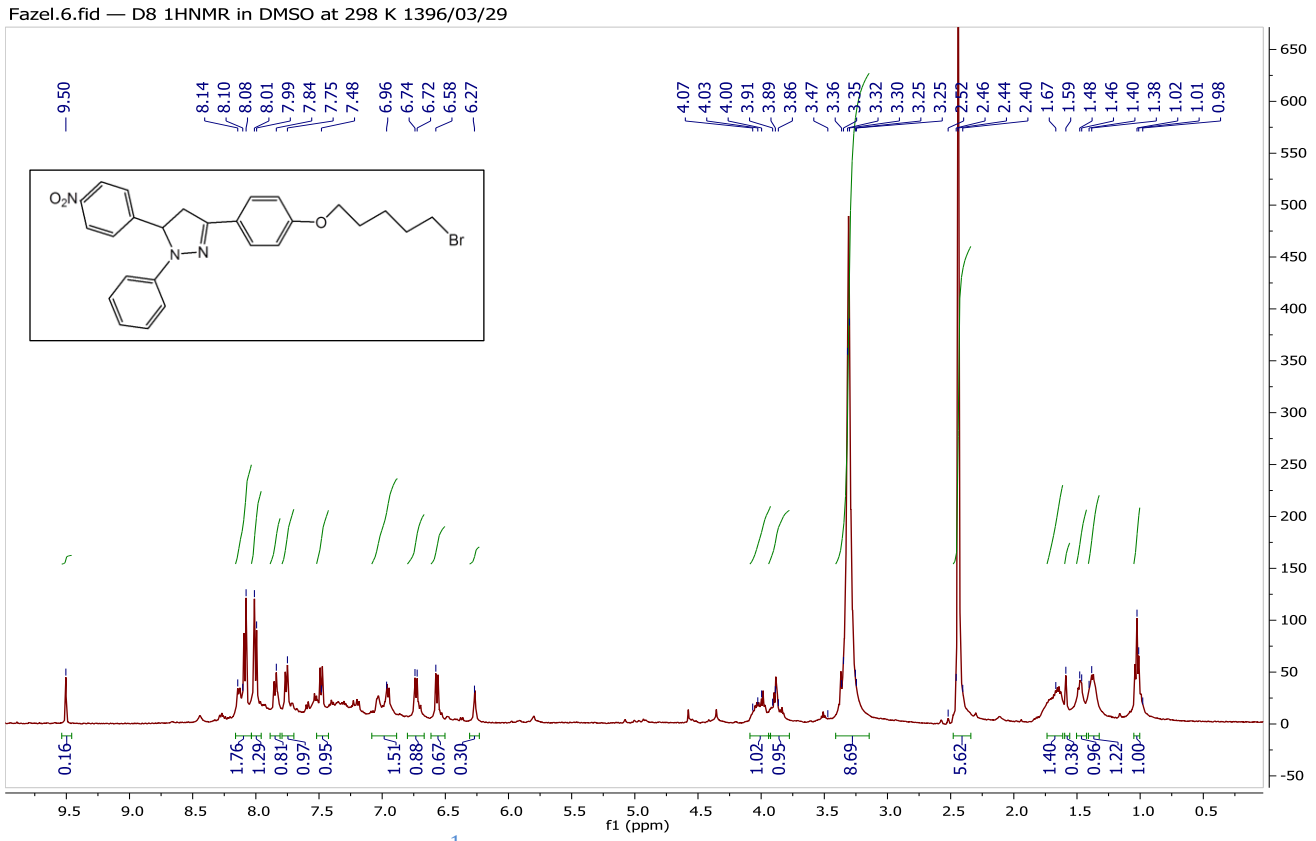


Figure (3-23): ^{1}H-NMR spectrum of compound (D8)

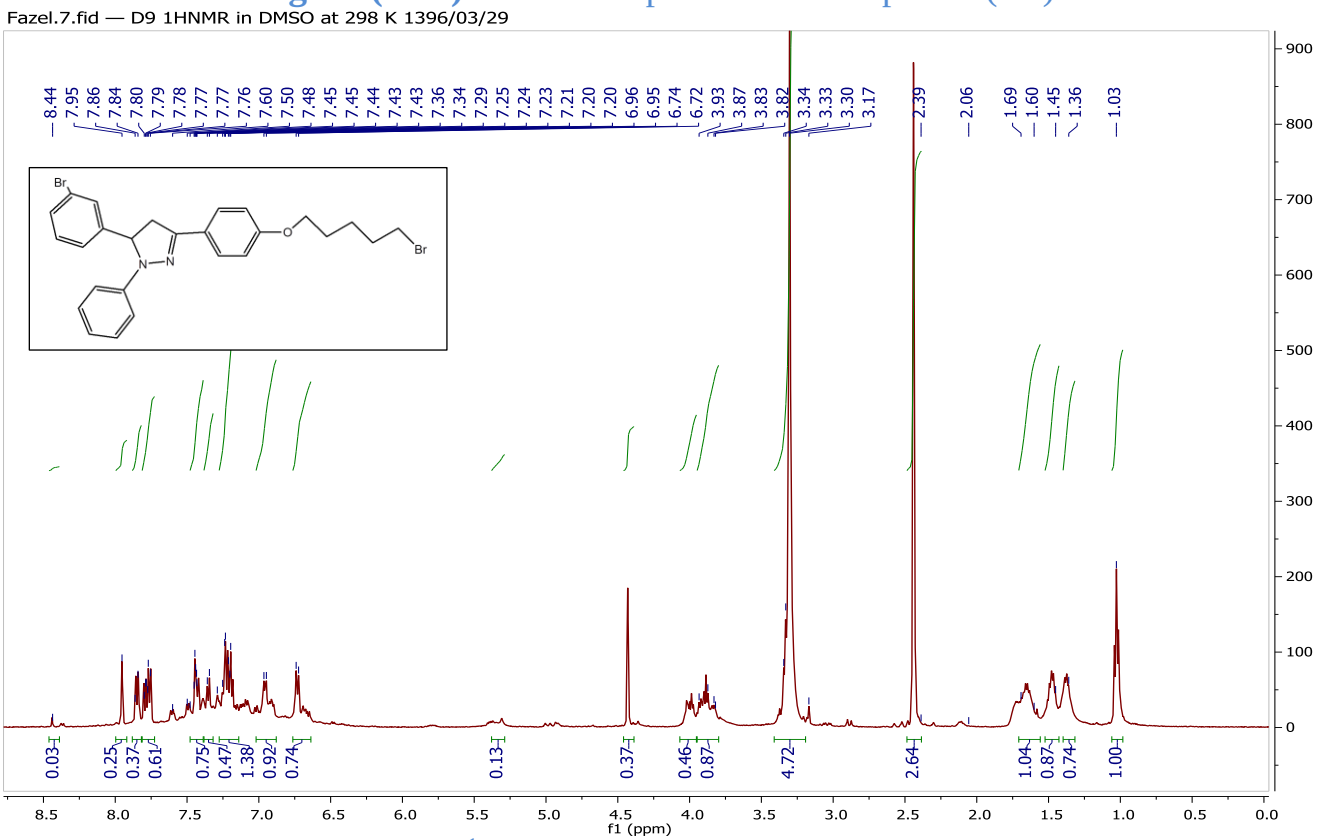


Figure (3-24): ^{1}H-NMR spectrum of compound (D9)

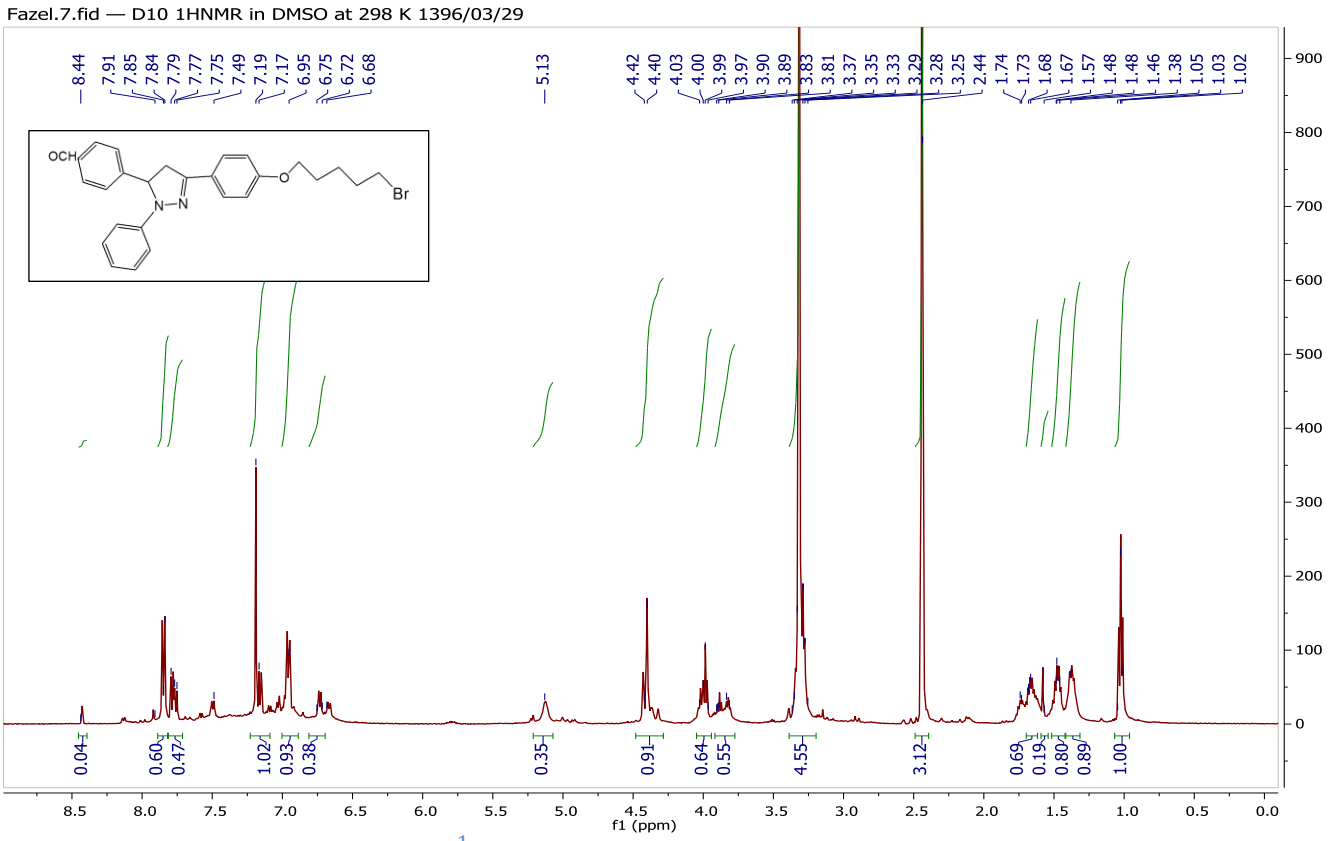


Figure (3-25): ^{1}H-NMR spectrum of compound (D10)

3.2.4.1.Characterization of 4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(substituted-phenyl)-1H-pyrimidin-2-one

The FT-IR spectra of compounds **(D11-D12)** have important characteristic bands at (3100 cm^{-1}) belong to (C-H) bonds of aromatic ring , aliphatic at (2943 cm^{-1}) and stretching vibration of carbonyl bond (C=O) at (1670 cm^{-1}). Another bands appeared at (1600 cm^{-1}) owing to (C=C) bond of stretching aromatic ring, Stretching vibration of (C=N) bond at (1624 cm^{-1}). Also the stretching vibration of (N-H) bond at (3430 cm^{-1}). [50] (Figure (3-26), (3-27) and Table (3-4)) showed the characteristic stretching vibration bands of the compounds (**D11-D12**).

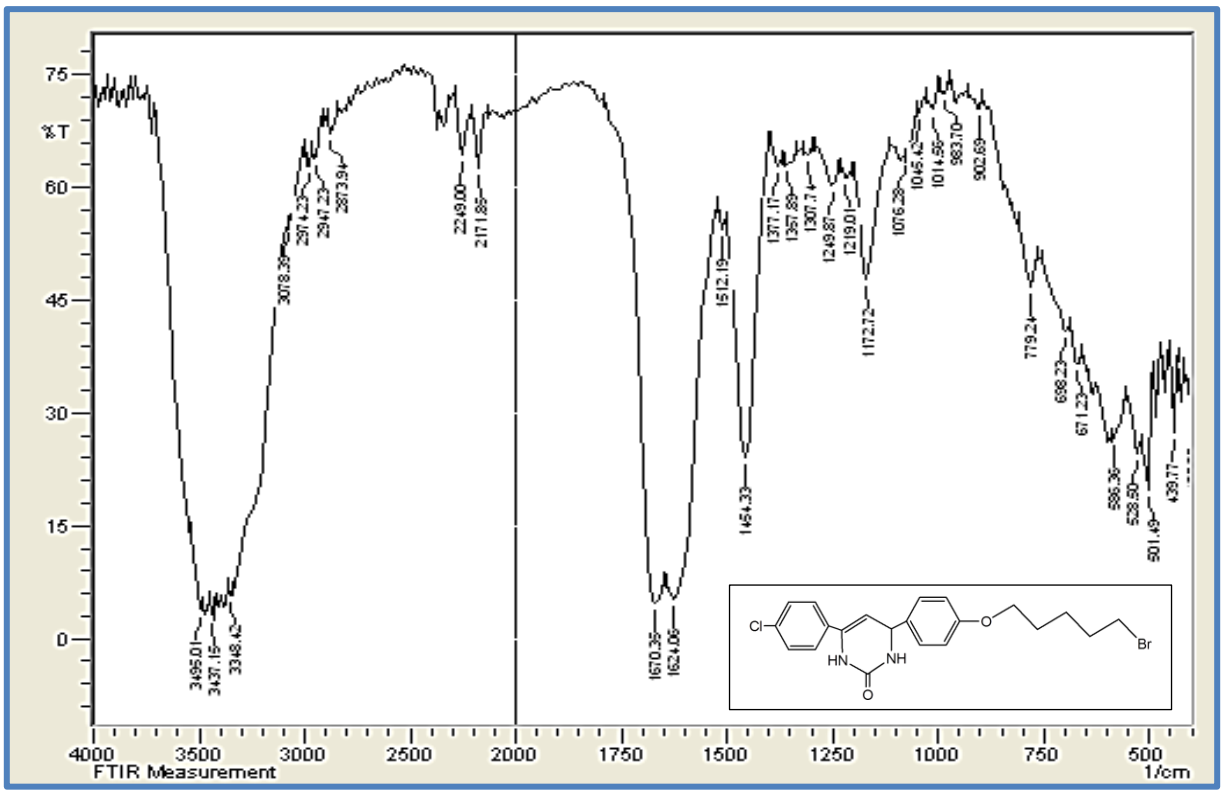


Figure (3-26): FT-IR spectrum of compound (D11)

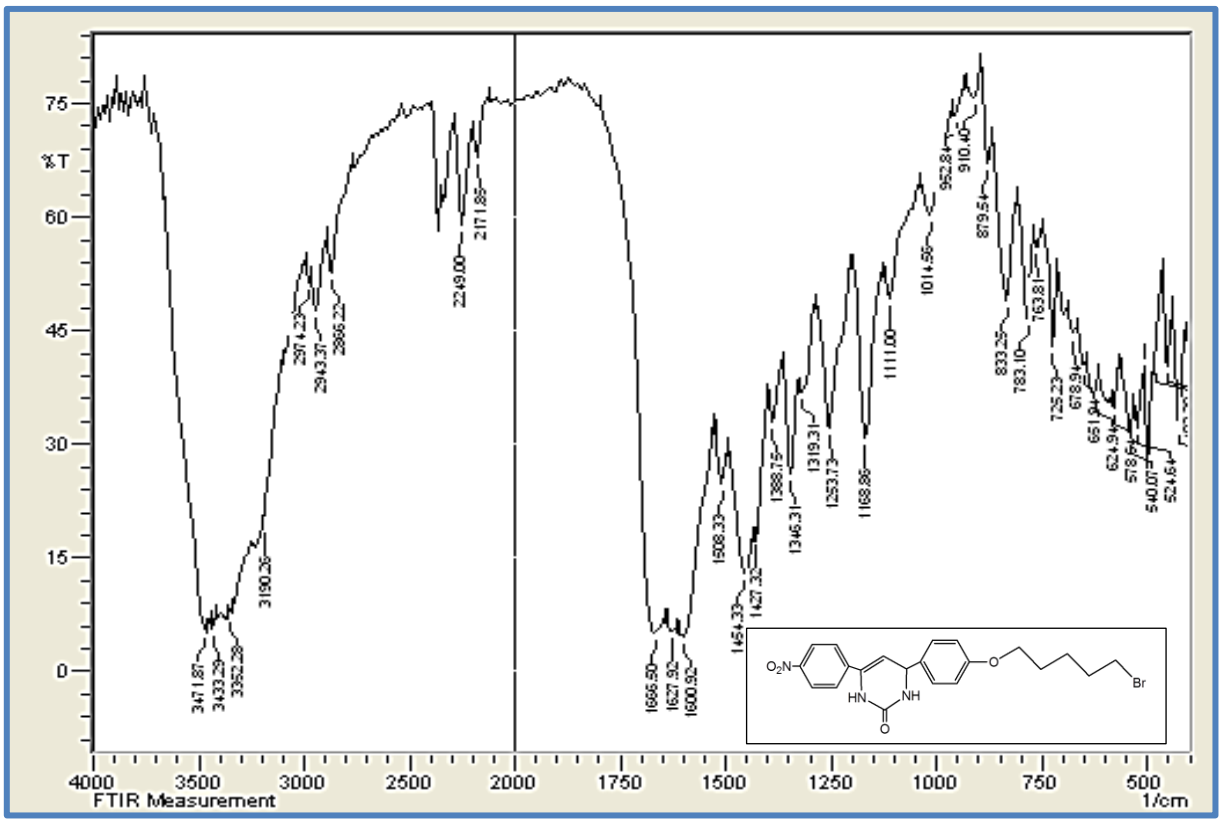


Figure (3-27): FT-IR spectrum of compound **(D12)**

Table 3-4: FTIR Spectral data of prepared compounds **(D11 – D12)** in cm^{-1}

Comp No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Aromatic	ν C=N	ν N-H	ν C-O	ν C=O
D11	3-26	3070	2947	1600	1624	3437	1249	1670
D12	3-27	3065	2947	1600	1627	3433	1253	1666

3.2.4.2. ^{1}H-NMR data of compound (D11) in ppm

8.5 (1H, NH); 6.3-8.5 (9H,d, C-H olefinic and aromatic); 5.5 (1H,d, CH_2-NH);4.0 (2H, CH_2-O); 3.8(2H, CH_2-Br); 1.0-1.6 (6H, CH_2-CH_2-CH_2).

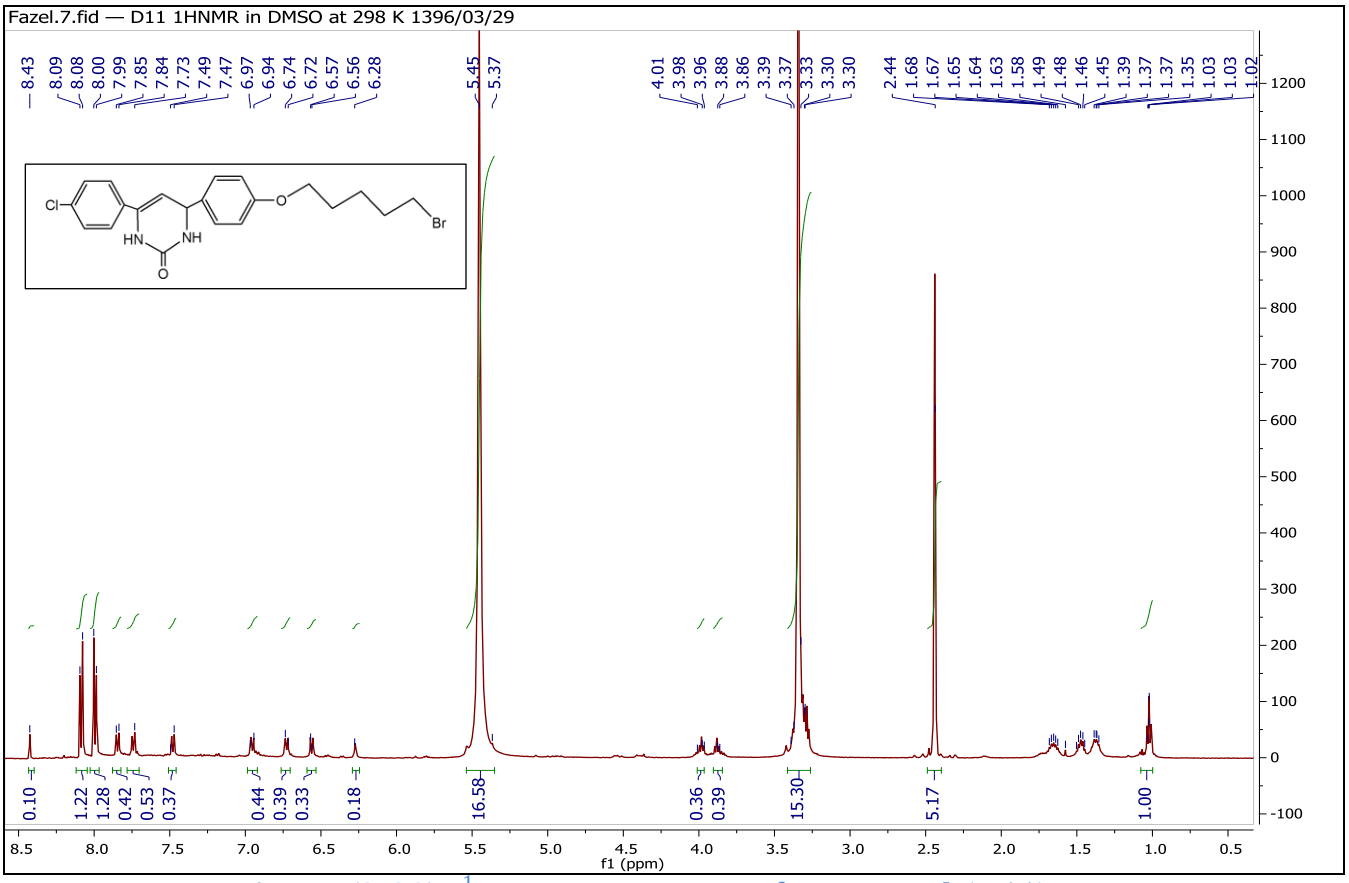


Figure (3-28): ^{1}H-NMR spectrum of compound (D11)

3.2.5.1 Characterization 4-[4-(5-Bromo-pentyloxy)-phenyl]-6-(substituted-phenyl)-1H-pyrimidin-2-one

The FT-IR spectra of compounds **(D13-D14)** showed important characteristic bands of the stretching vibration of (C-H) bonds of aromatic ring and olefin at (3100-2850 cm^{-1}), stretching vibration of (C=C) bond of aromatic ring at (1600 cm^{-1}), another bands appeared at (1662 cm^{-1}) due to (C=N) band , also the stretching vibration of (N-H) bond at (3430 cm^{-1}). It was good evidence for formation of compounds (**D13-D14**), when disappeared stretching bands of (C=O) group in FT-IR spectra of these compounds. [50] Figure (3-29), (3-30), and Table (3-6) show the interesting stretching vibration bands the compounds (**D13-D14**).

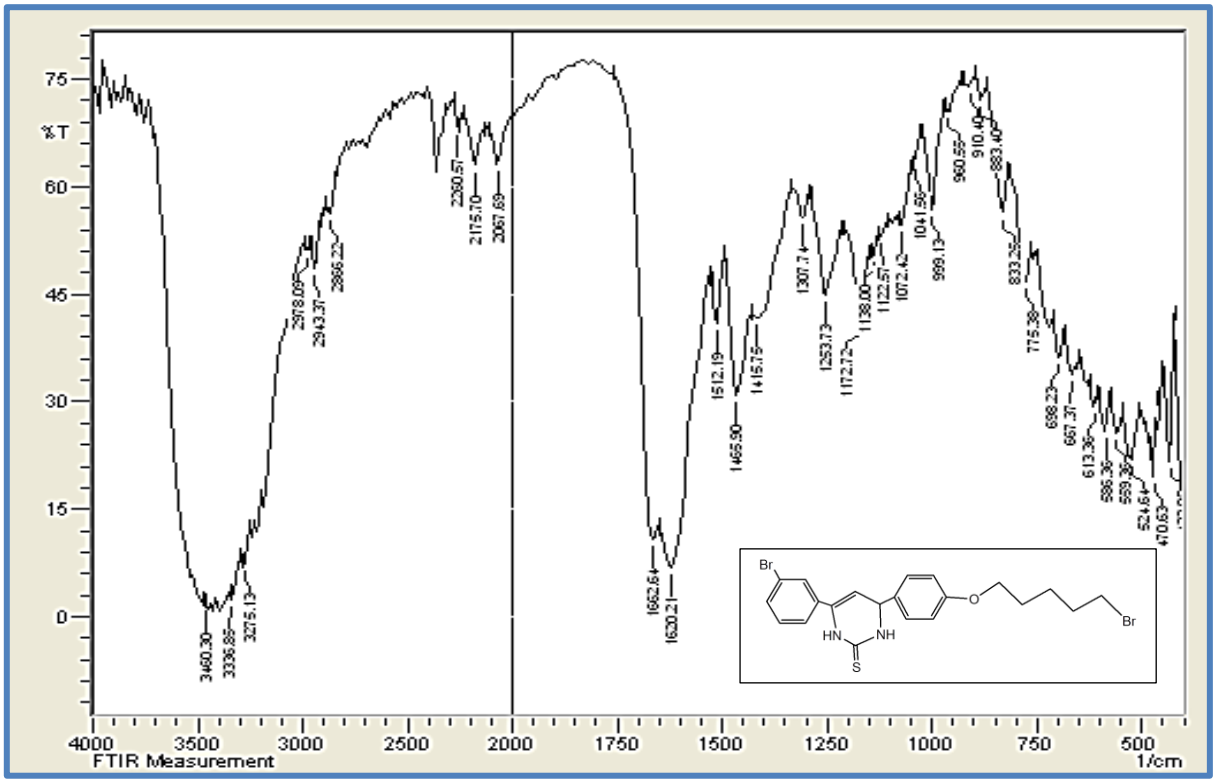


Figure (3-29): FT-IR spectrum of compound **(D13)**

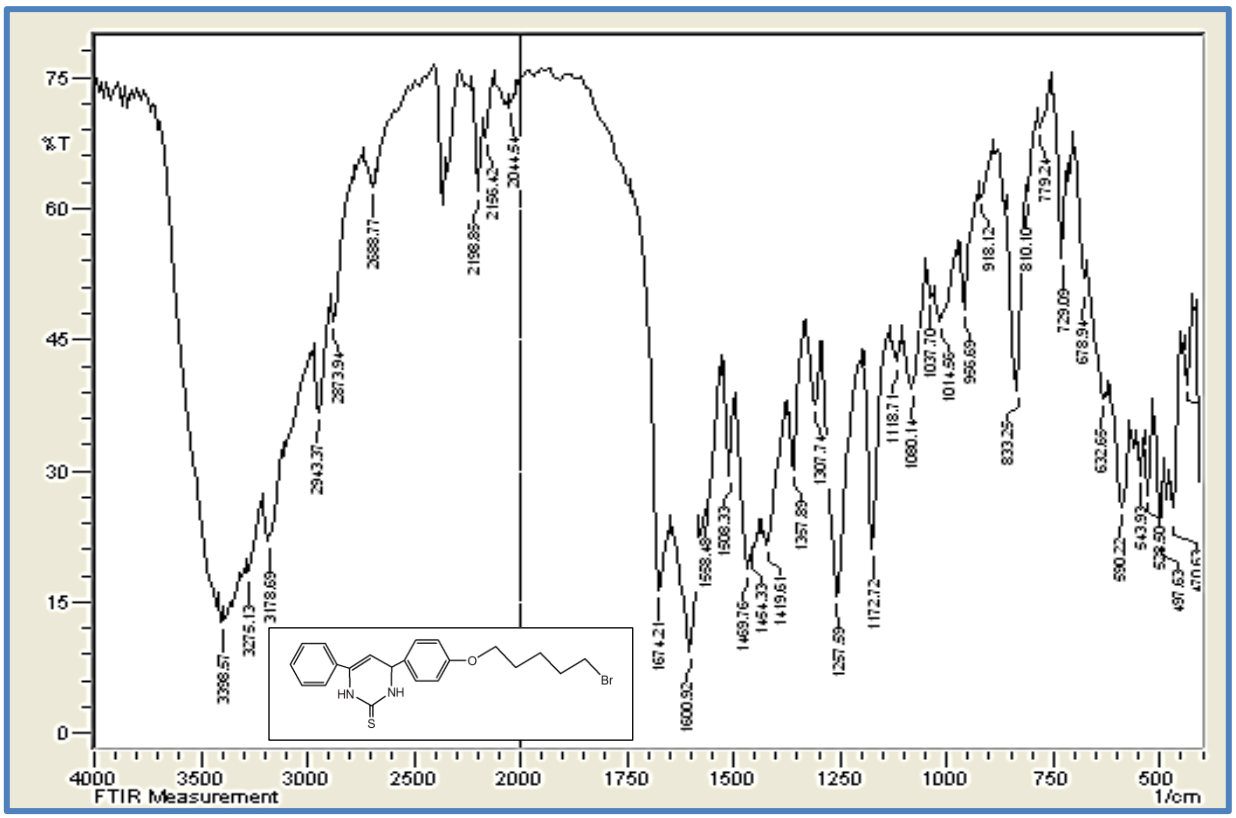


Figure (3-30): FT-IR spectrum of compound **(D14)**

Table 3-5: FTIR Spectral data of prepared compounds **(D13- D14)** in cm^{-1}

Compound No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Aromatic	ν C=N	ν N-H	ν C-O	ν C=S
D13	3-29	3000	2943	1620	1662	3460	1253	1138
D14	3-30	3050	2943	1600	1667	3398	1257	1357

3.2.5.2. ^{1}H-NMR data of compound (D14) in ppm

8.5 (1H,s, NH); 6.5-8.5 (10H, C-H olefinic and aromatic); 5.5 (1H,d, CH-NH); 4.5 (2H,t, CH_2-O); 4.0(2H,t, CH_2-Br); 1.0-1.6 (6H,m, CH_2-CH_2-CH_2).

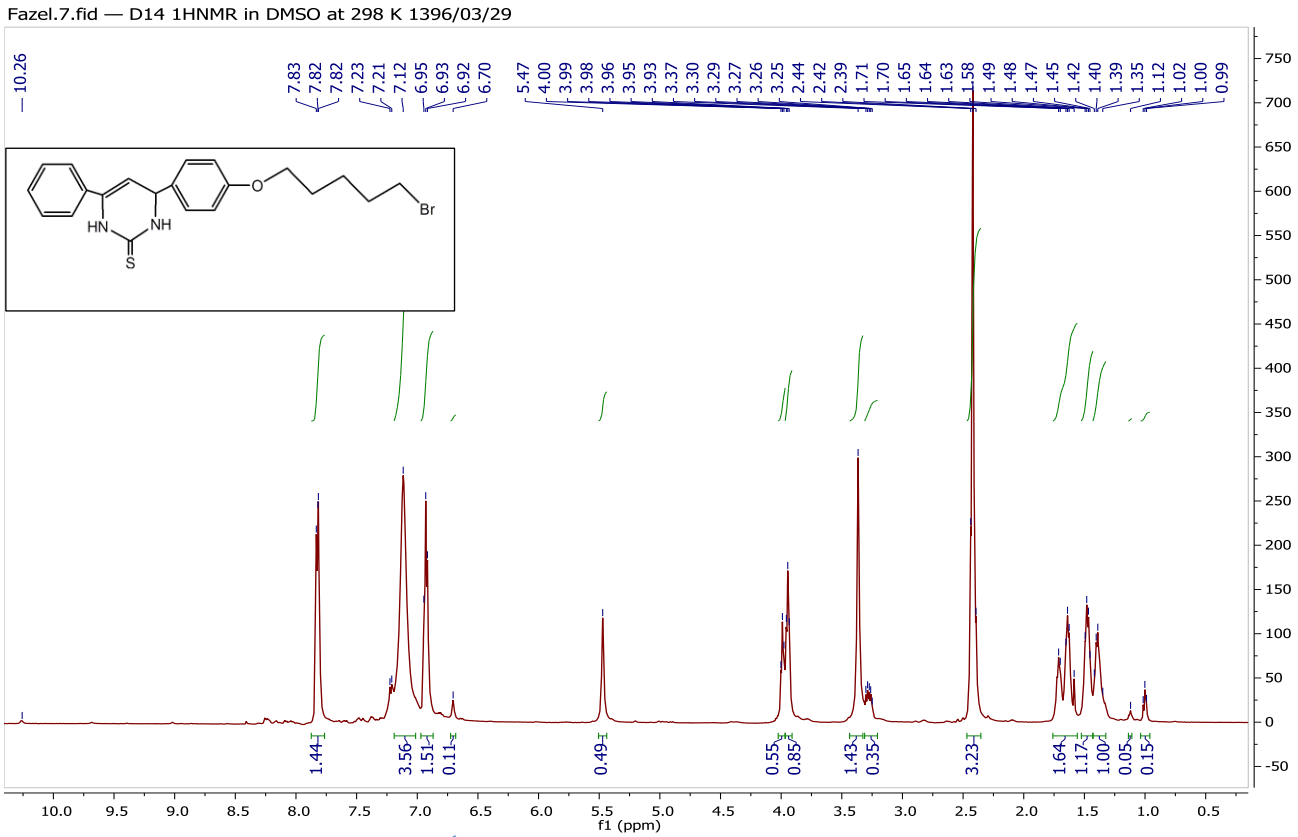


Figure (3-31): ^{1}H-NMR spectrum of compound (D14)

3.2.6.1. Characterization of 3-[4-(5-Bromo-pentyloxy)-phenyl]-5-phenyl-4,5-dihydro-isoxazole

The FT-IR spectrum of compound **(D15)** showed bands of the stretching vibration of (C-H) bonds of aromatic ring and olefin at (3040-2943 cm^{-1}) ,Also stretching vibration of (C=C) bond of aromatic ring at (1600 cm^{-1}), the stretching vibration of (C=N) bond at (1658 cm^{-1}) ,(C-O) (1249 cm^{-1}) and(C-O) endocyclic(1072 cm^{-1}). The bands of (C=O) was disappeared in the FT-IR spectrum of compound [50], Figure (3-32) showed the characteristic stretching vibration bands the compounds (**D15**) .

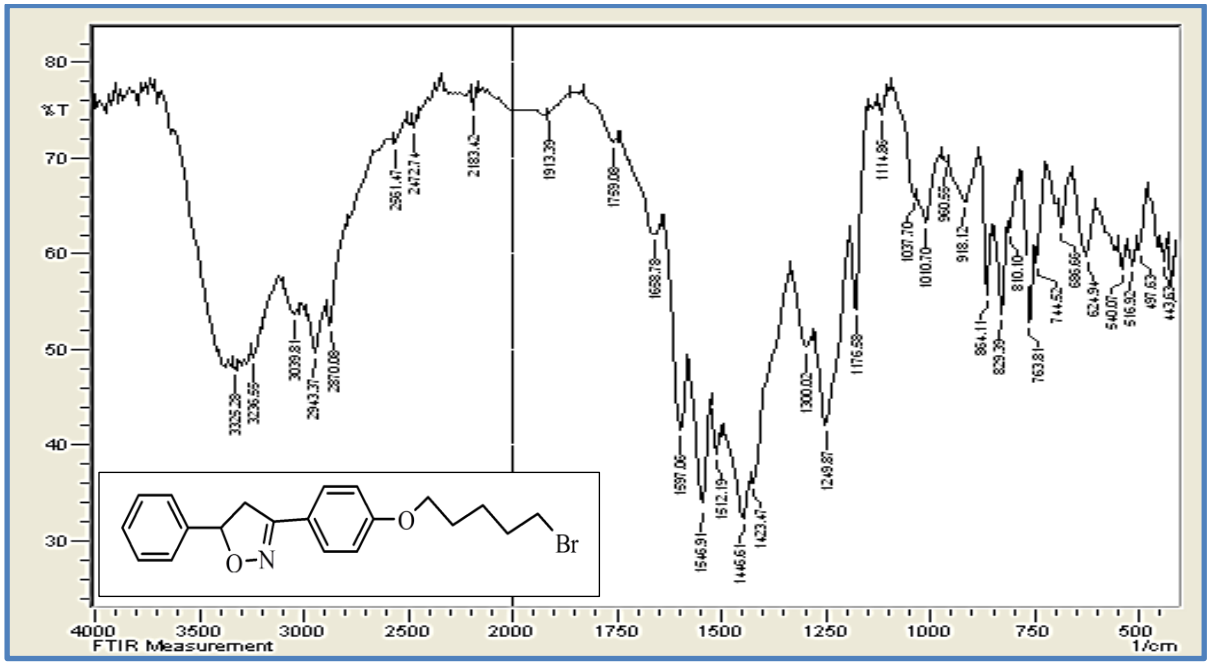


Figure (3-32): FT-IR spectrum of compound **(D 15)**

3.2.6.2. ^{1}H-NMR data of compound (D15) in ppm

6.7-8.1 (10H,d, C-H aromatic); 4.5 (2H,t, CH_2-O); 4.0(2H,t, CH_2-Br); 2.0 (2H,d, CH_2 oxazole ring); 5.4 (1H,t, CH- oxazole ring); 1.0-1.6 (6H,m, CH_2-CH_2-CH_2).

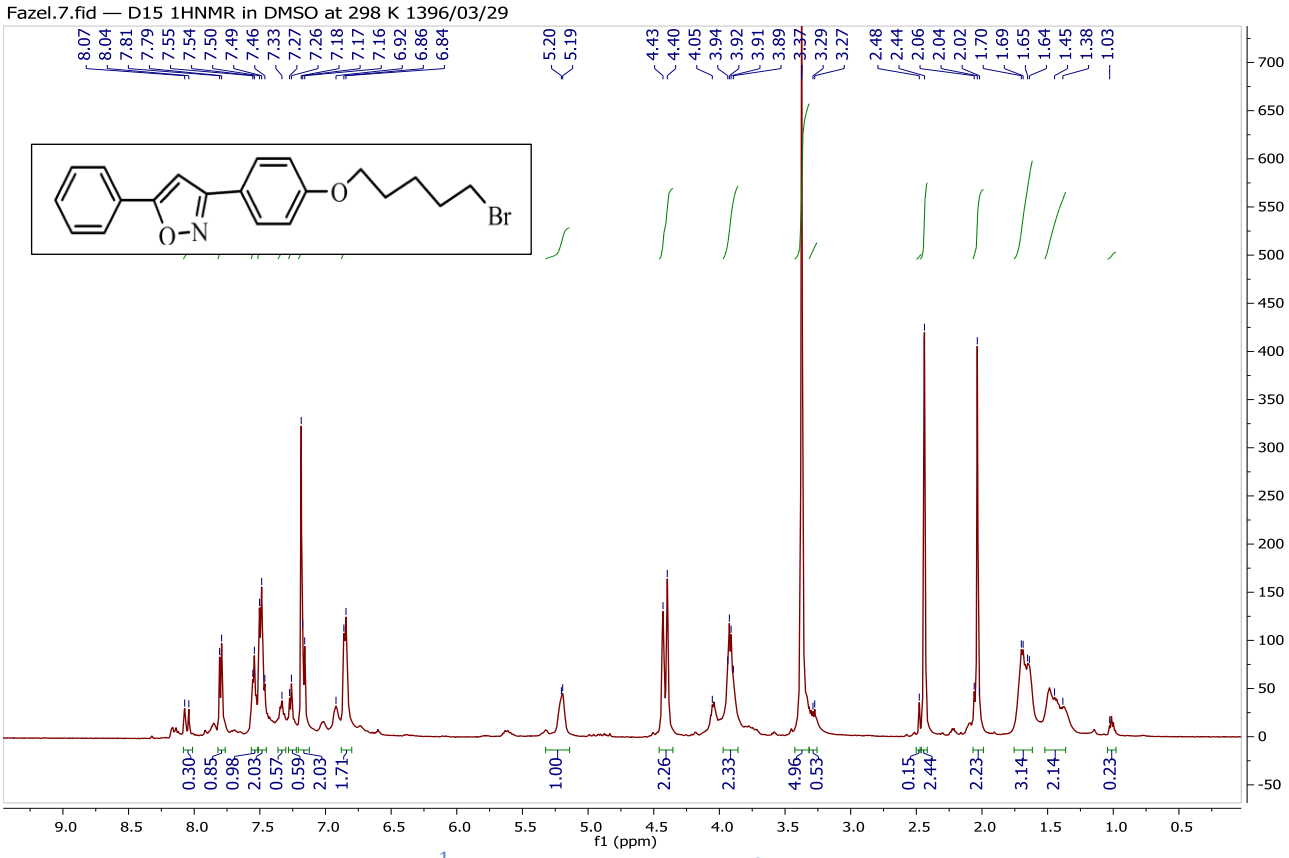
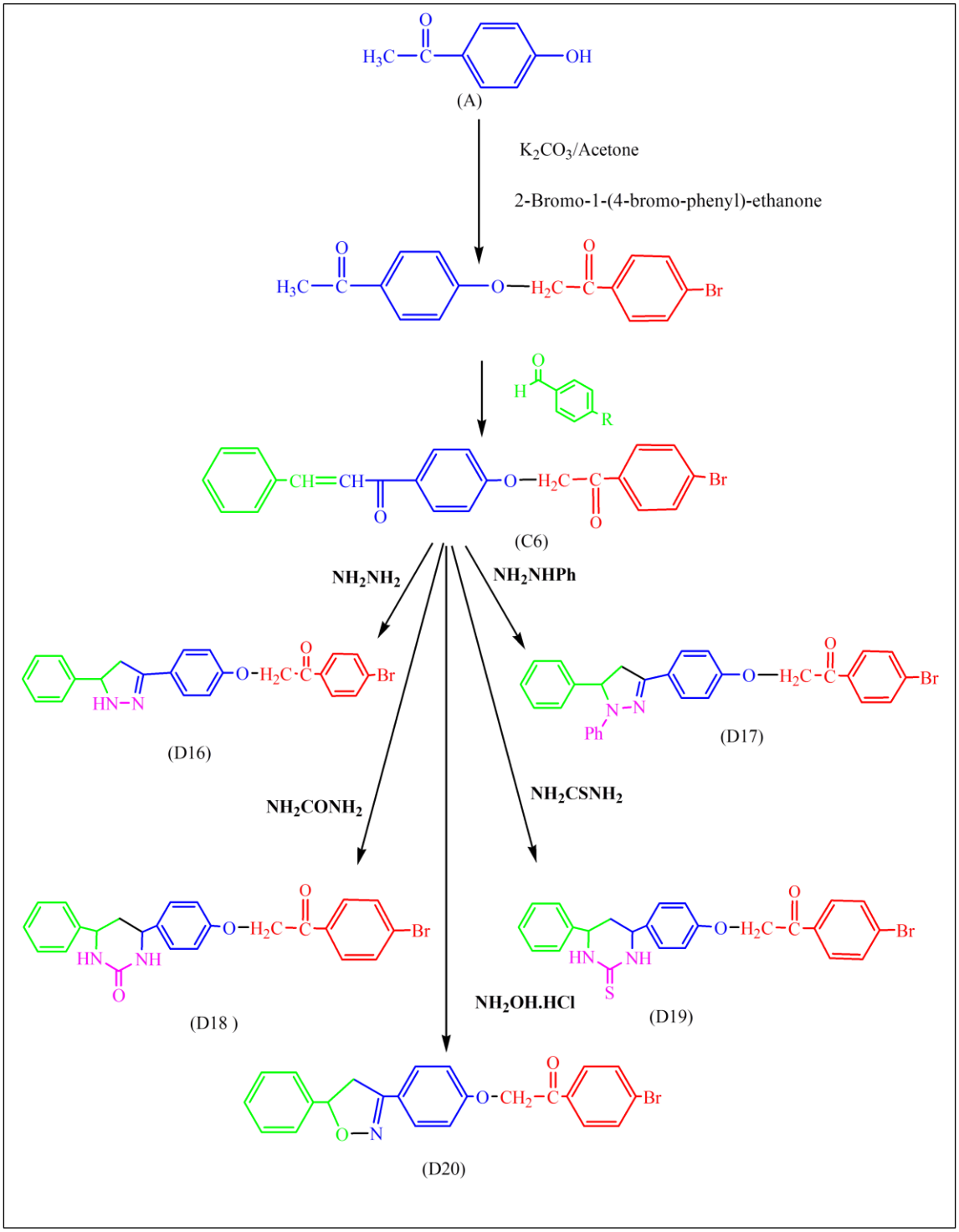


Figure (3-33): ^{1}H-NMR spectrum of compound (D15)

3.3 Synthesis of compounds (D16-D20):

The chemical steps for the synthesis of compounds **(D16-D20)** are shown in scheme 3-6



Scheme (3-6): The chemical steps for the synthesis of compounds **(D16-D20)**

3.4 The FT-IR spectra &^{1}H-NMR data of prepared compounds (D16-D20)

3.4.1. Characterization 2-(4-Acetyl-phenoxy)-1-(4-bromo-phenyl)-ethanone (B2).

The FT-IR spectra of compound (B2) has important characteristic identification by showing two stretching vibration bands at (C=O) bond at ketone (1705 cm^{-1}), (1658 cm^{-1}), and (1604cm^{-1}) to (C=C) aromatic stretching vibrations bond and (C-O) bond (1270 cm^{-1}) and stretching vibration bands at (2873,1947 cm^{-1})that relates to (C-H) of aliphatic bonds [50], (Figure (3-34).

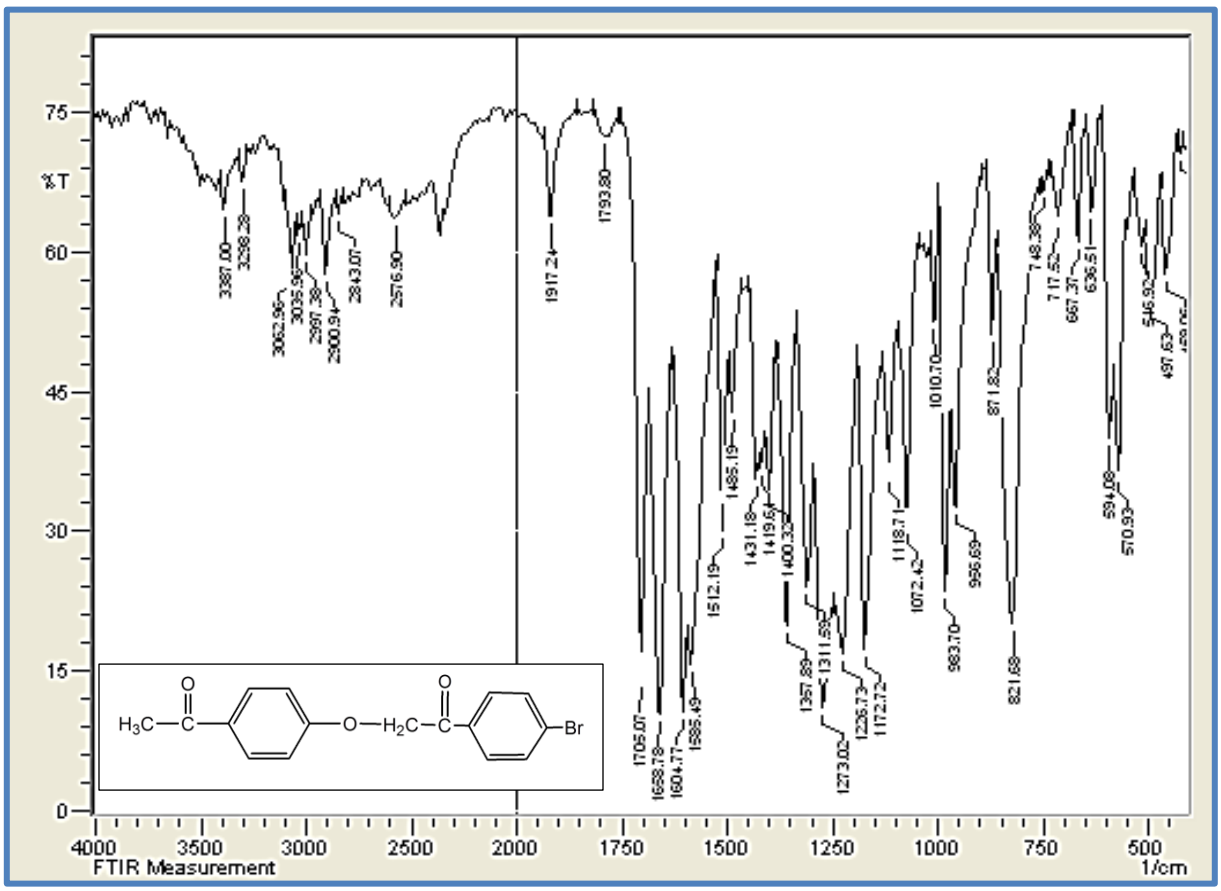


Figure (3-34): FT-IR spectrum of compound **(B2)**

3.4.2. Characterization of 1-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-3-phenyl-propan-1-one (C6).

The α,β unsaturated compound (C6) were prepared according to crossed Aldol condensation reaction . The FT-IR spectra of compound (C6) have important characteristic identification by shifting vibration band that corresponds to (C=O) (1681 cm^{-1}) band which are less than normal stretching vibration bands in (B2 ,1705 cm^{-1}) for carbonyl group of acetyl group and access shift in the carbonyl value because extend the conjugated system [50]. Figure (3-35) showed the characteristic stretching vibration bands for the α,β unsaturated compounds (C6) .

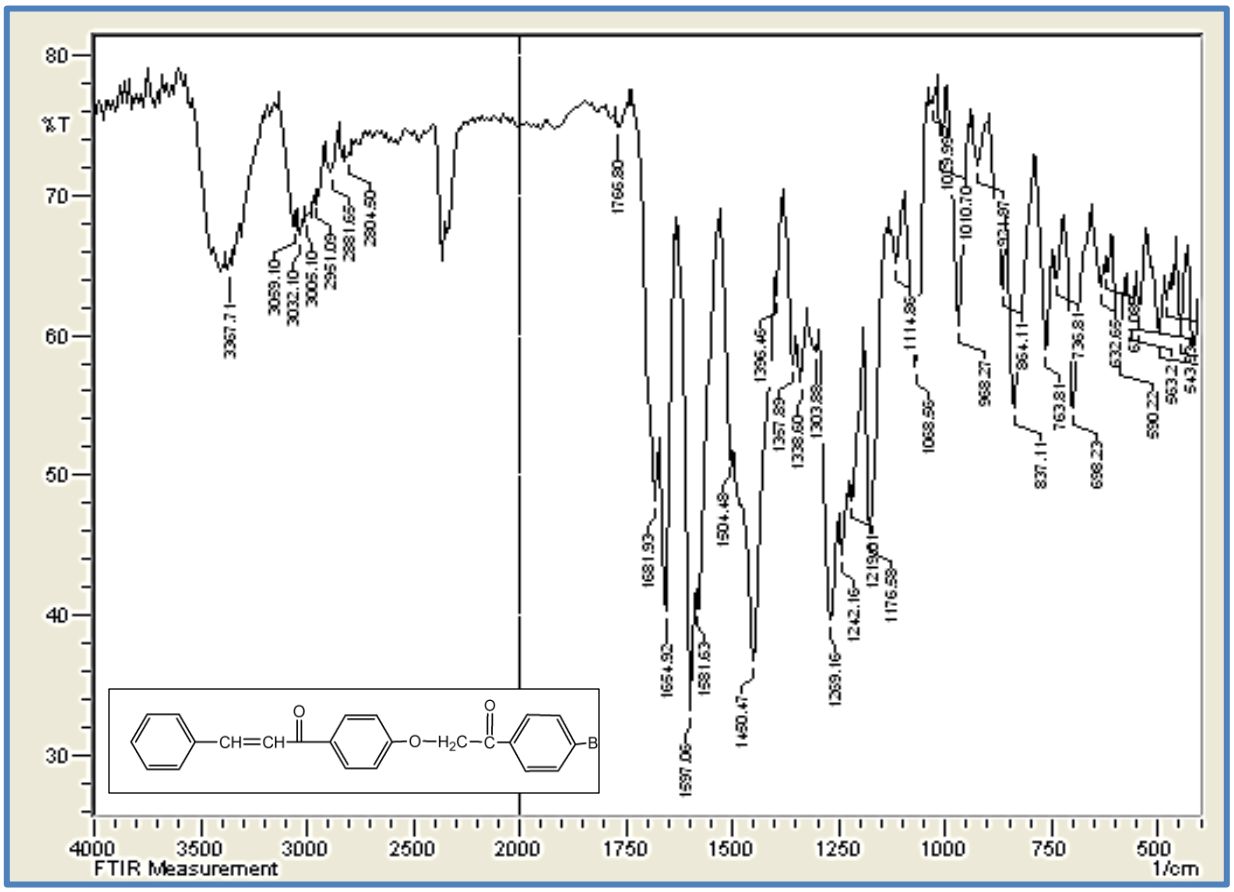


Figure (3-35): FT-IR spectrum of compound **(C6)**

3.4.3.1. Characterization 0f 1-(4-Bromo-phenyl)-2-[4-(5-phenyl-4,5-dihydro-1H-pyrazol-3-yl)-phenoxy]-ethanone (D16) and 1-(4-Bromo-phenyl)-2-[4-(1,5-diphenyl-4,5-dihydro-1H-pyrazol-3-yl)-phenoxy]-ethanone(D17)

The compounds (D16-D17) were prepared by cyclization reaction via hydrazine hydrate and phenyl hydrazine. The FT-IR spectra of compounds (D16-D17) revealed a medium stretching vibration band at(<1651 cm^{-1}) that corresponds to (C=O) , (>1651 cm^{-1}) that corresponds to (C=N) bond (see Figure (3-23) , Figure (3-24) and Table (3-7) .The FTIR spectrum of compounds (D16- D17) have important characteristic a broad stretching vibration bands as two other characteristic bond at (3062 cm^{-1}) , (1585 cm^{-1}) due to (C-H),(C=C) aromatic and at (3400 cm^{-1}) due to group stretching vibration band (N- H) . The stretching bands of (C=O) group was disappeared in the FT-IR spectra of compounds (D16 – D17) and this was good evidence to formation these compounds, [50] (Figure (3-36), (3-37), and Table (2-8) show the interesting stretching vibration bands for the pyrazole compounds (D16-D17).

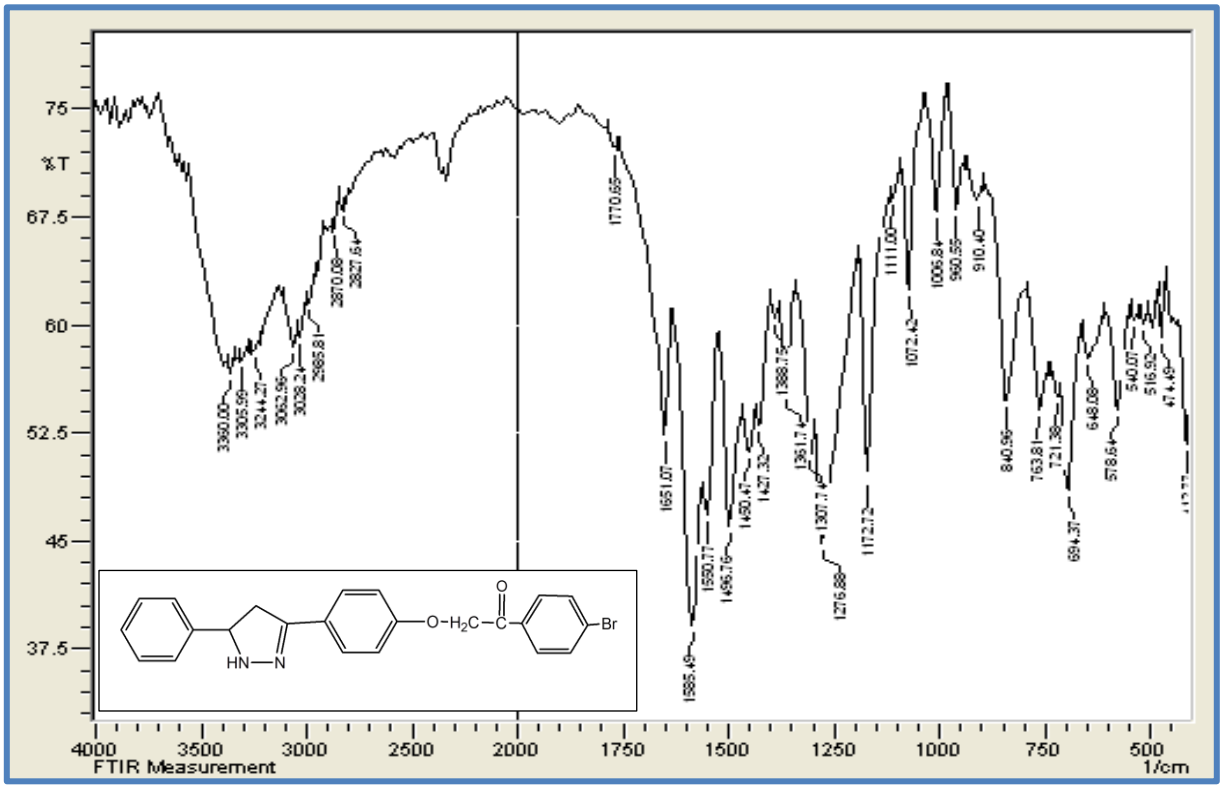


Figure (3-36): FT-IR spectrum of compound **(D16)**

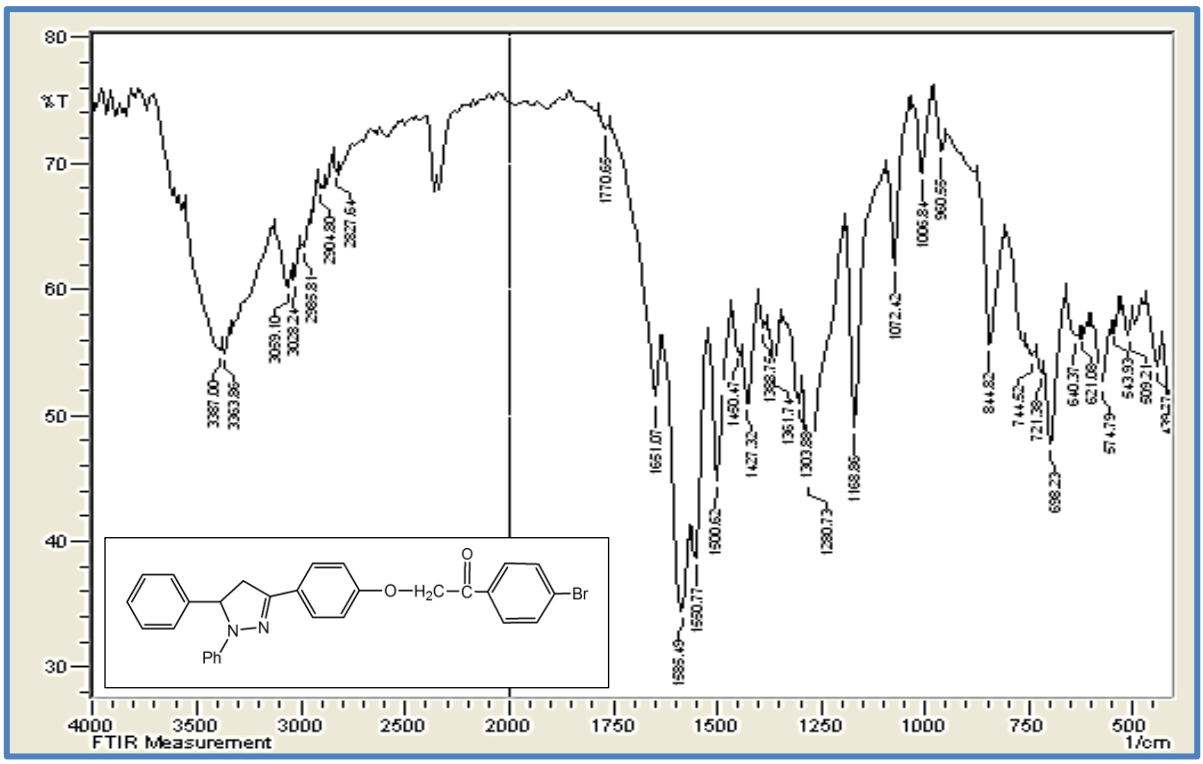


Figure (3-37): FT-IR spectrum of compound **(D17)**

Table 3-6: FTIR Spectral data of prepared compounds **(D16 – D17)** in cm^{-1}

Comp No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Aromatic	ν N-H	ν C-O	ν C=O
D16	3-39	3062	2980	1585	3383	1276	1651
D17	3-40	3062	2900	1585	3387	1280	1651

3.4.4.1.Characterization of 4-{4-[2-(4-Bromo-phenyl)-2-oxo-ethoxy]-phenyl}-6-phenyl-3,4-dihydro-1H-pyrimidin-2-one and 1-(4-Bromo-phenyl)-2-[4-(6-phenyl-2-thioxo-1,2,3,4-tetrahydro-pyrimidin-4-yl)-phenoxy]-ethanone (D18-D19)

The FT-IR spectrum of compounds **(D18-D19)** have important characteristic identification by showed the stretching vibration of (C-H) bonds of aromatic ring and olefin at (3000-3100 cm-1). Stretching vibration of (C=C) bond of aromatic ring and Aliphatic at (1600 cm^{-1} -1680 cm^{-1}), the stretching vibration of (N-H) bond at (3430 cm^{-1}) and have important characteristic stretching vibration two bands to (C=O) bond at (1678 cm^{-1}) and another at (1651) allowance for (C=O) (1681) in the chalcon (C6) which disappeared [50]Figure (3-38), Figure (3-39), and Table (3-10) show the interesting stretching vibration bands the compounds (**D18-D19**) .

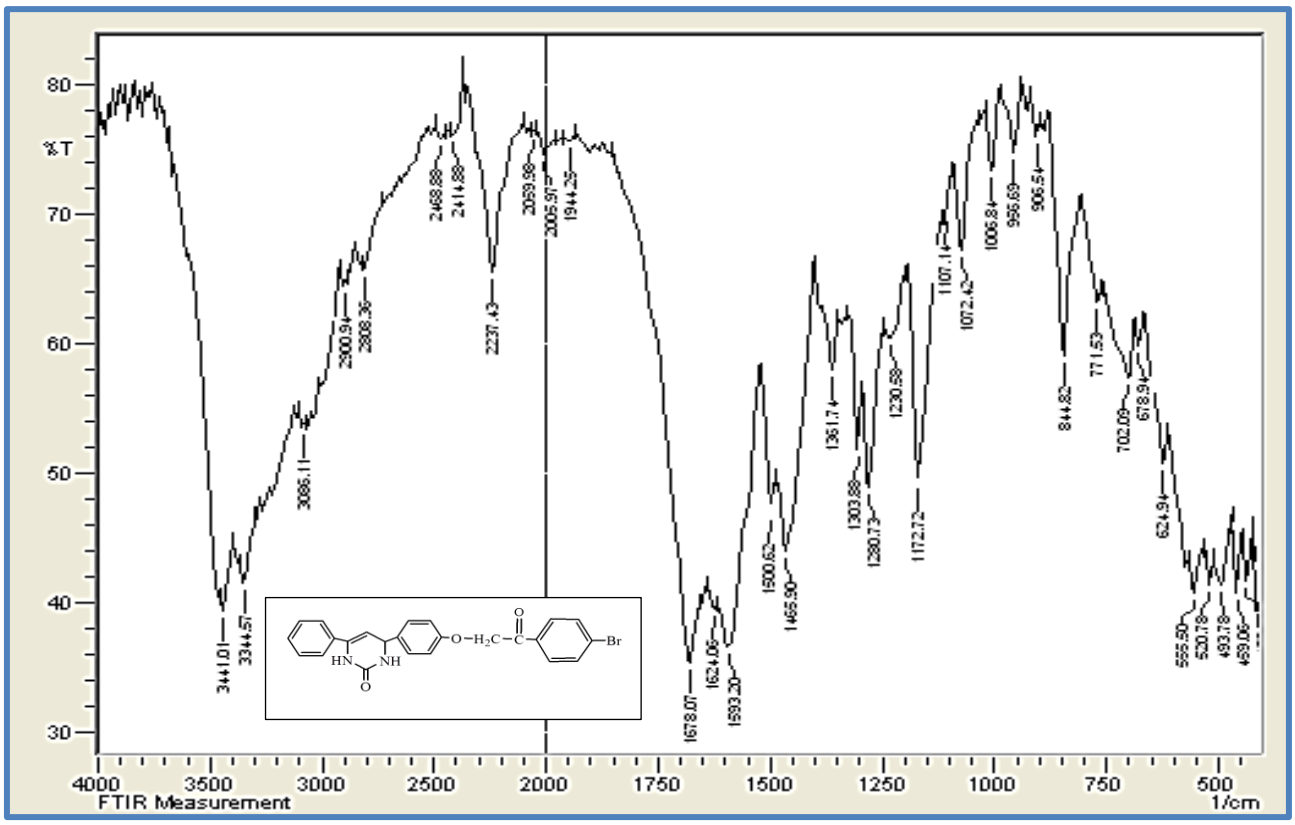


Figure (3-38): FT-IR spectrum of compound **(D18)**

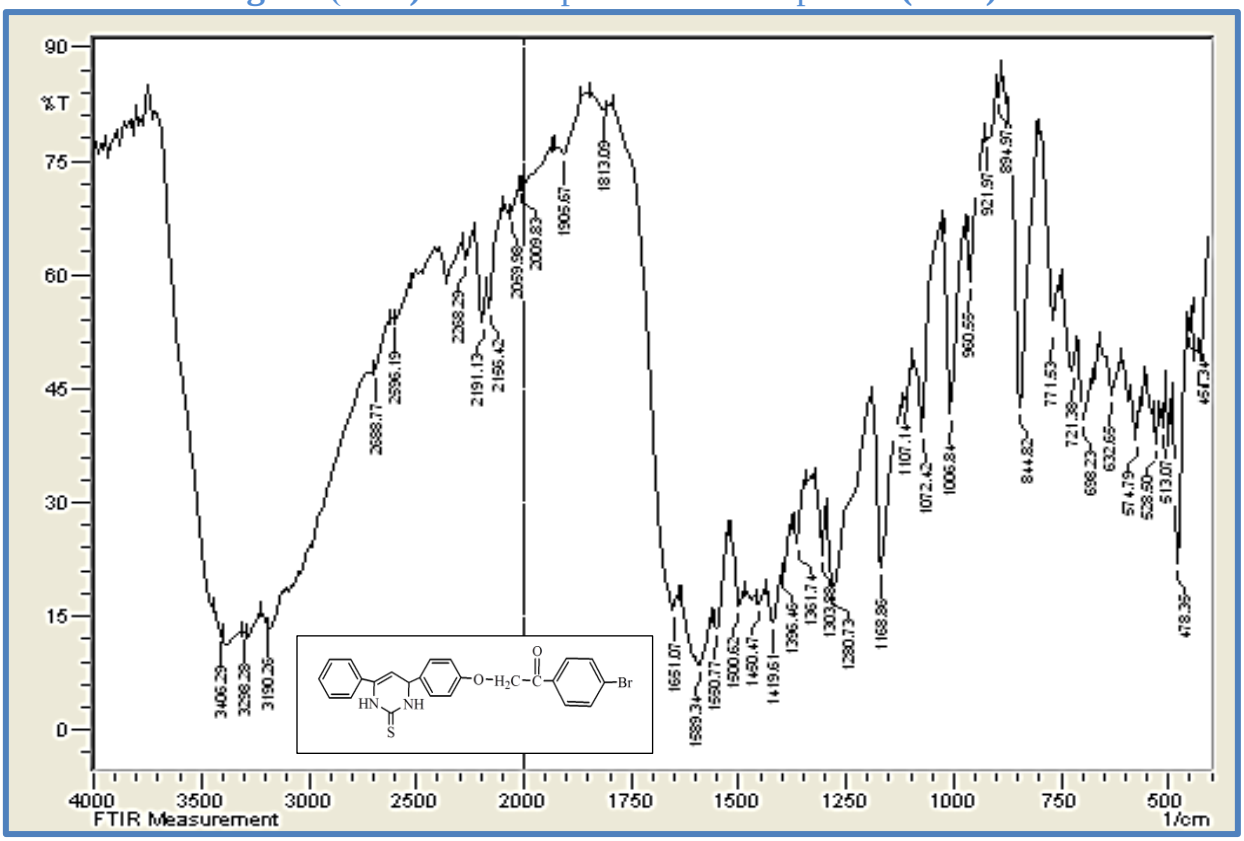


Figure (3-39): FT-IR spectrum of compound **(D19)**

Table 3-7: FTIR Spectral data of prepared compounds **(D18- D19)** in cm^{-1}

Comp No.	Fig. No.	ν C-H Aromatic	ν C-H Aliphatic	ν C=C Aromatic	ν N-H	ν C-O	ν C=O	ν C=S
D18	3-43	3086	2900	1593	3440	1280	1678	-
D19	3-44	3080	2900	1589	3400	1280	1651	1006

3.4.5.1. Characterization of 1-(4-Bromo-phenyl)-2-[4-(5-phenyl-4,5-dihydro-isoxazol-3-yl)-phenoxy]-ethanone(D20)

The FT-IR spectrum of compounds **(D20)** has important characteristic identification by showed the stretching vibration of (C-H) bonds of aromatic ring and olefin at (3040-2943 cm^{-1}) ,stretching vibration of (C=C) bond of aromatic ring at (1589cm^{-1}), the stretching vibration of (C=O) bond at (1662 cm^{-1})، and (C-O) bond at (1276 cm^{-1}) of ether ,and (1072 cm^{-1}) to(C-O) endocyclic [50], Figure (3-47) shows the interesting stretching vibration bands the compound (**D20**) .

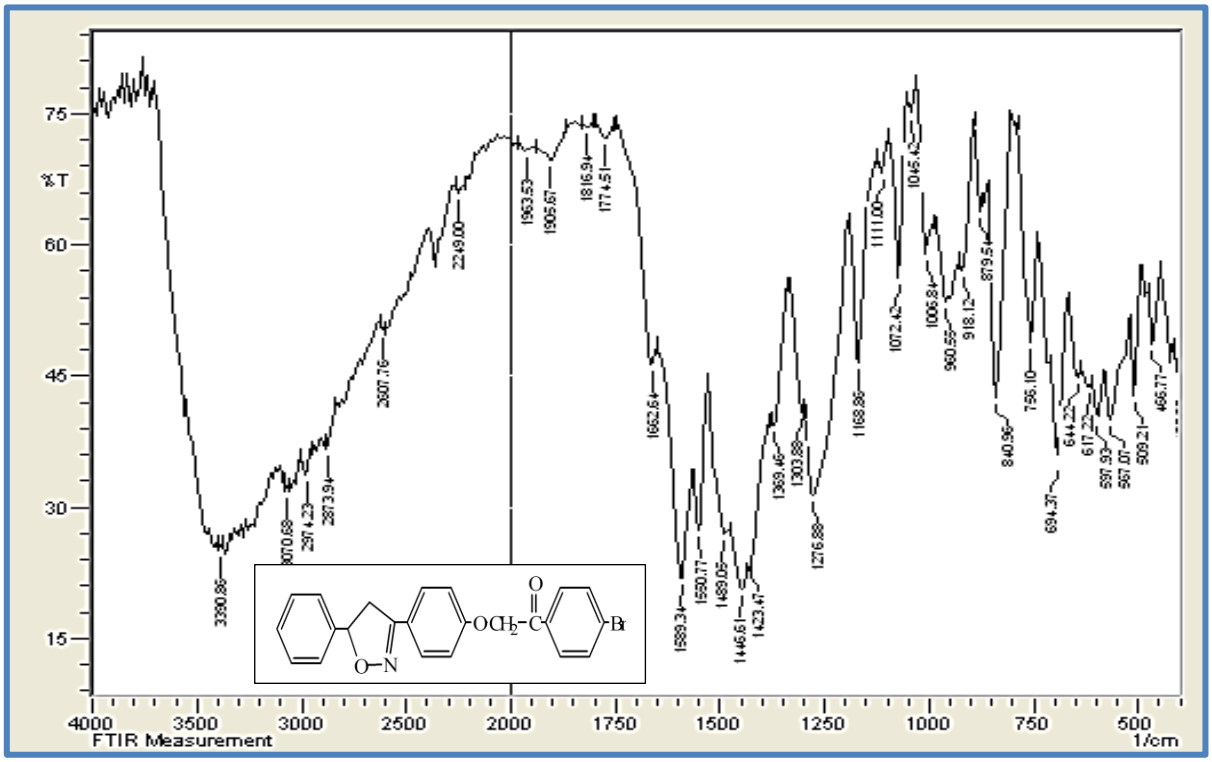


Figure (3-40): FT-IR spectrum of compound **(D20)**

3.4.5.2. ^{1}H-NMR data of compound (D20) in ppm

6.4-8.5 (13H,d, C-H aromatic); 4.5 (2H,s, CH_2-O); 2.0 (2H,d, CH_2 oxazole ring); 4.2 (1H,t, CH- oxazole ring).

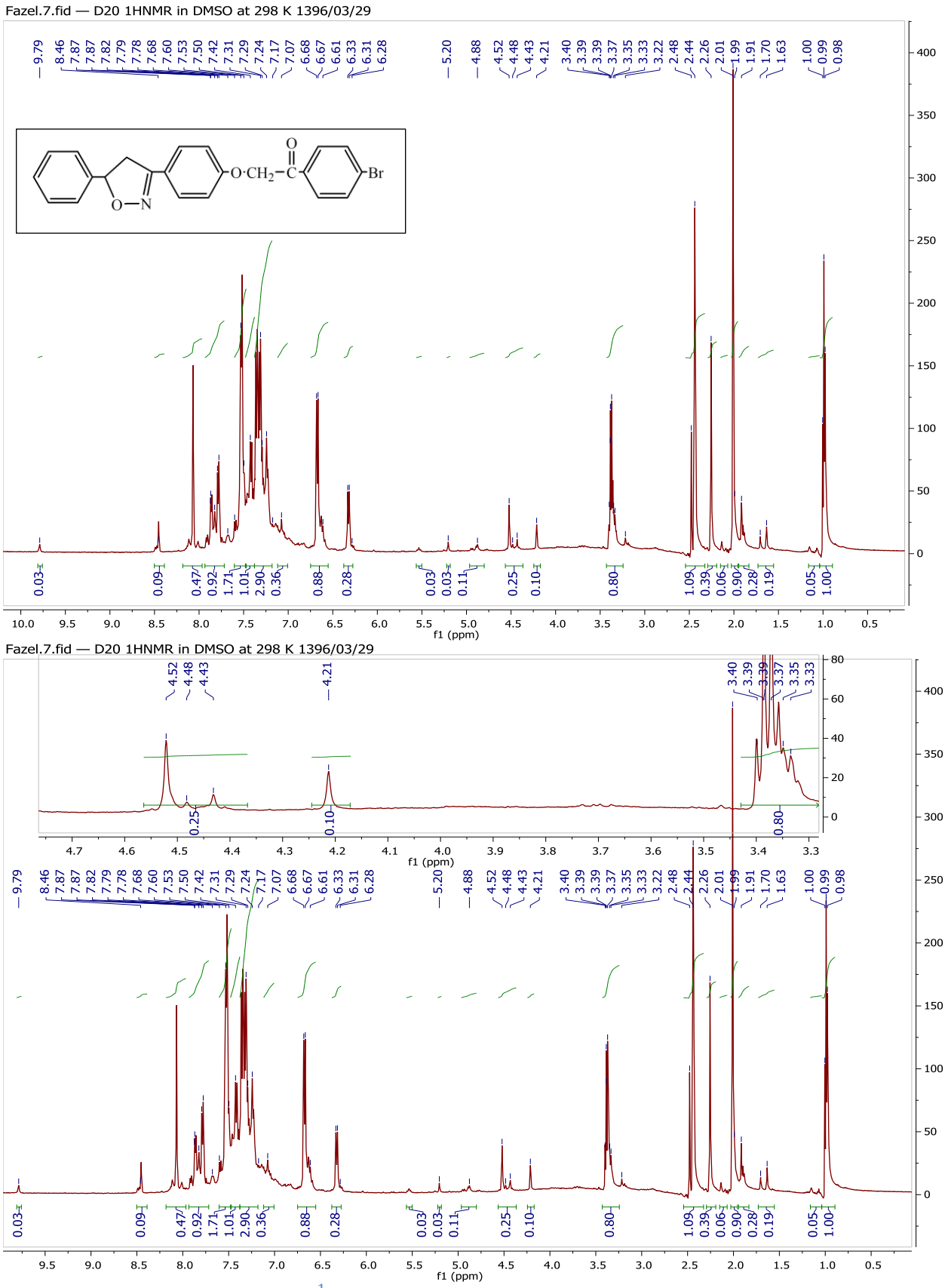
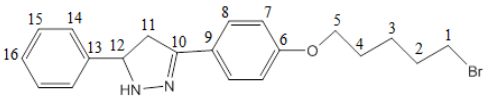
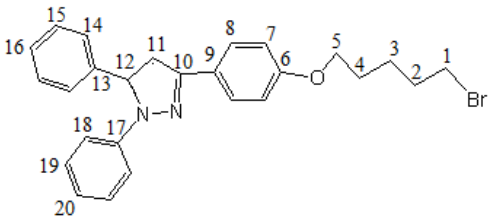
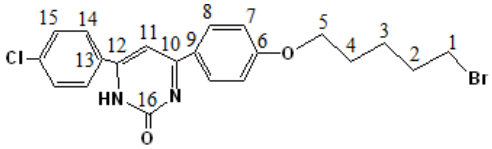
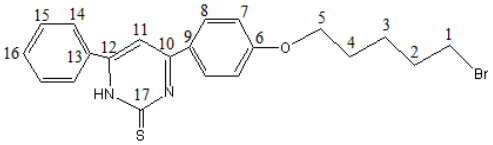
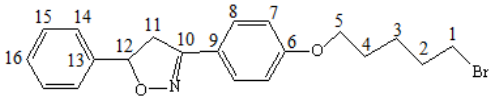


Figure (3-41): ^{1}H-NMR spectrum of compound (D20)

3.5. ^{13}C-NMR spectrum of compounds (D1,D6,D12,D14,D15)

^{13}C -NMR spectra of prepared organic compound containing heteroatoms **(**D1,D6,D12,D14,D15**)** are also used for confirming the structure of final products. Table (3-12) and Figures (3-49)-(3-53) , show the following characteristic chemical shifts (ppm , δ) for the compounds (D1,D6,D12,D14,D15) in DMSO-d_6 as a solvent.

Table (3-8): ^{13}C-NMR data of compounds (D1,D6,D12,D14,D15) in ppm ,δ

Comp. No.	Compound structure	^{13}C-NMR data	Fig. No.
D1		26-70 (C1-C5 and C11, C12); 110-160 (C6-C9 and C13-C16); 194 (C10).	3-49
D6		22-72 (C1-C5 and C11, C12); 115-165 (C6-C9, C16-C16 and C17-C20)); 196 (C10).	3-50
D12		22-70 (C1-C5); 114-155 (C6-C9 and C13-C15); 190 (C10); 110(C11): 160 (C12); 168(C16)	3-51
D14		22-69 (C1-C5); 127-131 (C6-C9 and C13-C16); 164 (C10); 114(C11): 160 (C12); 180(C17)	3-52
D15		22-87 (C1-C5 and C11, C12); 114-144 (C6-C9 and C13-C16); 153 (C10).	3-53

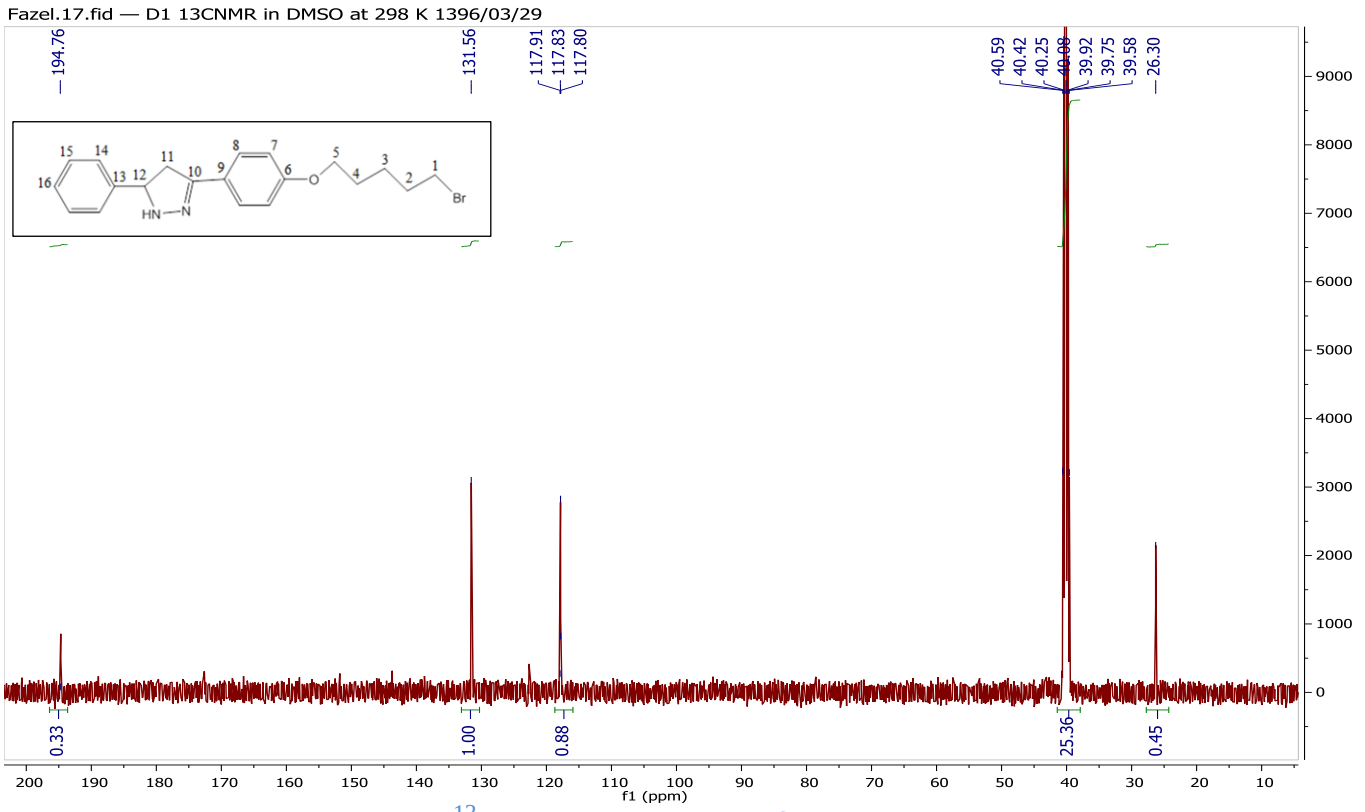


Figure (3-42): ^{13}C-NMR spectrum of compound (D1)

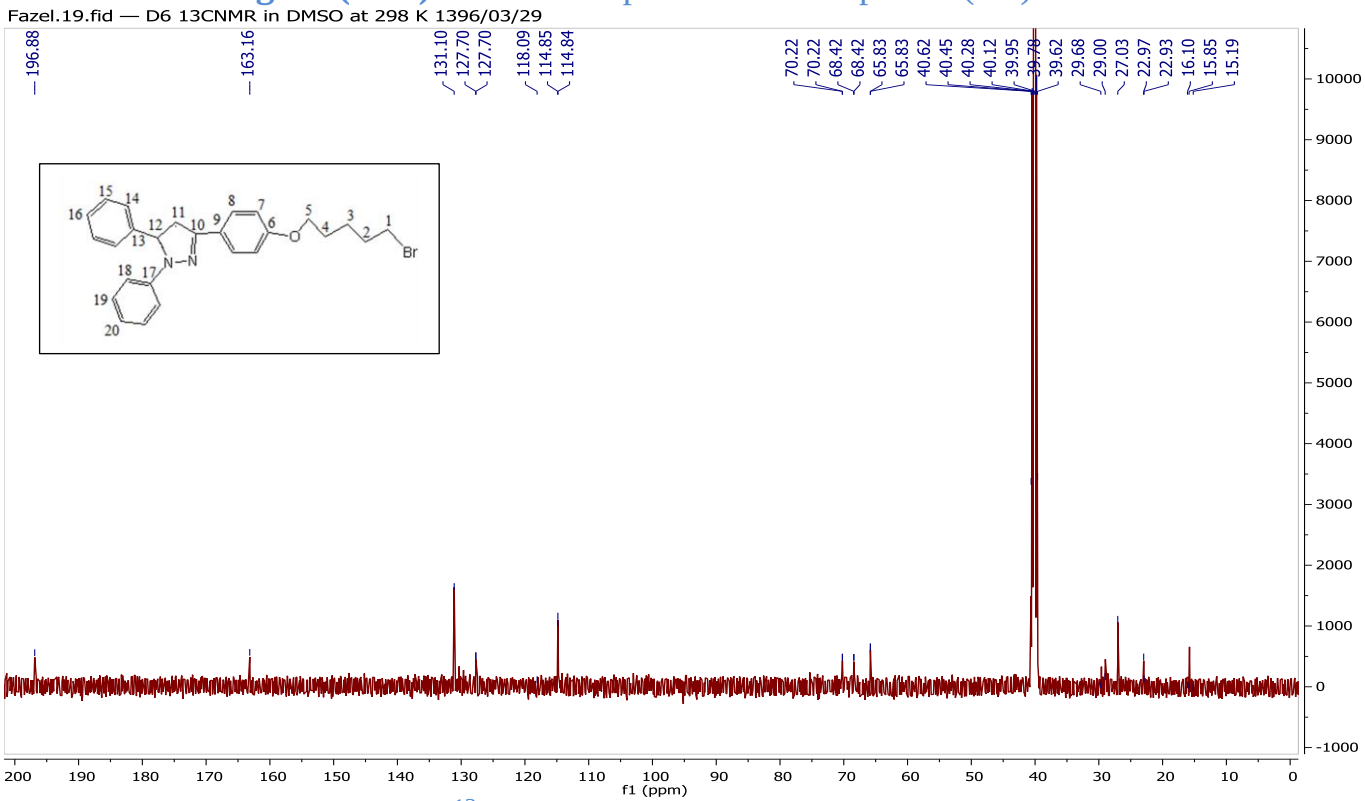


Figure (3-43): ^{13}C-NMR spectrum of compound (D6)

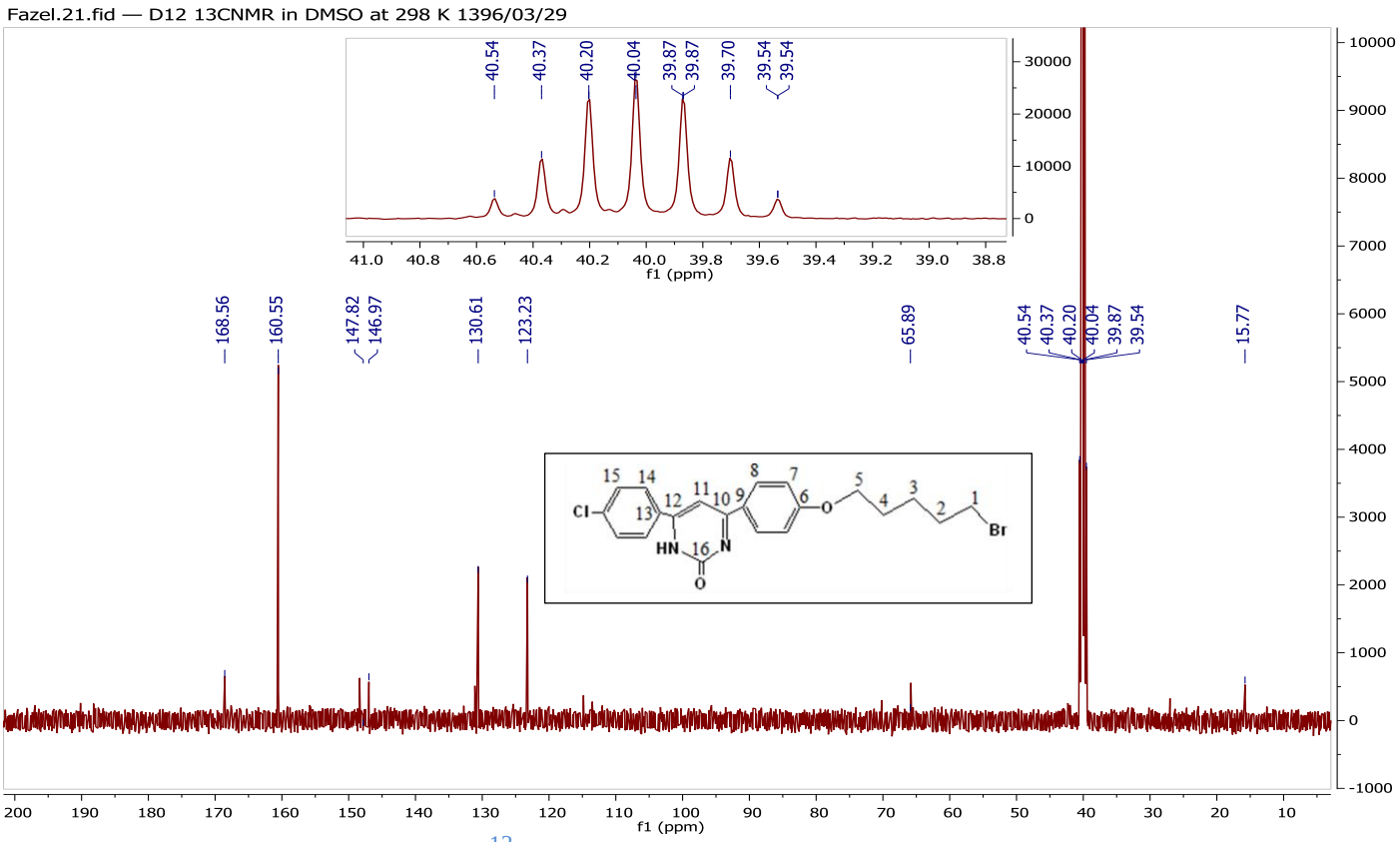


Figure (3-44): ^{13}C-NMR spectrum of compound (D12)

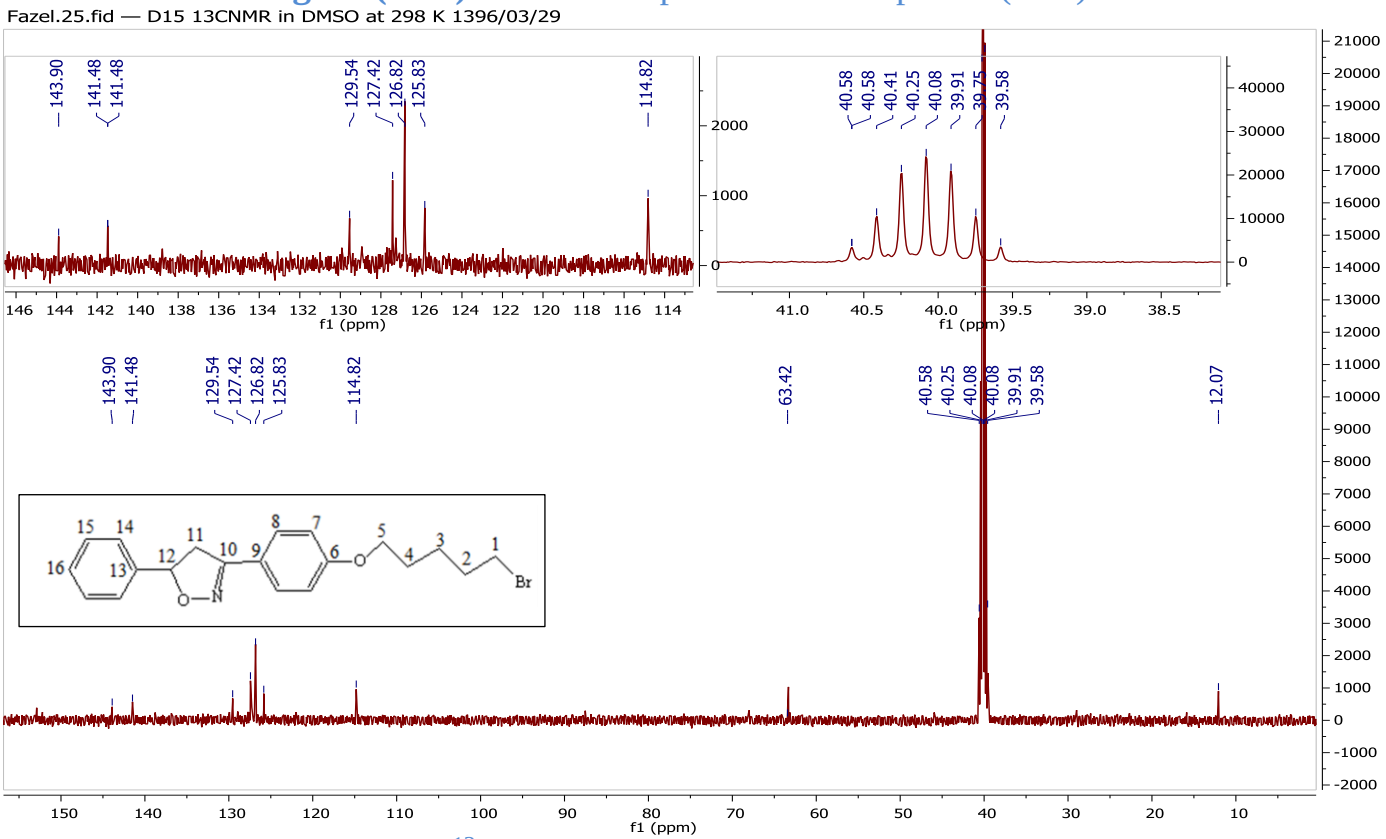


Figure (3-45): ^{13}C-NMR spectrum of compound (D15)

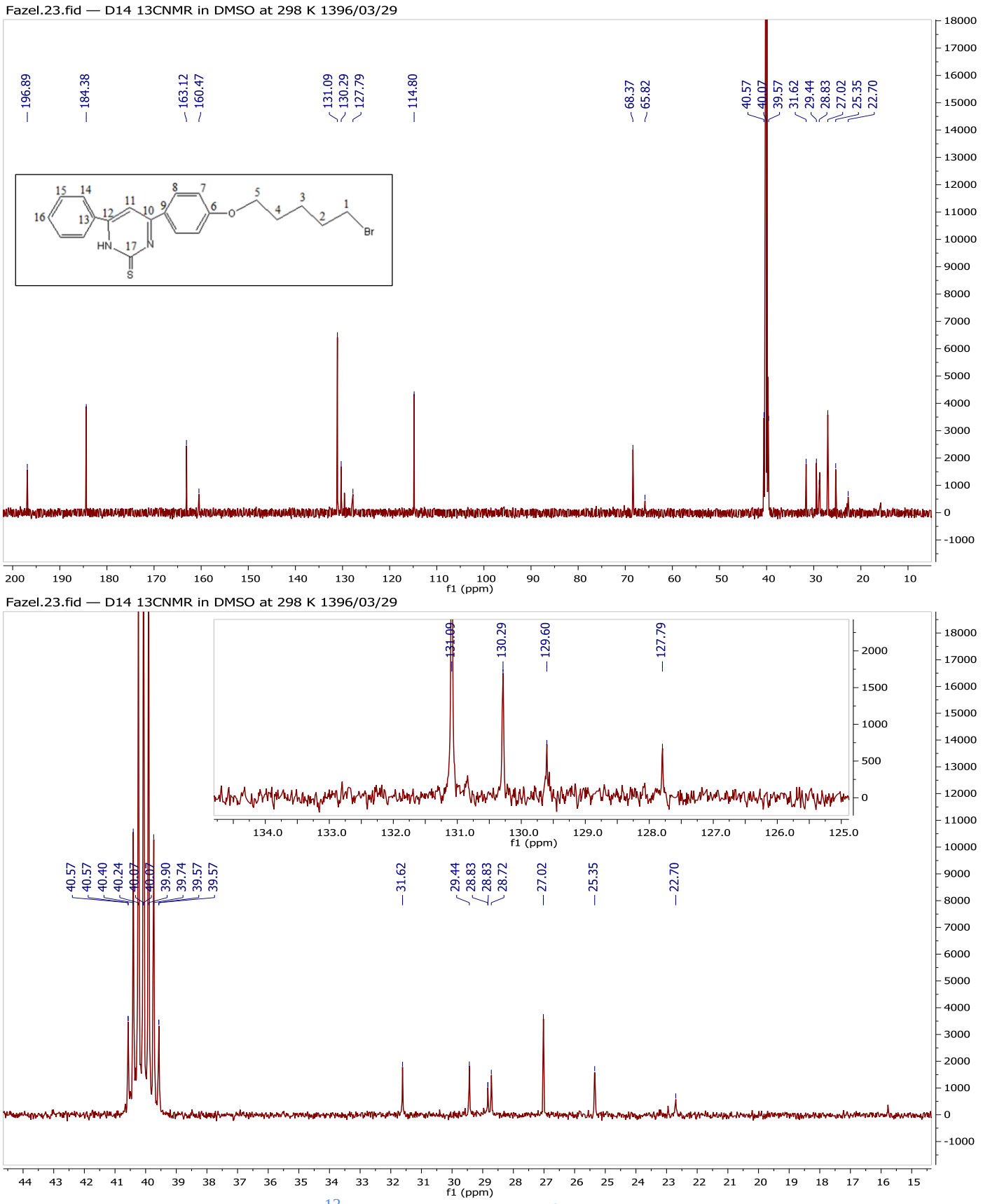


Figure (3-46): ^{13}C-NMR spectrum of compound (D14)

3.6. Weight loss measurements:

The prepared compounds **(D1- D20)** were used as inhibitors for the mild steel corrosion. To demonstrate the functionality of suggested inhibitors under the conditions prevailing in this study, weight loss measurements are tested the functional group of suggested inhibitors the values of rate of corrosion, surface coverage and inhibition efficiency from weight loss measurements at different concentrations of prepared compounds **(D1- D15** and **D16- D20)** after 24 hours immersion of mild steel in 1M H_2SO_4 at 30^{o}C are summarized in Table (3-12).

The rate of corrosion and inhibition efficiency of compounds **(D1- D20)** as a function of concentration are shown in Figures (3-54, 3-56, 3-58, 3-60), respectively. The results show that as the inhibitor concentration increases, the rate of corrosion decreases and the inhibition efficiency increases.

It can be concluded that these prepared compounds **(D1- D20)** act as corrosive inhibitor through adsorption on mild steel surface and formation of a protective layer between iron metal surface and the corrosive acidic media. The review of after effects of IE (%) in Table (3-12) demonstrates that the protection efficiency IE (%) increases with increasing the concentration of suggested inhibitors with the maximum inhibition efficiencies were mostly achieved at 10^{-2} M. These results could be explained by the effect of molecular structure of organic inhibitors **(D1- D20)** on inhibition efficiency, as well as adsorption process [52,53]. The surface protection of a metal surface depends upon how the inhibitor molecule will be adsorbed on this metal due to electronic density distribution (polarization) of the organic molecule [54]. The degree of surface coverage (θ) as function of concentration (C) of the inhibitor was studied graphically by fitting it to various adsorption isotherms to find the best adsorption isotherm. Langmuir adsorption isotherm was found to be the best description for organic inhibitors **(D1- D20)** for mild steel in 1M H_2SO_4. The

plot of (C/θ versus C) gave straight lines (Figure 3-55, 3-57,3-59, 3-61) with regression close to unity confirming that the adsorption of organic inhibitors **(D1- D20)** on the steel surface in 1M H_2SO_4 medium obeys the Langmuir adsorption isotherm. The data that obtained from Langmuir isotherm relationship (Eq. 2.3) have been used to calculate standard free energy of adsorption, ΔG^{o}_{ads} at 30◦C by using (Eq. 2.4). The calculated values of ΔG^{o}_{ads} over the temperature at 30◦C are recorded in Table (3-12). The negative values of ΔG°_{ads} indicate the spontaneous adsorption of inhibitors on the surface of steel surface [55, 56]. From the data of Table (3-12), ΔG°_{ads} values for organic inhibitors **(D1- D20)** are found to be in the ranges (-28 to -40) kJ mol^{-1}, indicating that adsorption process involving both physisorption and chemisorption [57-59].

The inhibition effects different concentrations of pyrazole, pyrimidine and isoxazole derivatives **(D1- D20)** on the reduction of corrosion of mild steel in 1M H_2SO_4 solution may be ascribed to the adsorption of these compounds at the metal surface at acidic solution. The basic types of interaction between an organic inhibitor and a metal surface are physisorption , chemisorption, or both. The adsorption of inhibitor is influenced by the nature of the metal, chemical structure of inhibitors, type of aggressive electrolyte, temperature, and the morphology of metal surface [60, 61]. The values of inhibition efficiency depend essentially on the electron density at the active center of the inhibitor molecule. The thermodynamic parameters showed that the adsorption of these inhibitors on the iron surface in 1M H_2SO_4 solution is both chemisorption and physisorption. Chemisorption of these inhibitors arises from the donor-acceptor interactions between the free electron pairs of heteroatoms and pi-electrons of multiple bonds as well as phenyl group and vacant d-orbital's of iron [62].

Table 3-9: Corrosion rate, inhibition efficiency, surface coverage (θ) and standard free energy of adsorption for mild steel in 1M H2SO4 by using weight loss measurements.

Concentration (M)	Corrosion rate ($mg.cm^{-2}.h^{-1}$)	IE%	Θ	$\Delta G°_{ads}$ ($kJ.mol^{-1}$)
Blank	1.342	-	-	-
(D1)				
5×10^{-4}	0.2179	83.8	0.838	-28.47 R^2=0.99
1×10^{-3}	0.1795	86.6	0.866	
5×10^{-3}	0.1191	91.1	0.911	
1×10^{-2}	0.0864	93.6	0.936	
(D2)				
5×10^{-4}	0.3580	73.3	0.733	-29.32 R^2=0.99
1×10^{-3}	0.1593	88.1	0.881	
5×10^{-3}	0.1191	91.1	0.911	
1×10^{-2}	0.0777	94.2	0.942	
(D3)				
5×10^{-4}	0.3398	74.7	0.747	-31.63 R^2=0.99
1×10^{-3}	0.1891	85.9	0.859	
5×10^{-3}	0.1238	90.8	0.908	
1×10^{-2}	0.0768	94.3	0.943	
(D4)				
5×10^{-4}	0.1593	88.1	0.881	-40.92 R^2=0.99
1×10^{-3}	0.1075	92.0	0.920	
5×10^{-3}	0.0864	93.6	0.936	
1×10^{-2}	0.0384	97.1	0.971	
(D5)				
5×10^{-4}	0.3398	74.7	0.747	-33.37 R^2=1
1×10^{-3}	0.1536	88.6	0.886	
5×10^{-3}	0.0681	94.9	0.949	
1×10^{-2}	0.0499	96.3	0.963	
(D6)				
5×10^{-4}	0.1449	89.2	0.892	-37.43 R^2=1
1×10^{-3}	0.1075	92.0	0.92	
5×10^{-3}	0.0960	92.8	0.928	
1×10^{-2}	0.0835	93.8	0.938	
(D7)				

5×10^{-4}	0.1718	87.2	0.872	-34.27 R^2=0.99
1×10^{-3}	0.1017	92.4	0.924	
5×10^{-3}	0.0700	94.8	0.948	
1×10^{-2}	0.0460	96.6	0.966	
(D8)				
5×10^{-4}	0.2140	84.0	0.84	-35.1256 R^2=0.99
1×10^{-3}	0.1526	88.6	0.886	
5×10^{-3}	0.1296	90.3	0.903	
1×10^{-2}	0.0576	95.7	0.957	
(D9)				
5×10^{-4}	0.1612	88	0.88	-34.27 R^2=0.99
1×10^{-3}	0.1372	89.8	0.898	
5×10^{-3}	0.1152	91.4	0.914	
1×10^{-2}	0.0796	94.1	0.941	
(D10)				
5×10^{-4}	0.1612	88.0	0.880	-33.37 R^2=0.99
1×10^{-3}	0.1296	90.3	0.903	
5×10^{-3}	0.0796	94.1	0.941	
1×10^{-2}	0.0307	97.7	0.977	
(D11)				
5×10^{-4}	0.1756	86.9	0.869	-40.46 R^2=0.99
1×10^{-3}	0.1257	90.6	0.906	
5×10^{-3}	0.1142	91.5	0.915	
1×10^{-2}	0.0844	93.7	0.937	
(D12)				
5×10^{-4}	0.1680	87.5	0.875	-34.66 R^2=0.99
1×10^{-3}	0.1123	91.6	0.916	
5×10^{-3}	0.1046	92.2	0.922	
1×10^{-2}	0.0499	96.3	0.963	
(C13)				
5×10^{-4}	0.2025	84.9	0.849	-34.27 R^2=1
1×10^{-3}	0.0960	92.8	0.928	
5×10^{-3}	0.0701	94.8	0.948	
1×10^{-2}	0.0489	96.4	0.964	
(C14)				

5×10^{-4}	0.1036	92.3	0.923	-33.94 R^2=0.99
1×10^{-3}	0.0931	93.1	0.931	
5×10^{-3}	0.0777	94.2	0.942	
1×10^{-2}	0.0268	98	0.98	
(D15)				
5×10^{-4}	0.4358	67.5	0.675	-29.88 R^2=0.99
1×10^{-3}	0.4224	68.5	0.685	
5×10^{-3}	0.2401	82.1	0.821	
1×10^{-2}	0.1372	89.8	0.898	
D16				
5×10^{-4}	0.3177	76.3	0.763	-33.37 R^2=0.99
1×10^{-3}	0.1977	85.3	0.853	
5×10^{-3}	0.1862	86.1	0.861	
1×10^{-2}	0.1315	90.2	0.902	
(D17)				
5×10^{-4}	0.3331	75.2	0.752	-31.63 R^2=0.99
1×10^{-3}	0.2601	80.6	0.806	
5×10^{-3}	0.2380	82.3	0.823	
1×10^{-2}	0.1708	87.3	0.873	
(D18)				
5×10^{-4}	0.2534	81.1	0.811	-33.37 R^2=0.99
1×10^{-3}	0.1891	85.9	0.859	
5×10^{-3}	0.1334	90.1	0.901	
1×10^{-2}	0.1036	92.3	0.923	
(D19)				
5×10^{-4}	0.0796	94.1	0.941	-37.43 R^2=1
1×10^{-3}	0.0499	96.3	0.963	
5×10^{-3}	0.0384	97.1	0.971	
1×10^{-2}	0.0345	97.4	0.974	
(D20)				
5×10^{-4}	0.4550	66.1	0.661	-28.86 R^2=0.99
1×10^{-3}	0.4416	67.1	0.671	
5×10^{-3}	0.2688	80.0	0.8	
1×10^{-2}	0.1564	88.3	0.883	

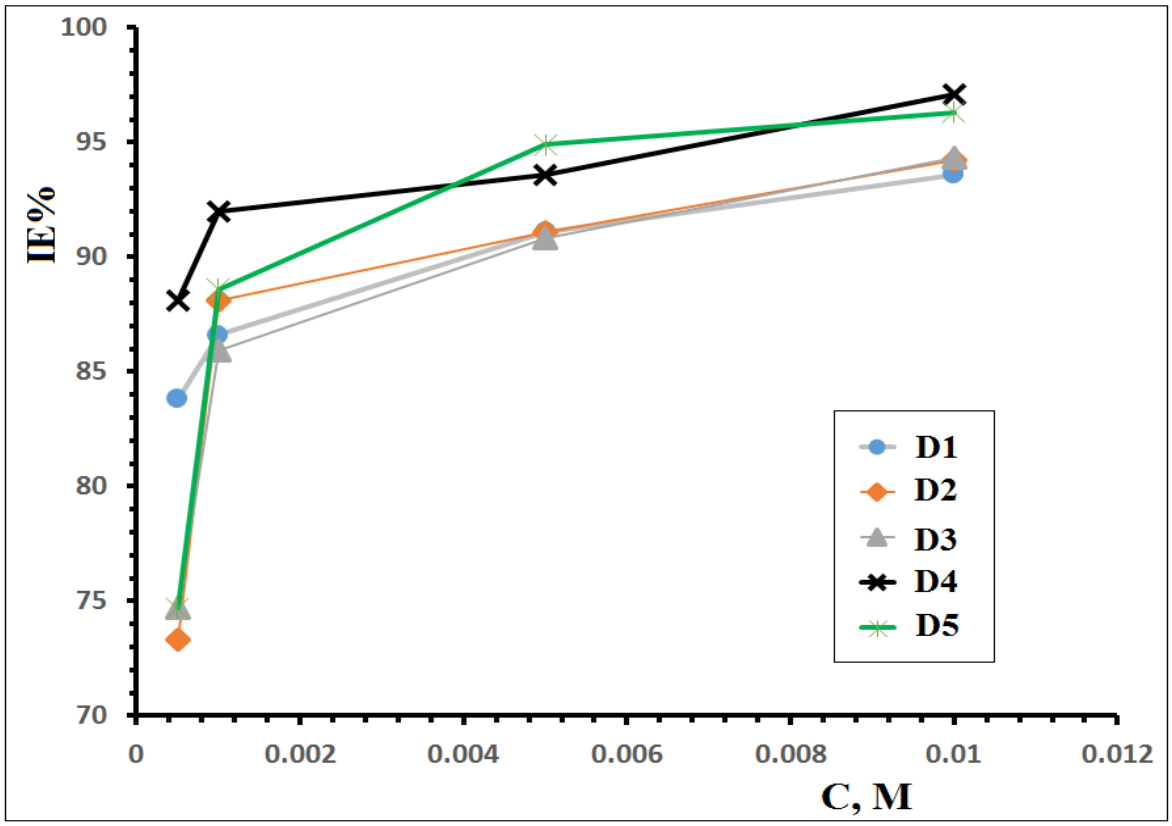


Figure (3- 47): Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M H_2SO_4 at 30°C for suggested inhibitors (**D1- D5**).

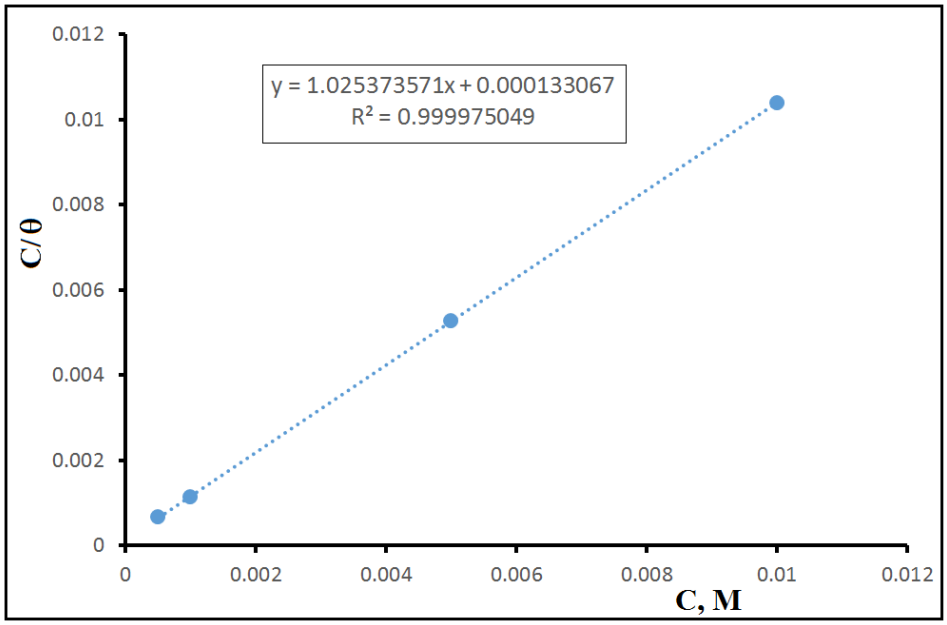


Figure (3-48): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (**D5**).

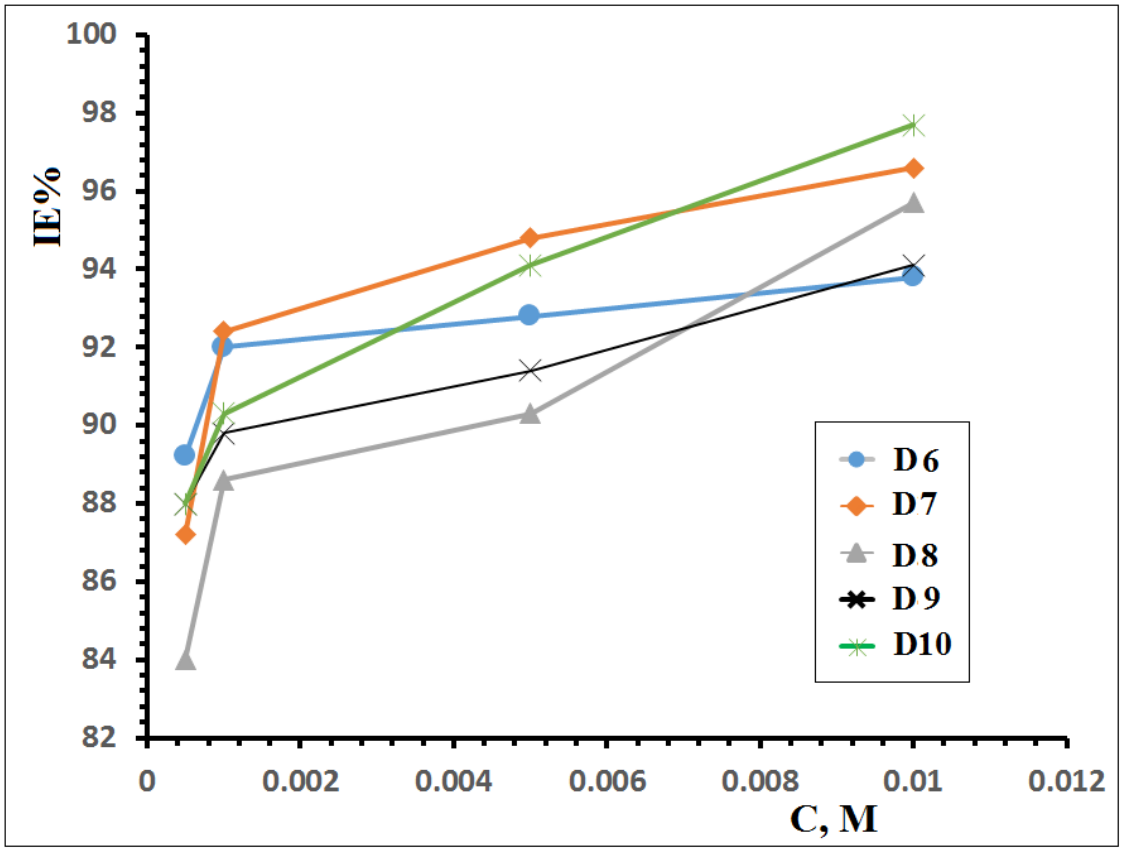


Figure (3-49): Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M H_2SO_4 at 30°C for suggested inhibitors (**D5- D10**).

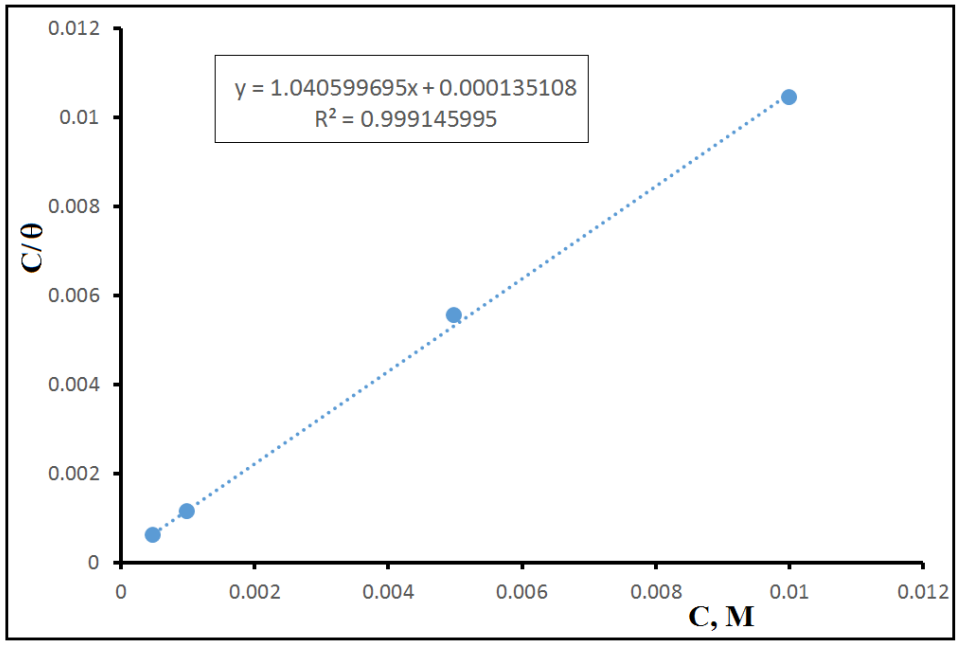


Figure (3-50): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (**D8**).

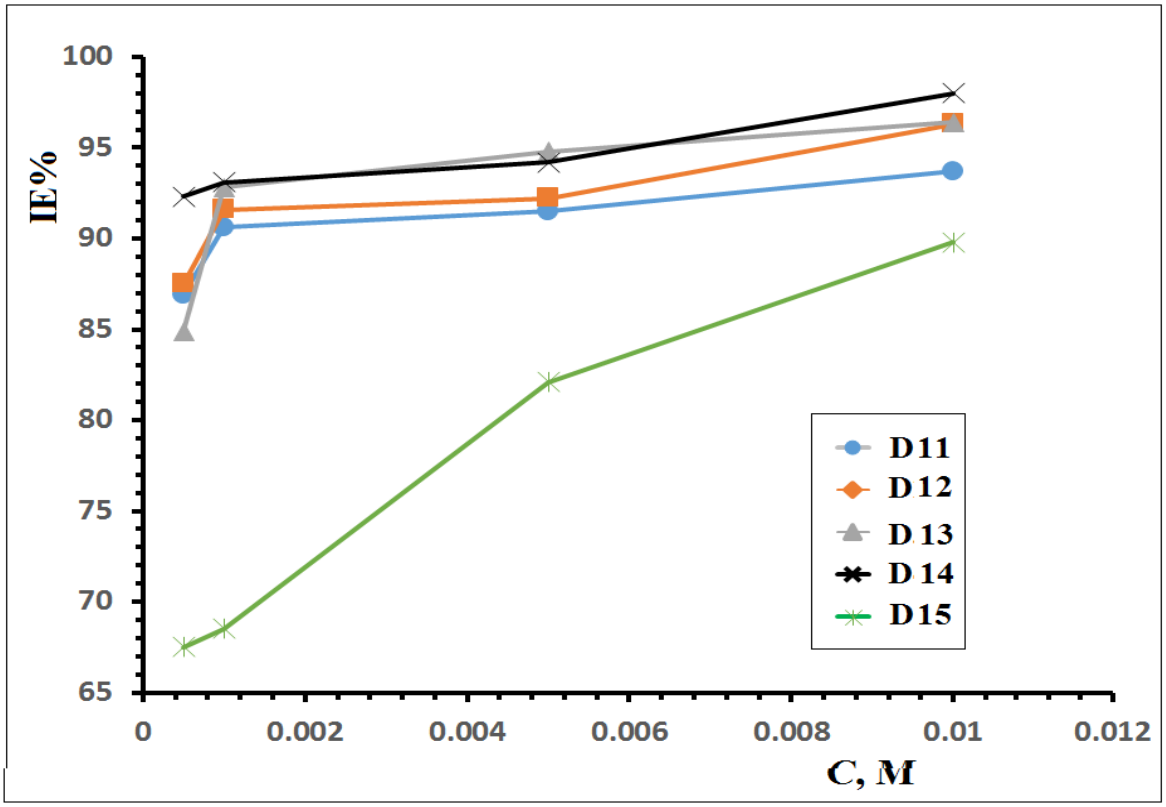


Figure (3-51): Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M H_2SO_4 at 30°C for suggested inhibitors (**D10- D15**).

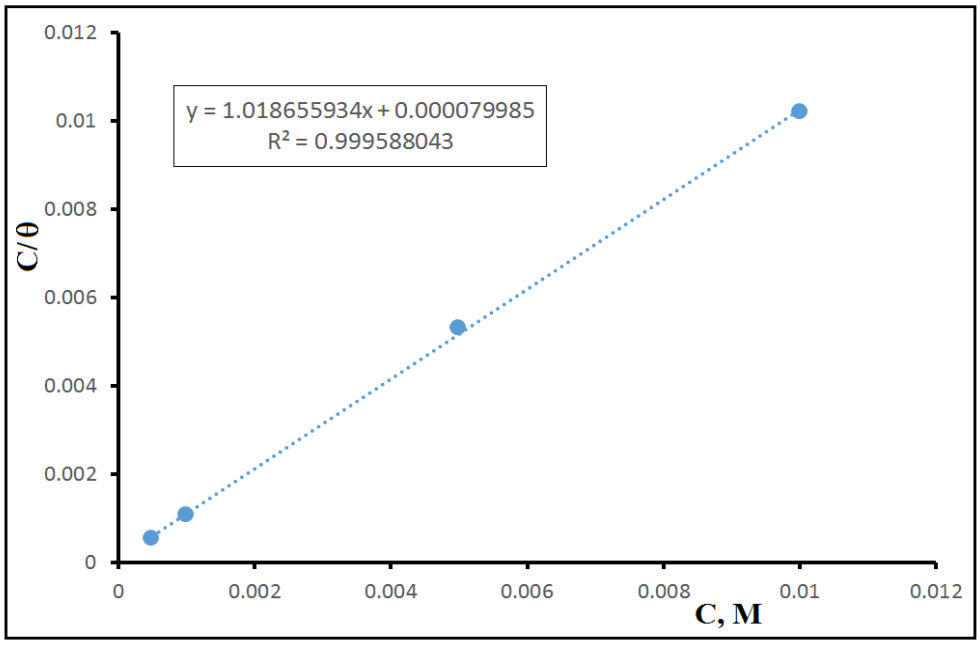


Figure (3-52): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (D14).

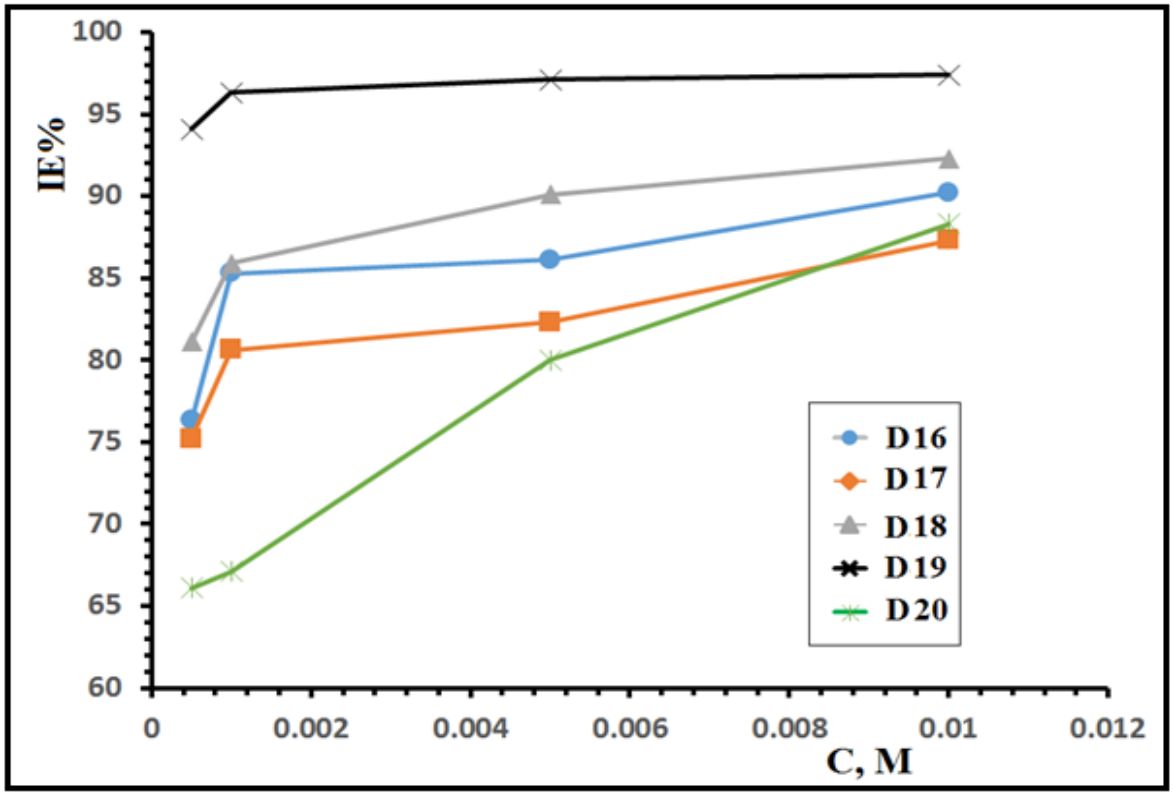


Figure (3-53): Effect of inhibitor concentrations on the inhibition efficiency for mild steel 1M H_2SO_4 at 30°C for suggested inhibitors (**D16- D20**).

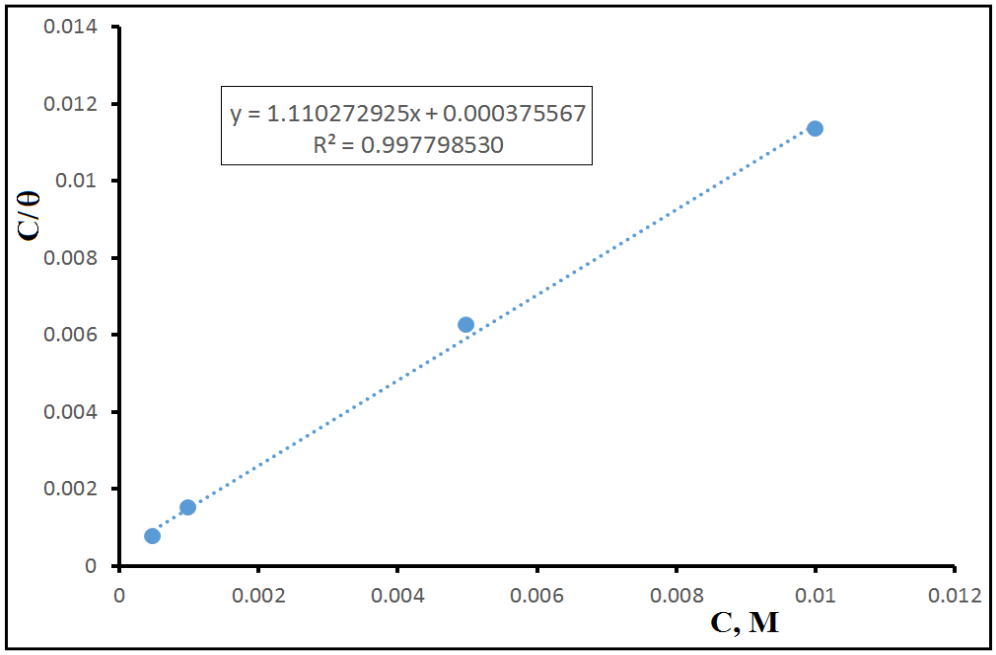


Figure (3-54): Langmuir adsorption isotherm plot for mild steel in 1M H_2SO_4 solution in the presence of various concentrations of inhibitor (**D20**).

3.7. Conclusion:

A series of heterocyclic compounds derivatives (pyrazole, pyrimidine and isoxazole) were synthesized, their structures were elucidated and tested as organic corrosion inhibitors for mild steel in acidic solution. Weight loss measurements were used to test the prepared heterocyclic derivatives. The results of weight loss tests revealed that prepared derivatives had excellent corrosion efficiencies especially at 0.01 M. In addition, the thermodynamic data showed spontaneous adsorption of organic corrosion inhibitors onto the surface of steel surface, as well as, adsorption process was involved both physisorption and chemisorption mechanisms.

3.8. Future Work:

1. Preparation of new organic compounds contains heterocyclic fragments containing N, S and O atoms.
2. Weight loss measurements are applied to study the inhibition efficiency of prepared compounds for mild steel in acidic media.

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ملخص

في هذه الدراسة تم تحضير بعض المركبات حلقية غير متجانسة من خلال عدة خطوات كالأتي :

اولاً : تحضير مركب الايثر (B1) من تفاعل (4-هايدروكسي فينون) مع الاكيل الهاليد (1و5- بومو بروبان) بوجود كاربونات البوتاسيوم والاسيتون .

ثانياً: تحضير مركب الايثر (B2) من تفاعل (4-هايدروكسي فينون) مع الاكيل الهاليد (4-برومو فنلسي برومايد) بوجود كاربونات البوتاسيوم والاسيتون .

ثالثاً: تحضير مشتقات الجالكونات (C1-C6) من خلال تفاعل تكاثف الالدول بين المركبات (B1 وB2) والالديهايدات المختلفة بوجود وسط قاعدي وتحريك مستمر بدرجات حرارة منخفضة .

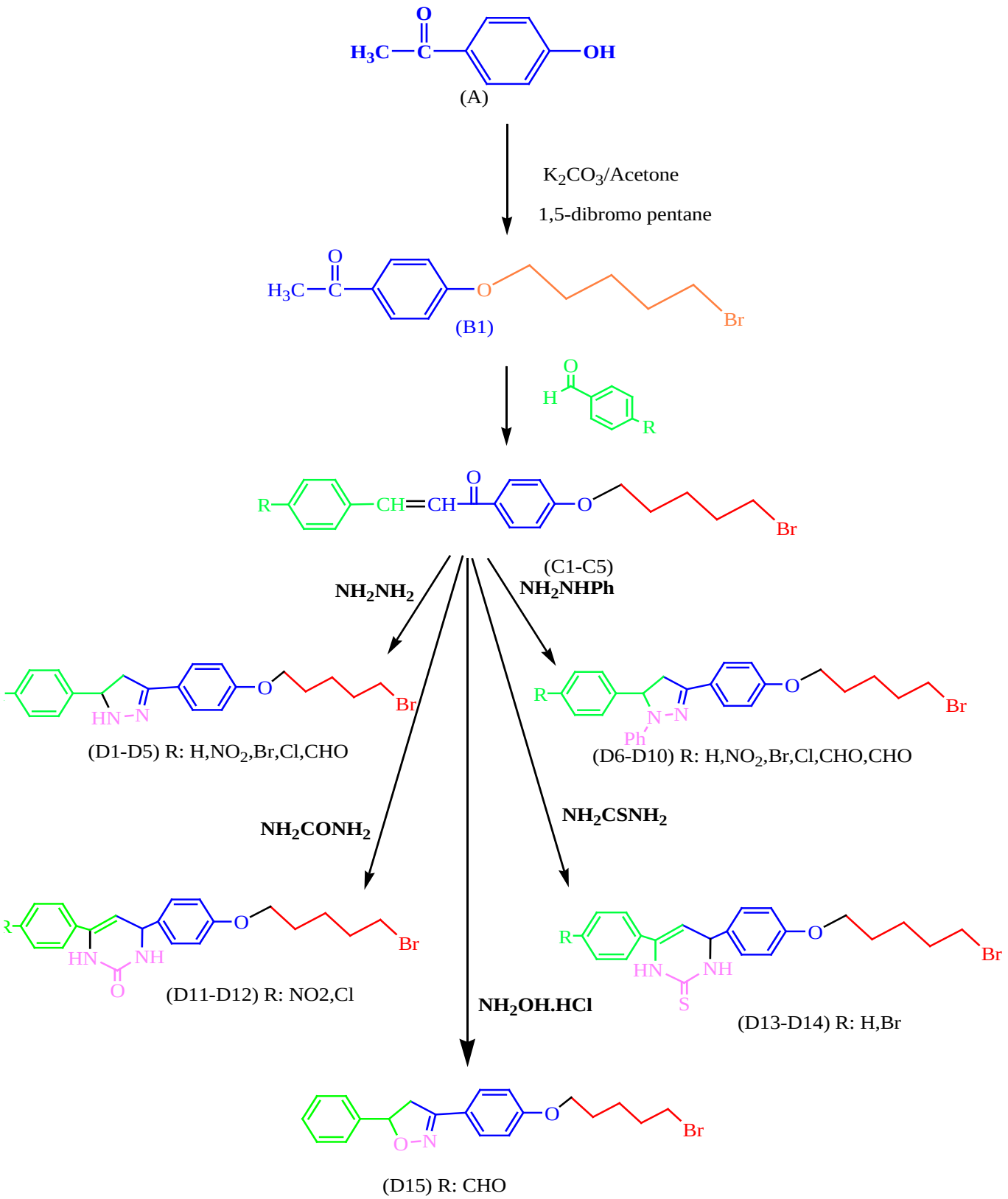
رابعاً: تحضير مشتقات البيرازول (D1-D10) و (D16- D17) من خلا تفاعل الجالكونات (C1-C6) مع هيدارزين معين (هيدرازين هتدريت و الفنل هيدرازين)

خامساً: تحضير مشتقات البرمدين (D11-D14) و (D18- D19) من خلا تفاعل الجالكونات (C1-C6) مع اليوريا والثايويوريا

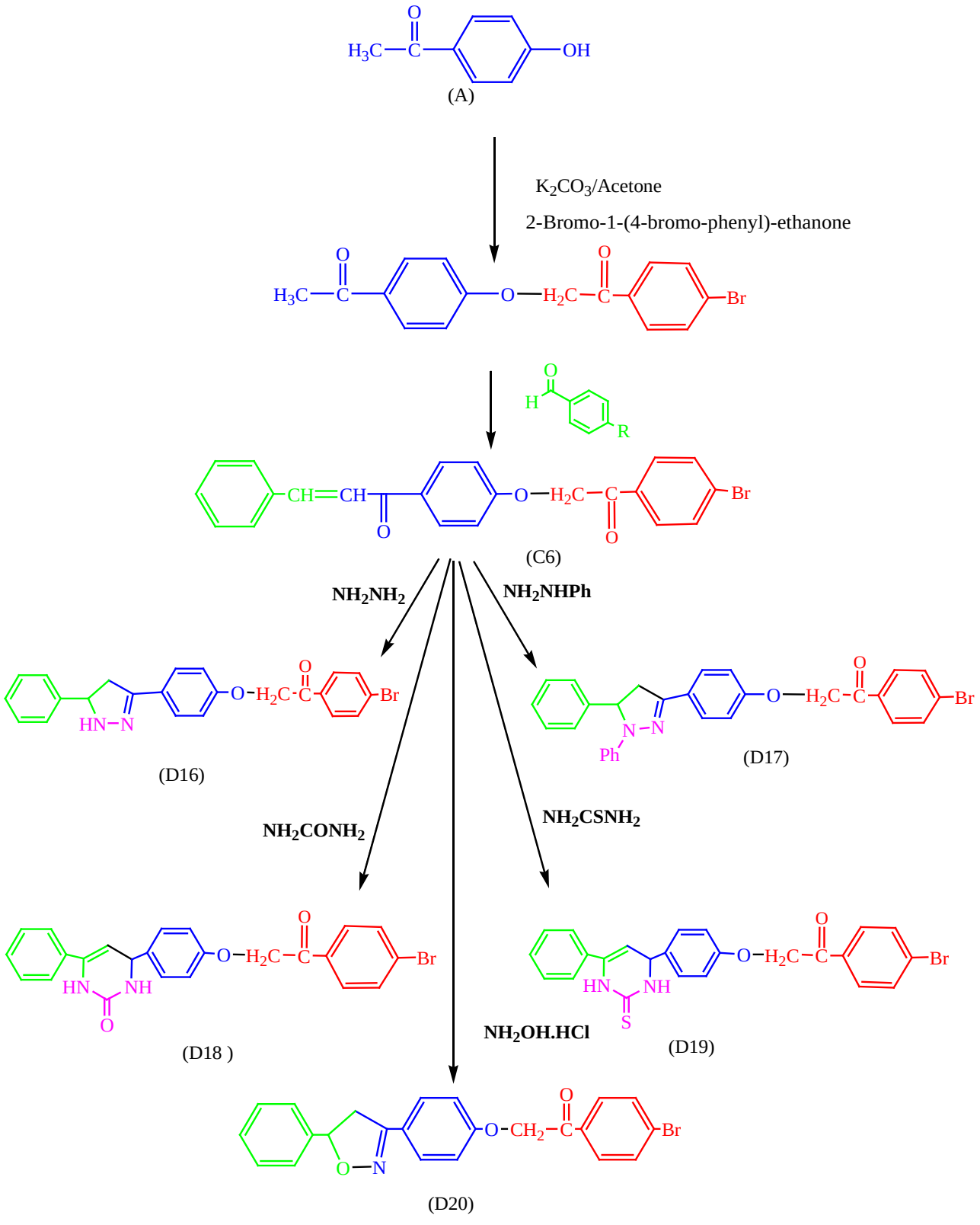
سادساً: تحضير مشتقات الازوكسازول (D15) و (D20) من خلا تفاعل الجالكونات (C5) و (C6) هيدروكسيد الامين .

تم تشخيص المركبات اعلاه من خلال قياس درجات الانصهار وطيف الاشعة فوق الحمراء وقيا سات بروتون الرنين المغناطيسي النووي وتقني تحليل النسبة المؤية لعاصر الكاربون والهيدروجين والنتروجين والكبريت في المركبات .

المركبات العضوية **(D1-D20)** تم استخدامها كمثبطات تاكل الحديد الصلب في محلول مائي لحامض الكبريتيك بتركيز امولاري ولمدة غمر 24 ساعة في درجة حرارة 30 درحة مؤية ، وتم استخدام طريقة فقدان الوزن لأختبار كفائة التثبيط للمركبات اعلاه . تم حساب قيم التغير في طاقة كبس الحرة للأمتزاز . وقدتم الحصول على معلومات للتنبؤ بالتفاعل الحاصل بين جزيئات المركبات العضوية وسطخ المعدن المستخدمة كمثبطات لتأكل سطح المعدن .



مخطط1: الخطوات الكيميائية لتحضير المركبات (B1),(C1-C5),(D1-D15)



مخطط2: الخطوات الكيميائية لتحضير المركبات (B2),(C6),(D16-D20)

جمهورية العراق

وزارة التعليم العالي والبحث العلمي

كليه العلوم / جامعة النهرين

قسم الكيمياء

تحضيرو تشخيص مركبات حلقية غير متجانسة كمثبطات للتآكل في الوسط الحامضي

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

من قبل

عقيل فاضل مطلك

بكلوريوس 2009 (جامعة النهرين)

بأشراف

أ. د.مهدي صالح شهاب

1439 2018