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and Scientific Research

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College of Science

Department of Chemistry

Synthesis and Characterization of Seven Membered Heterocyclic Derivatives from Chalcone Compounds.

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In Partial Fulfillment of the Requirements For The

Degree Of Master In Organic Chemistry

By

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B. Sc. Chemistry

University of Anbar- 2018

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2021 A.D 1443 A.H

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Synthesis and Characterization of Seven Membered Heterocyclic Derivatives from Chalcone Compounds

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Dedication

I would like to dedicate this work to:

The best of the wilderness and the example of Islam... Our Prophet Muhammad, may Allah bless him and grant him peace, peace be upon him.

Whoever drinks an empty cup to give me a drop of love.

Who gave his life to give us a moment of happiness.

Those who harvested thorns from my path to pave the path of knowledge for me

The big heart.....my father.

The meaning of love and the meaning of tenderness

For the smile of life and the secret of existence, for whom her supplication was the secret of my success and tenderness as a wound balm for my dear beloved ...my beloved mother.

Those who supported me in my life and the sweetness of my eyes, from which I derive hope and depend on it, and I feel keen to continue my academic career.... my dear husband.

Who gave me his knowledge and guided me to the path of knowledge... my supervisor...

My companions on the road and my support in times of adversity... my brothers and sister.

Those with whom I spent the best years of my life....my friends and colleagues.

Those who illuminate the darkness of ignorance with the light of knowledge....my teachers

Hanan

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Praise be to Allah, Lord of the Worlds, and prayers and peace be upon the Master of the Messengers, Muhammad, the Seal of the Prophets, and upon all his family and companions.

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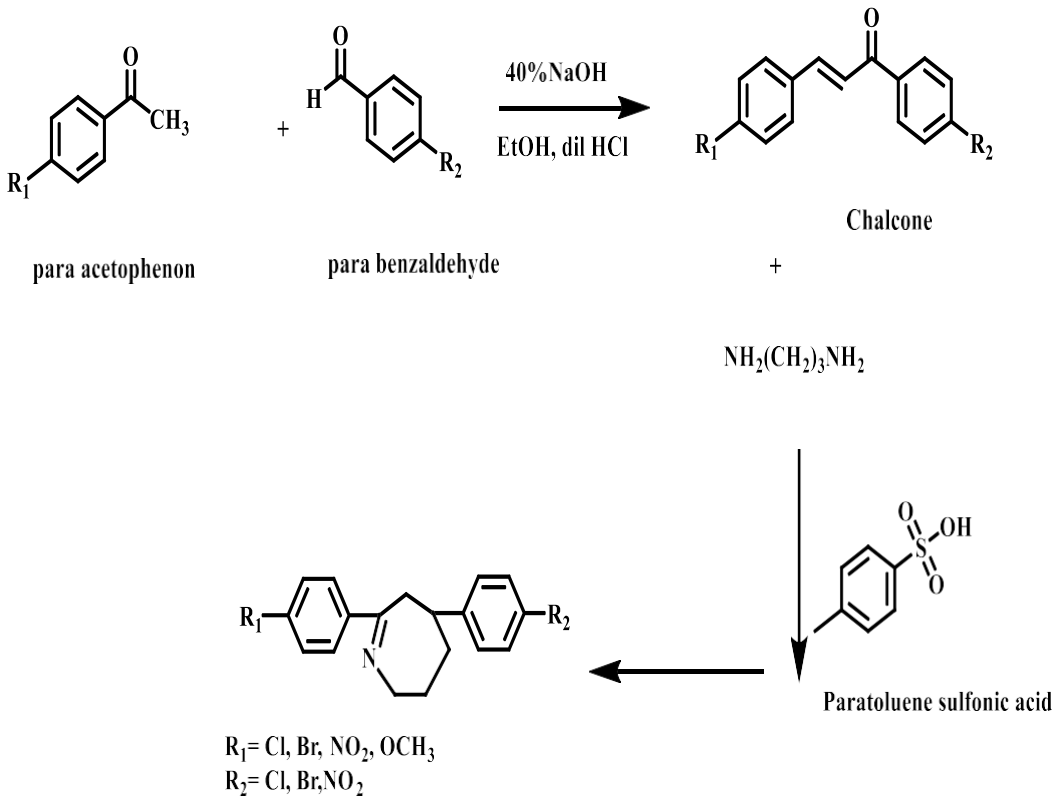
Abstract

The aim is to synthesize and characterized heterocyclic compounds and study their thermal stability as a step for future work. A preparation of chalcones synthesized warred out by mixing equal acetophenone with aldehydes. The second step (synthesized of 7- rings) was performed by reacting the chalcones with aliphatic diamines .

The results showed obtaining of 7- membered heterocyclic compounds, these compounds are charted using FT-IR, 1H-NMR, 13C-NMR, and TGA (thermal stability).

The TGA analysis shows the thermal stability of compound TGA peak appeared at a temperature certain this is an indication that the compound is thermally stable at this temperature.



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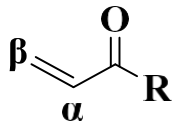
LIST OF ABBREVIATIONS

FT-IR	Fourier- transform Infrared
NMR	Nuclear Magnetic Resonance
ppm	part per million
s	Singlet
d	doublet
t	Triplet
M	multiplet
TGA	Thermogravimetric Analyzer
DTA	Differential Thermal Analysis
DSC	Differential Scanning Calorimetry
HIV	Human immunodeficiency virus
ABNO	Azabicyclo nonane-N-oxyl
DCM	Dilated Cardiomyopathy
DMF	Dimethyl formamide
TFA	Trade Facilitation Agreement
DNA	Deoxy nucleic Acid
RNA	Ribo nucleic Acid

1. Introduction.

1.1 Chalcone Compounds:

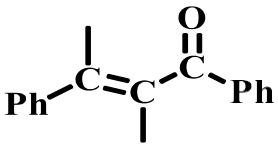
In chemical and biological chemistry, the carbonyl group is one of the most significant functional groups. Chalcone compounds are made when a carbonyl group (C=O) is paired with another functional group, especially the double bond (C=C), as in unsaturated alpha and beta carbonyl compounds[1, 2] (Figure 1.1).



(1)

Figure1.1: Group the general formula for the alpha-beta-unsaturated carbonyl.

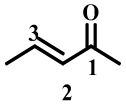
Chalcone, also known as benzylideneacetophenone or 1,3-diphenyl-2-propene-1-one, is a scaffold that consists of two aromatic rings connected by a three-carbon of unsaturated carbonyl bridge. It is often referred to as a natural product because it can be found in nature in a variety of free complex, and hybrid forms. In the nineteenth century, Kostanecki and Tambor synthesized a series of natural chromophoric products and named the term "Chalcone". The Chalcone scaffold is an open-chain intermediate in the aurone synthesis and serves as a precursor for flavonoids and isoflavonoids. In the presence of acid or base, Chalcones and flavanones are isomeric and readily interconvert [3] (Figure1.2).



(2)

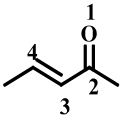
Figure1.2: compound(2).

The chemistry of Chalcones has remained attractive to researchers in the twenty-first century due to its simple chemistry, ease of synthesis, a large number of replaceable hydrogen to yield a large number of derivatives, and a variety of promising biological activities such as anti-diabetic, anti-neoplastic, antihypertensive, anti-retroviral, anti-inflammatory, anti-histaminic, anti-oxidant, anti-malarial, and so on [4, 5] (Figure1.3).



(3)

3,4-dimethylpent-3-en-2-one



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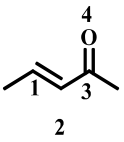
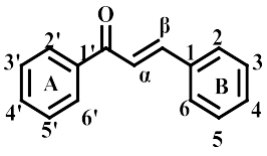
3,4-dimethylpent-3-en-2-one



(5)

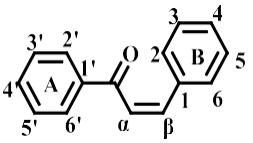
3,4-dimethylpent-3-en-2-one



(6)

(*E*)-chalcone

1-trans(E)



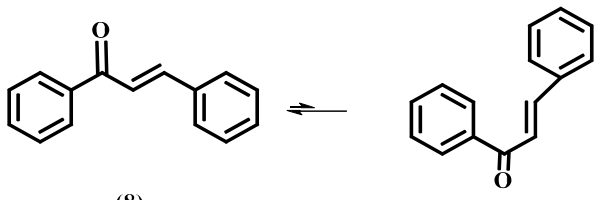
(7)

(*Z*)-chalcone

2-cis(Z)

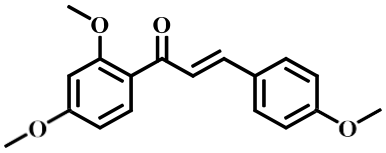
Figure1.3: Scaffold structural and numerical representations of Chalcone

The word "Chalcone" comes from the Greek word "chaos," which means "chalk." “Bronze,” is a term that refers to the colors of most natural objects. Chalcone compounds share a chemical structure. Chalconoid is a scaffold made up of 1, 3-diaryl-2-propen-1-one. There are trans and cis isomers of this substance. The trans isomer is more potent. It shows a thermodynamically more stable system[6] (Figure1.4).



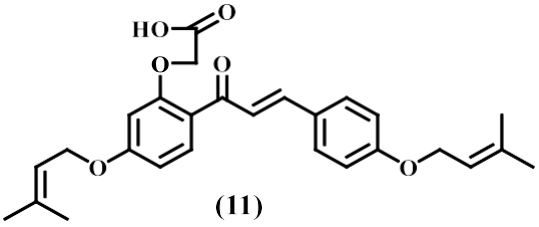
(8) (9)

(E)-chalcone



(10)

(*E*)-1-(2,4-dimethoxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one



(11)

(*E*)-2-(5-((3-methylbut-2-en-1-yl)oxy)-2-(3-(4-((3-methylbut-2-en-1-yl)oxy)phenyl)acryloyl)phenoxy)acetic acid

Figure1.4: Drugs Chalcone structures and two clinically approved Chalcone-based.

Alpha, beta-unsaturated carbonyl molecules are also found in diarylidene compounds. Crossed-aldol condensation using substituted aldehydes and acetone or any ketone molecule with two hydrogen atoms (alpha) acid is used to make these chemicals [7].

1.2. The most common ways to make Chalcone:

1.2.1. Synthesis in basic solution

Claisen-Schmidt condensation, a mixed aldol condensation in which aromatic aldehydes combine with aromatic ketones in the presence of a base (pyridine or piperidine) to generate aldehydes or alpha-beta unsaturated ketones,can be used to make Chalcones and their replacements[8, 9](Figure1.5).

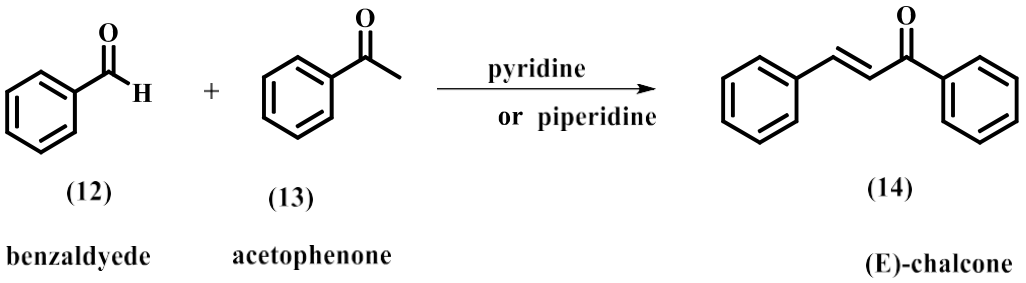


Figure 1.5: Preparing the Chalcone from the base

1.2.2. Preparation Chalcone in acid solution.

If an alkaline media is unavailable, alpha, beta-unsaturated carbonyl compounds, including Chalcones, Can be produced in an acidic medium. The following compound can be made in the presence of concentrated sulfuric acid [10, 11] (Figure 1.6).

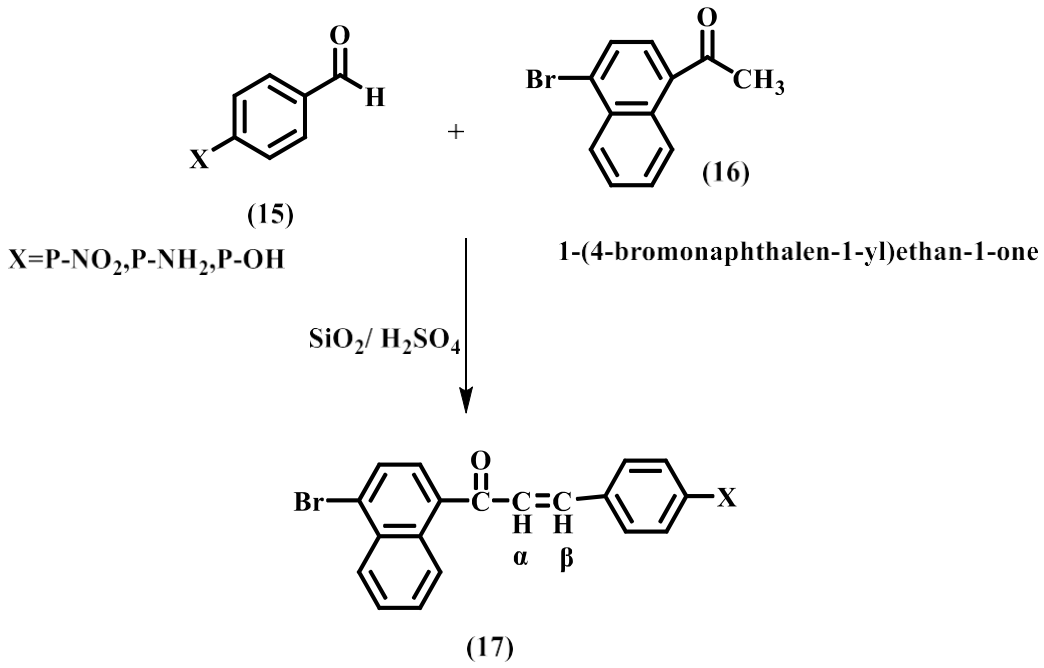


Figure 1.6: Chalcone Preparation in acid solution

1.3. Methods Preparation for Chalcones.

1.3.1. Coupling reaction.

A coupling reaction was used to perform several organic syntheses involving the synthesis of Chalcones. Covalent bonds between C and C-heteroatoms were formed via oxidative addition. Elimination of transmetalation is made by reductive transmetalation Sonogashira coupling, propargyl alcohols and aryl halide as reactants, catalyst PdCl2 (PPh3)2, yield (percentage) 57-98 [12] (Figure 1.7).

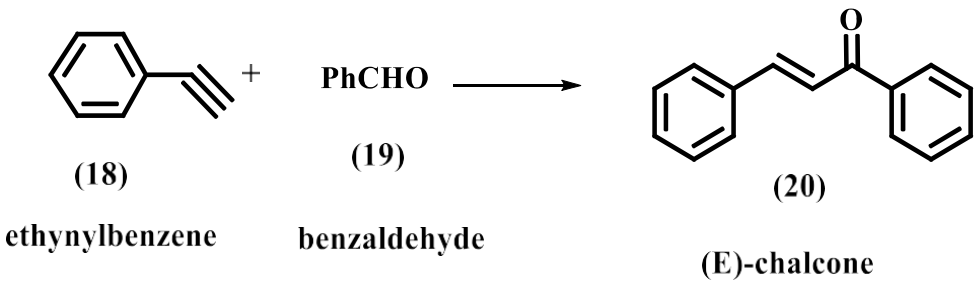
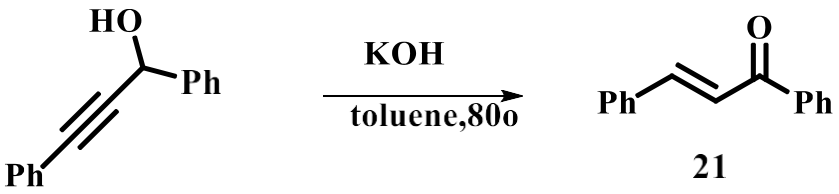


Figure 1.7: Coupling Reactions.

1.3.2. Rearrangement of Meyer-Schuster

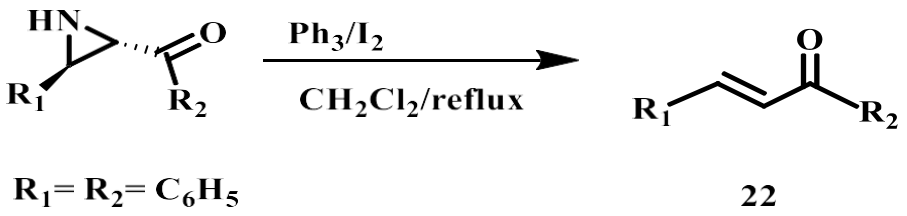
In recent decades, Mayer-Schuster rearrangement has attracted a lot of attention as a way to synthesize Chalcones from various sources. Propargyl alcohol, and propargyl acetate are examples of reactants, as well as siloxypropyne, which have various mechanistic arrangements compound(21). Hydroxyl's quick 1, 3-shift Propargylic alcohols have a unique functional group. From a Rupe reorganization, It used a variety of bases, including trimethylamine and KOH, as well as a catalyst [13] (Scheme1.1)



Scheme1.1: Compound (21).

1.3.3. Aziridine Deamination

Reaction with both cis- and trans-1-benzyl-2-benzoyl-3-aryl Aziridines gave the corresponding trans-alkenes [14, 15] (Scheme1.2).



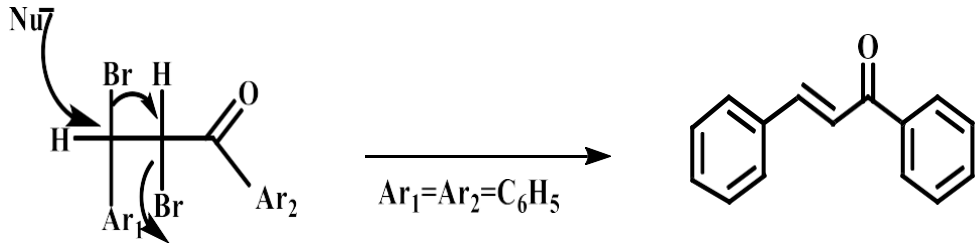
$R_1 = R_2 = C_6H_5$ **22**

Scheme1.2: Deamination of Aziridine.

1.3.4. Vicinal Dibromides Debromination.

Bromine classes removed the formation of 2, 3-dibromo-1,3-diphenylpropan-1-one from neighboring carbons which was demonstrated using a variety of catalysts, including, $BiCl_3$ Compoud, $BiCl_3$ compound is an inexpensive, non-toxic, water-resistant, and environmentally[16, 17]

Debromination of VIC-bromides results in the formation of Chalcone unsaturated compounds of Hantzsch ester and to achieve an 80 percent yield[18, 19] (Figure 1.8).

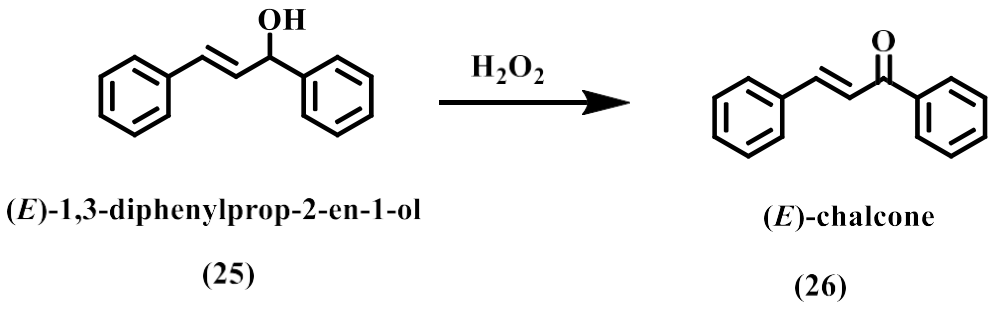


23 **24**

Figure 1.8: Debromination of vic-bromides.

1.3.5. Oxidation of Benzylic Alcohols.

The conversion of benzylic alcohols into the corresponding ketone in the synthesis of Chalcone was also investigated. An oxidant such as hydrogen peroxide must be present (Figure 1.9) [20]. The catalytic alteration was performed in a novel way. For example, 9-azabicyclo [3.3.1] nonane-N-oxyl (ABNO) was obtained by oxidation of benzylic alcohols [21]. KBr/O_3, TEMPO 99 percent yield [22].



(*E*)-1,3-diphenylprop-2-en-1-ol

(25)

(*E*)-chalcone

(26)

Figure 1.9: Oxidation of benzylic alcohol.

1.3.6. Wittig reaction

Is a chemical reaction that produces an alkene by combining an aldehyde or ketone with triphenylphosphonium yeild and the oxide of triphenylphosphine. Several changes have been made. Water, for example, has been documented in the Wittig reaction [23]. Phosphorus was substituted with arsenic, tellurium, and other elements in a previous analysis or antimony because their oxides quickly reduced due to bond strength. The major side effects are high toxicity and carcinogenicity of these compounds (29) [24] (Figure 1.10).

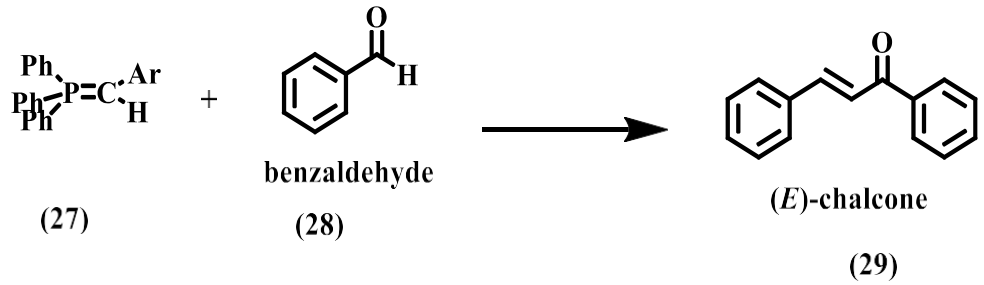


Figure 1.10: Wittig reaction

1.3.7. Claisen-Schmidt reactions or Condensation.

In general, Chalcones are made by base-catalyzed or acid-catalyzed Clausen-Schmidt condensation of aldehyde and ketone (Figure1.11) followed by dehydration to generate Chalcones [25].

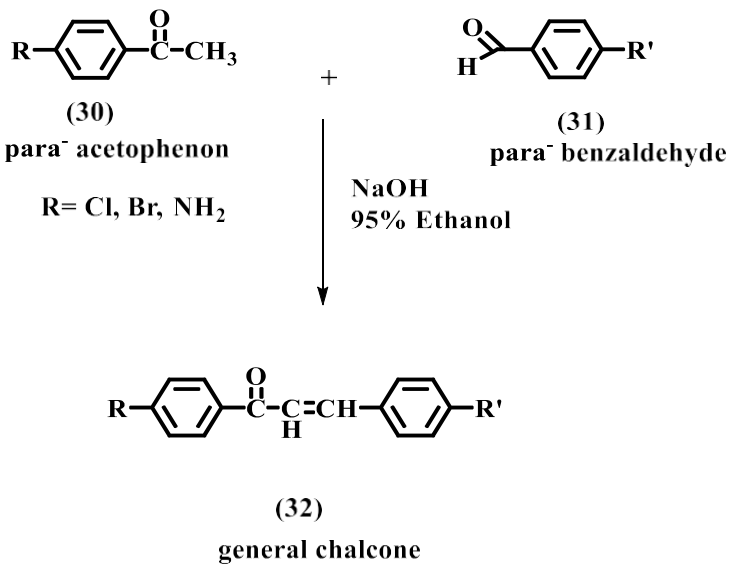


Figure1.11: Synthesis of Chalcones from Claisen-Schmidt reaction.

The synthesis of Chalcone derivatives is a simple condensation of acetophenone and aldehyde derivatives in the presence of acid or base catalysts in polar solvents at room temperature for several hours [26] (Figure1.12).

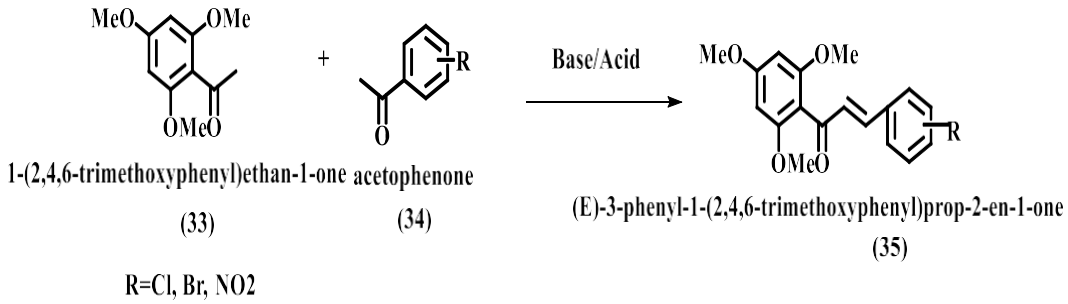
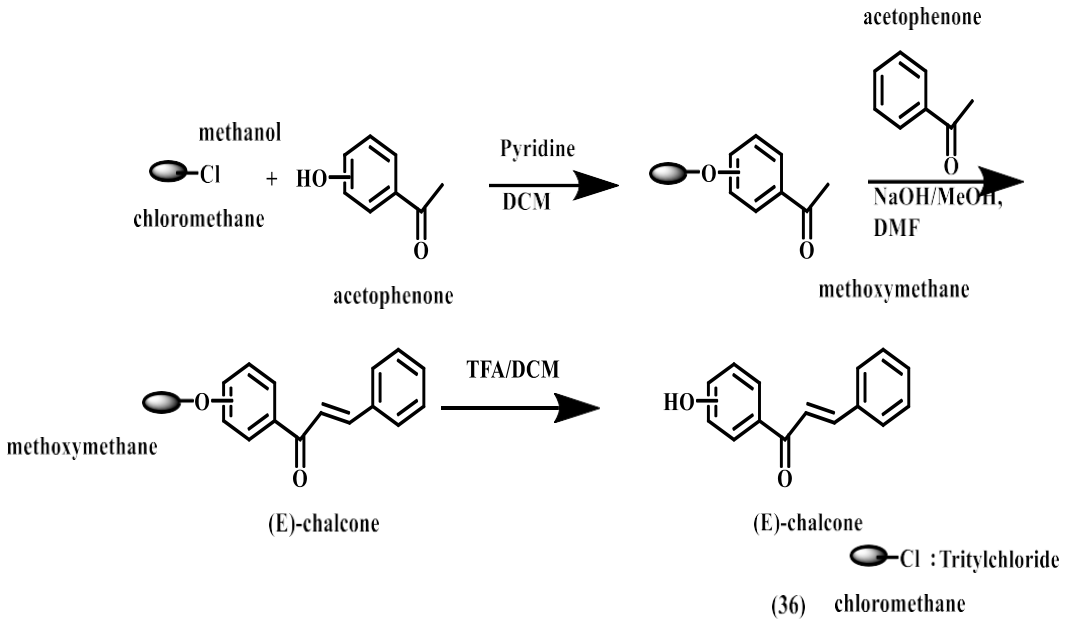


Figure1.12: Claisen–Schmidt reaction using a base/acid catalyst

The acetophenone derivative was first attached to the resin and then treated with benzaldehyde derivatives in this solid-phase condensation procedure. By the end of the process, the Chalcones were free of the resin. Using trifluoroacetic acid as a treatment [27] (Scheme1.3).



Scheme1.3: Compounds(36).

1.3.8. Aldol Reaction.

In basic media, the Aldol Reaction produced Chalcones by reacting ketones with aromatic aldehydes by combining ketones with ethanol with aromatic aldehyde[9, 28] (Figure1.13).

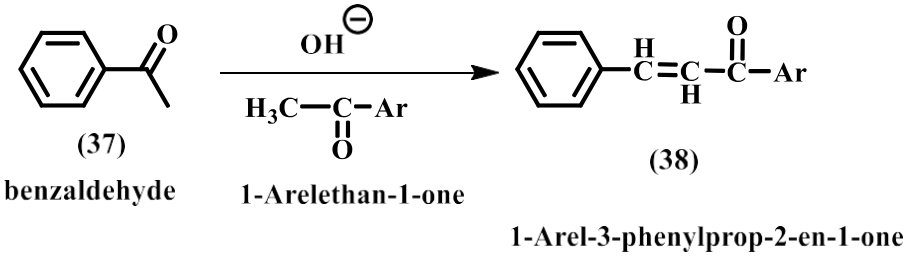


Figure1.13: General Aldol Reaction.

1.4 Chemical and physical characteristics of Chalcone

Chalcones can be found in all areas of the plant kingdom, including leaves, fruits, roots, stems, and flowers. Natural Chalcones are usually crystalline solids that come in a variety of colors, such as yellow, orange, and brown. Relative flavonoids and isoflavonoids are less stable than Chalcones. Alcohols, aqueous acidic and alkaline solutions, and alcohols are all good solvent sources of Chalcones. They turn a bright crimson or orange color in alkaline solutions acetone, chloroform, and dichloromethane, as well as organic solvents [27].

1.5. Reaction of Chalcone

1.5.1. Friedel–Crafts acylation:

Graft, Fridel $AlCl_3$ (aluminum chloride) is used to synthesis Chalcons[9] (Figure1.14).

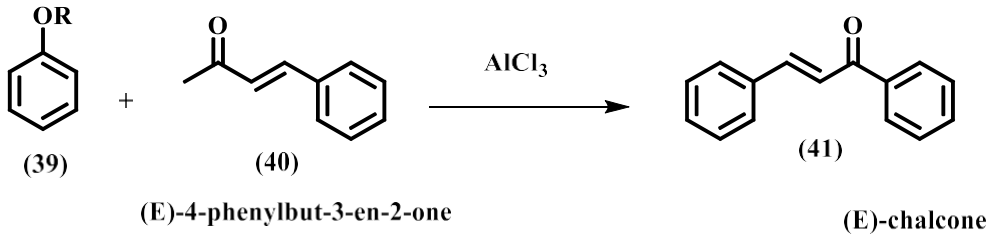


Figure1.14: Friedel–Crafts acylation is used to synthesize Chalcones.

1.5.2 Chalcone chemicals can be utilized in several applications

Using rings closure reactions. Many forms of heterocyclic rings can be created [29,30].

1.5.2.1 Chalcone cyclization with dinucleophile Chalcone cyclization with diamine compounds (Figure1.15).

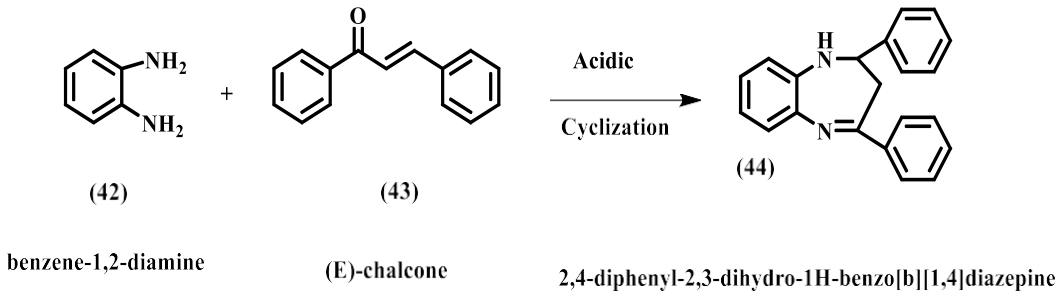


Figure1.15: Reaction of chalcon

1.5.2.2. Chalcone cyclization with diamine compounds to make cyclic molecules:

A cyclization method is used to produce Pyrimidine derivatives, pyrimidine derivatives, pyrimidine derivatives [31] (Figure1.16).

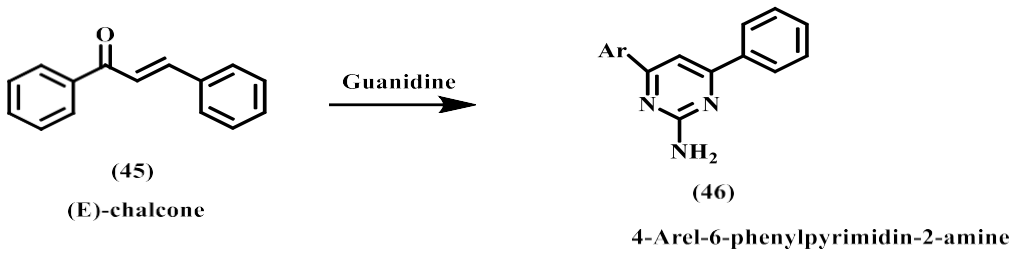


Figure1.16: Reaction of Chalcone cyclization

1.5.3 The reaction of chalcone to give pyrazoline

Pyrazoline is formed when Chalcone interacts with hydrazine.[9] (Figure1.17).

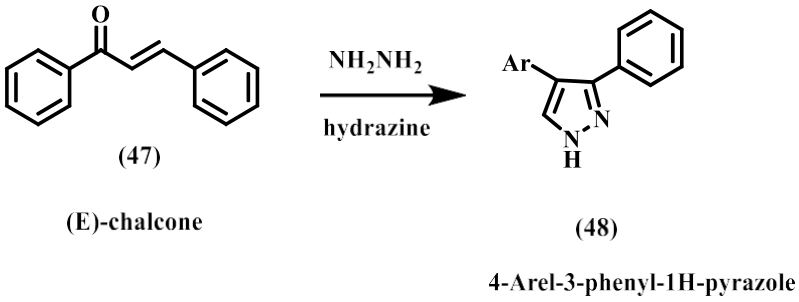
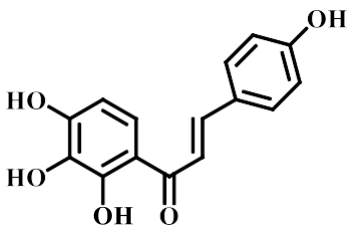


Figure1.17: The reaction of Chalcon to produce pyrazoline

1.6 Chalcone's Medical Applications

Chalcones and their derivatives have attracted a lot of attention in recent years. Many research studies have been published on Chalcones, and fresh pharmacological studies are still being conducted. Researchers have investigated new methods for producing Chalcone derivatives, which offer a wide range of pharmacological and biological properties. The antiviral activity of Chalcone derivatives appears to be significant compound(49) [32] (Figure1.18).

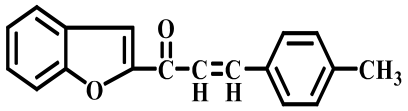


(49)

(E)-3-(4-hydroxyphenyl)-1-(2,3,4-trihydroxyphenyl)prop-2-en-1-one

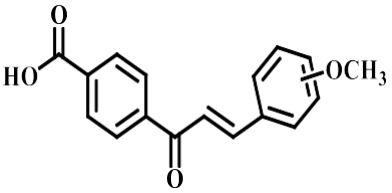
Figure1.18: Compound(49)

Other chalcone derivatives, on the other hand, showed higher antimicrobial activity compounds (50) and (51) [32] (Figures1.19).



(50)

1-(4H-chromen-2-yl)-3-(p-tolyl)prop-2-en-1-one

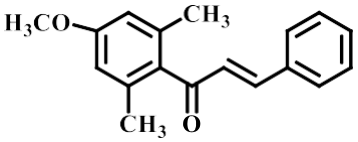


(51)

4-cinnamoylbenzoic acid

Figures1.19: Chalcone compounds(50) and (51) showed Antibacterial Activity.

A number of chalcone derivatives were examined as, antioxidants compound(52)[33] (Figure1.20).

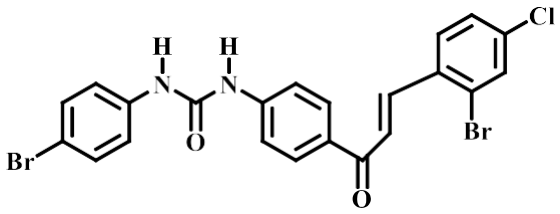


(E)-1-(4-methoxy-2,6-dimethylphenyl)-3-phenylprop-2-en-1-one

(52)

Figure1.20: A Chalcone compound(52) showed Antioxidants Activity

Some chalcone deductions showe of Antitubercular properties. However, some Chalcone derivatives [33] are toxic. Anti-inflammatory assays were also performed on Chalcone. Antitubercular and analgesic properties compound (53)[33](Figure1.21).

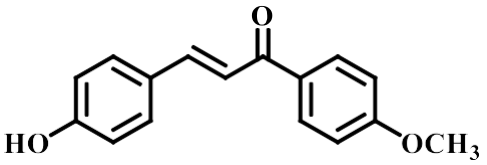


(E)-1-(4-(3-(2-bromo-4-chlorophenyl)acryloyl)phenyl)-3-(4-bromophenyl)urea

(53)

Figure1.21: Compound (53).

Anticancer properties Chalcone derivatives have been studied as anticancer agents with promising results as a medication compound(54) [34] (Figure1.22).

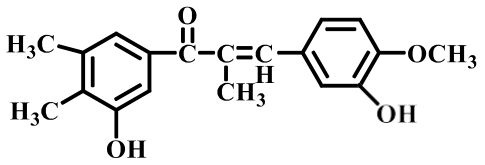


(E)-3-(4-hydroxyphenyl)-1-(4-methoxyphenyl)prop-2-en-1-one

(54)

Figure1.22: A Chalcone compound(54) showed Anticancer Activity

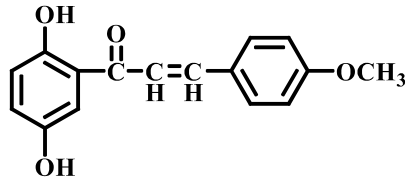
HIV antiviral action derivatives of Chalcone have been developed.and screened for anti-HIV antibodies, indicating due to positive outcomes in clinical trials as a medication compound(55) [35](Figure1.23).



1-(3-hydroxy-4,5-dimethylphenyl)-
3-(3-hydroxy-4-methoxyphenyl)-2-methylprop-2-en-1-one

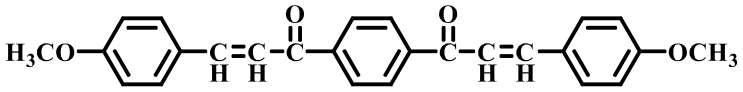
Figure1.23: A chalcone compound(55) showed Anti HIV.

Several Chalcone compounds showed antibacterial, antifungal, antimalarial, antiviral, antiinflammatory, antileishmanial, anti-tumor, and anticancer effects in a wide range of pharmacological and biological applications. Chalcones are biologically active due to their alpha, beta-unsaturated carbonyl system, as seen in compound(56). Bis-(Chalcone group) was prepared by other research compound(57) [36] (Figure1.24).



1-(2,5-dihydroxyphenyl)-3-(4-methoxyphenyl)prop-2-en-1-one

(56)



1,1'-(1,4-phenylene)bis(3-(4-methoxyphenyl)prop-2-en-1-one)

(57)

Figure1.24: Compound(56) and (57).

1.7. Heterocyclic Compounds

Heterocyclic compounds are cyclic organic compounds that contain at least one heteroatom; the most common heteroatoms are nitrogen, oxygen, and sulfur, but heterocyclic rings of other heteroatoms are also well-known. A carbocyclic Compound is a cyclic organic compound with all carbon atoms arranged in a ring. Heterocyclic compounds are one of the most important types of organic compounds. Due to its activity in a variety of illnesses, it is used in a variety of biological fields. The heterocyclic ring is present in the main skeleton of biological molecules such as DNA and RNA, chlorophyll, hemoglobin, vitamins, and many others. Many heterocyclic compounds have been used to treat a variety of diseases, including triazine derivatives, which have been used as antimicrobial herbicides and urinary tract infections [37].

1.7.1. Heterocyclic Rings with Seven Members:

The reactions of cyclic carboxylic acid anhydrides with imines generate the seven rings Oxazepines, such as the reactions of succinic, maleic, and phthalic anhydride with imines, as shown in the following equation compound(60) [38](Figure1.25).

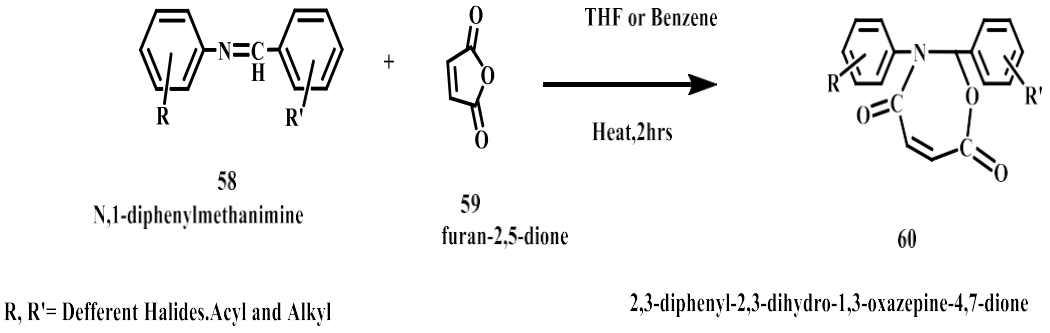


Figure1.25: Hept ring preparation of a Hetercyclic compound.

1.7.2 Compounds of Azepines

Spiro[indoline-3,7′-pyrrolo[1,2-a]azepines] were conveniently synthesized in satisfactory yields and with high diastereoselectivity from the three-component reaction of L-proline, isatins, and Chalcones, and sequential reaction with dimethyl but-2-ynedioate or methyl propiolate in refluxing methanol. The ferrocenyl-chalcones and dibenzylideneacetones were also successfully used in this one-pot two-step reaction to give novel ferrocenyl and styryl-substituted spiro compounds. The reaction mechanism included domino [3+2] cycloaddition reaction of azomethine ylide with Chalcone and the ring-expansion reaction of in situ generated spiro[indoline-3,3′-pyrrolizine] with electron-deficient alkynes compound (62)[39](Figure1.26).

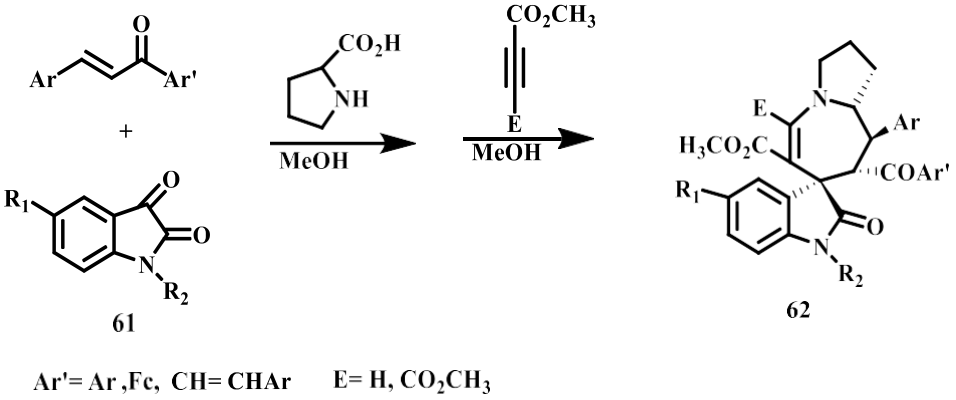


Figure1.26: Synthesis of compound(62) azepine

There are techniques for synthesizing the hepta-ring (oxazepine) from it by adding the compound (maleic anhydride) directly to the double bond (-C=N-)of Schiff's bases in ethanol as a solvent, and the result is 2,3-dihydro-1,3-oxazepine-4, 7- Diones, compound(Figure 1.27) (65) [40] as follows:

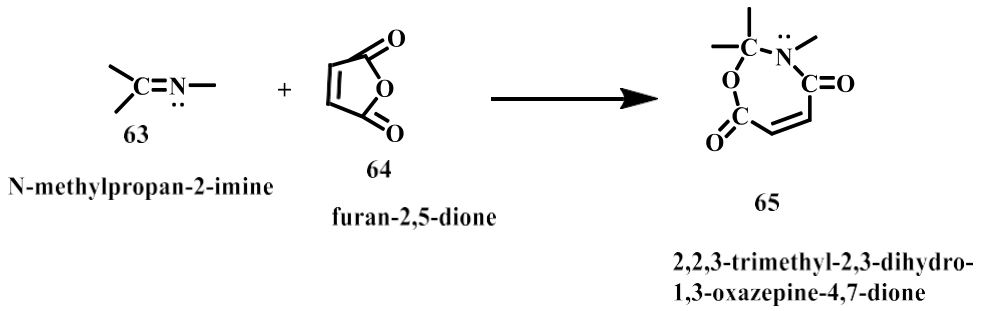


Figure 1.27: Prepration of compound(65) 1,3- oxazepine.

The reaction of Schiff bases with maleic anhydride or succinic anhydride gereroted certain compounds comprising two rings of 1,3-oxazepine-4-7-dione, as shown in the procedure below compound(68) [40] (Figure1.28).

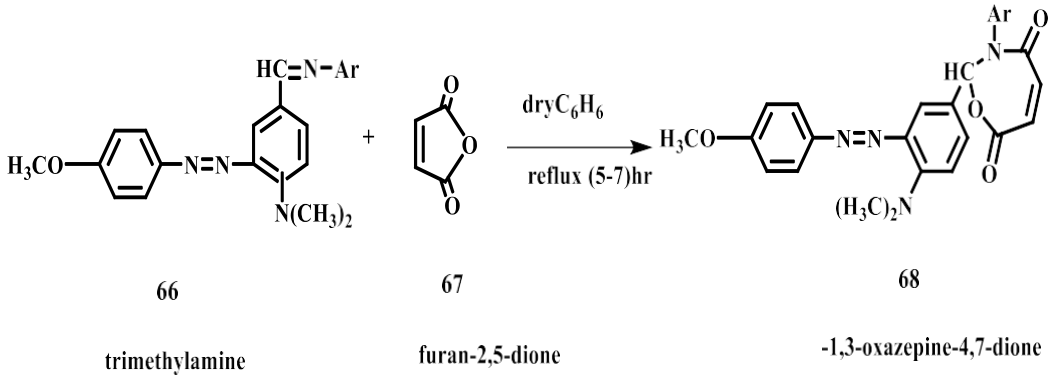
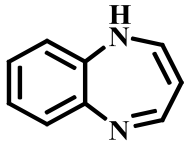


Figure 1.28: Synthesis of compound(68) 1, 3- oxazepine-dione

1.7.3. (1, 5-Benzodiazepines Compound):

1, 5-Benzodiazepines are bicyclic compounds with two nitrogen atoms at 1 and 5 positions in a seven-membered ring fused to a benzene ring. Benzo di azepines have attracted greater attention as an important class of heterocyclic compounds in the field of drugs and

pharmaceuticals. This nucleus is a pharmacophoric scaffold and represents a class of heterocycles with a wide range of biological applications. Many of them are widely used as anticonvulsants, antianxiety, sedatives, anti-depressive, hypnotic and neuroleptic agents. Some heterocycles containing benzodiazepines moiety were reported to possess anti-inflammatory, anti-viral, anti-HIV-1, antimicrobial, and antitumor activities. Other than their biological importance, benzodiazepines are valuable synthons for the preparation of fused ring compounds, such as triazole, thiazole, imidazole, and pyramid-benzodiazepines. It has been noticed that the introduction of an additional ring to the benzodiazepine core tends to exert profound influence in conferring novel biological activities in these molecules. Although many methods for synthesizing benzodiazepine ring systems have been reported, they continue to receive a great deal of attention compound(69) [41](Figure1.29).



1, 5-Benzodiazepines
69

Figure 1.29: Synthesis compound(69)

1.7.4. Seven-membered nitrogen-containing heterocycles.

Natural products and medications typically contain seven-membered nitrogen-containing heterocycles, particularly azepines and benzoazepines, which have considerable biological activity (Figure 1). 1 As a result, efficient and reliable assembly methods are being developed. The development of these handy scaffolds has sparked a lot

of attention, and Some tried-and-true procedures have been developed With these newly generated Chalcone-based pyridinium saltsin hand, we examined their reactivity by choosing as model substrates. When the reaction was conducted in CH_3CN at 60 °C with 1.2 equiv of 1,1,3,3-tetramethylguanidine (TMG) as the base, to our delight, the desired bridged benzodiazepine compound(72)[42] (Figure1.30).

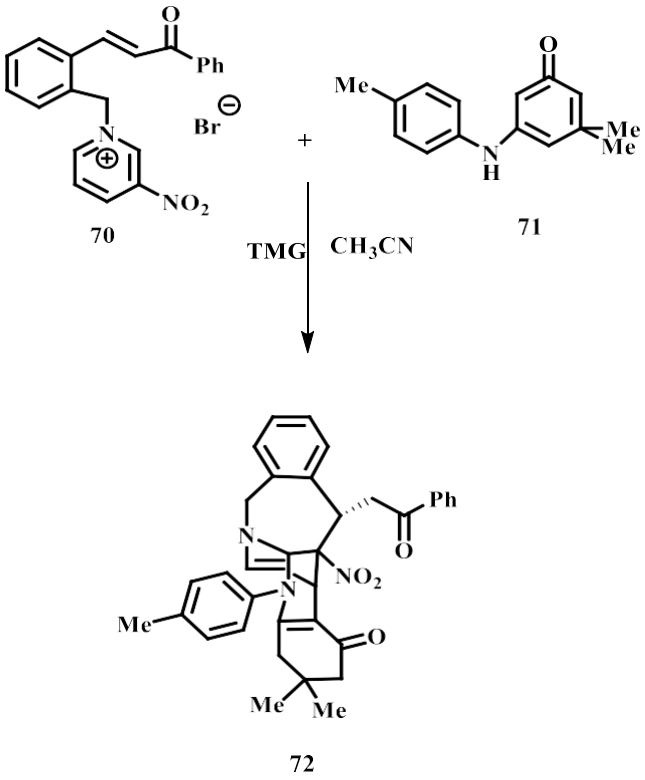
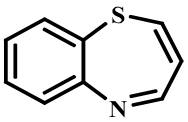


Figure1.30: Synthesis compound(72)

1.7.5 1,5-benzothiazepines biological activity:

Aimed to test the potency of Chalcone-based 1,5-benzothiazepines in inhibition of H1N1 neuraminidase through in vitro 4-methylumbelliferyl)- a-D-N-acetylneuraminic acid (MUNANA) assay. The in silico studies were also applied here to study the interactions of these compounds with the viral neuraminidase compound(73) [43] (Figure1.31).



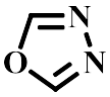
1,5-benzothiazepines

73

Figure1.31: Synthesis compound(73)

1.7.5 1,3,4-Oxadiazoles Activity:

1,3,4-Oxadiazoles are a type of heterocyclic compound that is useful in medicinal chemistry, pesticide chemistry, and field chemistry. of polymers. Oxadiazoles also have a number of properties. antitubercular, antimalarial, As a result, the synthesis and antibacterial properties of novel 1,3-benzoxazepine-1,5-diones bearing the biologically active 1,3,4-oxadiazole was reported in this article compound(74). [44](Figure1.32).



1,3,4-Oxadiazoles

74

Figure1.32: Synthesis compound(74).

1.8-Calorimetry:

Is a system for determining the quantify heat changes that caused by various processes. Calorimetric experiments, which are performed with calorimeters, can be used to obtain reliable thermal characteristics data in theory.

1.9-DTA:

Is a thermal analysis method that assesses the temperature difference between a sample and a reference at a predetermined temperature. Differential thermal scanning (DSC) is a thermal analysis method that determines the link between the energy difference and the temperature input to a sample and a reference under predetermined temperature settings. The two strategies have different physical meanings. Only the temperature's distinctive points, such as the phase transition temperature, can be tested with DTA. The temperature of the phase transition, as well as the temperature change during the phase change, can be measured using the DSC. The DTA curve's exothermic and endothermic peaks have no physical significance. The exothermic peak on the DSC curve represents heat release, while the endothermic peak represents heat absorption [45, 46].

1.10 The aim of the research

The aim of the research is to study the possibility of preparing some important heterocyclic compounds containing nitrogen atom. With a review of the literature about chalcones and their methods of interaction and preparation, and about heterocyclic compounds, a study of their importance and methods of preparation, and the possibility of studying its thermal stability for future use as medicines or in industry.

2. Experimental Part.

2.1: Chemicals.

The Chemicals used throughout the study for the synthesis of all intermediates and titled compounds are listed as below :

1.4-Aminobanzyldehyde (Sigma Aldrich-Germany 98 %)

2.4-Bromoacetophenon (Sigma Aldrich-Germany 99 %)

3. 4-Bromobanzyldehyde (Sigma Aldrich-Germany 98 %)

4. 4-Chloroacetophenon (Sigma Aldrich-Germany 99 %)

5.4-Chlorobanzyldehyde (Sigma Aldrich-Germany 98 %)

6.1, 3-diamino propane (Sigma Aldrich-Germany 97 %)

7. Ethanol (Sigma Aldrich-Germany 99 %)

8. HCl (Sigma Aldrich-Germany 99 %)

9.4-Hydroxybanzyldehyde (Sigma Aldrich-Germany 98 %)

10. NaOH (Sigma Aldrich-Germany 99 %)

11.4-Methoxyacetophenon (Sigma Aldrich-Germany 98 %)

12.4-Nitroacetophenon (Sigma Aldrich-Germany 98 %)

13. 4-Nitrobanzyldehyde (Sigma Aldrich-Germany 98 %)

14. Paratoluene sulfonic acid (Sigma Aldrich-Germany 96 %)

2.2 :Instruments

2.2.1 : Nuclear Magnetic Resonance Spectroscopy (^{1}HNMR, ^{13}C NMR)

Analyses were performed using a Bruker 400 MHz advanced spectrometer,at Turkey. (DMSO-d6) was used as a solvent, data for ^{1}H-NMR and ^{13}C-NMR spectra were reported as follows: chemical shift, multiplicity (s=singlet,d= doublet, t= triplet, and m= multiplet) Gazi University in Turkey

2.2.2 : Infrared Spectroscopy (FT-IR):

FT-IR spectra of the intermediate and the title compounds were recorded Thermo Scientific (Nicolet)(FT-IR) Gazi University in Turkey.

2.2.3 : Melting Point (M.P)

The melting points of the prepared compounds were determined using capillary tube. An electrolyte measuring device in the Faculty of Science, Department of the Chemistry University of Anbar.

2.2.4 : Microanalyses

Elemental analyses CHNX were carried out in a Thermo Flash 2000 CHNX Analyzer Gazi University in Turkey**.**

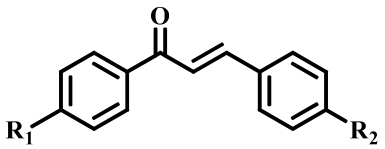
2.2.5 : Thermogravimetric Analyzer (TGA).

Item (TGA PT1000 Thermogravimetric Analyzer Company (Linseis Inc Catalog Number (TGA PT1000 / TGA PT1000 HiRes) was used for thermal sstability assess, Gazi University in Turkey.

2.3 : Methods:

The method of work includes two parts, the first step was the preparation of chalcones compounds, and the second step was done to close the rings as follows:

2.3.1 : The Synthesis of Chalcone:



75

Chalcone

Figure 2.1: Chalcone.

R_1= Cl, Br, NO_2, O-CH_3

R_2= NH_2, OH, NO_2, Cl, B

A solution of 0.01 mol paracetophenone and para-benzaldehyde was dissolved in ethanol (95%, 15 mL). An aqueous solution of sodium hydroxide (40%) was added to the solution and stirred for 12 hours, then drops of dilute hydrochloric acid were added to neutralize it and left overnight at room temperature. The reaction mixture was placed in water. A yellow-colored solid is precipitated from a solution. To obtain a transparent solution, the solid was dissolved in 15 ml ethanol and stirred for approximately 10 minutes. Yellow crystals in the form of a lump formed after leaving the solution in the air upon the gradual evaporation of the solvent, a layer that formed at the bottom of the tank. it, washing the product with distilled water, then drying it and recrystallizing it from ethanol [47-64].

2.3.1.1 : (E)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one: (1a). Yield 66.5 %, m.p 250-252, Molecular Weight: 258.7, Formula Weight $C_{15}H_{11}ClO_2$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2974.23 (C-H aliphatic), 1593.20 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 771.53(C-Cl).

2.3.1.2 : 1, 3-bis (4-chlorophenyl) prop-2-en-1-one: (2a). Yield 81.6 %, m.p 246-248, Molecular Weight: 277.1, Formula Weight $C_{15}H_{10}Cl_2O$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2974.23 (C-H aliphatic), 1593.20 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 771.53(C-Cl), 709.80 (C-Cl).

2.3.1.3 : 3-(4-bromophenyl)-1-(4-chlorophenyl) prop-2-en-1-one: (3a). Yield 85.9 %, m.p 238-240, Molecular Weight: 321.6, Formula Weight $C_{15}H_{10}BrClO$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2974.23 (C-H aliphatic), 1593.20 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 771.53(C-Cl)

2.3.1.4 :4-(E)-(4-Chlorophenyl)-3-(4-nitrophenyl)prop-2-en-1-one: (4a). Yield 80.4 %, m.p 255-257, Molecular Weight: 287.7, Formula Weight $C_{15}H_{10}ClNO_3$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2974.23 (C-H aliphatic), 1593.20 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 771.53(C-Cl).

2.3.1.5 : 3-(4-aminophenyl)-1-(4-chlorophenyl) prop-2-en-1-one: (5a). Yield 66.4 %, m.p 235-237, Molecular Weight: 257.7, Formula Weight $C_{15}H_{12}ClNO$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2974.23 (C-H aliphatic), 1593.20 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 771.53(C-Cl).

2.3.1.6 : 1-(4-bromophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one: (6a). Yield 76.2 %, m.p 245-247, Molecular Weight: 303.2, Formula Weight $C_{15}H_{11}BrO_2$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2924.08 (C-H aliphatic), 1600.92 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 682.80 (C-Br).

2.3.1.7 : 1-(4-bromophenyl)-3-(4-chlorophenyl) prop-2-en-1-one: (7a). Yield 66.8 %, m.p 250-252, Molecular Weight: 321.6, Formula Weight $C_{15}H_{10}BrClO$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2924.08 (C-H aliphatic), 1600.92 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 682.80 (C-Br), 767.67 (C-Cl).

2.3.1.8 : 1, 3- Bis(4-bromophenyl)prop-2-en-1-one: (8a). Yield 60.7 %, m.p 230-232, Molecular Weight: 366.1, Formula Weight $C_{15}H_{10}Br_2O$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2924.08 (C-H aliphatic), 1600.92 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 682.80 (C-Br).

2.3.1.9 : 1-(4-bromophenyl)-3-(4-nitrophenyl) prop-2-en-1-one: (9a). Yield 67.8 %, m.p 236-238, Molecular Weight: 332.2, Formula Weight $C_{15}H_{10}BrNO_3$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2924.08 (C-H aliphatic), 1600.92 (C=C aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 682.80 (C-Br).

2.3.1.10 : 3-(4-aminophenyl)-1-(4-bromophenyl) prop-2-en-1-one: (10a). Yield 66.5 %, m.p 238-240, Molecular Weight: 302.2, Formula Weight $C_{15}H_{12}BrNO$. FT-IR(cm^{-1}): 3059.10 (C-H aromatic), 2924.08 (C-H aliphatic), 1654.92 (C=C aromatic), 1600.92 (C=C

aromatic), 1654.92 (C=O), 1481.33 (C-H bending), 1442.75 (C-H bending), 682.80 (C-Br).

2.3.1.11 : 3-(4-hydroxyphenyl)-1-(4-methoxyphenyl) prop-2-en-1-one: (11a). Yield 70.5 %, m.p 240-242, Molecular Weight: 254.3, Formula Weight $C_{16}H_{14}O_3$. FT-IR(cm^{-1}): 3001.24 (C-H aromatic sp^2), 2974.24 (C-H aliphatic), 2935.66 (C-Hsp^3), 1585.49 (C=C aromatic), 1508.34 (C=C aliphatic), 1651.07 (C=O), 1458.19 (C-H bending), 1392.81 (C-H bending), 1249.88 (C-O stretch).

2.3.1.12 : 3-(4-chlorophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one: (12a). Yield 70.6 %, m.p 240-242, Molecular Weight: 272.7, Formula Weight $C_{16}H_{13}ClO_2$. FT-IR(cm^{-1}): 3001.24 (C-H aromatic sp^2), 2974.24 (C-H aliphatic), 2935.66 (C-Hsp^3), 1585.49 (C=C aromatic), 1508.34 (C=C aliphatic), 1651.07 (C=O), 1458.19 (C-H bending), 1392.81 (C-H bending), 1249.88 (C-O stretch).

2.3.1.13 : 3-(4-bromophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one: (13a). Yield 75.2 %, m.p 244-246, Molecular Weight: 317.2, Formula Weight $C_{16}H_{13}BrO_2$. FT-IR(cm^{-1}): 3001.24 (C-H aromatic sp^2), 2974.24 (C-H aliphatic), 2935.66 (C-Hsp^3), 1585.49 (C=C aromatic), 1508.34 (C=C aliphatic), 1651.07 (C=O), 1458.19 (C-H bending), 1392.81 (C-H bending), 663.52 (C-Br), 1249.88 (C-O stretch).

2.3.1.14 : 1-(4-methoxyphenyl)-3-(4-nitrophenyl) prop-2-en-1-one: (14a). Yield 86.5 %, m.p 250-252, Molecular Weight: 283.3, Formula Weight $C_{16}H_{13}NO_4$. FT-IR(cm^{-1}): 3001.24 (C-H aromatic sp^2), 2974.24 (C-H aliphatic), 2935.66 (C-Hsp^3), 1585.49

(C=C aromatic), 1508.34 (C=C aliphatic), 1651.07 (C=O), 1458.19 (C-H bending), 1392.81 (C-H bending), 1249.88 (C-O stretch).

2.3.1.15 : 3-(4-aminophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one: (15a) Yield 88.8 %, m.p 246-248, Molecular Weight: 253.3, Formula Weight $C_{16}H_{15}NO_2$. FT-IR(cm^{-1}): 3001.24 (C-H aromatic sp^2), 2974.24 (C-H aliphatic), 2935.66 (C-Hsp^3), 1585.49 (C=C aromatic), 1508.34 (C=C aliphatic), 1651.07 (C=O), 1458.19 (C-H bending), 1392.81 (C-H bending), 663.52 (C-Br), 1249.88 (C-O stretch).

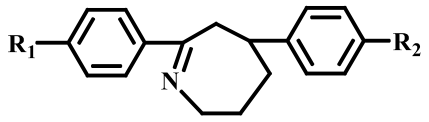
2.3.1.16 : 3-(4-hydroxyphenyl)-1-(4-nitrophenyl) prop-2-en-1-one): (16a). Yield 70.8 %, m.p 248-250, Molecular Weight: 269.3, Formula Weight $C_{15}H_{11}NO_4$. FT-IR(cm^{-1}): 3375.43 (-OH), 3113.11 (C-H aromatic), 2978.09 (C-H aliphatic), 1593.20 (C=C aromatic), 1442.75 (C=C aliphatic), 1654.92 (C=O), 1338.60 (C-H bending), 1276.88 (C-H bending), 1512.10 (NO stretch), 1338.60 (NO stretch).

2.3.1.17 : 3-(4-chlorophenyl)-1-(4-nitrophenyl) prop-2-en-1-one: (17a). Yield 87.8 %, m.p 255-257, Molecular Weight: 287.7, Formula Weight $C_{15}H_{10}ClNO_3$. FT-IR(cm^{-1}): 3375.43 (-OH), 3113.11 (C-H aromatic), 2978.09 (C-H aliphatic), 1593.20 (C=C aromatic), 1442.75 (C=C aliphatic), 1654.92 (C=O), 1338.60 (C-H bending), 1276.88 (C-H bending), 1512.10 (NO stretch), 1338.60 (NO stretch).

2.3.1.18 : 3-(4-aminophenyl)-1-(4-nitrophenyl) prop-2-en-1-one: (18a). Yield 87.8 %, m.p 258-260, Molecular Weight: 268.27, Formula Weight $C_{15}H_{12}N_2O_3$. FT-IR(cm^{-1}): 3375.43 (-OH), 3113.11 (C-H aromatic), 2978.09 (C-H aliphatic), 1593.20 (C=C aromatic),

1442.75 (C=C aliphatic), 1654.92 (C=O), 1338.60 (C-H bending), 1276.88 (C-H bending), 1512.10 (NO stretch), 1338.60 (NO stretch).

2.3.2 : Synthesis of 7 – membered Heterocyclic compounds



R1= Cl, Br, NO2, OCH3
R2= Cl, Br,NO2

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Figure 2.2: The formula for hetrocyclic seven membered ring.

The heterocyclic seven-rings were synthesized in a 100 mL circular flask with (0.01 mol) chalcone dissolved in (25 mL) absolute ethyl alcohol, followed by (0.01 mol) 1, 3-diamino propane and an amount as a catalyst, 0.02 g para toluene sulfonic acid. The reaction mixture was then heated until it reached the sublimation stage, and the back-distillation process was carried out at a temperature of 40 °C for 10 hours with continuous stirring after it cooled down and the product precipitated as a precipitate. The crystallization process can be performed using solvents. The solvent is suitable for the recrystallization process. The hepta -rings were characterized using (FT-IR, ^{1}H-NMR, ^{13}C-NMR) [65-70].

2.3.2. : Spectra FT-IR, ^{1}HNMR, ^{13}CNMR of Seven-Member Rings Heterocyclic compounds:

2.3.2.1 :5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine: (1b). Yield 83.5 %, m.p 258-260, Molecular Weight: 358.28, Formula Weight $C_{19}H_{20}BrNO$. FT-IR

(Lizer) (cm^{-1}): 3003.45 (C-H aromatic), 2935.63 (C-H aliphatic), 2844.22 (C-H aliphatic sp^3), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 1254.71, 1171.06 ($O-CH_3$), 665.08 (C-Br), 836.76 (C-H bending) ^{1}HNMR δ(ppm,DMSOd6): (C-H aromatic 7.7-8.3) (1H,p,H_2 3.4) (1H,t,$H_1$3.7) (1H,Q,$H_3$3.2) (2H,H_5,d,2.5) (2H,p,$H_4$1.17) (3H,s,$O-CH_3$3.9) ^{13}CNMR δ(ppm): ($O-CH_3$,55.7) (C_1,162.14) ($C_4$145.13) ($C_3$137) (C_{ph-Br} 131.83) ($C_{ph-OCH3}$127.5) ($C_5$119.43) ($C_2$114.64)

2.3.2.2 :7-(4-bromophenyl)-5-(4-chlorophenyl)-3,4,5,6-tetrahydro-2H-azepine: (2b). Yield 75.2 %, m.p 260-262, Molecular Weight: 362.70, Formula Weight $C_{18}H_{17}BrClN$. FT-IR (Lizer) (cm^{-1}): 3056.52 (C-H aromatic), 2935.63 (C-H aliphatic), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 714.35 (C-Cl), 658.62 (C-Br). ^{1}HNMR δ(ppm,DMSOd6): (1H,p,$H_2$3.0) (1H,t,$H_1$3.7) (1H,Q,$H_3$2.3) (2H,H_5,d,2.7) (1H,p,H_4 2.0) (C-H aromatic 7.7-8.3). ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) (C_{ph-Br} 131.83) (C_{ph-Cl} 133.62) ($C_5$119.43) ($C_2$114.64).

2.3.2.3 :5,7-bis(4-chlorophenyl)-3,4,5,6-tetrahydro-2H-azepine: (3b). Yield 71.8 %, m.p 270-272, Molecular Weight: 318.24, Formula Weight $C_{18}H_{17}Cl_2N$. FT-IR (Lizer) (cm-1): 3056.52 (C-H aromatic), 2950 (C-H aliphatic), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 977.79 (C-H bending), 791.85 (C-Cl), 772.53 (C-Cl),. ^{1}HNMR δ(ppm,DMSOd6): (1H,t,$H_1$3.5) (1H,p,$H_2$3.0) (1H,Q,$H_3$2.5) (2H,p,$H_4$1.84) (2H,d,$H_5$2.0) (C-H aromatic 7.7-8.3). ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) (C_{ph-Cl} 133.62) ($C_5$119.43) ($C_2$114.64) .

2.3.2.4:7-(4-bromophenyl)-5-(4-nitrophenyl)-3,4,5,6-tetrahydro-2H-azepine: (4b). Yield 79.2 %, m.p 250-252, Molecular Weight: 373.25, Formula Weight $C_{18}H_{17}BrN_2O_2$. FT-IR (Lizer) (cm^{-1}): 3006.40 (C-H aromatic), 2935.63 (C-H aliphatic), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 1324.34 (NO_2), 1254.73 (CH_2), 836.85 (C-H bending), 665.01 (C-Br). ^{1}HNMR δ(ppm,DMSOd6): (C-H aromatic 7.7-8.3) (1H,p,H_2 3.4) (1H,t,$H_1$3.7) (1H,Q,$H_3$3.2) (2H,H_5,d,2.5) (2H,p,$H_4$1.17) ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) (C_{ph-Br} 131.83) ($C_5$119.43) ($C_2$114.64) (C_{ph-NO2} 135.72) [73].

2.3.2.5 :5,7-bis(4-bromophenyl)-3,4,5,6-tetrahydro-2H-azepine: (5b). Yield 90.2 %, m.p 260-262, Molecular Weight: 407.15, Formula Weight $C_{18}H_{17}Br_2N$. FT-IR (Lizer)(cm^{-1}): 3090.95 (C-H aromatic), 2980.60 (C-H aliphatic), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 982.73 (C-H bending), 793.35(C-Br), 1324.68 (C=N). ^{1}HNMRδ(ppm,DMSOd6): (C-H aromatic 7.7-8.3) (1H,p,H_2 3.4) (1H,t,$H_1$3.7) (1H,Q,$H_3$3.2) (2H,H_5,d,2.5) (2H,p,$H_4$1.17). ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) (C_{ph-Br} 131.83) ($C_5$119.43) ($C_2$114.64) [73].

2.3.2.6 :5-(4-bromophenyl)-7-(4-chlorophenyl)-3,4,5,6-tetrahydro-2H-azepine: (6b). Yield 80.3 %, m.p 255-257, Molecular Weight: 362.70, Formula Weight $C_{18}H_{17}BrClN$. FT-IR (Lizer) (cm^{-1}): 3100.65 (C-H aromatic), 2910 (C-H aliphatic), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 832.25 (C-H bending), 811.20, 796.63 (C-Cl), 664.46 (C-Br). ^{1}HNMRδ(ppm,DMSOd6): (C-H aromatic 7.7-8.3) (1H,p,H_2

3.4) (1H,t,$H_1$3.7) (1H,Q,$H_3$3.2) (2H,H_5,d,2.5) (2H,p,$H_4$1.17). ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) ($C_{ph\text{-}Br}$ 131.83) (Cph-Cl 133.62) ($C_5$119.43) ($C_2$114.64) [74].

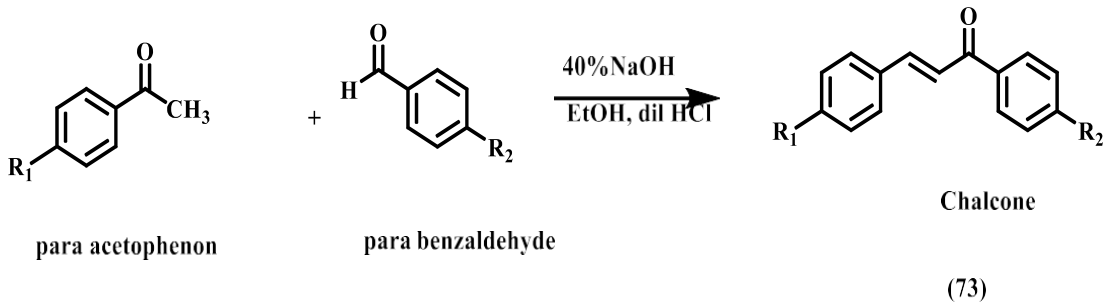
2.3.2.7 :5-(4-chlorophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine: (7b). Yield 80.3 %, m.p 250-252, Molecular Weight: 313.83, Formula Weight $C_{19}H_{20}ClNO$. FT-IR (Lizer) (cm-1): 3012.29 (C-H aromatic), 2980 (C-H aliphatic), 2844.22 (C-H aliphatic sp^3), 1590.33 (C=C aromatic), 1506.48 (C=C aliphatic), 1302.35 (C-H bending), 1656.54 (C=N), 1211.33,1167.81 (O-CH3), 823.30 (C-H bending), 720.43 (C-Cl). ^{1}HNMRδ(ppm,DMSOd6): (C-H aromatic 7.7-8.3) (1H,p,H_2 3.4) (1H,t,$H_1$3.7) (1H,Q,$H_3$3.2) (2H,H_5,d,2.5) (2H,p,$H_4$1.17) (3H,O-CH3,s,3.9). ^{13}CNMRδ(ppm): (C_1,162.14) ($C_4$145.13) ($C_3$137) ($C_{ph\text{-}Cl}$ 133.62) ($C_5$119.43) ($C_2$114.64) (O-CH3,55.7) .

3. Result and discussion.

3.1 Mechanism

3.1.1 Mechanism of preparing Chalcones

The Chalcone Compounds were synthesized by condensation reaction called (Claisen-Schmidt), which involved treating equivalent moles of the aromatic ketone Compound with an aldehyde (aromatic) in the presence of a base of 20 % KOH and ethanol as a solvent (Scheme 3.1)[9,71].

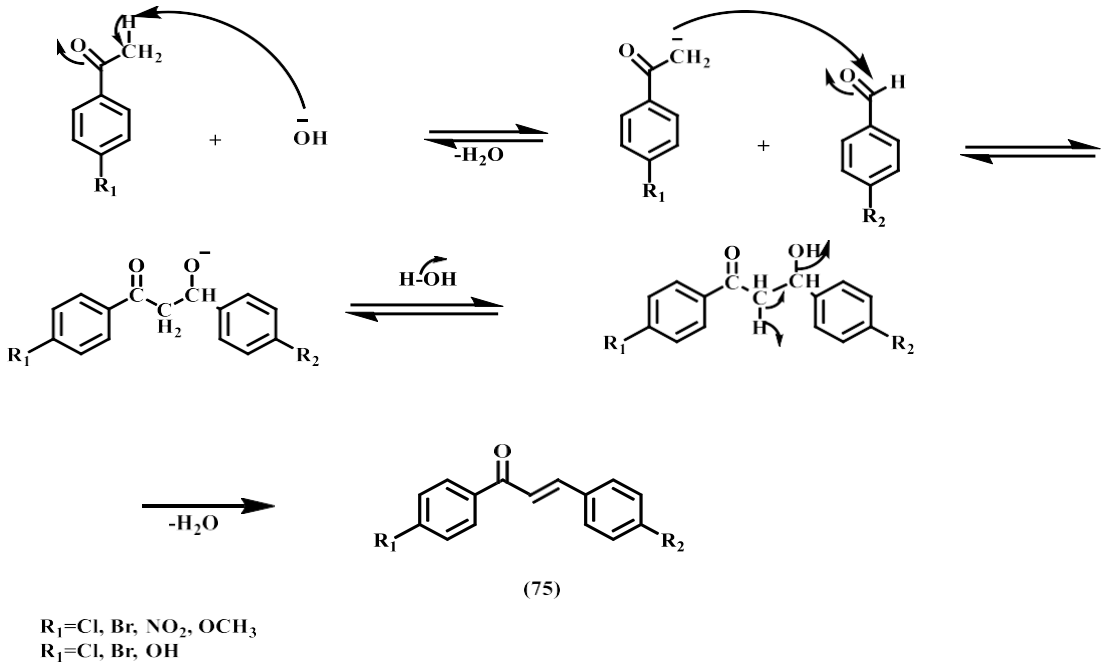


R_1= Cl, Br, NO_2, O-CH_3

R_2= NH_2, OH, NO_2, Cl, Br

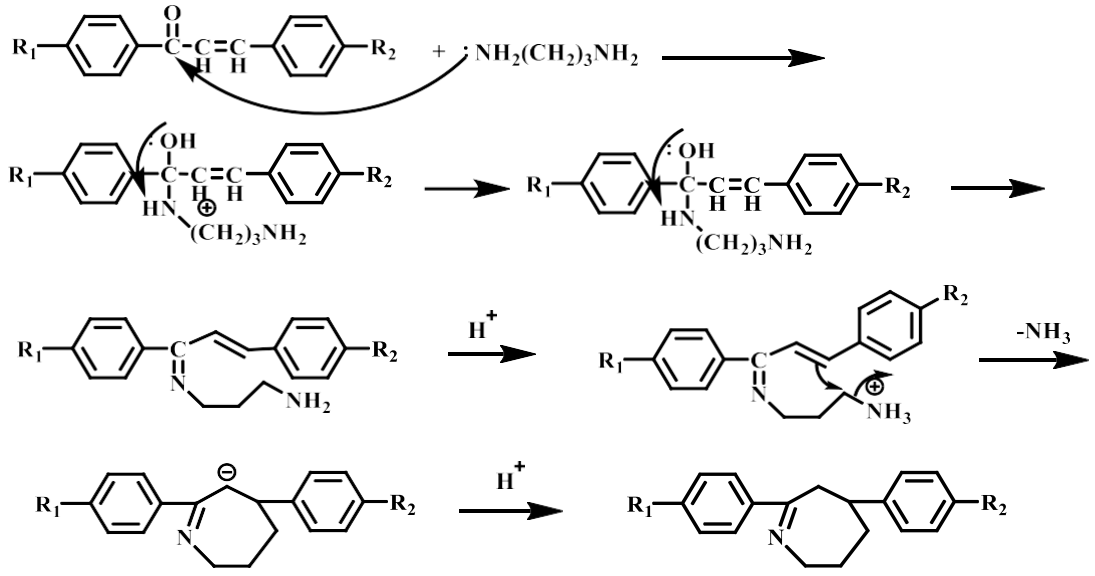
Scheme3.1: Preparation of Chalcone

The mechanism of chalcone formation via aldol condensation has four main steps that are deprotonation 1, addition, proton equilibration, and dehydration, where the dehydration process can be divided into two separate steps, deprotonation 2 and elimination [74].



Scheme 3.2: Mechanism of preparing chalcones

3.1.2 Mechanism of 7 – membered Heterocyclic compounds



R_1 = Cl, Br, NO_2, OCH_3

R_2 = Cl, Br

Scheme 3.3: Mechanism of 7 – membered Heterocyclic compounds.

3.2. Spectra FT-IR chalcone:

3.2.1 : (E)-1-(4-chlorophenyl)-3-(4-hydroxyphenyl) prop-2-en-1-one:

The FT-IR spectra of compounds 1a-5a are given in (Figures 3.1). The weak absorption band at 3059.10 cm^{-1},which is assigned to C-H stretching vibration,suggests the existence of hydrogen in the aromatic ring[75]. While the weak absorption bands for C-H aliphatic at 2974.23 cm^{-1}. The conjugated carbonyl group has a strong band at 1654.92 cm^{-1}. Another strong band, this one belonging to the carbon-carbon double bond, was discovered in 1593.20 cm^{-1} [76]. Wavenumber ranges of 1481.33 cm^{-1} and 1442.75 cm^{-1} are popular for aromatic C=C stretching vibrations [77], and the band C-Cl appear at 771.53 cm^{-1}, C-Cl 709.80 cm^{-1}. (Figure 3.1).

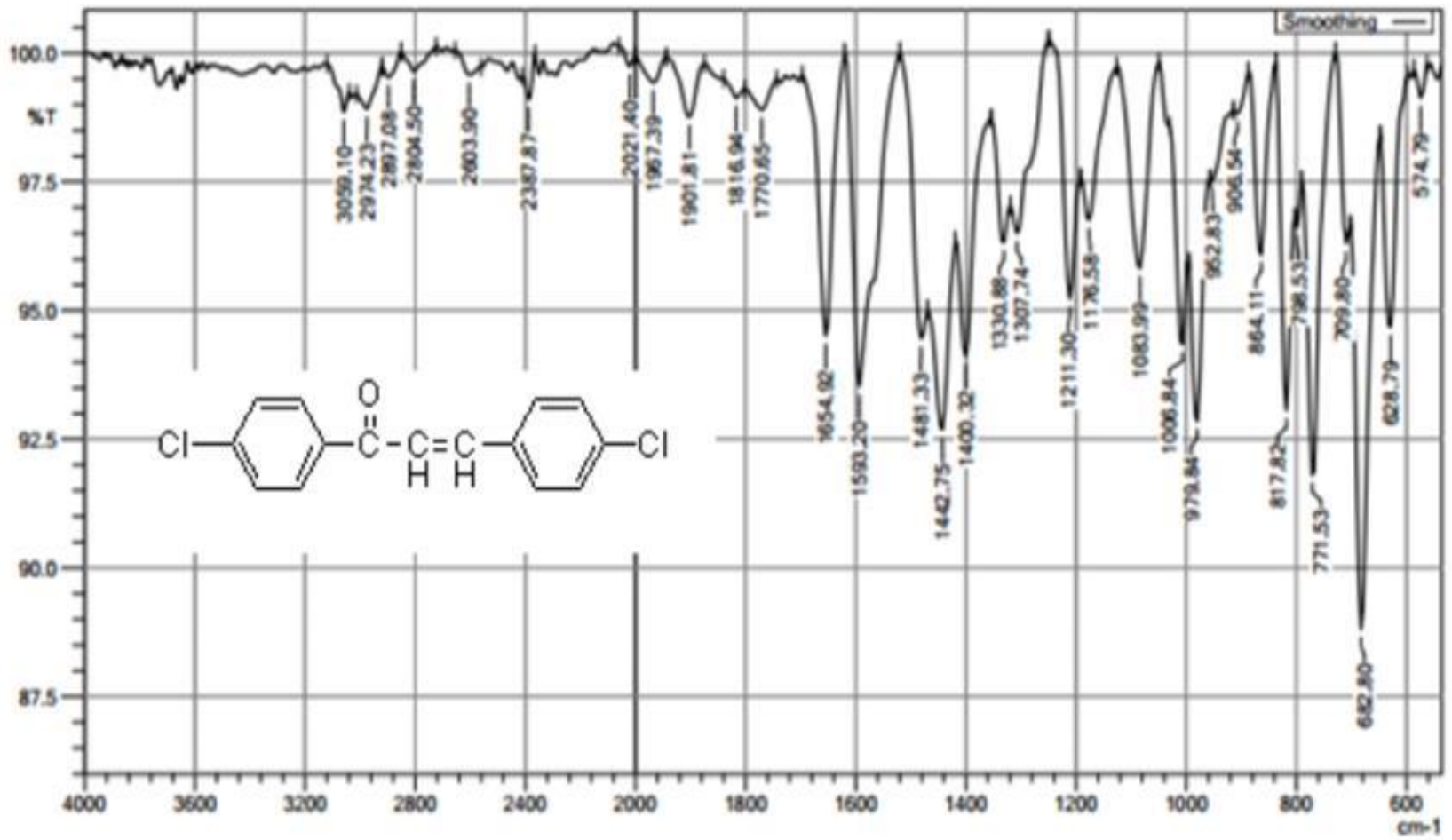


Figure 3.1: FT-IR 1, 3-bis (4-chlorophenyl) prop-2-en-1-one.

3.2.2. 1-(4-bromophenyl)-3-(4-chlorophenyl) prop-2-en-1-one:

The FT-IR spectra of compounds 6a-10a are given in (Figures 3.1). The weak absorption band at 3059.10 cm^{-1},which is assigned to C-H stretching vibration, suggests the existence of hydrogen in the aromatic ring[75]. While the weak absorption bands for C-H aliphatic at 2974.23 cm^{-1}. The conjugated carbonyl group has a strong band at 1654.92 cm^{-1}. Another strong band, this one belonging to the carbon-carbon double bond, was discovered in 1593.20 cm^{-1} [76]. Wavenumber ranges of 1481.33 cm^{-1} and 1442.75 cm^{-1} are popular for aromatic C=C stretching vibrations [77], and the band C-Cl appear at 771.53 cm^{-1} and the band C-Br appear at 682.80 cm^{-1} .(Figure 3.2)

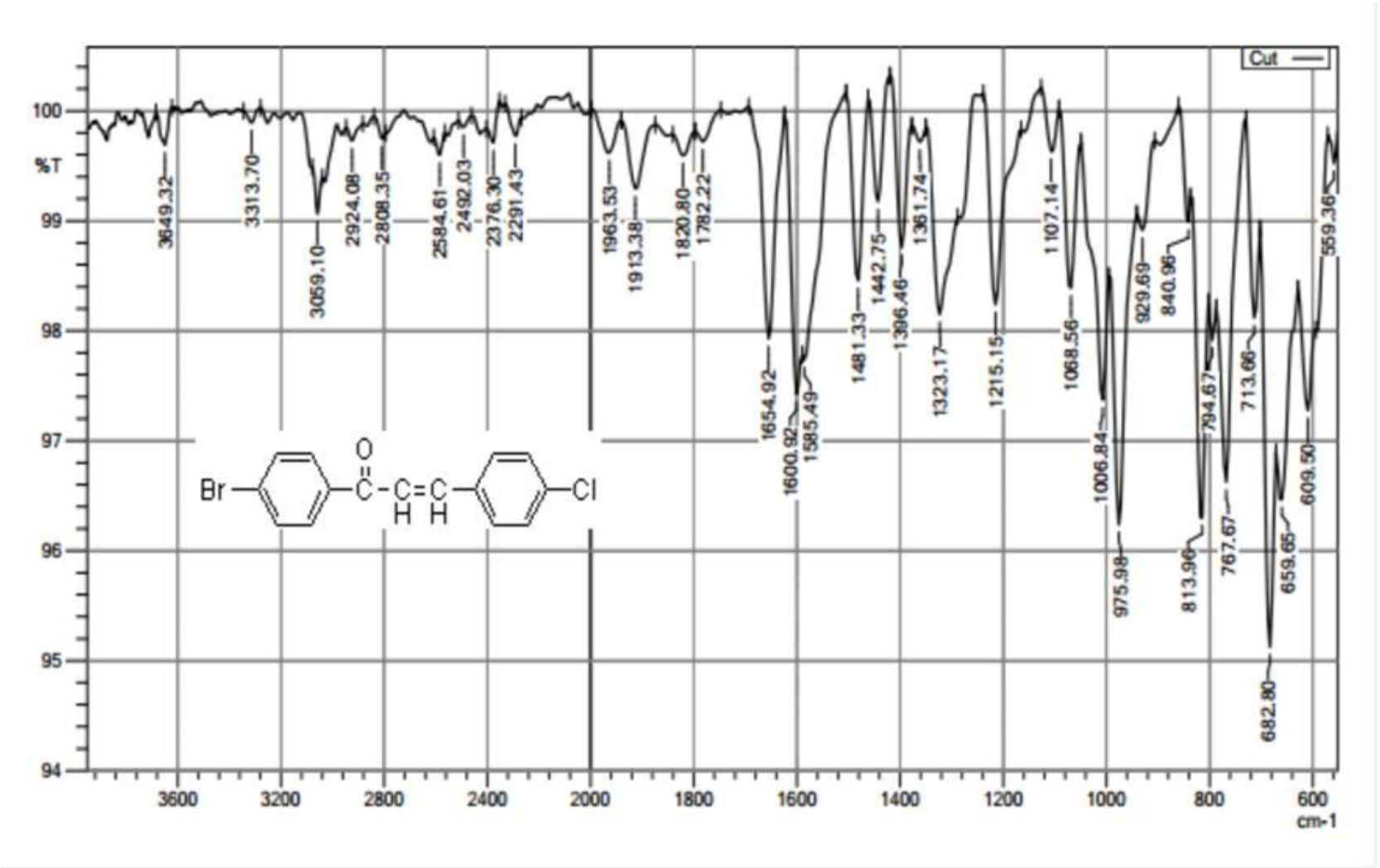


Figure 3.2: FT-IR1-(4-bromophenyl)-3-(4-chlorophenyl) prop-2-en-1-one.

3.2.3. 3-(4-bromophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one:

In the experimental section, FT-IR spectra for compounds 11a-15a are given in (Figures 3.3). The weak absorption band at 3001.24 cm^{-1}, which is assigned to C-H in the aromatic ring [75]. While the weak absorption bands for C-H aliphatic at 2974.24 cm^{-1}. The symmetric and asymmetric CH_3 bands appear at 2935.66 cm^{-1} in the frequency band. The conjugated carbonyl group has a strong band at 1651.07 cm^{-1}. Another strong band, this one belonging to the carbon-carbon double bond, was discovered in 1508.34 cm^{-1} [76]. Wavenumber ranges of 1585.49 cm^{-1} are popular for aromatic C=C stretching vibrations [77].

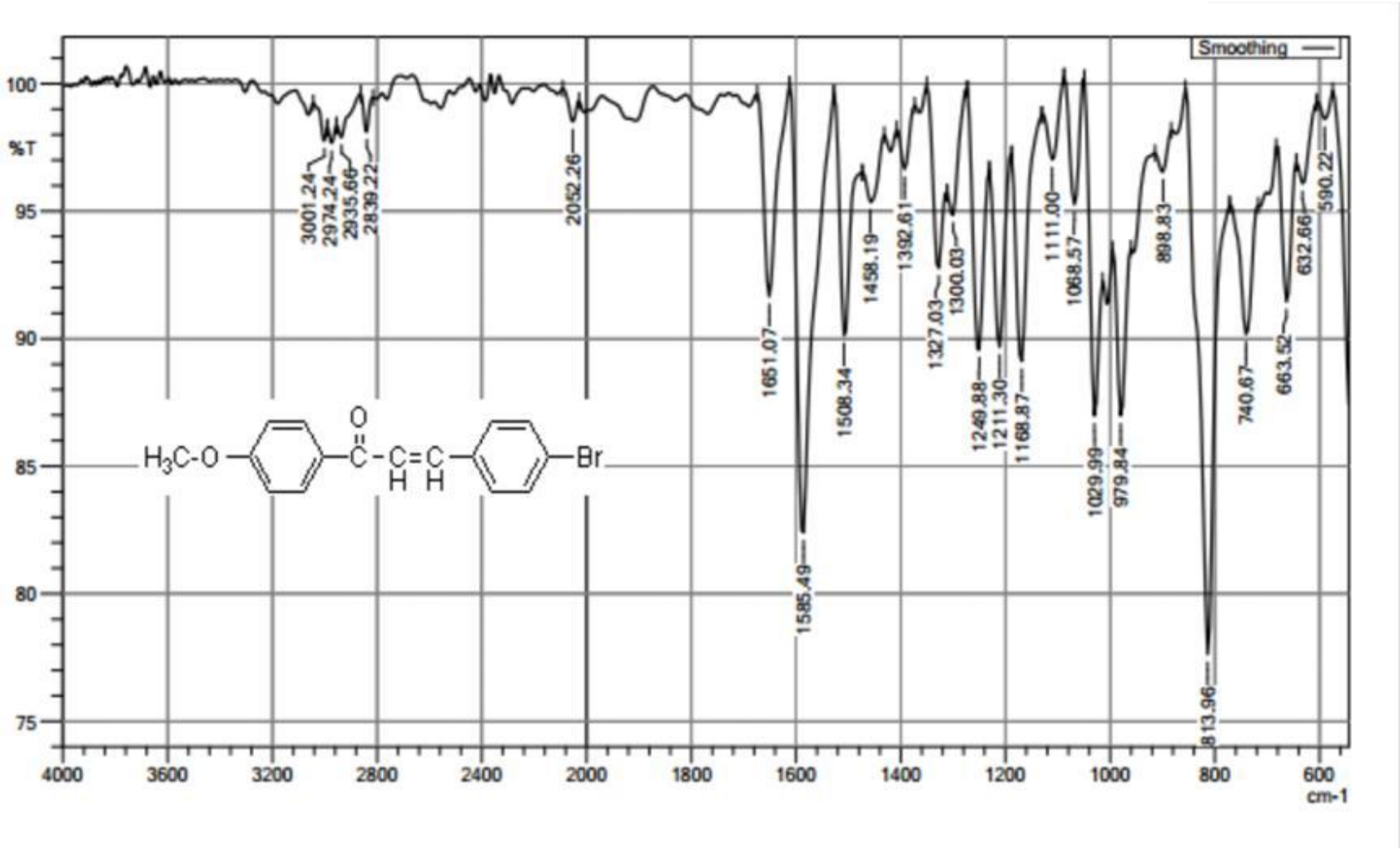


Figure 3.3.: FT-IR of 3-(4-bromophenyl)-1-(4-methoxyphenyl) prop-2-en-1-one.

3.2.4. 3-(4-hydroxyphenyl)-1-(4-nitrophenyl) prop-2-en-1-one.

In the experimental section, FT-IR spectra for compounds 16a-18a are given in (Figures 3.4). The wide pack at 3375.43 OH, The absorption band at 3113.11 cm^{-1}, which is assigned to C-H in the aromatic ring [75]. While the weak absorption bands for C-H aliphatic at 2978.09 cm^{-1}. The conjugated carbonyl group has a strong band at 1654.92 cm^{-1}. Another strong band, this one belonging to the carbon-carbon double bond, was discovered in 1442.75 cm^{-1} [76]. Wavenumber ranges of 1593.20 cm^{-1} are popular for aromatic C=C stretching vibrations [77].

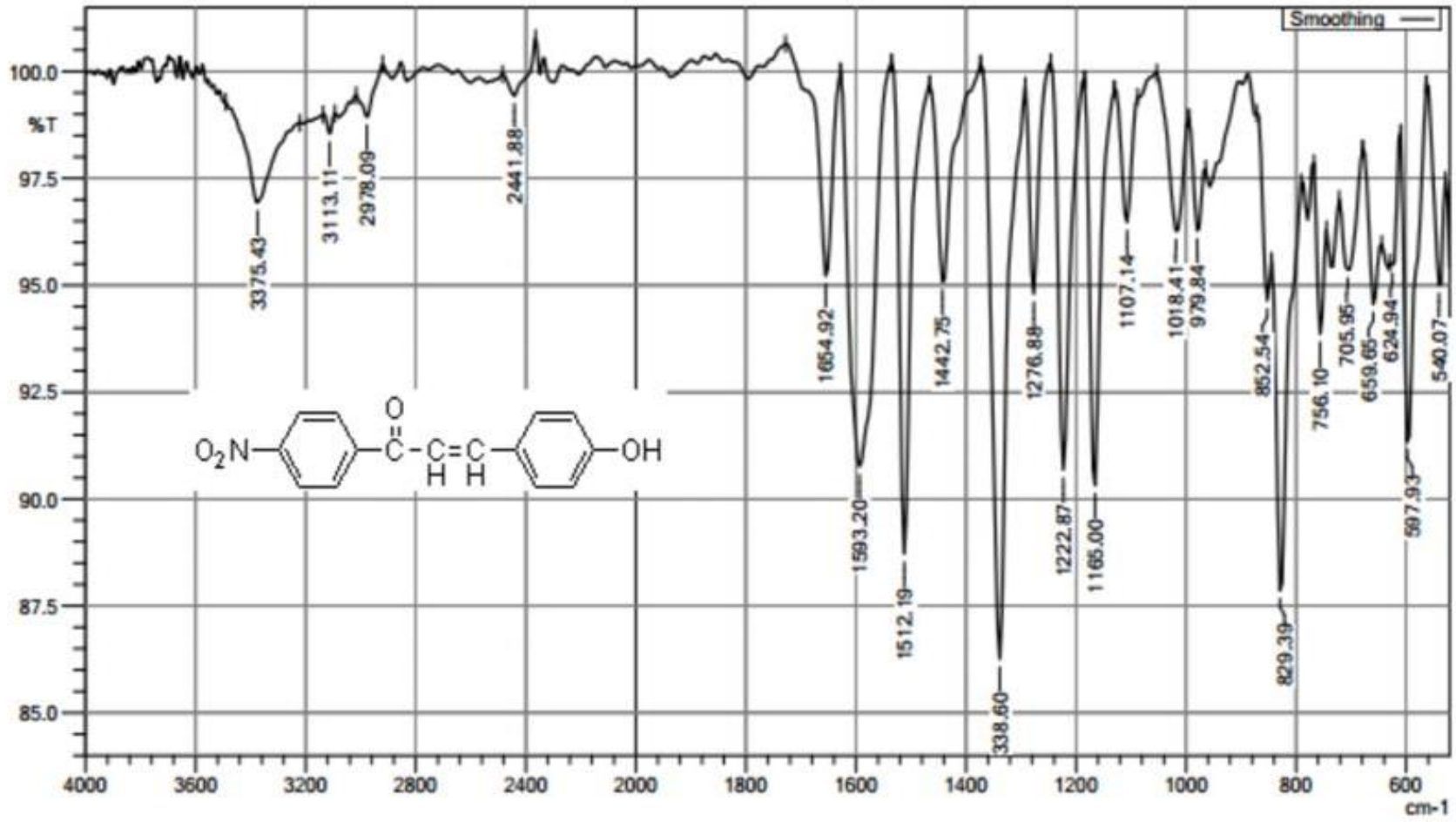


Figure 3.4: FT-IR of 3-(4-hydroxyphenyl)-1-(4-nitrophenyl) prop-2-en-1-one.

3.3. spectral data for compounds 1b-7b

3.3.1. FT-IR 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine.

The FT-IR data, of compounds 1b-7b, are recorded in the experimental section, while the selected FT-IR spectra of compounds 1b-7b are shown in Figures 3.5 . Aromatic ring C-H stretching modes occur in the range 3003.45 cm^{-1} [78]. The main absorption peaks at 2935.63 cm^{-1} and 2844.22 cm^{-1} were identified and assigned to asymmetric and symmetric CH_3 and CH_2 stretching, respectively [79]. In the frequency range of 1656.54 cm^{-1} band (C=N) appeared. At 1506.48 cm^{-1}, there is another strong band that belongs to the carbon-carbon double bond [76]. Aromatic rings indicate C=C skeletal stretching vibrations at 1590.33 cm^{-1}.

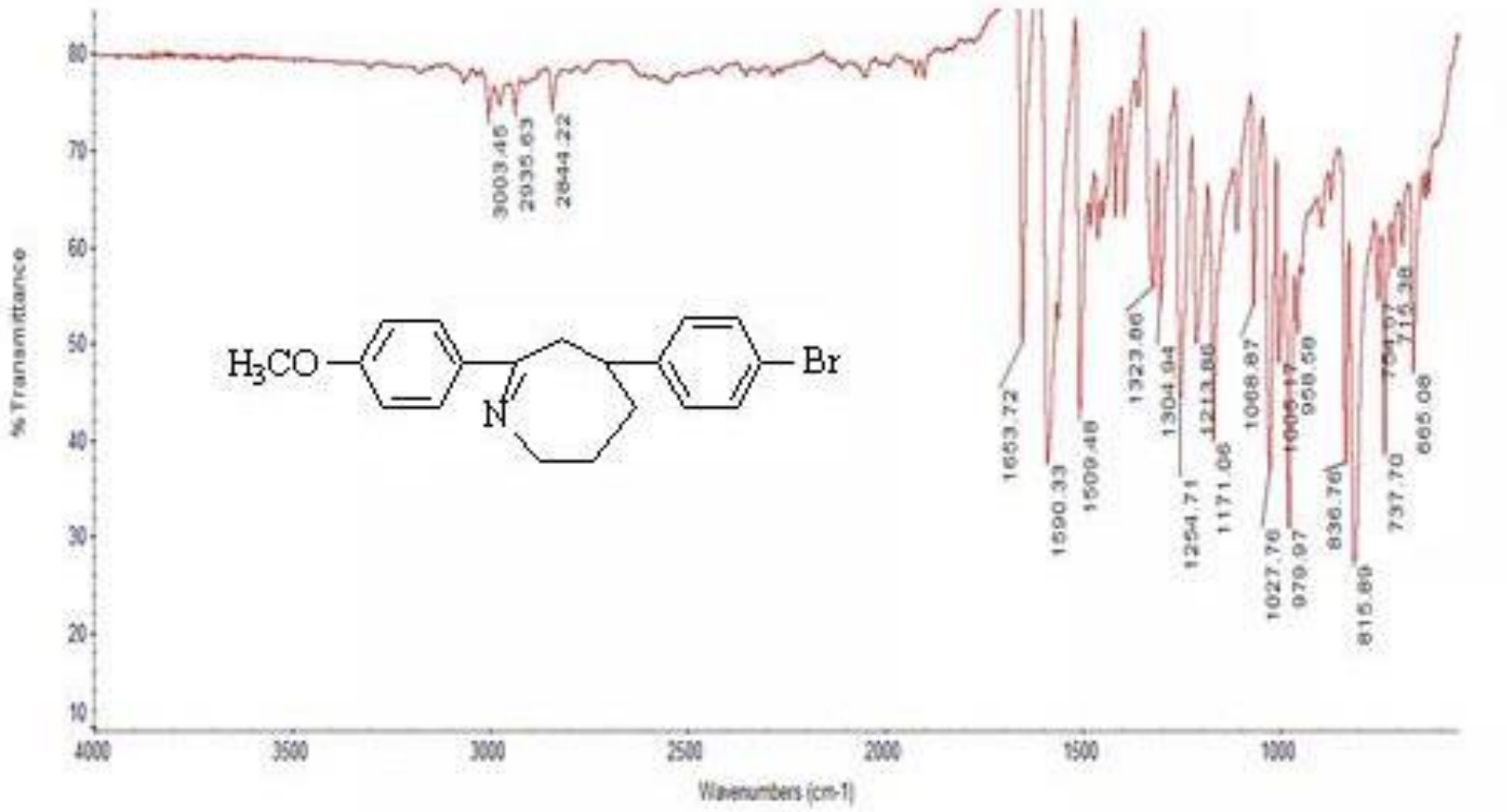


Figure 3.5: FT-IR of 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine.

3.3.2. ^{1}H-NMR 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine.

The ^{1}H-NMR spectra for all compounds 1b-7b are described in the experimental section, and the results are as follows, the signal in the rang at δ= 7.7-8.3 ppm can be ascribed to the presence C-H aromatic. The aromatic signals of protons H2 appeared as a multiplets in the δ= 3.4 ppm. The occurrence of the triblet at δ = 3.7 ppm can be ascribed to H1, while H5 appeared as a doublet at δ = 2.5 ppm , and a Qurtate signals for proton H3at the of δ= 3.2 ppm. Another observation multiplets at the chemical shift δ= 1.17 ppm is H4, while the singalet signal due to the protons O-CH_3 δ= 3.9 ppm. The ^{1}H-NMR spectrum of compounds 1b -7b is shown in Figures 3.6 [80,81].

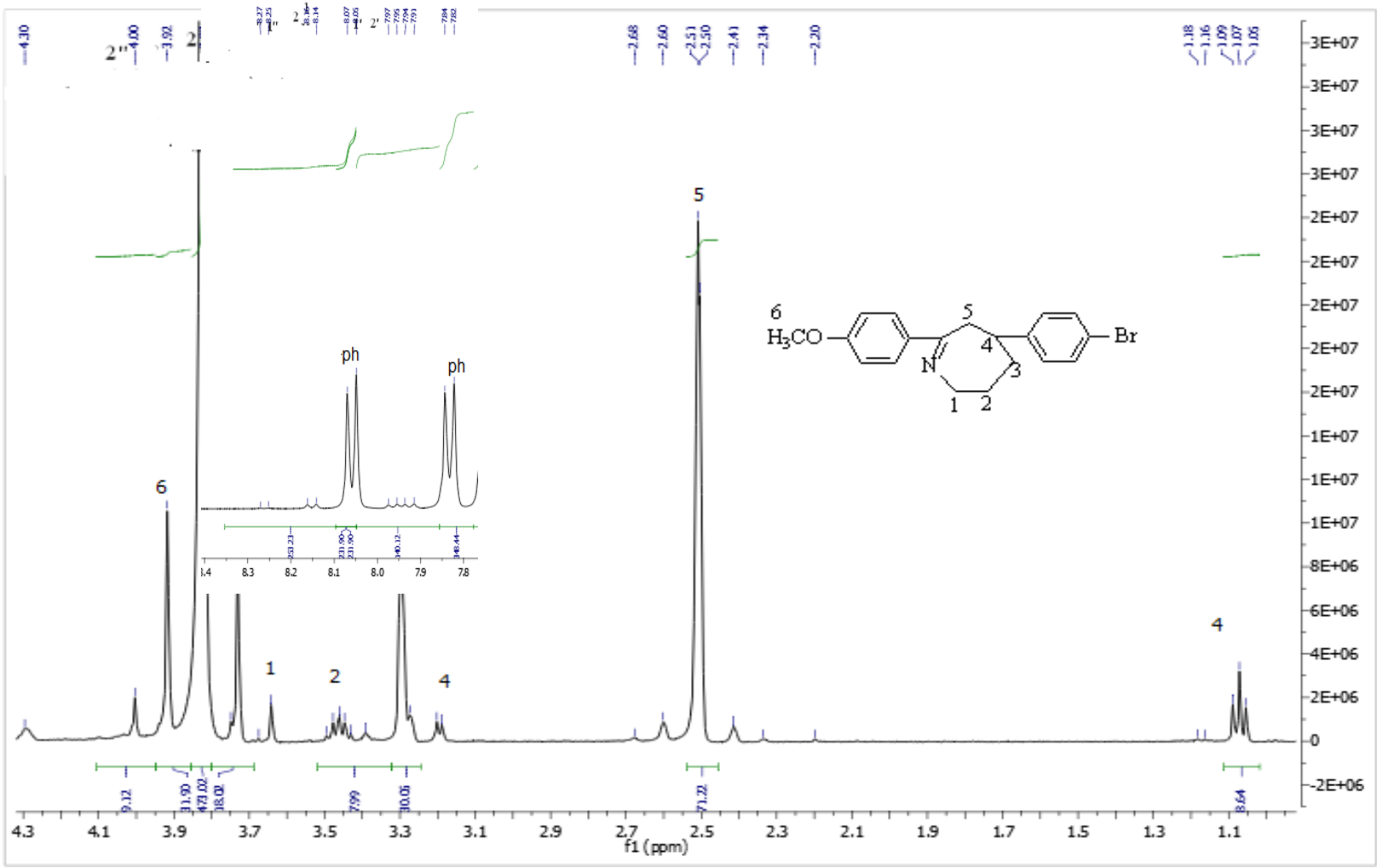


Figure 3.6: [1]HNMR of 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine.

3.3.3. ^{13}C-NMR 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6 tetrahydro-2H-azepine

The ^{13}C-NMR spectrum of compounds 1b-7b is shown in Figures 3.7 respectively. ^{13}C-NMR spectra of all compounds 1b-7b are listed in the experimental section as shown in the following results:The ^{13}C-NMR spectra are recorded in the experimental section that show the signals in the region of δ =55.7ppm distinctive for the O-CH_3. The resonances due to the aromatic carbons ph-Br aromaticon the chemical shift in the range of δ= 131.83 ppm, and ph-OCH_3 δ= 127.5 ppm, the chemical shift at δ =162.14 ppm attributed toC1. On the other hand, the chemical shift at δ = 145.13ppm is assigned to C4. The chemical shift which is at δ= 137 ppm is assigned to C3 At a high field, a singlet at range δ= 119.43 ppm due to the C5 , and C2 at δ= 114.64ppm.

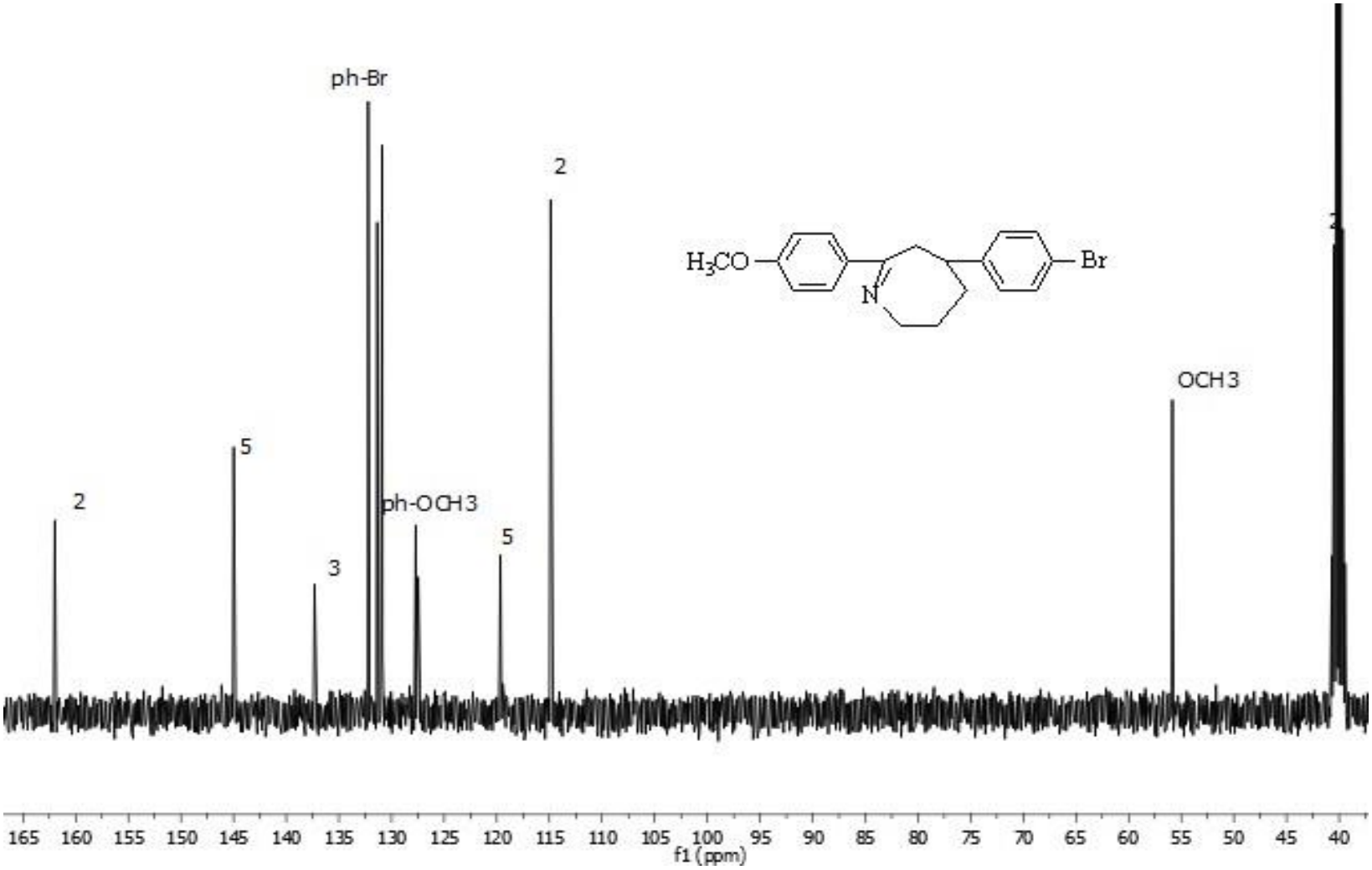


Figure3.7: 13CNMR of 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine.

Table 3.1: The CHNX of Chalcones.

no.	C%	H%	N%	X%
1a	69.6 (68.7)	4.3 (3.5)		Cl, 13.7 (12.9)
a2	64.9 (64.0)	3.6 (2.7)		Cl, 25.6 (24.9)
3a	55.9 (55.0)	3.1 (2.7)		Cl, 11.0 (10.5)
4a	62.6 61.5))	3.5 (2.7)	4.9 (3.9)	Cl, 12.3 (11.5)
a5	69.8 (68.9)	4.7 (3.7)	5.4, (4.7)	Cl, 13.8 (12.9)
6a	59.4 (58.7)	3.6 (2.7)		Br, 26.4 (25.7)
7a	55.9 (55.0)	3.1 (2.6)		Cl, 11.0 (10.3) Br, 24.8 (23.9)
8a	49.2 (48.5)	2.7 (1.9)		Br, 43.7 (42.9)

9a	54.2 (53.4)	3.0 (2.5)	4.2 (3.7)	Br, 24.1 (23.5)
10a	59.6 (58.9)	3.9 (3.0)	4.6 (3.7)	Br, 26.4 (25.5)
11a	75.5 (74.9)	5.5 (4.8)		
12a	70.4 (69.7)	4.7 (3.9)		Br, 12.99 (12.0)
13a	60.5 (59.7)	4.1 (3.3)		Br, 25.2 (24.5)
14a	67.8 (66.9)	4.6 (3.8)	4.9 (3.9)	
15a	75.8 (74.4)	5.9 (5.0)	5.5 (4.7)	
16a	66.8 (65.5)	4.1 (3.5)	5.2 (4.4)	
17a	62.6 (61.6)	3.5 (2.6)	4.9 (4.0)	
18a	67.1 (66.9)	4.5 (3.5)	10.4 (9.4)	

Table 3.2: The CHNX of 7 – membered Heterocyclic compounds.

NO.	**C%**	**H%**	**N%**	**X%**
1b	63.7 (62.8)	5.6 (4.8)	3.9 (3.0)	Br, 22.3 (21.4)
2b	59.6 (58.7)	4.7 (3.8)	3.9 (3.0)	Br, 22.0 (21.3) Cl, 9.8 (9.0)
3b	67.9 (66.9)	5.4 (4.6)	4.4 (3.5)	Cl, 22.3 (21.4)
4b	57.9 (56.9)	4.6 (3.9)	7.5 (6.9)	Br, 21.4 (20.6)
5b	53.1 (52.3)	4.2 (3.6)	3.4 (2.7)	Br, 39.3 (38.6)
6b	59.6 (58.8)	4.7 (3.9)	3.9 (3.0)	Br, 22.0 (21.3) Cl, 9.8 (8.9)
7b	72.7 (71.9)	6.4 (5.6)	4.5 (3.7)	Cl, 11.3 (10.5)

3.3.4: Spectra TGA of Seven-Member Rings Heterocyclic Compounds (1b-7b).

The thermal stablty of Compound TGA peak appeared at a temperature of 278.3, this is an indication that the compound is thermally stable at this temperature. The appearance of a small peak at 129 indicates the exit of carbon dioxide. From the foregoing information, it is clear that the compound is free of the groups of both types of water (adsorbent and absorbent), and also the temperature indicates the same degree that was determined as the melting point. (Figure3.8)

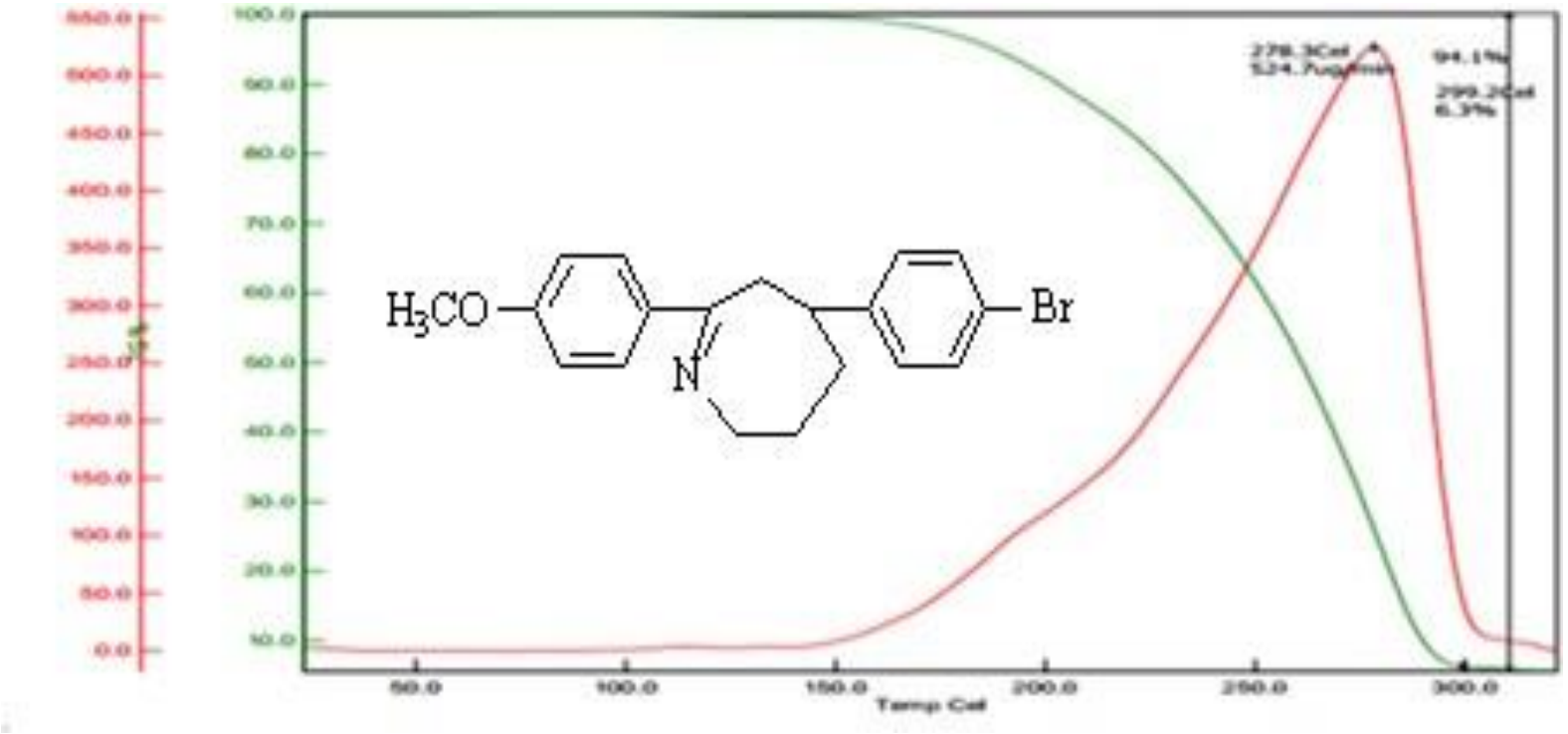


Figure 3.8: TGA of 5-(4-bromophenyl)-7-(4-methoxyphenyl)-3,4,5,6-tetrahydro-2H-azepine .

3.4. Conclusion

Synthesize and characterize new heterocyclic Compounds and study their thermal stability as a step for future work.

A reaction many warred out by mixing equal proportions of aromatic acetophenone that is substituted with aldehydes.

The second step was performed by reacting the last product with aliphatic diamines.

The results showed obtaining of 7-membered heterocyclic Compounds, these Compounds are charted using FT-IR ^{1}H-NMR, ^{13}C-NMR and TGA The Thermal stability.

The TGA analysis show the thermal stability of Compound TGA peak appeared at a temperature certain this is an indication that the compound is thermally stable at this temperature

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الخالصة

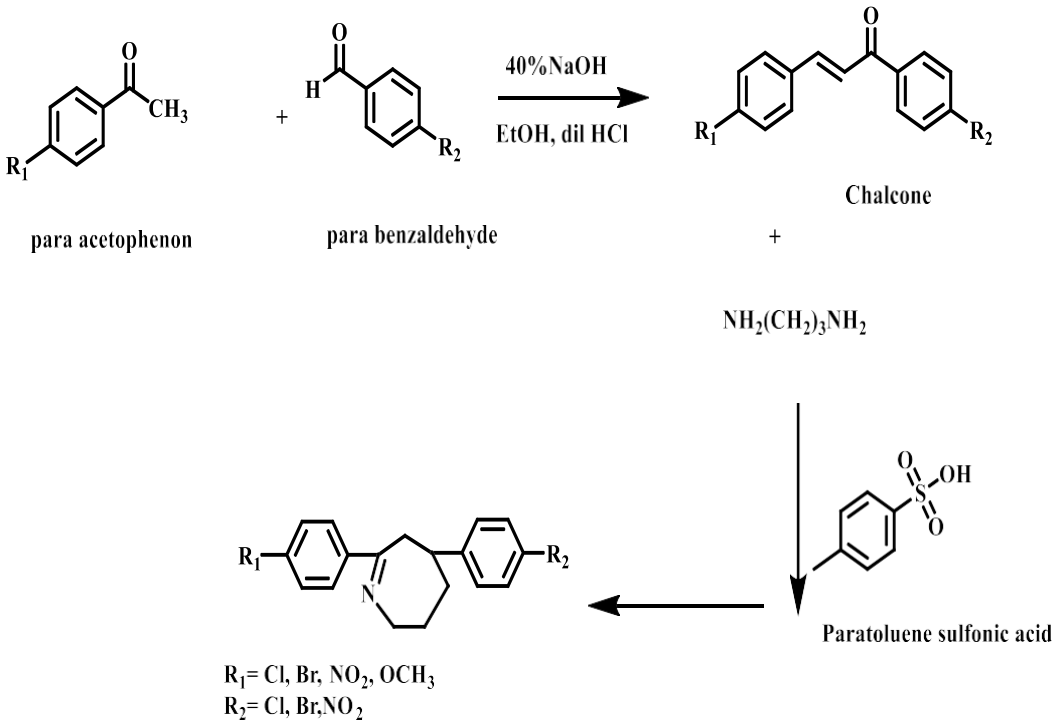
السمممال الريبيسممية لمرلبال الحلقية مير المتجانسممة ي أن بع الذرال أو للها مرتبطة في حلقال بما في ذلك ذرة واحدة من العناصر على أألقل بدَلً من الكربون.

الهدف التحضير مرلبال الجالكون باجراء تفاعل بموَلل متساوية من أألسيتوفينون مع أألد ايدال.

في الخطوة الثانية تم تحضير الحلقال السباعية عن طريق تفاعل الجالكون المحضر مع ثنايي امين أليفاتي.

أظهرل النتايج الحصول على حلقية سباعية مير متجانسة تم تشخيصها باستعمال FT-IR, ^{1}H- NMR, ^{13}C-NMR TGA والثبال الحراري .

يوضح تحليل التحليل الحراري الوزني)TGA(أن الثبال الحراري لقمة التحليل الحراري الوزني)TGA(ظهر عند درجة حرارة معينة ، و ذا مؤشر على أن المرلب مستقر حرارياً عند درجة الحرارة ذه.



جمهورية العراق

وزارة التعليم العالي والبحث العلمي

جامعة ألأنبار

كلية العلوم قسم

الكيمياء

تحضير وتشخيص مشتقات حلقية سباعية غير متجانسة من مركبات الجالكون

رسالة مقدمة الى كلية العلوم - جامعة ألأنبار وهي جزء من متطلبات نيل شهادة الماجستير في علوم الكيمياء

قدمت من قبل

حنان الطيف ياسين عبد الهيتي

بكالوريوس علوم كيمياء - جامعة االنبار 2018

إشراف

أ.م .د . مروان محمد فرحان

1443 م

2021 م