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# SYNTHESIS AND USES OF CHALCONE IN HETROCYCLIC SYNTHESIS

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## ABSTRACT

This review deals with synthetic methods of chalcones and their use in synthesis of heterocyclic compounds. The data and method of synthesis, chemical reaction and biological activities of these heterocycles published over the last years are reviewed here.

**KEYWORDS:** Chalcones, isoxazole, Pyrazoline, pyrimidone, thiopyrimodone, benzothiazepine, benzodiazepine.

## 1. INTRODUCTION

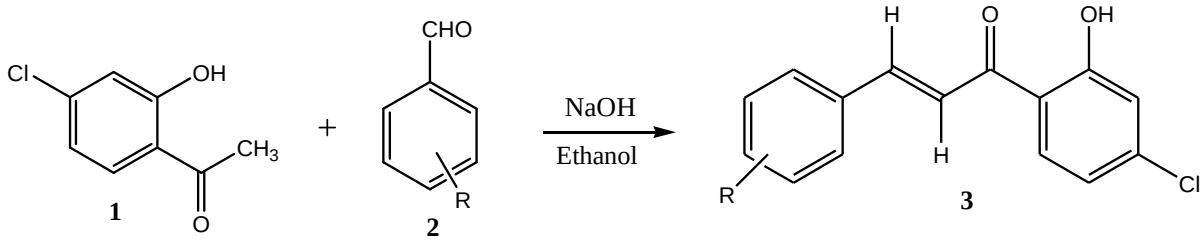
Chalcones are common natural pigment and one of the important intermediate of in biogenesis of Flavonoide. Chalcones have board spectrum of biolological activities such as Anticancer, Anti- inflamatory, Antioxidant, Antimicrobial, Antiplatalate and Antihyperglacemic activity. [1] The general structural formula is $Ar—CH=CH-CO-Ar$ and name chalcone was given by Kostanecki and Tambor.[2] The Chalcone bear very good synthon so that variety of novel heterocycles with good pharmaceutical activity have synthesized. One of the best methods to synthesize chalcone via Claisen-Schimidth Condensation.[3] Which involved cross Aldol Condensation of appropriate benzaldehyde and acetophenone in presence of base catalyst results in to αβ unsaturated carbonyl compound.

## 2. SYNTHETIC METHODS

There have been a number of practically important routes to synthesis of chalcones.

### 2.1) Synthesis of 4'-cloro, 2'-hydroxy chalcone

Anti bacterial 4'-cloro, 2'-hydroxy chalcone **3** extensively studied and reported by condensation of 2-hydroxyacetophenone **1** with different series of aldehyde **2 (scheme 1).**[4]

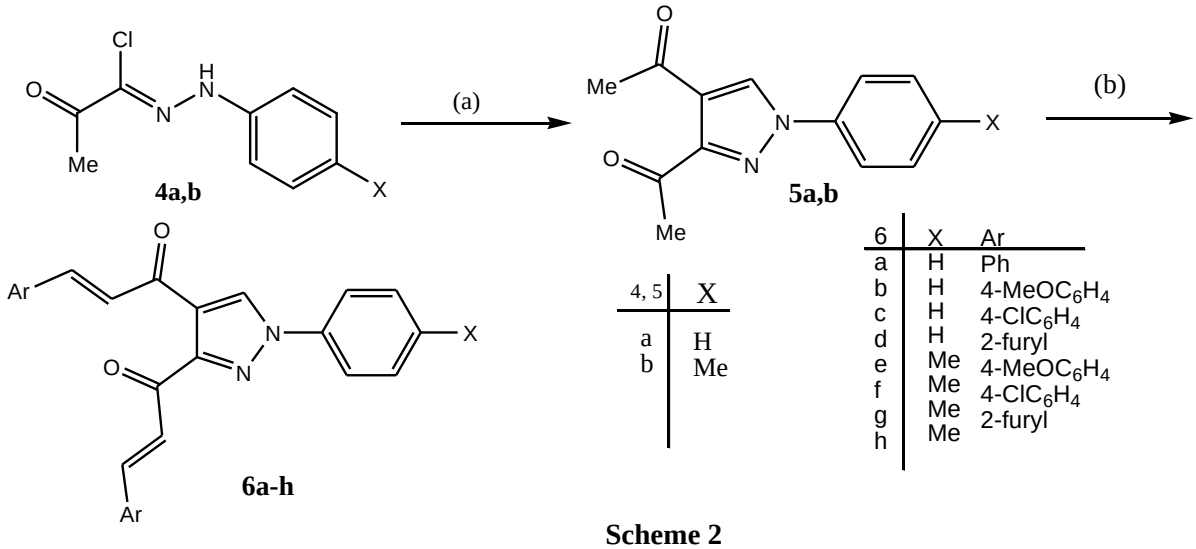



1R= H , 2R= 4-Cl , 3R= 2,4 -Cl , 4R= 2-$OCH_3$ 4-Cl

**Scheme 1**

### 2.2) N-arylpyrazoles 3, 4-Bis-chalcone:-

Microwave-assisted Synthesis of Novel N-arylpyrazoles 3,4-Bis-chalcones **6** were reported by condensation of pyrazolo[3,4-d] pyridazine derivatives **5** with series of aldehydes in the presence 10 % NaOH (scheme 2).[5]

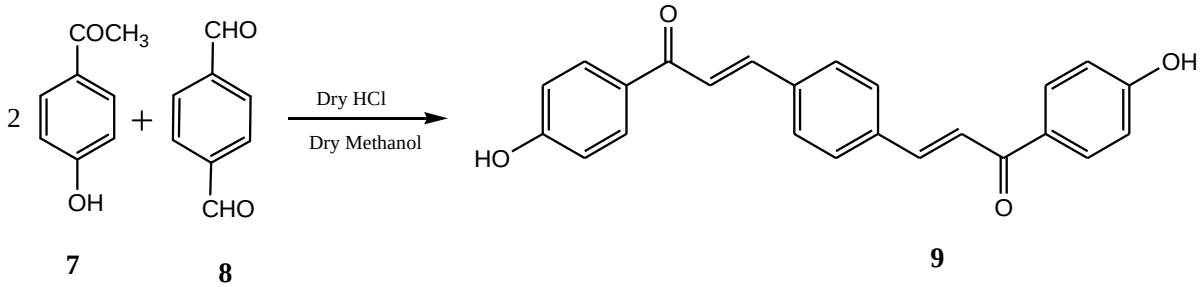



| 4, 5 | X |
|---|---|
| a | H |
| b | Me |

| 6 | X | Ar |
|---|---|---|
| a | H | Ph |
| b | H | 4-$MeOC_6H_4$ |
| c | H | 4-$ClC_6H_4$ |
| d | H | 2-furyl |
| e | Me | 4-$MeOC_6H_4$ |
| f | Me | 4-$ClC_6H_4$ |
| g | Me | 2-furyl |
| h | Me | |

**Scheme 2**

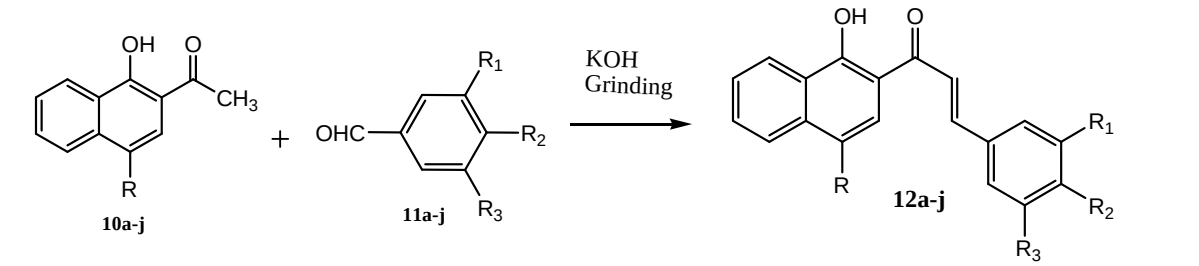
**2.3) Acid catalysed synthesis of Bis-chalcone:**-2 moles 4-hydroxyacetophenone **7** were treated with terephthaldehyde **8** in presence of HCl furnished to bis-chalcone **9**. (scheme 3).[6]




**Scheme 3**

### 2.4) Synthesis Chalcone by Grinding Technique

Series of chlacones **(12a-j)** were obtained by grinding acetyl-1-naphthol substituted 2-acetyl-1-naphthol (**10a-j**) with various substituted benzaldehydes at room temperature (**11a-j**) in the presence of solid KOH. (Scheme 4).[7]



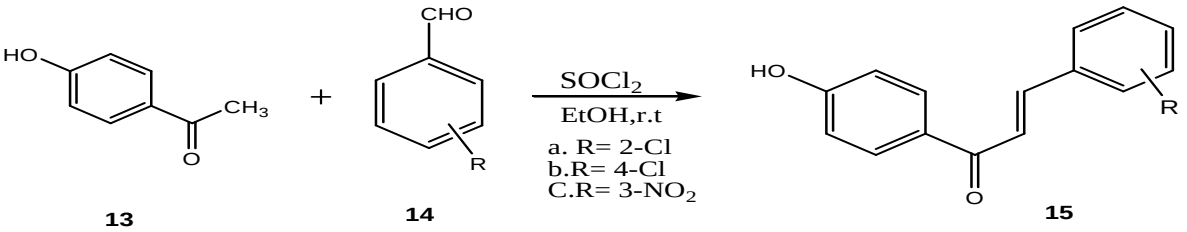

3a:R,$R_1$=H,$R_2$,$R_3$=$OCH_3$ 3b:R,$R_1$,$R_3$=H,$R_2$=$OCH_3$ 3c:R=I,$R_1$,$R_3$=H,$R_3$=$OCH_3$ 3d:R=Br,$R_1$=H,$R_2$,$R_3$=$OCH_3$ 3e:R=Br,$R_1$,$R_2$,$R_3$=$OCH_3$

3f:R,$R_1$,$R_3$=H,$R_2$=Cl 3g:R=I,R1,R3=H,R2=Cl 3h:R=Br,$R_1$,$R_3$=H,$R_2$=F 3i:$R_1$,$R_2$,$R_3$=H,$R_2$=F 3j:R=H,$R_1$,$R_2$,$R_3$=$OCH_3$

**Scheme 4**

### 2.5) $SOCl_2$ catalyzed synthesis of chalcone

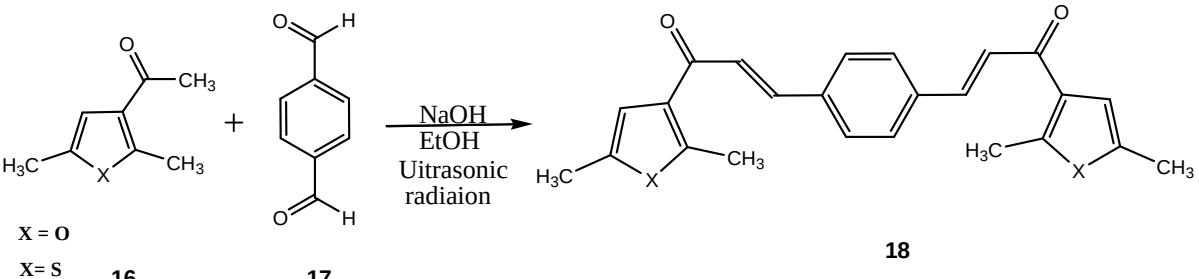
Reaction of 4-hydroxy acetophenone **13** with chloro benzaldehyde **14** in catalytic amount of $SOCl_2$ converted to 3 (2chlorophenyl)1(4hydroxyphenyl) prop-2en1one 15 (Scheme 5).[8]




**Scheme 5**

### 2.6) Ultrasonic radiation assisted synthesis of Bis-chalcones

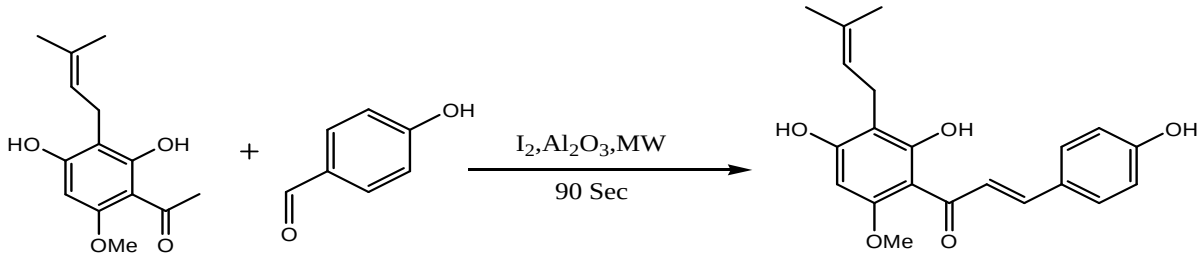
Photo physical and Electrochemically active Bis-chalcone derivative **18** were synthesized using aldol condensation reaction between acetyl-2,5-dimethylthiophene/3-acetyl-2,5-dimethylfuran **16** with terephthalaldehyde **17** via ultrasonic radiation (scheme 6).[9]




**Scheme 6**

### 2.7) Solvent free synthesis of chalcone

Highly bioactive prenylated hydroxychalcone Xanthohumol **21** was synthesized by the treatment of M-prynylated benzaldehyde **19** with p-hydroxyl benzaldehyde **20** in presence of iodine-alumina upon MW irradiation. (Scheme 7).[10]

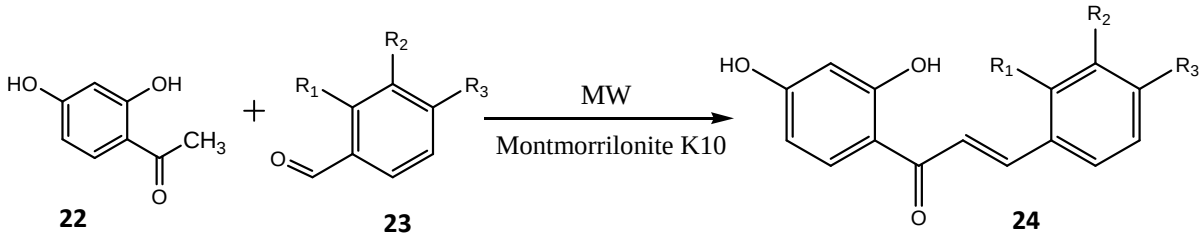



**19** **20** **21**

**Scheme 7**

### 2.8) Facile one pot synthesis of Chalcone

Reaction of dihydroxyacetophenone **22** with substituted aromatic aldehydes **23** in presence of catalytic amount of morpholine furnished to corresponding chalcones **24** (scheme8).[11]

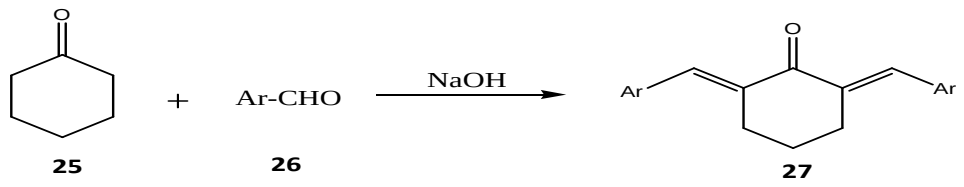



**22** **23** **24**

**Scheme 8**

### 2.9) Synthesis of bis-Chalcone

The bis chalcones 27 were synthesized from reaction of cyclohexanone **25** with subtitueded aldehydes 26 (scheme 9).[12]



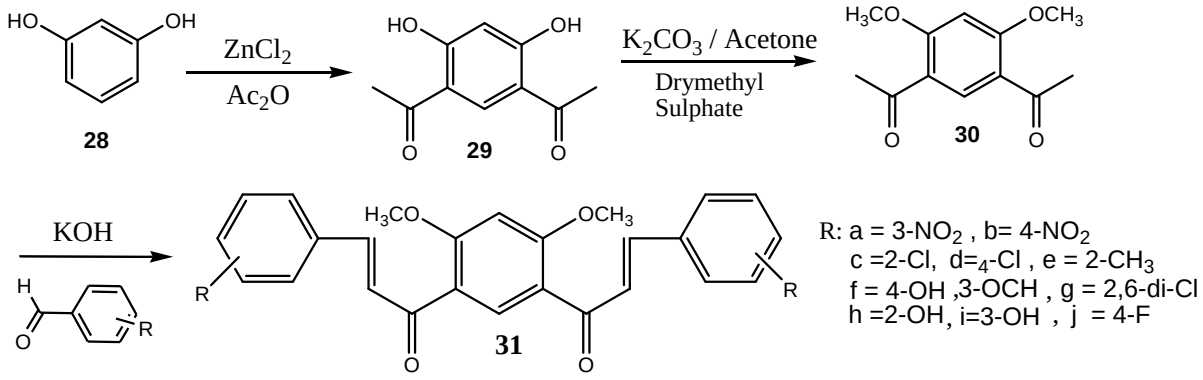

**25** **26** **27**

Ar = p-F-$C_6H_4$, p-Cl-$C_6H_4$, p-Br-$C_6H_4$, p-$CH_3$-$C_6H_4$, p-$OCH_3$-$C_6H_4$, p-$NO_2$-$C_6H_4$, $C_6H_5$-CH=CH, p-$N(CH_3)_2$-$C_6H_4$, H

**Scheme 9**

### 2.10) Synthesis of microbial active bis-chalcone

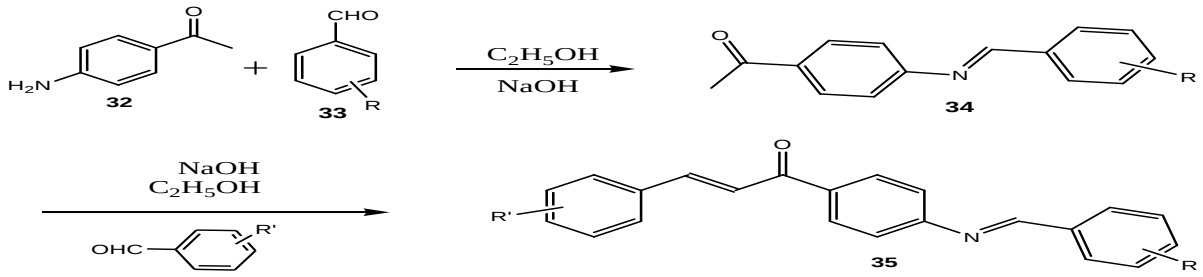
From the reaction of resorcinol **28** with acetic anhydride in presence of $ZnCl_2$ to afforded compound **29** which was reacted with $K_2CO_3$, Dimethyl sulphate furnished compound **30** which on treatment with aldehydes afforded the bioactive bis-chalcones 31 (scheme 10).[13]




**Scheme 10**

### 2.11) Synthesis of chalcone from Schiff base

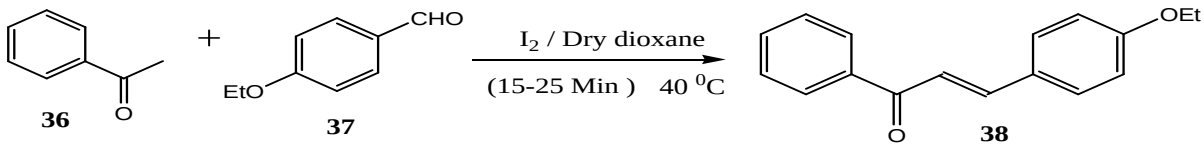
P-amino acetophenone **32** was treated with benzaldyde **33** resulted in to Schiff base **34** which on further reaction with benzaldyhde converted in to chalcone **35** (Scheme 11).[14]




**Scheme 11**

### 2.12) Iodine catalyzed synthesis of chalcone

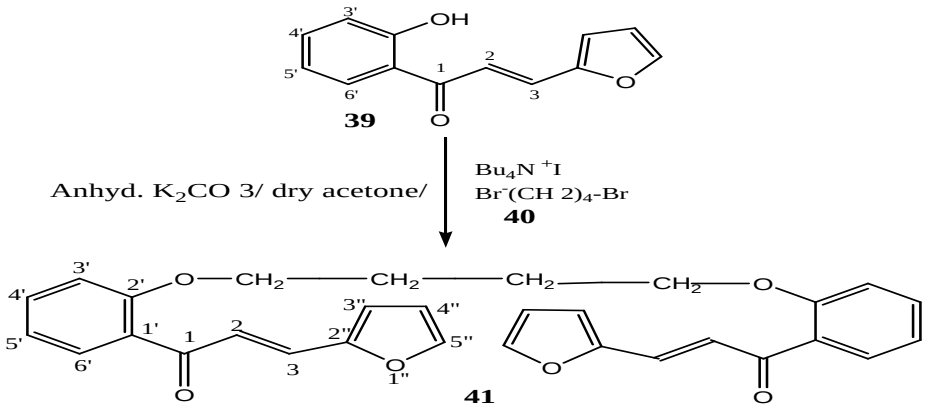
Synthesis of **38** was reported by reaction acetophenone **36** and 4-ethoxy benzaldehyde **37** in presence of catalytic amount of iodine (Scheme 12). [15]




**Scheme 12**

### 2.13) Synthesis of bis chalcone using PTC

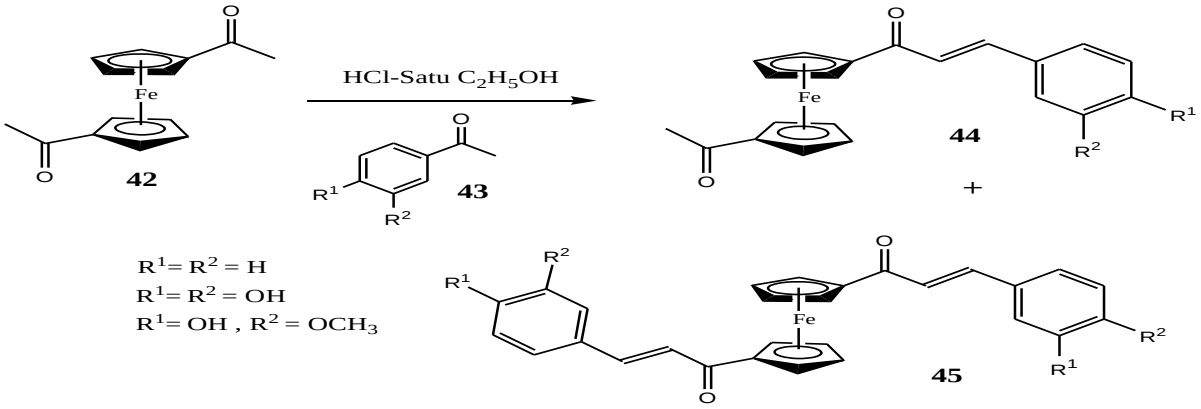
Furanyl chalcone **39** was reacted with 1,4-dibromobutane **40** presence of anhydrous $K_2CO_3$ and tetra butyl ammonium iodide (PTC) in dry acetone afforded to Antibacterial bis furanyl chalcone **41** (Scheme13). [16]




**Scheme 13**

### 2.14) Synthesis of chalcone using ferrocene

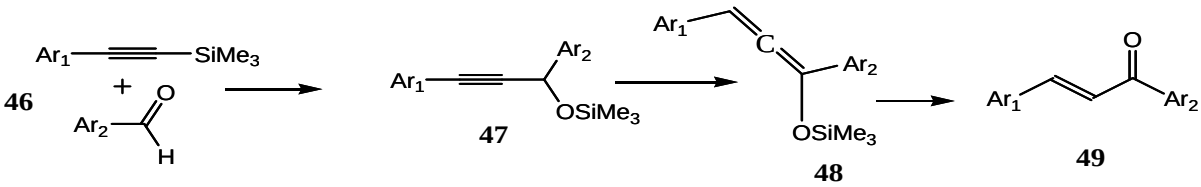
Treatment of diacetyl ferrocene **42** with benzaldehyde **43** furnished in to cinnamoyl ferrocene chalcone **44** and bis-cinnamoyl ferrocene chalcone **45** (Scheme 14).[17]




**Scheme 14**

### 2.15) One-pot synthesis of chalcone

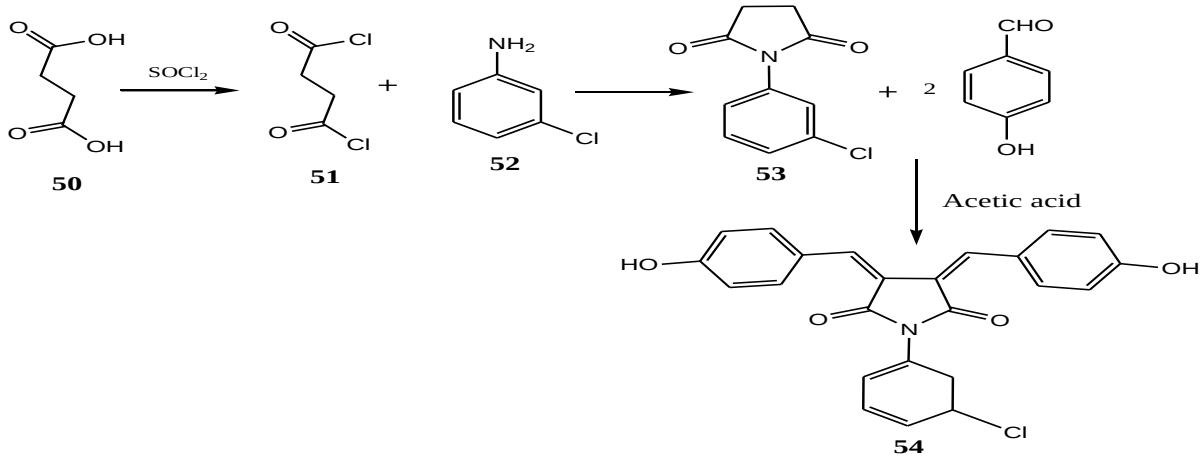
1,3-diaryl-2- propenyl sillyl ether **47** were obtained by the reaction of sillyl acetylenes **46** with aldehyde catalyzed by a chiral ammonium fluoride and potassium t-butoxide resulted in to corresponding siloxy allene **48** which on Acid treatment converted in to Z chalcones derivatives 49 (scheme 15).[18]




**Scheme 15**

### 2.16. Synthsis of bis-chalcone from succinamide

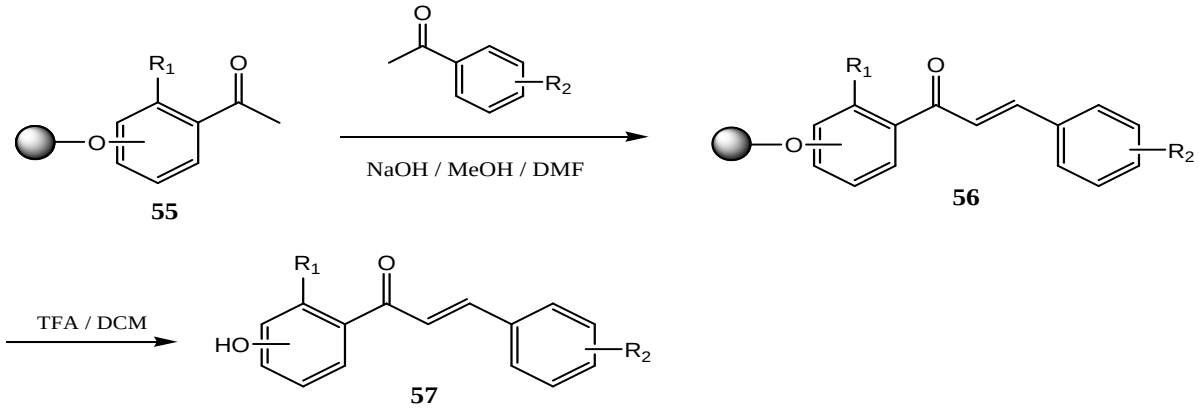
The three component reaction of succinic acid **50**, thionyl chloride **51** and Meta chloro aniline **52** furnished into phenyl substituted succinamide **53** which was treated with two moles of benzaldehydes afforded to bis-chalcone **54**. (Scheme 16).[19]




**Scheme 16**

### 2.17) Solid Phase Synthesis of Chalcones

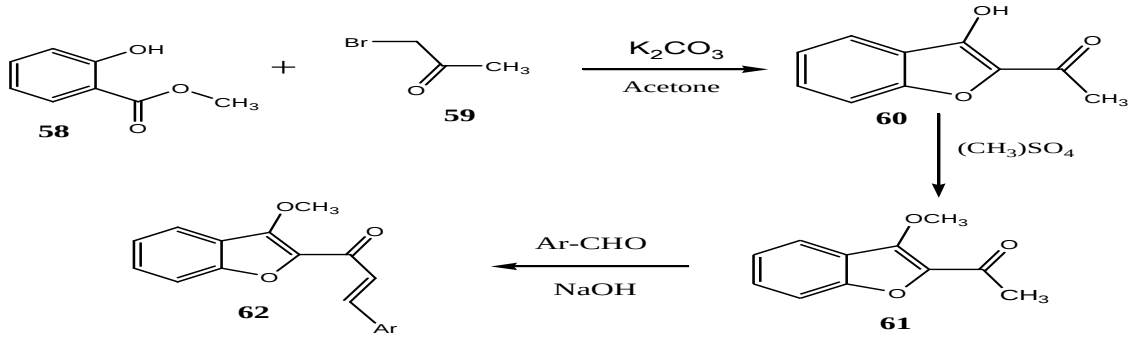
The resin-attached aldehydes **55** were condensed with either substituted methyl ketones**56** with NaOH in l0% MeOH-DMF at room temperature for 24 h converted to comp **56**. Resins were washed furnished in to chalcone **57**. (Scheme 17).[20]




**Scheme 17**

### 2.18) Synthesis using benzofuran

Methyl ortho hydroxyl benzoate **58** was reacted with α bromo ketone **59** in potassium carbonate cyclised in to 2-Hydroxy-3-methoxybezofuran **60** it was treated with methyl sulphate afforded to 2-Acetyl-3-methoxybezofuran **61** were condensed with aldehyde in 60% NaOH converted in to Bezofuranyl chalcones **62** (Scheme 18).[21]



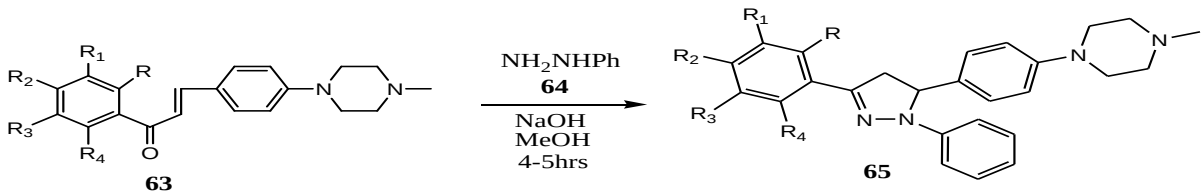

**Scheme 18**

## 3. USE IN HETEROCYCLIC SYNTHESIS (CHEMICAL REACTION)

### 3 .1) Synthesis of five member heterocyclic compound

#### 3.1.1) Synthesis pyrazoline by using chalcone

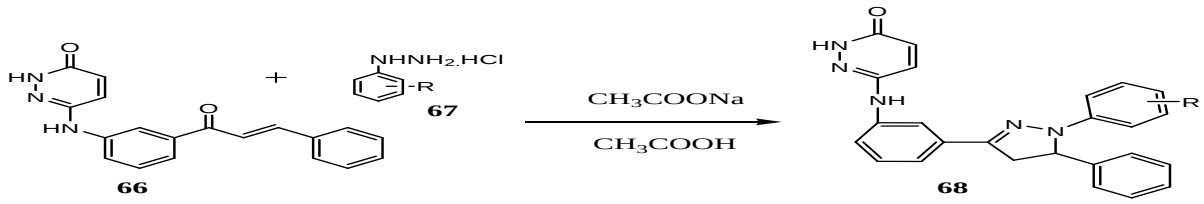
Synthesis of Pyrazole **65** was reported by treatment of chalcone **63** with phenyl hydrazine **64** in presence NaOH and ethanol (Scheme 19). [22]




**Scheme 19**

#### 3.1.2) Synthesis of pyridazine pyrazole

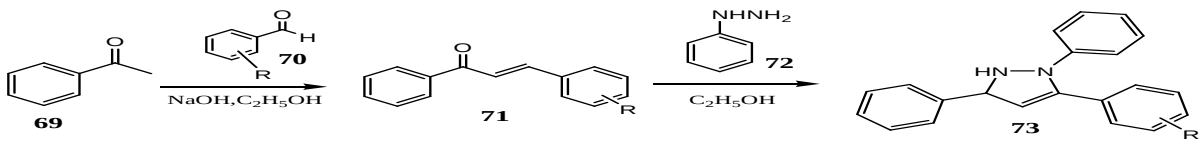
pyridazine chalcone **66** reacted with phenyl hydrazine **67** in presence sodium acetate and acetic acid furnished in to pyridazine pyrazole **68**. **(Scheme 20).** [23]




**Scheme 20**

#### 3.1.3) Synthesis of triphenyl pyrazole

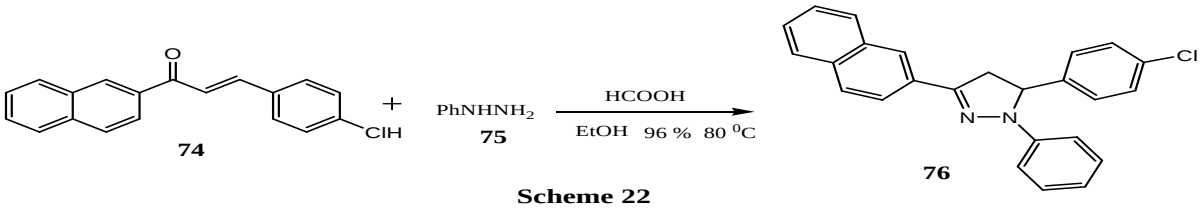
Reaction of Acetophenone **69** and benzaldehyde **70** in presence NaOH afforded chalcone **71** which was treatment with phenyl hydrazine**72** furnished in to in to triphenyl pyrazoline **73** (Scheme21). [24]




**Scheme 21**

### 3.1.4) Facile Synthesis tri substituted pyrazoline

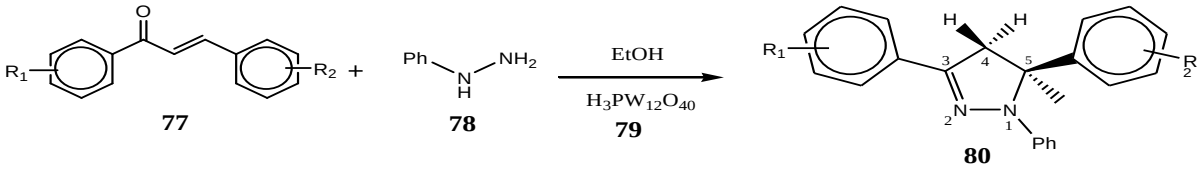
Synthesis of tri substituted pyrazoline derivative**76** was reported by condensation of chalcone **74** with phenyl hydrazine **75** in presence of formic acid under thermal condition (Scheme 22 ).[25]




**Scheme 22**

### 3.1.5) Synthesis of pyrazoline by heterogeneous catalyst

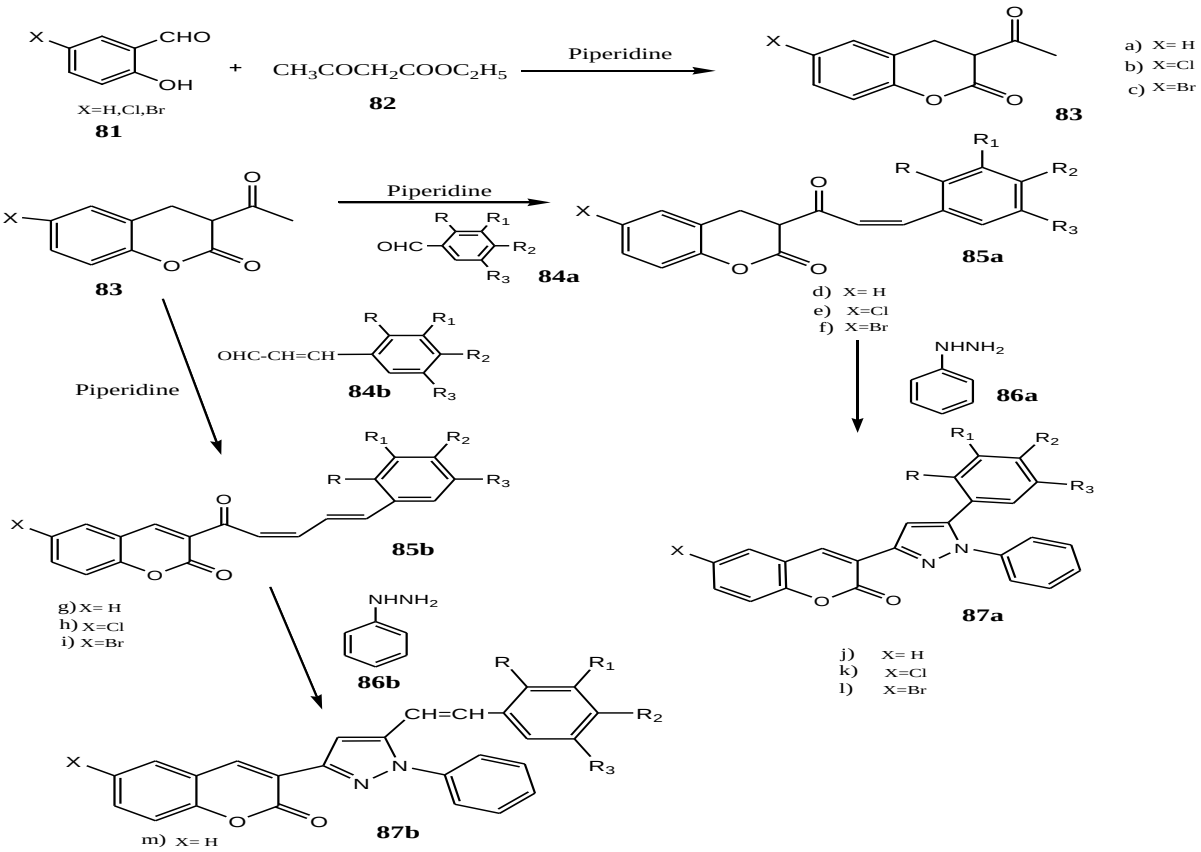
Novel 1,3,5- Triaryl-2-Pyrazoline **80** was extensively studied and reported by treatment of chalcone **77** with phenyl hydrazine **78** in presence of 4 mole % HTP ( $H_3PW_{12}O_{40}$ ) **79** heterogenous catalyst . (Scheme 23).[26]




**Scheme 23**

### 3.1.6) Synthesis pyrazole by cumarinyl chalcone

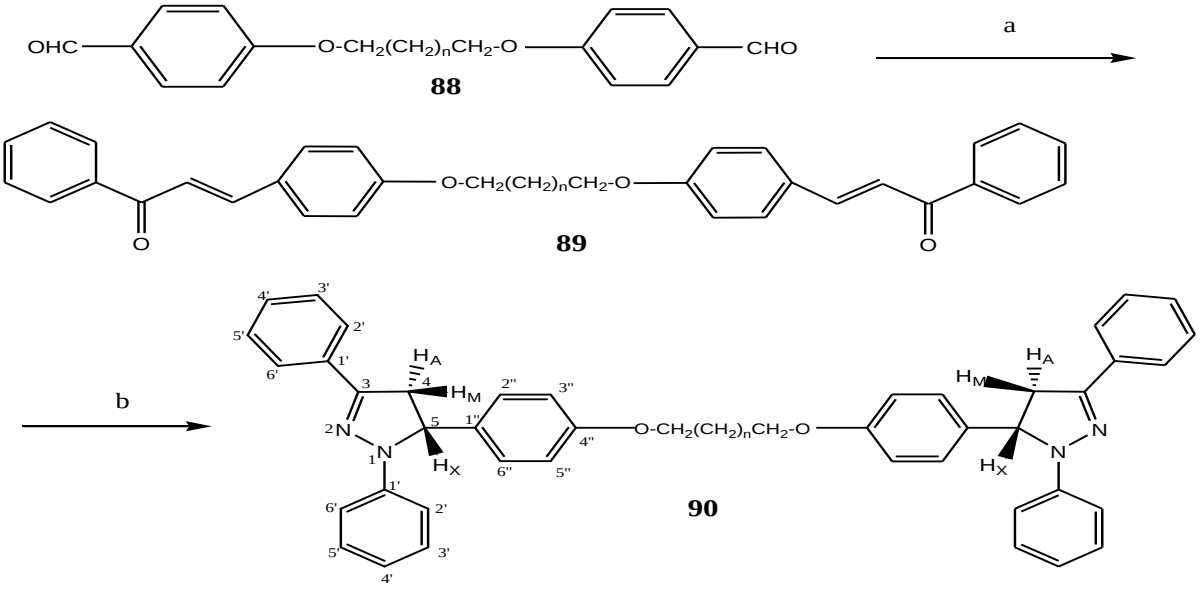
3-Acetyl-6-bromocoumarin **83** was prepared from of 5-bromosalicylaldehyde **81** and ethylacetoacetate **82** in presence of catalytic amount of piperidine. Aromatic aldehyde **83a** and **83b** upon microwave irradiation with compound **84a** & **84b** furnished to chalcones **85a** and **85b**. They were refluxed with phenyl hydrazine **86a** and **86b** afforded to pyrazole derivative 5-{(4'-N, N'-Dimetyl amino phenyl)-1-phenyl-2-pyrazoline} coumarin **87a,** 5-{(4'-N, N'-Dimetyl amino phenyl)-1-phenyl-2-pyrazoline-3"-yl} coumarin **87b** (Scheme 24).[27]




**Scheme 24**

### 3.1.7) Synthesis of Bis-pyrazoline from Bis-Chalcone

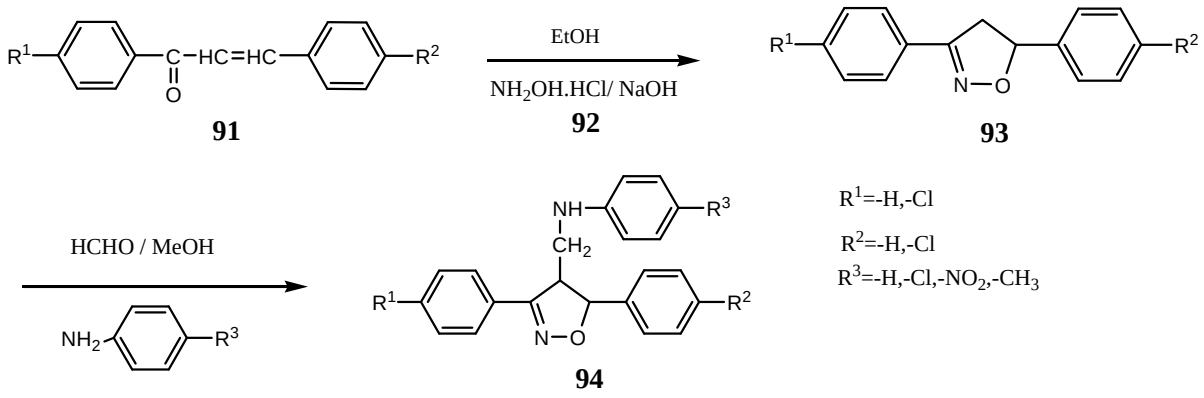
Synthesis of antibacterial and antifungal Bis-pyrazoline **90** was reported by reaction of bis-chalcone **89** with two moles phenyl hydrazine. Bis- chalcone was synthesized by reaction with bis- aldehyde 88 and acetophenone.(Scheme25).[28]




**Scheme 25**

### 3.2.1) Synthesis of isoxazoline from chalcone

Synthesis of Biologically active mannich base isoxazoline **94** was reported by reaction of isoxazoline **93.** The isoxazole 93 was synthesized by condensation of chalcone **91** with hydroxyl amine hydrochloride **92** (Scheme26).[29]

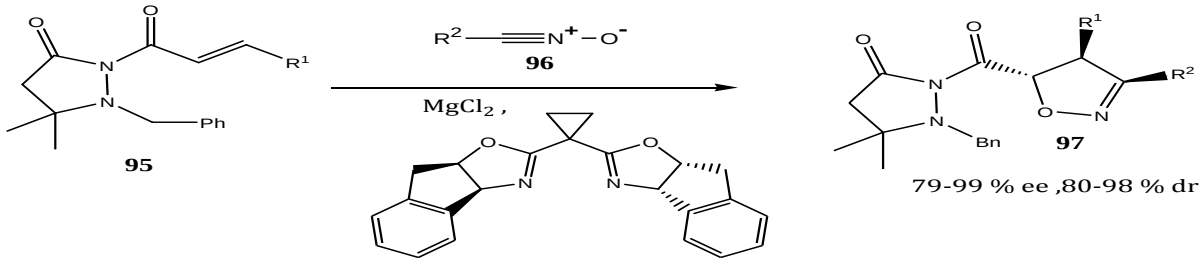



**91** **92** **93** **94**

**Scheme 26**

### 3.2.2) Synthesis of optically active isoxazoline from chalcone

Stereo selective synthesis of isoxazoline **97** was reported by [3+2] cycloaddition reaction of α β unsaturated amide chalcone **95** with nitrile oxide **96** (Scheme 27).[30]

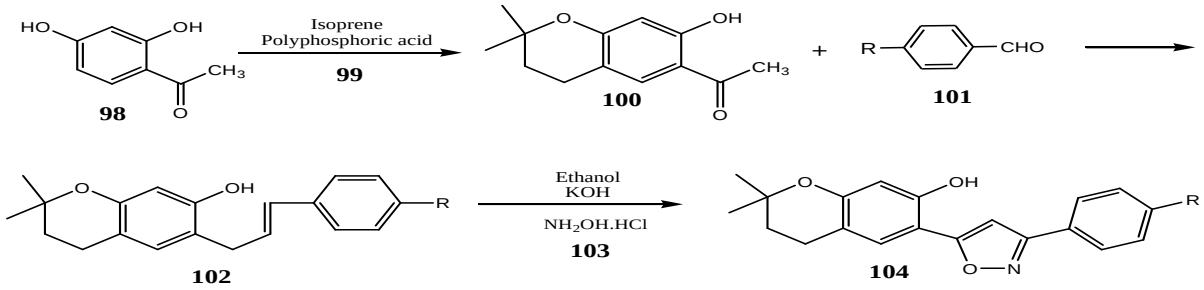



**95** **96** **97**

**Scheme 27**

### 3.2.3) Synthesis of novel isoxazole from chalcone

Synthesis of novel isoxazole **104** was reported by reaction of chalcone 102 with hydroxylamine hydrochloride. The chalcone **102** was synthesized from 2, 4 dihydroxy benzophenone. (Scheme 28).[31]

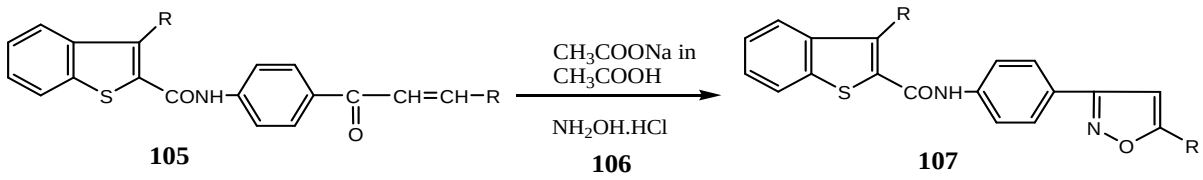



**98** **99** **100** **101** **102** **103** **104**

**Scheme 28**

### 3.2.4) Synthesis of isoxazole from chalcone

Microbially potent isoxazole **107** was extensively studied and reported synthesis by reaction of chalcone**105** with hydroxyl amine hydrochloride **106** in presence of sodium acetate in acetic acid. The chalcone was synthesized from the reaction of thiophenyl amino acetophenone with aromatic aldehydes (Scheme 29).[32]

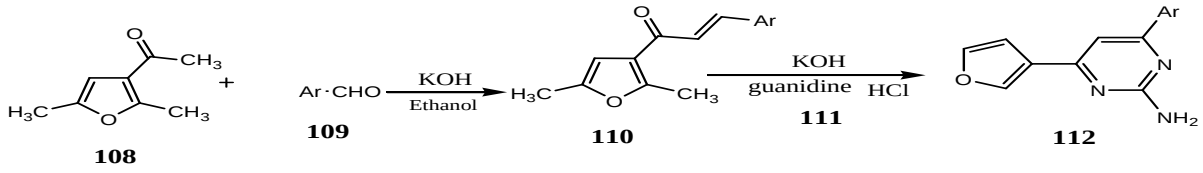



**Scheme 29**

### 3.3. Synthesis of six membered heterocycles

### 3.3.1) Synthesis of Furanyl pyrimidine from chalcone

Furanyl ketone **108** on treatment with aromatic aldehydes **109** afforded to chalcone **110** which was reacted with guanidine hydrochloride **111** in KOH furnished to pyrimidine **112**. (Scheme 30).[33]

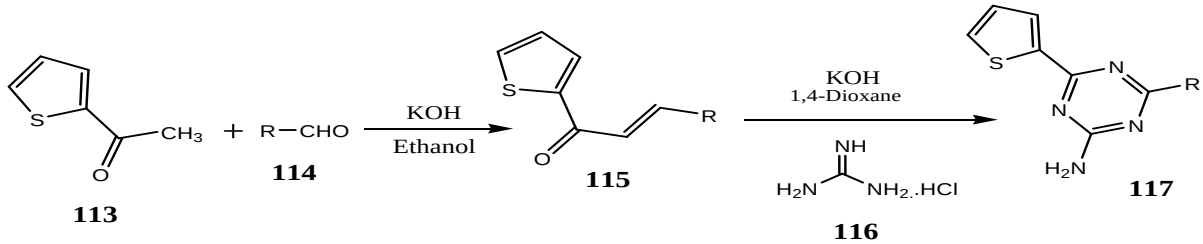



Ar = 3,4,5-trimethoxyphenyl
Ar = 4-chlorophenyl
Ar = 4-dimethylaminophenyl
Ar = 4-methylphenyl
Ar = 2,4-dichlophenyl

**Scheme 30**

### 3.3.2) Synthesis of thiopene pyrimidine from chalcone

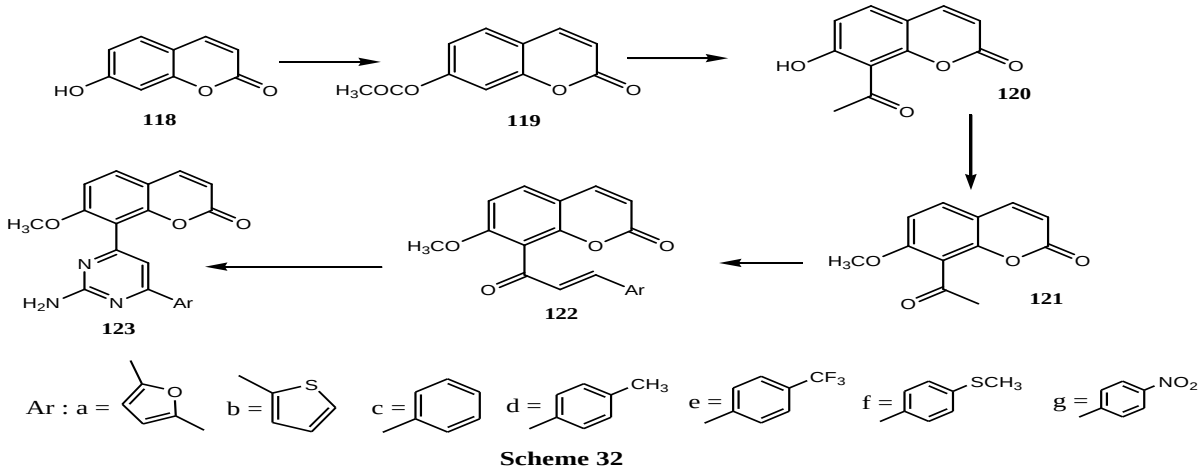
Synthesis of Analgesic and Antibacterial thiopene pyrimidine **117** was reported by condensation of chalcone **116** with guanidine hydrochloride **115**. Chalcone was obtained by reaction of thiophenyl ketone **113** with aldehyde **114** (Scheme 31).[34]




**Scheme 31**

### 3.3.3) Synthesis of coumarin pyrimidine from chalcone

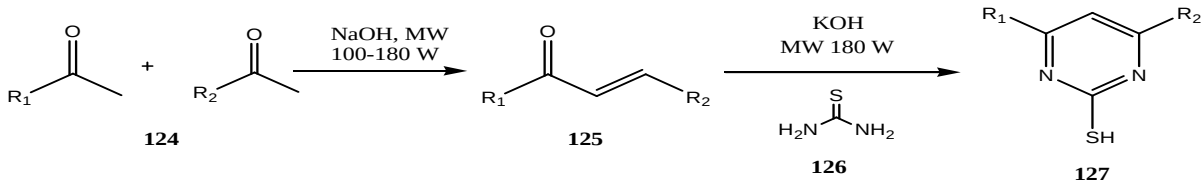
Synthesis of Vasorelaxsant coumarin pyrimidine **123** was reported in the given series of the reaction in which 7-hydroxy cumarin **118** on actylation converted to acetyl derivative of cumarin **119**, 8-acetyl-7-hydroxy cumarine **120** was obtained through fries rearrangement reaction. 8-acetyl-7-methoxy cumarine **121** was formed by reaction with $CH_3I$. It was treated with aromatic aldehyde afforded to chalcone **122** .which on treatment with guanidine hydrochloride afforded cumarin pyrimidine. (Scheme 32).[35]




**Scheme 32**

### 3.3.4) MW assisted Synthesis of thiopyrimidine from chalcone

Two moles aldehyde **124** in presence of NaOH upon MW irradiation converted to chalcone **125** which was on irradiated with thourea **126** afforded thiopyrimidine **127**. (Scheme 33). [36]

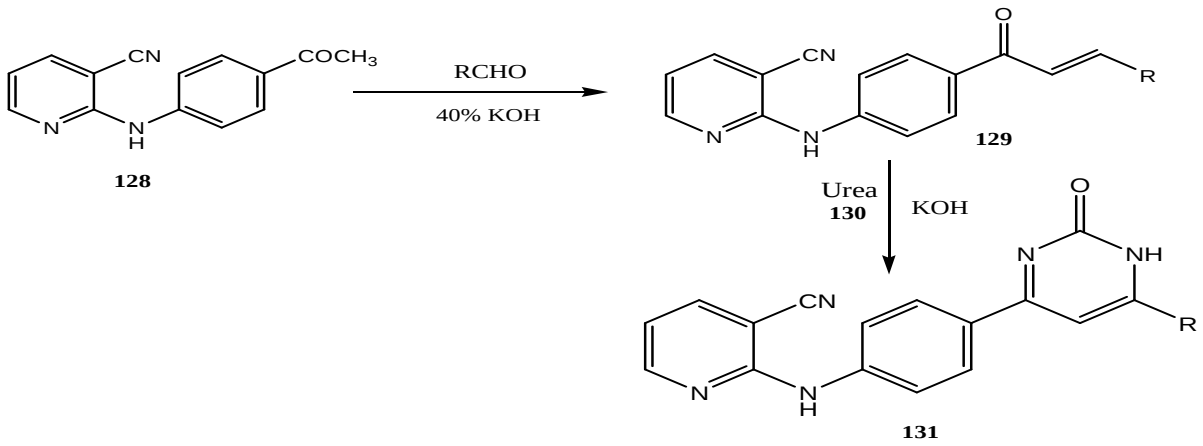



**Scheme 33**

### 3.4. Synthesis of pyrimidone derivative from chalcone

### 3.4.1) Synthesis of Phenyl amino pyridine pyrimidone

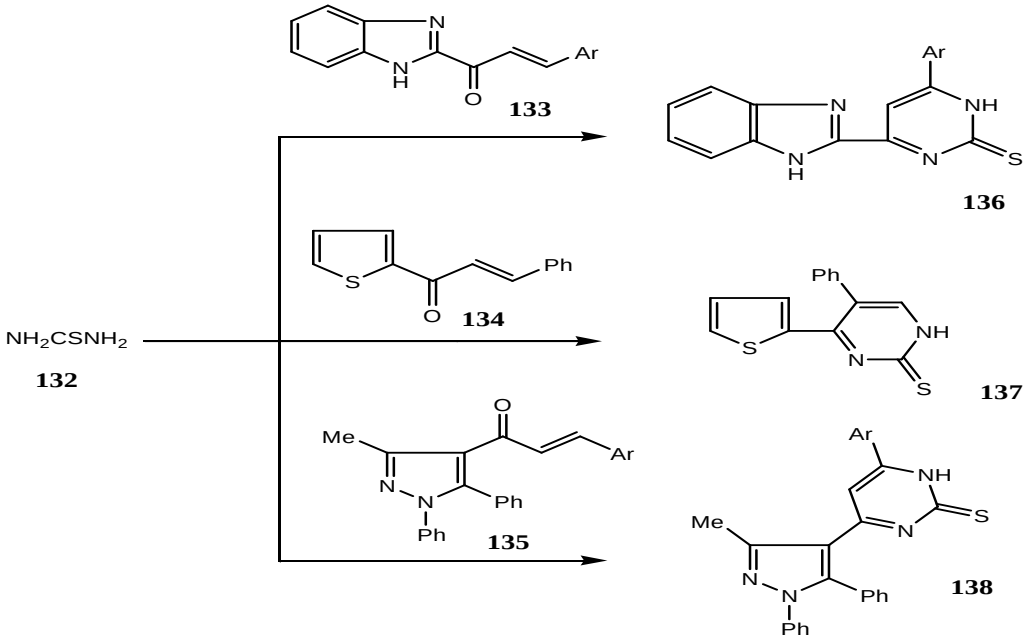
Phenyl amino pyridine ketone **128** condensed with aldehyde yielded chalcone **129** which was refluxed with urea **130** in alkaline medium converted to Antibacterial pyrimidone **131** (scheme 34).[37]




**Scheme 34**

### 3.4.2.) Synthesis of pyrimidone thione from chalcone

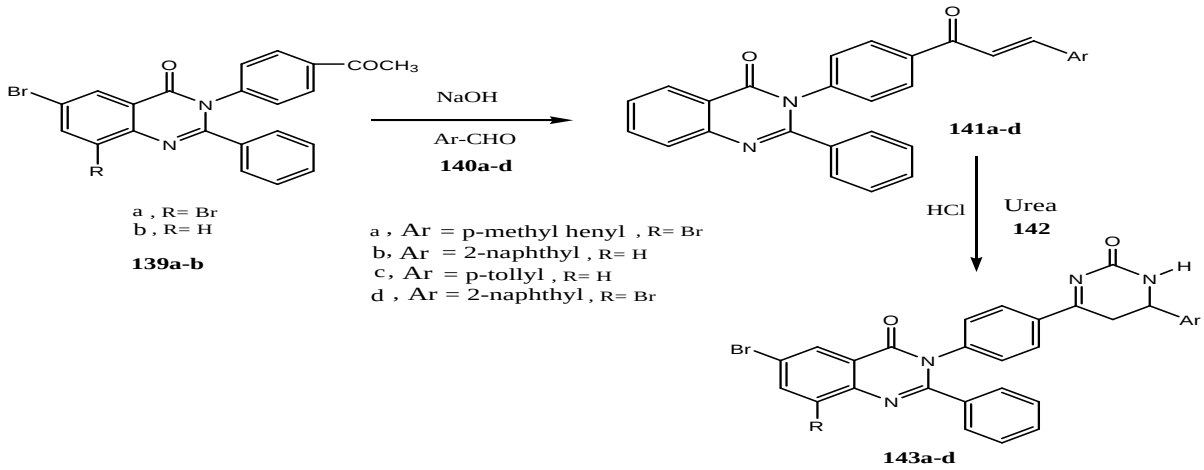
Thiourea **132** was condensed with Chalcone **133,134,135** converted in to pyrimidone thione **136,137,138** respectively. (Scheme 35).[38]




**Scheme 35**

### 3.4.3) Synthesis of Quionazole pyrimidone from chalcone

The compound 6,8-dibromo-2-phenyl-3-(4-acetylphenyl)-4(3H)-quinazolinone **139a-b** was achieved by fusion of the known, 6,8-dibromo-2-phenyl-4H-3,1-benzoxazin-4-one with p-aminoacetophenone. It was reacted with aldehyde **140a-d** converted to chalcone **141a-d.** It was refluxed with urea **142** resulted in to Anti-inflammatory and Analgesic Quionazole pyrimidone **143a-d**. (Scheme 36).[39]

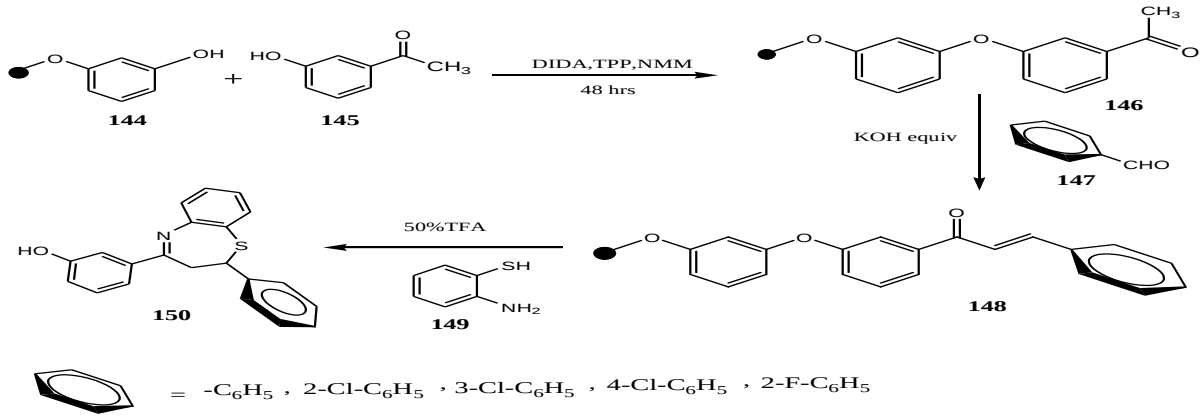



**Scheme 36**

### 3.5. Synthesis of seven membered heterocyclic compound

#### 3.5.1) Solid phase synthesis of benzothiazepine

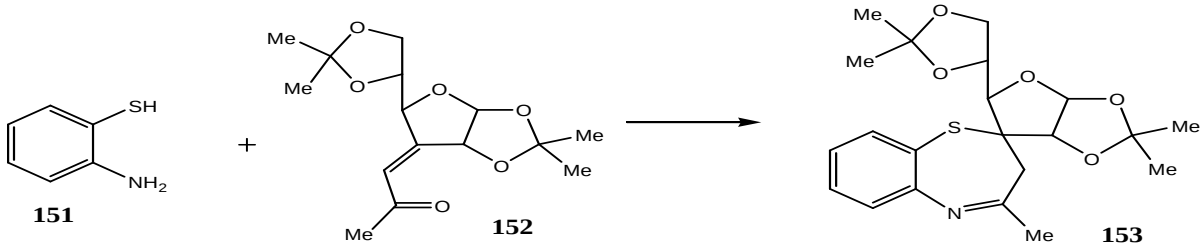
Reaction of comp **144** with acetophenone **145** gave compound **146** wich was on condensation with benzaldehyde **147** afforded chalcone **148.** The chalcone **148** on condensed with aminothiophenol **149** using resin as solid support furnished in to benzothiazepine **150** (Scheme 37).[40]




**Scheme 37**

#### 3.5.2) Synthesis of spiro benzothiazepine from chalcone

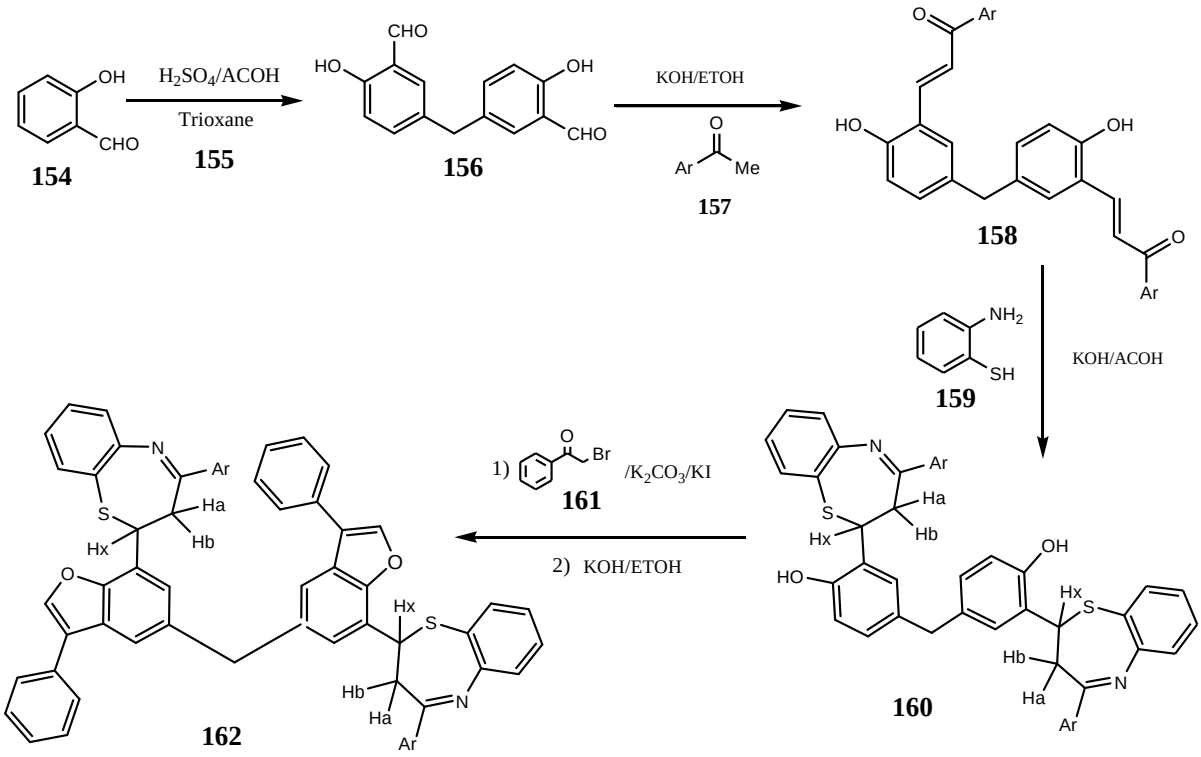
The aminothiophenol **151** was condensed chalcone **152** furnished in to spiro benzothiazepine **153**(Scheme 38).[41]




**Scheme 38**

### 3.5.3) Synthesis methylene-bis-benzofuranyl-[1,5]-benzothiazepines

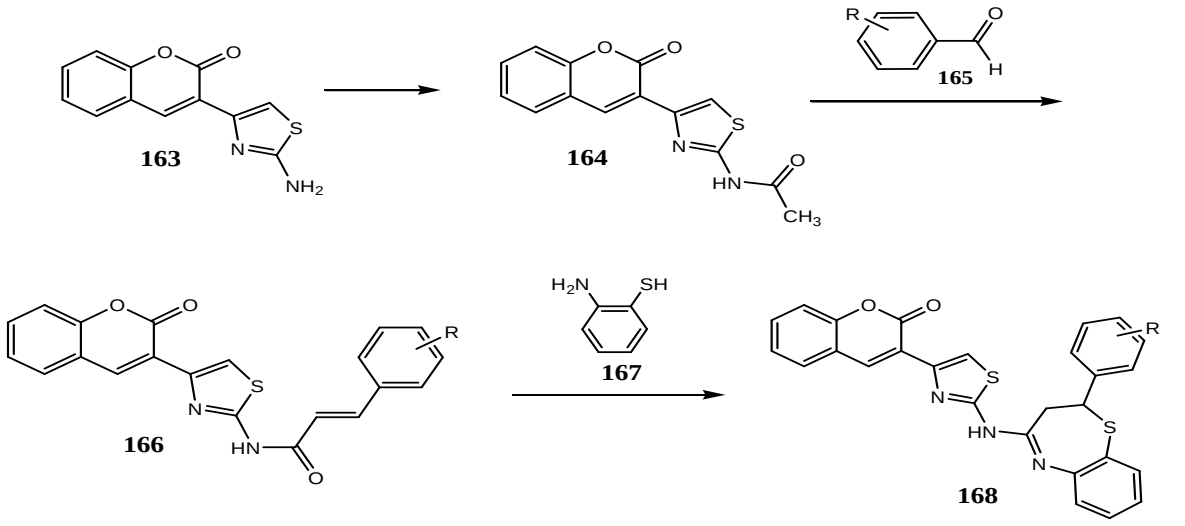
Synthesis of Bis- benzofuranyl benzothiazepine was reported by reaction of compound **154** with trioxane **155** in acidic condition afforded to compound **156.** It was further condensed with acetophenone **157** gave bis-chalcone **158.** It was reacted with aminothiophenol **159** converted to Bis-benzothiazepine **160** it was further reacted with Bromoacetophenone **161** in alkali media afforded the compound **162** (Scheme 39).[42]




**Scheme 39**

### 3.5.4) microwave assisted synthesis of benzothoazepine

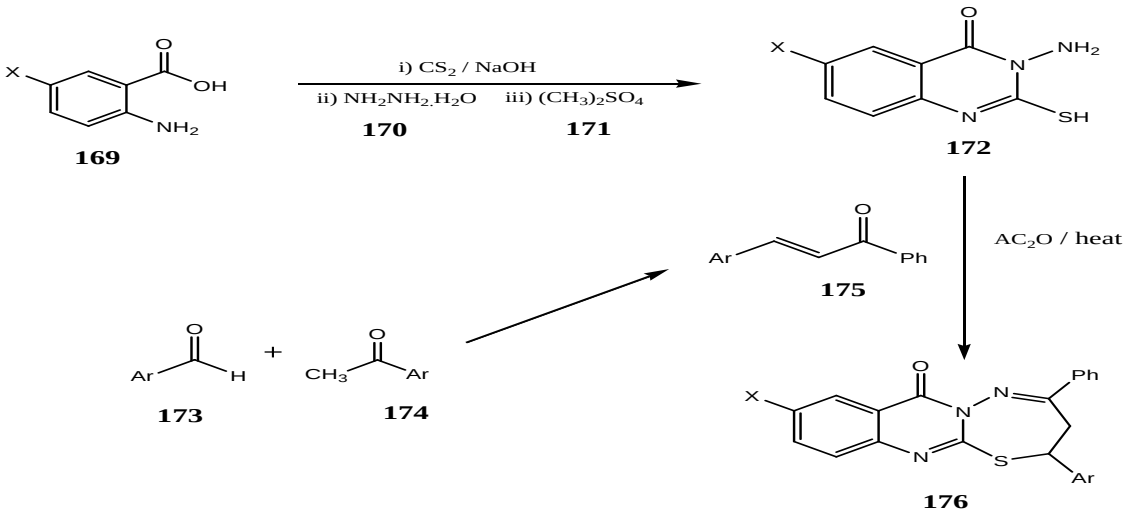
Study and synthesis of benzothoazepine **168** was reported by condensation of chalcone **166** with thioaminophenol **167** the corresponding chalcone was synthesized by acylation of compound **163** followed by treatment of aldehyde **165** (Scheme 40).[43]




**Scheme 40**

### 3.5.5) Synthesis of Quinazoline thiadiazepine

Substituted anthranilic acid **169** condensed with hydrazine hydrate**170** and dimethylsulphate**171** in alkaline carbon disulphide converted in to compound **172** which was refluxed with chalcone **175** furnished to Quinazolin Thiadiazepines **176**. The chalcone was prepared from compound **173** & **174** (Scheme 41).[44]

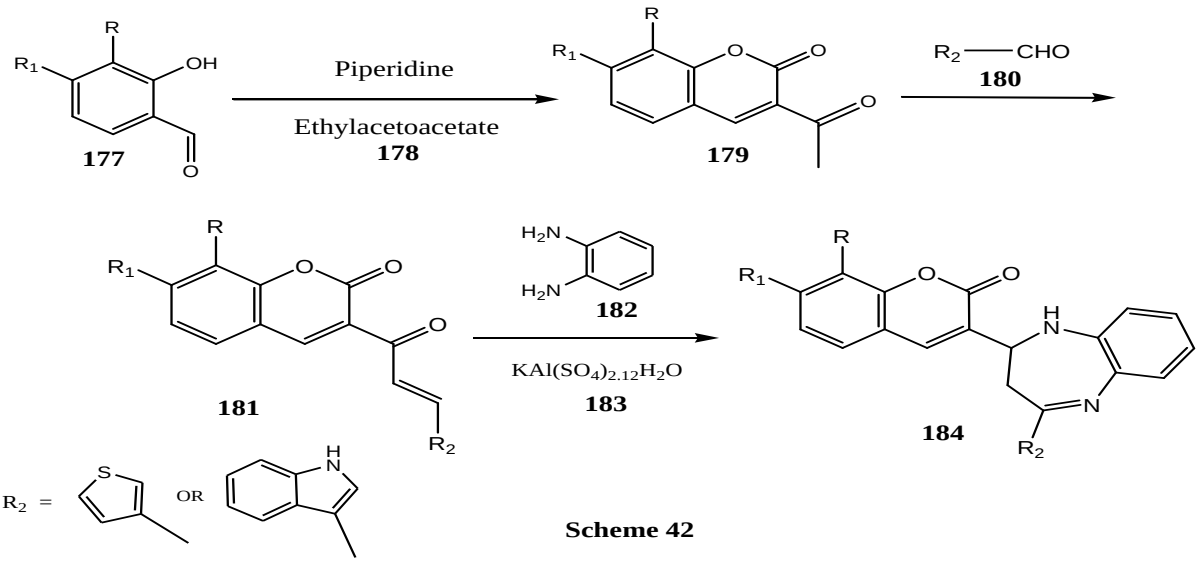



**Scheme 41**

### 3.6. Synthesis of benzodiazepine from chalcone

### 3.6.1) A S D catalyzed synthesis of benzodiazepine from chalcone

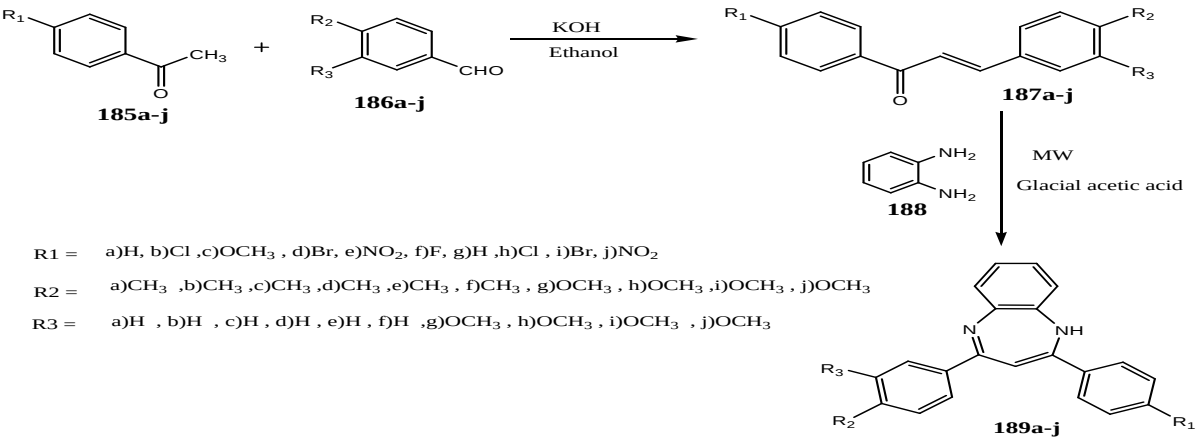
The compound **177** reacted with EAA **178** converted to compound **179.** It was treated with aldehydes **180** afforded to cumaryl chalcone **181.** The chalcone underwent ring closure with orthophenylene diamine 182 in presence of $KAl(SO_4)_2 12H_2O$ afforded the antioxidant benzodiazepine (Scheme 42).[45]




**Scheme 42**

### 3.6.2) MW assisted synthesis of 1,5-benzodiazepine

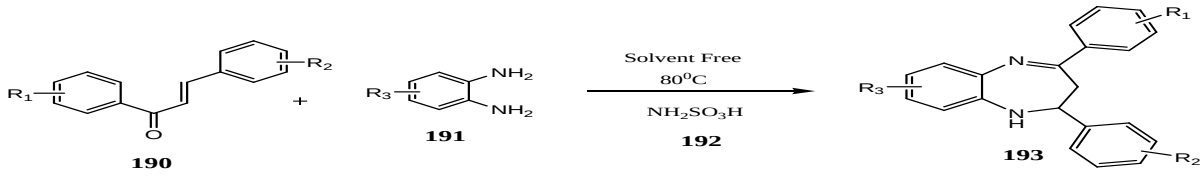
Microwave assisted synthesis of 1,5-benzodiazepine was reported by the reaction of **187a-j** with ortho phenylenediamine **188.** The chalcone was synthesized by reacting acetophenone **185a-j** with aldehyde **186a-j** (Scheme 43).[46]




**Scheme 43**

### 3.6.3) One Pot Synthesis of Benzo-[b]-1, 4-diazepines

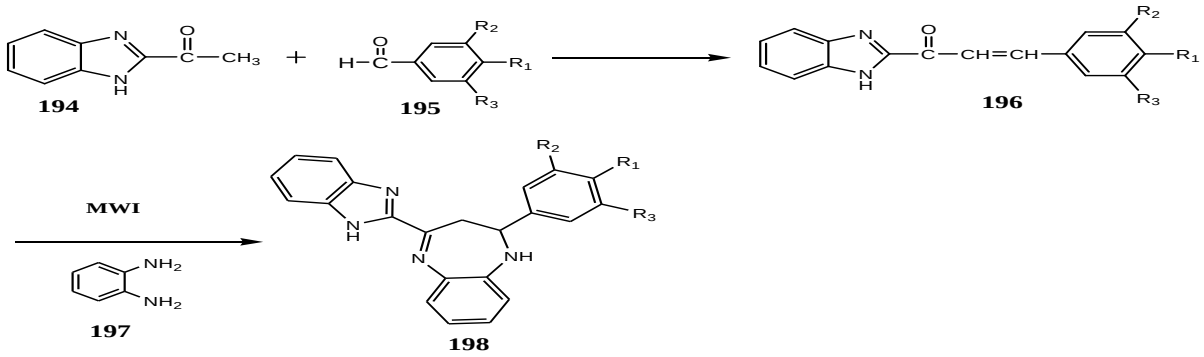
A mixture of α,β-unsaturated carbonyl compound **190,** O-Phenylenediamine **191** and sulfamic acid **192** were heated at 80 °C without any organic solvent for the appropriate time converted to Benzo-[b]-1,4-diazepines **193** (Scheme 44).[47]




**Scheme 44**

### 3.6.4) synthesis benzimidazole assembled 1, 5- benzodiazepine

Bezamidazolyl ketone**194** was condensed with aldehyde **195** afforded to chalcone **196** which on treatment with *o*-phenylenediamine **197** upon MW irradiation converted to bezamidazolyl 1,5- benzodiazepine **198.** (Scheme 45).[48]

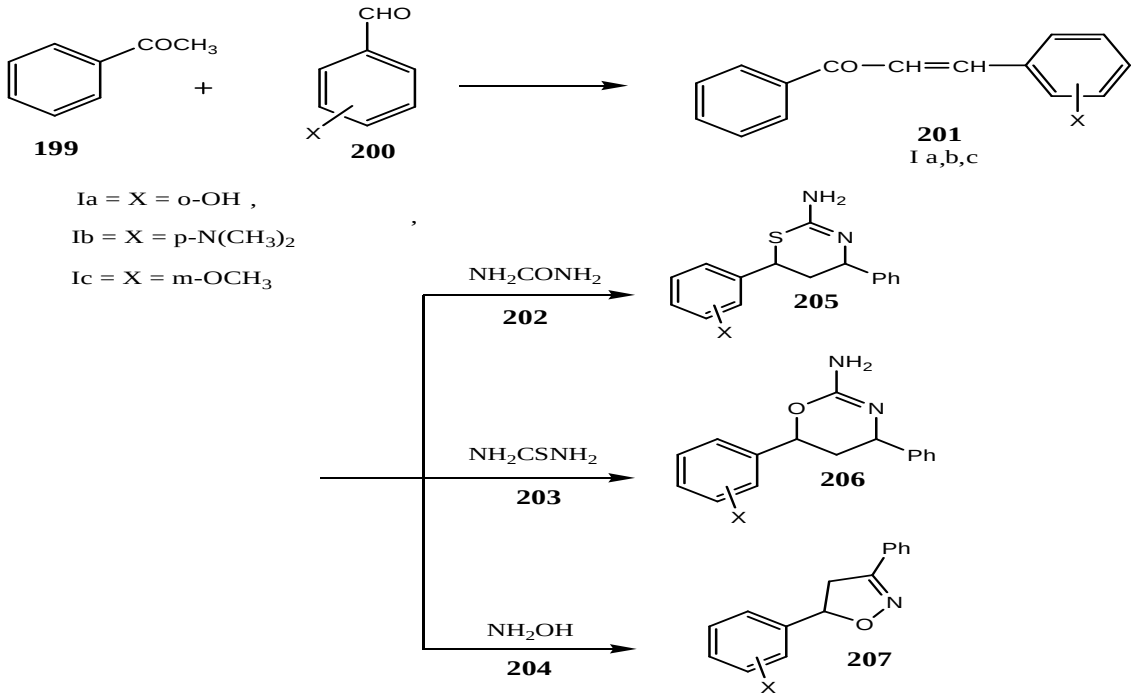



**Scheme 46**

## 4. MISCELLANEOUS REACTIONS

### 4.1) Synthesis of some heterocyclic compounds derived from chalcones

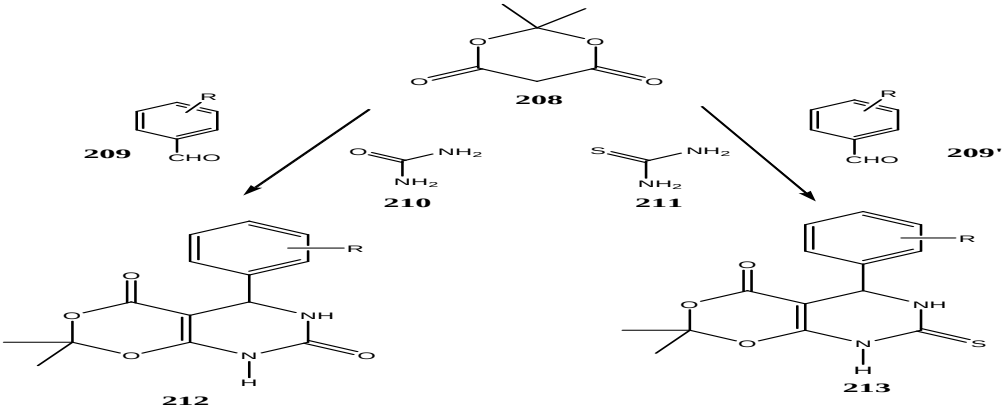
The reaction of Acetophenone **199** and substituted benzaldehyde **200** afforded chalcone **201.** It was treated with different ammonia derivatives **202, 203 & 204** afforded to Antibacterial heterocyles **205, 206 & 207** respectively (Scheme 46).[49]




**Scheme 49**

### 4.2) Green synthesis of biginelli products of meldrum acid

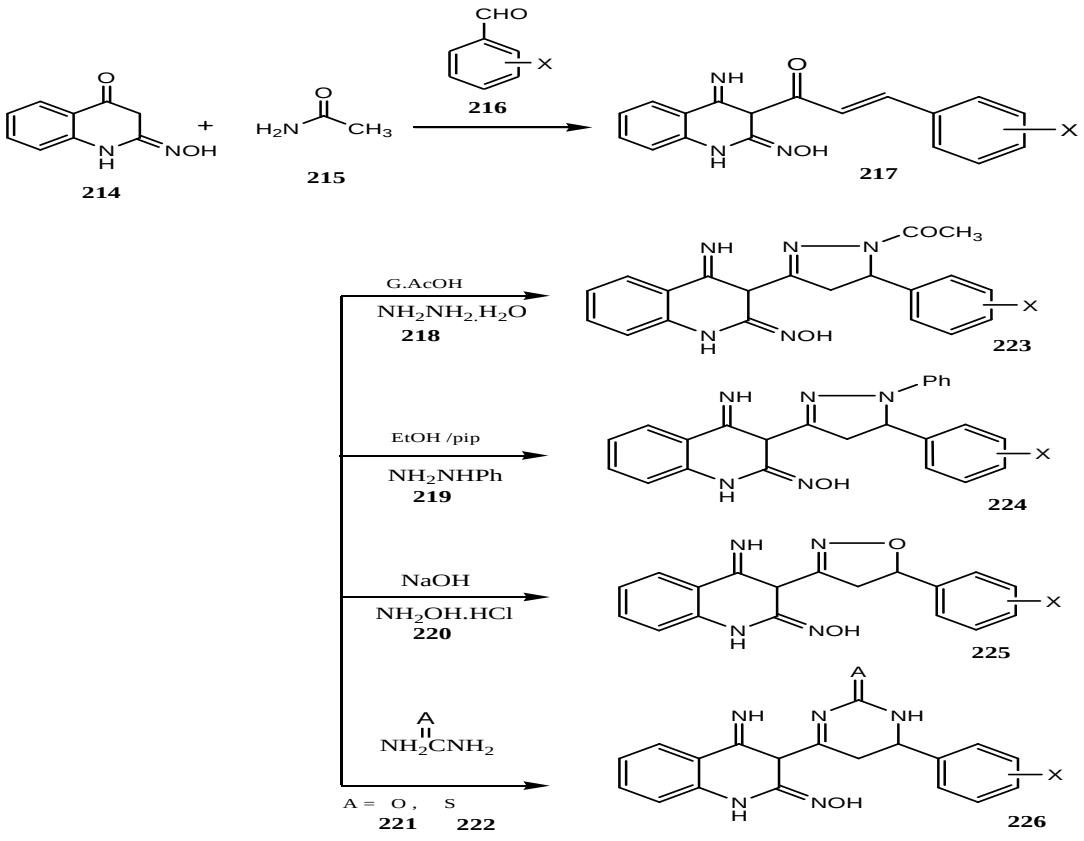
The multi component reaction of diketone **208** aldehyde **209** and urea **210** Thiourea **211** afforded to Antibacterial pyrimidone chalcone **212**, Thiopyrimidone chalcone **213**(Scheme 47).[50]




**Scheme 47**

### 4.3) Synthesis of 3-Substituted Benzpyrid-4-imino-2-oxime Derivatives

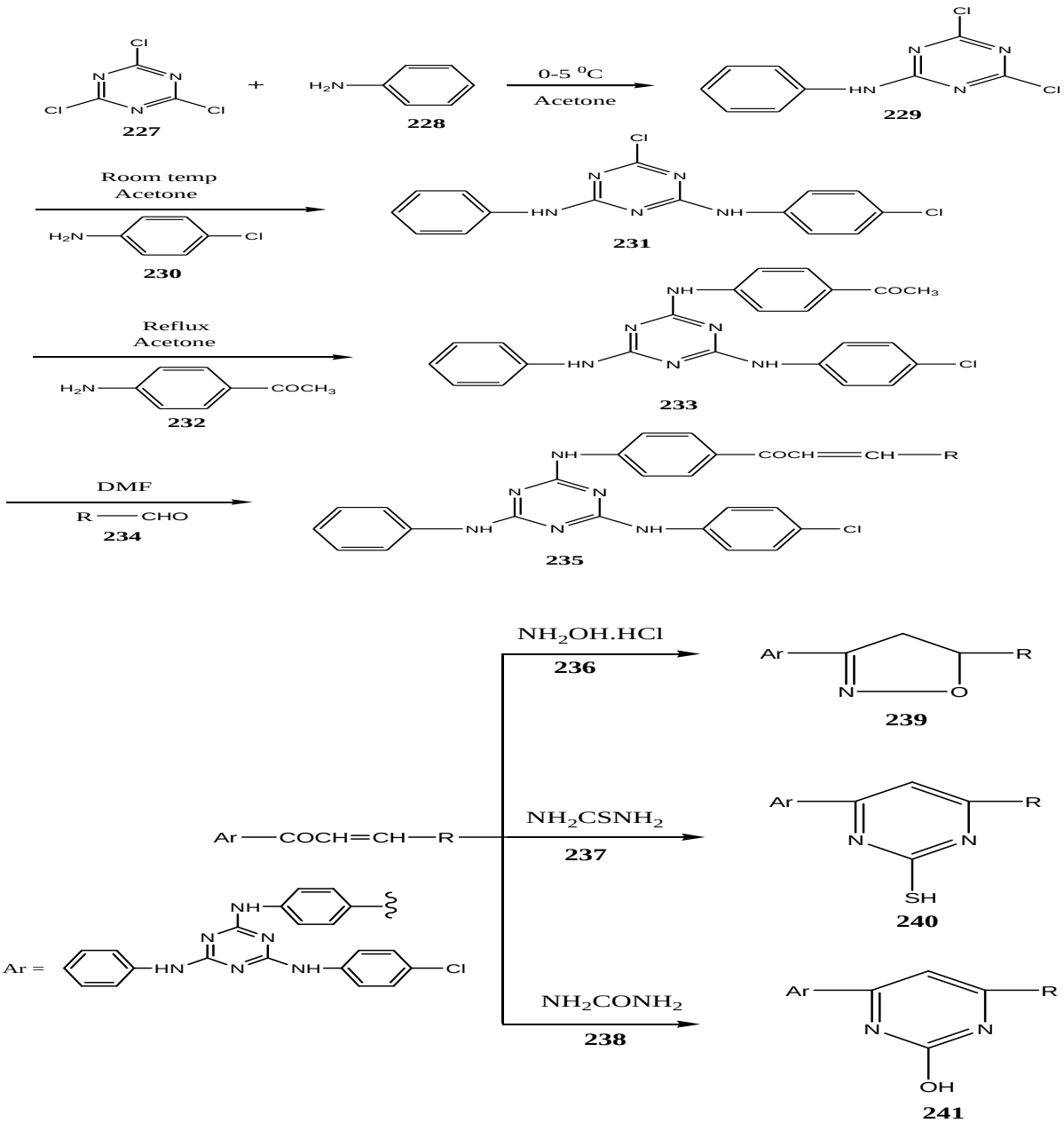
Three component reaction of comp **214,215,216** afforded to 3-Substituted Benzpyrid-4-imino-2-oxime chalcone **217** which was condensed with hydrazine hydrate **218**, phenyl hydrazine **219**, hydroxylamine hydrochloride **220**, Urea **221** ,Thiourea **222** converted to heterocyclic compounds **223,224,225,226,** respectively (Scheme 48).[51]




**Scheme 52**

**4.4) Synthesis, some novel isoxazoles, pyrimidinthiones and pyrimidinones**

Trichloro triazine **227** on treatment with aniline **228** in acetone at 0-5$^0$C formed the compound **229** which was further reacted with aniline **230** at room temp converted in to comp **231.** It was refluxed with p-aminoacetophenone **232** yielded the ketone **233.**Condensed of ketone **233** with aldehyde **234** afforded to chalcone **235.** It was refluxed with hydroxylamine hydrochloride **236**, Thiourea **237**, Urea **238** furnished to Antibacterial and antifungal isoxazole **239**, thiopyrimidine **240**, hydroxyl pyrimidine **241**. (Scheme49).[52]




**5. CONCLUSION**

This review has attempted to summarize the synthetic methods and reaction of chalcone; many biologically active compounds have been synthesized from that Chalcone. These

reactions greatly extended possibility in organic chemistry; Chalcones are easily synthesized and have high chemical reactivity and diverse synthetic application due to presence of enone system and reactive methylene group.

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