

SYNTHETIC APPROACHES FOR THE SYNTHESIS OF DIHYDROPYRIMIDINONES/ THIONES (BIGINELLI ADDUCTS): A CONCISE REVIEW

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ABSTRACT

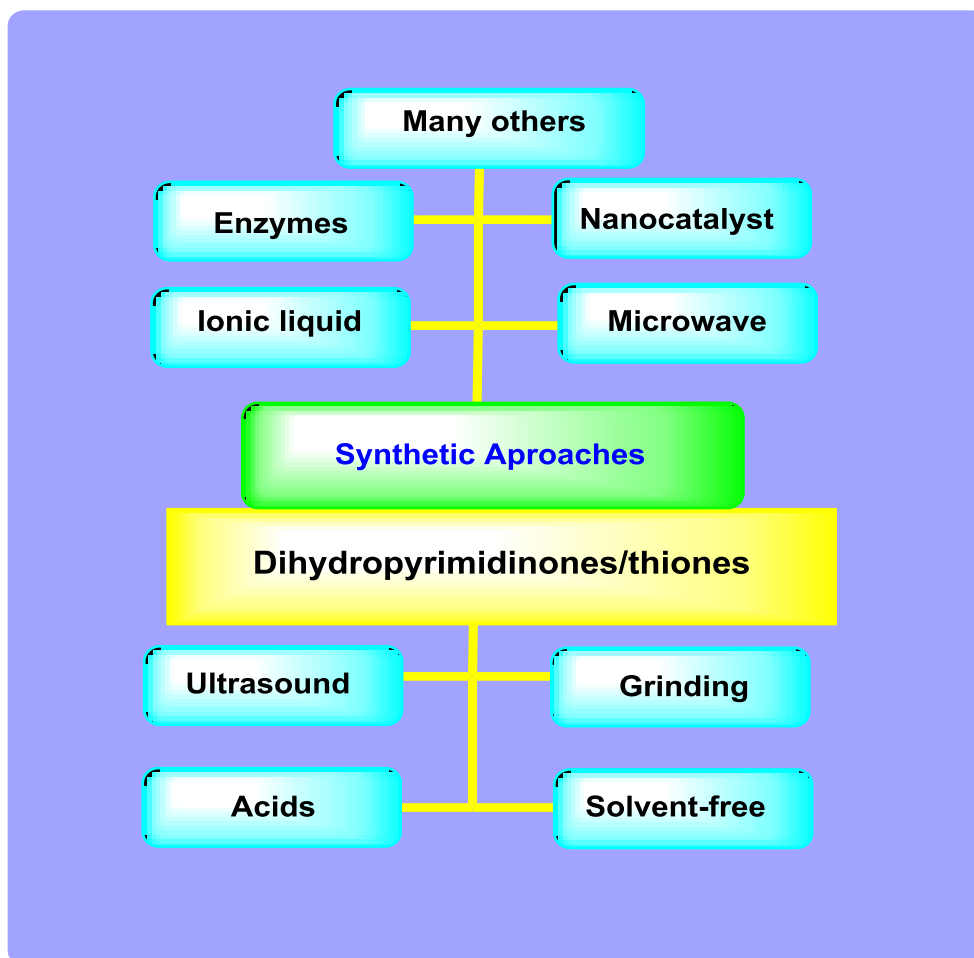
Dihydropyrimidinones are considered as vital biological scaffolds due to their involvement in various medicinal activities. As a result of the wide utilization of different Biginelli adducts in various fields the chemistry of the Biginelli motifs has been explored in drug discovery. The present review deals with the investigation of various synthetic methods used for the synthesis of dihydropyrimidinones (DHPMs). Various synthetic methods are discussed in this review to give clear understanding of pathways leading to the formation of Biginelli adducts.

KEYWORDS: Dihydropyrimidinones/thiones, Green chemistry, Biginelli reaction.

Highlights

1. A systematic review on synthetic approaches for the synthesis of dihydropyrimidinones.
2. More than 150 articles were included after screening.
3. Covers many synthetic methods which are used for the synthesis of dihydropyrimidinones/thiones
4. Green chemistry methods are discussed.

Graphical abstract



INTRODUCTION

The twelve Green Chemistry principles were first reported by Paul T. Anastas and John Warner^[1] and since then numerous scientific disclosures and inventions have ascended through “Green Chemistry”. The twelve green chemistry principles have given an extraordinary stepping stool for the creation of new research in the area of green chemistry.^[2] Green chemistry proficiently uses sustainable (usually) raw materials, reduces waste and stays away from the utilization of harmful and additionally risky reagents and solvents for the synthesis and application of synthetic products. Importantly, these twelve principles emphasize environmentally benign ideas from the planning of the desired product to its preparation, working, investigation, and its disposal after its use. One of the most unique fields of green chemistry is the improvement of scientific procedures. New approaches that are equipped for lessening the utilization of hazardous substances are the prime goal of green chemistry. Over the span of the latest couple of years, the chemistry network has been assembled to grow new sciences that are less perilous to human wellbeing and the earth. This

new methodology has gotten wide consideration. The 12 principles of green chemistry are depicted in **Figure 1**. Many synthetic approaches have been modified in last few years.^[3-25]

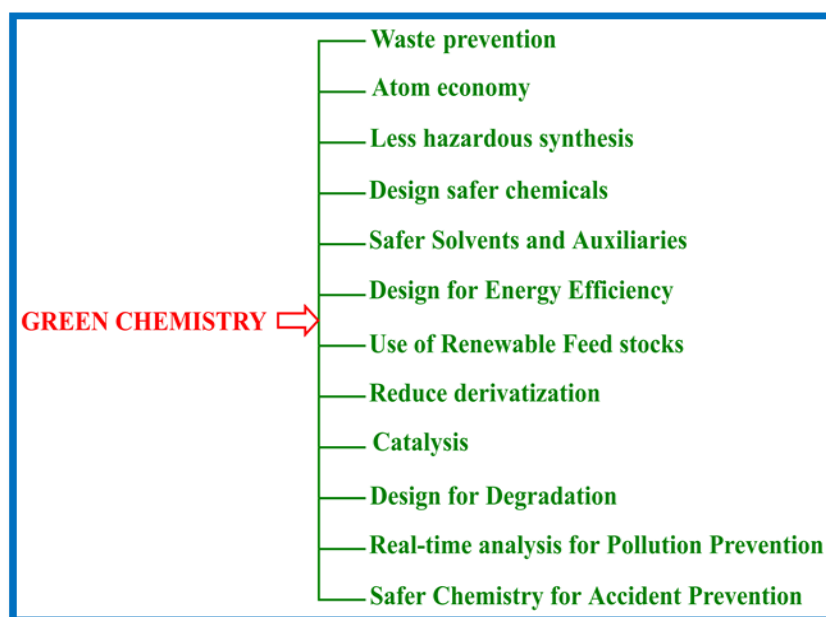
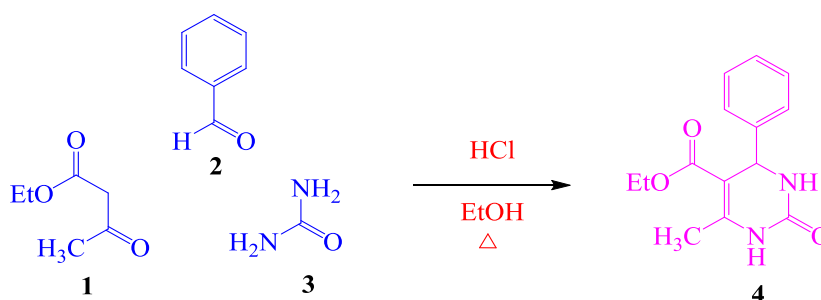


Figure 1: Twelve principles of green chemistry.

Multicomponent reactions (MCRs) are picking up significance in the field of organic synthesis. These reactions often referred to as green as they are expeditious and consequently give an improvement in the development of new synthetic procedures. The disclosure of recent MCRs is consequently most vital and researchers are showing very much interest. One such reaction is Biginelli 3,4-dihydropyrimidin-2-(1*H*)-one synthesis developed by Pietro Biginelli in 1893.^[26] A decade before the publication of Biginelli reaction, Hantzsch reported the synthesis of dihydropyrimidone which has a structure similar to dihydropyrimidinone. The classical version of Biginelli reaction involves the acid-catalyzed, three-component reaction between benzaldehyde; ethyl acetoacetate (EAA), and urea in ethanol at reflux condition inciting the formation of Biginelli adduct (**Scheme 1**).



Scheme 1.

The rising interest in the Biginelli reaction is basically a direct result of the therapeutic and pharmacological properties of Biginelli adducts, specifically, DHPMs.^[27, 28] Besides, various DHPMs had been seen to flaunt a huge spectrum of biological activities including antimalarial, antileishmanial, antitubercular, antiviral, antidiabetic, antiproliferative, anticancer, calcium channel inhibition, antioxidant, antimicrobial, antitumour, anti-inflammatory, antihypertensive, antineoplastic activities, etc. However, this reaction was overlooked to a great extent in the following years and hence the synthetic capabilities of dihydropyrimidinones stayed undiscovered till the 1970's. In the 1970's, interest consistently expanded, and since late 1980, an awesome concern has taken place as a result of an expansion in a variety of publications and patents. From that point forward numerous surveys on the synthesis and chemical properties of Biginelli adducts are revealed. A wide variety of reaction modifications have been developed for the synthesis of DHPMs, their thione analogues, and their heterocyclic derivative compounds. Biginelli adducts with great pharmacological potential have been reported.

In recent years, different varieties of building blocks have been accounted for the synthesis of Biginelli adducts and along these lines, the general proclamation about Biginelli reaction is, the reaction of aldehydes, 1,3-dicarbonyl compounds, and urea/thiourea to furnish 3,4-dihydropyridine-2(1*H*)-ones/thiones. The first review article on Biginelli dihydropyrimidinone synthesis was published by Oliver. C. Kappe in the year 1993 which has produced an extraordinary exposure to this subject.^[29] As a result of the wide utilization of different Biginelli adducts in various fields and their contribution as a base in DNA and RNA, the chemistry of the Biginelli motifs has been explored in drug discovery. Out of the five essential bases in nucleic acids three are pyrimidine derivatives which comprise of Cytosine which is found in DNA and RNA, Uracil in RNA and Thymine in DNA (**Figure 2**).

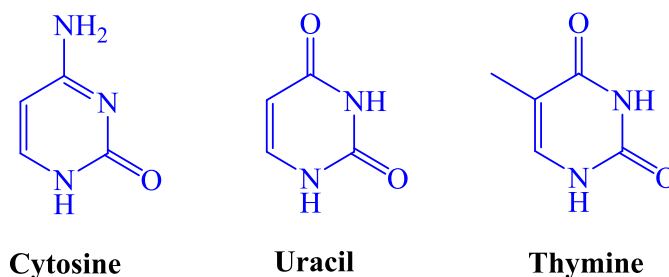


Figure 2.

Synthetic pathways to Biginelli adducts

The synthesis of Biginelli adducts can be carried out under variety of reaction conditions, and several improvements in the experimental procedures have been accounted for their synthesis in recent years. Despite the fact that it has been generally catalyzed by Brønsted acids, numerous other brilliant strategies have been reported in the literature over the span of last two decades.

Microwave irradiation methods

In the last two decades several strategies have been adopted to synthesize Biginelli adducts under microwave conditions. Liu and co-workers have synthesized dihydropyrimidin-2-thiones via biginelli reaction under solvent-free conditions using iodine as a catalyst.^[30] Kolvari and research group reported the synthesis of 3,4-dihydropyrimidin-2-(1*H*)-ones via Biginelli reaction catalyzed by nanomagnetic-supported sulfonic acid.^[31] The synthesis dihydropyrimidinones catalyzed by heteropolyanion-based ionic liquids under solvent-free and microwave conditions was reported by Fu and the research group.^[32] Kuraitheerthakumaran and group have developed new synthesis method for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and their corresponding 2(1*H*)-thiones using lanthanum oxide as a catalyst under solvent-free and microwave conditions.^[33] Pasunooti et al. have developed microwave-assisted, copper-catalyzed three-component synthesis of dihydropyrimidinones under mild conditions.^[34] Many other microwave synthesis methods have been accounted for the synthesis of Biginelli adducts.^[35-39]

Ultrasound irradiation methods

Ultrasound irradiation methods not only reduce the reaction time but also improve the reaction efficiency. Li et al. have reported the synthesis of 3,4-dihydropyrimidin-2-ones catalyzed by sulfamic acid using ultrasound irradiation.^[40] Yadav and research colleagues have modified the Biginelli reaction under ultrasound irradiation for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones using ceric ammonium nitrate.^[41] An efficient synthesis of 4-substituted pyrazolyl-3,4-dihydropyrimidin-2 (1*H*)-(thio) ones catalyzed by Mg(ClO₄)₂ under ultrasound irradiation was developed by Zhang and research group.^[42] Mandhane et al. have reported the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones catalyzed by using thiamine hydrochloride in water under ultrasound irradiation.^[43] Other ultrasound methods are also found to be very superior in terms of yield and reaction time.^[44-53]

Ionic liquid strategies

Ionic liquids are found to excellent media for the synthesis of variety of Biginelli adducts. Attri and research group have modified the synthesis of Biginelli adducts by using triethylammonium acetate ionic liquid.^[54] Polymer-supported benzimidazolium based ionic liquid: Brønsted acid catalyst has been reported for the synthesis of Biginelli adducts by Khiratkar and colleagues.^[55] Azimi et al. have developed solvent-free and one-pot Biginelli synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones and 3,4-dihydropyrimidin-2(1*H*)-thiones using ionic liquid N, N-diethyl-N-sulfoethan ammonium chloride {[Et₃N–SO₃H] Cl} as a green catalyst.^[56] Zhou et al. have also reported solvent-free synthesis of pyrimidinone derivatives using Bronsted acidic ionic liquid [C₃SO₃HDoim]HSO₄ in a three-component Biginelli-type reaction.^[57] Similarly some other ionic liquid catalyzed Biginelli transformations have also been accounted.^[58-65]

Nanoparticle based pathways

Nanoparticles are found to efficient catalysts for many cyclization reactions. There is numerous green chemistry methods based nanomaterials that have been employed for the synthesis of Biginelli scaffolds. Sapkal et al. have synthesized 3,4-dihydropyrimidine-2(1*H*)-ones via Biginelli reaction by using Nickel Nanoparticles.^[66] The nano-titanium dioxide catalyst has been proficiently used by Naik et al. for the synthesis of DHPMs.^[67] Alumina Nanoparticles are also used for the same purpose.^[68] Nasr-Esfahani and research colleagues have employed Fe₃O₄ nanoparticles as an efficient and magnetically recoverable catalyst for the synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones under solvent-free conditions.^[69] The ZnO nanoparticles embedded in SBA-15 have been efficiently used as heterogeneous catalyst for the synthesis of dihydropyrimidinones via Biginelli condensation reaction.^[70] Other Biginelli reactions are also carried out by using metal oxide nanoparticles.^[71-74]

Grinding and solvent-free methods

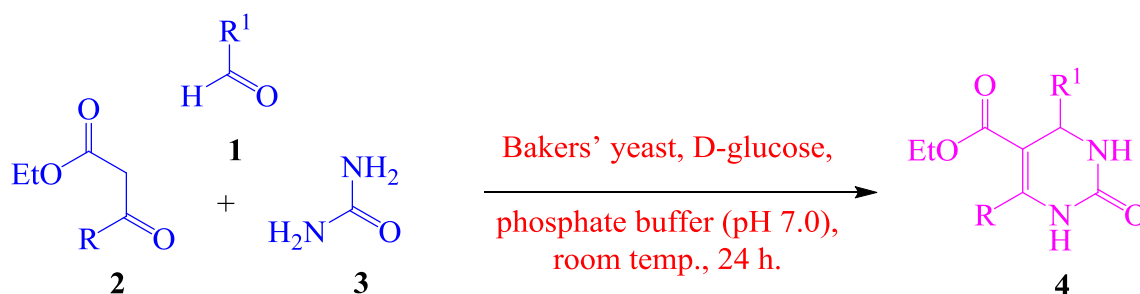
Grinding and solvent-free methods not only reduces cost but also makes the process simple. Numerous methods are found in literature for the synthesis of DHPMs.^[75-79] Sun et al. have reported a highly efficient solvent-free synthesis of dihydropyrimidinones catalyzed by zinc chloride.^[80] Wang et al. have modified the Biginelli reaction and employed Cu(NO₃)₂·3H₂O catalyst for the synthesis of Biginelli adducts under solvent-free conditions.^[81] The Ce(NO₃)₃·6H₂O-catalyzed solvent-free synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones were reported by the Adib research group.^[82] Bahram and research group have synthesized

Biginelli products by employing zinc oxide catalyst under solvent-free reaction conditions.^[83] Peng et al. have reported ionic liquids catalyzed Biginelli reaction under solvent-free conditions.^[82] An β -Cyclodextrin-assisted synthesis of Biginelli adducts under solvent-free conditions were reported by the Bahrami and colleagues.^[85]

Miscellaneous methods

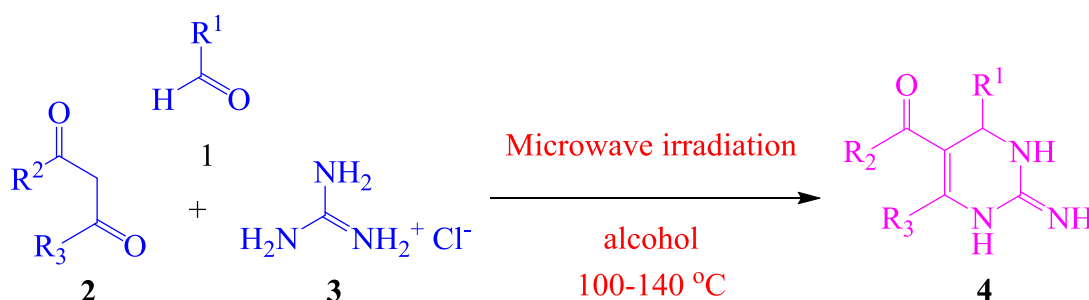
In the year 1987, Atwal et al. revealed a modified Biginelli reaction exhibiting higher yields.^[86, 87]

The first enzyme catalyzed Biginelli reaction (**Scheme 2**) was reported by Atul Kumar and Ram Awatar Maurya which offered Biginelli adducts in high yield.^[88]



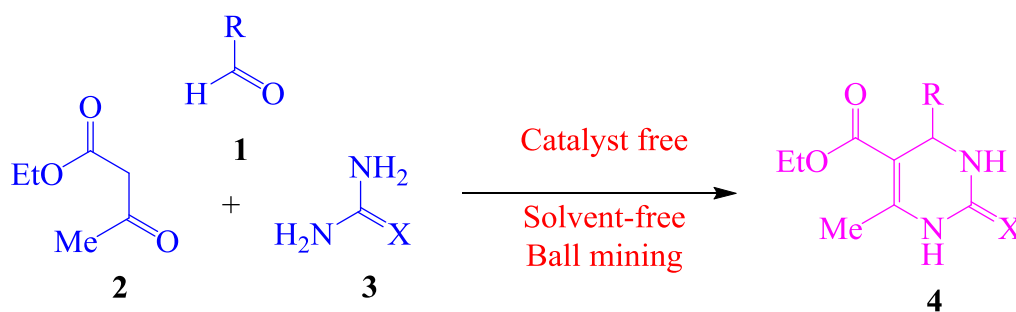
Scheme 2.

Fulvia Felluga and co-workers^[89], reported the synthesis of 2-aminodihydropyrimidines under microwave irradiation (**Scheme 3**).



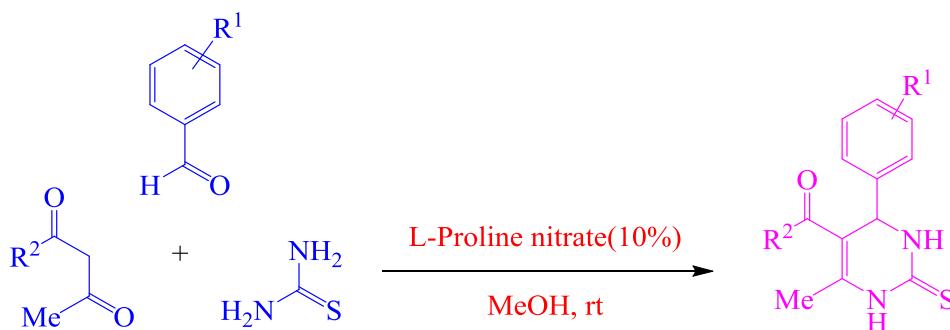
Scheme 3

Mohamed Ould M'hamed and co-workers.^[90], developed catalyst-free and solvent-free Biginelli reaction (**Scheme 4**) under ball milling conditions.



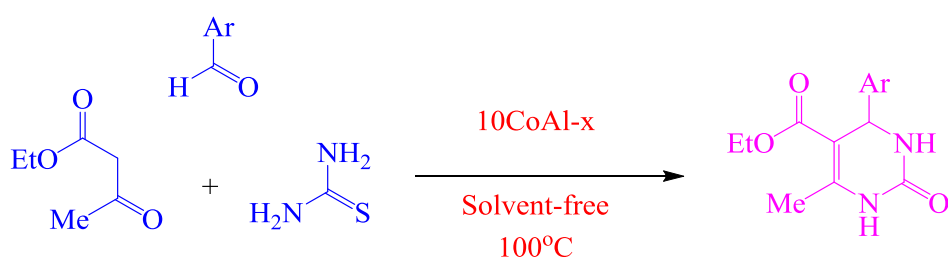
Scheme 4.

Hemant S. Chandak and co-workers^[91], modified Biginelli reaction (**Scheme 5**) by using L-proline nitrate as a recyclable catalyst.



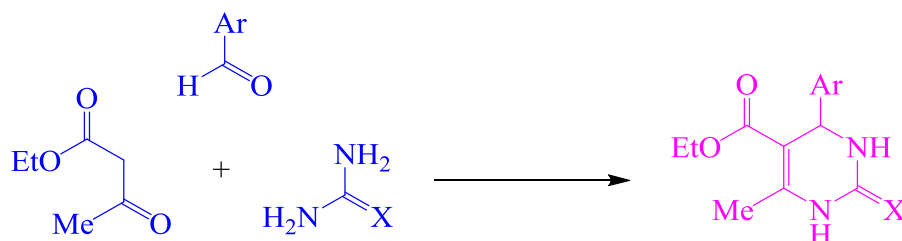
Scheme 5.

Chérifa Rabia et al.^[92] have built up a productive strategy for Biginelli reaction by using alumina supported cobalt catalyst (**Scheme 6**).



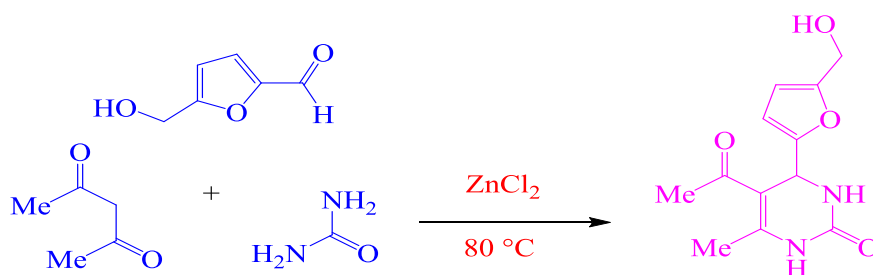
Scheme 6.

Kamali et al.^[93], reported the synthesis of various 3,4-dihydropyridine-2(1H)-ones derivatives under catalyst-free and solvent-free reaction conditions. Moreover, they demonstrated the Biginelli reaction by using various recyclable catalysts (**Scheme 7**).



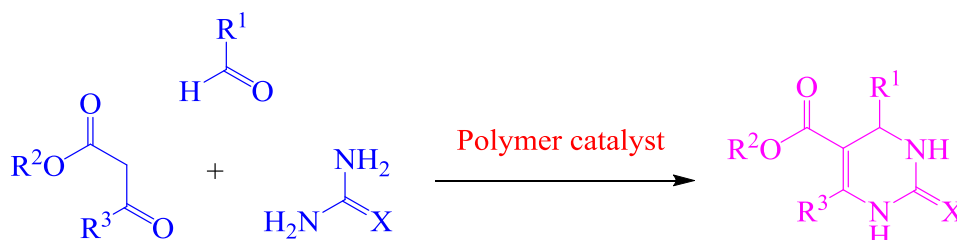
Scheme 7.

Florence Popowycz and co-workers^[94], reported the $ZnCl_2$ catalyzed Biginelli reaction (Scheme 8) using hydroxymethylfurfural sustainable raw material.



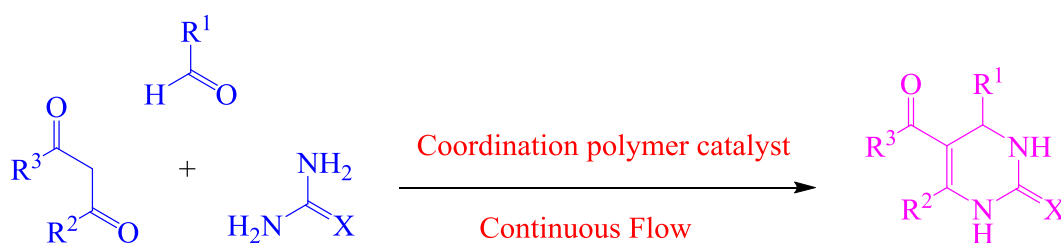
Scheme 8.

Polymer-supported catalysts (Scheme 9) have been found to be excellent for the synthesis of Biginelli adducts.^[95]



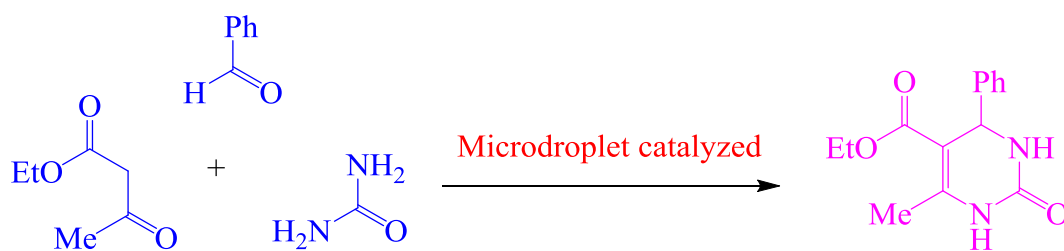
Scheme 9.

Brenno A. D. Neto et al.^[96], synthesized Biginelli adducts by using coordination polymers as a catalyst under continuous flow conditions (Scheme 10).



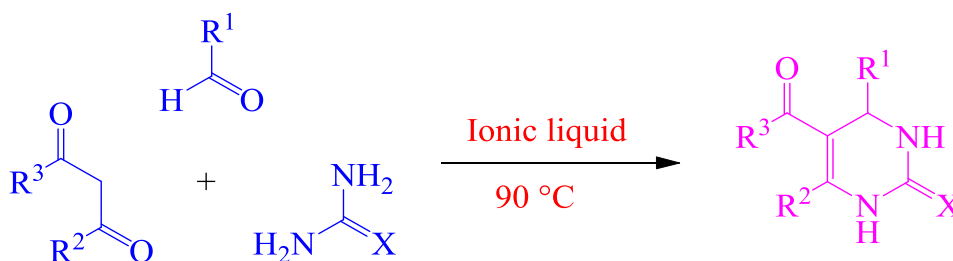
Scheme 10

David E. Clemmer et al.^[97] have reported the microdroplets' (produced by electrospray ionization) catalyzed Biginelli reaction (**Scheme 11**).



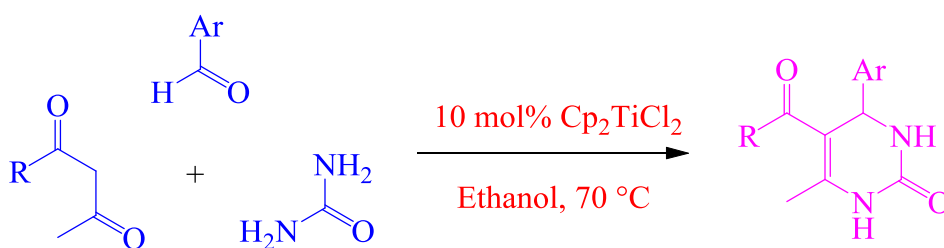
Scheme 11.

Brenno A. D. Neto and co-workers^[98], reported the Biginelli reaction by using various ionic liquids under homogeneous and heterogeneous catalysis (**Scheme 12**).



Scheme 12.

Ziwei Gao and co-workers^[99], reported the synthesis of Biginelli adducts by using activated titanocene as a catalyst (**Scheme 13**).



Scheme 13.

Nano bismuth pyromanganate catalyzed Biginelli transformation was also investigated.^[100]

Many catalytic Biginelli strategies have been modified to enhance and improve the reaction conditions. Some examples include FeCl_3 ^[100], HCOOH ^[102], ionic liquid^[103, 104] aluminatesulfonic acid^[105], $\text{SiO}_2\text{-CuCl}_2$ ^[106], $\text{Cu}(\text{OTf})_2$ ^[107], LiBr ^[108] $\text{In}(\text{OTf})_3$ ^[109], $\text{SiO}_2\text{-H}_2\text{SO}_4$ ^[110], $\text{HClO}_4\text{-SiO}_2$ ^[111], CuBr_2 ^[112], $[\text{L-AAIL}]/\text{AlCl}_3$ ^[113], MCM-41-HClO_4 ^[114], $\text{SiO}_2\text{-}$

ZnCl₂^[115], PPh₃^[116], Brønsted acid^[117], CAN^[118] titanocene^[119], TBAB^[120], and many other catalytic systems have also been reported for the synthesis of DHPM motifs presents their importance.^[121-153]

Concluding remarks

In summary, I conclude that there are various pathways that have been accounted for the synthesis of Biginelli adducts. Even though many methodologies have been reported still there is great scope to develop new methods. The most employed synthetic pathways are based on microwave and solvent-free based. This reaction has been performed by utilizing various sorts of catalytic systems. In current review, nearly all possible methods are discussed and this will attract readers from various fields.

Conflict of interest

The author has declared no conflict of interest.

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