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Recent Updates of Ionic Liquids as a Green and Eco-friendly Catalyst in the Synthesis of Heterocyclic Compounds: A Mini-Review

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ABSTRACT

This review papers aims to comprehensively address the various aspects of ionic liquids and supported ionic liquids, which constitute a significant branch within the expansive field of green catalyst. Specifically, it delves into the recent advancements made in this domain over the past three years for the synthesis of heterocyclic compounds. In the introduction section of this review, the discussion revolves around the structural diversity of ionic liquids with an acidic nature. Furthermore, the introduction presents a clear and definitive classification system for diverse types of acidic ionic liquids. In the last part of this review paper, a comprehensive literature review would be provided on the application of ionic liquids and supported ionic liquids for the synthesis of heterocyclic compounds. The primary objective of this review is to present a comprehensive perspective on the utilization of ionic liquid and supported ionic liquid in the synthesis of various heterocyclic compounds. Special attention is given to the pivotal role played by reusable supported ionic liquids in this process.

Keywords: *Ionic Liquid; green catalyst; organocatalyst; heterocyclic; synthesis*

1. Introduction

Since the 1999 review by Welton [1] titled "Room-Temperature Ionic Liquids: Solvents for Synthesis and Catalysis," a significant number of review papers with ionic liquids (ILs) in their titles have been published [2-10]. Over the past 15 years, the field of ionic liquids has emerged as a prominent area of research. An October 21th, 2023 search using Scopus for review papers with the term “Ionic Liquids” in the title part yielded 998 review paper. The definition of ionic liquid as a salt in the liquid state, as established by previous reviews, will be adhered to in this review as well for application of organocatalyst in the synthesis of heterocyclic compounds using multicomponent reactions. The term has been limited to salts with a melting point below an arbitrary temperature of 100 °C in certain contexts. Hence, it is of utmost importance to take into account different terminologies used to describe salts in their liquid form, including liquid electrolytes, room-temperature ionic liquid, liquid organic salt, molten salt, fused salt, ionic melts, fused salts, ionic fluids, and liquid salts. A comprehensive understanding of these terms is necessary to avoid confusion and ensure accurate communication. This review aims to provide a thorough analysis of a specific category of ionic liquids known as acidic ionic liquids or supported acidic ionic liquids for the synthesis of heterocyclic compounds. An acidic ionic liquid is characterized as an ionic salt with a low melting point and acidic properties. The acidity can be attributed to either Brönsted, Lewis, or a combination of Brönsted and Lewis acid types. Furthermore, the acidic functionality or group can be present in either the cation, anion, or both components of the ionic liquid. It is crucial to acknowledge that most of the ionic liquids documented in literature are neutral.

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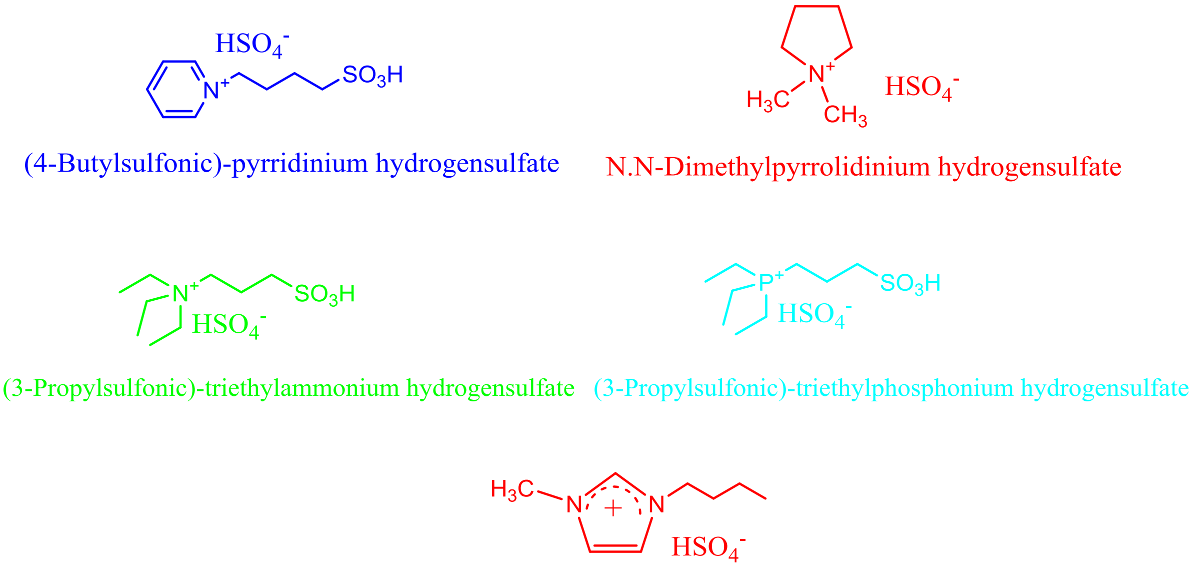
Therefore, this review will solely focus on the synthesis, and applications of the acidic ionic liquids for the synthesis of heterocyclic compounds. This comprehensive review aims to encompass various types of acidic ionic liquids and supported ionic liquids, including their synthesis and applications in organic synthesis. **Fig. 1** displays the chemical structures and nomenclature of various acidic ionic liquids that are commonly used in different research articles.

For description of importance of ionic liquids keyword, **Fig. 2** shows the interesting and strong increase of research about ionic liquids technology.

It is important to review the recent published review papers about ionic liquids keywords at the introduction. The article titled “A review of encapsulated ionic liquids for CO_2 capture” was published in 2023, and contains 131 references making it one of the more recent ten reviews in this sub group [9]. The second with title “Ionic liquid-based gels for biomedical applications” collected by Y. Gao and et al with 138 references appeared in 2023 in “Chemical Engineering Journal” [11]. Other review paper in 2023 with interesting topic were as follow: “Synthesis and Modification of Nanoparticles with Ionic Liquids: a Review” by K. J. Mahammed [12], “Ionic liquid electrolytes for sodium-ion batteries to control thermal runaway” by K. Sirengo [13], “Ionic liquid–based pretreatment of lignocellulosic biomass for bioconversion: A critical review” by S. Roy [14], “Covalently Supported Ionic Liquid Phases: An Advanced Class of Recyclable Catalytic Systems” by Giacalone [15], “Ionic Liquids in Asymmetric Synthesis: An Overall View from Reaction Media to Supported Ionic Liquid Catalysis**”** by Karimi [16], and “Ionic liquids in transdermal drug delivery system: Current applications and future perspectives” by Y. Zhang in 2023 [17]. The scope of the current review is about the application of ionic liquids and supported ionic liquids for the synthesis of different heterocyclic compounds. In this review paper, we would observe more acidic ionic liquids. This category of ionic liquids were divided in two subgroup as follow: Lewis acidic ionic liquids and Bronsted acidic ionic liquids. The acidity of Lewis acidic ionic liquids stems from an electron deficiency, while Brönsted acidic ionic liquids exhibit acidity as a result of ionizable protons. The electron accepting ability of Lewis acidic ionic liquids can be found in either the anion or cation. Nevertheless, the majority of the known Lewis acidic ionic liquids belong to the anion group in terms of their electron accepting ability. Some of these ionic liquids were investigated in review paper by J. Estager in 2014 [18]. **Fig. 3** displays a specific group of Lewis acidic ionic liquids that possess the capability to accept electrons in the anion. Typically, these Lewis acidic ionic liquids are synthesized through the reaction of a neutral ionic liquid with a Lewis acidic MXn in a completely dry environment.

A Brönsted acidic ionic liquid is an ionic liquid substance capable of donating a hydrogen ion (H^+) or proton. The Brönsted acidic ionic liquid can contain proton(s) that are easily released and can be found in various positions within its structure. These acidic proton(s) can be further categorized based on their specific location. Acidic protons are typically located in nitrogen or oxygen atoms, as well as in the anion and in acidic functional groups such as SO_3H and CO_2H that are attached to the cation. **Fig. 4** displays a specific group of Brönsted acidic ionic liquids.



(4-Butylsulfonic)-pyrridinium hydrogensulfate

N.N-Dimethylpyrrolidinium hydrogensulfate

(3-Propylsulfonic)-triethylammonium hydrogensulfate

(3-Propylsulfonic)-triethylphosphonium hydrogensulfate

Fig. 1. Common acidic ionic liquids

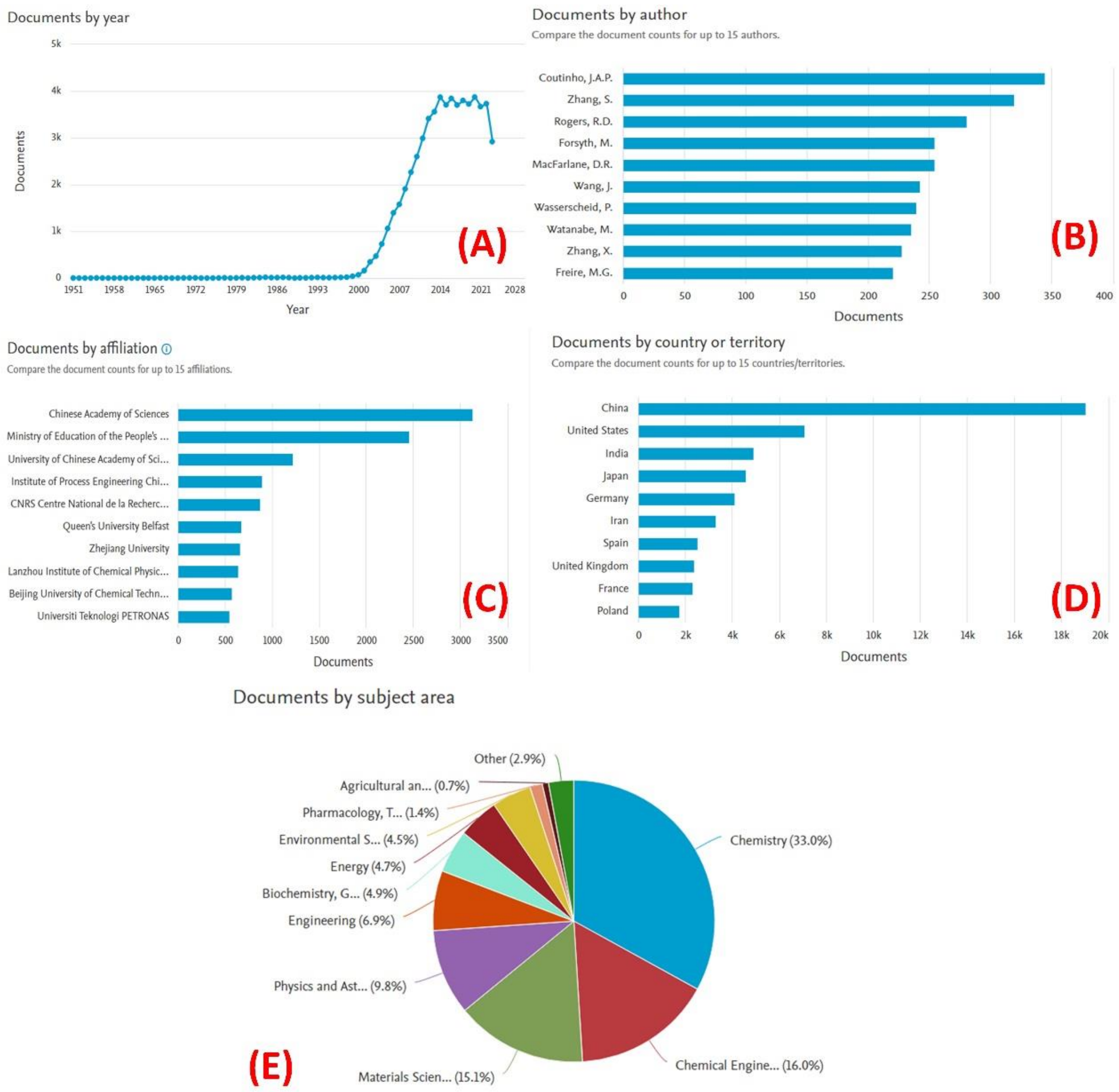


Fig. 2. Information and data extracted from Scopus database on October 2023, at about "Ionic Liquids" keywords: (A): Number of document per year from 1951 until October 2023 (B): Top ten of scientist in the field of ionic liquids (C): Top ten of academic center in ionic liquid field (D): Top ten of countries in ionic liquids field and (E): Distribution and application of ionic liquids in various sciences and technology

The fixation of acidic ionic liquids can be carried out on soluble or insoluble substrates. However, the majority of cases involve the use of insoluble substrates to produce heterogeneous acid catalyst systems. Often, these heterogeneous catalysts demonstrate enhanced size and positional selectivity compared to homogeneous catalysts, thanks to the solid support's capability to establish a tailored environment around the catalytic site [19]. Furthermore, the immobilization of the catalytic sites can effectively prevent molecular aggregation or bimolecular self-destruction reactions, thereby avoiding deactivation. One significant benefit of this approach is the convenient separation of the supported acidic ionic liquid from the reactants and products, allowing for its reuse. Silica, alumina, zeolites, and polystyrene type polymers are commonly employed as supports in this context. A comprehensive review published in 2014, titled "The use of supported acidic ionic liquids in organic synthesis," provides a comprehensive overview of the recent advancements in both inorganic and organic supported acidic ionic liquid in catalysis applications, backed by 79 references [19]. Silica and Fe_3O_4 serves as the predominant, practical, and acid-resistant solid support for Brönsted acidic ionic liquids, with limited instances of zeolites and metal organic frameworks being utilized [20]. Three fundamental methods of immobilization include the attachment of catalyst onto a silica surface, the creation of silica material through sol-gel formation, and the adsorption onto a solid surface. By utilizing a lengthier carbon chain, the attachment of Brönsted acidic ionic liquids onto a silica surface through grafting enables a more convenient approach to the acidic function [10, 21-27]. Another frequently employed method for immobilizing a catalyst onto silica involves the sol-gel synthesis through the hydrolysis of a blend of silicates such as tetraethyl orthosilicate (TEOS) and a catalytic function that is covalently bonded to a silicate compound. The successful application of this technique involves the immobilization of acidic ionic liquids. A notable example is the work of Miao and colleagues, who effectively immobilized 1-(3-propylsulfonic) imidazolium hydrogensulfate on silica-gel by utilizing tetraethyl orthosilicate as the primary silica source [28]. Another method for immobilizing a catalyst is through adsorption or entrapment in an inorganic support. This technique has also been utilized for acidic ionic liquids [29]. A catalyst comprising of $[(HSO_3)_3C_3(C_2)_3N]][NTf_2]$, an ionic liquid of the 3-propylsulfonic-trimethylammonium type, entrapped in silica gel was prepared by Marr and colleagues. This functionalized acidic ionic liquid embedded in silica gel was utilized as a reusable liquid phase catalyst for the dehydration of rac-1-phenyl ethanol. The efficacy of the catalyst was confirmed by hot filtration tests, which demonstrated that the activity was maintained within the gel [29]. Organic polymeric structures containing acidic ionic liquid immobilization have been identified. The typical method for producing acidic ionic liquid immobilized on polystyrene involves copolymerizing a blend of vinylbenzene with Brönsted acidic ionic liquids attachment and divinylbenzene [14]. The polystyrene based systems are extensively utilized organic supports. Furthermore, solid supports such as poly(vinylpyridine) and melamine resins have also been employed for acidic ionic liquid [14, 30-42].

Different modifiers influence distinct types of reactions in acid catalysis. For example, Friedel−Crafts alkylation is a reaction that is influenced by Lewis acid catalysis, while esterification is a reaction that is commonly observed in Brönsted acid catalysis. Lewis acid catalyzed reactions are characterized by the transfer of electrons towards an electron-deficient Lewis acid, resulting in the formation of a charge-separated complex. On the other hand, Brönsted acid catalyzed reactions involve proton transfer, which can enhance the electrophilicity of one of the reacting partners. There are two distinct manifestations of acid catalysis: specific

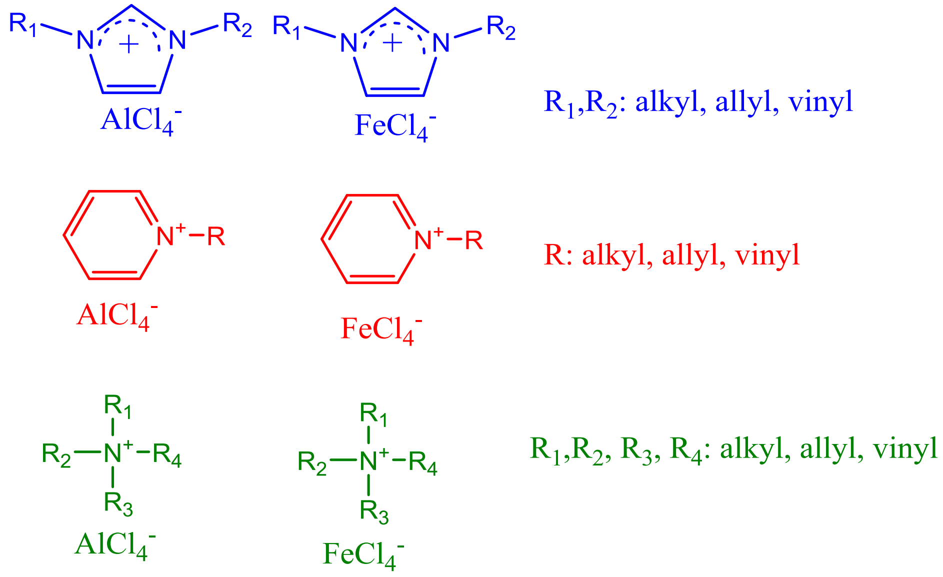


Fig. 3. Some of the Lewis acid ionic liquids

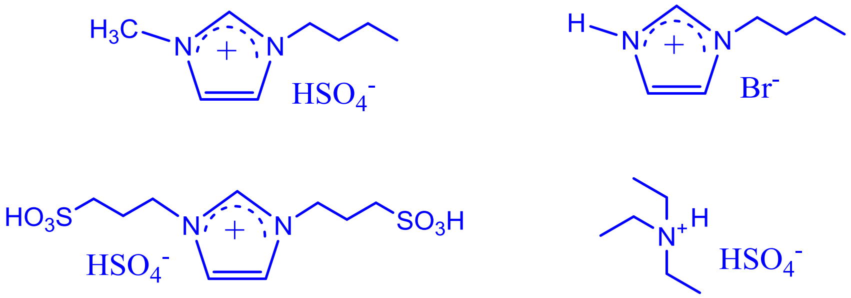


Fig. 4. Some of the Brönsted acidic ionic liquids

acid catalysis and general acid catalysis. In specific acid catalysis, the reaction rate relies on the particular acid that is present in the solution. The protonated form of the solvent in which a reaction is performed is typically the specific acid. General acid catalysis involves multiple species acting as acids. Acidic ionic liquids exhibit Lewis and Brönsted acid behavior and are utilized in various applications. They are also known to function as both homogeneous and heterogeneous acid catalysts. In numerous cases, the replacement of a typical acid with an acidic ionic liquid has resulted in improved yield, turnover number (TON), turnover frequencies (TOF), and catalyst recyclabilities, surpassing the performance of conventional counterparts in classical reactions. The application of Brönsted acidic ionic liquids in heterocyclic synthesis has been extensively documented. Numerous classical heterocyclic syntheses that were previously conducted using Lewis and Brönsted acids have been tested with Brönsted acidic ionic liquids, and in many instances, these ionic liquids have demonstrated superior catalytic properties compared to traditional acids. Several initial applications have been discussed in previous articles on ionic liquid reviews, as well as in the book "Ionic Liquids in Synthesis" [43-52]. A comprehensive account on the use of neutral, acidic, and basic ionic liquids as solvents and catalysts in the synthesis of various classes of heterocyclic compounds can be found in the 2008 review titled "Ionic Liquids in Heterocyclic Synthesis", which includes 367 references [53]. In this review paper, we decided to write a hot review paper in the application of ionic liquids and supported ionic liquids in the synthesis of heterocyclic compounds.

2. Synthesis of heterocyclic compounds catalyzed by ionic liquids and supported ionic liquids

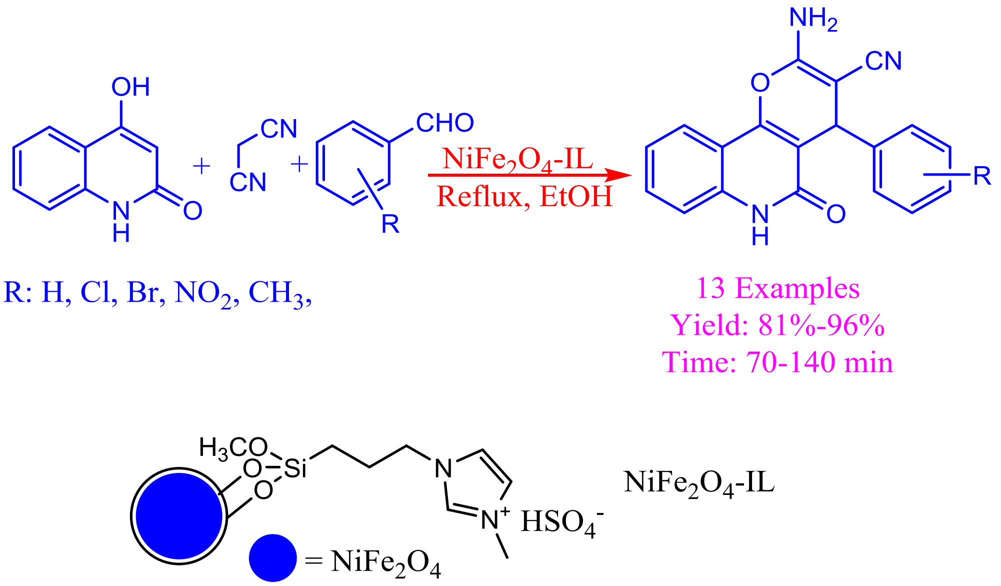
In 2023, Yousefi Ghaleh-Salimi and co-workers described the synthesis of pyrano[3,2-c]quinolone derivatives using $NiFe_2O_4@SiO_2$ attached ionic liquid [54] (**Scheme 1**). Pyrans and quinolines play a pivotal role in the development of bioactive substances that exhibit intriguing pharmacological effects. Notably, certain compounds incorporating quinoline fused with pyrans, specifically pyrano[3,2-c]quinolines, have demonstrated significant therapeutic properties. The presence of pyranoquinoline frameworks has been observed in essential natural compounds such as oricine, huajiaosimuline, and flindersine. In this method multicomponent reactions of malononitrile, 4-hydroxy-quinolin-2(1H)-one, and aromatic aldehydes were used in the presence of $NiFe_2O_4@SiO_2$ bonded ionic liquid. This process was conducted in ethanol under reflux conditions. After determining the optimal reaction conditions, a variety of pyrano[3,2-c]quinoline derivatives were synthesized utilizing 4-hydroxyquinolin-2(1H)-one, malononitrile, and aromatic aldehydes possessing both electron-donating and electron-withdrawing groups. Excellent yields (averaging 91%) were obtained from the reactions, which were closely monitored using thin layer chromatography (TLC). Notably, aldehydes featuring electron-withdrawing/halogen groups (NO_2, Cl, and Br) exhibited a slightly faster completion of TLC compared to those containing electron-donating groups (CH_3, OCH_3). The NMR and elemental analysis data provided further confirmation of the proposed product structures. The recovery of the catalyst from the reaction medium can be achieved through the use of an external magnet, allowing for its reuse in subsequent reactions aimed at the synthesis of pyrano[3,2-c]quinolone. The catalyst has demonstrated sustained efficacy over a significant number of cycles (9th catalytic cycle from 94% in first catalytic cycle to 87% in 9th catalytic cycle in 100 min).

In 2023, a functional ionic liquid, based on 1,2-benzisothiazol-3(2H)-one-1,1-dioxide (Saccharin), was synthesized, characterized, and designed to serve as a recyclable catalyst for the synthesis of Biginelli and Hantzcsh heterocycles at room temperature. The successful utilization of this novel catalyst was achieved. A developed method has been established for the synthesis of diverse N-containing heterocyclic compounds, such as dihydropyrimidins, tetrahydroquinazolines, hexahydroacridines, and thiadiazolo[3,2-a]pyrimidines (**Scheme 2**) in the presence of ([S*ac*-CH_3CO_2][Et_3NH]) [47]. This strategy is characterized by its green nature, being solvent-free, operationally simple, and highly efficient. The target products were obtained with high yields in all reactions, eliminating the need for column chromatography. This mechanosynthesis showcases environmentally friendly characteristics, including short reaction times, high efficiency, and the ability to conduct large-scale synthesis at ambient temperature, distinguishing it from classical reactions. The potential of recycling the [Sac-CH_3CO_2][Et_3NH] catalyst in the model reaction was finally examined. Following the formation of the product 5-acetyl-6-methyl-4-phenyl-3,4-dihydropyrimidin-2(1H)-one, 10 mL of distilled H_2O was added and stirred for 3 min. The reaction mixture was then extracted with ether to obtain the corresponding products. As the [Sac-CH_3CO_2][Et_3NH] catalyst salt is ionic and insoluble in ether, the residual ionic liquid was washed with ether (2 × 10 mL) and dried under vacuum for reuse in subsequent reactions without any further processing. These experimental findings demonstrate that the [Sac-CH_3CO_2][Et_3NH]

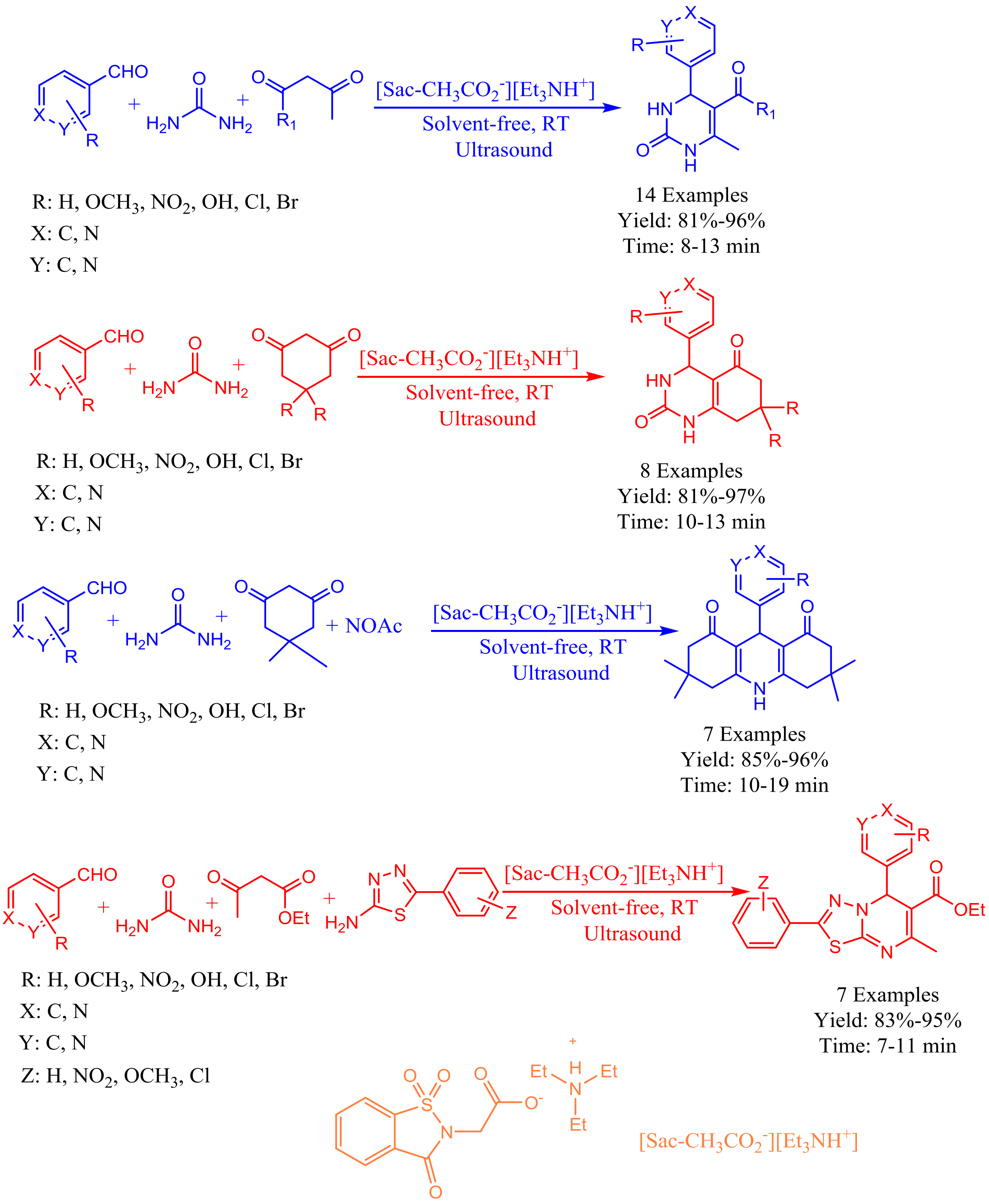
catalyst can be utilized for up to 4 cycles without any significant loss in its activity. The utilization of a ball mill enables the achievement of a sustainable reaction without the need for solvents. This strategic approach encompasses the reduction of waste and cost, as well as the implementation of straightforward operational procedures. The ball-milling method offers several advantages, such as the promotion of environmentally friendly reaction conditions, the attainment of excellent yields, a wide range of applicable substrates, and the utilization of a simple protocol.

Naderi and co-workers reported a green and efficient one-pot methodfor the synthesis of chromene and xanthene derivatives from benzylic alcohols (**Scheme 3**) [55]. A novel catalyst was synthesized and characterized using various techniques such as Fourier transform IR (FT-IR), inductively coupled plasma, X-ray diffraction (XRD), and thermogravimetric (TGA) analyses. The catalyst, which consisted of a Schiff base attached to an ionic liquid and a crown ether and coordinated to cobalt (II), was employed in the synthesis of xanthenes and chromenes using alcohols instead of aldehydes or ketones. The catalyst containing the crown ether and the ionic liquid exhibited superior activity compared to its analogs without them, owing to the increased solubility of the catalyst in the aqueous phase and its larger contact surface as a Lewis acid with the reactive species. This resulted in a faster alcohol oxidation process and higher reaction rates. Additionally, this method offers several advantages such as the ability to reuse the catalyst for up to six runs, short reaction times, the use of friendly environmentally green solvents, and good to excellent yields of products.

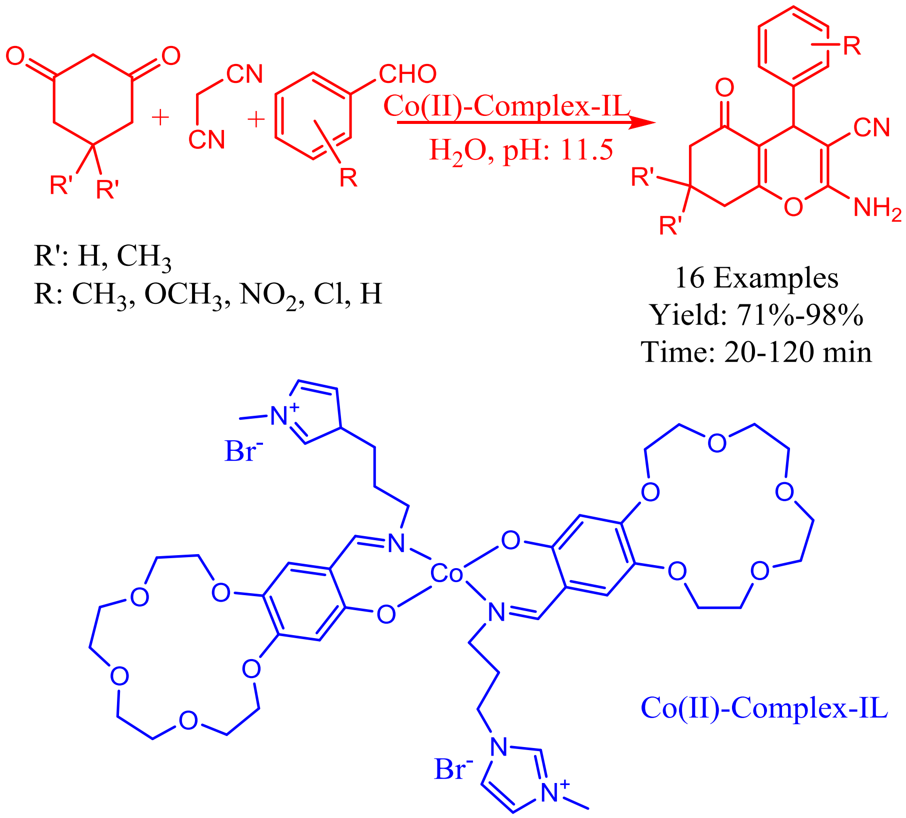
In 2023, Mohurle and co-workers described a highly effective diastereoselective one-pot multicomponent Mannich reaction using 6 mol% of [BCMIM][Cl] ionic liquid as a catalyst for the synthesis of β-amino ketones (**Scheme 4**) [56]. The reaction, which involved cyclohexanone, substituted aromatic aldehydes, and substituted aromatic amines, was carried out efficiently under solvent-free conditions at room temperature. The use of 6 mol% [BCMIM][Cl] catalyst resulted in excellent diastereoselectivity, high yields, rapid reaction times, and no need for purification by column chromatography. All synthesized derivatives underwent comprehensive characterization and validation through the utilization of ^{1}H NMR, ^{13}C NMR, and Fourier-transform infrared spectral techniques. Furthermore, the catalytic efficiency of the [BCMIM][Cl] ionic liquid catalyst remained intact even after undergoing reprocessing and being utilized for three consecutive cycles. In summary, a remarkably efficient synthesis of β-amino carbonyl compounds through a solvent-free Mannich reaction has been successfully developed. This innovative approach employs a mere 6 mol% of functionalized acid ionic liquid, resulting in enhanced efficiency and sustainability. The formation of β-amino carbonyl compounds was facilitated by the acid ionic liquid catalyst, which demonstrated enhanced catalytic activity, resulting in high yields and notable degrees of diastereoselectivity. The catalyst's catalytic activity remains intact even after being reused three times and recycled.



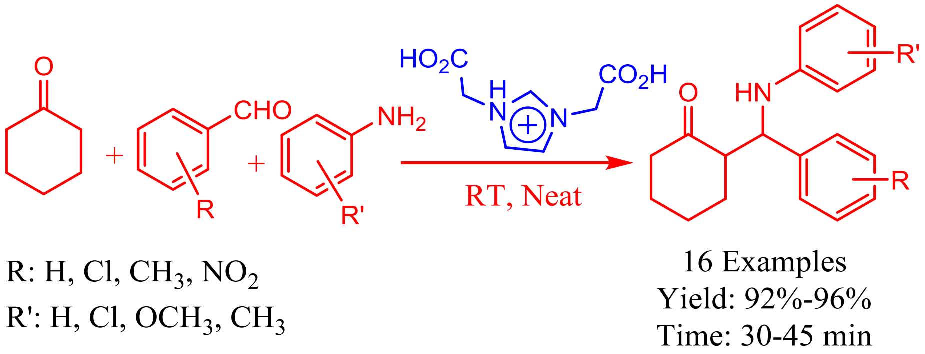
Scheme 1. Synthesis of pyrano[3,2-c]quinolone derivatives using NiFe$_2$O$_4$@SiO$_2$ attached ionic liquid



Scheme 2. Synthesis of dihydropyrimidins, tetrahydroquinazolines, hexahydroacridines, and thiadiazolo[3,2-a]pyrimidines using [Sac-CH_3CO_2][Et_3NH] under specific conditions



Scheme 3. Synthesis and preparation of xanthene derivatives in the presence cobalt (II) complex



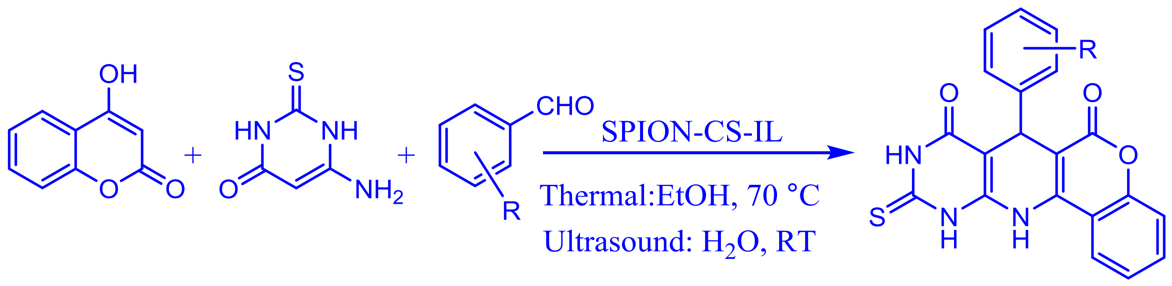
Scheme 4. Synthesis of β-amino carbonyl compounds using [BCMIM][Cl] ionic liquid catalyst

This approach offers several key advantages, including excellent atom economy, the use of relatively inexpensive reagents, a specially designed ionic liquid catalyst, mild reaction conditions, a quick reaction time, and the convenience of a single synthetic operation without the need for additional column purification.

The ultrasonic promoted approach was employed by Sayahi and co-workers [57] to modify the chitosan-functionalized ionic liquid with superparamagnetic iron oxide nanoparticles, resulting in the formation of a novel and reusable catalyst termed SPION@CS-IL. They presents the successful synthesis of SPION@CS-IL and highlights its potential applications. Vibrating-sample magnetometer (VSM), Transmission electron microscopy (TEM), Fourier transform infrared spectroscopy (FT-IR), energy-dispersive X-ray spectroscopy (EDX), X-ray powder diffraction (XRD), energy-dispersive X-ray spectroscopy (EDX), and thermogravimetric analysis (TGA) are employed for comprehensive characterization of SPION@CS-IL. The nanoparticles that were generated have been identified as a reusable heterogeneous superparamagnetic catalyst, which proves to be highly beneficial for the environmentally conscious one-pot synthesis of pyrido[2,3-d]pyrimidine derivatives. This efficient process involves a straightforward three-component reaction method that includes the utilization of thiobarbituric acid, 4-hydroxy coumarin, and a range of aromatic aldehydes (**Scheme 5**). The utilization of ultrasonic irradiation during the reaction analysis is being investigated, with the approach being an eco-friendly one that employs water as the solvent. The synthesized products offer highly favorable isolated yields. The catalyst exhibits exceptional reusability and can be effortlessly separated from the products through filtration after undergoing five consecutive runs. This eco-friendly process offers noteworthy advantages such as quick response times, minimal catalyst loadings, the ability to recycle the nanocatalyst up to five times, and the lack of hazardous chemical reagents.

Jahanbakhshi and Farahi synthesized the modified magnetic cellulose as a support for the Brønsted acidic ionic liquid, 1-(propyl-3-sulfonate) vinyl imidazolium hydrogen sulfate [58]. The novel supported ionic liquid catalyst underwent characterization through various techniques such as XRD, EDS, FTIR, VSM, SEM, TEM, TGA, and BET to determine its physical structure, composition, and functional groups. Due to the incorporation of nanosupport features and the utilization of flexible imidazolium linkers, the catalyst exhibited characteristics of a "quasi-homogeneous" nature, enabling it to efficiently facilitate the synthesis of triazolo[4,3-a]pyrimidine derivatives through a one-pot three-component reaction involving active methylene compounds (such as ethyl malononitrile or cyanoacetate), aryl aldehydes and, aminotriazole (**Scheme 6**). Various aryl aldehydes with electron-donating and electron-withdrawing groups were utilized in the reaction to explore the universality of this protocol. The desired products were obtained in good to excellent yields as the reaction progressed smoothly. The catalytic agent can be effortlessly retrieved with the aid of an external magnet and can be reused multiple times without any substantial decline in its catalytic efficiency.

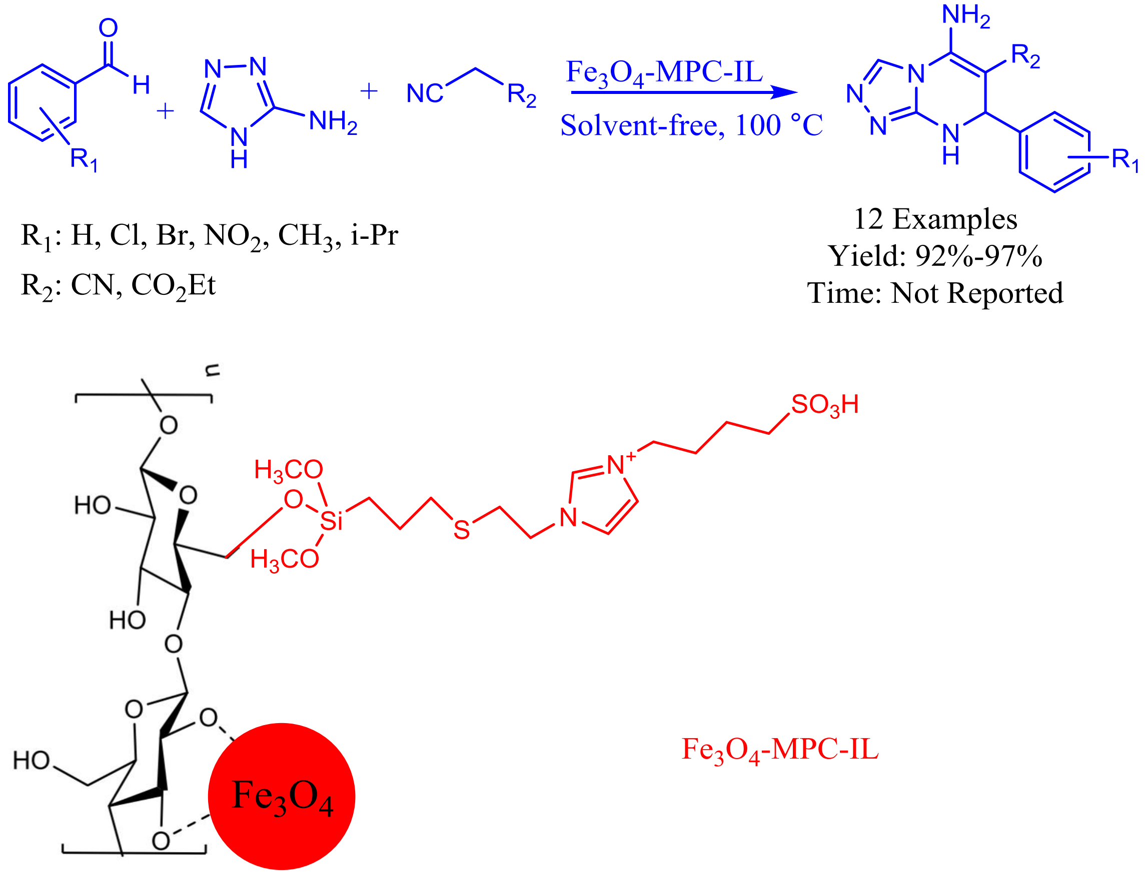
A new Bronsted acidic ionic liquid, $[HEPiPYBSA]^+HSO_4^-$, was synthesized by Shinde and colleagues. They investigated its catalytic effectiveness in the production of indenoquinoxalone tethered spiro-1,2,4-triazolidine-5-thiones through the reaction of 11H-[1,2-b]quinoxalin-11-one and thiosemicarbazide (**Scheme 7**) [59]. The DFT theory at B3LYP/6-31G∗ level was utilized to systematically optimize the synthesized ionic liquid (IL) $[HEPiPYBSA]^+$ HSO_4^-, resulting in the attainment of its most stable geometries. The method developed was tested for its generality with substituted indenoquinoxalone and thiosemicarbazide/substituted thiosemicarbazides under optimized reaction conditions. Unsubstituted indenoquinozalone demonstrates excellent reactivity when subjected to thiosemicarbazides, specifically N-methyl thiosemicarbazide and N-phenylthiosemicarbazide, resulting in rapid reaction times and the formation of products with remarkable yields. The corresponding spiro-1,2,4-triazolidine-5-thiones can be obtained in significant yield and a short reaction time by utilizing substituted indenoquinoxalone. The exploration of the formation mechanism of the product was prompted by the successful synthesis of spiro 1,2,4-triazolidine-5-thiones with diverse substitutions. The ionic liquid exhibited exceptional catalytic efficiency for up to five reaction cycles, while maintaining mild reaction conditions, high product yield, short reaction time, operational simplicity, and the use of non-toxic reagents and catalysts. These features collectively define the distinctive characteristics of the current methodology.



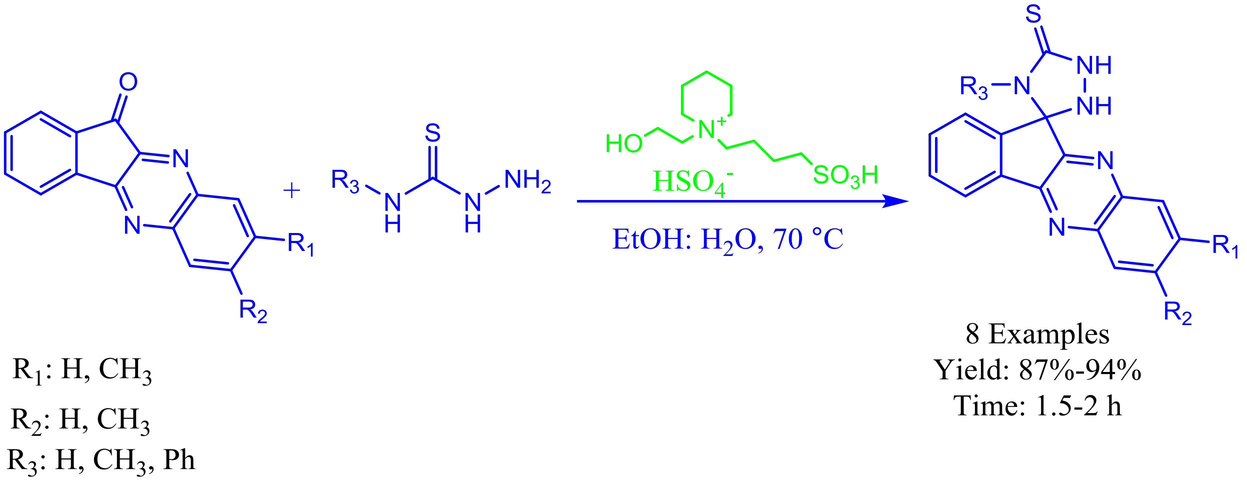
R: Cl, Br, NO_2, OCH_3, CN

10 Examples
Yield: 77%-89% Thermal
Yield: 84%-92% Ultrasound

Scheme 5. Synthesis of pyrido[2,3-d]pyrimidine derivatives using SPION@CS-IL catalyst



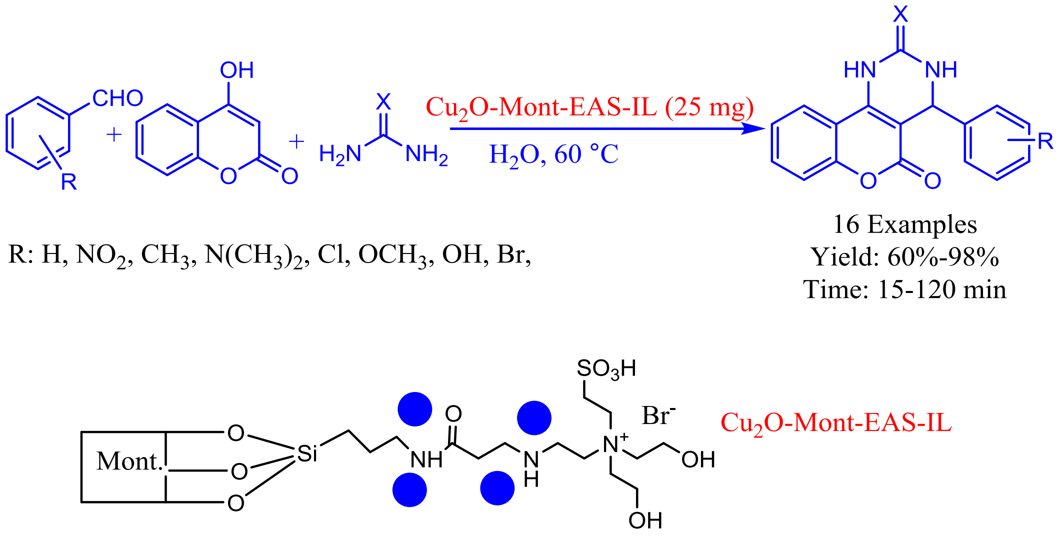
Scheme 6. Synthesis of triazolo [4,3-a]-pyrimidines derivatives using Fe_3O_4/MPC-[IL]



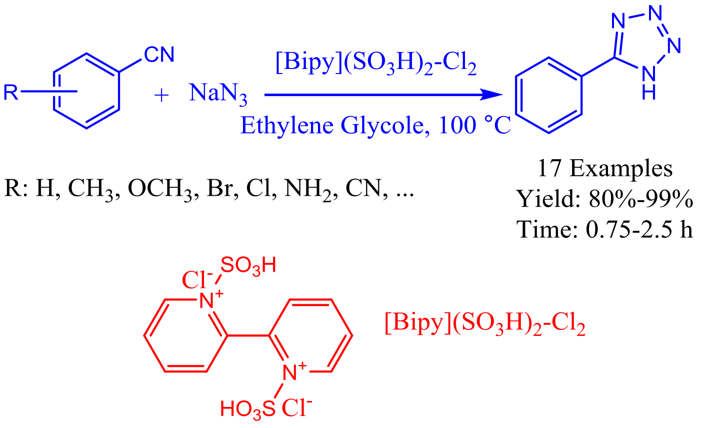
Scheme 7. Preparation of spiro indenoquinoxaline-1,2,4-triazolidine-5-thiones from 11H-[1,2-b]quinoxalin-11-ones and thiosemicarbazide

A novel catalyst, derived from natural sources, was synthesized by Besharati and co-workers [60]. This innovative catalyst involved the integration of Cu_2O nanoparticles into the acidic-ionic liquid functionalized Montmorillonite-K10, known as Cu_2O@Mont/EAS-IL. Cu_2O@Mont/EAS-IL underwent successful characterization using FTIR, BET, ICP-AES, XRD, FE-SEM, and TGA techniques. Subsequently, it was employed in the synthesis of benzopyranopyrimidines (BPP) via a one-pot reaction conducted under gentle conditions (**Scheme 8**). The activity of a newly synthesized catalyst, which is based on natural compounds and active metal copper, was investigated in the synthesis of benzopyranopyrimidines (BPP) compounds. The catalytic system exhibits superior performance in comparison to recently reported systems, boasting high catalytic capacity, a high percentage yield of isolated products, and a shorter reaction time under mild conditions. Furthermore, considering the mechanism and experimental findings, the quantity of copper present in the catalyst, serving as the active site, is sufficient to facilitate the progression of this reaction. The findings indicate that the acidic proton present in ionic liquids can serve as a co-catalyst, effectively enhancing the reaction. The comparison of this outcome with other conventional acid catalysts, such as pure CuI and Cu_2O@Mont, revealed that this catalytic system is not only effective but also safe, with no corrosive impact, and can be conveniently isolated. These findings suggest that the catalytic activity of Cu_2O@Mont/EAS-IL was enhanced due to the synergistic effect of the ionic liquid, Cu_2O, and Mont. In addition, this catalyst has the capability to expedite the production of the desired products compared to traditional thermal techniques. Cu_2O@Mont/EAS-IL offers several advantages, including its heterogeneous nature, ease of synthesis, and recyclability. The Cu_2O@Mont/EAS-IL catalyst exhibits the ability to be recovered and reused up to 5 times, while maintaining its catalytic activity without any notable decline.

A highly effective and environmentally friendly approach has been devised by Aali et al. to produce 5-substituted 1H-tetrazole derivatives via [2+3] cycloaddition reaction using 1-Disulfo-[2,2-bipyridine]-1,1-diium chloride ionic liquid (**Scheme 9**) [61]. This method yields excellent to good results and involves the use of different benzonitriles and sodium azide. The ionic liquid catalyst, $[BiPy](HSO_3)_2Cl_2$, based on 1-disulfo-[2,2-bipyridine]-1,1-diium chloride, has been effectively utilized to facilitate the synthesis of these highly sought-after products. This procedure offers notable benefits, such as the utilization of ethylene glycol as an environmentally friendly solvent. This method offers additional benefits such as cost-effectiveness, simplified catalyst preparation, gentle reaction parameters, environmentally-friendly reaction medium, effortless purification, swift reaction duration, and straightforward experimental procedure.



Scheme 8. Preparation of BPP derivatives catalyzed by Cu_2O@Mont/EAS-IL

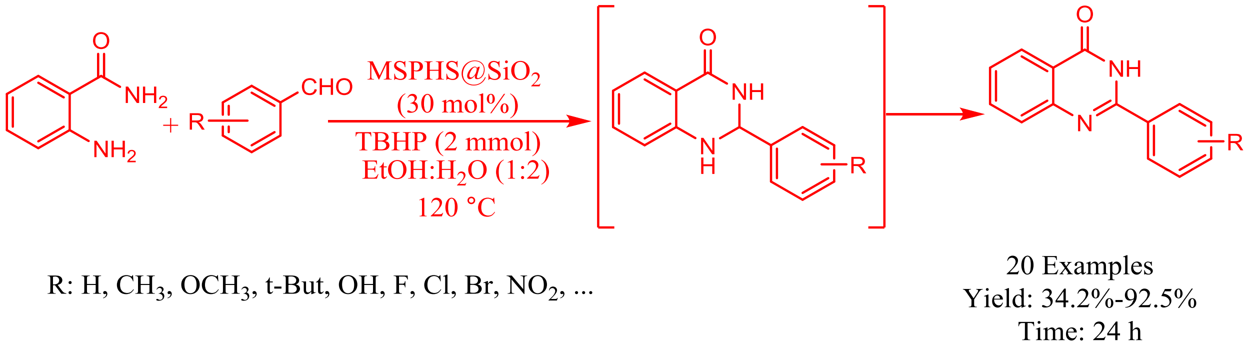


Scheme 9. Synthesis of 5-substituted-1*H*-tetrazoles in the presence of $[BiPy](SO_3H)_2$-Cl_2 in Ethyleneglycol.

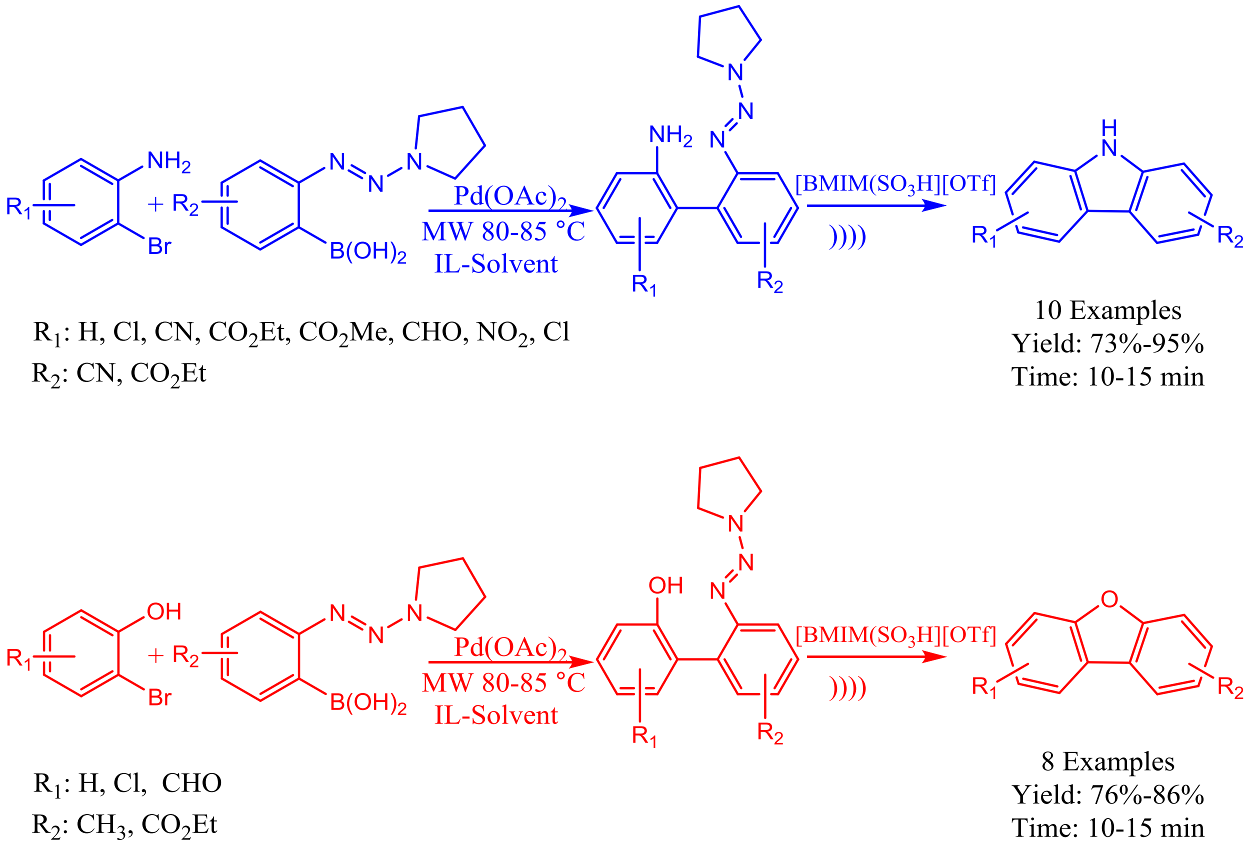
Huynh and co-workers prepared a novel catalyst 1-Methyl-1-(4-sulfobutyl)pyrrolidinium hydrogen sulfate supported onto silica gel (MSPHS@SiO_2) [62]. The initial step involved the synthesis of the first acidic ionic liquid, which contained sulfonyl groups derived from 1,4-butane sultone. To achieve this, 1-methylpyrrolidine was used as a nucleophilic reagent and reacted with electrophilic 1,4-butane sultone, resulting in the formation of a zwitterion intermediate. This zwitterion was then treated with sulfuric acid, leading to the formation of 1-methyl-1-(4-sulfobutyl)pyrrolidinium hydrogen sulfate ionic liquid. The next step involved grafting this ionic liquid onto the surfaces of silica gel, which was accomplished in the presence of tetraethyl orthosilicate (TEOS). The present investigation details the synthesis of 2-phenylquinazolin-4(3H)-ones using a recyclable Brønsted acidic ionic liquid immobilized onto silica (**Scheme 10**). The MSPHS@SiO_2 catalyst has been proven to be effective in the synthesis of 2-phenylquinazolin-4(3H)-ones by cyclizing aldehydes and 2-aminobenzamide. The MSPHS@SiO_2 (30 mol%) with TBHP (2 mmol) in a mixture of EtOH:H_2O (15 mL, 1:2) at 120 °C for 24 hours provided the optimized conditions. A diverse array of 2-phenylquinazolin-4(3H)-ones were successfully acquired through a straightforward recrystallization process, resulting in yields ranging from 34.2% to 92.5%. The MSPHS@SiO2 has demonstrated its efficacy as a green catalyst, enabling effective retrieval and reuse while maintaining its catalytic activity without any notable decline. In addition, the products were acquired through a straightforward recrystallization process. It is interesting that this method holds potential for large-scale production applications.

The synthesis of functionalized carbazoles and dibenzofurans utilizing biaryl-triazene as an intermediate was elucidated by Kim and colleagues, who employed Brønsted acidic Ionic liquid as a promoter (**Scheme 11**) [63]. The synthesis of 9H-carbazole-3-carboxylic acid ethyl ester involved the utilization of 2-bromoaniline and 5-(ethoxycarbonyl)-2-(pyrrolidin-1-yldiazenyl)phenyl)boronic acid, resulting in a high yield of 92%. To achieve the desired functionalized carbazole molecules, the boronic acid counterpart remained constant while the tolerance for functional groups on the bromoaniline moiety was varied. The biaryl intermediate is generated using the Suzuki-Miyaura protocol with the assistance of microwave in an ionic liquid (IL). Subsequently, the intermediate undergoes an aromatic nucleophilic substitution reaction in the presence of acidic IL under ultrasonication.

An imidazolium ionic liquids incorporating (L)-prolinamide were successfully synthesized and subsequently assessed as organocatalysts in the asymmetric Biginelli reaction involving benzaldehydes, urea, and β-keto esters by Aalam and co-workers (**Scheme 12**) [64]. The synthesized chiral ionic liquids underwent characterization using several techniques including FT-NMR, TGA, FT-IR, and HRMS. The Biginelli reaction was effectively catalyzed by a chiral ionic liquid containing adamantyl (L)-prolinamide, with $[BF_4]^-$ anion (5 mol%) and *p*-toluenesulfonic acid (5 mol%) as additives. This catalytic system yielded a diverse range of chiral 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs) in yields ranging from 16% to 74%, with enantiomeric excess (ee) values ranging from 7% to 85%. The reaction proceeded at room temperature for 48 hours. Notably, among the 30 chiral DHPMs products obtained, 18 of them were novel compounds. A plausible reaction mechanism and the existence of transition states or intermediates have been proposed and substantiated through the application of FT-NMR spectroscopy and DFT calculations. It is important that the (R)-absolute configuration of the Biginelli products was achieved through the favorable asymmetric induction resulting from the Re-face attack on the imine bond. In addition, the energy of the intermediates was determined through DFT calculations using the B3LYP/631-G* method.



Scheme 10. Synthesis of 2-phenylquinazolin-4(3H)-ones using MSPHS@SiO_2



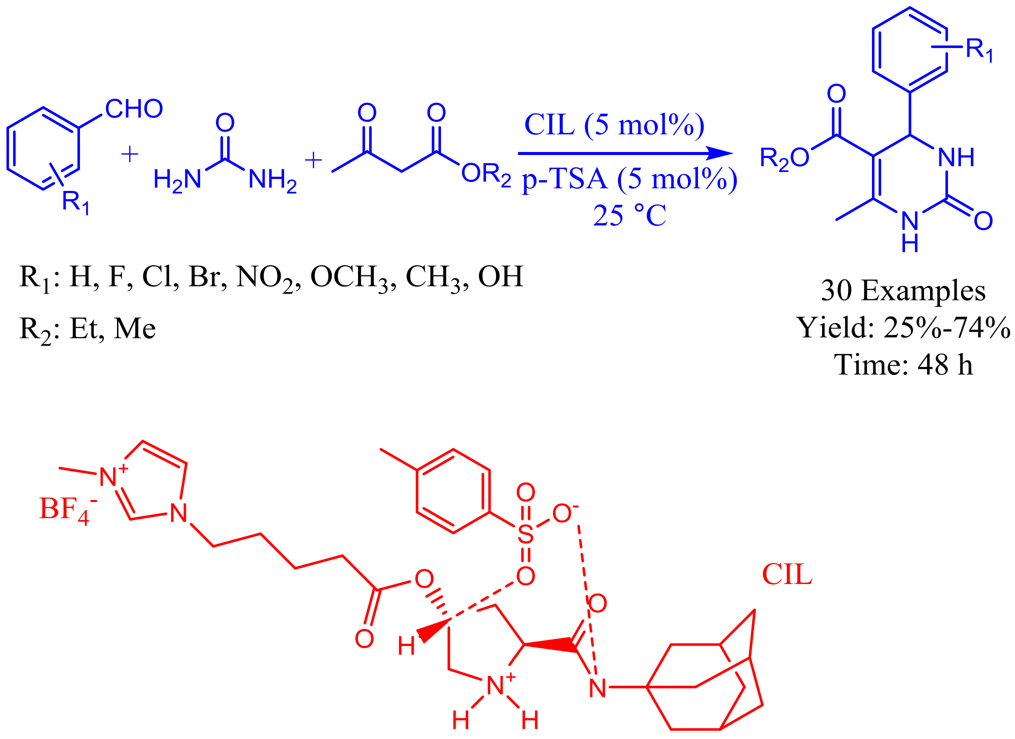
R_1: H, Cl, CN, CO_2Et, CO_2Me, CHO, NO_2, Cl
R_2: CN, CO_2Et

10 Examples
Yield: 73%-95%
Time: 10-15 min

R_1: H, Cl, CHO
R_2: CH_3, CO_2Et

8 Examples
Yield: 76%-86%
Time: 10-15 min

Scheme 11. Synthesis of carbazoles and dibenzofuran using [BMIM(SO_3H)][OTf]



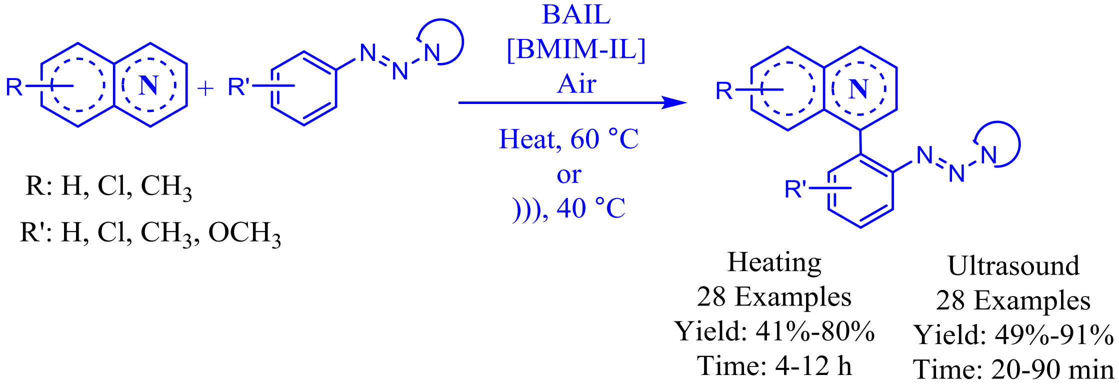
R_1: H, F, Cl, Br, NO_2, OCH_3, CH_3, OH
R_2: Et, Me

30 Examples
Yield: 25%-74%
Time: 48 h

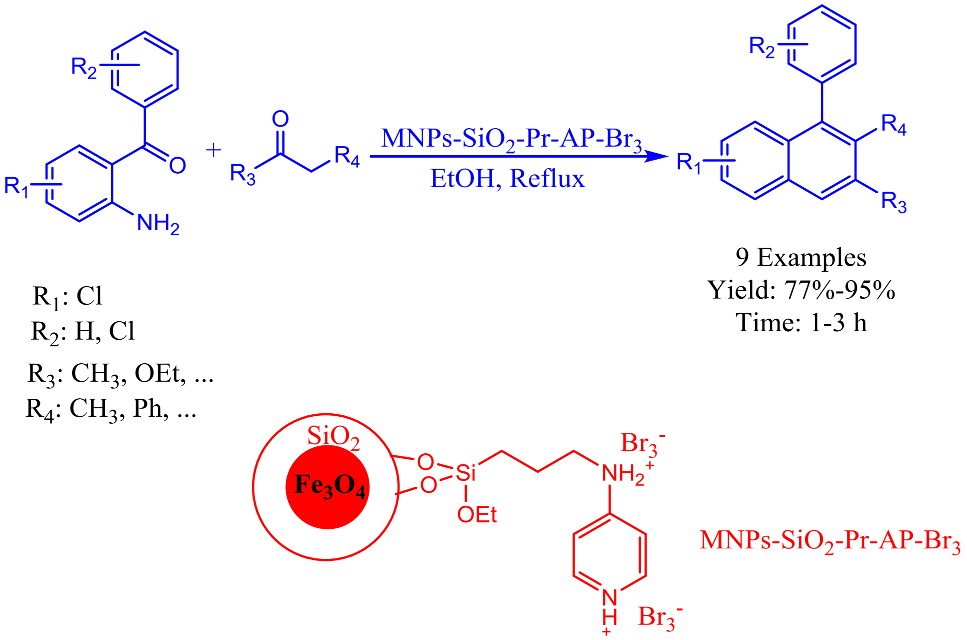
Scheme 12. Synthesis of chiral 3,4-dihydropyrimidin-2-(1H)-ones using chiral ionic liquid containing adamantyl (L)-prolinamide, with $[BF_4]^-$ anion and *p*-toluenesulfonic acid

Prabhala and colleagues have developed a highly efficient and convenient method for producing α-arylated N-heteroarenes. This method involves the use of ultrasound assistance and conventional heating in the presence of Imidazolium based ionic liquids. By utilizing this direct α-arylation protocol, not only does it serve as an acid promoter, but it also acts as a solvent, enabling the synthesis of α-arylated N-heteroarenes under aerobic conditions. The researchers evaluated this reaction using various structurally diverse N-heteroarenes and 1-aryltriazenes. Through this methodology, they were able to effectively establish a synthetic handle for a wide range of electron-rich and electron-deficient arylated N-heteroarenes, achieving high yields without the need for metal or peroxide. Furthermore, this methodology played a crucial role in the total synthesis of well-known oxoisoaporphine alkaloids, Menisporphine and Daurioxoisoporphine C. Notably, this approach offers several advantages, including being metal-free, utilizing a homogeneous ionic liquid medium, and providing environmentally friendly reaction conditions at moderate temperatures using both conventional and ultrasonic methods (**Scheme 13**) [65].

Kharazmi and co-workers prepared a new magnetic ionic liquid pyridinium-tribromide (MNPs@SiO_2-Pr-AP-tribromide) [66]. The provided catalyst was characterized by FT-IR, FE-SEM, TGA, XRD, EDS, EDX, TEM and VSM techniques. The one-pot reaction of 2-amino-5-chlorobenzophenone and pentane-2,4-dione resulted in the successful synthesis of quinoline derivatives using the highly efficient nanocatalyst (**Scheme 14**). This catalyst offers numerous benefits including convenient preparation, extensive surface area, renewability, exceptional thermal stability, heightened activity, reduced reaction time, enhanced efficiency, effortless purification, and gentle reaction conditions.



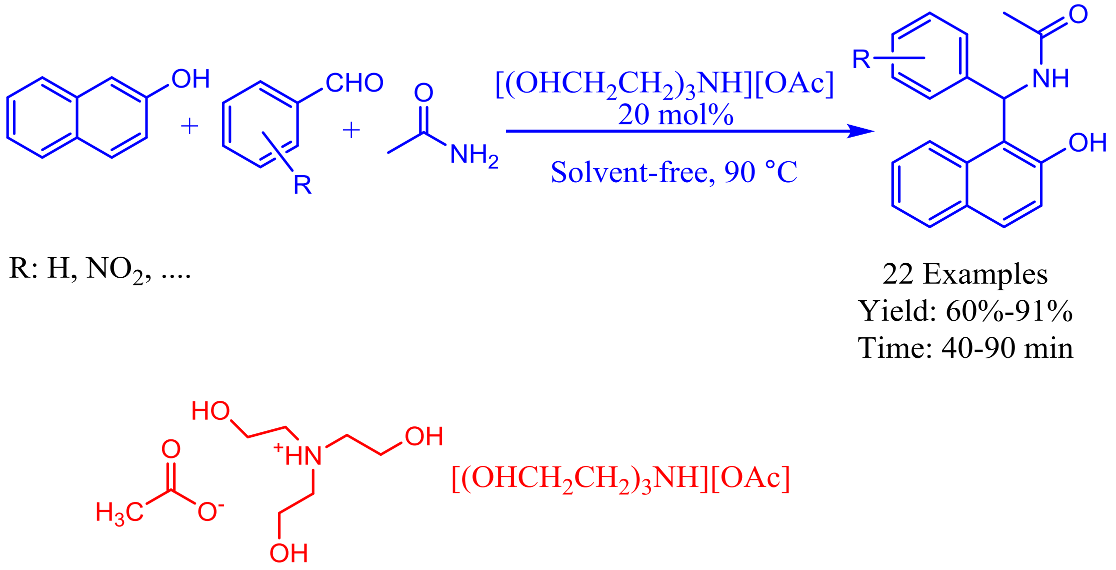
Scheme 13. The general and remark organic reactions catalyzed by [BMIM-IL]



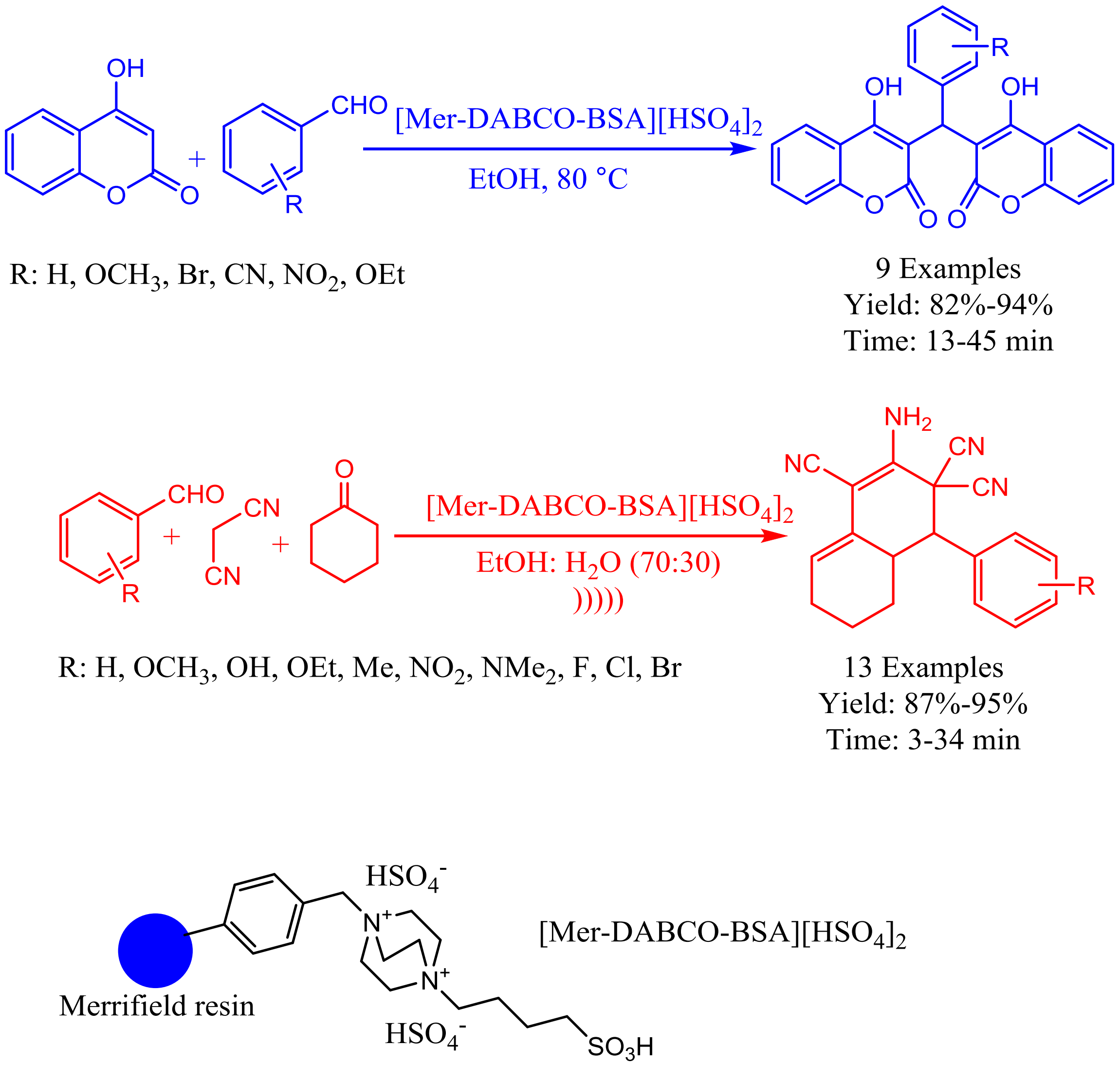
Scheme 14. Synthesis of quinoline derivatives using MNPs@SiO_2-Pr-AP-tribromide

Manavi and co-workers reported a highly efficient one-pot synthesis of amidoalkyl naphthol derivatives, along with their corresponding in vitro anti-Helicobacter pylori activity (**Scheme 15**) [67]. The reaction occurs through a multi-component condensation process involving 2-naphthol, (hetero) aromatic aldehydes, and various compounds such as urea, thiourea, acetamide, 2-aminothiazole, 4-nitrothiazol-2-amine, and 2-aminopyridine. This condensation takes place under solvent-free conditions. This protocol incorporates notable characteristics, including the utilization of triethanolammonium acetate ($[OHCH_2CH_2)_3NH][OAc]$) ionic liquid as an environmentally friendly, efficient, and recyclable catalyst. It offers advantageous attributes such as high yields, elimination of column chromatography, and cost-effectiveness. In an effort to expand the current protocol, the researchers endeavored to substitute urea with thiourea, acetamide, 2-aminothiazole, 4-nitrothiazol-2-amine, and 2-aminopyridine. These alternative compounds were subjected to the same reaction conditions, resulting in the successful synthesis of amidoalkyl naphthol derivatives with satisfactory yields ranging from moderate to good. The entire process was accomplished within a time frame of 40 to 90 minutes. The model reaction was also examined for the catalyst's reusability. Upon completion of the reaction, 6 mL of cold distilled H_2O was introduced to the reaction mixture and the solid product was filtered. The aqueous layer, comprising $[(OHCH_2CH_2)_3NH][OAc]$, was retrieved after rotary evaporation of water and was subsequently reused in subsequent reactions. The catalyst was recycled with remarkable yields and was employed in the aforementioned reaction for three cycles with satisfactory efficiency.

A new catalyst was synthesized by Patil and colleagues utilizing Merrifield resin that was functionalized with DABCO, 1,4-butane sultone, and concentrated H_2SO_4. The outcome was a Brønsted acidic ionic liquid catalyst that was supported by a polymer (**Scheme 16**) [68]. The confirmation of the synthesized catalyst's structure was achieved through the utilization of various techniques including FT-IR, XRD, SEM, XPS, EDX, TGA, and DTA. The catalytic efficiency of a newly developed Brønsted acidic catalyst, $[MerDABCO\text{-}BSA][HSO_4]_2$, was assessed in the synthesis of biscoumarins. This reaction involved the utilization of 4-hydroxycoumarin and aryl aldehydes as starting materials, with the reaction taking place in ethanol at a temperature of 80 °C. In addition, ortho-aminocarbonitriles were successfully synthesized by employing a combination of aromatic aldehydes, malononitrile, and cyclohexanone in an ethanol:water solvent mixture (70:30 v/v) under the influence of ultrasonic conditions. The catalyst demonstrates excellent stability when subjected to ultrasonic conditions and thermal. The recycled catalyst showcases efficient catalytic performance for four cycles, maintaining its activity without any notable decline. The current procedure presents numerous benefits, including operational simplicity, reduced reaction times, and enhanced product yields.



Scheme 15. Synthesis of amidoalkyl naphthol derivatives using $[(OHCH_2CH_2)_3NH][OAc]$



R: H, OCH$_3$, Br, CN, NO$_2$, OEt

9 Examples
Yield: 82%-94%
Time: 13-45 min

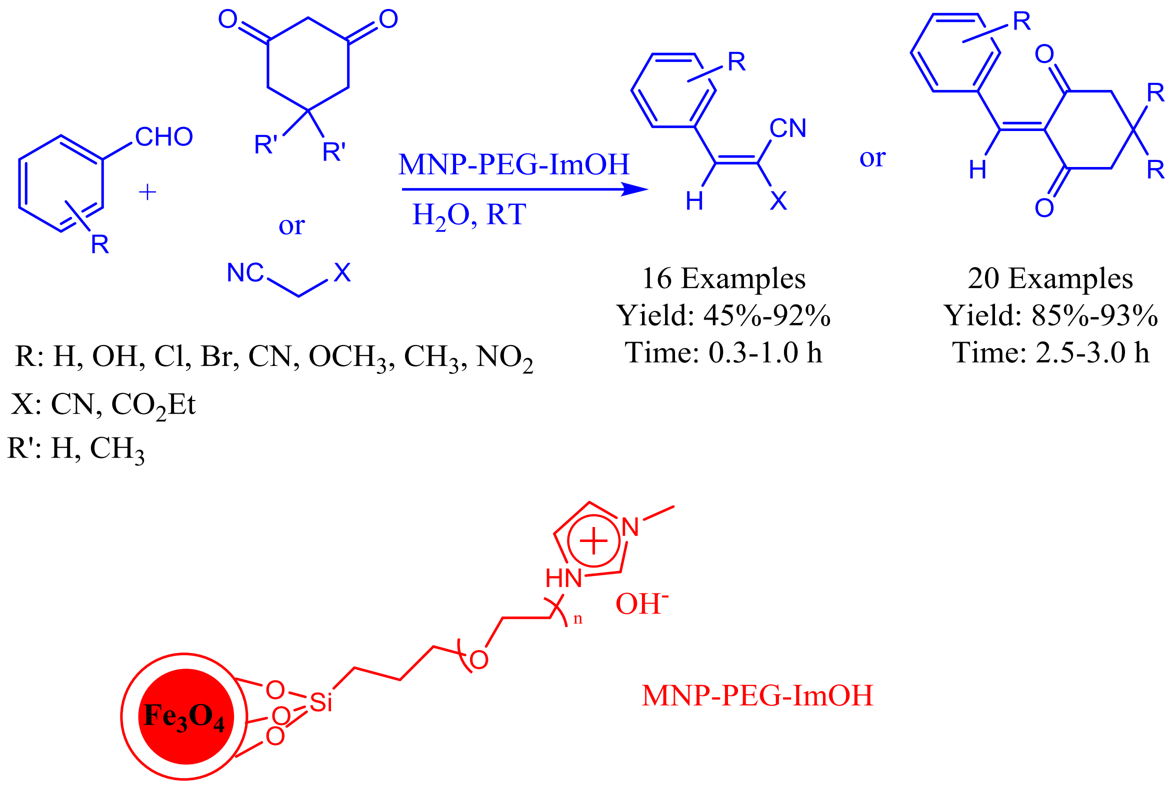
R: H, OCH$_3$, OH, OEt, Me, NO$_2$, NMe$_2$, F, Cl, Br

13 Examples
Yield: 87%-95%
Time: 3-34 min

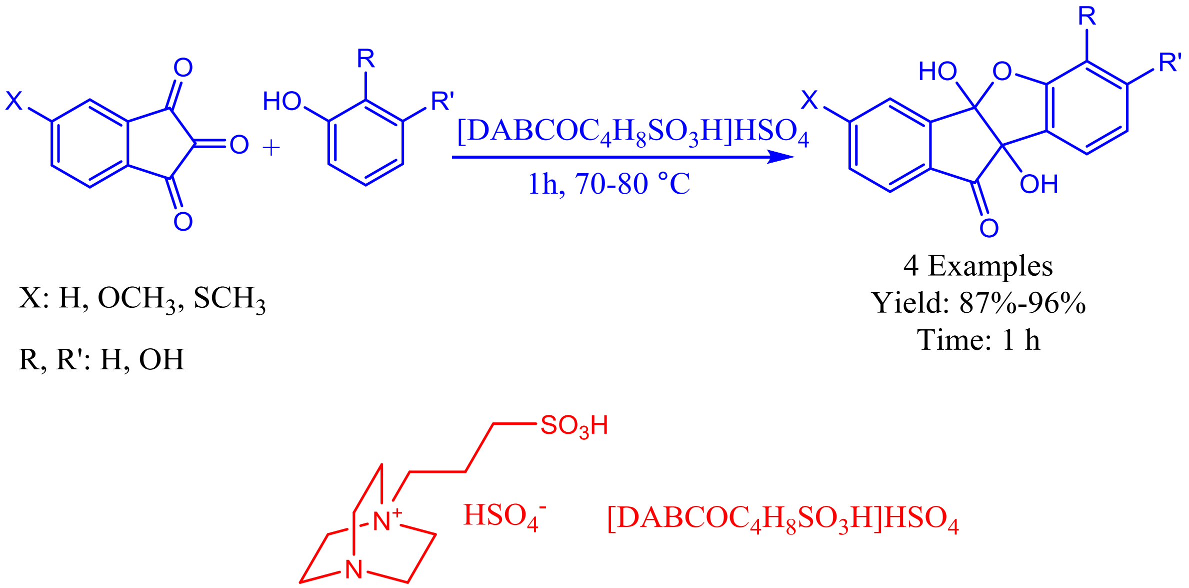
Scheme 16. Synthesis of biscoumarins and *ortho*aminocarbonitriles using [MerDABCO-BSA][HSO$_4$]$_2$

Fallah-Mehrjardi and co-workers focused on the synthesis and analysis of magnetic nanoparticles (MNP@PEG-ImOH) functionalized with polyethylene glycol-substituted 1-methyl imidazolium hydroxide [69]. The characterization of the synthesized catalyst was carried out using various techniques including FESEM, TGA, FT-IR, VSM, TEM, EDAX, and XRD. The examination of MNP@PEG-ImOH's catalytic activity was conducted in the Knoevenagel condensation process, involving active aromatic aldehydes and methylene compounds, within an aqueous medium at ambient temperature (**Scheme 17**). The catalytic system has proven to offer a multitude of advantages, including increased product yields, reduced reaction time, the ability to reuse and recycle the catalyst, simplified work-up procedures, and improved reaction conditions. The catalyst can be effortlessly separated from the reaction mixture using an external magnet and subsequently reused in subsequent reactions without any significant decrease in its effectiveness.

The exploration of an acidic catalyst based on DABCO (1,4-diaza bicycle [2.2.2] octane)-based ionic liquid enables the investigation of a straightforward and efficient approach for synthesizing indeno-benzofurans derivatives utilizing polyphenols and ninhydrins (**Scheme 18**) [70]. The utilization of catalysts is crucial for obtaining high yields in reactions of this nature. However, when DABCO-AIL is employed as a catalyst, the yields are exceptional, reaction times are shortened, and the reaction media are more environmentally friendly. The confirmation of product structures can be achieved through the utilization of IR, ^{1}H NMR, ^{13}C NMR, and mass spectrometry analysis. Oxidative stress has been implicated in the pathophysiology of various diseases, including diabetes, based on available evidence.



Scheme 17. Knoevenagel reaction catalyzed by MNP@PEG-ImOH

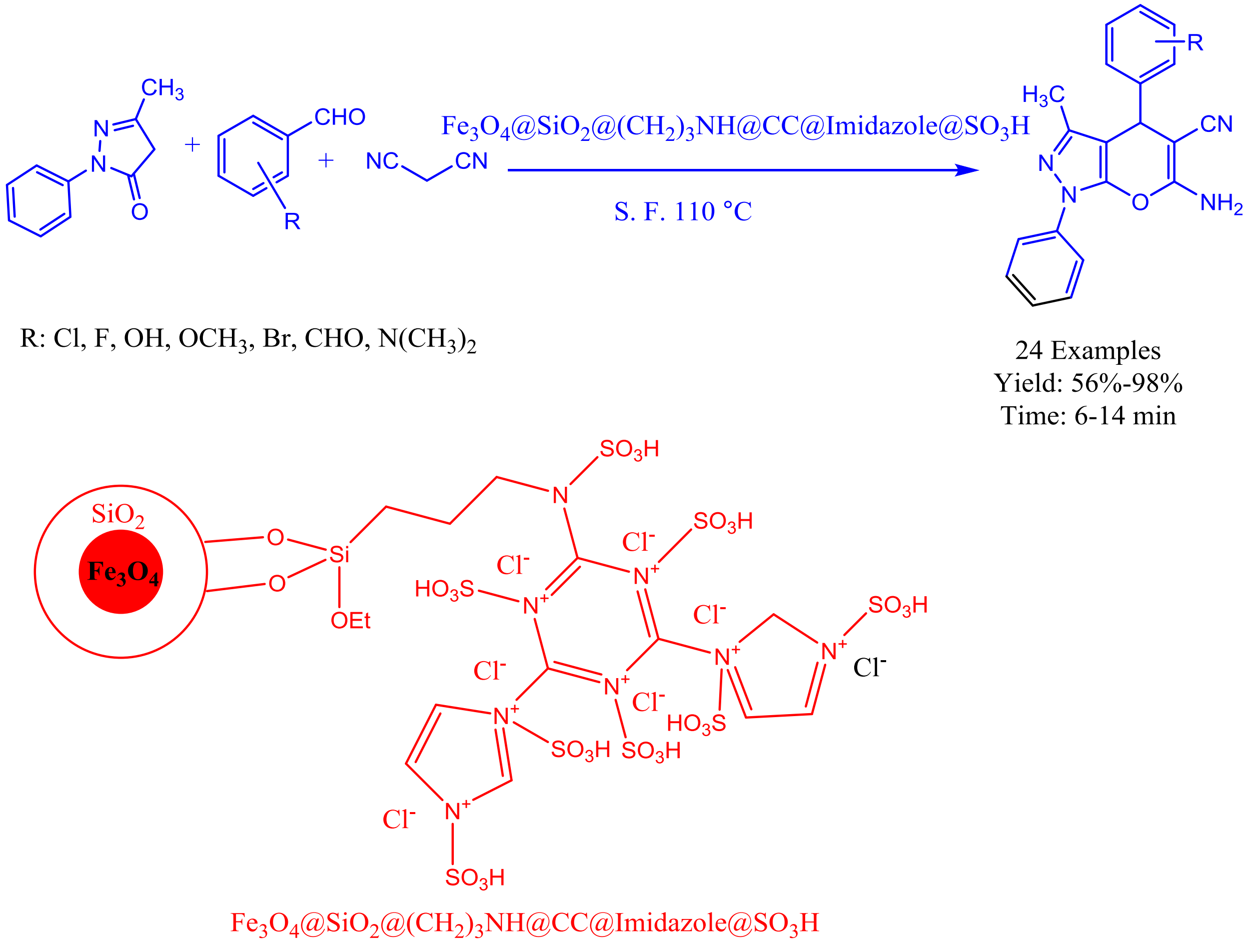


Scheme 18. Reactions of polyphenols and ninhydrin catalyzed by [DABCOC$_4$H$_8$SO$_3$H]HSO$_4$

The utilization of therapeutic antioxidants shows great potential in the prevention and treatment of various diseases. In order to assess the antioxidant capabilities of all synthesized derivatives, the DPPH assay involving 2,2-diphenyl-1-picrylhydrazylhydrazyl-hydrate was conducted.

A molecular engineering technique has been developed to synthesize a heterogeneous catalyst, $Fe_3O_4@SiO_2@(CH_2)_3NH@CC@Imidazole@SO_3H$, which is based on ionic liquids and nano-magnetic solid acids (**Scheme 19**) [71]. Various techniques were employed to characterize the synthesized catalyst, including IR, FESEM, TEM, EDX, EDX elemental mapping, TGA, DTA, and VSM. The synthesized catalyst's performance was assessed in the production of pyrano [2,3-c] pyrazole derivatives. It is conveniently retrievable with an external magnet and can be utilized multiple times. The stability of the as-synthesized catalyst was confirmed by the FTIR analysis, which remained unaffected even after undergoing five recovery steps. It was discovered that pyrano [2,3-c] pyrazole derivatives could be synthesized with high yield (56-98%) in a short amount of time. To optimize the reaction conditions, a systematic design of experiment (DOE) was implemented, which yielded exciting results.

A diverse collection of substituted quinolone-2-carboxylates, including 6-substituted quinoline dialkyl-2,4-dicarboxylates, 4,6-disubstituted quinolone-2-carboxylates, and 6-substituted 4-[2-methoxy-2-oxoethyl]quinoline-2-methylcarboxylates, was successfully synthesized using various one-pot and one-step multicomponent reactions (MCRs). These MCRs encompassed three different approaches: (a) a three-component reaction involving aromatic amines, dialkyl acetylenedicarboxylates, and terminal ketones/alkenes; (b) a pseudo three-component reaction involving dialkyl acetylenedicarboxylates and anilines; and (c) a pseudo three-component reaction involving methyl propiolate and anilines. Notably, all these reactions were carried out under solvent-free conditions at a temperature of 100°C. This synthetic strategy allowed for the efficient and convenient synthesis of a library of substituted quinolone-2-carboxylates with diverse structural motifs (**Scheme 20**) [72]. A new inorganic-organic core-shell, derived from silicated titanomagnetite, ethyl iodide, and, tryptophan amino acidserves as the catalyst for these annulation processes. The silicated titanomagnetite core ($Fe_{3-x}Ti_xO_4$-SiO_2) is embedded with tryptophan and then alkylated with ethyl iodide, resulting in the in situ formation of triethyltryptophanium iodide ionic liquid ($TrpEt3^+I^-$). The characterization of the ultimate nanohybrid, denoted as $Fe_{3-x}Ti_xO_4$-$SiO_2@TrpEt_3^+I^-$, was characterized by XRD, FT-IR, TGA, EDAX, and VSM analysis. The protocol showcases several notable features. Firstly, it enables the synthesis of a diverse array of substituted quinolines using a direct and uncomplicated method, all while operating under solvent-free conditions. Secondly, it allows for the utilization of a wide range of functional substrates, thereby expanding its applicability. Additionally, the nano promoter employed in this protocol can be easily separated using an external magnet, facilitating the

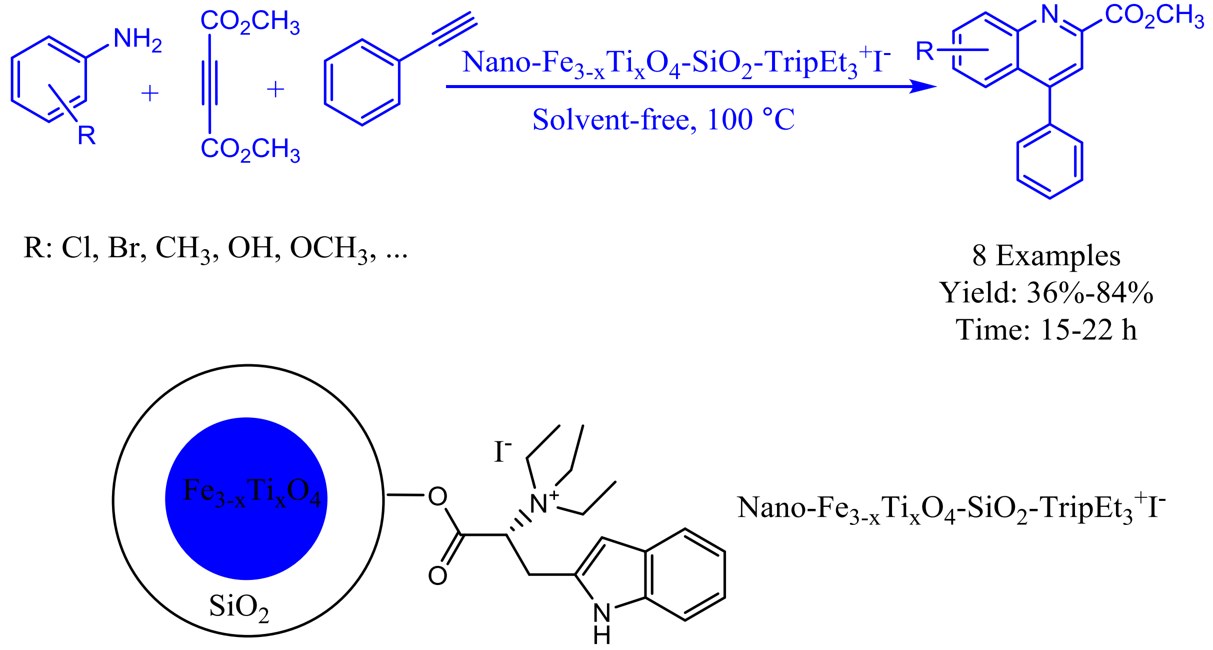


Scheme 19. Synthesis of pyrano [2,3-c] pyrazole derivatives catalyzed by $Fe_3O_4@SiO_2@(CH_2)_3NH@CC@Imidazole@SO_3H$

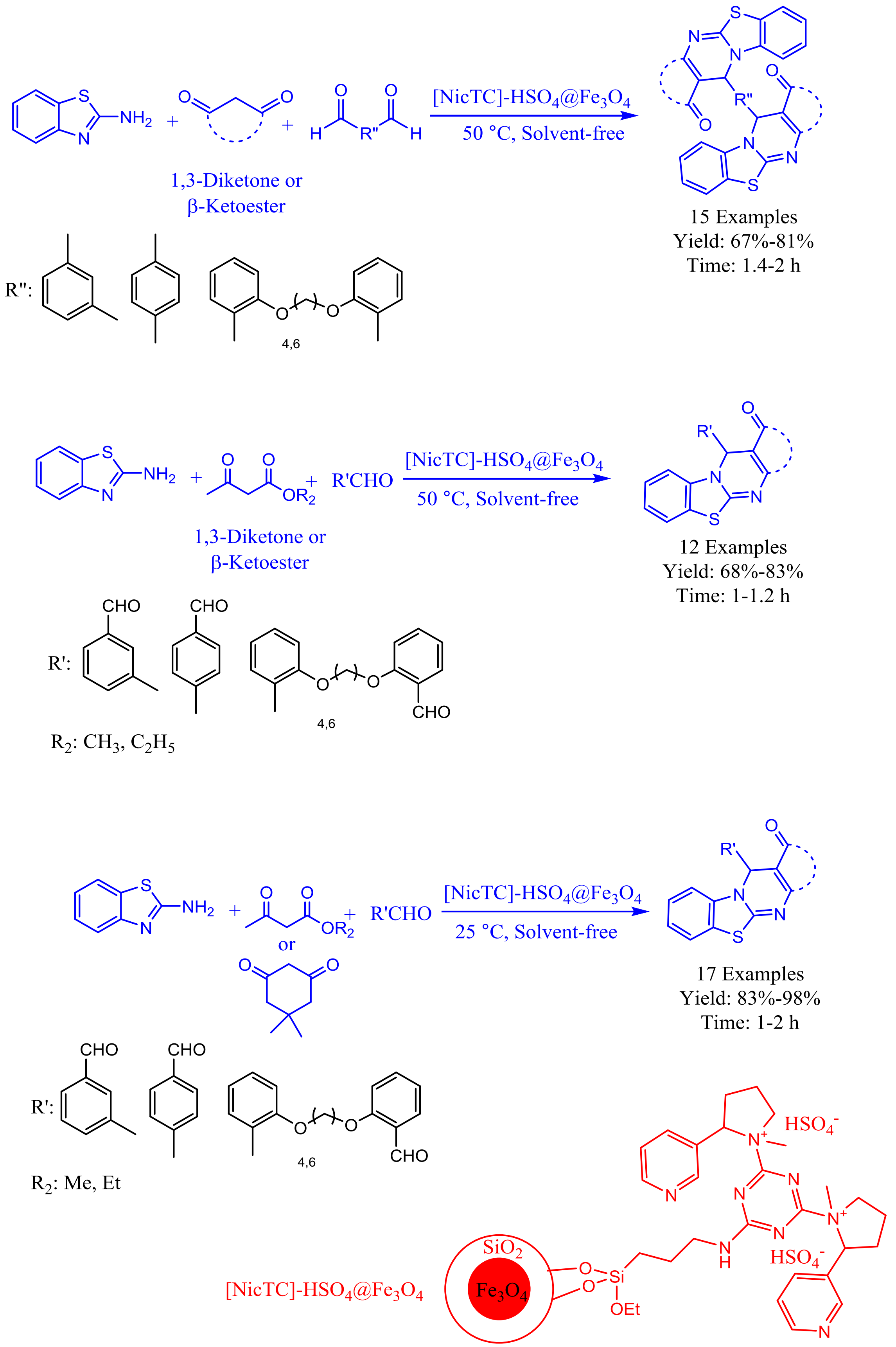
purification process. Moreover, the protocol exhibits regioselectivity in the cascade annulation procedure, ensuring precise control over the desired product formation. Lastly, the nanocomposite utilized in this protocol demonstrates remarkable recovery and reusability, maintaining its activity even after three consecutive runs without any significant loss.

A synthesis and characterization of [NicTC]HSO4@MNPs, as an ionic liquid based on nicotine with acidic properties, supported on magnetic nanoparticles, was conducted using various techniques. The catalyst's performance was assessed by Alishahi and co-workers in a multicomponent reaction involving aldehydes/dialdehydes, 2-aminobenzothiazole, and β-ketoesters/1,3-diketones, resulting in the synthesis of a range of innovative mono- and bis-4H-pyrimido[2,1-b]benzothiazole derivatives (**Scheme 21**) [73]. The exceptional reusability of [NicTC] HSO$_4$@MNPs catalyst in producing distinctive compounds through the reaction of 4-nitrobenzaldehyde, 2-aminobenzothiazole, and ethyl acetoacetate can be attributed to its superparamagnetic properties and impressive saturation magnetization value of 19.52 emu.g^{-1}. After the reaction concluded, the mixture underwent dilution with hot EtOH, and the catalyst was effortlessly separated using an external magnet. The separated catalyst was then washed with hot EtOH, dried, and subsequently reused in successive cycles. The catalyst demonstrates remarkable durability and effectiveness, as it can be utilized for a minimum of five cycles without experiencing any notable decline in its efficiency and activity. Furthermore, upon analyzing the FT-IR spectra of both the pristine and recycled catalyst, no discernible alterations in the catalyst's structure or characteristic bands were observed. This observation serves as evidence of the catalyst's stability under the prevailing reaction conditions. In addition, the method offers rapid response times, excellent yields, convenient work-up procedures, avoidance of toxic organic solvents, and the potential for catalyst recovery and reuse. These advantageous features render this approach an economically viable and environmentally friendly process for synthesizing such exquisite heterocycles.

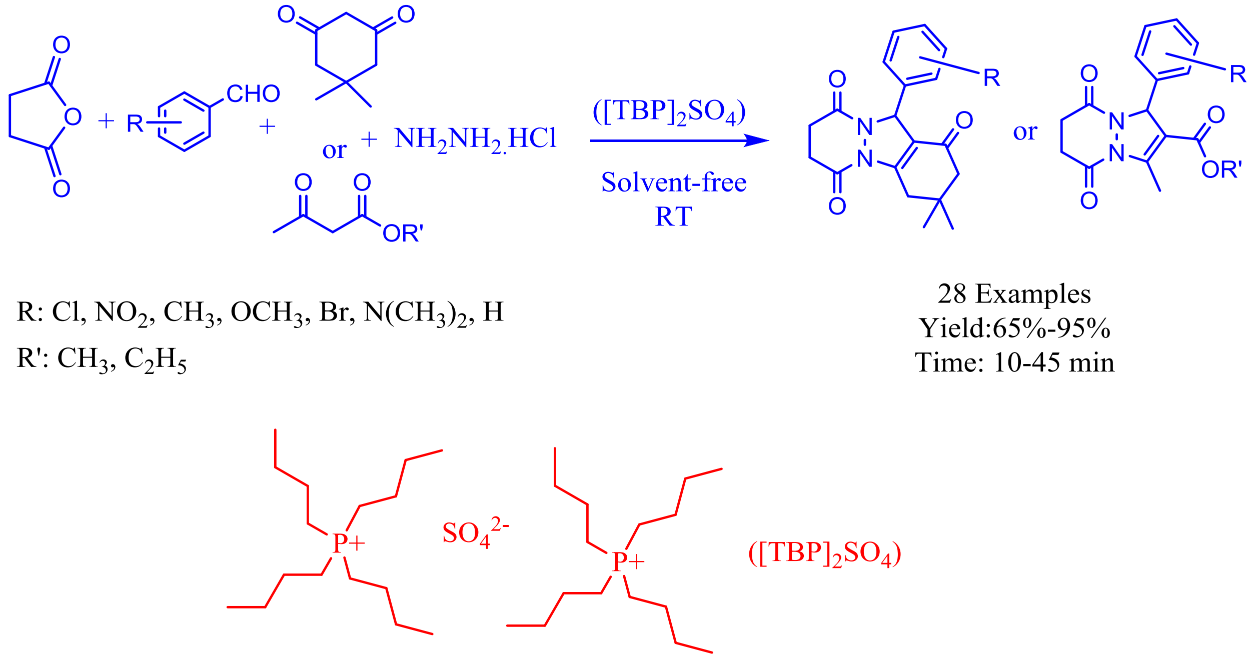
Tetrabutyl phosphonium sulfate, also known as [TBP]$_2$SO$_4$, was successfully synthesized in Amirmahani’s group as a novel room-temperature ionic liquid (RTIL) using a straightforward and cost-effective approach. The synthesized compound was thoroughly characterized using advanced analytical techniques such as ^{1}H, ^{13}C, ^{31}P NMR, and FT-IR spectrophotometry. The recently prepared catalyst demonstrated high efficiency when employed in several multicomponent reactions, such as the synthesis of indazolo[2,1-b]phthalazine, pyridazino[1,2-a]indazole, and pyrazolo[1,2-b]phthalazine (**Scheme 22**) [74]. This green approach offers numerous benefits, including rapid response time, utilization of straightforward techniques for catalyst and product preparation, effortless operation, and exceptional product efficiency. Furthermore, the catalyst can be effortlessly reclaimed and reused multiple times, resulting in reduced average activity.



Scheme 20. Synthesis of substituted quinolines in the presence of nano Fe$_{3-x}$Ti$_x$O$_4$-SiO$_2$@TrpEt$_3$$^+I^-$



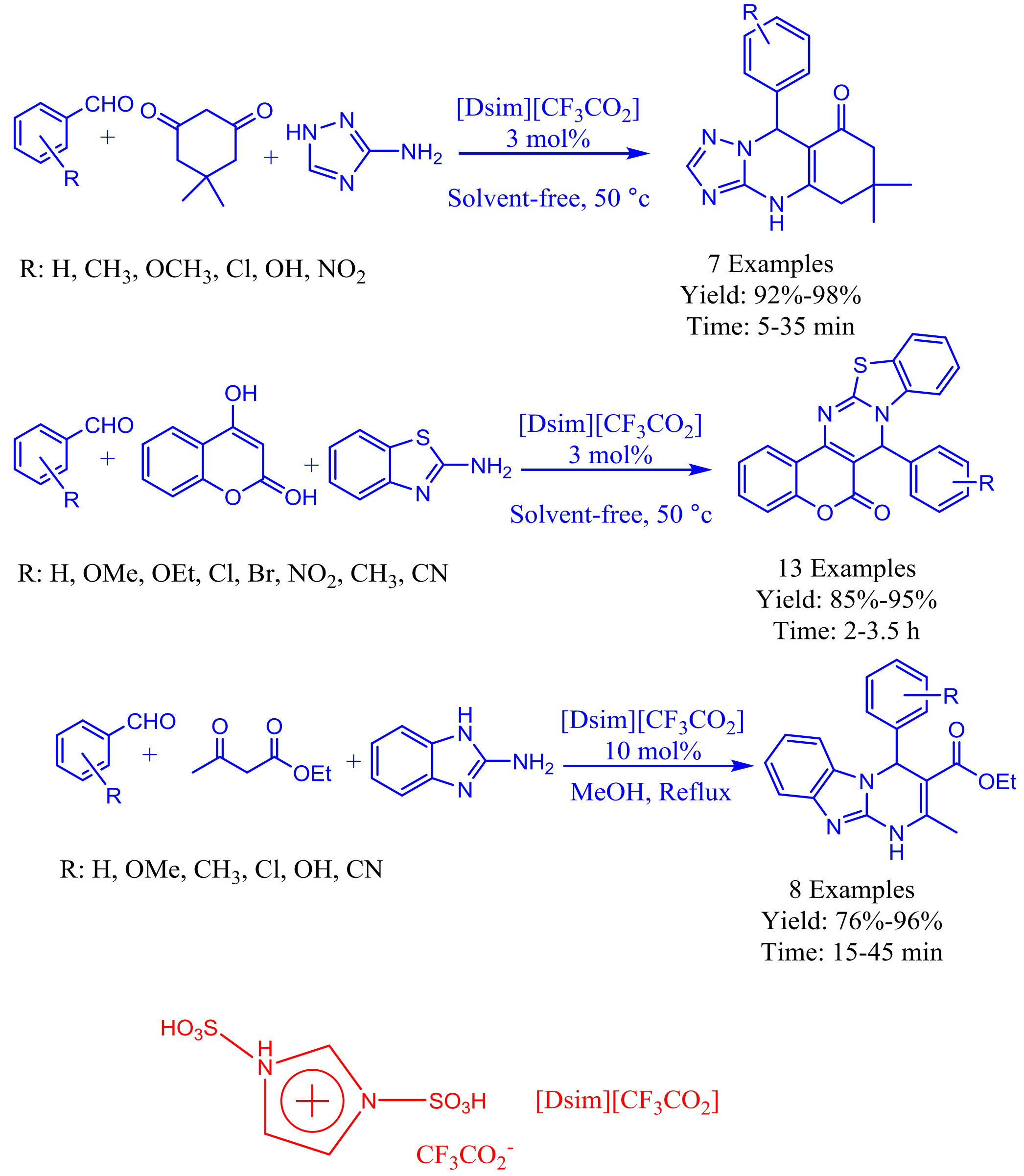
Scheme 21. Synthesis of a series of novel *mono*- and *bis*-4*H*pyrimido[2,1-*b*]benzothiazole derivatives catalyzed by [NicTC] HSO_4@MNPs



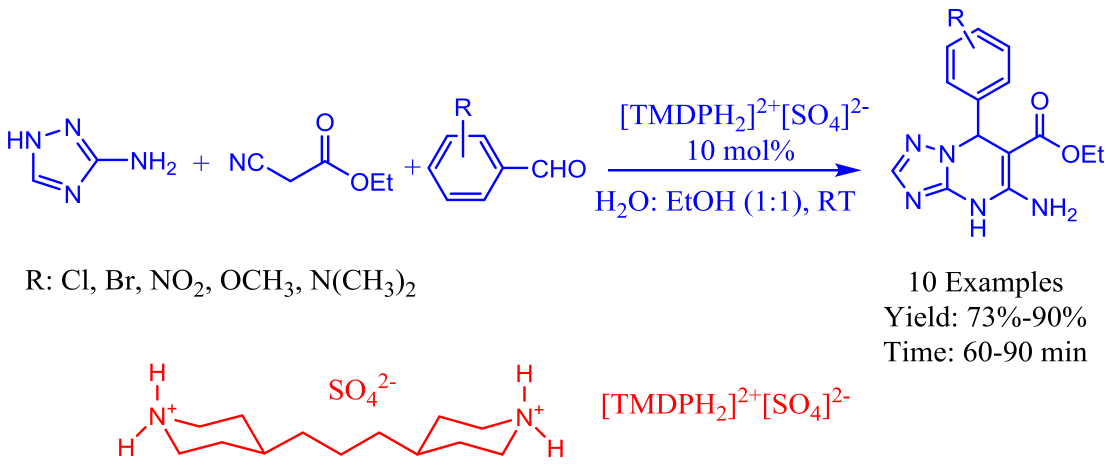
Scheme 22. Synthesis of 2*H*-pyridazino[1,2-*a*]indazole-1,6,9(11*H*)-triones, 2*H*-indazolo[2,1-*b*]phthalazine-1,6,11(13*H*)-triones derivatives catalyzed by $[TBP]_2SO_4$

$[Dsim][CF_3CO_2]$ proved to be a highly effective, uniform, and reusable ionic liquid catalyst in the production of chromeno[4,3-d]benzothiazolopyrimidines, triazoloquinazolinones, and benzoimidazopyrimidine derivatives through one-pot multi-component reactions without the need for solvents under heating conditions (**Scheme 23**) [75]. The catalyst exhibits exceptional catalytic properties, yielding favorable results within a brief reaction period and at a cost-effective rate. All products were acquired through recrystallization, eliminating the necessity for laborious work-up procedures. In addition, their focus shifted towards utilizing $[Dsim][CF_3CO_2]$ for synthesizing derivatives of benzoimidazopyrimidine in a subsequent endeavor. The one-pot three-component reaction involving 2-aminobenzoimidazole (1 mmol), benzaldehyde (1 mmol), and ethyl acetoacetate (1 mmol) was conducted utilizing $[Dsim][CF_3CO_2]$ (10 mol%) as a catalyst under various experimental conditions. The optimal outcome was achieved utilizing 10 mol% of the catalyst in methanol while under reflux circumstances. The method's efficiency and generality were demonstrated by utilizing the optimized conditions to condense ethyl acetoacetate and 2-aminobenzoimidazole with various aromatic aldehydes. The benzo[4,5]imidazo[1,2-a]pyrimidine derivatives can be obtained in good to high yields and relatively short reaction times by gently reacting aldehydes that contain both electron-withdrawing and electron-donating substituents. These methods offer numerous benefits, including generality, excellent efficiency, and high yields of reaction products, as well as safety, short reaction times, a clean reaction profile, easy handling, non-volatility, and economical use of the catalyst. Moreover, all products can be obtained through simple filtration, eliminating the need for column chromatography and reducing waste and environmental pollution.

A novel ionic liquid has been synthesized by Shahnavaz and colleagues, with its chemical structure being characterized through FTIR, 1D NMR, 2D NMR, and mass analyses [76]. The formation of 4,4′-trimethylene-N,N′-dipiperidinium sulfate was confirmed by the results, replacing 4,4′-trimethylene-N,N′-dipiperidinium hydrogen sulfate. The catalytic efficiency of a new ionic liquid was demonstrated through the successful synthesis of triazolo-pyrimidine derivatives under metal-free conditions at room temperature (**Scheme 24**). The desired products were extracted without resorting to high-cost column chromatography during the workup. The residual ionic liquid was recycled and reused in subsequent runs. Remarkably, the new ionic liquid displayed exceptional catalytic activity even after the fifth run, with no discernible alteration in its chemical structure.



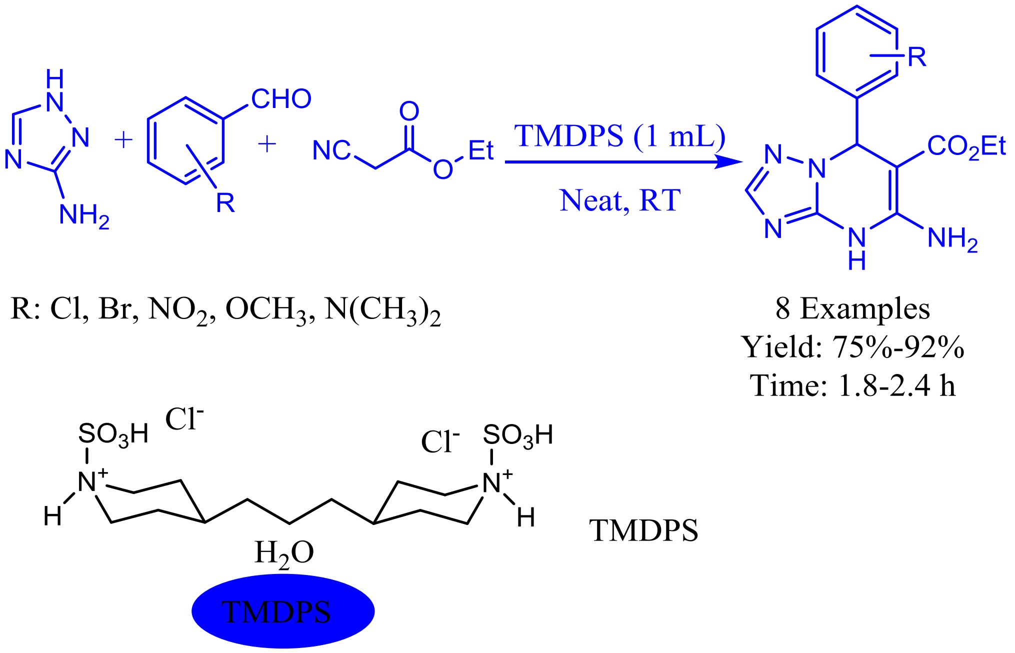
Scheme 23. Synthesis of triazoloquinazolinones, chromeno[4,3-d]benzothiazolopyrimidines, and benzoimidazopyrimidine derivatives catalyzed by [Dsim][CF_3CO_2]



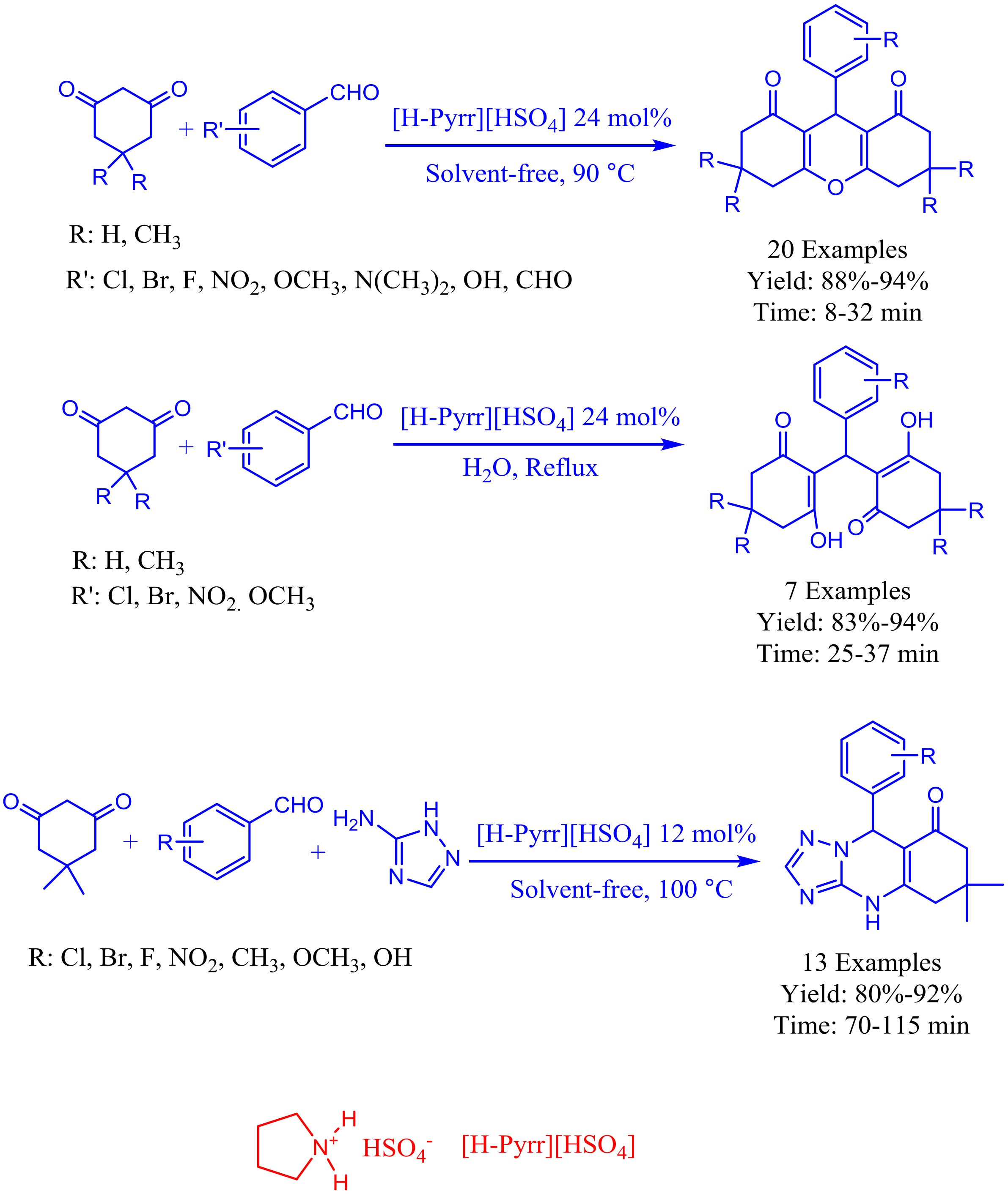
Scheme 24. Synthesis of triazolo[1,5-*a*]pyrimidines catalyzed by $[TMDPH_2]^{2+}[SO_4]^{2-}$

The viscosity of pure ionic liquids holds significant importance in their utilization as solvents for organic synthesis. This is due to the fact that a majority of these pure ionic liquids exhibit high viscosity, consequently leading to less efficient mass transfer of reactants. Zaharani and colleagues synthesized a range of innovative dihydro-[1,2,4]triazolo[1,5-a]pyrimidines employing a low-viscosity ionic liquid that was functionalized with acid groups (**Scheme 25**) [77]. The study demonstrated that the newly developed ionic liquid possesses the ability to function as an environmentally friendly solvent and acid catalyst, owing to its low viscosity and acid functionality. The resulting products were easily extracted, and the ionic liquid could be repeatedly recovered without compromising its catalytic efficiency. The significance of low viscous acid-functionalized ionic liquids in organic synthesis is highlighted by the current use of TMDPS in the dual solvent-catalyst approach for one-pot multicomponent reactions. It is anticipated that future investigations will uncover additional promising applications of TMDPS.

A straightforward and atom-efficient neutralization reaction of pyrrolidine and sulfuric acid resulted in the formation of Pyrrolidin-1-ium hydrogen sulfate ([H-Pyrr]$[HSO_4]$) [78]. This catalyst serves as a readily accessible, reusable, cost-effective, and environmentally friendly agent for facilitating the production of tetraketones, 1,8-dioxo-octahydroxanthenes, and triazolo[2,1-b]quinazolinone derivatives (**Scheme 26**). This method boasts significant benefits such as uncomplicated work-up procedure, effortless catalyst preparation, environmentally-friendly process, exceptional yields, and swift reaction times. The investigation of the structure and acidic properties of the ionic liquid catalyst prepared in this study involved the utilization of infrared spectra, ^1H and ^{13}C-NMR techniques, along with the determination of the Hammett acidity function. This approach circumvents the drawbacks associated with alternative techniques, including the use of extended reaction durations, organic solvents, surplus reagents, and suboptimal yields. Additionally, the current catalyst appears to offer superior advantages in terms of cost-effectiveness and availability. In summary, a new catalyst has been introduced for the synthesis of tetraketone, 1,8-dioxo-octahydroxanthene, and triazolo[2,1-b]quinazolinone derivatives. The catalyst, [H-Pyrr]$[HSO_4]$, is a room temperature Bronsted acidic ionic liquid that offers numerous advantages such as being highly efficient, cheap, simple, green, and homogeneous. The study also highlights the ease of preparation, handling, and recovery of the catalyst, short reaction times, cleaner reaction profiles, high yields of the products and easy work-up. To demonstrate the effectiveness of the chosen procedures, a comparison was made between our synthesized compounds in the presence of [H-Pyrr]$[HSO_4]$ and the results documented in existing literature.



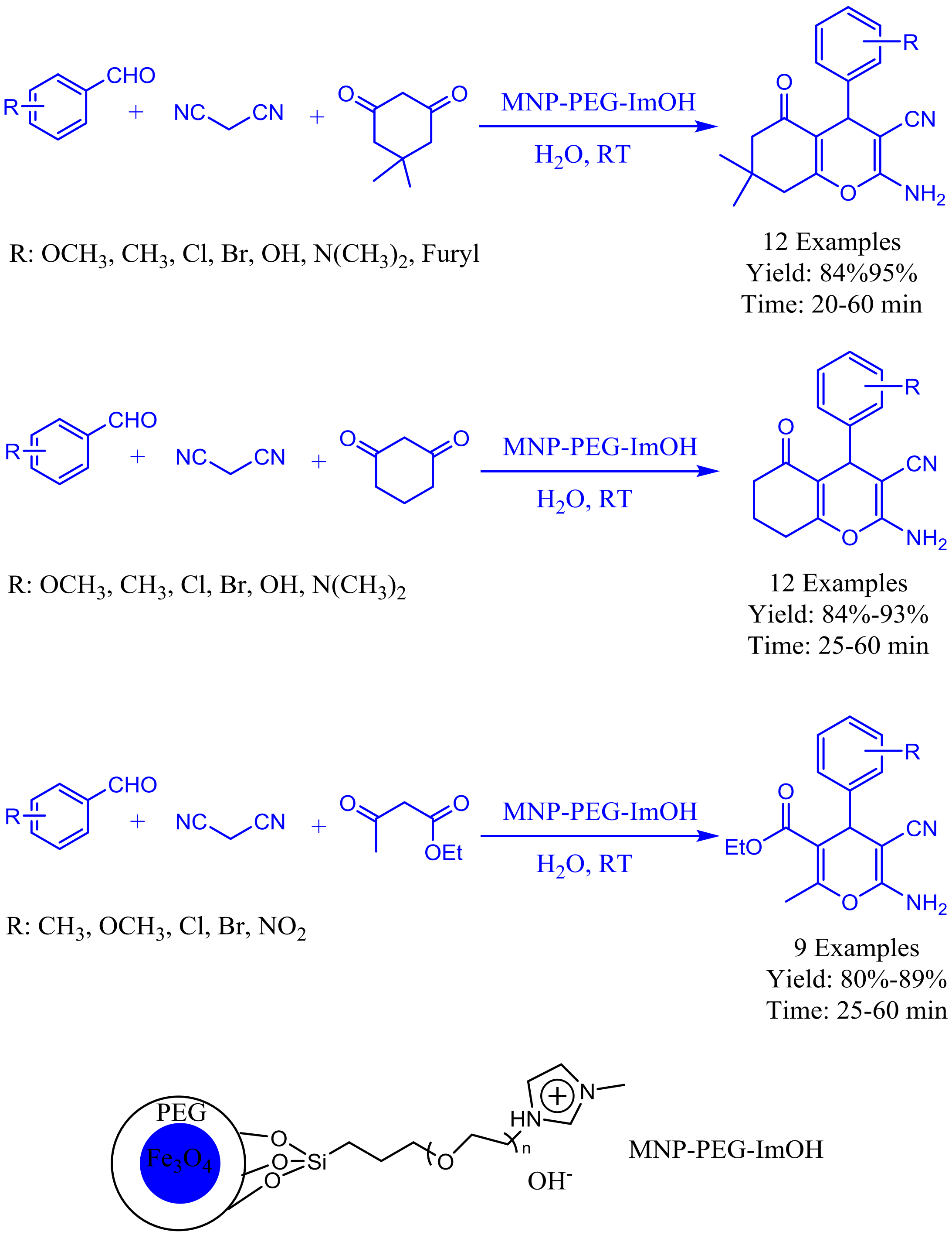
Scheme 25. Synthesis of 5-amino-7-aryl-4,7-dihydro-[1,2,4]triazolo[1,5-a]pyrimidine-6-carboxylates



Scheme 26. Synthesis of tetraketone, 1,8-dioxo-octahydroxanthene, and triazolo[2,1-b]quinazolinone derivatives catalyzed by ([H-Pyrr][HSO$_4$])

An optimized and simplified method has been devised to synthesize 2-amino-3-cyano-4H-pyrans through a convenient one-pot three-component reaction involving benzaldehydes, malononitrile, and 1,3-dicarbonyl compounds (**Scheme 27**) [79]. This innovative approach utilizes a novel nanomagnetite-supported organocatalyst (MNP@PEG-ImOH) in aqueous media, ensuring enhanced efficiency and ease of operation. The MNPs undergo comprehensive characterization through a range of techniques such as FT-IR, EDAX, FESEM, TEM, TGA, XRD, and VSM. The catalyst can be easily isolated from the reaction mixture using an external magnet and can be employed again in subsequent trials without any significant decline in its effectiveness. In summary, an efficient, thermally stable, and magnetically retrievable and reusable basic phase-transfer catalyst (MNP@PEG-ImOH) has been successfully synthesized and characterized. This magnetic nanocomposite was then utilized in a one-pot synthesis of 2-amino-3-cyano-4H-pyrans from the three-component reaction of malononitrile with aryl aldehydes and 1,3-dicarbonyl compounds at room temperature under an aqueous medium. The current catalytic system offers numerous advantages, including short reaction time, convenient separation, high yield, mild reaction conditions, straightforward work-up, and the ability to reuse the magnetic catalyst.

A novel method has been devised to synthesize L-proline triflate ionic liquid (L-ProTfO) in a straightforward, effective, and eco-conscious manner, employing ultrasound irradiation. The utilization of L-proline triflate ionic liquid technology in conjunction with microwave energy presents a compelling and expeditious substitute for the traditional acid-base-catalyzed thermal process.

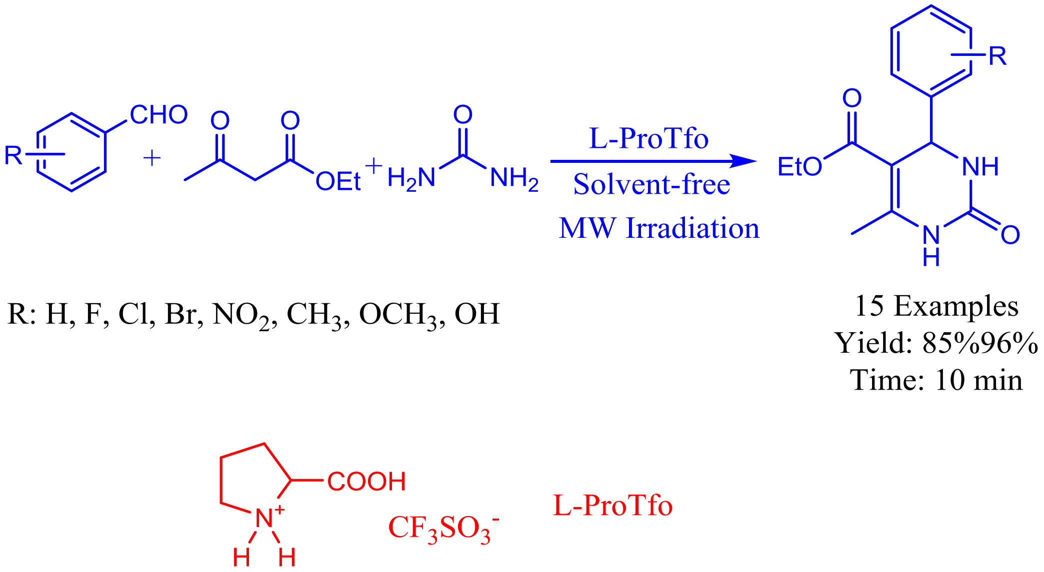


Scheme 27. Synthesis of 2-amino-3-cyano-4H-pyrans catalyzed by MNP@PEG-ImOH

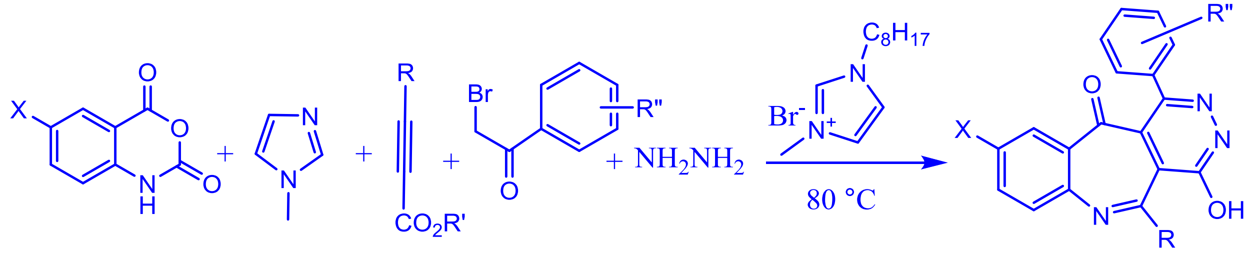
The present approach offers numerous benefits, such as a substantial yield, a brief reaction duration, and a straightforward work-up procedure. Furthermore, the L-proline triflate ionic liquid can be recycled and employed up to four times without any discernible decline in its catalytic efficacy. Both electron-withdrawing and electron-donating groups attached to the aryl ring of the aldehyde were examined and determined to exhibit reactivity. The presence of ortho- and para- electron-donating groups on the aryl ring of the aldehyde resulted in the formation of the desired products, namely o-Cl, p-Cl, p-Br, o-Br, o-Me, m-OMe, o-MeO, and p-OH, with yields that were comparably high, albeit slightly lower than the yield obtained with benzaldehyde. Furthermore, the presence of ortho and para electron-withdrawing groups on the aryl ring of the aldehyde resulted in the formation of the desired products, namely o-F, p-F, and p-NO_2, with exceptional yields surpassing that of benzaldehyde. On the other hand, m-substituted aldehydes, such as m-Cl, m-Br, and m-OH, yielded the desired products in lower quantities compared to benzaldehyde. However, m-Fluorobenzaldehyde exhibited a high yield of the desired product due to the electron-withdrawing properties of fluorine. An exploration was conducted on the recuperation and recycling of L-proline triflate in the Biginelli synthesis during the model reaction. A slight decline in catalytic activity was noted following the fourth cycle, indicating that the L-proline triflate catalyst can be utilized for a minimum of four cycles without any notable decrease in its effectiveness (**Scheme 28**) [80].

Dehbandi and colleagues conducted a study to explore the efficient synthesis of pyridazino benzazepine derivatives with high yields. The researchers employed a domino and one-pot reaction strategy, utilizing activated acetylenic compounds, N-methylimidazole, isatoic anhydride, alkyl bromides, and hydrazine as reactants. Notably, the reaction was carried out in an ionic liquid, serving as an environmentally friendly medium, at a temperature of 80°C (**Scheme 29**) [81]. The investigation of the antioxidation property of certain pyridazino benzazepines, attributed to their pyridazin and benzazepine core, was conducted through the utilization of diphenyl-picrylhydrazine radical trapping and ferric reduction experiments. Their procedure offers several advantages compared to the reported method, including a favorable reaction rate, high product efficiency, and easy separation of the product from the reaction mixture.

The ionic liquid [Bn-DBU][TFA] was obtained in almost quantitative yield through anion exchange of the resulting salt after the DBU was benzylated and treated with trifluoroacetate. This paragraph demonstrates its efficiency as a catalyst in the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones through the three-component reaction involving phthalhydrazide, active α-methylene nitriles, and aromatic aldehydes (**Scheme 30**) [82]. The three-step mechanism for this reaction has been confirmed by both DFT calculations at the B3LYP/SVP level and experimental results.



Scheme 28. Synthesis of 3,4-dihydropyrimidin-2(1*H*)-ones catalyzed by L-ProTfO



X: H, Cl, CH_3, NO_2

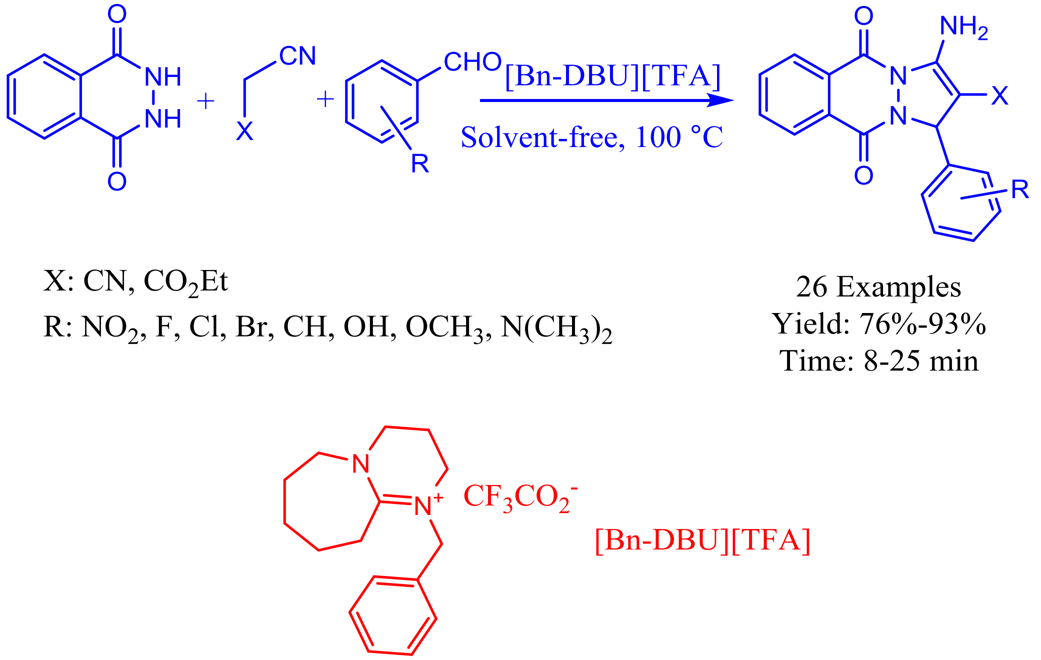
R: CO_2Me, CO_2Et, H

R': Me, Et

R": OCH_3, CH_3, NO_2, Br, Cl

14 Examples
Yield: 85%-95%
Time: 4 h

Scheme 29. Synthesis of pyridazino benzazepine derivatives



X: CN, CO_2Et

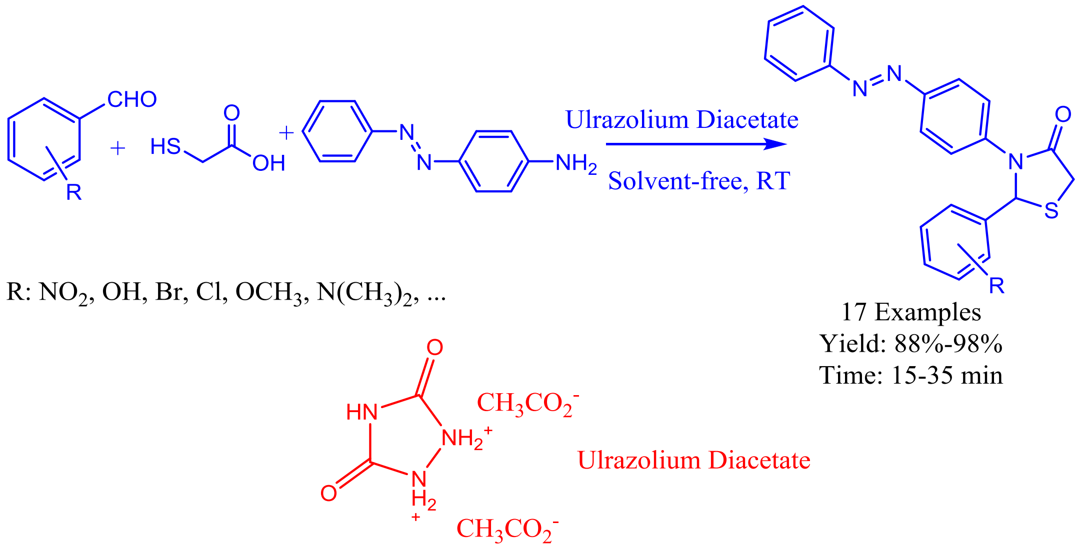
R: NO_2, F, Cl, Br, CH, OH, OCH_3, $N(CH_3)_2$

26 Examples
Yield: 76%-93%
Time: 8-25 min

Scheme 30. Synthesis of 1H-pyrazolo[1,2-b]-phthalazine-5,10-diones catalyzed by ionic liquid [Bn-DBU][TFA]

The catalytic effect, as per the DFT calculations, is primarily due to the intrinsic ionic properties of the ionic liquid, rather than its role as a basic catalyst. The calculations indicate the presence of two activated complexes with similar energies, whose rate determining functions and energies are influenced by their interaction with the anionic component of the ionic liquid. It has been observed that [Bn-DBU][TFA] exhibits greater catalytic activity compared to [Bn-DBU][OAc]. This mechanistic approach offers novel and encouraging perspectives on the logical development of ionic liquid catalysts for the production of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones. The presented synthetic technique possesses numerous notable benefits.

In a separated research, Zare and co-worker described a new route for the preparation of thiazolidine-4-ones derivative using ulrazolium diacetate at room temperature under solvent-free conditions (**Scheme 31**) [83]. A report has been made on the synthesis of new derivatives of 1,3-thiazolidine-4-ones (belonging to the azo dispersive dyes family) using urazolium diacetate as a catalyst. This synthesis involves a multicomponent reaction between various aldehydes, thioglycolic acid, and 4-aminoazobenzene, all under solvent-free conditions. The advantages of this method for synthesizing new thiazolidine-4-one derivatives include short reaction times, high yields, environmentally friendly and green chemistry practices, easy workup, solvent-free conditions, and convenient operation.

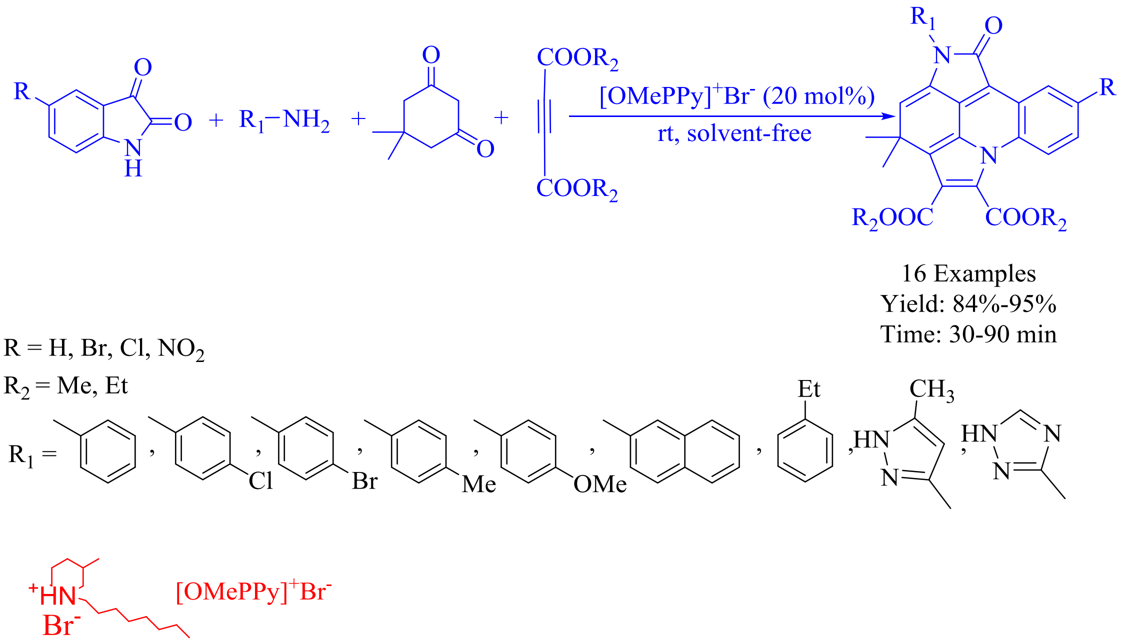


Scheme 31. Synthesis of thiazolidine-4-ones derivative using ulrazolium diacetate at room temperature under solvent-free conditions

In addition, Nokoofar and Shahriyari described a new approach for the providing of polycyclic fused acridines using [OMePPy]$^+$Br$^-$)] (**Scheme 32**) [84]. Various polycyclic fused acridines were synthesized in this study using a highly efficient and environmentally friendly one-step four-component reaction. The reaction involved isatins, dimedone, various amines, and dimethylacetylenedicarboxylates (DMAD/DEAD), all combined in the presence of a newly prepared ionic liquid called noctyl-3-methylpipyridinium bromide ([OMePPy]$^+$Br$^-$). Importantly, the reaction took place under solvent-free conditions at room temperature, ensuring an absolute green approach. The ionic liquid used in this study was thoroughly characterized using advanced techniques such as TGA/DTG, ^{13}C NMR, ^{1}H NMR, EDX, GC-MASS, and FESEM. By utilizing this eco-friendly and easily synthesized ionic liquid, the researchers were able to achieve good yields of a wide range of polycyclic fused acridines. This protocol highlights the green and economic aspects of the reaction media and the overall synthesis process.

Ghaffari Khaligh and co-workers described a novel approach for the synthesis of pyrano[4,3-b]pyrans, dihydropyrano[3,2-c]chromene, and tetrahydrobenzo[b]pyrans using a planetary ball mill under solvent-free conditions (**Scheme 33**) [85]. In the present study, a novel ionic liquid called 4,4′-trimethylene-N,N′-sulfonic acid-dipiperidinium chloride was synthesized and characterized using various techniques such as FTIR, 1D and 2D NMR, and Mass spectra. The properties of this new ionic liquid, including viscosity, pH, density, and solubility in common solvents, were determined. The catalytic activity of the ionic liquid was then demonstrated in the one-pot mechanosynthesis of dihydropyrano[3,2-c]chromene, pyrano[4,3-b]pyrans, and tetrahydrobenzo[b]pyrans using a planetary ball mill under solvent-free conditions. This innovative mechanosynthesis methodology combines the advantages of conventional multicomponent reactions with the ecological benefits and convenience of a simple mechanocatalytic procedure. Furthermore, the new ionic liquid could be easily recycled and reused multiple times without any significant loss of activity.

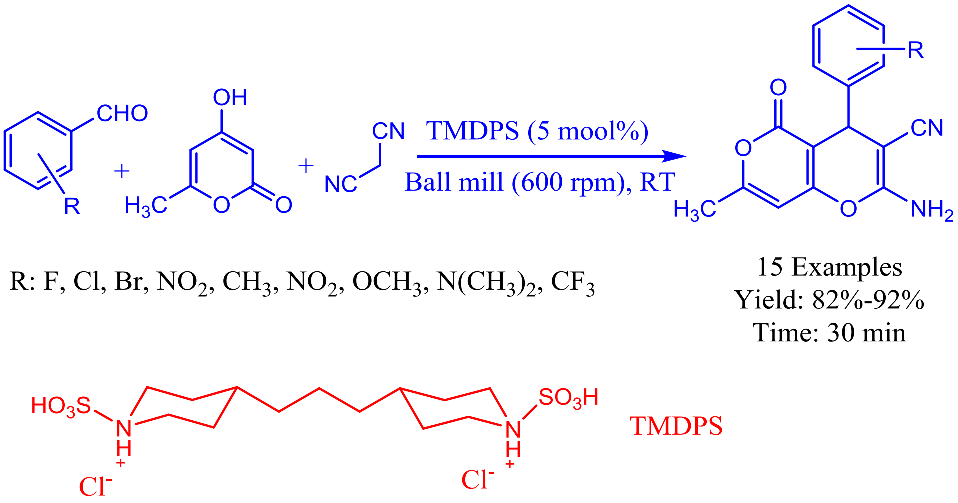
Liu and co-workers synthesized a diverse micro-mesoporous polymeric ionic liquids for the application in prins reaction (**Scheme 34**) [86]. In this research, a range of micro-mesoporous polymeric ionic liquids (PILs) were successfully synthesized through the copolymerization of anions and cations. These PILs were then characterized using various techniques such as SEM, FT-IR, N_2 adsorption-desorption isotherms, and TG. Additionally, the catalytic performance of the synthesized PILs was evaluated for the Prins reaction involving propylene and 1, 3, 5-trioxane. Out of the four PILs that were synthesized, VIMBs-DVB-SSA exhibited superior catalytic activity for the Prins reaction. Under the optimized conditions of 100°C, 8 wt%, 4 hours, and a mole ratio of propylene to 1, 3, 5-trioxane of 4:1, the conversion of formaldehyde reached 99.8% with a selectivity of 81.7% towards 4-methyl-1, 3-dioxane. Furthermore, the effects of reaction time, catalyst dosage, reaction temperature, and mole ratio of reaction substrates were also investigated. It is worth noting that the prepared catalyst demonstrated excellent thermal stability and can be easily reused, making it a promising candidate for future applications.



16 Examples
Yield: 84%-95%
Time: 30-90 min

R = H, Br, Cl, NO_2
R_2 = Me, Et
R_1 =

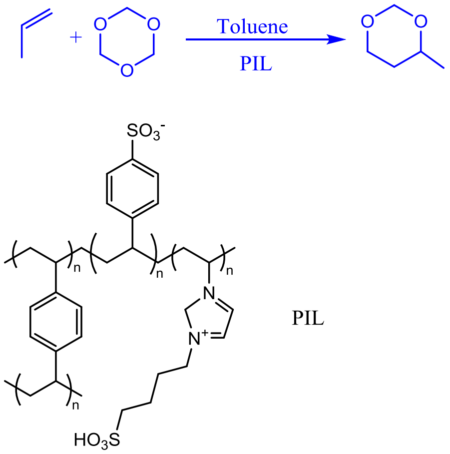
Scheme 32. Preparation of polycyclic fused acridines using [OMePPy]$^+$Br$^-$)]



R: F, Cl, Br, NO_2, CH_3, NO_2, OCH_3, $N(CH_3)_2$, CF_3

15 Examples
Yield: 82%-92%
Time: 30 min

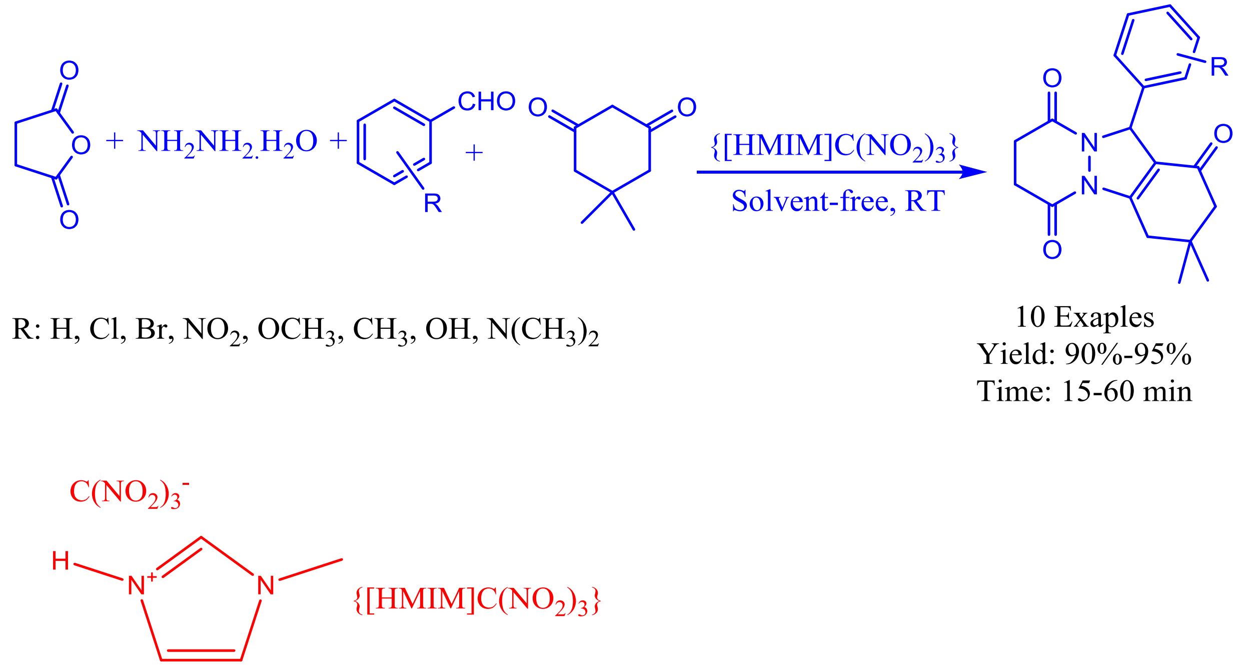
Scheme 33. Synthesis of one-pot mechanosynthesis of 4H-pyrans using TMDPS



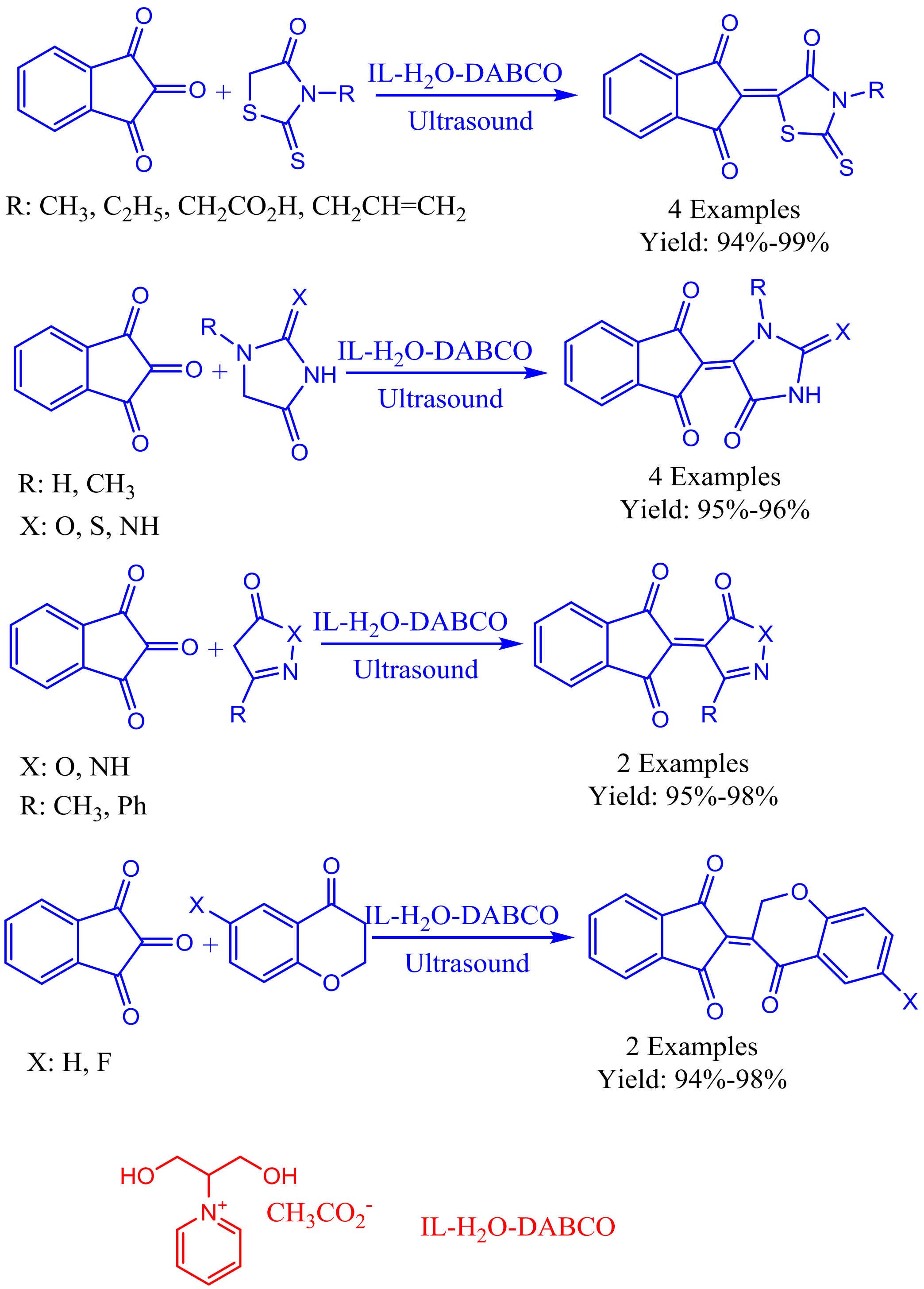
Scheme 34. The prins reaction in the presence of polymeric ionic liquid (PIL)

Majedi and co-workers described the synthesis of 3,4,7,8-tetrahydro-3,3-dimethyl-11-aryl-2H-pyridazino[1,2-a]indazole-1,6,9(11H)-triones using [[HMIM]C(NO_2)$_3$] (**Scheme 35**) [87]. A series of 3,4,7,8-tetrahydro-3,3-dimethyl-11-aryl-2H-pyridazino[1,2-a]indazole-1,6,9(11H)-triones were synthesized using a one-pot cyclocondensation method. The synthesis involved the reaction of succinic anhydride, hydrazine hydrate, benzaldehyde derivatives, and dimedone at room temperature, under solvent-free conditions. The reaction was catalyzed by 1-methyl imidazolium trinitromethanide {[HMIM]C(NO_2)$_3$}, which proved to be a highly effective ionic liquid catalyst. The synthesized compounds were soluble in DMSO and were tested for their antibacterial activity against *Salmonella enteritidis*, *Escherichia coli*, *Staphylococcus aureus*, and *Bacillus cereus*. The results demonstrated that the compounds exhibited antibacterial activity against the tested bacteria. Furthermore, the compounds were evaluated for their antioxidant activity using the DPPH free radical scavenging assay. The results indicated that most of the compounds displayed excellent dose-dependent antiradical properties. Based on the data obtained, the compounds showed moderate to excellent bactericidal effects against both Gram-positive and Gram-negative bacteria. Additionally, two compounds exhibited the highest antiproliferative potencies against A549 (*non-small lung carcinoma*), MCF-7 (*breast carcinoma*), and AGS (*gastric carcinoma*) cell lines.

In a interesting study, a unique dihydroxy ionic liquid ([Py-2OH]OAc) was synthesized by sonication of 2-chloropropane-1,3-diol with pyridine using sodium acetate as an ion exchanger. The effectiveness of ([Py-2OH]OAc) as a promoter for the sono-synthesis of a new library of condensed products through DABCO-catalyzed Knoevenagel condensation was then investigated under environmentally friendly conditions (**Scheme 36**) [88]. All reactions proceeded smoothly, resulting in high yields of Knoevenagel condensation compounds without the presence of aldol intermediates. Compared to traditional methods, this method offers several advantages, including mild reaction conditions, absence of by-products, use of eco-friendly solvents, excellent performance in green metrics, and suitability for large-scale synthesis. The reusability of the ionic liquid was also examined, with consistent high yields achieved over multiple runs. The newly obtained compounds were further evaluated for their potential as antitumor agents against three human tumor cell lines. The majority of the compounds exhibited potent activity at low doses, with those containing rhodanine or chromane moieties showing the most promising cytotoxic effects. In particular, the rhodanine carboxylic acid derivative demonstrated superior cytotoxicity compared to the reference drug. Additionally, docking simulation studies were conducted to support the experimental findings.



Scheme 35. Synthesis of 3,4,7,8-Tetrahydro-3,3-Dimethyl-11-Aryl-2*H*Pyridazino[1,2-*a*]Indazole-1,6,9(11*H*)-Triones using {[HMIM]C(NO_2)$_3$}

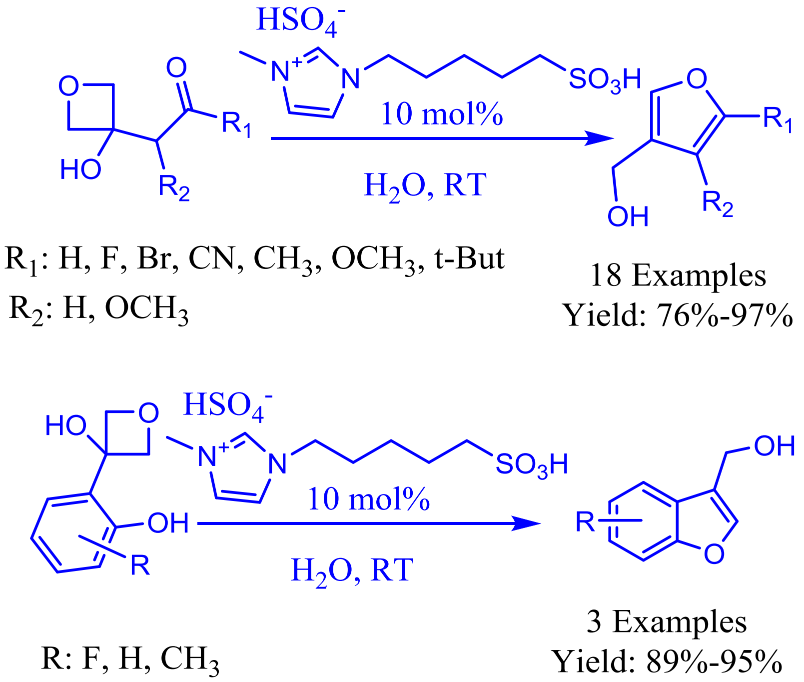


Scheme 36. DABCO-catalyzed Knoevenagel condensation process

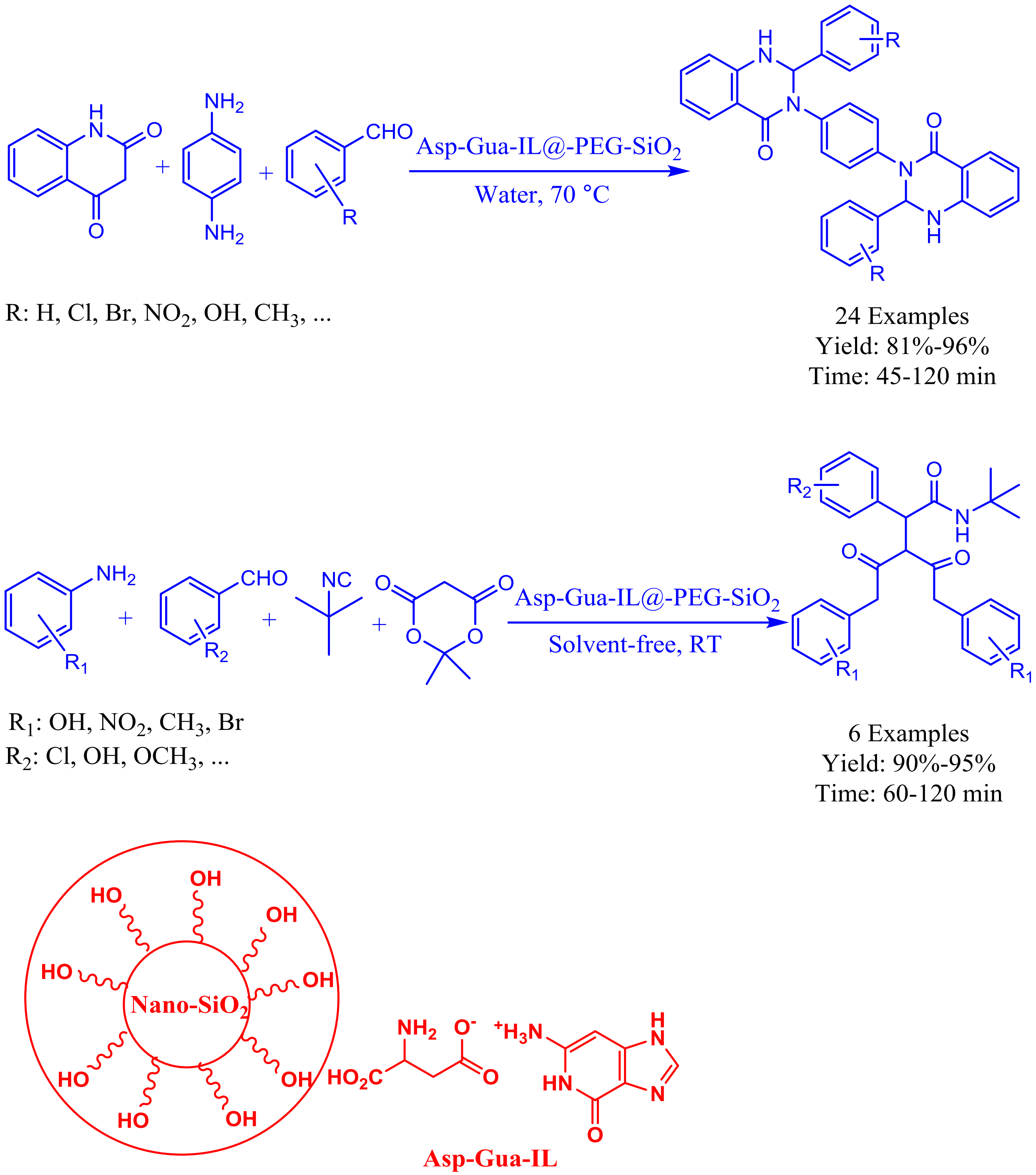
Ni and co-workers reported a new ionic liquid for ring opening of 3,3-disubstituted oxetanes in H_2O (**Scheme 37**) [89]. An environmentally friendly and efficient method for producing furans and benzofurans has been revealed, utilizing water as a solvent. This protocol involves the ring opening of 3,3-disubstituted oxetanes catalyzed by a Brønsted acid ionic liquid. The reaction takes place under mild conditions and demonstrates a wide range of substrates, resulting in high yields. Additionally, the catalyst used in this process, known as BAIL, can be effortlessly recovered through simple separation and reused up to six times without any noticeable decrease in its catalytic activity.

A novel nano structure, nano [(Asp-Gua) IL@PEG-SiO_2], has been developed using hydroxylated nano silica as the core and a unique guaninium aspartate ionic liquid as the shell (**Scheme 38**) [90]. This structure has been thoroughly characterized using various analytical techniques including FT-IR, EDAX, ^{1}H NMR, XRD, FE-SEM, TGA/DTG, and BET analysis. The organic-inorganic hybrid catalyzed synthesis of peptide-like tricarboxamides has been successfully achieved through a pseudo five-component condensation reaction involving aromatic aldehydes, aromatic amines, tert-butyl isocyanide, and Meldrum's acid. Importantly, this reaction was carried out under green solventless conditions at room temperature. The efficacy of this nano structure was demonstrated in the preparation of bis(2,3-dihydroquinazolin-4(1H)-one) derivatives via a one-pot pseudo five-component reaction of amines, aldehydes, and isatoic anhydride in aqueous media at 70°C. This protocol offers several advantages including a simple work-up procedure, short reaction times, economic feasibility, and environmental friendliness. These benefits are attributed to the utilization of green media and the ability to use a wide range of substrates. Additionally, the core-shell nano-promoter can be reused and recovered for up to 3 runs without significant loss of activity.

A collection of substituted quinolone-2-carboxylates, including 4,6-disubstituted quinolone-2-carboxylates, 6-substituted quinoline dialkyl-2,4-dicarboxylates, and 6-substituted 4-[2-methoxy-2-oxoethyl]quinoline-2-methylcarboxylates, was obtained using various one-pot and one-step multicomponent reactions (MCRs) (**Scheme 39**) [91]. These reactions included a three-component reaction involving dialkyl acetylenedicarboxylates, aromatic amines, and terminal alkenes/ketones, a pseudo three-component reaction involving dialkyl acetylenedicarboxylates, anilines and another pseudo three-component reaction involving anilines and methyl propiolate. All of these reactions were carried out under solvent-free conditions at a temperature of 100°C. The key component in these annulation processes is a unique inorganic-organic core-shell structure formed from silicated titanomagnetite, tryptophan amino acid, and ethyl iodide. The tryptophan embedded on the silicated titanomagnetite core ($Fe_{3-x}Ti_xO_4$-SiO_2) undergoes alkylation with ethyl iodide, resulting in the in situ preparation of a triethyltryptophanium iodide ionic liquid ($TrpEt_3^+I^-$). The final nanohybrid material ($Fe_{3-x}Ti_xO_4$-SiO_2@$TrpEt_3^+I^-$) was characterized using various techniques including FE-SEM, FT-IR, EDAX, TGA/DTG, vibrating sample magnetometer, and X-ray fluorescence. The notable features of this protocol are as follows: (1) synthesis of a wide range of substituted quinolines using a simple method and starting from readily available substrates under solvent-free conditions, (2) utilization of various functional groups as substrates, (3) easy separation of the nano promoter using an external magnet, (4) regioselectivity in the cascade annulation procedure, and (5) the ability to recover and reuse the nanocomposite for up to three runs without significant loss of activity.

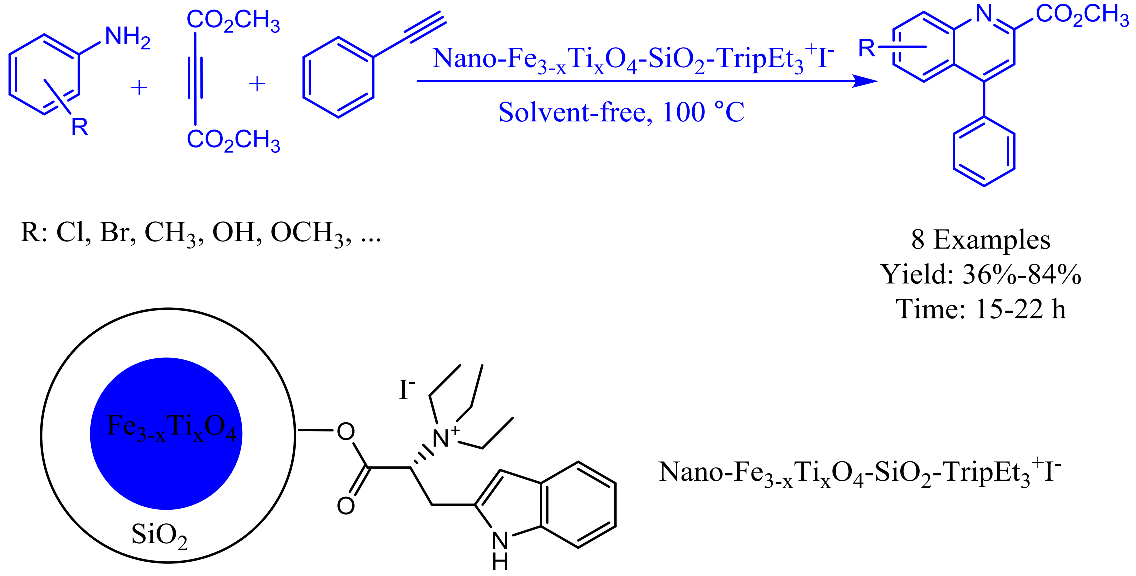


Scheme 37. Ring opening of 3,3-disubstituted Oxetanes in H_2O using acidic ionic liquid

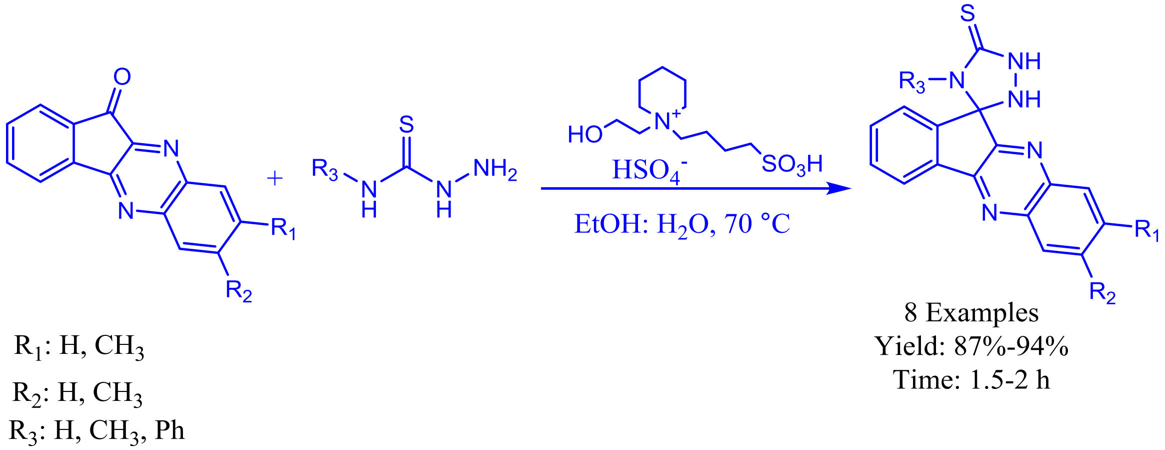


Scheme 38. Synthesis of tricarboxamides and bis(2,3-dihydroquinazolin-4(1H)-one) derivatives using nano ([(Asp-Gua) IL@PEG-SiO₂])

Shinde et al. have successfully produced a new type of Bronsted acidic ionic liquid called 1-(2-hydroxyethyl)-1-(4-sulfobutyl)piperidin-1-ium hydrogen sulfate, $[HEPiPYBSA]^{+}HSO_4^{-}$ (**Scheme 40**) [92]. They then investigated its effectiveness as a catalyst for the synthesis of indenoquinoxalone tethered spiro-1,2,4-triazolidine-5-thiones from the reaction between 11H-[1,2-b]quinoxalin-11-one and thiosemicarbazide. The most stable structures of the synthesized ionic liquid (IL) $[HEPiPYBSA]^{+}$ HSO_4^{-} were determined using the DFT theory at the B3LYP/6-31G* level. Additionally, a photoluminescence analysis of the synthesized spiro-1,2,4-triazolidine-5-thiones demonstrated their impressive fluorescent properties. This method offers several advantages, including a short reaction time, mild reaction conditions, the use of a reusable hydrophilic green catalyst, a benign solvent system, high atom efficiency, and a wide range of applicable substrates.



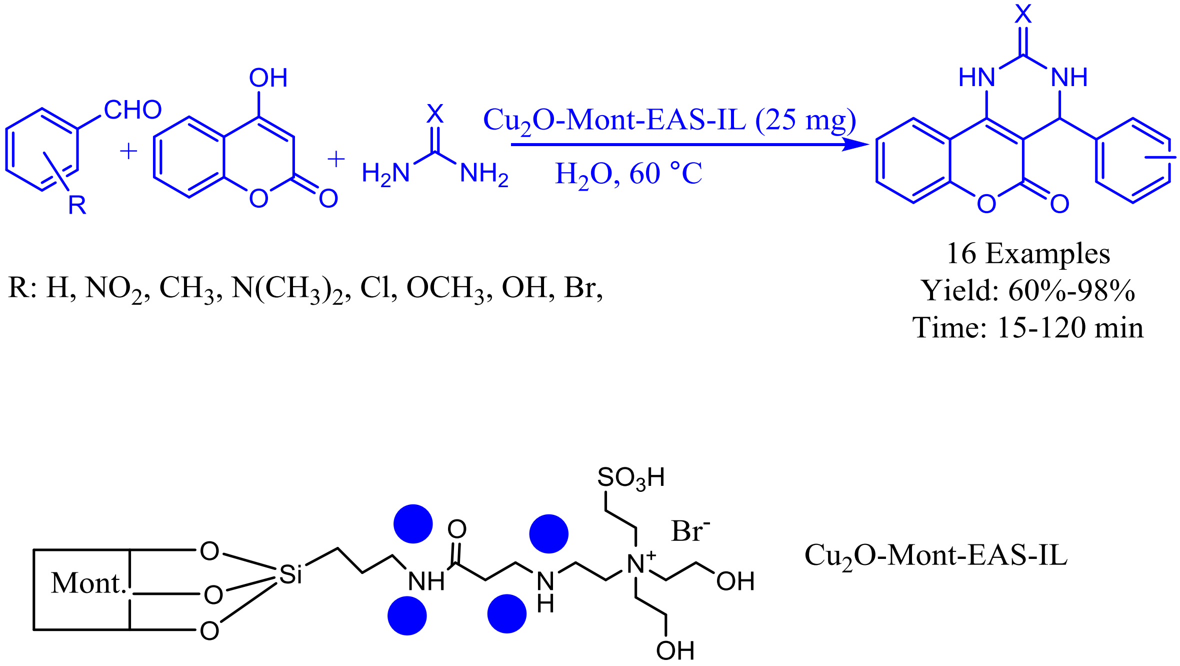
Scheme 39. Synthesis of 4-substituted quinoline-2-carboxylates and 4,6-disubstituted quinoline-2-carboxylates using ($Fe_{3-x}Ti_xO_4-SiO_2@TrpEt_3^+I^-$)



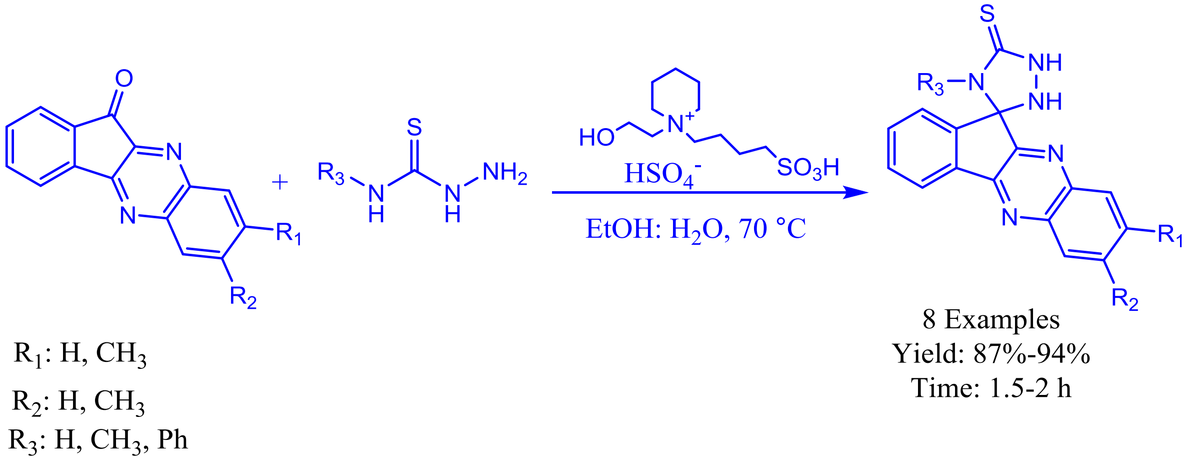
Scheme 40. Synthesis of spiro1,2,4-triazolidine-5-thiones using $[HEPiPYBSA]^+HSO_4^-$

Besharati and colleagues have successfully developed a new catalyst using a natural-based approach (**Scheme 41**) [60]. They incorporated Cu_2O NPs into Montmorillonite-K10, which was functionalized with an acidic-ionic liquid (Cu_2O@Mont/EAS-IL). The catalyst was thoroughly characterized using various techniques such as FTIR, ICP-AES, BET, XRD, FESEM, and TGA. It was then utilized in the synthesis of benzopyranopyrimidines (BPP) through a one-pot reaction conducted under mild conditions. The results demonstrated that the Cu_2O@Mont/EAS-IL catalyst achieved the highest product yields while requiring the lowest amount of catalyst. Additionally, the process exhibited easy workup and showed eco-friendly characteristics. The catalyst also displayed excellent recyclability, being able to be reused up to five times. Furthermore, the study confirmed that the Cu_2O@Mont/EAS-IL catalyst maintained its heterogeneous nature and did not leach significant amounts of copper during the reaction.

Rahmatizadeh and colleagues have successfully synthesized and characterized a new bis-imidazole-based acidic ionic liquid, $[H_2\text{-Bisim}][H_2PO_4]_2$ (**Scheme 42**) [93]. The characterization process involved various techniques such as FT-IR, 1H, ^{31}P, ^{13}C, NMR, and mass spectroscopy. This compound was then utilized as a cost-effective and reusable catalyst in the synthesis of arylidene malononitrile, ethyl (E)-3-(aryl)-2-cyanoacrylate, and tetrahydrobenzo[b]pyran derivatives. The procedure exhibited numerous advantages, including high yields, short reaction times, simple workup, and the use of a non-expensive and non-toxic catalyst. Furthermore, the ionic liquid could be recycled and reused without any significant decrease in its catalytic activity during the studied reactions.



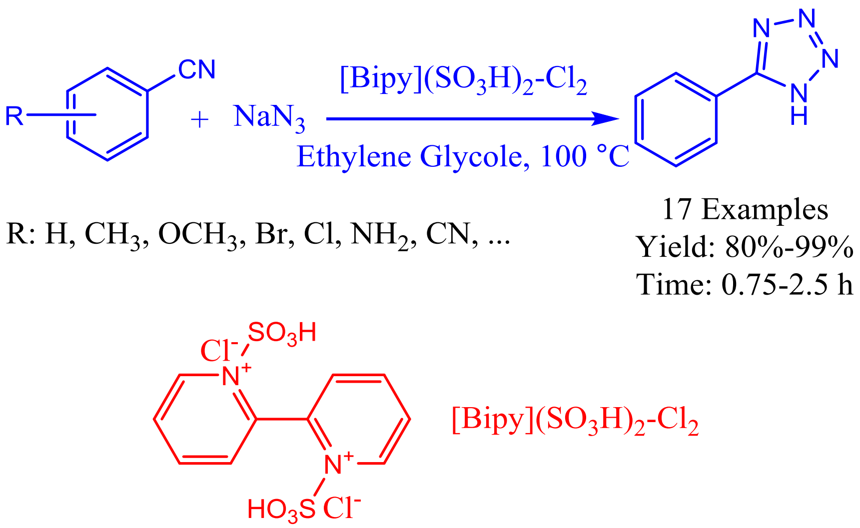
Scheme 41. Synthesis of benzopyranopyrimidines using (Cu_2O@Mont/EAS-IL)



Scheme 42. Synthesis of arylidene malononitrile, ethyl (*E*)-3-(aryl)-2-cyanoacrylate and tetrahydrobenzo[*b*]pyran using [H_2-Bisim][H_2PO_4]$_2$

A team of researchers led by Aali has developed a straightforward, environmentally friendly approach for synthesizing 5-substituted 1H-tetrazole derivatives (**Scheme 43**) [94]. This method involves a [2+3] cycloaddition reaction between different benzonitriles and sodium azide, resulting in high yields of the desired products. To facilitate this process, the researchers utilized a 1-disulfo-[2,2-bipyridine]-1,1-diium chloride ([BiPy](HSO_3)2Cl_2) system as an ionic liquid catalyst. This catalyst not only enables the formation of these valuable compounds but also offers several advantages. One notable advantage is the use of ethylene glycol as a green solvent. Additionally, this method is cost-effective, as the catalyst can be easily prepared and the reaction conditions are mild. The reaction takes place in a green reaction medium, and the subsequent workup is straightforward. Furthermore, the reaction time is short, and the experimental process is simple.

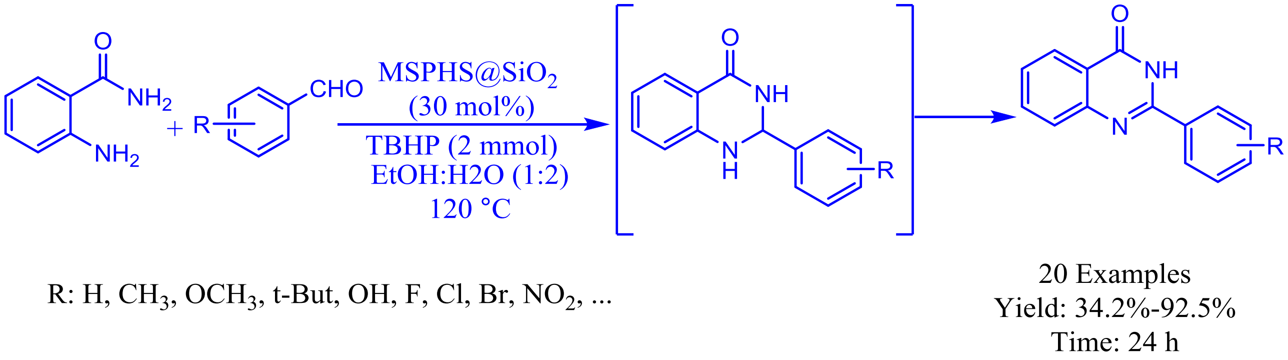
Extensive research has been conducted on the synthesis of 2-phenylquinazolin-4(3H)-ones (**Scheme 44**) [62]. However, previous methods involved the use of catalysts that could not be recycled, toxic organic solvents, and a costly purification step using column chromatography. In this current study, a new approach is presented for the preparation of 2-phenylquinazolin-4(3H)-ones using a recyclable Brønsted acidic ionic liquid grafted onto silica. The silica gel supported with 1-Methyl-1-(4-sulfobutyl)pyrrolidinium hydrogen sulfate (MSPHS@SiO_2) was prepared through a simple process.



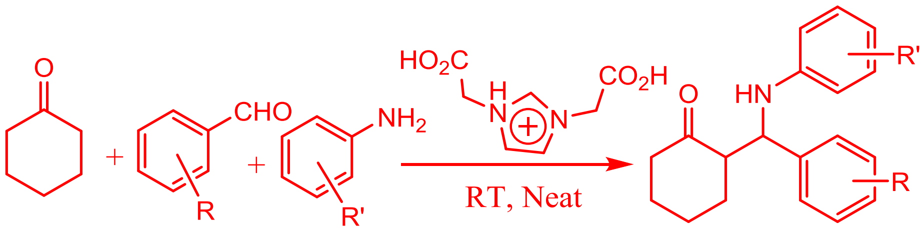
Scheme 43. Synthesis of 5-substituted 1*H*-tetrazoles using ([BiPy](HSO_3)$_2$$Cl_2$)

This material proved to be an effective catalyst for the cyclization of 2-aminobenzamide and aldehydes, resulting in the formation of 2-phenylquinazolin-4(3H)-ones. The optimized conditions for this reaction were found to be MSPHS@SiO_2 (30 mol%), TBHP (2 mmol), and a mixture of EtOH and H_2O (15 mL, 1:2) at a temperature of 120 °C for a duration of 24 hours. By employing a simple recrystallization process, a wide range of 2-phenylquinazolin-4(3H)-ones were obtained with yields ranging from 34.2% to 92.5%. The catalyst could be easily recycled, and a plausible mechanism for the reaction is proposed. Overall, MSPHS@SiO_2 proves to be an efficient and recyclable heterogeneous catalyst for the synthesis of 2-phenylquinazolin-4(3H)-ones using readily available and low-cost starting materials.

In this study conducted by Mohurle et al., a highly efficient diastereoselective one-pot multicomponent Mannich reaction was achieved using 6 mol% of 1,3-bis(carboxymethyl)imidazolium chloride [BCMIM][Cl] ionic liquid as a catalyst (**Scheme 45**) [95]. The reaction involved substituted aromatic aldehydes, cyclohexanone, and substituted aromatic amines, which underwent the Mannich reaction smoothly under solvent-free conditions at room temperature. The presence of 6 mol% [BCMIM][Cl] catalyst resulted in the formation of desired β-amino ketones. This process exhibited excellent diastereoselectivity, rapid reaction times, high yields, and eliminated the need for purification by column chromatography. All synthesized derivatives were thoroughly characterized and confirmed using ^{13}C NMR, ^{1}H NMR, and FT-IR spectral methods. Furthermore, the catalytic activity of the [BCMIM][Cl] ionic liquid catalyst remained intact even after being reused three times.



Scheme 44. Synthesis of 2-phenylquinazolin-4(3H)-ones using MSPHS@SiO_2



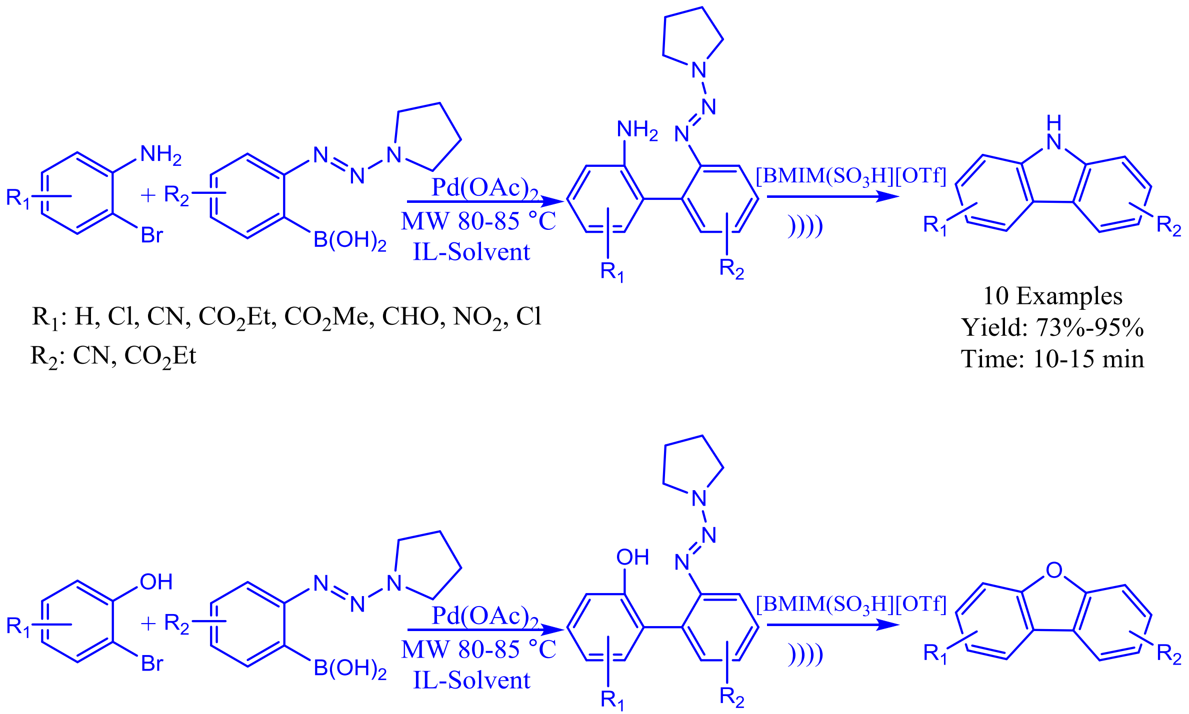
R: H, Cl, CH_3, NO_2
R': H, Cl, OCH_3, CH_3

16 Examples
Yield: 92%-96%
Time: 30-45 min

Scheme 45. Mannich reactions using [BCMIM][Cl]

Kim and his colleagues have published a study on the synthesis of functionalized carbazoles and dibenzofurans using a Brønsted acidic Ionic liquid as a catalyst (**Scheme 46**) [96]. They utilized a biaryl-triazene as an intermediate in the reaction. The key advantages of this method include a shorter reaction time, tolerance towards diverse functional groups, high yield, mild reaction conditions, and the use of microwave and ultrasonic assistance. Remarkably, the researchers achieved product yields ranging from 80% to 92% using this highly efficient and environmentally friendly technique. Additionally, the study also addresses the recycling and re-use of the ionic liquids.

(L)-Prolinamide-based imidazolium ionic liquids were synthesized and assessed as organocatalysts for the asymmetric Biginelli reaction involving benzaldehydes, urea, and β-keto esters (**Scheme 47**) [97]. The synthesized chiral ionic liquids were characterized using various techniques, including FT-IR, FT-NMR, TGA, and HRMS. The chiral ionic liquid, which contained adamantyl (L)-prolinamide with $[BF4]^-$ anion (5 mol %) and p-toluenesulfonic acid (5 mol %) as an additive, effectively catalyzed the Biginelli reaction. This catalytic system yielded a range of chiral 3,4-dihydropyrimidin-2-(1H)-ones (DHPMs) with yields ranging from 16% to 74% and enantiomeric excess (ee) values ranging from 7% to 85% after 48 hours at room



R_1: H, Cl, CN, CO_2Et, CO_2Me, CHO, NO_2, Cl
R_2: CN, CO_2Et

10 Examples
Yield: 73%-95%
Time: 10-15 min

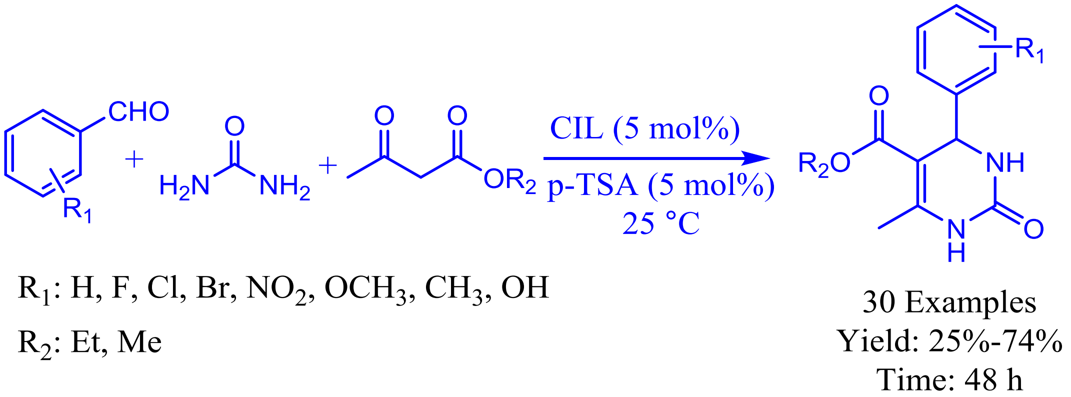
R_1: H, Cl, CHO
R_2: CH_3, CO_2Et

8 Examples
Yield: 76%-86%
Time: 10-15 min

Scheme 46. Synthesis of Carbazoles And Dibenzofurans using [BMIM(SO_3H)][OTf] ionic liquid temperature. Notably, among the 30 chiral DHPMs produced, 18 were novel compounds. The proposed reaction mechanism and transition states or intermediates were supported by FT-NMR spectroscopy and DFT calculations. The Re-face attack on the imine bond favored asymmetric induction, resulting in the formation of Biginelli products with (R)-absolute configuration. DFT calculations (B3LYP/631-G*) were employed to determine the energy of the intermediates.

Prabhala and his colleagues have developed an efficient and easy-to-use method for synthesizing α-arylated N-heteroarenes. This method utilizes ultrasound assistance and conventional heating, with the α-arylation protocol employing Imidazolium based ionic liquids as both acid promoter and solvent (**Scheme 48**) [98]. The researchers evaluated various structurally diverse N-heteroarenes and 1-aryltriazenes for this reaction. Remarkably, this methodology has proven successful in producing electron-rich and electron-deficient arylated N-heteroarenes in high yields, all without the need for metals or peroxides. Furthermore, this methodology played a crucial role in the total synthesis of Menisporphine and Daurioxoisoporphine C, two alkaloids belonging to the oxoisoaporphine class.

Recently, there has been a growing interest in the use of magnetic iron oxide nanoparticles that have been functionalized with various organic groups in the synthesis of organic compounds. In this particular study, Kharazmi and his colleagues successfully synthesized a new nano-catalyst called ionic liquid nano-magnetic pyridinium-tribromide (MNPs@SiO$_2$-Pr-AP-tribromide) (**Scheme 49**) [99]. The structure of this catalyst was determined through the use of various analytical techniques such as EDS, FT-IR, XRD, TEM, TGA, FE-SEM, EDX, and VSM analysis. The nanocatalyst proved to be highly efficient in the synthesis of quinoline derivatives through a one-pot reaction involving 2-amino-5-chlorobenzophenone and pentane-2,4-dione. This catalyst offers several advantages including a large surface area, high activity, easy preparation, renewability, improved efficiency, high thermal stability, shortened reaction time, easy purification, and mild reaction conditions.

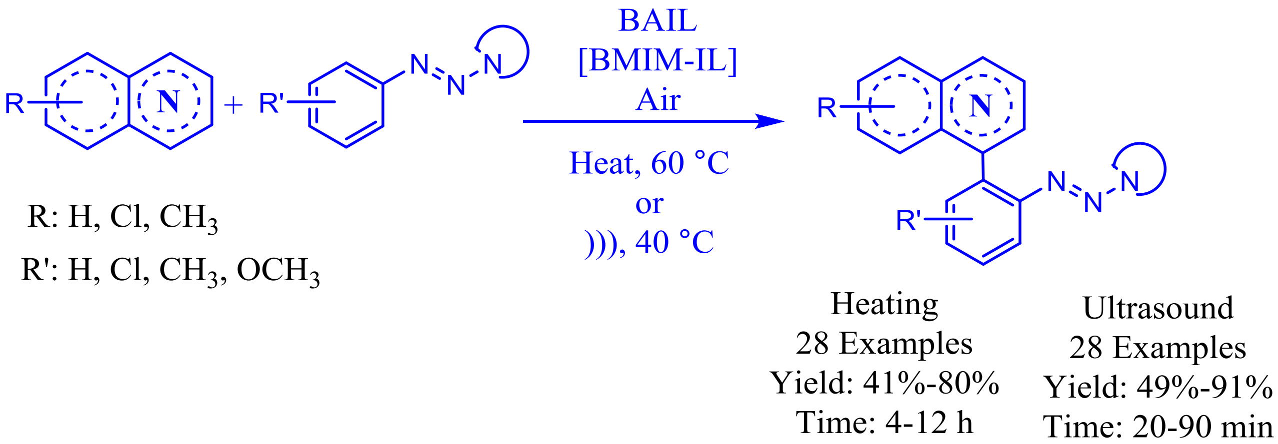


R$_1$: H, F, Cl, Br, NO$_2$, OCH$_3$, CH$_3$, OH

R$_2$: Et, Me

30 Examples
Yield: 25%-74%
Time: 48 h

Scheme 47. Enantioselective Biginelli Reaction using CIL



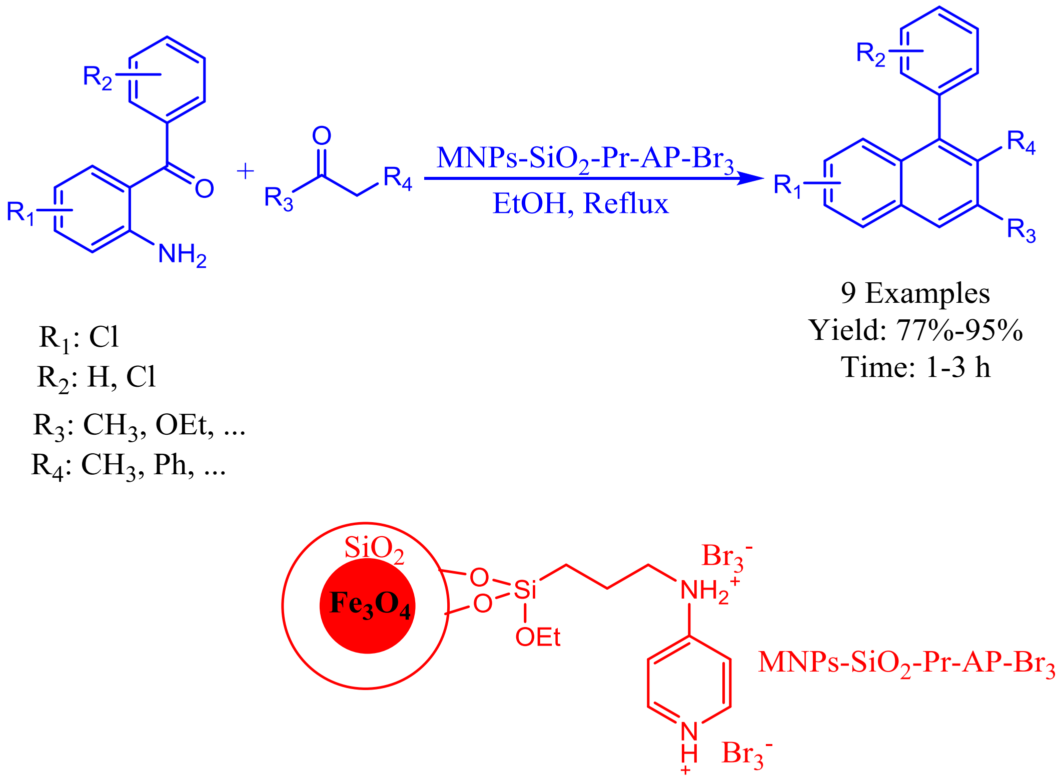
R: H, Cl, CH$_3$

R': H, Cl, CH$_3$, OCH$_3$

Heating
28 Examples
Yield: 41%-80%
Time: 4-12 h

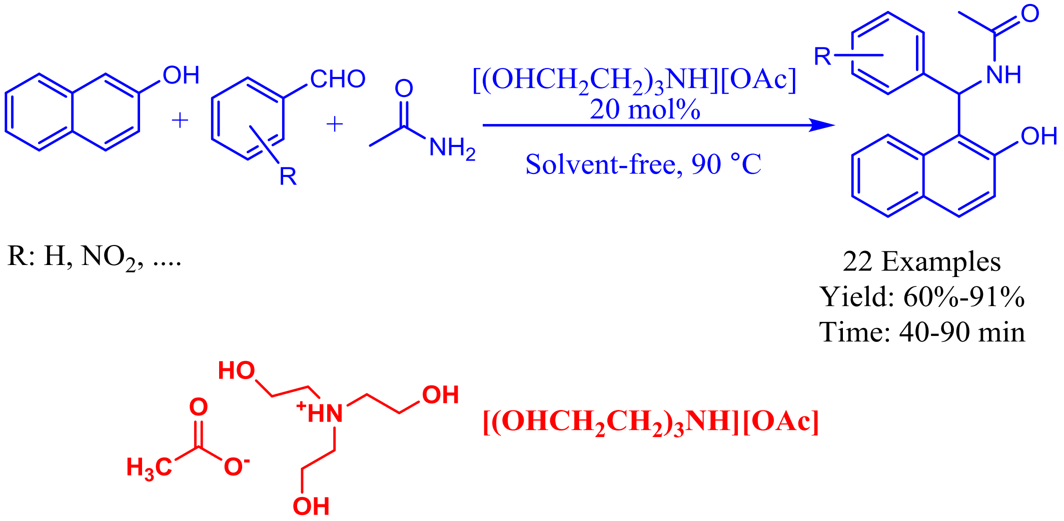
Ultrasound
28 Examples
Yield: 49%-91%
Time: 20-90 min

Scheme 48. **α**-Arylation of *N*-heteroarenes under ultrasound using [BMIM-IL]



Scheme 49. Synthesis of quinoline derivatives using MNPs@SiO$_2$-Pr-AP-tribromide

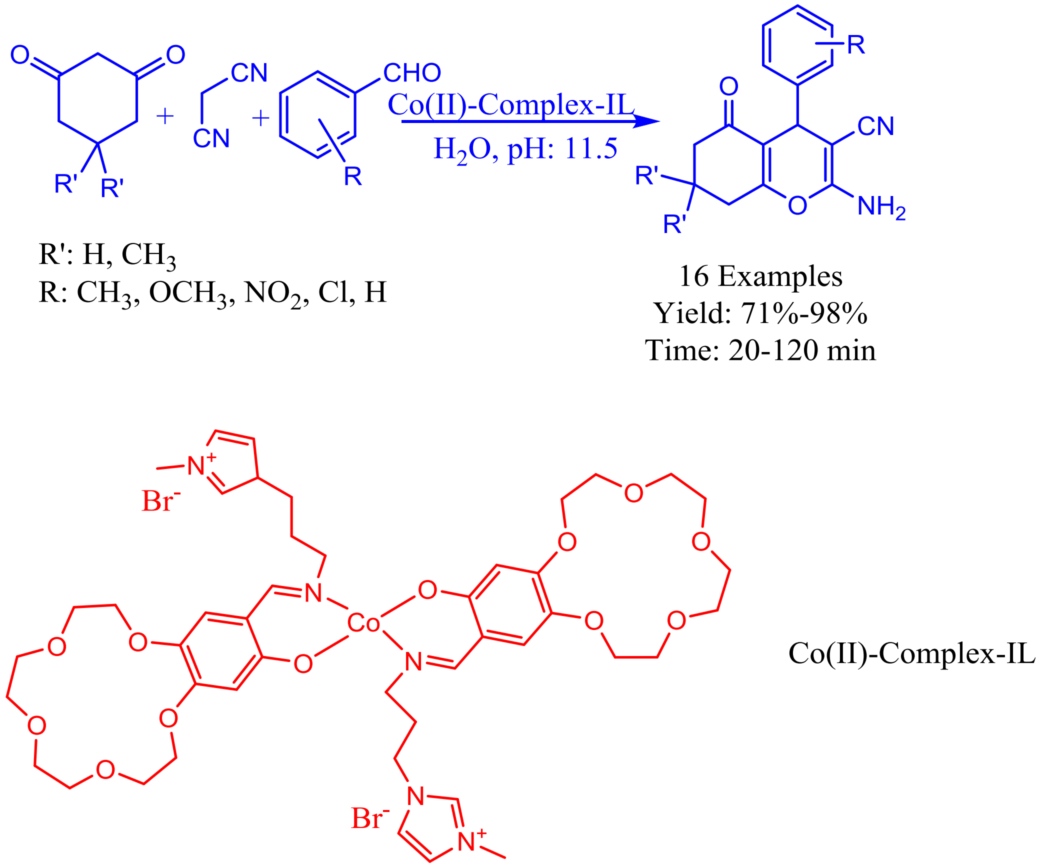
Approximately half of the global population has contracted Helicobacter pylori (H. pylori), which is recognized as the primary cause of chronic gastritis, duodenal ulcer disease, and stomach carcinoma. In this study, Manavi and colleagues have presented an effective, one-step synthesis of amidoalkyl naphthol derivatives and their in vitro activity against Helicobacter pylori (**Scheme 50**) [100]. The reaction occurs through a multi-component condensation of 2-naphthol, (hetero)/aromatic aldehydes, and various compounds such as urea, thiourea, 4-nitrothiazol-2-amine, acetamide, 2-aminothiazole, and 2-aminopyridine, all under solvent-free conditions. This methodology offers notable advantages, including the utilization of triethanolammonium acetate ([OHCH$_2$CH$_2$)$_3$NH][OAc]) ionic liquid as an environmentally friendly, efficient, and reusable catalyst, high yields, elimination of column chromatography, and cost-effectiveness. Through a comparison of the inhibition zones of the tested compounds, two specific compounds exhibit the most promising potential as anti-helicobacter agents.



Scheme 50. Synthesis of amidoalkyl naphthols using [OHCH$_2$CH$_2$)$_3$NH][OAc]

A novel Schiff base, which was linked to an ionic liquid and a crown ether and coordinated to cobalt (II), was synthesized and subsequently characterized using IR, inductively coupled plasma, XRD, and TGA (**Scheme 51**) [55]. This particular catalyst was employed in the synthesis of xanthenes and chromenes, wherein an alcohol was utilized in lieu of an aldehyde or a ketone. Throughout all the reactions, the catalyst containing the crown ether and the ionic liquid demonstrated superior activity compared to its counterparts lacking these components. The inclusion of the crown ether ring and the ionic liquid enhanced the solubility of the catalyst in the aqueous phase and augmented its contact surface as a Lewis acid with the reactive species. Consequently, this led to an increased alcohol oxidation process and a higher reaction rate. Additionally, this method offers the advantage of catalyst reusability for at least six runs, a short reaction time, the utilization of environmentally friendly green solvents, and the attainment of good to excellent product yields.

Patil and his colleagues have reported the synthesis of a new polymer supported Brønsted acidic ionic liquid catalyst in their recent work (**Scheme 52**) [101]. They achieved this by functionalizing Merrifield resin with DABCO, 1,4-butane sultone, and concentrated H_2SO_4. The structure of the catalyst was confirmed using various techniques such as XRD, EDX, XPS, FT-IR, SEM, TGA, and DTA. The efficiency of the novel Brønsted acidic [MerDABCO-BSA][HSO_4]$_2$ catalyst was evaluated in the synthesis of biscoumarins from aryl aldehydes and 4-hydroxycoumarin in EtOH at 80 °C. Additionally, they successfully synthesized ortho-aminocarbonitriles from malononitrile, cyclohexanone, and aromatic aldehydes in EtOH: H_2O (70:30 v/v) under ultrasonic conditions. The catalyst demonstrated good stability under both thermal and ultrasonic conditions. It was also found that the catalyst could be recycled and used for four cycles without significant loss in catalytic activity. This protocol offers several advantages including shorter reaction times, operational simplicity, and higher yields of the products.

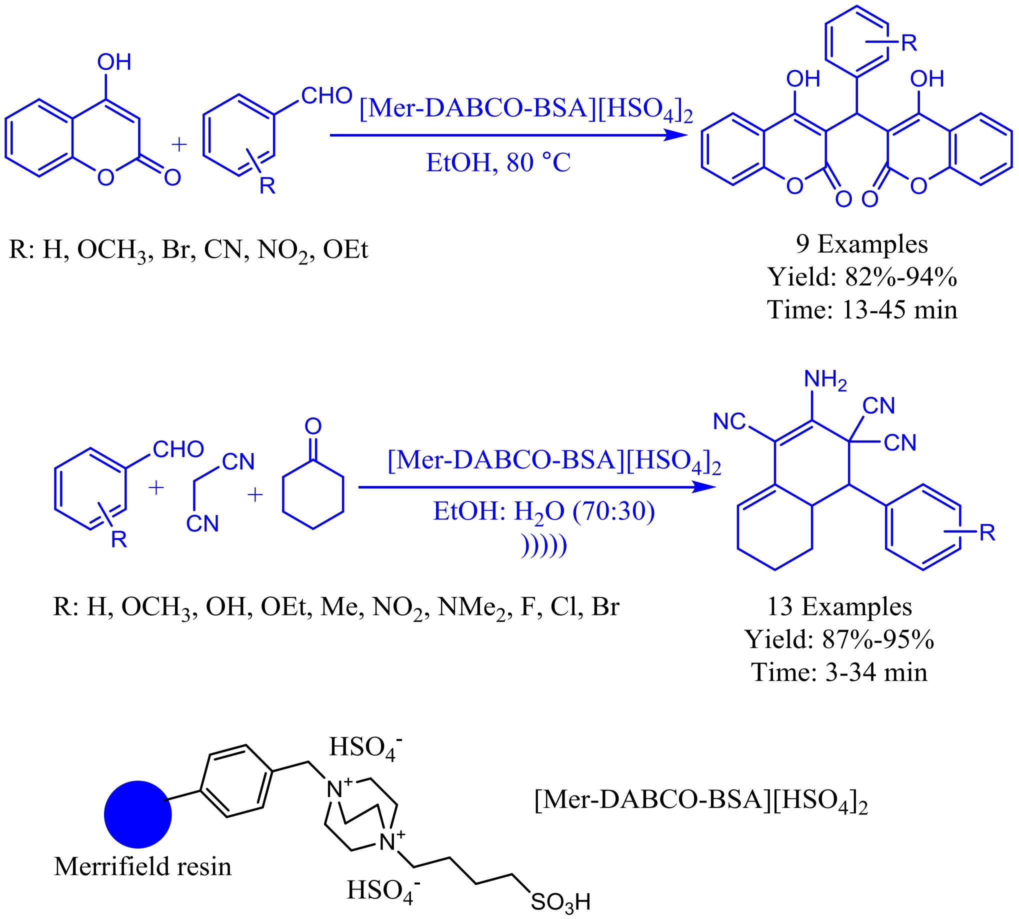


R': H, CH_3
R: CH_3, OCH_3, NO_2, Cl, H

16 Examples
Yield: 71%-98%
Time: 20-120 min

Co(II)-Complex-IL

Scheme 51. Synthesis of chromene and xanthene derivatives using Co(II)-Complex-Ionic Liquid

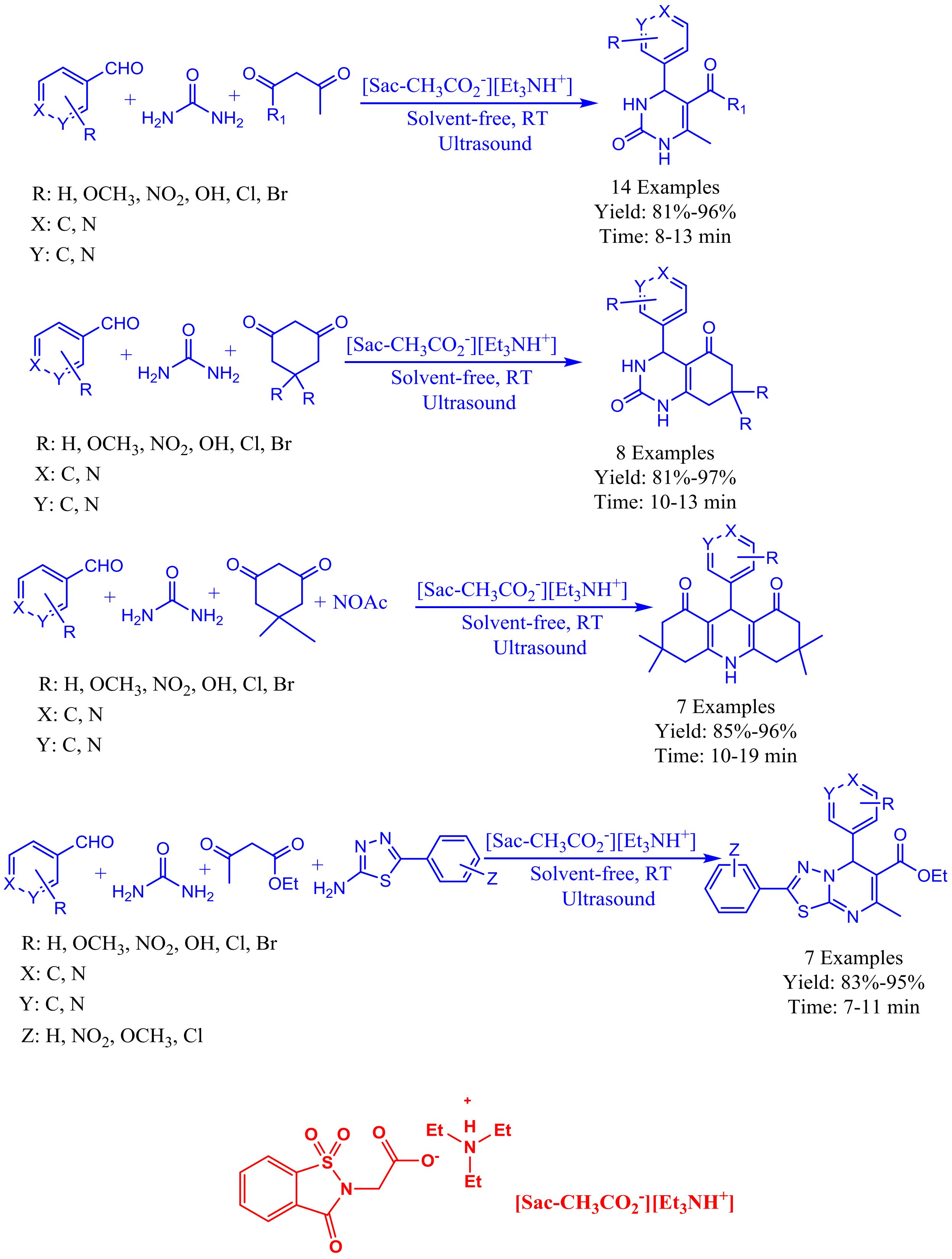


Scheme 52. Synthesis of biscoumarins and *ortho*-aminocarbonitriles using [MerDABCO-BSA][HSO$_4$]$_2$

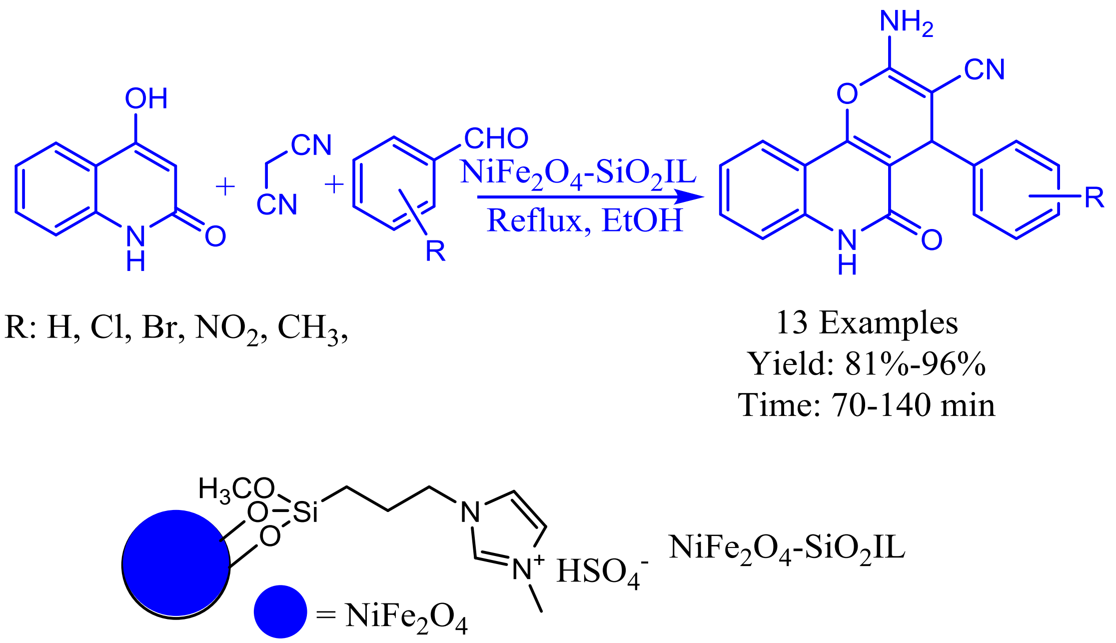
A novel 1,2-benzisothiazol-3(2H)-one-1,1-dioxide (Saccharin) has been utilized to create a functional ionic liquid. This ionic liquid has been successfully designed, synthesized, and characterized. Moreover, it has been effectively employed as a recyclable catalyst for the synthesis of Biginelli and Hantzcsh heterocycles at room temperature (**Scheme 53**) [47]. This innovative approach offers operationally simple, a green, solvent-free, and highly efficient strategy for assembling various N-containing heterocyclic compounds, such as hexahydroacridines, dihydropyrimidins, tetrahydroquinazolines, and thiadiazolo[3,2-a]pyrimidines. The presence of the triethylammonium 2-(1,1-dioxido-3-oxobenzo[d]isothiazol-2(3H)-yl)acetate ([Sac-CH$_3$CO$_2$][Et$_3$NH]) ionic liquid catalyst, under neat ball-milling conditions, enables the clean synthesis of the desired products in high yields, eliminating the need for column chromatography. This mechanosynthesis approach offers high efficiency, short reaction times, environmentally friendly characteristics, scalability, and ambient temperature conditions, distinguishing it from traditional reactions.

Ghaleh-Salimi and co-workers reported an efficient method for the synthesis of pyrano[3,2-c]quinolones in the presence of NiFe$_2$O$_4$@SiO$_2$ Bonded specific ionic liquid (**Scheme 54**) [54].

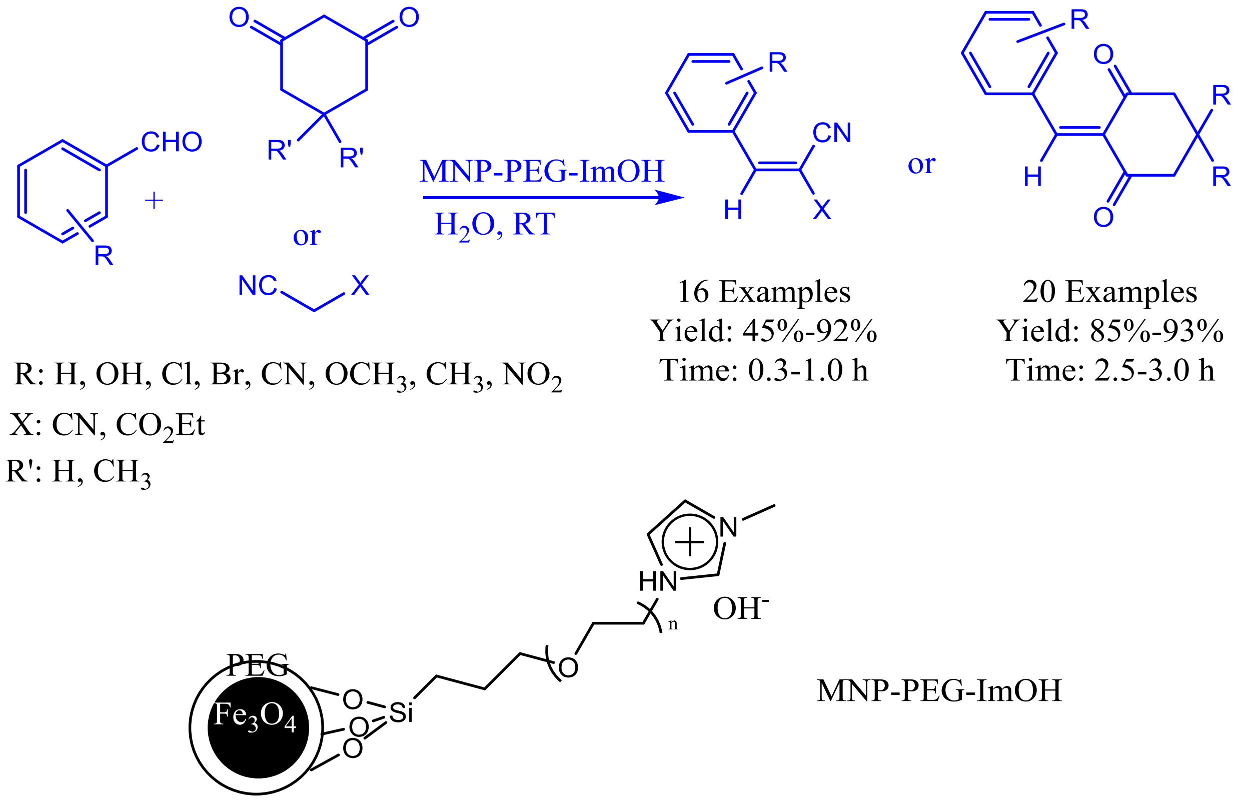
This research study focused on the synthesis and analysis of magnetic nanoparticles (MNP) supported with polyethylene glycol-substituted 1-methyl imidazolium hydroxide (PEG-ImOH) by Fallah-Mehrjerdi and co-workers (**Scheme 55**) [69]. The characterization of the MNP@PEG-ImOH was conducted using various techniques including FESEM, EDAX, TGA, FT-IR, TEM, VSM, and XRD. The catalytic performance of MNP@PEG-ImOH was evaluated in the Knoevenagel condensation reaction between active methylene compounds and aromatic aldehydes in an aqueous medium at room temperature. The results showcased several advantages of this catalytic system, such as enhanced product yields, reduced reaction time, catalyst reusability and recyclability, simplified work-up process, and favorable reaction conditions. Moreover, the catalyst could be easily separated from the reaction mixture using an external magnet and reused without significant loss of activity.



Scheme 53. Mechanosynthesis of Biginelli and Hantzcsh heterocycles using [Sac-CH_3CO_2][Et_3NH^+]



Scheme 54. Synthesis of Pyrano[3,2-c]quinolones using NiFe$_2$O$_4$@SiO$_2$-IL



Scheme 55. Knoevenagel Condensation using MNP-PG-ImOH

An investigation was conducted to explore a straightforward and efficient approach for synthesizing indeno-benzofurans derivatives. This method involved the use of polyphenols and ninhydrins, along with an acidic catalyst based on DABCO (1,4-diaza bicycle [2.2.2] octane)-based ionic liquid (**Scheme 56**) [70]. Without the catalyst, the yields of these reactions were found to be very low. However, when DABCO-AIL was employed, the yields improved significantly, the reaction times were reduced, and the resulting media were cleaner. The structures of the synthesized products were confirmed using various analytical techniques such as infrared (IR), proton nuclear magnetic resonance (1H NMR), Carbon-13 nuclear magnetic resonance (13C NMR), and mass spectrometry. It is worth noting that oxidative stress is believed to play a role in the development of numerous diseases, including diabetes. Therefore, therapeutic antioxidants hold promise as potential candidates for the prevention and treatment of such diseases. In order to investigate the antioxidant properties of all the synthesized derivatives, the 2,2-diphenyl-1-picrylhydrazylhydrazyl-hydrate (DPPH) assay was employed. Among the derivatives tested, two showed the highest antioxidant effect, with an IC50 value of 0.015 µmol/mL. These two derivatives were further evaluated for their anti-diabetic effect using the Bernfeld method. The most favorable outcome was observed at a concentration of 0.8 mg/mL for four derivatives. Additionally, the results of the 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide (MTT) test indicated that this concentration did not exhibit any cellular toxicity.

3. Conclusions

Over the past decade, the field of ionic liquids has expanded significantly, with acidic ionic liquids emerging as a crucial subfield within this domain. A comprehensive overview of the catalytic techniques employed in the synthesis of heterocyclic compounds utilizing ionic liquid and supported ionic liquid has been presented in this review. These catalysts are a versatile tool in synthesizing various heterocyclic compounds through diverse organic reactions. A range of organic reactions, including hydrolysis, oxidation, cyclization, dehydration, dehydrogenation, ring opening, etherification, addition, and esterification, along with the synthesis of diverse heterocyclic compounds, have been investigated in the presence of ionic liquids and supported ionic liquids, as previously mentioned. Furthermore, the aforementioned catalytic systems have demonstrated significant appeal as recoverable and reusable catalysts in organic reactions. In certain organic reactions, the proposed catalysts have the ability to create a new bond between carbon and carbon or heteroatom without the presence of any metal, which is particularly noteworthy. Several limitations in this context still require attention for future research. The primary trends in catalysts chemistry in the 21st century revolve around speed and sustainability. The demand for quicker results and the efficient utilization of resources has driven the push for miniaturization. This raises the question: what role do ionic liquids play in these trends and how do they contribute? In order to avoid repetition with other sections, a broader perspective on the potential applications of ionic liquids in chemistry is presented. This includes their involvement in CO2 removal, bio-fuel production, solar and fuel cell technologies, lubricants, as well as lanthanide and actinide separations, showcasing the remarkable adaptability of ionic liquids. However, it is important to address the cost of ionic liquids as a significant obstacle that needs to be overcome in the future.

Acknowledgements

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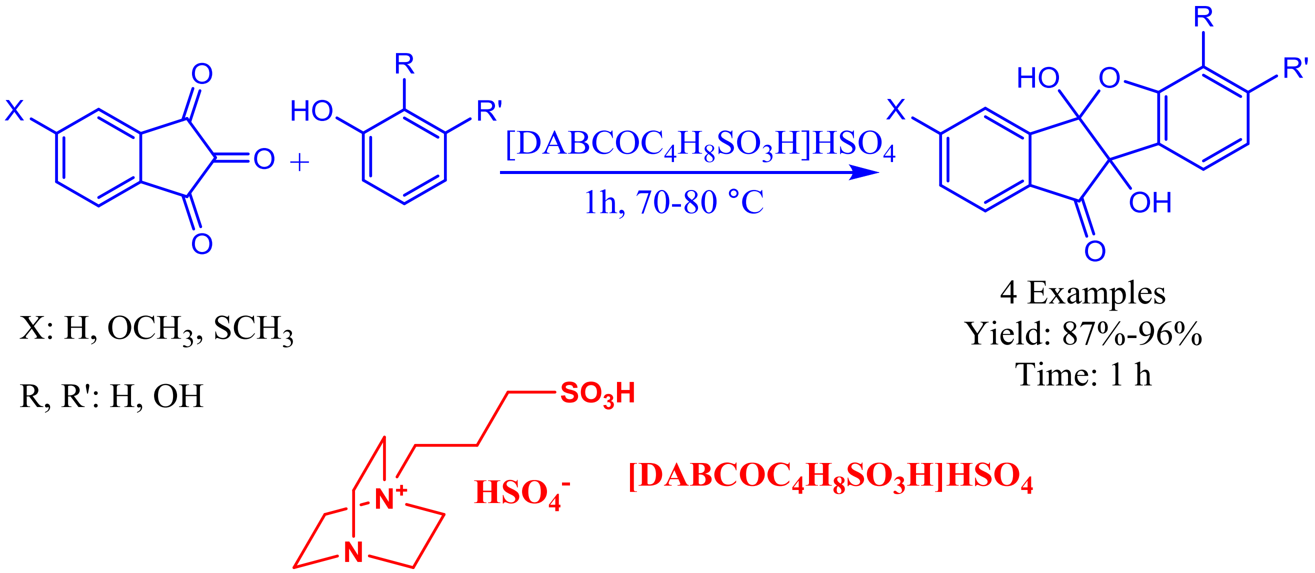

Scheme 56. Synthesis of indeno-benzofurans derivatives using [DABCOC$_4$H$_8$SO$_3$H]HSO$_4$

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