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Review

Greener organic synthetic methods: Sonochemistry and heterogeneous catalysis promoted multicomponent reactions

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ABSTRACT

Ultrasound is an essential technique to improve organic synthesis from the point of view of green chemistry, as it can promote better yields and selectivities, in addition to shorter reaction times when compared to the conventional methods. Heterogeneous catalysis is another pillar of sustainable chemistry being the recycling and reuse of the catalysts one of its great advantage. In the other hand, multicomponent reactions provide the synthesis of structurally diverse compounds, in a one-pot fashion, without isolation and purification of intermediates. Thus, the combination of these protocols has proved to be a powerful tool to obtain biologically active organic compounds with lower costs, time and energy consumption. Herein, we provide a comprehensive overview of advances on methods of organic synthesis that have been reported over the past ten years with focus on ultrasound-assisted multicomponent reactions under heterogeneous catalysis. In particular, we present pharmacologically important *N*- and *O*-heterocyclic compounds, considering their synthetic methods using green solvents, and catalyst recycling.

1. Introduction

Efforts to solve environmental problems have become more evident in the last decades. In this context, green chemistry, centered on its twelve principles [1,2], is central for the planning and execution of more environment friendly methods. Important factors associated with the development of greener processes are atom economy, efficiency, elimination of toxic intermediates/products and generation of as minimum waste as possible [3]. In this sense, multicomponent reactions (MCRs) have emerged as an interesting tool that allows for the straightforward synthesis of intricate molecules in a one-pot fashion, without the isolation and purification of intermediates, therefore leading to lower costs, time and energy consumption [4].

Moreover, the use of greener energy sources to promote chemical reactions has a prominent role [5], and, in this perspective, among other alternatives such as microwave irradiation and milling processes, ultrasound is highlighted [6]. The use of ultrasonic waves in synthesis usually results in shorter reaction time, and higher yield and selectivity when compared to conventional heating [7–13], besides facilitating, in many cases, the occurrence of organic transformations that would otherwise require drastic temperature conditions and pressure [5].

Ultrasound is characterized as any sound wave in frequencies above the normal hearing range of the human ear (i.e., above 16 kHz) [14] and the field of application of ultrasonic waves is surprisingly vast, such as in the pharmaceutical and food industries [15–20], extraction processes [16,21–31], waste treatment [32–46], materials chemistry [47–49], analytical chemistry [50–53], and nanoparticle synthesis [24,41,54–59]. All these examples, addressing the application of ultrasound for different purposes, serve as consolidating pillars for the importance of this tool for the progress of science and technology.

Sonochemistry is a field that studies phenomena and reactions induced by shock waves generated by localized pressure released quickly and by radicals formed in and/or around bubbles from the thermal decomposition of molecules in the system, both originated from ultrasonic cavitation [6], concept that will be discussed shortly in the next sections.

1.1. The phenomenon of acoustic cavitation

There are four theories to explain sonochemical effects: (1) hot-spot theory; (2)“electrical’’ theory; (3) “plasma discharge’’ theory and (4) supercritical theory [60]. These theories lead to various mode of reactivity: pyrolytic decomposition, OH^- oxidation, plasma chemistry, and supercritical water oxidation [60]. Nevertheless, the most accepted

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explanation for the promotion of reactions by ultrasonic radiation is based on the concept of an acoustic cavitation effect, which consists on the formation, growth and implosion of bubbles - with a life span of a few microseconds - at points located in the reaction medium, and makes the temperature and pressure reach levels on the order of 5000 °C and 10,000 atm, respectively [5,6,61]. The collapse of these bubbles eventually leads to reach the activation energy, allowing the occurrence of chemical reactions [5,6,61,62]. The cavitation process can be of several types (some examples are acoustic, hydrodynamic, optical and particle cavitation), depending on the generation method and the associated ultrasonic/experimental parameters (frequency, acoustic power, reactor shape, solvents, temperature, vapor pressure, surface tension and viscosity, etc.) [11,63,64].

Looking more closely at this phenomenon, acoustic cavitation can be divided into three consecutive steps: (i) nucleation, (ii) bubble growth, also known as expansion, and (iii) implosive collapse. Initially, microbubbles trapped in micro-slits of small particles within the liquid form cavitational nuclei, where the cavities are generated depending on the type and purity of the liquid. Then, after the microbubbles are formed, a small cavity can rapidly develop and expand by rectified diffusion when the acoustic intensity is low and lasts a few more acoustic cycles before expansion. The third moment occurs when the cavity has grown to a certain limit, and can no longer absorb energy, it is when a violent implosion occurs. At this point, the extremes of temperature and pressure provide an unusual environment or high energy microreactors that allow molecular fragmentation of the gases trapped in the collapsing cavities [14]. However, some chemical transformations have been observed that cannot be explained by the effect of cavitation [65,66]; in these cases, the need for a broader investigation of the aspects that make possible the occurrence of chemical reactions by irradiation of ultrasonic waves is implicit.

Based on how particles vibrate in the medium, the ultrasonic waves can be categorized in four ways: longitudinal compression waves, transverse/shear waves, surface/Rayleight waves and plate/Lamb waves [60,67]. With regard to frequency, ultrasound can be divided into three classes: power ultrasound (20–100 kHz), high frequency ultrasound (100 kHz –1 MHz), and diagnostic ultrasound (1–500 MHz), being the first track widely used to promote chemical and physical changes in systems [67]. Power also has an important influence on the cavitation process. In most cases, with increasing potency, the reaction rate also increases. When high ultrasonic power is applied, a great number of cavitation bubbles are generated in the solution [14]. The applied power density must be sufficient to provide the necessary pressure for cavitation, but not so drastic as to interrupt the growth dynamics of the cavitation bubbles, which can result in deficient cavitation and material growth [68]. Temperature is another parameter to be observed since, in many cases, the increase in temperature causes a decrease in cavitational effects.

A more in-depth discussion of the physical aspects involved in the acoustic cavitation process can be found in the reports by Luo et al. [69] and Pokhrel et al. [68], and for further information on other related parameters that govern this phenomenon see Sutkar et al. [70], Gogate et al. [71] Merouani et al. [72] and Bussemaker et al. [73].

1.2. *Ultrasonic waves promoting chemical reactions*

As in other chemical processes, sonochemistry also involves the dissociation and formation of chemical bonds [74]. When ultrasonic waves with frequencies above 20 kHz are radiated in a liquid, they can break chemical bonds (sonolysis) and produce free radicals, which will be able to promote a series of chemical transformations. In water as solvent, reduction–oxidation reactions occur and hydrogen and hydroxyl radicals are produced [75].

In the 1980′s, the Luche group began the investigations into the effects of ultrasound on chemical reactions and the mechanistic pathways involved in sonochemistry [66]. In this regard, in a seminal paper published in 1996, Luche and col. categorize sonochemical reactions into three groups [66]:

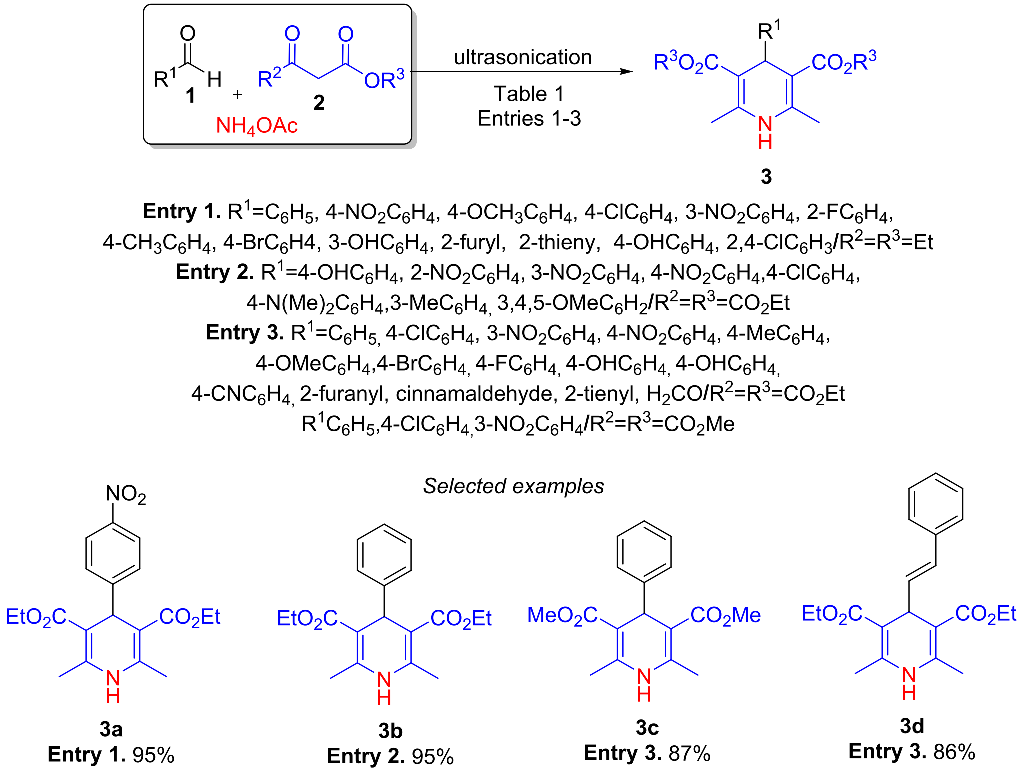
- homogeneous sonochemistry: reactions that fall into this category are governed by a radical route, in which the intermediates (radicals or radical ions) are generated by cavitation in homogeneous media. In this case, sonication would be able to promote reactions by means of radicals and ionic reactions could not be modified by such irradiation; this would be the “real” sonochemistry.
- heterogenous sonochemistry: reactions that would occur due to the mechanical effect of the waves propagating in a heterogeneous environment, i.e., the reactions that proceed via ionic intermediates would be stimulated by the effect of cavitational agitation; this would be the “false” sonochemistry.
- sonocatalysis: heterogeneous reactions with mixed mechanisms, that is, radical and ionic - the radical path would be improved by sonication, with cumulative application of the general mechanical effect of heterogeneous sonochemistry.

Once cavitation bubbles collapse, conditions at the center of the bubble or hot spots are very severe, for example large gradients in temperature, pressure and shear are experienced. Gases within the bubbles or in the interfacial region between the center of the bubble and the bulk liquid will lead to the formation of many radical species such as •OH, H• and hydroperoxyl radicals (•OOH) [74]. Sonolysis of water also produces H_2O_2 and H_2 gas via •OH and H•. Even though oxygen improves sonochemical activities, its presence is not essential for water sonolysis as sonochemical oxidation and reduction process can proceed in the presence of any gas. However, presence of oxygen could scavenge the H•, forming •OOH, which acts as oxidizing agents [60]. Pflieger et al. studied the generation of radicals (•OH) in water sonolysis at different frequencies. Such radicals were identified through the production of sonochemiluminescence via the addition of luminol near the cavitation bubbles [74,76]. In the same context, the Kavanal group has conducted a mechanistic study of the sonochemical oxidation of 2-aminopurine mediated by hydroxyl radical (•OH) in aqueous phase through a combination of DFT calculations and analysis of final products by the LC-Q-TOF-MS / MS method [77]. These examples attest that highly reactive radicals are capable of initiating various sonochemical reactions.

Pioneer studies on the use of ultrasound in organic synthesis were performed in 1950 by Miyagawa and Tsukida [6]. In the following decades, the number of publications in this area became abundant, including the appearance of books and reviews dealing with the topic [8,61,62,78–82].

With regard to the relationship between sonochemistry and catalysis, it appears that the cavitation bubble implosion process improves the dispersion of the catalyst in the medium, causing the appearance of non-passivated and highly reactive areas on the surface of the catalyst particles, as well as improving the spreading of reagents across the surface of this catalyst [83]. Combination of these processes effectively increases the rate of many chemical reactions, even making possible for those that do not normally occur due to low kinetic energy [83]. In some cases, there is a synergistic effect between the catalyst and the ultrasound, which is usually observed in the presence of solid catalysts. The formation of cavitation bubbles occurs preferentially on the surface of the particle via heterogeneous nucleation. In turn, the implosion of these bubbles is asymmetric, so that chemical and physical aspects resulting from this process end up inducing the generation or activation of catalytic sites [83].

Heterogeneous catalysis has unquestionably become a cornerstone within the Green Chemistry perspective, and in this sense, application of zeolites as catalysts in multicomponent reactions have been reviewed [84]. Moreover, Banerjee reported the recent developments on various nanoparticles catalyzed organic synthesis under the influence of ultrasonic irradiation [80]. Herein, the advances over the past ten years on ultrasound-assisted multicomponent reactions under heterogeneous



Entry 1. R^1=C_6H_5, 4-$NO_2C_6H_4$, 4-$OCH_3C_6H_4$, 4-ClC_6H_4, 3-$NO_2C_6H_4$, 2-FC_6H_4, 4-$CH_3C_6H_4$, 4-BrC6H4, 3-OHC_6H_4, 2-furyl, 2-thieny, 4-OHC_6H_4, 2,4-ClC_6H_3/R^2=R^3=Et

Entry 2. R^1=4-OHC_6H_4, 2-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$,4-ClC_6H_4, 4-$N(Me)_2C_6H_4$,3-MeC_6H_4, 3,4,5-$OMeC_6H_2$/R^2=R^3=CO_2Et

Entry 3. R^1=C_6H_5, 4-ClC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 4-MeC_6H_4, 4-$OMeC_6H_4$,4-BrC_6H_4, 4-FC_6H_4, 4-OHC_6H_4, 4-OHC_6H_4, 4-CNC_6H_4, 2-furanyl, cinnamaldehyde, 2-tienyl, H_2CO/R^2=R^3=CO_2Et
$R^1C_6H_5$,4-ClC_6H_4,3-$NO_2C_6H_4$/R^2=R^3=CO_2Me

Selected examples

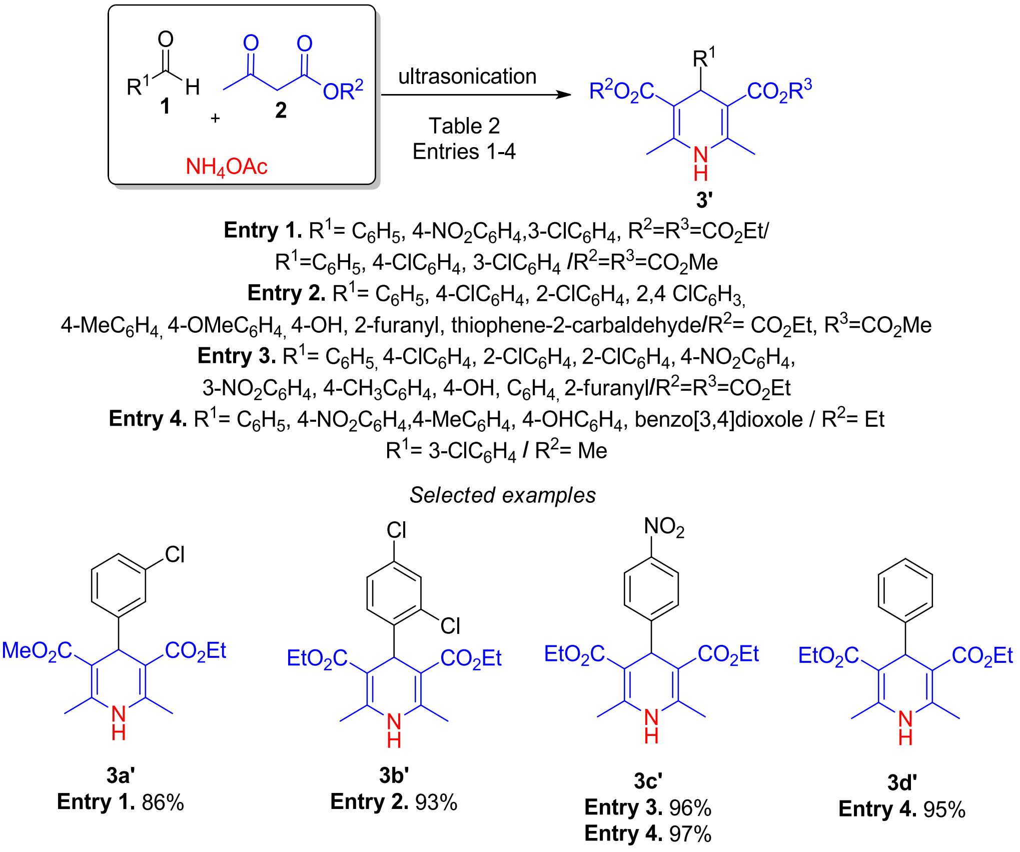
3a **Entry 1.** 95%

3b **Entry 2.** 95%

3c **Entry 3.** 87%

3d **Entry 3.** 86%

Scheme 1. Synthetic approaches mediated by ultrasound for the preparation of 1,4-DHPs (**3**) in greener conditions.



Entry 1. R^1= C_6H_5, 4-$NO_2C_6H_4$,3-ClC_6H_4, R^2=R^3=CO_2Et/
R^1=C_6H_5, 4-ClC_6H_4, 3-ClC_6H_4 /R^2=R^3=CO_2Me

Entry 2. R^1= C_6H_5, 4-ClC_6H_4, 2-ClC_6H_4, 2,4 ClC_6H_3, 4-MeC_6H_4, 4-$OMeC_6H_4$, 4-OH, 2-furanyl, thiophene-2-carbaldehyde/R^2= CO_2Et, R^3=CO_2Me

Entry 3. R^1= C_6H_5, 4-ClC_6H_4, 2-ClC_6H_4, 2-ClC_6H_4, 4-$NO_2C_6H_4$, 3-$NO_2C_6H_4$, 4-$CH_3C_6H_4$, 4-OH, C_6H_4, 2-furanyl/R^2=R^3=CO_2Et

Entry 4. R^1= C_6H_5, 4-$NO_2C_6H_4$,4-MeC_6H_4, 4-OHC_6H_4, benzo[3,4]dioxole / R^2= Et
R^1= 3-ClC_6H_4 / R^2= Me

Selected examples

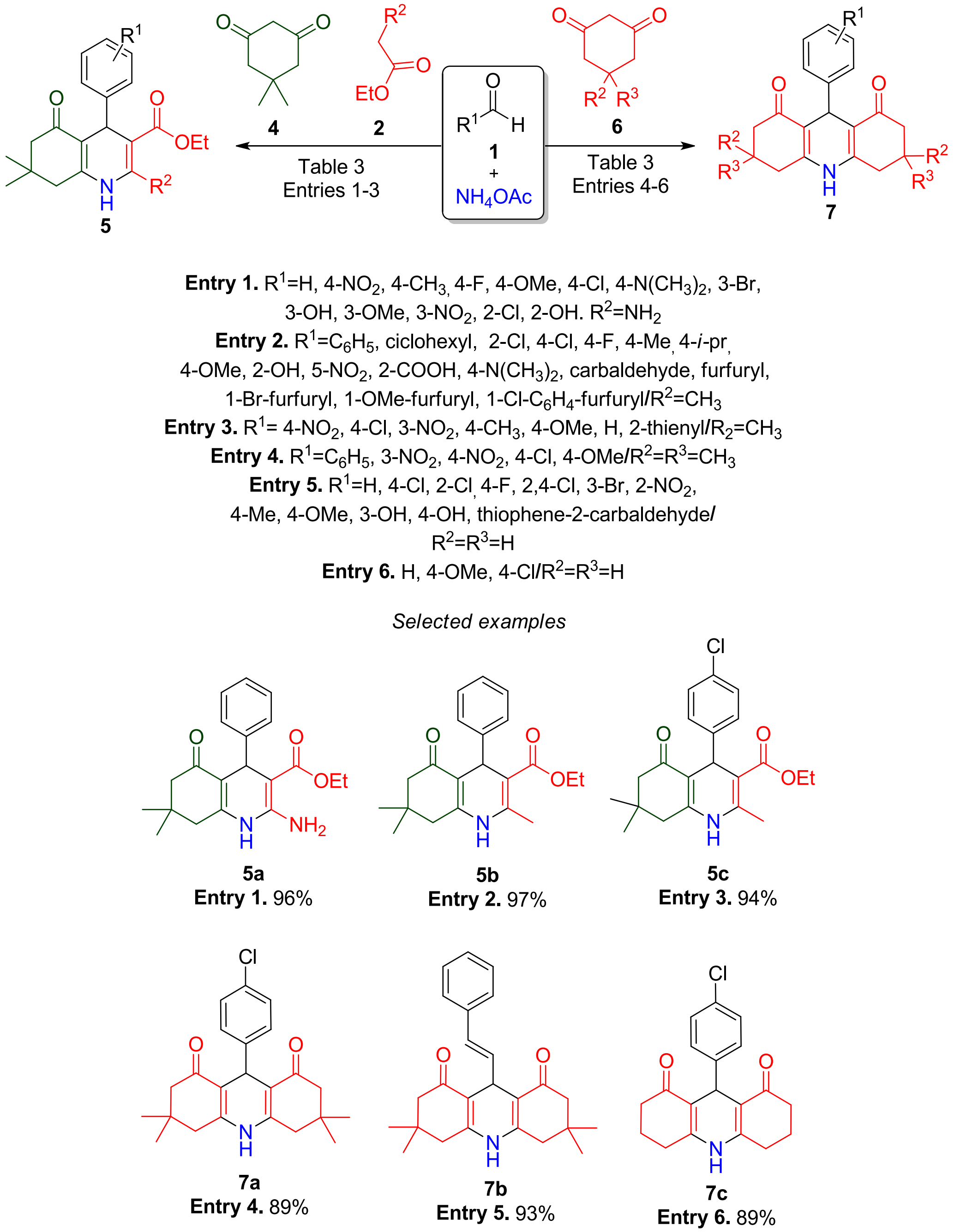
3a' **Entry 1.** 86%

3b' **Entry 2.** 93%

3c' **Entry 3.** 96% **Entry 4.** 97%

3d' **Entry 4.** 95%

Scheme 2. MCR procedures for obtaining 1,4-DHPs (**3**) under sonicated conditions.



Entry 1. R^1=H, 4-NO_2, 4-CH_3, 4-F, 4-OMe, 4-Cl, 4-$N(CH_3)_2$, 3-Br, 3-OH, 3-OMe, 3-NO_2, 2-Cl, 2-OH. R^2=NH_2

Entry 2. R^1=C_6H_5, ciclohexyl, 2-Cl, 4-Cl, 4-F, 4-Me, 4-*i*-pr, 4-OMe, 2-OH, 5-NO_2, 2-COOH, 4-$N(CH_3)_2$, carbaldehyde, furfuryl, 1-Br-furfuryl, 1-OMe-furfuryl, 1-Cl-C_6H_4-furfuryl/R^2=CH_3

Entry 3. R^1= 4-NO_2, 4-Cl, 3-NO_2, 4-CH_3, 4-OMe, H, 2-thienyl/R_2=CH_3

Entry 4. R^1=C_6H_5, 3-NO_2, 4-NO_2, 4-Cl, 4-OMe/R^2=R^3=CH_3

Entry 5. R^1=H, 4-Cl, 2-Cl, 4-F, 2,4-Cl, 3-Br, 2-NO_2, 4-Me, 4-OMe, 3-OH, 4-OH, thiophene-2-carbaldehyde/ R^2=R^3=H

Entry 6. H, 4-OMe, 4-Cl/R^2=R^3=H

Selected examples

5a **Entry 1.** 96%

5b **Entry 2.** 97%

5c **Entry 3.** 94%

7a **Entry 4.** 89%

7b **Entry 5.** 93%

7c **Entry 6.** 89%

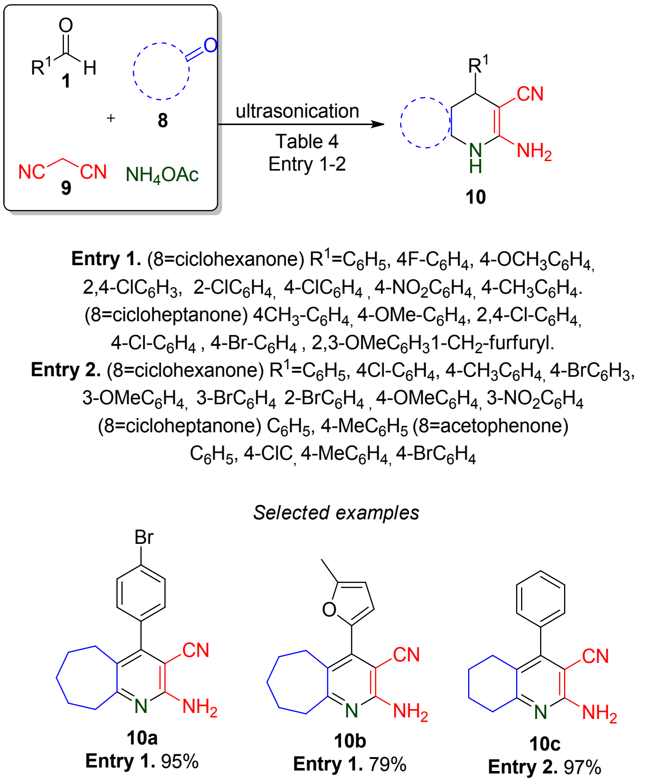
Scheme 3. Synthetic protocols for the preparation of polyhydroquinolines **5** and **7** promoted by ultrasonic waves.

catalysts is discussed. The MCRs are classified according to the class of compounds formed, with special attention to the *N*-heterocycles, and concerning the catalysts, zeolites and nanoparticles, among others, are presented considering their recycling capacity.

2. Ultrasound-assisted MCRs under heterogeneous catalysis

A strategy well aligned with the green chemistry principles and which has been gaining prominence in recent years in the field of heterogeneous catalysis is the immobilization of nanoparticles (NPs) on solid supports, such as porous silica [85–89], zeolites [84,90–93], polymers [94–96] and carbon-based supports, including carbon nanotubes (CNTs) [97–100], graphene [101–103], graphene oxide (GO) [104,105] and graphene nanosheets (GNSs) [103,106]. A notable peculiarity of many of these supports – as is the case with graphene - is the property of having the surface easily modifiable, which is only possible due to the presence of large points of nucleation or stabilization [103]. Other characteristics of these materials that make them remarkable interesting from the point of view of catalysis are porosity, low interaction with supported materials, and good mechanical resistance [105–109]. In turn, these mixed catalytic systems still have the benefit of being easily removable from the reaction medium, highlighting them in the search for more sustainable synthetic protocols [110].

Furthermore, combination of the use of ultrasound with these heterogeneous catalytic systems has proved to be a powerful strategy to increase reaction yields, and this is due in large part to the better dispersion of magnetic nanoparticles (MNPs) in the reaction mixture caused by ultrasonic irradiation, which results in a more active surface area to catalyze the reaction [111]. In this section, the ultrasound assisted synthesis of different classes of heterocyclic compounds using



Scheme 4. Synthesis of 2-amino-3-cyanopyridines (**10**) under mild conditions.

Table 1
Sonochemical and one-pot synthesis of 1,4-DHPs (**3**) mediated by heterogeneous nanocatalysis.

Entry	Catalyst	Conditions[a]	Examples	Yields (%)	Ref.
1	MWCNTs@meglumine	15–34 min	20	82–95	[115]
2	Celullose@pumice	10 min	11	93–97	[116]
3	Fe_3O_4/SiO_2-PDA	H_2O, 10 min, r.t	18	68–91	[111]

*Ultrasound parameters: Entry 1. Ultrasonic bath, r.t., with probe, diameter of 6 mm; frequency: 20 kHz; power: 70 W. Entry 2. Ultrasound device was not informed; reactions performed in ultrasound bath at r.t.; frequency: 60 kHz; power: 150 WL^{-1}. Entry 3. Ultrasound bath, r.t.; frequency: 50 kHz; power: 250 $W.L^{-1}$. [a]reactions carried out at r.t. and in EtOH as solvent.

heterogenous catalysts is discussed.

2.1. N-Heterocyclic compounds

2.1.1. 1,4-Dihydropyridines

Recently, several more environmentally friendly ultrasound-assisted protocols based on the Hantzch reaction have been developed for the one-pot synthesis of 1,4-dihydropyridines (1,4-DHPs), an extremely relevant class from a pharmacological point of view. These heterocycles have already demonstrated, for example, anti-cancer [112], anticoagulant, anti-microbial [113] and anti-thrombotic [114] activities. The synthetic approaches that will be discussed in this section are based on the condensation of aldehydes (**1**), 1,3-dicarbonyl compounds (**2**), ammonium acetate (Schemes 1–3), and malonitrile (**9**) (Scheme 4) in presence of green solvents such as EtOH and/or H_2O, promoted by highly efficient and reusable nanocatalysts.

Table 2
Protocols for the preparation of 1,4-DHPs (**3**) mediated by green solvents, innovative catalytic systems and ultrasonic irradiation.

Entry	Catalyst	Conditions[a]	Examples	Yields (%)	Ref.
1	SBA-15/SO_3H	Solvent-free, 8 min, 100 °C	5	80–86	[121]
2	Fe_3O_4@GA@IG	35–70 min	12	77–92	[118]
3	MCGC [b]	10–66 min, 40–42 °C	8	90–96	[119]
4	Cu-Fe/ZSM-5	H_2O, 5 min	6	93–99	[120]

*Ultrasound parameters: Entry 1. Ultrasound device equipped with a converter/transducer and titanium oscillator (horn),12.5 mm in diameter; frequency: 19.6 kHz; power: 600 W. Entry 2. Ultrasound device equipped with an ultrasonic probe sonicator; frequency: 20 kHz; power: 400 W, further details were not provided. Entry 3. Ultrasonic bath at temperature of 40–42 °C; frequency: 25 kHz; further details were not provided. Entry 4. The reactions were carried out using an ultrasonic processor probe at 20% power of the processor, further details were not provided. [a]reactions carried out at r.t. and in EtOH as solvent; [b]modified cyanoguanidine supported on chitosan.

In this perspective, for example, Moradi et al. [115] have designed a nanocatalyst based on a natural biopolymer supported on multi-walled carbon nanotubes (MWCNTs@meglumine), as a cheap and reusable catalyst, and employed it in the synthesis of the 1,4-DHPs. The developed catalytic system, used in a low amount (0.99 w/w %), has proved to be fundamental for the success of the method, since, in its absence, the desired product was obtained with very low yields (Table 1, Entry 1). Ultrasonication was performed in a device with probe with diameter of 6 mm that was immersed directly into the reaction mixture. The operating frequency was 20 kHz and the output power was 60–75 W through manual adjustment, and 70 W provided the best performance in the shortest reaction time. The reactions were carried out at room temperature. After a simple recycling process, the recovered nanocatalyst could be used four times, maintaining its efficiency and high yields.

Valadi et al. [116] have successfully developed a hybrid organic–inorganic nanocomposite of pumice stone immobilized on cellulose (pumicce@cellulose) and used this material (6.2 w/w %) in the preparation of 1,4-DHPs in EtOH as solvent at room temperature (Table 1, Entry 2). Pumice stone is a quite common natural mineral, having in its chemical composition silica, aluminum oxide, aluminum silicate and small amounts of other metal oxides, being rich in hydroxyl groups that can function efficiently as active sites when functionalized [116,117]. In the optimization study, the sonicated model reaction, under the same conditions, was performed first with cellulose only, in the absence of pumice, and then in the absence of cellulose and only pumice. In the first case, only traces of the product were identified, and in the second case, the product was formed, but with low yield, whereas in the presence of the pumicce@cellulose nanocomposite/ultrasound excellent yields of the product of interest were observed, in shorter reaction times. The reaction was carried out in an ultrasound bath with 60 kHz frequency and 150 W L^{-1} power density, and the temperature of the bath was maintained at r.t. by regular addition of ice (the ultrasound dispositive device was not informed). Studies investigating the co-participation of ultrasound in the catalytic activity of the nanocomposite were carried out, and the results led to the conclusion that there is a constructive synergistic effect between the active sites of the pumice stone and the ultrasonic waves. After recovering, the cellulose@pumice nanocomposite has shown an acceptable stability even after several cycles.

Magnetic nanoparticles (MNPs) of Fe_3O_4 can be embedded in the silica surface to prepare efficient nanocatalysts. In this regard, Taheri-Ledari and co-workers [111] have designed a new hybrid catalytic system with these MNPs using silica functionalized with pyrimidine-2,4-diamine (PDA) as matrix [Fe_3O_4/SiO_2-PDA], and applied it – in an amount of 2 w/w % - to obtain 1,4-DHP derivatives using EtOH as solvent (Table 1, Entry 3). Ultrasonic irradiation was performed in a bath at room temperature, with a frequency of 50 kHz and power of 250 WL^{-1}. In the absence of the nanocatalyst, only traces of the desired product were formed. After optimizing the method, the researchers investigated

Table 3
MCR procedures to the synthesis of polyhydroquinilines **5** and **7** by using hybrid heterogeneous nanocatalysts.

Entry	Catalyst	Conditions^a	Examples	Yields (%)	Ref.
1	Alum.poliborate	EtOH:H_2O, 45–50 min	13	86–96	[126]
2	LAIL@MNP	Solvent-free, 15–60 min, 80 °C	18	75–97	[125]
3	MWCNTs@meglumine	15–34 min, r. t.	7	85–94	[115]
4	Fe_3O_4/SiO_2-PDA	H_2O,10 min, r.t	5	85–89	[111]
5	Fe_3O_4@GA@IG	45–70 min	10	71–93	[118]
6	Fe_3O_4@GA@IG	50–60 min	3	61–89	[118]

*Ultrasound parameters: Entry 1. Ultrasound device with frequency of 33 kHz and power: 100 W, no further details were informed. Entry 2. Ultrasound device operating at frequency of 37 kHz and temperature of 80 °C; no further details were informed. Entry 3. Ultrasonic device equipped with probe, diameter of 6 mm; frequency: 20 kHz; power: 70 W. Entry 4. Ultrasound bath, r.t.; frequency: 50 kHz; power: 250 WL^{-1}. Entries 5 and 6. Ultrasound device equipped with an ultrasonic probe sonicator; frequency: 20 kHz; power: 400 W, further details were not provided. ^{a}reactions carried out at r.t. and in EtOH as solvent.

the effect of the association of the use of [Fe_3O_4/SiO_2-PDA], and the ultrasonic irradiation in the same reaction, and the results obtained confirmed that there is a constructive synergistic effect between the NH_2 groups (as active catalytic sites) and ultrasonic waves, at a frequency and power of 50 kHz and 250 W, respectively. The authors argued that the high catalytic activity of the nanocomposite is related to the increase in the binding capacity of the nitrogen atoms present, which is due to a constructive synergistic effect between PDA-NH_2 groups (as active catalytic sites) and ultrasonic waves, according to which the electronic resonance in the conjugated system of this charged heterocycle is likely to be accelerated. The nanocatalyst was recovered by simple magnetic separation and could be reused seven times without any measurable loss of catalytic activity.

Doustkhah et al. [89] have reported an interesting one-pot method to prepare 1,4-DHPs in presence of the inexpensive and reusable SBA-SO_3H/SBA-15 catalyst, a material based on functionalized sulfonic acid (SA) on mesoporous SBA-15 (Table 2, Entry 1). In this work, the authors showed that there was a synergistic effect between this catalytic system and ultrasound and suggested that the irradiation of ultrasonic waves in the mesoporous material led to changes in the SBA-SO_3H mesochannels, which started to behave as nanoreactors. With this, the mass transfer processes were accelerated, leading to a substantial increase in the catalytic activity of the nanocomposite, which made possible to obtain the products of interest with high yields and tolerance of various functional groups in short reaction time. The reaction was performed in a multi-wave ultrasonic generator, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating as continuous irradiation with a maximum power output of 600 W and frequency of 19.6 kHz. The amount of catalyst required was only 10 mol %. Studies have shown the feasibility of recovering and reusing the nanocatalyst, which maintained the catalytic properties up to six cycles.

It has recently been shown that certain types of proteinaceous materials can function efficiently as a support for nanoparticles, resulting in versatile heterogeneous catalysts. In this line, the Pourian group [118] obtained a hybrid catalytic system by immobilizing Fe_3O_4/NPs in Isinglas (IG) [Fe_3O_4@GA@IG], a type of collagen derived from the swimming bladders of tropical fish, and of great interest in catalysis, since it presents numerous acidic and basic groups in their helical structure, which can function as active sites when properly functionalized (Table 2, Entry 2). This nanobiocatalyst was successfully applied to establish a greener protocol for one-pot synthesis of 1,4-DHPs, in the presence of EtOH. The model reaction for optimization was carried out in the absence of catalysts, leading to the product with low yields, without sonication. When it was performed using the nanobiocatalyst (0.5 w/w %), under the same conditions, in the presence of EtOH and reflux, the yields remained low, in long reaction time. When performed in the presence of ultrasound, under the same conditions as before, the reaction led to high yields, in much shorter reaction times, showing that there is a synergism between nanocatalysis and ultrasonic irradiation. The reactions were carried out in an ultrasonic device, equipped with a probe sonicator (further details were not provided), operating a 20 kHz of frequency and 400 W of power. The Fe_3O_4@GA@IG catalyst was recovered using an external magnetic field, washed with ethyl acetate, dried, and then could be reused in up to six cycles, without appreciable loss in catalytic efficiency.

Stimulated by the interest in investigating the usefulness of biopolymers as an efficient support in nanocatalysis, Javanmiri et al. [119] have combined the qualities of chitosan - non-toxicity, biodegradability, biocompatibility - with the properties of magnetically modified cyanoguanidine (MCGC) to obtain a highly convenient heterogeneous nanocatalytic system, which has been successfully applied to the green synthesis of a series of 1,4-DHPs, in 0.5 w/w % loading, by using EtOH as a solvent (Table 2, Entry 3). The reaction was performed by using an ultrasonic cleaner bath at temperature of 40–42 °C, with a frequency of 25 kHz and the power was not informed. In comparison, using conventional heating using reflux, maintaining the same conditions, the reaction was twice longer, and lead to lower yields. The recycling process of the MCGC proved to be quite simple, by magnetic separation, followed by washing with EtOH and H_2O and drying. In terms of reuse, MCGC showed no change in catalytic properties even after eight reactions.

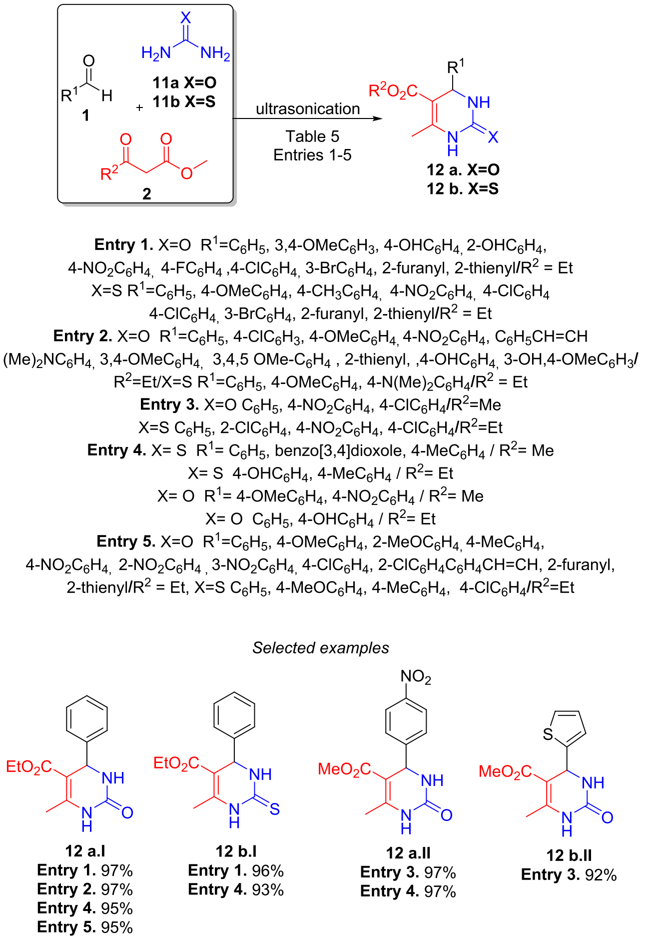
Safa et al. [120] promoted an aqua-mediated one-pot synthesis of Hantzsch DHPs sonocatalyzed by metal-supported nanocatalysts (Table 2, Entry 4). In this work they investigated under mild conditions some catalysts with different transition metals (Mn, Fe, Co, and Cu) and γ-alumina (γ-Al_2O_3), Zeolite Socony Mobil-5 (ZSM-5), as an aluminosilicate zeolite, and silicoaluminophosphate molecular sieve (SAPO-34) and different solvents at room temperature such as ethanol, ethanol/water, acetonitrile, acetonitrile/water, water, DCM, toluene and solvent-free (120 °C). The best results were obtained for Cu-Fe/ZSM-5 bimetallic catalyst (3 w/w %) in water under ultrasonic irradiation at room temperature at 20% power of the processor. The reuse of the catalyst was investigated and no decrease of its catalytic activity after three cycles was observed.

When the β-ketoester is replaced by an 1,3-dicarbonyl cyclic compound in the Hantzsch MCR more structurally complex 1,4-DHPs are formed, such as the polyhydroquinolines (PHQs) (**5** and **7**) [122]. The PHQs have received much attention in recent years, due to reports of various therapeutic properties associated with them, including antimalarial [123] and antidiabetic [124]. Among the synthetic methods of this nucleus, the use of heterogeneous catalysts under ultrasonic irradiation is highlighted. Examples in this category are two one-pot protocols developed by Aute et al. [125] and Nguyen and co-workers [126] using aldehydes (**1**), β-ketoesters (**2**), dimedone (**4**) or other cyclic diketones (**6**), and ammonium acetate as starting materials. In the first work, the researchers have synthesized a set of PHQs using an efficient catalytic system composed of aluminized polyborate (10 w/w %) as a way to increase the stability and improve the catalytic properties of the borate (Table 3, Entry 1). During optimization, the model reaction was reproduced in the absence of a catalyst, and there was no product formation. This method was compared with others reported in the literature for the synthesis of PHQs. It was found that the use of ultrasound provided the best yields in the shortest reaction times, in addition to greater operational simplicity, which makes this protocol highly efficient, and more benign for the environment. The reactions were performed in a device with maximum output of 100 W and frequency of 33 kHz, and no further details were provided. After the recovery processes, the catalyst can be successfully used in a cycle of five reactions without much decrease in its

Table 4
Synthesis of 2-amino-cianopyridines (**10**) under ultrasound and heterogeneous catalysis.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	SBA-15@ADMPT/HPA	EtOH, 3–5 min, r.t.	15	75–95	[127]
2	Fe_3O_4@g-C_3N_4-SA	H_2O, 8–15 min, r.t.	15	70–97	[128]

*Ultrasound parameters: Entry 1. Ultrasound device with probe, diameter of 6 mm; frequency: 20 kHZ, power: 50 W. Entry 2. Ultrasound device operating at frequency of 24 kHz and power of 250 W.



Scheme 5. One-pot protocols for ultrasound-based synthesis of DHMPs (**12**).

catalytic activity.

In the second case, the authors successfully designed and synthesized a mixed heterogeneous nanocatalyst, composed of ionic liquid immobilized in Fe_3O_4/MNPs (LAIL@/Fe_3O_4/MNPs), which proved to be highly efficient (2.8 w/w %) in promoting the PHQ synthesis in a solvent-free medium. In comparison with other methods available in the literature, this protocol proved to be more efficient in terms of reaction time and yield (Table 3, Entry 2). Ultrasonic irradiation-assisted reactions were performed at the frequency of 37 kHz and temperature of 80 °C, and no further details were informed. After the recovery process, the nanocomposite (LAIL@/Fe_3O_4/MNPs) was tested and kept the catalytic properties unchanged up to five reactions.

By using the catalysts previously shown in section 2.1.1, Moradi et al. [115], Taheri-Ledari et al. [111] (Table 3, Entries 3 and 4 respectively) and Pourian et al. (Table 3, Entries 5 and 6) also synthesized a series of PHQs (Scheme 3), with excellent yields.

Table 5
Sonochemical synthesis of DHMPs (**12**) using heterogeneous catalysts.

Entry	Catalyst	Conditions^a	Examples	Yields (%)	Ref.
1	NDL 5	EtOH:H_2O, 30–45 min, 45–50 °C	13^c	82-97^d	[131]
2	Polindole	s.f^b, 20–37 min, 45 °C	18	90–97	[132]
3	SBA-15/SO_3H	25 min, r.t.	17	88–97	[121]
4	Fe–Cu/ZSM-5	H_2O, 5 min, r.t.	9^e	92-97^f	[120]
5	Dendrimer-PWA	5–15 min, 50 °C	18	88–97	[133]

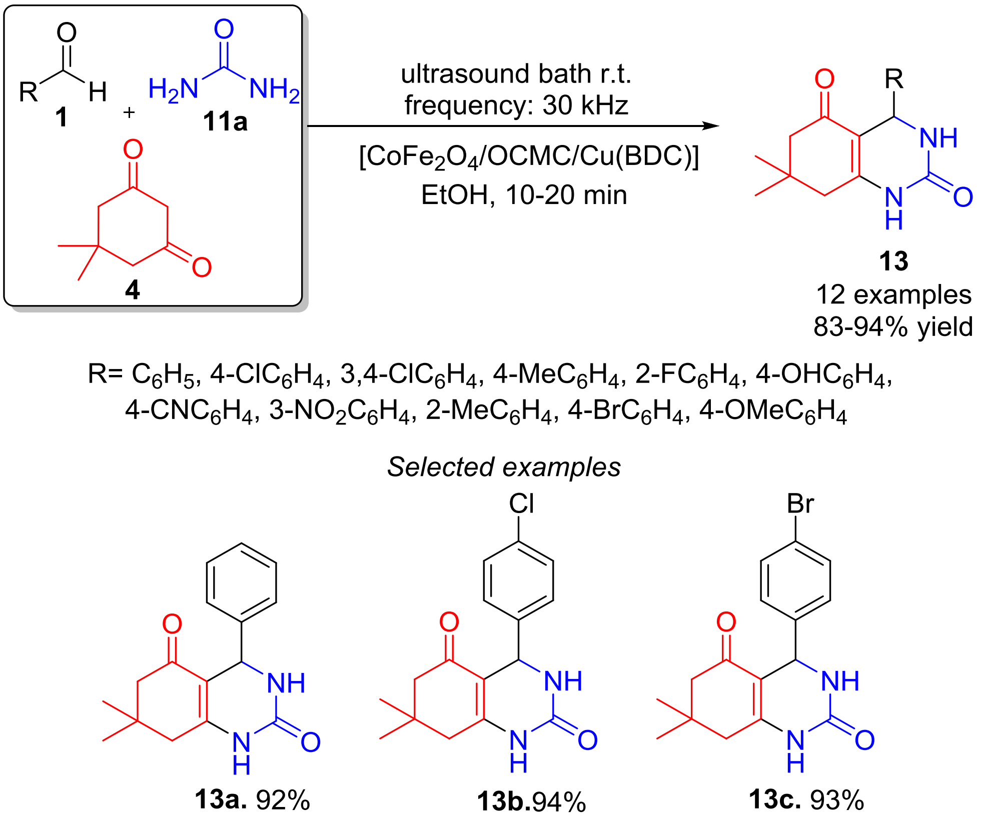
*Ultrasonication parameters: Entry 1. Ultrasonic bath with built-in heating, 45–50 °C; frequency: 35 kHz; power: 160/640 W. Entry 2. frequency: 33 kHz; power: 100 W, further details were not provided. Entry 3. Ultrasound device equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter; frequency: 19.6 kHz; power: 600 W. Entry 4. The reactions were carried out using an ultrasonic processor probe (SONOPULS Ultrasonic Homogenizers) at 20% power of the processor, further details were not provided. Entry 5. Ultrasound cleaning bath at 50 °C; frequency: 50 KHz, further details were not provided. ^{a}reactions carried out using only EtOH as solvent; ^{b} solvent-free; ^{c}X = O, 11/X = S, 2; ^{d}X = O, 82–97%/ X = S, 89–93%, ^{e}X = O, 4/X = S, 5, ^{f}X = O, 93–97%/ X = S, 92–95%.

More recently, highly effective procedures were developed for the synthesis of 2-amino-3-cyanopyridine (**10**) by the one-pot condensation of aldehydes (**1**), cyclic ketones (**8**), malononitrile (**9**) and ammonium acetate, in EtOH or water as solvent (Scheme 4). In one of them, Dastjerdi and co-workers [127] have designed and synthesized a hybrid catalytic system based on the heteropoly acid (HPA) $H_5PW_{10}V_2O_{40}$ immobilized on SBA-15@ADMPT (HPA/SBA-15@ADMPT) as an efficient nanocatalyst and EtOH as a solvent, at room temperature (Table 4, Entry 1). Ultrasonication was performed in a device equipped with a probe (diameter of 6 mm) at frequency of 20 kHz, power of 50 W and room temperature. The methodology provided excellent yields in a short reaction time. In the optimization study, the sonicated reaction was carried out separately in the presence of HPA or SBA-15, and, in both cases, the results showed that the products were obtained with low yield. However, with the hybrid nanocomposite HPA/SBA-15@ADMPT (0.47 w/w %) keeping constant the other conditions, the obtained yields were excellent. In the absence of ultrasound, the reaction was sixty times longer, with lower yield for the product of interest. After a simple recovery procedure, the catalyst showed a possibility of reusing in five reaction cycles.

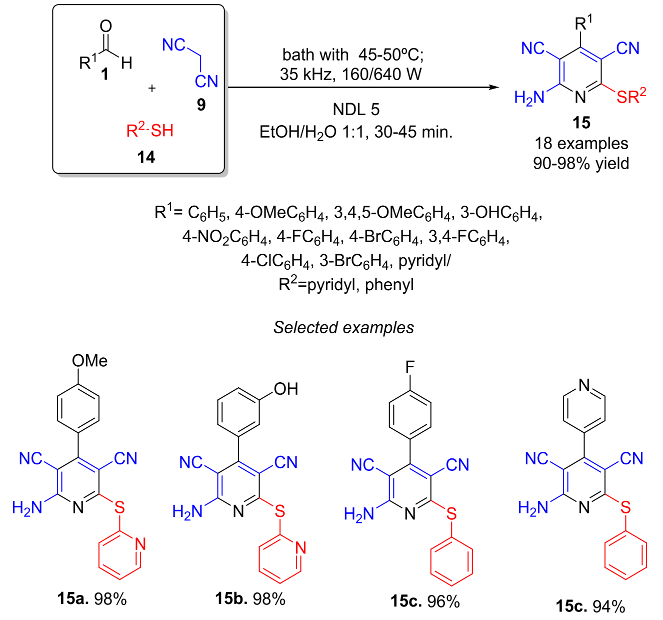
Likewise, the Edrisi group [128] have prepared a series of 2-amino-3-cyanopyridine using a modern and reusable heterogeneous catalyst composed of Fe_3O_4 nanoparticles embedded in a surface of sulfonated graphitic carbon nitride Fe_3O_4@g-C_3N_4-AS (0.96 mol%) (Table 4, Entry 2). This catalytic system combines the properties of carbon nitride surfaces (resistance to acid and basic media, and low toxicity, for example) with the excellent characteristics of Fe_3O_4/NPs as catalysts. To clarify the effect of using ultrasound, the reaction performed under conventional heating, at 60 °C, was fifty times longer than the one in the presence of ultrasonic waves. The reaction was performed in an ultrasonic homogenizer device with a frequency of 24 kHz and nominal power of 250 W. To investigate the influence of the ultrasound, the reaction was then carried out, under the same conditions, with an irradiation power of 50%, 80% and 100%, and the best results, in terms of yield, were obtained in the latter case. The developed catalytic could also be recycled, maintaining the catalytic activity even after five runs.

2.1.2. *Dihydropyrimidinones*

Under the perspective of green chemistry, very interesting methodologies for the synthesis of dihydropyrimidinones (DHMPs) via MCR have emerged in recent years. This scaffold belongs to a relevant class of heterocycles with a broad spectrum of biological activities, such as



Scheme 6. Nano-Co-ferrite catalyzed synthesis of substituted octahydroquinazolinones (**13**).



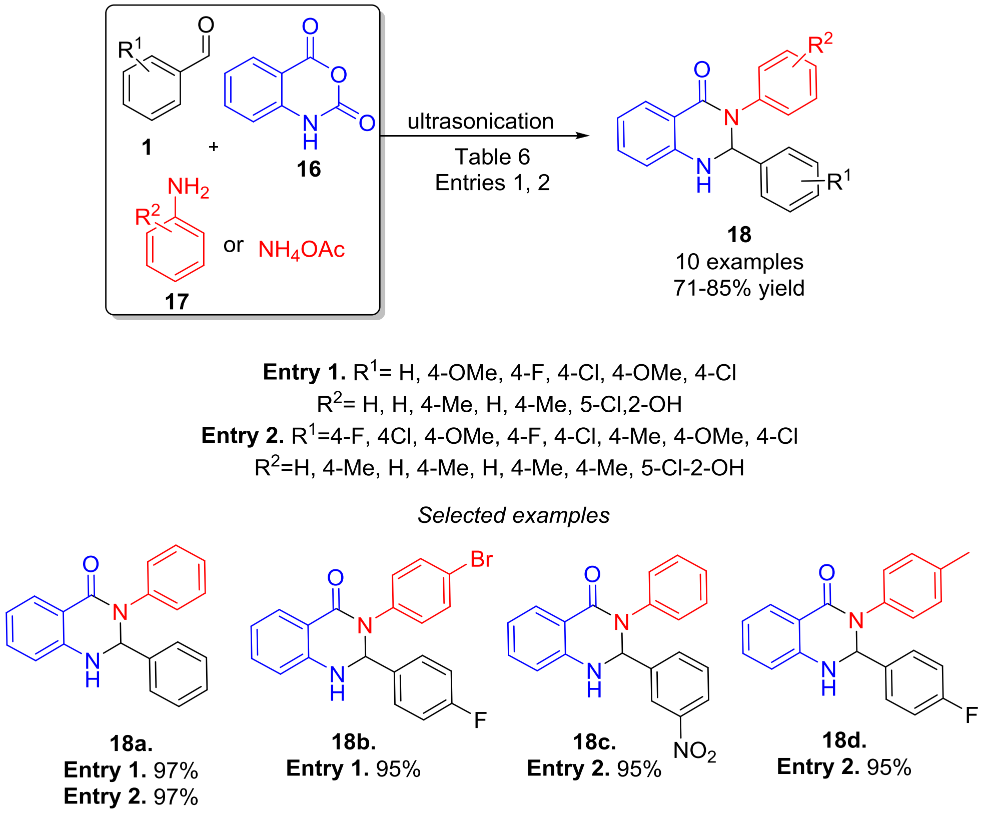
Scheme 7. Synthesis of sulfanylpyridines (**15**) in the presence of dolominte-limestone (NDL 5) and ultrasound.

antitumor [129] and anti-inflammatory [130]. In this section, the synthetic procedures that will be presented are based on the Biginelli reaction, which consists on the condensation between aldehydes (**1**), urea/thiourea or thiol (**11**) and β-ketoesters (**2**). These synthetic protocols, promoted by ultrasonic irradiation (Scheme 5), were established under mild reaction conditions, using green solvents and efficient heterogeneous catalysts, with easy recycling and high rate of reuse. In this context, Godugu et al. [131] have reported the use the mineral dolomite-lime (NDL) - a non-toxic and abundant material in nature - as a heterogeneous catalyst for the preparation of DHMPs in the presence of a mixture of EtOH/water as solvent (Table 5, Entry 1). The reaction was carried out by using ultrasonic bath with a frequency of 35 kHz and power of 160/640 W. In the optimization study, it was found that there was no product formation in the absence of the catalyst. When the reaction was carried out in the presence of the catalyst (5 w/w %) under traditional methods of stirring and/or heating and ultrasonic irradiation, the best condition was found when using EtOH, in the presence of ultrasound. The catalyst showed no significant loss in activity up to seven-reaction cycles (See Schemes 6).

Attracted by the interest in conducting polymers, the Handore group [132] has successfully developed a new approach promoted by a highly stable heterogeneous catalyst polyindole to synthesize a set of DHMP derivatives in a solvent-free reaction (Table 5, Entry 2). The ultrasound parameters informed were frequency of 33 kHz and power of 100 W. During the optimization, the catalytic potential of other conducting polymers was analyzed in separate with the use of ultrasound, but the polyindole (1.5 w/w %) showed superior catalytic activity, providing the achievement of DHMPs with high yields and a short reaction time. The polyindole showed the possibility of reuse in up to four reaction cycles with no noticeable loss in its catalytic activity.

Moreover, using the same catalyst previously mentioned (section 2.1.1), Doustkhah et al. (Table 5, Entry 3) [121] and Safa et al. (Table 5, Entry 4) [120] have synthesized a set of DHMPs, with excellent yields.

In a continuous effort to develop efficient and reusable nanocatalysts, Safaei-Ghomi et al. [133] reported a mixed system composed of dendrimer-attached phosphotungstic acid nanoparticles immobilized on nanosilica (Dendrimer-PWA) (Table 5, Entry 5). These authors emphasize the properties of dendrimer, which has been shown to be an appropriate support for nanoparticles, resulting in highly active



Scheme 8. Sonicated synthesis of dihydroquinazolinones (**18**) in ethanolic media.

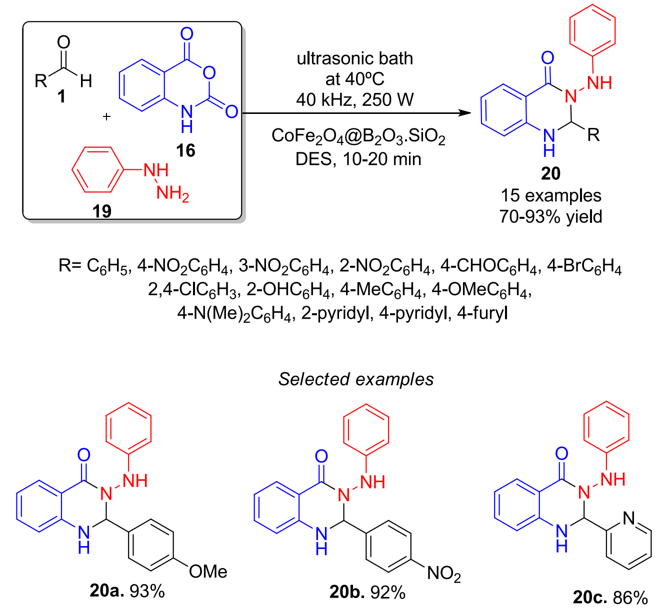
Table 6
Carbon Nanotube/NPs hybrid systems catalyzed one-pot ultrasound-assisted synthesis of dihydroquinazolinones (**18**).

Entry	Catalyst	Conditions[a]	Examples	Yield (%)	Ref.
1	Pt-MWCNTs	30–45 min, 60 °C	10	71–85	[138]
2	Co-CNTs	6–35 min, r.t.	19	81–97	[137]

*Ultrasound parameters: Entry 1. Ultrasound bath at 60 °C; further information was not provided. Entry 2. Ultrasound bath at 40 °C; frequency: 35 kHz; power: 90 W, further details were not provided. [a]reactions carried out using EtOH as solvent.

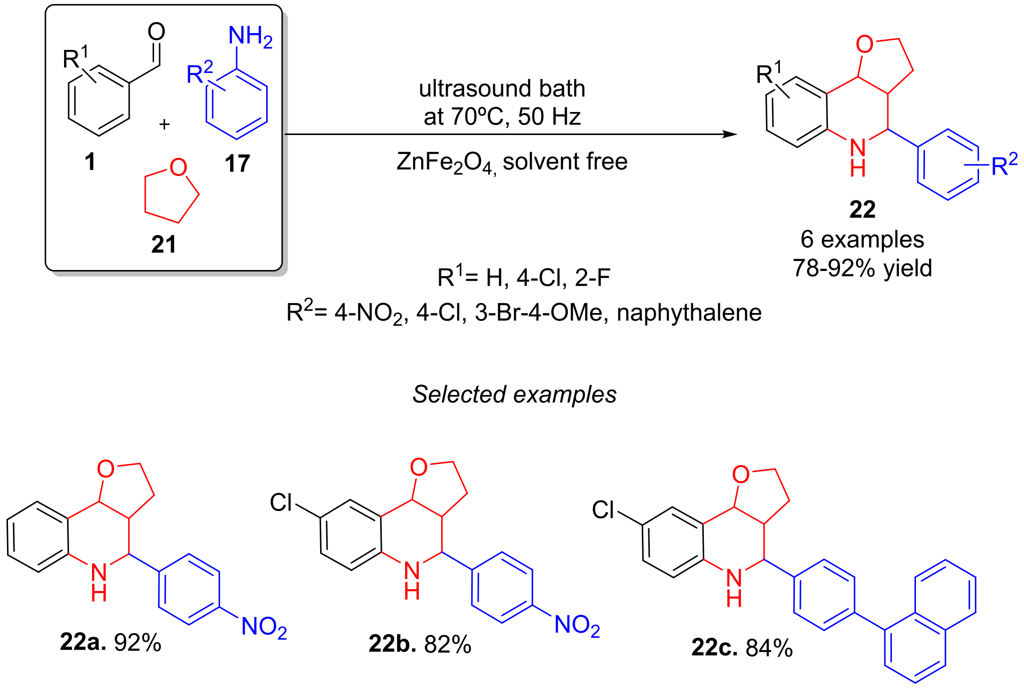
catalysts. The nanocomposite was able to successfully mediate the synthesis of DHMPs, in a protocol developed in the presence of EtOH. In the optimization study, the model reaction was performed in the presence of the Dendrimer-PWA using reflux or ultrasonic irradiation, under the same reaction conditions. In the second case, the reaction was nine times faster, with a considerably higher yield. Furthermore, the model reaction was performed in the presence of several catalysts, besides $H_3PW_{12}O_{40}$ nanoparticles and dendrimer-PWA (separately), all cases under ultrasonic irradiation, and the best yield for the product of interest was obtained when the nanocomposite (1.6 w/w %), showing a synergy between nanocatalysis and ultrasonic irradiation in promoting the reaction. The ultrasound apparatus was a cleaning bath at 50 °C, operating at frequency of 50 kHz, and further details were not provided. Dendrimer-PWA showed excellent recoverability and reusability, and the recovery process proved to be simple, consisting only of washing with EtOH and drying. This nanocomposite could be reused in up to eight reactions, maintaining its catalytic activity.

The Ghasemzadeh group [134] has developed an approach for the one-pot synthesis of octahydroquinazolinones (**13**), derived from DHMPs, obtained by the use of 1,3-cyclic dicarbonyl compounds in the Biginelli reaction (Scheme 5). This greener protocol is based in

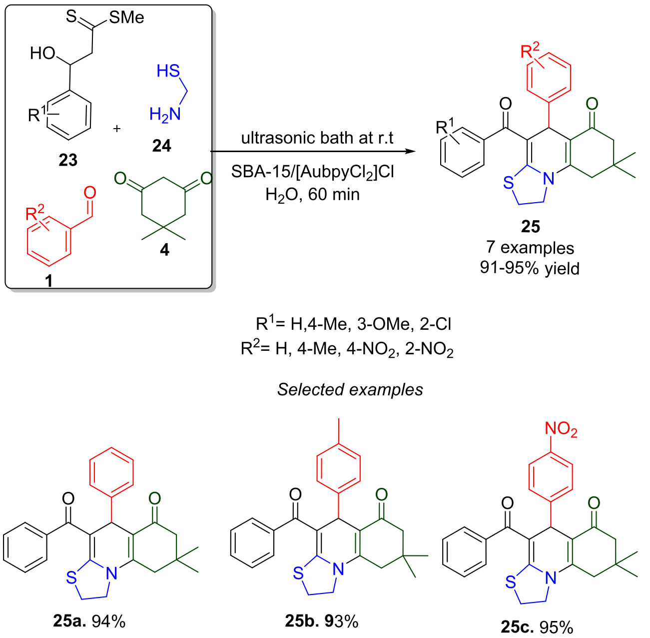


Scheme 9. Ultrasound-promoted preparation of dihydroquinazolinones (**20**) catalyzed by $CoFe_2O_4@B_2O_3.SiO_2$.

ultrasound, by using a highly, efficient and reusable shell/core/shell/ nanocomposite obtained from magnetic cobalt ferrite nanoparticles supported on *O*-carboxymethyl chitosan [$CoFe_2O_4$/OCMC/Cu(BDC)], via condensation of aldehydes (**1**), urea (**11a**), and dimedone (**4**) in presence of EtOH as solvent. In the optimization study, the model reaction was performed using ultrasound at the frequency of 30 kHz in the presence of several nanoparticles as catalysts. In all cases, the product of



Scheme 10. Ultrasound-mediated MCR for the synthesis of tetrahydropyranquinolines (**22**) using a $ZnFe_2O_4$ nanocatalyst.



Scheme 11. On water preparation of thiazoloquinolines (**25**) using SBA-15/[AubpyCl_2]Cl nanocatalyst under ultrasonic irradiation.

interest was obtained with good yields, which became excellent when the nanocomposite [$CoFe_2O_4$/OCMC/Cu(BDC)] (0.05 w/w%) was used, under the same conditions. The recovery of the nanocomposite was done by simple magnetic separation, and it could be reused six times without a significant loss in the performance of the catalytic activity.

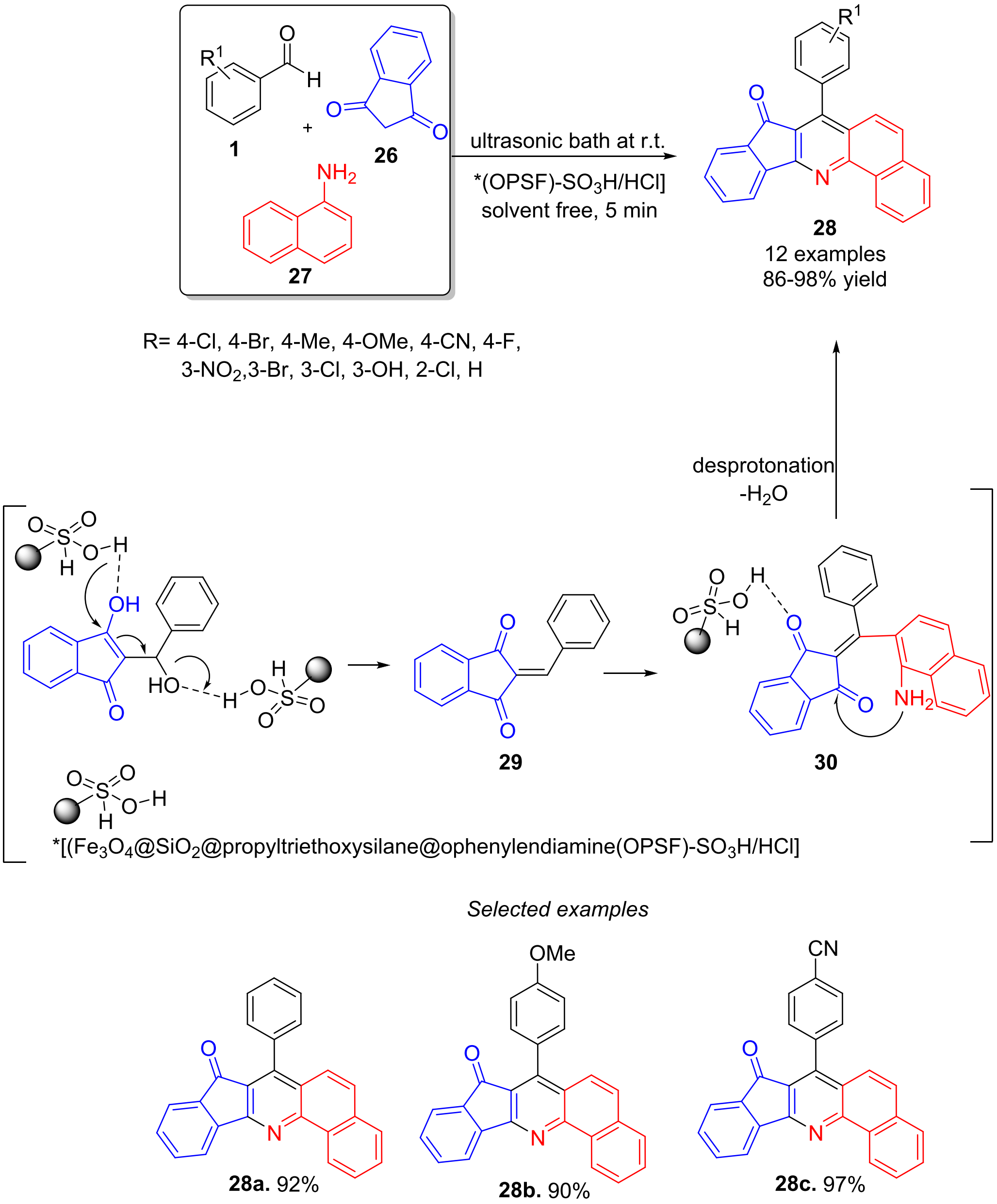
2.1.3. *2-Amino-4-(hetero)aryl-3,5-dicarbonitrile-6-sulfanylpyridines*

Exploring the already referenced methodology established for the synthesis of DHMPs (in section 2.1.2), Godugu et al. [131] synthesized a series of 2-amino-4-(hetero)aryl-3,5-dicarbonitrile-6-sulfanylpyridines (**15**) via condensation of aldehydes (**1**), malononitrile (**9**), and 2-mercaptopyridine (**14**). The desired products were obtained with excellent yields (above 90%) (Scheme 3).

2.1.4. *Dihydroquinazolinones*

Methodologies promoted by ultrasound and mediated by versatile and highly efficient heterogeneous catalysts have been reported to syntheses of dihydroquinazolinones (**18**, **20**). This important bicyclic framework has attracted interest because the wide range of biological activities associated with it, such as antimicrobial [135] and anticonvulsant [136]. The synthetic protocols discussed in this section are based on MCR between aldehydes (**1**), isatoic anhydride (**16**), and anilines (**17**), ammonium acetate or phenyl hydrazine (**19**) (Scheme 8). This is the case of the two procedures developed by Safari and co-workers [137,138], who have designed and synthesized a hybrid catalytic system based on metallic nanoparticles incorporated in Carbon Nanotube (CNTs) or Multi Wallet Carbon Nanotubes matrices (MWCNTs). CNTs/MWCNTs are very promising support materials in heterogeneous catalysis due to their extraordinary characteristics, such as high specific surface area, excellent electron conductivity incorporated with the good chemical inertia and high oxidation stability [97–100,139,140]. In the first case [137], a new nanocomposite hybrid of Pt-MWCNTs (0.93 w/w %) proved to be effective in promoting the synthesis of 2,3-dihydroquinazolin-4(1*H*)-one in EtOH under ultrasound irradiation (Scheme 8, Table 6, Entry 1). In the optimization study, the reaction was performed, under the same conditions, on ultrasonic irradiation and reflux, separately. As a result, it was found that, in the first case, the products were obtained in shorter reaction times, with a high yield. After a recycling process, the nanocomposite showed recyclability of up to four reaction cycles without considerable loss in catalytic activity.

Later, these same researchers [138] reported the synthesis and application of a nanostructure composed of cobalt/MNPs incorporated in CNTs (Co/CNTs) as heterogeneous catalyst in obtaining a series of 2,3-dihydroquinazolin-4(1*H*)-ones in EtOH under ultrasound irradiation (Table 6, Entry 2). The reaction was performed using conventional methods, but the results showed that under the same conditions, the reaction carried out with ultrasonic irradiation (frequency of 35 kHz and power of 90 W) always produced the best yields in the shortest reaction



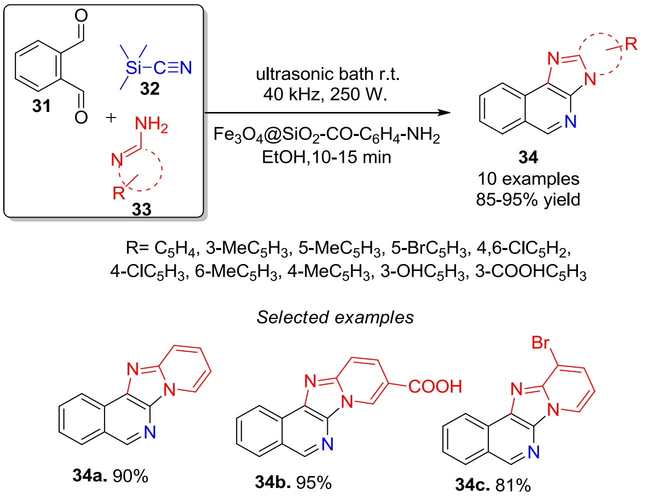
Scheme 12. Fe_3O_4/NPs incorporated on modified SiO_2 as functional catalyst in the sonochemical preparation of indenoquinolines (**28**).

times. Besides, a screening was performed with several MCNTs, however, the Co-CNT (9.15 w/w %) hybrid system was showed superior to the others. In terms of reuse, the recycled catalyst showed to be active even after five successive runs without an obvious loss of activity.

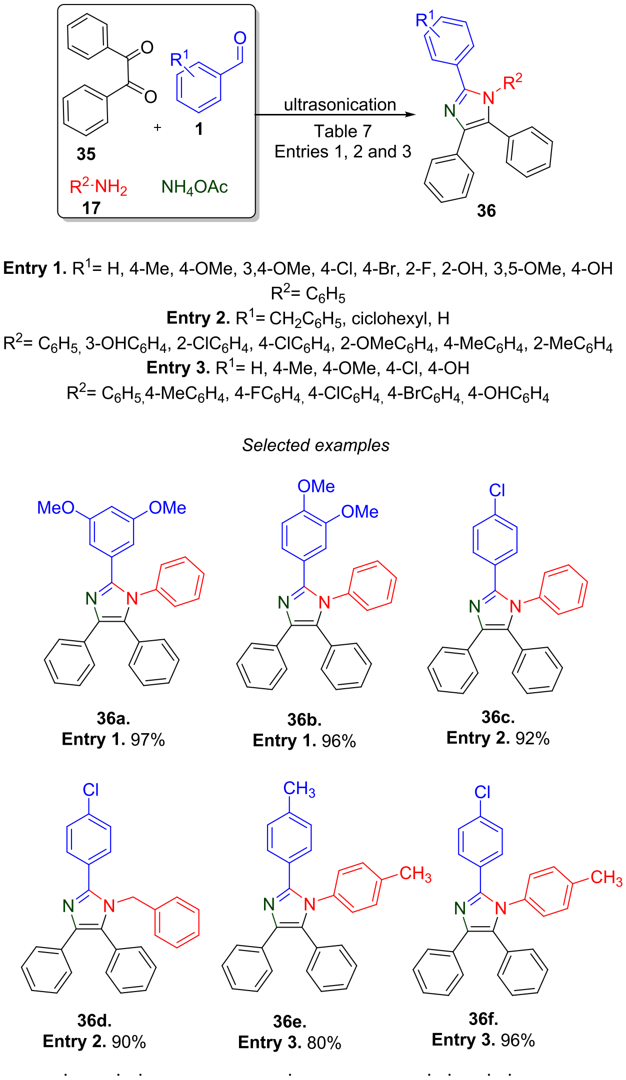
The Maleki group [141] has shown that glass–ceramic materials can also be used effectively as a solid support in heterogeneous catalysis. The researchers developed an innovative catalytic system that combines the paramagnetic properties of cobalt ferrite ($CoFe_2O_4$) with the features of glass-doped ceramic. This reusable nanomaterial - B_2O_3(Co-Fe_2O_4@B_2O_3.SiO_2 (5.5 w/w %) - has proved to be an effective catalyst for successful synthesis of 2-substituted-3-(phenylamino)-dihydroquinazolin-4(1*H*)-ones in presence of DES (deep eutectic solvent) (Scheme 9), and ultrasonic irradiation (cleaning bath at 40 °C, with a frequency of 40 kHz and power of 250 W). A study was carried out to compare the efficiency of this protocol with others reported in the literature for the synthesis of these dihydroquinazoline derivatives, which allowed to verify that the developed method was superior in terms of reaction times and yields. With regard to recyclability, the nanocatalyst could be reused six times without any significant reduction in product yield. In addition to the other advantages, the solvent could also be recycled, showing potential for application in a new reaction.

2.1.5. *Tetrahydropyranoquinolines*

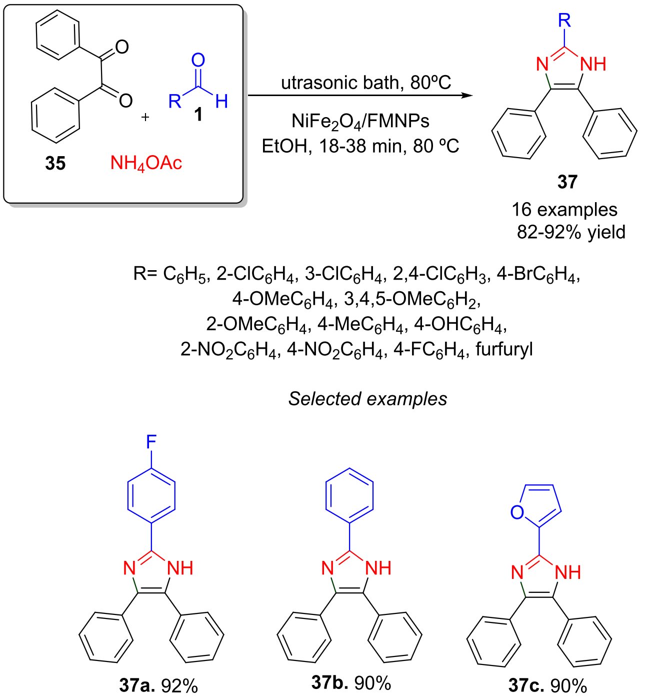
The Jadhav group [142] has synthesized a series of tetrahydropyranoquinolines (THQ) (**22**) via an easy and environmentally friendly ultrasound-assisted MCR based on the Povarov's hetero Diels-Alder reaction of substituted aromatic aldehydes (**1**), aromatic amines (**17**) and furan (**21**), in the absence of solvent (Scheme 10). In this case, the reactions were carried out in ultrasound bath (liquid holding capacity of bath, 5.5 L) at 70 °C and 50 Hz of frequency. These researchers have used a heterogeneous recyclable nanocomposite of $ZnFe_2O_4$ (10 mol %) as a catalyst in promoting this successful synthesis. The model reaction was not performed in the absence of the catalyst. After recovering process, Nano-$ZnFe_2O_4$ could be used in a cycle of up to five reactions without substantial loss in catalytic activity.



Scheme 13. Synthesis of pyridoimidazoisoquinolines (**34**) imidazoles in the presence of ultrasonic irradiation and $Fe_3O_4@SiO_2$-CO-C_6H_4-NH_2 nanocatalyst.



Scheme 14. Synthesis of substituted imidazoles (**36**) mediated by ultrasonic irradiation.



Scheme 15. Sonochemical preparation of imidazoles (**37**) catalyzed by $NiFe_2O_4$/FMNPs.

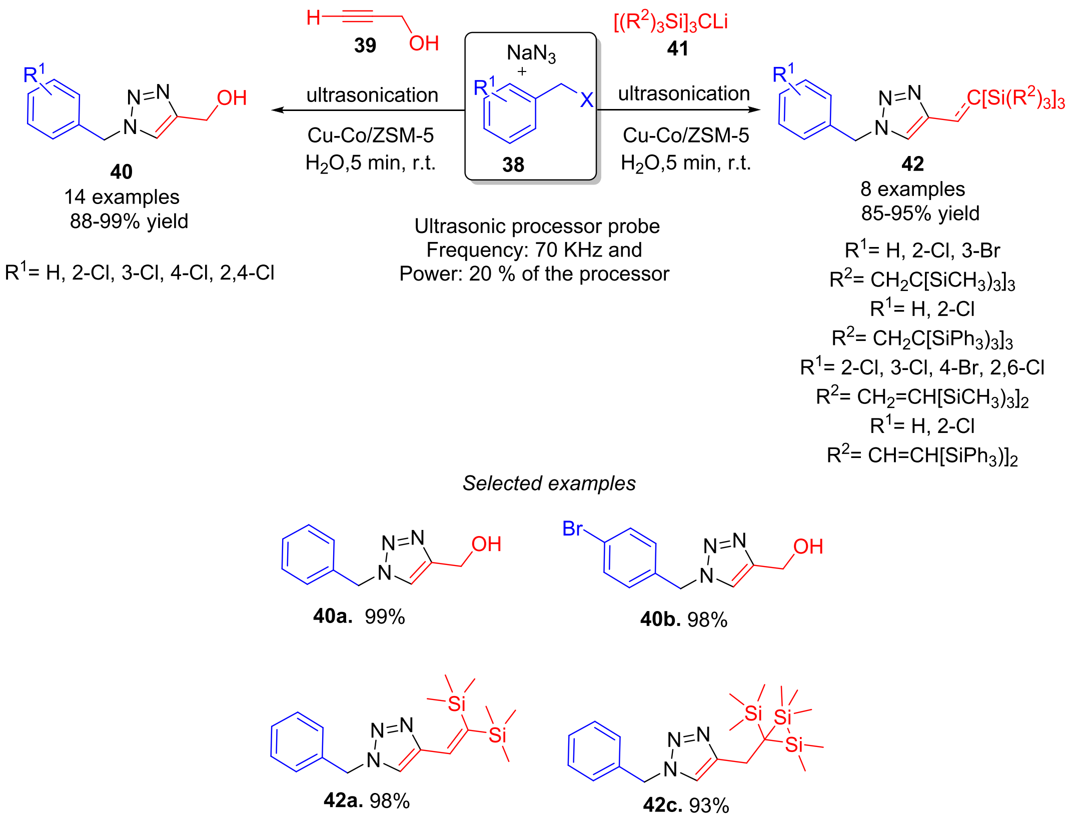
Table 7
One-pot synthesis of substituted imidazoles (**36**) mediated by ultrasound and nanocatalysts.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	Nano-$MgAl_2O_4$	EtOH,15–25 min, 60 °C	10	89–97	[148]
2	SBA-15/SO_3H	Solvent-free, 8 min, 100 °C	16	80–92	[121]
3	Cu/SAPO-34	H_2O, 4–8 min, r.t.	16	80–96	[149]

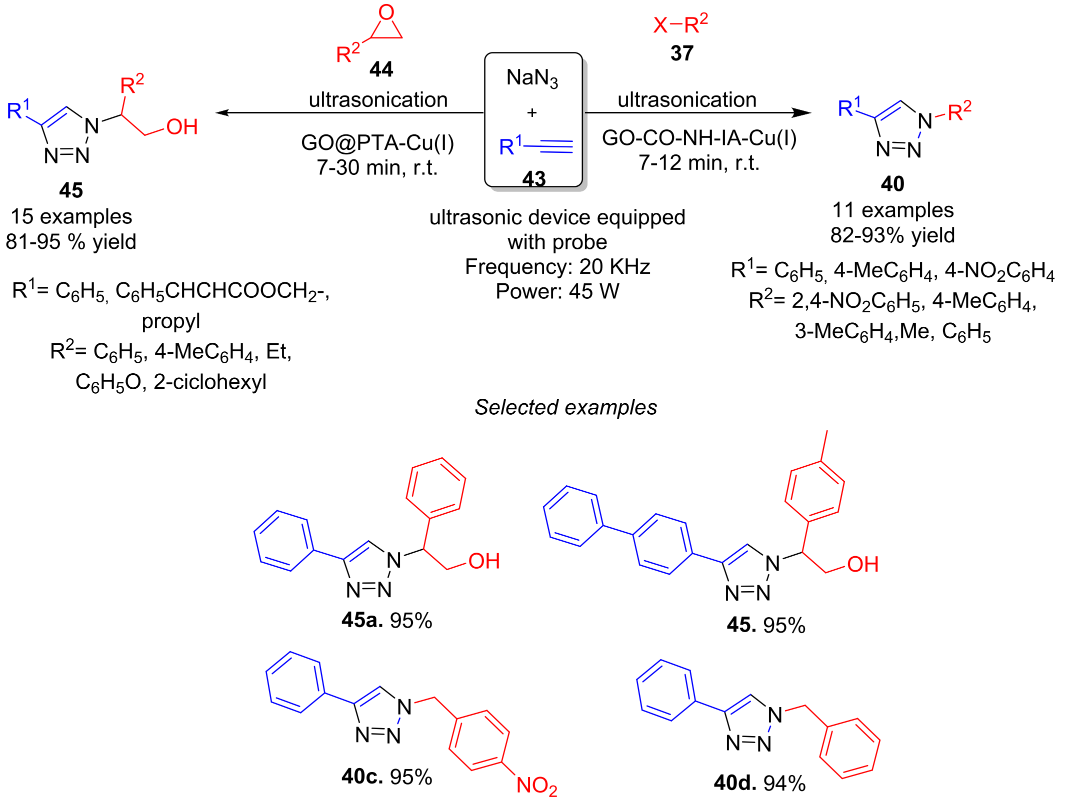
*Ultrasonic parameters: Entry 1. Ultrasonic bath at 60 °C; frequency: 50 kHz; power: 200 W. Entry 2. Ultrasound device equipped with a converter/transducer and titanium oscillator (horn),12.5 mm in diameter; frequency: 19.6 kHz; power: 600 W. Entry. 3. Ultrasonic processor probe device operating at 20% of the processor power, further information was not provided.

2.1.6. *Thiazoloquinolines*

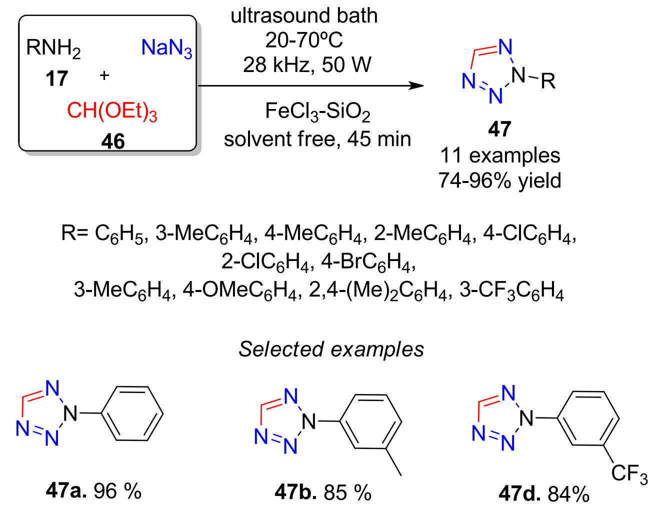
Sadeghzadeh and co-workers [143] have reported an ultrasound-promoted green MCR approach for the synthesis of thiazoloquinolines (**25**) in the presence of Au(III) dipyridine complex immobilized on mesoporous silica SBA-15 {SBA-15/[AubpyCl$_2$]Cl}as nanocatalysts at room temperature in aqueous media, by reaction between α-enolicdithioesters (**23**), cysteamine (**24**), aldehydes (**1**) and dimedone (**4**) (Scheme 11). During the optimization, it was verified that there was no product formation when the sonicated reaction was carried out in the absence of the nanocatalyst; in the presence of a free gold-pyridine complex, in the same conditions, the desired product was formed only in moderate yields, due to the formation of by-products. In this turn, when the reaction was carried out in concomitant presence of sonication and SBA-15/[AubpyCl$_2$]Cl (0.19 w/w %) hybrid nanocomposite, the product of interest was obtained with superior yield. This result indicated that the catalytic efficiency of gold-pyridine complex was increased by immobilization onto SBA-15. A comparative study was performed using the available methods for thiazoquinoline synthesis, which allowed to conclude that, at a lower temperature, the present



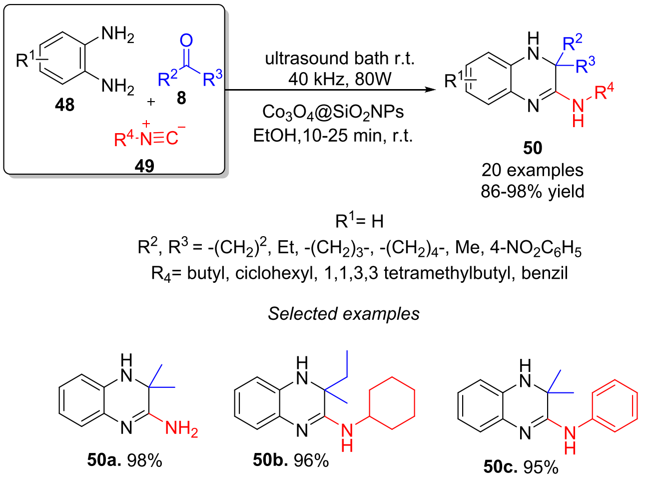
Scheme 16. On water-ultrasound mediated MCR protocols for the preparation of 1,2,3-triazoles **40** and **42** in presence of modified ZSM-5 zeolites as nanocatalyst.



Scheme 17. Cu(I) functionalized GO nanostructure as nanocatalyst in sonochemical synthesis of substituted triazoles **40** and **45** in a solvent-free media.



Scheme 18. One-pot synthesis of substituted 1,2,3,4-tetrazoles (**47**) under $FeCl_3$-SiO_2 nanocatalysis and ultrasound conditions.



Scheme 19. Preparation of dihydroquinoxalines (**50**) mediated by ultrasonic waves and Co_3O_4@SiO_2 nanocatalysis.

protocol is superior in terms of catalyst amount and reaction times. The recovered SBA-15/[AubpyCl$_2$]Cl nanocatalyst was reused for seven consecutive cycles without any significant loss in catalytic activity.

2.1.7. *Indenoquinolinones*

With a focus on the development of greener synthetic methods mediated by modern and reusable heterogeneous nanocatalysts, Maleki et al. [144] have reported the preparation of a hybrid magnetic organometallic nanocomposite composed of Fe_3O_4/NPs incorporated in a silica-coated stabilized *o*-phenylendiamine matrix [(Fe_3O_4@SiO_2@propyltriethoxysilane@ophenylendiamine(OPSF)-SO_3H/HCl], and its successful application in the one-pot synthesis of indenoquinolinenone derivatives (**28**) by condensation of aromatic aldehydes (**1**), 1,3-indanedione (**26**) and 1-naphthylamine (**27**), using ultrasonic irradiation, in a solvent-free media (Scheme 12). During optimization, the reaction was performed as follow: a) without sonication/catalyst and with stirring; b) with sonication, in the absence of a catalyst and c) also with sonication, but in the presence of Fe_3O_4@SiO_2 or OPSF-SO_3H, keeping constant the other reaction conditions. In all cases, with the exception of the first test, the product of interest was formed, with yields ranging from very low to high. When the same reaction was performed in using simultaneously ultrasound and the catalytic system (2.46 w/w%), there was a considerable increase in yield, showing the applicability of the combined use between heterogeneous catalysis and ultrasonic irradiation in this protocol. In the mechanistic proposal for the formation of the indenoquinolinones, the authors summarize that there is the formation, at first, of the intermediate **29** obtained via Knoevenagel condensation between aldehyde (**1**) and 1,3-indanedione (**26**), whose carbonyl groups are activated by the nanocatalyst. A Michael addition between this intermediate and 1-naphthylimine (**27**) leads to intermediate **30**, which, after deprotonation and water loss, leads to the desired product **28**. After each reaction, the catalyst was recovered by an external magnet and washed with ethanol, dried and reused in subsequent reactions at least eight times without any significant loss of its efficiency.

2.1.8. *Pyridoimidazoisoquinolines*

Maleki et al. [145] have synthesized a new nanocatalyst based on Fe_3O_4/NPs supported on SiO_2 modified with 4-aminobenzoylchloride (Fe_3O_4@SiO_2-CO-C_6H_4-NH_2), nanostructure that successfully mediated the ultrasound promoted synthesis of pyridoimidazoisoquinolines (**34**) by condensation of phthalaldehyde (**31**), trimethylsilylcyanide (**32**) and aminopyridines (**33**), in the presence of EtOH (Scheme 13). Initially, the reaction was performed in the presence of a catalytic amount of Fe_3O_4@SiO_2-CO-C_6H_4-NH_2 (5 mol%) in EtOH under ultrasonic irradiation (ultrasound cleaning with a frequency of 40 kHz and power of 250 W) leading to 90% yield of the desired product after 10 min. In order to compare the catalytic activity of the new nanostructure, the reaction was carried out under the same conditions already mentioned, in the presence of various catalysts such as protic solid acids, liquid acids and Lewis acids, in addition to Fe_3O_4 and Fe_3O_4@SiO_2 in different experiments. Among all cases, the results showed that the reaction yield in the presence of Fe_3O_4@SiO_2-CO-C_6H_4-NH_2 was the best. The nanocomposite could be easily recovered by magnetic separation, reused by five reaction cycles without significant loss of catalytic activity.

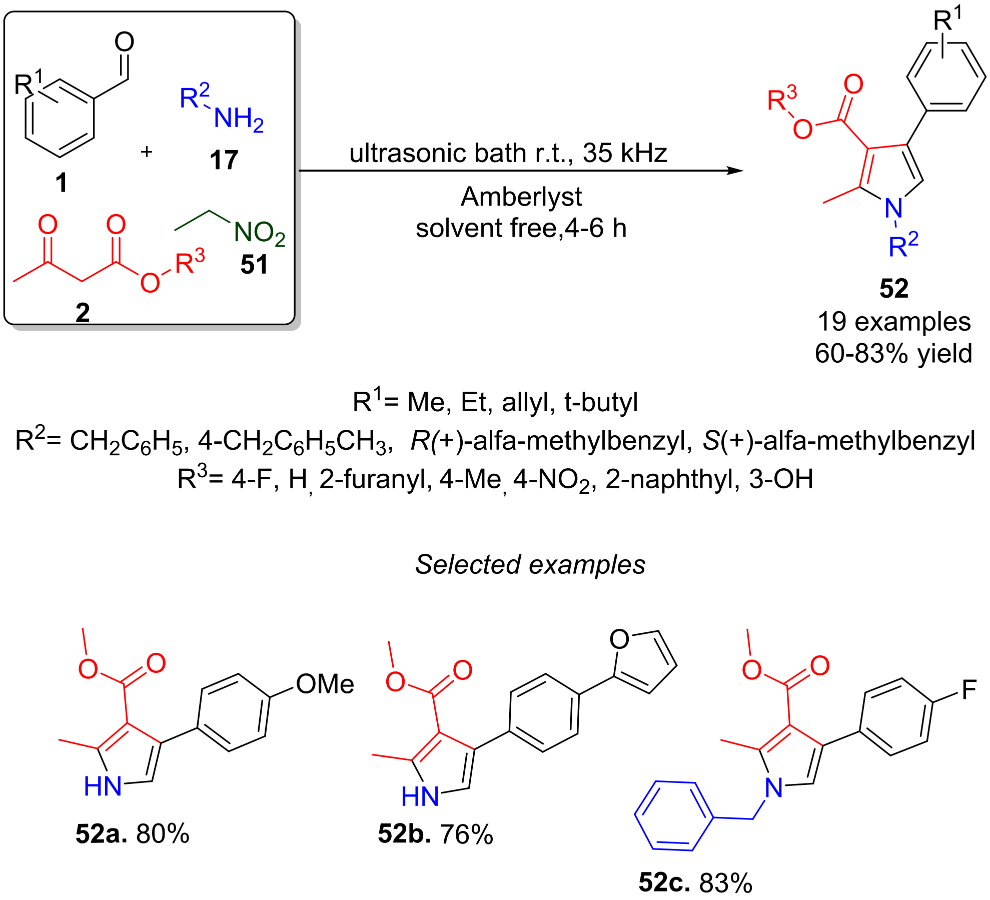
2.1.9. *Imidazoles*

Imidazoles have always occupied a prominent position in heterocyclic chemistry due to their versatile properties in synthesis and pharmacology, with several biological activities related to this nucleus, such as antibacterial [146] and antiepileptic [147]. Thus, in the context of heterogeneous catalysis, ultrasound-mediated MCR methods were developed for more environmentally friendly synthesis of imidazole derivatives **36** (Scheme 14) and **37** (Scheme 15), by condensation of diphenylethanedione (**35**), aldehydes (**1**) and aniline (**17**) or ammonium acetate, in the presence of green solvents. Safari et al. [148] have explored $MgAl_2O_4$/NPs as an efficient heterogenous catalyst in the straightforward and environmentally benign synthesis of these nuclei, by using EtOH as solvent (Tabe 7, Entry 1). In order to compare with conventional methods, the reaction was performed in the presence of ultrasonic irradiation (ultrasonic bath at 60 °C, frequency of 50 kHz and power of 200 W) and reflux, under the same conditions. In all cases, the use of ultrasonic waves made it possible to obtain the product of interest in high yields and shorter reaction times. Small amount of catalyst needed (only 0.035 mol%), mild conditions, simplicity of operation and easy work-up are some additional advantages of this protocol. The authors do not comment on the recycling and reuse of the nanocomposite.

By using the same catalyst previously discussed in the sections 2.1.1 and 2.1.2, Doustkhah et al. (Table 7, Entry 2) [121] also prepared a series of substituted imidazoles, with satisfactory yields.

In order to promote an efficient, eco-friendly synthesis of imidazoles, Safa and co-workers [149] developed a method using silicoaluminophosphate (SAPO-n) zeolites, via multicomponent reactions. They synthesized 16 examples of 1,2,4,5-tetraaryl imidazoles catalyzed by Cu/SAPO-34 nanocatalyst (5 wt%) in water under ultrasonic irradiation at room temperature at 20% of the processor power (ultrasonic processor probe device: ultrasonic homogenizers) (Table 7, Entry 3).

The Hajizadeh group [150] has explored the interesting catalytic



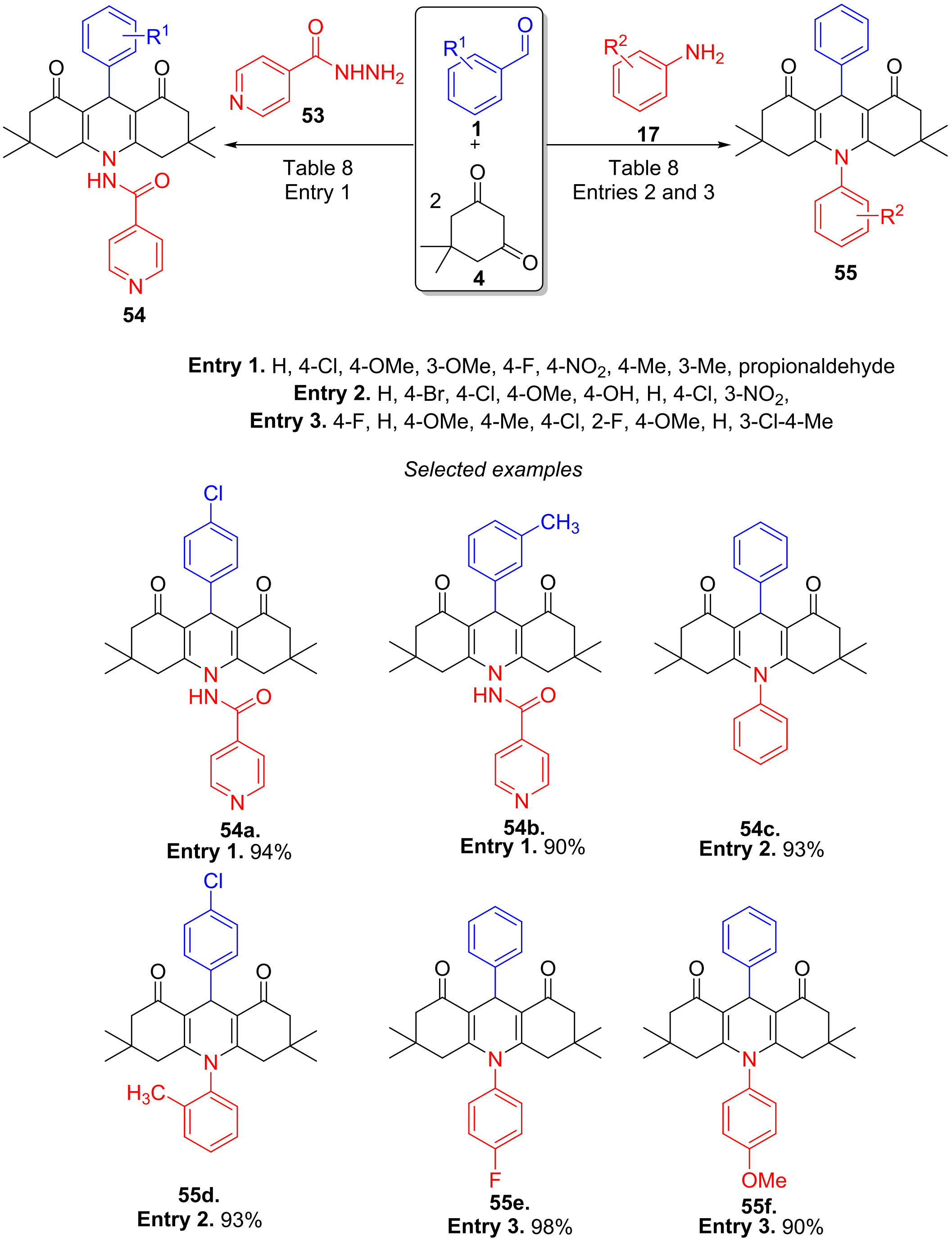
Scheme 20. Sonicated and solvent-free Amberlyst-15 catalyzed synthesis of substituted pyrroles (**52**).

properties of $NiFe_2O_4$ ferromagnetic nanoparticles (FMNPs). In this scenario, they have synthesized a modern green nanocatalyst composed of $NiFe_2O_4$/FMNPs incorporated in a based bentonite geopolymer support and applied it to the synthesis of imidazoles in the presence of EtOH (Scheme 15). The possible catalytic activity of bentonite, geopolymer and $NiFe_2O_4$/FMNPs were investigated separately, and the results showed that bentonite did not show any catalytic activity, whereas the geopolymer was moderately active. In turn, the hybrid nanocomposite $NiFe_2O_4$/FMNPs geopolymer (6.8 w/w %) showed an activity 3.25 times greater than that of the isolated geopolymer, under the same reaction conditions. The researchers proposed the occurrence of a synergistic effect between the hydroxyl groups present in the geopolymer structure and the $NiFe_2O_4$/FMNPs as an explanation for the effectiveness of this catalytic system. After a simple process of magnetic separation, washing with EtOH and drying, the nanocomposite was reused without noticeable reduction in catalytic activity in a cycle of eight reactions.

2.1.10. 1,2,3-Triazoles

The 1,2,3-triazoles and related compounds are of exceptional importance in organic synthesis, as they are part of the route to obtain many therapeutic agents. Derivatives of this nucleus are also biologically active, having exhibited anticancer [151] and antidiabetic [152] properties, for example. Traditional methods for obtaining these structures involve an “click” reaction of 1,3-dipolar cycloaddition of azide-alkene catalyzed by Cu(I)(CuAAC) [153]; however, protocols more aligned with the principles of green chemistry have recently been developed to obtain these structures, by using ultrasonic irradiation and heterogeneous catalysis (Scheme 16). These one-pot approaches were established by condensation of halides (**38**) or alkynes, propargilic alcohols (**39**) or tris(organosilyl)methyllithium compounds (**41**), sodium azide in presence of green solvents. For example, Safa and Mousazadeh [154] have synthesize a series of 1,2,3-triazole derivatives (**40** and **42**) by using Cu-Co modified zeolite ZSM-5 (5 w/w %) as effective, reusable and inexpensive catalyst in presence of water (Scheme 16). Among others, the advantage of this synthetic approach is the bimetallic nanocatalyst, that showed better properties and efficiency than those of traditional Cu catalysts for these transformations. The reaction model to optimization of this method was investigated under conditions of heating and ultrasonic irradiation in the presence of Cu-Co/ZSM-5. The corresponding products under ultrasound irradiation were obtained in short reaction times and good yields. When performed with sonication and in the presence of only pure HZMS-5, the model reaction did not occur even in a time interval twenty-four times longer than that sonicated and in the presence of Cu–Co ZSM-5. The reactions were carried out using an ultrasonic processor probe (12-mm-tip-diameter) operating a frequency of 70 kHz and at 20 % power of the processor and room temperature. The green nanocatalyst Cu-Co/ZSM-5 can be recovered by simple filtration and reused even after eighth times without significant loss of catalytic activity.

In the field of heterogeneous catalysis, carbon-based supports are on the rise. In this particular, graphene oxides (GOs) are specially interesting, due to the presence of hydrophilic functional groups such as carbonyl, carboxyl, epoxide and hydroxyl on their surface, easily modifiable, which assist in the immobilization of active species, responsible for the catalytic activity [103,105,106]. Keeping these properties in mind, Naeimi et al. [89,110] developed highly, efficient, and reusable green heterogeneous catalysts. In one of the works [110], they have used a Cu(I) functionalized (GO) [(GO@PTA-Cu(I)] (Scheme 17) in the successful synthesis of 1,2,3-triazole derivatives in presence of H_2O. This MCR protocol provided the desired products in high yields and short reaction times, with the amount of nanocomposite of only 0.017 mol%. No product was observed in the absence of the catalyst or



Scheme 21. Protocol for synthetic *N*-substituted 1,8-dioxo-decahydroacridines (**54** and **55**) catalyzed by *β*-CD or [$CoFe_2O_4$/OCMC/Cu(BDC)], under ultrasound irradiation.

sonication. Ultrasonication was carried out by device equipped with probe, diameter of 6 mm, 20 kHz of frequency and 45 W of power at room temperature. The effect of the frequency of ultrasonic irradiation on the model reaction was also investigated, and the best results were obtained when it was performed in the presence of GO@PTA-Cu (I) and ultrasonic irradiation at a power of 45 W. The recycled catalyst could be reused five times with no loss of catalytic activity.

In another publication [89], the authors have reported an one-pot procedure for the preparation of 1,2,3-triazoles (**40** and **45**) by using a synthetic nanocomposite of Cu(I) nanoparticles incorporated in an amino-functionalized graphene oxide matrix [Cu(I) GO-NH-IA] as catalyst and EtOH/H_2O as solvent (Scheme 17). To investigate the effects of ultrasonic irradiation and to compare heating with ultrasound-assisted method, the model reaction was carried out without sonication at 80 °C, for 90 min, and the desired product was obtained with low yield; when carried out at room temperature, for 120 min, no product formation was observed. However, in the presence of both [GO-NHIA-Cu (I)] (0.1 w/w %) and ultrasonic irradiation (70 W), the product of interest was obtained with excellent yield. The recyclability of this catalyst system was possible up to six runs without any loss of its catalytic activity.

2.1.11. 1,2,3,4-Tetrazoles

The tetrazole core has a wide spectrum of applications, ranging from

Table 8
Sonicated synthesis of acridine derivatives (**54** and **55**) mediated by heterogeneous catalysis.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	*β*- CD	H_2O, 61–90 min, 80 °C	9	56–94	[165]
2	*β*- CD	H_2O, 61–81 min, 80 °C	11	72–93	[165]
3	[$CoFe_2O_4$/OCMC/ Cu(BDC)]	EtOH, 10–13 min, r.t.	12	90–98	[134]

*Ultrasonication parameters: Entries 1 and 2. Ultrasonication by ultrasonic bath, at 80 °C; frequency: 35 kHz; power: 200 W. Entry 3. Ultrasound bath, frequency: 30 KHz, no more details were informed.

coordination chemistry [155,156] to propellant components of rockets based on their energetic properties [157]. The Habibi group [158] haa successfully synthesized a library of tetrazole derivatives (**47**) using $FeCl_3/SiO_2$ (3 w/w%) as a reusable, low-cost catalyst, under ultrasound or conventional methods, in a solvent-free media via MCR condensation of aryl amines (**17**), sodium azide and triethylorthoformate (**46**) (Scheme 18). In comparison with the use of reflux, the sonicated model reaction led to higher yields in shorter reaction times. Ultrasonication was performed in ultrasound bath with a frequency of 28 kHz and an output power of 50 W. The catalyst could be recovered by simple filtration and showed maintenance of catalytic activities in a cycle of three reactions.

2.1.12. *Dihydroquinoxalines*

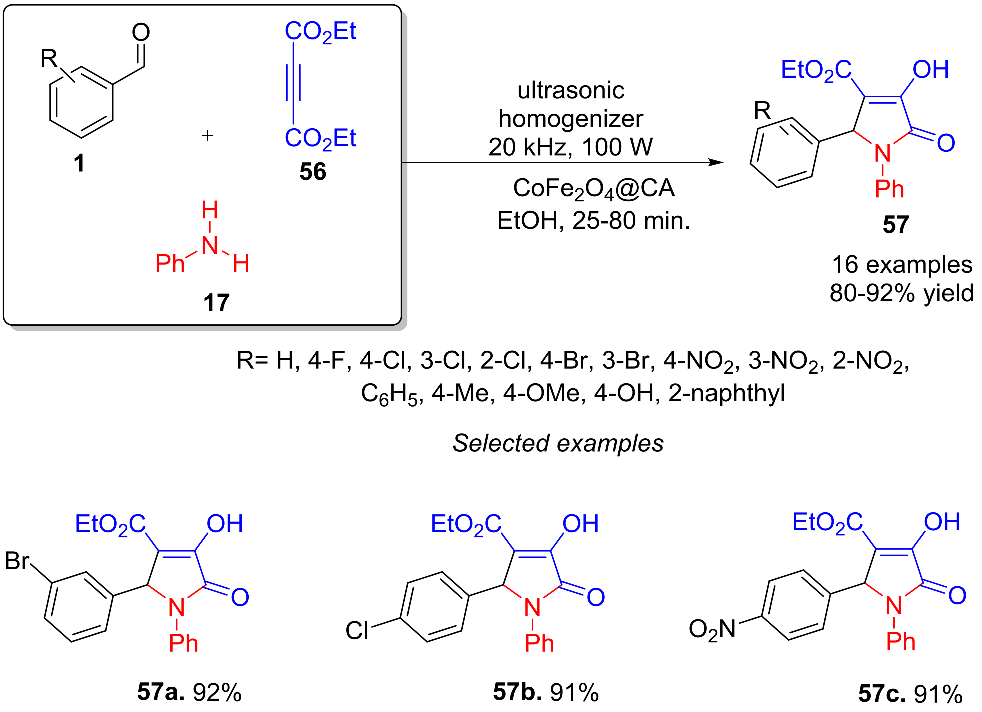
As already reported in several works cited throughout this review, magnetic nanoparticles assumed a prominent role in the scenario of heterogeneous catalysis. In this context, Ghasemzadeh et al. [159] have developed a greener ultrasound-assisted method to synthesize a series of dihydroquinoxalines (**50**) via a three-component reaction of *o*-penylenediamines (**48**), ketones (**8**) and isocyanides (**49**) in the presence of EtOH, using a magnetic Co_3O_4 nanocatalyst embedded in silica ($Co_3O_4@SiO_2$, 5 mol%) (Scheme 19). The reactions were sonicated at 40 kHz frequency and 80 W power at room temperature. The model reaction for optimization was tested in the presence of several catalysts, such as ZnO, CuI, MgO, Fe_3O_4, *p*-TSA, AgI, Mn_3O_4, SiO_2. The results showed that the compound of interest was obtained with high yield in the short reaction time only in the presence of $Co_3O_4@SiO_2$, whereas in the absence of a catalyst, traces of the desired product were obtained. In terms of recyclability, the nanocomposite remained active in a six-reaction cycle, with no noticeable loss in catalytic efficiency.

2.1.13. *Pyrroles*

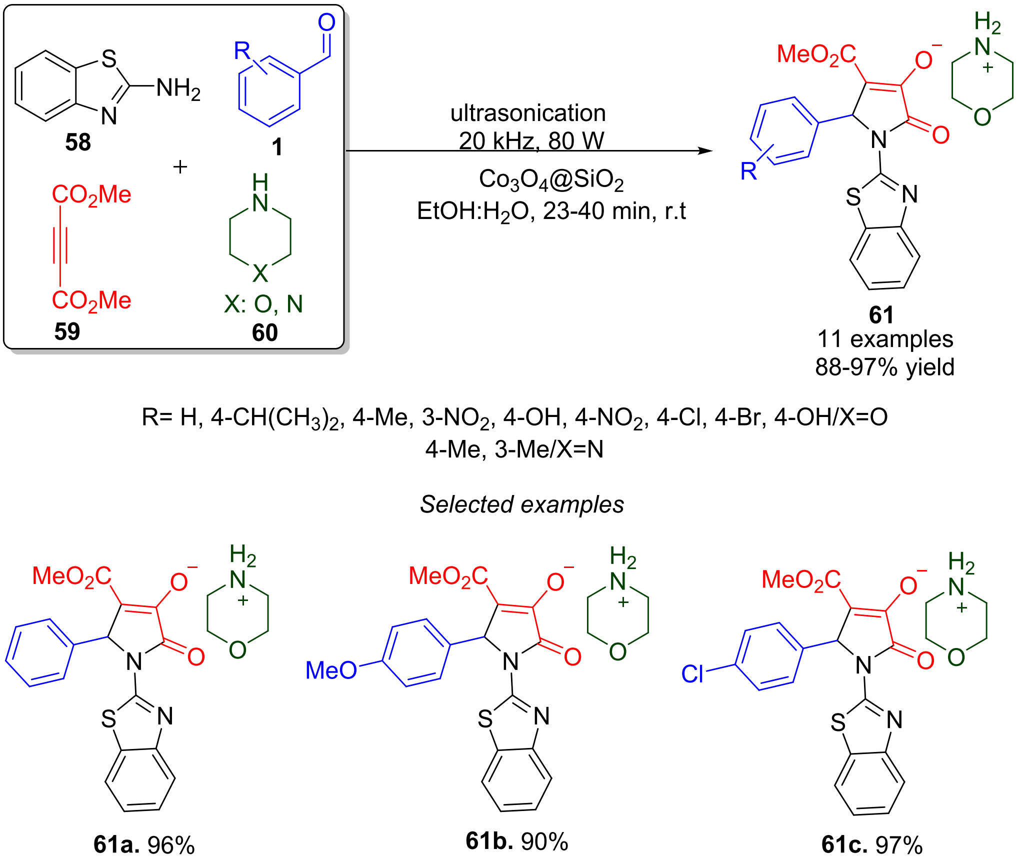
The pyrrole nucleus can be found in many natural products, including complex macromolecules, such as porphyrins, heme, chlorophyll, chlorines, etc., that present important biological activities [160]. The Murthi group [161] has developed a simple procedure for the synthesis of these important heterocycles via four-component reaction mediated by Amberlyst-1 as catalyst under ultrasound, by condensation of aromatic aldehydes (**1**), *β*-ketoesthers (**2**), primary amines (**17**) and nitromethane (**51**), which acted as reactant as well as solvent (Scheme 20). Due to the presence of acid and sulfonated groups on its surface, the resinous material Amberlyst 15 has been used successfully in heterogeneous catalysis to promote organic transformations [162-164]. The reaction was performed in an ultrasonic bath using irradiation of 35 kHz at room temperature. When the model optimization reaction was carried out in the absence of a catalyst, there was no formation of the expected product. On the other hand, under the same conditions, but now in the presence of Amberlyst 15 (10 % mol), the desired product was obtained with good yields. When performed with conventional heating, this reaction took six times longer to complete, compared to the one in which the ultrasound was used. In terms of recovery, Amberlyst could be easily recovered by simple filtration, proving fit for reuse in a cycle of three reactions without considerable losses in catalytic activity.

2.1.14. *Acridines*

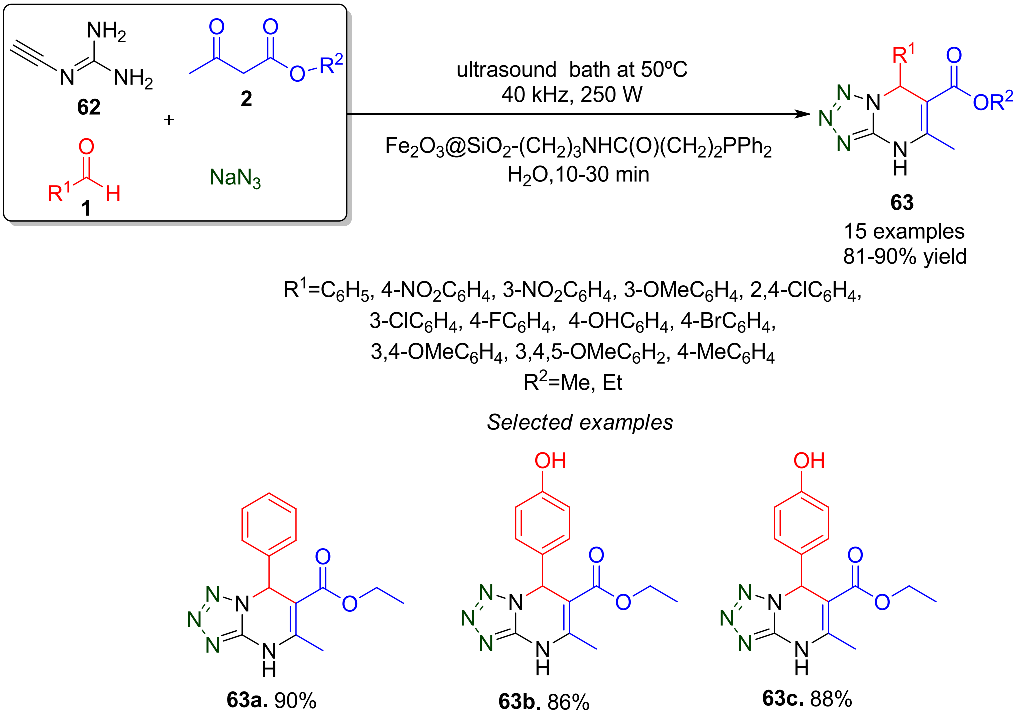
The 1,8-dioxo-decahydroacridine derivatives (**54** and **55**) were synthesized via MCR by the Chate group [165], via condensation using dimedone (**4**), aldehydes (**1**), aniline derivatives (**17**) or isoniazid (**53**) as starting materials (Scheme 21). They used the oligomer



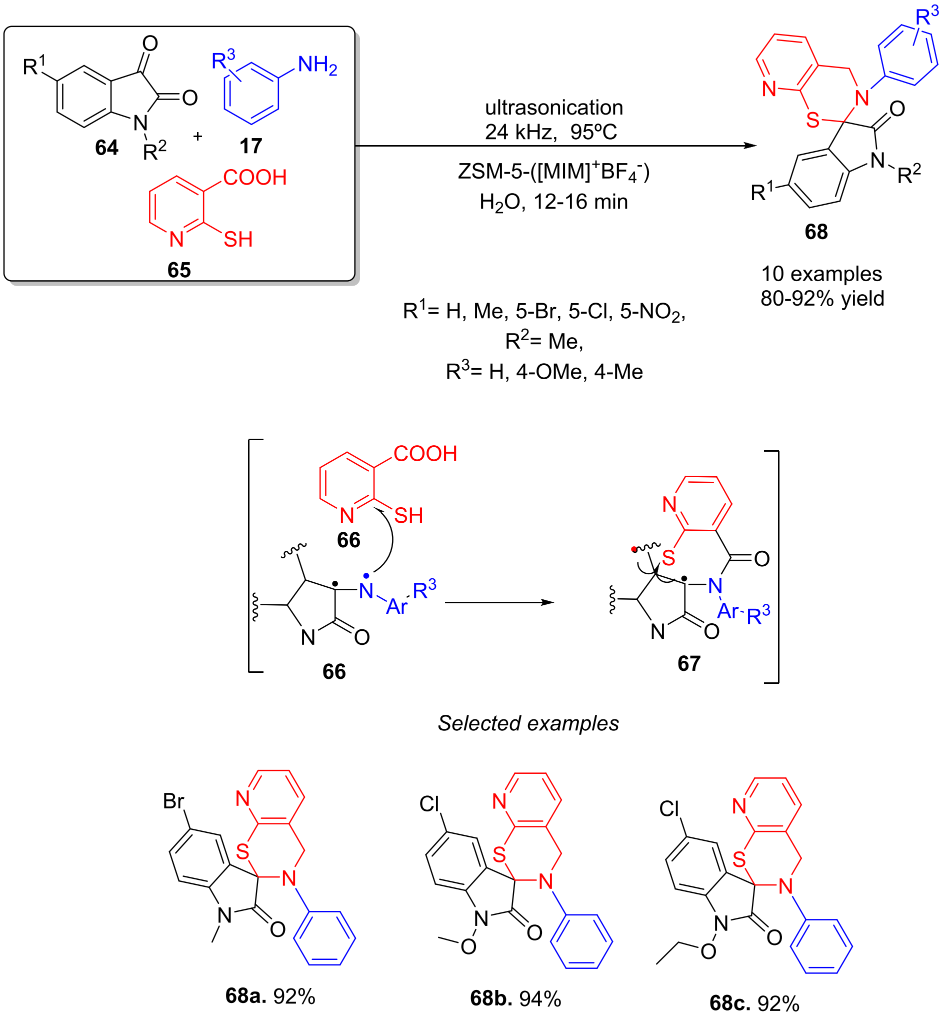
Scheme 22. Ultrasound-mediated 3-pyrrolin-2-ones (**57**) synthesis catalyzed by functionalized cobalt ferrite nanoparticles.



Scheme 23. Sonochemical preparation of 2-pyrrolidinones (**61**) mediated by $Co_3O_4@SiO_2$ nanocatalysis.



Scheme 24. Core-shell Fe_2O_3/MNPs hybrid nanocatalyst in the synthesis of tetrahydropyranquinolines (**63**) under ultrasonic irradiation.



68a. 92%
68b. 94%
68c. 92%

Scheme 25. Modified ZSM-5 zeolites as nanocatalyst in sonochemical preparation of spiro-oxindoles (**68**) in aqueous media.

β-cyclodextrin (β-CD) as catalyst (10 mol%) at 80 °C and water as a solvent. In the route with the use of isoniazid (Table 8, Entry 1), 9 derivatives were obtained with yields greater than 56%. In the reaction with the adoption of aniline derivatives (Table 8, Entry 2), it was possible to obtain 11 examples with yields ranging from 72 to 93% with a reaction period between 61 and 81 min. The reaction was performed in ultrasonic bath at 80 °C with a frequency of 35 kHz and a nominal power 200 W. In this protocol, α- and γ-cyclodextrins were also investigated, however, the β- proved to be more effective in obtaining the 1,8-dioxo-decahydroacridine derivatives. The catalyst had its reuse investigated and remained active in up to 3 cycles.

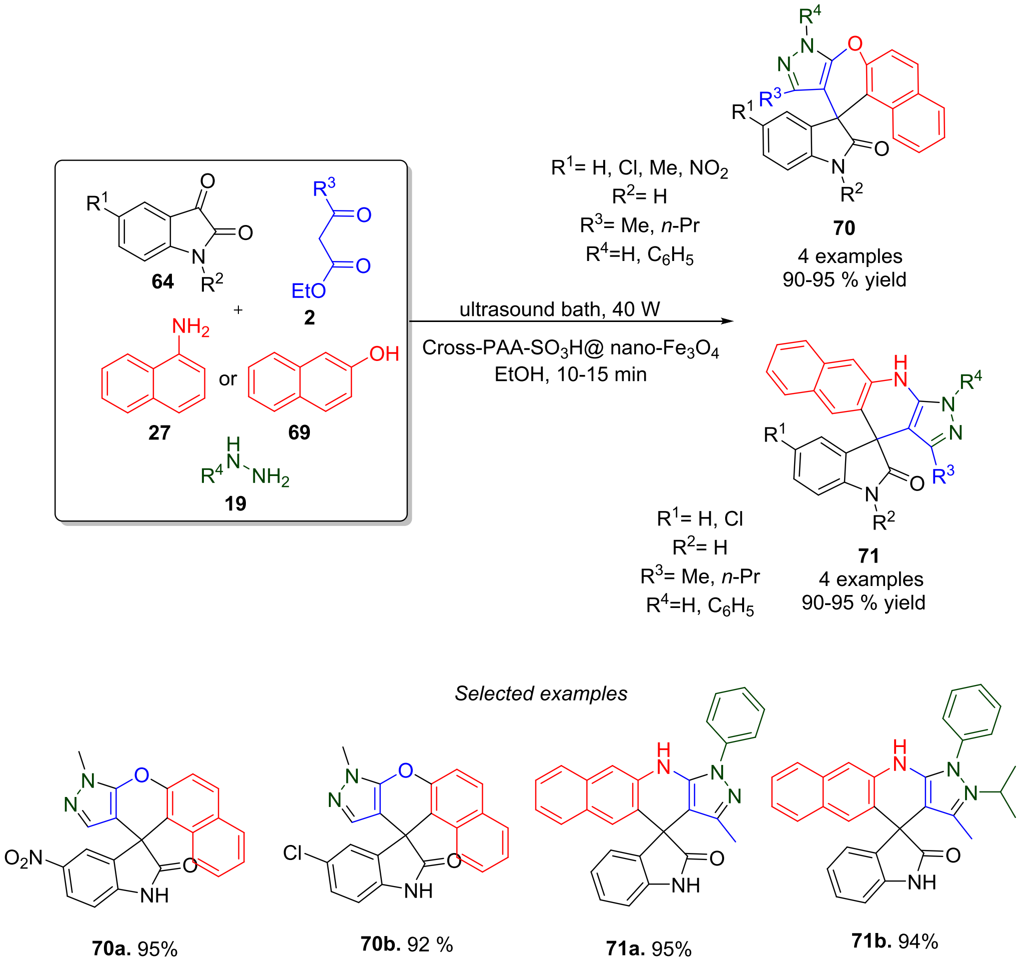
In the same methodology already mentioned in the section 2.1.2, Ghasemzadeh and co-workers (Scheme 22) [134] have synthesized a series of acridine derivatives, with yields above 90% (Table 8, Entry 3).

2.1.15. 3-Pyrrolin-2-ones

The Ahankar group [166] studied the synthesis of 3-pyrrolin-2-one-derivatives (**57**) via MCR using aniline (**17**), diethyl acetylenedicarboxylate (**56**) and aldehydes (**1**) as starting materials, mediated by ultrasound irradiation, and catalyzed by cobalt ferrite nanoparticles functionalized by citric acid ($CoFeO_4$@CA) (Scheme 22). The reaction was performed in an ultrasonic homogenizer at room temperature, frequency of 20 kHz and power of 100 W. The influence of ultrasound in this protocol was investigated, and the absence of ultrasound irradiation allowed the obtaining of the compounds of interest in 720 min with yields varying between 78 and 90%, in contrast with the use of ultrasound, the time of the reaction decreased significantly to 25–80 min. The method with the use of ultrasound irradiation in conjunction with $CoFeO_4$@CA (2.1 w/w %) allowed to obtain 16 examples of 3-pyrrolin-2-ones with yields between 80 and 92% (it was found that aromatic aldehydes with electron withdrawal groups reacted faster). The catalyst was separated by a magnet, dried after being washed with ethanol and acetone, and reused in up to five cycles without losing its activity.

2.1.16. 2-Pyrrolidinon-3-olates

Compounds with 2-pyrrolidinone core are interesting from a biological point of view, as is the case with some natural products [166] and also synthetic derivatives, which present antidepressant [167] and anticonvulsant [168] properties. Ghasemzadeh et al. [169] have developed an ultrasound-assisted one-pot protocol for obtaining these important structures by the condensation of 2-aminobenzothiazole (**58**), aromatic aldehydes (**1**), dimethyl acetylenedicarboxylate (**56**) and morpholine/piperidine (**60**) using a reusable and highly efficient nanocatalyst already mentioned in this review, the core–shell nanostructure Co_3O_4@SiO_2 (0.05 w/w %) in EtOH/H_2O media (Scheme 23). The reactions were carried out in a multi-wave ultrasonic generator, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with power of 80 W at room temperature. In the reaction optimization, a comparative study of the activity of Co_3O_4@SiO_2 was performed using six other catalysts, and ultrasonic irradiation (40 kHz and 80 W) under the same conditions. The



Scheme 26. Fe_3O_4/MNPs immobilized on modified polyacrilamide as heterogenous nanocatalyst for the ultrasound-mediated one-pot synthesis of spiro-indoles (**70** and **71**).

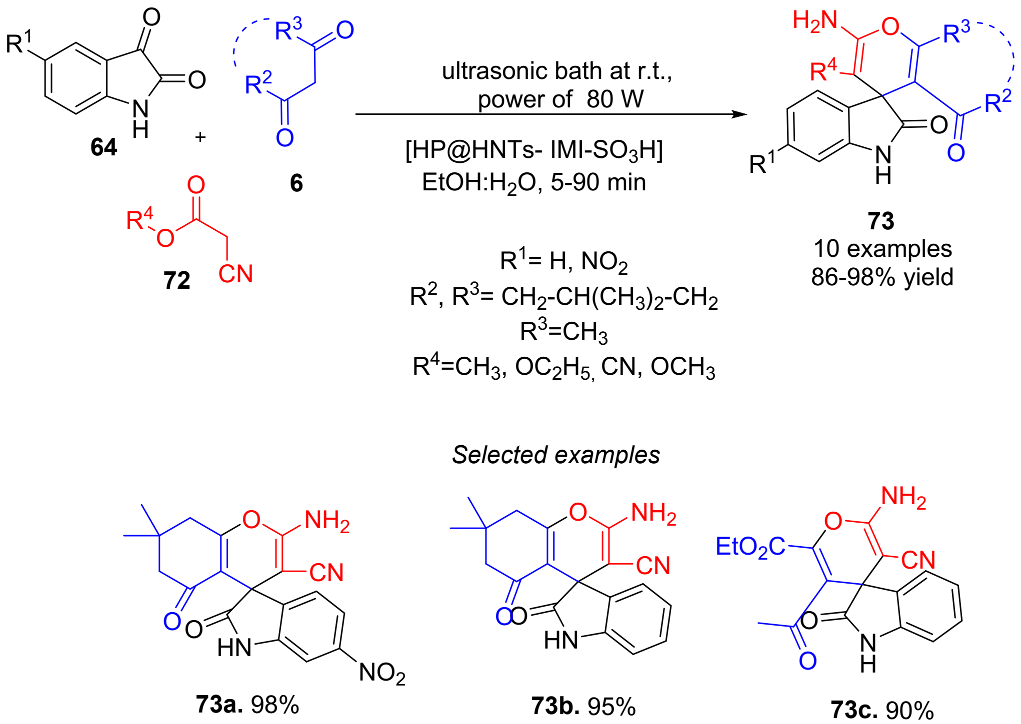
results showed that the expected product was obtained with high yields only in the experiment in which the use of nanocomposites was in conjunction with ultrasound. In the absence of catalysts, the product was formed only in trace amounts. Once the ideal condition was found, the reaction was also carried out by conventional heating, and the desired product was obtained with a yield about 25% lower, in a reaction time seventy-two times longer, in comparison with the sonicated reaction. The nanostructure $Co_3O_4@SiO_2$ was recycled via magnetic separation, followed by washing and drying, and remained active in a cycle of six reactions, without significant loss in catalytic activity.

2.1.17. Tetrazolopyrimidines

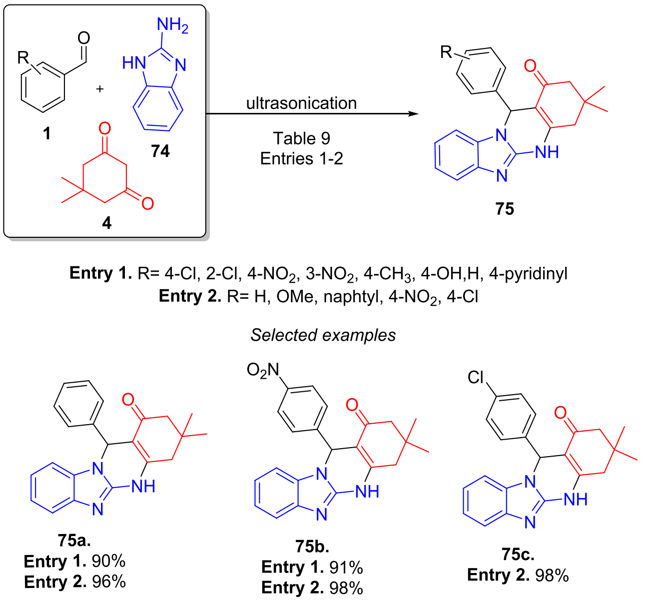
In connection with the interest in designing and developing more efficient, modern and ecological catalytic systems, the Maleki group [170] has synthesized a new organic–inorganic hybrid catalyst core shell, $[Fe_2O_3@SiO_2\text{-}(CH_2)_3NHC(O)(CH_2)_2PPh_2]$ for the sonochemical synthesis of tretrazolepyrimidine derivatives (**63**) via a four-component reaction of aldehyde (**1**), ethyl acetoacetate (**2**), 2-cyanoguanidine (**62**) and sodium azide in aqueous medium (Scheme 24). The reaction was studied in the presence of several catalysts, all in the same condition, using an ultrasound cleaning bath at 50 °C with a frequency of 40 kHz and power of 250 W. The best results were obtained for the reaction performed in the presence of the hybrid nanocomposite $[Fe_2O_3@SiO_2\text{-}(CH_2)_3NHC(O)(CH_2)_2PPh_2]$ (5 mol%). In the absence of catalysts, only traces of the product were observed in a much longer reaction time. On the other hand, when performed without sonication, keeping the other conditions unchanged, the reaction led to modest yields. The authors observed the occurrence of a synergism between ultrasound and nanocatalysis resulting in the success of this methodology. The catalyst was recovered quantitatively by simple magnetic separation and reused in subsequent reactions at least six times, with no noticeable loss of catalytic efficiency.

2.1.18. Spiro-oxindoles

Due to their unique structure, spiro-oxindoles have played a prominent role in the search for new anticancer agents [171], thus, it is highly desirable the advent of more environmentally friendly synthetic methodologies for obtaining these intriguing compounds. In this scenario, successful MCR protocols assisted by ultrasound and heterogeneous catalysis have been recently reported to obtain spiro-oxindoles in ethanolic or aqueous media. Arya and co-workers [172], for example, developed the catalyst ZSM-5-(IL), based on zeolite-supported Brønsted-acid ionic liquid, and applied it (0.3 mol%) in the preparation of *N*-substituted spiro[indole-pyrido[3,2-*e*]-thiazine (**68**) in water, by the condensation of isatins (**64**), aromatic amines (**17**) and 2-mercaptonicotinic acid (**65**) (Scheme 25). The reaction was performed in an ultrasonic processor equipped with a 3 × 140 mm probe that was immersed directly into the reaction mixture, operating at frequency of 24 kHz and the output power was 0–750 W through manual adjustment. The reaction was carried out at 95 °C. To compare the effect of ultrasound irradiation, the authors performed the reaction also under microwave irradiation and conventional heating, at the same conditions and verified that the reaction under sonication conditions was more efficient. They also point out that the efficiency and the yield of the reaction was



Scheme 27. MCR promoted by ultrasound for the synthesis of spiro-indoles (**73**) using HP@HNTs-IMI-SO_3H as nanocatalyst.



Scheme 28. Synthesis of benzimidazoloquinazolines (**75**).

higher for a shorter chain length ionic liquid cation ($[MIM]^+BF_4^-$) than those obtained in other ionic liquids with larger chain lengths. From a mechanistic point of view, the crucial step involves a radical route, where the intermediary **66**, generated *in situ* by reaction of the substituted isatin (**64**) and aromatic amines (**17**) under ultrasonication, reacts with 2-mercaptonicotinic acid (**65**) to give the diradical intermediate **67**, from which the product of interest is formed. It was found that the reaction rate in the presence of the radical scavenger *p*-benzoquinone decreased significantly, which supports the hypothesis of the radical mechanism. The catalyst ZSM-5-(IL) showed recyclability of up to five cycles without loss of catalytic activity.

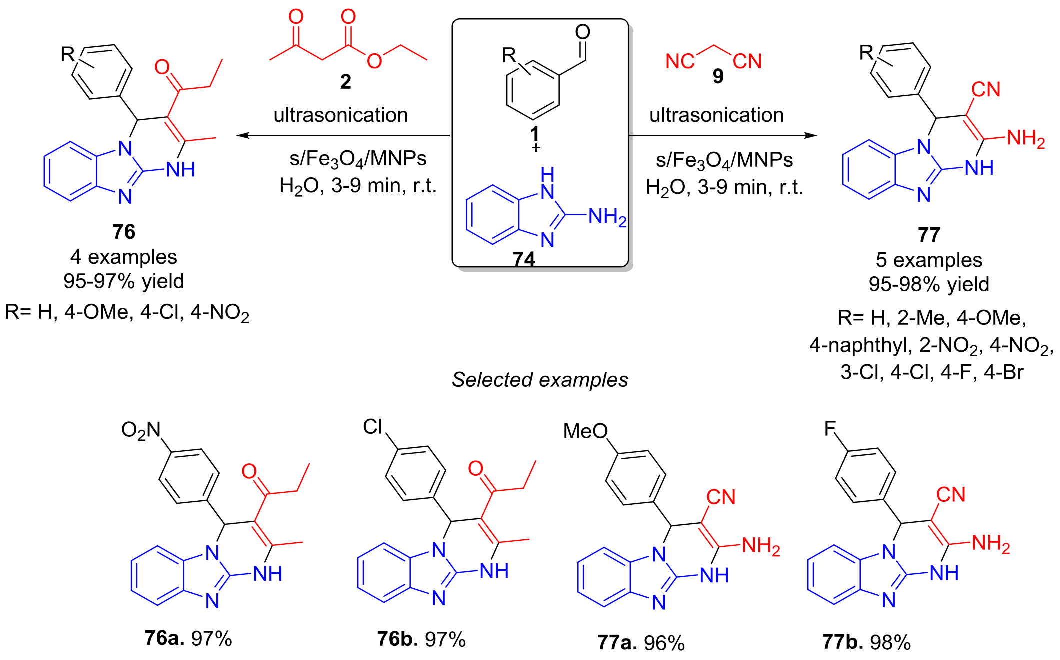
Table 9
Sonochemical preparation of benzimidazoloquinazolines (**75**) mediated by heterogeneous catalysis.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	MCGC	EtOH, 10–66 min, 40–42 °C	8	84–91	[119]
2	s/Fe_3O4/ MNPs	H_2O, 3–9 min, r.t.	5	95–98	[177]

*Ultrasonication parameters: Entry 1. Ultrasound bath at temperature of 30°-32 °C; frequency: 25 kHz, further details were not provided. Entry 2. Details were not informed.

In another method related to the same context, Shahbazi-Alavi et al. [173] have designed and synthesized a new heterogeneous nanocatalyst composed by Fe_3O_4/MNPs incorporated in cross-linked sulfonated polyacrylamide [Cross-PAA-SO_3H@ nano-Fe_3O_4] and successfully applied it to the synthesis of spiro-oxindoles (**70** and **71**) using isatins (**64**), ketoesters (**2**), naphthylamine (**27**) or 2-naphthol (**69**) and hydrazines (**19**) in the presence of EtOH (Scheme 26). This type of highly efficient and reusable nanocomposite, combines the aforementioned properties of MNPs with the characteristics of sulfonated polyacrylamides, such as high strength, hydrophilicity and proton conductivity [174]. In the optimization study, the reaction was carried out by sonication and in parallel using conventional heating methods, under the same conditions, in addition to various types of catalysts. In all cases, the sonicated reaction, with a power of 40 W, and catalyzed by [Cross-PAA-SO_3H@nano-Fe_3O_4] (0.06 w/w %) provided high yields in shorter times. The nanocatalyst could be easily separated using an external magnet and, after simple washing and drying, it could be reused in five reuse cycles, with maintenance of catalytic efficiency.

In the search for more environmentally benign synthetic protocols, Sadjadi and co-workers [175] have discovered a new and efficient hybrid nanocatalyst, combining (HPA), ionic liquid and halosite nanoclay (HNTs), [HP@HNTs-IMI-SO_3H], to promote the preparation, mediated by ultrasound, of spirooxindole derivatives (**73**) using isatins



Scheme 29. Preparation of benzimidazoles (**76** and **77**) in presence of ultrasonic waves and Fe_3O_4/MNPs/starch hybrid catalytic system.

(**64**), malononitrile (**9**) or cyanoacetic esters (**72**) and 1,3-dicarbonyl compounds (**2** or **6**), and a mixture of EtOH:H_2O as solvent at room temperature (Scheme 27). The apparatus applied was an ultrasonic bath at room temperature with power of 80 W, and further details were not informed. Initially, the sonicated reaction was carried out in the absence of the catalyst, and it was found that it proceeded very slowly and only traces of the desired product were obtained, confirming the need of the catalyst, whose adequate amount under the optimum conditions was 0.25 w/w %. The authors investigated the influence of ultrasound power, noting that the yield of the product was markedly dependent on it, since the increase of the power of ultrasonic irradiation to 80 W dramatically enhanced the yield of the product. Comparison of the results using this method with those of other already published in literature for the synthesis of spirooxindoles, attest the superiority of this protocol, in terms of reaction time and yields. Upon completion of the reaction, the nanocatalyst was simply filtered, washed, and dried, however could be reuse only on three reaction cycles, with a slight loss of catalytic activity.

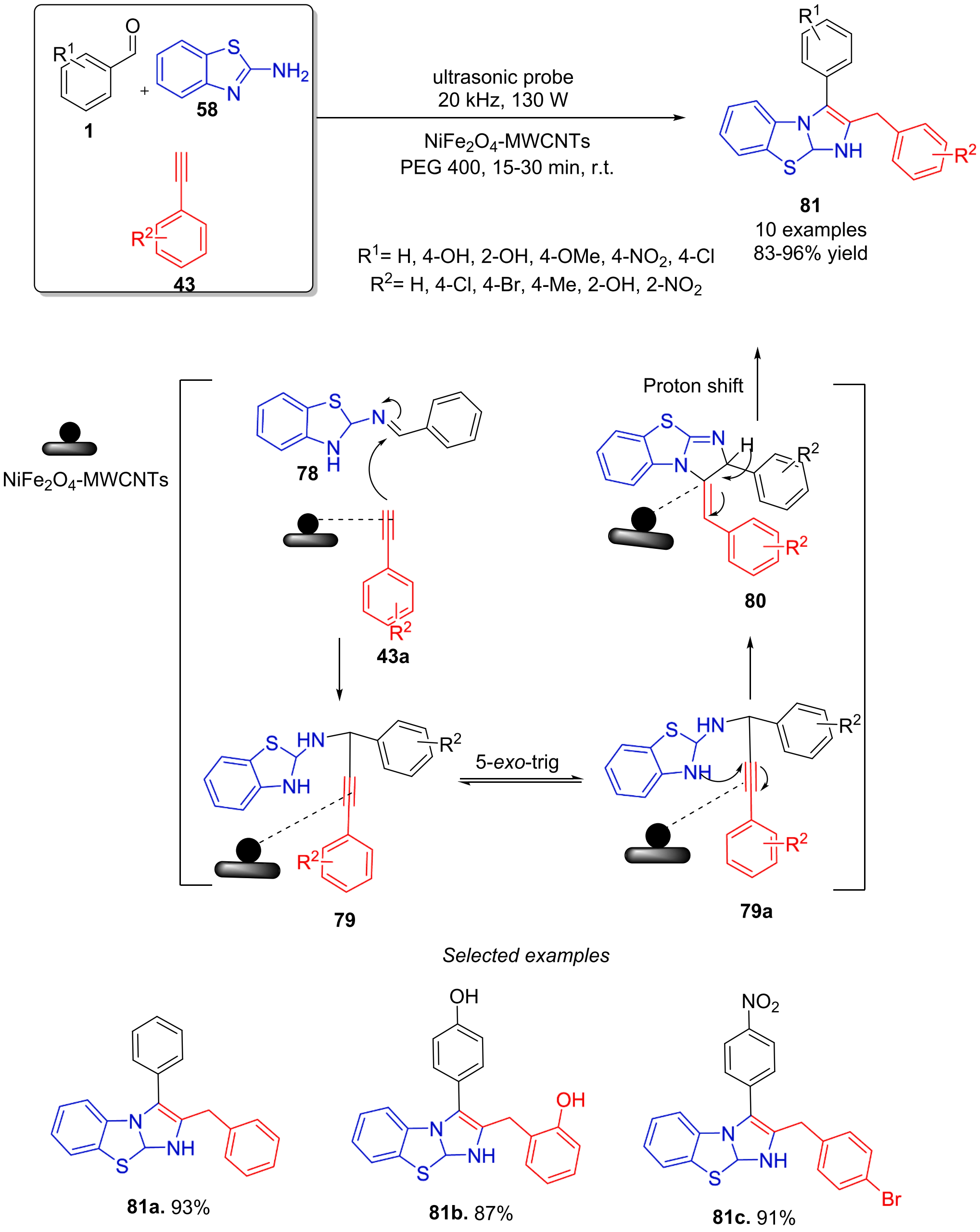
2.1.19. *Benzimidazoles*

The benzimidazoles are *N*-heterocycles with a wide spectrum of biological activities, such as anti-inflammatory and antitumor [176]. In the same work reported in section 2.1.1, Javanmiri et al. [119] synthesized a series of benzimidazoloquinazolines (**75**), with some modifications in the method, via MCR of 2-aminobenzimidazole (**76**), aldehydes (**1**) and dimedone (**4**) (Scheme 28 and Table 9, Entry 1). The efficiency of this protocol was compared with some of the methods previously reported in literature for the synthesis of benzimidazoloquinazolines, showing advantages in terms of the catalyst loading, solvent, temperature, in addition to reaction time and yield.

It has recently been demonstrated that polysaccharides can also function as agents for functionalization of MNPs, as reported by Verma et al. [177] in the development of a hybrid bionanocatalyst composed by F_3O_4/MNPs immobilized in starch (s-Fe_3O_4/MNPs) that was used in a green one-pot procedure for the synthesis of benzoimidazopyrimidine derivatives (**76** and **77**). The protocol, promoted by ultrasound, consists in the condensation of aromatic aldehydes (**1**), malononitrile (**9**) and 2-aminobenzimidazole (**74**), in water and at room temperature (Scheme 29, Table 9, Entry 2). The reaction was performed, in the same conditions, using reflux and ultrasonic irradiation to compare the effectiveness of this method, and when carried out under ultrasound, the reaction proceeded forty times faster and with a yield about 1.22 times higher. Small amount of the nanocatalyst (0.075 w/w %), easy isolation of products and chemoselectivity are differentials of this protocol. With regard to recycling, the nanocatalyst could be reused six times in a row without a significant loss on its catalytic activities.

2.1.20. *Benzo[d]imidazo[2,1-b]thiazoles*

In the search for greener catalytic systems, Geedkar and colleagues [178] proposed an efficient method for the synthesis of highly functionalized benzo[*d*]imidazo [1,2-b] thiazoles (**81**) using a nanocatalyst composed of multi-walled carbon nanotubes crowned with magnetic nickel ferrite nanoparticles ($NiFe_2O_4$-MWCNTs, 5 mol%), via condensation of arylaldehydes (**1**), phenylacetylene derivatives (**43**) and 2-aminobenzothiazole (**58**) in PEG 400 (Scheme 30). The reaction was carried out separately in the presence of $NiCl_2 \cdot 6H_2O$ and the nanocomposite $NiFe_2O_4$ MNPs, with formation of the product in reasonable quantities in both cases, although the yield was higher in the first case. In order to explore the role of ultrasonic irradiation, the reaction was also performed in the presence of $NiFe_2O_4$-CNTs under reflux. The reactions were performed using an ultrasonic processor with a maximum power of 130 W, operating at amplitude of 60% and frequency of 20 kHz. The results obtained showed that the reactions under ultrasonic irritation (70 KHz frequency) led to high yields in shorter reaction times. Concerning the mechanistic pathway, the authors proposed that the reaction starts with the nucleophilic attack of 2-aminobenzothiazole (**58**) to the aryl benzaldehyde (**1**), leading, after dehydration, to the Schiff's base (**78**). Parallel to this, coupling between the basic sites of the nanocomposite and the alkyne forms an acetylide complex **43a**, which attacks the Schiff's base to form the intermediate **79**, then undergoes a 5-*exo*-dig cyclization, leading to **80**, and finally furnishing the product of interest (**81**) after hydrogen shift. The reaction was evaluated using green chemistry metrics, such as atom economy, EcoScale score, and E-factor, which were in accordance with the sustainability of the process. After recovering the nanocomposite by magnetic separation, it could be used in a cycle of eight reactions without loss of loss in catalytic activity.



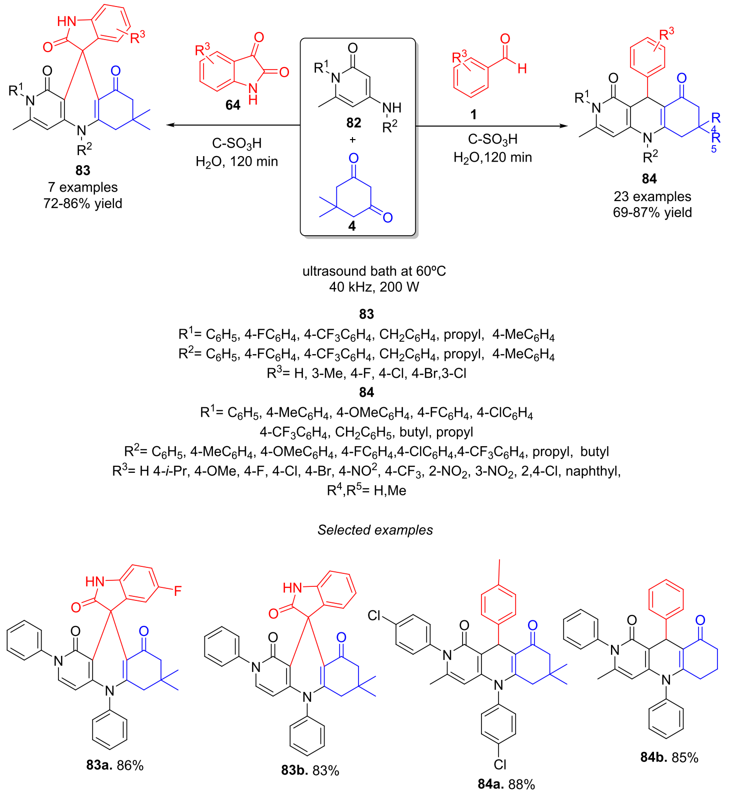
Scheme 30. $NiFe_2O_4$-MWCNTs nanocomposite in the synthesis of benzoimidazotiazoles (**81**) in presence of PEG-400 and ultrasonic irradiation.

2.1.21. 1,6-Naphthyridines

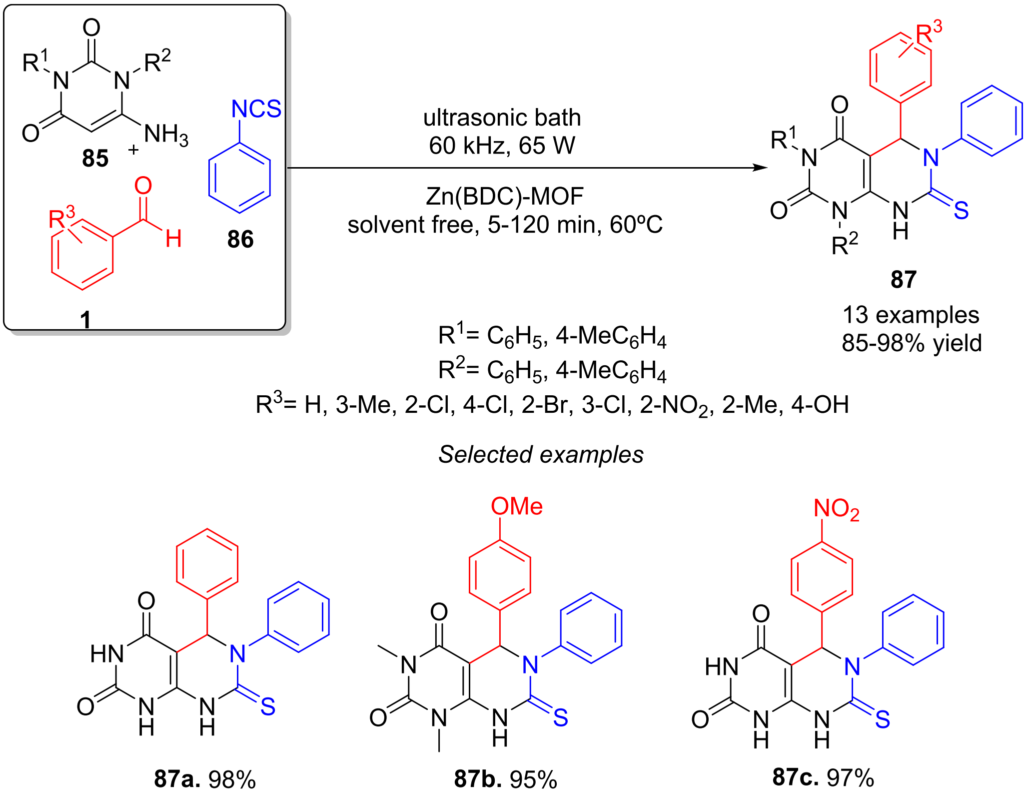
The 1,6-naphthyridine is a framework of great interest in medical chemistry, as present several biological properties, such as antitumor [179,180] and antiviral [181]. Solid acid carbonaceous materials (C-SO_3H) have emerged as heterogeneous catalysts of interest in greener organic synthesis, due to the fact that they combine acid catalytic properties with the possibility of more efficient recycling. In this perspective, Li et al. [182] have reported a viable protocol for the synthesis of 1,6-naphthyridine derivatives (**83** and **84**) using this type of material via one-pot condensation of 4-aminopyridinones (**82**), aromatic aldehyde (**1**) or isatin (**64**), and dimedone (**4**), in aqueous media (Scheme 31). The reaction was performed in an ultrasonic cleaner (40 kHz frequency, 200 W nominal power) at 60 °C and the temperature of the water bath was controlled at given temperature. When the reaction was performed in the absence of catalyst with sonication, or in the presence of the catalyst and absence of sonication, maintaining the other conditions, only traces of the product of interest were formed, in both cases. In this turn, combining the use of the C-SO_3H catalyst (0.28 w/w %) and ultrasound, the yields were satisfactory. The catalyst was recovered by filtration and washing and could be reused in a cycle of up to five reactions, with some loss of catalytic efficiency, due to contamination of active spits on its surface, according to the authors.

2.1.22. Pyrimido[4,5-d]pyrimidines

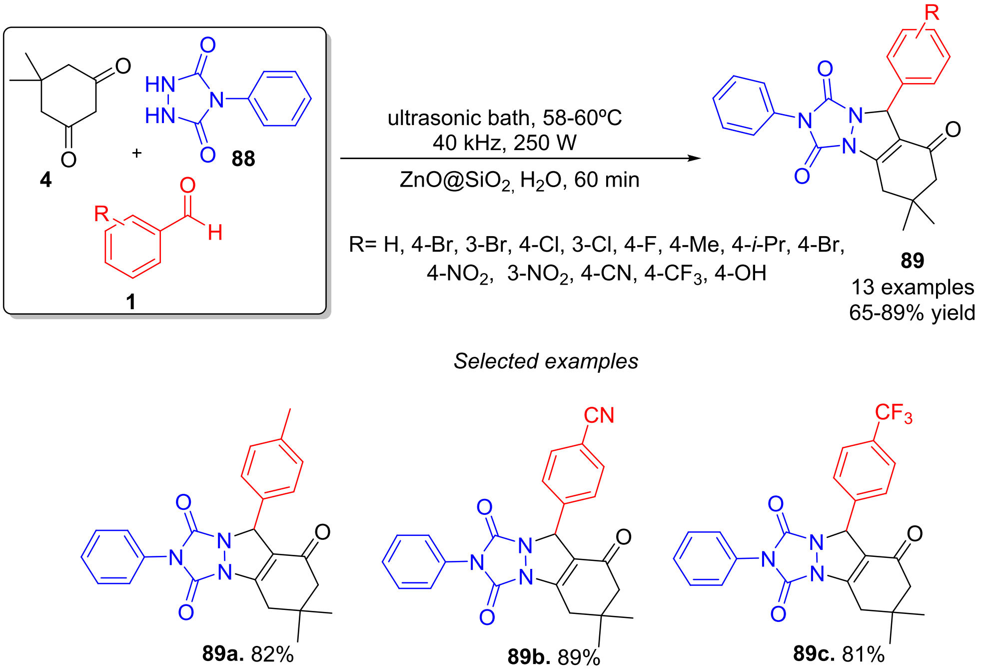
Metal-Organic Frameworks (MOFs) are a class of porous and polymeric materials, formed from the interaction between metallic ions or agglomerates and multitopic organic ligands [183]. They are compounds that have exceptionally high surface area, in addition to high thermal and chemical stability, being, for these reasons, quite interesting from the point of view of heterogeneous catalysis [184,185]. In this scenario, the Abdollahi-Basir group [186] has reported a synthetic approach mediated by ultrasound to obtain a series of pyrimid[4,5-*d*]



Scheme 31. Ultrasound-assisted MCR for the synthesis of 1,6-naphthyridine derivatives (**83** and **84**) by C-SO$_3$H catalysis.



Scheme 32. Sonochemical synthesis of pyrimid[4,5-*d*]pyrimidines (**87**) mediated by Zn/NPS/MOF hybrid nanocatalysist.



Scheme 33. MCR protocol to prepare triazolo[1,2-a]indazoletrione derivatives (**89**) promoted by ZnO@SiO$_2$ nanocatalysis and ultrasound.

pyrimidine (**87**) by condensation of 6-amino uracil (**85**), isothiocyanate (**86**) and aldehydes (**1**), using a catalytic system consisting of Zn NPs immobilized on 1,4-benzenedicarboxylate (BDC) [Zn (BDC)-MOF] in a solvent-free media (Scheme 32). The reactions were performed in ultrasound bath at 220 V, frequency of 60 kHz, power of 65 W and room temperature. In comparison with methodologies reported in the literature for the preparation of pyrimido[4,5-*d*] pyrimidines, this method proved to be superior in relation to reaction time and yields using a low catalyst loading (7.5 w/w %). After recovery by filtration and washing, the nanocomposite has remained active in only three reaction cycles.

2.1.23. *Triazolo[1,2-a]indazoletriones*

The Verma group [187] has established an synthetic protocol for the synthesis of triazole[1,2-a]indazoletriones (**89**) using silica-coated ZnO nanoparticles (ZnO@SiO$_2$) as heterogeneous catalyst in the presence of ultrasonic irradiation and in aqueous media via condensation of dimedone (**4**), 4-phenylurazole (**88**), and arylaldehydes (**1**) (Scheme 33). The reaction was performed in an ultrasound bath at 58–60 °C, with a frequency of 40 kHz and an output power of 250 W. During optimization, the reaction was monitored via UV–Vis and when carried out with sonication and in the absence of the nanocomposite, led to only 42% yield. In the cases where SiO$_2$ and Zn-NPs were used separately, the desired product was also obtained with low yields, whereas in presence of ZnO@SiO$_2$ (10 mol%) under sonication, the yield increased almost two times, in shorter reaction times. In terms of reuse, it was observed that nanocomposite ZnO@SiO$_2$ could be recycled up to six runs without much loss in its catalytic activity.

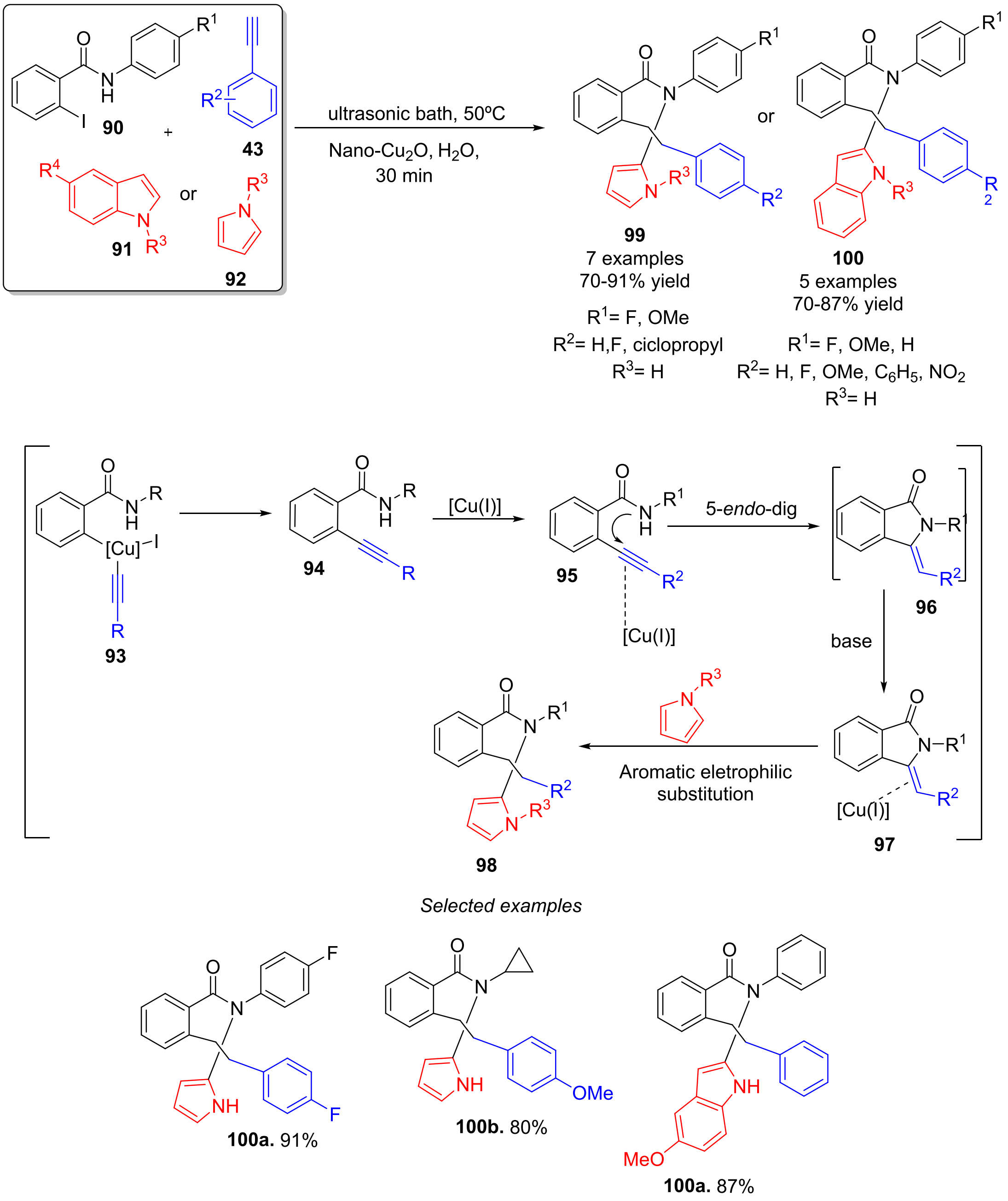
2.1.24. *Pyrrolyl/indolyl-dihydro-isoindolinones*

A greener MCR was developed by Sarkar and co-workers [188] for the ultrasound-mediated preparation of a series of 3-alkyl/aryl-3-(pyrrole-2-yl/indole-3-yl)-2-phenyl 2,3dihydroisoindolinones (**99** and **100**) in aqueous medium under cubic Cu$_2$O nanoparticles catalysis using 2-iodo-*N*-phenylbenzamides (**90**), terminal alkynes (**43**) and substituted indoles (**91**)/pyrroles (**92**) in aqueous media (Scheme 34). The amount of nanocomposite used was 10 mol %, and it does not require any surfactants or additional ligands, as in previous methods reported for synthesis of this class of compounds. The protocol showed high regioselectivity for substitution in C-2 and C-3, with pyrroles and indoles, respectively, but failed when substrates with a low nucleophilic content, such as furan or thiophene, were used. From a mechanistic point of view, the Sonogashira product **94** is obtained by the attack of phenylbenzamides on the π-alkyne Cu (I) acetylide complex (**93**) formed in the previous stage by the complexation between the nanocatalyst and the terminal alkyne (**43**). The triple bond of **95**, still activated, undergoes 5-*endo-dig* cyclization, in the presence of base, forming **96**. The nanocomposite now acts as Lewis acid activating the double bond of **97**, which leads to an electrophilic substitution with indole/pyrrole, giving the desired product **99** or **100**. In terms of reuse, the nanocomposite proved to be less efficient, with its catalytic activity significantly decreased in a successive cycle of four reactions; this is due, according to a study conducted by the authors, to the oxidation of Cu$_2$O.

2.1.25. *Benzopyranopyrimidine*

Immobilized Ag(0) nanoparticles were investigated for the synthesis of benzopyranopyrimidines. The Sadjadi group [189] obtained benzopyranopyrimidines adducts (**102**) via MCR using 4-hydroxycoumarin (**101**), benzaldehydes (**1**) and urea / thiourea (**11**). The reaction was carried out under ultrasound irradiation at 125 W power and 55 °C (the ultrasonic device was equipped with a temperature sensor and temperature was monitored during the reaction automatically; other parameters were not mentioned) and catalyzed by Ag@CDNS-SBA-15 (0.4 w/w %) using water as solvent at 55 °C (Scheme 35, Table 10, Entry 1). The catalyst was prepared by the immobilization of Ag(0) nanoparticles with SBA-15/cyclodextrin nanosponge and allowed to obtain 11 benzopyranopyrimidines (**102**) with yields varying from 80 to 95% in 25 to 50 min. The catalyst used in this protocol had its reuse capacity investigated and the results showed that it can be used up to four times, being the leaching of Ag(0) also verified.

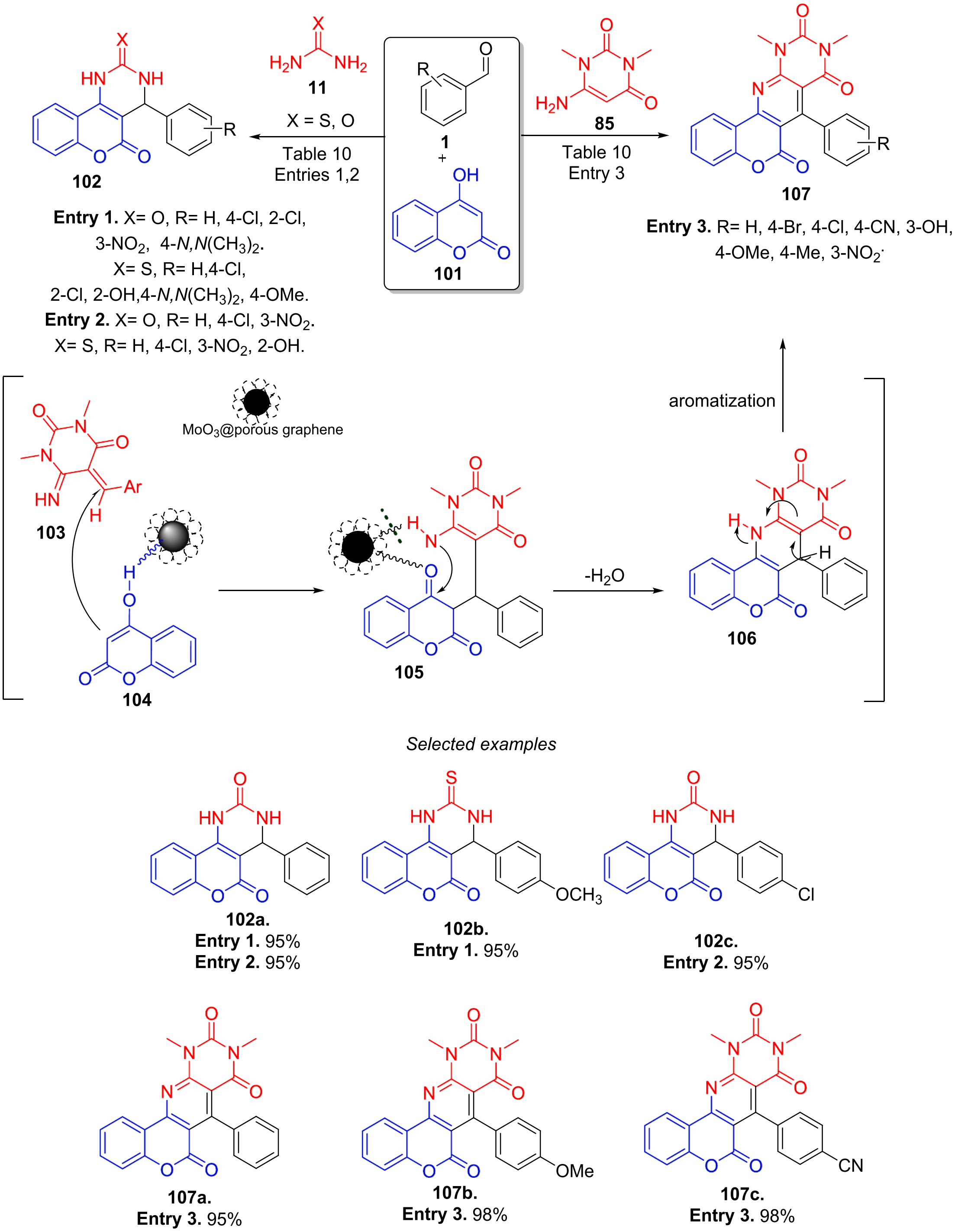
Sadjadi and co-workers [190] synthesized a hybrid HPA nanocatalyst immobilized in creatine-functionalized Halloysite nanotubes (HNTs), which was used in the aqueous MCR procedure for the preparation of benzopyranopyrimidines (102) from aldehydes (**1**), urea/thiourea (**11**) and 4-hydroxycoumarin (**101**) (Scheme 35, Table 10, Entry 2). The reactions were performed in an ultrasound bath at room temperature and power of 200 W (more details were not reported). The



Scheme 34. On water one-pot preparation of pyrrolyl/indolyl-dihydro-isoindolinones (**99** and **100**) by ultrasonic irradiation and nano-CuO_2 heterogeneous nanocatalysis.

desired product was not obtained in the absence of the nanocomposite, showing that the presence of this species (0.3 w/w %) is essential for the progress of the reaction. In this perspective, through this method it was possible to obtain 7 examples of benzopyranopyrimidines (**102**) with yields greater than 80% in 4–22 min. Regarding recyclability, the nanocatalyst showed catalytic activity in up to five reactions.

Encouraged by the interest in greener synthetic routes for obtaining heterocycles, the Abdolmohammadi group [191] developed a successful method for synthesis of benzopyranopyrido[*d*]pyrimidines (**107**) via one-pot condensation of aldehydes (**1**), 6-amino-1,3-dimethyluracil (**85**) and 4-hydroxycoumarin (**101**), using a heterogeneous reusable catalyst of MoO_3/NPs incorporated in porous biographene (MoO_3@porous graphene, 0.4 w/w %) (Table 10, Entry 3). The reaction was performed using on a multiwave ultrasonic generator, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, with an operation frequency of 20 kHz with a power output of 70 W. In the optimization study, the reaction was performed using conventional heating and the product of interest was not observed. According to the authors, this is related to the interruption of the reaction to form intermediate **105**, which occurs due to a hydrogen bond that prevents cyclization, confirmed by X-ray crystallography studies. The employment of ultrasonic irradiation (70 W) provided enough energy to break these interactions and promote the cyclization. In the proposed mechanism, the first step involves the nucleophilic attack of 6-amino-1,3-dimethyluracil (**85**) to the aldehyde (**1**) - whose carbonyl group was activated by the nanocatalyst, a potent Brønsted acid - leads to the alkene (**103**), which, in turn, reacts with 4-hydroxycoumarin (**101**) via Michael addition to produce intermediate **104**. An intramolecular cyclization in **105** leads to **106**, which generates the product **107** after the aromatization. After the recovery process, the nanocomposite was



Scheme 35. Methods for obtaining benzopyranopyrimidine derivatives (**102** and **107**) under heterogeneous catalysts and ultrasonic irradiation.

used successfully in four consecutive reaction cycles, with a negligible loss of catalytic activity.

Sadjadi and colleagues [190], in the same work, synthesized other benzopyranopyrimidines (**108**), with the use of 2-hydroxybenzaldehdes (**1**), malononitrile (**9**) and amines (**17**) (Scheme 36). This method achieved 8 examples of benzopyranopyrimidines, in 30–70 min with yields greater than 78 %. The authors reported a mechanistic proposal for obtaining these adducts, in which initially a Knovenagel condensation occurs between salicylaldehyde (**1**) and malononitrile (**9**) to form an arylidene as intermediate. Subsequently, the cyano group of this arylidene is attacked by the amine present in the medium forming a cyclic pyran intermediate, which in turn reacts with another molecule of salicylaldehyde present in the reaction medium with hydrogen transfer leading to the formation of benzopyranopyrimidine derivatives (**108**).

Recently, ultrasound-mediated syntheses of 1,4-dyhydropyrano/benzo-pyrazole derivatives (**110** and **115**) have been published (Scheme 37). In this perspective, Tabassum and col. [192] performed the synthesis of 1,4-dyhydropyrano [2,3-*c*]pyrazoles (**110**) by means of a MCR with aldehydes (**1**), 4-nitrophenylacetonitrile (**109**) and ethyl acetoacetate (**2**) using ethanol as solvent and the ZnO@PEG nanocatalyst (0.3 w/w %) (Scheme 37). The reaction was evaluated using reflux for 600 min, microwave irradiation (250 W) for 30 min, and ultrasound (ultrasonic bath operating at 35 kHz and 80 W and r.t.) for 15 min. In all cases the desired product was obtained with 65, 70 and 95%

Table 10
Synthesis of benzopyranopyrimidines (**102** and **107**) mediated by sonochemistry.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	Ag@CDNS-SBA-15	H_2O, 25–50 min, 55 °C	11	80–95	[189]
2	HPA@HNTs-C	H_2O, 4–22 min, r.t.	7	80–95	[190]
3	MoO_3@porous graphene	H_2O,10–66 min, r.t.	8	95–98	[191]

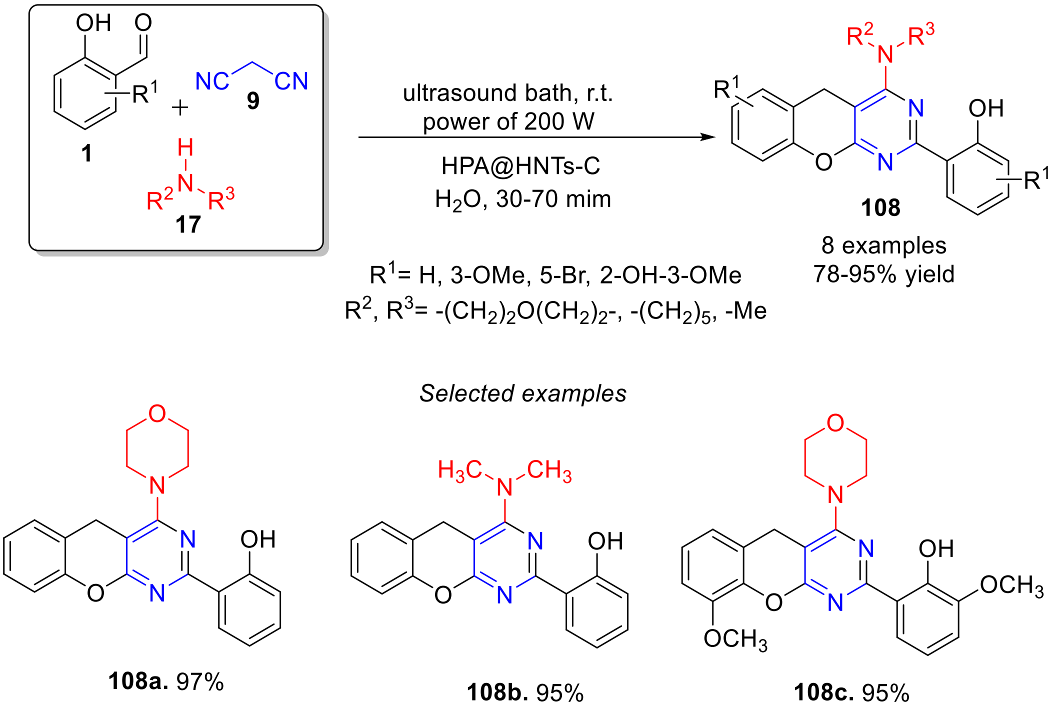
*Ultrasound parameters: Entry 1. Operating with a power of 125 W at a temperature of 55 °C and tip TT13, other ultrasound parameters were not mentioned. Entry 2. Ultrasound bath, at room temperature, and power of 200 W, further details were not informed. Entry 3. Ultrasonication device: Multiwave ultrasonic generator, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter; frequency: 20 kHz; power: 70 W.

yield, respectively, therefore the ultrasound was the most promising to obtain the adducts of interest. It was verified the importance of the immobilization of the nanoparticles for a better reaction progress. Using the optimized condition, 15 examples of 1,4-dihydropyrano[2,3-*c*]pyrazoles were obtained with yields varying between 87 and 97%. Regarding the reuse of the immobilized nanocatalyst, it remained active for five cycles.

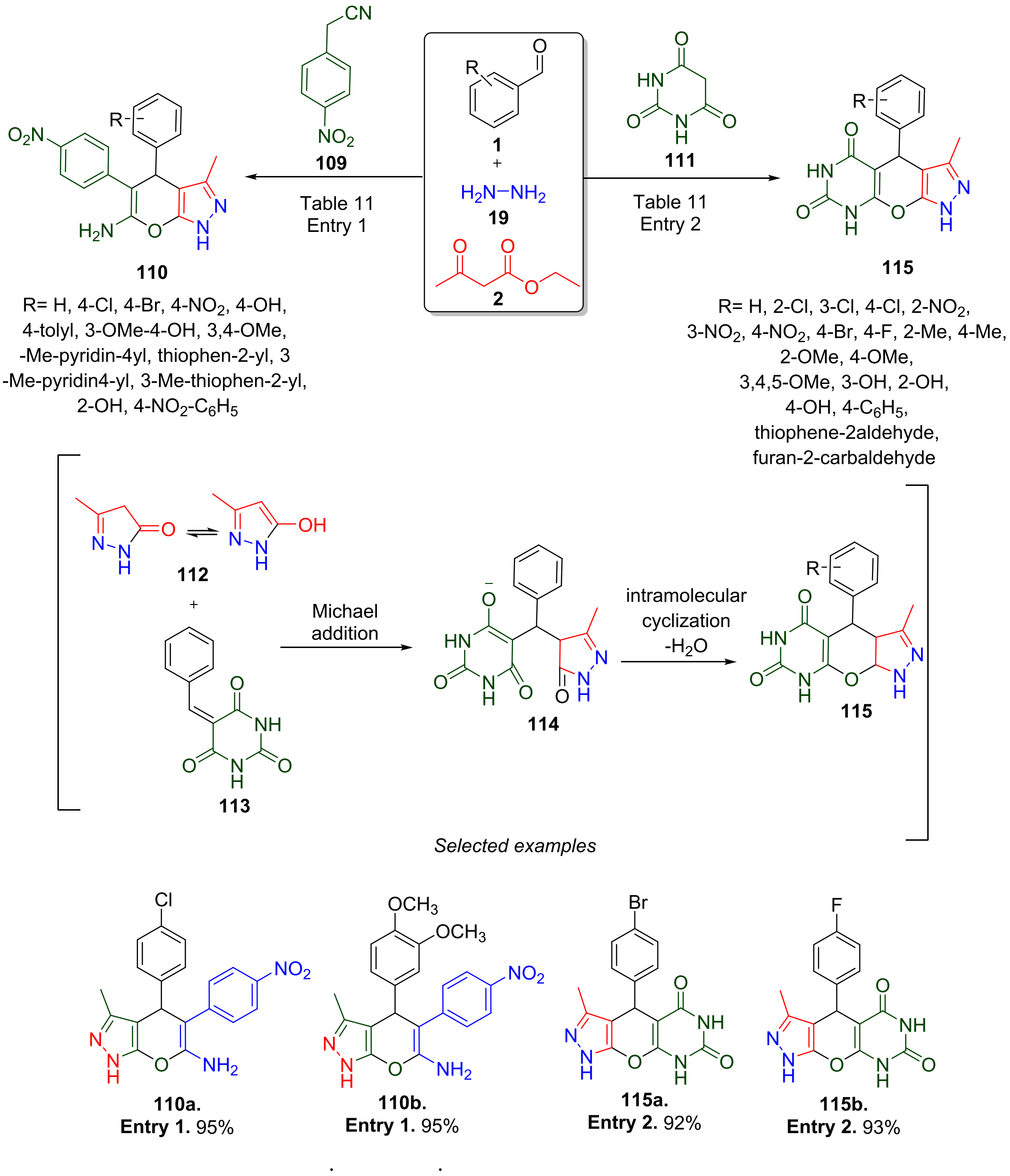
One type of polymer that has attracted attention in the field of heterogeneous catalysis in recent years is the cyclodextrin (CD)-nanosponges (CDNS), a material that has proven to be a very suitable support for nanoparticles [189,193]. Continuing the search for more sustainable synthetic protocols, Akolkar and co-workers [194] established an efficient method for the synthesis of of 1,4-dyhydropyrano/benzo-pyrimidine-pyrazole (**115**) mediated by ultrasonic irradiation and heterogeneous catalysis with *β*-cyclodextrin (*β*-CD) nanocomposite in aqueous medium, via condensation aromatic aldehydes (**1**), hydrazine hydrate (**19**), ethyl acetoacetate (**2**) and barbituric acid (**111**) (Scheme 37) (Table 11, Entry 2). In the optimization study, a screening of catalysts was carried out, in which the reaction was performed under ultrasonic irradiation (40 kHz, 50 °C) and in some cases, the product of interest was formed, in low to moderate yields. When *β*-cyclodextrin (20 mol%) was used, keeping all other variables constant, there was a notable improvement in the yield, in addition to shorter reaction time. According to the mechanistic proposal, formation of pyrazolopyranopyrimidines occurs via the intermediate **112** in equilibrium with its enolate by the condensation between ethyl acetoacetate (**2**) and hydrazine hydrate (**19**), previously activated by the catalyst. Parallel to this, there would be the formation of **113**, via Knoevenagel condensation between the aromatic aldehyde and barbituric acid (**111**), facilitated by the establishment of non-covalent reversible supramolecular complexes in the *β*-CD cavity. Then, **112** reacts with **113** through a Michael addition to generate **114**, which via intramolecular cyclization and dehydration, leads to the desired product (**115**). The authors further examined the catalytic efficiency of the methodology, performing the reaction on a gram scale (20 mmol) using the optimized condition with 89% yield in 30 min. The catalyst could be recovered by simple filtration, maintaining the efficiency up to four cycles.

2.1.26. *Azlactones*

Rostami and colleagues [195] performed the synthesis of 4-arylidene-2-phenyl-5(4)-oxazolones (azlactones) (**118**), by an MCR protocol that involves a condensation between aldehydes (**1**), hippuric acid (**117**) and acetic anhydride (**116**) (Scheme 38). In this MCR the catalytic medium was developed by a heterogeneous hybrid of ionic liquid with polyoxometalate hybrids ($[C_6(MIm)_2]_2W_{10}O_{32}\cdot 2H_2O$) (0.7 w/w %). The influence of ultrasound irradiation in the reaction medium was investigated and in its absence the product of interest was obtained with less than 5% yield, whereas under sonication, an excellent conversion to the product was verified. In this method, the reaction was promoted by an ultrasonic processor with a width of 3 mm and a probe of 140 mm in length, which was inserted into the reaction mixture. The operating frequency was 24 kHz and the output power 400 W. The effect of the solvent was also investigated, and it was noted that under solvent-free condition the best yield was obtained. Using the optimized condition, in short reaction time (8–25 min), it was possible to obtain 19 examples



Scheme 36. Synthesis of benzopyranopyrimidine derivatives (**108**) catalyzed by HPA@HNTs-C and promoted by ultrasonic irradiation in aqueous medium.



Scheme 37. Synthesis of 1,4-dihydropyrano[2,3-*c*]pyrazoles **110** and **115**.

Table 11
Strategies for obtaining 1,4-dihydropyrano[2,3-*c*]pyrazoles **110** and **115** promoted by ultrasound irradiation and heterogeneous catalysis.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	ZnO@PEG	EtOH, 15 min	15	87–97	[192]
2	*β*-cyclodextrin	H_2O, 25–70 min	21	84–93	[194]

*Ultrasound parameters: Entry 1. Ultrasound bath; frequency: 35 kHz; power: 80 W. Entry 2. Ultrasound bath, 50 °C; frequency: 40 kHz, no more details were provided.

of azlactone derivatives, with yields greater than 80%. Regarding the catalyst recycling, it was separated by filtration, and after washing with hot ethanol and drying at 80 °C under reduced pressure, it could be used in at least five cycles without significant loss in catalytic activity.

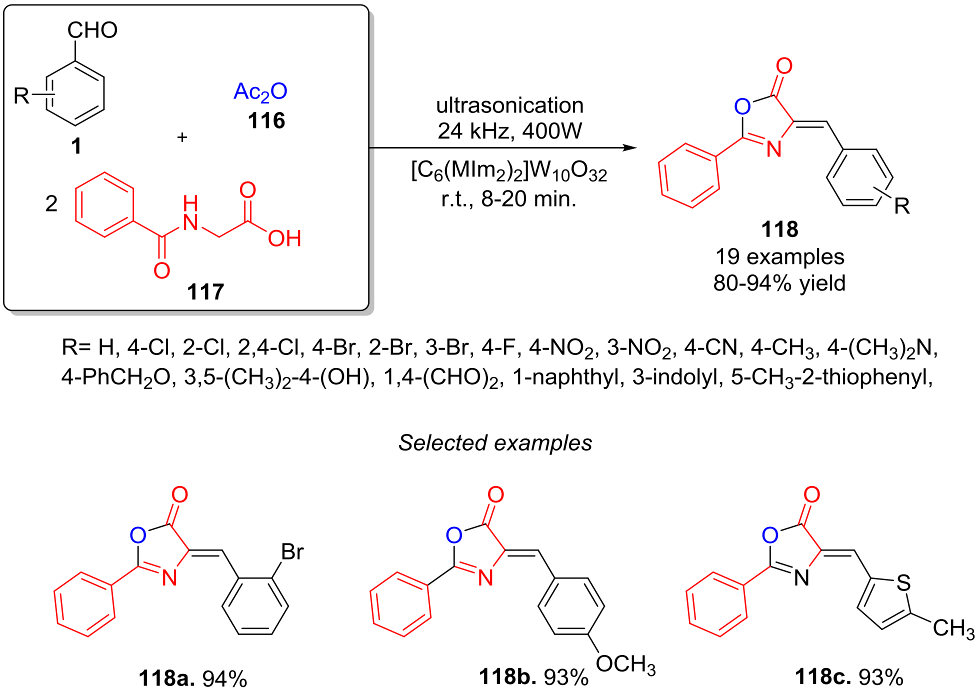
2.1.27. 3-Methyl-4-arylmethylene isoxazole-5(4H)-ones

The 3-methyl-4-arylmethylene isoxazole-5(4*H*)-ones (**119**) were obtained by the Ahmadzadeh group [196] via one-pot multicomponent cyclocondensation involving hydroxylamine hydrochloride, ethyl acetoacetate (**2**) and benzaldehyde derivatives (**1**) in water. The reactions were carried out in an ultrasonic bath with a frequency of 35 kHz and a nominal power of 100 W (Scheme 39). The nano-MMT-Sn catalyst was prepared by ion exchange between $SnCl_2$ and montmorillonite *K*10. Using this protocol, 12 examples were obtained in 87–96 % yield. The heterogeneous catalyst (0.2 w/w %) was separated by filtration and reused after dilution with ethyl acetate, showing to be efficient in up to six cycles.

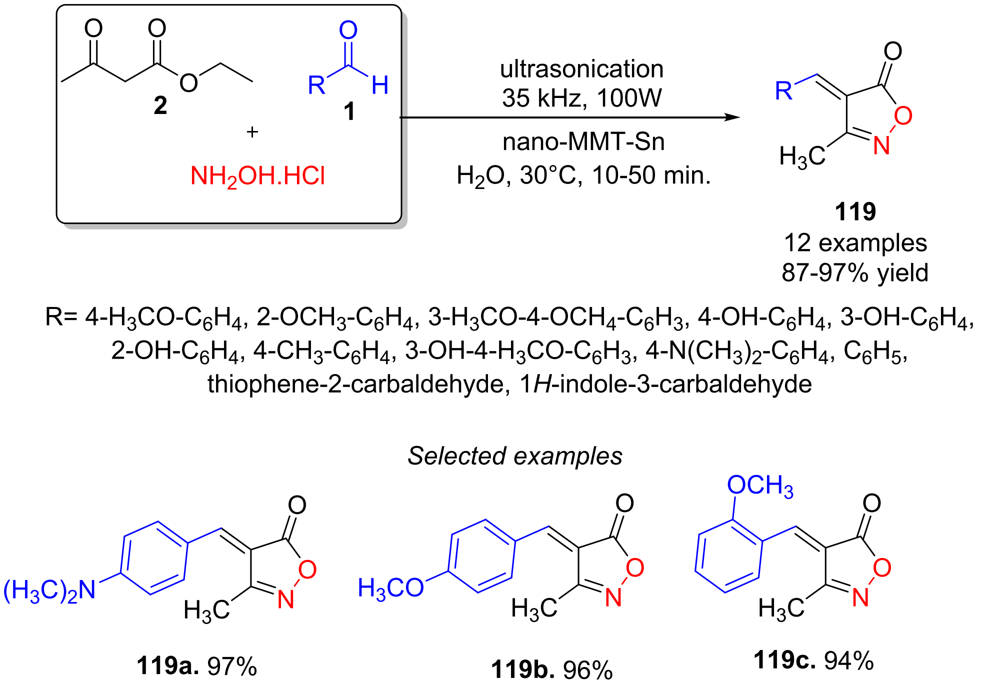
2.2. O-Heterocyclic compounds

2.2.1. Pyran derivatives

Pyrans have been extensively studied for their biological properties, such as antibacterial [197], antioxidant [198], antitumor [199], as well as against Hep G2/C3A [200]. This scaffold can also be found in natural products [201]. Due to the wide applicability of this class of compounds, studies focused on more selective and greener synthetic methods have



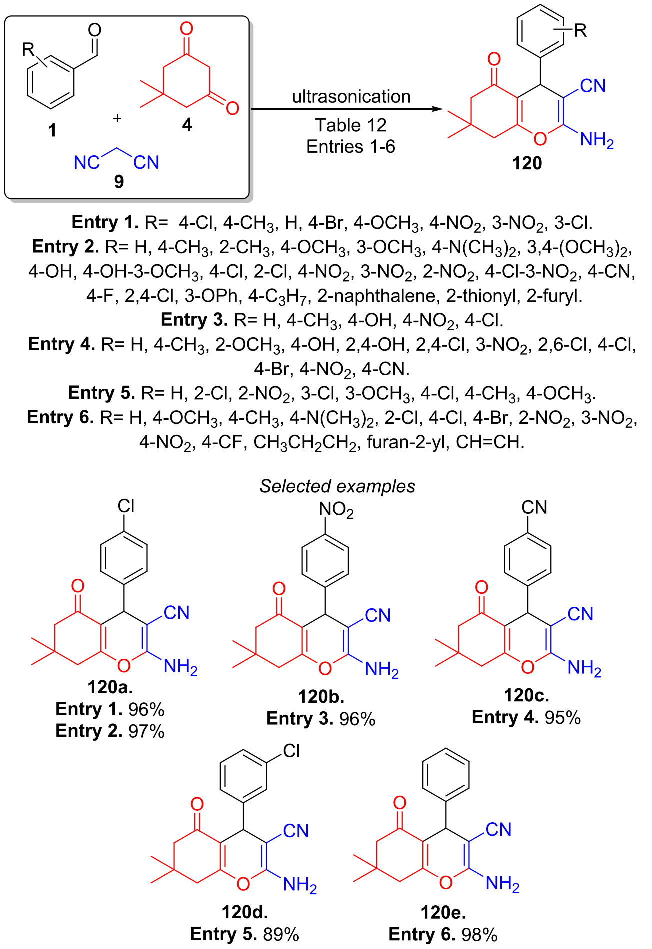
Scheme 38. Solvent-free MCR mediated by ultrasound irradiation to obtain azlactone derivatives (**118**) under heterogeneous catalysis.



Scheme 39. Synthesis of 3-methyl-4-arylmethylene isoxazole-5(4*H*)-ones (**119**) catalyzed by Sn^{II}-Mont *K*10 assisted by ultrasound.

been increasingly explored.

In the literature, several examples of synthesis of tetrahydrobenzo[*b*]pyran derivatives (**120**) via MCRs using aromatic aldehydes (**1**), malononitrile (**9**) and dimedone (**4**), under ultrasound irradiation (Scheme 40) are described. As, for example, Mohammadi et al. [202] developed a stable nanocatalyst based on ferrocene-modified magnetic nanoparticles containing benzimidazolium ionic liquid ($Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/NiCl_2$) (Table 12, Entry 1). In this study, the synthesis of tetrahydrobenzo[*b*]pyrans was investigated by conventional heating and by ultrasonic irradiation and it could be verified that under sonication the reaction was more effective, with shorter reaction times at room temperature and higher yields than the conventional heating. The reaction was carried out using a multiple wave ultrasonic generator equipped with a converter/titanium transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 10–60 W. This method allowed to obtain 8 examples, with yields varying between 86 and 96%, with a reaction time between 10 and 15 min. The small amount of catalyst (0.13 w/w %) is another highlight of this



Scheme 40. Ultrasonic irradiation for the synthesis of tetrahydrobenzo[*b*]pyrans (**120**) with the use of heterogeneous catalysts.

Table 12
Methods for obtaining tetrahydrobenzo[*b*]pyrans (**120**) under ultrasound and using recyclable catalysts.

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	$Fe_3O_4@SiO_2$-BenzIm-Fc[Cl]/$NiCl_2$	EtOH: H_2O,10–15 min, r.t	8	86–96	[202]
2	$Fe_3O_4@SiO_2$-Imid-PMA^n	H_2O, 4–14 min, r.t	24	89–97	[203]
3	$Fe_3O_4@Ph$-SO_3H	H_2O, 10–40 min, r.t	6	88–96	[204]
4	MNCACAs	EtOH, 10–30 min, 25 °C	12	85–95	[205]
5	$MgFe_2O_4$	EtOH, 10–15 min., 65 °C	8	85–92	[206]
6	n-TiO_2/$H_{14}[NaP_5W_{30}O_{110}]$	EtOH, 10–40 min., 40 °C	14	71–98	[207]

*Ultrasound parameters: Entry. 1 Use of an ultrasonic multiwave generator with a titanium converter / transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum output power of 10–60 W and the power levels were adjusted automatically. Entry. 2 Use of an ultrasonic cleaning bath with a frequency of 40 Hz at 220 V. Entry 3. Frequency, power, and device type were not reported. Entry 4. Irradiation performed in an ultrasonic bath at 60 Hz, with system temperature at 25 °C. Entry 5. Reaction was performed in an ultrasonic bath with a nominal power of 200 W and a frequency of 80 kHz. Entry 6. Process carried out in an ultrasound cleaner with a frequency of 35 kHz and an output power of 70 W.

synthetic procedure. The reuse of the nanocatalyst was investigated and remained active for 6 cycles.

In the same direction, the Esmaeil group [203] performed the synthesis of tetrahydrobenzo[*b*]pyran derivatives (**120**) via MCR (Table 12, Entry 2), using the $Fe_3O_4@SiO_2$-Imid-PMA^n magnetic nanocatalyst. In this method, the efficiency of ultrasound irradiation was investigated *vs* conventional heating. Through this investigation, the use of ultrasonic irradiation was applied more efficiently to obtain the compounds of interest with shorter reaction times and with higher yields. The reaction was performed in an ultrasonic cleaning bath with a frequency of 40 Hz at 220 V. The method under study made it possible to obtain a wide scope consisting of 24 examples of tetrahydrobenzo[*b*]pyrans (**120**) with yields greater than 89%. The nanocatalyst under study was reused in eight cycles, thus, using this method, it was possible to obtain a wide range of derivatives with good yields, short reaction times, and with the use of water as a solvent.

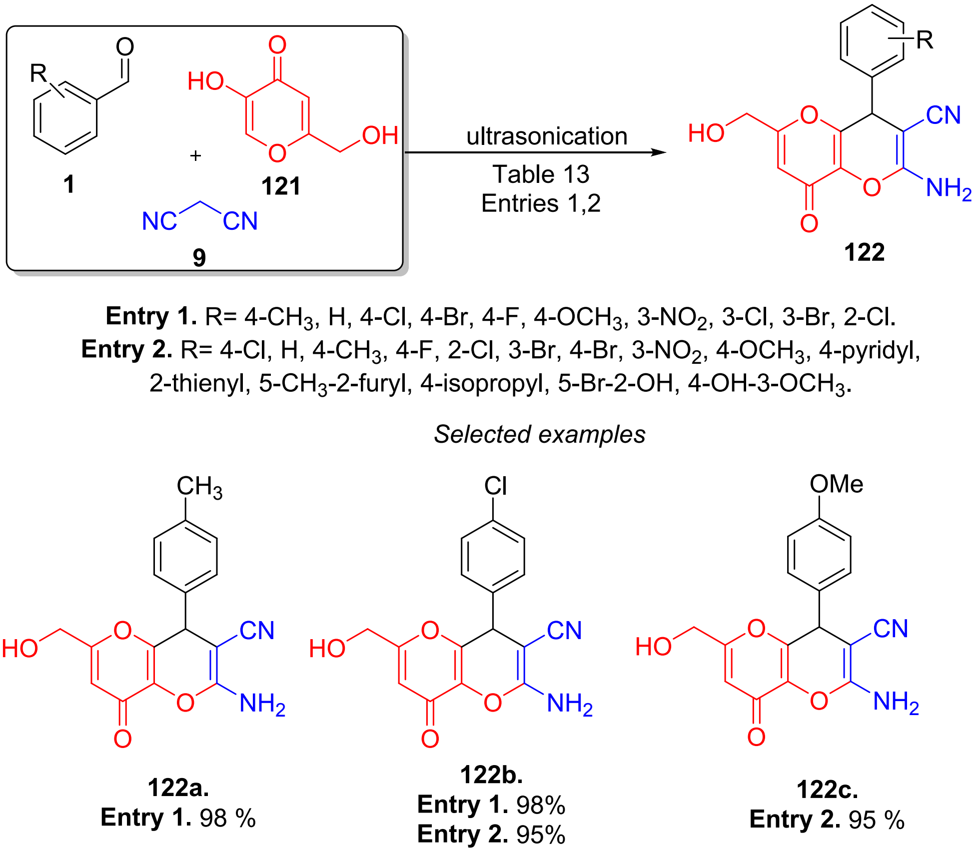
In this perspective, Elhamifar et al. [204] performed the synthesis of tetrahydrobenzo[*b*]pyrans (**120**) using a magnetic catalyst composed by iron oxide supported on phenylsulfonic acid in a core–shell structure ($Fe_3O_4@Ph$-SO_3H) (Table 12, Entry 3). The reaction was investigated under conventional heating at 50 °C and ultrasound irradiation at room temperature (frequency and power were not reported). It was found that the use of ultrasound irradiation promoted an improvement in the protocol, allowing to obtain 6 examples of tetrahydrobenzo[*b*]pyrans, with yields greater than 88%, low catalyst loading (0.4 w/w %) and reaction time between 10 and 40 min. The solvent used in this study was water and the reuse of the magnetic catalyst was investigated showing that the activity remained efficiently for up to 10 cycles.

Eivazzadeh and col. [205] also reported the synthesis of tetrahydrobenzo[*b*]pyrans (**120**) via one-pot method, using a calix[4]arene based magnetic nanocatalyst functionalized with amino groups (MNCACAs), under ultrasound irradiation (Table 12, Entry 4). The reaction was performed in an ultrasonic bath at 60 Hz at 25 °C. Employing the optimized conditions, it was possible to obtain 12 tetrahydrobenzo[*b*]pyrans, with the use of EtOH as solvent, at room temperature in 15 min. The nanocatalyst (0.35 w/w%) could be recovered and reused remaining active for five cycles.

The Eshtehardian group [206] reported the synthesis of tetrahydrobenzo[*b*]pyrans (**120**) under ultrasound irradiation, using as catalyst $MgFe_2O_4$ magnetic nanoparticles (0.08 w/w %) (Table 12, Entry 5). The reaction was performed in an ultrasonic bath with a nominal power of 200 W and a frequency of 80 kHz. Various solvents were studied, and the best results were obtained with ethanol at 65 °C. In this optimized condition it was possible to synthesize 8 examples of tetrahydrobenzo[*b*]pyrans with up to 85 % yield in 10–15 min. The magnetic nanoparticles were recovered with the aid of an external magnet, washed with acetone to remove the residual product, and then reused, remaining active for 4 cycles.

Furthermore, Azarifar and co-workers [207] studied the synthesis of tetrahydrobenzo[*b*]pyrans (**120**) mediated by ultrasound irradiation with the use of a nano-titania-supported catalyst n-TiO_2/$H_{14}[NaP_5W_{30}O_{110}]$. This protocol was carried out at 40 °C, using an ultrasound cleaner with a frequency 35 kHz and an output power of 70 W, and the most effective solvent was EtOH (Table 12, Entry 6). In this work, 14 derivates tetrahydrobenzo[*b*]pyran were obtained with yields greater than 71% in 10 to 40 min. After the completion, the reaction mixture was diluted in methanol and subsequently centrifuged to promote an effective separation of the catalyst. Then, the solid was washed with ethyl acetate, dried under reduced pressure, and reused in up to three cycles.

The synthesis of pyran[3,2-*b*]pyran derivatives (**122**) under ultrasound irradiation was explored by a one-pot condensation reaction of aromatic aldehyde (**1**), malononitrile (**9**) and kojic acid (**121**) (Scheme 41). In this context, the Nazari group [208] investigated the synthesis of bis-heterocyclic annulled derivatives via MCR using ultrasound irradiation. The reactions were carried out using a multiwave ultrasonic



Scheme 41. Synthesis of pyrano[3,2-*b*]pyran derivatives (**122**) by sonochemical-assisted MCR.

Table 13
Ultrasound-assisted synthesis of pyrano[3,2-*b*]pyrans (**122**).

Entry	Catalyst	Conditions[a]	Examples	Yields (%)	Ref.
1	Fe_3O_4@SiO_2-BenzIm-Fc[Cl]/$ZnCl_2$	8–12 min, r.t	10	86–98	[208]
2	SiO_2@Imd-Cl@Fc	15–20 min, 25 °C	15	84–95	[209]

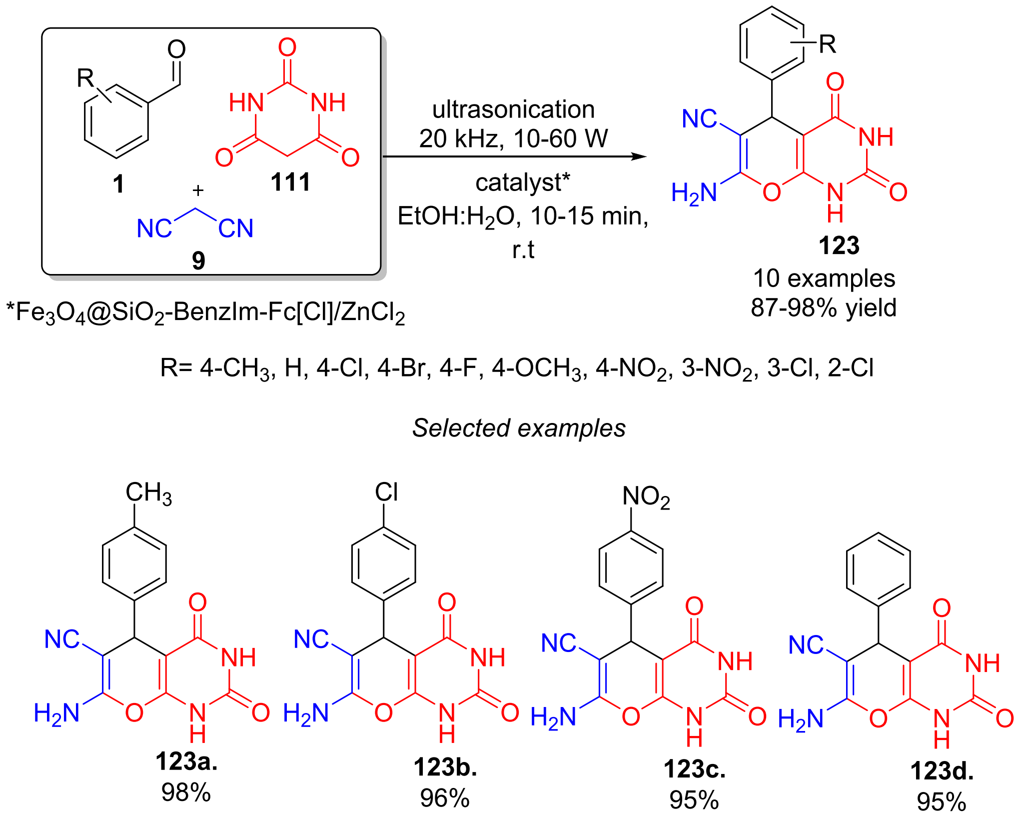
*Ultrasound parameters: Entry 1. The ultrasonic irradiations were obtained by a multiwave ultrasound equipped with a converter/transducer and a titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum output power of 10–60 W. Entry 2. The process was mediated by an ultrasonic multiwave generator equipped with a titanium converter / transducer and oscillator (horn) of 12.5 mm in diameter, operating at 20 kHz with maximum power of 10–60 W and power levels adjusted automatically. [a]a mixture of EtOH: H_2O was used as solvent.

generator equipped with a converter / transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum 10–60 W output power. The catalytic system was composed of magnetic nanoparticles coated with functionalized silica Fe_2O_4@SiO_2-BenzIm-Fc [Cl]/$ZnCl_2$, prepared by the coprecipitation method. The ideal amount of nanocomposite for the success of this synthetic approach was only 0.16 w/w%. After optimization for obtaining the pyrano[3,2-*b*]pyran derivatives, the reaction time varied between 8 and 12 min, a mixture of EtOH: H_2O (2: 1) was used as a solvent, and the desired products were obtained with yields greater than 86% (Table 13, Entry 1). The reuse of the nanocatalyst was investigated and it was noted that its catalytic activity remained for up to 6 cycles.

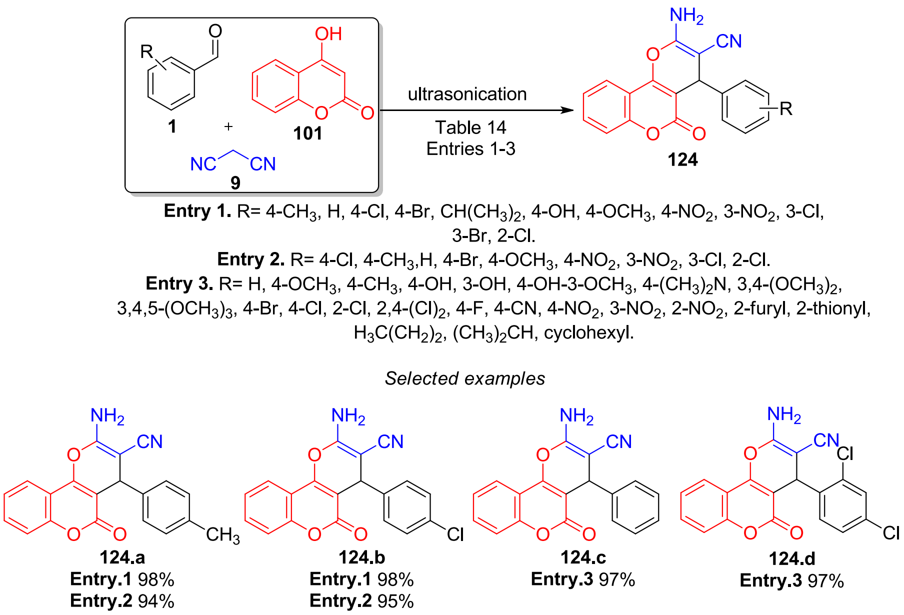
Mixed catalytic systems composed of supported ionic liquids (SILs) anchored on solid supports are also a privileged class of heterogeneous catalysts, presenting many advantages over free ILs, including an increase in the number in accessible catalyst active sites, reduction in the amount of necessary IL, and improvement in its ability to recover and reuse. In this regard, Teimuri-Mofrad et al. [209] have created a very active hybrid nanocatalyst based on ferrocene-containing ionic liquid supported on silica nanospheres (SiO_2@Imid-Cl@Fc) for the synthesis of pyrano[3,2-*b*]pyran derivatives (**122**) by one-pot condensation of aromatic aldehyde (**1**), malononitrile (**9**) and kojic acid (**121**) under ultrasound irradiation in EtOH/H_2O as solvent (Table 13, Entry 2). The reactions were carried out using an ultrasonic multiwave generator equipped with a converter/titanium transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 10–60 W and the power levels have been adjusted automatically. This catalytic system proved to be active in only 0.2 w/w% and could be recycled up to five times, with maintenance of the catalytic activity.

The Nazari group, in a work already mentioned in this review [208], evaluated the obtaining of pyran[3,2-*d*]pyrimidines (**123**) via ultrasound-assisted cyclocondensation of aromatic aldehydes (**1**), malononitrile (**9**) and barbituric acid (**111**) using a functionalized recyclable magnetic nanoparticles (Fe_2O_4@SiO_2-BenzIm-Fc[Cl]/$ZnCl_2$) (Scheme 42). This protocol made possible to obtain 10 examples of pyran[3,2-*d*]pyrimidines, with yields greater than 87%, with a reaction time between 10 and 15 min at room temperature.

Cyclocondensation reactions have also been explored to obtain pyran [3,2-*c*]chromenes (**124**) by means of a multicomponent reaction using aromatic aldehydes (**1**), malononitrile (**9**) and 4-hydroxycoumarin (**101**) (Scheme 43). In the work of the Nazari group [208], already discussed in this review, pyran[3,2-*c*]chromenes (**124**) were obtained with the use of magnetic nanoparticles coated with functionalized recyclable silica (Table 14, Entry 1). The method was carried out at room temperature and the solvent was a mixture of EtOH:H_2O, with a short reaction time (10–20 min), under ultrasound irradiation operating at 20



Scheme 42. MCR for the synthesis of pyran[3,2-*d*]pyrimidine derivatives (**123**) with the use of functionalized recyclable magnetic nanoparticles under ultrasound irradiation.



Scheme 43. Cyclocondensation to obtain pyran[3,2-*c*]chromenes (**124**) using sonochemistry and heterogeneous recyclable catalysts.

kHz with a maximum 10–60 W output power. Using this protocol, it was possible to obtain 12 examples of pyran[3,2-*c*]chromenes, with yields greater than 85%.

Mohammadi et al. [202] also evaluated the synthesis of pyran[3,2-*c*] chromenes (**124**) with a recyclable catalyst based on ferrocene-modified magnetic nanoparticles containing benzimidazolium ionic liquid (Fe_3O_4@ SiO_2@BenzIm-Fc[Cl]/$NiCl_2$), as already mentioned in this review. Using a mixture of EtOH:H_2O as solvent, with short reaction time (15–20 min) at 25 °C under ultrasound irradiation, it was possible to synthesize 9 examples of pyran [3,2-*c*]chromenes with yields between 87 and 95% (Table 14, Entry 2).

In this perspective, the Esmaeil group [203] also investigated the use of Fe_3O_4@SiO_2-Imid-PMA^n magnetic nanocatalyst in obtaining pyran [3,2-*c*]chromenes (**124**) via cyclocondensation, under ultrasound

Table 14
Synthetic protocols assisted by ultrasound to obtain pyran[3,2-*c*]chromenes (**124**).

Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	$Fe_3O_4@SiO_2$-BenzIm-Fc[Cl]/$ZnCl_2$	EtOH:H_2O, 10–20 min, r.t.	12	85–96	[208]
2	$Fe_3O_4@SiO_2$-BenzIm-Fc[Cl]/$NiCl_2$	15–20 min, 25 °C	9	87–95	[202]
3	$Fe_3O_4@SiO_2$-Imid-PMA^n	H_2O, 5–12 min, r.t	23	88–97	[203]

*Ultrasound parameters: Entries 1 and 2. Reactions were carried out using a multiple wave ultrasonic generator equipped with a converter / titanium transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum power output of 10–60 W and the power levels have been adjusted automatically. Entry 3. Ultrasound cleaning bath with frequency of 40 Hz at 220 V.

irradiations performed using an ultrasound cleaning bath with frequency of 40 Hz at 220 V. The adopted protocol allowed to obtain a broad scope consisting of 23 examples containing electron donors or withdrawing groups, with yields between 88 and 97%, in water and short reaction time (5–15 min) at room temperature (Table 14, Entry 3).

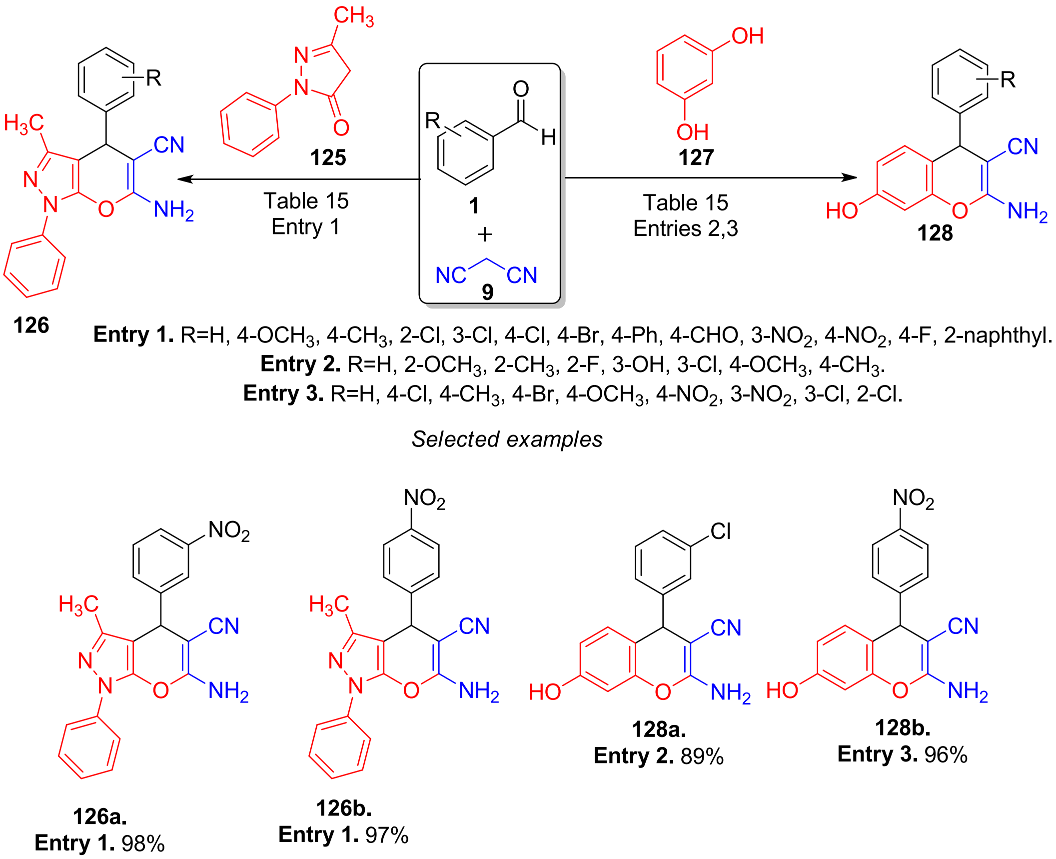
The Azarifar group also investigated the efficiency of the n-TiO2/$H_{14}[NaP_5W_{30}O_{110}]$ catalyst in obtaining dihydropyran[2,3-*c*]pyrazoles (**126**) (Scheme 44), under ultrasound irradiation, using EtOH as solvent at 40 °C (Table 15, Entry 1). In this protocol, it was possible to obtain 13 examples of dihydropyran [2,3-*c*]pyrazole (**126**) with yields greater 83%, with reaction time between 10 and 13 min [207].

The 2-amino-7-hydroxy-4*H*-chromene derivatives (**128**) have also been explored with the use of ultrasound irradiation and heterogeneous catalysis (Scheme 44). In the work by Estehardian et al. [206], already cited in this review with the study of the recyclable magnetic nanocatalyst $MgFe_2O_3$, it was also explored the synthesis of 2-amino-7-hydroxy-4*H*-chromene (**128**) via MRCs with the use of aldehydes (**1**), malononitrile (**9**) and resorcinol (**127**), with EtOH at 65 °C in 11–15 min (Table 15, Entry 2). In this work it was possible to obtain 8 2-amino-7-hydroxy-4*H*-chromene derivatives with 74–89 % yield. Moreover, the Mohammadi group [202] synthesized 2-amino-7-hydroxy-4*H*-chromene derivatives using the $Fe_3O_4@SiO_2$-BenzIm-Fc[Cl]/$NiCl_2$ catalyst, a mixture of EtOH/H_2O as solvent, at room temperature in 10–15 min. (Table 15, Entry 3). In this context, it was possible to obtain 9 derivatives

Table 15
Conditions for the synthesis of dihydropyran[2,3-*c*]pyrazoles (**126**) and 2-amino-7-hydroxy-4*H*-chromenes (**128**) under ultrasound irradiation.

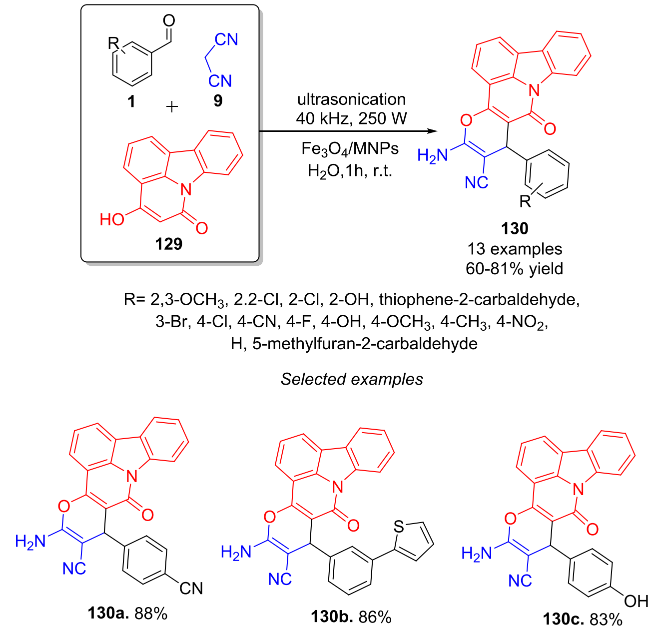
Entry	Catalyst	Conditions	Examples	Yields (%)	Ref.
1	n-TiO_2/$H_{14}[NaP_5W_{30}O_{110}]$	EtOH, 10–30 min., 40 °C	13	83–98	[207]
2	$MgFe_2O_4$	EtOH, 11–15 min., 65 °C	8	74–89	[206]
3	$Fe_3O_4@SiO_2$-BenzIm-Fc[Cl]/$NiCl_2$	EtOH: H_2O,10–15 min, r.t.	9	86–96	[202]

*Ultrasound parameters: Entry 1. Ultrasound cleaner with a frequency 35 kHz and an output power of 70 W. Entry 2. Performed in an ultrasonic bath with a nominal power of 200 W and a frequency of 80 kHz. Entry 3. The method was carried out in a multiwave ultrasonic generator equipped with a titanium converter / transducer and oscillator (horn), 12.5 mm in diameter, operating at 20 kHz with a maximum output power of 10–60 W.



Entry 1. R=H, 4-OCH_3, 4-CH_3, 2-Cl, 3-Cl, 4-Cl, 4-Br, 4-Ph, 4-CHO, 3-NO_2, 4-NO_2, 4-F, 2-naphthyl.
Entry 2. R=H, 2-OCH_3, 2-CH_3, 2-F, 3-OH, 3-Cl, 4-OCH_3, 4-CH_3.
Entry 3. R=H, 4-Cl, 4-CH_3, 4-Br, 4-OCH_3, 4-NO_2, 3-NO_2, 3-Cl, 2-Cl.

Scheme 44. Preparation of dihydropyran[2,3-*c*]pyrazoles (**126**) and 2-amino-7-hydroxy-4*H*-chromene derivatives (**128**) promoted by ultrasound irradiation and selected examples.



Scheme 45. Ultrasound-assisted approach to the synthesis of pyran-pyrido-carbazole derivatives (**130**) under Fe_3O_4/MNPs catalysis.

with 86–96% yield.

The Parmar group [13] recently reported the use of Fe_3O_4/MNPs (10 mol%) as a heterogeneous catalyst in the greenest preparation of a new class of pyrane-pyrido-carbazoles (**130**) via condensation of aryl aldehyde (**1**), malononitrile (**9**) and 4-hydroxypyridocarbazolone (**129**) under ultrasonic irradiation and use of water as solvent (Scheme 45). The reaction was performed in a medical ultrasound cleaner with a frequency of 40 kHz and output power of 250 W. The authors comment that the use of ultrasound increased the efficiency of the reaction, in comparison with other conventional methods of heating. It was also carried out without a catalyst by ultrasound, but in this case, it took a long time to complete the reaction, and still with product yield below 50%. In the mechanistic proposal for the formation of these interesting heterocycles, the authors argue that Fe_3O_4/MNPs assumes a double character: at first, as predicted, it behaves like Lewis acid due to the high electropositivity of Fe, coordinating with the oxygen of the carbonyl group of the aldehyde, and thus making the carbon more electrophilic. In a second step, Fe_3O_4/MNPs also assumes a basic character and, therefore, can abstract the proton from malonitrile acid. This statement is justified by potential calculations, which showed a negative charge on the surface of this nanocomposite. Thus, a Knoevenagel condensation between the anion generated by the deprotonation of malonitrile and the aldehyde, followed by Michael addition of 4-hydroxypyridocarbazolone (**129**) and intramolecular cyclization to give after tautomerization the final compound (**130**). Fe_3O_4/MNPs has proved to be an efficient heterogeneous catalyst in this reaction and can be recycled seven times without loss in its catalytic activity.

Shahbazi-Alavia and co-workers [210] have designed a new bimetallic nanocatalyst composed by Co_3O_4/NiO nanoparticles supported on quantum graphene points (GQDs), a new structure of the family of CNTs. This hybrid catalytic system (0.1 w/w %) was used in the one-pot protocol for the synthesis of pyranochromenes (**131**) and biscoumarins (**132**) by using benzaldehydes (**1**), 4-hydroxycoumarin (**101**) and ethyl cyanoacetate (**72**) under sonication (power of 40 W and other ultrasound parameters were not informed) in EtOH as solvent (Scheme 46). The reaction was also performed under conventional heating, but the use of ultrasound ensured shorter reaction times and higher yields of desired products. Furthermore, the authors carried out a comparison of the catalytic activity of the Co_3O_4/NiO nanocomposite with other catalysts reported in the literature for the synthesis of these recognized important heterocycles and the results indicated superior catalytic activity of the nanocomposite, which promoted the same reaction in a shorter reaction time and with better yields. Additional recyclability studies have shown that the nanocomposite could be reused several times without a noticeable loss of catalytic activity.

Still in the context of the synthesis of pyran derivatives, Gujar and co-workers [211] investigated the catalytic properties of molecular sieves (MS 4 Å) in the condensation of ethyl acetoacetate (**2**), hydrazine hydrate (**19**), aldehydes (**1**), and malanonitrile (**9**) (Scheme 47). They compared the MS 4 Å with other aluminate and silicate-based catalysts (amberlite, acid, basic and neutral alumina, silica gel, MS 3 Å and 10 Å) and without any catalyst, and carried out the reactions under ultrasonic waves and conventional heating. Furthermore, as a solvent they tested ethanol, toluene, acetonitrile, methanol, and water. The best result was found using MS 4 Å (1.3 w/w %) mediated by ultrasound waves in ethanol. The advantages of this one-pot two-step synthesis of dihydropyrano [2,3-*c*] pyrazole (**133**) are the high yield and the easy work-up procedure and isolation, beyond the MS 4 Å is a non-toxic, noncorrosive, commercially available, and inexpensive catalyst. The catalyst was recovered quantitatively simply by washing with ethyl acetate and reused in subsequent reactions at least five times, without significant loss of catalytic efficiency.

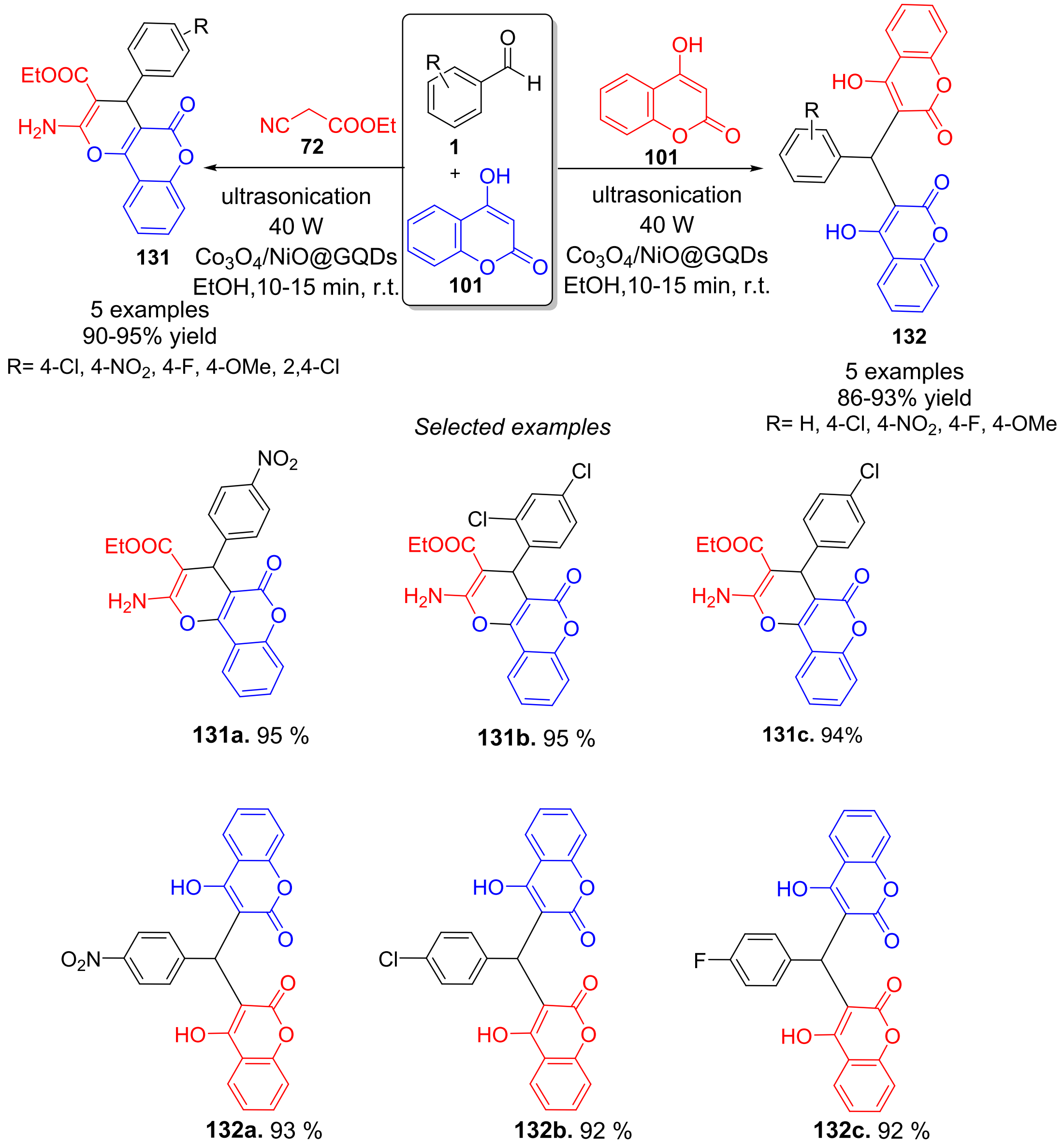
2.2.2. Benzo[b]furans

Benzo[*b*]furans motif is part of the structure of many natural products of interest in organic chemistry and pharmacology due to its wide spectrum of therapeutic actions [212], such as antimicrobial [213] and inflammatory [214]. The Sadjadi group [215] has developed a greener method to obtain these versatile compounds, using a new hybrid type bionanocatalyst, synthesized from the combination of hollow Fe_2O_3/MNPs nanospheres, ionic liquid and Ag/NPs (h-Fe_2O_3@SiO_2-IL/Ag) (Scheme 48). This protocol, mediated by ultrasound, consists of the one-pot condensation of salicylaldehyde (**1**), acetylene (**43**) and amine (**17**), in an aqueous medium. The reaction was carried out in the absence of the catalyst and using an ultrasonic bath at room temperature (with output power of 150 W and tip TT13) and the desired product has not been obtained. On the other hand, in the presence of h-Fe_2O_3@SiO_2-IL/Ag (0.45 w/w %) and sonication, the product of interest **134** was obtained in high yields. For comparative purposes, the reaction was performed using conventional methods of stirring and heating and ultrasound under the same conditions, and the results showed that the sonicated reaction led to higher yields, in shorter reaction times. After the recovery process by magnetic separation and washing with EtOH, the catalyst could be reused in a cycle of seven successful reactions with just slight loss of catalytic activity.

2.2.3. Xanthenes

Xanthene derivatives are very useful in several areas [216], in addition to exhibiting a wide spectrum of biological activities, such as antileukemic [217], insecticide [216] and antifungal [218]. In a methodology already discussed in the section 2.1.2, Ghasemzadeh and co-workers (Scheme 49) [134] have synthesized a series of these important heterocycles (**135**) with high yields (Table 16, Entry 1).

In the same trend, the Safa group [219], encouraged by the interest in environmentally friendly catalyst, has established a one-pot three-component protocol for the synthesis of biologically active xanthene derivatives (**136**) by reaction of aldehydes (**1**), cyclic 1,3-diketones (**6**) and β-naphthol (**69**) exploring a zeolite-supported on Fe and Cu (Fe-Cu/ZSM-5, 5–10 w/w %) as catalyst, under ultrasonic irradiation in water, at ambient temperature (Scheme 49, Table 16, Entries 2 and 3). The reactions were carried out in an ultrasonic processor probe, with 12-mm-tip diameter at room temperature and 40 % power of the processor. The authors verified that the incorporation of Fe into Cu/ZSM-5 increased the product yield and reduced the reaction time with decreased catalyst loading, and no product was observed in the absence



Scheme 46. Ultrasound-assisted MCR for the synthesis of pyranochromenes (**131**) and biscoumarins (**132**) in presence of GOD/ Co_3O_4/NiO nanocomposite as a catalyst.

of the catalyst. In terms of recyclability of the catalyst, it was found that no loss of catalytic activity was observed even after five reaction cycles.

2.2.4. 3-Cinnamoyl coumarins

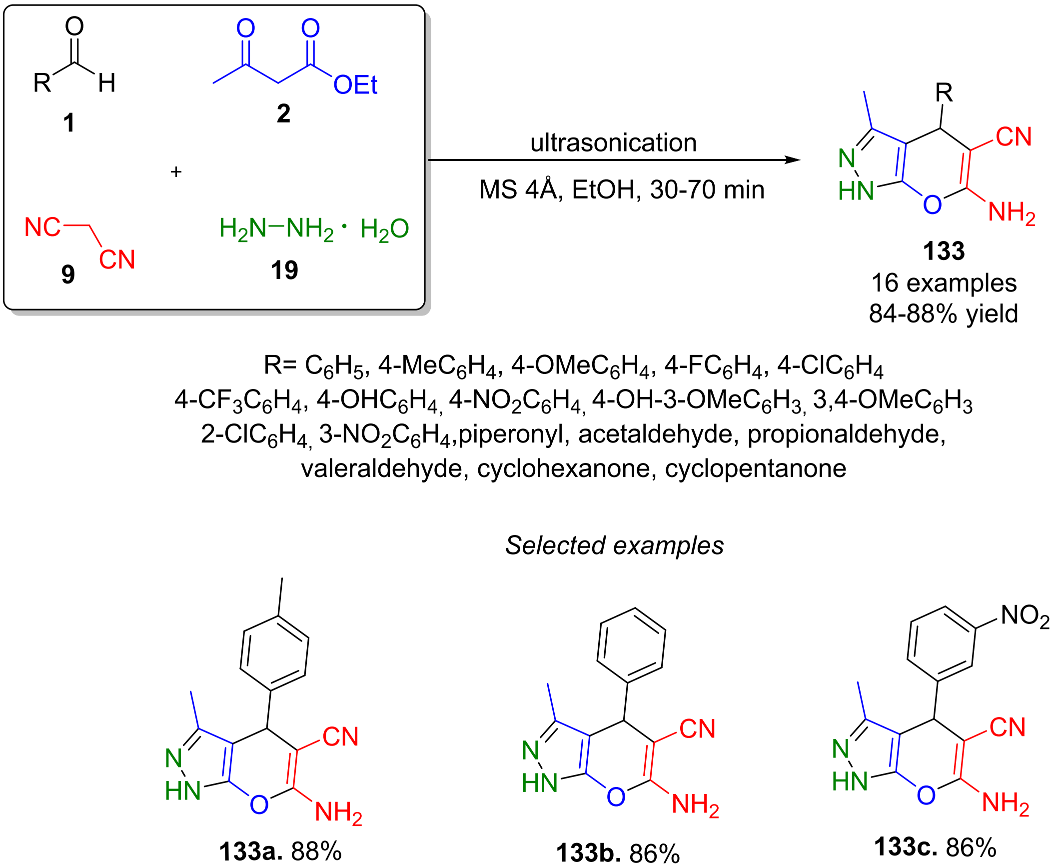
The 3-cinnamoyl coumarins (**137**) were synthesized by using a sonicated multicomponent reaction strategy via condensation of benzaldehydes (**1.a**), salicyaldehydes (**1.b**) and ethyl acetoacetate (**2**) (Scheme 50) [220] in presence of a new mesoporous catalyst $CoCl_2$NN'PhBIA/Al-SBA-15 (0.07 w/w %). The reactions were carried out in a multilayer ultrasound producer involving a Ti transformer and vibrator (horn) (diameter = 12.5 mm), working at 20 kHz and power of 55 W. Various solvents were studied, and among them ethanol was more effective. The reaction time to obtain the 3-cinnamoyl coumarins derivatives ranged from 10 to 15 min, in which it was possible to produce 13 derivatives of 3-cinnamoyl coumarins with yields greater than 89%. According to the authors, the high surface area of the $CoCl_2$NN'PhBIA/Al-SBA-15 catalyst improves the reaction condition together with the cavitation effect generated by ultrasonic irradiation. The adopted mesoporous catalyst had its reuse capacity studied, and remained its efficient activity in up to 8 cycles, and the structure of the catalyst was analyzed before and after reuse by FT-IR.

2.3. Miscellaneous

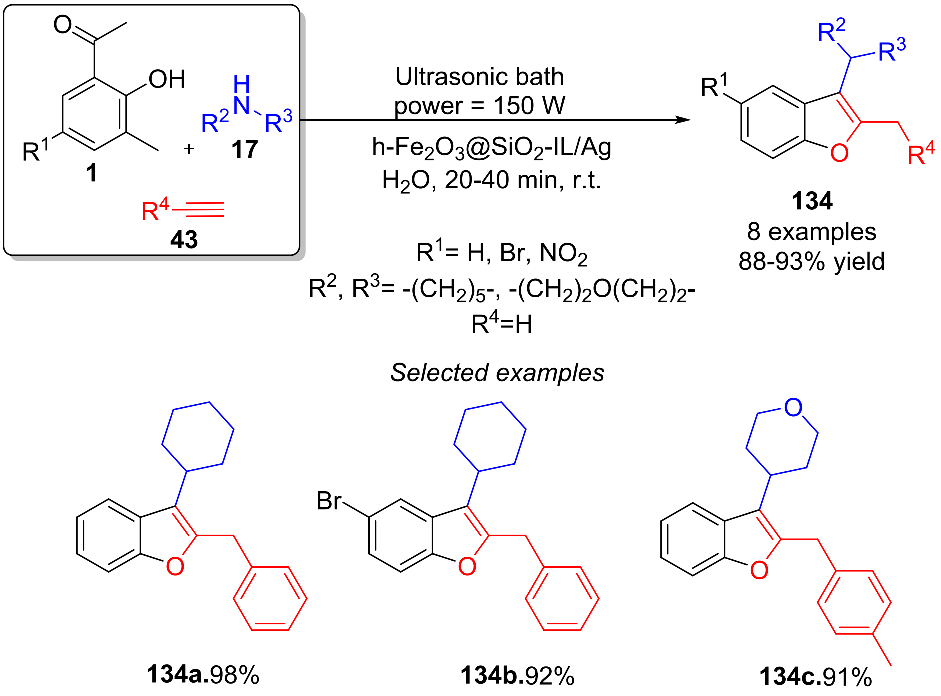
In this section, some examples of acyclic compounds prepared using MCRs under ultrasonic irradiation and heterogeneous catalysis are discussed.

2.3.1. β-Aminocarbonyl compounds

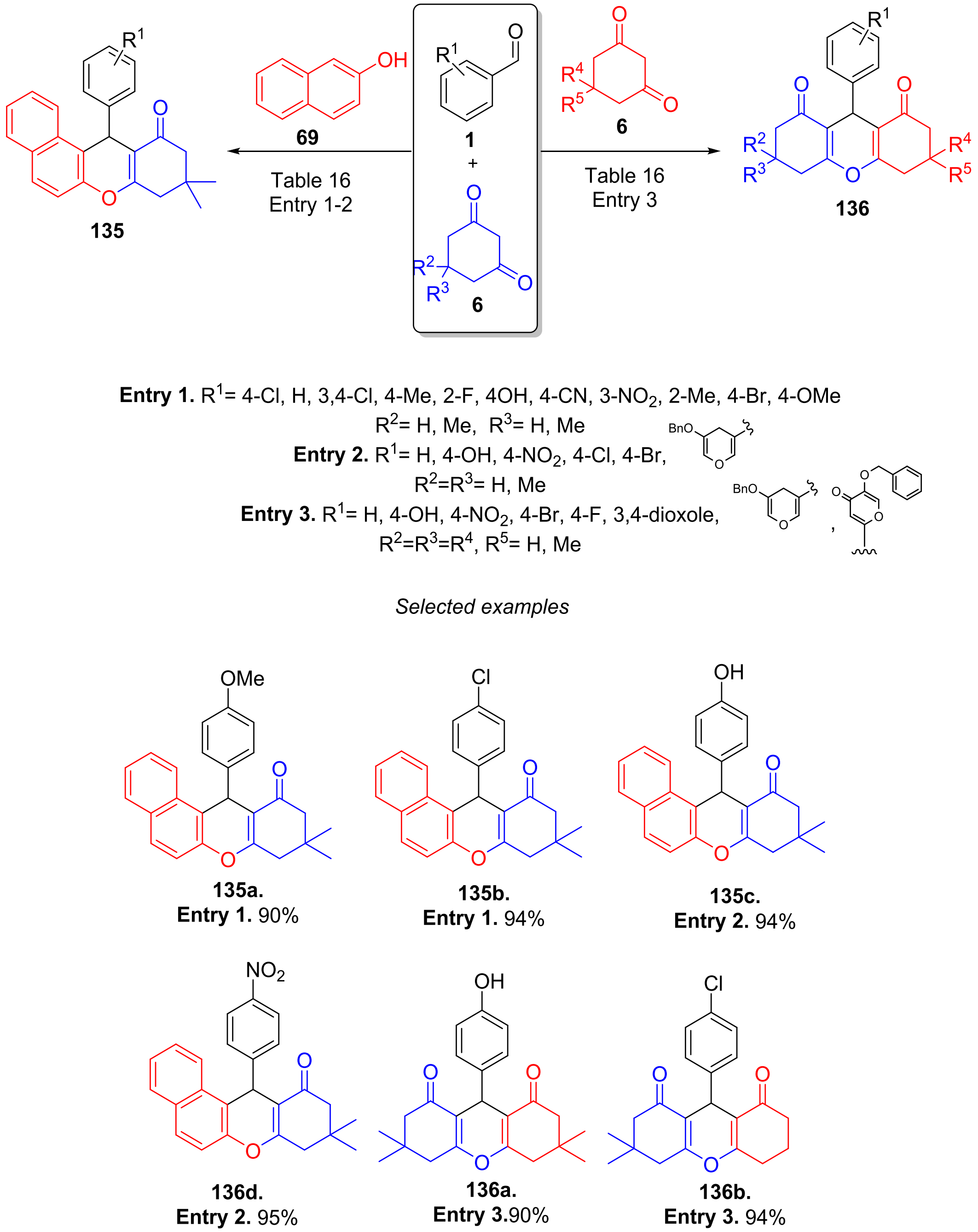
The β-amino carbonyl compounds are versatile synthetic intermediates, being found on the synthetic route of important pharmaceutical and natural products [221-223]. Achary and co-workers [104] have developed a cost-effective, environment friendly one-pot method based on the Mannich reaction for the ultrasound-assisted preparation of β-aminocarbonyl compounds (**138**) by copper oxide nanoparticles modified phosphate functionalized graphene (CuO/PGO, 10 mol %) catalysis, and under solvent-free conditions (Scheme 51). This method works via condensation of benzaldehyde (**1**), acetophenone (**8**) and



Scheme 47. One-pot two-step synthesis of dihydropyrano[2,3-*c*]pyrazole (**133**) in the presence of MS 4 Å and ultrasound waves.



Scheme 48. On water MCR for the synthesis of benzo[*b*]furans (**134**) by using ultrasound and Fe_2O_3@SiO_2-IL/Ag as nanocatalysis.



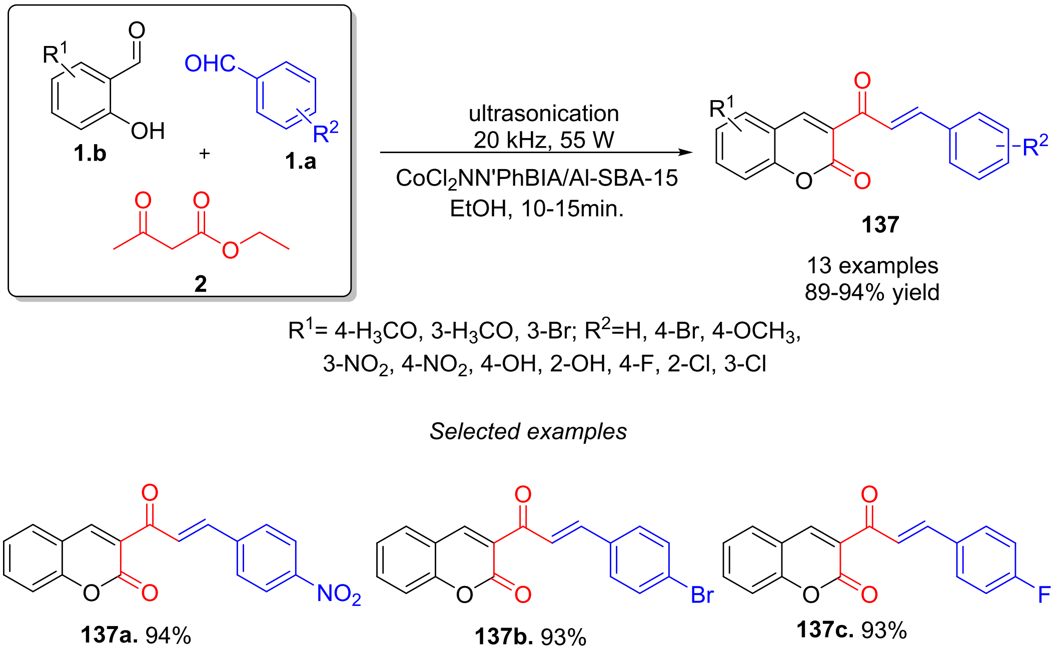
Scheme 49. One-pot protocol for the ultrasound-mediated synthesis of xanthenes **135** and **136** by using heterogeneous catalysis.

Table 16
MCR for the ultrasound-assisted synthesis of xanthene derivatives **135** and **136** by using reusable heterogeneous nanocatalysts.

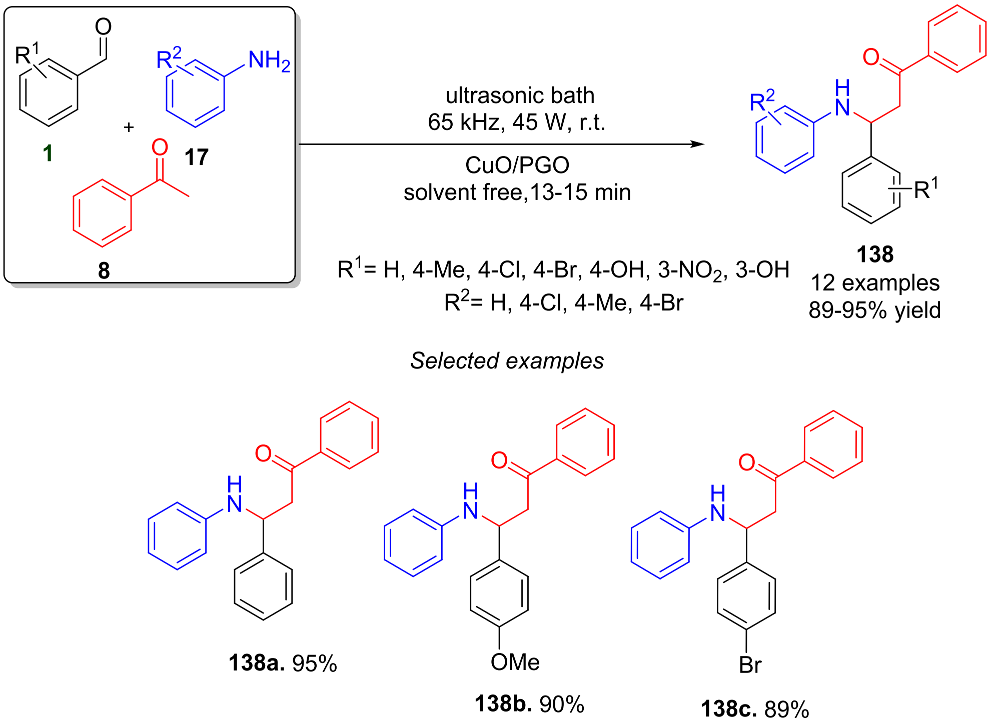
Entry	Catalyst	Conditions[a]	Examples	Yields (%)	Ref.
1	[CoFe$_2$O$_4$/OCMC/Cu(BDC)]	EtOH, 10–15 min	12	83–94	[134]
2	Fe-Cu/ZSM-5	H$_2$O, 5–9 min	6	94–95	[219]
3	Fe-Cu/ZSM-5	H$_2$O, 5–9 min	9	90–96	[219]

* Ultrasound parameters: Entry 1. ultrasound bath; frequency: 30 kHz, no more details were informed. Entries 2 and 3. Ultrasound device equipped with a processor probe, 12-mm-tip diameter; power: 40 % power of the processor. [a] reactions performed at r.t.

aniline (**17**). Ultrasonic syntheses were carried out in an ultrasonic cleaning bath (multi-frequency at 45 and 65 kHz). The reaction in the optimization phase was carried out in the presence of ultrasonic irradiation (45 W) and different catalytic systems, such as graphite only, GO only, PGO, CuO, physical mixture PGO + CuO and CuNPs; in all cases, there was only the formation of traces of the product. However, when combined the use of ultrasound with the mixed catalytic system CuO/PGO, the product of interest was obtained with excellent yields. The ultrasound-assisted reaction was also compared with other traditional stirring methods, and it was found that it provided greater gain in shorter reaction time, demonstrating the effective role of the ultrasonic process. The catalyst showed high stability and no significative lost in catalytic activity up to six reaction cycles.



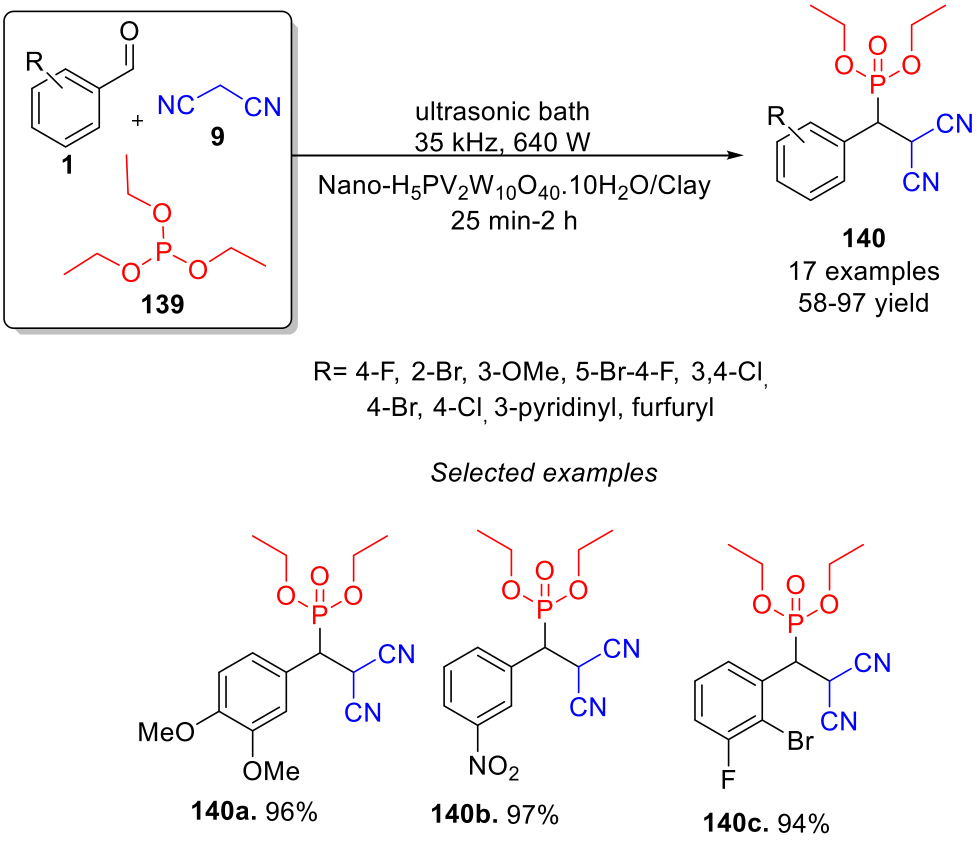
Scheme 50. Ultrasound-mediated MCR for the synthesis of 3-cinnamoyl coumarins (**137**) with the use of a mesoporous catalyst.



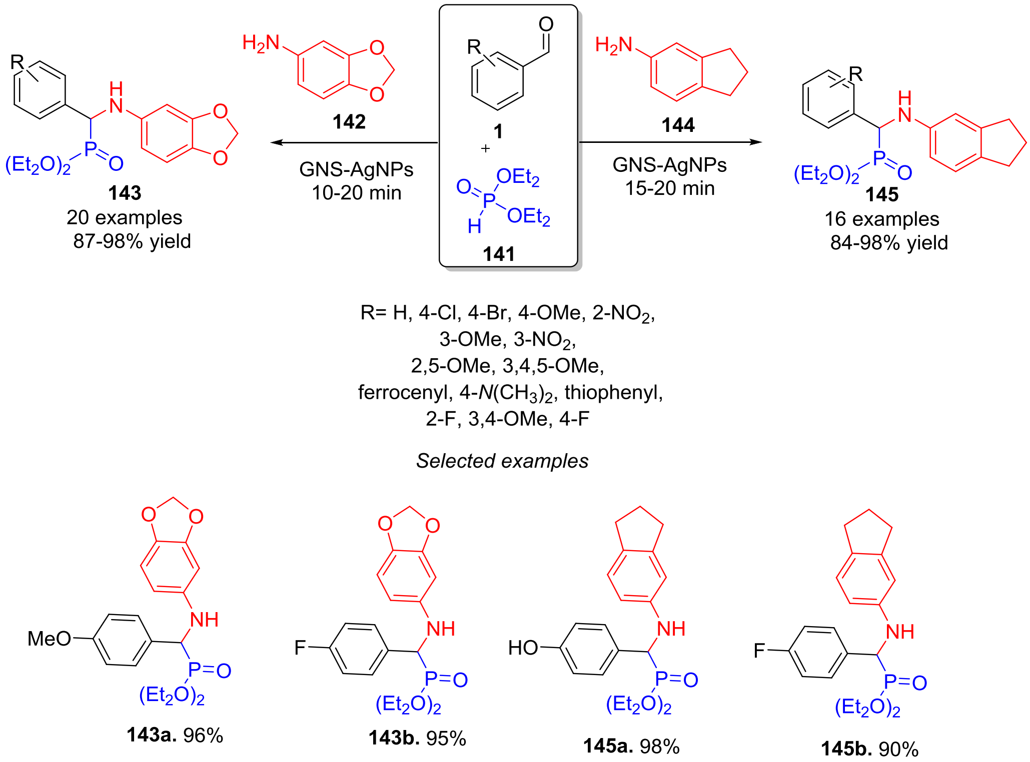
Scheme 51. Synthesis of β-aminocarbonyl compounds **138** by using CuO/PGO as catalyst and ultrasound in a solvent-free media.

2.3.2. *Phosphonate derivatives*

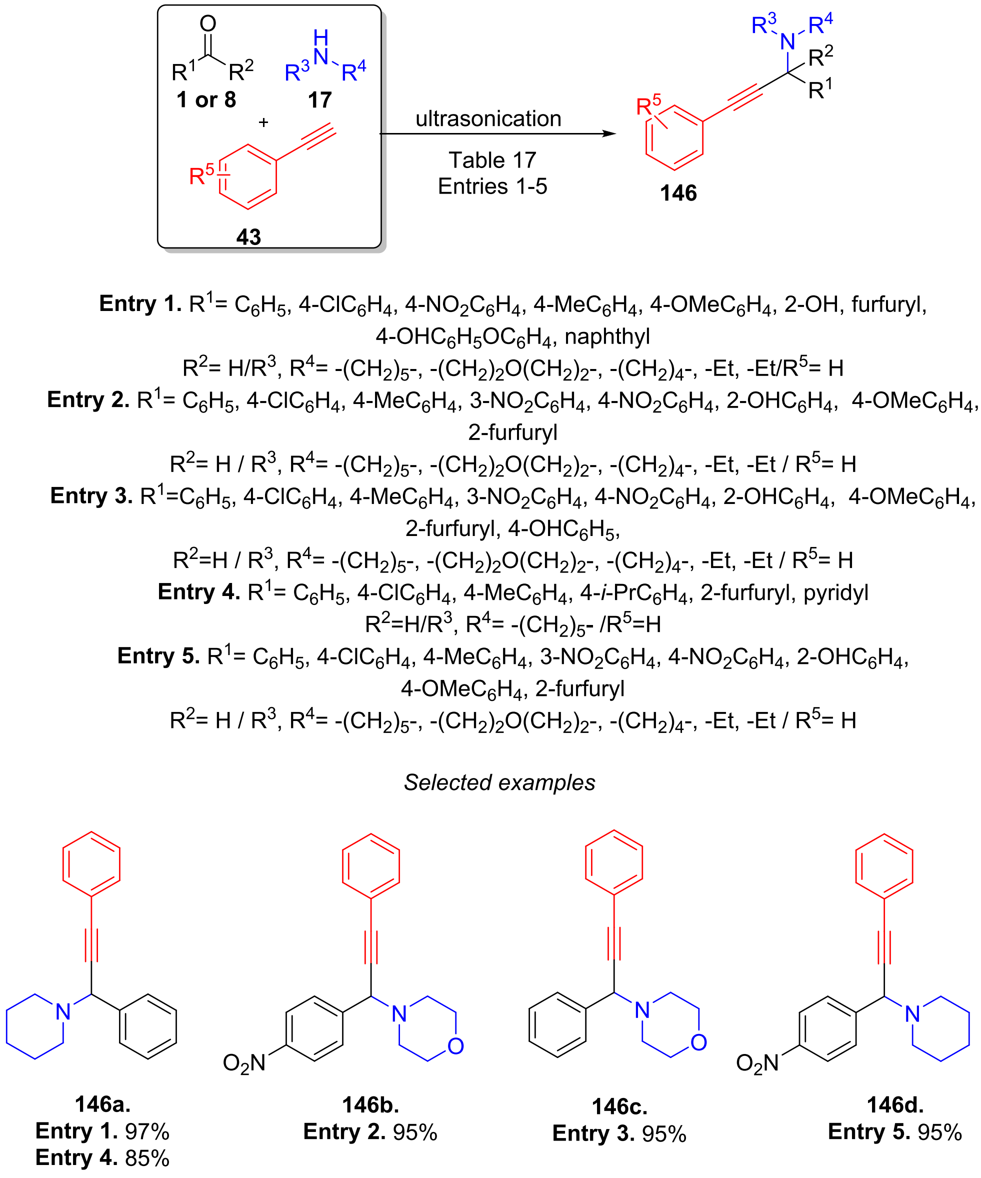
Phosphonates are important intermediates in organic synthesis, in addition to having an extensive list of biological activities [224–226]. In this scenario, the emergence of more ecologically viable synthetic methodologies to obtain these frameworks is desirable. Heteropolyacids (HPAs) are efficient catalysts in a series of chemical transformations [190,227–230], and having that in mind, Dar et al. (Scheme 52) [231] have combined the properties of HPAs and clay - material with wide application in heterogeneous catalysis as solid supports [232–234] – in the development of a nanocatalyst (Nano-$H_5PV_2W_{10}O_{40}\cdot 10H_2O$/Clay) for the synthesis of β-phosphonomalononitriles (**140**). The MCR was carried out using benzaldehyde (**1**), malononitrile (**9**), and triethyl phosphite (**139**) under ultrasonication, at room temperature and solvent-free media. The reactions were carried out in an ultrasonic bath dispositive at room temperature, frequency of 35 kHz and ultrasonic peak output of 640 W. The method, that works under low amount of the nanocatalyst (1.2 w/w %), furnished products with higher purity and yields and no need to purification via chromatographic column, but



Scheme 52. Synthesis of *β*-phosphonomalononitriles (**140**) in presence of nano-heteropoliacid-clay hybrid catalyst and ultrasonic irradiation.



Scheme 53. Graphene nanosheets-silver nanoparticles as nanocatalyst in the synthesis of *α*-aminophosphonates (**143** and **145**) by ultrasonic radiation.



Entry 1. R^1= C_6H_5, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 4-MeC_6H_4, 4-$OMeC_6H_4$, 2-OH, furfuryl, 4-$OHC_6H_5OC_6H_4$, naphthyl
R^2= H/R^3, R^4= -$(CH_2)_5$-, -$(CH_2)_2O(CH_2)_2$-, -$(CH_2)_4$-, -Et, -Et/R^5= H
Entry 2. R^1= C_6H_5, 4-ClC_6H_4, 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-OHC_6H_4, 4-$OMeC_6H_4$, 2-furfuryl
R^2= H / R^3, R^4= -$(CH_2)_5$-, -$(CH_2)_2O(CH_2)_2$-, -$(CH_2)_4$-, -Et, -Et / R^5= H
Entry 3. R^1=C_6H_5, 4-ClC_6H_4, 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-OHC_6H_4, 4-$OMeC_6H_4$, 2-furfuryl, 4-OHC_6H_5,
R^2=H / R^3, R^4= -$(CH_2)_5$-, -$(CH_2)_2O(CH_2)_2$-, -$(CH_2)_4$-, -Et, -Et / R^5= H
Entry 4. R^1= C_6H_5, 4-ClC_6H_4, 4-MeC_6H_4, 4-*i*-PrC_6H_4, 2-furfuryl, pyridyl
R^2=H/R^3, R^4= -$(CH_2)_5$- /R^5=H
Entry 5. R^1= C_6H_5, 4-ClC_6H_4, 4-MeC_6H_4, 3-$NO_2C_6H_4$, 4-$NO_2C_6H_4$, 2-OHC_6H_4, 4-$OMeC_6H_4$, 2-furfuryl
R^2= H / R^3, R^4= -$(CH_2)_5$-, -$(CH_2)_2O(CH_2)_2$-, -$(CH_2)_4$-, -Et, -Et / R^5= H

Selected examples

146a. **Entry 1.** 97% **Entry 4.** 85%

146b. **Entry 2.** 95%

146c. **Entry 3.** 95%

146d. **Entry 5.** 95%

Scheme 54. Sonochemical synthesis of propargylamines (**146**) mediated by heterogeneous catalysts.

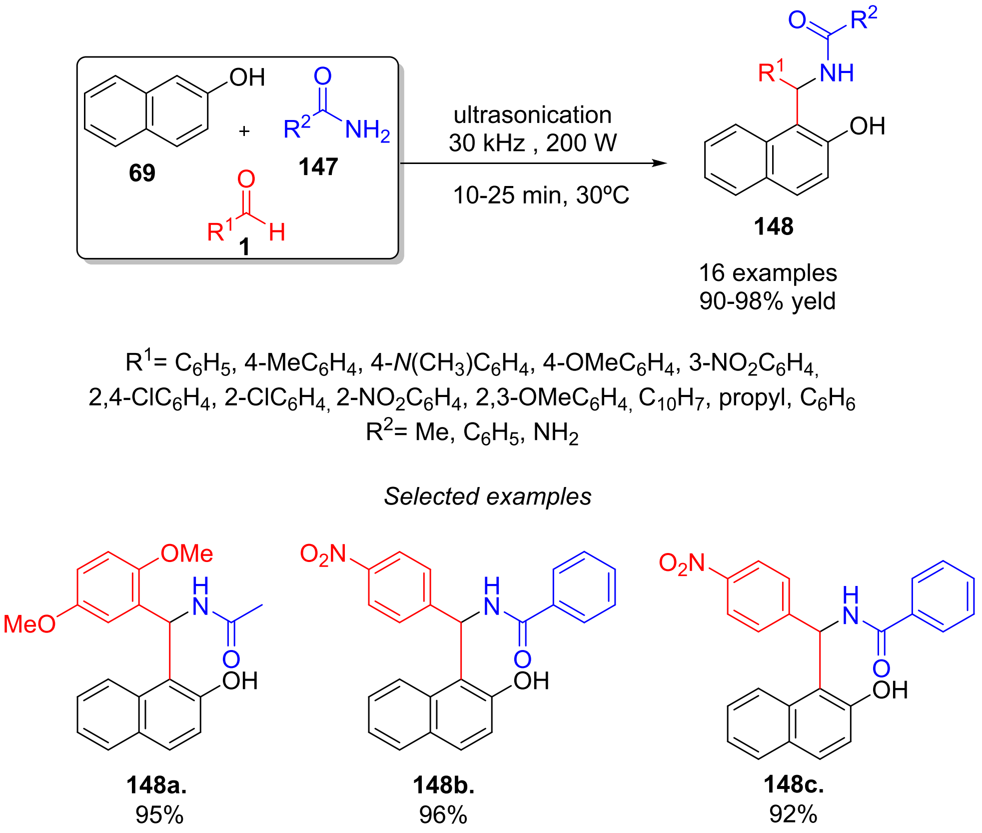
simply recrystallization., in short reaction time. Besides, the authors discussed that the catalyst could be easily recovered and reused in up to five cycles without significant loss of its catalytic activity.

In the same trend, the Rasal group [103] has synthesized a series of novel α-aminophosphonate derivatives (**143** and **145**) via a one-pot procedure based on Kabachnik–Fields reaction, by the consensation of 5-aminoindan (**142**) or 3,4-(methylenedioxy)aniline (**144**), aromatic aldehydes (**1**) and diethyl phosphite (**141**) by employing graphene nanosheets-silver nanoparticles (GNS-AgNPs) as nontoxic and versatile catalyst under ultrasonication, solvent-free and at room temperature (Scheme 53). The catalyst was prepared *in situ*, which is one more feature that adds more sustainability to the synthetic method. The reactions were performed using a multi-wave ultrasonic cell crusher, equipped by a converter/transducer and titanium oscillator (horn). When the reaction was performed in the absence of a catalyst and under ultrasonic irradiation, the product of interest was formed in low yields. However, when the ultrasound was associated with the use of the nanocatalyst GNS-AgNPs (2.4 w/w %) there was an important increase in the reaction yield. In a comparison made with other catalytic systems previously reported for the synthesis of α-aminophosphonates, GNS-

Table 17
Sonicated protocols for the synthesis of propargylamines (**146**) mediated by heterogeneous catalysts.

Entry	Catalyst	Conditions[a]	Examples	Yields (%)	Ref.
1	h-Fe_2O_3@SiO_2-CD/Ag	7–20 min	19	85–97	[238]
2	CuI@HNTs-2N	EtOH, 10–25 min	13	85–95	[239]
3	Ag@HNTs-T	18–37 min	40	82–95	[241]
4	LAIL@/Fe_3O_4/MNPs	Solvent-free, 45–90 min, 80 °C	8	39–85	[126]
5	h-Fe_2O_3@SiO_2-IL/Ag	8–30 min	40	80–95	[215]

*Ultrasound parameters: Entries 1 and 5. Ultrasound bath, 70 W of power; no more details were informed. Entry 2. Ultrasound bath at r.t.; power of 150 W, no more details were informed. Entry 3. Ultrasound bath, r.t.; power: 100 W, further details were not informed. Entry 4. Ultrasound device operating at frequency of 37 kHz and 80 °C; no further details were informed. [a]Reactions performed at r.t and using H_2O as solvent.



Scheme 55. Sonicated synthesis of 1-amidoalkyl-2-naphthol derivatives (**148**).

AgNPs showed superior catalytic behavior, providing the best yields. This system also showed excellent catalytic performance in the reaction performed on a gram scale. Regarding recyclability and reuse, the nanocomposite could be recovered and reused up to five times, without affecting the catalytic activity.

2.3.3. *Propargylamines*

Propargylamines are gaining more and more importance in the research field related to neurodegenerative diseases [235–237]. Seeking greener routes to obtain these important frameworks, efficient synthetic approaches assisted by ultrasound and mediated by modern and reusable nanocatalysts were developed, based on the one-pot condensation of aldehydes (**1**) or ketones (**8**), amines (**17**) and phenyl acetylene (**43**), in the presence of green solvents (Scheme 54). Sadjadi and co-workers, for example [238] have developed a reusable Fe_2O_3/MNPs/Ag-doped core–shell (h-Fe_2O_3@SiO_2-CD/Ag) nanocatalyst and use it in the establishment of a protocol for preparing the propargylamines **146** (Table 17, Entry 1). First, the reaction was performed in the presence of the nanocomposite via reflux and the product was obtained with good yield, which motivated the authors to investigate the influence of ultrasonic irradiation. Interestingly, the reaction carried out via ultrasound has considerably increased the yields, in a shorter reaction time. The power of the ultrasonic irradiation was also investigated, and the best value was 70 W. The efficiency of this protocol and the performance of h-Fe_2O3@SiO_2-CD/Ag to catalyze the reaction in only 0.09 w/w % was compared with that of some catalytic methodologies previously reported, showing its superiority. The nanocatalyst could be reused for up to four runs, with slight loss of catalytic activity.

Moreover, the Sadjadi group [239] has reported the use of CuI@amine-functionalized halloysite (CuI@HNTs-2 N) for one-pot preparation of propargylamines. The reaction was carried out primarily via reflux in EtOH, in the presence of the nanocomposite (9.2 w/w %), leading to a 93% yield (Table 17, Entry 2). When ultrasound was used, keeping the other parameters constant, this reaction led to obtaining the product of interest in greater yield and in a reaction time 1.5 times shorter. Ultrasonication were performed in a device with output power of 150 W and tip TT13. Also, in comparison with other catalysts reported in the literature to promote the same transformation, CuI@HNTs-2 N showed the best performance. The nanocomposite could be reused up to five runs of reactions, without significative loss in catalytic efficiency.

Continuing the studies with nanocatalysts based on Halloysite nanotubes, Malmir et al. [240] developed a novel heterogeneous catalyst for the green synthesis of propargylamines: Ag@HNTs-T (Table 17, Entry 3). In the optimization study, the reaction was carried out without ultrasound and catalyst, in which case the product was not formed. In the presence of catalyst (0.12 w/w %) and ultrasonic irradiation (100 W), the product was formed in short reaction times and with excellent yields. In terms of reuse, the Ag@HNTs-T was one of the most efficient nanocomposites among those mentioned in this review, since after a recovery process, consisting of EtOH washing and drying, this nanocomposite proved to be active in up to ten consecutive reactions, without severe losses in catalytic activity.

Using the methodology discussed in section 2.1.1, with some modifications, Nguyen et al. (Table 17, Entry 4) [126] also synthesized a series of propargylamines in high yields. Moreover, in a work already mentioned (section 2.2.2), Sadjadi and co-workers (Table 17, Entry 5) [215] have reported the preparation of propargylamines with excellent yields.

2.3.4. *1-Amidoalkyl-2-naphthol derivatives*

MCR methodologies mediated by ultrasonic irradiation and nanocatalysis were developed for the preparation of 1-amidoalkyl-2-naphthol derivatives (**48**), an important class of compounds that showed inhibition of acetyl- and butyrylcholinesterases (AChE and BChE, respectively) that are target to the treatment of neurodegenerative diseases [242]. These synthetic approaches are based on one-pot condensation between β-naphthol (**69**), aldehydes (**1**), and amides (**147**), under solvent-free conditions (Scheme 55). In this sense, the Safari group [243] skillfully synthesized a series of compounds using a new heterogeneous nanocatalyst composed of ionic liquid immobilized in Fe_3O_4/MNPs (MNPs-IL-OAc) in a solvent-free medium (Table 18, Entry 1). The reactions were carried out by a multiwave ultrasonic, equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 30 kHz with a maximum power output of 200 W. In the optimization study, the reaction was performed in the presence of several catalytic systems, and in all cases under ultrasonic irradiation at 60 °C. The results obtained indicated that, in the absence of catalyst, only traces of the product of interest were formed, but in the presence of nanoparticles of MNP-IL-OAc (0.19 w/w %), the reaction proceeded with high yield. To investigate the influence of ultrasonic irradiation on the method, the model reaction was also performed under optimized conditions under conventional heating, and the results showed superiority for the sonicated condition, in terms of yield of the desired product, but also and, mainly, in relation to reaction time. After a very simple recovery process, the nanocomposite showed potential for reuse in a cycle of up to seven consecutive reactions, showing a slight loss of catalytic efficiency after the third cycle.

3. Conclusion

The development of greener synthetic methods to achieve new structurally diverse compounds with remarkable biological properties has been extensively explored in the last decades. In this perspective, this review compiles multicomponent reactions to obtain *N*- and *O*-heterocyclic as well as acyclic compounds by greener protocols, with focus on ultrasonic irradiation, green solvents, and heterogeneous catalysis. The spectrum of applications of synthetic methods presented herein demonstrate the importance of this approach to promote more environmentally protocols, that results in short reaction times, less energy consumption and easy recycle of the heterogeneous catalysts.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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