Green Chemistry: Organic Transformation towards Sustainable Development

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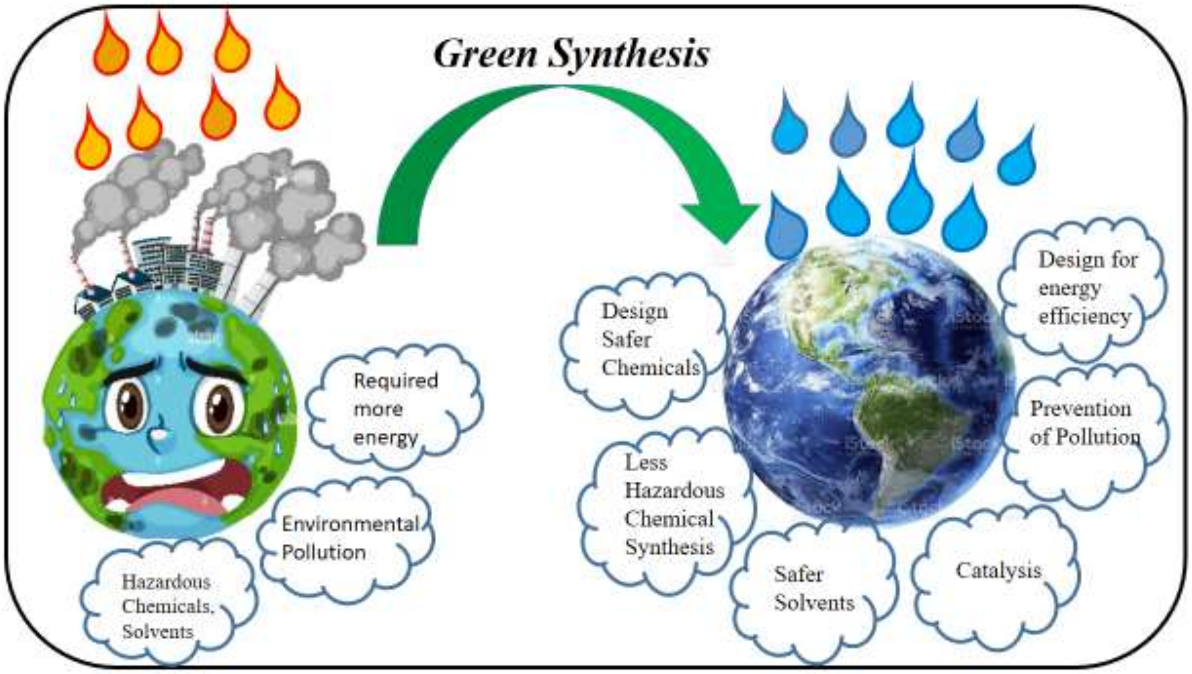
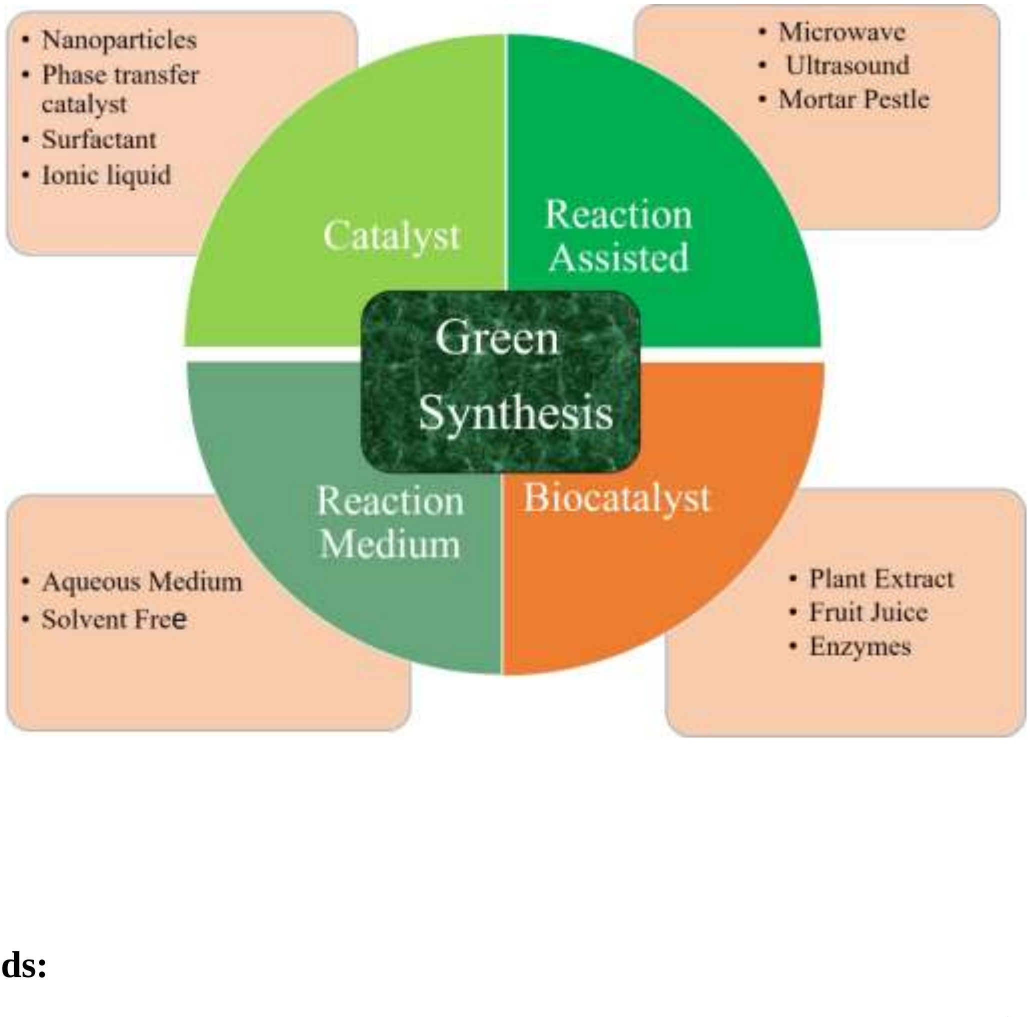


Abstract:

Traditionally, researchers used organic solvents and catalysts which are hazardous for human health and environment. Now-a-days researchers used water as a green solvent and many green catalyst such as nanoparticles, phase transfer catalyst, ionic liquid and biocatalyst, natural surfactant for organic transformation. Many reactants are insoluble in aqueous medium so reaction is not proceed, to overcome this problem there is need to add a substance which has hydrophilic property and tendency to dissolve all reactants in aqueous medium. Surfactant has such hydrophilic properties and it processed reactions in aqueous medium. Another greener method such as reaction assisted in microwave, ultra-sonicator and mortar pestle which are time reducing, eco-friendly method and renewable energy source. In this way we report herein synthesis of various biological active organic scaffolds by greener and environment benign methodology.

Graphical Abstract:



Keywords:

Biocatalyst, Ionic liquid, Microwave, Mortar pestle, Nanoparticles, PTC, Sonicator, Surfactant, Water.

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1. Introduction:

The main principle of green chemistry is the protection of environment from hazardous chemicals which are used in chemical reaction. Green chemistry means the elimination of hazardous solvent from chemical processes and eliminate of hazardous/organic catalyst by green catalyst [1]. The catalysis concept was given by the chemist Elizabeth Fulhane in 1794. In organic chemistry the first chemical reaction that utilized a catalyst was studied in 1811 by

Gottlieb Kirchhoff who invented the acid-catalyzed conversion of starch to glucose. Catalyst is used in chemical reaction for increase the rate of reaction. Catalysts are not consumed in the chemical reaction, it remains unchanged after the reaction. Catalysts react with one or more precursors which are used in chemical reaction to form intermediates and it gives the final reaction product.

There are three types of catalysis such homogeneous catalysis, heterogeneous catalysis and biocatalyst. Homogeneous catalysts means catalyst and reactant are in same phase. Generally, homogeneous catalysts are dissolved in a solvent i.e. it cannot be separable from reaction mixture. Homogeneous catalyst is similar to organometallic catalyst for inorganic chemist. Heterogeneous catalysis means catalyst and reactants of a reaction are in different phase. Most of the heterogeneous catalysts are solid in phase. Heterogeneous catalysts are supported catalyst means that the catalyst is dispel on the another material that increase the effectiveness or minimizes their cost [2]. Many heterogeneous catalysts are nanomaterials. Biocatalysts are the intermediate between homogeneous and heterogeneous catalysts, although homogeneous catalyst is soluble enzyme and the heterogeneous catalyst is membrane bound enzymes. An aqueous solution means the solution in which the water as a solvent. Because water is more abundant in nature and it is universal solvent.

Many scientists, use organic solvent for carry the organic reaction but it is dangerous for human health and environment also. From past decade, water is not used as solvent in organic synthesis owing to many organic compounds are not dissolve in water so reaction is not further carried out. Water is polar solvent and we know like dissolves likes [3]. So, only polar compounds are dissolved in water. But now a days scientists used water as a solvent for organic synthesis because it is natural solvent and it is environment friendly, this gives the production of organic compound by green method and follows all principles of green chemistry.

The great development in green synthesis is solvent-free reaction. But, although many reactions required the use of solvent. An ideal green solvent is water, it is non-flammable, non-toxic, easily available and inexpensive. Many reactions are performed at room temperature but it is time consuming. So, now-a-days greener and rapid techniques are used for perform the reactions such as microwave assisted reaction, ultrasound assisted reaction and also reaction carried out in mortar pestle. These organic synthesis carried out in aqueous as well as solvent free medium. There are the greener techniques and medium for carried out the organic synthesis. Traditionally, we used many organic solvent, catalyst which are hazardous for environment. So now we used the greener solvent and catalyst, such as ionic liquid, surfactant, hydrophilic auxiliary, phase transfer catalyst, nano-particles for synthesis of organic compound. Catalytic reactions processed in water assistance the field of sustainable organic synthesis.

Ionic liquids are used as a greener solvents for synthesis of organic compound. It is also used as biocatalyst in organic synthesis [4]. Biocatalysts considered as a green catalyst because of their low toxicity, low-flammability. Fruit juice, plant extract and enzyme are used as biocatalyst. Fruit juice like lemon, kiwi, pineapple, tamarind, sapindumtrifolistus, coconut are used as biocatalyst in synthesis [5]. Surfactant is used as a catalyst in organic synthesis. There are two types of surfactants, bio-surfactant and chemical surfactant. Bio-surfactant is much more efficient than chemical surfactant because bio-surfactant is ecofriendly, hazardless and less toxic. The chickpea leaf exudates is used as a bio-surfactant in organic transformation [6]. Phase transfer catalyst is applied in organic transformation. It is soluble in both solvents and returns them into the water phase. Due to this reactions processed under mild conditions with simple work up procedures. Therefore, the ionic liquids are used industrially. Crown ether, quaternary ammonium salts and phosphonium compounds are the examples of PTC [7].

Reactions conducted in aqueous medium but many reactants are not soluble in water so this restriction is overcome by the use of surfactants. The presence of micelles enables to accelerate the chemical reaction in aqueous media [3]. So it is a green approach towards the synthesis of organic compound.

Chemical reactions are act as the heart in all chemical processes in which reactant molecules are converted into the product by forming an intermediate. In the chemical processes catalyst plays an important role for formation of product without producing toxic material. In the chemical processes used green give the ecofriendly product.

In past decade the synthesis of chemical by stoichiometric reaction by using inorganic salt in synthesis such as metal like Na, Mg, Zn, Co and also used Lewis acid in the reaction which generate the waste from reaction is more than product yield. So catalysis used is reaction is more beneficial than stoichiometric reaction. Due to catalysis, there is minimization of energy in chemical reaction. So, use solid catalyst in organic synthesis which produced green product with fast rate and this catalyst work under mild reaction. Lots of wastes generated in many organic synthesis and they produced pollution in environment and posing serious health hazards. Many important green technologies are being explored to effectively control ill effects related to manufacture and use of chemicals. So, use of catalyst in organic synthesis is the best way for green synthesis.

Catalysis is the process of adding a catalyst to processed a reaction. Catalysis help to green chemical processes and also the demonstration of their value to reduce the environmental impact and reduce the costs of the processes will catalyze the greening of chemistry.

Catalyst is a substance that increases the rate of reaction by changing the reaction mechanism. A true catalyst is reform at the point in the reaction mechanism, and need only present in sub stoichiometric amount. Also, a true catalyst does not change. There are many characteristics of catalyst such as catalyst may undergo physical changes but not chemical, little amount of catalyst is sufficient for catalysis, catalyst activates the rate of reaction but cannot initiate it, catalytic activity is more at ambient temperature, in forward and backward reaction catalyst lowers the activation energy and also minimizes the threshold energy.

In this way the use of green solvent such as water and use of green catalyst such NPs, PTS etc. in the organic synthesis is useful for environment without any worse effect on human health and other organism in the environment. Sustainability is the aim of our research and green chemistry means to achieve this aim by synthesized the product by green method.

A review on this subject is presented herein with particular point up on the distinguished role of green solvent and green catalyst in a chemical reaction that have been advanced over the past decade.

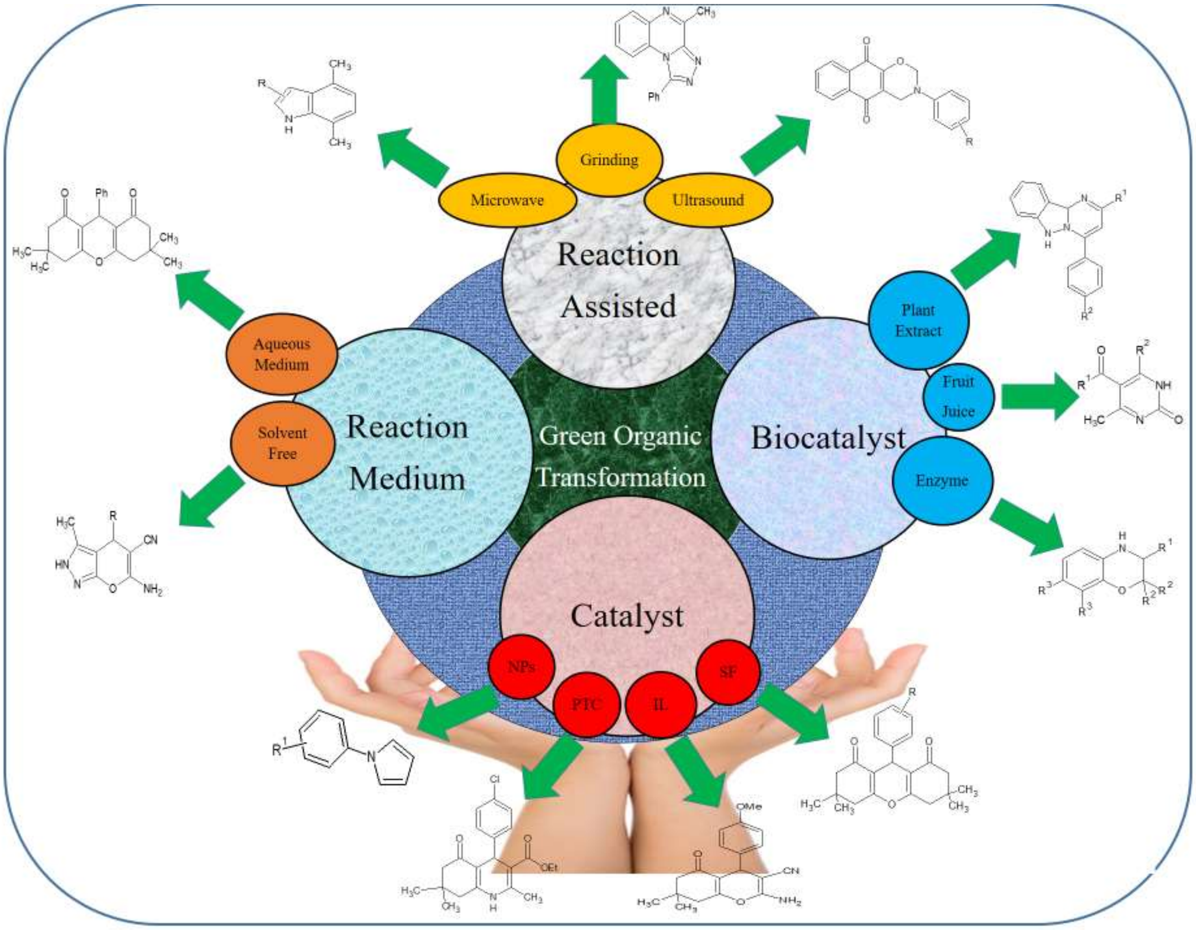


Fig. 1 Greener ways for organic transformations.

2. Catalyst:

Catalyst is a substance that speeds up a chemical reaction without itself being consumed during the reaction. Catalyst is used in chemical reaction then it increase the rate of chemical reaction and decrease the waste in reaction and gives more yield than conventional reaction. So, use of catalyst in reaction gives the green synthesis. There are three types of catalysis in organic synthesis such as homogeneous catalysis, heterogeneous catalysis and biological catalysis. Homogeneous catalyst means the reaction in which reactants and catalyst are in same phase. It cannot separated from reaction mixture. Heterogeneous catalyst means the reaction in which reactants and catalyst are in different phase. It can be separated from reaction mixture. It is reusable in another reaction. Biological catalysis is pH sensitive and more stable. Catalyst is classified as nanoparticles, ionic liquid, surfactant and phase transfer catalyst.

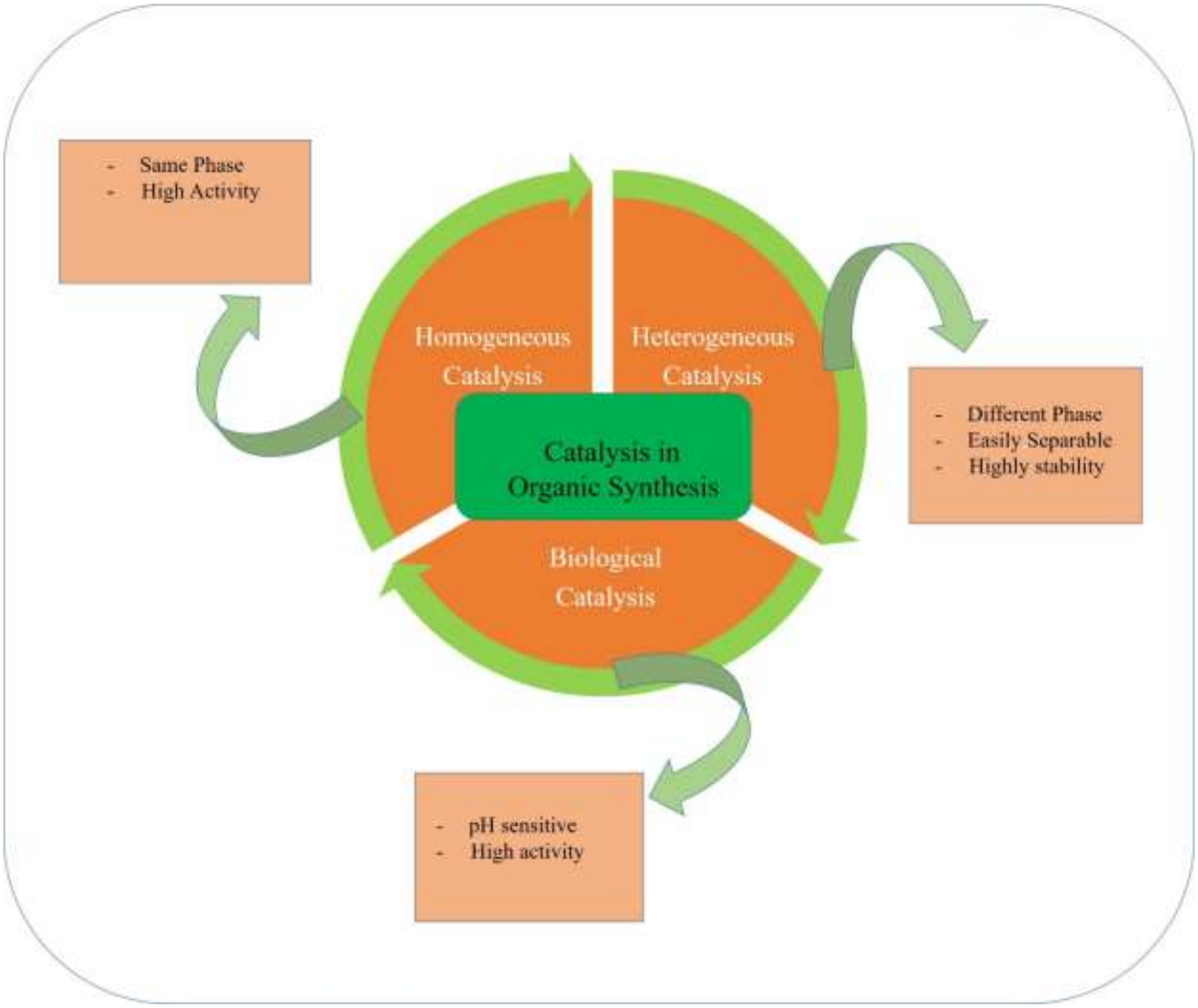


Fig. 2 Different types of catalysis and its application in organic transformations.

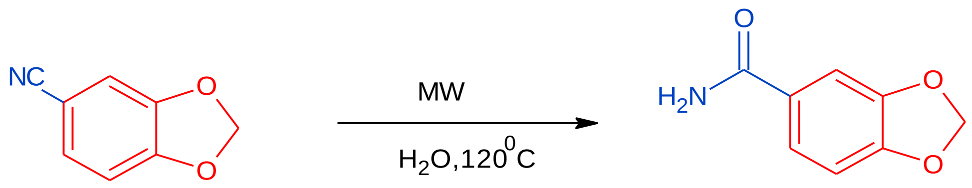
2.1 Nanoparticles:

Nanoparticles are more sustainable than conventional catalyst such as it provide high surface area, act as heterogeneous catalyst and give support for processed the reaction. Nano sized particles increase the contact between reactant and catalyst so gives the high yield of product. They are many types of nanoparticles such as metal NPs, bimetallic NPs etc.

The term nanotechnology is coined by the Nobel Laureate Richard Feynman. Nanotechnology give a various material with various nanoscale ranging from 1-100 nm. Nanoparticles contain a materials which has 0D (zero dimension), 1D, 2D and 3D. Nanoparticles are different in size, due to changing its physicochemical properties. As size of nanoparticle is changes then the appearance of nanoparticles also changes. Nanoparticles are small in size so when it used in the reaction and it provides the large surface area for reaction. Nanoparticles are classified into different types based on their morphology, size and its chemical properties. Mainly nanoparticles are classified into metal nanoparticles (MNPs), carbon-based NPs, ceramics NPs, polymeric NPs, and this classification is based on physical and chemical characteristics [8].

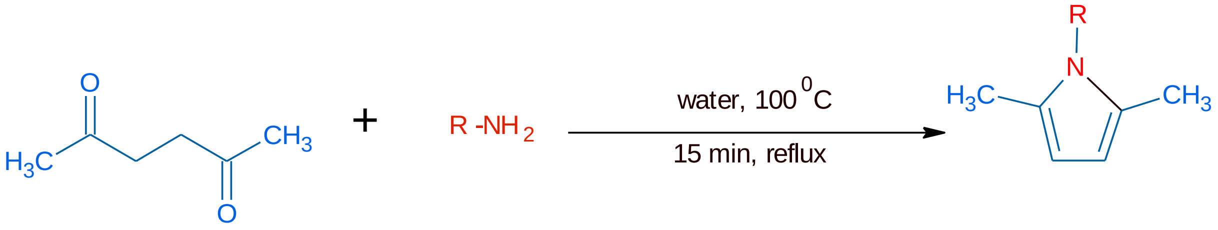
Nanoparticles are synthesized by two different methods such as top-down method and Bottom-up method. In top-down method, preparation of nanoparticles starting from larger molecules which are decomposed into smaller molecules then this molecules are converted into nanoparticles. Comparing both the methods, bottom-up method is green method for synthesis of nanoparticles. Because of their feasibility, less toxicity and cost effective. In this method, synthesis of nanoparticles by biological method such as by using plant extract and enzyme. The characterizations of nanoparticles are done by various methods like SEM, TEM and XRD etc.

Vivek polshettiwar and R. varma reported a use of Ruthenium hydroxide nanocatalyst which gave high activity for hydration of a range of activated, inactivated and heterocyclic nitriles in aqueous medium. The rate of reaction is not depend the nature of substituent on benzonitrile which proved the high catalytic activity and showed high chemoselectivity during hydration of benzonitrile containing dioxole ring. The reaction carried out in Mw in aqueous medium provide the high rate for reaction due to there is interaction of Mw with polar nanocatalyst. The catalyst used in reaction is paramagnetic in nature. So, catalyst is easily removed by external magnet without doing filtration (Scheme 1) [9].



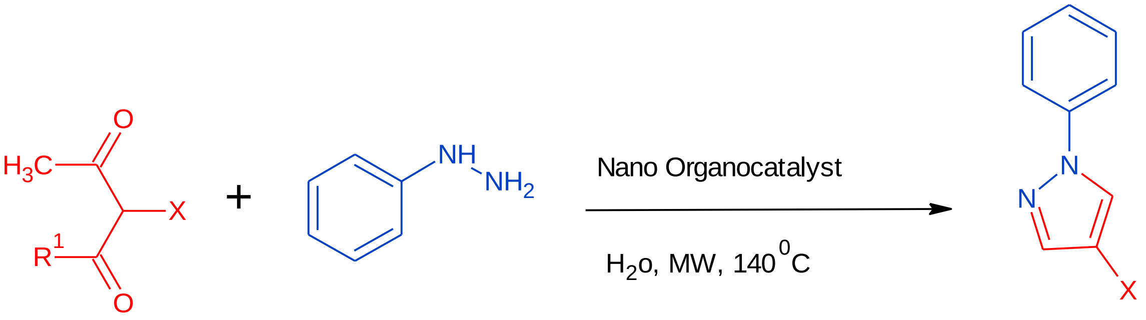
Scheme 1: The nano-Ru(OH)x catalysed hydration of cyanide.

Dilek Akbaşlar et al. reported a synthesis of pyrrole derivative from diketone and amine. The aqueous medium was used for the synthesis of pyrrole. It required 15 min for the completion of reaction. The reaction carried out in reflux at 100 °C. (Scheme 2) [10].



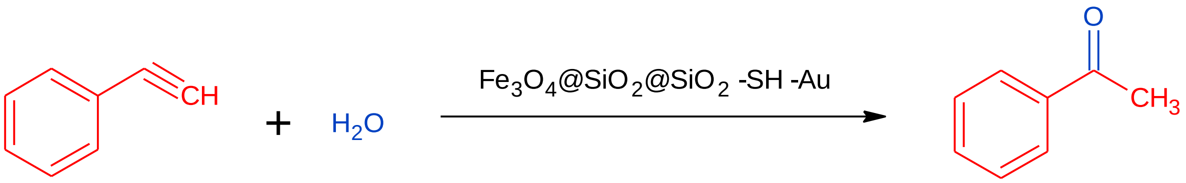
Scheme 2: Synthesis of pyrrole derivatives.

D. Gaikwad et al. developed a reaction in which hydrazine and 1, 3 diketones reacted to each other and produce pyrazole in good yield. These reaction processed in aqueous medium and take less than 20 min for completion. It is carried out under MW irradiation. The glutathione based nanoorganocatalyst was used for this reaction and this catalyst is paramagnetic in nature so it is easily separated by external magnet. Due to this use of organic solvent for catalyst recovery and product recovery is decreases (Scheme 3) [11].



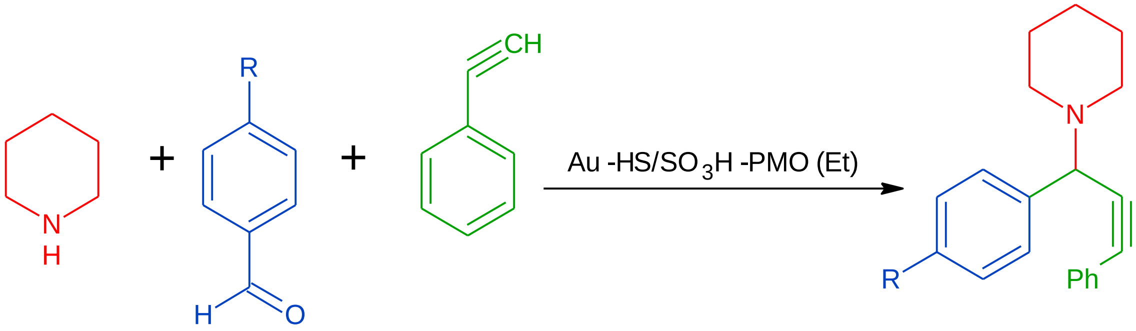
Scheme 3: Pyrazole synthesis using nanoorganocatalyst.

Shahnaz Rostamizadeh and co-workers reported a hydration of alkyne by using Fe_3O_4@ SiO_2 @ SiO_2-SH-Au super magnetic nanocatalyst. This reaction also carried out in solvent free condition. But the recyclability of catalyst was showed in hydration of phenylacetylene. The catalyst was recovered by magnet and it was used for next reaction (Scheme 4) [12].



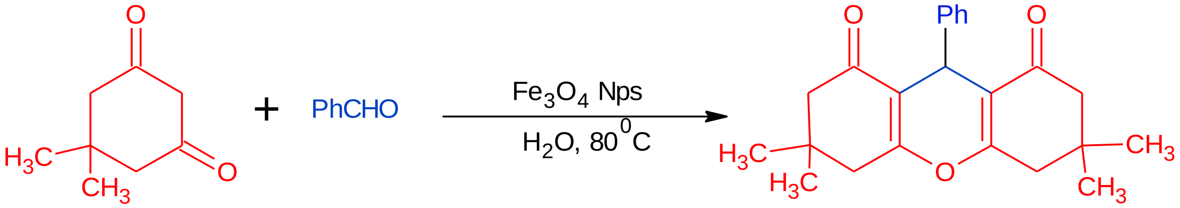
Scheme 4: Hydration of phenylacetylene by using Fe_3O_4@ SiO_2 @ SiO_2-SH-Au nanocatalyst.

Feng Zang et al. reported a “one pot” A^3- coupling reaction in presence of catalyst. In this reaction they used Au-NCP-MPs catalyst. In this reaction they used three reactant to form product. Au-NCP-MPs catalyst was more active than homogeneous catalyst. It provide high surface area. Reaction processed in aqueous media. The reaction carried out at 343 K temperature and required 48 hrs for completion (Scheme 5)[13].



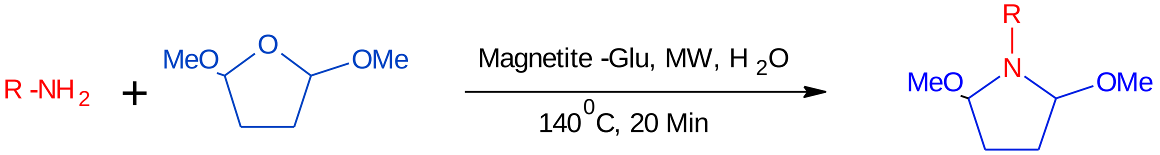
Scheme 5: One-pot A^3- coupling reaction in aqueous medium.

Karami group reported a synthesis of 9-aryl-substituted 1, 8-dioxo-octahydroxanthenes by using Fe_3O_4 NPs. Nanoparticles act as lewis acid and it do effect on the carbonyl group in aldehydes for nucleophilic attack. They found that the nanoparticles catalyzed condensation reaction between aldehyde and dimedone and give a product. The main characteristics of this reaction are it has simple workup procedure, short reaction time and high recyclability of catalyst. They carried out the reaction in aqueous medium so it follows or fulfill the principles of green chemistry (Scheme 6)[14].



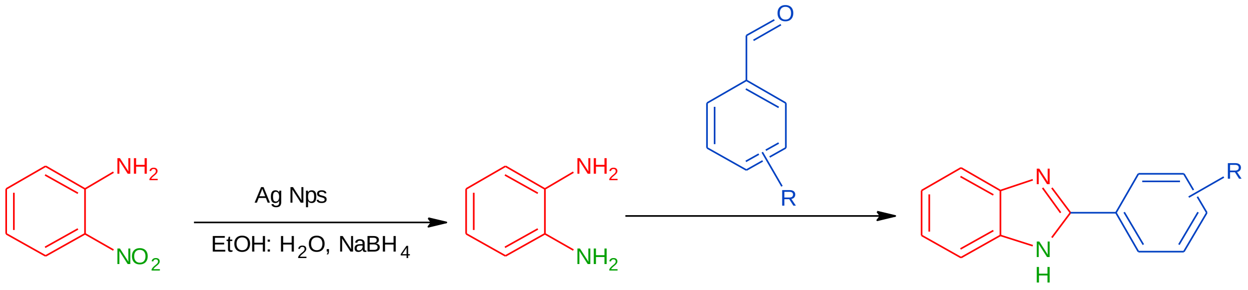
Scheme 6: Synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by Fe_3O_4 nanoparticles.

Polshettiwar and V. Varma reported a synthesis of 2, 5-dimethoxypyrrolidine by using magnetite-glu nanocatalyst. They carried out reaction in microwave and by using water as a solvent. Due to use of microwave it reduces the reaction time also due to use of water as a solvent it reduces the environmental pollution so synthesis of desired product by green method (Scheme 7) [15].



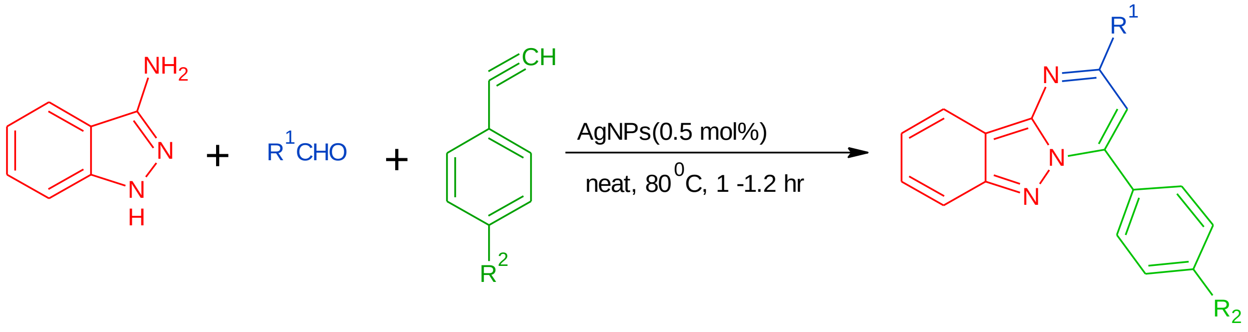
Scheme 7: Catalytic activity of Magnetite-Glu nanocatalyst.

Anju Arya and co-workers reported synthesis of 2-substituted benzimidazoles by using silver nanoparticles. They firstly reduced the 2-nitroaniline by using silver nanoparticles and sodium borohydride to obtain the product o-phenylenediamine. EtOH : H_2O used as a solvent for this reaction. The reduction of nitro group to amine group is confirmed by disappear yellow of reaction. After that substituted aldehyde is added to the mixture and mixture is heated to 80 °C for 10-12 hrs. The reaction was confirmed by TLC. This reaction is a green reaction (Scheme 8)[16].



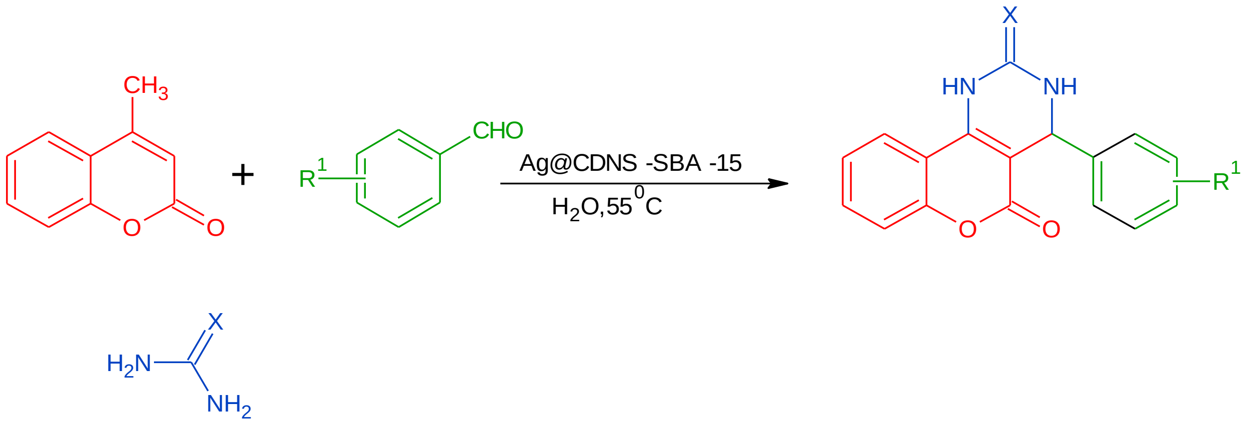
Scheme 8: Silver nanoparticles catalyzed synthesis of 2-substituted benzimidazoles.

Sandip Balwe and co-workers reported a synthesis of pyrimido[1,2-b]indazole by using silver nanoparticles under solvent free condition at 80 °C for 1-1.2 hrs. The 0.5% of silver nanoparticles are used in this reaction. The synthesis of product is achieved by three components i.e.3-aminoindazoles, aryl/heteroaryl/alicyclic aldehyde, and substituted phenyl acetylene by using Ag NPs. This reaction is carried out under room temperature. It follows protocols of green chemistry (Scheme 9)[17].



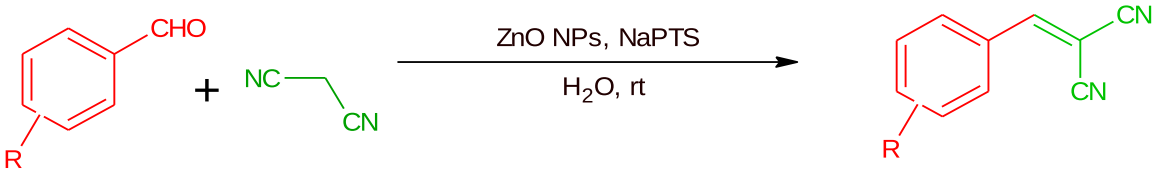
Scheme 9: Synthesis of pyrimido[1,2-b]indazole derivatives using Ag NPs under solvent free conditions.

Porco et al. reported the synthesis of cycloadduct from chalcone and diene by using Ag NPs. The Ag NPs are synthesized from via the reduction of $AgBF_4$ by using tetrabutyl ammonium borohydride with silica gel in DCM (Scheme 10)[18].



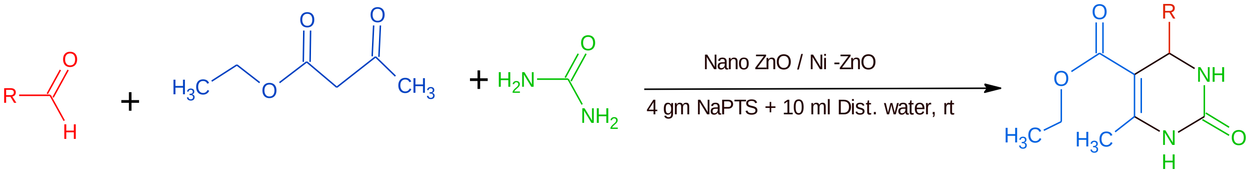
Scheme 10: Synthesis of benzopyranopyrimidines by using Ag NPs.

Suraj Attar et al. reported a synthesis of benzylidenemalonitrile in hydrotropic aqueous medium by using ZnO NPs. ZnO NPs were synthesized from neem (Azadirachta indica) leaf extract. Leaf extract act as capping agent. ZnO NPs were characterized by SEM, XRD, TGA-DTA and BET. The ZnO NPs were separated from reaction mixture by centrifuge method and used for another reaction (Scheme 11)[19].



Scheme 11: Synthesis of benzylidenemalonitrile (BMN).

Bipin Shinde et al. reported a synthesis of 3,4-dihydropyrimidin-2(1H)-ones by using ZnO flakes and Ni-ZnO nanoparticles. The nanoparticles were synthesized from chemical method and characterized by SEM, XRD and EDAX. Aqueous NaPTS used for this synthesis (Scheme 12)[20].



Scheme 12: The synthesis of 3, 4-dihydropyrimidin-2(1H)-ones.

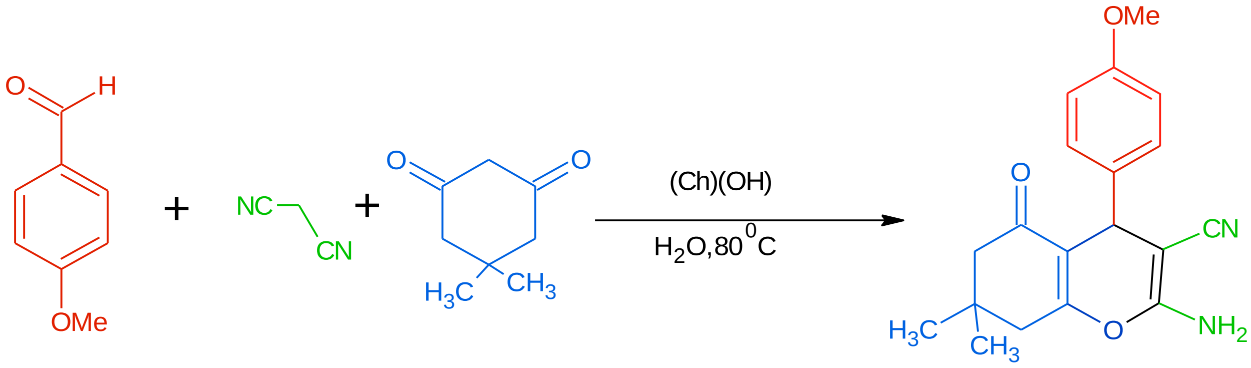
2.2 Ionic liquid:

Ionic liquid means compound consist of ions and liquid at room temperature. Ionic liquids are non-volatile, highly polar, hydrophilic and thermally stable. It was used as a solvent and catalyst in chemical reaction. It has attractive physical and chemical properties such as their high thermal stability, and very low vapor pressure make the liquids an environmentally attractive alternative to classical organic solvents for the development of green chemistry. Catalytic reactions in ionic liquid have been examined from last 20 years. The first use of ionic liquid catalyst in friedel-craft acylation reported in 1986. The ionic liquid is used as a catalyst because they exhibit very low pressure under all condition and they are non-volatile.

Ionic liquid melts below 100 °C which gives a compelling class of liquid substances and characterized by low vapor pressure. Ionic liquid is used as a solvent and catalyst in organic transformation. Ionic liquids are the materials with unique property comes from a complex interplay of coulombic, Van der waals and hydrogen bonding interaction is present between the ions [21].

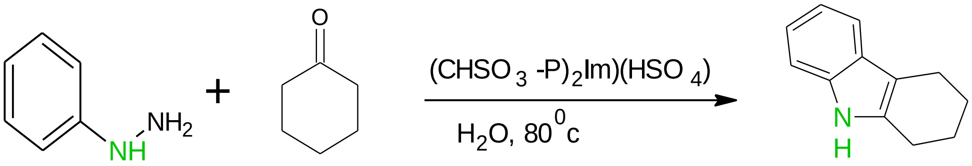
Ionic liquid is made up of anions due to this melting point of salt i.e. ionic liquid is low yields a structural variability of ionic liquids. Ionic liquid made up with cheap anions such as toluenesulfonates, octylsulfates and hydrogensulfates are used in synthesis, catalysis and separation techniques and has more applications. But ionic liquid with expensive functionalized, fluorinated and with chiral ions are used in small scale application. Ionic liquids have highly miscible properties as well as they are hydrophilic in nature. They do not miscible with organic solvent so use of ionic liquid in chemical synthesis is a green method of synthesis.

Huanan Hu et al. reported a reaction of synthesis of tetrahydrobenzo[b]pyran from three components such as benzaldehyde, malononitrile, dimedone in presence of ionic liquid used as a catalyst. They used choline hydroxide based ionic liquid. They prepared ionic liquid through anion exchange reaction [22]. They took different mol% of ionic liquid for the synthesis but 10 mol % ionic liquid gives more yield (Scheme 13).



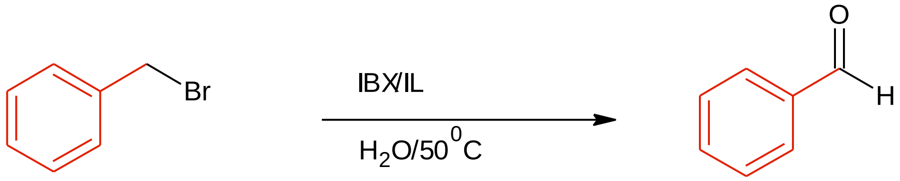
Scheme 13: Synthesis of tetrahydrobenzo [b] Pyran.

Dan-Qian Xu et al. reported a reaction of synthesis of Fischer indole synthesis from cyclohexanone and phenylhydrazine by using bronsted acidic ionic liquid as a catalyst in aqueous medium. The application of SO$_3$H-functionalized ionic liquids as bronsted acid catalyst is very few [23]. The bronsted acid ionic liquids are miscible with liquid (Scheme 14).



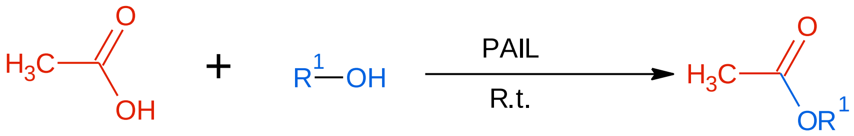
Scheme 14: The different ILS and acids catalyzed synthesis of fischer indole in aqueous medium.

Satish A. Dake et al. reported an oxidation of aryl halide to carbonyl compound in presence of IBX oxidant and phosphonium salt ionic liquid carried out the reaction in aqueous medium. The reaction completed in short time and gives excellent yield of product (Scheme 15) [24].



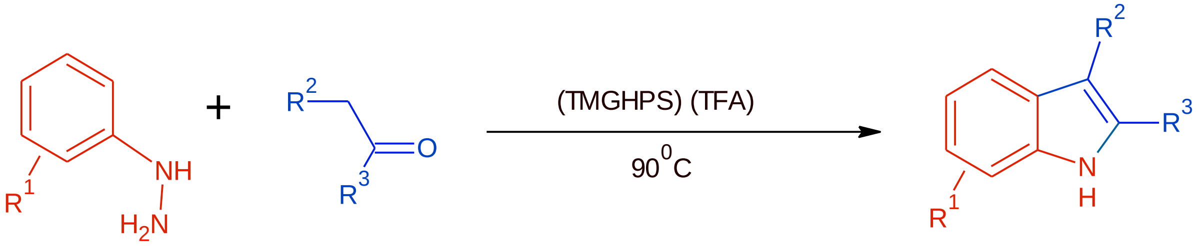
Scheme 15: Benzyl halide oxidation.

Xu et al. reported an esterification of alcohol by using acetic acid in room temperature in presence of bronsted acidic ionic liquids. The ionic liquid derived from protophilic amide [25]. For good conversion and excellent reaction rate is achieved by stabilizing the protonated acetic acid and limiting the alcohol protonation, protophilic amide ionic liquid (PAILS) accelerates the reaction (Scheme 16).



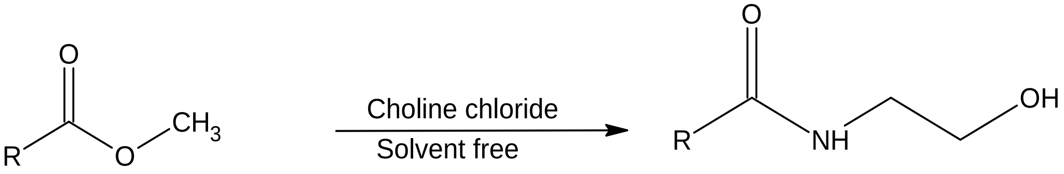
Scheme 16: Representative reaction for esterification.

William C. Neuhaus et al. reported a Fischer indole synthesis by using protonic ionic liquid. They used tetramethylguanidinium propanesulfonic acid trifluoromethylacetate ([TMGHPS] [TFA]) ionic liquid as a catalyst and reaction medium for the synthesis of indole. It is recyclable and reused catalyst for further reaction. The indole synthesis from hydrazine and ketone. The catalyst used for this reaction is ecofriendly (Scheme 17) [26].



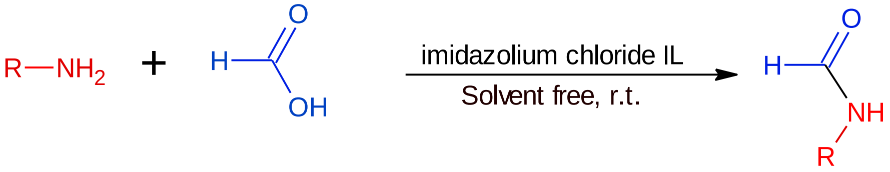
Scheme 17: Fischer indole synthesis.

Pramod patil and co-workers reported amidation of methyl ester in presence of choline chloride. The reaction carried out in the nitrogen atmosphere and in solvent free condition. In this reaction choline chloride is an ionic liquid. The reaction carried out in the oil bath between the ranges 90^0C to 110^0C. There is a green approach of reaction (Scheme 18) [27].



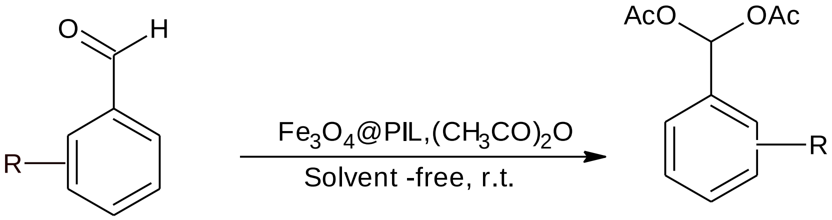
Scheme 18: Choline chloride catalyzed fatty acid ethanolamide.

Charu Garkoti and co-workers reported an N-formylation of amine in the presence of formic acid and supported imidazolium chloride ionic liquid under solvent free condition. They carried out the same reaction with unsupported catalyst then yield of product is in small amount. But when they used a supported imidazolium chloride ionic liquid catalyst then yield of product is maximum and short time is required for the reaction. As compared to other catalyst imidazolium chloride ionic liquid catalyst is easily separable by magnet and it has good catalytic activity (Scheme 19) [28].



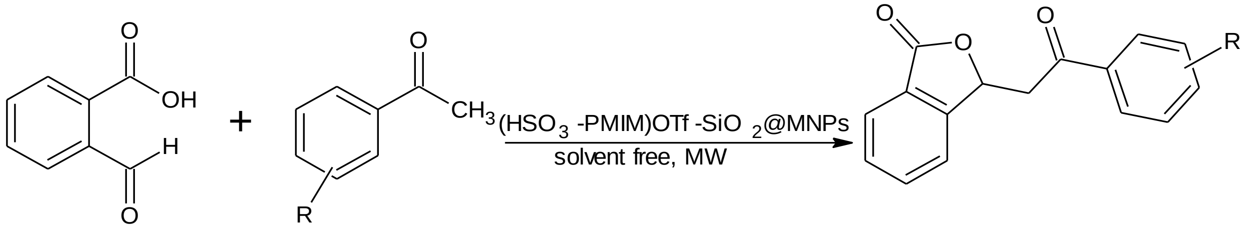
Scheme 19: Supported imidazolium chloride IL catalyzed N-formylation of amines.

Pourjavadi and co-workers reported an acylation of aldehyde by using ionic liquid. They used poly (Ionic liquid) coated magnetic Fe_3O_4 NPs. This catalyst is characterized by FT-IR, XRD, SEM and TEM. It gives morphology of synthesized magnetic catalyst. This catalyst contain highly coated polymer chain. The reaction carried out in the solvent free and at a room temperature so it follows the principle of green chemistry (Scheme 20) [29].



Scheme 20: Acylation using Fe_3O_4@PIL.

Forouz Rastegari and co-workers reported a synthesis of isobenzofuran-1(3H)-ones by using [HSO_3PMIM]OTf-SiO_2@MNPs. The reaction is carried out in the microwave and solvent free condition. So, the reaction required less time. The catalyst used in this reaction is highly reusable. The synthesized catalyst is characterized by TEM and XRD. The TEM image of [HSO3PMIM]OTf-SiO2@MNPs showed dark nano-Fe_3O_4 35 cores surrounded by grey silica shells. The TEM image of the reused catalyst gives its stability during the reaction. The histogram of size distribution shows the average diameter of nanoparticles is about 8-12 nm (Scheme 21) [30].



Scheme 21: The synthesis of Isobenzofuran-1(3H)-ones by using $(HSO_3PMIM)OTf-SiO_2@SMNPs$.

Hossein Naeimi et al. reported a synthesis of 2,4,5-trisubstituted imidazoles using supported $Fe_3O_4@SiO_2.HMSO_3H$ under solvent free condition at 110^0C. It is a multicomponent reaction. It is a green reaction (Scheme 22) [31].

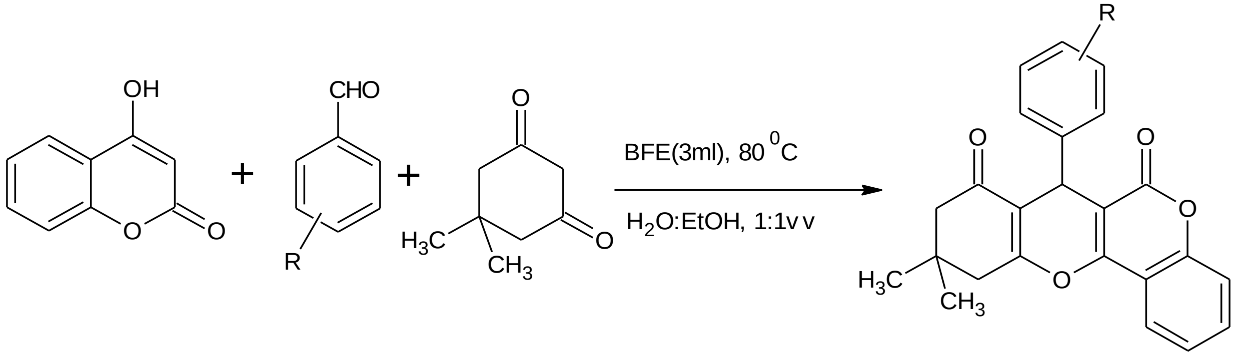
Scheme 22: Synthesis of 2,4,5- trisubstituted imidazoles using supported bronsted acidic IL.

2.3 Surfactant:

Many organic compounds are insoluble in water. So, this problem is overcome by using surfactant or surfactant like ligand. Surfactants are self-assembled compounds that depends on their structure and electric charge can interact as micelle with other substrate and due to this reason many organic compounds are soluble in water. So, many organic reactions are carried in water and it is one of the principle of green chemistry.

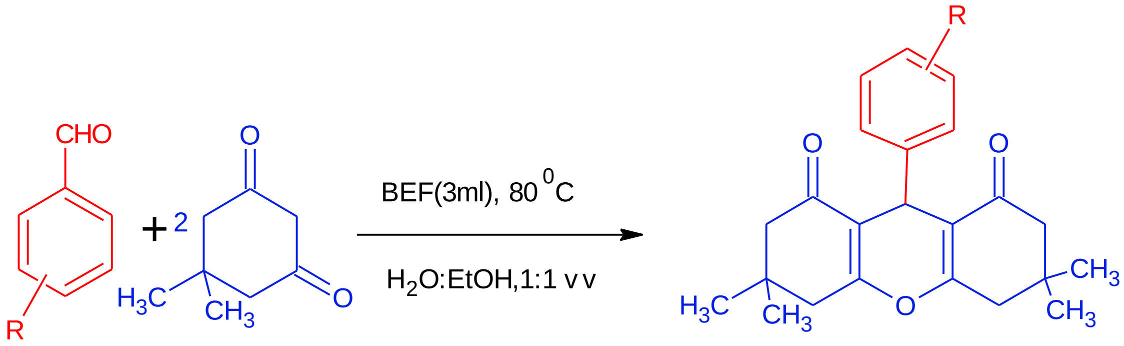
There is increase in environment pollution due to conventional use of chemical methods for synthesis of metal nanoparticles [32]. Nanoparticles are synthesized by the chemical and physical method, it is depend on the availability of material. Some are used hazardous chemicals for the synthesis of nanoparticles so it do the harmful effects on environment and human health also. Nanoparticles are synthesized by chemical method, during this process nanoparticles adsorb the hazardous chemicals so this types of particles are not used in biomedical equipment. So, there is a need of the synthesized nanoparticles by green method using fungi, bacteria and plant extract. Metal ion is reduced faster by plant extract than microorganism. Because plant extract contains biomolecules like protein, phenols etc. Due to aggregation property of plant extract, it do not form stable nanoparticles and small surface area leading to larger particle size. The surfactants are used to avoid these agglomeration of magnetic nanoparticles. To avoid these agglomeration of magnetic nanoparticles, surfactant is used. There are two types of surfactant, natural i.e. bio-surfactant and synthetic surfactant. Comparing both of surfactants, bio-surfactant follow the principle of green chemistry. The aqueous extract of Acacia concinna pods is a bio-surfactant and it play important role in stabilization of magnetic nanoparticles. The Fe NPs are synthesized by using aqueous extract of Baswellia Saarrta L. leaves as bio-surfactant and acacia concinna pods as stabilizing agent. Bio-surfactants are naturally occulting surfactant from plant, animals and microbial cells. They are used in oil recovery, food processing. The bilimbifruit extract is used as bio-surfactant in organic transformation which is more acidic due to presence of vitamin C in it [24].

Bhagyashree Patil et al. reported a synthesis of 10,11-dihydrochromeno[4,3-b] chromene-6,8(7H,9H)diones by using three components such as hydroxycoumarin aromatic aldehyde and dimedone in ethanolic aqueous medium at 80^0 C using BFE as a micellar biocatalyst (Scheme 23) [33].



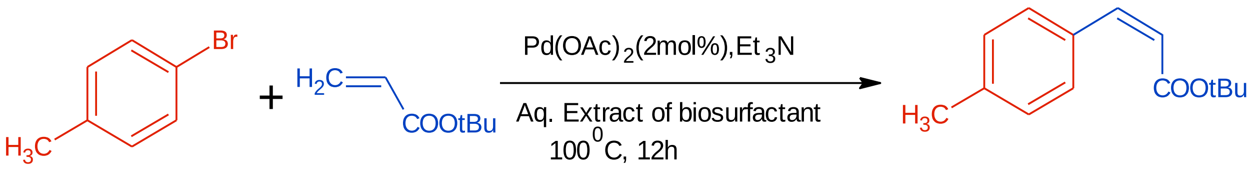
Scheme 23: Biosurfactant bilimbi fruit extract (BEF)-catalyzed synthesis of 10,11-dihydrochromeno[4,3-b]chromene-6,8(7H, 9H)-diones.

Bhagyashree Patil and co-workers reported this reaction in presence of BEF catalyst in 1:1 H_2O: EtOH (Scheme 24) [33] .



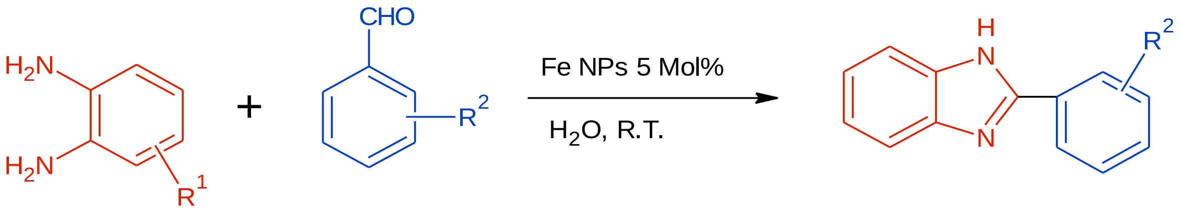
Scheme 24: BEF-catalyzed 1, 8-dioxo-octahydroxanthene synthesis.

Seema Patil and co-workers reported Mizoroki-Heck coupling reaction using pods of acacia concinna used as a bio-surfactant for this reaction (Scheme 25) [34].



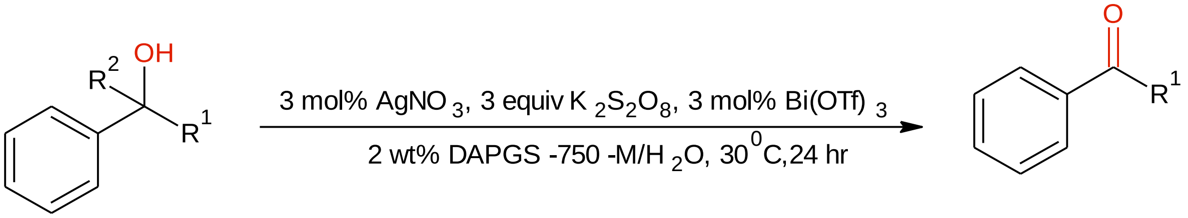
Scheme 25: Mizoroki-Heck Coupling reaction in aqueous extract of bio-surfactant.

Satyanarayan Arde et al. reported a synthesis of Fe NPs are synthesized by biological method during synthesis of NPs, Acacia concinna pod aqueous extract used as a bio-surfactant. Catalytic activity of Fe NPs is determined by synthesis of quinoxline. In absence of catalyst reaction give less amount of product. By adding the catalyst to the reaction, the yield of product is more and required short time (Scheme 26) [35].



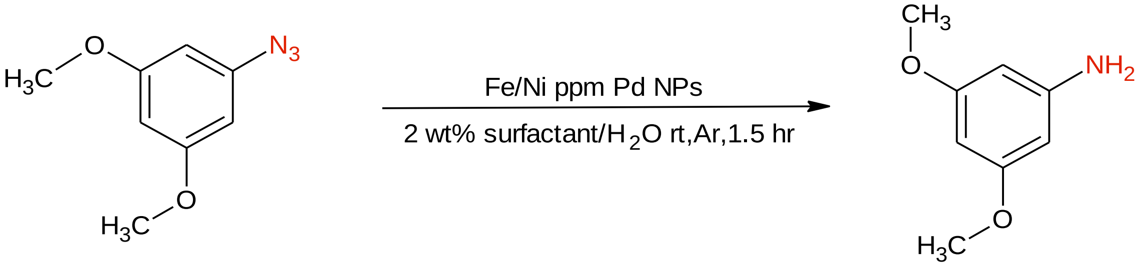
Scheme 26: Synthesis of quinoxaline.

Dengfeng Chen et al. reported an oxidation of tertiary alcohol by using DAPGS -750-M surfactant. This surfactant is more preferable than any other surfactant because it does not contain aliphatic long chain. These reaction is carried out in an aqueous medium to avoid any environmental issues by organic solvent (Scheme 27) [36].



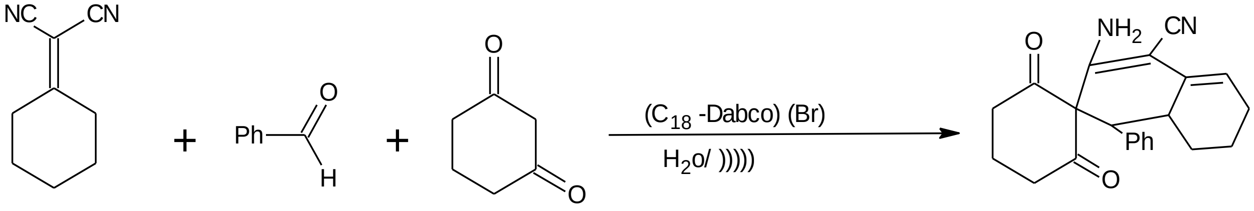
Scheme 27: Oxidation of tertiary alcohol.

Nicholas R. Lee and co-workers reported a reduction of aryl azide in the presence of coolade i.e. surfactant. Because the aryl azide is somewhat better solubility in surfactant. Due to use of surfactant reaction is carried out in aqueous medium and room temperature (Scheme 28) [37].



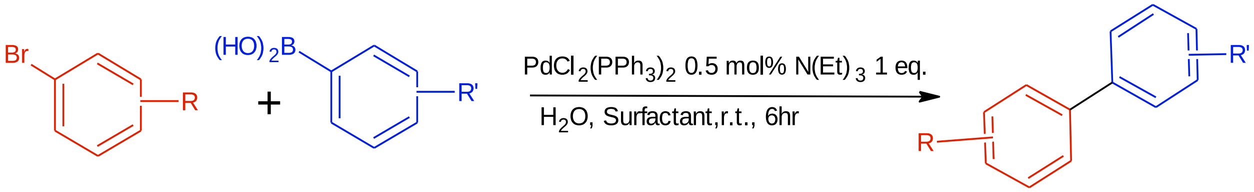
Scheme 28: Aryl azide reduction.

Trushant Lohar et al. reported a synthesis of spirocarbocycles by using DABCO based surfactant. This surfactant is cationic in nature. This reaction is carried out in an aqueous medium and in ultrasonicator (Scheme 29) [38].



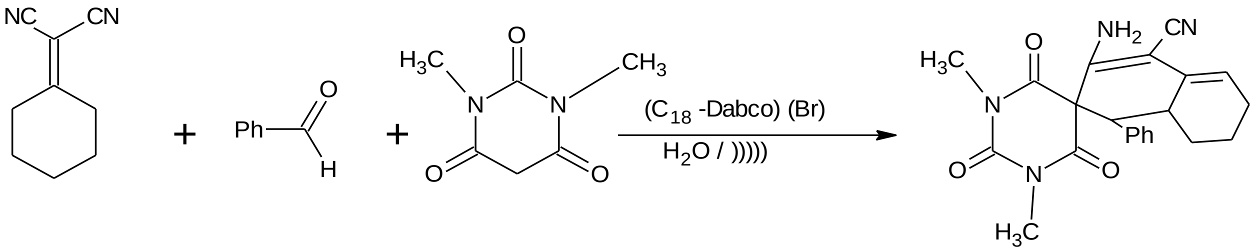
Scheme 29: Synthesis of spirocarbocycles by using (C_{18}- Dabco)(Br) surfactant in aqueous medium.

Tommaso Lorenzetto et al. reported a Suzuki coupling reactions between aryl bromides and aromatic bromic acid derivatives by using Sito-750-M as a surfactant. The reaction is carried out in aqueous medium (Scheme 30) [39].



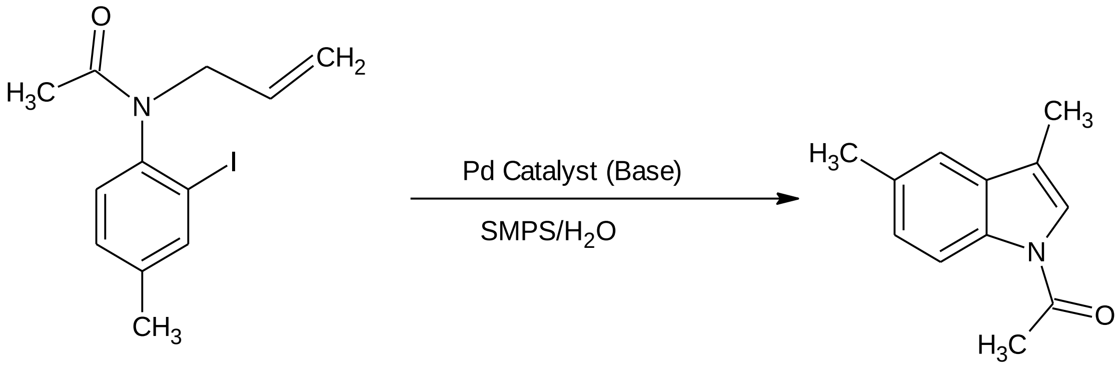
Scheme 30: Suzuki-Miyaura cross-coupling reaction in water.

Trushant Lohar et al. reported a synthesis of spirocarbocycles by using DABCO based surfactant. This surfactant is cationic in nature. This reaction is carried out in an aqueous medium and in ultrasonicator (Scheme 31) [38].



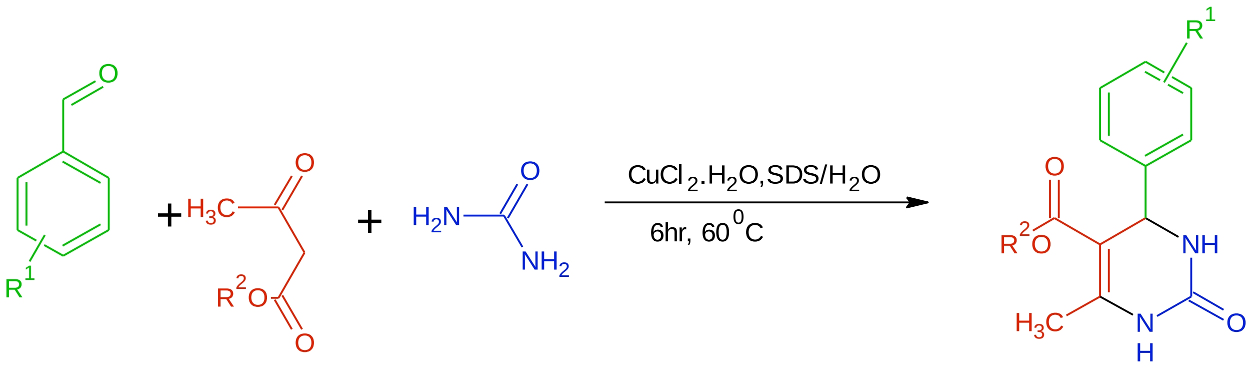
Scheme 31: Synthesis of spirocarbocycles using surfactant.

Singarajanahalli Mundarinti Krishna Reddy and co-workers reported a Csp^2- Csp^2 bond forming reaction by using SMPS surfactant. Stearyl methoxy PEG glycol succinate (SMPS) were synthesized by using readily available inexpensive aliphatic lipophilic alcohol and succinic anhydride. This reaction was carried out in an aqueous medium which minimizes the pollution of an environment (Scheme 32) [40].



Scheme 32: Csp^2- Csp^2 bond forming reaction by using surfactant.

Xu et al. reported a biginelli reaction catalyzed by lewis acid in presence of aqueous surfactant. After many optimization author selected $CuCl_2.2H_2O$ as a suitable catalyst and SDS as a micelles/ surfactant (Scheme 33) [74].



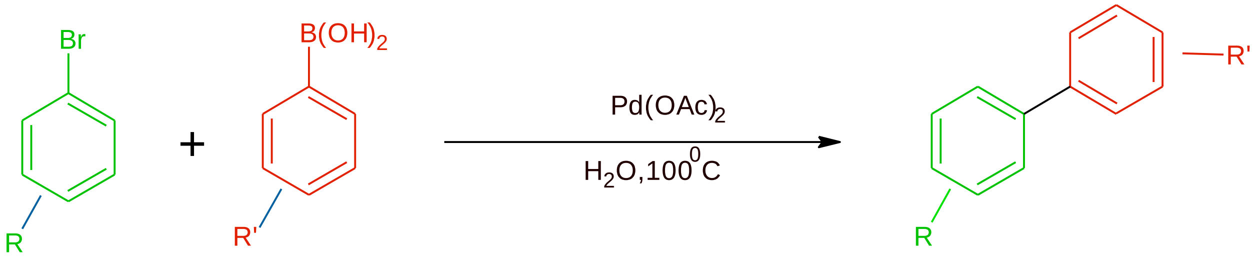
Scheme 33: The Biginelli reaction.

2.4 Phase transfer catalyst:

In chemistry, phase transfer catalyst means a catalyst that convert the reactant from one phase into another phase where reaction occurs. It is a form of heterogeneous catalyst. The reactants which are present in ionic form are often soluble in an aqueous phase but insoluble in an organic solvent in the absence of phase transfer catalyst. The catalyst act as a detergent for solubilizing the salts into the organic phase. PTC is used to the acceleration of the reaction. By using a PTC process, one can achieve faster reaction, obtain higher conversions or yield, make give less amount of byproducts, eliminate the need for expensive or dangerous solvents that will dissolve all the reactants in phase, eliminate the need for expensive raw materials.

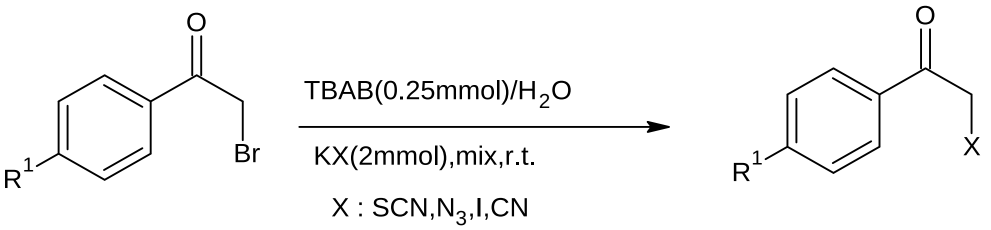
Phase transfer catalyst is a catalyst that accessibility the transition of reactant from one phase to another phase where reaction is takes place. Ionic reactants are soluble in water but insoluble in organic solvent in the absence of PTC. The PTC is act as a detergent for soluble the salt in organic phase [41]. The reaction is accelerated by using the PTC and more yield is obtained by it. It eliminate the expensive raw materials and minimize the waste. PTC is used in green chemistry by using water as reaction media and used of organic solvent is reduced. Quaternary ammonium salts is used as PTC. The PTC used in asymmetric alkylation which are catalyzed by quaternary ammonium salts which is derived from cinchona alkaloids.

Anamitra Chatterjee reported a Suzuki miyaura coupling reaction by palladium acetate. They carried out reaction in water at 100^0C.They used tridentate ligand Phenylphosphinacalix [3] trifuran for this reaction. (Scheme 34) [42].



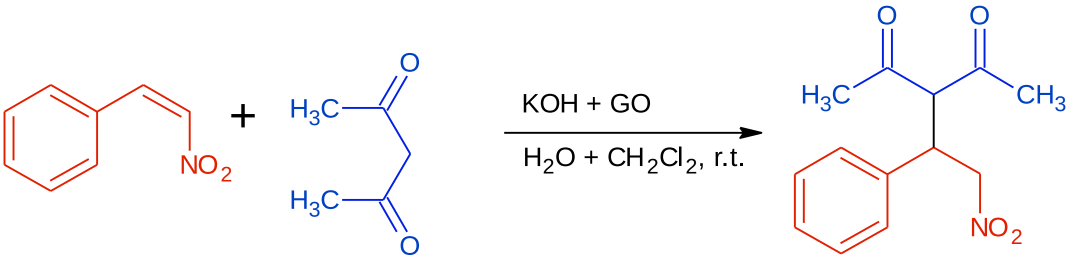
Scheme 34: Suzuki coupling reaction in water.

Soheil Sayyahi and Jafar saghanezhad reported a synthesis of phenacyl derivative in homogeneous PTC in aqueous media (Scheme 35) [43].



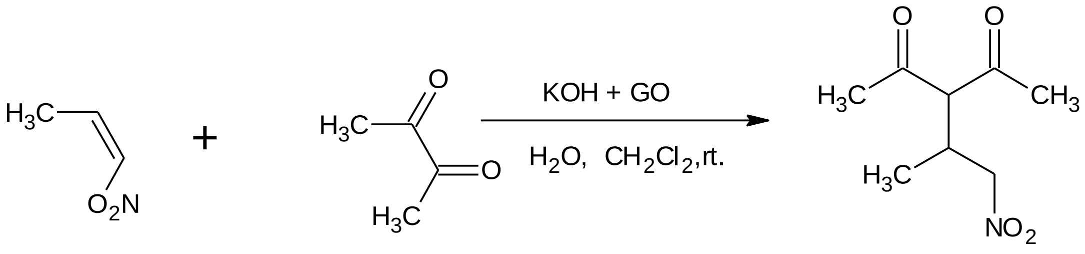
Scheme 35: Reaction with alpha bromoacetophenone with nucleophile.

Younamin Kim and co-workers developed a Michael addition reaction by graphene oxide as a recyclable PTC by using trans-β-nitrostyrene and 2,4-pentanedione (Scheme 36) [44].



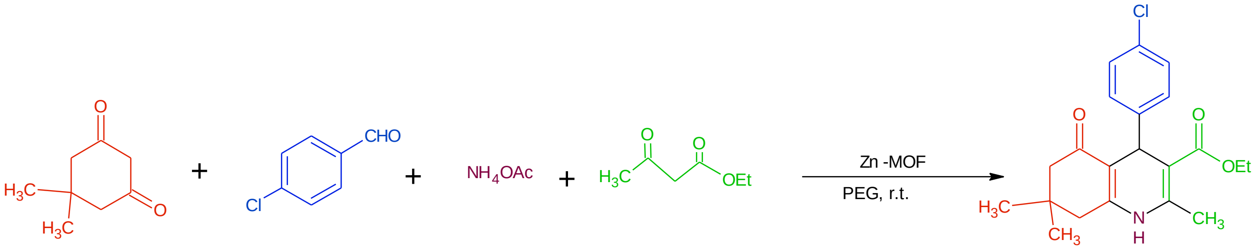
Scheme 36: Michael addition reaction of trans-β-nitrostyrene and 2,4-pentanedione.

Youngmin Kim et al. developed a Michael addition reaction for synthesis trans-β-nitroolefins. The reaction is carried out in aqueous medium i.e. in water by using KOH+GO, the reaction is processed and gives best yield due to presence of KOH+GO in water and the methylene chloride two phase system [44]. Two phase solvent system gives better yield and has provide short reaction time than one phase system (Scheme 37).



Scheme 37: Trans-β-Nitro-olefins as Michael acceptors.

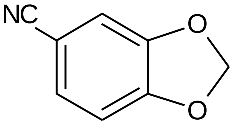
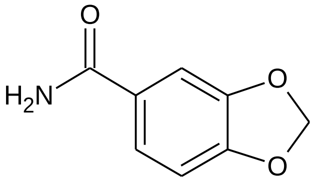
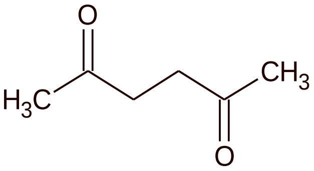
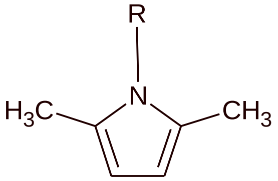
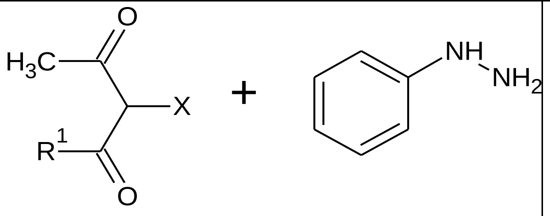
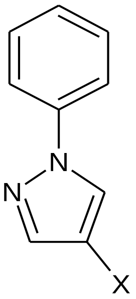
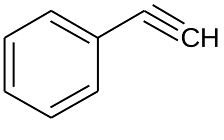
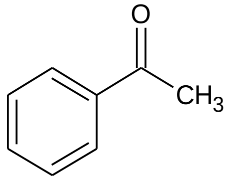
Sayed Mohammad Ramish et al. reported a synthesis of polyhydroquinolines by using four components such as dimedone, aldehyde, ethylacetoacetate and ammonium acetate. In this reaction Zn-MOF is used as a surfactant. The Zn-MOF porous microspheres is prepared by using 4,6-Diamino-2-pyrimidinethiol was dissolved in water and then, it was added to a solution of DMF containing 2 mmol of Zn(NO3)2.6H_2O salt. The reaction is carried out in PEG (Scheme 38) [45].

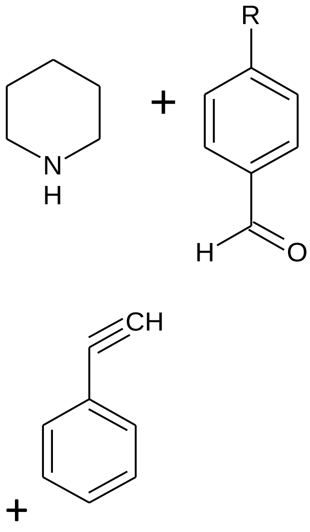
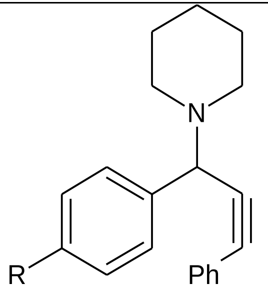
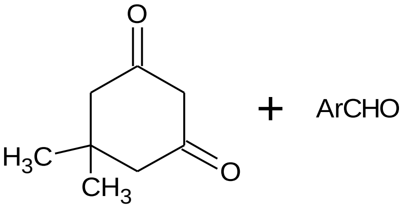
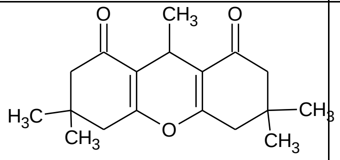
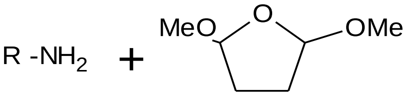
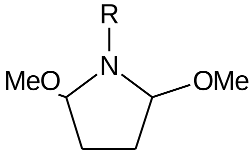
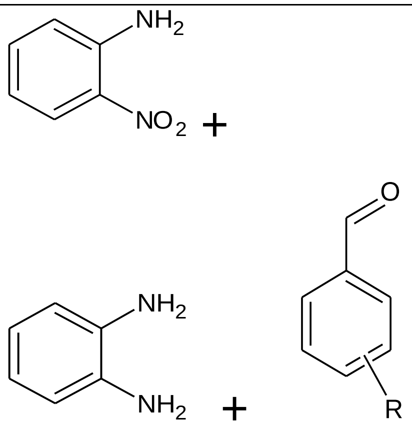
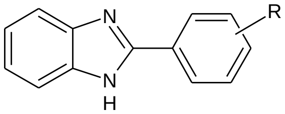


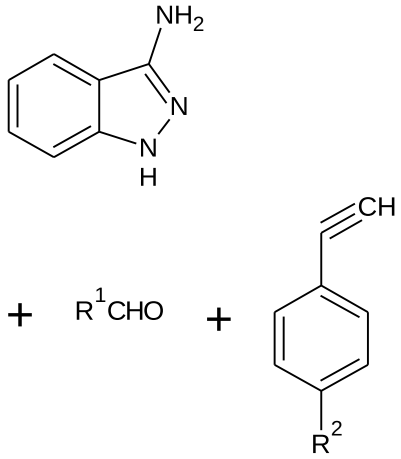
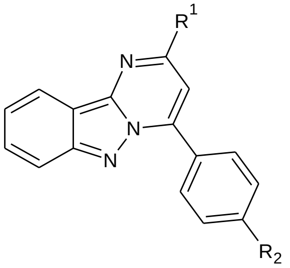
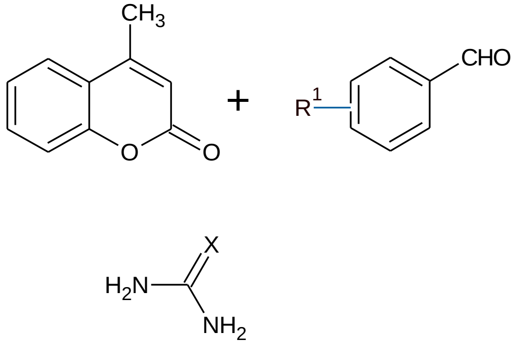
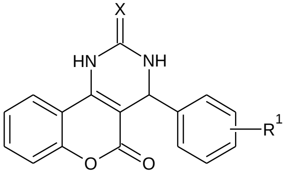
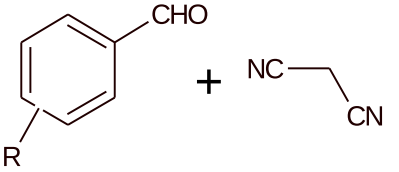
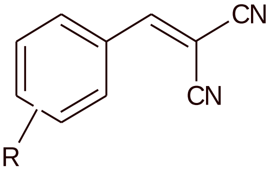
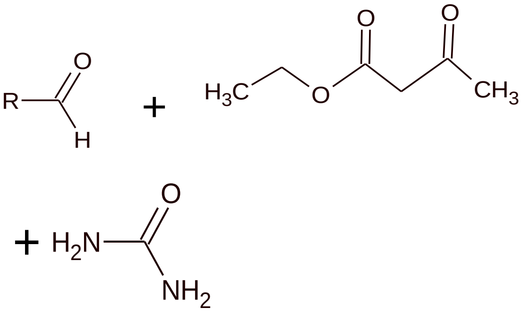
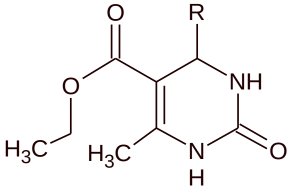
Scheme 38: Synthesis of polyhydroquinolines.

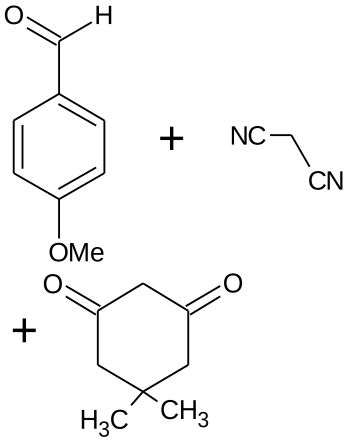
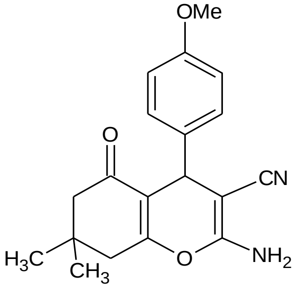
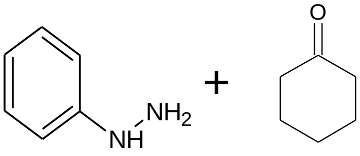
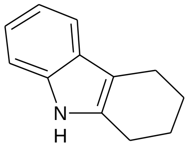
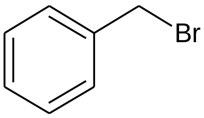
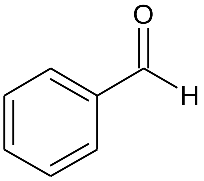
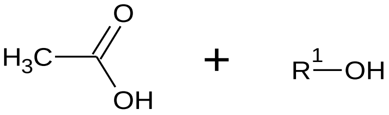
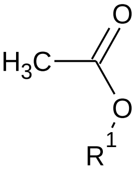
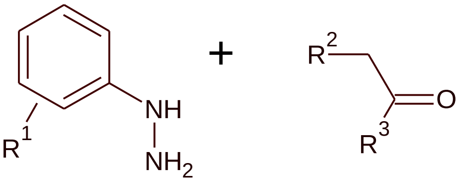
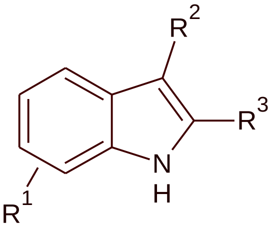
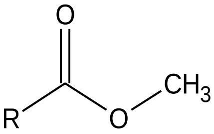
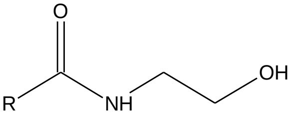
The short summary and overall progress of organic synthesis by nanoparticles, phase transfer catalyst, surfactant and ionic liquid in last decades are summarized in table number 1. The reactions summarized in table number 1 were carried out by green catalyst.

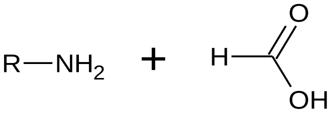
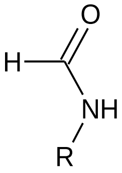
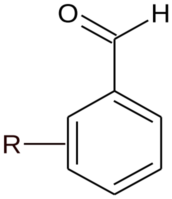
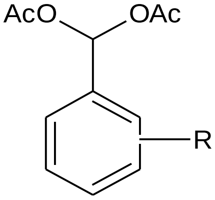
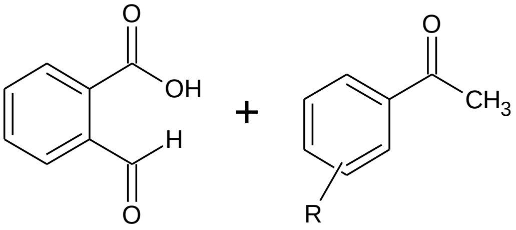
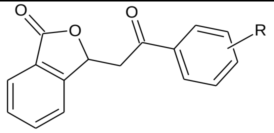
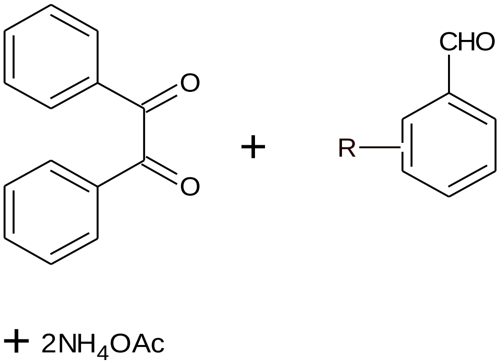
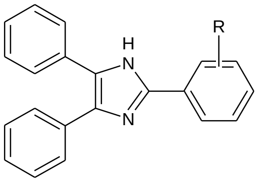
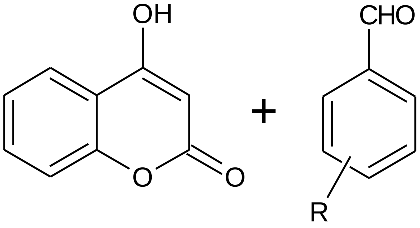
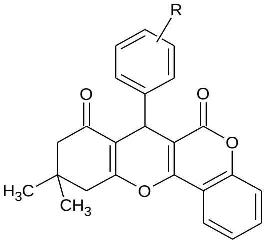
Table 1: Short summary of catalyst

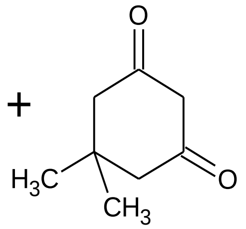
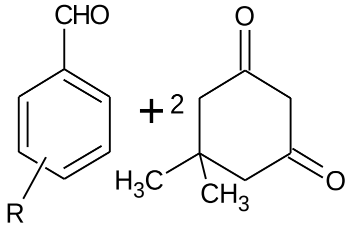
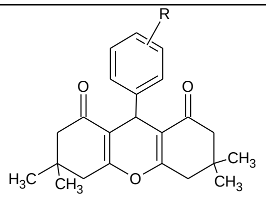
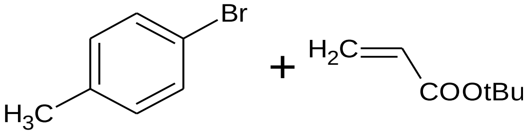
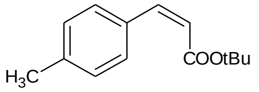
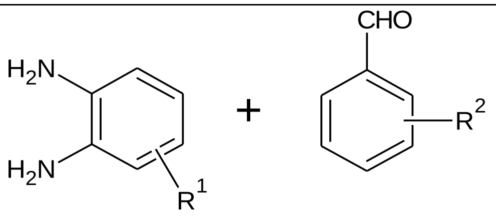
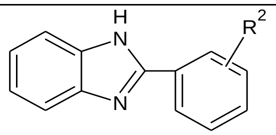
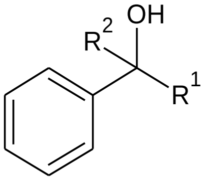
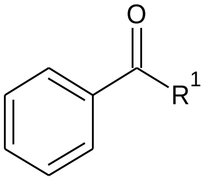
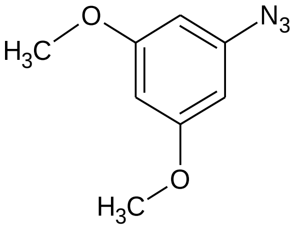
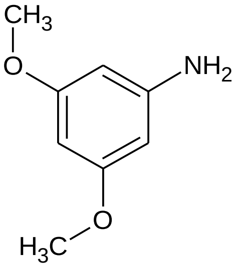
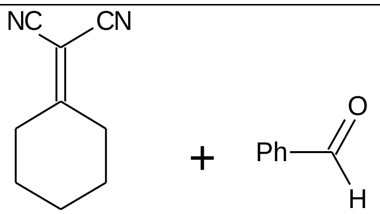
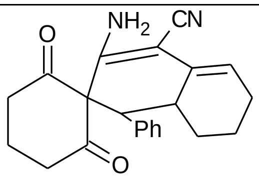
Scheme entry No.	Reactant	Condition	Product	References
1		MW, H_2O, 120^{0}C		[9]
2		H_2O, 100^{0}C, reflux		[10]
3		MW, H_2O, 140^{0}C		[11]
4		H_2O, 80^{0}C		[12]

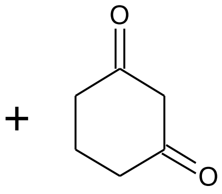
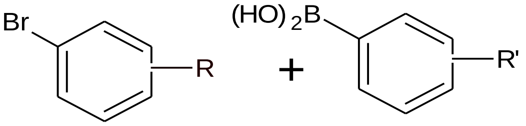
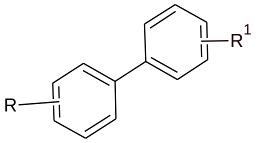
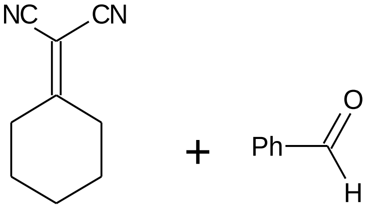
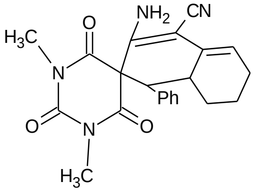
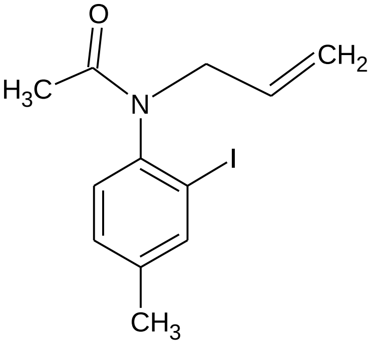
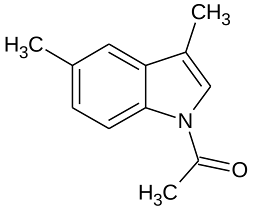
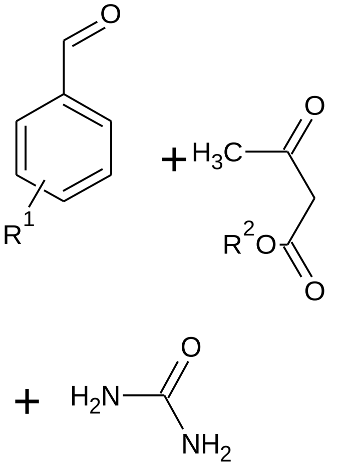
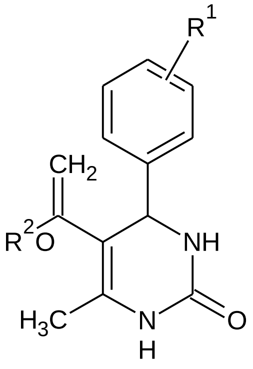
5		H_2O, 343 K		[13]
6		H_2O, 80^0C		[14]
7		MW, H_2O, 140^0C		[15]
8		EtOH:H_2O, 180^0C		[16]

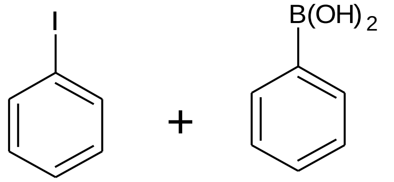
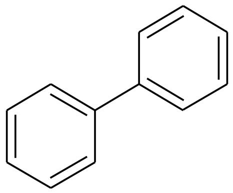
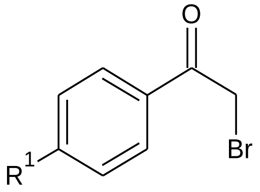
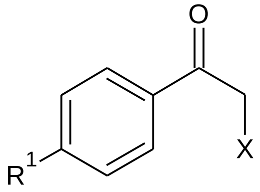
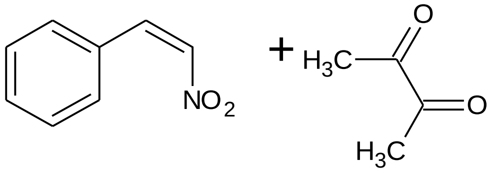
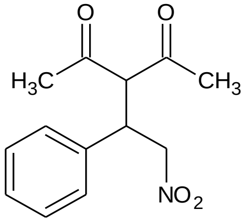
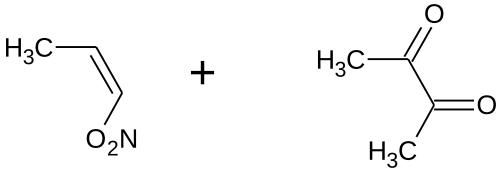
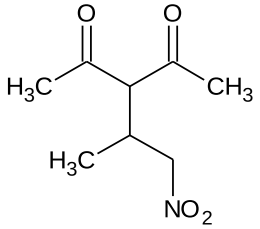
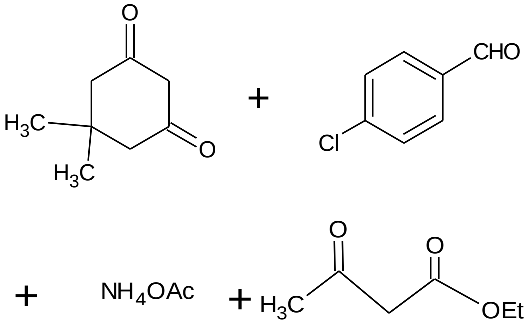
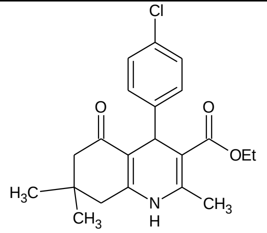
9		Solvent free, 80^{0}C		[17]
10		H_2O, 55^{0}C		[18]
11		H_2O, r.t., NaPTS		[19]
12		NaPTS, H_2O, r.t.		[20]

13		H_2O, 80^0C, IL		[22]
14		H_2O, 80^0C		[23]
15		H_2O, 50^0C		[24]
16		r.t., PAILS		[25]
17		IL, 90^0C		[26]
18		Choline chloride IL, Solvent free		[27]

19		Imidazolium chloride IL, Solvent free, r.t.		[28]
20		Solvent free, r.t., Fe_3O_4@PIL		[29]
21		Solvent free, MW		[30]
22		Solvent free, 110^{0}C, IL		[31]
23		H_2O:EtOH(1:1), 80^{0}C		[33]

				
24		H_2O:EtOH(1:1), 80^{0}C		[33]
25		Pd(OAc)$_2$, Et$_3$N, 100^{0}C		[34]
26		H_2O, r.t., Fe NPs, surfactant		[35]
27		H_2O, 30^{0}C		[36]
28		H_2O, r.t., Pd NPs, Surfactant		[37]
29		H_2O,)))), DABCO		[38]

		Based Surfactant		
30		H_2O, Surfactant, r.t.		[39]
31		H_2O,))))), DABCO based Surfactant		[38]
32		H2O, SMPS surfactant		[40]
33		SDS, H_2O, 60^0C		[74]

34		H_2O, Pd@CoF-QA PTC		[42]
35		H_2O, r.t.		[43]
36		GO, H_2O, r.t.		[44]
37		GO, H_2O, r.t.		[44]
38		Zn-MOF, PEG, r.t.		[45]

3. Biocatalyst:

Biocatalysis means the use of living systems or their parts of body to speed up chemical reactions. In this processes, natural catalyst such as enzymes are used for organic transformation.

The term catalysis is coined by the scientist Berzelius in 1836. Kuhne used the word enzyme in 1878 to indicate the catalysis taking place in the biological systems Isolations of enzyme system from cell-free extract of yeast was achieved in 1883 by Buchner. He named it as zymase which could convert sugar to alcohol. The biocatalyst is classified as oxidoreductases, transferases, Hydrolases, lyases, isomerases and ligase biocatalyst

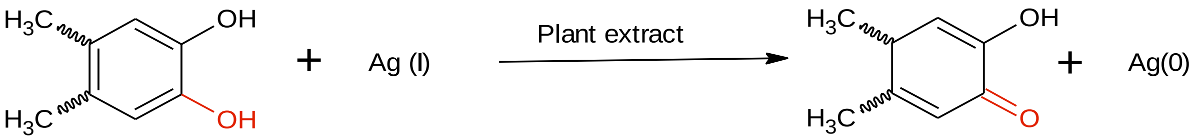
Preparing the organic product is a difficult task for chemists. So, there is a need to used catalysts which are non-hazardous, ecofriendly, easily available and inexpensive. The biocatalyst is a green catalyst. It is recovered from nature i.e. from fruit juice, plant extract and enzymes. Bow, many researchers used biocatalyst in organic transformation [46]. Biocatalyst achieve a great potential for regio- and stereo- specific conversion under mild conditions. There is no formation of any side products. There are many biocatalyst, among them beakers yeast is easily handle, low cost and it is used in green synthesis of 1,4-dihydropyridines, 4H-pyranes, benzimidazoles [47]. For the preparation of different chiral precurssors many biocatalytic methods are important. The whole cells and isolated enzymes of candida Sp. and yeast used for the synthesis of chiral compounds. Candida Sp. Is a important for oxidoreductases . Among known Candida Sp. Candida parapsilosis whole cell used as a biocatalyst for organic oxidation-reduction reactions. The products are enantiomerically pure molecules and which have many industrial applications [47]. Replacement of hazardous chemical catalysts by using biocatalyst and hazardous solvents by using green solvents such as ioni liquid. The use of both biocatalyst and ionic liquid which provide the sustainable approach for the organic transformations, particulary when the substrates have poor solubility in water [48]. Enzymatic transformation in organic solvent growing up the area of research for the production of industrial products. Organic solvents are harmful to living cells because they are able to bind the cell membrane and affect on its stability. So, researchers used many methods to modify enzymes in order to stay suitable with organic solvent [49]. Biotransformations are known from the time of Pasteur. But first microbial transformations discovered in 1950s [50]. Biocatalysts is a used of enzymes in organic transformations has a powerful tool in organic synthesis. They have high activity and having stereo-, region-. and chemo -selectivity observed in many biotransformation [51].

3.1 Plant Extract:

The plant extract is used for the synthesis of Ag NPs supported on graphene oxide. Abutilon hirtum leaf extract act as a reducing and capping agent without use of any toxic chemicals. The characterization of nanoparticles is done by the XRD. This NPs are used in reduction reaction. So, the synthesis of product by using a green catalyst [50]. The synthesis of Cu NPs on the surface of graphene oxide by using cuscutareflexa leaf extract. The synthesized NPs are characterized by many methods. Plant extract used in synthesis of many NPs and this NPs are used in organic transformations. Moringaoleifera leaves extract are used for the synthesis of Ni/ Fe_3O_4. Euphorbia Cheiradenia Boiss extract is used for the synthesis of Cu/rGo.

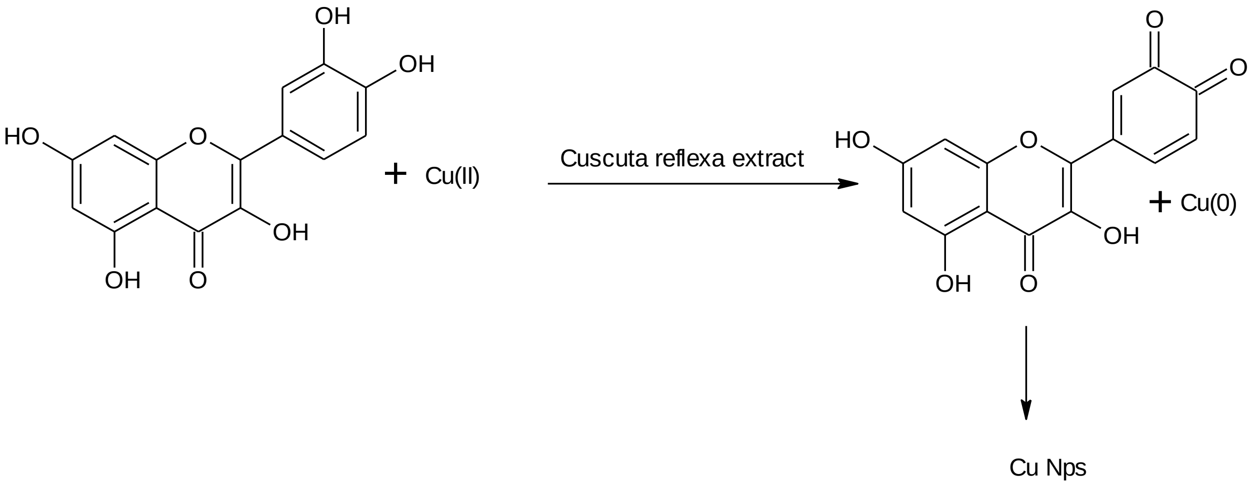
Lantana camara flower extract is used for the green synthesis of CuO NPs and this nanoparticles are used in aza-michael reaction [52]. Eucalptusglobulus leaf extract is used for the synthesis of TiO_2 NPs and this prepared NPs are used in synthesis of 4H-pyran derivative [53]. The synthesis of CuO NPs by using cordia Africana leaf extract for 4-nitrophenol reduction. For Suzuki-Miyaura coupling reaction, Pd based NPs are used. The use of organic solvent causes an environmental issues so, use of water as a solvent in this reaction. The synthesis of Pd NPs are done by the pulicariaglutinosa extract [54].

Mohboobe Maryami et al. reported a green synthesis of Ag NPs by the help of plant extract. He used Abutilon hirtum plant extract for synthesis of this nanoparticles. The prepared nanoparticles are confirmed by the surface plasmon resonance. Nanoparticles are characterized by UV-visible and FT-IR spectra (Scheme 39) [55].



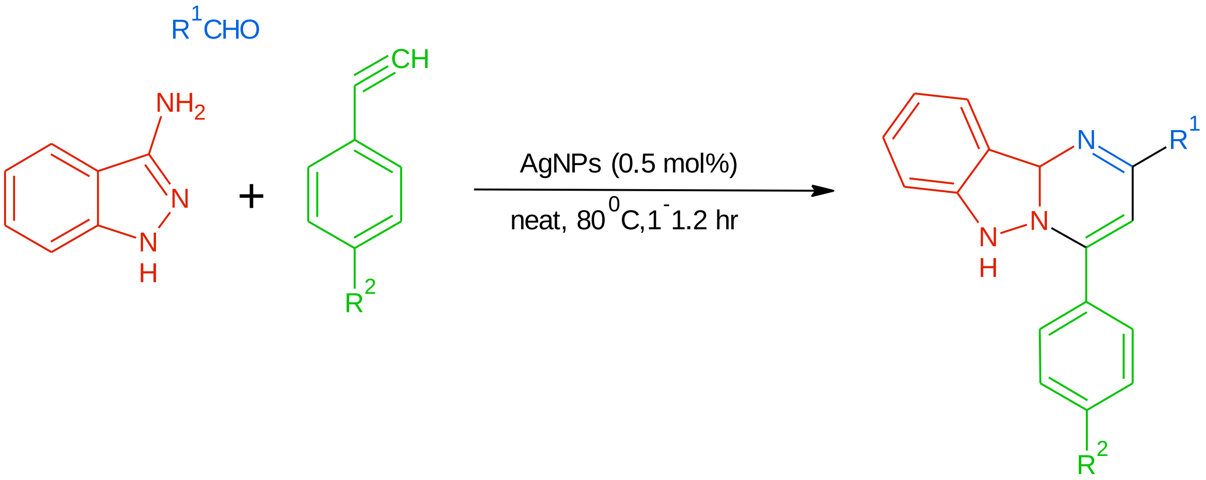
Scheme 39: Green synthesis of Ag NPs using plant extract.

Samira Naghdi et al. reported a synthesis of Cu NPs by using Cuscutareflexa plant extract. The prepared nanoparticles are monitored by using UV- visible technique (Scheme 40) [56].



Scheme 40: Biosynthesis of Cu NPs.

Balwea et al. synthesized pyriido(1,2-b) indazole derivatives using silver NPs. This Ag NPs are obtained from the plant extract of Raddix purariae. This plant extract was reacted with silver nitrate in presence of base and Ag NPs was characterized by using UV-Visible spectroscopy (Scheme 41) [17].



Scheme 41: Synthesis of pyrimido[1,2-b] indazole using Ag NPs under solvent free condition.

3.2 Fruit Juice:

Now a days many researchers developed a greener and eco-friendly methods for organic transformations which involves the use of alternative for the chemical catalyst, organic solvents and decrease the pollution of an environment and achieve the twelve principles of green chemistry. So, many researchers were used a fruit juices as a biocatalyst in organic transformations. The fruit juice is act as a homogeneous catalyst in organic reaction. The fruit juice like lemon, kiwi pineapple, coconut are used in an organic transformation. Lemon juice contain the citric acid so this is used in knoevenagel condensation, three-component synthesis of dihydropyrimidinones, triazoles. The fruit juice is a natural and biocatalyst and highly selective transformation and synthesis in environment friendly manner. Fruit juice is inexpensive and easily available and also easy to extract and used as a catalyst in the organic transformations. The growing interest in use of fruit juice as a biocatalyst in organic reaction because of its environmentally benign character, nonhazardous and cost effectiveness. Many fruit juice is acidic in nature [57].

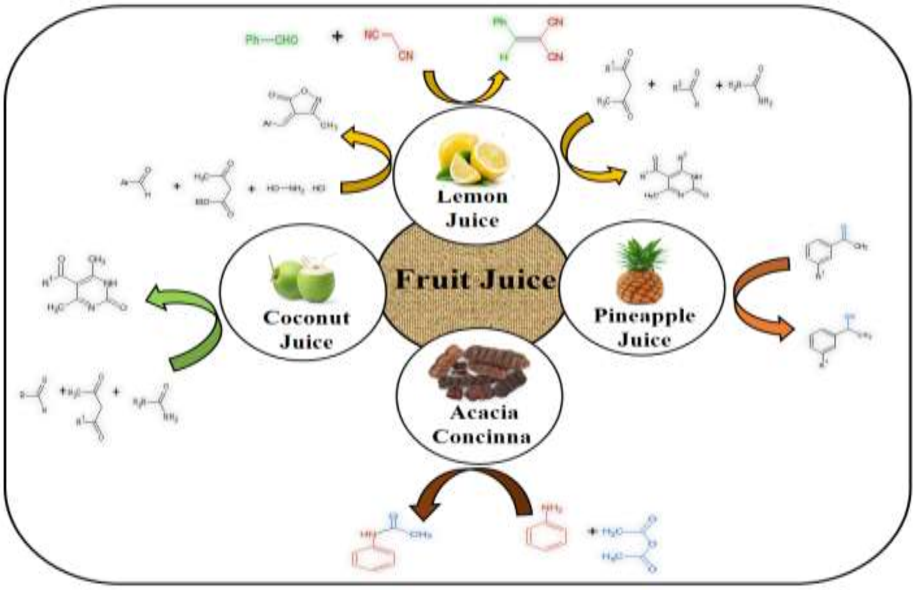
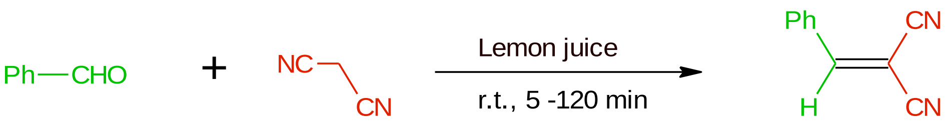


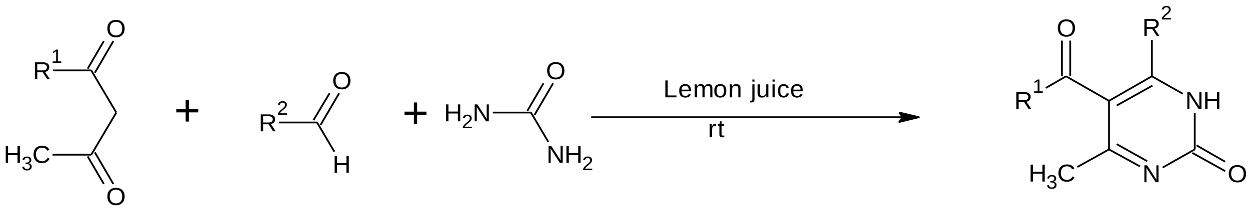
Fig. 3. Application of fruit juice in organic synthesis.

Rammohan pal reported the synthesis of product by knoevenagel condensation by using lemon juice extract. Deshmukh and co-workers studied that for the knoevenagel condensation reaction, lemon juice act as an homogeneous acid catalyst under solvent free condition (Scheme 42) [57].



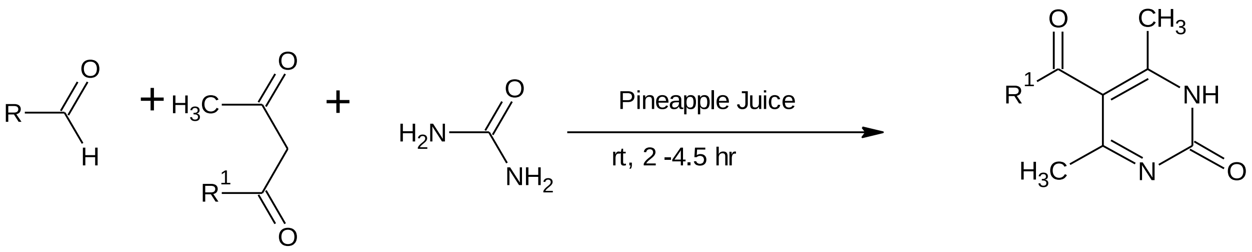
Scheme 42: Lemon juice catalyzed knoevenagel condensation.

M. Deshmukh et al. reported the synthesis of dihydropyrimidionone by using three components under solvent free conditions from aldehydes, 1,3-dicarbonyl compound and urea at room temperature by using lemon juice as a natural catalyst (Scheme 43) [58].



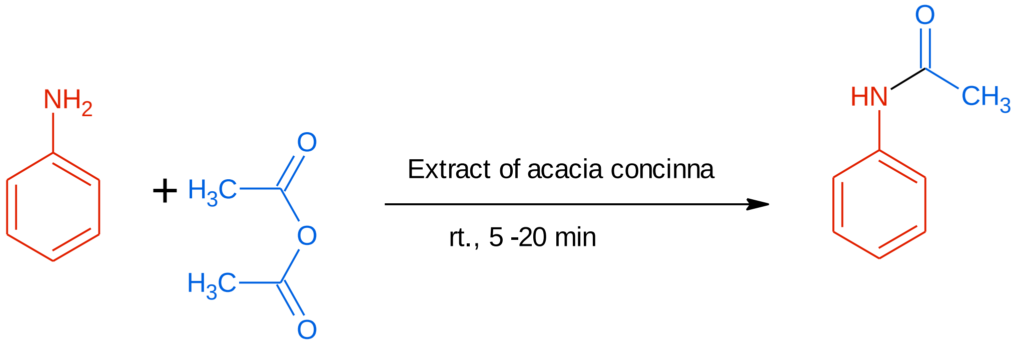
Scheme 43: The synthesis of dihydropyrimidinones by using lemon juice as a catalyst.

G. M. Nazeruddin and co-workers reported a synthesis of dihydropyrimidinones from aldehyde, diketone and urea in presence of pineapple juice at room temperature. The pineapple juice is an acidic in nature. It is used as a catalyst in this reaction (Scheme 44) [59].



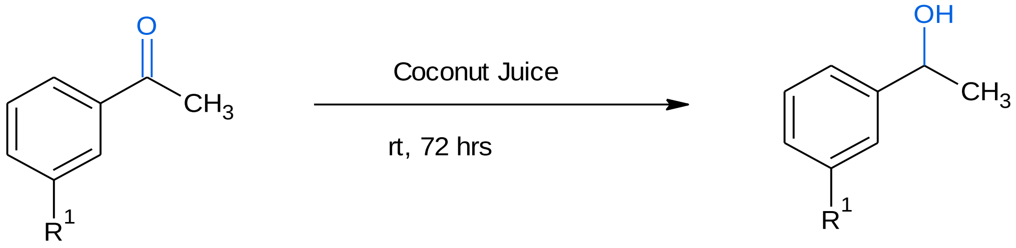
Scheme 44: Pineapple juice catalyzed synthesis of dihydropyrimidinones.

Patil et al. reported a synthesis of imine of aryl aldehyde and aromatic primary amine using extract of acacia concinna at room temperature and it gives good yield of product (Scheme 45) [57].



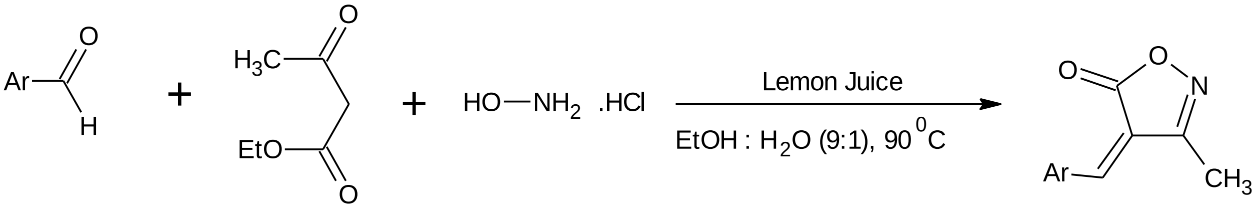
Scheme 45: Acylation of amines with Ac$_2$O catalyzed by pods of Acaaciaconcinna fruit.

Fonseca et al. developed a simple and green method for the selective bioreduction of aliphatic and aromatic aldehydes and ketones in high yield by using coconut juice as natural catalyst (Scheme 46) [57].



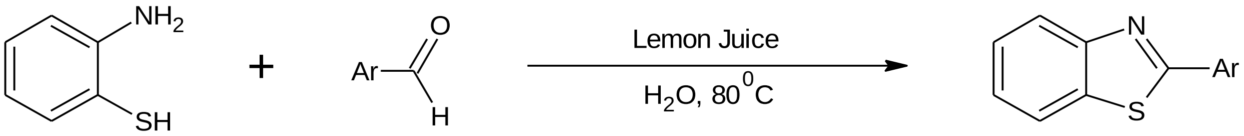
Scheme 46: Enantioselective reduction of aromatic ketone using coconut juice.

Vekariya, R. H. and co-workers reported a synthesis of isoxazole-5(4H)-ones by using three components such as aromatic aldehyde, ethylacetoacetate and hydroxylamine hydrochloride in presence of lemon juice and EtOH: H_2O (9:1) solvent proportion (scheme 47) [60].



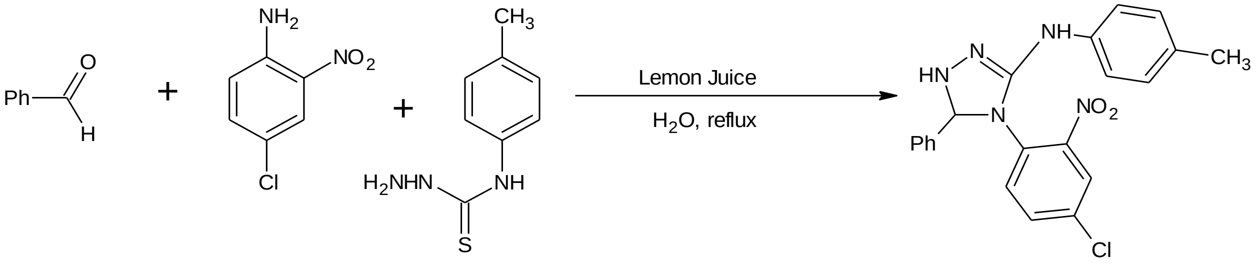
Scheme 47: Synthesis of substituted isoxazole – 5(4H)- ones.

Patil, MA et al. reported a synthesis of benzothiazoles by using lemon juice as a catalyst. The reaction is carried out in the aqueous medium at 80ºC. The reaction followed the protocol of green chemistry (scheme 48) [60].



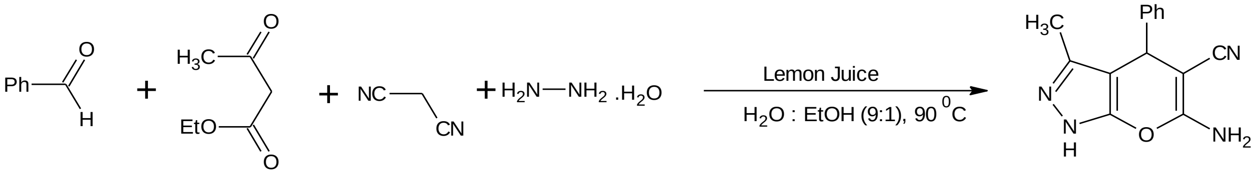
Scheme 48: Synthesis of benzothiazoles.

Sachdeva et.al. reported a synthesis of spiro indole-triazole by using three components such as aromatic aldehyde, thiosemicarbazide and 4-chloro,2-nitro aniline in presence of lemon juice used as a catalyst. The reaction was processed in the aqueous medium (Scheme 49) [61].



Scheme 49: Synthesis of spiro indole-triazole derivatives.

Vekariya and co-workers reported a synthesis of pyrano[2,3-c]-pyrazoles by using four components such as aromatic aldehyde, ethylacetoacetate, malononitrile and hydrazine hydrate. In this reaction lemon juice is used as a catalyst. The reaction carried out in an aqueous medium at 90°C (Scheme 50) [62].



Scheme 50: Synthesis of pyrano[2,3-c]-pyrazoles.

3.3 Enzymes:

Enzyme is used as a catalyst in organic reaction because it increase the rate of reaction. Enzyme is a biological molecule i.e. it is a green catalyst for many organic reaction. Mostly protein used as enzyme in reaction. Inside the enzyme, generally catalysis occurs at a localized site and this localized site is known as an active site. Many enzymes are made up with the proteins, either single protein or chain of proteins. Enzymes also incorporate the non-protein components such as metal ion known as cofactor. Many cofactors are vitamins. The important factors in enzyme catalysis include the general acid and base catalysis. Mechanism of enzyme catalysis is different but they are similar in the principle as compared to chemical catalysis. In enzyme catalysis the reagent binding with the enzyme restricts the conformational space of the reactants, they holding it with proper orientation and close to each other, so they are frequently collide to each other and with correct geometry so it increase the feasibility of the reaction. There are many advantages of enzymatic catalyst than biocatalyst because due to this reaction takes place at room temperature, easy to recovery of catalyst and it minimizes the waste water it minimizes the water washing step. So, the use of enzyme as a catalyst in chemical reaction is ecofriendly which follow the principles of green chemistry.

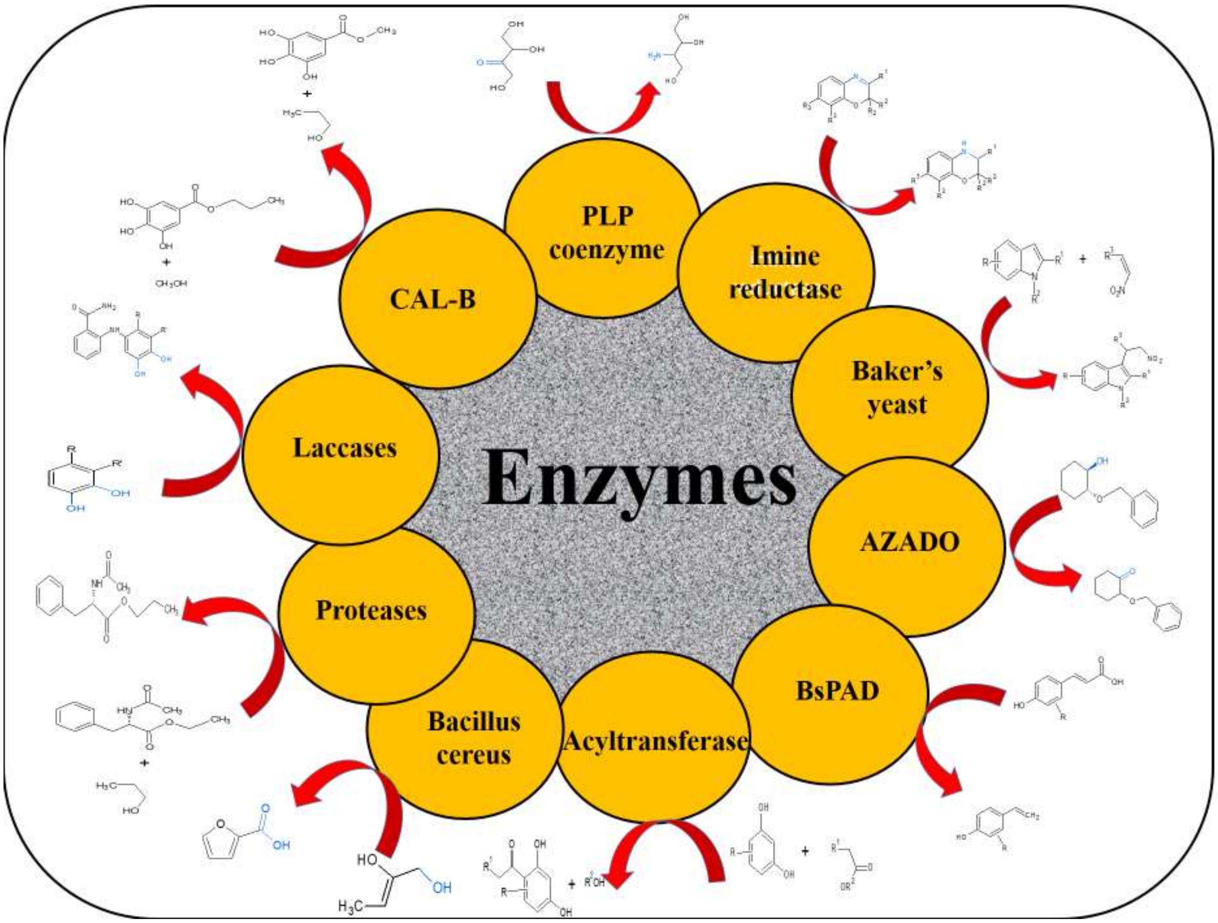
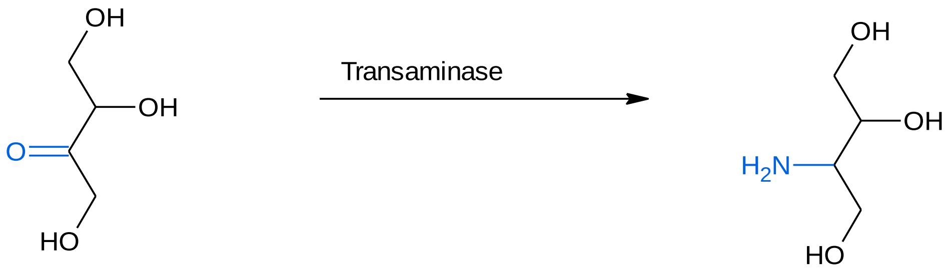


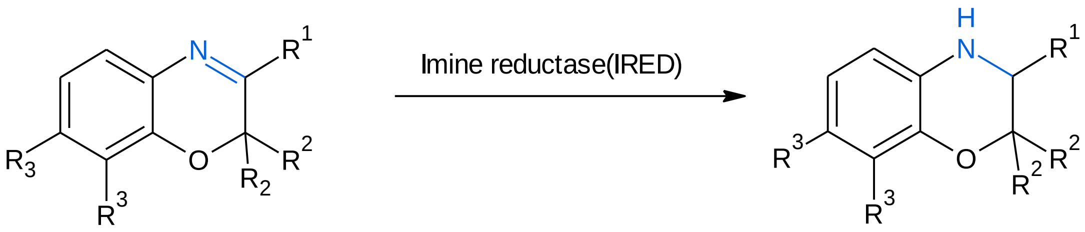
Fig.4. Organic transformation by using enzyme as a biocatalyst.

Ryan Cairns and co-workers reported a conversion of aldehyde and ketones to the corresponding amines by using amine transaminases in presence of puridoxyl-5-phosphate(PLP) coenzyme (Scheme 51 [63].



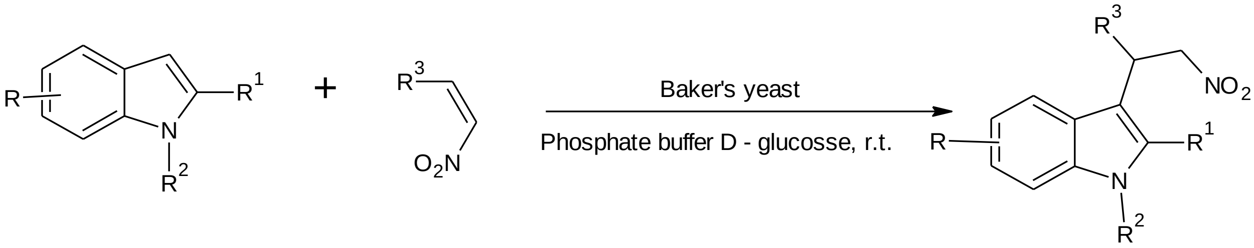
Scheme 51: Biocatalytic strategies for the direct amination of sugars.

Nadine Zumbragel and co-workers reported biocatalytic reduction 2H-1m4-benzoxazines 1 using imine reductase and in situ- cofactor is recycling by glucose dehydrogenase (Scheme 52) [64].



Scheme 52: Biocatalytic reduction of 2H-1,4-benzoxazines.

Ananda Mane and co-workers reported Michael addition of indoles to nitro-olefins in presence of fermented baker’s yeast. The reaction was carried out in presence of phosphate buffer (p^H=7) and-glucose at room temperature (Scheme 53) [65].

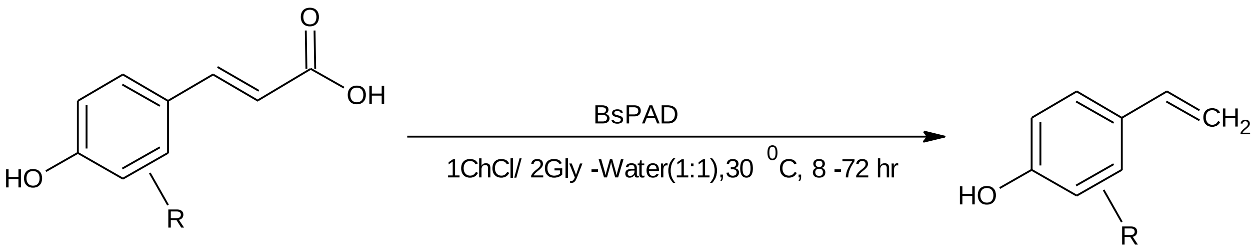


Scheme 53: Michael addition of indoles to nitroolefins in fermented baker's yeast.

Elisa Liardo and co-workers reported AZADO-catalyzed oxidation of trans-(±)-2-(benzyloxy)cyclohexanol (1b) with aq. NaOCl. 2-azaadamantane N-oxyl (AZADO) is an efficient catalyst for oxidation of hindered secondary alcohol (Scheme 54) [66].

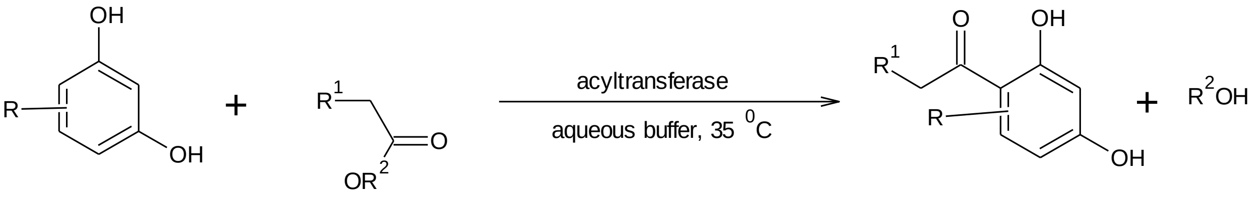
Scheme 54: Oxidation of trans-(±)-2-(benzyloxy)cyclohexanol (1b) by using AZADO catalyst in aq. NaoCl.

Schweiger et al. reported a decarboxylation of p-hydroxycinnamic acid by using BsPAD enzyme catalyst. BsPAD means Bacillus subtilis. This reaction is carried out in eutectic mixture choline chloride/glycerol (1ChCl/2Gly) at 30^{0}C (Scheme 55) [67].



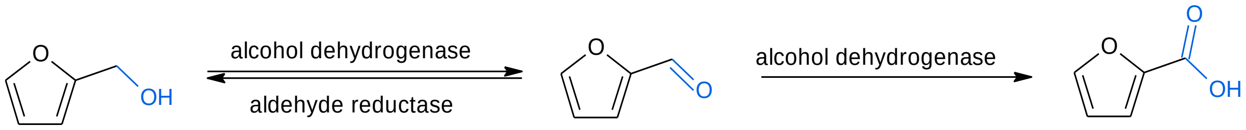
Scheme 55: Decarboxylation of p- hydroxycinnamic acids by using BsPAD in the 1ChCl/ 2Gly-water medium.

Christoph K. Winkler and co-workers reported the C- acylation of resorcinol derivative using acyltransferase enzyme catalyst. This reaction is carried out in aqueous buffer solution at 35°C. In this reaction enzyme used as a catalyst and aqueous medium used as a solvent so it follows all protocol of green reaction (Scheme 56) [68].



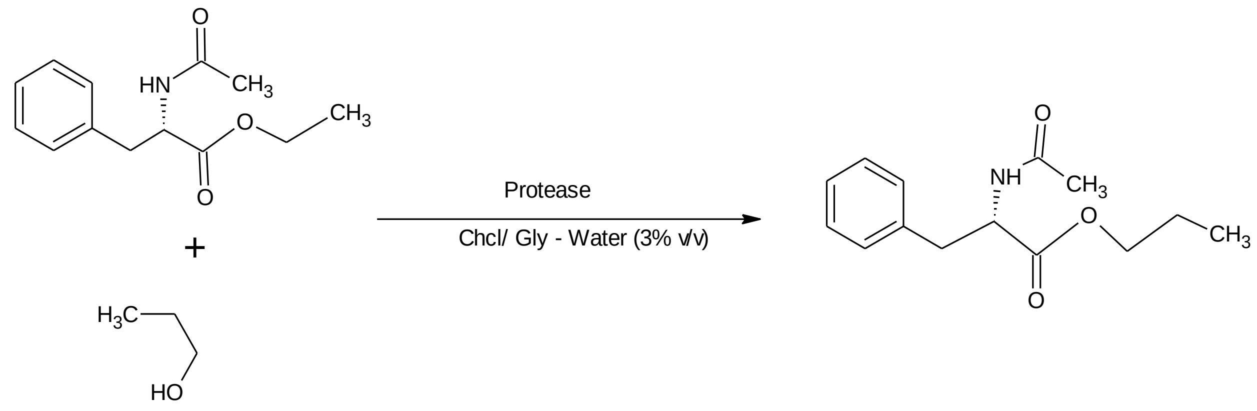
Scheme 56: Biocatalytic C- Acylation of Resorcinol derivatives using an Acyltransferase.

Alejandra Rodríguez M and co-workers reported a biotransformation of furfural using whole cells of Bacillus cereus. Whole cell is preferred than enzyme because cells are economical, more stable, and do not require complex regeneration systems (Scheme 57) [69].



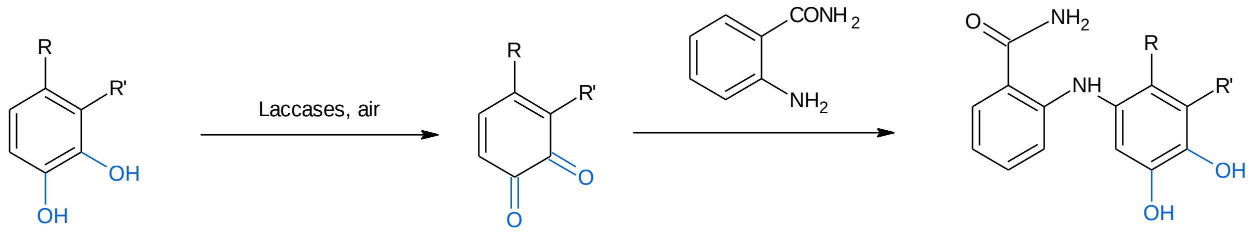
Scheme 57: Biotransformation of furfural using whole cells.

Pablo Domínguez de María and co-workers reported transesterification of N-acetyl-I-phenylalanine ethyl ester with 1-propanol by using proteases catalyst in DES. Deep eutectic solvents (DESs) has more practical,ecological advantages.It has less volatility, more thermal stability as like ionic liquid. Due to use of DES, biocatalyst show more activity (Scheme 58) [70].



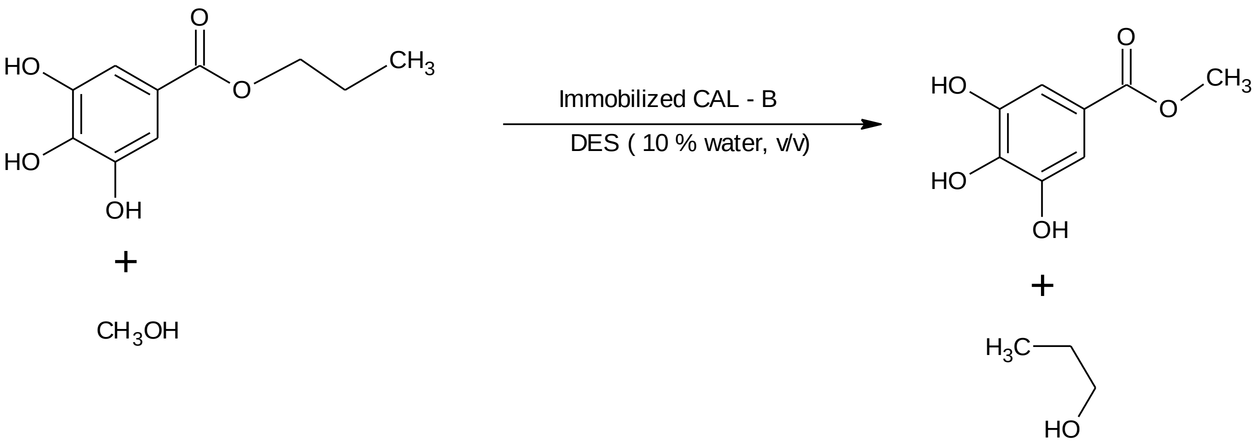
Scheme 58: Transesterification of N-acetyl-I-phenylalanine ethyl ester with 1-propanol by using proteases in DES.

Hahn, V and co-workers reported a nuclear amination with anilines by using laccase in presence of air (Scheme 59) [71].



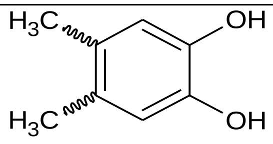
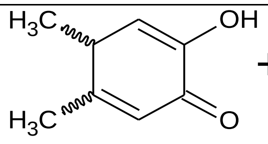
Scheme 59: Laccase – mediated nuclear amination with anilines.

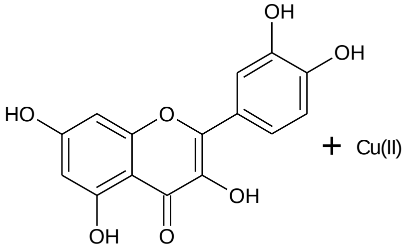
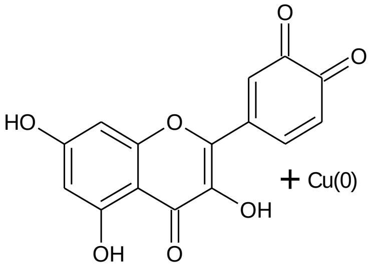
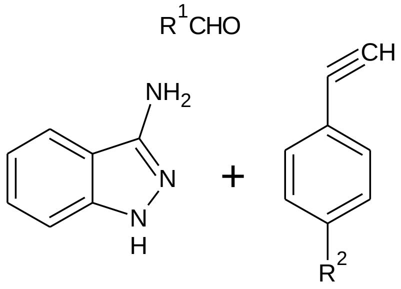
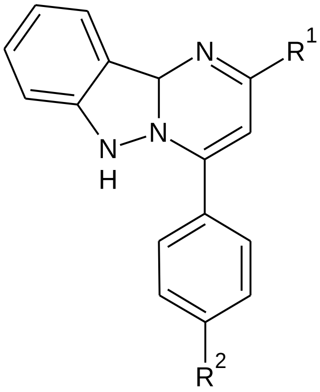
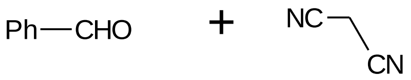
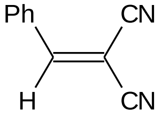
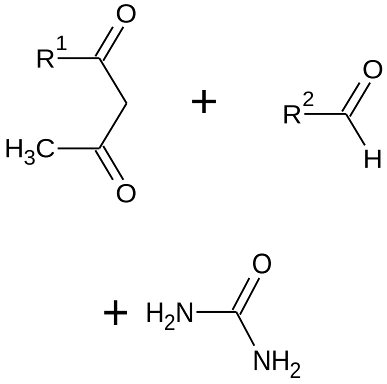
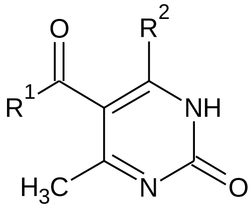
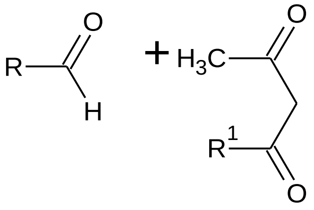
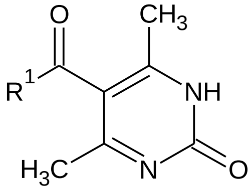
Pablo Domínguez de María and co-workers reported transesterification of propyl gallate with methanol by using immobilized in presence of DES. The stability and activity of enzymes in presence of DES is depends upon the enzyme type, substrate and reaction time. The lipase B from Candida antarctica (CAL-B) CAL-B shows good activity in presence of DES (Scheme 60) [70].

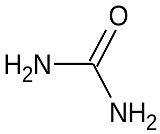
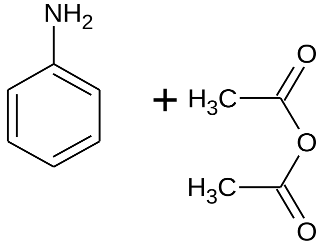
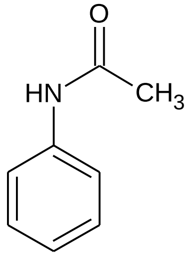
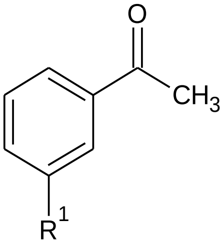
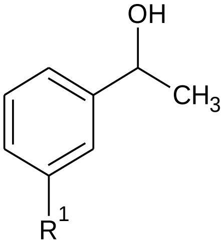
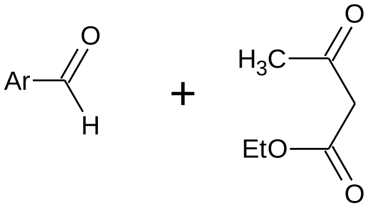
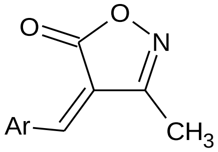
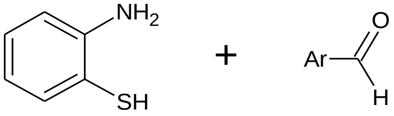
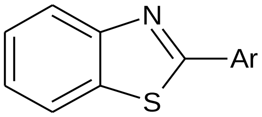
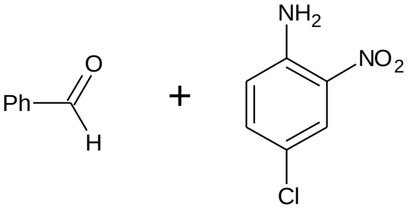
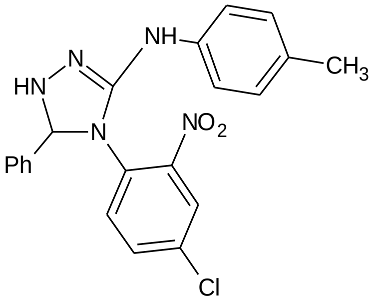


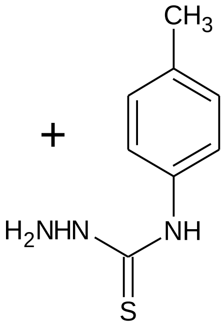
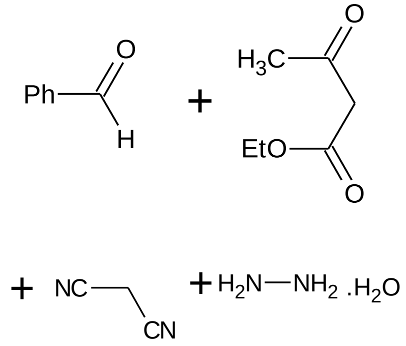
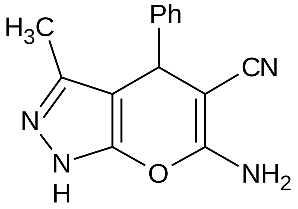
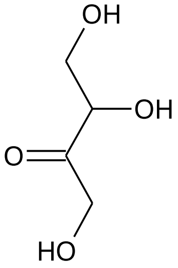
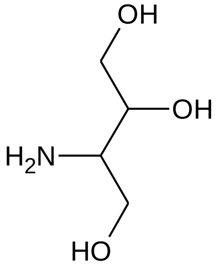
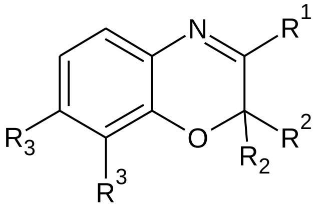
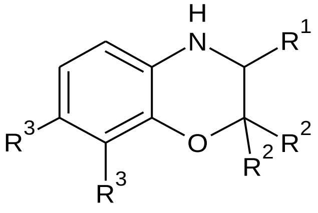
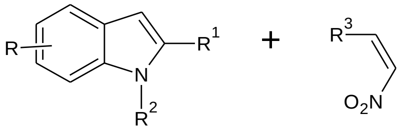
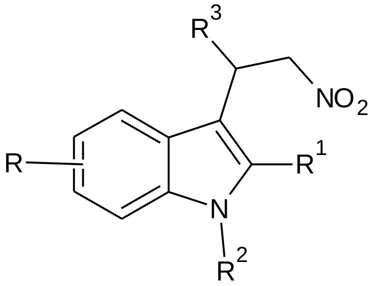
Scheme 60: Transesterification of propyl gallate with methanol by using immobilized CAL-B catalyst in DES.

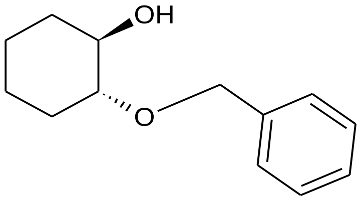
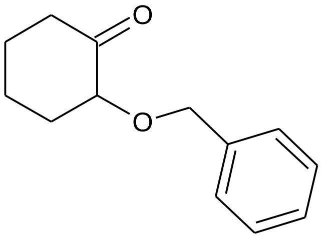
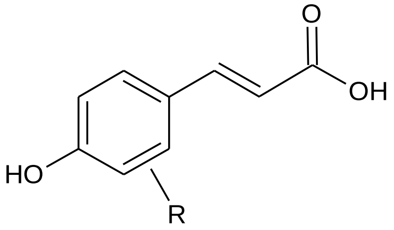
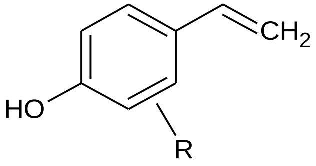
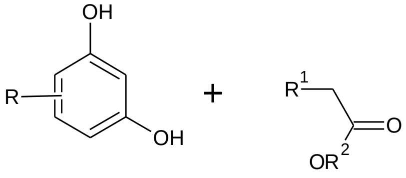
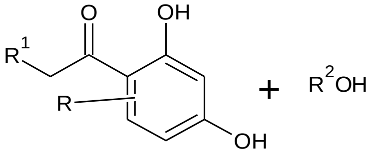
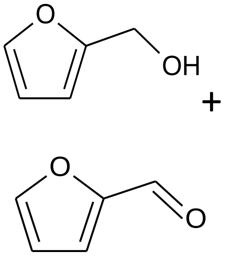
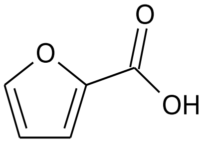
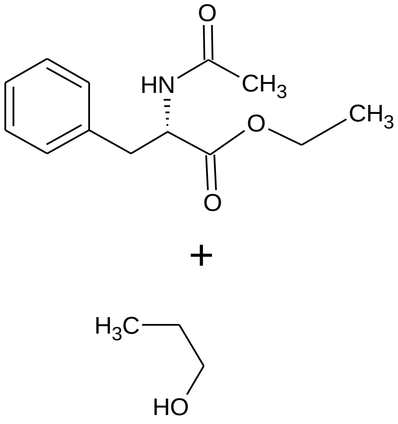
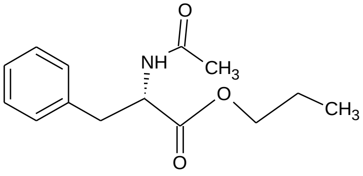
The short summary and overall progress of organic synthesis by biocatalyst in last decades are summarized in table number 2. The reactions summarized in table number 2 were carried out by using plant extract, enzyme and fruit juice.

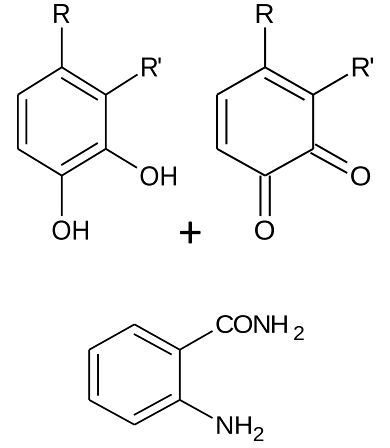
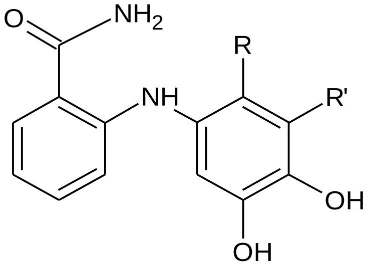
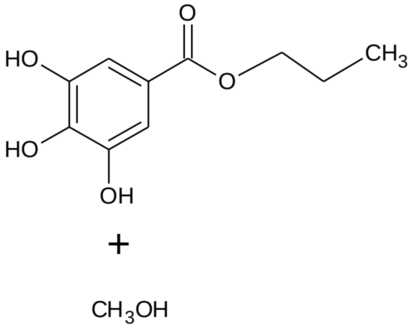
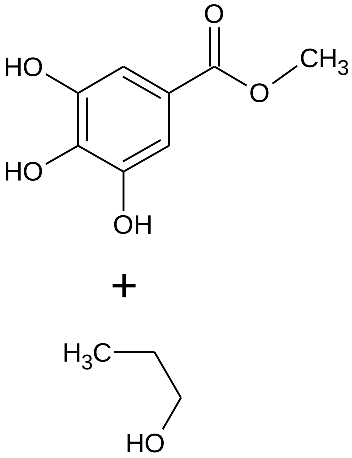
Table 2: Short summary of Biocatalyst				
Scheme entry No.	**Reactant**	**Condition**	**Product**	**Referen-ces**
39	 + Ag (I)	Plant extract, H_2O	 + Ag(0)	[55]

40		Cuscuta reflexa plant extract.		[56]
41		Neat, 80^{0}C		[17]
42		r.t., lemon juice		[57]
43		r.t., lemon juice		[58]
44		r.t., pineapple juice		[59]

				
45		r.t., acacia concinna plant extract		[57]
46		r.t., coconut juice		[57]
47	 + HO—NH$_2$ .HCl	EtOH:H$_2$O (9:1),90^{0}C		[60]
48		H$_2$O, 80^{0}C		[60]
49		H$_2$O, reflux		[61]

				
50		EtOH:H$_2$O (9:1),90^{0}C		[62]
51		Transamin-ases enzyme		[63]
52		Imine reductase		[64]
53		Baker's yeast, r.t.		[65]

54		Aq. NaOCl, r.t		[66]
55		Gly: H_2O (1:1), 30^{0}C		[67]
56		Aqueous buffer, 35^{0}C		[68]
57		Alcohol dehydrogenase		[69]
58		Gly-Water		[70]

59		Laccases, air		[71]
60		DES (10% water)		[70]

4. Reaction Medium:

There is need to use organic solvent in many organic synthesis which are hazardless to environment. Volatile organic compounds are evolved into environment by evaporation. So, more amount of volatile solvents are required for organic synthesis. To overcome this problem organic reaction are carried out in the absence of solvents or by use of non-volatile solvents which are less hazardous for environment. The ideal green solvent is hazardless, high B.P., naturally available and cheap.

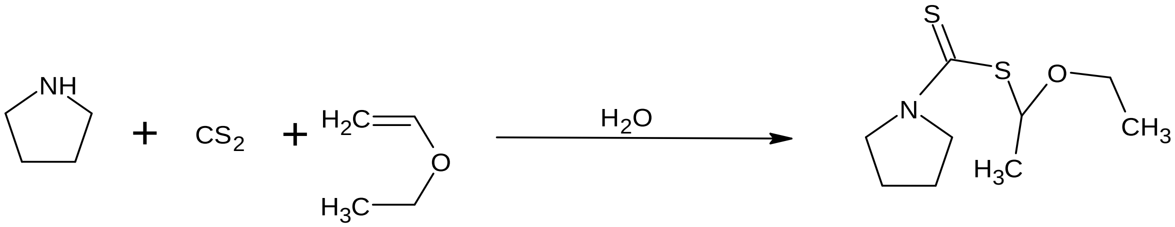
Organic reaction carried out in aqueous medium and solvent free condition also. Many scientist carried out organic reactions in organic solvent, this solvents are hazardous for environment and human health also. Now-a-days researchers used environment friendly solvent for reactions. So, there is need of use of ecofriendly solvent for organic reaction. So, now-a-days reactions are carried out in aqueous medium, Due to this all principles of green chemistry is followed.[72]

4.1 Aqueous Medium:

Now-a-days many researchers, organic transformations were carried out in aqueous medium. In aqueous medium comes many solvents such as water, ionic liquids, supercritical liquids, polyethylene glycol, ethanol : water (1:1) Water is the basis of life. In many organic reaction, water is used as a solvent. Water is cheap solvent, easily available in nature. Many organic solvents are expensive, hazardous and flammable. But as compared to this solvents, water has no any adverse properties. In organic reaction product is separated by phase separation method. It is also simple to control the temperature of reaction, since water has the highest heat capacity than any other solvent. The use of water in organic reaction reduced the hazardous substance and it is beneficial for environment. Ionic liquid is goof option for the organic solvents. Ionic liquids are appealing properties such as low vapour pressure, good chemical and thermal stability, they are inflammable and high ionic conductivity [72].

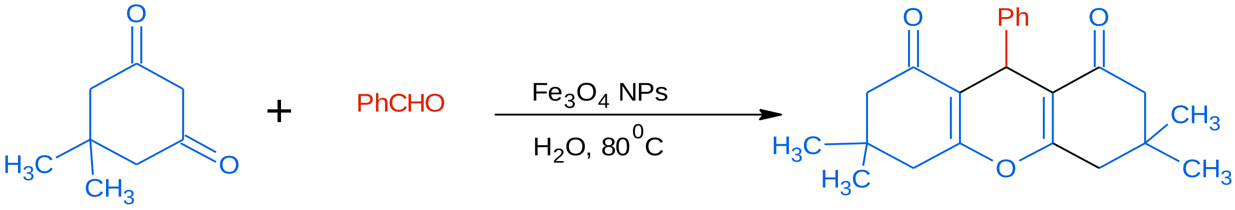
In conventional solvents consist of single molecules but ionic liquids consist of ions and liquids are room temperature. Use of protic ionic liquid in organic reactions act as an excellent reaction medium, dissolving both hydrophobic and hydrophilic molecules. Ionic liquid is green solvent used in many organic reaction, inorganic synthesis and polymer synthesis. Mixing of ionic liquid with other liquids is more easy for tuning their properties than the structural design of pure ionic liquids. Water is an important partner for ionic liquid because water has more variety of properties than pure ionic liquids. So, mixing of this solvents provide a large number of application for synthesis [73].

Azim Ziyaei Halimehjani and co-workers reported an efficient and environmentally friendly procedure for Markovnikov addition reaction of dithiocarbamate to alkyl vinyl ethers in aqueous medium without using any catalyst. They used different amines for formation of the designed product but when they used piperidine as an amine then high yield of product is formed (Scheme 61) [74].



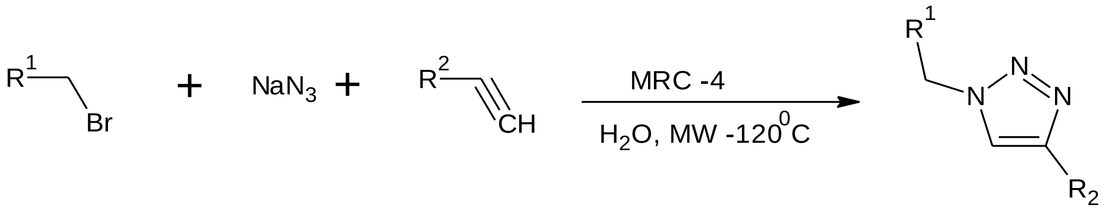
Scheme 61: Markovnikov addition reaction.

Karami group reported a synthesis of 1,8-dioxo-octahydroxanthenes by using Fe_3O_4 NPs. Nanoparticles acts as a lewis acid to activated carbonyl group present in aldehyde. There is a condensation reaction between aldehyde and diketone. The feature of this reaction is easy to work up, short reaction time and the reusability of this catalyst (Scheme 62) [14].



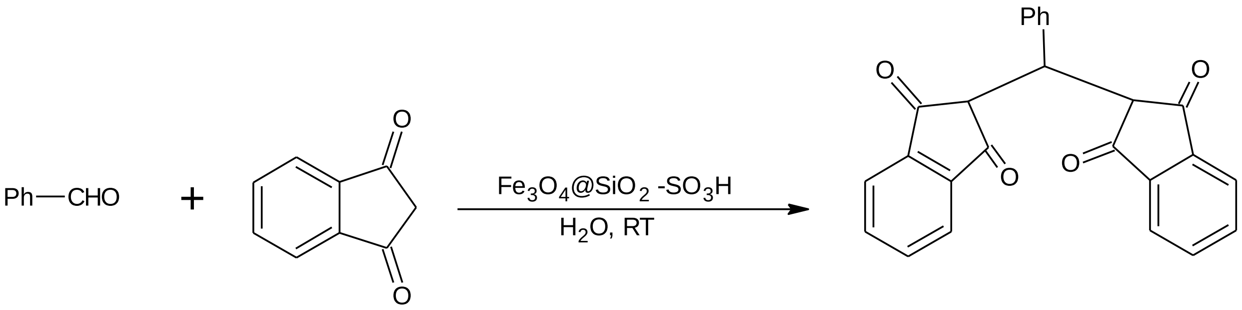
Scheme 62: The synthesis of 1,8-dioxo-octahydroxanthenes catalyzed by Fe_3O_4Nps.

Varma group reported azide-alkyne cycloaddition in water. They used Cu- functionalized MRC-4 and it is used in 1,3 dipolar cycloaddition. MRC-4 is prepared by glutathione anchored to Fe_3O_4 surfaces, followed by complexation of Cu ion (Scheme 63) [14].



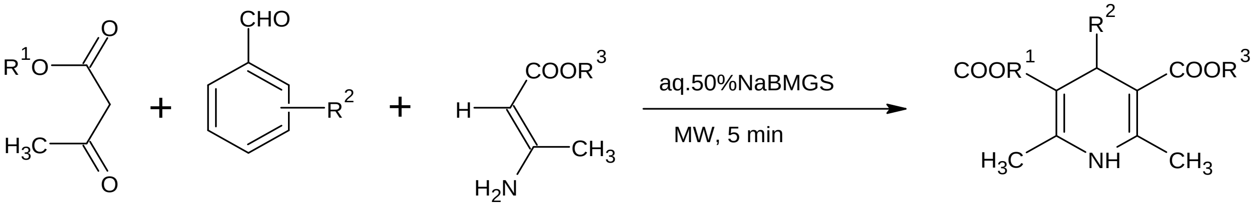
Scheme 63: Three component one-pot cycloaddition reaction.

Nemati group reported SiO_2 coated sulfonic acid act as a MRC. This catalyst used in synthesis of tetraketone derivative by knoevenagel condensation and Michael addition in water (Scheme 64) [14].



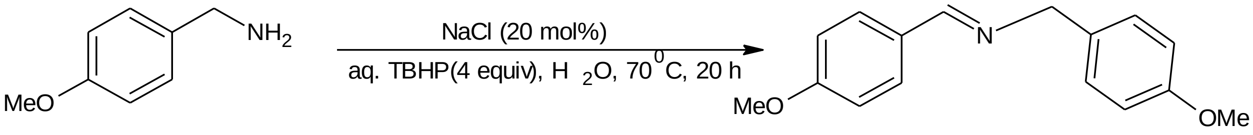
Scheme 64: The synthesis of tetraketones catalyzed by $Fe_3O_4@SiO_2\text{-}SO_3H$.

B.M. Khadikar et al. reported a synthesis hautzsch esters by using alkyl beta-aminocrotonate, aldehyde and alkyl acetoacetate in aqueous 50% sodium butyl-monoglycol sulfate. It was a hydrotropic solution. Reaction carried out in microwave (Scheme 65) [75].



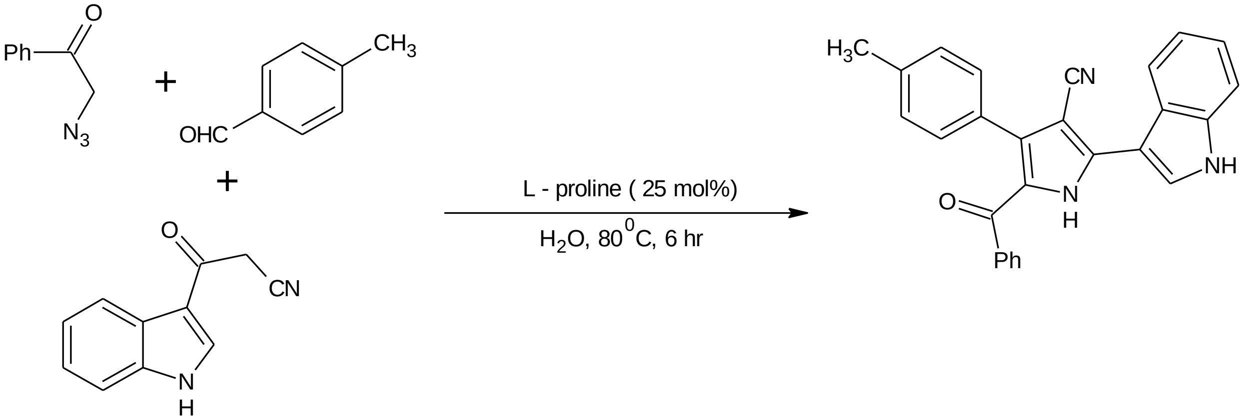
Scheme 65: Synthesis of dihydropyridine ester derivatives.

Susanta Hazra et al. reported the oxidation of primary amine to imines in presence of NaCl used as a catalyst. The catalyst is easily available or we used sea water also. The number of reactions were carried out to optimize the reaction conditions. They used of NaCl as a catalyst and TBHP in 90% of water was used as solvent for carried out the reaction (Scheme 66) [76].



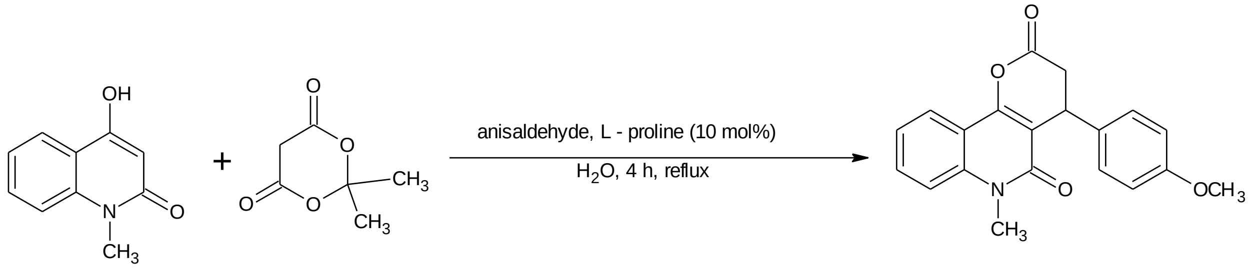
Scheme 66: Oxidation of primary amine to imines.

P. T. Perumal et al. reported a synthesis of tetrasubstituted pyrrole by using three components such as a-azido ketone, p-tolualdehyde and 3-cyanoacetylindole. This reaction is carried out in presence of L-proline in water is used as a catalyst at 80°C. The L-proline plays an important role in this transformation, it promote the initial knoevenagel condensation between p-tolualdehyde and 3-cyanoacetylindole followed by Michael addition (Scheme 67) [77].



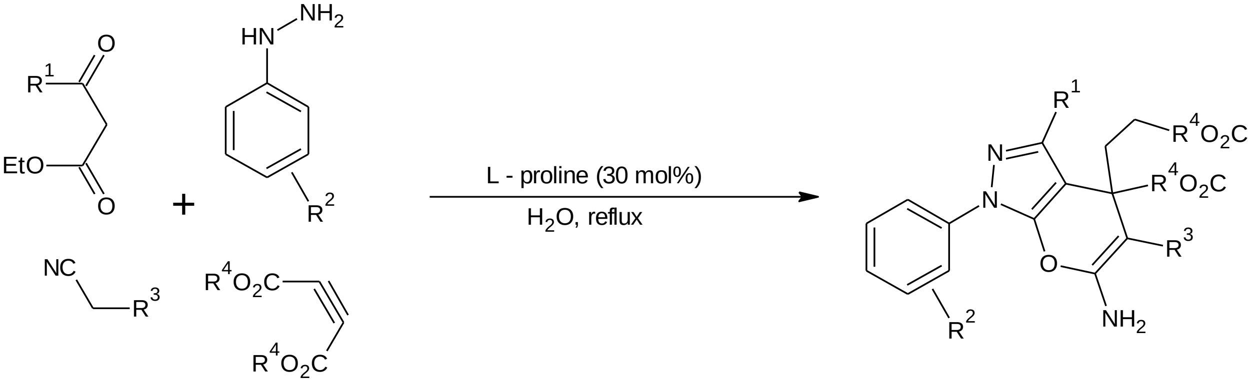
Scheme 67: Proline catalyzed synthesis of tetrasubstituted pyrrole.

Zhu et al. reported a synthesis of pyrano[3,2-c]quinolone-2,5-diones in presence of aqueous medium (Scheme 68) [77].



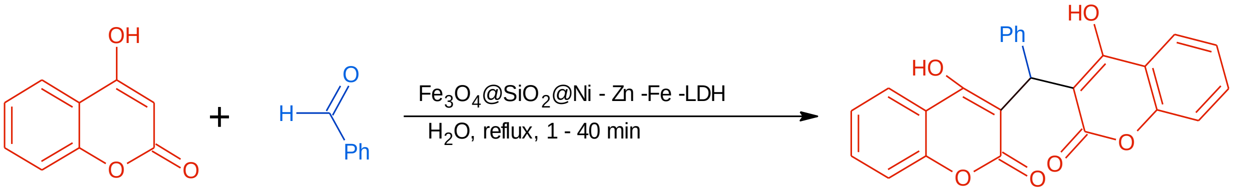
Scheme 68: Synthesis of pyrano [3,2-c]quinolone-2,5-diones.

B. S. Vachan et al. reported a synthesis of pyrano [2,3-c]pyrazoles by using four components in presence of proline as a catalyst and water as a solvent. So, this reaction fulfilled the condition of green chemistry (Scheme 69) [77].



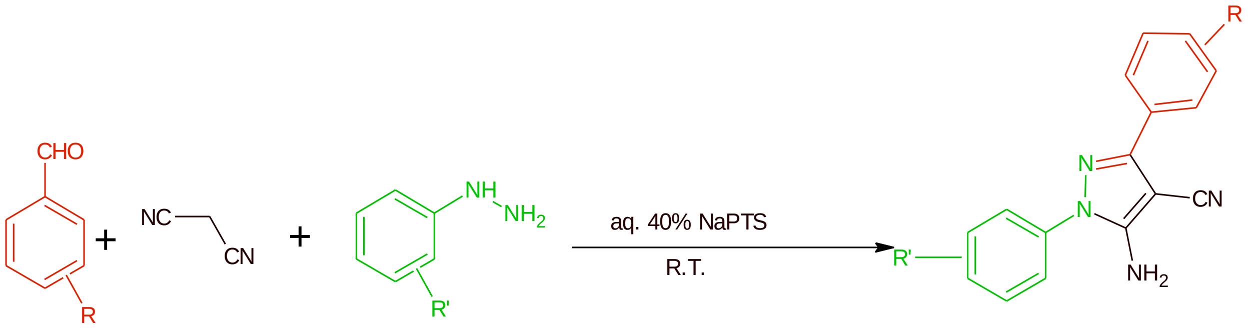
Scheme 69: Synthesis of highly functionalized pyrano [2,3-c]pyrazoles.

Masumeh Gilanizadeh et al. reported a synthesis of Biscoumarin by using Ni-Zn-Fe hydrotalcite supported on Fe_3O_4@SiO_2 nanoparticles. The reaction takes place between 4-hydroxycoumarin with aromatic aldehyde in refluxing water. It gives excellent yield of biscoumarin (Scheme 70) [79].



Scheme 70: Biscoumarin synthesis under LDH catalysis condition.

Aboli Sapkal et al. reported a synthesis of 5-aminopyrazole-4-carbonitrile in aqueous medium. They used sodium paratoulenesulfonate (NaPTS) hydrotrope for this synthesis. There were many advantages of this hydrotrope such as eco-friendly, less toxic, inexpensive and non-flammable. NaPTS is easily recoverable from reaction mixture. The synthesis of desired product from benzaldehyde, malononitrile and phenyl hydrazine (Scheme 71) [80].



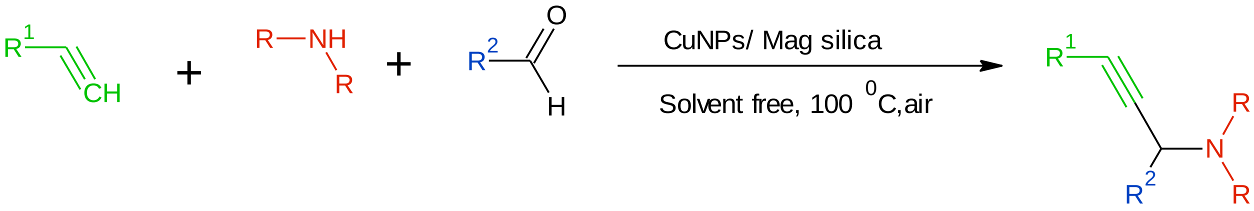
Scheme 71: Synthesis of 5-amino-pyrazole-4-carbonitrile.

4.2 Solvent free:

Many conventional organic transformation make a use of toxic and volatile solvents which are harmful for environment. So, there is a need of replacement of this hazardous solvent by green solvent or by without using solvent for reaction. It is the principle of green chemistry. With rising the environment awareness, the design solvent free green organic reaction. Many reactions are solvent free or solid state condition which reduced the pollution of environment. short time these reaction gained popularity and importance from researchers [13].

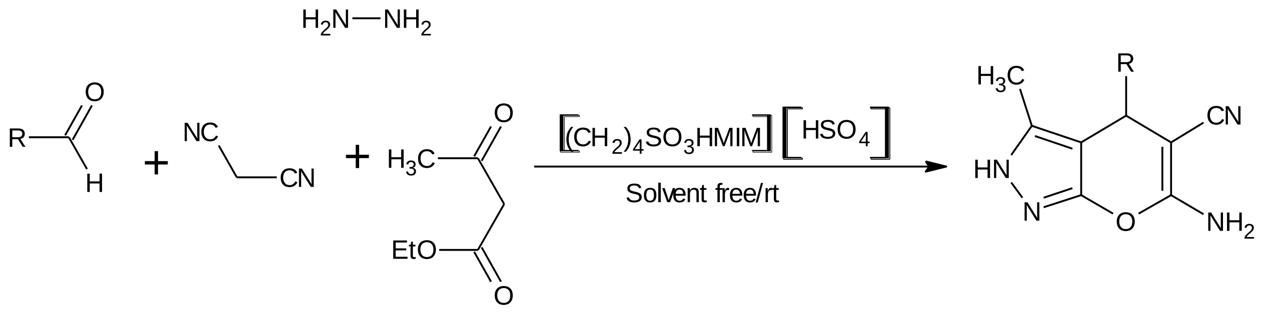
Many multicomponent reactions are carried out in solvent free condition by using catalyst. Solvent free reactions are carried out in mortar pestle and microwave also. So, it is reduce the time of reaction solvent free organic reactions make synthesis is simpler, prevent hazards, toxicity wastes. There are many advantages of solvent free reaction. It is cost saving. Lower consumption of energy and give pure product. These reaction processed by higher efficiency.

F. Nador and co-workers reported an alkyne coupling reaction. In this reaction they used copper based silica coated maghemite nanoparticles. This nanoparticles were magnetically recoverable. The synthesized nanoparticles were characterized by SEM, TEM, XRD and BET. In this reaction three component were used such as aldehyde, amine and terminal alkyne. The reaction carried out at 100°C in solvent free condition (Scheme 72) [81].



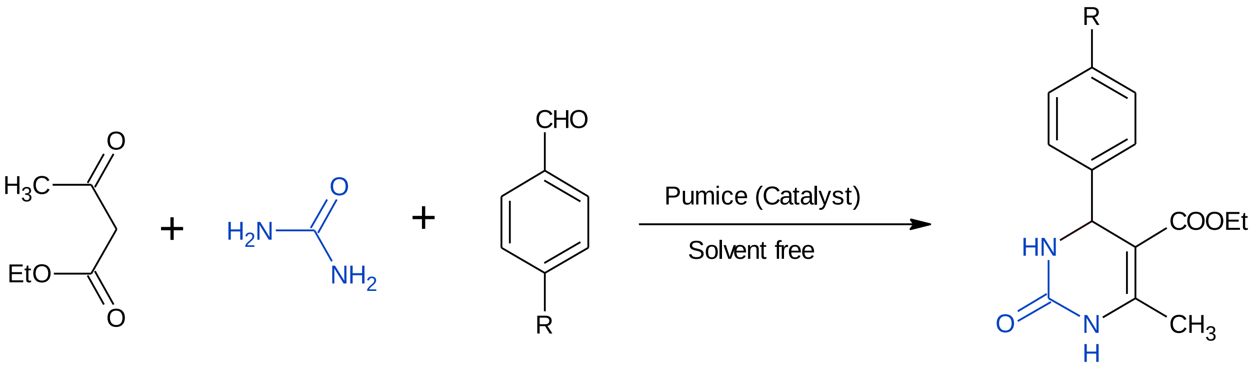
Scheme 72: Alkyne coupling reaction.

Javed Ebrahimi et al. reported a synthesis of pyranopyrazole. This was a four component reaction such as aldehyde, malononitrile, ethylacetoacetate and hydrazine. They carried out the reaction in presence of 3-methyl-1-(4-sulphonic acid) butylimidazolium hydrogen sulphate [(CH2)4SO3HMIM][HSO4] , ionic liquid catalyst. It is an acidic catalyst. The reaction carried out in solvent free condition (Scheme 73) [82].



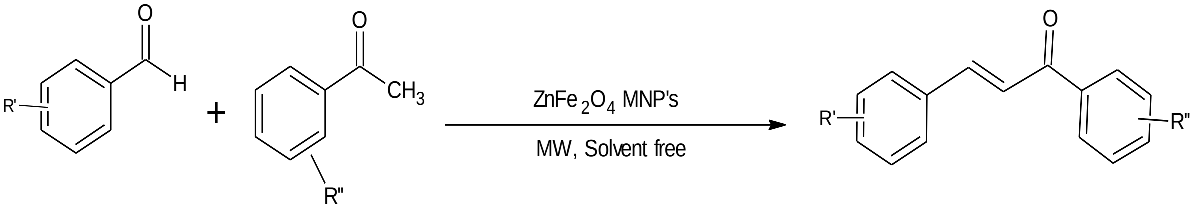
Scheme 73: Synthesis of Pyranopyrazoles.

Hany M. Abd El-Latee et al. reported a synthesis of 3,4-dihydropyrimidine-2(1H)-ones in presence of pumice catalyst. It is a natural heterogeneous catalyst. It was recyclable and effective in upto five reaction cycle. They used urea, aldehyde and ethylacetoacetate as a reactants for synthesis of pyrimidine derivative. They carried out reaction in solvent free condition (Scheme 74) [83].



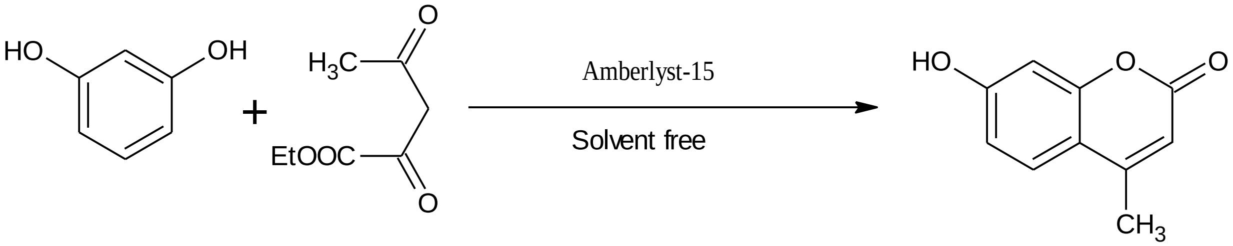
Scheme 74: Synthesis of 3,4-dihydropyrimidine-2(1H)-ones.

Ravikumar M Borade et al. reported a synthesis of chalcones. They used zinc ferrate nanoparticles for the synthesis of chalcones. It is claisen-schmidt condensation reaction. The reaction takes placed in microwave and in solvent free condition. So, the synthesis of chalcones by green method (Scheme 75) [84].



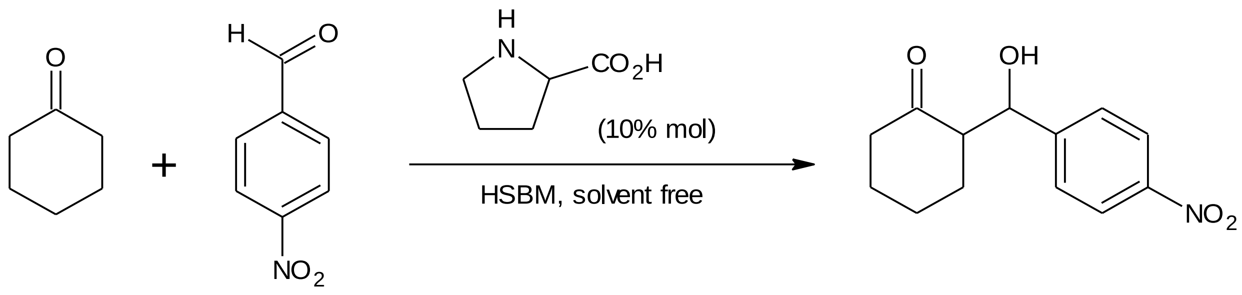
Scheme 75: Claisen-Schmidt condensation under solvent-free condition.

Souad Bouasla et al. reported a synthesis of 7-hydroxy-4-methylcoumarin derivatives. They used resorcinol and ethylacetoacetate in presence of amberlyst-15 heterogeneous catalyst for the synthesis of coumarin derivative. The amberlyst-15 is an acidic catalyst. This catalyst gave more yield compared with other acid catalyst. They carried out reaction in solvent free condition (Scheme 76) [85].



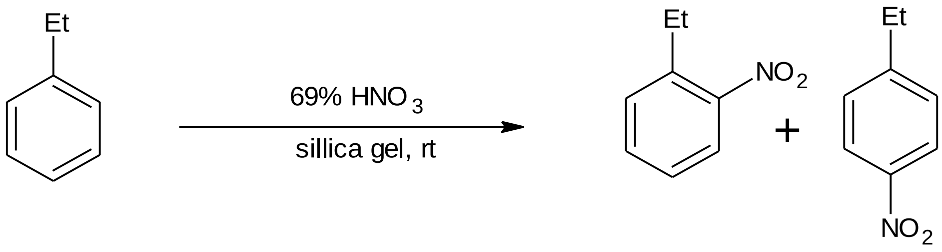
Scheme 76: Synthesis of 7-hydroxy-4-methylcoumarin derivatives under solvent free condition.

Claudia Gabriela Avila-Ortiz and co-workers reported asymmetric aldol reaction organocatalyzed by (S)-proline. The reaction is carried out under solvent free condition. The reaction carried out in short time. The reaction is green (Scheme 77) [86].



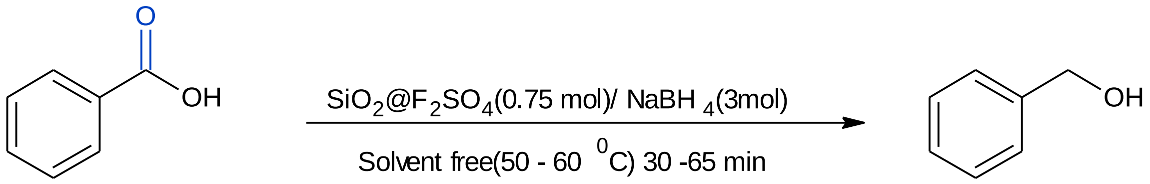
Scheme 77: (S)-proline organocatalyzed asymmetric aldol reaction.

Satoaki Onitsuka and co-workers reported the nitration of ethylbenzene with nitric acid on silica gel. 69% HNO_3 is used for nitration of ethylbenzene. If the percentage of nitric acid is decreases then the yield of product also decreases.500 mg silica gel is used for this reaction. The reaction carried out in solvent free condition and at room temperature (Scheme 78) [87].



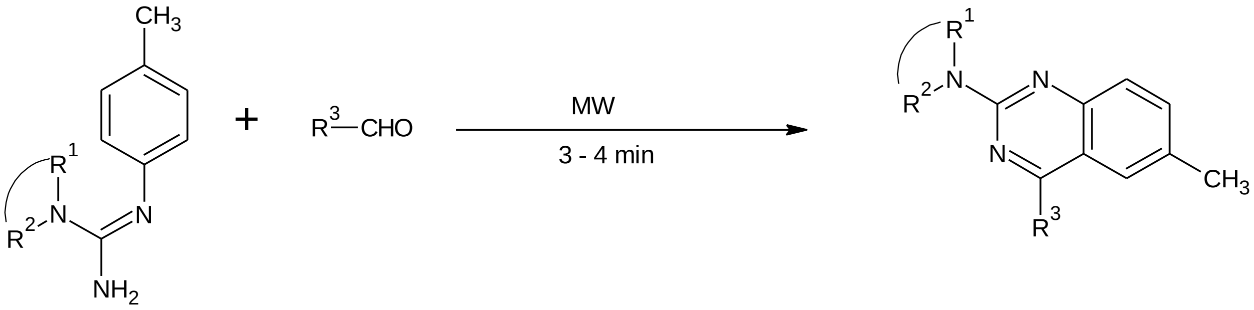
Scheme 78: The nitration of ethylbenzene in presence of nitric acid on silica gel.

Bagheri et al. reported the reduction of aromatic carboxylic acids to alcohols by using $NaBH_4$ in presence of SiO_2@$FeSO_4$ nanocatalyst. The various reagents were used for reduction of acid but it gave less yield, tedious work-up procedure and required drastic reaction conditions. These reagents were expensive and hazardous. But author reported a reduction of acid by using $NaBH_4$ in presence of SiO_2@$FeSO_4$ nanocatalyst in solvent free condition. (Scheme 79)



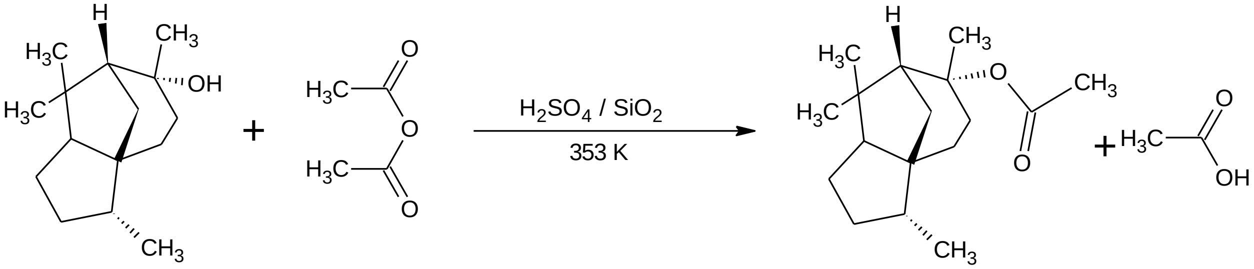
Scheme 79: Reduction aromatic carboxylic acids to alcohols.

Manoj B. Gawande et al. reported the synthesis of quinazolines in microwave. The reaction required 3-4 min for completion. The reaction was carried out in catalyst free and solvent free condition. The reaction followed protocol of green chemistry. (Scheme 80) [88].



Scheme 80: Synthesis of quinazolines using MW irradiation solvent free- catalyst free condition.

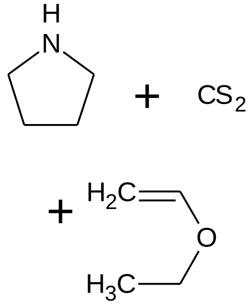
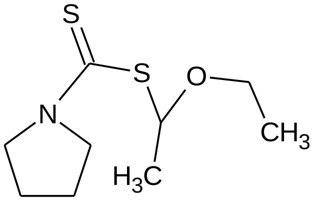
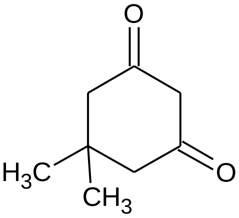
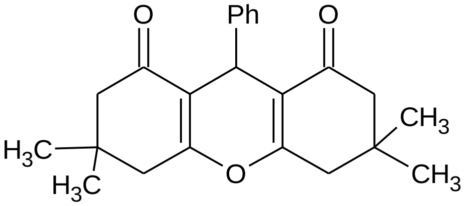
Rina Elvia and co-workers reported an acetylation of (+)-cedrol compound by using acetic anhydride as an acetylating agent in presence of H_2SO_4 / SiO_2 catalyst. Silica sulphuric acid is a reusable heterogeneous catalyst. The reaction carried out in solvent free condition (Scheme 81) [89].

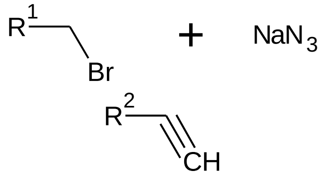
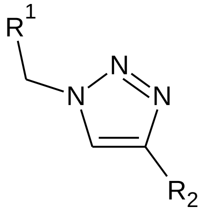
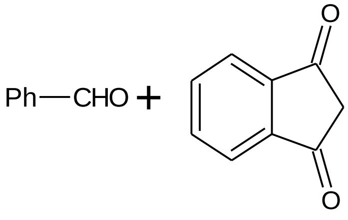
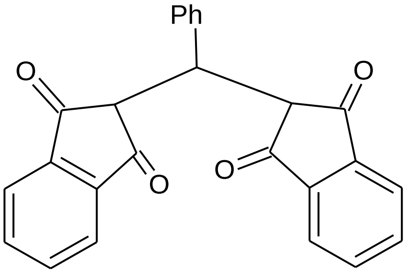
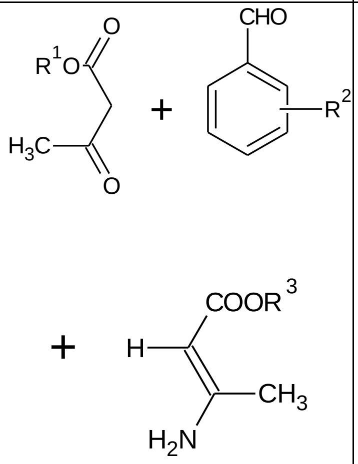
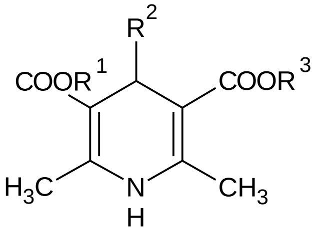
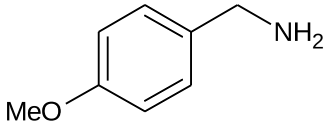
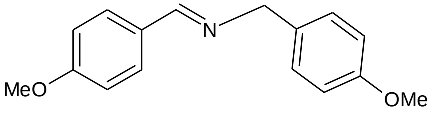
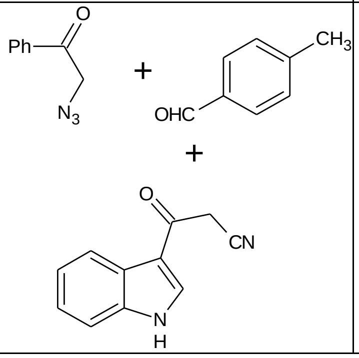
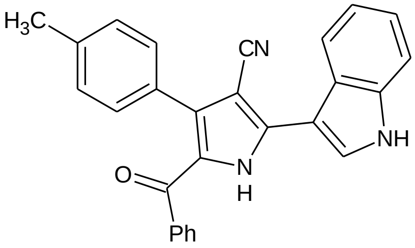


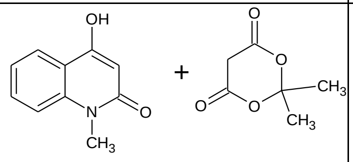
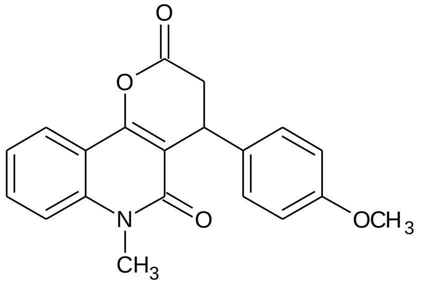
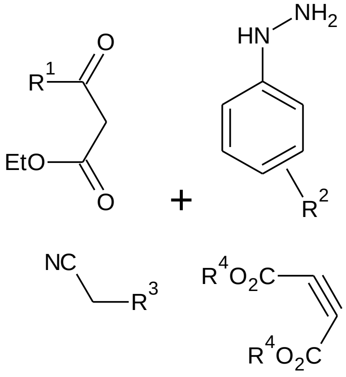
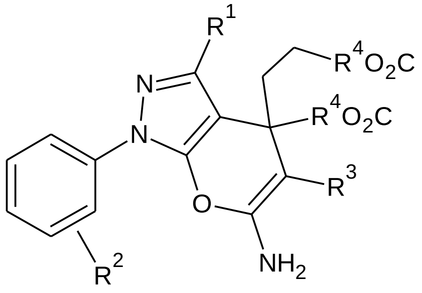
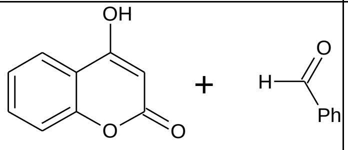
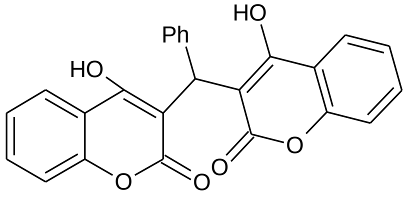
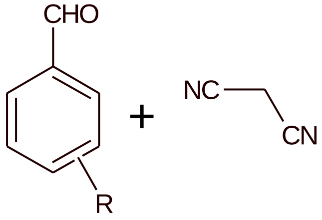
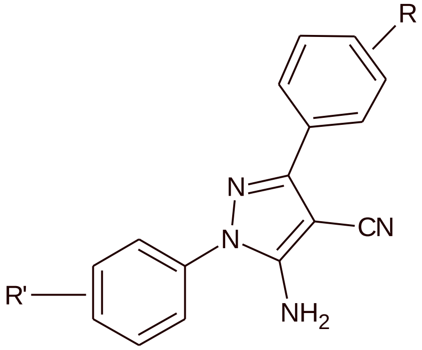
Scheme 81: Acetylation of (+)-cedrol compound.

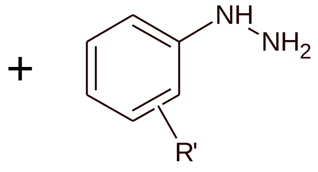
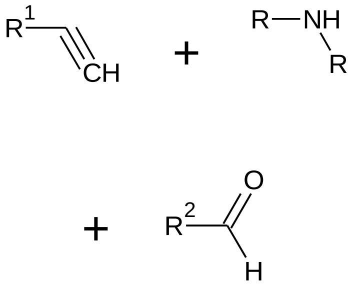
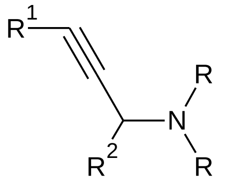
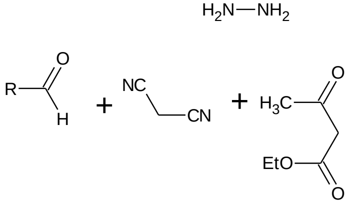
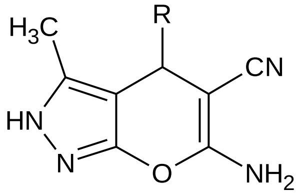
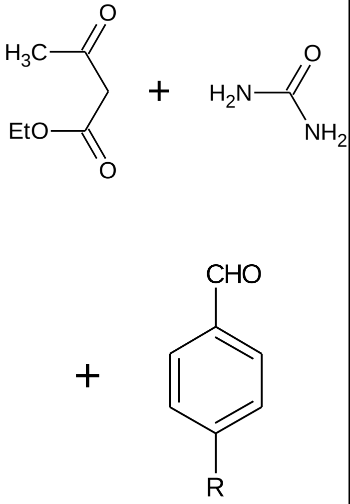
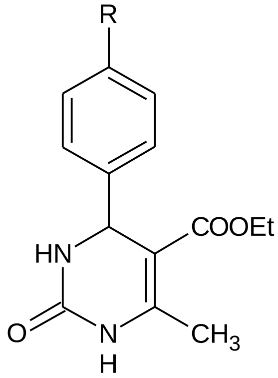
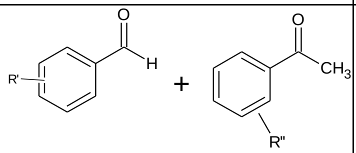
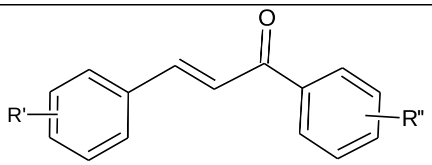
The organic reaction carried out in green medium such as aqueous medium and also carried out in solvent free condition which is summarized in table number 3.

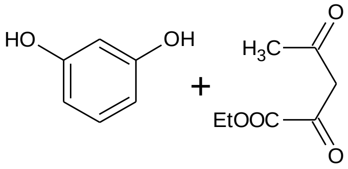
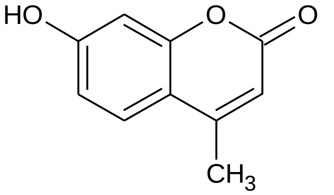
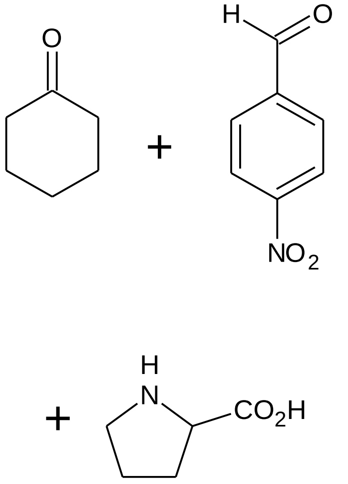
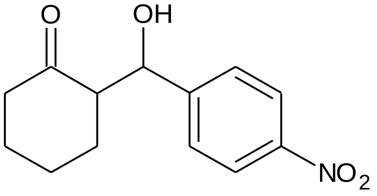
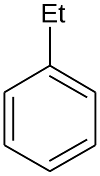
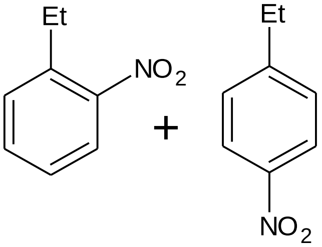
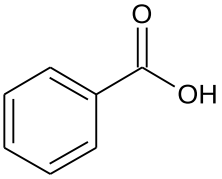
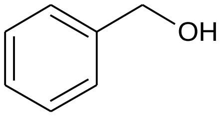
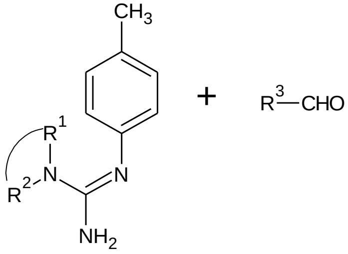
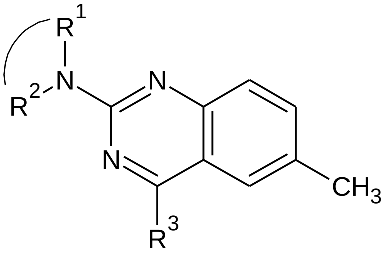
Table 3: Short summary of Reaction medium

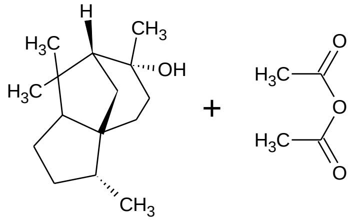
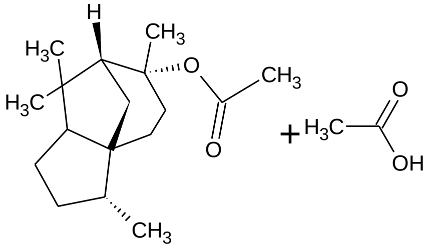
Scheme entry No.	Reactant	Condition	Product	References
61		H_2O		[74]
62		H_2O, 80^{0}C		[14]

63		MW, H_2O		[14]
64		H_2O, r.t.		[14]
65		MW, Hydrotropic solution		[75]
66		H_2O, 70^0C		[76]
67		H_2O, 80^0C		[77]

68		H_2O, Reflux		[77]
69		H_2O, Reflux		[77]
70		H_2O, Reflux		[79]
71		Aq. NaPTS, r.t.		[80]

				
72		Solvent free, 100^{0}C		[81]
73		Solvent free, r.t.		[82]
74		Solvent free		[83]
75		MW, Solvent free		[84]

76		Solvent free		[85]
77		Solvent free		[86]
78		Solvent free, r.t.		[87]
79		Solvent free, 50-60^{0}C		-
80		MW, Solvent free		[88]

81		Solvent free, 353 K		[89]

5. Reaction assisted

Organic reactions are carried out in microwave, ultrasonicator and mortar pestle.

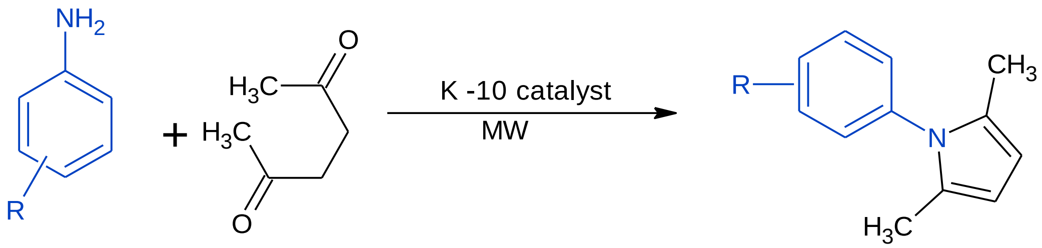
5.1 Microwave:

The organic reaction assisted in microwave which provide clean, simple, fast synthesis of organic compound. It increase the rate of reaction. It reduced the time required for reaction due to this it improve the yield and quality of the product. Reaction assisted in microwave which leads to ecofriendly. Conventional method needs to high temperature and more time for completion reaction but microwave assisted reaction eliminate this things and also reduced the environmental pollution [90].

In 1950's microwave is used for domestic and commercial purpose for heating and cooking the food. Cooking food by microwave is invented in 1940's. Tappan invented first microwave reaction oven in 1955. The first used microwave for synthesis is published in 1986. There is an important role of organic synthesis in research area from life of people to medication which provide better life. Now-a-days many novel methods used for synthesis of product provide environmentally and ecofriendly reaction. With number of big and complex of the problems and availability of newer and novel methods for completion of chemical reaction. Chemist used number of techniques such as photochemical, electrochemical, sonochemical and microwave methods.

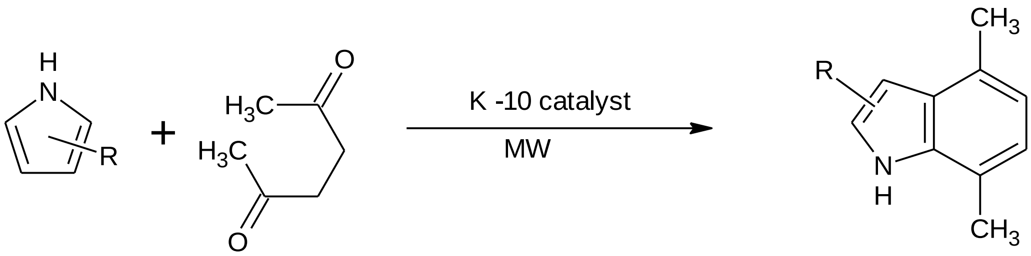
In organic reaction an aqueous emulsion polymerization of butyl acrylate, acrylic acid and methacrylic acid using electromagnetic radiation were the first application of microwave energy. In conventionally heating method, the heat is transfer from wall of the vessels then reacted to the solution and reactant. This method is slow for energy transferring. But in microwave heating method, microwave directly couple with molecules of reaction mixture which leads to rise in temperature and increase rate of reaction and gives product at short time. The reaction contents present in vessel are heated not vessel itself and heating of polar molecules is achieved [91]. Microwave processes were act as a green. It fulfill the principle of green chemistry.[92]

M. Abid et al. reported a synthesis of 2, 5-dimethyl-1-arylpyrroles by using K-10 catalyst with the help of hexan-2,5-dione used as cyclialkylating agent and aniline. This synthesis is carried out in MW. It gives 99% yield of product in 1 min. There is no formation of any byproduct. Minimum amount of heat is required for carried out the reaction (Scheme 82).



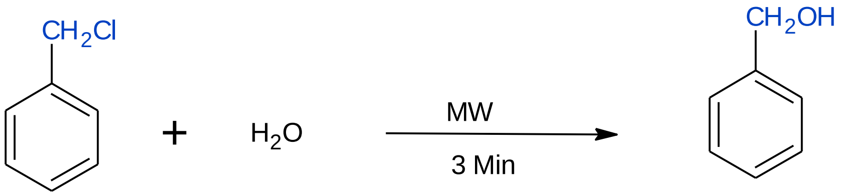
Scheme 82: Synthesis of trisubstitutedpyrrole by using Paal-knorr cyclization of aniline and 4-ethylaniline with 2,5-hexan-dione,

G.A. Somorjai et al. reported a synthesis of indole derivative with the help of pyrrole and hexan-2,5-dione by using K-10 catalyst and the reaction is carried out in the microwave (Scheme 83).



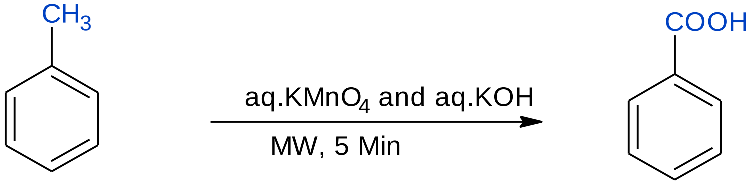
Scheme 83: Electrphillic annelation of pyrrole with 2,5-hexandione to 4,7- dimethylindole.

Smita Jauhari et al. reported a synthesis of benzyl alcohol from benzyl chloride by using water as a solvent and this reaction is carried out in microwave. The usual hydrolysis takes 35 min for completion of reaction but reaction carried out in MW so it takes 3 min for completion of the reaction (Scheme 84) [93].



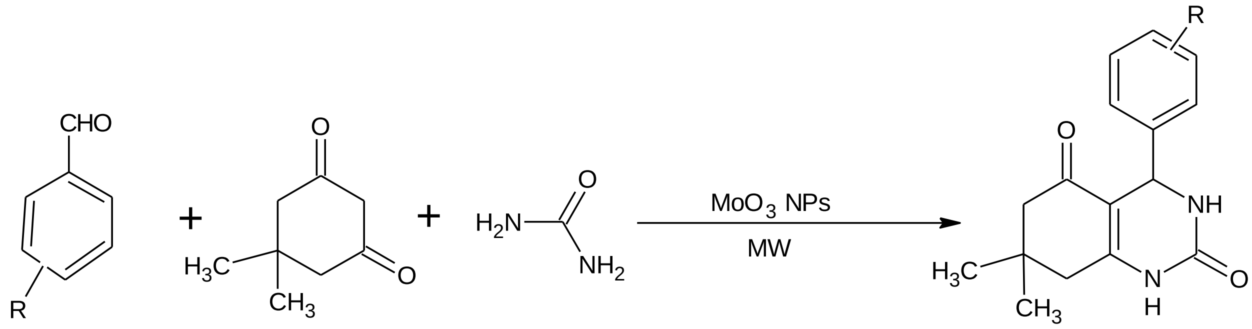
Scheme 84: Hydrolysis of benzyl chloride in microwave oven.

Smita Jauhari et al. reported a synthesis of benzoic acid by oxidation of toluene. The oxidising agent used for this reaction is $KMnO_4$. When the reaction is carried out in refluxing condition then it required 10-12 hr for completion the reaction but when reaction carried out in microwave then it completed in 5 min (Scheme 85) [93].



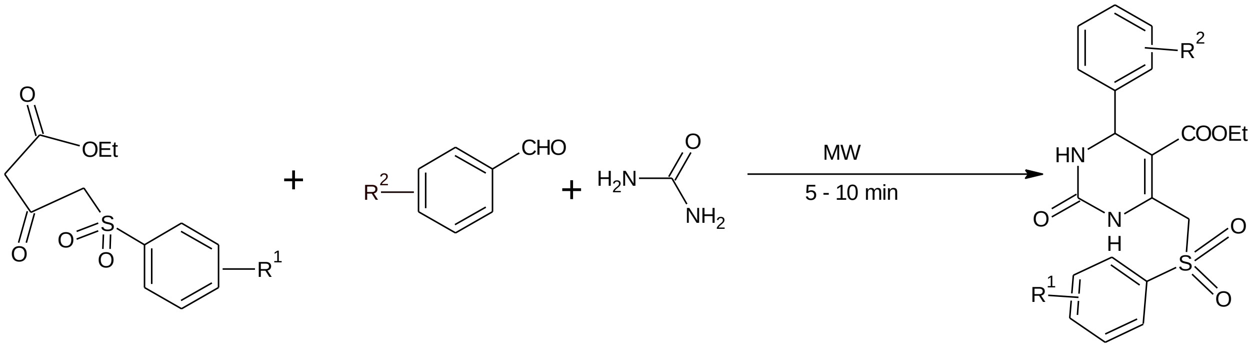
Scheme 85: Oxidation of toluene in presence of $KMnO_4$.

S. Jadhav et al. reported a synthesis of octahydroquinazolinone derivatives by using molybdenum oxide nanoparticles in solvent free condition. The reaction carried out in microwave at 360 W. The time required for the completion of reaction is only 2 minutes. It is a multicomponent reaction such as aldehyde, dimedone and urea (Scheme 86) [94].



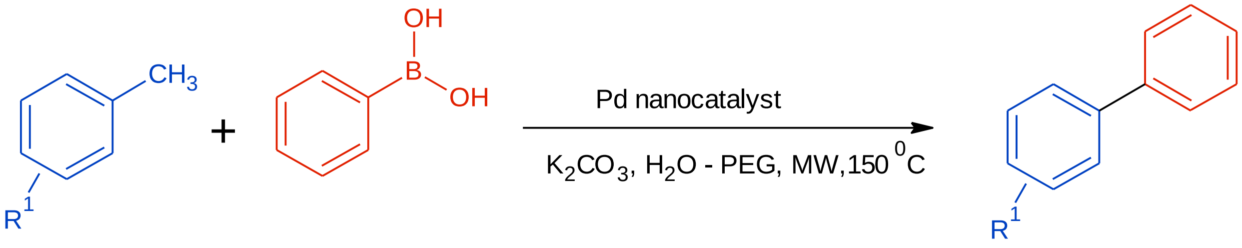
Scheme 86: Synthesis of octahydroquinazolinone by using MoO_3 nanoparticles.

Perumal et al. reported a synthesis of tetrahydropyrimidines in the microwave. The reaction required 5-10 min for completion. This reaction is solvent free and catalyst free. So, it is a green reaction (Scheme 87) [88].



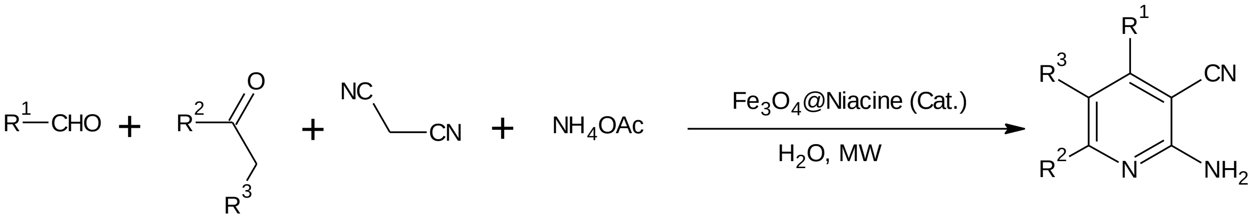
Scheme 87: Synthesis of tetrahydropyrimidines under MW irradiation.

Garcia et al. reported a reaction between arylhalides and phenylboronic acid by using Pd as a nanocatalyst. The reaction is carried out in microwave. Microwave provide facile and environment friendly condition to carried out the reaction. In this reaction water and PEG were used as a solvent (Scheme 88) [95].



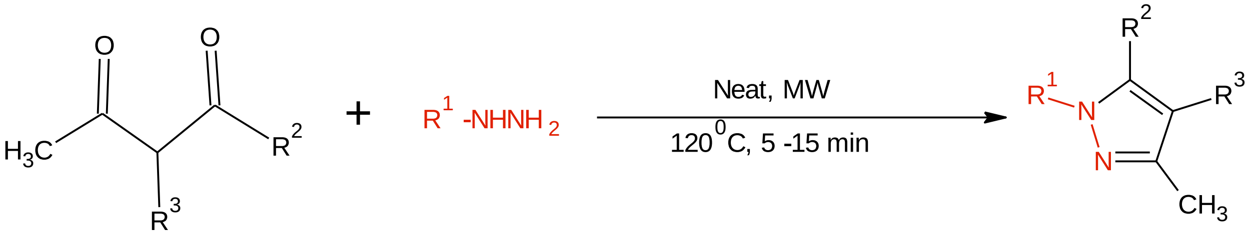
Scheme 88: Carbon-supported Pd nanocatalysts used in the reaction between arylhalides and phenylboronic acid under MW.

Mojgan Afradi et al. reported a synthesis of 2 – amino-3-cyanopyridine derivatives by using magnetic nanoparticles i.e. Fe_3O_4@Niacine. This catalyst is reusable and more efficient. The reaction is takes placed in microwave and water used as a solvent. The nanoparticles were prepared by co-precipitation method and it was characterized by SEM (Scheme 89) [96].



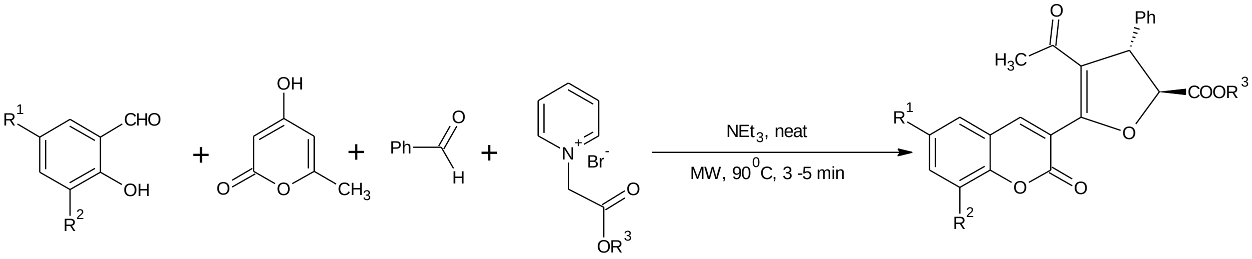
Scheme 89: Synthesis of 2 – amino-3-cyanopyridine derivatives in the presence of MNPs-niacin as catalyst.

Rajender S. Varma reported a synthesis of pyrazoles. The synthesis of desired product by solvent free and catalyst free condition. The reaction is carried out in microwave (Scheme 90) [97].



Scheme 90: Synthesis of pyrazoles.

Tangeti et al. reported a synthesis of substitute coumarin derivatives by using NEt_3. The reaction was carried out in solvent free condition and in microwave. The reaction required 3-5 min for completion (Scheme 91) [98].



Scheme 91: C-3 functionalized dihydrofuran substituted coumarin derivative in microwave.

5.2 Sonicator:

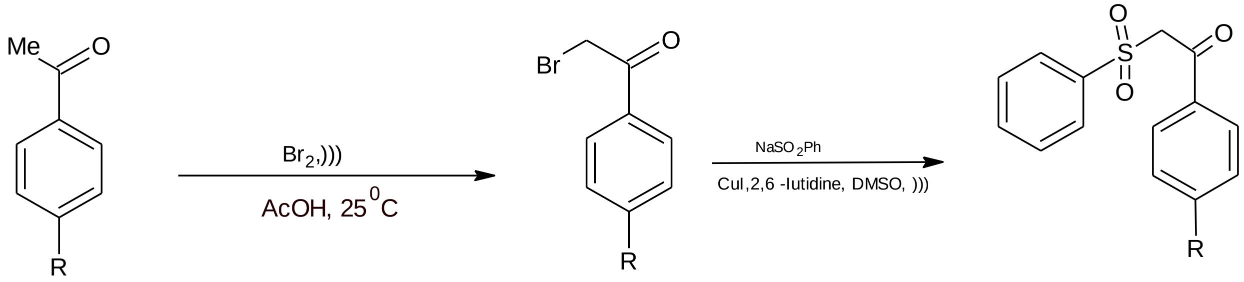
There are many conventional methods are used to carry out the organic reactions which has drawbacks such as long time reaction, less yield, more toxic solvents and costly reagents are required and also required high temperature. To overcome all this problems by using ultrasonicator for organic reaction.

Sonochemistry means the uses of sound waves with its chemical effect. The use of ultrasound waves in 1990’s by Richards and loomis. Ultrasound used between 20 KHz and 5 MHz frequency range to removal of biologically active compounds and formation of drugs. By use of ultrasound chemical reactivity is increases through formation and collision of bubbles in liquid medium. Ultrasound waves are propagate in aqueous medium in change compression as well as rarefaction cycle and form cavities [92].

Ultrasound assisted organic reactions are more advantageous than conventional method because of it gives high yield, increase rate of reaction and also purity of product is increased. Ultrasonic waves shows molecules oscillate around their mean position which increase distance between molecules.

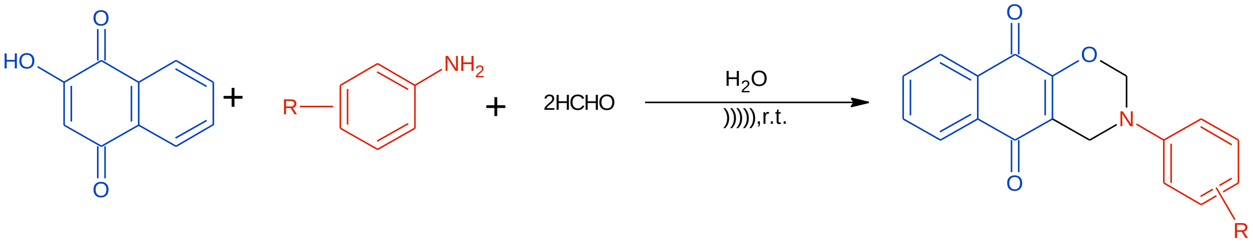
The application of ultrasonicator is to eliminate the use of catalyst in organic reaction. On the other hand researchers were used water for reaction. It is inexpensive, hazardless and easily available. Forming hydrogen bond. Water has high surface tension and hydrophobic in nature so reactants in water are bonded to each other and form aggregation which increase the rate of reaction. So, there is strong collaboration between ultrasonic radiation and used of aqueous media which gives environmental sustainability [99].

Neha Gharat and co-workers reported a sulphonation of α-bromoketones in the presence of CUI/2, 6-lutidine to gives β-keto-sulfones. The reaction takes placed in ultrasonicator in presence of aqueous medium. The reaction required less time and it is simple reaction as compared to traditional reaction (Scheme 92) [100].



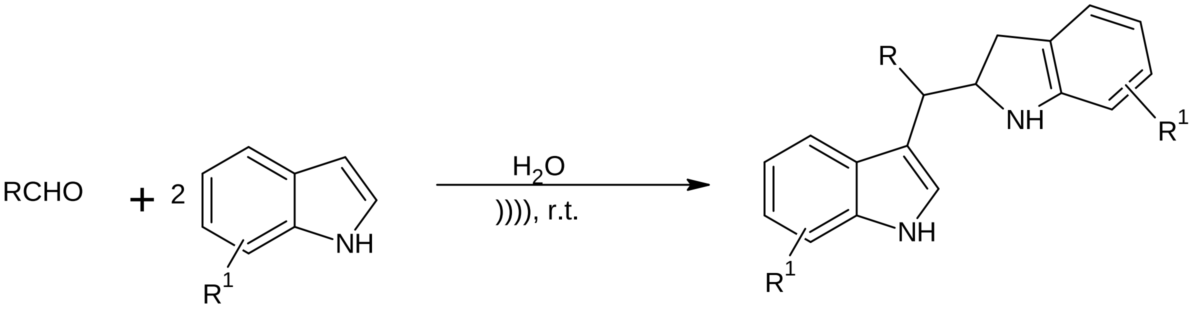
Scheme 92: Sulfonation of alpha-bromoketones in presence of ultrasonication.

Neha Gharat et al. reported a synthesis of naphthoquinone by combining oxazine derivative under aqueous medium by using ultrasonicator. It is an environmental safer reaction. It is a three components reaction. The components of reaction is 2-hydroxy-1,4-naphthoquinone, aromatic amine and formaldehyde (Scheme 93) [100].



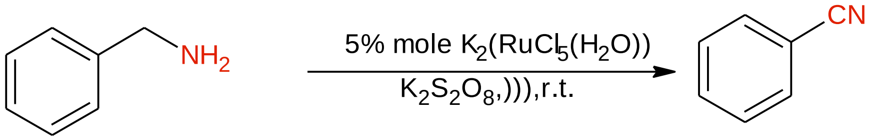
Scheme 93: Synthesis of naphthoquinone combined oxazine using ultrasound.

Neha Gharat and co-workers reported a synthesis of Bis(Indolyl)Methanes by using aldehyde and indole as a reactant in presence of aqueous medium under the sonication at room temperature. This reaction was carried out by without use of any catalyst. So, this reaction is used in industrial synthesis (Scheme 94) [101].



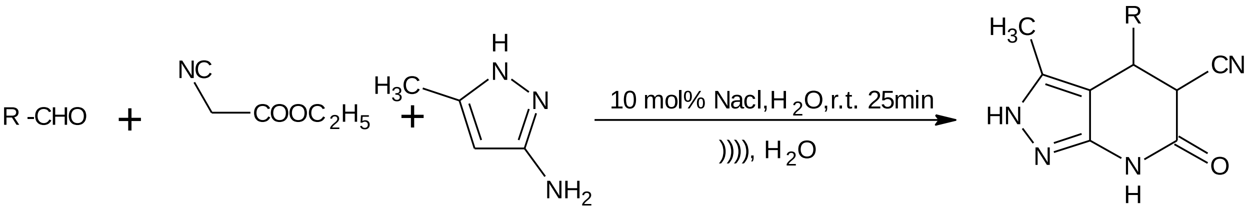
Scheme 94: Synthesis of Bis(Indolyl)Methanes by using aldehyde and ethyl lactate under ultrasonication.

Abdel Shoair reported a synthesis of aryl nitrile from benzyl amine by using oxidizing agent in the presence of catalyst. The catalyst $K_2(RuCl_5(H_2O))$ showed good catalytic activity and selectivity for the transformation of primary amine to the nitrile in 95% under ultrasound assisted irradiation technique at room temperature (Scheme 95) [102].



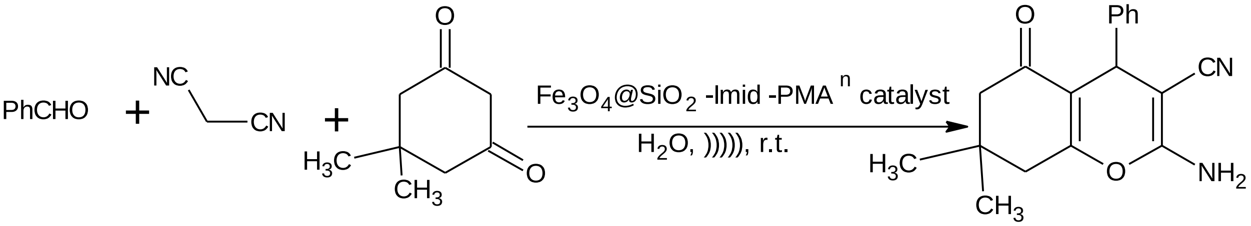
Scheme 95: Catalytic dehydrogenation of primary amines to nitriles by using ultrasound.

Bubun Banerjee reported a synthesis of pyrazolo(3,4-b) pyridine derivative by using aldehyde, ethyl cyanoacetate and 3-amino-5-methylpyrazole by using sodium chloride as a catalyst and reaction is carried out in the aqueous medium. The reaction is carried out in ultrasonicator. The reaction was completed in 25 min. (Scheme 96) [103].



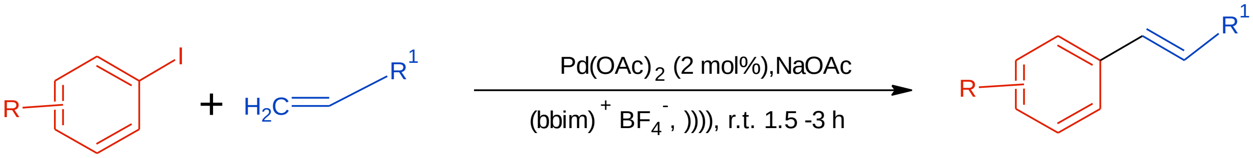
Scheme 96: Ultrasound-promoted synthesis of pyrazolo[3,4-b]pyridine derivatives in water.

Mohsen Esmaeilpour et al. reported a synthesis of derivatives of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-benzo[b]pyran by using three components such as aromatic aldehyde, malononitrile and dimedone in presence of $Fe_3O_4@SiO_2$-imid-PMA^n catalyst. The reaction was carried out in ultrasound.(Scheme 97) [104].



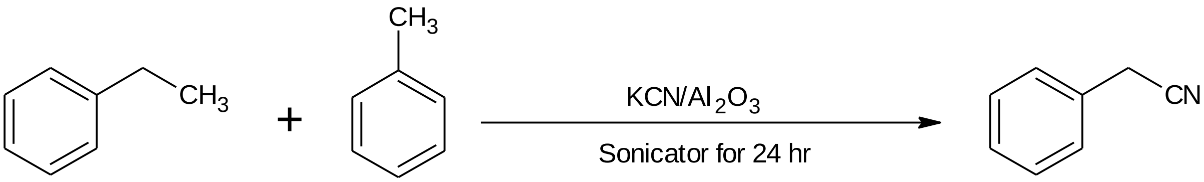
Scheme 97: Synthesis of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-benzo[b]pyran in the presence of $Fe_3O_4@SiO_2$-imid-PMA^n.

Srinivasan et al. reported a Heck reaction. The reaction is carried out in ionic liquid and in ultrasonicator. The reaction followed the protocol of green chemistry (Scheme 98) [97].



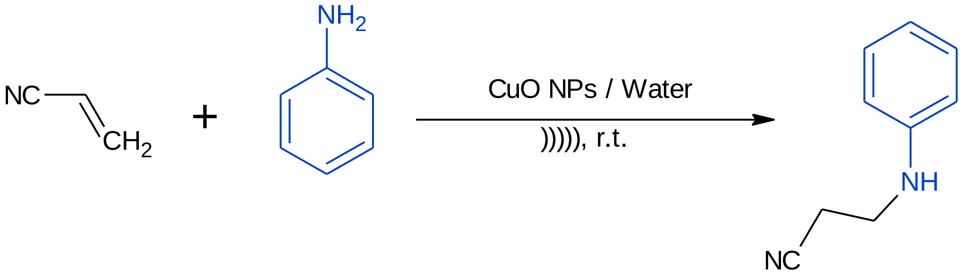
Scheme 98: Heck reaction in IL under ultrasound.

Rajender S. Varma reported a reaction of benzyl bromide with alumina-supported potassium cyanide in presence of toluene. The reaction is carried out in sonicator (Scheme 99) [97].



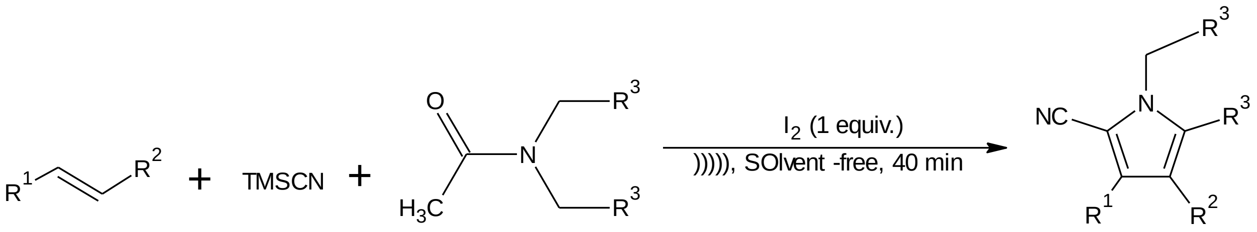
Scheme 99: Reaction of benzyl bromide with alumina-supported potassium cyanide.

Rakesh Chowdhury et al. reported the aza-michael reaction by using Cu NPs. The precursor used for synthesis of Cu NPs was Copper(II)acetate and NaOH is used as a hydrolyzing agent in the presence of flower extract of Lantana camara plant. The prepared nanoparticles characterized by SEM and TEM. The reaction is carried out in ultrasonicator (Scheme 100) [105].



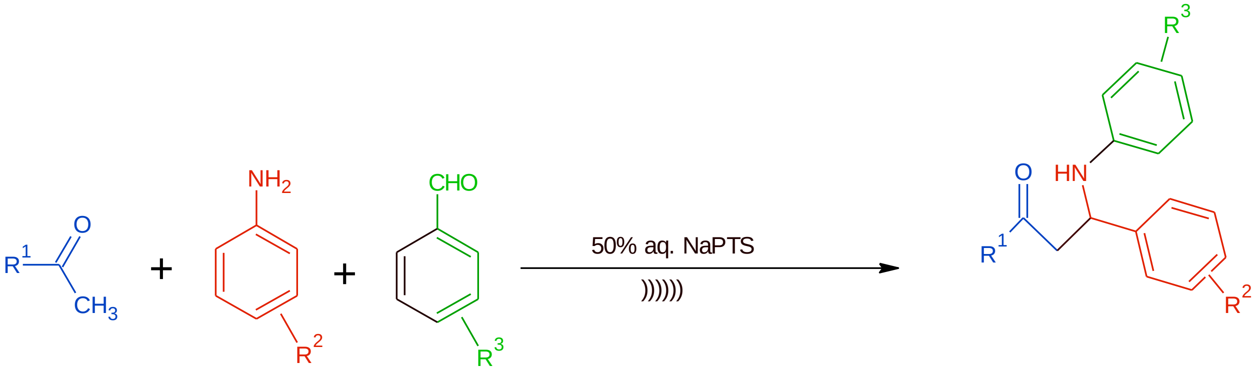
Scheme 100: Aza-Michael reaction under ultrasonic vibration.

Gui et al. reported a synthesis of polysubstituted pyrroles by using three components under solvent free condition and in presence of iodine as a catalyst. The reaction is carried out in ultrasonicator (Scheme 101) [106].



Scheme 101: Iodine-catalyzed one-pot three component routes to access pyrroles.

Santosh Kamble et al. reported a synthesis of β-amino carbonyl compounds in 50% aq. NaPTS. They used NaPTS as a hydrotope. It is high efficiency and reusable. The desired product is synthesized from substituted benzaldehyde, aniline and acetophenone. The benzaldehyde with electron withdrawing substituents then it gave high yield product. The reaction assisted in ultrasonicator (Scheme 102) [107].



Scheme 102: Synthesis of β-amino carbonyl compounds in hydrotrope.

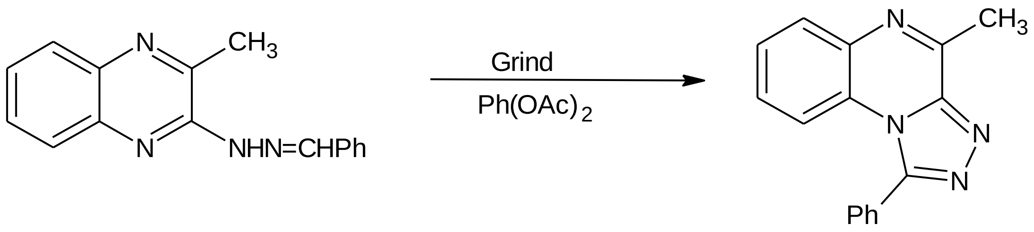
5.3 Mortar pestle:

Green chemistry concept has lots of challenges of protecting environment and human health. Green chemistry means utilization of 12 principles that reduce the hazardous substances from synthesis and design new less hazardous processes. So, for synthesis researchers used microwave, ultrasonic radiation, photocatalysts. They used greener reaction medium such as water, polyethylene glycol, microwave, ultrasonic radiation, photocatalysts. They used greener reaction medium such as microwave, ultrasonic, mortar pestle under solvent free condition which have result in sustainable pathways for organic synthesis.

Organic reactions are carried out by using mechanical energy is called mechanochemistry. The simple tool for mechanochemistry is use of mortar pestle is called grindstone chemistry [108].

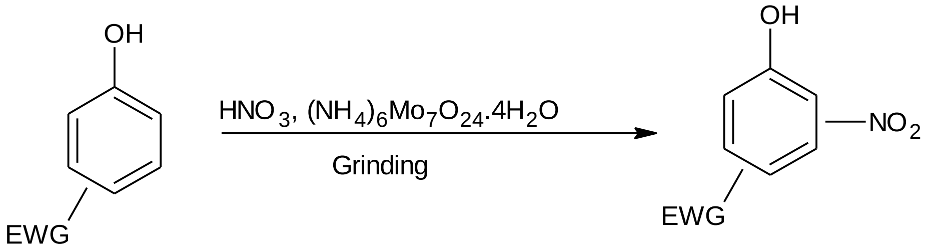
Grinding of two solid substances form a number of transformations mechanical energy is used for breaking the structure of substances and provide a new surfaces. When organic reaction is carried out in mortar pestle then it reduce the waste and solvents also or there is no need to use of solvent for this reaction also it provide the easy separation and purification of product. In mortar pestle reactions are carried out by mechanical energy. Now, these methods have become more famous for developed many multicomponent reaction.[109]

Rajender Varma reported a synthesis of 1-alkyl-4-methyl-1,2,4-triazolo(4,3-a) quinoxalines by the oxidation of arenecarbaldehyde3-methyl-quinoxalin-2-yl-hydrazones. The catalyst and reactant substance is grind in the mortar pestle to give yellow colored product. Few minutes required for completion of the reaction. These was rapid and solvent free reaction which gives green of product (Scheme 103) [108].



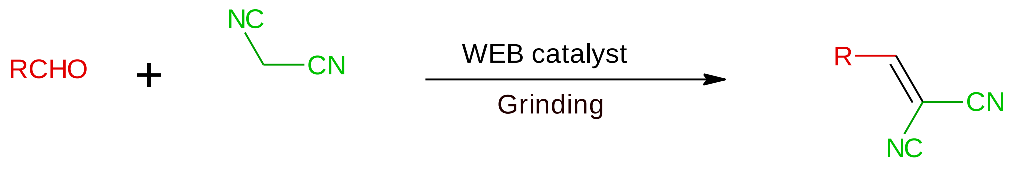
Scheme 103: Synthesis of 1-alkyl-4-methyl-1,2,4-triazolo[4,3-a]quinoxalines.

Sariah Sana et al. reported a nitration of organic compound by using ammonium molybdate. The reaction is carried out in mortar pestle so it is a green reaction (Scheme 104) [111].



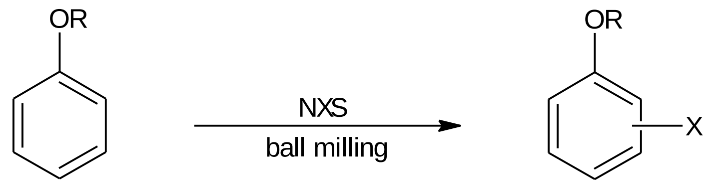
Scheme 104: Nitration of organic compounds catalyzed by group V and VI metal salts under solvent free condition.

K. Kantharaj et al. reported a knoevenagel condensation reaction to form 2- (phenyl methylene) malononitrile by using aldehyde and malononitrile. This reaction is carried out in the mortar pestle by using water extract of banana as a catalyst (Scheme 105) [110].



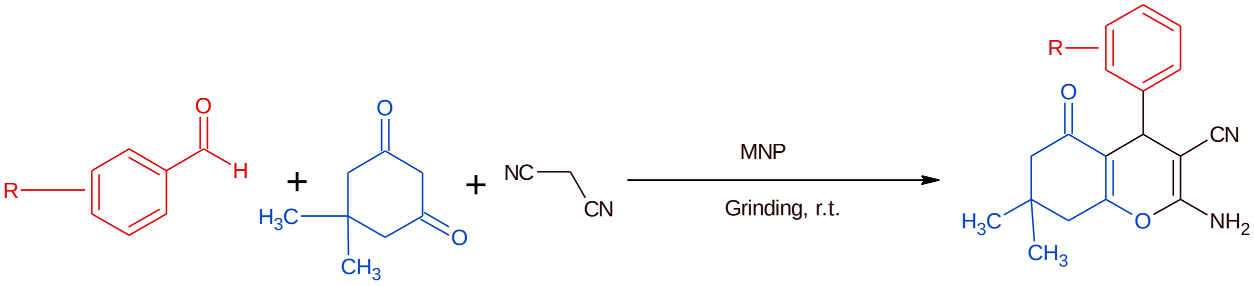
Scheme 105: WEB (Water extract of banana) catalyzed synthesis of Knoevenagel products.

Dharmendra Das and co-workers reported a halogenation reaction. This reaction is carried out in mortar pestle. This reaction is green reaction because it carried out in mortar pestle so it formed a product without any pollution. They carried out reaction by using mechanical energy. The large amount of product is formed in this reaction. This reaction follows principles of green chemistry (Scheme 106) [112].



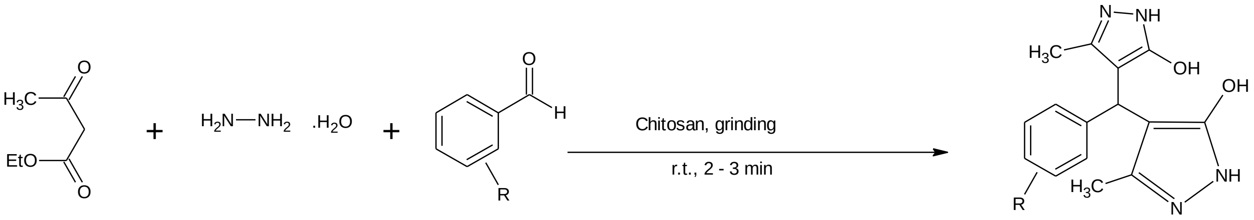
Scheme 106: Mechanochemical halogenation reaction with NXS.

Sobhan Rezayati et al. reported a synthesis of 2-amino-4H-benzo[b]pyrans by using magnetite nanoparticles. The reaction carried out in solvent free condition and in mortar pestle at room temperature. It is multicomponent reaction. It was synthesized from aldehyde, dimedone and malononitrile (Scheme 107) [113].



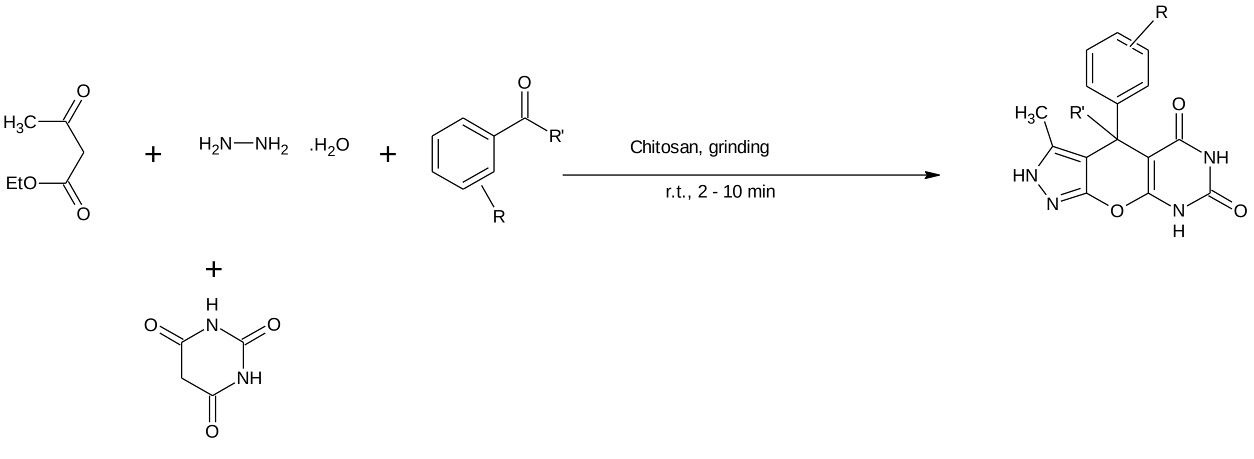
Scheme 107: Synthesis of 2-amino-4H-benzo[b]pyrans,

Bushra Chowhan et al. reported a synthesis of bis(pyrazol-5-ole) by using chitosan as a catalyst. This reaction is carried out in mortar pestle and it required 2-3 min for completion. The reaction was carried out in solvent free condition (Scheme 108) [98].



Scheme 108: Synthesis of bis(pyrazol-5-ole) by using chitosan as a catalyst.

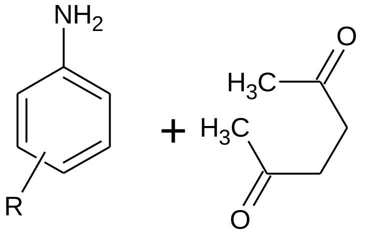
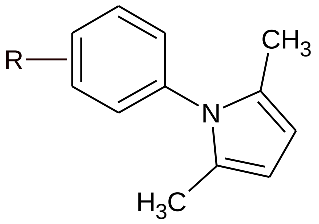
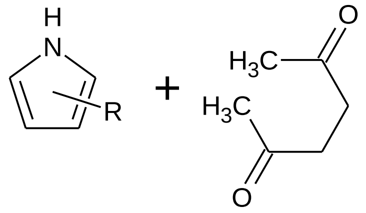
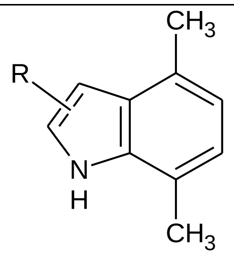
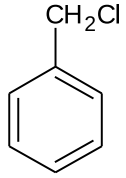
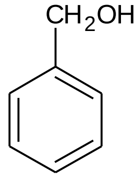
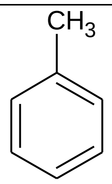
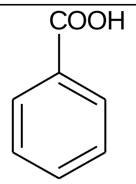
Bushra Chowhan et al. reported a synthesis of pyrazolopyranopyrimidine by using four components in presence of chitosan as a catalyst. The reaction is carried out in mortar pestle and 2-10 min was required for completion. This is a green reaction (Scheme 109) [98].

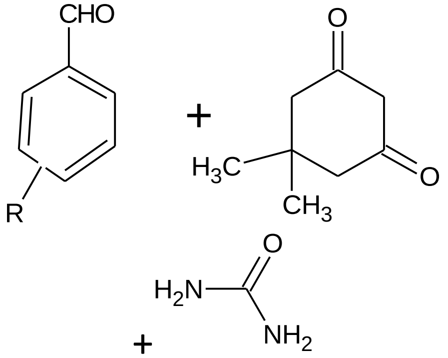
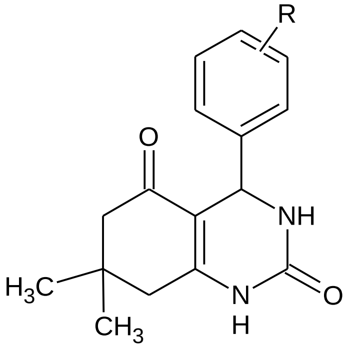
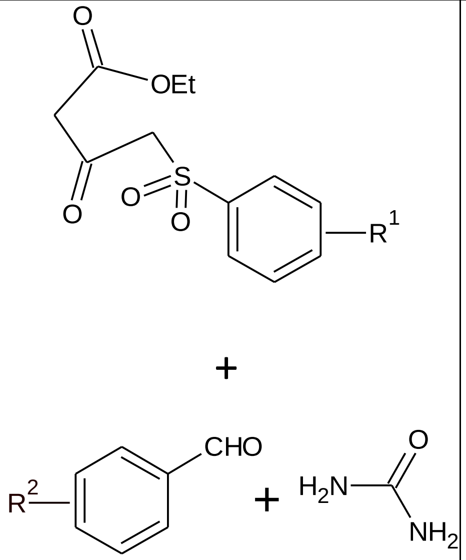
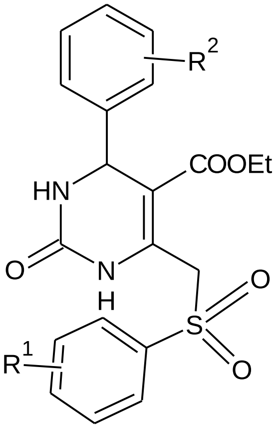
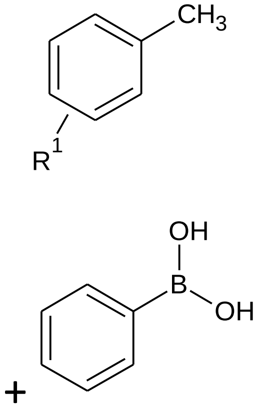
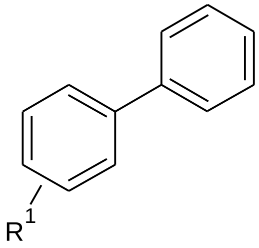


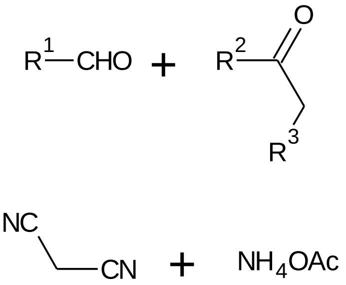
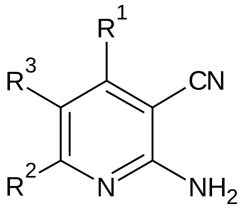
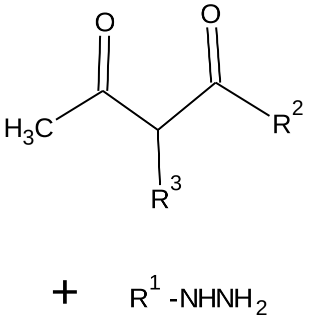
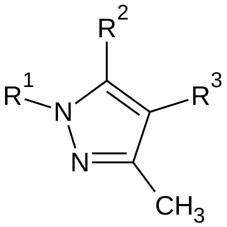
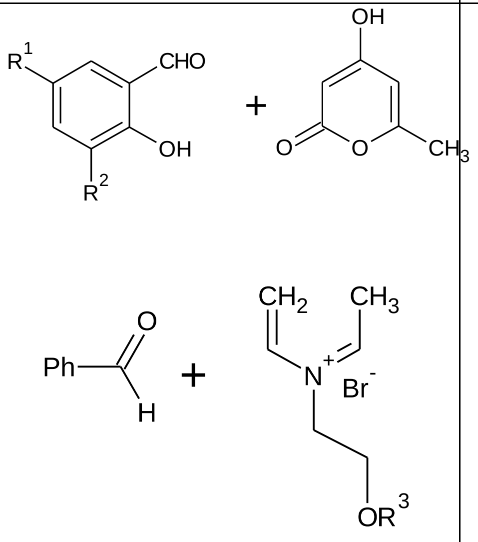
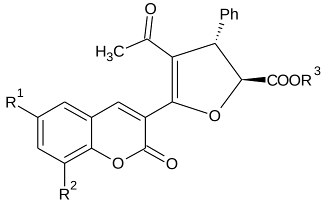
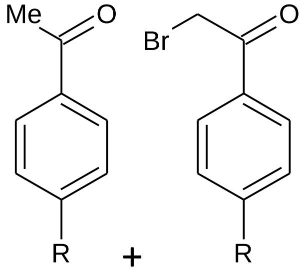
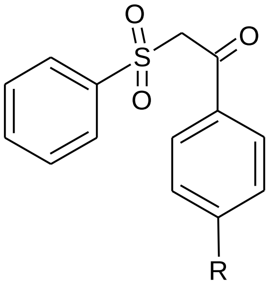
Scheme 109: Chitosan as a catalyst for the synthesis of pyrazolopyranopyrimidine.

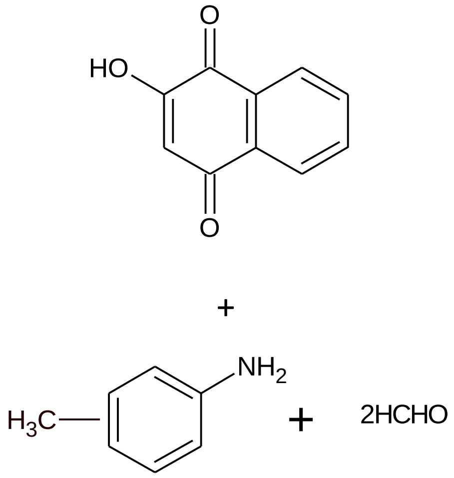
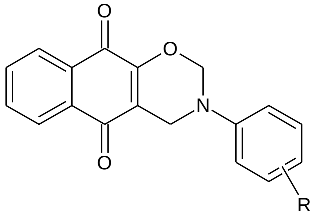
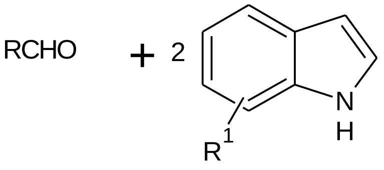
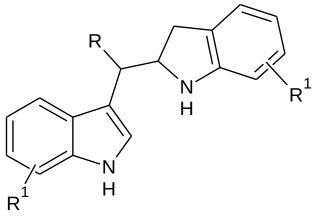
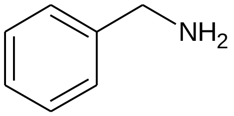
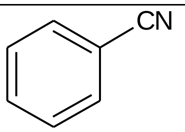
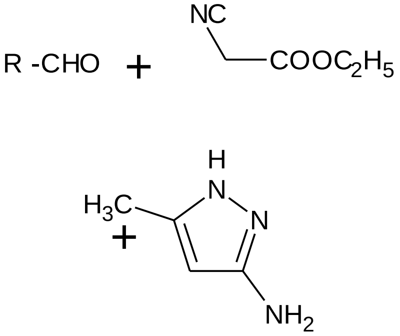
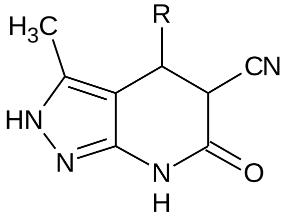
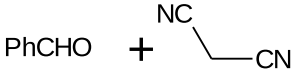
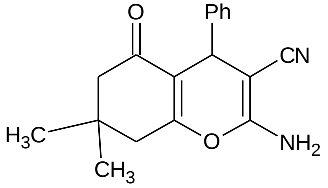
The organic transformation was carried out by the reaction assisted in microwave, ultra-sonicator and mortar pestle in last decades are summarized in table number 4. The reactions summarized in table number 4 were carried out by green method.

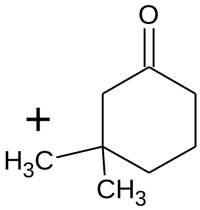
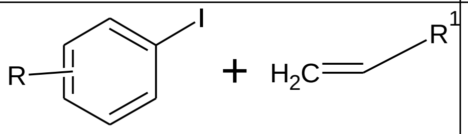
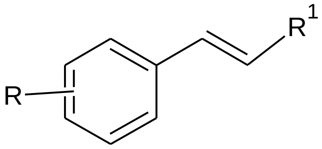
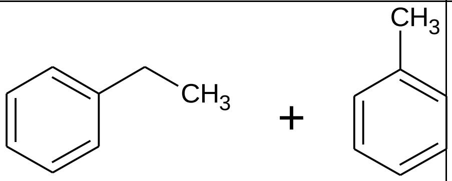
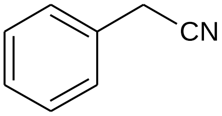
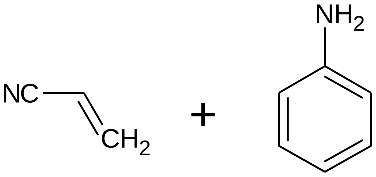
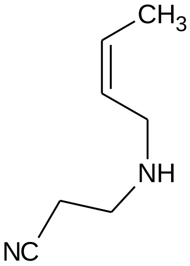
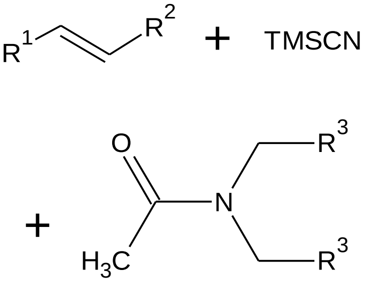
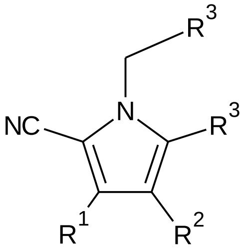
Table 4: Short summary of Reaction assisted

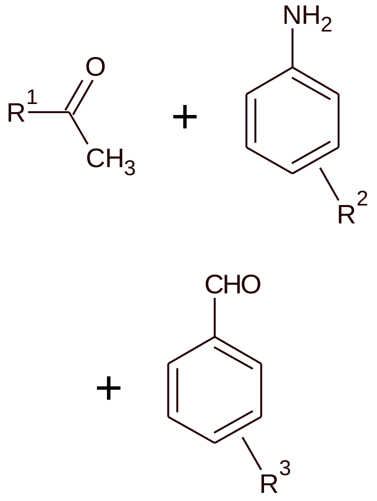
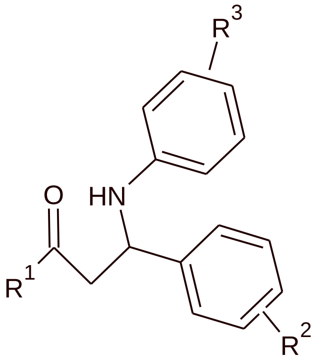
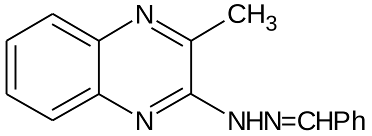
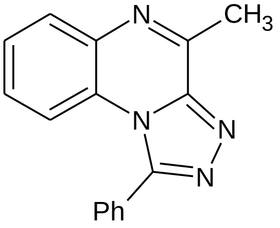
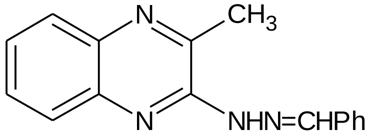
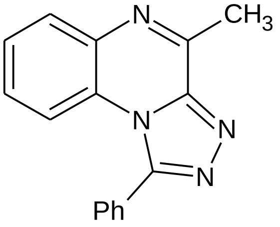
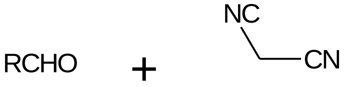
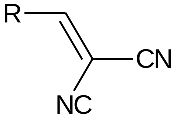
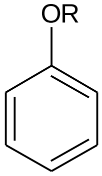
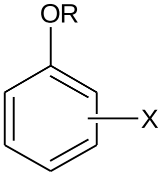
Scheme entry No.	Reactant	Conditi-on	Product	Referen-ces
82		MW, Solvent free		-
83		MW, Solvent free		-
84		MW,H_2O		[93]
85		MW, Aq.$KmnO_4$ + Aq. KOH		[93]

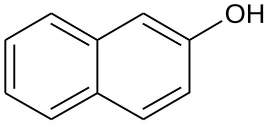
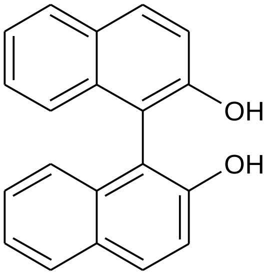
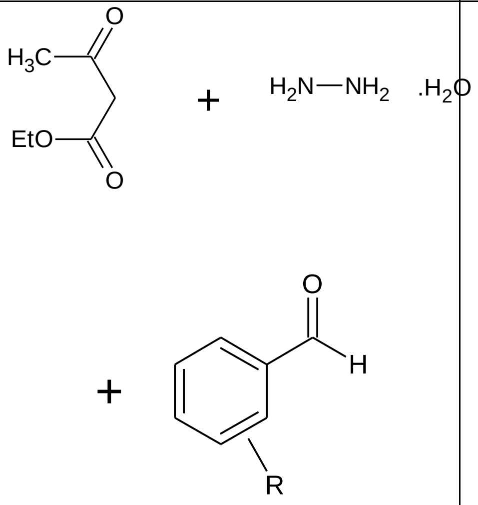
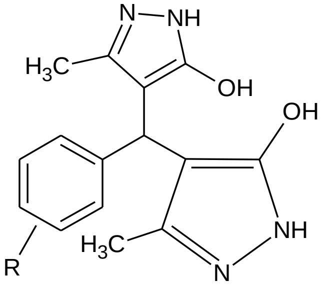
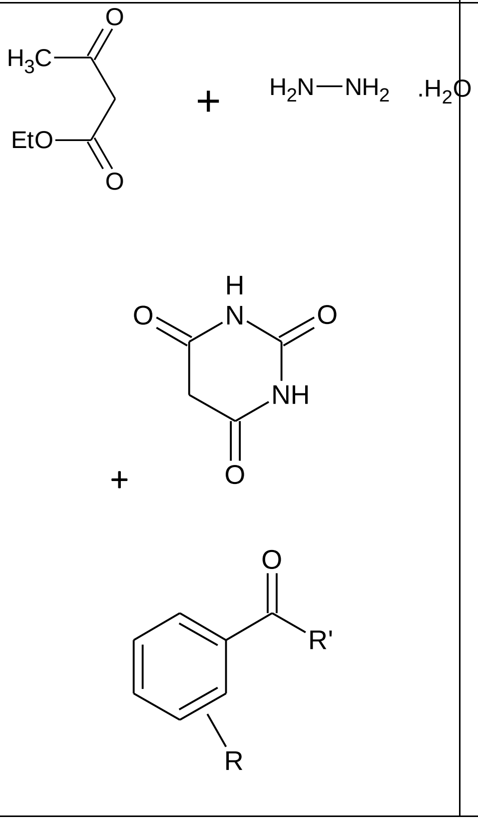
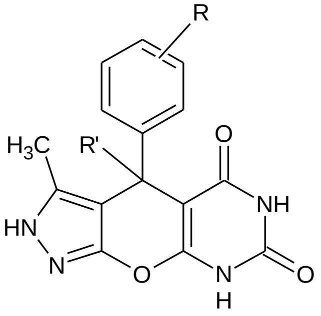
86		MW, Solvent free		[94]
87		MW, Solvent free, Catalyst free		[88]
88		MW, PEG-H_2O		[95]

89		MW, H_2O		[96]
90		MW, Solvent free, Catalyst free		[97]
91		MW		[98]
92		)))))), Aq. Medium		[100]

93		H_2O,)))), r.t.		[100]
94		H_2O,)))), r.t.		[101]
95		))))), r.t.		[102]
96		)))), H_2O		[103]
97		)))), H_2O, r.t.		[104]

				
98		IL,))))), r.t.		[97]
99		))))		[97]
100		H_2O,)))), r.t.		[105]
101		)))), Solvent free		[106]

102		)))), 50% aq. NaPTS		[107]
103		Solvent free, grinding		[108]
104		Solvent free		[111]
105		WEB		[110]
106		Grinding		[112]

107		r.t., Solvent free		[113]
108		r.t., Solvent free		[98]
109		r.t., Solvent free		[98]

6. Conclusion:

There is need to concentrate the environmental aspects during organic transformation because the hazardous chemicals which are used in organic transformation do adverse effect on environment and human being. Organic transformation means breaking of covalent bond of reactant to gives a new product. The organic transformation is important because to design new and selective product. To design a new product by organic transformation, green method is more beneficial than non-natural method because it has more advantages such as hazardless, inexpensive, environmentally friendly, time saving and avoid toxic chemicals. There are more benefits of green methodology, in these review we focused on green techniques such as nanoparticles, ionic liquid, surfactant, microwave assisted, ultra-sonication, aqueous medium, solvent free for doing organic transformation.

In this review we collect all green methodology which are beneficial in future to develop more greener methodology for organic transformation.

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8. References:

[1] G. Stavber and S. Stavber, “Towards Greener Fluorine Organic Chemistry: Direct Electrophilic Fluorination of Carbonyl Compounds in Water and Under Solvent-Free Reaction Conditions,” *Adv. Synth. Catal.*, vol. 352, no. 16, pp. 2838–2846, Nov. 2010, doi: 10.1002/adsc.201000477.

[2] V. Polshettiwar and R. S. Varma, “Green chemistry by nano-catalysis,” *Green Chem.*, vol. 12, no. 5, p. 743, 2010, doi: 10.1039/b921171c.

[3] F.-X. Zhu, W. Wang, and H.-X. Li, “Water-Medium and Solvent-Free Organic Reactions over a Bifunctional Catalyst with Au Nanoparticles Covalently Bonded to HS/SO $_3$ H Functionalized Periodic Mesoporous Organosilica,” *J. Am. Chem. Soc.*, vol. 133, no. 30, pp. 11632–11640, Aug. 2011, doi: 10.1021/ja203450g.

[4] D. E. Koeppe, “The uptake, distribution, and effect of cadmium and lead in plants,” *Science of The Total Environment*, vol. 7, no. 3, pp. 197–206, May 1977, doi: 10.1016/0048-9697(77)90043-2.

[5] R. Pal, “Fruit Juice: A Natural, Green and Biocatalyst System in Organic Synthesis,” *OJOC*, vol. 1, no. 4, p. 47, 2013, doi: 10.12966/ojoc.10.02.2013.

[6] R. C. Patil, S. A. Damate, D. N. Zambare, and S. S. Patil, “Chickpea leaf exudates: a green Brønsted acid type biosurfactant for bis(indole)methane and bis(pyrazolyl)methane synthesis,” *New J. Chem.*, vol. 45, no. 20, pp. 9152–9162, 2021, doi: 10.1039/D1NJ00382H.

[7] P. De-la-Torre *et al.*, “Ultrasound-assisted phase-transfer catalysis method in an aqueous medium to promote the Knoevenagel reaction: Advantages over the conventional and microwave-assisted solvent-free/catalyst-free method,” *Ultrasonics Sonochemistry*, vol. 21, no. 5, pp. 1666–1674, Sep. 2014, doi: 10.1016/j.ultsonch.2014.02.021.

[8] I. Khan, K. Saeed, and I. Khan, “Nanoparticles: Properties, applications and toxicities,” *Arabian Journal of Chemistry*, vol. 12, no. 7, pp. 908–931, Nov. 2019, doi: 10.1016/j.arabjc.2017.05.011.

[9] V. Polshettiwar and R. S. Varma, “Green chemistry by nano-catalysis,” *Green Chem.*, vol. 12, no. 5, p. 743, 2010, doi: 10.1039/b921171c.

[10] D. Akbaşlar, O. Demirkol, and S. Giray, “Paal–Knorr Pyrrole Synthesis in Water,” *Synthetic Communications*, vol. 44, no. 9, pp. 1323–1332, May 2014, doi: 10.1080/00397911.2013.857691.

[11] D. N. Gaikwad *et al.*, “A Brief Review on Microwave Assisted Synthesis of Pyrazole Derivatives,” 2019.

[12] S. Rostamizadeh, H. Estiri, and M. Azad, “Facile method for the synthesis of core/shell Fe3O4@SiO2@SiO2-SH-Au: a super magnetic nanocatalyst for water-medium and solvent-free alkyne hydration,” *J IRAN CHEM SOC*, vol. 13, no. 7, pp. 1367–1374, Jul. 2016, doi: 10.1007/s13738-016-0851-9.

[13] S. Zangade and P. Patil, “A Review on Solvent-free Methods in Organic Synthesis,” *COC*, vol. 23, no. 21, pp. 2295–2318, Jan. 2020, doi: 10.2174/1385272823666191016165532.

[14] T. Cheng, D. Zhang, H. Li, and G. Liu, “Magnetically recoverable nanoparticles as efficient catalysts for organic transformations in aqueous medium,” *Green Chem.*, vol. 16, no. 7, pp. 3401–3427, 2014, doi: 10.1039/C4GC00458B.

[15] M. B. Gawande, S. N. Shelke, R. Zboril, and R. S. Varma, “Microwave-Assisted Chemistry: Synthetic Applications for Rapid Assembly of Nanomaterials and Organics,” *Acc. Chem. Res.*, vol. 47, no. 4, pp. 1338–1348, Apr. 2014, doi: 10.1021/ar400309b.

[16] A. Arya, V. Mishra, and T. S. Chundawat, “Green synthesis of silver nanoparticles from green algae (Botryococcus braunii) and its catalytic behavior for the synthesis of benzimidazoles,” *Chemical Data Collections*, vol. 20, p. 100190, Apr. 2019, doi: 10.1016/j.cdc.2019.100190.

[17] S. G. Balwe, V. V. Shinde, A. A. Rokade, S. S. Park, and Y. T. Jeong, “Green synthesis and characterization of silver nanoparticles (Ag NPs) from extract of plant Radix Puerariae: An efficient and recyclable catalyst for the construction of pyrimido[1,2-b]indazole derivatives under solvent-free conditions,” *Catalysis Communications*, vol. 99, pp. 121–126, Aug. 2017, doi: 10.1016/j.catcom.2017.06.006.

[18] H. Cong and J. A. Porco, “Total Synthesis of (±)-Sorocenol B Employing Nanoparticle Catalysis,” *Org. Lett.*, vol. 14, no. 10, pp. 2516–2519, May 2012, doi: 10.1021/ol300800r.

[19] S. R. Attar, B. Shinde, and S. B. Kamble, “Enhanced catalytic activity of bio-fabricated ZnO NPs prepared by ultrasound-assisted route for the synthesis of tetraketone and benzylidenemalonitrile in hydrotropic aqueous medium,” *Res Chem Intermed*, vol. 46, no. 10, pp. 4723–4748, Oct. 2020, doi: 10.1007/s11164-020-04233-5.

[20] B. Shinde *et al.*, “Novel catalytic application of Ni@ZnO nanoparticles and ZnO nanoflakes in aqueous solution of NaPTS hydrotrope at room temperature via a green synthesis of 3,4-dihydropyrimidin-2(1H)-ones,” *Res Chem Intermed*, vol. 44, no. 5, pp. 3097–3113, May 2018, doi: 10.1007/s11164-018-3295-2.

[21] H.-P. Steinrück and P. Wasserscheid, “Ionic Liquids in Catalysis,” *Catal Lett*, vol. 145, no. 1, pp. 380–397, Jan. 2015, doi: 10.1007/s10562-014-1435-x.

[22] H. Hu, F. Qiu, A. Ying, J. Yang, and H. Meng, “An Environmentally Benign Protocol for Aqueous Synthesis of Tetrahydrobenzo[b]Pyrans Catalyzed by Cost-Effective Ionic Liquid,” *IJMS*, vol. 15, no. 4, pp. 6897–6909, Apr. 2014, doi: 10.3390/ijms15046897.

[23] D.-Q. Xu *et al.*, “Fischer indole synthesis catalyzed by novel SO3H-functionalized ionic liquids in water,” *Green Chem.*, vol. 11, no. 8, p. 1239, 2009, doi: 10.1039/b901010f.

[24] S. A. Dake *et al.*, “Phosphonium Ionic Liquid: A Novel Catalyst for Benzyl Halide Oxidation,” *Synthetic Communications*, vol. 39, no. 21, pp. 3898–3904, Oct. 2009, doi: 10.1080/00397910902840835.

[25] S. A. Dake *et al.*, “Phosphonium Ionic Liquid: A Novel Catalyst for Benzyl Halide Oxidation,” *Synthetic Communications*, vol. 39, no. 21, pp. 3898–3904, Oct. 2009, doi: 10.1080/00397910902840835.

[26] W. C. Neuhaus, I. J. Bakanas, J. R. Lizza, C. T. Boon, and G. Moura-Letts, “Novel biodegradable protonic ionic liquid for the Fischer indole synthesis reaction,” *Green Chemistry Letters and Reviews*, vol. 9, no. 1, pp. 39–43, Jan. 2016, doi: 10.1080/17518253.2016.1149231.

[27] P. Patil and A. Pratap, “Choline Chloride Catalyzed Amidation of Fatty Acid Ester to Monoethanolamide: A Green Approach,” *J. Oleo Sci.*, vol. 65, no. 1, pp. 75–79, 2016, doi: 10.5650/jos.ess15070.

[28] I. M. Walton, J. M. Cox, C. A. Benson, D. (Dan) G. Patel, Y.-S. Chen, and J. B. Benedict, “The role of atropisomers on the photo-reactivity and fatigue of diarylethene-based metal–organic frameworks,” *New J. Chem.*, vol. 40, no. 1, pp. 101–106, 2016, doi: 10.1039/C5NJ01718A.

[29] A. Pourjavadi, S. H. Hosseini, M. Doulabi, S. M. Fakoorpoor, and F. Seidi, “Multi-Layer Functionalized Poly(Ionic Liquid) Coated Magnetic Nanoparticles: Highly Recoverable and Magnetically Separable Brønsted Acid Catalyst,” *ACS Catal.*, vol. 2, no. 6, pp. 1259–1266, Jun. 2012, doi: 10.1021/cs300140j.

[30] F. Rastegari, I. Mohammadpoor-Baltork, A. R. Khosropour, S. Tangestaninejad, V. Mirkhani, and M. Moghadam, “1-Methyl-3-(propyl-3-sulfonic acid)imidazolium triflate supported on magnetic nanoparticles: an efficient and reusable catalyst for synthesis of mono- and bis-isobenzofuran-1(3H)-ones under solvent-free conditions,” *RSC Adv.*, vol. 5, no. 20, pp. 15274–15282, 2015, doi: 10.1039/C4RA14112A.

[31] H. Naeimi and D. Aghaseyedkarimi, “Ionophore silica-coated magnetite nanoparticles as a recyclable heterogeneous catalyst for one-pot green synthesis of 2,4,5-trisubstituted imidazoles,” *Dalton Trans.*, vol. 45, no. 3, pp. 1243–1253, 2016, doi: 10.1039/C5DT03488D.

[32] S. M. Arde, A. D. Patil, A. H. Mane, P. R. Salokhe, and R. S. Salunkhe, “Synthesis of quinoxaline, benzimidazole and pyrazole derivatives under the catalytic influence of biosurfactant-stabilized iron nanoparticles in water,” *Res Chem Intermed*, vol. 46, no. 11, pp. 5069–5086, Nov. 2020, doi: 10.1007/s11164-020-04240-6.

[33] B. M. Patil, S. R. Mali, B. M. Patil, and S. S. Patil, “*Averrhoa bilimbi* in Organic Transformation:A Highly Efficient and Green Biosurfactant for the Synthesis of Multi-Functional Chromenes and Xanthenes,” *Current Science*, vol. 118, no. 6, p. 931, Mar. 2020, doi: 10.18520/cs/v118/i6/931-945.

[34] S. P. Patil, S. N. Jadhav, C. V. Rode, R. V. Shejwal, and A. S. Kumbhar, “Bio-surfactant: a green and environmentally benign reaction medium for ligand-free Pd-catalyzed Mizoroki–Heck cross-coupling reaction in water,” *Transit Met Chem*, vol. 45, no. 6, pp. 403–411, Sep. 2020, doi: 10.1007/s11243-020-00392-x.

[35] S. M. Arde, A. D. Patil, A. H. Mane, P. R. Salokhe, and R. S. Salunkhe, “Synthesis of quinoxaline, benzimidazole and pyrazole derivatives under the catalytic influence of biosurfactant-stabilized iron nanoparticles in water,” *Res Chem Intermed*, vol. 46, no. 11, pp. 5069–5086, Nov. 2020, doi: 10.1007/s11164-020-04240-6.

[36] D. Chen, Y. Zhang, X. Pan, F. Wang, and S. Huang, “Oxidation of Tertiary Aromatic Alcohols to Ketones in Water,” *Adv. Synth. Catal.*, vol. 360, no. 18, pp. 3607–3612, Sep. 2018, doi: 10.1002/adsc.201800612.

[37] N. R. Lee *et al.*, "Coolade. A Low-Foaming Surfactant for Organic Synthesis in Water," *ChemSusChem*, vol. 12, no. 13, pp. 3159–3165, Jul. 2019, doi: 10.1002/cssc.201900369.

[38] T. Lohar, A. Kumbhar, A. Patil, S. Kamat, and R. Salunkhe, "Synthesis and characterization of new quaternary ammonium surfactant [C18-Dabco][Br] and its catalytic application in the synthesis of spirocarbocycles under ultrasonic condition," *Res Chem Intermed*, vol. 45, no. 3, pp. 1639–1651, Mar. 2019, doi: 10.1007/s11164-018-3690-8.

[39] T. Lorenzetto, D. Frigatti, F. Fabris, and A. Scarso, "Minimalistic β-sitosterol based designer surfactants for efficient cross-coupling in water," *Journal of Organometallic Chemistry*, vol. 964, p. 122316, Apr. 2022, doi: 10.1016/j.jorganchem.2022.122316.

[40] S. M. K. Reddy, J. Kothandapani, M. Sengan, A. Veerappan, and S. Selva Ganesan, "Exploring the influence of designer surfactant hydrophobicity in key C C/C N bond forming reactions," *Molecular Catalysis*, vol. 465, pp. 80–86, Mar. 2019, doi: 10.1016/j.mcat.2019.01.006.

[41] T. Hashimoto and K. Maruoka, "Recent Development and Application of Chiral Phase-Transfer Catalysts," *Chem. Rev.*, vol. 107, no. 12, pp. 5656–5682, Dec. 2007, doi: 10.1021/cr068368n.

[42] A. Chatterjee and T. R. Ward, "Recent Advances in the Palladium Catalyzed Suzuki–Miyaura Cross-Coupling Reaction in Water," *Catal Lett*, vol. 146, no. 4, pp. 820–840, Apr. 2016, doi: 10.1007/s10562-016-1707-8.

[43] S. Sayyahi and J. Saghanezhad, "An efficient method for synthesis of phenacyl derivatives under homogeneous phase transfer catalyst condition in aqueous media," *Chinese Chemical Letters*, vol. 22, no. 3, pp. 300–302, Mar. 2011, doi: 10.1016/j.cclet.2010.10.009.

[44] Y. Kim, S. Some, and H. Lee, "Graphene oxide as a recyclable phase transfer catalyst," *Chem. Commun.*, vol. 49, no. 50, p. 5702, 2013, doi: 10.1039/c3cc42787k.

[45] S. M. Ramish, A. Ghorbani-Choghamarani, and M. Mohammadi, "Microporous hierarchically Zn-MOF as an efficient catalyst for the Hantzsch synthesis of polyhydroquinolines," *Sci Rep*, vol. 12, no. 1, p. 1479, Jan. 2022, doi: 10.1038/s41598-022-05411-8.

[46] S. Gulati, R. Singh, J. Sindhu, and S. Sangwan, "Eco-friendly Preparations of Heterocycles Using Fruit Juices as Catalysts: A Review," *Organic Preparations and Procedures International*, vol. 52, no. 5, pp. 381–395, Sep. 2020, doi: 10.1080/00304948.2020.1773158.

[47] A. Chadha, S. Venkataraman, R. Preetha, and S. K. Padhi, "Candida parapsilosis: A versatile biocatalyst for organic oxidation-reduction reactions," *Bioorganic Chemistry*, vol. 68, pp. 187–213, Oct. 2016, doi: 10.1016/j.bioorg.2016.08.007.

[48] M. Potdar, G. Kelso, L. Schwarz, C. Zhang, and M. Hearn, "Recent Developments in Chemical Synthesis with Biocatalysts in Ionic Liquids," *Molecules*, vol. 20, no. 9, pp. 16788–16816, Sep. 2015, doi: 10.3390/molecules200916788.

[49] A. Kumar, K. Dhar, S. S. Kanwar, and P. K. Arora, "Lipase catalysis in organic solvents: advantages and applications," *Biol Proced Online*, vol. 18, no. 1, p. 2, Dec. 2016, doi: 10.1186/s12575-016-0033-2.

[50] M. Maryami, M. Nasrollahzadeh, E. Mehdipour, and S. M. Sajadi, "Preparation of the Ag/RGO nanocomposite by use of Abutilon hirtum leaf extract: A recoverable catalyst for the reduction of organic dyes in aqueous medium at room temperature," *International Journal of Hydrogen Energy*, vol. 41, no. 46, pp. 21236–21245, Dec. 2016, doi: 10.1016/j.ijhydene.2016.09.130.

[51] C. K. Winkler, J. H. Schrittwieser, and W. Kroutil, "Power of Biocatalysis for Organic Synthesis," *ACS Cent. Sci.*, vol. 7, no. 1, pp. 55–71, Jan. 2021, doi: 10.1021/acscentsci.0c01496.

[52] R. Chowdhury, A. Khan, and Md. H. Rashid, "Green synthesis of CuO nanoparticles using *Lantana camara* flower extract and their potential catalytic activity towards the aza-Michael reaction," *RSC Adv.*, vol. 10, no. 24, pp. 14374–14385, 2020, doi: 10.1039/D0RA01479F.

[53] S. Balaji, R. Guda, B. K. Mandal, M. Kasula, E. Ubba, and F.-R. N. Khan, "Green synthesis of nano-titania (TiO2 NPs) utilizing aqueous Eucalyptus globulus leaf extract: applications in the synthesis of 4H-pyran derivatives," *Res Chem Intermed*, vol. 47, no. 9, pp. 3919–3931, Sep. 2021, doi: 10.1007/s11164-018-03720-0.

[54] M. Khan *et al.*, “Plant Extract Mediated Eco-Friendly Synthesis of Pd@Graphene Nanocatalyst: An Efficient and Reusable Catalyst for the Suzuki-Miyaura Coupling,” *Catalysts*, vol. 7, no. 12, p. 20, Jan. 2017, doi: 10.3390/catal7010020.

[55] M. Maryami, M. Nasrollahzadeh, E. Mehdipour, and S. M. Sajadi, “Preparation of the Ag/RGO nanocomposite by use of Abutilon hirtum leaf extract: A recoverable catalyst for the reduction of organic dyes in aqueous medium at room temperature,” *International Journal of Hydrogen Energy*, vol. 41, no. 46, pp. 21236–21245, Dec. 2016, doi: 10.1016/j.ijhydene.2016.09.130.

[56] S. Naghdi, M. Sajjadi, M. Nasrollahzadeh, K. Y. Rhee, S. M. Sajadi, and B. Jaleh, “Cuscuta reflexa leaf extract mediated green synthesis of the Cu nanoparticles on graphene oxide/manganese dioxide nanocomposite and its catalytic activity toward reduction of nitroarenes and organic dyes,” *Journal of the Taiwan Institute of Chemical Engineers*, vol. 86, pp. 158–173, May 2018, doi: 10.1016/j.jtice.2017.12.017.

[57] R. Pal, “Fruit Juice: A Natural, Green and Biocatalyst System in Organic Synthesis,” *OJOC*, vol. 1, no. 4, p. 47, 2013, doi: 10.12966/ojoc.10.02.2013.

[58] M. B. Deshmukh, S. S. Patil, S. D. Jadhav, and P. B. Pawar, “Green Approach for Knoevenagel Condensation of Aromatic Aldehydes with Active Methylene Group,” *Synthetic Communications*, vol. 42, no. 8, pp. 1177–1183, Apr. 2012, doi: 10.1080/00397911.2010.537423.

[59] . G. M. N., . Y. I. S., . K. A., and . S. B. S., “Use of different Fruit juices as a Catalyst in Various Organic Synthesis (A Sustainable Development of Chemistry),” *JCPR*, vol. 9, no. 2, pp. 2805–2811, Feb. 2019, doi: 10.33786/JCPR.2019.v09i02.013.

[60] D. Das, “Lemon juice mediated efficient and eco-friendly organic transformations,” *Tetrahedron Letters*, vol. 61, no. 36, p. 152298, Sep. 2020, doi: 10.1016/j.tetlet.2020.152298.

[61] H. Sachdeva, R. Saroj, S. Khaturia, and D. Dwivedi, “Environ-Economic Synthesis and Characterization of Some New 1,2,4-Triazole Derivatives as Organic Fluorescent Materials and Potent Fungicidal Agents,” *Organic Chemistry International*, vol. 2013, pp. 1–19, May 2013, doi: 10.1155/2013/659107.

[62] R. H. Vekariya, K. D. Patel, and H. D. Patel, “Fruit juice of Citrus limon as a biodegradable and reusable catalyst for facile, eco-friendly and green synthesis of 3,4-disubstituted isoxazol-5(4H)-ones and dihydropyrano[2,3-c]-pyrazole derivatives,” *Res Chem Intermed*, vol. 42, no. 10, pp. 7559–7579, Oct. 2016, doi: 10.1007/s11164-016-2553-4.

[63] R. Cairns *et al.*, “Conversion of Aldoses to Valuable ω-Amino Alcohols Using Amine Transaminase Biocatalysts,” *ACS Catal.*, vol. 9, no. 2, pp. 1220–1223, Feb. 2019, doi: 10.1021/acscatal.8b04564.

[64] N. Zumbrägel, P. Machui, J. Nonnhoff, and H. Gröger, “Enantioselective Biocatalytic Reduction of 2 *H* -1,4-Benzoxazines Using Imine Reductases,” *J. Org. Chem.*, vol. 84, no. 3, pp. 1440–1447, Feb. 2019, doi: 10.1021/acs.joc.8b02867.

[65] A. Mane, T. Lohar, and R. Salunkhe, “Baker’s yeast as an efficient biocatalyst for regioselective 1,4-conjugate addition of indoles to nitroolefins in aqueous medium,” *Tetrahedron Letters*, vol. 57, no. 22, pp. 2341–2346, Jun. 2016, doi: 10.1016/j.tetlet.2016.04.057.

[66] E. Liardo, N. Ríos-Lombardía, F. Morís, and F. Rebolledo, “HYBRID ORGANO- AND BIO-CATALYTIC PROCESS FOR THE ASYMMETRIC TRANSFORMATION OF ALCOHOLS INTO AMINES IN AQUEOUS MEDIUM”.

[67] N. Ríos-Lombardía *et al.*, “DESign of Sustainable One-Pot Chemoenzymatic Organic Transformations in Deep Eutectic Solvents for the Synthesis of 1,2-Disubstituted Aromatic Olefins,” *Front. Chem.*, vol. 8, p. 139, Mar. 2020, doi: 10.3389/fchem.2020.00139.

[68] C. K. Winkler, J. H. Schrittwieser, and W. Kroutil, “Power of Biocatalysis for Organic Synthesis,” *ACS Cent. Sci.*, vol. 7, no. 1, pp. 55–71, Jan. 2021, doi: 10.1021/acscentsci.0c01496.

[69] A. Rodríguez M, L. Y. Rache, M. H. Brijaldo, G. P. Romanelli, R. Luque, and J. J. Martinez, “Biocatalytic transformation of furfural into furfuryl alcohol using resting cells of Bacillus cereus,” *Catalysis Today*, vol. 372, pp. 220–225, Jul. 2021, doi: 10.1016/j.cattod.2021.01.011.

[70] P. Domínguez de María, N. Guajardo, and S. Kara, “Enzyme Catalysis: In DES , with DES , and in the Presence of DES,” in *Deep Eutectic Solvents*, D. J. Ramón and G. Guillena, Eds., 1st ed.Wiley, 2019, pp. 257–271. doi: 10.1002/9783527818488.ch13.

[71] I. Bassanini, E. E. Ferrandi, S. Riva, and D. Monti, “Biocatalysis with Laccases: An Updated Overview,” *Catalysts*, vol. 11, no. 1, p. 26, Dec. 2020, doi: 10.3390/catal11010026.

[72] T. Deligeorgiev, N. Gadjev, A. Vasilev, S. Kaloyanova, J. J. Vaquero, and J. Alvarez-Builla, “Green Chemistry in Organic Synthesis”.

[73] P. N. Reddy, P. Padmaja, B. V. S. Reddy, and G. Rambabu, “Ionic liquid/water mixtures promoted organic transformations,” *RSC Advances*.

[74] A. Z. Halimehjani, K. Marjani, and A. Ashouri, “ChemInform Abstract: Synthesis of Dithiocarbamate by Markovnikov Addition Reaction in Aqueous Medium.,” *ChemInform*, vol. 41, no. 48, p. no-no, Nov. 2010, doi: 10.1002/chin.201048043.

[75] S. Kamat, Y. Indi, A. Kumbhar, and S. Kamble, “An aqueous hydrotropic solution as environmentally benign reaction medium for organic transformations: a short review,” *Res Chem Intermed*, vol. 48, no. 8, pp. 3223–3245, Aug. 2022, doi: 10.1007/s11164-022-04761-2.

[76] R. Behling, S. Valange, and G. Chatel, “Heterogeneous catalytic oxidation for lignin valorization into valuable chemicals: what results? What limitations? What trends?,” *Green Chem.*, vol. 18, no. 7, pp. 1839–1854, 2016, doi: 10.1039/C5GC03061G.

[77] B. S. Vachan *et al.*, “Proline and its Derivatives as Organocatalysts for Multi- Component Reactions in Aqueous Media: Synergic Pathways to the Green Synthesis of Heterocycles,” *Adv. Synth. Catal.*, vol. 362, no. 1, pp. 87–110, Jan. 2020, doi: 10.1002/adsc.201900558.

[78] P. Prasanna, S. Perumal, and J. C. Menéndez, “Chemodivergent, multicomponent domino reactions in aqueous media: l-proline-catalyzed assembly of densely functionalized 4H-pyrano[2,3-c]pyrazoles and bispyrazolyl propanoates from simple, acyclic starting materials,” *Green Chem.*, vol. 15, no. 5, p. 1292, 2013, doi: 10.1039/c3gc37128j.

[79] M. Gilanizadeh and B. Zeynizadeh, “Synthesis of Acridinediones and Biscoumarins Using Fe_3O_4 @SiO_2 @Ni–Zn–Fe LDH as an Efficient Magnetically Recoverable Mesoporous Catalyst,” *Polycyclic Aromatic Compounds*, vol. 41, no. 1, pp. 15–32, Jan. 2021, doi: 10.1080/10406638.2019.1567560.

[80] A. Sapkal and S. Kamble, “Greener and Environmentally Benign Methodology for the Synthesis of Pyrazole Derivatives,” *ChemistrySelect*, vol. 5, no. 42, pp. 12971–13026, Nov. 2020, doi: 10.1002/slct.202003008.

[81] F. Nador, M. A. Volpe, F. Alonso, A. Feldhoff, A. Kirschning, and G. Radivoy, “Copper nanoparticles supported on silica coated maghemite as versatile, magnetically recoverable and reusable catalyst for alkyne coupling and cycloaddition reactions,” *Applied Catalysis A: General*, vol. 455, pp. 39–45, Mar. 2013, doi: 10.1016/j.apcata.2013.01.023.

[82] J. Ebrahimi, A. Mohammadi, V. Pakjoo, E. Bahramzade, and A. Habibi, “Highly efficient solvent-free synthesis of pyranopyrazoles by a Brønsted-acidic ionic liquid as a green and reusable catalyst,” *J Chem Sci*, vol. 124, no. 5, pp. 1013–1017, Sep. 2012, doi: 10.1007/s12039-012-0310-9.

[83] H. M. A. El-Lateef *et al.*, “Pumice as a Novel Natural Heterogeneous Catalyst for the Designation of 3,4-Dihydropyrimidine-2-(1H)-ones/thiones under Solvent-Free Conditions,” *Molecules*, vol. 27, no. 18, p. 6044, Sep. 2022, doi: 10.3390/molecules27186044.

[84] R. M. Borade, S. B. Somvanshi, S. B. Kale, R. P. Pawar, and K. M. Jadhav, “Spinel zinc ferrite nanoparticles: an active nanocatalyst for microwave irradiated solvent free synthesis of chalcones,” *Mater. Res. Express*, vol. 7, no. 1, p. 016116, Jan. 2020, doi: 10.1088/2053-1591/ab6c9c.

[85] S. Bouasla *et al.*, “Coumarin Derivatives Solvent-Free Synthesis under Microwave Irradiation over Heterogeneous Solid Catalysts,” *Molecules*, vol. 22, no. 12, p. 2072, Nov. 2017, doi: 10.3390/molecules22122072.

[86] C. G. Avila-Ortiz and E. Juaristi, “Novel Methodologies for Chemical Activation in Organic Synthesis under Solvent-Free Reaction Conditions,” *Molecules*, vol. 25, no. 16, p. 3579, Aug. 2020, doi: 10.3390/molecules25163579.

[87] S. Onitsuka, Y. Z. Jin, A. C. Shaikh, H. Furuno, and J. Inanaga, “Silica Gel-Mediated Organic Reactions under Organic Solvent-Free Conditions,” *Molecules*, vol. 17, no. 10, pp. 11469–11483, Sep. 2012, doi: 10.3390/molecules171011469.

[88] M. B. Gawande, V. D. B. Bonifácio, R. Luque, P. S. Branco, and R. S. Varma, “Solvent-Free and Catalysts-Free Chemistry: A Benign Pathway to Sustainability,” *ChemSusChem*, vol. 7, no. 1, pp. 24–44, Jan. 2014, doi: 10.1002/cssc.201300485.

[89] C. Int, “Catalytic acetylation of (+)-cedrol with heterogeneous catalyst H2SO4/SiO2 under solvent free conditions,” Arabixiv, preprint, Apr. 2019. doi: 10.31221/osf.io/pbcey.

[90] A. K. Nagariya *et al.*, “Available online through www.jpronline.info,” *Journal of Pharmacy Research*, no. 3, 2010.

[91] M. A. Surati, S. Jauhari, and K. R. Desai, “A brief review: Microwave assisted organic reaction,” 2012.

[92] N. N. Gharat and V. K. Rathod, “Ultrasound-assisted organic synthesis,” in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Elsevier, 2020, pp. 1–41. doi: 10.1016/B978-0-12-819540-6.00001-2.

[93] M. A. Surati, S. Jauhari, and K. R. Desai, “A brief review: Microwave assisted organic reaction,” 2012.

[94] S. Jadhav, P. L. Anandgaonker, G. Kulkarni, S. T. Gaikwad, and A. S. Rajbhoj, “Microwave-Assisted One-Pot Synthesis of Octahydroquinazolinone Derivatives Using Molybdenum Oxide Nanoparticles in Solvent-Free Condition,” *J Clust Sci*, vol. 25, no. 5, pp. 1389–1399, Sep. 2014, doi: 10.1007/s10876-014-0716-2.

[95] A. K. Rathi, M. B. Gawande, R. Zboril, and R. S. Varma, “Microwave-assisted synthesis – Catalytic applications in aqueous media,” *Coordination Chemistry Reviews*, vol. 291, pp. 68–94, May 2015, doi: 10.1016/j.ccr.2015.01.011.

[96] M. Afradi, S. A. Pour, M. Dolat, and A. Yazdani-Elah-Abadi, “Nanomagnetically modified vitamin B $_3$ (Fe $_3$ O $_4$ @Niacin): An efficient and reusable green biocatalyst for microwave-assisted rapid synthesis of 2-amino-3-cyanopyridines in aqueous medium,” *Appl Organometal Chem*, vol. 32, no. 2, Feb. 2018, doi: 10.1002/aoc.4103.

[97] R. S. Varma, “Journey on greener pathways: from the use of alternate energy inputs and benign reaction media to sustainable applications of nano-catalysts in synthesis and environmental remediation,” *Green Chem.*, vol. 16, no. 4, p. 2027, 2014, doi: 10.1039/c3gc42640h.

[98] B. Borah, K. D. Dwivedi, B. Kumar, and L. R. Chowhan, “Recent advances in the microwave- and ultrasound-assisted green synthesis of coumarin-heterocycles,” *Arabian Journal of Chemistry*, vol. 15, no. 3, p. 103654, Mar. 2022, doi: 10.1016/j.arabjc.2021.103654.

[99] B. Banerjee, “Recent developments on ultrasound-assisted organic synthesis in aqueous medium,” *J Serb Chem Soc*, vol. 82, no. 7–8, pp. 755–790, 2017, doi: 10.2298/JSC170217057B.

[100] N. N. Gharat and V. K. Rathod, “Ultrasound-assisted organic synthesis,” in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Elsevier, 2020, pp. 1–41. doi: 10.1016/B978-0-12-819540-6.00001-2.

[101] N. N. Gharat and V. K. Rathod, “Ultrasound-assisted organic synthesis,” in *Green Sustainable Process for Chemical and Environmental Engineering and Science*, Elsevier, 2020, pp. 1–41. doi: 10.1016/B978-0-12-819540-6.00001-2.

[102] A. G. F. Shoair, “Ultrasonic-assisted ruthenium-catalyzed oxidation of some organic compounds in aqueous medium,” *Journal of Molecular Liquids*, vol. 206, pp. 68–74, Jun. 2015, doi: 10.1016/j.molliq.2015.01.023.

[103] B. Banerjee, “Recent developments on ultrasound-assisted one-pot multicomponent synthesis of biologically relevant heterocycles,” *Ultrasonics Sonochemistry*, vol. 35, pp. 15–35, Mar. 2017, doi: 10.1016/j.ultsonch.2016.10.010.

[104] M. Esmaeilpour, “A green one-pot three-component synthesis of tetrahydrobenzo [b]pyran and 3,4-dihydropyrano[c]chromene derivatives using Fe3O4@SiO2-imid-PMAn magnetic nanocatalystunder ultrasonic irradiationor reflux conditions,” *RSC Advances*.

[105] R. Chowdhury, A. Khan, and Md. H. Rashid, “Green synthesis of CuO nanoparticles using *Lantana camara* flower extract and their potential catalytic activity towards the aza-Michael reaction,” *RSC Adv.*, vol. 10, no. 24, pp. 14374–14385, 2020, doi: 10.1039/D0RA01479F.

[106] B. Borah and L. R. Chowhan, “Ultrasound-assisted transition-metal-free catalysis: a sustainable route towards the synthesis of bioactive heterocycles,” *RSC Adv.*, vol. 12, no. 22, pp. 14022–14051, 2022, doi: 10.1039/D2RA02063G.

[107] S. Kamble, A. Kumbhar, G. Rashinkar, M. Barge, and R. Salunkhe, “Ultrasound promoted efficient and green synthesis of β-amino carbonyl compounds in aqueous hydrotropic medium,” *Ultrasonics Sonochemistry*, vol. 19, no. 4, pp. 812–815, Jul. 2012, doi: 10.1016/j.ultsonch.2011.12.001.

[108] R. S. Varma, “Journey on greener pathways: from the use of alternate energy inputs and benign reaction media to sustainable applications of nano-catalysts in synthesis and environmental remediation,” *Green Chem.*, vol. 16, no. 4, p. 2027, 2014, doi: 10.1039/c3gc42640h.

[109] R. M. Borade, S. B. Kale, S. U. Tekale, K. M. Jadhav, and R. P. Pawar, “Cobalt ferrite magnetic nanoparticles as highly efficient catalyst for the mechanochemical synthesis of 2-aryl benzimidazoles,” *Catalysis Communications*, vol. 159, p. 106349, Nov. 2021, doi: 10.1016/j.catcom.2021.106349.

[110] K. Kantharaju, P. B. Hiremath, and S. Y. Khatavi, “WEB: A green and an efficient catalyst for Knoevenagel condensation under grindstone method,” *INDIAN J. CHEM.*, 2019.

[111] S. Sana, K. R. Reddy, K. C. Rajanna, M. Venkateswarlu, and M. M. Ali, “Mortar-Pestle and Microwave Assisted Regioselective Nitration of Aromatic Compounds in Presence of Certain Group V and VI Metal Salts under Solvent Free Conditions,” *IJOC*, vol. 02, no. 03, pp. 233–247, 2012, doi: 10.4236/ijoc.2012.23032.

[112] D. Das, A. A. Bhosle, A. Chatterjee, and M. Banerjee, “Automated grindstone chemistry: a simple and facile way for PEG-assisted stoichiometry-controlled halogenation of phenols and anilines using *N* -halosuccinimides,” *Beilstein J. Org. Chem.*, vol. 18, pp. 999–1008, Aug. 2022, doi: 10.3762/bjoc.18.100.

[113] S. Rezayati, G. Dinmohammadi, A. Ramazani, and S. Sajjadifar, “Mortar–Pestle Grinding Technique as an Efficient and Green Method Accelerates the Tandem Knoevenagel–Michael Cyclocondensation Reaction in the Presence of Ethylenediamine Immobilized on the Magnetite Nanoparticles,” *Polycyclic Aromatic Compounds*, pp. 1–23, Aug. 2022, doi: 10.1080/10406638.2022.2110506.