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Solvent-free Organic Reaction Techniques as an Approach for Green Chemistry

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Abstract: Unfortunately, many toxic solvents are used in chemistry laboratories and in the manufacturing of materials, which poses a serious risk to process safety, the natural environment, and human health. In this review, different tools for solvent-free organic reactions have been surveyed as an approach for green chemistry, where many of the solvents are known to upset our ecosystems so an enormous research effort has been exerted during the last decade to avoid the utilization of hazardous solvents and the number of publications on solvent-free reactions has increased nearly exponentially. Obviously, this reflects the great interest in solventless reactions. In our survey, we will highlight the solvent-free organic reaction as an approach for green chemistry to cover work published up to nearly 2022.

Keywords: Solvent-free reactions, green chemistry, mechanochemistry, microwave assisted synthesis, ultrasound assisted green synthesis, photochemical reactions.

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1. INTRODUCTION

We cannot deny that solvents play an important role in our life and are necessary for many applications such as cleaning, extraction, coatings, synthetic chemistry, separation of organic ingredients, etc. However, many of these solvents have a negative impact on our ecosystem because they cause ozone layer depletion, and contribute to tropospheric smog formation. In addition to the effect of these solvents on the human health, some of these solvents are neurotoxins, may cause sterility, or may cause cancer, so the utilization of these solvents is not accepted from environmental and health point of view (1–6).

We can say that there are no safe organic solvents, only more or less toxic ones. Table 1 shows the following: Aromatic hydrocarbons are the most dangerous solvents and most volatile organic compounds (VOC).

Solvents can harm the human body through the eyes, lungs, blood, skin, and kidneys. They are frequently between those (carcinogen, toxin, irritant, hepatotoxin, neurotoxin, and nephrotoxin). Therefore, different quality regulations force solvent producers to put well-known international labels on different solvents showing the extent of potential damage and how to handle, transport, and store different solvents (7). One of the major problems with using solvents is the time-consuming heating and recovery of the solvent after the reaction is complete (8).

In addition to the above, incorrect storage of solvents may cause fires or explosions. Most organic solvents have high flammability. Therefore, the pollution prevention Act of 1990 of environmental protection agency (U.S.EPA) encouraged the utilization of novel techniques to eliminate or reduce pollutants or waste and protect natural resources from depletion by increasing the efficiency of use.

Table 1: Some of the dangerous health effects resulting from solvents.

Health hazard	**Solvent and chemicals that create the hazard**
Carcinogen	Ethylene dichloride, methylene chloride, dioxin, chloroform, perchloroethane.
Toxic	Xylene, benzene, toluene
Irritant	Ammonium solution
Hepatotoxin	Dioxane, acetonitrile, carbon tetrachloride, phenol
Neurotoxin	Cresol, methylene chloride, xylene, carbon disulfide
Nephrotoxin	Ethylenediamine, chlorobenzene, dioxane, acetonitrile, Allyl alcohol, hexachloronaphthalene, phenol
Human organs that are harmed:	
1Blood	Nitrotoluene, benzene, cyanide, carbon monoxide
2Lung	Asbestos, silica, tars, dust
3Eyes or skin	Allyl alcohol, perchloroethane, ethyl butyl ketone, nitroethane, ethanolamine, propylene oxide.

As a result of the above-mentioned dangerous effect of solvents on human health and ecosystems, great efforts are made to find an innovative technique to eliminate or reduce the use of hazardous solvents or to use alternative safe solvents. From this approach, researchers worked to determine the role of alternative safe and green solvents like water, micellar medium, supercritical CO_2, ionic liquid in different chemical reactions (9). In addition to applied techniques (10) that reduce or prevent the use of solvents, such as solid-solid reaction (11,12), microwave assisted synthesis (13,14), and ultrasonic assisted reactions (15).

From the above aspects, we found the need for eliminating solvents in chemical reactions, so solvent less reactions are the key for solving all previously mentioned problems. Our review covers the recent advances of solvent-free organic reactions under different conditions as an approach to green chemistry.

Solvent-free reaction has many advantages (Fig.1) that are very important in industry:
1Reduced pollution (safe, nontoxic).
2Low costs.
3Simplicity in process (Renewable).
4Simplicity in handling (Easier to produce).
5Environmentally friendly.
6Reduced time.

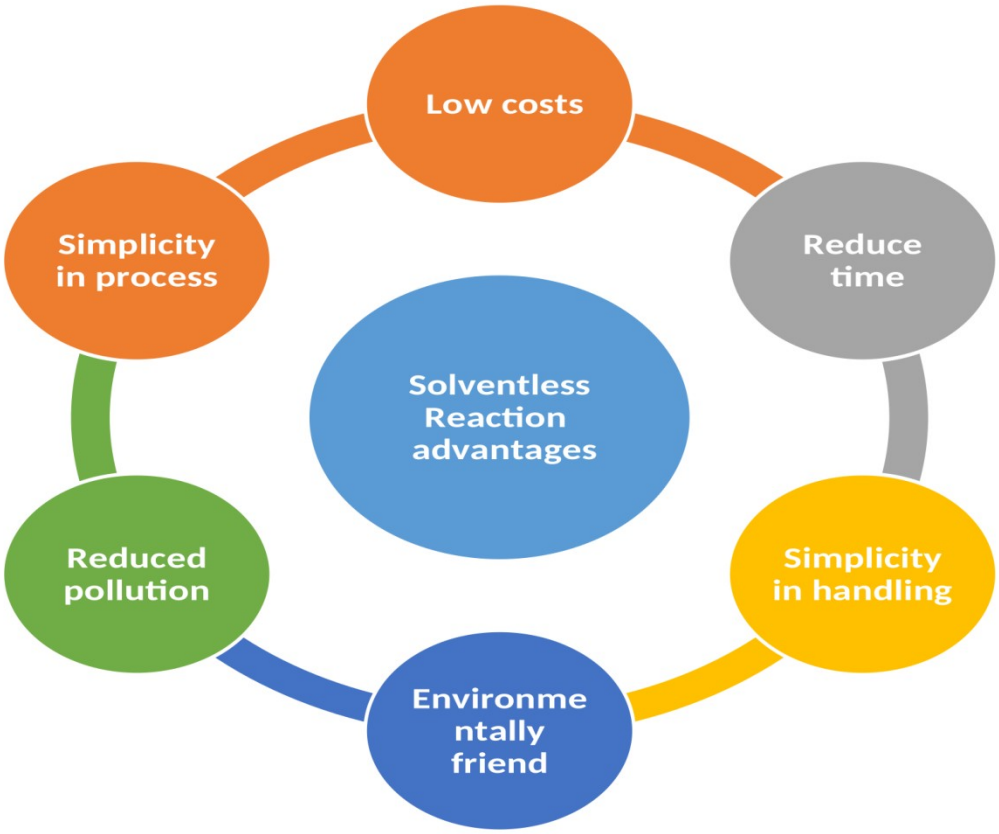


Figure 1: Advantages of solvent-free organic reactions.

2. APPLICATION OF ALTERNATIVE SOLVENTS

The process of replacing organic solvents with other systems is not easy, especially because most organic compounds are poorly soluble in natural solvents such as water, but there are many systems that are designed to skip the use of organic solvents, such as switchable solvents, supercritical fluids, ionic liquid systems, deep eutectic solvents (DES), and micellar systems.

2.1. Using Water as a Neutral Solvent

Water is an ideal alternative solvent in organic synthesis to verify some green chemistry principles (16–18) because water is safe from a health and environmental point of view. Unfortunately, the utilization of an aqueous medium instead of an organic solvent in organic synthesis is not a simple task. Many organic compounds are insoluble or sparingly soluble in water due to the high polarity of water, so many difficulties are faced.

2.2. Switchable Solvents

The liquids that can change their physical properties reversibly are defined as switchable solvents (19–21) where the reversible change between two different forms takes place by applying external stimulus (or trigger) such as changes in temperature and the addition or withdrawal of a gas (22, 23).

Although switchable solvents have many advantages, their use as reaction mediums is restricted to some specific reactions, such as the polymerization of styrene (24).

2.3. Supercritical Fluids

The most commonly used supercritical fluids are water and carbon dioxide, which are characterized by being inexpensive, nonflammable, and nonpoisonous, but the high cost of the used technology, especially for water, is because it needs to perform reactions at high temperature and pressure, which demand special equipment (25–28) .

2.4. Ionic Liquids

Ionic liquids' potential to take the place of common solvents as a reaction medium has been studied using a variety of organic processes. Ionic liquids are characterized by the catalytic activity of homogeneous transition-metal and the easy separation of the products of the reaction, but unfortunately, ionic liquids are not easily prepared, are expensive, and are sensitive to moisture, and some of them are hazardous (29–34).

2.5. Deep Eutectic Solvents

Deep eutectic solvents are considered a good alternative to ionic liquids because they have similar physicochemical properties. Deep eutectic

solvents are preferred over ionic liquids because they are biodegradable and much less expensive. Deep eutectic solvents (DES) were called "the organic reaction medium of the century" due to their simple, one-step purification-free production from readily available and renewable source chemicals. (35–39). But it is still uncommon and limited to some processes and reactions.

2.6 Micellar System

A micellar solution involves some aggregated surfactants, called micelles, in water as solvent. The micelle molecules have hydrophilic head and hydrophobic tail in aqueous solution. This system can perform internal reactions without resorting to organic solvents (40–42).

3. SOLVENTLESS ORGANIC REACTION TECHNIQUES

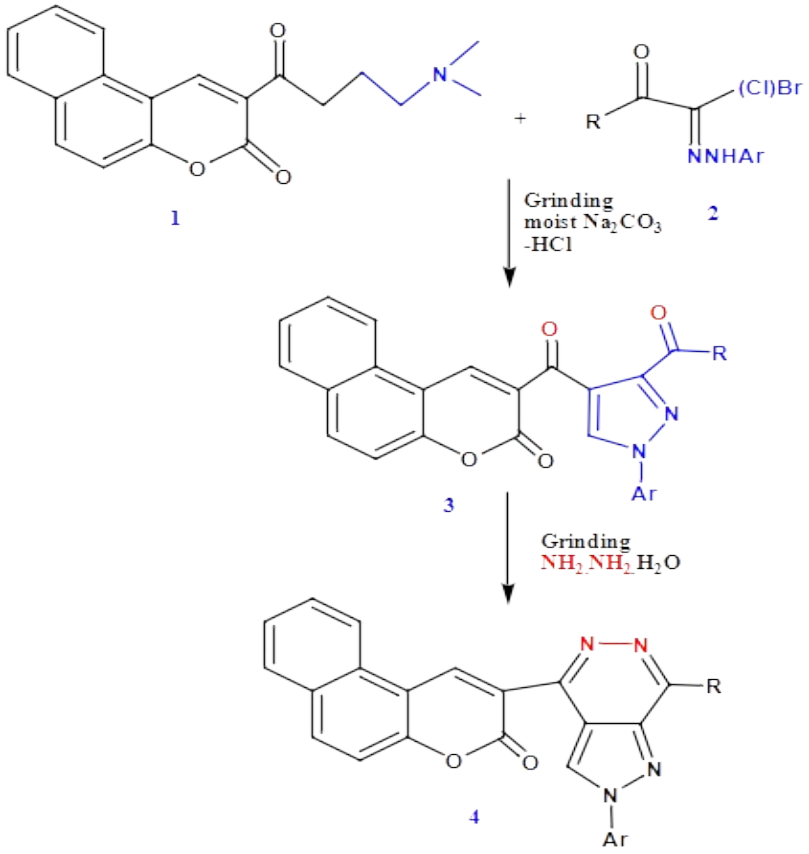
Many techniques have been exploited to go through chemical reactions without the need for solvents or using very small amounts compared to traditional methods (43). Grinding in a mortar (44) (mechanochemistry) is one of the oldest methods used to conduct reactions without solvents. Manual grinding has been developed into many automated methods that apply reactions by friction force, such as grinding by rotating mortar (45) and high-speed ball milling (46). Many other technologies have resorted to using energy to conduct reactions such as microwave-assisted reactions (47), reactions under ultrasonic waves (sonochemistry)(48), photochemistry, and electrochemistry (43), in addition to reactions that depend on microorganisms (biosynthesis)(49–51). In this section, we tried to shed light on the most important of these organic reactions that took place without harmful solvents as an approach to green chemistry.

3.1. Solventless Organic Reactions by Friction Force (Mechanochemistry)

The term “mechanochemistry” or “grindstone chemistry” is often used in a wide sense, covering the chemical reactions that depend on mechanical force as a source of energy (e.g., grinding, rotating mortar, and high-speed ball milling (52)).

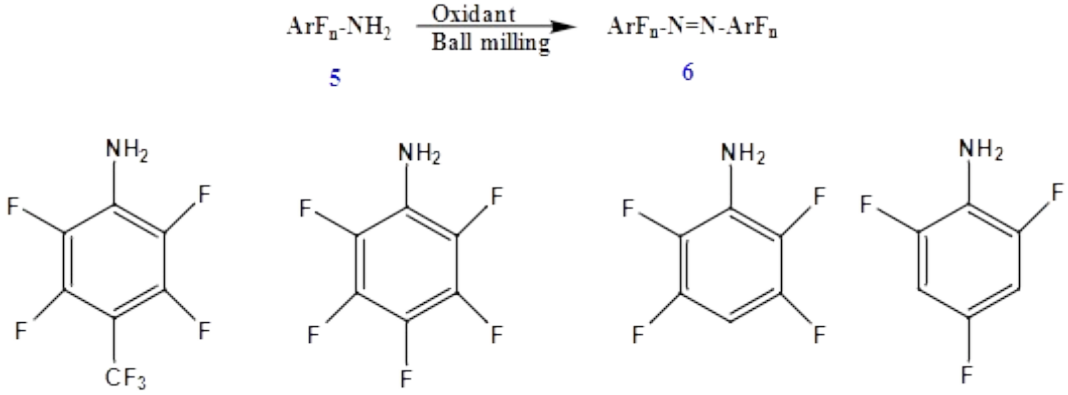
Studying mechanochemistry became very important because it can assist the reactions quickly and quantitatively under solventless conditions (53–56). It is obvious that mechanochemical reactions are effective and advantageous, so we can say that mechanochemistry could in the future develop a more conventional techniques in addition to the unsustainable dependence on solvents, which are hazardous and problematic (57,58).

By grinding chromen-3-one derivatives **1** with various reagents, a quick, inexpensive, clean, and environmentally acceptable method to synthesize novel pyrazoles, pyrazolopyridazines, and condensed pyrimidines was devised. (59) (Scheme 1).



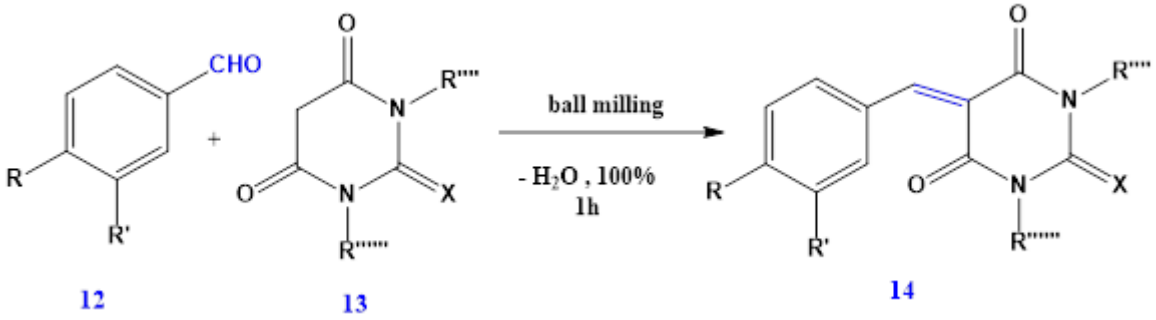
Scheme 1

Under solvent-free conditions, a quick and practical method for the mechanochemical oxidation of highly fluorinated anilines **5** to the corresponding symmetric azobenzene **6** was reported (60) (Scheme 2).



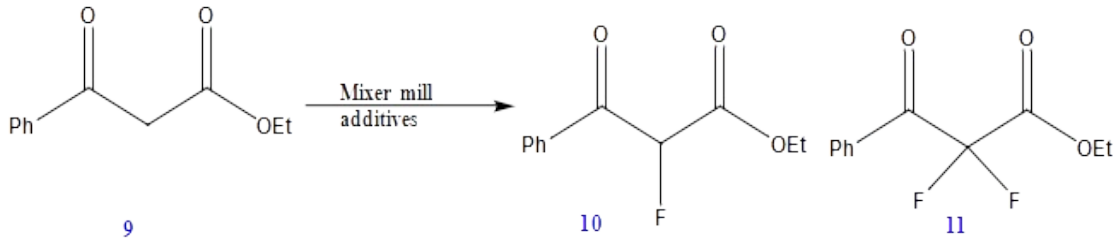
Scheme 2

The synthesis of physiologically active 2-amino-4*H*-benzo[b]pyrans **8**, a mild, ecofriendly green technique, has been established, using solid sodium ethoxide as the catalyst in solvent-free conditions at ambient temperature (61) (Scheme 3).



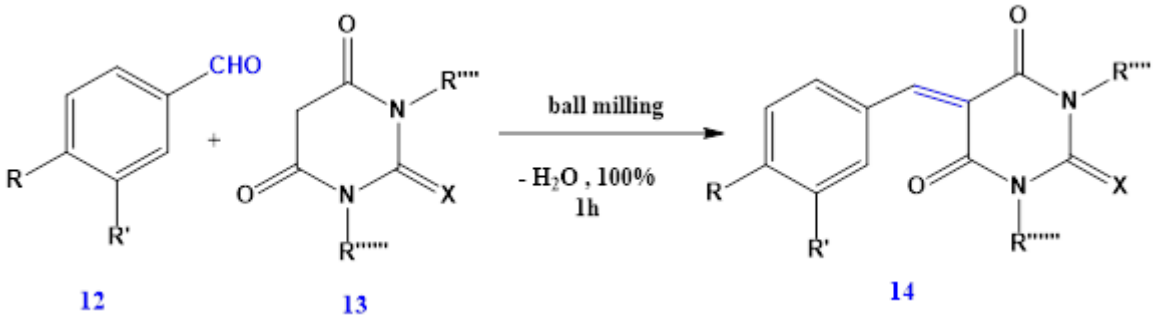
Scheme 3

By utilizing a grinding auxiliary, the mechanochemical fluorination of liquid β-ketoesters **9** has been accomplished. This led to good selectivity and good yields of mono- and difluorinated β-ketoesters **10,11** (62) (Scheme 4).



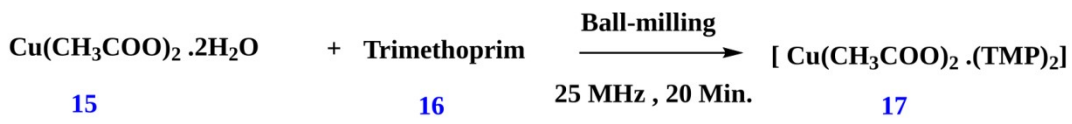
Scheme 4

The Knoevenagel condensation reaction is a significant C–C-bond forming **14**, produce α,β-unsaturated carbonyl organic compounds (63). A ball mill-based, solvent-free variant of this process was first introduced by Kaupp et al. He used the stoichiometric starting material amounts to produce the required results quantitatively. No work-up was necessary in this case, as well as in the alleged Michael additions, making these waste-free methods viable and environmentally friendly. (Scheme 5).



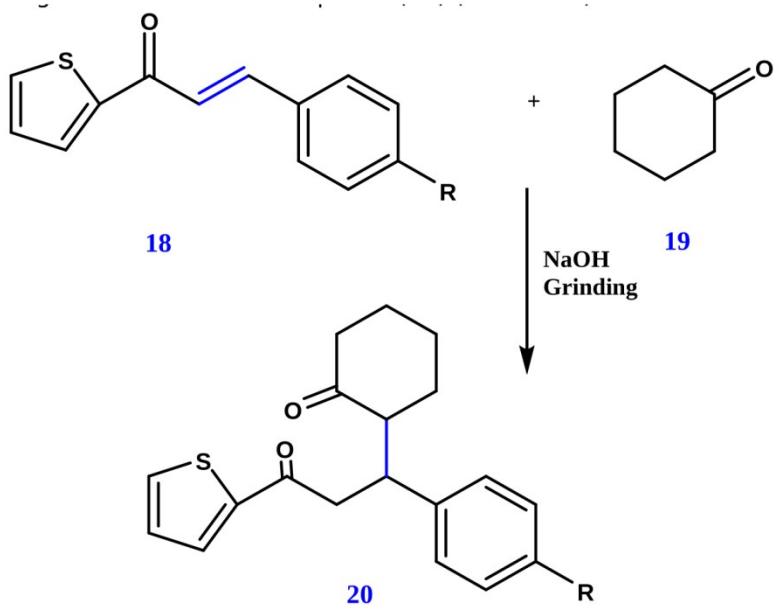
Scheme 5

Solvent-free synthesis of $[Cu(CH_3COO)_2(TMP)_2]$ and $[Ni(CH_3COO)_2(TMP)_2]$ **17** by ball milling of copper acetate dihydrate **15** and nickel acetate tetrahydrate with 5-(3,4,5-Trimethoxybenzyl)pyrimidine-2,4-diamine (Trimethoprim) **16** in the absence of solvent by ball-milling (64) (Scheme 6).



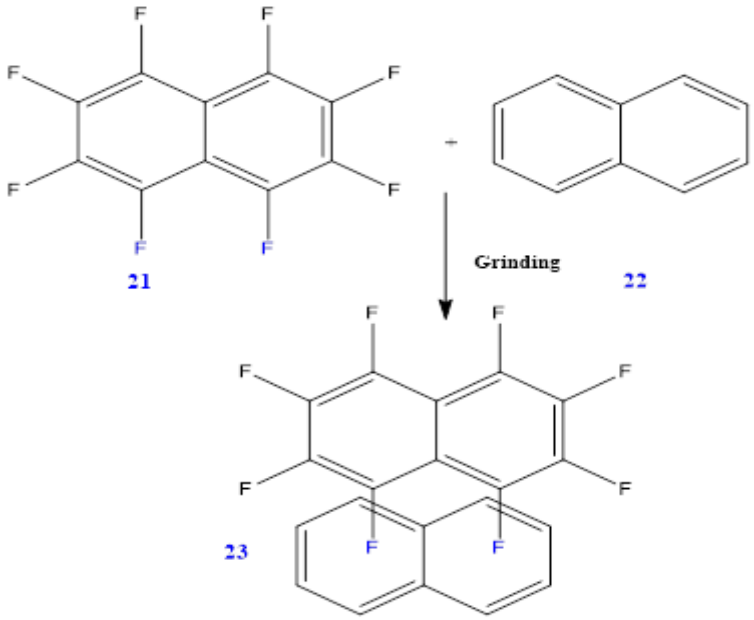
Scheme 6

1,5-diketones **20** were prepared by an efficient and ecofriendly method using mechanochemistry, where reactants are ground together in a mortar and pestle (65) (Scheme 7).



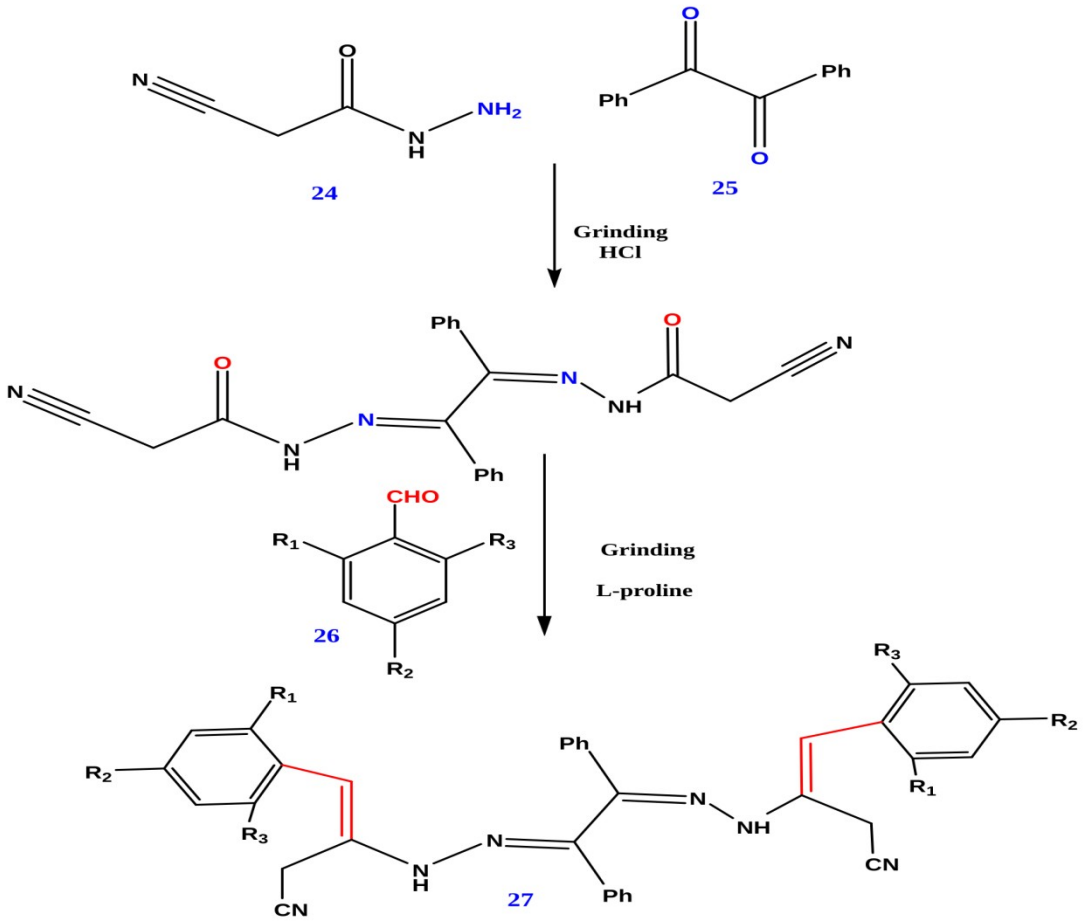
Scheme 7

Four π-π stacked arene-perfluoroarene co-crystals **23** made of naphthalene **22** or biphenyl, octafluoronaphthalene **21** or decafluorobiphenyl, and their mechanochemical synthesis are reported (66) (Scheme 8).



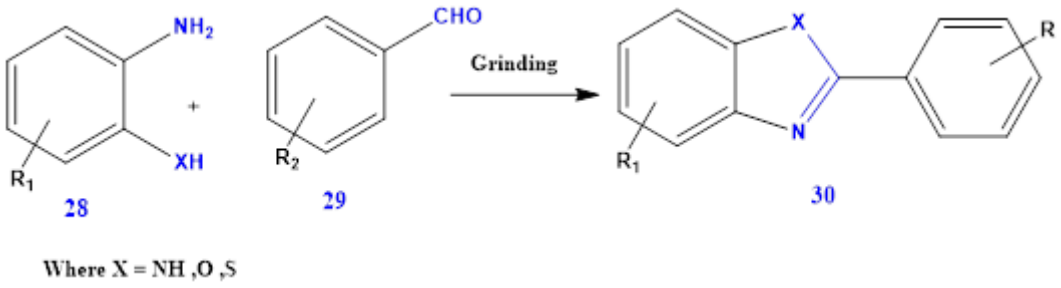
Scheme 8

The mechanochemical synthesis of benzil bis-hydrazones **27** occurred in two steps: the Schiff base reaction of 2-cyanoacetohydrazide **24** with benzil **25** in mole ratio 2:1, and the resulting grinding with benzaldehyde derivatives **26** (67). (Scheme 9).



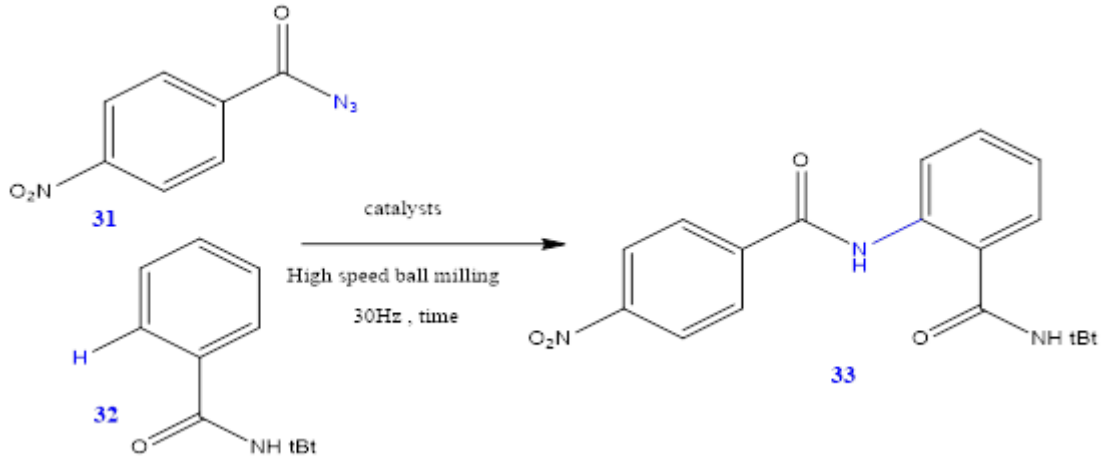
Scheme 9

Synthesis of benzimidazole **30** by grinding aromatic aldehyde **29** and ortho phenylenediamine **28** with very a high yield that reached 93% for forty-three substation samples in the percent of acetic acid (68) (Scheme 10).



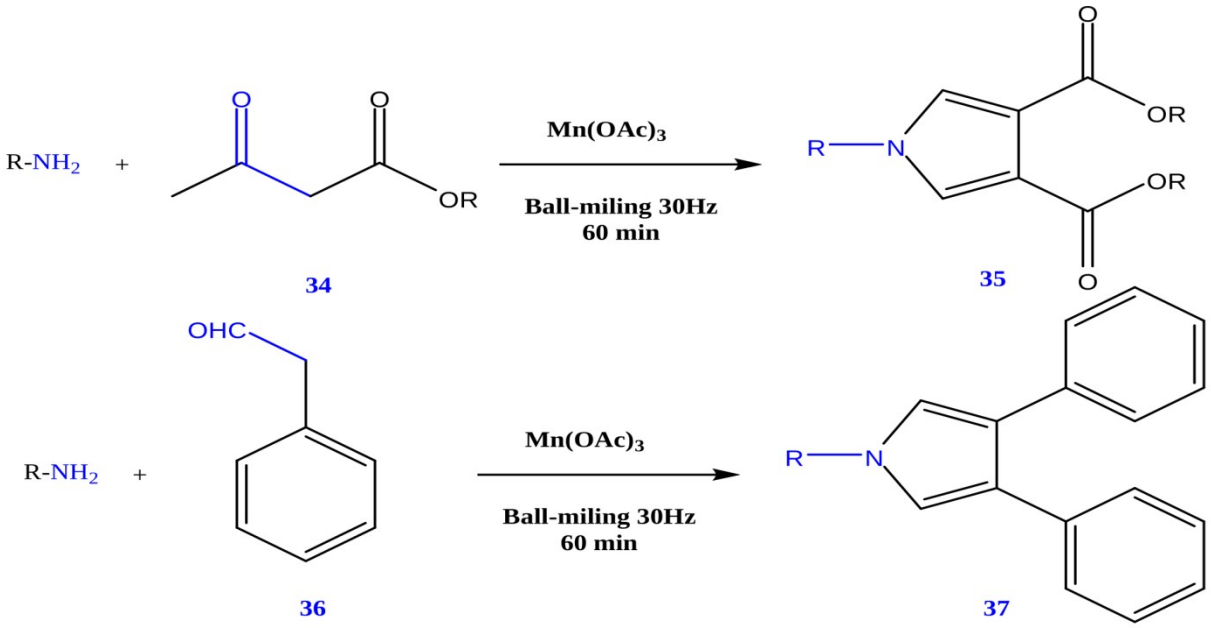
Scheme 10

High speed ball milling has been used to convert carbon-hydrogen bonding into amide **33** by the reaction of acyl azides **31** and different catalysts (69) (Scheme 11)



Scheme 11

Schiff base reaction of ketone or aldehyde and amine to form *N*-heterocyclic compounds **35, 37** have been developed by using solvent-less high-speed ball milling technique in the different forms of mechanism and present of manganese (III) acetate (70) (Scheme 12).



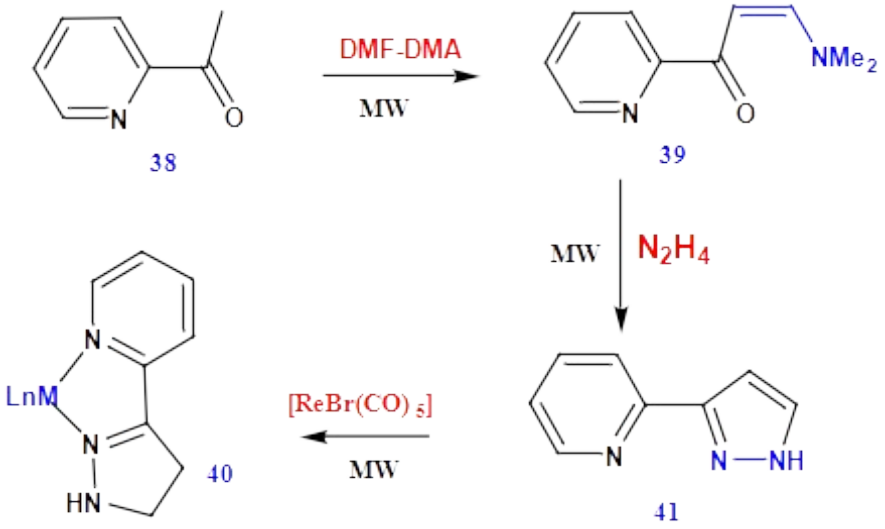
Scheme 12

3.2. Solventless organic reactions under microwave irradiation

Microwave-assisted organic synthesis (MAOS) has developed as a novel “approach” in solventless organic reactions. The process makes the synthesis of several organic compounds quick, easy, clean, effective, and affordable. Microwave assisted chemical reactions have become a new technique in the synthesis of organic compounds in recent years. The substantially increased reaction rate, faster reaction times, and improved product yield and quality are all significant benefits of this technique. The method used today is viewed as an important step toward green chemistry, especially with solventless reactions in industry (71–77).

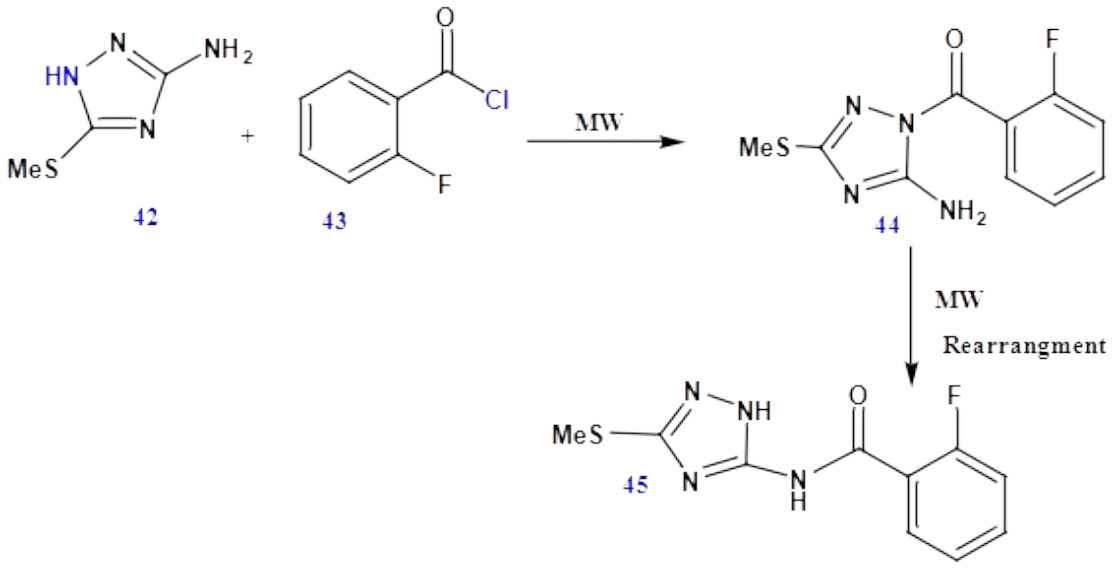
High frequency electromagnetic waves can be used in microwave ovens to heat materials. The wave's electric field component interacts with the material's charge particles to produce the heating. There are two mechanisms for heating materials: dipolar Polarization and ionic conduction. The biggest difference between conventional heating and microwave is the even distribution of heat, in addition to the absence of solvents and the speed of production(78,79).

By conventional procedures, 3-(2-pyridyl) pyrazole (pypzH) **41** synthesis requires refluxing at high temperatures for more than 16 hours, but a microwave-assisted synthesis reduces this to two subsequent phases of 2 hours at 100 °C and 10 minutes at 50 °C. Additionally, with MW assistance, it coordinates as a chelating ligand **40** to the "fac-$ReIBr(CO)_3$" and "$RuII(bipy)_2$" fragments in 5 or 10 min, respectively (80) (Scheme 13).



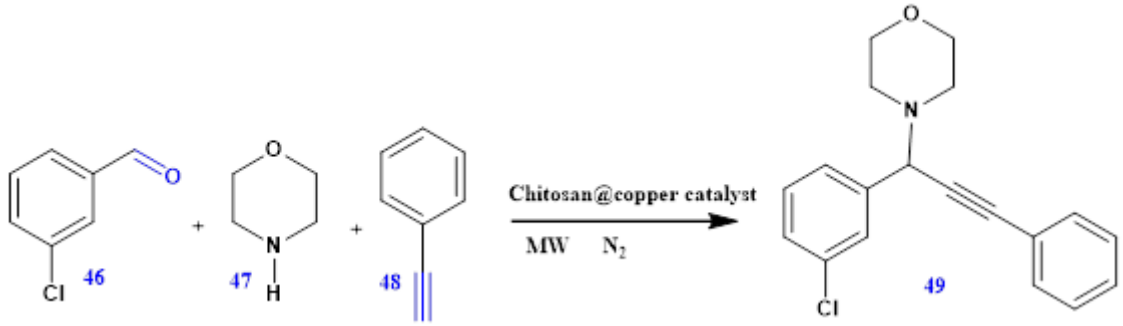
Scheme 13

Under catalyst- and solvent-free conditions, a microwave-assisted Fries rearrangement was employed to successfully create 2-fluoro-*N*-(3-methylsulfanyl-1*H*-1,2,4-triazol-5-yl) benzamide **45** from heterocyclic amide as a strategic intermediate (81) (Scheme 14).



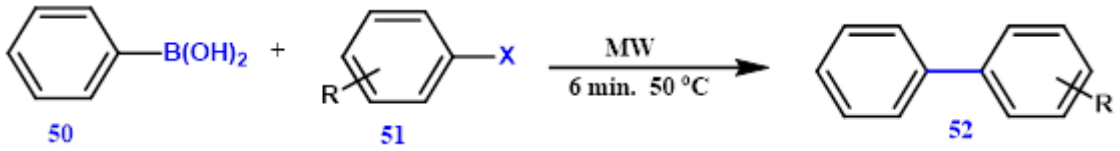
Scheme 14

A3-coupling and decarboxylative A3-coupling, chitosan-supported copper based heterogeneous catalysts have been studied. The established process uses minimal catalyst loading, a solventless environment, and a simple set-up to produce a variety of substituted propargylamines **49** (82) (Scheme 15).



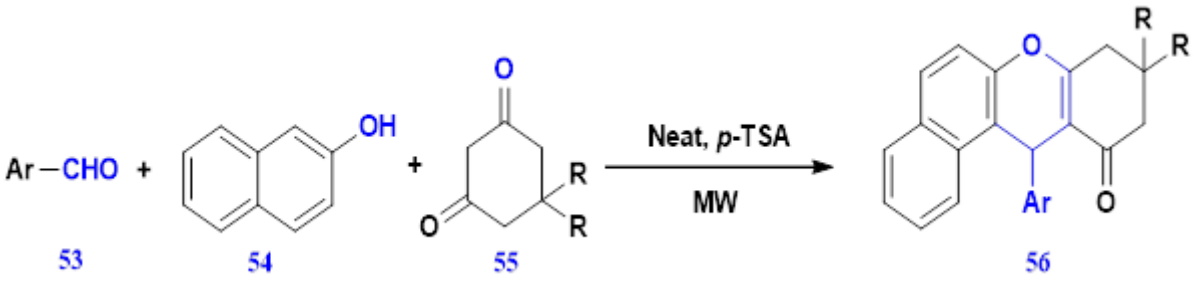
Scheme 15

Suzuki cross-coupling reactions are used to create twelve different biaryl compounds **52** using a microwave irradiation process that is safe, simple, and quick when a catalyst is present (83) (Scheme 16).



Scheme 16

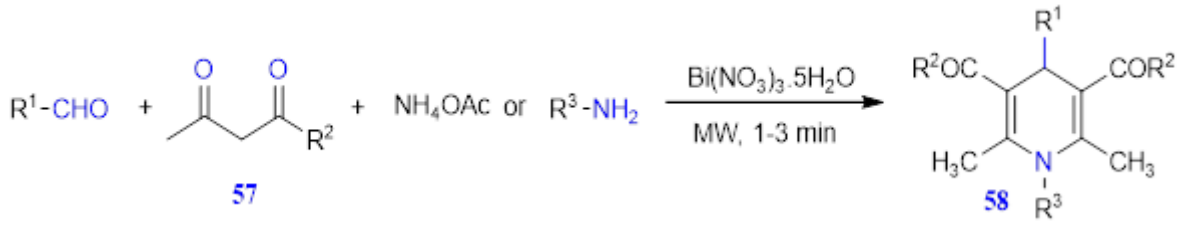
For the synthesis of 12-aryl-8, 9, 10, and 12-tetrahydrobenzo[a]xanthen-11-one **56** derivatives, convenient and environmentally friendly processes have been reported. These involve multi-component condensation reactions of aromatic aldehydes **53** with naphthol **54** and cyclic 1, 3-dicarbonyl compounds, specifically dimedone and cyclohexane-1, 3-dione **55**. using microwaves to condense *p*-toluenesulfonic acid in a clean environment. The green approaches described here avoid the harsh conditions posed by the more traditional existing technologies and demonstrate efficiency in terms of high yields, ease of operation, simple set-up, and quick reaction times (84) (Scheme 17).



Ar = C_6H_5, 4-ClC_6H_4, 4-BrC_6H_4, 4-FC_6H_4, 4-$CH_3OC_6H_4$, 4-CH_3C_6
4-OHC_6H_4, 4-$NO_2C_6H_4$, 3-ClC_6H_4, 3-BrC_6H_4, 2-BrC_6H_4
R = H, CH_3

Scheme 17

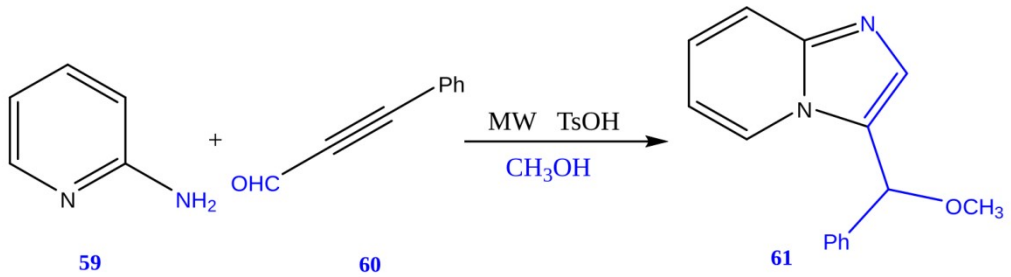
Bandyopadhyay et al. (85) reported an easy and incredibly quick technique for the synthesis of 1,4-dihydropyridines **58** under solvent-free conditions by reacting various carbonyl compounds and 1,3-dicarbonyl **57** compounds using aromatic amine/ammonium acetate as an ammonia source in the occurrence of catalytic amounts of bismuth nitrate pentahydrate using microwave irradiation (Scheme 18).



R1 = Aryl, Heteroaryl, Alkyl
R2 = Me, MeO, EtO
R3 = Aryl, Heteroaryl

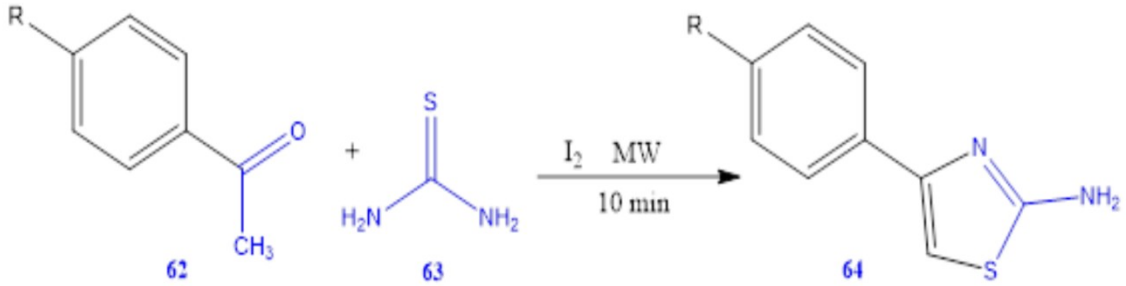
Scheme 18

Under solvent-free conditions, TsOH effectively catalyzes a three-component reaction involving pyridin-2-amine **59**, 3-phenylpropiolaldehyde **60**, and alcohol to produce imidazo[1,2-a] pyridines **61** in good yields. High efficiency and good functional group tolerance are seen in the reactions. This method offers a practical procedure for making functionalized imidazo[1,2-a]pyridine derivatives (86) (Scheme 19).



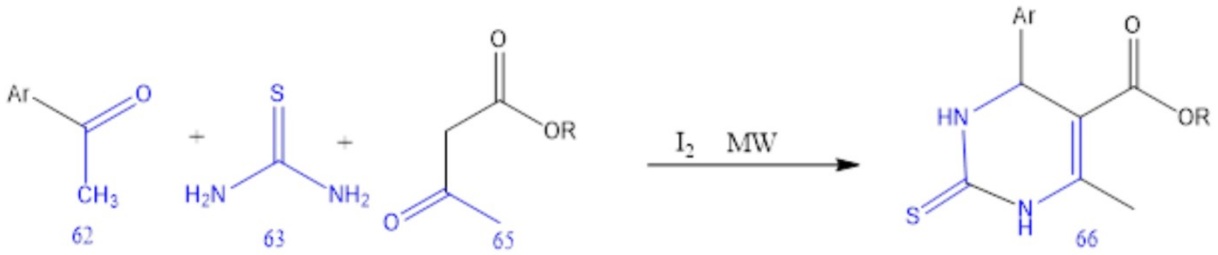
Scheme 19

P-substituted acetophenones **62** were reacted with thiourea **63** to produce 2-amino-4-arylthiazoles **64** in a single pot without the need for any solvents under microwave irradiation in the presence of iodine (87) (Scheme 20).



Scheme 20

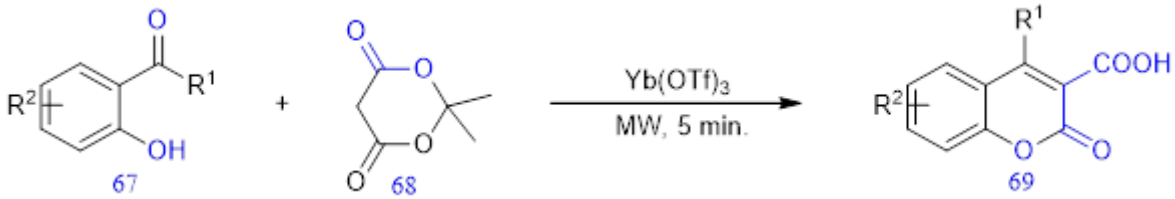
Biginelli reaction employing aldehydes **62**, acetoacetates **65**, and thiourea **63** in the presence of iodine under solvent-free conditions has been successfully microwave-assisted to produce 3, 4-dihydropyrimidin-2-thiones **66** with good yields and purity without chromatographic separation (88) (Scheme 21).



R = Me, Et
Ar = C_6H_5, 4-ClC_6H_4, 4-BrC_6H_4, 4-FC_6H_4, 4-$O_2NC_6H_4$, 3-$O_2NC_6H_4$, 2-$O_2NC_6H_4$, 4-$MeOC_6H_4$, 3-$MeOC_6H_4$, 4-OHC_6H_4, 4-OH-3-$MeOC_6H_3$

Scheme 21

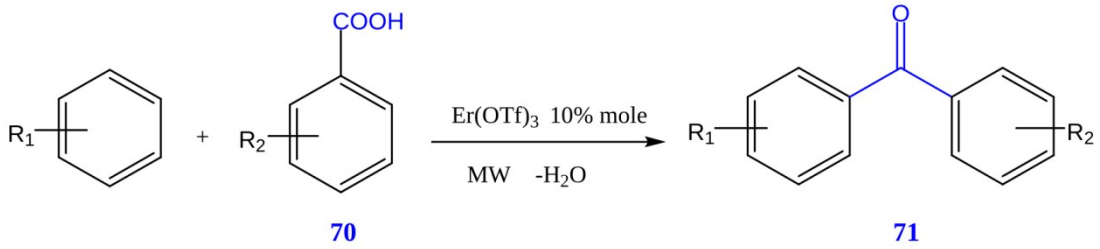
Under microwave irradiation and solvent-free conditions, coumarin-3-carboxylic acids **69** have been produced in good to high yields from differently substituted Meldrum's acid **68** and 2-hydroxybenzaldehydes or 2-hydroxyacetophenones **67** as starting materials in the presence of catalyst $Yb(OTf)_3$ hydrate with a concentration of 5% mol (89) (Scheme 22).



R1 = H, Me

Scheme 22

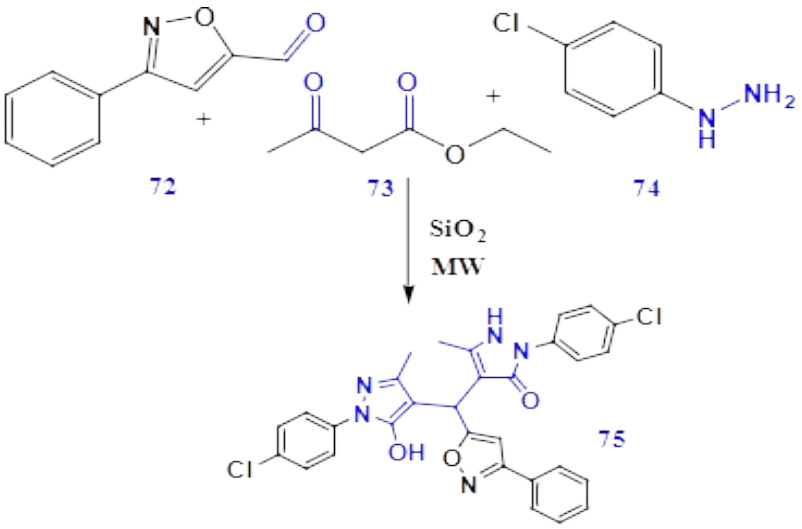
The Friedel-Crafts acylation of arenes containing electron-donating substituents employing aromatic carboxylic acids **70** as the acylating agents under microwave irradiation is shown to be boosted by the use of erbium trifluoromethane sulfonate as a catalyst. A variety of aryl ketones **71** can be prepared using an efficient, quick, and waste-free technique in good yields and with quick reaction times (90) (Scheme 23).



R_1 = Me, MeO, MeS, 1,2-di MeO, 1,3-di MeO, 1,4-di MeO
R_2 = H, 4-MeO, 2-MeO, 2-Cl, 2-F, 2-Br

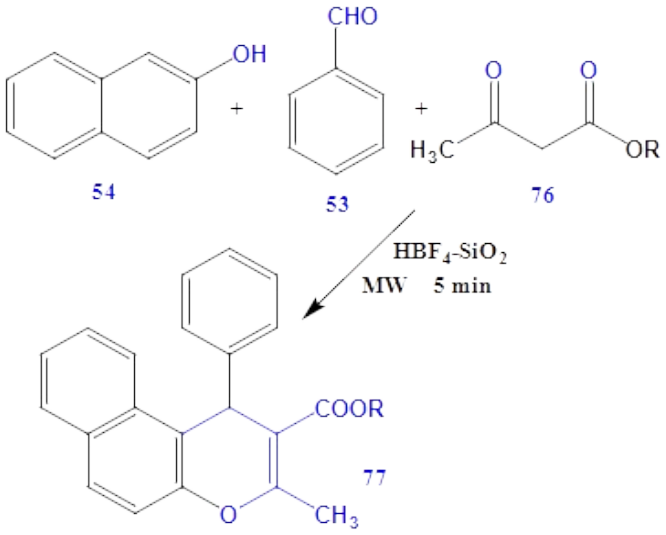
Scheme 23

Under microwave irradiation and solvent-free conditions, pyrazol-3(2*H*)-one derivatives **75** were produced from 3-phenylisoxazole-5-carbaldehyde **72**, ethyl acetoacetate **73**, and (4-chlorophenyl) hydrazine **74**. Silicon oxide was discovered to have excellent catalytic activity and dispersancy for the condensation reaction. Environmentally friendly reaction conditions, straightforward operation, a wide substrate, satisfactory yields, and the ability to reuse silica are some of this method's benefits.(91) (Scheme 24).



Scheme 24

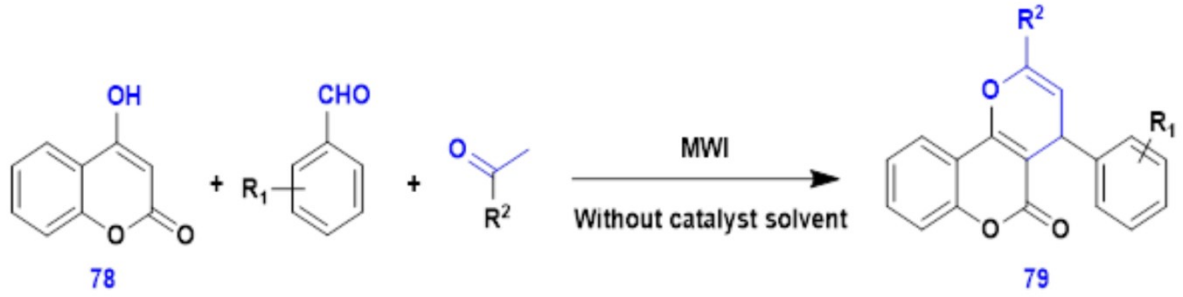
Using fluoroboric acid supported on silica under solvent-free conditions in a microwave reactor, a number of naphthopyrans **77** were synthesized. To improve the reaction conditions, the catalytic influence of HBF_4-SiO_2 was thoroughly explored (92) (Scheme 25).



R = C_2H_5

Scheme 25

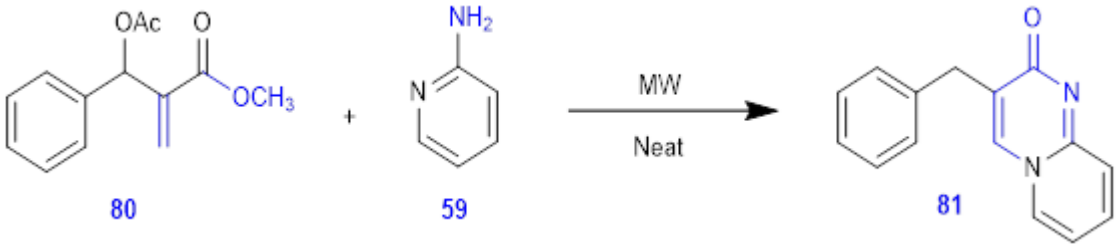
Using a one-pot, three-component reaction that involves acetophenones, 4-hydroxy-2*H*-chromen-2-one **78**, and aldehydes under microwave irradiation, to produce pyrano[3,2-c] chromen-5(4*H*)-ones **79** quickly and effectively. The current process has a number of benefits, including quick reaction times, straightforward operational procedures, avoiding hazardous solvents and catalysts, excellent product yields, and endurance of substrate diversity (93) (Scheme 26).



R_1 = 4-NO_2, 4-Cl, H
R_2 = 4-Me-C_6H_4, 4-MeO-C_6H_4, 2-Br-C_6H_4

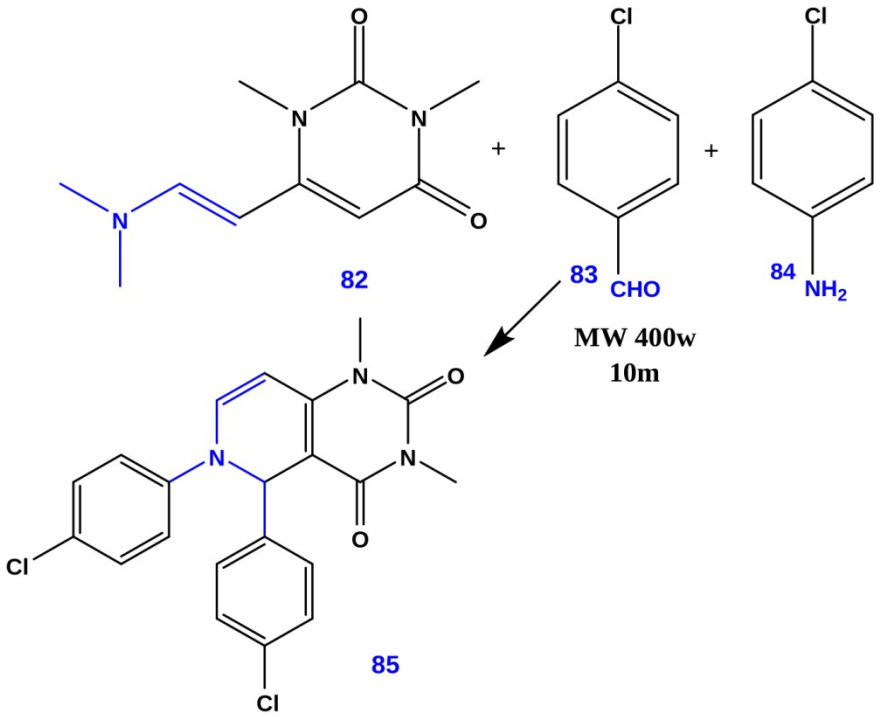
Scheme 26

For the rapid synthesis of pyrimidine derivatives, microwave-induced cyclocondensation of methyl 2-(acetoxy(phenyl) methyl) acrylate **80** with 2-aminopyridine **59** has been accomplished. excellent yields of pyrimidin-2-one **81** with high selectivity and rapid reaction times (94) (Scheme 27).



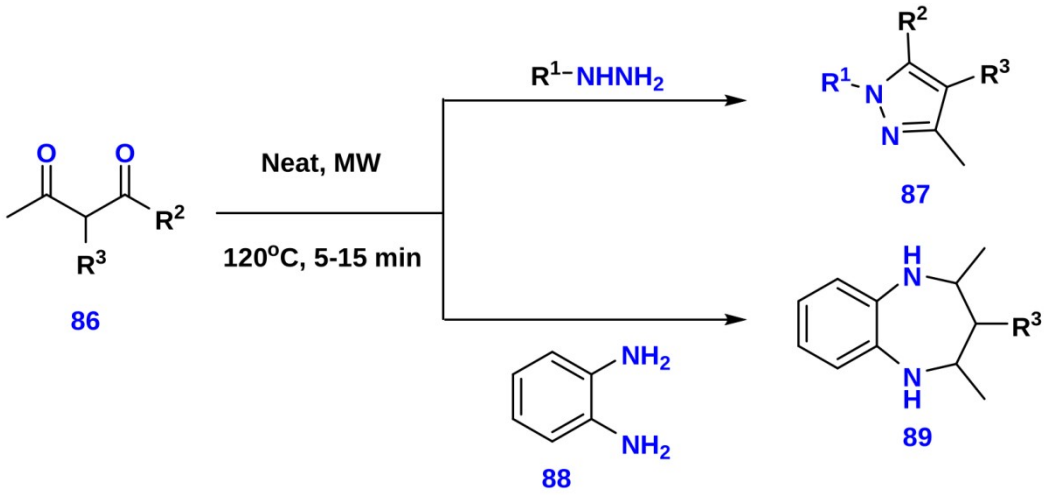
Scheme 27

Aza-Diels-Alder synthesis without a catalyst or solvent is reported. 1,3-dimethyluracil derivatives **82** combine with aldehyde and amine to quickly and efficiently produce dihydropyrido[4,3-d] pyrimidine derivatives **85** (95) (Scheme 28).



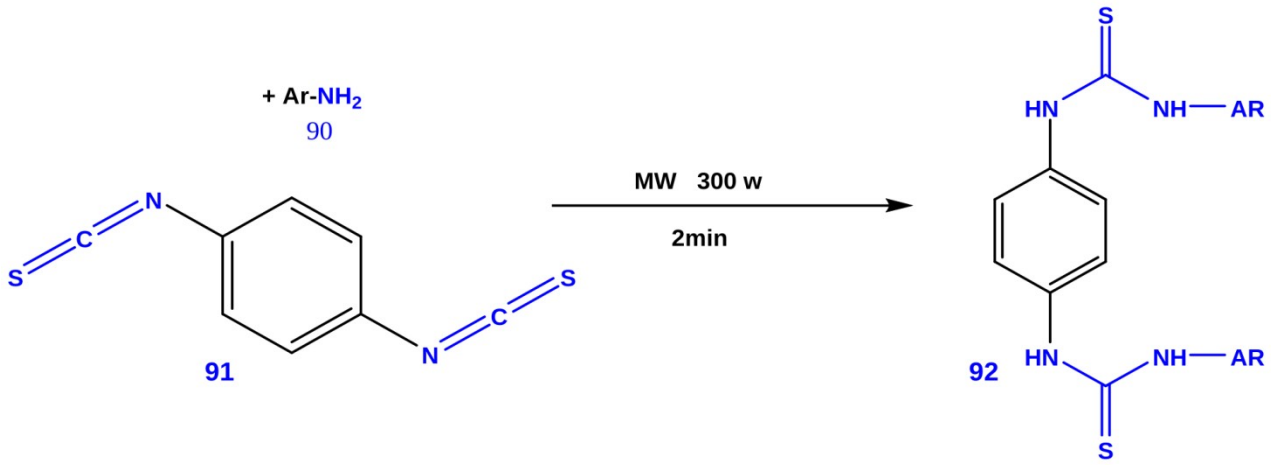
Scheme 28

Under microwave irradiation, hydrazines/hydrazides and diamines **88** can be quickly and easily combined with diketone **86** to produce pyrazoles and diazepines **87 ,89** in high yields without the use of a catalyst or reaction solvent (96) (Scheme 29).



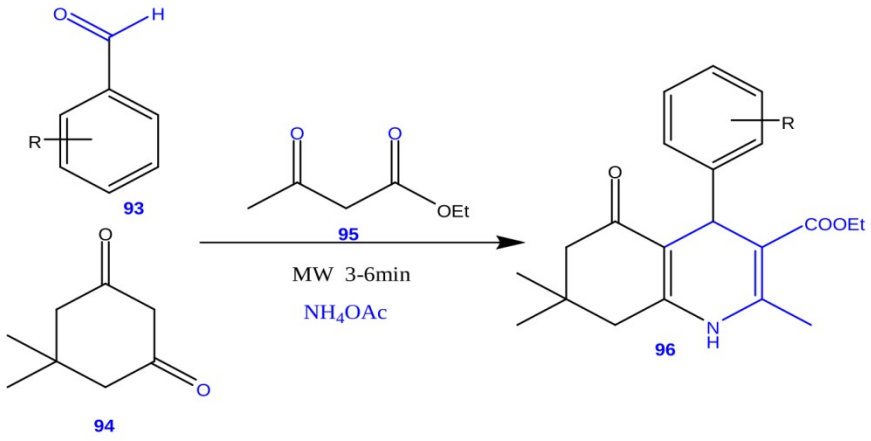
Scheme 29

1, 4-phenylenedithioureas **92** was prepared in solvent-free and catalyst-free conditions using microwave at 60 °C which exhibited the positive effect of microwave on yield and reaction time when compared to the traditional method (97) (Scheme 30).



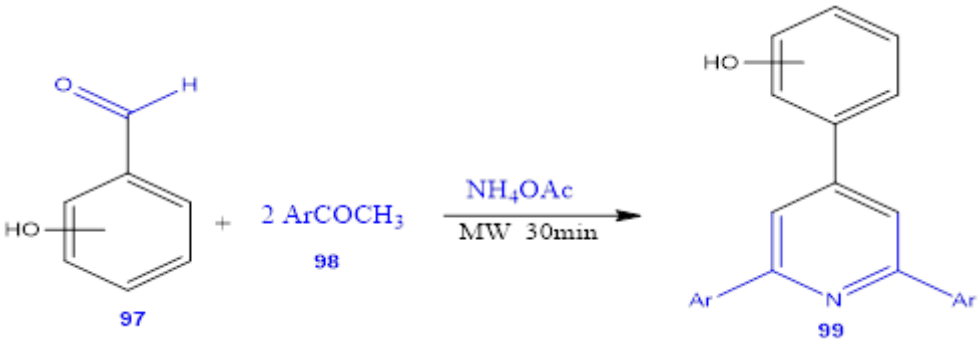
Scheme 30

When various aromatic aldehydes **93** were coupled with dimedone **94**, ethyl acetoacetate **95**, and ammonium acetate in the absence of a catalyst, under solvent-free, and microwave irradiation conditions, high yields of polyhydroquinolines **96** were produced (98) (Scheme 31).



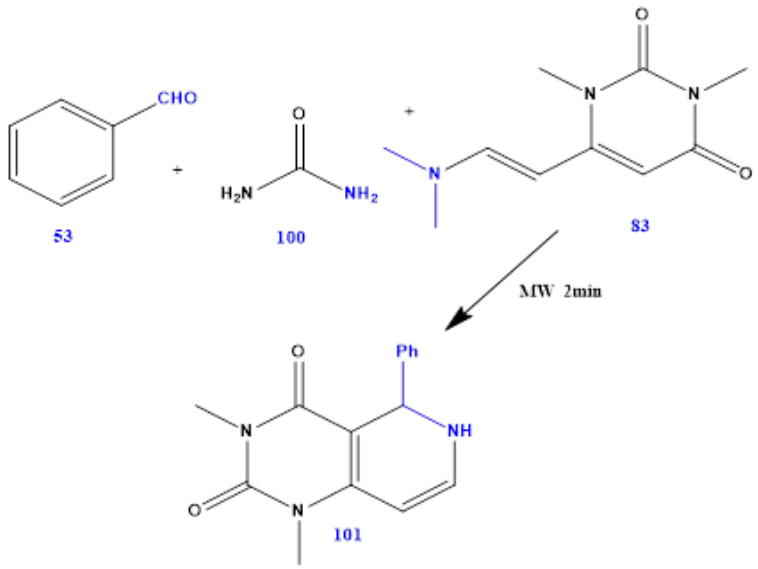
Scheme 31

Yin et al. studied the synthesis of a sequence of novel hydroxylated 2, 4, 6-trisubstituted pyridines using MW irradiation (99). Under ideal reaction conditions, 4-hydroxybenzaldehyde **97** and acetophenone **98** with ammonium acetate can be combined to form 4-(2, 6-Diphenylpyridin-4-yl) phenol **99** and its derivatives. in one pot**.** (Scheme 32).



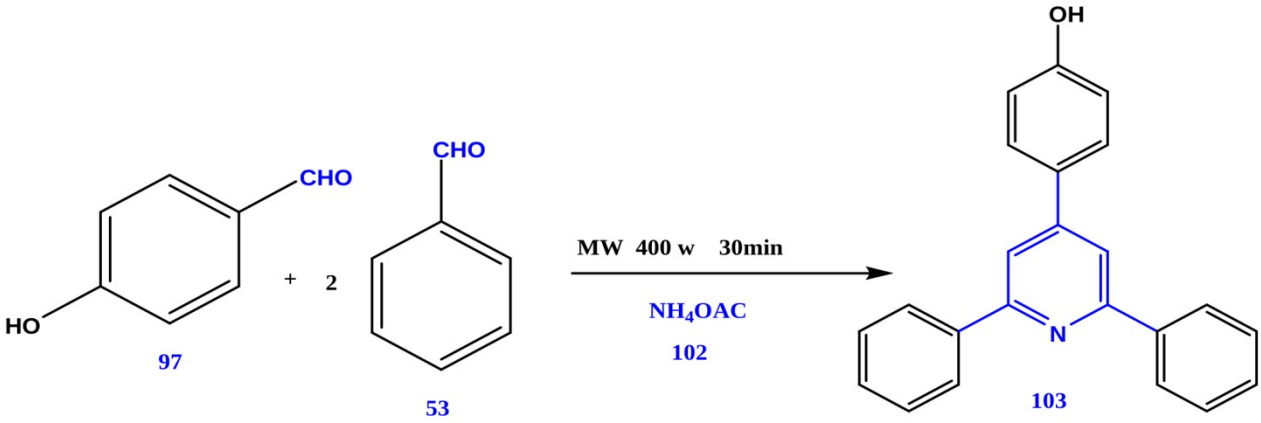
Scheme 32

Prajapati et al. developed the aza-Diels-Alder reaction under microwave irradiation by heating aldimines with 1,3-dimethyluracil **83** derivatives to produce pyrimidines **101** derivatives (100) (Scheme 33).



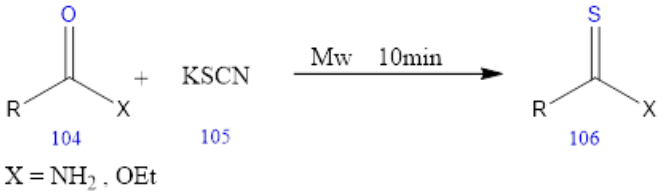
Scheme 33

Through a simple three-component condensation of 4-hydroxybenzaldehyde **97**, aldehyde **53**, and NH_4OAc **102**, a number of novel hydroxylated 2, 4, and 6-trisubstituted pyridines **103** were easily synthesized in high yield (83%) under MW irradiation (Scheme). Yin and his coworkers reported this work. (99) (Scheme 34).



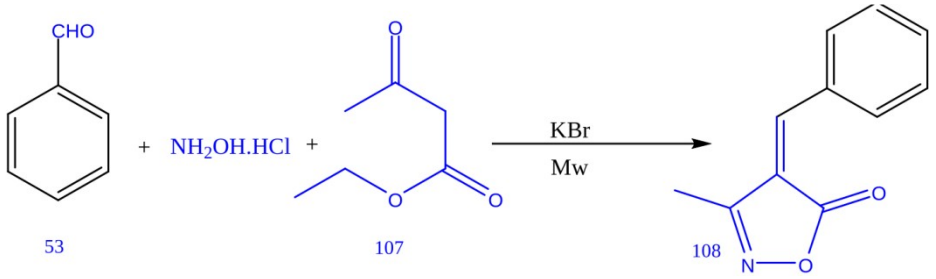
Scheme 34

Synthesis of a thioamides and thioester **106** under MW irradiation by reaction of esters and amides **104** with potassium thiocyanate **105** with yields in the range of 85-93% (101) (Scheme 35).



Scheme 35

3,4-disubstituted isoxazole **108** synthesis in a single pot with microwave irradiation in the presence of different catalysts such as potassium bromide (102,103) (Scheme 36).



Scheme 36

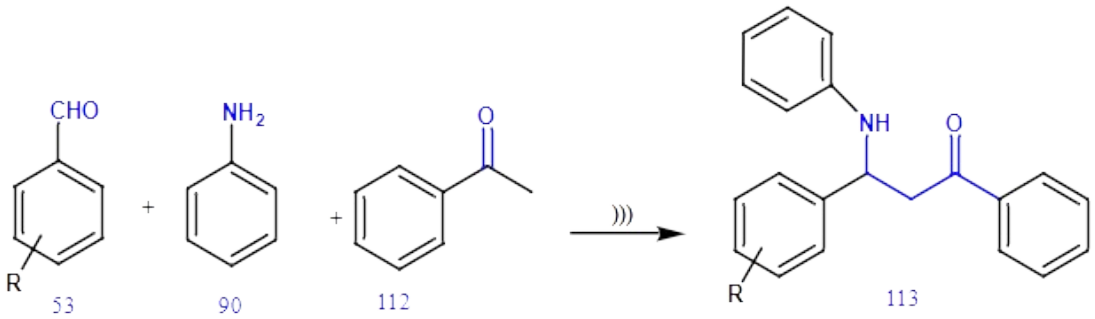
3.3. Solventless Organic Reactions under Ultrasonic Waves

Recent years have seen a lot of interest in the use of ultrasound in organic synthesis, which affects a number of organic reactions (104–109). It has been noted that ultrasonic lowers the reaction temperature, allowing for faster reaction speeds in ambient settings. This section discusses some of the most recent advances in ultrasound-based organic synthesis. There have been a lot of literary reviews recently that have discussed this method and its significance. Many literary reviews shed light on this technique and its importance in recent times (110–112).

As an easy, effective, and environmentally friendly technique toward N-alkylated amines **111**, ultrasound-assisted solventless oxidation/reductive amination of benzyl halides **109** was developed. (113) (Scheme 37).

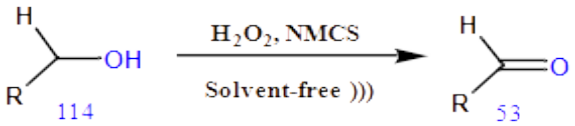
Scheme 37

Using an environmentally friendly ultrasonic process, a highly productive and active CuO nanoparticle decorated with phosphate functionalized graphene oxide (PGOCuO) nanocomposite was used as a catalyst in the Mannich reaction to synthesize β-amino carbonyl compounds **113** (114) (Scheme 38).



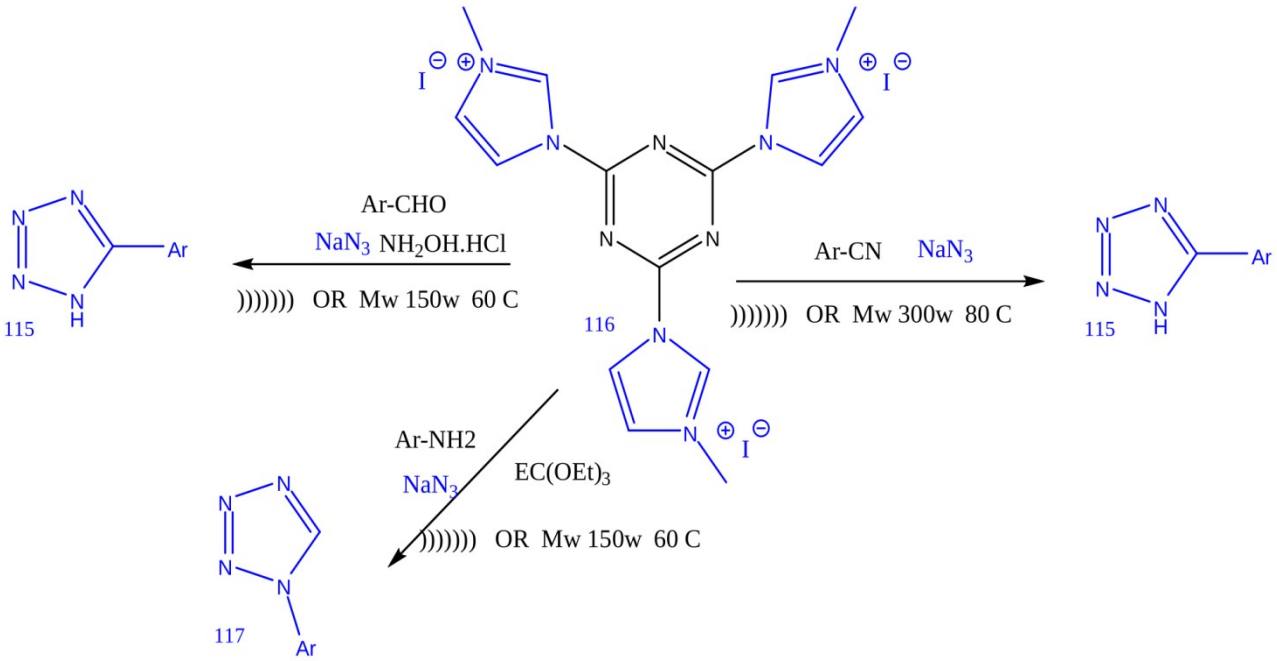
Scheme 38

MoO_3/Cu Schiff base complex nanocomposite (NMCS) was used to catalyze an atom-efficient and selective oxidation of alcohols **114** utilizing hydrogen peroxide under ultrasonic irradiation. Under solvent-free conditions, a structurally different set of alcohols was converted into the required aldehyde **53** and ketone products with high conversion and excellent selectivity. (115)(Scheme 39).



Scheme 39

Abdelkarim et al. used both microwave and ultrasonic techniques to synthesis 1 and 5 substituted-tetrazoles **116** under solvent free conditions (116) (Scheme 40).

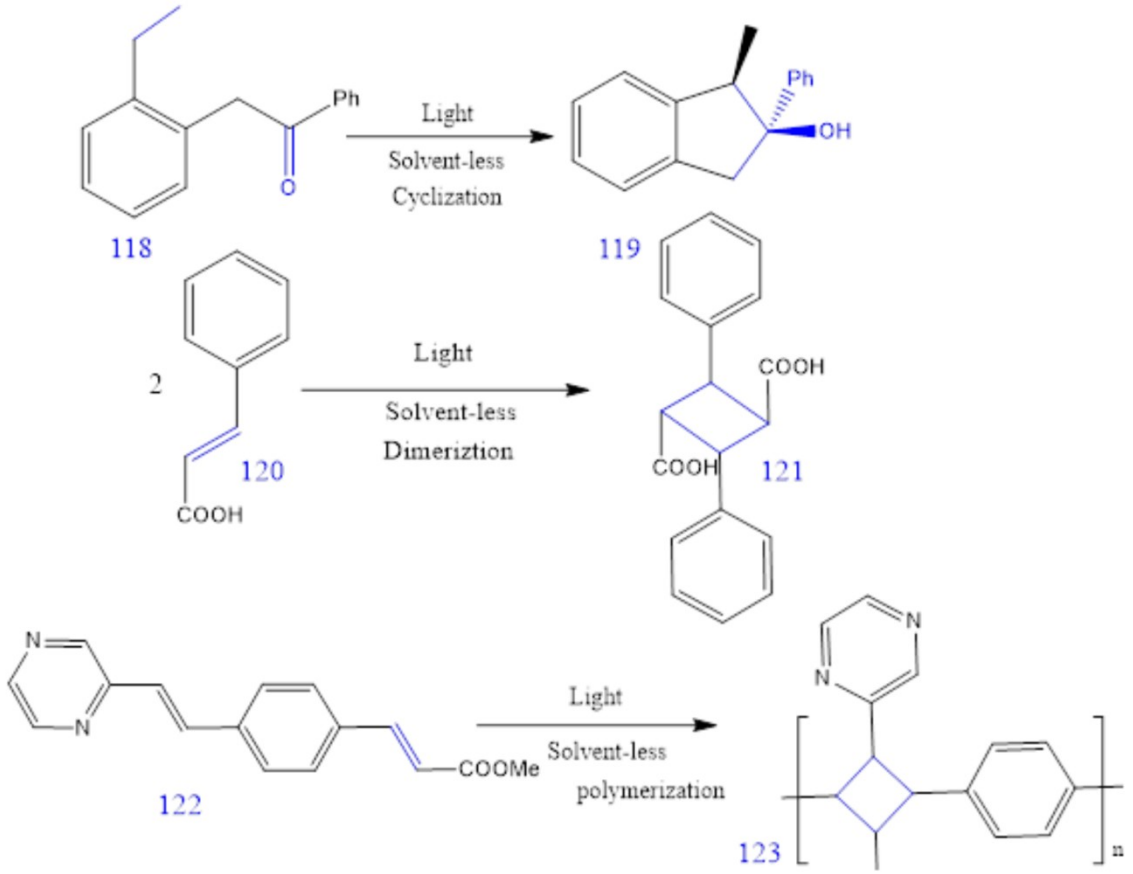


Scheme 40

3.4**Solventless Photochemical Organic Reactions**

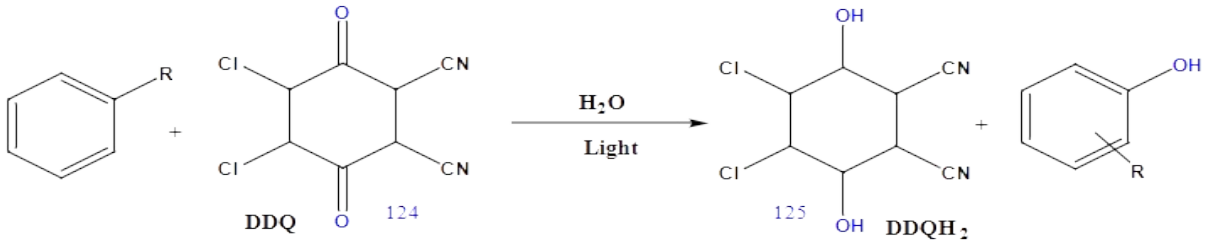
Furthermore, numerous photochemical procedures have been carried out without the need for solvents. Currently, typical synthetic chemists who are interested in creating compounds with considerable biological or catalytic activity are less interested in these processes. However, it is anticipated that the significance of photochemical processes will increase over the next few decades, particularly if sunlight can be exploited to speed up the process. In addition, several processes that are straightforward in a photochemical pathway cannot be carried out thermally (117–121).

Many reactions can be carried out with only light and without the need for solvents, such as polymerization, dimerization, and cyclization reactions (117) (Scheme 41).



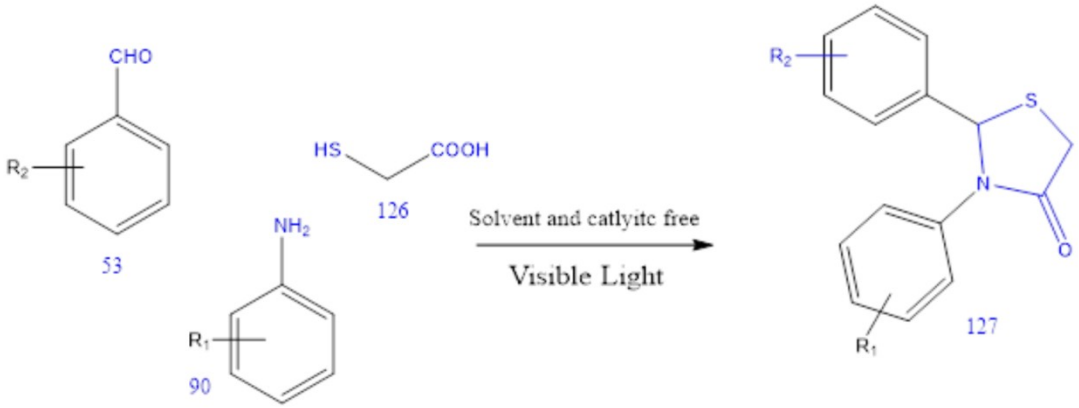
Scheme 41

Kei Ohkubo et al. (122) converted hydroquinone **124** function groups into di-hydroxide phenols **125** by xenon lamp in visible light (λ > 390 nm) with 99% conversion yield under solvent-free conditions (Scheme 42).



Scheme 42

Nazeef et al. (123) have developed a single pot, solvent-free photochemical reaction of aldehyde **53** and amine **90** in the presence of thioglycolic acid **126** to create thiazolidin-4-ones **127** ring without the use of a catalyst (Scheme 43).



Scheme 43

4. CONCLUSIONS

The main goal of green chemistry is to reach materials and products without polluting the environment or human health. Therefore, the approach of not using solvents in chemistry reactions has become the first priority in all industries and products. This approach saves time and safety in addition to reducing costs and pollutants. The techniques used start with the use of alternative organic solvents that do not harm the environment and technologies that require energy, such as microwave assisted synthesis and ultrasound assisted synthesis, in addition to directly using natural renewable energy, such as solventless photochemical organic reactions. From our review information, we find that there are many researchers who have focused their work on microwave reactions because of their high and fast effectiveness and the availability of the required devices, but there is some shortcoming in the trend towards ultrasound interactions, and this may be due to the lack of ultrasound devices or difficulty of application at a larger scale in industries.

5. CONFLICT OF INTEREST

No potential conflict of interest was reported by the authors.

6. ACKNOWLEDGMENTS

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