



Natural food additives as green catalysts in organic synthesis: a review

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Abstract

Catalysis is a pillar of green chemistry. Though there are many efficient catalysts reported, industrial engineers are now faced with the challenge of designing environmentally benign catalysts, which have a high reaction rate, can be recovered efficiently, and are biodegradable and cost-effective. Here we review food additives as catalysts in organic syntheses. Natural food additives offer a fruitful approach in implementing green chemistry, resulting in comparable reaction yields to conventional catalysts. We present the advantages of organic reactions performed using these green and efficient catalysts. In addition, reactions' yields are compared to various synthetic methods. Finally, we discuss the turn-over number, turn-over frequency and reaction mechanisms of selected organic reactions mediated by these catalysts.

Keywords Green chemistry · Food additives · Benign catalysts · Green synthesis · Organic synthesis

Abbreviations

H	Hydrogen
H ₂ O	Water
HOAc	Acetic acid
Me	Methyl
MeO	Methoxy
CN	Cyano
NO ₂	Nitro
NH ₂	Amino
NH ₄ OAc	Ammonium acetate
Cat-	Cation
H ⁺	Hydrogen ion
Ar	Aromatic
Ph	Phenyl
OH	Hydroxy
N	Nitrogen
Br	Bromine

Cl	Chlorine
F	Fluoro
NH ₃	Ammonia

List of symbols

g	Gram
mg	Milligram
mL	Milliliter
%	Percent
°C	Degree Celsius
h	Hour
h ⁻¹	Catalyst per unit time
r.t	Room temperature
mol%	Mole Percent
Fig.	Figure
o-	Ortho-
m-	Meta-
p-	Para-
β	Beta
α	Alpha
γ	Gamma
mins	Minutes
mol	Mole
mmol	Millimole

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Introduction

The chemical industry has utilized a majority of metals within the periodic table for chemical processes, such as in the manufacturing of chemicals, advanced materials, health care products, fuels and so on. As a society, we currently rely heavily on the use of metals and the intensive mining of these elements could cause environment burden, especially for end-of-life consumer products and industrial processes (Hunt et al. 2015). Inevitably, metals are being depleted, which will create a resource deficit in the future. Considering the environmental, societal and economic effects of intense metal mining on our earth, we need a dramatic change in our chemical processing methods to ensure a more sustainable chemical processes.

Due to the increasing environmental consciousness and more stringent regulations faced by the chemical and pharmaceutical industries, innovation of environmentally benign chemical processes has emerged as an important and demanding field in the modern era of organic synthesis research (Centi and Perathoner 2003; Lavilla et al. 2014). As such, increasing efforts have been devoted in the development of green synthetic endeavours that encompass the use of environmentally friendly reagents, solvents, and catalysts in performing organic processes. In recent years, chemists are faced with the challenge of developing environmentally benign catalysts, whose uses are in favor to maintain a sustainable environment. In fact, designing and developing sustainable catalysts are part of the fundamental aspect of green chemistry, resulting in cleaner, cheaper, and less energy used (Hutchings 2007; Khodabakhshi and Baghernejad 2013; Yu et al. 2020). Hence, cleaner and safer organic processes that emphasize the use of environmentally acceptable catalytic systems, that offer environmental and economic advantages over conventional organic processes are needed by the academia and industrial communities (Chen et al. 2020; Díaz-Sánchez et al. 2019; Kumar et al. 2019; Nongrum et al. 2019; Onuegbu et al. 2011; Paprocki et al. 2019; Peixoto et al. 2020).

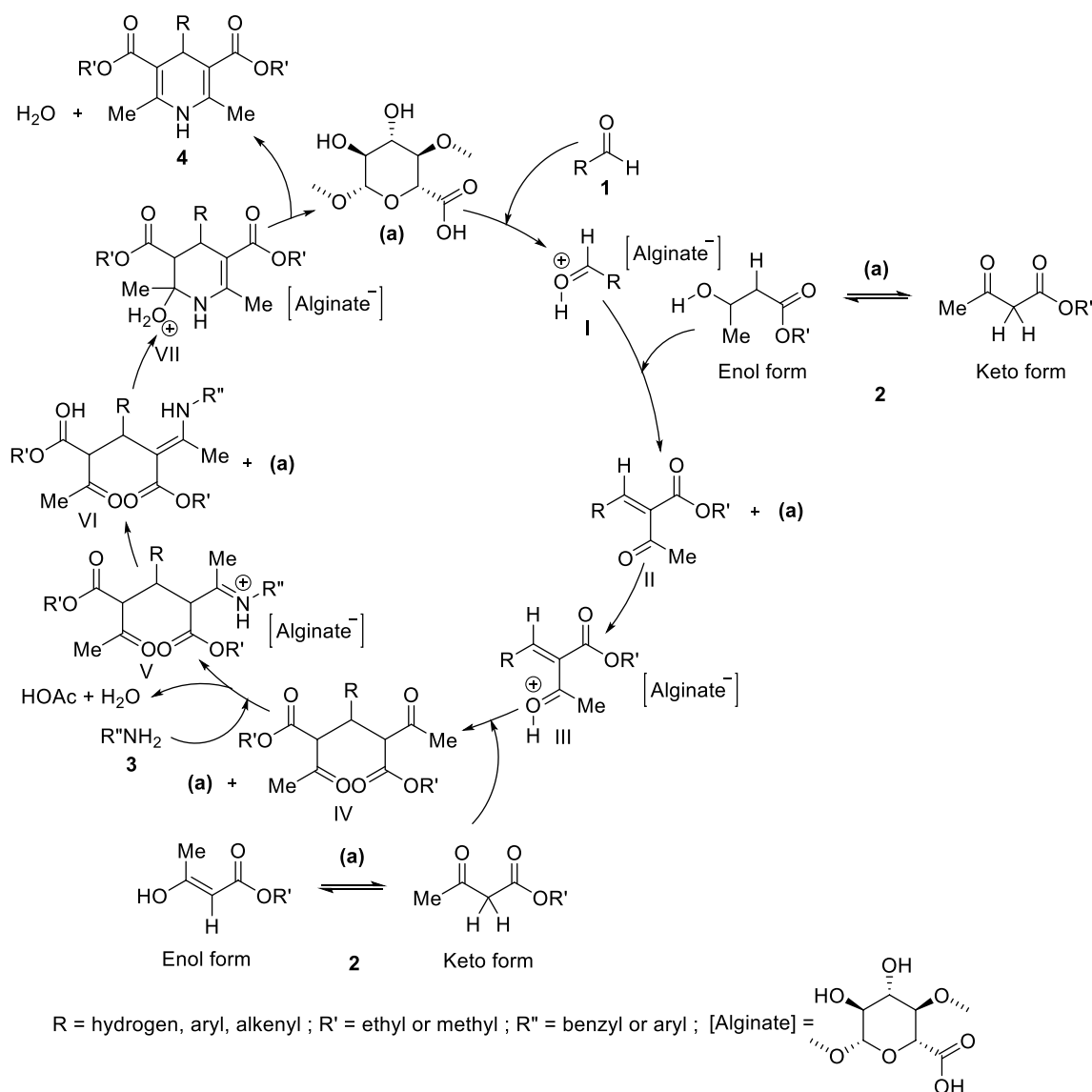
Food additives are chemical substances that are used to enhance the quality and safety of food. The use of food additives such as alginic acid (Dekamin et al. 2014), boric acid (Rezayati et al. 2014), tartaric acid (Gratzer et al. 2013), citric acid (Reddy et al. 2018), pectin (Pazhavelikkakath Purushothaman et al. 2018), oxalic acid (Dabiri et al. 2007) and saccharin (Banerjee et al. 2019) in achieving green organic reactions has gained much attention in recent years among researchers. These food additives represent a unique class of catalysts which are green, natural origin, low-cost, commercially available, biodegradable and at the same time have a large application in organic reactions. Though there have been many efficient catalysts

being reported, industrial engineers are still faced with the challenge of designing environmentally benign catalysts, which possess a higher reaction rate, efficient recovery of catalysts from the medium, biodegradable, and cost-effectiveness of the catalysts used. Hence, the use of environmentally benign and cost-effective catalysts is highly desirable. Herein, the literature of using food additives as unconventional green catalysts in organic synthesis was surveyed using multiple search terms and keywords to identify the relevant catalysts and their advantages in comparison with classical catalysts, in the development of green and eco-efficient chemical processes, are reviewed here.

Alginic acid

Alginic acid which is also known as an algin or alginate is an ionic polysaccharide that is commonly extracted from the cell walls of brown algae (Kariduraganavar et al. 2014). It can create a viscous gum when dissolves in water due to its capability of absorbing water easily till 200–300 times of its own weight and also soluble in water-miscible solvents such as ketones and alcohols. Besides, alginic acid has a very high demand in the food industry as it is commonly used as a thickener, emulsifiers, and also stabilizers (Kariduraganavar et al. 2014; Titlyanov et al. 2017). Dekamin et al. (2014) reported a highly efficient Hantzsch reaction using alginic acid (**a**) as a green bio-polymeric catalyst in 1,4-dihydropyridines **4** syntheses (Scheme 1). 1,4-dihydropyridines widely occur in nature, and drug molecules play an essential role in bioactivities and pharmaceutical activities (Wu et al. 2021). This environmentally friendly protocol provided the targeted compounds in high to excellent reaction yields (68–98%) via a Knoevenagel intermediate followed by Michael addition reaction. Overall, this reaction provides a mild and metal-free alternative to previous methods, as no solvents and metal-catalysts were used as well as a faster reaction rate was reported.

On top of that, the same authors also developed a synthesis protocol of polyhydroquinolines **9** via the Hantzsch reaction, which was mediated by alginic acid (Dekamin et al. 2018). The synthesis of polyhydroquinolines commenced with a four-component condensation of ethyl acetoacetate **5**, aldehyde **6**, ammonium acetate **7**, and cyclic diones **8**, catalyzed by alginic acid (**a**) under mild reaction conditions as shown in Scheme 2. The synthesis provided the targeted compounds in high to excellent yields (75–97%) through a Knoevenagel intermediate followed by Michael addition. The increase in the rate of reactions in polyhydroquinolines' syntheses was attributed to the charged-dipole interaction of alginic acid with reactants' intermediates. This has led to a high turnover number (9.5) and turnover frequency (22.8 h⁻¹) compared to previous studies. The result indicated



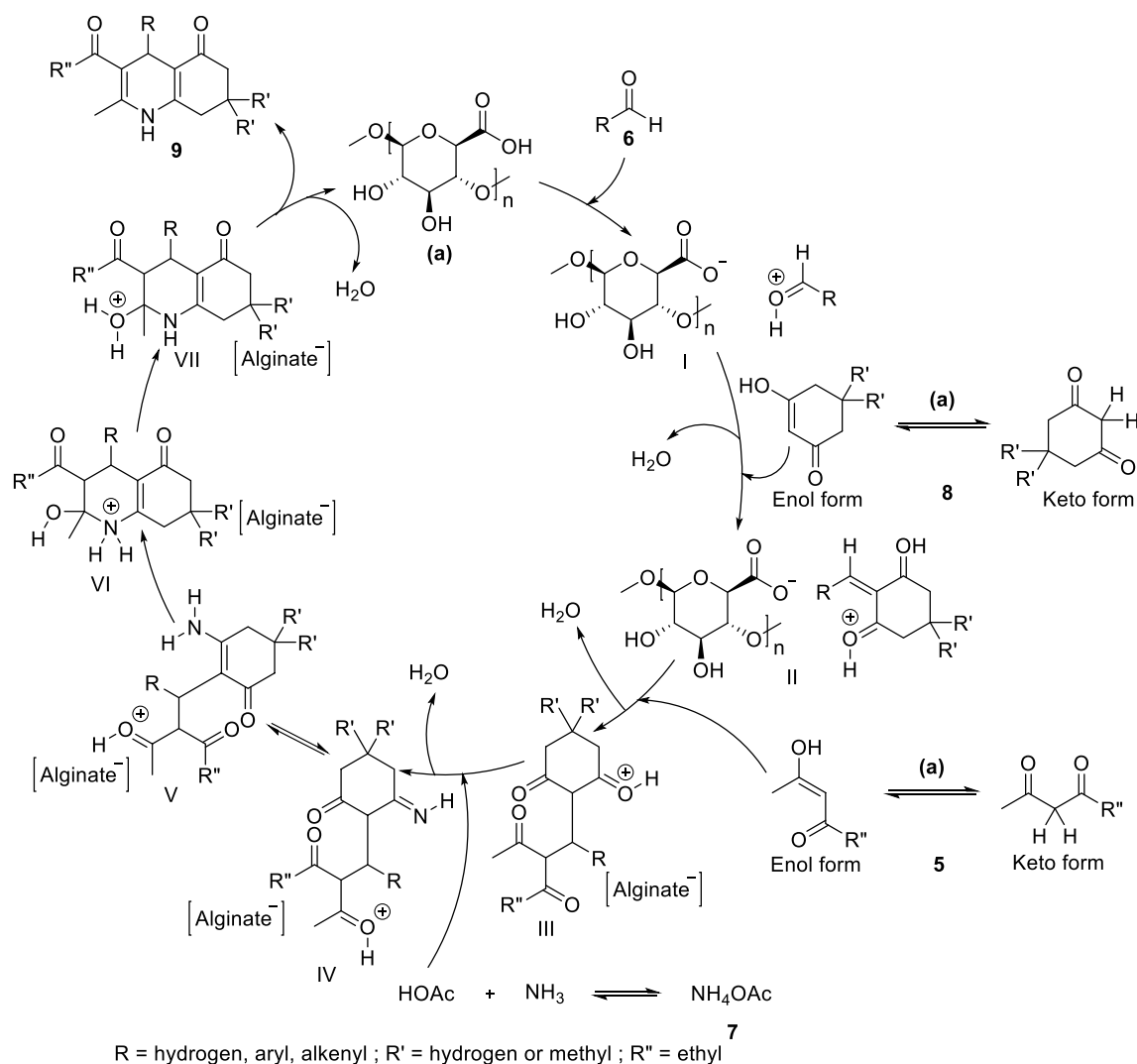
Scheme 1 Plausible mechanism of 1,4-dihydropyridines synthesis. *Notes:* Me (methyl), HOAc (acetic acid), H₂O (water), NH₂ (nitrogen source)

that alginic acid catalyst might meet the goal of green chemistry, which provides a more environmentally friendly and biodegradable method for organic catalysis (Hajizadeh and Maleki 2018; Maleki 2014, 2016, 2018; Maleki et al. 2016).

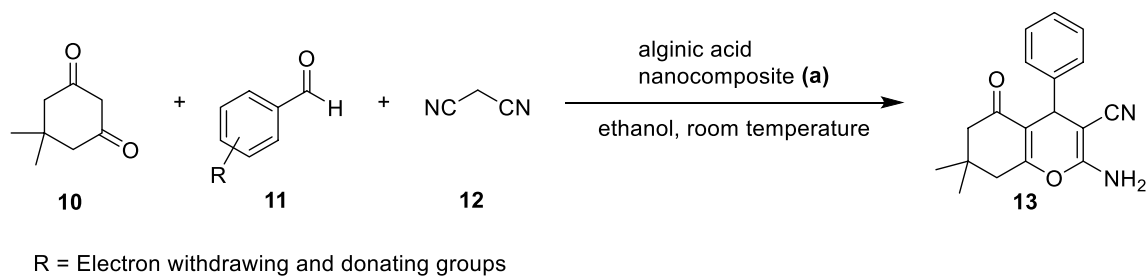
On the other hand, alginic acid (**a**) was also employed as a green catalyst in a study demonstrated by Maleki et al. (2019b), who reported the efficient and green synthesis of 2-amino-3-cyano-4H-pyran derivatives **13** as shown in Scheme 3, in which aldehydes **11**, 5,5-dimethyl-1,3-cyclohexanedione **10**, and malononitrile **12** were reacted in one-pot reaction in the presence of alginic acid nanocomposite (**a**). It was reported that the current synthesis has led to higher reaction yields (83–95%). Previously, the identical reaction suffered from long reaction times, difficult workup, and mediocre yields. Ironically, this protocol offers a mild

reaction condition, green and cost-effective nano-catalyst, shorter reaction time, easy workup with a simple procedure, and the catalyst was recoverable after five consecutive runs. In addition, the author also reported that the efficiency of the alginic acid nanocomposite, outperformed the single catalysts (alginic acid and zinc ferrite), though both can catalyze the reaction individually. The higher catalytic effect of alginic acid nanocomposite compared to individual catalyst was due to the synergy effect demonstrated by the nanocomposite employed in the protocol.

The same approach was employed by Srivastava et al. (2015) using alginic acid (**a**) as a green catalyst in catalysing reaction between indoles **15** and isoquinoline-1,3,4-triones **14** to form the hydroxyindolyl derivatives **17** as depicted in Scheme 4. Satisfactory reaction yields were



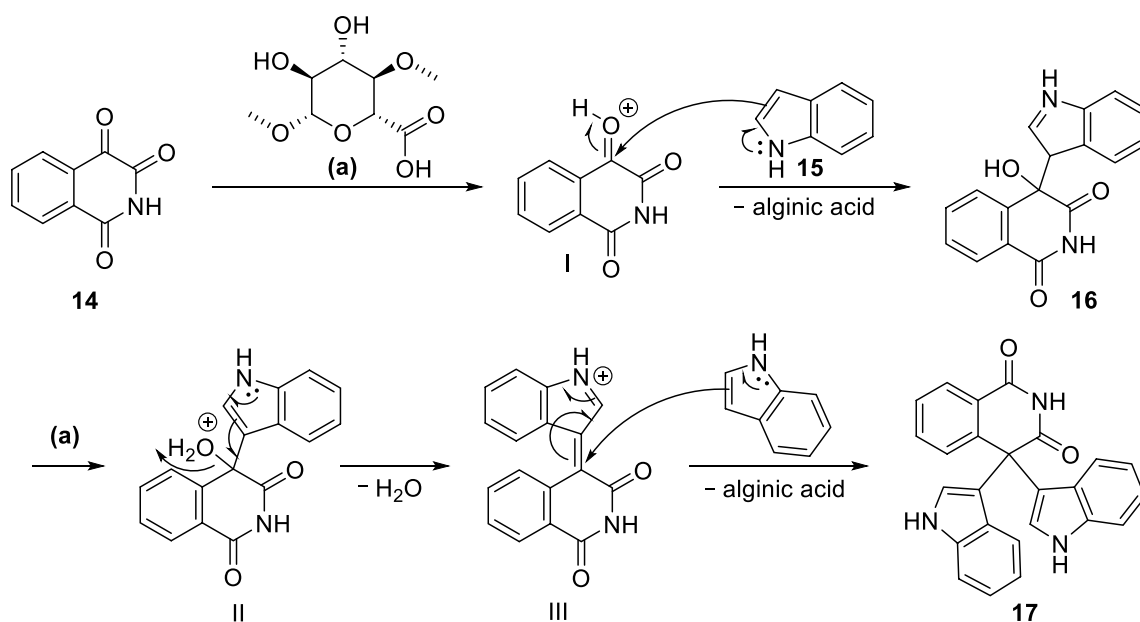
Scheme 2 Alginic acid-mediated polyhydroquinolines syntheses via multi-component Hantzsch reaction. *Notes:* NH_4OAc (ammonium acetate), NH_3 (ammonia), HOAc (acetic acid), H_2O (water)



Scheme 3 Synthesis of derivatives of 2-amino-3-cyano-4H-pyran. Reaction condition: dimedone (1.0 mmol), aldehyde (1.0 mmol), malononitrile (1.0 mmol), and catalyst (alginic acid nanocomposite, 5 mg) in ethanol (2 mL) at room temperature

recorded (57–82%) when the reactions were performed at 65 °C. In the past, the synthesis of hydroxyindolyl derivatives **17** employed metal-salt catalysts, harmful and

non-bio-degradable reagents. These methods are unfavorable due to the use of non-bio-degradable catalysts that can cause harm to the environment.



Scheme 4 Alginic acid-mediated isoquinoline-1,3,4-trione syntheses in water via Friedel–Crafts reaction of indoles. *Notes:* H₂O (water)

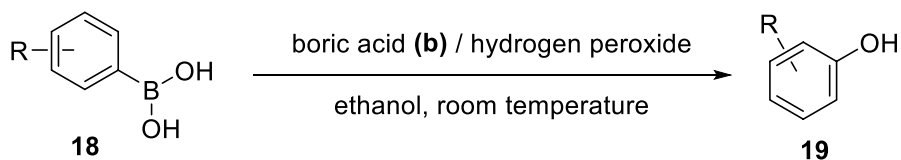


Fig. 1 Boric acid appears in white crystalline solid at room temperature

Boric acid

Boric acid (Fig. 1) is a food preservative employed in preserving the shelf life of meat products (Arslan et al. 2008). It is also used in starch gelatinization purposes and flavour enhancement (Yiu et al. 2008). Recently, boric acid is highly sought after in organic synthesis due to the eco-friendly, stability, excellent solubility in water, and inexpensive nature of this chemical substance. Gogoi et al. (2014) described a good example of boric acid (b) catalyzed *ipso*-hydroxylation process that employed hydrogen peroxide as an oxidant (Scheme 5), with turnover number (8.8) and turnover frequency (15.1 h⁻¹) reported for the optimized reaction condition. In this work, aryl boronic acids were all converted into the desired product 19 (80–95% yield) via oxidation reaction. The use of a greener approach such as the one described here is desired as it is metal-free, base-free, and the reaction can be carried out under room temperature conditions to prepare the corresponding phenols.

Scheme 5 The Synthesis of phenol. Reaction condition: aryl boronic acid (0.5 mmol), boric acid (0.1 mmol), hydrogen peroxide (2 mL) in ethanol (2 mL) at room temperature



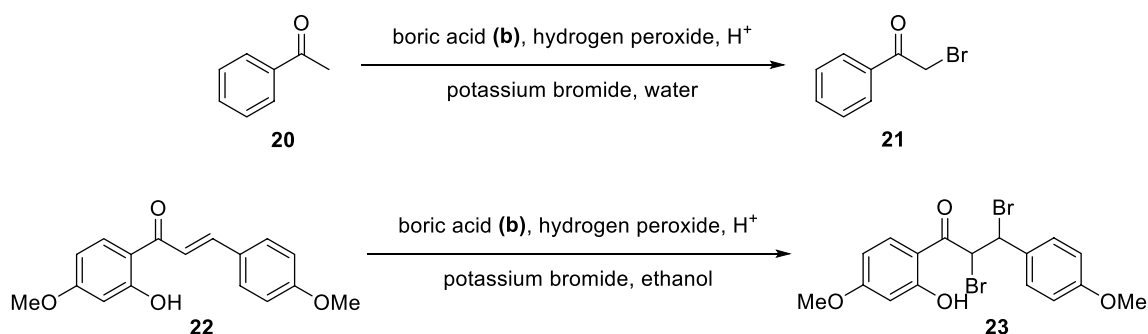
R = hydrogen, 3-methyl, 4-methyl, 2-methoxy, 4-cyano, 4-chloro, 4-nitro, 4-fluoro, aryl boronate esters, heteroaryl boronic acid

Apart from that, Nath and Chaudhuri (2008) have investigated a bromination protocol using boric acid as a green catalyst. The reaction was carried out involving potassium bromide as the bromide source and hydrogen peroxide as an oxidizing agent in the presence of boric acid (**b**) and ethanol as solvent (Scheme 6). This site-selective bromination of organic substrates has led to the high yields of desired products **21** and **23**. Based on the previous protocols for bromination of aryl compounds, most of these methods are unsustainable such as the use of corrosive and toxic reagents, which at times result in a large amount of waste production, leading to a 50% reduction of the atom efficiency (Vyas et al. 2003). However, the present work offers attractive advantages, such as cost-effective, eco-friendly, non-toxic, recyclable, safe to handle methods, and the reaction can be carried out effectively under mild conditions.

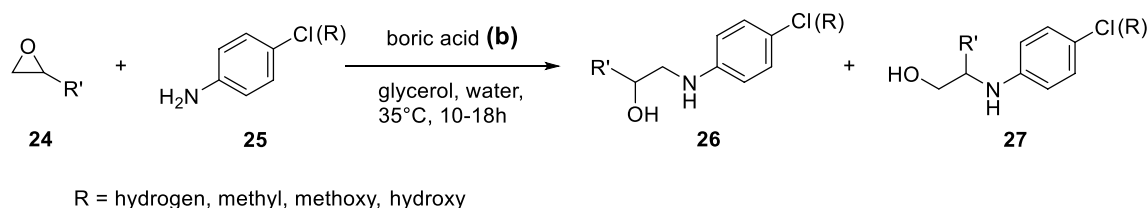
Furthermore, an efficient and regioselective ring-opening of epoxide reaction was also observed using boric acid as a catalyst (Halimehjani et al. 2012). Under this reaction, the 2,3-epoxypropyl ether **24** and aniline **25** were selected as model substrates and reacted in the presence of boric acid (**b**) (Scheme 7). In most cases, a satisfactory yield (93–100%) of derivatives **26** was obtained and various aromatic amines were tolerated under this protocol. Numerous efficient catalysts have been reported for a similar reaction. Yet, some drawbacks have been identified from those procedures such as the use of costly

catalysts, hazardous organic solvents, moisture-sensitive reactions, and so on. Alternatively, boric acid could act as a substitute due to its desirable characteristics such as inexpensive, water-soluble, easy to handle, commercially available, and environmentally friendly.

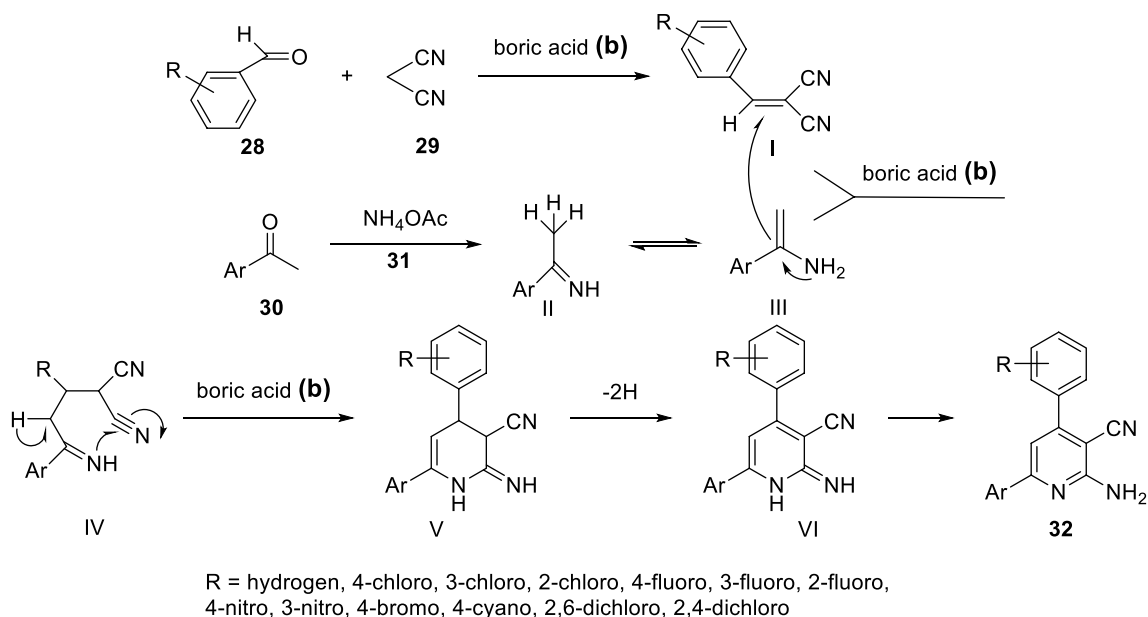
Another example was demonstrated by Hosseinzadeh et al. (2019), whom prepared the 2-amino-4,6-diarylnicotinonitriles **32** via a multicomponent reaction using boric acid (**b**) as a catalyst (Scheme 8). This environmentally benign protocol provided the targeted compounds in high yields (86–96%) via Knoevenagel condensation followed by air oxidation cyclization. Although various works of literature have been made on the synthetic protocol for 2-amino-4,6-diarylnicotinonitriles, these approaches suffered from the use of harsh reaction conditions, toxic solvents, with low reaction yields recorded. Consequently, the use of boric acid as a catalyst in the afore-mentioned reaction is superior to other protocols due to its excellent solubility in water, inexpensive catalyst, chemically stable and nontoxic nature, recyclable, and easy to handle. Besides, the current procedure takes place under a solvent-free condition which helps in pollution reduction, prevention of solvent waste, energy efficient, enhances the products yield and high atom economy. This is of scientific importance as no waste reactants were generated at the end of chemical processes (Maleki 2012, 2013; Maleki and Aghaei 2017; Maleki et al. 2018, 2019a).



Scheme 6 Production of bromoorganic compounds. Reaction condition: substrate (1.0 mmol), boric acid (0.05 mmol), hydrogen peroxide (3.0 mmol), potassium bromide (1.2 mmol) in water (2.5 mL) or ethanol (2.5 mL). Notes: H⁺ (hydrogen ion), OMe (methoxy)



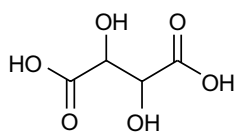
Scheme 7 Reaction of ring-opening of epoxides. Reaction condition: ring-opening of epoxides (2.5 mmol), aromatic amines (3.0 mmol), boric acid (0.3 mmol), glycerol (1–2 drops) in water (5 mL) within 10–18 h at 35 °C. Notes: h (hours), °C (degree Celsius)



Scheme 8 Tentative mechanism for the production of 2-amino-4,6-diarylnicotinonitrile. Reaction condition: aromatic aldehyde (1.0 mmol), malononitrile (1.5 mol), acetophenone (1.0 mmol),

ammonium acetate (NH_4OAc , 1.0 mmol), boric acid (1.0 mmol). Notes: Ar (Aromatic), H (hydrogen)

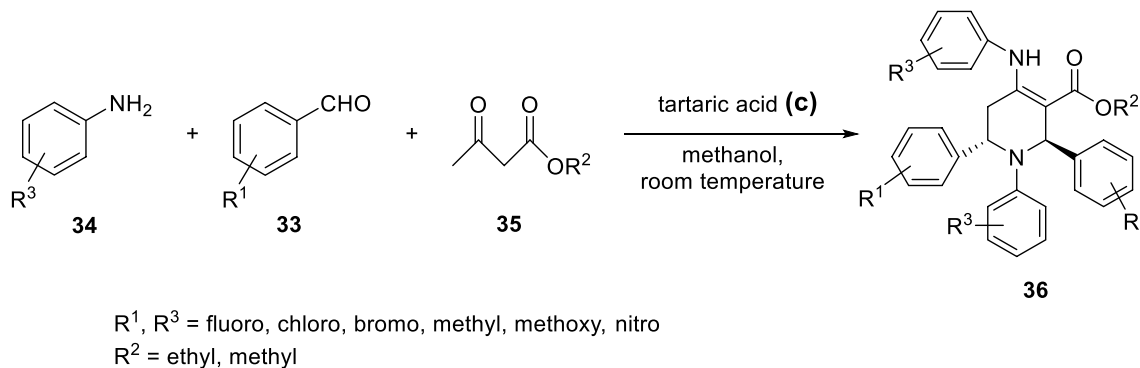
Fig. 2 Chemical structure of tartaric acid that is naturally found in grapes



Tartaric acid

Tartaric acid (Fig. 2) is one of the food additives that is added to enhance taste, acidity regulator, and also provide antioxidant properties in foods (Marchitan et al. 2010). Over the years, chemists have developed an eco-friendly method of organic reactions using tartaric acid

as a catalyst. According to the literature, tartaric acid was found to be an efficient catalyst in mediating the synthesis of piperidines **36** via a multi-component reaction (Aboonajmi et al. 2015). This reaction catalyzed by tartaric acid (**c**) involved aromatic aldehydes **33**, β -ketoesters **35**, and anilines **34** was carried out at room temperature (Scheme 9). Anilines as electron-donating groups reacted effectively with aldehydes to afford the piperidines in satisfactory yields (39–91%) via a domino process. Prior to that, the identical organic process suffered from low yields, the uses of toxic and expensive catalysts, and complicated workup procedures. Alternatively, this method offers more



Scheme 9 Synthesis of functionalized piperidines. Reaction condition: aromatic amine (2.0 mmol), aromatic aldehyde (2.0 mmol), and β -ketoester (1.0 mmol) with the presence of tartaric acid (0.075 g) in methanol (5 mL) at room temperature

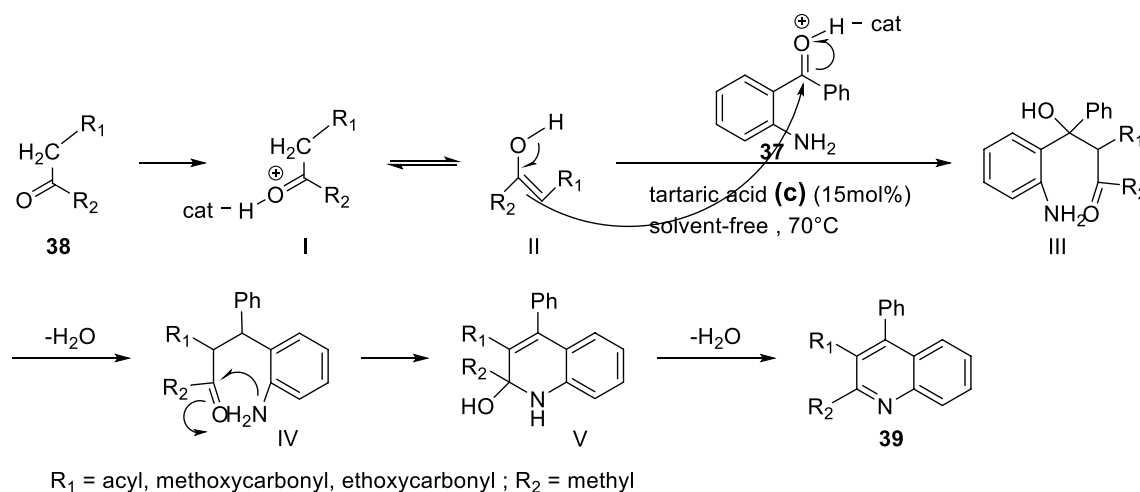
advantages which are simplicity in the workup procedure, cheap and the use of a biodegradable catalyst.

Likewise, a green synthesis using tartaric acid for the formation of poly-substituted quinolines **39** was reported lately (Mohamadpour et al. 2018). The reaction comprised of ketone **38** (1.0 mmol) and 2-aminobenzophenone **37** (1.0 mmol) in the presence of tartaric acid (**c**) as shown in Scheme 10 under neat condition. This one-pot four-component reaction gives excellent isolated yields (91–94%) via Friedländer condensation. Moreover, it has overcome some of the limitations encountered in previous protocols such as the uses of expensive and toxic catalysts, tedious workup procedure, the use of highly acidic conditions, prolonged reaction time, and low yields of isolated products. The current innovative method is scientifically significant, as it employed a non-toxic catalyst and column-free procedure. Furthermore, the poly-substituted quinoline synthesis mediated by tartaric acid was found to be in excellent reaction yield, which indicated that the current catalyst can act as a green alternative to other catalysts for the identical organic

reaction (Ahmad Ruslan et al. 2020). Previous methods in the synthesis of poly-substituted quinoline and their yields are summarized in Table 1.

In another work, tartaric acid was employed to synthesize the poly-substituted dihydropyrrrol-2-ones (Mohamadpour et al. 2016). Under the optimized reaction condition, formaldehyde **43**, dialkyl acetylenedicarboxylate **41**, and amines (aliphatic **40** or aromatic **42**) were reacted in the presence of tartaric acid (**c**) to afford the desired products **44** (Scheme 11) in excellent yields (74–93%), with 15 mol% of catalyst loading under ambient temperature. It is noteworthy that the previous methods involved the use of expensive and toxic catalysts, tedious work-up, prolonged reaction times, but resulted in low yields of products. In contrast, the current developed method is known to be environmentally benign, cost-effective, highly efficient, shorter reaction times, and led to high yields of products.

Tartaric acid (**c**) was also being employed as a catalyst in the green synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones **47**, which involved 2-aminobenzamide **46** and



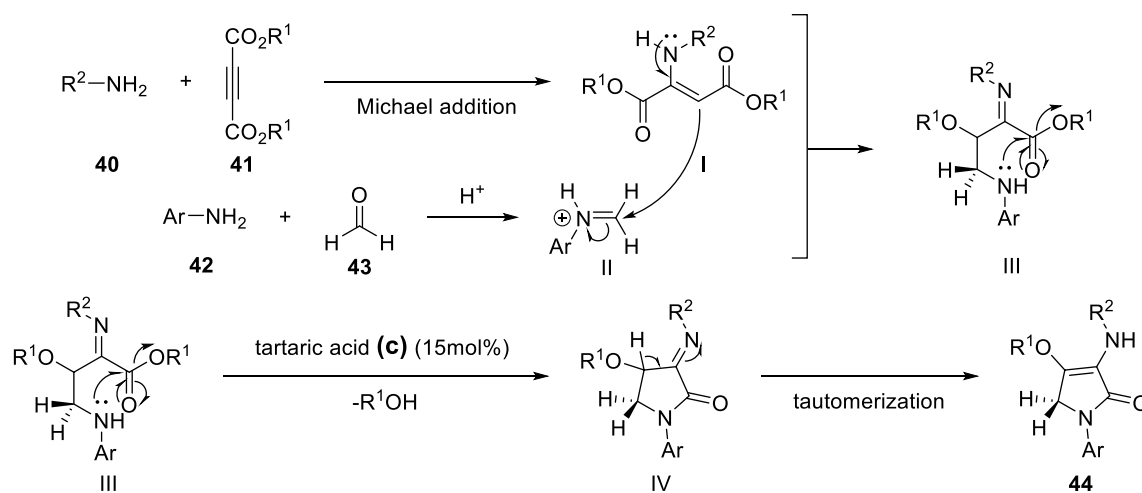
Scheme 10 Proposed mechanism in the formation of poly-substituted quinolines via Friedländer condensation. Reaction condition: ketone (1.0 mmol), 2-aminobenzophenones (1.0 mmol), tartaric

acid (0.15 mmol) at 70 °C under solvent-free condition. *Notes:* H₂O (water), Ph (phenyl), mol% (mole percent), °C (degree Celsius), cat- (cation)

Table 1 Comparison of previous methods and their reactions' yields in the synthesis of poly-substituted quinolines

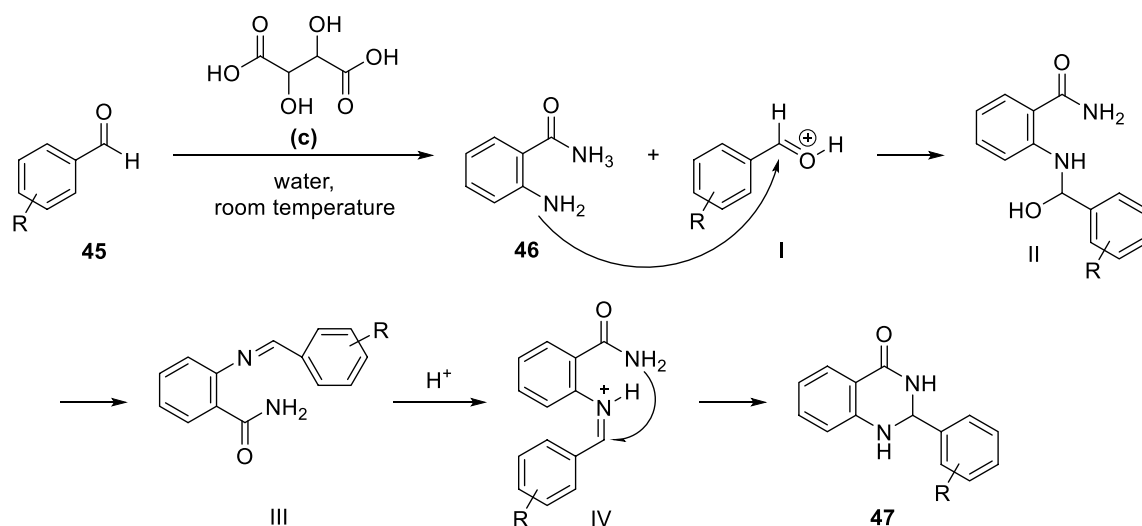
Catalysts	Conditions	Time (min)	Yield (%)	References
Sulfonate ionic liquid	Solvent-free, 70 °C	25	89	Shirini et al. (2014)
Zeolite-supported transition metal catalyst	Ultrasound Irradiation	7	92	Safa et al. (2016)
Lanthanum(III) chloride/chloroacetic acid	Solvent-free, 70 °C	10	96	Pouramiri et al. (2017)
Zwitterionic-type ionic liquid	Solvent-free, 100 °C	17	94	Rafiee and Shahebrahimi (2019)
Polyvinylpyrrolidonium triflate	Toluene, 110 °C	300	85	Khaksar et al. (2014)
Potassium fluoride/clinoptilolite nanoparticles	Solvent-free, 80 °C	60	92	Balou et al. (2019)
Tartaric acid	Solvent-free, 70 °C	10	89	Mohamadpour et al. (2018)

min (minute), °C (degree Celsius), % (percent)



R^1 = methyl, ethyl ; R^2 = phenyl, 4-bromo-benzyl, 4-fluoro-benzyl, 4-methoxy-benzyl, 4-methyl-benzyl, n-butyl, benzyl

Scheme 11 Synthesis of poly-substituted dihydropyrrol-2-ones. Reaction condition: amine (1.0 mmol), dialkyl acetylenedicarboxylate (1.0 mmol), formaldehyde (1.5 mmol), tartaric acid (0.15 mmol). *Notes:* Ar (Aromatic), OH (hydroxy), mol% (mole percent)



R = hydrogen, 4-methyl, 4-methoxy, 4-hydroxyl, 4-chloro, 4-fluoro, 4-nitro, 4-N,N-dimethyl, 3-chloro, 3-methoxy, 3-hydroxyl, 2-hydroxyl

Scheme 12 Synthesis of 2,3-dihydroquinazolin-4(1*H*)-ones. Reaction condition: aromatic aldehyde (1.0 mmol), 2-aminobenzamide (1.0 mmol), tartaric acid (0.2 mmol) in water (5 mL) at room temperature. *Notes:* H^+ (hydrogen ion)

various aromatic aldehydes **45** (Scheme 12) (Singh et al. 2018). In the proposed mechanism, tartaric acid aided in activating the carbonyl group of the aldehydes, which further enhances the electrophilic character of aldehyde followed by cyclization, and the desired products were recorded in high to excellent yields (85–95%). The use of

costly catalysts, prolong reaction times, and harsh reaction conditions are among the disadvantages associated with the previous protocols. This approach is more superior to the former protocols as the catalyst used is far safer, efficient, and eco-friendly compared to the previous protocols.

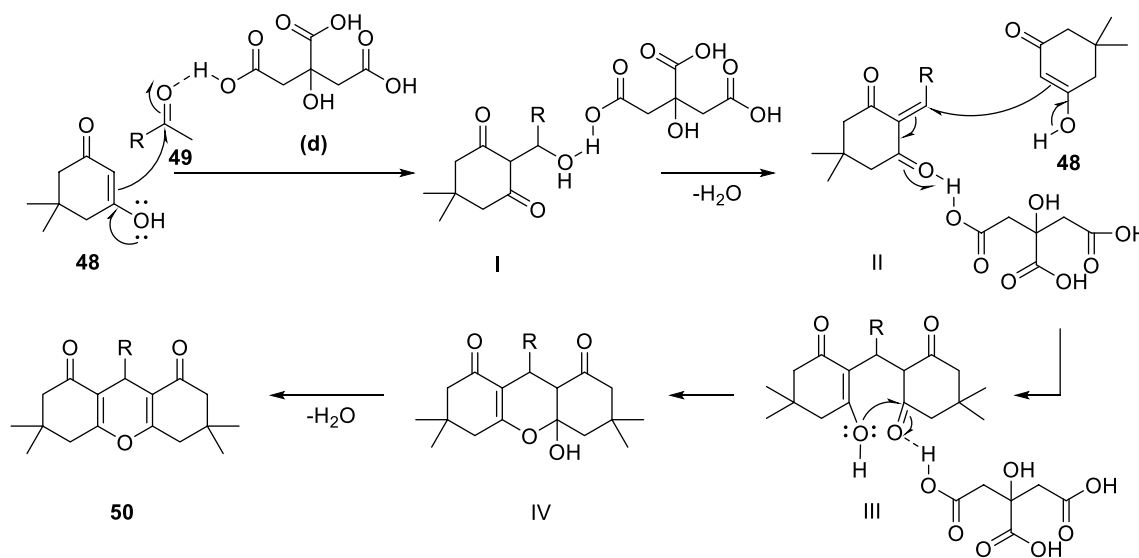
Citric acid

Citric acid is a natural preservative, anti-caking agent, acidity regulator and antioxidant agent in food processing industry. In the food industry, citric acid is usually employed in the production of fruit juice, jelly, candies, marmalade, as well as aid in suppressing the browning process in fruits (Navarro et al. 2013). According to a recent literature, many organic reactions have been achieved by using citric acid as a catalyst (Bafti and Khabazzadeh 2014). This catalyst is found to be low-cost, stable, non-volatile as well as eco-friendly additive compared to other catalysts in catalyzing identical organic reactions. One of the remarkable examples was reported in the synthesis of 1,8-dioxo-octahydroxanthenes **50** (Navarro et al. 2013). The reaction takes place between aldehyde **49** and dimedone **48** in the presence of citric acid (**d**). A plausible mechanism for the synthesis is presented in Scheme 13. At the end of the synthesis, high yields (73–85%) of the desired compounds were obtained via the intramolecular cyclization step. This protocol was found to be greener and efficient, as the conventional methods described in previous literatures suffer from several limitations including the need for catalyst preparation, use of expensive catalysts and reagents, tedious reaction workup, harsh reaction condition, and prolonged reaction times. In the present method, citric acid was selected as a green catalyst as it is non-volatile, cost-effective, readily available, and reusable.

Besides, this procedure offers a milder reaction condition and minimizing the production of wastes.

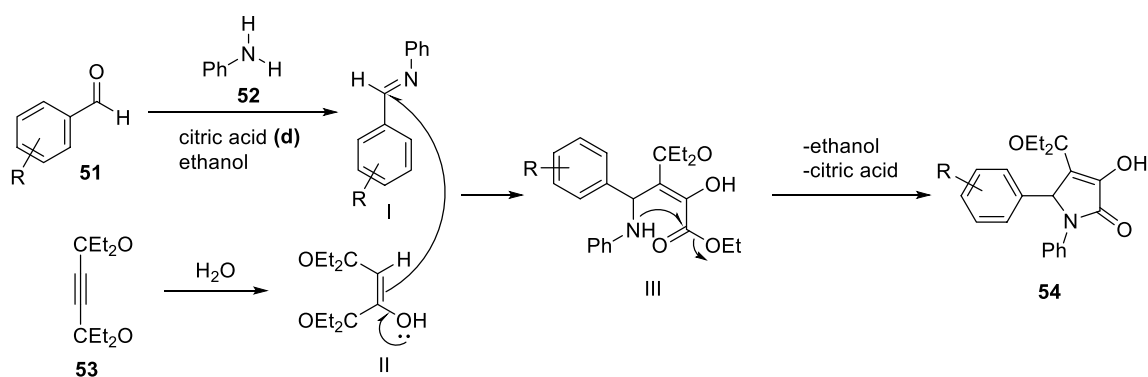
The role of citric acid as a green catalyst was also investigated in the synthesis of 3-pyrrolin-2-ones **54** (Ahankar et al. 2016). These reactions involved aromatic aldehydes **51**, aniline **52**, and diethyl acetylene-dicarboxylate **53** were carried out successfully under microwave irradiation, with citric acid (**d**) as catalyst. Scheme 14 shows the mechanism of formation for the 3-pyrrolin-2-ones. The elimination of ethanol and citric acid molecules at the final stage of the reaction resulted in high yields (80–92%) of the targeted products. In many cases, the use of harsh reaction conditions, non-eco-friendly catalysts, toxic solvents, and low yields of end-products were commonly encountered in the previous method for the identical organic reaction. With the aid of citric acid, this green catalyst helps to increase reactions yields within a short reaction time. Moreover, this green catalyst is inexpensive and eco-friendly, commercially available additives, and resulted in high purity of the targeted products.

In addition, Shaikh et al. (2014) also demonstrated the preparation of amidoalkyl naphthols **58** using citric acid (**d**). Amidoalkyl naphthols have been attracting interest among researchers due to their useful pharmacological and biological properties. Previously, the use of unsustainable methods have been employed in the amidoalkyl naphthols syntheses, such as the use of molecular iodine (Das et al. 2007), ferric hydrogen sulfate (Shaterian et al. 2008), strontium



R = benzaldehyde, 4-methoxybenzaldehyde, 4-dimethylaminobenzaldehyde, 3,4,5-trimethoxybenzaldehyde, piperonal, 4-bromobenzaldehyde, 4-chlorobenzaldehyde, 4-nitrobenzaldehyde, 2-nitrobenzaldehyde, 2-pyridinecarbaldehyde, 2-thiophenecarbaldehyde

Scheme 13 Formation of 1,8-dioxo-octahydroxanthenes Reaction condition: aldehyde (0.5 mmol) and dimedone (1.0 mmol) with the presence of citric acid (2 mL). Notes: H₂O (water)

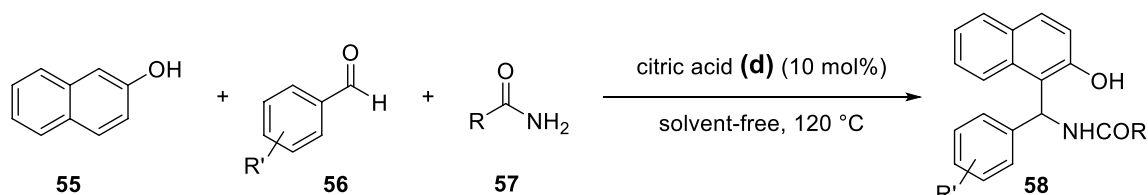


R = phenyl, 4-methyl-benzyl, 2-naphthal, 4-chloro-benzyl, 3-chloro-benzyl, 2-chloro-benzyl, 4-fluoro-benzyl, 4-bromo-benzyl, 3-bromo-benzyl, 4-nitro-benzyl, 3-nitro-benzyl, 2-nitro-benzyl, 4-phenyl-benzyl, 4-hydroxy-benzyl, 4-methylsulfonyl-benzyl, 4-methoxy-benzyl

Scheme 14 Mechanism of formation of 3-pyrrolin-2-ones. Reaction condition: aromatic aldehyde (1.0 mmol), aniline (1.0 mmol), diethyl acetylene-dicarboxylate (1.0 mmol), citric acid (2.0 mmol) in ethanol (4 mL). Notes: Ph (phenyl), H₂O (water)

bis(trifluoromethanesulfonate) (Shaikh et al. 2014), disulfonamide catalyst (Ghorbani-Vaghei and Malaekhepour 2010) and magnetic nanoparticle-supported sulfuric acid (Safari and Zarnegar 2013). However, some of these methods required prolonged reaction times, high catalyst loading, the use of expensive and corrosive reagents, and strongly acidic conditions. Due to these problems, citric acid has been attracting the attention of chemists as an alternative green catalyst. Under the improved protocol, citric acid (**d**) catalyzed the three-component reaction involving aromatic aldehyde **56**, acetamide **57**, and 2-naphthol **55** under the neat condition to synthesize the desired compound in high yields (87–94%) as shown in Scheme 15. Moreover, citric acid is more favourable than other catalysts, as it is a biodegradable, cheap, non-corrosive, and non-toxic. In this experiment, the calculated turnover number (8.7) and turnover frequency (34.8 h⁻¹) demonstrated that the optimized reaction condition was achieved with the use of 10 mol% of citric acid as catalyst and heated under 120 °C.

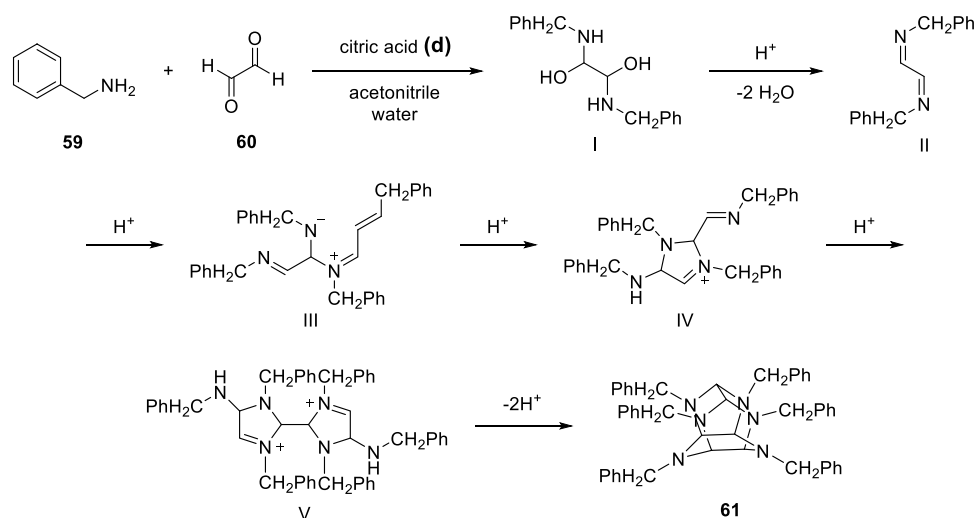
Next, a citric acid-mediated synthesis of hexabenzyl hexaazaisowurtzitane **61** was developed (Shokrollahi et al. 2016) via the condensation of benzylamine **59** with glyoxal **60** (Scheme 16). The synthesis of hexabenzyl hexaazaisowurtzitane was reported to have the best results when only 5 mol% of citric acid (**d**) catalyst was used and with acetonitrile–water as the solvent. Besides, the reaction takes 5 min with ultrasonic power of 150 W producing high yields (89%) of the desired hexabenzyl hexaazaisowurtzitane. Previous methodologies utilized formic acid as a catalyst for the synthesis of hexabenzyl hexaazaisowurtzitane. However, the formic acid has been proven to be corrosive to most alloys including stainless steel (Shokrollahi et al. 2016; Singh et al. 2018). Therefore, citric acid is a more favourable catalyst as it is non-toxic and biodegradable, as well as well known to catalyze a variety of organic reactions. When coupled with ultrasound irradiation, the reaction was found to have good reaction yields and completed within a shorter reaction time as demonstrated in this work.



R = methyl, phenyl, amino ; R' = phenyl, 4-chloro-benzyl, 4-methoxy-benzyl, 4-nitro-benzyl, 2-nitro-benzyl, 2-chloro-benzyl, 4-methyl-benzyl

Scheme 15 Synthesis of amidoalkyl-2-naphthols. Reaction condition: 2-naphthol (1.0 mmol), aromatic aldehyde (1.0 mmol), amide (1.2 mmol), citric acid (10 mol%) at 120 °C under solvent-free conditions. Notes: °C (degree Celsius), mol% (mole percent)

Scheme 16 Mechanism of formation of hexabenzyl hexaazaisowurtzitane. Reaction condition: benzylamine (8.5 mmol), glyoxal (3.75 mmol), citric acid (0.05 mmol) in acetonitrile (7.75 mL) and water (0.775 mL) under conventional stirring and ultrasonic radiation condition. Notes: H⁺ (hydrogen ion), H₂O (water), Ph (phenyl)



Pectin

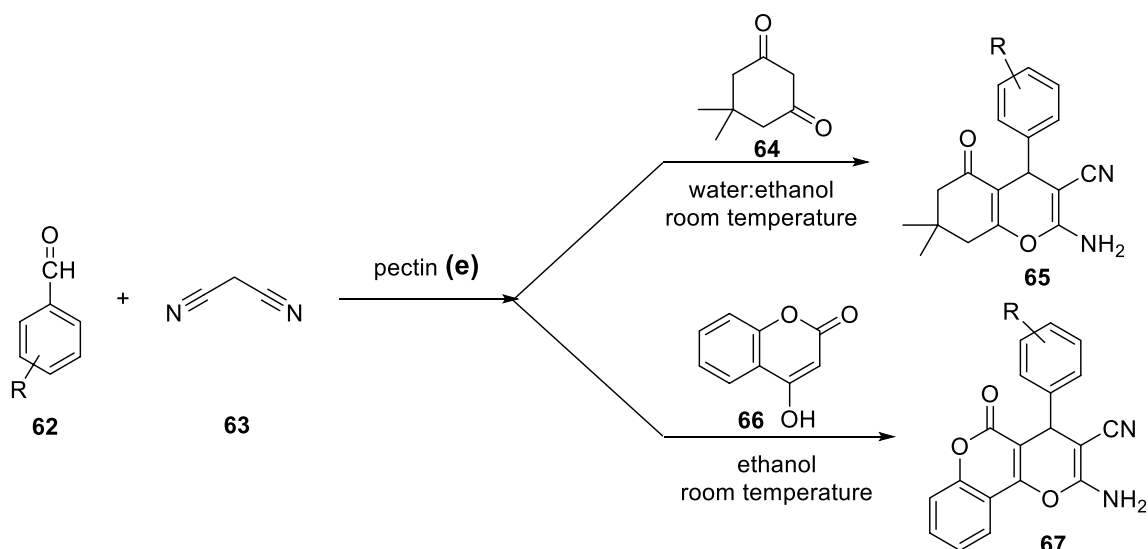
Pectin is a naturally occurring polymer that has applications in the fields of medical, pharmaceutical, and biotechnology industries. In the food and beverage industry, pectin is used as thickening, bulking and colloidal stabilizer agent. The source of commercial pectin is from the citrus rind (Thakur et al. 1997; Sriamornsak 2007). Over the past years, the use of pectin in organic synthesis has received considerable attention among chemists due to its biodegradable and green nature as an organic catalyst. One of the examples was found on the synthesis of tetrahydrobenzo[*b*]pyran **65** and 3,4-dihydropyrano[*c*]chromene **67** (Kangani et al. 2016) using this environmentally benign catalyst. A one-pot three-component reaction of benzaldehyde **62** with malononitrile **63**, and dimedone **64** or 4-hydroxycoumarin **66** exclusively lead to the targeted products, **65** and **67**, respectively (Scheme 17). Scheme 18 shows the plausible mechanism for the production of **65**. The great interest in this catalyst was due to the green and biodegradable property of pectin (**e**) as an organic catalyst. Furthermore, the tetrahydrobenzo[*b*]pyran **65** and 3,4-dihydropyrano[*c*]chromene **67** syntheses mediated by pectin (**e**) were found to be in excellent reaction yields, which indicated that the current catalyst can act as green alternative to other catalysts for the identical organic reactions (Table 2).

The presence of food additives as catalysts in organic reactions also has the utility for organic reactions to be performed at room temperature. One such reaction was identified in the pectin (**e**) catalyzed oxopyroles and furan-2(5H)-one's syntheses (Kangani et al. 2018). The result of this finding showed that the reaction can be carried out successfully at room temperature, which was desirable in minimizing the economic and environmental impact. Scheme 19 shows a proposed mechanism for the synthesis of dihydro-2-oxopyroles **72**.

Oxalic acid

Oxalic acid or commonly known as oxalate is a compound that occurred naturally in plants. Oxalic acid is usually found in vegetables such as spinach, carrots, rhubarb and bamboo shoots. Dabiri et al. (2007) prepared quinolines **75** via the *Friedländer* annulation in the presence of oxalic acid (**f**) as an organic catalyst. The reaction pathway involved 2-aminobenzophenone **73** and ethyl acetoacetate **74** which leads to the formation of quinolines **75** under solvent-free condition as shown in Scheme 20. The result showed that the desired compounds can be efficiently furnished and obtained in excellent yields (88–95%) via condensation reaction followed by cyclodehydration steps. The uniqueness of employing oxalic acid in mediating this reaction including eco-friendly nature, inexpensive and solvent-free condition, which makes this catalyst more superior than the use of toxic catalysts and solvents in the previous studies. Table 3 summarizes the previous methods and their yields in the synthesis of quinoline.

The use of oxalic acid for organic transformation is recommended by chemists as the reaction can be carried out in a solvent-free condition. One of these examples was demonstrated by Sarkate et al. (2013), which successfully employed oxalic acid (**f**) as a green catalyst for the synthesis of 1,5-benzodiazepines **78** under the solvent-free condition at 80 °C. The reaction commenced by reacting *o*-phenylenediamine **76** and α , β -unsaturated ketones **77** as presented in Scheme 21. Excellent yields (76–96%) of the desired product were achieved within a short reaction time. A plausible mechanism for the synthesis of 1,5-benzodiazepines is illustrated in Scheme 22. In the reported literature, previous methods have suffered from several drawbacks and limitations in using costly and toxic catalysts or reagents, associated with tedious work-up and resulting in low product yields. Alternatively, the present method developed by

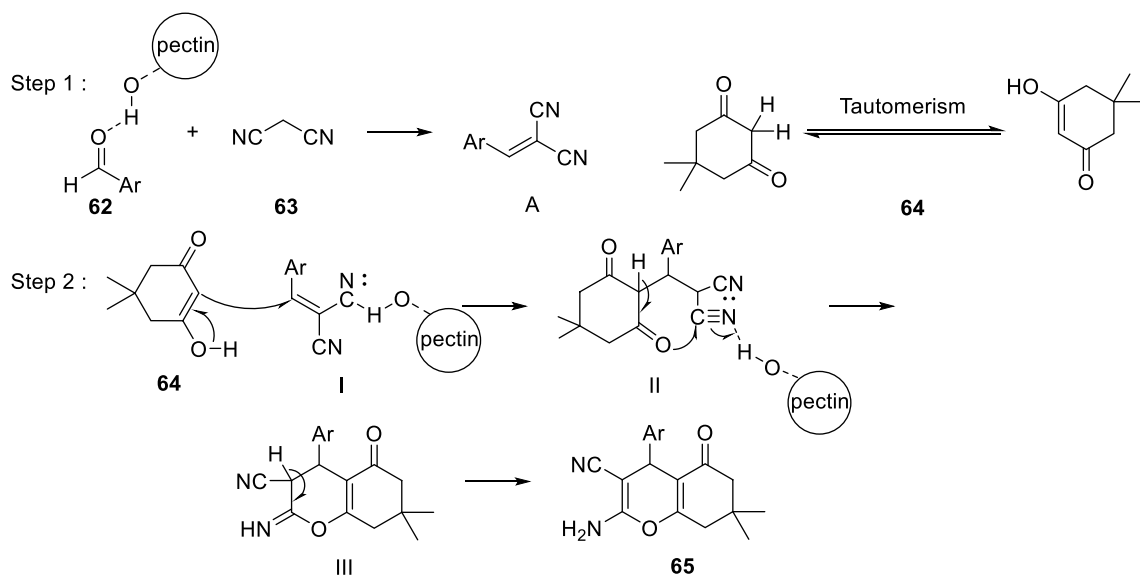


R (**65**) = phenyl, 2-chlorobenzyl, 4-chlorobenzyl, 2,4-dichlorobenzyl, 2-nitrobenzyl, 3-nitrobenzyl, 4-nitrobenzyl, 4-methylbenzyl, 4-methoxybenzyl, 2,3-dimethoxybenzyl, 4-hydroxy-3-methoxybenzyl, 4-(dimethylamino)benzyl, 2,3-methoxybenzyl, 4-hydroxybenzyl, thiophene-2-carbaldehyde, 3-furaldehyde

R (**67**) = phenyl, 3-nitrobenzyl, 4-nitrobenzyl, 4-methylbenzyl, 3,4-dimethoxybenzyl, 2-chlorobenzyl, 4-chlorobenzyl, 2,4-dichlorobenzyl, 4-hydroxybenzyl, 2-fluorobenzyl, thiophene-2-carbaldehyde, thiophene-3-carbaldehyde

Scheme 17 Synthesis of tetrahydrobenzo[*b*]pyran **65** and 3,4-dihydropyrano[*c*]chromene **67**. Reaction condition: aromatic aldehyde (1.0 mmol), malononitrile (1.0 mmol), dimedone

(1.0 mmol) or 4-hydroxycoumarin (1.0 mmol), pectin (0.05 g) in water:ethanol or ethanol solvent system at room temperature



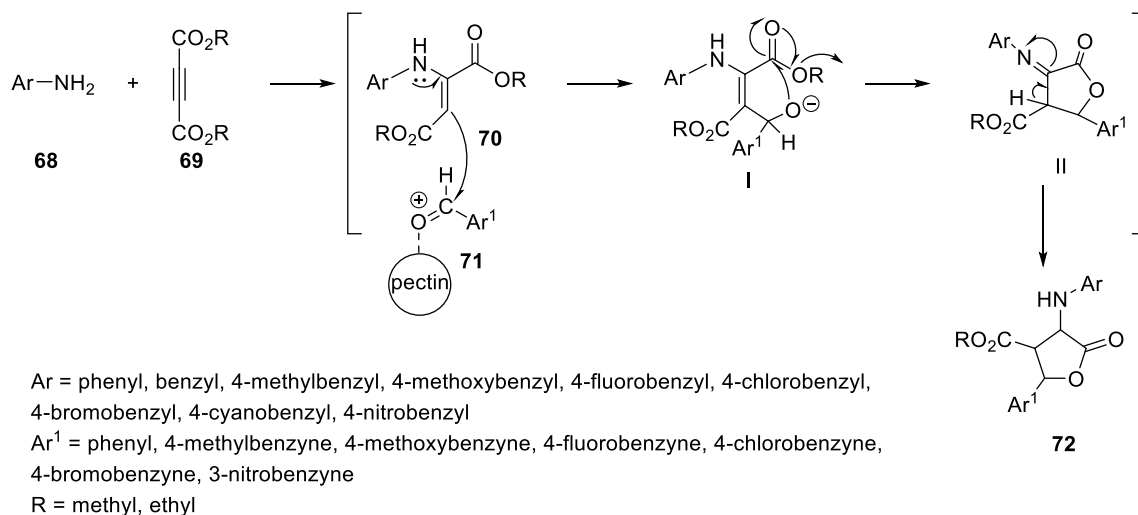
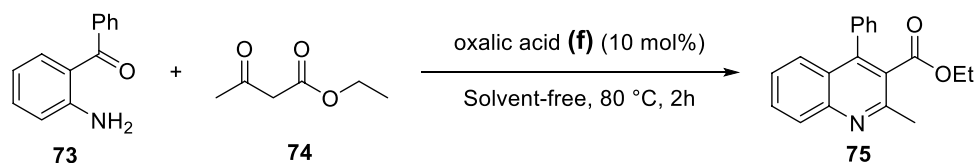
Ar = phenyl, 2-chlorobenzyl, 4-chlorobenzyl, 2,4-dichlorobenzyl, 2-nitrobenzyl, 3-nitrobenzyl, 4-nitrobenzyl, 4-methylbenzyl, 4-methoxybenzyl, 2,3-dimethoxybenzyl, 4-hydroxy-3-methoxybenzyl, 4-(dimethylamino)benzyl, 2,3-methoxybenzyl, 4-hydroxybenzyl, thiophene-2-carbaldehyde, 3-furaldehyde

Scheme 18 Mechanism of formation for tetrahydrobenzo[*b*]pyran **65**. Notes: the reaction were catalyzed by pectin in ethanol–water solvents system. Ar (Aromatic)

Table 2 Comparison of previous methods and their reaction yields in the syntheses of tetrahydrobenzo[*b*]pyran **65** and 3,4-dihydropyrano[*c*]chromene **67**

Product	Catalysts	Conditions	Time (min)	Yield (%)	References
65	Basic ionic liquid catalyst	Water, 60 °C	15	95	Yang et al. (2015)
65	Triethylamine	Ultrasound Irradiation	120	98	Auria-Luna et al. (2020)
65	γ -cyclodextrin/deep eutectic solvent	Solvent-free, 60 °C	15	98	Xiong et al. (2019)
65	Trifluoroethanol	Reflux	300	90	Khaksar et al. (2012)
67	Cobalt Orthophosphate	Water/Ethanol, 80 °C	25	97	El Hallaoui et al. (2019)
67	1,4-diaza-bicyclo[2.2.2]octane-based bis-dicationic ionic salt	Water, 100 °C	20	95	Zabihzadeh et al. (2020)
67	Ammonium acetate	Ionic liquid, 100 °C	50	94	Mhiri et al. (2020)
67	Piperazine	Water, 90 °C	135	96	Yousefi et al. (2018)
65	Pectin	Water/Ethanol, r.t	60	90	Kangani et al. (2016)
67	Pectin	Water/Ethanol, r.t	10	90	Kangani et al. (2016)

min (minute), r.t (room temperature), % (percent)

**Scheme 19** Tentative mechanism of dihydro-2-oxypyroles syntheses. Reaction condition: mixture of amine (1.0 mmol), dialkyl acetylene-dicarboxylate (1.0 mmol), aldehyde (1.5 mmol), pectin (0.05 g) in water:ethanol (1:3) at room temperature. *Notes:* Ar (Aromatic)**Scheme 20** Synthesis of quinolines. Reaction condition: 2-aminobenzophenone (1.0 mmol), ethyl acetoacetate (1.1 mmol), oxalic acid (0.1 mmol), heated at 80 °C under solvent-free conditions for 2 h. *Notes:* h (hours), °C (degree Celsius), Ph (phenyl), mol% (mole percent)

the authors offers advantages which includes a more environmentally friendly procedure, cost-effective catalysts, easy work-up, shorter reaction time, and reduction of waste production.

Another example of this approach was found in the preparation of 2-(substituted phenyl) phthalazin-1(*2H*)-ones **81**

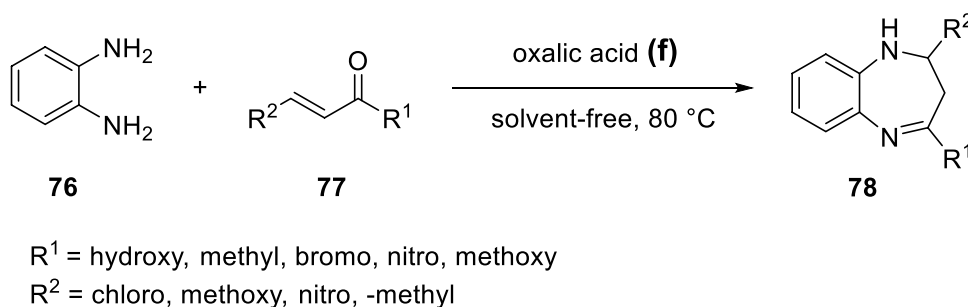
using oxalic acid (Sangshetti et al. 2015). A model reaction of substituted phenyl hydrazine **80** and phthalaldehydic acid **79** was established using water as a solvent in the presence of oxalic acid (**f**) (Scheme 23). This environmentally benign protocol afforded the targeted compound in excellent yields (95–98%) via dehydrative cyclization. The presence

Table 3 Comparison of previous methods and their reaction yields in the syntheses of quinoline **75**

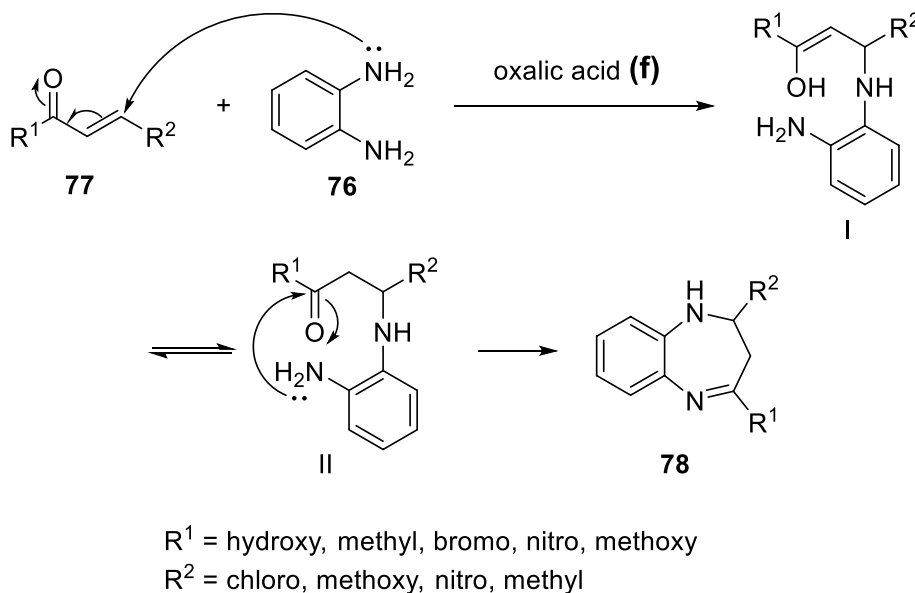
Catalysts	Conditions	Time (min)	Yield (%)	References
L-proline/1,3-dimethylimidazolium methyl sulfate ionic liquid	90 °C	30	98	Tasqeeruddin and Asiri (2020)
4-Toluenesulfonic acid	Water/Ethanol, 80 °C	720	99	Zhou et al. (2018)
Calcium trifluoromethanesulfonate/ Tetrabutylammonium hexafluorophosphate	Solvent-free, 120 °C	300	98	Singh and Yaragorla (2017)
Functionalized imidazolium salt	Solvent-free, 100 °C	960	96	Gisbert et al. (2019)
4-Imidazol-1-yl-butane-1-sulfonic acid	Toluene, 50 °C	30	94	Khaligh et al. (2018)
Nafion NR50	Microwave/Ethanol	60	92	Chan et al. (2020)
Oxalic acid	Solvent-free, 80 °C	120	90	Dabiri et al. (2007)

min (minute), °C (degree Celsius), % (percent)

Scheme 21 Synthesis of 1,5-benzodiazepines. Reaction condition: *o*-phenyldiamine (10.0 mmol), α , β -unsaturated ketones (10.0 mmol), oxalic acid (0.1 mmol), heated at 80 °C under solvent-free conditions. *Notes:* °C (degree Celsius)



Scheme 22 Mechanism of formation for 1,5-benzodiazepines catalyzed by oxalic acid

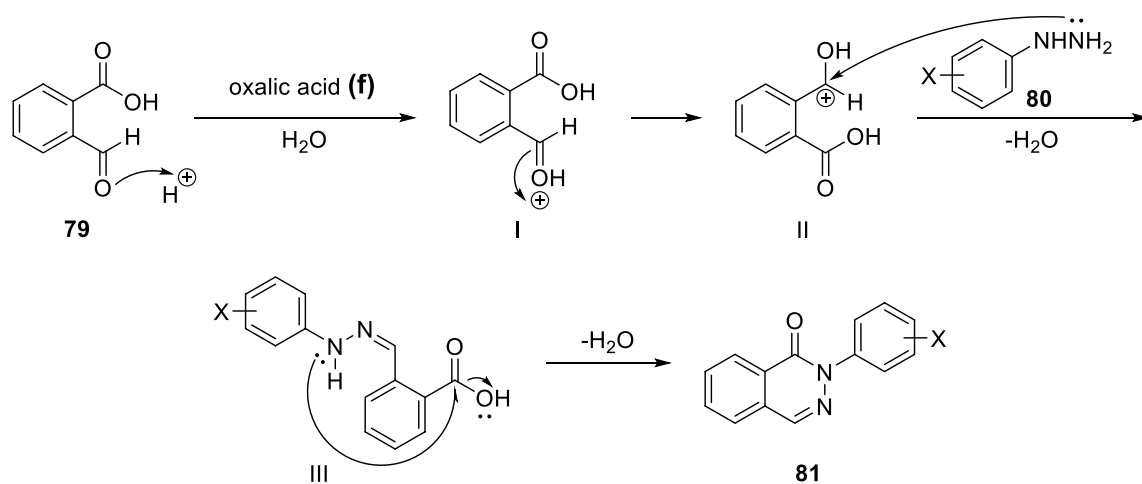


of oxalic acid in the synthetic route helps in the protonation at the carbonyl carbon of phthalaldehydic acid (stage I). Several synthetic methods for the synthesis of phthalazinones have been identified in the literatures. However, these synthetic methods involve harsh reaction conditions, prolonged reaction times, and required strong acids and bases. The use of oxalic acid in organic reactions is economical, mild, and easy to handle. In addition, the advantage of this catalyst is

also associated with a marked decrease in reaction time and only requires water as the sole solvent.

Saccharin

Over the past, saccharin plays a role as an artificial sweetener to enhance the sweet taste of the food (Tripathi et al. 2006). Besides, it is also generally used as a calorie-free additive



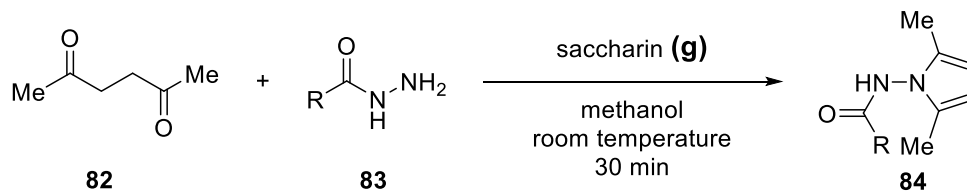
Scheme 23 Mechanism of 2-(substituted phenyl) phthalazin-1(2H)-one's syntheses. Reaction condition: phthalaldehyde (10.0 mmol), substituted phenyl hydrazine (10.0 mmol), oxalic acid (0.1 mmol) in water (15 mL) as solvent. Notes: H₂O (water)

in beverages and food products (Larsen 2012). Recently, saccharin has gained attention among researchers as it has high catalytic applicability in organic transformations as it is easily available, requires very mild reaction condition, and efficiently water-soluble. Bhandari and Gaonkar (2015) was the first to report on the synthesis of pyrroles derivatives achieved using saccharin as a green catalyst. The synthesis of *N*-substituted 2,5-dimethylpyrroles **84** involved the reaction of various hydrazides **83** and hexane-2,5-dione **82** in the presence of saccharin (**g**) (Scheme 24). This synthetic protocol leads to good reaction yields (80–92%) of the targeted products via Paal-Knorr condensation, with turnover number (3.4) and turnover frequency (6.9 h⁻¹) reported for the optimized reaction condition. A close inspection of previous methods for the Paal-Knorr condensation, they often involved the use of strong acids, expensive and toxic reagents. The present work offers more advantages compared to the previous methods where the use of saccharin displayed a cost-effective, non-toxic, and easy to handle method.

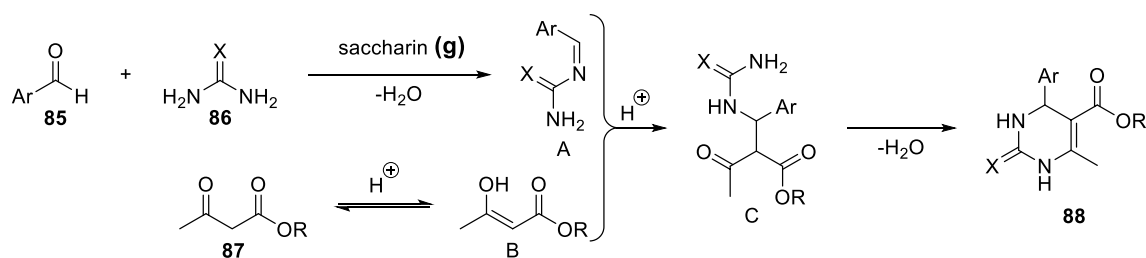
Moreover, it is recyclable for another two runs without significant loss in its activity.

Another saccharin-mediated approach was identified in the work of Mohamadpour et al. (2016). An efficient solvent-free 3,4-dihydropyrimidine-2-(1*H*)-ones **88** method was developed, when urea/thiourea **86**, aromatic aldehydes **85**, and alkyl acetoacetate **87** were reacted in one-pot in the presence of saccharin (**g**) as catalyst. Under this protocol, the turnover number (4.6) and turnover frequency (18.2 h⁻¹) were reported for the optimized reaction condition. In addition, various types of benzaldehydes were tolerable and reacted following the Biginelli manner, which afforded the targeted compounds in high yields (80–93%). The solvent-free and the use of the inexpensive catalyst of this protocol provides attractive advantages compared to previous protocols. The mechanism for the formation of **88** catalyzed by saccharin is illustrated in Scheme 25. A multicomponent reaction involving phthalamide **89**, aldehydes **91**, hydrazine hydrate **90**, and malononitrile **92** under

Scheme 24 Synthesis of *N*-substituted 2,5-dimethylpyrroles. Reaction condition: hexane-2,5-dione (6.0 mmol), hydrazide (4.0 mmol), saccharin (1.0 mmol) in methanol (6 mL) while stirred for 30 min at room temperature via Paal-Knorr condensation reaction, Notes: Me (methyl), min (minute)



R = 1-(4-fluorophenyl)-5-methyl-1,3-dihydroisobenzofuran, 2-methylbenzofuran, 2-methylfuran, 2-methylthiophene, 2,4-dimethylthiazole, toluene, *p*-xylene, 2,6-dichloro-*N*-(2-ethylphenyl)aniline, 1-methoxy-4-methylbenzene, 1-bromo-4-methylbenzene, 1-chloro-4-methylbenzene, 1-fluoro-4-methylbenzene



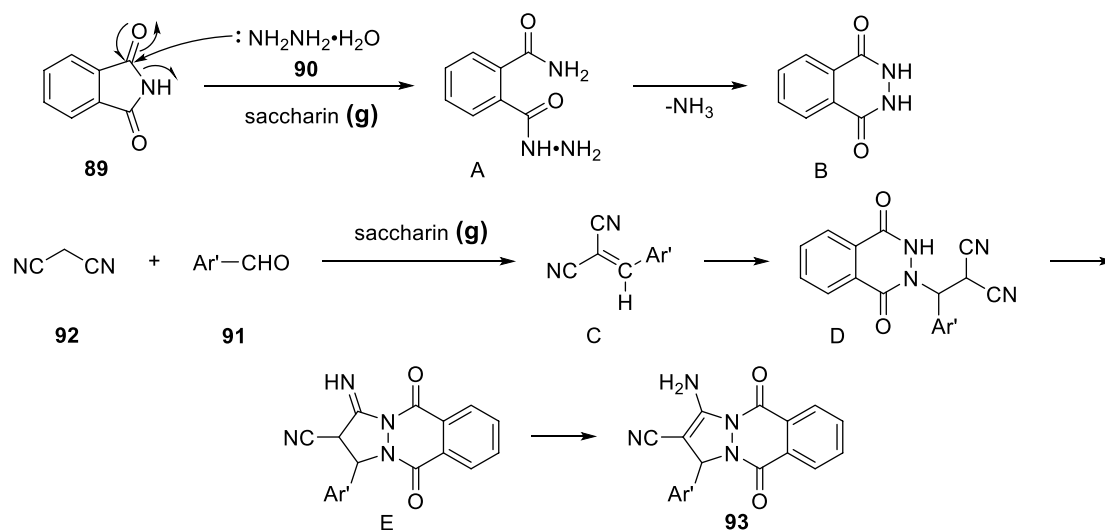
X = oxygen, sulfur

R = methyl, ethyl

Ar = 2-chlorobenzyl, phenyl, 4-methoxybenzyl, 4-hydroxybenzyl, 4-nitrobenzyl, 3-methoxybenzyl, 4-fluorobenzyl, 4-(dimethylamino)benzyl, 4-chlorobenzyl, 3-chlorobenzyl, 4-methylbenzyl,

Scheme 25 Mechanism of formation for the synthesis of 3,4-dihydropyrimidine-2-(1*H*)-ones. Reaction condition: aromatic aldehyde (1.0 mmol), urea/thiourea (1.5 mmol), ethyl/methyl acetoacetate

(1.0 mmol), saccharin (0.15 mmol) under solvent-free conditions. *Notes:* H₂O (water), H⁺ (hydrogen ion), Ar (Aromatic)



Ar' = 2-thienyl, 3-fluorobenzyl, phenyl, 3-nitrobenzyl, 4-bromobenzyl, 2-chlorobenzyl, 3-bromobenzyl, 3-methoxybenzyl, 2-nitrobenzyl, 3-methylbenzyl, 2,4-dichlorobenzyl, 4-nitrobenzyl, 3,4,5-trimethoxybenzyl, 4-fluorobenzyl, 4-methylbenzyl, 4-hydroxybenzyl, 4-chlorobenzyl, 3-chlorobenzyl

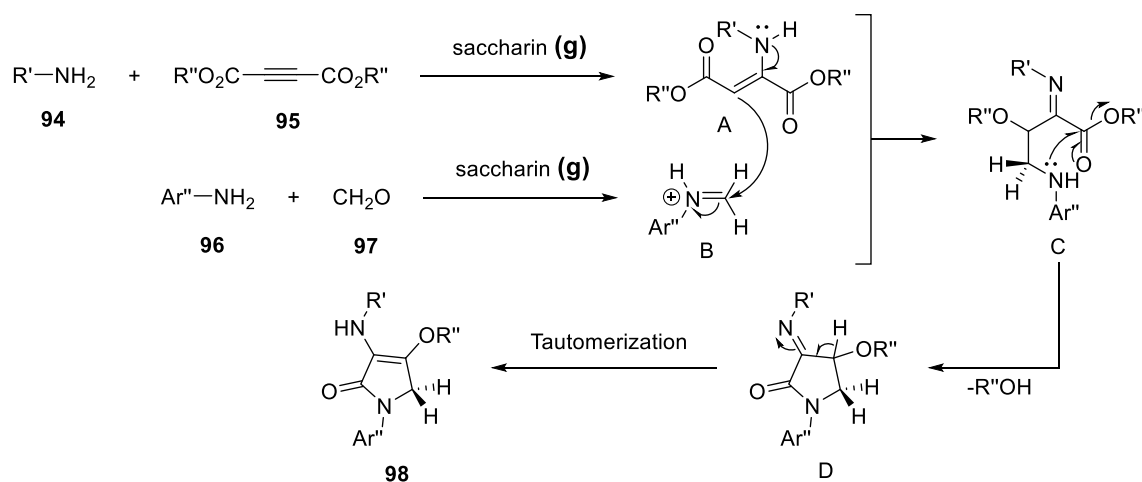
Scheme 26 Mechanism of formation for the pyrazolo[1,2-*b*]-phthalazine-5,10-diones. Reaction condition: phthalimide (1.0 mmol), hydrazine monohydrate (1.0 mmol), aromatic aldehyde (1.0 mmol), malonitrile (1.0 mmol), in the presence of saccharin (0.2 mmol). *Notes:* Ar (Aromatic), NH₃ (ammonia)

Ar (Aromatic), NH₃ (ammonia)

solvent-free conditions were reported by the same author to afford pyrazolo[1,2-*b*]-phthalazine-5,10-dione **93** in the presence of saccharin (Scheme 26). Surprisingly, this green approach afforded an excellent yield (82–93%) of the desired products within a shorter reaction time. Generally, the use of saccharin is much safer than previous protocols for the identical organic reaction.

Inspired by the previous study, the same authors (Mohammadpour et al. 2016) have synthesized a series of dihydro-2-oxypyrrrole **98** via a one-pot four-component reaction, involving aromatic **94**, aliphatic amines **96**, formaldehyde **97**, and dialkyl acetylenecarboxylate **95** in the presence of

saccharin (**g**) as organic catalyst (Scheme 27). Excellent reaction yields (85–94%) were recorded using saccharin as a green catalyst. A close inspection on the previous methods revealed that the majority of the literatures reported on the use of unsustainable methods, such as the use of tetrachlorobis(tetrahydrofuran)zirconium (Sajadikhah et al. 2016), silica gel-supported tungstic acid (Reddy et al. 2014), Brønsted acidic ionic liquid (Zhang et al. 2015), sulfonic acid functionalized nanoporous silica (Ziarani et al. 2014), and molecular iodine (Ziarani et al. 2014) as catalysts. This has prompted the current investigation towards an environmentally friendly method, which uses saccharin as a green



Ar'' = phenyl, 4-chlorobenzyl, 4-fluorobenzyl, 4-methylbenzyl, 4-methoxybenzyl, 4-bromobenzyl, 3,4-dichlorobenzyl
 R' = phenyl, 4-chlorobenzyl, 4-fluorobenzyl, 4-methylbenzyl, 4-methoxybenzyl, 4-bromobenzyl, n-butyl, benzyl
 R'' = methyl, ethyl

Scheme 27 Mechanism of formation for the synthesis of dihydro-2-oxypyrrrole. Reaction condition: amine (1.0 mmol), dialkyl acetylenedicarboxylate (1.0 mmol), aromatic amine (1.0 mmol), formalde-

hyde (1.5 mmol), in the presence of saccharin (0.15 mmol). *Notes:* Ar (Aromatic), OH (hydroxy)

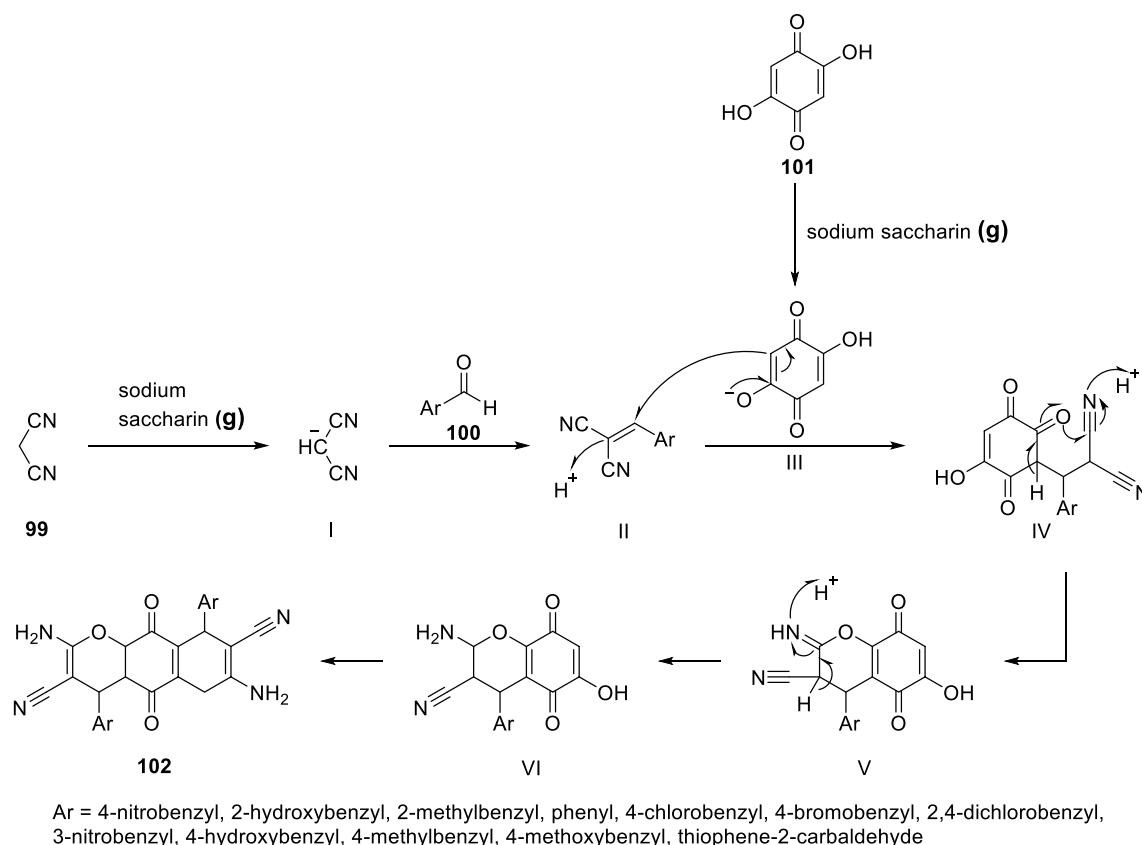
catalyst because it is a cost-effective and non-toxic catalyst but without compromising on catalytic activity.

Last but not least, the use of saccharin was also demonstrated by Moradi and Aghamohammad Sadegh (2017) whereby the synthesis of dihydropyrano[2,3-g]chromenes **102** was carried out by using sodium saccharin. The one-pot five-component reaction between aryl aldehyde **100**, 2,5-dihydroxy-1,4-benzoquinone **101**, and malononitrile **99** in the presence of sodium saccharin (**g**) under microwave irradiation was developed to obtain **102** (Scheme 28). This efficient and eco-friendly approach enables the synthesis of **102** in excellent yields (78–90%). The benefits of the current method include simplicity in reaction workup, cost-effective catalysts, and producing high reactions yields within short reaction times. Table 4 summarizes the different methods and their yields performed by the author in the synthesis of dihydropyrano[2,3-g]chromenes **102** (Moradi and Aghamohammad Sadegh 2017).

Conclusion

At industry level, the growing demand for the finite elemental resources such as metals for industrial processes has led to concerns over the sustainability of the supply of these elements. Furthermore, intensive mining of these elements has increased the burden on the environment and at times lead to the issue of environmental pollution. Therefore, there are calls to search for greener alternatives to reduce the use of elemental resources for chemical

processes in the industries. Food additives, on the other hand, have been gaining interest not only in the food industry but also in the chemical industry as elemental substitutes contributing to sustainable organic reactions. The involvement of food additives as green catalysts for preparative organic reactions has raised the interest of today's scientists for the development of environmentally benign methodologies. Generally, food additives are regarded as “green catalyst” in organic syntheses and we believed that the next decade will mark a major development of using a green and sustainable method in promoting organic transformations, for both academia and industries alike. Thus, the use of food additives can act as the alternative catalysts in achieving the goals of green and sustainable chemistry, as many benefits and green features described previously by scientists in this field. This review article specifically addresses the use of non-metals, biodegradable and green catalysts, namely the natural food additives that is significant to address the issue of sustainable chemical processes at industrial and academia levels. In recent years, with more researchers increasingly investigating the chemical properties of food additives, their future applications have been evident and prominent in organic catalysis and green nanoparticle synthesis preparation. The current finding of this review identify one of the future challenges in the use of food additives as green catalyst is the stability and miscibility of the food additives, especially in large-scale operation, with deemed to be researched and reported in the future.



Scheme 28 Mechanism of dihydropyrano[2,3-g]chromenes synthesis. Reaction condition: malononitrile (2.0 mmol), aryl aldehyde (2.0 mmol), 2,5-dihydroxy-1,4-benzoquinone (1.0 mmol), sodium saccharin (0.1 mmol) under microwave irradiation. *Notes:* Ar (Aromatic)

Table 4 Comparison of different methods and their reactions' yields in the syntheses of dihydropyrano[2,3-g]chromenes **102**

Catalysts	Conditions	Time (min)	Yield (%)
Meglumine	Water/Ethanol/Microwave	15	43
1-Butyl-3-methylimidazolium tetrafluoroborate	Water/Ethanol/Microwave	8	57
Sodium phthalimide	Water/Ethanol/Microwave	10	70
Sodium benzoate	Water/Ethanol/Microwave	25	64
Triethylamine	Water/Ethanol/Microwave	20	75
Saccharin	Water/Ethanol/Microwave	30	52
Sodium saccharin	Water/Ethanol/Microwave	8	90

min (minute), % (percent)

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Compliance with ethical standards

Conflict of interest There is no conflict of interest to be declared in this manuscript.

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