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REVIEW

Generation of new carbon–carbon and carbon–heteroatom bonds mediated by agro-waste extracts: a review

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Abstract

Agro-waste extracts are considered green solvents since they are easy to handle, readily accessible from natural waste feedstock, biodegradable and recyclable. Therefore, the employment of these extracts in reaction media has emerged as the most useful and eco-friendly alternative in modern organic chemistry. Here, we review recent developments for the generation of new carbon–carbon and carbon–heteroatom bonds mediated by agro-waste extracts. We show that these aqueous extracts have great applicability in several transformations, including condensations, oxidations, multicomponent and coupling reactions. The challenges and advantages on the use of water of agro-waste extracts in synthetic methodologies is also detail.

Keywords Agro-waste extracts · Biorenewable extracts · Sustainable methodologies · Green · Chemistry

Introduction

The 12 principles of green chemistry formulated by Anastas and Warner (1998) have enabled the design of environmentally benign products and processes over the last years (Anastas and Eghbali 2010; Anastas and Zimmerman 2006). The application of these concepts has notably received special attention in organic synthesis due to their applicability as green reaction media in the development of sustainable methodologies (Sheldon 2012). In particular, the "use of safer solvents and auxiliaries" (5th principle) associated with the "use of renewable feedstocks" (7th principle) has been considered a powerful advance in modern organic chemistry (Ruslan et al. 2021).

In this regard, several biomass-based organic solvents have been applied for the generation of new carbon–carbon and carbon–heteroatom bonds (Sydnes 2019; Gamdeepan et al. 2019; Corrêa et al. 2015). The most commonly bio-derived solvents used are cyrene (Camp 2018), ethyl lactate (Asthana et al. 2005; Mäki-Arvela et al. 2014), glycerol (Sonnati et al. 2013; Díaz-Álvarez et al. 2014) and 2-methyltetrahydrofuran (Alcantara and de Maria 2018). Furthermore, biomass-based organic solvents have efficiently replaced traditional solvents improving the selectivity and yield in several transformations (Henderson et al. 2011; Prat et al. 2013). For instance, Cyrene which is obtained from cellulose may substitute dipolar aprotic solvents such as *N*-methyl-2-pyrrolidone, dimethyl sulfoxide or dimethylformamide (Sherwood et al. 2014; Khoo et al. 2015). Despite the good applicability of these biomass-based organic solvents, unwanted organic waste is still generated after the reaction workup.

To minimize the generation of unwanted organic solvents, biobased aqueous solvents derived from fruits have been employed for this purpose (Misra et al. 2012; Gulati et al. 2020a, b; Nasrollahzadeh et al. 2020; Das 2020a). In this context, several fruit juices have been successfully applied to solve this issue, for instance, by using pineapple (Patil et al. 2011), watermelon, coconut (Halder et al. 2019; Fonseca et al. 2009), tamarind and lemon (Saha et al. 2018; Vekariya et al. 2016; Kumari et al. 2020; Khan et al. 2018; Dutta et al. 2019a) in the reaction media.

Likewise, the use of water in organic reactions can definitely decrease environmental pollution because this solvent is highly abundant, inexpensive, nonvolatile, nonflammable, inexpensive and very safe (Kitanosono et al. 2018; Simon and Li 2012; Li and Chen 2006). Notably, the use of agro-waste ashes associated with aqueous solution or simply known as water of agro-waste extracts has emerged as a sustainable alternative in modern synthetic organic chemistry

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(Hooshmand et al. 2019). The employment of water of agro-waste extracts is also advantageous comparing to traditional organic solvents since theses extracts are readily prepared from natural waste materials, avoiding high-cost industry processes. (Talukdar and Deka 2016; Schmitt et al. 2021). Thus, undoubtedly, the use of water of agro-waste extracts is highly desirable in organic synthesis.

In 2017, Bora and coworkers revised previous achievements regarding the application of water of agro-waste extracts in organic synthesis (Sarmah et al. 2017a). However, a number of publications related to the application of these extracts in organic chemistry have significantly increased since the advances related to the formation of new carbon–carbon and carbon–heteroatom bonds are updated day by day (Venkateswarlu 2021).

Considering the relevance of carbon–carbon and carbon–heteroatom bond-forming reactions and the eco-friendly aspects of water of agro-waste extracts, herein we present an overview focus on the development of synthetic methodologies mediated by water of agro-waste extracts. For a better discuss, this review was divided into 4 sections: (i) general aspects, (ii) carbon–carbon bond-forming reactions, (iii) carbon–heteroatom bond formation and (iv) multicomponent reactions.

General aspects of agro-wastes

The development of appropriate destinations of agricultural biomass wastes has attracted special attention since it usually demands further treatment which is associated with high cost (Udugama et al. 2020; Cattaneo et al. 2021; Freitas et al. 2021). However, these agricultural biomass wastes could be converted into respective ashes which provide them several applications (Balakrishnan et al. 2011; Swain et al. 2019; Vivek et al. 2019; Patil et al. 2020). For instance, they have been successfully used in solid state fermentation (Sadh et al. 2018), biofertilizer (Lim and Matu 2015) and the chemical industry (Azat et al. 2019; Guzmán et al. 2016; Roselló et al. 2017). In this context, heterogeneous catalysis is the most common application of agro-waste ashes in applied chemistry (Roldan-Carmona et al. 2014; Nath et al. 2019; Halder et al. 2020a; Das et al. 2020b; Lalhmangaihzuala et al. 2021; Laskar et al. 2019a).

In terms of its economic feasibility, the employment of ashes is very desirable because the oxides might be produced directly from municipally biomass wastes, avoiding the high feedstock and transportation costs (Freitas et al. 2021; Lai et al. 2017). Furthermore, the use of agro-waste ashes is preferable than the conventional inorganic catalysts since it can be obtained from renewable resources, which also generates environmental and economic benefits (Abdullah et al. 2017; Udugama et al. 2020; Nabora et al. 2019).

Similarly, water of agro-waste extracts has attracted special since these extracts are inexpensive, biodegradable, inexpensive and easily obtained from biomass residues. According to literature reports, water of agro-waste extracts has a basic nature, containing different alkaline and alkaline earth metal carbonates and/or hydroxides (Deka et al. 2007; Jenkins et al. 1996). These peculiarities of water of agro-waste extracts might provide them unique applications in a wide range of reactions.

Regardless the type of water of agro-waste extracts, generally it has been used a standard protocol for the preparation of desired aqueous extracts (Boruah et al. 2015a). In fact, water of agro-waste extracts are prepared by burning the biomass residue into respective ashes, which are further suspended in distilled water in a glass erlenmeyer and stirred from 15 to 120 min at room temperature, depending on the nature of agro-waste. Afterward, the filtration of this aqueous mixture provides the corresponding water of agro-waste extracts (Fig. 1). The final solution has a unique basic nature and generally contains a stable mixture of alkali metal carbonates which are particularly useful as a basic catalytic media (Deka et al. 2007; Neog and Deka 2013).

In spite the sole procedure for the preparation of water of agro-waste extracts, the composition of these aqueous solution is most likely variable and it depends on several features, including diversity of soils, cultivation form, precipitation levels and difference in the plant species (Vassilev et al. 2013). Moreover, the origin of the plants is also particularly relevant due to different availability and metallic composition of the soil (Laing et al. 2009; Delaquis et al. 2016). Thus, different water agro-waste extracts are study over the world and notably applied in organic synthesis. The following sections will disclose the relevance of aqueous extracts in the generation of new carbon–carbon and carbon–heteroatom bonds.

Carbon–carbon bond formation

The formation of new carbon–carbon bonds is a well-recognized challenge in organic chemistry and several methods have been developed over the last years (Ravelli et al. 2016). More recently, carbon–carbon bond-forming reactions employing eco-friendly conditions have received special attention in modern organic chemistry (Kamanna and Khatavi 2020). In this section, we will discuss and summarize the peculiarities of agro-waste extracts for the construction of new carbon–carbon bonds in a series of transformations such as cross-coupling, condensations and Michael addition reactions.

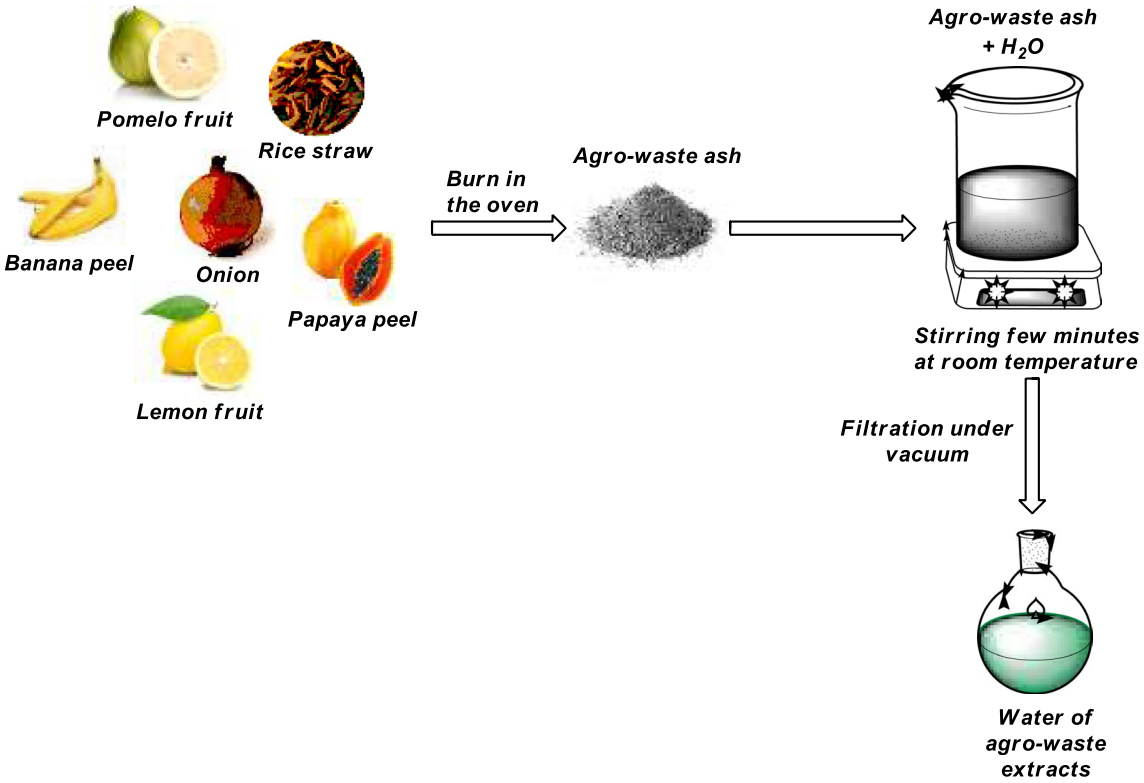


Fig. 1 Extraction of aqueous solutions from agro-waste. Basically, the biomass waste is burned into respective ash which are further suspended in distilled water in an erlenmeyer and stirred for few minutes at room temperature. Next, the filtration of this solution affords the respective water of agro-waste extracts

Cross-coupling reactions

Transition metal-catalyzed reactions are a well-recognized approach to form carbon–carbon bonds, and several methodologies have been reported (Seechurn Johansson et al. 2012; Magano et al. 2011; Nahra and Cazin 2021), including Claisen rearrangement (Shi et al. 2021), conversion of aldehydes to ketones (Yan et al. 2021), synthesis of heterocyclic compounds (Naveen 2021) and cross-coupling transformations (Sebastián and Morales 2019; Mohjer et al. 2021). In particular, the Suzuki–Miyaura cross-coupling reaction has become one of the most applicable methodologies for the construction of new carbon–carbon bonds under mild conditions (Sherwood 2020; Aabaka et al. 2021).

In 2015, Boruah and coworkers described a suitable protocol for the Suzuki–Miyaura cross-coupling reaction in the presence of water extract of banana catalyzed by palladium acetate (Boruah et al. 2015b). The cross-coupling reaction proceeded very well in extract of banana at room temperature, allowing the preparation of desired products in high yields in very short reaction times (Fig. 2, method A). Interestingly, the reaction was carried out without the use of any external base most likely due to the basic nature of the aqueous extract.

In another publication, the same research group presented other advances in this cross-coupling transformation using water extract of rice straw ash in the reaction media (Boruah et al. 2015a). Similarly, interesting results were achieved and the corresponding biaryl compounds were obtained from 45 to 90% yields (Fig. 2, method B). Moreover, a significant feature of this work was the reusability of the catalytic system, which proved to be highly efficient until the 5th cycle with no significant loss of activity. An improvement in the Suzuki–Miyaura reaction revealed a better activity of pure rice straw ash compared with its aqueous extract, most likely due the generation in situ of palladium nanoparticles (Mahanta et al. 2016). Nonetheless, further studies disclosed that water of agro-waste extracts is also useful for the reduction of palladium(II) into respective nanoparticles through a green process (Dewan et al. 2018). Despite the efficiency of agro-waste extracts in reductive processes, these extracts have essential importance as base in the Suzuki–Miyaura reaction due their inherent alkaline nature.

Another interesting protocol for the generation of new carbon–carbon bonds via Suzuki–Miyaura reaction was described by Bora's group (Sarmah et al. 2016). In this work, the authors reported the synthesis of biaryl compounds via a

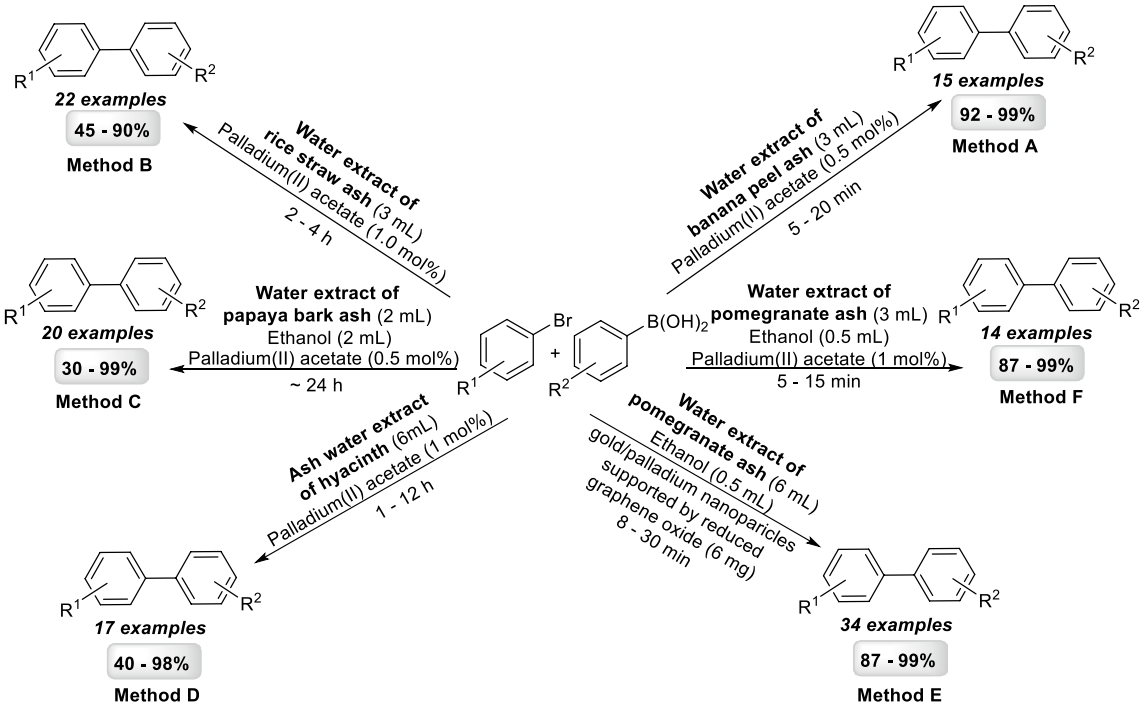


Fig. 2 Different methodologies for Suzuki–Miyaura reaction in the presence of agro-waste extracts catalyzed by palladium. Aryl boronic acids and aryl bromides reacted efficiently under optimized conditions, furnishing the corresponding biaryl compounds in good yields

cross-coupling between aryl halides and boronic acids in the presence water extract of papaya bark ash. The reaction was carried out employing 0.5 mol% of palladium(II) acetate and a mixture of extract and ethanol (1:1), which afforded the corresponding products in good yields (Fig. 2, method C). Later, the same research group also applied ash water extract of hyacinth as an eco-friendly base source in the same cross-coupling reaction and they also achieved very fruitful results (Sarmah et al. 2017b). In this regard, 17 examples of coupled products were efficiently synthesized from 40 to 98% yields (Fig. 2, method D).

Appa et al. applied water extract of pomegranate ash as a green medium for the Suzuki–Miyaura reaction catalyzed by gold–palladium nanoparticles supported by reduced graphene oxide (Appa et al. 2021a). The reaction could tolerate both electron-donating and electron-withdrawing substituents on the aromatic ring of boronic acid as well as aryl bromide, affording the desired products in very high yields (Fig. 2, method E). Experimental results also suggest that the cross-coupling reaction involves a heterogeneous process. In fact, the recyclability of the gold–palladium nanoparticles supported by reduced graphene oxide–water extract of pomegranate ash system was evaluated and no significant loss in catalytic activity was observed until the 3rd cycle.

Following their studies on the application of water extract of pomegranate ash, Lakshmidevi et al. also explored a series of palladium–mesoporous silica catalysts in the same cross-coupling reaction (Lakshmidevi et al. 2021). In this sense, the protocol was applicable to substrates bearing both electron-donating and electron-withdrawing substituents, furnishing the corresponding products in very good yields.

In addition, Venkateswarlu's group has also successfully applied palladium(II) acetate as a catalyst for the Suzuki–Miyaura reaction in the presence of water extract of pomegranate ash (Appa et al. 2019a). Similarly, the combination of palladium catalyst and water extract of pomegranate ash proved to be a renewable system for the preparation of biaryl compounds, affording the desired products in very good yields (Fig. 2, method F). Very recently, biaryl compounds have also been efficiently obtained via Suzuki–Miyaura reaction mediated by water extract of radish leaves (Kempasiddaiah et al. 2021).

The Sonogashira reaction is another common and important cross-coupling transformation to accomplish new carbon–carbon bonds (Mohajer et al. 2021). Due to the high demand for the development of green synthetic approaches, the use of agro-waste extracts in this reaction has also become highly desirable.

In this context, Dewan et al. reported a palladium-catalyzed Sonogashira cross-coupling reaction in the presence of water extract of banana peel ash (Dewan et al. 2016a). Various reaction parameters were evaluated in this

transformation, and the best results were found by using 1 mol% of palladium(II) acetate and a mixture of water extract of banana peel ash/ethanol in a 1:1 ratio at 60 °C. The reaction tolerated a variety of aryl iodides containing both electron-withdrawing and electron-releasing substituents, as well as aromatic and aliphatic alkynes, furnishing the respective products in very high yields (Fig. 3, method A).

Water extract of papaya bark ash has also been successfully applied in the Sonogashira cross-coupling reaction (Dewan et al. 2016b). According to the author's findings supported by experimental evidence, this extract played an essential dual role in this reaction, furnishing the alkaline medium and acting simultaneously as a reducing agent, generating in situ of palladium nanoparticles. Thus, the preparation of the desired products was accomplished in the absence of any external base, ligand and/or copper catalyst. In general, the reaction was carried out smoothly, providing the corresponding cross-coupled products in good yields (Fig. 3, method B).

Very recently, Liu and coworkers have described a new protocol for palladium-catalyzed cross-coupling reaction of indoles and iodoarenes in the presence of water extract of pomelo peel ash (Sun et al. 2021). A systematic study developed by the authors showed a better selectivity and reaction efficiency in three-component mixed solvents. In fact, the cross-coupling reaction preferred to take place at position 2 of indole by carrying the reaction with 10 mol% of palladium(II) chloride, 100 °C and dimethyl sulfoxide/acetonitrile/water extract of pomelo peel ash (0.5:0.5:1.0 mL). The reaction well tolerated both electron-releasing and electron-withdrawing substituents attached on the aromatic rings of iodoarenes, affording the corresponding products in very good yields (Fig. 4). Similarly, substituted indoles containing methyl, methoxy and halides groups reacted very smoothly with iodobenzene, giving the respective cross-coupling products in 59–89% yields.

On the other hand, the Ullman reaction is also a convenient catalyzed coupling reaction widely applied for the generation of new carbon–carbon bonds and it allows the preparation of biaryl compounds (Chen et al. 2017). In a pioneering work, Lakshmidevi et al. reported a novel and eco-friendly medium based on water extract of pomegranate ash for this coupling reaction (Lakshmidevi et al. 2018).

The influence and activity of different agro-waste water extracts, such as water extract of rice straw ash, water extract of banana peel ash, water extract of papaya bark ash and water extract of lemon fruit shell ash, employing 4-iodoanisole as a standard substrate were deeply studied (Fig. 5). In this regard, water extract of pomegranate ash was the best extract option affording the desired product in 99% yield. Experimental analysis of X-ray photoelectron spectroscopy and X-ray spectroscopy disclosed the presence of potassium, magnesium, calcium, carbon, oxygen and chlorine in the water extract of pomegranate ash. These findings also revealed the highest amount of potassium in water extract of pomegranate ash solution among all extracts.

The generality of the Ullman reaction was also evaluated by applying various substituted aryl halides, containing

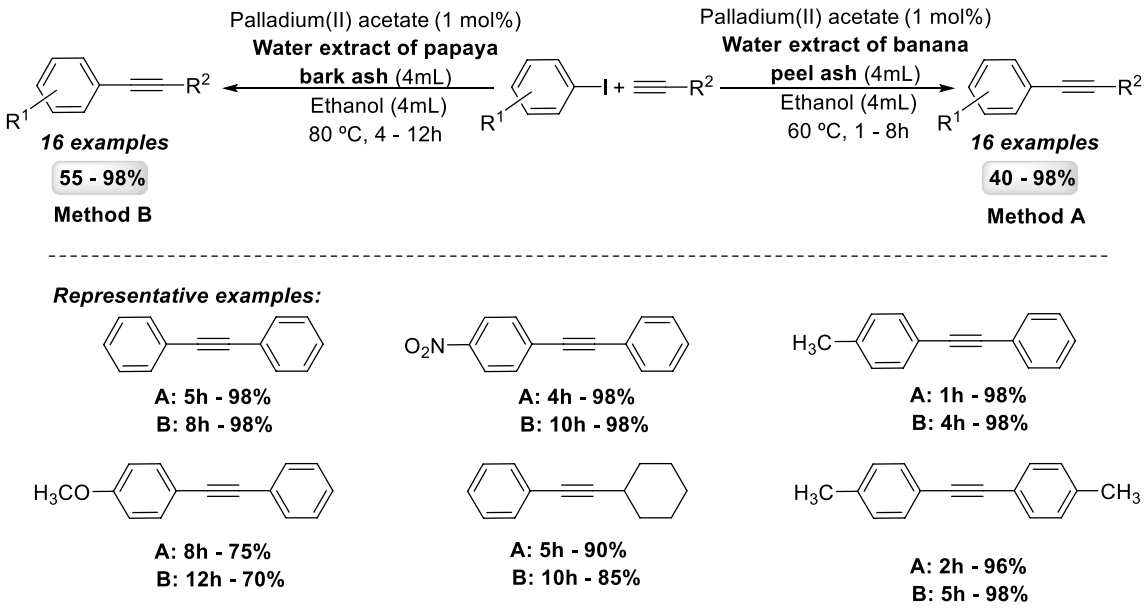


Fig. 3 Sonogashira cross-coupling reaction in agro-waste extracts. A variety of aryl iodides reacted smoothly with boronic acids in water extract of banana peel ash, affording the respective products in 55–98% yields (method A). Aryl iodides and terminal alkynes were coupled efficiently in the presence of water extract of papaya bark ash, furnishing the desired products in 40–98% yields (method B)

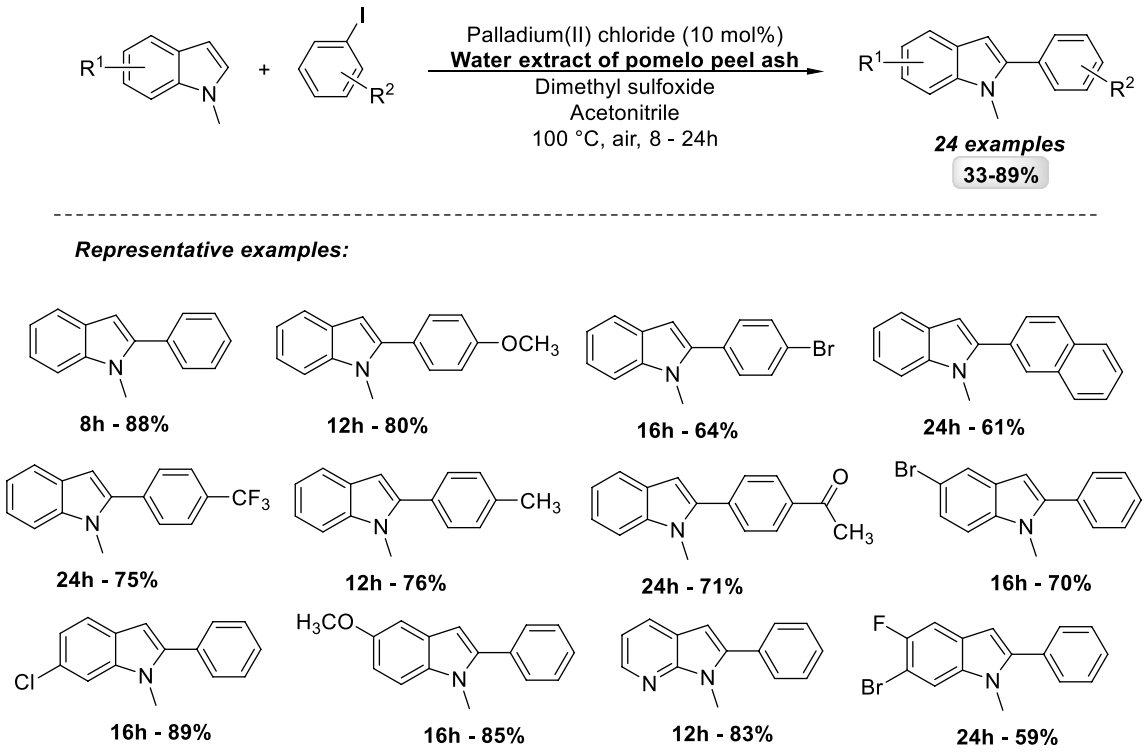


Fig. 4 Cross-coupling of indole and iodoarenes in water extract of pomelo peel ash. A variety of indoles were treated with iodoarenes to afford the corresponding products in moderate to high yields

electron-releasing and electron-withdrawing groups attached to the aromatic ring. In general, aryl halides were much more reactive than bromides and chloride analogs, affording the corresponding coupling products in higher yields.

Likewise, symmetrical biaryl compounds can also be accessed by homocoupling of aryl boronic acids (Vasconcelos et al. 2019). As an eco-friendly example, these compounds were recently obtained via palladium-catalyzed aerobic homocoupling of aryl boronic acids mediated by water extract of pomegranate ash (Appa et al. 2021b). A wide range of desired products were synthesized in very good yields via sp^2-sp^2 homocoupling reaction by using 1 mol% of palladium(II) acetate at room temperature in the presence of water extract of pomegranate ash (Fig. 6).

Aldol and condensation reactions

Aldol and condensation reactions are well-known alternatives for the generation of new carbon–carbon bonds and the catalytic fashion of these transformations has been widely reported over the years (Yao et al. 2018; Poole et al. 2019; Li et al. 2019). Among them, the Henry reaction, which is also well recognized as a nitro aldol reaction, has been widely applied for the generation of new carbon–carbon bonds (Rajkumari et al. 2019).

In 2016, Surneni et al. described a sustainable protocol for this reaction employing water extract of banana and water extract of rice straw ash in the reaction media (Surneni et al. 2016). Both natural feedstock extracts exhibited a dual role in this nitro aldol reaction, acting as a base as well as solvent. It should be noted that water extract of banana was the best extract option when compared to water extract of rice straw ash, since the desired products were efficiently obtained in lower reaction times under similar reaction conditions (Fig. 7).

In 2019, Dwivedi's group described a novel methodology for the preparation of 3-hydroxy-oxindole by decarboxylative aldol reaction of *β*–ketoacid and isatin derivatives promoted by water extract of rice straw ash (Dwivedi et al. 2019a). The reaction pathway occurs mainly due to the alkaline nature of extract, which contributes to the decarboxylation of *β*–ketoacid and allows in situ formation of methyl enolate **I**, which is the key intermediate for this transformation. Next, this intermediate smoothly reacts with isatin derivatives via an aldol-type reaction to give the respective products. Notably, the protocol was applicable for the preparation of 17 target molecules in very high yields (Fig. 8). Moreover, a further experiment at the gram scale provided the respective 3-hydroxy-oxindole in quantitative yield, which is also a great advance from a synthetic point of view.

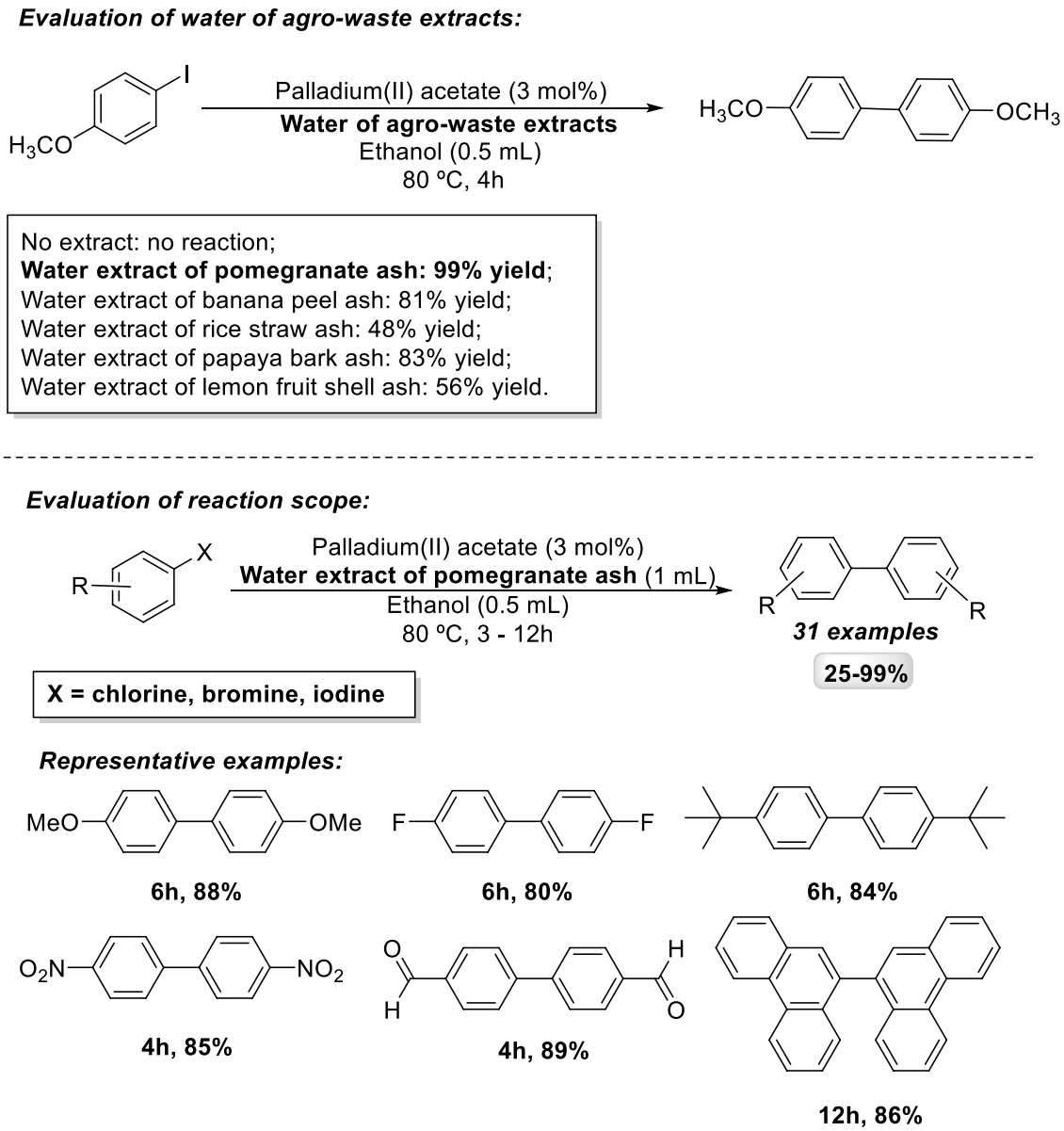


Fig. 5 Ullmann reaction in the presence of water extract of pomegranate ash. Palladium(II) catalyzed efficiently the homocoupling of aryl halides, and the desired products were obtained in moderate to excellent yields (25–99%)

Dutta et al. reported a very efficient method for the preparation of α-diazo-β-hydroxy esters via aldol condensation of aldehydes with ethyl diazoacetate promoted by a water extract of banana–dimethyl sulfoxide system (Dutta et al. 2019b). The reaction proceeded very smoothly furnishing the respective α-diazo-β-hydroxy esters from 43 to 85% yields (Fig. 9). The protocol was tolerant to both electron-donating and electron-withdrawing substituents present on the aromatic ring of aldehyde. Regarding the synthetic applicability, the sequential conversion of α-diazo-β-hydroxy esters into the respective β-keto esters was also described. Moreover, the generality of the protocol was also extended for the synthesis of imidazo[1,2-a]pyridine-3-carboxylates via a one-pot approach.

In recent years, the use of water of agro-waste extracts has become a cleaner alternative for condensation reactions (Patil et al. 2021). In this context, Chia's group developed a suitable catalytic system for the condensation of aldehydes with 4-hydroxycoumarins or indoles promoted by the water extract of onion peel (Chia et al. 2018). In this regard, the reaction between aromatic aldehydes and a series of 4-hydroxycoumarins provided the corresponding bisenols in 62–94% yields (Fig. 10, method A). Analogously, a variety of indoles underwent condensation reactions in the presence of aromatic aldehydes in the presence of the same water

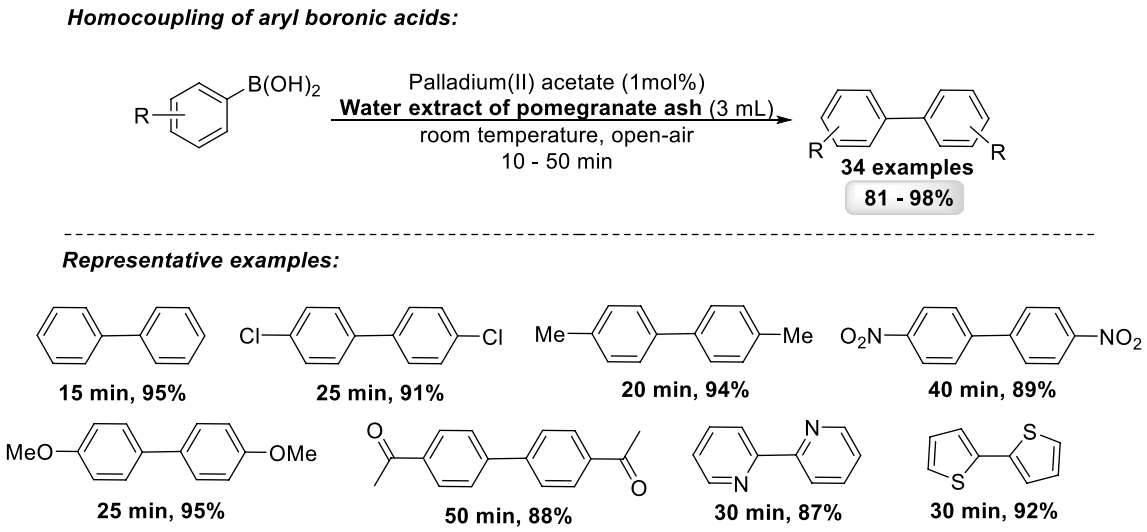


Fig. 6 Homocoupling of aryl boronic acids in water extract of pomegranate ash. The homocoupling reaction of aryl boronic acids was efficiently carried out employing 1 mol% of palladium(II) acetate, furnishing the respective products in high yields (81–98%)

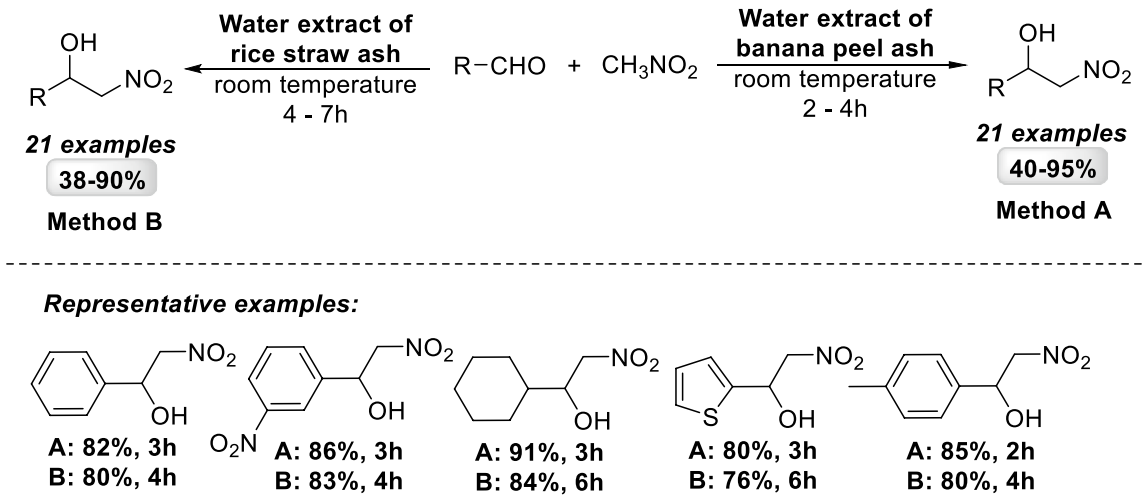


Fig. 7 Henry reaction promoted by water extract of banana or water extract of rice straw ash. Both aqueous extracts were efficient base and solvent for the preparation of nitro aldol adducts in moderate to high yields

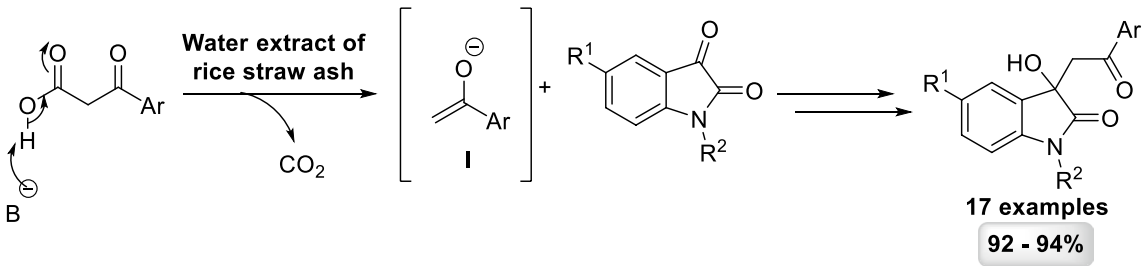


Fig. 8 Decarboxylative aldol reaction of *β*–ketoacid and isatin in water extract of rice straw ash. The desired 3-hydroxy-oxindoles were obtained in 92–94% yields through decarboxylative aldol reaction of *β*–ketoacid and isatin derivatives

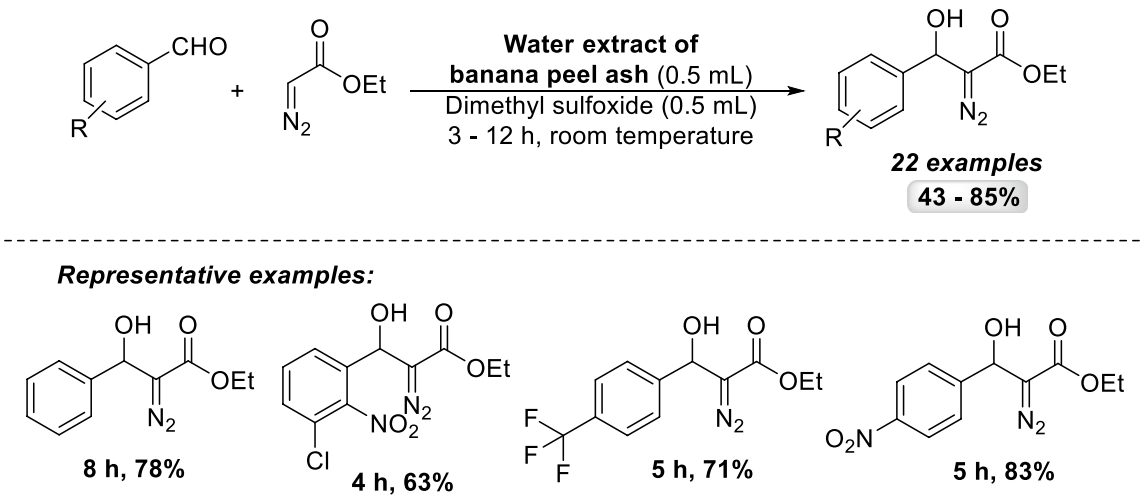


Fig. 9 Preparation of α-diazo-β-hydroxy esters by water extract of banana–dimethyl sulfoxide system. The reaction proceeded very well in the mixture of water extract of banana and dimethyl sulfoxide (0.5 mL:0.5 mL), affording in respective products in up to 85% yield

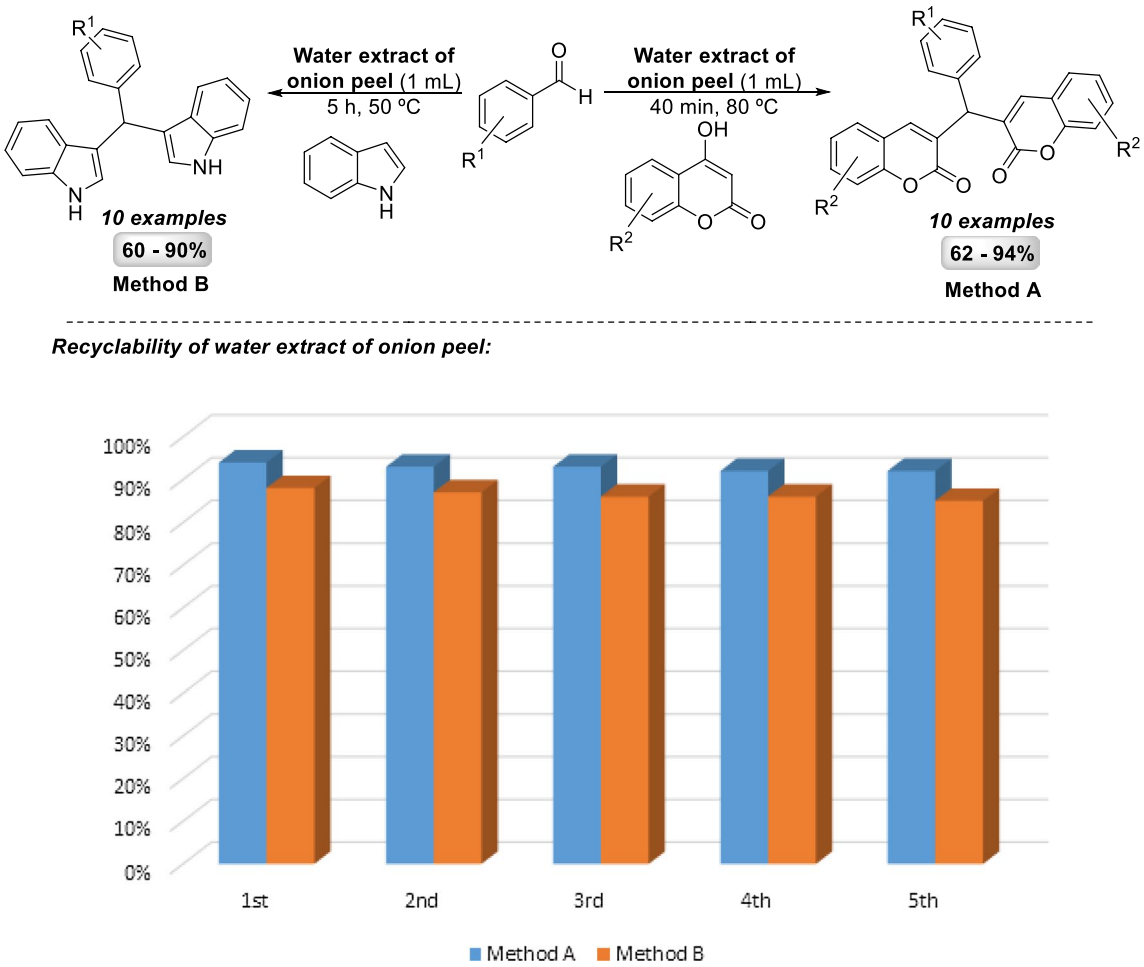


Fig. 10 Condensation reaction promoted by water extract of onion peel. The condensation of aldehydes with both 4-hydroxycoumarins and indoles was highly efficient, affording the corresponding products in 60–94% yields. The water extract of onion peel was also recovered and reused for up to five times without loss of activity

extract of onion peel catalytic system (Chia et al. 2019). Generally, the reaction also proceeded well furnishing the desired products in very good yields (Fig. 10, method B).

Moreover, in both methodologies, the water extract of onion peel was also recovered and reused in further experiments. Remarkably, water extract of onion peel conserved its catalytic activity and efficiency for up to five recycling experiments. Thus, this extract was considered a green alternative for the construction of carbon–carbon bonds via condensation reactions. Further studies also demonstrated that waste curd water might be a suitable reaction promoter for the condensation of aldehydes with indoles (Rajput et al. 2019).

Badiger and Kamanna (2021) developed a Knoevenagel condensation of aromatic/heteroaromatic aldehydes with malononitrile promoted by water extract of orange fruit peel ash. By this approach, 16 examples of unsaturated benzylidene derivatives were successfully prepared employing 3 mL of this extract. In general, the protocol was applicable for various substituted aromatic aldehydes and the respective Knoevenagel adducts were obtained in 82–96 yields (Fig. 11). Additionally, it was also observed a dual role of water extract of orange fruit peel ash and the extract acts as a catalyst and solvent in the condensation reaction.

Michael addition reaction

The Michael addition reaction is a particularly valuable approach for the generation of new carbon–carbon bonds and several synthetic strategies have been well documented (Wadhwa et al. 2018; Denisov et al. 2021; Das et al. 2021). For example, synthesis of 2-arylacetonitriles derivatives (Chen et al. 2021), asymmetric addition of aldehydes to β-nitrostyrenes (Gorde et al. 2021) and *anti*selective γ-nitroaldehydes (Schnitzer et al. 2020). Similarly, nitroalkanes have emerged as versatile and useful reagents in a wide range of transformations (Ballini and Palmieri 2018).

In this context, Kumar et al. reported a straightforward protocol for the Michael addition of nitroalkanes (Kumar et al. 2018). The methodology was tolerant for several functional groups on the phenyl ring of 3-methyl-4-nitro-5alkenyl-isoxazole, furnishing the respective products in 76 to 92% yields. Remarkably, in this reaction water extract of rice straw ash has shown a dual role, acting as a solvent and base.

In terms of the reaction mechanism, the carbonate anions from the aqueous extract abstract a proton from nitromethane, affording the respective nitrate ion. Next, this species undergoes conjugation addition with 3-methyl-4-nitro-5alkenyl-isoxazole, furnishing the conjugated addition product (Fig. 12). Furthermore, the protocol was also applicable for the preparation of 4-nitro butyric acid, which is a synthetic intermediate used for the synthesis of Bacoflen.

The development of synthetic approaches for functionalization of indole cores has significantly increased due to the wide range of applications of this heterocycle (Mondal et al. 2020; Abenante et al. 2020; Galardon 2021). In this context, the incorporation of a 2H-chromene ring at the position 3 of the indole core has attracted special attention from several researchers (Paul et al. 2014; Kumar et al. 2017; Rao et al. 2018; Gore et al. 2012). From an environmental point of view, water extract of lemon has been efficiently used as a promoter in the functionalization of indoles with substituted chromene derivatives (Vasantha et al. 2020). The versatility and efficiency of the protocol was investigated by

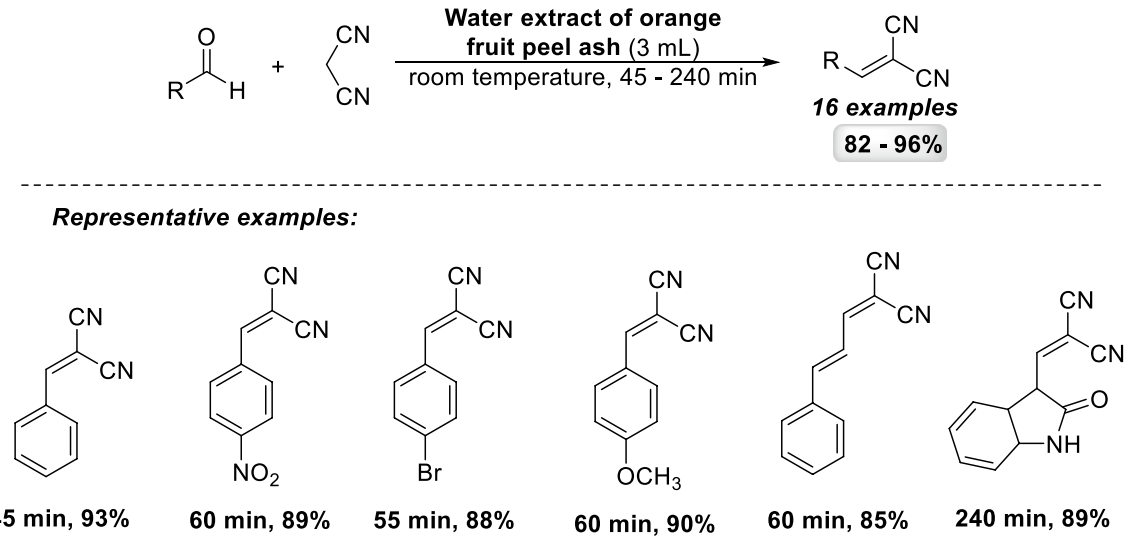


Fig. 11 Knoevenagel condensation promoted by water extract of orange fruit peel ash. Aromatic and heteroaromatic aldehydes react smoothly with malononitrile to afford the respective benzylidene derivatives in 82–96% yields

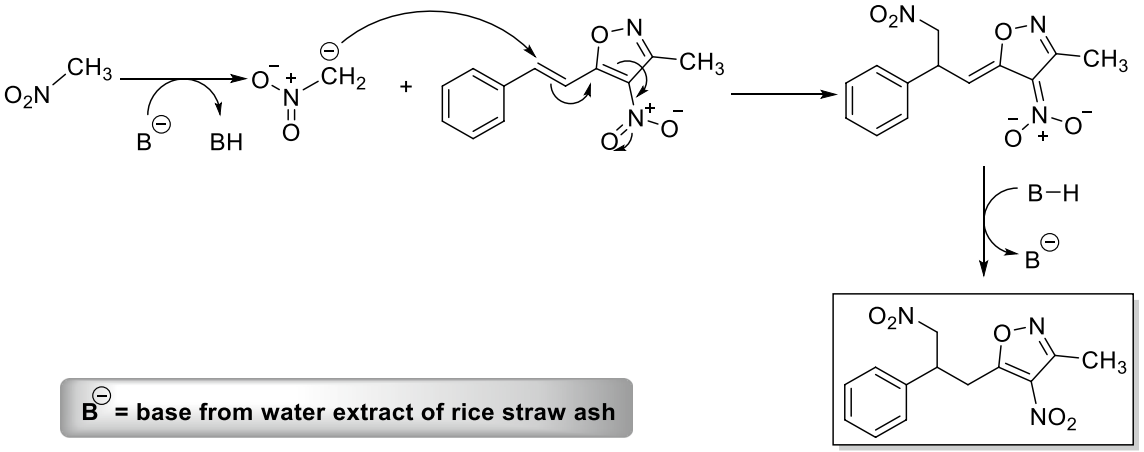


Fig. 12 1,6-Michael addition of nitro-alkane to 3-methyl-4-nitro-5-styryl-isoxazoles in water extract of rice straw ash. The base from the aqueous extract abstracts a proton from nitromethane to afford nitrate ion. Subsequently, nitrate undergoes conjugation addition with 3-methyl-4-nitro-5alkenyl-isoxazole to afford the reaction product (Kumar et al. 2018)

preparing 8 examples of alkyl-4-(1H-indol-3yl)-2-alkyl-4H-chromene-3-carboxylate derivatives (Fig. 13). In this view, the desired products were achieved with very good yields at room temperature.

Carbon–heteroatom bond formation

The development of new strategies for the generation of new carbon–heteroatom bonds is directly associated with accomplishing privileged organic compounds which might present biological, pharmaceutical and synthetic applications (Silva et al. 2020; Martins et al. 2020). In this regard, a wide range of methodologies that involve different reagents as well as solvents have been reported in the literature (Richards et al. 2021). Various eco-friendly methodologies for the generation of carbon–oxygen, carbon–nitrogen, carbon–sulfur and carbon–bromine will be accordingly summarized and discussed in this section.

Carbon–oxygen bond formation

The generation of new carbon–oxygen bonds is particularly valuable in modern organic synthesis since the respective products have shown unique biological and synthetic applications (Pan et al. 2019; Jiang et al. 2020). For example, phenols and their derivatives are important target molecules which contains a range of applications, including pharmaceuticals (Razavi-Azarkhiavi et al. 2016; Jarial et al. 2016; Tungmunnithum et al. 2018; Patra and Singh 2018), antioxidant (Wright et al. 2001; Amorati et al. 2003; Zeb 2020) and flavoring agents (Roston and Kissinger 1981; Maga 1992; Liang et al. 2009; Hayes et al. 2019).

As a consequence of phenols relevance, the development of new strategies to achieve these kinds of compounds has been broadly investigated (Batra et al. 2021). Among them, the oxidative hydroxylation of arylboronic acids has been considered a promising strategy to access phenols moieties (Upadhyay et al. 2021; Mahanta et al. 2021).

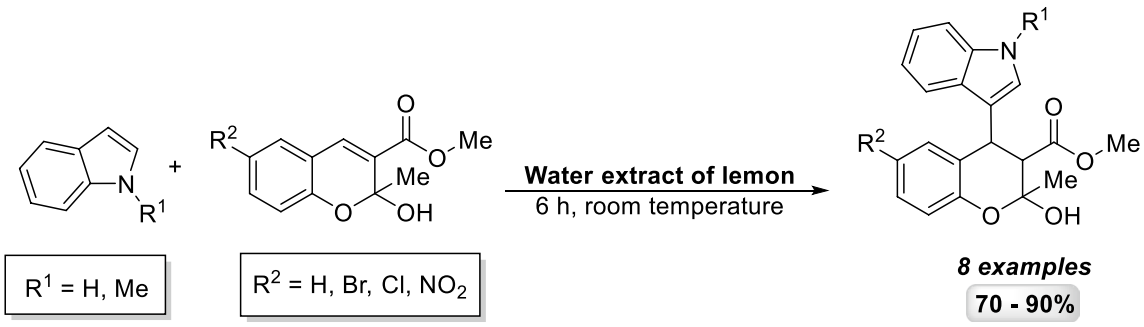


Fig. 13 Functionalization of indoles with chromenes promoted by water extract of lemon. Indoles were treated with substituted chromene derivatives during 6 h at room temperature, affording the corresponding products in 70–90% yields (Vasantha et al. 2020)

In this context, an elegant synthetic pathway to obtain phenols via *ipso*-hydroxylation of arylboronic acids was reported by Saikia et al (2015a). The reaction involves the treatment of aryl/heteroarylboronic acids with 30% aqueous hydrogen peroxide as an oxidant in the presence of water extract of rice straw ash. This straightforward procedure allowed the preparation of desired phenols in very high yields (Fig. 14, method A).

Furthermore, water extract of rice straw ash was also recovered from the reaction media and reused for the next transformations. In this study, it was observed that this extract maintained its efficiency until the 5th cycle without significant loss of extract activity.

Further studies developed by the same group demonstrated that water extract of banana peel ash is also green catalytic alternative for the *ipso*-hydroxylation of arylboronic acids (Saikia et al. 2016). In fact, 12 different examples of functionalized phenols were obtained from 90 to 97% yields under optimized reaction conditions (Fig. 14, method B). Moreover, the reusability of water extract of banana peel ash was also evaluated and the extract conserved its catalytic activity until the 5th reaction run.

Another interesting work for the preparation of phenol derivatives was described by Saikia and Borah (2015). In this study, the authors reported a new protocol for the preparation of respective phenols through the oxidation of aromatic aldehydes using hydrogen peroxide–water extract of rice straw ash as an oxidative system via the Dakin reaction (Fig. 15, method A). Alternatively, the Dakin reaction was also described employing water extract of banana peel ash under aerobic conditions (Saikia et al. 2015b). In this regard, hydrogen peroxide–water extract of banana also proved to be a very efficient system, affording phenol derivatives in 90–98% yields (Fig. 15, method B).

Regardless of the use of agro-waste extracts in the Dakin reaction, mechanistically, the extract has shown two important roles. First, the extract is mainly responsible for deprotonation of hydrogen peroxide due its well-known base nature. Furthermore, in the last step of the mechanism the extract most likely acts in hydrolyses of the aldehyde affording the corresponding product. Additionally, grape pomace extract was also applied in the oxidation of arylboronic acids, which efficiently replaced the activity of tannic acid in this reaction (Scoccia et al. 2016).

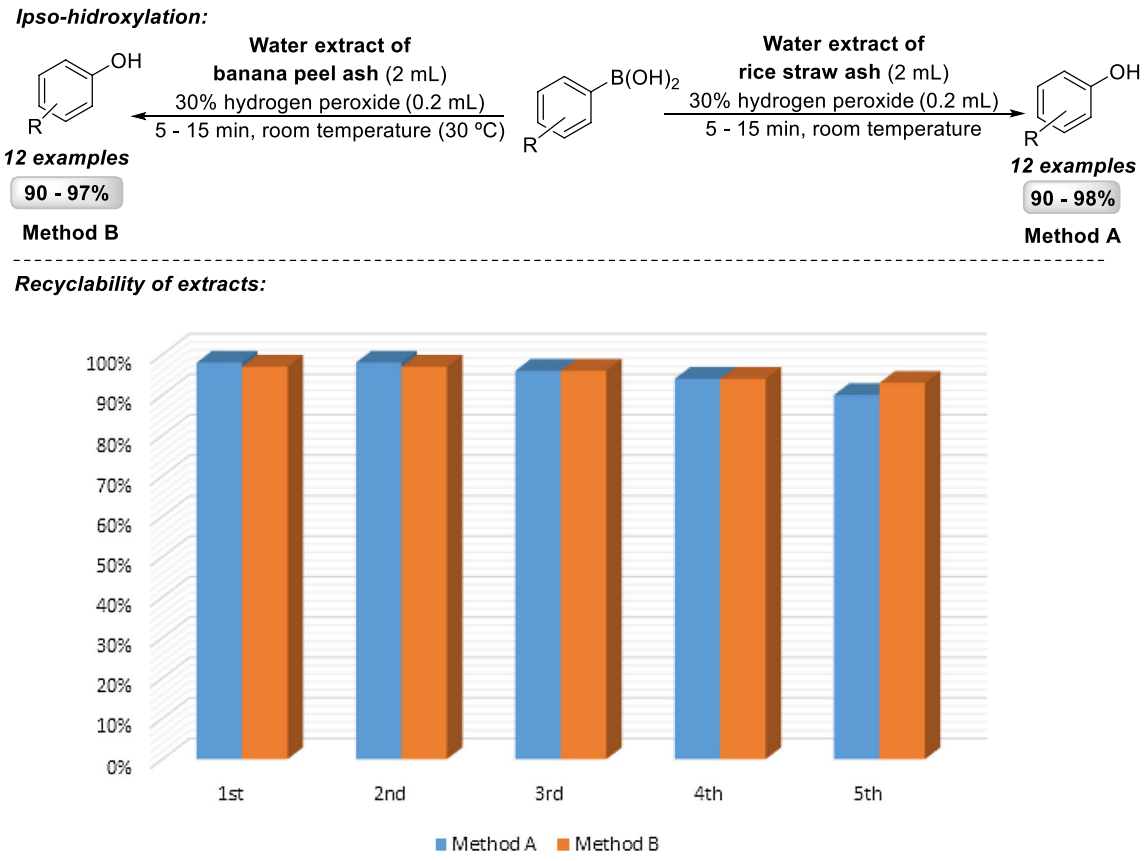


Fig. 14 *Ipso*-hydroxylation of arylboronic acids in agro-waste extracts. Water extract of rice straw ash and water extract of banana peel ash were efficient catalytic media for the *ipso*-hydroxylation of arylboronic acids, affording the corresponding products in 90–98%yields. Both aqueous extracts were recovered and reused in further experiments without significant loss of activity

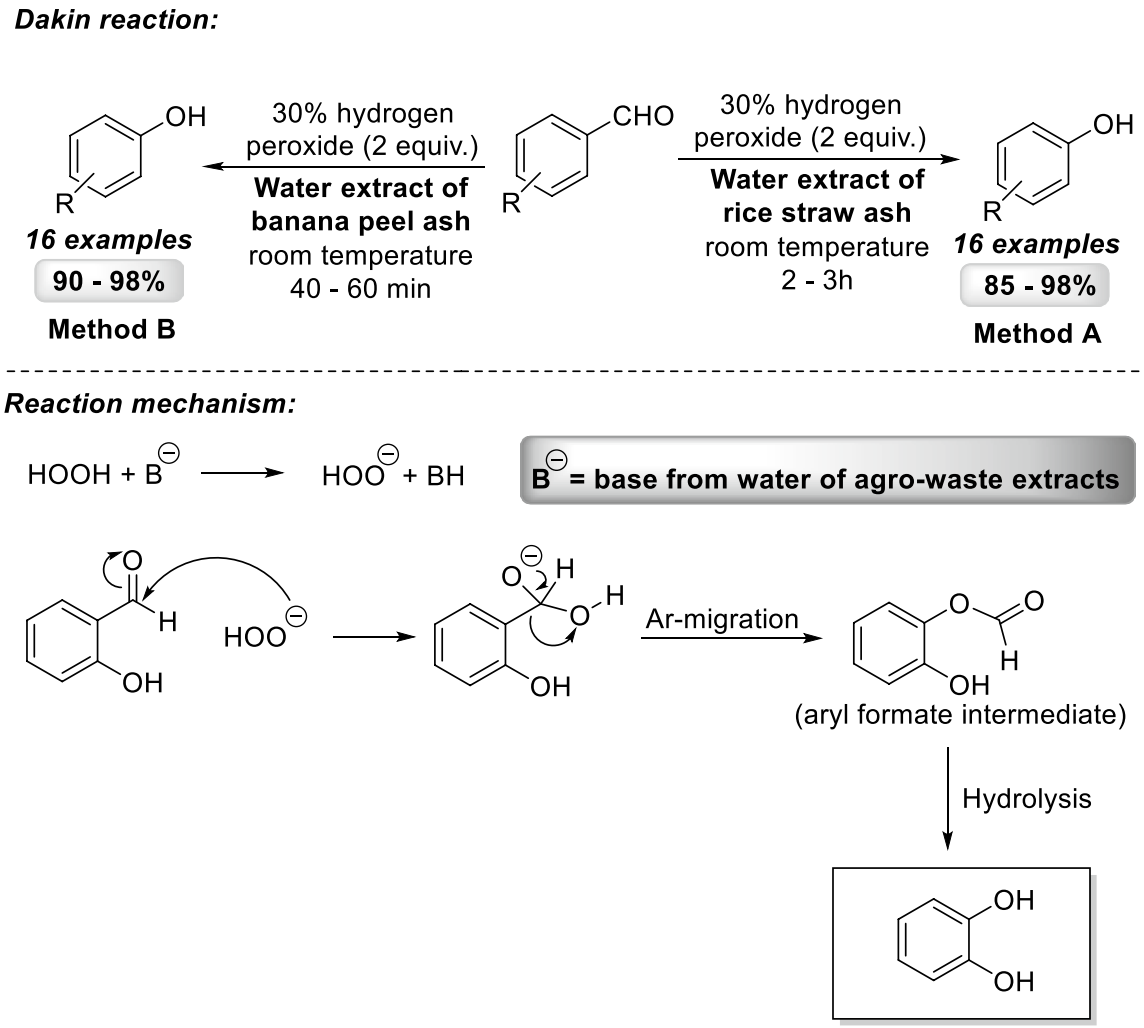


Fig. 15 Dakin reaction promoted by extract of rice straw ash and water extract of banana peel ash. Phenols were efficiently achieved through the oxidation of aromatic aldehydes using 2 equivalents of hydrogen peroxide in the presence of water of agro-waste extracts

On the other hand, benzamide derivatives have become attractive target molecules that have innumerous biological and pharmacological properties, including antimicrobial (Narayana et al. 2004), anticonvulsant (Foster et al. 1999), analgesic (Coats et al. 2004) and antitumor activities (Xu et al. 2006). In this regard, the synthesis of these kinds of compounds has been widely explored (Wang et al. 2011; Zeng and Guan 2011; Bhunia et al. 2017; Mitrofanov et al. 2017; Balbom et al. 2019). Generally, benzamide derivatives are conveniently obtained by reaction of aromatics and aliphatics alcohols with aniline (Wang et al. 2011), Beckmann rearrangement (Owston et al. 2007) or aminocarbonylation of aryl halides (Wu et al. 2010).

From an environmental point of view, Sun and coworkers reported a straightforward approach for the hydration of nitriles, which was promoted by water extract of pomelo peel ash (Sun et al. 2019). The methodology was very efficient, furnishing the respective benzamide derivatives in good yields without using any base, metal or organic solvent (Fig. 16). This protocol was also applicable for the preparation of selected aliphatic amides under similar reaction conditions.

Aiming to increase the versatility of the protocol, the authors also studied the recyclability of the extract. After completion of the reaction, the water extract of pomelo peel ash was recovered and reused for subsequent runs. In fact, the reused aqueous extract was very efficient until the fourth reaction run. In addition to the reusability study, three experiments were realized on a gram scale, and the corresponding amides were obtained in very good yields.

Bora and coworkers have notably developed convenient applications of calcined burnt peel ashes or their respective extracts for the preparation of a diversity of target molecules (Laskar et al. 2019b; Dewan et al. 2018). Recently, Das's group has reported a general and robust alternative for the construction of new carbon–oxygen bonds using water

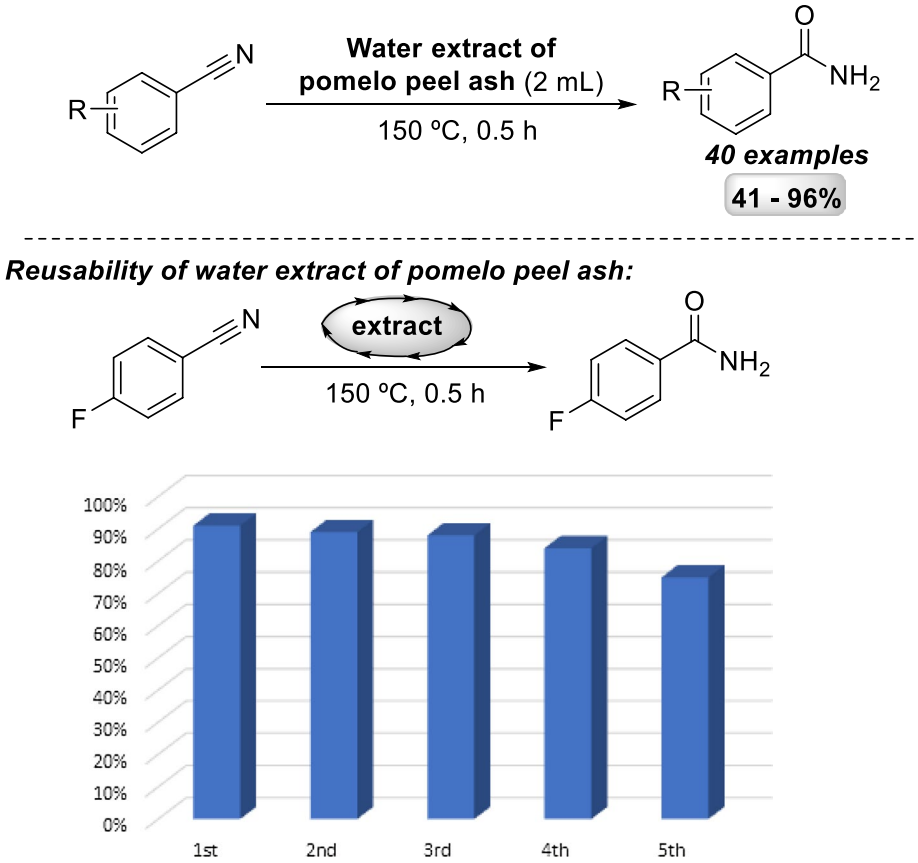


Fig. 16 Synthesis of benzamide derivatives promoted by water extract of pomelo peel ash. The desired amides were achieved in 41–96%yields at 150 °C via hydration of nitriles. Water extract of pomelo peel ash was recovered and efficiently reused until the fourth reaction run

extract of teak leaf (Das et al. 2020c). More specifically, the protocol was highly efficient for the hydration of nitriles and *ipso*-hydroxylation of arylboronic acids, affording the desired products in very good yields under mild reaction conditions (Fig. 17).

Notably, the authors found a dual role of water extract of teak leaf in all these transformations, acting as a base as well as solvent in the reaction media. In addition to carbon–oxygen bond formation water extract of teak leaf was also applicable as a greener alternative for *N*-arylation of imidazoles with phenylboronic acids and condensation of Knoevenagel condensation of aryl aldehydes with malononitrile under similar reaction conditions.

Carbon–nitrogen bond formation

Peptides represent an interesting class of nitrogen compounds that have shown great relevance from synthetic and biological points of view (Lenstra et al. 2014). Therefore, the preparation of peptides via carbon–nitrogen bond formation between two amino acid molecules has become particularly useful in modern organic chemistry (Bader et al. 2020; Gisemba and Aldrich 2020). Generally, traditional protocols for peptide synthesis require the use of bases, activating agents and coupling agent catalysts (Todorovic 2020).

In contrast, Konwar's group described an eco-friendly methodology for the peptide bond formation reaction using water extract of banana peel ash and ethylene glycol without any external base (Konwar et al. 2016). Several reaction parameters were tested for the peptide coupling reaction and the combination of water extract of banana peel ash and *N*-ethyl-*N*′-(3-dimethylaminopropyl) carbodiimide hydrochloride (EDC.HCl) in the presence of ethylene glycol proved to be the best option at room temperature. Remarkably, different benzoyl-protected amino acids smoothly reacted with amino acid methyl ester hydrochloride salts, affording the corresponding peptides in 58–95% yields (Table 1).

In addition, the recyclability of the water extract of banana peel ash/ethylene glycol catalytic system was also evaluated and it was efficient until the third reaction run. More recently, banana peel ash/ethylene glycol catalytic system has also been described as a green approach for the amide bond formation under microwave irradiation (Kamanna et al. 2020).

On the other hand, β-amino carbonyl/nitrile compounds have gained special attention since they are useful synthetic intermediates in several organic transformations (Yadav et al. 2003). In this context, Talukdar and Deka (2020) reported a convenient protocol for the synthesis of

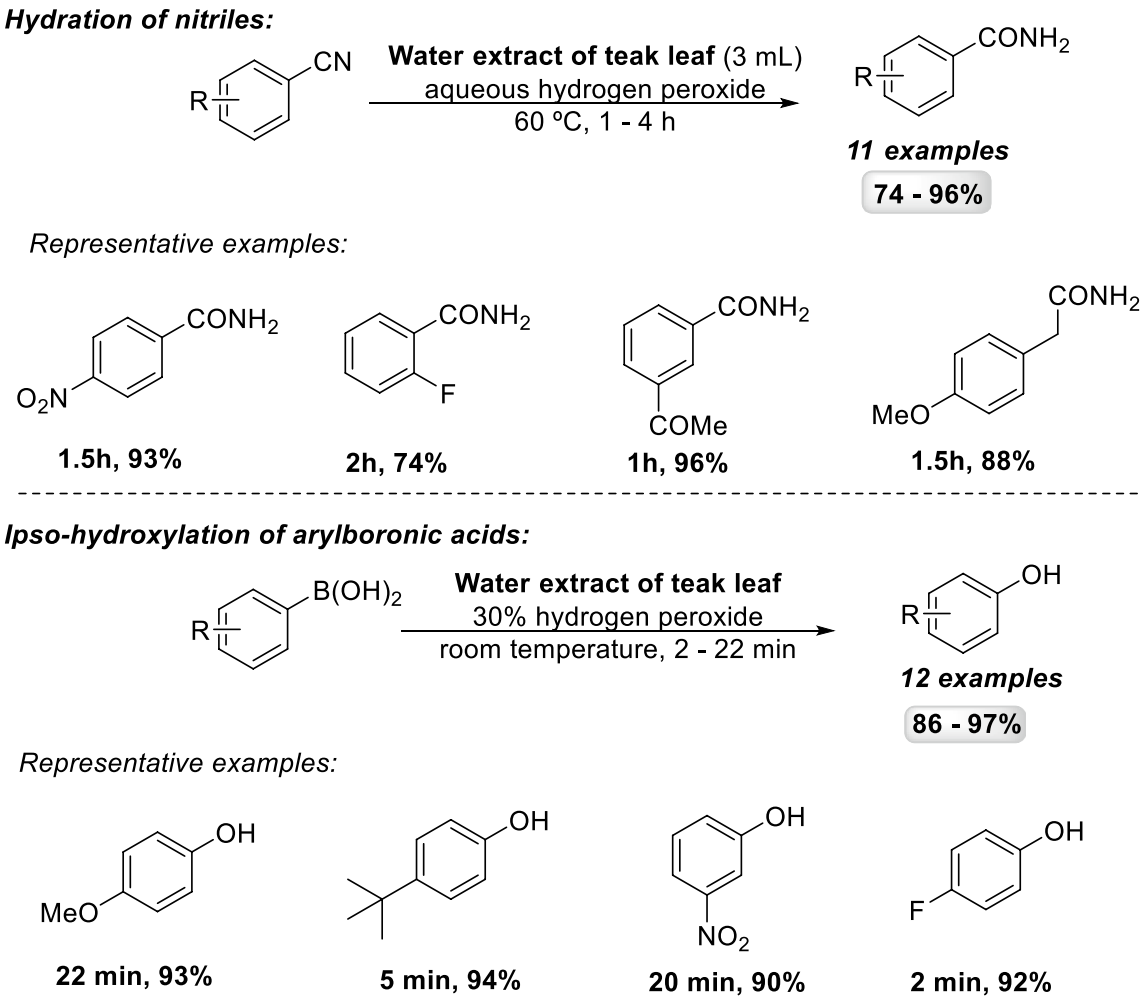


Fig. 17 Synthesis of amides and phenols promoted by water extract of teak leaf. Amides were obtained in 74–96% yields by the hydration of nitriles at 60 °C. Phenols were achieved in 86–97% yields by *ipso*-hydroxylation of arylboronic acids at room temperature

these compounds by the aza-Michael reaction catalyzed by water hyacinth ash.

Interestingly, amines reacted very smoothly with α,β-unsaturated carbonyl/nitrile compounds affording the corresponding Michael adducts in very good yields, under neat conditions (Fig. 18). Moreover, Baylis–Hillman adducts were also appropriate substrates furnishing the desired products from 87 to 96% yields under optimized conditions.

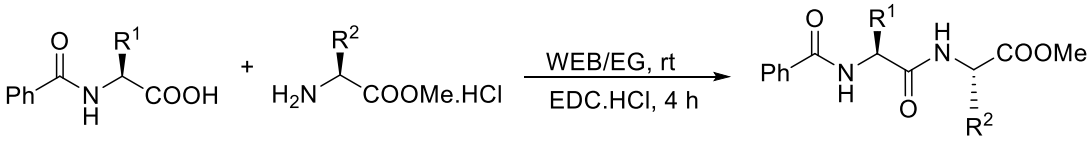
It is well recognized that the development of new synthetic strategies for the preparation of aryl azides is very important, since these kinds of compounds are versatile building blocks in organic synthesis (Bräse and Banert 2010; Ge et al. 2020). Because of the importance of aryl azides, several methodologies for the preparation of these kinds of compounds have been described (Jin et al. 2011; Hajipour and Mohammadsaleh 2014; Prieto et al. 2017).

In this context, Saikia described a copper-catalyzed approach for the synthesis of aryl azides by the treatment of aryl boronic acids with sodium azide in the presence water extract of banana peel ash (Saikia 2018). Remarkably, potassium and sodium carbonates present in water extract of banana peel ash most likely act as a base in this transformation. This protocol was applicable for a variety of substituted aryl boronic acids containing both electron-releasing and electron-withdrawing groups, affording the corresponding aryl azides in excellent yields. Some representative examples are illustrated in Fig. 19.

Very recently, Vekateswarlu and coworkers have described a sustainable protocol for the preparation of chiral *tert*-butanesulfinyl aldimines mediated by water extract of pomegranate ash (Naidu et al. 2021). Notably, water extract of pomegranate ash efficiently catalyzed the condensation of *tert*-butanesulfinamides and aldehydes in the presence of water and ethanol, affording desired products in up to 99% yields (Fig. 20).

The authors also proposed a plausible reaction mechanism for this transformation. The catalytic cycle of the reaction starts with the deprotonation of the *tert*-butanesulfinamide

Table 1 Synthesis of several peptides[a]

Entry	R^1	R^2	Yield (%)
			
WEB/EG = Water extract of banana peel ash/ethylene glycol EDC.HCl = *N*-ethyl-*N*'-(3-dimethylaminopropyl) carbodiimide hydrochloride			
1	-H	-H	95
2	$-CH_3$	$-CH_3$	71
3	-H	$-CH_3$	67
4	$-CH_3$	-H	76
5	$-CH_2Ph$	-H	58
6	$-CH_2Ph$	$-CH_3$	61
7	$-CH(CH_3)_2$	-H	76
8	$-CH(CH_3)_2$	$-CH_3$	72
9	$-CH_2CH(CH_3)_2$	-H	68
10	$-CH_2CH(CH_3)_2$	$-CH_3$	77

Reaction conditions: benzoyl-protected amino acid (1 mmol), amino acid methyl ester hydrochloride (1.5 mmol), *N*-ethyl-*N*'-(3-dimethylaminopropyl) carbodiimide hydrochloride (1 mmol) in water extract of banana peel ash (3 mL) and ethylene glycol (0.2 mL)

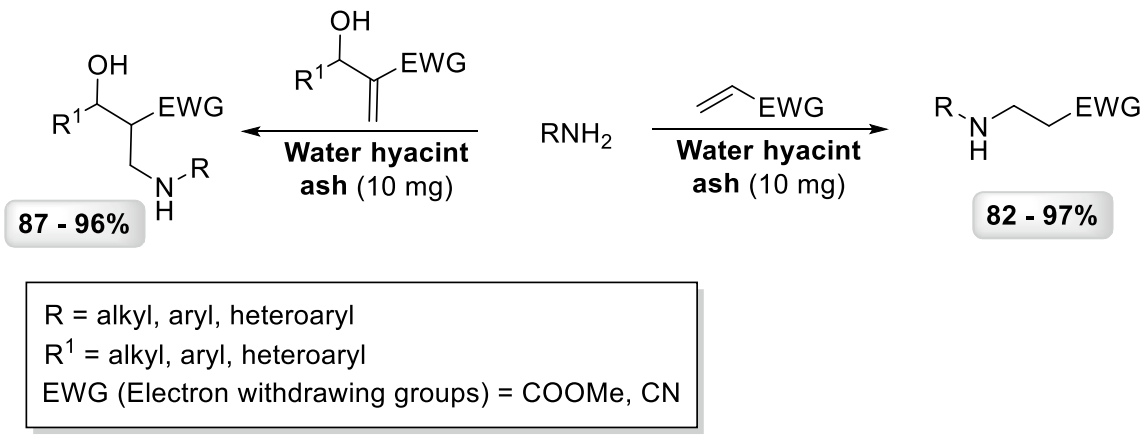


Fig. 18 Aza-Michael reaction catalyzed by water hyacinth ash. The treatment of amines with α,β-unsaturated carbonyl/nitrile compounds in the presence of water hyacinth ash furnished the corresponding Michael adducts in 82–97% yields

by the base from water extract of pomegranate ash, furnishing the respective intermediate **A**. Subsequently, this intermediate undergoes to a nucleophilic addition step with aldehyde, generating α-sulfinylamino alkoxide **B**. This transitory specie is readily converted into α-sulfinylaminol **C** with concomitant regeneration of the base, completing the catalytic cycle. Finally, **C** is readily converted into respective *tert*-butanesulfinyl aldimines through the elimination of water.

Moreover, the regeneration of the base in the reaction media was also supported by further recyclability studies, which showed water extract of pomegranate ash efficiency until 5th catalytic cycle.

Carbon–sulfur bond-forming reactions

Organosulfur compounds have shown unique properties and have been notably used as privileged substrates in the synthesis of several bioactive substances (Nielsen et al. 2017; Colle et al. 2013). They have also been employed as valuable intermediates in a wide range of organic reactions (Prochnow et al. 2019; Amri and Wirth 2021), including

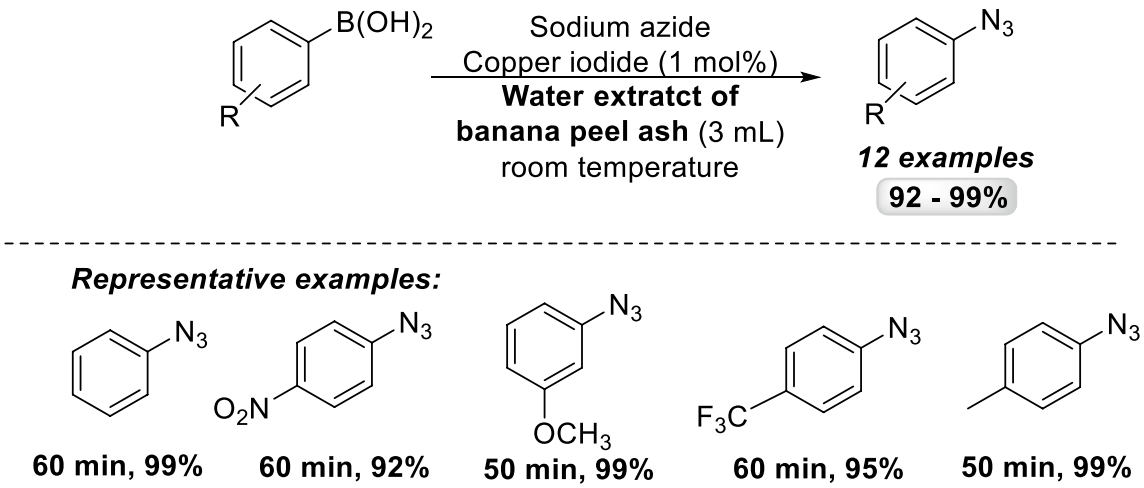


Fig. 19 Synthesis of aryl azides in water extract of banana peel ash. The desired products were efficiently obtained in very high yields through a copper-catalyzed reaction between aryl boronic acids and sodium azide

cross-coupling reactions (Qin et al. 2021) and total synthesis (Silva et al. 2018; Pearson et al. 2004).

Because of organosulfur importance, several strategies to accomplish these kinds of compounds have been widely reported in the literature (Azeredo et al. 2013; Zupanc and Jereb 2021; Lanfranco et al. 2021). Among them, hydrothiolation reaction have become one of the most useful and atom economical pathway to afford the desired organosulfur compounds under greener conditions (Rocha et al. 2017; Peixoto et al. 2020; Shigeno et al. 2021).

Similarly, the development of new synthetic methods for new carbon–sulfur bond formation using water of agro-waste extracts has become particularly valuable in organosulfur chemistry (Leitemberger et al. 2019). In this context, our research group has reported a straightforward methodology for the hydrothiolation of alkynes in the presence of agro-waste extracts (Godoi et al. 2019). In particular, water extract of rice straw ash proved to be the best aqueous extract option for the synthesis of the desired vinyl thioethers. Generally, terminal alkynes and thiol derivatives were excellent reaction partners, affording the corresponding products in good yields with high stereoselectivity (Fig. 21). Moreover, water extract of rice straw ash could be easily recovered from the reaction media and reused for further reactions. Indeed, this aqueous extract conserved its activity up to the fourth cycle, furnishing the corresponding thioether with good yield and high stereoselectivity.

Very recently, we have elucidated the main behavior of by water extract of rice straw ash in the hydrothiolation of alkynes, combining the experimental design and some well-known techniques of characterization and metal quantification (Silveira et al. 2021). In fact, experimental evidence supported by inductively coupled plasma optical emission spectrometry and X-ray fluorescence analysis revealed a slight variation in the concentration between the metals present in the rice ashes and in their water extracts. Nonetheless, these differences in metallic compositions might be associated with different factors including the pH of soils, differences in rice species, precipitation, weather as well as cultivation form (Zhang et al. 2020; Makela et al. 2016).

Furthermore, the effect of the metals from by water extract of rice straw ash on the hydrothiolation of phenylacetylene was also investigated by employing ANOVA response, coefficient of determination, linear regression model and Fischer's test. The combination of statistical analysis and experimental design allowed us to correlate the concentration and effects of the independent variables present in the aqueous extract. In this regard, calcium (II) was found to be the most important metal for the hydrothiolation reaction when by water extract of rice straw ash was used as a solvent.

Notably, a good agreement between our experimental results and this theoretical analysis was observed. Based on these findings as well as control experiments, a plausible mechanism for the hydrothiolation of alkynes was also proposed (Fig. 22). Remarkably, a synergistic effect between by water extract of rice straw ash and light would be responsible for the generation of thiyl radical (**I**) in the reaction media. Next, this sulfur intermediate would react with **II** giving the respective species **III**. Then, this radical reacts with thiol furnishing the corresponding product with concomitant regeneration of thiyl radical, completing the mechanism.

Carbon–bromine bond formation

It is well known that aromatic and heteroaromatic bromides are important substrates in a wide range of organic reactions (Chang et al. 2012; Yang et al. 2013; Uchida

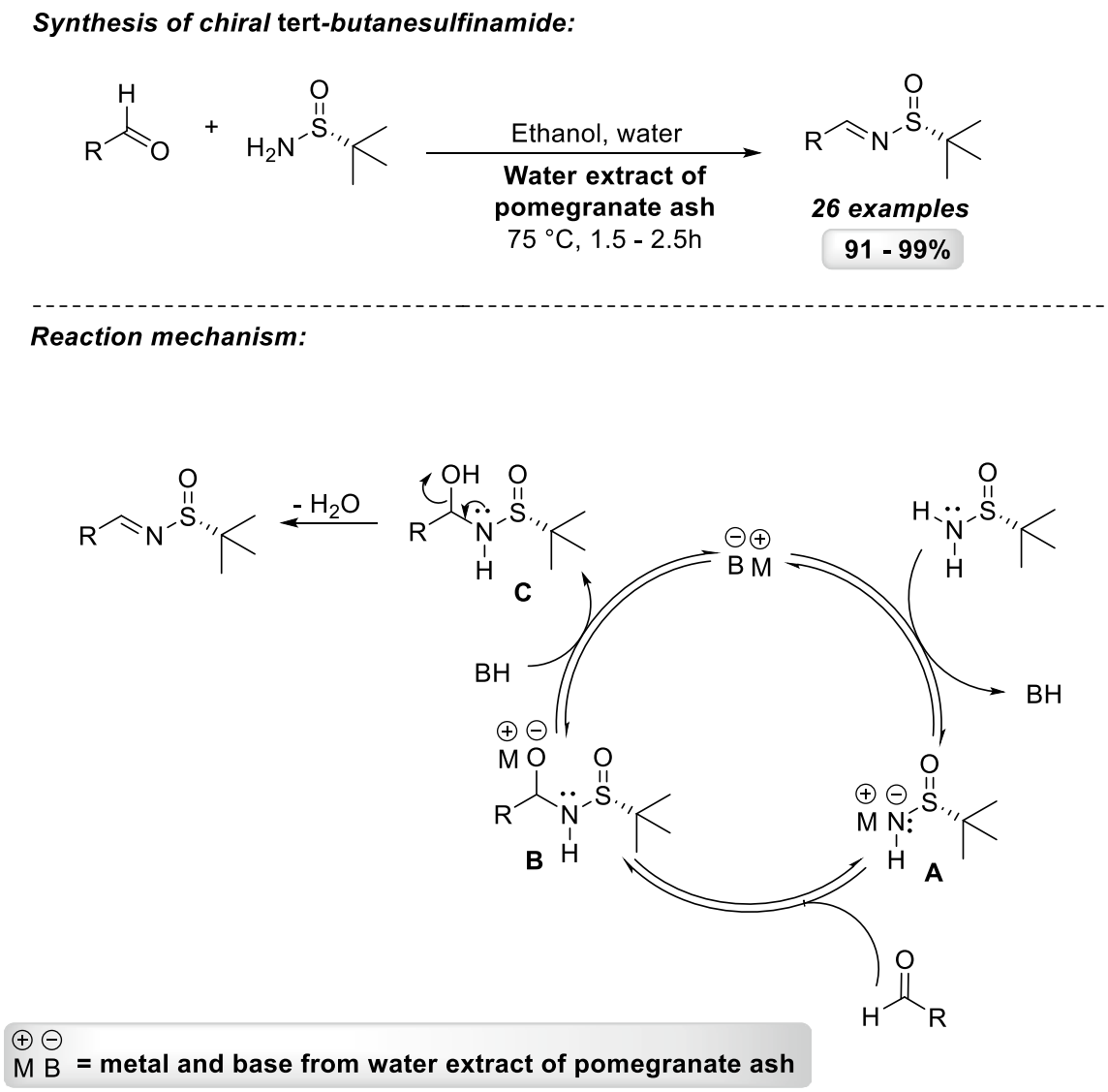


Fig. 20 Synthesis of chiral *tert*-butanesulfinyl aldimines catalyzed by water extract of pomegranate ash. *Tert*-butanesulfinamides react efficiently with different aldehydes, giving the desired products in 91–99% yields (Naidu et al. 2021)

and Togo 2019; Mondal et al. 2021). In this regard, the aromatic electrophilic substitution has become the most straightforward protocol to synthesize these bromides derivatives (Mendoza et al. 2016; Xiao et al. 2021; Schammel et al. 2021).

Within this context, Appa et al. (2019b) developed a convenient methodology for the monobromination of aromatic compounds employing *N*-bromosuccinimide in the presence of water extract of pomegranate ash. Although the role of this extract was not fully understood, the authors presented a plausible reaction pathway for the bromination reaction (Fig. 23). It was believed that the metal basic species from water extract of pomegranate ash would be responsible for the generation of succinimide and the bromine intermediate. Subsequently, this intermediate undergoes electrophilic substitution reaction, furnishing the respective aromatic compound as a final product.

Multicomponent reactions for carbon–carbon and carbon–heteroatom bond formation

Domino processes have emerged as a useful tool for the synthesis of a variety of target molecules and have become one of the most efficient methods for the generation of new carbon–carbon and carbon–heteroatom bonds (Shylaja et al. 2018; Yang et al. 2017; Pan et al. 2021). In this context, multicomponent reactions (MCRs) have presented major advantages over conventional stepwise approaches,

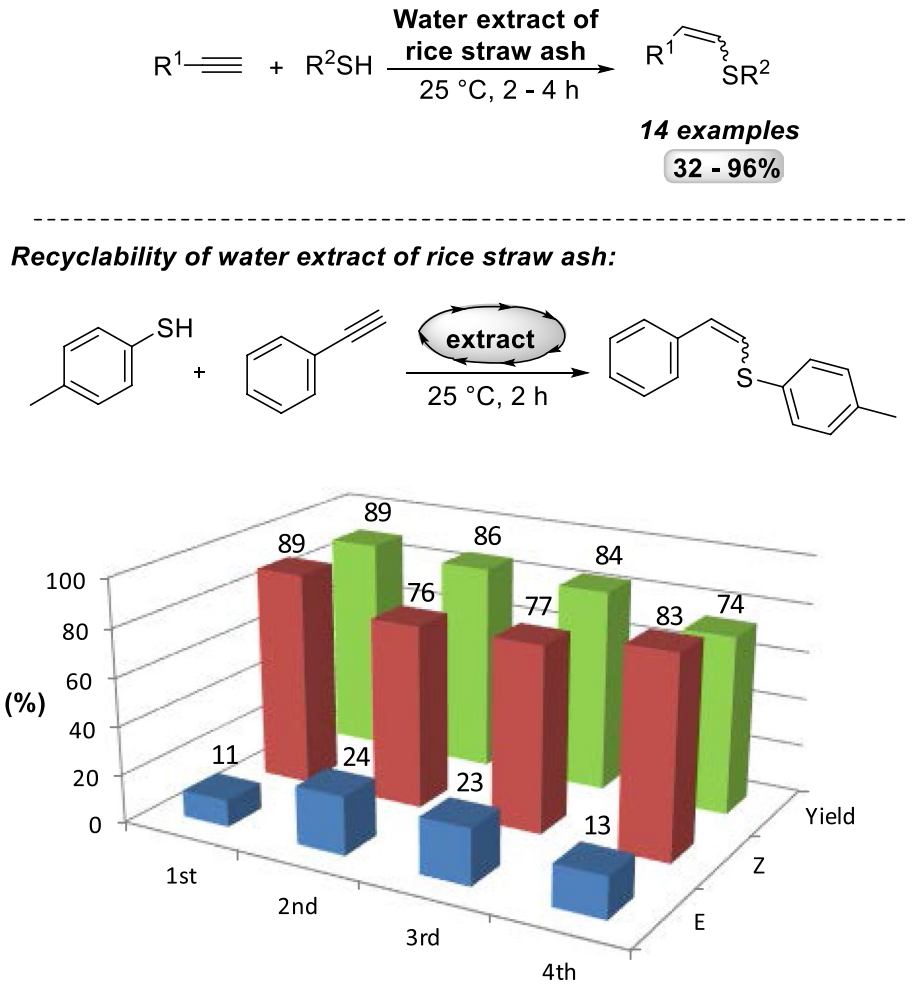


Fig. 21 Hydrothiolation of terminal alkynes promoted by water extract of rice straw ash. Several thioethers were prepared by reacting alkynes with thiols at room temperature. The aqueous extract was recovered from the reaction media and reused up to 4th run without significant loss of its activity (Leitemberger et al. 2019)

Z: it refers to configuration of vinyl thioether (from *zusammen*, the German word for together).
E: it refers to configuration of vinyl thioether (from *entgegen*, the German word for opposite).

and they have been demonstrated to be a useful method to prepare complex organic substances with high atom efficiency (Fontecha-Tarazona et al. 2015; Cioc et al. 2014; Hayashi 2016).

Bordoloi and coworkers described a suitable approach for the preparation of functionalized imidazole and dihydropyrimidine derivatives through a three-component transformation promoted by water extract of pomelo (Tamuli et al. 2017). Of particular importance, both methodologies required only equivalent amount of water extract of pomelo to provide the respective products efficiently without the use of any extra additives, cocatalysts or solvents. The generality of the reaction was also evaluated and both electron-donating and electron-withdrawing substituents attached to the aromatic ring of benzaldehyde furnished the respective products in very high yields (Fig. 24).

More recently, Hiremath and Kamanna (2020) have reported another interesting multicomponent reaction promoted by agro-waste extracts. In this regard, a microwave-assisted synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones through condensation of aldehyde with malononitrile and phthalhydrazide catalyzed by water extract of mango peel ash was described. By this three-component process, the desired products could be efficiently achieved in good yields employing water extract of mango peel ash as a base source (Fig. 25).

Very recently, Hiremath and Kantharaju (2020) have described a high-yielding three-component approach for the preparation of 2-amino-4H-pyran and tetrahydrobenzo[b]pyran derivatives employing water extract of muskmelon fruit shell ash as a catalyst. The synthesis of both 2-amino-4H-pyran and tetrahydrobenzo[b]pyran derivatives is

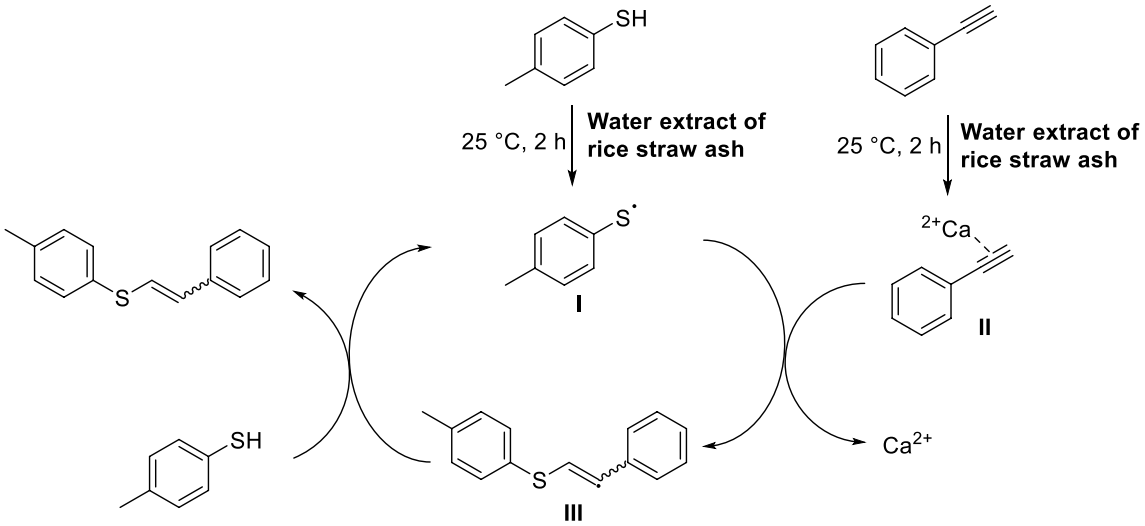
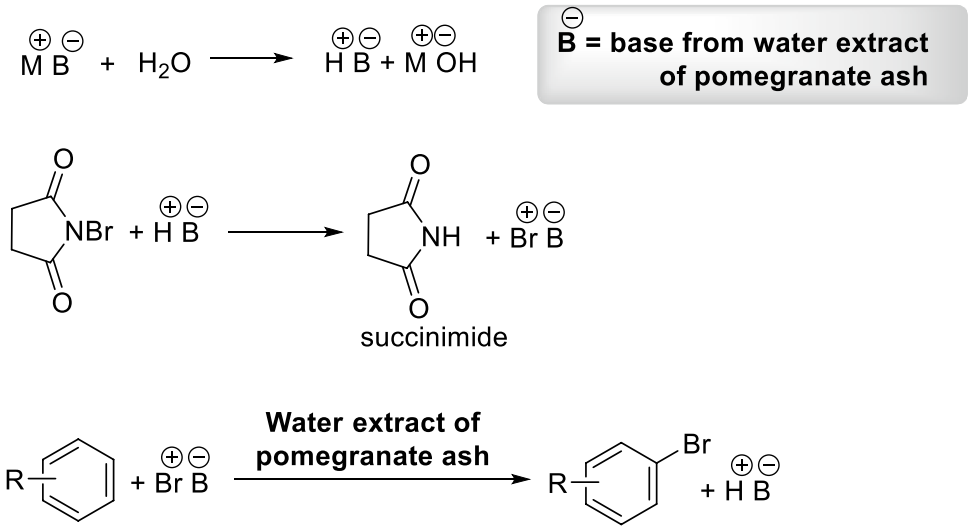


Fig. 22 Plausible reaction mechanism for the hydrothiolation of phenylacetylene. The thiyl radical (I) generated in the reaction media reacts with II to afford the intermediate III. Subsequent reaction of this intermediate with 4-methylbenzenethiol provides the desired product, completing the mechanism (Silveira et al. 2021)

Fig. 23 Reaction pathway of bromination of aromatic compounds in water extract of pomegranate ash. The base from water extract of pomegranate ash reacts with *N*-bromosuccinimide to form succinimide and the bromine intermediate. Next, this intermediate undergoes electrophilic substitution reaction to afford the desired product (Appa et al. 2019b)



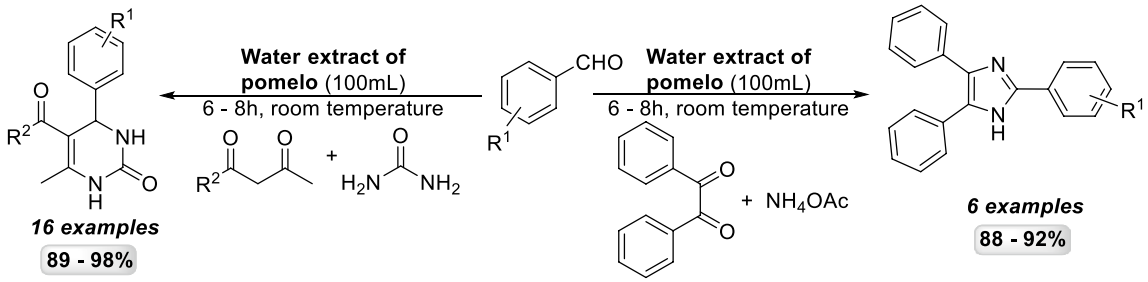


Fig. 24 Three-component transformation promoted by water extract of pomelo. Imidazole derivatives were obtained by the reaction between aldehydes and 1,2-diketone in the presence of ammonium acetate. Aldehydes were condensed with 1,3-diketones and urea to give the respective dihydropyrimidines in 89–98% yields

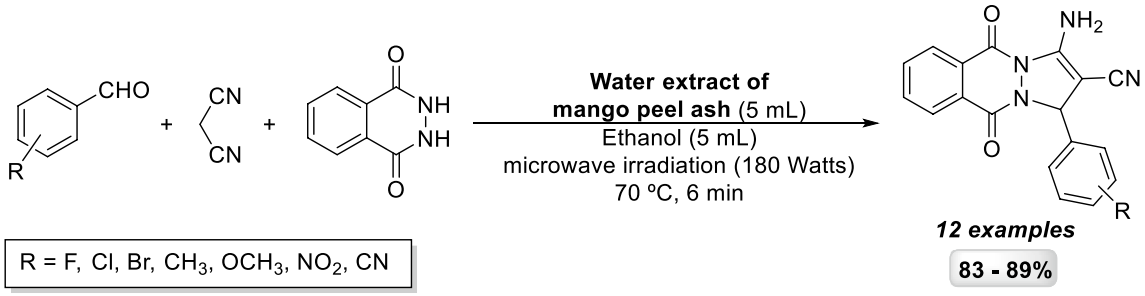


Fig. 25 Synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones promoted by water extract of mango peel ash. The condensation reaction of aldehyde with malononitrile and phthalhydrazide catalyzed by water extract of mango peel ash provided the desired products in up to 89% yield in only 6 min (Hiremath and Kamanna 2020)

accomplished with in situ generation of benzylidene malononitrile via Knoevenagel condensation (Fig. 26).

A wide range of desired products were synthesized under standard conditions and the reaction well-tolerated electron-withdrawing as well as electron-donating substituents in the aldehyde moiety. Moreover, the reusability of water extract of muskmelon fruit shell ash was also evaluated and it shows high efficiency until the 4th reaction cycle without significant decrease in the yield value of desired product.

Water extract of *tamarindus indica* seed ash also proved to be a suitable aqueous extract for the one-pot three-component synthesis of 4H-pyran derivatives (Halder et al. 2020b). The protocol was simple and convenient to prepare a range of 4H-pyran derivatives in up to 95% yield through a one-pot reaction between 1,3-cyclohexanediones, aryl aldehydes and malononitrile in the presence of water extract of *tamarindus indica* seed ash and ethanol as a reaction media.

Mechanistically, *tamarindus indica* seed ash is essential for the abstraction of proton from malononitrile which is subsequently converted into intermediate **A** by a Knoevenagel-type condensation reaction. Next, this intermediate reacts with 4-hydroxycoumarin by a Michael addition reaction mediated by base, giving the species **B**. Finally, the intramolecular cyclization reaction followed by an isomerization step affords the desired 4H-pyran derivative (Fig. 27).

Dwivedi and coworkers described a one-pot methodology for the preparation of pyrano[2,3-c]pyrazole employing arylidene malononitrile and pyrazolone assisted by water extract of banana peels ash (Dwivedi et al. 2019b). The variation of the reaction scope in terms of arylidene malononitrile moiety demonstrated that a broad range of functional groups could be tolerated and 17 different examples were efficiently synthesized in excellent yields (Fig. 28). Mechanistically, water extract of banana peels ash showed an important role in this reaction, acting as a base source in the first step, generating enol **A**, which further undergoes Michael addition with arylidene malononitrile to furnish intermediate **B**. Subsequently, this intermediate abstract a

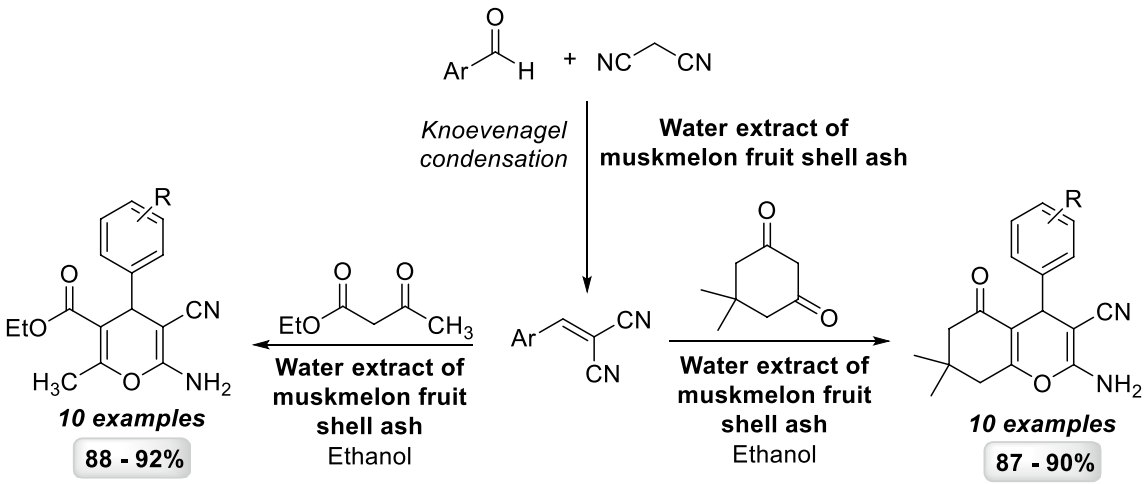


Fig. 26 Synthesis of 2-amino-4H-pyran and tetrahydrobenzo[b]pyran derivatives in water extract of muskmelon fruit shell ash. First, benzylidene malononitrile in generated in situ by condensation of aldehyde with malononitrile. Next, benzylidene malononitrile is smoothly converted into corresponding products by reaction with dicarbonyl compounds

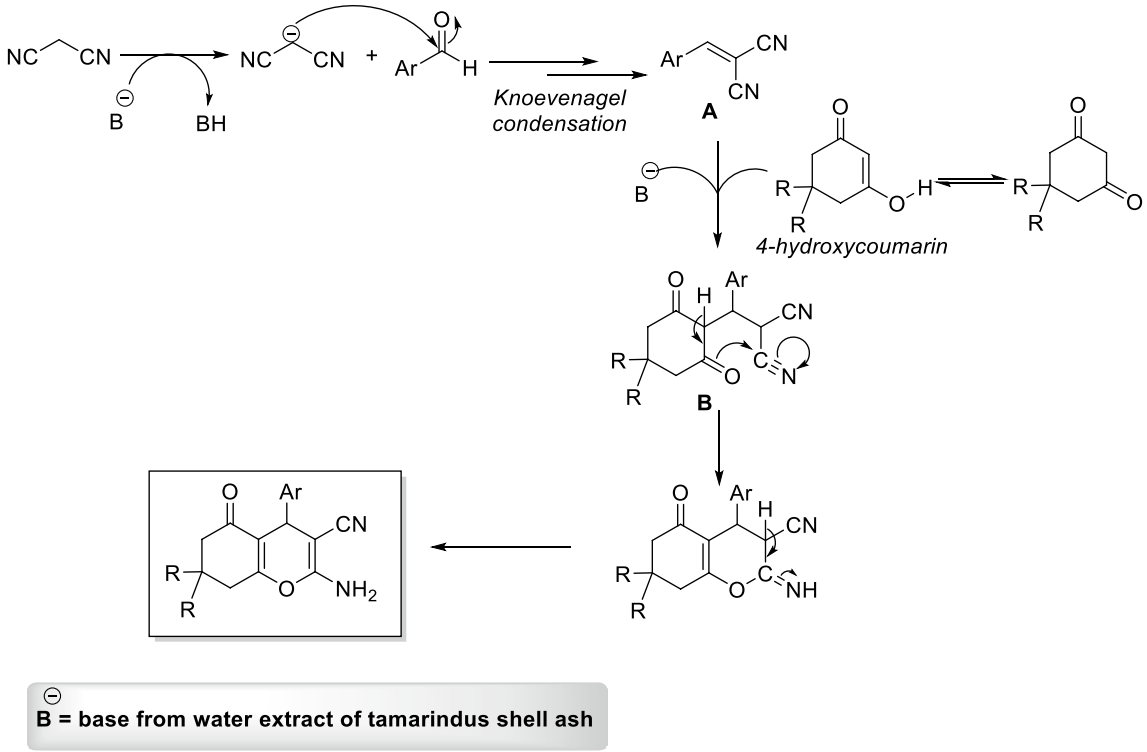


Fig. 27 Plausible mechanism for the synthesis of 4H-pyran derivatives. Benzylidene malononitrile (**a**) is generated through Knoevenagel condensation of aldehyde with malononitrile. Next, this intermediate reacts with 4-hydroxycoumarin to afford the species **b**. Finally, the final product is achieved by the intramolecular cyclization reaction of **b** followed by an isomerization step

proton from extract to generate the species **C**, which is submitted to intramolecular cyclization to provide **D**. Finally, through an isomerization step, the corresponding product is conveniently obtained.

On the other hand, Bendre's group described a one-pot methodology for the synthesis of 3-carboxycoumarins promoted by water extract of banana peels (Bagul et al. 2017). In this regard, alkali metal carbonates such as sodium carbonate and potassium carbonate present in water extract of banana peels solution act as internal bases in the condensation reaction. A series of 3-carboxycoumarins were synthesized via Knoevenagel condensation and intramolecular cyclization of 2-hydroxybenzaldehydes with meldrum's acid in very good yields (Fig. 29, method A).

Later, the same research group also described the preparation of 3-carboxycoumarins in the presence of water extract of rice straw ash (Patil et al. 2018). In this study, the corresponding 3-carboxycoumarins were synthesized in up to 94% yield using 10% of water extract of rice straw ash in ethanol at room temperature (Fig. 29, method B).

Additionally, water extract of lemon fruit shell ash has also been applied as a basic catalytic medium in the same condensation reaction (Khatavi and Kantharaju 2018). The protocol resulted in good to excellent isolated yields of the desired 3-carboxycoumarins within 3–6 min under microwave irradiation (Fig. 29, method C).

More recently, interesting results have also been demonstrated by Kantharaju et al. (2019). In this regard, water extract of nilgiri bark was employed as a green catalyst alternative for the preparation of 3-carboxycoumarins. The reaction proceeded well, affording the corresponding products in good yields at room temperature (Fig. 29, method D). In addition to the production of 3-carboxycoumarins, the methodology was extended to the synthesis of benzylidinemalononitrile derivatives. As an aside study, Kantharaju's group also reported the synthesis of these compounds in the presence of water extract of banana peel ash under the grindstone method (Kantharaju et al. 2019).

Owing the alkaline nature of water of agro-waste extracts it also been employed as based catalysts in the preparation of chromene scaffolds. In this regard, the synthesis of 2-amino-4H-chromene derivatives was reported via a multicomponent reaction promoted by bael fruit extract (Shinde et al. 2017). Notably, a wide range of desired products were achieved through the condensation of aryl aldehydes with malononitrile and naphthol derivatives promoted by bael fruit extract (Fig. 30, method A). The authors also investigated the recyclability of extract, and the catalytic system

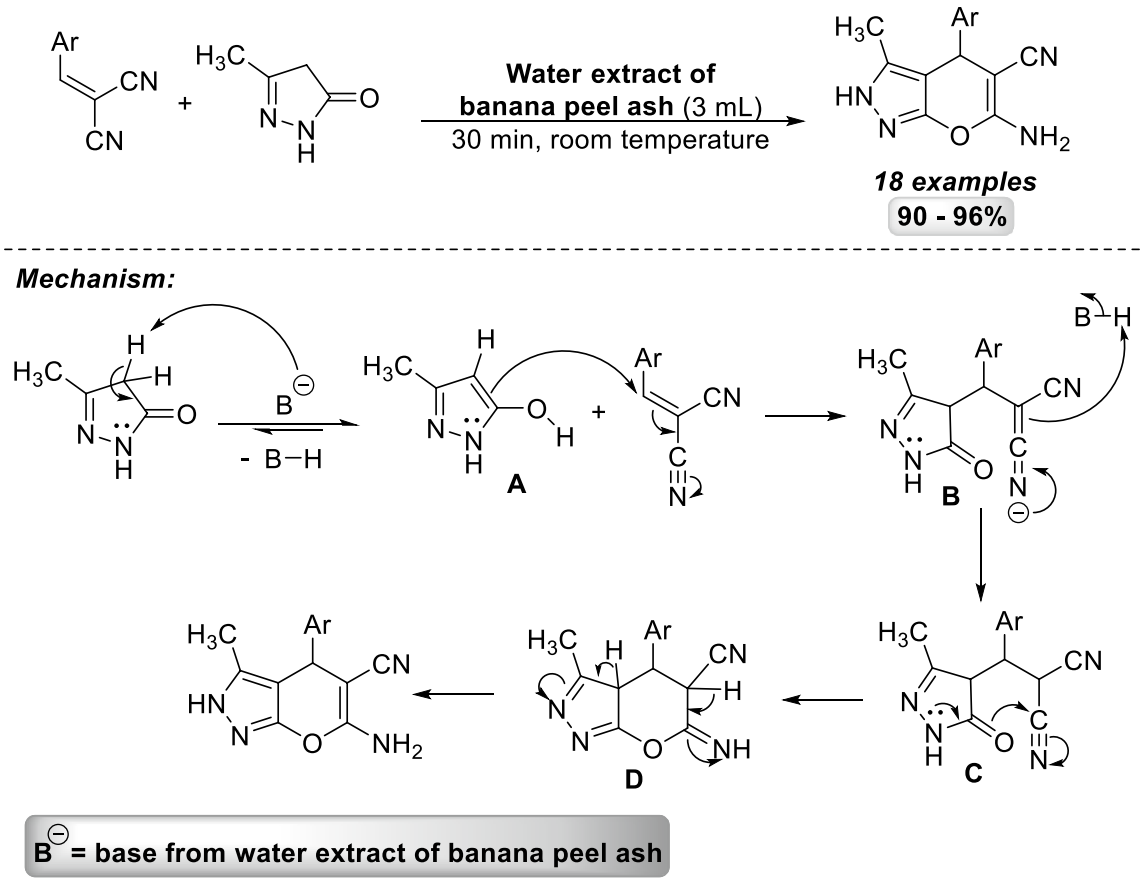


Fig. 28 Synthesis of pyrano[2,3-c]pyrazole promoted by water extract of banana peels ash. Deprotonation of pyrazolone generates enol **a**, which further undergoes to conjugate addition with arylidene malononitrile to give the intermediate **b**. This intermediate is further protonated to generate the specie **c**, which is converted into **d** by intramolecular cyclization step. Finally, the corresponding product is achieved through an isomerization step (Dwivedi et al. 2019b)

proved to be efficient until the 5th cycle. In further studies, the same group also described the effect of bael fruit ash in this reaction (Patil et al. 2021).

Likewise, 2-amino-4H-chromene derivatives were also successfully obtained via multicomponent process in the presence of water extract of pomegranate peel ash (Hiremath et al. 2019). The methodology was applicable for a broad scope of chromene scaffolds which were delivered in very good yields under microwave irradiation (Fig. 30, method B).

Water extract of agave leaf ash has also provided to be very efficient for the synthesis of 2-amino-4H-chromene derivatives (Patil et al. 2019). Hence, aryl aldehydes reacted smoothly with malononitrile and naphthol derivatives in the presence of water extract of agave leaf ash, affording the corresponding products in very high yields (Fig. 30, method C). In addition, this protocol was also highly useful for the synthesis of pyrano[2,3c]pyrazoles under similar reaction conditions.

More recently, water extract of banana peel ash has also been applied as a green catalyst for the multicomponent synthesis of 2-amino-3,5-dicarbonitrile-6-thio-pyridine derivatives (Allahi and Akhlaghinia 2020). This methodology allowed the preparation of a variety of the desired products in very good yields by a one-pot process.

In terms of the reaction mechanism, it was assumed that water extract of banana peel ash would act as a base due to the presence of metal carbonates in the extract composition. Thus, the generation of the species **A** was proposed by deprotonation of the acid proton from malononitrile, which is further converted into respective Knoevenagel adduct **B** by a condensation step. Next, the Knoevenagel adduct undergoes a Michael addition reaction with another equivalent of **A** to give compound **C**. This intermediate reacts with the thiolate anion to afford intermediate **D**. Subsequently, an intramolecular cyclization reaction followed by protonation generates the most stable tautomeric form of dihydropyridine (**E**). Last, the formation of desired product was assumed to occur through an air oxidative aromatization step (Fig. 31).

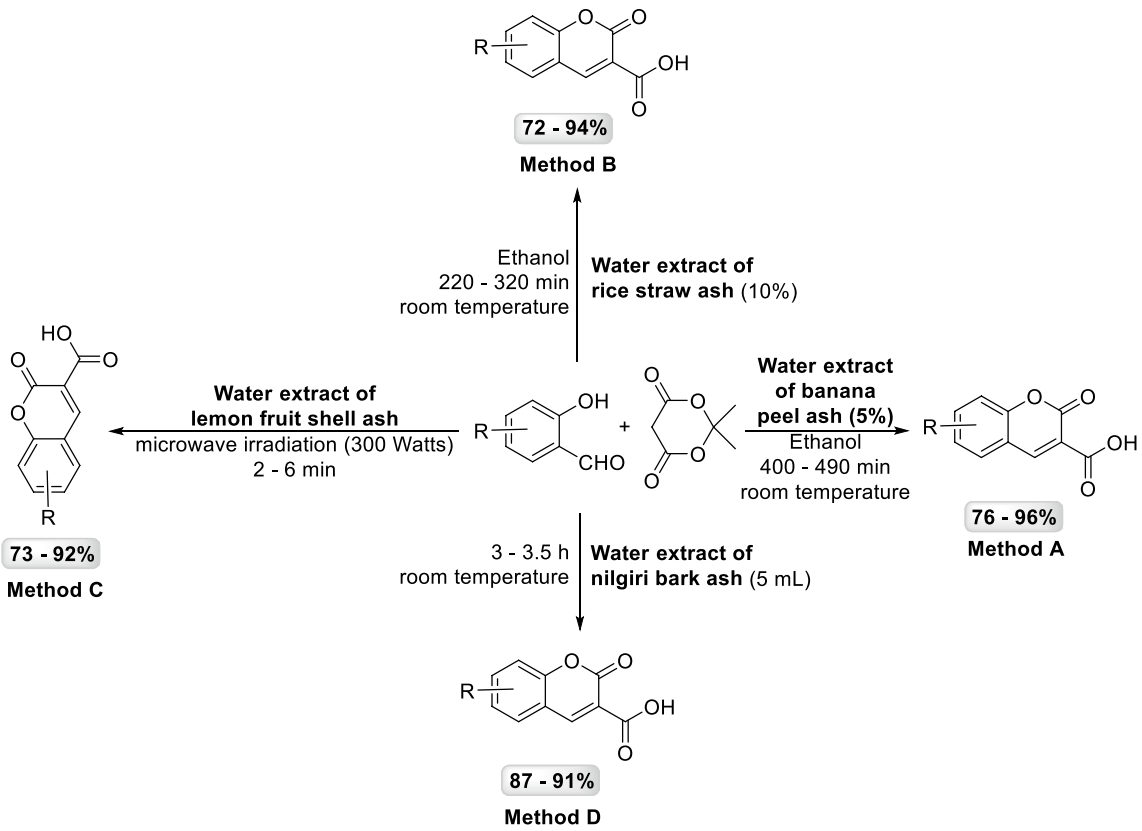


Fig. 29 Synthesis of 3-carboxycoumarins promoted by agro-waste extracts. 2-Hydroxybenzaldehydes were successfully converted into respective 3-carboxycoumarins in the presence of meldrum's acid and different water agro-waste extracts, including nilgiri bark, lemon fruit, banana peel and rice straw ashes

Conclusion

In summary, in this review a significant increase in the development of environmentally benign synthetic approaches for the generation of new carbon–carbon and carbon–heteroatom bonds was observed. The recent literature has demonstrated a series of advantages of the use of agro-waste extracts as a green alternative for carbon–carbon and carbon–heteroatom bond-forming reactions. In this context, the use of these biomass residues in organic synthesis has several benefits, including: (1) easy access from natural waste feedstock, (2) mild conditions, (3) high catalytic efficiency and (4) recyclability.

In spite the well effectiveness of agro-waste extracts in a series of transformations, some articles are focus only on development of synthetic methodologies and the role of metal in the reaction media is not fully discussed. Also, the organochalcogen chemistry might be further explored, since only few works have been reported to date. On the other hand, the employment of agro-waste extracts in the reaction medium overcome any limitation in the protocols reported in the literature once these aqueous extracts are nontoxic, highly recyclable, simple workup, biodegradable and readily available from natural waste feedstock. Thus, owing to the notable applications of these extracts, a great trend is growing the studies on this topic and extending to other areas of chemistry.

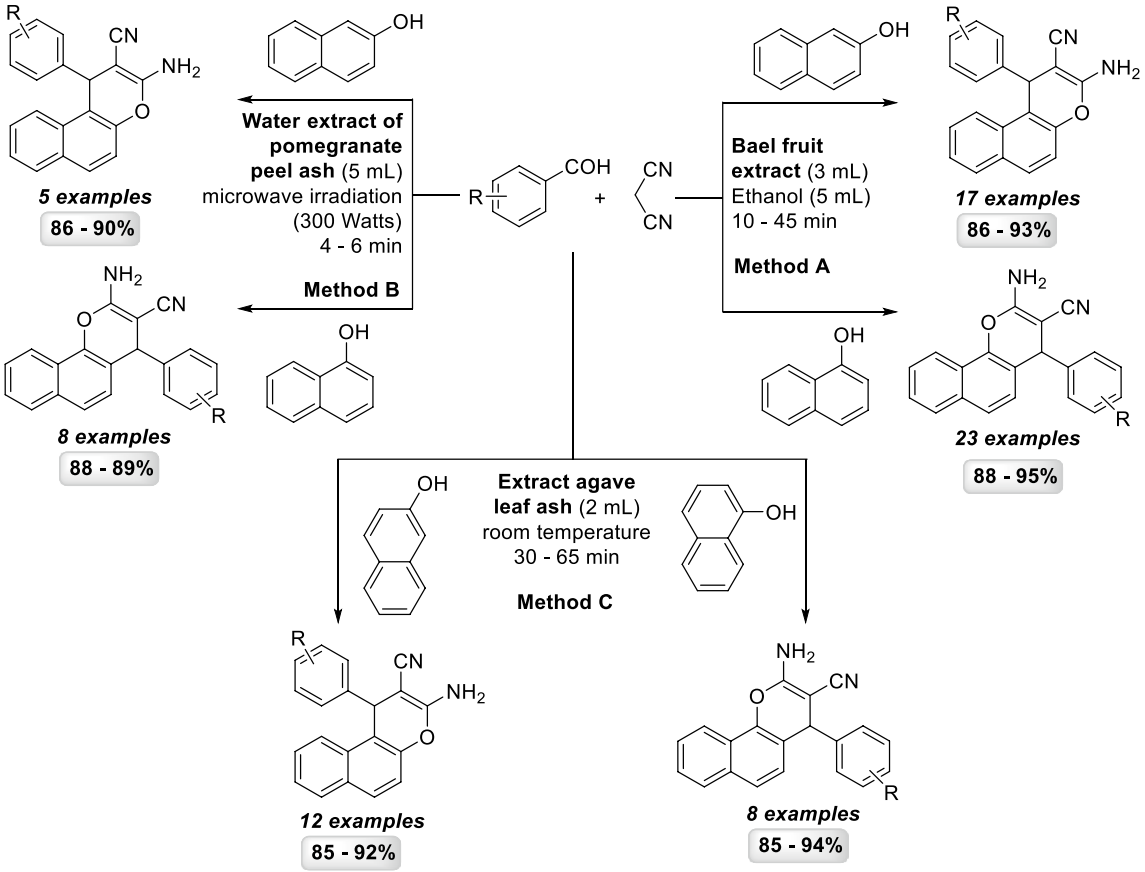


Fig. 30 Synthesis of chromene scaffolds in agro-waste extracts. 2-Amino-4H-chromene derivatives were obtained through the condensation of aryl aldehydes with malononitrile and naphthol derivatives under conventional heating in the presence of bael fruit or agave leaf extracts (methods A and C, respectively). The combination of water extract of pomegranate peel ash and microwave irradiation was efficient for the preparation of desired chromene scaffolds in 86-9o% yields (method B)

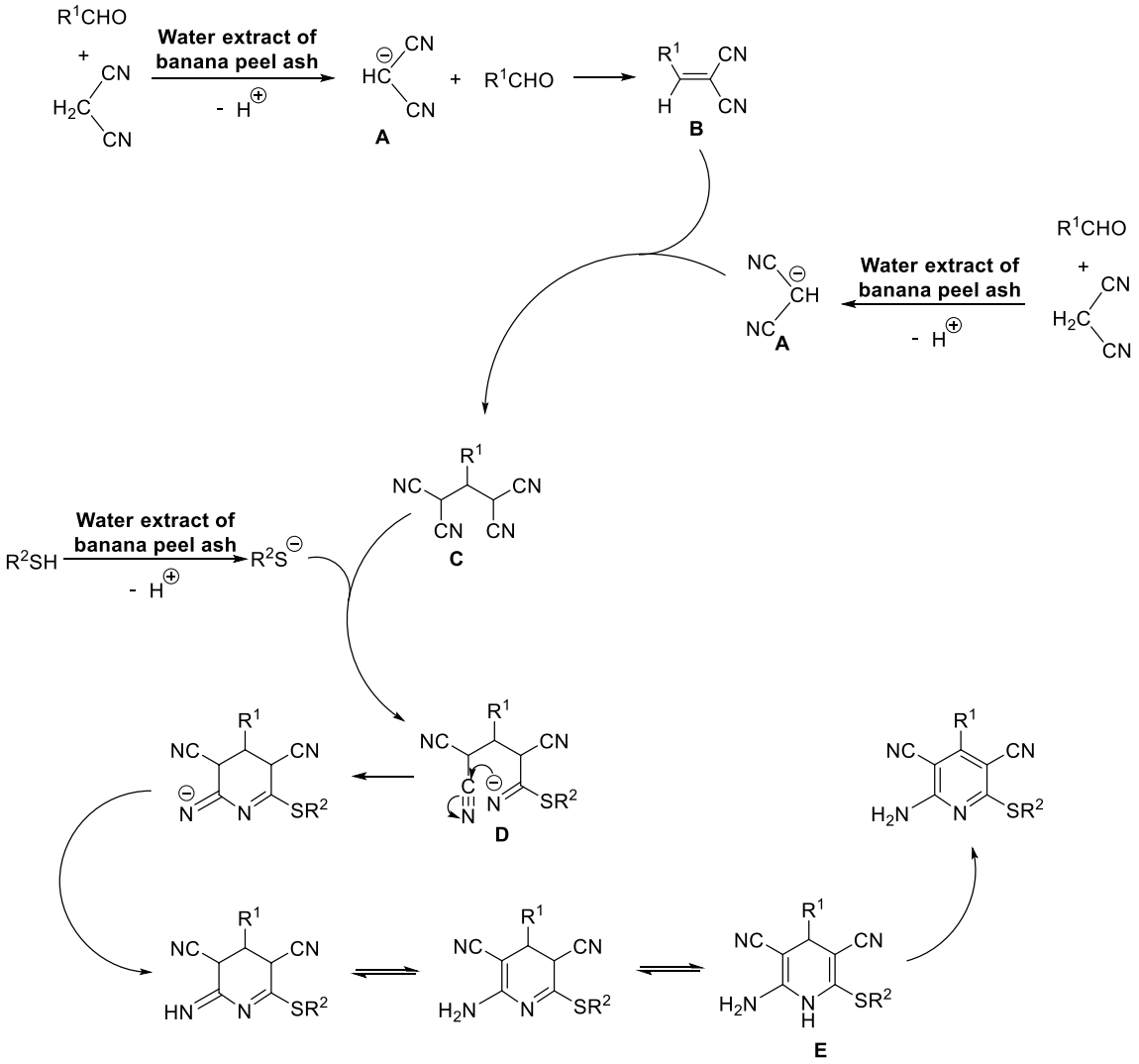


Fig. 31 Proposed mechanism for the synthesis of 2-amino-3,5-dicarbonitrile-6-thio-pyridines. The mechanism involves the formation of Knoevenagel adduct (**b**) by a condensation step. Next, this compound undergoes a Michael addition reaction with **a** to give the intermediate **c**. This specie reacts with the thiolate anion to furnish **d**. Finally, through an intramolecular cyclization reaction followed by an oxidative aromatization step the desired product is achieved (Allahi and Akhlaghinia 2020)

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Declarations

Conflict of interest The authors declared that there is no conflict of interest.

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