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REVIEW

Ashes from organic waste as reagents in synthetic chemistry: a review

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Abstract

The decline of fossil- and ore-based materials is calling for more recycling of waste into new materials. Here, I review the recycling of ashes from biomass into reagents for chemical synthesis and biodiesel production. Biomass includes banana, pomegranate, rice, papaya, century plant, water hyacinth, bael fruit, nilgiri, mango, onion, muskmelon fruit, pomelo, lemon fruit, teak and tamarind. Chemical reactions include Knoevenagel condensation, Suzuki–Miyaura cross-coupling, Sonogashira reaction, Dakin reaction, Henry reaction, Ullmann coupling, Pd-catalyzed homocoupling, aromatic bromination, hydroxylation of arylboronic acids, hydration of nitriles and azide–alkyne click reaction. The synthesis of peptide bonds, disulfides, aminochromenes, carboxycoumarins, diazohydroxy esters, imidazopyridines, pyranopyrazoles, chalcones, flavones and bisenols is described.

Keywords Ashes of organic waste · Biorenewable resources · Industrially relevant transformations · Waste utilization · Sustainable strategy

Introduction

The global population has been projected to be 9.7 and 11.0 billion by 2050 and 2100 from the current 7.7 billion (Desa 2019). Huge quantity of waste can be generated due to the rising population by the consumption of energy, food, fiber, feed, etc. In accordance with the World Bank's announcement, the waste created in 2018 is ~ 2017 metric tons and is expected to be ~ 2586 and ~ 3040 metric tons by 2030 and 2050 (Millati et al. 2019). Nearly 40–50% of this waste is made up of organic matter, and its discharge into landfills associates significant environmental issues as liberation of greenhouse gases, contamination of both the surface and ground water, odor effusion and transmission of vector via birds and insects (Khanal et al. 2020). Therefore, the transformation of the waste using physical and chemical methods to beneficial derivatives like fuels, feed and biochemical or chemical feedstocks is highly demanding and necessary task toward the environmental sustainability (Abdel-Shafy and Mansour 2018; Khanal et al. 2020). Moreover, the dwindling supply attending to the growing demand for fossil-based depleting materials drive in hunt for bio-based renewable resources for chemical substances.

The application of biorenewable resources in chemical transformations is highly challenging and the utilization of metabolites (primary and secondary) of natural sources (plants, animals, marine organism and microorganism) as renewable feedstocks in the complete/semi-synthesis of important complex organic compounds including natural products is long been known (Kühlborn et al. 2020; Natte et al. 2020). Further, these metabolites are the significant biopotential compounds, sources of drugs, dyes, renewable solvents, essential oils, biofuels, polymers, energy-based materials, etc. (Al-Jumaili et al. 2018; Spierling et al. 2018; Mgaya et al. 2019; Bansal and Rosenholm 2020; Kühlborn et al. 2020; Natte et al. 2020; Solanilla-Duque et al. 2020). Application of the bio-derived compounds as solvents is another exciting area in industrially relevant chemical transformations, but the similar properties of these solvents as petroleum-based organic compounds or sometimes high boiling points (which makes complication in recovery) are the major drawback in these cases (Sarmah et al. 2017b; Part et al. 2016; Oklu et al. 2019).

On the other hand, the ashes of renewable materials are utilized for several purposes and are well known for their use

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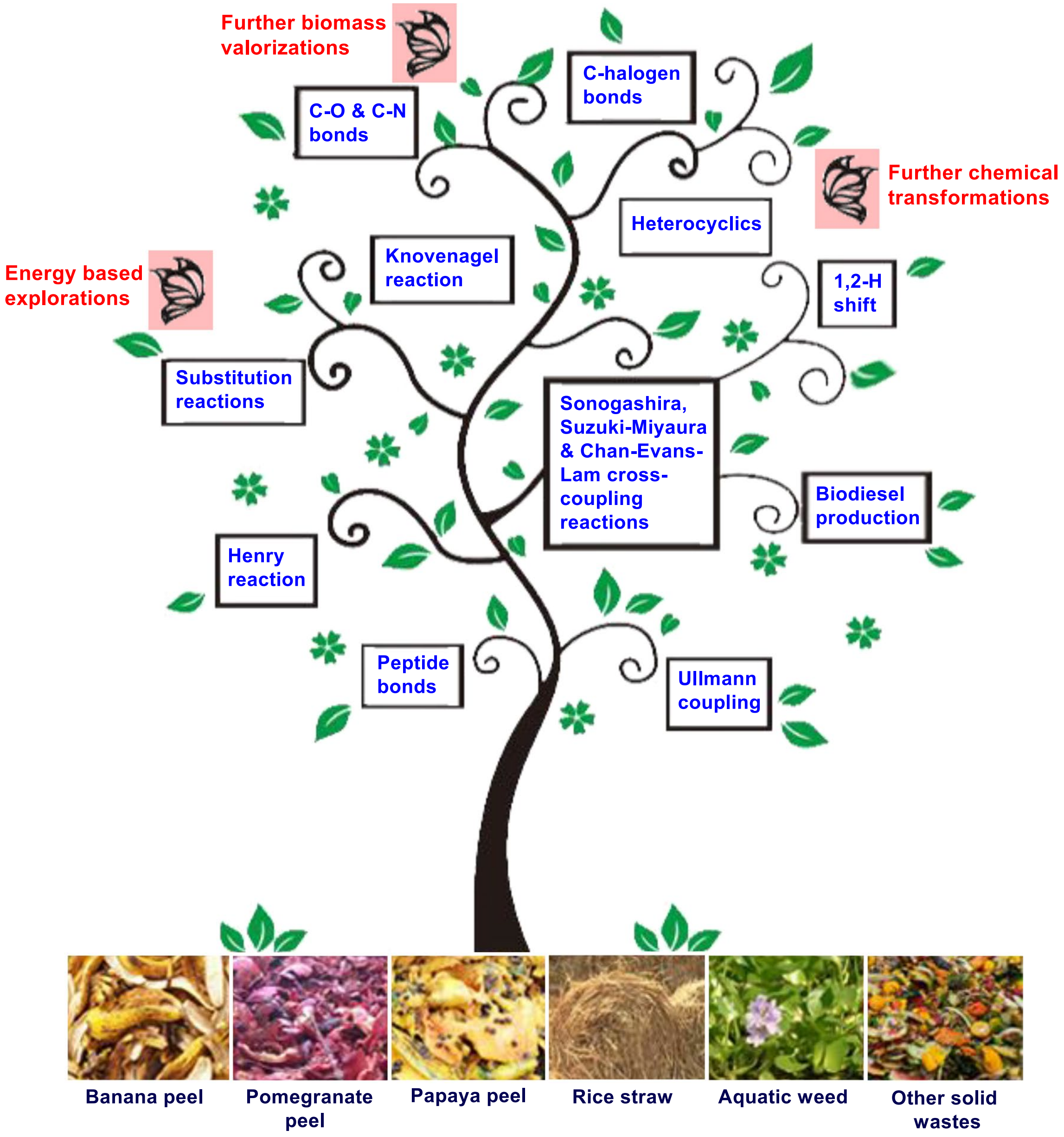
in fertilizers (Brod et al. 2012; Patel et al. 2019; Abelenda et al. 2021), cement-based products (Banu et al. 2020; Athira et al. 2021), water treatment (Bhatnagar et al. 2015; Mor et al. 2016; Anton et al. 2020; Abelenda et al. 2021), cosmetics (Tiwari and Pradhan 2017), healthcare products (Foo and Hameed 2009), detergents (Hui and Chao 2006; Meshram et al. 2015), separation of inorganic materials like silica (Hossain et al. 2019; Rovani et al. 2019; Temeche et al. 2020; Farirai et al. 2021) and zeolites (Hui and Chao 2006; Meshram et al. 2015; Belviso 2018; Sivalingam and Sen 2020), solar cells (Gao et al. 2020; Wu et al. 2020; Farirai et al. 2021), quality upgradation of biogas (Baruah et al. 2017; Juárez et al. 2018; He et al. 2019; Zhu et al. 2020), etc. These are also well documented for their utility in biodiesel production (Vadery et al. 2014; Basumatary et al. 2018; Pathak et al. 2018; de Barros et al. 2020; Gohain et al. 2020a; Madai et al. 2020) (Sect. 17).

Since the water extract of banana peel ash was appeared for its application in external base-free Suzuki–Miyaura cross-coupling reaction of arylboronic acids and aryl bromides (Boruah et al. 2015b), a moderate attention has been spent by the chemists in utilizing these ashes in various chemical transformations besides their large possible scope. Moreover, the strategy of applying ashes of biorenewable wastes to industrially relevant chemical transformations seems to be a highly sustainable technology in the clearance of solid organic waste. In most of these studied cases, aqueous media has been explored and hence this strategy utilizes nature's preferred solvent such as water (Chanda and Fokin 2009; Butler and Coyne 2010; Simon and Li 2012; Smith et al. 2017; Romney et al. 2018; Elorriaga et al. 2020; Petkova et al. 2020; Venkateswarlu and Rao 2021). Even though water is the responsible media for the endurance of life, the synthetic organic chemists treat water as enemy by claiming that it shows difficulty in reproducibility of reactions and decreases the product yields (Romney et al. 2018). Chemists take all the pains in removing the trace amounts of water in solvents, and it appears only during the workup of the reactions (Romney et al. 2018). The Mother nature has developed several optimized reactions of high selectivity and specificity at mild conditions using water as the media, but never utilizes organic solvents for this purpose (Smith et al. 2017; Petkova et al. 2020). In fact, the organic volatile solvents cover nearly 85% of the chemicals utilized in the pharmaceutical industries and are merely recovered 50–80% are detrimental in environmental pollution (Sheldon 2005; Appa et al. 2018, 2019a). Hence, the replacement of the volatile organic solvents in the industrial or its relevant process can ultimately decrease the environmental pollution.

Combining both the highly environment friendly technologies such as the utilization of water and renewable materials can definitely have great impact in reducing the necessity of volatile organic compounds, which are largely based on depleting sources thereby routing the scope of high environment sustainability and provide a solution to the linear economy caused by the industrialization, rapid urbanization, growth of population and rise in living standards. This review strives to allure the focus of the researchers toward further exploration of this technique in academically or industrially important chemical processes and technology. These processes can become highly environment friendly technique by the reduction of waste and delivering low-cost media, catalysts and bases. The systematic review of the reported work on the titled area has been discussed here (Sects. 2–16). However, few reviews have been covered some of the work in the selected area of this review (Hussain et al. 2016; Sarmah et al. 2017b; Hooshmand et al. 2019; Gulati et al. 2020), but they are appeared to be very narrow in scope or discussed very few reports and hence this review undertake to provide a comprehensive information about all the reported investigations. In view of the significance and huge scope, the recent developments on the application of organic waste-derived ashes or their modifications in biofuel production are also summarized in Sect. 17 of this review.



Banana ash

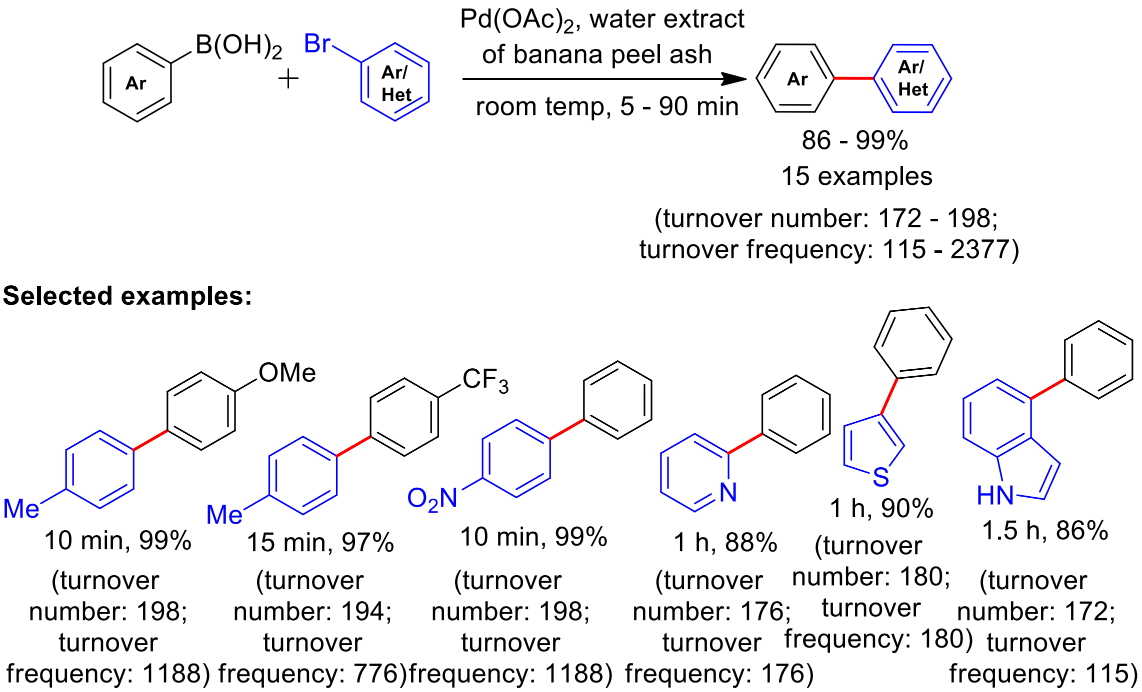
Banana peel ash contains potassium and sodium carbonates, potassium oxide and chlorides in significant amounts along with minor quantities of other metallic and non-metallic substances (Deka and Talukdar 2007; Pathak et al. 2018). Water extract of banana peel ash was investigated by Boruah et al. for its effective application as sustainable base and media for the room temperature Suzuki–Miyaura cross-coupling reaction of arylboronic acids and (hetero)aryl bromides under Pd(OAc)$_2$ catalysis (Scheme 1) (Boruah et al. 2015b). It seems to be the first report on the exploitation of water extracts of ash of waste for the organic transformations of industrial relevance and after which a very moderate efforts were appeared from various scientific teams on exploitation of these ashes/extracts for multifarious chemical transformations. Further, the biaryls formed in the Suzuki–Miyaura cross-coupling reaction are highly biologically and industrially important molecules, agrochemicals, functional materials and special chemicals (Rao et al. 2017a; Baran and Sargin 2020; Abaka et al. 2021) which is the Nobel Prize (2010) winning transformation in chemistry (Seechurn et al. 2012). Suzuki–Miyaura cross-coupling reaction is the widely used cross-coupling transformation among the others due to the use of readily available arylboronic acids which are fairly stable, nontoxic and highly reactive, and feasibility of a wide range of catalytic systems.

The reactions of Boruah and co-worker's method gave high yields (86–99%) of biaryls in the absence of external ligand, additives and organic solvents using aqueous media at ambient and non-inert conditions. A very good substrate scope was identified with quick reactions (5–90 min) in this investigation. The consumption of base of water extract of banana peel ash during the catalytic process of Pd-catalyzed Suzuki–Miyaura cross-coupling reaction was observed to restrict the reusability of water extract of banana peel ash, but it was evidenced the involvement (and necessity) of base of water extract of banana peel ash in the process. The high reactivity of arylboronic acids with aryl/heteroaryl bromides was proposed due to the presence of bases such as potassium and sodium carbonates and promoters such as sodium and potassium chlorides. This method also shows high calculated turnover number values as 172–198 and turnover frequency values as 115–2377.

Transition metal-promoted cross-couplings are evidenced as the prevailed strategies in the synthesis of C–C bonds (Choi and Fu 2017; Rao et al. 2017b). In this connection, banana peel ash-immobilized $PdCl_2$ was reported for the Suzuki–Miyaura cross-coupling reaction of benzeneboronic acid and 4-bromoanisole in ethanol at 100 °C using 2 eq. of K_2CO_3 to provide 49% of 4-methodybiphenyl in 24 h (Scheme 2) (Rosa et al 2019). This transformation shows the values of turnover number as 98 and turnover frequency as 4.

Saikia et al. implemented water extract of banana peel ash as renewable basic media to Dakin reaction using H_2O_2 as oxidant (Saikia et al. 2015a) (Scheme 3). Dakin reaction is an *ipso*-hydroxylation reaction of carbonyl function on *o*-/*p*-hydroxyaryl aldehydes/ketones using base (such as NaOH) and an oxidant (usually H_2O_2). In the developed oxidative hydroxylation process of aryl aldehydes by Saikia et al., water extract of banana peel ash plays a critical role as base catalyst and subsequently avoids the necessity of commercial base, NaOH (Saikia et al. 2015a). The water extracts of various parts of banana such as trunk, peels and rhizome have been studied in this investigation on Dakin reaction. The polyhydroxylated aromatics (phenols) formed in this process are fundamental substrates in making agrochemicals, agents of flavor, antioxidants, drugs, fine chemicals, etc. (Rappoport 2003; Das et al. 2004; Saikia et al. 2015a; Zeng et al. 2020), and this development can be performed at room temperature under mild conditions which is observed as an advantage over the necessity of harsh reaction conditions under traditional procedures (Dakin 1909; Chen and Foss Jr 2012). The polyhydroxylated aromatics are formed with excellent yields (90–98%) in 40–60 min using this protocol.

Surneni et al. established a nitro-aldol (Henry) reaction of (hetero)aryl/alkyl aldehydes and nitromethane using water extract of banana peel ash as reaction media and catalyst to produce *β*-nitroalcohols (Scheme 4) (Surneni et al. 2016). The *β*-nitroalcohols with multifunctional groups serve as important substrates in the synthesis of complex organic compounds (Mokhtar et al. 2020). The reported methods display disadvantages like the requirement of commercial bases/metal-based catalysts/harsh reaction conditions/

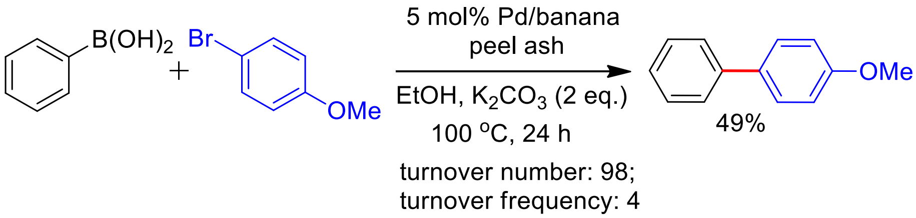


Scheme 1 $Pd(OAc)_2$-catalyzed Suzuki–Miyaura cross-coupling in water extract of banana peel ash

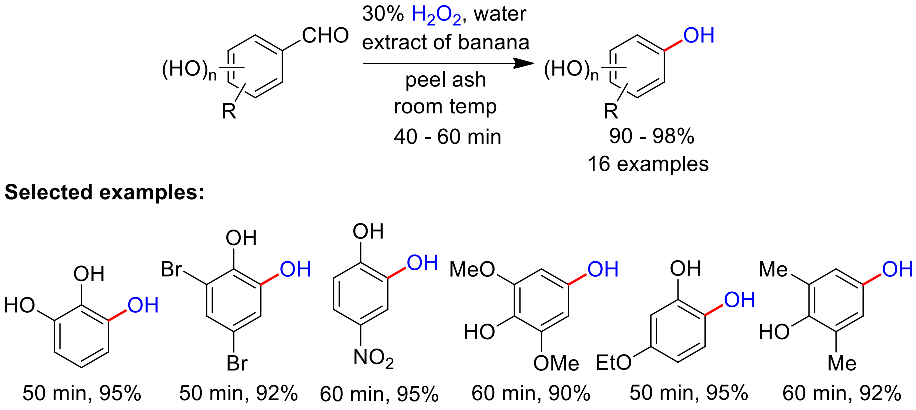
unconventional catalysts/organic solvents or suffers with less scope of substrates (Davis et al. 2001; Soengas and Silva 2012; Ganesan et al. 2014; Mokhtar et al. 2020). The method of Surneni et al. displays significant advantages as quick reaction profiles (2–4 h), good-to-excellent isolated product yields (40–95%), wide substrate scope, ambient condition and avoid of external catalyst and organic solvents. The reaction of cinnamaldehyde with nitromethane gave a product (**I**) via the Michael addition followed by Henry reaction is a unique example of this method. A variety of aldehydes attached to aryl, aliphatic, olefin and ester functions are examined to deliver high yields of Henry addition products using this sustainable protocol. In case of aryl aldehydes, the aryl moiety with electron-withdrawing substituents showed high yields over other aryl aldehydes. Pathak and co-workers also reported the Henry reaction using in situ synthesized iron-magnetic nanoparticles on water extract of banana peel ash (water extract of banana peel ash@Fe_3O_4 nanoparticles) as heterogeneous catalyst under solvent-free conditions (Scheme 5) (Pathak et al. 2019). The catalyst was systematically characterized using various spectroscopic and other physical techniques. 50 mg of catalyst loading was used for the 1 mmol of aldehyde to give high yields of *β*-nitroalcohols (70–99%) in 70–114 min, and the catalyst reusability studies showed 99%, 95% 89% and 85% of yields in 1–4 cycles using 4-nitrobenzaldehyde and nitromethane. A variety of aldehydes (including aliphatic and aromatic) and nitromethane/nitroethane/1-methylnitroethane are reported to show good results using this heterogeneous catalyst-assisted protocol.

The peptide bond formation is one of the elementary and widely employed transformations in organic synthesis in making biologically significant complex molecules, agrochemicals and industrially important substances (Tang and Becker 2014; Bryan et al. 2018). Development of convenient protocols for the peptide bond synthesis in water is a difficult and challenging task (Gabriel et al. 2015; Bryan et al. 2018). Water extract of banana peel ash has been reported for its

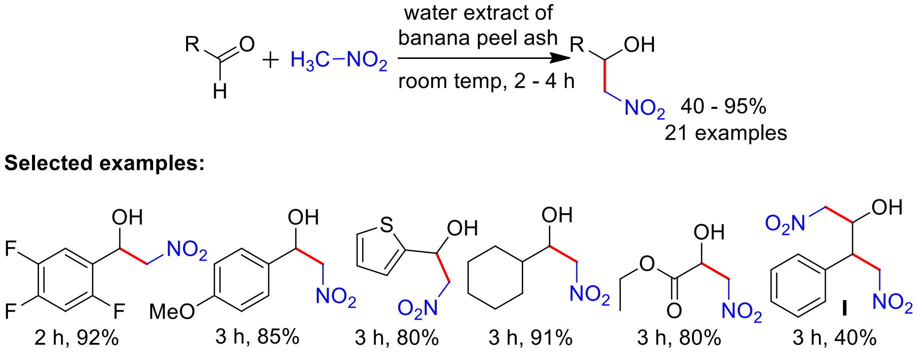
Scheme 2 Pd/banana peel ash-catalyzed Suzuki–Miyaura cross-coupling reaction



Scheme 3 Dakin reaction using H_2O_2–water extract of banana peel ash



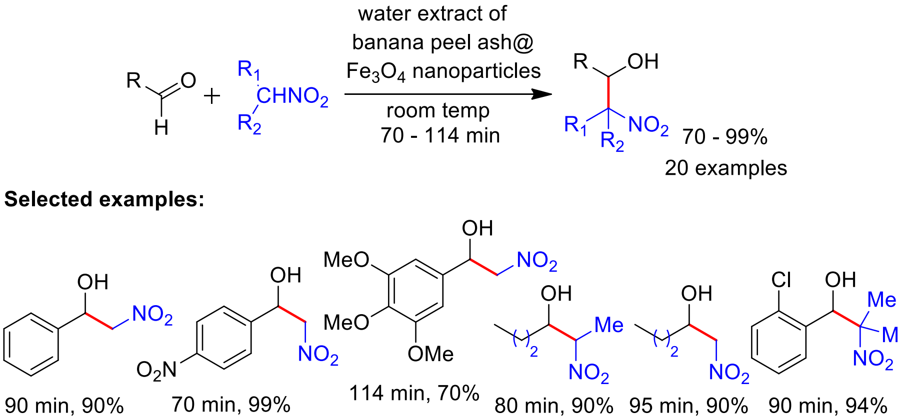
Scheme 4 Henry reaction in water extract of banana peel ash



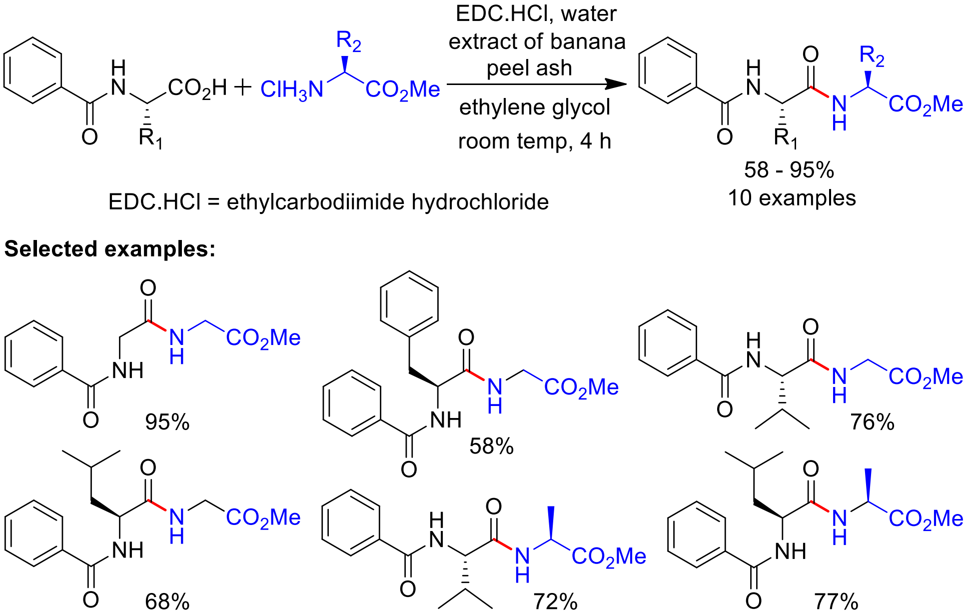
significant role as base and aqueous medium in peptide bond formation between *N*-benzoyl amino acids and hydrochlorides of methyl esters of amino acids using ethylcarbodiimide hydrochloride and ethylene glycol at room temperature (Scheme 6) (Konwar et al. 2016). The necessity of water extract of banana peel ash, ethylcarbodiimide hydrochloride (dehydrating agent) and ethylene glycol in the synthesis of peptide bond was systematically determined by the authors. This process using aqueous medium represents the natural synthesis of peptide since the peptides are made in biological systems using water as solvent. This water extract of banana peel ash-assisted synthesis of peptide bonds shows advantages as the avoid of external base, use of aqueous conditions, high yields (58–95%) of biologically/pharmaceutically/industrially important peptides, conduct of reactions at ambient conditions and exploration of biorenewable waste-derived catalyst.

Dewan et al. developed a sustainable, added base- and ligand-free cross-coupling process of monosubstituted alkynes (with alky or aryl substituents) and aryl bromides/iodides (Sonogashira cross-coupling) in water extract of banana peel ash under Pd(OAc)$_2$ catalysis at 60 °C (Scheme 7) (Dewan et al. 2016a). The Sonogashira cross-coupling can usually be catalyzed by palladium in the presence of copper-based co-catalysts and a phosphine ligand to synthesize disubstituted alkynes from organic halides and terminal alkynes, and the Sonogashira cross-coupling products are the highly important substrates in the synthesis of dyes, pharmaceuticals, polymers, natural products, sensors and heterocyclic compounds (Dewan et al. 2016a; Bonacorso et al. 2018; Krishnan et al. 2019; Kanwal et al. 2020). The water extract of banana peel ash-assisted protocol shows certain advantages as the development of economical, convenient and highly sustainable procedure which avoids copper-based catalyst as co-catalysts, ligands, external base and volatile organic solvents. The substituted alkynes are formed using this protocol with good-to-excellent yields (40–98%) in 1–8 h (Scheme 7). The addition of ethanol as

Scheme 5 Henry reaction in water extract of banana peel ash@Fe$_3$O$_4$ nanoparticles



Scheme 6 Peptide bond formation in water extract of banana peel ash

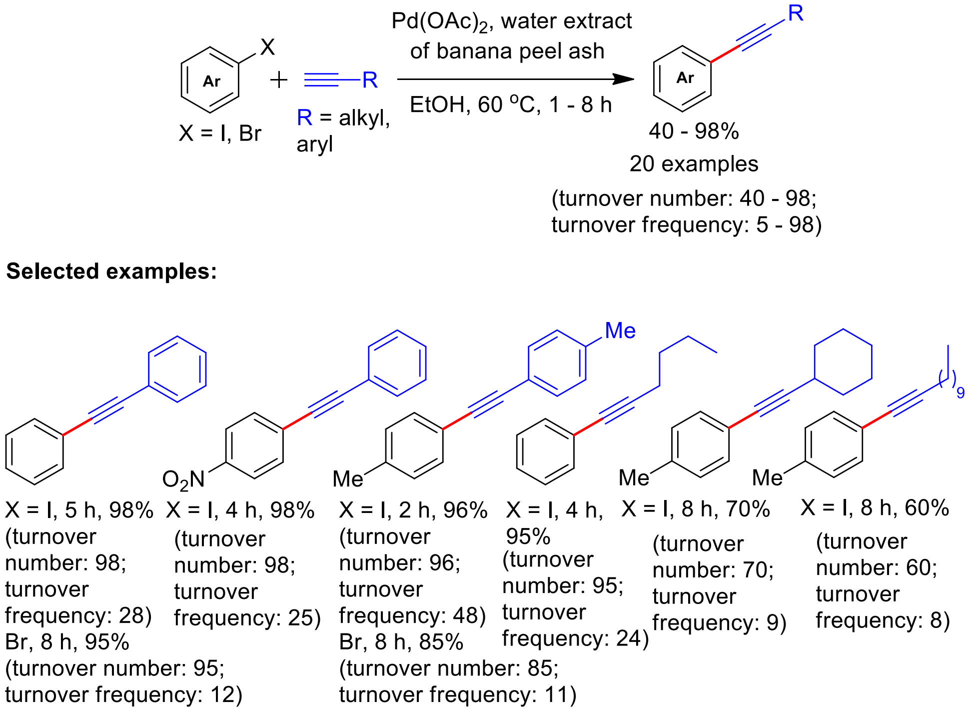


co-solvent showed best results and aryl iodides are observed as the best substrates than aryl bromides in this development. The turnover number and turnover frequency values of this method are observed as 40–98 and 5–98.

Water extract of banana peel ash was also reported as catalyst and medium for the oxidative deborylative hydroxylation (*ipso*-hydroxylation) reaction of (hetero) arylboronic acids employing H_2O_2 as external oxidant (Scheme 8) (Saikia et al. 2016). It is an attractive alternative method to the transition metal, external base and organic solvent-based traditional methods of *ipso*-hydroxylation of (hetero)arylboronic acids to produce synthetically and pharmaceutically valuable phenols (Hao et al. 2019; Muhammad et al. 2020) with high yields (88–97%) in 5–15 min. The easy availability and high stability of arylboronic acids (Rao and Venkateswarlu 2018) are an added advantage in this protocol. Several (hetero)arylboronic acids with electron-releasing and electron-withdrawing functional groups are converted conveniently into phenols using this protocol (Scheme 8). A good reusability of the catalytic media, water extract of banana peel ash was observed up to five cycles and showed 97%, 97%, 96%, 94% and 93% of yields of phenol from benzeneboronic acid in 1–5 cycles. Banana peel ash was also reported for the oxidative hydroxylation (*ipso*-hydroxylation) of (hetero)arylboronic acids in water using 30% H_2O_2 (Scheme 9) (Das et al. 2020b). The fair reusability of banana peel ash–H_2O system up to five cycles was studied to produce 96%, 94%, 91%, 90% and 86% yields of phenol from benzeneboronic acid in 1–5 cycles. The comparison of banana peel ash-assisted *ipso*-hydroxylation process of arylboronic acids with some reported heterogeneous catalysts-assisted protocols is shown in Table 1, and it indicates the present method avoids the necessity of external catalysts to access phenols at mild and sustainable conditions.

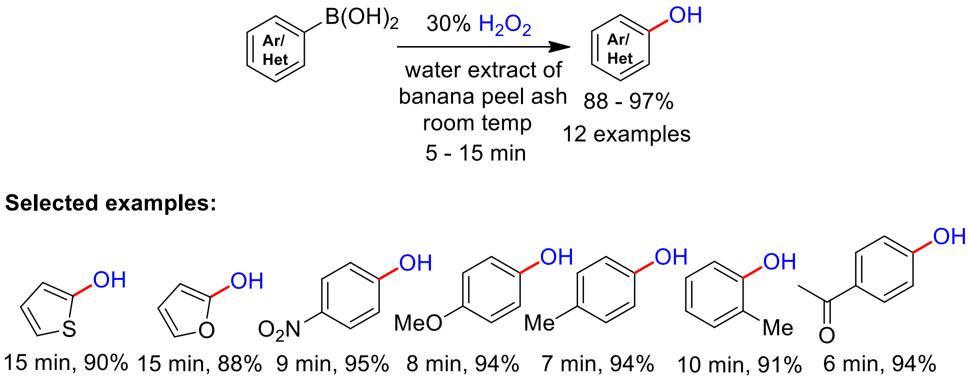
The synthesis of a variety of 3-carboxycoumarins using water extract of banana peel ash as catalytic media was reported by Bagul and co-workers (Bagul et al. 2017). The reaction of salicylaldehydes with Meldrum's acid was used for the preparation of 3-carboxycoumarins with 76–96% yields in 6.7–8.2 h employing water extract of banana peel ash–EtOH mixture (Scheme 10) at room temperature. Coumarins constitute a prominent class of natural products and possess a wide range of biological properties including antioxidant, anti-acetylcholinesterase (AChE), antifungal, antipyretic and anti-inflammatory (Trost and Toste 1996; Gover and Jachak 2015; Wienhold et al. 2021). Coumarins are also well known for their application in food as additives, pharmaceuticals, cosmetics, perfumes, fluorescent dyes and optical brighteners (Myung et al. 2013; Bagul et al. 2017). A variety of catalysts including NH_4OAc (Alvim et al. 2005), $SnCl_2 \cdot 2\ H_2O$ (Karami et al. 2012), K_3PO_4 (Undale et al. 2012), $FeCl_3$ (He et al. 2015) and $LiClO_4$–LiBr (Bandgar et al. 2002) are reported for the synthesis of coumarins from substituted salicylaldehydes and Meldrum's acid. These protocols required additional catalysts/promoters and hence the water extract of banana peel ash-assisted protocols is an important contribution for the synthesis of coumarins with the application of bio-derived base at ambient conditions. Further, the compounds are purified by recrystallization

Scheme 7 $Pd(OAc)_2$-assisted Sonogashira reaction in water extract of banana peel ash

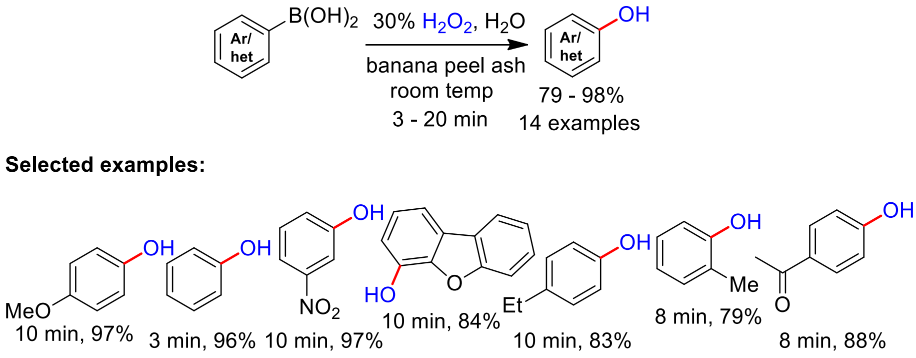


technique avoiding extraction and column chromatographic separations.

A natural feedstock-based azidification reaction of arylboronic acids was reported by Saikia (Saikia 2018) using CuI as catalyst in water extract of banana peel ash. The organic azides are the prominent substrates in making a variety of nitrogen heterocycles including tetrazoles and triazoles (Saikia 2018), and these are the important sources for the nitrogen compounds such as amides, imines, amines, phosphazenes and aziridines (Saikia 2018). Arylboronic acids are

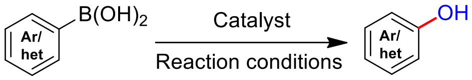


Scheme 8 *Ipso*-hydroxylation reaction of (hetero)arylboronic acids with water extract of banana peel ash–H_2O_2



Scheme 9 Banana peel ash-assisted *ipso*-hydroxylation of (hetero)arylboronic acids using H_2O_2

Table 1 Comparison of results of *ipso*-hydroxylation of arylboronic acids using banana peel ash and other reported catalysts[a]

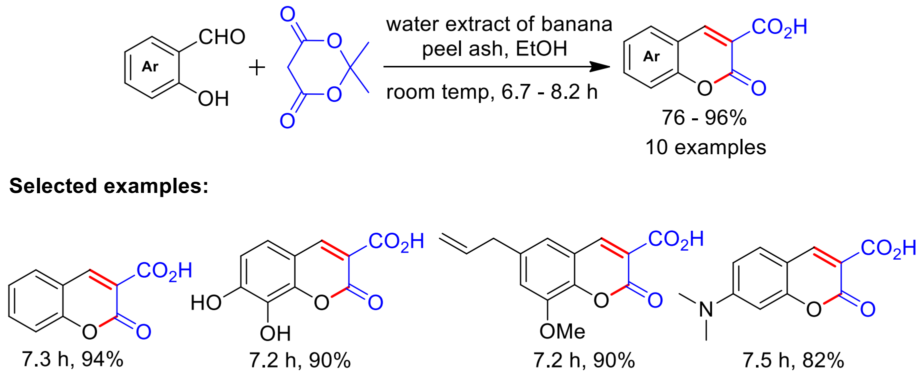


Entry	Catalyst	Reaction conditions	% Yield	Recyclability of the catalyst	Ref
1	Pd-chitosan–carbon nanotubes (10 wt%[b] Pd-content, 3 mg)	H_2O_2 (3 mL), room temp, 15 min	48–94	Up to 6th cycle	Shin et al. (2019)
2	Fe_2O_3@SiO_2 (4 mg)	H_2O (4 mL), O_2, 50 °C, 2–5 h	86–98	Up to 5th cycle	Saikia et al. (2017)
3	Ag nanoparticles@ montmorillonite K-10 (5 mg)	30% H_2O_2 (0.5 mL), room temp, 15–35 min	85–95	Up to 7th cycle	Begum et al. (2015)
4	Carbon nanotubes–chitosan film (10 mg)	$CuSO_4{\cdot}5H_2O$ (0.1 mmol), KOH (3 eq.) H_2O (5 mL), room temp, under air, 24 h	85–95	Up to 5th cycle	Kim et al. (2018)
5	Ni(benzene-1,3,5-tricarboxylate)4,4’-bipyridine metal organic framework (30 wt%[b])	H_2O_2 (0.4 mmol), EtOH (1 mL), room temp, 10 min	72–98	Up to 5th cycle	Latha et al. (2020)
6	Banana peel ash (10 wt%[b])	H_2O (2 mL), 30% H_2O_2 (0.5 mL), room temp, under air, 3–20 min	79–98	Up to 5th cycle	Das et al. (2020b)

[a] This table has been reproduced from Das et al. (2020b) with permission from the Elsevier

[b] wt% = weight percent

Scheme 10 Synthesis of 3-carboxycoumarins in water extract of banana peel ash

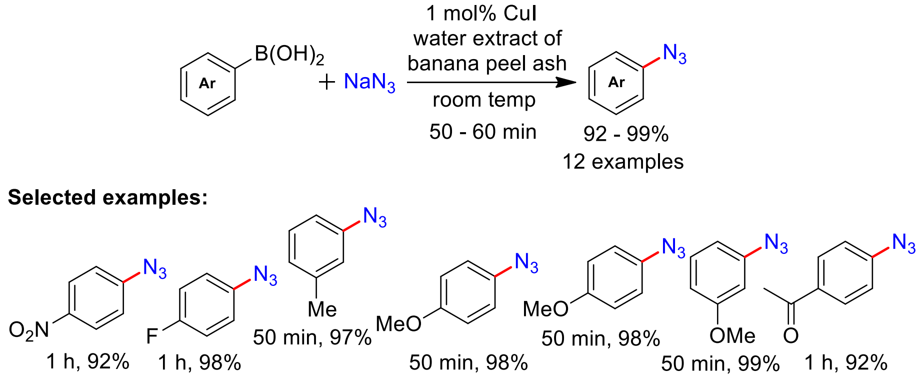


the highly reactive substrates in making aryl azides using an azide source (e.g., $TMSN_3$ and NaN_3), and the conversion requires a copper-based catalyst, solvent (usually CH_3OH)/base/promoter and heating conditions (Saikia 2018). The method of Saikia is a sustainable example to the conventional heating methods, and this process proceeds at room temperature. This process avoids the toxic CH_3OH as solvent or co-solvent and external base/promoters/additives. High yield of the aryl azides (92–99%) was achieved in short reaction times (≥ 1 h) (Scheme 11). The crude product (phenyl azide or 4-azidoanisole) in water extract of banana peel ash was also studied for the click reaction with phenyl acetylene and found successful for the formation of 1,4-diaryl-1,2,3-trizole derivatives in 80 and 85% yields using 1 eq. of $CuSO_4{\cdot}5H_2O$ and sodium ascorbate (1 eq.) (Scheme 12) (Saikia 2018). The reaction mixture of azidification reaction directly investigated for the click reaction is another example of the external base-free reaction in natural feedstocks.

A multicomponent method for the preparation of 2-amino-4*H*-chromenes from phenols, malononitrile and aryl aldehydes has been reported by Kantharaju and Khatavi using water extract of banana peel ash as catalytic media under microwave irradiation (300 W) (Kantharaju and Khatavi 2018a). In this method the product yields are observed as 68–79% in 2.2–4.0 min (Scheme 13). A grindstone method was also established in the same article, but the reactions require 15–25 min for the completion. The 2-amino-4*H*-chromenes are also tested for in vitro antimicrobial activity and found to show good activity against *Klebsiella*, *Escherichia coli*, *Aspergillus niger* and *Candida*. This multicomponent strategy avoids the external catalysts as necessary with the reported procedures (Mohammadi et al. 2019; Tahmassebi et al. 2019; Ebrahimiasl and Azarifar 2020) can be operated at mild and aqueous conditions.

Pathak et al. reported the application of banana peel ash as sustainable catalyst (heterogeneous) for the biodiesel production from soybean oil via the transesterification phenomenon (Scheme 14a) (Pathak et al. 2018). The soybean oil was converted to its corresponding fatty acid methyl ester (biodiesel) with 98.95% conversion using 0.7 weight percent banana peel ash and methanol. The catalyst was studied for reusability and found the decreased activity; ~ 52.16% conversion was observed in 4th cycle due to the loss of potassium and calcium. Banana peel ash was also reported for the biodiesel production using soybean oil and methanol by Fan et al. (2019) (Scheme 14b). This transesterification showed 95.1% conversion of soybean oil to biodiesel in 1 h at 65 °C employing 1.5 weight percent of banana peel ash and methanol to oil ratio as 15:1. The banana peel ash was characterized to exist well-dispersed microstructured K_2O–KCl; due to this the banana peel ash shows high catalytic activity over the physically mixed K_2O and KCl catalysts. The reusability

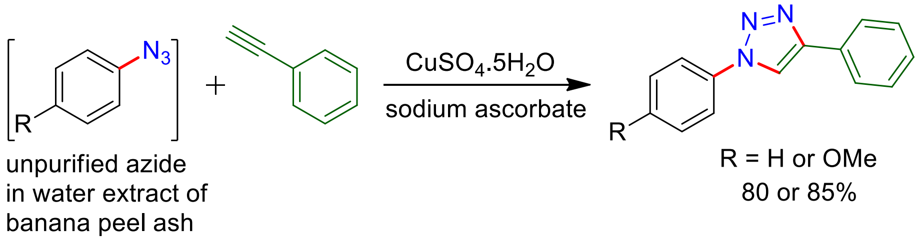
Scheme 11 Synthesis of aryl azides from arylboronic acids using CuI–water extract of banana peel ash system



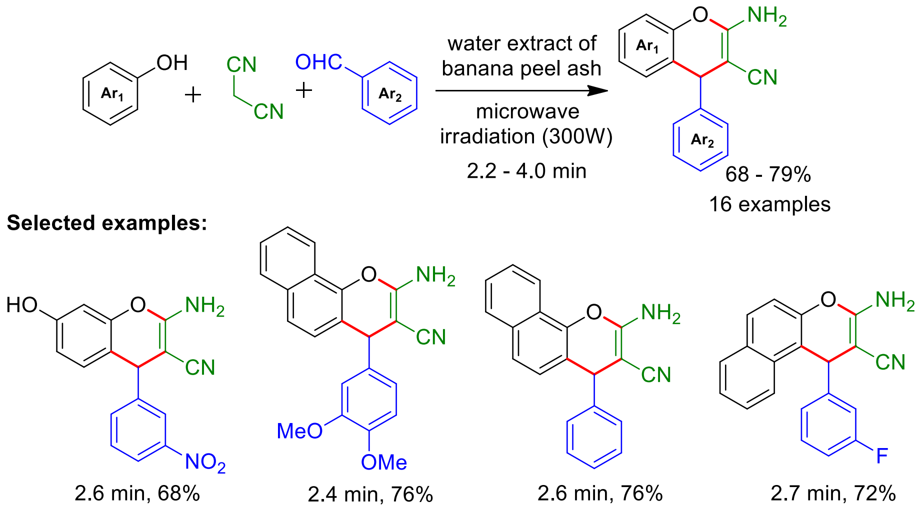
studies of the banana peel ash showed 75.5% biodiesel conversion in 4th cycle.

The condensation reaction of (hetero)aryl aldehydes and malononitrile (Knoevenagel condensation) was reported by Kantharaju et al. for the synthesis of α,β-unsaturated nitriles using water extract of banana peel ash employing grindstone method (Scheme 15) (Kantharaju et al. 2018). This method shows advantages as the use of renewable catalyst and medium, evade of external catalysts and organic solvents which are based on the depleting petro chemicals, ambient conditions, high product yields (80–93%) and short reaction times (4–10 min). The products are purified by non-chromatographic method (filtration and recrystallization).

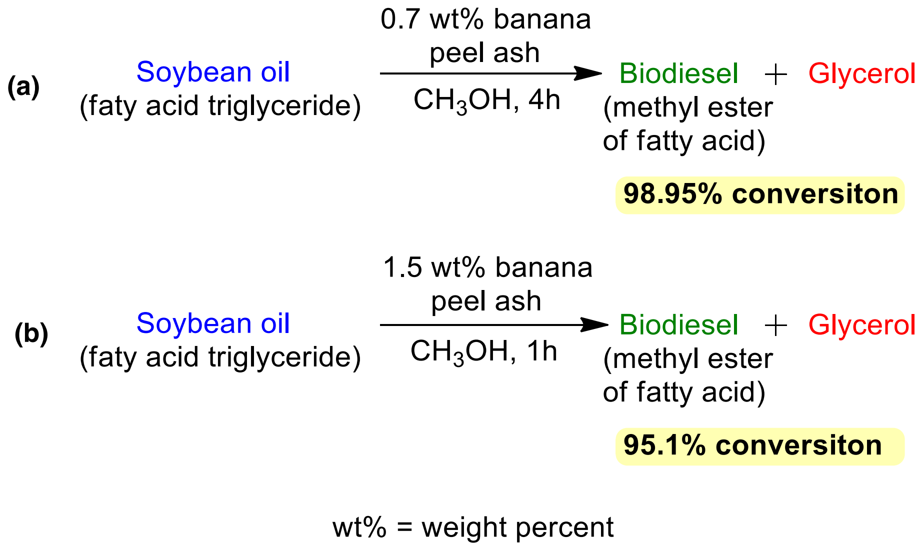
Banana peel ash was also reported for the Knoevenagel condensation reaction in EtOH at 50 °C (Scheme 16) (Laskar et al. 2019). The aryl/heteroaryl aldehydes showed high reactivity with malononitrile/nitromethane/acetyl acetone/diethyl malonate. The reactions are reported to proceed



Scheme 12 One-pot azide–alkyne click reaction in water extract of banana peel ash



Scheme 13 Synthesis of 2-amino-4*H*-chromenes in water extract of banana peel ash under microwave irradiation



Scheme 14 Preparation of biodiesel from soybean oil using banana peel ash as catalyst

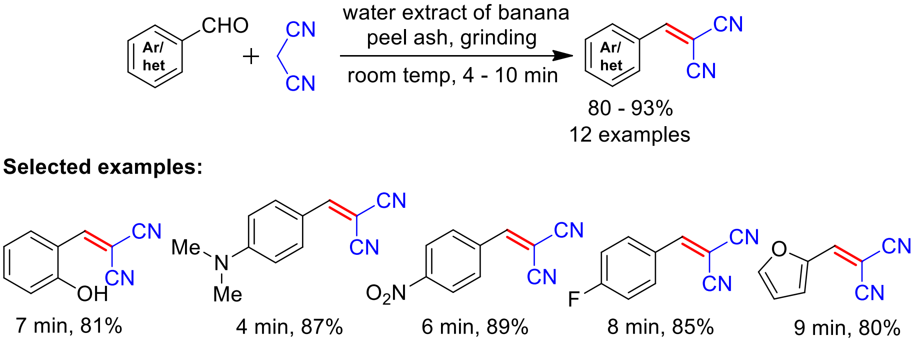
in 10–30 min to provide their corresponding condensation products in 74–96% yields. The banana peel ash was reused and found to be efficient up to six cycles; 86% of the product was observed in sixth cycle, and 96%, 96%, 95%, 93% and 90% of product yield was observed in 1–5 cycles using benzaldehyde and malononitrile as substrates. Table 2 shows the significance of this method over the other recent reports.

Leitemberger et al. established a straightforward procedure for the oxidative synthesis of diorganic disulfides in open air using water extract of banana peel ash as a renewable media and oxidant (Scheme 17) (Leitemberger et al. 2019). The organic disulfides are the motifs in several biomolecules shows high biological and synthetic significance (Leitemberger et al. 2019). These are accessed using oxidants and metal (e.g., iron, gold, palladium, copper and cobalt)-based catalysts at heating conditions in unconventional/volatile solvents (Leitemberger et al. 2019). The method of Leitemberger et al. is an excellent example of the exploration of waste-derived, natural oxidizing agent (such as water extract of banana peel ash) to valuable organic transformations. The interesting prospects of this work are the evade of external oxidant, toxic/problematic organic solvents and catalysts, high yields of products in several examples (up to 99%), wide substrate scope including heteroaryl, aryl and alkyl thiols, good biological and industrial significance of the products, mild reaction conditions, exploitation of waste and the use of aqueous media. The proposed mechanism of disulfide synthesis in water extract of banana peel ash is presented in Fig. 1.

Aldol-type addition reaction of aldehydes and ethyl diazoacetate in water extract of banana peel ash–dimethyl sulfoxide system was developed by Dutta et al. to produce *α*-diazo-*β*-hydroxy esters (Scheme 18) (Dutta et al. 2019). This reaction was reported using bases like lithium diisopropylamide, NaH, BuLi, KOH, KOtBu, 1,8-diazbicyclo-[5.4.0]undec-7-ene (DBU), Bu_2Mg, Et_3N-diisopropylamine, etc. (Dutta et al. 2019). But, the protocol of Dutta et al. uses natural base and it is also studied to be reusable up to five cycles with a slight variation in yields. This method was also extended for the one-pot, two-step access to *β*-keto esters via the $Pd(PPh_3)_4$-catalyzed 1,2-hydrogen shift, and the *β*-keto esters are formed in 50–80% yields (Scheme 19) (Dutta et al. 2019). Further, this method was investigated for the effective formation of imidazo[1,2-*a*]pyridine-3-carboxylic acid ethyl esters by three-step, one-pot sequential process via aldol-type reaction of aldehydes and ethyl diazoacetate, and Pd-catalyzed hydrogen 1,2-shift followed by reacting with 2-aminopyridines [under *N*-bromosuccinimide catalysis] in water extract of banana peel ash–dimethyl sulfoxide system (Scheme 20) (Dutta et al. 2019). This sustainable preparation of *α*-diazo-*β*-hydroxy esters and one-pot sequential reactions of *α*-diazo-*β*-hydroxy esters to produce further valuable compounds under waste-derived catalyst media with high pot-economy are the strengths of this report (Dutta et al. 2019).

Dwivedi et al. developed a new protocol for the preparation of pyrano[2,3-*c*]pyrazoles from pyrazolones and

Scheme 15 Knoevenagel condensation using water extract of banana peel ash at grinding condition



Scheme 16 Knoevenagel condensation using banana peel ash in EtOH

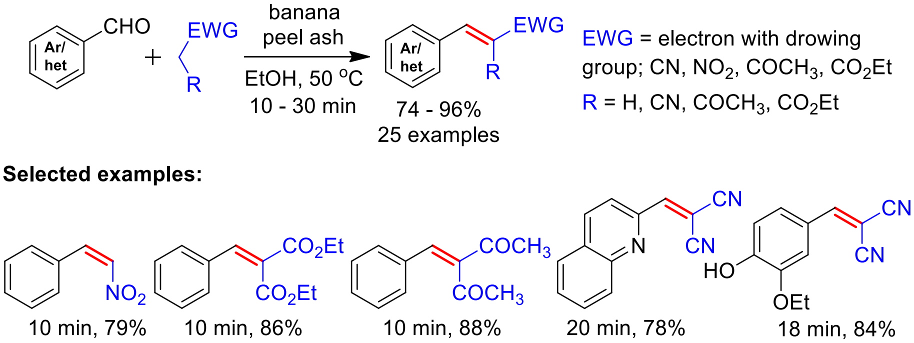
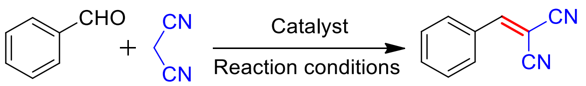


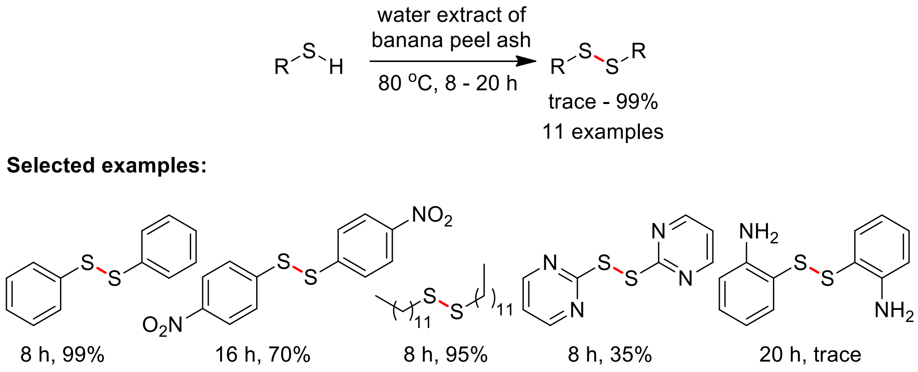
Table 2 Comparison of results of Knoevenagel reaction of benzaldehyde and malononitrile using banana peel ash with other reports[a]



Entry	Catalyst	Solvent	Time (min)	Temp (°C)	Yield (%)	Ref
1	Metal organic framework-Pd	Dimethyl sulfoxide	5	25	42.5	Ezugwu et al. (2016)
2	Metal organic framework-NH_2	Dimethyl formamide	270	80	51	Taher et al. (2016)
3	Chitosan	EtOH	360	40	99	Sakthivel and Dhakshinamoorthy (2017)
4	Pd@Aluminum oxyhydroxide	H_2O:MeOH (1:2)	25	Room temp	85	Göksu and Gülteki (2017)
5	Magnetic nanoparticles-diethylenetriamine tribromide	H_2O	50	70	94	Shiri et al. (2017)
6	NH_2-MgAl-layered double hydroxide nanosheets	Toluene	60	40	95.6	Jia et al. (2018)
7	Banana peel ash	EtOH	10	50	96	Laskar et al. (2019)

[a] This table has been reproduced from Laskar et al. (2019) with permission from the Elsevier

Scheme 17 Disulfide synthesis from oxidative coupling of thiols in water extract of banana peel ash



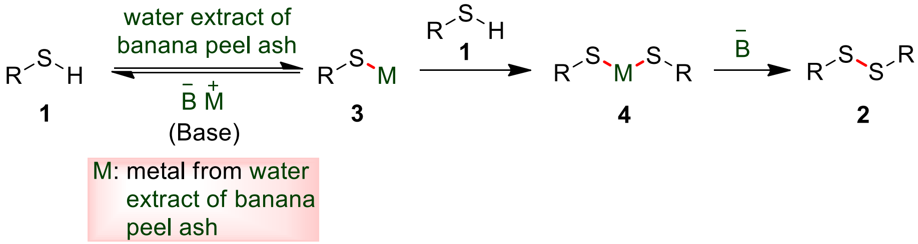
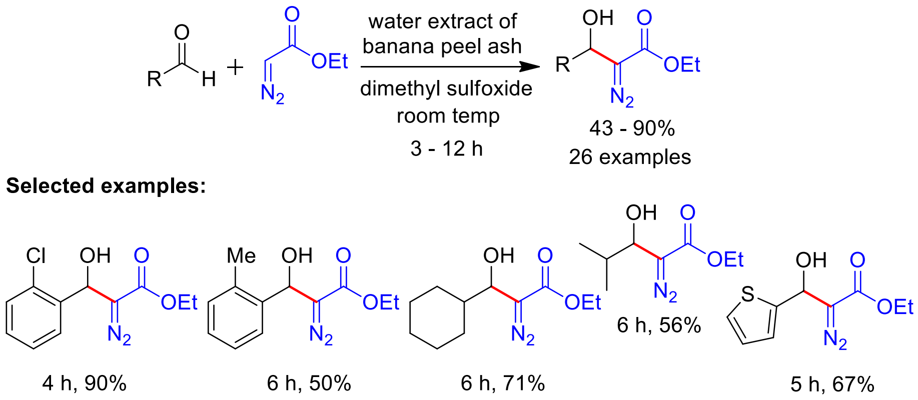


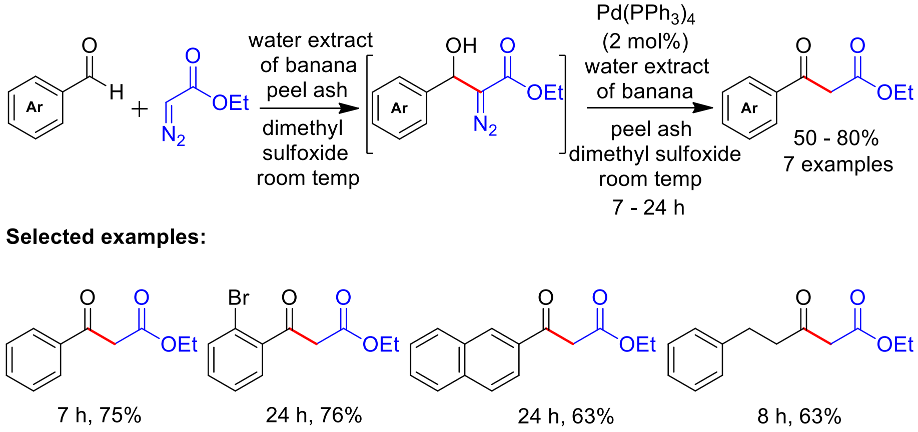
Fig. 1 Plausible mechanism of disulfide synthesis in water extract of banana peel ash. In this mechanism, the disulfides (**2**) are formed from thiols (**1**) via the intermediates, metal (from water extract of banana peel ash) thiolate **3** by deprotonation of thiol and metal dithiolate **4** by further deprotonation of thiol. The mechanism was evidenced to proceed through the ionic mechanism using some control experiments; the reaction is successful using radical scavengers such as (2,2,6,6-tetramethylpiperin-1-yl)oxidanyl (TEMPO), hydroquinone and 2,6-bis(1,1-dimethylethyl)-4-methylphenol (BHT) (Leitemberger et al. 2019). This figure has been reproduced from Leitemberger et al. (2019) with permission from the John Wiley & Sons

α,β-unsaturated nitriles using water extract of banana peel ash as catalytic media (Scheme 21) (Dwivedi et al. 2020). The pyranopyrazoles constitute a unique class of nitrogen heterocycles with the fused pyrazole and pyran rings. These are the well-known motifs in medicinally important compounds shows a broad range of biological properties like anti-HIV, anticancer, analgesic, insecticidal, etc. activities (Dwivedi et al. 2020). This conversion was reported by using catalysts such as L-proline, Et_3N, Mg nanoparticles, piperidine, morpholine, cupreine, cyclodextrin, etc. (Dwivedi

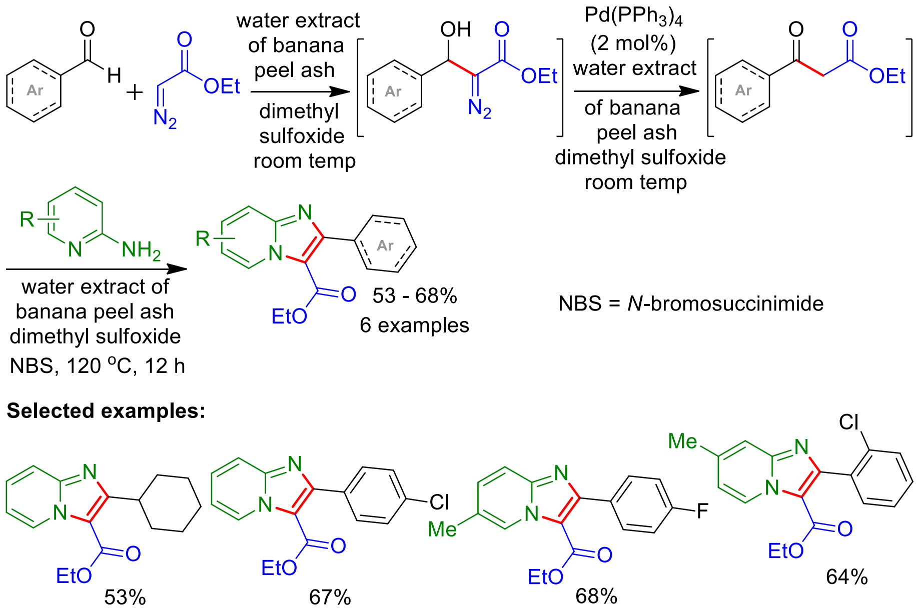
Scheme 18 Synthesis of *α*-diazo-*β*-hydroxy esters in water extract of banana peel ash–dimethyl sulfoxide system



Scheme 19 One-pot two-step synthesis of *β*-keto esters in water extract of banana peel ash–dimethyl sulfoxide system



Scheme 20 One-pot three-step synthesis of imidazopyridines in water extract of banana peel ash–dimethyl sulfoxide system



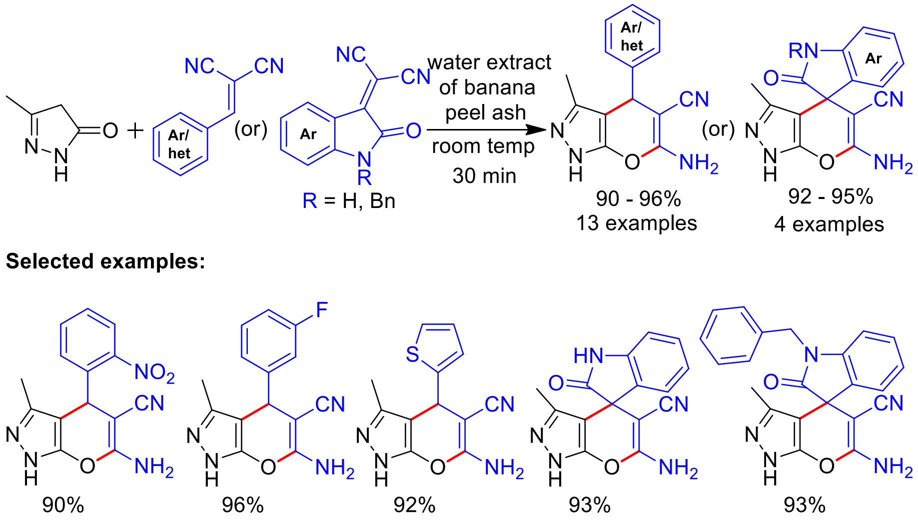
et al. 2020). But, this method uses renewable catalyst. This method can be performed at room temperature and the products are purified by non-chromatographic, recrystallization technique. Pyrano[2,3-*c*]pyrazoles are formed in high yields (90–96%) in 30 min in this development.

A heterogeneous lithium calcium oxide iron sulfate [Li-CaO/$Fe_2(SO_4)_3$] supported on banana peel ash was reported as efficient catalyst for the biodiesel synthesis from neem seed oil (Scheme 22) (Madai et al. 2020). 99.8% transformation of neem seed oil as biodiesel (methyl ester of fatty oil) was observed using 8:1, oil/CH_3OH ratio using catalyst load: 1.7 weight percent of banana peel ash–1.3 weight percent of Li-CaO/$Fe_2(SO_4)_3$ in 53 min at 60 °C. This banana peel ash–metal oxide system was studied to show 75.6% conversion of neem seed oil to biodiesel in fifth cycle is a noteworthy advantage of this development.

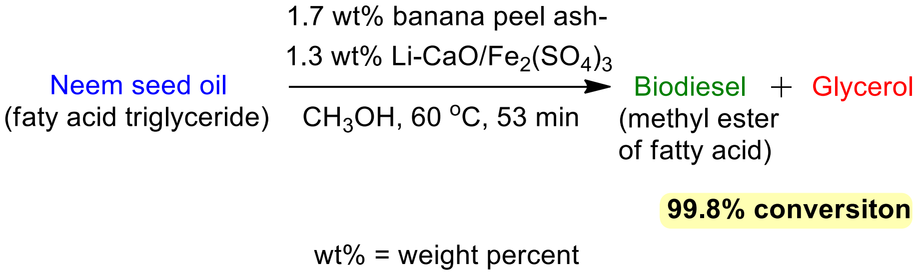
Pyridine-based compounds are the widely distributed among all the nitrogen heterocycles in a variety of biologically active natural products and hence the development protocols for the preparation of these moieties has high synthetic importance (Hill 2010). The four-component route using malononitrile, aldehydes and thiols is an important technique to access highly substituted pyridines and was reported using catalysts: $NaNH_2$, $ZrClO_2$, silica nanoparticles, CuI nanoparticles, $Sc(OTf)_3$, Al_2O_3, CH_3COONa, Zn(II) and Cd(II) metal organic frameworks, boric acid, $ZnCl_2$, Cao nanoparticles, etc., typically in volatile organic/unconventional solvents (Evdokimov et al. 2007; Ali et al. 2020; Ebrahimiasl et al. 2020; Allahi and Akhlaghinia 2021). Allahi and Akhlaghinia reported this multi(four) component reaction using water extract of banana peel ash as catalyst and medium for an effective synthesis of 2-amino-3,5-cyano-6-thiopyridines at 65 °C (Scheme 23) (Allahi and Akhlaghinia 2021). This investigation displays the advantages as the use of waste-derived catalyst, evade of toxic and volatile organic solvents, wide substrate scope, unnecessitating the metal-based or costly catalysts, application of inexpensive materials and mild conditions. The aryl aldehydes (with electron attracting and electron releasing groups) and heteroaryl aldehydes showed high isolated product yields of pyridines (80–90%) in 10–45 min (Scheme 23). Similarly, a wide range of thiols (aryl and alkyl) showed impressive results using water extract of banana peel ash-catalyzed protocol.

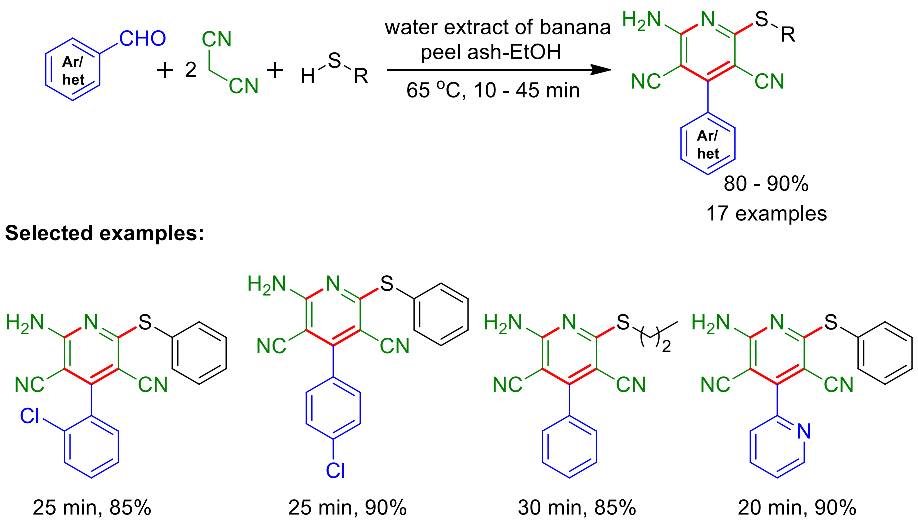
Water extract of banana peel ash has also been reported for the synthesis of chalcones and flavones via Claisen–Schmidt condensation of (hetero)aryl aldehydes and aryl methyl ketones at room temperature (Scheme 24) (Tamuli et al. 2020). The flavones and chalcones are the naturally available biopotent compounds and are the usual building blocks in industrially important chemical transformations (Wen et al. 2018; Qin et al. 2020; Tamuli et al. 2020; Zaragozá et al. 2020). Two different banana species Malbhog and *Musa champa* are studied individually in this method. Water extract of Malbhog peel ash (**I**) showed slightly better activity than water extract of *Musa champa* peel ash (**II**) (Scheme 24). Flavones are synthesized in the presence of O_2 (1 atm) as an external oxidant in water extract of banana peel ash. Large substrate scope, high product

Scheme 21 Preparation of pyrano[2,3-*c*]pyrazoles employing water extract of banana peel ash as catalytic media



Scheme 22 Biodiesel preparation from neem seed oil using banana peel ash–Li-CaO/$Fe_2(SO_4)_3$ system

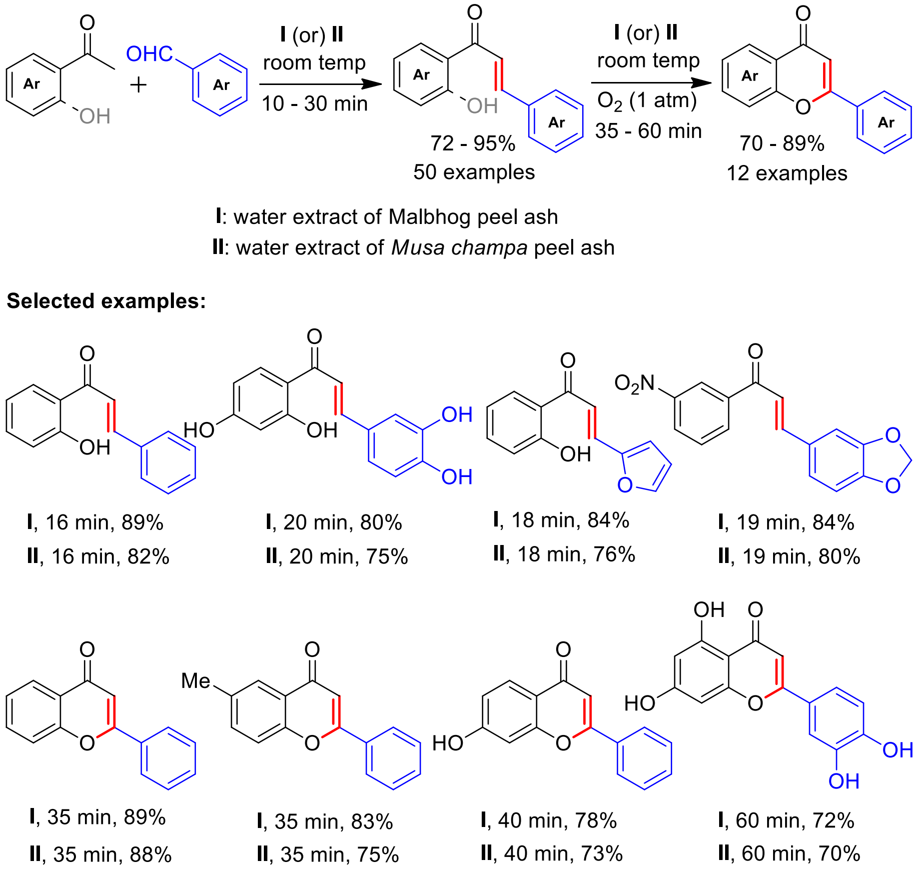




Scheme 23 Synthesis of polysubstituted pyridenes under water extract of banana peel ash catalysis

yields, nature-inspired conditions, exploration of waste, characterization of banana ashes and high reaction rates are the advantages this method. It avoids harsh reaction conditions, costly catalysts/reagents, inert atmosphere and organic solvents of reported protocols (Golshani et al. 2017; Bentahar et al. 2020; Halpani and Mishra 2020; Tamuli et al. 2020).

Das et al. developed a green protocol for the hydration of aryl nitriles to give amides using water extract of banana peel ash as reaction medium and H_2O_2 as source of oxygen at 60 °C (Das et al. 2021) (Scheme 25). Recently, some metal (ruthenium and palladium)-based catalysts were appeared in the literature for the preparation of amides by a controlled hydration of nitriles (Matsuoka et al. 2015; Rao et al. 2016; Jia et al. 2017; Sharley and Williams 2017).



Scheme 24 Synthesis of chalcones and flavones in water extract of banana peel ash

Products yields are reported with 70–97% in 1–7 h. The proposed mechanism of hydration of aryl nitriles using water extract of banana peel ash–H_2O_2 system is shown in Fig. 2. The comparison of this method with the recently reported methods is shown in Table 3 toward indicating the merits of this water extract of banana peel ash-based protocol.

Banana (*Musa bulbasiana*) stem ash has also been demonstrated as highly economical alternative in biogas-producing plants to improve the quality of biogas by the effective reduction of CO_2 (capable to 20%) from biogas (Baruah et al. 2017). The presence of significant amounts of potassium and calcium in banana stem ash is responsible for the efficient removal of CO_2. Difference in the amount of CO_2 absorption was identified by changing the weight of ash and height of bed of scrubber material. This process with effective absorption of CO_2 from biogas enhanced its gross calorific value (GCV).

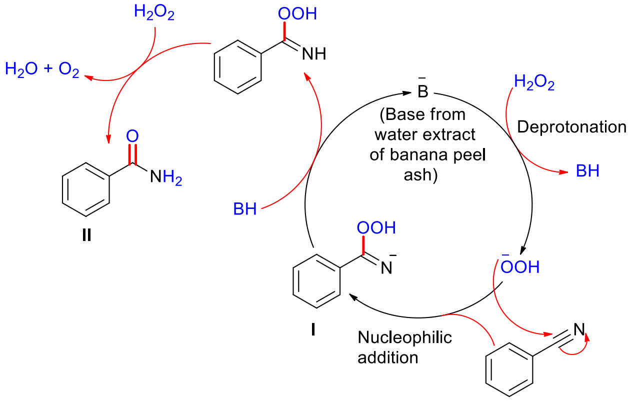


Fig. 2 Proposed mechanism of hydration of aryl nitriles using water extract of banana peel ash–H_2O_2. Initially, the base of water extract of banana peel ash and H_2O_2 generates α-hydroperoxyimine intermediate **I** from nitrile via a nucleophilic reaction of nitrile with hydroperoxide ion of water extract of banana peel ash–H_2O_2 system. The intermediate **I** gives amide (**II**) in the presence of H_2O_2 via the protonation followed by the loss of oxygen and tautomerization. This figure has been reproduced from Das et al. (2021) with permission from the Elsevier

Pomegranate peel ash

Lakshmidevi et al. developed water extract of pomegranate peel ash-promoted Ullmann coupling reaction of aryl halides (Scheme 26) (Lakshmidevi et al. 2018). It was reported to present the potassium, magnesium, calcium, carbon, oxygen and chlorine as major constituents of water extract of pomegranate peel ash by X-ray photoelectron spectroscopy and energy-dispersive X-ray analysis (Lakshmidevi et al. 2018), and the presence of major constituents as K_2O, Cl, Na_2O, SO_3, MgO, CaO and SiO_2 was also identified using X-ray fluorescence analysis (Appa et al. 2021a). The water extract of pomegranate peel ash played a significant role as critical base (due to the presence of basic components) and aqueous media in Ullmann coupling reaction under added ligand-, base- and π-acid-free, mild conditions (Lakshmidevi et al. 2018). The formation of biaryls in excellent yields (up to 99%) at moderate temperate (80 °C) and low catalyst loading (3 mol%) (usually the Ullmann reaction of aryl halides needs elevated temperature and stoichiometric amounts of catalysts such as copper or palladium) and wide substrate scope are the significant advantages of this protocol. The formation of protodehalogenation and hydroxydehalogenation products is also reported in this finding. The order of reactivity of aryl halides was reported as Ar–I > Ar–Br >>> Ar–Cl, and a constructive comparison of reported Pd-catalyzed Ullmann couplings was made to unveil the effectiveness of water extract of pomegranate peel ash-mediated Ullmann coupling (Lakshmidevi et al. 2018). Turnover number and turnover frequency values of this method have been observed as 8–33 and 1–17. The mechanism of Pd-catalyzed Ullmann coupling in water extract of pomegranate ash is shown in Fig. 3. The comparison of reported Ullmann coupling protocols using palladium-based catalysts is represented in Table 4.

Appa et al. used water extract of pomegranate ash for the construction of biaryls via the Suzuki–Miyaura cross-coupling reaction of arylboronic acids and aryl bromides/

Scheme 25 Hydration reaction of aryl nitriles using water extract of banana peel ash–H_2O_2

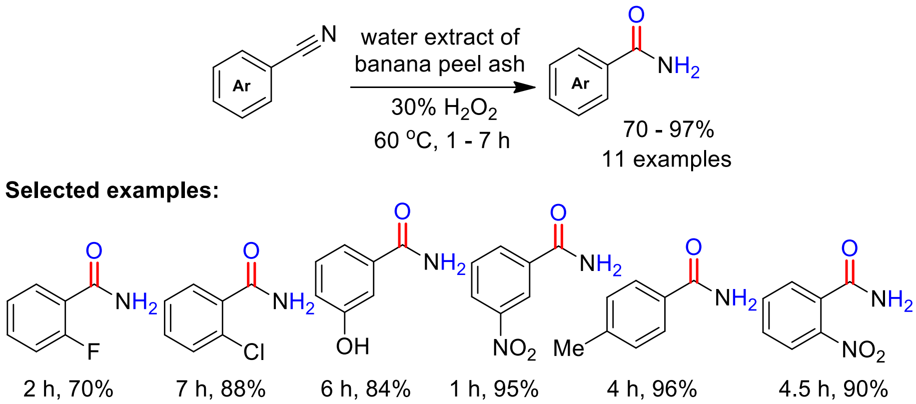
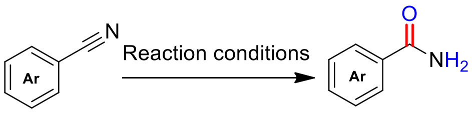


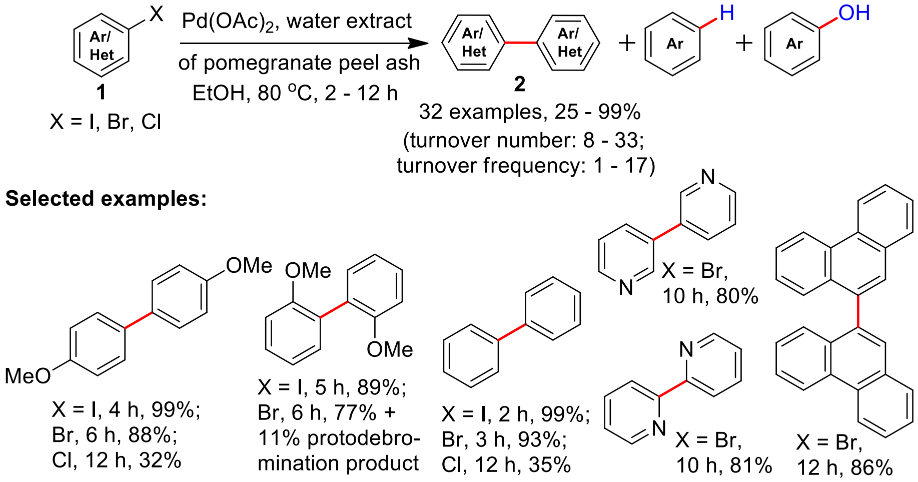
Table 3 Comparison of the results of water extract of banana peel ash–H_2O_2 system with some recent reports in hydration of nitriles[a]



Entry	Reaction conditions	Yield (%)	Ref
1	Ru catalyst, NaOH, ^{i}PrOH, 80 °C, 4 h	72–93	Jia et al. (2017)
2	Chitin-supported ruthenium (Ru/chitin), H_2O, 120 °C, N_2 atmosphere, 20–60 h	23–98	Matsuoka et al. (2015)
3	$Pd(OAc)_2$, 2,2'-bipyridyl, H_2O, 70 °C, 24 h	77–98	Sharley and Williams (2017)
4	$PdMPAV_1$[b]@TiO_2, H_2O, 140 °C, 6 h	52–97	Rao et al. (2016)
5	Water extract of banana peel ash, 30% H_2O_2, 60 °C, 1–7 h	70–97	Das et al. (2021)

[a] This table has been reproduced from Das et al. (2021) with permission from the Elsevier

[b] $PdMPAV_1$ = Palladium-exchanged vanadium-incorporated molybdophosphoric acid



Scheme 26 $Pd(OAc)_2$-catalyzed Ullmann coupling in water extract of pomegranate peel ash

iodides (Scheme 27) (Appa et al. 2019b). High chemo- and regioselectivity has been reported in these reactions. Some examples of chemo- and regioselectivity of this investigation are presented in Fig. 4. Wide substrate scope and conduct of reactions at ambient conditions using biorenewable base-media are further advantages shown in this protocol. Bulky aryl halides also produced very high yields of their corresponding Suzuki–Miyaura cross-coupling reaction products at room temperature using this sustainable methodology. This protocol shows high turnover number and turnover frequency values as 870–990 and 2610–11,880. The mechanism of water extract of pomegranate ash-assisted Suzuki–Miyaura cross-coupling reaction is presented in Fig. 5.

The homogeneous Suzuki–Miyaura cross-coupling reaction struggles with severe drawbacks such as the difficulty in purifying the active pharmaceuticals from palladium contamination and less possibility for the reuse of catalysts (Hussain et al. 2016; Shi and Cai 2018). The heterogeneous supported Pd nanoparticles-based catalysts are the attractive alternatives, but these are still wrestles with the unwanted homogeneous mechanism during the catalytic process results the palladium leaching and low substrate scope (Zhang and Wang 2006; Saptal et al. 2019). Hence, the new developments in the Suzuki–Miyaura cross-coupling reaction using heterogeneous catalysts have great importance in synthetic organic chemistry. Recently, Appa et al. reported a protocol for the heterogeneous Suzuki–Miyaura cross-coupling reaction in water extract of pomegranate peel ash using reduced graphene oxide supported Au–Pd bimetallic nanoparticles (Au@Pd nanoparticles/reduced graphene oxide) under ligand less ambient conditions (Scheme 28) (Appa et al. 2021b). Au@Pd nanoparticles/reduced graphene oxide has been synthesized employing chemical reduction with methylamine borane using $AuCl_3·3H_2O$, K_2PdCl_4 and reduced graphene oxide, and the catalyst was characterized using X-ray diffraction (XRD), transmission electron microscopy

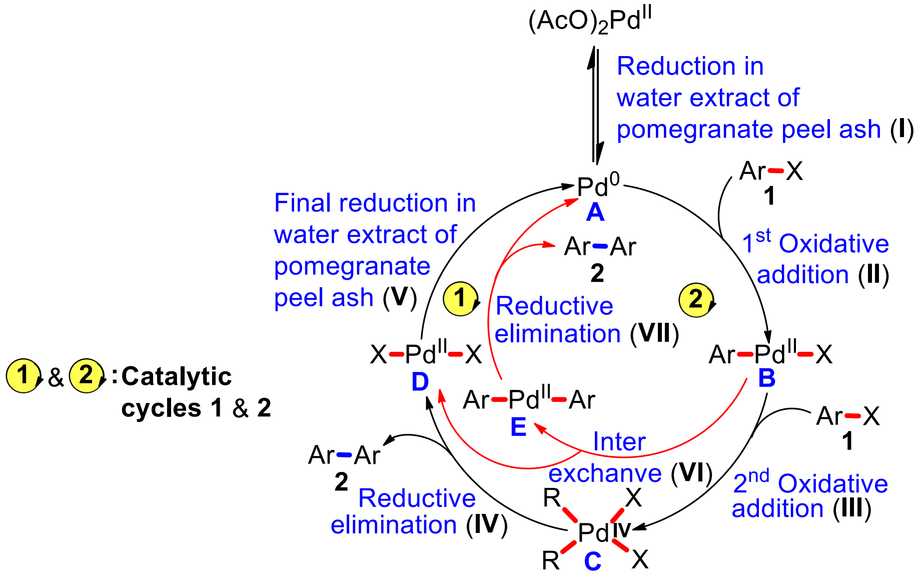


Fig. 3 Proposed mechanism of Ullmann coupling in water extract of pomegranate ash. The Pd^0 (**A**) species formed in water extract of pomegranate peel ash from $Pd(OAc)_2$ involves in oxidative addition with aryl halide (**1**) to give intermediate **B**. **B** results Pd(II) and (or) Pd(IV) intermediates **E** and (or) **C** via inter exchange (**VI**) or 2nd oxidative addition (**III**) steps. **E** and (or) **C** gives biaryl (**2**) and active catalyst principal **A** via the reduction in water extract of pomegranate peel ash. This figure has been reproduced from Lakshmidevi et al. (2018) with permission from the Royal Society of Chemistry

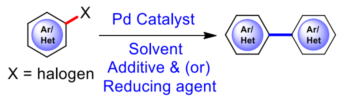
(TEM), high-resolution transmission electron microscopy (HRTEM), plasma-optical emission spectroscopy (ICP-OES) and cyclic voltammetric (CV) techniques. The formation of ~ 5.8 nm sized Au–Pd core–shell bimetallic particles was identified using these characterizations. The coupling products were reported with 91–99% in 5–30 min with high substrate feasibility in this development (Scheme 28). Reusability studies displayed 99%, 98%, 95% and 91% yields of biaryl from benzeneboronic acid and 3-bromoanisole in 1–4 cycles which indicates high reusability of catalyst in the 1st and 2nd cycle due to the effective recapture phenomenon of Pd when Au is present (Nemygina et al. 2018).

Lakshmidevi et al. also developed a new Pd-KIT-6-catalyzed Suzuki–Miyaura cross-coupling reaction using water extract of pomegranate peel ash as an aqueous reaction media and renewable base (Scheme 29) (Lakshmidevi et al. 2021). This protocol was reported to display high stability of catalyst under nature-derived basic conditions in the absence of added ligand, additive and commercial base. The effective reusability of the catalyst was reported in this Pd-KIT-6-catalyzed procedure and retain of Pd^0 after the use of the catalyst in Suzuki–Miyaura cross-coupling reaction was confirmed by X-ray photoelectron spectroscopy analysis. It seems to be a good example of the real heterogenization of Suzuki–Miyaura cross-coupling reaction under sustainable conditions showing several advantages over other silica-supported Pd heterogeneous catalysts (Lakshmidevi et al. 2021), and a comparison of reported results of silica-supported Pd catalysts of this article is reproduced in Table 5. Turnover number and turnover frequency values of this method have been observed as 120–392 and 10–1267.

A novel $Pd(OAc)_2$-assisted sustainable (hetero)arylboronic acids self-coupling reaction was reported by Appa et al. in water extract of pomegranate peel ash (Scheme 30) (Appa et al. 2021a). This homocoupling reaction carried out at room temperature shows high chemoselectivity with quick reaction profiles (10–50 min) and high yields (81–98%). This method shows high prevalence over the significant reports (Cheng et al. 2007; Jin et al. 2009; Puthiaraj et al. 2014; Appa et al. 2021a), and the comparison of the most of the reported methods using Pd catalysts in self-couplings of (hetero)arylboronic acids discussed in this manuscript is reproduced in Table 6. A considerable effort has also been made toward heterocoupling of arylboronic acids in this development (Appa et al. 2021a). The reduction of $Pd(OAc)_2$ to Pd^0 was observed in water extract of pomegranate peel ash and was characterized using X-ray photoelectron spectroscopy, and Pd^0 was assumed as responsible chemical species for the quick formation of biaryls. The plausible mechanism of this process is represented in Fig. 6.

The bromination of (hetero)aromatic substrates is widely used transformation in organic synthesis. Appa et al. established a highly chemo- and regioselective, room temperature bromination reaction of activated aromatics/heteroaromatics including, phenols, anilines, aryl methyl ethers, and heterocyclics using *N*-bromosuccinimide in water extract of pomegranate peel ash (Scheme 31) (Appa et al. 2019a). The (hetero)aryl bromides are one among the most reactive substrates in synthetic organic transformations and are highly stable. This method shows several merits than the reported significant bromination protocols, and the comparison of the reported methods with water extract of pomegranate peel ash-assisted protocol is shown in Table 7. Further, the critical role of water extract of pomegranate peel ash as catalyst and media was systematically evaluated in this method. Avoid of external catalysts, volatile organic solvents and additives, large substrate scope with 91% to

Table 4 Comparison of methods for Pd-catalyzed homocoupling (Ullmann) reaction of aryl halides[a].



Entry	Catalyst	Base	Solvent	Additive and (or) Reducing agent	Temp (°C)	Time (h)	Yields (%)	Ref	Remarks
1	Pd–C	NaOH-AcONa	H_2O	Surfactant	95	24	30–65	Bamfield and Quan (1978)	External base and surfactant were required Low-to-moderate yields of products
2	$Pd(OAc)_2$	Cs_2CO_3	Dimethylacetamide	Hydroquinone and ligand: $P(o\text{-tol})_3$ or $As(o\text{-tol})_3$	100	2–48	37–99	Hennings et al. (1999)	External base, organic solvent, ligand and reducing agent were compulsory
3	Pd–C	–	Acetone-H_2O	Zn	Room temp	0.5	70–94	Venkatraman and Li (1999)	10 mol% Pd and 300 mol% Zn were required
4	$Pd(OAc)_2$	K_2CO_3 or Et_3N	Dimethyl formamide -H_2O	$^nBu_4NBr$ and ^iPrOH	115	7–50	42–95	Penalva et al. (1998)	External base, organic solvent and TBAB are required
5	Pd–C	–	H_2O	Zn—liquid CO_2	Room temp	12	42–92	Li et al. (2002)	High pressure—liquid CO_2, Zn (200 mol%) was necessary
6	Pd–C	–	H_2O	Zn—liquid CO_2	Room temp	8–96	78-quant	Li et al. (2003)	High pressure—liquid CO_2, Zn are required
7	$PdCl_2(PhCN)_2$	TDAE[b]	Dimethyl formamide	TDAE[b]	50	2–42	trace-98	Kuroboshi et al. (2003)	Organic solvent and external base cum reducing agent (TDAE[b]) were required Trace amount of yields of product was reported with aryl chlorides
8	Sulfur-palladacycles	K_3PO_4	Dimethyl formamide	–	100	87–143	12–96	Silveira et al. (2002)	External base, S-palladacycles, large reaction time and organic solvent were necessary
9	$Pd(dba)_2$	–	Dimethyl formamide	$^nBu_4NF$	90	12	0–94	Seganish et al. (2005)	300 mol% of $^nBu_4NF$ and organic solvents were required. Only aryl iodides and aryl bromides were studied

Table 4 (continued)

Entry	Catalyst	Base	Solvent	Additive and (or) Reducing agent	Temp (°C)	Time (h)	Yields (%)	Ref	Remarks
10	Pd(OAc)$_2$	K_2CO_3	PEG^c 4000	–	120	4–28	82–97	Wang et al. (2006)	Use of base and PEG^c 4000 was critical Only aryl iodides and aryl bromides were studied
11	$PdCl_2$	K_2CO_3	EtOH-H_2O	EDTA^d—ascorbic acid	Reflux	4–11	15–84	Ram and Singh (2006)	External base, EDTA^d and ascorbic acid (100 mol%) were required
12	$Pd_2(dba)_3$	^{t}BuONa	Diglyme	Phosphite ligand	130	12	10–80	Moon et al. (2007)	Phosphite-based ligand, external base and organic solvent are compulsory
13	$PdCl_2$	Et_3N or ^{i}PrONa	Ionic liquid	Ionic liquid-OPPh$_2$ ligand	80	0.25–20	58–95	Iranpoor et al. (2008)	Requirement of external base, ionic liquid and ligand are detrimental
14	Pd(OAc)$_2$	K_2CO_3	2-Butanone	–	120	5	65–91	Wang and Lu (2009)	External base, inert (N_2) atmosphere and organic solvent are obligatory
15	Pd$_{colloids}$	^{n}Bu$_4$NAc	^{n}Bu$_4$NAc	Aldehyde	90	2–7	81–92	Calò et al. (2009)	Added base and reducing agent were compulsory Aryl chlorides show no reactivity
16	Pd(OAc)$_2$	Et_3N	Dimethyl formamide	Biphenyl phosphine ligand	100	5	<5-quant	Nadri et al. (2011)	Inert atmosphere, organic base and solvent and phosphine ligand were necessary. Limited examples with only aryl bromides
17	Pd(OAc)$_2$	Cs_2CO_3	Dimethyl formamide or CH_3CN	Benzoin, PPh_3 and ^{n}Bu$_4$NAc	120	1–2	56–96	Park et al. (2011a)	External base, organic solvent, ligand and ^{n}Bu$_4$NAc were essential
18	$PdCl_2$	^{n}Pr$_3$N	Ionic liquid	–	100	0.5–15	45–96	Iranpoor et al (2012a)	Organic base and ionic liquid were necessary

Table 4 (continued)

Entry	Catalyst	Base	Solvent	Additive and (or) Reducing agent	Temp (°C)	Time (h)	Yields (%)	Ref	Remarks
19	Pd–C	NaOH	H_2O	–	MWI^e-150	1	20–95	Gädda et al. (2012)	Base and microwave irradiation are obligatory Hydrodehalogenation was always associates Studies were limited only for aryl iodides
20	Pd@poly-CN-PF_6^{f}	NaOH	H_2O	Ascorbic acid	100	9–24	8–95	Wang et al. (2013)	External base and reducing agent (ascorbic acid) were necessary
21	$Pd(OAc)_2$	–	H_2O	Mg and paraformaldehyde	70	12	21–87	Bhattacharjya et al. (2015)	Reducing agent—Mg and paraformaldehyde were detrimental Only aryl iodides were tested
22	$Pd(OAc)_2$	Cs_2CO_3	1,4-Butanediol	1,4-Butanediol	75	1.5–24	39–94	Huang et al. (2016)	External base and organic solvent cum reducing agent were necessarily required
23	Hydrotalcite supported Pd-Au nanocatalyst	KOH	^{i}PrOH	–	40	2–22	80–97	Wang et al. (2017a)	Use of base and organic solvent was necessary
24	Au–Pd nanochain network	K_2CO_3	H_2O-EtOH	–	80	4	77–98	Wang et al. (2017b)	External base and Au–Pd nanochain networks were necessary
25	Pd@Fe_3O_4-SiO_2 nanocatalyst	K_2CO_3	H_2O	–	Room trmp	1–2	52–95	Moghaddam et al. (2018)	Synthesis of magnetic nanoparticle supported palladium and the use of external base are critical
26	Pd-PVP^g/MCM-48	K_2CO_3	Dimethyl formamide	–	100	12	55–90	Mosaddegh and Yavari (2018)	Base and organic solvents were used for the limited number (only seven) of substrates

Table 4 (continued)

Entry	Catalyst	Base	Solvent	Additive and (or) Reducing agent	Temp (°C)	Time (h)	Yields (%)	Ref	Remarks
27	Pd(OAc)$_2$	Water extract of pomegranate peel ash–EtOH		–	80	2–12	25–99	Lakshmidevi et al. (2018)	Use of novel renewable base (derived from agro-waste) and benign reaction media Exploitation of aryl iodides, aryl bromides and aryl chlorides Avoiding the addition of base, ligand, reducing agent and toxic (organic) solvent

[a] This table has been reproduced from Lakshmidevi et al. (2018) with permission from the Royal Society of Chemistry

[b] TDAE = tetrakis(dimethylamino)ethylene

[c] PEG = poly(ethylene glycol)

[d] EDTA = ethylenediaminetetraacetic acid

[e] MWI = microwave irradiation

[f] poly-CN-PF$_6$ = poly-3-(cyanomethyl)-1-vinylimidazolium hexafluorophosphate

[g] PVP = poly(*N*-vinyl-2-pyrrolidone)

Scheme 27 Pd(OAc)$_2$-catalyzed Suzuki–Miyaura cross-coupling reaction in water extract of pomegranate ash

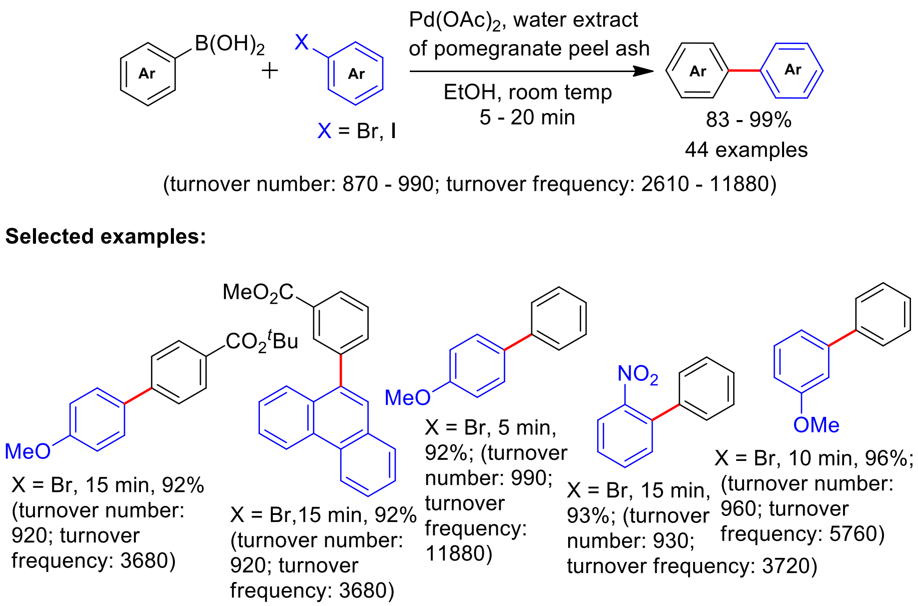
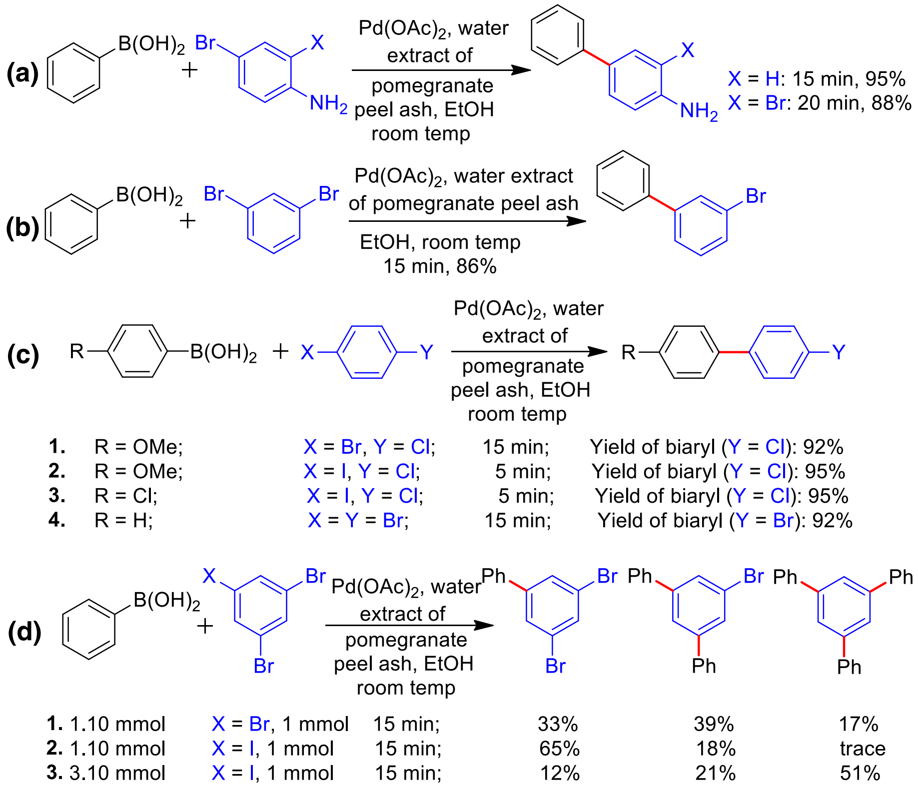


Fig. 4 Examples of chemo-/regioselectivity in Appa et al. (2019b). **(a)** High regio- and (or) chemoselectivity in the Suzuki–Miyaura cross-coupling reaction of 4-bromoaniline and 2,4-dibromoaniline. **(b)** High regioselectivity in the Suzuki–Miyaura cross-coupling reaction of 1,3-dibromobenzene. **(c)** High regio- and (or) chemoselectivity in the Suzuki–Miyaura cross-coupling reactions of 1,4-dibromobenzene and mixed 1,4-dihalobenzene. **(d)** Considerable chemo- and (or) regioselectivity in the Suzuki–Miyaura cross-coupling reaction of 1,3,5-tribromobenzene or 1,3-dibromo-5-iodobenzene



quantitative yields, high regioselectivity and quick reaction times (1–15 min) are the reported advantages of this protocol.

A multicomponent reaction for the preparation of biopotent 2-amino-4*H*-chromenes from aryl aldehydes, malononitrile and phenols was reported by the application of water extract of pomegranate peel ash under microwave irradiation (Scheme 32) (Hiremath and Kamanna 2019). The utilization of water extract of pomegranate peel ash was crucial as base catalyst in this report, and the products are purified by simple filtration and recrystallization by avoiding column chromatography. The products are obtained in high yields (86–94%) in just 3–6 min (Scheme 32).

Sravani et al. utilized water extract of pomegranate peel ash for the neutralization of high acidity of graphene oxide prepared from natural graphite via chemical treatment (Sravani

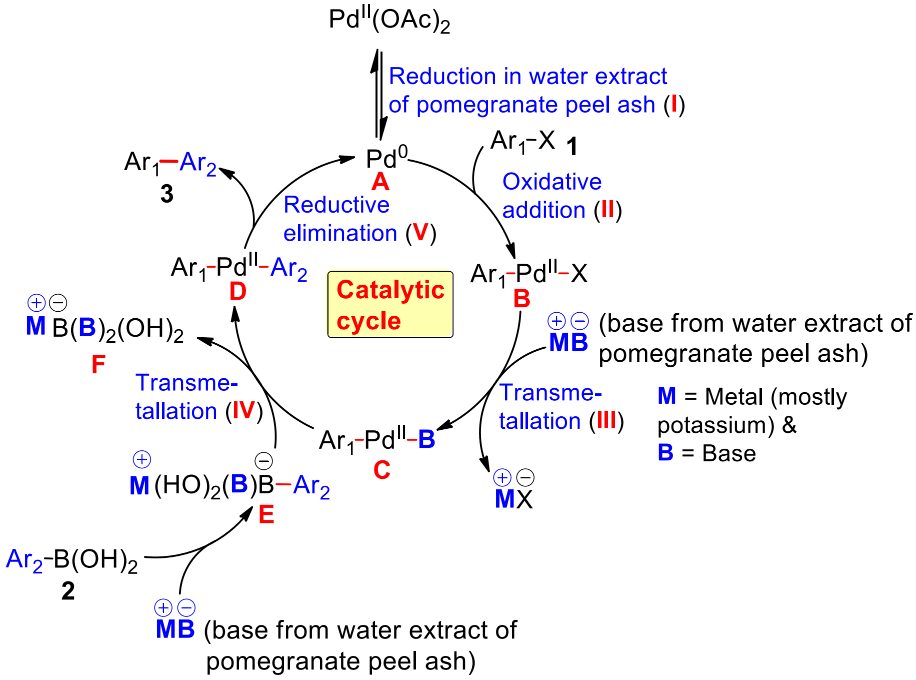
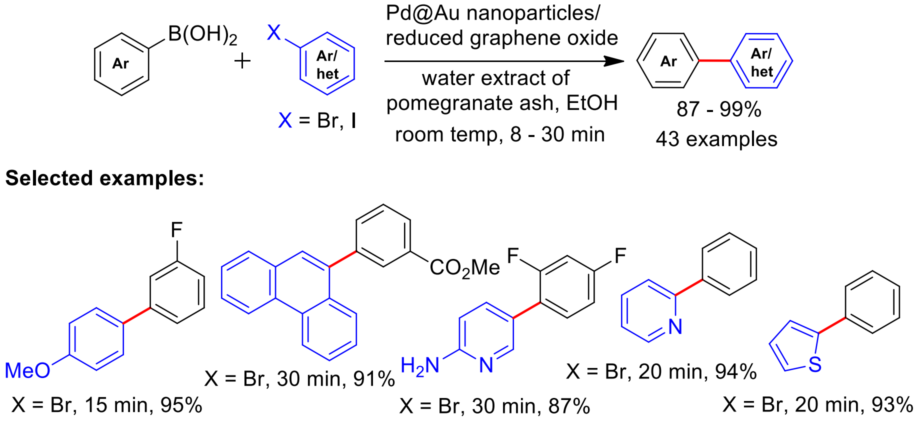
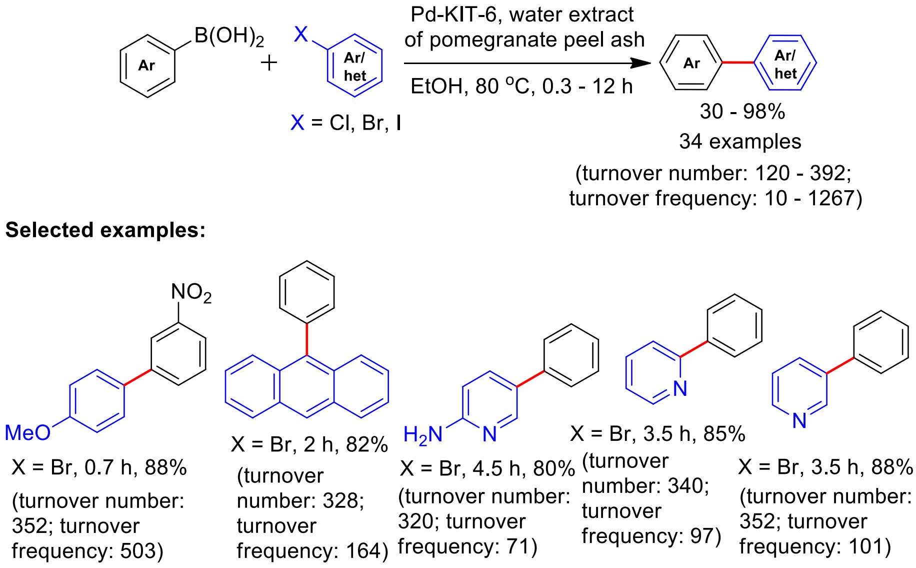


Fig. 5 Proposed mechanism of Pd(OAc)$_2$-catalyzed Suzuki–Miyaura cross-coupling reaction in water extract of pomegranate peel ash. The Pd^0 reactive species, **A** obtained by the reduction of Pd(OAc)$_2$ in water extract of pomegranate ash. **A** forms Pd^{II} species **C** via the oxidative addition with aryl halide (**1**) followed by transmetallation with the base of water extract of pomegranate ash (Appa et al. 2019b). Further transmetallation of **C** with the intermediate **E** formed from arylboronic acid (**2**) and base of water extract of pomegranate ash gives diarylpalladium intermediate **D**. Finally, **D** results the biaryl, **3** and Pd^0 active principal, **A**. This figure has been reproduced from Appa et al. (2019b) with permission from the John Wiley & Sons

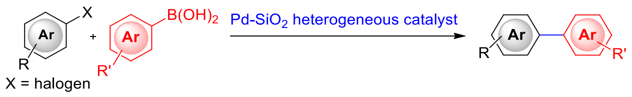


Scheme 28 Au@Pd nanoparticles/reduced graphene oxide-catalyzed Suzuki–Miyaura reaction in water extract of pomegranate ash



Scheme 29 Pd-KIT-6-catalyzed Suzuki–Miyaura reaction in water extract of pomegranate peel ash

Table 5 Comparison of reports on Suzuki–Miyaura cross-coupling reaction using Pd-silica-based heterogeneous catalysts[a].



Entry	Catalyst	Base	Solvent	Temp (°C)	Time	Yield (%)	Pd-particle size (nm)	Ref	Remarks
1	Pd nanoparticles@ polyvinylpyrlidone-SiO_2	NaOAc	CH_3CN-H_2O	100	12 h	> 95	2.9 ± 1.4	Gude and Narayanan (2010)	External base and large reaction time were required. No recyclability of the catalyst, only one aryl iodide was used
2	Pd nanoparticles@ H_2N–SiO_2	K_2CO_3	H_2O	60–70	2–3 h	70–96	5 ± 6	Veerakumar et al. (2013)	External base and tetra-n-butylammonium bromide are required
3	Pd nanoparticles@ PPh_2–SiO_2	K_2CO_3	^iPrOH-H_2O	60	3–4 h	58–98	10 ± 15	Sahu and Das (2015)	External base and organic solvent were required. Only aryl bromides were studied
4	Pd@SBA-15	K_2CO_3	EtOH-H_2O	85	5 h	99	10	Han et al. (2007)	External base was required. Only aryl bromides were studied
5	Pd-Au@SiO_2	–	H_2O	80	2–4 h	48–53	Not reported	Speziali et al. (2013)	Low yields of coupling products and instability of the catalyst were reported. Only aryl bromides were studied
6	Pd nanoparticles@ SiO_2	K_2CO_3	Acetone-H_2O	75–100	5–24 h	78–92	3.5 ± 1.0	Basu and Paul (2013)	Organic solvent and external base were essential
7	Pd-MCM-48	NaOAc	H_2O	80	87–143 h	85–99	4 ± 7	Banerjee et al. (2010)	External base was used. No recyclability of catalyst
8	SilicaCat-Pd	K_2CO_3	EtOH-H_2O	Reflux	5 min	99	Not reported	Lemay et al. (2010)	External base was required. Only one example was studied
9	SilicaCat silicadiphenyl phosphinite-Pd	K_2CO_3	EtOH	Reflux	2 h	88	Not reported	Lemay et al. (2010)	External base was used. Only one example was studied
10	Pd(0)/silicadiphenyl phosphinite	NaOH	EtOH	Reflux	4–11 h	89–99	8	Iranpoor et al. (2012b)	Requirement of external base and no recyclability of catalyst

Table 5 (continued)

Entry	Catalyst	Base	Solvent	Temp (°C)	Time	Yield (%)	Pd-particle size (nm)	Ref	Remarks
11	MCM-48-pyridinyl-methanimine-Pd	K_2CO_3	EtOH-H_2O	90	5 h	89–96	Not reported	Sarkar et al. (2015b)	External base was compulsory. Aryl chlorides were not studied
12	Pd-citosan@SiO_2	K_2CO_3	EtOH	80	1–10 h	68–95	> 100	Jadhav et al. (2015)	External base, long reaction time, large particle sizes were observed
13	Pd(II)-MCM-41	Na_2CO_3	EtOH-H_2O	60	2–24 h	2–99	Not reported	Bhunia et al. (2010)	External base was necessary. Trace amount of yield of products were reported with aryl chlorides
14	KIT-6(60/130)-SH.Pd	K_2CO_3	Dimethyl formamide-H_2O	80	4–5 h	–	Not reported	McQuarrie et al. (2010)	Added base and organic solvent, inert condition were compulsory. Only one example was studied
15	Pd-poly(2-hydroxyethyl methacrylate)/KIT-6	K_2CO_3	H_2O	40	1–12 h	85–97	Not reported	Kalbasi and Mosaddegh (2012)	External base and solvent was necessary. Limited examples were studied
16	Hollow Pd-silica spheres	K_3PO_4	EtOH	Reflux	3–24 h	90–99	10	Kim et al (2002)	10 mol% of catalyst, external base, 50 ml of solvent, were required. Only four examples were studied
17	SiO_2/tetra(ethylene glycol)/Pd	K_3PO_4	Toluene	110	5 h	5–98	2–5	Kim et al. (2004)	Use of externalbase and organic solvent, high temperature was compulsory. Trace amount of yields of products were reported with aryl chlorides
18	Pd@pSiO_2 yolk-shell nanocatalyst	CS_2CO_3	Dimethyl formamide-H_2O	199	3 h	61–100	3.6	Park et al. (2011b)	External base, organic solvent and extremely high temperature were mandatory. Limited examples with aryl bromides and chlorides were reported

Table 5 (continued)

Entry	Catalyst	Base	Solvent	Temp (°C)	Time	Yield (%)	Pd-particle size (nm)	Ref	Remarks
19	Pd^0-aminopropyl- siliceous mesocellular foam	K_2CO_3	EtOH-H_2O	90	30 min	0–95	–	Bratt et al. (2014)	Added base and microwave irradiation were obligatory
20	Pd@meso-SiO_2	K_2CO_3	EtOH	80	3 min -5 h	Trace-99.5	2–10	Chen et al. (2012)	External base was required and only aryl iodides were studied
21	Pd nanoparticles-silica-starch substrate	NaOH	H_2O-Dimethyl formamide	Reflux	1–8 h	86–96	Not reported	Khalafi-Nezhad and Panahi (2012)	1.2 mol% of catalyst, external base and organic solvents were necessary
22	SiO_2-acac-Pd nanoparticles	$NaHCO_3$	H_2O	Reflux	8 min-9.5 h	66–94	6–12	Hajipour et al. (2014)	External base was required. Limited examples were studied
23	Pd@MCM-41 nanoporous silica	K_2CO_3	–	100	4 min-2 h	80–97	Not reported	Nejat et al. (2015)	External base was compulsory. Studied only aryl chlorides and aryl bromides
24	Pd^0-ethylene diamine-SiO_2/cellulose substrate	K_2CO_3	H_2O	100	18–60 min	75–93	Not reported	Bhardwaj et al. (2015)	2.5 mol% of catalyst, additive and base were required. Limited examples with aryl bromides were reported
25	Pd nanoparticles@ silica-dendrimers	K_2CO_3	EtOH	78	0.5–36 h	Trace-99	10–20	Xu et al. (2013)	External base was used. Long reaction time was reported
26	Pd-diazabicyclo[2.2.2] octane (DABCO) complex@SiO_2	K_2CO_3	EtOH	80	1–15 h	60–96	Not reported	Kumbhar et al. (2012)	External base was required
27	Pd@SBA-15	K_2CO_3	H_2O	80	1 h	21–98	3–6	Zhang et al. (2013)	External base was required. Only aryl bromides were studied
28	Pd@mSiO_2 yolk-shell nanoreactor	K_2CO_3	EtOH-H_2O	80	5 min-12 h	25–99	5	Wei et al. (2015)	External base was necessary. Limited examples were studied
29	MCM-41–3-(2-aminoethylamino) propyl-Pd(II) complex	K_2CO_3	Xylene	90–110	2–10 h	71–97	Not reported	Zhao et al. (2011)	Organic solvent and external base were obligatory. Limited examples with only aryl bromides has been reported

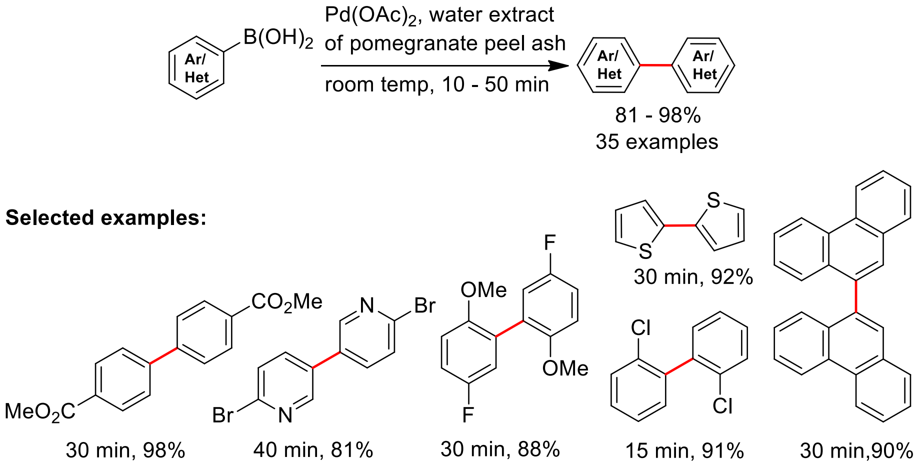
Table 5 (continued)

Entry	Catalyst	Base	Solvent	Temp (°C)	Time	Yield (%)	Pd-particle size (nm)	Ref	Remarks
30	Pd@NH_2- SiO_2	K_2CO_3	Dimethyl formamide-H_2O	100	3.4 h	94	5.1	Cornejo et al. (2014)	External base and organic solvents were necessary. Only one example was studied
31	Pd@PPh_2-SiO_2	K_2CO_3	Dimethyl formamide-H_2O	100	3.4 h	96	5.1	Cornejo et al. (2014)	External base and organic solvents were necessary. Only one example was studied
32	Pd nanoparticles@ PEG[b] functionalized silica	K_2CO_3	Dimethyl formamide	100	3–10 h	88–92	12–14	Dutta and Sarkar (2011)	Use of external base and organic solvent. Only aryl iodides and aryl bromides were studied. PEG[b] used for the preparations of catalyst
33	Pd@SBA-16	K_2CO_3	EtOH-H_2O	90	6 h	88–94	Not reported	Sarkar et al. (2015a)	External base was required. Only few examples were studied
34	Pd(1%)-KIT-6, Pd(5%)-KIT-6, Pd(10%)-KIT-6, Pd(5%)-SBA-15, Pd(5%)-SBA-16	Water extract of pomegranate peel ash–EtOH		80	2–12 h	25–99	2.2 (SBA-15), 3.5 (KIT-6) and 1.5 (SBA-16)	Lakshmidevi et al. (2021)	Green and sustainable reaction media, added base- and ligand-free conditions, high stability of the catalysts, 0.25 mol% of catalysts, pure heterogeneous mechanism and wide substrate scope

[a] This table has been reproduced from Lakshmidevi et al. (2021) with permission from the Elsevier

[b] PEG = poly(ethylene glycol)

Scheme 30 $Pd(OAc)_2$-catalyzed self-coupling of (hetero)arylboronic acids in water extract of pomegranate peel ash



et al. 2020). The synthesized water extract of pomegranate peel ash-derived graphene oxide was used directly with metal precursors to obtain well-dispersed Pt_3Co/reduced graphene oxide and Pt_3Ni/reduced graphene oxide nanoparticles, which are investigated for oxygen reduction reaction. These water extracts of pomegranate peel ash-derived reduced graphene oxide-supported systems are reported as stable and durable in oxygen reduction reaction process (Sravani et al. 2020).

The pomegranate peel ash was reported for the condensation of aryl aldehydes to cyclic ketones (cyclopentanone/cyclohexanone/α-tetralone) toward the formation of pharmaceutically important bisbenzylidenecycloalkanones/alkylidene-α-tetralones in water at reflux condition (Scheme 33) (Patil et al. 2020). This method also reported for the purification of products by non-chromatographic method such as filtration followed by recrystallization. Non-chromatographic purification of products, wide reactants scope, renewable catalyst, aqueous media, quick reactions (25 min–5 h) and impressive isolated yields (65–98%) of the products, efficient utilization of waste are made this protocol as a sustainable and effective alternate to the existing procedures, and the importance of this protocol has been indicated by a comparison with some reported methods: I_2-CH_2Cl_2 (Das et al. 2006a), TiO_2-HOAc-EtOH (Tabrizian et al. 2016), NaOH-cetyl trimethyl ammonium bromide-H_2O (Shrikhande et al. 2008), sodium-modified fluorapatite-H_2O-microwave irradiation (Mounir et al. 2018), $Cu(TFA)_2{\cdot}4H_2O$ (Song et al. 2009) and SiO_2-OK (Jin et al. 2006) for the synthesis of 2,6-bis(4-methoxybenzylidine)cyclohexanone from 4-methoxybenzaldehyde and cyclohexanone (Patil et al. 2020).

Rice-based ashes

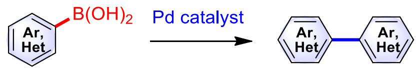
Rice straw ash was reported to contain potassium, sodium, magnesium and calcium from its energy-dispersive X-ray analysis (Mahanta et al. 2016). Boruah et al. reported the utilization of water extract of rice straw ash for the sustainable, room temperature $Pd(OAc)_2$-catalyzed Suzuki–Miyaura cross-coupling reaction of arylboronic acids and (hetero)aryl bromides (Scheme 34) (Boruah et al. 2015a). This article was presented the study of reusability of the catalytic system in water extract of rice straw ash for Suzuki–Miyaura cross-coupling reaction up to six consecutive cycles with the yield of 4-methoxybiphenyl as 88%, 86%, 86%, 80%, 74% and 65% from 4-bromoanisole and benzeneboronic acid. This development showed advantages as the application of natural feedstock, large substrate scope, good yields (45–90%) of industrially important biaryls and ambient conditions. The rice straw ash was also been utilized directly for the Suzuki–Miyaura cross-coupling reaction of arylboronic acids and (hetero)aryl bromides in water and isopropanol mixture using $Pd(OAc)_2$ as catalyst (Scheme 35) (Mahanta et al. 2016). The in situ formation of metallic palladium nanoparticles (Pd nanoparticles) with 5–10 nm size was also observed in this case.

Saikia and Borah was reported a sustainable Dakin reaction of aryl aldehydes using H_2O_2 as an external oxidant in water extract of rice straw ash (Scheme 36) (Saikia and Borah 2015). Use of renewable material, good scope of substrates, ambient conditions, high yields (85–98%) of the products in 2–3 h and easy preparation of catalyst such as water extract of rice straw ash are the observed advantages of this protocol.

Ipso-hydroxylation of (hetero)arylboronic acids has also been reported using water extract of rice straw ash as a catalyst and H_2O_2 as an oxidant by Saikia et al. (2015b) (Scheme 37). The catalyst was effectively reused up to five cycles with the yields of phenol as 98%, 98%, 96%, 94% and 90% from benzeneboronic acid. The effective reusability of the biorenewable catalyst is the notable advantage of this protocol.

Water extract of rice straw ash has also been reported with water extract of banana peel ash for Henry reaction

Table 6 Comparison of reports on Pd-catalyzed homocoupling reactions[a]



Entry	Pd-catalyst	Media	Additive/base	Temp (°C)	Time (h)	Yield (%)	Ref	Remarks
1	$Pd(OAc)_2$	$EtOH\text{-}H_2O$	$Cu(OAc)_2/Na_2CO_3$ or $Ba(OH)_2$	Room temp	72	6–84	Smith et al. (1997)	Base and $Cu(OAc)_2$/low product yields[b] and large reaction times
2	$Pd(OAc)_2$	Dimethyl formamide/toluene	Phosphine ligand/K_2CO_3	60–120	1.7–4	12–85	Wong and Zhang (2001)	Base and ligand/high temperature, low yields[a] and hazardous solvent
3	$PdCl_2$	$EtOH\text{-}H_2O$	*p*-Toluenesulfonyl chloride/Na_2CO_3	Room temp	12	56–97	Kabalka and Wang (2002)	Base and additive/low yields[b] and large reaction times
4	$Pd(PPh_3)_2Cl_2$	Tetrahydrofuran-H_2O	$Bu_4NF{\cdot}H_2O$	Room temp	8–12	59–81	Punna et al. (2004)	Additive/low yields,[b] large reaction times and hazardous solvent
5	$Pd(OAc)_2$	Acetone-H_2O	K_2CO_3	Room temp	24	0–97	Xu et al. (2008)	Base and volatile solvent/large reaction times and low yields[b]
6	Cyclopalladated ferrocenylimines	$^iPrOH\text{-}H_2O$	$K_3PO_4{\cdot}7H_2O$	15	12–24	14–99	Mu et al. (2009)	Base and low temperature/low yields[b] and extended reaction times
7	CpPd(N-heterocyclic carbene)Cl	^iPrOH	^tBuOK	Room temp	24	28–98	Jin et al. (2009)	Base/low yields[b] and large reaction times
8	$Pd(OAc)_2$	$[bmim][PF_6]$[c]	Ethyl bromoacetate/K_2CO_3	60	3	68–97	Cheng et al. (2007)	Base, additive and ionic liquid/heating condition and moderate yields[b]
9	$Pd(OAc)_2$	Dimethyl formamide-H_2O	*p*-Benzoquinone	80	0.2–2.1	32–99	Amatore et al. (2008)	Oxidant (*p*-benzoquinone)/hazardous solvent, heating and low yields[b]
10	$[Pd(Phbz)(X)(PPh_3)]$[d]	Tetrahydrofuran	–	Room temp	24	27–97	Kapdi et al. (2014)	Complex catalytic system/large reaction times, hazardous tetrahydrofuran and low yields[b]
11	$Pd(OAc)_2$	H_2O	Isopropyl myristate (phase transfer catalyst)-K_2CO_3	Room temp	0.25	47–99	Dwivedi et al. (2014)	Base and phase transfer catalyst /low product yields[b]
12	$Pd(OAc)_2$	PEG[e] 2000	PPh_3	70	8	0–94	Xia et al. (2015)	PEG[e] 2000 and ligand/heating, large reaction times and low product yields[b]
13	Pd Colloids	$CH_3CN\text{-}H_2O$	K_2CO_3	80	24	50–96	Sable et al. (2017)	Base/heating, large reaction times, low yields[b] and problematic solvent

Table 6 (continued)

Entry	Pd-catalyst	Media	Additive/base	Temp (°C)	Time (h)	Yield (%)	Ref	Remarks
14	[{Pd(μ-OH)Cl(IPr)}$_2$][f]	EtOH	KOH	40	6	70–99	Ostrowska et al. (2018)	Base and complex catalytic system/large reaction times
15	Pd(OAc)$_2$	H_2O	Tert-butyl hydroperoxide	Room temp	1	0–98	Xu et al. (2018)	Oxidant/low product yields[b]
16	Pd(OAc)$_2$	Water extract of pomegranate peel ash		Room temp	0.17–0.83	81–98	Appa et al. (2021a)	Use of renewable catalyst and aqueous media, high, wide substrate scope, excellent yields in short reaction time, low catalyst load and chemo-/regioselectivity

[a] This table has been reproduced from Appa et al. (2021a) with permission from the Elsevier

[b] Low/moderate product yields with certain substrates

[c] [bmim][PF$_6$] = 1-butyl-3-methylimidazolium hexafluorophosphate

[d] [Pd(Phbz)(X)(PPh$_3$)] = [Pd(*N*-phenylbenzaldimine)(imidate or acetate)(PPh$_3$)]

[e] PEG = poly(ethylene glycol)

[f] [{Pd(μ-OH)Cl(IPr)}$_2$] = [{Pd(μ-OH)Cl(bis(2,6-diisopropylphenyl)imidazolin-2-ylidene)}$_2$]

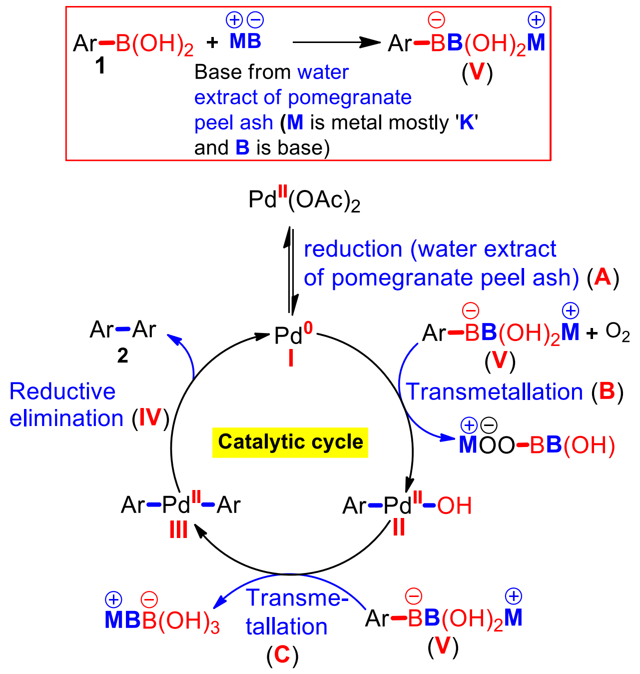


Fig. 6 Proposed mechanism of $Pd(OAc)_2$-catalyzed self-coupling of (hetero)arylboronic acids in water extract of pomegranate peel ash. The Pd^0 (**I**) formed from $Pd(OAc)_2$ in water extract of pomegranate peel ash involves in transmetallation with intermediate **V** (formed in water extract of pomegranate peel ash from arylboronic acid) to give palladium(II) intermediate, **II** which is on further transmetallation with **V** provides diaryl palladium(II) intermediate, **III** (Appa et al. 2021a). Final reduction of **III** gives biaryl (**2**) and Pd^0 catalytically active species. This figure has been reproduced from Appa et al. (2021a) with permission from the Elsevier

of nitromethane and aldehydes by Surneni et al. (Scheme 4 and 38) (Surneni et al. 2016), but the rate of this reaction is slow when compared to water extract of banana peel ash-catalyzed reactions (Scheme 4). These reactions also showed similar trend in reactivity of nitromethane with aldehydes as in the water extract of banana peel ash case (Scheme 4) and also reported a Michael addition followed by Henry reaction of cinnamaldehyde and nitromethane.

Pharmaceutically and industrially significant 3-carboxycoumarins are synthesized from *o*-hydroxybenzaldehydes and Meldrum's acid using water extract of rice straw ash as sustainable media at room temperature (Scheme 39) (Patil et al. 2018). This method uses highly abundant agro-waste (i.e., rice straw)-based derivative showing high yields (72–94%) of the isolated products in 3.7–5.3 h under the mild reaction conditions, and the products are purified by recrystallization technique.

A Michael addition reaction of 3-methyl-4-nitro-5-styrylisoxazoles with nitroalkanes was reported by Kumar et al. using water extract of rice straw ash as a base and reaction media (Scheme 40) (Kumar et al. 2018). This method is a sustainable alternative to the reported methods in the synthesis of pharmaceutically important γ-nitrobutyric acid derivatives. The previous reports to this method suffer with the drawbacks such as the requirement of expensive catalysts/reagents, solvents, large reaction times and inert conditions (Kumar et al. 2018). On the other hand, this reaction proceeds in aqueous media using renewable catalyst. The reactions proceed to give high yields (76–92%) of Michael addition products in 3 h at ambient conditions. The proposed mechanism of water extract of rice straw ash-assisted mechanism of Kumar et al. is represented in Fig. 7.

Rice husk ash-immobilized $PdCl_2$ (Pd/rice husk ash) was developed for the effective Suzuki–Miyaura cross-coupling reaction of arylboronic acids and aryl halides at 100 °C in ethanol (Scheme 41) (Rosa et al 2019). The fair reusability of Pd/rice husk ash up to five recycles was the advantage of this protocol. The stability of Pd^0 in the catalytic system was evaluated using Hg^0 poisoning and the soluble Pd^{II} by hallow fiber method. Based on these facts, a synergistic action in the catalysis between leached Pd^{II} and Pd^0 on rice husk ash was proposed. The aryl iodides are observed to be most reactive substrates than aryl bromides under this agro-waste-derived catalytic condition. The turnover number and turnover frequency values of this protocol are observed as 60–198 and 2–65.

Scheme 31 Aromatic nuclear bromination using *N*-bromosuccinimide in water extract of pomegranate peel ash

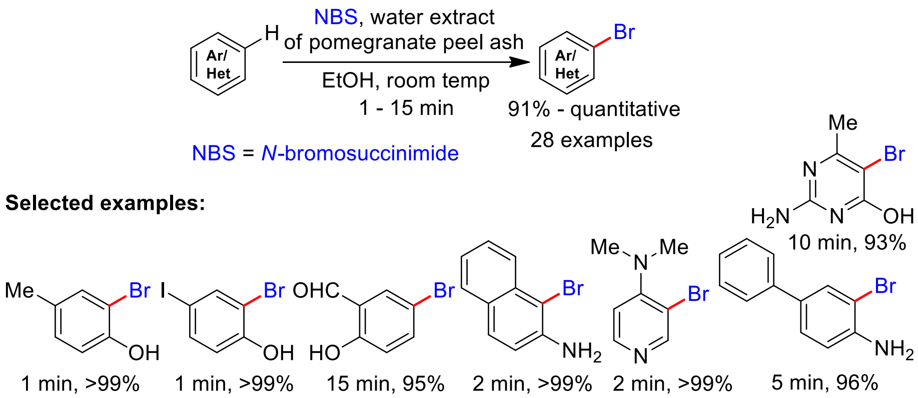
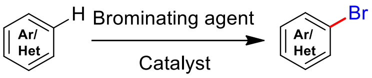


Table 7 Comparison of some methods for (hetero)aromatic bromination[a]



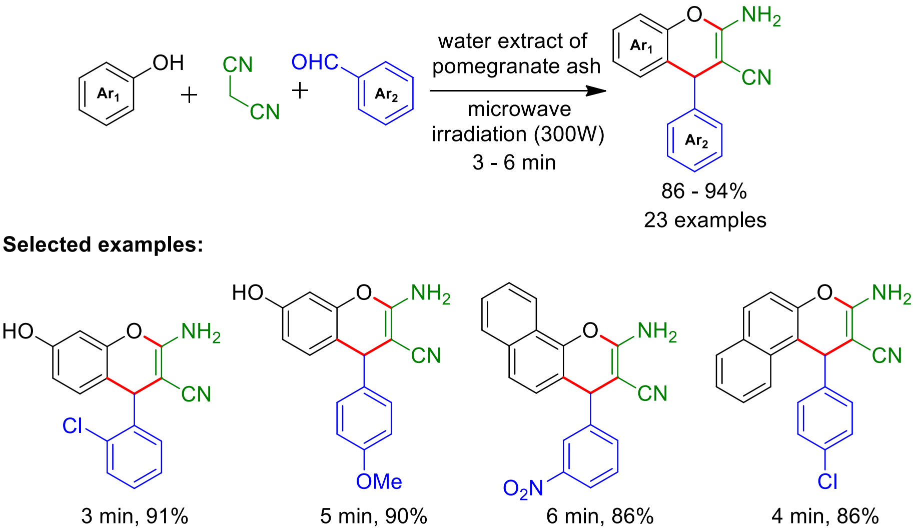
Entry	Brominating agent/catalyst	Solvent	Time	Yield (%)	Remarks
1	NBS[b]/sulfonic-acid-functionalized silica, (Das et al. 2006b)	CH_3CN-Et_2O (1:3)	1 min–3 h	67–99	Requires added catalyst and organic solvent
2	NBS[b] /NH_4OAc (Das et al. 2007)	CH_3CN	1 min–1.25 h	81–99	Requires catalyst and organic solvent
3	NBS[b]/PEG[c] 400 (Venkateswarlu et al. 2009)	PEG[c] 400	1 min–2.5 h	80–99	Requires external catalytic medium
4	NH_4Br/oxone (Naresh et al. 2013)	MeOH-H_2O (1:1)	2–90 min	16–98	External oxidant and problematic solvent are necessary
5	$CuBr_2$/oxone (Li et al. 2013a, b)	CH_3CN	3–24 h	25–90	Necessity of oxidant, CH_3CN and low yields in some examples
6	HBr/H_2O_2-AcOH (Koini et al. 2011)	Petroleum ether	0.5–3 h	64–96	Non-conventional reagent and external oxidant, catalyst and organic solvents are detrimental
7	Br_2/$CaBr_2$ (Kumar et al. 2011)	H_2O/ CH_3CN	10–30 min	91–99	Used non-conventional reagent and no control over selectivity
8	NBS[b]/*p*-toluenesulfonic acid (Bovonsombat et al. 2008)	Dioxane/ CH_3CN	6–18 h	2–78	Formation of multiple bromo compounds and requirement of organic solvent are the drawbacks
9	Br_2/lithium tetramethylpiperidide (LiTMP) (Menzel et al. 2006)	Tetrahydrofuran	2 h	10–62	Non-conventional reagent system and organic solvent are required
10	NH_4Br/H_2O_2/AcOH (Mohan et al. 2004)	AcOH	2.5–22 h	54–99	Formation of multiple bromo derivatives and requirement of oxidant and catalytic systems are the drawbacks
11	Br_2/layered double hydroxide-WO_4/ H_2O_2 (Choudary et al. 2003)	Dichloroethane	0.5–1 h	74–97	The use of organic solvent, external catalyst and oxidant are obligatory
12	NBS[b]/PhSSPh (or $PhSSiMe_3$) (Hirose et al. 2019)	CH_3CN	1–24 h	35–quant	Non-conventional catalyst and organic solvent are necessary. Dibromo compounds are formed (no selectivity) in several cases
13	NBS[b]/indoles (Shi et al. 2018)	n-Heptane	12 h–5 days	81–99	Requires of additional catalyst and organic solvents
14	NBS[b]/hexafluoroisopropanol (Tang et al. 2018)	Hexafluoro-2-propanol	5 min–16 h	74–99	Requirement of large reaction times and non-conventional solvent are the drawbacks
15	NBS[b]/I_2 (Pramanick et al. 2017)	CH_3CN	6–48 h	78–quant	Large reaction time and requirement of organic solvents are obligatory
16	NaBr/H_2O_2/AcOH/sonication (Lima et al. 2017)	Dimethyl formamide-AcOH	5–10 min	60 – quant	Requires of external oxidant, catalyst, sonication and dimethyl formamide
17	1,2-Ethanediylbis(triphenylphosphonium)-ditribromide (Salmasi et al. 2016)	Dichloromethane-MeOH (2:1)	< 5 min	85–98	Organic solvent and non-conventional catalysts are necessary
18	Water extract of pomegranate peel ash–NBS[b] (Appa et al. 2019a)		1–15 min	91–quant	No added catalyst and problematic solvent systems; excellent yields of products in short reaction time

[a] This table has been reproduced from Appa et al. 2019a with permission from the Springer Nature

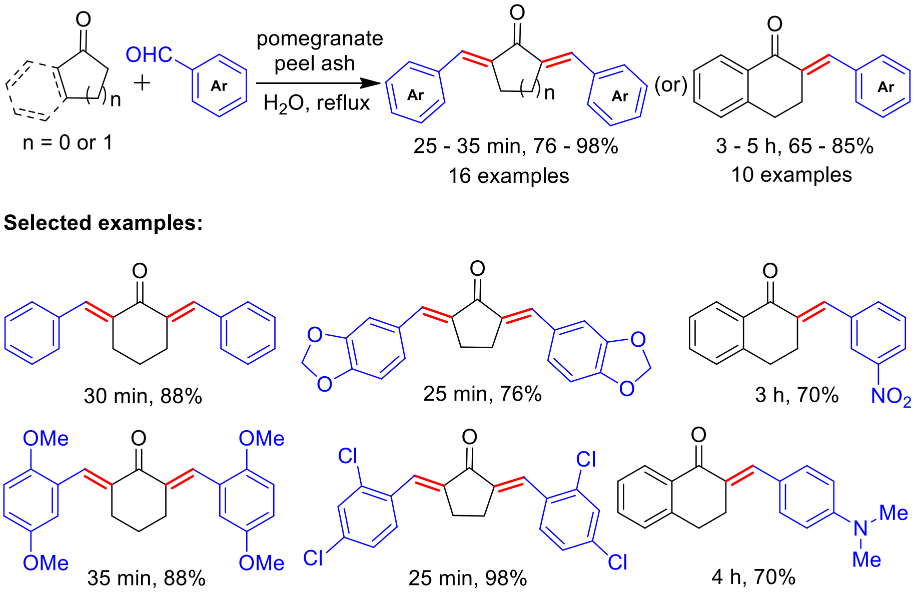
[b] NBS = *N*-bromosuccinimide

[c] PEG = poly(ethylene glycol)

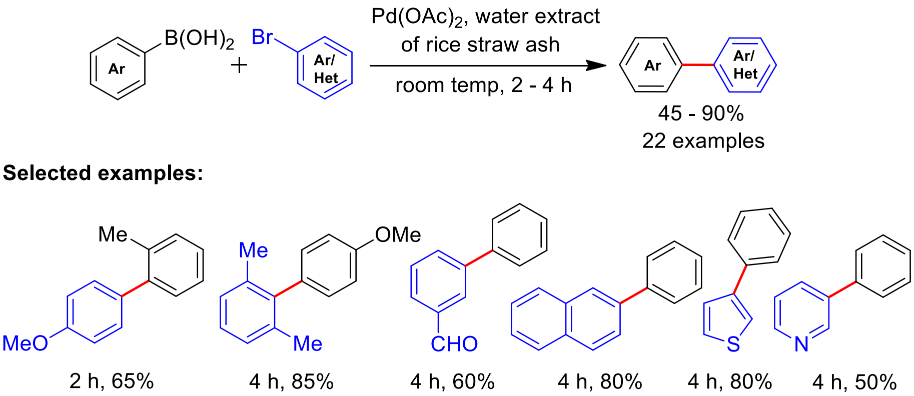
Scheme 32 Sustainable access to 2-amino-4*H*-chromenes in water extract of pomegranate peel ash using microwave irradiation



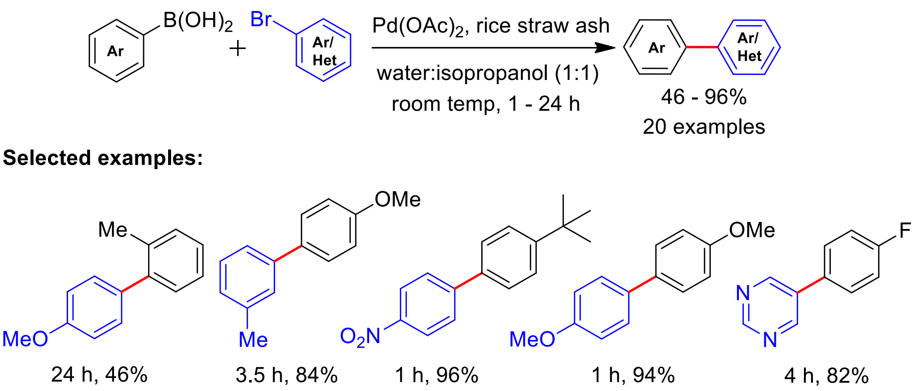
Scheme 33 Synthesis of (bis) alkylidenecycloalkanones using pomegranate peel ash in water



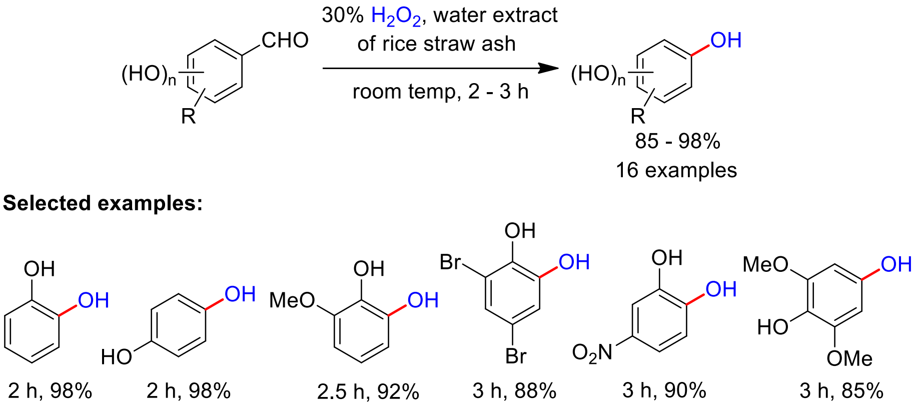
Scheme 34 Pd$(OAc)_2$-catalyzed Suzuki–Miyaura cross-coupling reaction in water extract of rice straw ash



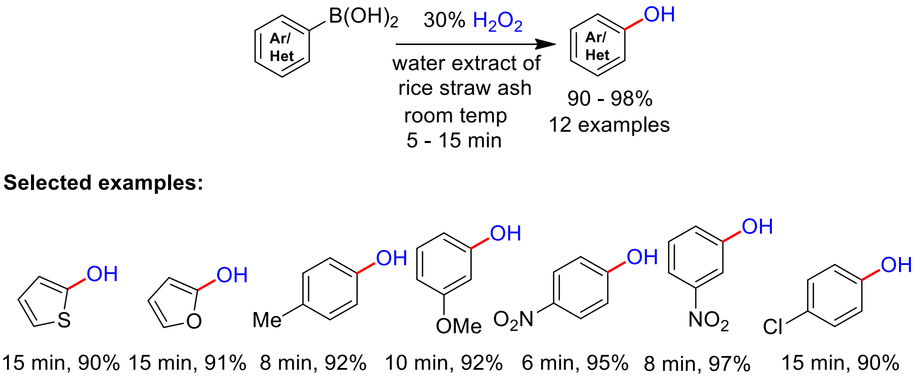
Scheme 35 Pd(OAc)$_2$-catalyzed Suzuki–Miyaura cross-coupling reaction using rice straw ash



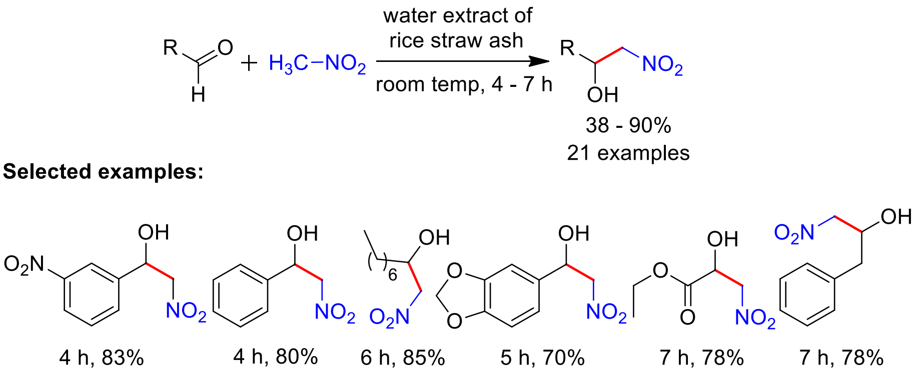
Scheme 36 Dakin reaction using H$_2$O$_2$–water extract of rice straw ash



Scheme 37 *Ipso*-hydroxylation of (hetero)arylboronic acids using water extract of rice straw ash–H$_2$O$_2$

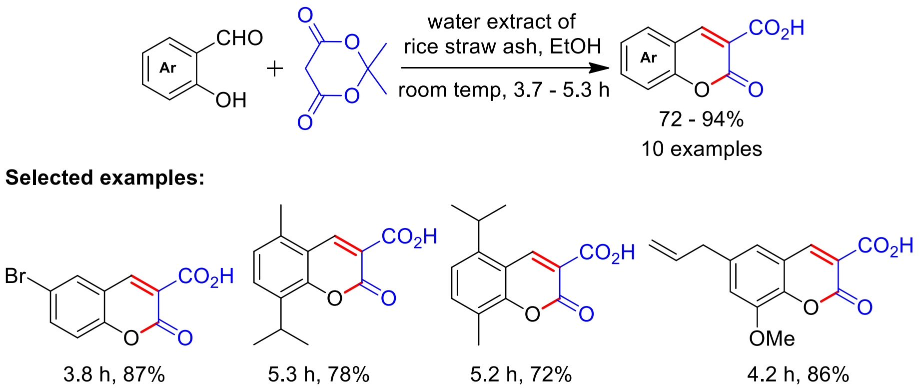


Scheme 38 Henry reaction in water extract of rice straw ash

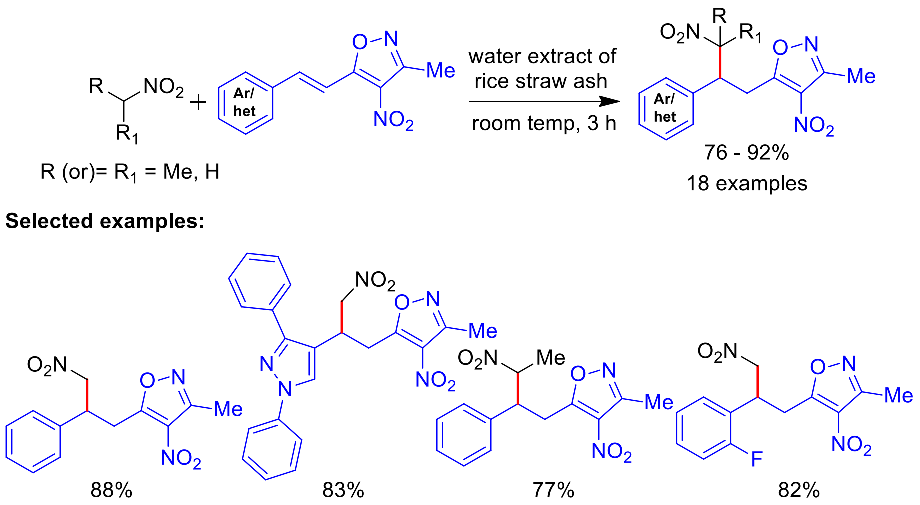


Decarboxylative aldol addition reaction of (hetero)aryloylacetic acids with *N*-protected or unprotected isatins has been reported by Dwivedi et al. for the production of *β*-hydroxy(hetero)aryloyl derivatives of isatins using water extract of rice straw ash (Scheme 42) (Dwivedi et al. 2019). The *β*-hydroxy(hetero)aryloyl derivatives are well known for their biological functions including antioxidant and radical scavenging activities (Dwivedi et al. 2019). The reported synthetic processes of these compounds require metal catalysts, organic solvents, heating conditions, amine-thiourea systems and ligands (Dwivedi et al. 2019). However, the development of Dwivedi et al. can be performed at room

Scheme 39 Synthesis of 3-carboxycoumarins using water extract of rice straw ash



Scheme 40 Michael addition reaction in water extract of rice straw ash



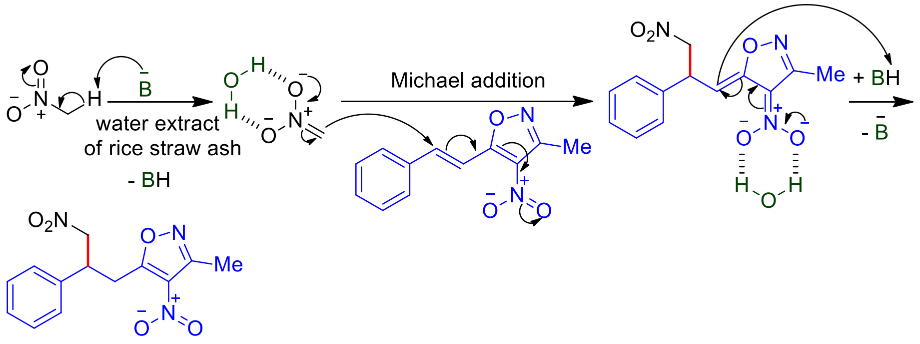


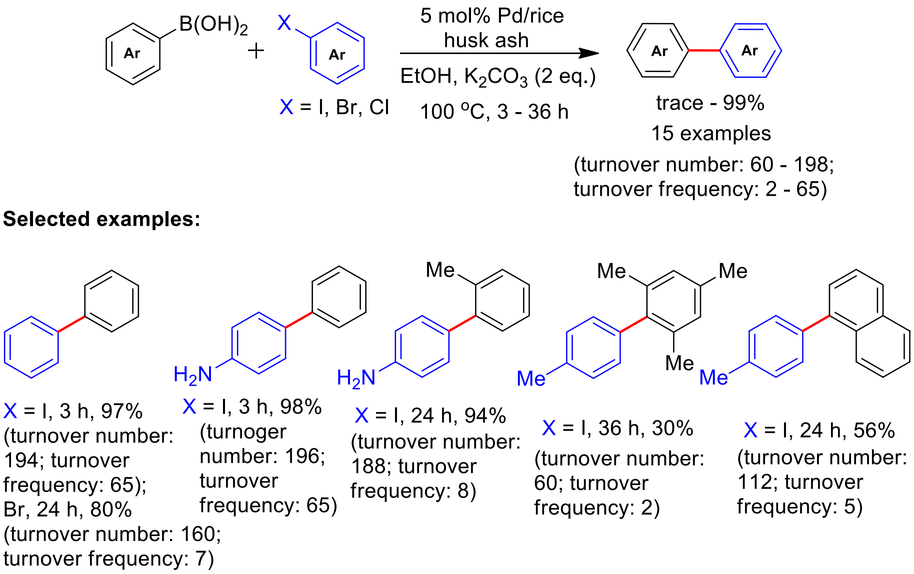
Fig. 7 Proposed mechanism of water extract of rice straw ash-catalyzed Michael addition reaction. As can be seen, the base of water extract of rice straw ash generates the nucleophile from the nitroalkane which participate in 1,4-addition with 3-methyl-4-nitro-5-styrylisoxazole to provide the Michael addition product (*γ*-nitrobutyric acid derivatives). The intermediates during this process are stabilized in water via hydrogen bonding (Fig. 7). This figure has been reproduced from Kumar et al. (2018) with permission from the John Wiley & Sons

temperature using waste-based renewable catalyst (water extract of rice straw ash), and the products are formed with high yields (91–99%) in 70 min (Scheme 42). This method was also found to be successful for the large scale (up to 10 mmol) synthesis of aldol addition products. The green chemistry parameters like E-factor, atom economy, mass efficiency and process mass intensity of this protocol are calculated to be 0.158, 85.86%, 85.86% and 1.2333 representing the effectiveness of this method (Dwivedi et al. 2019). Proposed mechanism of Dwivedi et al. is shown in Fig. 8.

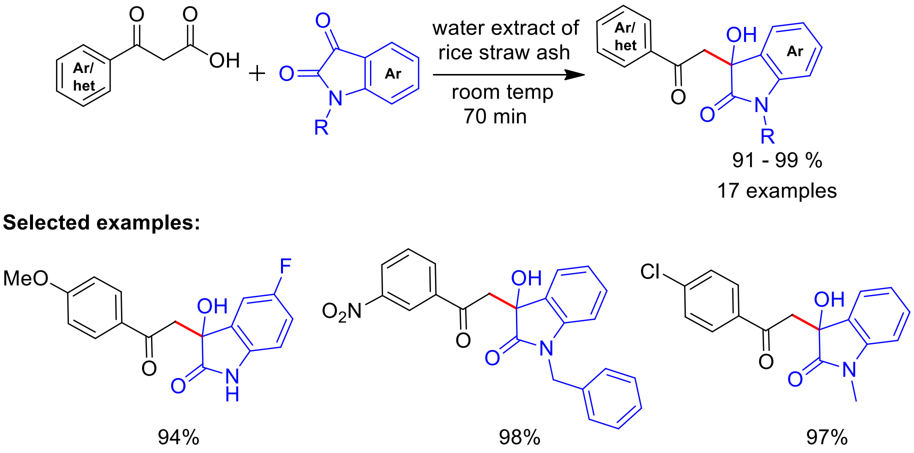
(3-Glycidyloxypropyl)trimethoxysilane-functionalized Ni^{II}-immobilized aminated Fe_3O_4@TiO_2 yolk-shell nanoparticles were reported for the synthesis of diethyl (hetero)arylphosphonates, diethyl alkenylphosphonates or diethyl alkynylphosphonates (Scheme 43) (Ghasemzadeh and Akhlaghinia 2019). The C-P bond formation between the (hetero)aryl halides or arylboronic acids or alkenes or alkynes and diethyl phosphite (or triethyl phosphite) is the key step in these reactions and can be achieved at 90 °C. The reactions of triethyl phosphite are reported to be faster on comparison with diethyl phosphite for the synthesis of diethyl (hetero)arylphosphonates, diethyl alkenylphosphonates or diethyl alkynylphosphonates. The catalyst also found its successful reusable application up to seven cycles (the isolated product yields are reported as 95%, 95%, 95%, 90%, 90%, 85% and 85% in 1–7 cycles), and this method also avoids the necessity of organic solvents in the case of reported methods (Ghasemzadeh and Akhlaghinia 2019).

Godoi and co-workers have been reported a hydrosulfidation reaction of alkynes/alkenes with aryl/alkyl thiols in the presence of water extract of rice straw ash at room temperature toward the synthesis of sulfides (Scheme 44) (Godoi et al. 2019; Silveira et al. 2021). The sulfides are the important intermediates in organic synthesis possess significant biological properties (Li et al. 2013a, b; Velasco et al. 2018; Godoi et al. 2019). This method is an attractive alternative to the existing harsh and costly procedures (Rodygin et al.

Scheme 41 Pd/rice husk ash-catalyzed Suzuki–Miyaura cross-coupling reaction



Scheme 42 Decarboxylative aldol addition reaction in water extract of rice straw ash



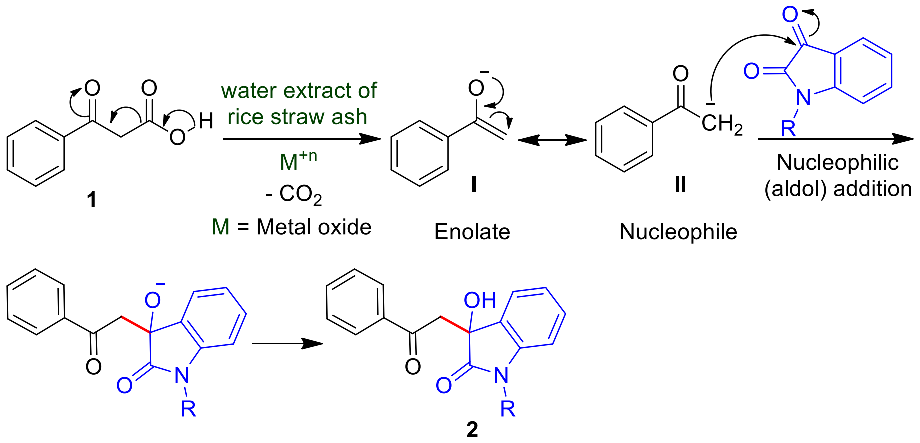


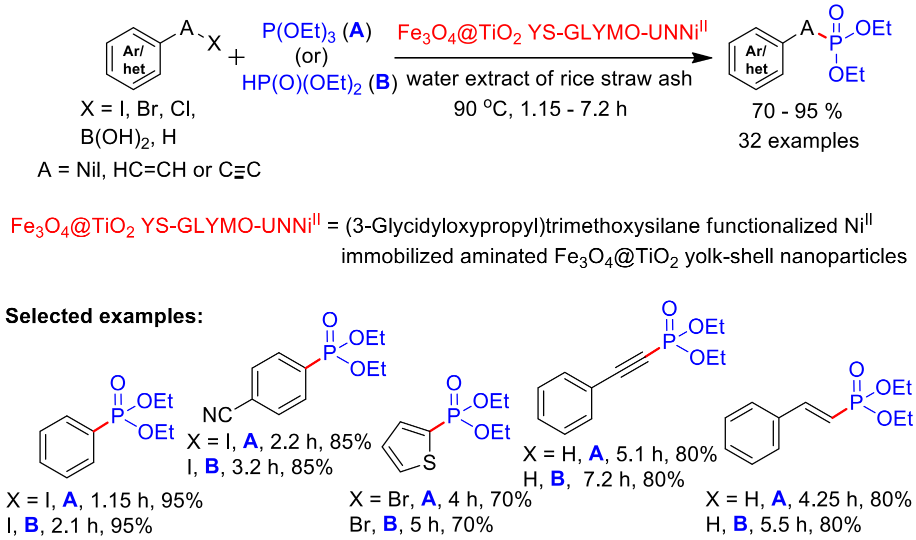
Fig. 8 Proposed mechanism of water extract of rice straw ash-catalyzed aldol addition reaction. Proposed mechanism of Dwivedi et al. is shown in Fig. 8. The decarboxylation of aryloylacetic acids (**1**) generates the enolate (**I**) in water extract of rice straw ash can rearranges to the nucleophile, **II** and **II** on aldol reaction with isatin products the *β*-hydroxy(hetero)aryloyl derivative (**2**). This figure has been reproduced from Dwivedi et al. (2019) with permission from the John Wiley & Sons

2017; Sahharova et al. 2020; Tolley et al. 2021) and explores agro-waste-based products at ambient conditions. The reusability study of water extract of rice straw ash for this conversion delivered the product (from 4-methylbenzenethiol and phenylacetylene) yields as 89%, 86%, 84% and 74% in 1–4 cycles (Godoi et al. 2019).

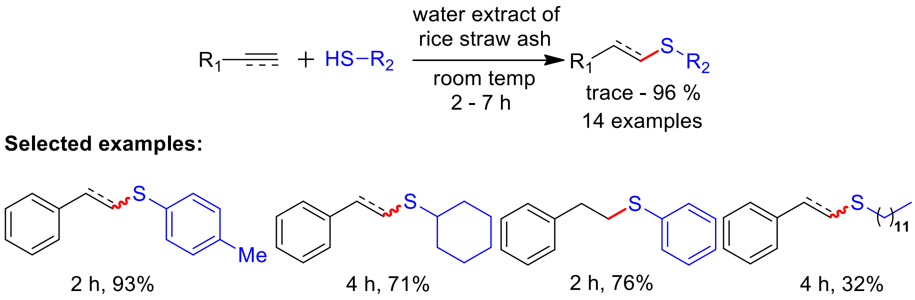
Papaya-based ashes

The presence of sodium, magnesium, potassium, calcium, copper and oxygen was identified in papaya bark ash by its energy-dispersive X-ray and ion-exchange chromatographic analysis (Sarmah et al. 2016). Water extract of papaya bark ash has been reported by Sarmah et al. for the external base and ligand-free Suzuki–Miyaura cross-coupling reaction of aryl bromides and (hetero)arylboronic acids using $Pd(OAc)_2$ at room temperature (Scheme 45) (Sarmah et al. 2016). The reported advantages of this Suzuki–Miyaura cross-coupling reaction based on water extract of papaya bark ash–$Pd(OAc)_2$ system include the avoid of ligand, additive and organic solvents, conduct of reactions at ambient conditions with no side reactions and application of nature-abundant feedstock. Further, the reusability of $Pd(OAc)_2$-water extract of papaya bark ash system was found with a very slight loss of the catalytic activity up to five cycles. (The isolated product yields from 1-bromo-4-nitrobenzene and benzeneboronic acid have been reported as 97%, 97%, 92%, 85% and 78%.)

Scheme 43 C-P band synthesis using (3-glycidyloxypropyl) trimethoxysilane-functionalized Ni^{II}-immobilized aminated $Fe_3O_4@TiO_2$ yolk-shell nanoparticles in water extract of rice straw ash



Scheme 44 Hydrosulfidation reaction in water extract of rice straw ash



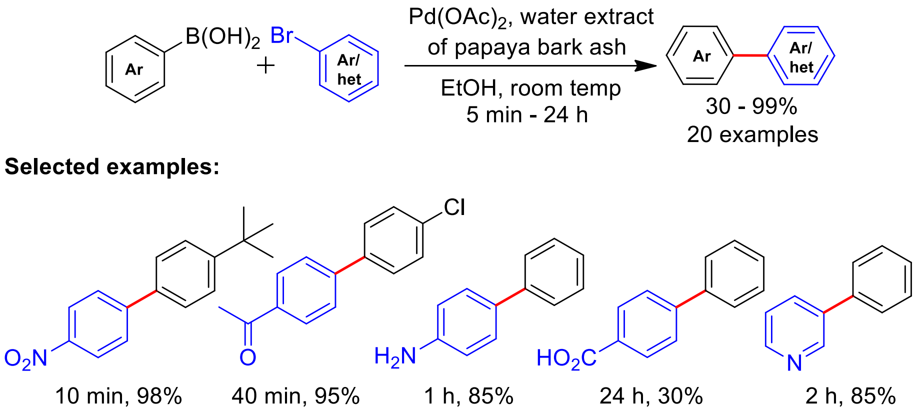
A copper and ligand-free Sonogashira cross-coupling reaction of aryl iodides and terminal alkynes at room temperature was discovered by Dewan et al. using water extract of papaya bark ash and Pd(OAc)$_2$ (Scheme 46) (Dewan et al. 2016b). The reaction of aryl bromides was also reported with terminal alkynes but these transformations require 80 °C. The substituted alkynes are formed in 30–90% yields in 4–12 h using the developed conditions. The aryl bromides with electron-withdrawing groups and *o*-substituted aryl iodide gave low yields of the products under water extract of papaya bark ash–Pd(OAc)$_2$-assisted Sonogashira cross-coupling. The in situ formation of palladium nanoparticles (Pd nanoparticles) was also observed during the formation of products, and the Pd nanoparticles were characterized using transmission electron microscopy analysis. The Pd nanoparticles formed with the size 10–20 nm range were crystallized in spherical shape which are assumed to be responsible for the effective coupling of alkynes and aryl halides at Cu-free conditions (Dewan et al. 2016b).

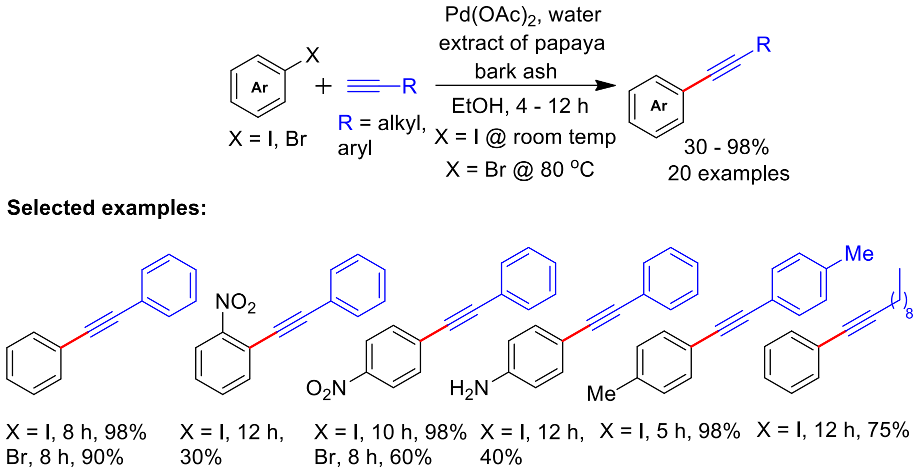
Papaya stem ash showed the presence of large quantities of potassium, calcium and sodium along with minor quantities of magnesium and silicon by energy dispersive X-ray analysis (Gohain et al. 2020a). Papaya stem ash was utilized for the Knoevenagel condensation reaction of aryl aldehydes and malononitrile at 55 °C in ethanol (Scheme 47) (Gohain et al. 2020a). Papaya stem ash (2 weight percent) was also reported as sustainable catalyst for the biodiesel production from waste cooking oil and *Scenedesmus obliquus* lipid with 95.23% and 93.33% conversion using CH$_3$OH/oil as 9:1 in 3 h at 60 °C (Scheme 48) (Gohain et al. 2020a). The reusability of the catalyst was found to be up to 5–6 cycles in Knoevenagel reaction and biodiesel productions.

Century plant leaf ash

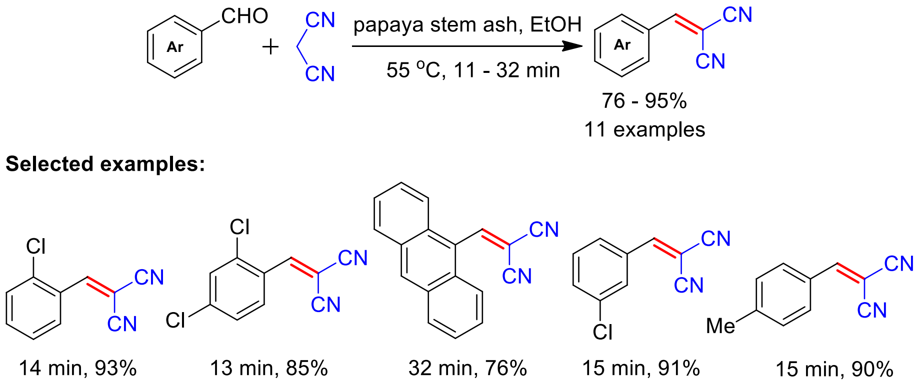
The literature investigations suggested the presence of potassium, calcium, magnesium, sodium, zinc and phosphorous in considerable amounts in the leaf of century plant (*Agave americana*), and the basic nature of the ash of these leaves is also used by the Himalayan people for the washing of clothes (Patil et al. 2019). Water extract of century plant leaf ash has been reported for the multicomponent (three-component) reaction of naphthols, aldehydes and malononitrile at room temperature to give 2-amino-4*H*-chromenes in 30–65 min with 85–94% yields (Scheme 49) (Patil et al. 2019). A four-component reaction of aldehydes, malononitrile, ethyl acetoacetate and hydrazine hydrate (or phenylhydrazine) toward the synthesis of pyrano[2,3-*c*]pyrazoles at room temperature was also reported in the same report by Patil et al. (Scheme 50) (Patil et al. 2019). The application of nature-derived basic media at ambient temperature for the conduct of

Scheme 45 Pd(OAc)$_2$-catalyzed Suzuki–Miyaura cross-coupling reaction in water extract of papaya bark ash

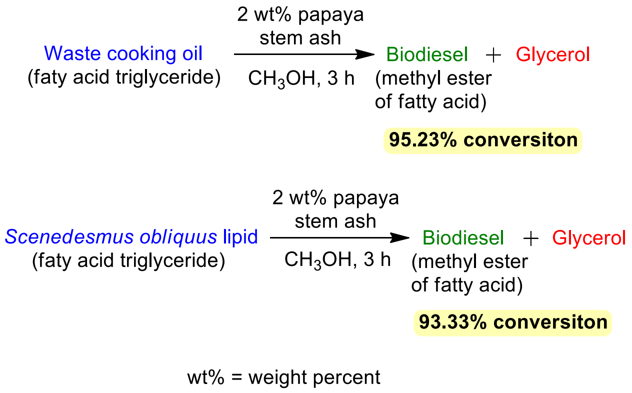




Scheme 46 $Pd(OAc)_2$-catalyzed Sonogashira cross-coupling reaction in water extract of papaya bark ash



Scheme 47 Knoevenagel condensation reaction using papaya stem ash



Scheme 48 Biodiesel preparation from waste cooking oil and *Scenedesmus obliquus* lipid using papaya stem ash

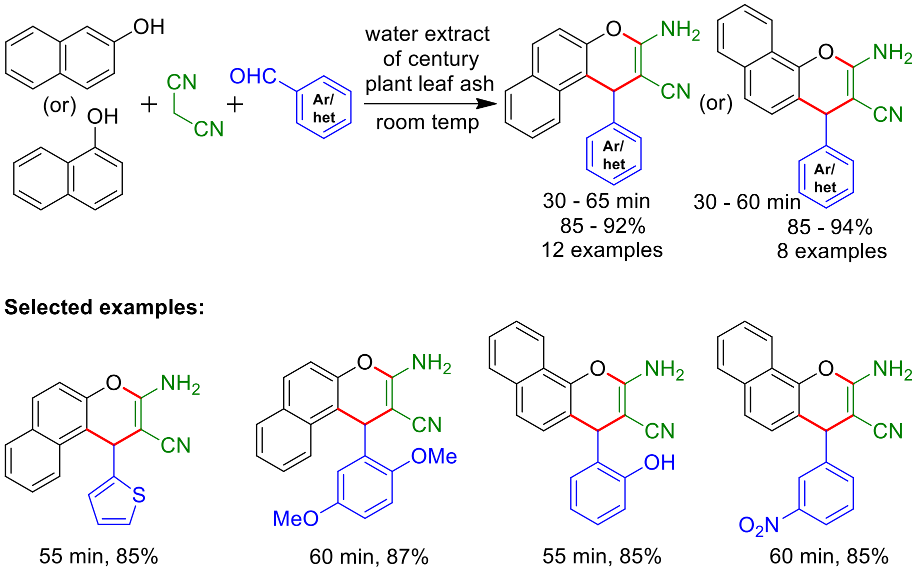
multicomponent reactions with high product yields under added catalyst and organic solvent-free conditions is the advantage of this procedure. Further, the compounds are purified without using column chromatography. Reusability studies indicated the effectiveness of the catalyst up to four cycles with the yields of pyrano[2,3-*c*]pyrazole in 94%, 92%, 89% and 83% using ethyl acetoacetate, hydrazine hydrate, 4-chlorobenzaldehyde and malononitrile.

Water hyacinth ash

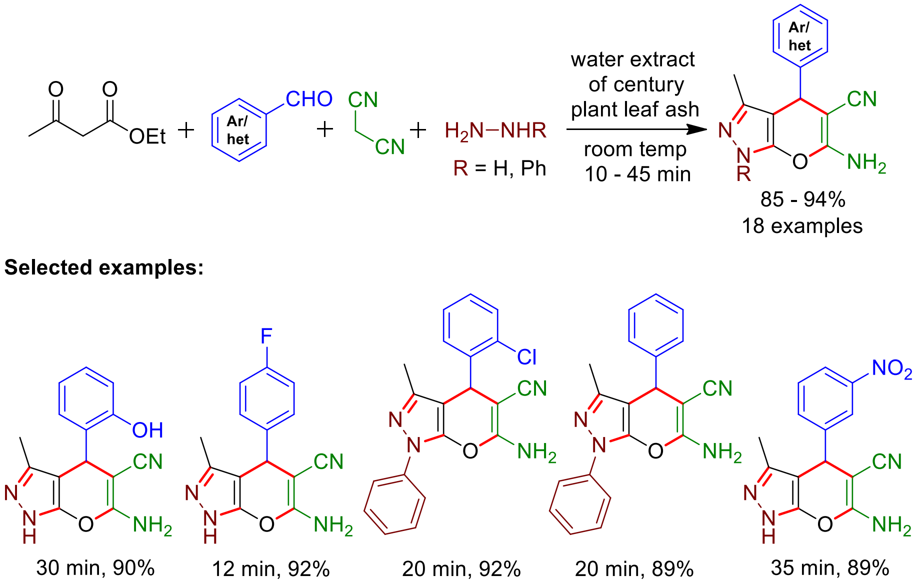
The water hyacinth (*Eichhornia crassipes*) is a highly abundant aquatic weed, and its ash showed the presence of large quantities of potassium, magnesium, calcium and copper by energy-dispersive X-ray analysis (Sarmah et al. 2017a). The water extract of water hyacinth ash was utilized by Sarmah et al. for the successful transformation of arylboronic acids and aryl halides into biaryls (Suzuki–Miyaura cross-coupling reaction) with 40–98% yields in 1–12 h using $Pd(OAc)_2$ at room temperature (Scheme 51) (Sarmah et al. 2017a). The use of naturally abundant weed, and ligand- and base-free ambient conditions are the advantages of this Suzuki–Miyaura cross-coupling reaction. Aryl iodides showed high reactivity over aryl bromides, and aryl chlorides are not found to participate in Suzuki–Miyaura cross-coupling reaction under the developed conditions.

The application of water hyacinth roots ash for solvent-free *aza*-Michael reaction of amines and α,β-unsaturated nitriles or acrylonitrile or Morita–Baylis–Hillmann adducts with amines has been reported for the synthesis of substituted amines with 82–97% yields in 0.25–7 h (Scheme 52)

Scheme 49 Synthesis of 2-amino-4*H*-benzochromenes in water extract of century plant leaf ash



Scheme 50 Synthesis of pyrano[2,3-*c*]pyrazoles in water extract of century plant leaf ash

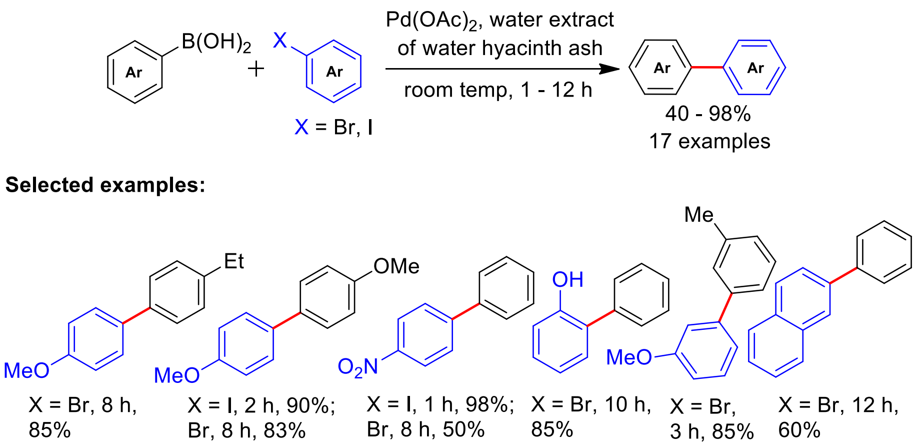


(Talukdar and Deka 2020). The catalyst was studied for its reuse using methyl acrylate and 2-aminoethanol as substrates and found the gradual decrease of its activity during five consecutive cycles (isolated yields of product: 95%, 88%, 80%, 70% and 50% in 1–5 cycles). Solvent-free conditions, easy separation of the products, high yields, application of weed-based natural feedstock as catalyst, absence of external (metal-based) catalysts and volatile organic solvents and highly economical reaction conditions are reported advantages of this work over the other reported methods using catalysts such as $InCl_3$, $Yb(OTf)_3$, $Bi(NO_3)_3$, $LiClO_4$, $Cu(OTf)_2$, SiO_2-H_2SO_4, SmI_2, etc. (Talukdar and Deka 2020).

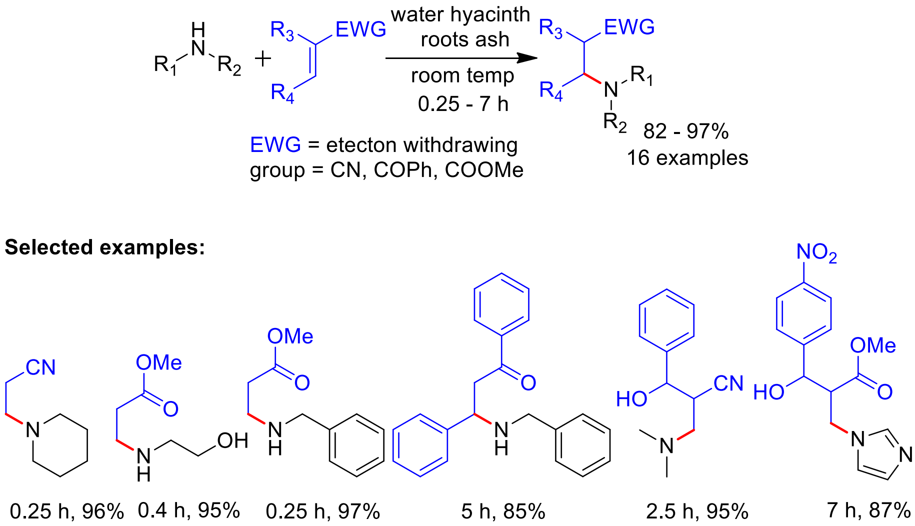
Bael fruit ash

The bael fruit ash was reported for the presence of potassium, calcium, magnesium, sodium and phosphorous in large quantities by flame atomic absorption spectroscopic analysis (Shinde et al. 2017). Water extract of bael fruit ash was reported by Shinde et al. for the synthesis of 2-amino-4*H*-benzochromenes and 2-amino-4*H*-chromenes using two types of multicomponent reactions (Shinde et al. 2017). 2-Amino-4*H*-benzochromenes are synthesized from naphthols, aryl/heteroaryl aldehydes and malononitrile at room temperature (Scheme 53), and 2-amino-4*H*-chromenes are synthesized from *o*-hydroxybenzaldehydes and 2 eq. of malononitrile (or ethyl acetoacetate) or 1 eq. malononitrile

Scheme 51 Pd(OAc)$_2$-catalyzed Suzuki–Miyaura cross-coupling reaction in water extract of water hyacinth ash



Scheme 52 *Aza*-Michael reaction-catalyzed by water hyacinth roots ash



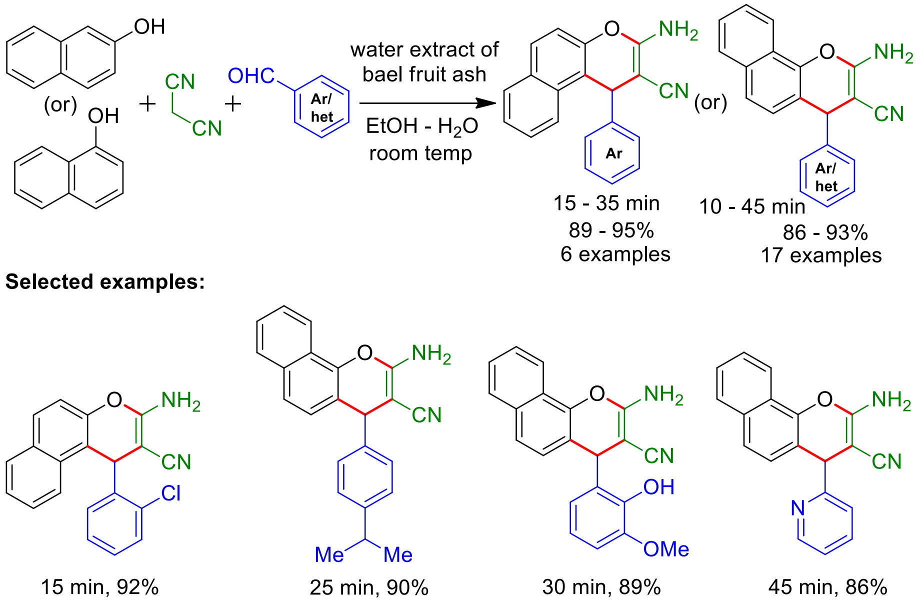
and nitromethane at room temperature (Scheme 54). These methods are highly economical by the application of readily available materials and are safe by the use of renewable catalyst and media. This method showed several advantages over the reported protocols using other catalysts, and the comparison of the results of the reported methods is presented in Table 8. Reusability study of water extract of bael fruit ash was reported with the yields 94%, 94%, 93%, 93% and 91% in 1–5 cycles.

Shinde et al. also developed two different four-component reactions for the synthesis of pyrano[2,3-*c*] pyrazoles and pyrazolyl-4*H*-chromenes using bael fruit ash in water at room temperature (Schemes 55, 56 and 57) (Shinde et al. 2018). A four-component reaction of aryl/heteroaryl aldehydes, malononitrile, ethyl acetoacetate and hydrazine hydrate was used for the synthesis of pyrano[2,3-*c*]pyrazoles (Scheme 55), while the four-component reaction of *o*-hydroxybenzaldehydes, malononitrile, ethyl acetoacetate and hydrazine hydrate was used for the synthesis of pyrazolyl-4*H*-chromenes (Scheme 56). The reactions of aryl/heteroaryl 1,2-dials produced bis(pyrano[2,3-*c*]pyrazoles) (Scheme 57). The application of nature derived base in water as media is identified to be critical for these transformations, and the reactions are conducted at room temperature in open air. A comparison of several reported methods in connection to this work has also been provided in this article, which indicates the clear advantages of this protocol over others (Shinde et al. 2018).

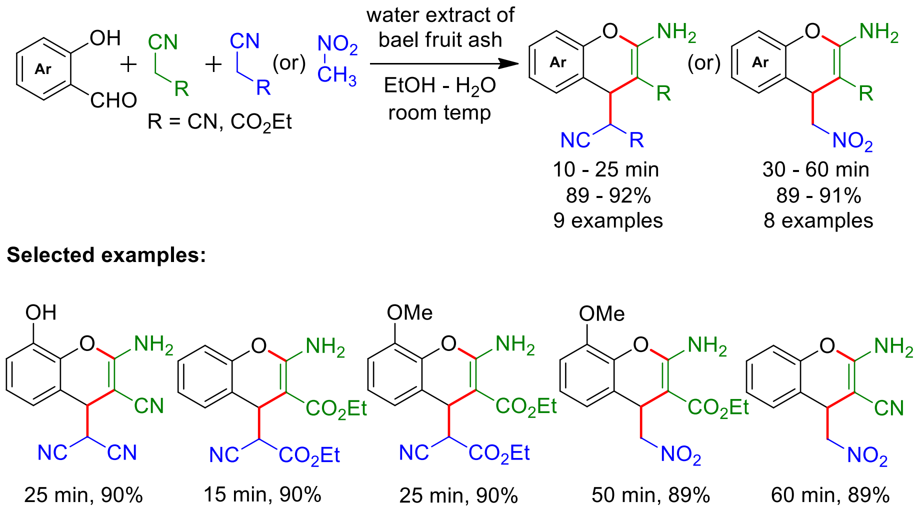
Nilgiri bark ash

Water extract of nilgiri bark ash has been reported for the sustainable synthesis of 3-carboxycoumarins from 2-hydroxybenzaldehydes and Meldrum's acid at room

Scheme 53 Synthesis of 2-amino-4*H*-benzochromenes in water extract of bael fruit ash



Scheme 54 Synthesis of 2-amino-4*H*-chromenes in water extract of bael fruit ash

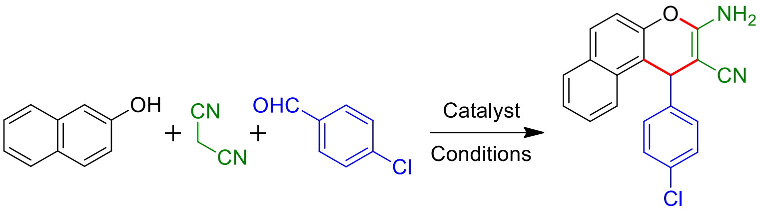


temperature (Scheme 58) (Kantharaju and Hiremath 2020). Water extract of nilgiri bark ash was also reported for the Knoevenagel condensation of aryl aldehydes and malononitrile at room temperature (Scheme 59) (Kantharaju and Hiremath 2020). This method has been reported with the advantages as the conduct of reactions at ambient conditions, column-free purification of the compounds, use of renewable materials, added catalyst and organic solvent-free conditions and high yields of the products in short reaction times. Further the ash of nilgiri was studied to contain calcium, magnesium, potassium, sodium, carbon and copper in considerable to large quantities (Kantharaju and Hiremath 2020). This report also presented a comparison of the results with the reported procedures.

Mango peel ash

Mango peel ash was characterized to contain large quantity of potassium and considerable amounts of magnesium, phosphorous and silicon by energy-dispersive X-ray analysis (Hiremath and Kamanna 2021). The water extract of mango peel ash has been reported as suitable catalyst for the synthesis of 1*H*-pyrazo[1,2-*b*]phthalazine-5,10-diones from phthalhydrazide, malononitrile and aryl aldehydes

Table 8 Comparison of the results of water extract of bael fruit ash-catalyzed method with some reports[a]

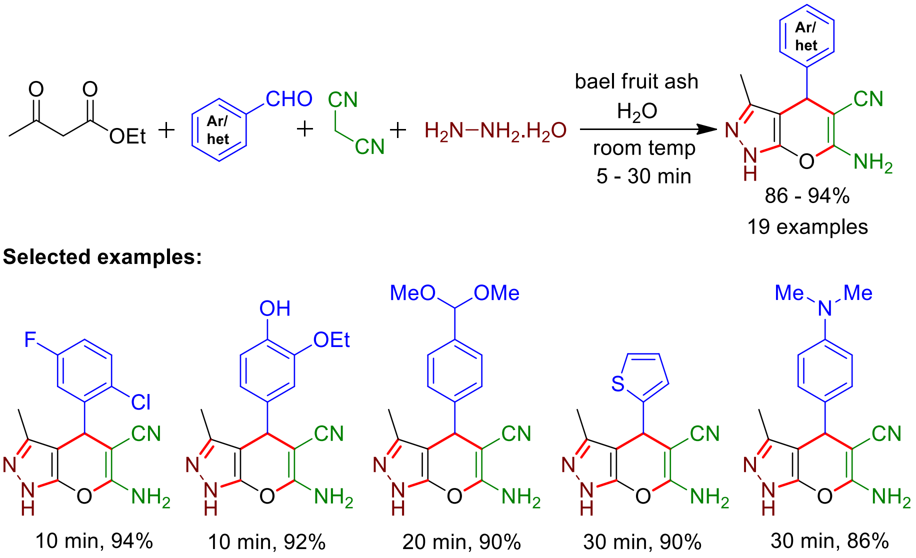


Entry	Catalyst	Solvent	Temp	Time	Yield (%)	Ref
1	*p*-Toluenesulfonic acid	CH_3CN	Reflux	4 h	91	Baghernejad et al. (2009)
2	Methanesulfonic acid	CH_3CN	Reflux	4 h	91	Elinson et al. (2008)
3	Cetyltrimethylammonium chloride	H_2O	110 °C	6 h	74	Ballini et al. (2001)
4	$H_{14}[NaP_5W_{30}O_{110}]$	H_2O	Reflux	4 h	91	Heravi et al. (2007)
5	[bmim]OH[b]	H_2O	Reflux	5 min	96	Gong et al. (2008)
6	γ-Alumina	H_2O	Reflux	3 h	84	Maggi et al. (2004)
7	Water extract of bael fruit ash	EtOH	Room temp	30 min	94	Shinde et al. (2017)

[a] This table has been reproduced from Shinde et al. (2017) with permission from the Royal Society of Chemistry

[b] [bmim]OH = 1-butyl-3-methylimidazolium hydroxide

Scheme 55 Synthesis of pyrano[2,3-*c*]pyrazoles in water using bael fruit ash

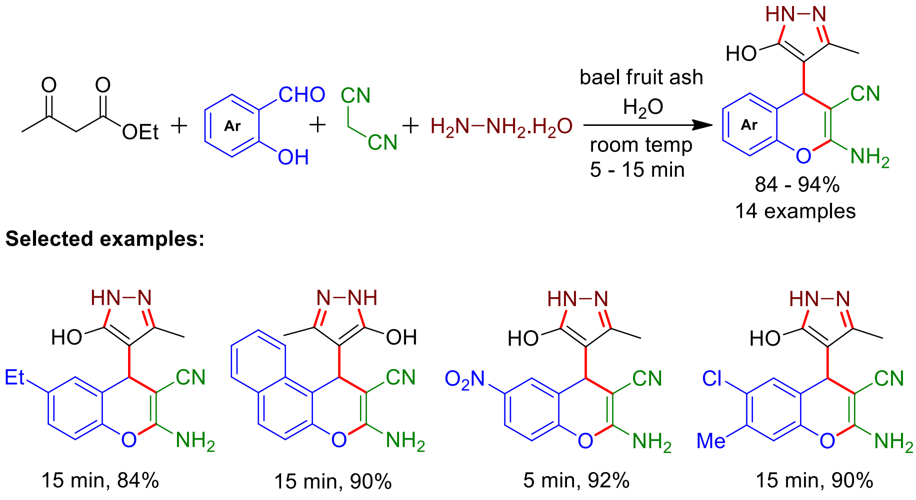


under microwave irradiation (Scheme 60) (Hiremath and Kamanna 2021). The reported advantages of this protocol include the application of agro-waste-derived media for multicomponent reaction, costly catalyst and toxic solvent-free conditions with excellent yields (83–89%) of the products in 6–8 min reaction time.

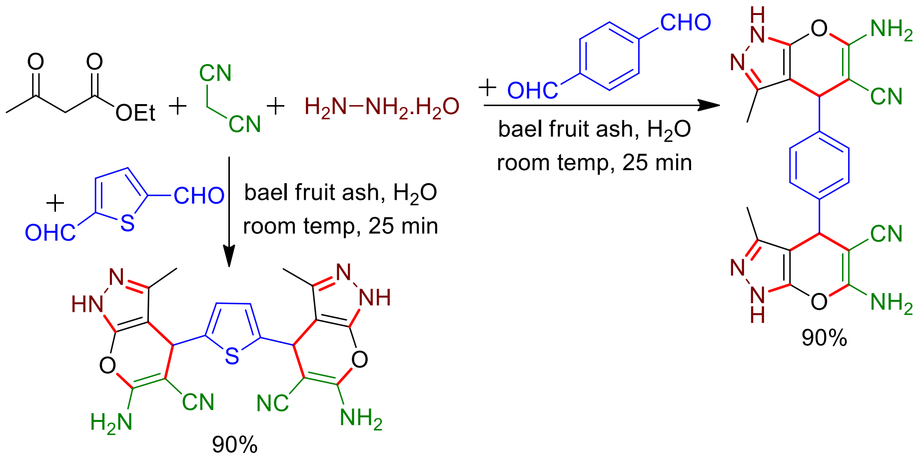
Onion peel ash

Bisenols of 4-hydroxycoumarins and aryl aldehydes were reported in water extract of onion peel ash at 80 °C (Scheme 61) (Chia et al. 2018). This method evades the

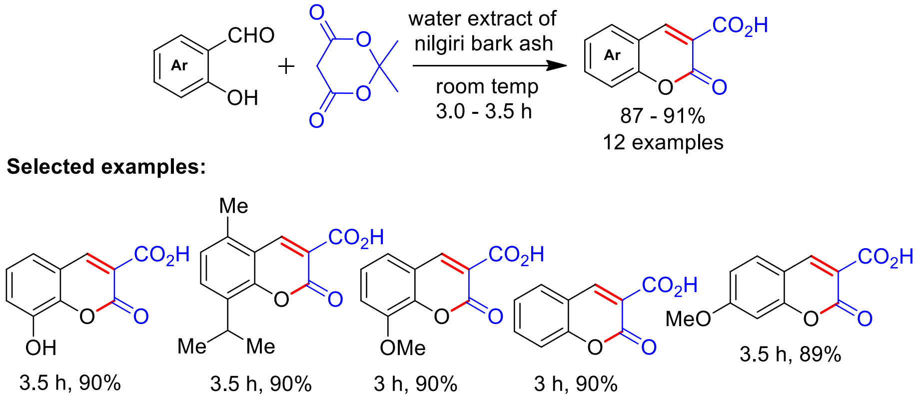
Scheme 56 Synthesis of pyrazolyl-4*H*-chromenes in water using bael fruit ash



Scheme 57 Synthesis of bis(pyrano[2,3-*c*]pyrazoles) in water using bael fruit ash

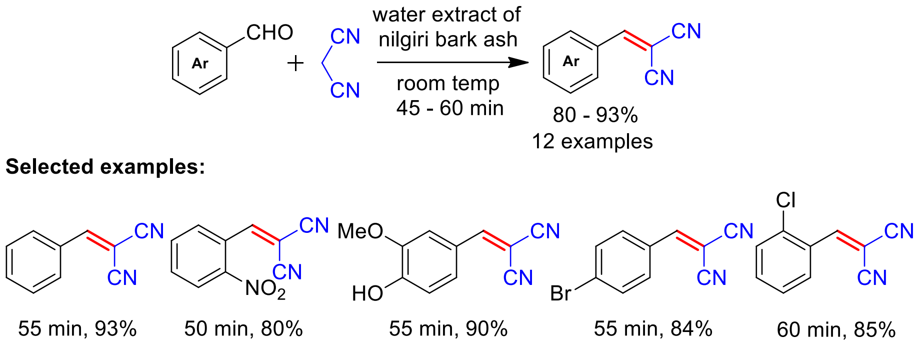


Scheme 58 Synthesis of 3-carboxycoumarins in water extract of nilgiri bark ash at room temperature

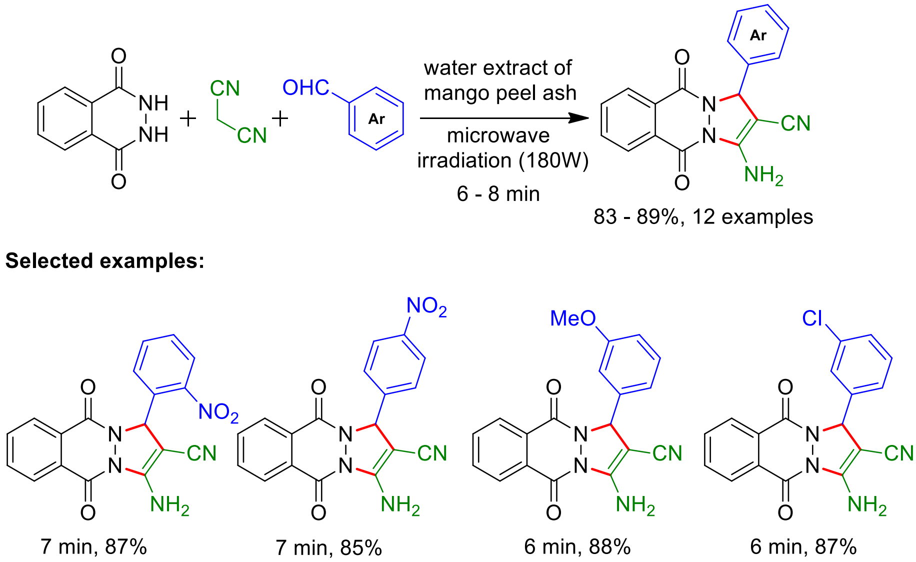


external catalysts and organic solvents. The formation of high yields of products (62–94%) in 40 min by the use of waste-derived catalytic media is the advantage over existing methods for the synthesis of bisenols of 4-hydroxycoumarins and aldehydes (Chia et al. 2018). The catalytic system has been reused without much decrease of yield up to five cycles and the yields of bisenol of 4-hydroxycoumarin, and benzaldehyde was reported as 94%, 93%, 93%, 92% and 92% in 1–5 cycles (Chia et al. 2018).

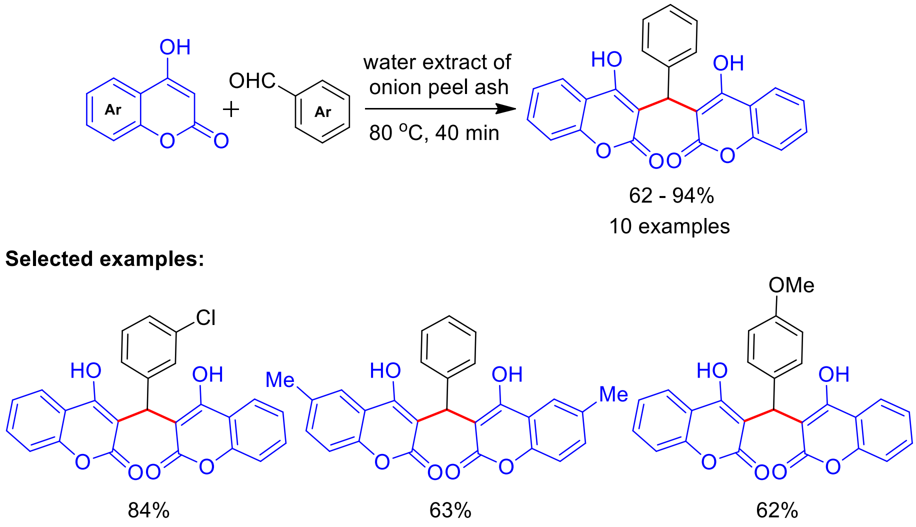
Scheme 59 Knoevenagel condensation reaction in water extract of nilgiri bark ash at room temperature



Scheme 60 Synthesis of pyrazophthalazine diones in water extract of mango peel ash under microwave irradiation



Scheme 61 Synthesis of bisenols in water extract of onion peel ash at 80 °C



Muskmelon fruit shell ash

Muskmelon fruit shell ash was studied to contain calcium, magnesium, sodium and potassium in large quantities by energy-dispersive X-ray analysis (Hiremath and Kantharaju 2020). The water extract of muskmelon fruit shell ash has also been reported for the room temperature synthesis of 2-amino-4*H*-pyrians and tetrahydrobenzo[*b*] pyranes (Hiremath and Kantharaju 2020). The reaction of aryl aldehydes with malononitrile and ethyl acetoacetate was yielded 2-amino-4*H*-pyrians (in 88–92% yields), while the use of dimedone instead of ethyl acetoacetate produced tetrahydrobenzo[*b*]pyranes (in 86–90% yields) (Scheme 62). The catalyst reusability study in the synthesis of 2-amino-4*H*-pyrian from benzaldehyde, ethyl acetoacetate and benzaldehyde showed 92%, 91%, 90% and 87% in 1–4 cycles. The comparison of the results of this method with the reported methods is also represented in Table 9 (Hiremath and Kantharaju 2020).

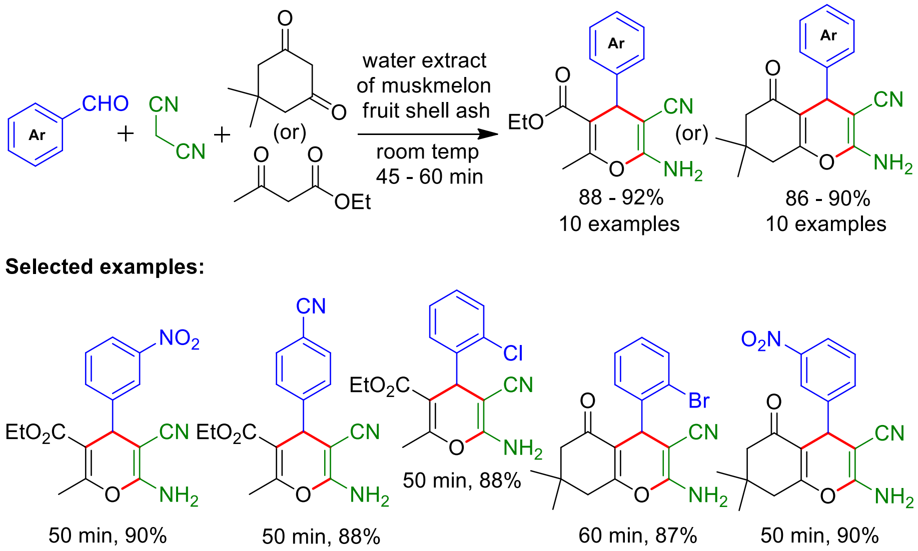
Pomelo peel ash

Sun et al. reported a selective and mild hydrolysis of a variety of nitriles (including aryl, heteroaryl, alkyl and alkenyl nitriles) to form amides using water extract of pomelo peel ash at 150 °C (Scheme 63) (Sun et al. 2019). The X-ray photoelectron spectroscopy analysis of water extract of pomelo peel ash suggested the presence of potassium, calcium, phosphorous, carbon, oxygen, silicon, chlorine and silicon in large to considerable amounts (Sun et al. 2019). Water extract of pomelo peel ash shows significance over the other ashes-based aqueous extracts and the high selectivity in the formation of amide over acids has been found under basic water extract of pomelo peel ash condition. The water extract of pomelo peel ash was also studied for the reusability using 4-fluorobenzonitrile and observed to form the product, 4-fluorobenzamide in 91%, 89%, 88%, 84% and 75% yields in 1–5 cycles. This method displayed the advantages as wide substrate scope, use of waste-derived catalytic medium, avoid of metals and oxidizing agents (such as peroxides), mild conditions, ease of preparation of the catalyst and high yields (41–96%) of selective hydrolysis products.

Lemon fruit shell ash

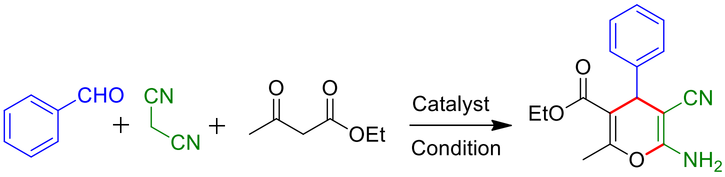
The lemon fruit shell ash contains magnesium, potassium, sodium and potassium as major constituents (Kantharaju and Khatavi 2018b). Water extract of lemon fruit shell ash has been reported by Kantharaju and Khatavi for the synthesis of 2-amino-4*H*-chromenes from phenols (such as α-naphthol, β-naphthol and resorcinol), malononitrile and aryl aldehydes under microwave irradiation (300 W) (Scheme 64) (Kantharaju and Khatavi 2018b). The reaction was studied under mechanical stirring, grindstone and microwave irradiation methods, and the microwave irradiation process was found effective under water extract of lemon fruit shell ash-catalyzed condition which delivered the benzochromene derivatives with 72–89% yields in 2–8.3 min.

Water extract of lemon fruit shell ash was also investigated for the synthesis of 3-carboxycoumarins via the condensation of salicylaldehydes and Meldrum's acid under microwave irradiation (300 W) by Khatavi and Kantharaju (Scheme 65) (Khatavi and Kantharaju 2018). The reported advantages of this process include the quick reactions (2–6 min), easy separation of the products, high product yields (73–92%) and application of biorenewable catalyst.



Scheme 62 Synthesis of 2-aminopyrians and tetrahydrobenzopyranes in water extract of muskmelon fruit shell ash

Table 9 Comparison of the results of water extract of muskmelon fruit shell ash with other protocols[a]



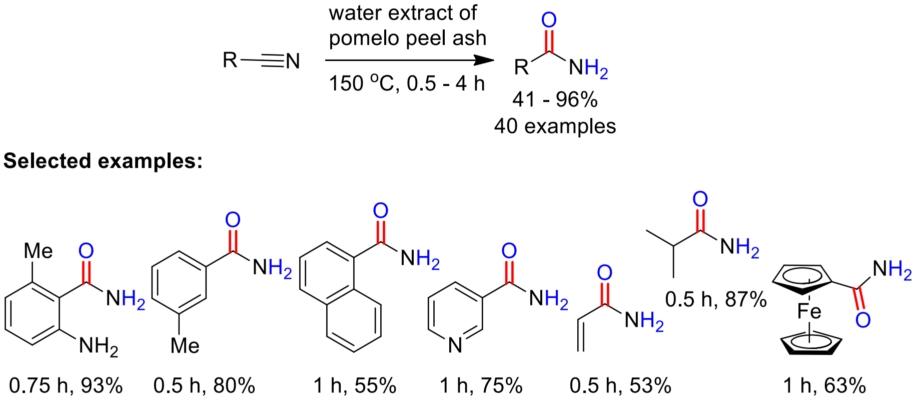
Entry	Catalyst	Solvent/ method	Temp (°C)	Time (min)	Yield (%)	Ref
1	KF-Al_2O_3	EtOH	Room temp	180	77	Kharbangar et al. (2012)
2	Borax	EtOH, H_2O	Room temp	30	84	Molla et al. (2013)
3	NH_4OAc	Neat, grinding	Room temp	15	78	Smits et al. (2013)
4	Piperazine	H_2O	90	7	96	Yousefi et al. (2018)
5	Fe_3O_4@glutaraldehyde@isinglass	EtOH	Reflux	50	88	Pourian et al. (2018)
6	[bmim]OH[b]	Neat	60	45	90	Khurana and Chaudhary (2012)
7	Fe_3O_4@g-C_3N_4[c]	EtOH	60	190	80	Azizi et al. (2018)
8	K_2CO_3/montmorillonite	EtOH, H_2O, ultrasound	50	25	95	Pham et al. (2017)
9	[2-aemim][PF_6][d]	H_2O, microwave irradiation	100	3	87	Peng and Song (2007)
10	Water extract of muskmelon fruit shell ash	EtOH	Room temp	45	92	Hiremath and Kantharaju (2020)

[a] This table has been reproduced from Hiremath and Kantharaju (2020) with permission from the John Wiley & Sons

[b] [bmim]OH = 1-butyl-3-methylimidazolium hydroxide

[c] Fe_3O_4@g-C_3N_4 = magnetite supported graphitic carbon nitride

[d] [2-aemim][PF_6] = 1-(2-aminoethyl)-3-methylimidazolium hexafluorophosphate

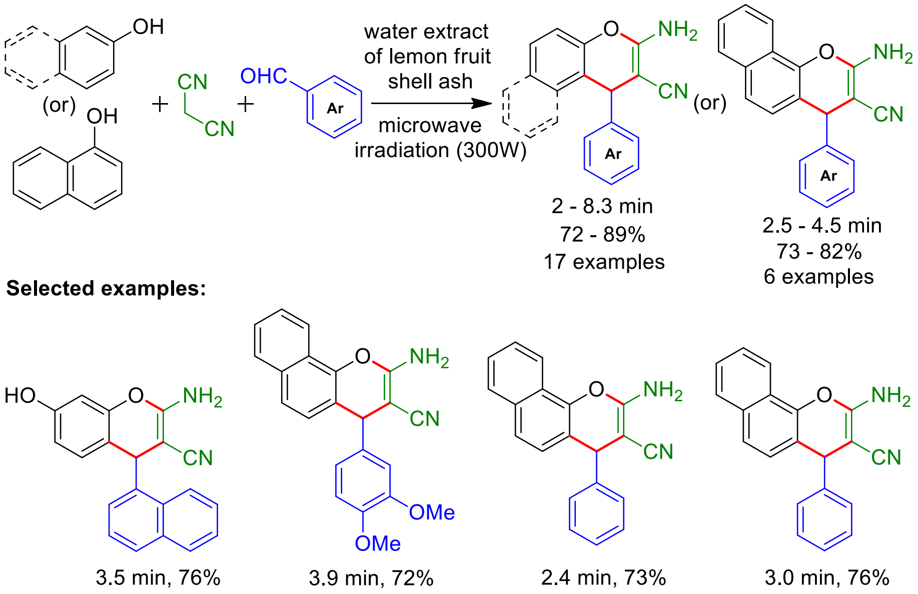


Scheme 63 Hydration reaction of nitriles in water extract of pomelo peel ash

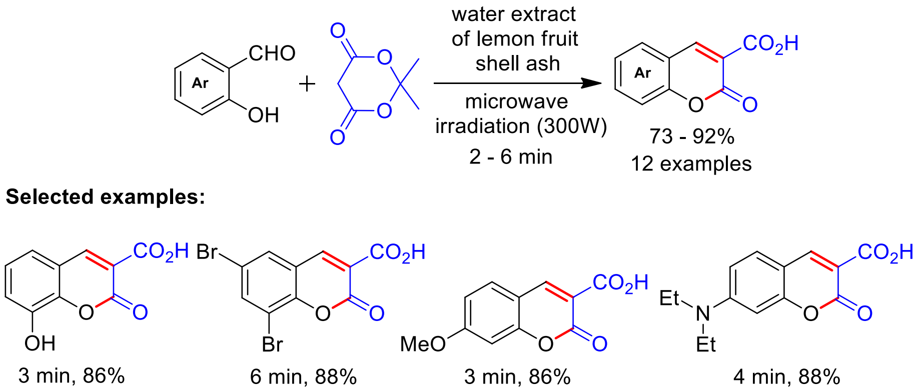
Teak leaf ash

Energy-dispersive X-ray analysis of teak leaf ash showed the presence of calcium, potassium, magnesium, silicon and oxygen in good quantities (Das et al. 2020a). Das et al. reported the application of water extract of teak leaf ash for the successful conversion of arylboronic acids into phenols with 86–97% yields in 2–22 min using H_2O_2 as hydroxide source at room temperature (Scheme 66) (Das et al. 2020a). The synthesis of aryl/alkyl amides with 74–96% yields in 1–4 h from aryl/alkyl nitriles was also reported in the same article using H_2O_2 at 60 °C (Scheme 67). The Knoevenagel condensation of aryl aldehydes and malononitrile with 85–95% product yields in 15–21 min at 60 °C (Scheme 68) and the Cu(OAc)$_2$-catalyzed Chan–Evans–Lam amination of imidazoles (and benzimidazoles) with 68–87% product yields in 8–12 h using arylboronic acids (Scheme 69) are also included in this

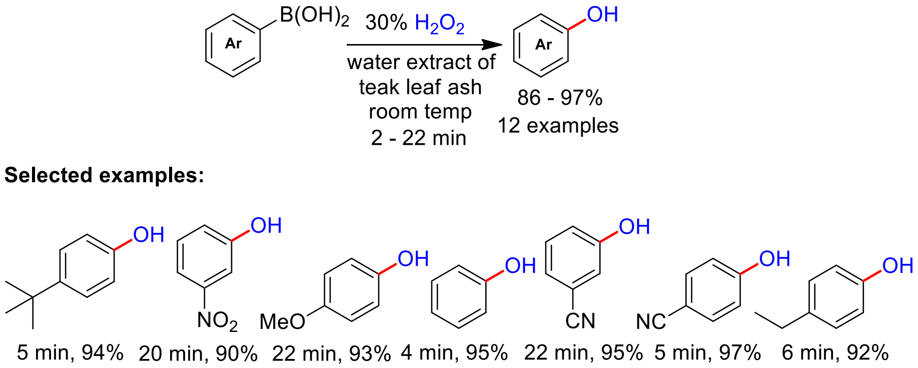
Scheme 64 Synthesis of 2-amino-4*H*-benzochromenes in water extract of lemon fruit shell ash under microwave irradiation



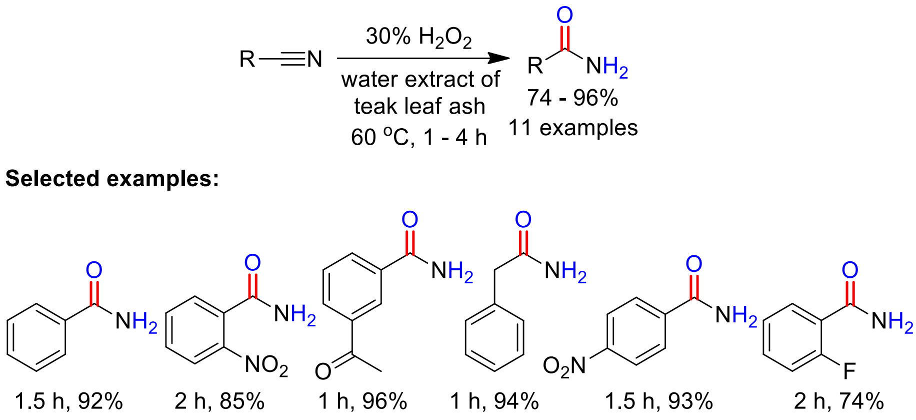
Scheme 65 Synthesis of 3-carboxycoumarins using water extract of lemon fruit shell ash under microwave irradiation



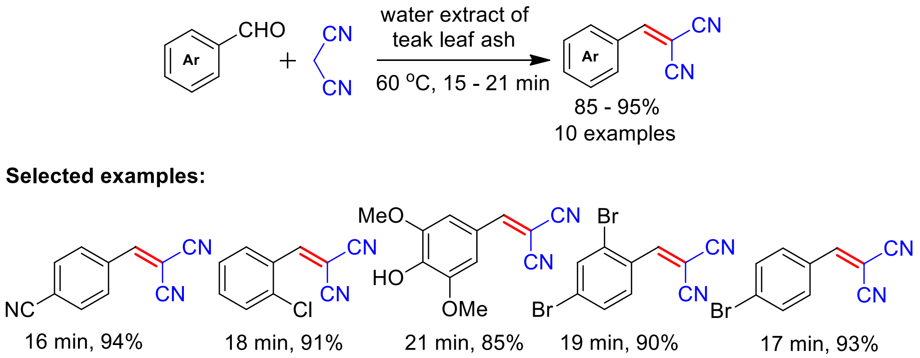
Scheme 66 Synthesis of phenols from arylboronic acids using water extract of teak leaf ash–H_2O_2



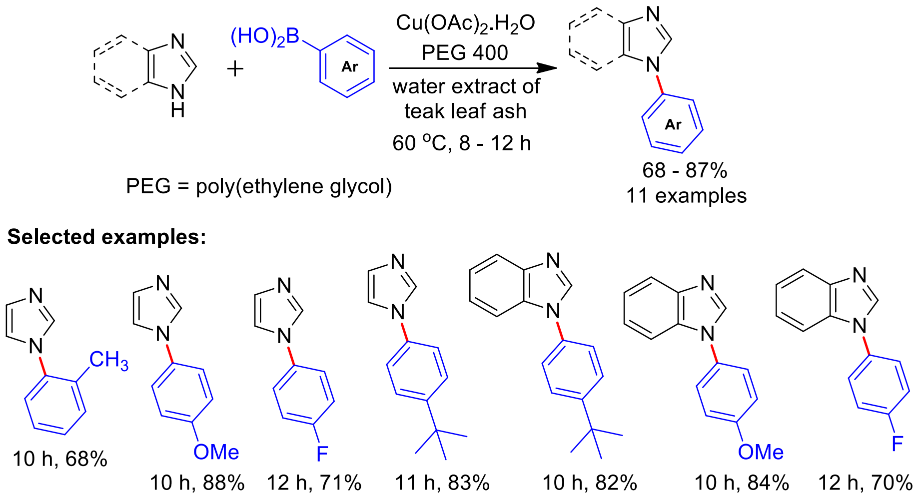
report. The Chan–Evans–Lam coupling was performed in poly(ethylene glycol) (PEG) 400 and water extract of teak leaf ash mixture at 60 °C. In each of these reactions, the broad applicability was confirmed using a wide range of substrates. These nature-inspired processes based on water extract of teak leaf ash were reported with the advantages such as the application of renewable basic media/catalyst, avoid of volatile solvents/ligands/auxiliaries and formation of products in high yields (Das et al. 2020a).



Scheme 67 Hydration reaction of nitriles using water extract of teak leaf ash–H_2O_2



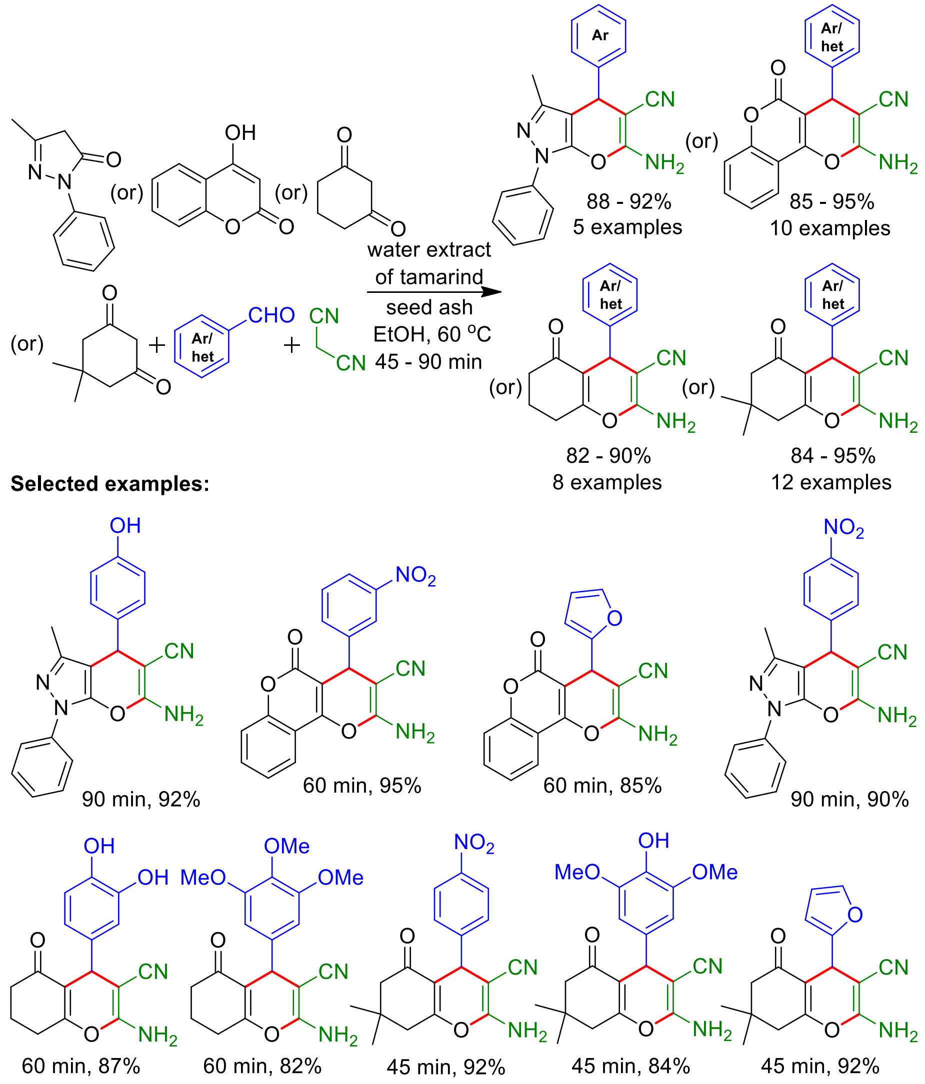
Scheme 68 Knoevenagel condensation using water extract of teak leaf ash



Scheme 69 Cu-catalyzed Chan–Evans–Lam coupling in water extract of teak leaf ash–poly(ethylene glycol) 400

Tamarind seed ash

Tamarind seed ash showed the presence of magnesium as major constituent along with minor constituents as potassium, calcium and sodium by energy-dispersive X-ray analysis (Halder et al. 2021). Water extract of tamarind seed ash has been reported by Halder et al. for the synthesis of 2-amino-4*H*-chromenes from enol equivalents (such as dimedone, cyclohexane-1,3-dione, 4-hydroxycoumarin and 1-phenyl-3-methylpyrazolone), (hetero)aryl aldehyde and malononitrile (Halder et al. 2021) (Scheme 70). The reactions are conducted at 60 °C to form high yields of 2-amino-4*H*-chromenes (82–95%) in 45–90 min (Scheme 70). The observed reusability of catalyst up to four cycles (95%, 92%, 90% and 88% yields of 2-amino-4*H*-chromene from 4-methoxybenzaldehyde, dimedone and malononitrile) using



Scheme 70 Synthesis of 2-aminopyrians using water extract of tamarind seed ash

waste-derived inexpensive catalyst shows predominance over commercial catalyst-based methods using external catalysts such as urea, borax, ZrO_2 nanoparticles, ferrite-supported glutathione, Fe_2O_3-proline magnetic nanoparticles, etc. (Halder et al. 2021).

Application of ashes in biodiesel production

In addition to the applications of ashes of organic solid waste or their derivatives in industrially relevant chemical transformation, a parallel and huge amount of work has been appeared in the use of the ashes of organic waste and their derivatives as catalysts in biodiesel productions. Few reviews have covered the most of the developments in this area, and they are appeared in 2018 (Basumatary et al. 2018) and 2020 (Alrobaian et al. 2020; Etim et al. 2020b; Hamza et al. 2020). Due to the high importance, scope and explorations, this review also undertakes to present the reported processes from the year 2020 in addition to the explorations of organic waste-based ashes/ash derivatives that are presented in Sects. 2–16. Table 10 displays the representative highlights of these works appeared on this area from the year 2020 to till date.

Perspectives

Through the literature reports and own experience of the author by working with the waste-derived ashes in the development of new/novel methods for industrially relevant chemical transformations, the following are supposed to be the future perspectives in this area of research.

a) In the development of novel protocols, the ashes or their derivatives play a crucial role as catalysts facilitating to evade the additional chemical substances as catalyst/oxidant/metal/ligand/additive/volatile solvents.

Table 10 Organic waste-based ash/ash-derived systems in biodiesel production since 2020

Entry	Biodiesel feedstocks	Catalyst	Calcination temp (°C)	Catalyst load (wt%[a])	MeOH/oil ratio	Temp (°C)	Time (h)	Conversion (%)	Ref
1	Waste cooking oil	Arecanut husk ash	750	1	15:1	65	2	96.5	Vinu and Binitha (2020)
2	Waste cooking oil	*Tectona grandis* leaves ash	700	2.5	6:1	60	3	100	Gohain et al. (2020b)
3	Coconut oil	Moringa leaves ash	500	2	9:1	60	2.5	98.18	Taslim et al. (2020)
4	Honne oil	Cocoa pod husk-plantain peel ash	500	4.5	15:1	65	2.5	99.12	Olatundun et al. (2020)
5	Soybean oil	Orange peel ash	Burnt in air	7	6:1	Room temp	7	98	Changmai et al. (2020)
6	Soybean oil	Pineapple leaves ash	600 and 900	4	40:1	60	0.5	98	de Barros et al. (2020)
7	Soybean oil	Banana trunk ash	Burnt in air	7.15	6:1	Room temp	6	98.39	Rajakumari and Rokhum (2020)
8	Soybean oil	Mango peel ash	Burnt in air	6	6:1	Room temp	4	98	Laskar et al. (2020)
9	*Calophyllum inophyllum* oil	Sugarcane leaf ash	Burnt in air	5	19:1	64	3	97	Arumugan and Sankaranarayanan (2020)
10	Pangi oil	Durian rind ash	Burnt in air	5	8:1	65	1	96.21	Yanti et al. (2020)
11	Sunflower oil	Walnut shell ash	800	5	12:1	60	0.1	98	Miladinović et al. (2020)
12	Palm oil	Sugar cane bagasse ash	500–800	6	20:1	65	3	93.8	Mutalib et al. (2020)
13	Rubber seed oil	Durian peel ash	600	10	8:1	65	1	96.5	Fitriani et al. (2020)
14	Sunflower oil	Banana peduncle ash	700	1.98	9.2: 1	60	1	99.36	Balajii and Niju (2020)
15	Waste cooking oil	Rice husk char-(20%) K_2O-(5%)Fe	450	4	12:1	75	4	98.6	Hazmi et al. (2020)
16	Palm oil	Rice husk ash	800	5	1:1	65	1	99.73	Ngaini et al. (2020)
17	*Irvingia gabonensis–Pentaclethra macrophylla–Elais guineesis* oil blend	Egg shell–snail shell–wood mixed ash	900	4.5	8:1	61.61	1.1	97.22	Adepoju et al. (2020)
18	Palm oil	Durian skin ash	800	4	6:1	50–70	2	90.14	Said et al. (2020)
19	Waste cooking oil	Papaya peel ash	700	3.5	12:1	65	1	97.5	Etim et al. (2020a)
20	*Jatropha curcas* oil	Kesseru branch ash	550 and 850	7	12:1	65	1.1	97.75	Basumatary et al. (2021)
21	Soybean oil	Moringa leaves ash	500	6	6:1	65	2	86.7	Aleman-Ramirez et al. (2021)

Table 10 (continued)

Entry	Biodiesel feedstocks	Catalyst	Calcination temp (°C)	Catalyst load (wt%[a])	MeOH/oil ratio	Temp (°C)	Time (h)	Conversion (%)	Ref
22	*Calophyllum inophyllum–Annona muricata* oil blend	Waste wood ash	1100	2	1:2.4	70	1	99.15	Adepoju (2021)
23	Sunflower oil	Waste ginger leaves ash	–	1.6	6:1	–	1.5	93.83	John et al. (2021)
24	Waste cooking oil	Fe_3O_4@orange peel ash	Burnt in air	6	6:1	65	3	98	Changmai et al. (2021)

[a] wt% = weight percent

b) Large-scale separation of the constituents of ashes may be undertaken by investigating suitable procedures or instrumental methods. The modification of the constituents of ashes to other valuable products is also possible by simple chemical derivatization(s). Novel catalytic systems for significant transformations of material science and industrial relevance may also be developed using the ashes.
c) The applicability of various solid organic waste-based ashes should be studied for their applicability as renewable feedstocks/reagents/catalysts/solvents in chemical synthesis, energy-based applications and other environment sustainable chemical/physical transformations.
d) Investigations of chemical processes using ashes or ash derivatives and the subsequent study of the constituents of ashes may enroot a new avenue in modifying the existing procedures.
e) The scope of establishing natural alternative to the existing base/super base-assisted systems in organic synthesis may also be under taken using these ashes.
f) These systems may further drive toward developing cost-effective and energy-efficient protocols in organic synthesis using water as sustainable solvent at ambient conditions.
g) Development of effective and economical catalytic systems using ashes/modified ashes in the biodiesel production and biomass transformation to useful products is the prominent scope in this area.
h) It is also possible to develop highly economic and renewable absorbents for CO_2, H_2S, etc., with enhanced biogas quality using these ashes by minimizing the energy consumption and greenhouse gases emission.
i) Since a very limited work has been appeared on the utilization of the ashes/extracts of ashes of renewable organic wastes in synthetic organic chemistry, there will be a huge opportunity in developing novel reactions that are not reported yet.

Conclusion

In conclusion this article provides a brief review on the reported methods of industrially important transformations that are appeared by the utilization of solid waste-derived ashes/ash extracts. As can be seen, it is a sustainable strategy in chemical synthesis and biodiesel production by the utilization of biorenewable materials. This also appears to be a novel and prominent approach for the management of solid waste.

The reported explorations of waste-derived ashes to industrially relevant transformations are limited to few chemical transformations. These include Suzuki–Miyaura, Chan-Evans-Lam, Ullmann, Sonogashira, Michael, aldol-type, Knoevenagel and Henry reactions; *ipso*-functionalizations of aryl aldehydes/arylboronic acids; sulfidifications of thiols, alkynes or alkenes; azide–alkyne click reaction; 3-carboxycoumarin synthesis; peptide bond making; biodiesel production; pyridines preparation; flavones and chalcones synthesis; C–Br and C-P bond making; hydration of nitriles; bisenol preparation; pyrazophthalazines synthesis; arylboronic acids/heteroarylboronic acids homocouplings; and synthesis of pyranes. Several of these processes are appeared as reputation with the alternative waste-derived products.

As mentioned in the future perspectives (Sect. 18), there is a huge scope in utilization of the solid waste-derived products as bases to the industrially relevant chemical transformation and bulk process may be undertaken for the extraction of chemical constituents from these extracts. Further, the presence of a variety of metallic or non-metallic constituents (including oxides and chlorides) in these extracts may be evaluated for the novel transformations that are not discovered yet and in which the ingredients of ashes may work as promoters, redox reagents, feedstocks, phase transfer agents, catalysts, etc.

The chemistry reported by using these ashes/extracts appears to be tiny instead their scope. The chemical/physical transformations that are developed using these ashes/extracts may be encouraged without much comparison to the results of ash-based derivatives, since the solid waste is not of a particular fruit (e.g., banana, mango, pomegranate, etc.) or not a particular weed or plant, it may be anything. How best the solid waste can be utilized as valuable product is highly important in the green chemistry/sustainable environment perspective than which waste has been utilized.

The reported processes presented in this review along with the great future scope may attain the attention of synthetic chemists toward exploration of this sustainable technology to industrially relevant chemical transformations, waste valorization and energy-related applications.

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