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COMPREHENSIVE REVIEW

Development of green methodologies for Heck, Chan–Lam, Stille and Suzuki cross-coupling reactions

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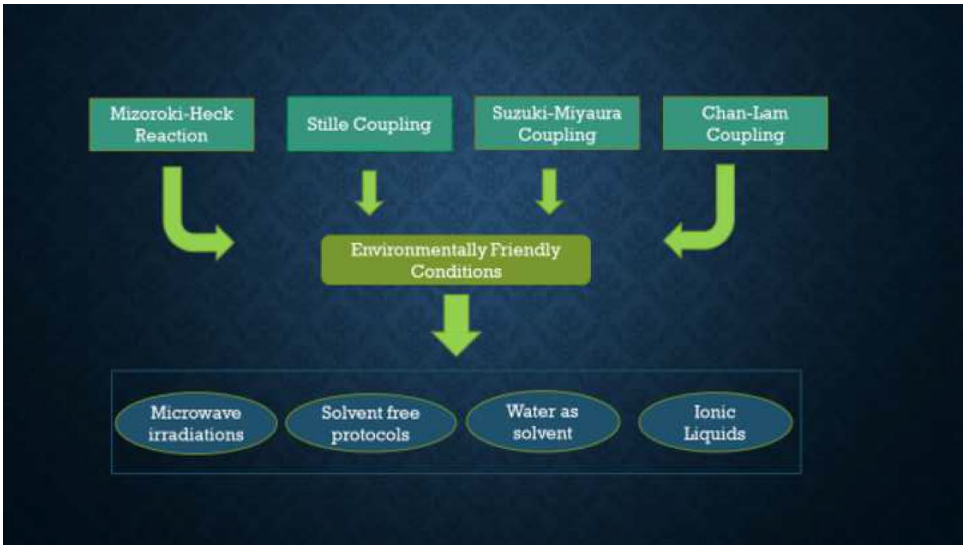
Abstract

Organic reactions under green conditions have become popular day by day because of increased use of harmful chemicals leading to environmental hazards. This review focuses the implementation of green chemistry in Suzuki–Miyaura, Heck, Stille and Chan–Lam cross-coupling reactions incorporating a variety of strategies in which ionic liquids, water and microwave irradiations are extensively used.

Graphic abstract



Keywords Transition metals · Green chemistry · Nanoparticles · Microwave irradiations · Heterogeneous catalyst

Introduction

Palladium-based catalysts have gained tremendous importance in modern organic chemistry. The wide spread use of palladium-catalyzed reactions (such as Suzuki–Miyaura, Mizoroki–Heck and Stille cross-coupling reaction) shows their importance for further research to develop new molecules. These reactions are playing dynamic role in the construction of natural as well as synthetic polymers besides pharmaceutical products [1–8]. Exploration in bioconjugation of the coupling reaction is due to its broad functional groups tolerance in aqueous media [9].

In recent past, a number of economical chemical processes have been adopted in which microwave irradiation is used for heating purpose and water is preferred over organic solvents being inexpensive, nonflammable and non-toxic

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[10–14]. On the other hand, reactions subjected to microwave irradiations give maximum yield within short time. Gedye and Giguere group [15, 16] at first pronounced the efficacy of these radiations in 1986 to enhance chemical transformations. However, latest scientific apparatuses have overcome the problems like low yield and accidents following improper control as faced by old microwave units [17].

Similarly, ligand, additive and solvent-free protocols are becoming popular nowadays to obtain maximum conversion in an eco-friendly manner. This review article focuses the green synthetic routes discovered by different organic chemists from 2013 to 2018 for Suzuki–Miyaura, Heck, Stille and Chan–Lam cross-coupling reactions.

Brief overview of the metal-catalyzed reactions under green conditions

Heck cross-coupling reaction (Table 1)

Polystyrene-supported palladium(II) dithizone complex **1** (Fig. 1) obtained from the reaction of chloromethylated polystyrene with dithizone effectively catalyzed Heck reaction of aryl halides with methyl acrylates under environmentally friendly conditions. Water was used as the only solvent along with triethyl amine (base) to obtain 80–98% yield of the respective products at 70 °C [18].

The role of iron in metal-catalyzed reactions has been often studied due to its air and moisture stability, less toxicity and environmentally friendly nature. It is an inexpensive metal as compared to palladium, cobalt and nickel. However, till 2013, it was not in use to catalyze the Mizoroki–Heck reaction. In 2013, Hajipour and Azizi [19] prepared iron-based heterogeneous catalyst **2** (Fig. 2) by treating silica acac (prepared by grafting methodology) with $FeCl_3{\cdot}6H_2O$ and then tested it for the reaction between aryl iodides and different olefins. Poly(ethylene glycol) (PEG) was used as the only solvent at 130 °C. Potassium carbonate was selected as suitable base to get 69–85% yield of the required cross-coupling products. The reaction proved to be environmentally friendly having highly active iron catalyst which is easily recoverable and recyclable.

To increase the efficacy of the Heck reaction, Keshipour et al. [20] prepared required catalyst (PdNPs@EDACs) by using ethylenediamine-functionalized cellulose as stabilizing material for the palladium nanoparticles. Heck reaction proceeded very well by using water as green reaction media and potassium carbonate as base. By maintaining temperature at 100 °C, the desired cross-coupling compounds were obtained in 91–99% yield. However, the excellent yield (99%) of product **5** was obtained by the reaction of *p*-nitrophenyl iodide or 4-iodotoluene with styrene **4** (Scheme 1).

Focusing the green synthetic routes, solvent-free protocols are of great interest. In 2013, Khazaei et al. [21] examined the reaction between iodobenzene and butyl acrylate by using pectin-supported palladium nanoparticles (PdNPs/pectin) and tripropyl amine base. 94% yield of the required product was obtained after 5 min with 100% conversion of the iodobenzene. After achieving good results, the authors applied this methodology on different substrates to attain desired substituted alkenes in 57–94% yield.

The research group of Li [22] performed Heck reaction between salt **6** and acrylate **7** or styrene **8** by using aluminum hydroxide stabilizing palladium nanoparticles in ethanol. Resultantly, the required cross-coupling products **9** and **10** were afforded in 60–99% and 23–99% yields, respectively, (Scheme 2). The main advantages of this protocol involved base and ligand-free condition in addition to easy preparation of the desired catalyst (PdNPs/$Al(OH)_3$).

Increasing interest in water-soluble catalysts due to their easy separation from water-insoluble organic products has triggered considerable attention to insert the water-soluble functional groups in ligands. Therefore, Liu et al. [23] prepared ligand ($mPEG_{16}MeImI$) **11** (Fig. 3) which along with palladium acetate efficiently run the reaction of aryl halides and styrene. 38–98% yield range was obtained at 373 K in K_2CO_3, H_2O and 1:5 mixture of $Pd(OAc)_2$/ligand **11**.

In Heck cross-coupling reaction, arenediazonium salts emerged as efficient precursors instead of aryl halides because N_2 is better leaving group than the halogens as demonstrated by Matsuda's group. Therefore, Salabert et al. [24] utilized a variety of arenediazonium salts and alkenes as coupling partners to obtain 10–95% yield range of the respective products. However, the excellent yield (95%) was obtained by the coupling of arenediazonium salt **12** with alkene **13** at 25 °C using 1 mol % palladium acetate catalyst and water as solvent (Scheme 3).

Successful contribution of Betti bases in organic synthesis has received attention from synthetic chemists because of easy preparation and extensive utilization in the synthesis of organometallic compounds. However, no strategy was developed till 2013 in which Betti bases could be used to catalyze the Heck reaction. Hence for the first time, Zhang and coworkers [25] scrutinized the reaction of different halides and olefins by using $PdCl_2$ with Betti base **17**. To carry out the reaction smoothly, temperature was maintained at 120 °C using K_2CO_3 and H_2O solution. The reaction proved to be quite efficient by attaining 56–95% yield range (Scheme 4).

Polymers especially microgels are widely accepted as solid support because these microgels with specific ligand enhance the catalytic activity of the palladium catalyst as reported by Yang et al. [26]. The authors prepared Fe_3O_4@PUNP-Pd catalyst to carry out the reaction between aryl iodide **19** and acrylic acid **20** under argon atmosphere. It was found that only 0.1 mol% quantity of the catalyst was

Table 1 Summary of the green reaction conditions in Mizoroki–Heck reaction

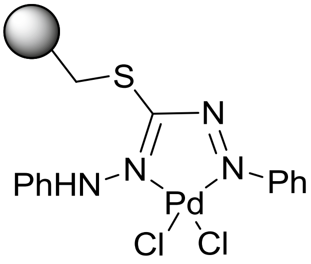
Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Aryl halides, methyl acrylates	Heat	Polystyrene-supported palladium(II) dithizone complex	–	Water	70 °C	5 h	80–98%	[18]
Aryl iodides, methyl acrylate, methyl methacrylate	Heat	Silica-supported iron catalyst	–	Poly(ethylene glycol)	130 °C	1–7 h	69–85%	[19]
Aryl halides, methylvinyl ketone, styrene	Heat	Palladium nanoparticles supported on ethylenediamine-functionalized cellulose (PdNPs@EDACs)	–	Water	100 °C	8 h	91–99%	[20]
Aryl halides, *n*-butyl acrylate	Heat	Palladium nanoparticles supported on pectin	–	Solvent free	140 °C	5 min–18 h	57–94%	[21]
Arenediazonium tetrafluoroborate, styrene, methyl acrylate, *n*-butyl acrylate	–	Aluminum hydroxide stabilizing palladium nanoparticles	–	Ethanol	25 °C	24–48 h	23–99%	[22]
Aryl halides, styrene	Heat	Palladium acetate	ligand (mPEG$_{16}$MeImI)	Water	373 K	1–24 h	38–98%	[23]
Diazonium salts, alkenes	–	Palladium acetate	–	Water	25 °C	16 h	10–95%	[24]
Aryl halides, olefins	Heat	Palladium chloride	1-(Morpholin-1-yl-pyridin-2-yl-methyl)-2-naphthol	Water	120 °C	12 h	56–95%	[25]
Aryl iodides and bromides, acrylic acid, styrene	Heat	Palladium supported on a magnetic microgel (Fe_3O_4@PUNP-Pd)	–	Water	Reflux	12 h	89–96%	[26]
Aryl halides, styrene, butyl acrylate	Heat	Palladium nanoparticles supported on agarose-functionalized magnetic nanoparticles of Fe_3O_4	–	PEG 200	80–130 °C	1–24 h	60–94%	[27]
5-Iodo-2′-deoxyuridine, acrylate	MW	Palladium acetate	–	Water	80 °C	30 min	35–90%	[28]
Aryl halides, styrene, methyl acrylate	–	Pd nanocatalyst (PdNs-H40-PCL-PEG UMs)	–	Water	25 °C	1–1.5 h	85–99%	[29]
Aryl halides, alkenes	Heat	Imidazolium ionic liquid-tagged Schiff base complex of palladium	–	Water	80 °C	3.5–6.5 h	76–98%	[30]
Aryl iodides, bromides, methyl acrylate	Heat	Palladium acetate	–	Ethylene and propylene carbonates	100 °C	24 h	–	[31]

Table 1 (continued)

Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Aryl bromide, alkene	Heat	Palladium nanoparticles supported on triazine-functionalized mesoporous covalent organic polymer (MCOP)	–	1:1 mixture of DMSO-H_2O	90 °C	10–16 h	80–98%	[32]
Aryl bromides, chlorides	Heat	Noncovalently functionalized graphene supported palladium nanoparticles (PCA-GNS-Pd)	–	Water	90 °C	5–30 h	41–92%	[33]
Aryl halides, styrene, methyl and ethyl acrylates	Heat	β-Cyclodextrin-capped palladium nanoparticle	–	3:7 Mixture of the β-cyclodextrin and *N*-methylurea	85 °C	2–10 h	55–96%	[34]
Aryl halides, olefins	MW	Cellulose-supported palladium nanoparticles	–	Water	80 °C	15–20 min	87–89%	[35]
Aryl halides, ethyl and *n*-butyl acrylates	Heat	*Bis*(N-substituted oxamate) palladate(II) complexes	–	Tetra-*n*-butyl ammonium bromide	120 °C	5–15 min and 1.5 and 4 h	75–99%	[36]
Aryl halides, *n*-butyl acrylate	Heat	Gelatin/pectin-stabilized palladium nanoparticles	–	Solvent free	140 °C	3 min–16 h	72–98%	[37]
Arenediazonium tosylate, alkene	MW	Palladium acetate	–	Water	75 °C	1–50 min	50–97%	[38]
Aryl iodides and bromides, allylphosphonate	Heat	$[PdCl_2(NH_3)_2]$	–	Water	80 °C	36 h	39–99%	[39]
Non-activated alkyl iodides, alkenes	UV light	–	–	Water	50 °C	40 min	10–86%	[40]
Aryl iodides and bromides, olefins	Heat	Poly(1-aminoethyl-3-vinylimidazolium bromide)-supported palladium catalyst (Pd/Fe_3O_4@PIL-NH_2)	–	Solvent free	120 °C	25 min–24 h	34–97%	[41]
Aryl halides, *n*-butyl acrylate, styrene	Heat	Nano-tetraimine Pd(0) complex	–	Water	90 °C	0.5–7 h	84–96%	[42]
Iodobenzene, *n*-butyl acrylate	MW	Palladium nanoparticles supported on laponite clay	–	Solvent free	–	5–10 min	–	[43]
Aryl halides, olefins	Heat	Pd/CuO nanoparticles	–	DMF	110 °C	20 h	80–98%	[44]

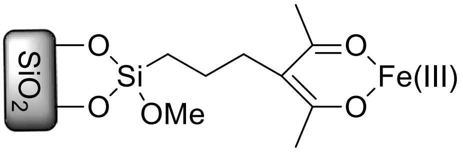
Table 1 (continued)

Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Aryl halides, alkenes	Heat	Palladium nanoparticle-β-cyclodextrin-graphene nanosheet (Pd@CD-GNS)	–	Water	90 °C	15–24 h	60–95%	[45]
Aryl halides, olefins	Heat	ᴅ-Glucosamine-derived pyridyl-triazole@palladium catalyst	–	Solvent free	80 °C	6–24 h	62–96%	[46]
Aryl halides, *n*-butyl acrylate	Heat	Palladium nanoparticles stabilized by *Pistacia atlantica kurdica* gum	–	Water	80 °C	24 h	60–98%	[47]
Aryl halides, acrylic acids	Heat	Magnetic polymer nanocomposite-supported palladium catalyst (Fe_3O_4@PUVS-Pd)	–	Water	Reflux	12–24 h	48–97%	[48]
Aryl iodides, methyl acrylate, acrylic acid, styrene	Heat	Glucose-derived palladium nanoparticles	–	3:1 Mixture of water and acetonitrile	100 °C		23–100%	[49]
Aryl halides, butyl acrylate, acrylonitrile	Heat	Palladium-S-propyl-2-aminobenzothioate immobilized on Fe_3O_4 magnetic nanoparticles	–	Polyethylene glycol	100–120 °C	40–2880 min	81–98%	[50]
Aryl halides, *n*-butyl acrylate	Heat	Palladium nanoparticles stabilized by lignin PEDOT-NFs@Pd	–	Solvent free	140 °C	5 min–18 h 15–75 min	55–94%	[51]
Aryl halides, *n*-butyl acrylate, styrene	Ultrasonic irradiation	Palladium acetate	–	Water	25 °C	24 h	68–96%	[52]
Aryl halide, styrene, methyl acrylate	–	Palladium supported on phosphine-functionalized ZrO_2 nanoparticles (ZrO_2@ECP-Pd) $Pd(PPh_3)_4$	NHC ligand	Water	70 °C	30–180	35–91%	[53]
Aryl halides, methyl and *n*-butyl acrylate	Heat		–	[bmim]PF_6	100 °C		70–98%	[54]
Aryl halides, olefins	Heat	$PdCl_2(NH_3)_2$	–	Water	98 °C	3–12 h	40–93%	[55]
Aryl iodides and bromides, dialkyl vinylphosphonate	Heat		–	Water	80–120°C	6 h	35–98%	[56]



1

Fig. 1 Structure of polystyrene-supported palladium(II) dithizone complex **1**



2

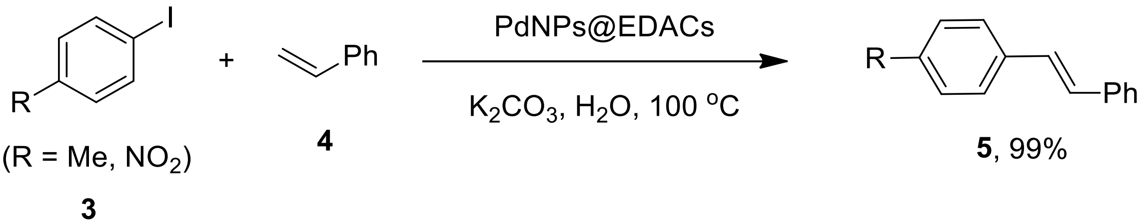
Fig. 2 Structure of heterogeneous iron catalyst **2**

sufficient to attain 96% yield of the required cinnamic acid derivative **21** (Scheme 5).

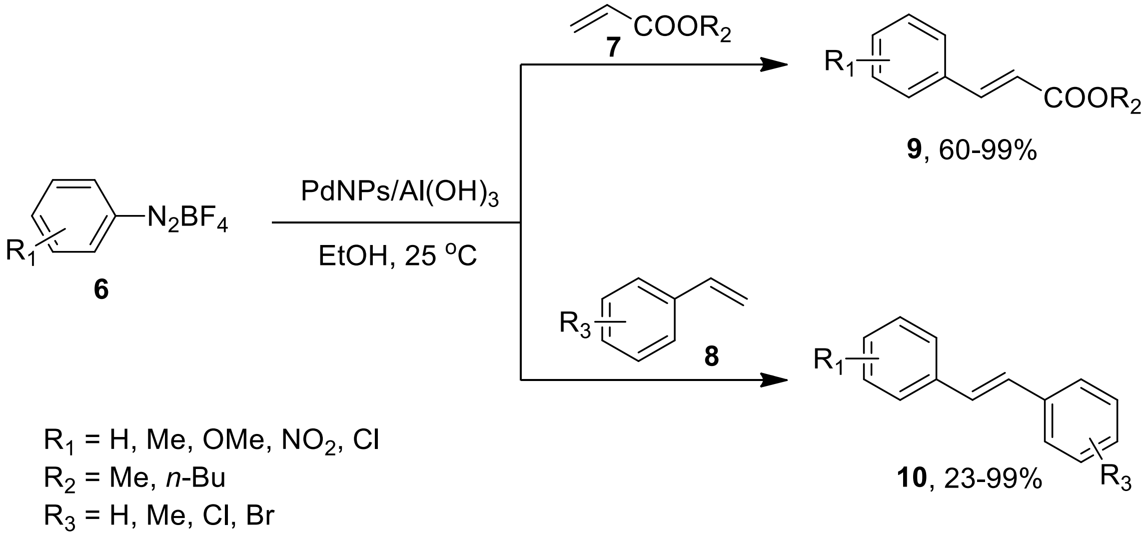
The reaction between different aryl halides and styrene or butyl acrylate was efficiently carried out in the presence of palladium nanoparticles which were supported on agarose-functionalized magnetic nanoparticles of Fe_3O_4. 60–94% yield range of the required products were attained under optimized reaction conditions (K_2CO_3, PEG 200, 80 °C for aryl iodides and 120 °C for aryl bromides). However, *p*-chlorotoluene on treatment with styrene and butyl acrylate at 130 °C gave 87% and 76% yields, respectively [27].

Len and Hervé reported a direct, simple and selective approach for the reaction between uridine **22** and acrylate **13** (Scheme 6) [28]. The reaction was facilitated under microwave irradiations (for 30 min), by maintaining temperature at 80 °C. To achieve the complete conversion, 10 mol% $Pd(OAc)_2$, 2 equiv. triethyl amine and water were the necessary optimized reagents. In addition to this, an antiviral drug BVDU (brivudine) was efficiently synthesized by using this ligand-free methodology.

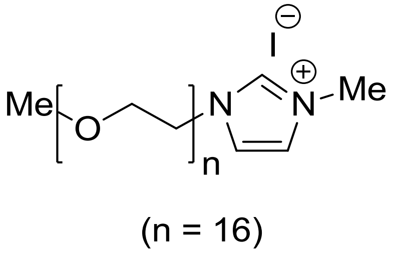
Nabid and Bide utilized PdNPs@H40-PCL-PEG UMs catalyst for the reaction of different aryl halides with styrene and methyl acrylate [29]. The reaction was processed in



Scheme 1 PdNPs@EDACs-catalyzed Mizoroki–Heck reaction



Scheme 2 Heck reaction of arenediazonium tetrafluoroborate salt **6** with acrylate **7** or styrene **8**



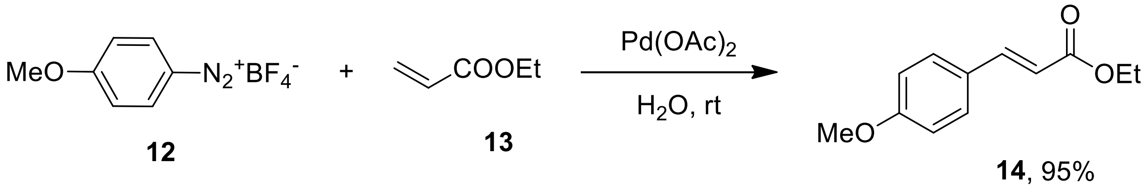
11

Fig. 3 PEG-functionalized ligand (mPEG$_{16}$MeImI) **11**

K_2CO_3 and H_2O solution to attain maximum yield (99%) of the product at room temperature. 85–99% yield range proved the efficacy and wide substrate scope of this methodology.

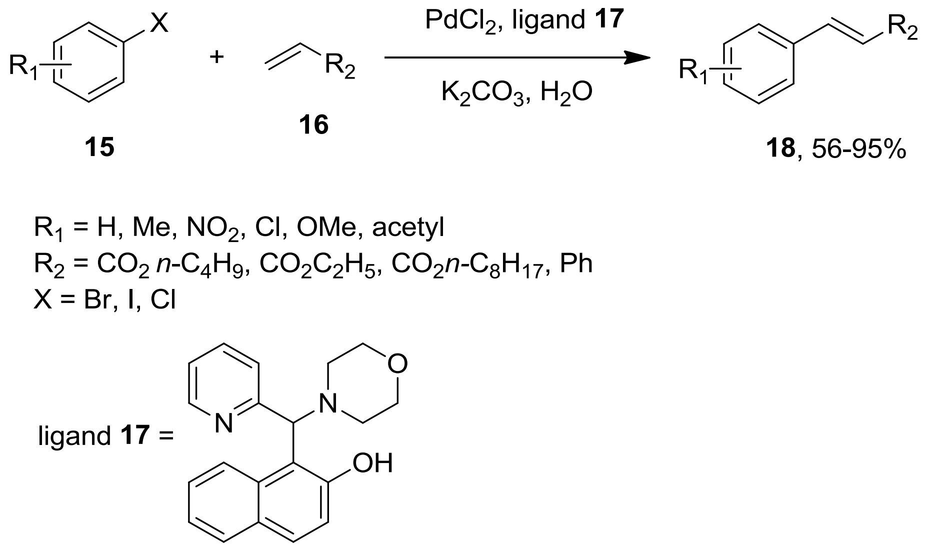
Nehra et al. [30] reported a Heck cross-coupling reaction of phenyl iodide **24** with alkene **25** performed in water. Schiff base palladium complex **26** (1 mol%) was used as catalyst with potassium carbonate as base. By maintaining temperature at 80 °C, product **27** was obtained in 98% yield within 4 h (Scheme 7). Besides achieving excellent yield range, air stability, water solubility and easy reusability up to six runs were the primary traits of the catalyst.

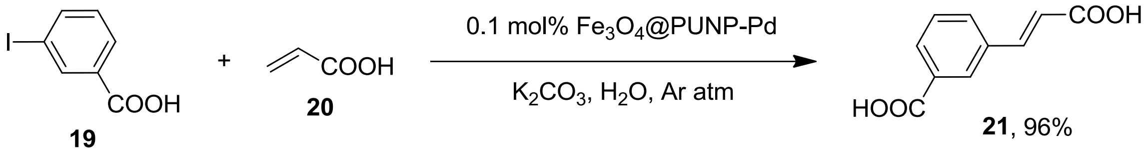
The characteristics features of cyclic carbonates (such as biodegradability, low vapor pressure, less toxicities and odor levels) make them attractive candidates as green reaction media in organic synthesis. Their low cost and extensive use on industrial level encouraged Hunt and colleagues [31] to assess potential applicability of these carbonates for Heck cross-coupling reaction. To achieve complete conversion and maximum yield, palladium acetate and triethyl amine were used at 100 °C. The impact of different solvents (cyclohexanone, DMF, DMSO, ethylene carbonate, propylene carbonate, toluene and *N*-methylpyrolidone (NMP)) was tested and results declared ethylene and propylene carbonates at the top



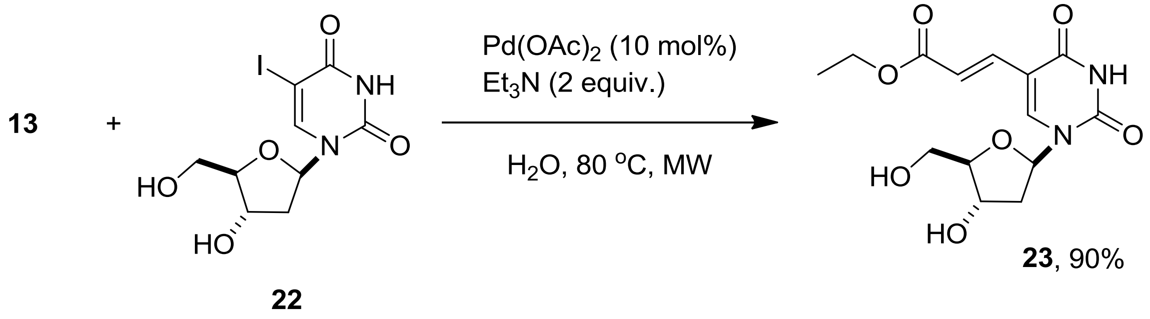
Scheme 3 Coupling of salt **12** with ethyl acrylate **13** in the presence of palladium acetate

Scheme 4 Heck reaction catalyzed by $PdCl_2$ with ligand **17**

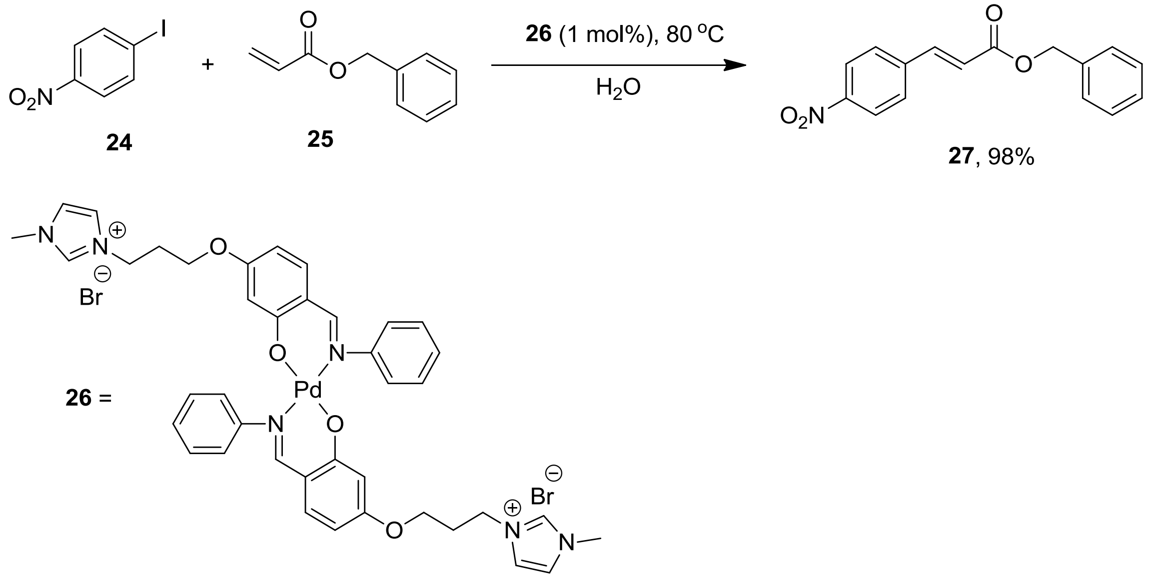




Scheme 5 Fe_3O_4@PUNP-Pd-catalyzed Heck reaction



Scheme 6 Reaction between uridine **22** and ethyl acrylate **13** in the presence of palladium acetate



Scheme 7 Heck cross-coupling of phenyl iodide **24** with alkene **25** in the presence of ionic liquid-tagged palladium complex **26**

with high productivity and 100% conversion as compared to other solvents especially NMP.

Pitchumani and Puthiaraj [32] reported a convenient approach for the Heck reaction using mesoporous covalent organic polymer (MCOP) **28** (Fig. 4) for the stabilization of palladium nanoparticles. To facilitate this protocol, optimized reaction conditions involved potassium carbonate as base, 1:1 mixture of DMSO-H_2O and 90 °C temperature.

In 2014, Sharavath and Ghosh [33] have made a novel contribution toward Heck cross-coupling reaction by using noncovalently functionalized grapheme-supported palladium nanoparticles (PCA-GNS-Pd). The reaction between bromobenzene **29** and alkene **30** was completed in 92% yield by using 0.2 mol% PCA-GNS-Pd, TBAB, H_2O and sodium carbonate (Scheme 8).

Keen interest in cyclodextrins in the present era reveals their extensive applications in organic synthesis especially to conduct metal-catalyzed reactions by stabilizing the transition metal nanoparticles. In this regard, Zhao and coworkers [34] investigated β-cyclodextrin-capped palladium nanoparticle-catalyzed Heck reaction. 90–96% yield range was obtained when different aryl iodides were treated with 4-Cl and 4-F styrenes; however, in case of methyl acrylate, iodobenzene afforded 94% yield within 2 h. While treating aryl bromides with methyl or ethyl acrylates, 55–76% yield range was attained. For this protocol, triethyl amine as base and 3:7 mixture of the β-cyclodextrin and *N*-methylurea were used as effective reaction media.

The extensive use of plant extract for the synthesis of metal nanoparticles has remained the goal of many research groups due to the presence of flavonoids and polyphenols (in plant extract) which are capable to fulfill the requirement of reducing agents. Considering this on the top priority, Konwar and colleagues [35] utilized oxyresveratrol (an active bio-reductant) along with $PdCl_2$ and nanoporous cellulose to prepare the targeted catalyst (Pd(0) NPs cellulose) whose

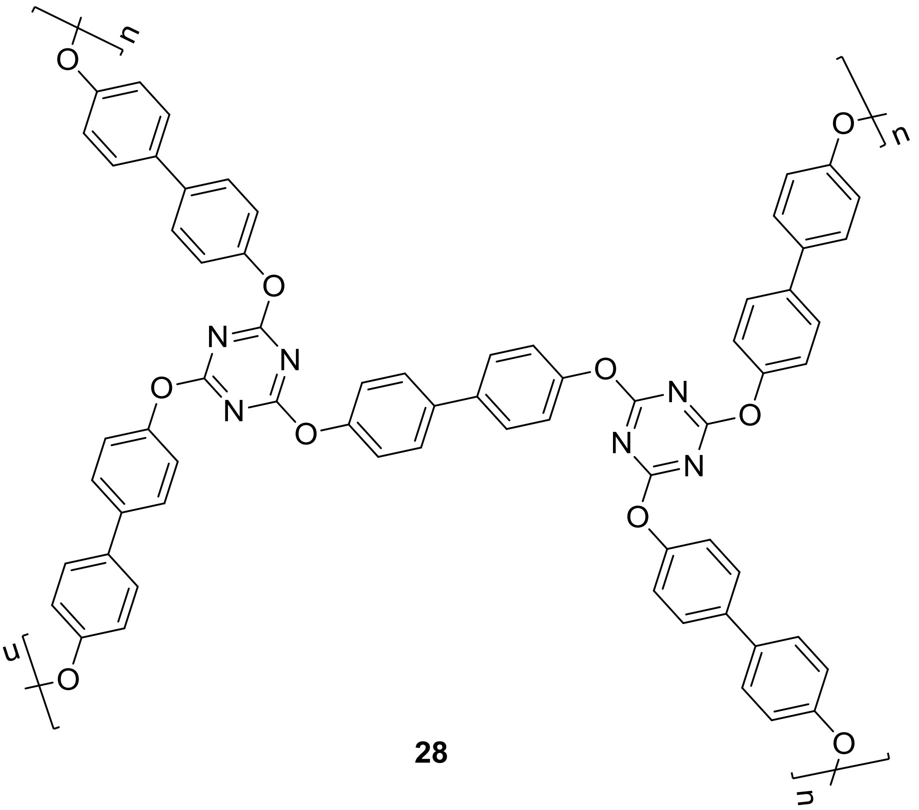
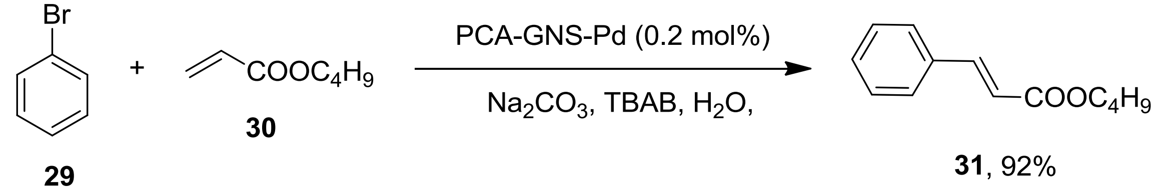


Fig. 4 Structure of mesoporous covalent organic polymer (MCOP) **28**

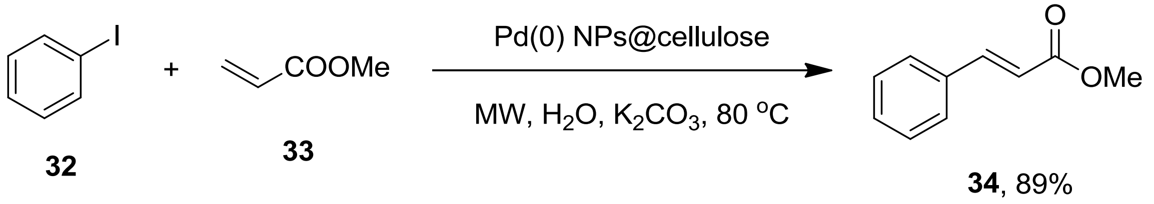


Scheme 8 Heck cross-coupling between bromobenzene **29** and alkene **30** via noncovalently functionalized graphene catalyst (PCA-GNS-Pd)

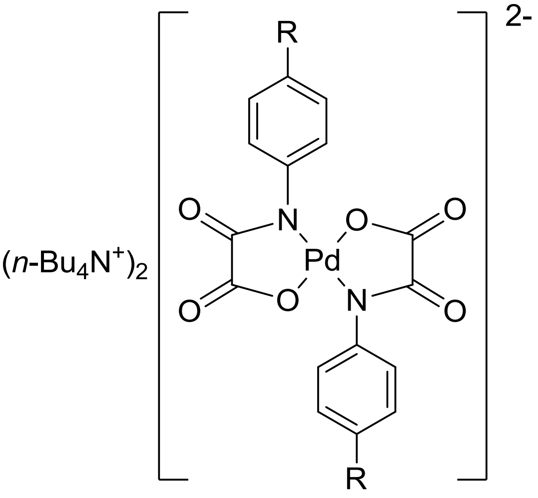
efficiency was checked by treating phenyl iodide **32** with methyl acrylate **33**. Maximum yield (89%) was observed by consuming 0.5 mol% Pd(0) NPs@ cellulose in potassium carbonate and water solution. The reaction was carried out under microwave irradiation by maintaining temperature at 80 °C (Scheme 9).

Fortea-Pérez et al. [36] synthesized *bis*(oxamato) palladate(II) complexes (**35–39**) (Fig. 5) and tested their catalytic activities in Heck cross-coupling reaction using triethyl amine (2 equiv.) and n-Bu_4NBr as solvent at 120 °C. As a result, high yields were observed within short reaction time (5–15 min) in case of aryl iodides, while 4-MeO- and 4-F-substituted aryl bromides gave desired products in 1.5 and 4 h, respectively.

The enhanced catalytic activity of palladium nanoparticles functionalized by carbohydrate-based solid support



Scheme 9 Pd(0) NPs@cellulose-catalyzed Heck cross-coupling



35, R = 4-F
36, R = 4-Cl
37, R = 4-Br
38, R = 4-MeO
39, R = isopropyl

Fig. 5 Heck cross-coupling reaction catalyzed by complexes (**35–39**)

encouraged Khazaei and colleagues [37] to assess the efficacy of the mixture of gelatin (protein) and pectin (polysaccharide) for stabilizing the required PdNPs. The synthesized catalyst efficiently catalyzed the Mizoroki–Heck cross-coupling in the presence of tripropyl amine. As a result, the expected coupling adducts gave good-to-excellent yield range (72–98%).

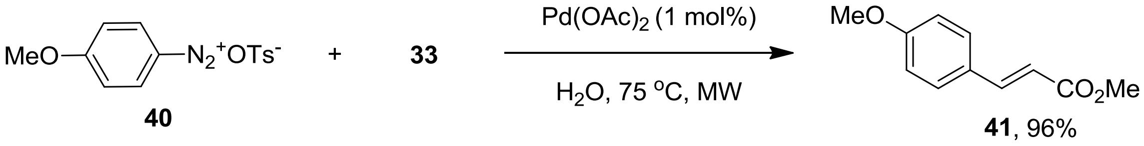
Postnikov and colleagues [38] investigated the reaction of arenediazonium tosylate **40** with methyl acrylate **33** using water as an effective reaction medium. The reaction was carried out at 75 °C with 1 mol % Pd(OAc)$_2$, resultantly, required alkene **41** was obtained in 96% yield (Scheme 10). The methodology covered a wide range of substrate to afford 50–97% yield under microwave irradiation.

Tsai and co-workers reported the reaction between aryl iodide **43** and diethyl allylphosphonate **42** in the mixture of 5 mol % [PdCl$_2$(NH$_3$)$_2$], *i*-Pr$_2$NH (base) and water [39]. Resultantly, the corresponding product **44** was afforded in 99% yield at 80 °C (Scheme 11). Moreover, 39–99% yield range proved the substrate scope of this methodology.

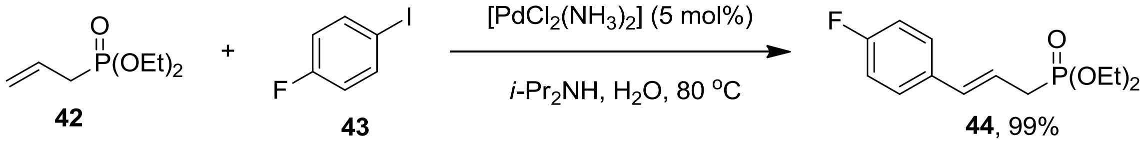
Li and co-workers [40] conducted Heck-type coupling of a wide range of alkenes with alkyl iodides under metal-free conditions. The reaction worked very well using NaO*t*-Bu and water at 50 °C for 40 min. Maximum yield (86%) was afforded by the use of UV radiations under argon atmosphere.

Ionic liquids (ILs) have received a lot of importance nowadays by stabilizing and enhancing the activity of catalytic species in metal-catalyzed reactions. Besides their broad range applications, they are fluently used in heterogeneous catalytic system as solid support. In this regard, Bian and co-workers [41] utilized poly(1-aminoethyl-3-vinylimidazolium bromide) as solid support to prepare palladium catalyst Pd/Fe$_3$O$_4$@PIL-NH$_2$ which efficiently catalyzed the Heck reaction. 95% yield of the desired alkene was obtained using triethyl amine as base under solvent-free conditions. Reaction was completed after 40 min by maintaining temperature at 120 °C. To evaluate the substrate scope, the methodology was then applied on different aryl halides and concluded that the reaction environment was well-tolerated by aryl iodides giving 34–97% yield range. While using 4-bromonitrobenzene and 3-bromoquinoline, 80% and 79% yields were obtained, respectively. However, an attempt to conduct the reaction with 4-chloronitrobenzene, trace amount of the respective product was attained.

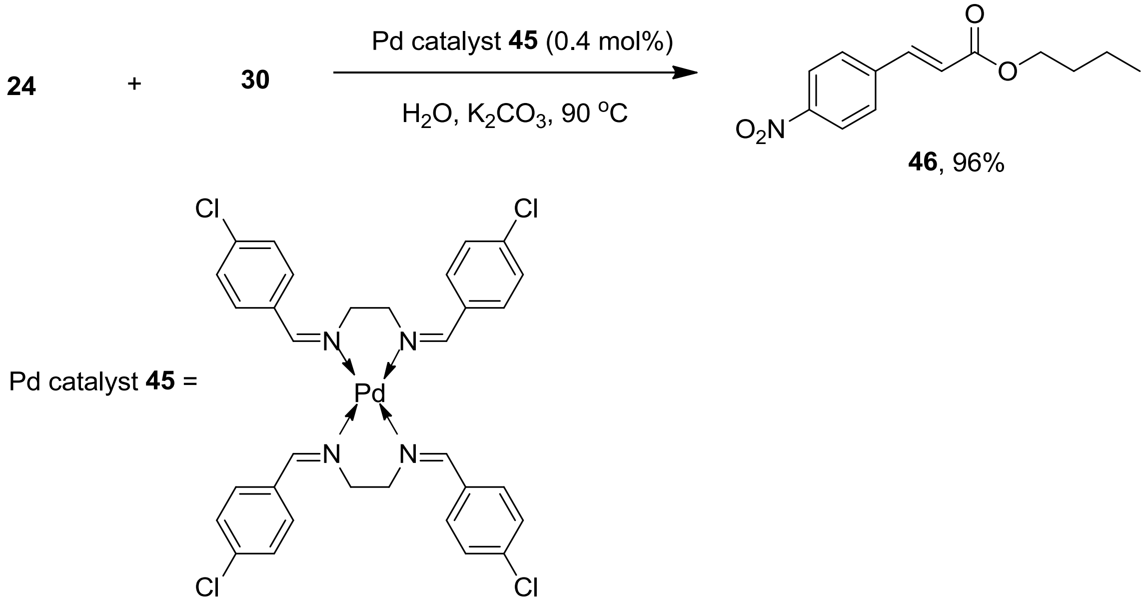
The research group of Asadi [42] synthesized a nanotetraimine Pd(0) complex **45** and proved that 0.4 mol %



Scheme 10 Matsuda-Heck reaction of diazonium salt **40** with methyl acrylate **33**



Scheme 11 Synthesis of aryl-substituted allylphosphonate **44** through palladium-catalyzed Heck reaction



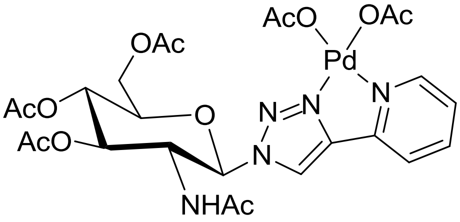
Scheme 12 Heck reaction catalyzed by palladium complex **45**

loading of the catalyst was quiet sufficient to increase the efficacy of the reaction of aryl iodide **24** with acrylate **30**. To achieve maximum yield (96%) of the desired product **46**, temperature had to be raised to 90 °C using water as green reaction media and potassium carbonate as base (Scheme 12).

Garcia and co-workers [43] studied the effect of Pd nanoparticles functionalized with laponite clay (as solid support) in microwave-assisted Mizoroki–Heck reaction. They started their investigation by treating iodobenzene with butyl acrylate using triethyl amine as base. The reaction was conducted under solvent-free condition by empowering the microwave irradiations from 5 to 10 min. Complete conversion of the starting materials was achieved at 75 W power of microwave; however, in this way, the recovery of the catalyst was decreased at lower level. A number of experiments were performed to adjust the microwave irradiation power from 25 to 75 W, and it was found that the catalyst could be reused after eight cycles with quantitative yields at 25 W.

To synthesize Pd/CuO nanoparticles through green approach, the seed extract of *Theobroma cacao* L. was mixed with $PdCl_2/CuCl_2{\cdot}2H_2O$. The reducing and stabilizing capability of the seed extract facilitated the pathway to attain the targeted nanoparticles at 50 °C within 7 min. After that the activity of these particles was tested by phosphine-free Heck reaction. The reaction gave maximum yield (98%) under aerobic condition at 110 °C using Et_3N and DMF [44].

The potential applicability of graphene to synthesize heterogeneous catalysts was checked by Ghosh and co-workers [45]. The authors described an efficient and green synthesis of palladium nanoparticle-β-cyclodextrin-graphene nanosheet (Pd@CD-GNS) and used them for Heck reaction in water. The reaction gave 60–95% yield of the corresponding products at 90 °C in sodium carbonate, TBAB and 0.05 mol% catalytic mixture.



47

Fig. 6 Triazole-based palladium catalyst **47**

D-Glucosamine-derived pyridyl-triazole@palladium catalyst **47** (Fig. 6) synthesized by Shen et al. [46] facilitated the reaction of aryl halides with olefins. For example, 62–96% yield of the required products was afforded using 0.1 mol % catalyst **47** and 3 mmol triethyl amine under solvent-free condition. Moreover, the scope for this new chemistry is expedient for synthesizing Axitinib (a marketed drug used to treat cancer of the vascular endothelial cells) from palladium-catalyzed Migita cross-coupling followed by the Heck reaction in overall 70% yield.

The use of *Pistacia atlantica kurdica* gum as solid support in the synthesis of palladium nanoparticles was examined by Veisi and colleagues [47]. The mixture of P. a. kurdica with $PdCl_2$ was refluxed in ethanolic solution at 80 °C to obtain the targeted catalyst within 2 h. After that the applicability of the catalyst was studied by the Heck reaction. The reaction mixture was prepared in water containing potassium carbonate as base and different aryl halides and *n*-butyl acrylate as starting precursors. As a result, good-to-excellent (60–98%) yield of the corresponding products was obtained only with 0.1 mol % palladium loading.

The research group of Bian [48] reported the reaction of a variety of aryl halides with acrylic acid using Fe_3O_4@PUVS-Pd **48** catalyst. The representative catalyst was prepared by immobilization of Pd(II) on Fe_3O_4@PUVS particles, and then its catalytic performance was tested by the reaction of aryl iodide **24** with acrylic acid **20**. Excellent yield (97%) using water as the only solvent and potassium carbonate as base proved the efficacy of the catalyst (Scheme 13).

The use of reducing sugar for the stabilization of palladium nanoparticles in Mizoroki–Heck reaction was examined by Camp and co-workers [49]. After a number of experiments among fructose, cellulose, sucrose and glucose, it could be inferred that glucose (4 mol%) gave the maximum yield when used with palladium acetate to catalyze the reaction of iodobenzene with methyl acrylate. Scope of this method was further explored by treating a variety of aryl iodides (having electron-donating (NH_2) and electron-withdrawing substituents (CN, CHO, NO_2)) with methyl acrylate, acrylic acid and styrene, resultantly, 23–100% yield of the corresponding products was obtained within 16 h at 100 °C using triethyl amine and 3:1 mixture of water and acetonitrile.

To develop an efficient heterogeneous catalytic system, Ghorbani-Choghamarani and colleagues [50] synthesized palladium-*S*-propyl-2-aminobenzothioate immobilized on Fe_3O_4 MNPs (Pd-ATBA-MNPs) **50** (Fig. 7) and evaluated its utility for the Mizoroki–Heck reaction. 1.64 Mol % Pd-ATBA-MNPs, polyethylene glycol (PEG) and Na_2CO_3 were the selected reagents to obtain 81–98% yield of the cross-coupling products.

Synthesis and evaluation of catalytic activity of lignin@PdNPs were described by Marulasiddeshwara and Kumar [51]. For this purpose, iodobenzene and *n*-butyl acrylate were selected as ideal substrates. To achieve 100% conversion within short time (~ 5 min), *n*-Pr_3N was used as suitable base under solvent-free condition. As a result, maximum yield (94%) was afforded by maintaining temperature at 140 °C.

Ultrasonic waves have the ability to accelerate the chemical reaction greater than the usual thermal process with high yields. As well as, environmentally friendly behavior and minimum formation of waste products are the main advantages of the ultrasound-assisted reactions. In this regard, the influence of ultrasound irradiation on the Heck reaction was studied by Rezaei [52]. As expected, the protocol gave 68–96% yield range under mild reaction conditions (K_2CO_3, H_2O, 170 W US power at 25 °C). In addition to this, PEDOT-NFs@Pd was used as green catalyst in this methodology to attain the products within short time (15–75 min). The representative catalyst was synthesized (by the polymerization reaction between EDOT (3,4-ethylenedioxythiophene) and $FeCl_3$ with subsequent addition of

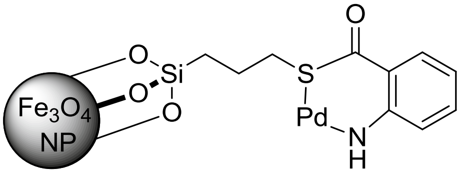


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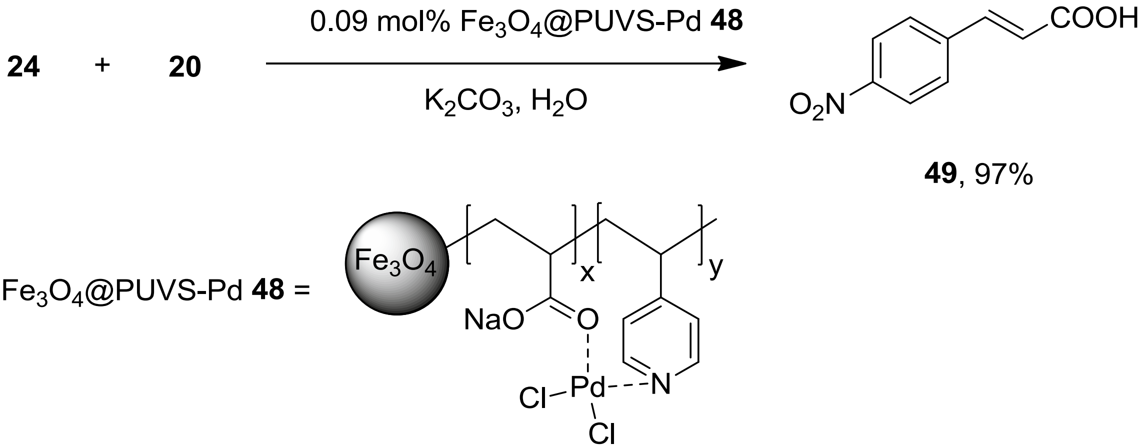
Fig. 7 Palladium-*S*-propyl-2-aminobenzothioate immobilized on Fe_3O_4 MNPs (Pd-ATBA-MNPs) **50**



Scheme 13 Fe_3O_4@poly(undecylenic acid-*co*-4-vinyl pyridine-*co*-sodium acrylate) (Fe_3O_4@PUVS)Pd **48** catalyzed reaction of aryl iodide **24** with acrylic acid **20**

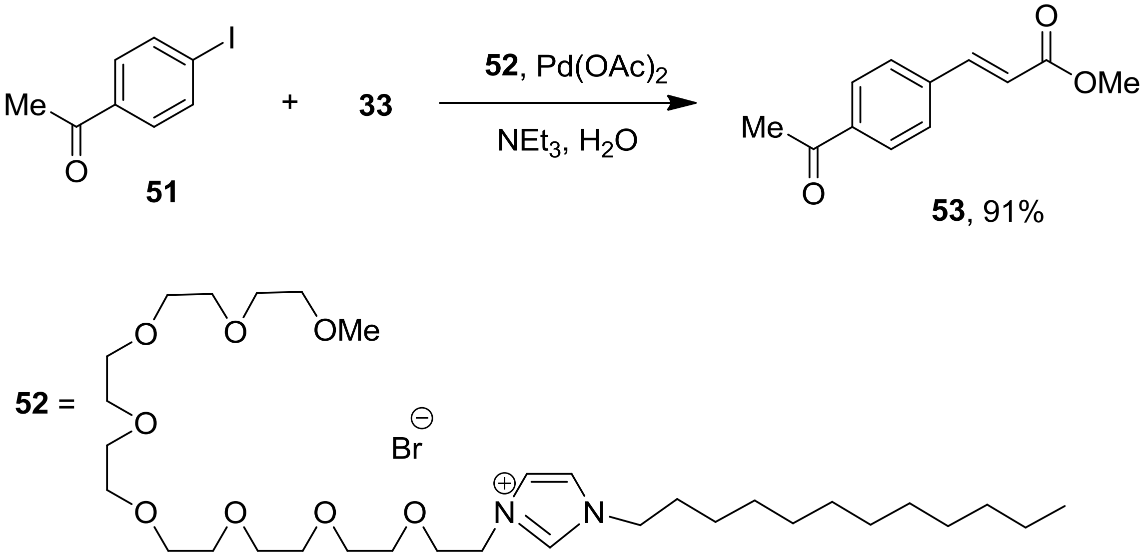
palladium(II) nitrate in this mixture) and used on a broad scale level due its unique properties such as easy recovery, reusability, high stability and minimum palladium leaching.

Increasing interest in hydrophilic-functionalized *N*-heterocyclic carbenes (NHC) due to their extensive catalytic properties has triggered considerable attention to synthesize such types of ligands under mild reaction conditions. One representative example demonstrated that the reaction of imidazole with 1-bromododecane gave 1-dodecylimidazole which was further treated with $Br(CH_2CH_2O)_8CH_3$ to obtain the surface-active NHC ligand **52**. Palladium acetate with ligand **52** efficiently catalyzes the reaction of phenyl iodide **51** with methyl acrylate **33**. The process afforded the desired product **53** in 91% yield using Et_3N in H_2O (Scheme 14) [53].

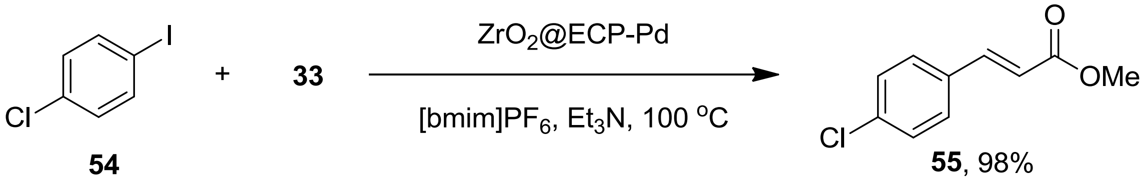
Akhlaghinia and Zarghani prepared palladium supported on phosphine-functionalized ZrO_2 nanoparticles (ZrO_2@ECP-Pd), and the efficacy of the newly synthesized catalyst was attested by Heck cross-coupling reaction using nucleophile **33** with aryl iodide **54** (Scheme 15). The reaction worked very well in the presence of triethyl amine and [bmim]PF_6 solvent which was selected by comparing the time range and eco-friendly behavior of the following solvents (DMF, EtOH, H_2O, MeCN). Temperature was maintained at 100 °C to attain 98% yield of the respective cross-coupling product **55** within 30 min [54].

Jadhav and Rode [55] reported an efficient methodology for the Mizoroki–Heck reaction under aerobic condition using triethyl amine, water and 2 mol % $Pd(PPh_3)_4$ without any additional additive. This approach has a wide substrate scope, allowing the preparation of a variety of substituted alkenes by keeping temperature at 98 °C.

Lee et al. [56] investigated mono and double Heck reaction for the formation of alkenylphosphonates under aqueous medium. Different aryl iodides and bromides were treated with dialkyl vinylphosphonates using $PdCl_2(NH_3)_2$, *i*-Pr_2NH and water. In case of aryl bromides, 35–83% yield range was obtained with 5 mol % catalyst loading at 120 °C; however, by maintaining temperature at 80 °C with 1 mol % quantity of the catalyst, aryl iodides were completely converted into corresponding products. On the other hand, for double arylation, the quantity of the aryl iodide (2.5 mmol) was increased as compared to the other coupling partner (1.0 mmol) using 5 mol% $PdCl_2(NH_3)_2$ at 80 °C.



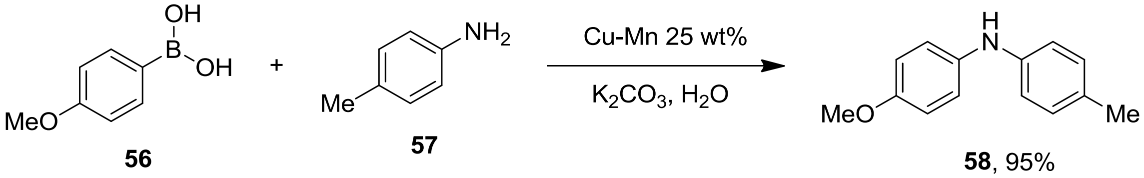
Scheme 14 Heck reaction of phenyl iodide **51** with methyl acrylate **33**



Scheme 15 Palladium-supported phosphine-functionalized ZrO_2 nanoparticles (ZrO_2@ECP-Pd) as catalyst

Table 2 Summary of the green reaction conditions in Chan–Lam cross-coupling reaction

Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Aryl boronic acids, amines	–	Cu–Mn bimetallic catalyst	–	Water	25 °C	3–4 h	70–95%	[57]
Aryl boronic acids, anilines, imidazoles	–	Copper-salen complex	–	Water/*i*-PrOH	25 °C	10–24 h	63–95%	[58]
Aryl boronic acids, aliphatic and aromatic sulfonamides	Heat	$Cu(OAc)_2 \cdot H_2O$	–	Water	Reflux	2–10 h	12–95%	[59]



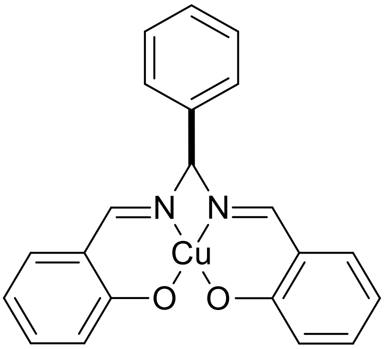
Scheme 16 Reaction of aryl boronic acid **56** with aniline **57** using 25 wt% Cu-Mn catalyst

Chan–Lam cross-coupling reaction (Table 2)

The utilization of copper-manganese spinels in metal-catalyzed reactions has become a suitable method since the last few years due to their remarkable catalytic properties. Compared to homogeneous system, the catalyst (Cu–Mn) is recyclable, reusable and escapes from expensive ligands. In this regard, the research group of Sawat [57] developed an environmentally friendly strategy for the cross-coupling of a variety of aryl boronic acids with different amines. 70–95% yield was obtained in all studied examples, and one representative model reaction is illustrated in scheme 16, affording 95% yield of the cross-coupling product **58** with 25 wt% catalyst loading.

Recently, interest in the synthesis of nitrogen-containing molecules has significantly increased due to their extensive utilization in medicinal and natural products. More efficient and broadly applicable methodologies have been developed especially for imidazoles because of their role in the construction of *N*-heterocyclic carbenes and ionic liquids. Recent advances in Chan–Lam reaction, particularly the development of chiral ligands led to the formation of *N*-arylimidazoles by the cross-coupling of imidazoles with aryl boronic acids. The conditions were optimized by using *i*-PrOH as solvent, K_2CO_3 and copper-salen complex **59** (Fig. 8) as catalyst. 63–94% yield range was obtained by maintaining the temperature at 25 °C under aerobic condition. However, by using water as solvent instead of *i*-PrOH, anilines were efficiently used as starting precursors to obtain required diaryl amines in 71–95% yield [58].

Sulfonamides, medicinally important scaffolds, are involved in the treatment of multiple diseases by inhibiting the growth of β-secretase (responsible for Alzheimer's disease), dipeptidyl peptidase IV (cause diabetes) and HCV NS5B polymerase (source of acute hepatitis). Besides antibacterial agents, they also show cytotoxic properties by controlling insulin-like growth factor receptor (IGF-IR) which is responsible for cancer. To overcome these diseases, a variety of sulfonamide derivatives have been reported yet using mild and green reaction conditions. A general procedure for the synthesis of *N*-arylated sulfonamides was recently developed in the laboratory of Nasrollahzadeh, [59] in which $Cu(OAc)_2 \cdot H_2O$ efficiently catalyzed the reaction of a variety of sulfonamides with different boronic acids (boronic acids having 4-Me, 3-CF_3, 4-MeO, 2-MeO, 2,6-di Me, 3-pyridinyl, 3-thienyl groups) via Chan–Lam cross-coupling under ligand-free condition. Both aliphatic and aromatic sulfonamides were well-tolerated by this methodology, affording maximum yield (95%) of the desired product in the presence of water and potassium carbonate.



59

Fig. 8 Copper-salen complex **59**

Table 3 Summary of the green reaction conditions in Stille cross-coupling reaction

Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Aryl halides, alkenyl halides, organotin compounds	–	$Pd(P(t\text{-}Bu)_3)_2$, DABCO	–	Water	25 °C/50–60 °C	1–24 h	39–98%	[60]
Aryl iodides and bromides, aryltributylstannanes	Heat	$PdCl_2(NH_3)_2$	Cationic 2,2′-bipyridyl ligand	Water	110 °C	3–48 h	56–98%	[61]

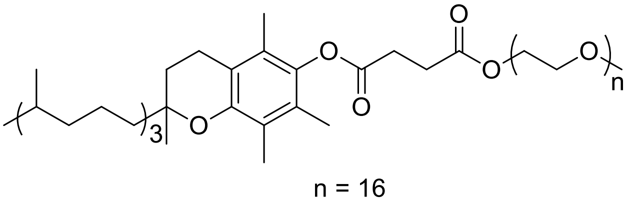


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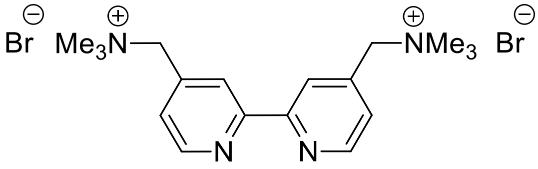
Fig. 9 Structure of TPGS-750-M (polyethanol-α-tocopherylsuccinate) **60**



61

Fig. 10 Cationic 2,2′-bipyridyl **61** as effective ligand for Stille reaction

Stille cross-coupling reaction (Table 3)

Lipshutz's team [60] has devoted their efforts to recommend TPGS-750-M (polyethanol-α-tocopherylsuccinate) **60** (Fig. 9) as a suitable surfactant for Stille cross-coupling reaction. They began their investigation by treating 3-chlorotoluene with 2-furyltributyltin at room temperature. After testing different catalysts and additives, the mixture of $Pd(P(t\text{-}Bu)_3)_2$, DABCO and NaCl proved to be quiet efficient one. The reaction was processed in an aqueous TPGS-750-M solution to afford maximum yield of the product. Moreover, these conditions satisfied a variety of substrates generally affording 39–98% yield of the required cross-coupling products.

The research group of Tsai [61] conducted palladium-catalyzed Stille cross-coupling using cationic 2,2′-bipyridyl ligand **61** (Fig. 10). The representative catalytic environment was established by mixing equimolar ratio of $PdCl_2(NH_3)_2$ with ligand **61** which was used for the coupling of aryl iodides with aryltributylstannanes. As a result, 59–98% yield range was afforded in case of aryl iodides, while aryl bromides gave 56–97% yield range in the given condition ($NaHCO_3$, H_2O, 110 °C). Besides good yield range, mild reaction conditions and easy separation of catalyst from required product makes this methodology more effective toward C–C bond formation reactions.

Suzuki cross-coupling reaction (Table 4)

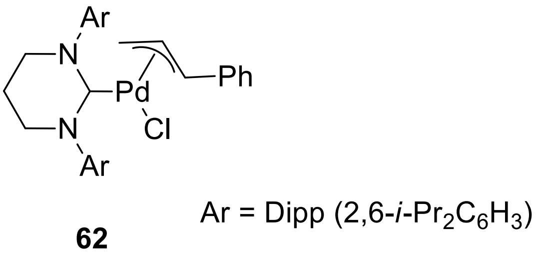
Kolychev et al. [62] prepared *N*-heterocyclic carbene (NHC) complex of palladium ((6-Dipp)Pd(cinn)Cl (cinn = 3-phenylallyl)) **62** (Fig. 11) and used it as catalyst for Suzuki reaction of heteroaryl halides and aryl boronic acids. They have described an efficient method of the Suzuki coupling reaction employing optimized reagents such as sodium bicarbonate, TBAB, H_2O water with 0.5 mol% quantity of the catalyst to obtain 39–99% yield of the respective cross-coupling products under aerobic condition. The highlights of this catalytic system include air and moisture stability with easy availability and high catalytic activity.

Garg and colleagues [63] have reported a coupling of heterocyclic halides with aryl boronic acids in the presence of 5–10 mol% $NiCl_2(PCy_3)_2$ and K_3PO_4. The authors used 2-Me-THF and *t*-amyl alcohol as solvents and observed their effect on the required yield range. It was found that 35–100% yield range was attained in case of *t*-amyl alcohol, while 2-Me-THF gave 49–100% yield range.

Sartori et al. [64] have achieved ligand-free Na_2PdCl_4-catalyzed cross-coupling reactions of 5-iodo-2′-deoxyuridine with different aryl boronic acids in the presence of potassium hydroxide as base and water as solvent. As a result, a variety of 5-aryl-2′-deoxyuridines were prepared in 17–80% yield by using 0.1 mol % quantity of the catalyst, while 0.05 mol % catalyst loading afforded 13–86% yield range. Veerakumar et al. [65] achieved palladium-catalyzed cross-coupling of aryl halides (having CH_3, OCH_3, $COCH_3$

Table 4 Summary of the green reaction conditions in Suzuki–Miyaura cross-coupling reaction

Substrates	Energy supply	Catalyst	Ligand	Solvent	Temp	Time	Yield	References
Heteroaryl chlorides and bromides, aryl boronic acids	Heat	Diaminocarbene palladium complex ((6-Dipp)Pd(cinn)Cl (cinn = 3-phenylallyl))	–	Water	Reflux	1–3 h	39–99%	[62]
		$NiCl_2(PCy_3)_2$						
Heterocyclic halides, aryl boronic acids	Heat	Na_2PdCl_4	–	2-Me-THF and *t*-amyl alcohol	100 or 120 °C	12 h	35–100%	[63]
				Water				
5-Iodo-2′-deoxyuridine, aryl boronic acids	Heat		–		100 °C	0.25–24 h	13–86%	[64]
Aryl halides, aryl boronic acids	Heat	Silica-supported PEI-capped nanopalladium ($Pd/NH_2–SiO_2$)	–	Water, DMF	60–110 °C	45 min–6 h	70–96%	[65]
Aryl chlorides, aryl boronic acids	–	Zwitterionic palladium complex	–	4/1 Mixture of 1,4-dioxane and water	25 °C	2–12 h	33–> 99%	[66]
Aryl halides, aryl boronic acids	Heat	Aminophosphine palladium(0) complex supported on ZrO_2 nanoparticles (ZrO_2@$AEPH_2$-PPh_2-Pd(0))	–	Water	80 °C	20 min–24 h	30–95%	[67]

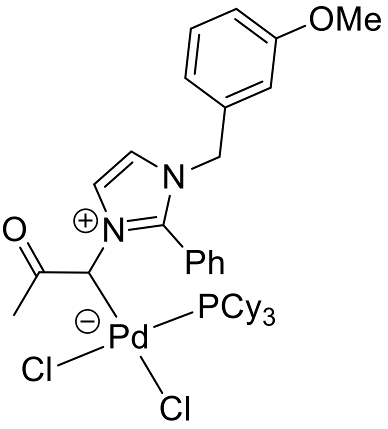


62

Fig. 11 NHC palladium complex **62** for Suzuki cross-coupling

and NO_2 groups) with aryl boronic acids using TBAB as phase-transfer catalyst in water with as low as 0.05 mol% $Pd/NH_2–SiO_2$ catalyst. Resultantly, 82–96% yield range was observed for aryl iodides and 70–90% yield range for aryl bromides.

Lee and co-workers [66] have used zwitterionic palladium complex **63** (Fig. 12) as a catalyst for Suzuki cross-coupling of aryl chlorides with aryl boronic acids in the presence of potassium hydroxide in 4/1 mixture of 1,4-dioxane and water as green reaction media. The aforementioned catalyst **63** has been prepared first, by the reaction of chloroacetone and imidazole derivative; resultantly, a monodentate ligand was obtained which coordinated with $PdCl_2$ to give the required catalyst.



63

Fig. 12 Zwitterionic palladium complex **63**

Razavi et al. [67] have described a highly effective direct coupling of aryl halides with aryl boronic acids catalyzed by ZrO_2@$AEPH_2$-PPh_2-Pd(0) complex. (Aminophosphine palladium(0) complex supported on ZrO_2 nanoparticles.) Temperature was maintained at 80 °C to acquire 30–95% yield range. Substrate scope was evaluated by taking a variety of aryl iodides, bromides and chlorides having electron-donating and electron-withdrawing groups. Resultantly, aryl iodides and bromides gave 80–95% and 70–95% yield ranges, respectively. On the other hand, chlorobenzene and 4-chlorobenzaldehyde afforded 30% and 45% yields, respectively, and trace amount of the product was observed in case of 4-chloroaniline.

Conclusion/future perspective

Metal-catalyzed reactions (especially, Suzuki–Miyaura, Heck, Stille and Chan–Lam couplings) play a vital role in carbon–carbon bond formation. However, to conduct these reactions under environmentally friendly conditions is of great interest. In order to find green reaction conditions, organic researchers have contributed a lot in this field. This review article outlines and highlights the importance of green reaction conditions such as water, microwave irradiations and solvent-free protocols. In spite of all the efforts brought forward by various research groups in developing green conditions for aforementioned cross-coupling reactions, the authors are of the view that synthetic applications of cross-coupling reactions toward biologically relevant (Drugs, natural products, etc.) is a less investigated area and a lot of research can be done in this field.

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