



# Multi-functionalized ionic liquid with in situ-generated palladium nanoparticles for Suzuki, Heck coupling reaction: a comparison with deep eutectic solvents

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## Abstract

A new catalytic system for Suzuki and Heck coupling has been developed from multi-functionalized task specific ionic liquid (TSIL) and in situ formed palladium nanoparticles (PdNps). The generated PdNPs were characterized by UV–Visible spectroscopy and transmission electron microscopy (TEM) analysis. These PdNPs have found size below 10 nm and exhibited a excellent catalytic activity in the cross-coupling of aryl halide without using external phosphine ligand. Along with electron deficient olefins, electron rich olefins were also undergo smooth reaction giving excellent yield. The results obtained in ionic liquid are compared with results obtained in deep eutectic solvents. Progress of reaction was found very smooth in ionic liquid rather than in deep eutectic solvents. The aqueous system containing ionic liquid along with PdNPs was recycled for seven times, without any significant loss.

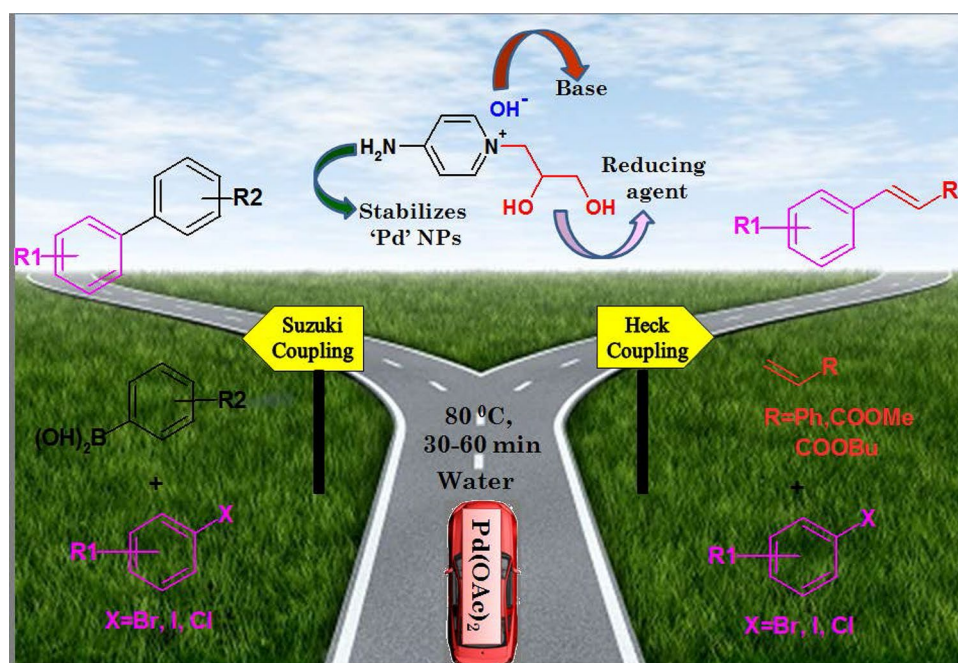
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## Graphical abstract



**Keywords** Multi-functionalized ionic liquid · Suzuki–Miyaura · Heck–Mizoroki · Palladium nanoparticles · Deep eutectic solvents · Transmission electron microscopy

## Introduction

The utilization of metal nanoparticles (MNPs) is of gigantic significance in the diverse field including energy conversion and storage, chemical manufacturing, biological applications, and environmental technology [1–4]. Looking in to these diverse applications of MNPs, we can state that it has a very potential and intense future. Coming towards its efficiency in organic reactions as a catalyst, recently scientific experts are having significant interest in the terms of green chemistry because of their tender character, effortlessness of preparation and availability of large surface area [5–7]. Presently many active scientists are working on immobilization MNPs in ionic liquids to prove its synergetic activity in case of hydrogenation, oxidation, acetylation, and C–C coupling reactions under both single-phase and multiphase conditions [8–11]. Alongside this there are some interesting reviews of MNPs considering its preparation, characterization, and use as catalyst (soluble or insoluble MNPs) in ILs [12–14]. In the many of the synthesis of MNPs in ionic liquids, the functionalized ionic liquids which are also called as task specific ionic liquids (TSILs) used as both ligands and supporting for immobilization and recycling of MNPs [15, 16]. The reason is because functionalized ILs can provide stronger stabilization for the MNPs without losing their catalytic properties;

in addition ILs possesses several distinctive properties, such as negligible vapor pressure, no miscibility with non-polar solvents, and reasonable thermal and chemical stability with excellent electrical conductivity [17–20]. Owing to these exceptional properties, more attention has been focused on the synthesis of new ILs with functional groups, so-called TSILs which will act as reducing as well as stabilizing agent for MNPs.

In all above discussion ILs are used as recyclable medium, besides this recently Deep Eutectic Solvents (DES) are also entering in this era. These DES plays a similar role as like that of ILs [21, 22]. These can also be recycled many times without losing its activity and main advantage of using is their biodegradable nature. Some of the ILs are not biodegradable but most of the DES has biodegradability nature [23–25]. So research communities are focusing to continue the research in the same. The use of DES in the field of coupling reactions is still under primary level because of stability of palladium catalyst used during the reaction. There are few research articles which they have focused in using DES only as a reaction medium for the palladium catalyzed reactions [26–28]. Some of research group have utilized carbohydrate based DES as a reaction medium, e.g., D-mannose-urea, L-Carnitine-urea [29, 30]. But these all earlier reports possess drawbacks such as use

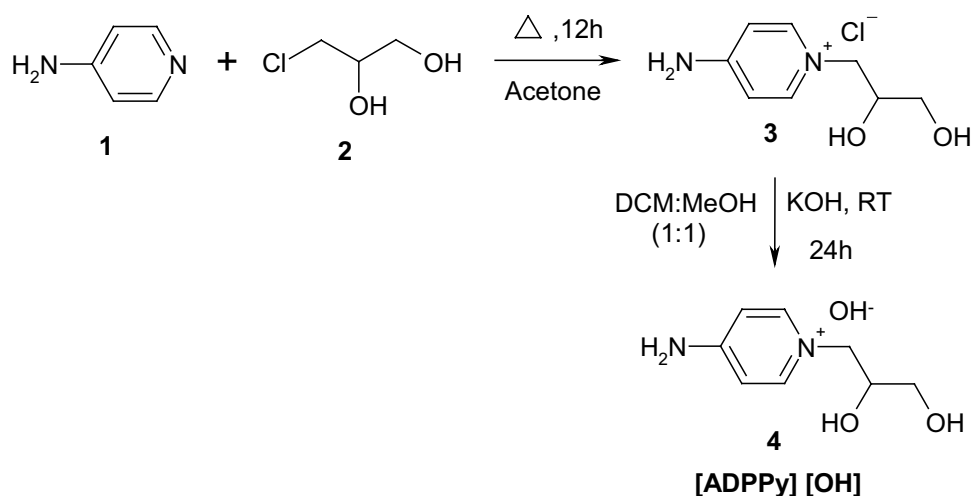
of external ligand, external reducing agent, and external base and long reaction time to carry out very effective coupling reaction. Research articles also failed to reproduce the results obtained with traditional Palladium catalysts and not stated effective recycling method. Hence here ILs provides all the solution to these questions. In the present manuscript we have designed such IL which will act as reducing, stabilizing agent and also act as a base for palladium catalyzed Suzuki, Heck coupling reaction.

In continuation with our earlier work in the field of IL, [31, 32] herein we disclose a novel protocol for the Suzuki and Heck coupling reaction using synthesized multi-functionalized ionic liquid in aqueous conditions. The desired carbon–carbon bond formation proceeded under mild conditions with high efficiency and good functional group tolerance. Results obtained in different ILs are also compared with the results obtained of reaction in DES.

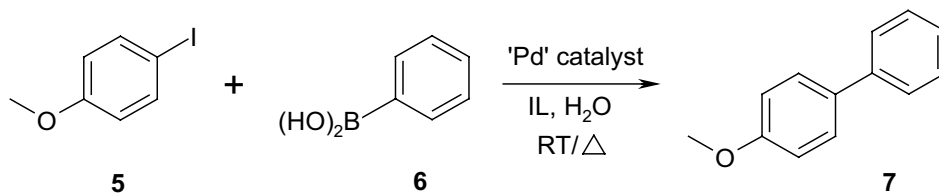
## Results and discussion

Initially we have synthesized a multi-functionalized ionic liquid. In the first step quaternisation of 4-amino pyridine and 3-chloro-1,2-propanediol in acetone at reflux temperature was carried out and increased the basicity of the ionic liquid by incorporating  $\text{OH}^-$  on reaction with potassium hydroxide (Scheme 1). The introduction of diol functionality has some added advantages over other non hydroxyl ILs.

**Scheme 1** Synthesis of multi-functionalized ionic liquid



**Scheme 2** Typical Suzuki–Miyaura coupling



Literature investigation reveals that the hydroxyl-functionalized ILs possess high solvent polarities, high dielectric constants than non-functionalized ILs, higher hydrogen-bond acidity which increases the hydrophilicity of the ILs [33–35]. The Dyson group [36] reported that, hydroxyl-functionalized ILs act as reducing agent and formed highly stable, small PdNPs with a narrow size distribution. Hence due to these advantages of the hydroxyl group we targeted to synthesis such ionic liquid which will fulfill all requirements for carrying out coupling reaction smoothly. The formation of IL was confirmed by characterizing its  $^1\text{H}$  and  $^{13}\text{C}$  NMR, and we delighted that spectra confirmed the formation of desired multifunctional IL.

## Suzuki–Miyaura coupling

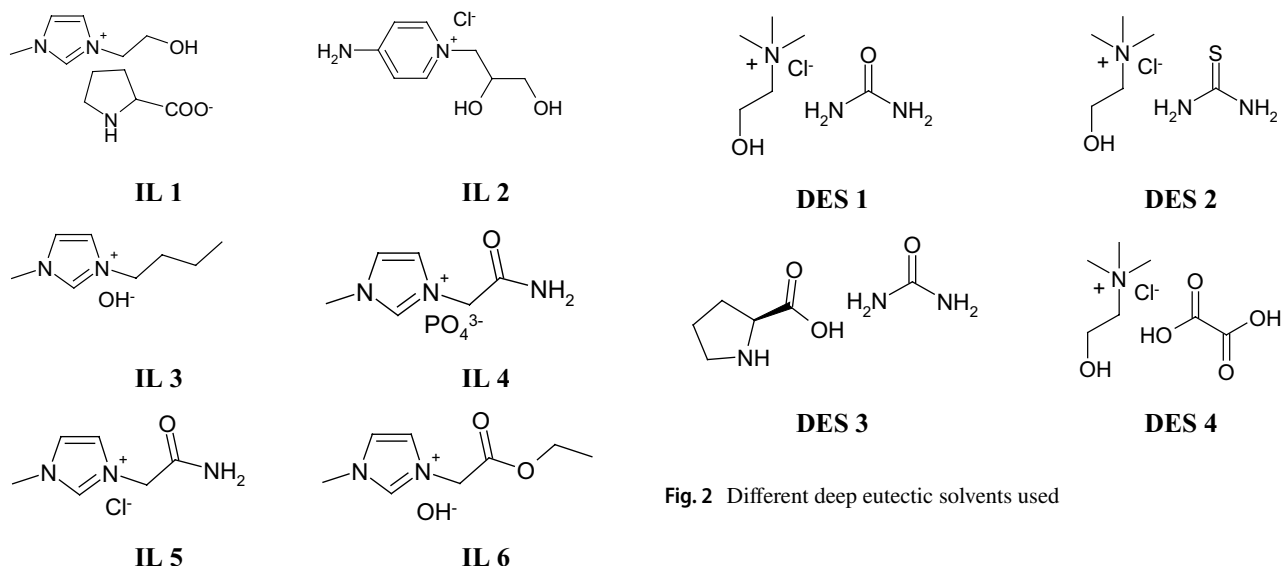
As we all know, water is cheap, readily available, nontoxic, non-flammable and environment friendly solvent. Furthermore, water can provide several other advantages, such as inertness against oxidation and reduction, high polarity and high solution ability [37, 38]. In the present study we have used water as a solvent and different ILs for carrying out Suzuki coupling reaction. We explored effect of synthesized ILs with model reaction of 4-iodo anisole, phenyl boronic acid, and different palladium sources in water (Scheme 2). When reaction was carried out at room temperature after prolonged time we observed inferior results, but when the same carried out at 80 °C giving very promising results. To

**Table 1** Optimization of the reaction conditions

Entry	Catalyst (2 mol%)	Base (mol %)	Temp. (°C)	Time (h)	Yield (%) <sup>a</sup>
1	Pd(PPh <sub>3</sub> ) <sub>4</sub>	[ADPPy][OH] (20)	RT	7	20
2	Pd(PPh <sub>3</sub> ) <sub>4</sub>	[ADPPy][OH] (20)	80	5	60
3	Pd <sub>2</sub> (dba) <sub>3</sub>	[ADPPy][OH] (20)	80	7	40
4	Pd/C	[ADPPy][OH] (20)	80	8	10
5	Pd(OAc) <sub>2</sub>	[ADPPy][OH] (20)	RT	4	45
6	Pd(OAc) <sub>2</sub>	[ADPPy][OH] (20)	80	1	99
7	Pd(OAc) <sub>2</sub>	[ADPPy][OH] (30)	80	1	99
8	PdCl <sub>2</sub>	[ADPPy][OH] (30)	80	1	90
9	Pd(OAc) <sub>2</sub>	IL 2 (20)	80	8	35
10	Pd(OAc) <sub>2</sub>	IL 1 (20)	80	1.5	60
11	Pd(OAc) <sub>2</sub>	IL 3 (20)	80	1	89
12	Pd(OAc) <sub>2</sub>	IL 4 (20)	80	2	75
13	Pd(OAc) <sub>2</sub>	IL 5 (20)	80	5	30
14	Pd(OAc) <sub>2</sub>	IL 6 (20)	80	1	85

Reaction conditions: 4-iodoanisole (1 mmol), phenylboronic acid (1.1 mmol), water (5 mL)

<sup>a</sup>Isolated yields

**Fig. 1** Different ionic liquids (ILs) studied

carry out reaction with ILs other than [ADPPy][OH] we have to use external base or any stabilizing agent for catalyst. But only a mixture of IL [ADPPy][OH] and water gave us excellent results. Achievements of all these preliminary survey are shown in Table 1.

Reaction with other ILs also studied, ILs containing basic functionality got us excellent results. All results are summarized in Table 1. All the ILs are synthesized (Fig. 1) using earlier reported procedures [39–43]. Achieving success in IL: water medium we carried out similar reaction in diverse Deep Eutectic Solvents (DES) (Fig. 2). Nowadays these DES are considered as excellent reaction medium for carrying

**Fig. 2** Different deep eutectic solvents used

out organic reactions than ILs. So we focused to carry out reaction in these with similar model reactants. As discussed earlier we didn't observe any promising results with DES. All results are summarized in Table 2. To all these reactions require external phosphine ligand and base for completion of reaction. So here our synthesized IL looks to be better than DES. The DES used during this study are synthesized using earlier reported procedures [44, 45].

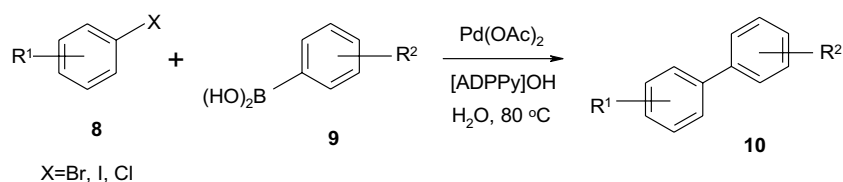
When we used Pd(OAc)<sub>2</sub> (2 mol%), IL [ADPPy][OH] (20 mol%), and heating at 80 °C, got 99% of desired product (Entry 6, Table 1). Having these optimized reaction conditions in hand, we next proceeded to examine the scope and limitation of catalytic system in the Suzuki cross-coupling reaction of various types of iodo-, bromo-, and chloro aryl derivatives and aryl boronic acids (Table 3). In general, all of the coupling products were

**Table 2** Suzuki coupling reaction in deep eutectic solvent

Sr. No.	Catalyst (2 mol%)	Base (2 mmol)	Ligand (5 mol%)	Solvent	Temp.	Time in h	Yield % <sup>a</sup>
1	Pd(OAc) <sub>2</sub>	NaOH	–	DES 1	RT	6	55
2	Pd(OAc) <sub>2</sub>	NaOH	Triphenyl phosphine	DES 1	RT	3	80
3	Pd(OAc) <sub>2</sub>	Na <sub>2</sub> CO <sub>3</sub>	Triphenyl phosphine	DES 1	RT	3	75
4	Pd(OAc) <sub>2</sub>	Triethyl amine	Xanthphos	DES 1	RT	3	79
5	Pd(OAc) <sub>2</sub>	Triethyl amine	Xphos	DES 1	RT	3	76
6	Pd(OAc) <sub>2</sub>	Triethyl amine	Triphenyl phosphine	DES 1	80 °C	1.5	95
7	Pd(OAc) <sub>2</sub>	Triethyl amine	Triphenyl phosphine	DES 2	80 °C	2	92
8	Pd(OAc) <sub>2</sub>	Triethyl amine	Triphenyl phosphine	DES 3	80 °C	2	94
9	Pd(OAc) <sub>2</sub>	Triethyl amine	Triphenyl phosphine	DES 4	80 °C	5	50

Reaction conditions: 4-Iodoanisole (1 mmol), phenylboronic acid (1.1 mmol), water (5 mL)

<sup>a</sup>Isolated yields

**Table 3** Reactions of aryl halides and phenyl boronic acids under the optimized reaction conditions

Entry	Aryl halide (8)	Boronic acid (9)	Time, h	Yield (%) <sup>a</sup>	TON	TOF
10a	R <sup>1</sup> =H, X=I	R <sup>2</sup> =H	1	96	48	48
10b	R <sup>1</sup> =H, X=Cl	R <sup>2</sup> =4-OMe	2	80	40	20
10c	R <sup>1</sup> =H, X=Br	R <sup>2</sup> =4-Me	1	95	47.5	47.5
10d	R <sup>1</sup> =4-Me, X=Br	R <sup>2</sup> =H	1	92	46	46
10e	R <sup>1</sup> =4-Me, X=I	R <sup>2</sup> =4-OMe	1.5	89	44.5	29.66
10f	R <sup>1</sup> =4-OMe, X=I	R <sup>2</sup> =H	1.5	88	44	29.33
10g	R <sup>1</sup> =4-OMe, X=I	R <sup>2</sup> =4-OMe	1	85	42.5	42.5
10h	R <sup>1</sup> =4-CN, X=Br	R <sup>2</sup> =H	1.5	84	42	28
10i	R <sup>1</sup> =4-NO <sub>2</sub> , X=I	R <sup>2</sup> =H	2	87	43.5	21.75
10j	R <sup>1</sup> =4-COMe, X=Br	R <sup>2</sup> =H	1.5	90	45	30
10k	R <sup>1</sup> =4-OMe, X=Br	R <sup>2</sup> =4-Me	1	87	43.5	43.5
10l	1-Naphthyl Iodie	R <sup>2</sup> =H	2	80	40	20

Reaction conditions: aryl halide (1 mmol), boronic acid (1.1 mmol), Pd(OAc)<sub>2</sub> (2 mol%), [ADPPy][OH] (20 mol%), Water (5 mL) at 80 °C

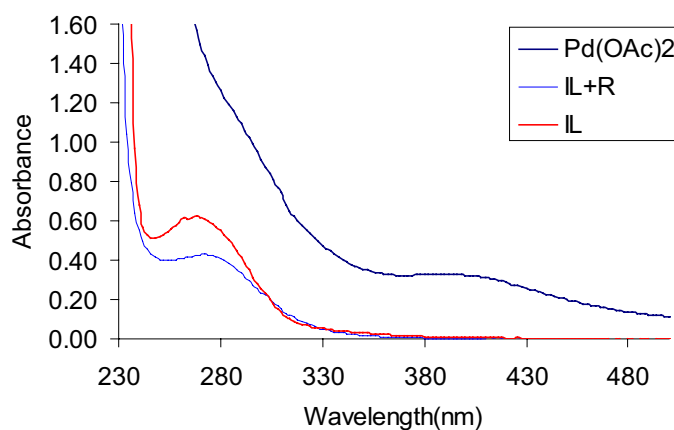
<sup>a</sup>Isolated yield

obtained in good to excellent yields. A variety of electron donating, electron withdrawing aryl halides, different substituted phenyl boronic acids were then explored as substrates and the results are listed in Table 3. We found that aryl bromides and iodides reacted with phenyl boronic acid efficiently, giving the good to excellent yields. Remarkably, no product arising from the homocoupling of aryl boronic acids or product from hydrolytic deboration was detected in these substrates. The turnover frequency and turnover number of the reaction (TON = Mole of product/IL mole; TOF = TON/time in h)

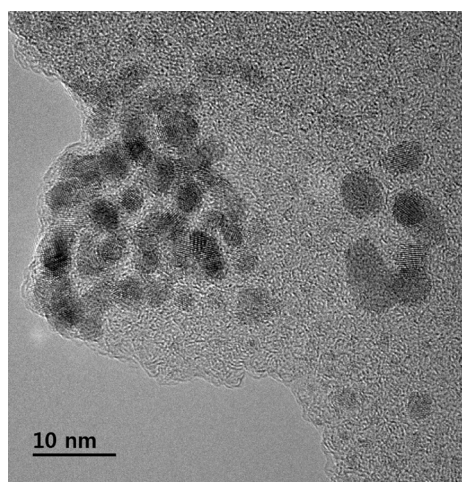
also calculated and we delight to report here reaction fits well in these calculations.

During the progress of the reaction we observed change in color of reaction from yellow to dark brownish black. Hence there might be formation of Pd-NPs in situ during the completion of reaction. After the completion of reaction, we extracted the reaction mixture by diethyl ether to separate the synthesized biaryls. Then the aqueous phase have been analyzed by recording UV–Vis spectrum in acetone medium and compared the same with that of Pd(OAc)<sub>2</sub> (Fig. 3a). The absorption at 405 nm due to Pd(OAc)<sub>2</sub> disappeared from

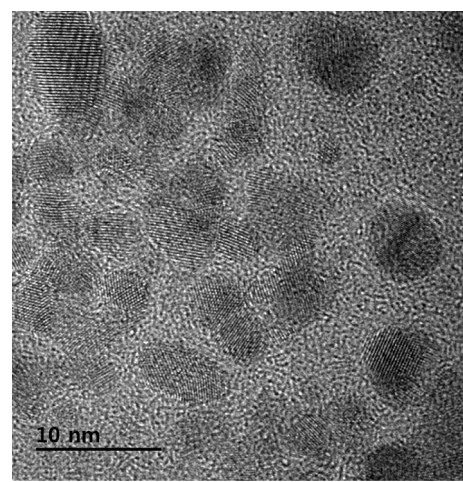
**Fig. 3** **a** UV–Vis spectra of reaction mixture after completion of reaction. **b, c** TEM analysis of separated Pd-NPs



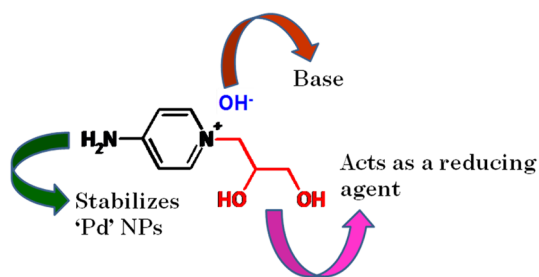
(a)



(b)



(c)



**Fig. 4** Versatility of ionic liquid

the reaction mixture due to the formation of Pd-NPs. These obtained Pd-NPs is characterized by transmission electron microscopy (TEM) analysis as shown in Fig. 3b, c, and it was found that there is formation of Pd-NPs of around size 10 nm.

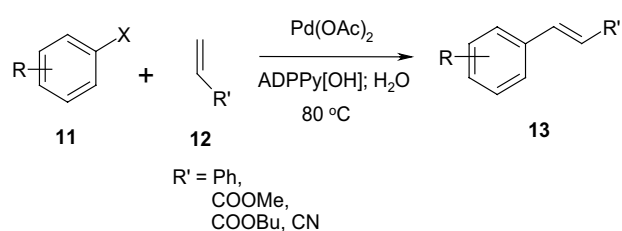
The ionic liquid used during the advancement of reaction performs many roles (Fig. 4). The anion  $\text{OH}^-$  acts as a base required for Suzuki coupling reaction. As discussed above

regarding hydroxyl functionality of the ionic liquid, it acts as reducing agent for formation of Pd-NPs in situ. The  $-\text{NH}_2$  group from cation act as well stabilizing agent for formed nanoparticles.

To verify the formation of Pd-NPs and successful completion of reaction, we performed the mercury poisoning test [46] with  $\text{Hg}(0)$  based on the deactivation of metal via amalgam formation. The addition of  $\text{Hg}(0)$  to the Suzuki reaction with Pd-NPs showed a complete inhibition of the catalytic activity.

### Heck-Mizoroki coupling

After initial success in Suzuki–Miyaura coupling, we next focused our attention to carry out Heck coupling under the similar optimized reaction conditions (Scheme 3). We are delighted to report here that the same catalytic system is very much effective in Heck-Mizoroki coupling with aryl halide and electron deficient olefins to absolutely giving E-isomer as a major product (Table 4). The formation of

**Scheme 3** Heck–Mizoroki coupling

E-isomer was confirmed by  $^1\text{H}$  NMR analysis of the product as it shows coupling constant above 8 Hz. Reaction worked well with both electron donating as well as electron withdrawing aryl halides. All the products are isolated from reaction mixture by column chromatography using silica (mesh size 100:200) as stationary phase and ethyl acetate:hexane (1:9) as mobile phase.

Reaction progressed much better with electron deficient olefins hence we tried the Heck arylation of electron

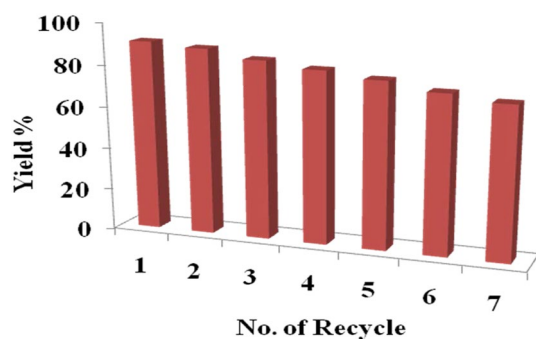
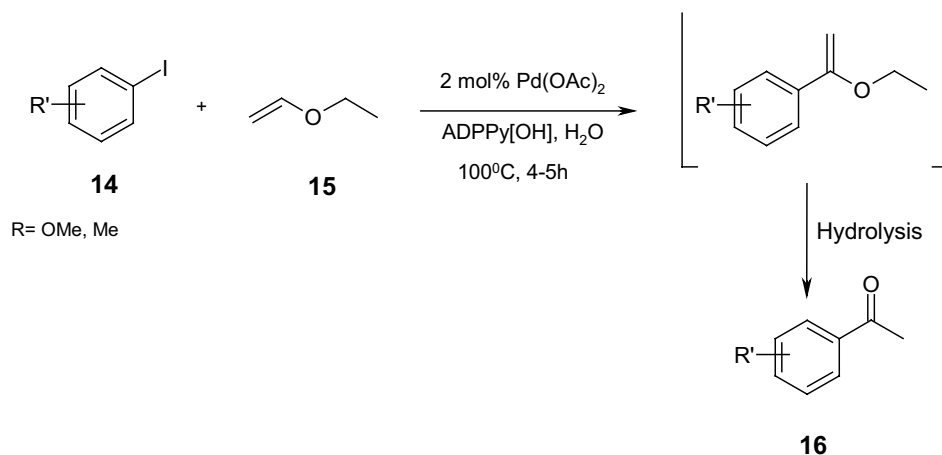
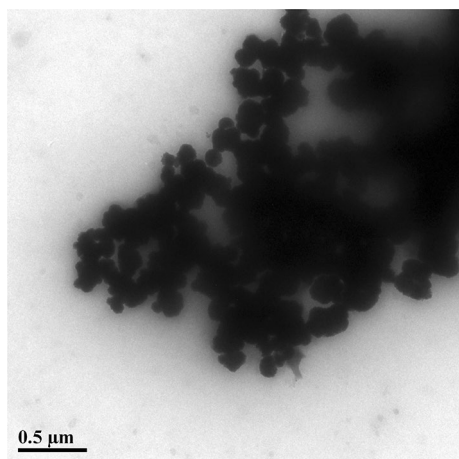
donating olefins *viz* ethyl vinyl ether with aryl halides (Entry 13 m, **13n** Table 4) under optimized reaction conditions (Scheme 4). After hydrolysis, we observed formation of corresponding arylmethylketones with 100%  $\alpha$ -regioselectivity and the product was characterized by  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR.

It is one of the principal of Green chemistry, that catalyst used should be reused to carry out number of reactions with excellent efficiency. Hence in this standpoint, recycling of catalyst is highly warranted. We carried out the recyclability study of ionic liquid-PdNps catalytic system for the model reaction. For reusability study we choose to study reaction between 4-iodo anisole and phenylboronic acid under the optimized reaction conditions. Grati-fyingly, it was observed that the catalytic system can be reused effectively for 7 times without any significant loss of activity providing excellent yields of products (Fig. 5). After 7th run we analyzed the Pd-NPs and we found some aggregation of Pd-NPs (Fig. 6).

**Table 4** Reactions of aryl halides and olefins under the optimized reaction conditions

Entry	Aryl halide (11)	Olefin (12)	Time h	Yield <sup>a*</sup> %	TON	TOF
13a	R = H, X = Br	R' = Ph	2	98	49	24.5
13b	R = 4-COMe, X = Br	R' = Ph	3	95	47.5	15.83
13c	R = 4-NO <sub>2</sub> , X = I	R' = Ph	3	92	46	15.33
13d	R = 4-NO <sub>2</sub> , X = I	R' = COOMe	4	90	45	11.25
13e	R = H, X = Cl	R' = COOMe	8	75	37.5	4.68
13f	R = 4-COMe, X = Cl	R' = COOMe	8	70	35	4.37
13g	R = 4-OMe, X = I	R' = COOMe	3	87	43.5	14.5
13h	R = 1-Naphthyl, X = I	R' = COOMe	3	86	43	14.33
13i	R = 4-COMe, X = Cl	R' = CN	9	65	32.5	3.61
13j	R = H, X = Cl	R' = CN	8	70	35	4.37
13k	R 4-CN, X = Br	R' = COOBu	3	90	45	15
13l	R = H, X = I	R' = COOBu	2	95	47.5	23.75
13m			4	80 <sup>a</sup>	40	10
13n			4	78 <sup>a</sup>	39	9.75

Reaction conditions: Aryl halide (1 mmol), styrene/acrylate/acrylonitrile (1.1 mmol), Pd(OAc)<sub>2</sub> (2 mol %), ADPPy[OH] (20 mol%), temp.: 100 °C; <sup>a</sup>:100% regioselectivity (isolated yields), \*Isolated Yield

**Scheme 4** Heck arylation of ethylvinylether with aryl halides**Fig. 5** Reusability of catalytic system (ionic liquid and Pd-NPs)**Fig. 6** TEM analysis of Pd-NPs after 7th run

## Conclusions

In conclusion, we have developed an eco-benign method for Suzuki–Miyaura and Heck–Mizoroki coupling by

employing an IL-PdNPs catalytic system. In situ generation of PdNPs is assisted by multi-functionalized ionic liquid which also reduces and stabilizes them. The catalytic system can be reused at least for 7 times without any significant loss in catalytic activity which is one of the green aspects of method. Novelty of the protocol is exploration of novel efficient catalytic system for coupling reaction along with additional features viz. operational simplicity, reusability of the catalytic system, shorter reaction time, avoidance of conventional volatile organic solvents, 100% atom economy, easy work up procedure, etc. Thus we believe that our findings indicate significant gains toward achieving ideal transformations.

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