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In-situ-generated palladium nanoparticles in novel ionic liquid: an efficient catalytic system for Heck–Matsuda coupling

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Abstract A green, convenient, ecological and recyclable method comprising dual functionalized, task-specific, ionic liquid (IL)-triggered, in situ-generated Pd nanoparticles (NPs) and their catalytic application for Heck–Matsuda coupling of olefins is described. Both arenediazonium tetrafluoroborate and silica sulphate salts are coupled with olefins under ligand-free and aerobic conditions at ambient temperature furnishing excellent yields of products. The Ionic liquid used acts as a reducing as well as stabilizing agent for in situ-generated Pd NPs. The formed NPs were characterized by transmission electron microscopy (TEM) analysis, having a size below 50 nm, and exhibited high catalytic activity. The catalytic system can be reused for eight times effectively without any significant loss of activity. The method was found to be highly stereo-specific, giving exclusively the 'E' isomer.
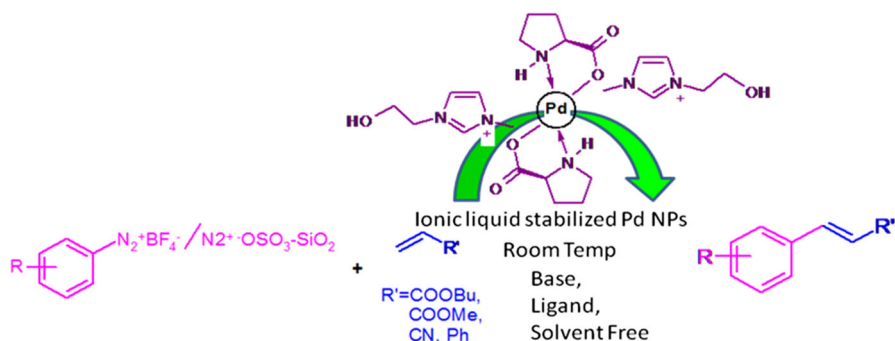
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Graphical Abstract

Ionic liquid stabilized Pd NPs

Room Temp
Base,
Ligand,
Solvent Free

R'=COOBu,
COOMe,
CN, Ph

Keywords Heck–Matsuda · Stereospecific · Nanoparticles · Task-specific IL

Introduction

The attention towards room temperature task-specific Ionic Liquids (TSILs) has appreciably increased over the last decade as environmental concerns originated from usual synthetic procedures inspired the researchers to investigate alternatives to conventional organic solvents [1, 2]. Some unique characteristics of TSILs such as adjustable physico-chemical properties, negligible vapor pressure and high polarity merged with hydrophobicity provide good solubility for a wide range of organic, inorganic and organometallic compounds [3–6]. ILs have been found in numerous applications not only as environmentally benign reaction media, but also as catalysts and reagents [7].

Furthermore, the highly polar nature of ILs in biphasic system ensures immiscibility with many organic solvents or in certain cases, also with aqueous media, offering unique opportunities for recycling and phase-switching techniques [8–10]. On the catalysis front, many reactions ranging from transition metal-mediated processes to Friedel–Crafts reactions, C–C bond-forming condensations, and cycloadditions are dramatically accelerated in ILs. Because of these particular features, ILs are very attractive liquid media to carry out a plethora of organic transformations. In this perspective, several review articles in the field of catalysis have captured much attention on the utility of this media [11, 12]. The first experiment in IL catalysis was carried out a way back more than 30 years ago and thereafter the field has experienced a fabulous growth, especially over the last decade [13].

The palladium-catalyzed C–C coupling of olefins and aryl or alkenyl halides, universally referred to as the "Heck–Mizoroki coupling", and has received immense attention in the past decade because it is a selective method for formation of new C–C bonds in a single operational step [14, 15]. Nowadays, instead of using aryl or alkenyl halides, diazonium salts are being widely used as precursors to carry out coupling reactions including Heck–Matsuda coupling [16–30]. However,

homogeneous catalysts and non-volatile solvents have been of limited use, mainly because of the difficulty of separation of products from the reaction mass that in turn may lead to economical/environmental problems especially in case of expensive or toxic metal catalysts. Therefore, the development of greener approaches is highly essential which will offer recovery of solvent as well as catalyst.

Kaufmann et al. [31] for the first time used ILs (tetraalkylammonium and tetraalkylphosphonium bromides) as reaction media for the palladium-catalyzed Heck coupling, giving moderate to high yields of product. In such coupling reactions, the IL is believed to stabilize the palladium catalyst, and no precipitation of palladium was observed even after complete conversion of the aromatic halide to the product.

It is well known that transition metal nanoparticles (MNPs) are utilized to carry out coupling reactions [32–34] due to their superiority over traditional metal catalytic systems with respect to controllable size, more degrees of freedom and small surface with active sites accessible to reactants [35, 36].

Although different catalytic systems consisting of other than IL systems and MNPs are reported in literature [37, 38], a recently combined system of TSILs and a Pd source (especially palladium NPs) is being extensively employed to efficiently catalyze coupling reactions [32, 39–41]. The TSILs acts as a versatile component because they behave as a reducing as well as stabilizing agent for palladium NPs.

Till today, a variety of TSILs have been reported; however, hydroxyl-functionalized IL possess added advantages over the rest of the ILs. These offer higher polarities and high dielectric constants resulting in increased hydrophilicity, increased H bond acidity and basicity with no change in dipolarity (the Kamlet–Taft scale) [42–45]. It has been observed that hydroxyl-functionalized ILs act as good reducing agents and lead to formation of highly stable Pd NPs with a narrow size distribution [46].

Amino acids (AAs) are one of the most versatile classes of natural, bio-renewable, and non-toxic raw materials. Other additional benefits viz low cost, biodegradability [47], biological activity [48] induce utilization of AAs as precursors for designer IL synthesis. Due to these reasons, AA-functionalized ILs have become popular amongst the scientific community and are being developed as reagents and catalysts to mediate chemical transformations [49–52].

Though varieties of AAs are available, proline is widely utilized as a precursor for ILs, as it is cheaper and easily available. Thus, prolinate-functionalized ILs have become a prime choice of researchers and are being used to synthesize organometallic catalysts for organic transformation [53–60]. In this context and in continuation with our earlier work in ILs and MNPs [61, 62], herein we have synthesized novel dual-functionalized TSILs and explored their catalytic activity for Heck–Matsuda coupling (Scheme 1).

Initially, attention was focused towards synthesis of TSILs for Heck–Matsuda coupling reaction which would induce in situ generation of Pd NPs as well as stabilize them through ligand coordination interactions. As discussed earlier, hydroxyl functionality possesses reducing properties; we decided to incorporate hydroxyl functionality in the cationic core. While selecting a suitable precursor as an IL cation, it was observed in literature that in most of the cases, imidazolium-
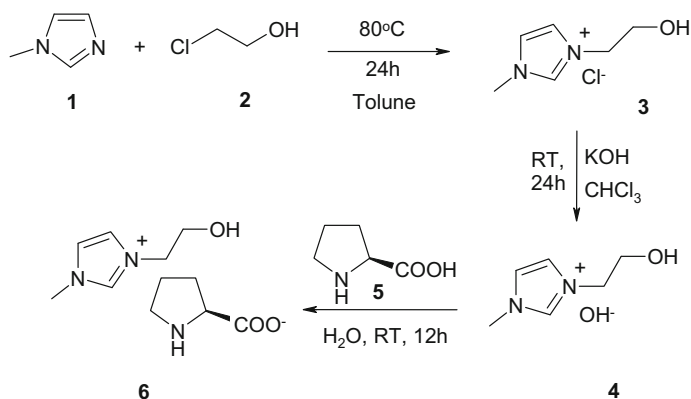
Scheme 1 Synthesis of prolinate-functionalized TSIL

based cations lead to room temperature ILs. Hence, for our experiment, the synthesis of IL was carried out using 1-methyl imidazole as a precursor. In order to stabilize the Pd NPs, prolinate functionality as an anion was incorporated in the IL via metathesis reaction. The synthetic route of novel dual-functionalized TSIL 1-hydroxylethyl-1-methylimidazolium prolinate [HEMIM][Pro] is outlined in Scheme 1. Thus, synthesized IL was equipped with cations having pendant hydroxyl functionality. This induces the coupling reaction and also acts as a reducing agent with prolinate functionality as an anion. This, in turn, serves as a ligand which stabilizes and/or activates the in situ-formed Pd NPs. The formation of IL was confirmed by ^1H and ^{13}C nuclear magnetic resonance (NMR) analysis.

After the synthesis of TSIL, we targeted our attempt towards application of TSIL for the coupling reaction. In order to discover suitable reaction conditions and to examine the activity of the catalyst, the coupling of benzenediazonium tetrafluoroborate salt (1 mmol) and styrene (1 mmol) using $PdCl_2$ (2 mol%) as a Pd source was used as a model reaction. We used IL as a reaction medium and as a ligand to stabilize the palladium catalyst and, surprisingly, 89% yield of coupling product was observed within 1 h. During the progress of the reaction, we had observed the change in initial yellowish brown color of the reaction mixture to grayish black, which was supposed to be due to in situ formation of Pd NPs. To verify this, after completion of the reaction. diethyl ether was added to the reaction mixture to extract the product, and the IL phase was analyzed by transmission electron microscopy (TEM) analysis. The TEM analysis confirmed the formation of Pd NPs having size below 50 nm (Fig. 1).

The size and shape of generated MNPs depends on several factors, such as reaction conditions (temperature, metal concentration, time, etc.), type of metal precursor, reducing agent, and the nature of the IL. However, there is evidence indicating that the relative size of MNPs is directly related to the volume of the IL (polar and nonpolar sphere). Certainly, metal precursors tend to be dissolved in the polar IL sphere, and, thus, the size is directly related to the volume of the anion of the imidazolium-based IL [32, 63–65]. Several groups have reported the use of ILs
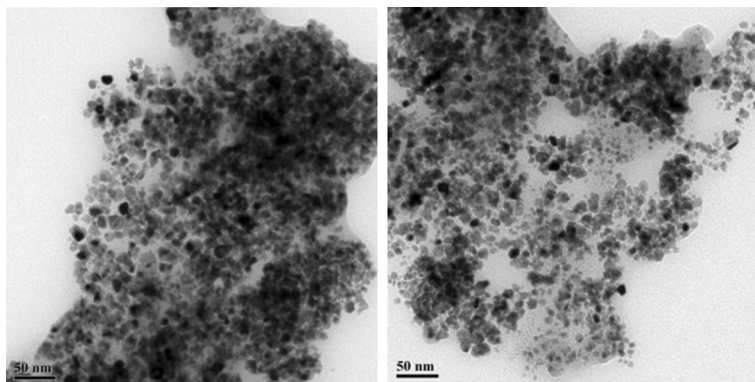
Fig. 1 TEM Image of in situ-generated Pd NPs

as solvents for the Heck reaction [66–69]. In the present work, we used prolinate-functionalized IL which performs a dual role, i.e. as a reducing as well as a stabilizing agent for Pd NPs for Heck–Matsuda reaction. Hence, it was not necessary to use any external ligand, stabilizing agent, any organic co-solvent or nitrogenous atmosphere to carry out the reaction, which are the green aspects of the protocol.

The palladium loading is an important aspect of the coupling reaction as it is an expensive metal. While optimizing the reaction, we observed that Pd loading less than 2 mol% gave inferior results. The best result with 99% of desired product was obtained employing 3 mol% of palladium acetate at room temperature. It is noteworthy that even at room temperature reactions took place smoothly within 1 h, furnishing excellent yields, and no self-coupling products were observed. Thereafter, to investigate the effect of the Pd source on the reaction, other Pd sources viz. Pd/C, Pd(PPh$_3$)$_4$, PdCl$_2$ etc. were also screened under optimized conditions (Fig. 2), but no significant increment in the reaction yield was observed.

To check the effect of prolinate-functionalized IL, we carried out similar reactions with other synthesized ILs, i.e. with compound 3 and compound 4 (Scheme 1), but we obtained inferior results as compared to the reaction with prolinate-functionalized IL (Table 1, entries A′ and B′). Hence, it is worthy to mention that prolinate IL is very effective in carrying out the coupling reaction. After obtaining the best reaction conditions, we carried out the reaction of arenediazonium silica sulfate salt (1 mmol) and styrene (1 mmol) using Pd(OAc)$_2$ and IL (2 mL) at room temperature (Scheme 2). It's our great pleasure to report here that the reaction worked well, giving a yield of about 97% of desired product. Hence, the protocol is applicable to both tetrafluoroborate and silica sulfate salts.

In order to verify the generality of the method, differentially substituted arenediazonium tetrafluoroborates as well as silica sulfate salts and various electron-deficient olefins were reacted under optimized conditions (Scheme 3). Gratifyingly, the reaction worked well with all types of substrates and olefins furnishing excellent yields of corresponding products (Tables 1, 2). It is worth mentioning that the reaction is stereospecific, giving only E-isomer as a single product.
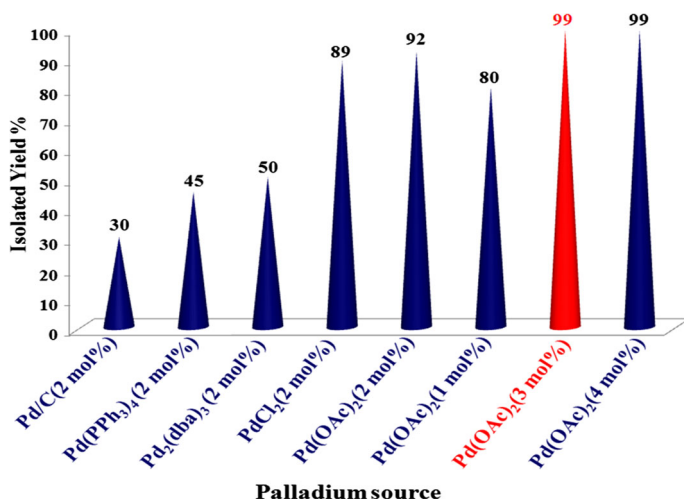
Fig. 2 Effect of different palladium sources on the Heck–Matsuda coupling. Reaction condition: benzenediazonium salt (1 mmol), styrene (1 mmol), palladium source (mol%), IL (2 mL), room temperature

Table 1 Heck–Matsuda reaction with different substituted arenediazonium tetrafluoroborate salts

Entry	Diazonium tetrafluoroborate salt (**7**) **R**	Olefin (**8**) **R′**	Product (**9**)	Time (min)	Yield (%)[a]
A′	H	Ph	9A′	180	20
B′	H	Ph	9B′	120	60
a	H	Ph	9a	30	99
b	H	COOMe	9b	30	99
c	H	COOBu	9c	30	99
d	4-Cl	Ph	9d	50	93
e	4-Cl	CN	9e	45	90
f	2,6-Me	COOBu	9f	40	95
g	2,6-Me	Ph	9g	40	96
h	3-NO$_2$	Ph	9h	50	87
i	3-NO$_2$	COOBu	9i	50	88
j	1-Naphthyl amine	COOMe	9j	55	90
k	4-Me	Ph	9k	35	93
l	4-Me	CN	9l	45	85
m	4-OMe	COOBu	9m	35	96

Reaction condition: for entry A′: compound 3 (IL 3) used as solvent arenediazonium salt (1 mmol), olefin (1 mmol), Pd(OAc)$_2$ (3 mol%), at room temperature for entry B′: compound 4 (IL 4) used as solvent arenediazonium salt (1 mmol), olefin (1 mmol), Pd(OAc)$_2$ (3 mol%), at room temperature for entry a–m: arenediazonium salt (1 mmol), olefin (1 mmol), Pd(OAc)$_2$ (3 mol%), prolinate functionalized IL (2 mL), at room temperature. [a] Isolated yield
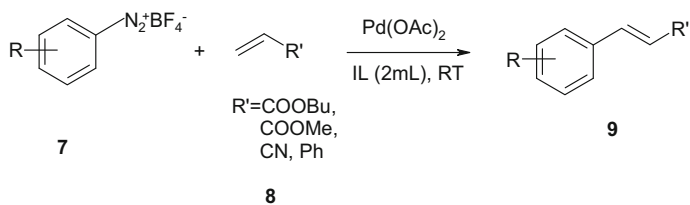
Scheme 2 Reaction with arenediazonium tetrafluoroborate salts
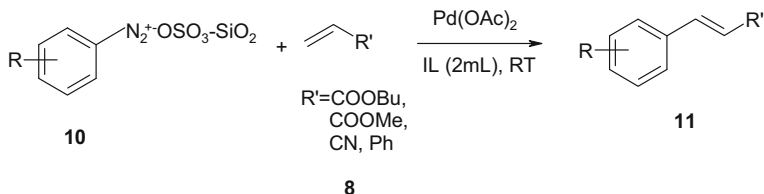
Scheme 3 Reaction with arenediazonium silica sulphate salts

Table 2 Heck–Matsuda reaction with different substituted arenediazonium silica sulphate salts

Entry	Diazonium silica sulphate salt (10) R	Olefin (8)	Product (11)	Time (min)	Yield (%)[a]
a	H	Ph	11a	30	99
b	H	COOMe	11b	30	99
c	H	COOBu	11c	30	99
d	4-OMe	CN	11d	45	89
e	4-OMe	COOMe	11e	40	91
f	4-COMe	COOMe	11f	55	86
g	4-COMe	Ph	11g	55	84
h	2-Me	COOBu	11h	35	94
i	2-Me	COOMe	11i	35	92
j	4-Br	CN	11j	45	88
k	4-Br	Ph	11k	50	90
l	3-NO$_2$	Ph	11l	50	85
m	2,6-Me	COOMe	11m	40	91

Reaction condition: arenediazonium salt (1 mmol), olefin (1 mmol), Pd(OAc)$_2$ (3 mol%), prolinate functionalized IL (2 mL), at room temperature. [a] Isolated yield

Although the catalytic system is highly efficient, green chemistry legislations direct us to minimize the waste and enhance conservation of energy. From this standpoint, recycling of catalyst is highly warranted. Hence, we carried out a recyclability study of an IL-Pd NP catalytic system for the model reaction. Gratifyingly, it was observed that the catalytic system can be reused effectively for eight times without significant loss of activity, providing excellent yield of products
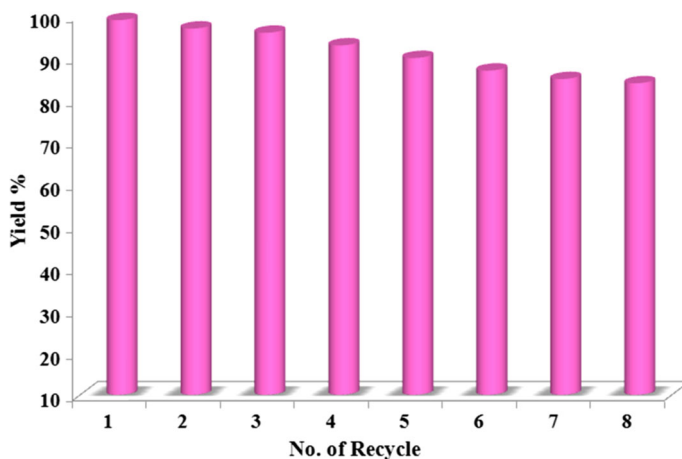
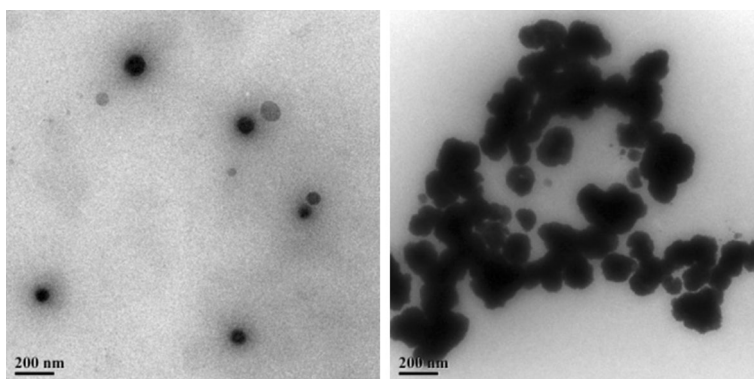**Fig. 3** Reusability of catalytic system (IL and Pd NPs)

Fig. 4 TEM Image of Pd NPs after the eighth run

(Fig. 3). After the eighth run, we analyzed the separated Pd NPs by TEM analysis which exhibited the aggregation of the Pd NPs (Fig. 4). This exemplifies the greener aspect and high efficacy of the protocol.

Conclusion

In conclusion, we have developed an eco-benign method for Heck–Matsuda coupling by employing a novel IL-Pd NP catalytic system. In situ generation of Pd NPs is assisted by a novel dual-functionalized TSIL which also act as reducing and stabilizing agents for them. The catalytic system can be reused at least for eight times without any significant loss in catalytic activity, which is one of the green aspects of the method. The reaction proceeds smoothly with both tetrafluoroborate as well as silica sulphate salts equipped with diverse functionalities. The novelty of

the protocol is the exploration of a novel, efficient, catalytic system for Heck–Matsuda coupling along with additional features viz. operational simplicity, reusability of the catalytic system, shorter reaction time, avoidance of conventional volatile organic solvents, no waste formation, 100% atom economy, easy work-up procedure, etc. Thus, we believe that our findings portend significant gains toward achieving ideal transformations.

General information

Chemicals (Spectrochem, Mumbai) and palladium sources (Spectrochem, Mumbai) were used as received. All reactions were carried out in aerobic condition in predried glassware. Infrared (IR) spectra were recorded on a Perkin-Elmer FT-IR-783 spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC spectrometer (300 MHz for ^{1}H NMR and 75 MHz for ^{13}C NMR), using CDCl$_3$ as solvent and tetramethylsilane (TMS) as an internal standard. Chemical shifts (δ) are expressed in parts per million (ppm) and coupling constants are expressed in hertz (Hz).

Typical procedure for the preparation of 1-(2-hydroxyethyl)-1-methylimidazolium prolinate [HEMIM][Pro] ionic liquid

To a vigorously stirred solution of 1-methylimidazole (10 mmol) in toluene (25 mL), 2-chloroethanol (11 mmol) was slowly added at room temperature and quarternisation was carried out at 80 °C for 24 h, after which it was cooled at room temperature for 1 h. Toluene was decanted and the remaining viscous oil was repeatedly washed with diethyl ether to yield colourless viscous IL, which was dried in vacuum, furnishing 1-(2-hydroxylethyl)-1-methylimidazolium chloride [HEMIM][Cl].

1-(2-Hydroxylethyl)-1-methylimidazolium chloride (10 mmol) was then dissolved in dichloromethane and cooled at 0 °C followed by addition of potassium hydroxide (11 mmol) and stirring for 24 h at room temperature. The suspension was filtered to remove the precipitated potassium chloride salt and the solvent was evaporated under reduced pressure, furnishing 1-(2-hydroxylethyl)-1-methylimidazolium hydroxide; [HEMIM][OH]. Finally, 1-(2-hydroxylethyl)-1-methylimidazolium hydroxide (5 mmol) was dissolved in water, and L-proline (5 mmol) was added slowly at room temperature; after addition, it was stirred at room temperature for 12 h. The solvent was removed in vacuum to furnish desired IL viz 1-hydroxylethyl-1-methylimidazolium prolinate [HEMIM][Pro].

General procedure for the Heck–Matsuda coupling

To a 50-mL round bottom flask, IL (2 mL), Pd(OAc)$_2$ (3 mol %), olefin (1 mmol), and aryldiazonium tetrafluoroborate salt/aryldiazonium silica sulfate salt (1 mmol) was added and stirred at room temperature under aerobic conditions. After completion of the reaction [monitored by thin layer chromatography (TLC)], the reaction mixture was extracted with diethyl ether (2 × 20 mL) while the IL-Pd NPs

remained the same in the reaction flask. The combined organic fractions were washed with water, dried over anhydrous sodium sulfate, and evaporated to obtain corresponding crude product. The crude product was purified by column chromatography with hexane/ethyl acetate (9:1) as eluent. Synthesized products were confirmed from physical constant, IR, ^{1}H, ^{13}C NMR and mass analysis.

General procedure for the reusability of catalytic system in the Heck–Matsuda coupling

A mixture of butyl acrylate (1 mmol), benzenediazonium tetrafluoroborate salt (1 mmol), Pd(OAc)$_2$ (3 mol %), and IL (2 mL) was stirred at room temperature under aerobic condition. After completion of reaction (TLC), the reaction mixture was extracted by diethyl ether (2 × 20 mL). The combined organic layer was concentrated under reduced pressure, and the residue was isolated by column chromatography hexane/ethyl acetate (9:1) as eluent to afford the product. The reaction residue consisting of IL-Pd NPs was loaded with the fresh reactants for the next run under the same reaction conditions. The catalytic system was reused for eight subsequent runs without any loss of catalytic activity.

Spectral data

1-(2-hydroxyethyl)-1-methylimidazolium prolinate [HEMIM][Pro] IL

^{1}H NMR (D$_2$O, 300 MHz): δ 1.90 (m, 2H), 2.24 (m, 1H), 3.29 (m, 2H), 3.8 (s, 3H), 3.9 (m, 1H), 4.02 (m, 2H), 4.22 (t, 2H), 7.37 (d, 1H), 7.43 (d, 1H), 8.68 (s, 1H); ^{13}C NMR (D$_2$O, 75 MHz): δ 21.58, 26.79, 33.56, 43.91, 49.35, 57.60, 59.03, 120.27, 121.42, 134.17, 172.35.

Table: 1

Entry 9a: (1,1′-(*E*)-ethene-1,2-diyldibenzene)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.10 (s, 1H), 7.26 (s, 1H), 7.33–7.38 (m, 5H), 7.50–7.53 (m, 5H); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 126.51(4C), 127.62(2C), 128.68(4C), 128.71(2C), 137.33(2C); MS(EI): 180(m/z), 181(M + 1), 173, 159, 147.

Entry 9c: (Butyl (2*E*)-3-phenylacrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.97 (t, 3H), 1.40–1.47 (m, 2H), 1.63–1.70 (m, 2H), 4.18 (t, 2H), 6.37–6.42 (d, 1H, *J* = 15 Hz), 7.32–7.35 (m, 3H), 7.47–7.50 (m, 2H), 7.61–7.67 (d, 1H, *J* = 18 Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 13.82, 19.23, 30.85, 64.05, 118.34, 127.96 (2C), 128.75 (2C), 130.00, 134.54, 144.33, 166.34; MS(EI): 205(m/z), 189, 158, 150, 133, 104, 91, 78, 56, 51.

Entry 9h: (1-Nitro-3-[(*E*)-2-phenylvinyl]benzene)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 7.08–7.13 (d, 1H, *J* = 15 Hz), 7.19–7.25 (d, 1H, *J* = 18 Hz), 7.30–7.31 (d, 1H, *J* = 3 Hz), 7.33–7.40 (m, 2H), 7.48–7.53 (m, 3H),

7.76–7.78 (d, 1H, $J = 6$ Hz), 8.07–8.11 (dd, 1H, $J = 3$ Hz, $J = 9$ Hz,), 8.34–8.35 (t, 1H, $J = 3.6$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 120.88, 121.95, 126.03, 126.83 (2C), 128.52, 128.82 (2C), 129.43, 131.81, 131.99, 136.21, 139.14, 148.81; MS(EI): 225(m/z) (M$^+$), 206, 191, 178, 165, 152, 139, 115, 102, 89, 76, 63, 51.

Entry 9i: (Butyl (2E)-3-(3-nitrophenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.99 (t, 3H), 1.42–1.5 (m, 2H), 1.67–1.76 (m, 2H), 4.24 (t, 2H), 6.54–6.60 (d, 1H, $J = 18$ Hz), 7.57–7.62 (t, 1H, $J = 15$ Hz), 7.69–7.74 (d, 1H, $J = 15$ Hz), 7.82–7.84 (d, 1H, $J = 6$ Hz), 8.22–8.26 (dt, 1H, $J = 3$ Hz, $J = 6$ Hz,), 8.39–8.40 (t, 1H, $J = 3$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 13.72, 19.17, 30.72, 64.67, 121.52, 122.33, 124.36, 129.82, 133.41, 136.26, 141.52, 148.75, 165.85; MS(EI): 249(m/z), 221, 204, 193, 176 (M$^+$), 160, 146, 129, 118, 102, 97, 76, 57.

Entry 9f: (Butyl (2E)-3-(2,6-dimethylphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 1.01 (t, 3H), 1.45–1.52 (m, 2H), 1.70–1.79 (m, 2H), 2.39(s, 6H), 4.27 (t, 2H), 6.09–6.14 (d, 1H, $J = 15$ Hz), 7.08–7.19 (m, 3H), 7.86–7.92 (d, 1H, $J = 18$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 13.79, 15.92, 19.25, 21.06, 30.78, 64.54, 120.12, 123.94, 128.23, 128.58, 136.64, 143.33, 166.99; MS(EI): 232(m/z), 217, 159 (M$^+$), 130, 115, 105, 91, 77, 65, 53.

Entry 9j: (Methyl (E)-3-(1-naphthyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.87 (s, 3H), 6.53 (d, 1H, $J = 16$ Hz), 7.44–7.59 (m, 4H), 7.74 (d, 1H, $J = 7$ Hz), 7.85–7.89 (m, 2H), 8.20 (d, 1H, $J = 8$ Hz), 8.54 (d, 1H, $J = 15.6$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 51.68, 96.17, 120.41, 123.39, 124.93, 125.39, 126.19, 126.84, 128.70, 130.51, 131.44, 133.68, 141.81, 167.04.

Entry 9m: (Butyl (2E)-3-(4-methoxyphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.95 (t, 3H), 1.39–1.47 (m, 2H), 1.62–1.69 (m, 2H), 3.80(s, 1H), 4.16 (t, 2H), 6.22–6.28 (d, 1H, $J = 18$ Hz), 6.80–6.85 (m, 2H), 7.41–7.44 (m, 2H), 7.55–7.60 (d, 1H, $J = 15$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 13.80, 19.21, 30.88, 54.99, 63.84, 114.17 (2C), 115.76, 127.21, 129.52 (2C), 143.98, 161.20, 166.67; MS(EI): 234(m/z), 178 (M$^+$), 161, 134, 121, 103, 90, 77, 63, 51.

Table: 2

Entry 11e: (Methyl (E)-3-(4-methoxyphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 3.79 (s. 3H), 3.83 (s, 3H), 6.28 (d, 1H, $J = 16$ Hz), 6.86–6.91 (dd, 2H, $J = 8.7$ Hz, $J = 11.4$ Hz), 7.44–7.48 (m, 2H), 7.63 (d, 1H, $J = 16$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 51.46, 55.20, 96.14, 114.26(2C), 115.25, 127.12, 129.66(2C), 144.46, 161.32, 167.48.

Entry 11f: (Methyl (*E*)-3-(4-acetylphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.58 (s, 3H), 3.79 (s, 3H), 6.47 (d, 1H, $J = 16$ Hz), 7.57 (d, 2H, $J = 8$ Hz), 7.66 (d, 1H, $J = 16$ Hz), 7.92 (d, 2H, $J = 8$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 26.50, 51.72, 120.28, 128.04 (2C), 128.79, 128.95, 137.99, 143.17, 166.50, 196.46.

Entry 11g: (1-{4-[(*E*)-2-phenylvinyl]phenyl}ethanone)
^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm): 2.61 (s, 3 H), 7.09–7.40 (m, 5H), 7.52–7.59 (m, 4H), 7.95 (d, 2H, $J = 8.4$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm): 26.49, 126.45 (2C), 126.79 (2C), 127.41, 128.28, 128.76 (2C), 128.85 (2C), 131.45, 135.95, 136.64, 141.92, 196.85.

Entry 11h: (Butyl (2*E*)-3-(2-methylphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 0.99 (t, 3H), 1.42–1.49 (m, 2H), 1.66–1.73 (m, 2H), 2.45 (s, 3H), 4.22 (t, 2H), 6.32–6.38 (d, 1H, $J = 18$ Hz), 7.17–7.28 (m, 3H), 7.55 (t, 1H, $J = 9$ Hz), 7.94–7.99 (d, 1H, $J = 15$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 13.79, 19.23, 19.76, 30.83, 64.23, 119.32, 126.27, 126.37, 129.86, 130.71, 133.45, 137.44, 142.18, 166.83; MS(EI): 218(m/z), 162, 145, 127, 117 (M$^+$), 107, 91, 77, 57.

Entry 11i: (Methyl (2*E*)-3-(2-methylphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.46 (s, 3H), 3.81 (s, 3H), 6.31–6.36 (d, 1H, $J = 15$ Hz), 7.17–7.25 (m, 3H), 7.51–7.54 (d, 1H, $J = 9$ Hz), 7.93–7.98 (d, 1H, $J = 15$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 19.76, 51.52, 118.84, 126.31, 126.37, 129.96, 130.74, 133.36, 137.49, 142.44, 167.15; MS(EI): 176(m/z) (M$^+$), 160, 146, 129, 118, 102, 97, 76, 57.

Entry 11m: (Methyl (2*E*)-3-(2,6-dimethylphenyl)acrylate)
^{1}H NMR (CDCl$_3$, 300 MHz): δ 2.36 (s, 6H), 3.82 (s, 3H), 6.03–6.09 (d, 1H, $J = 18$ Hz), 7.03–7.13 (m, 3H), 7.81–7.86 (d, 1H, $J = 15$ Hz); ^{13}C NMR (CDCl$_3$, 75 MHz): δ 16.10, 21.12, 51.62, 120.02, 123.42, 128.40, 128.57, 133.85, 136.49, 143.74, 152.53, 167.04; MS(EI): 190(m/z), 175, 159, 130 (M$^+$), 115, 103, 91, 77, 64, 51.

References

1. P. Wasserscheid, T. Welton, *Ionic Liquids in Synthesis* (Wiley-VCH, Weinheim, 2008)
2. S. Toma, M. Meciarova, R. Sebesta, Eur. J. Org. Chem. **3**, 321–327 (2009)
3. J. Dupont, R.F. de Souza, P.A.Z. Suarez, Chem. Rev. **102**, 3667–3692 (2002)
4. R. Sheldon, Chem. Commun. **23**, 2399–2407 (2001)
5. P. Wasserscheid, W. Kein, Angew. Chem. Int. Ed. **39**, 3772–3789 (2000)
6. T. Welton, Chem. Rev. **99**, 2071–2083 (1999)
7. R. Giernoth, Angew. Chem. Int. Ed. **49**, 2834–2839 (2010)
8. J.D. Holbrey, K.R. Seddon, Clean Prod. Process. **1**, 223–236 (1999)

9. P. Wasserscheid, W. Keim, Angew. Chem. **112**, 3926–3945 (2000)
10. P. Wasserscheid, W. Keim, Angew. Chem. Int. Ed. **39**, 3772–3789 (2000)
11. H. Olivier-Bourbigou, L. Magna, J. Mol. Catal. **182**, 419–437 (2002)
12. R. Hayes, G.G. Warr, R. Atkin, Chem. Rev. **115**, 6357–6426 (2015)
13. G.W. Parshall, J. Am. Chem. Soc. **94**, 8716–8719 (1972)
14. W. Cabri, I. Candiani, Acc. Chem. Res. **28**, 2–7 (1995)
15. W.A. Hermann, C. Brossmer, Angew. Chem. Int. Ed. **34**, 1844–1848 (1995)
16. X.-F. Wu, H. Neumann, M. Beller, Chem. Commun. **47**, 7959–7961 (2011)
17. B. Panda, T. Sarkar, Chem. Commun. **46**, 3131–3133 (2010)
18. G. Fabrizi, A. Goggiamani, A. Sferrazza, S. Cacchi, Angew. Chem. Int. Ed. **49**, 4067–4070 (2010)
19. K. Selvakumar, A. Zapf, A. Spannenberg, M. Beller, Chem. Eur. J. **8**, 3901–3906 (2002)
20. F. Babudri, G.M. Farinola, F. Naso, D. Panessa, J. Org. Chem. **65**, 1554–1557 (2000)
21. R.G. Kalkhambkar, K.K. Laali, Tetrahedron Lett. **52**, 1733–1737 (2011)
22. J.G. Taylor, A.V. Moro, C.R.D. Correia, Eur. J. Org. Chem. **8**, 1403–1428 (2011)
23. M.B. Andrus, Y. Ma, Y. Zang, C. Song, Tetrahedron Lett. **43**, 9137–9140 (2002)
24. D.M. Willis, R.M. Strongin, Tetrahedron Lett. **41**, 6271–6274 (2000)
25. M.B. Andrus, C. Song, Org. Lett. **3**, 3761–3764 (2001)
26. E. Peyroux, F. Berthiol, H. Doucet, M. Santelli, Eur. J. Org. Chem. **5**, 1075–1084 (2004)
27. J.T. Kuethe, K.G. Childers, Adv. Synth. Catal. **350**, 1577–1586 (2008)
28. M. Kosugi, K.J. Fugami, Organomet. Chem. **653**, 50–53 (2002)
29. K. Kikukawa, K. Kono, F. Wada, T. Matsuda, J. Org. Chem. **48**, 1333–1336 (1983)
30. K. Cheng, C. Wang, Y. Ding, Q. Song, C. Qi, X.-M. Zhang, J. Org. Chem. **76**, 9261–9268 (2011)
31. D.E. Kaufmann, M. Nouroozian, H. Henze, Synlett **11**, 1091–1092 (1996)
32. J.D. Scholten, B.C. Leal, J. Dupont, ACS Catal. **2**, 184–200 (2012)
33. A. Balanta, C. Godard, C. Claver, Chem. Soc. Rev. **40**, 4973–4985 (2011)
34. M. Planellas, R. Pleixats, A. Shafira, Adv. Synth. Catal. **354**, 651–662 (2012)
35. C. Zhou, J. Wang, L. Li, R. Wang, M. Hong, Green Chem. **13**, 2100–2106 (2011)
36. Y.Z. Chen, L. Liang, Q. Yang, M. Hong, Q. Xu, S.H. Yua, H.L. Jiang, Mater. Horiz. **2**, 606–612 (2015)
37. S. Handa, E.D. Slack, B.H. Lipshutz, Angew. Chem. Int. Ed. **54**, 11994–11998 (2015)
38. S. Handa, M.P. Andersson, F. Gallou, J. Reilly, B.H. Lipshutz, Angew. Chem. Int. Ed. **55**, 4914–4918 (2016)
39. V.I. Parvulescu, C. Hardacre, Chem. Rev. **107**, 2615–2665 (2007)
40. B. Xinab, J. Hao, Chem. Soc. Rev. **43**, 7171–7187 (2014)
41. C.W. Scheeren, G. Machado, S.R. Teixeira, J. Morais, J.B. Domingos, J. Dupont, J. Phys. Chem. B **110**, 13011–13020 (2006)
42. S. Tang, G.A. Baker, H. Zhao, Chem. Soc. Rev. **41**, 4030–4066 (2012)
43. P. Twu, Q. Zhao, W.R. Pitner, W.E. Acree, G.A. Baker, J.L. Anderson, J. Chromatogr. A **1218**, 5311–5318 (2011)
44. Q. Zhao, J. Eichhorn, W.R. Pitner, J.L. Anderson, Anal. Bioanal. Chem. **395**, 225–234 (2009)
45. M.A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N.H. Hassan, J.P. Hallett, P.A. Hunt, H. Niedermeyer, J.M. Perez- Arlandis, M. Schrems, T. Welton, R. Wilding, Phys. Chem. Chem. Phys. **13**, 16831–16840 (2011)
46. M.M. Huang, Y. Jiang, P. Sasisanker, G.W. Driver, H. Weingartner, J. Chem. Eng. Data **56**, 1494–1499 (2011)
47. N. Gathergood, M.T. Garcia, P.J. Scammells, Green Chem. **6**, 166–175 (2004)
48. K.M. Docherty, C.F. Kulpa Jr., Green Chem. **7**, 185–189 (2005)
49. P. Moriel, E.J. Garcia-Suarez, M. Martinez, A.B. Garcia, M.A. Montes-Moran, V. Calvino-Casilda, M.A. Banares, Tetrahedron Lett. **51**, 4877–4881 (2010)
50. N.A. Larionova, A.S. Kucherenko, D.E. Siyutkin, S.G. Zlotin, Tetrahedron **67**, 1948–1954 (2011)
51. N. Ferlin, M. Courty, A.N. Van Nhien, S. Gatard, M. Pour, B. Quilty, M. Ghavre, A. Hai, K. Kummerer, N. Gathergood, S. Bouquillon, RSC Adv. **3**, 26241–26251 (2013)
52. K.R. Roshan, T. Jose, D. Kim, K.A. Cherian, D.W. Park, Catal. Sci. Technol. **4**, 963–970 (2014)
53. A. Morel, E. Silarska, A.M. Trzeciak, J. Pernak, Dalton Trans. **42**, 1215–1222 (2013)
54. J. Yan, L. Wang, Synthesis **3**, 447–452 (2010)
55. W. Liu, F. Hou, Appl. Organometal. Chem. **29**, 368–371 (2015)
56. K. Azizi, A. Heydari, RSC Adv. **4**, 6508–6512 (2014)

57. G. Zhang, Y. Luan, X. Han, Y. Wang, X. Wen, C. Ding, Appl. Organometal. Chem. **28**, 332–338 (2014)
58. A.R. Hajipour, E. Boostania, F. Mohammadsaleh, RSC Adv. **5**, 24742–24748 (2015)
59. K.R. Reddy, C.V. Rajasekhar, G. Gopi, Krishna. Synth. Commun. **37**, 1971–1976 (2007)
60. M.M. Heravi, M.H. Tehrani, K. Bakhtiari, H.A. Oskooie, Catal. Commun. **8**, 1341–1344 (2007)
61. D.S. Gaikwad, Y.K. Park, D.M. Pore, Tetrahedron Lett. **53**, 3077–3081 (2012)
62. J.D. Patil, S.N. Korade, S.A. Patil, D.S. Gaikwad, D.M. Pore, RSC Adv. **5**, 79061–79069 (2015)
63. E. Redel, R. Thomann, C. Janiak, Inorg. Chem. **47**, 14–16 (2008)
64. G.S. Fonseca, G. Machado, S.R. Teixeira, G.H. Fecher, J. Morais, M.C.M. Alves, J. Dupont, J. Colloid Interface Sci. **301**, 193–204 (2006)
65. P. Migowski, D. Zanchet, G. Machado, M.A. Gelesky, S.R. Teixeira, J. Dupont, Phys. Chem. Chem. Phys. **12**, 6826–6833 (2010)
66. F. Bellina, C. Chiappe, Molecules **15**, 2211–2245 (2010)
67. A.J. Carmichael, M.J. Earle, J.D. Holbrey, P.B. McCormac, K.R. Seddon, Org. Lett. **1**, 997–1000 (1999)
68. S.L. Yingjie, L.H. Xie, S. Zhang, J. Xu, Org. Lett. **8**, 391–394 (2006)
69. J. Ruan, J. Xiao, Acc. Chem. Res. **44**, 614–626 (2011)