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Polymeric β-alanine incarcerated Pd(II) catalyzed allylic etherification in water: A mild and efficient method for the formation of C(sp^3)-O bond

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A new heterogeneous palladium(II) catalyst has been developed through a convenient and economic way. The catalyst was synthesized by confining palladium metal with polystyrenal β-alanine-imine network and characterized by FT-IR spectroscopy, thermogravimetric analysis, field emission scanning electron microscopy, energy dispersive X-ray, and elemental analysis. Polymeric imine can be prepared easily from chloromethylated polystyrene and β-alanine. Using this polymer incarcerated palladium (II) catalyst a useful and efficient procedure for stereospecific synthesis of allyl-aryl ether has been developed. The benzylic, aromatic, and heteroaromatic phenols react with various substituted allyl acetates by this procedure to furnish a library of allyl-aryl and allyl-hetero-aryl ethers in high yields. The catalyst could be recovered easily and reused five times without any considerable loss of its catalytic activity.

Introduction

Homogeneous palladium complexes have been used successfully for a variety of reactions in organic synthesis.[1] But due to the chance of metal contamination with the end product and the difficulty to recover and reuse the homogeneous catalyst, heterogeneous Pd catalyst has emerged as sustainable alternative. Thus the immobilization of palladium on a heterogeneous support has received considerable attention to provide an effective catalyst overcoming the drawbacks of homogeneous catalysis.[2] Furthermore, the use of water as the reaction medium has gained top priority because of its unique reactivity and selectivity which is different from those in organic solvents, in addition to its environmental acceptability and low cost.[3] Thus, the combination of heterogeneous, inexpensive, ligand-free, robust, recyclable catalysts and water as a solvent for a chemical transformation is highly desirable in the context of environmental and industrial concerns. Recently, polymer-supported phosphine and amine ligand have been developed to immobilize palladium metals onto polymers.[4] Our group has explored few polymer supported metal catalyst for hydrogenation,[5] C-C and C-N cross coupling reaction[6] and catalytic oxidation.[7] We report here a simple preparation and characterization of a new polymeric β-alanine-imine incarcerated highly active Pd(II) catalyst and exemplified its application for the stereo-specific allylic etherification reactions in water under mild condition. The catalyst was prepared easily by two step reaction. The initial step is the formation of polymeric imine by the condensation of chloromethylated polystyrene with readily available and inexpensive β-alanine. Finally the PS-Pd-ala catalyst was prepared by the immobilizing the palladium metal on polymeric imine, for the first time.

The construction of C(sp^3)-O bond is very important in organic synthesis as it constitutes the key step in the synthesis of many pharmaceuticals.[8] Allyl ethers are employed as useful starting material in a wide variety of reactions such as 1,3-hydrogen shift, [3,3]-sigmatropic rearrangement, and polymerization reactions.[9] They are also found as core units of several biologically active molecules and natural products.[10] In addition, allyl groups act as efficient protecting groups for phenol derivatives.[11] Usually allylation is performed using allyl alcohol derivatives or halides.[12] But, easy availability and configurational stability of allyl acetate make it preferable allylating agents compared to highly activated, unstable allyl halides and tosylates.[13] Transition metal-catalyzed allylation of carbon, nitrogen and sulfur nucleophile is one of the most frequently employed transformations in organic synthesis.[14-17] Generally, allyl ethers are prepared by the reaction between alkyl halide and phenols using strong base e,g metal alkoxide.[18] However, allylation with soft phenolic nucleophile has received less attention. Few transition metal complexes such as Pd,[19] Ru,[20] Ir,[21] Ni[22] have been explored as the catalysts for the synthesis of allyl ethers. In fact, majority of the methods involved non recyclable, costly homogeneous transition metal catalyst. Therefore an alternative sustainable heterogeneous catalyst is highly desirable for the synthesis of allyl ether. Verma *et al* reported a mild procedure for the general *O*-allylation of phenols with allyl acetates using

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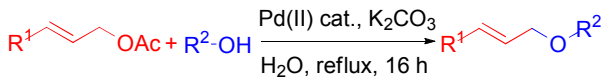
Electronic Supplementary Information (ESI) available: Copies of ^{1}H NMR and ^{13}C NMR spectra of all products listed in Tables 2, Scheme 3, 4 and 5. See DOI: 10.1039/x0xx00000x

magnetically separable heterogeneous Pd catalyst.[23] Here we report the application of our catalyst for a mild and efficient allylic C(sp^3)-O bond formation (Scheme 1).



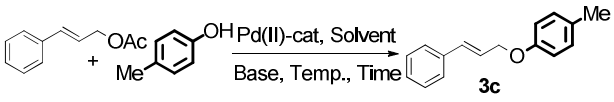
Scheme 1 Palladium catalyzed allylic etherification

Results and discussion

2.1 Allylic etherification

To probe the optimum reaction conditions, a series of experiments were performed with variation of reaction parameters such as base, solvent, temperature and time for a representative *O*-allylation of cinnamyl acetate (**1b**) with *p*-cresol (**2b**). The results are summarized in Table 1. Water was found to be best solvent among THF, DMF, toluene, 1,4-dioxane, CH_3CN, NMP and DMSO tried for this reaction. Among various bases K_2CO_3 was found more effective than Cs_2CO_3 and K_3PO_4 under identical condition. $NaHCO_3$ shows almost similar activity compared to K_2CO_3.

Table 1 Standardization of reaction conditions[a]



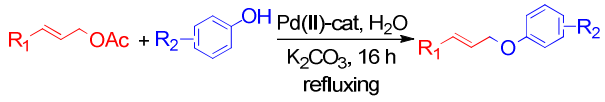
Entry	Solvent	Base	Temp. (°C)	Time (h)	Yield[a] (%)
1	THF	K_2CO_3	70	16	39
2	DMF	K_2CO_3	110	16	62
3	Toluene	K_2CO_3	110	16	18
4	Dioxane	K_2CO_3	105	16	43
5	MeCN	K_2CO_3	80	16	16
6	NMP	K_2CO_3	110	16	38
7	DMSO	K_2CO_3	110	16	44
8	H_2O	K_2CO_3	100	16	90
9	H_2O	K_3PO_4	100	16	42
10	H_2O	Cs_2CO_3	100	16	37
11	H_2O	$NaHCO_3$	100	16	85
12	H_2O	K_2CO_3	100	30	91
13	H_2O	K_2CO_3	rt	30	-
14	H_2O	K_2CO_3	70	20	83
15[b]	H_2O	K_2CO_3	100	12	-
16[c]	H_2O	K_2CO_3	100	16	88
17[d]	H_2O	K_2CO_3	100	16	76

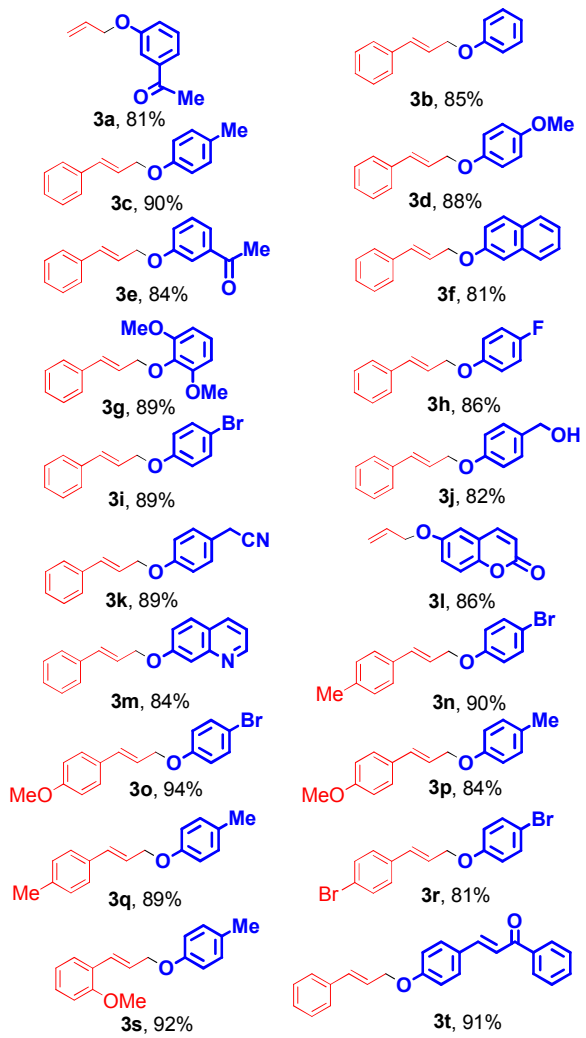
[a]Yields refer to those of purified products characterized by ^1H and ^{13}C NMR spectroscopic data. [b]Without using catalyst. [c]In presence of TEMPO.[d]Palladium(II) acetate was used as a catalyst.

The reaction failed to initiate at room temperature and these are then carried out under refluxing condition. There was no reaction in the absence of supported Pd(II) catalyst (Table 1, entry 15). The yield of the product (**3c**) was not affected after the addition of 1 equiv. of TEMPO (Table 1, entry 16). Best yield was obtained using H_2O as a solvent and 10 mol% Pd(II) catalyst in presence of K_2CO_3 under reflux for 16 h (argon atmosphere) (Table 1, entry 8). In our preliminary screening, it was exciting to demonstrate that polymer incarcerated Pd(II) catalyst was slightly more reactive than the homogeneous Pd(II) acetate catalyst (Table 1, entry 17).

Both aliphatic and aromatic allyl acetates were found to be efficient substrates for the *O*-allylation reaction. The allyl acetate bearing phenyl with an electron-donating group at *para*- position

Table 2 Synthesis of allyl aryl ether using Pd catalyst[a]

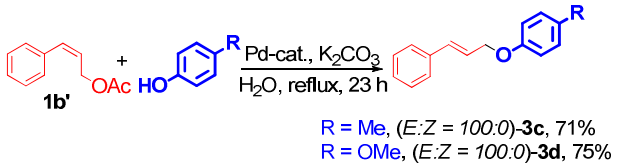




[a]Yields refer to those of purified products characterized by ^1H and ^{13}C NMR spetroscopic data

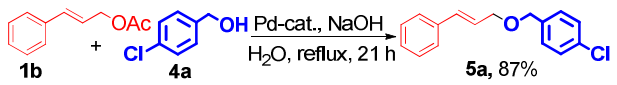
formed the product in good yield and the reactions are more facile than those with unsubstituted one. Significantly, the reaction is uniform with *ortho*- and *para*-substituted cinnamyl acetates. The *O*-allylation of (*E*)-3-(4-bromophenyl)allyl acetate is highly chemoselective as the attack of nucleophile occurs only at allylic position leaving -Br group on the aromatic ring unaffected (Table 2, **3r**).[24] A series of diversely substituted phenols underwent reactions with substituted allyl acetates by this procedure to provide the corresponding allyl-aryl ethers. The phenols bearing various electron donating (-Me, -OMe,) and withdrawing moieties (-F, -COMe) at the different positions of the aromatic ring underwent coupling with allyl and cinnamyl acetates without any difficulty (Table 2). With an *ortho*-2,6-dimethoxy-substituted phenol, the cinnamyl acetate (**1b**) gave a reasonable yield of the allylation product, although the nucleophile is more sterically hindered (Table 2, **3g**). It was found that the reactivity of hydroxy groups attached with aromatic system is greater than aliphatic one. We performed the reaction of cinnamyl acetate with 4-(hydroxymethyl)phenol and (4-(cinnamyloxy)phenyl)methanol was obtained as the single product (Table 2, **3j**). We also investigated the reactions of several heterocyclic phenols with allyl and cinnamyl acetates and the coupling reaction occurs without any difficulty (Table 2, **3l** and **3m**).

Significantly, the (*E*)- cinnamyl acetates and substituted phenol produced the corresponding (*E*)- allyl aryl ether with complete retention of stereochemistry. Interestingly, the (*Z*)- cinnamyl acetates also provided (*E*) products with excellent stereospecificity (Scheme 2)



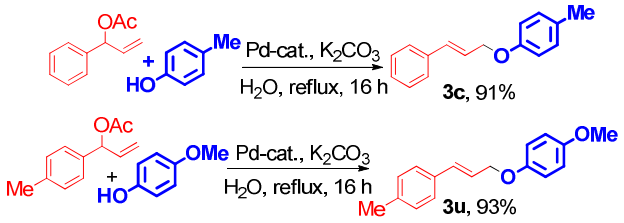
Scheme 2 Synthesis of (*E*)-allyl-aryl ether using (*Z*)-cinnamyl acetate.

Substituted benzyl alcohols also coupled with cinnamyl acetate successfully to produce the corresponding ethers (Scheme 3, **5a**). In this reaction we have used strong base like NaOH instead of K_2CO_3 for the completion of reaction**.**



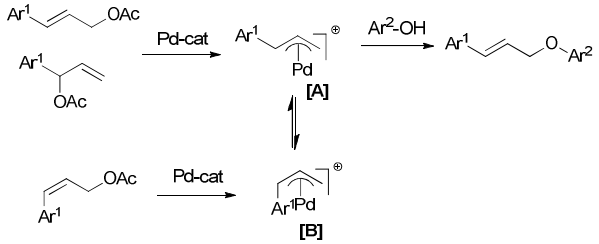
Scheme 3 Synthesis of benzyl-allyl ether using benzyl alcohol.

In case of branched allyl acetate (Scheme 4, **3c**, **3u**), this reaction shows equal efficiency to provide linear allyl-aryl ether which also supports the mechanism that entails the intermediacy of an η^3-π-allyl Pd complex as the key intermediate in the reaction (Scheme 5).



Scheme 4 *O*-Allylation using branched cinnamyl acetate.

We suggest that the reaction proceeds through an interaction of Pd(II) with allyl acetate followed by oxidative addition with substituted phenol resulting a η^3-π-allyl complex, which undergoes reductive elimination to give the product (Scheme 5).[17a] In case of *trans*-allyl acetate, it is predicted that the direct interaction of π-allyl complex [**A**] with phenol, followed by reductive elimination gives the *trans* product. However in case of *cis*-allyl acetate, the intermediate [**B**], formed after the oxidative addition, is likely to equilibrate with stable, less congested intermediate [**A**] and finally gives the *trans* product**.**

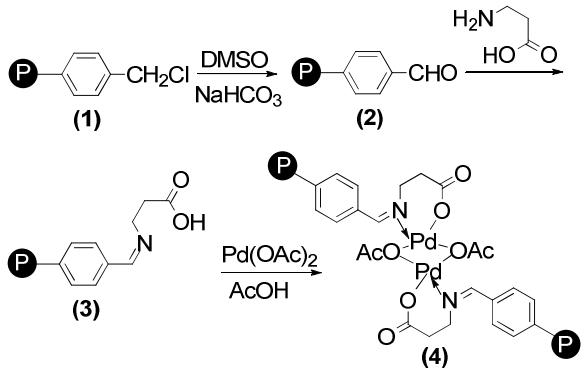


Scheme 5 Plausible mechanism.

Experimental

3.1 Loading of metal ions on to the polymeric ligand

Polymeric ligand (**3**) (1 gm) was stirred for 20 h with palladium acetate (20 mg) in acetic acid (10 mL) at 100 °C (Scheme 6). At the end of the reaction, the resulting metal-loaded polymer was filtered, washed with water, followed by methanol and finally dried under vacuum for 6 h at 90 °C.



Scheme 6 Outline for the synthesis of polymer incarcerated palladium(II) catalyst

3.2 Characterization of supported palladium(II) complex

Due to insolubility of the polymer supported Pd(II) complex in all common organic solvents, characterization was limited to the physicochemical properties, chemical analysis, SEM, TGA, IR, and UV-Vis spectral data. Elemental analysis data for polymer supported ligand and catalyst are tabulated in Table 3. Amount of metal was determined by stripping the bound metal from the support and analysis by using atomic absorption spectrophotometer. Palladium content was found in the catalyst is 10.34 wt% of Pd analyzed by AAS (Table 3). Palladium content remained almost unchanged even after recycling the catalyst for five cycles.

Table 3 Chemical composition of polymer supported ligand **(3)** and Pd-PS-ala catalyst **(4)**

Compound	C%	H%	N%	Pd%
Ligand **(3)**	74.96	6.36	4.61	-
Pd-PS-ala **(4)**	71.94	6.97	4.78	10.34 (10.23[a])

[a]Palladium content of recycled catalyst after 5th cycles

3.2.1 IR study

The mode of attachment of β-alanine and palladium metal onto the support was confirmed by IR spectral bands (Figure 1). In the FT-IR spectrum of aldehyde functionalized polymer (**2**), a new peak appeared at 1705 cm^{-1} that was assigned to carbonyl C=O bond stretching vibration of the aldehyde group. In the polymer (**2**) the sharp C-Cl peak due to -CH_2Cl group at 1264 cm^{-1} was absent.[25] The formation of the Schiff base moiety on the polymeric support (**3**) is indicated by a peak at 1,633 cm^{-1} assigned to C=N stretching frequency. This band shifted to lower wave numbers after complexation with palladium metal. The polymer supported Pd-catalyst (**4**) exhibited IR peaks at 1574 cm^{-1}, 1423 cm^{-1} (ν COO bridged).[26] It suggests that, Schiff base coordinated to the central palladium ion through the azomethine nitrogen.

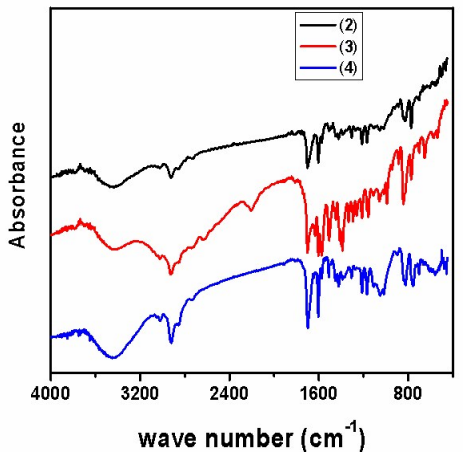


Figure 1. FT-IR spectra of (**2**) aldehyde functionalised polymer, (**3**) polymer supported schiff base ligand and (**4**) polymer supported Pd(II) catalyst, Pd-PS-ala.

3.2.2 DRS-UV study

The electronic spectrum (Figure 2) of the polymer supported Schiff base ligand and palladium catalyst (Pd-PS-ala) have been recorded in the diffuse reflectance spectrum mode as $MgCO_3/BaSO_4$ disc due to its solubility limitations in common organic solvents. In the catalyst, broad bands around 260 to 350 nm are observed. This absorption bands may be attributed to π→π* and n→π* transition in phenyl moiety. The bands at 390-430 nm arise due to LMCT.

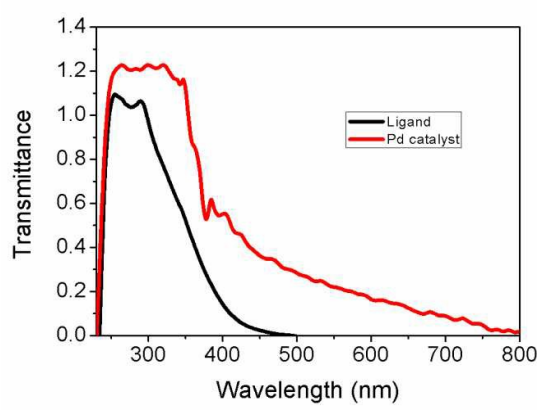
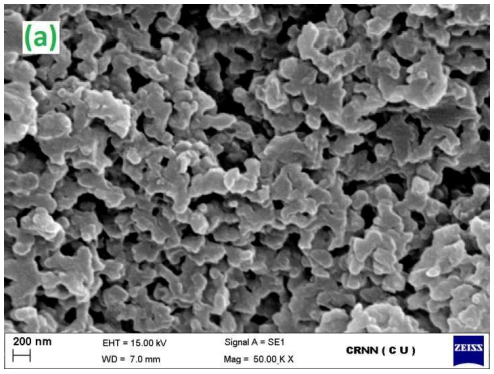
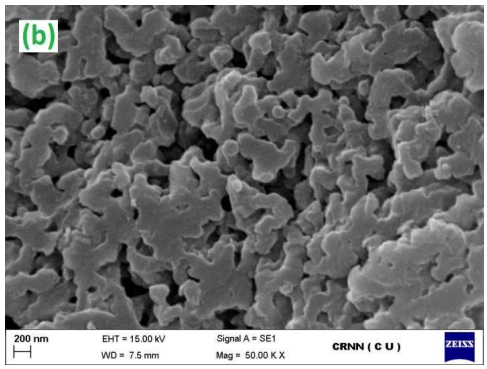


Figure 2. DRS-UV-Visible spectra of ligand and Pd-PS-ala catalyst.

3.2.3 Scanning electron micrographs (SEM) and energy dispersive X-ray analysis (EDX)

The morphology of the catalyst was studied using Scanning Electron Microscope (SEM). The micrographs of the polymer anchored *β*-alanine ligand and palladium(II) catalyst obtained from the scanning electron microscope are presented in Figures 3a and 3b respectively. The morphological changes in the polymer supported ligand and polymer supported catalyst are quite evident from these images. The micrograph of five time reused Pd-PS-ala catalyst is also presented in figure 3c. Quite uniform and negligible variation in size is observed throughout the both specimens. Energy dispersive spectroscopy analysis of X-rays (EDAX) data for the polymer supported palladium complex is given in Figure 4. The EDAX data also inform the attachment of palladium on the surface of the polymer matrix.





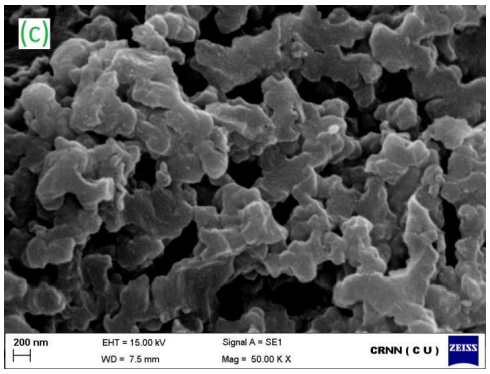


Figure 3. SEM images of (a) Polymer supported schiff base ligand, (b) Polymer supported Pd(II) catalyst, Pd-PS-ala, (c) Five times recycled polymer supported Pd(II) catalyst, Pd-PS-ala.

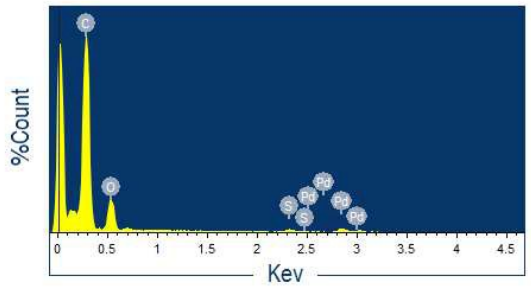


Figure 4. EDAX data of polymer supported Pd(II) catalyst, Pd-PS-ala.

3.2.4 TGA Analysis

Thermal stability of the complex was investigated using TGA at a heating rate of 10 ^{o}C/min in air over a temperature range of 30-600 ^{o}C. TGA curve of the polymer supported Pd(II) catalyst is shown in Figure 5. The Pd(II)-complex is stable up to 370-390 ^{o}C and above that temperature it is decomposed. Thermogravimetric study suggests that the polymer supported palladium complex degrade at considerably higher temperature.

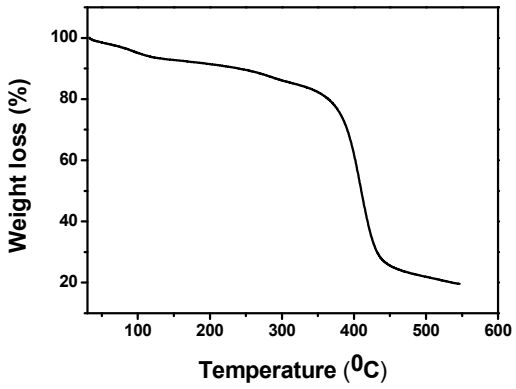


Figure 5. TGA plots for Pd-PS-ala catalyst.

3.3 General Procedure for Coupling of Phenol with Allyl acetate

A mixture of polymer supported Pd(II) catalyst (30 mg), cinnamyl acetate (1 mmol), *p*-cresol (1 mmol), potassium carbonate (2 mmol) and water (3mL) was placed in a 10 mL round bottom flask and was stirred for 16 h at 110 ^{o}C. The reaction was monitored by TLC. After completion of reaction, the catalyst was removed by simple filtration through celite-545. Then ethyl acetate was added to the reaction mixture and the organic layer was separated from water. The desired product was isolated from the extracted organic part by column chromatography over silica gel (ethyl acetate/hexane) to provide pure 1-(cinnamyloxy)-4-methylbenzene as colourless oil; yield: 209 mg (90%). The spectroscopic data (^{1}H NMR and ^{13}C NMR) of this product are in good agreement with those of an authentic sample.

3.4 Heterogeneity Test

To verify the heterogeneity of the catalyst, 1 mmol *p*-cresol, 1 mmol cinnamyl acetate and 30 mg catalyst were allowed to stir in 3 mL water at 110 ^{o}C. The reaction was stopped after 8 h, and the conversion was found to be 56 % by GC-analysis. At this stage, the catalyst was separated from the reaction medium and the reaction was continued with the filtrate for next 8 h. After total 16 h the extent of conversion was found to remain the same. Moreover, UV-Visible spectra of the catalyst free reaction mixture did not show any absorption peak responsible for palladium. This information indicates that the reaction was followed by a heterogeneous pathway. Further, the leaching of palladium from the catalyst was checked by analyzing (EDX, IR) the used catalyst. Analysis of the used catalyst did not show appreciable loss in palladium content as compared to that of fresh catalyst. Beside, IR-spectrum of the recycled catalyst was quite similar to that of the fresh sample indicating the heterogeneous nature of the catalyst. The UV-Visible spectroscopy was also used to determine the stability of the catalyst. The metal content of the recycled catalyst was determined with the help of AAS and it was found that palladium content of the recycled catalyst remained almost unchanged. These observations strongly suggest that the catalyst is truly heterogeneous in nature.

3.5 Recovery of Catalyst

At the end of the reaction, the reaction mixture was filtered. Then the recovered catalyst was thoroughly washed with methanol, dried

and then further washed with diethyl ether to remove any traces of organic materials. The catalyst was then finally dried at 55 °C for 5 h under vacuum to activate. The catalyst can be recycled for five times without losing the activity (Figure 6).

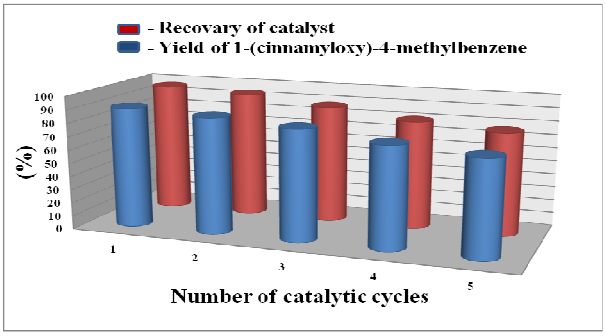


Figure 6. Recyclability chart for Pd-PS-ala catalyst.

The known compounds were identified by comparison of their spectra with those of authentic samples 3a[27a], 3b[23a], 3c[27b], 3d[27b], 3f[23a], 3i[27c], 3l[27d], 3o[27e], 3p[23a], 3q[19f], 3u[27f]. The unknown compounds were properly characterized by their spectroscopic data (IR, ^{1}H NMR, ^{13}C NMR and HRMS) data and elemental analysis and these data are provided below in order of their numbers in the respective tables and schemes.

1-[3-(3-phenyl-allyloxy)-phenyl]-ethanone (Table 3, 3e): Yellow viscous oil; IR (neat): 3415, 3027, 2923, 2853, 1684, 1580, 1484, 1438, 1356, 1269, 1212, 1018 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.46 (s, 3 H), 4.59 (d, J = 5.6 Hz, 2 H), 6.24-6.31 (m, 1 H), 6.62 (d, J = 15.6 Hz, 1 H), 7.02-7.29 (m, 7 H), 7.42 (d, J = 7.6 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 26.7, 68.9, 113.6, 120.3, 121.4, 124.0, 126.7 (2C), 128.1, 128.7 (2C), 129.7, 133.4, 136.4, 138.6, 158.9, 197.9; HR-MS (EI): m/z=275.1046 ($M+Na^+$), calcd. for $C_{17}H_{16}O_2$: 275.1048.

1,3-Dimethoxy-2-(3-phenyl-allyloxy)-benzene (Table 3, 3g): Pale Yellow Solid; IR (KBr): 3417, 3036, 2989, 2958, 2865, 1889, 1609, 1510, 1460, 1252, 1241, 1177, 1112, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.78 (s, 6 H), 4.59 (d, J = 6.0 Hz, 2 H), 6.45-6.53 (m, 1 H), 6.65 (dd, J_1 = 7.6 Hz, J_2 = 16 Hz, 3 H), 6.91 (d, J = 8.4 Hz, 1 H), 7.41 (d, J = 15.6 Hz, 2 H), 7.45-7.51 (m, 3 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1 (2C), 73.8, 105.4 (2C), 123.7, 123.9, 126.5 (2C), 128.2, 128.65 (2C), 129.1, 132.9, 152.6 (2C), 153.8; anal. calcd. for $C_{17}H_{18}O_3$: C 75.53, H 6.71; found: C 74.98, H 6.65%.

1-Fluoro-4-(3-phenyl-allyloxy)-benzene (Table 3, 3h): White Solid; IR (KBr): 3564, 3390, 3020, 2854, 1635, 1506, 1215 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.59 (d, J = 1.2 Hz, 2 H), 6.31-6.36 (m, 1 H), 6.65 (d, J = 16 Hz, 1 H), 6.81-6.84 (m, 2 H), 6.89-6.93 (m, 2 H), 7.18-7.21 (m, 2 H), 7.24-7.27 (m, 2 H), 7.33-7.35 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.5, 114.2, 116.0 (d, J = 18.7 Hz, 2C), 116.1, 124.5 (2C), 126.7 (2C), 128.7 (2C), 133.3, 136.6, 155.8 (d, J = 207.5 Hz, 1C), 158.7; anal. calcd. for $C_{15}H_{13}FO$: C 78.93, H 5.74; found: C 78.81, H 5.82%.

(4-(cinnamyloxy)phenyl)methanol (Table 3, 3j): Yellowish viscous liquid; IR (neat): 3645, 3583, 3415, 3361, 3294, 3242, 2927, 2856, 1747, 1650, 1508 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (s, 2H), 4.73 (d, J = 6.5 Hz, 2H), 6.41-6.47 (m, 1H), 6.76 (d, J = 16.0 Hz, 1H), 6.98 (d, J = 8.4 Hz, 1H), 7.26-7.34 (m, 5H), 7.36 (d, J = 7.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 65.2, 68.9, 115.1 (2C), 124.5, 126.7, 128.1 (2C), 128.7 (2C), 128.8 (2C), 133.2, 136.6, 158.4; anal. calcd. for $C_{16}H_{16}O_2$: C 79.97, H 6.71; found: C 80.06, H 6.68%.

2-(4-(cinnamyloxy)-phenyl)-acetonitrile (Table 3, 3k): White Solid; IR (KBr): 3406, 2924, 2853, 2251, 1953, 1731, 1612, 1512, 1462, 1247, 1014 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.62 (s, 2 H), 4.63 (d, J = 5.6 Hz, 2 H), 6.31-6.35 (m, 1 H), 6.66 (d, J = 16 Hz, 1 H), 6.89 (d, J = 8.4 Hz, 2 H), 7.16-7.35 (m, 7 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.8, 68.7, 114.0, 115.4 (2C), 118.1, 122.0, 124.1, 126.6 (2C), 127.9, 128.6 (2C), 129.1 (2C), 133.3, 158.4; anal. calcd. for $C_{17}H_{15}NO$: C 81.90, H 6.06, N 5.62; found: C 81.88, H 6.11, N 5.66%.

7-(3-phenyl-allyloxy)-quinoline (Table 3, 3m): Dirty white solid; IR (KBr): ν 3382, 3066, 2959, 2863, 2752, 2682, 1634, 1598, 1442, 1381, 1221, 1040 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.69 (d, J = 6 Hz, 2 H), 6.36-6.41 (m, 1 H), 6.68 (d, J = 16 Hz, 1 H), 7.27-7.48 (m, 7 H), 7.68 (d, J = 5.6Hz, 1 H), 7.83 (d, , J = 8.8 Hz, 1 H), 8.28 (d, J = 5.6Hz, 1 H), 9.09 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.7, 108.3, 120.6, 123.7, 124.2, 126.5, 126.9 (2C), 128.4, 128.6, 129.0, 129.1 (2C), 131.1, 133.4, 140.3, 150.8, 156.7; anal. calcd. for $C_{18}H_{15}NO$: C 82.73, H 5.79, N 5.36; found: C 81.78, H 5.66, N 5.41%.

(*E*)-1-bromo-4-((3-(*p*-tolyl)-allyl)-oxy)-benzene (Table 3, 3n): White solid; IR (KBr): 3375, 2933, 2863, 1742, 1650, 1606, 1509, 1463, 1380, 1287, 1241, 1175, 1105, 1063, 1032 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.97 (s, 3 H), 4.58 (d, J = 6.0 Hz, 2 H), 6.26 (m, 1 H), 6.61 (d, J = 16.0 Hz, 1 H), 6.76 (d, J = 8.8 Hz, 2 H), 7.06 (d, J = 8.0 Hz, 2 H), 7.23 (d, J = 8.0 Hz, 2 H), 7.29-7.32 (m, 2 H).; ^{13}C NMR (75 MHz, $CDCl_3$): δ 21.8, 68.9, 114.0, 116.6 (2C), 122.8, 126.5, 126.6 (2C), 129.3 (2C), 132.2 (2C), 133.5, 137.9, 157.7; anal. calcd. for $C_{16}H_{15}BrO$: C 63.38, H 4.99; found: C 63.41, H 4.83%.

1-(4-bromocinnamyloxy)-4-bromobenzene (Table 3, 3r): White Solid; IR (KBr): 3368, 3081, 2932, 2854, 1780, 1604, 1591, 1496, 1463, 1378, 1290, 1175, 1117 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.65 (d, J = 4.4 Hz, 2 H), 6.36-6.39 (m, 1 H), 6.66 (d, J = 16 Hz, 1 H), 6.83 (dd, J_1 = 2 Hz, J_2 = 4.8 Hz, 2 H), 7.27 (d, J = 7.6 Hz, 2 H), 7.38 (d, J = 4.8 Hz, 2 H), 7.45 (d, J = 6.8 Hz, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 67.6, 113.0, 115.5, 120.8, 123.7, 127.7, 127.1, 130.7, 130.9, 131.3, 138.3, 156.7; anal. calcd. for $C_{15}H_{12}Br_2O$: C 48.95, H 3.29; found: C 48.88, H 3.34%.

1-(2-methoxycinnamyloxy)-4-methyl benzene (Table 3, 3s): Pale yellow solid; IR (KBr): 3397, 3031, 2958, 2914, 2840, 2052, 1895, 1655, 1606, 1510, 1461, 1383, 1328, 1283, 1241, 1177, 1111, 1031 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.21 (s, 3 H), 3.77 (s, 3 H), 4.59 (d, J = 0.8 Hz, 2 H), 6.33-6.4 (m, 1 H), 6.78-6.87 (m, 4 H), 6.95-7.02 (m, 3 H), 7.14-7.18 (m, 1 H), 7.39 (dd, J_1 = 1.2 Hz, J_2 = 7.6 Hz, 1 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 22.3, 55.0, 68.9, 110.5, 114.3 (2C), 120.2, 125.0, 125.2, 126.8, 127.7, 128.5, 129.6 (2C), 129.5, 156.3, 156.4; anal. calcd. for C17H18O2: C 80.28, H 7.13; found: C 80.67, H 7.11%.

(2*E*)-3-(4-(cinnamyloxy)-phenyl)-1-phenylprop-2-en-1-one (Table 3, 3t): White Solid; IR (KBr): 3393, 3026, 2923, 2853, 1904, 1660, 1631, 1601, 1509, 1445, 1381, 1333, 1290, 1248, 1178, 1113, 1070, 1008 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.76 (dd, J_1 = 1.2 Hz, J_2 = 6 Hz, 2 H), 6.38-6.45 (m, 1 H), 6.75 (d, J = 16 Hz, 1 H), 6.99 (d, J = 8.8 Hz, 2 H), 7.26-7.28 (m, 1 H), 7.32-7.36 (m, 2 H), 7.41-7.44 (m, 3 H), 7.48-7.52 (m, 2 H), 7.56-7.58 (m, 1 H), 7.59-7.63 (m, 2 H), 7.79 (d, J = 15.6 Hz, 1 H), 8.00-8.02 (m, 2 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 68.7,

115.2 (2C), 119.9, 123.7, 126.6 (2C), 127.8, 128.0, 128.3 (2C), 128.4 (2C), 128.5 (2C), 130.2 (2C), 132.5, 133.4, 136.2, 138.5, 144.6, 160.7, 190.5; HR-MS (EI): m/z=341.1542 ($M+H^+$), calcd. for $C_{24}H_{20}O_2$: 341.1540.

1-Chloro-4-(3-phenyl-allyloxymethyl)-benzene (Scheme 4, 5a): Yellow viscous liquid; IR (neat): 3355, 3050, 2952, 2920, 2760, 1911, 1605, 1490, 1468, 1360, 1298, 1288, 1274, 1109, 1085 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 4.26 (d, J = 4.4 Hz, 2 H), 4.59 (s, 2 H), 6.27-6.34 (m, 1H), 6.56 (d, J = 16.0 Hz, 1 H), 7.21-7.36 (m, 9 H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 63.0, 63.7, 126.0 (2C), 127.3, 127.8 (2C), 127.9, 128.1 (4C), 130.7, 132.8, 136.3, 138.9; anal. calcd. for $C_{16}H_{15}ClO$: C 74.27, H 5.84; found: C 74.21, H 5.66%.

Conclusions

In conclusion, we have demonstrated the synthesis of polymer supported air- and moisture-stable, oxygen-insensitive and reusable palladium(II) catalyst and its application for the *O*-allylation of allyl/cinnamyl acetates with substituted phenol under refluxing condition in water. Ease of recovery and reuse of the catalyst make this method an economic and environmentally-benign process. In addition, high yields, excellent stereo- specificity, use of water as solvent, scope of wide functionalization and simple work-up procedure make this method more attractive and valuable to the existing methodologies for allylic C-O coupling reactions.

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Notes and references

1 (a) J. Tsuji, *Palladium Reagents and Catalysts*. New Perspectives for the 21st Century; Wiley: Chichester, 2004. (b) E. Negishi and A. de Meijre, *Organopalladium Chemistry for Organic Synthesis*; Wiley: New York, 2002; (c) J. Hartwig, *Organotransition Metal Chemistry*; University Science Books: Sausalito, CA, 2010 (d) N. Miyaura and A. Suzuki, *Chem. Rev*., 1995, **95**, 2457; (e) N. Selander and K. J. Szabo, *Chem. Rev*. 2011, **111**, 2048-2076; (f) T. W. Lyons and M. S. Sanford, *Chem. Rev*., 2010, **110**, 1147-1169.

2 (a) M. J. Climent, A. Corma and S. Iborra, *RSC Adv*., 2012, **2**, 16-58; (b) N. Mizuno and M. Misono, *Chem. Rev*., 1998, **98**, 199-217; (c) J. Lu and P. H. Toy, *Chem. Rev*., 2009, **109**, 815-838.

3 (a) P. A. Grieco, Organic Synthesis in Water; Blackie Academic and Professional: London, 1998.; (b) Z. P. Demko and K. B. Sharpless, *J. Org. Chem*., 2001, **66**, 7945; (c) C. J. Lee, *Chem. Rev*., 2005, **105**, 3095.

4 (a) B. M. Trost, *J. Am. Chem. Soc.* 1979, **101**, 6432- 6433; (b) Y. Uozumi, H. Danjo and T. Hayashi, *Tetrahedron Lett.* 1997, **38**, 3557-3560; (c) M. Zecca, R. Fisera, G. Palma, S. Lora, M. Hronec and M. Kra'lik, *Chem.-Eur. J.* 2000, **6**, 1980-1986; (d) C. A. Parrish and S. L. Buchwald, *J. Org. Chem.* 2001**, 66**, 3820-3827; (e) Y. Niu, L. K. Yeung and R. M. Crooks, *J. Am. Chem. Soc.* 2001, **123**, 6840-6846; (f) A. M. Jansson, M. Grotli, K. M. Halkes and M. Meldal, *Org. Lett.* 2002, **4**, 27-30.

5 S. M. Islam, A. S. Roy, P. Mondal and N. Salam, *Applied Organometallic Chemistry,* 2012**, 26,** 625-634.

6 (a) A. S. Roy, J. Mondal, B. Banerjee, P. Mondal, A. Bhaumik and S. M. Islam, *Applied Cetalysis A: General*, 2014, **469***,* 320-327; (b) S. M. Islam, S. Mondal, P. Mondal, A. S. Roy, K. Tuhina, M. Mobarok, S. Paul, N. Salam and D. Hossain, *Catalysis letters*, 2011, **141,** 1171-1181.

7 S. M. Islam, A. S. Roy, P. Mondal and N. Salam, *Journal of Molecular Catalysis A: General,* 2012, **358**, 38-48.

8 (a) J. Buckingham, *Dictionary of Natural Products*, University Press, Cambridge, MA, 1994; (b) B. M. Trost and P. Renaud, *J. Am. Chem. Soc.*, 1982, **104**, 6668-6672; (c) B. M. Trost and J. P. Geneˆt, *J. Am. Chem. Soc.*, 1976, **98**, 1816-1817.

9 (a) J. Tsuji, *In Handbook of Organopalladium Chemistry for Organic Synthesis*, (Eds. : E. Negishi), Wiley, New York, 2002, Vol. 5, pp. 1669-1687; (b) B. M. Trost and D. L. VanVranken, *Chem. Rev.,* 1996, **96**, 395-422; (c) S. A. Godleski, in: *Comprehensive Organic Synthesis*, (Eds. : B. M. Trost, I. Fleming), Pergamon, Oxford, 1991, Vol. 4, pp. 585-661.

10 (a) A. Monte, M. S. Kabir, J. M. Cook, M. Rott, W. R. Schwan and L. U.S. Defoe, *Pat. Appl. Publ.,* 2007, **37**; (b) O. E. O. Hormi and L. Hirvela, *Tetrahedron Lett*., 1993, **34**, 6463-6466; (c) D. Gopal and K. Rajagopalan, *Tetrahedron Lett*., 1987, **28**, 5327-5330.

11 (a) S. Tanaka, H. Saburi, Y. Ishibashi and M. Kitamura, *Org. Lett*., 2004, **6**, 1873-1875.

12 (a) A. Heumann, *In Transition Metals for Organic Synthesis*; M. Beller, C. Bolm, Eds.; *Wiley-VCH*: Weinheim, Germany, 2004; vol. 1, p 251; (b) B. M. Trost and T. S. Scanlan, *Tetrahedron Lett*., 1986, **27**, 4141-4144; (c) B. M. Trost and D. L. Van Vranken, *Chem. Rev*., 1996, **96**, 395-422; (d) M. Johannsen and K. A. Jorgensen, *Chem. Rev*., 1998, **98,** 1689-1708; (e) Y. Yatsumonji, Y. Ishida, A. Tsubouchi and T. Takeda, *Org. Lett*. 2007, **9**, 4603-4606; (f) C. Juslen and T. Enkvist, *Acta Chem. Scand*., 1958, **12**, 287-297; (g) B. C. Ranu and R. Jana, *Adv. Synth. Catal*., 2005, **347**, 1811-1818; (h) S. Vijaikumar and K. Pitchumani, *J. Mol. Catal. A: Chem*., 2004, **217**, 117-120; (i) R. N. Salvatore, R. A. Smith, A. K. Nischwitz and T. Gavin, *Tetrahedron Lett.,* 2005, **46**, 8931-8935; (j) R. S. Varma and T. I. Reddy, *Chem. Commun*. 1997, 621-622.

13 B. M. Trost and T. R. Verhoeven, *J. Am. Chem. Soc*. 1980, **102**, 4730-4743.

14 (a) J. Tsuji, *Transition Metal Reagents and Catalysts*; Wiley: New York, 2000; (b) S. A. Godleski, *In Comprehensive Organic Synthesis*; B. M. Trost, I. Fleming, Eds.; Pergamon: Oxford, 1991, Vol. 4, p. 585. (c) M. Shibasaki, *In Advances in Metal-Organic Chemistry*; Liebeskind, L. S., Ed.; JAI: Greenwich, CT, 1996; Vol. 5; (d) P. J. Harrington, *In Comprehensive Organometallic Chemistry II*; E. W. Abel, F. G. A. Stone, G. Wilkinson, Eds.; Pergamon: Oxford, 1995; Vol. 12, p. 798-903. (e) *Comprehensive Asymmetric Catalysis*; E. N. Jacobsen, A. Pfaltz, H. Yamamoto, Eds.; Springer: Berlin, 1999; Vol. 2; (f) J. Tsuji, *Palladium Reagents and Catalysts: Innovations in Organic Synthesis*, John Wiley and Sons, New York, 1995.

15 (a) B. M. Trost, R. Madsen, S. D. Guile and B. Brown, *J. Am. Chem. Soc*., 2000, **122**, 5947-5956; (b) T. M. Pedersen, E. L. Hansen, J. Kane, T. Rein, P. Helquist, P.-O. Norrby and D. Tanner, *J. Am. Chem. Soc*., 2001, **123**, 9738-9742; (c) M. E.

Krafft, A. M. Wilson, Z. Fu, M. J. Procter and O. A. Dasse, *J. Org. Chem.,* 1998, **63**, 1748-1749; (d) H. Nakamura, K. Aoyagi, J.-G. Shim and Y. Yamamoto, *J. Am. Chem. Soc*., 2001, **123**, 372-377.

16 (a) S. L. You, X. Z. Zhu, Y. M. Luo, X. L. Hou and L. X. Dai, *J. Am. Chem. Soc.,* 2001, **123**, 7471-7472; (b) T. Konno, K. Nagata, T. Ishihara and H. J. Yamanaka, *Org. Chem*., 2002, **67**, 1768-1775; (c) L. F. Tietze, H. Schirok, M. Wohrmann and K. Schrader, *J. Org. Chem*., 2000, **65**, 2433-2444; (d) M.-C. Liao, X.-H. Duan and Y.-M Liang, *Tetrahedron Lett*., 2005, **46**, 3469-3472.

17 (a) S. Ahammed, A. Saha and B. C. Ranu**,** *RSC Adv*., 2012, **2,** 6329-6335; (b) Y. Yatsumonji, Y. Ishida, A. Tsubouchi and T. Takeda, *Org. Lett*., 2007, **9**, 4603-4606; (c) S. Divekar, M. Safi, M. Soufiaoui and D. Sinou, *Tetrahedron,* 1999, **55**, 4369-4376; (d) T. Ishiyama, M. Mori, A. Suzuki and N. Miyaura, *J. Organomet. Chem*., 1996**, 525,** 225-232; (e) H. Danjo, D. Tanaka, T. Hayashi and Y. Uozumi, *Tetrahedron,* 1999, **55***,* 14341-14352.

18 A. W. Williamson, *J. Chem. Soc.,* 1852, **4**, 229-239.

19 (a) R. Akiyama and S. Kobayashi, *J. Am. Chem. Soc.,* 2003, **125**, 3412-3413; (b) T. Satoh, M. Ikeda, M.Miura and M. Nomura, *J. Org. Chem.,* 1997, **62**, 4877-4879; (c) C. Goux, M. Massacret, P. Lhoste and D. Sinou, *Organometallics*, 1995, **14**, 4585-4593; (d) Y. Kayaki, T. Koda and T. Ikariya, *J. Org. Chem.,* 2004, **69**, 2595-2597; (e) H. Kim and C. Lee*, Org. Lett.,* 2002, **4**, 4369-4371; (f) F. L. Lam, T. T.-L. Au-Yeung, F. Y. Kwong, Z. Zhou, K. Y. Wong and A. S. C. Chan, *Angew. Chem. Int. Ed.,* 2008, **47**, 1280-1283.

20 (a) H. Saburi, S. Tanaka and M. Kitamura, *Angew. Chem. Int. Ed*., 2005, **44**, 1730-1732; (b) Z. Sahli, N. Derrien, S. Pascal, B. Demerseman, T. Roisnel, F. Barriere, M. Achard and C. Bruneau, *Dalton Trans.,* 2011, **40**, 5625-5630; (c) J. A. v. Rijn, E. v. Stapele, E. Bouwman and E. Drent, *J. Catal*., 2010, **272**, 220-226; d) R. C. v. d. Drift, M. Vailati, E. Bouwman and E. Drent, *J. Mol. Catal. A: Chem*., 2000, **159**, 163-177; (e) J. A. v. Rijn, M. A. Siegler, A. L. Spek, E. Bouwman and E. Drent, *Organometallics,* 2009, **28**, 7006-7014; (f) M. Austeri, D. Linder and J. Lacour, *Adv. Synth. Catal.,* 2010, **352**, 3339-3347.

21 H. Nakagawa, T. Hirabayashi, S. Sakaguchi and Y. Ishii, *J.Org. Chem.,* 2004, **69**, 3474-3477.

22 Y. Yatsumonji, Y. Ishida, A. Tsubouchi and T. Takeda, *Org. Lett.*, 2007, **9**, 4603-4606.

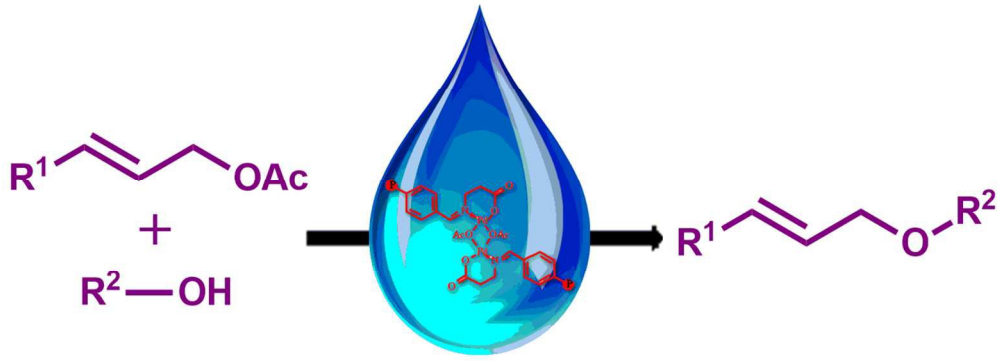
23 (a) A. Saha, J. Leazer and R. S. Varma, *Green Chem*., 2012, **14**, 67-71; (b) R. B. N. Baig and R. S. Varma, *Ind. Eng. Chem. Res*. 2014, **53**, 18625−18629.

24 M. A. Zolfigol, V. Khakyzadeh, A. R.eza Moosavi-Zare, A. Rostami, A. Zare, N. Iranpoor, M. H. Beyzavie and R. Luque, *Green Chem*., 2013, **15**, 2132-2140.

25 M. D. Angelino and P. E. Laibinis, *Macromolecules,* 1998, **31**, 7581-7587.

26 P. A. Stephenson and G. Wilkinson, *Inorg. Nucl. Chem.,* 1967, **29**, 2122-2123.

27 (a) T.-W.Tsai, E.-C. Wang, S.-R. Li, Y.-H. Chen, Y.-L. Lin, Y.-F. Wang and K.-S. Huang, *J. Chinese Chem. Soc.,* 2004, **51**, 1307-1318; (b) W. Wang, R. Zhou, Z.-J. Jiang, K. Wang, H.-Y. Fu, X.-L. Zheng, H. Chen and R.-X. Li, *Adv. Synth. Catal.,* 2014, **356**, 616-622; (c) E. Lindstedt, R. Ghosh and B. Olofsson, *Org. Lett.,* 2013, **15***,* 6070-6073; (d) F. Carta, A. Maresca, A. Scozzafava and C. T. Supuran. *Bioorg. Med. Chem.,* 2012, **20***,* 2266-2273; (e) K. Watanabe, T. Mino, T. Abe, T. Kogure and M. Sakamoto, *J. Org. Chem.,* 2014**, 79***,* 6695-6702; (f) T. Mino, H. Shindo, T. Kaneda, T. Koizumi, Y. Kasashima, M. Sakamoto, T. Fujita, *Tet. Lett*. 2009, **50**, 5358-5360.



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