Journal of Organometallic Chemistry 822 (2016) 189–195

Contents lists available at ScienceDirect

Journal of Organometallic Chemistry

journal homepage: www.elsevier.com/locate/jorganchem

Recyclable Pd(II)complex catalyzed oxidative *sp*^{2} C–H bond acylation of 2-aryl pyridines with toluene derivatives

Pullaiah C. Perumgani [a], Sai Prathima Parvathaneni [a, *], Srinivas Keesara [b], Mohan Rao Mandapati [a, **]

[a] *Catalysis Laboratory, Inorganic and Physical Chemistry Division, CSIR-Indian Institute of Chemical Technology (IICT), Tarnaka, Hyderabad 500 607, India*
[b] *School of Chemistry, University of Hyderabad, Hyderabad 500046, India*

ARTICLE INFO

Article history:
Received 28 June 2016
Received in revised form
24 August 2016
Accepted 25 August 2016
Available online 31 August 2016

Keywords:
Polymer-anchored Pd(II) complex C
Ortho-acylation
2-Aryl pyridines
Cross dehydrogenative coupling
Toulene
TBHP

ABSTRACT

A recyclable polymer–anchored Pd(II) complex **C** was synthesized and characterized using different spectroscopic techniques. In addition the catalytic efficiency of the Pd (II) complex **C** was evaluated for *ortho*-acylation of 2-aryl pyridines with toluene derivatives to form aryl ketones via cross dehydrogenative coupling. In this catalytic process toluene acts as an effective coupling partner upon *sp*^{3} C–H bond oxidation for *sp*^{2} C–H bond acylation of 2-aryl pyridines in the presence of Pd(II)/TBHP system on water. Furthermore, the catalyst **C** was highly stable and could be easily recovered and reused for four cycles with no significant decrease in its activity and selectivity.

1. Introduction

The direct aromatic C–H bond functionalization is one of the most challenging and reliable strategy to construct C–C and C–heteroatom bonds [1]. Among the various C–H activation techniques, the directing group assisted C–H bond activation and dehydrogenative cross-coupling are most facile methods that has gained considerable attention over traditional cross-coupling methods [2]. Benzophenones constitute prominent structural motifs of top 200 most-sold pharmaceuticals that exhibit broad spectrum of biological activities including cholesterol regulation(-Tricor), anti-inflammatory effects (Sector), and selective estrogen receptor modulation (Evista) [3]. Several methods for the introduction of a carbonyl moiety have been developed, including the traditional Friedel–Crafts acylation, the coupling of aryl compounds with aliphatic olefins and carbon monoxide in presence of Ru has been generally employed [4]. These methods however showed poor selectivity and formation of waste materials due to the use of excess Lewis acids. Further the use of expensive ruthenium catalyst, handling of carbon monoxide and generation of high reaction temperature suggests that new sustainable methods are highly desirable.

In order to solve the selectivity issue, direct transformations such as arylation, olefination, halogenation, and amination with the assistance of conventional directing groups like pyridines, amides, esters, imines, ketones, oxazolines, and nitriles have been reported [5]. In contrast carbonylative C–H bond functionalizations (acylation) have been investigated to a lesser extent. Transition metal catalyzed C–H activation of arenes has been achieved mostly by employing palladium, ruthenium, rhodium, copper and Iron catalysts [6]. To the best of our knowledge aldehydes, alcohols, α-oxocarboxylic acids, arylmethyl amines, carboxylic acids, diketones, benzylic ethers and CO with PhI as acyl sources for transition-metal-catalyzed carbonylative coupling reactions of directed group assisted arene C–H bonds have been described [7]. Among them, the catalytic cycle between Pd(II) and Pd(IV) is one of the major pathways [8], in which a number of oxidants such as $K_2S_2O_8$, TBHP, BQ, DDQ, PIDA have been widely employed. Organic reactions conceded 'On-water' have become one of the most intriguing area of research in green chemistry as it is universal medium for all chemical reactions of life [9]. The pioneering work for rate

---

* Corresponding author.
** Corresponding author.
E-mail addresses: saiprathimaiict@gmail.com (S.P. Parvathaneni), mandapati@iict.res.in (M.R. Mandapati).

http://dx.doi.org/10.1016/j.jorganchem.2016.08.028
0022-328X/© 2016 Elsevier B.V. All rights reserved.

enhancements “on water” was first demonstrated by Breslow and Sharpless inspired the intense research “on water” catalysis [10]. Design and development of efficient catalytic processes with energy minimization, replacement of toxic catalysts and hazardous solvents with relatively benign solvents such as water, catalyst-free synthesis, and high atom economy are some of the most essential components of an ideal green synthesis [11].

Despite great achievements in green catalysis, most of the organic transformations are incompatible with water since most of the organic compounds do not dissolve in water while solubility is generally considered a prerequisite for reactivity. This tends to be an important challenge and emerging as an attractive area of research for organic chemists.

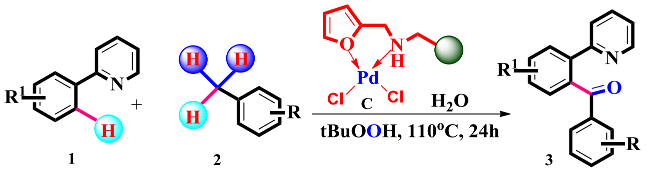
Polystyrene is one of the most commonly employed reliable polymeric support due to its low cost, ready availability and chemical inertness in recent years. A variety of polymer-supported metal catalysts for the C–C coupling reactions were reported [12].

In terms of green and environmental perspective cross dehydrogenative coupling, commercially available alkyl benzenes as acylating agents is considered as ideal, eco-economical protocol. Carbon-carbon bond formation via C–H activation in water is another potential clean process that can have both high atom efficiency and easy recycling of the catalyst.

Recently, palladium-catalyzed oxidative *ortho*-acylation of inactive C(sp2)–H bonds via C–H, C–C, and C–O bond cleavage of toluenes was reported for the synthesis of aromatic ketones [13].

In view of minimizing the waste/side product formation the use of toxic gaseous carbon monoxide and homogeneous Pd catalyst stands as hindrance for economical and sustainable chemistry for the reported methods. In all the above-mentioned procedures for ortho-acylation reactions, the Pd catalysts used are homogeneous in nature and suffer from several drawbacks, such as they may easily be destroyed during the course of the reaction [14]. So, the catalysts are not easily separable from reaction mixtures and they are non-recyclable. In order to overcome the problems associated with homogeneous catalysts and with the growing demand for sustainable synthesis the direct catalytic C–H functionalization under mild reaction conditions becomes highly essential. More Recently homogeneous conditions were replaced with supported palladium nanoparticles in ortho-directed CDC reactions of alkyl benzenes [15]. The main advantage of the given polymeric complex of palladium (II) **C** over palladium (0) nanoparticles catalyst is mainly in twice less loading and better recyclability.

We mainly focused on developing simple, economical, green pathway for carbonylation reaction/ortho-acylation of 2-phenylpyridine. In view of continuous interest to develop simple recyclable polymer bound metal complexes [16], herein we report a facile synthesis of benzophenone derivatives by Pd-catalyzed acylation of 2-phenyl pyridines by employing toluene derivatives as the simple coupling partners. However, ortho-acylation product was obtained in excellent yields with recyclable, heterogeneous Palladium complex under on-water conditions with toluene as an acylating partner (Scheme 1). This protocol is highly appreciable due to being atom and step economic for the direct conversion of C–H bonds to C–C bonds for aryl ketone synthesis.



Scheme 1. Palladium-catalyzed direct *ortho*-acylation of arenes. DG = directing group.

Herein, we report the synthesis and characterization of a new polymer supported furan-2-ylmethanamine derived palladium(II) complex (PS-FMA–Pd) as an effective and highly reusable catalyst for the synthesis of benzophenone derivatives from toluene derivatives and TBHP as the oxidant under on-water conditions. Thus, the synthesized polymer-anchored Pd(II) catalyst showed efficient catalytic application towards a carbonylation reaction in a green pathway without employing carbon monoxide or base or solvent under phosphine free conditions.

2. Experimental

2.1. Material and instruments

Analytical-grade reagents and freshly distilled solvents were used throughout the experiment. The reagents were supplied by Sigma-Aldrich Chemicals Company, USA and Merck Co. Liquid substrates were redistilled and dried with appropriate molecular sieves. Distillation and purification of the solvents and substrates were done by standard procedures.[16] The starting materials and reagents were purchased from various commercial sources and used without further purification. ACME silica gel (60–120 mesh) was used for column chromatography. Analytical thin-layer chromatography (TLC) was performed on pre-coated TLC plates with silica gel 60-F_{254} plates and visualized by UV-light. ^1H NMR and ^{13}C NMR spectra were recorded, using tetramethylsilane (TMS) in the solvent of $CDCl_3$ as the internal standard on a 400, 500 MHz spectrometer (^1H NMR: TMS at 0.00 ppm, $CDCl_3$ at 7.26 ppm; ^{13}C NMR: $CDCl_3$ at 77.00 ppm). Chemical shifts (δ) were recorded in ppm with respect to TMS as an internal standard and coupling constants are quoted in Hertz (Hz). Mass spectra were recorded on a mass spectrometer by the electron spray ionization (ESI) and the data acquired in positive ionization mode. HRMS spectra were determined on TOF type mass analyzer. FTIR spectra of the samples were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. A EXSTAR TG/DTA7200 instrument was used for the thermogravimetric (TGA) analysis. Powder X-ray diffraction patterns of the pure functionalized materials were recorded on a Bruker D-8 Advance diffractometer operated at 40 kV voltage and 40 mA current using a Cu tube ($\lambda = 0.15406$ nm) as the radiation source. TEM analysis was carried out by using a JEOL 2010 TEM operated at 200 kV. The metal content in the catalyst was determined using a Varian AA240 atomic absorption spectrophotometer (AAS).

2.1.1. Synthesis of the catalyst

Preparation of polymer-supported furan-2-ylmethanamine (B) (PS-FMA): A 250 mL round-bottomflask equipped with a magnetic stirrer was charged with CH_3CN (100 mL). To this 1% DVB-crosslinked chloromethylated polystyrene (0.5 g, 2.25 mmol/Cl), furan-2-ylmethanamine A (2.3 mL, 22.5 mmol), and NaI (14.9 mg, 0.1 mmol) were added and the mixture was refluxed for 48 h. The mixture was filtered and the residue was washed sequentially with CH_3CN (3 × 20 mL), 1:1 CH_3OH–1M aq K_2CO_3 (3 × 20 mL), 1:1 CH_3OH–H_2O (3 × 20 mL), and Et_2O (3 × 10 mL), and then dried in an oven.

2.1.2. Preparation of polystyrene-supported Pd(II) complex (C) (PS-FMA-Pd)

To the polystyrene-supported furan-2-ylmethanamine B (0.5 g), EtOH (100 mL) was added and kept for 30 min. A solution of $Pd(CH_3CN)_2Cl_2$ (0.5 g) in EtOH (10 mL) was then added, and the (1:1) mixture was refluxed for 12 h. The polymer-anchored brown colored metal complex, impregnated with the metal, was filtered, washed thoroughly with EtOH (3 × 30 mL), and finally dried in vacuum at 70 °C for 24 h (Scheme 2).

2.1.3. General procedure for carbonylation catalyzed by polymer anchored-Pd(II) C

A dried round bottomed flask equipped with a magnetic stir bar was charged with 25 mg Polymer anchored-Pd(II) C catalyst (PS-FMA-Pd), 2-phenyl pyridine (0.5 mmol), toluene (1.0 mmol), TBHP (2.0 mmol) and water (0.5 mL) were added to a reaction vessel. The mixture was stirred at 110 °C for 24 h, then cooled to room temperature and catalyst was filtered, the filtrate was extracted with ethyl acetate (3 × 10 mL). The combined organic layers were extracted with water, and dried over anhydrous Na_2SO_4. The organic layers were evaporated under reduced pressure and the resulting crude product was purified by column chromatography by using ethyl acetate/hexane(1:4) as eluent to give the corresponding ortho-acylation products. The products were characterized by ^1H NMR, ^{13}C NMR and HRMS.

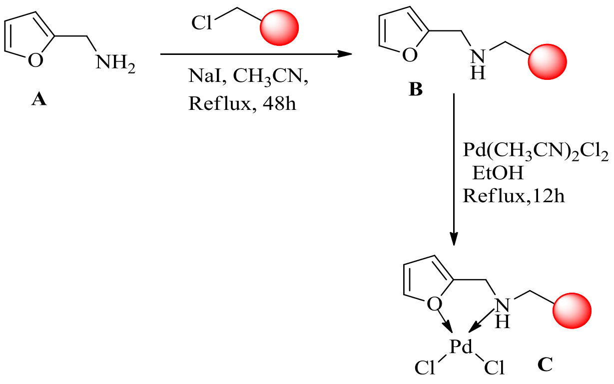
3. Results and discussion

3.1. Synthesis and characterization of the polymer supported Pd(II) catalyst C

The new polymer supported Pd(II) catalyst C was prepared in two steps according to the reported procedure [16]. Complex C was fully characterized by chemical analysis, SEM-EDX, TGA, AAS and IR spectroscopic techniques. The complexation ratio of palladium to PS-FMA is 1:1. The exact palladium content of the heterogeneous catalyst was determined by atomic absorption spectroscopy (AAS) suggests 5.33% of metal per gram. The coordination of palladium metal on polymer supported ligand was confirmed by FT-IR spectra. We observed a sharp peak at 1263 cm^{-1} in chloromethylated polystyrene IR spectrum, which corresponding to C–Cl group. This peak was practically eliminated after the introduction of furan-2-ylmethanamine, and palladium onto the polymer. The decreasing IR value of the NH group (from 3448 cm to 1 to 3423 cm−1) in polystyrene-supported ligand to complex is indicating the formation of Pd–N bond.

Scanning electron micrographs were reported for PS-FMA ligand and the supported PS-FMA–Pd catalyst to study the morphological changes. The SEM images of the polymer supported ligand and Pd(II) catalyst clearly showed the morphological change on the surface of polystyrene after loading of metal on it (Fig. 1).

An energy dispersive spectroscopy analysis of X-rays (EDX) data for the PS-FMA and PS-FMA–Pd catalyst is given in Fig. 2 (A, B). The EDX data also inform that the attachment of palladium metal on the surface of the polymer matrix. The EDX image of the PS-FMA–Pd complex (Fig. 2B) confirms the presence of the respective atoms: C, N, O, Cl and Pd.



Scheme 2. Synthesis of polymer-bound furan-2-ylmethanamine derived Pd(II) complex.

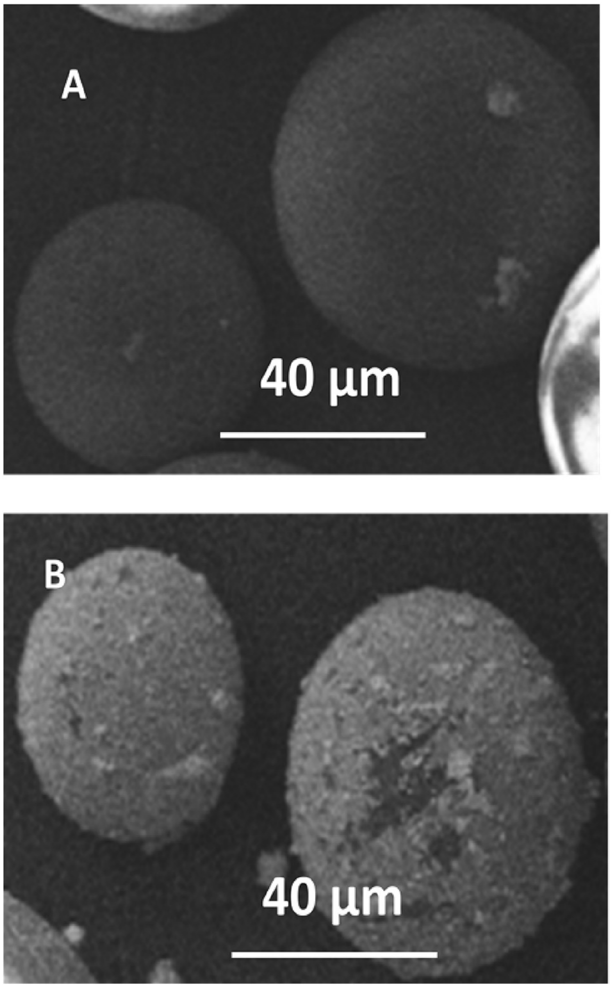


Fig. 1. SEM images of the polymer anchored ligand PS-FMA (A) and PS-FMA–Pd (B) complex.

3.2. Catalytic activity

Thermal stability of the complex was investigated using thermogravimetric analysis (TGA) at a heating rate of 10 °C min-^{1} over a temperature range of 30–500 °C. The TGA curve of the polymer anchored catalyst is shown in Fig. 3. The initial sharp weight loss up to 150 °C may be due to the pore occupancy by solvent molecules and moistures. The complex C is stable up to 330 °C and thermal decomposition of the catalyst starts above this temperature. Thermogravimetric study of the complex **C** suggests that the polymer anchored catalyst is very useful for high temperature reactions.

As polymer anchored metal complexes exhibit efficient catalytic activity with broad applicability they have been extensively studied and reported in the literature. In our previous reports we have studied their catalytic activity in the field of coupling reactions [15]. Now we decided to investigate the catalytic activity of the PS-FMA–Pd catalyst to prepare benzophenones via the carbonylation reaction with toulenes without using carbon monoxide.

Initial experiments were carried out using 2-phenylpyridine **1a** as a model substrate, Toulene **2a** as acyl coupling partner with Pd (II) complex C and water as solvent. Different oxidants such as H_2O_2, $K_2S_2O_8$, O_2, *tert*-butyl hydroperoxide (TBHP), *tert*-butyl

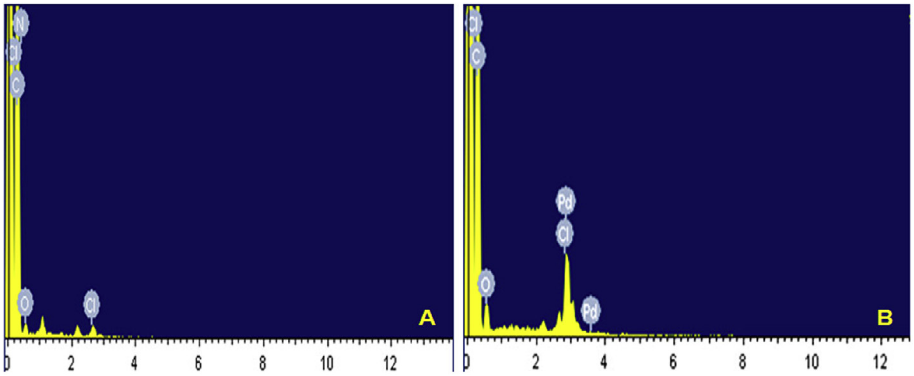


Fig. 2. EDX image of the polymer anchored ligand PS-FMA (A), polymer anchored complex PS-FMA–Pd(B).

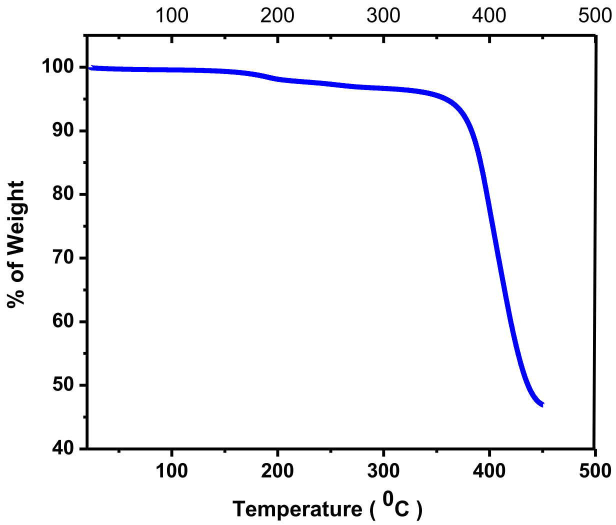
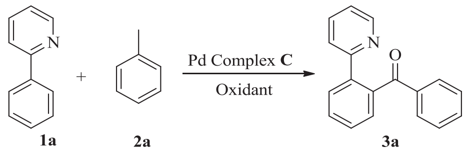


Fig. 3. TGA curve of a Polymer anchored Pd(II) catalyst.

peroxybenzoate (TBPB) were screened under various temperatures as shown in Table 1. However with oxidants such as H_2O_2, $K_2S_2O_8$, O_2, *tert*-butyl peroxybenzoate (TBPB) the desired product was not obtained even at 110 °C for 24 h (entries 1–3 and 5). To our delight, *tert*-butyl hydroperoxide (TBHP) proved to be the best oxidant at 110 °C for about 24 h and 2-phenylpyridine was obtained in 88% yield in the presence of Pd complex **C** (entry 4). But TBHP was ineffective at room temperature with no yield (entry 6) and low yield at 80 °C (entry 7). There was no considerable change in yields by increasing the temperature from 110 °C to 130 °C and reaction time from 24 to 48 h (entry 8 and 10). Notably lowering the reaction time from 24 to 12 h resulted only in 60% yield (entry 9). As expected the desired product was not obtained even in trace amounts in absence of oxidant, TBHP and catalyst, Pd complex **C** (entries 11–12). But gave good yield of the desired product in 80% even in absence of solvent (entry 13). To know the applicability of the catalyst under various solvent conditions the reaction was carried with different solvents such as DMSO, EtOH, THF, CH_3CN and $CHCl_3$. Among them EtOH, DMSO, CH_3CN gave the desired products 68%, 64% and 54% yields within 24 h, where as $CHCl_3$ and THF took 48 h as shown in Table 2. The above optimization studies shows TBHP at 110 °C on-water, in presence of Pd complex **C** for 24 h gave the desired product **3a** in 88% yield (entry 4, Table 1).

The direct ortho acylation of 2-phenylpyridine with toulene was conducted under optimized reaction conditions, and the results are summarized in Scheme 4. The reactions with toluene derivatives bearing electron-donating groups and electron-withdrawing substituents at the aromatic ring proceeded to give the desired products in good to excellent yields (Scheme 3). There is considerable influence on the yields for *ortho*, *para* and *meta* isomers of toluene derivatives. The *ortho* isomers containing products delivered low yields (**3d**, **3g**, **3j** and **3m**) when compared to *para* or *meta* isomers

Table 1
Screening of reaction conditions.[a]



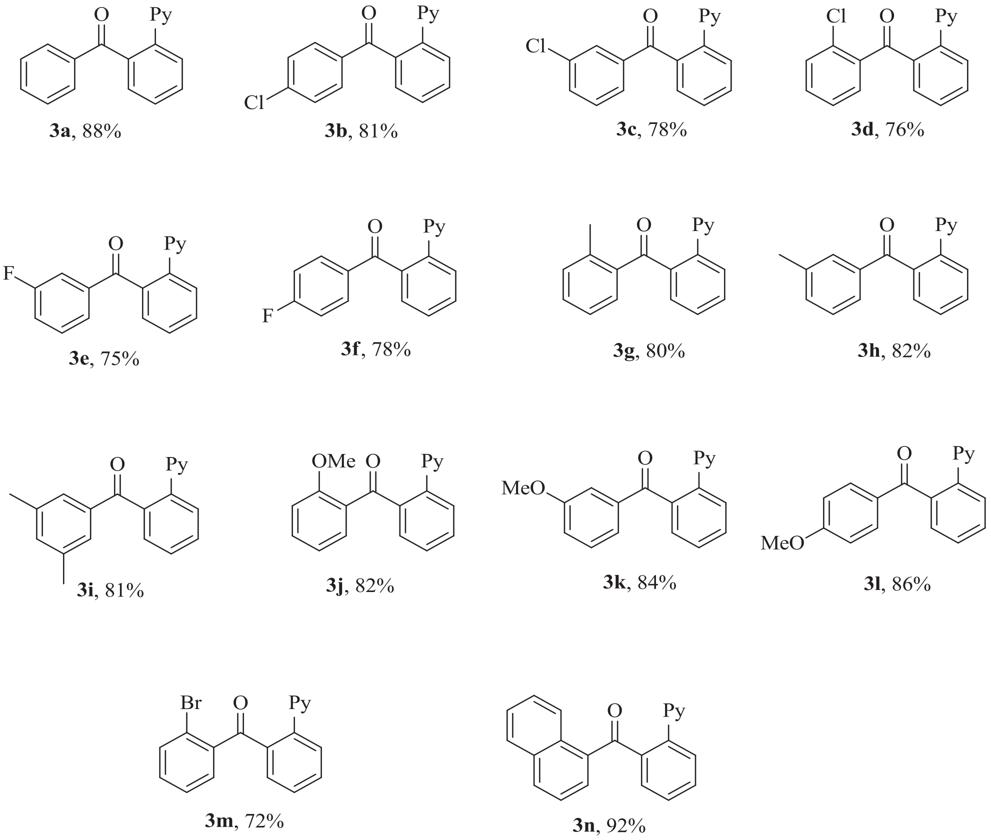
Entry	Oxidant	Temp (°C)	Time (h)	Yield (%)[b]
1	H_2O_2	110	24	10
2	$K_2S_2O_8$	110	24	–
3	O_2 (1 atm)	110	24	–
4	TBHP	110	24	88
5	TBPB	110	24	–
6	TBHP	RT	24	–
7	TBHP	80	24	50
8	TBHP	130	24	86
9	TBHP	110	12	61
10	TBHP	110	48	86
11	–	110	24	–[c]
12	TBHP	110	24	–[d]
13	TBHP	110	24	80[e]

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (25 mg), oxidant (2.0 mmol), water (0.5 mL), air, 24 h.
[b] Isolated yield.
[c] No oxidant.
[d] No catalyst.
[e] No solvent.

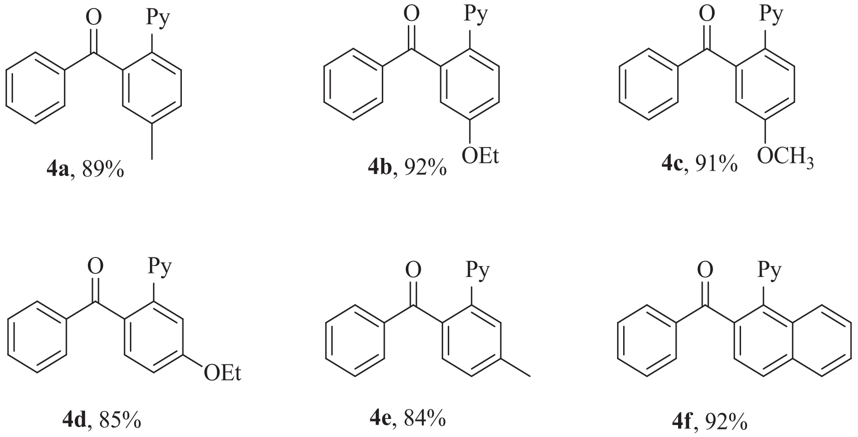
Table 2
Screening of solvents.[a]

Entry	Oxidant	Solvent	Time (h)	Yield (%)[b]
1	TBHP	DMSO	24	64
2	TBHP	EtOH	24	68
3	TBHP	THF	48	10
4	TBHP	CH_3CN	24	54
5	TBHP	$CHCl_3$	48	51

[a] Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (25 mg), solvent (0.5 mL).
[b] Isolated yield.



Scheme 3. Substrate scope for acylation of 2-phenyl pyridine.



Scheme 4. Scope for acylation of substituted 2-Phenyl pyridines.

due to steric hindrance (**3b**, **3f**, **3l** and **3c**, **3e**, **3h**, **3k**). However electron-donating groups substituted toluene products (OMe, CH_3) gave better yields than electron withdrawing substituents (F, Cl and Br). The OMe substituted *para*, *meta*, *ortho* gave (**3l**) 86%, (**3k**) 84%, (**3j**) 82% and Me substituted *meta*, *ortho* resulted in (**3h**) 82%, (**3g**) 80% yields of the desired products. In case of *chloro* substituted *para*, *meta*, *ortho* the desired product was achieved in (**3b**) 81%, (**3c**) 78%, (**3d**) 76% and *fluoro* substituted *para*, *meta* with (**3f**) 78%, (**3e**) 75%, where as *meta* substituted *bromo* gave (**3m**) 72% respectively. The most interesting result is that Ar—Br (**3m**), group tolerated since Pd species might be expected to cleave C—Br bonds easily. Notably disubstituted methyl and napthyl substituted toluene derivatives (**3i**) and (**3n**) gave 79% and 92% yields of acylated products.

In addition, the directed aroylation of 2-arylpyridine with a set of substituted aryl pyridines was performed under the optimized reaction conditions, and the results are presented in Scheme 4. The functional groups including methyl, methoxy, ethoxy and naphthyl were compatible and the desired products were achieved in excellent yields. For example, substituted aryl pyridines with 4-methyl, ethoxy, methoxy (which bears a strong electron-donating group) afforded the desired products **4a**, **4b** and *4c* in 89%, 92% and 91% respectively. Whereas **4d**, **4e** were obtained in 85% and 84% and **4f** in a yield of 92% yield. Thus the aroylation reaction selectively gave the monoacylated products with variety of 2-phenyl pyridines.

The recyclability of the polymer–anchored Pd(II) complex C was tested in the aroylation of 2-phenyl pyridine **1a** and toluene **2a**. As shown in Fig. 4, the catalyst can be reused for five cycles with only 5% decline of activity after the 5th recycle. The leaching of palladium from the polymer anchored palladium(II) complex C was confirmed by carrying out an (EDX, IR and AAS) analysis of the used catalyst as well as the product mixtures. The analytical data of used catalyst did not show appreciable loss in the palladium content as compared to the fresh catalyst. The EDX and IR spectrum of the recycled catalyst was relatively similar to that of the fresh sample, representing the heterogeneity nature of this complex. The metal content of the recycled catalyst was determined with the help of AAS and it was found that there is no considerable loss in palladium content of the recycled catalyst.

To understand the possible reaction pathway, control experiments were conducted in the presence of radical scavenger TEMPO under solvent free conditions. It was observed that desired acylation product **3a** was found in <5%, indicating the possible radical pathway. This clearly demonstrates the dual role of TBHP as an oxidant and a radical initiator.

However during the course of the reaction formation of benzaldehyde was observed that could be possibly via radical oxidation of toluene. Basing on the reported literature [17] and from our studies a tentative mechanism to rationalize this transformation is clearly depicted in Scheme 5. Initially Pd(II) complex **C** activates the *ortho* C–H bond of 2-phenyl pyridine to generate chelation-directed C–H intermediate **D**, which reacts with TBHP resulting in the formation of **E**. This in turn reacts with aldehyde which is produced from the oxidation of toluene, forming the acyl intermediate **F**. This will undergo reductive elimination followed by rapid oxidation generates the product **3a** with regeneration of the catalyst **C**.

4. Conclusion

In summary, we have described an efficient aroylation reaction of 2-phenyl pyridines with toluene derivatives as acylating partners under "on water" conditions. The simple Polymer anchored Pd(II) complex was synthesized and found to be active for selective acylation of ortho-directed CDC reaction of 2-phenyl pyridines with toluene derivatives affording diverse range of aromatic ketones in high yields. This heterogeneous catalyst is stable and can be reused for five cycles without appreciable loss of activity, indicating effective anchoring of the polymer. All the reactions were carried out without any solvent, recyclable Pd complex, TBHP as oxidant with broad substrate scope, low metal loadings, on-water conditions and excellent yields. This eco-economical conditions makes this protocol highly valuable over the existing methods.

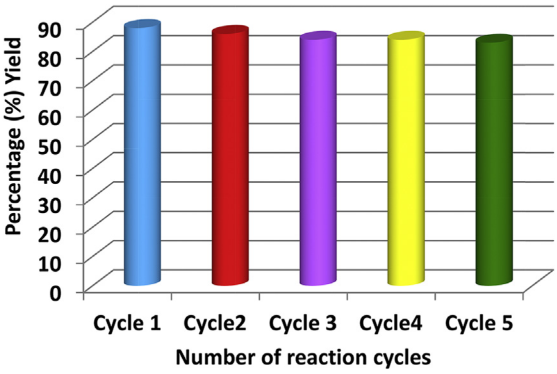
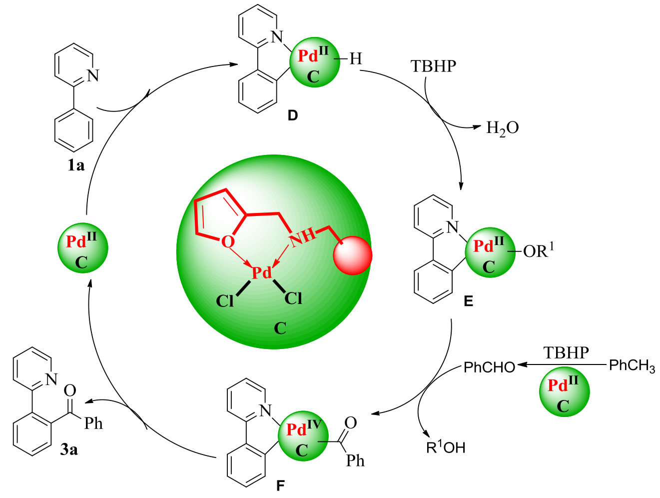


Fig. 4. Recyclability of the Polymer anchored Pd(II) complex **C**.



Scheme 5. Possible reaction mechanism.

Acknowledgements

P. S. P gratefully acknowledge to the financial assistance provided by CSIR-Senior Research Associateship (Scientist's Pool Scheme) CSIR-SRA (IA-27520), New Delhi and PCP (UGC-SRF), thanks for the fellowship provided by UGC, Govt of India. We also acknowledge director IICT for providing infrastructural facilities.

References

[1] (a) C.S. Yeung, V.M. Dong, Chem. Rev. 111 (2011) 1215;
(b) M.M. Diaz-Requejo, P.J. Pérez, Chem. Rev. 108 (2008) 3379;
(c) P. Muller, C. Fruit, Chem. Rev. 103 (2003) 2905;
(d) T. Naota, H. Takaya, S.I. Murahashi, Chem. Rev. 98 (1998) 2599;
(e) L. Ackermann, R. Vicente, A.R. Kapdi, Angew. Chem. Int. Ed. 48 (2009) 9792;
(f) L. Ackermann, Chem. Commun. 46 (2010) 4866.
[2] (a) J.J. Mousseau, A.B. Charette, Acc. Chem. Res. 46 (2013) 412;
(b) D.A. Colby, R.G. Bergman, J.A. Ellman, Chem. Rev. 110 (2010) 624;
(c) O. Daugulis, H.Q. Do, D. Shabashov, Acc. Chem. Res. 42 (2009) 1074;
(d) J.A. Ashenhurst, Chem. Soc. Rev. 39 (2010) 540;
(e) C.J. Scheuermann, Chem. Asian J. 5 (2010) 436.
[3] (a) McGrath, M. Brichacek, J.T. Njardarson, J. Chem. Educ. 87 (2010) 1348;
(b) S. Gmouh, H. Yang, M. Vaultier, Org. Lett. 5 (2003) 2219.
[4] (a) H. Heaney, in: B.M. Trost, I. Fleming (Eds.), Comprehensive Organic Synthesis, vol. 2, Pergamon Press, Oxford, 1991, p. 733;
(b) G.A. Olah, Friedel–crafts and Related Reactions, Wiley-Interscience, New York, 1963;
(c) E.J. Moore, W.R. Pretzer, T.J. O'Connell, J. Harris, L. La-Bounty, L. Chou, S.S. Grimmer, J. Am. Chem. Soc. 114 (1992) 5888;
(d) N. Chatani, T. Fukuyama, F. Kakiuchi, S. Murai, J. Am. Chem. Soc. 118 (1996) 493;
(e) T. Fukuyama, N. Chatani, F. Kakiuchi, S. Murai, J. Org. Chem. 62 (1997) 5647;
(f) N. Chatani, Y. Ie, F. Kakiuchi, S. Murai, J. Org. Chem. 62 (1997) 2604;
(g) Y. Ie, N. Chatani, T. Ogo, D.R. Marshall, T. Fukuyama, F. Kakiuchi, S. Murai, J. Org. Chem. 65 (2000) 1475.
[5] (a) P. Gandeepan, K. Parthasarathy, C.H. Cheng, J. Am. Chem. Soc. 132 (2010) 8569;
(b) T. Nishikata, A.R. Abela, S.L. Huang, B.H. Lipshutz, J. Am. Chem. Soc. 132 (2010) 4978;
(c) F.W. Patureau, F. Glorius, J. Am. Chem. Soc. 132 (2010) 9982;
(d) J. Wen, S. Qin, L.F. Ma, L. Dong, J. Zhang, S.S. Liu, Y.S. Duan, S.Y. Chen, C.W. Hu, X.Q. Yu, Org. Lett. 12 (2010) 2694;
(e) B. Tang, R. Song, C. Wu, Y. Liu, M. Zhou, W. Wei, G. Deng, D. Yin, J.H. Li, J. Am. Chem. Soc. 132 (2010) 8900;
(f) T. Nishikata, B.H. Lipshutz, Org. Lett. 12 (2010) 1972;
(g) X. Chen, K.M. Engle, D.H. Wang, J.Q. Yu, Angew. Chem. Int. Ed. 48 (2009) 5094;
(h) Y.H. Zhang, J.Q. Feng, C.J. Li, J. Am. Chem. Soc. 130 (2008) 2900;

(i) L.V. Desai, K.J. Stowers, M.S. Sanford, J. Am. Chem. Soc. 130 (2008) 13285;
(j) G.W. Wang, T.T. Yuan, X.L. Wu, J. Org. Chem. 73 (2008) 4717;
(k) G.J. Deng, L. Zhao, C.J. Li, Angew. Chem. Int. Ed. 47 (2008) 6278;
(l) A.S. Tsai, R.G. Bergman, J.A. Ellman, J. Am. Chem. Soc. 130 (2008) 6316;
(m) X. Chen, X.S. Hao, C.E. Goodhue, J.Q. Yu, J. Am. Chem. Soc. 128 (2006) 6790;
(n) X.B. Wan, Z.X. Ma, B.J. Li, K.Y. Zhang, S.K. Cao, S.W. Zhang, Z.J. Shi, J. Am. Chem. Soc. 128 (2006) 7416;
(o) H.Y. Thu, W.Y. Yu, C.M. Che, J. Am. Chem. Soc. 128 (2006) 9048;
(p) K. Dipannita, N.R. Deprez, L.V. Deprez, M.S. Sanford, J. Am. Chem. Soc. 127 (2005) 7330.

[6] (a) T.W. Lyons, M.S. Sanford, Chem. Rev. 110 (2010) 1147;
(b) X. Chen, K.M. Engle, D.-H. Wang, J.-Q. Yu, Angew. Chem. Int. Ed. 48 (2009) 5094;
(c) S. Murai, F. Kakiuchi, S. Sekine, Y. Tanaka, A. Kamatani, M. Sonoda, N. Chatani, Nature 366 (1993) 529;
(d) D.A. Colby, R.G. Bergman, J.A. Ellman, Chem. Rev. 110 (2010) 624;
(e) C. He, S. Gou, L. Huang, A. Lei, J. Am. Chem. Soc. 132 (2010) 8273;
(f) M. Sai, H. Yorimitsu, K. Oshima, Angew. Chem. Int. Ed. 50 (2011) 3294;
(g) C.L. Sun, B.J. Li, Z.J. Shi, Chem. Rev. 111 (2011) 1293;
(h) N. Xu, P. Li, Z. Xie, L. Wang, Chem. Eur. J. 22 (2016) 2236;
(i) J.P. Yao, G.W. Wang, Tetrahedron Lett. 57 (2016) 1687;
(j) F.X. Xiong, C. Qian, D. Lin, W. Zeng, X. Lu, Org. Lett. 15 (2013) 5444;
(k) Z.J. Cai, C. Yang, S.Y. Wang, S.J. Ji, J. Org. Chem. 80 (2015) 7928;
(l) H. Tang, C. Qian, D. Lin, H. Jiang, W. Zeng, Adv. Synth. Catal. 356 (2014) 519.

[7] (a) X. Chen, X. Cui, Y. Wu, Org. Lett. 18 (2016) 2411;
(b) Y. Wu, L. Sun, Y. Chen, Q. Zhou, J.W. Huang, H. Miao, H.B. Luo, J. Org. Chem. 81 (2016) 1244;
(c) Y. Wu, B. Li, F. Mao, X. Li, F.Y. Kwong, Org. Lett. 13 (2011) 3258;
(d) Z.Y. Li, D.D. Li, G.W. Wang, J. Org. Chem. 78 (2013) 10414;
(e) M. Kim, J. Park, S. Sharma, A. Kim, E. Park, J.H. Kwak, Y.H. Jung, I.S. Kim, Chem. Commun. 49 (2013) 925;
(f) P. Fang, M. Li, H. Ge, J. Am. Chem. Soc. 132 (2010) 11898;
(g) Y. Shin, S. Sharma, N.K. Mishra, S. Han, J. Paek, H. Oh, J. Ha, H. Yoo, Y.H. Jung, I.S. Kim, Adv. Synth. Catal. 357 (2015) 594;
(h) S. Sharma, M. Kim, J. Park, M. Kim, J.H. Kwak, Y.H. Jung, J.S. Oh, Y. Lee, I.S. Kim, Eur. J. Org. Chem. (2013) 6656;
(i) M. Kim, N.K. Mishra, J. Park, S. Han, Y. Shin, S. Sharma, Y. Lee, E.-K. Lee, J.H. Kwak, I.S. Kim, Chem. Commun. 50 (2014) 14249;
(j) Q. Zhang, F. Yang, Y. Wu, Chem. Commun. 49 (2013) 6837;
(k) J. Lu, H. Zhang, X. Chen, H. Liu, Y. Jiang, H. Fu, Adv. Synth.Catal 355 (2013) 529;
(l) W. Zhou, H. Li, L. Wang, Org. Lett. 14 (2012) 4594;
(m) S. Han, S. Sharma, J. Park, M. Kim, Y. Shin, N.K. Mishra, J.J. Bae, J.H. Kwak, Y.H. Jung, I.S. Kim, J. Org. Chem. 79 (2014) 275;
(n) A. Tlili, J. Schranck, J. Pospech, H. Neumann, M. Beller, Angew. Chem. Int. Ed. 52 (2013) 6293.

[8] (a) A.B. Weinstein, S.S. Stahl, Catal. Sci. Technol. 4 (2014) 4301;
(b) K.J. Stowers, A. Kubota, M.S. Sanford, Chem. Sci. 3 (2012) 3192.

[9] (a) T. Head-Gordon, G. Hura, Chem. Rev. 102 (2002) 2651;
(b) U.M. Lindstrom, Chem. Rev. 102 (2002) 2751;
(c) Y. Hayashi, Angew. Chem. Int. Ed. 45 (2006) 8103;
(d) J. Mlynarski, S. Bas, Chem. Soc. Rev. 43 (2014) 577.

[10] (a) R. Breslow, Acc. Chem. Res. 24 (1991) 159;
(b) R. Breslow, Acc. Chem. Res. 37 (2004) 471;
(c) S. Narayan, J. Muldoon, M.G. Finn, V.V. Fokin, H.C. Kolb, K.B. Sharpless, Angew. Chem. Int. Ed. 44 (2005) 3275.

[11] B.M. Trost, Angew. Chem. Int. Ed. 34 (1995) 259.

[12] (a) M. Bakherad, A. Keivanloo, B. Bahramian, S. Jajarmi, J. Organomet. Chem. 724 (2013) 206;
(b) Y. He, C. Cai, J. Organomet. Chem. 696 (2011) 2689;
(c) S.M. Islam, P. Mondal, A.S. Roy, S. Mondal, D. Hossain, Tetrahedron Lett. 51 (2010) 2067.

[13] (a) S. Guin, S.K. Rout, A. Banerjee, S. Nandi, B.K. Patel, Org. Lett. 14 (2012) 5294;
(b) H. Song, D. Chen, C. Pi, X. Cui, Y. Wu, J. Org. Chem. 79 (2014) 2955;
(c) Y. Wu, P.Y. Choy, F. Mao, F.Y. Kwong, Chem. Commun. 49 (2013) 689;
(d) Y. Wu, L.J. Feng, X. Lu, F.Y. Kwong, H.B. Luo, Chem. Commun. 50 (2014) 15352.

[14] (a) X.F. Jia, S.H. Zhang, W.H. Wang, F. Luo, J. Cheng, Org. Lett. 11 (2009) 3120;
(b) O. Basle, J. Bidange, Q. Shuai, C.J. Li, Adv. Synth. Catal. 352 (2010) 1145;
(c) C.L. Li, L. Wang, P.H. Li, W. Zhou, Chem. Eur. J. 17 (2011) 10208;
(d) Y.X. Yang, B. Zhou, Y.C. Li, Adv. Synth. Catal. 354 (2012) 2916;
(e) C.W. Chan, Z.Y. Zhou, W.Y. Yu, Adv. Synth. Catal. 353 (2011) 2999;
(f) A.B. Paula, F.G. Areli, C. Arkaitz, M. Ruben, J. Am, Chem. Soc. 132 (2010) 466.

[15] Y.S. Bao, D. Zhang, M. Jia, B. Zhaorigetu, Green Chem. 18 (2016) 2072.

[16] (a) K. Balaswamy, P.C. Pullaiah, M.M. Rao, Appl. Catal. A General 483 (2014) 110;
(b) K. Balaswamy, P.C. Pullaiah, K. Srinivas, M.M. Rao, Inorg. Chim. Acta 423 (2014) 95;
(c) K. Balaswamy, P.C. Pullaiah, M.M. Rao, Appl. Organometal. Chem. 28 (2014) 756.

[17] (a) F. Xiao, Q. Shuai, F. Zhao, O. Basle, G. Deng, C.J. Lu, Org. Lett. 13 (2011) 1614;
(b) D.J. Cárdenas, B.M. Matute, A.M. Echavarren, J. Am. Chem. Soc. 128 (2006) 5033;
(c) B. Mariampillai, J. Alliot, M.Z. Li, M.A. Lautens, J. Am. Chem. Soc. 129 (2007) 15372;
(d) K.M. Gericke, D.I. Chai, N. Bieler, M. Lautens, Angew. Chem. Int. Ed. 121 (2009) 1447;
(e) R. Kishore, M. Lakshmi Kantam, J. Yadav, M. Sudhakar, S. Laha, A. Venugopal, J. Mol. Catal. A Chem. 379 (2013) 313.