Research paper

Polystyrene supported Dichloro-(8-aminoquinoline)-Palladium(II) complex catalyzed C-H bond activation for *ortho*-acylation of 2-aryl pyridines

C. Pullaiah Perumgani, Sai Prathima Parvathaneni, Balaswamy Kodicherla, Srinivas Keesara, Mohan Rao Mandapati

PII: S0020-1693(16)30664-8
DOI: http://dx.doi.org/10.1016/j.ica.2016.10.014
Reference: ICA 17307

To appear in: *Inorganica Chimica Acta*

Received Date: 3 August 2016
Revised Date: 3 October 2016
Accepted Date: 7 October 2016

Please cite this article as: C. Pullaiah Perumgani, S. Prathima Parvathaneni, B. Kodicherla, S. Keesara, M. Rao Mandapati, Polystyrene supported Dichloro-(8-aminoquinoline)-Palladium(II) complex catalyzed C-H bond activation for *ortho*-acylation of 2-aryl pyridines, *Inorganica Chimica Acta* (2016), doi: http://dx.doi.org/10.1016/j.ica.2016.10.014

Polystyrene supported Dichloro-(8-aminoquinoline)-Palladium(II) complex catalyzed C-H bond activation for *ortho*-acylation of 2-aryl pyridines

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

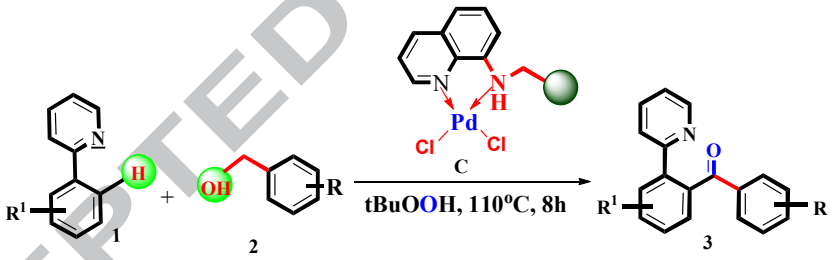
[a]*Catalysis Laboratory, Inorganic and Physical Chemistry Division*

CSIR-Indian Institute of Chemical Technology (IICT),Tarnaka, Hyderabad –500 607, India,

[b]*School of Chemistry, University of Hyderabad, Hyderabad 500046, India.*

Fax: +91-040-27160921, Tel: (+) 91 40 27193181
E-mail: saiprathimaiict@gmail.com, mandapati@iict.res.in

Abstract: Polystyrene-supported Dichloro-(8-aminoquinoline)-Pd(II) complex **C** was synthesized and its catalytic efficiency was evaluated for *ortho*-acylation of 2-aryl pyridines with alcohols to form aryl ketones *via* cross dehydrogenative coupling. In addition in the presence of Pd (II) complex, toluene derivatives were also employed as an effective coupling partner for synthesis of aromatic ketones. Furthermore, this catalyst was highly stable and could be easily recovered by simple filtration and reused for four cycles with no significant decrease in its activity and selectivity.



Scheme 1

Introduction:

Direct C-H bond functionalisation of aromatic motifs *via* introduction of carbonyl groups will be a more challenging, environmentally friendly, complementary to Friedel-Crafts acylation for aryl ketone synthesis [1]. Aryl ketones are predominantly employed in the fragrance, dye and pharmaceutical industries [2]. Directing group assisted C-H bond functionalisation and cross dehydrogenative coupling (CDC) are commonly employed methods to achieve selective C-H bond functinalisations [3-5]. Ru, Rh, Cu and Pd are commonly employed transition-metals for carbon-carbon bond forming processes [6-7]. Among these, the palladium complexes are

preferred catalysts for directed C-H functionalisation reactions due to their high compatibility and exceptional stability towards moisture and air [8]. Recently, research group of Kim has developed transition metal catalysed oxidative sp^2 C-H bond acylations with aldehydes for synthesis of aromatic ketones [9]. Encouraged by these findings, it further occurred to us that alcohols can be potentially utilized as ideal acylation reagents since alcohols can be readily oxidized into aldehydes [10]. Kim, Yuan and Li groups have reported oxidative *ortho*-acylations of aryl moieties with alcohols as acyl source through palladium-catalyzed synthesis of aromatic ketones [11-15]. Most of the reported methods for C-H bond acylation are under homogeneous conditions [16-18]. However, oxidative acylation on aromatic sp^2 C-H bonds with the exploitation of recyclable heterogenous catalysts are extremely rare. Thus there is a wide scope for improvement of new heterogeneous catalysts for oxidative acylations.

Our research group mainly interested in developing simple recyclable polymer bound metal complexes, and its applications for C-C bond formation reactions [19]. Recently, we have reported polystyrene-supported N,N-dimethylethylenediamine with Cu and Pd complexes (**E** and **F**) as catalysts for Sonogashira, A^3, Suzuki coupling reactions and N-phenylpiperazine-Cu(II) complex **D** for KA^2 coupling (figure 1) [20-23].

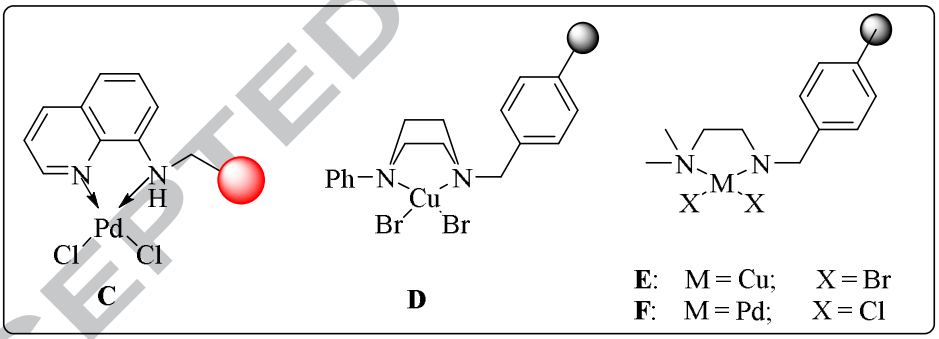


Fig. 1 Polymer supported copper and palladium complexes (**C, D, E** and **F**).

Herein, we report polymer supported Pd(II) complex **C** as an efficient and highly reusable heterogeneous catalyst for *ortho*-acylation of 2-phenyl pyridines by employing alcohol derivatives as the simple coupling partners. The main advantage of the present polymeric palladium (II) **C** complex over existing methods is mainly less catalytic loading, better recyclability and broad scope with excellent yields (Scheme 1).

Experimental

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. 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. ^{1}H 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 (^{1}H 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.

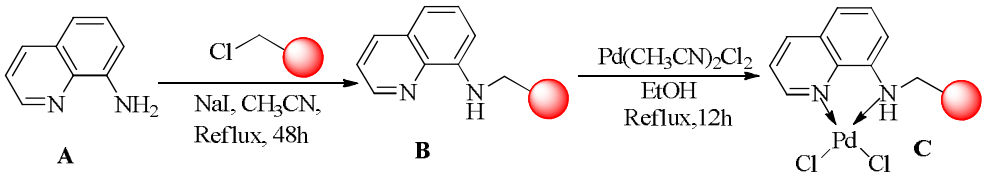
Preparation of polymer-supported 8-Aminoquinoline (B) (PS-8-AQ)

A 250 mL round bottom flask containing CH_3CN (50mL), equipped with a magnetic stirrer bar is added with chloromethylated polystyrene (1 g, 1.2 mmol g^{-1} of Cl) and 8-Aminoquinoline (5 mmol) and NaI (0.1 mmol). The reaction mixture was refluxed for 48 h and was subsequently 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.

Preparation of polystyrene-supported Pd(II) complex (C) (PS-8-AQ-Pd)

To the polystyrene-supported 8-Aminoquinoline **B** (0.5g), 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).



Scheme 2. Synthesis of polymer-bound 8-Aminoquinoline derived Pd(II) complex **C**.

General procedure for carbonylation reaction catalyzed by Polymer anchored-Pd(II) C:

A dried round bottomed flask equipped with a magnetic stir bar was charged with 15 mg Polymer anchored-Pd(II) **C** catalyst (PS-8-AQ-Pd), 2-phenyl pyridine (0.5 mmol), benzyl alcohol (1.0 mmol) and TBHP (2.0 mmol) were added to a reaction vessel. The mixture was stirred at 110 ^{o}C for 8 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 ^{1}H NMR, ^{13}C NMR and HRMS.

Results and discussion

The new polymer supported Pd(II) catalyst **C** was prepared in two steps which is clearly represented in Scheme 2. 8-Aminoquinoline functionalized polystyrene resin **B** was formed by heating a mixture of chloromethylated polystyrene and 8-Aminoquinoline **A** in CH_3CN for 48 h. This polymer-supported 8-Aminoquinoline **B** is insoluble in common organic solvents. Reaction of **B** with EtOH and $Pd(CH_3CN)_2Cl_2$ in 1 : 1 molar ratio for 12 h resulted in covalent attachment of palladium to give functionalized polymer anchored-Pd(II) complex C. The complex was characterized by chemical analysis, SEM-EDX, TGA, AAS and IR spectroscopic techniques. The complexation ratio of palladium to PS-8-AQ is 1:1. The amount of palladium incorporated into the polymer was determined by atomic absorption spectroscopy (AAS), which showed a value of 4.93%. This complex formation was confirmed by FT-IR analysis. In the IR spectrum of chloromethylated polystyrene, the two characteristic peaks at 1263 and 670 cm^{-1} were due to stretching and bending vibrations of C–Cl group. They were practically eliminated after the

introduction of 8-Aminoquinoline and palladium onto the polymer. Compared to the IR spectrum of $Pd(CH_3CN)_2Cl_2$, the peaks at 2330 cm^{-1} (C–N, CH_3CN), and 2918 cm^{-1} (C–H, CH_3CN) are absent in the case of complex. The decrease in IR value of the NH group of polystyrene supported ligand **B** (from 3431 cm^{-1} to 3407 cm^{-1}) to the complex **C** indicates the formation of Pd–N bond (Supporting information).

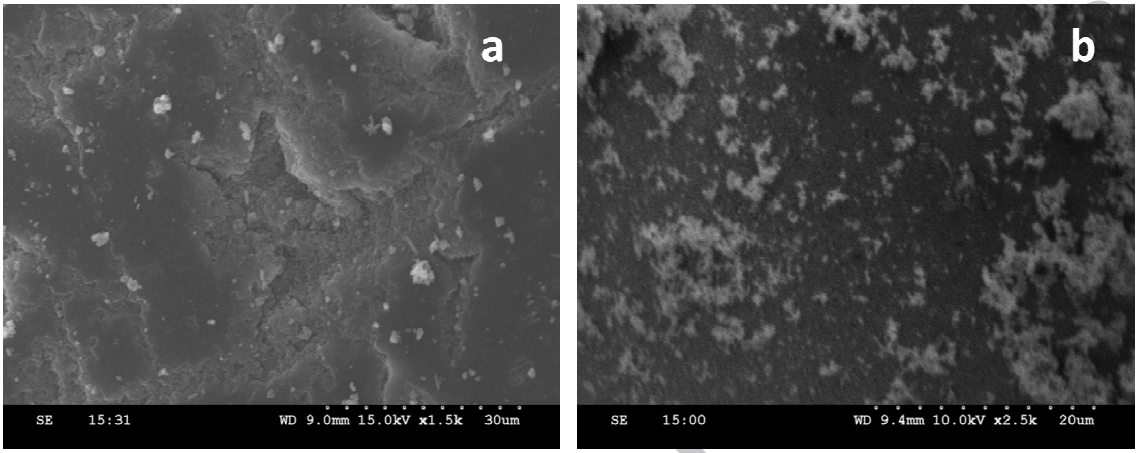


Fig. 2 SEM images of **(a)** polymer anchored ligand (PS-8-AQ); **(b)** palladium complex (PS-8-AQ-Pd).

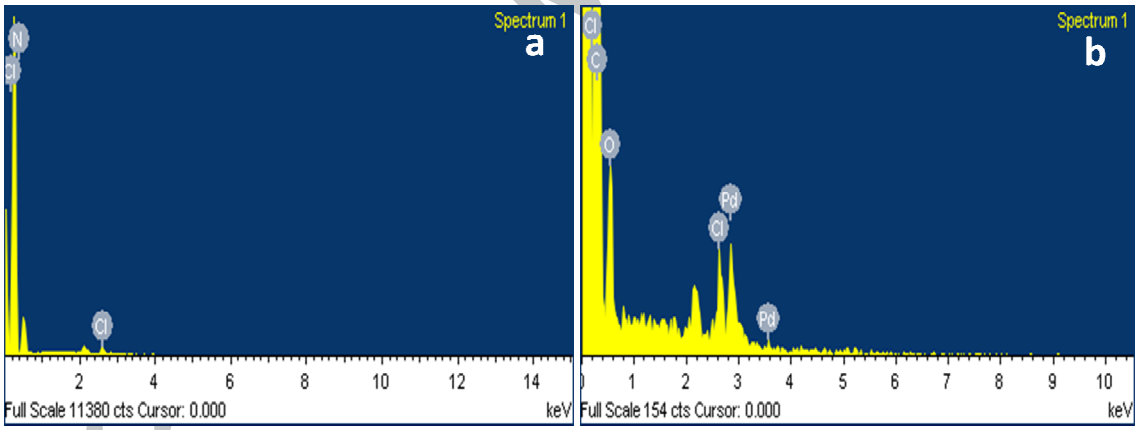


Fig. 3 EDX image of **(a)** polymer anchored ligand (PS-8-AQ); **(b)** polymer anchored complex (PS-8-AQ-Pd).

Scanning electron micrographs were shown in figure 2 for PS-8-AQ ligand and the supported Pd complex. The SEM image (b) clearly indicate the change in the morphology of polymer supported Pd(II) catalyst **C,** which is due to the bonding of Pd on the surface of polystyrene supported ligand. An energy dispersive spectroscopy analysis of X-rays (EDX) data for the polymer anchored ligand (PS-8-AQ) (**B**) and (PS-8-AQ-Pd) (**C**) catalyst is given in Fig. 3.

The EDX data also inform that the attachment of palladium metal on the surface of the polymer matrix. The EDX spectrum of the PS-8-AQ-Pd complex (Fig. 3) confirms the presence of the respective atoms: C, N, Cl and Pd.

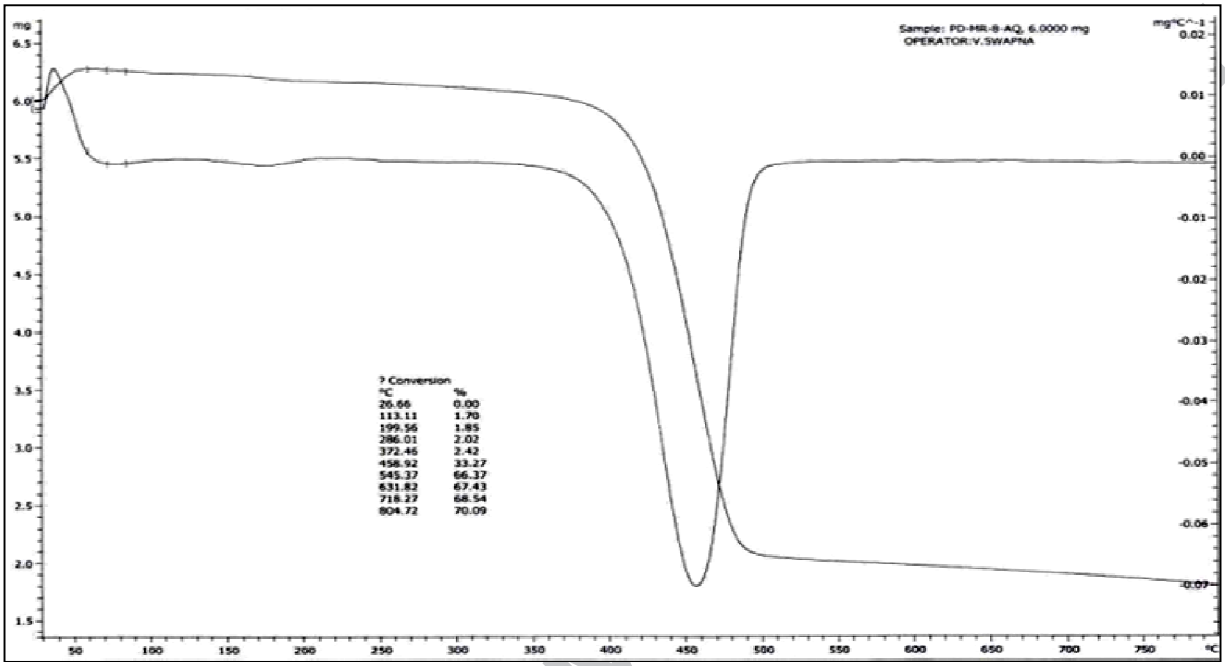


Fig. 4 TGA of polymer supported (PS-8-AQ-Pd) **C** complex.

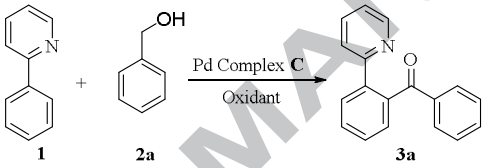
Thermal stability of the complex was investigated using thermogravimetric analysis (TGA) at a heating rate of 10 °C min^{-1} over a temperature range of 30-800 °C. The TGA curve of the polymer anchored catalyst is shown in Fig. 4. The initial negligible weight loss up to 370 °C may be due to the removal of solvent molecules. The complex **C** is stable up to 400 °C and above which thermal decomposition takes place.

Catalytic activity

As polymer anchored metal complexes exhibit efficient catalytic activity they have been extensively studied and reported in the field of coupling reactions. In our present work, we investigated the catalytic activity of the PS-8-AQ–Pd catalyst to prepare benzophenones with benzyl alcohols without using carbon monoxide. Initially, we examined the carbo-acylation of 2-phenyl pyridine reaction with alcohols in the presence of polymer supported Pd (II) complex **C** under a variety of reaction conditions. We have chosen 2-phenyl pyridine **1** and benzyl alcohol **2a** as model substrates for *ortho* acylation (Table 1). Several oxidants such as H_2O_2, $K_2S_2O_8$,

O_2, tert-butyl hydroperoxide (TBHP), and tert-butyl peroxybenzoate (TBPB) were screened at various temperatures as shown in Table 1. However in presence of $K_2S_2O_8$, O_2, H_2O_2, tert-butyl peroxybenzoate (TBPB) the desired product was not obtained even at 120 °C for 24h (entries 1-3 and 5). Among the screened, *tert*-butyl hydroperoxide (TBHP) proved to be the best oxidant at 110 °C for about 8h and desired product was obtained in 91 % yield in the presence of Pd complex **C** (entry 4). But TBHP was unsuccessful at room temperature (entry 6) and low yield at 80 °C (entry **7**). There is considerable change in yields by increasing the reaction time from 5 to 8h at 110 °C (entry 8 and 4). However the desired product was not obtained in absence of oxidant and Pd complex **C** (entries 9-10). Therefore TBHP at 110 °C in presence of Pd complex **C** for 12h gave the desired product **3a** in 91 % yield under solvent free conditions (entry 4, Table 1).

Table 1. Optimization of reaction conditions[a]

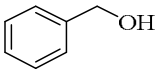
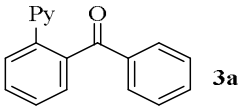
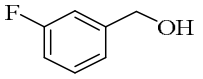
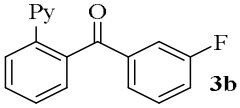
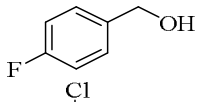
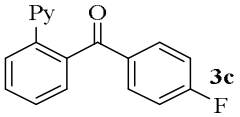
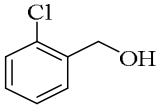
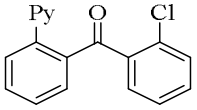
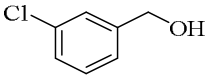
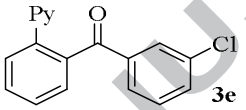
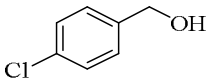
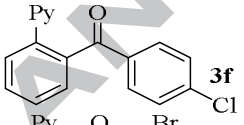
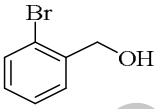
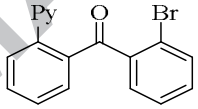
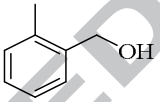
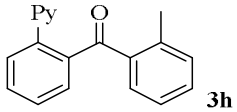
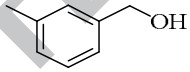
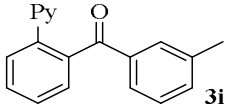
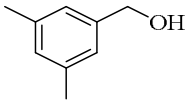
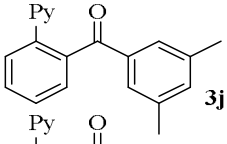
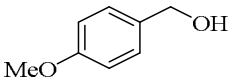
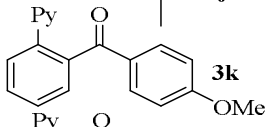
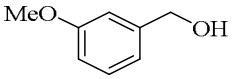
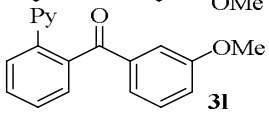
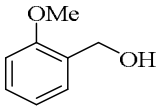
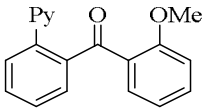


1 2a 3a

Entry	Oxidant	Temp (°C)	Time (h)	Yield (%)[b]
1	H_2O_2	110	12	–
2	$K_2S_2O_8$	110	12	–
3	O_2 (1atm)	110	18	–
4	TBHP	110	8	91
5	TBPB	110	12	–
6	TBHP	RT	24	–
7	TBHP	80	12	35
8	TBHP	110	5	65
9	–	110	12	–[c]
10	TBHP	110	12	–[d]

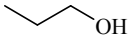
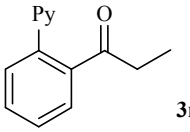
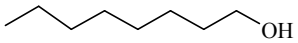
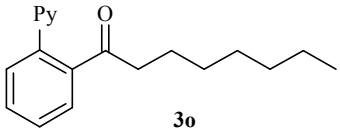
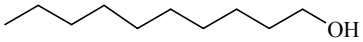
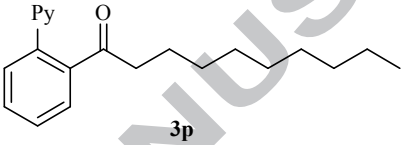
[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (15 mg), oxidant (2.0 mmol), [b]Isolated yield, [c]No Oxidant, [d]No Catalyst.

Table 2. Acylation reaction of 2-phenyl pyridine with a various benzyl alcohols[a]

Entry	Alcohol	Product	Yield (%)[b]
1		 **3a**	91
2		 **3b**	80
3		 **3c**	82
4		 **3d**	78
5		 **3e**	80
6		 **3f**	83
7		 **3g**	75
8		 **3h**	80
9		 **3i**	82
10		 **3j**	84
11		 **3k**	91
12		 **3l**	85
13		 **3m**	82

[a]Reaction conditions: **1** (0.5 mmol), **2a** (1.0 mmol), catalyst (15 mg), oxidant (2.0 mmol),110 °C for 8 h, [b]Isolated yield.

Table 3 Acylation reaction of 2-phenyl pyridines with aliphatic alcohols[a]

Entry	Alcohol	Product	Yield (%)[b]
14		 **3n**	trace
15		 **3o**	72
16		 **3p**	78

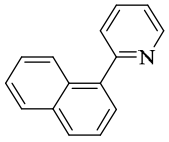
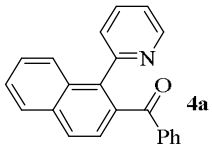
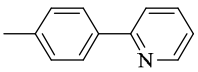
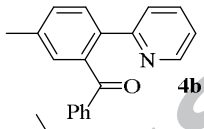
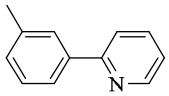
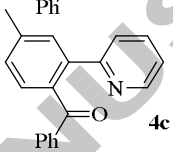
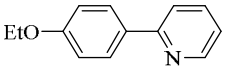
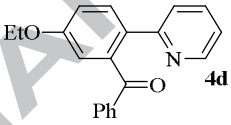
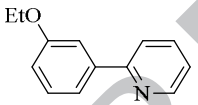
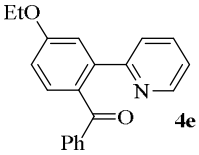
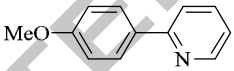
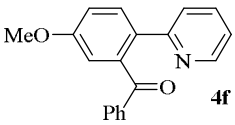
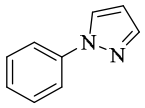
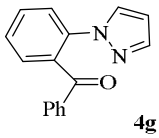
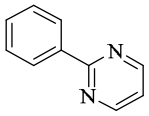
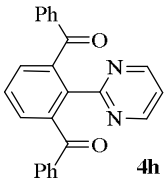
[a]Reaction conditions: **1** (0.5 mmol), **2** (1.0 mmol), catalyst (15 mg), oxidant (2.0 mmol),110 ^{o}C for 8 h, [b]Isolated yield.

We have extended the reaction with more challenging aliphatic alcohols for direct aroylation of 2-phenylpyridines under the optimized reaction conditions, and the results are represented in Table 3. It should be noted that propanol resulted in trace amount of the desired product (Table 3, entry 14) whereas 1-octanol and 1-decanol gave the mono acylation product with (**3o**) 72% and (**3p**) 78% yields respectively (Table 3, entries 15 and 16).

The scope of direct *ortho* acylation of 2-phenylpyridine with various substituted benzyl alcohols was conducted under the optimized reaction conditions, and the results are summarized in Table 2. The reactions with benzylic alcohols bearing electron-donating groups (entries 8-13) and electron withdrawing substituents at the aromatic ring (entries 2-7) proceeded to give the desired products in good to excellent yields. However electron-donating groups substituted acylated products (OMe, CH_3) gave better yields than electron withdrawing substituents (F, Cl and Br). The OMe substituted *para*, *meta*, *ortho* gave (**3k**) 91%, (**3l**) 85%, (**3m**) 82% and Me substituted *meta*, *ortho* resulted in (**3i**) 82%, (**3h**) 80% yields of the desired products. In case of methyl disubstituted, the acylated product (**3j**) was obtained in 84% yield. However *chloro* substituted *para*, *meta*, *ortho* the desired product was achieved in (**3f**)

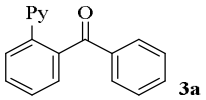
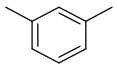
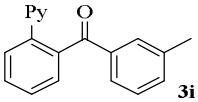
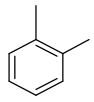
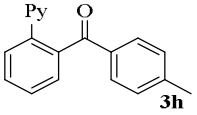
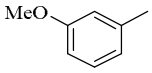
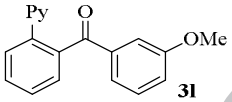
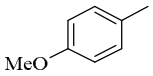
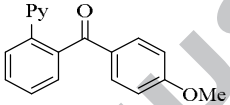
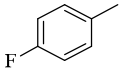
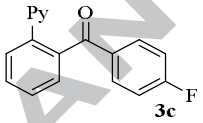
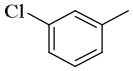
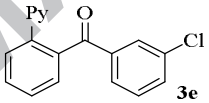
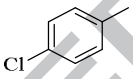
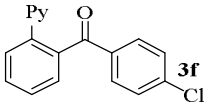
83%, (**3e**) 80%, (**3d**) 78% respectively. But *fluoro* substituted *para*, *meta* with (**3c**) 82%, (**3b**) 80%, where as *ortho* substituted *bromo* gave (**3g**) 75% of acylated products.

Table 4 Acylation reaction of variety of N-directing groups with benzyl alcohol[a]

Entry	Starting Material	Product	Yield (%)[b]
1		 **4a**	91
2		 **4b**	88
3		 **4c**	84
4		 **4d**	86
5		 **4e**	81
6		 **4f**	90
7		 **4g**	82
8		 **4h**	78

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (15 mg), oxidant (2.0 mmol), 110 °C for 8 h, [b]Isolated yield.

Table 5. Acylation reaction of 2-phenyl pyridine with toluene derivatives[a]

Entry	Toluene	Product	Yield (%)[b]
1		 **3a**	78
2		 **3i**	70
3		 **3h**	75
4		 **3l**	76
5		 **3k**	80
6		 **3c**	70
7		 **3e**	65
8		 **3f**	68

[a]Reaction conditions: **1a** (0.5 mmol), **2a** (1.0 mmol), catalyst (15 mg), oxidant (2.0 mmol), 110 °C for 24 h, [b]Isolated yield.

In addition, we also studied the reaction with various substituted aryl pyridines, pyrazole and pyrimidine for the directed aroylation of 2-arylpyridines under the optimized conditions, and the results are presented in Table 4. The functional groups including Me, OEt, OMe and naphthyl were well-suited 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 **4b**, **4c**, **4d**, **4e**, **4f** in 88%, 84%, 86%, 81% and 90% respectively. In case of naphthyl substituted pyridine the desired product **4a** was obtained in 91% yield and 1-phenyl-1*H*-pyrazole (entry 7) gave 82% yield. As expected 2-phenylpyrimidine (entry 8) gave only diacylated product in 78% yield due to the presence of two *ortho* directing nitrogen atoms. Thus the

aroylation reaction gave acylated products with variety of 2-phenyl pyridines in high yields.

Further, we extended the scope of the reaction with toluene derivatives as acylating partners. To our surprise both electron-donating and electron-withdrawing substituents at the aromatic ring proceeded to give the desired products in good to excellent yields (Table 5). However electron-donating groups substituted toluene products (OMe, CH_3) gave better yields than electron withdrawing substituents (F and Cl). The Me substituted *ortho* and *meta* gave 75%, 70%, and OMe substituted *meta*, *para* resulted in 76%, 80% yields of the desired products. In case of *chloro* substituted *para*, *meta* the desired product was achieved in 68%, 65% and *para*, substituted *fluoro* with 70% respectively.

The recyclability of the polymer–anchored Pd (II) complex **C** was tested in the acylation of 2-phenyl pyridine **1** and benzyl alcohol **2a**. It was found that the catalyst can be reused for four cycles with only 4% decline of activity after the 4th recycle as shown in Fig 5. The AAS analytical data of used catalyst **C** did not show appreciable loss in the palladium content.

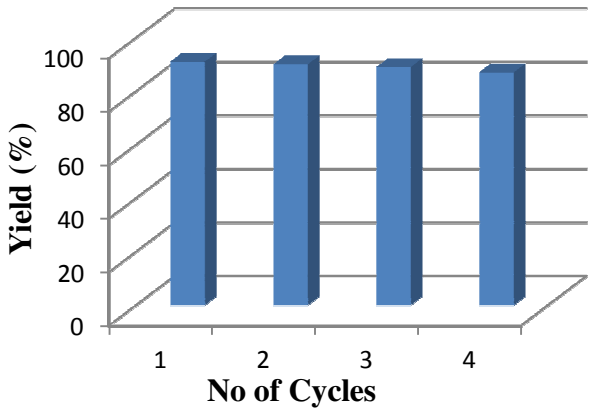


Fig 5: Recyclability of Pd(II) catalyst **C**

Conclusion

In summary, we have developed a simple recyclable heterogeneous Pd(II) complex **C** as versatile, active and stable catalyst for selective *ortho*-acylation of 2-phenyl pyridines with benzyl alcohol and toluene derivatives as cheap acylation source. Thus this represents as an efficient and eco-economical protocol for the carbonylation reaction as it afforded the *ortho*-

acylation products in excellent yields with high selectivity under solvent/carbon monoxide free conditions with broad substrate scope.

Acknowledgements

P. S. P gratefully acknowledge to the financial assistance provided by CSIR-Senior Research Associateship (Scientist's Pool Scheme), 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.

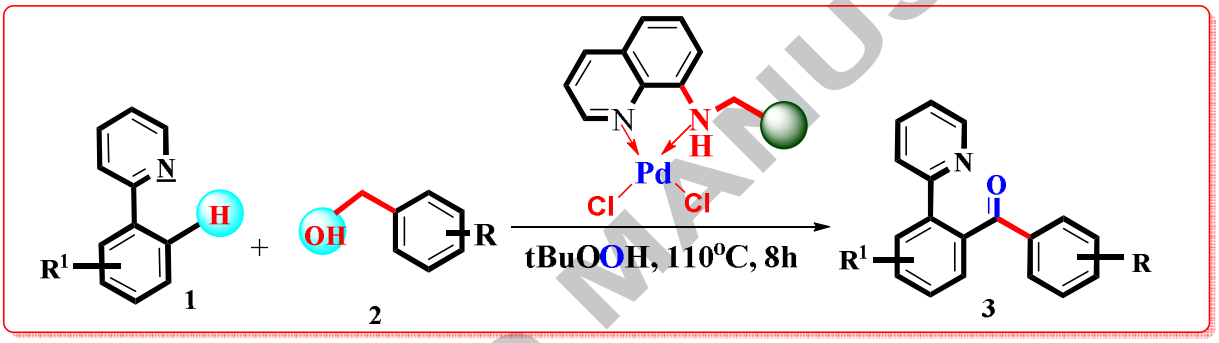
References:

[1] Sartori, G.; Maggi, R. Advances in Friedel-Crafts Acylation Reactions; CRC Press: FL, 2010.
[2] Surburg, H.; Panten, J. Common Fragrance and Flavor Materials, 5th ed.; Wiley-VCH: Weinheim, Germany, 2006.
[3] O. Daugulis, H. Q. Do, D. Shabashov, Acc. Chem. Res. 42 (2009) 1074.
[4] D. A.; Colby, Bergman, R. G.; Ellman, J. A. Chem. Rev. 110 (2010) 624.
[5] C. J. Li, Acc. Chem. Res. 42 (2009) 335.
[6] P. B. Arockiam, C. Bruneau, P. H. Dixneuf, Chem. Rev. 112 (2012) 5879.
[7] C. Liu, J. Yuan, M. Gao, S. Tang, W. Li, R. Shi, A. Lei, Chem. Rev. 115 (2015) 12138.
[8] T. W. Lyons, M. S. Sanford,Chem. Rev. 110 (2010) 1147.
[9] 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.
[10] G. Dobereiner, R. Crabtree, Chem. Rev. 110 (2010) 681.
[11] J. Park, A. Kim, S. Sharma, M. Kim, E. Park, Y. Jeon, Y. Lee, J. H. Kwak, Y. H. Jung, I. S. Kim, Org. Biomol. Chem. 11 (2013) 2766.
[12] M. Kim, S. Sharma, J. Park, M. Kim, Y. Choi, Y. Jeon, J. H. Kwak, I. S. Kim, Tetrahedron 69 (2013) 6552.
[13] 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.
[14] F. Xiao, Q. Shuai, F. Zhao, O. Baslé, G. Deng, C.-J. Li, Org. Lett. 13 (2011) 1614.
[15] Y. Yuan, D. Chen, X. Wang, Adv. Synth. Catal. 353 (2011) 3373.
[16] X. F. Wu Chem. Eur. J. 21 (2015)12252.
[17] X. F. Wu Chem. Rec. 15 (2015) 949.
[18] X. F. Wu, J. L.Gong, X. Qi Org. Biomol. Chem, 12 (2014) 5807.

[19] K.Srinivas, P.Sai Prathima, D. Govardhan, M. Mohan Rao. J. Organomet. Chem. 765 (2014) 31.
[20] K. Balaswamy, P. C. Pullaiah, M. Mohan Rao, Appl. Catal. A 483 (2014) 110.
[21] K. Balaswamy, P. C. Pullaiah, K. Srinivas, M. Mohan Rao, Inorg. Chim. Acta 423 (2014) 95.
[22] K. Balaswamy, P. C. Pullaiah, M. Mohan Rao, Appl. Organometal. Chem. 28 (2014) 756.
[23] P. C. Pullaiah, K. Srinivas, P. Saiprathima, M. Mohan Rao, New J. Chem. 40 (2016) 5113.

Graphical Abstract:

Polystyrene-supported Dichloro-(8-aminoquinoline)-Pd(II) complex **C** was synthesized and its catalytic efficiency was evaluated for *ortho*-acylation of 2-aryl pyridines with alcohols to form aryl ketones *via* cross dehydrogenative coupling. In addition in the presence of Pd (II) complex **C**, toluene derivatives were also employed as an effective coupling partner for synthesis of aromatic ketones. Furthermore, the catalyst **C** was highly stable and could be easily recovered by simple filtration and reused for four cycles with no significant decrease in its activity and selectivity.



Highlights:

Efficient Recyclable Polystyrene-supported Dichloro-(8-aminoquinoline)-Pd(II) complex

Low metal loadings with high recyclability

C-H bond acylation with benzyl alcohols as coupling partner

Broad Scope with high yields

sp^2 C-H bond activation