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Polymer anchored 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex: An efficient catalyst for the copper and solvent free Sonogashira cross-coupling reaction

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ABSTRACT

An efficient copper and solvent free Sonogashira cross-coupling reaction catalyzed by polymer supported 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex **4** (PS-bpt-Pd) was reported. This inexpensive and simply synthesized heterogeneous catalyst **4** afforded excellent yields of the cross-coupling products under mild reaction conditions. We have achieved high yields for aryl iodide coupling reactions with terminal alkynes at room temperature under copper and solvent-free conditions. In addition, we also observed moderate to good yields for aryl bromides as coupling partner. This insoluble PS-bpt-Pd(II) catalyst **4** can be easily recovered by simple filtration and reused up to five times with stable catalytic activity. In addition to this, heterogeneous Pd (II) complex is even applicable on a gram scale for cross-coupling with high catalytic efficiency.

1. Introduction

Sonogashira cross-coupling reaction is one of the most popular palladium-catalyzed C–C bond forming reaction [1]. This involves the cross-coupling reaction of aryl halides with terminal alkynes, playing a vital role in the production of many industrially important chemicals and substituted alkyne compounds with high synthetic value in the organic chemistry. These moieties are abundant in biologically active natural products, pharmaceutical products and materials [2]. Over the past decade, notable achievements have been made in the development of Pd catalysts for the Sonogashira transformations in both homogeneous and heterogeneous conditions. Homogeneous palladium catalysts associated with some of the difficulties, like unwanted palladium contamination, separation and recovery of the catalysts from the products. Heterogeneous metal catalysts are emerging as an alternative to the existing homogeneous ones. A number of heterogeneous palladium catalysts have been reported for the C–C bond formation reactions with different solid supports such as polymers [3], metal oxides [4], zeolites [5], silica-starch [6], clay [7], montmorillonite [8], magnetic nanoparticles [9] and carbon nanofiber [10].

Polymer supported Pd catalysts are very attractive due to facile synthesis, stability and easy separation from the reaction mixture makes growing their applications in heterogeneous catalysis. Therefore, a number of polymer anchored palladium complexes have been synthesized with diverse donor functionalities and their catalytic activity have been studied for the C–C bond forming reactions [11]. It is well known that the nature of ligands in polymer supported Pd complexes could have a substantial effect on the catalytic behaviour [12].

Most of the Pd catalysts have been reported for Sonogashira coupling reaction, along with copper salts as co-catalysts under different organic solvents [13]. Copper co-catalyst is responsible for the formation of undesired homo-coupling products through the Glaser coupling in palladium catalyzed Sonogashira reaction [14]. The use of organic solvents as medium shows severe health and environmental problems from their associated waste. The main target of research in this field is to avoid the use of copper co-catalyst and organic solvents to achieve economical and environmental safety [15]. In this point of view, a small number of efficient reusable palladium catalytic systems have been reported for Sonogashira cross-coupling reactions under copper and solvent free conditions. M. Bakherad and co-workers reported different

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polystyrene-supported palladium catalysts for copper and solvent free Sonogashira coupling reactions [16]. R. S. Salunkhe and co-workers have published Sonogashira coupling reaction with Merrifield resin supported Pd-NHC complex under copper- and solvent-free conditions [17].

Herein, we report the synthesis of polystyrene supported 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex **4** (PS-bpt-Pd(II) complex **4**) and its application to the Sonogashira cross-coupling reaction under copper and solvent free conditions. Formerly, we have reported homogeneous and heterogeneous thiopseudourea Pd(II) complexes as catalysts for different C–C cross-coupling reactions [18].

2. Experimental

2.1. General information

All materials were commercial reagent grade. Chloromethylated polystyrene (1% cross-linked, 200–400 mesh with 1.0–1.3 mmol/g) was a product of Alfa-Aesar. Aryl halides and terminal alkynes were obtained from Aldrich. Laboratory grade acetone was purchased from S.D Fine. The amount of catalyst **4** we used according to molecular weight of palladium. Thermo gravimetric analysis was recorded on a TG/DTA-7300, HITACHI, Japan. Samples were heated from 30 °C to 800 °C ascent at 20 °C/min under N_2 atmosphere. IR spectra were obtained in KBr wafers on Thermo Nicolet Nexus 670 spectrophotometer respectively. Field emission scanning electron microscope (FESEM) images were obtained from a Carl Zeiss model Merlin compact microscope using a 30 keV electron beam. Energy dispersive x-ray (EDX) spectra were recorded using Oxford Instruments X-MaxN SDD (50 mm2) system and INCA analysis software. The ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz, respectively. The chemical shifts are reported in ppm downfield to TMS ($\delta = 0$) for ^{1}H NMR and $CDCl_3$ ($\delta = 77.0$) for ^{13}C NMR. High-resolution mass spectra (HRMS) were recorded on ESI-TOF maXis.

2.2. Preparation of the catalyst

2.2.1. General procedure for the synthesis of ligand **2**

To a solution of 4-amino-1-benzylpiperidine (5 mmol) in 20 mL of acetone, benzoyl isothiocyanate (5 mmol) was added dropwise at 0 °C and allowed to stir for 3 h at room temperature. The reaction mixture was concentrated to a solid; water (50 mL) was added, and extracted with ethyl acetate (50 mL). The organic layer was washed with brine (20 mL), dried over $MgSO_4$, and filtered, after which the solvent was removed under reduced pressure. The crude product was purified by column chromatography on silica gel using ethyl acetate/hexane as the eluent to give the corresponding coupling products (Scheme 1).

*2.2.1.1. 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiourea (**2**).* ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 10.7 (s, 1H), 8.89 (s, 1H), 7.76 (d, $J = 7.57$ Hz, 2H), 7.54 (t, $J = 7.07$ Hz, 1H), 7.43 (t, $J = 7.07$ Hz, 2H), 7.25–7.18 (m, 5H), 4.26 (s, 1H), 3.45 (s, 2H), 2.72 (s, 2H), 2.18 (t, $J = 10.61$ Hz, 2H), 2.06 (d, $J = 11.87$ Hz, 2H), 1.63 (dd, $J = 11.36$ Hz, 2H);^{13}C NMR (100 MHz, $CDCl_3$) δ 178.9, 167.1, 136.9, 133.5, 131.7, 129.4, 129.0, 128.4, 127.5, 127.1, 62.7, 60.4, 51.5, 30.3; IR (cm^{-1}): $\tilde{\nu}$(CONHCSNH) 3417, 3239, $\tilde{\nu}$(C=O)1670, $\tilde{\nu}$(C=S) 796. HRMS: exact mass calculated for $C_{20}H_{23}N_3OS$ $[M+H]^+ = 354.1640$, found $m/z = 354.1644$.

2.2.2. Synthesis of PS-bpt ligand (**3**)

To a 250-mL round bottom flask containing DMF (50 mL), equipped with magnetic stirrer bar is added with chloromethylated polystyrene (1 g, 1.25 mmol/g of Cl) and 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiourea (1.5 mmol). The reaction mixture was stirred for 24 h at 110 °C and was subsequently filtered and washed thoroughly with DMF, dried in oven at 80 °C for 24 h to form the PS-bpt (Scheme 1).

2.2.3. Synthesis of PS-bpt-Pd(II) complex (**4**)

To a 250-mL round bottom flask containing CH_2Cl_2 (50 mL), equipped with magnetic stirrer bar is added with PS-bpt ligand **3** (1.3 g) and $Pd(OAc)_2$ (1 mmol). The resulting mixture was allowed to stir at room temperature for 24 h. This mixture was filtered and washed with acetonitrile to obtain PS-bpt-Pd(II) complex **4** (Scheme 1).

2.3. General procedure for the Sonogashira cross-coupling reaction of aryl iodides

A mixture of aryl iodide (1.0 mmol), phenylacetylene (1.2 mmol), Et_3N (2.0 mmol) and 0.005 mmol (10 mg) of Pd(II) complex **4** was stirred at room temperature for a desired reaction time. Further, the reaction mixture was extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane as eluent to give the corresponding coupling products.

2.4. General procedure for the Sonogashira cross-coupling reaction of aryl bromides

A mixture of aryl iodide (1.0 mmol), phenylacetylene (1.2 mmol), TMG (2.0 mmol), water (2 mL) and 0.01 mmol (20 mg) of Pd complex **4** was stirred at 80 °C temperature for a desired reaction time. Further, the reaction mixture was extracted with ethyl acetate and dried over $MgSO_4$. The solvent was removed under reduced pressure and the residue was purified by column chromatography on silica gel using hexane as the eluent to give the corresponding coupling products.

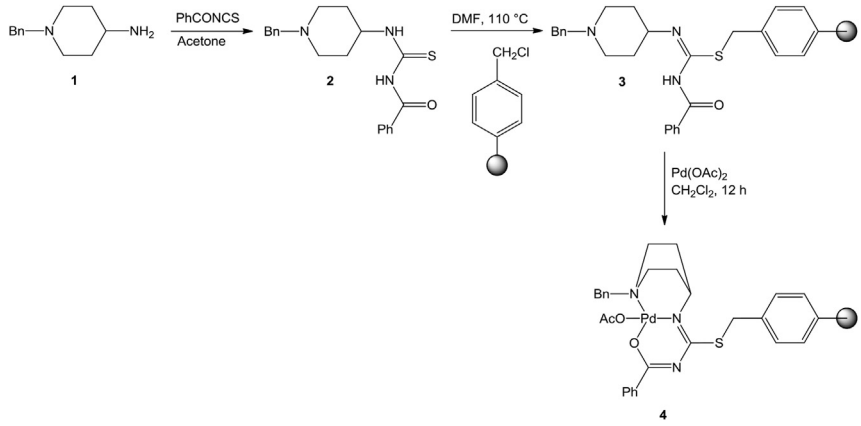
2.5. Procedure for CS_2 poisoning test

A 25 mL round bottom flask was charged with iodobenzene (1.0 mmol), phenylacetylene (1.2 mmol), 0.005 mmol (10 mg) of Pd complex **4** and 0.2 mL of CS_2 (0.8 equiv comparative to palladium) from a freshly prepared solution in Et_3N. This reaction mixture was stirred at room temperature for 10 h and no conversion takes place as indicated by TLC analysis.

3. Results and discussion

The new thiourea ligand **2** was prepared by following one step procedure as shown in Scheme 1. This involves the reaction between benzoyl isothiocyanate and 4-amino-1-benzylpiperidine in acetone under nitrogen atmosphere at 0 °C to afford the thiourea compound **2**. The light yellow solid was obtained in 95% yield after purification by column chromatography. Compound **2** was characterized by NMR, IR and Mass spectroscopic techniques.

In Scheme 1, we have represented the steps involved in the preparation of new polystyrene supported thiopseudourea Pd(II) complex **4**. A 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea functionalized polystyrene resin (PS-bpt) (2% DVB) was formed by heating a mixture of chloromethylated polystyrene and 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiourea in DMF solvent at 110 °C for 24 h. This solid polymer-supported thiopseudourea **3** is insoluble in common organic solvents. Reaction of polymer-bound thiopseudourea with DCM and $Pd(OAc)_2$ in 1: 1 M



Scheme 1. Synthesis of PS-bpt-Pd(II) complex **4**.

molar ratio for 12 h at room temperature resulted in covalent attachment of palladium to give the functionalized polymer. The literal complex formation was confirmed by FT-IR analysis. The FT-IR spectrum of polystyrene, PS-bpt ligand **3** and PS-bpt-Pd(II) complex **4** is revealed in supplementary information. A sharp peak at 1263 cm^{-1} corresponding to C—Cl peak completely disappeared in polymer-bound thiopseudourea Pd complex indicates the introduction of thiourea on the polymer. In addition, the stretching vibration of the C═N and C═O double bond peaks observed at 1600 and 1724 cm^{-1} corresponds to the formation of polystyrene-supported thiopseudourea palladium complex [19].

Scanning electron micrographs (SEM) were reported for pure chloromethylated polystyrene, and polymer anchored thiopseudourea-Pd(II) complex **4** to study the morphological changes. Usually the pure polymer bead had a smooth and flat surface, while the anchored polymeric complex showed roughening of the top layer. The complete morphology change in the complex **4** indicates the presence of palladium metal on the surface of polymer (Fig. 1(A) and (B)). Next we studied the Energy Dispersive X-ray Spectroscopy (EDX) analysis of PS-bpt-Pd(II) **4,** which showed catalyst was composed with palladium, carbon, nitrogen, oxygen, and sulphur. This confirms that the thiopseudourea-Pd(II) complex anchored to the polymer matrix (Fig. 2(a) and (b)).

Thermal stability of the complex **4** was investigated by TGA. The

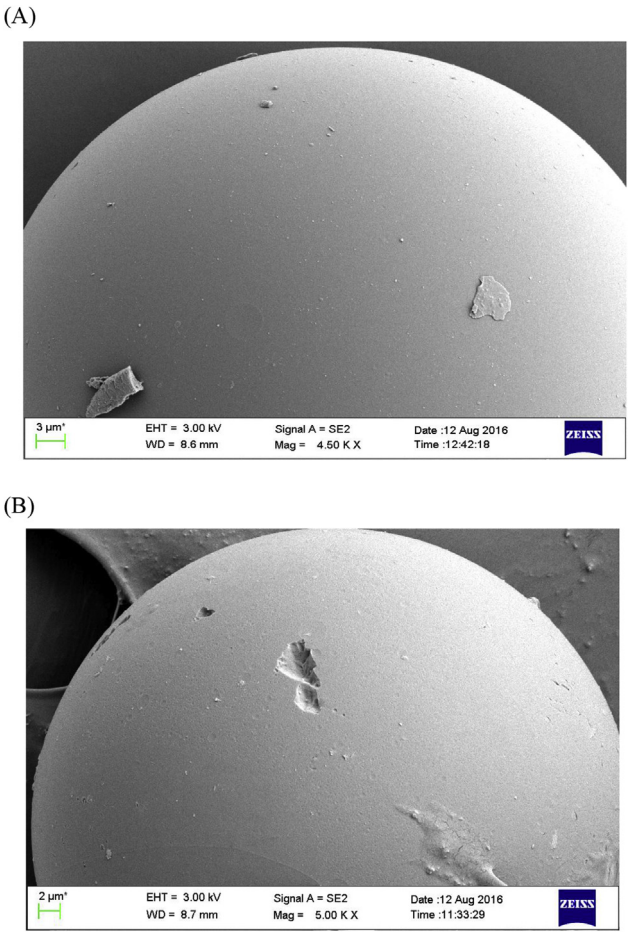


Fig. 1. SEM images of (A) Chlomethylated polystyrene (B) PS-bpt-Pd(II) complex **4**.

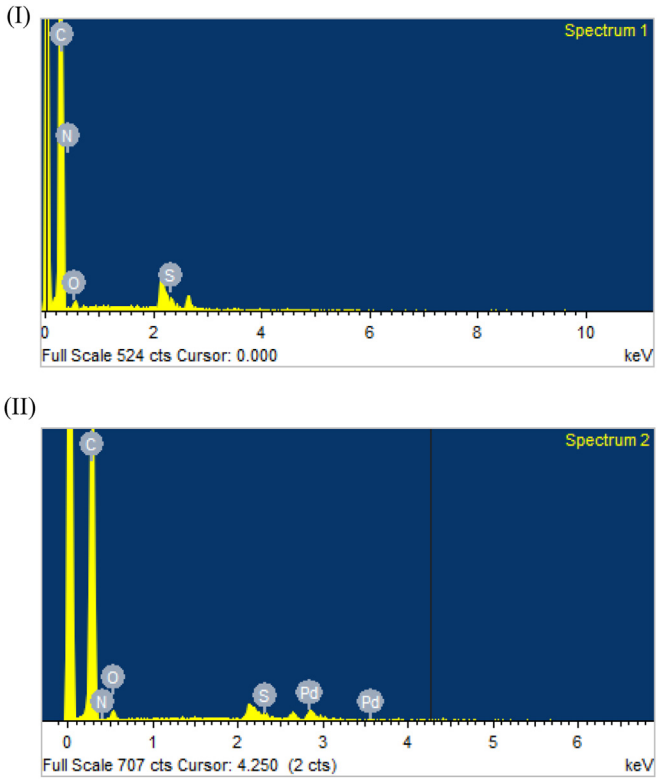


Fig. 2. EDX analysis of: (a) PS-bpt ligand **3** (b) PS-bpt-Pd(II) complex **4**.

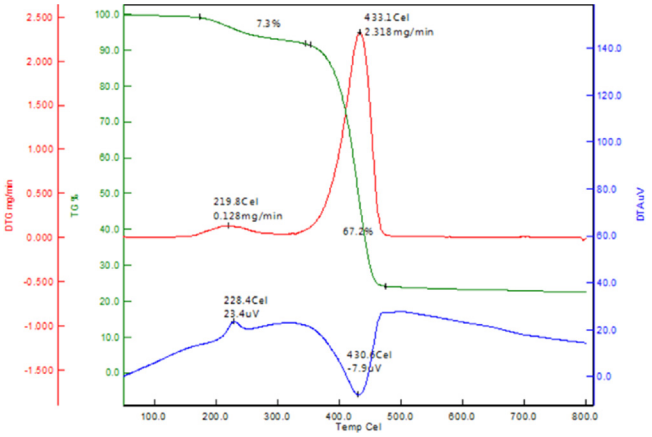


Fig. 3. TG-DTA analysis of PS-bpt-Pd(II) complex **4**.

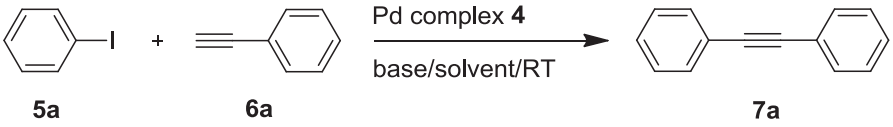
negligible weight loss below 200 °C is due to the physically adsorbed solvent molecules. Thermogravimetric analysis shows stability of the PS-bpt-Pd(II) complex (**4**) up to 320 °C and further weight loss at a higher temperature (above 320 °C) was attributed to the decomposition of complex (Fig. 3). The exact concentration of palladium incorporated into the polymer was determined by atomic absorption spectroscopy (AAS), which showed the value of about 6.46% (0.609 mmol/g).

Initially we tested the catalytic activity of PS-bpt-Pd(II) complex **4** in the solvent and copper-free Sonogashira cross-coupling reaction. We have chosen iodobenzene and phenylacetylene as model substrates to optimize the reaction conditions (Table 1). To choose a suitable base, we screened different bases using 0.005 mmol of catalyst **4** in water at room temperature. No coupling product **7a** was observed in case of inorganic bases and NaOAc.$3H_2O$ employed reactions (Table 1, entries 1–4). High yields were observed with all the organic amine bases (TMG, DABCO, DBU, and Et_3N) (Table 1, entries 5–8) [20]. The organic amine bases were more favourable towards aryl halide and alkyne cross-coupling in our reaction conditions due to fast hydrogen halide formation. As expected no coupling product **7a** was obtained under base free conditions (Table 1, entry 9). Next we screened various organic solvents with Et_3N base. The reaction proceeded well with all the organic solvents and gave the coupling product **7a** in moderate to excellent yields (Table 1, entries 10–16). Next we studied the same reaction under solvent-free conditions with Et_3N as the base. Effective coupling product was observed with in 5 h under these reaction conditions without any formation of Glaser-type oxidative homo coupling product (Table 1, entry 17).

Further, we studied the scope of coupling of aryl iodides with phenylacetylene under the above optimized reaction conditions (Table 2). We observed high yields of coupling products for both electron rich and electron deficient aryl iodides reactions under solvent free conditions. Substituent effect was not prominent for the coupling reaction of *para* and *meta* substituted aryl iodides with phenylacetylene which resulted the corresponding products **7a-7g** in excellent yields (Table 2, entries 1–7). Due to steric effect low yield of the coupling product **7h** was obtained for the 2-bromoiodobenzene reaction with phenylacetylene. We observed slight improvement in yield (from 40% to 65%) for the same experiment when carried out in water (Table 2, entry 8). Next we investigated the effect of various aryl iodides using 4-ethynyltoluene as the substrate led to good yield of the desired products **7b** and **7i-7n** (Table 2, entries 9–15).

Encouraged by these results, further we extended the scope of the catalyst **4** to Sonogashira coupling reaction of aryl bromides Table 3. As expected, the above optimized reaction conditions were ineffective for the bromobenzene coupling reaction with phenylacetylene. Aryl bromides are less reactive compared to aryl iodides in Sonogashira cross-coupling reactions. Efficient coupling was observed with TMG base and water as solvent at 70 °C (Table 3, entry 1). All the reactions of aryl bromides with phenylacetylene and 1-ethynyl-4-methylbenzene furnished good yields of coupled products **7b-7d** and **7i-7k** by varying reaction times (Table 3, entries 2–8). No coupling product was observed for chlorobenzene

Table 1
Optimization reaction of the of iodobenzene with phenylacetylene.[a]

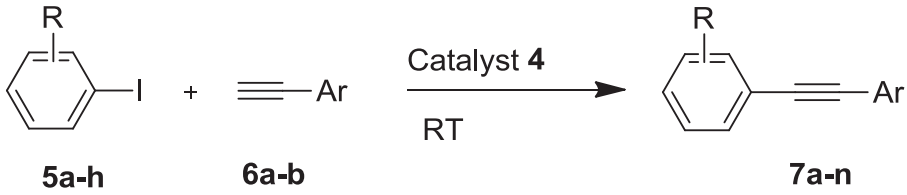


5a **6a** **7a**

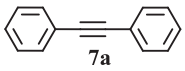
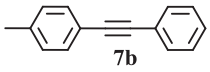
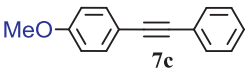
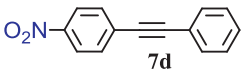
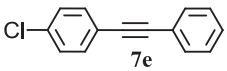
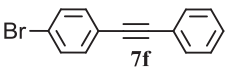
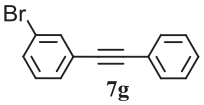
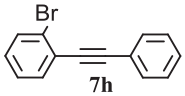
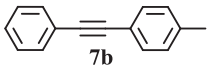
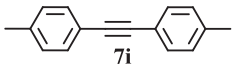
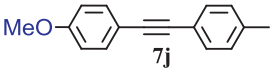
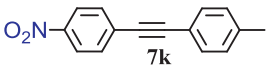
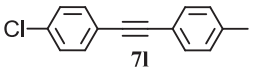
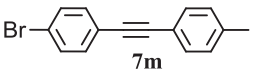
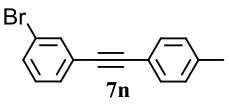
Entry	Base	Solvent	Time (h)	Yield (%)[b]
1	K_2CO_3	H_2O	12	Nr[c]
2	K_3PO_4	H_2O	12	Nr[c]
3	$LiOH·H_2O$	H_2O	12	Nr[c]
4	$NaOAc·3H_2O$	H_2O	12	Nr[c]
5	TMG	H_2O	6	98
6	DABCO	H_2O	6	90
7	DBU	H_2O	6	98
8	Et_3N	H_2O	6	97
9	–	H_2O	6	Nr[c]
10	Et_3N	MeOH	8	72
11	Et_3N	EtOH	8	80
12	Et_3N	DMF	8	94
13	Et_3N	DMSO	8	95
14	Et_3N	THF	8	95
15	Et_3N	Dioxane	8	96
16	Et_3N	Toluene	8	94
17	Et_3N	–	5	99

[a] Reaction conditions: Iodobenzene (1 mmol), Phenylacetylene (1.2 mmol), base (2 mmol), catalyst **4** (0.005 mmol), solvent (1 mL) at room temperature.
[b] Isolated yield.
[c] No reaction.

Table 2
Sonogashira coupling of different aryl iodides catalyzed by complex **4**.[a]



5a-h **6a-b** **7a-n**

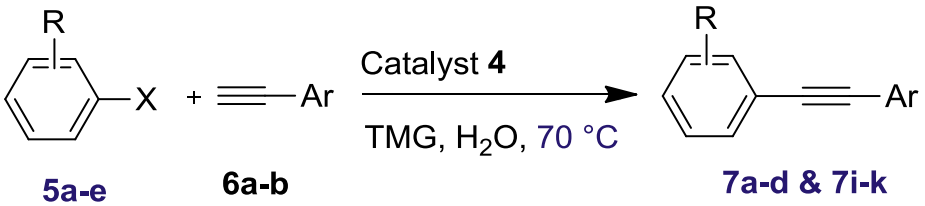
Entry	R	Ar	Product	Yield (%)[b,c]
1	H (**5a**)	Ph (**6a**)	 **7a**	99, 97[c]
2	4-Me (**5b**)	**6a**	 **7b**	96, 95[c]
3	4-OMe (**5c**)	**6a**	 **7c**	86, 84[c]
4	4-NO_2 (**5d**)	**6a**	 **7d**	96, 95[c]
5	4-Cl (**5e**)	**6a**	 **7e**	98, 97[c]
6	4-Br (**5f**)	**6a**	 **7f**	97, 97[c]
7	3-Br (**5g**)	**6a**	 **7g**	96, 94[c]
8	2-Br (**5h**)	**6a**	 **7h**	40, 65[c]
9	**5a**	4-$CH_3C_6H_5$ (**6b**)	 **7b**	98
10	**5b**	**6b**	 **7i**	90
11	**5c**	**6b**	 **7j**	88
12	**5d**	**6b**	 **7k**	96
13	**5e**	**6b**	 **7l**	95
14	**5f**	**6b**	 **7m**	98
15	**5g**	**6b**	 **7n**	95

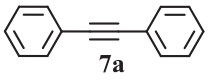
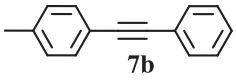
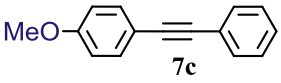
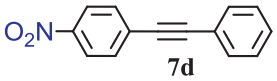
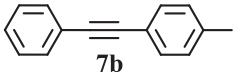
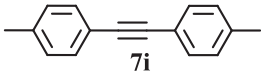
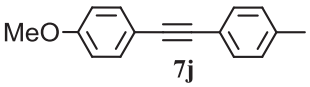
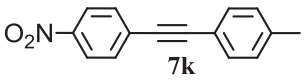
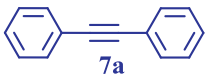
[a] Reaction conditions: Aryl iodide (1 mmol), alkyne (1.2 mmol), catalyst 4 (0.005 mmol %), Et_3N (2 mmol) at room temperature for 6 h.
[b] Isolated yield.
[c] Water as solvent (1 mL).

coupling reaction (Table 3, entry 9).

In order to disclose the effectiveness of this catalyst, we conducted different reactions with iodobenzene and phenylacetylene under solvent free conditions up to 10 mmol millimole

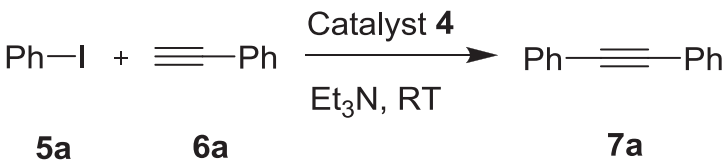
Table 3
Sonogashira coupling of different aryl bromides catalyzed by complex **4**.[a]



Entry	R	Ar	Product	Yield (%)[b]
1	**5a**	**6a**	 **7a**	82
2	**5b**	**6a**	 **7b**	80
3	**5c**	**6a**	 **7c**	72
4	**5d**	**6a**	 **7d**	81
5	**5a**	**6b**	 **7b**	78
6	**5b**	**6b**	 **7i**	70
7	**5c**	**6b**	 **7j**	66
8	**5d**	**6b**	 **7k**	79
9	**5e**[c]	**6a**	 **7a**	Nr

[a] Reaction conditions: Aryl bromide (1 mmol), alkyne (1.2 mmol), catalyst **4** (0.01 mmol), TMG (2 mmol) at 70 °C temperature for 15 h.
[b] Isolated yield.
[c] Chlorobenzene (1 mmol) used as substrate. Nr = No reaction.

Table 4
Sonogashira coupling of iodobenzene with phenylacetylene catalyzed by complex **4**.[a]



Entry	Reaction scale	Catalyst **4** (mmol)	Time	Yield (%)[b]
1	1 mmol	0.005	6	99
2	2 mmol	0.005	8	98
3	3 mmol	0.005	12	97
4	4 mmol	0.005	20	94
5	5 mmol	0.005	32	92
6	10 mmol	0.005	60	90
7	10 mmol	0.01	40	96

[a] Iodobenzene (1.0 equiv), phenylacetylene (1.2 equiv), Et_3N (2 eq) at room temperature.
[b] Isolated yields.

scale (Table 4). Iodobenzene (1–5 and 10 mmol scale) was transformed into product **7a** with 0.005 mmol of catalyst **4** for all the reactions and obtained excellent yields with time variation (Table 4, entries 1–6). Herein we observed that the reaction time was increased with increasing number of millimoles of substrates. Next we increased catalyst loading from 0.005 mmol to 0.01 mmol for 10 mmol scale reaction resulted decreasing reaction time from 60 h to 40 h (Table 4, entries 7).

3.1. Recyclability of the catalyst

Economical and industrial point of view, recyclability of the catalyst is a significant factor. The recycling efficiency of the catalyst **4** was investigated for the coupling of iodobenzene with phenylacetylene under the above optimized reaction conditions. After every experiment, this heterogeneous catalyst was easily separated from the reaction mixture by simple filtration and washed with acetonitrile. The air-dried catalyst can be reused directly without any additional treatment. We observed stable catalytic activity of catalyst **4** for the first five cycles and thereafter decreased gradually (6–10 cycles) (Fig. 4). After consecutive runs, no perceptible loss of the weight of the catalyst is observed.

Next we determined the leaching of Pd metal from the polymer supported catalyst into the Sonogashira reaction mixture by using. After ten consecutive experiments, we observed 8.7% amount of Pd loss into the reaction mixture with excellent reusability of the heterogeneous catalyst.

3.2. Confirming the heterogeneity of catalyst *4*

The reaction mixture of Sonogashira coupling was filtered and analyzed AAS of the filtrate to identify the presence of palladium in the solution phase. However, no palladium was observed in the AAS examination. Next we conducted CS_2 poisoning test for catalyst **4** to determine the nature of catalyst (homogeneous or heterogeneous). For heterogeneous catalyst less than 1.0 equiv. of CS_2 (per metal atom) is capable to poison the catalyst [21]. Here 0.8 equiv of CS_2 (comparative to palladium) is enough to inhibit catalytic activity of catalyst **4** for iodobenzene coupling reaction with phenylacetylene. The above results proved that the catalyst **4** is heterogeneous in nature and Sonogashira coupling is catalyzed by **4**, under heterogeneous conditions.

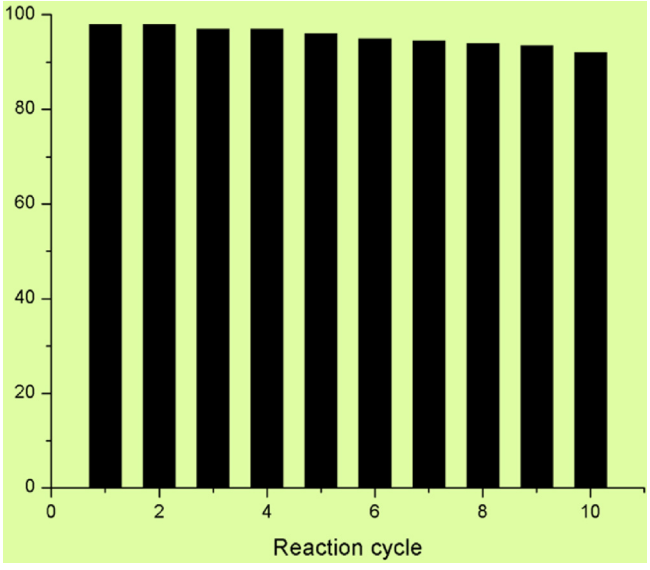


Fig. 4. The recyclability of the catalyst **4** in the preparation of **7a**.

4. Conclusions

In conclusion, we have reported efficient polymer supported 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex **4** as a heterogeneous catalyst for copper/solvent free Sonogashira reaction. The use of environmental benign catalyst **4** for Sonogashira cross-coupling reaction may considerably decrease the cost of energy in the chemical industry and serves as useful alternative to the reported procedures. In addition to this, it is even applicable for gram scale reactions with excellent yields of coupling products.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2016.08.029.

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