

Microwave Assisted Fluoride-Free Hiyama Cross-Coupling Reaction Catalyzed by Pd (0)–PVP Nanoparticles

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Abstract: Fluoride-free Hiyama cross-coupling reactions of phenyltrimethoxysilane with aryl halides were performed in water using sodium hydroxide as the activator at 110 °C. The reactions, catalyzed by PVP stabilized colloidal palladium nanoparticles, show enhanced rate under microwave heating and proceed quickly (6 min). The progress of the reactions was monitored by GC-MS and parameters such as catalyst concentration, effect of base, recyclability etc. were investigated. Excellent yields were obtained with a variety of substrates and the products, after isolation, were characterized by ¹H NMR.

Keywords: Hiyama cross-coupling, Microwave heating, Pd (0)–PVP Nanoparticles, Reaction catalyzed

1. INTRODUCTION

Palladium-catalyzed carbon-carbon bond formation reactions are useful tools for constructing materials and drugs in modern chemistry [1, 2]. Several types of cross-coupling reactions such as Kumada [3-4], Negishi [5, 6], Stille [7, 8], Suzuki [9, 10], Hiyama [11, 12], Sonogashira [13, 14], and other related couplings [15-18], based on the transmetalation of a variety of hard or soft organometallic nucleophiles, have been developed so far. Among them, Suzuki and Stille reactions are the most studied and utilized. However, they have several disadvantages when applied to practical organic synthesis. Stille coupling makes use of toxic tin reagents and their byproducts need to be removed. By using boronic acids, the Suzuki reaction puts an end to problems which stems from reagent toxicity but boronic acids are difficult to synthesize and purify [19]. Therefore, Hiyama coupling reactions, which make use of organosilicon reagents, have several attractions. The organosilicon reagents are nontoxic, available at low cost, can be prepared easily and are stable under reaction conditions. However, C-Si bond of alkylsilanes requires corrosive fluoride anion for activation. To increase the activity of C-Si bond alkenylfluorosilanes [20], alkenylalkoxysilanes [21-23], and organosilanols [24-26] have been explored, the reaction being catalyzed by palladium or nickel in the presence of phosphine ligands [27-31]. Most of these ligands are expensive, thus, significantly limiting the industrial application of these reactions. The development of inexpensive and efficient catalytic system for the Hiyama cross-coupling reactions, hence, became an important objective.

In the last decade, the use of metal nanoparticles as efficient catalysts has attracted considerable interest. The high surface-to-volume ratio of nanoparticles provides larger number of active sites per unit area compared to their heterogeneous counterparts, as we and many others have

recently shown in the case of Suzuki [32] and Hiyama [33] cross-couplings. Polymers such as polyvinylpyrrolidone (PVP) are efficient stabilizers for metal nanoparticles. PVP is a relatively inexpensive linear polymer and palladium nanoparticles stabilized by it have proven their effectiveness in the catalysis of C–C coupling reactions [34-35]. El-Sayed and co-workers [36-39] have deeply investigated the size, structure and catalytic activity of Pd-PVP nanoparticles, especially in the case of Suzuki reaction. Lei Wang et al. [40] have reported Sonogashira cross-coupling reaction using Pd/PVP as a catalyst in a ligandless and copper free-system with high yields. Martins *et al.* [41] reported Heck reaction using Pd (0)-PVP as a catalyst in ligand free conditions.

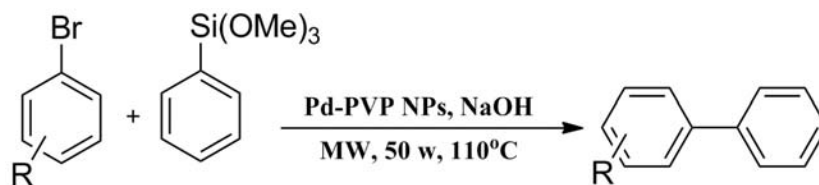
In the present case, we examine the catalytic activity and stability of the Pd (0)–PVP nanoparticles towards base catalyzed Hiyama reaction between phenyltrimethoxysilane and aryl halides under conventional and microwave heating. Effect of various parameters such as nature of base, concentration of catalyst and recyclability were also investigated.

2. EXPERIMENTAL

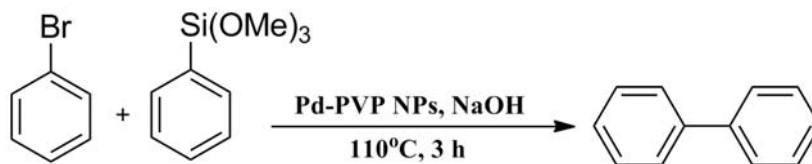
All chemicals used were of analytical grade or of the highest purity available. All glassware was thoroughly cleaned with freshly prepared 3:1 HCl/HNO₃ (aqua-regia) and rinsed with Millipore-Q water. Phenyltrimethoxysilane was purchased from Aldrich. The aryl bromides were obtained from BDH and Merck. All aryl bromides and chlorides were of 98–99% purity. Dichloromethane (DCM), diethyl ether (Et₂O), and NaOH were purchased from Finar Chemicals. Water used in all experiments was purified by the Millipore system.

High resolution transmission electron microscopy (HR-TEM) pictures were taken using a Hitachi (H-7500) instrument. GC–MS measurements were carried on Perkin Elmer USA Auto system XL carrier gas Helium, Column PE - 5 MS, oven temp varied from 70 to 280 °C at 10 °C per min. ¹H NMR spectra were recorded on a Bruker Advance II 400 NMR spectrometer. CEM benchmate microwave reactor was used for microwave heating.

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Scheme (1). Hiyama reaction catalysed by Pd (0)–PVP colloidal NPs.



Scheme (2). Hiyama reaction catalysed by Pd (0)–PVP NPs between bromobenzene and phenyltrimethoxysilane under conventional heating.

2.1. Synthesis of PVP-Pd Nanoparticles

The PVP-Pd nanoparticles were synthesized by reduction of palladium ions with ethanol similar to that described previously [42]. H_2PdCl_4 employed as the palladium precursor, was prepared by adding 0.1 mmol of PdCl_2 in 1.0 mL of 0.2 M HCl and the solution diluted to 50 mL with Millipore water. A solution containing 15 mL of H_2PdCl_4 solution, 21 mL of Millipore water, 0.0666 g of PVP (Average MW of PVP 40,000) and 14 mL of ethanol was refluxed in a round bottom flask. This resulted in a dark brown colloidal solution of palladium nanoparticles (Pd (0)–PVP NPs) in about 3h. A drop of this solution was placed onto a 200 mesh carbon coated copper grid and solvent evaporated. TEM was used to characterize the size of the nanoparticles.

2.2. Hiyama Reaction

2.2.1. Hiyama Reaction Under Microwave Irradiation

Into a 10 mL vial, aryl bromide (1 mmol), phenyltrimethoxysilane (1.5 mmol), 5 mL Pd (0)–PVP NPs (0.003 mmol Pd) were taken. 1mL of 3M NaOH, (3 mmol) was added dropwise while stirring the reaction mixture vigorously. The vial was then heated in CEM microwave (50 w, 110 °C, stirring on) for 6-8 min (Scheme 1). The reaction mixture was cooled to room temperature and extracted with Et_2O / DCM (2×5mL). The organic layer was dried over MgSO_4 and the solvent removed by rotaevaporator. The crude products thus isolated were recrystallized from appropriate solvents.

2.2.2. Hiyama Reaction Under Conventional Heating

A 10 mL round-bottomed flask equipped with a reflux condenser was filled with bromobenzene (1 mmol), phenyltrimethoxysilane (1.5 mmol) and 5 mL of Pd (0)–PVP NPs (0.003 mmol of Pd) solution. 1mL of 3M NaOH (3 mmol) was added dropwise while stirring the reaction mixture vigorously. The flask was then placed in an oil bath, and the mixture heated for 3 h at 110 °C (Scheme 2). After cooling the reaction mixture to room temperature, the product was extracted in Et_2O (2×5mL). The ethereal layer was dried over MgSO_4 and the solvent removed by rotaevaporator. The

crude product, thus isolated, was purified by recrystallization.

2.3. Effect of Various Parameters on Catalyst Activity

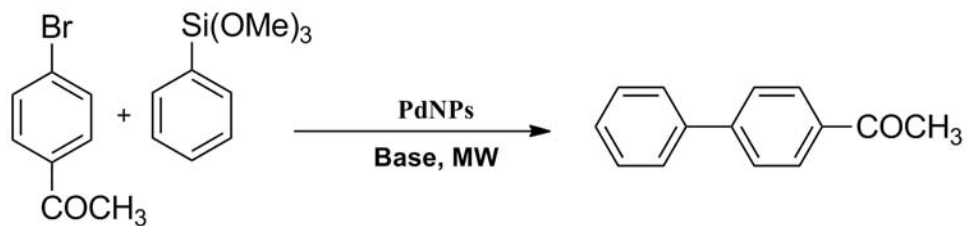
Effect of various parameters such as time, catalyst concentration, base, etc. was studied for the coupling reaction between 4-bromoacetophenone and phenyltrimethoxysilane. Into three 10 mL vials, 4-bromoacetophenone (1.0 mmol), phenyltrimethoxysilane (1.5 mmol), sodium hydroxide (1 mL, 3 M), ethanol (1.5 mL) and catalyst (5 mL Pd(0)–PVP colloidal NPs,) were taken and heated in a CEM microwave reactor for a hold time of 2, 4, and 6 min, respectively (Scheme 3). The reactions were quenched by filtering the hot solution in 10 mL cold water and the aqueous solution for each run was extracted with Et_2O (2× 5 mL). The combined extracts were dried over anhydrous MgSO_4 , and products analyzed by GC–MS. The effect of catalyst concentration was also studied by taking different amounts of catalyst while keeping the other parameters constant.

3. RESULTS AND DISCUSSION

The procedure reported by Miyake *et al.* [42] was followed in order to prepare the Pd (0)–PVP colloidal NPs. Palladium chloride was employed as the palladium source, ethanol as the reducing agent and PVP as the stabilizer. After refluxing for 3 h, the solution acquired a dark brown colour and remained stable for weeks at room temperature. Following this methodology, we could obtain nanoparticles with size ranging between 2 to 5 nm as revealed by TEM analysis (Fig. 1).

3.1. Catalytic Activity

Microwave irradiation is a simple, rapid and effective way of energy transfer to a reaction medium, provided it has enough polarity to suffer the absorption of MW energy [43]. Its application in several cases has led to acceleration of the reaction rate, improvement in yields and selectivity [44]. In the present case, we studied the catalytic activity of the Pd (0)–PVP nanoparticles for the Hiyama cross-coupling of bromobenzene with phenyltrimethoxysilane under microwave as well as conventional heating (Scheme 1 and 2).



Scheme (3). Hiyama reaction of 4- bromoacetophenone with phenyltrimethoxysilane.

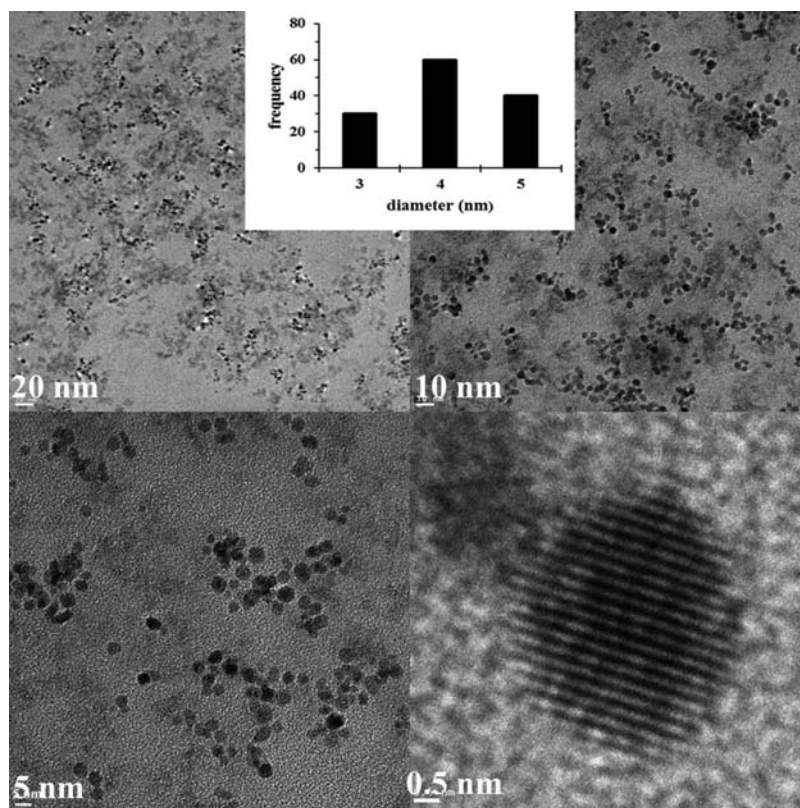
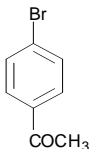
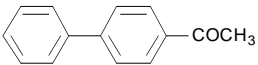
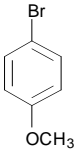
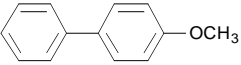
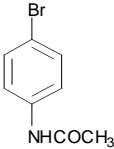
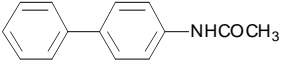
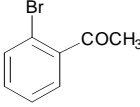
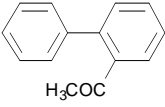
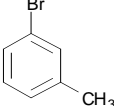
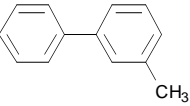

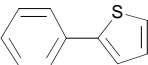
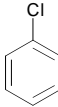
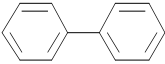
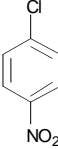
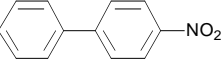


Fig. (1). TEM image of the Pd(0)-PVP nanoparticles.

Table 1. Hiyama cross-coupling of phenyltrimethoxysilane with different aryl halides under microwave heating.

No.	Aryl halide	Product	T (min)	Yield*(%)
1	<chem>BrC1=CC=C(C=C1)</chem>	<chem>C1=CC=C(C=C1)-C2=CC=C(C=C2)</chem>	6	96
2	<chem>BrC1=CC=C(C=C1)C=O</chem>	<chem>C1=CC=C(C=C1)-C2=CC=C(C=C2)C=O</chem>	6	90
3	<chem>BrC1=CC=C(C=C1)[N+](=O)[O-]</chem>	<chem>C1=CC=C(C=C1)-C2=CC=C(C=C2)[N+](=O)[O-]</chem>	6	90

Table 1. contd...

No.	Aryl halide	Product	T (min)	Yield*(%)
4			6	85
5			6	90
6			6	90
7			7	90
8			6	85
9			8	85
10			9	88
11			9	90

[a] phenyltrimethoxysilane (1.5 mmol), Aryl halides (1 mmol), base (3 mmol), catalyst, Pd(0)-PVP NPs 5 mL (0.003 mmol of Pd), at P = 50 W, 110 °C under microwave
 [b] * isolated yield

It was discovered that reaction time was greatly reduced under microwave heating (6 min) compared to conventional heating (3 hrs). Isolated yield of biphenyl under conventional heating was only 86% in contrast to 96% isolated under microwave heating. Thus, using microwave heating, the reaction can be performed at a faster pace and with higher yield as compared to conventional heating.

The excellent results obtained under microwave heating prompted us to screen further, the coupling of phenyltrimethoxysilane, with various substituted aryl halides. Both, electron-deficient and electron-rich aryl bromides produced the corresponding biphenyls in excellent yields. The results are summarized in Table 1. The effect of variation of aryl

halide was also studied and it was noticed that aryl chlorides with electron withdrawing groups gave higher yields of corresponding biphenyls

All the products were of high purity and were characterized by matching their ^1H NMR spectra with the reported data. The results have been provided in Supporting Information. In majority of the reactions, power of microwave was maintained between 45 to 50W and temperature at 110 °C. The temperature and potency profile for the reactions under microwave irradiation is shown in Fig. (2).

Nature of the base and its quantity has a great effect on the yield of the biphenyl. A wide range of different bases has

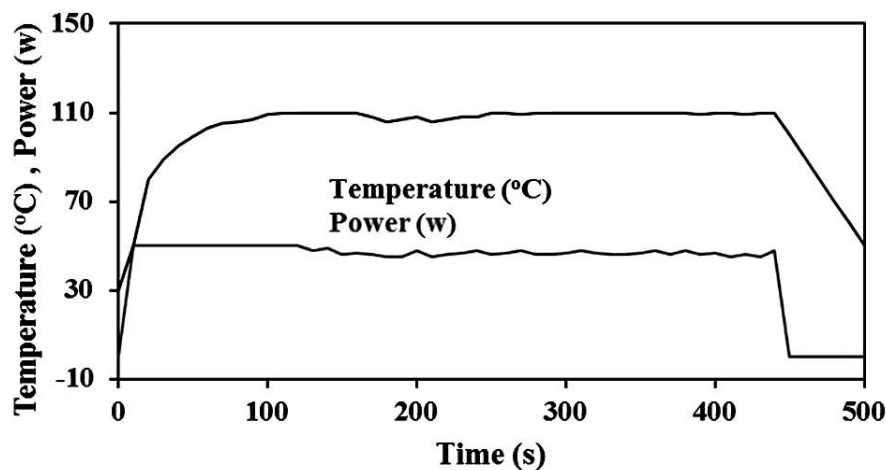


Fig. (2). Temperature and potency profile for the microwave-assisted Hiyama reactions catalyzed by Pd (0)–PVP.

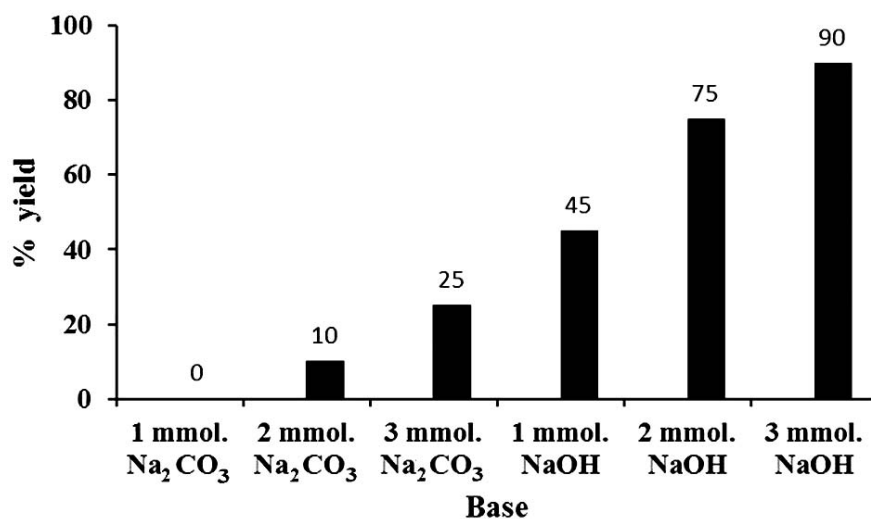


Fig. (3). Effect of base on the yield (GC determined) of 4-bromoacetophenone in Hiyama reactions.

been reported as activator in Hiyama cross-coupling reaction. In this case, two common inorganic bases viz. sodium hydroxide and sodium carbonate in different molar ratios were tried. It was observed that, the conversion to 4-acetylbiphenyl was incomplete when sodium carbonate was used as base. However, in the case of NaOH, % yield was high (as monitored by GC/MS) and maximum conversion was achieved using 3M NaOH. The results are shown in (Fig. 3).

The catalytic activity Pd (0)–PVP NPs was investigated by varying the amount of catalyst while keeping the other parameters constant. The results are shown in (Fig. 4). The highest yield was obtained using 5 mL (0.003 mmol of Pd) of Pd (0)–PVP colloidal solution. Using the obtained results, we calculated the TON and TOF (h^{-1}) values which were found to be 330 and 3300 respectively.

The kinetics of the reaction was studied by analyzing the reaction mixture at different intervals of time and confirmed by the GC-MS at the end of reaction (Fig. 5) Total conversion of 4-bromoacetophenone was obtained after 6 min. The GC-MS analysis of the ether extract showed that 4-

acetylbiphenyl is the sole product (retention time = 19.07 min). The mass spectrum of this peak (retention time = 19.07 min) showed its molecular ion peak at m/z 196 and other prominent peaks at m/z 181, 152, 127, 91, 76.

3.2. Recycling of Pd (0)–PVP NPs

The recycling of Pd (0)–PVP NPs was also studied. After quenching the reaction, products were extracted into organic phase. The Pd (0)–PVP NPs settled at the bottom was separated by centrifugation and heated again with 5 mL of fresh ethanol. The catalyst gets dispersed and was reused after adding fresh amount of reactants. The Pd (0)–PVP nanoparticles were reused for at least four runs without any significant decrease in the catalytic activity and performance (Fig. 6).

4. CONCLUSIONS

We have demonstrated that Pd (0)–PVP colloidal solution is an efficient catalyst for Hiyama cross-coupling reaction under microwave irradiation. The corresponding biaryls were obtained in good yield (80–96%) and short

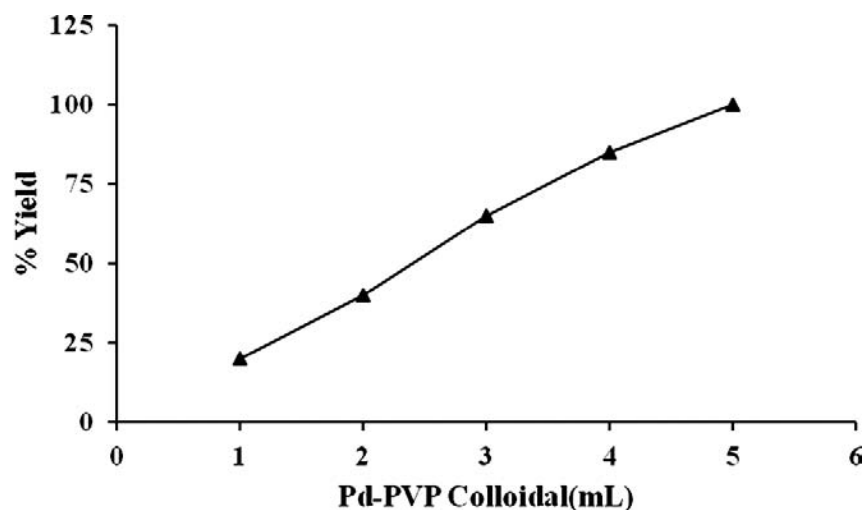


Fig. (4). Effect of Pd(0)-PVP Colloidal Catalyst Concentration on the yield (GC determined) of 4-bromoacetophenone.

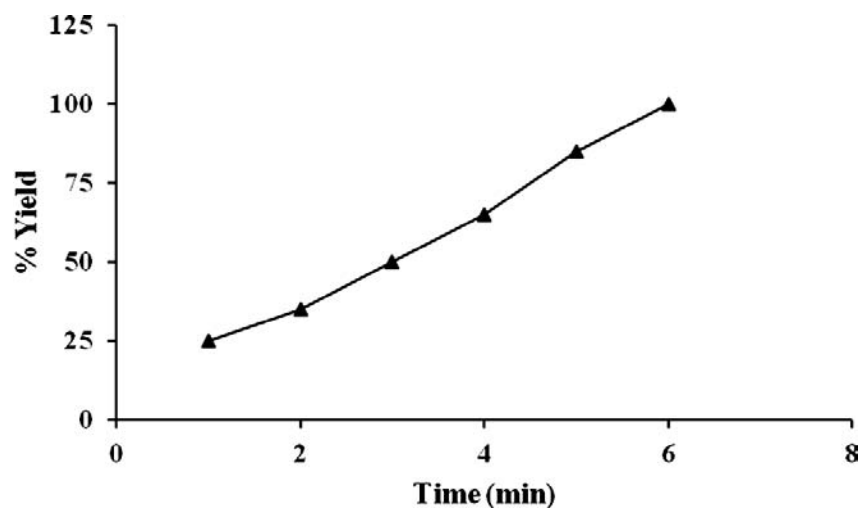


Fig. (5). Effect of Time on the yield (GC determined) of 4-bromoacetophenone.

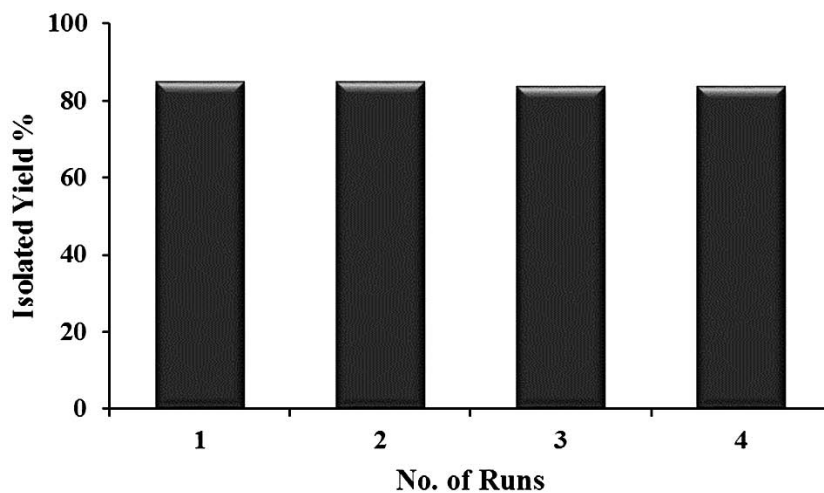


Fig. (6). Reuse of Pd(0)-PVP NPs in Hiyama reaction of 4-bromoacetophenone and phenyltrimethoxysilane.

times (6 - 8 min) from aryl bromides and aryl chlorides. Compared to water soluble palladium complex, Pd(0)-PVP colloidal solution is not only easy to synthesize but also

recyclable. There was no need to use fluoride ions as activators. However, the yield of the product strongly depends on the type of base used.

CONFLICT OF INTEREST

The authors confirm that this article content has no conflict of interests.

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