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A dithizone-functionalized polystyrene resin-supported Pd(II) complex as an effective catalyst for Suzuki, Heck, and copper-free Sonogashira reactions under aerobic conditions in water

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ABSTRACT

A novel polystyrene-supported palladium(II) dithizone complex is found to be a highly active catalyst for the Suzuki, Heck, and Sonogashira reactions of aryl halides in water. By this protocol, aryl halides, coupled with phenyl boronic acid (Suzuki reaction), alkenes (Heck reaction) or terminal alkyne (Sonogashira reaction), smoothly affords the corresponding cross-coupling products in good to excellent yields. Furthermore, the catalyst shows good thermal stability and recyclability. The catalyst was recycled for the Suzuki, Heck, and Sonogashira reactions for five runs without appreciable loss of its catalytic activity and negligible metal leaching.

1. Introduction

Regarding the C—C bond formation reactions, particular attention has been paid to the coupling of aryl halides with organoboronic acids (Suzuki coupling reaction) [1–7], alkenes (Heck reaction) [8–14], and alkynes (Sonogashira coupling reaction) [15–19], respectively. These Pd-catalyzed coupling reactions are ranked today among the most general transformations in organic synthesis, which have great industrial potential for the synthesis of chemicals, therapeutic drugs, and their intermediates.

The original Heck, Suzuki, and Sonogashira reactions generally proceed in the presence of a homogeneous palladium catalyst, which makes its separation and recovery tedious, if not impossible, and might result in unacceptable palladium contamination of the products. A way to overcome this difficulty would be the use of a heterogeneous palladium catalyst.

From the standpoint of green chemistry, development of more environmentally benign conditions for the reaction such as the use of a heterogeneous palladium catalyst would be desirable [20–23]. Palladacycles have recently emerged as one of the most promising classes of catalysts or catalyst precursors in the Pd catalyzed C—C bond forming reactions such as Heck-Mizoroki [24–34], Suzuki-Miyaura [1,35–41], and Sonogashira reactions [42–49].

The immobilization methods used to deposit palladium into heterogeneous solid beds have been studied extensively, and diverse supports such as clay [50], carbon nanofiber [51], montmorillonite [52], magnetic mesoporous silica [53], zeolite [54], and metal oxides [55] have been investigated.

A current challenge in this area is the development of efficient immobilized systems that could simultaneously fulfill the usual targets of achieving high TON values and facilitate recovering and reuse as well as the need for obtaining Pd-free final products [56,57], meeting the strict purity specifications for the pharmaceutical industry [58,59].

In this regard, different types of heterogeneous catalysts have been prepared with the goal of achieving catalyst recovery and recycling [60,61].

To date, development of green chemistry through organic reactions conducted in water has become one of the most exciting research endeavors in organic synthesis [62–65]. Several examples of Pd-catalyzed Suzuki-Miyaura, Mizoroki-Heck, and Sonogashira reactions in aqueous media have been reported [66–69].

Recently, Xia et al. described cross-linked polymer supported Palladium catalyzed carbonylative Sonogashira coupling reaction in water [70]. Singh et al. reported synthesis and characterization

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of recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for Mizoroki-Heck and Sonogashira reactions in ionic liquid media [71]. Furthermore, Iranpoor et al. illustrated Palladium nano-particles supported on agarose as efficient catalyst and bioorganic ligand for C—C bond formation *via* solvent less Mizoroki-Heck reaction and Sonogashira reaction in polyethylene glycol (PEG 400) [72]. Wu et al. exemplified ionic liquid functionalized phosphine-ligated Palladium complex for the Sonogashira reactions under aerobic and copper-free conditions [73]. Above all the methods provide good yield, but some of these reactions are sluggish requiring at least 24 h for completion, lengthy work-up procedure, harsh reaction conditions and require absolutely dry and inert media.

So far, polystyrene-supported palladium catalysts have successfully been used for the Heck [74] and Suzuki [75–78] reactions, and have shown lower levels of palladium leaching during cross-coupling. To date, a few palladium complexes on functionalized polystyrene support have been prepared and successfully used in Sonogashira reaction [79–85]. Very recently, our research team have reported the synthesis of the polystyrene-supported bidenate phosphine palladium(0) complex [abbreviated as PS-dpp-Pd(0), and the polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi-carbazone complex [abbreviated as PS-ppdot-Pd(II)], and found that these complexes are a highly active and recyclable catalyst for Sonogashira reaction of aryl iodides [86,87] or benzoyl chlorides [88,89] with terminal alkynes.

Our approach was guided by three imperatives: (i) the support should be easily accessible; (ii) develop an efficient synthetic process for the facile conversion of Heck, Suzuki, and Sonogashira coupling reactions; and (iii) the ligand anchored on the support should be thermal stability, air-stable at room temperature, which should allow its storage in normal bottles with unlimited shelf-life.

Herein, we report the synthesis of polystyrene-supported palladium(II) dithizone complex [abbreviated as PS-dtz-Pd(II)] catalyst and its application to cross-couplings such as Suzuki-Miyaura, Mizoroki-Heck, and copper-free Sonogashira reactions in water under aerobic conditions. The ease of preparation of the complex, its long shelf-life, stability toward air, and compatibility with a wide variety of aryl halides and alkynes make it ideal for the above mentioned reactions.

2. Experimental

All materials were commercial reagent grade. Chloromethylated polystyrene (4–5% Cl and 2% cross-linked with divinylbenzene) was a product of Merck. Alkyne and aryl halide compounds were obtained from Merck or Fluka.

2.1. Preparation of polymer-anchored PS-dtz-Pd(II) 3

To a 250-ml of round bottom flask equipped with a magnetic stirrer bar and containing DMF (50 ml), were added chloromethylated polystyrene (2 g, 1.25 mmol/g of Cl) and dithizone (7.5 mmol). The reaction mixture was stirred for 24 h at 100 °C, and was subsequently filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. The dithizone functionalized polymer **2** (3.0 g) was treated with ethanol (50 ml) for 30 min. An ethanolic solution of $PdCl_2(PhCN)_2$ (1.2 g) was added, and the resulting mixture was heated to 80 °C for 15 h. The resulting bright yellow colored polymer, impregnated with the metal complex, was filtered and washed with ethanol to obtain PS-dtz-Pd(II) **3** (Scheme 1).

2.2. General procedure for the Suzuki coupling reaction

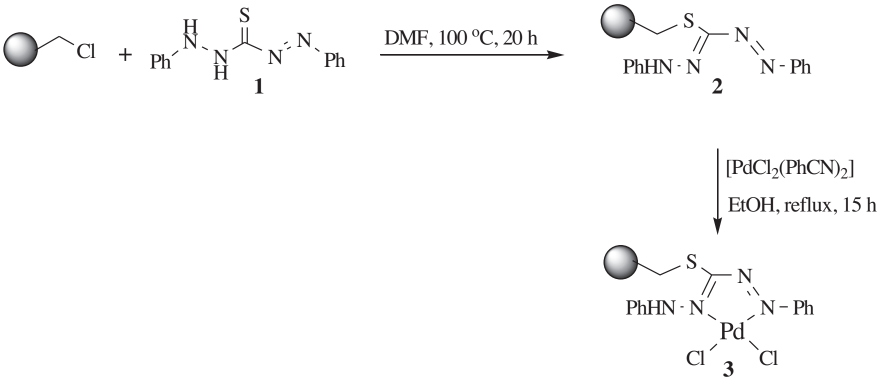
A mixture of aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), PS-dtz-Pd(II) (0.001 mmol), K_2CO_3 (2 mmol), and water (3 ml) was stirred at 70 °C for 5 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using $CHCl_3$—CH_3OH (97:3) as eluent to afford the pure product.

2.3. General procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), methyl acrylate (1.5 mmol), PS-dtz-Pd(II) (0.001 mmol), K_2CO_3 (2.0 mmol), and water (3 ml) was stirred at 70 °C for 5 h. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude product was subjected to silica gel column chromatography using $CHCl_3$—CH_3OH (97:3) as eluent to afford the pure product.

2.4. General procedure for the Sonogashira coupling reaction

An aryl halide (1.0 mmol) and a terminal alkyne (1.2 mmol) were added to a mixture of PS-dtz-Pd(II) (0.001 mmol), piperidine (2.0 mmol), and water (3 ml) in a glass flask under vigorous stirring. The mixture was stirred at room temperature for 3 h under aerobic conditions. After completion of the reaction, the mixture was filtered to recover the catalyst. The polymer was washed with water and acetonitrile, vacuum dried, and stored for a new run. After GC analysis, the solvent was removed under vacuum, and the crude



Scheme 1. Preparation of the heterogeneous catalyst PS-dtz-Pd(II) **3**.

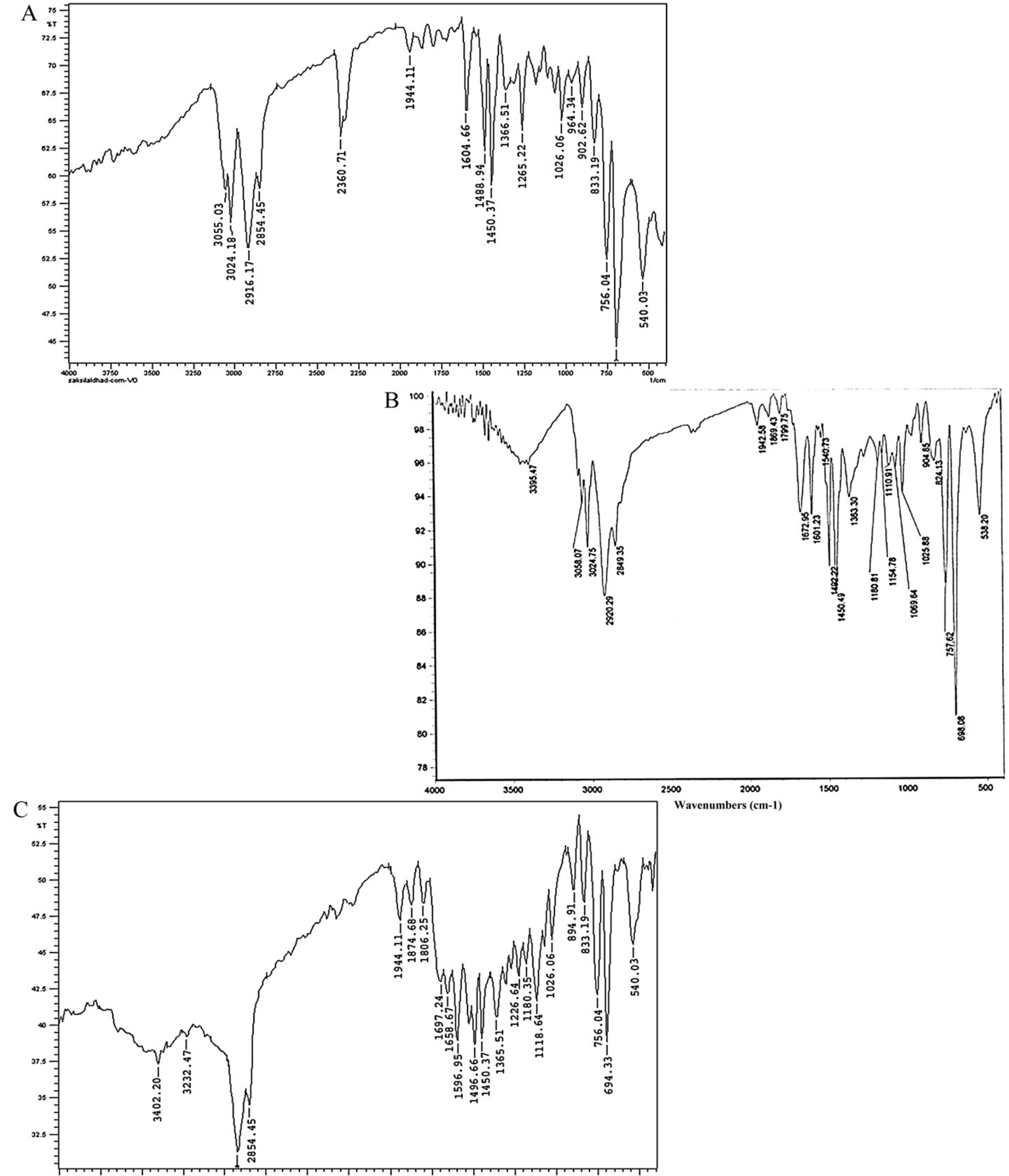


Fig. 1. FT-IR spectra of: (A) chloromethylated polystyrene (B) polystyrene-dithizone ligand (C) supported Pd-dithizone complex.

product was subjected to silica gel column chromatography using $CHCl_3—CH_3OH$ (97:3) as eluent to afford the pure product.

3. Results and discussion

3.1. Characterization of PS-dtz-Pd(II)

A polystyrene divinylbenzene resin anchored with a chelating regent dithizone has been reported by Grote and Kettrup [90]. They have used this support for the sorption of gold and platinum group metals and base metals like copper, nickel, and zinc.

We report here anchoring of dithizone on crosslinked polystyrene polymer (Scheme 1). The chelating polymeric matrix is further used for Suzuki, Heck, and Sonogashira reactions. A polystyrene resin (2% DVB) functionalized with dithizone groups was formed by heating a mixture of chloromethylated polystyrene and dithizone in DMF at 100 °C for 24 h. The polymer-supported dithizone is insoluble in common organic solvents. Reaction of polymer-bound dithizone with a solution of $[PdCl_2(C_6H_5CN)_2]$ in ethanol under reflux conditions resulted in covalent attachment of palladium onto functionalized polymer. The N content of resin was obtained to be 2.8% (1.98 mmol/g), which indicates that only 40% of total chlorines was substituted by amine). The amount of palladium incorporated into the polymer was also determined by inductively coupled plasma (ICP), which showed the value of about 3.1%.

The difference in the amount of chlorine in chloromethylated polystyrene and the dithizone anchored support is due to the chemical binding of dithizone to the support by chlorine displacement. This was further confirmed through FT-IR analysis of the copolymer and copolymer loaded with dithizone.

In the FT-IR spectrum of polymer-bound dithizone, the sharp C—Cl peak (due to $—CH_2Cl$ groups) at 1265 cm^{-1} (Fig. 1A) in the starting polymer was practically omitted or seen as a weak band after introduction of dithizone on the polymer. The stretching vibrations of the C=N double bonds appear at 1672 cm^{-1} for polystyrene-dithizone ligand, respectively (Fig. 1B). The NH group of polystyrene-dithizone in the IR spectrum is 3395 cm^{-1}, whereas the NH group of dithizone palladium complex (Fig. 1C) in the IR spectrum is 3402 cm^{-1} indicating that the Pd-N bond has been established.

Scanning electron micrographs (SEM) were reported for a single bead of pure chloromethylated polystyrene, and polymer-anchored complex to observe the morphological changes. As expected, the pure polystyrene bead had a smooth and flat surface, while the anchored complex showed roughening of the top layer (Fig. 2).

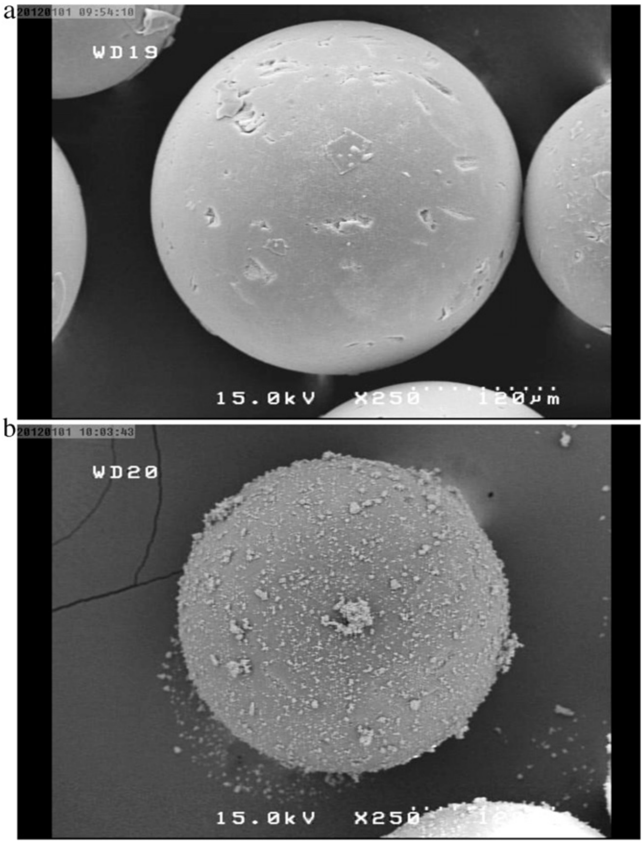


Fig. 2. Scanning electron micrograph of (a) chloromethylated polystyrene; (b) PS-dtz-Pd(II) complex.

3.2. Catalytic activity

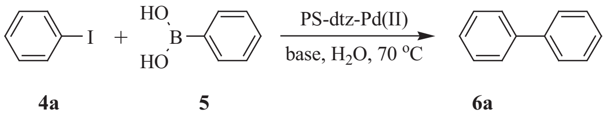
Efficiency of the dithizone-functionalized polystyrene resin-supported Pd(II) complex **3** was tested in Suzuki, Heck, and Sonogashira reactions.

3.2.1. Catalytic Suzuki cross-coupling reactions

In the initial investigations, we examined the Suzuki-Miyaura coupling reaction of the model substrate phenyl iodide **4a** with phenylboronic acid **5** using PS-dtz-Pd(II) complex (0.1 mol%) as the catalyst in water at 70 °C for 5 h (Table 1). As it can be seen in Table 1, from the bases screened, K_2CO_3 showed the best result, and the corresponding coupling product **6a** was obtained in 99% yield (Table 1, entry 8). Effect of temperature on the activity of PS-dtz-Pd(II) complex was also studied. As the temperature decreased from 70 to 25 °C, the yield of product **6a** decreased from 99% to 60% (entry 9). A low palladium concentration gave a decreased yield (entry 10).

Thus at the optimal reaction conditions PS-dtz-Pd(II) complex (0.1 mol%) as the catalyst, K_2CO_3 (2.0 equiv) as the base, and water (3 ml) as the solvent are used at the temperature of 70 °C. With the optimal reaction conditions in hand, we firstly explored the scope and limitations of the reaction with a set of aryl iodides and phenylboronic acid. We were pleased to find out that all reactions afforded the desired coupling products **6** in excellent yields within 5 h, and the substituents, either an electron-donating group such as methoxy group (Table 2, entry 7) or an electron-withdrawing group such as Cl, NO_2, or COMe on the phenyl ring of **4** had almost no significant effect on these reactions (Table 2, entries 3–6). To extend the scope of our work, we next investigated the coupling reaction of various aryl bromides with phenyl boronic acid. The less reactive

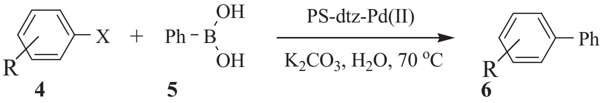
Table 1
Optimization of the conditions for Suzuki reaction of iodobenzene with phenyl boronic acide[a].



Entry	Base	Cat (mol%)	Yield (%)[b]
1	Et_3N	0.1	95
2	DIEA	0.1	90
3	Pyridine	0.1	86
4	Piperidine	0.1	94
5	Pyrrolidine	0.1	90
6	KOH	0.1	93
7	Na_2CO_3	0.1	95
8	K_2CO_3	0.1	99
9[c]	K_2CO_3	0.1	60
10	K_2CO_3	0.05	90

[a] Conditions: iodobenzene (1.0 mmol), phenylboronic acide (1.2 mmol), base (2.0 mmol), H_2O (3 ml), 5 h at 70 °C.
[b] GC yield.
[c] Reaction at 25 °C.

Table 2
Suzuki reaction of aryl halides with phenyl boronic acid using PS-dtz-Pd(II) complex[a].



Entry	R	X	Product	Yield (%)[b]	TON
1	H	I	**6a**	99	990
2	4-Br	I	**6b**	98	980
3	4-Cl	I	**6c**	99	990
4	4-MeCO	I	**6d**	100	1000
5	4-NO_2	I	**6e**	100	1000
6	3-NO_2	I	**6f**	100	1000
7	4-MeO	I	**6g**	98	980
8	H	Br	**6a**	68	680
9	4-CHO	Br	**6h**	92	920
10	4-CN	Br	**6i**	90	900
11	4-NO_2	Br	**6e**	80	800
12	3-NO_2	Br	**6f**	90	900
13	4-MeO	Br	**6g**	60	600

[a] Reaction conditions: aryl halide (1.0 mmol), phenyl boronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), PS-dtz-Pd(II) (0.001 mmol), H_2O (3 ml), 5 h at 70 °C.
[b] GC yield.

bromobenzene showed low yield (entry 8). However, the activated aryl bromides, 4-bromobenzaldehyde, 4-bromobenzonitrile, 4-nitrobromobenzene and 3-nitrobromobenzene gave the corresponding product in high yield (Table 2, entries 9–12).

3.2.2. Catalytic Heck reaction

The scope of this methodology was further extended for Heck reaction. Using PS-dtz-Pd(II) complex as catalyst bases like K_2CO_3 (94%), KOH (93%), Et_3N (97%), diisopropylethylamine (92%), pyridine (85%), and piperidine (87%), in water at 70 °C were screened for the standard reaction. It was observed that the reaction was more favorable using Et_3N as the base, and the protocol was applied for coupling of methylacrylate with aryl halides.

Using the optimized reaction conditions, we explored the general applicability of PS-dtz-Pd(II) complex with methyl acrylate and aryl halides containing electron withdrawing or donating substituents, and the results were tabulated in Table 3. Among the various substituted aryl iodides, both deactivated (electron-rich) and activated (electron-poor) examples were converted efficiently to the desired products in excellent yields (entries 1–4). As expected, aryl iodides were more reactive than aryl bromides, and the substituent effects in the aryl iodides appeared to be less significant than in the aryl bromides. As shown in Table 3, activated aryl bromides such as *p*-nitrobromobenzene underwent the Heck reaction with methyl acrylate under similar conditions to afford the corresponding product in 95% yield (entry 6) whereas, unactivated aryl bromides such as *p*-methoxybromobenzene gave 80% yield (entry 7).

3.2.3. Catalytic Sonogashira reactions

We next investigated the PS-dtz-Pd(II) complex catalytic system for the copper-free Sonogashira cross-coupling reaction. The catalytic activity of the PS-dtz-Pd(II) complex **3** (0.1 mol%) was studied at room temperature under aerobic conditions in a copper-free Sonogashira reaction using phenylacetylene and aryl halides in the presence of various bases in water. Our optimization data is shown in Table 4.

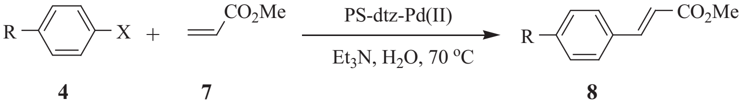
When the reaction of phenylacetylene with phenyl iodide was performed with piperidine as base, an excellent 99% yield of the product was obtained (entry 4). Since aryl bromides are cheaper and more readily available than aryl iodides, and hence are synthetically more useful as educts, we examined the reaction of phenyl bromide with phenylacetylene under the above conditions, and piperidine was found to be the best choice of base amongst those tested (entry 13).

After the optimized conditions were found, we explored the general applicability of the PS-dtz-Pd(II) complex **3** as a catalyst for copper-free coupling of different alkynes **9** with aryl iodides and bromides **4** containing electron withdrawing or donating substituents. The results are shown in Table 5. The coupling of phenylacetylene with iodobenzene took place smoothly at room temperature in the presence of piperidine (2 mmol) and 0.1 mol% palladium of the PS-dtz-Pd(II) complex **3** to give an excellent yield of diphenylacetylene (entry 1). The Sonogashira coupling of phenylacetylene with *p*-iodoanisol bearing electron-donating groups at their *p*-positions gave the corresponding biarylacetylenes **10g** in 97% yield, (entry 7). *p*-Nitroiodobenzene, and *m*-nitroiodobenzene, having electron-deficient aromatic rings, also underwent the Sonogashira coupling with phenylacetylene under similar conditions to afford the corresponding biarylacetylenes **10b**, and **10c** in excellent yields (100%) (entries 2 and 3).

When the less reactive acetylene, 1-hexyne, and propargyl alcohol were used, the coupling product was produced efficiently. Coupling of *p*-substituted iodobenzene having nitro, chloro, bromo, and methoxy groups took place with 1-hexyne to give the corresponding products **10i**–**m** in excellent yields (entries 9–13). Propargyl alcohol also reacted efficiently with aryl iodides providing excellent yields of the desired products (entries 14–16).

To extend the scope of our work, we next investigated the coupling of various aryl bromides with terminal alkynes. As shown in Table 5, high catalytic activity was observed in the coupling of unactivated aryl bromides such as nitrobromobenzenes (entries 18, 19, 24, 25, and 29) and *p*-bromoanisole (entries 22, 27, and 30) as well as the activated nitroiodobenzenes (entries 2, 3, 9, 10, and 15) and *p*-iodoanisol (entries 7, 13, and 16). Moreover,

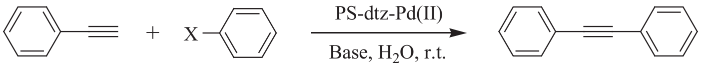
Table 3
Heck reactions of aryl halides with methyl acrylate using PS-dtz-Pd(II) complexe[a].



Entry	R	X	Product	Yield(%)[b]	TON
1	H	I	**8a**	97	970
2	Cl	I	**8b**	98	980
3	NO_2	I	**8c**	98	980
4	MeO	I	**8d**	95	950
5	H	Br	**8a**	90	900
6	NO_2	Br	**8c**	95	850
7	MeO	Br	**8d**	80	800

[a] Conditions: aryl halide (1.0 mmol), methyl acrylate (1.5 mmol), PS-dtz-Pd(II) (0.001 mmol), Et_3N (2.0 mmol), H_2O (3 ml), 5 h at 70 °C.
[b] GC yield.

Table 4
Copper-free Sonogashira reaction of phenylacetylene with aryl halides in the presence of different bases[a].

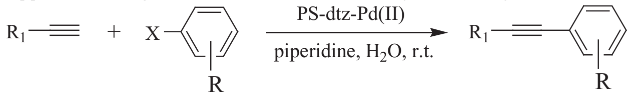


9a **10a**

Entry	X	Base	Yield[b] (%)
1	I	DIEA	80
2	I	Et_3N	96
3	I	Pyridine	52
4	I	Piperidine	99
5	I	Pyrrolidin	42
6	I	Butylamin	64
7	I	K_2CO_3	97
8	I	Na_2CO_3	95
9	I	KOH	93
10	Br	DIEA	60
11	Br	Et_3N	75
12	Br	Pyridine	53
13	Br	Piperidine	99
14	Br	Pyrrolidin	55
15	Br	Butylamin	43
16	Br	K_2CO_3	95
17	Br	Na_2CO_3	90
18	Br	KOH	87

[a] Reaction conditions: phenylacetylene (1.2 mmol), halobenzene (1.0 mmol), base (2.0 mmol), PS-dtz-Pd(II) (0.001 mmol), H_2O (3 ml), 3 h at room temperature, aerobic conditions.
[b] GC yield.

Table 5
Copper-free Sonogashira reactions of terminal alkynes with aryl halides[a].



9 **4** **10**

Entry	R	X	Y	Product	Yield[b] (%)	TON
1	Ph	I	H	**10a**	99	990
2	Ph	I	4-NO_2	**10b**	100	1000
3	Ph	I	3-NO_2	**10c**	100	1000
4	Ph	I	4-Cl	**10d**	99	990
5	Ph	I	4-Br	**10e**	99	990
6	Ph	I	4-$COCH_3$	**10f**	99	990
7	Ph	I	4-OCH_3	**10g**	97	970
8	n-C_4H_9	I	H	**10h**	98	980
9	n-C_4H_9	I	4-NO_2	**10i**	100	1000
10	n-C_4H_9	I	3-NO_2	**10j**	100	1000
11	n-C_4H_9	I	4-Cl	**10k**	99	990
12	n-C_4H_9	I	4-Br	**10l**	98	980
13	n-C_4H_9	I	4-OCH_3	**10m**	98	980
14	CH_2OH	I	H	**10n**	99	990
15	CH_2OH	I	4-NO_2	**10o**	100	1000
16	CH_2OH	I	4-OCH_3	**10p**	98	980
17	Ph	Br	H	**10a**	97	970
18	Ph	Br	4-NO_2	**10b**	98	980
19	Ph	Br	3-NO_2	**10c**	97	970
20	Ph	Br	4-Cl	**10d**	97	970
21	Ph	Br	4-F	**10q**	96	960
22	Ph	Br	4-OCH_3	**10g**	92	920
23	n-C_4H_9	Br	H	**10h**	96	960
24	n-C_4H_9	Br	4-NO_2	**10i**	97	970
25	n-C_4H_9	Br	3-NO_2	**10j**	97	970
26	n-C_4H_9	Br	4-Cl	**10k**	96	960
27	n-C_4H_9	Br	4-OCH_3	**10m**	95	950
28	CH_2OH	Br	H	**10n**	92	920
29	CH_2OH	Br	4-NO_2	**10o**	92	920
30	CH_2OH	Br	4-OCH_3	**10p**	90	900

[a] Reaction conditions: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), PS-dtz-Pd(II) (0.001 mmol), piperidine (2.0 mmol), H_2O (3 ml), 3 h, room temperature, aerobic conditions.
[b] GC yield.

Table 6
The Suzuki, Heck and Sonogashira reactions catalyzed by the recycled catalyst.[a]

Entry	Cycle	Suzuki yield (%)[b]	Heck yield (%)	Sonogashira yield (%)
1	1	99	97	99
2	2	99	97	99
3	3	98	95	99
4	4	96	92	98
5	5	93	90	98

[a] Reaction conditions: phenyl boronic acid (Suzuki reaction) (1.2 mmol), methyl acrylate (Heck reaction) (1.5 mmol), phenyl acetylene (Sonogashira reaction) (1.2 mmol), iodobenzene (1.0 mmol), PS-dtz-Pd(II) (0.001 mmol), base (2.0 mmol), H_2O (3 ml), 70 °C (for Suzuki and Heck reactions), room temperature (for Sonogashira reaction).

[b] GC yield.

p-chlorobromobenzene, and *p*-fluorobromobenzene having electron-deficient aromatic rings also underwent Sonogashira coupling reaction with terminal alkynes under similar conditions to afford the corresponding products in excellent yields.

In all reactions, only 0.1 mol% of PS-dtz-Pd(II) based on the aryl halides was used, and the molar turnover numbers (TON) were larger than those in the corresponding coupling reaction catalyzed by other polystyrene-supported catalysts reported [91–94].

3.3. *Recycling of the catalyst*

One of the purposes for designing this heterogeneous catalyst is to enable recycling of the catalyst for use in subsequent reactions. The reusability of the catalyst was tested upon the reaction of phenyl iodide with phenylboronic acid (Suzuki reaction), phenyl iodide with methyl acrylate (Heck reaction) and phenyl iodide with phenylacetylene (Sonogashira reaction) as the representative reactants and in the presence of 0.1 mol% of PS-dtz-Pd(II) in order to study the recyclability of this heterogeneous catalyst. Similarly, the reactions for the repeated runs were conducted after separation of the organic compounds from the reaction mixture by extraction, and the recovered solid catalyst was recycled for another run. The recycling process was repeated for five cycles with some decrease in the catalytic activity of the catalyst (Table 6).

In order to determine the absolute amount of the palladium species dissolved in solution caused by leaching, the crude reaction mixtures were evaporated to dryness and analyzed using ICP-AE. The amount of palladium leaching after the first run (for Suzuki reaction) was determined by ICP analysis to be only 0.2%, and after five repeated recycling was 5%, which shows the average amount of leaching of palladium per cycle has been around 1.0%.

4. Conclusion

The first example of Suzuki, Heck, and Sonogashira reactions catalyzed by cheap, and air stable PS-dtz-Pd (II) complex as catalyst was described. The ease of preparation of the complex, indefinite shelf life, and stability toward air make it an ideal complex for the above transformations. The system works equally well for a wide variety of aryl halides and alkynes, and tolerates a variety of functional groups. All the reactions were conducted in the air without the use of an organic solvent. Moreover, the catalyst could be reused for five consecutive cycles without a significant loss of its catalytic activity. These advantages make the process highly valuable from the synthetic and environmental points of view.

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