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Suzuki, Heck, and copper-free Sonogashira reactions catalyzed by 4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin-supported Pd(II) under aerobic conditions in water

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ABSTRACT

4-amino-5-methyl-3-thio-1,2,4-triazole-functionalized polystyrene resin-supported Pd(II) complex was found to be an efficient catalyst in the palladium-catalyzed Suzuki–Miyaura coupling reactions of aryliodides and bromides, Mizoroki–Heck reactions of aryliodides and bromides, and copper-free Sonogashira reactions of aryliodides and bromides in water. Under appropriate conditions, all of these reactions give the desired products in moderate to excellent yields. The catalyst is air-stable and easily available. The palladium catalyst is easily separated, and can be reused for several times without a significant loss in its catalytic activity.

1. Introduction

Palladium-catalyzed cross-coupling reactions are versatile and efficient methods for carbon–carbon bond formations [1]. Among them, the Suzuki–Miyaura [2–4], Mizoroki–Heck [5–7], and Sonogashira [8–10] coupling reactions play important roles in modern synthetic chemistry.

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.

Development of recoverable and recyclable catalysts for industrial applications has become important from both the environmental and economical viewpoints, and has been well-reviewed in the literature [11]. To achieve this objective, several catalysts have been anchored or immobilized onto polymeric and inorganic supports [12,13]. Despite the advantages and progress, homogeneous catalysis has a share of less than 20% in industrial processes, because of the issues related to recoverability and recyclability of expensive metal catalysts.

In contrast, heterogeneous catalysis exhibits the advantage of easy separation of the catalyst from the products, and it can be easily adapted to continuous flow processes [14,15].

Palladacycles have recently emerged as one of the most promising classes of catalysts or catalyst precursors in the Pd-catalyzed C–C bond formation reactions such as the Heck–Mizoroki [16–19], Suzuki–Miyaura [20–23], and Sonogashira reactions [24–26].

Improvement of these reactions greatly relies on reactivity of the palladium catalyst using increasingly efficient supporting ligands. To date, many efforts have been made to the search for more efficient ligands. During the past decades, the most common ligands used for these coupling reactions have been the phosphine-based ones [27,28]. Since most of the phosphine-based ligands are air and/or moisture-sensitive, in recent years, phosphine-free ligands as N-heterocyclic carbenes (NHCs) have also been employed [29–31].

To date, development of green chemistry through organic reactions conducted in water has become one of the most exciting research endeavors in organic synthesis [32–34]. Nevertheless, only a few examples of Suzuki–Miyaura, Mizoroki–Heck, and Sonogashira reactions by using water as the solvent have been reported in the literature [35,36].

Very recently, Chungu Xia et al. have described cross-linked polymer supported Palladium-catalyzed carbonylative Sonogashira coupling reactions in water [37]. Vasundhara Singh et al.

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have reported synthesis and characterization of recyclable and recoverable MMT-clay exchanged ammonium tagged carbapalladacycle catalyst for Mizoroki–Heck and Sonogashira reactions in ionic liquid media [38]. Furthermore, Nasser Iranpoor et al. have illustrated palladium nano-particles supported on agarose as an efficient catalyst and a bioorganic ligand for C–C bond formation via the solventless Mizoroki–Heck reaction and Sonogashira reaction in polyethylene glycol (PEG 400) [39]. Haihong Wu et al. have exemplified ionic liquid functionalized phosphine-ligated palladium complex for the Sonogashira reactions under aerobic and copper-free conditions [40].

Polystyrene is one of the most popular polymeric supports used in synthetic organic chemistry because of its in expense, ready availability, mechanical robustness, chemical inertness, and facile functionalization. S. M. Islam et al. have described synthesis and characterization of reusable polystyrene anchored Pd(II) azo complex catalyst for Suzuki and Sonogashira coupling reaction in water medium [41]. Moreover, Ying He et al. have developed successful copper-free Sonogashira coupling reaction catalyzed by a reusable polystyrene-supported macrocyclic Schiff base palladium complex in water [42]. Recently, our research team have reported synthesis of the polystyrene-supported bidentate phosphine palladium(0) complex and the polystyrene-supported palladium(II) 1-phenyl-1,2-propanedione-2-oxime thiosemi–carbazone complex, and found that these complexes are highly active and recyclable catalysts for Sonogashira reaction of aryl iodides [43,44] or benzoyl chlorides [45,46] with terminal alkynes. Although all these methods provide good yields, some of the reactions are sluggish, requiring high temperature for completion, and the reactions must be performed in the presence of a relatively large amount of palladium.

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

In the continuation of our interest in the development of new ligands for Pd-catalyzed C–C bond formation reactions, we report synthesis of the PS-tazo-Pd(II) catalyst and its application to cross-couplings such as the 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, its stability toward air, and its compatibility with a wide variety of aryl halides, and alkynes make it ideal for the above-mentioned reactions.

2. Results and discussion

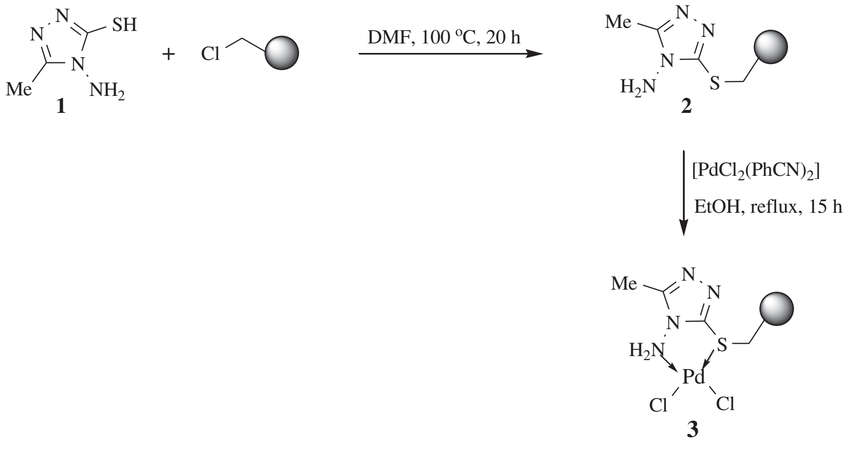
First polystyrene-bound triazole (PS-tazo) **2** was prepared by treating chloromethylated polystyrene (cross-linked with 2% divinylbenzene, 4–5% Cl content, 1.14–1.40 mmol/g Cl) with an appropriate quantity of 4-amino-3-methyl-5-mercaptotriazole **1** in DMF for 20 h at 100 °C. PS-tazo prepared was characterized by elemental analysis. The nitrogen content of this resin was 5.13%. According to this value, the degree of triazole introduced into the polymer was 0.916 mmol/g of the support. This shows that only 65–80% of the total chlorine content have been substituted by triazole. Then triazole-functionalized polystyrene resin-supported Pd(II) [PS-tazo-Pd(II)]complex **3** was prepared by stirring a suspension of PS-tazo in a solution of $PdCl_2(PhCN)_2$ in refluxing EtOH for 15 h (Scheme 1). The catalyst prepared, PS-tazo-Pd(II), was characterized by FT-IR, SEM, and ICP. The amount of palladium incorporated into the polymer was also determined by inductively coupled plasma (ICP), which showed a value of 0.28 mmol/g of the heterogenized catalyst.

Presence of the triazole ligand on the polystyrene was confirmed by FT-IR spectra. The sharp C–Cl peak (due to $-CH_2Cl$ groups) at 1264 cm^{-1} in the starting polymer was practically omitted after introduction of the triazole ligand on the polymer. The IR spectra of chloromethylated polystyrene-supported triazole ligand show sharp bands around 3347 cm^{-1} due to the N–H vibrations (Fig. 1).

Scanning electron micrograph (SEM) was recorded to understand the morphological changes occurring on the surface of the polymer. The images showed that polystyrene microspheres have been broken upon attachment of the triazole and palladium complex (Fig. 2).

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

Initial studies were performed upon the Suzuki–Miyaura coupling reaction of phenyliodide **4a** with phenylboronic acid **5** as a model reaction using PS-tazo-Pd(II) complex (0.1 mol%) as the catalyst in water at 70 °C for 10 h (Table 1). As it can be seen in this table, from the bases screened, K_2CO_3 shows the best result, and the corresponding coupling product **6a** was obtained in 99% yield (Table 1, entry 6). When the amount of the catalyst was decreased from 0.1 to 0.05 mmol %, the yield of **6a** was decreased to 75% (entry 7). However using 0.1 mmol% of PS-tazo-Pd(II), biphenyl was obtained with 99% in 10-h (entry 6). Almost similar yield was achieved when escalating the catalyst amount from 0.1 to 0.15 mmol% (entry 8). Effect of temperature on the activity of PS-tazo-Pd(II) complex was also studied. As the



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

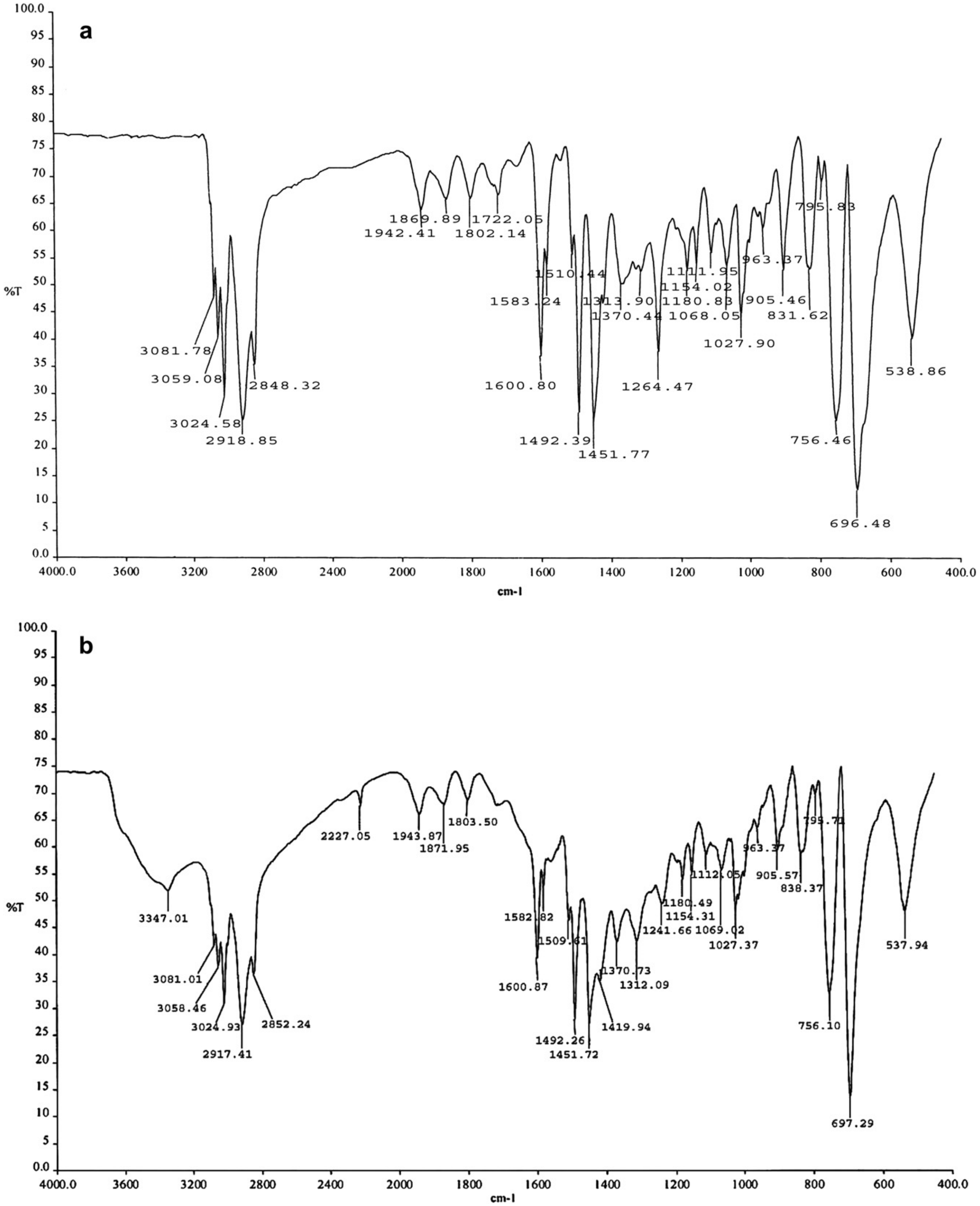


Fig. 1. FT-IR spectra of (a) chloromethylated polystyrene, and (b) supported Pd-tazo complex.

temperature decreased from 70 to 25 °C, the yield of product **6a** decreased from 99% to 70% (entry 9).

Using the optimized reaction conditions, we explored the general applicability of PS-tazo-Pd(II) complex with phenylboronic acid and aryl iodides containing electron withdrawing or donating substituents, and the results were tabulated in Table 2. We were pleased to find out that all reactions afforded the desired coupling products **6** in excellent yields within 10 h, and the substituent,

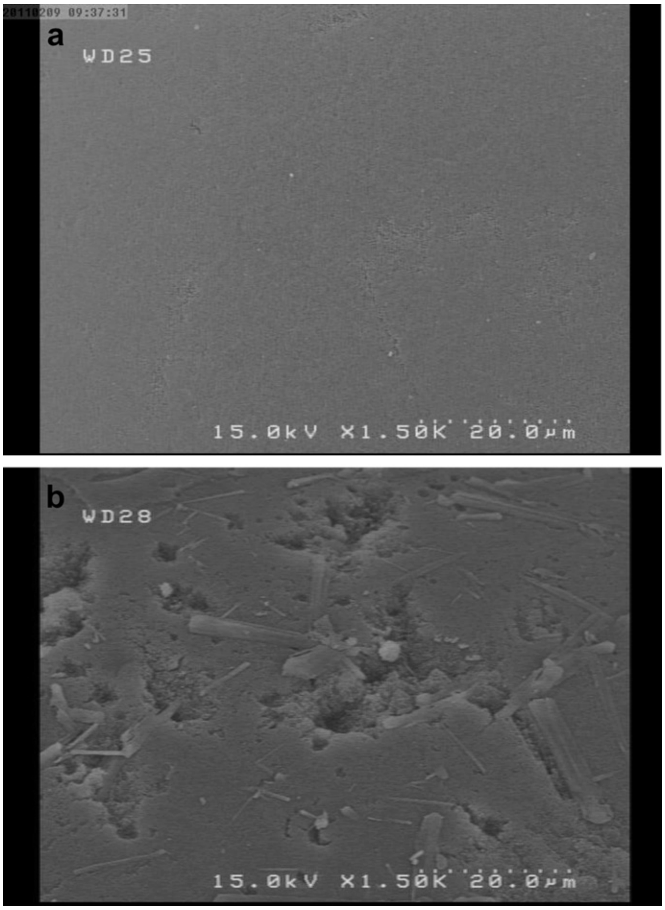
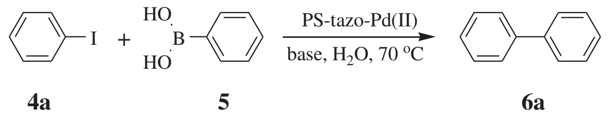


Fig. 2. Scanning electron micrograph of (a) chloromethylated polystyrene (b) supported Pd-tazo complex.

either an electron-donating group such as methoxy group (entry 7) or an electron withdrawing group such as NO_2, COMe, or Cl (entries 2–5) on the phenyl ring of **4** had almost no significant effect on these reactions. To extend the scope of our work, we next investigated the coupling reactions of various aryl bromides with phenylboronic acid. The Suzuki reactions of electron withdrawing and electron-rich aryl bromides with phenylboronic acid proceeded smoothly to give the corresponding coupling products in high yields (entries 9–14).

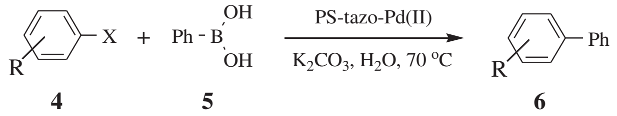
Table 1
Optimization of the conditions for Suzuki reaction of phenyliodide with phenylboronic acid[a].



Entry	Base	Time (h)	Catalyst (mol%)	Yeild[b] (%)
1	DIEA	10	0.1	64
2	Et_3N	10	0.1	85
3	Piperidine	10	0.1	90
4	Pyrrolidin	10	0.1	74
5	Na_2CO_3	10	0.1	97
6	K_2CO_3	10	0.1	99
7	K_2CO_3	10	0.05	75
8	K_2CO_3	7	0.15	99
9[c]	K_2CO_3	10	0.1	70

[a] Conditions: phenyliodide (1.0 mmol), phenylboronic acid (1.2 mmol), base (2.0 mmol), H_2O (3 ml), 10 h at 70 °C.
[b] GC yield.
[c] Reaction at 25 °C.

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



Entry	R	X	Product	Yield[b] (%)	TON
1	H	I	**6a**	99	990
2	3-NO_2	I	**6b**	99	990
3	4-NO_2	I	**6c**	99	990
4	MeCO	I	**6d**	99	990
5	Cl	I	**6e**	97	970
6	Br	I	**6f**	96	960
7	MeO	I	**6g**	96	960
8	H	Br	**6a**	98	980
9	3-NO_2	Br	**6b**	99	990
10	4-NO_2	Br	**6c**	99	990
11	4-CN	Br	**6h**	98	980
12	4-CHO	Br	**6i**	98	980
13	Cl	Br	**6e**	97	970
14	MeO	Br	**6g**	95	950

[a] Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), K_2CO_3 (2.0 mmol), PS-tazo-Pd(II) (0.001 mmol), H_2O (3 ml), 10 h at 70 °C.
[b] GC yield.

Furthermore, under these optimized conditions, we investigated the usefulness of PS-tazo-Pd(II) complex in the Heck reaction involving cross-coupling of an aryl halide with methyl acrylate. Table 3 illustrates that the reaction is effective in the presence of a wide variety of functional groups on the aryl iodides and aryl bromides, giving good to excellent conversions to the corresponding products.

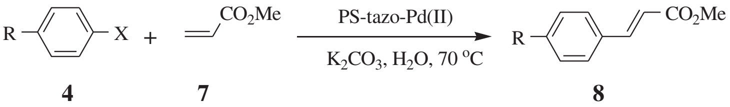
Among the various substituted aryl iodides, both activated (electron-poor) and deactivated (electron-rich) examples were converted efficiently to the desired products in excellent to good yields (entries 2–5). As expected, aryl iodides were more reactive than aryl bromides, and the substituent effects in the aryl iodides appear 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 98% yield (entry 7) whereas, unactivated aryl bromides such as *p*-bromoanisole gave 90% yield (entry 8).

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

When the reaction of phenylacetylene with iodobenzene was performed with K_2CO_3 as the base, an excellent 99% yield of the product was obtained (entry 5).

After the optimized conditions were found, we explored the general applicability of the PS-tazo-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 phenyliodide took place smoothly at room temperature in the presence of K_2CO_3 (2.0 mmol) and 0.1 mol% palladium of the PS-tazo-Pd(II) complex **3** to give an excellent yield

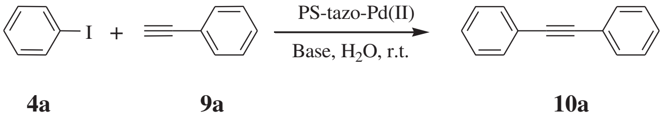
Table 3
Heck reactions of aryl halides with methyl acrylate using PS-tazo-Pd(II) complex[a].



Entry	R	X	Product	Yield[b] (%)	TON
1	H	I	**8a**	97	970
2	NO_2	I	**8b**	99	990
3	Cl	I	**8c**	98	980
4	Br	I	**8d**	97	970
5	MeO	I	**8e**	92	920
6	H	Br	**8a**	95	950
7	NO_2	Br	**8b**	98	980
8	MeO	Br	**8e**	90	900

[a] Conditions: aryl halide (1.0 mmol), methyl acrylate (1.5 mmol), PS-tazo-Pd(II) (0.001 mmol), K_2CO_3 (2.0 mmol), H_2O (3 ml), 10 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].



Entry	Base	Yeild[b] (%)
1	DIEA	70
2	Et_3N	95
3	Piperidine	85
4	Pyrrolidin	95
5	K_2CO_3	99
6	Na_2CO_3	96

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

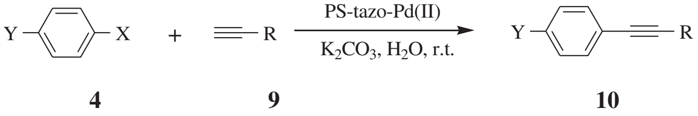
of diphenylacetylene (entry 1). The Sonogashira coupling of phenylacetylene with *p*-iodoanisol (electron-rich) gave the corresponding biarylacetylenes **10d** in 97% yield, (entry 4).

p-bromoiodobenzene and *p*-chloroiodobenzene also underwent the Sonogashira coupling reaction with phenylacetylene under similar conditions to afford the corresponding biarylacetylenes **10b** and **10c** in excellent yields (99%) (entries 2 and 3).

When the less reactive acetylene, 1-hexyne, was used, the coupling product was produced efficiently. Coupling of *p*-substituted iodobenzene having bromo, chloro, and methoxy groups took place with 1-hexyne to give the corresponding products **10h–j** in excellent yields (entries 10–12).

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 aryl bromides such as nitrobromobenzenes (entries 6 and 14) and *p*-bromoanisole (entries 8 and 16) as well as the iodobenzenes. Moreover, *p*-nitrobromobenzene and *p*-bromobenzonitrile having electron-deficient aromatic rings also underwent Sonogashira coupling reactions with terminal

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



Entry	R	X	Y	Product	Yield[b] (%)	TON
1	Ph	I	H	**10a**	99	990
2	Ph	I	Br	**10b**	99	990
3	Ph	I	Cl	**10c**	99	990
4	Ph	I	MeO	**10d**	97	970
5	Ph	Br	H	**10a**	91	910
6	Ph	Br	NO_2	**10e**	96	960
7	Ph	Br	CN	**10f**	95	950
8	Ph	Br	MeO	**10d**	95	950
9	*n*-C_4H_9	I	H	**10g**	99	990
10	*n*-C_4H_9	I	Br	**10h**	99	990
11	*n*-C_4H_9	I	Cl	**10i**	98	980
12	*n*-C_4H_9	I	MeO	**10j**	98	980
13	*n*-C_4H_9	Br	H	**10g**	98	980
14	*n*-C_4H_9	Br	NO_2	**10k**	98	980
15	*n*-C_4H_9	Br	CN	**10l**	99	990
16	*n*-C_4H_9	Br	MeO	**10j**	98	980

[a] Reaction conditions: aryl halide (1.0 mmol), terminal alkyne (1.2 mmol), PS-tazo-Pd(II) (0.001 mmol), K_2CO_3 (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	Sonogashira yeild[b] (%)	Suzuki yeild[b] (%)	Heck yeild[b] (%)
1	1	99	99	99
2	2	99	97	98
3	3	95	90	95
4	4	90	85	90
5	5	90	85	87

[a] Reaction conditions: phenyliodide (1.0 mmol), phenylacetylene (Sonogashira reaction) (1.2 mmol), phenylboronic acid (Suzuki reaction) (1.2 mmol), methyl acrylate (Heck reaction) (1.5 mmol), PS-tazo-Pd(II) (0.001 mmol), K_2CO_3 (2.0 mmol), H_2O (3 ml), room temperature (for Sonogashira reaction), 70 °C (for Suzuki and Heck reactions).

[b] GC yield.

alkynes under similar conditions to afford the corresponding products in excellent yields (entries 6, 7, 14 and 15).

The reusability of the catalyst is a very important theme, especially for commercial applications. Therefore, the recovery and reusability of the catalyst were investigated using the reaction of iodobenzene with phenylboronic acid (Suzuki reaction), iodobenzene with methyl acrylate (Heck reaction), and iodobenzene with phenylacetylene (Sonogashira reaction) as the representative reactants, and in the presence of 0.1 mol% of PS-tazo-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).

To determine the degree of leaching of the metal from the heterogeneous catalyst, the catalyst was removed by filtration after the reaction (for Suzuki reaction) was completed and the palladium content of the filtrate was determined by ICP. It was shown that less than 0.2% of the total amount of the original palladium species was lost into solution during the course of a reaction. This leaching level was negligible which was also confirmed by the excellent recoverability and reusability of this heterogeneous catalyst.

3. Conclusion

In conclusion, we developed a clean and safe protocol for the Suzuki, Heck, and copper-free Sonogashira reactions catalyzed by the PS-tazo-Pd(II) complex. The catalyst used is easily separated, and can be reused for several times without a noticeable change in its activity. The ease of preparation of the complex, indefinite shelf-life, and stability toward air make it an ideal complex for the above transformations. Further work is in progress to broaden the scope of this catalytic system for aryl chlorides and other organic transformations.

4. 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.

4.1. Preparation of polymer-anchored PS-tazo-Pd(II) ***3***

To a 250-ml 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 4-amino-5-methyl-3-thio-1,2,4-triazole (5.0 mmol). The reaction mixture was stirred for 20 h at 100 °C, and was subsequently filtered and washed thoroughly with DMF, and dried in vacuo for 12 h. The triazole-functionalized polymer **2** (1.5 g) was treated with ethanol (50 ml) for 30 min. An ethanolic solution of $PdCl_2(PhCN)_2$ (1.5 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-tazo-Pd(II) **3** (Scheme 1).

4.2. General procedure for the Suzuki coupling reaction

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.2 mmol), PS-tazo-Pd(II) (0.001 mmol), K_2CO_3 (2.0 mmol), and water (3 ml) was stirred at 70 °C for 10 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 (98:2) as eluent to afford the pure product.

4.3. General procedure for the Heck reaction

A mixture of aryl halide (1.0 mmol), methyl acrylate (1.5 mmol), PS-tazo-Pd(II) (0.001 mmol), K_2CO_3 (2.0 mmol), and water (3 ml) was stirred at 70 °C for 10 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 (98:2) as eluent to afford the pure product.

4.4. 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-tazo-Pd(II) (0.001 mmol), K_2CO_3 (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 product was subjected to silica gel column chromatography using $CHCl_3$–CH_3OH (98:2) as eluent to afford the pure product.

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