Suzuki and Sonogashira Cross-Coupling Reactions in Water Medium with a Reusable Poly(*N*-vinylcarbazole)-Anchored Palladium(II) Complex

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Abstract: Poly(3,6-dibenzaldimino-*N*-vinylcarbazole)-anchored palladium(II) complex has been synthesized and characterized by different physicochemical and spectroscopic techniques. The present complex shows excellent catalytic activities for Suzuki and Sonogashira coupling reactions under phosphine-free and copper-free reaction conditions in water medium. This immobilized catalyst can be easily separated and reused for further reactions for more than five times without noticeable loss in the catalytic activity.

Key words: heterogeneous catalysis, Schiff base, palladium complex, cross-coupling, biaryls

The Suzuki and Sonogashira cross-coupling reactions are among the most important carbon-carbon bond-forming processes in organic synthesis.¹ It features applications that range from the preparation of hydrocarbons and industrial production of pharmaceuticals to advanced synthesis of natural products.² The continuing depletion of natural resources and growing environmental awareness has necessitated changes in the practices of both the chemical industry and academia. One strategy that addresses these issues is the replacement of deleterious molecular solvents with environmentally more benign, reaction enhancing alternatives. Of the novel solvents that have emerged, water has shown great promise.³ Actually, water is an attractive alternative to traditional organic solvents because it is inexpensive, nonflammable, nontoxic, and environmentally sustainable by alleviating the problem of pollution by organic solvents. While a considerable progress is being achieved in water medium, the vast majority of examples of catalytic reactions in aqueous medium still use homogeneous catalysis.⁴ It is clear that green chemistry not only requires the use of friendly solvents but also it is very convenient to convert homogeneous catalysis into heterogeneous catalysis in order to recover and reuse the catalyst. Many immobilization methods and supported materials have been reported in literature,⁵ among them charcoal, silicas, zeolites, hydrotalcites, and polymers are widely exploited.

Polymer-supported organotransition metal catalysts offer several significant advantages in synthetic and industrial chemistry; among these, the ease of separation of catalyst from the desired reaction products and the recovery and reuse of the catalyst are most important.⁶ Palladium as catalyst plays an important role in organic synthesis.⁷ Palladium exhibits good catalytic activity in carbon–carbon bond-formation reactions. Various polymer-supported palladium catalysts for the Suzuki and Sonogashira crosscoupling reaction have been reported.⁸ However, most of them are related to the palladium(II) complexes in combination with phosphine ligand. Despite tertiary phosphines are effective in controlling reactivity and selectivity in organometallic chemistry and heterogeneous catalysis, they require air-free handling to prevent their oxidation. Therefore, the development of phosphine-free heterogeneous palladium catalysts having a high activity and good stability is a topic of enormous importance.⁹

Here, we report the heterogeneous Suzuki coupling and copper-free Sonogashira coupling reactions of aryl halides over a polymer-anchored palladium(II) Schiff base complex catalyst in water medium under aerobic condition.

Preparation and Characterization of $[Pd(C_6H_4CH=N-P)(PhCN)CI]$ Complex [P = poly(N-vinylcarbazole)]

Schematic illustration for the synthesis of the catalyst is presented in Scheme 1. The functionalized poly(N-vinylcarbazole amine) 2 was prepared according to the method of King and Sweet,¹⁰ which was converted to the polymeranchored ligand 3 by reaction with benzaldehyde in anhydrous toluene under reflux. The preparation of poly(N-vinylcarbazole)-anchored palladium(II) complex 4 was done by reaction of **3** with a methanolic solution of Pd(Ph-CN)₂Cl₂.¹¹ The catalyst **4** showed characteristic IR peaks at 1620 cm⁻¹ (C=N imine), 1590 cm⁻¹ (C=C stretching, aromatic), 720 cm⁻¹ (orthometalation), ¹² 2290 cm⁻¹ (C=N of benzonitrile), 455 cm⁻¹ (Pd–N),¹³ and 355 cm⁻¹ (Pd–Cl),¹⁴ which support the formation of palladium(II) complex. The metal content of polymer-anchored palladium(II) complex determined by AAS suggested 12.80 wt% metal loading in the immobilized palladium complex.

Suzuki Cross-Coupling Reactions

To explore the catalytic activity of the present catalyst, initially the Suzuki coupling reaction¹⁵ of bromobenzene with phenylboronic acid was studied as a model reaction and the role of various solvents, temperatures, and bases was screened using this catalyst (Scheme 2). Several sol-

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Scheme 1 Synthesis of polymer-anchored $[Pd(C_6H_4CH=N-$ P)(PhCN)Cl] complex

vents such as DMF, MeCN, NMP, MeOH, DMSO, toluene, and water was investigated and it was found that water was the best solvent for this coupling reactions using the present catalyst. With polar solvents like NMP, MeCN, DMF, DMSO, and MeOH, yields were comparatively good (Table 1, entries 1–5). In contrast, the catalytic performance was not acceptable when a nonpolar solvent toluene was employed (Table 1, entry 6). This coupling reaction was found to be highly sensitive to the reaction temperature. At lower temperatures $(30-60 \ ^{\circ}C)$ only low to moderate yield was obtained (Table 1 entries 7–10). A reaction temperature of 70 °C was found to be optimal for the model reaction. The effect of base on the reaction was also important, because the desired crosscoupling products were not obtained in any noticeable amounts in the absence of base. The addition of inorganic carbonate base, K₂CO₃, resulted in excellent conversion (95%, Table 1, entry 11); however, organic bases like Et₃N and piperidine gave lower conversion (Table 1, entries 16, 17). The addition of other inorganic bases gave moderate to low conversions of bromobenzene. The quantity of K_2CO_3 was also found to be important. The basesubstrate molar ratio of 2:1 was found to be ideal for the present catalytic system.



Scheme 2 Suzuki coupling reaction of aryl halides with arylboronic acid

To examine the scope for this coupling reaction, a variety of aryl halides, iodides, bromides, and chlorides, were coupled with arylboronic acids under optimize reaction conditions (K₂CO₃, H₂O, 70 °C) and good to excellent re-

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Table 1 Optimal Conditions for $[Pd(C_6H_4CH=N-P)(PhCN)Cl]$ -Catalyzed Suzuki Cross-Coupling Reaction^a

Entry	Base	Solvent	Time	Temp (°C)	Yield (%)
1	K ₂ CO ₃	DMF	12	100	84
2	K ₂ CO ₃	MeCN	12	110	75
3	K ₂ CO ₃	NMP	12	reflux	71
4	K ₂ CO ₃	MeOH	10	70	80
5	K ₂ CO ₃	DMSO	12	110	61
6	K ₂ CO ₃	toluene	24	110	21
7	K ₂ CO ₃	H_2O	8	30	12
8	K ₂ CO ₃	H_2O	8	40	34
9	K ₂ CO ₃	H_2O	8	50	68
10	K ₂ CO ₃	H_2O	8	60	82
11	K ₂ CO ₃	H ₂ O	8	70	95
12	Cs ₂ CO ₃	H_2O	8	70	87
13	K ₃ PO ₄ ·7H ₂ O	H_2O	8	70	68
14	NaOH	H_2O	8	70	58
15	NaOAc	H_2O	8	70	65
16	Et ₃ N	H_2O	8	70	39
17	piperidine	H_2O	8	70	17

^a Reaction conditions: bromobenzene (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (1.0 mol% Pd), base (2.0 mmol), solvent (6 mL). Yields refer to GC and GC-MS analysis using dodecane as internal standard (average of two runs).

sults were obtained (Table 2). A control experiment indicated that the coupling reaction did not occur in the absence of catalyst. Aryl iodides containing electrondonating and electron-withdrawing groups readily coupled with phenylboronic acid in rather short time (Table 2, entries 2 and 3). Although the reaction became slower, bromobenzene gave 95% of biaryl products after eight hours (Table 2, entry 4). The effect of substituents in bromobenzene was also examined in this reaction (Table 2, entries 5–11). The less active electron-rich 4-bromotoluene and 4-bromoanisole produced moderate yield while electron-deficient 4-bromoacetophenone and 4-bromonitrobenzene gave excellent yield of coupled products. Steric effects did not influence the yield significantly, for example, in the reaction of o- and m- nitrobromobenzene with phenylboronic acid, the corresponding coupled products were obtained in 90% and 94% yield, respectively (Table 2, entries 10 and 11). Heteroaryl bromide, such as 2-bromopyridine, coupled effectively with phenylboronic acid providing 94% biaryl product (Table 2, entry 12). The reactivity pattern of bromobenzene with a variety of substituted boronic acids was also examined (Table 2, entries 13 and 14), which indicates that the electron-donating substituents increase the yield of the reactions. It is

noteworthy that the water-soluble aryl bromide, 4-bromophenol, gave good yields in only four hours (Table 2, entry 9). We also tested the catalytic activity of the present catalyst for the coupling of aryl chlorides. Aryl chlorides are generally unreactive in the coupling reactions. Less reactive chlorobenzene gave poorer conversion compared to aryl bromides or iodides while electron-deficient 4-chloroacetophenone gave moderate yield of coupled product under these reaction conditions (Table 2, entries 15 and 16).

Sonogashira Cross-Coupling Reaction

We further extended the catalytic activity of the present catalyst in copper-free Sonogashira cross-coupling reactions.^{1c,16} In our initial experiments, we tested the Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene as model reaction in the presence of polymer-anchored palladium(II) catalyst **4** under a phos-

phine-free and copper-free reaction condition (Scheme 3). Addition of a small amount of TBAB (tetrabutylammonium bromide) in the reaction medium enhanced the rate of the reaction and increased the conversion. Model reaction was carried out under different systems to optimize the reaction conditions (Table 3). Several solvents, such as DMF, methanol, NMP, toluene, and H₂O, were tested for this coupling reaction and H₂O was found to be the best solvent based on conversion, reaction temperature, and reaction time (Table 3, entries 1-5). Next we examined the effect of different bases for the Sonogashira coupling reactions. The reaction works very well when organic bases, such as Et₃N and piperidine, were used (Table 3, entries 5, 6), with the best result obtained in the case of Et_3N as base (Table 3, entry 5). Inorganic bases such as NaOAc, K_2CO_3 , and $K_3PO_4 \cdot 7H_2O$, were substantially less effective and gave moderate to low conversion (Table 3, entries 7-9).

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$R^{7} \xrightarrow{X + (OH)_{2}B} \xrightarrow{R^{2}} R^{2} \xrightarrow{K_{2}CO_{3}, \text{ catalyst}} R^{7} \xrightarrow{R^{7}} R^{2}$						
Entry	ArX	ArB(OH) ₂	Product ^b	Time (h)	Conv. (%) ^c	Yield (%)
1		B(OH)2	la	5	100	~100
2	0 ₂ N-	B(OH)2	0 ₂ N-{>-{>>}-{>>}-{>>}-{>>}-{>>}-{>>}-{>>}-	4	100	~100
3	MeO	B(OH)2	MeO-	5	98	97
4	Br	B(OH)2		8	95	95
5	MeO-Br	B(OH)2	MeO-	8	94	94
6	Br	B(OH)2		8	94	94
7	O ₂ N-Br	B(OH)2	0 ₂ N-	6	98	97
8	MeOC-Br	B(OH)2	MeOC	6	99	99
9	HO-Br	B(OH)2	HO-	4	98	98
10	O ₂ N Br	B(OH)2		6	96	94

Table 2 Suzuki Cross-Coupling Reactions of Aryl Halides with Arylboronic Acids with $[Pd(C_6H_4CH=N-P)(PhCN)Cl]$ Complex Catalysta(continued)



^a Reaction conditions: aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), catalyst (1.0 mol% Pd), K₂CO₃ (2.0 mmol), H₂O (6 mL), 70 °C. ^b Products were identified by comparison of their IR and ¹H NMR spectral data with those reported in the literature.

^c Conversion of reactant was determined by GC and GC-MS analysis using dodecane as internal standard.



Scheme 3 Sonogashira coupling reactions of aryl halides with phenylacetylene

To examine the scope of this coupling reaction, phenylacetylene was coupled with different aryl halides in H₂O in the presence of polymer-anchored palladium(II) catalyst 4 at 70 °C (Scheme 3). The experimental results are summarized in Table 4. As shown in Table 4, the electron-neutral, electron-rich and electron-poor aryl iodides reacted with phenylacetylene very well to generate the corresponding cross-coupling products in excellent yields under the standard reaction conditions (Table 4, entries 1-6). Trace amount of homocoupled product was detected in the reaction medium. This cross-coupling was also tolerant of ortho substitution in aryl iodides and led to moderate yields (Table 4, entry 6). Activated aryl bromides reacted with phenylacetylene to generate the corresponding products in good yields (Table 4, entries 8-10). For electron-rich aryl bromides, relatively lower yield was obtained under the present reaction conditions (Table 4, entries 11 and 12). Heteroaromatic compound such as 2bromopyridine also reacted with palladium(II) catalyst to give cross-coupling product in 78% yield (Table 4, entry 13). These results indicate that a variety of important functional groups could be well tolerated under the present reaction conditions. Unfortunately, only a very small amount of the cross-coupled product was isolated, when aryl chlorides were coupled with phenylacetylene under the same reaction conditions (Table 4, entries 14 and 15).

Table 3 Optimal Conditions for $[Pd(C_6H_4CH=N-P)(PhCN)Cl]$ -Catalyzed Sonogashira Cross-Coupling Reaction^a

Entry	Base	Solvent	Time	Temp (°C)	Yield (%) ^b
1	Et ₃ N	DMF	12	100	78
2	Et ₃ N	MeOH	10	70	82
3	Et ₃ N	NMP	12	reflux	67
4	Et ₃ N	toluene	24	80	12
5	Et ₃ N	H ₂ O	10	70	99
6	piperidine	H_2O	10	70	93
7	NaOAc	H_2O	10	70	39
8	K_2CO_3	H_2O	10	70	52
9	K_3PO_4 ·7 H_2O	H_2O	10	70	41

^a Reaction conditions: iodobenzene (1.0 mmol), phenylacetylene (2.0 mmol), catalyst (1.0 mol% Pd), base (2.0 mmol), TBAB (1.0 mmol), solvent (6 mL).

^b Yield refers to GC and GC-MS analysis using dodecane as internal standard (average of two runs).

$ \begin{array}{c c} & & \\ & $							
Entry	ArX	Product ^b	Time (H)	Conv. (%) ^c	Yield (%)		
1		2a	10	100	99		
2	O ₂ N-	$o_2N - $	10	100	98		
3	MeOC		10	100	99		
4	MeO	MeO-	10	95	93		
5		-	10	96	95		
6		\sim	12	86	83		
7	Br	2a	12	88	88		
8	O ₂ N-Br	0 ₂ N-{}	12	93	92		
9	MeOC Br		12	95	95		
10	NC	NC-	12	93	91		
11	MeO-	мео-	12	87	87		
12	——————Br	<>>-=-<>>2f	12	85	84		
13	⟨Br	2h	12	80	78		
14	CI	2a	24	18	18		
15	MeOC-CI		24	35	34		

^a Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (2.0 mmol), catalyst (1.0 mol% Pd), Et₃N (2.0 mmol), TBAB (1.0 mmol), H₂O (6 mL), 70 °C.

^b Products were identified by comparison of their IR and ¹H NMR spectral data those reported in the literature.

^c Conversion of reactant was determined by GC and GC-MS analysis using dodecane as internal standard.

 $[\]label{eq:constraint} Table 4 \quad Sonogashira Cross-Coupling Reactions of Aryl Halides with Phenylacetylene with [Pd(C_6H_4CH=N-P)(PhCN)Cl] Complex Catalyst^a (C_6H_4CH=N-P)(PhCN)Cl] Complex Catalyst^a (C_6H_4CH=N-P)(PhCN)Cl] (C_6H_4CH=N-P)(PhCN)$

Table 5 Comparison of Catalytic Activity of the Present Catalyst with Other Related Reported Systems

Entry	Reaction type	Catalyst	Reaction conditions	Yield (%)	Refer- ence
1	Suzuki	[Pd(C ₆ H ₄ CH=N–P)(PhCN)Cl]	cat. (1.0 mol%), K ₂ CO ₃ , H ₂ O, 8 h, 70 °C	94	this work
	(4-bromotoluene + phenylboronic acid)	chitosan-g-mPEG350Pd(0)	cat. (0.5 mol%), H ₂ O, NaOH, 5 h, 150 $^\circ\mathrm{C}$	66	_17a
		Pd-1/FSG	cat. (0.1 mol%), K ₂ CO ₃ ,H ₂ O, 12 h, 100 °C	90	_17b
2	Sonogashira	[Pd(C ₆ H ₄ CH=N–P)(PhCN)Cl]	cat. (1.0 mol%), Et ₃ N,H ₂ O, 10 h, 70 °C	99	this work
	(iodobenzene + phenylacetylene)	Pd-silica	cat. (0.01 mmol), Et ₃ N, H ₂ O, 12 h, 70 °C	87	_17c
		Pd-salen	cat. (0.01 mmol), Cs ₂ CO ₃ , H ₂ O, 9 h, 60 $^{\circ}\text{C}$	95	_17d
		PdCl ₂	cat. (1.0 mol%), H ₂ O, pyrrolidine, 24 h, 50 °C	294	_17e

Comparison of Catalytic Activity with Other Reported Systems

Table 5 provides a comparison of the results obtained for our present catalytic system with those reported in the literature. The present catalyst exhibited higher conversions and selectivities compared to the other reported systems. Reactions conducted at lower temperature^{17a,b} and shorter reaction time^{17b,c,e} were required in both the Suzuki and Sonogashira coupling reactions.

Heterogeneity Tests

A hot-filtration test was performed in the Suzuki crosscoupling reaction of 4-bromotoluene with phenylboronic acid. After completion of the reaction, the solid catalyst was filtered off and the filtrate was tested in another reaction cycle. No conversion was detected in the filtrate, confirming the truly heterogeneous nature of the polymersupported catalyst.

Catalyst Reuse

Catalyst lifetime and the ability to easily recycle the catalyst are highly desirable for industrial applications. The recycle efficiency of present polymer-anchored palladium(II) complex **4** was investigated in the coupling reactions of 4-bromotoluene with phenylboronic acid and iodobenzene with phenylacetylene, respectively. After the first run, the catalyst was separated by filtration, washed thoroughly, and then dried under vacuum. The catalytic run was repeated with further addition of substrates in appropriate amount under optimum reaction conditions and the nature and yield of the final products were comparable to that of the original one. The catalytic results revealed that the activity of the catalyst remained almost unchanged over five reaction cycles (Figure 1).

In conclusion, we have developed a highly active and easily recoverable poly(3,6-dibenzaldimino-*N*-vinylcarbazole) palladium(II) complex catalyst for the Suzuki and Sonogashira cross-coupling reactions. The catalyst is ca-



Figure 1 Recycling activity of polymer-anchored palladium(II) complex catalyst towards the Suzuki cross-coupling reaction of 4-bromotoluene with phenylboronic acid and Sonogashira cross-coupling reaction of iodobenzene with phenylacetylene.

pable of performing well in neat water medium under aerobic and phosphine-free conditions. This polymer-anchored catalyst is easy to make, air-stable, inexpensive, and nonpolluting solid. The remarkable advantages with the use of the catalyst are the ready accessibility of the catalysts, its reusability, and storage. The high activity, broad substrate scope, and the successful recycling of this catalyst makes it a more economic and environmentally friendly process for the synthesis of different fine chemicals. Further studies of other coupling reactions catalyzed by this system are currently in progress.

Analytical grade reagents and freshly distilled solvents were used throughout the experiment without further purification unless stated otherwise. Poly(*N*-vinylcarbazole) (Art. No. 368350-5) was supplied by Aldrich Chemical Company, U.S.A. Pd(PhCN)₂Cl₂ was purchased from Arora Matthey and was used as such without further purification. All other chemicals used in this investigation were of analytical grade procured from E-Merck.

The FTIR spectra were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. A Perkin-Elmer 2400C elemental analyzer was used to collect microanalytical data (C, H, and N). The metal loading in the polymer was analyzed using a Varian AA240 atomic absorption spectrophotometer (AAS). Morphology and particle size of different functionalized polystyrene samples were analyzed using a scanning electron microscope (SEM) (ZEISS EVO40, England) equipped with EDX facility. The thermal stability of the immobilized catalyst was determined using a Mettler Toledo TGA/ DTA 851. Diffuse reflectance UV-Vis spectra were taken using a Shimadzu UV-2401PC doubled beam spectrophotometer having an integrating sphere attachment for solid samples. The reaction products were analyzed by Varian 3400 gas chromatograph equipped with a 30 m CP-SIL8CB capillary column and a frame ionization detector and Trace DSQ II GC-MS equipped with a 60 m TR-50MS capillary column. Flash chromatography was performed on silica gel (230-400 mesh).

Poly(N-vinylcarbazole amine) (2)

Poly(N-vinylcarbazole) (5 g, 1.67 mmol) was taken in 1,2-dichloroethane (100 mL). A mixture containing concd HNO₃ (25 mL) and 50 mL of glacial AcOH (50 mL) was added dropwise at r.t. to the above suspension with constant stirring and then the reaction mixture was refluxed for 12 h. The resulting yellowish brown poly(3,6dinitro-N-vinylcarbazole) (1) was filtered, washed thoroughly with AcOH, H₂O, THF, and acetone in that order and then dried under vacuum. A solution of SnCl₂ (1.0 g, 5.27 mmol) in concd HCl (12 mL) was added to the suspension of yellowish brown 1 (5 g, 1.12 mmol) in AcOH (20 mL). The mixture was stirred at r.t. for 48 h. The resulting yellow polymer was filtered, washed successively with H₂O, THF, MeOH, and acetone. The yellow polymer obtained as the amine hydrochloride was dried under vacuum. Poly(N-vinylcarbazole-3,6-diamine) hydrochloride was treated with 5% alcoholic NaOH solution for 6 h. The amine 2 thus obtained was filtered, washed successively with H2O, MeOH, and finally dried under vacuum; yield: 4.2 g (84%).

Polymer-Anchored Ligand 3

The polymer-anchored ligand **3** was prepared by the reaction of **2** (3 g, 0.9 mmol) with benzaldehyde (10 mL) in anhyd toluene (30 mL) under reflux condition for 72 h under N_2 ; yield: 2.7 g (90%).

Poly(N-vinylcarbazole)-Anchored Palladium(II) Complex 4

For the preparation of poly(N-vinylcarbazole)-anchored palladium(II) complex **4**, a methanolic solution (25 mL) of Pd(PhCN)₂Cl₂ (0.7 g, 1.82 mmol) was mixed with **3** (2 g, 0.5 mmol) and the reaction mixture was first stirred for 24 h at r.t. and then refluxed in a water bath for 12 h; yield: 1.6 g (80%).

Suzuki Cross-Coupling Reaction in Water Medium; General Procedure

A mixture of aryl halide (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol), H_2O (6.0 mL) and 1.0 mol% of Pd catalyst **4** was stirred at 70 °C under air. To study the progress of the reaction, the reaction mixtures were collected at different time interval and quantified by GC analysis. At the end of the reaction, the catalyst was separated by simple filtration. The filtrate was extracted with CH_2Cl_2 (3 × 10 mL) and passed through a pad of silica gel. The organic phase thus collected was dried (Na_2SO_4), filtered, concentrated, and the residue was purified by GC-MS and ¹H NMR spectroscopy. All prepared compounds are known and compared with authentic samples (Table 2).

Sonogashira Cross-Coupling Reaction in Water Medium; General Procedure

To a suspension of the polymeric Pd(II) catalyst **4** (1.0 mol% of Pd) in H₂O (6.0 mL), aryl halide (1.0 mmol), phenylacetylene (2.0 mmol), TBAB (1.0 mmol), and Et₃N (2.0 mmol) were added. The reaction mixture was stirred at the prearranged temperature for appropriate reaction time. Progress of the reaction was monitored by GC analysis at different time interval of the reaction. After completion of the reaction, the reaction mixture was cooled to r.t., diluted with H₂O (10 mL), and extracted with CH₂Cl₂ (3 × 10 mL). The organic phase thus collected was dried (Na₂SO₄) and concentrated. The crude material was purified by flash column chromatography on silica gel. The product was analyzed by GC-MS and ¹H NMR spectroscopy. All prepared compounds are known and compared with authentic samples (Table 4).

Reuse of the Catalyst

The Suzuki reaction was carried out with 4-bromotoluene (1.0 mmol), phenylboronic acid (1.5 mmol), K_2CO_3 (2.0 mmol) and Pdcarbazole catalyst 4 (1.0 mol%) in H_2O (6 mL). The Sonogashira reaction was carried out with iodobenzene (1.0 mmol), phenylacetylene (2.0 mmol), Et_3N (2.0 mmol), TBAB (1.0 mmol) and Pdcarbazole catalyst 4 (1.0 mol%) in H_2O (6 mL). Each reaction mixture was stirred at 70 °C in air atmosphere. After completion of the reaction, the mixture was cooled and the catalyst was separated from the liquid mixture by filtration. The filtrate was analyzed by gas chromatography to determine the yield of the product. The recovered catalyst was washed thoroughly with acetone and H_2O , and dried under vacuum. After that, the recovered catalyst was reused for the next reaction under the same reaction conditions as mentioned above.

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