This article was downloaded by: [University of Glasgow] On: 20 May 2013, At: 02:36 Publisher: Taylor & Francis Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



# Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry

Publication details, including instructions for authors and subscription information: http://www.tandfonline.com/loi/lsyc20

Polystyrene-Anchored Palladium(II) Schiff Base Complex: A Reusable Catalyst for Phosphine-Free and Copper-Free Sonogashira Cross-Coupling Reaction in Aqueous Medium

Manirul Islam<sup>a</sup>, P. Mondal<sup>a</sup>, A. Singha Roy<sup>a</sup>, K. Tuhina<sup>b</sup>, S. Mondal<sup>a</sup> & D. Hossain<sup>a</sup>

<sup>a</sup> Department of Chemistry, University of Kalyani, Nadia, India <sup>b</sup> Department of Chemistry, B.S. College, Danapur, India

Published online: 29 Jun 2011.

To cite this article: Manirul Islam , P. Mondal , A. Singha Roy , K. Tuhina , S. Mondal & D. Hossain (2011): Polystyrene-Anchored Palladium(II) Schiff Base Complex: A Reusable Catalyst for Phosphine-Free and Copper-Free Sonogashira Cross-Coupling Reaction in Aqueous Medium, Synthetic Communications: An International Journal for Rapid Communication of Synthetic Organic Chemistry, 41:17, 2583-2593

To link to this article: <u>http://dx.doi.org/10.1080/00397911.2010.515331</u>

# PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <u>http://www.tandfonline.com/page/terms-and-conditions</u>

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae, and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings,

demand, or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.



Synthetic Communications<sup>®</sup>, 41: 2583–2593, 2011 Copyright © Taylor & Francis Group, LLC ISSN: 0039-7911 print/1532-2432 online DOI: 10.1080/00397911.2010.515331

# POLYSTYRENE-ANCHORED PALLADIUM(II) SCHIFF BASE COMPLEX: A REUSABLE CATALYST FOR PHOSPHINE-FREE AND COPPER-FREE SONOGASHIRA CROSS-COUPLING REACTION IN AQUEOUS MEDIUM

Manirul Islam,<sup>1</sup> P. Mondal,<sup>1</sup> A. Singha Roy,<sup>1</sup> K. Tuhina,<sup>2</sup> S. Mondal,<sup>1</sup> and D. Hossain<sup>1</sup>

<sup>1</sup>Department of Chemistry, University of Kalyani, Nadia, India <sup>2</sup>Department of Chemistry, B.S. College, Danapur, India

## GRAPHICAL ABSTRACT



R=H, COMe, CH<sub>3</sub>, OMe, CN, NO<sub>2</sub>

Abstract A novel polystyrene-supported palladium(II) complex, an excellent and recyclable catalyst, was synthesized for Sonogashira reactions. The present complex shows high catalytic activity for Sonogashira cross-coupling reaction of aryl halides with phenylacetylene under phosphine-free and copper-free reaction conditions in aqueous ( $DMF-H_2O$ ) medium. The catalyst could be reused for at least six reaction cycles with almost unchanged catalytic properties.

Keywords Aqueous medium; aryl halides; palladium(II) complex; Sonogashira cross-coupling

#### INTRODUCTION

Palladium-catalyzed reactions have been recognized as powerful tools in multiple organic transformations.<sup>[1–5]</sup> Despite the remarkable utility of Pd catalysts in organic synthesis, they suffer from one significant drawback: They often remain in the organic products at the end of the reaction. In recent years, the search for environmentally benign chemical processes or methodologies has received much attention from chemists, because they are essential for the conservation of the global ecosystem. Homogeneous palladium–catalyst system suffers from a major drawback in that the catalyst recovery and/or its reuse is difficult, affecting the overall economics of the process.<sup>[6–8]</sup> Heterogeneous catalysts, which are widely used in industry, have good thermal stability, can be easily separated from the reaction mixture, and often can be regenerated and reused. Therefore, heterogenizing homogeneous metal

Received February 22, 2010.

Address correspondence to Dr. Manirul Islam, Department of Chemistry, University of Kalyani, Kalyani, Nadia, 741235, W.B., India. E-mail: manir65@rediffmail.com

complex by supporting it on an insoluble support has attracted a lot of interest as a suitable method for solving many practical problems, including recovery of the catalyst from the reaction mixture and recycling. Palladium supported on materials such as carbon,<sup>[9]</sup> amorphous silicates,<sup>[10]</sup> polymers,<sup>[11]</sup> and zeolites<sup>[12]</sup> is commonly employed in heterogeneous catalysis.

The palladium-catalyzed coupling of terminal acetylenes with aryl and vinyl halides (Sonogashira reaction) is one of the important and widely used carbon-carbon bond-forming reactions in organic synthesis.<sup>[13–19]</sup> The most commonly used catalytic systems for this transformation include PPh<sub>3</sub> as ligand together with CuI as the cocatalyst. The main disadvantages of the palladium catalysts containing simple phosphine ligands is of high cost of phosphine, air- and thermosensitivity, low activity toward deactivated substrates, and contamination of the products with the phosphine-based by-products. The presence of copper iodide in the reaction mixture also has several drawbacks: Oxidative homocoupling of acetylenes (Glaser-type reaction) cannot be avoided in a copper-mediated reaction,<sup>[20,21]</sup> in which by-products (diaryldiacetylenes) are generally difficult to separate from the desired products, and copper acetylide is a potentially explosive reagent. Use of water as a reaction medium for transition-metalcatalyzed reactions is very attractive for organic synthesis because water is a readily available, safe, and environmentally friendly solvent. In water or water-organic solvent mixtures, the Sonogashira reaction is very effectively catalyzed by palladium catalyst containing no copper salt and/or phosphine ligands.<sup>[22-28]</sup>

Herein, we have reported a truly heterogeneous palladium catalyst for the Sonogashira cross-coupling reactions in aqueous medium under copper-free and phosphine-free reaction conditions. The catalyst shows good catalytic activity in the coupling reactions of various aryl halides with phenylacetylene. Furthermore, easy catalyst recovery and excellent recycling efficiency of the catalyst make it an ideal system for coupling reactions in the aqueous phase.

The synthesis of the polymer-anchored Schiff base palladium(II) catalyst is illustrated in Scheme 1. It was readily prepared through a two-step procedure. The polystyrene amine (1 g) was reacted with benzaldehyde (3 mL) in dry toluene (10 mL) under reflux conditions for 72 h to afford polymer Schiff base ligand (2). This polymer Schiff base ligand (1 g) subsequently reacted with palladium acetate (0.5 g) in acetic acid (10 mL) at 80 °C for 10 h to generate the corresponding polystyrenesupported palladium(II) catalyst.



Scheme 1. Synthesis of polymer-anchored Pd(II) Schiff base complex.

Because of insolubility of the polymer-anchored Pd(II) complex in all common organic solvents, its structural investigations was limited only to its physicochemical properties, SEM-EDX, TGA-DTA, infrared (IR), and ultraviolet-visible (UV-vis) spectral data. The complete incorporation of the organic substructure in the material was confirmed by elemental analysis. The metal content of polymer anchored Pd(II) complex determined by atomic absorption spectrometry (AAS) suggested 2.23 wt% metal loading in the immobilized palladium complex. The SEM images of polymer-anchored ligand and metal complex clearly show the morphological change that occurred on the surface of the polymer matrix after loading of the metal (Fig. 1). EDX data also support the metal attachment on the surface of polymer matrix (Fig. 2).

The catalyst is thermally stable up to  $250 \,^{\circ}$ C. The IR spectrum of polymeranchored Schiff base ligand showed characteristic IR peak at  $1635 \,\mathrm{cm}^{-1}$ , which may be assigned to the -C=N stretching vibration of imine which on complexation with metal shifted toward lower frequency to  $1615 \,\mathrm{cm}^{-1}$ . This suggested bond formation between Pd and ligand. Other characteristic peaks at  $1585 \,\mathrm{cm}^{-1}$ ,  $1430 \,\mathrm{cm}^{-1}$ ( $\nu$  COO bridged),  $720 \,\mathrm{cm}^{-1}$  (orthometallation),<sup>[29]</sup> and  $455 \,\mathrm{cm}^{-1}$  ( $\nu$  Pd-N)<sup>[30]</sup> also support the formation of the palladium(II) complex. The UV-vis spectra provided further evidence for the presence of palladium(II) on polymer support. The absorption maxima at 295 nm may be attributed to the  $\pi \rightarrow \pi^*$  transition in polymer and phenyl moiety, and the absorption at higher range (370–440 nm) may be due to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions of imine system in conjugation with the aromatic nuclei.

In our previous study of cross-coupling reactions, it was found that the present catalyst is highly efficient for the Suzuki cross-coupling reaction, which furnished biaryl products with good yields.<sup>[31]</sup> Therefore, continuing the search for further catalytic reactions, we decided to investigate the catalytic activity of the present catalyst for the Sonogashira reaction. We began our investigation of the Sonogashira coupling reaction with the present catalyst using the coupling of bromobenzene with phenylacetylene as a model reaction (Scheme 2). Because the performance of a successful metal-catalyzed cross-coupling reaction is known to be governed by a number



Figure 1. FE SEM image of polymer-anchored Schiff base ligand (A) and  $PS-[(C_6H_4CH=N)Pd(OAc)]_2$  complex (B).



Figure 2. EDX spectrum of PS-[(C<sub>6</sub>H<sub>4</sub>CH=N)Pd(OAc)]<sub>2</sub> complex.

of factors, at first the effects of various bases, solvents, temperatures, and catalyst concentrations on the Sonogashira cross-coupling reaction were surveyed. Using tetrabutylammonium bromide (TBAB) as an additive enhanced the rate of the reaction. All the reactions were carried out under an air atmosphere.

We first examined the effect of reaction temperature on the Sonogashira coupling reaction. The results are reported in Table 1. At room temperature, very poor yield of the cross-coupled product was obtained. As expected, raising the temperature substantially increased the conversion of bromobenzene, and a temperature of 70 °C provided the greatest conversion. The reaction was carried out under an air atmosphere.

To verify the solvent effect in Sonogashira coupling reactions, we have investigated a series of reactions by taking the model reaction in different solvents (Table 1). The results showed that the nonpolar solvents such as toluene or p-xylene gave moderate to low amount of conversions (entries 5 and 6). Quantitative yields were observed with polar solvents such as dimethylsulfoxide (DMSO), dimethylformanide (DMF), or methanol (entries 7–9). The catalytic activity was also observed in neat water, and the desired product was obtained in 70% yields. The reaction performed in DMF–H<sub>2</sub>O (1:1) was found to be the best for the present catalytic system



Scheme 2. Sonogashira reaction of phenylacetylene with bromobenzene.

Entry	Temperature (°C)	Solvent	Base	Base–substrate ratio	Time (h)	Yield (%)
1	30	DMF-H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	2:1	12	Trace
2	50	DMF-H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	2:1	12	23
3	60	$DMF-H_2O(1:1)$	Et <sub>3</sub> N	2:1	12	75
4	70	DMF-H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	2:1	12	97
5	120	p-xylene	Et <sub>3</sub> N	2:1	24	22
6	110	Toluene	Et <sub>3</sub> N	2:1	24	14
7	100	DMF	Et <sub>3</sub> N	2:1	12	87
8	100	DMSO	Et <sub>3</sub> N	2:1	12	79
9	70	Methanol	Et <sub>3</sub> N	2:1	12	76
10	70	$H_2O$	Et <sub>3</sub> N	2:1	12	70
11	70	DMF-H <sub>2</sub> O (1:1)	K <sub>2</sub> CO <sub>3</sub>	2:1	12	69
12	70	$DMF-H_2O(1:1)$	$K_3PO_4$	2:1	12	57
13	70	DMF-H <sub>2</sub> O (1:1)	NaOH	2:1	12	34
14	70	$DMF-H_2O(1:1)$	No base	2:1	24	No reaction
15	70	DMF-H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	0.5:1	12	26
16	70	DMF-H <sub>2</sub> O (1:1)	Et <sub>3</sub> N	1:1	12	32

**Table 1.** Optimal conditions for polymer-anchored Pd(II) Schiff base complex–catalyzed Sonogashira reaction of bromobenzene and phenylacetylene<sup>*a*</sup>

<sup>*a*</sup>Reaction conditions: bromobenzene (1.0 mmol), phenylacetylene (2.0 mmol), catalyst (1.0 mol% Pd), and solvent (6 mL). Yields determined by GC analysis.

(entry 4), as the greatest conversion was obtained in this mixed aqueous-organic solvent.

The base usually plays an important role in the Sonogashira cross-coupling reaction. Thus, different kinds of bases were screened, and the results are summarized in Table 1. From the results, it is seen that triethylamine is the most effective base in the present catalytic system. Inorganic bases are less effective and gave moderate yield of the coupled product. No conversion was observed in the absence of base. The effect of base substrate ratios on the coupling reaction was also examined. Using a base–substrate molar ratio of 2:1, the greatest conversion of bromobenzene was obtained.

We next evaluated the catalytic activity of the present catalyst using a variety of aryl halides under optimized reaction conditions, and the results obtained were collected as shown in Table 2. From the results, it is seen that the reaction was effective in the presence of a wide variety of functional groups on the aryl iodides, bromides, and chlorides, giving good to excellent conversions to the corresponding products. Electron-poor aryl halides were coupled with phenylacetylene efficiently in the presence of catalyst. The electron-rich arylhalides also afford moderate to good conversions. The electronically neutral iodo and bromobenzene produced a large amount of the desired product when coupled with phenylacetylene. The ortho-substituted aryl halide, 2-bromotoluene, gave good yields of coupled product but requires longer reaction times, which might be due to steric hindrance. Under the same reaction conditions, heteroaryl bromide such as 2-bromopyridine furnished the desired coupled product in good yields. In addition, 1-bromonaphthalene was successfully coupled with phenylacetylene to afford the corresponding coupled product in 89% yields. The less reactive chlorobenzene showed low conversion. The activated

Entry	ArX	Time (h)	Product <sup><math>b</math></sup> (no.)	Conv. <sup><i>c</i></sup> (%)	Isolated yield (%)
1		8	((2a)	100	100
2	Br	12	(2a)	100	100
3	MeOC-	8	меос	100	99
4	H <sub>3</sub> C	8	H <sub>3</sub> C-{>	96	95
5	H <sub>3</sub> C-	12	H <sub>3</sub> C-{>	95	95
6	MeO-Br	12	MeO	88	87
7	NC Br	12		92	92
8	O <sub>2</sub> N — Br	12	0 <sub>2</sub> N-(2f)	98	98
9	MeOC Br	12	меос	99	99
10	CH <sub>3</sub> Br	24	NO <sub>2</sub>	87	83
11	⟨Br	12	$\langle N = \langle N \rangle_{(2h)}$	89	88
12	Br	15	(2i)	91	89
13	CI CI	24	()(2a)	42	42
14	MeOC CI	24	MeOC	71	70

**Table 2.** Sonogashira cross-coupling reaction of aryl halides with phenylacetylene with polymer-anchored Schiff base complex catalyst<sup>a</sup>

<sup>*a*</sup>Reaction conditions: aryl halide (1.0 mmol), phenylacetylene (2.0 mmol), catalyst (1.0 mol% Pd), Et<sub>3</sub>N (2.0 mmol), TBAB (1.0 mmol), and DMF–H<sub>2</sub>O (1:1, 6 mL) at 70 °C.

<sup>b</sup>Products were identified by comparison of their GC-MS and <sup>1</sup>H NMR spectral data with those reported in the literature.

<sup>c</sup>Conversion of reactant was determined by GC and GCMS analysis using dodecane as internal standard.

aryl chloride, 4-chloroacetophenone, gave the corresponding coupled product in moderate yields. However, in both reactions high temperature and longer reaction time were required.

The main advantage of the present polymer-anchored Pd(II) Schiff base complex catalyst for the Sonogashira coupling compared to previous literature reports<sup>[11,32]</sup> is that it achieves good yields and selectivity of Sonogashira coupling products in the absence of toxic copper salt and expensive phosphine ligands. The reaction was carried out in an aqueous medium in open air instead of an inert atmosphere.

To determine whether the catalyst is actually functioning in a heterogeneous manner, a hot-filtration test was performed for the Sonogashira coupling reaction of bromobenzene and phenylacetylene. During the reaction, the solid catalyst was separated from the reaction mixture by filtration after 4h of reaction, and the determined conversion was 55%. The obtained filtrate was continually stirred under the same reaction conditions for a further 3h. The gas chromatographic analysis showed no increase in the conversion. Atomic absorption spectrometric analysis of the filtrate confirms that no metal is present. These results confirm that no leaching of the metal from the catalyst takes place during the catalytic reaction.

The lifetime is an important point concerning the use of the catalyst both for industrial and pharmaceutical applications. As the solid catalyst can be recovered easily from the reaction mixture, we examined the reuse of the present catalyst using the reaction of bromobenzene and phenylacetylene. The capability of recycling the polymer-anchored Pd(II) Schiff base complex was confirmed after six consecutive reactions in DMF–H<sub>2</sub>O (1:1) medium. After the first run, the catalyst was separated by filtration, washed thoroughly, dried under vacuum, and then subjected to the next run under the same reaction conditions. The results summarized in Fig. 3 demonstrate that there was almost no change in catalytic activity even after the sixth run. The metal content of the recycled catalyst remained almost unaltered, indicating no leaching of the metal from the polymer support.



Figure 3. Recycling activity of PS-[ $(C_6H_4CH=N)Pd(OAc)$ ]<sub>2</sub> complex catalyst toward the Sonogashira cross-coupling reaction of bromobenzene with phenylacetylene. Reaction conditions: bromobenzene (1.0 mmol), phenylacetylene (2.0 mmol), catalyst (1.0 mol% Pd), Et<sub>3</sub>N (2.0 mmol), TBAB (1.0 mmol), and DMF-H<sub>2</sub>O (1:1, 6 mL) at 70 °C.

#### M. ISLAM ET AL.

In conclusion, we have developed a mild copper-free Sonogashira coupling reaction of arylhalides and acetylene in aqueous medium (DMF–H<sub>2</sub>O, 1:1) using  $Et_3N$  as base under aerobic conditions using polymer-anchored Schiff base complex catalyst. The main advantages associated with this catalyst are (i) easy preparation and handling of the catalyst and commercial availability of the support; (ii) no need for copper salt and phosphine ligand in the catalytic system; and (iii) excellent yield and selectivity in an aqueous medium. Easy product recovery and the recycling efficiency, along with high selectivity of this catalyst, may be useful for the synthesis of different fine chemicals under ecofriendly conditions.

#### **EXPERIMENTAL**

The reagents and solvents were obtained from commercial sources and were generally used without further purification. Poly(styrene-co-divinyl benzene) and palladium acetate were supplied by Aldrich Chemical Company, USA, and other organic reagents were purchased from Merck.

Surface morphology and particle size of the samples were analyzed using a scanning electron microscope (Zeiss EVO40, England) equipped with EDX facility. Thermogravimetric analysis (TGA) of the immobilized catalyst was determined using a Mettler Toledo TGA 851. The Fourier transform (FT–IR) spectra were recorded on a Perkin-Elmer FTIR 783 spectrophotometer using KBr pellets. Diffuse reflectance UV-vis spectra were taken using a Shimadzu UV-2401PC doubled-beam spectrophotometer having an integrating sphere attachment for solid samples. A Perkin-Elmer 2400C elemental analyzer was used to collect microanalytical data (C, H, and N). Palladium content in the catalyst was determined using Varian AA240 atomic absorption spectrophotometer. The <sup>1</sup>H NMR spectra were recorded on 250-, 300-, or 500-MHz spectrometers. The chemical shifts were measured in parts per million (ppm), using tetramethylsilane (TMS) as an internal standard and CDCl<sub>3</sub> as the solvent.

## General Procedure for the Conduct of Sonogashira Cross-Coupling Reaction in DMF–H<sub>2</sub>O (1:1) Medium

To a suspension of the polymeric Pd(II) catalyst (1.0 mol% of Pd) in DMF– H<sub>2</sub>O (6.0 mL, 1:1), aryl halides (1.0 mmol), phenylacetylene (2.0 mmol), TBAB (1.0 mmol), triethylamine (2.0 mmol), and n-dodecane (15–20 mg) as an internal gas chromatography (GC) standard were added. The resulting mixture was stirred at the prearranged temperature for the appropriate reaction time. Samples were withdrawn periodically and analyzed by GC. GC yield was determined using n-dodecane as an internal standard and based on the amount of aryl halide employed. After completion of the reaction, the reaction mixture was cooled to room temperature and extracted with Et<sub>2</sub>O three times. The organic phase in the combined filtrates was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent was evaporated under reduced pressure, and the crude material was purified by flash column chromatography on silica gel. The product was analyzed by GC-MS and <sup>1</sup>H NMR. All prepared compounds were known and compared with authentic samples.

#### Sonogashira Coupling Products

**Diphenylacetylene (2a).** White solid, mp: 54 °C (lit. mp<sup>[33]</sup> 54–55 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) 7.75–7.52 (m, 4H), 7.36–7.33 (m,6H). GC-MS: m/z 178.

**1-Acetyl-4-phenylethynyl-benzene (2b).** Pale yellow solid, mp: 98–99 °C (lit. mp<sup>[34]</sup> 97 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>; 250 MHz):  $\delta$  (ppm) 7.93 (d, 2H,), 7.62–7.54 (m, 4H), 7.38–7.35 (m, 3H), 2.60 (s, 3H). GC-MS: m/z 220.

**4-Phenylethynyl-toluene (2c).** White solid, mp: 70–72 °C (lit. mp<sup>[35]</sup> 72–73 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) 7.55–7.52 (m, 2H), 7.44 (d, 2H), 7.36–7.32 (m, 3H), 7.16 (d, 2H), 2.38 (s, 3H). GC-MS: m/z 192.

**1-Methoxy-4-phenylethynyl-benzene (2d).** Pale yellow solid, mp: 59–60°C (lit. mp<sup>[36]</sup> 59–60°C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) 7.55–7.48 (m, 4H), 7.37–7.33 (m, 3H), 6.90 (d, 2H), 3.83 (s, 3H), GC-MS: m/z 208.

**1-Cyano-4-phenylethynyl-benzene (2e).** White solid; mp 105–106°C (lit. mp<sup>[28]</sup> 106–108 °C). <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  7.36–7.39 (m, 3H), 7.52–7.59 (m, 2H), 7.61–7.62 (m, 4H); GC-MS: m/z 203.

**1-Nitro-4-phenylethynyl-benzene (2f).** Yellow solid, mp: 119 °C (lit. mp<sup>[36]</sup> 119–120 °C). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 300 MHz):  $\delta$  (ppm) 7.38–7.40 (m, 3H), 7.54–7.58 (m, 2H), 7.65 (d, 2H), 8.21(d, 2H); GC-MS: m/z 223.

**1-Phenylethynyl-toluene (2g).** White solid. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm)7.44–7.39 (m,3H), 7.25–7.21 (m, 3H), 7.12–7.10 (m, 2H), 7.08–7.04 (m,1H), 2.41 (s, 3H). GC-MS: *m/z* 192.

**2-Phenylethynyl-pyridine (2h).** Yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 250 MHz): δ (ppm) 8.55 (d, 1H), 7.64–7.54 (m, 3H), 7.50 (d, 1H), 7.34–7.29 (m, 3H), 7.22–7.14 (m, 1H). GC-MS: *m*/*z* 179.

**1-(1-Naphthyl)-2-phenylacetylene (2i).** Yellow oil. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz): δ (ppm) 8.44 (d, 1H), 7.83 (ddd, 2H), 7.75 (d, 1H), 7.64 (d, 2H), 7.58 (t, 1H), 7.52 (t, 1H), 7.44 (t, 1H), 7.39–7.34 (m, 3H). GC-MS: *m/z* 228.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the Department of Science and Technology (DST), the Council of Scientific and Industrial Research (CSIR), and the University Grant Commission (UGC), New Delhi, India, for funding. One of the authors, K. T., is thankful to the UGC (eastern region), India, for financial support. We also thank the DST and UGC, New Delhi, India, for providing instrumental support under the Funding for Infrastructure in Science and Technoloy (FIST) and SAP program.

#### REFERENCES

- 1. Tsuji, J. Palladium Reagents and Catalysts; Wiley: Chichester: New York, 1995.
- Malleron, J. L.; Fiaud, J. C.; Legros, J. Y. Handbook of Palladium-Catalyzed Organic Reactions; Academic Press: London, 1997.

#### M. ISLAM ET AL.

- 3. Diederich, F.; Stang, P. J. *Metal-Catalyzed Cross-coupling Reactions*; Wiley-VCH: Weinheim, 1999.
- 4. Negishi, E.; de Meijere, A. Handbook of Organopalladium Chemistry for Organic Synthesis; Wiley-Interscience: New York, 2002.
- 5. Yin, L.; Liebscher, J. Carbon-carbon coupling reactions catalyzed by heterogeneous palladium catalysts. *Chem. Rev.* **2007**, *107*, 133–173.
- Guan, J. T.; Weng, T. Q.; Yu, G. A.; Liu, S. H. Copper-free PdCl<sub>2</sub>/PPh<sub>3</sub>-catalyzed Sonogashira coupling reaction of aryl bromides with terminal alkynes in water. *Tetrahedron Lett.* 2007, 48, 7129–7133.
- 7. Bhattacharya, S.; Sengupta, S. Palladium-catalyzed alkynylation of aryl halides (Sonogashira reaction) in water. *Tetrahedron Lett.* **2004**, *45*, 8733–8736.
- Bakherad, M.; Keivanloo, A.; Bahramian, B.; Hashemi, M. Copper-free Sonogashira coupling reactions catalyzed by a water-soluble Pd-salen complex under aerobic conditions. *Tetrahedron Lett.* 2009, 50, 1557–1559.
- 9. Novak, Z.; Szabo, A.; Repasi, J.; Kotschy, A. Sonogashira coupling of aryl halides catalyzed by palladium on charcoal. J. Org. Chem. 2003, 68, 3327–3329.
- Polshettiwar, V.; Len, C.; Fihri, A. Silica-supported palladium: Sustainable catalysts for cross-coupling reactions. *Coord. Chem. Rev.* 2009, 253, 2599–2626.
- Kim, J. H.; Lee, D. H.; Jun, B. H.; Lee, Y. S. Copper-free Sonogashira cross-coupling reaction catalyzed by polymer-supported N-heterocyclic carbene palladium complex. *Tetrahedron Lett.* 2007, 48, 7079–7084.
- 12. Djakovitch, L.; Rollet, P. Sonogashira cross-coupling reactions catalysed by copper-free palladium zeolites. *Adv. Synth. Catal.* **2004**, *346*, 1782–1792.
- Sonogashira, K.; Tohda, Y.; Hagihara, N. A convenient synthesis of acetylenes: Catalytic substitutions of acetylenic hydrogen with bromoalkenes, iodoarenes, and bromopyridines. *Tetrahedron Lett.* 1975, 16, 4467–4470.
- Sonogashira, K.; Yatake, T.; Tohda, Y.; Takahashi, S.; Hagihara, N. Novel preparation of σ-alkynyl complexes of transition metals by copper(I) iodide-catalysed dehydrohalogenation. J. Chem. Soc., Chem. Commun. 1977, 291–292.
- Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. A convenient synthesis of ethynylarenes and diethynylarenes. *Synthesis* 1980, 627–630.
- Siemsen, P.; Livingston, R. C.; Diederich, F. Acetylenic coupling: A powerful tool in molecular construction. *Angew. Chem., Int. Ed.* 2000, 39, 2632–2657.
- 17. Chinchilla, R.; Nájera, C. The Sonogashira reaction: A booming methodology in synthetic organic chemistry. *Chem. Rev.* 2007, 107, 874–922.
- Tykwinski, R. R. Evolution in the palladium-catalyzed cross-coupling of sp- and sp<sup>2</sup>hybridized carbon atoms. *Angew. Chem.*, *Int. Ed.* 2003, 42, 1566–1568.
- Negishi, E.; Anastasia, L. Palladium-catalyzed alkynylation. *Chem. Rev.* 2003, 103, 1979–2017.
- Siemsen, P.; Livingston, R. C.; Diederich, F. Acetylenic coupling: A powerful tool in molecular construction. *Angew. Chem., Int. Ed. Engl.* 2000, *39*, 2632–2657.
- 21. Hay, A. S. Oxidative coupling of acetylenes, II. J. Org. Chem. 1962, 27, 3320-3321.
- 22. Ye, Z. W.; Yi, W. B. Polymer-supported palladium perfluorooctanesulfonate [Pd(OPf)<sub>2</sub>]: A recyclable and ligand-free palladium catalyst for copper-free Sonogashira coupling reaction in water under aerobic conditions. *J. Fluorine Chem.* **2008**, *129*, 1124–1128.
- Gil-Moltó, J.; Karlström, S.; Nájera, C. Di(2-pyridyl)methylamine–palladium dichloride complex covalently anchored to a styrene-maleic anhydride co-polymer as recoverable catalyst for C–C cross-coupling reactions in water. *Tetrahedron* 2005, *61*, 12168–12176.
- Liang, B.; Huang, M.-W.; You, Z.-J.; Xiong, Z.-C.; Lu, K.; Fathi, R.; Chen, J.-H.; Yang, Z. Pd-catalyzed copper-free carbonylative Sonogashira reaction of aryl iodides with

alkynes for the synthesis of alkynyl ketones and flavones by using water as a solvent. *J. Org. Chem.* **2005**, *70*, 6097–6100.

- Thathagar, M. B.; Rothenberg, G. One-pot Pd/C-catalyzed "domino" HALEX and Sonogashira reactions: A ligand- and Cu-free alternative. Org. Biomol. Chem. 2006, 4, 111–115.
- Djakovitch, L.; Rollet, P. Sonogashira cross-coupling reactions catalyzed by heterogeneous copper-free Pd-zeolites. *Tetrahedron Lett.* 2004, 45, 1367–1370.
- Kim, J. H.; Lee, D. H.; Jun, B. H.; Lee, Y. S. Copper-free Sonogashira cross-coupling reaction catalyzed by polymer-supported N-heterocyclic carbene palladium complex. *Tetrahedron Lett.* 2007, 48, 7079–7084.
- Sotiriou-Leventis, C.; Wang, X.; Mulik, S.; Thangavel, A.; Leventis, N. Immobilization of Pd catalysts on mesoporous silica for amine- and copper-free Sonogashira coupling reactions. *Synth. Commun.* 2008, *38*, 2285–2298.
- Onue, H.; Moritani, I. Ortho-Metalation reactions of N-phenylbenzaldimine and its related compounds by palladium(II) acetate. J. Organomet. Chem. 1972, 43, 431–436.
- Durig, J. R.; Layton, R.; Sink, D. W.; Mitchell, B. R. Far infrared spectra of palladium compounds, I: The influence of ligands upon the palladium chloride stretching frequency. *Spectrochim. Acta* 1965, *21*, 1367–1378.
- Islam, S. M.; Mondal, P.; Singha Roy, A.; Mondal, S.; Mobarak, M. An effcient and reusable polymer-supported palladium catalyst for the Suzuki cross-coupling reactions of aryl halides. J. Chem. Res. 2009, 756–760.
- Polshettiwar, V.; Hesemann, P.; Moreau, J. J. E. Palladium containing nanostructured silica functionalized with pyridine sites: A versatile heterogeneous catalyst for Heck, Sonogashira, and cyanation reactions. *Tetrahedron* 2007, 63, 9784–6790.
- Komáromi, A.; Novák, Z. Effcient copper-free Sonogashira coupling of aryl chlorides with palladium on charcoal. *Chem. Commun.* 2008, 4968–4970.
- Jana, S.; Dutta, B.; Bera, R.; Konar, S. Imobilization of palladium in mesoporous silica matrix: Preparation, characterization, and its catalytic efficacy in carbon-carbon coupling reactions. *Inorg. Chem.* 2008, 47, 5512.
- Agawa, T.; Miller, S. Reaction of silver acetylide with acylpyridinium salts: N–Benzoyl-2phenylethynyl-1,2-dihydropyridine. J. Am. Chem. Soc. 1961, 83, 449.
- Yanga, F.; Cuia, X.; Lia, Y.; Zhanga, J.; Rena, G.; Wu, Y. Cyclopalladated ferrocenylimines: Efficient catalysts for homocoupling and Sonogashira reaction of terminal alkynes. *Tetrahedron* 2007, 63, 1963.