

A Simple and Efficient One-Pot Synthesis of Substituted Benzo[*b*]furans by Sonogashira Coupling–5-*endo-dig* Cyclization Catalyzed by Palladium Nanoparticles in Water Under Ligand- and Copper-Free Aerobic Conditions

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A simple and efficient procedure for the synthesis of 2-substituted benzo[*b*]furan derivatives has been developed by the reaction of 2-iodophenols and arylacetylenes in water catalyzed by palladium nanoparticles generated in situ in open air. The reaction does not require any additive, ligand, or co-

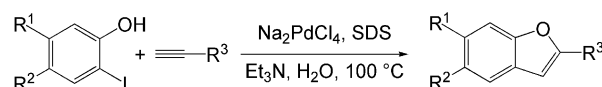
catalyst. The reaction occurs through Sonogashira coupling of 2-iodophenols with phenylacetylenes followed by 5-*endo-dig* cyclization. A series of functionalized benzo[*b*]furan derivatives was obtained in high yields by this procedure.

Introduction

Benzo[*b*]furan derivatives have received considerable attention, as several molecules containing the benzofuran moiety show remarkable activities against asthma, ulcers, tumors, cardiovascular disease, type 2 diabetes, migraines, etc.^[1] Moreover, a wide range of natural products contain benzofuran as their core unit.^[2] Thus, this molecule has become a very popular synthetic target and several methods have been developed.^[3] Most of these are based on transition-metal-catalyzed Sonogashira coupling of *o*-halophenols and phenylacetylenes followed by cyclization. A variety of reagents/catalysts such as *N*-heterocyclic carbene–palladium complex/Cs₂CO₃ in DMSO,^[3a] Pd(PPh₃)₂Cl₂/CuI in DMF,^[3b] Pd(PPh₃)₂Cl₂/CuI in THF,^[3c] Pd(PPh₃)₂Cl₂/CuI in diisopropylamine,^[3d] Pd(PPh₃)₂Cl₂/CuI in Et₃N,^[3e] Pd(PPh₃)₂Cl₂/CuI/Et₂NH in DMF,^[3f] 10% Pd-C/PPH₃/CuI/(*S*)-prolinol in water,^[3g] and Pd⁰ nanoparticles in CH₃CN under sonication.^[3h] Although these methods are quite efficient, all of them except one^[3g] involve hazardous organic solvents and many of them require a co-catalyst and ligands.

The use of water as a reaction medium for organic reactions has received wide acceptability^[4] because of environmental concerns, its low cost, and its unique reactivity and selectivity that cannot be attained by organic solvents.^[5] Nevertheless, a one-pot multistep reaction in water is highly desirable in the context of green chemistry. On the other hand, the use of metal nanoparticles as efficient catalysts in organic reactions has attracted considerable interest in recent times because of their benign character and ease of preparation.^[6] As part of our continuing activities in this

area,^[7] we report here a one-pot Pd nanoparticle catalyzed reaction of 2-iodophenols and arylacetylenes in water in the absence of any ligand or copper co-catalyst leading to benzofurans (Scheme 1).



Scheme 1. Synthesis of benzo[*b*]furans.

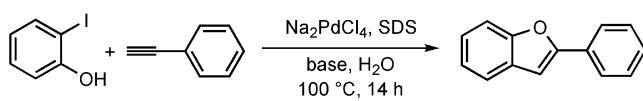
Results and Discussion

The experimental procedure is very simple. A mixture of Na₂PdCl₄, sodium dodecyl sulfate, 2-iodophenol, and arylacetylene in water was heated to reflux in the presence of triethylamine for a certain period of time as required to complete the reaction (TLC). Standard workup and purification by filtration through a short column of silica gel provided the product. Among a variety of bases investigated, triethylamine was found to provide the best yield (Table 1, Entry 4).

To determine the active catalytic species in this reaction, an extract from the reaction mixture of 2-iodophenol and phenylacetylene after 5 h from the start of the reaction showed the formation of nanoparticles, 5–6 nm in size by TEM (transmission electron microscopy; Figure 1). The identity of these particles as palladium was confirmed by EDX (energy dispersive X-ray) analysis (Figure 2), which is an important tool used to characterize metals and other elements. The amount of Pd⁰ nanoparticles was optimized to 4 mol-% for an efficient reaction. Nevertheless, Pd⁰ nanoparticles are generated in situ by the reduction of Na₂PdCl₄ by sodium dodecyl sulfate (SDS) in water.^[7c] SDS also acts as a stabilizer here.

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Table 1. Effect of base on the synthesis of benzofurans.



Entry	Base	Yield (%)
1	K ₃ PO ₄	30
2	NaOH	50
3	K ₂ CO ₃	35
4	Et ₃ N	82
5	Cs ₂ CO ₃	45

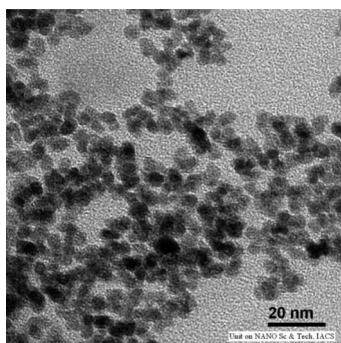


Figure 1. TEM image of Pd nanoparticles.

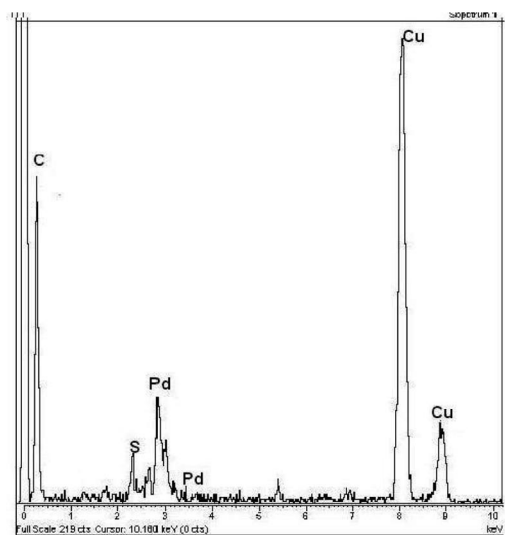
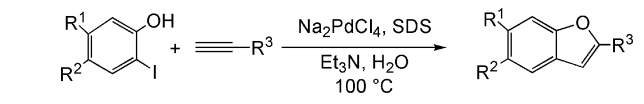


Figure 2. EDX spectra of Pd nanoparticles on Cu grid.

A series of substituted 2-iodophenols underwent reactions with a variety of diversely functionalized arylacetylenes by this procedure to produce the corresponding substituted benzofurans. The results are summarized in Table 2. Obviously, the reaction proceeds through Sonogashira coupling followed by subsequent 5-*endo-dig* cyclization. The reaction is highly selective with respect to halo couplings; only iodobenzene reacts. Thus, the Br group present in the

aromatic ring of 2-iodophenol remained inert and did not take part in the coupling process (Table 2, Entry 11). The electron-withdrawing CO₂Et group and electron-donating CH₃ group did not affect the reactivity of the catalyst in the reaction. A smooth reaction with a variety of substituted phenylacetylenes provided easy access to a library of functionalized benzofurans. Several functionalities such as Cl, Br, F, and OMe on the aromatic ring of the arylacetylenes are compatible with this process.

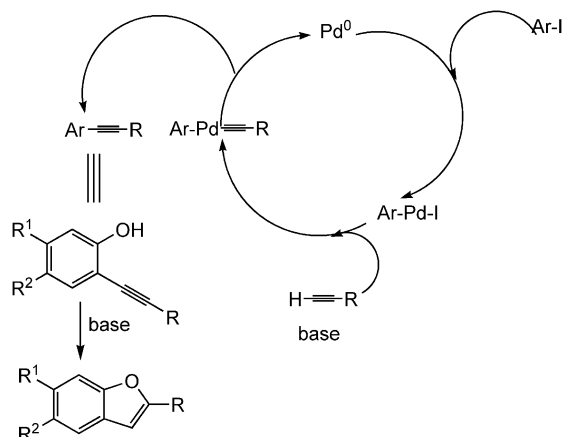
Table 2. Synthesis of benzo[*b*]furans.


Entry	R ¹	R ²	R ³	Time [h]	Yield [%] ^[a]	Ref.
1	H	H	C ₆ H ₅	14	82	[3h]
2	H	H	3-BrC ₆ H ₄	16	75	[8]
3	H	H	4-ClC ₆ H ₄	12	80	[9]
4	H	H	4-FC ₆ H ₄	14	82	[9]
5	H	H	4-MeC ₆ H ₄	12	80	[9]
6	H	H	4-MeOC ₆ H ₄	17	82	[9]
7	H	H	1-naphthyl	16	83	[10]
8	CO ₂ Et	H	C ₆ H ₅	14	84	–
9	H	C ₆ H ₅	C ₆ H ₅	18	86	[11]
10	H	Me	C ₆ H ₅	18	80	[12]
11	H	Br	C ₆ H ₅	16	81	[12]

[a] Yield refers to that of the purified isolated product characterized by spectroscopy (IR, ¹H NMR, and ¹³C NMR).

In general, the reactions are very clean and high yielding. The pure compounds are obtained by simple filtration of the crude product through a short column of silica gel. For comparison, this Pd⁰ nanoparticle catalyzed reaction in water under aerial atmosphere is more efficient than the one using Pd⁰ nanoparticles in CH₃CN under sonication and argon,^[3h] as indicated by the reactions of 4-methyl-2-iodophenol and 2-iodophenol with phenylacetylene (Table 2, Entries 1 and 11), where our method provides 82 and 80% yield, whereas the other one furnished 42 and 40% yield of the product together with 18 and 13% yield of the 1,3-diyne. We have not isolated any 1,3-diyne in any of these reactions. This clearly demonstrates the unique characteristics of the combination of Pd nanoparticles and water over organic solvents. Although earlier, a similar reaction using 10% Pd-C in water was reported,^[3g] it uses triphenylphosphane as ligand, CuI co-catalyst, and expensive (*S*)-prolinol, whereas our method involves only Pd nanoparticles and does not require any ligand, co-catalyst, or additive like (*S*)-prolinol.

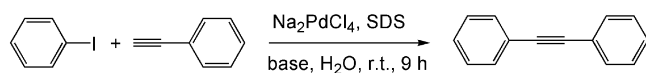
We believe that the reaction proceeds through a standard pathway^[3h] of oxidative addition of 2-iodophenol to Pd⁰ followed by transmetalation, reductive elimination, and cyclization to give the product with regeneration of Pd⁰ for the next cycle, as outlined in Scheme 2.



Scheme 2. Plausible mechanism.

We also studied the normal Sonogashira coupling^[13] of aryl iodides with aryl/alkylacetylenes by using this catalyst system. It was found that sodium hydroxide was equally effective as triethylamine for this reaction (Table 3, Entry 2). Thus, sodium hydroxide, being less expensive and easily available, was chosen as the base for these reactions. The reactions are also accomplished at room temperature. A wide range of substituted aryl iodides and phenylacetylenes participated in this reaction to provide the corresponding substituted acetylenes. The results are reported in Table 4. A variety of substituents such as F, Br, OCF₃, NH₂, NO₂, and COCH₃ on the phenyl ring of the aryl iodides are compatible with this procedure, and both electron-donating and electron-withdrawing groups are uniformly reactive. A heteroaryl iodide (Table 4, Entry 9) also produced the corresponding product in high yield. Aliphatic acetylenes (Table 4, Entries 12–14) underwent reactions by this procedure without any difficulty.

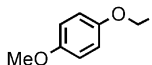
Table 3. Optimization of base in the Sonogashira reaction.



Entry	Base	Yield [%]
1	K ₃ PO ₄	65
2	NaOH	86
3	K ₂ CO ₃	51
4	Et ₃ N	80
5	Cs ₂ CO ₃	70

The aqueous suspension containing the catalyst after the Sonogashira reaction as well as cyclization to benzofuran was recycled for three runs with gradual loss of efficiency

Table 4. Sonogashira coupling between aryl iodides and acetylene.

Ar-I + R ¹ -C≡C-R		Na ₂ PdCl ₄ , SDS NaOH, H ₂ O, r.t.		Ar-C≡C-R ¹	
Entry	Ar	R ¹	Time [h]	Yield [%] ^[a]	Ref.
1	C ₆ H ₅	C ₆ H ₅	9	86	[13a]
2	3-FC ₆ H ₄	C ₆ H ₅	8	84	[13a]
3	4-BrC ₆ H ₄	C ₆ H ₅	10	84	[14]
4	4-OCF ₃ C ₆ H ₄	C ₆ H ₅	10	82	—
5	2-NH ₂ C ₆ H ₄	C ₆ H ₅	11	84	[15]
6	4-MeC ₆ H ₄	C ₆ H ₅	11	78	[13a]
7	4-O ₂ NC ₆ H ₄	C ₆ H ₅	12	76	[13a]
8	4-MeOCC ₆ H ₄	C ₆ H ₅	7	92	[13a]
9		C ₆ H ₅	10	85	[16]
10	C ₆ H ₅	4-ClC ₆ H ₄	8	88	[13a]
11	C ₆ H ₅		10	85	[17]
12	C ₆ H ₅		9	78	[18]
13	C ₆ H ₅		10	82	[19]
14	C ₆ H ₅		12	80	—

[a] Yield refers to that of the purified isolated product characterized by spectroscopy (IR, ¹H NMR, and ¹³C NMR).

as demonstrated by a representative reaction of 2-iodophenol and phenylacetylene in Figure 3. The loss of activity of the Pd nanoparticles is due to the agglomeration of the nanoparticles after each cycle. The catalytic efficiency of the nanoparticles is very much dependent on the particle size. Usually, an increase in the size of the nanoparticles results in a decrease in the activity.^[20] In this reaction, the Pd nanoparticles after the third recycle were found to be largely agglomerated as shown by the TEM image (Figure 4), and thus, their activity was greatly reduced.

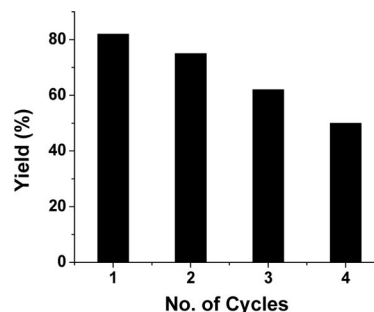


Figure 3. Recyclability diagram for the reaction of 2-iodophenol and phenylacetylene.

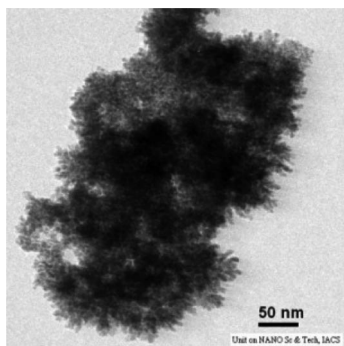


Figure 4. TEM image of agglomerized Pd nanoparticles after third recycle.

Conclusions

We have developed a one-pot, very simple and efficient procedure for the synthesis of functionalized benzo[*b*]furans through a Sonogashira coupling–5-*endo-dig* cyclization catalyzed by in situ generated palladium nanoparticles in water and open air without any ligand or co-catalyst. A wide range of substituted aryl iodides and phenylacetylenes underwent this reaction to provide easy access to a library of benzofurans. The simple, eco-friendly reaction conditions, high yields of products, reusability of the catalyst, no requirement for a ligand, co-catalyst, or special device, and the superior efficiency of the reaction compared to similar reported procedures^[3g,3h] make this procedure more attractive. Most significantly, better performance of Pd nanoparticles in water than CH₃CN^[3h] is noteworthy.

Experimental Section

Representative Procedure for the Synthesis of Benzo[*b*]furan: To a mixture of Na₂PdCl₄ (12 mg, 0.0408 mmol) and sodium dodecyl sulfate (144 mg, 0.5 mmol) in water (3 mL) was added 2-iodophenol (220 mg, 1 mmol), phenylacetylene (123 mg, 1.2 mmol), and Et₃N (303 mg, 3 mmol). The mixture was heated to reflux (oil bath) for 14 h (TLC). After cooling, the reaction mixture was extracted with ethyl acetate (3 × 10 mL). The extract was washed with water and brine and dried with Na₂SO₄. Evaporation of the solvent left the crude product, which was purified by column chromatography over silica gel (hexane/ether, 92:8) to afford pure 2-phenylbenzo[*b*]furan (159 mg, 82%) as a white solid (m.p. 120 °C). The spectroscopic data (¹H and ¹³C NMR) are in good agreement with those reported for the authentic sample.^[3h] The aqueous part containing the catalyst was reused in three subsequent runs without appreciable loss of efficiency (Figure 3). This procedure was followed for the synthesis of all the products listed in Table 2. Although the general experimental procedure was based on a 1-mmol-scale reaction, multimolar reactions produced similar results. The known compounds were identified by comparison of their spectra with those reported earlier (see references in Table 2).

Ethyl 2-Phenylbenzofuran-6-carboxylate: White solid, m.p. 87 °C. IR (KBr): $\tilde{\nu}$ = 2982, 2853, 2276, 1705, 1447, 1366, 1298, 1225, 1190 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 1.42 (t, *J*_{H,H} = 7.13 Hz, 3 H, CO₂CH₂CH₃), 4.40 (q, *J*_{H,H} = 7.13 Hz, 2 H, CO₂CH₂CH₃), 7.01 (s, 1 H, 3-H), 7.34–7.48 (m, 3 H, 3-H, 4-H of 2-Ph), 7.57 (d, *J*_{H,H} = 8.19 Hz, 1 H, 2-H of 2-Ph), 7.86 (d, *J*_{H,H} =

7.6 Hz, 2 H, 4-H), 7.95 (d, *J*_{H,H} = 8.17 Hz, 1 H, 5-H), 8.20 (s, 1 H, 7-H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 14.4, 61.0, 101.3, 112.7, 120.3, 124.4, 125.3 (2 C), 126.4, 128.9 (2 C), 129.3, 129.8, 133.5, 154.3, 158.8, 166.8 ppm. HRMS: calcd. for C₁₇H₁₄O₃ [M + Na]⁺ 289.0841; found 289.0845. See Table 2, Entry 8.

Representative Experimental Procedure for the Sonogashira Coupling Reaction of Iodobenzene with Phenylacetylene to Produce Diphenylacetylene: To a mixture of Na₂PdCl₄ (12 mg, 0.0408 mmol) and sodium dodecyl sulfate (144 mg, 0.5 mmol) in water (3 mL) was added iodobenzene (204 mg, 1 mmol), phenylacetylene (123 mg, 1.2 mmol), and NaOH (120 mg, 3 mmol). The mixture was stirred at room temperature for 9 h (TLC). The reaction mixture was extracted with ethyl acetate (3 × 10 mL). The extract was washed with water and brine and dried with Na₂SO₄. Evaporation of the solvent left the crude product, which was purified by column chromatography over silica gel (hexane) to afford pure diphenylacetylene (153 mg, 86%) as a white solid (m.p. 62 °C). The spectroscopic data (¹H and ¹³C NMR) are in good agreement with those reported for the authentic sample.^[13a]

Many of these products are known compounds and were identified by comparison of their spectra with those reported earlier (see references in Table 4). The new compounds were characterized by IR, ¹H NMR, and ¹³C NMR spectroscopy and HRMS, which are provided below in order of their entries in Table 4.

1-Phenylethynyl-4-trifluoromethoxybenzene: White solid, m.p. 68–70 °C. IR (KBr): $\tilde{\nu}$ = 3431, 1587, 1529, 1498, 1444, 1277, 1205, 1165 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 7.21 (d, *J*_{H,H} = 8.27 Hz, 2 H, 3-H), 7.36–7.38 (m, 3 H, 3'-H, 4'-H), 7.53–7.58 (m, 4 H, 2-H, 2'-H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 88.0, 90.3, 118.8, 120.8 (2 C), 122.2, 123.0, 128.5 (2 C), 128.7, 131.8 (2 C), 133.3 (2 C), 149.0 ppm. C₁₅H₉F₃O (262.06): calcd. C 68.70, H 3.46; found C 68.68, H 3.49. See Table 4, Entry 4).

1-Methoxy-4-(3-phenylprop-2-ynoxy)benzene: Brownish yellow solid, m.p. 83 °C. IR (KBr): $\tilde{\nu}$ = 2958, 2926, 2910, 2855, 1512, 1441, 1379, 1288, 1230, 1219 cm⁻¹. ¹H NMR (300 MHz, CDCl₃, 25 °C): δ = 3.78 (s, 3 H, OCH₃), 4.87 (s, 2 H, CH₂), 6.87 (d, *J*_{H,H} = 9 Hz, 2 H, 2-H), 6.99 (d, *J*_{H,H} = 9.3 Hz, 2 H, 3-H), 7.30–7.32 (m, 3 H, 3'-H, 4'-H), 7.43–7.45 (m, 2 H, 2'-H) ppm. ¹³C NMR (75 MHz, CDCl₃, 25 °C): δ = 55.6, 57.4, 84.2, 86.9, 114.5 (2 C), 116.2 (2 C), 122.3, 128.2 (2 C), 128.6, 131.7 (2 C), 151.9, 154.3 ppm. HRMS: calcd. for C₁₆H₁₄O₂ [M + H]⁺ 239.1094; found 239.1067. See Table 4, Entry 14.

Acknowledgments

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