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Recyclable Pd/$CuFe_2O_4$ nanowires: a highly active catalyst for C–C couplings and synthesis of benzofuran derivatives†

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Pd/$CuFe_2O_4$ nanowire-catalyzed cross coupling transformations are described. Notably, these reactions showed excellent functional group tolerance. Further, the protocol is applied to a one-pot synthesis of benzofurans *via* a Sonogashira coupling and intramolecular etherification sequence. The catalyst was reused and found to maintain its activity and stability.

Introduction

The ability to form various C–C bonds under transition metal catalysis is important in organic synthesis. Particularly, one-pot construction of heterocyclic core structures of biological relevance is indispensable.[1] In this context, Pd is one of the most widely used transition metals for a variety of coupling transformations. When compared with homogeneous counterparts, heterogeneous catalysts enable the formation of less contaminated products and promote green chemistry.[1–3] In the recent past, heterogeneous catalysis, for the formation of C–C, C–O, C–N and C–S bonds, became the central part of synthetic chemistry. Amongst them all, carbon–carbon (C–C) bond forming reactions for the preparation of carbon scaffolds are of high importance from the organic synthetic viewpoint.

Supported nanocatalysts have become an integral part of heterogeneous catalysis for various organic transformations and industrial applications.[4–7] Especially, metal oxide supported heterogeneous nanocatalysts are preferred because of their activity, better selectivity, and high stability over conventional metal based catalyst frameworks.[8] Unsupported nanocatalysts face problems due to issues related recovery and recyclability from the reaction mixture.[9] This problem can be resolved by immobilizing the active species on a support having high surface area materials such as nano-metal oxides,[10] carbon nano-materials,[11,12] polymers[13] *etc.* Among all the supporters, nano-metal oxide supported nanocatalysts are easily separable from the reaction mixture.[14,15] Especially, the substitution of the copper ion into the ferrite lattice constitutes a well-developed category of the mixed metal ferrites for catalysis in organic reactions.[16,17] In this context, we designed $CuFe_2O_4$ support for organic transformation reactions (C–C couplings).

The biaryls and diarylacetylenes are useful scaffolds that constitute pharmaceuticals, agrochemicals and biologically active compounds.[17,18] The Suzuki–Miyaura cross-coupling reactions of aryl halides with aryl boronic acids and Sonogashira coupling reactions of aryl halides with arylacetylenes are considered to be important carbon–carbon bond forming strategies, for constructing biaryls and internal acetylenes, respectively.[19–21] However, most of these reactions made use of toxic ligands in conjunction with Pd-salts or Pd nanoparticles and Pd/Cu nanoparticles.[22] Benzofuran derivatives are an important class of heterocyclic compounds, due to their miscellaneous biological profile, such as analgesia, antitumor, antimicrobial, kinase inhibitor and antihyperglycemic activities.[23–28] Recently, the research group of Mariusz Jan Bosiak showed the utility of benzofurans in photovoltaic and optoelectronic properties, wherein benzofurans absorb and emit the light.[29–32] While, one-pot synthesis of benzofurans, under homogeneous catalysis, is well established. Recently, the synthetic community turned their interest to develop new methods for the synthesis of benzofurans by means of heterogeneous catalytic conversion.[33–39] Very recently, there have been various reports described that the catalytic activity of Pd nanoparticles can be retained, the stability of the Pd nanoparticles also enhanced to some extent by using magnetic nanomaterials as a supporter for immobilization of Pd nanoparticles.[40–46] Recently, we have developed Pd/$CuFe_2O_4$ nanowires and showed its synthetic utility toward Heck couplings.[47] Herein, we present the applicability of catalyst for various C–C bond forming reactions (Suzuki, Sonogashira). Further, this catalyst applied for the one-pot synthesis of benzofurans *via* intermolecular Sonogashira followed by intramolecular cyclization. Initially, a comparative study of as prepared catalyst with other recently reported Pd supported catalysts for Suzuki coupling

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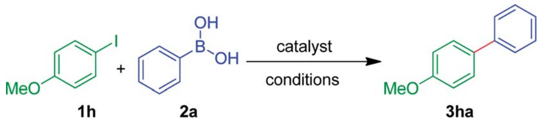
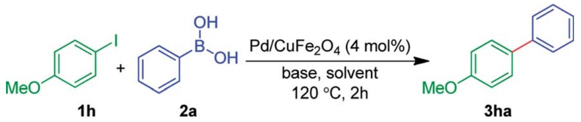
† Electronic supplementary information (ESI) available: Details of catalyst synthesis, characterization and experimental studies. ^1H, ^{13}C-NMR spectra of all isolated products. See DOI: 10.1039/c8ra03697g

Table 1 Comparison of the catalytic activity of Pd/$CuFe_2O_4$ nanowires with other reported recent catalysts for Suzuki couplings



Entry	Catalyst	Conditions	Yield (%)	Ref.
1	PdO/GO	K_2CO_3, DMSO, 120 °C, 10 min	88	48
2	Pd-SBT@MCM	K_2CO_3, PEG, 80 °C, 175 min	96	49
3	GO/Fe_2O_4/Pd composite	K_2CO_3, H_2O/EtOH, 80 °C, 20 min	95	50
4	Pd@CQD@Fe_3O_4	*t*-BuOK, EtOH : H_2O (1 : 1), 120 °C, 60 min	95	51
5	Pd/C@Fe_2O_4	K_2CO_3, H_2O, 100 °C, 30 min	96	52
6	Pd@PVP	K_2PO_4, H_2O/EtOH (1 : 3), 80 °C, 3–18 h	93	53
7	Fe_3O_4@SiO_2–Pd	CaO, H_2O/EtOH (1 : 1), 85 °C, 20 min	93	54
8	Pd/Celite-PANI	K_2CO_3, TBAB (10%), dioxane : H_2O (1 : 1), 90 °C, 4 h	94	55
9	Pd/TiO_2	Na_2CO_3, NMP : H_2O, 120 °C, 4 h	95	56
10	HMMS-salpr-Pd	K_2CO_3, H_2O/EtOH (1 : 1), 70 °C, 60 min	94	57
11	**Pd/$CuFe_2O_4$ nanowires**	**K_2CO_3, DMSO, 120 °C, 10 min**	**98**	**this work**

Table 2 Optimization studies for the formation of biphenyl **3ha**[a]



Entry	Base	Solvent	Yield[b] **3aa**(%)
1	**K_2CO_3**	**DMSO**	**98**
2	K_2CO_3	DMF	95
3	K_2CO_3	DMA	67
4	K_2CO_3	Toluene	52
5	K_2CO_3	1,4-Dioxane	76
6	K_2CO_3	THF	72
7	K_2CO_3	Acetonitrile	63
8	Cs_2CO_3	DMSO	67
9	K_3PO_4	DMSO	40
10	NaOH	DMSO	31

[a] Reaction conditions: aryl iodides **1h** (0.25 mmol), arylboronic acid **2a** (0.5 mmol), Pd/$CuFe_2O_4$ (4 mol%), base (0.5 mmol) and solvent (1 mL) at 120 °C. [b] Isolated yields of product **3ha**.

reactions was shown in Table 1. As shown in Table 1, most of the Pd supported nanocatalysts produces the yields 88–96% (Table 1, entries 1–10). Whereas, with our catalyst Pd/$CuFe_2O_4$ nanowires we got near quantitative yields (98%) (Table 2, entry 11).

Results & discussion

To begin with, the optimization of Suzuki–Miyaura coupling was planned. For this purpose, 4-methoxy iodobenzene **1h** and phenylboronic acid **2a** were chosen as the model substrates. Recently, we reported that Pd/$CuFe_2O_4$ nanowires showed the best catalytic activity for Heck couplings.[47] Thus, the reaction was carried out between 4-methoxy iodobenzene **1h** and phenylboronic acid **2a** in the presence of Pd/$CuFe_2O_4$ nanowires (4 mole%), K_2CO_3 (2 equiv.) and in DMSO (1 mL) at 120 °C for 2 h. Gratifyingly, the reaction was quite successful and furnished the biaryl product **3ha**, in near quantitative yield (Table 2, entry 1). On the other hand, other solvents, such as DMF, DMA, toluene, 1,4-dioxane, THF and acetonitrile were inferior (Table 2, entries 2 to 7). While the reaction gave fair, moderate and poor yields of the product **3ha** with other bases, such as Cs_2CO_3, K_3PO_4, and NaOH respectively (Table 2, entries 8 to 10).

Further to optimize the mol% of the Pd/$CuFe_2O_4$ catalyst, for the formation of **3ha**, the reaction was performed between 4-methoxy iodobenzene **1h** and phenylboronic acid **2a** with 0, 1, 2, 4, 6, 8, and 10 mol% of Pd in Pd/$CuFe_2O_4$, under standard conditions. Among all, it was observed that the reaction yields were more or less same with ≥4 mol% of Pd in Pd/$CuFe_2O_4$ (Fig. 1). Thus it was concluded that the 4 mol% of Pd was an optimal load to drive the reaction.

With these best conditions in hand, the scope was extended for the Suzuki–Miyaura coupling with various iodoarenes **1a–l** and arylboronic acids **2a–d**. Gratifyingly, the reaction was found to be amenable and afforded the corresponding biaryls **3aa–lb**, in fair to near quantitative yields (Table 3). Interestingly, the reaction was successful with simple iodobenzene **1a** and amenable with abroad range of functional groups (COOMe, NO_2, OMe, F & Cl) on aromatic ring **1b–j**, which reveals a wide functional group tolerance of this reaction. Notably, heteroaromatic iodide **1l**, gave the products **3lb**, in excellent yield. Significantly, protecting group free iodopyridine **1k** was also tolerable and afforded the products **3ka–kc** (Table 3). Interestingly, the reaction was also amenable to simple arylboronic acids **2** bearing broad range of functional moieties on the aromatic ring [*i.e.* OMe, F and Cl, (Table 3)]. To demonstrate the utility of the strategy, the Suzuki coupling reaction was explored with bromoarenes **1s–u** with simple boronic acid **2a**, under established conditions. Gratifyingly, biphenyls **3aa**, **3da** and **3ha** were isolated in 82%, 70% and 68% yields (Table 3), respectively. Which ascertains the usefulness of Pd(0)/$CuFe_2O_4$

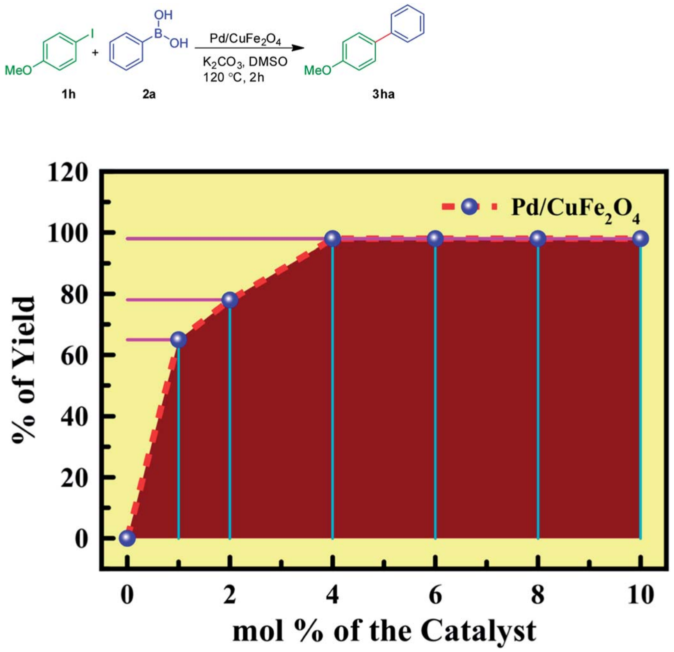


Fig. 1 Optimization of loading the catalyst for Suzuki-coupling reaction.

nanowires catalyst. Whereas the coupling with chlorobenzene **1v** and *meta*-chloronitrobenzene **1w** as reacting partners with the boronic acid **2a**, furnished the desired biaryls **3aa** and **3da** in poor yields (25% & 27% respectively, Table 3). It is noteworthy to mention that in case of **1v** and **1w**, the homo coupling of boronic acid **2a** was also noticed. In addition, the chloroarenes **1v** and **1w** were not completely consumed even after 24 h.

The recovery of the catalyst was done by centrifugation and washing with ethyl acetate and acetone followed by drying in a hot air oven at 60 °C for 12 h. The recovered Pd/$CuFe_2O_4$ nanowires catalyst was then subjected to the next catalytic cycles. It is worth mentioning that the catalyst retains its activity, which is evident with nearly no loss of activity even after fifth reaction cycle (Fig. 2). The marginal loss of activity after the fifth cycle (<3%) may be due to loss of some amount of the catalyst during the recovery of Pd/$CuFe_2O_4$ nanowires. The catalyst was recycled five times without an appreciable change in the product **3ha** yield, under the established conditions at 120 °C. Thus, based on the above results it is confirmed that Pd/$CuFe_2O_4$ nanowires catalyst is stable enough and can be reused.

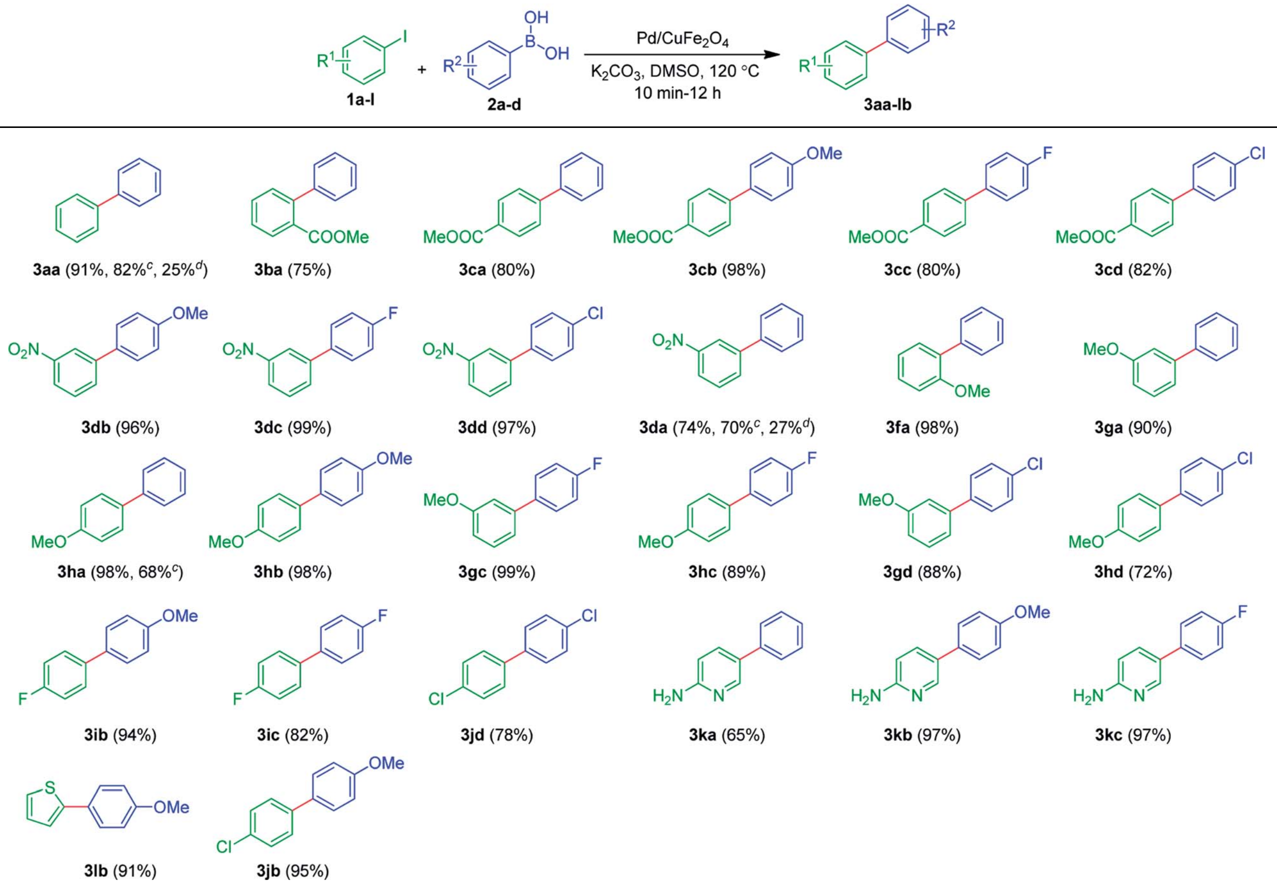
The relation between catalytic properties and structure of Pd/$CuFe_2O_4$ nanowires

The mechanism for the relation between catalytic properties (Suzuki coupling reaction) and structure of Pd/$CuFe_2O_4$ nanowires is shown in Scheme 1. The first step would be the oxidative addition of Pd(0)/$CuFe_2O_4$ nanowires to the 4-methoxy iodobenzene **1h** to form Pd(II) species **A.** In most cases the oxidative addition is the rate determining step of a catalytic cycle. During this step, the Pd is oxidized from Pd(0) to Pd(II). Further, the reaction with base gives the intermediate **B**, which on coupling with the activated boronic acid derivative **C** (produced by reaction of the boronic acid **2a** with K_2CO_3 base), gives transmetalation complex **D.** Finally, the reductive elimination of D affords the coupled product **3ha** restores the active Pd(0)/$CuFe_2O_4$ nanowires, thus completes the catalytic cycle.

After successful synthesis of biaryls using Suzuki–Miyaura coupling, in order to check the efficiency of the Pd/$CuFe_2O_4$ nanowires catalyst, we aimed at Sonogashira coupling between iodoarenes and arylacetylenes. Therefore, initially, the reaction was explored between 2-amino iodobenzene **1m** and phenylacetylene **4a**, under established conditions as above (see; Table 2, entry 1). The reaction was quite successful and furnished the 2-amino diphenylacetylene product **5ma**, in good yield (Table 4, entry 1). On the other hand, the reaction was found to be inferior with the other solvents, such as DMF, DMA, toluene, 1,4-dioxane, THF and acetonitrile (Table 4, entries 2 to 7). While the reaction with bases Cs_2CO_3 and KOH gave moderate yields of the product **5ma** (Table 4, entries 8 and 9).

With the above optimized conditions, for Sonogashira coupling, to demonstrate the utility of the strategy, the activity of Pd/$CuFe_2O_4$ catalyst was assessed for the reaction between iodoarenes **1a–q** and phenylacetylene **4a.** The results of the catalytic reactions are as depicted in Table 5, which showed broad substrate scope and delivered the corresponding internal acetylenes **5aa–qa**, in fair to very good yields. For example, iodoarenes bearing electron-withdrawing groups (*meta*-COOMe, *para*-COOMe, *meta*-NO_2) were found to be smooth and afforded the products (**5ba**, **5ca** & **5da**) moderate yields (Table 5). In addition, the reaction was quite successful with electron releasing groups as well (**5fa**, **5ga** & **5ha**, Table 5). Notably, the reaction was tolerable to protecting group free NH_2 moiety on pyridine ring (**5ka**, Table 5). To our delight, 2-iodobenzylalcohol

Table 3 Synthesis of biphenyls with aryl iodide and arylboronic acid[a,b]



3aa (91%, 82%[c], 25%[d]) **3ba** (75%) **3ca** (80%) **3cb** (98%) **3cc** (80%) **3cd** (82%)

3db (96%) **3dc** (99%) **3dd** (97%) **3da** (74%, 70%[c], 27%[d]) **3fa** (98%) **3ga** (90%)

3ha (98%, 68%[c]) **3hb** (98%) **3gc** (99%) **3hc** (89%) **3gd** (88%) **3hd** (72%)

3ib (94%) **3ic** (82%) **3jd** (78%) **3ka** (65%) **3kb** (97%) **3kc** (97%)

3lb (91%) **3jb** (95%)

[a] Reaction conditions: aryl iodides (0.25 mmol), arylboronic acid (0.5 mmol), Pd/CuFe$_2$O$_4$ (4 mol%), K$_2$CO$_3$ (0.5 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of chromatographically pure products **3aa–lb**. [c] Isolated yields of products when bromoarenes **1s–u** were used. [d] Isolated yields of products when chloroarenes **1v–w** were used.

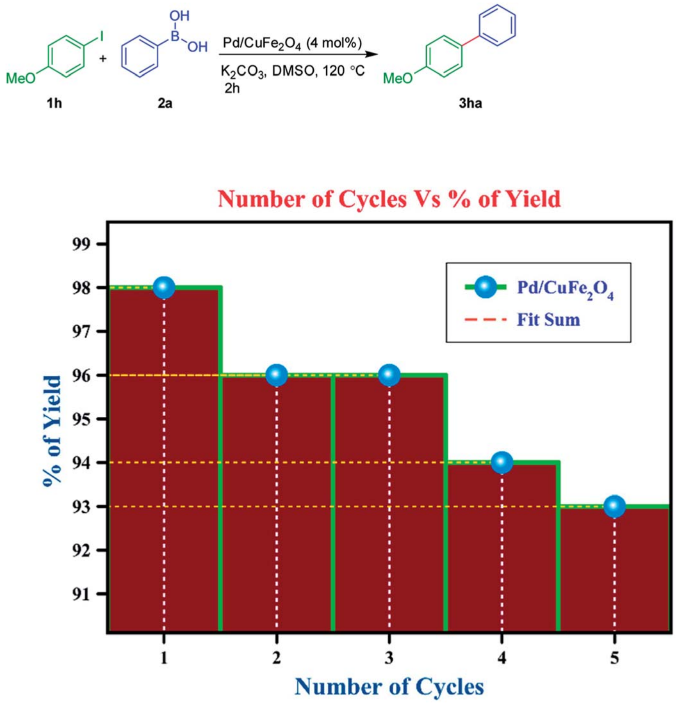
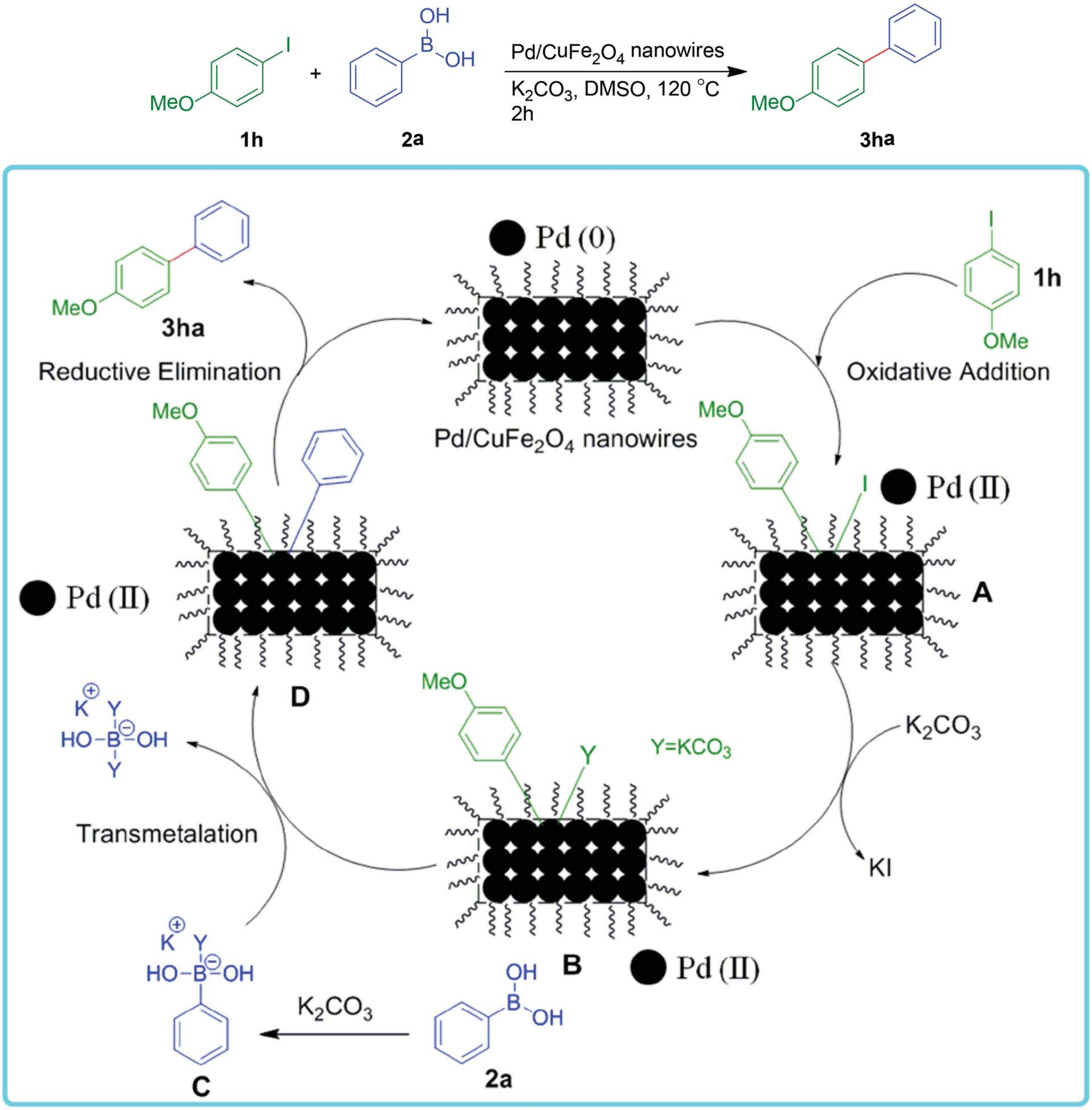


Fig. 2 Recyclability of the catalyst Pd/CuFe$_2$O$_4$ nanowires in Suzuki reaction.

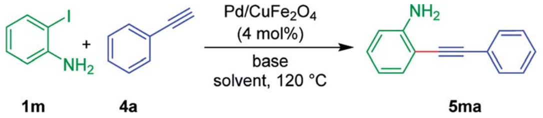


Scheme 1 The mechanism for the relation between catalytic properties (Suzuki coupling reaction) and structure of Pd/$CuFe_2O_4$ nanowires.

2n coupled with phenylacetylene **4a** and gave the product **5na**, in very good yield (Table 5). Further, we have explored Sonogashira coupling between bromobenzene **1s** and phenylacetylene **4a**. Notably, the reaction was smooth and yielded diphenylacetylene **5aa**, in yields 68%. Even the reaction was also successful *meta*-bromonitrobenzene **1t** and *para*-methoxybromobenzene **1u** with **4a**. While, the reaction is somewhat sluggish with chloroarenes. Therefore, the present catalyst seems to be active enough and could promote the reactions with bromoarenes as well. To further check the selectivity of the process, it was planned to test the substituent susceptibility. Thus, the reaction was conducted with 1-chloro-4-iodobenzene **1j** in the presence of phenylacetylene **4a**, in very good yields (Table 5). To our delight, the reaction was found to be smooth and selective and gave the product **5jb**, in which relatively more reactive iodo substituent was selectively involved in the coupling reaction. It is worth mentioning that the reaction with ethyl propiolate as coupling partner, did not lead to any product and only starting materials were recovered. This may be due to the fact that less nucleophilicity of acetylenic β-carbon of ethyl propiolate.

Benzofurans are ubiquitous oxygen-containing heterocyclic motifs that constitute many natural products, pharmaceuticals, biologically important compounds and organic materials. In this context, many synthetic strategies have been established for their synthesis. Notably, transition metal-catalyzed (Pd,[58–66] Rh,[67] Ru,[68–71] Ir,[72] Au[73] and Cu[74–76]) annulations proved to be powerful strategies for the synthesis of benzofurans. Quite

Table 4 Optimization studies for the formation of 2-(phenyl ethynyl) aniline **5ma**[a]

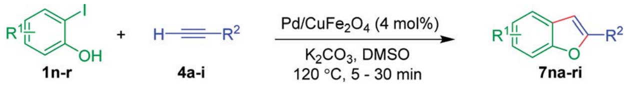


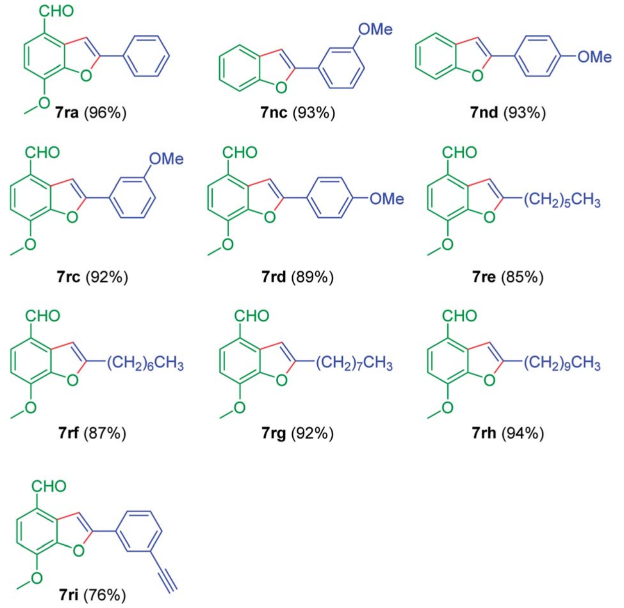
Entry	Base	Solvent	Yield (**5ma**)[b]	Time (h)
1	**K_2CO_3**	**DMSO**	**75**	**12**
2	K_2CO_3	DMF	60	12
3	K_2CO_3	DMA	35	24
4	K_2CO_3	Toluene	—[c]	48
5	K_2CO_3	1,4-Dioxane	36	24
6	K_2CO_3	THF	30	24
7	K_2CO_3	CH_3CN	32	24
8	Cs_2CO_3	DMSO	55	12
9	KOH	DMSO	48	12

[a] Reaction conditions: aryl iodides **1m** (0.5 mmol), phenylacetylene **4a** (1 mmol), Pd/CuFe$_2$O$_4$ (4 mol%), base (1 mmol) and solvent (1 mL) at 120 °C. [b] Isolated yields of product **5ma**. [c] No progress was observed.

interestingly, when 2-iodophenols **1n–r** were treated with terminal acetylenes **4a–i**, benzofurans were obtained as the products (Table 6). For example, the reaction was amenable to different arylacetylenes (**4a**, **4c** & **4d**) and furnished the corresponding benzofurans **7ra–rd** (Table 6). Notably, the reaction was also successful with terminal alkyl acetylenes **4e–h** and

Table 6 Synthesis of benzofurans **7ra–ri** from 2-iodophenols **1n–r** and aryl alkynes **4a–i**[a,b]

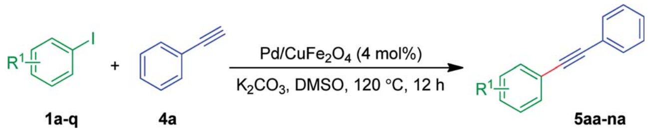


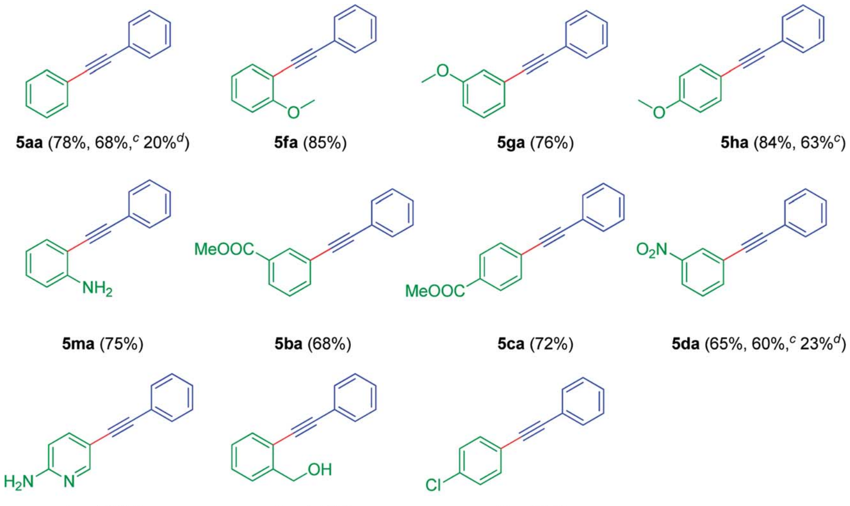


7ra (96%) **7nc** (93%) **7nd** (93%)
7rc (92%) **7rd** (89%) **7re** (85%)
7rf (87%) **7rg** (92%) **7rh** (94%)
7ri (76%)

[a] Reaction conditions: 2-iodophenols **1n–r** (0.5 mmol), aryl alkynes **4a–i** (0.5 mmol), Pd/CuFe$_2$O$_4$ nanowires (4 mol%), K$_2$CO$_3$ (1 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of product **7na–ri**.

Table 5 The Pd/CuFe$_2$O$_4$ nanowires catalyzed Sonogashira coupling reaction between iodoarenes **1a–q** and phenylacetylene **4a**[a,b]

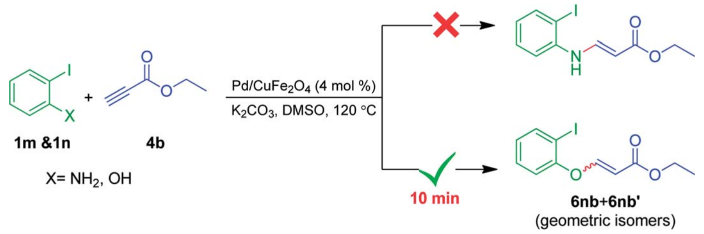




5aa (78%, 68%,[c] 20%[d]) **5fa** (85%) **5ga** (76%) **5ha** (84%, 63%[c])
5ma (75%) **5ba** (68%) **5ca** (72%) **5da** (65%, 60%,[c] 23%[d])
5ka (68%) **5qa** (86%) **5ja** (86%)

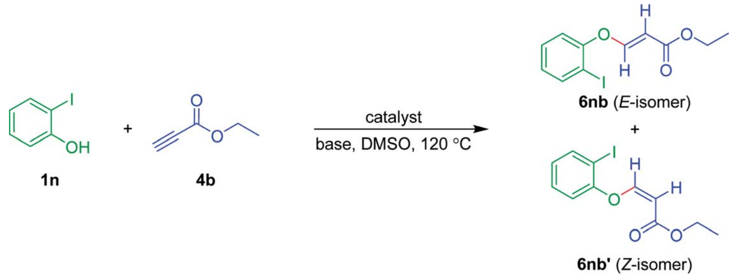
[a] Reaction conditions: aryl iodides **1a–q** (0.5 mmol), phenylacetylene **4a** (1 mmol), Pd/CuFe$_2$O$_4$ (4 mol%), K$_2$CO$_3$ (1 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of product **5aa–5qa**. [c] Isolated yields of products when bromoarenes **1s–u** were used. [d] Isolated yields of products when chloroarenes **1v–w** were used.

Table 7 Attempting for Sonogashira reaction between iodoarenes **1m–n** and ethyl propiolate **4b**[a,b]



[a] Reaction conditions: aryl iodides **1m** & **1n** (0.5 mmol), ethyl propiolate **4b** (1 mmol), Pd/CuFe$_2$O$_4$ (4 mol%), K$_2$CO$_3$ (1 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of products **6**.

Table 8 Screening conditions for the formation of **6nb**+**6nb′** from iodophenol **1n** and ethyl propiolate **4b**[a,b]



				Yield (%)	
Entry	Catalyst (Pd/CuFe$_2$O$_4$)	Base (K$_2$CO$_3$)	Solvent (DMSO)	**6nb** (*E*)	**6nb′** (*Z*)
1	4 mol%	2 eq.	1 mL	57	39
2	—	2 eq.	1 mL	32	16
3	—	2 eq.	—	35	18
4	4 mol%	2 eq.	—	53	35
5	—	—	1 mL	—	—
6	4 mol%	—	1 mL	—	—
7	—	—	—	—	—

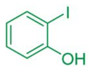
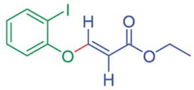
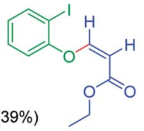
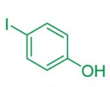
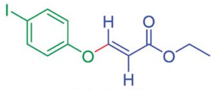
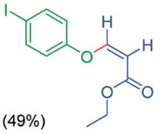
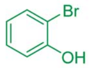
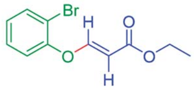
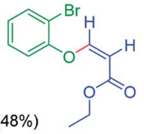
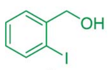
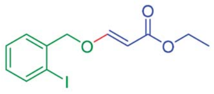
[a] Reaction conditions: aryl iodides **1n** (0.5 mmol), ethyl propiolate **4b** (1 mmol), Pd/CuFe$_2$O$_4$ (4 mol%), K$_2$CO$_3$ (1 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of products **6**.

afforded the benzofurans **7re–rh**, in very good to excellent yields (Table 6). Significantly, the reaction was tolerable to the aldehyde functionality on the aromatic ring of 2-iodophenol derivative **1r**. Significantly, 3-hydroxy-2-iodo-4-methoxybenzaldehyde **1r** coupled with 1,3-diethynylbenzene **4i**, in which only one acetylene group was reacted and gave **7ri** as an exclusive product (Table 6).

Moreover, to check the scope and generality of Sonogashira coupling, 2-iodophenol was treated with ethyl propiolate **4b**. Surprisingly, no Sonogashira product was formed; instead, Michael addition product **6nb** was obtained as major diastereomer *via* nucleophilic attack of the hydroxyl group of phenol (Table 7). This sort of nucleophilic 1,4-addition of phenolic hydroxyl across the activated triple/double bonds is already established in the literature.[77–79] Whereas, when 2-iodoaniline was reacted with ethyl propiolate **4b**, we could not observe any required product. The reaction was inconclusive from the TLC.

To understand the nature of the reaction and whether or not the palladium is necessary to drive this Michael addition reaction, the reaction was performed under varying conditions, as illustrated in Table 8. The reaction under standard conditions, furnished the product **6nb**+**6nb′** (57 + 39) (Table 8, entry 1). The reaction was also successful without Pd-catalyst, but with the base and solvent, albeit there was a drop in the yields [**6nb**+**6nb′** (32 + 16), Table 8, entry 2]. In addition, the reaction was smooth, under neat conditions with base and without catalyst [**6nb**+**6nb′** (35 + 18), Table 8, entry 3]. While the yield of the product was good with both catalyst and base and without solvent [**6nb**+**6nb′** (53+35), Table 8, entry 4]. Only with solvent and without base and catalyst, no progress was noted (Table 8, entry 5). Similarly, with the catalyst and solvent, without base, no progress was seen (Table 8, entry 6). The reaction did not proceed without the catalyst, base and solvent (Table 8, entry 7).

Table 9 Attempting for Sonogashira reaction between iodoarenes and ethyl propiolate **4b**[a,b]

	6 (*E* isomer)	**6'** (*Z* isomer)
 **1n**	 **6nb** (57%)	 **6nb'** (39%)
 **1o**	 **6ob** (50%)	 **6ob'** (49%)
 **1p**	 **6pb** (50%)	 **6pb'** (48%)
 **1q**	 **6qb** (72%)	--[c]

[a] Reaction conditions: aryl iodides **1n–q** (0.5 mmol), ethyl propiolate **4b** (1 mmol), Pd/$CuFe_2O_4$ (4 mol%), K_2CO_3 (1 mmol) and DMSO (1 mL) at 120 °C. [b] Isolated yields of products **6**. [c] Only single *E*-isomer **6qb** was formed.

To further confirm this sort of reactivity, the reaction was explored with different halophenols (**1n**, **1o**, **1p** & **1q**) with ethyl propiolate **4b**, under standard reaction conditions. As anticipated, furnished the corresponding arylvinyl ethers as *Z* and *E* diastereomeric mixture, as minor and major isomers, respectively (Table 9). Surprisingly, when 2-iodobenzylalcohol **1q** was used as the nucleophile, exclusively, gave the *E* isomer in 72% yield (Table 9).

Conclusions

In summary, we have demonstrated a facile route for the synthesis of biphenyls, diphenylacetylene and 2-aryl/alkyl benzofuran derivatives *via* ligand-free Suzuki, Sonogashira coupling reactions using the catalyst Pd/$CuFe_2O_4$ nanowires. The Suzuki cross-coupling reaction furnished the biphenyls with excellent to near quantitative yields. Further, the optimized conditions were applied for Sonogashira coupling followed by the intramolecular nucleophilic attack for the formation benzofurans. It was also demonstrated for the unusual formation arylvinyl ethers *via* nucleophilic attack of the hydroxyl group of phenol onto the triple bond of ethyl propiolate.

Conflicts of interest

There is no conflict of interest.

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