RSC Advances



PAPER

View Article Online
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Cite this: RSC Adv., 2018, 8, 21030

Recyclable Pd/CuFe₂O₄ nanowires: a highly active catalyst for C-C couplings and synthesis of benzofuran derivatives†

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Received 30th April 2018 Accepted 1st June 2018

DOI: 10.1039/c8ra03697g

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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. Unsupported nanocatalysts face problems due to issues related recovery and recyclability from the reaction mixture. 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. 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 CuFe₂O₄ 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/CuFe2O4 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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 $[\]dagger$ Electronic supplementary information (ESI) available: Details of catalyst synthesis, characterization and experimental studies. $^1H,\ ^{13}C\text{-NMR}$ spectra of all isolated products. See DOI: 10.1039/c8ra03697g

Table 1 Comparison of the catalytic activity of Pd/CuFe₂O₄ nanowires with other reported recent catalysts for Suzuki couplings

Entry	Catalyst	Conditions	Yield (%)	Ref.
1	PdO/GO	K ₂ CO ₃ , DMSO, 120 °C, 10 min	88	48
2	Pd-SBT@MCM	K ₂ CO ₃ , PEG, 80 °C, 175 min	96	49
3	GO/Fe ₂ O ₄ /Pd composite	K ₂ CO ₃ , H ₂ O/EtOH, 80 °C, 20 min	95	50
4	Pd@CQD@Fe ₃ O ₄	t-BuOK, EtOH: H ₂ O (1:1), 120 °C, 60 min	95	51
5	Pd/C@Fe ₂ O ₄	K ₂ CO ₃ , H ₂ O, 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 ₃ O ₄ @SiO ₂ -Pd	CaO, H ₂ O/EtOH (1 : 1), 85 °C, 20 min	93	54
8	Pd/Celite-PANI	K ₂ CO ₃ , TBAB (10%), dioxane : H ₂ O (1 : 1), 90 °C, 4 h	94	55
9	Pd/TiO ₂	Na ₂ CO ₃ , NMP : H ₂ O, 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 ₂ O ₄ nanowires	K ₂ CO 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 ₂ CO 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/CuFe₂O₄ (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/CuFe₂O₄ 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/CuFe₂O₄ 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/CuFe₂O₄ 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/CuFe₂O₄ 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/CuFe₂O₄, under standard conditions. Among all, it was observed that the reaction yields were more or less same with \geq 4 mol% of Pd in Pd/CuFe₂O₄ (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, NO₂, OMe, F & Cl) on aromatic ring 1b-j, which reveals a wide functional group tolerance of this reaction. Notably, heteroaromatic iodide 11, gave the products 31b, 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)/CuFe2O4

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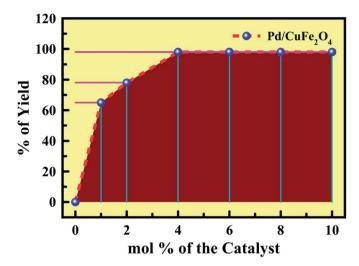


Fig. 1 Optimization of loading the catalyst for Suzuki-coupling reaction.

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/CuFe₂O₄ 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/CuFe₂O₄ 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/CuFe₂O₄ nanowires catalyst is stable enough and can be reused.

The relation between catalytic properties and structure of Pd/CuFe₂O₄ 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 \mathbf{B} , which on coupling with the activated boronic acid derivative \mathbf{C} (produced by reaction of the boronic acid $2\mathbf{a}$ with K_2CO_3 base), gives transmetalation complex \mathbf{D} . Finally, the reductive elimination of D affords the coupled product $3\mathbf{ha}$ 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 4n, under established conditions as above (see; Table 2, entry 1). The reaction was quite successful and furnished the 2-amino diphenylacetylene product 5mn, 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 5mn (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/CuFe₂O₄ 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*-NO₂) 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 NH₂ moiety on pyridine ring (**5ka**, Table 5). To our delight, 2-iodobenzylalcohol

Table 3 Synthesis of biphenyls with aryl iodide and arylboronic $acid^{a,b}$

^a Reaction conditions: aryl iodides (0.25 mmol), arylboronic acid (0.5 mmol), Pd/CuFe₂O₄ (4 mol%), K₂CO₃ (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.

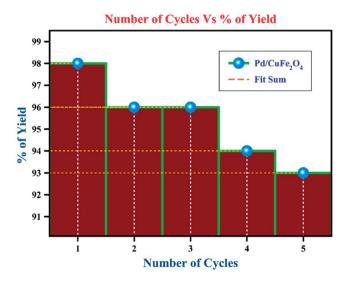


Fig. 2 Recyclability of the catalyst Pd/CuFe₂O₄ nanowires in Suzuki reaction.

Scheme 1 The mechanism for the relation between catalytic properties (Suzuki coupling reaction) and structure of Pd/CuFe₂O₄ nanowires.

2a

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

K2CO3

and selective and gave the product $5\mathbf{jb}$, 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 Au⁷³ and Cu⁷⁴⁻⁷⁶) 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 ₂ CO ₃	DMSO	75	12
2	K ₂ CO ₃	DMF	60	12
3	K ₂ CO ₃	DMA	35	24
4	K ₂ CO ₃	Toluene	<u></u> c	48
5	K_2CO_3	1,4-Dioxane	36	24
6	K_2CO_3	THF	30	24
7	K_2CO_3	CH ₃ CN	32	24
8	Cs_2CO_3	DMSO	55	12
9	КОН	DMSO	48	12

^a Reaction conditions: aryl iodides 1m (0.5 mmol), phenylacetylene 4a (1 mmol), Pd/CuFe₂O₄ (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 $4a-i^{a,b}$

 a Reaction conditions: 2-iodophenols **1n-r** (0.5 mmol), aryl alkynes **4a-i** (0.5 mmol), Pd/CuFe₂O₄ nanowires (4 mol%), K₂CO₃ (1 mmol) and DMSO (1 mL) at 120 $^{\circ}$ C. b Isolated yields of product **7na-ri**.

Table 5 The Pd/CuFe₂O₄ nanowires catalyzed Sonogashira coupling reaction between iodoarenes **1a-q** and phenylacetylene **4a**^{a,b}

	R ¹ + 1	Pd/CuFe ₂ O ₄ (4 m K ₂ CO ₃ , DMSO, 120	°C, 12 h R ¹	igaa-na
5aa (78%, 68%,° 20% ^d)	5fa (85%)	5ga (76%)	5ha (84%, 63%°)
	MeOOC.	MeOOC	O ₂ N	
	5ma (75%)	5ba (68%)	5ca (72%) 5	ida (65%, 60%, ^c 23% ^d)
H₂N	N (69%)	OH CI	Fin (969/)	
	5ka (68%)	5qa (86%)	5ja (86%)	

^a Reaction conditions: aryl iodides **1a-q** (0.5 mmol), phenylacetylene **4a** (1 mmol), Pd/CuFe₂O₄ (4 mol%), K₂CO₃ (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}

Table 8 Screening conditions for the formation of 6nb+6nb' from iodophenol 1n and ethyl propiolate 4b^{a,b}

Entry	Catalyst (Pd/CuFe $_2$ O $_4$)	Base (K ₂ CO ₃)	Solvent (DMSO)	Yield (%)	
				6nb (<i>E</i>)	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/CuFe₂O₄ (4 mol%), K₂CO₃ (1 mmol) and DMSO (1 mL) at 120 °C. ^b Isolated yields of products **6**.

afforded the benzofurans 7**re-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 1**r**. Significantly, 3-hydroxy-2-iodo-4-methoxybenzaldehyde 1**r** coupled with 1,3-diethynylbenzene 4**i**, in which only one acetylene group was reacted and gave 7**ri** 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).

^a Reaction conditions: aryl iodides **1m** & **1n** (0.5 mmol), ethyl propiolate **4b** (1 mmol), Pd/CuFe₂O₄ (4 mol%), K₂CO₃ (1 mmol) and DMSO (1 mL) at 120 °C. ^b Isolated yields of products **6**.

Table 9 Attempting for Sonogashira reaction between iodoarenes and ethyl propiolate ${\sf 4b}^{a,b}$

To further confirm this sort of reactivity, the reaction was explored with different halophenols $(\mathbf{1n}, \mathbf{1o}, \mathbf{1p} \& \mathbf{1q})$ with ethyl propiolate $\mathbf{4b}$, 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 $\mathbf{1q}$ 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/CuFe₂O₄ 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.

Acknowledgements

B. L. Narayana would like to thanks to University Grant Commission (UGC), New Delhi, for awarding Junior & Senior Research Fellowship (JRF & SRF).

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^a Reaction conditions: aryl iodides **1n-q** (0.5 mmol), ethyl propiolate **4b** (1 mmol), Pd/CuFe₂O₄ (4 mol%), K₂CO₃ (1 mmol) and DMSO (1 mL) at 120 °C. ^b Isolated yields of products **6.** ^c Only single *E*-isomer **6qb** was formed.

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