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Cite this: *RSC Adv.*, 2024, **14**, 21269

Recyclable $LaF_3 \cdot Pd$ nanocatalyst in Suzuki coupling: green synthesis of biaryls from haloarenes and phenylboronic acids†‡

Smitabala Panda,§ Sagarika Patra,§ Swadhin Swaraj Acharya, Ganngam Phaomei* and Bibhuti Bhusan Parida*

Received 26th January 2024
Accepted 13th June 2024

DOI: 10.1039/d4ra00686k

rsc.li/rsc-advances

Herein we prepared the novel $LaF_3 \cdot Pd$ nanocatalyst characterized by XRD and TEM analysis. The nanocatalyst was applied in Suzuki coupling reaction for the synthesis of biaryls in aqueous medium from readily available aryl halides (bromides and iodides) and substituted phenylboronic acids in the presence of K_2CO_3 as the base at 70 °C. The present method is capable of giving the C–C coupled product in good to excellent yields (up to 97%). The reactions were conducted under green conditions in aqueous medium and the nanocatalyst used in this study was recyclable. The recyclability and reusability of the catalyst was checked for seven consecutive cycles without significant loss in reactivity.

Introduction

$C(sp^2)$–$C(sp^2)$ bond forming reactions[1] are very important strategies to construct complex scaffolds in natural products,[2] drug discovery, medicinal chemistry,[2b] functional materials, *etc.* Various transition metals have been used extensively in many reactions *i.e.*, C–H activations,[3] cross-coupling reactions, *etc.* to construct C–C bonds having moderate to complex motifs in many usual organic transformations. Palladium-catalyzed coupling reactions play a very important role in organic synthesis. The 2010 Nobel prize in chemistry supports the popularity, success, and importance of this field.[4] Among all, the Suzuki coupling reaction is one of the most celebrated and frequently encountered reactions in the laboratory as well as industry for the construction of C–C bonds to synthesize biaryls.[5] Biaryl-containing scaffolds as a backbone constitute a subunit in many organic frameworks, and are widely distributed in many natural products,[6] functional materials, catalysts-ligands,[7] pharmaceuticals and drugs,[8] agrochemicals,[9] *etc.* (Fig. 1). The biaryl-based scaffolds have been documented to exhibit a broad range of biological activities.[10]

Discovering greener approaches in organic synthesis is always a challenge to organic chemists. The demand for developing green and sustainable methods has been increasing in recent years. In this context, the use of green energy, solvents, one-pot processes with minimal waste production with high atom and step-economy, and the use of recyclable nanocatalysts are considered to be the better alternatives.[5e] In the literature the Suzuki coupling is well documented with the combination of various homogeneous catalysts and ligands, which also comes with some limitations such as expensive ligands, additional steps for ligand synthesis, metal contamination in the products, metal leaching.[5d] In recent years, transition metal-derived nanocatalysts have received a great deal of attention from synthetic chemists because of their high activity, and sustainable aspects as compared to homogeneous catalysts. They are frequently used in organic synthesis.[11] In this backdrop, the Pd-based nanoparticles proved to be an excellent candidate in the coupling reaction for the formation of C–C bonds. Several coupling reactions such as Suzuki–Miyaura, Heck and Sonogashira reactions have been successfully conducted in the presence of Pd-nanocatalysts.[12]

The lanthanide-based nanoparticles (LNPs)[13–15] are widely known for their optical properties and they find applications in bioimaging, optical sensing, image-guided therapy, biosensing, and optogenetics. Apart from biological applications, the LNPs have been utilized as efficient catalysts in organic synthesis.[16–18] Therefore, in continuation of our research interest in lanthanide-based nanoparticles and C–C bond forming methodology development,[19] we are interested in utilizing the LNP $(LaF_3 \cdot Pd)_3$ as a catalyst to carry out Suzuki coupling reactions and to our delight the LNP showed good catalytic activity and it was recovered from the reaction system and reused up to seven consecutive runs without significant loss of reactivity.

Department of Chemistry, Berhampur University, Bhanja Bihar-760007, Odisha, India. E-mail: bbp.chem@buodisha.edu.in

† The manuscript is dedicated to 70th Birth Anniversary of Prof. Satyaban Jena (Former Professor, Department of Chemistry, Utkal University, Odisha).

‡ Electronic supplementary information (ESI) available. See DOI: **https://doi.org/10.1039/d4ra00686k**

§ Equal contribution in the work.

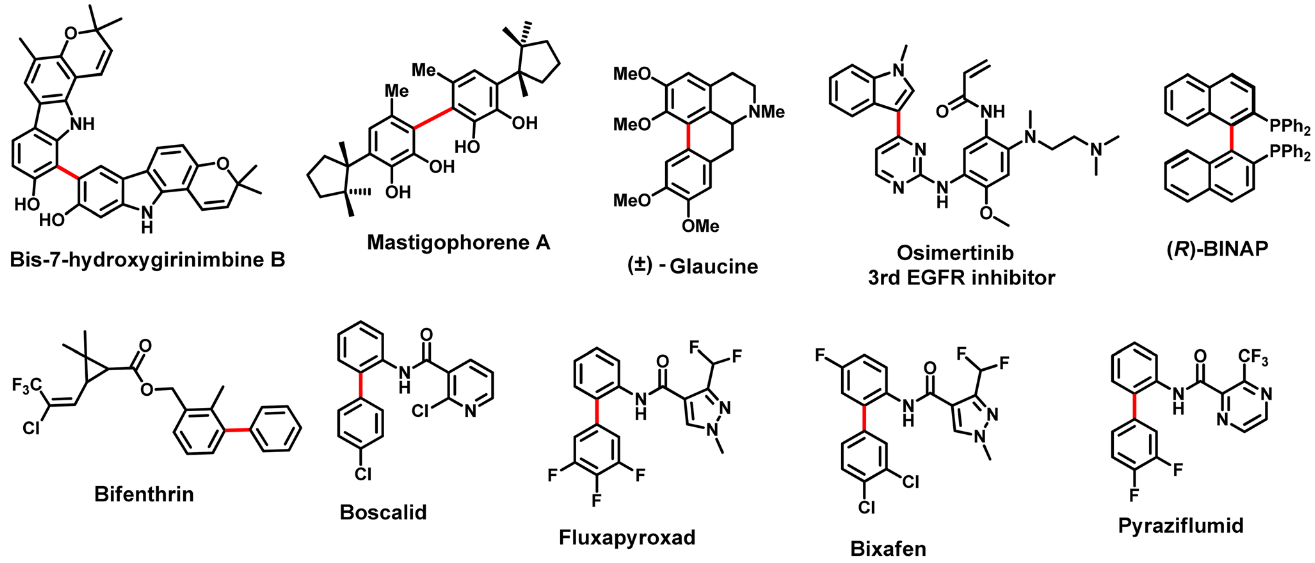


Fig. 1 Representative examples of biaryls in naturally occurring molecules, catalysts, drugs, and agrochemicals with biaryl scaffolds.

Results and discussion

Synthesis and characterization of $LaF_3 \cdot Pd$ nanocatalyst

The La–Pd bimetallic nanoparticles were prepared from the reaction of La_2O_3, $Pd(OAC)_2$, and NH_4F in the presence of 50% NH_4OH at 120 °C in autoclave as displayed in Scheme 1.

XRD study

XRD patterns of synthesized $LaF_3 \cdot Pd$ is shown in Fig. 2. From the diffraction pattern it is obvious that the nanoparticles are highly crystalline and the diffraction peaks correspond to that of pure LaF_3 hexagonal system (JCPDS No. 076-0510). The lattice parameters, cell volume and particle size calculated using Scherrer equation are given in the Table 1. The peaks from other phases were not detected in the as-prepared sample indicating that the as-prepared sample is pure. However the nanoparticles after used as catalyst some new peaks are appeared (marked with asterisk) indicating changes in the LaF_3 nanoparticles. This change may be due to the formation of some LaF_3 to $LaFCO_3$ nanoparticle (JCPDS-074-0985) since K_2CO_3 is used in the reaction.

TEM image

The TEM image (Fig. 3b) of $LaF_3 \cdot Pd$ nanoparticles reveal that particles are spherical in shape with a diameter maximum about 8 nm (Fig. 3d). The high magnification TEM image (Fig. 3a) shows the lattice fringes of the nanoparticles corresponding to the lattice fringes (100) and (101) plane of hexagonal Lanthanum fluoride (JCPDS No. 076-0510). The lattice planes are also assigned in the SAED pattern Fig. 3c corresponding to the (100), (101), (110) and (112) plane. The lattice fringes in the HRTEM and SAED pattern indicated the well crystallinity of the particles.

$$La_2O_3 + Pd(OAc)_2 + NH_4F \xrightarrow[120\ ^{o}C,\ overnight]{50\%\ NH_4OH} LaF_3.Pd\ 5\%\ nanoparticles$$

Scheme 1 Preparation of the $LaF_3 \cdot Pd$ 5 at % nanoparticles.

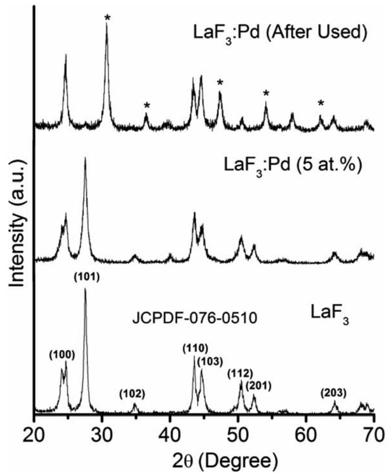


Fig. 2 XRD pattern of $LaF_3 \cdot Pd$.

Table 1 The lattice parameters, cell volume and particle size of $LaF_3 \cdot Pd$

	a (Å)	b (Å)	c (Å)	Cell volume	Particle size
JCPDF-076-0510	4.148	4.148	7.354	109.58	
LaF_3	4.157	4.157	7.352	110.06	17.05
LaF_3:Pd	4.150	4.150	7.360	109.78	11.50
LaF_3:Pd (after used)	4.161	4.161	7.350	110.21	14.17

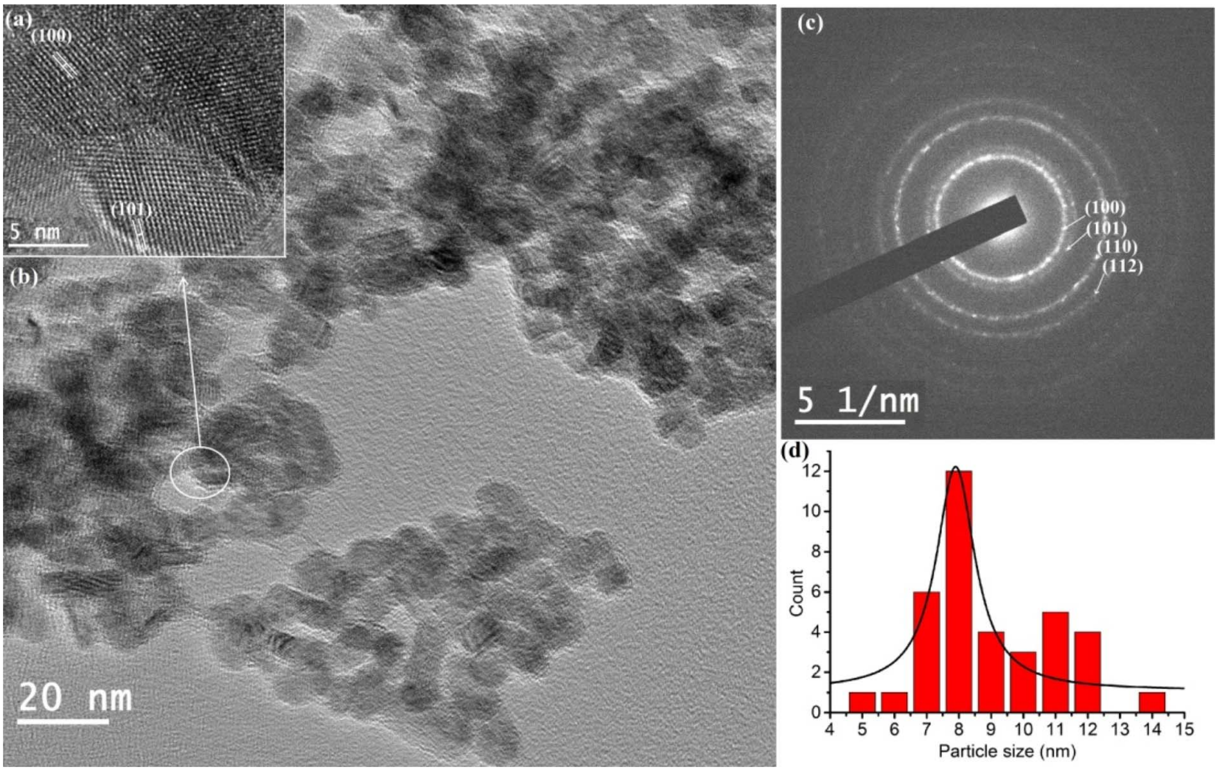


Fig. 3 (a) HRTEM image (b) TEM image (c) SAED pattern (d) histogram of particle size of $LaF_3 \cdot Pd$.

Palladium doped LaF_3 nanoparticles for catalysis

From the X-ray photoelectron spectroscopy (XPS) spectrum in the Fig. 4a and b it clearly indicates the presence of La and Pd ions in the prepared nanoparticles. The La 3d binding energy around 853 and 837 eV of La $3d_{3/2}$ and La $3d_{5/2}$ respectively. From the Pd 3d scan the existence of metallic Pd(0) and Pd(II) is also confirmed where the binding energies of $3d_{5/2}$ are 336 eV, 337 eV and for that of $3d_{3/2}$ are 342 eV, 343 eV respectively. The PP at% are found to be La $3d_{5/2} = 0.37$ at%, F 1s = 1.8 at%, Pd $3d_{3/2} = 0.09$ and Pd $3d_{5/2} = 0.06$ at% (Fig. 4).

Optimization of reaction condition using the $LaF_3 \cdot Pd$ nanocatalyst

With the LNP ($LaF_3 \cdot Pd$) in hand, we were interested in exploring the catalytic efficiency of the LNP in Suzuki coupling. With this objective, we commenced the optimization study for the Suzuki coupling reaction by taking 4-bromophenol **1f** (1.0 mmol), and phenylboronic acid **2a** (1.5 mmol) as the standard substrates in the presence of 40 mg of the catalyst, in the presence of NaOH in aqueous medium under room temperature, pleasingly **3f** was isolated in 81% yield (entry 1, Table 2).

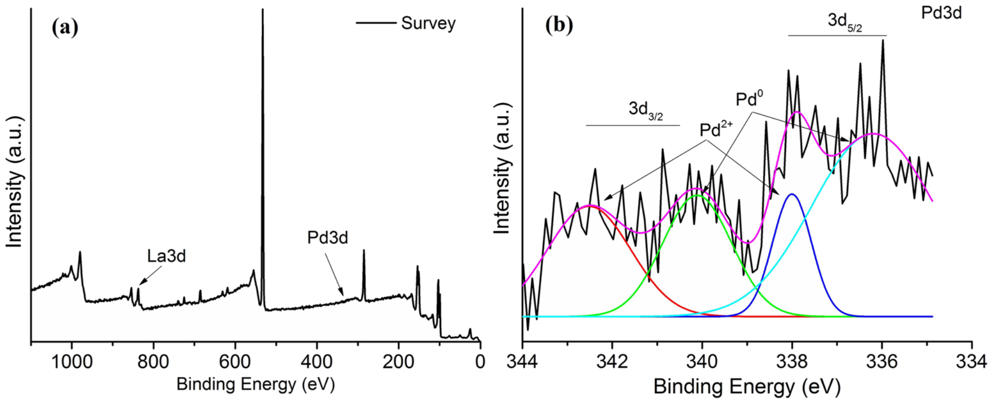
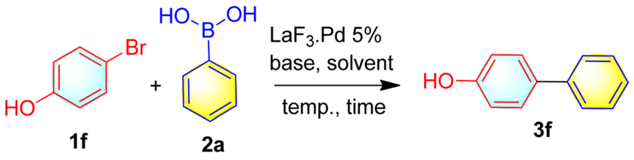


Fig. 4 (a) X-ray photoelectron spectroscopy spectra (b) magnified XPS of $LaF_3 \cdot Pd$.

Table 2 Optimization Table with **1f**



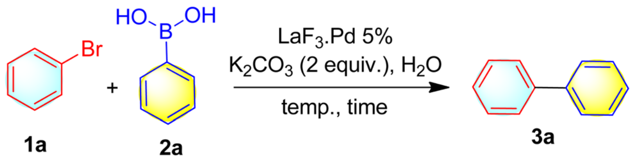
Entry	Catalyst loading (mg)	Base (equiv.)	Solvent	Temperature (°C)	Time (hours)	Yield^{a,b} (%)
1	40	NaOH (2)	H_2O	RT	1	81
2	40	KOH (2)	H_2O	RT	1	83
3	40	K_2CO_3 (2)	H_2O	RT	1	97
4	40	Na_2CO_3 (2)	H_2O	RT	1	82
5	40	Et_3N (2)	H_2O	RT	1	84
6	30	K_2CO_3 (2)	H_2O	RT	1	97
7	20	K_2CO_3 (2)	H_2O	RT	1	97
8	**15**	**K_2CO_3 (2)**	**H_2O**	**RT**	**1**	**97**
9	15	K_2CO_3 (2)	Dioxane	RT	1	90
10	15	K_2CO_3 (2)	DMSO	RT	1	81
11	15	K_2CO_3 (2)	DMF	RT	1	79

[a] Reaction conditions: **1f** (1 mmol), **2a** (1.5 mmol) in 3 mL of solvent. [b] Isolated yield.

The structure of **3f** was characterized by recording ^{1}H and ^{13}C NMR spectra. Then by keeping all the parameters same and varying the base such as KOH, K_2CO_3, Na_2CO_3, and Et_3N the product **3f** was isolated in 83%, 97%, 82%, and 84% yields respectively (entries 2–5, Table 2). From the screening of the bases the K_2CO_3 was found as the best choice. Next, to check the optimum amount of catalyst by keeping all the parameters the same and varying the catalyst loading, the amount of catalyst was decreased gradually from 30 mg to 15 mg and found that 15 mg is the optimum amount of catalyst needed for the current study (entries 6–8, Table 2). Then we turned our attention to check whether any other solvent can be employed to get enhanced yield and with less reaction time. So various solvents such as dioxane, DMSO, and DMF were screened by keeping the catalyst loading 15 mg and all other parameters constant (entries 9–11, Table 2), and found that no solvent gives better results than H_2O. With this optimum condition for **3f** (15 mg catalyst, H_2O, K_2CO_3, RT for 1 hour), we turned our attention to study the substrate scope. Surprisingly, the optimum condition is not suitable for **3a** (entry 1, Table 3).

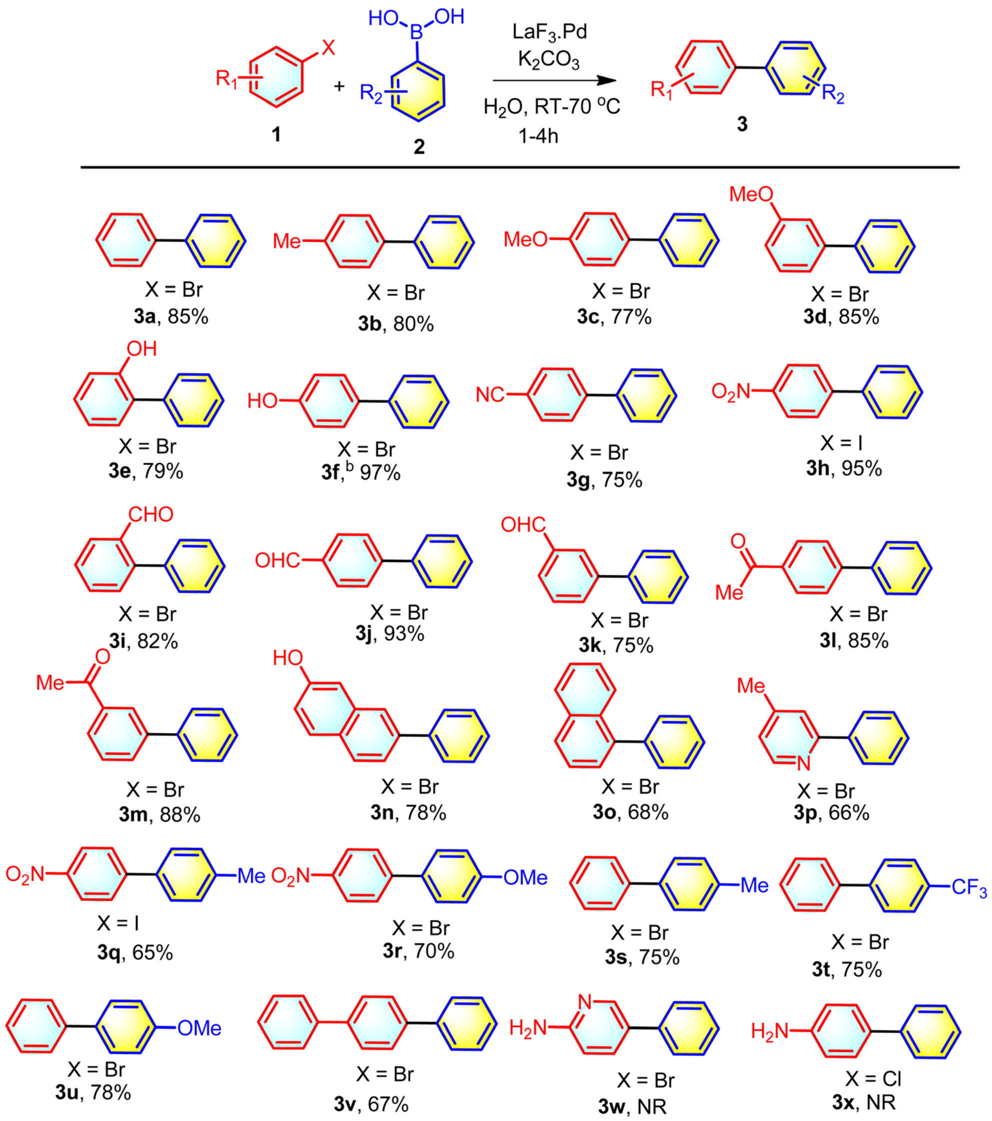
Therefore, optimum conditions were further investigated by taking bromobenzene **1a**, and **2a**. Under the study, the base, catalyst loading, and the solvent were kept constant, and increased the temperature from 50–100 °C (entries 1–5, Table 3). At 50 °C, the product **3a** was isolated in 62% yield (entry 2, Table 3). Then with increase in temperature to 70 °C **3a** was isolated in 85% yield (entry 3, Table 3) and further increase in temperature up to 100 °C improved the product yield further

Table 3 Optimization table with **1a**



Entry	Catalyst loading (mg)	Base (equiv.)	Solvent	Temperature (°C)	Time (hours)	Yield^{a,b} (%)
1	15	K_2CO_3 (2)	H_2O	RT	40	8
2	15	K_2CO_3 (2)	H_2O	50	4	62
3	**15**	**K_2CO_3 (2)**	**H_2O**	**70**	**4**	**85**
4	15	K_2CO_3 (2)	H_2O	80	4	85
5	15	K_2CO_3 (2)	H_2O	100	4	85

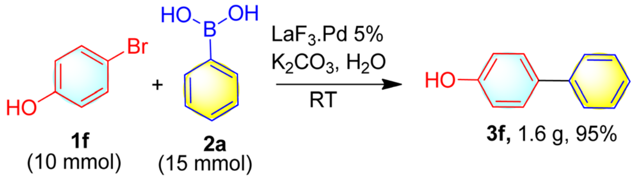
[a] Reaction conditions: **1a** (1 mmol), **2a** (1.5 mmol) in 3 mL of solvent. [b] Isolated yield.



Scheme 2 Substrate scope for the $LaF_3 \cdot Pd$ nanocatalyzed synthesis of biaryls. [a]Reaction conditions: **1** (1.0 mmol), **2** (1.5 mmol), $LaF_3 \cdot Pd$ (15 mg), K_2CO_3 (2.0 mmol) and H_2O (3.0 mL) were added in a 10 mL round-bottom flask and fitted with reflux condenser. The reaction mixture was stirred vigorously at 70 °C until the completion of the reaction (by TLC monitoring). [b]In case of **3f** the reaction was performed at room temperature. NR: no reaction.

(entries 4 and 5, Table 3). Thus, 70 °C was found to be optimum temperature for the reaction (entry 3, Table 3). To our delight, this optimum condition worked well for all the substrates under the study.

Then, to check the electronic and steric effect, at first the bromobenzenes with electron donating substituents 1-bromo-4-methylbenzene **1b** was reacted with **2a** at 70 °C and 80% yield of the product was observed. Next, bromobenzene with 4-OMe and 3-OMe substituent were reacted with phenylboronic acid **2a** and pleasingly the corresponding products **3c** and **3d** were



Scheme 3 Gram scale synthesis of **3f**.

Table 4 Recyclability of the catalyst and the isolated yields

No. of runs	Catalyst used	Catalyst recovered	Yields (%)
1st run	30 mg	28 mg	84
2nd run	28 mg	27 mg	85
3rd run	27 mg	25 mg	83
4th run	25 mg	24 mg	84
5th run	24 mg	22 mg	83
6th run	22 mg	21 mg	82
7th run	21 mg	19 mg	82

Table 5 Comparison of recently reported works with the present work

Sl. no	Catalyst	Reaction condition	Time	Yield	Ref.
1	Nano-Fe_3O_4@CA-Pd	K_2CO_3, EtOH : H_2O, 75 °C	25 min	Trace-98%	20
2	Fe_3O_4@SiO_2–NHC–Pd(II) NPs	K_2CO_3, H_2O, 60 °C	1–16 h	69–97%	21
3	5%Pd/TiO_2, anatase type	Cs_2CO_3, DMA, 80 °C, under Ar, sealed, 1000 rpm	24 h	42–98%	22
4	Fe_3O_4@SiO_2-NMIM-Pd	K_2CO_3, EtOH, 80 °C	1.5–5 h	27–97%	23
5	Ni-TC@ASMNP	K_3PO_4, dioxane, PPh_3, 100 °C	10–15 h	75–97%	24
8	Pd NPs@APC	K_2CO_3, solvent-free, microwave	5 min	52–99%	25
9	Fe_3O_4@SiO_2–Pd	CaO, EtOH : H_2O (1 : 1), 85 °C	20–70 min	87–96%	26
10	Fe_3O_4@NC/Pd	KOH, H_2O, 90 °C	0.5 h	53–99%	27
11	ZrO_2@$AEPH_2$-PPh_2-Pd(0)	K_2CO_3, H_2O, 80 °C	20 min–24 h	Trace-95%	28
12	Fe_3O_4@boehmite-NH_2-Co^{II} NPs	KOH, H_2O, 80 °C	25 min–9 h	15–95%	29
13	Cu–ninhydrin@GO–Ni MNPs	Na_2CO_3, H_2O, 80 °C	50 min–7 h	89–97%	30
14	Pd/$CuFe_2O_4$ nanowires	K_2CO_3, DMSO, 100 °C	10 min–12 h	27–99%	31
15	Pd-SBT@MCM-41	PEG-400, 80 °C	1–5 h	87–98%	32
16	Pd@CQD@Fe_3O_4 NPs	*t*-BuOK, EtOH : H_2O (1 : 1) 60–120 °C	2–24 h	88–100%	33
17	Pd@4PVP	K_3PO_4, EtOH/H_2O (3 : 1) 80 °C	3–18 h	29–99%	34
18	**$LaF_3\cdot$Pd nanocatalyst**	**K_2CO_3, H_2O, RT-70 °C**	**1–4 h**	**66–97%**	**This work**

isolated in 77% and 85% yields. Next, the 2-OH and 4-OH substituted bromobenzene were reacted with **2a**. The respective biaryls **3e** and **3f** were isolated in 79% and 97% yields. Then the haloarenes with various electron withdrawing groups were tested. 4-CN substituted bromobenzene gave 75% yield of the corresponding biaryl **3g**. Iodobenzene with 4-NO_2 substitution resulted the corresponding biaryl **3h** in 95% yield. Other electron withdrawing groups on the bromobenzene such as 2-CHO, 4-CHO, 3-CHO, 4-C(O)Me. 3-C(O)Me were also capable of resulting the corresponding biphenyls **3i**, **3j**, **3k**, **3l**, **3m** in 82%, 93%, 75%, 85%, 88% yields respectively. Next, the fused biphenyls were also screened for synthesizing the biaryl systems. For this, 7-bromonaphthalen-2-ol and 1-bromonaphthalene were subjected to react with **2a**. Pleasingle the corresponding fused aromatics based biaryls **3n** and **3o** were isolated in good yields (78% and 68% respectively). The heteroaromatic systems are important candidates in drug discovery, thus to check whether the present method can be applied for coupling with heteroaromatic halides, a reaction was performed between 2-bromo-4-methylpyridine and **2a**. The corresponding coupled product **3p** was isolated in 66% yield. After checking the substrate scope of haloarenes, we then turned our attention to check the substrate scope for the substituted phenylboronic acid. For that We have reacted 4-nitroiodobenzene with the phenylboronic acid with 4-Me and 4-OMe substitution and the expected coupled products **3q** and **3r** were obtained in 65% and 70% yield. Then, bromobenzene was reacted with the phenylboronic acid with 4-Me, 4-CF_3 and 4-OMe substitutions and the respective coupled products **3s**, **3t** and **3u** were isolated in 75%, 75% and 78% yields respectively. Next, 4-bromo-1,1′-biphenyl was reacted with **2a** and pleasingly the coupled product 1,1′:4′,1″-terphenyl **3v** was isolated in 67% yield. Apart from the bromo and iodobenzene derivatives, we have also studied the scope of chloro aromatic and heteroaromatics. The 2-amino-5-chloropyridine and 4-chloroaniline were subjected to react with phenylboronic acid **2a** in the developed reaction condition. But the coupled product **3w** and **3x** were not formed (Scheme 2).

Scale-up experiment

To further check, whether the present method can be applied to synthesize the biaryls in large scale, a reaction was performed by taking the 4-bromophenol **1f** (10 mmol), phenylboronic acid **2a** (15 mmol) at room temperature. To our delight, the corresponding biaryl **3f** was isolated in 95% yield (1.6 g) (Scheme 3).

Recyclability test

The nanocatalysts in recent years are becoming popular for their recyclability up to several cycles. Also owing to easy to handle, sustainable and green aspect, they are becoming popular in industries. Thus to check whether the present nanocatalyst $LaF_3\cdot$Pd can be recycled and reused, the reaction was performed by taking **1a** (2.0 mmol) and **2a** (3.0 mmol) in the presence of 30 mg of the catalyst under the optimized reaction condition. After completion of the reaction, the catalyst was recovered by centrifuge and dried and further utilized in the synthesis of **3a**. Pleasingly, the catalyst was recovered and reused for seven consecutive cycles without significant loss in the catalytic activity and the product yield (Table 4).

Comparison

The nanocatalyzed Suzuki reaction is getting attention from synthetic chemists owing to its green aspects such as reusability. In this regard, there are many reports frequently published on the nanocatalyzed C–C bond formation by Suzuki coupling. Thus, to check the efficacy of our catalyst $LaF_3\cdot$Pd with the recent reported literature, we summarized the results of various nanocatalyzed Suzuki reactions with the present work (Table 5).[20–34] It is clear from the table that the present catalyst is efficient enough for the synthesis of biaryls in terms of product yield and reaction time and also this can be recycled and reused.

Conclusion

To summarize, we synthesized the $LaF_3\cdot$Pd 5% nanocatalyst and characterized by XRD and TEM analysis. To check the catalytic efficiency of the synthesized nanocatalyst, we applied the nanocatalyst for the synthesis of biaryls *via* Suzuki coupling in the aqueous medium, a greener condition. To our delight, the catalyst is efficient enough to result the products in good to excellent yields within 1–4 hours. Also, the catalyst was recycled from the reaction medium and reused for seven consecutive runs without any significant decrease in the catalytic activity and product yield. This green and sustainable aspect of the present method meets the requirement of industrial applications. Thus, we believe the present report will be a valuable addition to the green and sustainable methodologies in synthetic organic transformation.

Data availability

The data that support the finding of the present study are available in ESI‡ of this article.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

B. B. P. is thankful to SERB (SRG/2019/002032), New Delhi, S&T Department Project-Odisha (ST-SCST-0061/2018/2724), UGC (F. 30-484/2019) (BSR) and G. P. is thankful to OURIIP-Odisha for funding. S. S. A. is thankful to CSIR India for junior research fellowship. The authors are grateful to Berhampur University for infrastructure. We acknowledge IISER Berhampur for NMR and sample characterization facilities. The authors are thankful to Alisha Rani Tripathy and Akash Bisoyi of IISER Thiruvananthapuram for their timely help.

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