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Recyclable $\text{LaF}_3 \cdot \text{Pd}$ nanocatalyst in Suzuki coupling: green synthesis of biaryls from haloarenes and phenylboronic acids†‡

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Herein we prepared the novel $\text{LaF}_3 \cdot \text{Pd}$ 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.

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Introduction

$\text{C}(\text{sp}^2)\text{--C}(\text{sp}^2)$ bond forming reactions¹ 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 ($\text{LaF}_3 \cdot \text{Pd}$)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.

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§ Equal contribution in the work.



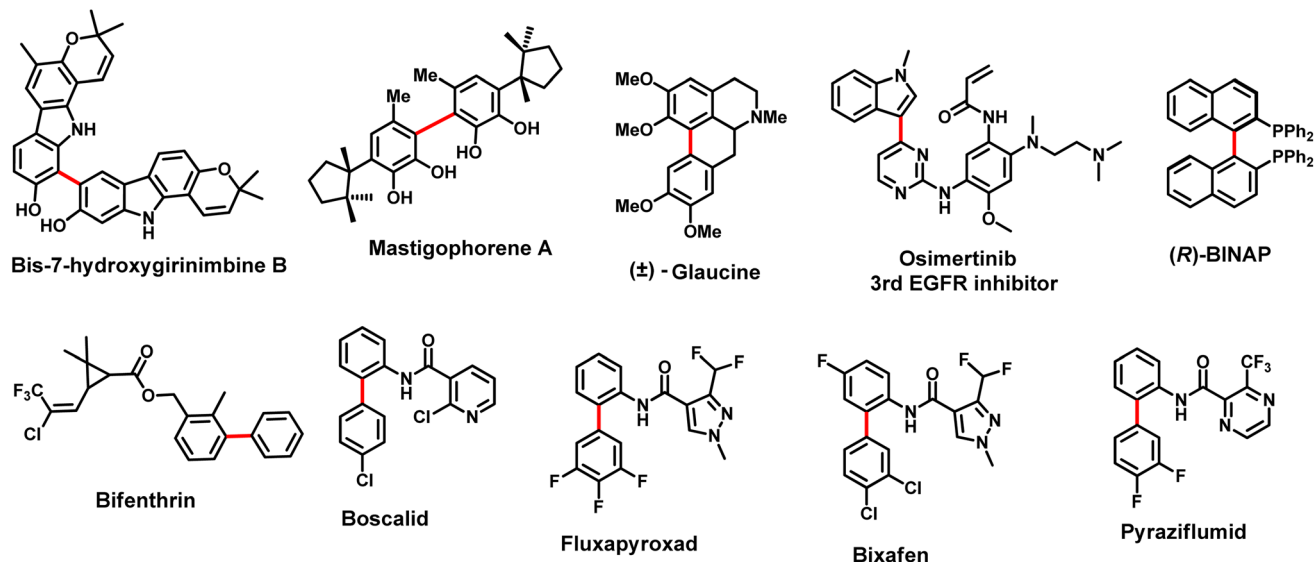


Fig. 1 Representative examples of biaryl in naturally occurring molecules, catalysts, drugs, and agrochemicals with biaryl scaffolds.

Results and discussion

Synthesis and characterization of $\text{LaF}_3 \cdot \text{Pd}$ nanocatalyst

The La-Pd bimetallic nanoparticles were prepared from the reaction of La_2O_3 , $\text{Pd}(\text{OAc})_2$, 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 $\text{LaF}_3 \cdot \text{Pd}$ 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 $\text{LaF}_3 \cdot \text{Pd}$ 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.

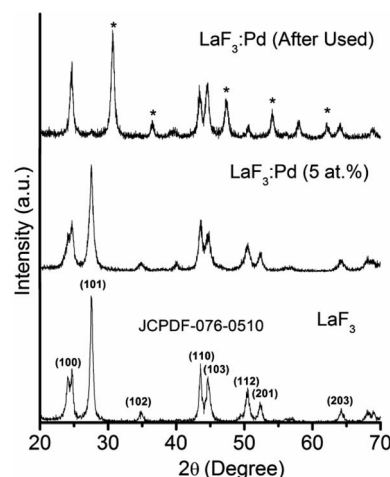
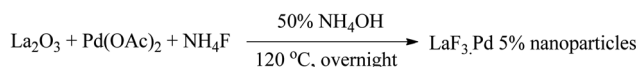


Fig. 2 XRD pattern of $\text{LaF}_3 \cdot \text{Pd}$.

Table 1 The lattice parameters, cell volume and particle size of $\text{LaF}_3 \cdot \text{Pd}$

| | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (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 |
| $\text{LaF}_3 \cdot \text{Pd}$ | 4.150 | 4.150 | 7.360 | 109.78 | 11.50 |
| $\text{LaF}_3 \cdot \text{Pd}$ (after used) | 4.161 | 4.161 | 7.350 | 110.21 | 14.17 |



Scheme 1 Preparation of the $\text{LaF}_3 \cdot \text{Pd}$ 5 at % nanoparticles.



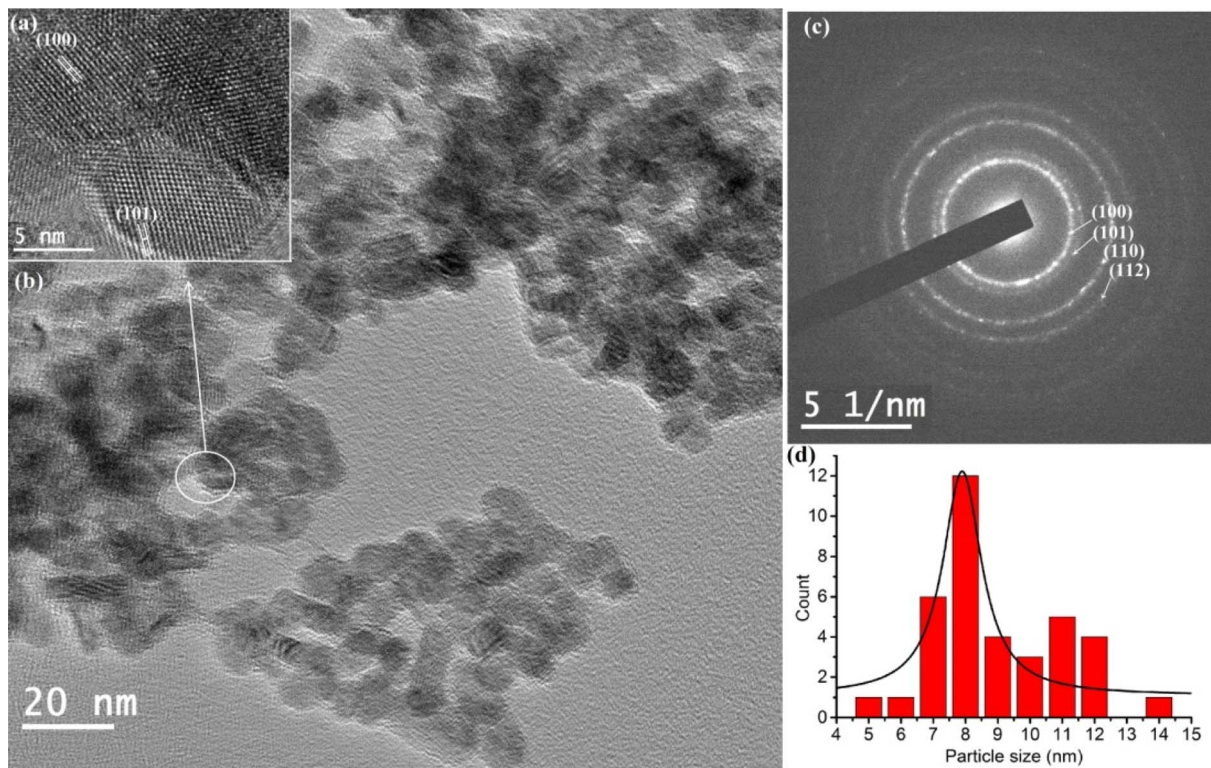


Fig. 3 (a) HRTEM image (b) TEM image (c) SAED pattern (d) histogram of particle size of $\text{LaF}_3 \cdot \text{Pd}$.

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 $\text{LaF}_3 \cdot \text{Pd}$ nanocatalyst

With the LNP ($\text{LaF}_3 \cdot \text{Pd}$) 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).

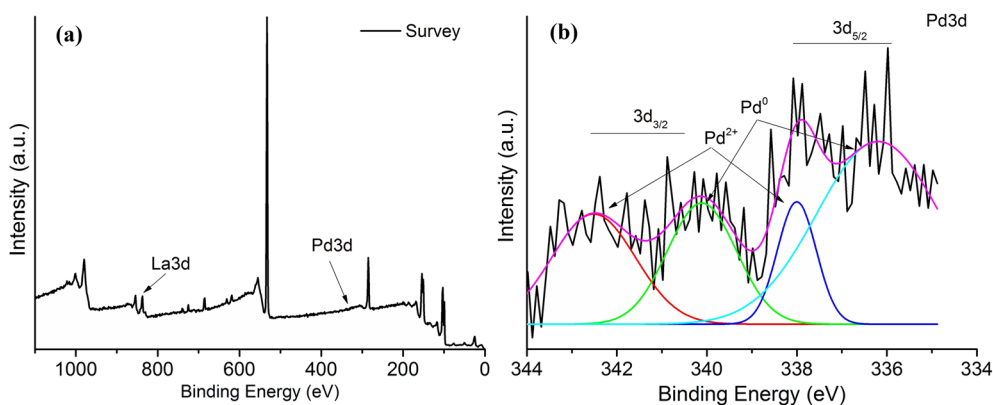
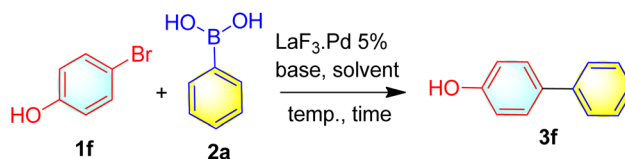


Fig. 4 (a) X-ray photoelectron spectroscopy spectra (b) magnified XPS of $\text{LaF}_3 \cdot \text{Pd}$.

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 ₂ O | RT | 1 | 81 |
| 2 | 40 | KOH (2) | H ₂ O | RT | 1 | 83 |
| 3 | 40 | K ₂ CO ₃ (2) | H ₂ O | RT | 1 | 97 |
| 4 | 40 | Na ₂ CO ₃ (2) | H ₂ O | RT | 1 | 82 |
| 5 | 40 | Et ₃ N (2) | H ₂ O | RT | 1 | 84 |
| 6 | 30 | K ₂ CO ₃ (2) | H ₂ O | RT | 1 | 97 |
| 7 | 20 | K ₂ CO ₃ (2) | H ₂ O | RT | 1 | 97 |
| 8 | 15 | K ₂ CO ₃ (2) | H ₂ O | RT | 1 | 97 |
| 9 | 15 | K ₂ CO ₃ (2) | Dioxane | RT | 1 | 90 |
| 10 | 15 | K ₂ CO ₃ (2) | DMSO | RT | 1 | 81 |
| 11 | 15 | K ₂ CO ₃ (2) | DMF | RT | 1 | 79 |

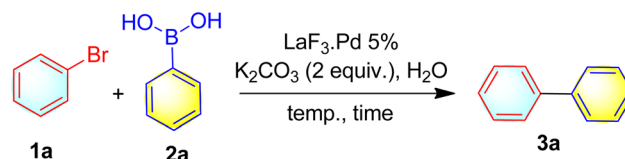
^a Reaction conditions: **1f** (1 mmol), **2a** (1.5 mmol) in 3 mL of solvent. ^b Isolated yield.

The structure of **3f** was characterized by recording ¹H and ¹³C NMR spectra. Then by keeping all the parameters same and varying the base such as KOH, K₂CO₃, Na₂CO₃, and Et₃N 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 K₂CO₃ 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 H₂O. With this optimum condition for **3f** (15 mg catalyst, H₂O, K₂CO₃, 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

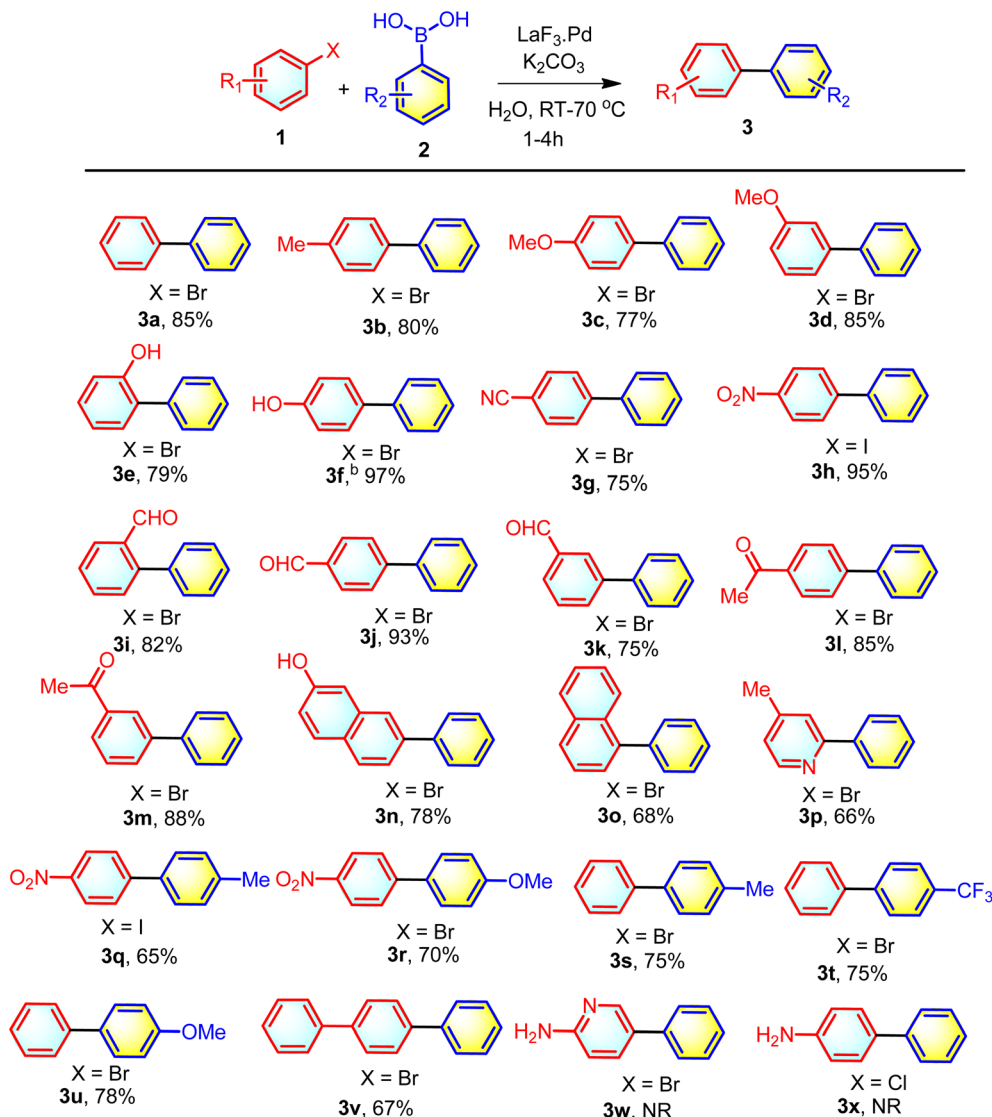
Table 3 Optimization table with 1a



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

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



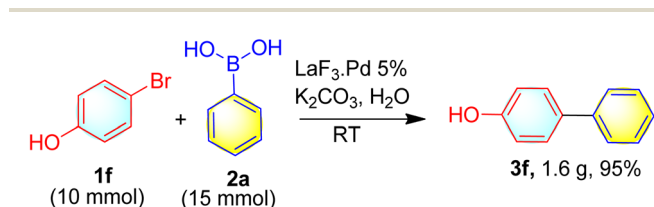


Scheme 2 Substrate scope for the $\text{LaF}_3 \cdot \text{Pd}$ nanocatalyzed synthesis of biaryls. ^aReaction conditions: **1** (1.0 mmol), **2** (1.5 mmol), $\text{LaF}_3 \cdot \text{Pd}$ (15 mg), K_2CO_3 (2.0 mmol) and H_2O (3.0 mL) were added in a 10 mL round-bottom flask and fitted with reflux condenser. The reaction mixture was stirred vigorously at 70 °C until the completion of the reaction (by TLC monitoring). ^bIn 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 ₃ O ₄ @CA-Pd | K ₂ CO ₃ , EtOH : H ₂ O, 75 °C | 25 min | Trace-98% | 20 |
| 2 | Fe ₃ O ₄ @SiO ₂ -NHC-Pd(II) NPs | K ₂ CO ₃ , H ₂ O, 60 °C | 1–16 h | 69–97% | 21 |
| 3 | 5%Pd/TiO ₂ , anatase type | Cs ₂ CO ₃ , DMA, 80 °C, under Ar, sealed, 1000 rpm | 24 h | 42–98% | 22 |
| 4 | Fe ₃ O ₄ @SiO ₂ -NMIM-Pd | K ₂ CO ₃ , EtOH, 80 °C | 1.5–5 h | 27–97% | 23 |
| 5 | Ni-TC@ASMNP | K ₃ PO ₄ , dioxane, PPh ₃ , 100 °C | 10–15 h | 75–97% | 24 |
| 8 | Pd NPs@APC | K ₂ CO ₃ , solvent-free, microwave | 5 min | 52–99% | 25 |
| 9 | Fe ₃ O ₄ @SiO ₂ -Pd | CaO, EtOH : H ₂ O (1 : 1), 85 °C | 20–70 min | 87–96% | 26 |
| 10 | Fe ₃ O ₄ @NC/Pd | KOH, H ₂ O, 90 °C | 0.5 h | 53–99% | 27 |
| 11 | ZrO ₂ @AEPH ₂ -PPh ₂ -Pd(0) | K ₂ CO ₃ , H ₂ O, 80 °C | 20 min–24 h | Trace-95% | 28 |
| 12 | Fe ₃ O ₄ @boehmite-NH ₂ -Co ^{II} NPs | KOH, H ₂ O, 80 °C | 25 min–9 h | 15–95% | 29 |
| 13 | Cu-ninhydrin@GO-Ni MNPs | Na ₂ CO ₃ , H ₂ O, 80 °C | 50 min–7 h | 89–97% | 30 |
| 14 | Pd/CuFe ₂ O ₄ nanowires | K ₂ CO 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 ₃ O ₄ NPs | <i>t</i> -BuOK, EtOH : H ₂ O (1 : 1) 60–120 °C | 2–24 h | 88–100% | 33 |
| 17 | Pd@4PVP | K ₃ PO ₄ , EtOH/H ₂ O (3 : 1) 80 °C | 3–18 h | 29–99% | 34 |
| 18 | LaF ₃ ·Pd nanocatalyst | K ₂ CO ₃ , H ₂ O, 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-NO₂ 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**. Pleasingly 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-CF₃ 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 hetero-aromatics. 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 LaF₃·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 LaF₃·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 LaF₃·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.

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