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## Xantphos-coordinated palladium dithiolates: Highly efficient catalyst for decarboxylative Sonogashira reaction into corresponding alkynes

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This work reports Xantphos-coordinated palladium dithiolate complexes as catalysts for decarboxylative Sonogashira coupling reaction of phenyl propiolic acid and 2-butynoic acid with various iodoarenes. These palladium aryl dithiolate complexes were synthesized and characterized by <sup>1</sup>H and <sup>31</sup>P nuclear magnetic resonance (NMR) spectroscopy, melting point, and elemental analysis (CHNS). Synthetic utility for the reported protocol is explored for the effect of various functional groups on the yield of corresponding heteroaryl alkynes. The current protocol showed excellent catalytic activity towards decarboxylative alkynylation reaction with high turn-over number (TON) up to  $10^5$  and turn-over frequency (TOF) up to  $10^4$  h<sup>-1</sup>. The catalyst could be recycled up to six recycles without losing its catalytic activity. The in situ generation of palladium nanoparticles (PdNPs) was observed after the third recycle, and the amount was significant after the sixth recycle, which were confirmed and characterized by powder X-ray diffraction (XRD), scanning electron microscope (SEM), and energy-dispersive X-ray (EDX) analysis and high-resolution transmission electron microscopy (HR-TEM). The catalytic activity of the reaction is attributed to the formation of PdNPs.

#### K E Y W O R D S

decarboxylative Sonogashira reaction, dithiolate, recyclable, TON and TOF, Xantphos

## **1** | INTRODUCTION

Substituted alkynes are fundamental structural motifs, which serve as versatile building blocks in the synthesis of pharmaceuticals, natural products, agrochemicals, and functional materials.<sup>[1,2]</sup> Over the past three decades, the Sonogashira cross-coupling reaction plays the most efficient and reliable approach for Csp–Csp<sup>2</sup> bond formation in the synthesis of substituted alkynes.<sup>[3,4]</sup> Generally, the catalytic system for these reactions includes phosphine ligated palladium complexes and copper salts as cocatalyst with an excess amount of amine as a base or

solvent. However, the use of copper salts facilitates the Sonogashira reaction. But it leads to the formation of the homocoupling reaction of terminal alkynes through a Cu-mediated Hay/Glaser reaction.<sup>[5]</sup> Furthermore, the presence of an excess amount of amine, either as a base or solvent, is not environmentally friendly.<sup>[6,7]</sup> To surmount the impediments, numerous kinds of Sonogashira reactions have been reported to enhance the protocol's catalytic efficiency involving amine and copper-free systems in the chemical literature.<sup>[8,9]</sup>

Alkynyl carboxylic acids represent a potential candidate for terminal alkynes as they are readily available,

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stable, and easy to handle and store.<sup>[10,11]</sup> Moon and coworkers employed the first decarboxylative Sonogashira coupling methodology between alkynyl carboxylic acids with aryl halides in 2008 by using Pd(dba)<sub>3</sub> catalyst and phosphine ligand.<sup>[12]</sup> Since then, several catalytic systems have been achieved to yield internal alkynes.<sup>[11,13–18]</sup>

The Pd-catalyzed cross-coupling reactions are being known as an attractive and versatile tool for organic transformations. The tolerance of many functionalities present on the substrates under mild reaction conditions, and owing to the facile oxidation state of Pd(0) to Pd(II) or Pd(II) to Pd(IV), palladium became a center of attraction in the group of transition metal catalysts.<sup>[19,20]</sup> Phosphines and their improved systems attracted significant attention in the early development of homogeneous Pd catalysts.<sup>[21,22]</sup> Subsequently, numerous research works initiated to develop palladium complexes based on N-containing ligands, N-heterocyclic carbenes, imines, oximes, and palladacycles have arisen as highly effective catalysts in C–C bond forming reactions (Scheme 1).<sup>[23–26]</sup>

Palladium complexes with S and Se-based ligands are recognized as valuable phosphine-free complexes owing to the family of moisture-insensitive, air-stable, and efficient catalysts.<sup>[27-30]</sup> Similarly to the previous misbelief, sulfur-based ligands are known as catalyst promoters<sup>[31]</sup> rather than acting as catalytic poison.<sup>[32]</sup> Due to the electron-donating property of sulfur and the strong Pd–S bond in palladium thiolate complexes holding improved stability, easier handling and preparation shows better and vigorous catalytic activity than amine, thioether, carbene, selenium-ligand-based complexes.<sup>[33]</sup> Numerous Pd catalysts derived from hybrid thiolate (PS, NS) and carbene-thiolate-based ligands are appreciated in C–C cross-coupling reactions.<sup>[34,35]</sup>

However, thiolate ligands being less explored as to their tendency to form insoluble polymeric complexes. Moreover, with the appropriate design of thiolate moiety and its coligands, soluble discrete molecules of



**SCHEME 1** Decarboxylative coupling

Pd(II) complexes can be constructed. Recently, we have synthesized the supramolecular Pd dithiolate complexes capping with diphosphine ligands wide-bite angles.<sup>[36]</sup> However, owing to the larger bite angle, Xantphoscapped Pd dithiolate complexes exhibited better catalytic activity in Suzuki<sup>[36]</sup> and Heck<sup>[37]</sup> cross-coupling reactions compared with dppe analogue<sup>[38,39]</sup> and offered a high turn-over number (TON). Besides, these stable and highly soluble complexes provided excellent catalytic activity in carbonylative Suzuki-Miyaura reactions<sup>[40,41]</sup> as well as in amino and phenoxycarbonylation.<sup>[42]</sup> However, organochalcogen ligated palladium catalysts have rarely been reported for Csp-Csp<sup>2</sup> cross-coupling reaction.<sup>[43,44]</sup> in particular for decarboxylative Sonogashira cross-coupling reaction.

Encouraged by the above results, we utilized Xantphos-coordinated Pd dithiolate complexes (Scheme 2) as catalysts to explore decarboxylative Sonogashira coupling reactions between alkynyl carboxylic acids and aryl halides with Cu-free conditions. The various reaction parameters were screened to get optimized reaction conditions followed by different aryl halide coupling partners at lower catalyst loading. The comparison between catalytic activity of synthesized macrocycles with conventional Pd catalysts was studied. The reusability of these catalysts, the formation and characterization of palladium nanoparticles (PdNPs), and their active participation have been discussed here. The compositions of catalysts Pd(1) {[Pd(Xantphos)(1,4-SC<sub>6</sub>H<sub>4</sub>SH)]<sub>2</sub>(OTf)<sub>2</sub> (I) and  $[Pd_2(Xantphos)_2(1,4-SC_6H_4S)]_2(OTf)_4$  (II)} and Pd(2)  $[Pd_2(Xantphos)_2(4,4'-SC_{12}H_8S)]_2(OTf)_4$  (II) are shown in Scheme 2.<sup>[36]</sup>

### 2 | EXPERIMENTAL

## 2.1 | Decarboxylative Sonogashira reaction

To the oven-dried round bottom (RB) flask, aryl halide (0.6 mmol), phenyl propiolic acid (0.5 mmol),  $K_2CO_3$  (1.2 equiv), palladium complex (0.1 mol%), and 3 ml of solvent were added, and the content was stirred on an oil bath for 10 h at 100°C. Afterwards, the reaction was cooled. The reaction mixture was diluted with distilled water and solvent ethyl acetate (3 × 15 ml) used to extract the product. The solvent of the extract was evaporated under reduced pressure to obtain a crude product. The purification was carried out by column chromatography (100–200 mesh size, silica gel) using petroleum ether/ethyl acetate as the mobile phase. Then the products were analyzed by GC–MS and <sup>1</sup>H and <sup>13</sup>C nuclear magnetic resonance (NMR) spectroscopy.

**SCHEME 2** Xantphos-coordinated palladium dithiolate complexes applied as catalysts in decarboxylative Sonogashira reaction. <sup>a</sup>Bite angle and flexibility range in parentheses (in degrees), Mane et al.<sup>[36]</sup>



### 2.2 | Catalyst recycling

The recyclability of any catalyst plays a crucial role. Hence, the developed catalyst Pd(2) was evaluated for recyclability with optimal reaction conditions. To the oven-dried 50-ml RB flask, starting materials, catalyst, and later the solvent were added. After completion of the reaction, it was allowed to cool. The solvent was evaporated under vacuum, and the product was extracted in ethyl acetate. The aqueous layer was centrifuged and decanted; the obtained catalyst was washed with distilled water, followed by n-hexane and diethyl ether, and dried. Then it was used for the next consecutive recycle run by charging the flask with starting materials. However, the catalyst could be reused up to the sixth cycle. After the sixth cycle, the black residue obtained was analyzed with powder X-ray diffraction (XRD), scanning electron microscope (SEM), and transmission electron microscopy (TEM) technique.

## 3 | RESULTS AND DISCUSSION

The catalysts Pd(1) and Pd(2) complexes were prepared and analyzed according to the reported method.<sup>[36]</sup> In case of Pd(1) of phenylene-1,4-dithiolate, the complexes I and II exist in equal proportions in the solution, as shown by the <sup>31</sup>P NMR spectrum (Figure S1). However, only complex II exists for the catalyst Pd(2) with 4,4'biphenyldithiolate.

Initially, we performed the reaction between phenyl propiolic acid 1a and iodobenzene 2a to optimize the reaction conditions, and the effects of various parameters such as base, time, temperature, and solvents have been analyzed. The obtained results are shown in Table 1. In the progress of the reaction, solvent plays a crucial role. We have explored the effect of various solvents to get maximum conversion of starting materials on the model reaction. Initially, we have used K<sub>2</sub>CO<sub>3</sub> as a base and Pd(2) catalyst, and the content was heated at 120°C for 12 h with different solvents. The polar aprotic solvents such as acetonitrile (45%), dimethylacetamide (60%), dimethylformamide (78%), and dimethyl sulfoxide (DMSO) (92%) provided good to the excellent conversion of 2a (Table 1, entries 1, 3, 2, and 4, respectively). However, the use of 1,4-dioxane as a solvent provided only 26% of conversion of 2a, and no conversion of starting materials was obtained by using toluene as a solvent (Table 1, entries 6 and 5). Excellent conversion (92%) of 2a was achieved using DMSO as polar aprotic solvent; hence, it was chosen for further optimization studies. A base screening study with organic and inorganic bases revealed that K<sub>2</sub>CO<sub>3</sub> (92%) provided excellent conversion compared with other bases such as Na<sub>2</sub>CO<sub>3</sub> (60%), Et<sub>3</sub>N (46%), DIPEA (15%), and DBU (88%) (Table 1, entries 7-11).

#### TABLE 1 Optimization of reaction parameters for decarboxylative Sonogashira coupling reaction



Entry	Solvent	Base	Time (h)	Temp (°C)	Conversion <sup>a</sup> (%)	Yield <sup>a</sup> (%)
Effect of solvent						
1	ACN	K <sub>2</sub> CO <sub>3</sub>	12	120	45	42
2	DMF	K <sub>2</sub> CO <sub>3</sub>	12	120	78	75
3	DMA	K <sub>2</sub> CO <sub>3</sub>	12	120	60	56
4	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	120	92	90
5	Toluene	K <sub>2</sub> CO <sub>3</sub>	12	120	NR	NR
6	1,4-Dioxane	K <sub>2</sub> CO <sub>3</sub>	12	120	26	23
Effect of base						
7	DMSO	Na <sub>2</sub> CO <sub>3</sub>	12	120	60	57
8	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	120	92	90
9	DMSO	Et <sub>3</sub> N	12	120	46	42
10	DMSO	DIPEA	12	120	15	11
11	DMSO	DBU	12	120	88	86
Effect of temperature						
12	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	60	40	36
13	DMSO	$K_2CO_3$	12	80	76	73
14	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	100	92	90
15	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	120	92	90
Effect of time						
16	DMSO	K <sub>2</sub> CO <sub>3</sub>	6	100	65	62
17	DMSO	K <sub>2</sub> CO <sub>3</sub>	8	100	79	75
18	DMSO	K <sub>2</sub> CO <sub>3</sub>	10	100	92	90
19	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	100	92	90
$20^{\rm b}$	DMSO	K <sub>2</sub> CO <sub>3</sub>	12	100	-	-
21	EtOH	K <sub>2</sub> CO <sub>3</sub>	10	100	65	60
22	MeOH	K <sub>2</sub> CO <sub>3</sub>	10	100	28	25

Note: Reaction condition: 1a (0.5 mmol), 2a (0.6 mmol), base (1.2 equiv), catalyst (0.1 mol%), solvent (3 ml).

<sup>a</sup>Conversion and yield of product determined by GC and product identified by GC–MS.

 $^{b}$ In the absence of Pd(2) catalyst.

Further, the effect of temperature and time was screened on the model reaction using  $K_2CO_3$  as a base and DMSO as a solvent. As we decreased the reaction temperature from  $120^{\circ}C$  to  $100^{\circ}C$ , no considerable

changes were noted in the conversion of **2a** (Table 1, entries 14 and 15). However, further decreasing the reaction temperature from  $100^{\circ}$ C to  $60^{\circ}$ C, the conversion of **2a** was lowered to 40% (Table 1, entries 12 and 14).

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It was found that 100°C is the optimal reaction temperature for maximum conversion. However, when the reaction time was increased from 10 to 12 h, there was no change in the conversion of 2a (Table 1, entries 18 and 19). Thus, based on these results, 10-h duration and 100°C temperature are sufficient to complete the reaction with excellent conversion and hence, the yield of the product. Further, there was no conversion of 2a observed, and the reaction does not proceed in the absence of palladium catalyst, which shows the catalyst's requirement. Thus, the optimized reaction parameters for the synthesis of substituted alkynes through decarboxylative Sonogashira reaction are 1a (0.5 mmol), 2a (0.6 mmol), Pd (0.1 mol%), K<sub>2</sub>CO<sub>3</sub> (1.2 equiv), and DMSO (3 ml) at 100°C for 10 h. Later, the effect of protic solvents like methanol and ethanol was investigated on optimal reaction, and their results are shown in Table 1 (entries 21 and 22).

Subsequently, we investigated the substrate scope study concerning the various aryl iodides and alkynyl carboxylic acids (with R = Ph and Me) under the optimum reaction conditions. At the beginning of the study, we performed the cross-coupling reaction of different aryl iodides with phenyl propiolic acid for the decarboxylative alkynylation process, and the obtained results are shown in Table 2. The simple iodobenzene reacted smoothly with phenyl propiolic acid to give biphenyl acetylene with 90% yield (**3a**). Then the aryl iodides with electron-donating functionality such as p-CH<sub>3</sub> and p-OMe well coupled with phenyl propiolic acid to give corresponding internal alkynes **3b** and **3c** providing 89% and 87% yields, respectively (entries 2 and 3).

Next, the electron-deficient functional groups such as  $p-NO_2$ , p-CN, p-acetyl,  $m-NO_2$ , and m-CHO on aryl iodides showed improved conversion and provided coupling products in significant yields of the corresponding internal alkynes about 76% to 92% (entries 4–8); this may be achieved due to the electron-withdrawing nature of functionality. Furthermore, heteroaryl iodides having N, O, and S on the aryl group were also successfully coupled to give respective products (entries 9–11). Similarly, various aryl iodides, coupled with 2-butynoic acid, also gave a good yield of respective products 78% (**31**), 74% (**3m**), and 75% (**3n**) (entries 12–14).

However, the reaction of aryl bromides with phenyl propiolic acid and 2-butynoic acid provided only traces of the coupled product (entries 15-17) under the same reaction conditions. The comparison study of the Xantphos-coordinated Pd catalysts, Pd(1) and Pd(2), with conventional palladium precursors, has been investigated. Both the catalysts show comparable activity as evident from Table 3. 4-Nitro iodobenzene containing electron-withdrawing group gave 92% and 90% yield

(entries 4 and 5) or the 4-iodo anisole containing electrondonating group yielded 87% and 85% (entries 6 and 7) when catalyzed by catalysts Pd(**2**) and Pd(**1**), respectively.

Both the catalysts are found to be stable enough in the solid state, which was evaluated from the thermogravimetric analysis. The thermogravimetric curves reveal that the thermal stability and the decomposition phase start after 320°C for catalyst Pd(**2**) and after  $305^{\circ}$ C for catalyst Pd(**1**)<sup>[36]</sup> (Figures S2 and S3). However, under the optimal reaction conditions, these catalysts show superior activity as compared with traditional Pd catalysts, such as Pd(OAc)<sub>2</sub>, PdCl<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>, and PdCl<sub>2</sub> (Table 3).

Subsequently, the consequence of catalyst loading was investigated on the present protocol (Table 4). The effect of catalyst loading experiments on the yield of substituted alkynes was explored using the coupling reaction of 4-iodonitrobenzene with phenyl propiolic acid by using tetranuclear complex Pd(2). When decreasing the catalyst loading of Pd(2) from 1 to 0.01 mol% of Pd, the yield of the product was achieved to be 87% (Table 4, entry 3). Further reduction of catalyst loading to 0.001 mol% of Pd, 68% of the considerable yield of the product was obtained, and TON was found to be  $6.8 \times 10^4$ . The maximum TON  $4.6 \times 10^5$  and turn-over frequency (TOF)  $4.6 \times 10^4 \text{ h}^{-1}$  could be achieved by using 0.0001 mol% of Pd, yielding 46% of the respective product (Table 4, entry 5). The recyclability of the complex Pd(2) was examined; the reaction between 4-iodonitrobenzene and phenyl propiolic acid to yield the corresponding alkyne was chosen as a model reaction. After completion of the zero cycle of the reaction, the solvent was evaporated under vacuum, and extraction of the coupling product with ethyl acetate. The catalyst was separated, washed, and dried in the oven, and it was used to check the recyclability with optimal reaction conditions. The flask containing the Pd catalyst was charged with the required quantities of starting materials for the first cycle of the reaction, which provided 91% of the coupling product. Similarly, 89% and 87% of the product were obtained for the second and third cycles, respectively (Table S1). The catalyst effectively works by providing good conversion of the product. However, the catalyst can be recycled up to six successive runs with a slight decrease in its catalytic activity. After the third recycle, black particles were isolated and characterized by PXRD pattern.

The formation of PdNPs was characterized by intense peaks found at  $2\theta \sim 28.8^{\circ}$ ,  $40^{\circ}$ ,  $46.5^{\circ}$ , and  $68.2^{\circ}$ . Similarly, after the sixth recycle, the obtained black residue was analyzed by PXRD pattern. The more intense peaks were observed at  $2\theta \sim 28.8^{\circ}$ ,  $40^{\circ}$ ,  $46.5^{\circ}$ , and  $68.2^{\circ}$  (Figure S5). They were attributed to the planes (111), (200), and (220) of the cubic face-centered structure of





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## **TABLE 2** (Continued)



(Continues)



## TABLE 2 (Continued)





3k

## TABLE 2 (Continued)



(Continues)



*Note*: Reaction conditions: **1** (0.5 mmol), **2** (0.6 mmol),  $K_2CO_3$  (1.2 equiv), catalyst (0.1 mol%), DMSO (3 ml). <sup>a</sup>Isolated yield of the product.

PdNPs.<sup>[45]</sup> The formation of PdNPs serves as a reservoir of active catalytic species<sup>[46]</sup> for high activity of the decarboxylative Sonogashira reaction. The morphology of the PdNPs was revealed by SEM (Figure 1a,b), which shows the spherical shape of the product. The HR-TEM analysis of PdNPs (Figure 1c,d) reveals that PdNPs are well dispersed and spherical.

However, the average size of these NPs are ranging from 5 to 10 nm. The EDAX (energy-dispersive X-ray analysis) spectrum shows the presence of major and minor constituent elements as Pd and S in a 9:1 ratio of atom% (Figure S4). The S of the thiolate group may be present as capping group of PdNPs, which are generated after the loss of thiolate ligands from the dithiolate complex of Pd(II).

The hot filtration test and Hg poison test were examined to investigate the nature of catalysis process in the coupling reaction. The hot filtration test<sup>[47]</sup> was carried out (Sr. No. 3 in the supporting information) on model reaction using the catalyst Pd(2). The hot filtration test was performed for the third cycle, which showed PdNPs, the filtrate exhibited incomplete conversion (28%) reaction indicating that some Pd catalyst is decomposed to NPs. The reaction in the third cycle happens through "cocktail" reaction system. Moreover, the filtrate was subjected to ICP-AES (inductively coupled plasma-atomic emission spectroscopy) analysis to check the palladium leaching. No detectable amount of palladium (below 0.01 ppm) was found, signifying negligible amount of catalyst remained in the solution. Similar experiment was done at zero cycle. Interestingly, the filtrate after separation can show the maximum conversion of 2a, signaling the presence of soluble Pd species, in turn, demonstrating homogeneous pathway for the reaction. Further, the

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#### **TABLE 3** Comparative study of Pd complexes 1 and 2 with commercial palladium precursors



4 2a′ Pd(2) 92 920 92 5 2a' Pd(1)90 900 90 6 4-Iodoanisole (2a") Pd(2) 87 870 87 7 2a″ Pd(1) 85 850 85

*Note*: Reaction conditions: **1a** (0.5 mmol), **2a** (0.6 mmol),  $K_2CO_3$  (1.2 equiv), catalyst (0.1 mol%), DMSO (3 ml). <sup>a</sup>Yield of product calculated by GC and GC–MS.





Note: Reaction conditions: 1a (0.5 mmol), 2a (0.6 mmol), K<sub>2</sub>CO<sub>3</sub> (1.2 equiv), DMSO (3 ml).

<sup>a</sup>Conversion and yield were determined based on GC-GC-MS.

mercury poison test<sup>[48]</sup> (Sr. No. 4 in the supporting information) was examined on the optimal reaction using an excess of the elemental Hg (Pd:Hg = 1:400). The reaction of Hg with PdNPs separated after the third recycle using

Pd(2) catalyst suppresses the coupling of phenyl propiolic acid and iodobenzene. It implies that the catalytic process was quenched in the presence of Hg(0), indicating the heterogeneous pathway is involved in the reaction.



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**FIGURE 2** Recycle study of catalyst Pd(2)

However, another experiment similar to the above procedure employing Pd(**2**) catalyst was performed. The reaction of Pd complex  $[Pd_2(Xantphos)_2(4,4'-SC_{12}H_8S)]_2(OTf)_4$  with excess of Hg at zero cycle does not cease the coupling reaction. The later result exhibits the homogeneous nature of the catalysis process, which may proceed via the Pd(0)/Pd(II) mechanism. However, the formation PdNPs at subsequent cycles suggest the presence of "cocktail"-type catalytic system, which can undergo both homogeneous and heterogeneous catalysis processes, as discussed by others (Figure 2).<sup>[49,50]</sup>

### 4 | CONCLUSION

In summary, Xantphos-coordinated Pd complexes of dithiolate ligands employed as highly stable and efficient catalysts for the synthesis of substituted alkynes through the decarboxylative Sonogashira reaction with various aryl iodides. This current protocol works well without the use of external ligand and copper as cocatalyst. Thermally stable, moisture, and air-insensitive complexes are effective catalysts for decarboxylative Sonogashira coupling reactions. Catalyst tolerates both electron-rich and -poor substituents. The catalyst remains highly active with low concentration yielding high TON ( $4.6 \times 10^5$ ) and TOF up to  $10^4$  h<sup>-1</sup>. Comparative study of Pd complexes with conventional Pd precursors shows that Pd(2)maintains superior catalytic activity at low catalyst loading (0.1 mol%) with higher conversion of the product. The developed catalyst could be recycled for six cycles. The in situ formation of PdNPs during the catalysis has been confirmed. The activation of decarboxylative Sonogashira coupling by these NPs independently supports their role in catalysis.

# 4.1 | Electronic supplementary information

All the details of general materials, the procedure for catalysts preparation, and their thorough data of characterization are summarized, procedure for the hot filtration test and Hg poison test, the curves of thermogravimetric analysis of catalysts Pd(1) and Pd(2), EDAX spectrum of PdNPs, the table data of recyclability, PXRD pattern of catalyst Pd(2), and for all the decarboxylative Sonogashira coupling products <sup>1</sup>H and <sup>13</sup>C NMR spectra and GC–MS (gas chromatography-mass spectrometers).

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### AUTHOR CONTRIBUTIONS

**Manjunath Lokolkar:** Conceptualization; data curation; formal analysis; investigation; methodology; visualization. **Pravin Mane:** Data curation; formal analysis; methodology. **Sandip Dey:** Conceptualization; data curation; investigation; project administration; resources; supervision. **BM Bhanage:** Conceptualization; data curation; funding acquisition; investigation; project administration; resources; administration; resources; supervision.

#### DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available in the supporting information of this article.

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### SUPPORTING INFORMATION

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