

# KCC-1/BPT/PD AS A NEW NANO CATALYST FOR ONE-POT SYNTHESIS OF N-SUBSTITUTED 1,4-DIHYDROPYRIDINES AND 2-VINYLFURANS

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## Abstract:

*KCC-1/bpt/Pd catalyst was readily prepared for first time from inexpensive starting materials in aqueous media which catalyzed the synthesis 1,4-dihydropyridines and 2-vinyl furans. 1,4-Dihydropyridine (DHP) and furans scaffold represents the heterocyclic unit of remarkable pharmacological efficiency. 1,4-Dihydropyridines are widely used clinically as calcium channel blockers for the treatment of cardiovascular diseases, such as, nifedipine and nitrendipine are used for the treatment of hypertension and angina pectoris, nisoldipine is a potent vasodilator and nimodipine exhibits selectivity for cerebral vasculature. Also, furans are important structural motifs in a number of biologically active natural products and medicinal agents such as nakadomarin A<sup>1</sup> and Sumiki's acid. High catalytic activity and ease of recovery from the reaction mixture using filtration, and several reuse times without significant losses in performance are additional eco-friendly attributes of this catalytic system.*

**Keywords:** Nano catalyst; Heterogeneous catalyst; One-pot synthesis; Green chemistry; Multicomponent cyclization

## 1. Introduction

Furans are an important group of five-membered oxygen containing heterocycles that are found in a variety of natural products such as kallolides [1], combranolides [2], pheromones [3], commercial pharmaceuticals, flavours, fragrances, insecticides, and anti-leukemic agents [4–6], Furans also have wide utility as synthetic intermediates or synthons for numerous functional groups such as carboxylic acids,  $\beta$ -ketoesters, and aromatics. [7–10] Another interesting class of these compounds is 2-vinyl furans which have been utilized as synthetic reagents in polymer chemistry, being used in producing resins and polymers [11].

1,4-dihydropyridines (1,4-DHPs) are important class of compounds in the field of drugs and pharmaceuticals [12], The DHP moiety is common to numerous bioactive compounds which include various antihypertensive, vasodilator, antimutagenic, antitumor and antidiabetic agents [13-16], 1,4-DHPs are generally synthesised by classical Hantzsch method, which involves cyclocondensation of an aldehyde,  $\beta$ -ketoester and ammonia either in acetic acid or in refluxing ethanol for long reaction times which typically leads to low yields [17,18].

The metal complex has strong catalytic activities that for this property has been a topic of research [19–23]. Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their

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catalysis related properties, which can be leveraged in various usage. Among the reported metal used in catalysis, palladium is the most stable catalyst, and have been widely studied because of their catalysis related properties, which can be leveraged in various usage such as Sonogashira [24-26], Suzuki-Miyaura [27-29], Heck [30-32], Hiyama [33-35], Larock heteroannulation [36-39], degradation of pollutants [40], hydrogenation [41], and fuel cells [42]. In recent years, it has been proved that the use of complex functional groups either grafted or smeared on the solid supports played an important role in preventing the aggregation of metal catalysts.[43-45] Fibrous nano-silica (KCC-1), which possibilities a high surface area and easy availability through its fibers is reported by Polshettiwar et al. [46]. This would be an ideal catalyst support troth for the making of noble metal based catalysts that represent high availability of active sites and excellent catalytic activity. Herein, we report the synthesis of KCC-1 supported 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea-Pd(II) complex (KCC-1/bpt/Pd) and its application for synthesis 1,4-dihydropyridines and 2-vinyl furan in aqueous media (Scheme 1).

## 2. Material and methods

Chemical materials were purchased from Fluka and Merck in high purity. Melting points were determined in open capillaries using an Electrothermal 9100 apparatus and are uncorrected. FTIR spectra were recorded on a VERTEX 70 spectrometer (Bruker) in the transmission mode in spectroscopic grade KBr pellets for all the powders. The particle size and structure of nano particle was observed by using a Philips CM10 transmission electron microscope operating at 100 KV. Powder X-ray diffraction data were obtained using Bruker D8 Advance model with Cu K $\alpha$  radiation. The thermogravimetric analysis (TGA) was carried out on a NETZSCH STA449F3 at a heating rate of 10 °C min<sup>-1</sup> under nitrogen. <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a BRUKER DRX-300 AVANCE spectrometer at 300.13 and 75.46 MHz, BRUKER DRX-400 AVANCE spectrometer at 400.22 and 100.63

MHz, respectively. Elemental analyses for C, H, and N were performed using a Heraeus CHN-O-Rapid analyser. The purity determination of the products and reaction monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates. Mass spectra were recorded on Shimadzu GCMS-QP5050 Mass Spectrometer.

### General Procedure for the Preparation of KCC-1 Nanoparticles

TEOS (2.5 g) was dissolved in a solution of cyclohexane (30 mL) and 1-pentanol (1.5 mL). A stirred solution of cetylpyridinium bromide (CPB 1 g) and urea (0.6 g) in water (30 mL) was then added. The resulting mixture was continually stirred for 45 min at room temperature and then placed in a teflon-sealed hydrothermal reactor and heated 120 °C for 5 h. The silica formed was isolated by centrifugation, washed with deionized water and acetone, and dried in a drying oven. This material was then calcined at 550 °C for 5 h in air.

### General procedure for the preparation of KCC-1/3-chloropropylsilane NPs

KCC-1 (2 mmols) and THF (20 mL) were mixed together in a beaker, and then NaH (20 mmol) was dispersed in to the mixture by ultrasonication. 3-chloropropyltriethoxysilane (22 mmol) was added drop-wise at room temperature and stirred for another 16 h at 60°C. The resultant products were collected and washed with ethanol and deionized water in sequence, and then dried under vacuum at 60 °C for 2 h for further use.

### General procedure for the preparation of KCC-1/bpt NPs

KCC-1/3-chloropropylsilane (1g), 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiourea (1.5mmols), and DMF (50 mL) were mixed together with magnetic stirrer bar. The reaction mixture was stirred for 12h at 110°C and was subsequently filtered and washed thoroughly with DMF, dried in oven at 80oC for 24h to form the KCC-1/bpt.

### General procedure for the preparation of KCC-1/bpt/Pd NPs

KCC-1/bpt/Pd structures were prepared by reaction 1 g of KCC-1/bpt with 1 mmol of

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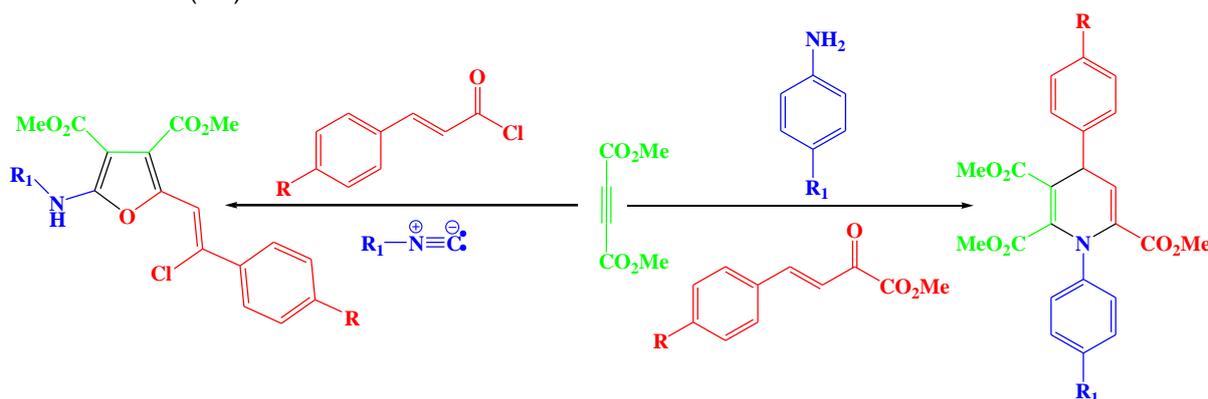
$\text{Pd}(\text{OAc})_2$  were mixed with 20 mL of  $\text{CH}_2\text{Cl}_2$  at room temperature for 24 h. This mixture was filtered and washed with acetonitrile to obtain KCC-1/bpt/Pd(II) complex.

#### General Procedure for the Synthesis of N-substituted-1,4-dihydropyridines

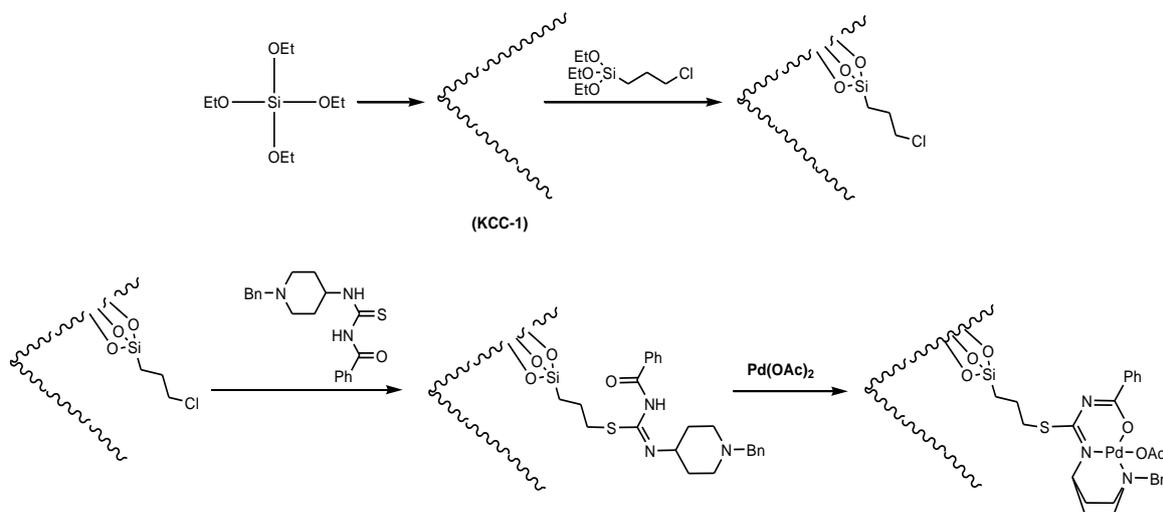
A solution of primary amine (1 mmol), dimethyl acetylenedicarboxylate (1 mmol), and KCC-1/bpt/Pd NPs (0.1 mg) was stirred vigorously at room temperature for 10 min then methyl (arylmethylidene) pyruvates (1 mmol) in water (20 mL) was added and the mixture was heated under reflux for 1 h. The solvent was removed under reduced pressure, and produced an oil, which was purified by prep TLC plates (20×20 cm) (Eluent hexane/ethyl acetate 3:1). Further purification was done by recrystallization in mixture of methanol/water (9:1).

#### General Procedure for the Synthesis of 2-vinyl furan

A mixture of dimethyl acetylenedicarboxylate (1 mmol) and cinnamoyl chloride (1 mmol), and isocyanide (1 mmol), and KCC-1/bpt/Pd NPs (0.1 mg) were stirred at room temperature under solvent-free conditions for the 30 min. Upon completion, the progress of the reaction was monitored by TLC when the reaction was completed, EtOH was added to the reaction mixture and the nano KCC-1/bpt/Pd NPs were separated by filtration. The solvent was removed under reduced pressure, and the residue was purified by flash column chromatography over silica gel (EtOAc/Hexanes, 1:5) to yield the desired 2-vinyl 5-amino furan.



Scheme 1. Synthesis of 1,4-dihydropyridines and 2-vinyl furans in the presence of nano KCC-1/bpt/Pd



Scheme 2. Schematic illustration of the synthesis for KCC-1/bpt/Pd nanoparticles

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### 3. Results and Discussion

The synthesis of KCC-1/bpt/Pd NPs involved several steps. The fibers of KCC-1 have many Si-OH groups on the surfaces; thus, it was expected that the KCC-1 could be easily functionalized with 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea to form KCC-1/bpt. Furthermore, 3-benzoyl-1-(1-benzylpiperidin-4-yl)-2-thiopseudourea groups on the KCC-1/bpt could supported palladium(II) complex. The synthesized nano KCC-1/bpt/Pd was then characterized by different methods such as XRD, TEM, SEM, FTIR and TGA (Scheme 2). FT-IR spectroscopy was

employed to determine the surface modification of the synthesized catalyst (Figure 1). The Si-O-Si symmetric and asymmetric stretching vibrations at  $802\text{ cm}^{-1}$  and  $1103\text{ cm}^{-1}$  and the O-H stretching vibration at  $3444\text{ cm}^{-1}$  were observed for the KCC-1 (Figure 1a). The successful functionalization of the bpt based organic-inorganic hybrid on KCC-1 surface is evidenced by two broad peaks at about  $1000\text{--}1150\text{ cm}^{-1}$ , assigned to Si-O stretching vibrations, as well as the presence of C-H stretching at  $2950\text{ cm}^{-1}$  and C-H bending vibration at approximately  $1450\text{ cm}^{-1}$  observed in Figure 1b.

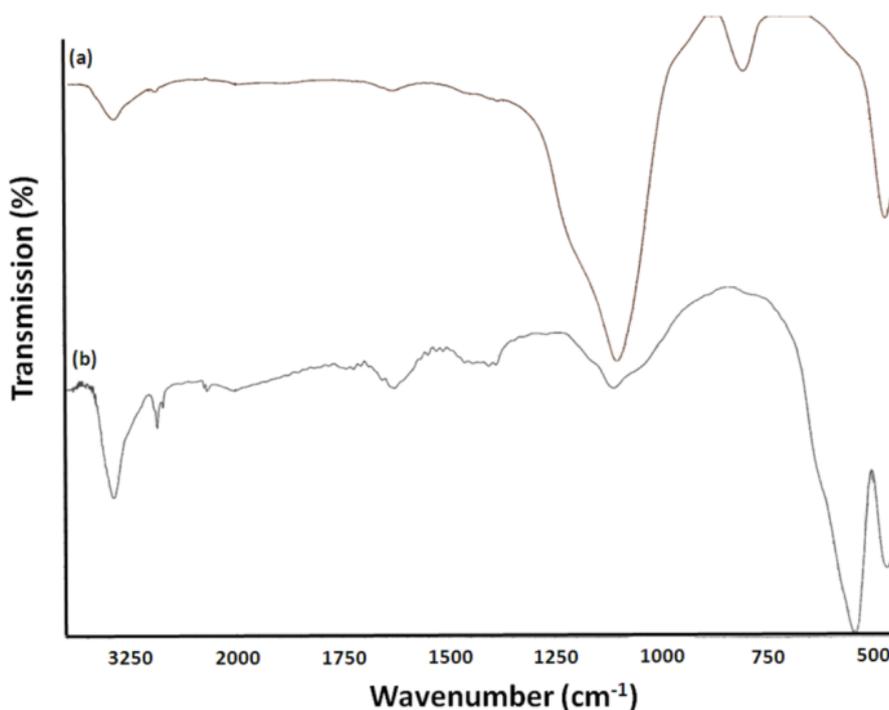


Figure 1. FTIR spectra of (a) KCC-1 NPs, and (b) KCC-1/bpt/Pd NPs

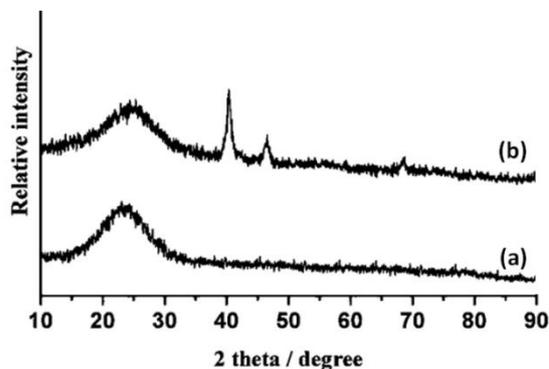


Figure 2 XRD analysis of (a) KCC-1 NPs, and (b) KCC-1/bpt/Pd NPs

The XRD patterns of KCC-1 NPs, and KCC-1/bpt/Pd NPs catalyst were shown in Figure 2. The broad peak between  $20\text{--}30^\circ$  corresponds to amorphous silica (Figure 2a). Moreover, new peaks at  $2\theta = 40.1^\circ$ ,  $46.5^\circ$  and  $68^\circ$  interferences of Pd (JCPDS 05-0681) (Figure 2b) crystal were observed for KCC-1/bpt/Pd confirming the successful growth of Pd (II) on the surface of KCC-1/bpt.

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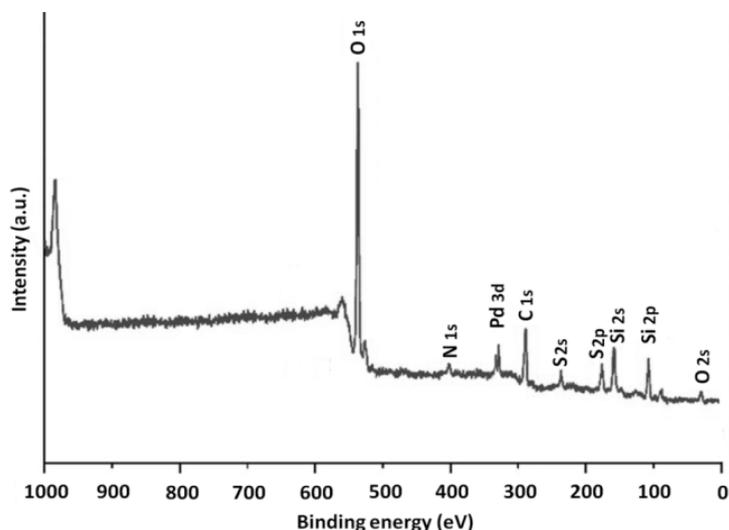


Figure 3 XPS spectra of KCC-1/bpt/Pd NPs

XPS was used to investigate the chemical elements on the surface of KCC-1/bpt/Pd NPs. A full-scan XPS spectrum for the as prepared catalyst is illustrated in Figure 3. Peaks corresponding to Si, O, C, S, N, and Pd can be clearly observed, and the presence of N 1s, S 2s, and S 2p further confirmed that KCC-1 had been successfully functionalized by the bpt. Also, XPS Pd 3d spectrum displays a doublet indicative of metallic Pd.

To confirm the thermal stability of the KCC-1/bpt/Pd, the thermogravimetric analysis of this material was performed at temperatures ranging from room temperature to 700°C (Figure 4). As seen in figure 4, two weight loss stages were observed in flow air. About 4 wt% weight loss was observed in the first stage (40–250°C)

corresponding to the loss of small molecules such as physically absorbed water. In the second stage (250–400°C), weight loss is about 10wt%, which can be attributed to the organic group derivatives. These data are in good agreement with the results of FT-IR analysis and confirmed the incorporation of bpt groups into the material frame work as well as their high stability during preparation and purification stages.

The structures of the synthesized KCC-1/bpt/Pd NPs were analyzed by TEM. The as prepared KCC-1/bpt/Pd NPs microspheres with fibrous structure were uniform and monodispersed (Figure 5). The average diameter of the microspheres was about 200-220nm. TEM image shown in figure 5 further clarifies that the distance between the two fibers was about 10-15nm.

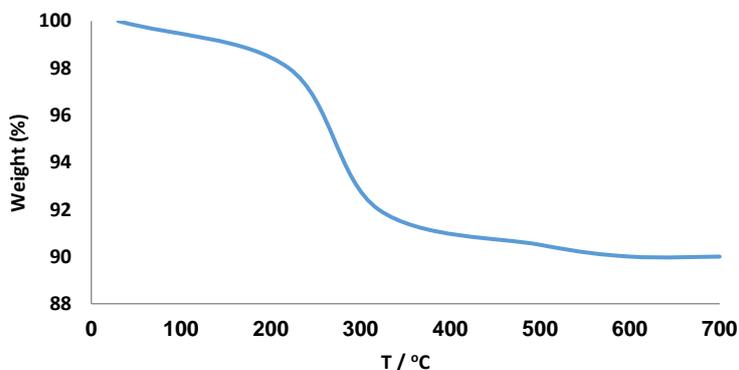
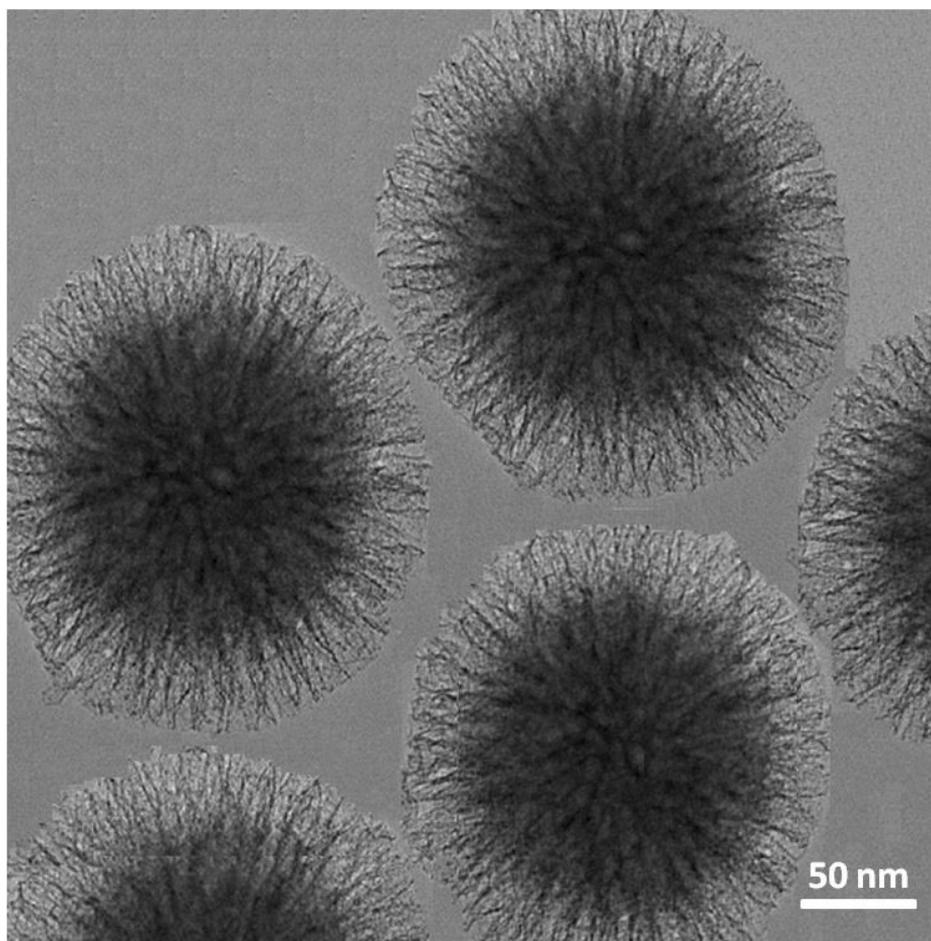


Figure 4 TGA diagram of KCC-1/bpt/Pd NPs

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**Figure 5** TEM images of KCC-1/bpt/Pd NPs.

The N<sub>2</sub> adsorption–desorption isotherms of KCC-1/bpt/Pd NPs showed characteristic type IV curve, which is consistent with literature reports on standard fibrous silica spheres. As for KCC-1, the BET surface area, total pore volume, and BJH pore diameter are obtained as 439m<sup>2</sup>/g, 1.49 cm<sup>3</sup>/g, and 14.78nm respectively, whereas the corresponding parameters of KCC-1/bpt/Pd NPs have decreased to 328m<sup>2</sup>/g, 1.07cm<sup>3</sup>/g, and 12.32nm. The nitrogen sorption analysis of KCC-

1/bpt/Pd NPs also confirms a regular and uniform mesostructure with a decrease in surface area, pore diameter and pore volume parameters in comparison with that of pristine KCC-1. With the functionalization by bpt-Si, the corresponding pore volumes are drastically reduced. This could be ascribed to increased loading with the sensing probe, which occupies a large volume inside the silica spheres (Table 1).

**Table 1** Structural parameters of KCC-1 and KCC-1/bpt/Pd materials determined from nitrogen sorption experiments.

Catalysts	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	V <sub>t</sub> (cm <sup>3</sup> g <sup>-1</sup> )	D <sub>BJH</sub> (nm)
<b>KCC-1</b>	439	1.49	14.78
<b>KCC-1/bpt/Pd</b>	328	1.07	12.32

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Table 2 The effect of solvent and temperature for synthesis of 1,4-dihydropyridine.<sup>[a]</sup>

Entry	Solvent	Temp. (°C)	Yield (%) <sup>[b]</sup>
1	EtOH	Reflux	64
2	H <sub>2</sub> O	Reflux	93
3	H <sub>2</sub> O	80	87
4	H <sub>2</sub> O	60	61
5	H <sub>2</sub> O	r.t.	-
6	CH <sub>3</sub> CN	Reflux	36
7	THF	Reflux	25
8	CH <sub>2</sub> Cl <sub>2</sub>	Reflux	29
9	EtOAc	Reflux	43
10	DMF	Reflux	24
11	Toluene	Reflux	27
12	<i>n</i> -Hexane	Reflux	18
13	Benzene	Reflux	9
14	CCl <sub>4</sub>	Reflux	17
15	Cyclohexane	Reflux	12
16	CHCl <sub>3</sub>	Reflux	43
17	DMSO	Reflux	32
18	MeOH	Reflux	72
19	Dioxane	Reflux	24
20	<i>i</i> -PrOH	Reflux	55
21	solvent-free	100	-

[a] Reaction conditions: Reaction conditions: alkyl methyl (arylmethylidene) pyruvates (1.0 mmol), aniline (1.0 mmol), and dimethyl acetylene-dicarboxylate (1.0 mmol), catalyst (0.1 mg), 2 h; [b] GC yields [%].

Then the amount of catalyst necessary to promote the reaction efficiently was examined. It was observed that the variation for KCC-1/bpt/Pd NP had an effective influence. The best amount of KCC-1/bpt/Pd NP was 0.1mg which afforded the desired product in 93% yields (Figure 4). Under the optimal conditions, the reaction progress in the presence of 0.1mg of KCC-1/ bpt/Pd NP was monitored by GC. Using this catalyst system, excellent yields of 1,4-dihydropyridine can be achieved in 60 min (Figure 5). No apparent by-

products were observed by GC in all the experiments and the 1,4-dihydropyridine was obtained cleanly in 93% yield.

We examined the effect of solvent on the synthesis of 1,4-dihydropyridine using the KCC-1/bpt/Pd NPs at heating under reflux (Table 1). Solvent does affect on catalysts performance. *n*-Hexane, benzene, CCl<sub>4</sub>, or cyclohexane, a non-polar solvent, gave 1,4-dihydropyridine a lower yield than that obtained in under solvent-free conditions (Table 1, entry 12-15). CH<sub>3</sub>CN, THF,

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CH<sub>2</sub>Cl<sub>2</sub>, DMF, Toluene, Dioxane, CHCl<sub>3</sub>, EtOAc, and DMSO, aprotic polar solvents, gave also 1,4-dihydropyridine in low yields. The reaction was do better in protic solvent. *i*-PrOH, and ethanol gave 1,4-dihydropyridine in average yields (Table 1, entries 1 and 20). In contrast, the use of methanol resulted in an increased yield of 72% the yield was remarkably increased up to 93% when H<sub>2</sub>O was used as the solvent respectively in the presence of KCC-1/bpt/Pd NPs. In this study, it was found that water is a more efficient (Table 1, entry 2) over other organic solvents. A solvent that stabilizes one of two competing transition states that control the selectivity should enhance the selectivity of the product obtained via the stabilized transition state. For example, in multicomponent reactions higher

reaction rates and selectivities are often obtained in polar solvents compared to non-polar solvents, which has been attributed to enhanced hydrogen bonding between the solvent and the transition state, as well as to enforced hydrophobic interactions when conducted in water, which facilitates alignment of the substrates. The ability to use water as the reaction medium greatly increases the green credentials of the method. We also investigated the crucial role of temperature in the synthesis of 1,4-dihydropyridine in the presence of KCC-1/bpt/Pd NP as a catalyst. Results clearly indicated that the catalytic activity is sensitive to reaction temperature. The best temperature for this reaction was at reflux condition (Table 1, entry 2-5).

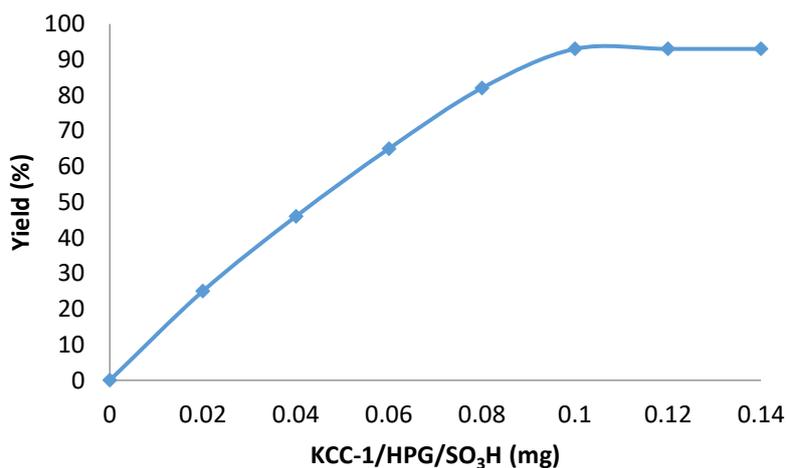


Figure 4 Effect amount of catalyst on yield of 1,4-dihydropyridine

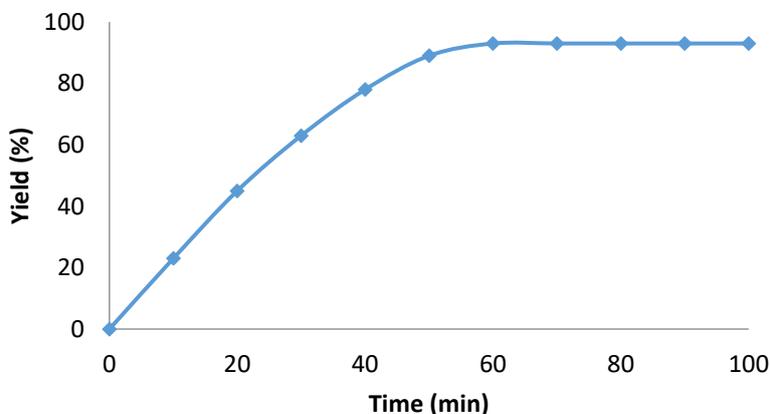


Figure 5 Effect of time on yield of 1,4-dihydropyridine

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After optimization of the reaction conditions, to delineate this approach, particularly in regard to library construction, this methodology was evaluated by using different alkyl methyl (arylmethylidene) pyruvates, variety of different substituted primary amine and of dimethyl acetylenedicarboxylate in the presence of KCC-1/bpt/Pd NPs under similar conditions. As can be

seen from (Table 2), electronic effects and the nature of substituents on the alkyl methyl (arylmethylidene) pyruvates and primary amine did not show strongly obvious effects in terms of yields under the reaction conditions. The three-component cyclocondensation reaction proceeded smoothly.

**Table 2** The reaction of alkyl methyl (arylmethylidene) pyruvates, and aniline with dimethyl acetylenedicarboxylates.<sup>a</sup>

Entry	R	R <sub>1</sub>	Product	Yield (%) <sup>b</sup>
1	CH <sub>3</sub>	H	4a	93
2	CH <sub>3</sub>	OCH <sub>3</sub>	4b	91
3	CH <sub>3</sub>	Br	4c	92
4	OCH <sub>3</sub>	H	4d	90
5	OCH <sub>3</sub>	OCH <sub>3</sub>	4e	87
6	OCH <sub>3</sub>	Br	4f	89
7	Cl	H	4g	94
8	Cl	OCH <sub>3</sub>	4h	91
9	Cl	Br	4i	92

<sup>a</sup> Reaction conditions: alkyl methyl (arylmethylidene) pyruvates, primary amines, dimethyl acetylenedicarboxylate, and nano KCC-1/bpt/Pd (0.1 mg) in water (20 mL) was added and the mixture was heated under reflux for 1 h; <sup>b</sup> Isolated yield

The catalytic potential of the nano KCC-1/bpt/Pd was evaluated in condensation reactions. In order to optimize the reaction conditions, we examined reaction of dimethyl acetylenedicarboxylate, cinnamoyl chloride, and *t*-Butyl isocyanide as a model compound using under various reaction conditions in terms of time and product yield (Table 3). Catalytic amount of nano KCC-1/bpt/Pd (0.1 mg) under solvent-free conditions at room temperature for 30 min was found to be ideal the reaction conditions for the complete synthesis of 2-vinyl furan.

In light of the above-mentioned chemistry and properties of 2-vinyl furans, the development of new and efficient approaches for the synthesis of these compounds, from simple, readily available starting materials is desirable. We investigated the intermolecular trapping of zwitterion intermediates generated from the reaction of isocyanide and

DMAD with trans-cinnamoyl chloride for the construction of novel 2-vinyl furans. Herein, we describe the reaction of isocyanides with dialkyl acetylenedicarboxylates (DAAD) and trans-cinnamoyl chlorides leading to novel 2-vinyl furans, via three-component reaction in good yields (Table 4).

It is important to note that the heterogeneous property of nano KCC-1/bpt/Pd facilitates its efficient recovery from the reaction mixture during work-up procedure. The activity of the recycled catalyst was also examined under the optimized conditions. After the completion of reaction, the catalyst was separated by filtration, washed with methanol and dried at the pump. The recovered catalyst was reused for ten consecutive cycles without any significant loss in catalytic activity (Figure 6).

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**Table 3** Optimization of the reaction conditions for the synthesis of 2-vinyl furan in terms of temperature, amount catalyst, time and product yield.<sup>a</sup>

Entry	Solvent	Temp. (°C)	Time (min)	Amount catalyst (mg)	Yield (%) <sup>b</sup>
1	Solvent-free	r.t.	10	0.14	43
2	Solvent-free	r.t.	20	0.14	78
3	Solvent-free	r.t.	30	0.14	96
4	Solvent-free	r.t.	40	0.14	96
5	Solvent-free	r.t.	30	0.12	96
6	Solvent-free	r.t.	30	0.1	96
7	Solvent-free	r.t.	30	0.8	87
8	Solvent-free	r.t.	30	0.6	79
9	Solvent-free	50	30	0.1	96
10	Solvent-free	100	30	0.1	96
11	H <sub>2</sub> O	r.t.	30	0.1	69
12	<i>i</i> -PrOH	r.t.	30	0.1	53
13	MeOH	r.t.	30	0.1	62
14	EtOH	r.t.	30	0.1	54
15	THF	r.t.	30	0.1	32
16	CH <sub>2</sub> Cl <sub>2</sub>	r.t.	30	0.1	29
17	CH <sub>3</sub> CN	r.t.	30	0.1	trace
18	THF	r.t.	30	0.1	23
19	CH <sub>2</sub> Cl <sub>2</sub>	r.t.	30	0.1	26
20	EtOAc	r.t.	30	0.1	46
21	DMF	r.t.	30	0.1	19
22	Toluene	r.t.	30	0.1	25
23	<i>n</i> -Hexane	r.t.	30	0.1	16
24	Benzene	r.t.	30	0.1	11
25	CCl <sub>4</sub>	r.t.	30	0.1	15
26	Cyclohexane	r.t.	30	0.1	-
27	CHCl <sub>3</sub>	r.t.	30	0.1	40
28	DMSO	r.t.	30	0.1	36
29	Dioxane	r.t.	30	0.1	29

<sup>a</sup> Reaction conditions: dimethyl acetylenedicarboxylate, cinnamoyl chloride, and *t*-Butyl isocyanide; <sup>b</sup> Isolated yields.

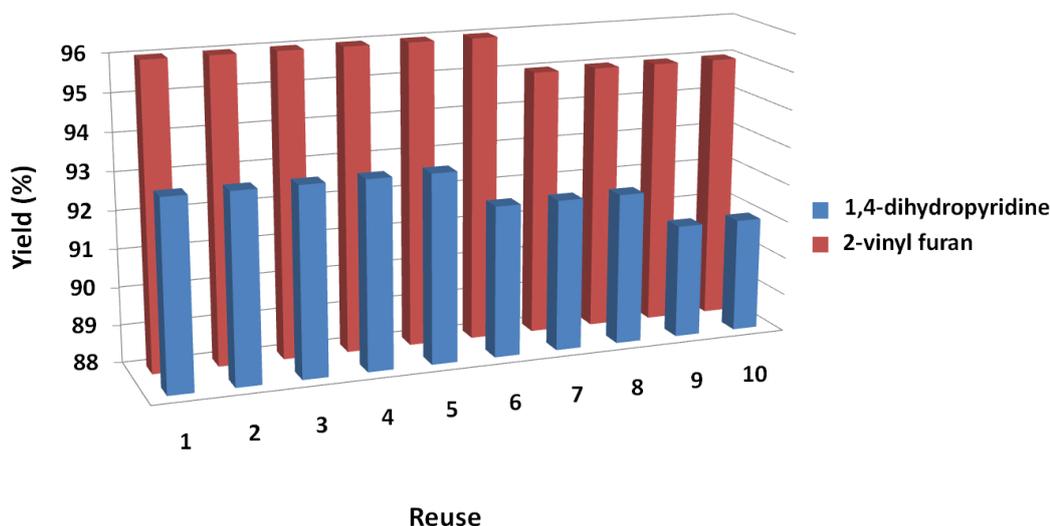
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**Table 4 Reaction of cinnamoyl chlorides with dialkyl acetylenedicarboxylates and isocyanides.**

Entry	R	R <sub>1</sub>	Yield (%) <sup>a</sup>
1	H	Cyclohexyl	92
2	Me	Cyclohexyl	93
3	H	<i>t</i> -Butyl	96
4	Me	<i>t</i> -Butyl	94
5	OMe	<i>t</i> -Butyl	91
6	H	1,1,3,3-tetramethyl butyl	83
7	Me	1,1,3,3-tetramethyl butyl	85

<sup>a</sup> Isolated yield



**Figure 6. Reuses performance of the catalysts**

#### 4. Conclusions

KCC-1/bpt/Pd nanoparticle, can be easily prepared using a polymerization method under safe conditions. The spectral and analysis data confirmed the effectiveness of the method for the preparation of KCC-1/bpt/Pd nanoparticle by preventing the grain growth or agglomeration of the particles. The KCC-1/bpt/Pd nanoparticle, as an effective and reusable heterogeneous catalyst,

can provide an environmentally friendly alternative for the heterogeneous synthesis of 1,4-dihydropyridine and 2-vinyl furan derivatives under mild conditions. 1,4-Dihydropyridine (DHP) and furans scaffold represents the heterocyclic unit of remarkable pharmacological efficiency.

#### Conflict of interests

The authors have no conflict of interest.

#### References

- [1] Kallolide A, Look SA, Burch MT, Fenical W, Qitai Z, Clardy J, *J. Org. Chem.* 1985; 50: 5741-7646.
- [2] Fenical W, Okeeda RK, Basnadurraga MM, Culver P, Jacobs RS, *Science* 1981; 212: 1512-1514.
- [3] Mori K, *Tetrahedron* 1989; 45: 3233-3612.

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- [4] Sargent MV, Dean FM, Furans and their benzo derivatives. In: Katritzky AR, Rees CW (eds) Comprehensive heterocyclic chemistry. Pergamon, New York; 1984.
- [5] Hou XL, Yang Z, Wong HNC, Furans and benzofurans. In: GribbleGW, Gilchrist TL (eds) Progress in heterocyclic chemistry, vol 14. Pergamon, Oxford.
- [6] Donnelly DMX, Meegan MJ, Five-membered rings with two heteroatoms, each with their fused carbocyclic derivatives. In: Katritzky AR, Rees CW (eds) Comprehensive heterocyclic chemistry, vol 4. Pergamon, New York; 1984.
- [7] Nakanish K, Natural products chemistry. Kodansha Ltd, Tokyo; 1974.
- [8] Vernin G, The chemistry of heterocyclic flavoring and aroma compounds. Ellis Horwood, Chichester; 1982.
- [9] Kubo I, Lee YW, Nakanishi K, Chapyra A, J. Chem. Soc. Chem. Commun. 1976; 949-950.
- [10] Schulte G, Schener PJ, McConnel O, Helv. Chim. Acta. 1980; 63: 2159-2167.
- [11] Choura M, Belgacem NM, Gandini A, Macromolecules 1996; 29: 3839-3850.
- [12] Reddy GM, Shiradkar M, Chakravarthy AK, Curr. Org. Chem. 2007; 11: 484-487.
- [13] Janis RA, Trigg DA, J. Med. Chem. 1983; 25: 775-785.
- [14] Bocker RH, Guengerich FP, J. Med. Chem. 1986; 28: 1596-1603.
- [15] Gaudio AC, Korolkovas A, Tkahata Y, J. Pharm. Sci. 1994; 83: 1110-1115.
- [16] Gordeev MF, Patel DV, Gordon EM, J. Org. Chem. 1996; 61: 924-928.
- [17] Dondoni A, Massi A, Minghini E, Bertolasi V, Tetrahedron 2004; 60: 2311-2326.
- [18] Love B, Sander KM, J. Org. Chem. 1965; 30: 1914-1916.
- [19] Wang ML, Jiang TT, Lu Y, Liu HJ, Chen Y, J. Mater. Chem. A 2013; 1: 5923-5933.
- [20] Zhang X, Su Z, Adv. Mater. 2012; 24: 4574-4577.
- [21] de Pedro ZM, Diaz E, Mohedano AF, Casas JA, Rodriguez JJ, Appl. Catal. B: Environ. 2011; 103: 128-135.
- [22] Liu YM, Tsunoyama H, Akita T, Xie SH, Tsukuda T, ACS Catal. 2011; 1: 2-6.
- [23] Yang X, Huang C, Fu ZY, Song HY, Liao SJ, Su YL, Du L, Li XJ, Appl. Catal. B: Environ. 2013; 140: 419-425.
- [24] Negishi E, Anastasia L, Chem. Rev. 2003; 103: 1979-2017.
- [25] Lee DH, Lee YH, Harrowfield JM, Lee IM, Lee HI, Lim WT, Kim Y, Jin MJ, Tetrahedron 2009; 65: 1630-1634.
- [26] Sonogashira K, J. Organomet. Chem. 2002; 653: 46-49.
- [27] Pomeisl K, Holy A, Pohl R, Horska K, Tetrahedron 2009; 65: 8486-8492.
- [28] Tapolcsanyi P, Krajsovsky G, Ando R, Lipcsey P, Horvath G, Matyus P, Riedl Z, Hajos G, Maes BUW, Lemiere GLF, Tetrahedron 2002; 58: 10137-10143.
- [29] Nielsen TE, Quement SL, Meldal M, Tetrahedron Lett. 2005; 46: 7959-7962.
- [30] Miyazaki F, Uotsu K, Shibasaki M, Tetrahedron 1998; 54: 13073-13078.
- [31] Kalinski C, Umkehrer M, Schmidt J, Ross G, Kolb J, Burdack C, Hiller W, Hoffmann SD, Tetrahedron Lett. 2006; 47: 4683-4686.
- [32] Garcia A, Rodriguez D, Castedo L, Saa C, Dominguez D, Tetrahedron Lett. 2001; 42: 1903-1905.
- [33] Gordillo A, Jesus ED, Mardomingo CL, Org. Lett. 2006; 8: 3517-3520.
- [34] Denmark SE, Baird JD, Chem. Eur. J. 2006; 12: 4954-4963.
- [35] Csapo A, Bodor A, Rabai J, J. Fluor. Chem. 2012; 137: 85-92.
- [36] Wang C, Sperry J, Tetrahedron 2013; 69: 4563-4577.
- [37] Larock RC, Yum EK, Refvik MD, J. Org. Chem. 1998; 63: 7652-7662.
- [38] Larock RC, Yum EK, J. Am. Chem. Soc. 1991; 113: 6689-6690.
- [39] Joucla L, Batail N, Djakovitch L, Adv. Synth. Catal. 2010; 352: 2929-2936.
- [40] Yang MQ, Pan X, Zhang N, Xu YJ, CrystEngComm, 2013; 15: 6819-6828.
- [41] Dong Z, Le X, Dong C, Zhang W, Li X, Ma J, Appl. Catal., B, 2015; 162: 372-380.
- [42] Antolini E, Energy Environ. Sci., 2009; 2: 915-931.
- [43] Zhou L, Gao C, Xu W, Langmuir 2010; 26: 11217-11225.
- [44] Chen Z, Zhou L, Zhang F, Yu C, Wei Z, Applied Surface Science 2012; 258: 5291-5298.
- [45] Du Q, Zhang W, Ma H, Zheng J, Zhou B, Li Y, Tetrahedron 2012; 68: 3577-3584.
- [46] Polshettiwar V, Cha D, Zhang X, Basset JM, Angew. Chem. Int. Ed. 2010; 49: 9652-9656.