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Graphical Abstract

Efficient *in situ* palladium nano catalysis for Z-selective semi transfer hydrogenation of internal alkynes using 1, 4-butanediol

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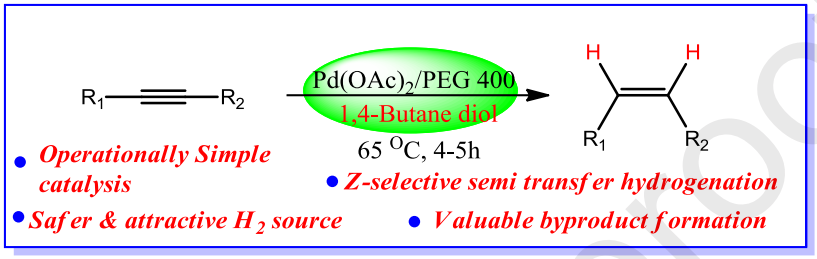

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Efficient *in situ* palladium nano catalysis for Z-selective semi transfer hydrogenation of internal alkynes using safer 1, 4-butanediol

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ABSTRACT

Simple and efficient *in situ* generated palladium nanoparticles (PdNPs) in PEG-4OO catalyzed semi transfer hydrogenation of internal alkynes to Z-alkenes with excellent selectivity along with the formation of beneficial γ-butyrolactone as a byproduct using low quantity of safer and attractive 1, 4-butanediol as a hydrogen source was described.

Constructing the Z-alkenes having versatile applications in pharmacologically active constituents, materials and organic synthesis [1], through the selective semi hydrogenation of alkynes has always been an attracting and motivating assignment to the scientific and industrial community. Though, the Lindlar's catalyst is a common and good selection for this persistence till today [2], few limitations including (i) the use of a toxic Pb salt (ii) excess of quinoline to suppress the over-hydrogenation, (iii) low substrate tolerance (iv) isomerization of the (Z)-olefins to the (E)-olefines and (v) less stability concerns have stimulated the chemists to develop other alternative V [3], Cr [4],Fe [5], Co [6], Ni [7], Cu [8], Nb [9], Ru [10], Rh [11] and Au [12] catalysts.

Specifically, palladium has been recognized as the most active and appropriate catalyst, due to the stronger adsorption of the C≡C (compare to C=C group) on Pd metal surface permits the inhibition of the over-reduction of alkene. Accordingly, numerous heterogeneous nano Pd-catalysts [13] were developed for this perseverance. Nonetheless, all these Pd-catalysts have shown high activity and selectivity, several reasonable shortcomings were found, such as slightly complicated and tedious materials preparation [13a-n & 13p], none [13h-k, 13m & 13o-p] or little recyclability [13e-g & 13l] and the use of external H_2 gas [13a-o] that consist of special handling and storage matters. Therefore, the development of easily accessible nano Pd-catalysis for the selective semi transfer hydrogenation of alkynes using more attractive and safer hydrogenating agent is a desirable objective.

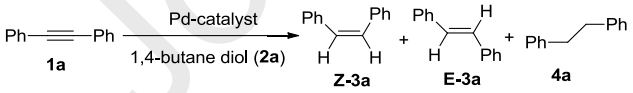
1, 4-Butanediol is a proficient and benign hydrogen source that readily accessible as of renewable biomass derivatives [14]. The loss of two equivalents of molecular hydrogen from 1, 4-butanediol upon its dehydrogenation yields γ-butyrolactone (GBL) as a sole product [15]. Owing to the substantial role of lactones in natural products and polymers [16], their synthesis by catalytic transfer dehydrogenation of diols was considered as an eco-friendly method [17]. Remarkably, the irreversible nature of the 1, 4-butanediol as understood by resulting lactone formation is a significant benefit and thus 1, 4-butanediol have become a good alternative to formic acid in transfer hydrogenations. Consequently, several metal catalyzed transfer hydrogenations of nitrile [18], nitro [19], carbonyl [20-21], olefin [21] and imine [21] compounds were successively accomplished by means of 1, 4-butanediol. To the best of our knowledge, there is no precedence of metal catalyzed selective semi transfer hydrogenation of alkynes using 1, 4-butanediol as a hydrogen source. Herein, we first time describe the catalytic ability of simple and efficient *in situ* generated PdNPs [$(Pd(OAc)_2$/PEG-400)] system for the selective conversion of internal alkynes to Z-alkenes *via* transfer hydrogenation pathway using attractive and safer 1.4-butanediol along with the formation of beneficial λ-butyrolactone as a bi-product.

At the outset, we have concentrated on the selection of suitable Pd-catalysts for the semi transfer hydrogenation (STH), choosing diphenylacetylene **(1a)** and 1, 4-butanediol (**2a**) are model substrates. As shown in table 1, using 3 mol % of homogeneous Pd-catalysts like $PdCl_2$, $Pd(OAC)_2$ and

Pd

(17-31%) of Stilbene (**3a)** that associated with low to moderate selectivity (58-72%) of Z-stilbene (**Z-3a**) was found, even after 8 hours (Table 1, entries 1-3). The effect of ionic liquids combined with $PdCl_2(PPh_3)_2$ catalyst was also none in the STH of **1a** (Table 1, entries 4). Interestingly, the addition of polyethylene glycol-400 (PEG-400) solvent to the 1 mol% of $PdCl_2$, $Pd(OAC)_2$ and $PdCl_2(PPh_3)_2$ have greatly allowed the formation of high yield (84-92%) of **3a** with excellent selectivities (89-94%) of **Z-3a**, at 65 °C after 4 hour only (Table 1, entries 5-7). However, the $PdCl_2(PPh_3)_2$ in PEG-400 system has been found to best (Table 1, entry 7), we have interested to select $Pd(OAC)_2$ for the further optimization study, since it does not require any additives such as base and phosphine ligand etc., (Table 1, entry 6). Further, the combination of $Pd(OAc)_2$ and PEG-200 system has decreased the yield of **3a** and selectivity of **Z-3a** to little extent. On the other hand, no change in the yield of the **3a** and selectivity of **Z-3a** was obtained, when we used $Pd(OAC)_2$+PEG-600 system (Table 1, entry 9). Particularly, in the presence of PEGs, the color of the crude reaction mixture was reddish brown, that indicated us the formation of possible *in situ* nano-palladium particles (Table 1, entries 5-11). Previously, the use poly ethylene glycols (PEGs) as efficient synthetic and stabilizing agents for the PdNPs has been well established [22].The TEM study revealed that the size of *in situ* generated Pd nanoparticles [1 mol% $Pd(OAC)_2$ + PEG-400] system in the range of 2.5-3.0 nm (Figure S1, ESI). The high yield of **3a** and excellent selectivity of **Z-3a** may be attributed to the formation of very small size PdNPs and their subsequent steric stabilization by PEG-400 (Table 1, entry 6). Besides, the reaction was not considerable at room temperature and 45 °C (Table 1, entry 10-11). There was also found that increasing in the reaction time up to 6 hours, the yield of **3a** and selectivity of **Z-3a** remains intact (Table 1, entry 12). We have also prepared *ex situ* PdNPs according to literature procedure [23] and then directly utilized for the model reaction under the optimal conditions to afford 83% yield of **3a** (Table 1, entry 13) which indicates that *in situ* formed PdNPs are highly active catalytic species as compared to *ex situ* PdNPs. Finally the addition of Hg (100 equiv to Pd) to model reaction under the optimal conditions has led to completely prevent the STH, indicating that the actual active catalytic system is likely to be nanopalladium (Table 1, entry 14).

Table 1. Selection of suitable Pd-catalyst

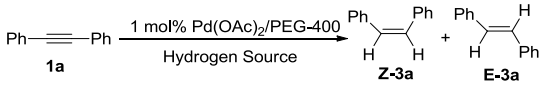


Entry	Catalyst (mol%)	Time	3a/4a Yield(%)[b]	Selectivity (%)[c] Z-(3a)/E-(3a)
1	$PdCl_2$ (3)	8	17/12	58/42[d]
2	$Pd(OAc)_2$ (3)	8	23/11	63/37[d]
3	$PdCl_2(PPh_3)_2$(3)	8	33/9	72//28[d]
4	$PdCl_2(PPh_3)_2$(3)/bmimBF_4	8	33/9	72//28[d]
5	$PdCl_2$ (1)/PEG-400	4	84/0	89/11[d]
6	$Pd(OAc)_2$(1)/ PEG-400	4	92/0	94/6 [d]
7	$PdCl_2(PPh_3)_2$(1)/PEG-400	4	94/0	95/5 [d]
8	$Pd(OAc)_2$(1)/ PEG-200	4	92/0	94/6 [d]
9	$Pd(OAc)_2$(1)/ PEG-600	4	92/0	94/6 [d]
10	$Pd(OAc)_2$(1)/ PEG-400	12	Trace	-
11	$Pd(OAc)_2$(1)/PEG-400	8	59/0	86/14 [d,e]
12	$Pd(OAc)_2$(1) /PEG-400	6	92/0	94/6 [d,f]
13	*Ex situ* PdNPs	7	83/0	92/8[g]
14	$Pd(OAc)_2$(1) /PEG-400	6	trace	-[h]

[a]The reaction was conducted in 1 mL of THF at reflux temperature; [b]Yields were determined by ^{1}H NMR; [c] Z/E ratio was Determined by ^{1}H NMR; [d]The reaction was carried out in 2 mL of corresponding PEG at 65 °C; [e]Reaction was carried out at RT; [f]Reaction was carried out at 45 °C; [g]Pre-prepared PdNPs; [h]100 mmol of Hg was added.

Using the above optimized catalytic system, we then investigated the hydrogenation capability of few mono and di-hydric alcohols. The findings suggested that the transfer hydrogenation of **1a** using excess (3-5 equivalents) of isopropanol and 2-butanol was not fruitful even after 12 hours (Table 2, entries 1-4). Surprisingly, all the 1 equivalent diols used in the STH of **1a**, have afforded the moderate to high yields (47-92%) of desired **3a**, where excellent selectivities of **Z-3a** (91-94%) were also found (Table 2, entries 5-8). Among all the diols, 1, 4-butanediol has provided appreciable results in the present approach (Table 2, entry 6). The efficacy of low quantity of 1, 4-butanediol as an efficient hydrogen source in several transfer hydrogenation reactions, because of possible equilibrium determined through the formation of GBL was well elucidated previously.[18-21]

Table 2. Selection of suitable hydrogen-source



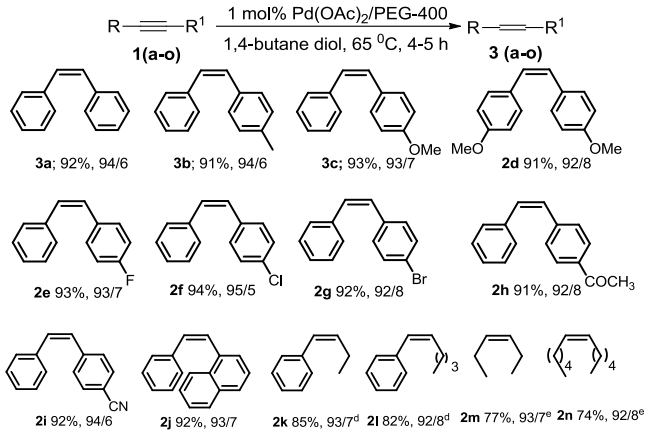
Entry	H-source(eq)	Time	Yield 3a (%)[b]	Selectivity **(Z.3a/E-3a)**[c]
1	Iso-propanol (3)	12	11	71/29
2	2-butanol (3)	12	16	79/21
3	Iso-propanol (5)	12	17	78/22
4	2-butanol (5)	12	22	83/17
5	1,4-butanediol (1)	4	92	94/6
6	1,6-hexanediol (1)	4	47	91/9
7	1,5-pentanediol (1)	4	58	93/7

[a]The reaction was conducted using 2 mL of PEG-400 at 65 °C temperature; [b]Yields were determined by ^{1}H NMR; [c]Z/E ratio was Determined by ^{1}H NMR;

The above optimized conditions in our hand, we further extended our protocol to examine the compatibility of various internal alkynes. From the table 3, it was understood that all internal alkynes used were found to well suited in the present protocol, to give excellent selectivities (>90%) of corresponding Z-alkenes. Among all internal alkynes, the diaryl alkynes were more reactive and provided high yields of corresponding olefins (Table 3, entries 2-11). The nature of substituents (electron releasing/electron withdrawing) on aryl internal alkynes has not much effective in the present STH. Conversely, with increasing in the aliphatic nature of internal alkynes, the yields of alkenes have been decreased progressively (Table 3, entries 12-15).

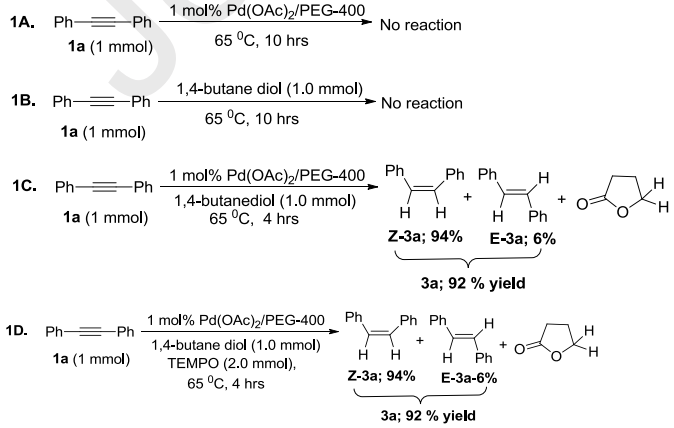
Noti ture functionalities/groups present on the diaryl alkynes was not accomplished, indicating that our present approach could selectively reduce the C≡C alkynes only, under the chosen optimized conditions (table 3, entries 5-10).

Table 3. Substrate scope



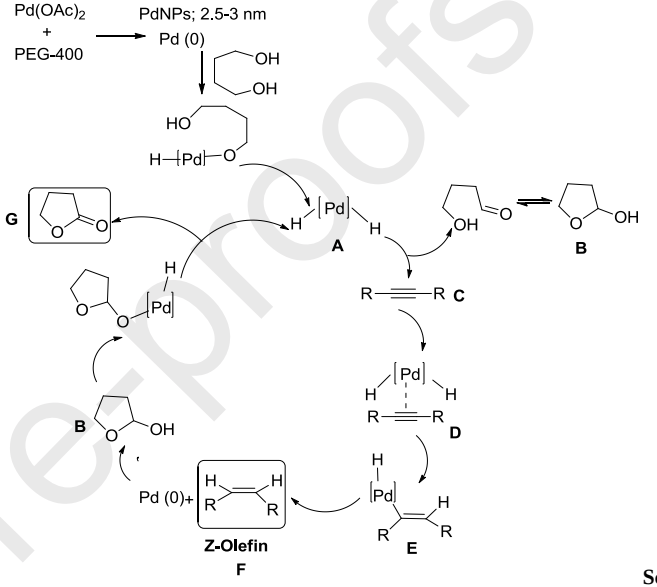
[a]The reaction was conducted using 1 mol% $Pd(OAc)_2$ and 2 mL of PEG-400 solvent at 65 ^oC for 4 h; [b]Yields were determined by ^1H NMR; [c]Z/E ratio was determined by ^1H NMR; [d]Reaction time was 4.5 h; [e]The reaction time was 5 h.

To understand the possible transfer hydrogenation path, we have carried out some controlled (**1A-1D, scheme 1**). Though, the PEG-400 polymer is a polar protic solvent, no reduction of **1a** was achieved indicating that PEG-400 couldn't serve as hydrogen source in the present PdNPS catalyzed STH reaction (**1A, scheme 1**). Besides, the transfer hydrogenation of **1a** using 1, 4-butanediol without using any catalyst was also unsuccessful, which specify that the Pd-catalyst is necessary for the activation of 1, 4-butanediol to allow its two H-atoms for the semi-hydrogenation of **1a (1B, scheme 1)**. Furthermore, *in situ* PdNPS catalyzed STH of **1a** by means of 1, 4-butanediol, has provided the 92% of **3a,** that contains 94% of **Z-3a**, along with the formation of γ-butyro lactone (GBL) byproduct confirmed that 1,4-butane diol acts as hydrogenating agent in the present STH approach (**1C, scheme 1**). The formation of (GBL) bi-product was analyzed ^1H NMR spectrum (ESI) and consistent with previous data.[23] The addition of radical scavenger 2, 2, 6, 6-Tetramethyl-piperidin-1-yl)oxyl (TEMPO) to the reaction mixture has not altered yield of **3a** as well as selectivity of **Z-3a**, that indicate our transformation don't proceed through radical intermediates (**1D, scheme 1**).



Scheme 1. Some supporting studies

[17a, 18, 22f & 24] we proposed a plausible mechanism (**Scheme 2)**. Initially, 1, 4-butanediol reacts with active PdNP catalytic species to form Pd-H_2 species (**A**) by yielding tetrahydrofuran-2-ol (**B**). Next, the addition of **A** to the internal alkyne **C** gives σ-vinyl palladium adduct **E** through the formation of activated intermediate **D**. Finally, the adduct **E** undergoes reductive elimination to give desired Z-olefin with the regeneration of active PdNPs. These PdNPs further react with **B** to form another Pd-H_2 species (**A**) along with the formation of GBL (**G**) byproduct. At this juncture, the newly formed Pd-H_2 species (**A**) continues the semi transfer hydrogenation of new internal alkyne molecule.



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Sheme 2. Proposed reaction pathway

In order to demonstrate the competence of this procedure, recyclability of the established *in situ* generated PdNPs catalytic system was studied using **1a** as a substrate (Figure 1). After first investigation, the reaction mixture was extracted with diethyl ether (4 X 10 mL) and solidified $Pd(OAc)_2$/PEG 400 was further allowed to a second catalytic run using same substrate. We have detected that transformation is faster, after the first catalytic run, by giving high yields of **3a** could be due to the generation of *in situ* PdNPs. Interestingly, no appreciable loss in the yield of **3a** was observed, using the present PdNPs catalytic system up to six recycle runs.

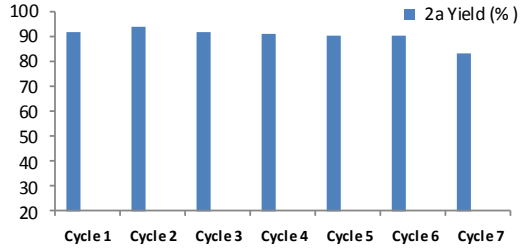

Figure 1. Recyclability of $Pd(OAc)_2$ + PEG-400 catalytic system

In conclusion, we first time established a simple and efficient palladium nanoparticles catalyzed semi transfer hydrogenation of alkynes to achieve highly selective Z-alkenes in good to excellent yields using stoichiometric amount of safer 1,4-

during the synthesis of Z-olefins makes our protocol attractive. Furthermore, the established catalytic system worked well up to 6 recycle runs.

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A Supplementary data

Experimental details, characterization data, TEM image of *in situ* PdNPs, copies of ^{1}H and ^{13}C NMR spectra of products can be found, in the online version, at http://dx.doi.org/

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- Operationally simple catalysis
- Safer and attractive H_2-source
- Z-selective semi transfer hydrogenation
- Valuable byproduct formation