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Palladium nanoparticles as efficient catalyst for C–S bond formation reactions†

Mei-Na Zhang, Shahid Khan, Junjie Zhang and Ajmal Khan *

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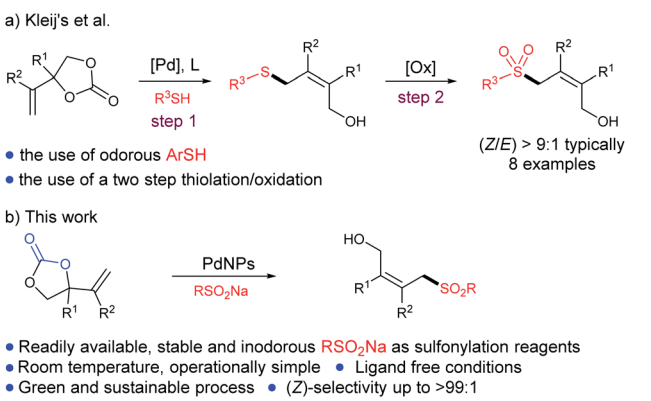
The development of green, economical and sustainable chemical processes is one of the primary challenges in organic synthesis. Herein, we report an efficient and heterogeneous palladium-catalyzed sulfonylation of vinyl cyclic carbonates with sodium sulfinates *via* decarboxylative cross-coupling. Both aliphatic and aromatic sulfinate salts react with various vinyl cyclic carbonates to deliver the desired allylic sulfones featuring tri- and even tetrasubstituted olefin scaffolds in high yields with excellent selectivity. The process needs only 2 mol% of $Pd_2(dba)_3$ and the *in situ* formed palladium nano-particles are found to be the active catalyst.

Introduction

The development of green, economical and sustainable organic processes that can be performed under ambient conditions in which the desired products can be obtained by the utilization of simple and readily available starting materials is one of the most important objectives in organic synthesis. Efforts to develop green processes and our ongoing interest in nano-catalysis, we focused to develop a practical and effective method for the formation of allylic sulfones since they have an important role in pharmaceuticals and biologically active drug agents,[1] such as anticancer,[1a] antibacterial,[1b] and weed control herbicides.[1c] Moreover, there have been several reports on the use of substituted allylic sulfones in asymmetric catalytic processes, providing useful synthesis of chiral sulfones.[2] Therefore; the development of effective methodologies to synthesize allylic sulfones has drawn considerable interest both in organic reactions[3] and in the pharmaceutical industry.[4] Reported methods included the use of transition metal-catalysed allylic substitution,[5] nucleophilic/radical addition,[6] hydrosulfination of allenes,[7] or alkynes,[8] and many others[9] by using toxic and expensive ligands. From the view point of economy and environmental concerns, the development of greener synthetic procedures using readily available, environmentally benign and inexpensive feedstock is highly appealing.

Since the initial reports,[10] many groups have found interest in vinyl cyclic carbonate chemistry to develop useful synthetic procedures for the synthesis of valuable building blocks.[11] Among them, Kleij and Yang's *et al.* have together reported the homogeneous palladium-catalysed thiolation, sulfonylation of vinyl cyclic carbonates to form allylic sulfones (Scheme 1a).[12] Regardless of their importance, these methods have few drawbacks. For example, the need of the bulky ligands to accomplish smooth conversions and the use of odorous thiols makes them limited towards the green and economical synthesis. The fast-growing field of palladium-nanocatalysis[13] could solve these issues, which has increasing interest in both industry field and organic reactions, due to its stability, recyclability and unique reactivity. Furthermore, two-dimensional nano-materials has become an important platform to design efficient single site catalysts for various applications, such as, CO_2 reduction and CO oxidation *etc.*[14]

In this context, we have proposed a "green", so-called "ligandless", palladium nano-catalyst, which has shown good reactivity without the addition of any external ligand or stabilizer. We planned to examine the catalytic activity of PdNPs in C–S bond formation reactions, since very few reports are



Scheme 1 Cross coupling of vinyl cyclic carbonates for C–S bond formation. (a) Homogeneous catalysis (b) heterogeneous catalysis.

Department of Applied Chemistry, School of Science, Xi'an Key Laboratory of Sustainable Energy Materials Chemistry, MOE Key Laboratory for Nonequilibrium Synthesis and Modulation of Condensed Matter, Xi'an Jiao Tong University, Xi'an 710049, P. R. China. E-mail: ajmalkhan@xjtu.edu.cn

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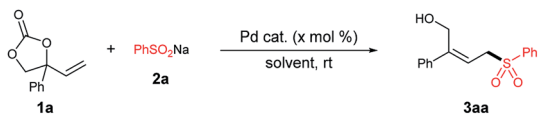
available for nanoparticle-catalyzed C–S bond formation,[15] and, to the best of our knowledge, no report is existing for PdNPs-catalyzed C–S bond formation reaction, which involves no additional stabilizer and or external ligand at ambient temperature.[16] In our continuing interest in green chemistry[17] and efforts towards the formation of quaternary all-carbon centers,[18] we herein report an external ligand-free palladium-catalyzed C–S bond formation reaction for the synthesis of allylic sulfones featuring tri- and or tetrasubstituted olefin scaffold in excellent yields and stereoselectivities at room temperature (Scheme 1b).

Results and discussion

With the expectation to obtain trisubstituted allylic sulfone **3aa**, we selected vinyl cyclic carbonate **1a** and sodium benzenesulfinate **2a** as model substrates. To our delight, the expected product **3aa** can be obtained in 12% isolated yield when the reaction was conducted in THF at room temperature using $PdCl_2$ as a catalyst (Table 1, entry 1). The effect of palladium-catalysts was screened, with the attempt to improving the yield and selectivity. Different palladium-catalysts were used under ligand free conditions at room temperature (Table 1, entries 2–4). Among them, only $Pd_2(dba)_3$ provided the desired trisubstituted allylic sulfone at an 92% isolated yield with >19 : 1 *Z*/*E* selectivity (Table 1, entry 4). The reaction was also performed in pure water, but only 42% of the desired product was isolated (Table 1, entry 5). The reaction efficiency did not improve further in other solvents (Table 1, entries 6–9). Furthermore, no desired product was detected when sodium benzenesulfinate was replaced by benzenesulfinic acid, which means the reaction worked as a simple nucleophilic addition.

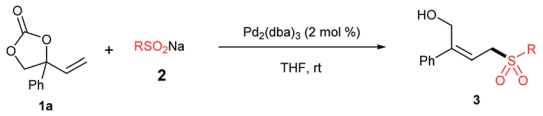
Table 1 Optimization of the reaction conditions[a]



Entry	Pd catalyst	Solvent	Yield[b] (%)	*Z*/*E*[c] (%)
1	$PdCl_2$	THF	12	3 : 1
2	$Pd(OAc)_2$	THF	32	3 : 1
3	$Pd(acac)_2$	THF	15	5 : 1
4	$Pd_2(dba)_3$	THF	92	19 : 1
5	$Pd_2(dba)_3$	H_2O	42	4 : 1
6	$Pd_2(dba)_3$	EtOH	48	8 : 1
7	$Pd_2(dba)_3$	Toluene	15	8 : 1
8	$Pd_2(dba)_3$	DCM	40	10 : 1
9	$Pd_2(dba)_3$	CH_3CN	85	17 : 1

[a] Reaction conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), 5 mol% of palladium-catalyst was used (entries 1–3), 2 mol% of palladium-catalyst was used (entries 4–9), solvent (1.0 mL), rt, 15 h. [b] The yields are of isolated materials for the mixture of the stereoisomers. [c] Determined by ^{1}H NMR of crude reaction mixture.

Table 2 Sodium sulfinate substrate scope[a]



Entry	2	3	Yield[b] (%)	Z/*E*[c]
1[d]	**2a** (R = Ph)	**3aa**	90	>19 : 1
2	**2b** (R = 4-MeC_6H_4)	**3ab**	90	>25 : 1
3	**2c** (R = 4-PhC_6H_4)	**3ac**	93	>25 : 1
4	**2d** (R = 4-ClC_6H_4)	**3ad**	88	>19 : 1
5	**2e** (R = 4-FC_6H_4)	**3ae**	82	>19 : 1
6	**2f** (R = 4-$NO_2C_6H_4$)	**3af**	94	>25 : 1
7	**2g** (R = 2,4-MeOC_6H_4)	**3ag**	95	>25 : 1
8	**2h** (R = 3,4-ClC_6H_4)	**3ah**	92	>19 : 1
9	**2i** (R = 3,5-$CF_3C_6H_4$)	**3ai**	93	>19 : 1
10	**2j** (R = 3-BrC_6H_4)	**3aj**	82	>19 : 1
11	**2k** (R = 2-ClC_6H_4)	**3ak**	85	>25 : 1
12	**2l** (R = 2-FC_6H_4)	**3al**	81	>25 : 1
13	**2m** (R = 2-naphthyl)	**3am**	92	>25 : 1
14	**2n** (R = 3-pyridine)	**3an**	93	>19 : 1
15	**2o** (R = 2-thiophene)	**3ao**	95	>19 : 1
16	**2p** (R = Me)	**3ap**	82	10 : 1
17	**2q** (R = Et)	**3aq**	86	>19 : 1
18	**2r** (R = ^{i}Pr)	**3ar**	90	>19 : 1
19	**2s** (R = cyclopropyl)	**3as**	87	>19 : 1
20	**2t** (R = $CH_3OCOCH_2CH_2$)	**3at**	82	10 : 1

[a] Reaction conditions: **1a** (0.20 mmol), **2** (0.30 mmol), $Pd_2(dba)_3$ (2 mol%), THF (1.0 mL), rt, 15 h. [b] The yields are of isolated materials for the stereoisomers. [c] Determined by ^{1}H NMR of crude reaction mixture. [d] The reaction was performed on gram-scale synthesis. The (*Z*)-configuration of **3ab** was determined by X-ray crystallography, those of the other products were assigned by analogy (see ESI for more details).

With the optimized reaction condition (Table 1, entry 4), the generality of the substrate scope of the decarboxylative cross-coupling reaction was investigated and the results are summarized in Table 2. A variety of sodium sulfinates (**2**) reacted effectively to provide the desired allylic sulfones (**3**) in high yield with excellent (*Z*)-selectivity. Both electron-donating and electron-withdrawing substituents on phenyl ring of sulfinate salts could react with vinyl cyclic carbonate **1a**, affording the corresponding products in excellent yields and stereoselectivities (Table 2, entries 2–12). The (*Z*)-configuration of allylic sulfone **3ab** was confirmed by X-ray analysis (see ESI† for details). In addition, sulfinate salts with bulky naphthyl and heteroaryl moieties were also tolerated under the optimized conditions supported by the formation of products **3am–3ao** (Table 2, entries 13–15).

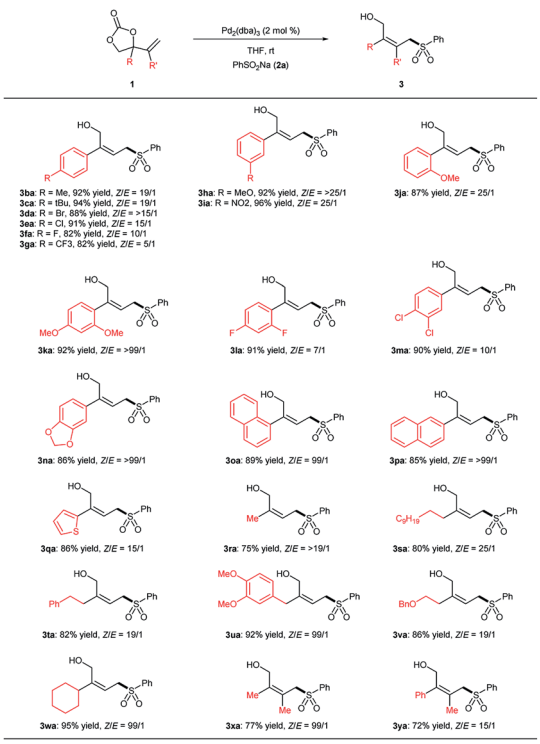
Furthermore, it is noteworthy that the alkyl sulfinate salts, which has posed great challenge in the synthesis of allylic sulfones due to their low reactivity, were also suitable nucleophiles in our reaction conditions.[5–9] Both primary and secondary alkyl sulfinate salts worked well under the optimized condition providing the corresponding allylic sulfones in high yield with excellent regioselectivities (Table 2, entries 16–19). Notably, upon employing a more functionalized sodium

sulfinate **2t** as the sulfonylation partner, the linear allylic sulfone **3at** was isolated in 82% yield with 10 : 1 (*Z*)-selectivity. The reaction leading to allylic sulfone **3aa** was easily scaled up to gram scale without any loss of the stereoselectivity and yield (5 mmol scale: 1.3 g, 90% yield, >19 : 1 *Z*/*E*, Table 2, entry 1).

As described in Table 3, various vinyl cyclic carbonates were tested under the optimized conditions to further examine the reaction scope. A variety of phenyl-substituted vinyl cyclic carbonates, with different electronic and steric properties, were tolerated to provide the desired allylic sulfones (**3ba–3na**) in high yields with excellent stereoselectivities. Vinyl cyclic carbonates with bulky naphthyl group also worked well to provide allylic sulfones **3oa** and **3pa** in high yields with excellent (*Z*)-selectivity. Vinyl cyclic carbonate with versatile furan moiety also reacted smoothly to furnish the desired product **3qa** in high yield with high stereoselectivity (86% yield, 15 : 1 *Z*/*E*).

Furthermore, the conditions were also suitable for the reaction of alkyl substituted vinyl cyclic carbonates (**2ra–2ya**), providing the corresponding products in high yields and excellent stereoselectivities. In the case of methyl-substituted cyclic carbonate **1r**, the formation of branched allylic sulfone was observed which affected the linear product yield. With vinyl carbonate bearing longer alkyl chain, the expected allylic sulfone was also obtained in high yield and regioselectivity (80% yield, >25 : 1 *Z*/*E*, **3sa**). Vinyl cyclic carbonates **1t**, **1u** and **1v** that have different substituents in the alkyl chain were allowed to react with sulfinate salt **2a**, good yield and stereoselectivity were obtained (**3ta**, **3ua** and **3va**). In addition, cyclic carbonate with cyclohexyl-substituent afforded the desired product in high yield (95% yield, **3wa**) with excellent (*Z*)-selectivity. Furthermore, the substitution of alkyl group (R = Me) at the β-position of the olefin scaffold is workable with excellent stereoselectivity (**3xa** and **3ya**).

Table 3 Vinyl cyclic carbonate substrate scope[a,b,c]



[a] Reaction conditions: **1a** (0.20 mmol), **2** (0.30 mmol), $Pd_2(dba)_3$ (2 mol%), THF (1.0 mL), rt, 15 h. [b] The yields are of isolated materials for the stereoisomers. [c] Determined by ^1H NMR of crude reaction mixture. The (*Z*)-configuration of **3ab** was determined by X-ray crystallography, those of the other products were assigned by analogy (see ESI for more details).

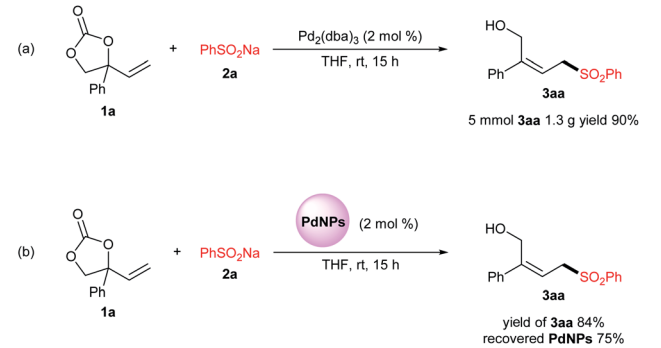


Fig. 1 (a) Gram-scale synthesis and (b) recyclability of PdNPs.

To demonstrate the synthetic use of the present methodology, gram scale synthesis was carried out (Fig. 1a). Compound **3aa** was synthesized from **1a** and **2a** (5.0 mmol scale) over $Pd_2(dba)_3$ (2 mol%) at an 90% yield (1.3 g). At the end of reaction, the mixture was filtered and washed to give a dark black solid, from which palladium nano-particles were observed with size of 5–70 nm upon TEM analysis.[19] Furthermore, we evaluated the recyclability of these free-formed palladium nanoparticles, replacing $Pd_2(dba)_3$, showing a small decline in the catalytic activity in a test reaction (Fig. 1b) which clearly indicate that catalyst is free from any sort of agglomeration. Notably, a small decrease in the recovered PdNPs might be attributed due to workup and recovery procedures.

In order to gain insight into the reaction mechanism, especially for the high activity of the palladium catalyst, transmission electron microscopy (TEM) analysis was carried out in this decarboxylative cross coupling reaction.[19] The Pd(0) precursor serve as source of PdNPs due to the decomposition of $Pd_2(dba)_3$ in the solid state to release (dba) and formation of Pd black: $Pd_2(dba)_3 \rightarrow dba + [Pd]$.[20] Analysis by TEM confirmed the

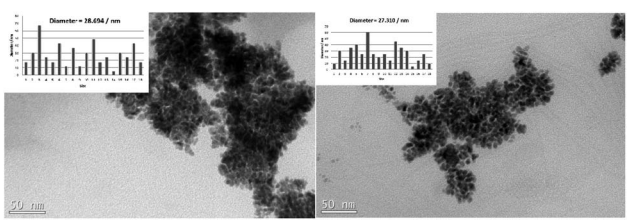


Fig. 2 TEM images of PdNPs for the coupling of **1a** with **2a** in THF. A sample taken after 30 minutes (right). A sample taken after 15 hours (left).

presence of palladium nano-particles with dimensions of 5–70 nm as shown in Fig. 2. These results revealed that $Pd_2(dba)_3$ was reduced to form palladium nano-particles and the PdNPs are likely stabilized by dba.

Conclusions

In conclusion we have developed a palladium nanoparticle catalyzed cross-coupling of vinyl cyclic carbonates with sodium sulfinates under external ligand free conditions and without the addition of any stabilizer at room temperature. We are able to construct allylic sulfones in high yield and (*Z*)-selectivity. We found that a broad range of substitution is tolerated on either coupling partner. Taken together with its cost efficient, environmentally friendly, broad substrate scope, chemo-selectivity, readily available and stable starting materials and operational simplicity, this green methodology will find practical use in synthetic setting.

Conflicts of interest

The authors declare no conflicts of interest.

Acknowledgements

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