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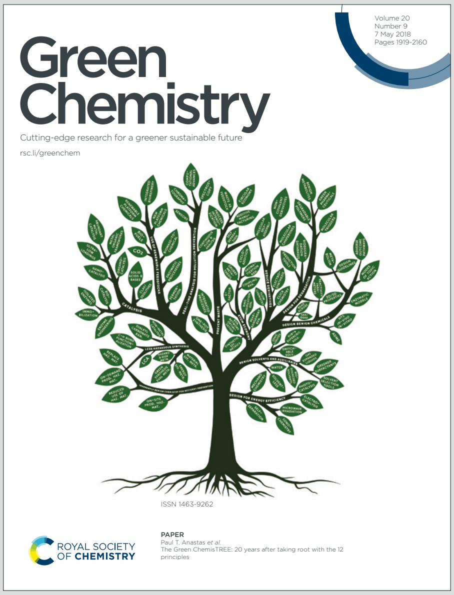

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COMMUNICATION

Palladium nano-particles as recyclable catalyst for C-O bond formation under solvent free conditions

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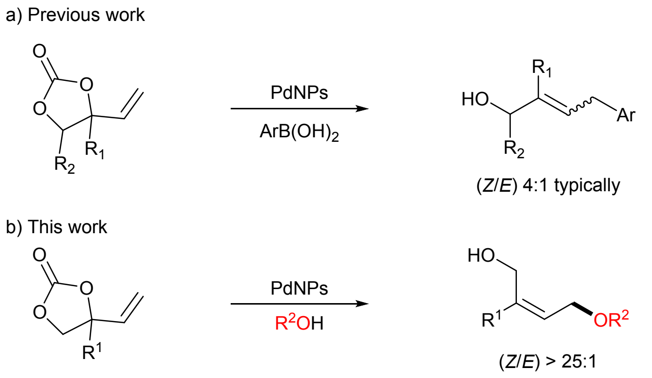
The development of green, economical and sustainable chemical processes is one of the primary challenges in organic chemistry. Herein, we report a recoverable heterogenous palladium catalysis for the stereoselective synthesis of multi-functionalized allylic ethers under solvent free conditions. This method is based on an *in situ* generated PdNPs catalyzed O-allylation of alcohols with vinyl cyclic carbonates. The solvent-free conditions, easily recoverable catalyst, efficient recycling, and operational simplicity renders the protocol green, economic and sustainable.

The development of green and economical organic processes that can be performed under solvent-free, and at ambient conditions in which the catalyst can be recovered by simple filtration without the loss of catalytic activity is highly desirable in organic synthesis. Efforts to develop economical and green procedures, we focused to develop a practical method for the preparation of allylic ethers since it can be used as starting material in many organic reactions for the synthesis of valuable building blocks.[1] Generally, preparation of allyl aryl ethers relies on Williamson-type ether synthesis that uses highly active allyl halides and strongly basic alkoxide anions.[2] Therefore, considerable efforts have been committed to their synthesis by employing transition metal-catalysed allylic substitution reactions.[3] However, most of these reported methods are carried out by using a homogeneous non-recyclable catalyst with expensive ligands and toxic organic solvents. In the context of low cost and environmental acceptability, the development of cost-efficient, heterogeneous and recyclable catalysis under solvent-free conditions is highly desirable and essential.



Recyclable, Green, Regio- and Stereoselective Catalysis
Solvent and ligand-free conditions, Easily accessed materials

Scheme 1 Cross coupling reactions of vinyl cyclic carbonates catalyzed by palladium nano-catalyst.

Recently, vinyl cyclic carbonates have found great importance in organic synthesis serving as dipole precursors to generate π-allyl palladium intermediate after decarboxylation and hence provide direct access to a variety of synthetically as well as medicinally important compounds.[4] Most recently, Kleij and co-workers have reported a homogeneous palladium-catalyzed decarboxylative etherification by the utilization of vinyl cyclic carbonates to form allylic ethers.[5a] However, the use of bulky phosphine ligands and nonrecyclable homogeneous Pd-catalyst create economic and environmental problems to extending their scope. The fast-growing field of palladium nano-catalysis could address these difficulties, which has increasing interest in both organic reactions and industry field, due to its stability, recyclability and unique reactivity.[6] In this account, we have proposed a "green'', so-called "ligandless", palladium nano-catalyst, which has shown good reactivity and recyclability without the addition of any stabilizer or base under solvent free conditions. We planned to examine the catalytic activity of PdNPs in C–O bond formation reactions, since very few reports are available for nanoparticle-catalysed C–O bond formation,[7] and, to our knowledge, no report is existing for PdNPs-catalysed C–O bond formation, which

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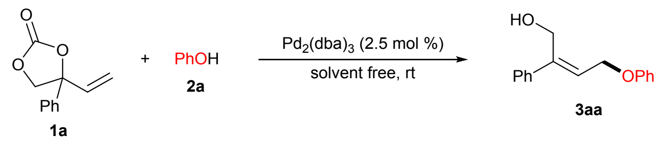
involves no additional stabilizer, base and phosphine ligand under solvent free conditions.[8] Our interest in green chemistry and efforts toward PdNPs catalysed sustainable organic reactions (Scheme 1a),[9] we herein report an external ligand-free and reusable PdNPs catalysed C–O bond formation reaction for the synthesis of allylic ethers with excellent yields and stereoselectivities under solvent-free conditions at room temperature (Scheme 1b).

Table 1 Optimization of reaction conditions[a]



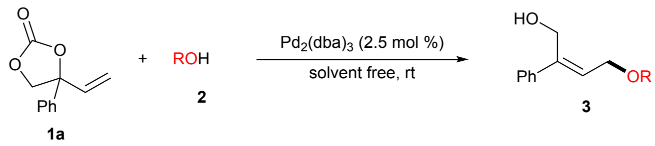
Entry	Deviation from optimal conditions	Yield[b] [%]	Z/E[c]
1	Without palladium source	0	--
2	No deviation	93	19:1
3	$PdCl_2$	< 15	5:1
4	$Pd(OAc)_2$	20	5:1
5	$Pd(acac)_2$	< 10	5:1
6	Solvents = THF, DMF, toluene	< 10	ND
7	H_2O used as solvent	20	8:1
8	Amount of $Pd_2(dba)_3$ = 1%, 0.5%	76, 54	19:1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), rt, 15 hours. [b] The yields are of isolated materials for the mixtures of the stereoisomers. [c] Determined by ^1H NMR of crude reaction mixture. The (*Z*)-configuration was confirmed by the comparison of ^1H-NMR with that of the reported literature.[5]

Firstly, we use the reaction of Phenyl substituted vinyl cyclic carbonate (**1a**) with phenol (**2a**) as model substrates to optimize the reaction conditions (Table 1). Different palladium-precursors, $Pd_2(dba)_3$, $PdCl_2$, $Pd(OAc)_2$ and $Pd(acac)_2$ were used under external ligand and solvent-free conditions at room temperature (Table 1, entries 2-5). Among them, only $Pd_2(dba)_3$ provided the desired trisubstituted allyl aryl ether (**3aa**) at an 93% isolated yield with 19:1 *Z/E* ratio. The use of other palladium-precursors resulted in lower conversion (Table 1, entry 3-5). The solvent effect and catalyst loading were next investigated. The reaction efficiency was decreased dramatically in organic solvents like THF, DMF and toluene (Table 1, entry 6). The reaction was also performed in pure water, but only 20% of the desired product was obtained (Table 1, entry, 7). When the catalyst amount decreased from 5 mol% to 2 mol% and 1 mol%, the isolated yield of the desired product **3aa** dropped from 93% to 76 % and 54% respectively (Table 1, entry 8). During the optimization studies we found that palladium was essential for promoting the reaction; in the absence of palladium source, the reaction did not proceed at all and only starting materials were collected (Table 1, entry 1). The (*Z*)-configuration of **3aa** was confirmed by the comparison of ^1H-NMR with that of reported in literature.[5a] The high (*Z*)-selectivity in these transformations was found, because of the in situ formation of a six-member palladacycle conformed by DFT calculations reported in the previously related literature.[5b-c]

With the optimized reaction conditions developed, 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 phenols reacted effectively to provide the desired allyl aryl ethers in high yield with excellent (*Z*)-selectivity. Both electron-donating and electron-withdrawing substituents on phenols could react with **1a**, affording the corresponding products in high yields and stereoselectivities (Table 2, entry 2-13). As for the *p*-substituted phenols, the products **3ab**, **3ac**, **3ad**, **3ae** and **3af** were produced in high yields (91%, 96%, 88%, 92%, and 93%) with excellent stereoselectivities. In the cases of phenols with substituents on *ortho*-position, allylic ethers **3ag**, **3ah** and **3ai** were smoothly produced in 84%, 89% and 82% yield respectively with excellent (*Z*)-selectivity. Furthermore, the bi-substituted and tri-substituted phenol furnished the desired product **3aj** and **3ak** in 90% and 72% yields with excellent (*Z*)-selectivity. The lower yield obtained in case of tri-substituted phenol could be possibly due to the steric hindrance effect. Moreover, 1-naphthol and 2-naphthol gave **3al** and **3am** in 94% and 92% yields, respectively with excellent stereoselectivity. It should be mentioned that methanol, which posed great challenge to be installed into allylic ethers due to their low reactivity, were also suitable substrate in our optimized condition (**3an**). Unfortunately, *iso*-propanol and *tert*-butanol could not provide the desired products (**3ao** and **3ap**) and in both cases, the conversion was less than 5%.

Table 2 Alcohol substrate scope[a]



Entry	2 (R)	3	Yield[b] (%)	Z/E[c]
1	**2a** (R = Ph)	**3aa**	93	19:1
2	**2b** (R = 4-MeC_6H_4)	**3ab**	91	25:1
3	**2c** (R = 4-$MeOC_6H_4$)	**3ac**	96	25:1
4	**2d** (R = 4-BrC_6H_4)	**3ad**	88	19:1
5	**2e** (R = 4-$NO_2C_6H_4$)	**3ae**	92	15:1
6	**2f** (R = 4-CNC6H4)	**3af**	93	10:1
7	**2g** (R = 2- $NO_2C_6H_4$)	**3ag**	84	25:1
8	**2h** (R = 2- PhC_6H_4)	**3ah**	89	25:1
9	**2i** (R = 2- $CHOC_6H_4$)	**3ai**	82	25:1
10	**2j** (R = 4-allyl-2-MeO-C_6H_3)	**3aj**	90	25:1
11	**2k** (R = 2,3,4-trimethyl-C_6H_2)	**3ak**	72	25:1
12	**2l** (R = 1-naphthyl)	**3al**	94	25:1
13	**2m** (R = 2-naphthyl)	**3am**	92	25:1
14	**2n** (R = Me)	**3an**	78	19:1
15[d]	**2o** (R = ^iPr)	**3ao**	> 5	ND
16[d]	**2p** (R = ^tBu)	**3ap**	> 5	ND

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Pd_2(dba)_3$ (2.5 mol%), rt, 15 hours. [b] The yields are of isolated materials for the mixtures of the stereoisomers. [c] Determined by ^1H NMR of crude reaction mixture. [d] ^1H-NMR-yield. The (*Z*)-configuration of **3aa** and **3ac** was confirmed by the comparison of ^1H-NMR with that of the reported literature,[5a] those of the other products were assigned by analogy.

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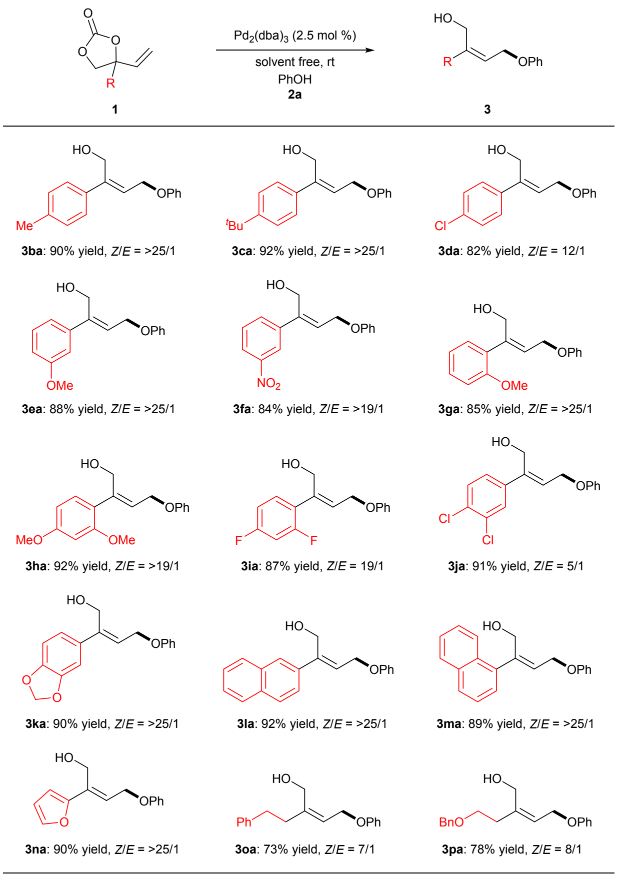
As described in Table 3, various vinyl cyclic carbonates were tested under the optimized conditions to further examine the reaction scope. A variety of phenyl-substituted vinyl cyclic carbonates, with different electronic and steric properties, were tolerated to provide the desired allyl aryl ethers **3ba**-**3ka** in high yields with excellent stereoselectivities. Vinyl cyclic carbonates with bulky naphthyl group also worked well to provide allylic ethers **3la** and **3ma** in high yields with excellent (*Z*)-selectivity. Vinyl cyclic carbonate with versatile furan moiety also reacted smoothly to furnish the desired product **3na** in high yield with high stereoselectivity. Furthermore, the conditions were also suitable for the reaction of alkyl substituted vinyl cyclic carbonates (**1o**-**1p**), providing the corresponding products in good yields albeit with comparatively low stereoselectivities.

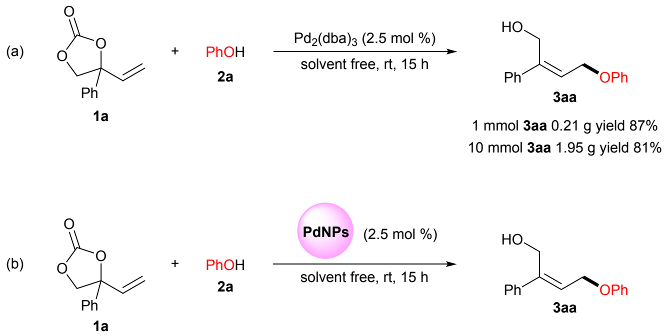
Table 3 Vinyl cyclic carbonate substrate scope[a]



3ba: 90% yield, *Z*/*E* = >25/1
3ca: 92% yield, *Z*/*E* = >25/1
3da: 82% yield, *Z*/*E* = 12/1
3ea: 88% yield, *Z*/*E* = >25/1
3fa: 84% yield, *Z*/*E* = >19/1
3ga: 85% yield, *Z*/*E* = >25/1
3ha: 92% yield, *Z*/*E* = >19/1
3ia: 87% yield, *Z*/*E* = 19/1
3ja: 91% yield, *Z*/*E* = 5/1
3ka: 90% yield, *Z*/*E* = >25/1
3la: 92% yield, *Z*/*E* = >25/1
3ma: 89% yield, *Z*/*E* = >25/1
3na: 90% yield, *Z*/*E* = >25/1
3oa: 73% yield, *Z*/*E* = 7/1
3pa: 78% yield, *Z*/*E* = 8/1

[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.3 mmol), $Pd_2(dba)_3$ (2.5 mol%), rt, 15 hours. [b] The yields are of isolated materials for the mixtures of the stereoisomers. [c] Determined by ^1H NMR of crude reaction mixture. The (*Z*)-configuration of **3ba** was confirmed by the comparison of ^1H-NMR with that of the reported literature,[5] those of the other products were assigned by analogy.

To demonstrate the application of the present protocol, gram scale transformation was carried out (Fig. 1a). The compound **3aa** can be prepared from **1a** and **2a** (1.0 mmol) over $Pd_2(dba)_3$ (2.5 mol%) at an 87% yield (0.21 g). This procedure can be directly enlarged to 10 mmol scale, producing **3aa** at an 81.4% isolated yield (1.95 g). At the end of reaction on 10 mmol, the mixture was filtered and washed to give a dark black solid, from which palladium nano-particles were observed with size of 5-50 nm upon TEM analysis.[10] In addition, we evaluated the recyclability of these free-formed palladium nano-particles, replacing $Pd_2(dba)_3$, showing no appreciable loss in the catalytic activity in a test of five cycles (Fig. 1b and Fig. S5) which clearly indicate that catalyst is free from any sort of agglomeration. Notably, a small decrease in the product yields in the subsequent catalytic cycles might be attributed the minor loss of PdNPs catalyst during workup and recovery procedures.



cycle	yeild of **3aa**	recovered **PdNPs**
1	89%	85%
2	85%	82%
3	82%	84%
4	78%	75%
5	75%	76%

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

Furthermore, in the kinetic study for the coupling reaction, a hot filtration test was used to examine the heterogeneity of Pd-catalyst (Fig. S6).[10] To understand whether the reaction is catalyzed by heterogeneous or a leached catalyst, a hot filtration experiment was performed for the preparation of **3aa**. A set of four reactions were separately carried out and catalyst was removed from the reaction mixtures through centrifugation after 30 minutes for first reaction (30%, NMR yield), after 60 minutes for second reaction (56%, NMR yield), after 2 hours for third reaction (65%, NMR yield), after 5 hours for fourth reaction (82%, NMR yield), and after 10 hours for fifth reaction (91%, NMR yield). The remaining reaction mixtures were further allowed to react for next 13 h. However, no improvements in the yields were observed in all five reactions. This confirms that no leaching of PdNPs catalyst was observed during the course of reactions.

Transmission electron microscopy (TEM) analysis was carried out to determine the reason for the high activity of the palladium catalyst in this decarboxylative cross coupling reaction. 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].[11] Analysis by TEM confirmed the presence of palladium nano-particles with dimensions of 5-50 nm as shown in

Figure 2.[10] These results revealed that $Pd_2(dba)_3$ was reduced to form palladium nano-particles and the PdNPs are likely stabilized by dba.

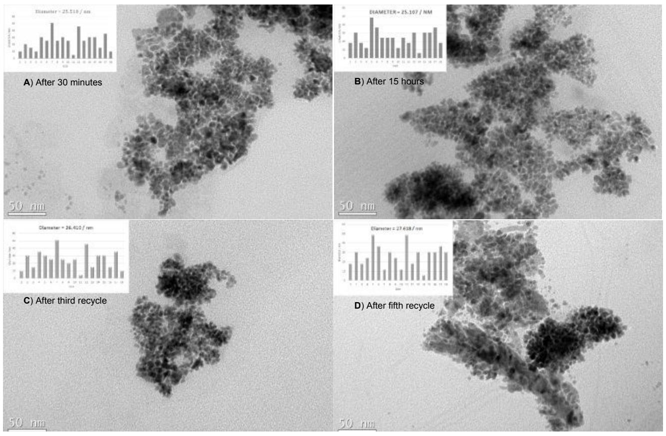


Fig. 2 TEM images of PdNPs for the coupling reaction of **1a** with **2a** under solvent and external ligand free-conditions. A sample taken after 30 minutes (A). A sample taken after 15 hours (B). A sample taken after third recycles (C). A sample taken after fifth recycles (D).

Conclusions

In summary, we have developed an efficient, practical and green method for the synthesis of allyl aryl ethers featuring tri-substituted olefin scaffolds from phenols and vinyl cyclic carbonates using inexpensive $Pd_2(dba)_3$ as the catalyst under ligand and solvent free-conditions. The reaction need only 2.5 mol% of catalyst and the in situ formed PdNPs are found to be active catalyst. The catalytic system shows good tolerance towards both aryl and alkyl-substituted vinyl cyclic carbonates and phenols, providing the corresponding allylic products in high yields and stereoselectivities. This protocol can be easily scaled-up and applied, as a demonstration, in the synthesis of tri-substituted allyl aryl ether **3aa** at a yield of “1.95g”.

Conflicts of interest

There are no conflicts to declare.

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