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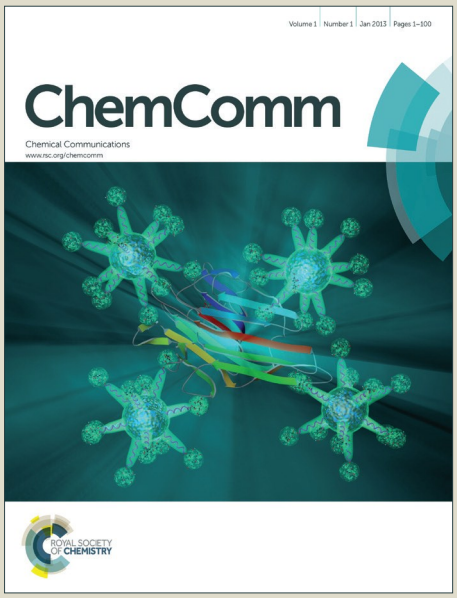




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ARTICLE TYPE

# Palladium-Catalyzed Aerobic Oxidative Double Allylic C-H Oxygenation of Alkenes: A Novel and Straightforward Route to α,β-Unsaturated Esters

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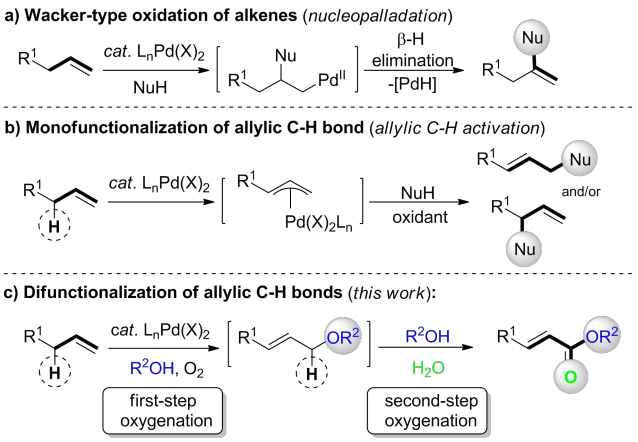
**A mild tandem oxidative functionalization of allyl aromatic hydrocarbons was accomplished in the catalytic system of Pd(OAc)$_2$/DMA under 1 atm $O_2$. The green twofold C-O bond formation involving double allylic C-H oxygenation, unlocks opportunities for markedly different synthetic strategies. Moreover, the reaction affords aryl *α,β*-unsaturated esters directly from readily available terminal olefins in moderate to good yields with excellent chemo- and stereoselectivities.**

Carbon-carbon double bond of alkenes is one of the basic functional groups, selective catalytic oxidative transformations of its hydrocarbons enabling a significant streamlining of the synthesis of complex molecules.[1, 2] Among the various transition metal-catalyzed selective oxidation functionalization of C-H bonds, Pd catalysts have displayed encouraging versatility in the construction of diverse carbon-carbon and carbon-heteroatom bonds.[3] In particular, the Pd-catalyzed Wacker-oxidation[4,5] and functionalization of allylic C-H bond[6] of terminal olefins have received much attention because of useful protocols for direct functionalization at the C2 and C1 or C3 positions. Mechanistically such reactions are believed to proceed through two distinctive routes: (i) nucleopalladation (Scheme 1a), (ii) palladium-catalyzed allylic C-H activation (Scheme 1b). Commonly, once the alkene is coordinated to palladium, the formation of an intermediate π-allyl-palladium complex is typically not observed, since the ensuing π-olefin-palladium complex has a propensity to undergo nucleophilic attack at the more substituted vinylic carbon providing Wacker-type products.[7] In this context, controlling the selectivity of palladium catalysts in oxidative alkene functionalization to constitute valuable building blocks in organic synthesis remains challenging and rewarding.

Recently, significant progress has been made in the evolution of Pd(II)-catalyzed monofunctionalization reactions of allylic C-H bond of alkenes.[8-14] However, no general method has been reported for tandem allylic C-H functionalization, due to poor reactivity and competitive over-oxidation of alkene substrates and their products. To overcome these limitations, we hypothesized that intermolecular dioxygen-coupled oxidative oxygenation of olefins with alcohol would be capable of generating linear allylic ether. The new formation of C-O bond, together with double bonds at the *β*-position, has an activating effect to the adjacent C-H bonds, which enables these compounds to serve as precursors that undergo next functionalization in the presence of Pd(II), thereby overcoming the low inherent reactivity of *β*-functionalized allylic alkenes. Moreover, the use of molecular oxygen[15, 16] as terminal oxidant overcomes the key limitations of the undesired over-oxidation. Herein, we report the discovery and development of a strategically distinct approach to *α,β*-unsaturated esters through palladium-catalyzed aerobic oxidative double allylic C-H oxygenation of alkenes (Scheme 1c).




**Scheme 1.** Pd-catalyzed oxidative functionalization of C-H bond of alkenes.

On the basis of our previous work on palladium-catalyzed direct functionalization of allylic C-H bonds of alkenes,[8n,11,16e,16f] the investigation was started by searching for a suitable catalyst/solvent combination using allylbenzene **1a** and *n*-butanol **2a** as model substrates in the presence of $Pd^{II}$ (10 mol %) using 1 atm dioxygen as the oxidant (Table 1). To our delight, the expected product **3aa** was obtained in a promising 11% yield under the initial conditions (Table 1, entry 1). The concomitant formation of small amounts of oxidative Wacker product **6a** and alkene monooxygenation product **5aa** was also observed in the reaction. Screening of various solvents indicated that *N,N*-dimethylacetamide (DMA) was optimal[17] and the yield of **3aa** significantly increased to 84% without **5aa** detected, while in other solvents such as 1-methyl-2-pyrrolidinone (NMP), *N,N*-dimethylformamide (DMF), dioxane, toluene, none or only trace amount of the target butyl cinnamate **3aa** was detected (Table 1, entries 2-6). Attempts to use alternative catalysts such as $PdCl_2$, $PdI_2$, $PdBr_2$ and $Pd(TFA)_2$ proved less efficient affording **3aa** in

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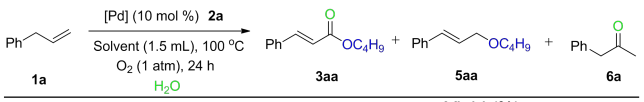
**Table 1.** Effects of Solvents and Catalysts.[a]

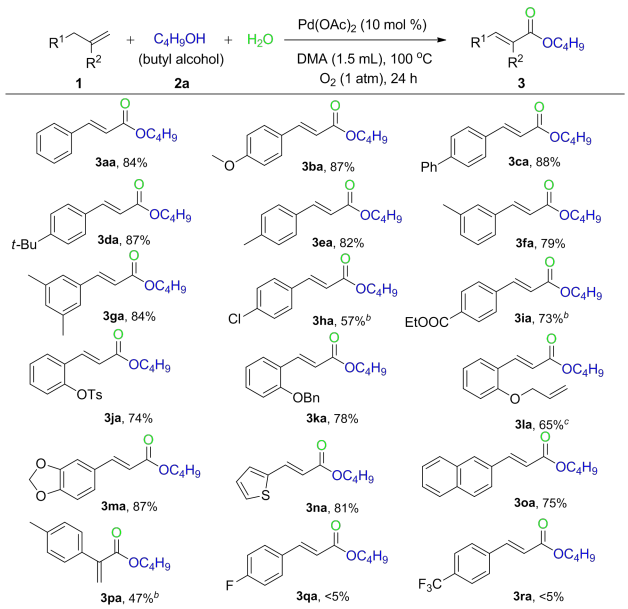



| Entry | [Pd] | Solvent | Yield (%) 3aa | 5aa | 6a |
|---|---|---|---|---|---|
| 1 | $Pd(OAc)_2$ | DMSO | 11 | 53 | 5 |
| 2 | $Pd(OAc)_2$ | DMA | 84 | n.d. | 2 |
| 3 | $Pd(OAc)_2$ | NMP | 23 | 13 | n.d. |
| 4 | $Pd(OAc)_2$ | DMF | n.d. | n.d. | 38 |
| 5 | $Pd(OAc)_2$ | Dioxane | n.d. | 10 | 7 |
| 6 | $Pd(OAc)_2$ | Toluene | n.d. | 6 | 3 |
| 7 | $PdCl_2$ | DMA | 7 | 6 | 18 |
| 8 | $PdI_2$ | DMA | 5 | 11 | 10 |
| 9 | $PdBr_2$ | DMA | 5 | 7 | 11 |
| 10 | $Pd(TFA)_2$ | DMA | n.d. | 5 | 23 |
| 11 | - | DMA | n.d. | n.d. | n.d. |
| 12[b] | $Pd(OAc)_2$ | DMA | 51 | 5 | 9 |

[a] Reaction conditions: [Pd] (10 mol %), **1a** (0.5 mmol), **2a** (0.5 mL), $H_2O$ (1.5 equiv.), $O_2$ (1 atm), 24 h. Yield determined by GC using diphenyl ether as the internal standard. n.d. = not detected. [b] Reaction run at 90 °C.

lower yields (Table 1, entries 7-10). No product formation was observed in the absence of $Pd^{II}$-catalyst (Table 1, entry 11). Lowering the temperature to 90 °C just led to a lower yield (Table 1, entry 12).

**Table 2.** Substrate Scope of Alkenes [a]

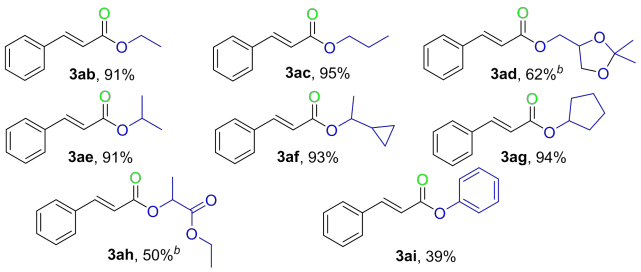



[a] Reaction conditions: **1** (0.5 mmol), **2a** (0.5 mL), $Pd(OAc)_2$ (10 mol %), DMA (1.5 mL), $H_2O$ (1.5 equiv.), $O_2$ (1 atm) at 100 °C. Yields referred to isolated yields. [b] Reaction run at 110 °C. [c] Reaction run at 80 °C.

With the optimized conditions established, the scope of the terminal alkenes was first examined. As summarized in Table 2, a series of substituted allyl arenes, including some with electron-donating groups (Me, Ph, $^t$Bu, OMe) and some with electron-withdrawing groups (Cl, COOEt), were converted into the corresponding *α,β*-unsaturated esters in moderate to good yields (**3aa-3ia**). But the substrate with electron-withdrawing substituent was less reactive than that with electron-donating substituent in this transformation. And the substituents at the *para*, *meta*, and *ortho* positions of the arene ring did not affect the efficiencies (**3ea**, **3fa, 3ja-3la**). Heteroaryl-substituted propenes such as 5-allylbenzo[d][1,3]-dioxole (**1m**) and 2-allylthiophene (**1n**) also produced the desired products in good yields. Interestingly, 2-naphthylpropene could give the corresponding product in 75% yield (**3oa**). The transformation of 1-methyl-4-(prop-1-en-2-yl)benzene proceeded efficiently under the optimized conditions affording the desired product (**3pa**) in moderate yield. Unfortunately, 1-allyl-4-fluorobenzene (**1q**) and 1-allyl-4-(trifluoromethyl)benzene (**1r**) afforded only trace amount of the desired products.[18] And terminal alkyl olefins such as 1-octene, led to the formation of ketones through the Wacker process, instead of the desired product.

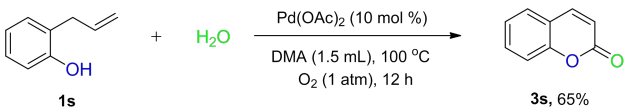
Next, we examined the generality of this novel reaction process with respect to aliphatic alcohols (Table 3). Various primary aliphatic alcohols transferred to the corresponding functionlization products in high yields with excellent chemo- and stereoselectivities (**3ab**, **3ac**). Remarkably, substituted methanols bearing acetal group was tolerated in this transformation (**3ad**). The reaction of **1a** with simple secondary alcohols, such as isopropanol, 1-cyclopropylethanol and cyclopentanol also proceeded smoothly to afford the desired *α,β*-unsaturated esters in good to excellent yields (**3ae**, **3af**, and **3ag**). Ethyl lactate was also compatible, and the desired product **3ah** was obtained in 50% yield. Unexpectedly, phenol also proceeded efficiently under the optimized conditions albeit in a low yield (**3ai**).

**Table 3.** Substrate Scope of Aliphatic Alcohols and Phenol [a]




[a] Reaction conditions: 1a (0.5 mmol), 2 (3 equiv.), $Pd(OAc)_2$ (10 mol %), DMA (1.5 mL), $H_2O$ (1.5 equiv), $O_2$ (1 atm) at 100 °C. Yields referred to isolated yields. [b] Reaction run at 110 °C.

This catalytic system was also found to be applicable to intramolecular oxidative cyclizations. 2-Allylphenol was smoothly converted into 2*H*-chromen-2-one (**3s**) in a moderate yield and a small quantity of Wacker-type cyclization product, 2-methylbenzofuran, was also detected (Scheme 2).




**Scheme 2.** Intramolecular Allylic C-H Dioxygenation of 2-Allylphenol.

Further, competition experiments were performed between the intra- and intermolecular reactions. When 2-allylphenol, together with butan-1-ol, was added to this catalytic system, both **3s** and **4ta** were detected. 2-Allylphenol derivative bearing common protecting groups, such as trimethylsilyl, readily engaged in intermolecular esterification combined with the subsequent intramolecular Wacker oxidation cyclization producing the benzofuran-2-carboxylate derivatives with alcohols of different chain length (Scheme 3). Additionally, the high yield of intermolecular esterification uncovers the rate of intermolecular

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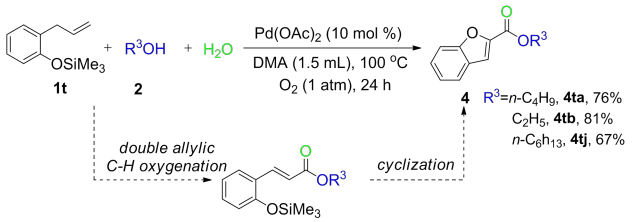
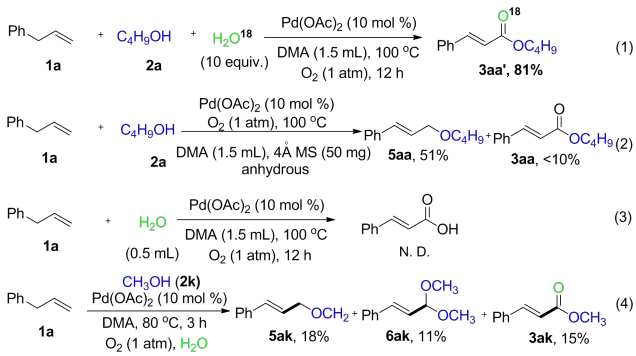
esterification is prior to intramolecular Wacker oxidation in this catalytic system.




**Scheme 3.** Applications of the Novel Synthetic Sequence to Benzofuran-2-carboxylate.

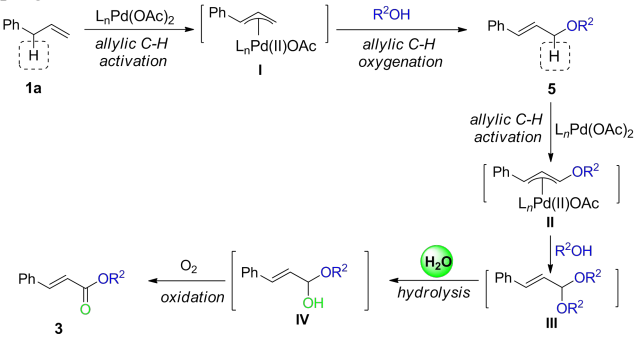
Several control experiments were performed to gain some mechanistic insight into the present reaction (Scheme 4): (i) the reaction of **1a** and **2a** adding $H_2O^{18}$ under the standard conditions, afforded $O^{18}$-labled product **3aa'** in good yield; (ii) the reaction of **1a** with **2a** was carried out in anhydrous DMA, affording **5aa**[19] in 51% yield, and less than 10% yield of **3aa**[20]; (iii) the reaction of **1a** was carried out without alcohols, cinnamyl acid was not detected. It indicated that it does not follow the traditional esterification route involving coupling preoxidized carboxylic acid and alcohol fragments;[21] (iv) a standard condition reaction of allylbenzene **1a** with methanol **2k** was performed, surprisingly, the corresponding acetal was detected by GC-MS after 3 h and it vanished after 16 h. These results indicated the possibility that nucleophilic attack of alcohols to π-allyl-palladium species occurred to form the corresponding allyl ethers and allyl acetal species.




**Scheme 4.** Control Experiments.

According to these results, we proposed the mechanism shown in Scheme 5. First, Pd(II) reacts with allylbenzene **1a** to produce the corresponding π-allyl-palladium species **I** through the allylic C-H bond activation.[22] Next, intermediate **I** is subjected to the nucleophilic attack of alcohol to afford the oxidative allylic oxygenation product **5**, which subsequently undergoes allylic C-H bond activation to give π-allyl-palladium species **II**. Intermediate **II** engages in the formation of the second C-O bond by reacting with another molecule alcohol affording corresponding allyl acetal species **III** and then, hydrolysis of intermediate **III** gives intermediate **IV**. Finally, oxidation-dehydrogenation of **IV** by dioxygen provides the target product **3**. Simultaneously, dioxygen plays a role in oxidating Pd(0) to regenerate the active catalyst species Pd(II).

In summary, we have developed a catalytic system of $Pd(OAc)_2$/DMA under 1 atm $O_2$ double allylic C-H oxygenation reaction, which represents a significant advance in catalytic reactions for the expedient and selective synthesis of a broad range of linear aryl *α,β*-unsaturated esters, wherein alkene was utilized as the carbonyl carbon source of acylating reagent with $O_2$ as a benign oxidant. Preliminary studies indicated that the process is *via* *β*-oxygenation allylic alkenes with alcohols forming a linear allylic ether, followed by Pd-catalyzed allylic C-H oxygenation with another alcohol, then, hydrolysis and finally oxidation-dehydrogenation to the corresponding products. Works along this line, further investigations to expand the scope of this transformation and elucidate the detailed mechanism are in progress.




**Scheme 5.** Plausible Reaction Mechanism.

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## Notes and references

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† Electronic Supplementary Information (ESI) available: Experimental section, characterization of all compounds, copies of $^1H$, $^{19}F$ and $^{13}C$ NMR spectra for selected compounds. See DOI: 10.1039/b000000x/

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18 The precise reason that fluorine atoms shut down reactivity is unclear in the present stage and remains to be elucidated.

19 When anhydrous DMSO was used as the solvent, the reaction mainly led to (*E*)-butyl cinnamyl ether **5aa** and its derivatives. For details, see the Supporting Information Table 4.

20 The detection of a small amount of **3aa** can be explained that only a little water which generated from the first-step oxygenation process, underwent the second-step oxygenation.

21 (a) J. Otera, *Esterification*; Wiley-VCH: Weinheim, 2003 and referencestherein; (b) K. Ishihara, *Tetrahedron*, 2009, **65**, 1085.

22 (a) J. W. Faller, M. E. Thomsen and M. J. Mattina, *J. Am. Chem. Soc.*, 1971, **93**, 2642; (b) B. M. Trost, M. R. Machacek and A. Aponick, *Acc. Chem. Res.*, 2006, **39**, 747.