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Allylic C–H Acetoxylation with a 4,5-Diazafluorenone-Ligated Palladium Catalyst: A Ligand-Based Strategy to Achieve Aerobic Catalytic Turnover

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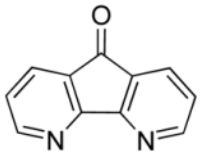
Abstract

Pd-catalyzed C–H oxidation reactions often require the use of oxidants other than O_2. Here, we demonstrate a ligand-based strategy to replace benzoquinone with O_2 as the stoichiometric oxidant in Pd-catalyzed allylic C–H acetoxylation. Use of 4,5-diazafluorenone (**1**) as an ancillary ligand for $Pd(OAc)_2$ enables terminal alkenes to be converted to linear allylic acetoxylation products in good yields and selectivity under 1 atm O_2. Mechanistic studies reveal that **1** facilitates C–O reductive elimination from a π-allyl-Pd^{II} intermediate, thereby eliminating the requirement for benzoquinone in this key catalytic step.

The selective oxidation of C–H bonds in organic molecules is an important and growing field.[1] Many of the emerging methods utilize palladium catalysts in combination with stoichiometric organic or transition-metal oxidants, such as $PhI(OAc)_2$, benzoquinone, Cu^{II} or Ag^{I}.[2] Mechanistic studies suggest that these oxidizing agents often react with organopalladium(II) intermediates and promote reductive elimination of carbon-carbon or carbon-heteroatom bonds.[3] Replacement of these oxidants with molecular oxygen represents a significant fundamental challenge that has important implications for environmentally-benign, large-scale applications of these methods.[4,5] Here, we present a ligand-based strategy to replace benzoquinone (BQ) with O_2 as an oxidant in Pd-catalyzed allylic C–H acetoxylation reactions. Preliminary mechanistic studies reveal that the use of 4,5-diazafluorenone (**1**) as an ancillary ligand facilitates C–O bond formation from π-allyl-palladium(II) species and, thereby, permits O_2 to be used as the oxidant in a Pd^{II}/Pd^{0} catalytic cycle without requiring BQ.[6]



4,5-diazafluorenone (**1**)

Pd-catalyzed allylic acetoxylation reactions represent a prominent class of C–H oxidations that have been the subject of extensive historical[7] and contemporary[8,9] interest. The vast majority of these reactions utilize BQ as a stoichiometric or cocatalytic oxidant. Fundamental studies implicate at least three possible roles for BQ in the catalytic mechanism (Scheme 1): (1) to promote nucleophilic attack by acetate on a π-allyl-Pd^{II}

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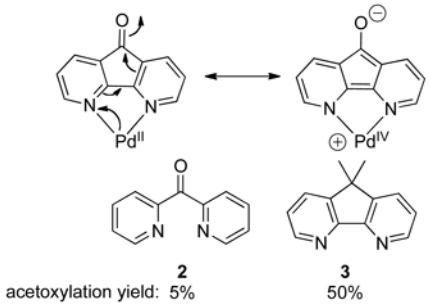
Supporting Information Available: Experimental procedures, screening data, and characterization data for of all new compounds. This information is available free of charge via the internet at: http://pubs.acs.org.

species (step II),[3a,d] (2) to displace the allylic acetate product from Pd^0 following reversible C–O bond formation (step III),[8d] and (3) to oxidize Pd^0 to Pd^{II} (step IV).[10] Because molecular oxygen is also capable of oxidizing Pd^0 to Pd^{II},[6] we reasoned that an aerobic allylic C–H oxidation process could be achieved by identifying a ligand for Pd that could eliminate the requirement for BQ in steps II and III.

Pyridine, phenanthroline (phen) and related nitrogenous ligands have been widely used in Pd-catalyzed aerobic oxidation reactions.[11] Such ligands were tested recently by Lin, Labinger and Bercaw in allylic acetoxylation reactions,[8d] and a bipyrimidine-$Pd(OAc)_2$ catalyst was shown to be effective with 2 equiv of BQ as the oxidant. We reevaluated ligands of this type under 1 atm of O_2 to test their ability to support aerobic Pd-catalyzed acetoxylation of allyl benzene (Table 1). Pyridine (entry 2), bipyridine (bpy, entry 3), phenanthroline (phen, entry 8), bipyrimidine (bpm, entry 11) and a number of bpy and phen derivatives (entries 4–7, 9, 10) were almost completely ineffective; mostly unreacted allyl benzene was obtained at the end of the reaction. The lack of Pd black in these reactions suggested the problem is a lack of reactivity, not catalyst decomposition. A noteworthy exception to these poor results was obtained with 4,5-diazafluorenone (**1**), which led to an 81% yield of the linear acetoxylation product (entry 12). This ligand was included in the screen based on the hypothesis that the carbonyl group could promote backbonding from the Pd^{II} center. We reasoned that contribution from the Pd^{IV} resonance structure (eq 1) might facilitate C–O reductive elimination from a π-allyl-Pd^{II} intermediate and enable BQ-free catalytic turnover (cf. Scheme 1, step II). Subsequent control experiments failed to validate this hypothesis, however. For example, use of di-2-pyridyl ketone, **2**, another ligand capable of backbonding, afforded the allylic acetoxylation product in only 5% yield, whereas use of another diazafluorene ligand, **3**, in which the carbonyl group in **1** was replaced with two methyl substituents, resulted in a moderate yield of the acetoxylation product (50%). The latter result is not as good as the acetoxylation yield obtained with **1**, but it is substantially better than the yield with **2** or the other ligands in Table 1. These results suggest that geometric properties of **1** (e.g., the bite angle), rather than backbonding, underlie the effectiveness of this ligand.



(1)

Successful aerobic acetoxylation of allyl benzene provided the basis for further optimization of the reaction conditions and evaluation of the substrate scope. It was possible to decrease the temperature to 60 °C and replace AcOH with dioxane as the reaction solvent; the optimized conditions featured 5 mol % $Pd(OAc)_2$, 16 equiv of AcOH and a catalytic amount of NaOAc (20 mol%) under 1 atm of O_2 (see Supp. Info. for additional optimization data). These Pd-catalyzed allylic acetoxylation conditions were then tested with a number of other alkenes (Table 2). Successful reactivity was observed with naturally occurring allyl benzene derivatives estragole and methyl eugenol (entries 2 and 3) as well as simple hydrocarbon-

based α-olefins (entries 4 and 5). Silyl ethers were well tolerated, as were esters, acetals, amides, and carbamates (entries 6–11). Nearly all of the substrates examined produced the linear acetoxylation product exclusively in good yields and exhibited a strong preference for formation of the *E* isomer of the alkene. The reactivity appears selective for terminal olefins, as β-methyl styrene, cyclohexene, methyl crotonate and methylenecyclohexane gave little to no desired product.

These allylic oxidation reactions enable anti-Markovnikov hydration of α-olefins to be achieved via tandem O_2/H_2- coupled redox steps. This net transformation represents a long-standing challenge in the field of catalysis,[12] and it can be achieved in a straightforward one-pot process consisting of Pd-catalyzed allylic acetoxylation, removal of the acetate under basic conditions and hydrogenation of the alkene (Scheme 2A). No additional catalyst is required for the hydrogenation step; addition of activated carbon to the crude reaction mixture, which still contains Pd from the acetoxylation reaction, and stirring under 1 atm of H_2 results in efficient hydrogenation of the alkene. Good yields of terminal alcohols were obtained for three representative substrates utilizing this sequence (Scheme 2B). The isolated yield of the alcohol essentially matches that of the initial acetoxylation step.

Mechanistic studies have begun to provide insights into the ability of the diazafluorenone ligand (**1**) to support aerobic BQ-free catalytic turnover. Two similar [(L)Pd^{II}(η^3-allyl)]OAc complexes, **4** (L = diazafluorenone, **1**) and **5** (L = *t*Bu_2bpy), were prepared in order to compare the effects of O_2 and BQ on the reactivity of the π-allyl-Pd^{II} complexes under catalytically relevant conditions (Figures 1 and 2). In the first set of experiments, the ability of **4** and **5** to undergo stoichiometric acetoxylation of the allyl ligand was probed by ^{1}H NMR spectroscopy under three separate conditions: in the absence of an oxidant (1 atm N_2), under 3 atm O_2[13] and in the presence of 2 equiv BQ (Figure 1). The diazafluorenone complex reacts to form allyl acetate in good yield under all conditions (70–90%); however, the reaction time varied from 24 h (N_2) to 3 h (O_2) to 1 h (BQ).[14] Complex **5**, with the catalytically incompetent *t*Bu_2bpy ligand, is completely unreactive in the presence of N_2 and O_2; however, it undergoes acetoxylation in the presence of 2 equiv BQ (88%).

A second set of experiments probed the possibility of reversible C–O bond formation by monitoring the ability of π-allyl-Pd^{II} complexes **4** and **5** to mediate acetate-d_3 incorporation into cinnamyl acetate (Figure 2A). The proposed Pd-mediated mechanism for acetate exchange is shown in Figure 2B, and the data are summarized in Figure 2C. The diazafluorenone complex **4** mediated extensive acetate exchange (76% in 3 h) in the absence of an oxidant; however, this reactivity was eliminated by the presence of O_2 or BQ.[15] Acetate exchange decreased systematically as the O_2 pressure increased (Figure 2D), presumably reflecting the ability of O_2 to trap the Pd^0-alkene complex (***k*$_{ox}$**, Figure 2B) and inhibit exchange. Negligible acetate exchange was observed with the *t*Bu_2bpy complex **5**, even in the absence of an oxidant.

These results provide insights into the catalytic steps that have been proposed to involve BQ (Scheme 1, steps II and III). The reactivity of **5** in the stoichiometric acetoxylation study (Figure 1) reveals that BQ can induce acetoxylation of an otherwise unreactive π-allyl-Pd^{II} complex. O_2 is not an effective BQ surrogate in this reaction. The stoichiometric reactivity of **4** reveals that BQ is not required for the C–O bond-forming step when diazafluorenone is the ancillary ligand. We speculate that the distorted bite angle of the diazafluorenone ligand[16] destabilizes Pd^{II} and allows the π-allyl ligand to undergo nucleophilic attack in the absence of BQ. Computational studies to probe this hypothesis will be the focus of future studies. The qualitative rate differences for the acetoxylation of **4** in the presence of N_2, O_2 and BQ (Figure 1) can be rationalized in two ways. O_2 and BQ can enhance the rate by trapping the putative Pd^0-alkene species and preventing reversion to the π-allyl-Pd^{II}

complex.[17] Alternatively, the faster rate with BQ relative to O_2 could reflect the ability of BQ to promote acetoxylation of the π-allyl-Pd^{II} complex, in addition to trapping the Pd^0 intermediate.

Further work will be needed to probe the effect of ancillary ligands on other steps of the catalytic mechanism, such as C–H activation, and their influence on the identity of the turnover-limiting step and the catalyst resting state. Nevertheless, the results presented here provide clues into the ability of an ancillary ligand to enable catalytic turnover with O_2, rather than BQ, as the stoichiometric oxidant, and a plausible catalytic cycle is shown in Scheme 3.

This study points to a potentially versatile ligand-based strategy to achieve aerobic Pd-catalyzed C–H oxidation. For example, BQ and other oxidants have been proposed to promote C–C reductive elimination in oxidative cross-coupling reactions.[3g,j,k] On the basis of the present results, we anticipate that it might be possible to identify ancillary ligands that facilitate reductive elimination from Pd^{II} and thereby eliminate the requirement for undesirable stoichiometric oxidants. Efforts to test this hypothesis have been initiated.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

Acknowledgments

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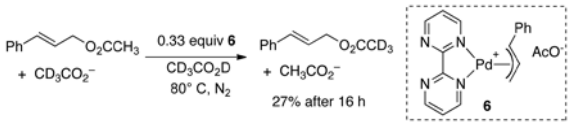
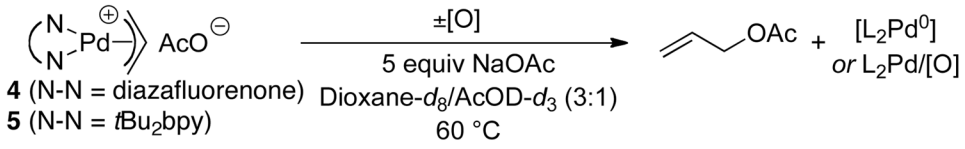
13. Poor gas-liquid mixing in 5 mm NMR tubes required the use of 3 atm O_2 to ensure the presence of approx. 1 equiv of dissolved O_2 in solution.
14. In the absence of oxidant, Pd black is observed at the end of the reaction, whereas the reaction mixture remains homogeneous in the presence of oxidant, presumably due to the formation of ligated $Pd^{II}(OAc)_2$ species. Separately, it was noted that the reaction of **4** was unaffected by the presence of excess ligand 1 (5 equiv) in solution, suggesting that formation of allyl acetate does not proceed via pre-equilibrium dissociation of 1 from the Pd center.
15. Lin et al.[8d] have previously reported that the (bpm)Pd(η^3-cinammyl) complex **6** (eq 2) mediates acetate exchange in cinnamyl acetate in the absence of an oxidant. In addition, they demonstrated that **6** is stable toward stoichiometric acetoxylation under N_2, but it releases cinammyl acetate in the presence of BQ under conditions somewhat different from ours (AcOH, 80° C) (cf. Figure 1). The reactivity of **6** in the presence of O_2 was not reported. Preliminary studies suggest (bpm)Pd(allyl) complexes react differently under our conditions. Further work will be needed to make a direct comparison between ligand **1** with bipyrimidine in allylic acetoxylation reactions.



(2)

16. The BF_4^- salts of **4** and **5** have been characterized by X-ray crystallography. For a summary of structural data, see Figure S6 and additional data in the Supp. Info.
17. Previous studies in our lab have demonstrated the reaction of O_2 with Pd0-alkene complexes to afford η^2-peroxo species relevant to this process. See ref. 6b and (a) Popp BV, Thorman JL, Stahl SS. J Mol Catal A: Chem. 2006; 251:2–7. (b) Popp BV, Morales CM, Landis CR, Stahl SS. Inorg Chem. 2010; 49 ASAP. 10.1021/ic100806w



N N ligand	yield of allyl acetate		
	1 atm N_2	3 atm O_2	2 equiv BQ
(**1**)	70% (24 h)	90% (3 h)	88% (1 h)
^{t}Bu, ^{t}Bu	0% (24 h)	0% (24 h)	88% (24 h)

Figure 1.

Ligand effects on stoichiometric acetoxylation of well-defined π-allyl-Pd complexes in the absence of an oxidant (1 atm N_2) and in the presence of O_2 (3 atm) and benzoquinone (2 equiv). The indicated reaction time indicates the time needed for >95% conversion of **4** or **5**.

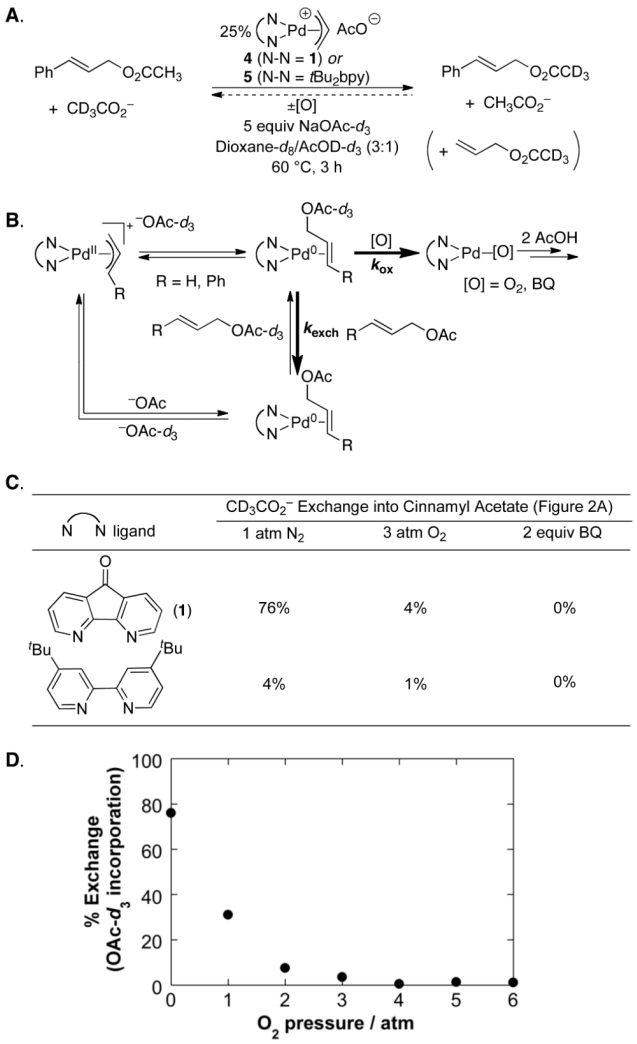
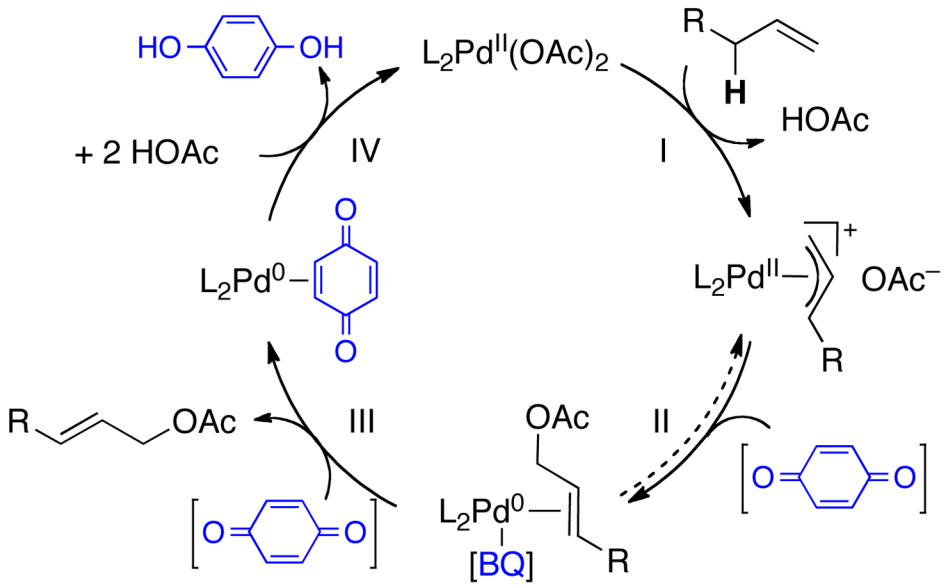
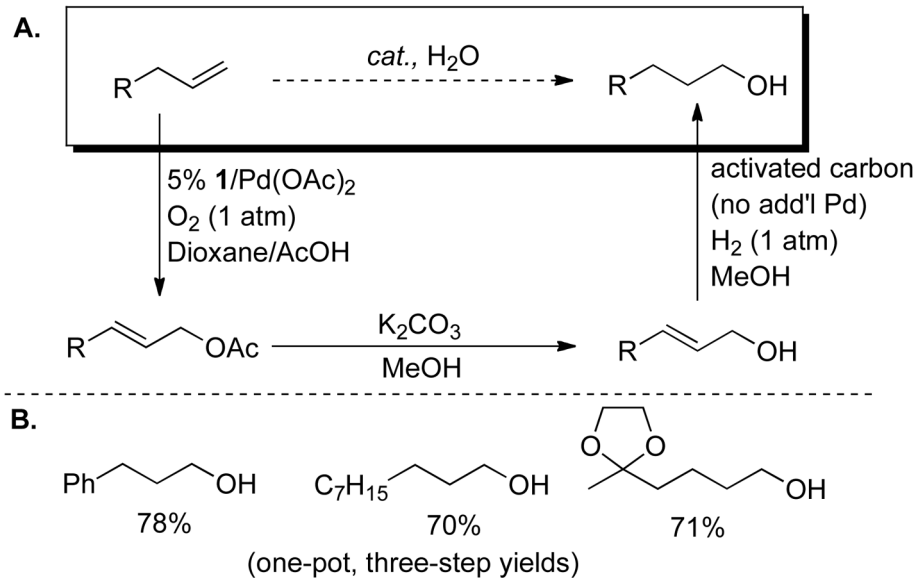


Figure 2.

Experiments designed to probe the reversibility of C–O bond formation from (L)Pd(η^3-allyl) complexex. (A) Acetate exchange into cinnamyl acetate in the presence of a (L)Pd(η^3-allyl) complex; (B) Mechanistic basis for (L)Pd(η^3-allyl)-catalyzed acetate exchange in cinnamyl acetate and the influence of an oxidant on the extent of exchange; (C) Extent of acetate exchange with different (L)Pd(η^3-allyl) complexes in the absence and presence of an oxidant; (D) O_2 pressure effects on the extent of acetate exchange for the reaction in Figure 2A [(L)Pd(η^3-allyl) = **4**].

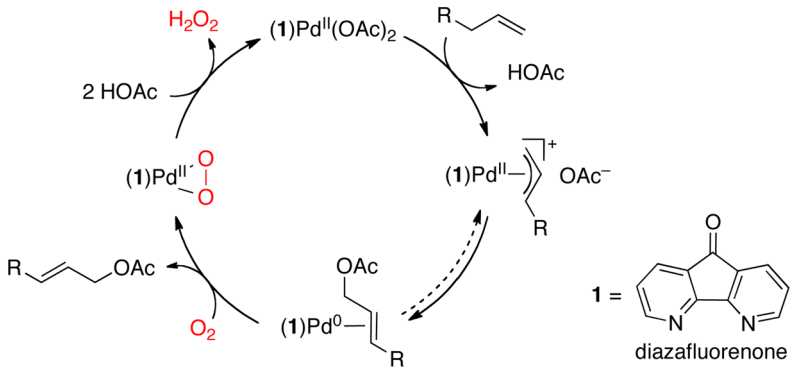


Scheme 1.
Proposed Mechanism for Palladium-Catalyzed Allylic Acetoxylation.



Scheme 2.

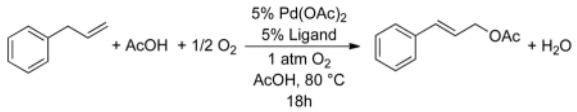
Net Anti-Markovnikov Hydration of Terminal Alkenes via a One-Pot, Three-Step Sequence.



Scheme 3.
Proposed Mechanism for Palladium-Catalyzed Aerobic Allylic Acetoxylation.

Table 1

Identification of a Ligand for Palladium-Catalyzed Aerobic Allylic Acetoxylation.[a]



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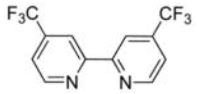
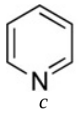
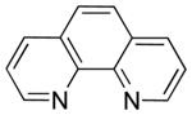
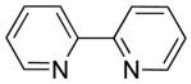
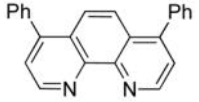
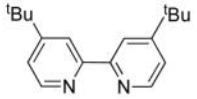
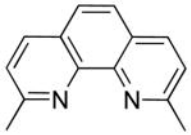
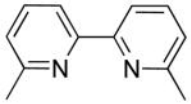
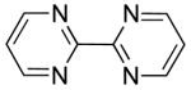
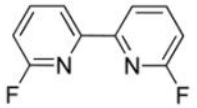
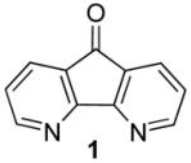
1	None	4%	7		0%
2	 [c]	4%	8		9%
3		4%	9		0%
4		0%	10		0%
5		0%	11		4%
6		3%	12	 1	**81%**

[a] 5% $Pd(OAc)_2$ (3 mg, 0.0134 mmol), 5% ligand (0.0134 mmol), allyl benzene (35 μL, 0.268 mmol), AcOH (1 mL), 1 atm O_2, 80 °C, 18h.

[b] GC (internal std = nitrobenzene).

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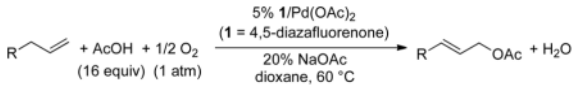
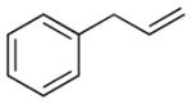
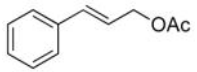
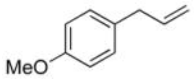
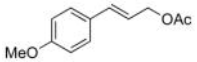
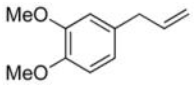
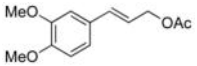
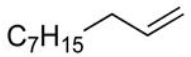
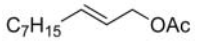
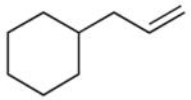
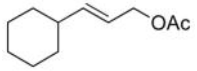
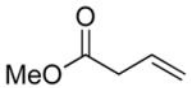
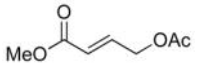
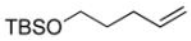
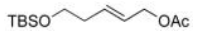
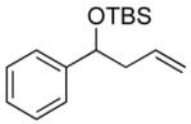
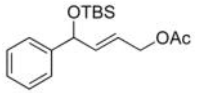
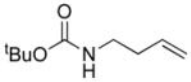
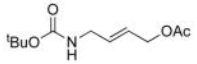
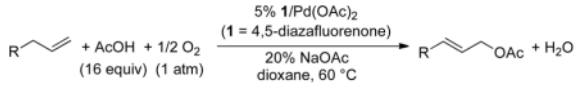
$c_{10\%}$

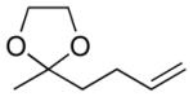
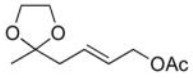
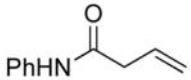
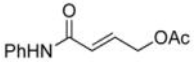
Table 2

Aerobic Allylic Acetoxylation of Terminal Olefins.[a]



Entry	Substrate	Time (h)	Product	*E:Z*[b]	Yield[c]
1		24		17:1	81% (89%)
2		24		14:1	79% (87%)
3		24		6:1	68% (68%)
4		48		10:1	76% (82%)[d]
5		24		19:1	70% (76%)
6		24		21:1	84% (92%)
7		48		6:1	52% (72%)
8		48		29:1	76% (87%)
9		24		7:1	76% (84%)[e]



Entry	Substrate	Time (h)	Product	*E:Z*[b]	Yield[c]
10		48		36:1	71% (84%)
11		24		16:1	74% (86%)

[a] Reaction conditions: 5 mol % $Pd(OAc)_2$ (0.05 mmol), 5 mol % **1** (0.05 mmol), 20 mol % NaOAc (0.20 mmol), substrate (1.0 mmol), dioxane (2.8 mL), AcOH (0.9 mL, 16 mmol), 1 atm O_2, 60 °C.

[b] Based on GC analysis of the crude mixture.

[c] Isolated yields. GC yields are given in parenthesis.

[d] 3:1 mixture of allylic and homoallylic acetates.

[e] 4 atm O_2. 5:1 mixture of linear and branched isomers.