Synlett F. Louafi et al. Letter

Dichotomous Reaction Pathways for the Oxidative Palladium(II)-Catalyzed Intramolecular Acyloxylation of Alkenes

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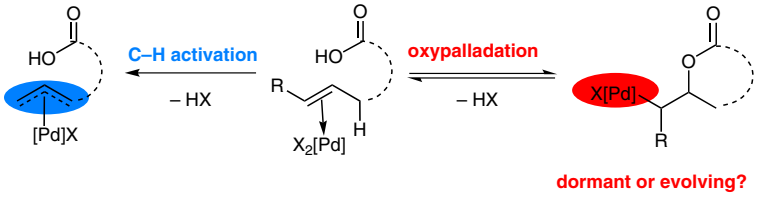

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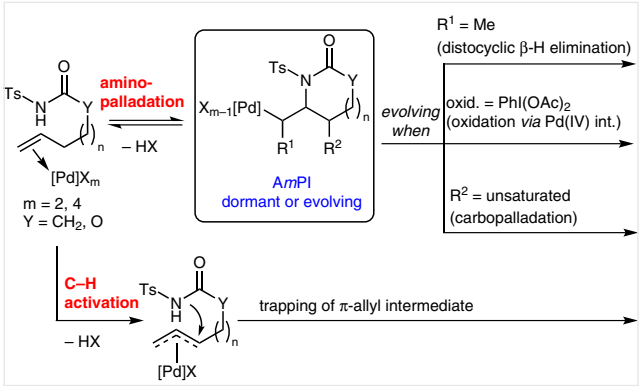
Abstract This work provides an in-depth investigation of the Pd(II)-catalyzed oxidative cyclization of various alkenoic acids bearing different tethers between the carboxylic acid moiety and the olefin function, showcasing how different mechanistic pathways (oxypalladation or allylic C–H activation) can be operative. The factors biasing toward one or the other of these reactivities are rationally discussed and compared with our recent studies on the Pd(II)-catalyzed intramolecular amination.

Key words palladium(II), C–H activation, oxypalladation, reaction mechanisms, alkenoic acids

Pd(II)-catalyzed addition of nucleophiles to olefins has emerged as an attractive research domain in the past decades.[2] However, the mechanism of these transformations is not always clear, since nucleopalladation[3] and allylic C–H activation[4] are two competing pathways sharing the same substrate type as well as reaction conditions. Therefore, we started a study aiming at understanding the detailed mechanisms of Pd(II)-catalyzed oxidative cyclizations.[5] We recently studied the behavior of unsaturated amine derivatives such as *N*-sulfonyl carbamates and carboxamides under oxidative Pd(II) catalysis [$Pd(OAc)_2$, White's disulfoxide ligand[6] and a terminal oxidant such as phenylbenzoquinone (PhBQ) or $PhI(OAc)_2$ in AcOH[7]] (Scheme 1).

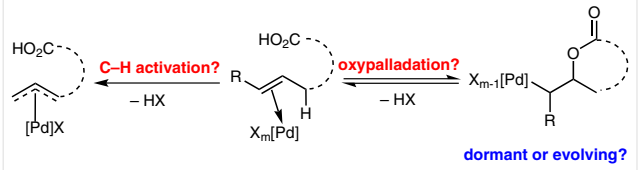
This study indicated that after activation of the unsaturation, two main mechanistic pathways can be operative: namely, aminopalladation, which affords the corresponding cyclic aminopalladated intermediate (A*m*PI). This latter can either evolve along diverse pathways such as distocyclic[8] β-H elimination,[9] oxidation by a strong oxidant like $PhI(OAc)_2$,[10] and carbopalladation (Scheme 1, top), or lay



Scheme 1 'Dormant' versus 'evolving' aminopalladated intermediates A*m*PI (previous work)

'dormant'. In this latter case, being the A*m*PI in equilibrium with the substrate,[11] C–H allylic activation followed by intramolecular trapping of the transiently generated π-allyl–Pd(II) intermediate[4] can alternatively become the only observed reactivity (Scheme 1, bottom).

To verify if such dichotomous behavior is common to a broader range of substrates, we decided to extend the above investigation to unsaturated alkenoic acids. Our results are reported in this letter (Scheme 2).

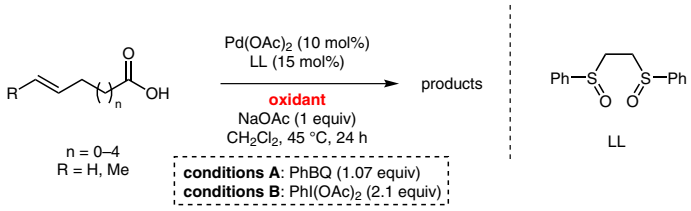


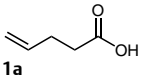
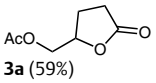
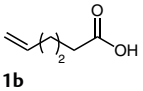
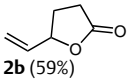
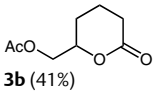
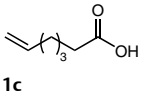
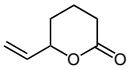
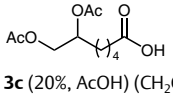
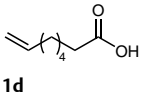
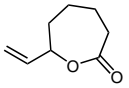
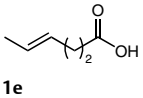
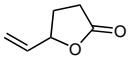
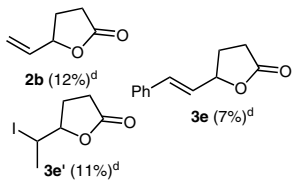
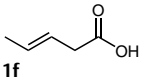
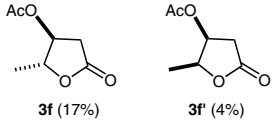
Scheme 2 Possible paths for the Pd(II)-catalyzed intramolecular acyloxylation (this work)

We began our study by using our previous standard reaction conditions, namely: 10 mol% of $Pd(OAc)_2$, 15 mol% of $PhS(O)(CH_2)_2S(O)Ph$ as the ligand and 1.07 equivalents of PhBQ (conditions A) or 2.1 equivalents of $PhI(OAc)_2$ (conditions B) as the oxidant. The influence of the nature of the solvent (AcOH, CH_2Cl_2) and of a base (NaOAc) was first investigated in preliminary experiments (see supporting information), the best results being obtained [for both PhBQ and $PhI(OAc)_2$], in CH_2Cl_2 with one equivalent of NaOAc. Various alkenoic acids were then reacted under these conditions and the results are summarized in Table 1 according to the terminal oxidant used.

First, following conditions A (PhBQ as oxidant), pent-4-enoic acid (**1a**) did not react (Table 1, entry 1), whereas hex-5-enoic acid (**1b**), hept-6-enoic acid (**1c**) and oct-7-enoic acid (**1d**) gave the corresponding vinyl lactones **2b–d** with moderate yields[12] (Table 1, entries 2–4). These results indicate that, under such reaction conditions, a direct allylic acyloxylation occurred.[13] Carboxylic acids bearing internal alkenes were then tested. (*E*)-Hex-4-enoic acid (**1e**) led to vinyl lactone **2b** in a moderate 49% yield (Table 1, entry 5). However, under the same conditions, (*E*)-pent-3-enoic acid (**1f**) only led to degradation (Table 1, entry 6). Conditions B [$PhI(OAc)_2$] were next tested. Acetoxylated lactones **3a**,**b**,**f**, and **3f′** were obtained starting from carboxylic acids **1a**,**b**,

Table 1 Pd(II)-Catalyzed Intramolecular Acyloxylation of Alkenes



Entry	Substrate	Products method A[a]	Products method B[a]
1	 **1a**	–[b]	 **3a** (59%)
2	 **1b**	 **2b** (59%)	 **3b** (41%)
3	 **1c**	 **2c** (39%)	 **3c** (20%, AcOH) (CH_2Cl_2)[c]
4	 **1d**	 **2d** (7%)	–[c]
5	 **1e**	 **2b** (45%)	 **2b** (12%)[d] **3e** (7%)[d] **3e′** (11%)[d]
6	 **1f**	–[c]	 **3f** (17%) **3f′** (4%)

[a] Isolated yields.
[b] Starting material was recovered.
[c] Degradation was observed.
[d] Compounds **2b**, **3e** and **3e′** were obtained as inseparable mixtures.

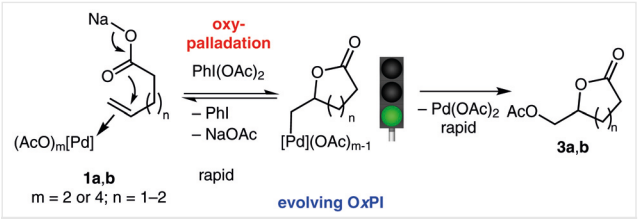
and **1f** (Table 1, entries 1–2 and 6),[14,15] whereas acids **1c** and **1d** only gave intractable material in CH_2Cl_2 (Table 1, entries 3 and 4) or, in the case of **1c**, diacetoxylated product **3c** in AcOH.[16] Finally, carboxylic acid **1e** gave a mixture of 5-vinyl- (**2b**), 5-styryl- (**3e**) and 5-(1-iodoethyl)- (**3e′**) γ-butyrolactone (Table 1, entry 5).

Similarly to the Pd(II)-catalyzed intramolecular amination, the above results become coherent if we consider the existence of a rapid equilibrium between the substrate and the corresponding cyclic oxypalladated intermediate (OxPI), which can be off-cycle (dormant) or in-cycle (evolving), depending on several factors. Thus, under the reaction conditions of conditions A, due to the impossibility of β-H elimination (forbidden proxicyclic, no external β-H available for distocyclic), the substrates **1b**–**d** are slowly but irreversibly consumed through an allylic C–H activation path, leading to the corresponding vinyl lactones **2b**–**d** (Scheme 3).[4,13] The formation of the four-membered lactone appears highly disfavored, especially if the transient β-allyl intermediate takes place via an inner-sphere mechanism,[17] thus accounting for the absence of reactivity of acid **1a**.

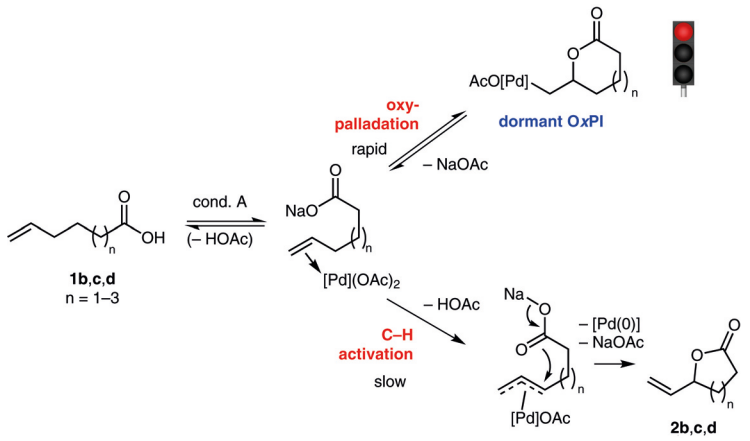
Further information came from the experiments carried out in the presence of $PhI(OAc)_2$. Indeed, the 'dormant' OxPI intermediate could be 'awakened' by this oxidant, which allowed obtaining the acetoxylated lactones **3a**,**b** through a double bond oxypalladation–reductive elimination sequence likely involving a Pd(IV)[18] [or dimeric Pd(III)][19] intermediate (Scheme 4).[20] However, only five- or six-membered acetoxylated lactones were isolated, while medium-rings were not obtained. These results lead us to assume that the oxypalladation–reductive elimination process is much faster than the previously observed C–H activation reactivity, and reversibility of the oxypalladation step is lost, be it Pd(II)- or Pd(IV)-catalyzed.

Let us consider now the results obtained for the carboxylic acids, **1e**,**f**, having an internal double bond. Under conditions A, substrate **1e** provided uneventfully the vinyl lactone **2b**. In this case, both the competing paths (allylic C–H activation–nucleophilic trapping and oxypalladation) may in principle lead to the same product. However, as the disulfoxide ligand is not expected to induce the C–H activation of an internal allylic position in a linear alkene, it follows that the reaction transits through the cyclic OxPI intermediate, which in turn evolves to the final product via a distocylic β-H elimination (Scheme 5).[21] The same lactone **2b** is formed from **1e** when using $PhI(OAc)_2$ as oxidant, too. However, in this case, **2b** is accompanied by 5-styryl- (**3e**) and 5-(1-iodoethyl)- (**3e′**) β-butyrolactone. While **3e** is likely to derive from carbopalladation of **2b** with in situ generated PhPdI,[22] **3e′** may result from a (non Pd-catalyzed) $PhI(OAc)_2/I^-$ mediated direct iodolactonization of **1e**.[23] As to the evolution of the cyclic OxPI, the distocyclic β-H elimination appears in this case to be faster than the alternative Pd oxidation step.

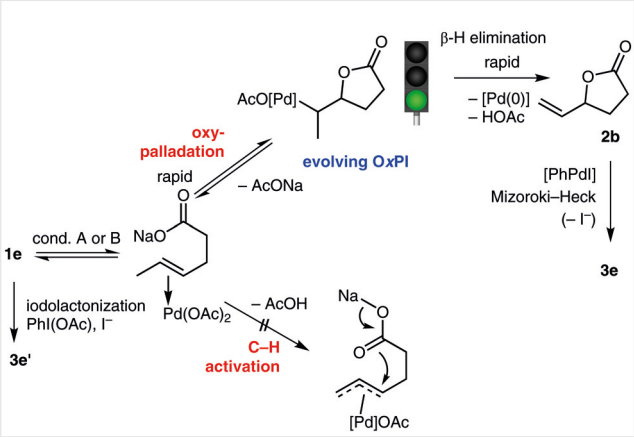
Finally, treatment of **1f** under conditions A only gave degradation products, whereas under conditions B, two separable diastereoisomers **3f** (*trans*) and **3f′** (*cis*) could be isolated. The formation of these compounds is in agreement with an oxidative cyclization passing through a nonselective (*trans* or *cis*) oxypalladation[24] and/or a nonselective (reductive elimination type or nucleophilic substitution type)[25] oxylation (Scheme 6).[26]



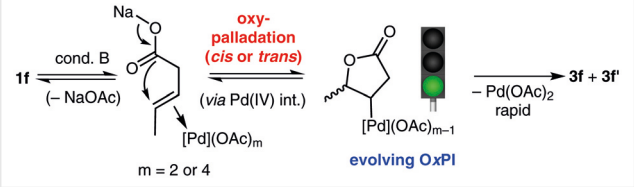
Scheme 4 'Waking-up' the cyclic OxPI with $PhI(OAc)_2$



Scheme 3 Allylic C–H activation of compounds involving a dormant OxPI



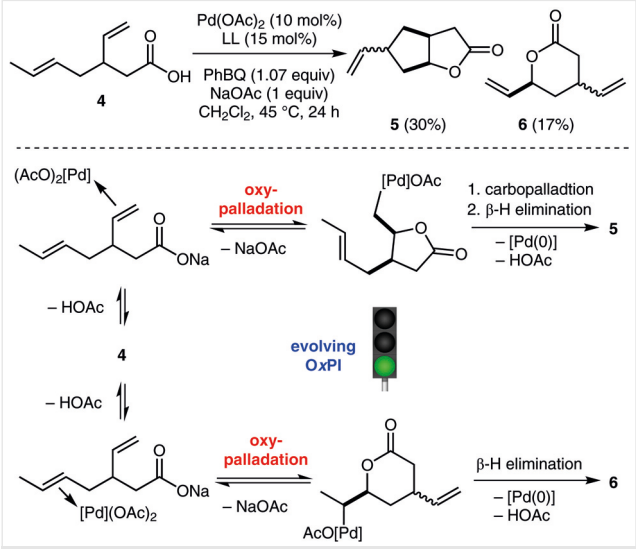
Scheme 5 'Waking-up' the cyclic OxPI via distocyclic β-H elimination, and competition with iodolactonization



Scheme 6 Behavior of carboxylic acid **1f** under conditions B

To further confirm the involvement of a cyclic O*x*PI, and by analogy with our previous work on the nitrogen series,[5a] we reasoned that an appropriately placed unsaturation in the substrate could 'awaken' the O*x*PI without relying on an exogenous parameter such as the replacement of the oxidant. Accordingly, the dienic carboxylic acid **4** was planned as ideal candidate.[27] Indeed, when **4** was submitted to conditions A, the predicted domino sequence[28] took place, leading to bicyclic γ-lactone **5** together with the some dienic δ-lactone **6** (Scheme 7),[29] the latter product coming from a oxypalladation–distocyclic dehydropalladation shunt path (Scheme 5). These results are in full accord with the formation of a latent cyclic O*x*PI, thereby validating our speculation.

In summary, the present study on oxidative Pd(II)-catalyzed intramolecular acyloxylation well complements our previous work on the intramolecular amination,[5] providing an unified mechanistic picture of the behavior of a broad range of unsaturated nucleophiles, spanning from alkenoic acids, to *N*-sulfonyl carbamates and carboxamides, as a function of the starting material and the operating conditions (Scheme 8). Thus, after activation of the unsaturation by a Pd(II) or Pd(IV) complex, to give intermediate **I**, a rapid nucleopalladation occurs, leading to a cyclic σ-alkyl–palladium(II) or σ-alkyl-palladium(IV) intermediate **II** (A*m*PI or O*x*PI). On the one hand, if possible, evolution via distocyclic



Scheme 7 'Waking-up' the cyclic OxPI via intramolecular carbopalladation

β-H elimination takes place affording the final unsaturated product **A** (right, top), or via a carbopalladation–dehydropalladation sequence, leading to bicyclic product **B** (bottom right). Both paths involve the reduction of Pd(II) to Pd(0), whose oxidation by a terminal oxidant (such as a quinone derivative) closes the catalytic cycles. Alternatively, in the presence of a hypervalent iodine(III) reagent a pre- or post-nucleopalladative Pd(II)-to-Pd(IV) oxidation can take place, whose evolution affords the acetoxylated product **C** (right, bottom). On the other hand, if **II** cannot evolve via one of the above paths, **I** is slowly but irreversibly depleted through an allylic C–H activation, and nucleophilic trapping of the thus generated π-allyl–Pd(II) intermediate **IV** leads to the allylated product **D** (left). In this case, due to the reversibility of the nucleopalladation step, intermediate **II** remains an off-cycle species. These studies further confirm the existence of the reversible formation of cyclic nucleopalladated Pd(II) intermediates, which can evolve or lay 'dormant' depending on the reaction conditions and the nature of the substrate.[30]

Acknowledgment

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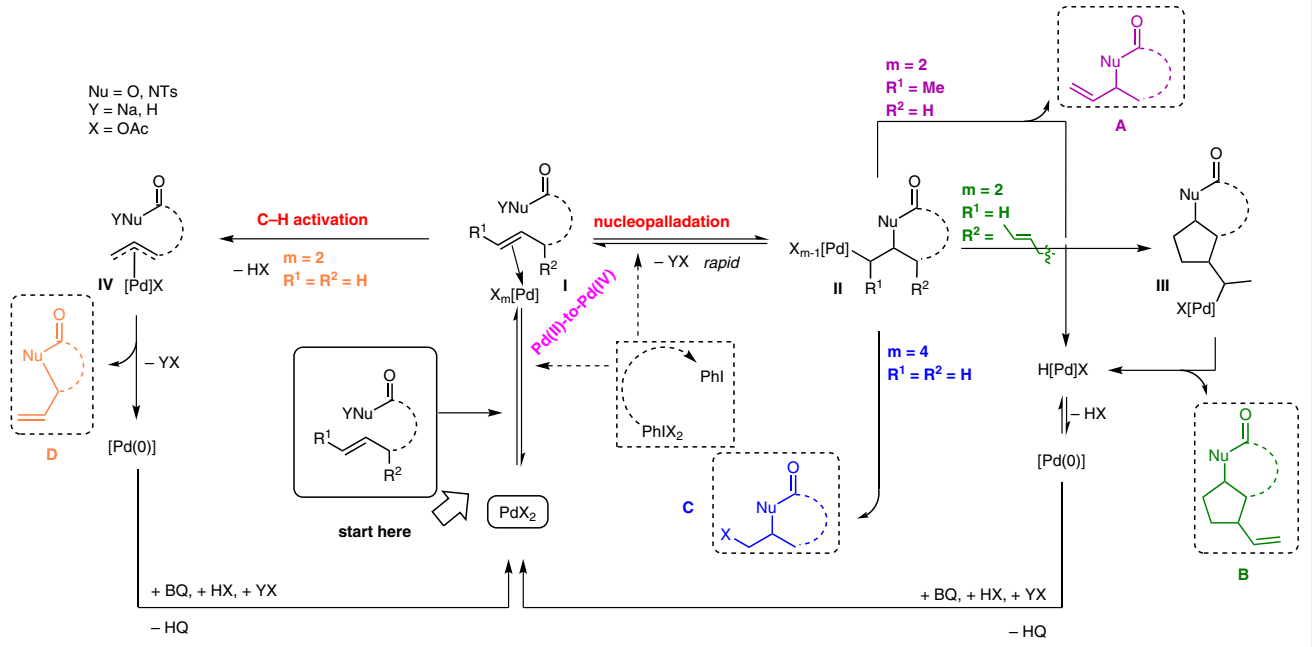
Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0035-1560071.



Scheme 8 A unified mechanistic scenario in Pd(II)-catalyzed intramolecular acyloxylation and amination of unsaturated substrates

References and Notes

(1) On leave from UR-CHEMS, Université Constantine 1, 25000 Constantine, Algeria.

(2) For books on this topic, see: (a) Bäckvall, J.-E. In *Modern Oxidation Methods*; Wiley-VCH: Weinheim, **2004**. (b) Tsuji, J. In *Palladium Reagents and Catalysts*; Wiley: New York, **2004**, 2nd ed.. (c) Negishi, E.-I. In *Handbook of Organopalladium Chemistry for Organic Synthesis*; John Wiley & Sons, Inc: New York, **2002**.

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(5) (a) Rajabi, J.; Lorion, M. M.; Ly, V. L.; Liron, F.; Oble, J.; Prestat, G.; Poli, G. *Chem. Eur. J.* **2014**, *20*, 1539. (b) Lorion, M. M.; Nahra, F.; Ly, V. L.; Mealli, C.; Messaoudi, A.; Liron, F.; Oble, J.; Poli, G. *Chim. Oggi* **2014**, *32*, 30.

(6) Chen, M. S.; Prabagaran, N.; Labenz, N. A.; White, M. C. *J. Am. Chem. Soc.* **2004**, *126*, 1346.

(7) The initial reaction conditions of this project were inspired by our work on direct intramolecular allylic amination. See: (a) Nahra, F.; Liron, F.; Prestat, G.; Mealli, C.; Messaoudi, A.; Poli, G. *Chem. Eur. J.* **2009**, *15*, 11078. (b) See also: Alexanian, E. J.; Lee, C.; Sorensen, E. J. *J. Am. Chem. Soc.* **2005**, *127*, 7690.

(8) We have proposed the terms *distocyclic* and *proxicyclic* to unequivocally distinguish between β-H eliminations involving a hydrogen atom either on a linear fragment or on a cyclic structure, respectively.

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(30) (a) **General Procedures; Conditions A**: In a sealed tube, under an argon atmosphere, were added the carboxylic acid (1.0 equiv), $Pd(OAc)_2$ (0.1 equiv), bis-sulfoxide ligand (0.15 equiv), *p*-phenylbenzoquinone (1.07 equiv), NaOAc (1.0 equiv) and CH_2Cl_2 (0.5 M). The tube was sealed and the reaction was allowed to stir at 45 °C. After 24 h, the reaction mixture was filtered on a plug of celite. The filtrate was treated with a sat. aq solution of 5% K_2CO_3 and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic layers were dried over anhyd $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash silica gel column chromatography afforded the desired vinyl lactone. **Analytical Data for 2b**: Yield: 59%; colorless oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 5.86 (ddd, *J* = 17.1, 10.5, 6.0 Hz, 1 H), 5.33 (dt, *J* = 17.2, 1.2 Hz, 1 H), 5.22 (dt, *J* = 10.5, 1.1 Hz, 1 H), 4.87–4.95 (m, 1 H), 2.50 (ddd, *J* = 8.0, 6.9, 1.1 Hz, 2 H), 2.31–2.46 (m, 1 H), 1.87–2.07 (m, 1 H). These data are in good agreement with those reported in the literature (ref. 11). **Conditions B**: In a sealed tube, under an argon atmosphere, were added the carboxylic acid (1.0 equiv), $Pd(OAc)_2$ (0.1 equiv), bis-sulfoxide ligand (0.15 equiv), iodobenzene diacetate (2.1 equiv), NaOAc (1.0 equiv) and CH_2Cl_2 (0.5 M). The tube was sealed and the reaction was allowed to stir at 45 °C for 24 h. The mixture was filtered over a small pad of celite. The filtrate was treated with a sat. aq solution of 5% K_2CO_3 and the aqueous layer was extracted with CH_2Cl_2 (3 ×). The combined organic layers were dried over anhyd $MgSO_4$, filtered and concentrated under reduced pressure. Purification by flash silica gel column chromatography afforded the acetoxylated product. **Analytical Data for 3b**: yield: 41%; yellow oil. ^1H NMR (300 MHz, $CDCl_3$): δ = 4.45–4.53 (m, 1 H), 4.18 (dd, *J* = 12.0, 3.8 Hz, 1 H), 4.12 (dd, *J* = 12.0, 5.8 Hz, 1 H), 2.30–2.74 (m, 2 H), 2.04 (s, 3 H), 1.70–2.00 (m, 3 H), 1.50–1.71 (m, 1 H). (b) These data are in good agreement with those reported in the literature: Ha, H. J.; Park, Y. S.; Park, G. S. *ARKIVOC* **2001**, *(i)*, 55.