

# Palladium-Catalyzed Intermolecular Oxyarylation of Vinylacetates with Retention of an Alkenyl Moiety

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**(5)** Supporting Information

**ABSTRACT:** Palladium-catalyzed intermolecular oxyarylation reaction of vinylacetates with retention of the double bond in the final product is developed. Under the optimized reaction conditions, the desired products of multisubstituted vinylesters could be obtained in moderate to high yields.



D irect oxidative functionalization of sp<sup>2</sup> alkenes via the oxidative Heck reaction has been shown to be a powerful method for olefin functionalization because it avoids the need to use prefunctionalized alkenes such as alkenylhalides and/or alkenyl organometallics.<sup>1</sup> Inspired by the pioneering work of Gusevskaya<sup>2</sup> and Ishii,<sup>3</sup> research groups of Loh,<sup>4</sup> Glorious,<sup>5</sup> Yu,<sup>6</sup> Shi,<sup>7</sup> Georg,<sup>8</sup> Liu,<sup>9</sup> Giuaizeau,<sup>10</sup> Iwasawa,<sup>11</sup> Bäckvall,<sup>12</sup> and others have developed transition-metal-catalyzed vinyl C–H bond direct functionalization methods (Scheme 1, eq 1).<sup>13</sup> In



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connection with our interest in the synthesis of trisubstituted alkenes,<sup>4,14</sup> we are interested in the sequential  $\alpha$ - and  $\beta$ -sp<sup>2</sup> C–H bond difunctionalization of simple alkenes.<sup>15</sup> This proves to be more difficult than we anticipated.<sup>16</sup> Another approach is to obtain a difunctionalized vinyl ester via one-pot C–H bond functionalization followed by an exchange with a nucleophile. As a proof of concept, we exchanged the acetate group with other functionalized esters. In this work, we would like to communicate the results of a palladium-catalyzed intermolecular arylation and esterification of vinylacetates with retention of the double bond after reaction (Scheme 1, eq 2). Using different acids allowed us to introduce a different functional group in the ester functional group of the product.

Initially, we searched for optimized reaction conditions for the oxyarylation of vinylacetate **1a** with cheap and commercially available iodobenzene and pivalic acid as the efficient nucleophile. The results are summarized in Table 1. In the presence of  $Pd(PPh_3)_4$ ,  $Ag_2O$ , and Xantphos in *p*-xylene solution,

the oxyarylated product 4a could be obtained in 53% yield (Table 1, entry 1). However, in the absence of Ag<sub>2</sub>O, no desired product could be obtained even though a stoichiometric amount of Pd(0)catalyst was used (Table 1, entries 2-4). To our delight, a very high yield could be achieved by using  $Pd(OAc)_2$  as catalyst (Table 1, entry 5). Subsequently, other halobenzenes were tested in this reaction; only product 4a' generated from p-xylene reacting with 1a could be detected after the reaction (Table 1, entries 6-8). Therefore, benzene was employed as the aryl source, and compound 4a was isolated in 33% yield (Table 1, entry 9). Other corresponding oxyarylated products also were obtained in low yields using *p*-xylene and mesitylene (Table 1, entries 10 and 11). Next, it was observed that reducing the amount of pivalic acid used will lead to a decrease in yield of the product. Other silver bases and Pd(II) catalysts were also found to be efficient to afford the desired product (Table 1, entries 13-16). It was noted that reducing the loading of the palladium catalyst and Xantphos ligand (Table 1, entry 17) or replacing Xantphos with PPh<sub>2</sub> (Table 1, entry 18) as well as changing the solvent (Table 1, entries 19 and 20) all led to a slight decrease in the yield of the product. Control experiments were also carried out; no desired product was found in the absence of palladium catalyst, while in the absence of silver oxide, an isolated 21% yield of product could be observed (Table 1, entries 21 and 22).

After optimization of the reaction conditions, various acids were screened in this reaction. It was found that the phenylacetic acid and its derivatives could react well with vinylacetate **1a** to give the desired products in good yields regardless of substituents present on the acid. Further screening of the acid-containing heteroatom on the substituted chain will lead to dramatic decrease in product yields. Only 29 and 52% yields were obtained when 2-acetoxyacetic acid and 5-acetamidopentanoic acid were applied, respectively, in this reaction (Chart 1, **4f** and **4k**). Other acids such as pentanoic acid and cyclopropanecarboxylic acid could also smoothly provide the corresponding products in

**Received:** May 23, 2015

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|       |                        | + PhX<br>1.2 equiv       | [Pd]/L/Ag<br>PivOH (5 equiv)<br>solvent, 80 °C, 24 h | →<br>→<br>→<br>→<br>→<br>→<br>→<br>→<br>→ |                  |                 |
|-------|------------------------|--------------------------|--|---|------------------|-----------------|
| entry | [Pd] (mol %)           | Ag (equiv)               | PhX  | L (mol %)                                 | solvent          | yield $(\%)^b$  |
| 1     | $Pd(Ph_3P)_4$ (10)     | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | p-xylene         | 53              |
| 2     | $Pd(Ph_3P)_4(10)$      |                          | PhI  | Xantphos (10)                             | <i>p</i> -xylene | NR              |
| 3     | $Pd(Ph_{3}P)_{4}(100)$ |                          | PhI  |   | <i>p</i> -xylene | NR              |
| 4     | $Pd(dba)_2$ (100)      |                          | PhI  |   | <i>p</i> -xylene | NR              |
| 5     | $Pd(OAc)_2(10)$        | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 93              |
| 6     | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) | PhBr   | Xantphos (10)                             | <i>p</i> -xylene | с               |
| 7     | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) | PhCl   | Xantphos (10)                             | <i>p</i> -xylene | с               |
| 8     | $Pd(OAc)_2(10)$        | Ag <sub>2</sub> O (0.65) | PhF  | Xantphos (10)                             | <i>p</i> -xylene | с               |
| 9     | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) |  | Xantphos (10)                             | PhH              | 33              |
| 10    | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) |  | Xantphos (10)                             | <i>p</i> -xylene | с               |
| 11    | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) |  | Xantphos (10)                             | mesitylene       | d               |
| 12    | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 81 <sup>e</sup> |
| 13    | $Pd(OAc)_2(10)$        | $Ag_2CO_3$ (0.65)        | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 89              |
| 14    | $Pd(PPh_3)Cl_2(10)$    | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 63              |
| 15    | $Pd(CH_3CN)Cl_2)$ (10) | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 88              |
| 16    | $Pd(TFA)_2(10)$        | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | 91              |
| 17    | $Pd(OAc)_2(5)$         | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (5)                              | <i>p</i> -xylene | 80              |
| 18    | $Pd(OAc)_2(10)$        | Ag <sub>2</sub> O (0.65) | PhI  | $PPh_3(20)$                               | <i>p</i> -xylene | 85              |
| 19    | $Pd(OAc)_2(10)$        | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | DCE              | 82              |
| 20    | $Pd(OAc)_2$ (10)       | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | dioxane          | 75              |
| 21    |                        | Ag <sub>2</sub> O (0.65) | PhI  | Xantphos (10)                             | <i>p</i> -xylene | NR              |
| 22    | $Pd(OAc)_2$ (10)       |                          | PhI  | Xantphos (10)                             | p-xylene         | 21              |
|       |                        |                          |  |   |                  |                 |

<sup>*a*</sup>Reaction conditions: A mixture of **1a** (0.3 mmol), catalyst, ligand, and additive in solution was allowed to stir for 24 h at 80 °C under argon atmosphere. <sup>*b*</sup>Isolated yields. <sup>*c*</sup>2-(2,5-Dimethylphenyl)-3,4-dihydronaphthalen-1-yl pivalate (**4a**') was obtained as the final product in 22–26% yield. <sup>*d*</sup>2-Mesityl-3,4-dihydronaphthalen-1-yl pivalate (**4a**'') was isolated as the final product in <15% yield. <sup>*e*</sup>Pivalic acid was used in 3 equiv.

Chart 1. Palladium-Catalyzed Oxyarylation of Vinylacetate Using Different Acids $^{a,b}$ 



<sup>*a*</sup>Reaction conditions: To a mixture of **1a** (0.3 mmol), **2a** (0.36 mmol, 1.2 equiv), **3** (1.5 mmol, 5 equiv), Xantphos (0.03 mmol, 10 mol %), and Ag<sub>2</sub>O (0.195 mmol, 0.65 equiv) was added anhydrous *p*-*x*ylene (1 mL) and allowed to stir for 24 h at 80 °C under argon atmosphere. <sup>*b*</sup>Isolated yields.

excellent yields (Chart 1, 4g and 4i). However, the aryl acid, such as benzoic acid, gave the product in a slightly decreased yield

(Chart 1, 4h). Furthermore, low reactivity was observed when more acidic formic acid was used (Chart 1, 4j).

Next, different aryl iodides were screened as the aryl source (Chart 2). It was noted that substrates with an electronwithdrawing group on the phenyl ring would favor the desired product's formation (Chart 2, 5a-5i). Moreover, other functional groups such as halides, esters, and cyano are tolerated in the final products, which will allow the products to be further transformed in subsequent steps. However, only moderate yield of the product could be found for the substrate with a strong electron-donating group. It is important to note that product 51(Chart 2) could also be achieved in a reasonable yield when 1,4diiodobenzene was used in the current reaction.

Finally, the substrate scope of vinylacetates was examined (Chart 3). Due to their important use of 3,4-dihydronaphthalen-1-yl acetate structural subunits as major building blocks in the synthesis of bioactive molecules and pharmaceutical compounds,<sup>17</sup> heteroatom-substituted vinylacetates **1** were investigated. It was found that electron-rich substrates provided the desired products in high yields (Chart 3, 6a), while only moderate yields were obtained for the substrate with electronwithdrawing groups (Chart 3, 6b and 6c). Acyclic vinylacetates were also utilized to react with iodobenzene and pivalic acid, and products 6e and 6f could be obtained in 83 and 66% yields, respectively, and with Z-configuration.<sup>18</sup>

To better understand this oxyarylation reaction, a series of control experiments were carried out to clarify the possible mechanistic pathway. First, it was observed that the starting material 1a would be completely recovered after heating a mixture of vinylacetate 1a and pivalic acid in *p*-xylene for 24 h.

Chart 2. Palladium-Catalyzed Oxyarylation of Vinylacetate with Various Iodobenzene Derivatives  $^{a,b}$ 



<sup>*a*</sup>Reaction conditions: To a mixture of 1a (0.3 mmol), 2 (0.36 mmol, 1.2 equiv), 3a (1.5 mmol, 5 equiv), Xantphos (0.03 mmol, 10 mol %), and Ag<sub>2</sub>O (0.195 mmol, 0.65 equiv) was added anhydrous *p*-xylene (1 mL) and allowed to stir for 24 h at 80 °C under argon atmosphere. <sup>*b*</sup>Isolated yields.

Chart 3. Palladium-Catalyzed Oxyarylation of Different Vinylacetates with Iodobenzene $^{a,b}$ 



<sup>*a*</sup>Reaction conditions: To a mixture of **1** (0.3 mmol), **2a** (0.36 mmol, 1.2 equiv), **3a** (1.5 mmol, 5 equiv), Xantphos (0.03 mmol, 10 mol %), and Ag<sub>2</sub>O (0.195 mmol, 0.65 equiv) was added anhydrous *p*-xylene (1 mL) and allowed to stir for 24 h at 80 °C under argon atmosphere. <sup>*b*</sup>Isolated yields.

The possibility of ester group exchange before the reaction could be excluded (Scheme 2, eq 3). When the 2-phenyl-3,4dihydronaphthalen-1-yl acetate 7 was prepared and used to react with pivalic acid in the presence of palladium catalyst and silver oxide, no desired product (4a) was detected after stirring the mixture for 24 h, which indicated that the step-by-step C–O bond cleavage/regeneration was unlikely (eqs 4 and 5). Furthermore, 3,4-dihydronaphthalen-1-yl pivalate 8 and 3,4dihydronaphthalen-1-yl benzoate 9 were tested to couple with iodobenzene in the presence of acetic acid and pivalic acid, respectively; in both cases, the oxyarylation reaction occurred and the desired products could be formed in high yields (eqs 6 and 7, respectively). It was also found that no reaction occurred

# Scheme 2. Control Experiments for Exploring the Possible Reaction Pathway



when 2-phenyltetralone was added into the reaction as starting material.

Based on the above results, a plausible mechanism for this oxyarylation reaction is proposed, as shown in Scheme 3. At the





beginning, the active Pd(0) catalyst generated via reduction with the Xantphos ligand reacts with iodobenzene **2a** to give the arylpalladium species **I**, which could coordinate with **1a**.<sup>19</sup> Subsequently, the carbopalladium intermediate **III** could be generated via a *trans*-attack of carboxylate.<sup>20</sup> Following that, the reductive elimination will release the Pd(0) catalyst into the next catalytic cycle and lead to the formation of intermediate **IV**, then E2 elimination of the original carboxylate group can take place to afford the desired product.

In conclusion, we have developed a novel palladium-catalyzed intermolecular oxyarylation reaction of vinylacetates. According to this method, the double bond could be retained in the final products, resulting in the difunctionalization of alkenes. The ability to introduce functional groups in the ester group could expand the synthetic utility of this reaction. It also provides an efficient and simple method for preparation of multisubstituted vinyl esters. Reactions using different nucleophiles to trap the intermediate are in progress.

### ASSOCIATED CONTENT

#### **Supporting Information**

Experimental procedures and spectral data for all new compounds (<sup>1</sup>H NMR, <sup>13</sup>C NMR, IR, HRMS). The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.Sb01507.

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

We gratefully acknowledge the funding support of the National Science Foundation for Young Scientists of China (21202156), and the State Key Program of National Natural Science Foundation of China (21432009).

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