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# Allylic Carbon–Carbon Double Bond Directed Pd-Catalyzed Oxidative *ortho*-Olefination of Arenes

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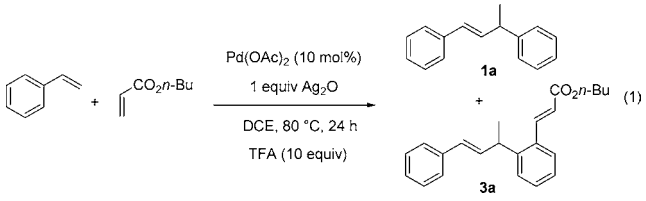
Supporting Information

**ABSTRACT:** Pd-catalyzed selective *ortho*-olefination of arenes assisted by an allylic C–C double bond at room temperature using $O_2$ as a terminal oxidant is described. A possible mechanism involving the initial coordination of allylic C=C bond to Pd followed by selective *o*-C–H bond metalation is proposed.

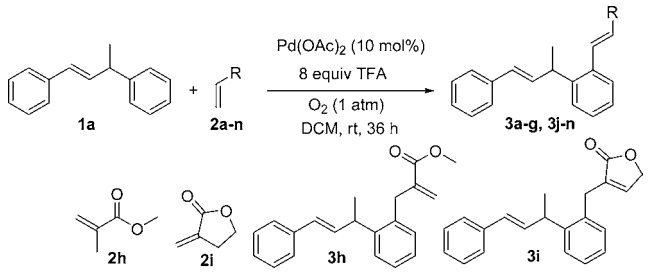
Selective activation of C–H bonds catalyzed by transition metal complexes has shown great potential for the construction of value-added molecules through C–C or carbon–heteroatom bond formation.[1] This methodology is of interest for the chemical and pharmaceutical industries, because it can significantly simplify and shorten the synthetic route and also allow the utilization of less expensive, more readily available, and environmentally benign starting materials. In particular, oxidative cross-coupling between arenes and olefins, commonly known as the Fujiwara–Moritani reaction,[2] is a powerful variant of the classical Mizoroki–Heck reaction[3] that avoids the need for the use of aryl halides and reduces the generation of salt waste. In general, regioselectivity of the Fujiwara–Moritani reaction can be achieved either through the introduction of a directing group[4] or by use of an external ligand.[5] Such directors are usually N- or O-containing functional groups. The search for new variants to assist selective C–H bond functionalization is expected to extend the scope of the synthetic application. Our ongoing interest in finding new organic transformations through C–H bond activation[6] prompts us to examine the utilization of the C=C bond as a director for selective C–H functionalization reaction. Here, we report a Pd-catalyzed regioselective *ortho*-olefination of arenes at ambient temperature using molecular oxygen as the terminal oxidant. The reaction appears to proceed unprecedentedly using the allylic C=C bond as the director for the C–H activation and functionalization.

Our investigation started with the reaction of styrene with butyl acrylate **2a** using 10 mol% $Pd(OAc)_2$ along with 1 equiv of $Ag_2O$ in 1,2-dichloroethane (DCE) at 80 °C for 12 h. When trifluoroacetic acid (TFA) was used as an additive, head-to-tail homodimerization product styrene[7] **1a** and olefination product **3a** were observed in 37 and 18% yields, respectively (eq 1).




To optimize the formation of **3a**, we examined the reaction under various conditions. Optimized reaction conditions were found to include **1a** (0.5 mmol) and **2a** (1.5 mmol) in dichloromethane (DCM, 3 mL) in the presence of $Pd(OAc)_2$ (10 mol%) and TFA (8 equiv) at room temperature for 36 h under 1 atm of $O_2$. Under these conditions, the reaction gave **3a** in 91% isolated yield (Table 1, entry 1). There are two

**Table 1. Scope of Activated Alkenes 2 in the Pd-Catalyzed Olefination of 1a**[a]




| entry | 2 | product 3 | yield, %[b] |
|---|---|---|---|
| 1 | R = $CO_2n$-Bu, **2a** | **3a** | 91 |
| 2 | R = $CO_2$Et, **2b** | **3b** | 93 |
| 3 | R = $CO_2$Me, **2c** | **3c** | 95 |
| 4 | R = $CO_2t$-Bu, **2d** | **3d** | 23 + (66)[c] |
| 5 | R = $CO_2C_6H_{11}$, **2e** | **3e** | 43 + (49)[c] |
| 6 | R = $CO_2CH_2Ph$, **2f** | **3f** | 62[d] |
| 7 | R = $CO_2H$, **2g** | **3g** | 64[d] |
| 8 | **2h** | **3h** | 63[d] |
| 9 | **2i** | **3i** | 56[d] |
| 10 | R = $C(O)NH_2$, **2j** | **3j** | 40 (73)[e] |
| 11 | R = $C(O)NMe_2$, **2k** | **3k** | 69 |
| 12 | R = $C(O)NHCH_2Ph$, **2l** | **3l** | 56[f] |
| 13 | R = CN, **2m** | **3m** | 48[d] |
| 14 | R = $SO_2Ph$, **2n** | **3n** | 67[d] |

[a]Unless otherwise mentioned, all reactions were carried out using **1a** (0.50 mmol), alkene **2** (1.5 mmol), $Pd(OAc)_2$ (0.050 mmol), TFA (4.0 mmol), and DCM (3.0 mL) at 25 °C in an $O_2$ atmosphere for 36 h. [b]Isolated yields. [c]Yield of hydrolyzed product **3g**. [d]Reaction time was 60 h. [e]Reaction was carried out using **1a** (1.0 mmol) and alkene **2j** (0.50 mmol), and the yield is calculated on the basis of **2j**. [f]1.0 mmol of alkene **2l** was used.

phenyl groups in **1a**, and the olefination appears to occur on an *ortho*-carbon of the phenyl ring near the methyl group. The

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**Table 2. Scope of Alkene 1 in the Pd-Catalyzed Olefination with 2**[a]


| entry | 1 | 2 | product 3 | yield [%][b] |
|---|---|---|---|---|
| 1 | R = Me, **1b** | **2a** | R = Me, **3ba** | 87 |
| 2 | R = C(CH$_3$)$_3$, **1c** | **2a** | R = C(CH$_3$)$_3$, **3ca** | 89 |
| 3 | R = F, **1d** | **2a** | R = F, **3da** | 73 |
| 4 | R = Ph, **1e** | **2a** | R = Ph, **3ea** | 76[c] |
| 5 | R = OMe, **1f** | **2a** | R = OMe, **3fa** | 83 |
| 6 | R = OMe, **1g** | **2a** | R = OMe, **3ga** | 91 |
| 7 | R = Cl, **1h** | **2a** | R = Cl, **3ha** | 63 |
| 8 | **1i** | **2a** | **3ia** | 69[c] |
| 9 | R = H, **1j** | **2a** | R = H, **3ja** | 81 |
| 10 | R = Me, **1k** | **2a** | R = Me, **3ka** | 86 |
| 11 | R = 2-Me, **1l** | **2a** | R = 2-Me, **3la** | 71 |
| 12 | R = 4-Me, **1m** | **2a** | R = 4-Me, **3ma** | 83 |
| 13 | R = 4-*t*-Bu, **1n** | **2a** | R = 4-*t*-Bu, **3na** | 79 |
| 14 | R = 4-F, **1o** | **2a** | R = 4-F, **3oa** | 72 |
| 15 | **1p** | **2a** | **3pa** | 79 |
| 16 | **1q** | **2c** | **3qc** | 56 |
| 17 | **1r** | **2a** | **3ra** | 82 |
| 18 | **1j** | **2k** | X = C(O)NMe$_2$, **3jk** | 71 |
| 19 | | **2m** | X = CN, **3jm** | 56[c] |
| 20 | | **2n** | X = SO$_2$Ph, **3jn** | 61[c] |
| 21 | **1s** | **2a** | **3sa** | 0 |

[a]Unless otherwise mentioned, all reactions were carried out using **1a** (0.50 mmol), alkene **2** (1.5 mmol), Pd(OAc)$_2$ (10 mol %), TFA (4.0 mmol), and DCM (3.0 mL) at 25 °C in an O$_2$ atmosphere for 36 h. [b]Isolated yields. [c]Reaction time was 60 h.

structure of **3a** was confirmed by its $^1$H and $^{13}$C NMR and mass data. As shown below, the structures of similar products **3g,l** were further supported by NOE experiments and X-ray structural determination, respectively. To our knowledge, this is the first report of the use of allylic C=C bond as a director for the Pd-catalyzed C−H activation reaction.[8]

The choice of solvent and oxidant is crucial for the success of the present catalytic reaction. A series of solvents or solvent combinations and oxidants were examined for the reaction of **1a** with **2a** (see Supporting Information). It appears that TFA (8 equiv) in DCM gave the highest yield (91%) of **3a**. The reaction was totally ineffective in the absence of TFA. However, higher TFA concentration led to lower product yield of **3a**. When pure TFA was used as the solvent under an O$_2$ atmosphere, **3a** was obtained in 17% yield. The use of weaker acids like AcOH and PivOH as additives instead of TFA totally suppressed the formation of **3a**. Of the oxidants tested, O$_2$ appeared to be the best for this catalytic reaction. Other oxidants such as Ag$_2$O and Cu(OAc)$_2$ are less effective, affording **3a** in 11 and 16% yield, respectively. In addition to Pd(OAc)$_2$, Pd sources such as PdCl$_2$, PdCl$_2$(PPh$_3$)$_2$, and PdCl$_2$(CH$_3$CN)$_2$ were also examined, but only PdCl$_2$(CH$_3$CN)$_2$


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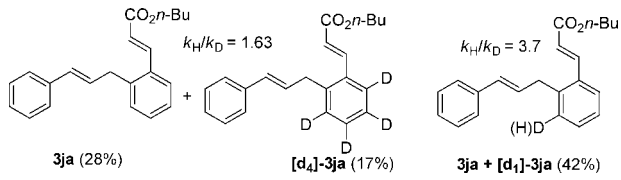
showed catalytic activity, producing **3a** in 16% yield; the others were completely inactive.

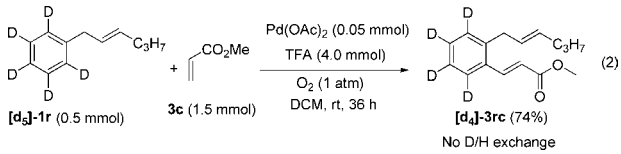
Under the optimized reaction conditions, various electron-deficient olefins (**2b**−**n**) also reacted with dimer **1a** smoothly to give the corresponding olefinated products in good to excellent yields. Thus, ethyl (**2b**) and methyl acrylate (**2c**) afforded the corresponding olefination products **3b**,**c** in 93 and 95% yields, respectively. Similarly, *tert*-butyl and cyclohexyl acrylate reacted efficiently with **1a** to give **3d**,**e**, but part of the products underwent hydrolysis to give **3g**. The reaction of benzyl acrylate **2f** with **1a** also proceeded, although the corresponding product **3f** was obtained in slightly lower yield (Table 2, entries 1−6). Interestingly, acrylic acid **2g** also underwent the same transformation to afford the corresponding product **3g** in 64% yield (entry 7). It is important to mention that the reaction of **1a** with $\alpha$-substituted acrylates **2h**,**i** proceeded to form **3h**,**i** (entries 8, 9) rather than the isomers with structures similar to **3a**−**g**. Unlike $\alpha$-substituted acrylates, $\beta$-substituted acrylate is not active for the transformation under similar reaction conditions. In addition to acrylates, acrylamide (**2j**), *N*,*N*-disubstituted acrylamide (**2k**), and *N*-benzyl acrylamide (**2l**) also reacted smoothly with **1a** to provide the desired products **3j**−**l** in moderate to good yields (entries 10−12). The structure of **3l** was further confirmed by X-ray diffraction. Acrylonitrile **2m** and phenyl vinyl sulfone **2n** were also successfully employed in this transformation to give the corresponding products **3m**,**n** in 48 and 67% yields, respectively (entries 13, 14). However, electronically neutral alkenes such as 1-hexene and styrene are not suitable substrates for this transformation.

We next examine the scope of substrate **1** in the present catalytic reaction. The results of these studies are shown in Table 2. Substrates **1b**−**i** were prepared byhomodimerization of the corresponding substituted styrene.[7c] Under the optimized reaction conditions shown in Table 1, these substrates underwent olefination with acrylate **2a** to give the corresponding products **3** in good to excellent yields. The results indicate that electron-donating substituents such as methyl, *tert*-butyl, and methoxyl groups enhance the reactivity and increase the product yields (entries 1, 2, 5, and 6); a less electron-donating substituent appears to decrease the reactivity of the substrate, but with a longer reaction time, high conversion and yield can still be achieved (entries 3, 4 and 7, 8). For substrates with a substituent at the *meta* position, olefination occurs only at the less hindered *ortho* position. Presumably, the regioselectivity was controlled by the steric effect of the *meta* substituent (entries 6, 7). Substrates **1j**−**o** without a methyl group on the aliphatic chain also reacted efficiently with **2a** to give the expected olefination products in good yields (entries 9−14). Interestingly, sterically hindered tri- and tetrasubstituted alkenes **1p**,**q** also drive the *ortho*-olefination reaction to give the respective products **3pa**,**qc** in good yields of 79 and 56% (entries 15, 16). The reaction is not restricted to styrene derivatives; it is also compatible with alkyl-substituted alkenes. Thus, treatment of hex-2-enylbenzene (**1r**) with **2a** afforded *ortho*-olefination product **3ra** in 82% yield (entry 17). The *E*:*Z* ratio of the C=C bond on substrate **1r** does not change after the catalytic reaction. In addition to acrylate **2a**, acrylic amide **2k**, acrylonitrile **2m**, and vinyl sulfone **2n** also react smoothly with 1,3-diphenylpropene **1j** to give **3jk**−**jn**, respectively, in moderate to good yield. The results in Tables 1 and 2 show clearly that it is the allylic C=C bond attached to an arene ring that activates the *o*-C−H bond of the arene. Under the reaction conditions, a vinylic C=C bond does not activate the arene C−H bond. As shown in Table 2, entry 21, we also examined the possibility of a butenylic C=C bond as a director for C−H bond activation with **2a**. However, we failed to observe any expected product **3sa**.

To understand the mechanism of this catalytic reaction, we first performed competition reactions using allylic substrates **1n** and **1o**, **1j** and **1r**, and **1c** and **1d** with **2a**. The results of these three sets of reactions revealed that substrates **1c**, **1n**, and **1r**, with an electron-richer substituent on the allylic arene ring or on the C=C bond gave a higher product yield than **1o**, **1j** and **1d**, respectively (Supporting Information). The observations support the coordination of C=C to Pd(II) and an electrophilic C−H activation during the reaction (see proposed mechanism, Scheme 2).[9] Next, we examined possible D/H exchange for the reaction of [$\mathbf{d}_5$]-**1r** with **2c** under standard reaction conditions. The reaction gave [$\mathbf{d}_4$]-**3rc** in 74% yield with no D/H exchange, as indicated by its $^1$H NMR and mass spectra (eq 2). This result ruled out the possibility of non-regioselective C−H activation followed by *ortho*-selective olefin insertion/reductive elimination. Finally, we measured the kinetic isotopic effects (KIEs) of the catalytic reaction by carrying out competition reaction inter- and intramolecularly. An intermolecular KIE $k_H/k_D$ = 1.63 was observed for the competition reaction of **1j** and deuterium-labeled [$\mathbf{d}_5$]-**1j** with **2a** (Scheme 1). On the other hand, an intramolecular competition experiment of [$\mathbf{d}_1$]-**1j** with **2a** showed $k_H/k_D$ = 3.7. The observed large difference in the inter- and intramolecular KIE values implies that the coordination of the C=C bond occurs prior to C−H palladation in the catalytic cycle.[10] If palladation takes place before C=C bond coordination, similar KIE values for the inter- and intramolecular competitions should be observed.[10]

**Scheme 1. Isotope Effect for the Pd-Catalyzed Oxidative Coupling of 1j with 2a**




Based on the experiment results and known transition metal catalyzed C−H activation reactions,[2−4,11] a possible mechanism employing **1j** and **1a** as the substrates is proposed to account for the present catalytic reaction (Scheme 2). The highly electrophilic [Pd(TFA)]$^+$ is expected to be generated in the presence of TFA.[2h,12] This cationic species should greatly facilitate coordination of the C=C bond and enhance metalation of the aromatic C−H bond. Thus, coordination of the C=C bond in **1j** and then the C−C $\pi$ bond between the *ortho* and *ipso* carbons to the Pd(II) center to give intermediate **A** is expected.[13] Subsequent cyclometalation forms Pd(II) $\sigma$-aryl complex **B**. Insertion of activated olefin into the C−Pd bond in intermediate **B**, followed by $\beta$-hydride elimination, affords the corresponding product **3ja** and H-Pd(TFA) species. Oxidation by $O_2$ regenerates the active Pd(II) species.[11]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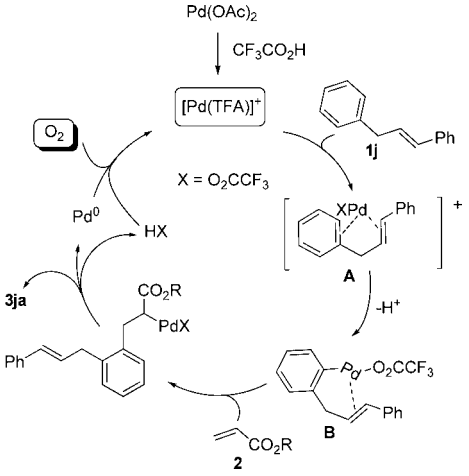
**Scheme 2. Proposed Mechanism for the Pd-Catalyzed Olefination Reaction**




In conclusion, we have demonstrated an effective Pd-catalyzed carbon−carbon double bond assisted selective *o*-C−H olefination of arenes at room temperature using $O_2$ as the oxidant. The reaction appears to be the first example employing an allylic alkenyl double bond as a directing group for C−H activation. In addition, we have observed that a *β*-C═C bond instead of an *α*-C═C bond is important to the *o*-C−H bond activation of arenes. Further applications of this methodology to other coupling partners and a detailed mechanistic investigation are in progress.

## ■ ASSOCIATED CONTENT

### Supporting Information

General experimental procedure and characterization details. This material is available free of charge via the Internet at http://pubs.acs.org.

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### Notes

The authors declare no competing financial interest.

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