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Highly Effective Pd-Catalyzed *ortho* Olefination of Acetanilides: Broad Substrate Scope and High Tolerability

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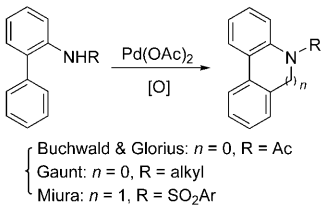
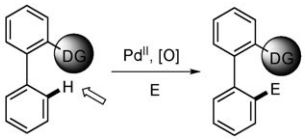
In recent years, direct functionalization of C–H bonds in organic compounds has emerged as an efficient, atom-economical, and environmentally friendly synthetic tool, with widespread applications in the preparation of natural products, pharmaceuticals, and organic materials. In particular, direct activation/functionalization of C–H bonds in aromatic compounds has attracted the most attention[1] and is noteworthy for its application in industrial settings.[2] As a representative example in this context, oxidative cross-coupling reaction between arenes and olefins, commonly known as the Fujiwara–Moritani reaction,[1c,g,3] is a powerful variant of the classical Mizoroki–Heck reaction[4] which circumvents the use of preformed or less readily accessible aryl halides. In general, regioselectivity in Fujiwara–Moritani reactions can be achieved either through the coordinative nature of a directing group that resides in the aromatic system,[5] or through the use of external ligands.[6] While significant advances have been made since the discovery of the Fujiwara–Moritani reaction with greatly improved efficiency and less drastic reaction conditions,[7–8] broad substrate scope and wide functional group compatibility are yet to be realized. Herein, we report the discovery of a highly effective protocol for the Pd-catalyzed Fujiwara–Moritani reaction of substituted acetanilides with unprecedented substrate scope.[7i]

In view of the recent reports on the C–H activation of 2-arylanilines under palladium catalysis [Eq. (1)],[9] we speculated that these substrates could partake in an analogous mechanistic pathway to afford 2′-substitued 2-arylanilnes in the presence of an electrophile [Eq. (2)]. More specifically, in the presence of an α,β-unsaturated substrate as a coupling partner (e.g., E = acrylate), we anticipated the formation of the corresponding 2′-alkenyl-2-arylanilines as the Fujiwara–Moritani product.



(1)



(2)

Along this line of thought, as illustrated in Scheme 1, we began our investigations using 2-phenylacetanilide (**1a**) and methyl acrylate as the test substrates. Much to our surprise, when a solution of **1a** in TFA (0.1 M) was treated with $Pd(OAc)_2$ (5 mol%), $K_2S_2O_8$ (1.0 equiv), and methyl acrylate (2.0 equiv) at room temperature,[10] none of the expected C2′-substituted Fujiwara–Moritani product **2a′** nor its cyclized heterocyclic derivative **2a″** was detected. Instead, the C2-substituted Fujiwara–Moritani product **2a** was observed as the sole product (by ^1H NMR analysis). This unexpected finding is of great interest since it is well documented that Pd-catalyzed C–H functionalizations of *ortho*-substituted acetanilides, such as *o*-methylacetanilide, *o*-methoxyacetanilide, *o*-trifluoromethylacetanilide, and *N*-Ac-1-naphthylamine are drastically impeded by the *ortho* substituents, resulting in very low or no conversion even at elevated temperature.[7b–e,8]

Based on this serendipitous finding, we subsequently channeled our efforts to elucidate the possible contributors

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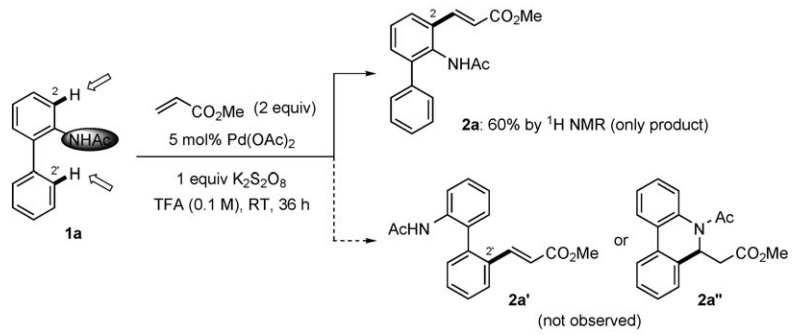
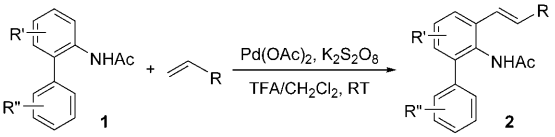


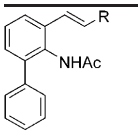
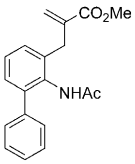
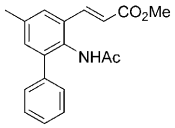
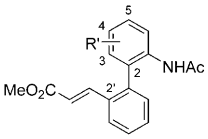
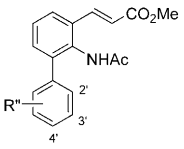
Scheme 1. Unexpected C–H activation at the C2 position instead of the anticipated C2′ position.

to the success of this unexpected oxidative cross-coupling reaction. First, among a variety of nitrogen protecting groups examined, the acetyl group was found as the protecting group of choice (for details, see the Supporting Information). Second, $Pd(OAc)_2$ proved to be the most effective palladium catalyst for this cross-coupling reaction, and no reaction was observed in the absence of $Pd(OAc)_2$. The unique combination of solvent system [TFA/CH_2Cl_2 (4:1)], high concentration (0.5 M), and the choice of oxidant ($K_2S_2O_8$) was also key to the optimized reaction conditions (for details, see the Supporting Information). TFA as the source of acid proved superior among all the acids examined, either as a solvent/cosolvent or as an additive.

With the optimized reaction conditions in hand, we set out to explore the substrate scope of this process and the results are shown in Table 1. In all cases, reactions between 2-arylacetanilide **1a** and activated olefins proceeded smoothly to afford 2-alkenyl-6-phenylacetanilides with exclusive *E* stereoselectivities in moderate to good yields (Table 1, **2a**–**d**). Double bond isomerized product **2e** was obtained when methyl methacrylate was employed as the activated olefin, albeit in a lower yield. Acetanilides bearing strongly electron-withdrawing groups (e.g., 4-nitro or 5-nitro) required more forcing conditions (60 °C) for the cross-coupling reactions to take place, and resulted in the preferential formation of C2′-functionalized products presumably because the anilide aromatic system is strongly deactivated (Table 1, **2g**,**h**). Acetanilides with substitution on the 2-aryl domain also displayed good reactivity, where both electron-donating and electron-withdrawing substituents were well tolerated (Table 1, **2i**–**p**). The structure of cross-coupling product **2p** was unambiguously confirmed by X-ray crystallographic analysis.[11] Equally noteworthy is the fact that this process can tolerate a variety of functionalities including methoxy, halogen, ketone, and nitro groups (Table 1, **2g**–**p**). In the case of halogenated substrates, only C2-alkenylation products were observed (Table 1, **2n**,**o**), uncomplicated by dehalogenation or Heck-type processes which could potentially take place at the halogenated positions. As such, this functional group tolerance should permit further elaboration of the cross-coupling products, and enable greater structural diversity.

Table 1. Pd-catalyzed oxidative cross-coupling between 2-arylacetanilides and activated olefins.

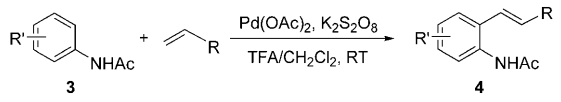


Product		Yield [%][e]
	**2a**: R = CO_2Me	72[a]
	2b: R = CO_2Et	64[a] (72)[a,b]
	2c: R = CO_2nBu	77
	2d: R = $CONMe_2$	59
	**2e**	37
	**2f**	65[a]
	**2g**: R′ = 4-NO_2	42[b,c]
	2h: R′ = 5-NO_2	44[b,c]
	**2i**: R″ = 4′-MeO	71
	2j: R″ = 3′-MeO	71[b]
	2k: R″ = 2′-MeO	70
	2l: R″ = 4′-Me	52 (15)[d]
	2m: R″ = 4′-Ac	80
	2n: R″ = 4′-Cl	75
	2o: R″ = 4′-F	66[a]
	2p: R″ = 3′-NO_2	63

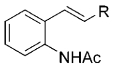
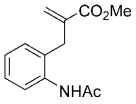
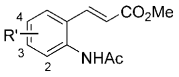
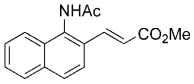
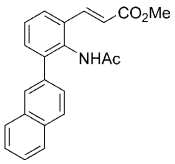
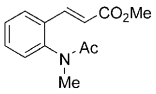
Reaction conditions: **1** (1 equiv), olefin (2 equiv), $Pd(OAc)_2$ (10 mol%), and $K_2S_2O_8$ (1 equiv) in TFA/CH_2Cl_2 (4:1, 0.5 M) at 25 °C for 24–48 h, unless otherwise noted. [a] With 5 mol% $Pd(OAc)_2$. [b] In TFA (0.5 M). [c] At 60 °C. [d] Yield of diolefination product at both C2 and C2′ positions. [e] Yield of isolated product.

(Table 2, **4a**–**e**). Methyl vinyl ketone also proved to be a suitable substrate, affording the corresponding alkenylated product **4d**. Acrylonitrile, (*E*)-ethyl crotonate, and styrenes were less effective substrates for the cross-coupling reactions, giving little or no conversions (20–35% by ^1H NMR)

Table 2. Pd-catalyzed oxidative cross-coupling between acetanilides and activated olefins.



3 4

Product		Yield [%][f]
	**4a**: R = CO_2Me	87 (94)[a]
	4b: R = CO_2nBu	80
	4c: R = $CONMe_2$	67
	4d: R = COMe	71[a,b]
	**4e**	43
	**4f**: R′ = 4-Me	83 (93)[a]
	4g: R′ = 3-Me	75
	4h: R′ = 2-Me	88[a]
	4i: R′ = 4-MeO	86 (92)[a]
	4j: R′ = 3-MeO	71[c] (81)[a,c]
	4k: R′ = 2-MeO	71 (84)[a]
	4l: R′ = 4-Cl	70
	4m: R′ = 3-Cl	70[a]
	4n: R′ = 4-F	76
	4o: R′ = 4-NO_2	50[a,d]
	**4p**	82
	**4q**	58[a]
	**4r**	52[a,e]

Reaction conditions: **3** (1 equiv), olefin (2 equiv), $Pd(OAc)_2$ (5 mol%), and $K_2S_2O_8$ (1 equiv) in TFA/CH_2Cl_2 (4:1, 0.5 M) at 25 °C for 20–48 h, unless otherwise noted. [a] With 10 mol% $Pd(OAc)_2$. [b] In TFA/CH_2Cl_2 (1:1, 0.5 M). [c] In TFA/CH_2Cl_2 (1:2, 0.5 M). [d] At 40 °C in TFA (0.5 M). Yield was determined by ^{1}H NMR of the crude mixture using trichloroethylene as an internal standard. Isolation failed owing to the nearly same R_f value as that of starting material. [e] At 60 °C in TFA (0.5 M). [f] Yield of isolated product.

even at elevated temperature (50 °C). Similar to the 2-arylacetanilides discussed earlier, acetanilides bearing electron-donating or -withdrawing substituents were once again well tolerated, giving cross-coupling product **4f–o** in moderate to good yields. Excellent regioselectivity was observed for *meta*-substituted acetanilides with the reaction taking place at the sterically less encumbered aryl C–H bond (Table 2, **4g**, **4j**, and **4m**). Noteworthy is the remarkable effectiveness of this developed protocol in the cross-coupling reactions of electron-deficient substrates (i.e. 3-chloro-, 4-chloro-, 4-fluoro-, 4-nitroacetanilide), giving the corresponding products (Table 2, **4l–o**) which could not be easily obtained under the reported Pd-catalyzed Fujiwara–Moritani reaction conditions.[7–8] Furthermore, as mentioned earlier, *ortho*-substituted substrates traditionally have been extremely challenging in the context of the Pd-catalyzed Fujiwara–Moritani reaction;[7b–e,8] therefore, the successful preparation of **4h**, **4k**, **4p**, and **4q** is a true testament of the power of this newly established protocol. Lastly, *N*-methylacetanilide, a substrate previously reported to be inert in the Pd-catalyzed Fujiwara–Moritani reaction[7b–c,e–f] also proceeded uneventfully to give product **4r** in 52% yield.

The anilide moiety has been demonstrated to be an effective directing group in C–H activation,[7] whereas TFA serves to enhance the electrophilicity of the palladium center and its metalation of the aromatic C–H bond.[1c,3f,12] We were delighted to find that, upon treatment of **1a** with $Pd(OAc)_2$ in TFA, palladacycle **I** was isolated in 80% yield [Eq. (3)] and its structure was validated by X-ray crystallographic analysis (Figure 1).[11] In support of the C–H activation mechanism, indeed palladacycle **I** underwent stoichiometric C2-alkenylation with methyl acrylate to give the cross-coupling product **2a** in 65% yield [Eq. (4)]. Palladacycle **I** could also catalyze the oxidative coupling of **1a** with methyl acrylate to afford **2a** in 70% yield [Eq. (4)]. Furthermore, kinetic isotope experiments suggest that cleavage of the C–H bond at the *ortho* position is involved in the rate-determining step (for details, see the Supporting Information).[7c]

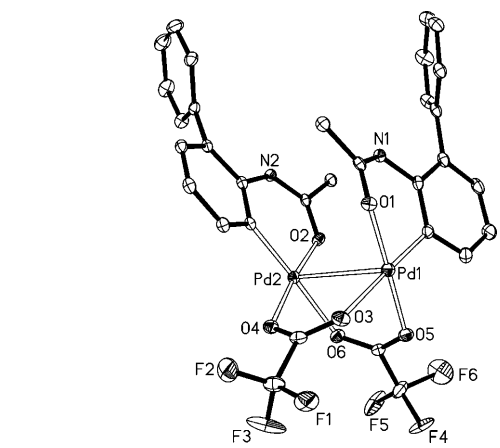
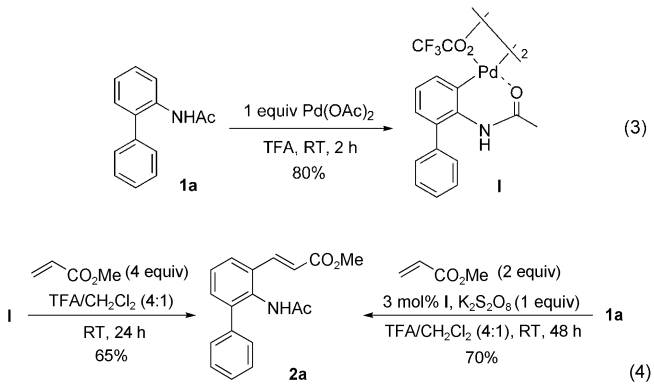


Figure 1. Molecular structure of **I**. Thermal ellipsoids are shown at the 30% probability level.



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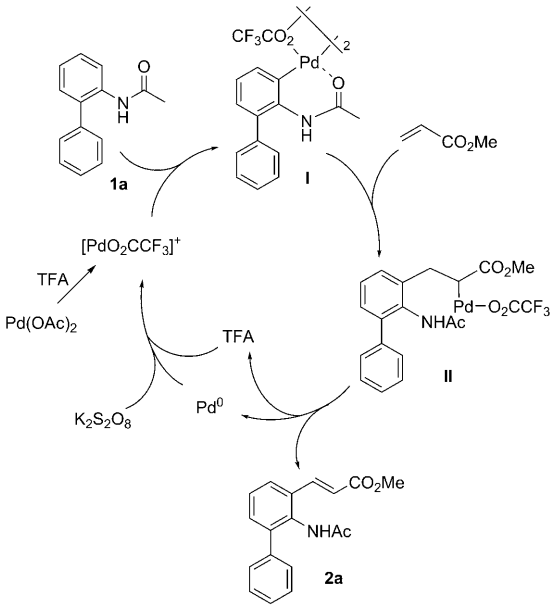
Scheme 2 outlines a plausible mechanism for the Pd-catalyzed oxidative cross-coupling reaction between acetanilide **1a** and methyl acrylate. Based on our experimental findings,



Scheme 2. Proposed mechanism for the Pd-catalyzed *ortho* olefination of acetanilides.

the cationic palladium species $[PdO_2CCF_3]^+$ generated from $Pd(OAc)_2$/TFA participates in the *N*-Ac-directed *ortho* cyclopalladation and leads to the formation of palladacycle **I**. The electronic dependence of the anilide system supports the electrophilic attack at the palladium center during the *ortho*-palladation step. Carbopalladation of methyl acrylate by palladacycle **I** followed by β-hydride elimination then affords the cross-coupling product **2**, where the newly generated Pd^0 is reoxidized to Pd^{II} in the presence of $K_2S_2O_8$. Although the mechanism presented here invokes a Pd^0/Pd^{II} catalytic cycle,[7,12b] an alternative or synergistic mechanistic pathway involving either a Pd^{II}/Pd^{III} or Pd^{II}/Pd^{IV} catalytic cycle[13] cannot be completely excluded.

In summary, we have developed an effective Pd-catalyzed *ortho* olefination of acetanilides and demonstrated unprecedented substrate scope. In particular, this newly established reaction protocol overcame the deficiencies in the previously reported Pd-catalyzed Fujiwara–Moritani reactions with regard to *ortho*-substituted and electron-deficient acetanilides. Furthermore, functional group compatibility should enable further elaboration of the cross-coupling product, thereby allowing rapid access to highly functionalized arenes. In view of the privileged aromatic motifs found in a number of natural and designed compounds with important biological and physical implications, such a synthetic methodology is particularly attractive and valuable.

Experimental Section

General procedure for Pd-catalyzed oxidative coupling reactions of *N*-Ac-2-aminobiaryls with electron-deficient olefins via C–H bond activation: To a solution of *N*-Ac-2-aminobiaryl (**1**) in TFA and CH_2Cl_2 (4:1, 0.5 M) were added olefin (2 equiv), $Pd(OAc)_2$ (5–10 mol%), and $K_2S_2O_8$ (1 equiv). The resulting mixture was stirred at room temperature for the reported time. After the reaction was completed, the reaction mixture was poured into water and basified with sat. $NaHCO_3$, and then the product was extracted with CH_2Cl_2 (three times), dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel to afford the corresponding product **2**.

Acknowledgements

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Keywords: acetanilides · C–H activation · olefination · palladium

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