ChemPubSoc Europe

DOI: 10.1002/chem.201503284

CHEMISTRY A European Journal Full Paper

C–H Activation

Palladium(II)-Catalyzed Acetoxime Directed *ortho*-Arylation of Aromatic Alcohols

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Abstract: Biaryls, which contained a benzyloxy motif, were directly constructed through a ligand-promoted Pd^{II}-catalyzed *ortho*-arylation of masked aromatic alcohols. A variety of acetoxime ethers could be coupled with a diverse range of arylboronic acid pinocol esters, giving direct access to bioactive biaryls in modest to good yield. Not only could acetoxime be subsequently removed without a separation, functionalized hydroxylamine derivatives could also be obtained.

Introduction

Development of controlling site-specific functionalization of C–H bonds offers an innovative approach to construct the core structures of pharmaceutical agents, natural products, and organic materials.[1] Harnessing a directing group to enable site-selective C–H functionalization is one of the most successful strategies;[2] however, such transformations are sometimes in conflict with the directing groups available in a particular starting material. Despite great efforts that have been made in the last few decades to exploit varieties of auxiliaries for amines,[3] acids,[4] and ketones[5] in transition-metal-catalyzed direct C–H functionalization, it remains a significant challenge to develop alcohol or masked alcohol-directed C–H oxidation and C–C formation reactions,[6] due to the possible oxidation of the hydroxyl group, weak coordination of alcohols with Pd^{II}, and the constraints of introducing suitable surrogate groups for alcohols.

In 2010, breakthroughs were achieved by Yu and co-workers, who made a series of reports on Pd^{II}-catalyzed hydroxy-directed *ortho*-olefination,[7] intramolecular cyclization,[8] and carbonylation[9] of phenethyl alcohols. However, the use of secondary- or primary alcohols afforded lower yields. Meanwhile, Hartwig and co-workers developed a practical hydroxyl-directed *ortho*-silylation of benzyl alcohols by employing an Ir catalyst, followed by a separate Hiyama-type coupling of the benzoxasiloles with aryl halides.[10] Despite these advances, there is still a demand to more efficiently and directly construct biaryls containing a benzyloxy motif, which are the omnipresent component of many drug candidates, for example, in known HNF-4α modulators,[11] JTT-305,[12] and VEGF receptor inhibitors[13] (Figure 1; HNF = hepatocyte nuclear factor, VEGF = vascular endothelial growth factor). Recently, our group reported acetoxime directed *ortho*-olefination of masked aromatic alcohols through a six- or seven-membered *exo*-palladacycle (Scheme 1 A).[14] Though the crystallization of *exo*-palladacycle intermediate demonstrated the ability of *exo*-directing mode, we have not tapped its potential. Herein, we report the first Pd^{II}-catalyzed cross-coupling of *O*-benzylacetoximes with arylboron reagents, in which oxime serves as an *exo*-type directing

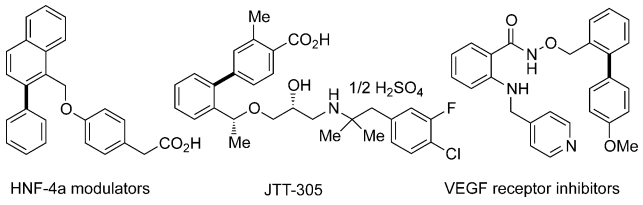
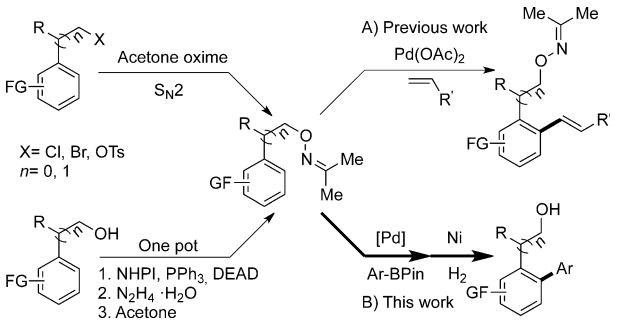


Figure 1. Biologically active compounds containing a benzyloxy motif.



Scheme 1. Pd^{II}-catalyzed acetoxime-assisted C–H functionalization. NHPI = *N*-hydroxyphthalimide, DEAD = diethyl azodicarboxylate.

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Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201503284.

group, and can be subsequently removed without a separation (Scheme 1 B).

While oxime is well-known for transition-metal-catalyzed C–H activation of masked ketones,[5,15] Dong and co-workers developed the first *exo*-oxime-directed acetoxylation of masked alcohols under Pd^{II}/Pd^{IV} catalysis.[16] In this seminal report, they developed a catalytic alcohol β-C(sp^3)–H activation and C–O formation reaction, where using a 2,6-dimethoxylbenzaldoxime as novel bidentate directing group was found to be crucial.[16a] Later, they expanded its application in Pd-catalyzed *ortho*-acetoxylation of masked benzyl alcohol.[16b] However, we envisioned that using concise acetoxime as monodentate directing group should also be beneficial to the arene C–H activation, because 1) *O*-benzylacetoximes are simple and readily available, which can be easily synthesized from an S_N2 reaction of benzyl halides with acetone oxime,[17] or prepared from widely available alcohols though a one-pot procedure (Scheme 1); 2) the acidic α-hydrogens in acetoxime are rather stable under mild oxidative conditions;[14] 3) tuning the reactivity and selectivity of catalysts can be achieved through the use of external ligands;[18] 4) not only is acetoxime used as a traceless directing group, but hydroxylamine[13,19] also exists in bioactive molecules.

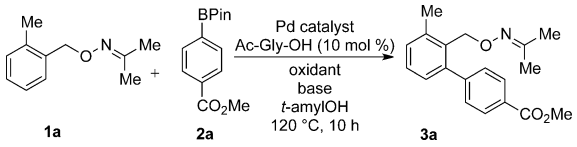
Results and Discussion

Initially, we treated acetoxime ether **1a** with phenylboronic acid pinacol ester **2a** at 120 °C for 10 h with a combination of different oxidants, bases, and ligands (Table 1). Preliminary results revealed that the use of $Pd(TFA)_2$ (10 mol%), Ac-Gly-OH (10 mol%), and Ag_2CO_3 (2 equiv) in *t*-amylOH (0.5 mL) gave the *ortho*-arylation product **3a** in 85% yield (Table 1, entry 1). In a further investigation into the performance of different bases, no positive effect was observed in the presence of common weak bases (entries 2–8). Interestingly, the addition of KBF_4 facilitated this transformation, giving **3a** in 93% yield (entry 9). Although the reason needs to be further explored, we speculated that the KBF_4 would play the role of a pH buffer in the catalytic cycle, which would stabilize the palladium intermediate. Among the palladium catalysts screened, though $Pd(OAc)_2$, $Pd(PPh_3)Cl_2$, $Pd(CH_3CN)_2Cl_2$, and $PdCl_2$ resulted in moderate to good yield (entries 10–13), $Pd(TFA)_2$ was found to be superior. Because of competitive Pd^{II}-mediated protonation and homocoupling of the arylboron reagents, the use of 10 mol% of catalyst was deemed necessary (entries 9 and 14). Having identified the best catalyst, we proceeded to evaluate the optimal oxidant. The oxidants such as AgOAc, Ag_2O, $Cu(OAc)_2$, and 1,4-benzoquinone (BQ) were all tested (entries 15–18); however, Ag_2CO_3 still turned out to be the best. From previous studies, the ligands can adjust the steric and electronic properties of coordinated Pd^{II} centre.[18d,e,g,20] Thus, the ligand of Ac-Gly-OH, which could significantly promote C(sp^2)–H activation and subsequent coupling reactions, was indispensable (entries 9 and 19). In the absence of a palladium catalyst, the control experiment gave no product (entry 20).

With optimized conditions for the cross-coupling in hand, various masked aromatic alcohols were prepared and examined to test the generality of this methodology (Scheme 2). To our great delight, the electron-rich arenes provided the corresponding arylated products in moderate to good yield (**3c–g,i,j**). In particular, both *meta*- and *para*-substituted benzyl alcohol derivatives afforded the corresponding mono-arylated products in good yield (64%–83%). Trace diarylated products were also observed in the reaction system (**3e–h**). It is probable that the steric hindrance and coordinated effect inhibited the further arylation reaction. Furthermore, the α-substituted benzyl alcohols were all well-tolerated, affording arylated products in good to excellent yield (**3k–m,q**). In particular, the acetoxime-protected 1,4-benzenedimethanol gave the mono-arylated product **3o** in a synthetically acceptable yield. Rather disappointingly, *O*-phenylacetoxime would be completely decomposed into undetectable smaller molecules under Pd^{II}/Pd^0 catalysis (**3p**). In contrast, the acetoxime-protected phenethyl alcohol afforded the arylated product in good yield with 2.5 equiv of **2a**, which may go through a rare seven-membered *exo*-palladacycle intermediate.[14]

The efficiency of this acetoxime-assisted C–H transformation encouraged us to evaluate the scope of arylboronic acid pinacol esters (Ar-BPins). In general, various *para*- and *meta*-substituted Ar-BPins were tolerated in this transformation, affording the corresponding products in good to excellent yield (Scheme 3). Gratifyingly, this synthetic protocol is compatible with various functional groups, including F, Cl, Ac, CF_3, SO_2Me,

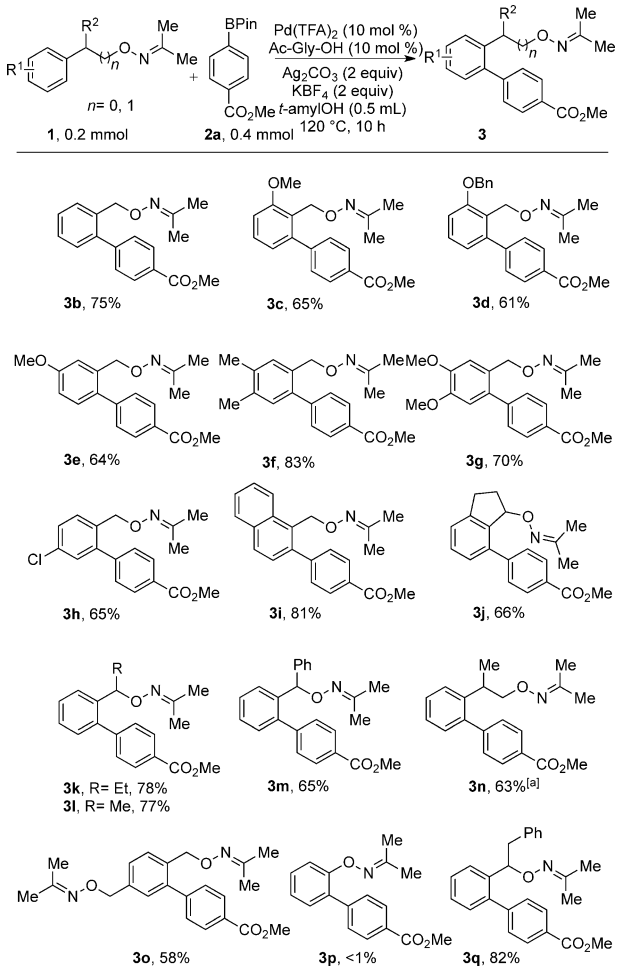
Table 1. Optimization of reaction conditions.[a]



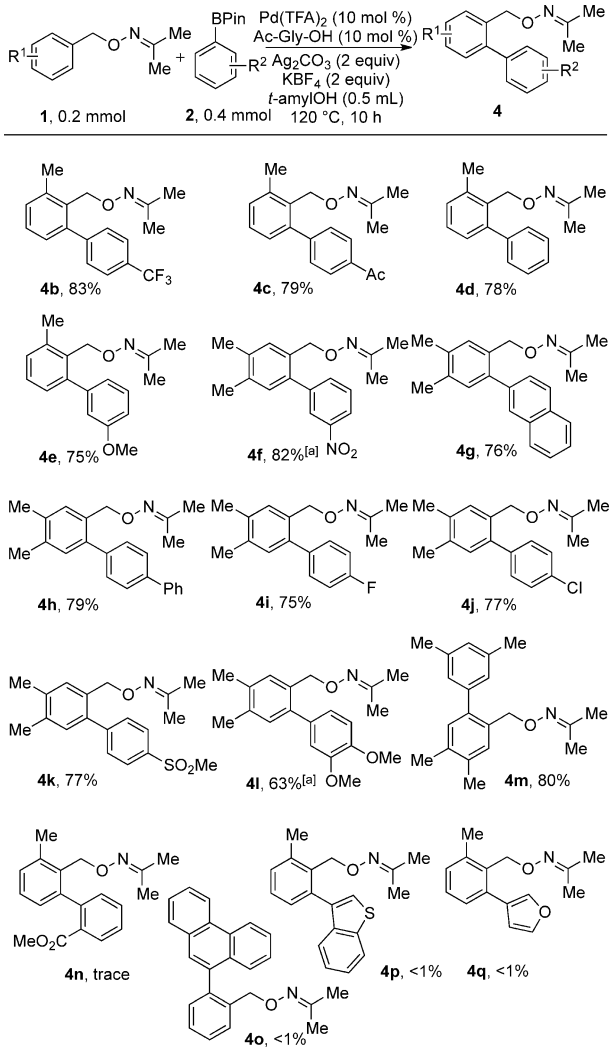
1a 2a 3a

Entry	Catalyst	Oxidant	Base	Yield[b] [%]
1	$Pd(TFA)_2$	Ag_2CO_3	–	85
2	$Pd(TFA)_2$	Ag_2CO_3	K_3PO_4	5
3	$Pd(TFA)_2$	Ag_2CO_3	K_2HPO_4	31
4	$Pd(TFA)_2$	Ag_2CO_3	KH_2PO_4	83
5	$Pd(TFA)_2$	Ag_2CO_3	$NaHCO_3$	49
6	$Pd(TFA)_2$	Ag_2CO_3	Na_2CO_3	38
7	$Pd(TFA)_2$	Ag_2CO_3	Li_2CO_3	87
8	$Pd(TFA)_2$	Ag_2CO_3	$NaBF_4$	84
9	**$Pd(TFA)_2$**	**Ag_2CO_3**	**KBF_4**	**93**
10	$Pd(OAc)_2$	Ag_2CO_3	KBF_4	51
11	$Pd(PPh_3)Cl_2$	Ag_2CO_3	KBF_4	77
12	$Pd(CH_3CN)_2Cl_2$	Ag_2CO_3	KBF_4	80
13	$PdCl_2$	Ag_2CO_3	KBF_4	77
14[c]	$Pd(TFA)_2$	Ag_2CO_3	KBF_4	84
15	$Pd(TFA)_2$	Ag_2O	KBF_4	18
16	$Pd(TFA)_2$	AgOAc[d]	KBF_4	39
17	$Pd(TFA)_2$	$Cu(OAc)_2$	KBF_4	12
18	$Pd(TFA)_2$	BQ	KBF_4	3
19[e]	$Pd(TFA)_2$	Ag_2CO_3	KBF_4	8
20	-	Ag_2CO_3	KBF_4	0

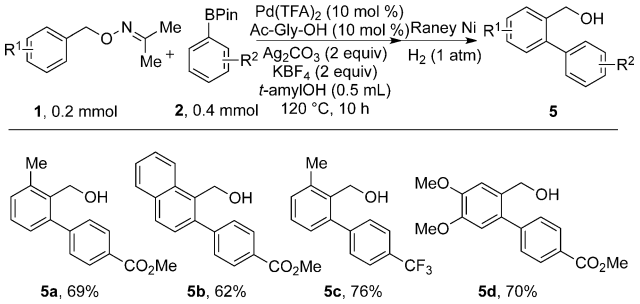
[a] Reaction conditions: **1a** (0.2 mmol), **2a** (0.4 mmol), Pd catalyst (10 mol%), oxidant (2.0 equiv), base (2.0 equiv) in *t*-amylOH (0.5 mL), 120 °C, 10 h. [b] GC yield determined using tridecane as internal standard. [c] $Pd(TFA)_2$ (5 mol%), Ac-Gly-OH (5 mol%). [d] AgOAc (4 equiv). [e] Without Ac-Gly-OH.



Scheme 2. C(sp^2)–H cross-coupling of Ar-BPin with various functionalized acetoxime ethers. [a] Reaction was carried out with **2a** (0.5 mmol).



Scheme 3. C(sp^2)–H cross-coupling of acetoxime ethers with different Ar-BPins. [a] Reaction was carried out with **2** (0.5 mmol).



Scheme 4. Sequential arylation and removal of directing group.

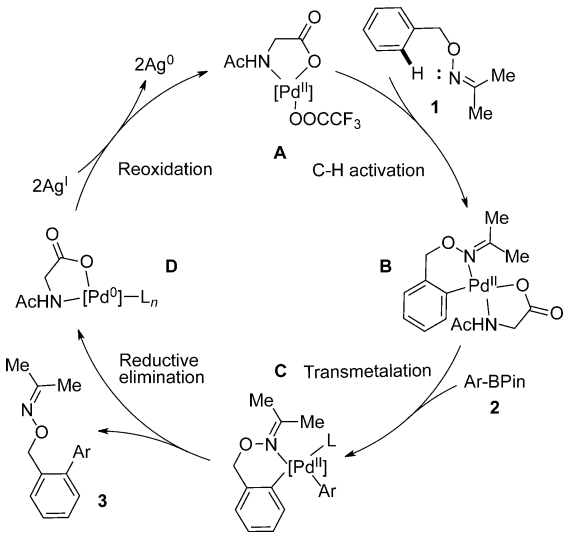
NO_2, Me, and OMe. Moreover, the 2-naphthylboronic acid pinacol ester gave the corresponding coupling product in good yield (**4g**). Unfortunately, poor conversions were obtained for *ortho*-substituents on account of steric hindrance (**4n** and **4o**). Similarly, heteroarylboronates that contained thianaphthene (**4p**) and furan (**4q**) were unreactive under this condition.

To further demonstrate the synthetic simplicity and versatility of the acetoxime group, we developed a sequential procedure, which could accomplish arylation and removal of the directing group with one separation, to access arylated benzyl alcohols (Scheme 4). The key to make this protocol successful depends on the reduction of acetoxime by Raney Ni catalyst.[14] Alternatively, hydrolysis of acetoxime could obtain hydroxylamine derivatives.[21]

Based on the above results and pioneering studies,[3f,g,h,5a,16,18d,22] the mechanism of acetoxime-directed *ortho*-arylation reaction is proposed as depicted in Scheme 5.To begin with, the Pd^{II} species **A**, which is bound by amino acid ligand, coordinates with the substrate **1** and subsequently activates the *ortho*-C–H bond, forming a six-membered *exo*-palladacycle intermediate **B**.[14] Transmetalation with Ar-BPin **2** produces intermediate **C**,[18d,3h] followed by reductive elimination, releases the target molecule **3**, with concomitant generation of Pd^0 species **D**. Reoxidation with 2 equiv of Ag^I regenerates the active Pd^{II} species **A** for another catalytic cycle.

Conclusion

We have developed the first example of acetoxime-directed *ortho*-arylation of masked aromatic alcohol derivatives via the



Scheme 5. Proposed catalytic cycle.

possible six- and seven-membered *exo*-palladacycle intermediate. A variety of acetoxime ethers can be coupled with a diverse range of arylboronic acid pinocol esters giving direct access to bioactive biaryls containing a benzyloxy motif under ligand-accelerated palladium catalysis. Impressively, either acetoxime can be subsequently removed without a separation, or functionalized hydroxylamine derivatives can be obtained. To gain insight into the reaction mechanism and explore the potential of *exo*-type acetoxime directing group in transition-metal-catalyzed C–H activation, further investigations are currently in progress in our lab.

Experimental Section

General procedure for the palladium(II)-catalyzed acetoxime-directed *ortho*-arylation of aromatic alcohols (Schemes 2 and 3)

To a 20 mL sealed tube (with a Teflon cap) equipped with a magnetic stir bar, the following were added sequentially: $Pd(TFA)_2$ (6.6 mg, 0.02 mmol, 10 mol%), Ac-Gly-OH (2.3 mg, 0.02 mmol, 10 mol%), Ag_2CO_3 (110.3 mg, 0.4 mmol, 2.0 equiv), KBF_4 (50.4 mg, 0.4 mmol, 2.0 equiv), phenylboronic acid pinacol ester **2** (0.4 mmol, 2.0 equiv), and acetoxime ether **1** (0.2 mmol, 1.0 equiv). *t*-AmylOH(0.5 mL) was carefully added to rinse the chemical on the inner side wall of the tube. The tube was then capped and submerged in a preheated 120 °C oil bath. The reaction was stirred for 10 h and cooled down to room temperature. The crude reaction mixture was diluted with EtOAc (6 mL) and filtered through a short pad of Celite. The sealed tube and Celite pad were washed with an additional 10 mL of EtOAc. The filtrate was concentrated in vacuo, and the resulting residue was purified by flash column chromatography or preparative TLC using EtOAc/hexane 1:50 as the eluent.

Acknowledgements

We gratefully acknowledge the Natural Science Foundation of Jiangsu Province of China (BK20130294), the Young National Natural Science Foundation of China (No. 21402133), and PAPD for financial support.

Keywords: alcohols · arylation · C–H activation · cross-coupling · synthetic methods

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Received: August 19, 2015
Published online on October 9, 2015