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Palladium-Catalyzed Regioselective *ortho*-Acylation of Azoxybenzenes with Aldehyde Derivatives

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Abstract: An efficient strategy for the regioselective *ortho*-acylation of azoxybenzenes with various aldehydes in the presence of palladium catalysts has been developed and furnishes good to excellent yields. The reaction proceeds smoothly and can tolerate a variety of functional groups.

Keywords: *ortho*-acylation; aldehydes; azoxybenzenes; C–H bond cleavage; palladium catalysis

During the development of methods for organic synthesis, the emergence of direct functionalization of unreactive C–H bonds by transition metal catalysts provides an atom-economic strategy, which dramatically shortens the pathway to the construction of carbon-carbon or carbon-heteroatom bonds and has achieved great progress in the synthesis of many useful polyfunctional compounds.[1,2] Generally, most of the established approaches to regio- and chemoselective C–H bond cleavage involving directing group-assisted activation have been extensively investigated, with groups such as acetyl,[3] acetamino,[4] carboxylic acid,[5] ester,[6] aldehydes,[7] ketones,[8] nitriles,[9] oxazolyl,[10] pyridyl[11] and imino[12] moieties. Hence, the elegant combination of suitable transition metals and directing groups is very crucial to realize C–H bond cleavage and further transformations. To the best of our knowledge, azoxy compounds with two directing groups[13] (N or O), which represents an extreme challenge in the control of two different kinds of C–H bond activation, have rarely been studied in the field of C–H functionalization.[14]

Azoxy compounds, which are key materials in electronic devices, have wonderful liquid crystalline properties,[15] and have also wide applications in dyes, polymer inhibitors and stabilizers.[16] Although numerous methods for the synthesis of azoxy compounds have been developed,[17] exploration in the functionalization of azoxybenzenes is very limited. Very recently, as part of the development of group-directed C–H bond activation, Wang and co-workers first reported a Pd-catalyzed functionalization of azoxybenzenes with oxocarboxylic acids,[14a] and subsequently developed a Ru-catalyzed alkenylation of azoxybenzenes.[14b] As far as we know, there are only the two above reports on C–H bond functionalization of azoxy compounds. Considering the importance of azoxy compounds and the significant bioactive motifs of aryl ketones,[18] it is necessary to develop a new method to realize C–H bond activation of azoxybenzenes, and the coupling partner should be very cheap and accessible. Pursuing our interest in the cleavage of inert chemical bonds,[19] herein we report a direct, novel and efficient approach to establish a strategy for the *ortho*-acylation of a number of different azoxy compounds *via* nitrogen atom-directed Pd-catalyzed C–H bond activation with various commercially accessible aldehydes (Scheme 1).

Our initial investigation focused on the model reaction of azoxybenzene (**1a**, 1.0 equiv.) and benzaldehyde (**2a**, 2.0 equiv.) with TBHP (3.0 equiv.) in the presence of 10 mol% $Pd(OAc)_2$ in DCE at 60 °C for 24 h (Table 1, entry 1). To our delight, the desired product **3a** was isolated in 28% yield, and further screening of additives showed an obvious increase in yield when trifluoroacetic acid was added (Table 1, entry 2). Furthermore, different Pd catalysts were also investigated, among which $Pd(TFA)_2$ possessed the highest catalytic activity, and the corresponding product was obtained in 85% yield (Table 1, entries 3–6). It was very important to demonstrate that the reaction temperature is very crucial to this transformation, and increasing or lowering the temperature suppressed the efficiency, for example, increasing the temperature to 80 °C brought a distinct reduction in

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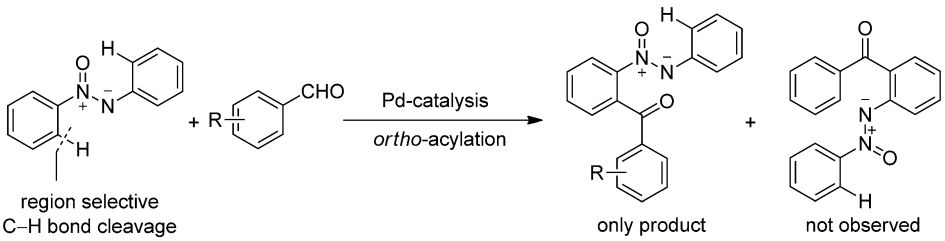
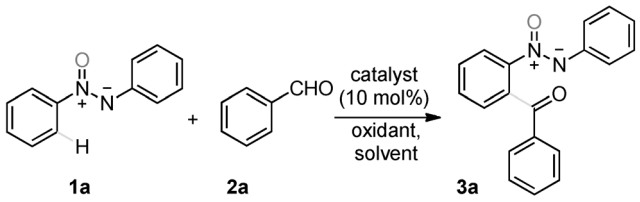


Scheme 1. Pd-catalyzed *ortho*-acylation of azoxybenzenes with benzaldehydes.

Table 1. Optimization of the reaction conditions.[a]



1a **2a** **3a**

Entry	Catalyst	Oxidant	Solvent	Yield [%][b]
1	$Pd(OAc)_2$	TBHP	DCE	28
2	$Pd(OAc)_2$	TBHP	DCE	71[c]
3	$PdCl_2$	TBHP	DCE	30
4	$PdCl_2(MeCN)_2$	TBHP	DCE	28
5	$Pd(PPh_3)_4$	TBHP	DCE	24
6	**$Pd(TFA)_2$**	**TBHP**	**DCE**	**85**
7	$Pd(TFA)_2$	TBHP	DCE	54[d]
8	$Pd(TFA)_2$	TBHP	DCE	66[e]
9	$Pd(TFA)_2$	TBHP	toluene	trace
10	$Pd(TFA)_2$	TBHP	dioxane	trace
11	$Pd(TFA)_2$	TBHP	MeCN	n.r.
12	$Pd(TFA)_2$	TBHP	AcOH	30
13	$Pd(TFA)_2$	TBHP	neat	56
14	$Pd(TFA)_2$	DTBP	DCE	9
15	$Pd(TFA)_2$	DDQ	DCE	trace
16	$Pd(TFA)_2$	$(NH_4)_2S_2O_8$	DCE	trace
17	$Pd(TFA)_2$	$PhI(OAc)_2$	DCE	<5
18	$Pd(TFA)_2$	TBHP	DCE	75[f]

[a] All the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.4 mmol of **2a** and 0.6 mmol of TBHP in 1.0 mL DCE at 60 °C under Ar.
[b] Isolated yields.
[c] 1.0 equiv. of TFA was added.
[d] At 40 °C.
[e] At 80 °C.
[f] Under air conditions.

yield (Table 1, entries 7 and 8). It should be noted that this transformation works well only in the presence of DCE, however, other solvents such as toluene, dioxane, MeCN, or AcOH were less effective or impeded the reaction (Table 1, entries 9–12). Afterwards, we also tested this transformation under neat conditions which only afforded the desired product in 56% yield (Table 1, entry 13). Meanwhile, the oxidants also played a very important role in this catalytic procedure, and other common oxidants reduced or failed to participate in this reaction (Table 1, entries 14–17). It is gratifying that this catalytic procedure was also effective under air conditions, although the isolated yield was slightly lower (Table 1, entry 18). Finally, the optimized conditions for the C–H *ortho*-functionalization of azoxybenzenes were determined to be 60 °C for 24 h in DCE with 10 mol% $Pd(TFA)_2$ as the catalyst and 3.0 equiv. of TBHP as the oxidant.[20]

To explore the applicability of this protocol, various aromatic aldehydes were surveyed and the results are summarized in Table 2. To our delight, the C–H acylation of azoxybenzenes with different aldehydes could proceed smoothly and moderate to excellent yields were obtained for most cases. The substitution on the aromatic ring demonstrated that no significant electronic effect of the *para*-substituted azoxybenzenes was present (Table 2, **3ab**, **3af**–**3ah**, **3ak**), except for 4-cyanobenzaldehyde and 4-nitrobenzaldehyde, which showed obvious deleterious effects (Table 2, **3ai** and **3aj**). It is worth noting that the bromo group remained intact in this procedure with an excellent yield, which could be used for further transformations into other important structures. And fortunately, a representative structure of **3ah** was confirmed by X-ray single crystal analysis (see the Supporting Information for more details). Surprisingly, the steric hindrance effect was not observed when *meta*- and *ortho*-substituted aromatic aldehydes were involved in the reaction, and the corresponding products were obtained in 81% (**3ac**) and 80% (**3ad**) yields, respectively. Also, 1-naphthaldehyde was tested in the reaction and the yield of the product was acceptable (Table 2, **3ae**). Encouraged by the above results, an aliphatic aldehyde, such as *n*-butyraldehyde, was evaluated and a moderate yield of the product was isolated (Table 2, **3am**). However, when heterocyclic-substituted aldehydes were exposed under the reaction conditions, the corresponding products were obtained in low efficiency. For example, the product **3an** was isolated in 20% yield, which did not change even with higher temperature or longer reaction time.

Next, we tested the scope of different azoxy compounds in this procedure with benzaldehyde under our best conditions. The results demonstrated that azoxy derivatives with electron-donating groups gave better yields than those with electron-withdrawing groups. For example, 4,4′-dimethylazoxybenzene and

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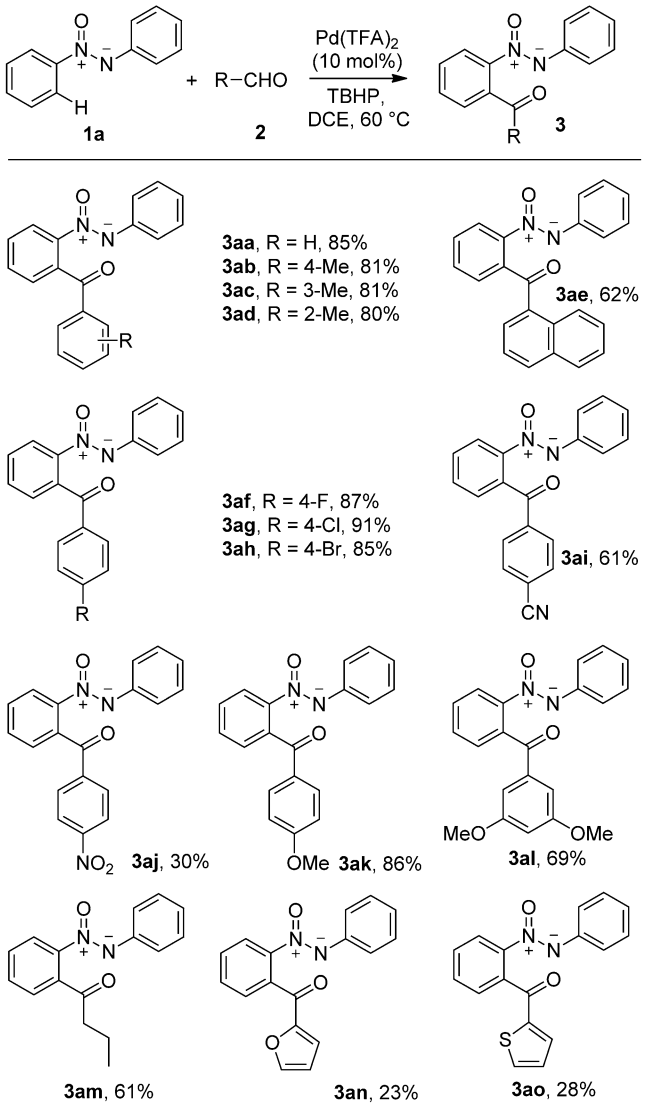
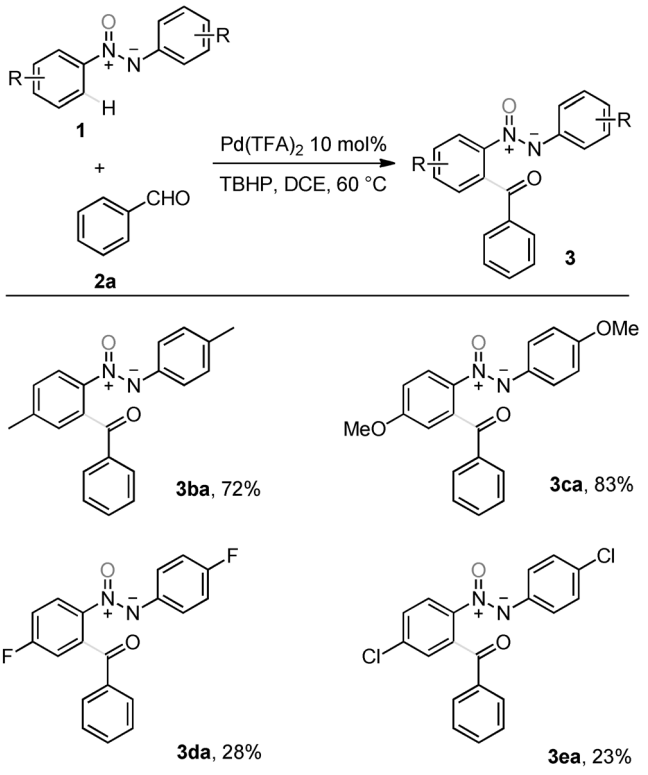
Table 2. Scope of the *ortho*-acylation of azoxybenzene with aldehydes.[a,b]



[a] All the reactions were carried out in the presence of 0.2 mmol of **1a**, 0.4 mmol of **2** and 0.6 mmol of TBHP in 1.0 mL DCE at 60 °C under Ar.
[b] Isolated yields.

Table 3. Scope of azoxy compounds with benzaldehyde.[a,b]



[a] All the reactions were carried out in the presence of 0.2 mmol of **1**, 0.4 mmol of **2a** and 0.6 mmol of TBHP in 1.0 mL DCE at 60 °C under Ar.
[b] Isolated yields.

4,4′-azoxydianisole provided the desired products in excellent yields (Table 3, **3ba** and **3ca**), while sharply reduced yields were observed with electron-deficient substituents at the *para*-positions of azoxybenzenes, such as F and Cl (Table 3, **3da** and **3ea**).[21] Unfortunately, other electron-deficient groups, such as CF_3 and CO_2Me were not beneficial for this transformation, and almost no desired products were isolated.

On the basis of our experimental results and previous literature,[14,22] a plausible mechanism pathway for the Pd-catalyzed C–H functionalization of azoxybenzenes is depicted in Scheme 2. Although two kinds of potential C–H bonds exist in the azoxybenzene based on the regions of the N and O atoms, the real directing group is N, which is generally considered to be a better coordinating atom than O when complexed with Pd(II). So it is reasonable to assume first that the reaction is probably initiated by N-assisted *ortho*-selective cyclometalation on the arene ring by $Pd(TFA)_2$, followed by reaction with the acyl radicals, which were generated *in situ* by abstraction of hydrogen atom of aldehydes. Second, the intermediate **II** was formed *via* oxidation of Pd(II) to Pd(IV) or dimeric Pd(III).[23] Finally, reductive elimination of acyl and aryl groups provides the *ortho*-acylated products and the active Pd(II) was regenerated. To prove the existence of radical intermediates, TEMPO (2,2,6,6-tetramethyl-piperidyl-1-oxyl) was added as a radical scavenger and the reaction was suppressed completely.[24]

Due to the unique biological activity of indazoles as liver X receptor agonists[22,25] and a previous report,[14a] the various *ortho*-acylation products can be easily transformed into the corresponding indazoles under reduction conditions, which afforded a more efficient and economical method to construct the backbone of indazoles (Scheme 3).

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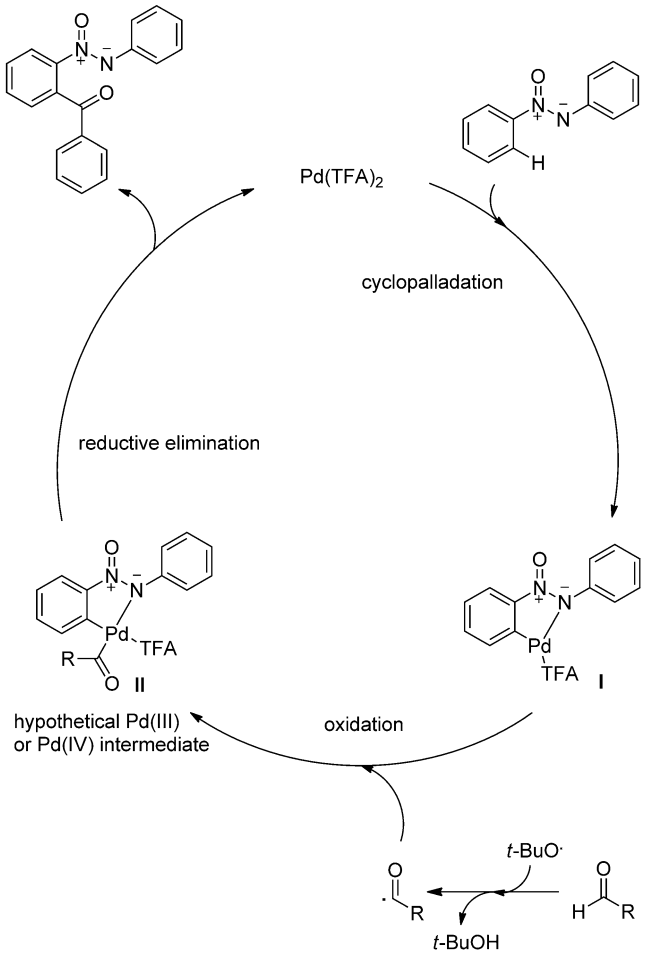
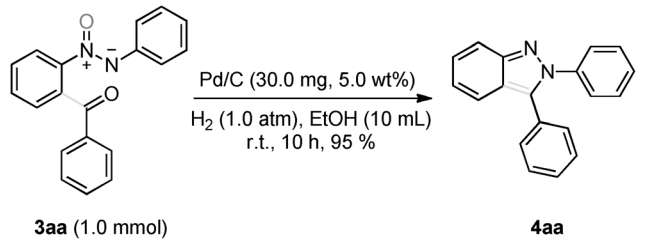


Scheme 2. Proposed reaction mechanism.



Scheme 3. Transformation of *ortho*-acylated azoxybenzene into indazole.

In conclusion, we have developed a novel catalytic system for the *ortho*-acetyl functionalization of azoxybenzenes *via* N atom-directed activation of C–H bond with TBHP as an oxidant. This procedure was highly efficient and easy to handle. The availability of the aldehydes and the extensive scope observed make this strategy attractive to synthetic chemists. Further studies on applications of this approach and other functionalizations of azoxy compounds are ongoing in our laboratory.

Experimental Section

General Procedure

An oven-dried 10-mL screw-capped vial was charged with $Pd(TFA)_2$ (6.6 mg, 0.02 mmol, 10 mol%), azoxybenzene (39.6 mg, 0.2 mmol, 1.0 equiv.), and benzaldehyde (42.4 mg, 0.4 mmol, 2.0 equiv.) under a gentle stream of argon. Then TBHP (108 μL, 5.5 M, 0.6 mmol, 3.0 equiv.) and DCE (1 mL) were added to the vial by a syringe. The vessel was heated in an oil bath at 60 °C for 24 h followed by cooling. The contents were subjected to flash chromatography to give the corresponding product (85%) as a pale yellow oil. The purified material was dried under an oil-pump vacuum.

Acknowledgements

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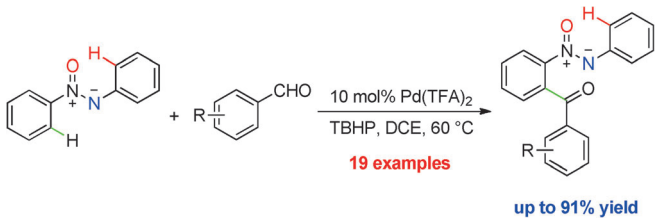

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