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Palladium-Catalyzed Acylation of 2-Aryl-1,2,3-triazoles with Aldehydes

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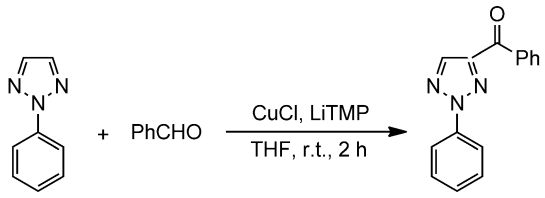
Abstract: The palladium-catalyzed acylation of 2-aryl-1,2,3-triazoles with aldehydes *via* C–H bond activation is described. A wide variety of products was isolated in good to excellent yields. This finding provides a new and useful strategy for the synthesis of aromatic ketones.

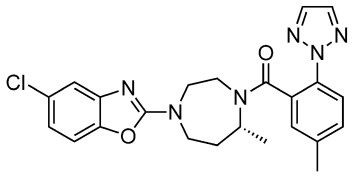
Keywords: acylation; 2-aryl-1,2,3-triazoles; catalysis; C–H activation; palladium

Transition metal-catalyzed direct C–H bond functionalization has emerged as an important transformation in organic chemistry.[1] Palladium-catalyzed regioselective C–H functionalization has been extensively exploited.[2] The combination of transition metals and directing groups is a useful method to facilitate C–H bond cleavage.[3] Recently, Cheng reported a palladium-catalyzed direct access to ketones from aldehydes *via* the C–H cleavage of arenes.[4] Later, Kim described the palladium-catalyzed oxidative *ortho*-acylation of triflamide-protected benzylamines with aryl and alkyl aldehydes *via* C–H bond activation.[5] At the same time, Fu reported a novel and efficient palladium-catalyzed synthesis of aromatic ketones and isoindolobenzimidazoles *via* selective aromatic C–H bond acylation with readily available carboxylic acids.[6] In 2012, Floris Chevallier reported that 2-phenyl-2*H*-1,2,3-triazole prepared *in situ* from CuCl and LiTMP by using a lithium-copper base produced a phenyl ketone under particular reaction conditions (Scheme 1).[7]

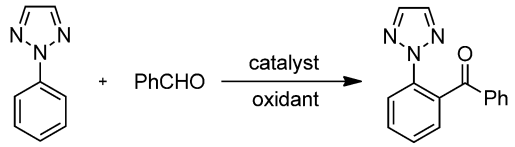
To the best of our knowledge, the direct acylation of 1,2,3-triazole rings is limited to 2-aryl-1,2,3-triazoles. In a broad spectrum of biologically active products, 1,2,3-triazoles function as useful structural elements.[8] Recently, Ye reported the application of 1,2,3-triazole-4-carboxylic acid derivatives as alternative auxiliaries in adjusting the palladium-catalyzed C–H activation.[9] In 2008, Ackermann reported carboxylic acids as cocatalysts for generally applicable direct arylations in apolar solvents.[10] In 2009, Ackermann also reported the ruthenium-catalyzed direct arylations of *N*-aryl-1,2,3-triazoles with aryl chlorides as electrophiles.[11] 1,2,3-Triazoles, which have been known for decades, have become one of the most important heterocycles in current chemical research.[12] Recently, these compounds have found applications in biological science,[13] material chemistry,[14] and medicinal chemistry[15] (Scheme 2). Reports on the reaction of a C–H bond with C-hetero unsaturated bonds are rare.[16] Moreover, the catalytic and direct introduction of carbonyl functional groups into the phenyl ring *via* C–H bond cleavage is appealing in organic chemistry.[17] Many directing groups, such as acetyl,[18] acetamino,[19] and carboxyl[20] groups, have been used in C–H bond activation, especially in *ortho*-aromatic C–H bond functionalization.[21] Given the electron-poor nature of the triazole ring, the direct acylation



Scheme 1. Synthesis of phenyl(2-phenyl-2*H*-1,2,3-triazol-4-yl)methanone.



Scheme 2. Suvorexant.



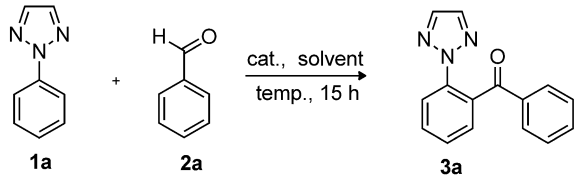
Scheme 3. Transition metal-catalyzed oxidative acylation.

of 2-aryl-1,2,3-triazole has not yet been reported. Inspired by our recent studies on transition metal-catalyzed oxidative acylation of 2-aryl-1,2,3-triazoles with aldehydes,[15c–h] we report herein the palladium-catalyzed *ortho*-acylation of 2-aryl-1,2,3-triazoles *via* C–H bond activation (Scheme 3).

Our initial investigations focused on the reaction of 2-phenyl-2*H*-1,2,3-triazole (**1a**) with benzaldehyde (**2a**). The combination of 2-phenyl-2*H*-1,2,3-triazole (**1a**, 1 equiv.) with benzaldehyde (**2a**, 1.1 equiv.), TBHP (2 equiv.), and $Pd(OAc)_2$ (10 mol%) in DCE at 80 °C for 15 h generated the acylated product [2-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (**3a**) with a yield of 80% (Table 1, entry 1). Based on this initial finding, further investigations on the effect of various reaction conditions were performed, as shown in Table 1. Considering the stability of **1a**, the use of $Pd(OAc)_2$ and *tert*-butyl hydroperoxide (TBHP, 70 wt% in water) was necessary in the model reaction. Solvent screening showed that an improved chemical yield could be obtained by using DCE as the solvent, whereas other solvents, such as DMSO, benzene, MeCN, 1,2-dioxane, and DMF, were less effective (Table 1, entries 2–6). The oxidants had a critical function in this reaction. Aldehydes are very sensitive to several oxidants. Thus, the choice of oxidant is crucial for the reaction conditions.[22] When various oxidants were used, TBHP gave the best results, whereas α,α-dimethylbenzyl hydroperoxide (DTBP), H_2O_2 (70 wt% in water), benzoyl peroxide (BPO), lauroyl peroxide (LPO), dicumyl peroxide (DCP), $Cu(OAc)_2$, Ag_2CO_3, $K_2S_2O_8$, and O_2 were all found to be inferior (Table 1, entries 7–15). On the other hand, the use of oxidants such as $Cu(OAc)_2$ and Ag_2CO_3 was inefficient (Table 1, entries 12 and 13).

The effect of various transition metal catalysts was further investigated. The catalyst $NiCl_2$ only gave a 10% yield (Table 1, entry 16). The use of $Cu(OAc)_2$, $FeCl_2$, and $AgNO_3$ was ineffective for this reaction (Table 1, entries 17–19). When $PdCl_2$ was used as the catalyst in the reaction, **3a** was obtained with a yield of 52% (Table 1, entry 20). $Pd(OAc)_2$ showed excellent activity among these catalysts. When the amount of TBHP (1 equiv.) was decreased, the conversion of the reaction increased up to 85% (Table 1, entry 21). More TBHP was able to oxidize the aldehydes. When the temperature was either increased or decreased, an obvious decline was observed in the yield (Table 1, entries 22–25). Meanwhile, when we decreased the amount of $Pd(OAc)_2$ (5 mol%), the yield decreased (Table 1, entry 26). The best result was obtained using 10 mol% of $Pd(OAc)_2$ and 1 equiv. of TBHP in DCM at 80 °C for 15 h to afford **3a** in high yield (85%), as shown in entry 21.

Table 1. Selected optimization of reaction conditions.[a]



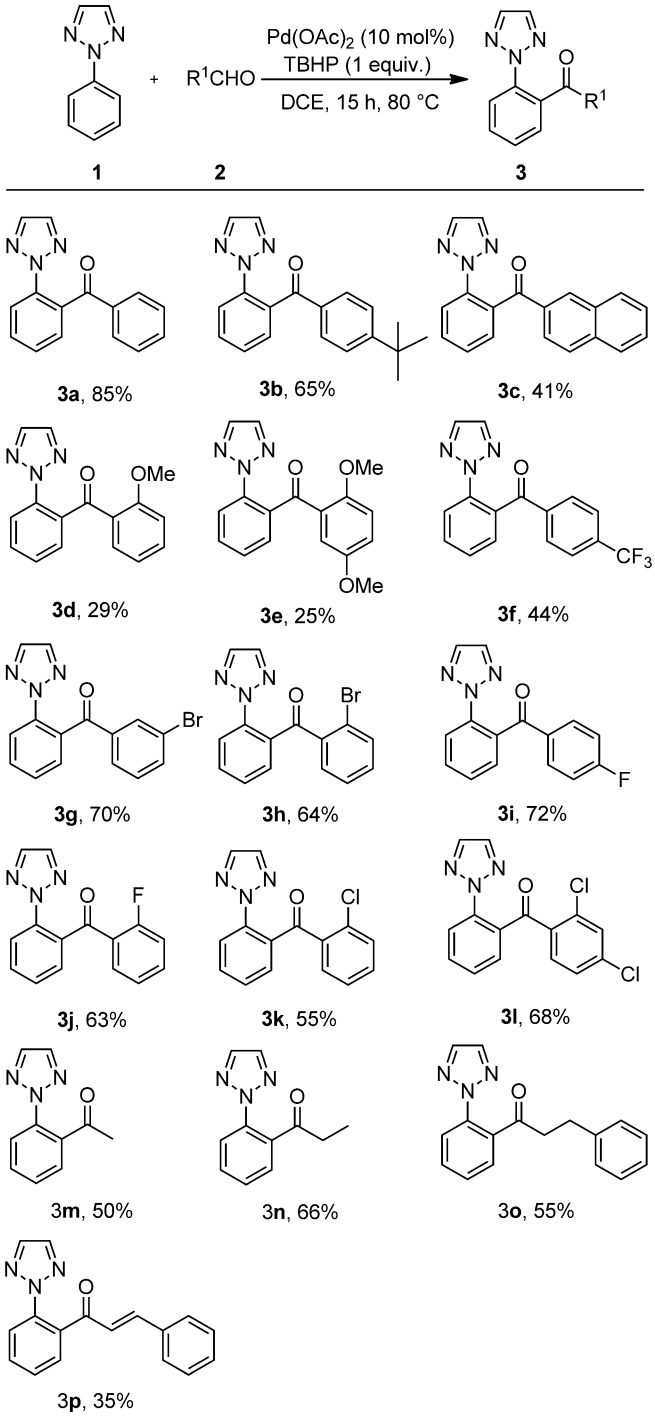
1a **2a** **3a**

Entry	Solvent	Oxidant (equiv.)	Cat. (mol%)	Temp. [°C]	Yield [%][b]
1	DCE	TBHP (2)	$Pd(OAc)_2$ (10)	80	80
2	DMSO	TBHP (2)	$Pd(OAc)_2$ (10)	80	trace
3	Benzene	TBHP (2)	$Pd(OAc)_2$ (10)	80	25
4	MeCN	TBHP (2)	$Pd(OAc)_2$ (10)	80	18
5	1,4-dioxane	TBHP (2)	$Pd(OAc)_2$ (10)	80	38
6	DMF	TBHP (2)	$Pd(OAc)_2$ (10)	80	0
7	DCE	DTBP (2)	$Pd(OAc)_2$ (10)	80	52
8	DCE	H_2O_2 (2)	$Pd(OAc)_2$ (10)	80	10
9	DCE	BPO (2)	$Pd(OAc)_2$ (10)	80	45
10	DCE	LPO (2)	$Pd(OAc)_2$ (10)	80	12
11	DCE	DCP (2)	$Pd(OAc)_2$ (10)	80	43
12	DCE	$Cu(OAc)_2$ (2)	$Pd(OAc)_2$ (10)	80	0
13	DCE	Ag_2CO_3 (2)	$Pd(OAc)_2$ (10)	80	0
14	DCE	$K_2S_2O_8$ (2)	$Pd(OAc)_2$ (10)	80	15
15	DCE	O_2	$Pd(OAc)_2$ (10)	80	20
16	DCE	TBHP (2)	$NiCl_2$ (10)	80	10
17	DCE	TBHP (2)	$Cu(OAc)_2$ (10)	80	trace
18	DCE	TBHP (2)	$FeCl_2$ (10)	80	trace
19	DCE	TBHP (2)	$AgNO_3$ (10)	80	trace
20	DCE	TBHP (2)	$PdCl_2$ (10)	80	52
21	**DCE**	**TBHP (1)**	**$Pd(OAc)_2$ (10)**	**80**	**85**
22	DCE	TBHP (1)	$Pd(OAc)_2$ (10)	r.t.	55
23	DCE	TBHP (1)	$Pd(OAc)_2$ (10)	60	50
24	DCE	TBHP (1)	$Pd(OAc)_2$ (10)	100	60
25	DCE	TBHP (1)	$Pd(OAc)_2$ (10)	120	67
26	DCE	TBHP (1)	$Pd(OAc)_2$ (5)	80	76

[a] *Reaction conditions:* **1a** (0.4 mmol), **2a** (0.44 mmol), catalyst (quantity noted), oxidant (quantity noted), solvent (2 mL) for 15 h in a pressure tube.
[b] Isolated yield.

Having these optimized conditions in hand, we explored different substituted aldehydes, which were reacted with 2-phenyl-2*H*-1,2,3-triazole (**1a**) to generate the desired *ortho* C–H bond acylation product, as shown in Table 2. Various substituted aldehydes produced moderate yields. Although we have not carried out a detailed study of substituent effects, benzaldehyde gave higher yields than those with electron-withdrawing or electron-donating groups. The use of substituents with strong electron-withdrawing character (e.g., CF_3) resulted in low yields. The use of 4-nitrobenzaldehyde, *N,N*-dimethylformamide (DMF) and formaldehyde failed to deliver the acylation product *via* this procedure. Remarkably, halogen-substituted aldehydes were smoothly converted to the corresponding products **3g–l**, which were obtained with

Table 2. Scope of aldehydes for Pd-catalyzed C–H acylation.[a]



[a] *Reaction conditions:* **1a** (0.4 mmol), **2a–p** (0.44 mmol), $Pd(OAc)_2$ (10 mol%), TBHP (0.4 mmol, 70 wt% in water), DCE (2 mL) at 80 °C for 15 h in a pressure tube.
[b] Isolated yield.

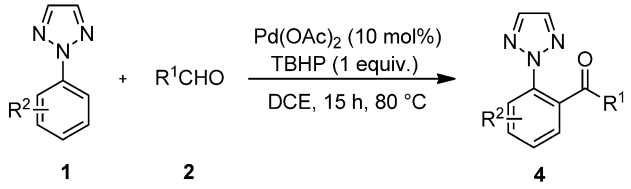
yields of 55–72%. Different substituent positions of the benzaldehydes affected the yield of the products. Thus, **3g–k** were isolated in yields of 55–72%. The presence of an *ortho*-substituted group was not suitable in this C–H activation reaction. Moreover, the steric effects of the *ortho*-substituted group was more pronounced compared with those of the *para*-substituted group. To our delight, this reaction was not limited to aryl aldehydes. Aliphatic aldehydes also participated in this reaction (**3m--3p**). The tolerance of the reaction to these functional groups in the substrates provides the possibility for the further useful transformation of the products.

To evaluate further the substrate scope of this process, a variety of 2-aryl-1,2,3-triazoles (**1b–f**) and aldehydes (**2b**, **2n**, **2q**) in identical reaction conditions were screened, as shown in Table 3. As expected, a series of functional groups on the phenyl ring of 2-aryl-1,2,3-triazoles, such as Me, OMe, Cl, CF_3 and COOMe, were compatible with this procedure, and the acylation products were isolated in moderate to good yields (Table 2, entries 1–10). An interesting regioselectivity was observed when a *meta*-substituent existed at 2-phenyl-2*H*-1,2,3-triazole, in which only the acylation at the *para*-position of this substituent took place because of the steric hindrance (**4a**, **4d**). The substituted aldehydes with electron-withdrawing groups on the benzene rings (e.g., **2q**) were favored in the reaction to form the desired products in good yields (Table 3, entries 4–7). By contrast, electron-donating aldehydes **2b** were relatively less reactive in these reaction conditions. We believe that this reaction may be blocked by the electrophilic attack of the Pd(II) center to the phenyl ring. The hindrance on the aryl group of 2-aryl-1,2,3-triazoles limited the yield of the reaction.

Based on previous studies and our observations, a proposed mechanism is outlined for the Pd-catalyzed C–H acylation in Scheme 4. First, through the chelate-directed C–H activation of 2-phenyl-2*H*-1,2,3-triazole, a five-membered cyclopalladated intermediate **A**, which was confirmed by many previous reports, is formed.[4,21b,23] In fact, a similar metalocycle is obtained through the use of a coordinating group that helps direct the subsequent transition metal C–H bond insertion.[24] The high regioselectivity, as well as the high catalytic activity of the isolated cyclopalladated complex **A**, provides a strong evidence that supports this step.[25] The reaction of benzaldehyde with TBHP generates a reactive benzoyl radical, which reacts with intermediate **A** to carry out the oxidation of Pd(II) to the dimeric Pd(III) or Pd(IV) **B**.[2d] Finally, the intermediate **B** undergoes reductive elimination to generate the acylation product. At the same time, Pd(II) is regenerated for the next catalytic cycle.[26]

In conclusion, we have demonstrated a simple and efficient method for the Pd-catalyzed oxidative *ortho*-acylation of 2-aryl-1,2,3-triazoles with aldehydes *via* C–H bond activation. This method is very convenient

Table 3. Scope of 2-aryl-1,2,3-triazoles.



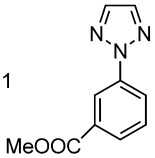
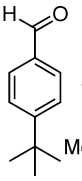
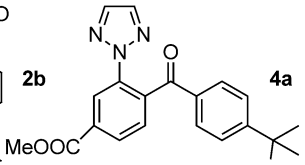
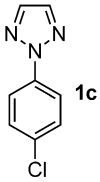
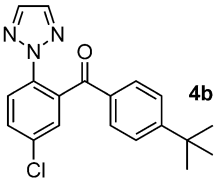
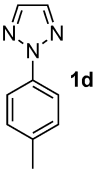
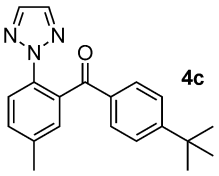
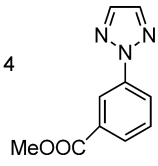
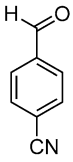
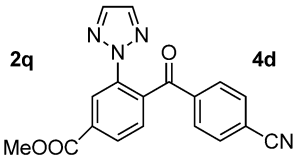
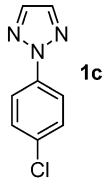
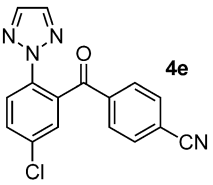
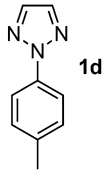
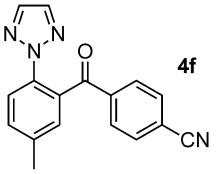
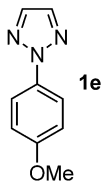
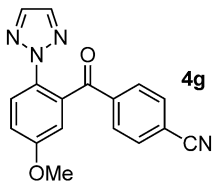
Entry	1	2	4	Yield [%][b]
1				43
2				73
3				71
4				82
5				80
6				71
7				85

Table 3. (Continued)

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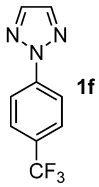
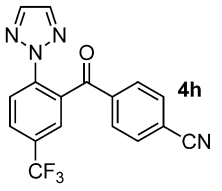
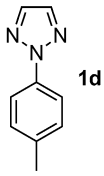
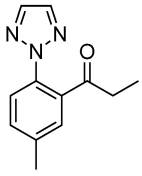
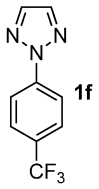
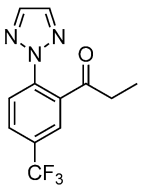
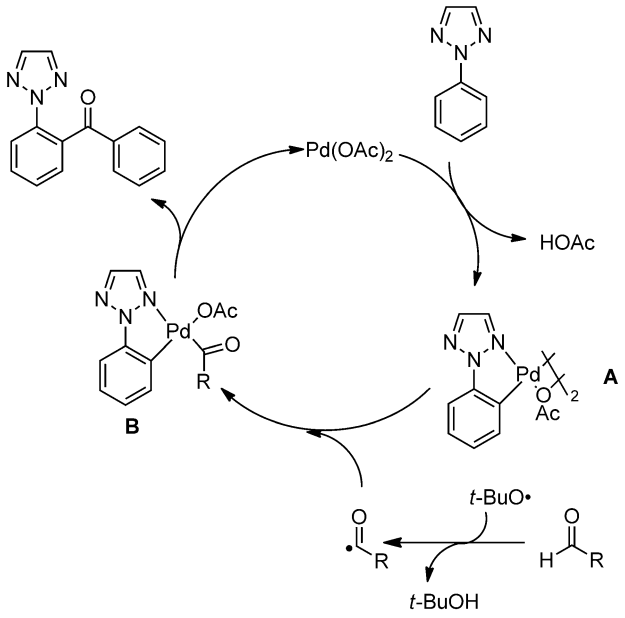
8				52
9				73
10				62

[a] *Reaction conditions:* **1** (0.4 mmol), **2** (0.44 mmol), $Pd(OAc)_2$ (10 mol%), TBHP (0.4 mmol, 70 wt% in water), DCE (2 mL) at 80 °C for 15 h in pressure tubes.
[b] Isolated yield.

and atom-economic for the direct synthesis of aromatic ketones from aldehydes. The oxidant TBHP, which is inexpensive and environmentally benign, was employed in these reactions. The reaction exhibited good functional group tolerance. The mild reaction conditions employed in this reaction provide future poten-



Scheme 4. Plausible mechanism.

tial applications of this method in the synthesis of natural products and other useful compounds. Ongoing work seeks to gain further insights into the mechanism of this reaction and to expand the scope to the acylation of unactivated sp^3 C–H bonds.

Experimental Section

Typical Procedure for the Acylation of 2-Aryl-1,2,3-triazoles

Benzaldehyde (**2a**) (46.64 mg, 0.44 mmol, 1.1 equiv.) was added to an oven-dried, sealed tube charged with 2-phenyl-2*H*-1,2,3-triazole (**1a**) (58 mg, 0.4 mmol, 1 equiv.), $Pd(OAc)_2$ (9 mg, 0.04 mmol, 10 mol%), and TBHP (51.4 mg, 0.4 mmol, 1 equiv.) in DCE (2 mL). The reaction mixture was stirred at 80 °C for 15 h. After the reaction was completed (as monitored by TLC), the mixture was cooled to room temperature. The solvent was then evaporated under vacuum. The resulting residue was purified *via* flash column chromatography (petroleum ether/ethyl acetate = 10:1, *v/v*) to yield [2-(2*H*-1,2,3-triazol-2-yl)phenyl](phenyl)methanone (**3a**).

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