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Cycloisomerization

Palladium-Catalyzed Oxidative Cycloisomerization of 2-Cinnamyl-1,3-Dicarbonyls: Synthesis of Functionalized 2-Benzyl Furans

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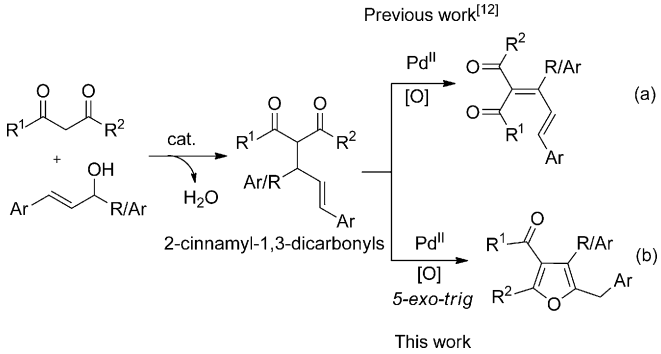
Abstract: A new palladium-catalyzed intramolecular oxidative cycloisomerization of readily available starting materials, 2-cinnamyl-1,3-dicarbonyls, has been demonstrated for the creation of structurally diverse 2-benzyl furans. The cycloisomerization occurs by a regioselective 5-*exo*-trig pathway. The reaction shows a broad substrate scope with good to excellent yields. Furthermore, a one-pot procedure has been executed by using readily available cinnamyl alcohols and 1,3-diketones.

Substituted furans are endowed with a broad spectrum of biologically active natural products and pharmaceuticals.[1] They have been extensively used as building blocks in organic synthesis[2] and materials science.[3] Consequently, there has been a long-standing interest in rapid and reliable construction of functionalized furans, aimed at achieving a greater level of molecular complexity in a convergent and atom-economical fashion from readily accessible starting materials.[4–6] Among various approaches for the synthesis of furans, considerable attention has been paid to develop the intramolecular cycloisomerization of 2-substituted-carbonyl precursors, particularly from 2-alkynyl-[4] or 2-allenylcarbonyl species.[5] Despite the tremendous progress in Pd-catalyzed oxidative addition of carbonyls to alkenes,[7] the aforementioned transformation of 2-alkenylcarbonyls by oxidative cycloisomerization has rarely been reported. Nevertheless, alkenyl species are more readily accessible and manipulable than alkynes or allenes. The pioneering oxidative cycloisomerization of 2-alkenyl-1,3-dione reported by Han and Widenhoefer is the sole example in this regard.[8] However, the method has limited substrate scope with respect to both 1,3-dicarbonyls and their allyl counterparts.

Intrigued by the easy accessibility of 2-cinnamyl-1,3-dicarbonyls, from cinnamyl alcohol (Scheme 1) or cinnamyl bromide and commercially available 1,3-dicarbonyls,[9,10] as well as our continuing interest in developing oxidative cycloisomerization reactions,[11] we embarked on the study of palladium-catalyzed oxidative cycloisomerizations of 2-cinnamyl-1,3-dicarbonyls for the synthesis of highly functionalized 2-benzyl furans by a selective *5-exo*-trig cyclisation pathway (Scheme 1b). However, the competitive formation of α,β,γ,δ-dienones instead of annulation to provide the furan poses a formidable challenge (Scheme 1a).[12]



Scheme 1. Oxidation (a) and oxidative cycloisomerization (b) of 2-cinnamyl-1,3-dicarbonyls.

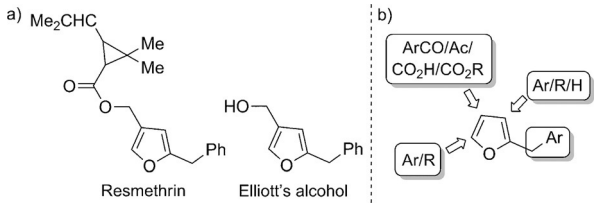


Figure 1. a) Bioactive 2-benzyl furans; b) an array of highly functionalized furans are accessible by the current strategy.

2-Benzyl furans are important privileged scaffolds in many bioactive molecules (Figure 1 a).[13] However, although this core skeleton is useful, a limited number of strategies for its synthesis from easily available precursors are currently known.[14] Furthermore, because of its inherent low reactivity, functionalization at the 3-position of furans has proven difficult,[15] and the synthesis of tetrasubstituted furans remains a challenge.[16]

In our initial attempt to synthesize the furans, we probed a 2-step sequence by using a model reaction of 2-cinnamyl-1,3-dione **1 j** (Table 1). In the presence of benzoquinone (BQ) as oxidant and DMF as solvent, Pd^{II} catalysts, such as $Pd(OAc)_2$, $PdCl_2$, and $[PdCl_2(CH_3CN)_2]$, were tested, the last of which providing the best conversions into the desired product **3 j** (Table 1, entries 1–3). To further improve the yield, $[PdCl_2(CH_3CN)_2]$ catalyst was examined in the presence of a variety of additives (Table 1, entries 4–9) and solvents (entries 9–14). Interestingly, acids played a vital role here and *p*-toluenesulfonic acid monohydrate (PTS) was found to be better than

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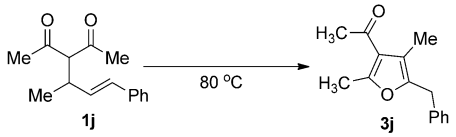
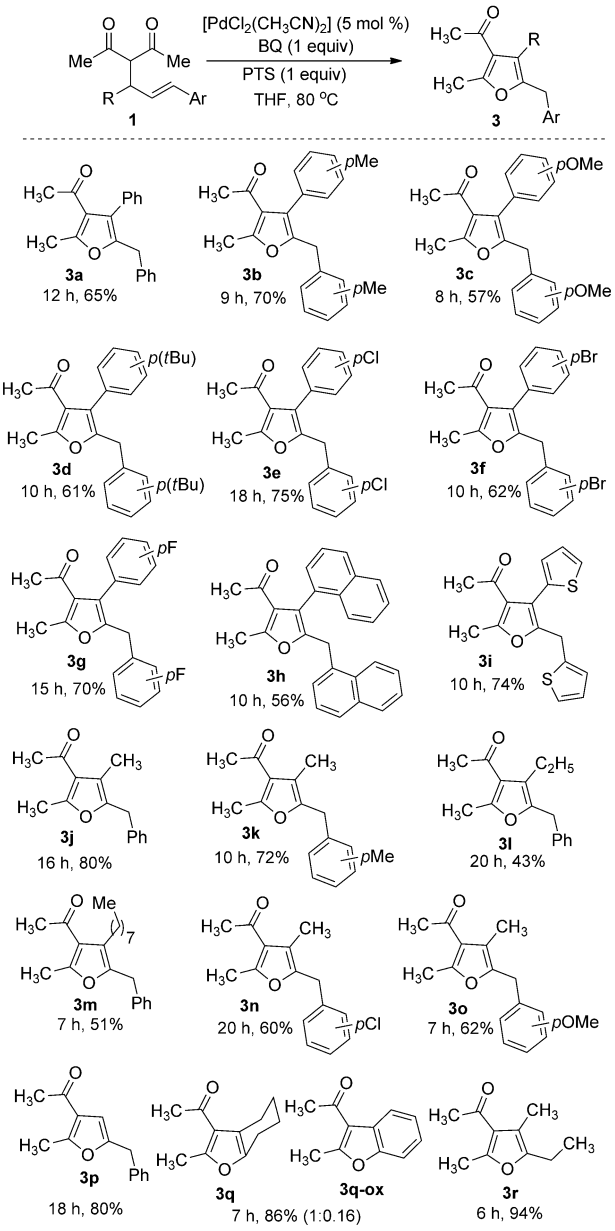
Table 1. Catalyst optimization.



1j 3j

Entry	Catalyst	Additive (1 equiv)	Oxidant (1 equiv)	Solvent	Yield [%][a]
1	$Pd(OAc)_2$	–	BQ	DMF	<5
2	$PdCl_2$	–	BQ	DMF	<5
3	$[PdCl_2(CH_3CN)_2]$	–	BQ	DMF	17
4	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	DMF	46
5	$[PdCl_2(CH_3CN)_2]$	AcOH	BQ	DMF	19
6	$[PdCl_2(CH_3CN)_2]$	TFA	BQ	DMF	21
7	$[PdCl_2(CH_3CN)_2]$	PivOH	BQ	DMF	<5
8	$[PdCl_2(CH_3CN)_2]$	LiCl	BQ	DMF	7
9	$[PdCl_2(CH_3CN)_2]$	K_2CO_3	BQ	DMF	0
10	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	DCE	28
11	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	MeOH	59
12	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	dioxane	77
13	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	toluene	16
14	**$[PdCl_2(CH_3CN)_2]$**	**PTS**	**BQ**	**THF**	**85 (79)[b]**
15	$[PdCl_2(CH_3CN)_2]$	-	BQ	THF	23
16	$[PdCl_2(CH_3CN)_2]$	PTS	BQ	THF (RT)	32
17	$[PdCl_2(CH_3CN)_2]$	PTS	O_2	THF	<5
18	$[PdCl_2(CH_3CN)_2]$	PTS	$Cu(OAc)_2$	THF	9
19	$[PdCl_2(CH_3CN)_2]$	PTS	Ag_2O	THF	–
20	$[PdCl_2(CH_3CN)_2]$	TfOH	BQ	THF	82
21	–	TfOH	BQ	THF	0

[a] The yields were determined based on ^1H NMR spectra of the reaction mixture using diphenylacetonitrile as internal standard; [b] value in parentheses refer to yield of product isolated by column chromatography.

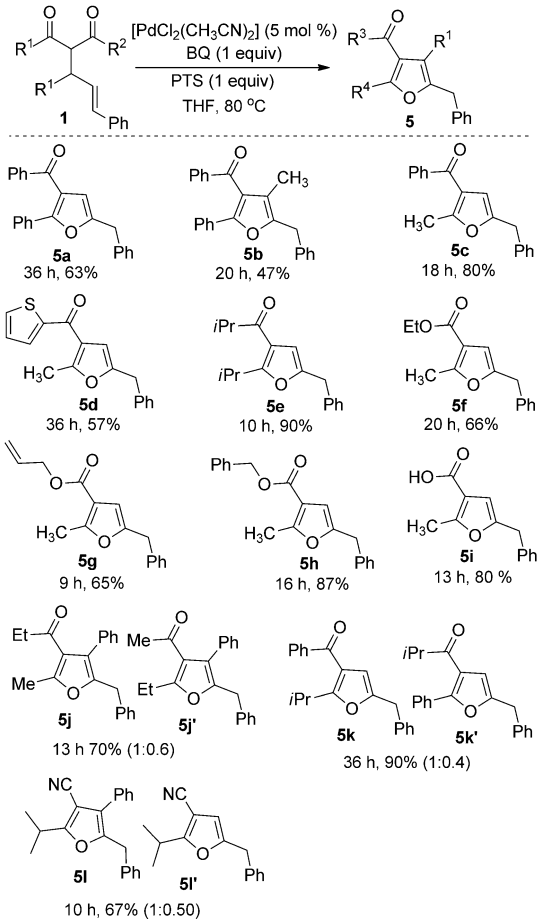


Scheme 2. Variation of cinnamyl moiety. Reaction conditions: 2-Cinnamyl-1,3-dione (0.15 mmol), $[PdCl_2(CH_3CN)_2]$ (5 mol%), BQ (1 equiv), PTS (1 equiv), THF (1.0 mL). Yields refer to products isolated by column chromatography.

acetic acid, trifluoroacetic acid (TFA), and pivalic acid (PivOH; Table 1, entries 4–7). Benzoquinone (BQ) was a better oxidant than O_2, $Cu(OAC)_2$, and Ag_2O (Table 1, entries 17–19 vs. entry 14). After the above screening, 5 mol% of $[PdCl_2(CH_3CN)_2]$ catalyst, 1 equivalent of BQ as the oxidant and 1 equivalent of PTS as the additive in THF solvent at 80 °C were chosen as the optimal reaction conditions (Table 1, entry 14). Under these conditions, **3j** was obtained in 79% yield. Another stronger acid, TfOH, was also examined for the current cyclization process, and the desired furan was formed in a similar manner (entry 20). However, the reaction did not work at all in the absence of Pd catalyst (entry 21).

With the optimized conditions in hand (Table 1, entry 14), the scope of this reaction with respect to the cinnamyl moiety was examined (Scheme 2). The dimethyl-1,3-dicarbonyl unit attached to various symmetrical diaryl–cinnamyl functionalities gave the corresponding 2-benzyl-3-aryl-4-acyl-5-methyl furans (**3a**–**i**) in good yields. Besides H (**3a**), electron-rich substituents on the aryl moiety, such as Me (**3b**), MeO (**3c**), and *t*Bu (**3d**), as well as electron-deficient halide substituents, such as Cl (**3e**), Br (**3f**), and F (**3g**), were well tolerated, affording the desired furans in 57–75% yields. Fortunately, halide substituents Br (**3f**) and Cl (**3e**), which are sensitive to palladium-catalyzed reactions and are also potential substrates for further transition metal-catalyzed functionalizations, did not give rise to any complications under such mild reaction conditions. Other types of aryl moiety, such as 1-naphthyl (**3h**), and heteroaryl moiety, such as 2-thiophene (**3i**), were equally applicable to provide the functionalized furans in good yields. By retaining the same 1,3-dicarbonyl moiety in the 2-cinnamyl-1,3-dicarbonyl substrate, various unsymmetrical cinnamyl groups were employed for the current furan synthesis. Corresponding 2-benzyl-3-alkyl-4-acyl-5-methyl furans (**3j**–**o**) were efficiently synthesized in good yields. Apart from 2-benzyl furans, the corresponding 2-alkyl furans can potentially be synthesized by using the same reaction conditions, as shown in cases of **3q** and **3r**.

To further explore the substrate scope, various 1,3-dicarbonyl moieties of the 2-cinnamyl-1,3-dicarbonyl substrates were



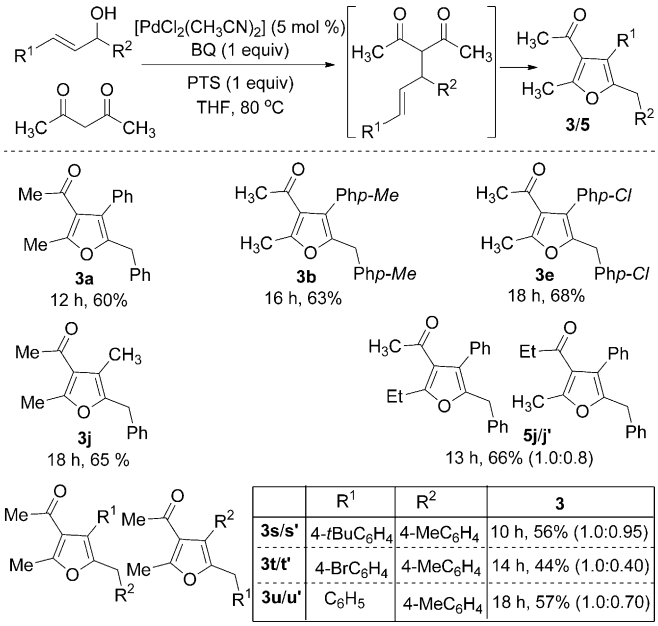
Scheme 3. Variation of 1,3-Dicarbonyl Counterpart. Reaction conditions: 2-Cinnamyl-1,3-dione (0.15 mmol), $[PdCl_2(CH_3CN)_2]$ (5 mol%), BQ (1 equiv), PTS (1 equiv), THF (1.0 mL). Yields refer to products isolated by column chromatography.

then investigated (Scheme 3). 1,3-Dicarbonyls bearing aryl/aryl (**5a**,**b**), aryl/alkyl (**5c**), heteroaryl/alkyl (**5d**) and alkyl/alkyl (**5e**) substituents delivered the corresponding furans in good yields. Particularly, 1,3-dicarbonyls bearing an ester functionality, such as ethyl (**5f**), allyl (**5g**) and benzyl (**5h**) esters, provided the desired furans without any problem. Notably, allyl and benzyl esters, which are generally sensitive to palladium-catalyzed reaction conditions, did not give rise to any complications under such mild reaction conditions. In the case of *tert*-butyl ester, the desired oxidative cyclization occurred, but the *tert*-butyl group was deprotected, providing the corresponding carboxylic acid-substituted furan **5i**. 1,3-Dicarbonyls bearing unsymmetrical alkyl groups, such as methyl/ethyl, led to product mixtures containing two regioisomers (**5j/j'** and **5k/k'**). When, instead of 1,3-dicarbonyls, a 2-cyanocarbonyl species was utilized under the current reaction conditions, encouragingly, the desired furan **5l** was formed, along with a dearylated analogue **5l'**, as an inseparable mixture.

Next, we examined the one-pot, sequential *C*-alkylation of 1,3-dicarbonyls with cinnamyl alcohols followed by oxidative cyclization for the palladium-catalyzed synthesis of furans (Scheme 4). Various tetrasubstituted furans were synthesized in good yields.

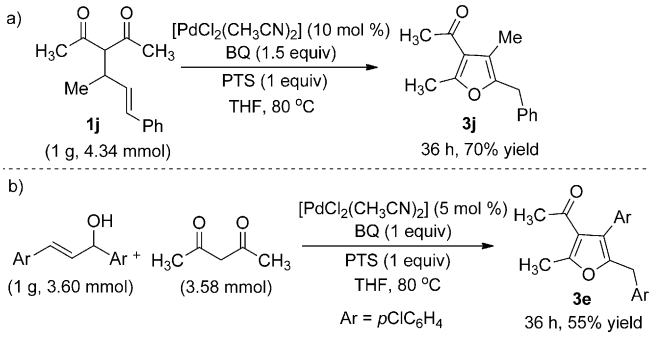
To test the practicality of this approach, a gram-scale synthesis of **3j** from the corresponding 2-cinnamyl-1,3-dicarbonyl species **1j** was performed (Scheme 5a). Furthermore, a gram-scale synthesis of **3e** was carried out from the corresponding allyl alcohol and acetylacetone, also catalyzed by $[PdCl_2(CH_3CN)_2]$ (Scheme 5b).

A proposed reaction pathway for the oxidative cycloisomerization of 2-cinnamyl-1,3-dicarbonyls to form functionalized 2-benzyl furans, based on the aforementioned results, is depicted in Scheme 6. An acid-mediated tautomerization of 2-cinnamyl-1,3-dicarbonyl **1** generates the enol tautomer **1′** which reacts with the Pd^{II} species to provide palladium–enolate **I**. Then, **I** undergoes intramolecular 5-*exo*-trig cyclization to give species **II**. However, Pd^{II} might also act as a π-acid to activate the C=C bond for the intramolecular 5-*exo*-trig cyclization to generate species **II**. Subsequently, **II** can be transformed into the desired product by β-hydride elimination to give inter-

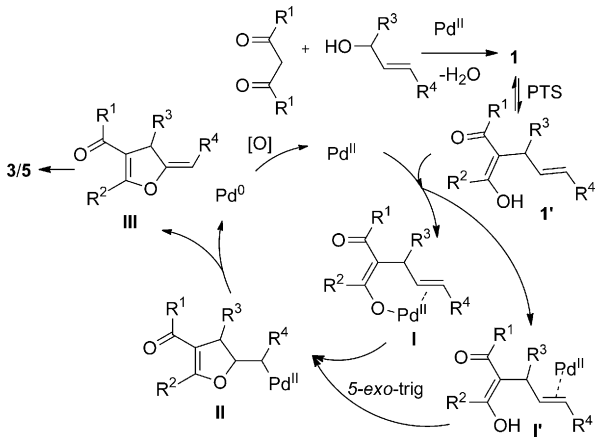


	R^1	R^2	3
3s/s'	4-*t*BuC_6H_4	4-MeC_6H_4	10 h, 56% (1.0:0.95)
3t/t'	4-BrC_6H_4	4-MeC_6H_4	14 h, 44% (1.0:0.40)
3u/u'	C_6H_5	4-MeC_6H_4	18 h, 57% (1.0:0.70)

Scheme 4. One-pot reaction. Reaction conditions: Alcohol (0.15 mmol), 1,3-dicarbonyl compound (0.15 mmol), $[PdCl_2(CH_3CN)_2]$ (5 mol%), BQ (1 equiv), PTS (1 equiv), THF (1.0 mL). Yields refer to products isolated by column chromatography.



Scheme 5. Gram-scale syntheses of **3j** (a) and **3e** (b). Yields refer to products isolated by column chromatography.



Scheme 6. Proposed mechanism for current process.

mediate **III**, followed by isomerization. Furthermore, Pd^0 was assumed to be oxidized by benzoquinone to regenerate the active Pd^{II} catalyst. In the one-pot protocol, the Pd^{II} species also catalyzes the dehydrative coupling between 1,3-dicarbonyls and cinnamyl alcohols to form the product **1**. The alternate pathway, whereby α,β,γ,δ-dienones are generated from substrate **1** followed by cyclization to provide the furans, is ruled out based on the control experiment (see the Supporting Information).

In summary, a versatile catalytic method for the synthesis of highly functionalized 2-benzyl furans through palladium-catalyzed intramolecular oxidative annulation of 2-cinnamyl-1,3-dicarbonyls has been disclosed. A one-pot, sequential synthesis of 2-cinnamyl-1,3-dicarbonyls, starting from the corresponding cinnamyl alcohols and 1,3-dicarbonyls, has also been demonstrated. In view of the high pharmaceutical importance of the functionalized 2-benzyl furans, this simple and practical synthetic strategy should be valuable to both pharmaceutical and agrochemical industries. Furthermore, it will significantly impact the step economy in the synthesis of bioactive compounds.

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Keywords: cycloisomerization · furans · heterocycles · oxidation · palladium

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