Synthetic Methods

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Oxidative Cross-Coupling of Allenyl Ketones and Organoboronic Acids: Expeditious Synthesis of Highly Substituted Furans**

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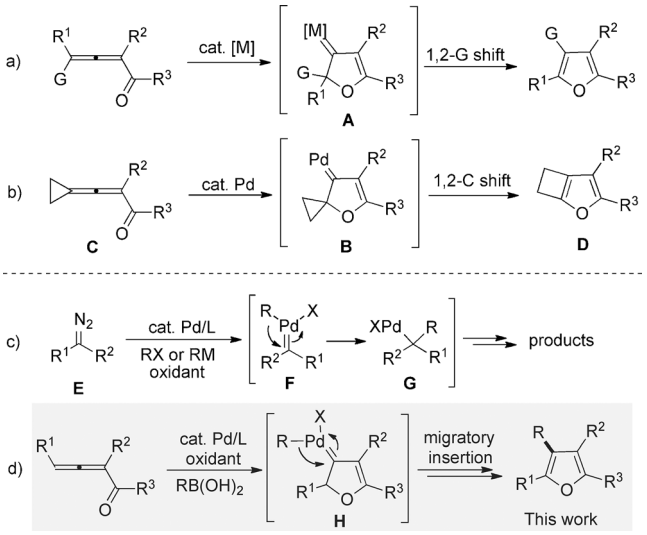
Abstract: *Allenyl ketones are employed as coupling partners in palladium-catalyzed oxidative cross-coupling reactions with organoboronic acids. This reaction constitutes an efficient methodology for the synthesis of highly substituted furan derivatives. Palladium-carbene migratory insertion is proposed as the key step in this transformation.*

Furans are highly important structural motifs because they exist in a variety of natural products and synthetic pharmaceuticals, and some furan derivatives have been found to have potential uses in materials science or as building blocks in synthetic chemistry.[1] Therefore, concise and efficient synthesis of highly substituted furans has attracted extensive attention over the decades.[2,3] Among the various methods to synthesize furans, the transition-metal-catalyzed cycloisomerization of 1,2-allenyl ketones is particularly attractive.[4–9] The reaction may proceed via cyclic metal carbene intermediates. Marshall et al. and Hashmi et al. demonstrated that allenyl ketones could undergo a formal 1,2-hydride shift to produce furan derivatives (G = H, M = Rh^I, Ag^I, Pd^{II}; Scheme 1 a).[5,6] Gevorgyan and co-workers have developed a series of transition-metal-catalyzed cyclizations of allenyl ketones which undergo a 1,2-shift to form functionalized furans (G = alkyl, aryl, halide, acyloxy, silyl, etc., M = Au^I, Ag^I, Cu^I, etc.; Scheme 1 a).[7] Recently, Wu and co-workers reported that the palladium-catalyzed reaction of allenyl ketones bearing a cyclopropyl moiety (**C**) proceeds through a 1,2-carbon shift of the carbene species **B**, thus giving the furan-fused cyclobutene **D** (Scheme 1 b).[8] These pioneering studies demonstrate that the metal-mediated cycloisomerization of allenyl ketones is a general approach to the cyclic metal carbene species.

In contrast, transition-metal-catalyzed cross-coupling reactions involving carbene migratory insertion have recently been demonstrated to be an important methodology in organic synthesis.[10,11] Generally, the common carbene precursors in these transformations are diazo compounds.[12,13] With palladium as the catalyst, diazo compounds can participate in coupling reactions with a wide range of electrophiles, such as aryl halides, benzyl halides, and allyl halides. In the presence of suitable oxidants, diazo compounds can also be employed as carbene precursors to participate in palladium-catalyzed oxidative cross-coupling reactions with various nucleophiles, which include aryl boronic acids,[13a–c] terminal alkynes,[13d] and others.[13e–g] In addition, a series of cascade reactions have also been developed.[10f,14] The palladium carbene formation and the subsequent migratory insertion are considered to be key steps in these transformations (Scheme 1 c).

Based on the importance of the furan synthesis and our interest in palladium carbene chemistry, we envisioned that novel methods for furan synthesis might be achieved by integrating transition-metal-catalyzed cycloisomerization of allenyl ketones with carbene migratory insertion reactions. We have recently demonstrated that conjugated enynones can be employed as carbene precursors to participate in palladium-catalyzed cross-coupling reactions with organohalides as electrophiles.[15,16] Herein we show that by utilizing allenyl ketones as carbene precursors, palladium-catalyzed oxidative cross-coupling of allenyl ketones with organoboronic acids can be developed, thus providing an alternative method for highly substituted furans (Scheme 1 d).



Scheme 1. Furan synthesis by transition-metal-catalyzed reactions of allenyl ketones.

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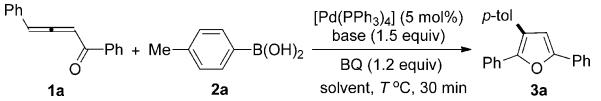
At the outset of this investigation, we used the 1,2-allenyl ketone **1a** and *p*-tolylboronic acid (**2a**) as the substrates to optimize the reaction conditions (Table 1). Reaction conditions similar to those we previously reported, in our study on palladium-catalyzed oxidative cross-coupling reactions between aryl boronic acids and diazo compounds, were first used for the current reaction.[13a] To our delight, we obtained the target furan product **3a** in 25% yield (Table 1, entry 1). Encouraged by this initial result, we further optimized the reaction conditions. Changing the solvent from toluene to other solvents failed to improve the reaction (Table 1, entries 2–4). Then the effect of base was examined, and iPr$_2$NEt was found to be superior to iPr$_2$NH, and the yield could be improved to 52% (Table 1, entries 5–7). Changing the ratio of the two substrates from 1:1 to 1:1.5 resulted in a higher yield (Table 1, entries 8–10). Furthermore, we found that the reaction was slightly affected by temperature (Table 1, entries 11 and 12). Further lowering the temperature led to a diminished yield (Table 1, entry 13). Subsequently, we inspected the effect of the reaction concentration and found that the reaction could be improved at low concentration, thus affording **3a** in 67% yield at 0.03 mol L^{-1} (Table 1, entries 14–16). Slow addition of **1a**, over 5 minutes, to the reaction system increased the yield to 76%, presumably because the low concentration of the carbene precursor reduced the occurrence of side reactions (Table 1, entry 17). Finally, lowering the palladium catalyst loading from 5 mol% to 2.5 mol% afforded a similar result (Table 1, entry 18), and only a slightly diminished yield was observed when the loading of catalyst was further reduced to 1 mol% (Table 1, entry 19).

Thus, the reaction conditions given in entry 18 of Table 1 were chosen as the optimized reaction conditions for this reaction, and a variety of allenyl ketone derivatives (**1a–h**) were used to investigate the scope of the reaction (Table 2). As illustrated in Table 1, good to excellent yields were obtained in all the cases. We were delighted to find that the tenfold scaled-up reaction afforded a comparable result, wherein the product **3a** was obtained in 90% yield (Table 2, entry 1). The substituent on the aromatic ring appended to the allene moiety has little influence on this reaction. Both electron-donating and electron-withdrawing groups are well tolerated in this transformation (Table 2, entries 2 and 3). Apart from aryl-substituted allenes, a methyl-substituted allene and a terminal allene were both suitable substrates for this reaction (Table 2, entries 4 and 5). It is noteworthy that tetrasubstituted furans could also be synthesized by this method in 81–93% yields (Table 2, entries 6 and 7). In addition, the substituents appended to the keto moiety are not limited to aryl groups. For example, the allene **1h**, bearing a methyl ketone moiety, can be smoothly converted into the corresponding product under the optimized reaction conditions (Table 2, entry 8).

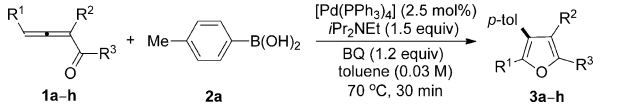
Table 1: Optimization of reaction conditions.[a]

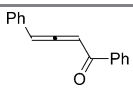
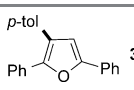
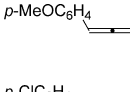
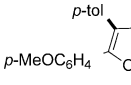
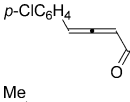
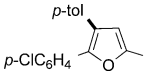
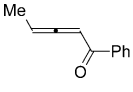
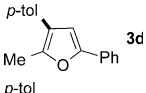
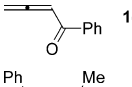
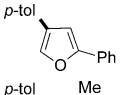
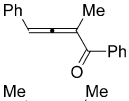
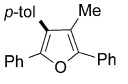
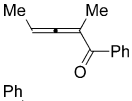
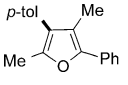
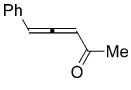
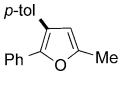


Entry	Solvent	Base	**1a**/**2a**	T [°C]	c [mol L^{-1}]	Yield [%][b]
1	toluene	iPr$_2$NH	1:1	80	0.1	25
2	1,4-dioxane	iPr$_2$NH	1:1	80	0.1	21
3	MeCN	iPr$_2$NH	1:1	80	0.1	trace
4	DCE	iPr$_2$NH	1:1	80	0.1	15
5	toluene	iPr$_2$NEt	1:1	80	0.1	52
6	toluene	K_2CO_3	1:1	80	0.1	32
7	toluene	Et_3N	1:1	80	0.1	41
8	toluene	iPr$_2$NEt	1:1.3	80	0.1	57
9	toluene	iPr$_2$NEt	1:1.5	80	0.1	61
10	toluene	iPr$_2$NEt	1.5:1	80	0.1	55
11	toluene	iPr$_2$NEt	1:1.5	90	0.1	61
12	toluene	iPr$_2$NEt	1:1.5	70	0.1	62
13	toluene	iPr$_2$NEt	1:1.5	50	0.1	53
14	toluene	iPr$_2$NEt	1:1.5	70	0.2	48
15	toluene	iPr$_2$NEt	1:1.5	70	0.05	62
16	toluene	iPr$_2$NEt	1:1.5	70	0.03	67
17[c]	toluene	iPr$_2$NEt	1:1.5	70	0.03	76
18[c,d]	toluene	iPr$_2$NEt	1:1.5	70	0.03	75[f]
19[c,e]	toluene	iPr$_2$NEt	1:1.5	70	0.03	69

[a] The reaction was carried out on a 0.1 mmol scale, and **1a** was added as a solution with a concentration of about 0.5 M. [b] Yield of product isolated after column chromatography. [c] **1a** was added as a solution over 5 min. [d] The loading of [Pd(PPh$_3$)$_4$] is 2.5 mol%. [e] The loading of [Pd(PPh$_3$)$_4$] is 1 mol%. [f] Average yield of three runs. BQ = 1,4-benzoquinone; DCE = 1,2-dichloroethane.

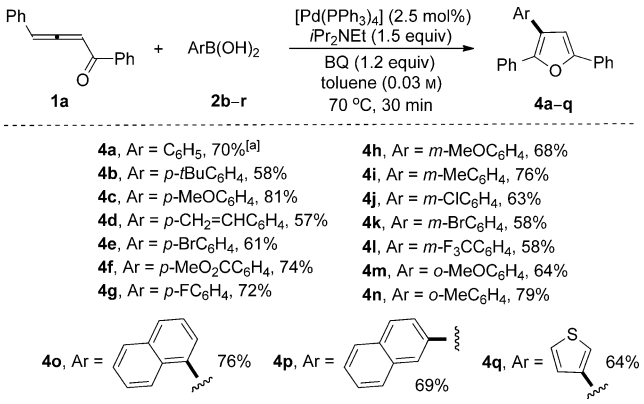
Table 2: Scope of the reaction of allenyl ketones with *p*-tolylboronic acid (**2a**).[a]



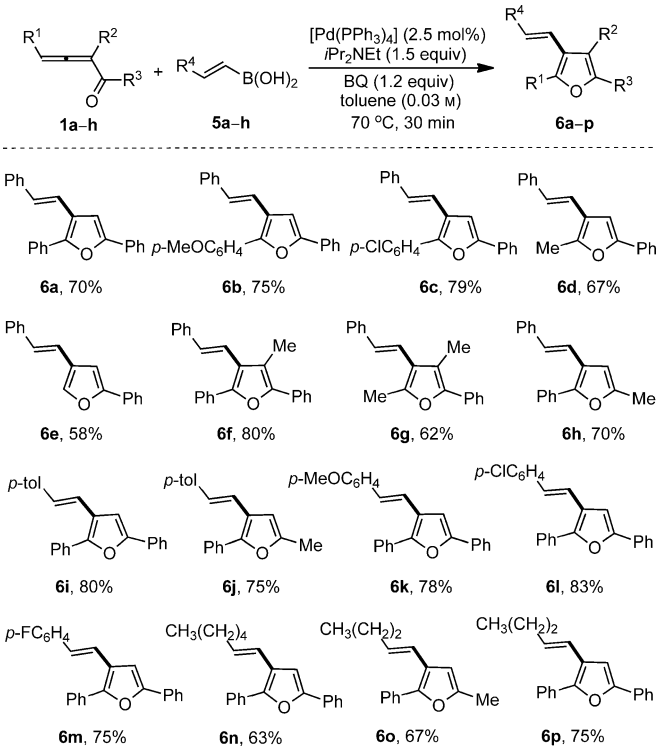
Entry	Allenyl ketone	Product	Yield [%][b]
1	 **1a**	 **3a**	75 (90)[c]
2	 **1b**	 **3b**	69
3	 **1c**	 **3c**	69
4	 **1d**	 **3d**	72
5	 **1e**	 **3e**	63
6	 **1f**	 **3f**	93
7	 **1g**	 **3g**	81
8	 **1h**	 **3h**	79

[a] The reaction was carried on an 0.1 mmol scale with 1 equiv of **1a–h** and 1.5 equiv of **2a**. [b] Yield of product isolated after column chromatography. [c] The yield within parentheses was obtained on a 1.0 mmol scale.

We next explored the reaction scope with a series of aryl boronic acids (**2b–r**) by using **1a** as carbene precursor (Scheme 2). To our delight, the reactions proceeded well under the optimized reaction conditions, thus affording versatile furan derivatives with moderate to good yields.



Scheme 2. Reaction scope of aryl boronic acids with the allenyl ketone **1a**. Reactions were carried out under the reaction conditions described in Table 2. Yields are those of the products isolated after column chromatography.



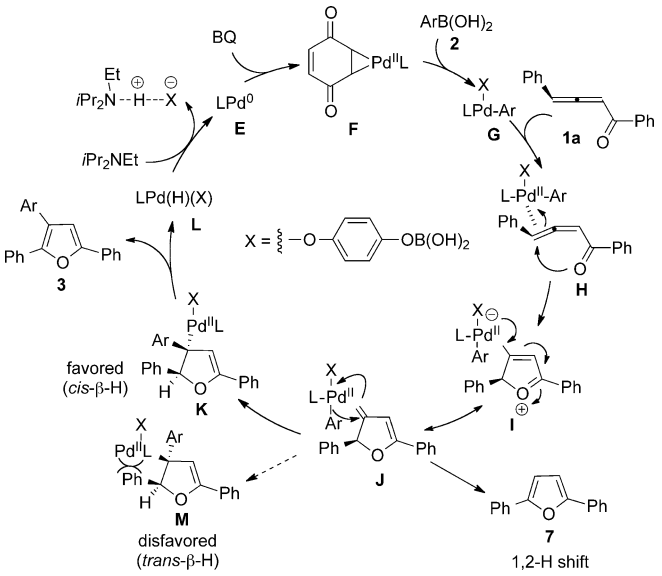
Scheme 3. Reaction scope of allenyl ketones with alkenyl boronic acids. Reactions were carried out under the reaction conditions described in Table 2. Yields are those of the products isolated after column chromatography.

The position of the substituents on the aromatic ring of the aryl boronic acids has little effect on this transformation. Aryl boronic acids bearing *para* (**4b–g**), *meta* (**4h–l**), and *ortho* (**4m–n**) substituents with different electronic properties can be employed in this reaction, thus smoothly generating the cross-coupling products in 57–81% yields. It is noteworthy that the compatibility of the functional groups is rather good for this reaction. Even a terminal olefin (**4d**) and an aryl boronic acid bearing halogen substituents (**4e,j,k**), groups which are generally sensitive to palladium-catalyzed reaction conditions, are well tolerated. Moreover, naphthyl boronic acids (**4o,p**) and a heteroarylboronic acid (**4q**) are also suitable substrates, thus affording the corresponding products in 64–76% yields.

Since alkenyl boronic acids have reactivity similar to that of aryl boronic acids in palladium-catalyzed cross-coupling reactions, we proceeded to extend the reaction scope to alkenyl boronic acids. To the best of our knowledge, there have been no reports on using alkenyl boronic acids in palladium-catalyzed carbene migratory insertion reactions. To our delight, alkenyl boronic acids showed good reactivity in this palladium-catalyzed reaction. This type of reaction provides an alternative approach to the synthesis of 3-alkenyl-substituted furans.

As illustrated in Scheme 3, a variety of alkenyl boronic acids (**5a–h**) reacted smoothly with allenyl ketones under the same reaction conditions, thus affording 3-alkenyl-substituted furans in 58–83% yields. *E*-styrylboronic acid (**5a**) was firstly subjected to the reaction with a series of allenyl ketones (**1a–h**), thus producing 3-alkenyl-substituted furans bearing different substituents on the furyl rings (**6a–h**). The substituents on the styryl boronic acids show little influence on the reaction as both electron-donating (**6i–k**) and electron-withdrawing (**6l–m**) groups are well tolerated. In addition, the 2-alkyl-substituted alkenyl boronic acids can also be used as substrates in this reaction, thus affording the corresponding 3-alkenyl-substituted furans **6n–p**.

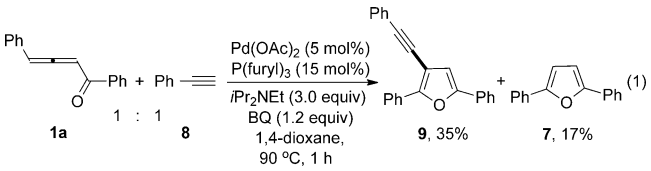
We have proposed a plausible mechanism for the palladium-catalyzed oxidative cross-coupling reaction of boronic acids and allenyl ketones (Scheme 4). The reaction is initiated



Scheme 4. Proposed reaction mechanism.

by the oxidation of the Pd^0 species **E** by 1,4-benzoquinone (BQ), thus generating the Pd^{II} species **F** which undergoes transmetallation with aryl boronic acids to afford the aryl palladium intermediate **G**.[13a] The species **G** coordinates to **1a** to give **H**, in which the allene moiety is bent, thus resulting in a decrease of the distance between the carbonyl oxygen atom and the terminal allene carbon atom.[6a] At this point, an oxypalladation of the double bond would lead to the formation of the zwitterionic intermediate **I**, which is a resonance structure to the γ-donor substituted vinyl carbene complex **J**. Next, the aryl migration from palladium to the carbenic carbon atom occurs in a stereoselective manner to generate the intermediate **K**,[10] in which the steric hindrance between palladium ligand and the phenyl group is avoided (in contrast, **M** is not favored). The intermediate **K** has a *cis*-β-hydrogen, which then undergoes *β*-hydride elimination to form the furan product **3**. Finally, the generated Pd^{II} species **L** undergoes reductive elimination to regenerate **E** with the aid of the base, thus completing the catalytic cycle.

During the optimization of this reaction, 2,5-diphenylfuran (**7**) was observed as a side product, and is likely generated from the direct 1,2-H shift or *β*-hydride elimination followed by reductive elimination of the palladium carbene intermediate **J**.[6a,17] Previous mechanistic investigations using DFT calculations have suggested that palladium carbene migratory insertion is a highly facile process with an energy barrier of less than 5 kcal mol^{-1}, which is favorable to that of the 1,2-H shift process.[15] This data is in consistent with the experimental results of this study. Furthermore, under reaction conditions similar to those of our previously reported palladium-catalyzed oxidative cross-coupling reaction between terminal alkynes and diazo compounds,[13d] phenylacetylene (**8**) can also react with **1a** to afford the 2-alkynyl furan **9** in 35% yield along with the formation of the 1,2-H shift byproduct **7** in 17% yield [Eq. (1)]. These preliminary results also support the proposed mechanism involving carbene migratory insertion process. Nevertheless, a mecha-



nism involving the formation of a π-allyl palladium species and subsequent intramolecular nucleophilic substitution cannot be ruled out at present.[18] Further investigation is needed to unambiguously establish the mechanism of this reaction.

In conclusion, we have developed a novel palladium-catalyzed oxidative cross-coupling reaction between allenyl ketones and organoboronic acids. The reaction tolerates various functional groups, thus providing a novel methodology to the efficient synthesis of highly substituted furans and 3-alkenyl-substituted furan derivatives. Mechanistically, palladium carbene migratory insertion is most likely involved in this transformation. This study further demonstrates that carbene migratory insertion is a rather general process regardless of the source of carbene precursors. This work should open up more possibilities in the future.

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Keywords: allenes · carbenes · cross-coupling · furans · palladium

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