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Palladium-Catalyzed Addition/Cyclization of (2-Hydroxyaryl)boronic Acids with Alkynylphosphonates: Access to Phosphacoumarins

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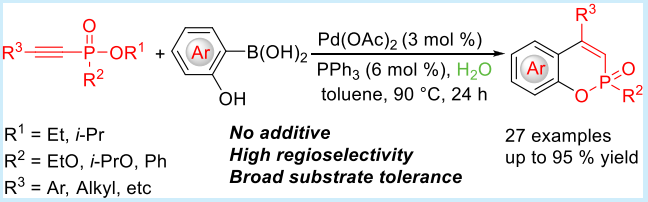
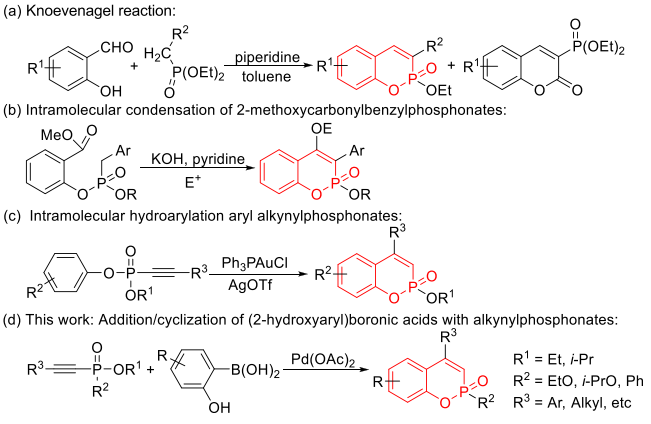
ABSTRACT: A facile palladium-catalyzed addition/cyclization of (2-hydroxyaryl)boronic acids with alkynylphosphonates has been developed, providing an effective strategy to construct a series of valuable phosphacoumarins. This methodology features excellent regioselectivity and broad substrate tolerance.



Phosphorus-containing heterocycles, as an emerging group of organophosphorus compounds, have drawn widespread attention due to their wide applicability in organic synthesis,[1] medicinal chemistry,[2] and material science.[3] In particular, phosphacoumarins, the phosphorus analogues of coumarin, are made of an important subclass of phosphorus heterocycle compounds. Phosphacoumarins are endowed with unique biological activities[4,7a] and exhibit high flame-retarding performance.[5] However, reliable synthetic methods for phosphacoumarins are still limited to date. Traditionally, phosphacoumarins are mainly obtained from the intermolecular reaction of suitable starting materials[6] or from predesigned complex phosphorus precursors via intramolecular functionalization.[7] Chen and Rodios' groups have employed salicylaldehydes and phosphonoacetates for the preparation of phosphacoumarins via the Knoevenagel reaction, which afforded only low yields (<21%) followed by the formation of phosphonocoumarins (Scheme 1a).[6a,b] Fu's group reported that the intramolecular condensation of 2-methoxycarbonylbenzylphosphonates delivered a diverse series of 4-*O*-substituted phosphacoumarins, which suffer from the requirement of multistep reactions to prepare the precursors (Scheme 1b).[7a] Moreover, Mironov's group revealed the intramolecular coupling of readily hydrolyzable arylenedioxytrihalogenphosphoranes or hexacoordinated phosphorus derivatives with terminal alkynes leading to phosphacoumarin derivatives.[6c−g] In 2013, Lee's group established the gold-catalyzed hydroarylation of aryl alkynylphosphonates for the synthesis of phosphacoumarins (Scheme 1c),[7b] but its general use poses severe limitations due to the noble gold/silver catalysts. Thus developing a facile and efficient method for the synthesis of phosphacoumarin derivatives from readily available and cheap starting materials is continuously desirable and essential.

Scheme 1. Synthetic Strategies toward Phosphacoumarins



The transition-metal-catalyzed conjugate addition of organoboron reagents to unsaturated alkenes and alkynes is one of the most useful synthetic strategies to form a C−C bond over the past several decades.[8] Among them, the palladium-catalyzed addition/cyclization reaction involving organoborons and alkynes provides one of the most straightforward pathways for the formation of carbocycles and heterocycles.[9] In 2008, Yamamoto's group reported the construction of arylcoumarins via Cu-catalyzed hydroarylation with arylboronic acids.[10] Inspired by these excellent contributions and in line with our constant interest in the construction of heterocyclic compounds bearing a phosphorus atom,[9a,11] herein we revealed that the Pd-catalyzed addition/cyclization reaction of arylbor-

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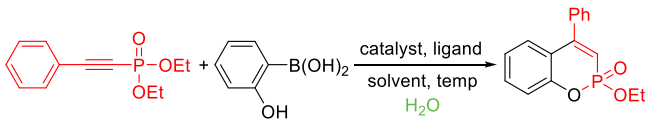
onic acids bearing an *ortho*-hydroxyl group with various alkynylphosphonates, which could be prepared conveniently,[12] led to privileged phosphacoumarin scaffolds. Compared with the known methods, this novel protocol has the advantages of operational simplicity, excellent regioselectivity, and broad substrate tolerance and could be an attractive practical method. To the best of our knowledge, this approach is the first example of a Pd-catalyzed addition/cyclization reaction of (2-hydroxyaryl)boronic acid with alkynylphosphonates into phosphacoumarins.

Initially, the reaction was carried out with diethyl-(phenylethynyl)phosphonate (**1a**) and (2-hydroxyphenyl)-boronic acid (**2a**) in the presence of 3 mol % $Pd(OAc)_2$ and 6 mol % dppb in 1,4-dioxane at 60 °C (Table 1, entry 1). To

Table 1. Optimization of the Reaction Conditions[a]



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

entry	catalyst	ligand	solvent	temp (°C)	yield (%)[b]
1	$Pd(OAc)_2$	dppb	1,4-dioxane	60	52
2	$Pd(OAc)_2$	dppb	1,4-dioxane	80	65
3	$Pd(OAc)_2$	dppb	1,4-dioxane	90	75
4	$Pd(OAc)_2$	dppb	1,4-dioxane	100	70
5	$PdCl_2$	dppb	1,4-dioxane	90	16
6	$Pd(PPh_3)_4$	dppb	1,4-dioxane	90	70
7	$Cu(OAc)_2$	dppb	1,4-dioxane	90	0
8	$Ni(OAc)_2$	dppb	1,4-dioxane	90	0
9		dppb	1,4-dioxane	90	0
10	$Pd(OAc)_2$	dppp	1,4-dioxane	90	78
11	$Pd(OAc)_2$	PPh_3	1,4-dioxane	90	80
12	$Pd(OAc)_2$		1,4-dioxane	90	39
13	$Pd(OAc)_2$	PPh_3	CH_3CN	90	40
14	$Pd(OAc)_2$	PPh_3	DMF	90	32
15	$Pd(OAc)_2$	PPh_3	DCE	90	90
16	**$Pd(OAc)_2$**	**PPh_3**	**toluene**	**90**	**95**
17[c]	$Pd(OAc)_2$	PPh_3	toluene	90	61
18[d]	$Pd(OAc)_2$	PPh_3	toluene	90	89
19[e]	$Pd(OAc)_2$	PPh_3	toluene	90	90

[a]Reaction conditions: **1a** (0.3 mmol), **2a** (0.45 mmol), catalyst (3 mol %), ligand (6 mol %), H_2O (2 equiv), and solvent (2 mL), 24 h, under Ar. [b]Isolated yields. [c]1 mol % of $Pd(OAc)_2$ was used. [d]Under air. [e]Reaction run on a 1 mmol scale.

our delight, the desired product **3a** was obtained in 52% yield. Subsequently, we tried to improve the yield of **3a** by increasing the temperature. Pleasantly, the yield was significantly improved to 75% at 90 °C (entries 1−3). However, a slight decrease in the yield was observed at 100 °C (entry 4). Screening other palladium complexes such as $PdCl_2$ and $Pd(PPh_3)_4$ gave yields of 16 and 70%, respectively (entries 5 and 6). Other metal salts such as $Cu(OAc)_2$ and $Ni(OAc)_2$ were tested, which both failed to generate the desired product (entries 7 and 8). Without a catalyst, no product was observed (entry 9), indicating that palladium salt is indispensable for this transformation. Next, we examined the effect of the ligand on the reaction (entries 10 and 11). It implied that PPh_3 was the best choice for the reaction, delivering the desired product **3a** in 80% yield (entry 11). Nevertheless, the yield dramatically reduced to 39% in the absence of the ligand (entry 12). Subsequently, the effect of the solvent was studied. Solvents such as CH_3CN, DMF, 1,2-dichloroethane (DCE), and toluene (entries 13−16) were explored, indicating that toluene could improve the yield to 95% (entry 16). It is interesting that the replacement of coordinating solvents (e.g., CH_3CN) with noncoordinating solvents (e.g., toluene) could lead to an enhancement of the activity, probably due to the use of noncoordinating solvents minimizing the competition for coordination with the catalyst.[13] In addition, the loading of $Pd(OAc)_2$ was also evaluated, showing that decreasing the amounts of $Pd(OAc)_2$ into 1 mol % afforded a significant loss of yield (entry 17). Notably, ambient air proved to be competent for constructing phosphacoumarins without a significant loss of yield (entry 18). It is noticeable that the addition of the aryl group took place exclusively at the β-position of the alkynylphosphonates, which might be attributed to the α-position carbanion stabilization by the phosphonyl group. Finally, a 1 mmol scale reaction was further examined, affording a 96% yield of **3a** (entry 19).

With the optimal reaction conditions in hand (Table 1, entry 16), the scope of alkynylphosphonates was first surveyed. As demonstrated in Scheme 2, a variety of alkynylphosphonates readily reacted with phenylboronic acid **2a**, generating the corresponding phosphacoumarins in moderate to excellent yields. Arylalkynylphosphonates bearing 2-methyl, 4-methyl, 4-*tert*-butyl, and 4-methoxy groups on the phenyl ring were suitable reaction partners in this transformation, leading to the corresponding products **3b**−**3e** in 52−84% yields. It is noteworthy that steric hindrance significantly affected the efficiency. For example, the diethyl (*p*-tolylethynyl)-phosphonate **1b** produced the target product **3b** in a high yield of 84%, but the sterically demanding meta-substituted counterpart **1c** gave the expected compound **3c** in only 52% yield. Additionally, halogen groups like fluoro (F), chloro (Cl), and bromo (Br) smoothly underwent this reaction and constructed the desired products **3f**−**3h** in 60−88% yields. The alkynylphosphonates with electron-withdrawing groups such as trifluoromethyl (CF_3), nitrile (CN), and nitro (NO_2) were also compatible with this protocol, giving the corresponding products in moderate to good yields of 53−80% (**3i**−**3k**). Notably, the addition of an isopropoxy group to compound **1** is capable of serving as a leaving group in this reaction to obtain the target products (**3j**−**3l**). Interestingly, both polycyclic and heterocyclic aromatic-substituted alkynyl-phosphonates (**1m** and **1n**) were also allowed to generate the expected phosphacoumarins in moderate yields. Alkynyl-phosphonate containing a thiophene group afforded the desired heterocyclic product **3o** in only 30% yield, probably due to the poisoning of the transition-metal catalyst caused by the thiophene group. It is noteworthy that this strategy was an effective route to tolerate ether and ketone functional groups on the phosphacoumarin scaffold, leading to **3p** with a good yield of 72%. Moreover, both aliphatic-substituted and cycloalkane-substituted alkynylphosphonates were also applicable to offer the target products in yields of 48−62% (**3q**−**3t**).

The versatility of the reaction was further evaluated by the use of different arylboronic acid derivatives (Table 2). Various arylboronic acids bearing methyl, chloro, and fluoro groups were investigated in combination with diethyl(phenylethynyl)-phosphonate **1a** or diisopropyl (phenylethynyl)phosphonate **1l**, which provided the desired six-substituted phosphacoumarin in yields of 36−95% (**3u**−**3y**). Moreover, the halogen substituents (**3w**, **3x**, and **3y**) could offer numerous possible

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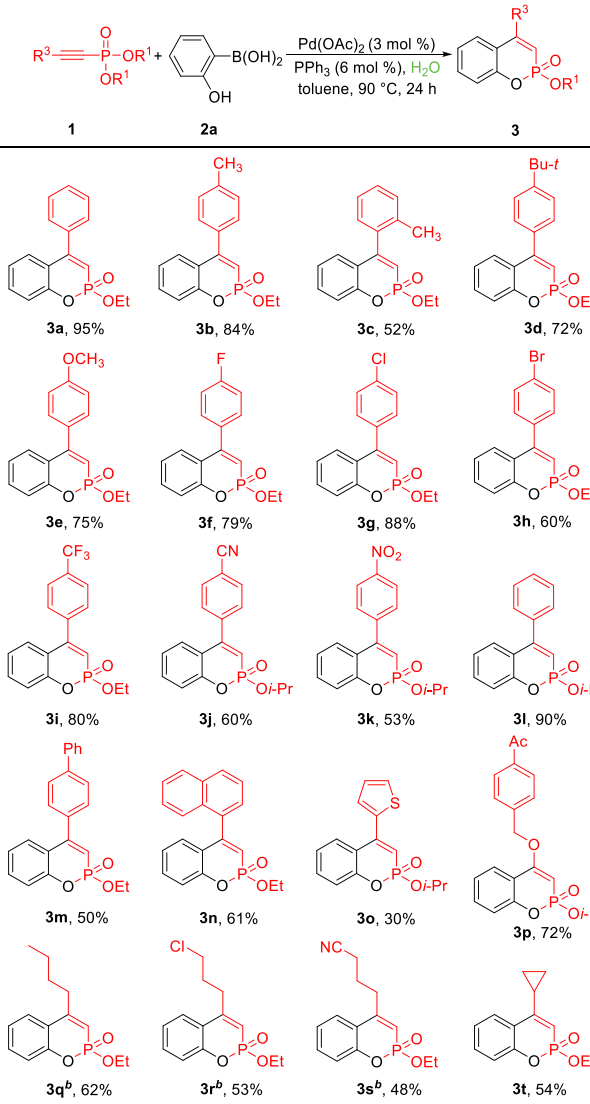
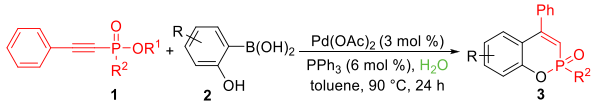
Scheme 2. Palladium-Catalyzed Addition/Cyclization of Alkynylphosphonates with 2a[a]



[a]Reaction conditions: **1** (0.3 mmol), **2a** (0.45 mmol), $Pd(OAc)_2$ (3 mol %), PPh_3 (6 mol %), H_2O (2 equiv) and toluene (2 mL) at 90 °C for 24 h under Ar. [b]At 120 °C for **3q**–**3s**.

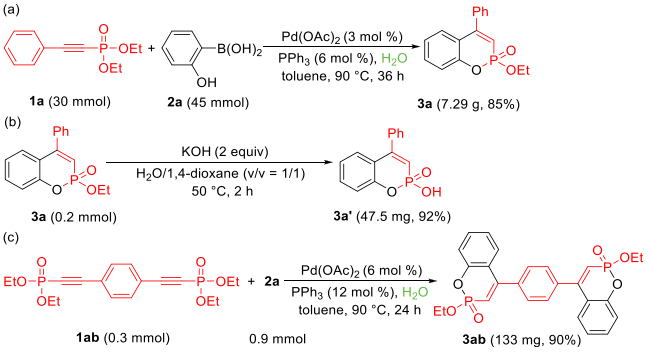
Table 2. Palladium-Catalyzed Addition/Cyclization of 1 with (2-Hydroxyaryl)boronic Acids[a]



entry	alkynylphosphonate **1**	arylboronic acid **2**	product **3**	yield (%)[b]
1	**1a**	**2b**	**3u**	60
2	**1l**	**2b**	**3v**	95
3	**1a**	**2c**	**3w**	58
4	**1a**	**2d**	**3x**	36
5	**1l**	**2d**	**3y**	45
6	**1u**	**2a**	**3z**	73

[a]Reaction conditions: **1** (0.3 mmol), **2** (0.45 mmol), $Pd(OAc)_2$ (3 mol %), PPh_3 (6 mol %), H_2O (2 equiv), and toluene (2 mL) at 90 °C for 24 h under Ar. [b]Isolated yields.

Scheme 3. Application Studies



postfunctionalizations of the phosphacoumarin scaffold. In addition, ethyl phenyl(phenylethynyl)phosphinate **1u** could also react with (2-hydroxyphenyl)boronic acid **2a**, generating the expected product **3z** in 73% yield.

To demonstrate the synthetic application potential of this method, a gram-scale experiment was carried out. As shown in Scheme 3a, 7.29 g of **3a** could be obtained in a yield of 85%. The stability of phosphacoumarin **3a** was preliminary evaluated in the presence of the strong base KOH (Scheme 3b), with the finding that **3a** was hydrolyzed into phosphonic acid **3a′**, preserving the phosphacoumarin framework in an excellent yield of 92%, indicating the strong stability of the phosphacoumarin scaffold under these alkaline conditions. Furthermore, **2a** could react with diyne **1ab** to generate a novel bisphosphacoumarin-4-yl-benzene framework (**3ab**) in an excellent yield of 90%, which could be of interest in the material field (Scheme 3c).[14]

To gain insight into the mechanism, several control experiments were conducted. Initially, we performed the reaction of **1a** with **2a** through decreasing the temperature to 60 °C in the presence of 3 mol % $Pd(OAc)_2$ and 6 mol % PPh_3 in toluene. We found that the desired product **3a** was obtained in a yield of 70%; simultaneously, the intermediate phosphoalkene **3aa** was isolated in 24% yield (Scheme 4a). Next, the treatment of the intermediate phosphoalkene **3aa** in the absence of $Pd(OAc)_2$ and PPh_3 could give the expected product **3a** in an equivalent yield of 98% under heating (Scheme 4b). These results indicated that **3aa** is the key intermediate during this process and the intramolecular nucleophilic substitution of **3aa** yielding **3a** could be performed effectively in the absence of catalyst and ligand. Subsequently, phenylboronic acid-d_2 (**2a′**, 99.8% D) was employed to determine the source of the hydrogen on the vinylic carbon. Notably, it turned out that **2a′** with **1l** gave only

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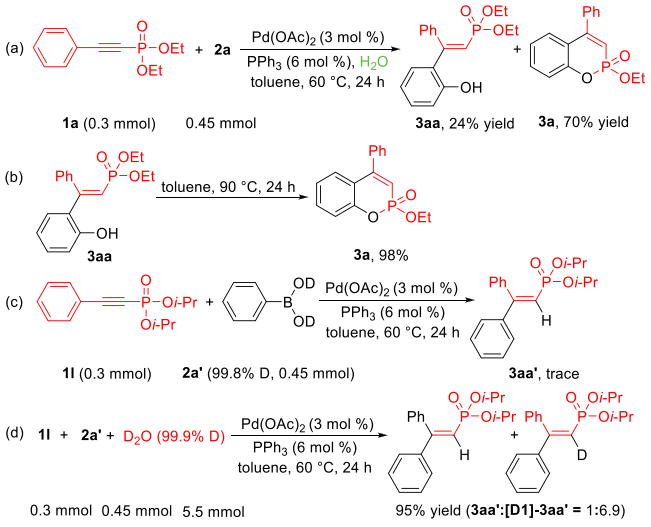
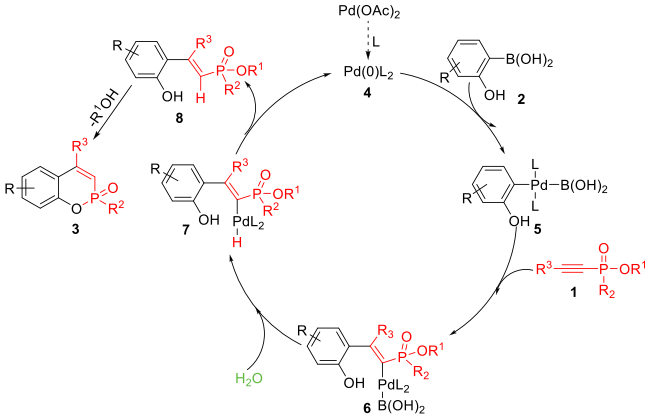
Scheme 4. Control Experiments



a trace of phosphoalkene **3aa′** under strictly anhydrous conditions, indicating that the hydrogen on the double bond is not from boronic acid (Scheme 4c). The addition of 100 μL of D_2O (99.9% D) to the reaction system led to the products **3aa′**/[**D1**]-**3aa′** in a total yield of 95% with a ratio of **3aa′**/[**D1**]-**3aa′** of 1:6.9 determined by ^{1}H NMR analysis (Scheme 4d). These results clearly revealed that the hydrogen on the vinylic carbon is derived from water.

On the basis of these experimental results and previous reports,[8c,g,15] a plausible mechanism is proposed in Scheme 5.

Scheme 5. Plausible Mechanistic Pathway



Initially, the oxidative addition of Pd(0) species **4** with (2-hydroxyaryl)boronic acid **2** readily took place to deliver the intermediate **5**.[8d,15,16] Next, the selective insertion of alkynylphosphonate **1** into the Pd−C in a syn fashion generated the intermediate **6**. Then, the hydrogen from water was abstracted by **6** to form the intermediate **7**. The reductive elimination of **7** led to the intermediate alkene **8** along with the reproduction of the active Pd(0) species. Finally, an intramolecular nucleophilic substitution of **8** resulted in the formation of the desired product **3**, accompanied by the release of one molecular alcohol.

In conclusion, a convenient and efficient one-pot method for the construction of a variety of valuable phosphacoumarins has been successfully established via a palladium-catalyzed addition/cyclization reaction. In this reaction, both readily available aromatic and aliphatic alkynylphosphonates could smoothly deliver the desired phosphacoumarins in moderate to excellent yields. This transformation features operational simplicity, high regioselectivity, and a broad substrate tolerance, showing great potential for wide application in material science and biological research. Further studies on mechanistic investigations as well as research applications are currently underway in our laboratory.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.0c03151.

General experimental procedures, characterization details, and copies of ^{1}H, ^{13}C, and ^{31}P NMR spectra of compounds (PDF)

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Author Contributions

All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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