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## ARTICLE

# Palladium-Catalyzed Oxidative Deacetonative Coupling of 4-Aryl-2-methyl-3-butyn-2-ols with H-phosphonates

Cite this: DOI: 10.1039/x0xx00000x

Received 00th January 2012,  
Accepted 00th January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

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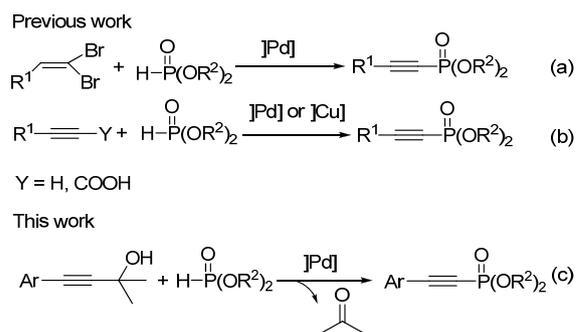
An efficient and general applicable protocol for palladium-catalyzed oxidative deacetonative coupling of 4-aryl-2-methyl-3-butyn-2-ols with dialkyl H-phosphonates has been developed. This methodology provides a new and practical route to alkynylphosphonates using the inexpensive 4-aryl-2-methyl-3-butyn-2-ols as the alkyne sources. This reaction could also be performed from aryl bromides, 2-methyl-3-butyn-2-ol and dialkyl H-phosphonates using the cheap 2-methyl-3-butyn-2-ol as an alkyne source.

## Introduction

Alkynylphosphonates as extremely valuable synthetic precursors could be easily further functionalized on the triple bond through conjugate-addition, cyclo-addition and other reactions, making them potentially useful in organic synthetic, pharmaceutical and biological applications.<sup>1</sup> Given the extremely important value and broad applications of alkynylphosphonates, the development of practical and efficient methods for their preparation from common and commercially available alkyne sources is highly desirable in organic synthesis. The classic Csp-P bond forming tools are the Michaelis-Arbuzov and Michaelis-Becker reaction, which suffer from poor functionality group tolerance and multistep synthetic routes.<sup>2,3</sup> To address these issues, considerable efforts have been made to develop new and efficient methods for the preparation of alkynylphosphonates.<sup>4-8</sup> Typically, the direct Csp-P bond forming reactions using 1,1-dibromo-1-alkenes,<sup>5</sup> terminal alkynes<sup>6</sup> or arylpropionic acids with H-phosphonates<sup>7</sup> have been achieved (Scheme 1, a and b). However, some of the alkyne sources employed in these methods are expensive and difficult to prepare, unstable, or sensitive to air and moisture.

On the other hand, 4-aryl-2-methyl-3-butyn-2-ols were considered as one of the reliable and inexpensive alkyne sources have significantly grown in popularity, because they could generate corresponding terminal alkynes by releasing an acetone under proper conditions,<sup>9</sup> and can be easily prepared from the coupling of aryl halides with 2-methyl-3-butyn-2-ol.<sup>10</sup> Recently, palladium-catalyzed deacetonative coupling reaction of 4-aryl-2-methyl-3-butyn-2-ols with aryl halides or alkenes have been realized for the synthesis of diaryl acetylene or ene-yne compounds.<sup>11,12</sup> To date, the current research interest on this type of deacetonative reaction is mainly focused on Csp-C bond forming reaction, and the direct construction of Csp-P bond using this deacetonative strategy remains unexplored (Scheme 1c). As part of our continuing research program on the chemistry of 4-aryl-2-methyl-3-butyn-2-ols, we envisioned a new and practical synthesis of alkynylphosphonates via oxidative deacetonative coupling using 4-aryl-2-methyl-3-butyn-2-ols as the

alkyne sources, which would be an important complement to the current Csp-P bond forming methodologies.



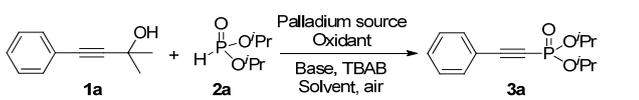
Scheme 1 The synthetic routes to alkynylphosphonates

## Results and Discussion

Initially, we performed a reaction of 4-phenyl-2-methyl-3-butyn-2-ol (**1a**) with diisopropyl H-phosphonate (**2a**) in DMSO in the presence of 5 mol% of Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub>, 1.5 equiv of Ag<sub>2</sub>CO<sub>3</sub>, 3 equiv of K<sub>2</sub>CO<sub>3</sub> and 1 equiv of TBAB, and the desired product was obtained in 15% yield (Table 1, entry 1). After screening of the solvent (e.g., DMA, Dioxane, THF, and DCE), to our delight, DCE could greatly promote the reaction, affording the desired product in 71% yield (Table 1, entries 2–5). Subsequently, we checked some other oxidants, Ag<sub>2</sub>O and AgOAc could give the desired product in yields of 83% and 51%, respectively, but other commercially available oxidant including Cu(OAc)<sub>2</sub>, BQ, K<sub>2</sub>S<sub>2</sub>O<sub>8</sub>, and O<sub>2</sub> could not facilitate the reaction at all (Table 1, entries 6–11). In this catalyst system, Ag<sub>2</sub>O not only can serve as the oxidant but also accelerate the deacetonative step to form the alkynyl silver (I) species, and obviously, the typical oxidant Cu(OAc)<sub>2</sub> can not act as these characters (Table 1, entries 6 and 8). Then, different bases (e.g.,

$\text{Cs}_2\text{CO}_3$ ,  $\text{Na}_2\text{CO}_3$ ,  $\text{KOH}$ , and  $\text{K}_3\text{PO}_4$ ) were also checked, and  $\text{K}_3\text{PO}_4$  exhibited the highest activity affording the desired product in 86% yield (Table 1, entries 12–15). Finally, some controlling experiments were performed. For example, performing the reaction under base-, TBAB-, or palladium-free conditions as well as decreasing the temperature to 100 °C could only generate the desired product in a lower yields ranging from 30% to 68% (Table 1, entries 16–19). Note that  $\text{Ag}_2\text{O}$  can also partly promote the reaction *via* the direct coupling of alkynyl silver (I) with H-phosphonate, affording the product in about 30% yield under palladium-free conditions (Table 1, entry 18). Some other commercially available palladium catalysts such as  $\text{Pd}(\text{OAc})_2$ ,  $\text{PdCl}_2$ , and  $\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$  were also evaluated, and the coupling products were obtained in relatively lower yields of 71%, 73%, and 55%, respectively (Table 1, entries 20–22).  $\text{CuI}$  was finally checked as the catalyst, and the desired product was only obtained in a lower yield of 15% (Table 1, entry 23).

**Table 1** Optimization of the reaction conditions<sup>a</sup>



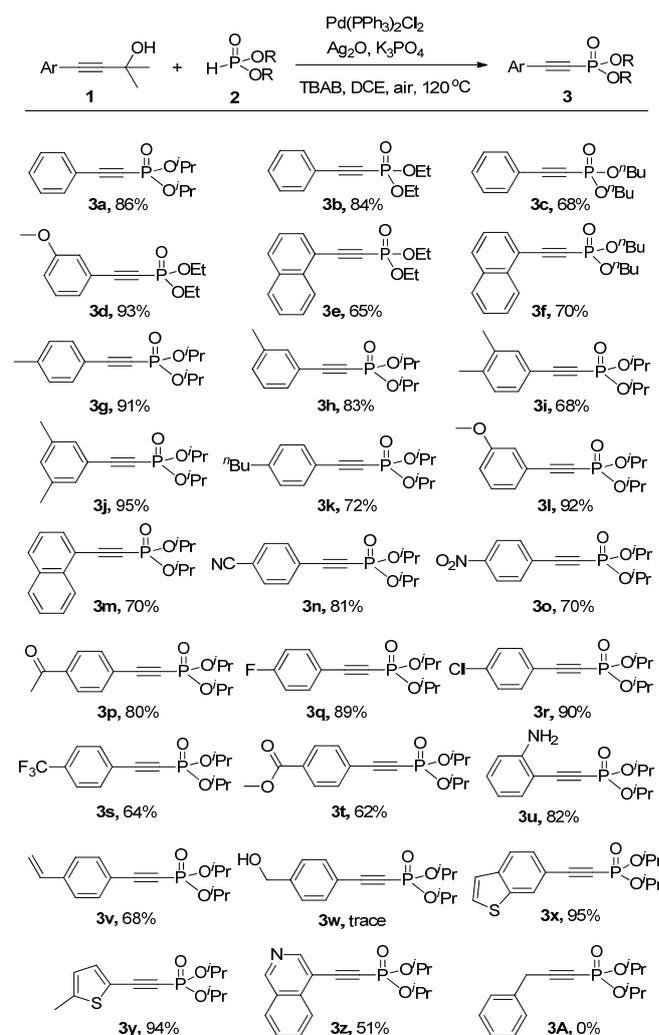
Entry	Catalyst	Oxidant	Base	Solvent	Yield
1	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	DMSO	15
2	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	DMA	Trace
3	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	Dioxane	10
4	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	THF	Trace
5	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{CO}_3$	$\text{K}_2\text{CO}_3$	DCE	71
6	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_2\text{CO}_3$	DCE	83
7	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{AgOAc}$	$\text{K}_2\text{CO}_3$	DCE	51
8	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Cu}(\text{OAc})_2$	$\text{K}_2\text{CO}_3$	DCE	Trace
9	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	BQ	$\text{K}_2\text{CO}_3$	DCE	Trace
10	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{K}_2\text{S}_2\text{O}_8$	$\text{K}_2\text{CO}_3$	DCE	Trace
11	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{O}_2$	$\text{K}_2\text{CO}_3$	DCE	Trace
12	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	86
13	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{Cs}_2\text{CO}_3$	DCE	56
14	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{Na}_2\text{CO}_3$	DCE	61
15	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{KOH}$	DCE	70
16	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	-	DCE	65
17 <sup>c</sup>	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	45
18	-	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	30
19 <sup>d</sup>	$\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	68
20	$\text{PdCl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	71
21	$\text{Pd}(\text{OAc})_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	73
22	$\text{Pd}(\text{CH}_3\text{CN})_2\text{Cl}_2$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	55
23	$\text{CuI}$	$\text{Ag}_2\text{O}$	$\text{K}_3\text{PO}_4$	DCE	15

<sup>a</sup> Reaction conditions: **1a** (0.3 mmol), **2a** (0.2 mmol), catalyst (5 mol%), oxidant (0.3 mmol), base (0.6 mmol), TBAB (0.2 mmol), and solvent (2 mL) at 120 °C under air for 12 h. <sup>b</sup> Isolated yield. <sup>c</sup> Without TBAB. <sup>d</sup> At 100 °C.

Under the optimized conditions, we next explored the substrate scope and the results are summarized in Table 2. Generally, the reaction of dialkyl H-phosphonates with 4-aryl-2-methyl-3-butyn-2-ols could work well, and the electronic effect of 4-aryl-2-methyl-3-butyn-2-ols has no obvious influence on this deacetonative coupling. For example, either electron-donating groups (e.g.,  $\text{CH}_3$ ,  $^t\text{Bu}$ , and  $\text{OCH}_3$ ) or electron-withdrawing functional groups (e.g.,  $\text{CN}$ ,  $\text{NO}_2$ ,

$\text{COCH}_3$ ,  $\text{F}$ ,  $\text{Cl}$  and  $\text{CF}_3$ ) could be well tolerated (Table 2, **3g–3s**). Moreover, the substrates bearing more sensitive groups ( $\text{COOCH}_3$ ,  $\text{NH}_2$  and alkene) and some heterocycle-containing substrates such as thienyl ring and isoquinoline could also be converted into the corresponding products in moderate to good yields (Table 2, **3t–3v**, **3x–3z**). However, the substrate 4-(4-(hydroxymethyl)phenyl)-2-methylbut-3-yn-2-ol only gave a mixture products containing trace amount of desired product determined by HRMS (Table 2, **3w**). And unfortunately, when the alkyl-substituted 2-methyl-5-phenylpent-3-yn-2-ol was used, the reaction did not occur at all (Table 2, **3A**).

**Table 2** Deacetonative coupling of 4-aryl-2-methyl-3-butyn-2-ols with dialkyl H-phosphonates<sup>a,b</sup>



<sup>a</sup> Reaction conditions: aryl propargyl alcohol **1** (0.3 mmol), H-phosphonate **2** (0.2 mmol),  $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$  (5 mol %),  $\text{Ag}_2\text{O}$  (1.5 equiv),  $\text{K}_3\text{PO}_4$  (3.0 equiv), TBAB (1.0 equiv), DCE (2.0 mL) at 120 °C under air for 12 h. <sup>b</sup> Isolated yield.

In recent years, the consecutive reactions have attracted much attention, because apart from the economy-efficiency and time-efficiency, subjecting the crude product directly to the next step would be interesting and promising.<sup>13</sup> Since synthesis and purification of 4-aryl-2-methyl-3-butyn-2-ols compounds are tedious and time consuming processes, and thus direct

adding in situ generated 4-aryl-2-methyl-3-butyn-2-ols from Sonogashira reaction of aryl bromides to the deacetonative coupling without purification would be an attractive choice. After the first report of deacetonative reaction by Chow's group in 2001,<sup>11a</sup> Kotschy and co-workers also reported this tandem

**Table 3** Consecutive Sonogashira/deacetonative coupling reactions<sup>[a,b]</sup>

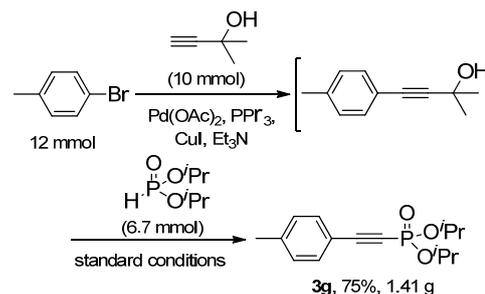
Entry	Ar	Product	Yield (%)
1			80
2			86
3			81
4			60
5			90
6			77
7			75
8			84
9			55
10			85

<sup>a</sup> Reaction conditions for Sonogashira reaction step: aryl bromide **4** (0.36 mmol), 2-methyl-3-butyne-2-ol **5** (0.3 mmol), Pd(OAc)<sub>2</sub> (1 mol%), PPh<sub>3</sub> (3 mol%), CuI (1 mol%), diisopropyl H-phosphonate **2** (0.2 mmol). <sup>b</sup> Isolated yield based on the amount of diisopropyl H-phosphonate.

Sonogashira/deacetonative reaction using 2-methyl-3-butyne-2-ol and aryl halides as the substrates, and the diarylacetylenes were obtained in good yields.<sup>14</sup> Following this view of point, we would like to apply this method to the Sonogashira/deacetonative phosphonation reactions. Typically, this consecutive reaction was performed in two steps: upon

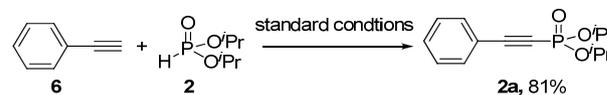
completion of the Sonogashira reaction between aryl bromides and 2-methyl-3-butyne-2-ol and removal of the solvent in vacuum, the crude product was directly subjected to the deacetonative coupling reaction affording the desired alkynylphosphonates in moderate to high yield (Table 3). This synthetic strategy would greatly diminish the cost of the expensive alkyne source, and one cheap terminal alkyne: 2-methyl-3-butyne-2-ol would be enough for most of deacetonative Csp-P bond forming process.

To demonstrate the application of this consecutive Sonogashira/deacetonative coupling, a gram-scale reaction of 4-bromotoluene (**4g**), 2-methyl-3-butyne-2-ol and diisopropyl H-phosphonate (**2a**) was performed. This two-step reaction could generate alkynylphosphonate (**3g**) as the desired product in an overall yield of 75% based on the amount of 4-bromotoluene (**4g**) (Scheme 2).



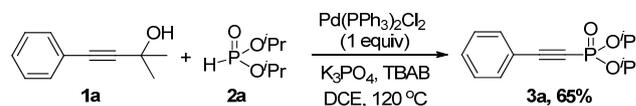
**Scheme 2** A gram-scale experiment

To further investigation of the mechanism of this reaction, we performed a controlling experiment using the phenylacetylene (**6**) and diisopropyl H-phosphonate (**2**) as the starting materials. The desired product **2a** was obtained in 81% yield, which indicated that phenylacetylene might be produced in the process of oxidative deacetonative coupling (Scheme 3).



**Scheme 3** Controlling experiment using phenylacetylene as the starting material

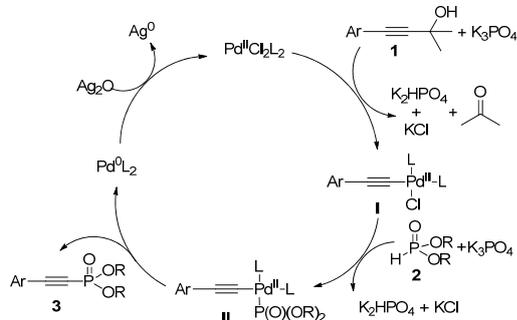
Moreover, when the reaction was performed under silver-free conditions with 1 equiv Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> as the catalyst, the desired product could also be obtained in a 65% yield, this might indicate that the active alkynyl-palladium species is the key intermediate in the catalytic cycle (Scheme 4).



**Scheme 4** Controlling experiment under silver-free conditions

On the basis of the previous report and our own works,<sup>7a,11f,15</sup> a proposed mechanism was outlined as Scheme 5. First, deacetonative reaction of the aryl propargyl alcohol (**1**) occurred in the presence of a base, and the ligand exchange between Pd(II) species and the in situ formed alkyne anion took place to form the alkynyl-palladium intermediate **I**. Then, this

highly active alkynyl-palladium species **I** reacted with the phosphonate anion generated from H-phosphonate (**2**) and a base to afford the intermediate **II**. The reductive elimination of the intermediate **II** would lead to the desired product (**3**) and release the Pd(0) species. Finally, the Pd(0) species would be oxidized to the active Pd(II) species with the assistance of silver oxide to fulfill the catalytic cycle.



Scheme 5 Proposed mechanism

## Conclusions

In conclusion, a new and convenient protocol for the synthesis of alkynylphosphonates through deacetonative reaction of 4-aryl-2-methyl-3-butyn-2-ols with dialkyl H-phosphonates was established for the first time. Notably, this reaction could also be performed as a consecutive Sonogashira/deacetonative process of aryl bromides, 2-methyl-3-butyn-2-ol and dialkyl H-phosphonates using the cheap 2-methyl-3-butyn-2-ol as an alkyne source.

## Experimental Section

### General Methods.

$^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  NMR spectra were recorded on a Bruker DPX-400 spectrometer with  $\text{CDCl}_3$  as the solvent and TMS as an internal standard. High-resolution mass spectra were measured on a MALDI-FTMS. Ethyl acetate and hexane (analytical grade) were used for column chromatography without purification. The other chemicals were bought from commercial sources and used as-received unless otherwise noted.

### Typical Procedure for the Palladium-Catalyzed Oxidative Deacetonative Coupling of 4-Aryl-2-methyl-3-butyn-2-ols with Dialkyl H-phosphonates

Aryl propargyl alcohol (0.3 mmol), H-phosphonate (0.2 mmol),  $\text{Pd}(\text{PPh}_3)\text{Cl}_2$  (5 mol%),  $\text{Ag}_2\text{O}$  (1.5 equiv),  $\text{K}_3\text{PO}_4$  (3.0 equiv), and TBAB (1.0 equiv) were added to a 10 mL round-bottomed flask and then DCE (2.0 mL) was added. The reaction mixture was stirred at 120 °C (oil bath temperature) under reflux for 12 h. After the reaction was complete, the mixture was added into  $\text{H}_2\text{O}$  (25 mL) and extracted with  $\text{CH}_2\text{Cl}_2$  three times. The combined organic layer was dried with anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated in vacuum. The crude product was purified by flash chromatography on silica gel using

hexane/ethyl acetate as the eluent to give the pure product (Yield: 51%–95%).

### Typical Procedure for the Consecutive Reaction

Under a nitrogen atmosphere, a mixture of aryl bromide (0.4 mmol), 2-methyl-3-butyn-2-ol (0.3 mmol),  $\text{Pd}(\text{OAc})_2$  (1 mol%),  $\text{PPh}_3$  (3 mol%),  $\text{CuI}$  (1 mol%) in  $\text{Et}_3\text{N}$  (2.0 mL) was added to a 5 mL round-bottomed flask. After stirred at refluxing temperature for 12 h, the resulting mixture was evaporated to remove the solvent in vacuum. The residue was transferred into a 5 mL round-bottomed flask, and then a mixture of diisopropyl H-phosphonate (0.2 mmol),  $\text{Pd}(\text{PPh}_3)\text{Cl}_2$  (5 mol%),  $\text{Ag}_2\text{O}$  (1.5 equiv),  $\text{K}_3\text{PO}_4$  (3.0 equiv), and TBAB (1.0 equiv) in DCE (2 mL) was added. After the resulting mixture was stirred vigorously at 120 °C (oil bath temperature) under reflux for 12 h, the mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered through a short pad of celite, and evaporated to remove the solvent in vacuum. The crude product was purified by column chromatography to afford the desired product (Yield: 55%–90%).

### Typical Procedure for the Consecutive Reaction on Gram-Scale

Under a nitrogen atmosphere, a mixture of aryl bromide (12 mmol), 2-methyl-3-butyn-2-ol (10 mmol),  $\text{Pd}(\text{OAc})_2$  (1 mol%),  $\text{PPh}_3$  (3 mol%),  $\text{CuI}$  (1 mol%) in  $\text{Et}_3\text{N}$  (25 mL) was added to a 100 mL round-bottomed flask. After stirred at reflux temperature for 12 h, the resulting mixture was evaporated to remove the solvent in vacuum. The residue was transferred into a 100 mL round-bottomed flask, and then a mixture of diisopropyl H-phosphonate (6.7 mmol),  $\text{Pd}(\text{PPh}_3)\text{Cl}_2$  (5 mol%),  $\text{Ag}_2\text{O}$  (1.5 equiv),  $\text{K}_3\text{PO}_4$  (3.0 equiv), and TBAB (1.0 equiv) in DCE (30 mL) was added. After the resulting mixture was stirred vigorously at 120 °C (oil bath temperature) under reflux for 24 h, the mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered through a short pad of celite, and evaporated to remove the solvent in vacuum. The crude product was purified by column chromatography to afford the desired product (1.41 g, 75%).

### Acknowledgements

We are grateful to the National Natural Science Foundation of China (Nos. 21172200, 21102134) for financial support to this research.

### Notes and references

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† Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI:10.1039/b000000x/

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