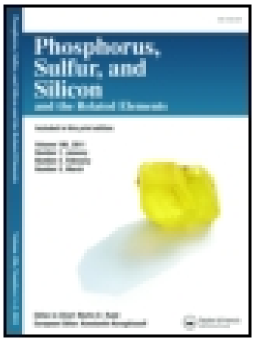

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# Solvent-free $Zn(OTf)_2$-catalyzed dehydrative cross coupling of propargyl alcohols with diarylphosphine oxides to afford allenylphosphine oxides

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# Solvent-free $Zn(OTf)_2$-catalyzed dehydrative cross coupling of propargyl alcohols with diarylphosphine oxides to afford allenylphosphine oxides

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**Abstract** *A less expensive and more environmentally friendly $Zn(OTf)_2$-catalyzed dehydrative coupling reaction of propargyl alcohols with diarylphosphine oxides is reported. The reaction takes place under mild and solvent free conditions, and features a high regioselectivity to provide an effective method for the synthesis of some diarylphosphinyl allenes in moderate to high yields.*

**Keywords** allenylphosphoryl compound; zinc catalysis; dehydrative coupling; solvent-free synthesis; regioselectivity

## INTRODUCTION

Allenylphosphoryl compounds are structurally interesting and have many applications in organic synthesis due to the presence of the unique allenic structure and the versatile organophosphorus functionality.[1-6] They can undergo selective additions with nucleophiles and electrophiles to afford stereodefined functionalized olefins.[1-3] Particularly, the catalytic asymmetric hydroarylation of diphenylphosphinylallenes can produce valuable chiral organophosphorus compounds.[4] Furthermore, some of these compounds have also been applied in cyclization reactions to access other structurally advanced organophosphorus compounds.[5,6]

A classical method for the synthesis of allenylphosphoryl compounds is the Horner-Mark [2,3]-rearrangement reaction of propargyl phosphates. This method was first discovered in the 1960s by researchers from industry (Scheme 1A).[7] Although this method is still frequently used today, it suffers from low yields and limited scopes,

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and requires the use of highly toxic, moisture-sensitive and odorous phosphorus chlorides. These drawbacks stimulate the search for new methods.[8-14] In 2010, Stawinski[8] reported a Pd-catalyzed cross-coupling reaction of propargylic chlorides (carbonates) with the stable and readily available P(O)H compounds to produce allenylphosphonates and related compounds based on the well-known Pd-catalyzed propargylic substitution involving allenyl- and propargyl-palladium intermediates (Scheme 1B, eq. a). However, the use of expensive palladium catalyst and bidentate ligand (DPEPhos) limited its use. In 2016, we reported a cheap Cu-catalyzed propargylic substitution of propargylic acetates with P(O)H compounds *via* allenylidene intermediates to afford allenylphosphoryl compounds in high yields (Scheme 1C, eq. b).[9,10] Propargyl acetates bearing very sterically hindering substituents at the propargylic position and a variety of P(O)H compounds including H-phosphonates, H-phosphinates and diarylphosphine oxides all can be used for the reaction, yet internal propargylic acetates cannot be applied.

The direct dehydrative C-P coupling reaction of propargyl alcohols with P(O)H compounds represents the most advanced method (Scheme 1C). The benefit of this approach is evident since it employs readily available and low-cost alcohols without wasteful prefunctionalization and principally produces water as the only byproduct.[11] Very recently, the groups of Zhao[12] and Yang[13] achieved such catalytic dehydrative C-P couplings of some propargylic alcohols with P(O)H compounds by using $Cu(OTf)_2$ and AgOTf as the catalysts. Meanwhile, we found that $CdCl_2$ is an active catalyst capable of promoting the dehydrative coupling of several propargyl alcohols with diarylphosphine oxides.[14] Comparably, our Cd-catalyzed system is particularly advantageous for propargyl alcohol substrates which bear sterically demanding substituents at the triple bond terminus to afford the allenyl products in high yields most likely due to a distinct mechanism involving the formation of propargyl phosphate intermediates.[14] However, the use of the hazardous and non-environmental-friendly cadmium catalyst becomes a major concern when applying this method.[15] As a continued effort, herein we report our recent

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finding on an alternative Zn-catalyzed reaction of propargyl alcohols with diarylphosphine oxides. We find that Zn(OTf)$_2$ can be used as the catalyst for the dehydrative coupling of propargyl alcohols and diarylphosphine oxides to generate allenylphosphine oxides under solvent free conditions. Because the zinc catalyst is much less toxic and cheaper, the reaction catalyzed by this metal should be more practically useful.

**Scheme 1** The development of synthetic methods to access allenylphosphoryl compounds

## RESULTS AND DISCUSSION

We initially found that ZnCl$_2$ was incapble of catalyzing the C-P coupling of 3-*tert*-butyl-1-phenylprop-2-yn-1-ol (**1a**) with Ph$_2$P(O)H (**2a**) in DCE to produce the allenylphosphine oxide **3a** (Table 1, entry 1). A close study reveals that the solvent plays a significant role in the reaction outcome. When MeCN was used as the solvent, the allenyl product **3a** was formed in 73% yield (Table 1, entry 7). When the reaction was performed under solvent free conditions, the desired product **3a** was also formed, but in a lower yield (Table 1, entry 8). The use of other solvents such as toluene, THF, dioxane, DMF and DMSO all gave poor results (Table 2-6). When we investigated the catalytic effect of the more cationic Zn(OTf)$_2$, we found that the reaction performed in the presence of 10 mol% Zn(OTf)$_2$ under solvent free conditions afforded the product **3a** in 92% yield (Table 1, entry 10). However, the use of a solvent has a negative impact on the product yield of the reaction (Table 1, entries 11-13). Even when the reaction was performed in MeCN, which is a suitable solvent for the ZnCl$_2$-catalyzed reaction, only a trace amount of the expected product was detected (Table 1, entry 11). Although the product yield was slightly improved when 2 equiv of **1a** was used (Table 1, entry 9), we noted that the use of a more amount of the propargyl alcohol that could keep a good state of stirring of the reaction mixture benefited for the re-productivity of the yields. The reaction of **1a** and **2a** in a 1/1 molar ratio sometimes gave a decreased yield, because it became difficult to maintain a good state of continuous stirring due to the formation of a very slurry mixture when the reaction proceeded. Thus we finally defined the optimal conditions as

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follows: **1a**/**2a**: 2/1, 10 mol% of Zn(OTf)$_2$, no solvent, 100 $^o$C, 12 h.

**Table 2** Optimization of the reaction conditions of **1a** and **2a**[a]

Table 2 shows the results of the Zn(OTf)$_2$-catalyzed C-P coupling reaction of a variety of propargyl alcohols with diphenylphosphine oxide (**2a**). In addition to **1a**, propargyl alcohols **1b**-**1e** bearing the *t*-butyl group and electron-deficient phenyl groups at the propargylic position reacted smoothly with **2a** affording the expected products in high yields (Table 2, entries 2-5). The reactions of propargyl alcohols **1g**-**1i** bearing the *n*-butyl group at the triple bond terminus also react well with **2a** to afford the corresponding products **3g**-**3i** in good yields (Table 2, entries 7-9). However, the reaction of the propargyl alcohol **1f** or **1j** that bears an electron-rich phenyl group at the propargylic position took place with poor selectivity. The reactions mainly gave the propargyl diphenylphosphine oxides as the major products (Table 2, entries 6 and 10). The reaction can also be applied to propargyl alcohols with two aryl groups at the propargylic position. As shown in entries 11 and 12, the products **3k** and **3l** were successfully prepared in good to high yields. Probably due to a low reactivity, the reaction of **1m** catalyzed by Zn(OTf)$_2$ only gave a trace amount of the product. Under the conditions using ZnCl$_2$ as the catalyst, the reaction could give rise to the product in 26% yield (Table 2, entry 13). In addition, the reactions of propargyl alcohols bearing a phenyl group or cyclopropyl group at the triple bond terminus also produce the corresponding products in low yields (Table 2, entries 14 and 15).

**Table 2** Zn(OTf)$_2$-catalyzed C-P coupling of propargylic alcohols **1** with diarylphosphine oxide **2a**[a]

We also examined the reactions of other substituted diarylphosphine oxides. As shown in Table 3, typical diarylphosphine oxides which bear electron-donating and electron-withdrawing substituents on the phenyl rings are all good substrates to give rise to the expected products **3p**-**3s** in high yields. The reactions of substrates bearing different aryl groups also took place smoothly to give the corresponding products **3t** and **3u** in high yields. Since

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diarylphosphine oxides can be easily obtained in high yields from the reaction of the cheap and easily-handled diethyl phosphite with Grignard reagents *via* substituition reactions,[16] this method should facilitate the introduction of a relatively broad scope of the diarylphosphinyl functionality into the allenic framework.

**Table 3** $Zn(OTf)_2$-catalyzed C-P coupling of **1a** with diarylphosphine oxides **2b**-**2g**[a]

We further performed a control experiment to understand the reaction mechanism (Scheme 2). An equal molar mixture of **1a**, **1g** and **2a** was heated to 100 $^{o}$C for 12 h in the presence of 10 mol% of $Zn(OTf)_2$. Analysis of the crude mixture by $^{31}$P NMR shows that a mixture of **3a** and **3g** with a ratio of 1.42/1 was formed. In light of the steric factor of the two substrate (**1a** *vs* **1g**), this result indicates that a $S_N2$'-type mechanism by the direct attack of the phosphorus nucleophile to the triple bond is less likely.

**Scheme 2** The competition experiment

Accordingly, we believe that the present reaction may proceed via a similar mechanism as the previously reported Cd-catalyzed reaction.[14] The catalytic cycle is outlined in Scheme 3. The coordination of zinc cation to propargyl alcohol **1** may activate and enable the cleavage of the C-O bond to generate the propargylic carbon cation **B** (resonance structure **B'**) and **C**. $Ar_2P(O)H$ **2** is in equilibrium with its tautomer **2'**, and may react with **B** and **C** to produce the propargylic phosphonite intermediate **D** via the attack of oxygen atom to the propargylic position and generate one molecule of water. The intermediate **D** finally undergoes the classical [2,3]-rearrangement to give the allenyl product **3**.

**Scheme 3** The proposed mechanism

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## CONCLUSIONS

In summary, we have found that $Zn(OTf)_2$ is a competent catalyst to promote the dehydrative coupling of propargyl alcohols with diarylphosphine oxides under solvent free conditions. The reaction could generate the allenylphosphine oxides with high selectivity from several propargyl alcohols and diarylphosphine oxides in moderate to high yields. Since the zinc catalyst is less expensive and more environmentally friendly, this reaction should be useful for the preparation of these products.

## EXPERIMENTAL

*General information:* all reactions were performed under dry $N_2$ atmosphere. Anhydrous solvents were distilled prior to use: THF was distilled from sodium using benzophenone as the indicator; MeCN, DCM and DMF were distilled from $CaH_2$. Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. $^1H$ (400 MHz), $^{13}C$ (100 MHz) and $^{31}P$ NMR (162 MHz) spectra were recorded on a Bruker Ascend(TM) 400 MHz NMR spectrometer in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Chemical shifts are expressed in ppm and $J$ values are given in Hz. HRMS analysis of the products (ESI-TOF) was performed at the Analytical Center of State Key Laboratory of Materials-Oriented Chemical Engineering at Nanjing Tech University, China. The Supplemental Materials contains the full experimental procedures and copies of $^1H$, $^{13}C$ and $^{31}P$ NMR spectra of the products **3** (Figures S 2 – S 40).

*A typical procedure for the $Zn(OTf)_2$-catalyzed reaction of propargyl alcohols with diarylphosphine oxide (Synthesis of **3a**):* An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with $Zn(OTf)_2$ (7.3 mg, 0.02 mmol), propagylic alcohol **1a** (75.4 mg, 0.4 mmol,) and diphenylphosphine oxide **2a** (40.4 mg, 0.2 mmol). The Schlenk tube was sealed and then evacuated and backfilled with $N_2$ (3 cycles). The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 $^oC$. After the reaction was heated for 12 h, the mixture was disolved in DCM and transferred into a round-bottom flask. Removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (petroleum ether/ethyl acetate 3/1 to 1/1) to afford 69.2

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mg of **3a** (yield 93%), which is a known compound.[12]

**(4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl)bis(4-methoxyphenyl)phosphine oxide (3t):** 63.9 mg (yield 82%), prepared from 75.4 mg of **1a** (0.4 mmol) and 44.0 mg of **2f** (0.2 mmol) according to the typical procedure for the synthesis of **3a**. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.79-7.57 (m, 4H), 7.54-7.31 (m, 2H), 7.26–7.17 (m, 4H), 7.13-7.08 (m, 1H), 7.03-6.98 (m, 2H), 6.89-6.84 (m, 1H), 6.06-6.01 (m, 1H), 1.34 (s, 4.5H), 1.33 (s, 4.5H). $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ = 29.13, 29.08. HRMS (ESI-TOF): *m/z* = 391.1618, calcd for $C_{25}H_{25}FOP$ [$MH^+$] 391.1627.

**(4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl)bis(4-methoxyphenyl)phosphine oxide (3u):** 67.8 mg (yield 84%), prepared from 75.5 mg of **1a** (0.4 mmol) and 46.4 mg of **2g** (0.2 mmol) according to the typical procedure for the synthesis of **3a**. $^1$H NMR ($CDCl_3$, 400 MHz): $\delta$ = 7.77-7.39 (m, 6H), 7.25-7.161 (m, 4H), 7.02–6.93 (m, 3H), 6.72-6.69 (m, 1H), 6.03-5.99 (m, 1H), 3.84 (s, 1.5H), 3.68 (s, 1.5), 1.33 (s, 9 H). $^{31}$P NMR ($CDCl_3$, 162 MHz): $\delta$ = 30.1, 29.9. HRMS (ESI-TOF): *m/z* = 403.1819, calcd for $C_{26}H_{28}O_2P$ [$MH^+$] 403.1827.

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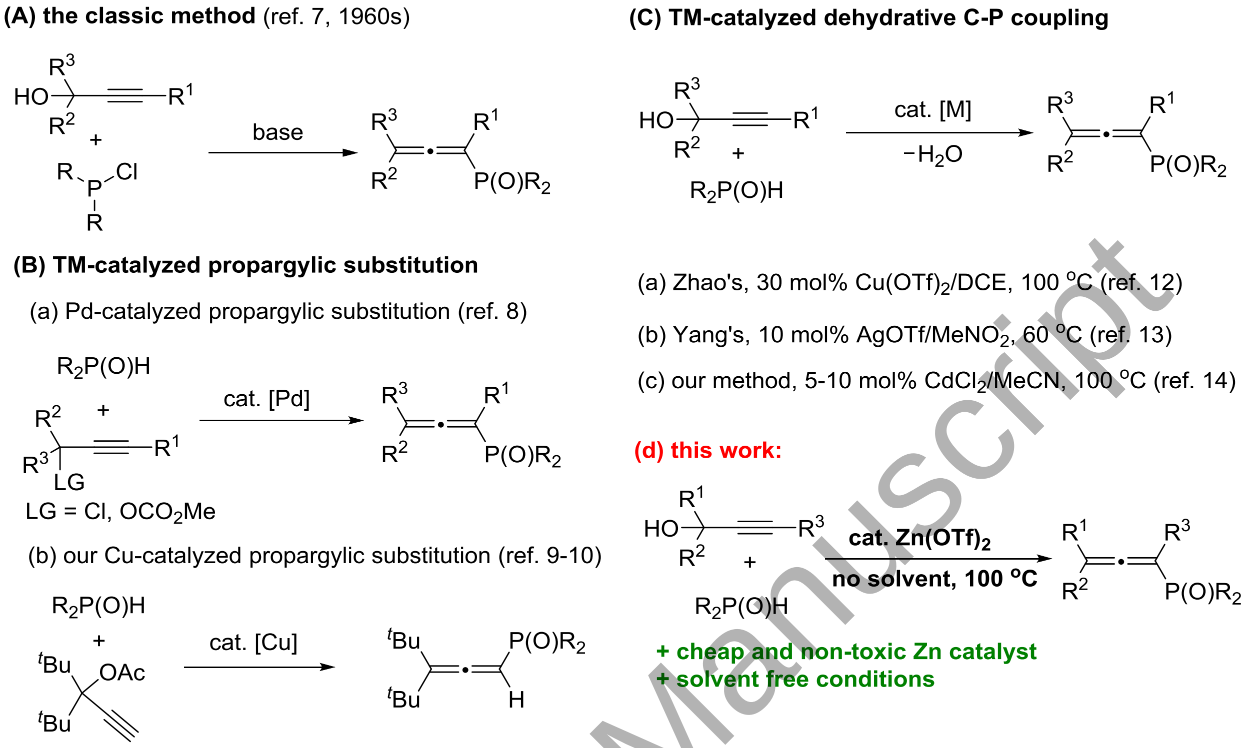

**Scheme 1**. The development of synthetic methods to access allenylphosphoryl compounds

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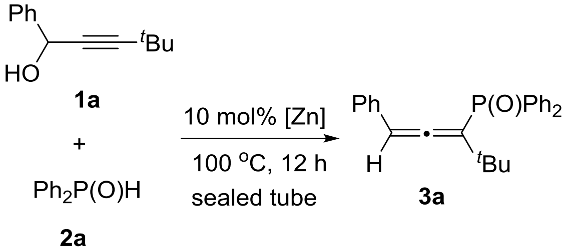
**Table 1**. Optimization of the reaction conditions of **1a** and **2a**[a]



| entry | [Zn] | solvent | yield (%)[b] |
|---|---|---|---|
| 1 | $ZnCl_2$ | DCE | trace |
| 2 | $ZnCl_2$ | toluene | trace |
| 3 | $ZnCl_2$ | THF | trace |
| 4 | $ZnCl_2$ | dioxane | trace |
| 5 | $ZnCl_2$ | DMSO | 0 |
| 6 | $ZnCl_2$ | DMF | trace |
| 7 | $ZnCl_2$ | MeCN | 73 |
| 8 | $ZnCl_2$ | NS[c] | 59[d] |
| 9 | $Zn(OTf)_2$ | NS[c] | 92(93)[e] |
| 10 | $Zn(OTf)_2$ | MeCN | trace[f] |
| 11 | $Zn(OTf)_2$ | DCE | trace |
| 12 | $Zn(OTf)_2$ | dioxane | trace |

[a] Reaction conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), [Zn] (10 mol%), solvent (2 mL).

[b] Isolated yields.

[c] NS: no solvent.

[d] 1-(diphenylphosphoryl)-4,4-dimethyl-1-phenylpentan-3-one was isolated in 12% yield.

[e] **1a** (0.4 mmol) and **2a** (0.2 mmol) were used.

[f] 1-(diphenylphosphoryl)-4,4-dimethyl-1-phenylpentan-3-one was isolated in 44% yield.

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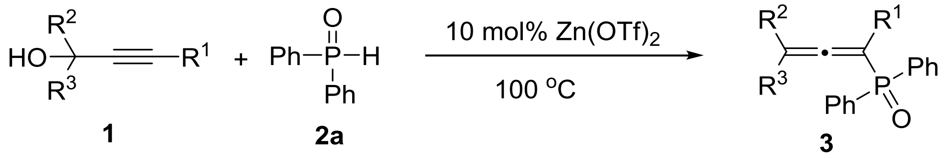
**Table 2**. Zn(OTf)$_2$-catalyzed C-P coupling of propargylic alcohols **1** with diarylphosphine oxide **2a**[a]



| entry | **1** | R$^1$ | R$^2$ | R$^3$ | **3**, yield (%) |
|---|---|---|---|---|---|
| 1 | **1a** | $^t$Bu | Ph | H | **3a**, 93 |
| 2 | **1b** | $^t$Bu | 4-ClC$_6$H$_4$ | H | **3b**, 95 |
| 3 | **1c** | $^t$Bu | 4-FC$_6$H$_4$ | H | **3c**, 94 |
| 4 | **1d** | $^t$Bu | 4-BrC$_6$H$_4$ | H | **3d**, 95 |
| 5 | **1e** | $^t$Bu | 2-ClC$_6$H$_4$ | H | **3e**, 81 |
| 6 | **1f** | $^t$Bu | 4-MeOC$_6$H$_4$ | H | **3f**, 87[b] |
| 7 | **1g** | $^n$Bu | Ph | H | **3g**, 74 |
| 8 | **1h** | $^n$Bu | 4-FC$_6$H$_4$ | H | **3h**, 72 |
| 9 | **1i** | $^n$Bu | 4-CF$_3$C$_6$H$_4$ | H | **3i**, 47 |
| 10 | **1j** | $^n$Bu | 4-MeOC$_6$H$_4$ | H | **3j**, 78[b] |
| 11 | **1k** | $^t$Bu | Ph | Ph | **3k**, 95 |
| 12 | **1l** | $^n$Bu | Ph | Ph | **3l**, 67 |
| 13 | **1m** | $^t$Bu | -(CH$_2$)$_5$- |  | **3m**, trace (26)[c] |
| 14 | **1n** | Ph | Ph | H | **3n**, 20 (trace)[c] |
| 15 | **1o** | C$_3$H$_5$ | Ph | H | **3o**, 37 (15)[c] |

[a] unless otherwise noted, the reaction conditions: **1** (0.4 mmol), **2** (0.2 mmol), Zn(OTf)$_2$ (10 mol%), no solvent, 100 °C; Isolated yields are given.

[b] Combined yields of the mixture of allenyl diphenylphosphine oxide and propargylic diphenylphosphine oxide isomer (ratio: ca. 1/5).

[c] **1** (0.4 mmol), **2** (0.2 mmol), ZnCl$_2$ (10 mol%), MeCN (2 mL), 100 °C.

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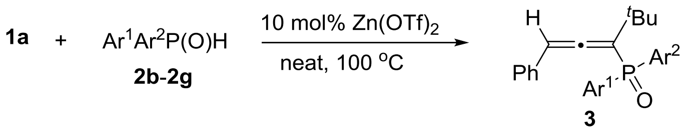
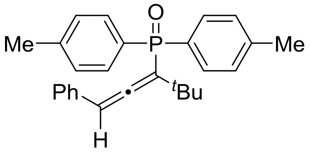
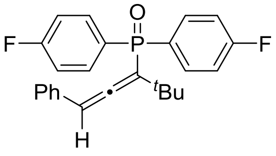
**Table 3**. $Zn(OTf)_2$-catalyzed C-P coupling of **1a** with diarylphosphine oxides **2b**-**2g**[a]

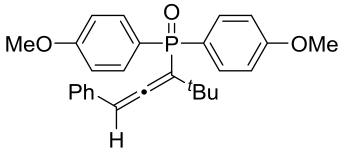




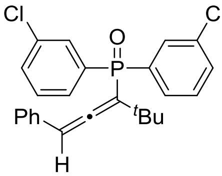
**3p**, 79%



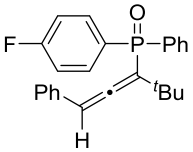
**3q**, 85%



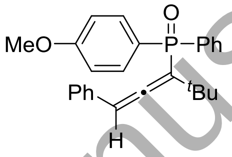
**3r**, 90%



**3s**, 82%



**3t**, 82% (dr:1/1)[b]



**3u**, 84% (dr: 1/1)[b]

[a] Reaction conditions: **1a** (0.4 mmol), **2** (0.2 mmol), $Zn(OTf)_2$ (10 mol%), no solvent, 100 °C; Isolated yields are given.[b] The dr value was determined from $^{31}P$ NMR spectra of the product.

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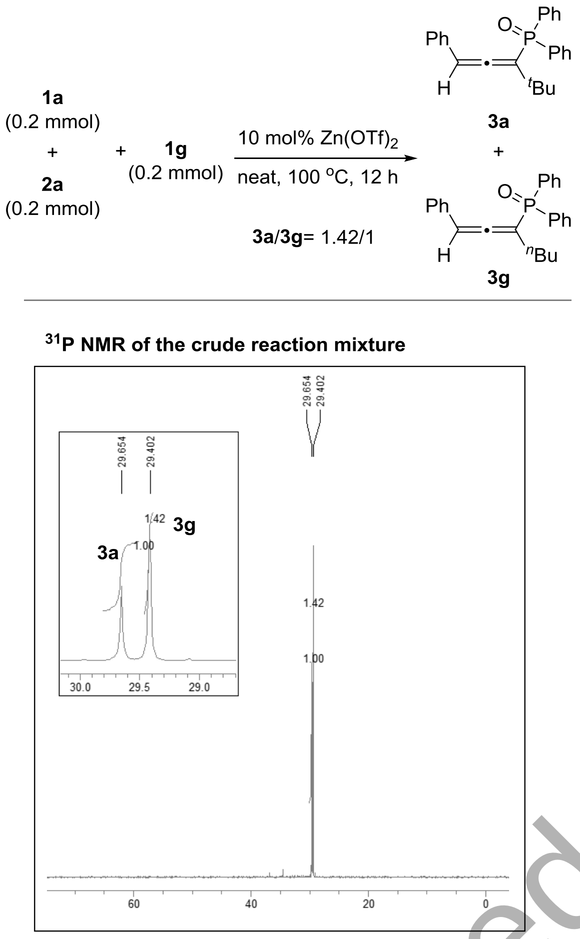
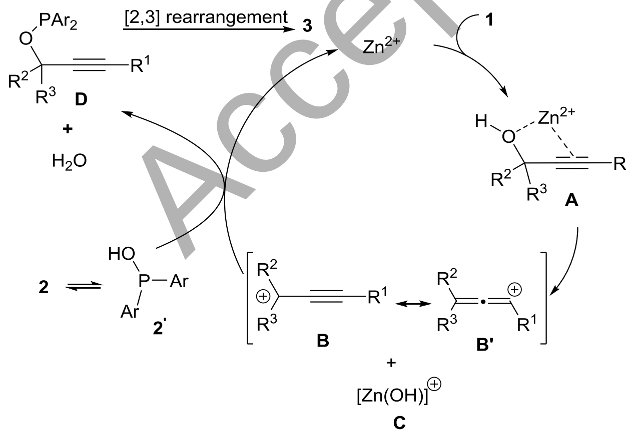


**Scheme 2.** The competition experiment



**Scheme 3**. The proposed mechanism

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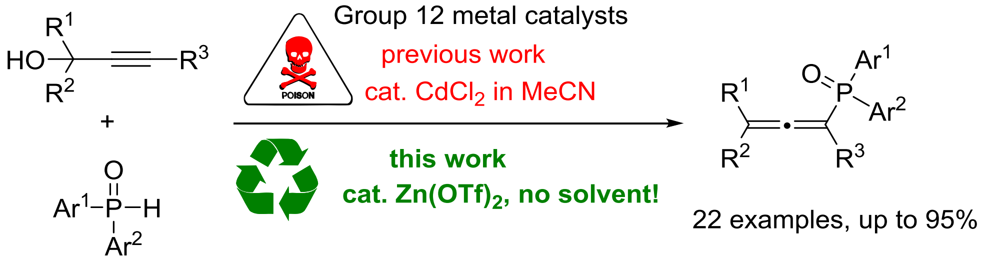

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