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Cadmium(II) Chloride-Catalyzed Dehydrative C-P Coupling of Propargyl Alcohols with Diarylphosphine Oxides to Afford Allenylphosphine Oxides

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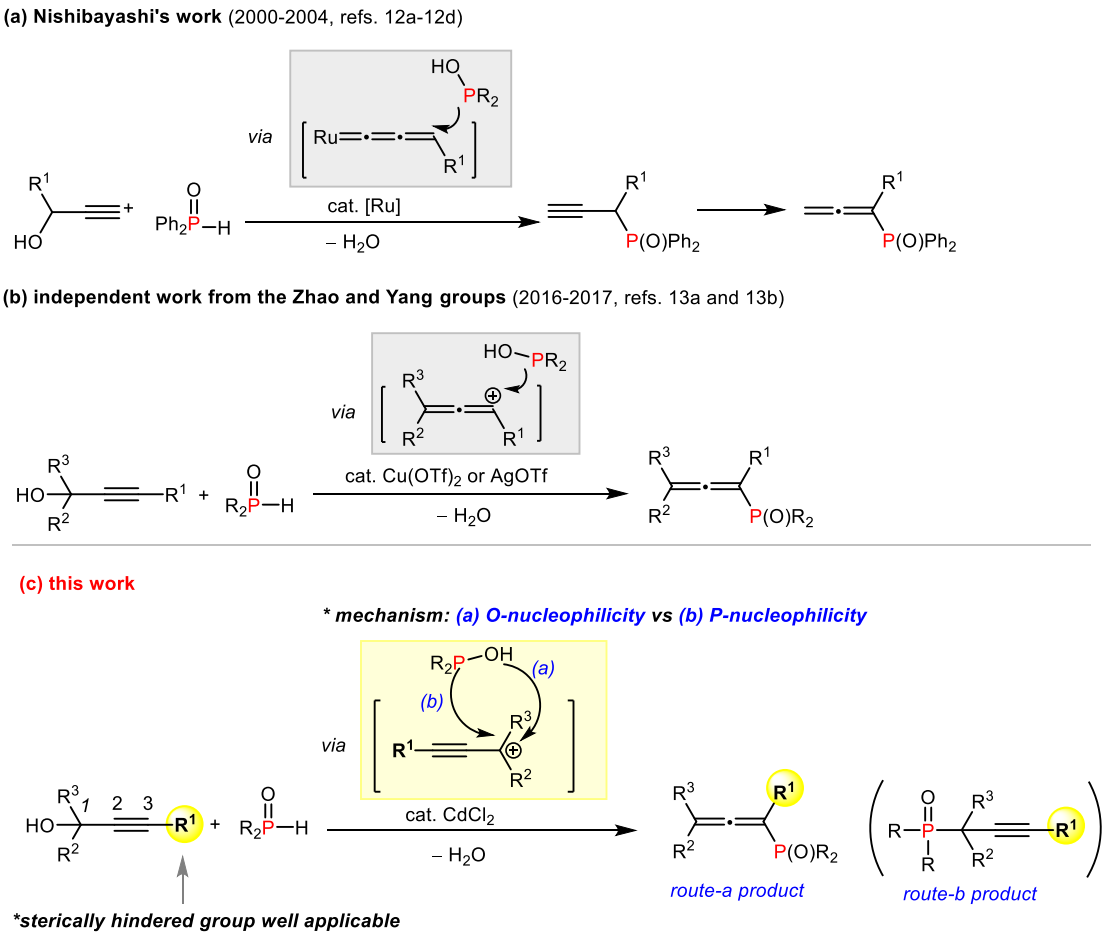
Abstract: The cadmium(II) chloride-catalyzed dehydrative C-P cross-coupling reaction of propargyl alcohols with diarylphosphine oxides is reported. Several propargyl alcohols including those bearing the sterically demanding *tert*-butyl group at the triple bond terminus can be used as good substrates in the reaction to produce the corresponding allenylphosphine oxides in good to high yields in acetonitrile at 100 ºC. The reaction can also be easily scaled up to a gram-scale synthesis. A mechanism study indicates that the reaction may proceed through a process of propargylic substitution to generate phosphonite intermediates followed by [2,3] sigmatropic rearrangement to produce the allenyl products, rather than through a common allenylative substitution resulting from P-nucleophilicity.

Keywords: allenylphosphoryl compound; dehydration; organophosphorus; propargyl alcohol; selectivity

Introduction

Organophosphorus compounds are of fundamental importance in organic synthesis and catalysis, and also have wide utility in biology, agrochemistry and material science.[1] Phosphoryl allenes are amongst a special class of P-functionalized unsaturated compounds that have received significant attention in recent years.[2-5] Indeed, the properties arising from the unique allenic structure and the phosphorus functionality render them valuable intermediates in many synthetic applications, such as the formation of highly functionalized olefins via selective additions with electrophiles or nucleophiles,[2] chiral organophosphorus compounds via transition metal-catalyzed asymmetric additions,[3] and other structurally sophisticated phosphorus compounds via Diels–Alder or other related cyclizations.[4,5] A traditional and universal preparation of these compounds is through the Horner-Mark [2,3]-rearrangement reaction which was developed in 1960s.[6] However, this method requires the use of moisture-sensitive and highly toxic phosphorus halides, and often suffers from low yields, harsh conditions and limited scope. These drawbacks thus stimulate the search for new alternative mild methods. Stawinski[7] and our group[8] have developed several effective catalytic transformations of P(O)H compounds with propargylic compounds such as propargylic halides, acetates and epoxides to afford allenylphosphoryl compounds in high yields with high selectivity.

On the other hand, the catalytic dehydrative coupling reaction of a C-OH bond with a Nu-H bond has recently emerged as a powerful tool to construct new C-C and C-heteroatom bonds.[9-11] The methodology is synthetically appealing as it employs readily available and low-cost alcohols without the need for wasteful prefunctionalization and principally generates water as the sole byproduct. Accordingly, a more direct and ideal method for the synthesis of phosphoryl allenes would be a catalytic dehydrative C-P coupling of propargyl alcohols with the stable and readily available P(O)H compounds. In this aspect, Nishibayashi first demonstrated in a study the Ru-catalyzed dehydrative propargylic substitution of propargyl alcohols with $Ph_2P(O)H$ to provide propargyl phosphine oxides (Scheme 1a).[12] Mechanistically, the reaction takes place as a result of the nucleophilic attack of the phosphorus atom to the C^3 atom of the Ru-allenylidene intermediate.[12b] The resultant propargyl phosphine oxides could undergo a facile alkyne-allene isomerization under their conditions to generate phosphoryl allenes for further transformations.[12c,12d] The direct synthesis of phosphoryl allenes via a dehydrative C-P coupling protocol has been realized very recently by the groups of Zhao and Yang independently, using $Cu(OTf)_2$ and AgOTf as the catalysts (Scheme 1b).[13]



Scheme 1. Transition metal-catalyzed dehydrative C-P cross coupling reactions of propargyl alcohols with P(O)H compounds.

Both the reactions were believed to proceed via the attack of the phosphorus atom to the C_3 atom of the allenic carbon cation (in resonance with the corresponding propargylic carbon cation) to form the C-P bond based on the P-nucleophility of the P(O)H compounds. Thus, low yields were often observed for substrates bearing R^1 as the sterically hindered group.

As our recent advance in this area,[7] here we report a $CdCl_2$-catalyzed dehydrative coupling of propargyl alcohols with P(O)H compounds (Scheme 1c). A remarkable feature of this reaction is the good compatibility of propargyl alcohols that bear sterically demanding substituents at the triple bond terminus (C^3) as substrates to produce the allenyl products in high yields. More intriguingly, a mechanism study reveals that the reaction may proceed as a process of propargylic substitution of propargyl alcohols by $R_2P(O)H$ based on their O-nucleophilicity to form phosphonite intermediates followed by [2,3] sigmatropic rearrangement to produce the allenyl products, rather than as the common allenylative substitution resulting from P-nucleophilicity.[7,12,13] To our knowledge, such a distinct reactivity is seldom demonstrated.

Results and Discussion

Our study began with examination on the reaction of 3-*tert*-butyl-1-phenylprop-2-yn-1-ol (**1a**) as the alcohol partner and $Ph_2P(O)H$ (**2a**) as the nucleophile using zinc salts as catalysts. We initially questioned whether the steric hindrance of the big *t*-Bu substituent at C^3 in **1a** would trigger the occurring of the C-P bond formation event at C^1. Unfortunately, initial experiments showed that $ZnCl_2$ and $Zn(OTf)_2$ were both ineffective to promote the reaction (Table 1, entries 1 and 2). To our surprise, when $CdCl_2$, a similar group 12 inorganic metallic salt, was used, the reaction afforded allenyl product **3a** in 62% yield (Table 1, entry 3). The reaction demonstrated excellent regioselectivity as the ^{31}P NMR spectroscopy of the crude product shows only one new peak at 29.2 ppm assigned to be **3a**. With these encouraging results, we then examined the catalytic activity of two other commercially available Cd salts. The reaction catalyzed by CdI_2 proceeded more quickly but the yield was low due to the formation of some unidentified byproducts of large polarity (Table 1, entry 4). However, $Cd(OAc)_2$ was proved ineffective (Table 1, entry 5). Using $CdCl_2$ as the catalyst, the solvent effect was investigated (Table 1, entries 6-11). The results show that the solvent also

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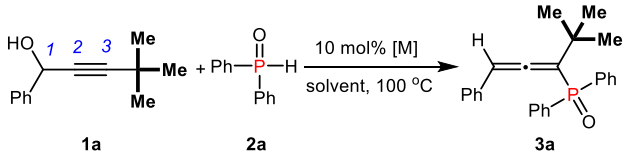
Table 1. Effect of the catalysts and solvents on the dehydrative C-P coupling reaction of **1a** and **2a**.[a]



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

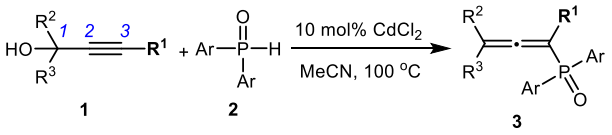
run	M	solvent	time (h)	**3a**, yield (%)[b]
1	$ZnCl_2$	DCE	12	trace
2	$Zn(OTf)_2$	DCE	12	trace
3	$CdCl_2$	DCE	12	62
4	CdI_2	DCE	4	36
5	$Cd(OAc)_2$	DCE	12	0
6	$CdCl_2$	toluene	12	trace
7	$CdCl_2$	THF	12	0
8	$CdCl_2$	Dioxane	12	0
9	**$CdCl_2$**	**MeCN**	**12**	**85**
10	$CdCl_2$	DMF	12	0
11	$CdCl_2$	DMSO	12	0
12	$CdCl_2$[c]	MeCN	16	80
13	$CdCl_2$[d]	MeCN	24	58

[a]Conditions: **1a** (0.24 mmol), **2a** (0.2 mmol), [M] (10 mol%), solvent (2 mL).
[b]Isolated yields.
[c] 5 mol% of the catalyst was used.
[d] 1 mol% of the catalyst was used.

has a significant influence on the outcome of the reaction. The best result was obtained when MeCN was used as the solvent; A very clean transformation was observed and **3a** was obtained in 85% yield (Table 1, entry 9). However, all the other solvents we checked gave negative results. For example, the reaction performed in toluene generated a very complex mixture and only a trace amount of the product was detected (Table 1, entry 6). When the reaction was performed in THF or dioxane, propargyl alcohol **1a** decomposed and **3a** was not formed (Table 1, entries 7 and 8). When DMF or DMSO was used as the solvent, no reaction took place (Table 1, entries 10 and 11). Furthermore, we also checked the effect of the catalyst loading on the reaction. When the reaction was conducted in the presence of 5 mol% of $CdCl_2$, the reaction gave rise to the product **3a** in 80% yield in 16 h (Table 1, entry 12). Further decrease in the catalyst loading to 1 mol% led to a reduced yield to 58% in 24 h (Table 1, entry 13).

Table 2 shows the results of the $CdCl_2$-catalyzed dehydrative C-P coupling reactions of a variety of propargyl alcohols with diarylphosphine oxides under the optimal conditions. Thus, propargyl alcohols **1** bearing haloaryl substituents reacted cleanly with **2a**, producing the corresponding allenyl products **3b-3f** highly selectively. The yields (**3b-3d**) were generally

Table 2. $CdCl_2$-catalyzed C-P coupling of propargyl alcohols with diarylphosphine oxides. [a]



1 **2** **3**

3a (R = H), 85%
3b (R = 4-Cl), 92%
3c (R = 4-F), 96%
3d (R = 4-Br), 96%
3e (R = 2-Br), 78%
3f (R = 2-Cl), 63%
3g (R = 4-MeO), 72%[b,c]
3h (R = 2-OMe), 44%[b,d]

3i (R = H), 82%
3j (R = 4-F), 86%
3k (R = 2-F), 83%
3l (R = 4-CF_3), 73%
3m (R = 3-Me, 5-Me), 66%[b,e]

3n (R = ^{t}Bu), 18%[f]
3o (R = ^{n}Bu), 20%[f]

3p (R = ^{t}Bu), 43%[f]
3q (R = ^{n}Bu), 39%[f]

3r (R = Ph), 70%
3s (R = ^{n}Bu), 0%

3t, 78%

3u (R = Me), 82%
3v (R = F), 79%
3w (R = OMe), 83%

3x, 28%

3y, 71%

the propargylic products

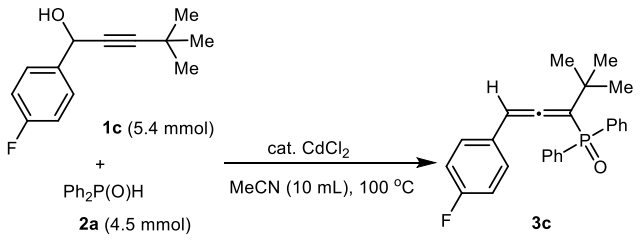
3g' (R = 4-MeO)
3h' (R = 2-MeO)

3m'

[a]Conditions: **1** (0.24 mmol), **2** (0.2 mmol), $CdCl_2$ (10 mol%) in MeCN (2 mL). Isolated yields are given.
[b]Combined yields of a mixture of the allenyl and propargyl products.
[c] **3g/3g'** = 4/1.
[d] **3h/3h'** = 2/1.
[e] **3m/3m'** = 1.5/1.
[f] ca. 40−60% of **2a** recovered.

high for substrates bearing *para*-substituted phenyl groups, while substrates with *ortho*-substituted phenyl groups gave moderate yields (**3e** and **3f**). The reactions of 3-butyl-1-arylprop-2-yn-1-ols with **2a** also took place smoothly to selectively produce the allenyl products **3i**-**3l** in good to high yields. However, the use of alcohols bearing electron-rich phenyl groups at C^1 afforded mixtures of allenyl and propargyl products likely due to electronic effect. For example, the reaction of 1-(4-methoxyphenyl)-4,4-dimethylpent-2-yn-1-ol (**1g**) with **2a** produced a mixture of **3g** and **3g'** with a ratio of 4/1. Mixture of products were also obtained from the reactions of 1-(2-methoxyphenyl)-4,4-dimethylpent-2-yn-1-ol (**1h**) and 1-(3,5-dimethylphenyl)hept-2-yn-1-ol (**1m**) with **2a**. On the other hand, the use of 1,1-disubstituted propynols also resulted in the formation of the allenyl products **3n**-**3q**, but in low yields due to the decomposition of the propargyl alcohols. Furthermore, 1-phenylprop-2-yn-1-ols bearing a phenyl or cyclopropanyl substituent at C^3 both successfully gave the expected products **3r** and **3t** in good yields. However, no reaction took place when undec-6-yn-5-ol (**1s**) was employed because of its low reactivity. The present reaction could be applied to other diarylphosphine oxides.[14] Typical substrates bearing electron-donating and electron-withdrawing substitutes on the phenyl rings were all proved as good substrates to provide the expected products **3u**, **3v**, **3w** and **3y** in high yields, but **2e** bearing two *o*-tolyl groups gave **3x** in a low yield due to the steric effect. The obtained products were characterized by ^1H, ^{13}C and ^{31}P NMR, HRMS, and the sturcture of **3y** was further confirmed by X-ray crystallography.[15]

The present reaction can be easily scaled up for a gram-scale synthesis (Scheme 2). For example, the reaction of **1c** and **2a** performed on a 4.5 mmol scale in 10 mL of MeCN afforded 1.546 g of **3c** (88%) using 10 mol% of the catalyst. When 5 mol% of the catalyst was employed, the reaction still took place smoothly and 1.524 g of **3c** was obtained.



catalyst amount	obtained weight	isolated yield
10 mol%	**1.546 g**	88%
5 mol%	**1.524 g**	87%

Scheme 2. The gram-scale synthesis of **3c**.

Figure 1 shows a comparison on the performance of the Cd catalyst with the known Cu and Ag catalysts on the reactions of **1a** or **1i** with **2a**. Clearly, the present reaction is distinguished from the known methods by its effectiveness for both substrates **1a** and **1i** bearing different sterically demanding groups at the C^3 position (*t*-Bu *vs* *n*-Bu). However, significant loss of product yields was observed in reactions of **1a** and **2a** promoted by the Cu and Ag catalysts. This obvious difference led us to the assumption that the present reaction should proceed via a different mechanism from the Cu or Ag catalysis.

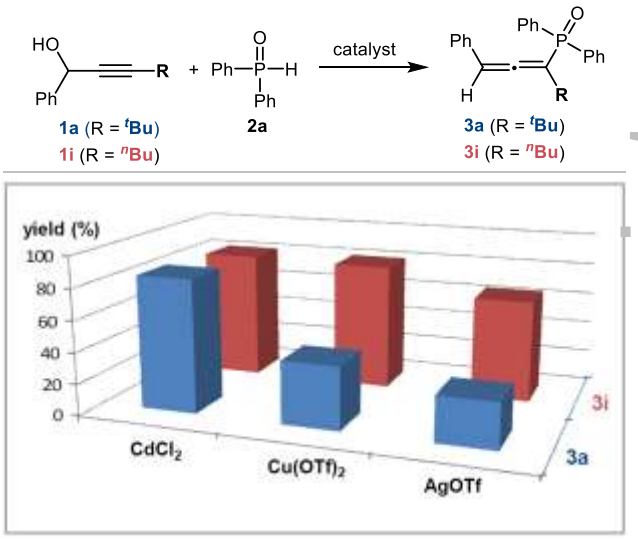
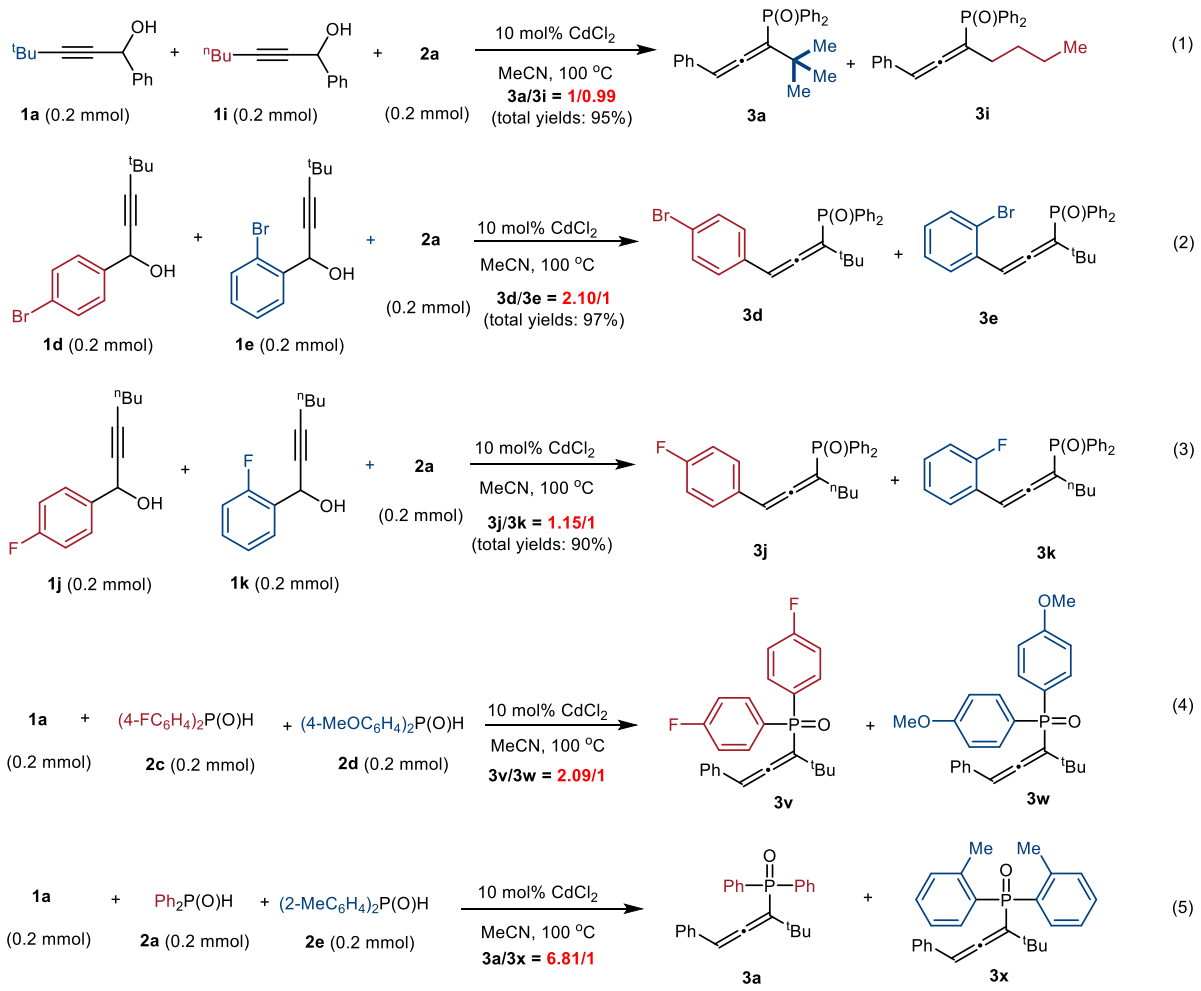


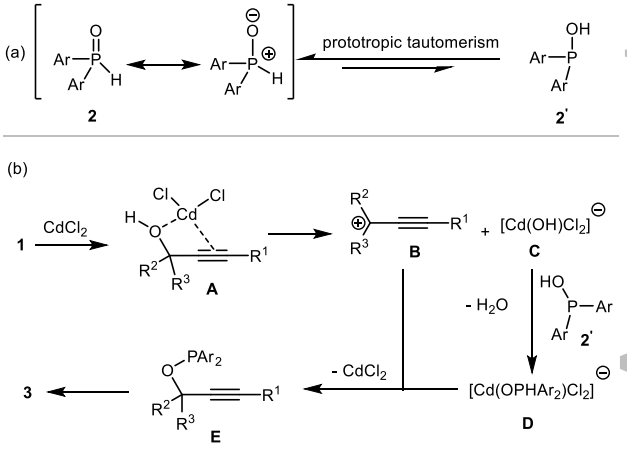
Figure 1. The steric effect: a comparison on the performance of Cd, Cu and Ag catalysts for the dehydrative C-P coupling reactions of **1a**/**2a** and **1i**/**2a**.

In order to gain more insight into the mechanism, some competition experiments were then conducted and noted as follows. 1) The reaction of **1a**, **1i** and **2a** with equal molar amount was performed under the catalytic conditions. Analysis of the crude reaction mixture by ^{31}P NMR shows that **3a** and **3i** were formed in a ratio of 1/0.99 in a combined yield of 95% (Scheme 3, eq. 1). This result indicates that the steric effect at C^3 has no influence on the reaction.[16] 2) In comparison, the reaction is sensitive to steric effect of the substitute at C^1. Thus, the treatment of an equal molar amount of **1d**, **1e** and **2a** with the catalyst resulted in the formation of **3d** and **3e** in a ratio of 2.10/1 (Scheme 3, eq. 2). When mixed substrates (**1j** and **1k**) bearing the small fluorine atom were examined, **3j** and **3k** were formed in a ratio of 1.15/1 (Scheme 3, eq. 3). 3) Another noteworthy observation arose from the competition reaction of **1a**, **2c** and **2d** that gave a mixture of products in favor of the formation of **3v** (**3v**/**3w** = 2.09/1, Scheme 3, eq. 4). This result suggests that $Ar_2P(O)H$ bearing electron-withdrawing groups reacts preferentially to form the product, contradicting the level of their nucleophilic ability. 4) The reaction of an equal molar amount of **1a**, **2a** and **2e** led to the formation of **3a** predominately (Scheme 3, eq. 5). This result is expectable considering the steric effect of the P(O)H compounds.



Scheme 3. Competition experiments for a mechanism study (for details, see the Supporting Information).

Based on these observations, we proposed a possible mechanism as shown in Scheme 4. The coordination of $CdCl_2$ to alcohol **1** may activate and enable the cleavage of the C-O bond to generate the carbon cation **B** and $[Cd(OH)Cl_2]$ anion **C**.[17] $Ar_2P(O)H$ **2** is in equilibrium with its tautomer **2'** (Scheme 3a),[18] and may react with **C** to form $[Cd(OPAr_2)Cl_2]$ anion **D**. The reaction of **B** and **D** then produces a propargyl phosphonite intermediate **E**, which undergoes the classical [2,3]-rearrangement to give the allenyl product **3** (Scheme 4b). It is noteworthy that the introduction of electron-withdrawing groups in **2** generally leads to a shift in equilibrium towards **2'** and increases the acidity of **2'** (Scheme 4a), thus enhancing its reactivity to the reaction with **C**.[18a] This fact accounts for the preferred formation of **3v** in the competition reaction of **1a**, **2c** and **2d** (Scheme 3, eq. 4). On other hand, the differentitation of the intermediates **B** due to the electronic effect of the substitutes at C^1 should have an important influence on the selectivity of the reaction as experimentally observed from the reactions of **1g**, **1h** and **1m**. The reasons for this unexpected result are unclear at present and need further study.



Scheme 4. (a) Tautomeric equilibrium between **2** and **2'**; (b) The proposed mechanism.

Conclusion

In conclusion, we have disclosed a $CdCl_2$-catalyzed dehydrative C-P cross-coupling reaction of

propargyl alcohols with P(O)H compounds. A remarkable advantage of the reaction is the good applicability of propargyl alcohols that bear sterically demanding substituents at the triple bond terminus to provide products in high yields. The reaction may involve a process of propargylic substitution in favor of a distinct and high level of O-nucleophilic selectivity to form phosphonite intermediates followed by [2,3] rearrangement to selectively give the allenyl products. Further investigation into the reaction scope and detailed mechanism will be pursued.

Experimental Section

General Information

Unless otherwise specified, all reactions were performed under dry N_2 atmosphere. Anhydrous solvents were distilled prior to use: THF, dioxane and toluene were distilled from sodium using benzophenone as the indicator; MeCN, DCE, DMF and DMSO were distilled from CaH_2. Propargyl alcohols **1a-1t** were prepared following a procedure reported by Hailes.[19] A typical procedure was given in the Supporting Information (Page 8 in SI). Diarylphosphine oxides **2** were purchased from commercial sources or prepared following known method.[8a] Flash chromatography was performed on silica gel using petroleum ether and EtOAc as eluent. ^{1}H, ^{13}C and ^{31}P NMR spectra were recorded on a 400 MHz spectrometer. 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 was obtained from the Analytical Center of State Key Laboratory of Materials-Oriented Chemical Engineering at Nanjing Tech University.

General Procedure for the $CdCl_2$-Catalyzed Dehydrative Reaction of Propargyl Alcohols with Diarylphosphine Oxides

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with anhydrous $CdCl_2$ (3.7 mg, 10 mol %). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 0.5 mL of MeCN was injected with vigrous stirring. Then **1** (0.24 mmol) and **2** (0.2 mmol) dissolved in 1.5 mL of MeCN was added. The Schlenk tube was sealed and immersed in an oil bath which was heated to 100 °C. After the reaction was complete (monitored by TLC, 12 h), 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 the product **3**. *Note: the residual waste containing the hazardous cadmium salts should be disposed properly.*

(4,4-Dimethyl-1-phenylpenta-1,2-dien-3-yl)diphenyl phosphine oxide (3a).[13a] 63.2 mg (yield 85%), prepared from 45.1 mg of **1a** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.73 (m, 2H), 7.66–7.60 (m, 2H), 7.52–7.48 (m, 1H), 7.45–7.40 (m, 2H), 7.30–7.15 (m, 6H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.02 (d, *J* = 11.2 Hz, 1H), 1.34 (s, 9H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.2.

(1-(4-Chlorophenyl)-4,4-dimethylpenta-1,2-dien-3-yl) diphenylphosphine oxide (3b). 74.6 mg (yield 92%), prepared from 53.3 mg of **1b** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79–7.74 (m, 2H), 7.63–7.58 (m, 2H), 7.52–7.49 (m, 1H), 7.49–7.42 (m, 2H), 7.31–7.27 (m, 1H), 7.23–7.17 (m, 4H), 6.90 (d, *J* = 8.0 Hz, 2H), 5.98 (d, *J* = 10.8 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.0 (d, $J_{P\text{-}C}$ = 7.5 Hz), 133.8 (d, $J_{P\text{-}C}$ = 105.7 Hz), 133.3 (d, $J_{P\text{-}C}$ = 102.5 Hz), 132.9 (d, $J_{P\text{-}C}$ = 2.4 Hz), 131.7 (d, $J_{P\text{-}C}$ = 2.1 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.5 Hz), 131.4 (d, $J_{P\text{-}C}$ = 3.2 Hz), 131.3 (d, $J_{P\text{-}C}$ = 7.4 Hz), 131.2 (d, $J_{P\text{-}C}$ = 9.6 Hz), 128.7, 128.3 (d, $J_{P\text{-}C}$ = 13.0 Hz), 128.0 (d, $J_{P\text{-}C}$ = 12.0 Hz), 127.6 (d, $J_{P\text{-}C}$ = 2.4 Hz), 112.5 (d, $J_{P\text{-}C}$ = 93.8 Hz), 96.6 (d, $J_{P\text{-}C}$ = 14.1 Hz), 37.5 (d, $J_{P\text{-}C}$ = 4.8 Hz), 30.8 (d, $J_{P\text{-}C}$ = 3.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.0. HRMS (ESI-TOF): *m/z* = 407.1305, calcd for $C_{25}H_{25}ClOP$ [MH^+] 407.1332.

(1-(4-Fluorophenyl)-4,4-dimethylpenta-1,2-dien-3-yl) diphenylphosphine oxide (3c). 76.2 mg (yield 96%), prepared from 49.5 mg of **1c** (0.24 mmol) and 40.4 mg of 2a (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81–7.76 (m, 2H), 7.64–7.59 (m, 2H), 7.55–7.51 (m, 1H), 7.48–7.43 (m, 2H), 7.32–7.27 (m, 1H), 7.24–7.19 (m, 2H), 6.97–6.90 (m, 4H), 6.02 (d, *J* = 11.2 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.9 (dd, $J_{P\text{-}C}$ = 6.9 Hz, $J_{F\text{-}C}$ = 2.2 Hz), 162.0 (dd, $J_{F\text{-}C}$ = 245.9 Hz, $J_{P\text{-}C}$ = 1.7 Hz), 133.8 (d, $J_{P\text{-}C}$ = 106.3 Hz), 133.3 (d, $J_{P\text{-}C}$ = 103.4 Hz), 131.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.4 Hz), 131.26 (d, $J_{P\text{-}C}$ = 9.4 Hz), 131.23 (d, $J_{P\text{-}C}$ = 3.2 Hz), 128.6 (dd, $J_{F\text{-}C}$ = 6.5 Hz, $J_{P\text{-}C}$ = 2.6 Hz), 128.2 (d, $J_{P\text{-}C}$ = 13.0 Hz), 127.84 (d, $J_{F\text{-}C}$ = 7.8 Hz, $J_{P\text{-}C}$ = 2.2 Hz), 127.78 (d, $J_{P\text{-}C}$ = 9.3 Hz), 115.4 (d, $J_{P\text{-}C}$ = 22.7 Hz), 112.1 (d, $J_{P\text{-}C}$ = 94.0 Hz), 96.5 (d, $J_{P\text{-}C}$ = 14.3 Hz), 37.4 (d, $J_{P\text{-}C}$ = 5.5 Hz), 30.7 (d, $J_{P\text{-}C}$ = 4.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.3. HRMS (ESI-TOF): *m/z* = 391.1632, calcd for $C_{25}H_{25}FOP$ [MH^+] 391.1627.

(1-(4-Bromophenyl)-4,4-dimethylpenta-1,2-dien-3-yl) diphenylphosphine oxide (3d). 86.3 mg (yield 96%), prepared from 64.1 mg of **1d** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79–7.73 (m, 2H), 7.62–7.57 (m, 2H), 7.54–7.43 (m, 3H), 7.34–7.27 (m, 3H), 7.24–7.20 (m, 2H), 6.84 (d, *J* = 8.0 Hz, 2H), 5.97 (d, *J* = 11.2 Hz, 1H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.9 (d, $J_{P\text{-}C}$ = 7.1 Hz), 133.7 (d, $J_{P\text{-}C}$ = 105.5 Hz), 133.3 (d, $J_{P\text{-}C}$ = 103.1 Hz), 131.8 (d, $J_{P\text{-}C}$ = 7.3 Hz), 131.65 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.58 (d, $J_{P\text{-}C}$ = 1.7 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.4 Hz), 131.3 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.2 (d, $J_{P\text{-}C}$ = 9.5 Hz), 128.2 (d, $J_{P\text{-}C}$ = 12.6 Hz), 127.9 (d, $J_{P\text{-}C}$ = 8.3 Hz), 127.8 (d, $J_{P\text{-}C}$ = 1.4 Hz), 120.9 (d, $J_{P\text{-}C}$ = 1.7 Hz), 112.5 (d, $J_{P\text{-}C}$ = 93.6 Hz), 96.5 (d, $J_{P\text{-}C}$ = 14.0 Hz), 37.5 (d, $J_{P\text{-}C}$ = 5.0 Hz), 30.8 (d, $J_{P\text{-}C}$ = 3.9 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.1. HRMS (ESI-TOF). *m/z* = 451.0798, calcd for $C_{25}H_{25}BrOP$ [MH^+] 451.0826.

(1-(2-Bromophenyl)-4,4-dimethylpenta-1,2-dien-3-yl) diphenylphosphine oxide (3e). 74.0 mg (yield 78%), prepared from 80.1 mg of **1e** (0.3 mmol) and 41.5 mg of **2a** (0.21 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz). δ = 7.81–7.76 (m, 2H), 7.60–7.40 (m, 6H), 7.29–7.25 (m, 1H), 7.20–7.14 (m, 3H), 7.08 (d, *J* = 7.2 Hz, 1H), 7.03–6.99 (m, 1H), 6.47 (d, *J* = 11.2 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.3 (d, $J_{P\text{-}C}$ = 7.4 Hz), 133.5 (d, $J_{P\text{-}C}$ = 106.7 Hz), 133.1 (d, $J_{P\text{-}C}$ = 102.4 Hz), 132.8, 132.4 (d, $J_{P\text{-}C}$ = 7.7 Hz), 131.7 (d, $J_{P\text{-}C}$ = 3.3 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.4 Hz), 131.25 (d, $J_{P\text{-}C}$ = 9.5 Hz), 131.24 (d, $J_{P\text{-}C}$ = 2.0 Hz), 128.5 (d, $J_{P\text{-}C}$ = 1.5 Hz), 128.3 (d, $J_{P\text{-}C}$ = 12.9 Hz), 127.8 (d, $J_{P\text{-}C}$ = 10.7 Hz), 127.7, 127.2, 122.0 (d, $J_{P\text{-}C}$ = 3.9 Hz), 112.0 (d, $J_{P\text{-}C}$ = 93.7 Hz), 96.5 (d, $J_{P\text{-}C}$ = 13.9 Hz), 37.4 (d, $J_{P\text{-}C}$ = 5.2 Hz), 30.8 (d, $J_{P\text{-}C}$ = 3.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.2; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.2. HRMS (ESI-TOF): *m/z* = 451.0820, calcd for $C_{25}H_{25}BrOP$ [MH^+] 451.0826.

(1-(2-Chlorophenyl)-4,4-dimethylpenta-1,2-dien-3-yl) diphenylphosphine oxide (3f). 52.8 mg (yield 63%), prepared from 53.3 mg of **1f** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.82–7.77 (m, 2H), 7.61–7.52 (m, 3H), 7.49–7.45 (m, 2H), 7.29–7.06 (m, 7H), 6.46 (d, *J* = 11.2 Hz, 1H), 1.34 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.4 (d, $J_{P\text{-}C}$ = 8.0 Hz), 133.7 (d, $J_{P\text{-}C}$ = 107.0 Hz), 133.3 (d, $J_{P\text{-}C}$ = 103.0 Hz), 131.8 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.7 (d, $J_{P\text{-}C}$ = 3.0 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.0 Hz), 131.32 (d, $J_{P\text{-}C}$ = 10.0 Hz), 131.28 (d, $J_{P\text{-}C}$ = 3.0 Hz), 130.7 (d, $J_{P\text{-}C}$ = 7.0 Hz), 129.6 (d, $J_{P\text{-}C}$ = 1.0 Hz), 128.34 (d, $J_{P\text{-}C}$ = 4.0 Hz), 128.32 (d, $J_{P\text{-}C}$ = 12.0 Hz) , 127.8 (d, $J_{P\text{-}C}$ = 12.0 Hz), 127.7 (d, $J_{P\text{-}C}$ = 2.0 Hz), 126.7 (d, $J_{P\text{-}C}$ = 2.0 Hz), 112.1 (d, $J_{P\text{-}C}$ = 93.0 Hz), 93.9 (d, $J_{P\text{-}C}$ = 14.0 Hz), 37.4 (d, $J_{P\text{-}C}$ = 4.0 Hz), 30.8 (d, $J_{P\text{-}C}$ = 3.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.1. HRMS (ESI-TOF): *m/z* = 407.1337, calcd for $C_{25}H_{25}ClOP$ [MH^+] 407.1332

Diphenyl(1-phenylhepta-1,2-dien-3-yl)phosphine oxide (3i). [13a] 30.5 mg (yield 82%), prepared from 25.6 mg of **1i**

(0.13 mmol) and 20.2 mg of **2a** (0.1 mmol) in 1 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.69 (m, 4H), 7.51–7.38 (m, 3H), 7.35–7.32 (m, 2H), 7.27–7.24 (m, 2H), 7.21–7.17 (m, 1H), 7.09 (d, J = 8.0 Hz, 2H), 6.11 (dt, J_1 = 11.2 Hz, J_2 = 3.2 Hz, 1H), 2.49–2.33 (m, 2H), 1.60–1.52 (m, 2H), 1.37–1.29 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.5.

(1-(4-Fluorophenyl)hepta-1,2-dien-3-yl)diphenyl phosphine oxide (3j). 67.3 mg (yield 86%), prepared from 49.5 mg of **1j** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79–7.74 (m, 2H), 7.71–7.65 (m, 2H), 7.52–7.50 (m, 1H), 7.46–7.39 (m, 3H), 7.35–7.32 (m, 2H), 7.05–7.02 (m, 2H), 6.97–6.92 (m, 2H), 6.09 (dt, J_1 = 10.8 Hz, J_2 = 3.2 Hz, 1H), 2.50–2.29 (m, 2H), 1.60–1.48 (m, 2H), 1.38–1.31 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.9 (dd, $J_{P\text{-}C}$ = 6.4 Hz, $J_{F\text{-}C}$ = 1.9 Hz), 162.1 (dd, $J_{F\text{-}C}$ = 245.6 Hz, $J_{P\text{-}C}$ = 1.3 Hz), 131.71 (d, $J_{P\text{-}C}$ = 104.7 Hz), 131.9 (d, $J_{P\text{-}C}$ = 3.3 Hz), 131.8 (d, $J_{P\text{-}C}$ = 2.8 Hz), 131.6 (d, $J_{P\text{-}C}$ = 10.3 Hz), 131.4 (d, $J_{P\text{-}C}$ = 10.4 Hz), 131.3 (d, $J_{P\text{-}C}$ = 104.7 Hz), 128.5 (dd, $J_{F\text{-}C}$ = 6.5 Hz, $J_{P\text{-}C}$ = 2.3 Hz), 128.3 (d, $J_{P\text{-}C}$ = 12.2 Hz), 128.1 (d, $J_{P\text{-}C}$ = 13.0 Hz), 128.0 (d, $J_{F\text{-}C}$ = 7.9 Hz, $J_{P\text{-}C}$ = 2.0 Hz), 115.5 (d, $J_{P\text{-}C}$ = 21.8 Hz), 103.3 (d, $J_{P\text{-}C}$ = 97.7 Hz), 96.4 (d, $J_{P\text{-}C}$ = 14.2 Hz), 30.4 (d, $J_{P\text{-}C}$ = 5.6 Hz), 27.8 (d, $J_{P\text{-}C}$ = 5.5 Hz), 22.3, 13.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.5. HRMS (ESI-TOF): m/z = 391.1616, calcd for $C_{25}H_{25}FOP$ [MH^+] 391.1627.

(1-(2-Fluorophenyl)hepta-1,2-dien-3-yl)diphenyl phosphine oxide (3k). 65.0 mg (yield 83%), prepared from 49.4 mg of **1k** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.68 (m, 4H), 7.50–7.46 (m, 1H), 7.42–7.38 (m, 3H), 7.35–7.30 (m, 2H), 7.17–7.08 (m, 2H), 7.04–6.93 (m, 2H), 6.26 (dt, J_1 = 11.2 Hz, J_2 = 3.4 Hz, 1H), 2.48–2.29 (m, 2H), 1.59–1.52 (m, 2H), 1.38–1.29 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.6 (dd, $J_{P\text{-}C}$ = 6.0 Hz, $J_{F\text{-}C}$ = 1.4 Hz), 159.4 (dd, $J_{F\text{-}C}$ = 248.6 Hz, $J_{P\text{-}C}$ = 3.3 Hz), 131.86 (d, $J_{P\text{-}C}$ = 3.5 Hz), 131.80 (d, $J_{P\text{-}C}$ = 105.1 Hz), 131.74 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.53 (d, $J_{P\text{-}C}$ = 9.8 Hz), 131.42 (d, $J_{P\text{-}C}$ = 10.5 Hz), 131.40 (d, $J_{P\text{-}C}$ = 104.0 Hz), 128.7 (dd, $J_{F\text{-}C}$ = 8.0 Hz, $J_{P\text{-}C}$ = 1.5 Hz), 128.3 (d, $J_{P\text{-}C}$ = 10.2 Hz), 128.13 (d, $J_{P\text{-}C}$ = 11.1 Hz), 128.12, 124.1 (d, $J_{P\text{-}C}$ = 3.2 Hz), 120.3 (d, $J_{F\text{-}C}$ = 12.1 Hz, $J_{P\text{-}C}$ = 7.2 Hz), 115.5 (d, $J_{P\text{-}C}$ = 21.2 Hz), 102.8 (d, $J_{P\text{-}C}$ = 97.5 Hz), 96.0 (dd, $J_{P\text{-}C}$ = 13.8 Hz, $J_{F\text{-}C}$ = 5.8 Hz), 30.4 (d, $J_{P\text{-}C}$ = 5.0 Hz), 27.7 (d, $J_{P\text{-}C}$ = 6.3 Hz), 22.3, 13.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.6. HRMS (ESI-TOF): m/z = 391.1618, calcd for $C_{25}H_{25}FOP$ [MH^+] 391.1627.

Diphenyl(1-(4-(trifluoromethyl)phenyl)hepta-1,2-dien-3-yl)phosphine oxide (3l). 64.3 mg (yield 73%), prepared from 76.8 mg of **1l** (0.3 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.79–7.66 (m, 4H), 7.54–7.40 (m, 6H), 7.52–7.50 (m, 1H), 7.36–7.31 (m, 2H), 7.16 (d, J = 8.4 Hz, 2H), 6.13 (dt, J_1 = 9.2 Hz, J_2 = 3.2 Hz, 1H), 2.52–2.32 (m, 2H), 1.59–1.50 (m, 2H), 1.37–1.32 (m, 2H), 0.84 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.3 (d, $J_{P\text{-}C}$ = 6.4 Hz), 136.7 (d, $J_{P\text{-}C}$ = 5.8 Hz), 132.08 (d, $J_{P\text{-}C}$ = 3.4 Hz), 131.93 (d, $J_{P\text{-}C}$ = 2.7 Hz), 131.65 (d, $J_{P\text{-}C}$ = 105.0 Hz), 131.55 (d, $J_{P\text{-}C}$ = 9.2 Hz), 131.37 (d, $J_{P\text{-}C}$ = 9.3 Hz), 131.24 (d, $J_{P\text{-}C}$ = 103.4 Hz), 128.4 (d, $J_{P\text{-}C}$ = 12.0 Hz), 128.3 (d, $J_{P\text{-}C}$ = 12.21Hz), 126.7 (d, $J_{P\text{-}C}$ = 1.8 Hz), 126.0 (d, $J_{F\text{-}C}$ = 225.2 Hz), 125.5 (d, $J_{P\text{-}C}$ = 2.9 Hz), 104.3 (d, $J_{P\text{-}C}$ = 96.7 Hz), 96.4 (d, $J_{P\text{-}C}$ = 13.0 Hz), 30.5 (d, $J_{P\text{-}C}$ = 5.2 Hz), 27.8 (d, $J_{P\text{-}C}$ = 5.9 Hz), 22.3, 13.7. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.6. HRMS (ESI-TOF): m/z = 441.1591, calcd for $C_{26}H_{25}F_3OP$ [MH^+] 441.1595.

(4,4-Dimethyl-1,1-diphenylpenta-1,2-dien-3-yl)diphenyl phosphine oxide (3n). 16.4 mg (yield 18%), prepared from 63.4 mg of **1n** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN; 23.1 mg of **2a** recovered. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.61–7.56 (m, 4H), 7.40–7.36 (m, 2H), 7.28–7.25 (m, 10H), 6.97–6.94 (m, 4H), 1.35 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.1 (d, $J_{P\text{-}C}$ = 7.5 Hz), 135.3 (d, $J_{P\text{-}C}$ = 7.0 Hz), 133.7 (d, $J_{P\text{-}C}$ = 103.4 Hz), 133.4 (d, $J_{P\text{-}C}$ = 8.2 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.7 Hz), 128.3, 128.0 (d, $J_{P\text{-}C}$ = 14.1 Hz), 127.9, 127.6, 112.0 (d, $J_{P\text{-}C}$ = 14.8 Hz), 110.6 (d, $J_{P\text{-}C}$ = 93.5 Hz), 38.0 (d, $J_{P\text{-}C}$ = 5.9 Hz), 30.9 (d, $J_{P\text{-}C}$ = 4.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.0. HRMS (ESI-TOF): m/z = 449.2027, calcd for $C_{31}H_{30}OP$ [MH^+] 449.2034.

(1,1-Diphenylhepta-1,2-dien-3-yl)diphenylphosphine oxide (3o). 18.2 mg (yield 20%), prepared from 63.4 mg of **1o** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN; 24.3 mg of **2a** recovered. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66–7.61 (m, 4H), 7.46–7.42 (m, 2H), 7.34–7.26 (m, 10H), 6.99–6.97 (m, 4H), 2.47–2.41 (m, 2H), 1.67–1.59 (m, 2H), 1.35–1.31 (m, 2H), 0.83 (t, J = 7.4 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.8 (d, $J_{P\text{-}C}$ = 5.9 Hz), 135.3 (d, $J_{P\text{-}C}$ = 6.8 Hz), 131.79 (d, $J_{P\text{-}C}$ = 103.2 Hz), 131.76 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.3 Hz), 128.4, 128.2 (d, $J_{P\text{-}C}$ = 12.0 Hz), 128.1 (d, $J_{P\text{-}C}$ = 2.5 Hz), 127.7, 112.7 (d, $J_{P\text{-}C}$ = 14.6 Hz), 102.0 (d, $J_{P\text{-}C}$ = 98.4 Hz), 30.6 (d, $J_{P\text{-}C}$ = 5.9 Hz), 28.1 (d, $J_{P\text{-}C}$ = 7.4 Hz), 22.4, 13.8. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.9. HRMS (ESI-TOF): m/z = 449.2038, calcd for $C_{31}H_{30}OP$ [MH^+] 449.2034.

(1-Cyclohexylidene-3,3-dimethylbut-1-en-2-yl)diphenyl phosphine oxide (3p). 32.5 mg (yield 43%), prepared from 43.2 mg of **1p** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN; 12.8 mg of **2a** recovered. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.69–7.64 (m, 4H), 7.48–7.38 (m, 6H), 1.99–1.91 (m, 2H), 1.76–1.88 (m, 2H), 1.42–1.24 (m, 4H), 1.20 (s, 9H), 1.09–1.00 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 203.8 (d, $J_{P\text{-}C}$ = 8.8 Hz), 134.7 (d, $J_{P\text{-}C}$ = 102.0 Hz), 131.4 (d, $J_{P\text{-}C}$ = 9.0 Hz), 131.0 (d, $J_{P\text{-}C}$ = 2.5 Hz), 127.9 (d, $J_{P\text{-}C}$ = 11.2 Hz), 105.2 (d, $J_{P\text{-}C}$ = 100.3 Hz), 104.5 (d, $J_{P\text{-}C}$ = 13.6 Hz), 36.2 (d, $J_{P\text{-}C}$ = 7.2 Hz), 30.8 (d, $J_{P\text{-}C}$ = 3.5 Hz), 30.1 (d, $J_{P\text{-}C}$ = 6.3 Hz), 26.3 (d, $J_{P\text{-}C}$ = 3.4 Hz), 25.4. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 31.6. HRMS (ESI-TOF): m/z = 387.1860, calcd for $C_{24}H_{29}OPNa$ [MNa^+] 387.1854.

(1-Cyclohexylidenehex-1-en-2-yl)diphenylphosphine oxide (3q). 29.4 mg (yield 39%), prepared from 43.2 mg of **1q** (0.24 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN; 16.2 mg of **2a** recovered.. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.73–7.68 (m, 4H), 7.50–7.41 (m, 6H), 2.24–2.19 (m, 2H), 2.01–1.93 (m, 2H), 1.85–1.80 (m, 2H), 1.47–1.41 (m, 4H), 1.34–1.28 (m, 4H), 1.06–0.98 (m, 2H), 0.84 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 204.0 (d, $J_{P\text{-}C}$ = 7.6 Hz), 137.6 (d, $J_{P\text{-}C}$ = 102.8 Hz), 131.6 (d, $J_{P\text{-}C}$ = 8.7 Hz), 131.4 (d, $J_{P\text{-}C}$ = 2.5 Hz), 128.2 (d, $J_{P\text{-}C}$ = 12.1 Hz), 104.8 (d, $J_{P\text{-}C}$ = 14.6 Hz), 96.3 (d, $J_{P\text{-}C}$ = 103.3 Hz), 30.4 (d, $J_{P\text{-}C}$ = 5.7 Hz), 30.1 (d, $J_{P\text{-}C}$ = 5.5 Hz), 27.2 (d, $J_{P\text{-}C}$ = 7.9 Hz), 26.4 (d, $J_{P\text{-}C}$ = 3.3 Hz), 25.5, 22.1, 13.9. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 32.1. HRMS (ESI-TOF): m/z = 365.2016, calcd for $C_{24}H_{30}OP$ [MH^+] 365.2034.

(1,3-Diphenylpropa-1,2-dien-1-yl)diphenylphosphine oxide (3r). [13a] 54.9 mg (yield 70%), prepared from 62.5 mg of **1r** (0.3 mmol) and 40.4 mg of **2a** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.80–7.72 (m, 4H), 7.68 (d, J = 8.0 Hz, 2H), 7.48–7.44 (m, 1H), 7.39–7.21 (m, 11H), 7.12 (d, J = 7.6 Hz, 2H), 6.29 (d, J = 10.8 Hz, 1H). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.6.

(1-Cyclopropyl-3-phenylpropa-1,2-dien-1-yl)diphenyl phosphine oxide (3t). 83.4 mg (yield 78%), prepared from 61.9 mg of **1s** (0.36 mmol) and 60.6 mg of **2a** (0.3 mmol) in 3 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.81–7.73 (m, 4H), 7.51–7.48 (m, 1H), 7.43–7.32 (m, 5H), 7.27–7.17 (m, 3H), 7.06 (d, J = 8.0 Hz, 2H), 6.16 (dd, J_1 = 10.8 Hz, J_2 = 1.6 Hz, 1H), 1.65–1.57 (m, 1H), 0.86–0.81 (m, 2H), 0.62–0.60 (m, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 207.2 (d, $J_{P\text{-}C}$ = 7.2 Hz), 132.6, 132.3 (d, $J_{P\text{-}C}$ = 6.7 Hz), 131.83 (d, $J_{P\text{-}C}$ = 2.7 Hz), 131.73 (d, $J_{P\text{-}C}$ = 4.2 Hz), 131.70 (d, $J_{P\text{-}C}$ = 103.9 Hz), 131.65 (d, $J_{P\text{-}C}$ = 10.2 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.8 Hz), 128.6 (d, $J_{P\text{-}C}$ = 1.5 Hz), 128.2 (d, $J_{P\text{-}C}$ = 6.8 Hz), 128.1 (d, $J_{P\text{-}C}$ = 7.3 Hz), 127.5 (d, $J_{P\text{-}C}$ = 1.3 Hz), 126.6 (d, $J_{P\text{-}C}$ = 2.6 Hz), 107.4 (d, $J_{P\text{-}C}$ = 99.6 Hz), 99.0 (d, $J_{P\text{-}C}$ = 13.3 Hz), 9.0 (d, $J_{P\text{-}C}$ = 18.4 Hz), 9.03, 8.9 (d, $J_{P\text{-}C}$ = 1.5 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.8. HRMS (ESI-TOF): m/z = 357.1395, calcd for $C_{24}H_{22}OP$ [MH^+] 357.1408.

(4,4-Dimethyl-1-phenylpenta-1,2-dien-3-yl)di-p-tolyl phosphine oxide (3u). 65.4 mg (yield 82%), prepared from 45.1 mg of **1a** (0.24 mmol) and 45.9 mg of **2b** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.62 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.50 (dd, J_1 = 12.0 Hz, J_2 = 8.0 Hz, 2H), 7.22–7.16 (m, 5H), 7.01–7.98 (m, 4H), 6.00 (d, J = 11.2 Hz, 1H), 2.38 (s, 3H), 2.21 (s, 3H), 1.33 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.9 (d,

$J_{P\text{-}C}$ = 7.8 Hz), 141.8 (d, $J_{P\text{-}C}$ = 3.1 Hz), 141.5 (d, $J_{P\text{-}C}$ = 2.6 Hz), 133.0 (d, $J_{P\text{-}C}$ = 7.7 Hz), 131.5 (d, $J_{P\text{-}C}$ = 9.0 Hz), 131.3 (d, $J_{P\text{-}C}$ = 9.5 Hz), 130.8 (d, $J_{P\text{-}C}$ = 108.0 Hz), 130.0 (d, $J_{P\text{-}C}$ = 105.8 Hz), 128.8 (d, $J_{P\text{-}C}$ = 12.2 Hz), 128.5 (d, J = 12.9 Hz), 128.4 (d, $J_{P\text{-}C}$ = 1.6 Hz), 127.1 (d, $J_{P\text{-}C}$ = 1.7 Hz), 126.5 (d, $J_{P\text{-}C}$ = 2.0 Hz), 112.0 (d, $J_{P\text{-}C}$ = 94.7 Hz), 97.3 (d, $J_{P\text{-}C}$ = 13.7 Hz), 37.3 (d, $J_{P\text{-}C}$ = 5.7 Hz), 30.8 (d, $J_{P\text{-}C}$ = 4.3 Hz), 21.4 (d, $J_{P\text{-}C}$ = 18.1 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.5. HRMS (ESI-TOF): *m/z* = 401.2058, calcd for $C_{27}H_{30}OP$ [MH^+] 401.2034.

(4,4-Dimethyl-1-phenylpenta-1,2-dien-3-yl)bis(4-fluorophenyl)phosphine oxide (3v). 64.3 mg (yield 79%), prepared from 45.1 mg of **1a** (0.24 mmol) and 47.0 mg of **2c** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77–7.71 (m, 2H), 7.63–7.57 (m, 2H), 7.27–7.20 (m, 3H), 7.16–7.11 (m, 2H), 7.00 (d, J = 8.0 Hz, 2H), 6.92-6.87 (m, 2H), 6.05 (d, J = 11.6 Hz, 1H), 1.33 (s, 9 H). *Due to the coupling of F-C and P-C, the ^{13}C NMR spectra show very complex peaks not easily interprepted.* Typical signals belong to the allenyl unit: δ = 209.1 (d, $J_{P\text{-}C}$ = 7.9 Hz), 111.9 (d, $J_{P\text{-}C}$ = 96.4 Hz), 97.7 (d, $J_{P\text{-}C}$ = 14.3 Hz)). Signals belong to the *t*-Bu group: δ = 37.5 (d, $J_{P\text{-}C}$ = 6.2 Hz), 30.7 (d, $J_{P\text{-}C}$ = 4.1 Hz). A full list of the ^{13}C NMR data: ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.18, 209.10, 166.14, 166.11, 165.90, 165.86, 163.63, 163.60, 163.39, 163.34, 133.96, 133.88, 133.86, 133.75, 133.67, 133.65, 133.56, 132.39, 132.32, 130.23, 130.20, 129.89, 129.85, 129.15, 129.11, 128.83, 128.79, 128.62, 128.60, 128.44, 127.63, 127.61, 127.00, 126.41, 126.39, 115.77, 115.63, 115.55, 115.42, 115.38, 115.25, 115.17, 115.04, 112.37, 111.41, 97.78, 97.63, 37.49, 37.43, 30.76, 30.72. ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 27.8. HRMS (ESI-TOF): *m/z* = 409.1511, calcd for $C_{25}H_{24}F_2OP$ [MH^+] 409.1533.

(4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl)bis(4-methoxyphenyl)phosphine oxide (3w). 73.3 mg (yield 83%), prepared from 47.0 mg of **1a** (0.25 mmol) and 53.9 mg of **2d** (0.21 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.66 (dd, J_1 = 11.6 Hz, J_2 = 8.8 Hz, 2H), 7.52 (dd, J_1 = 11.6 Hz, J_2 = 8.8 Hz, 2H), 7.24–7.14 (m, 3H), 7.00 (d, J = 7.6 Hz, 2H), 6.92 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 2H), 6.68 (dd, J_1 = 8.8 Hz, J_2 = 2.4 Hz, 2H), 5.99 (d, J = 11.6 Hz, 1H), 1.33 (s, 9 H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.0 (d, $J_{P\text{-}C}$ = 7.7 Hz), 162.1 (d, $J_{P\text{-}C}$ = 3.2 Hz), 161.8 (d, $J_{P\text{-}C}$ = 2.9 Hz), 133.3 (d, $J_{P\text{-}C}$ = 11.0 Hz), 133.1 (d, $J_{P\text{-}C}$ =11.2 Hz), 132.9 (d, $J_{P\text{-}C}$ = 7.0 Hz), 128.4, 127.1 (d, $J_{P\text{-}C}$ = 1.5 Hz), 126.4 (d, $J_{P\text{-}C}$ = 2.3 Hz), 125.3 (d, $J_{P\text{-}C}$ = 112.7 Hz), 124.7 (d, $J_{P\text{-}C}$ = 110.2 Hz), 113.6 (d, $J_{P\text{-}C}$ = 13.0 Hz), 113.3 (d, $J_{P\text{-}C}$ = 12.8 Hz), 112.3 (d, $J_{P\text{-}C}$ = 95.6 Hz), 97.1 (d, J = 13.5 Hz), 55.1 (d, J = 11.7 Hz), 37.2 (d, $J_{P\text{-}C}$ = 5.6 Hz), 30.7 (d, $J_{P\text{-}C}$ = 3.4 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.8. HRMS (ESI-TOF): *m/z* = 433.1960, calcd for $C_{27}H_{30}O_3P$ [MH^+] 433.1933.

(4,4-Dimethyl-1-phenylpenta-1,2-dien-3-yl)di-o-tolyl phosphine oxide (3x). 22.3 mg (yield 28%), prepared from 45.1 mg of **1a** (0.24 mmol) and 46.0 mg of **2e** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77 (d, J = 8.0 Hz, 2H), 7.62–7.57 (m, 1H), 7.42–7.05 (m, 10H), 5.31 (d, J = 11.2 Hz, 1H), 2.63 (s, 3H), 2.50 (s, 3H), 0.74 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 208.4 (d, $J_{P\text{-}C}$ = 6.7 Hz), 143.2 (d, $J_{P\text{-}C}$ = 8.5 Hz), 142.8 (d, $J_{P\text{-}C}$ = 8.0 Hz), 132.8 (d, $J_{P\text{-}C}$ = 6.2 Hz), 132.4 (d, $J_{P\text{-}C}$ = 3.4 Hz), 132.2 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.9 (d, $J_{P\text{-}C}$ = 10.2 Hz), 131.55 (d, $J_{P\text{-}C}$ = 101.5 Hz), 131.77 (d, $J_{P\text{-}C}$ = 11.5 Hz), 131.53 (d, $J_{P\text{-}C}$ = 2.9 Hz), 131.46 (d, $J_{P\text{-}C}$ = 101.7 Hz), 131.2 (d, $J_{P\text{-}C}$ = 3.2 Hz), 128.2, 127.1 (d, J = 1.4 Hz), 126.5 (d, $J_{P\text{-}C}$ = 12.1 Hz), 124.9 (d, $J_{P\text{-}C}$ = 13.6 Hz), 124.4 (d, $J_{P\text{-}C}$ = 13.0 Hz), 110.4 (d, $J_{P\text{-}C}$ = 92.7 Hz), 97.1 (d, $J_{P\text{-}C}$ = 14.2 Hz), 37.3 (d, $J_{P\text{-}C}$ = 5.1 Hz), 31.0 (d, $J_{P\text{-}C}$ = 2.7 Hz), 21.9 (d, $J_{P\text{-}C}$ = 4.6 Hz), 21.8 (d, $J_{P\text{-}C}$ = 4.6 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 36.7. HRMS (ESI-TOF): *m/z* = 401.2059, calcd for $C_{27}H_{30}OP$ [MH^+] 401.2034.

bis(3-Chlorophenyl)(4,4-dimethyl-1-phenylpenta-1,2-dien-3-yl)phosphine oxide (3y). 61.2 mg (yield 71%), prepared from 45.1 mg of **1a** (0.24 mmol) and 54.0 mg of **2f** (0.2 mmol) in 2 mL MeCN. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.77–7.73 (m, 1H), 7.64–7.56 (m, 2H), 7.51–7.37 (m, 3H), 7.29–7.13 (m, 5H), 7.03 (d, J = 8.0 Hz, 1H), 6.11 (d, J = 11.8 Hz, 1H), 1.34 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 209.3 (d, $J_{P\text{-}C}$ = 7.4 Hz), 135.7 (d, $J_{P\text{-}C}$ = 104.0 Hz), 135.3 (d, $J_{P\text{-}C}$ = 101.5 Hz), 134.8 (d, $J_{P\text{-}C}$ = 15.7 Hz), 134.5 (d, $J_{P\text{-}C}$ = 16.1 Hz), 132.0 (d, $J_{P\text{-}C}$ = 3.1 Hz), 131.9 (d, $J_{P\text{-}C}$ = 8.2 Hz), 131.6 (d, $J_{P\text{-}C}$ = 2.5 Hz), 131.3 (d, $J_{P\text{-}C}$ = 10.2 Hz), 131.1 (d, $J_{P\text{-}C}$ =10.6 Hz), 129.7 (d, $J_{P\text{-}C}$ = 13.1 Hz), 129.5 (d, $J_{P\text{-}C}$ = 8.4 Hz), 129.4 (d, $J_{P\text{-}C}$ = 13.9 Hz), 129.2 (d, $J_{P\text{-}C}$ = 8.8 Hz), 128.7, 127.7 (d, $J_{P\text{-}C}$ = 1.4 Hz), 126.4 (d, $J_{P\text{-}C}$ = 2.2 Hz), 111.2 (d, J = 96.5Hz), 98.2 (d, $J_{P\text{-}C}$ = 14.4 Hz), 37.5 (d, J = 6.3 Hz), 30.7 (d, $J_{P\text{-}C}$ = 4.0 Hz). ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 27.3. HRMS (ESI-TOF): *m/z* = 441.0935, calcd for $C_{25}H_{24}Cl_2OP$ [MH^+] 441.0942.

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[14] The reaction of diethyl phosphonate [$(EtO)_2P(O)H$)] or methyl phenylphosphinate [(MeO)PhP(O)H] with **1a** did not produce the expected allenylphosphoryl products.

[15] CCDC 1558550 contains the crystallographic data of compounds **3y**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[16] In comparision, the competition reaction of **1a**, **1i** and **2a** catalyzed by $Cu(OTf)_2$ afforded a mixture of **3a** and **3i** in a ratio of ca. 4/1 (ca. 3/1 by AgOTf), indicative of a significant steric effect of the substituent R^1 on the reaction.

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UPDATE

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