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Copper-Catalyzed Allenylation-Isomerization Sequence of Penta-1,4-diyn-3-yl Acetates with P(O)H Compounds: Facile Synthesis of 1-Phosphonyl 2,4-Diynes

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Abstract: The copper-catalyzed reaction of 5-substituted penta-1,4-diyn-3-yl acetates with P(O)H compounds to efficiently give a new class of phosphonyl diynes is reported. The reaction may take place through a regioselective nucleophilic attack of phosphorus nucleophiles on Cu-allenylidene intermediates to form allenyl intermediates followed by a rapid allene-alkyne isomerization process. The synthetic utility of the obtained products is demonstrated.

Keywords: allenes; copper catalysis; C–P bond formation; diynes; organophosphorus compounds

Introduction

The importance of organophosphorus compounds in organic synthesis, biology and material science has stimulated extensive studies on developing new and efficient C–P bond-forming reactions for introducing a phosphorus functionality into organic molecules.[1] To this end, the catalytic reactions of P(O)H compounds such as H-phosphonates, H-phosphinates and secondary phosphine oxides with functional groups of unsaturated C-C or C-heteroatom bonds represent a powerful tool.[2] Particularly, the transition metal (TM)-catalyzed reactions of P(O)H compounds with alkynes are extremely useful as this methodology could enable the formation of a wide range of valuable unsaturated phosphorus compounds (Figure 1).[3–5,8] For example, the TM-catalyzed additions of P(O)H compounds to the C≡C triple bonds, which have been studied for more than 20 years, could provide vinylphosphorus compounds with almost arbitrary regio- and stereoselectivity by choosing suitable catalysts and conditions (Figure 1a).[3] The C_{sp}–P couplings of P(O)H compounds with terminal or functionalized alkynes were extensively explored in recent years, and some extremely useful methods have been established for alkynylphosphorus compounds (Figure 1b).[4]

In comparison, the straightforward methods for the synthesis of phosphonyl 1,3-dienes and 1,2-dienes (allenes) *via* catalytic transformations of P(O)–H bonds remain underdeveloped (Figure 1c and d). Particularly, there is only one report in the literature describing the access of phosphonyl 1,3-dienes from a Ni-catalyzed reaction of propargyl alcohols with P(O)H compounds, whereby the regioselectivity is not satisfactory.[5] The high demand for these compounds in cyclizations and related reactions for constructing structural-

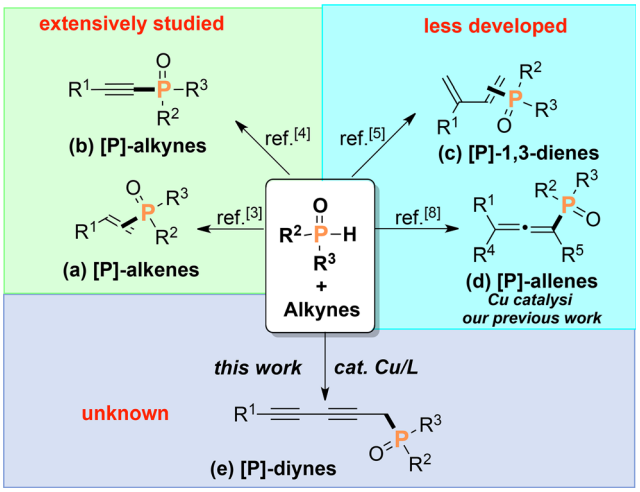


Figure 1. Transition metal-catalyzed reactions of alkynes with P(O)H compounds: a brief background.

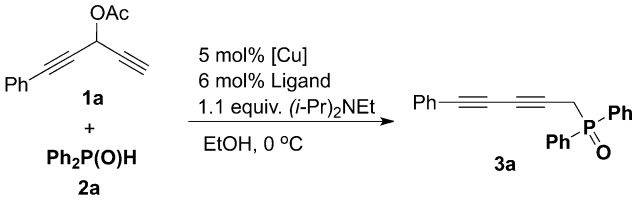
ly more sophisticated organophosphorus compounds consequently stimulates the development of alternative methods.[6,7] A few synthetic methods for phosphonyl 1,3-dienes have been recently reported based on the transformations of phosphonyl allenes.[6a–c]

As an interest in developing new C–P bond-forming reactions for efficient organophosphorus synthesis,[8] we recently reported a highly selective Cu-catalyzed propargylic substitution of propargyl acetates with P(O)H compounds to address the synthesis of allenylphosphorus compounds (Figure 1d).[8a,9] The new reaction is believed to proceed *via* a unique nucleophilic interception of *in situ* generated Cu-allenylidene intermediates by phosphorus nucleophiles. While most of the propargyl acetates studied were found to be selectively transformed to the corresponding allenyl derivatives in high yields under mild and green conditions, during the course of our further study on the reaction we came across a different outcome from the reaction of 5-substituted penta-1,4-diyn-3-yl acetates, which gave 1-phosphonyl 2,4-diynes as the products (Figure 1e). We reason that an interesting facile catalytic allenylation–isomerization sequence may happen in the reaction thus ultimately leading to the formation of these new products. Recognizing the versatile reactivity of the conjugated diyne unit[10] and the phosphorus functionality,[1a,b] we consider that these diyne derivatives would be useful building blocks to access valuable compounds with advanced molecular structures upon further synthetic manipulation. As a result, we report herein the results of this study, namely, the preparation and synthetic application of a new class of 1-phosphonyl 2,4-diyne derivatives from an efficient Cu-catalyzed allenylation and allene–alkyne isomerization reaction of 5-substituted penta-1,4-diyn-3-yl acetates with P(O)H compounds (Figure 1e). To the best of our knowledge, such a highly efficient transformation based on P(O)H compounds and alkynes has not been disclosed and there is no report on the synthesis of phosphoryl 1,3-diynyl compounds.

Results and Discussion

As shown in Table 1, when 5-phenylpenta-1,4-diyn-3-yl acetate (**1a**) and diphenylphosphine oxide (**2a**) were treated with a catalytic amount of CuI and TMEDA in the presence of 1.1 equiv. of $(i\text{-Pr})_2$NEt in EtOH at 0 °C for 2 h, the reaction gave the phosphonyl diyne **3a** in 81% yield highly selectively (entry 1). The reaction could also be promoted by the combination of other copper salts and and ligands. For example, the use of CuBr and CuCl with TMEDA gave **3a** in 81% and 80% yield, respectively. Divalent Cu salts $Cu(OAc)_2$ and $CuCl_2$ are also active to promote the reaction, albeit giving **3a** in slightly low yields. With

Table 1. Effect of the Cu-catalytic systems on reaction of **1a** and **2a**.[a]



Entry	[Cu]/Ligand	Time [h]	Yield [%][b]
1	CuI/TMEDA	2	81
2	CuBr/TMEDA	2	81
3	CuCl/TMEDA	2	80
4	$Cu(OAc)_2$/TMEDA	2	78
5	$CuCl_2 \cdot 2\,H_2O$/TMEDA	2	76
6	CuI/2,2'-bpy	4	80
7	CuI/1,10-Phen	4	76
8	CuI/DPPE	4	trace

[a] *Reaction conditions:* **1a** (0.24 mmol), **2a** (0.2 mmol), [Cu] (5 mol%), ligand (6 mol%) and $(i\text{-Pr})_2$NEt (0.22 mmol), EtOH (2 mL).
[b] Isolated yields.

regard to the ligand, 2,2′-bpy and 1,10-Phen were found to be active to catalyze the reaction with CuI and gave the product in comparable yields in 4 h.[10] Nevertheless, only a trace amount of **3a** was detected when a bisphosphine ligand DPPE was used. In addition, no reaction took place in the absence of a copper catalyst. Compound **3a** was characterized by ^{1}H, ^{13}C, ^{31}P NMR and HR-MS, and the proposed linear conjugated diyne structure was unambiguously confirmed by the X-ray diffraction analysis of a single crystal of the product (Figure 2).[11]

Table 2 summarizes the results of some typical diynylphosphorus compounds, prepared from 5-substituted penta-1,4-diyn-3-yl acetates with P(O)H compounds, by taking advantage of the present Cu-catalyzed method. Thus, in addition to **2a**, other diaryl-

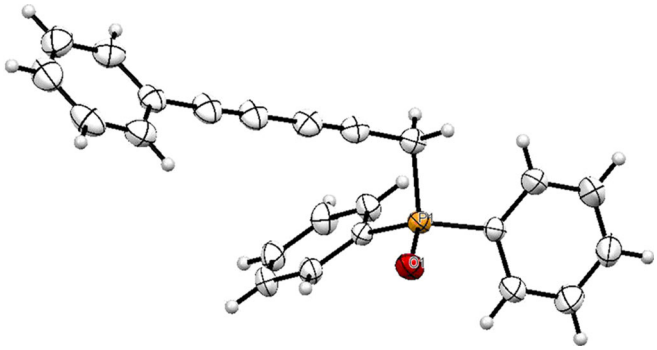
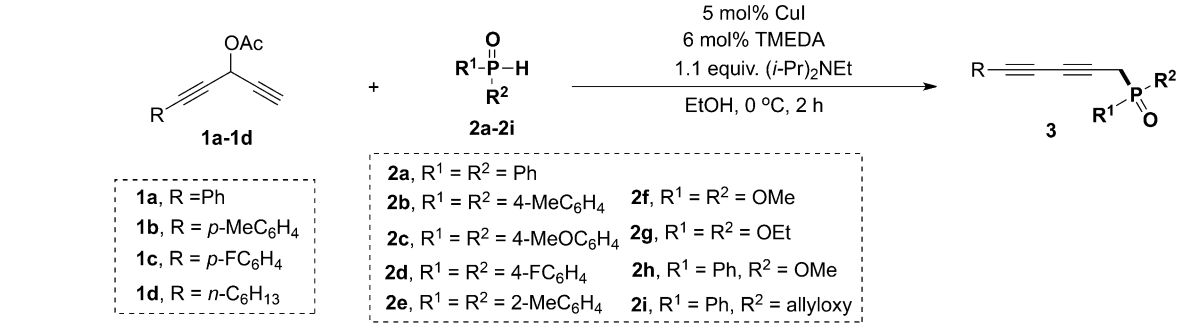
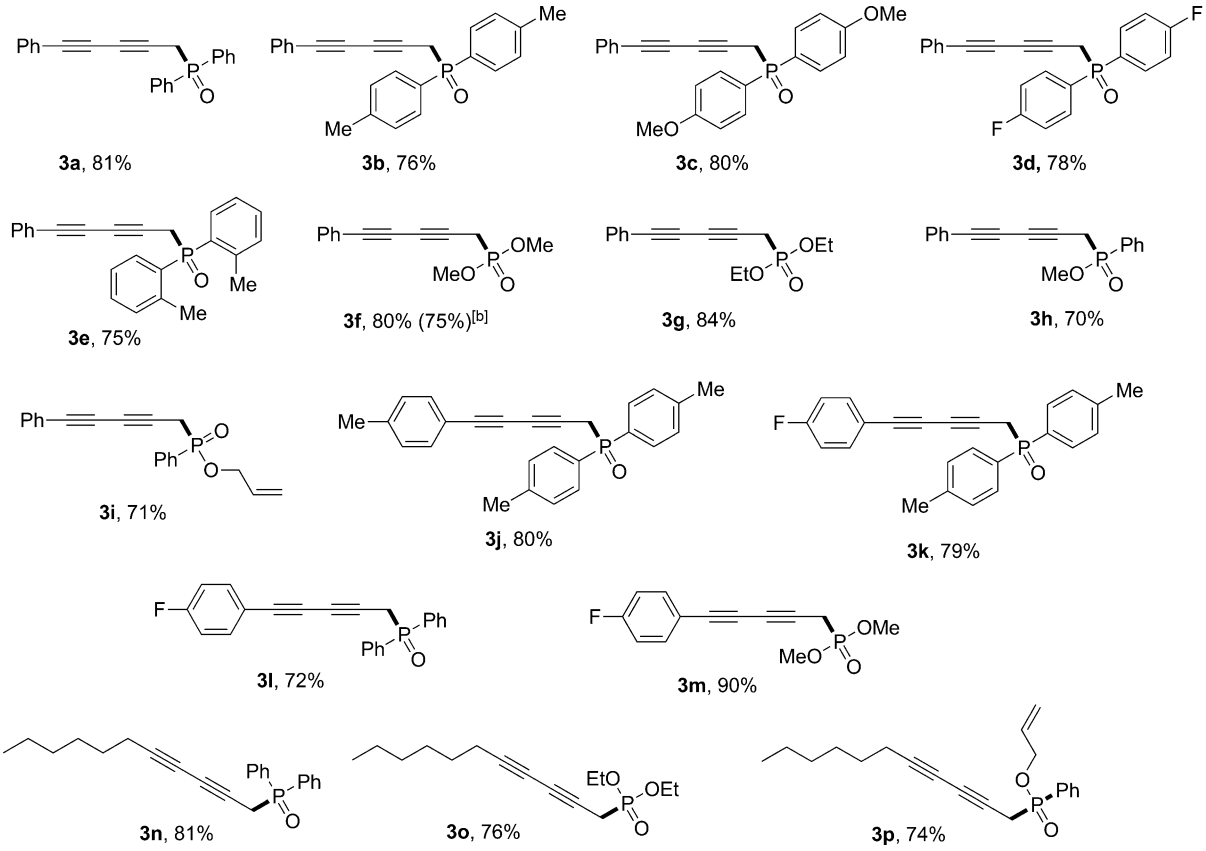


Figure 2. Molecular structure of compound **3a** (ellipsoids are drawn at 30% probability).

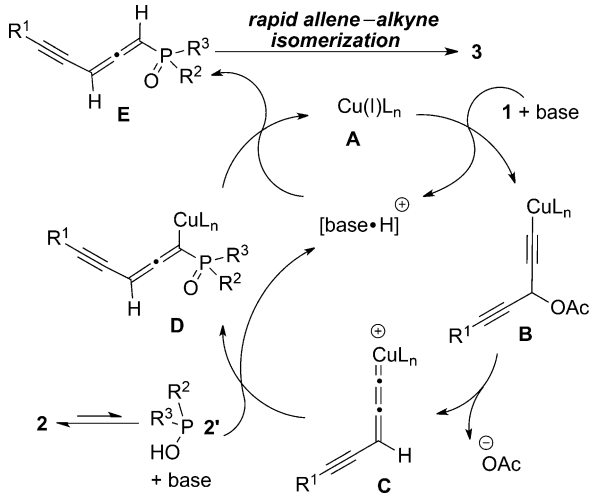
Table 2. Scope of the reaction.[a]



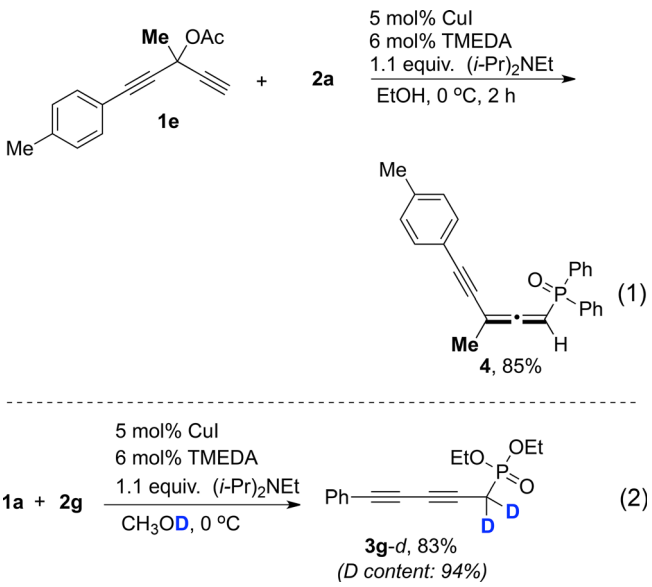


[a] *Reaction conditions:* **1** (0.24 mmol), **2** (0.2 mmol), CuI (5 mol%), TMEDA (6 mol%) and $(i\text{-Pr})_2$NEt (0.22 mmol), EtOH (2 mL). Isolated yields are given.
[b] 10 mmol scale.

phosphine oxides (**2b**–**2e**) bearing either electron-donating or electron-withdrawing substitutes on the phenyl rings are applicable to produce the desired products in good yields. Particularly, the reaction of the more sterically hindered substrate **2e** which bears two *o*-tolyl substituents also took place smoothly to give the product **3e** in 75% yields. Furthermore, H-phosphonates and H-phosphinates also readily reacted with **1a** to give the desired products in good to high yields (**3f**–**3i**). For example, the reaction of dimethyl phosphonate (**2f**) with **1a** gave dimethyl (5-phenylpenta-2,4-diyn-1-yl) phosphonate (**3g**) in 80% yield. Notably, the reaction is also easily scaled up to a gram-scale, to give 1.85 g of the desired product **3f** in 75% isolated yield. The reaction of H-phosphinate **2i** enables the successful synthesis of the phosphorus-tethered 1,7,9-ene-diyne products **3i** and **3p** in 71% and 74% yields, respectively. With regard to **1**, the substrates with the electron-donating (**1b**, R = *p*-MeC_6H_4) and electron-withdrawing phenyl substituents (**1c**, R = *p*-FC_6H_4) at the 5-position were examined, which gave the products **3j**–**3m** in good to high yields. Furthermore, the alkyl substituted substrate **1d** (R = *n*-C_6H_{13}) was also applicable, producing the de-



Scheme 1. A plausible mechanism.



sired products **3n**–**3p** in good yields without any loss of efficiency.

A plausible mechanism for the reaction is proposed in Scheme 1, based on literature precedents[12] and a report of our previous work.[8a] In the presence of a base, the active Cu(I) species **A** generated from the reaction of the copper salt with TMEDA first reacts with **1** to produce the Cu-acetylide complex **B**. Loss of an acetyl group from **B** would form a copper allenylidene complex **C**.[12d] The reaction of **2** with **C** *via* a regioselective nucleophilic attack then produces the yne-allenyl Cu-intermediate **D**, protodemetallation of which gives the yne-allenyl intermediate **E** and regenerate the copper catalyst. The unstable **E** finally undergoes an allene–alkyne isomerization to give the product **3**.

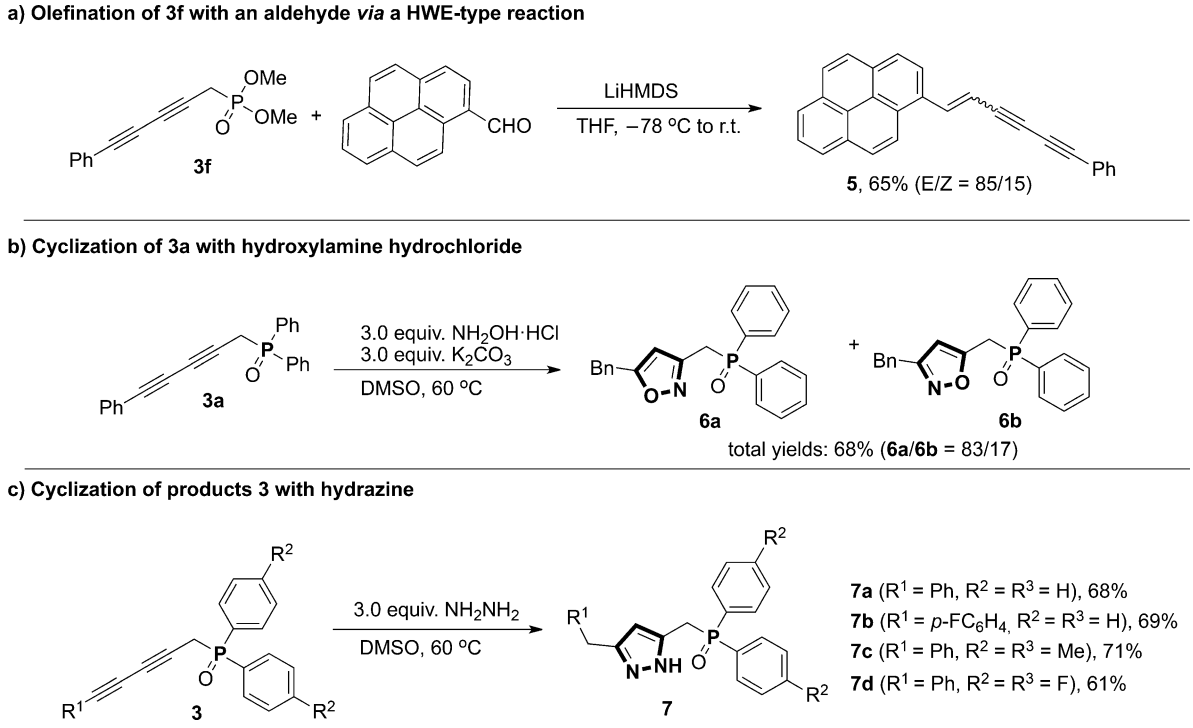
It is impossible to trap the intermediate **E** by shortening the reaction time due to the rapid rate of the isomerization process.[13] Nevertheless, the reaction of 3-methyl-5-(*p*-tolyl)penta-1,4-diyn-3-yl acetate (**1e**) with **2a** produced yne-allenyl product **4** in 85% yield [Eq. (1)], confirming the proposed route involving the formation of intermediate **E**.[8a] In addition, the participation of the solvent proton during the isomerization process is evident as the reaction of **1a** and **2g** performed in CH_3OD gave the deuterated product **3g**-*d* (α-D *ca.* 94%) in 83% yield [Eq. (2)].

It should be noted that the resulting 1-phosphonyl 2,4-diynes are highly useful in organic synthesis due to the vesertile reactivity of the conjugated diyne unit and the phosphorus functionality. For example, the products could serve as valuable precusors for introducing an ene-diyne unit into an organic molecule *via* Horner–Wadsworth–Emmons (HWE) type reactions. As shown in Scheme 2a, treatment of **3f** with 1.1 equiv. of LiHMDS at −78 °C followed by the addition of 1-pyrenecarbaldehyde successfully gave the olefinic product **5** in 65% yield. In light of the wide occurrence of the ene-diyne unit in bioactive molecules and functional materials, such a transformation would find utility in related areas.[14]

On the other hand, the conjugated diynes are valuable building blocks for heterocyclic synthesis.[10] Accordingly, the synthetic value of the obtained products is further highlighted as promising precursors to access heterocycle-containing organophosphorus compounds. As shown in Scheme 2b, the cyclization of **3a** with hydroxylamine afforded the isoxazole-tethered phosphine oxides **6a** and **6b** in 68% yield with a selectivity of 83/17.[15] Upon treatment of the 1-phosphonyl 2,4-diyne products with hydrazine, pyrazole-tethered phosphine oxides **7a**–**7d** were successfully obtained in good yields with excellent regioselectivity (Scheme 2c). Products **6** and **7** are characterized by ^{1}H, ^{13}C, ^{31}P NMR and HR-MS, and the structures are further confirmed by the single crystal X-ray diffraction analyses of the representative compounds **6a** and **7a** (Figure 3).[16] It is worth noting that further reduction of the P=O functionality of these products should enable an access to N,P-bidentate ligands.

Conclusions

In conclusion, we have disclosed a highly efficient copper-catalyzed reaction of 5-substituted penta-1,4-diyn-3-yl acetates with P(O)H compounds to afford a facile synthesis of a new class of phosphonyl 1,3-diynes. The reaction takes place efficiently under mild conditions, and the products are useful to access advanced molecular structures with further elaboration. We believe that this reaction will attract attention from many research disciplines due to the broad utility of the 1,3-diynes and the organophosphorus compounds.



Scheme 2. Synthetic transformation of the products.

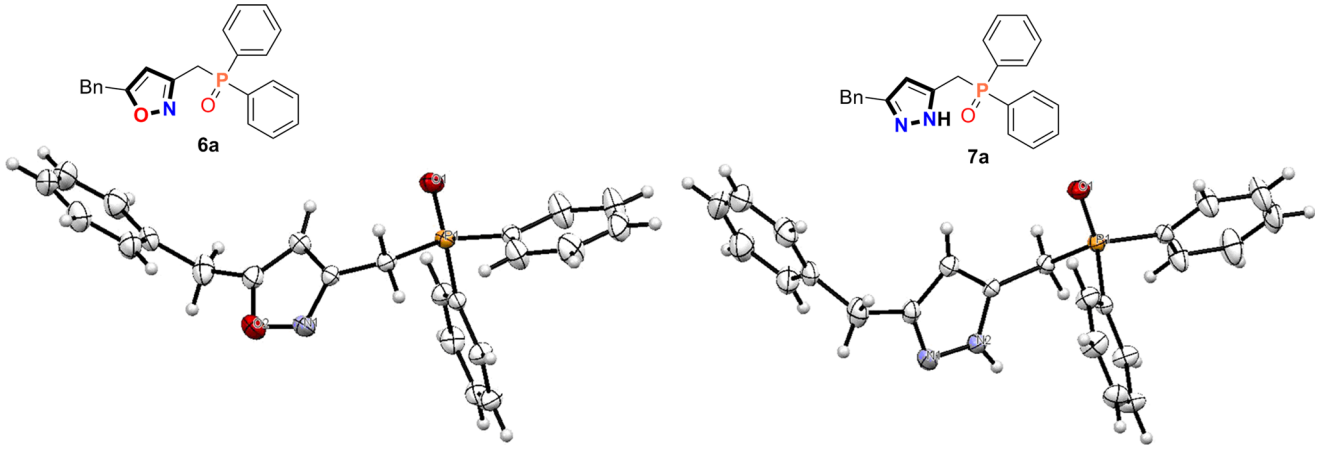


Figure 3. Molecular structures of compounds **6a** and **7a** (ellipsoids are drawn at 30% probability).

Experimental Section

General Information

Unless otherwise specified, all reactions were performed under a dry N_2 atmosphere. The substrates **2a**, **2f** and **2g** are commercially available and were used as received. Other P(O)H compounds were all known and prepared following known methods.[17] Copper salts, TMEDA, 2,2′-bpy, 1,10-Phen, dppe and $(i\text{-Pr})_2$NEt are all commercially available and used as received. Absolute alcohol was used after degassing. 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 Bruker Advance 400 spectrometer. Chemical shifts were recorded with tetramethylsilane (TMS) as the internal reference standard. Chemical shifts are expressed in ppm and *J* values are given in Hz. HR-MS were obtained from the Analytical Center of the Department of Chemistry of Zhejiang University, P.R. China.

Synthetic Procedure for the Propargyl Acetate 1a

n-Butyllithium (4 mL, 2.5 M in hexane) was added to a solution of ethynylbenzene (1.122 g, 11 mmol) in THF (30 mL)

at −78 °C under an N_2 atmophere. The reaction mixture was allowed to stir at this temperature for 30 min. 3-(Trimethylsilyl)propiolaldehyde (1.262 g, 10 mmol) was then slowly added and the reaction mixture was stirred at −78 °C for 30 min, naturally warmed to room temperature and kept stirring overnight. After being quenched by saturated NH_4Cl solution, extracted with Et_2O and concentrated to dryness, the residue was dissolved in THF and cooled to 0 °C. A solution of tetrabutylammonium fluoride (*ca.* 10 mmol, 85% purity containing water) in THF was added dropwise. After stirred at 0 °C for 2 h, the reaction mixture was quenched with water and extracted with ether. The organic layers were dried with $MgSO_4$, and concentrated under vacuum. Pure 1-phenylpenta-1,4-diyn-3-ol was obtained after column chromategraphy on silica gel (PE/EtOAc 8:1 v/v); yield: 1.250 g (80%).

To a solution containing the above prepared alcohol (5 mmol, 780.0 mg), acetic acid (6 mmol, 360.0 mg) and *N*, *N*-dimethylpyridin-4-amine (DMAP, 0.5 mmol, 61.0 mg) in CH_2Cl_2 (10 mL) was added a solution of dicyclohexylmethanediimine (DCC, 6 mmol, 1.236 g) in CH_2Cl_2 at 0 °C. After the addition was complete, the reaction was stirred at 0 °C for 2 h. The reaction mixture was filtered and concentrated. The residue was purified by column chromatography on silica gel (PE/EtOAc 20:1 v/v) to afford 1-phenylpenta-1,4-diyn-3-yl acetate **1a** as a liquid; yield: 851.4 mg (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.50–7.47 (m, 2H), 7.36–7.31 (m, 3H), 6.28 (d, J = 2.4 Hz, 1H), 2.62 (d, J = 2.4 Hz, 1H), 2.17 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.1, 132.1, 129.2, 128.3, 121.4, 85.4, 82.1, 77.5, 73.7, 53.3, 20.8; HR-MS (EI-TOF): m/z = 198.0683, calcd. for $C_{13}H_{10}O_2$ [M^+]: 198.0681.

Compounds **1b**–**1d** were prepared following a similar procedure described as above. **1a**–**1d** are stable at least for 8 months at 0 °C stored in a refrigerator.

1-(*p*-Tolyl)penta-1,4-diyn-3-yl acetate (1b): Yield: 922.1 mg (87%); liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.37 (d, J = 8.4 Hz, 2H), 7.13 (d, J = 8.4 Hz, 2H), 6.27 (d, J = 2.4 Hz, 1H), 2.61 (d, J = 2.0 Hz, 1H), 2.35 (s, 3H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.1, 139.4, 131.9, 129.0, 118.3, 85.6, 81.5, 77.7, 73.5, 53.4, 21.5, 20.8; HR-MS (EI-TOF): m/z = 212.0837, calcd. for $C_{14}H_{12}O_2$ [M^+]: 212.0837.

1-(4-Fluorophenyl)penta-1,4-diyn-3-yl acetate (1c): Yield: 874.8 mg (81%); liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.48–7.45 (m, 2H), 7.04–6.99 (m, 2H), 6.25 (d, J = 2.4 Hz, 1H), 2.61 (d, J = 2.0 Hz, 1H), 2.16 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.0, 163.0 (d, J = 249.3 Hz), 134.1 (d, J = 8.4 Hz), 117.4 (d, J = 3.4 Hz), 115.6 (d, J = 22.2 Hz), 84.3, 82.0, 77.4, 73.7, 53.2, 20.7; HR-MS (EI-TOF): m/z = 216.0588, calcd for $C_{13}H_9O_2F$ [M^+]: 216.0587.

Undeca-1,4-diyn-3-yl acetate (1d): Yield: 855.0 mg (83%); liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 6.01 (dd, J_1 = 4.0 Hz, J_2 = 2.0 Hz, 1H), 2.53 (d, J = 2.0 Hz, 1H), 2.22 (td, J_1 = 7.6 Hz, J_2 = 2.0 Hz, 2H), 2.12 (s, 3H), 1.55–1.27 (m, 8H), 0.88 (t, J = 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 169.2, 87.1, 78.2, 73.6, 73.0, 53.3, 31.3, 28.5, 28.1, 22.5, 20.8, 18.7, 14.0; HRMS (EI-TOF): m/z = 206.1304, calcd. for $C_{13}H_{18}O_2$ [M^+]: 206.1307.

General Procedure for the Cu-Catalyzed Preparation of Phosphoryl 1,3-Diynes

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with CuI (1.9 mg, 5 mol%). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 1.0 mL of ethanol was injected, followed by the injection of TMEDA (2 μL) and (i-Pr)$_2$NEt (38 μL) under stirring. The mixture was stirred for 10 min and cooled to 0 °C. Then **1** (0.24 mmol) and **2** (0.2 mmol) dissolved in 1.0 mL of ethanol were injected. The reaction was kept stirring at the same temperature and monitored by TLC. After the reaction was complete, removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (PE/EtOAc 3:1 to 1:1 v/v) to afford the product **3**.

Diphenyl(5-phenylpenta-2,4-diyn-1-yl)phosphine oxide (3a): Yield: 55.1 mg (81%); white solid; mp 152–153 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.87–7.81 (m, 4H), 7.60–7.49 (m, 6H), 7.44–7.42 (m, 2H), 7.33–7.26 (m, 3H), 3.44 (d, J = 16.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 132.5, 132.4 (d, $J_{P,C}$ = 2.1 Hz), 131.1 (d, $J_{P,C}$ = 102.3 Hz), 131.2 (d, $J_{P,C}$ = 9.4 Hz), 129.1, 128.6 (d, $J_{P,C}$ = 12.3 Hz), 128.3, 121.3 (d, $J_{P,C}$ = 1.3 Hz), 76.3 (d, $J_{P,C}$ = 3.6 Hz), 74.2 (d, $J_{P,C}$ = 11.6 Hz), 73.7 (d, $J_{P,C}$ = 5.5 Hz), 69.4 (d, $J_{P,C}$ = 9.2 Hz), 23.8 (d, $J_{P,C}$ = 67.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 28.1; HR-MS (EI-TOF): m/z = 340.1022, calcd. for $C_{23}H_{17}OP$ [M^+]: 340.1017.

(5-Phenylpenta-2,4-diyn-1-yl)di-*p*-tolylphosphine oxide (3b): Yield: 56.0 mg (76%); white solid; mp 147–148 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.70–7.65 (m, 4H), 7.42–7.39 (m, 2H), 7.33–7.24 (m, 7H), 3.36 (d, J = 17.2 Hz, 2H), 2.39 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 143.0 (d, $J_{P,C}$ = 2.5 Hz), 132.4, 132.3 (d, $J_{P,C}$ = 9.5 Hz), 129.3 (d, $J_{P,C}$ = 12.0 Hz), 129.1, 128.2, 127.3 (d, $J_{P,C}$ = 104.9 Hz), 121.3 (d, $J_{P,C}$ = 1.4 Hz), 76.2 (d, $J_{P,C}$ = 3.4 Hz), 74.5 (d, $J_{P,C}$ = 11.3 Hz), 73.8 (d, $J_{P,C}$ = 6.7 Hz), 69.1 (d, $J_{P,C}$ = 8.5 Hz), 23.5 (d, $J_{P,C}$ = 67.8 Hz), 21.6; ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 29.8; HR-MS (EI-TOF): m/z = 368.1336, calcd. for $C_{25}H_{21}OP$ [M^+]: 368.1330.

Bis(4-methoxyphenyl)(5-phenylpenta-2,4-diyn-1-yl) phosphine oxide (3c): Yield: 64.1 mg (80%); white solid; mp 160–161 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.78–7.73 (m, 4H), 7.46–7.44 (m, 2H), 7.37–7.28 (m, 3H), 7.03–7.00 (m, 4H), 3.87 (s, 6H), 3.38 (d, J = 16.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 162.7 (d, $J_{P,C}$ = 2.3 Hz), 133.2 (d, $J_{P,C}$ = 11.0 Hz), 132.5, 129.1, 128.3, 122.3 (d, $J_{P,C}$ = 109.3 Hz), 121.4, 114.2 (d, $J_{P,C}$ = 13.2 Hz), 76.2 (d, $J_{P,C}$ = 2.6 Hz), 74.8 (d, $J_{P,C}$ = 10.7 Hz), 73.8 (d, $J_{P,C}$ = 6.8 Hz), 69.1 (d, $J_{P,C}$ = 9.3 Hz), 55.3, 24.1 (d, $J_{P,C}$ = 67.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ = 28.7; HR-MS (EI-TOF): m/z = 400.1222, calcd. for $C_{25}H_{21}O_3P$ [M^+]: 400.1228.

Bis(4-fluorophenyl)(5-phenylpenta-2,4-diyn-1-yl) phosphine oxide (3d): Yield: 58.6 mg (78%); white solid; mp 146–147 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 7.88–7.82 (m, 4H), 7.46–7.44 (m, 2H), 7.36–7.21 (m, 7H), 3.44 (d, J = 17.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 165.4 (dd, $J_{F,C}$ = 252.7 Hz, $J_{P,C}$ = 2.9 Hz), 133.8 (dd, $J_{F,C}$ = 11.2 Hz, $J_{P,C}$ = 8.9 Hz), 132.6, 129.3, 128.4, 126.9 (dd, $J_{P,C}$ = 105.9 Hz, $J_{F,C}$ = 3.6 Hz), 121.1, 116.2 (dd, $J_{F,C}$ = 21.2 Hz, $J_{P,C}$ = 13.2 Hz), 76.7 (d, $J_{P,C}$ = 3.9 Hz), 73.7 (d, $J_{P,C}$ = 11.7 Hz), 73.4 (d, $J_{P,C}$ = 7.1 Hz), 69.8 (d, $J_{P,C}$ = 8.3 Hz), 24.1 (d, $J_{P,C}$ = 68.4 Hz);

^{31}P NMR ($CDCl_3$, 162 MHz): δ=26.9 (br); HR-MS (EI-TOF): m/z=376.0834, calcd. for $C_{23}H_{15}OPF_2$ [M^+]: 376.0829.

(5-Phenylpenta-2,4-diyn-1-yl)di-*o*-tolylphosphine oxide (3e): Yield: 55.2 mg (75%); white solid; mp 138–139 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.69–7.63 (m, 2H), 7.49–7.41 (m, 4H), 7.33–7.26 (m, 7H), 3.55 (d, J=16.0 Hz, 2H), 2.46 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=142.3 (d, $J_{P,C}$=8.3 Hz), 132.5, 132.4 (d, $J_{P,C}$=2.4 Hz), 132.1 (d, $J_{P,C}$=10.9 Hz), 131.8 (d, $J_{P,C}$=11.2 Hz), 129.6 (d, $J_{P,C}$=100.2 Hz), 129.1, 128.3, 125.7 (d, $J_{P,C}$=12.1 Hz), 121.5 (d, $J_{P,C}$=1.2 Hz), 76.4 (d, $J_{P,C}$=3.2 Hz), 74.2 (d, $J_{P,C}$=12.2 Hz), 73.8 (d, $J_{P,C}$=5.6 Hz), 69.7 (d, $J_{P,C}$=8.7 Hz), 23.5 (d, $J_{P,C}$=67.4 Hz), 21.3 (d, $J_{P,C}$=3.8 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=34.2; HR-MS (EI-TOF): m/z=368.1331, calcd. for $C_{25}H_{21}OP$ [M^+]: 368.1330.

Dimethyl (5-phenylpenta-2,4-diyn-1-yl)phosphonate (3f): Yield: 39.7 mg (80%); yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.40 (m, 2H), 7.31–7.21 (m, 3H), 3.80 (d, J=10.4 Hz, 6H), 2.90 (d, J=22.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=132.5 (d, $J_{P,C}$=1.3 Hz), 129.2, 128.3, 121.3 (d, $J_{P,C}$=1.4 Hz), 76.0 (d, $J_{P,C}$=3.8 Hz), 73.7 (d, $J_{P,C}$=7.6 Hz), 72.9 (d, $J_{P,C}$=15.8 Hz), 67.6 (d, $J_{P,C}$=10.4 Hz), 53.6 (d, $J_{P,C}$=6.8 Hz), 18.0 (d, $J_{P,C}$=144.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=22.6; HR-MS (EI-TOF): m/z=248.0604, calcd. for $C_{13}H_{13}O_3P$ [M^+]: 248.0602.

Diethyl (5-phenylpenta-2,4-diyn-1-yl)phosphonate (3g): Yield: 46.4 mg (84%); yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.42–7.40 (m, 2H), 7.30–7.21 (m, 3H), 4.19–4.11 (m, 4H), 2.87 (d, J=22.4 Hz, 2H), 1.31 (d, J=7.2 Hz, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=132.5 (d, $J_{P,C}$=1.4 Hz), 129.1, 128.3, 121.4 (d, $J_{P,C}$=1.5 Hz), 75.8 (d, $J_{P,C}$=3.2 Hz), 73.8 (d, $J_{P,C}$=7.2 Hz), 73.4 (d, $J_{P,C}$=14.7 Hz), 67.4 (d, $J_{P,C}$=10.7 Hz), 63.1 (d, $J_{P,C}$=6.4 Hz), 19.0 (d, $J_{P,C}$=143.3 Hz), 16.4 (d, $J_{P,C}$=5.9 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=20.0; HR-MS (EI-TOF): m/z=276.0917, calcd. for $C_{15}H_{17}O_3P$ [M^+]: 276.0915.

Methyl phenyl(5-phenylpenta-2,4-diyn-1-yl) phosphinate (3h): Yield: 41.1 mg (70%); yellow slurry solid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.93–7.87 (m, 2H), 7.63–7.61 (m, 1H), 7.57–7.52 (m, 2H), 7.49–7.46 (m, 2H), 7.36–7.29 (m, 3H), 3.80 (d, J=11.2 Hz, 3H), 3.22–3.02 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=133.1 (d, $J_{P,C}$=2.4 Hz), 132.5 132.0 (d, $J_{P,C}$=9.4 Hz), 129.1, 128.7 (d, $J_{P,C}$=13.2 Hz), 128.3, 128.2 (d, $J_{P,C}$=130.2 Hz), 121.4 (d, $J_{P,C}$=1.5 Hz), 76.0 (d, $J_{P,C}$=3.7 Hz), 73.7 (d, $J_{P,C}$=7.6 Hz), 73.6 (d, $J_{P,C}$=12.9 Hz), 68.1 (d, $J_{P,C}$=8.7 Hz), 52.1 (d, $J_{P,C}$=6.5 Hz), 22.7 (d, $J_{P,C}$=98.0 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=36.8; HR-MS (EI-TOF): m/z=294.0812, calcd. for $C_{18}H_{15}O_2P$ [M^+]: 294.0810.

Allyl phenyl(5-phenylpenta-2,4-diyn-1-yl)phosphinate (3i): Yield: 45.4 mg (71%); yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.93–7.88 (m, 2H), 7.64–7.60 (m, 1H), 7.57–7.51 (m, 2H), 7.48–7.46 (m, 2H), 7.37–7.27 (m, 3H), 6.03–5.93 (m, 1H), 5.41 (dd, J_1=16.8 Hz, J_2=1.2 Hz, 1H), 5.41 (dd, J_1=10.4 Hz, J_2=0.8 Hz, 1H), 4.70–4.64 (m, 1H), 4.54–4.47 (m, 1H), 3.22–3.04 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=133.0 (d, $J_{P,C}$=2.2 Hz), 132.5, 132.4 (d, $J_{P,C}$=7.4 Hz), 131.9 (d, $J_{P,C}$=9.8 Hz), 129.1, 128.7 (d, $J_{P,C}$=132.8 Hz), 128.6 (d, $J_{P,C}$=13.2 Hz), 128.3, 121.4 (d, $J_{P,C}$=1.4 Hz), 118.4, 75.9 (d, $J_{P,C}$=3.6 Hz), 73.8 (d, $J_{P,C}$=5.2 Hz), 73.7 (d, $J_{P,C}$=12.2 Hz), 68.2 (d, $J_{P,C}$=9.2 Hz), 65.9 (d, $J_{P,C}$=5.3 Hz), 23.2 (d, $J_{P,C}$=96.4 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=35.7; HR-MS (EI-TOF): m/z=320.0964, calcd. for $C_{20}H_{17}O_2P$ [M^+]: 320.0966.

Di-*p*-tolyl(5-(*p*-tolyl)penta-2,4-diyn-1-yl)phosphine oxide (3j): Yield: 61.0 mg (80%); white solid; mp 144–145 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.74–7.69 (m, 4H), 7.34–7.29 (m, 6H), 7.09 (d, J=8.0 Hz, 2H), 3.39 (d, J=16.8 Hz, 2H), 2.41 (s, 6H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=142.8 (d, $J_{P,C}$=3.2 Hz), 139.5, 132.4, 131.3 (d, $J_{P,C}$=10.4 Hz), 129.3 (d, $J_{P,C}$=12.6 Hz), 129.1, 128.0 (d, $J_{P,C}$=104.6 Hz), 118.3 (d, $J_{P,C}$=1.4 Hz), 76.5 (d, $J_{P,C}$=3.7 Hz), 74.2 (d, $J_{P,C}$=11.1 Hz), 73.3 (d, $J_{P,C}$=6.5 Hz), 69.3 (d, $J_{P,C}$=8.9 Hz), 24.0 (d, $J_{P,C}$=67.3 Hz), 21.6, 21.5; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=28.5; HR-MS (EI-TOF): m/z=382.1494, calcd. for $C_{26}H_{23}OP$ [M^+]: 382.1487.

[5-(4-Fluorophenyl)penta-2,4-diyn-1-yl]di-*p*-tolyl phosphine oxide (3k): Yield: 61.0 mg (79%); white solid; mp 149–150 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.73–7.68 (m, 4H), 7.43–7.40 (m, 2H), 7.33–7.30 (m, 4H), 7.00–6.96 (m, 2H), 3.39 (d, J=16.4 Hz, 2H), 2.41 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=162.8 (d, $J_{F,C}$=250.3 Hz), 142.9 (d, $J_{P,C}$=3.2 Hz), 134.5 (d, $J_{F,C}$=7.3 Hz), 131.2 (d, $J_{P,C}$=9.9 Hz), 129.3 (d, $J_{P,C}$=12.2 Hz), 127.9 (d, $J_{P,C}$=105.3 Hz), 117.5 (d, $J_{F,C}$=1.1 Hz), 115.7 (d, $J_{F,C}$=22.4 Hz), 75.0 (d, $J_{P,C}$=2.7 Hz), 74.6 (d, $J_{P,C}$=11.9 Hz), 73.6 (d, $J_{P,C}$=6.5 Hz), 68.9 (d, $J_{P,C}$=8.5 Hz), 23.9 (d, $J_{P,C}$=66.5 Hz), 21.5; ^{31}P NMR ($CDCl_3$, 162 MHz): δ=28.5; HR-MS (EI-TOF): m/z=386.1242, calcd. for $C_{25}H_{20}OPF$ [M^+]: 386.1236.

[5-(4-Fluorophenyl)penta-2,4-diyn-1-yl]diphenyl phosphine oxide (3l): Yield: 51.6 mg (72%); white solid; mp 155–156 °C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.86–7.81 (m, 4H), 7.60–7.50 (m, 6H), 7.45–7.41 (m, 2H), 7.01–6.97 (m, 2H), 3.44 (d, J=16.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.0 (d, $J_{F,C}$=250.1 Hz), 134.6 (d, $J_{F,C}$=8.7 Hz), 132.5 (d, $J_{P,C}$=2.0 Hz), 131.3 (d, $J_{P,C}$=9.6 Hz), 131.2 (d, $J_{P,C}$=102.7 Hz), 128.7 (d, $J_{P,C}$=12.0 Hz), 117.5 (d, $J_{F,C}$=3.7 Hz), 115.8 (d, $J_{F,C}$=22.3 Hz), 75.3 (d, $J_{P,C}$=3.7 Hz), 74.3 (d, $J_{P,C}$=11.2 Hz), 73.6 (d, $J_{P,C}$=8.1 Hz), 69.2 (d, $J_{P,C}$=8.1 Hz), 23.9 (d, $J_{P,C}$=67.2 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=28.0; HR-MS (ESI-TOF): m/z=359.1018, calcd. for $C_{23}H_{17}OPF$ [MH^+]: 359.1001.

Dimethyl [5-(4-fluorophenyl)penta-2,4-diyn-1-yl]phosphonate (3m): Yield: 47.9 mg (90%); yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.47–7.43 (m, 2H), 7.02–6.97 (m, 2H), 3.85 (d, J=11.2 Hz, 6H), 2.95 (d, J=22.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=163.0 (d, $J_{F,C}$=250.1 Hz), 134.6 (dd, $J_{F,C}$=8.8 Hz, $J_{P,C}$=1.4 Hz), 117.6 (dd, $J_{F,C}$=3.4 Hz, $J_{P,C}$=1.4 Hz),115.8 (d, $J_{F,C}$=22.5 Hz), 75.0 (d, $J_{P,C}$=3.6 Hz), 73.5 (d, $J_{P,C}$=7.2 Hz, $J_{F,C}$=1.5 Hz), 73.0 (d, $J_{P,C}$=16.2 Hz), 67.5 (d, $J_{P,C}$=9.9 Hz), 53.6 (d, $J_{P,C}$=6.8 Hz), 18.1 (d, $J_{P,C}$=144.1 Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): δ=22.5. HR-MS (EI-TOF): m/z=266.0505, calcd. for $C_{13}H_{12}O_3PF$ [M^+]: 266.0508.

Diphenyl(undeca-2,4-diyn-1-yl)phosphine oxide (3n): Yield: 56.3 mg (81%); yellow liquid; ^{1}H NMR ($CDCl_3$, 400 MHz): δ=7.83–7.78 (m, 4H), 7.58–7.54 (m, 2H), 7.51–7.47 (m, 4H), 3.35 (d, J=17.2 Hz, 2H), 2.21–2.18 (m, 2H), 1.50–1.42 (m, 2H), 1.36–1.21 (m, 6H), 0.86 (t, J=6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=132.4 (d, $J_{P,C}$=3.0 Hz), 131.3 (d, $J_{P,C}$=9.5 Hz), 130.9 (d, $J_{P,C}$=101.6 Hz), 128.6 (d, $J_{P,C}$=12.0 Hz), 79.5 (d, $J_{P,C}$=3.3 Hz), 69.9 (d, $J_{P,C}$=9.1 Hz), 66.8 (d, $J_{P,C}$=11.4 Hz), 64.7 (d, $J_{P,C}$=5.6 Hz), 31.2, 28.4, 28.0, 23.3 (d, $J_{P,C}$=68.8 Hz), 22.4, 19.1, 13.9; ^{31}P NMR

($CDCl_3$, 162 MHz): $\delta = 29.2$; HR-MS (EI-TOF): $m/z =$ 348.1643, calcd. for $C_{23}H_{25}OP$ [M^+]: 348.1643.

Diethyl undeca-2,4-diyn-1-ylphosphonate (3o): Yield: 43.2 mg (76%); yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 4.21–4.14$ (m, 4H), 2.81 (d, $J = 22.4$ Hz, 2H), 2.45–2.40 (m, 2H), 1.53–1.46 (m, 2H), 1.36–1.24 (m, 12H), 0.86 (t, $J =$ 6.8 Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 78.9$ (d, $J_{P,C} =$ 3.5 Hz), 67.8 (d, $J_{P,C} = 9.7$ Hz), 66.1 (d, $J_{P,C} = 15.3$ Hz), 64.8 (d, $J_{P,C} = 7.3$ Hz), 63.0 (d, $J_{P,C} = 6.7$ Hz), 31.2, 28.4, 28.0, 22.4, 19.1, 18.6 (d, $J_{P,C} = 144.5$ Hz), 16.3 (d, $J_{P,C} = 5.7$ Hz), 13.9; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 20.5$; HR-MS (EI-TOF): $m/z = 284.1545$, calcd. for $C_{15}H_{25}O_3P$ [M^+]: 284.1541.

Allyl phenyl(undeca-2,4-diyn-1-yl)phosphinate (3p): Yield: 48.5 mg (74%); yellow liquid; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.90–7.85$ (m, 2H), 7.62–7.58 (m, 1H), 7.54–7.49 (m, 2H), 6.01–5.92 (m, 1H), 5.39 (dd, $J_1 = 17.2$ Hz, $J_2 =$ 1.2 Hz, 1H), 5.26 (d, $J = 10.4$ Hz, 1H), 4.67–4.61 (m, 1H), 4.51–4.44 (m, 1H), 3.09–2.91 (m, 2H), 2.26–2.22 (m, 2H), 1.54–1.47 (m, 2H), 1.39–1.24 (m, 6H), 0.89 (t, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 132.9$ (d, $J_{P,C} =$ 3.0 Hz), 132.6 (d, $J_{P,C} = 6.5$ Hz), 132.0 (d, $J_{P,C} = 9.5$ Hz), 129.1 (d, $J_{P,C} = 131.5$ Hz), 128.6 (d, $J_{P,C} = 12.0$ Hz), 118.2, 79.1 (d, $J_{P,C} = 3.7$ Hz), 68.7 (d, $J_{P,C} = 10.0$ Hz), 66.5 (d, $J_{P,C} = 12.8$ Hz), 65.8 (d, $J_{P,C} = 6.5$ Hz), 64.9 (d, $J_{P,C} = 6.6$ Hz), 31.2, 28.4, 28.1, 22.9 (d, $J_{P,C} = 96.9$ Hz), 22.5, 19.2, 14.0; ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 35.7$; HR-MS (EI-TOF): $m/z = 328.1596$, calcd. for $C_{20}H_{25}O_2P$ [M^+]: 328.1592.

Procedure for the Olefination Reaction of Dimethyl (5-Phenylpenta-2,4-diyn-1-yl)phosphonate (3f) with 1-Pyrenecarbaldehyde to Produce 1-(6-Phenylhexa-1-en-3,5-diyn-1-yl)pyrene (5)

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with dimethyl (5-phenylpenta-2,4-diyn-1-yl)phosphonate (124.0 mg, 0.5 mmol). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 3.0 mL of dry THF were injected, and the solution was cooled to −78 °C. A solution of LiHMDS (0.55 mmol, 1 M in THF) was then injected under stirring. The mixture was stirred for 2 h at the same temperature. Then 1-pyrenecarbaldehyde (57.5 mg, 0.25 mmol) dissolved in 2.0 mL of dry THF was added dropwise. The reaction was slowly warmed to room temperature, and stirred overnight. The reaction was quenched with aqueous NH_4Cl, extracted with EtOAc (10 mL × 3). The combined organic layers were dried with Na_2SO_4. Removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica to afford the product **5**; yield: 57.4 mg (65%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 8.39$ (d, $J = 9.2$ Hz, 0.85H), 8.31 (d, $J = 9.2$ Hz, 0.15H), 8.27–8.01 (m, 9H), 7.57–7.55 (m, 1.7H), 7.52–7.49 (m, 0.3H), 7.39–7.34 (m, 3H), 6.54 (d, $J =$ 16.0 Hz, 0.85H), 6.17 (d, $J = 12.0$ Hz, 0.15H); HR-MS (EI-TOF): $m/z = 352.1257$, calcd. for $C_{28}H_{16}$ [M^+]: 352.1252.

Procedure for the Cyclization of 3a and Hydroxylamine to Produce 6a and 6b

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with **3a** (68.0 mg, 0.2 mmol), K_2CO_3 (82.8 mg, 0.6 mmol) and hydroxylamine hydrochloride (41.4 mg, 0.6 mmol). The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 1.0 mL of DMSO was injected. The mixture was stirred at 60 °C overnight. After the reaction was complete (monitored by TLC), water was added. The mixture was extracted with EtOAc (10 mL × 3 times). The combined organic layers were washed with water, brine and dried with Na_2SO_4. Removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica to afford the unseperable mixture of **6a** and **6b**; yield: 50.7 mg (total: 68%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.75–7.67$ (m, 4H), 7.52–7.41 (m, 6H), 7.29–7.21 (m, 3H), 7.13–7.11 (m, 2H), 6.05 (s, 0.83H), 5.97 (d, $J = 2.0$ Hz, 0.17H), 3.95 (s, 1.66H), 3.88 (s, 0.34H), 3.77 (s, $J = 14.0$ Hz, 0.34H), 3.69 (d, $J = 13.2$ Hz, 1.66H); ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 28.1$, 27.2; HR-MS (ESI-TOF): $m/z = 374.1308$, calcd. for $C_{23}H_{21}NO_2P$ [MH^+]: 374.1310.

General Procedure for the Cyclization of Phosphoryl 1,3-Diynes 3 with Hydrazine

An oven-dried Schlenk tube containing a Teflon-coated stir bar was charged with phosphoryl 1,3-diyne **3**. The Schlenk tube was sealed and then evacuated and backfilled with N_2 (3 cycles). 1.0 mL of DMSO was injected, followed by the injection of hydrazine (3.0 equiv., 80 wt% in water). The mixture was stirred at 60 °C overnight. After the reaction was complete (monitored by TLC), water was added. The mixture was extracted with EtOAc (10 mL × 3). The combined organic layers were washed with water, brine and dried with Na_2SO_4. Removal of the solvent under vacuum left a slurry residue, which was purified by flash chromatography on silica (PE/EtOAc-1:3 v/v) to afford **7**.

5-Benzyl-3-[(diphenylphosphanyl)methyl]-1*H*-pyrazole (7a): Prepared from 68.0 mg of **3a** (0.2 mmol); yield: 50.6 mg (68%); white solid; mp 217–218 °C; ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.70–7.65$ (m, 4H), 7.51–7.47 (m, 2H), 7.41–7.37 (m, 4H), 7.26–7.16 (m, 3H), 7.09 (d, $J =$ 6.8 Hz, 2H), 5.79 (s, 1H), 3.88 (s, 2H), 3.67 (d, $J = 12.8$ Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 138.9$, 131.9 (d, $J_{P,C} =$ 3.4 Hz), 131.8 (d, $J_{P,C} = 100.2$ Hz), 131.0 (d, $J_{P,C} = 9.2$ Hz), 128.6, 128.4 (d, $J_{P,C} = 5.7$ Hz), 126.3, 105.3 (d, $J_{P,C} = 4.2$ Hz), 33.2, 29.9 (d, $J_{P,C} = 68.3$ Hz); ^{31}P NMR ($CDCl_3$, 162 MHz): $\delta = 30.0$; HR-MS (ESI-TOF): $m/z = 373.1459$, calcd. for $C_{23}H_{22}N_2OP$ [MH^+]: 373.1470.

{[5-(4-Fluorobenzyl)-1*H*-pyrazol-3-yl]methyl}diphenylphosphine oxide (7b): Prepared from 40.0 mg of **3k** (0.11 mmol); yield: 29.5 mg (69%); white solid; mp 214–215 °C; ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 12.4$ (br, 1H), 7.81–7.76 (m, 4H), 7.56–7.47 (m, 6H), 7.12–7.05 (m, 4H), 5.59 (s, 1H), 3.80 (d, $J = 14.8$ Hz, 2H), 3.78 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 161.4$ (d, $J_{P,C} = 243.1$ Hz), 134.8 (d, $J_{P,C} = 3.4$ Hz), 131.9 (d, $J_{P,C} = 2.2$ Hz), 131.7 (d, $J_{P,C} = 100.4$ Hz), 131.0 (d, $J_{P,C} = 9.4$ Hz), 129.9 (d, $J_{P,C} =$ 8.0 Hz), 128.5 (d, $J_{P,C} = 11.8$ Hz), 115.0 (d, $J_{P,C} = 21.3$ Hz), 105.1, 32.5, 29.7 (d, $J_{P,C} = 68.0$ Hz); ^{31}P NMR (DMSO-d_6, 162 MHz): $\delta = 26.8$. HR-MS (ESI-TOF): $m/z = 391.1362$, calcd. for $C_{23}H_{21}N_2OPF$ [MH^+]: 391.1376.

[(5-Benzyl-1*H*-pyrazol-3-yl)methyl]di-*p*-tolylphosphine oxide (7c): Prepared from 36.8 mg of **3b** (0.1 mmol); yield: 28.5 mg (71%); white solid; mp 228–229 °C; ^1H NMR (DMSO-d_6, 400 MHz): $\delta = 12.4$ (br, 1H), 7.66–7.62 (m, 4H), 7.27–7.22 (m, 6H), 7.19–7.15 (m, 1H), 7.09 (d, $J = 6.8$ Hz,

2H), 5.62 (s, 1H), 3.80 (s, 2H), 3.74 (s, J=13.6 Hz, 2H), 2.31 (s, 6H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=147.5 (br), 142.2 (d, $J_{P,C}$=2.4 Hz), 139.1, 138.3 (br), 131.0 (d, $J_{P,C}$=9.1 Hz), 129.2 (d, $J_{P,C}$=12.8 Hz), 128.6 (d, $J_{P,C}$=99.9 Hz), 128.4 (d, $J_{P,C}$=29.8 Hz), 126.1, 105.1 (d, $J_{P,C}$=4.2 Hz), 33.3, 29.9 (d, $J_{P,C}$=67.8 Hz), 21.5; ^{31}P NMR (DMSO-d_6, 162 MHz): δ=27.0; HR-MS (ESI-TOF): m/z=401.1779, calcd. for $C_{25}H_{26}N_2OP$ [MH$^+$]: 401.1783.

[(5-Benzyl-1*H*-pyrazol-3-yl)methyl]bis(4-fluorophenyl)-phosphine oxide (7d): Prepared from 37.6 mg of **3d** (0.1 mmol); yield: 25.0 mg (61%); white solid; mp 212–213 °C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ=12.4 (br, 1H), 7.88–7.82 (m, 4H), 7.36–7.32 (m, 4H), 7.27–7.17 (m, 3H), 7.09–7.07 (m, 2H), 5.62 (s, 1H), 3.83 (d, J=14.8 Hz, 2H), 3.81 (s, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz): δ=165.0 (dd, $J_{F,C}$=252.6 Hz, $J_{P,C}$=2.7 Hz), 138.6, 133.5 (dd, $J_{F,C}$=10.6 Hz, $J_{P,C}$=9.5 Hz), 128.5, 128.4, 127.5 (d, $J_{P,C}$=103.9 Hz), 126.4, 115.9 (d, $J_{F,C}$=21.6 Hz, $J_{P,C}$=12.6 Hz), 105.3, 33.0, 29.7 (d, $J_{P,C}$=69.7 Hz); ^{31}P NMR (DMSO-d_6, 162 MHz): δ=26.1; HR-MS (ESI-TOF): m/z=409.1274, calcd. for $C_{23}H_{20}N_2OPF_2$ [MH$^+$]: 409.1281.

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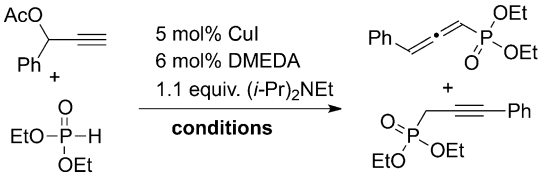

conditions	combined yields	distribution (**allene/alkyne**)
(a) EtOH, 0 °C, 5 h	95	98/2
(b) EtOH, 0 °C to r.t., 12 h; then 60 °C, 8 h	96 96	89/11 57/43
(c) DCE, 0 °C to r.t., 12 h	25	100/0
(d) DCE, 60 °C, 8 h	96	85/15

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