



## Ni-catalyzed regiodivergent hydrophosphorylation of enynes

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### ABSTRACT

A regiodivergent hydrophosphorylation of enynes with phosphites has been developed using earth-abundant nickel catalyst. The manipulation of regioselectivity can be achieved by regulating the insertion order of alkyne bonds with  $(RO)_2P(O)-Ni-H$  or  $R_2P(O)O-Ni-H$  species, respectively. Under the Ni/Xantphos catalysis, 4,1-hydrophosphorylation is selectively obtained while the adding of acid can promote reactions towards 1,2-addition. By employing an additional Pd-H catalysis, 2,1-hydrophosphorylation is also an accessible task in one-pot reaction. Mechanistic studies and analysis have also been performed to interpret the origin of the regioselective regulation. This work highlights the arts in accessing different regioisomers by diverting common elementary reaction steps.

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Owing to the versatile biological activities, organophosphorus has wide applications in medicinal and agricultural chemistry [1–5]. Besides, many phosphine compounds also serve as useful building blocks, ligands as well as organocatalysts in numerous synthetic transformations [6–9]. Therefore, considerable efforts have been devoted to their selective synthesis under catalysis [10–25]. Among all the developed protocols, the transition-metal catalyzed hydrophosphorylation of unsaturated C–C bonds represents one of the most atom-economic and straightforward tools [26–31]. In this regard, many intellectual achievements have been contributed to the selective hydrophosphorylation of alkenes [32–38], alkynes [39–53], allenes [54–56] and 1,3-dienes [57–61] over the past years. However, the regioselective hydrophosphorylation of conjugated enynes was rather rare [62,63]. Compared with alkene or alkyne surrogates, the hydrophosphorylated products from enynes usually contain at least two unsaturated C–C bonds that can facilitate the rapid assembly of molecular complexity by their further modification.

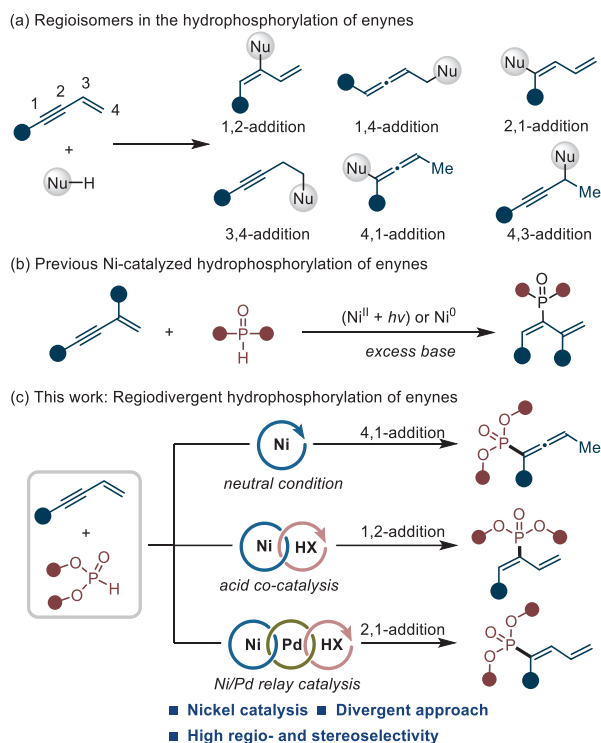
The regiodivergent hydrofunctionalization of enynes is by no means an easy work and considerable hurdles impede its development [64–67]. The competitive insertion between alkene and alkyne bonds often complicates most of the established methods. The existence of various  $\pi$ -metal tautomerisms also poses

substantial challenges in regioselective control (Scheme 1a). Although some success have been achieved to forge the C–C [68–76], C–N [77–79], C–Si [80,81] or C–B [82–86] bonds, the selective construction of C–P bonds is limited. Recently, Zhu and co-workers developed a light-induced nickel catalysis for the 1,2-hydrophosphorylation of conjugated enynes with phosphine oxides in the presence of excess base [62]. Very recently, Zhang's group also disclosed a base-required nickel catalysis for 1,2-hydrophosphorylation of conjugated enynes (Scheme 1b) [63]. It should be noted that only one major isomer in hydrophosphorylation could be accessed under the above two protocols. On the basis of our continuous research interests in functionalization of alkenes/alkynes [87–92], herein we reported a regiodivergent strategy for selective hydrophosphorylation of conjugated enynes with phosphites (Scheme 1c). By manipulating the order of elementary reaction step, switchable regulation of 4,1- or 1,2-addition could be realized, respectively. With the help of an additional Pd–H catalysis, 2,1-hydrophosphorylation was also an accessible task in our protocol.

Initially, we designed this regiodivergent and atom-economic hydrophosphorylation on the basis of Ni-hydride catalysis depicted in Scheme 2A [45,61,63]. In the absence of acid, the direct oxidative addition between Ni(0) and phosphite (**1**) may deliver Ni-hydride species **Int A**, which then coordinates with enyne (**2**) and gives complex **Int B** (pathway A). Due to the bulkiness of tertiary phosphorus motif, the **Int B** is crowded and tends to occur P–Ni bond insertion with alkyne bond to release steric encumbrance and generate **Int C** or its tautomerism **Int C'**. Subsequently, the reduc-

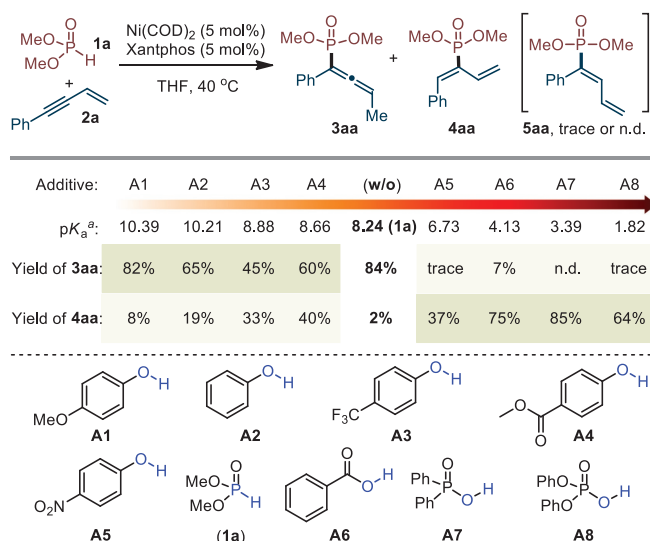
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**Scheme 1.** Catalytic regioselective hydrophosphorylation of enynes.

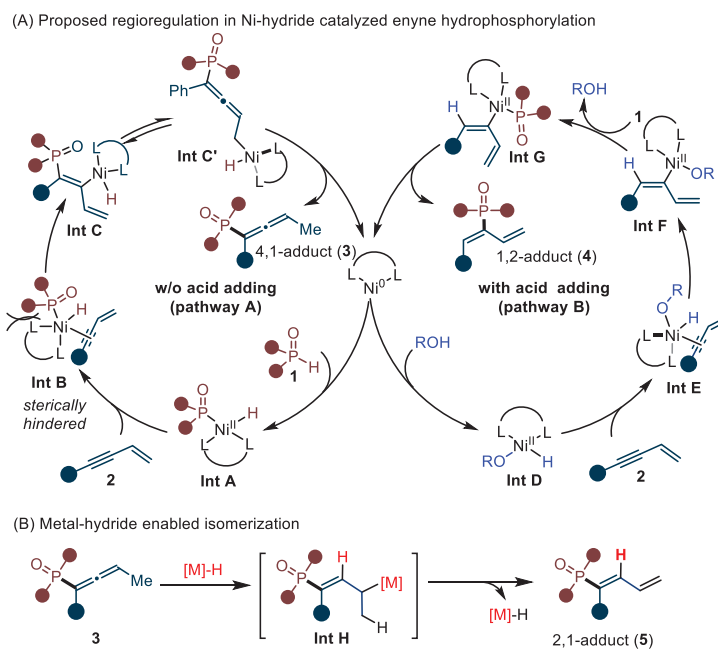
tive elimination from less hindered **Int C'** may lead to 4,1-addition product **3** and regenerate Ni(0) species. With the aid of a Brønsted acid, the oxidative addition probably occurs first between Ni(0) and acid to yield **Int D** (pathway B). Next, coordination of **Int D** with enyne (**2**) furnishes complex **Int E**. Compared with **Int B**, the **Int E** is less crowded and Ni-H insertion with alkyne bond may take place preferentially in this case to produce **Int F**. Then, **Int G** can be obtained through the ligand exchange between phosphite (**1**) and **Int F**, followed by a final reductive elimination to deliver the 1,2-adduct **4**. Notably, the 2,1-hydrophosphorylation may also be



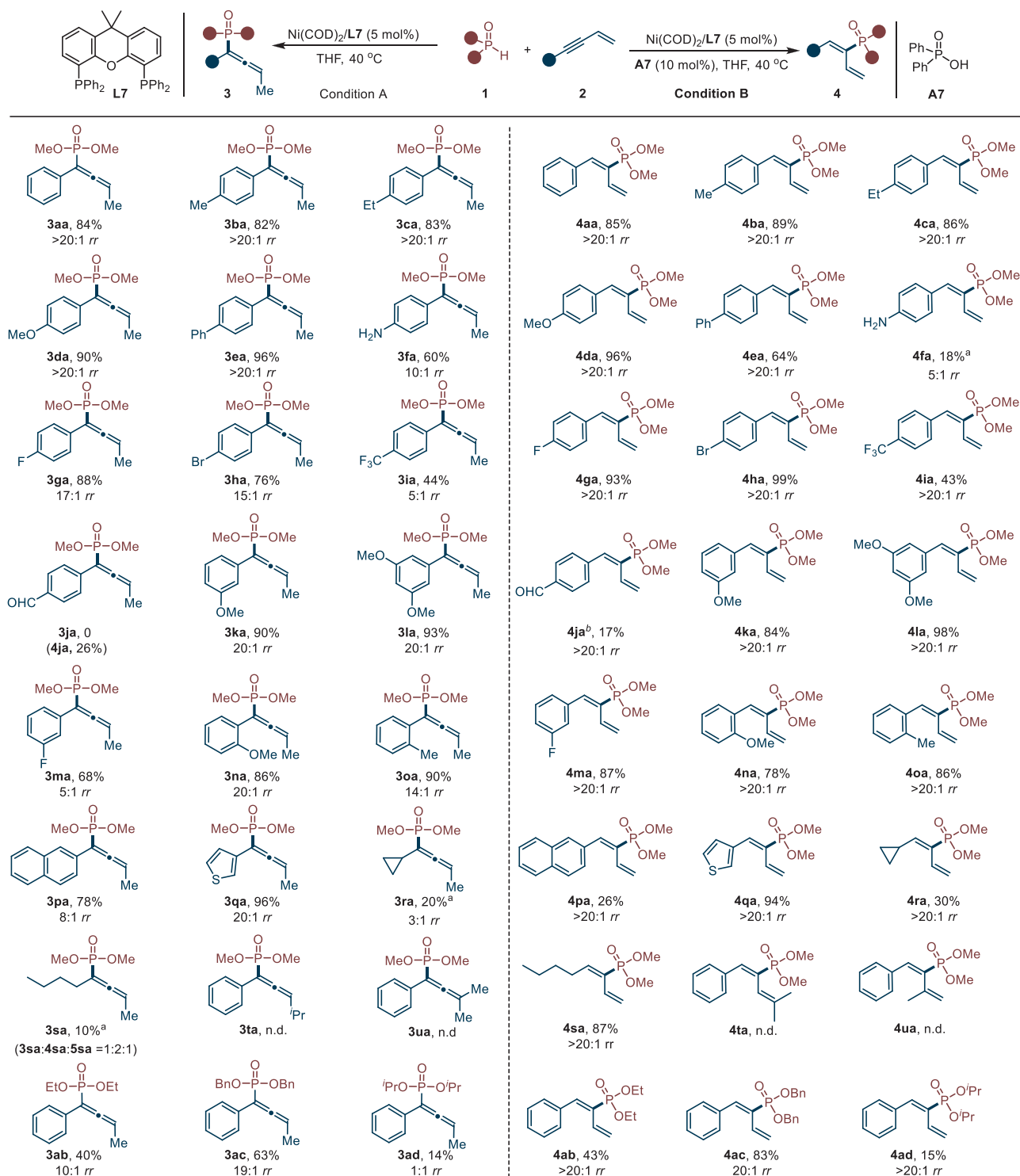
**Scheme 3.** Evaluation of reaction conditions. Conditions: **1a** (0.20 mmol), **2a** (0.30 mmol), Ni(COD)<sub>2</sub> (5 mol%), Xantphos (5 mol%), additive (10 mol%), THF (0.5 mL), 40 °C, 20 h, N<sub>2</sub>. Yield was determined by HPLC with naphthalene as the internal standard. <sup>a</sup> Predicted value with H<sub>2</sub>O as the solvent, see ref. [93].

available by metal-hydride mediated alkene isomerization via **Int H** (Scheme 2B).

With this proposal in mind, we explored the regiodivergent hydrophosphorylation with the coupling between dimethyl phosphite (**1a**) and enyne (**2a**) and by using Ni(COD)<sub>2</sub> as catalyst precursor in THF at 40 °C. After the careful evaluation of various ligands (for details, see Table S1 in Supporting information), we found that Xantphos (**L7**) displayed best performance in terms of reactivity and the reaction could give allene **3aa** in excellent selectivity. To manipulate the regioselectivity, phenols and acids with different  $pK_a$  value were then examined (Scheme 3) [93]. Indeed, the electron-rich phenols with higher  $pK_a$  value than **1a** all gave **3aa** as major product (**A1** and **A2**). In contrast, the yield of **4aa** increased while the electron-deficient phenols employed (**A3** and **A4**) and became



**Scheme 2.** Proposed regiodivergent enyne hydrophosphorylation under Ni-hydride catalysis.

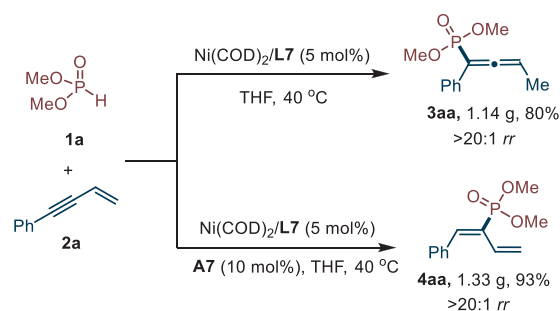


**Scheme 4.** Substrate scope towards 1,2-adducts and 4,1-adducts. Condition A: **1** (0.20 mmol), **2** (0.30 mmol), Ni(COD)<sub>2</sub> (5 mol%), L7 (5 mol%), THF (0.5 mL), 40 °C, 20 h; Condition B: **1** (0.20 mmol), **2** (0.30 mmol), Ni(COD)<sub>2</sub> (5 mol%), L7 (5 mol%), A7 (10 mol%), THF (0.5 mL), 40 °C, 20 h. Isolated yield of the major product was given in all cases. Regioselectivity was determined by <sup>31</sup>P NMR analysis of the crude mixture. <sup>a</sup> Isolated product together with regioisomer, the yield of corresponding product has been adjusted accordingly. <sup>b</sup> CsOAc (10 mol%) was used instead of (Ph)<sub>2</sub>PO<sub>2</sub>H.

majority when the loaded phenol bearing pK<sub>a</sub> value lower than that of dimethyl phosphite (**A5** vs. **1a**). These results inspired us to further screen some more acidic additives. It was found that the reaction with diphenylphosphinic acid (**A7**) could successfully furnish **4aa** in 85% yield with excellent regioselectivity. Notably, in all case the 2,1-addition product **5aa** could not be detected or only obtained in trace amount. Besides, NiCl<sub>2</sub>/Zn combined system is

not suitable for current reactions (for details, see Table S2 in Supporting information).

Under the standard conditions, we then sought out to examine the generality of enyne substrates for 4,1-addition (Scheme 4, condition A). A variety of enynes bearing electron-donating groups could couple with dimethyl phosphite **1a** smoothly and led to alkenes in good yields and regioselectivities (**3aa–3fa**). Halides such



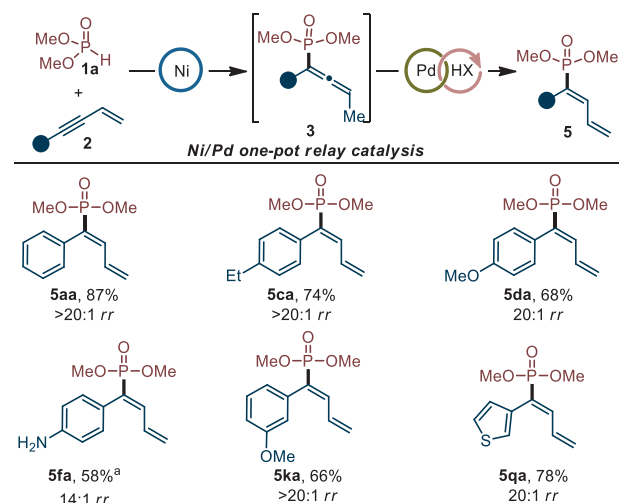
Scheme 5. Gram-scale reactions.

as -F (**3ga**) and -Br (**3ha**) were also applicable substituents for the current conversion. However, when substrates having the stronger electron-withdrawing groups, such as -CF<sub>3</sub> (**3ia**) and -CHO (**3ja**), the reaction proceeded sluggishly. Substituents at the *meta*- or *ortho*-position of phenyl rings were compatible as well (**3ka**–**3oa**). On replacing the phenyl group with 2-naphthalenyl or 3-thienyl group, the substrates were transformed into product **3pa** and **3qa** in 78% and 96% yield, respectively. Aliphatic enynes could couple with **2a** but resulted in low selectivity (**3ra** and **3sa**). As illustrated by **3ta** and **3ua**, the reactions failed to proceed when enyne substrates bearing substituent on alkene group. When reactions were carried out with bulkier alkyl phosphites under condition A, the reactivities and regioselectivities were both decreased (**3ab**–**3ad**). This result is probably due to steric repulsion between alkoxy group and phenyl group (Scheme 2, **Int C**), which makes P–Ni bond insertion step unfavorable.

With the Ni/acid catalysis, aryl enynes with various substituents at the phenyl rings successfully resulted in a range of 1,3-dienes **4aa**–**4pa**. In most case, substrates with either electron-donating or electron-withdrawing groups all delivered products in high yields and excellent regioselectivities. However, when the enynes bearing reactive groups, such as -NH<sub>2</sub> (**4fa**) and -CHO (**4ja**), the reactions proceeded with low yields. Delightfully, the bromo group (**4ha**), which is a fragile substituent in many nickel catalysis, could remain intact under current conditions and produced corresponding product in 99% yield. This reaction was also feasible to the 3-thienyl enyne and led to **4qa** in 94% yield. In addition, aliphatic enyne could react with dimethyl phosphite as well, furnishing hydrophosphorylated product **4ra** and **4sa** in excellent selectivity. The enynes having substituent on alkene unit were also not tolerated under this condition (**4ta** and **4ua**). In addition, the bulkiness of alkyl groups showed no obvious difference in regioselectivity (**4ab**–**4ad**,  $\geq 20:1$  *rr* in all case). However, it was found that the bulkier alkyl group had the lower reactivity (**4aa** vs. **4ad**). Based on the above-mentioned pathway B, the regioselectivity under acid condition was determined by the Ni–H insertion process. This step is not concerned with alkyl phosphites and therefore the regioselectivity keeps in high level. But the bulky substituents can affect the ligand exchange step, which may result in the low yield when (*i*PrO)P(O)H employed (**4ad**).

Under the optimal reaction conditions, this regiodivergent hydrophosphorylation could be easily conducted in a gram-scale (Scheme 5). Under nickel catalysis, the reaction between dimethyl phosphite (**1a**) and enyne (**2a**) could successfully deliver product **3aa** in 1.14 g with 80% yield and  $>20:1$  *rr*. In the presence of acid, diene product **4aa** could also be obtained in 93% yield (1.33 g) and  $>20:1$  *rr*.

To shed light on the mechanism, we also performed deuterium-labeling experiments (Scheme S1 in Supporting information). When subjecting deuterated dimethyl phosphite (**1a-d**) to couple with enyne (**2a**) under the standard condition A or condition B, respectively, it was found no obvious deuterium scrambling was de-



Scheme 6. 2,1-Hydrophosphorylation by Ni/Pd one-pot relay catalysis. Step 1: **1a** (0.30 mmol), **2** (0.20 mmol), Ni(COD)<sub>2</sub> (5 mol%), **L7** (5 mol%), dioxane, 40 °C, 20 h. Step 2: Pd(OAc)<sub>2</sub> (10 mol%), PPh<sub>3</sub> (20 mol%), PhCOOH (40 mol%), 1,4-dioxane, 120 °C, 6 h. Isolated yield of the major product was given in all cases. Regioselectivity was determined by <sup>31</sup>P NMR analysis of the crude mixture. <sup>a</sup> Isolated product together with regioisomer **4fa**, total yield was given.

tected in the products **3aa**–**d** and **4aa**–**d** as well as recovered **2a**. These results indicate a less possibility of a reversible process between Ni–hydride insertion and  $\beta$ -hydride elimination. Then, kinetic studies were also performed to gain further insights on reaction profiles (Fig. S4A in Supporting information). With the increase of the reaction time, the yield of **4aa** raised rapidly during the initial time under condition B, while slow linear growing was observed for **3aa** under condition A. These results indicate that the reaction for 1,2-addition is rather faster than that for 4,1-addition. No transitional product being detected excludes the possibility of an interchange conversion between **3aa** and **4aa**.

When replacing the nickel catalyst with palladium, only 1,2-addition product was found whether acid was added or not, suggesting the unique regioregulated ability of nickel catalysis (Fig. S4B, Eqs. 1 and 2 in Supporting information). Besides, it was also found that the reaction with acid apparently exhibited higher efficiency. This is in according with kinetic experiments and previous Han's work that the adding of acid can accelerate the hydrophosphorylation process [42]. This conclusion also meets with the results when subjecting 1-phenylpropyne **6** to react with **1a** under standard nickel catalysis, in which higher yields of hydrophosphorylation products (**7a** and **7b**) were obtained under the acid condition (Fig. S4B, Eqs. 3 vs. 4). Instead, no any hydrophosphorylation product could be detected in the coupling reaction between 1-phenyl-1,3-butadiene **8** and **1a** (Fig. S4B, Eq. 5), suggests that current catalysis may not favor the alkene insertion process. Moreover, diene intermediate **9** was synthesized to react with **1a** under standard condition and the 6% yield of **4aa** was furnished, supports the rationality of proposed pathway B (Fig. S4B, Eq. 6).

As we mentioned in Scheme 3, the selective 2,1-hydrophosphorylation of enynes was extremely difficult to be accessed by direct addition reaction. However, we conceived an indirect way—the one-pot late-stage isomerization of allene products [94,95]. With this imagination in mind, the evaluation of compatibility of Ni catalysis with isomerization catalysis was subsequently carried out (for details, see Table S5 in Supporting information). Pleasingly, it was found that under Pd(OAc)<sub>2</sub>/PPh<sub>3</sub>/PhCOOH combined catalysis, various 2,1-hydrophosphorylated products could be successfully obtained in moderate to good yields and decent regioselectivities (Scheme 6). The current relay catalysis was also

featured by its easy handle and allene intermediate products were not needed to be separated in this one-pot way.

In conclusion, we have developed a practical strategy for the regioselective hydrophosphorylation of enynes. Under Ni/Xantphos catalysis, 4,1-addition could be selectively obtained whereas the adding of acid switched reactions towards 1,2-addition. Mechanistic studies showed that the regioselectivity was probably governed by the alkyne insertion step between (RO)<sub>2</sub>P(O)-Ni-H and (R)<sub>2</sub>P(O)O-Ni-H species. With the help of Ni/Pd relay catalysis, the 2,1-hydrophosphorylation could also be realized in one-pot reaction. Further investigations on more mechanistic details and the extension of this regioselectivity controlled strategy are now in progress in our laboratory.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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### Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.ccl.2022.107914.

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