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Dynamic coordination drives regiodivergent dienylation of propargylic esters with phosphine oxides

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ABSTRACT

Transition-metal-catalyzed substitution of propargylic electrophiles with secondary phosphine oxides (SPOs) has emerged as a powerful strategy to phosphorus-containing frameworks. However, precise regiocontrol remains elusive due to competing pathways in allenyl-metal intermediates and SPO tautomerism. Herein, we report a dynamic coordination strategy that leverages the tunable binding modes of SPOs to achieve regiodivergent dienylation of propargylic esters, thereby accessing a diverse range of 1,3-dienyl phosphines. Through fine-tuning of ligands and the strategic use of Brønsted or Lewis acid-assisted catalytic systems, we demonstrate switchable *C2- versus C3*-selective dienylation, governed by dynamic control over the coordination modes and reactivities of SPOs. Mechanistic studies reveal that the dynamic inner- or outer-sphere coordination dictates the regiochemical outcome, which proceeds *via* relay catalysis or bimetallic cooperative catalysis pathways, thus offering a rationale for the observed regiodivergence. This method provides a robust and modular platform for synthesizing multisubstituted 1,3-dienyl phosphines with broad substrate scope and excellent regio- and stereoselectivity, underscoring the potential of coordination-controlled reactivity in complex bond-forming processes.

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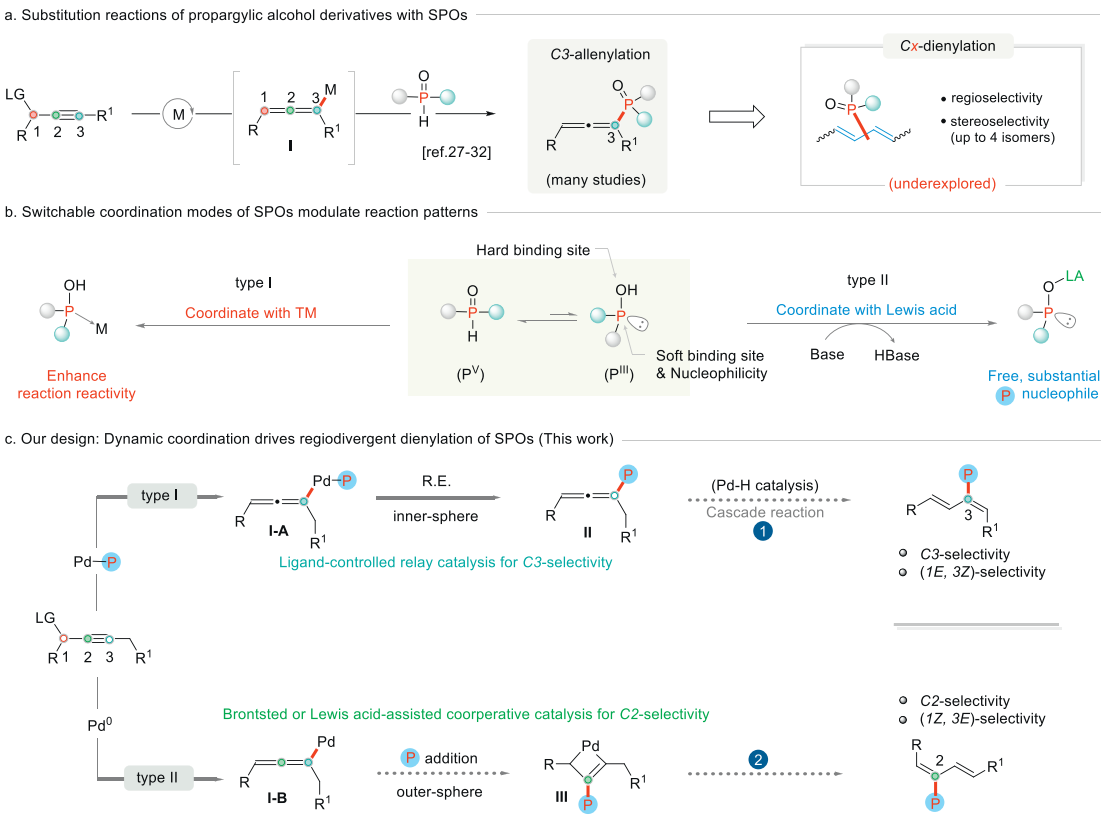
The continuous development of phosphorus chemistry remains an important theme in both industrial and academic contexts, with widespread applications across organic chemistry [1,2], materials science [3–7], and medicinal chemistry [8–10]. The strategic incorporation of phosphorus atoms enables significant modulation of the physicochemical properties of organic molecules, thereby enhancing molecular functionalities while simultaneously expanding structural diversity and complexity. As a result, molecular phosphating has emerged as a powerful and versatile strategy for designing and synthesizing structurally sophisticated molecules [11–16].

Among organophosphorus compounds, vinyl phosphines serve as key synthetic precursors for constructing essential molecular frameworks [12–14]. Notably, 1,3-dienyl phosphines featuring conjugated diene moieties represent a privileged structural class that functions as versatile synthetic building blocks (*e.g.*, Diels-Alder cycloaddition) [2,3,16–20] and biologically active reagents [15,21,22]. Despite this significance, synthetic routes to 1,3-dienyl phosphorus compounds remain exceptionally limited [14,23–25].

Transition-metal catalyzed substitution of readily accessible propargylic electrophiles with synthetically versatile and air-stable secondary phosphine oxides (SPOs) constitutes a powerful strategy for constructing phosphorus-containing frameworks (Scheme 1a) [26–32]. While significant progress has been predominantly achieved in the highly regioselective synthesis of propargyl- [26] or allenyl-phosphines [27–32], the development of synthetic methodologies for synthetically useful 1,3-dienyl phosphines remains substantially underdeveloped (Scheme 1a). To date, the high regioselective dienylation of SPOs still suffers considerable challenges: (1) The dynamic tautomeric equilibrium of SPOs between pentavalent (phosphine oxide) and trivalent (phosphinous acid) forms imparts complex coordination behavior with catalytic metals [33,34], potentially generating unpredictable Type I/II catalytic pathways that compromise reaction selectivity and substrate compatibility (Scheme 1b) [35–37]. (2) The inherent complexity of allenyl-metal intermediates **I** (Scheme 1a), featuring multiple potential reactive sites (*C1*, *C2*, and *C3*), makes regiocontrol particularly demanding [38–45]. (3) Controlling *E/Z*-stereoselectivity in conjugated diene

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Scheme 1. Difficulties and improvements in the synthesis of phosphinylated dienes.

systems represents a fundamental challenge, especially for non-terminal multisubstituted dienes that may generate up to four stereoisomers [46,47]. Guo's group made an elegant contribution by developing a ligand-controlled strategy for the dienylation of SPOs with propargylic carbonates under acidic conditions, affording 1,3-dienyl phosphines with *C2*-selectivity [30]. Furthermore, Li and Ma groups strategically employed allenylic acetates and SPOs to achieve the synthesis of terminal 1,3-dienyl phosphines with high regio-selectivity [48]. Considering the limitations and challenges, establishing robust synthetic protocols to access structurally diverse 1,3-dienyl phosphines would significantly expand the available chemical space, enabling the exploration of novel molecular architectures with enhanced complexity and functionality.

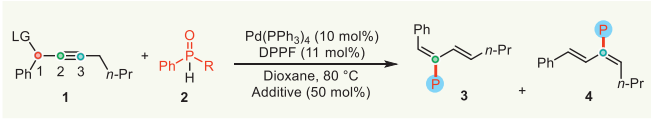
We disclose our contribution to developing an efficient strategy for the dienylation of SPOs with propargylic esters in a predictable regio- and stereoselective manner, thereby providing a new entry point into diverse 1,3-dienyl phosphines. Inspired by the dynamic equilibrium effects of SPOs (Scheme 1b), we envision that tunable coordination patterns may provide a reliable means for regulating regioselectivity (Scheme 1c) [49,50]. Typically, in the precedent work, the preferred allenyl-type products [27–32,38] were generated *via* an inner-sphere reductive elimination of the M-P bond (**I-A**, Scheme 1c) through the high binding affinity of the P-center coordination mode (type I, Scheme 1b). Allene is a versatile synthetic intermediate for various transformations in organic synthesis, especially for Pd-H catalysis [51–57]. We imagined that if the *in-situ* generated allenyl phosphines intermediate **II** [27–32] could engage in Pd-H-catalyzed cascade transformations, which might provide an ideal synthetic route to *C3*-selective 1,3-dienyl phosphines (Scheme 1c, top). To our knowledge, this Pd-H-catalyzed cascade process remains unprecedented, particularly for configurationally challenging trisubstituted allenes—a formidable obstacle.

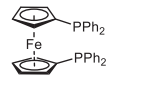
On the other hand, we have recently developed a transition metal-catalyzed regioselective dienylation of propargylic electrophiles, which typically proceeds through the regioselective nucleophilic addition at the central *C2*-carbon of allenyl-metal complex to furnish diversely functionalized 1,3-dienes [58]. Notably, the oxygen atom of SPOs has been used as a suitable ligand for early transition metals [49]. Accompanying the deprotonation with a base, which might potentially favor the formation of substantial free P-centered nucleophiles (type II, Scheme 1b) [50]. This process facilitates nucleophilic attack by SPOs at the *C2*-position of allenyl-metal intermediate **I-B** *via* an outer-sphere pathway, forming metallacyclobutene **III** [59–61]. Subsequent ring-opening/β-H elimination then affords *C2*-selective dienylation product (Scheme 1c, bottom) [41–43,62–64]. Moreover, suppressing reductive elimination from intermediate **I-A** favors pathway divergence, redirecting the mechanism from the original inner-sphere route to the outer-sphere pathway (**I-B** → **III**). These outer-sphere pathways exclusively afford *C2*-dienylation products, demonstrating distinct regioselectivity from the *C3*-selective inner-sphere pathway (Scheme 1c).

Thus, this switchable coordination model of SPOs enables the regiodivergent transformation of propargyl esters into site-selectivity-tunable, non-terminal 1,3-dienyl phosphines. Significantly, the successful implementation of this work, controlled by the dynamic coordination of SPOs, not only expands accessible phosphine architectures but also establishes a strategic blueprint for precise regiocontrol in allenyl-metal intermediate transformations.

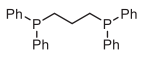
To demonstrate our hypothesis, we start our investigation by using propargylic carbonate **1** and SPOs **2** as pilot substrates (Table 1, see Tables S1 and S2 in Supporting information for details). Notably, conventional catalytic systems strongly favor the formation of allenyl-type product **5** [27–32] without an additive (Table 1, en-

Table 1
Preliminary discovery of dynamic modulation of regioselectivity.[a]

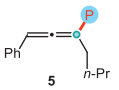




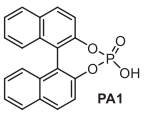
DPPF (ßn = 99°)



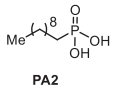
DPPP (ßn = 91°)



5



PA1



PA2

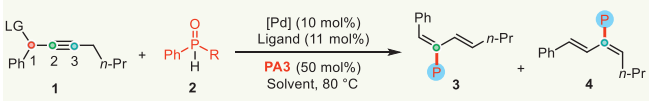


PA3

Entry	Change of conditions	**3/4**	**5**
1	No DPPF, no additive	0/0	0
2	No Additive	0/0	70
3	NEt_3	0/0	80
4	**PA1**	<5/27	0
5	**PA2**	<5/54	0
6	**PA3**	7/73	0
7	DPPF/**PA3**	42/16	0
8	$Zn(OTf)_2$[b]	56/0	0

[a] For details of the experiment, please refer to Supporting information. Unless otherwise noted, **1a** (LG = OBoc), **2a** (R = *n*-Bu) were used.
[b] **1p** (LG = OPiv), **2f** (R = Ph) were used at 120 °C.

Table 2
Further optimization of the *C2*-site selectivity.[a]



Entry	[Pd]	Ligand	Solvent	**3**:**4**[b]	Yield (%)[c]
1	$Pd(PPh_3)_4$	Binap	Dioxane	1:1	35
2[d]	$Pd(PPh_3)_4$	Xantphos	Dioxane	/	<5
3	$Pd(PPh_3)_4$	DCyPB	Dioxane	2.5:1	40
4	$Pd(PPh_3)_4$	DPPP	Dioxane	2.5:1	58
5	$Pd(PPh_3)_2(OAc)_2$	DPPP	Dioxane	3.5:1	53
6	$Pd(PPh_3)_2(OAc)_2$	DPPP	CPME	5:1	56
7	$Pd(PPh_3)_2(OAc)_2$	DPPP	Toluene	5:1	54
8[e]	$Pd(PPh_3)_2(OAc)_2$	DPPP	*i*-Pr_2O	10:1	54
9[f]	$Pd(PPh_3)_4$	DPPF	*i*-Pr_2O	/	0
10[f]	$Pd(PPh_3)_4$	DPPF	DMF	>20:1	85
11[f]	$Pd(PPh_3)_4$	DPPP	DMF	>20:1	78
12[f]	$Pd(PPh_3)_4$	DPPF	DMA	>20:1	87

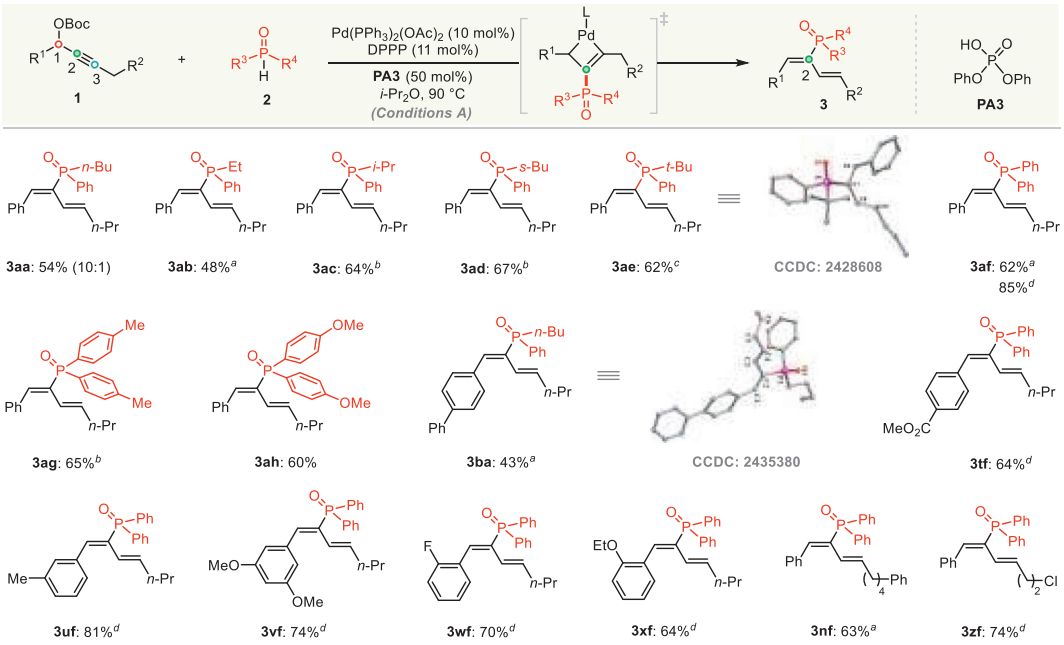
[a] Conditions unless otherwise noted: **1a** (0.1 mmol, LG = OBoc), **2a** (0.12 mmol, R = *n*-Bu), [Pd] (10 mol%), ligand (11 mol%), **PA3** (50 mol%), solvent (0.025 mol/L), 80 °C, N_2, 12 h. For details of the experiment, please refer to Supporting information. DCyPB: 1,4-Bis-(dicyclohexylphosphino)butane.
[b] The proportion was identified by ^1H NMR test.
[c] Isolated yields of the mixtures **3** and **4** after column chromatography are shown.
[d] Allene **5** is a major product.
[e] At 90 °C.
[f] Change of conditions: $Zn(OTf)_2$ was used instead of **PA3**; **1p** (0.1 mmol, LG = OPiv), **2f** (0.3 mmol, R = Ph) were used at 120 °C for 10 h.

try 2), particularly in the presence of an abundant base (Table 1, entry 3), which facilitates the rapid anion exchange of SPOs to palladium and accelerates the reductive elimination of C-P [27]. Building upon the dynamic coordination effect of SPOs, we propose two feasible regulatory strategies to change this inherent reaction behavior. Firstly, it is well-precedented that phosphoric acids typically preferentially bond to a metal catalyst, followed by anion exchange with SPOs [65–67]. Inspired by this, our initial hypothesis aimed to introduce phosphoric acid to occupy the coordinate site of the palladium center and, at the same time, to alter the reaction path by regulating the anion exchange ability with SPOs. This approach yielded only minor amounts of *C2*-phosphinylated diene **3** (Table 1, entries 4–6), with *C3*-selectivity (**4**) dominating. This selectivity likely stems from proton migration in allenyl intermediate **5** *via* Pd-H catalysis, a process accelerated by phosphonic acid derivatives [66].

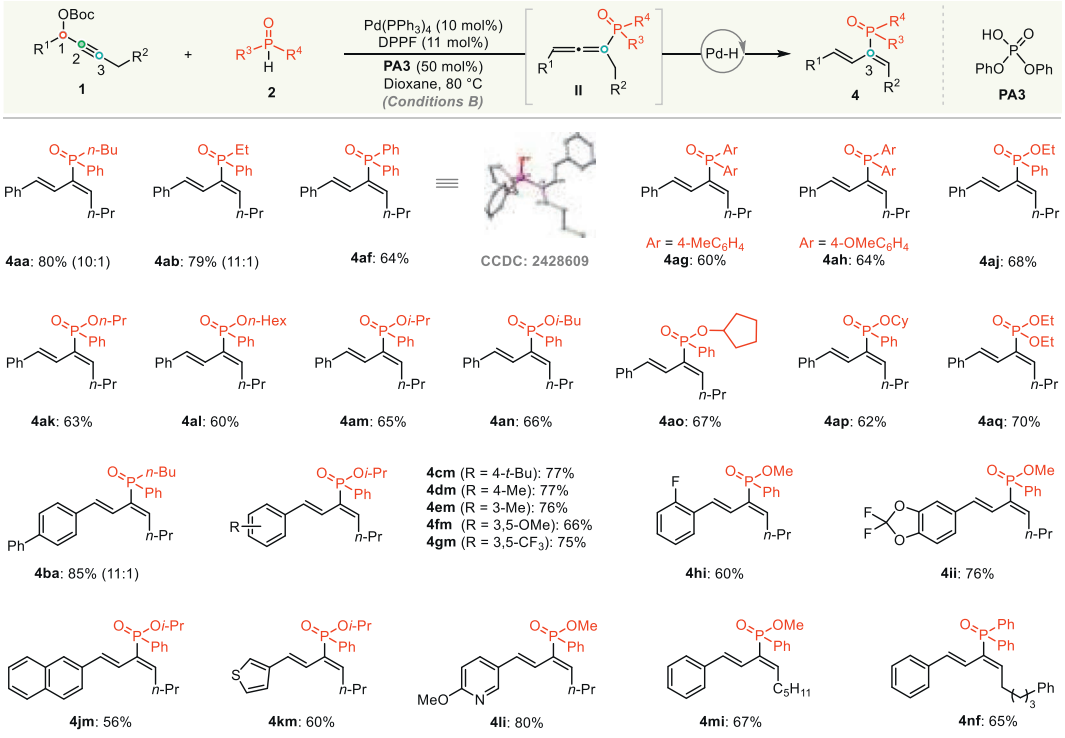
Notably, Brønsted acid with low steric hindrance and high acidity (**PA3**) exhibited superior efficacy in promoting this migration to afford product **4** (Table 1, entry 6). Secondly, to our surprise, the employment of narrower-bite-angle ligand DPPP ($\beta_n = 91°$) [68–70] in conjunction with **PA3** essentially switched the regioselectivity from *C3* to *C2*-site, compared with the wider-bite-angle DPPF ($\beta_n = 99°$) (Table 1, entries 6 and 7) [68], demonstrating the potential feasibility of modulating regioselectivity through ligand-bite-angle. Additionally, the introduced Lewis acids could synergistically deprotonate the SPOs [50], liberating free nucleophilic phosphine species (type II, Scheme 1b), thereby enhancing the likelihood of *C2*-site selectivity in an outer-sphere manner (Scheme 1c). The extensive screening of Lewis acid catalysts revealed that $Zn(OTf)_2$ enables a complete regioselectivity switching toward the *C2*-site product under elevated reaction temperatures, giving product **3** with excellent regio- and stereoselectivity (Table 1, entry 8, see Supporting information for more details).

After realizing a cascade reaction system that enables the highly *C3*-selective synthesis of 1,3-dienyl phosphines based on preliminary attempts at the aforementioned modulation strategies (Table 1, entry 6), we subsequently turned our interest to *C2*-selectivity. To further promote the selectivity of *C2*-site phosphinylation, based on our preliminary results (Table 1, entry 7), we first attempt to examine bidentate ligands with different bite angles (Table 2). The mixture of products **3** and **4** (1:1) was obtained when Binap ($\beta_n = 93°$) [68] was used. Notably, using Xantphos ($\beta_n = 108°$) [68] as the ligand exclusively delivered the allenyl-phosphine **5** and even hindered the proton transfer process to dienes (Table 2, entry 2). DPPP remained the most favorable ligand for *C2*-selectivity in ligand screening (Table 2, entries 1–4). Subsequently, by systematically adjusting the reaction parameters, we successfully achieved the efficient construction of *C2*-site phosphinylated diene product **3** in high regioselectivity (Table 2, entry 8, see Supporting information for more details). We speculate that the narrower-bite-angle coordination weakens the nucleophile binding of SPOs [69,70], thus allowing a relatively free phosphine nucleophile. On the other hand, excellent yield and selectivity can be obtained by using dipolar solvents in Lewis acid-modified conditions (Table 2, entries 10–12). The palladium cation was stabilized by the solvation effect to inhibit the chance of the phosphine anion coordination [71], thereby enhancing its free nucleophilic property. Clearly, ligand bite-angle regulation is not the dominant factor in such Lewis acid-modified systems (Table 2, entries 10 and 11, see Supporting information for more details).

Building upon the established strategies, we first evaluated the substrate scope of *C2*-site selective dienylation across diverse coupling partners (Scheme 2). Both aryl-alkyl and diaryl-substituted secondary phosphine oxides exhibit excellent compatibility, maintaining robust *C2*-site selectivity under different catalytic protocols. Notably, aryl–*tert*–butyl secondary phosphine oxide demonstrated inherent steric control advantages in our strategy (**3ae**). By employing propargylic esters with varying substitution patterns, we achieved flexible functional group diversification at both terminals of the diene products (**3ba** and **3tf**-**3zf**), establishing a highly efficient platform for structural diversity. Single-crystal X-ray analyses of representative products (**3ae**, **3ba**) provided unambiguous confirmation of regio- and stereoselectivity. Moreover, the preparation protocols with **PA3** or $Zn(OTf)_2$ as additives give consistent results on the NMR spectra (**3af**), revealing remarkable structural consis-



Scheme 2. *C2*-site phosphinylation/dienylation of propargylic carbonates with SPOs. Conditions A: **1** (0.2 mmol), **2** (0.24 mmol), $Pd(PPh_3)_2(OAc)_2$ (10 mol%), DPPP (11 mol%), **PA3** (50 mol%), iPr_2O (0.025 mol/L), 12 h under N_2 atmosphere at 90 °C. No isomers were observed unless otherwise noted. The regio-selectivity (*C2*:*C3*) is shown in parentheses. [a] At 80 °C. [b] There is a small amount of olefin isomers, **3**: isomer ≥ 10:1. [c] Change of conditions: $Pd(PPh_3)_4$ and DPPF were used, dioxane as solvent, at 80 °C. [d] Change of conditions: OPiv was used instead of OBoc, **2** (0.6mmol), $Pd(PPh_3)_4$ and DPPF were used, $Zn(OTf)_2$ as additive, DME as solvent, at 120 °C for 10 h.

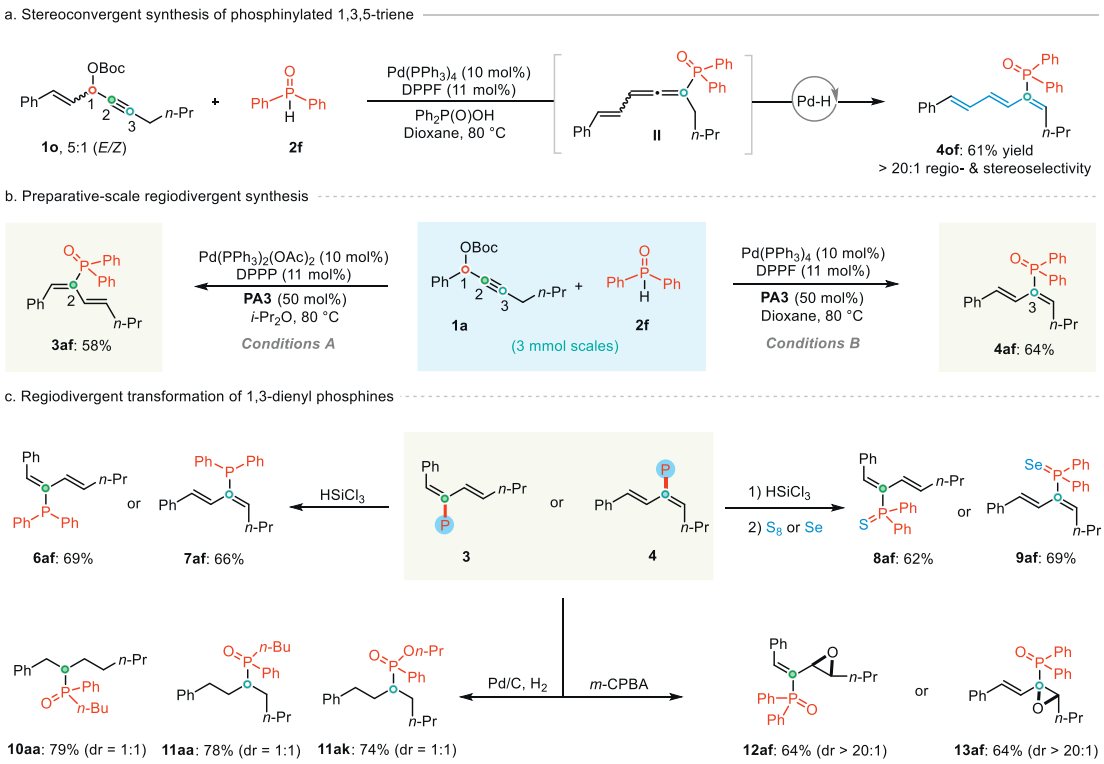


Scheme 3. *C3*-site phosphinylation/dienylation of propargylic carbonates with SPOs. Conditions B: **1** (0.2 mmol), **2** (0.24 mmol), $Pd(PPh_3)_4$ (10 mol%), DPPF (11 mol%), **PA3** (50 mol%), dioxane (0.025 mol/L), 12 h under N_2 atmosphere at 80 °C. No isomers were observed unless otherwise noted. The regio-selectivity (*C3*:*C2*) is shown in parentheses.

tency across different catalytic modes. These results underscore the broad applicability and precision of our strategy.

Using a relay catalysis strategy, we further expanded the scope to *C3*-site selective dienylation (Scheme 3). Through adjustments to the catalytic system (*e.g.*, ligands), previously explored coupling partners readily switched from *C2*- to *C3*-site selectivity while maintaining broad compatibility and high chemo-, regio-, and stereo-selectivity. Single-crystal studies revealed that while the substitution site could be toggled, the olefin geometry of dienes followed analogous stereo-chemical trends, which is consistent with steric minimization principles during the reaction.

Inspired by the robustness of this method, the reaction was applied to the skipped enyne-type propargylic ester **1o**, which was used as a 5:1 *E*/*Z* mixture (Scheme 4a). This



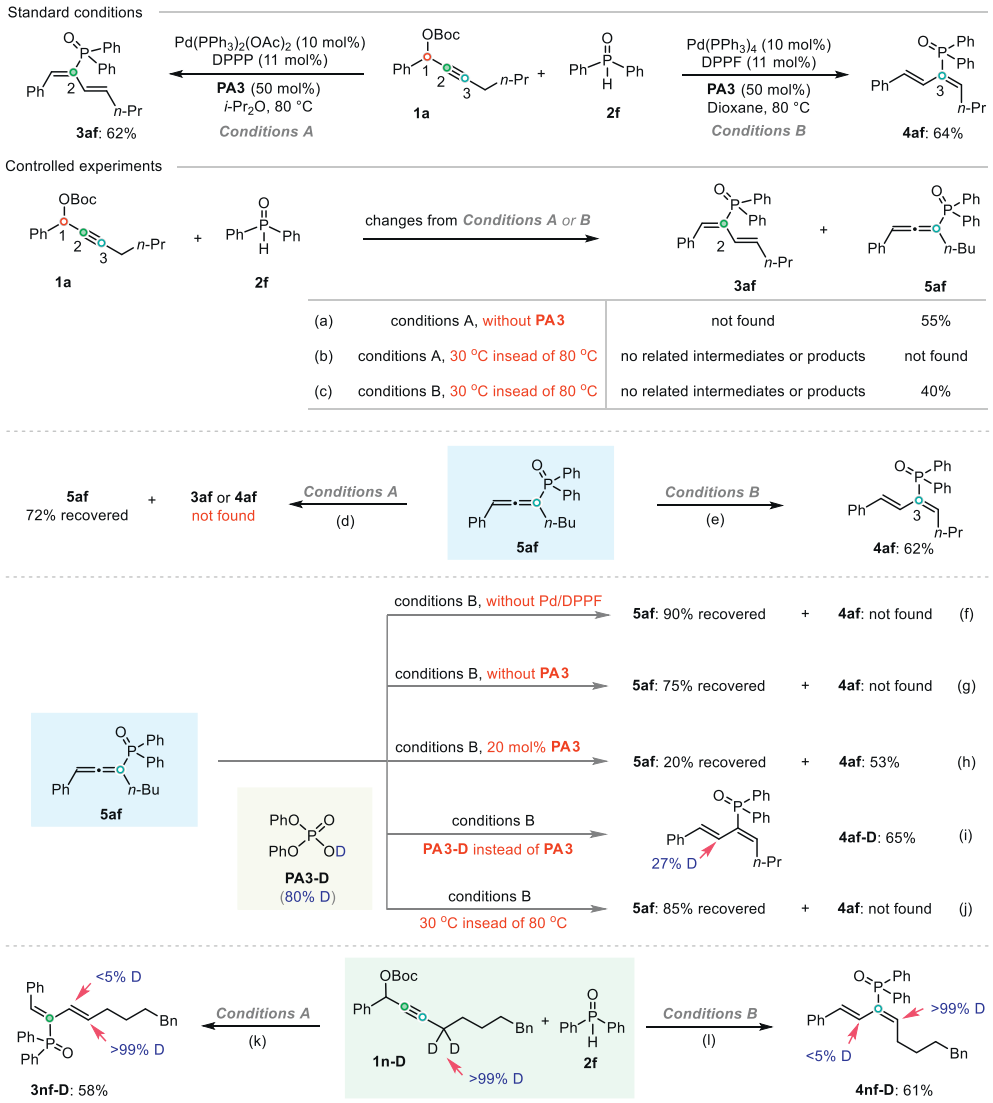
Scheme 4. Synthetic transformations.

cinnamaldehyde-derived substrate presented significant stereochemical challenges due to dynamic isomerization among complex η^1-σ-, η^3-π-allyl-Pd/propargyl-Pd/allene-Pd intermediates. Pleasingly, the palladium-catalyzed cascade reaction proceeded efficiently, affording phosphinylated 1,5-diene **4of** with excellent regio- and stereoselectivity (>20:1). This result highlights the superior selectivity control of our catalytic system and its utility for the stereoconvergent synthesis of polyconjugated alkenes from *E/Z*-mixed alkene precursors. Moreover, preparative-scale syntheses delivered equally favorable outcomes, demonstrating the synthetic efficiency and scalability of this approach (Scheme 4b). The significance of 1,3-dienyl phosphine stems from its structural flexibility and diverse reactive sites. The phosphine oxide portion can be readily transformed under conventional reduction conditions to achieve the trivalent phosphorus species (**6af**, **7af**), yielding products that serve as potential phosphine ligands or precursors for their preparation, or upon integration with chalcogens (sulfur or selenium) to generate aryl-phosphine sulfides/selenides incorporating conjugated diene moieties (**8af**, **9af**). Such distinctive molecular backbone architecture may offer organic electrode materials with enhanced performance [72,73]. Additionally, the double bond moiety undergoes efficient hydrogenation under Pd/C catalysis to furnish branched alkyl-substituted phosphine oxide frameworks (**10aa**, **11aa,** and **11ak**). Notably, the epoxidation of these conjugated dienes selectively occurs on the individual double bonds with alkyl substitution, without being affected by the position of phosphinyl substitution (**12af**, **13af**) [74]. These transformations collectively illustrated the versatility of 1,3-dienyl phosphine-derived products.

To elucidate the specific reaction path of each condition and the mechanism of site selectivity, we conducted a series of experimental studies (Scheme 5). Although standard conditions A and B exhibit nearly identical reaction profiles with different phosphine ligands, they demonstrate divergent site selectivity, suggesting distinct reaction pathways. Initial condition optimization (Table 1, entry 2, w/o additive) and control experiment (Scheme 5a) revealed that removing phosphonic acid from either conditions A or B consistently terminated the reaction at the allene product stage. These findings indicate that ligand-bite-angle modulation (DPPP *vs.* DPPF) alone cannot fully suppress reductive elimination, and latent bases in leaving groups accelerate anion coordination of SPOs, thereby promoting the transmetallation event and subsequent reductive elimination. These observations strongly imply that phosphonic acid participates in pathway regulation from the outset: Its anionic coordination preferentially occupies the fourth vacant orbital of palladium. Consequently, the reaction initially forms an allene-Pd-X intermediate (H-X = **PA3**). Subsequent anion exchange step with SPOs delays the transmetallation event, enabling pathway bifurcation.

Subsequent studies showed that the allene intermediate **5af**, under standard conditions A using a narrower-bite-angle DPPP as the ligand, cannot further convert to products **3af** or **4af** (Scheme 5d). In contrast, conditions B, which utilize a wider-bite-angle DPPF as the ligand, enable the smooth conversion of allene intermediates to the target product **4af** (Scheme 5e). These findings suggest that the allene intermediate **5af** is not the precursor of the *C2*-selective product **3af**, but is likely responsible for forming the *C3*-selective product **4af**. These results also indicate that the nature of the ligand played a key role in reaction patterns. At this stage, we reasonably assume that the bite-angle of the ligand can largely affect the reductive elimination ability of the allenyl-Pd-SPO transition state. Our control experiment demonstrates that ligands with a narrower bite angle (DPPP) may fail to weaken the Pd-**PA3** coordination affinity sufficiently [69,70], thereby inhibiting allenyl-Pd-SPO formation through anion exchange with SPOs and favoring the formation of product **3af** with excellent *C2*-selectivity. Validation experiments (Schemes 5f-h) confirm the necessity of a Pd catalyst and phosphonic acid, indicating a cooperative mechanism involving Pd/phosphonic acid.

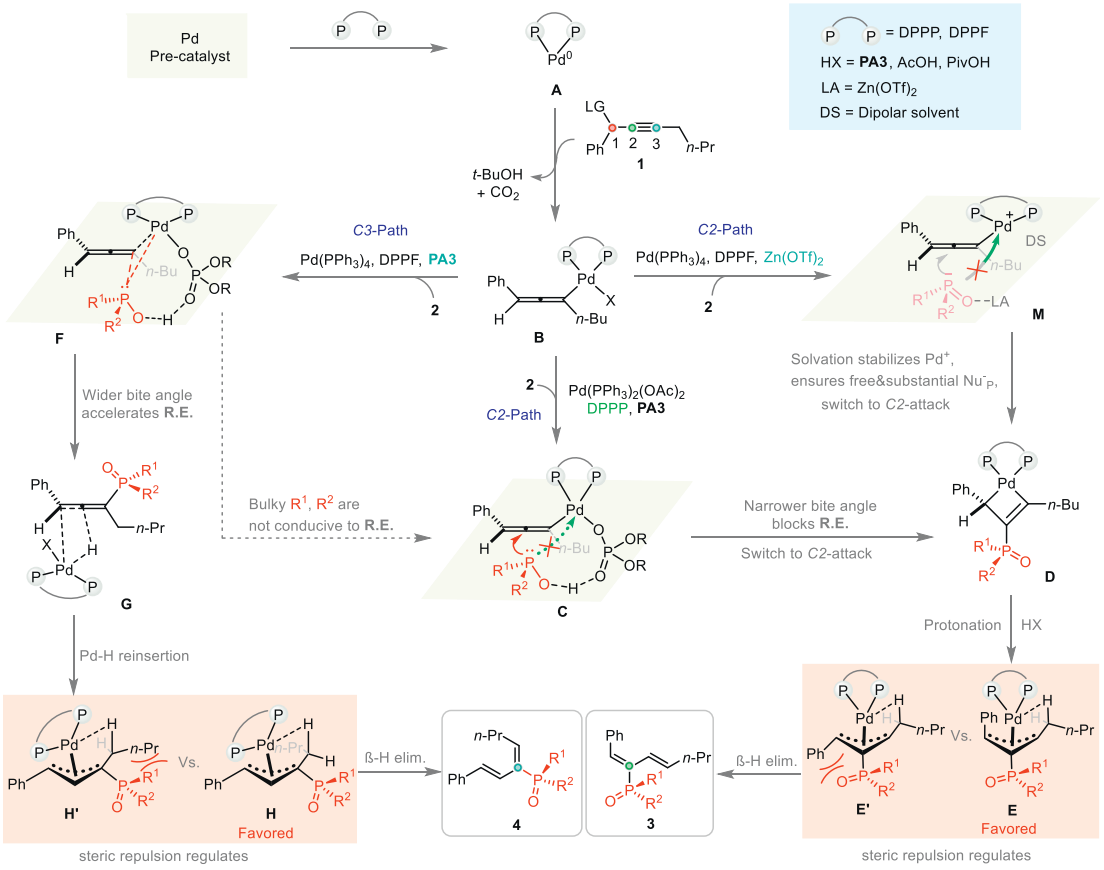
Further isotopic labeling experiments employing deuterated phosphonic acid (**PA3-D**) provided compelling evidence for a credible Pd–H insertion/elimination mechanism (Scheme 5i) govern-



Scheme 5. Controlled experiments and mechanistic studies.

ing the allene-to-diene isomerization. However, the lower reaction temperature is not conducive to the occurrence of this isomerization from allene **5af** (Scheme 5j). At the same temperature, the reaction remained capable of initiating and stably forming the allene intermediate (Scheme 5c). Notably, even when the generation of the allene intermediate was hindered by the use of a narrower-bite-angle ligand (DPPP), no intermediates or products attributable to Pd–H-mediated pathways were detected (Scheme 5b). These results imply that while prior studies of synergistic catalysis of Pd/phosphonic acid suggested preferential generation of Pd–H species to trigger hydro- or phosphinyl-palladation of alkynes [31], the putative Pd–H-involved pathway in our system requires a relatively high activation energy and does not dominate over the oxidative addition pathway under the investigated conditions. Experiments using propargylic deuterium-labeled substrates (Schemes 5k-l) under either conditions A or B fail to detect significant deuteration at the remaining site of the product, suggesting rapid flow of deuterium into the system after β-D elimination (rich in protons from secondary phosphine reagents, phosphonic acid, and solvent). Additionally, both conditions (A and B) indicate the final product of dienylation, and both are mediated by acidic reaction systems, suggesting that the reaction mechanism differs significantly from previous work [30].

Based on the above results and prior research [42,43,58,62–64], we propose the mechanism of this palladium-catalyzed divergent synthesis (Scheme 6). The process initiates with the oxidative addition of the active palladium species **A** to the propargylic esters, generating the cationic allenyl-Pd intermediate **B** [75], and then branching into different reaction paths depending on the ligand and additive used. By employing narrower-bite-angle ligand DPPP, hindered anion exchange likely drives SPOs attack at the allene central carbon (in the intermediate **C**), forming the palladacyclobutene species **D** [59–61]. For SPO with a bulky group (such as *tert*–butyl), the anion exchange process is similarly hindered, thus also favoring *C2*-site nucleophilic pathway even in the case of using wider-bite-angle ligand (Scheme 2, **3ae**). Subsequent protonation opens the palladacycle [42,43,63], yielding an η^3-π-allylpalladium intermediate **E** or **E'** (dynamic transformation of the two). Here, steric repulsion between adjacent substituents favors a *trans*-configured intermediate (intermediate **E**), which undergoes β-H elimination with high stereoselectivity to afford the *C2*-site phosphinylated diene product. On the contrary, accelerated reductive elimination is feasible with a wider-bite-angle ligand DPPF in intermediate **F**. The forming allene intermediate then undergoes Pd-H reinsertion *via* relay catalysis [51– 53] to generate a η^3-π-allylpalladium intermediate **H** or **H'**. A similar steric effect enforces the *trans*-configured intermediate **H**, ensuring stereo-selective β-



Scheme 6. Plausible mechanism.

H elimination to deliver the *C3*-site phosphinylated diene product. Separately, a Lewis acid-assisted deprotonation strategy [50] combined with the stabilization of the palladium cation by using dipolar solvent [71] generates a freely accessible, stabilized, and nucleophilically enhanced phosphine reagent, enabling priority to the *C2*-site selective attack in intermediate **M**. However, this pathway requires elevated temperatures to dissociate the coordinating anion of palladium and facilitate deprotonation, which is concerted with the action of a Lewis acid. At lower temperatures, it would inherently terminate in allene intermediate **5** (for details, see Table S2) and fail to proceed toward diene formation due to the absence of a palladium-hydride species required for further transformation.

In summary, we have developed a dynamic coordination-directed strategy that enables palladium-catalyzed highly regiodivergent dienylation of propargylic esters with secondary phosphine oxides, providing efficient access to structurally diverse 1,3-dienyl phosphines with excellent regio- and stereoselectivity. By modulating ligand-bite-angle and employing Brønsted/Lewis acid-assisted dual catalysis to tune the coordination models of SPOs, we achieved precise control over *C2- versus C3*-selectivity, demonstrating the important role of metal-phosphine oxide coordination patterns in determining regiochemical outcomes. Our mechanistic investigations revealed that this regiodivergent dienylation proceeds through relay catalysis or bimetallic cooperative pathways, which are tuned by the dynamic inner- or outer-sphere coordination of phosphine oxides with palladium. This transformation exhibits broad compatibility with diverse coupling partners while delivering high levels of chemo-, regio-, and stereoselectivity, thereby offering efficient access to complex dienyl- and polyconjugated ene-substituted phosphines. This work not only expands the synthetic toolbox for functionalized dienyl phosphines that were previously unattainable by conventional methods but also underscores the potential of coordination-controlled reactivity in addressing challenges in selective transformations. Meanwhile, the construction of dienyl phosphine compounds containing *P*-stereogenicity is ongoing in our laboratory.

CRediT authorship contribution statement

Chen Zhou: Responsible for the initial exploration of the project and main experimental work, data collection, and the organization of supporting information. **Yuxuan Shi:** Responsible for the main experimental work, data collection, and the organization of supporting information; Also be responsible for conducting supplementary experiments and collecting and organizing data during the revision of the manuscript. **Leyang Zhang:** Take on part of the experimental implementation tasks. **Mengfu Dai:** Responsible for part of the experimental guidance and data analysis. **Lanzhu Tai:** Responsible for the initial exploration of the project. **Qiang Dai:** Designed, optimized and determined this project; mainly responsible for guiding the experimental work of graduate students, formulating research plans, supervising the progress of the project, and solving experimental problems; Completed the original draft of the manuscript, and undertook the tasks of reviewing, editing and submitting. **Liang-An Chen:** Designed, optimized and determined this project; Responsible for project supervision, guidance and planning, as well as review and polishing of the manuscript. All authors discussed the results and commented on the paper.

Declaration of competing interest

All the authors in this manuscript 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

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