Nickel-catalyzed switchable 1,3-dienylation and enantioselective allenylation of phosphine oxides

The development of general catalytic methods for the regio- and stereo-selective construction of phosphoryl derivatives from identical substrates remains a formidable challenge in organic synthesis. Enabled by the newly developed BDPP-type ligands, we disclosed a nickel-catalyzed allenylation of phosphine oxides rationally and predictably, allowing the construction of versatile chiral allenylphosphoryl derivatives with high enantiopurity (up to 94% e.e.). Alternatively, using an achiral phosphine ligand dcypbz under acidic conditions, we achieved a regiochemical switch of the 1,3-dienylation to afford functionalized phosphinoyl 1,3-butadienes (up to 93% yield). The salient features of this method include switchable reactivity, broad substrate scope, readily available feedstock, single-step preparation, and high asymmetric induction.

Optically active allene-containing organic compounds have found widespread application in organic synthesis and materials chemistry\(^1\)\(^-\)\(^3\). A synthetic method that can rapidly lead to chiral substituted allenes from simple and readily available starting materials is highly desirable\(^4\)\(^-\)\(^8\). Concerning efficiency and versatility, transition metal catalysis has emerged as an attractive method to transform propargylic alcohol derivatives into propargylated\(^9\)\(^-\)\(^19\), 1,3-dienyl\(^20\)\(^-\)\(^21\), or allenyl products\(^22\)\(^-\)\(^31\) through the use of various nucleophiles\(^32\)\(^-\)\(^34\). However, control of regioselectivity in catalytic propargylic substitution reactions has rarely been demonstrated\(^35\)\(^,\)\(^36\). We hypothesized that it might be possible to tune the desired selectivities through careful choice of phosphine ligand, leading to the formation of phosphoryl derivatives with functional diversity.

Allenlyphosphine oxides and phosphinoyl 1,3-butadienes are widely recognized as synthetic intermediates\(^37\)\(^-\)\(^39\), chiral ligands\(^40\)\(^,\)\(^41\), and biologically active reagents\(^42\). Therefore, the development of enantioselective methods to access diverse allenlyphosphoryl derivatives rapidly and efficiently is highly desirable. Classical synthetic avenues toward allenlyphosphine oxide synthesis usually rely on [2,3]-sigmatropic rearrangement\(^43\)\(^-\)\(^44\). The process hitherto developed still suffers from severe limitations, such as multistep synthetic sequences, the use of relatively unstable and hazardous phosphorus chlorides, and poor tolerance of functional groups. Enantioselective couplings of propargylic alcohol derivatives with various nucleophiles have been reported to afford chiral allenes (Fig. 1A)\(^45\)\(^-\)\(^50\). Despite extensive efforts, there is no extant catalytic protocol for constructing enantiomerically enriched allenlyphosphoryl derivatives from two readily available fragments. On the other hand, transition metal-catalyzed propargylic substitution reactions have been established for carbon-phosphorus bond formation in racemic versions\(^51\)\(^-\)\(^56\). Recently, Sakata, Nishibayashi, and coworkers described the chiral ruthenium complex-catalyzed enantioselective phosphinylation of terminal propargylic alcohols delivering propargyl derivatives with high regio- and enantioselectivity (Fig. 1B)\(^57\). The Murakami group reported a seminal nickel-catalyzed reaction of propargylic carbonates with phenols for the synthesis of aryloxy-1,3-dienes\(^21\). Therefore, the development of a simplified and stereospecific strategy to access various phosphoryl derivatives would be warranted to further widen the synthetic potential of these scaffolds and build up molecular complexity. However, several challenges have to be overcome, such as (1) the selective generation of different products from identical substrates; (2) catalytic regioselective protocols utilizing ligands rather than substrate control;
and (3) the identification of reaction conditions that afford high enantioselectivities.

The allenylnickel complex, as revealed by recent elegant reports, was proposed as the key intermediate in nickel-catalyzed asymmetric propargylic substitution reactions. Therefore, we speculated that the nickel-catalytic system with the rational design and development of chiral ligands would meet the challenges above to achieve carbon-phosphorus bond formation in an asymmetric manner. In this work, we report the successful introduction of nickel-catalyzed 1,3-dienylation and enantioselective allenylation, providing phosphinoyl 1,3-butadiene with excellent chemo- and regioselectivity (Fig. 1C).

Results

Reaction optimization

In an initial experiment, the coupling reaction of racemic propargylic carbonate 1a and diphenylphosphine oxide 2a was examined (Table 1). The use of (S,S)-Ph-BPE (L1) afforded trisubstituted allylphosphine oxides 3a and phosphinoyl 1,3-buta- dienes and allylphosphine oxides with excellent chemo- and regioselectivity (Fig. 1C).

![Fig. 1](image_url)

**Fig. 1** Nickel-catalyzed regioselective strategy for 1,3-dienylation and enantioselective allenylation. A Pd-catalyzed enantioselective allenylation. B Ru-catalyzed enantioselective propargylic phosphorylation. C This work: Ni-catalyzed 1,3-dienylation and enantioselective allenylation.
Enantioselectivity was observed with the use of chiral ligand \( \text{L24} \). Further optimization studies revealed that the chiral backbone of the phosphine ligands \( \text{L25} \) and \( \text{L26} \) showed remarkable effects on the outcome of the reaction, and finally, \( \text{L23} \) was identified as the optimal choice.

Notably, the use of HCO\(_2\)Li as an additive can dramatically enhance the activity of the reaction to afford \( \text{3a} \) with 89% yield and 82% e.e. (Table 2, entry 2 vs 1). Among all the additives examined (entries 3–6), 1,3-DCP was found to give the optimum results with desired product \( \text{3a} \) obtained in 81% yield with 88% e.e. (entry 6). An increase in stereoselectivity was observed by fine-tuning the reaction conditions (entry 7).

**Substrate scope**

Having optimized the reaction conditions for the regioisomeric allylation, we next investigated the generality of the reaction substrates (Fig. 3A). A diverse array of propargylic carbonates with various alkyl substituents performed well in the presence of nickel catalyst, affording the desired products in high yields and excellent enantioselectivities (\( \text{3a-3f} \)). Propargylic carbonates with electron-donating or electron-withdrawing substituents on the benzene ring also proved to be suitable nucleophiles in the coupling reactions, thus furnishing the corresponding allenylphosphine oxides in 70–86% yield and 87–90% e.e. (\( \text{3g-3j} \)). The meta substituted propargylic carbonates also survived our catalytic conditions (\( \text{3k and 3l} \)). This method was compatible with furan and thiophene heterocycle-substituted \( \text{3m and 3n} \). Moreover, various dialkyl substituted propargylic carbonates were well tolerated, leading to the corresponding products in good yields with excellent enantioselectivity (\( \text{3o-3s} \)).

Table 1 | Condition evaluation

| Entry | \( \text{L} \) | Solvent | \( \text{3a/4a} \) | Yield (%)\(^a\) | e.e. of \( \text{3a} \) (%) |
|-------|-------------|---------|----------------|----------------|-----------------|
| 1     | \( \text{L1} \) | dioxane | 1:2            | 26             | 12              |
| 2     | \( \text{L2} \) | dioxane | 1:3            | 20             | 28              |
| 3     | \( \text{L3} \) | dioxane | <1:20          | 45             | -               |
| 4     | \( \text{L4} \) | dioxane | 3:1            | 45             | 28              |
| 5     | \( \text{L5} \) | dioxane | 7:1            | 51             | 16              |
| 6     | \( \text{L6} \) | dioxane | >20:1          | 52             | 18              |
| 7     | \( \text{L7} \) | dioxane | >20:1          | 51             | 24              |
| 8     | \( \text{L8} \) | dioxane | >20:1          | 52             | 43              |
| 9     | \( \text{L9} \) | dioxane | 3:1            | 31             | -               |
| 10    | \( \text{L10} \) | dioxane | 1:3            | 42             | -               |
| 11\(^b\) | \( \text{L3} \) | DMF     | <1:20          | 65             | -               |
| 12\(^b\) | \( \text{L10} \) | DMF     | <1:20          | 78             | -               |
| 13\(^d\) | \( \text{L8} \) | dioxane | >20:1          | 34             | 48              |
| 14\(^d\) | \( \text{L8} \) | DCM     | >20:1          | 35             | 69              |

Reactions were conducted by using Ni(COD)\(_2\) (10 mol%), \( \text{L} \) (12 mol%), \((\text{rac})-1\text{a} (0.3 \text{mmol})\), and \( 2\text{a} (0.1 \text{mmol}) \) at 80 °C, 24 h. e.e. values were determined by high-performance liquid chromatography analysis.

\(^a\)Isolated yield of the mixture \( \text{3a} \) and \( \text{4a} \) after chromatography are shown.

\(^b\)(rac)-1\text{a} (0.12 \text{mmol}), 2\text{a} (0.1 \text{mmol}), \text{Ni(COD)}\(_2\) (5 mol%), and \( \text{L3} (6 \text{mol}) \) was used.

\(^c\)(rac)-1\text{a} (0.12 \text{mmol}), 2\text{a} (0.1 \text{mmol}), \text{Ni(COD)}\(_2\) (10 mol%), \( \text{L10} (12 \text{mol}) \), and \( \text{Ph}_2\text{P(O)}\text{OH} (0.5 \text{equiv}) \) was used at 100 °C.

\(^d\)Quinuclidine (1.0 equiv) was used at 25 °C. DMF = N,N-dimethylformamide, DCM = dichloromethane.
Fig. 2 | Investigation of BDPP-type ligands in enantioselective allenylation. Reactions were conducted by using Ni(COD)$_2$ (10 mol%), L* (12 mol%), (rac)-1a (0.3 mmol), 2a (0.1 mmol), and quinuclidine (1.0 equiv) in DCM (1 mL) at 25 °C for 24 h. e.e. values were determined by high-performance liquid chromatography analysis. The isolated yields of after chromatography are shown. NR = no reaction.

Table 2 | Further optimization

| Entry | Additive | Yield (%) | e.e. of 3a (%) |
|-------|----------|-----------|---------------|
| 1     | –        | 16        | 80            |
| 2     | HCO$_2$Li (0.2 equiv) | 89        | 82            |
| 3     | HCO$_2$Li (0.2 equiv) and MeOH (3.0 equiv) | 82        | 82            |
| 4     | HCO$_2$Li (0.2 equiv) and EtOH (3.0 equiv) | 84        | 82            |
| 5     | HCO$_2$Li (0.2 equiv) and TFE (3.0 equiv) | 71        | 87            |
| 6     | HCO$_2$Li (0.2 equiv) and 1,3-DCP (3.0 equiv) | 81        | 88            |
| 7*    | HCO$_2$Li (0.2 equiv) and 1,3-DCP (3.0 equiv) | 90        | 90            |

Reactions were conducted by using Ni(COD)$_2$ (10 mol%), L23 (12 mol%), (rac)-1a (0.3 mmol), 2a (0.1 mmol), and quinuclidine (1.0 equiv) in DCM (1 mL) at 25 °C. Isolated yield of after chromatography are shown. *Quinuclidine (3.0 equiv), 10 °C, 84 h. TFE = 2,2,2-thifluoroethanol, 1,3-DCP = 1,3-dichloropropan-2-ol.
**Fig. 3** | Nickel-catalyzed enantioselective allenylation. Reactions were performed by using Ni(COD)$_2$ (10 mol%), L$_{23}$ (12 mol%), (rac)-1 (0.3 mmol), 2 (0.1 mmol), HCO$_2$Li (0.2 equiv), quinuclidine (3.0 equiv), and 1,3-DCP (30 μL) in DCM (1 mL) at 10 °C. Isolated yields after chromatography are shown. e.e. values were determined by HPLC analysis. Quinuclidine (5.0 equiv), without 1,3-DCP, 0 °C.
our attention to complementary regioselective 1,3-dienylation with the phosphine ligand dcpybz (L10). Under the optimized reaction conditions (Table 1, entry 12), a broad range of propargylic carbonates and phosphine oxides were investigated (Fig. 4). Various substituted propargylic carbonates smoothly underwent this transformation, delivering phosphinoyl 1,3-butadienes in high yields (4a–4h). The structure of 4b was confirmed by X-ray single-crystal diffraction. Phosphine oxides with different substituents on the aromatic ring also afforded good results (4i–4o).

**Synthetic applications**

To further demonstrate the practical utility of our protocol, a scale-up reaction was carried out under standard reaction conditions, furnishing 3a in 71% yield with 90% e.e. (Fig. 5A). In addition, the treatment of allenylphosphine oxide 3a with PhSeCl gave rise to desired selenohydroxylation product 5 in 86% yield with a maintained e.e.4a, and the absolute configuration of 5 was assigned by single-crystal X-ray diffraction analysis. Exposure of allenylphosphine oxide 3a to iodine in MeCN/H2O afforded 6, which was subsequently treated with acetic anhydride to generate ester 7 in high yield without loss of enantiopurity. Subsequently, the Suzuki coupling of 7 with phenylboronic acid in MeCN afforded 8 with 90% e.e. in 86% yield. 7 could also be readily reduced and then oxidized in the presence of elemental selenium and sulfur to obtain the corresponding phosphine selenide 10 and phosphine sulfide 11, respectively. In addition, propargylic carbonate 1b was subjected to 1,3-dienylation on a large scale, and the corresponding adduct 4b was obtained in 65% yield (Fig. 5B). Hydrogenation of 4b in the presence of a catalytic amount of Pd/C generated the corresponding phosphine oxide 12 in 87% yield. Furthermore, the treatment of 4b with trichlorosilane furnished the corresponding phosphine 13, which was then oxidized in the presence of elemental selenium to obtain phosphine selenide 14 in a high yield.

**Mechanistic studies**

A series of experiments were conducted to gain a better understanding of the mechanistic details of this process (Fig. 6). The reactions carried out with the racemate and both enantiomers of propargylic carbonate 1p produce good graphical overlay in the kinetic data (Fig. 6A), and under all conditions, (S)-3p was obtained in essentially identical e.e. (92% e.e.) monitored over different reaction times. Furthermore, reactions of (rac)-1p, (R)-1p (96% e.e.), and (S)-1p (93% e.e.) were separately conducted under the standard reaction conditions (Fig. 6B), and e.e. of the recovered 1p was essentially unchanged throughout the reaction process, suggesting that the irreversible oxidative addition process occurred under the reaction conditions. All these results established that the chiral ligand effectively controls the absolute configuration of the
product, regardless of the stereochemistry of the starting electrophilic substrates. The relationship between the e.e. value of L23 and that of 3p was then investigated using a ligand with different levels of enantiopurity (Fig. 6C, racemic, 20%, 40%, 50%, 60%, 80%, and >99% e.e.). Indeed, the nonlinear effect study revealed a linear relationship between the e.e. of the product, regardless of the stereochemistry of the starting electrophilic substrates. The nature of the phosphine ligands and the additives65-68. As shown in Fig. 7, the proposed catalytic cycle for the generation of allenylphosphine oxide 3 begins with the Ni-mediated decarboxylation of propargylic carbonate 1 under basic conditions with L23 as the ligand (left cycle), the in situ generated tert-butoxy anion could deprotonate hydroxydiphenylphosphine to generate the diphenyldiphosphinite anion. Therefore, the nucleophilicity of oxygen is higher than that of phosphine in 2', which might favor nickel-catalyzed O-propargylation62. Therefore, nucleophilic addition of hydroxyphosphine anion 2' onto phosphine L23-bound allenylnickel intermediate 1 provides a stereoselective route to access chiral propargyl phosphinate II62, and the following [2,3]-sigmatropic rearrangement furnishes the final allenylphosphine oxide 369. Alternatively, under acidic conditions with L10 as the ligand (right cycle), the allenylphosphine oxide 3 can be expected to be accessible by an alternative rearrangement pathway66.

Fig. 5 | Synthetic versatility of the catalytic system. A Derivatization of product 3a. B Derivatization of product 4b.
The ligand exchange of allyl nickel intermediate V with 2° and subsequent reductive elimination of nickel complex VI regenerates the nickel catalyst and furnishes final 1,3-dienyl isomer 4.

Discussion

In summary, a nickel-catalyzed 1,3-dienylation and enantioselective allenylation of phosphine oxides have been developed. The employment of different phosphine ligands allows for the highly regio- and stereoselective formation of allenylphosphoryl frameworks with excellent enantioselectivity (up to 94% e.e.) using a highly efficient type of chiral BDPP-type ligand. The high efficiency, stereoselectivity, and operational simplicity of this transformation, coupled with the rational design of chiral ligands, are expected to render this method a valuable tool in asymmetric synthesis.

Methods

General procedure for nickel-catalyzed enantioselective allenylation

In a 10 mL Schlenk tube, Ni(COD)₂ (2.8 mg, 0.01 mmol, 10 mol%), L23 (7.6 mg, 0.012 mmol, 12 mol%), and 1,3-DCP (30 μL) were stirred in 1 mL anhydrous DCM under argon at room temperature for 20 min. Propargylic carbonate 1 (0.3 mmol), phosphine oxide 2 (0.1 mmol, 1.0 equiv), quinuclidine (33.3 mg, 0.3 mmol), and HCO₂Li (1.4 mg, 0.02 mmol) were then added successively. The reaction mixture was stirred at 10 °C until the reaction was complete (monitored by TLC). The reaction mixture was concentrated, and the residue was purified by column chromatography to afford the corresponding product 3.

General procedure for nickel-catalyzed 1,3-dienylation

In a 10 mL Schlenk tube, Ni(COD)₂ (2.8 mg, 0.01 mmol, 10 mol%) and dcyplbz L10 (5.6 mg, 0.012 mmol, 12 mol%) were stirred in 1 mL anhydrous DMF under argon at 80 °C for 10 min. Propargylic carbonate 1 (0.12 mmol), phosphine oxide 2 (0.1 mmol, 1.0 equiv) and HOP(O)Ph₂ (10.9 mg, 0.05 mmol) were then added successively. The reaction mixture was stirred at 100 °C until the reaction was complete (monitored by TLC). The reaction mixture was concentrated, and the residue was purified by flash column chromatography on silica gel to give the desired product 4.

Table 3 | Additive effect on the outcome of the reaction

| Entry | L     | Additive   | Yield (%) | 3a/4a  |
|-------|-------|------------|-----------|--------|
| 1     | L4    | quinuclidine | 95        | >20:1  |
| 2     | L4    | none       | 70        | 3:1    |
| 3     | L4    | Ph₂P(O)OH  | 39        | <1:20  |
| 4     | L10   | quinuclidine | 93        | 4:1    |
| 5     | L10   | none       | 42        | 1:3    |
| 6     | L10   | Ph₂P(O)OH  | 40        | <1:20  |

Reactions were conducted by using Ni(COD)₂ (10 mol%), L (12 mol%), (rac)-1a (0.3 mmol), 2a (0.1 mmol), in dioxane (1 mL) with quinuclidine (1.5 equiv) or diphenylphosphinic acid (0.5 equiv) as additives at 80 °C, 24 h. Isolated yield of the mixture 3a and 4a after chromatography are shown.
Fig. 7 | Proposed catalytic cycle. Pathways are shown for the catalytically afforded reactive species from propargylic carbonate with nickel catalysts. Under basic condition, the phosphine L23-bound allenynickel intermediate I can react with hydroxyphosphine anion 2' to produce 3 (left cycle). Under the acidic condition, an allyl nickel intermediate V undergoes the reaction with 2'' to furnish the final 1,3-dienyl isomer 4 (right cycle).

Data availability
All data generated or analyzed during this study are included in the published Article and Supplementary Information. Crystallographic data for the structures reported in this Article have been deposited at the Cambridge Crystallographic Data Centre, under deposition numbers CCDC 2106890 (L23), 2131762 (4b) and 2120142 (5). Copies of the data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/.

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Author contributions
C.G. conceived and designed the study, and wrote the paper. J.Z., X.C., X.X., H.W., and L.P. performed the experiments and analyzed the data. All authors discussed the results and commented on the manuscript.

Competing interests
The authors declare no competing interests.

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