Angewandte Chemie International Edition

Angewandte International Edition Chemie

How to cite: *Angew. Chem. Int. Ed.* **2026**, e7982002
doi.org/10.1002/anie.7982002

COMMUNICATION

Phosphine-Catalyzed Unsymmetric [2 + 2] Annulation of Allenyl Phosphonates for Highly Substituted Cyclobutenes

Shao-Han Sun[1,2] | Sa-Na Yang[1,3] | Heng Liu[1] | Zhi-Yuan Ding[1,2] | Yilitabaier Julaiti[1,2] | Xiang-Ping Hu[1,2] | Qing-An Chen[1,2]

[1]Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, China | [2]University of Chinese Academy of Sciences, Beijing, China | [3]Avic Harbin Aircraft Industry Group Co., Ltd., Harbin, China

Correspondence: Heng Liu (liuheng@dicp.ac.cn) | Xiang-Ping Hu (xiangping@dicp.ac.cn) | Qing-An Chen (qachen@dicp.ac.cn)

Received: 3 February 2026 | **Revised:** 27 May 2026 | **Accepted:** 3 June 2026

Keywords: allene | annulation | chemistry | cycloaddition | cyclobutane | deprotonation | double bond | isomerization | Lewis acids and bases | zwitterion

ABSTRACT

Allenes, as versatile intermediates with unique cumulative double bond systems, have been widely used in cycloaddition reactions for constructing various cyclic skeletons, yet the selective synthesis of cyclobutenes via double allenes [2 + 2] annulation still remains a long-standing challenge. Herein, we report a phosphine-catalyzed unsymmetric [2 + 2] annulation of allenyl phosphonates for the efficient construction of highly substituted cyclobutenes. The reaction exhibits broad substrate scope, delivering the target cyclobutenes in moderate to good yields with exceptional *Z*/*E* selectivities and diastereoselectivities. Mechanistic studies reveal that the reaction proceeds via phosphine-induced zwitterion formation and deprotonation of allene. The Lewis acid enables precise control of diastereoselectivity, while silane effectively suppresses allene isomerization to conjugated dienes and prevents catalyst deactivation, thus ensuring reaction efficiency. Furthermore, the synthesized cyclobutene derivatives demonstrate good structural modifiability through diverse transformations. This work enriches the field of phosphine-catalyzed allene chemistry, fills a gap in allene-based [2 + 2] cyclization modes, expands the methodological toolbox for cyclobutene synthesis, and provides a versatile platform for accessing complex cyclobutene-containing molecules.

1 | Introduction

Since their discovery, allenes have been successfully employed in the synthesis of highly complex target molecules of biological and industrial significance owing to their unique reactivity [1–5]. These compounds feature a cumulative double bond system and possess a central sp-hybridized carbon atom flanked by two sp^2-hybridized carbons. This distinctive structural arrangement, which contains two perpendicular π bonds, endows allenes with higher electron density and reaction accessibility compared to alkenes bearing delocalized π-electron systems. Consequently, allenes exhibit remarkably enhanced reactivity relative to alkenes. Moreover, the electronic properties and reaction activity of each carbon center in allenes can be modulated through substitution patterns, enabling their dual role as both nucleophiles and electrophiles in diverse transformations [6–10]. Particularly, allenes have emerged as versatile intermediates in organic synthesis due to their ability to participate in a wide range of cycloaddition reactions, such as [2 + 1] [11–13], [2 + 2] [14–19], [3 + 2] [20–24], [4 + 2] [25–30], and [4 + 3] cycloadditions [31–34], which have been successfully applied to the total synthesis of natural products containing three-, four-, five-, six-, and seven-membered rings, respectively (Figure 1a) [35–40]. However, examples of constructing natural products bearing cyclobutene moieties via allene-based cycloaddition reactions remain scarce. This is partly attributed to the insufficient development of methods for cyclobutene synthesis directly from allenes.

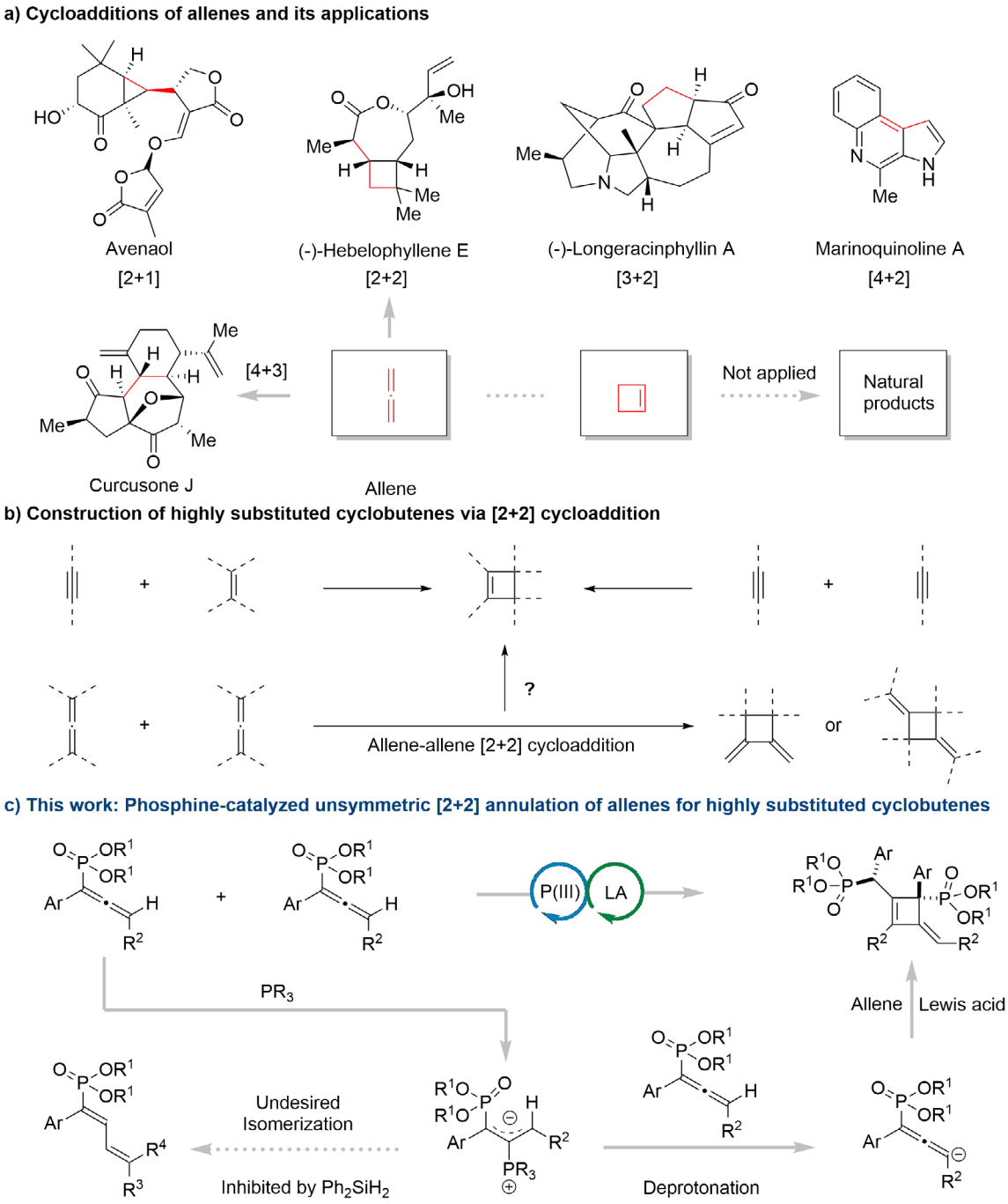
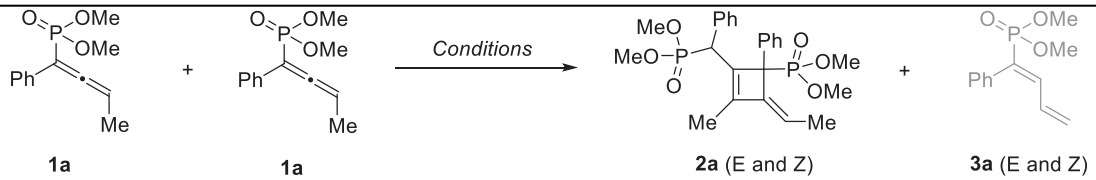


FIGURE 1 | Cycloadditions of allenes and cyclobutene constructions.

Cyclobutenes are not only prevalent in numerous natural products, bioactive metabolites, pharmaceuticals, and organic dyes [41–44] but also serve as valuable synthetic intermediates owing to their inherent ring strain and high reactivity [45–50]. In recent years, significant progress has been achieved in the direct construction of cyclobutene frameworks [51–54]. Traditional strategies primarily rely on [2 + 2] cycloaddition reactions of alkenes with alkynes or reductive [2 + 2] cycloadditions of alkynes (Figure 1b) [55–58]. Our group previously reported the synthesis of cyclobutene-containing butafulvenes from alkynes via allene intermediates [59]. However, the selective construction of a single cyclobutene product from allenes remains challenging. Current reports on the [2 + 2] cycloaddition of allenes themselves are limited to the formation of cyclobutanes, with scarce examples of cyclobutene synthesis. This deficiency stems from the underdeveloped methodologies for cyclobutene construction directly from allenes, which is hampered by the following obstacles: (1) control of reaction sites: similar to the [2 + 2] cycloaddition of allenes themselves to form cyclobutanes, the presence of cumulative double bonds in allenes often leads to the formation of mixtures derived from the reaction of different double bonds [60], thereby reducing reaction efficiency and complicating product separation. (2) Diastereoselectivity control: Unsymmetric [2 + 2] cycloadditions of unsymmetrical allenes typically generate multiple stereo centers upon double bond saturation [61], and the lack of control over these stereoselectivity severely restricts

TABLE 1 | The discovery of phosphine-catalyzed unsymmetric [2 + 2] annulation of allene.



1a + **1a** → **2a** (E and Z) + **3a** (E and Z)

Entry	Base	Yield of 2a	dr Ratio of 2a	Z/E ratio of 2a	Yield of 3a
1	^{t}BuONa	41%	1.7:1	2.5:1	n.d.
2	MeONa	35%	1.8:1	2.6:1	n.d.
3	DIPEA	n.d.	n.d.	n.d.	n.d.
4	Et_3N	n.d.	n.d.	n.d.	n.d.
5	PMe_3	38%	1:1	> 20:1	33%
6[a]	PMe_3	66%	1.4:1	> 20:1	n.d.

Note: Reaction conditions: **1a** (0.10 mmol), base (10 mol%), THF (0.50 mL), 40°C under N_2, 20 h.

[a]Ph_2SiH_2 (0.05 mmol), PMe_3 (20 mol%). Yields were determined by HPLC analysis with naphthalene as an internal standard.

their applications, especially in natural product synthesis. (3) Formation of endocyclic alkenes: Since the basic unit of allenes is carbon–carbon double bonds, [2 + 2] cycloaddition of two double bonds usually produces cyclobutanes [62–66]. Therefore, the formation of endocyclic alkenes requires avoiding this process.

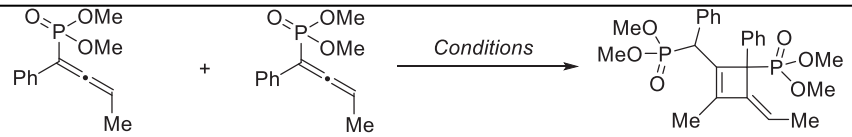
Motivated by the synthetic potential of allenes and the significance of cyclobutenes, we herein report a phosphine-catalyzed unsymmetric [2 + 2] cyclization of allenyl phosphonates for the efficient construction of highly substituted cyclobutenes (Figure 1c). The reaction proceeds through phosphine addition to allenes to form zwitterionic intermediates, which act as bases to deprotonate another allene molecule. The deprotonated allene then serves as a nucleophile to undergo nucleophilic addition with a second allene, followed by intramolecular cyclization to afford cyclobutenes. Notably, the diastereoselectivity of the reaction is effectively controlled through the coordination between Lewis acids and phosphonates. Furthermore, it was found that silanes can suppress the isomerization of allenes to conjugated dienes and prevent catalyst deactivation, ensuring the efficiency of the cycloaddition pathway. This strategy provides a convenient route to highly substituted cyclobutenes, expands the methodological toolbox for cyclobutene synthesis, and fills a gap in the [2 + 2] cyclization modes of allenes.

2 | Results and Discussion

Considering the significance of organophosphorus compounds and the easy accessibility of substrates, a phosphonate-substituted allene that can be readily synthesized via our previously developed protocol was selected as the model substrate [67]. It was initially discovered that allenyl phosphonate **1a** could perform a formal [2 + 2] reaction in the presence of a catalytic amount of ^{t}BuONa, albeit with poor *Z*/*E* selectivity and diastereoselectivity (Table 1, entry 1). Other alkoxide bases, such as MeONa, were subsequently investigated and yielded similar results (entry 2). Although the addition of amines failed to afford any desired products (entries 3 and 4), the use of trimethylphosphine (PMe_3) as a catalyst resulted in a 43% yield with excellent *Z*/*E* selectivity (> 20:1, entry 5). However, diene **3a** was identified as the major side product, arising from the isomerization of **2a** under Lewis base catalysis. Given that this isomerization [6, 68, 69] proceeds via successive proton transfer steps, proton abstraction is deemed necessary to suppress the side reaction. Silanes are known to react with various proton sources under basic conditions to form Si–O or Si–C coupling products alongside hydrogen gas [70–72]. Consequently, diphenylsilane (Ph_2SiH_2) was selected as a proton scavenger, which not only enhanced the yield of **2a** to 66% but also effectively inhibited the allene isomerization pathway (entry 6). Both PPh_3 and P(4-CF_3-C_6H_4)$_3$ failed to catalyze this reaction (Table S2, entries 10 and 12). P(4-OMe-C_6H_4)$_3$ could drive the cyclization process yet delivered a lower product yield than PMe_3 (Table S2, entry 13).

To optimize the diastereoselectivity of [2 + 2] annulation, a range of Lewis acids was screened. Strong Lewis acids such as $BF_3{\cdot}Et_2O$ and $InCl_3$ were unable to yield any products due to their ligation with PMe_3 (Table 2, entries 2 and 3). Weaker Lewis acid, on the other hand, did manage to improve the diastereoselectivity of **2a** with either yield or *Z*/*E* selectivity diminished (entries 4–7). $Fe(OTf)_2$ was eventually selected as the desired additive for its superior ability to control both diastereoselectivity and geometric selectivity. Solvents with different polarity were then investigated. When replacing THF with more polar solvents like MeCN and DMF, a dramatic decrease of both reactivity and selectivity was observed (entries 8 and 9). Using DCE would slightly decrease the yield of **2a** to 60% with moderate geometric control (entry 10). The reaction proceeded with excellent selectivity in toluene (entry 11). However, the yield of **2a** was less satisfactory compared to that in 1,4-dioxane, which also afforded good diastereoselectivity and geometric selectivity (entry 12). It was found that the number of hydrogen atoms in the silane also exerted a significant impact on the reaction outcome. Ph_3SiH reduced only the yield of **2a** while preserving good selectivity, whereas $PhSiH_3$ led to inferior results in both reactivity and selectivity (entries 13 and 14). Further optimizations were conducted by adjusting the catalyst loading,

TABLE 2 | Optimization of phosphine-catalyzed unsymmetric [2 + 2] annulation of allene.



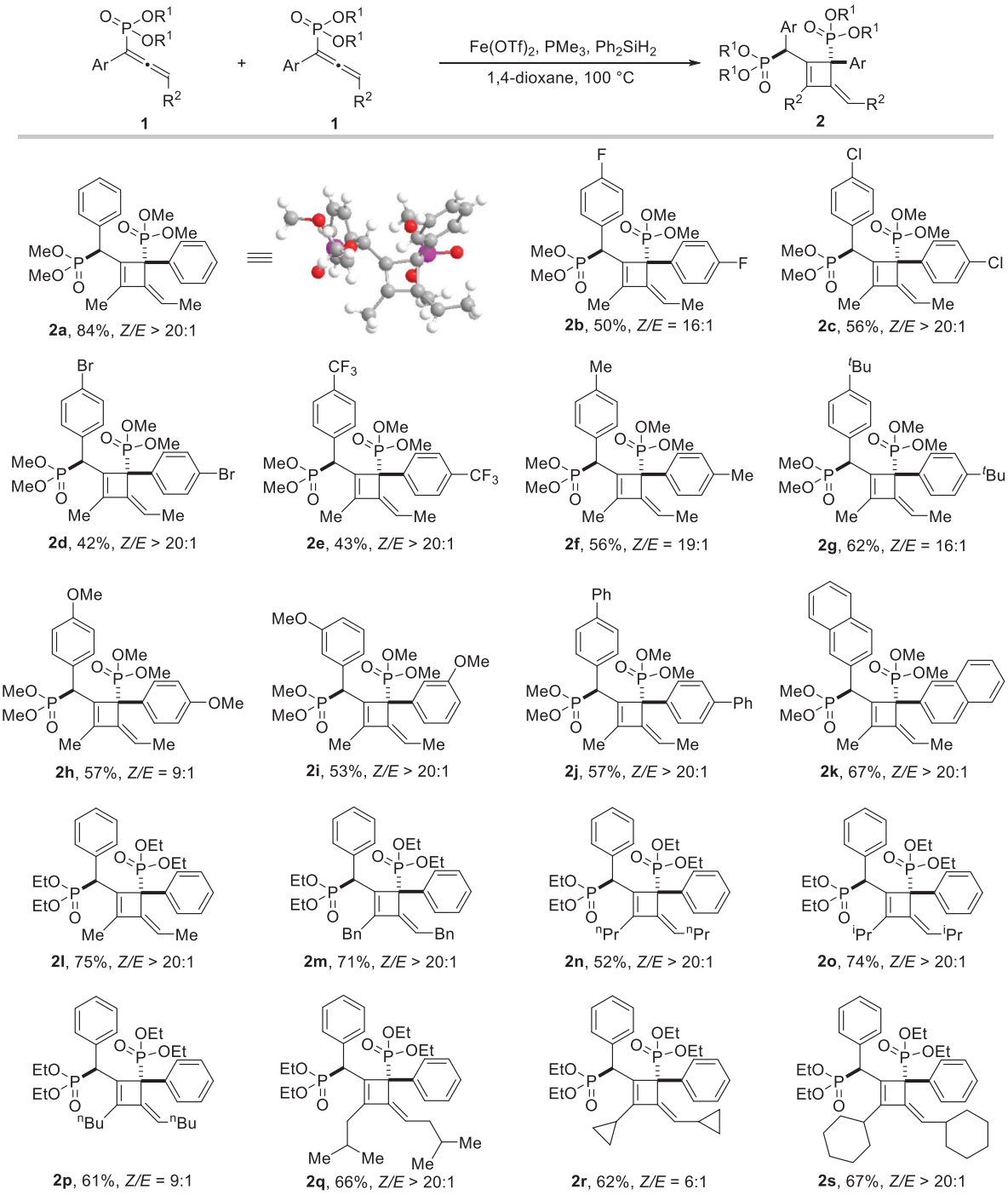
1a **1a** **2a** (E and Z)

Entry	Lewis acid	Silane	Solvent	Yield of 2a	dr of 2a	Z/E of 2a
1	None	Ph_2SiH_2	THF	66%	1:1	> 20:1
2	$BF_3{\cdot}Et_2O$	Ph_2SiH_2	THF	n.d.	n.d.	n.d.
3	$InCl_3$	Ph_2SiH_2	THF	8%	> 20:1	> 20:1
4	BPh_3	Ph_2SiH_2	THF	63%	10:1	14:1
5	$ZnCl_2$	Ph_2SiH_2	THF	39%	> 20:1	1.2:1
6	$FeCl_2$	Ph_2SiH_2	THF	62%	> 20:1	8:1
7	$Fe(OTf)_2$	Ph_2SiH_2	THF	44%	> 20:1	> 20:1
8	$Fe(OTf)_2$	Ph_2SiH_2	MeCN	28%	3:1	6:1
9	$Fe(OTf)_2$	Ph_2SiH_2	DMF	4%	n.d.	n.d.
10	$Fe(OTf)_2$	Ph_2SiH_2	DCE	60%	> 20:1	6:1
11	$Fe(OTf)_2$	Ph_2SiH_2	Toluene	43%	> 20:1	> 20:1
12	$Fe(OTf)_2$	Ph_2SiH_2	1,4-dioxane	63%	> 20:1	> 20:1
13	$Fe(OTf)_2$	$PhSiH_3$	1,4-dioxane	55%	10:1	7:1
14	$Fe(OTf)_2$	Ph_3SiH	1,4-dioxane	27%	> 20:1	> 20:1
15[a]	$Fe(OTf)_2$	Ph_2SiH_2	1,4-dioxane	82%	> 20:1	> 20:1

Note: Reaction conditions: **1a** (0.10 mmol), PMe_3 (20 mol%), Lewis acid (10 mol%), silane (0.05 mmol), solvent (0.50 mL), 80°C, N_2, 20 h.
[a]PMe_3 (10 mol%), 1,4-dioxane (0.10 mL), 100°C. Yields were determined by HPLC analysis with naphthalene as an internal standard.

reactant concentration, and reaction temperature. Ultimately, reducing the PMe_3 loading to 10 mol% while increasing the concentration of **1a** to 1.0 M at 100°C afforded product **2a** in 82% yield with excellent diastereoselectivity and geometric selectivity (entry 15).

With the optimal condition in hand, the generality of the substrate was then investigated (Figure 2). The model substrate afforded the target product **2a** in 84% isolated yield, and the product structure was unambiguously verified by X-ray single crystal analysis (CCDC: 2515075). Since halogen-substituted aryl compounds can undergo diverse subsequent transformations to enhance product modifiability, substrates bearing halogen substituents (F, Cl, Br) were first examined. All halogen-containing aryl substrates were compatible with the reaction, delivering the corresponding cyclobutene-containing products (**2b**–**2d**) in moderate yields (42%–56%). When the aryl ring was substituted with a strong electron-withdrawing group (trifluoromethyl, -CF_3), the reaction outcome (**2e**, 43%) was comparable to that of halogen-substituted substrates. In contrast, substrates with electron-donating substituents on aryl rings afforded products (**2f**–**2i**) in slightly higher yields (53%–62%) than those with electron-withdrawing groups. Notably, the substitution position of the substituents had no significant impact on the reaction efficiency or selectivity (**2h** and **2i**). Both biaryl- and naphthyl-substituted allenes also readily underwent smooth conversion to the target products (**2j** and **2k**). Replacing the methyl phosphonate group of **1a** with an ethyl phosphonate group had no major influence on the substrate's reactivity and would lead to the formation of **2l** with a 75% yield. Different γ-substituted alkyl chains were also examined in this reaction. The benzyl and isopropyl groups were well tolerated and produced **2m** and **2o** in 71% and 74% yield, respectively. Increasing the chain length of γ-substituents would result in an improvement of reactivity as indicated by **2n** (52%) and **2p** (61%). The steric bulkiness of γ-substituents had no obvious influence on product yield since isobutyl substituted **2q** and cyclohexyl substituted **2s** both gave satisfying results (66% and 67%, respectively). Besides, the strained cyclopropyl group could also serve as a suitable γ-substituent (**2r**, 62%) without the observation of ring-opening side products, which excluded the participation of γ-radical species. The phosphonate-substituent is regarded as an electron-withdrawing group that modulates the electron density of carbon atoms in allenes and boosts their electrophilicity. Allene substituted with another electron-withdrawing group, such as sulfonyl group, could be converted into the corresponding cyclobutene product (Figure S5, **2t**, 44%). In contrast, ester-substituted allene was incapable of yielding the target product (Figure S5, **2u**), which is presumably ascribed to the inherent nucleophilicity of the oxygen atom on the ester moiety in zwitterionic species [73]. To further probe the role of aryl substituents, substrates with aryl moieties replaced by alkyl groups or hydrogen were synthesized. However, none of these substrates were compatible with standard conditions (**2v**, **2w**). Notably, in the absence of $Fe(OTf)_2$, **1v** was recovered in 65% yield while the alkyne **4w** was isolated in 17% yield (Figure S5). These experimental results indicate that the aryl group likely plays a



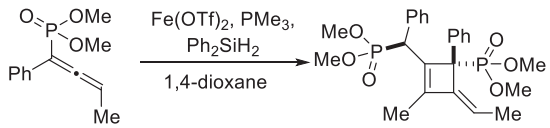
Reaction conditions: **1** (0.20 mmol), $Fe(OTf)_2$ (10 mol%), PMe_3 (10 mol%), Ph_2SiH_2 (50 mol%), 1,4-dioxane (0.20 mL), 100 °C, 20 h.

FIGURE 2 | Substrate scope of phosphine-catalyzed unsymmetric [2 + 2] annulation of allene.

crucial role in stabilizing the zwitterionic intermediate. A cross-annulation experiment was also performed with trisubstituted allene **1a** and tetrasubstituted allene **1x**. Nevertheless, no cross product was detected, and only the homo-annulation product of **1a** was obtained (Supporting Information, Section 4.2).

To investigate the reaction mechanism, control experiments were performed to determine the roles of additives. As expected, no reaction occurred in the absence of PMe_3 (Figure 3a, entry 2). Removal of Lewis acid would reduce diastereoselectivity to 2:1 (Figure 3a, entry 3). Although silane was not a necessary component for the reaction to proceed, it played a significant role in promoting the reactivity of **1a** as indicated by entries 1 and 4 (Figure 3a). Deuterium labeling experiments were then performed to shed light on the reaction pathway (Figure 3b). When Ph_2SiD_2 was used as an additive, no deuterium incorporation was observed in product **2a** (Figure 3b), indicating that silane was unlikely to directly participate in product formation.

(a) Control experiments

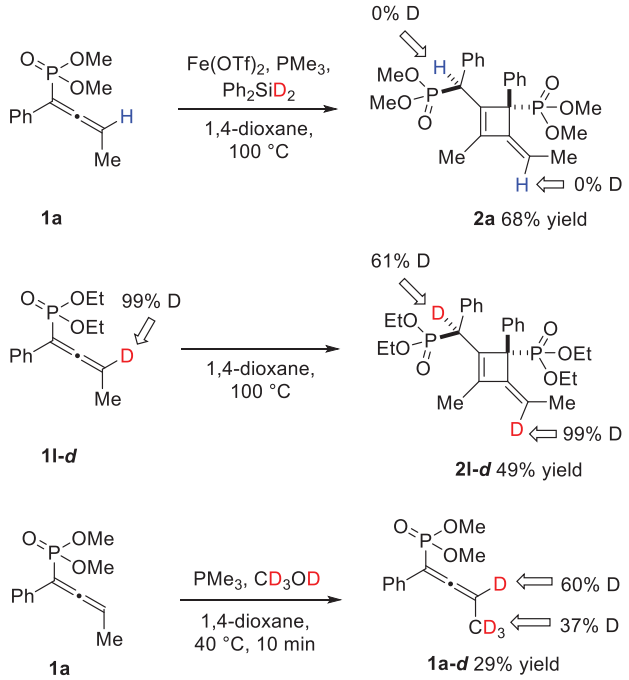


1a 2a

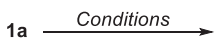
Entry	Variation of conditions	Yield of 2a	dr
1	None	82%	>20:1
2	w/o PMe_3	n.d.	n.d.
3	w/o $Fe(OTf)_2$	64%	2:1
4	w/o Ph_2SiH_2	n.d.	n.d.

Reaction conditions: **1a** (0.10 mmol), $Fe(OTf)_2$ (10 mol%), PMe_3 (10 mol%), Ph_2SiH_2 (50 mol%), 1,4-dioxane (0.10 mL), 100 °C, 20 h.

(b) Deuterium labelling experiments

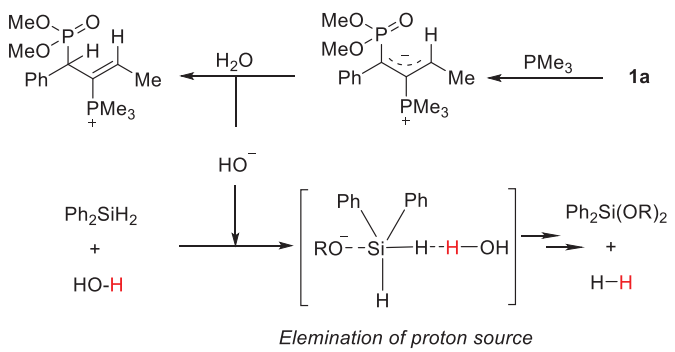


(c) Mechanism for inhibition of allene isomerization

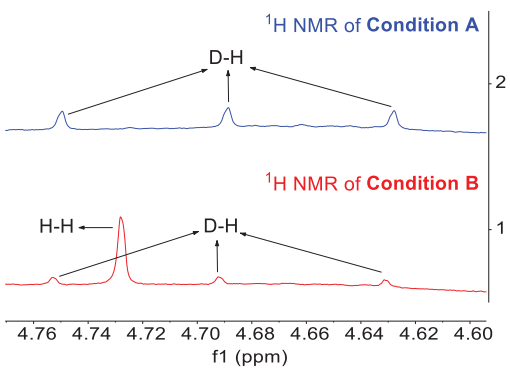


Entry	Variation of conditions	Yield of 2a	Yield of 3a
1	with H_2O	28%	48%
2	w/o H_2O	38%	33%

Reaction conditions: **1a** (0.10 mmol), PMe_3 (10 mol%), H_2O (0.02 mmol), 1,4-dioxane (0.50 mL), 40 °C.

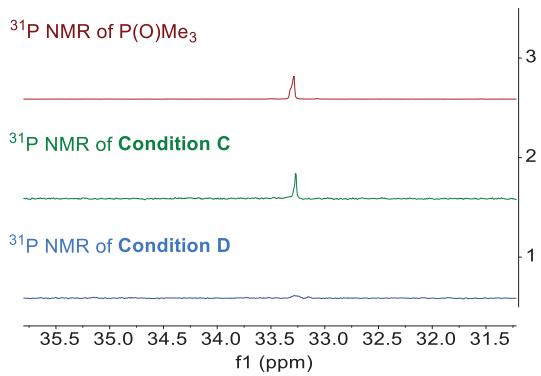


(d) Ph_2SiH_2 as proton scavenger



Condition A: **1a** (0.10 mmol), PMe_3 (1 mol%), Ph_2SiD_2 (0.05 mmol), H_2O (0.10 mmol), 1,4-dioxane (0.5 mL).
Condition B: **1a** (0.10 mmol), PMe_3 (1 mol%), Ph_2SiH_2 (0.05 mmol), D_2O (0.10 mmol), 1,4-dioxane (0.5 mL).

(e) Ph_2SiH_2 as reductant for $P(O)Me_3$



Condition C: **1a** (0.10 mmol), PMe_3 (0.01 mmol), 1,4-dioxane-d_8 (0.50 mL).
Condition D: **1a** (0.10 mmol), PMe_3 (0.01 mmol), Ph_2SiH_2 (0.05 mmol), 1,4-dioxane-d_8 (0.50 mL).

FIGURE 3 | Mechanistic studies.

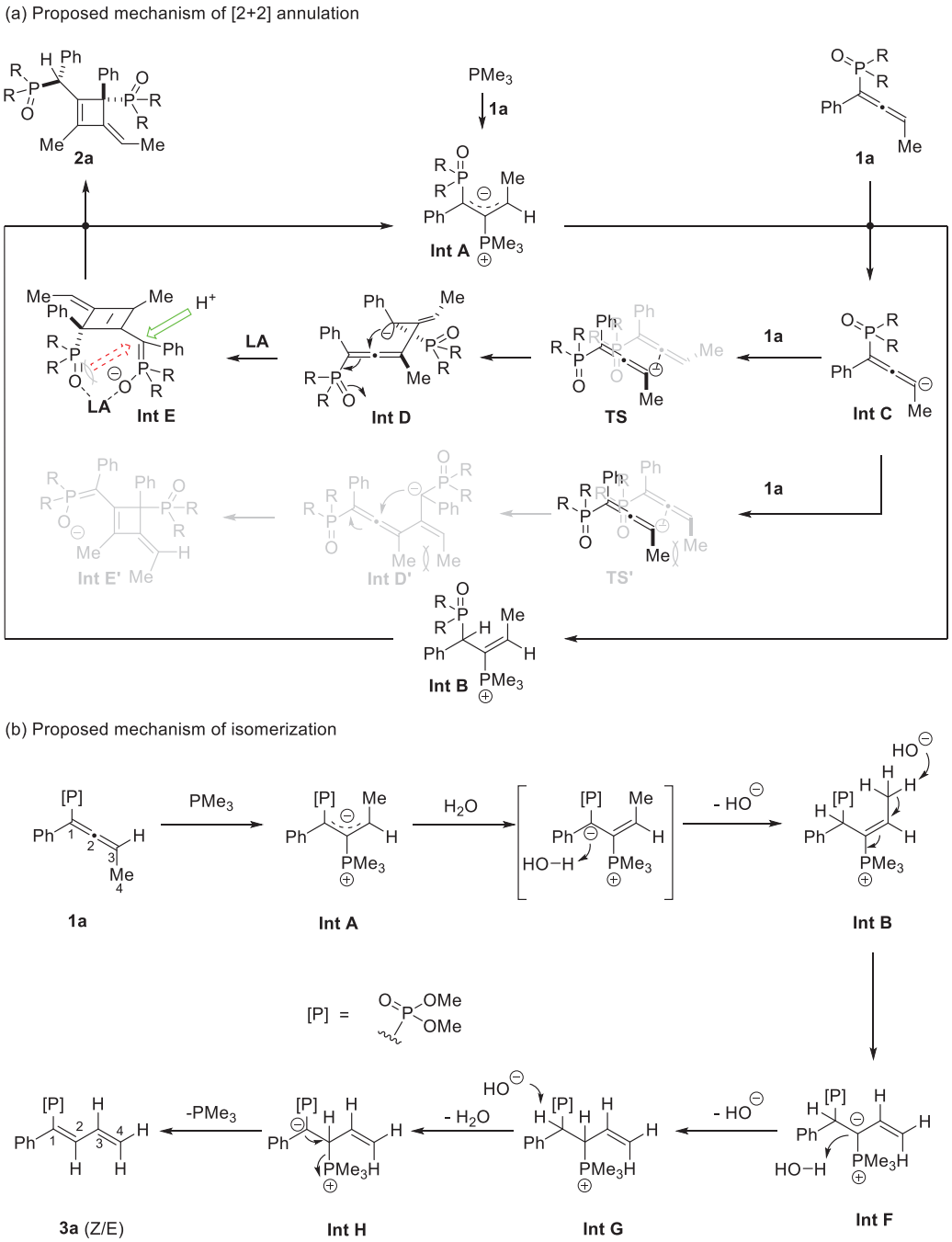


FIGURE 4 | Proposed mechanism of [2 + 2] annulation and isomerization of allenyl phosphonate.

No deuterium loss was observed at the alkenyl position when γ-deuterated **1l** was used as substrate while partial scrambling activity took place at α-carbon of the phosphonate group (Figure 3b). Importantly, γ-deuterated **1a** could be separated in 29% yield when **1a** was subjugated with CD_3OD under the catalysis of PMe_3 (Figure 3b). These findings indicated a potential deprotonation of allene under basic conditions. Kinetic profiles (Figure 3c) demonstrated a fast production of **2a** in the first 40 min at 40°C without the participation of Lewis acid (Figure S8). In the absence of silane, a slower generation of **2a** was observed (Figure S9). Besides, no inter-transformation between **2a** and side-product **3a** was detected, which ruled out the possibility of **3a** as an intermediate (Table S11).

The mechanism of silane's ability to inhibit isomerization was also studied. As previously reported, organophosphine-catalyzed allene isomerization proceeds via proton transfer [68, 69]. Furthermore, Yu et al. have demonstrated that trace water in solvents can facilitate proton transfer of allenes in phosphine-catalyzed systems [74]. Accordingly, we speculate that trace water within the solvent promotes the allene isomerization process. The control experiment demonstrated that the addition of water would significantly enhance the selectivity of the isomerization product (Figure 3c, entries 1 and 2). Silane is believed to scavenge the water under the catalysis of in situ formed carbanion, thereby inhibiting allene isomerization. When allene **1a**, Ph_2SiD_2 and H_2O were mixed with a catalytic amount of PMe_3 (Figure 3d,

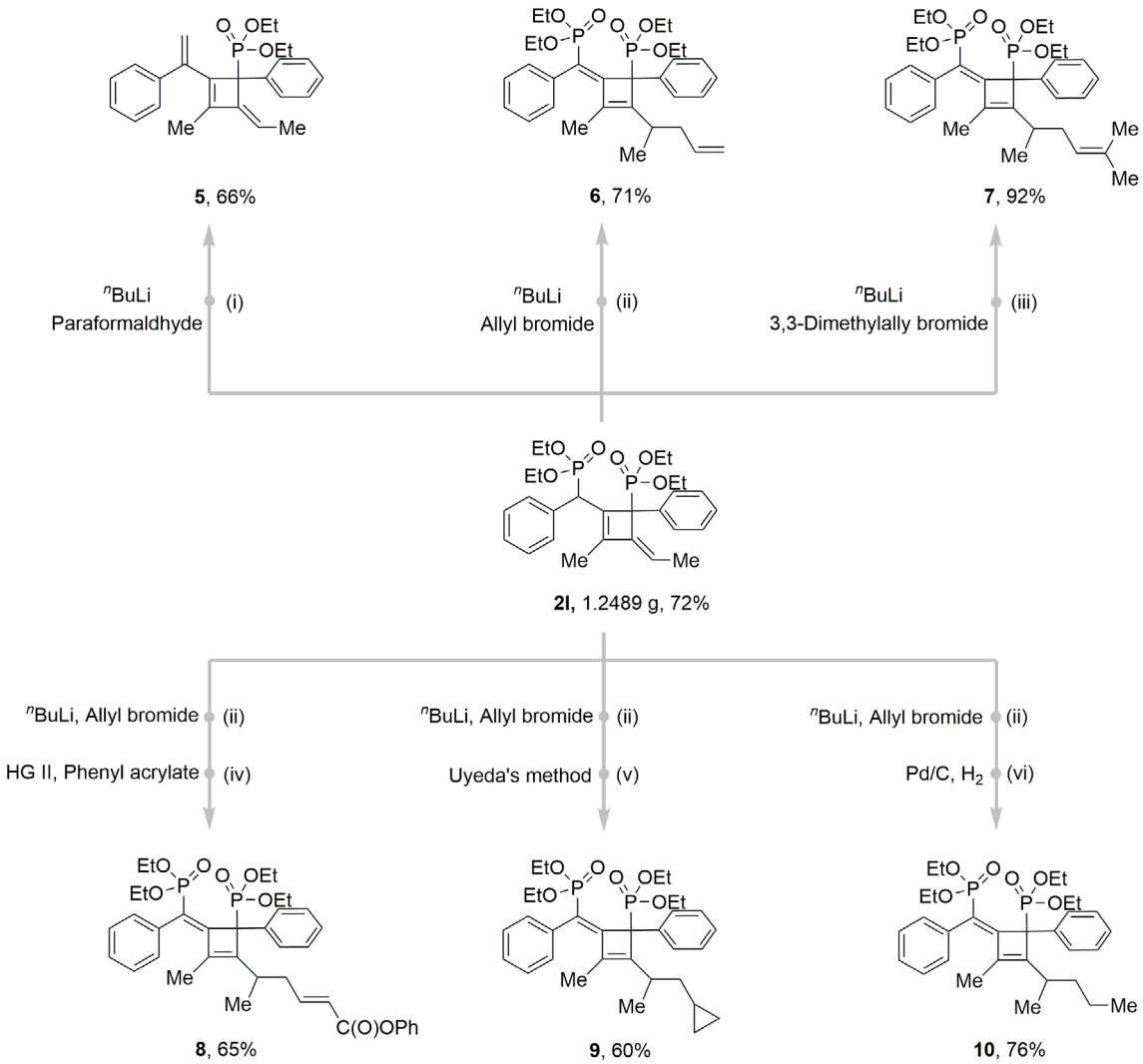


FIGURE 5 | Synthetic transformations. (i) **2l** (0.30 mmol), paraformaldehyde (3.0 mmol), ^{n}BuLi (0.30 mmol), THF (3.0 mL), 0°C to r.t.; (ii) **2l** (0.10 mmol), allyl bromide (0.50 mmol), ^{n}BuLi (0.10 mmol), THF (1.0 mL), 0°C to r.t.; (iii) **2l** (0.12 mmol), 3,3-dimethylallyl bromide (0.50 mmol), ^{n}BuLi (0.10 mmol), THF (1.0 mL), 0°C to r.t.; (iv) **6** (0.10 mmol), phenyl acrylate (0.30 mmol), second generation Hoveyda–Grubbs catalyst (0.005 mmol), DCM (1.0 mL), r.t.; (v) **6** (0.10 mmol), CH_2Br_2 (0.11 mmol), $CoBr_2$ (0.01 mmol), Et-PDI (0.01 mmol), zinc powder (0.20 mmol), THF (0.50 mL), r.t.; (vi) **6** (0.20 mmol), Pd/C (0.02 mmol), H_2 (200 psi), MeOH (1.0 mL), r.t.

condition A), rapid gas emission was observed in the course of 1 min. Subsequent ^{1}H NMR experiment demonstrated clear evidence of the formation of D-H (4.7 ppm, t, $J = 42$ Hz). Similarly, using Ph_2SiH_2 and D_2O as reactants could also produce D-H (Figure 3d, condition B). No gas emission was detected without the addition of either **1a** or PMe_3. The requirement of high loading suggested that silane might have additional roles in this reaction. When replacing PMe_3 with $P(O)Me_3$, **2a** could still be produced in 56% yield (Table S12). This finding indicated that silane could also serve as a reductant and produce PMe_3 in situ. The ^{31}P NMR spectra of a series of control experiments are presented in Figure 3e. In the absence of silane, a distinct signal corresponding to $P(O)Me_3$ was clearly observed. In contrast, this characteristic peak disappeared upon the addition of 50 mol% silane. This observation further confirms that silane acts as a reducing agent to reduce $P(O)Me_3$, thereby preserving the catalytic activity of PMe_3 and preventing its deactivation via oxidative side reactions.

Based on the results of mechanistic studies, a plausible mechanism for the phosphine-catalyzed [2 + 2] annulation of allene is proposed (Figure 4a). The phosphine catalyst will attack the β-carbon of allene to form a zwitterion species **Int A**. Given the deuterium-labeling experiment (Figure 3b, Equation 3), zwitterion **Int A** preferentially acts as a base to deprotonate **1a**, generating phosphonium ion **Int B** and allenyl carbanion **Int C**, rather than engaging in a nucleophilic reaction with **1a**. Subsequently, **Int C** dimerizes with another molecule of allene **1a** through a less congested transition state **TS** to form **Int D**. Then carbanion **Int D** undergoes intramolecular Michael addition to afford **Int E** with a cyclobutene framework and a functional group resembles an ylide. In the presence of Lewis acid, the phosphonate group and the yilde-like group are positioned at the same side of the cyclobutene plane where one side of carbon-phosphorus double bond is shielded by the bulky phosphonate group. **Int B** then approaches the nucleophilic carbon center from the less congested side, resulting in the formation of good

diastereoselectivity of **2a**. Simultaneously, the zwitterion and Lewis acid are released to participate in another catalytic cycle. A similar mechanism could also be proposed for the geometric isomer of **2a**. However, due to the significant steric hindrance of **TS'**, this pathway is kinetically less favored, thus leading to a predominant *Z*-selectivity. Based on reported literature [69, 74] and experimental results, a plausible mechanism is proposed for isomerization of **1a** (Figure 4b). Nucleophilic attack of C2 by phosphine catalyst leads to the formation of **Int A**. The protonation of **Int A** produces **Int B**, which is deprotonated at C3 and forms **Int F**. Under the mediation of proton source, a formal 1,2-proton shift is accomplished via **Int G** and **Int H**. The subsequent elimination of PMe_3 produces diene **3a**.

To demonstrate the structural modifiability of the products, various transformations of the cyclobutene derivatives were attempted. Notably, the reaction maintained a good yield when conducted on a gram scale (Figure 5). After isolating 1.2489 g of product **2l** in 72% yield, the Horner-Wadsworth-Emmons (HWE) reaction was successfully performed using paraformaldehyde as a reactant, affording triene **5** in 66% yield. Due to the steric-congested nature of the HWE intermediate generated by **2l**, further increasing the bulkiness of the aldehyde would severely hamper the reactivity. Allyl bromide was also utilized as an electrophile in constructing a *tetra*-substituted carbon center adjacent to phosphonate group. Surprisingly, the exocyclic double bond was functionalized and gave high functionalized cyclobutane **6** in 71% yield. A prenyl group could be selectively introduced for the formation of product **7** through the reaction with 3,3-dimethylallyl bromide as a substrate. The non-conjugated alkenyl group of **6** could easily perform cross metathesis reaction and produce internal alkene **8** in 65% yield. Under the cobalt catalyzed protocol developed by Uyeda et al. [75], cyclopropanation of **6** was successfully carried out and delivered cyclopropane **9** in 60% yield. A facile hydrogenation of **6** under the catalysis of Pd/C was conducted and gave desired product **10** in 76% yield. The success of these transformations demonstrates that our products exhibit excellent structural modifiability, thereby enabling the synthesis of a variety of complex compounds bearing a cyclobutene scaffold.

In summary, we have successfully developed a phosphine-catalyzed unsymmetric [2 + 2] annulation of allenyl phosphonates, offering an efficient and selective strategy for the construction of highly substituted cyclobutenes. The rational combination of phosphine catalysis, Lewis acid modulation, and silane-mediated proton scavenging enables the selective formation of endocyclic alkenes in cyclobutenes. The protocol exhibits good substrate generality, which underscores the robustness of the catalytic system and its potential for applications in complex molecule synthesis. Mechanistic studies have elucidated the reaction pathway, involving zwitterion formation, deprotonation, dimerization, and intramolecular cyclization. This proposed mechanism provides valuable insights for the design of analogous phosphine-catalyzed annulation reactions. In addition, the synthesized cyclobutene derivatives demonstrate excellent structural modifiability, highlighting the utility of the products as versatile intermediates for accessing complex cyclic scaffolds. This work enriches the field of phosphine-catalyzed allene chemistry, fills a gap in allene [2 + 2] cyclization modes, and expands the synthetic toolbox for cyclobutenes.

Author Contributions

Shao-Han Sun: conceptualization, methodology, investigation, writing – original draft, data curation. **Sa-Na Yang**: conceptualization, methodology. **Heng Liu**: supervision, project administration, funding acquisition, writing – review and editing, writing – original draft, formal analysis. **Zhi-Yuan Ding**: writing – review and editing, validation, investigation. **Yilitabaier Julaiti**: writing – review and editing, investigation, validation. **Xiang-Ping Hu**: supervision, project administration, writing – review and editing. **Qing-An Chen**: supervision, project administration, funding acquisition, writing – review and editing, conceptualization, writing – original draft, resources.

Acknowledgments

This work was financial support by the National Natural Science Foundation of China (22402191), the Natural Science Foundation of Liaoning Province (2024JH3/50100006), and the Dalian Science and Technology Talent Innovation Support Policy Project (2024RQ088).

Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting File 1: anie73234-sup-0001-SuppMat.pdf.