SCIENCE CHINA
Chemistry

•ARTICLES•
SPECIAL ISSUE: In Honor of Professor Lixin Dai on the Occasion of His 100th Birthday

October 2023 Vol.66 No.10: 2810–2816
https://doi.org/10.1007/s11426-023-1744-2

Palladium-catalyzed allylic alkylation enabled by ketone umpolung *via* Pudovik addition/[1,2]-phospha-Brook rearrangement

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Received June 30, 2023; accepted August 10, 2023; published online September 11, 2023

Palladium-catalyzed allylic alkylation enabled by ketone umpolung *via* Pudovik addition/[1,2]-phospha-Brook rearrangement with phosphites has been developed. The protocol offers a straightforward method for the synthesis of potentially bioactive homoallylic alcohol phosphonates in an efficient and economical way. This cascade reaction proceeds under mild conditions with excellent functional group compatibility. Furthermore, the catalytic asymmetric version has also been explored.

palladium, umpolung, allylic alkylation, Pudovik addition, [1,2]-phospha-Brook rearrangement

Citation: Zhang J, Su JY, Liu YZ, Li H, Wang Q, Deng WP. Palladium-catalyzed allylic alkylation enabled by ketone umpolung *via* Pudovik addition/[1,2]-phospha-Brook rearrangement. *Sci China Chem*, 2023, 66: 2810–2816, https://doi.org/10.1007/s11426-023-1744-2

1 Introduction

Transition-metal (TM) catalyzed allylic alkylation has emerged as a powerful tool for the construction of both carbon–carbon and carbon–heteroatom bonds *via* the π-allyl-transition-metal species (Scheme 1a) [1]. In this field, the development of different nucleophilic species has been a research focus. Notably, the novel nucleophilic species generated *via* carbonyl umpolung stand out as a key building block in constructing complex molecules and pharmaceuticals [2]. Therefore, the application of these nucleophilic species in transition-metal catalyzed allylic substitution attracts intense attention. Recently, Ohmiya *et al*. [3], Liu *et al*. [4], and Ye *et al*. [5] realized the desired umpolung allylic alkylations of aldehyde compounds *via* creative NHC/TM cooperative catalysis systems (Scheme 1b). Last year, Hasegawa and Sawamura [6] reported visible-light-induced copper-catalyzed umpolung allylic alkylations with pre-prepared acylsilanes (Scheme 1b). Besides, Ohmiya *et al*. [7] developed a Cu/Pd cooperative catalyzed umpolung allylation to produce a homoallylic secondary alcohol. Despite these preceding extensive studies, the homoallylic tertiary alcohol derivatives, which have extensive application for the synthesis of natural products [8], could not be furnished by the umpolung allylic alkylation of ketones so far (Scheme 1c). In this regard, the development of TM catalyzed allylic alkylation enabled by ketone umpolung to furnish homoallylic tertiary alcohol derivatives is still in great hunger.

Pudovik addition/[1,2]-phospha-Brook rearrangement is an efficient method to synthesize tertiary alcohol phosphonates from ketones *via* a umpolung progress (Scheme 2a) [9]. In previous reports by Terada [10], Johnson, Ooi [11], Liu, Feng [12], and other groups [13], the active umpolung nucleophilic intermediates were trapped by stable electrophilic species or proton and numerous valuable organic phosphorus compounds were constructed, which are key frameworks in plentiful potential bioactive molecules [14]. Hence, we envisaged that the employment of *in situ* generated π-allyl-palladium species to catch the umpolung nucleophilic intermediates, which is produced from ketones and phosphites *via* Pudovik addition/[1,2]-phospha-Brook rearrangement,

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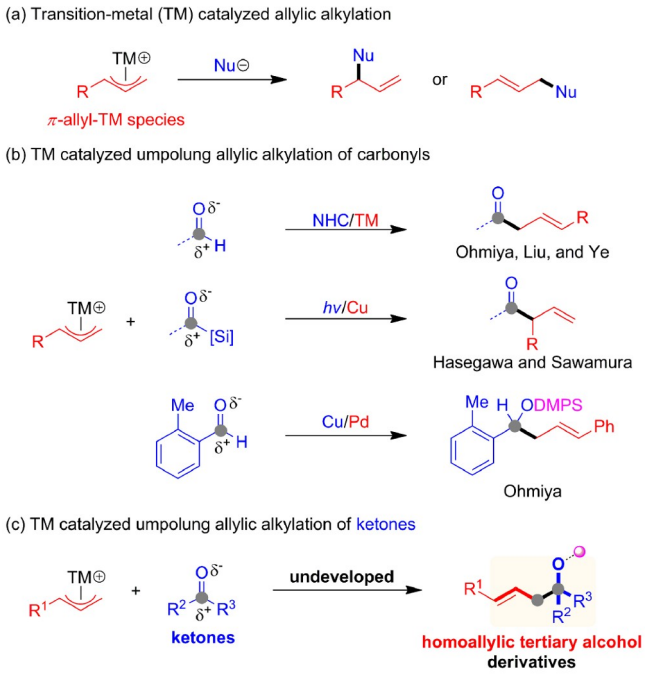
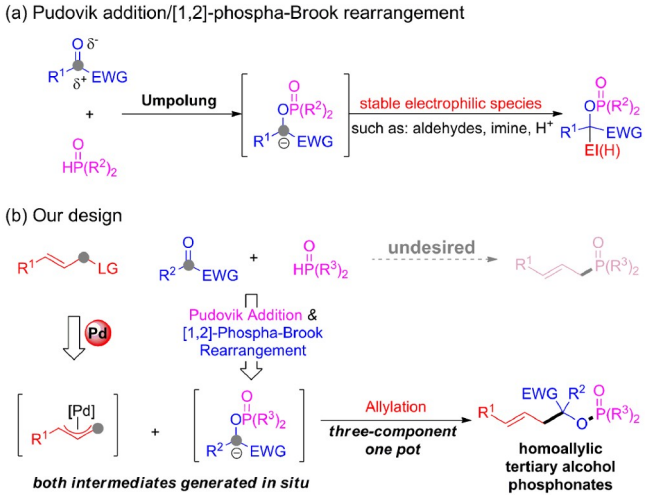
which could provide a series of the desired potentially bioactive homoallylic alcohol phosphonates (Scheme 2b). Although this protocol is theoretically feasible, there are still some obstacles. Both the nucleophilic species and the π-allyl-palladium electrophilic species are generated *in situ*, their reactivity should be matched. Besides, in this three-component reaction, the direct allylations of phosphine reagent will compete with the target reaction, which make the chemo-selectivity challenging [15]. Finally, the potential coordination of phosphine compounds with palladium may cease the reaction.



Scheme 1 Transition-metal catalyzed allylic alkylations (color online).



Scheme 2 Palladium-catalyzed allylic alkylation enabled by ketone umpolung (color online).

2 Experimental

General procedure for the synthesis of **4**. Under nitrogen atmosphere, a dried Schlenk tube (10 mL) with a magnetic stir bar was charged with $Pd_2dba_3{\cdot}CHCl_3$ (2.6 mg, 0.0025 mmol, 2.5 mol%), **L7** (3.7 mg, 0.006 mmol, 6 mol%) and anhydrous tetrahydrofuran (1.0 mL). The mixture was stirred at room temperature for 30 min. Then the reaction mixture was cooled to 0 °C in an ice bath, and allyl carbonates **1** (0.11 mmol, 1.1 equiv.), α-ketoesters **2** (0.15 mmol, 1.5 equiv.), phosphites **3** (0.10 mmol, 1.0 equiv.), and LiHMDS (0.1 mL, 0.10 mmol, 1.0 equiv., 1.0 M in tetrahydrofuran (THF)) were added subsequently. After that, the reaction mixture was stirred at room temperature. Once completion (all cases finished within 1 h), the reaction mixture was diluted with ethyl acetate, and filtered through a celite pad. The filter cake was washed with ethyl acetate and the combined organic phase was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford products **4**. More details can be found in the Supporting Information online.

General procedure for the synthesis of **7**. Under nitrogen atmosphere, a dried Schlenk tube (10 mL) with a magnetic stir bar was charged with $Pd_2dba_3{\cdot}CHCl_3$ (2.6 mg, 0.0025 mmol, 2.5 mol%), **L7** (3.7 mg, 0.006 mmol, 6 mol%) and anhydrous tetrahydrofuran (1.0 mL). The mixture was stirred at room temperature for 30 min. Then the reaction mixture was cooled to 0 °C in an ice bath, and *tert*-butyl cinnamyl carbonate **1C** (0.12 mmol, 1.2 equiv.), isatins **6** (0.10 mmol, 1.0 equiv.), diethyl phosphite **3a** (0.12 mmol, 1.2 equiv.) and LiHMDS (0.12 mL, 0.12 mmol, 1.2 equiv., 1.0 M in THF) were added subsequently. After that, the reaction mixture was stirred at room temperature. Once completion (all cases finished within 2 h), the reaction mixture was diluted with ethyl acetate, and filtered through a celite pad. The filter cake was washed with ethyl acetate and the combined organic phase was concentrated under reduced pressure. The crude residue was purified by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 10:1) to afford products **7**. More details can be found in the Supporting Information online.

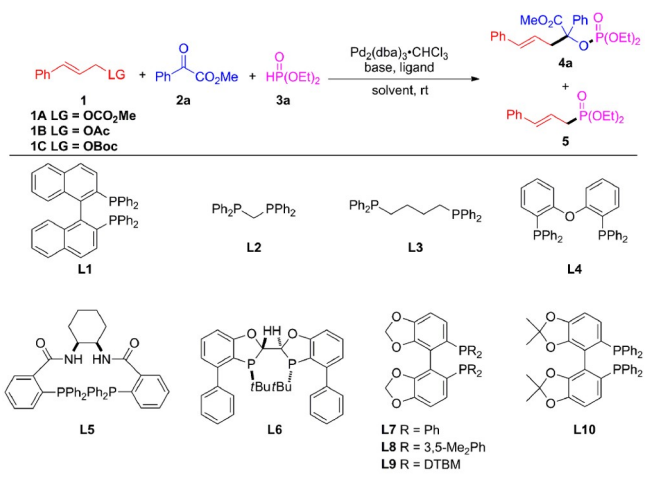
3 Results and discussion

3.1 Optimization studies

We commenced our study by employing allyl methyl carbonate **1A** (1.0 equiv.), phenyl α-ketoester **2a** (1.5 equiv.), and diethyl phosphite **3a** (1.5 equiv.) as model substrates with $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%), **L1** (Binap) (6 mol%), and LiHMDS (1.5 equiv., 1.0 M in THF) in tetrahydrofuran (1.0 mL) at 0 °C to room temperature. Gratifyingly, the

desired Pudovik addition/[1,2]-phospha-Brook rearrangement/allylation cascade reaction proceeded smoothly with excellent chemo- and regio-selectivity, producing the desired product **4a** in *E*-configuration in 71% yield (Table 1, entry 1). Encouraged by the result, various bases were evaluated to improve the yield, revealing that LiHMDS exhibited the optimal reactivity (Table 1, entries 2–4; more details shown in Table S1, entries 3–7, Supporting Information online). A panel of bidentate phosphine ligands were screened for this reaction. The usage of **L2** (DPPM) did not work (Table 1, entry 5) perhaps due to the difficulties in forming stable bidentate coordination with palladium. The reaction with **L3** (DPPB) and **L4** (DPEphos) failed to give better results (**L3** 61% yield, Table 1 entry 6; **L4** 65% yield, Table 1, entry 7). Notably, when **L5** (Trost ligand) was used, no target product **4a** was detected. We think the amide hydrogen of the **L5** may be captured by the LiHMDS, which destroy the coordination between ligand and metal. However, the reaction afforded the byproduct **5** (9% yield), which did not be detected in our study before, *via* allylation of diethyl phosphite **3a** (Table 1, entry 8). The usage of **L6** (BIBOP) resulted in 46% yield for **4a** (Table 1, entry 9) [16]. To our delight, the usage of **L7** (Segphos) improved the yield of **4a** to 78% (Table 1, entry 10) and the modification on **L7** gave slightly reduced yields (Table 1, entries 11–13). Other screening of mono or bidentate phosphine ligands did not enhance the yields of **4a** inferior to **L7** (details shown in Table S1, entries 14–19). Additionally, two bisoxazoline ligands were evaluated and the yields of **4a** were unsatisfactory (details shown in Table S1, entries 20 and 21). By the way, the reaction performed with $Pd(PPh_3)_4$ without any extra ligands provided **4a** in only low level of yield (28%) (Table 1, entry 14). Then, the molar ratios of **1a**, **2a**, **3a**, and LiHMDS were investigated. The reaction with a **1a**/**2a**/**3a**/LiHMDS molar ratio of 1.1:1.5:1.0:1.0 gave a better yield (90%) (Table 1, entry 15). To test the effect of the leaving group (Ac, Boc) on the allyl moiety in this reaction, various cinnamyl alcohol derivatives were subjected to the reaction conditions (Table 1, entries 16 and 17). The reaction conducted with *tert*-butyl cinnamyl carbonate (**1C**) gave **4a** in the highest yield (94%) (Table 1, entry 17). Further investigation of the effect of different solvents (Table 1, entries 18 and 19) uncovered that tetrahydrofuran was optimal. In addition, control experiments revealed the necessities of $Pd_2dba_3{\cdot}CHCl_3$ and ligand **L7** (Table 1, entries 20 and 21). Ultimately, the optimum conditions found consisted of performing this reaction with allyl carbonates **1** (1.1 equiv.), α-ketoesters **2** (1.5 equiv.), phosphites **3** (1.0 equiv.), and LiHMDS (1.0 equiv.) in tetrahydrofuran (*c* 0.1 M) at 0 °C to room temperature in the presence of $Pd_2dba_3{\cdot}CHCl_3$ (2.5 mol%), **L7** (6 mol%).

Table 1 Optimization of the reaction conditions [a]



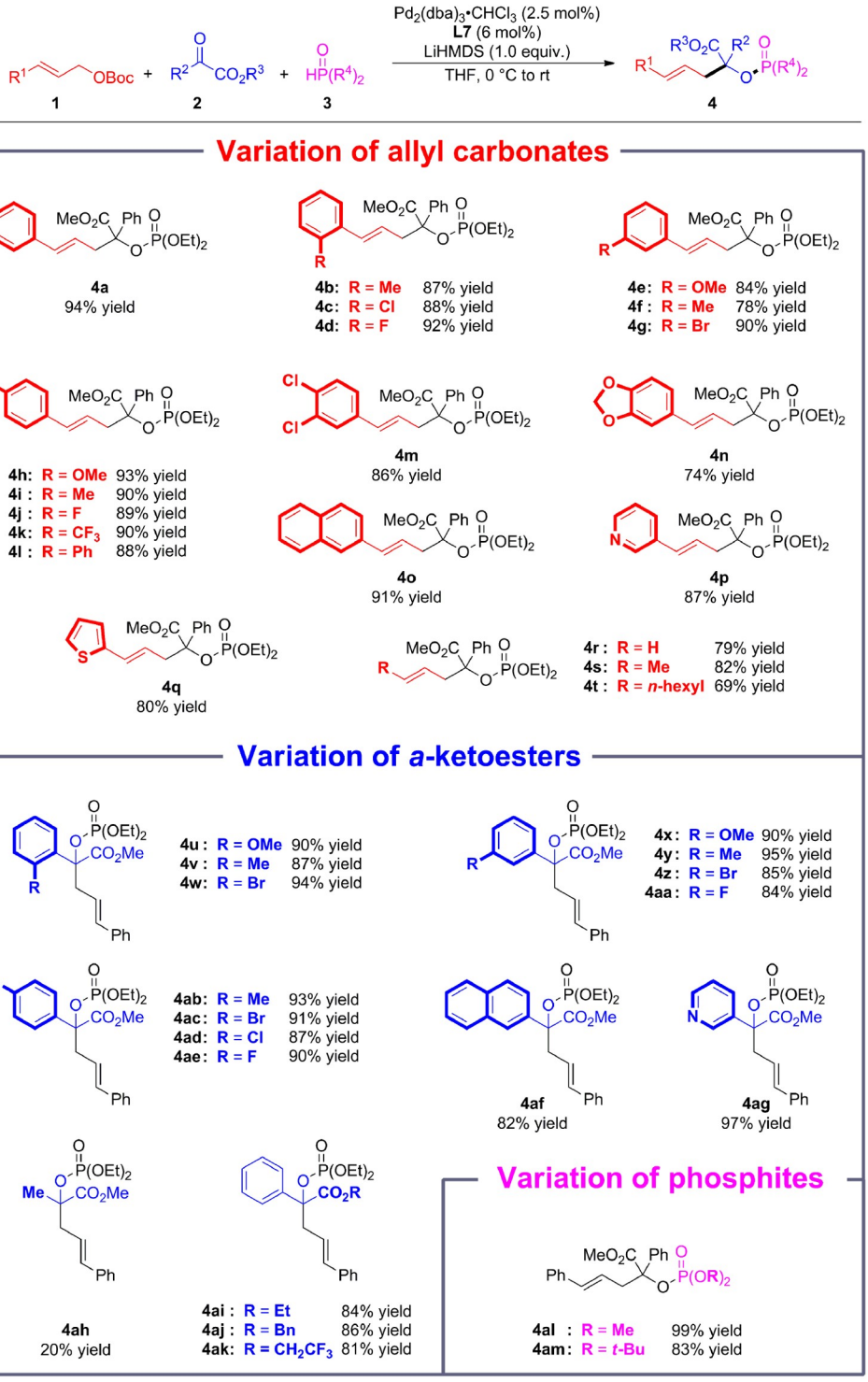
Entry	Base	Ligand	LG	Solvent	Yield (**4a**) [b]
1	LiHMDS	**L1**	OCO_2Me	THF	71
2	LiO*t*Bu	**L1**	OCO_2Me	THF	60
3	DBU	**L1**	OCO_2Me	THF	Trace
4	DIPEA	**L1**	OCO_2Me	THF	–
5	LiHMDS	**L2**	OCO_2Me	THF	Trace
6	LiHMDS	**L3**	OCO_2Me	THF	61
7	LiHMDS	**L4**	OCO_2Me	THF	65
8	LiHMDS	**L5**	OCO_2Me	THF	–
9	LiHMDS	**L6**	OCO_2Me	THF	46
10	LiHMDS	**L7**	OCO_2Me	THF	78
11	LiHMDS	**L8**	OCO_2Me	THF	71
12	LiHMDS	**L9**	OCO_2Me	THF	74
13	LiHMDS	**L10**	OCO_2Me	THF	73
14 [c]	LiHMDS	-	OCO_2Me	THF	28
15 [d]	LiHMDS	**L7**	OCO_2Me	THF	90
16 [d]	LiHMDS	**L7**	OAc	THF	69
17 [d]	LiHMDS	**L7**	OBoc	THF	94
18 [d]	LiHMDS	**L7**	OBoc	DCM	Trace
19 [d]	LiHMDS	**L7**	OBoc	Toluene	33
20 [d], [e]	LiHMDS	**L7**	OBoc	THF	–
21 [d]	LiHMDS	–	OBoc	THF	–

a) Reactions conditions: **1** (0.10 mmol), **2a** (0.15 mmol), **3a** (0.15 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (0.0025 mmol), ligand (0.006 mmol), and base (0.15 mmol) in solvent (1.0 mL) at 0 °C to room temperature for 1 h unless otherwise noted. b) Isolated yield of **4a**. c) $Pd(PPh_3)_4$ (5 mol%) instead of $Pd_2dba_3{\cdot}CHCl_3$. d) **1** (0.11 mmol), **2a** (0.15 mmol), **3a** (0.10 mmol), LiHMDS (0.10 mmol). e) Without $Pd_2dba_3{\cdot}CHCl_3$.

3.2 Versatility

After the optimum conditions identified, we next examined the substrate scope. As summarized in Table 2, an array of allyl carbonates containing with electron-rich and electron-deficient substituents in the *ortho* (*o*-Me, *o*-Cl, *o*-F), *meta* (*m*-OMe, *m*-Me, *m*-Br), and *para* (*p*-OMe, *p*-Me, *p*-F, *p*-CF_3,

Table 2 Substrate scope of Pudovik addition/[1, 2]-phospha-Brook rearrangement/allylation cascade reaction [a)]



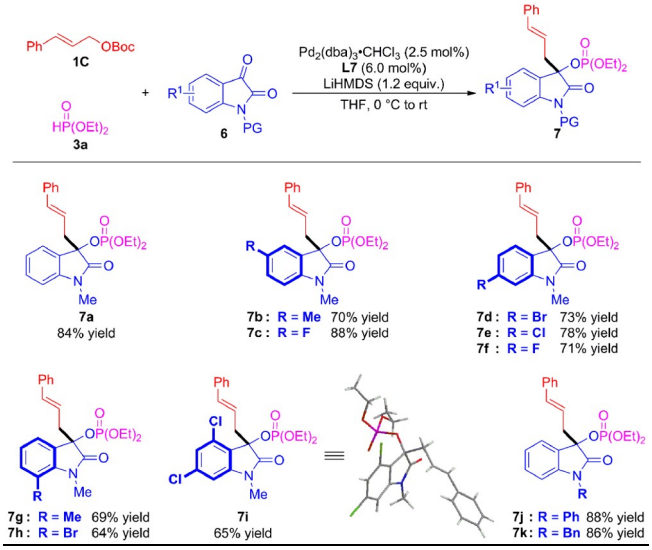
a) Reaction conditions: **1** (0.11 mmol), **2** (0.15 mmol), **3** (0.10 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (0.0025 mmol), **L7** (0.006 mmol), and LiHMDS (0.10 mmol, 1.0 M in THF) in tetrahydrofuran (1.0 mL) at 0 °C to room temperature for 1 h.

p-Ph) positions of the phenyl ring proceeded smoothly and delivered the corresponding products **4b-l** in good to excellent yields (78%–93%). Moreover, high yield (**4m** 86%) was obtained for the allyl carbonate bearing disubstituted aryl group (3,4-Cl_2Ph). The substrate derived from the piperonyl aldehyde was also well-tolerated, providing **4n** with slight decrease in yield (74%). As showcased by examples **4o–4q**, fused-ring (β-naphthyl) and heteroaryl allylic carbonates (3-pyridine, 2-thienyl) also worked well, providing good to high yields (80%–91%). To our delight, the reactions

with aliphatic *tert*-butyl carbonates proceeded smoothly, furnishing **4r**–**4t** in 69%–82% yields. Attention was then paid to the substituted α-ketoesters. Various monosubstituted aryl α-ketoesters bearing electron-rich and electron-deficient groups on the phenyl rings, were employed. All the reactions afforded corresponding substituted products **4u**–**4ae** in good to excellent yields (84%–94%), regardless of the substitution pattern at the *ortho* (*o*-OMe, *o*-Me, *o*-Br), *meta* (*m*-OMe, *m*-Me, *m*-Br, *m*-F), or *para* (*p*-Me, *p*-Br, *p*-Cl, *p*-F) positions. It is worthnoting that the reaction has also proved to be compatible with substrates uniting β-naphthyl or 2-pyridine moieties, which furnished the desired products with comparable results (**4af** 82% yield, **4ag** 97% yield). In addition, despite that the methyl substituted α-ketoesters bearing active hydrogen at the carbonyl α-position, which would lead to elusive chemo-selectivity, **4ah** could also be furnished in acceptable yield (20%). Moreover, ethyl, benzyl, and trifluoroethyl ester substituted α-ketoesters were all tolerated (**4ai** 84% yield, **4aj** 86% yield, **4ak** 81% yield). Further attempts at expanding the scope of the reaction of the carbonyl compounds bearing electron-deficient groups on the α-site failed (details shown in Supporting Information online, Page 28); benzyl gave only the trace amount of product. The β,γ-unsaturated α-ketoester, *N*,*N*-dimethylbenzamide and 2,2,2-trifluoro-1-phenylethan-1-one gave a complex reaction mixture. Having established a broad scope regarding the reaction of allyl carbonates and α-ketoesters, we then explored the scope with respect to phosphites **3**. Gratifyingly, the reactions of phosphites bearing a dimethyl or di-*tert*-butyl group occurred smoothly to give products in good to excellent yield (**4al** 99% yield, **4am** 83% yield). Disappointingly, diarylphosphine oxides (diphenyl) could not work in this reaction (details shown in Supporting Information online, Page 28).

To deliver diverse homoallylic alcohol phosphonates with this synergistically catalytic strategy, *N*-methyl isatins **6** were used as the replacement of α-ketoester substrates, which would afford isatin-incorporated homoallylic alcohol phosphonates **7**. Although the phospha-Brook rearrangement employing isatins is slow compared to the one with α-ketoesters, target product **7a** could be obtained in high yield (84%) under the optimized conditions with the simple adjustment of substrate equivalent. Then, the generality of this reaction was investigated by initially looking at various isatins (Table 3). A wide range of monosubstituents on the isatins **6** were well-tolerated in the reaction and **7b**–**7h** bearing various substituents (5-Me, 5-F, 6-Br, 6-Cl, 6-F, 7-Me, 7-Br) were isolated in moderate to high yields (64%–88%). 4,6-Dichloro isatin **6i** was also smoothly converted into the product **7i** in acceptable yield (65%) and the structure of **7i** was determined by X-ray crystallography (see Supporting Information online, Page 40). In addition, when *N*-phenyl isatin **6j** and *N*-benzyl isatin **6k** were used, the reaction furnished product **7j** and **7k** in high yields (88% and 86%).

Table 3 Substrate scope of Pudovik addition/[1, 2]-phospha-Brook rearrangement/allylation cascade reaction with isatins [a)]



a) Reaction conditions: **1C** (0.12 mmol), **6** (0.10 mmol), **3a** (0.12 mmol), $Pd_2dba_3{\cdot}CHCl_3$ (0.0025 mmol), **L7** (0.006 mmol), and LiHMDS (0.12 mmol, 1.0 M in THF) in tetrahydrofuran (1.0 mL) at 0 °C to room temperature for 2 h.

3.3 Gram-scale synthesis and synthetic transformations

To illustrate the potential synthetic utility of the current catalytic system, gram-scale synthesis and several transformations were performed. Notably, the catalyst loading could be lowered to 1.0 mol% without serious influence on the reactivity in the gram-scale synthesis of **4a** (1.88 g, 90% yield). Next, the transformations of **4a** were conducted as shown in Scheme 3. Treatment of **4a** with sodium methoxide in methanol provided corresponding alcohol **8** in good yield (90%). Additionally, **9** (96% yield) was afforded by the elimination of **4a** in the presence of TfOH. Moreover, the phosphonate and ester functionalities could be reduced by $LiAlH_4$, and the corresponding dihydroxy compound **10** was afforded in 92% yield.

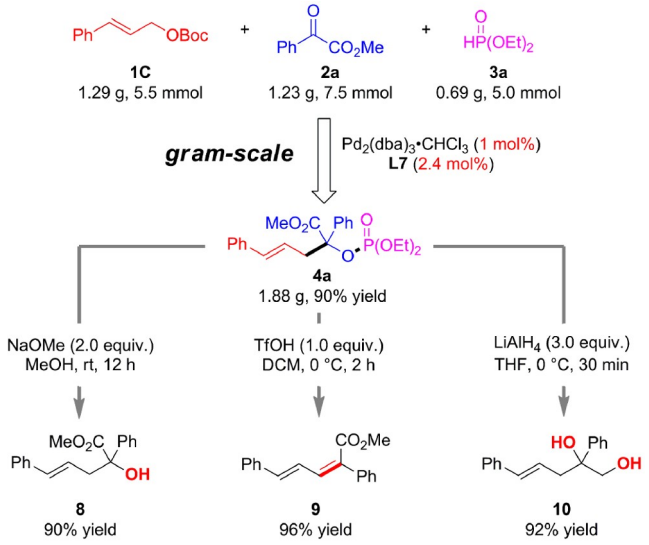
3.4 Preliminary investigation on the catalytic asymmetric version

Furthermore, the catalytic asymmetric Pudovik addition/[1, 2]-phospha-Brook rearrangement/allylation cascade reaction version has also been explored, and a number of chiral ligands were screened (see Table S1 for details). The reaction of methyl cinnamyl carbonate **1A**, phenyl α-ketoester **2a** and diethyl phosphite **3a** provided moderate enantioselectivity (30% *ee*) with $Pd_2dba_3{\cdot}CHCl_3$ as the catalyst in the presence

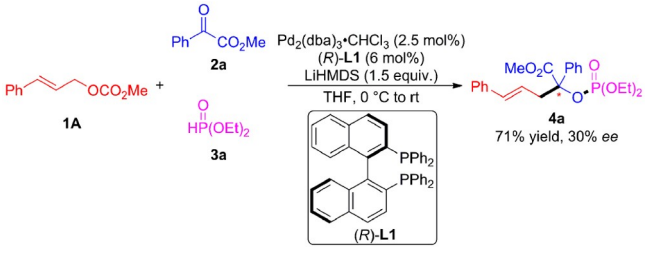
of chiral ligand (*R*)-**L1** (Scheme 4).

3.5 Proposed mechanism

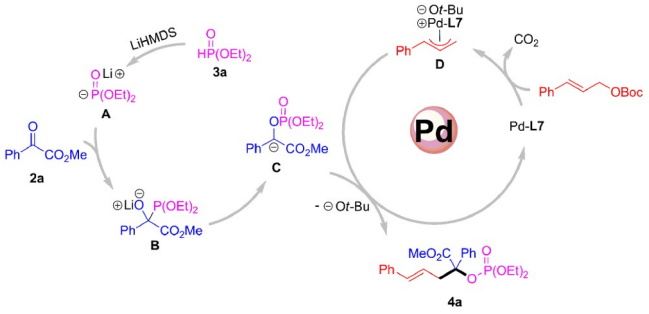
On the basis of the experimental observations, a plausible mechanism was proposed in Scheme 5 by utilizing the formation of **4a** as an example. First, the deprotonation of diethyl phosphite **3a** by a LiHMDS followed by the Pudovik addition of the resulting nucleophilic species **A** to a keto moiety of α-ketoester **2a** provides the intermediate **B**. Subsequently, the [1, 2]-phospha-Brook rearrangement proceeds to generate nucleophilic species **C**. Concurrently, the palladium catalyst generates *in situ* by $Pd_2dba_3{\cdot}CHCl_3$ and **L7**, which undergoes oxidative addition to *tert*-butyl cinnamyl carbonate **1C** and furnishes π-allyl-palladium intermediate **D**. Finally, the attack of the **C** to **D** *via* an outer sphere pathway provides the adduct **4a** along with the regeneration of the palladium catalyst [17].



Scheme 3 Product derivations (color online).



Scheme 4 Preliminary investigation on the catalytic asymmetric version (color online).



Scheme 5 Proposed catalytic cycle (color online).

4 Conclusions

In summary, we have developed a palladium-catalyzed allylic alkylation of initiated by ketones umpolung *via* Pudovik addition/[1, 2]-phospha-Brook rearrangement with phosphites. A series of diverse potentially bioactive homoallylic alcohol phosphonates were obtained in an efficient (up to 99% yield) and economical way with excellent chemo- and regio-selectivity. The cascade reaction also features a broad substrate scope (50 examples) and mild conditions. More exploration of strategies to realized TM-catalyzed asymmetric umpolung allylic alkylation of carbonyls were ongoing in our lab.

Acknowledgements This work was supported by the National Key Research and Development Program of China (2021YFA0804900), the Leading Innovative and Entrepreneur Team Introduction Program of Zhejiang (2022R01007), and Shanghai Frontiers Science Center of Optogenetic Techniques for Cell Metabolism.

Conflict of interest The authors declare no conflict of interest.

Supporting information The supporting information is available online at chem.scichina.com and link.springer.com/journal/11426. The supporting materials are published as submitted, without typesetting or editing. The responsibility for scientific accuracy and content remains entirely with the authors.

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