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手性 P,N,N-配体/钯催化的不对称烯丙基取代反应

秦 浩[a] 侯传金*,[a,b] 梁丁化[a] 何心伟[b]
李 玲*,[a,c] 胡向平*,[c]
([a]大连工业大学轻工与化学工程学院 辽宁大连 116034)
([b]安徽师范大学功能分子固体教育部重点实验室 安徽芜湖 241000)
([c]中国科学院大连化学物理研究所 辽宁大连 116023)

摘要 P,N,N-配体是近年来发展起来的在不对称催化反应中具有广泛应用的一类手性配体. 将手性 P,N,N-配体应用于钯催化不对称烯丙基取代反应研究. 结果表明, 在较温和条件下, 含 C、N 和 O 的各类亲核试剂均能顺利发生反应, 获得良好的产率和对映选择性(产率高达 97%, 93% *ee*).
关键词 P,N,N-配体; 不对称烯丙基取代; 钯

Chiral P,N,N-Ligands for Pd-Catalyzed Asymmetric Allylic Substitutions

Qin, Hao[a] Hou, Chuanjin*,[a,b] Liang, Dinghua[a] He, Xinwei[b]
Li, Ling*,[a,c] Hu, Xiangping*,[c]
([a] *School of Light Industry and Chemical Engineering, Dalian Polytechnic University, Dalian, Liaoning 116034*)
([b] *Key Laboratory of Functional Molecular Solids, Ministry of Education, Anhui Normal University, Wuhu, Anhui 241000*)
([c] *Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian, Liaoning 116023*)

Abstract Chiral P,N,N-ligands are a new type of ligands developed in recent years, which have been widely used in asymmetric catalytic reactions. In this study, chiral P,N,N-ligands were applied to palladium-catalyzed asymmetric allylic substitution reactions. The results showed that under mild conditions, various nucleophiles containing carbon, nitrogen and oxygen could react smoothly, achieving good yields (up to 97% yield) and enantioselectivities (up to 93% *ee*).
Keywords P,N,N-ligands; asymmetric allylic substitution; palladium

1 Introduction

Chiral compounds play a pivotal role in the manufacture of pharmaceuticals, agrochemicals and other fine chemicals.[1] Therefore, the unique potential value of the chiral products has made countless researchers working for it. Chiral compounds obtained by asymmetric allylic substitutions are an extremely useful class of molecules that have been used as widespread building blocks in organic synthesis for more than 50 years.[2] Accordingly, the allylic substitution has become a significant reaction in transition-metal-catalyzed asymmetric reactions, which has satisfied the growing demand for enantioselective synthesis of the chiral compounds in recent decades.[3] In 1977, Trost *et al*.[4] reported the first palladium-catalyzed asymmetric allylic alkylation with chiral phosphine ligands, opening up a new side of the field. Since then, significant progress had been made in the asymmetric allylic substitutions which focus on the substrate scope, nucleophile diversity, catalyst structure and ligand design.[5] In this regard, the efficiency of transition-metal catalyzed asymmetric reactions relied mainly on the choice of chiral ligands. Tremendous efforts had been directed towards developing chiral ligands design and synthesis.[6] Various chiral ligands were developed and showed excellent performance in asymmetric allylic substitutions, such as Trost's ligand,[7] BINAP,[8] Segphos,[9] SKP,[10] PHOX,[11] Phosferrox,[12] Josiphos[13] and FerroNPS.[14] Despite of these developments, the discovery of

* Corresponding authors. E-mail: houcj@dlpu.edu.cn; 18840836643@163.com; xiangping@dicp.ac.cn
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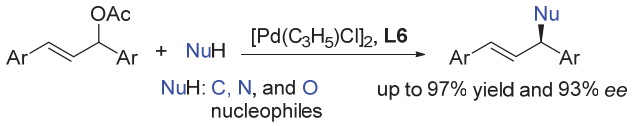
more efficient ligands for different allylic substitution reactions with broad range of substrates and nucleophiles scope is still of great importance.

Chiral P,N,N-ligands represented a new class of ligands developed in recent years, which were widely used in asymmetric catalytic reactions. In 2011, Zhou *et al.*[15] reported the iridium-catalyzed asymmetric hydrogenation of various ketones with chiral spiro P,N,N-ligands (SpiroPAP) (Figure 1), which showed excellent enantioselectivities and extremely high turn over number (TON) (as high as 4550000). Later, Zhang *et al.*[16] developed a ferrocenyl P,N,N-ligands, f-amphox (Figure 1), and applied them in the iridium-catalyzed asymmetric hydrogenations. In 2016, we[17] reported a type of sterically hindered chiral ferrocenyl P,N,N-ligands (Figure 1) and successfully employed them in the iridium-catalyzed asymmetric hydrogenation of *α*-alkyl-*β*-aryl-*β*-ketoesters via dynamic kinetic resolution. In 2019, Liu *et al.*[18] discovered a series of copper-catalyzed asymmetric radical coupling reactions with chiral alkaloid-derived P,N,N-ligands (Figure 1). In 2019, Li *et al.*[19] reported the cobalt-catalyzed regio- and enantioselective allylic amination with chiral P,N,N-ligand bisoxazolinephosphine (Figure 1). Excellent performance of these P,N,N-ligands in asymmetric allylic substitutions was then demonstrated by Li *et al.*[20] Recently, we have developed a series of phenylethylamine (PEA)-derived P,N,N-ligands (Figure 1) which showed excellent diastereo- and enantioselectivities in the copper-catalyzed asymmetric propargylic substitutions[21] and cycloadditions.[22] Inspired by the previous work, we would like to report the palladium-catalyzed asymmetric allylic substitution with the PEA-derived P,N,N-ligands using nucleophiles containing carbon, nitrogen and oxygen (Scheme 1).

2 Results and discussion

At the outset, 1,3-diphenyl-2-propenyl acetate (**1a**) and dimethyl malonate (**2a**) were chosen as the model substrates



Scheme 1 Pd-catalyzed asymmetric allylic substitutions with PEA-derived P,N,N-ligands using C, N and O nucleophiles

to investigate palladium-catalyzed asymmetric allylic alkylation. The reaction was performed in toluene at 50 ℃ for 12 h with *N*,*O*-bis(trimethylsilyl)acetamide (BSA) and NaOAc as base in the presence of Pd-catalyst prepared *in situ* from $[Pd(C_3H_5)Cl]_2$ and chiral ligands. The effect of chiral ligands on the reaction was first examined (Scheme 2). Although the chiral P,N-ligands[23] are the most widely studied and used ligands in asymmetric allylic substitutions, P,N-ligands **L1**～**L3** showed disappointing results with low *ee* values (0～43% *ee*). To our delight, the use of PEA-derived P,N,N-ligands **L4**～**L6** resulted in better yields and enantioselectivities. Good result (71% yield and 82% *ee*) was obtained with the sterically hindered P,N,N-ligand **L6**.

To improve the reactivity and stereoselectivity, further optimization of palladium source, base, reaction temperature and solvent was investigated (Table 1). The results indicated that $[Pd(C_3H_5)Cl]_2$ was the best palladium source (Entry 1), while other palladium, including $Pd(OAc)_2$, $Pd_2(dba)_3$ and $Pd[P(C_6H_5)_3]_4$, provided **3a** in low yields and enantioselectivities (Entries 2～4). Next, *N*,*O*-bis(trimethylsilyl)acetamide (BSA) activators effect were investigated (Entries 5～8) and the best result was obtained with NaOAc as base activator in terms of reactivity and enantioselectivity (Entry 1). The reaction temperature also has a significant impact, obtaining decreased yields or *ee* values at higher or lower temperature (Entries 9, 10). The followed screening of solvents such as tetrahydrofuran (THF), CH_3CN, 1,4-dioxane, Et_2O and CH_2Cl_2 (Entries 11～16) revealed that THF was the best choice, and 90% yield and 91% *ee* were obtained (Entry 11). Thus, the optimized re-

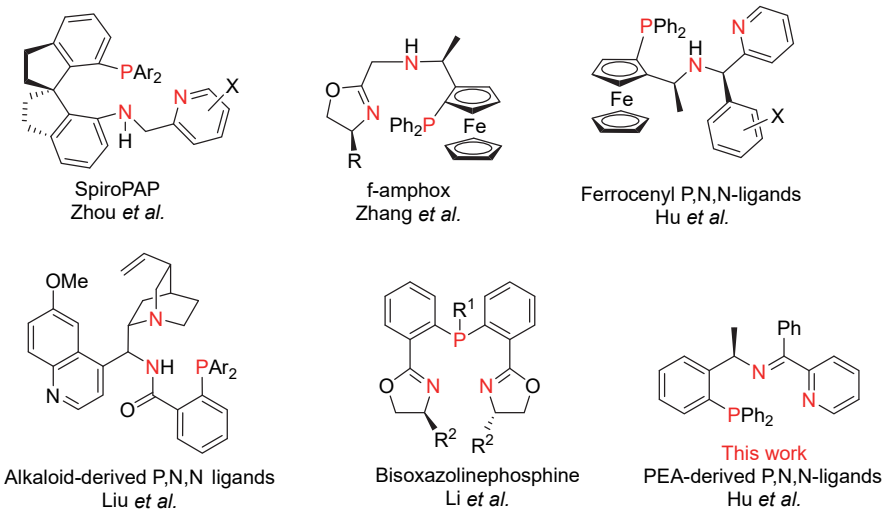
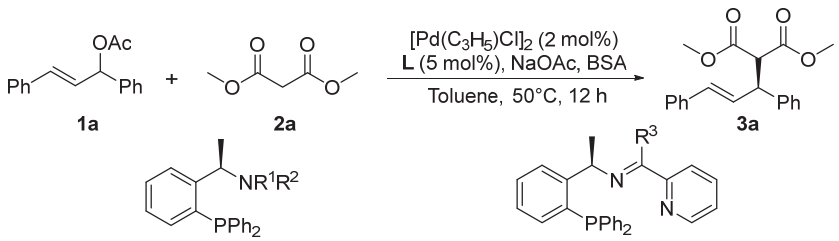


Figure 1 Some representative chiral P,N,N-ligands



L1: R^1 = H, R^2 = H, 86% yield, 43% *ee*
L2: R^1 = H, R^2 = Me, 94% yield, 39% *ee*
L3: R^1 = Me, R^2 = Me, 51% yield, 0% *ee*

L4: R^3 = H, 34% yield, 49% *ee*
L5: R^3 = Me, 92% yield, 61% *ee*
L6: R^3 = Ph, 71% yield, 82% *ee*

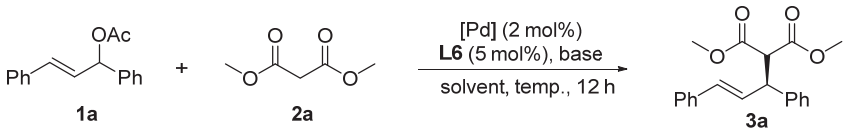
Scheme 2 Screening of ligands in the palladium-catalyzed asymmetric allylic alkylation

action conditions were finally established as: $[Pd(C_3H_5)Cl]_2$ as metal precursor, P,N,N-ligand **L6**, THF as solvent, 50 ℃, BSA as base and NaOAc as activator.

Under the optimal reaction conditions, the substrate scope and limitation of various 1,3-diaryl-2-propenyl acetates **1** was examined. The results are summarized in Table 2. It was pleased to find that all the allylic alcohol acetates **1a**～**1g** reacted smoothly with dimethyl malonate (**2a**), giving the corresponding products **3a**～**3g** in 72%～97% yields with 76%～92% *ee*, regardless of the electronic effects and substitution pattern of the substituent on the phenyl ring. The absolute configuration of **3c** was determined as *S* by X-ray analysis (CCDC 2283367). Meanwhile, 2-naphthyl substrate (**1h**) and heteroaryl substrate (**1i**) also performed well, providing the allylic alkylation products with 89% *ee* (**3h**) and 71% *ee* (**3i**), respectively. Other carbon containing nucleophiles, such as diethyl malonate (**2b**), dimethyl 2-methylmalonate (**2c**), pentane-2,4-dione (**2d**) and malononitrile (**2e**) also worked well and good to excellent enantioselectivities (**3j**～**3m**, 77%～93% *ee*) were achieved, although only moderate yields were achieved for **3l** and **3m**. However, unsymmetrical allylic substrate, phenyl methyl substituted acetate (**2n**) for example, was successful transformed into the corresponding product **3n** in good yield but with significantly reduced enantioselectivities (18% *ee*).

Encouraged by these results, the asymmetric allylic substitutions with nucleophiles containing nitrogen and oxygen were then investigated (Table 3). However, the first attempt of the reaction of 1,3-diphenyl-2-propenyl acetate (**1a**) and benzylamine (**4a**) with BSA/NaOAc in THF did not proceed at all. Fortunately, after several reaction conditions screening, the product **5a** was obtained in good results (85% *ee*) in the presence of K_2CO_3 in CH_2Cl_2. Then, we thought to explore the range of nucleophiles that could be used in this transformation. The aliphatic amine, morpholine (**4b**)

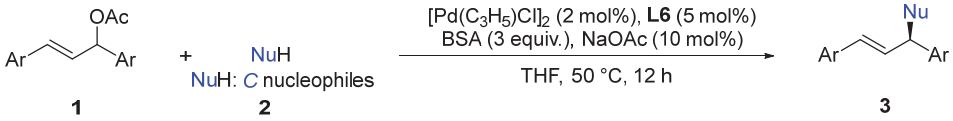
Table 1 Optimization of the reaction conditions of asymmetric allylic alkylation[a]



Entry	[Pd]	Base	Solvent	Temperature/℃	Yield[b]/%	*ee*[c]
1	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	Toluene	50	71	82
2	$Pd(OAc)_2$	BSA, NaOAc	Toluene	50	28	33
3	$Pd_2(dba)_3$	BSA, NaOAc	Toluene	50	NR	
4	$Pd[P(C_6H_5)_3]_4$	BSA, NaOAc	Toluene	50	35	48
5	$[Pd(C_3H_5)Cl]_2$	BSA, KOAc	Toluene	50	30	82
6	$[Pd(C_3H_5)Cl]_2$	BSA, K_2CO_3	Toluene	50	86	72
7	$[Pd(C_3H_5)Cl]_2$	BSA, Na_2CO_3	Toluene	50	17	77
8	$[Pd(C_3H_5)Cl]_2$	BSA	Toluene	50	56	79
9	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	Toluene	80	84	35
10	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	Toluene	r.t.	61	82
11	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	THF	50	90	91
12	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	CH_3CN	50	90	55
13	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	1,4-Dioxane	50	76	85
14	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	CH_3OH	50	NR	
15	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	Et_2O	50	95	73
16	$[Pd(C_3H_5)Cl]_2$	BSA, NaOAc	CH_2Cl_2	50	70	86

[a] The reactions were carried out with **1a** (0.3 mmol), **2a** (0.9 mmol), [Pd] (2 mol%), **L6** (5 mol%), BSA (3 equiv.) and catalytic amount of activator (10 mol%) in solvent (2.0 mL) at *T* ℃. [b] Isolated yield. [c] Determined by chiral HPLC.

Table 2 Substrate scope of various 1,3-diaryl-2-propenyl acetates **1** with carbon nucleophiles **2**



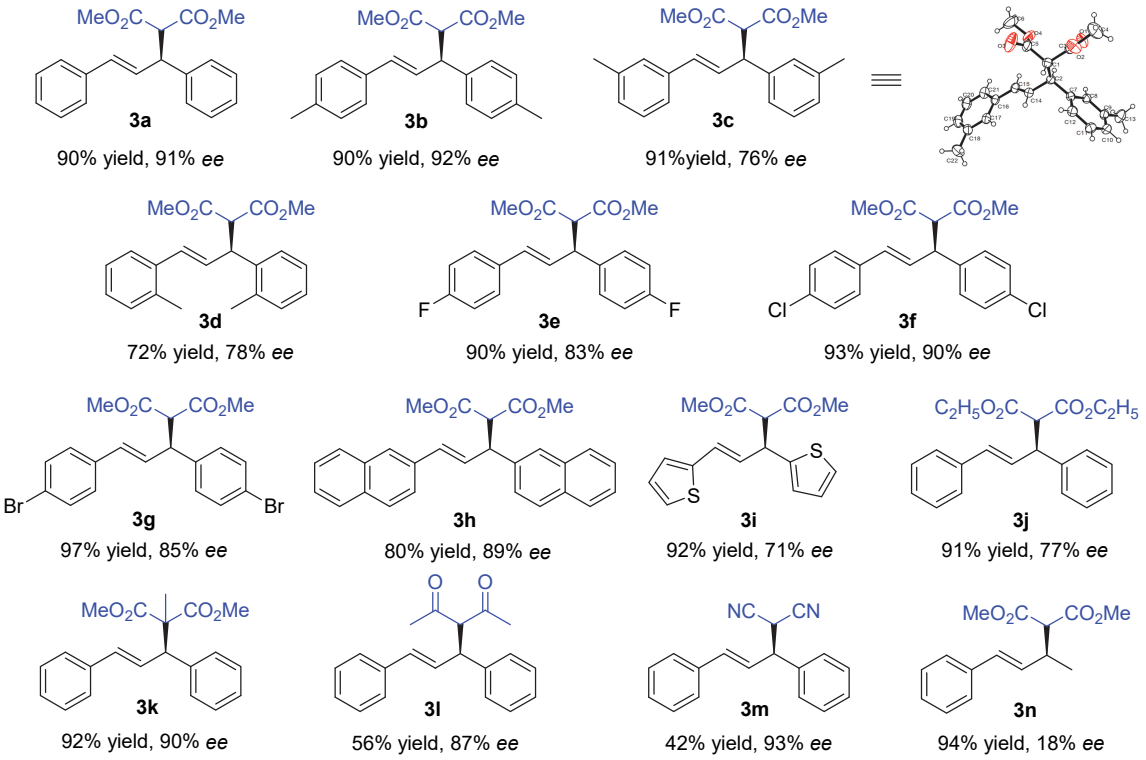
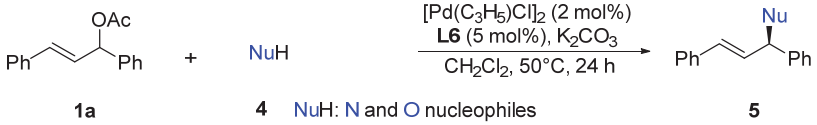
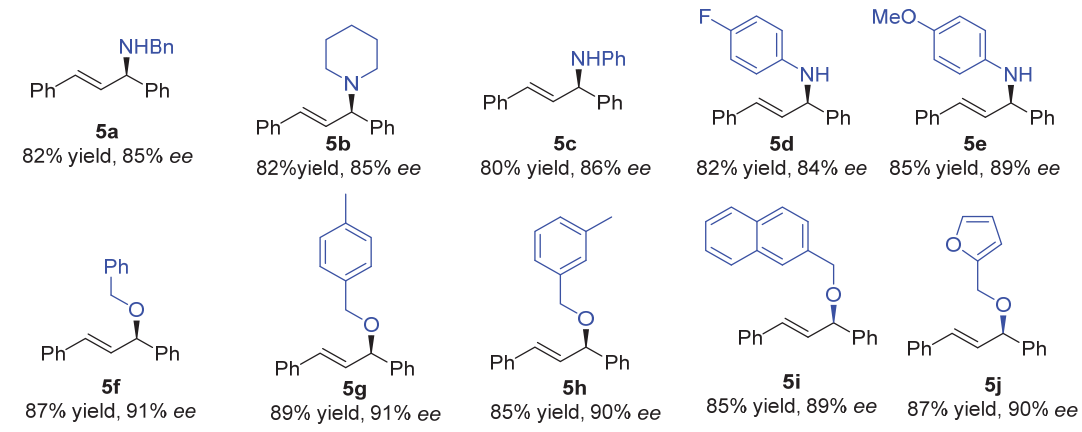


Table 3 Substrate scope of nucleophiles containing nitrogen and oxygen **4**

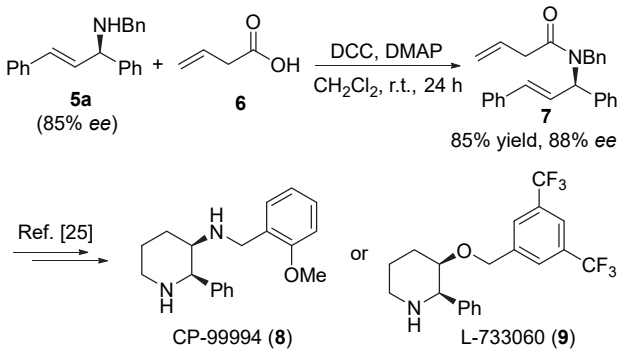




performed well and good enantioselectivity (**5b**, 85% *ee*) was observed. The aromatic amines were also suitable for the reaction. The aniline substrates (**4c**～**4e**) with electron-withdrawing and electron-donating substituents reacted smoothly and afforded the allylic amination products with good enantioselectivities (**5c**～**5e**, 84%～89% *ee*).

Additionally, the oxygen nucleophiles of benzyl alcohols **4f**～**4h** were also investigated, and the corresponding products **5f**～**5h** were obtained with excellent enantioselectivities (90%～91% *ee*). Furthermore, 2-naphthyl substrate (**4i**) and 2-furyl substrate (**4j**) were also effectively converted to the allylic etherification products with 89% *ee* (**5i**) and 90% *ee* (**5j**), respectively.

To demonstrate the synthetic utility of this methodology, the allylic amination product **5a** was subjected to react with 3-butenoic **6** in the presence of dicyclohexyl carbodiimide (DCC) and 4-dimethylaminopyridine (DMAP), and converted to the corresponding amide **7**[24] in excellent enantioselectivity (Scheme 3). Notably, amide **7** could be further transformed to piperidine analogues CP-99994 (**8**) and L-733060 (**9**), which have excellent affinity and selectivity with human neurokinin-1 (NK1) receptor.[25]



Scheme 3 Synthetic application of the asymmetric allylic amination product **5a**

3 Conclusion

In summary, we have developed the palladium-catalyzed asymmetric allylic substitutions of 1,3-diaryl-2-propenyl acetates with PEA-derived chiral P,N,N-ligands. The results showed that good to excellent yields and enantioselectivities could be achieved with nucleophiles containing carbon, nitrogen and oxygen (up to 97% yield and 93% *ee*) under mild conditions. This reaction provided an efficient method for the asymmetric formation of C—C, C—N and C—O bonds. Further studies on the applications in asymmetric catalysis with these ligands are underway in our laboratory.

4 Experimental section

4.1 General information

Unless otherwise noted, all the experiments were carried out under nitrogen (N_2) atmosphere. All reactions were carried out in oven-dried flask sealed with rubber septa using standard Schlenk techniques. All the solvents were purified according to standard procedure. The other commercial chemicals were used directly without any further purification. Flash column chromatography was performed using 200～300 mesh silica gel. ^{1}H NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported in δ value with tetramethyl silane (TMS) as the internal standard. High-pressure liquid chromatography (HPLC) analysis was performed using Agilent 1260 series instrument with chiral columns [HPLC: Chiralpak AD-H column, Chiralcel OJ-H column or Chiralcel OD-H column) with hexane and *i*-PrOH as solvents. Copies of NMR spectra and HPLC analysis were given in the supporting information.

4.2 General procedure for Pd-catalyzed asymmetric allylic substitutions (AAS)

4.2.1 General procedure for Pd-catalyzed AAS with *C*-nucleophiles

Ligand **L6** (5 mol%) and $[Pd(C_3H_5)Cl]_2$ (2 mol%) were dissolved in THF (1 mL) in a Schlenk tube under N_2. After stirring at room temperature for 1 h, allylic acetate **1** (0.30 mmol) was added, followed by **2** (0.90 mmol), NaOAc (0.03 mmol), BSA (0.90 mmol) and THF (2.0 mL). The mixture was stirred at 50 ℃ for 12 h, and then purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product **3**.

Dimethyl (*S*,*E*)-2-(1,3-diphenylallyl)malonate (**3a**):[26] Colorless oil, 90% yield, 91% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V* = 90 ∶ 10), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=10.7 min (minor), t_R=13.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.31 (s, 4H), 7.27 (s, 6H), 6.49 (d, *J*=15.6 Hz, 1H), 6.34 (dd, *J*=15.2, 8.4 Hz, 1H), 4.28 (t, *J*=10.0 Hz, 1H), 3.96 (d, *J*=10.8 Hz, 1H), 3.72 (s, 3H), 3.53 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-di-*p*-tolylallyl)malonate (**3b**):[26] Colorless oil, 90% yield, 92% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=85∶15), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=10.1 min (minor), t_R=12.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21 (t, *J*=8.4 Hz, 4H), 7.14～7.08 (m, 4H), 6.44 (d, *J*=16.0 Hz, 1H), 6.27 (dd, *J*=15.2, 8.4 Hz, 1H), 4.23 (t, *J*=9.6 Hz, 1H), 3.94 (d, *J*=10.8 Hz, 1H), 3.71 (s, 3H), 3.55 (s, 3H), 2.32 (s, 6H).

Dimethyl (*S*,*E*)-2-(1,3-di-*m*-tolylallyl)malonate (**3c**):[27] White solid, m.p. 85～87 ℃. 91% yield, 76% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=15.4 min (minor), t_R=17.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.24～7.10 (m, 6H), 7.05 (t, *J*=6.8 Hz, 2H), 6.47 (d, *J*=16.0 Hz, 1H), 6.33 (dd, *J*=15.2, 8.4 Hz, 1H), 4.25 (t, *J*=9.6 Hz, 1H), 3.98 (d, *J*=10.8 Hz, 1H), 3.72 (s, 3H), 3.56 (s, 3H), 2.34 (d, *J*=8.0 Hz, 6H).

Dimethyl (*S*,*E*)-2-(1,3-di-*o*-tolylallyl)malonate (**3d**):[27] Colorless oil, 72% yield, 78% *ee* [HPLC: Chiralcel OD-H, hexane/isopropanol (*V*∶*V*=95∶5), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=6.0 min (minor), t_R=6.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (s, 1H), 7.26～7.17 (m, 4H), 7.16～7.12 (m, 3H), 6.68 (d, *J*=15.6 Hz, 1H), 6.04 (dd, *J*=15.2, 8.4 Hz, 1H), 4.59 (t, *J*=10.0 Hz, 1H), 4.09 (d, *J*=11.2 Hz, 1H), 3.75 (s, 3H), 3.54 (s, 3H), 2.50 (s, 3H), 2.30 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-bis(4-fluorophenyl)allyl)malonate

(**3e**):[26] Colorless oil, 90% yield, 83% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=85∶15), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=10.2 min (minor), t_R=14.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.27 (q, *J*=7.6 Hz, 4H), 7.04～6.95 (m, 4H), 6.43 (d, *J*=15.6 Hz, 1H), 6.23 (dd, *J*=15.6, 8.4 Hz, 1H), 4.26 (t, *J*=9.2 Hz, 1H), 3.90 (d, *J*=10.8 Hz, 1H), 3.72 (s, 3H), 3.55 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-bis(4-chlorophenyl)allyl)malonate (**3f**):[26] Colorless oil, 93% yield, 90% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=16.9 min (minor), t_R=24.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.30 (d, *J*=7.6 Hz, 2H), 7.24 (t, *J*=10.8 Hz, 6H), 6.41 (d, *J*=15.6 Hz, 1H), 6.27 (dd, *J*=15.6, 8.4 Hz, 1H), 4.25 (t, *J*=9.6 Hz, 1H), 3.90 (d, *J*=10.4 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-bis(4-bromophenyl)allyl)malonate (**3g**):[26] Colorless oil, 97% yield, 85% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=85∶15), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=16.7 min (minor), t_R=23.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (dd, *J*=20.8, 8.0 Hz, 4H), 7.18 (d, *J*=8.0 Hz, 4H) 6.40 (d, *J*=15.6 Hz, 1H), 6.29 (dd, *J*=15.2, 8.4 Hz, 1H), 4.24 (t, *J*=9.2 Hz, 1H), 3.90 (d, *J*=10.8 Hz, 1H), 3.71 (s, 3H), 3.56 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-di(naphthalen-2-yl)allyl)malonate (**3h**):[28] White solid, m.p. 72～74 ℃. 80% yield, 89% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=25.1 min (minor), t_R=33.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.86～7.75 (m, 7H), 7.70 (s, 1H), 7.56 (d, *J*=8.8 Hz, 1H), 7.51～7.41 (m, 5H), 6.71 (d, *J*=15.6 Hz, 1H), 6.57 (dd, *J*=15.2, 8.4 Hz, 1H), 4.54 (t, *J*=9.6 Hz, 1H), 4.16 (d, *J*=10.4 Hz, 1H), 3.76 (s, 3H), 3.52 (s, 3H).

Dimethyl 2-((*S*,*E*)-1,3-di(thiophen-2-yl)allyl)malonate (**3i**): Colorless oil, 92% yield, 71% *ee* [HPLC: Chiralcel AD-H, hexane/isopropanol (*V*∶*V*=85∶15), flow rate 0.8 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=9.9 min (minor), t_R=13.1 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.21～7.14 (m, 2H), 6.94 (s, 4H), 6.65 (d, *J*=15.6 Hz, 1H), 6.19 (dd, *J*=15.2, 8.8 Hz, 1H), 4.54 (t, *J*=9.6, 1H), 3.90 (d, *J*=10.4 Hz, 1H), 3.72 (s, 3H), 3.64 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.7, 167.6, 143.2, 141.5, 127.8, 127.4, 126.9, 126.1, 125.5, 124.9, 124.6, 124.5, 58.5, 52.8, 52.7, 44.1. HRMS calcd for $C_{16}H_{16}NaO_4S_2$ $[M+Na]^+$ 359.0382, found 359.0378.

Diethyl (*S*,*E*)-2-(1,3-diphenylallyl)malonate (**3j**):[26] Colorless oil, 91% yield, 77% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 1.0 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=10.4 min (minor), t_R=14.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.32～7.19 (m, 10H), 6.49 (d, *J*=15.6 Hz, 1H), 6.35 (dd, *J*=15.6, 8.8 Hz, 1H), 4.27 (t, *J*=9.6 Hz, 1H), 4.18 (q, *J*=6.0 Hz, 2H), 4.01～3.92 (m, 3H) 1.22 (t, *J*=6.4 Hz, 3H), 1.02 (t, *J*=6.8 Hz, 3H).

Dimethyl (*R*,*E*)-2-(1,3-diphenylallyl)-2-methylmalonate (**3k**):[26] Colorless oil, 92% yield, 90% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=97∶3), flow rate 1.0 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=10.0 min (major), t_R=10.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.39～7.21 (m, 10H), 6.72 (dd, *J*=15.6, 9.2 Hz, 1H), 6.50 (d, *J*=15.6, 1H), 4.34 (d, *J*=8.8 Hz, 1H), 3.73 (s, 3H), 3.65 (s, 3H), 1.52 (s, 3H).

Dimethyl (*S*,*E*)-3-(1,3-diphenylallyl)pentane-2,4-dione (**3l**):[26] White solid, m.p. 46～48 ℃. 56% yield, 87% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=95∶5), flow rate 1.0 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=11.6 min (minor), t_R=12.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45～7.20 (m, 10H), 6.45 (d, *J*=16.0 Hz, 1H), 6.21 (dd, *J*=16.4, 6.0 Hz, 1H), 4.37 (s, 2H), 2.27 (s, 3H), 1.94 (s, 3H).

Dimethyl (*S*,*E*)-2-(1,3-diphenylallyl)malononitrile (**3m**):[29] Colorless oil, 42% yield, 93% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=70∶30), flow rate 1.0 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=17.2 min (minor), t_R=19.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48～7.30 (m, 10H), 6.73 (d, *J*=15.6 Hz, 1H), 6.49 (dd, *J*=15.2, 7.6 Hz, 1H), 4.15～4.08 (m, 2H).

Dimethyl (*S*,*E*)-2-(4-phenylbut-3-en-2-yl)malonate (**3n**):[28] Colorless oil, 94% yield, 18% *ee* [HPLC: Chiralcel OD-H, hexane/isopropanol (*V*∶*V*=98∶2), flow rate 0.8 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=11.7 min (minor), t_R=12.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.37～7.29 (m, 4H), 7.26～7.23 (m, 1H), 6.48 (d, *J*=8.0 Hz, 1H), 6.15 (dd, *J*=16.0, 8.0 Hz, 1H), 3.77 (s, 3H), 3.70 (s, 3H), 3.43 (d, *J*=8.0 Hz, 1H), 3.18～3.12 (m, 1H), 1.22 (d, *J*=8.0 Hz, 1H).

4.2.2 General procedure for Pd-catalyzed AAS with *N*- and *O*-nucleophiles

Ligand **L6** (5 mol%) and $[Pd(C_3H_5)Cl]_2$ (2 mol%) were dissolved in CH_2Cl_2 (1 mL) in a Schlenk tube under N_2. After stirring at room temperature for 1 h, allylic acetate **1a** (0.30 mmol) was added, followed by **4** (0.90 mmol), K_2CO_3 (1.5 mmol), and CH_2Cl_2 (2.0 mL). The mixture was stirred at 50 ℃ for 24 h, and then purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product **5**.

Dimethyl (*R*,*E*)-*N*-benzyl-1,3-diphenylprop-2-en-1-amine (**5a**):[26] Colorless oil, 82% yield, 85% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=85∶15), flow rate 0.5 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=14.4 min (minor), t_R=16.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.47 (d, *J*=7.6 Hz 2H), 7.40～7.36 (m, 8H), 7.32～7.22 (m, 5H), 6.62 (d, *J*=15.6 Hz 1H), 6.36 (dd, *J*=15.6, 7.2 Hz, 1H), 4.44 (d, *J*=7.2 Hz, 1H), 3.82 (t, *J*=15.2 Hz, 2H), 1.85 (s, 1H).

Dimethyl (*R*,*E*)-1-(1,3-diphenylallyl)piperidine (**5b**):[30] White solid, m.p. 102～104 ℃. 82% yield, 85% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=97∶

3), flow rate 0.8 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=6.0 min (minor), t_R=6.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, J=8.0 Hz, 2H), 7.40～7.29 (m, 8H), 6.56 (d, J=16.0 Hz, 1H), 6.38 (q, J=7.2, 1H), 3.85 (d, J=8.4 Hz, 1H), 2.46 (d, J=48.0 Hz, 4H), 1.61 (s, 4H), 1.47 (s, 2H).

Dimethyl (*R*,*E*)-*N*-(1,3-diphenylallyl)aniline (**5c**):[26] Colorless oil, 80% yield, 86% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=95∶5), flow rate 1.0 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=7.8 min (minor), t_R=9.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.48 (d, J=8.0 Hz, 2H), 7.42～7.41 (m, 4H), 7.34 (t, J=7.2 Hz 3H), 7.28 (d, J=7.2 Hz 1H), 7.20 (t, J=7.6 Hz 2H), 6.78～6.66 (m, 4H), 6.45 (dd, J=15.6, 5.6 Hz, 1H), 5.14 (d, J=5.6 Hz, 1H), 4.19 (s, 1H).

Dimethyl (*R*,*E*)-*N*-(1,3-diphenylallyl)-4-fluoroaniline (**5d**):[31] Colorless oil, 82% yield, 84% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=98∶2), flow rate 1.0 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=18.0 min (minor), t_R=24.0 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46～7.38 (m, 6H), 7.32 (t, J=6.8 Hz 3H), 7.27 (d, J=6.8 Hz, 1H), 6.87 (t, J=8.0 Hz 2H), 6.62 (q, J=16.0, 3H), 6.51 (q, J=4.4 Hz, 1H), 5.04 (d, J=5.2 Hz, 1H), 4.13 (s, 1H).

Dimethyl (*R*,*E*)-*N*-(1,3-diphenylallyl)-4-methoxyaniline (**5e**):[26] White solid, m.p. 75～77 ℃. 85% yield, 89% *ee* [HPLC: Chiralpak AD-H, hexane/isopropanol (*V*∶*V*=95∶5), flow rate 1.0 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=14.0 min (minor), t_R=18.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46 (d, J=7.6 Hz, 2H), 7.40～7.38 (m, 4H), 7.34～7.25 (m, 5H), 6.78 (t, J=18.0 Hz 2H), 6.64 (t, J=13.2, 3H), 6.42 (dd, J=15.2, 4.4 Hz, 1H), 5.03 (d, J=6.0 Hz, 1H), 3.75 (s, 3H).

Dimethyl (*R*,*E*)-(3-(benzyloxy)prop-1-ene-1,3-diyl)-dibenzene (**5f**):[26] Colorless oil, 87% yield, 91% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=98∶2), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=19.5 min (minor), t_R=22.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.45 (d, J=7.6 Hz, 2H), 7.40 (t, J=8.0 Hz, 7H), 7.34～7.27 (m, 6H), 6.65 (d, J=15.6 Hz, 1H), 6.36 (dd, J=15.6, 6.8 Hz, 1H), 5.03 (d, J=6.8 Hz, 1H), 4.60 (s, 2H).

Dimethyl (*R*,*E*)-(3-((4-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5g**):[14] Colorless oil, 89% yield, 91% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=98∶2), flow rate 0.75 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=19.5 min (minor), t_R=23.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.50～7.48 (m, 2H), 7.42 (t, J=7.2 Hz, 4H), 7.37～7.27 (m, 6H), 7.22 (d, J=8.0 Hz, 2H), 6.67 (d, J=15.6 Hz 1H), 6.39 (dd, J=15.6, 6.4 Hz, 1H), 5.06 (d, J=6.4 Hz, 1H), 4.59 (s, 2H), 2.40 (s, 3H).

Dimethyl (*R*,*E*)-(3-((3-methylbenzyl)oxy)prop-1-ene-1,3-diyl)dibenzene (**5h**):[14] Colorless oil, 85% yield, 90% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=96∶4), flow rate 0.75 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=10.8 min (minor), t_R=12.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.49～7.40 (m, 6H), 7.34 (t, J=14.8 Hz, 3H), 7.27 (d, J=7.6 Hz, 2H), 7.23～7.13 (m, 3H), 6.67 (d, J=16.0 Hz, 1H), 6.39 (dd, J=15.6, 6.8 Hz, 1H), 5.06 (d, J=6.4 Hz, 1H), 4.60 (s, 2H), 2.40 (s, 3H).

Dimethyl (*R*,*E*)-2-(((1,3-diphenylallyl)oxy)methyl)-naphthalene (**5i**):[32] Colorless oil, 85% yield, 89% *ee* [HPLC: Chiralcel OD-H, hexane/isopropanol (*V*∶*V*=98∶2), flow rate 0.8 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=10.2 min (minor), t_R=15.4 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.87 (t, J=7.2 Hz, 4H), 7.57～7.50 (m, 5H), 7.43 (t, J=13.6 Hz, 4H), 7.37～7.33 (m, 3H), 7.18 (d, J=7.6 Hz, 1H), 6.70 (d, J=16.0 Hz, 1H), 6.42 (dd, J=15.6, 6.8 Hz, 1H), 5.10 (d, J=6.8 Hz, 1H), 4.79 (s, 2H).

Dimethyl (*R*,*E*)-2-(((1,3-diphenylallyl)oxy)methyl)furan (**5j**):[26] Colorless oil, 87% yield, 90% *ee* [HPLC: Chiralcel OJ-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 1.0 mL/min, λ=254 nm, 25 ℃]. Retention times: t_R=12.9 min (minor), t_R=13.8 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.46～7.38 (m, 7H), 7.32 (t, J=14.4 Hz, 3H), 7.26 (d, J=7.2 Hz, 1H), 6.65 (d, J=15.6 Hz, 1H), 6.36 (d, J=11.2, 3H), 5.06 (d, J=6.4 Hz, 1H), 4.50 (s, 2H).

4.3 Synthetic application of the asymmetric allylic amination product **5a**

The product **5a** (0.4 mmol) and 3-butenoic **6** (0.4 mmol) were dissolved in CH_2Cl_2 (2 mL) in a Schlenk tube under N_2. DCC (0.4 mmol), DMAP (0.08 mmol) and CH_2Cl_2 (2.0 mL) were added. The mixture was stirred at room temperature for 24 h, and then purified by flash column chromatography directly, eluting with petroleum ether and ethyl acetate to afford the corresponding product dimethyl (*R*,*E*)-*N*-benzyl-*N*-(1,3-diphenylallyl)but-3-enamide (**7**),[25] colorless oil, 85% yield, 88% *ee* [HPLC: Chiralcel AD-H, hexane/isopropanol (*V*∶*V*=90∶10), flow rate 0.8 mL/min, λ=254 nm, 40 ℃]. Retention times: t_R=12.7 min (major), t_R=18.8 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.41～7.32 (m, 4H), 7.32～7.24 (m, 6H), 7.24～7.18 (m, 3H), 7.17～7.10 (m, 2H), 6.76～6.66 (m, 1H), 6.65～6.33 (m, 1H), 6.33～6.10 (m, 1H), 6.10～5.77 (m, 1H), 5.32～5.03 (m, 2H), 5.00～4.64 (m, 1H), 4.61～4.27 (m, 1H), 3.51～2.99 (m, 2H).

Supporting Information Experimental procedures, characterization data, copies of HPLC analysis and NMR spectra. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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(Lu, Y.)

