ChemPubSoc Europe

DOI: 10.1002/ejoc.201600045

EurJOC European Journal of Organic Chemistry

Full Paper

Asymmetric Catalysis

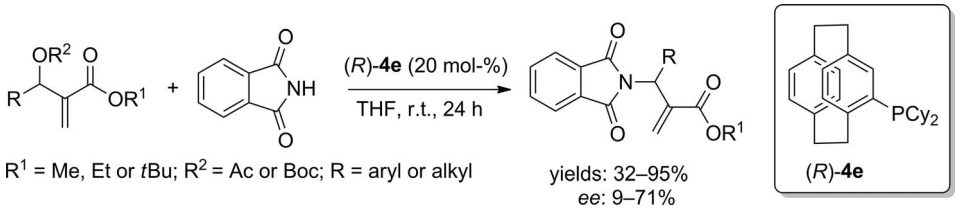
Enantioselective Allylic Substitution of Morita–Baylis–Hillman Adducts Catalyzed by Chiral Bifunctional Ferrocenylphosphines

Linglong Zhu,[a] Haiwen Hu,[a] Liang Qi,[a] Yi Zheng,[a] and Weihui Zhong*[a]

Abstract: A series of air-stable chiral ferrocenylphosphines (**LB1**–**LB4**) were prepared and used in the asymmetric allylic substitution of Morita–Baylis–Hillman (MBH) adducts with phthalimide under mild reaction conditions; the (R,S_{Fc})-ferrocenylphosphine **LB4** afforded the desired amination products **3** in moderate yields with excellent enantioselectivities. The absolute configuration of **3o** was confirmed by X-ray analysis.

Introduction

The Morita–Baylis–Hillman (MBH) reaction has emerged as an attractive approach for the preparation of α-methylene-β-hydroxycarbonyl compounds, which are versatile synthetic building blocks in organic synthesis.[1] In recent decades, great effort has been devoted to the synthesis of these chiral compounds through the following two approaches: the asymmetric Morita–Baylis–Hillman (MBH) reaction[2] and the asymmetric substitution of MBH adducts.[3] Owing to the broader range of substrates, increasing attention has been paid to the asymmetric substitution of MBH adducts. Notably, great progress have been achieved in the organophosphine-catalyzed allylic amination and allylic alkylation of MBH acetates and carbonates.[4] In 2004, Krische and co-workers[5] first reported the asymmetric amination of MBH acetates with phthalimide catalyzed by chiral phosphanes, which provided the corresponding substitution products in good yields along with moderate *ee* values. Inspired by the elegant work of Krische, Hou and Shi independently studied the asymmetric transformation of MBH adducts to build highly functionalized γ-butenolides from MBH acetates or carbonates. In 2007, Hou and co-workers[6] reported the enantioselective substitution of MBH adducts derived from acrylate with phthalimide, catalyzed by planar chiral [2,2]-paracyclophane monophosphanes to give the allylic amination products with high regioselectivities but poor-to-moderate enantioselectivities (9–71 % *ee*); however, the absolute configuration of these amination products was not disclosed (Scheme 1). Later, Shi and co-workers[7,8] developed a set of highly active chiral phosphane organocatalysts, containing both Lewis basic and Brönsted acidic sites, which can achieve highly enantioselective allylic amination of acetates of MBH alcohols derived from methyl vinyl ketone (MVK) or ethyl vinyl ketone (EVK) to afford the target products in good yields and up to 90 % *ee* (Scheme 2). To date, methodologies for the highly enantioselective substitution of carbonates or acetates of MBH alcohols derived from MVK and EVK have been well-established and can be achieved readily, but the asymmetric reactions of MBH adducts derived from acrylate with phthalimide have remained a challenge. Thus, the discovery of new catalysts to achieve the highly enantioselective substitution of MBH acetates or carbonates derived from acrylate is still a highly desirable goal. Very recently, our group reported a highly enantioselective [3+2] cycloaddition reaction catalyzed by the chiral bifunctional ferrocenylphosphine **LB2** (Scheme 3).[9] The catalysts containing five-membered heteroaryl rings and amide moieties presented higher catalytic activities owing to a favorable steric interaction be-

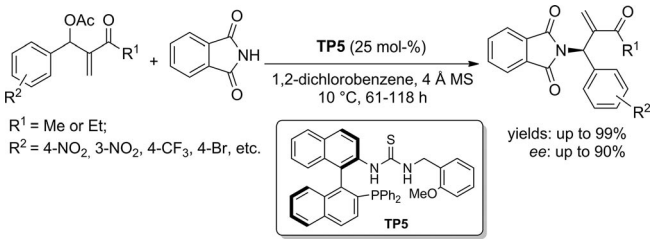


Scheme 1. Previous work by Hou and co-workers.

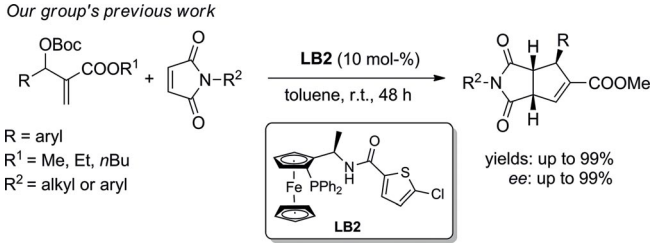
[a] *Collaborative Innovation Center of Green Pharmaceutical Engineering, College of Pharmaceutical Sciences, Zhejiang University of Technology, Chao Wang Road 18th, 310014, Hangzhou, P. R. China*
E-mail: weihuizhong@zjut.edu.cn
www.zjut.edu.cn

Supporting information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/ejoc.201600045.

tween the diphenylphosphine and heteroaryl moieties. On the basis of these results, in this work, we chose the best structural pattern and modified the five-membered heteroaryl ferrocenylphosphine catalyst and then investigated if the highly enantioselective amination of MBH adducts derived from acrylate with phthalimide could be achieved (Figure 1).



Scheme 2. Previous work by Shi and co-workers.



Scheme 3. Asymmetric [3+2] cycloaddition reaction catalyzed by ferrocenylphosphines.

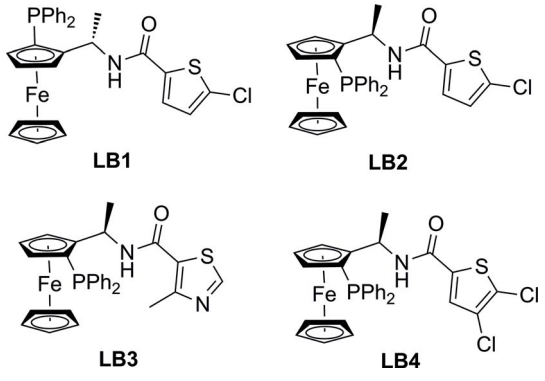
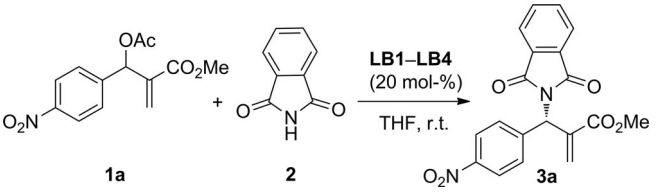


Figure 1. The structures of the chiral bifunctional ferrocenylphosphines.

Results and Discussion

The initial assays were performed with MBH adduct **1a** and phthalimide (**2**) in the presence of the chiral bifunctional ferrocenylphosphines **LB1**–**LB4** (Table 1). Pleasingly, the allylic amination product **3a** was obtained in 65 % yield and 91 % *ee* with **LB2** (20 mol-%) as the catalyst in tetrahydrofuran (THF) at room temperature for 120 h (Table 1, Entry 2). In addition, **LB1** as the catalyst resulted in a decrease in both yield and enantioselectivity (Table 1, Entry 1). Catalyst **LB3** was also effective for this reaction and afforded the desired product **3a** in moderate yield but good *ee* (Table 1, Entry 3). Delightfully, the dichloro-substituted catalyst **LB4** showed the best enantioselectivity in this reaction and afforded the corresponding product **3a** in 73 % yield with 94 % *ee* (Table 1, Entry 4). A slight increase of both yield and *ee* was observed for a prolonged reaction time of 240 h (Table 1, Entry 5). Notably, decreased catalyst loadings and temperature had little influence on this reaction (Table 1, Entries 6–9). The further exploration of the effect of the solvent suggested that $CHCl_3$ can significantly promote the reaction to afford the corresponding product **3a** in 74 % yield and 96 % *ee* (Table 1, Entries 10–13).

Table 1. Screening of chiral phosphines for the allylic substitution of MBH adduct **1a** with phthalimide **2**.[a]



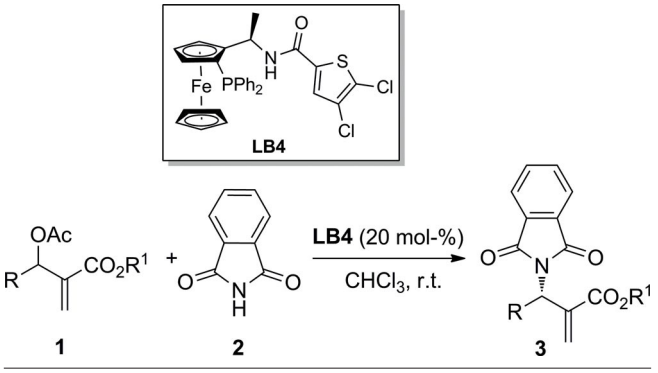
Entry	Catalyst [mol-%]	Time [h]	*T* [°C]	Solvent	**3a** Yield[b] [%]	**3a** *ee*[c] [%]
1	**LB1** (20)	120	r.t.	THF	64	–86
2	**LB2** (20)	120	r.t.	THF	65	91
3	**LB3** (20)	120	r.t.	THF	58	92
4	**LB4** (20)	120	r.t.	THF	73	94
5	**LB4** (20)	240	r.t.	THF	74	96
6	**LB4** (10)	120	r.t.	THF	52	96
7	**LB4** (20)	240	0	THF	42	96
8	**LB4** (20)	120	40	THF	75	94
9	**LB4** (20)	120	40	$CHCl_3$	74	96
10	**LB4** (20)	120	r.t.	CH_2Cl_2	42	94
11	**LB4** (20)	120	r.t.	Et_2O	34	75
12	**LB4** (20)	120	r.t.	$CHCl_3$	74	96
13	**LB4** (20)	120	r.t.	toluene	53	92

[a] Unless otherwise specified, the reactions were performed with **1a** (0.5 mmol), **2** (1.5 mmol), and catalysts **LB1**–**LB4** (0.1 mmol) in THF (2.5 mL) at room temperature. [b] Isolated yield. [c] The *ee* was determined by HPLC analysis with a chiral column.

With the optimal reaction conditions in hand (Table 1, Entry 12), the scope of this reaction was then explored with a series of MBH acetates **1** derived from acrylate in the reaction with **2** (Table 2). A variety of substituted MBH adducts **1** bearing electron-withdrawing or -donating groups on aromatic ring or different ester groups on the side chain all proceeded smoothly after 120 h to afford the corresponding products (**3a**–**3p**) in moderate-to-good yields (up to 74 %) and excellent *ee* values (up to 96 % *ee*). We found that the substrate derived from methyl acrylate delivered a better result than the substrates derived from ethyl acrylate and butyl acrylate (Table 2, Entries 1–3). Notably, electron-withdrawing aromatic MBH adducts were more reactive than electron-donating ones (Table 2, Entries 1, 11, 13, and 15). In addition, multisubstituted aromatic rings (Table 2, Entries 12 and 16) also afforded the corresponding products in moderate yields along with high *ee* values. Owing to steric hindrance, the *ortho*-heterosubstituted MBH adducts gave lower yields than those of *meta*- or *para*-substituted products (Table 2, Entries 6–10). Notably, the *ortho*-nitro-substituted MBH adduct could not undergo this reaction (Table 2, Entry 4). A naphthyl group was tolerated in this reaction, and the corresponding product **3p** was obtained in moderate yield

and *ee* (Table 2, Entry 17). Unfortunately, for the aliphatic MBH acetate, the product was not obtained even if the reaction was performed at a higher temperature (40 or 60 °C) or with a higher catalyst loading (Table 2, Entry 18). The absolute configuration of **3o** was determined to be *R* by X-ray analysis (Figure 2). Interestingly, the absolute configuration of most of products **3** should be (+)-*S* according to their specific rotation (Table 2).

Table 2. Asymmetric allylic substitution reaction of MBH adducts with phthalimide catalyzed by **LB4**.[a]



Entry	R/R[1]	Yield[b] [%]	*ee*[c] [%]	Absolute configuration
1	4-$NO_2C_6H_4$/Me	74 (**3a**)	96	(–)-*S*
2	4-$NO_2C_6H_4$/Et	65 (**3b**)	72	(+)-*S*
3	4-$NO_2C_6H_4$/*n*Bu	60 (**3c**)	73	(–)-*S*
4	2-$NO_2C_6H_4$/Me	–	–	–
5	4-FC_6H_4/Me	39 (**3d**)	72	(+)-*S*
6	2-ClC_6H_4/Me	35 (**3e**)	90	(–)-*R*
7	3-ClC_6H_4/Me	36 (**3f**)	82	(+)-*S*
8	4-ClC_6H_4/Me	51 (**3g**)	75	(+)-*S*
9	4-BrC_6H_4/Me	46 (**3h**)	73	(+)-*S*
10	3-BrC_6H_4/Me	41 (**3i**)	89	(+)-*S*
11	4-MeC_6H_4/Me	56 (**3j**)	73	(+)-*S*
12	3,4-$Me_2C_6H_3$/Me	36 (**3k**)	91	(+)-*S*
13	4-$MeOC_6H_4$/Me	41 (**3l**)	62	(+)-*S*
14	C_6H_5/Me	46 (**3m**)	92	(+)-*S*
15	4-$F_3CC_6H_4$/Me	71 (**3n**)	89	(+)-*S*
16	2,4-$Cl_2C_6H_3$/Me	57 (**3o**)	94	(–)-*R*
17	1-naphthyl/Me	31 (**3p**)	78	(+)-*S*
18	phenylpropyl/Me	Trace	–	–

[a] Unless otherwise specified, the reactions were performed with **1** (0.5 mmol), **2** (1.5 mmol), and **LB4** (0.1 mmol) in $CHCl_3$ (2.5 mL) at room temperature. [b] Isolated yield. [c] The *ee* was determined by HPLC analysis with a chiral column.

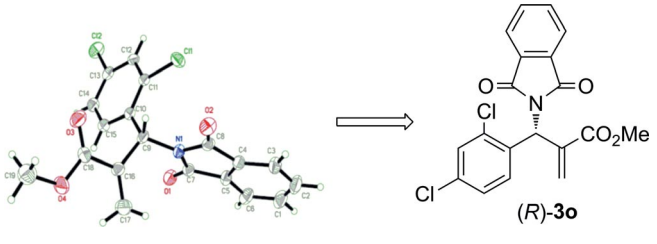
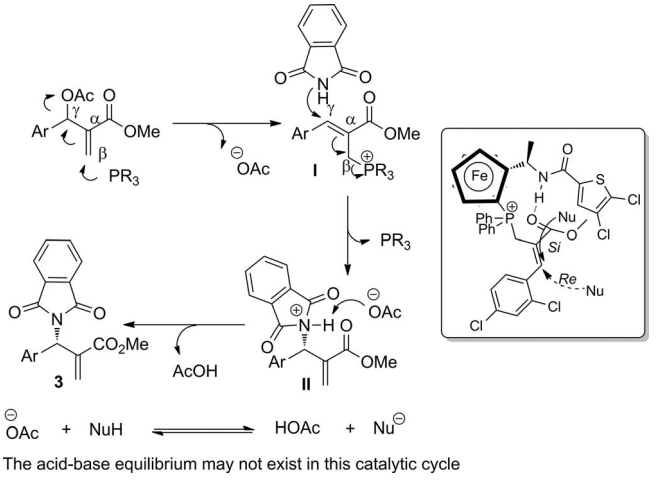


Figure 2. X-ray crystal structure of (*R*)-**3o**.

On the basis of the experimental results[10] and previous work,[5,8,11] a plausible mechanism and an activation model are outlined in Scheme 4. The direct nucleophilic addition of the chiral bifunctional ferrocenylphosphine catalyst to the MBH acetate generates the intermediate **I** and an acetate ion. The acetate ion engages in an acid–base equilibrium involving deprotonation of the pronucleophile, as proposed by Krische. In our case, the pK_a of the pronucleophile phthalimide (pK_a = 8.3)[12] is higher than that of acetic acid (pK_a = 4.8);[13] therefore, the acetate should not deprotonate the phthalimide. Thus, we propose that the phthalimide directly attacks the γ position of the olefin from the *Re* face of the olefin owing to a steric repulsion between the aromatic group of the catalyst and the phthalimide to offer intermediate **II**, which undergoes deprotonation to afford the final product **3**.



Scheme 4. Possible mechanism.

Conclusions

We have developed a series of chiral ferrocenylphosphines to promote the enantioselective allylic substitution of MBH adducts with phthalimide, and the chiral ferrocenylphosphine **LB4** showed good catalytic activity for this reaction. Furthermore, **LB4** is reasonably air-stable in solution and in the solid state.[14] Efforts are in progress to use the chiral ferrocenylphosphine catalysts for other asymmetric reactions.

Experimental Section

Materials and General Experimental Details: All starting materials were commercially available and used without further purification. Melting points were determined with a Büchi B-540 capillary melting-point apparatus. Optical rotations were determined with an Autopol V polarimeter. The ^1H and ^{13}C NMR spectra of samples in $CDCl_3$ were recorded with a Varian-400 spectrometer at 400 and 100 MHz with tetramethylsilane (TMS, δ = 0 ppm) as an internal standard. The chemical shifts are reported in ppm, and coupling constants *J* are expressed in Hertz. The ^{31}P NMR spectra of samples in $CDCl_3$ with 85 % H_3PO_4 as an internal standard were recorded with a Varian 400 spectrometer at 161.9 MHz. Solution mass spectra were obtained with a Trace DSQ mass spectrometer in ESI mode and a Trace quadrupole mass spectrometer in EI mode. High-resolution mass spectra were acquired with an Agilent 6210 TOF mass spectrometer. The enantiomeric excesses of the target molecules were determined through chiral-phase HPLC analysis with an

Agilent 1100 HPLC system (Daicel Chiralcel AD-H, OD-H, or AS-H column and eluted with *n*-hexane/*i*PrOH) with a UV diode array detector (DAD). The X-ray analysis was performed with Xcalibur and Gemini instruments.

The MBH adducts **1** were prepared by the literature procedure.[15]

(*S*)-5-Chloro-*N*-[1′-(*R*)-2′-(diphenylphosphanyl)ferrocenyl]ethylthiophene-2-carboxamide (LB1): A mixture of 5-chlorothiophene-2-carboxylic acid (0.24 g, 1.5 mmol), bis(trichloromethyl)carbonate (0.22 g, 0.75 mmol), and *N*,*N*-dimethylformamide (DMF; 1.10 mg, 0.015 mmol) in toluene (5 mL) was heated to 110 °C. Then, the generated 5-chlorothiophene-2-carbonyl chloride was cooled to room temperature and added to a solution of (*S*)-1-(*S*)-[diphenylphosphinoferrocenyl]ethylamine (0.21 g, 0.50 mmol) in CH_2Cl_2 (5 mL), and the reaction mixture was stirred at 0 °C for 1 h. After the completion of the reaction, water was added to quench the reaction. The reaction mixture was then filtered and extracted with CH_2Cl_2 (3 × 10 mL), and the combined organic extracts were dried with Na_2SO_4, filtered, and concentrated. The residue was purified by flash column chromatography to afford **LB1** (0.24 g, 86 %) as a yellow solid, m.p. 118.5–120.5 °C. $[\alpha]_D^{20}$ = +323.2 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.57–7.49 (m, 2 H), 7.40 (d, *J* = 5.2 Hz, 3 H), 7.19 (d, *J* = 3.2 Hz, 5 H), 7.14 (s, 1 H), 6.99 (d, *J* = 3.6 Hz, 1 H), 6.80 (d, *J* = 2.4 Hz, 1 H), 5.25 (q, *J* = 6.0 Hz, 1 H), 4.54 (s, 1 H), 4.36 (s, 1 H), 4.02 (s, 5 H), 3.86 (s, 1 H), 1.41 (d, *J* = 6.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.0, 138.7, 138.0, 136.3, 135.0, 134.8, 134.6, 132.6, 132.4, 129.4, 128.3 (2 C), 128.2, 126.7 (2 C), 95.7, 95.5, 73.9, 73.8, 72.2, 71.3, 70.0 (5 C), 69.6, 46.0, 23.0 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ = –23.73 ppm. MS (ESI): *m*/*z* (%) = 580.6 (100) $[M + Na]^+$. HRMS (ESI): calcd. for $C_{29}H_{25}ClFeNNaOPS$ $[M + Na]^+$ 580.0325; found 580.0322.

Catalyst **LB2** was prepared as a yellow solid by a similar procedure. $[\alpha]_D^{20}$ = –328.0 (*c* = 0.5, $CHCl_3$).

(*R*)-3-Methyl-*N*-[1′-(*S*)-2′-(diphenylphosphanyl)ferrocenyl]ethylthiazole-2-carboxamide (LB3): By following a similar procedure as that for **LB1**, **LB3** (0.24 g, 92 %) was obtained a yellow solid, m.p. 58.8–60.8 °C. $[\alpha]_D^{20}$ = –339.2 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.63 (s, 1 H), 7.55–7.48 (m, 2 H), 7.38 (d, *J* = 5.2 Hz, 3 H), 7.18–7.08 (m, 5 H), 6.71–6.62 (m, 1 H), 5.33 (q, *J* = 5.2 Hz, 1 H), 4.53 (s, 1 H), 4.35 (t, *J* = 2.4 Hz, 1 H), 4.03 (s, 5 H), 3.88–3.81 (m, 1 H), 2.68 (s, 3 H), 1.45 (d, *J* = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 159.7, 155.8, 151.6, 138.8, 136.4, 135.0, 134.7, 132.4, 132.2, 129.3, 128.2, 128.2, 128.1, 125.9, 95.4, 95.1, 74.4, 74.3, 72.3, 71.0, 70.0 (5 C), 69.5, 45.9, 22.7, 17.5 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ = –24.60 ppm. MS (ESI): *m*/*z* (%) = 561.2 (100) $[M + Na]^+$. HRMS (ESI): calcd. for $C_{29}H_{27}FeN_2NaOPS$ $[M + Na]^+$ 561.0823; found 561.0845.

(*R*)-4,5-Dichloro-*N*-[1′-(*S*)-2′-(diphenylphosphanyl)ferrocenyl]ethylthiophene-2-carboxamide (LB4): By following a similar procedure as that for **LB1**, **LB4** (0.26 g, 87 %) was obtained as a yellow solid, m.p. 85.5–87.8 °C. $[\alpha]_D^{20}$ = –340.4 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.54–7.47 (m, 2 H), 7.38 (d, *J* = 4.8 Hz, 3 H), 7.18 (d, *J* = 4.0 Hz, 5 H), 6.56 (s, 1 H), 6.54–6.49 (m, 1 H), 5.33 (q, *J* = 6.8 Hz, 1 H), 4.53 (s, 1 H), 4.35 (t, *J* = 2.4 Hz, 1 H), 4.03 (s, 5 H), 3.87–3.83 (m, 1 H), 1.47 (d, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 158.1, 138.9, 136.2, 135.8, 134.9, 134.7, 132.6, 132.4, 129.4, 129.3, 128.5, 128.3, 128.2, 126.1, 123.9, 94.8, 94.6, 74.8, 74.7, 72.4, 70.9, 70.1 (5 C), 69.6, 46.1, 21.9 ppm. ^{31}P NMR (162 MHz, $CDCl_3$, 85 % H_3PO_4): δ = –24.67 ppm. MS (ESI): *m*/*z* (%) = 630.5 (100) $[M + K]^+$. HRMS (ESI): calcd. for $C_{29}H_{24}Cl_2FeNOPS$ $[M + K]^+$ 613.9936; found 613.9951.

General Procedure for the Enantioselective Allylic Substitution: To a flame-dried Schlenk tube charged with the corresponding MBH acetate **1** (0.5 mmol), **2** (1.5 mmol, 220.5 mg), and chiral ferrocenylphosphine **LB4** (59.1 mg, 0.1 mmol) was added anhydrous $CHCl_3$ (2.5 mL). The reaction mixture stirred at room temperature under an argon atmosphere for 120 h. The reaction was monitored by TLC. After the starting substrates were consumed, the solvent was removed under reduced pressure, and the residue was purified by silica gel column chromatography (eluent: *n*-hexane/EtOAc/CH_2Cl_2 8:1:1) to give the corresponding amination adduct **3**.

Sixteen chiral products were synthesized, of which 12 were new compounds (**3c, 3d**–**3f**, **3h**–**3l**, and **3n**–**3p**).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-nitrophenyl)allyl]phthalimide (3a): Yellow oil. $[\alpha]_D^{20}$ = –10.4 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.4 Hz, 2 H), 7.84–7.87 (m, 2 H), 7.74–7.76 (m, 2 H), 7.61 (d, *J* = 8.4 Hz, 2 H), 6.63 (s, 1 H), 6.52 (s, 1 H), 5.67 (s, 1 H), 3.73 (s, 3 H) ppm. MS (EI): *m*/*z* (%) = 366 (5), 334 (97), 147 (18), 104 (95), 76 (35). The *ee* was determined by HPLC with a chiral OD-H column (λ = 218 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 25.045 min, t_{minor} = 32.678 min; *ee* = 96 %).

(*S*)-*N*-[2-(Ethoxycarbonyl)-1-(4′-nitrophenyl)allyl]phthalimide (3b): Yellow oil. $[\alpha]_D^{20}$ = +2.8 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.21 (d, *J* = 8.8 Hz, 2 H), 7.84–7.87 (m, 2 H), 7.74–7.76 (m, 2 H), 7.62 (d, *J* = 8.8 Hz, 2 H), 6.63 (d, *J* = 1.2 Hz, 1 H), 6.51 (s, 1 H), 5.63 (d, *J* = 1.6 Hz, 1 H), 4.21–4.12 (m, 2 H), 1.19 (t, *J* = 7.2 Hz, 3 H) ppm. MS (EI): *m*/*z* (%) = 380 (3), 334 (60), 306 (100), 104 (36), 76 (25). The *ee* was determined by HPLC with a chiral OD-H column (λ = 218 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 19.380 min, t_{minor} = 23.288 min; *ee* = 72 %).

(*S*)-*N*-[2-(Butoxycarbonyl)-1-(4′-nitrophenyl)allyl]phthalimide (3c): Yellow oil. $[\alpha]_D^{20}$ = –7.2 (*c* = 0.5, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.18 (d, *J* = 7.2 Hz, 2 H), 7.83 (d, *J* = 2.4 Hz, 2 H), 7.73 (d, *J* = 2.8 Hz, 2 H), 7.60 (d, *J* = 7.6 Hz, 2 H), 6.62 (s, 1 H), 6.50 (s, 1 H), 5.63 (s, 1 H), 4.12 (d, *J* = 5.6 Hz, 2 H), 1.57–1.54 (m, 2 H), 1.29–1.26 (m, 2 H), 0.87 (t, *J* = 6.4 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.4 (2 C), 165.0, 147.6, 144.2, 136.7, 134.4 (2 C), 131.6, 129.7 (2 C), 129.4 (2 C), 123.7 (2 C), 123.6 (2 C), 65.4, 54.0, 30.7, 19.3, 13.8 ppm. ES (EI): *m*/*z* (%): 408 (4), 334 (58), 306 (100), 104 (52), 76 (20). HRMS (ESI): calcd. for $C_{22}H_{20}N_2NaO_6$ $[M + Na]^+$ 431.1214; found 431.1226. The *ee* was determined by HPLC with a chiral OD-H column (λ = 218 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 15.775 min, t_{minor} = 18.969 min; *ee* = 73 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-fluorophenyl)allyl]phthalimide (3d): Colorless oil. $[\alpha]_D^{20}$ = +71.7 (*c* = 0.4, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.83 (m, 2 H), 7.71 (m, 2 H), 7.43 (m, 2 H), 7.01–7.05 (m, 2 H), 6.56 (d, *J* = 1.6 Hz, 1 H), 6.38 (s, 1 H), 5.63 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6, 165.7, 163.4, 161.0, 137.3, 134.0 (2 C), 132.7, 131.6, 130.4 (2 C), 129.1 (2 C), 123.3 (2 C), 115.6, 115.4, 54.0, 52.2 ppm. MS (EI): *m*/*z* (%) = 339 (6), 306 (80), 278 (72), 250 (100), 104 (38), 76 (35). HRMS (ESI): calcd. for $C_{19}H_{14}FNNaO_4$ $[M + Na]^+$ 362.0799; found 362.0792. The *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 75:25; flow rate: 0.8 mL/min; t_{major} = 8.737 min, t_{minor} = 14.274 min; *ee* = 72 %).

(*R*)-*N*-[2-Methoxycarbonyl-1-(2′-chlorophenyl)allyl]phthalimide (3e): Colorless oil. $[\alpha]_D^{20}$ = –9.0 (*c* = 0.2, $CHCl_3$). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.84–7.86 (m, 2 H), 7.73–7.76 (m, 2 H), 7.51–7.53 (m, 1 H), 7.38–7.40 (m, 1 H), 7.27–7.29 (m, 2 H), 6.77 (s, 1 H), 6.60 (s, 1 H), 5.62 (s, 1 H), 3.73 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6 (2 C), 165.6, 136.2, 134.4, 134.2 (2 C), 133.6, 131.6 (2 C), 130.2, 129.7, 129.5, 128.8, 126.7, 123.5 (2 C), 52.4, 52.2 ppm. MS (EI): *m*/*z* (%) = 355 (1), 319 (100), 288 (32), 260 (19), 104 (16), 76 (10). HRMS (ESI): calcd. for $C_{19}H_{14}ClNNaO_4$ $[M + Na]^+$ 378.0504; found 378.0518. The

ee was determined by HPLC with a chiral OJ-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 33.296 min, t_{minor} = 26.925 min; *ee* = 90 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(3′-chlorophenyl)allyl]phthalimide (3f): Colorless oil. $[\alpha]_D^{20}$ = +73.3 (*c* = 0.15, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.85 (m, 2 H), 7.72–7.73 (m, 2 H), 7.42 (s, 1 H), 7.28–7.32 (m, 3 H), 6.59 (s, 1 H), 6.37 (s, 1 H), 5.65 (s, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (2 C), 165.8, 139.0, 137.0, 134.6, 134.2 (2 C), 131.7, 129.9 (2 C), 129.8, 128.8, 128.4, 126.9, 123.6 (2 C), 54.3, 52.5 ppm. MS (EI): *m/z* (%) = 355 (13), 295 (88), 267 (36), 207 (100), 104 (70), 76 (45). HRMS (ESI): calcd. for $C_{19}H_{14}ClNNaO_4$ $[M + Na]^+$ 378.0504; found 378.0514. The *ee* was determined by HPLC with a chiral OJ-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 95:5; flow rate: 0.8 mL/min; t_{major} = 34.998 min, t_{minor} = 32.733 min; *ee* = 82 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-chlorophenyl)allyl]phthalimide (3g): Colorless oil. $[\alpha]_D^{20}$ = +74.7 (*c* = 0.8, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.84 (m, 2 H), 7.70–7.73 (m, 2 H), 7.30–7.39 (m, 4 H), 6.57 (d, *J* = 1.6 Hz, 1 H), 6.37 (s, 1 H), 5.64 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H) ppm. MS (EI): *m/z* (%) = 355 (5), 325 (15), 297 (20), 295 (100), 104 (33), 50 (2). Th *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.6 mL/min; t_{major} = 13.926 min, t_{minor} = 19.816 min; *ee* = 75 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-bromophenyl)allyl]phthalimide (3h): Colorless oil. $[\alpha]_D^{20}$ = +38.3 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.84 (m, 2 H), 7.70–7.72 (m, 2 H), 7.47 (d, *J* = 8.4 Hz, 2 H), 7.32 (d, *J* = 8.4 Hz, 2 H), 6.57 (d, *J* = 0.8 Hz, 1 H), 6.36 (s, 1 H), 5.64 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.7 (2 C), 165.8, 137.1, 136.0, 134.2 (2 C), 131. 8 (2 C), 131.7, 130.4 (2 C), 129.5 (2 C), 123.5 (2 C), 122.3, 54.2, 52.5 ppm. MS (EI): *m/z* (%) = 399 (7), 339 (96), 311 (26), 104 (66), 76 (100). HRMS (ESI): calcd. for $C_{19}H_{14}BrNNaO_4$ $[M + Na]^+$ 421.9998; found 422.0004. The *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 10.880 min, t_{minor} = 14.623 min; *ee* = 73 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(3′-bromophenyl)allyl]phthalimide (3i): Colorless oil. $[\alpha]_D^{20}$ = +89.2 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.84 (m, 2 H), 7.70–7.72 (m, 2 H), 7.57 (s, 1 H), 7.36–7.44 (m, 2 H), 7.20–7.24 (m, 1 H), 6.59 (s, 1 H), 6.36 (s, 1 H), 5.66 (s, 1 H), 3.73 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.0 (2 C), 165.1, 138.8, 136.5, 133.8 (2 C), 131.3 (2 C), 130.9 (2 C), 129.8, 129.4, 127.0, 123.2 (2 C), 122.4, 54.3, 52.6 ppm. MS (EI): *m/z* (%) = 399 (6), 369 (28), 341 (42), 231 (100), 104 (66), 76 (42). HRMS (ESI): calcd. for $C_{19}H_{14}BrNNaO_4$ $[M + Na]^+$ 421.9998; found 422.0015. The *ee* was determined by HPLC with a chiral OJ-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 98:2; flow rate: 0.8 mL/min; t_{major} = 60.731 min, t_{minor} = 55.895 min; *ee* = 89 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-methylphenyl)allyl]phthalimide (3j): Colorless oil. $[\alpha]_D^{20}$ = +76.5 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.83 (m, 2 H), 7.68–7.71 (m, 2 H), 7.32 (d, *J* = 8.0 Hz, 2 H), 7.15 (d, *J* = 8.0 Hz, 2 H), 6.55 (d, *J* = 1.6 Hz, 1 H), 6.36 (s, 1 H), 5.66 (d, *J* = 1.6 Hz, 1 H), 3.73 (s, 3 H), 2.37 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8 (2 C), 166.1, 137.9, 137.7, 134.0 (2 C), 131.9 (3 C), 129.3 (3 C), 128.6 (2 C), 123.4 (2 C), 54.7, 52.4, 21.4 ppm. MS (EI): *m/z* (%) = 335 (5), 304 (9), 276 (15), 275 (100), 76 (27). HRMS (ESI): calcd. for $C_{20}H_{17}NNaO_4$ $[M + Na]^+$ 358.1050; found 358.1064. The *ee* was determined by HPLC with a chiral OD-H column (λ = 218 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 12.303 min, t_{minor} = 14.144 min; *ee* = 73 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(3,4-dimethylphenyl)allyl]phthalimide (3k): Colorless oil. $[\alpha]_D^{20}$ = +21.2 (*c* = 0.2, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.81–7.83 (m, 2 H), 7.68–7.70 (m, 2 H), 7.17–7.18 (m, 2 H), 7.10 (d, *J* = 8.4 Hz, 1 H), 6.54 (d, *J* = 1.2 Hz, 1 H), 6.33 (s, 1 H), 5.66 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H), 2.24 (s, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.3 (2 C), 165.5, 137.3, 136.4, 136.1, 134.0, 133.6 (2 C), 131.5 (2 C), 129.5 (2 C), 129.0, 125.8, 123.1 (2 C), 54.8, 52.5, 20.5, 20.1 ppm. MS (EI): *m/z* (%) = 349 (11), 289 (100), 260 (83), 232 (10), 104 (49). HRMS (ESI): calcd. for $C_{21}H_{19}NNaO_4$ $[M + Na]^+$ 372.1206; found 372.1211. The *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.6 mL/min; t_{major} = 16.840 min, t_{minor} = 21.436 min; *ee* = 91 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-methoxyphenyl)allyl]phthalimide (3l): Colorless oil. $[\alpha]_D^{20}$ = +78.7 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.80–7.82 (m, 2 H), 7.68–7.70 (m, 2 H), 7.38 (d, *J* = 8.4 Hz, 2 H), 6.87 (d, *J* = 8.4 Hz, 2 H), 6.54 (d, *J* = 1.6 Hz, 1 H), 6.34 (s, 1 H), 5.65 (d, *J* = 2.0 Hz, 1 H), 3.81 (s, 3 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.8 (2 C), 166.0, 159.3, 137.9, 134.0 (2 C), 131.9, 130.0 (3 C), 129.1 (2 C), 123.4 (2 C), 114.0 (2 C), 55.4, 54.4, 52.3 ppm. MS (EI): *m/z* (%) = 351 (13), 291 (100), 290 (57), 262 (32), 104 (41), 76 (29). HRMS (ESI): calcd. for $C_{20}H_{17}NNaO_5$ $[M + Na]^+$ 374.0999; found 374.1007. The *ee* was determined by HPLC with a chiral OD-H column (λ = 218 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 22.411 min, t_{minor} = 17.828 min; *ee* = 62 %).

(*S*)-*N*-[(2-Methoxycarbonyl-1-phenyl)allyl]phthalimide (3m): Yellow oil. $[\alpha]_D^{20}$ = +82.4 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.82–7.84 (m, 2 H), 7.69–7.71 (m, 2 H), 7.30–7.44 (m, 5 H), 6.56 (d, *J* = 1.6 Hz, 1 H), 6.39 (s, 1 H), 5.63 (d, *J* = 1.6 Hz, 1 H), 3.71 (s, 3 H) ppm. MS (EI): *m/z* (%) = 321 (2), 289 (33), 261 (100), 104 (26), 76 (10). The *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 70:30; flow rate: 0.8 mL/min; t_{major} = 10.306 min, t_{minor} = 24.835 min; *ee* = 92 %).

(*S*)-*N*-[2-Methoxycarbonyl-1-(4′-trifluoromethylphenyl)allyl]-phthalimide (3n): White solid; m.p. 80.2–81.0 °C. $[\alpha]_D^{20}$ = +77.2 (*c* = 0.5, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.85 (m, 2 H), 7.71–7.73 (m, 2 H), 7.58 (dd, *J* = 18.8, 8.4 Hz, 4 H), 6.60 (s, 1 H), 6.47 (s, 1 H), 5.64 (s, 1 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.6 (2 C), 165.7, 140.9, 136.9, 134.3 (2 C), 131.7, 129.7 (2 C), 129.1 (3 C), 125.6 (3 C), 123.6 (2 C), 54.3, 52.5 ppm. MS (EI): *m/z* (%) = 389 (4), 328 (100), 300 (51), 104 (76), 76 (47). HRMS (ESI): calcd. for $C_{20}H_{14}F_3NNaO_4$ $[M + Na]^+$ 412.0767; found 412.0769. The *ee* was determined by HPLC with a chiral OD-H column (λ = 222 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 9.544 min, t_{minor} = 10.887 min; *ee* = 89 %).

(*R*)-*N*-[2-Methoxycarbonyl-1-(2,4-dichlorophenyl)allyl]-phthalimide (3o): White solid; m.p. 105.1–106.0 °C. $[\alpha]_D^{20}$ = –52.6 (*c* = 1.0, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.83–7.85 (m, 2 H), 7.72–7.74 (m, 2 H), 7.46 (d, *J* = 8.4 Hz, 1 H), 7.39 (d, *J* = 2.4 Hz, 1 H), 7.23–7.25 (m, 1 H), 6.70 (s, 1 H), 6.59 (d, *J* = 1.2 Hz, 1 H), 5.64 (d, *J* = 1.6 Hz, 1 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 166.9 (2 C), 164.8, 135.7, 134.4, 134.1, 133.9 (2 C), 132.6, 131.2 (2 C), 131.0, 129.2, 128.4, 126.7, 123.3 (2 C), 52.7, 51.9 ppm. MS (EI): *m/z* (%) = 355 (75), 266 (40), 206 (11), 73 (100), 59 (5). HRMS (ESI): calcd. for $C_{19}H_{14}Cl_2NO_4$ $[M + H]^+$ 390.0294; found 390.0284. The *ee* was determined by HPLC with a chiral OD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 85:15; flow rate: 0.8 mL/min; t_{major} = 11.435 min, t_{minor} = 23.534 min; *ee* = 94 %).

(*S*)-*N*-[(2-Methoxycarbonyl-1-naphthyl)allyl]phthalimide (3p): Colorless oil. $[\alpha]_D^{20}$ = +52.7 (*c* = 0.4, $CHCl_3$). ^1H NMR (400 MHz, $CDCl_3$): δ = 7.98 (d, *J* = 8.4 Hz, 1 H), 7.82–7.88 (m, 4 H), 7.69–7.72 (m, 2 H), 7.64 (d, *J* = 7.2 Hz, 1 H), 7.44–7.55 (m, 3 H), 7.23 (s, 1 H), 6.59 (d, *J* =

0.8 Hz, 1 H), 5.63 (d, J = 1.6 Hz, 1 H), 3.72 (s, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 167.9 (2 C), 166.0, 137.1, 134.1 (2 C), 133.8, 132.0, 131.7, 130.9, 129.4 (2 C), 129.0 (2 C), 126.9, 126.8, 125.7, 125.1, 123.5 (2 C), 123.1, 52.5, 51.5 ppm. MS (EI): m/z (%) = 355 (3), 327 (6), 207 (100), 165 (87), 104 (25). HRMS (ESI): calcd. for $C_{23}H_{17}NNaO_4$ $[M + Na]^+$ 394.1050; found 394.1048. The *ee* was determined by HPLC with a chiral AD-H column (λ = 220 nm; eluent: *n*-hexane/*i*PrOH 90:10; flow rate: 1.0 mL/min; t_{major} = 25.194 min, t_{minor} = 23.630 min; *ee* = 78 %).

Supporting Information (see footnote on the first page of this article): Spectroscopic data and chiral HPLC traces of the compounds shown in Tables 1 and 2, X-ray crystallographic data for **3o**, and detailed descriptions of the experimental procedures.

Acknowledgments

The authors thank the National Natural Science Foundation of China (NSFC) (grant number 21276238) for financial support.

Keywords: Asymmetric catalysis · Amination · Phosphanes · Configuration determination

[1] For selected reviews on the MBH reaction, see: a) K. Morita, Z. Suzuki, H. Hirose, *Bull. Chem. Soc. Jpn.* **1968**, *41*, 2815; b) D. Basavaiah, P. D. Rao, R. S. Hyma, *Tetrahedron* **1996**, *52*, 8001–8062; c) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–891; d) C. K. W. Kwong, R. Huang, M.-J. Zhang, M. Shi, P. H. Toy, *Chem. Eur. J.* **2007**, *13*, 2369–2376; e) V. Declerck, J. Martinez, F. Lamaty, *Chem. Rev.* **2009**, *109*, 1–48; f) D. Basavaiah, B. S. Reddy, S. S. Badsara, *Chem. Rev.* **2010**, *110*, 5447–5674; g) Q.-Y. Zhao, Z. Lian, Y. Wei, M. Shi, *Tetrahedron* **2012**, *68*, 4899–4905; h) X.-Y. Chen, F. Xia, S. Ye, *Org. Biomol. Chem.* **2013**, *11*, 5722–5726; i) P. Verma, P. Verma, R. B. Sunoj, *Org. Biomol. Chem.* **2014**, *12*, 2176–2179; j) J. Chen, J.-J. Li, J.-Z. Wang, H. Li, W. Wang, Y.-W. Guo, *Org. Lett.* **2015**, *17*, 2214–2217.

[2] For selected reviews on the asymmetric MBH reaction, see: a) P. Langer, *Angew. Chem. Int. Ed.* **2000**, *39*, 3049–3052; *Angew. Chem.* **2000**, *112*, 3177; b) Y.-H. Liu, L.-H. Chen, M. Shi, *Adv. Synth. Catal.* **2006**, *348*, 973–979; c) M. Shi, G.-N. Ma, J. Gao, *J. Org. Chem.* **2007**, *72*, 9779–9781; d) G. Masson, C. Housseman, J.-P. Zhu, *Angew. Chem. Int. Ed.* **2007**, *46*, 4614–4628; *Angew. Chem.* **2007**, *119*, 4698; e) M.-J. Qi, T. Ai, M. Shi, G.-G. Li, *Tetrahedron* **2008**, *64*, 1181–1186; f) Z.-Y. Lei, X.-G. Liu, M. Shi, M.-X. Zhao, *Tetrahedron: Asymmetry* **2008**, *19*, 2058–2062; g) Y.-H. Liu, M. Shi, *Adv. Synth. Catal.* **2008**, *350*, 122–128; h) M. Shi, X.-G. Liu, *Org. Lett.* **2008**, *10*, 1043–1046; i) X.-Y. Guan, Y. Wei, M. Shi, *Chem. Eur. J.* **2010**, *16*, 13617–13621; j) X.-Y. Guan, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2010**, 4098–4105; k) X.-Y. Han, Y.-Q. Wang, F.-R. Zhong, Y.-X. Lu, *Org. Biomol. Chem.* **2011**, *9*, 6734–6740; l) Y.-L. Yang, Y. Wei, M. Shi, *Org. Biomol. Chem.* **2012**, *10*, 7429–7438; m) G. Martelli, M. Orena, S. Rinaldi, *Eur. J. Org. Chem.* **2012**, 4140–4152; n) Y. Wei, M. Shi, *Chem. Rev.* **2013**, *113*, 6659–6690; o) F.-L. Hu, M. Shi, *Org. Chem. Front.* **2014**, *1*, 587–595; p) Y.-N. Gao, Q. Xu, M. Shi, *ACS Catal.* **2015**, *5*, 6608–6614.

[3] For recent reports on the asymmetric substitution of MBH adducts, see: a) D. Basavaiah, N. Kumaragurubaran, D. S. Sharada, R. M. Reddy, *Tetrahedron* **2001**, *57*, 8167–8172; b) G. W. Kabalka, B. Venkataiah, G. Dong, *Organometallics* **2005**, *24*, 762–764; c) Z. Shafiq, L. Liu, Z. Liu, D. Wang, Y.-J. Chen, *Org. Lett.* **2007**, *9*, 2525–2528; d) M. Lakshmi Kantam, K. B. Shiva Kumar, B. Sreedhar, *J. Org. Chem.* **2008**, *73*, 320–322; e) S.-J. Zhang, H.-L. Cui, K. Jiang, R. Li, Z.-Y. Ding, Y.-C. Chen, *Eur. J. Org. Chem.* **2009**, 5804–5809; f) W.-S. Sun, L. Hong, C.-X. Liu, R. Wang, *Org. Lett.* **2010**, *12*, 3914–3917; g) F.-J. Wang, S.-K. Li, M.-L. Qu, M.-X. Zhao, L.-J. Liu, M. Shi, *Chem. Commun.* **2011**, *47*, 12813–12815; h) L. Huang, Y. Wei, M. Shi, *Org. Biomol. Chem.* **2012**, *10*, 1396–1405; i) M.-X. Zhao, M.-X. Chen, W.-H. Tang, D.-K. Wei, T.-L. Dai, M. Shi, *Eur. J. Org. Chem.* **2012**, 3598–3606; j) N.-J. Zhong, L. Liu, D. Wang, Y.-J. Chen, *Chem. Commun.* **2013**, *49*, 3697–3699; k) A.-J. Lin, J.-Y. Wang, H.-B. Mao, Y. Shi, Z.-J. Mao, C.-J. Zhu, *Eur. J. Org. Chem.* **2013**, 6241–6245; l) G.-Y. Ma, M. K. P. Sibi, *Org. Chem. Front.* **2014**, *1*, 1152–1156; m) P. Putaj, I. Ticha, I. Cisarova, J. Vesely, *Eur. J. Org. Chem.* **2014**, 6615–6620; n) S.-X. Ma, Y. Zhong, S.-L. Wang, Z.-Q. Xu, M. Chang, R. Wang, *Acta Chim. Sinica* **2014**, *72*, 825–829; o) L. Yao, C.-J. Wang, *Adv. Synth. Catal.* **2015**, *357*, 384–388.

[4] For recent reports on the organophosphine-catalyzed allylic amination and allylic alkylation of MBH acetates or carbonates, see: a) Y.-Q. Jiang, Y.-L. Shi, M. Shi, *J. Am. Chem. Soc.* **2008**, *130*, 7202–7203; b) Y.-L. Yang, C.-K. Pei, M. Shi, *Org. Biomol. Chem.* **2011**, *9*, 3349–3358; c) H.-P. Deng, M. Shi, *Eur. J. Org. Chem.* **2012**, 183–187.

[5] C.-W. Cho, J.-R. Kong, M. J. Krische, *Org. Lett.* **2004**, *6*, 1337–1339.

[6] T.-Z. Zhang, L.-X. Dai, X.-L. Hou, *Tetrahedron: Asymmetry* **2007**, *18*, 1990–1994.

[7] G.-N. Ma, S.-H. Cao, M. Shi, *Tetrahedron: Asymmetry* **2009**, *20*, 1086–1092.

[8] H.-P. Deng, Y. Wei, M. Shi, *Eur. J. Org. Chem.* **2011**, 1956–1960.

[9] H.-W. Hu, S.-X. Yu, L.-L. Zhu, L.-X. Zhou, W.-H. Zhong, *Org. Biomol. Chem.* **2016**, *14*, 752–760.

[10] The absolute configuration of **3o** was determined to be *R* by X-ray analysis, but the absolute configuration of most of products **3** should be (+)-*S* according to their specific rotation (see the Supporting Information).

[11] H. Park, C.-W. Cho, M. J. Krische, *J. Org. Chem.* **2006**, *71*, 7892–7894.

[12] R. P. Bell, W. C. E. Higginson, *Proc. R. Soc. London Ser. A* **1949**, *197*, 141–159.

[13] J. F. J. Dippy, S. R. C. Hughes, A. Rozanski, *J. Chem. Soc.* **1959**, 2492–2498.

[14] The second NMR spectrum of **LB4** was recorded after it was exposed to air for 3 d, and a trace amount of phosphine oxide was detected.

[15] J. T. M. Correia, M. T. Rodrigues, H. Santos, C. F. Tormena, F. Coelho, *Tetrahedron* **2013**, *69*, 826–832.

Received: January 12, 2016
Published Online: April 6, 2016

