DOI: 10.1002/ejoc.200800321

A Fast Catalytic Asymmetric Aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imines with Methyl Vinyl Ketone in the Presence of Chiral Bifunctional Phosphane Lewis Bases

Zhi-Yu Lei,[a] Guang-Ning Ma,[b] and Min Shi*[a,b]

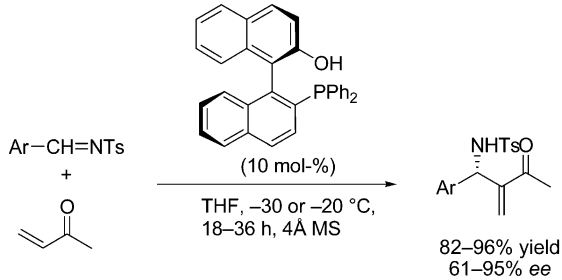
Keywords: Asymmetric catalysis / Aza-Morita–Baylis–Hillman reaction / Ketones / Lewis bases

A series of novel bifunctional chiral phosphane Lewis bases having one phenyl group and an electron-donating alkyl group on the phosphorus atom was designed and successfully synthesized. The use of these bifunctional chiral phosphane Lewis bases in catalytic asymmetric aza-Morita–Baylis–Hillman reactions (aza-MBH reactions) of *N*-sulfonated imines with methyl vinyl ketone affords the corresponding adducts in good-to-excellent yields and moderate-to-good enantioselectivities within a few hours at room temperature. To the best of our knowledge, this is the fastest catalytic asymmetric MBH reaction reported thus far.

Introduction

The asymmetric Morita–Baylis–Hillman reaction is one of the most useful and attractive C–C bond-forming reactions used to give enantiomerically enriched β-hydroxy carbonyl compounds or β-amino carbonyl compounds bearing an α-alkylidene group, which are valuable building blocks in the synthesis of medicinally relevant compounds.[1] Because of the great potential of the products and the superior mild reaction conditions, the catalytic asymmetric version of the aza-Morita–Baylis–Hillman (aza-MBH) reaction has attracted increasing attention and has undergone remarkable progress during the past decade.[2–4] Thus far, many kinds of chiral bifunctional catalysts have been developed and some excellent catalytic systems for the aza-MBH reaction that are able to achieve high enantioselectivities have been reported. Among these reported chiral catalysts, the chiral BINOL-[3] and NOBIN-derived[4] bifunctional catalysts developed by our group, Sasai, and others displayed excellent catalytic activities with wide substrate scopes and excellent enantioselectivities.

Nevertheless, the catalytic asymmetric aza-MBH reaction is often hampered by a low reaction rate (>15 h) and a great deal of chiral catalyst loading (>10 mol-%) is usually required. Hence, the development of more efficient chiral catalysts still remains a great challenge. For example, previously, we reported that the catalytic asymmetric aza-MBH reaction of *N*-sulfonated imines with methyl vinyl ketone (MVK) produced the adducts in 82–96% yield and 61–95%*ee* at –30 or –20 °C within 18–36 h in THF by using (*R*)-2′-diphenylphosphanyl-1,1′-binaphthalen-2-ol as a chiral bifunctional phosphane Lewis base catalyst (10 mol-%) in the presence of 4 Å molecular sieves (Scheme 1).[3a,3c] On the basis of this result, we envisaged that the reaction rate of this aza-MBH reaction can be accelerated by replacing one phenyl group with an electron-donating alkyl group to enhance the nucleophilicity of the phosphorus atom. Herein, we wish to report an efficient catalytic asymmetric aza-MBH reaction of *N*-sulfonated imines with MVK by using 2′-[alkyl(phenyl)phosphanyl]-1,1′-binaphthalen-2-ol as the catalysts to give the corresponding adducts in good-to-excellent yields and moderate-to-good enantioselectivities (up to 88%*ee*) within only 1–5 h at room temperature. To the best our knowledge, this is the fastest asymmetric MBH or aza-MBH reaction reported thus far.



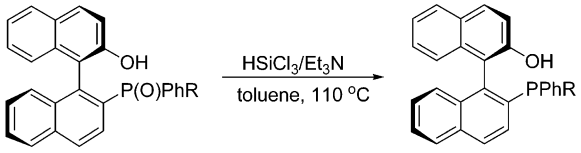
Scheme 1. Catalytic asymmetric aza-MBH reaction in the presence of chiral bifunctional phosphane Lewis base.

[a] School of Chemistry & Molecular Engineering, East China University of Science and Technology, Laboratory for Advanced Materials and Institute of Fine Chemicals,
130 Mei Long Road, Shanghai 200237, China
E-mail: Mshi@mail.sioc.ac.cn
[b] State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, Chinese Academy of Sciences,
354 Fenglin Road, Shanghai 200032, China
Fax: +86-21-64166128

Supporting information for this article is available on the WWW under http://www.eurjoc.org or from the author.

Results and Discussion

As show in Scheme 2, we first designed and synthesized a series of chiral bifunctional phosphane Lewis bases **L1**–**L4** bearing an alkyl group on the phosphorus atom. These phosphane compounds can be easily prepared by reduction of the corresponding phosphane oxides[5] in the presence of Et_3N and $HSiCl_3$.[6] The chirality at phosphorus atom is lost during the reduction of the phosphane oxide. A pair of inseparable diastereoisomers (diastereoisomeric ratio is about 1:1) was acquired and used for the asymmetric aza-MBH reaction. The detailed experimental procedures and the spectroscopic data are summarized in the Supporting Information.



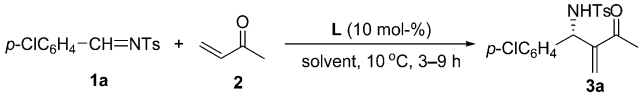
L1: R = Et, 64%
L2: R = *i*Pr, 58%
L3: R = *n*Bu, 67%
L4: R = Cy, 61%

Scheme 2. Preparation of chiral bifunctional phosphane Lewis bases.

Firstly, the catalytic activity of **L1** was examined in the reaction of *N*-[(4-chlorophenyl)methylene]-*N*-tosylamine (**1a**) and MVK (**2**) as a model at room temperature (10 °C) in a variety of solvents. The results of these experiments are presented in Table 1, and THF was found to be the best solvent in terms of both yield and *ee* of the corresponding aza-MBH adduct **3a** (Table 1, Entries 1–5). In dichloromethane, acetonitrile, toluene, or ether, **3a** was formed in 48–98% yield and 27–52%*ee* under identical conditions (Table 1, Entries 2–5). Next studies were aimed at determining the efficiency of other chiral bifunctional phosphane Lewis bases **L2**–**L4** in THF. As shown in Table 1, chiral phosphane Lewis base **L3** produced the corresponding aza-MBH adduct **3a** in 97% yield and 68%*ee* after 3 h (Table 1, Entry 7). Under the same reaction conditions, chiral bifunctional phosphane Lewis base **L2** produced adduct **3a** in lower *ee* though high catalytic ability was also observed (Table 1, Entry 6). In addition, more sterically encumbered chiral bifunctional phosphane Lewis base **L4** did not show any improvement in enantioselectivity, affording **3a** in only 34%*ee* (Table 1, Entry 8). These results indicate that the steric bulkiness around the phosphorus atom in the catalysts is crucial for this catalytic asymmetric reaction. Moreover, it should be also noted that although the chirality on the phosphorus atom is lost during the reduction with $HSiCl_3$ and Et_3N under reflux in toluene, the enantioselectivity of **3a** is introduced by the axial chirality of the BINOL scaffold.

By using **L3** as the catalyst under the optimized reaction conditions, we next carefully examined the temperature effect on this reaction. The results are outlined in Table 2. No

Table 1. Optimization of the reaction conditions in the asymmetric aza-MBH of *N*-[(4-chlorophenyl)methylene]-*N*-tosylamine (**1a**) with MVK (**2**).

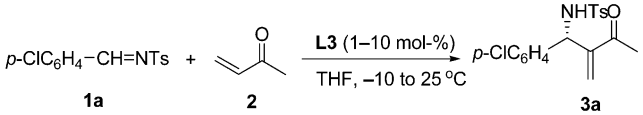


Entry	L	Solvent	Time [h]	Yield [%][a]	*ee*/ [%][b]	Absolute configuration
1	**L1**	THF	4	99	60	*S*
2	**L1**	CH_2Cl_2	5	48	52	*S*
3	**L1**	MeCN	7	98	52	*S*
4	**L1**	PhMe	8	62	27	*S*
5	**L1**	Et_2O	9	76	37	*S*
6	**L2**	THF	3	99	43	*S*
7	**L3**	THF	3	97	68	*S*
8	**L4**	THF	4	94	34	*S*

[a] Isolated yields. [b] Determined by chiral HPLC.

significant improvement in yield or enantioselectivity could be realized at 25, 0, or –10 °C, although the reaction rate was accelerated significantly with the rising of the temperature (Table 2, Entries 1–3). At 25 °C, the reaction was complete within 1 h to afford **3a** in 99% yield and 68%*ee* (Table 2, Entry 1). Having the partially optimized reaction conditions in hand, the loading of phosphane Lewis base **L3** was also examined from the range of 1 to 10 mol-% (Table 2, Entries 1, 4–6). It was found that the reaction rate was accelerated significantly with an increase in catalyst loading to afford **3a** with similar *ee* values. The yield of **3a** could be maintained upon prolonging the reaction time in the cases of less catalyst loading. In the presence of **L3** (5 mol-%), corresponding adduct **3a** was obtained in 96% yield and 67%*ee* within 1.5 h (Table 2, Entry 4). Moreover, adduct **3a** could be attained in 98% yield and 66%*ee* after a prolonged reaction time (5 h) with a catalyst loading of 1 mol-%. Overall, we established the optimized reaction conditions: 5–10 mol-% of **L3** as the catalyst and THF as the solvent at 25 °C.

Table 2. Optimization of the reaction conditions in the asymmetric aza-MBH of *N*-[(4-chlorophenyl)methylene]-*N*-tosylamine (**1a**) with MVK (**2**).

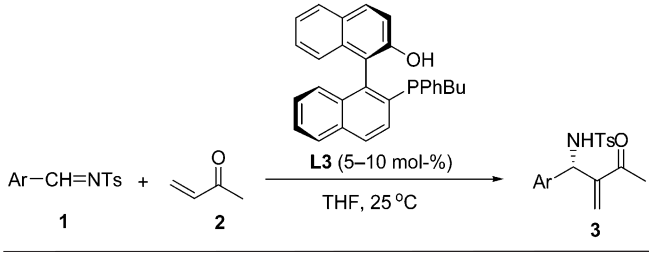


Entry	**L3** [mol-%]	*T* [°C]	Time [h]	Yield [%][a]	*ee* [%][b]
1	10	25	1	99	68
2	10	0	6	98	67
3	10	–10	10	98	67
4	5	25	1.5	96	67
5	3	25	2	97	67
6	1	25	5	98	66

[a] Isolated yields. [b] Determined by chiral HPLC.

To investigate the scope and limitations of this highly efficient catalytic asymmetric aza-MBH reaction of *N*-sulfonated imines with MVK, we examined several other imines under the optimized conditions. The results of these experiments are summarized in Table 3. When *N*-sulfonated imines **1** contained an electron-donating group, such as a methyl or methoxy group, on the aromatic ring, the corresponding adducts **3c** and **3d** were obtained within 4–5 h in the presence of 10 mol-% of **L3** in nearly quantitative yield with *ee* values of 51 and 44%, respectively (Table 3, Entries 2 and 3). As for *N*-sulfonated imines **1** bearing an electron-withdrawing group on the aromatic ring, the reaction proceeded smoothly to afford the corresponding adducts in excellent yields and moderate-to-good *ee* values within 1–2 h in the presence of 5.0 mol-% of **L3** (Table 3, Entries 4–12). Substituents in the *ortho*, *meta*, or *para* position of the aromatic ring in the employed imines did not affect the outcome of the reactions, and higher enantioselectivities were observed when *ortho*-substituted imines were treated with MVK under the standard conditions (Table 3, Entries 6–9 and 12). In particular, *N*-sulfonated imines derived from 2-chlorobenzaldehyde and 2,4-dichlorobenzaldehyde gave the corresponding aza-MBH adducts in 88% *ee* within 2 h, which is the highest enantioselectivity achieved in this interesting catalytic system (Table 3, Entries 7 and 8). Naphthalene-1-carbaldehyde-, heteroaromatic aldehyde-, and aliphatic aldehyde-derived imines gave the corresponding aza-MBH adducts **3n**–**p** in good-to-high yields and moderate enantioselectivities within 3–5 h under identical conditions (Table 3, Entries 13–15).

Table 3. Asymmetric aza-MBH reactions of *N*-tosylaldimines **1** with **2** catalyzed by **L3**.



Entry	Ar	**L3** [mol-%]	*t* [h]	Product	Yield [%][a]	*ee* [%][b]	Absolute configuration
1	C_6H_5	10	3	**3b**	93	52	*S*
2	4-MeC_6H_4	10	4	**3c**	98	51	*S*
3	4-MeOC_6H_4	10	5	**3d**	97	44	*S*
4	4-BrC_6H_4	5	2	**3e**	98	68	*S*
5	3-BrC_6H_4	5	2	**3f**	98	80	*S*
6	2-BrC_6H_4	5	2	**3g**	90	81	*R*
7	2-ClC_6H_4	5	2	**3h**	89	88	*R*
8	2,4-$Cl_2C_6H_3$	5	2	**3i**	91	88	*R*
9	2-FC_6H_4	5	2	**3j**	90	78	*R*
10	4-$NO_2C_6H_4$	5	1	**3k**	96	69	*S*
11	3-$NO_2C_6H_4$	5	1	**3l**	91	69	*S*
12	2-$NO_2C_6H_4$	5	1	**3m**	92	78	*R*
13	1-naphthyl	5	5	**3n**	91	65	*S*
14	2-furyl	5	3	**3o**	89	64	*R*
15	(*E*)-C_6H_5CH=CH	10	4	**3p**	80	61	*S*

[a] Isolated yields. [b] Determined by chiral HPLC.

Conclusions

We designed and synthesized a series of novel chiral bifunctional phosphane Lewis base catalysts having one phenyl group and an electron-donating alkyl group on the phosphorus atom for the catalytic asymmetric aza-MBH reaction. We found that these chiral bifunctional phosphane catalysts are very effective in this reaction under mild and concise conditions to produce the corresponding adducts in good-to-excellent yields and moderate-to-good enantioselectivities within 1–5 h. To the best of our knowledge, this is the fastest catalytic asymmetric MBH reaction reported thus far. Efforts are in progress to elucidate the mechanistic details of this reaction and to study its scope and limitations.

Experimental Section

General Remarks: ^{1}H, ^{31}P, and ^{13}C NMR spectra were recorded with a Varian Mercury vx-300 spectrometer for solution in DMSO or $CDCl_3$ with tetramethylsilane (TMS) as an internal standard. Chiral HPLC was performed with a SHIMADZU SPD-10A series with chiral columns. Elementary analyses (C, H, N) were performed with a Carlo–Erba 1106 analyzer. Mass spectra were recorded by EI and HRMS was measured with a HP-5989 instrument. Flash column chromatography was performed by using silica gel (300–400 mesh). Melting points are uncorrected. All solvents were purified by distillation under the standard conditions. Unless otherwise noted, all commercially obtained reagents were used without further purification. All reactions were carried out under an argon atmosphere. Imines[2a,3a,3c] and phosphane oxides[5] were synthesized according to literature procedures. Products **3a**–**f**, **3h**, **3i**, **3k**–**p** are known compounds.[2a,3a,3c,4a]

General Procedure for the Reduction of Phosphane Oxides: At 0 °C, $HSiCl_3$ (8.0 mmol, 0.8 mL) was carefully added to a mixture of phosphane oxide (2.0 mmol) and triethylamine (16 mmol, 2.1 mL) in toluene (50 mL) in a three-necked round-bottom flask under an argon atmosphere. The reaction mixture was heated to reflux for 16–24 h. After being cooled to room temperature, the mixture was diluted with Et_2O and quenched with a small amount of saturated $NaHCO_3$. The resulting suspension was filtered through Celite, and the solid was washed with Et_2O. The combined organic layer was dried with anhydrous $MgSO_4$ and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2; EtOAc/petroleum ether, 1:10) to give the product as a colorless solid (a pair of diastereoisomers).

(*R*)-2′-[Ethyl(phenyl)phosphanyl]-1,1′-binaphthalen-2-ol (L1): White solid. Yield: 520 mg (64%). M.p. 168–170 °C. $[a]_D^{25}$ = –16.4 (*c* = 0.93, CH_2Cl_2). IR (CH_2Cl_2): $\tilde{\nu}$ = 3054, 2927, 1708, 1621, 1595, 1514, 1434, 1144, 815 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.79–0.89 (m, 3 H, CH_3), 1.01 (dt, *J* = 7.2, 17.4 Hz, 3 H, CH_3), 1.92 (q, *J* = 7.5 Hz, 2 H, CH_2), 2.06 (q, *J* = 7.2 Hz, 2 H, CH_2), 4.50 (br., 1 H, OH), 4.84 (br., 1 H, OH), 6.54 (d, *J* = 8.4 Hz, 1 H, ArH), 6.86–7.05 (m, 7 H, ArH), 7.14–7.38 (m, 14 H, ArH), 7.46–7.51 (m, 2 H, ArH), 7.64–7.78 (m, 3 H, ArH), 7.86–8.01 (m, 7 H, ArH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ = –20.41, –20.83 ppm. MS (EI): *m*/*z* = 406.1 (40.59) $[M]^+$, 405.1 (26.48) $[M - 1]^+$, 390.2 (25.11) $[M - 16]^+$, 389.1 (100) $[M - 17]^+$, 252.1 (13.55) $[M - 154]^+$. HRMS (EI): calcd. for $C_{28}H_{23}OP$ 406.1487; found 406.1487.

(*R*)-2′-[isopropyl(phenyl)phosphanyl]-1,1′-binaphthalen-2-ol (L2): White solid. Yield: 486 mg (58%). M.p. 149–150 °C. $[a]_D^{25}$ = –13.0 (c = 0.58, CH_2Cl_2). IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 2944, 1714, 1621, 1595, 1515, 1434, 1144, 815 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.83–0.99 (m, 8 H, CH_3), 1.12–1.19 (m, 4 H, CH_3), 2.58–2.66 (m, 2 H, CH), 4.25 (br., 1 H, OH), 4.84 (br., 1 H, OH), 6.28 (d, J = 9.0 Hz, 1 H, ArH), 6.72–6.78 (m, 1 H, ArH), 6.93–7.07 (m, 6 H, ArH), 7.12–7.51 (m, 16 H, ArH), 7.78 (d, J = 8.1 Hz, 1 H, ArH), 7.88–7.96 (m, 7 H, ArH), 8.03 (t, J = 8.7 Hz, 2 H, ArH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ = –10.03, –12.40 ppm. MS (EI): m/z = 420.2 (58.95) $[M]^+$, 403.2 (100) $[M - 17]^+$, 377.1 (80.13) $[M - 43]^+$, 252.1 (25.60) $[M - 168]^+$. HRMS (EI): calcd. for $C_{29}H_{25}OP$ 420.1643; found 420.1643.

(*R*)-2′-[Butyl(phenyl)phosphanyl]-1,1′-binaphthalen-2-ol (L3): White solid. Yield: 584 mg (67%). M.p. 68–70 °C. $[a]_D^{25}$ = –14.3 (c = 0.83, CH_2Cl_2). IR (CH_2Cl_2): $\tilde{\nu}$ = 3057, 2969, 1719, 1588, 1509, 1419, 1140, 940 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.68 (t, J = 6.9 Hz, 3 H, CH_3), 0.84 (t, J = 6.9 Hz, 3 H, CH_3), 1.11–1.15 (m, 4 H, CH_2), 1.34–1.43 (m, 4 H, CH_2), 1.88 (t, J = 7.5 Hz, 2 H, CH_2), 2.04 (t, J = 7.5 Hz, 2 H, CH_2), 4.54 (br., 1 H, OH), 4.83 (br., 1 H, OH), 6.54 (d, J = 8.7 Hz, 1 H, ArH), 6.87–7.06 (m, 7 H, ArH), 7.15–7.38 (m, 14 H, ArH), 7.47–7.52 (m, 2 H, ArH), 7.60–7.64 (m, 1 H, ArH), 7.71–7.79 (m, 2 H, ArH), 7.87–8.02 (m, 7 H, ArH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ = –24.68 ppm. MS (EI): m/z = 434.2 (53.07) $[M]^+$, 417.2 (100) $[M - 17]^+$, 377.1 (25.42) $[M - 57]^+$, 268.1 (53.69) $[M - 166]^+$. HRMS (EI): calcd. for $C_{30}H_{27}OP$ 434.1800; found 434.1780.

(*R*)-2′-[Cyclohexyl(phenyl)phosphanyl]-1,1′-binaphthalen-2-ol (L4): White solid. Yield: 560 mg (61%). M.p. 74–76 °C. $[a]_D^{25}$ = –18.8 (c = 0.54, CH_2Cl_2). IR (CH_2Cl_2): $\tilde{\nu}$ = 3055, 2926, 1708, 1619, 1596, 1513, 1433, 1144, 814 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 0.92–1.43 (m, 8 H, CH_2), 1.51–1.78 (m, 12 H, CH_2), 2.25–2.44 (m, 2 H, CH), 4.24 (br., 1 H, OH), 4.81 (br., 1 H, OH), 6.31 (d, J = 8.7 Hz, 1 H, ArH), 6.74–6.79 (m, 1 H, ArH), 6.95–6.97 (m, 5 H, ArH), 7.03–7.53 (m, 17 H, ArH), 7.76–8.05 (m, 10 H, ArH) ppm. ^{31}P NMR (121 MHz, $CDCl_3$, 85% H_3PO_4): δ = –15.35, –17.26 ppm. MS (EI): m/z = 460.2 (85.00) $[M]^+$, 443.2 (100) $[M - 17]^+$, 377.1 (89.54) $[M - 83]^+$, 268.1 (55.87) $[M - 192]^+$. HRMS (EI): calcd. for $C_{32}H_{29}OP$ 460.1956; found 460.1956.

Typical Reaction Procedure for L3-Catalyzed Aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imine 1a with MVK: To a solution of imine **1a** (58.6 mg, 0.2 mmol) and **L3** (4.3 mg, 0.01 mmol) in THF (1.0 mL) was added methyl vinyl ketone (34 μL, 0.4 mmol). The reaction mixture was stirred at 25 °C. When the reaction was completed, as monitored by TLC, the solvent was removed under reduced pressure, and the residue was purified by a flash column chromatography (SiO_2; EtOAc/petroleum ether, 1:3) to afford **3a** as a white solid. Yield: 70.1 mg (96%). M.p. 91.2–91.8 °C. $[a]_D^{25}$ = +18.6 (c = 0.85, CH_2Cl_2) for 67%*ee*. ^1H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.14 (s, 3 H, Me), 2.41 (s, 3 H, Me), 5.26 (d, J = 9.0 Hz, 1 H), 6.02 (d, J = 9.0 Hz, 1 H), 6.07 (s, 1 H), 6.09 (s, 1 H), 7.04 (d, J = 8.7 Hz, 2 H, Ar), 7.14 (d, J = 8.7 Hz, 2 H, Ar), 7.22 (d, J = 8.1 Hz, 2 H, Ar), 7.62 (d, J = 7.8 Hz, 2 H, Ar) ppm. HPLC (Chiralcel AD; hexane/*i*PrOH, 70:30; 0.7 mL/min; 230 nm,): t_{major} = 13.61 min, t_{minor} = 15.99 min.

Supporting Information (see footnote on the first page of this article): Experimental procedures and spectroscopic and analytical data for the compounds shown in Tables 1–3.

Acknowledgments

We thank the Shanghai Municipal Committee of Science and Technology (04JC14083, 06XD14005) and the National Natural Science Foundation of China for financial support (20472096, 203900502, 20672127, and 20732008).

[1] For reviews on the MBH or aza-MBH reaction, see: a) D. Basavaiah, P. D. Rao, R. S. Hyma, *Tetrahedron* **1996**, *52*, 8001–8062; b) S. E. Drewes, G. H. P. Roos, *Tetrahedron* **1988**, *44*, 4653–4670; c) E. Ciganek, *Org. React.* **1997**, *51*, 201–350; d) P. Langer, *Angew. Chem. Int. Ed.* **2000**, *39*, 3049–3051; e) J.-X. Cai, Z.-H. Zhou, C.-C. Tang, *Huaxue Yanjiu* **2001**, *12*, 54–64; f) Y. Iwabuchi, S. Hatakeyama, *J. Synth. Org. Chem. Jap.* **2002**, *60*, 2–14; g) D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–892; h) G. Masson, C. Housseman, J. Zhu, *Angew. Chem. Int. Ed.* **2007**, *46*, 4614–4628; i) D. Basavaiah, K. V. Rao, R. J. Reddy, *Chem. Soc. Rev.* **2007**, *36*, 1581–1588; j) Y. L. Shi, M. Shi, *Eur. J. Org. Chem.* **2007**, *18*, 2905–2916.

[2] a) M. Shi, Y.-M. Xu, *Angew. Chem. Int. Ed. Engl.* **2002**, *41*, 4507–4510; b) S. Kawahara, A. Nakano, T. Esumi, Y. Iwabuchi, S. Hatakeyama, *Org. Lett.* **2003**, *5*, 3103–3105; c) J. E. Imbriglio, M. M. Vasbinder, S. J. Miller, *Org. Lett.* **2003**, *5*, 3741–3743; d) D. Balan, H. Adolfsson, *Tetrahedron Lett.* **2003**, *44*, 2521–2524; e) S. J. Miller, *Acc. Chem. Res.* **2004**, *37*, 601–610; f) M. Shi, Y.-M. Xu, Y.-L. Shi, *Chem. Eur. J.* **2005**, *11*, 1794–1802; g) J. Wang, H. Li, X. H. Yu, L. S. Zu, W. Wang, *Org. Lett.* **2005**, *7*, 4293–4296; h) I. T. Raheem, E. N. Jacobsen, *Adv. Synth. Catal.* **2005**, *347*, 1701–1705; i) A. Berkessel, K. Roland, J. M. Neudörfl, *Org. Lett.* **2006**, *8*, 4195–4198; j) A. Nakano, K. Takahashi, J. Ishihara, S. Hatakeyama, *Org. Lett.* **2006**, *8*, 5357–5360; k) R. Gausepohl, P. Buskens, J. Kleinen, A. Bruckmann, C. W. Lehmann, J. Klankermayer, W. Leitner, *Angew. Chem. Int. Ed.* **2006**, *45*, 3689–3692; l) N. Utsumi, H. Zhang, F. Tanaka, C. F. Barbas III, *Angew. Chem. Int. Ed. Engl.* **2007**, *46*, 1878–1880.

[3] a) M. Shi, L. H. Chen, *Chem. Commun.* **2003**, 1310–1311; b) K. Matsui, S. Takizawa, H. Sasai, *J. Am. Chem. Soc.* **2005**, *127*, 3680–3681; c) M. Shi, L. H. Chen, C.-Q. Li, *J. Am. Chem. Soc.* **2005**, *127*, 3790–3800; d) M. Shi, C.-Q. Li, *Tetrahedron: Asymmetry* **2005**, *16*, 1385–1391; e) M. Shi, L.-H. Chen, W.-D. Teng, *Adv. Synth. Catal.* **2005**, *347*, 1781–1789; f) K. Matsui, S. Takizawa, H. Sasai, *Synlett* **2006**, 761–765; g) Y.-H. Liu, L.-H. Chen, M. Shi, *Adv. Synth. Catal.* **2006**, *348*, 973–979; h) K. Matsui, K. Tanaka, A. Horii, S. Takizawa, H. Sasai, *Tetrahedron: Asymmetry* **2006**, *17*, 578–583; i) K. Ito, K. Nishida, T. Gotanda, *Tetrahedron Lett.* **2007**, *48*, 6147–6149; j) Y.-H. Liu, M. Shi, *Adv. Synth. Catal.* **2008**, *350*, 122–128.

[4] a) Y.-L. Shi, M. Shi, *Adv. Synth. Catal.* **2007**, *349*, 2129–2135; b) M.-J. Qi, T. Ai, M. Shi, G. Li, *Tetrahedron* **2008**, *64*, 1181–1186.

[5] a) C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei, C. H. Senanayake, *Org. Lett.* **2005**, *7*, 4277–4280; b) T. K. Olszewski, B. Boduszek, S. Sobek, H. Kozłowski, *Tetrahedron* **2006**, *62*, 2183–2189; c) J. Bigeault, L. Giordano, G. Buono, *Angew. Chem. Int. Ed. Engl.* **2005**, *44*, 4753–4757.

[6] Y. Uozumi, A. Tanahashi, S.-Y. Lee, T. Hayashi, *J. Org. Chem.* **1993**, *58*, 1945–1948.

Received: March 27, 2008
Published Online: June 25, 2008

