

Asymmetric Aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imines with Activated Olefins Catalyzed by Chiral Phosphine Lewis Bases Bearing Multiple Phenol Groups

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Abstract: In the aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines (*N*-arylmethylidene-4-methylbenzenesulfonamides) with methyl vinyl ketone (MVK), ethyl vinyl ketone (EVK), and acrolein, we found that, through the use of catalytic amounts of chiral phosphine Lewis bases bearing multiple phenol groups, the corresponding adducts could be obtained in good yields with >90% ee at –20 °C or at room temperature in THF. The mechanism of this process was investigated by ³¹P NMR spectroscopic analysis. The phenoxide or the key enolate intermediate, which

is stabilized by intramolecular hydrogen bonding with phenol groups, was observed by ³¹P NMR spectroscopy. Thus, the most effective bifunctional LBBA (Lewis base and Brønsted acid) phosphine-Lewis base promoter system reported to date has been identified for such catalytic, asymmetric aza-Morita–Baylis–Hillman reactions.

Keywords: asymmetric catalysis; aza-Morita–Baylis–Hillman reaction; chiral phosphine; Lewis base; organocatalysts; phenol groups; *N*-sulfonated imines

Introduction

Recently, the design and synthesis of multifunctional organocatalysts for the aza-Morita–Baylis–Hillman (aza-MBH) reaction have received much attention,^[1] and several excellent reaction systems using chiral nitrogen and phosphine Lewis bases as such multifunctional organocatalysts to achieve high enantioselectivities in aza-MBH reactions have been reported.^[2] However, to the best of our knowledge, asymmetric aza-MBH reactions still suffer from slow reaction rates and limited substrate applicability because less electrophilic *N*-tosylaldimines bearing strongly electron-donating groups on the aromatic ring do not react with high reaction rate or afford high ee. Therefore, the development of better multifunctional organocatalysts for catalytic, asymmetric aza-MBH reactions is a very attractive and competitive field of research. Previously, Hine and Kelly reported that double hydrogen bonding can accelerate the reaction of phenyl glycidyl ether with diethylamine and some Diels–Alder reactions by 1,8-biphenylenediol, respectively.^[3] In our previous report of chiral phosphine Lewis base [(*R*)-2'-diphenylphosphanyl-[1,1']binaphthalenyl-2-ol]-catalyzed asymmetric aza-MBH reac-

tions, we also disclosed that a phenolic hydroxy group played a key role in this LBBA (Lewis base and Brønsted acid) bifunctional organocatalyst, with intramolecular hydrogen bonding affording the corresponding aza-MBH adduct in high ee.^[2b, f] On the basis of these results, we envisioned that chiral phosphine Lewis base, such as chiral phosphinyl BINOL,^[2b, f] bearing multiple phenol groups might accelerate the reaction rates and overcome the drawback of the limited substrates in the catalytic, asymmetric aza-MBH reaction since we believe these possibly hydrogen bond donating groups can significantly stabilize the key phosphonium enolate and produce the corresponding adducts in good yields and high ee (Figure 1).

Herein, we report the synthesis of chiral phosphine Lewis bases (**CPLBs**) bearing multiple phenol groups and their application in catalytic, asymmetric aza-MBH reactions. These new chiral phosphine Lewis bases are more effective than those previously reported^[2f] in such reactions. The phenoxide or the key enolate intermediates of these reactions were observed by ³¹P NMR spectroscopy.

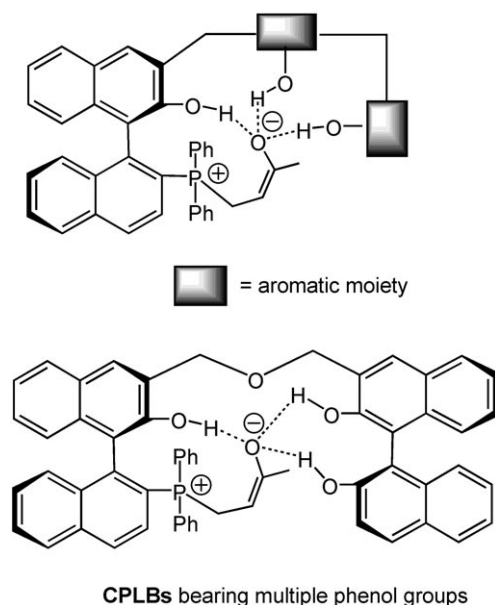


Figure 1. A plausible hydrogen bonding structure in chiral phosphine Lewis bases bearing multiple phenol groups.

Results and Discussion

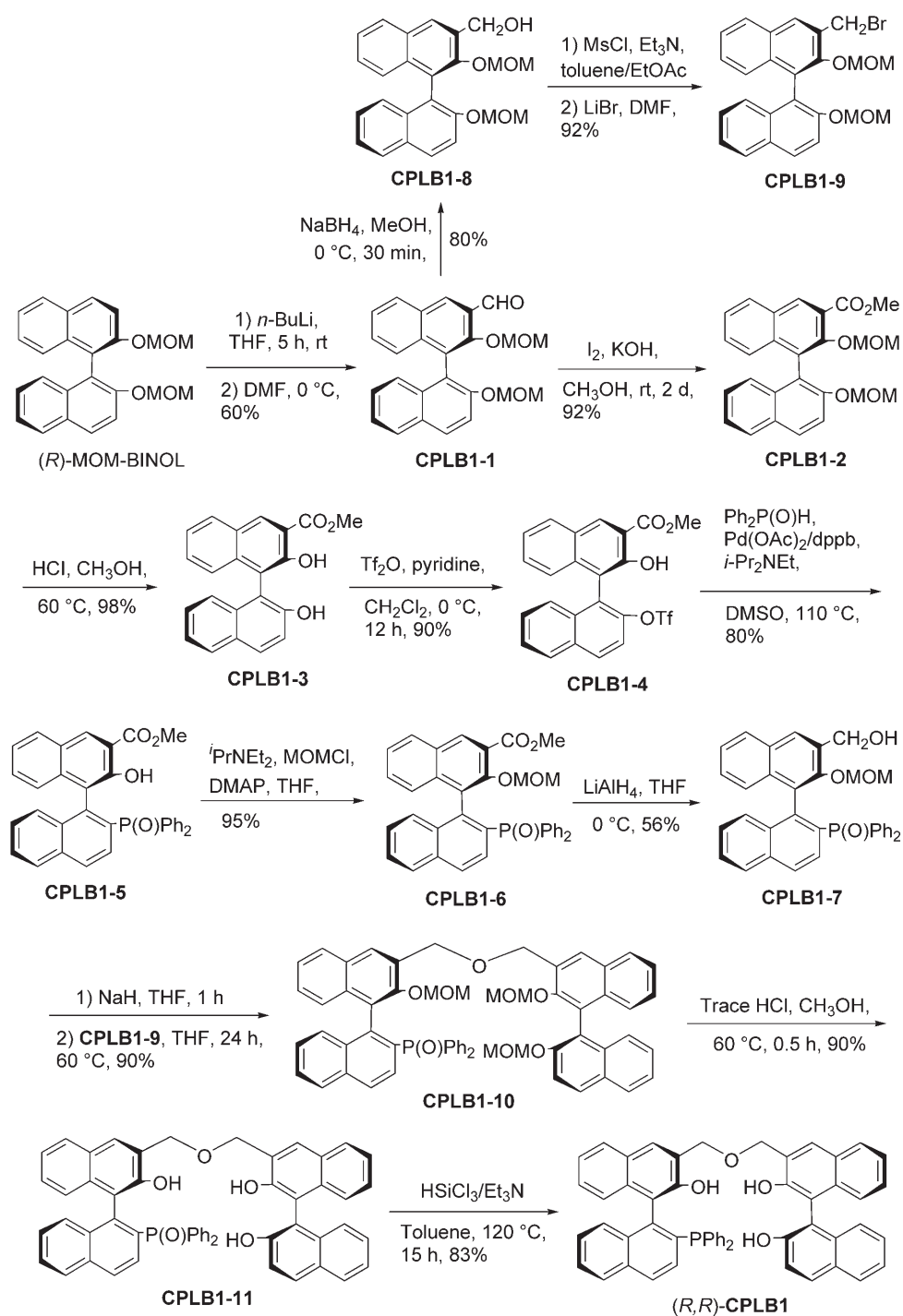
The synthesis of the chiral phosphine Lewis base (CPLB) having multiple phenol groups, **CPLB1**, is shown in Scheme 1. First, compound **CPLB1-1** was synthesized from MOM-protected (*R*)-BINOL by treatment with butyllithium in anhydrous tetrahydrofuran (THF) at room temperature, followed by *N,N*-dimethylformamide (DMF) at 0 °C. The aldehyde group in **CPLB1-1** was converted to the corresponding methyl ester by oxidation of **CPLB1-1** with iodine in methanol in the presence of potassium hydroxide at room temperature for 2 days to afford compound **CPLB1-2** in 90% yield. Deprotection of the MOM-protecting group with aqueous HCl solution in methanol at 60 °C produced compound **CPLB1-3** in 98% yield. Compound **CPLB1-4** was obtained in 90% yield by the reaction of **CPLB1-3** with TiF_4 in the presence of pyridine in dichloromethane at 0 °C. The coupling reaction of **CPLB1-4** with diphenylphosphine oxide afforded compound **CPLB1-5** in 80% yield. The phenol group was then protected by MOMCl to give compound **CPLB1-6**, which was treated with LiAlH_4 in THF to afford alcohol **CPLB1-7** in 56% yield (Scheme 1). Alternatively, reduction of **CPLB1-1** with NaBH_4 in methanol at 0 °C produced alcohol **CPLB1-8** in 80% yield, and this could be transformed into bromide **CPLB1-9** by treatment with methanesulfonyl chloride (MsCl) in the presence of Et_3N in toluene/ EtOAc followed by LiBr in DMF (Scheme 1). The etherification of **CPLB1-7** by **CPLB1-9** was achieved by treatment of **CPLB1-7** with NaH in THF followed by addition of **CPLB1-9**

to provide compound **CPLB1-10** in 90% yield. Removal of the MOM group with aqueous HCl in methanol at 60 °C produced the corresponding phosphine oxide compound **CPLB1-11** in 90% yield. Reduction of phosphoryl group of **CPLB1-11** by HSiCl_3 and Et_3N in toluene at 120 °C (oil bath) afforded the desired compound **CPLB1** in 83% yield (Scheme 1).^[4] Using similar synthetic procedures, a variety of **CPLBs** (Scheme 2) was synthesized in good yields. Their syntheses procedures and spectroscopic data are summarized in the Supporting Information.

With *p*-chlorobenzylidene-4-methylbenzenesulfonamide (**1e**) as substrate, the catalytic asymmetric aza-MBH reaction with methyl vinyl ketone (MVK) was examined by use of 10 mol % of these chiral phosphine Lewis bases in THF at room temperature (25 °C) for 12 h. The results are summarized in Scheme 2. The corresponding aza-MBH adduct **2e** was obtained in >90% yield and >90% ee with chiral phosphine Lewis bases bearing multiple phenol groups such as **CPLB1**, **CPLB2**, **CPLB3** and **CPLB4** (bearing one phenolic hydroxy group and one aliphatic hydroxy group), all of which are much improved compared to our previously reported chiral phosphine Lewis base **CPLB5** under identical conditions (Scheme 2).^[2f,5] It should be noted that **CPLB2**, a diastereomeric isomer of **CPLB1**, produced adduct **2e** in slightly lower yield and ee compared to **CPLB1**. This result suggests that the chirality of the second binaphthol moiety do not influence the ee of the products significantly. In addition, Lewis base catalyst **CPLB4** having one phenolic hydroxy group and one aliphatic hydroxy group, and **CPLB3** having two phenol groups and two diphenylphosphinyl moieties also afforded **2e** in higher yield and ee than the original chiral phosphine Lewis base **CPLB5** under identical conditions. The best result was given by Lewis base catalyst (*R,R*)-**CPLB1**. All these results suggest that chiral phosphine Lewis bases bearing hydroxy groups can indeed improve the yield and ee of aza-MBH reactions.

Using (*R,R*)-**CPLB1** as chiral Lewis base promoter, the catalytic asymmetric aza-MBH reaction of a variety of *N*-sulfonated aldimines **1** with MVK was examined in THF at −20 °C.^[2f] The results are summarized in Table 1. For all of the substrates, >90% ee was achieved in good to high yield (Table 1, entries 1–13). In several cases, 95–96% ee was realized (Table 1, entries 2–6, and 11). For *N*-sulfonated aldimines bearing a strongly electron-donating group on the aromatic ring, such as *p*-methoxybenzylidene-4-methylbenzenesulfonamide (**1c**), 95% ee was achieved in 70% yield using the standard conditions (Table 1, entry 3).

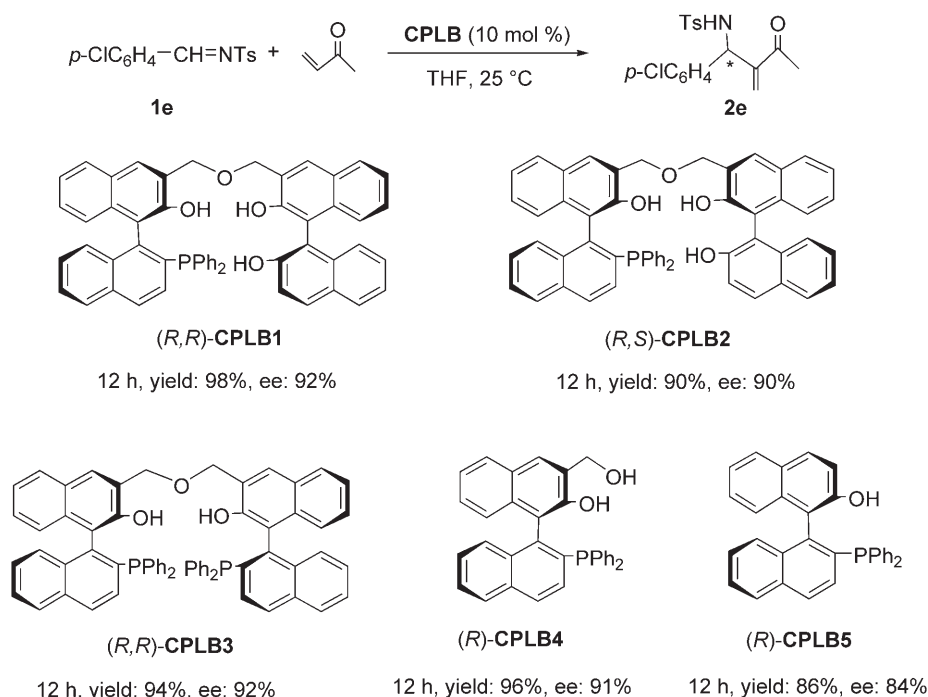
Under these optimized reaction conditions (−20 °C in THF), we next examined the aza-MBH reaction of *N*-tosylated aldimines **1** with ethyl vinyl ketone (EVK), a less reactive Michael acceptor in aza-MBH reactions. The results of these reactions are summarized in Table 2. The corresponding aza-MBH adducts **3a–d** were ob-

Scheme 1. Synthesis of chiral **CPLB1**.

tained in > 90% ee and good yields (Table 2, entries 1–4).

Moreover, we also examined the aza-MBH reaction of *N*-tosylated aldimines **1** with acrolein in the presence of **CPLB1**. In this type of aza-MBH reaction, THF is the best solvent and the reaction temperature can significantly affect the ee and yield according to our previous investigations.^[2] Using *N*-(4-bromobenzylidene)-4-

methylbenzenesulfonamide (**1f**) as substrate, temperature effects were examined in THF. We found that the corresponding aza-MBH reaction adduct **3e** was obtained in higher yield and ee at room temperature (25 °C) (Table 2, entries 5–7). At –20 °C, the achieved ee decreased dramatically under otherwise identical conditions (Table 2, entries 5–7). We believe that, in this case, the equilibrium of the Baylis–Hillman reaction



Scheme 2. Asymmetric aza-MBH reaction with chiral phosphine Lewis bases bearing multi-phenolic hydroxy groups in THF at 25 °C.

leans toward the reaction product at higher temperature whereas, at lower temperature, the equilibrium leans toward the opposite way. Thus, we carried out the aza-MBH reactions of other *N*-tosylated aldimines **1** with acrolein at room temperature (25 °C). These results are summarized in Table 2 (entries 8 and 9). The corresponding adducts **3f** and **3g** were obtained in 99% and 85% ee, respectively, in good yields.

A control experiment was carried out using **CPLB6** (Scheme 3), which is partially *O*-methylated and synthesized in a manner analogous to that shown in Scheme 1 (see Supporting Information), in the aza-MBH reaction of **1e** with MVK. The corresponding adduct **2e** was formed in 55% yield with 88% ee under the standard conditions (Scheme 3). This result suggests that the two phenolic hydroxy groups on the second binaphthalene moiety indeed play a significant role in improving yields and enantioselectivities of the aza-MBH reaction.

Another control experiment was carried out using 10 mol % of **CPLB5** in conjunction with 10 mol % (*R*)-BINOL in the aza-MBH reaction of **1e** with MVK under the standard conditions (Scheme 4). We found that the corresponding adduct **2e** was formed in 89% yield and 84% ee. These results are similar to those using **CPLB5** as a sole chiral Lewis base promoter.^[2f]

These control experiments suggest that the multiple phenol groups in **CPLB1** do indeed play a significant role in the aza-MBH reactions to give the desired adducts in higher yield and ee.

In order to gain mechanistic insight into these reactions, we carried out a ³¹P NMR spectroscopic analysis of **CPLB1** in the absence and presence of MVK, as we did previously with **CPLB5**.^[2f] We found that the ³¹P NMR (CDCl₃, 85% H₃PO₄) spectroscopic data of **CPLB1** showed a signal at −12.07 ppm (Figure S1 in Supporting Information), but the ³¹P NMR spectroscopic data of **CPLB1** with MVK (molar ratio = 1:5) showed a new signal at +26.36 ppm, which is believed to correspond to the phosphonium phenoxide, which is in an equilibrium with the corresponding *in situ* formed phosphonium enolate, an active species in the aza-MBH reaction stabilized by intramolecular hydrogen bonding (Figure S2).^[2f,6] However, in the ³¹P NMR spectroscopic data of **CPLB6** under the same conditions, no such signal could be observed in the presence of MVK (Figures S3 and S4). In the ³¹P NMR spectrum of **CPLB1**, the fact that the new signal appeared in the positive region upon the addition of MVK indicated that a positively charged phosphorus species was formed. A significant feature in the ³¹P NMR spectrum of **CPLB1** with the addition of MVK is the exclusive appearance of the new signal at +26.36 ppm because in the ³¹P NMR spectrum of the original chiral phosphine Lewis base **CPLB5**, the new signal appeared in the positive field upon addition of MVK, along with the signal in the negative field (free phosphine ligand) in a ratio of 1:1, which indicated that the formed phosphonium phenoxide is in an equilibrium with the free chiral phosphine

Table 1. Asymmetric aza-MBH reaction of *N*-tosylaldimines with MVK in the presence of chiral phosphine Lewis base **CPLB1**.

Reaction scheme: $\text{Ar-CH=N-R} + \text{CH}_2=\text{CH-CO-CH}_3 \xrightarrow[\text{THF, -20 } ^\circ\text{C}]{\text{CPLB1 (10 mol \%)}} \text{Ar-CH(R)-CH}_2\text{-CO-CH}_3$

Entry	Ar	R	Time [h]	Yield [%] ^[a] 2	ee [%] ^[b]	Absolute configuration ^[c]
1	C ₆ H ₅	1a , Ts	36	2a , 97	92	S
2	<i>p</i> -C ₂ H ₅ C ₆ H ₄	1b , Ts	48	2b , 94	96	S
3	<i>p</i> -MeOC ₆ H ₄	1c , Ts	48	2c , 70	95	S
4	<i>p</i> -FC ₆ H ₄	1d , Ts	24	2d , 83	96	S
5	<i>p</i> -ClC ₆ H ₄	1e , Ts	24	2e , 94	96	S
6	<i>p</i> -BrC ₆ H ₄	1f , Ts	24	2f , 85	95	S
7	<i>o</i> -ClC ₆ H ₄	1g , Ts	24	2g , 97	92	<i>R</i>
8	<i>m</i> -ClC ₆ H ₄	1h , Ts	24	2h , 87	94	S
9	<i>p</i> -NO ₂ C ₆ H ₄	1i , Ts	24	2i , 93	93	S
10	<i>o</i> -NO ₂ C ₆ H ₄	1j , Ts	36	2j , 85	90	<i>R</i>
11	<i>m</i> -NO ₂ C ₆ H ₄	1k , Ts	24	2k , 89	96	S
12	<i>trans</i> -C ₆ H ₅ CH=CH	1l , Ts	36	2l , 97	90	S
13	<i>p</i> -ClC ₆ H ₄	1m , Ms	36	2m , 90	91	S

^[a] Yield of isolated product^[b] Determined by chiral HPLC.^[c] Determined by the sign of specific rotation.^[2f]

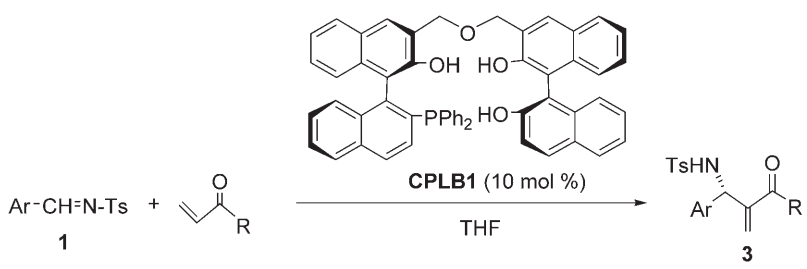
Lewis base **CPLB5** as well.^[2f] In the case of **CPLB1**, only a trace of the free phosphine ligand signal was observed, indicating that an interaction (hydrogen bonding) between multiple phenol groups and the oxygen atom of MVK does indeed exist, which strongly stabilizes the formed phosphonium phenoxide, which is in an equilibrium with the corresponding *in situ* formed phosphonium enolate stabilized by intramolecular hydrogen bonding, and drives the equilibrium largely to the formation of the phosphonium phenoxide or enolate intermediate stabilized by intramolecular hydrogen bonding.^[2f] We believe that this is the key factor for why these chiral phosphine Lewis bases bearing multiple phenol groups are more effective catalysts than **CPLB5**.

For chiral phosphine Lewis base **CPLB6**, no spectroscopic alteration was observed upon the addition of MVK, indicating that one phenolic hydroxy group is not enough to significantly interact with the oxygen atom of MVK through hydrogen bonding, although the new signal was observed with **CPLB5** upon the addi-

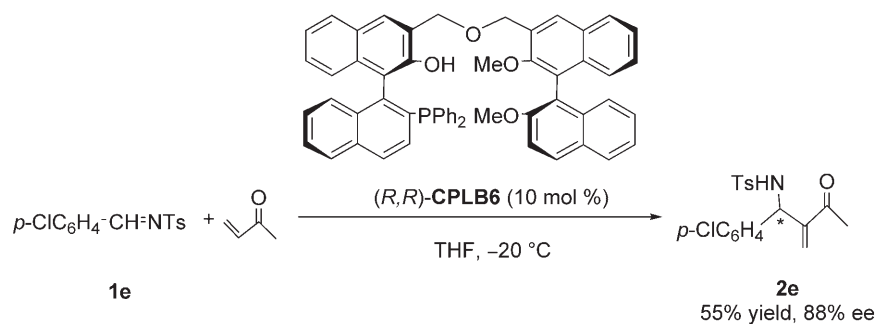
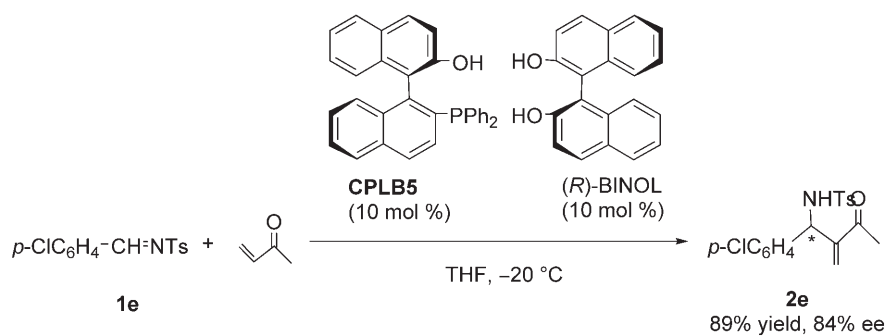
tion of MVK,^[2f] presumably due to the steric hindrance in **CPLB6**.

Conclusion

In conclusion, we found that in the aza-MBH reaction of *N*-sulfonated aldimines **1** with MVK using **CPLB1**, bearing multiple phenol groups as a chiral phosphine Lewis base promoter, the corresponding adducts can be obtained in >90% ee and good to high yields at –20 °C or room temperature (25 °C) in THF for most of the substrates using MVK, EVK, or acrolein as a Michael acceptor. The multiple phenol groups played a key role in these reactions and in order to achieve high enantioselectivities and yields. Efforts are underway to elucidate additional mechanistic details of this process and the key factors of chiral Lewis bases in aza-MBH reactions and to disclose their scope and limitations.

Table 2. Asymmetric aza-MBH reaction of *N*-tosylaldimines with EVK and acrolein in the presence of chiral phosphine Lewis base **CPLB1**.


Entry	Ar	R	Temp. [°C]	Time [h]	Yield [%] ^[a]	ee [%] ^[b]	Absolute configuration ^[c]
1	<i>p</i> -FC ₆ H ₄ , 1d	Et	−20	84	3a , 86	92	S
2	<i>m</i> -FC ₆ H ₄ , 1n	Et	−20	84	3b , 83	90	S
3	<i>m</i> -ClC ₆ H ₄ , 1h	Et	−20	84	3c , 83	90	S
4	<i>p</i> -BrC ₆ H ₄ , 1f	Et	−20	84	3d , 88	93	S
5	<i>p</i> -BrC ₆ H ₄ , 1f	H	25	12	3e , 90	90	S
6	<i>p</i> -BrC ₆ H ₄ , 1f	H	10	5	3e , 67	86	S
7	<i>p</i> -BrC ₆ H ₄ , 1f	H	−20	12	3e , 74	72	S
8	<i>p</i> -FC ₆ H ₄ , 1d	H	25	4	3f , 75	99	S
9	<i>p</i> -ClC ₆ H ₄ , 1e	H	25	4	3g , 67	85	S

^[a] Isolated yield ^[b] Determined by chiral HPLC.^[c] Determined by the sign of specific rotation.^[2f]**Scheme 3.** Asymmetric aza-MBH reaction of *N*-tosylated aldimine **1e** with MVK catalyzed by **CPLB6** (10 mol %).**Scheme 4.** Asymmetric aza-MBH reaction of *N*-tosylated aldimine **1e** with MVK catalyzed by **CPLB5** (10 mol %) and (*R*)-BINOL (10 mol %), respectively.

Experimental Section

General Remarks

Melting points were obtained with a Yanagimoto micro melting point apparatus and are uncorrected. Unless otherwise stated, all reactions were carried out under an argon atmosphere. All solvents were purified by distillation. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. ^1H NMR spectra were recorded on a Bruker AM-300 spectrometer as a solution in CDCl_3 with tetramethylsilane (TMS) as an internal standard; J values are in Hz. Mass spectra were recorded with an HP-5989 instrument and HR-MS were measured by a Finnigan MA + mass spectrometer. *N*-Sulfonated imines **1** were prepared according to the literature.^[7] All of the solid compounds reported in this paper gave satisfactory CHN microanalyses with a Carlo-Erba 1106 analyzer. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF₂₅₄ silica gel coated plates. Flash column chromatography was carried out using 200–300 mesh silica gel at increased pressure. The optical purities of the aza-Morita–Baylis–Hillman adducts were determined by HPLC analysis using a chiral stationary phase column (column, Daicel Co. Chiralcel AD, AS, TBB and OJ; eluent: hexane/2-propanol mixture; flow rate, 0.7 mL min⁻¹; detection, 254 nm or 220 nm light) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.^[21]

Typical Reaction Procedure for CPLB-Catalyzed Aza-Baylis–Hillman Reaction of *N*-Sulfonated Imines with MVK

A 10-mL Schlenk tube containing *N*-(benzylidene)-4-chlorobenzenesulfonamide (**1e**) (0.5 mmol) and 3-(2'-diphenylphosphanyl-2-hydroxy-[1,1']binaphthalenyl-3-ylmethoxymethyl)-[1,1']binaphthalenyl-2,2'-diol **CPLB1** (0.05 mmol) was degassed and the reaction vessel was protected under an argon atmosphere. Then, THF (1.0 mL) was added. After the reaction mixture was cooled to -30°C , methyl vinyl ketone (MVK) (1.5 mmol) was added into the Schlenk tube. The reaction mixture was stirred at -20°C for 24–48 hours. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2 , eluent: EtOAc/petroleum ether = 1/5) to yield the corresponding aza-Baylis–Hillman adduct as a colorless solid, which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess. For microanalysis, all these products were recrystallized from acetone and *n*-hexane.

Supporting Information Available

^{13}C and ^1H NMR spectroscopic and analytical data for chiral phosphine Lewis bases **CPLB1–CPLB4** and **CPLB6**, aza-Morita–Baylis–Hillman reaction products, experimental details, Figures S1–S4, and chiral HPLC traces of the compounds shown in Tables 1 and 2 and Schemes 2 and 3 are presented in the Supporting Information.

Acknowledgements

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