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Dendritic Chiral Phosphine Lewis Bases-Catalyzed Asymmetric Aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imines with Activated Olefins

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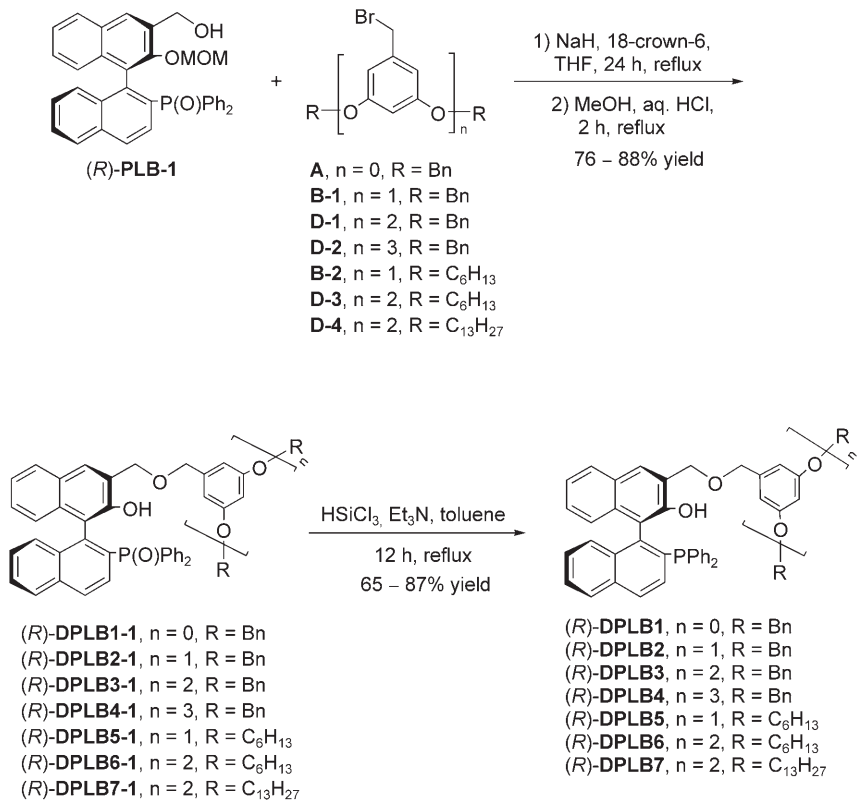
Abstract: A series of polyether dendritic chiral phosphine Lewis bases was synthesized, and successfully applied to the asymmetric aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines (*N*-arylmethylidene-4-methylbenzenesulfonamides) with methyl vinyl ketone (MVK), ethyl vinyl ketone (EVK), and acrolein to give the adducts in good to excellent yields along with up to 97% *ee*, which are more effective than our previously reported original chiral phosphine Lewis bases. In addition, the dendrimer-supported chiral phosphine Lewis bases can be easily recovered and reused.

Keywords: activated olefins; asymmetric catalysis; aza-Morita–Baylis–Hillman reaction; dendritic chiral phosphine Lewis bases; *N*-sulfonated imines; organocatalysts

Introduction

The asymmetric Morita–Baylis–Hillman (MBH) or aza-Morita–Baylis–Hillman (aza-MBH) reaction is one of the most useful and interesting carbon-carbon bond forming reactions to give enantiomerically enriched β-hydroxy carbonyl compounds or β-amino carbonyl compounds bearing an α-alkylidene group with enormous potential synthetic utility under mild reaction conditions.[1] Over the last decade, great progress has been made in catalytic asymmetric versions of these reactions and several excellent multifunctional organocatalysts for aza-MBH to achieve high enantioselectivities have been reported.[2] However, the asymmetric aza-MBH reaction is often hampered by a low reaction rate and limited substrate applicability because it is still highly sensitive to the substitution at both imine and Michael acceptor. Therefore, the design and synthesis of efficient organocatalysts for the aza-MBH reaction is still a challenge for organic chemists. In our previous report, we disclosed that chiral phosphine Lewis base [(*R*)-2′-diphenylphosphanyl-[1,1′]binaphthalenyl-2-ol] [(*R*)-**PLB8** shown below in Scheme 3] having a phenolic hydroxy group is an effective chiral phosphine Lewis base for the catalytic, asymmetric aza-MBH reaction.[2b,h] The significant advantage in this chiral phosphine Lewis base system is that it is a "structure-tunable" organocatalyst,[2h,3] and through modification of the catalyst framework, several excellent results have been reported by our group.[4] Recently, we have focused on the search for a more effective, useful, recoverable and reusable chiral phosphine Lewis base system for the aza-MBH reaction. Dendrimers are highly branched and well-defined macromolecules with controllable structure, which offer a unique tool for fine-tuning the catalytic activity through the microenvironment.[5] To the best of our knowledge, in the field of asymmetric aza-MBH reactions, a dendritic organocatalytic system has not been investigated so far. Therefore, we attempted to anchor chiral phosphine Lewis bases onto a dendrimer supporter and investigate their catalytic activity in aza-MBH reactions. Herein, we report the synthesis of chiral phosphine Lewis bases supported by a polyether dendrimer and their application in catalytic, asymmetric aza-MBH reactions. Compared to the bifunctional chiral phosphine Lewis base core,[2b,h] a positive dendrimer effect is observed along with a higher *ee* of the aza-MBH products and these organocatalysts can be easily recovered and reused.



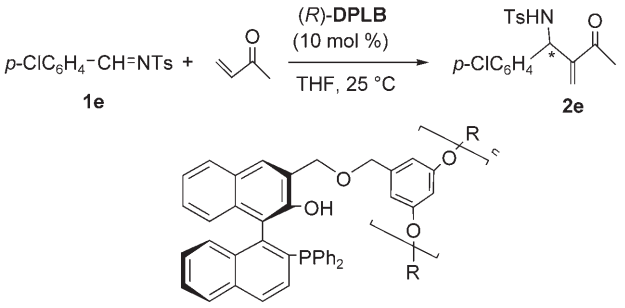
Scheme 1. Synthesis of polyether dendrimer supported chiral Lewis bases (*R*)-**DPLBs**.

Results and Discussion

The synthetic route of the chiral phosphine Lewis bases supported by polyether dendrimers is shown in Scheme 1. The synthesis of MOM-protected chiral *p*hosphine *L*ewis *b*ase (*R*)-**PLB-1** bearing one aliphatic hydroxy group has been reported in our previous paper.[4] After treatment of (*R*)-**PLB-1** with NaH in THF, the brominated polyether dendrimers **A**, **B-1**, **B-2**, **D-1**, **D-2**, **D-3**, and **D-4**[6] were added to produce the corresponding etherified products, which could give the corresponding precursors of various *d*endritic chiral *p*hosphine *L*ewis *b*ases (*R*)-**DPLB1-1**, (*R*)-**DPLB2-1**, (*R*)-**DPLB3-1**, and (*R*)-**DPLB4-1** in 76–88% yields after removal of the MOM protecting group with aqueous HCl in methanol. Reduction of the phosphoryl group of (*R*)-**DPLB1-1**, (*R*)-**DPLB2-1**, (*R*)-**DPLB3-1**, and (*R*)-**DPLB4-1** by $HSiCl_3$ and Et_3N in toluene afforded the corresponding dendritic chiral phosphine Lewis bases (*R*)-**DPLB1-4** in good yields (65–87%). As for the preparation of (*R*)-**DPLB5-7** (Scheme 1), the corresponding precursors (*R*)-**DPLB5-1**, (*R*)-**DPLB6-1**, and (*R*)-**DPLB7-1** were directly used for the reduction with $HSiCl_3$ and Et_3N in toluene without isolation. The synthetic procedures are quite simple. Their detailed experimental procedures and the spectroscopic data are summarized in the Supporting Information.

To investigate their catalytic activities in asymmetric aza-MBH reaction with these polyether dendritic chiral phosphine Lewis bases [(*R*)-**DPLB1-7**], an initial examination was carried out using *p*-chlorobenzylidene-4-methylbenzenesulfonamide **1e** and methyl vinyl ketone (MVK) as the substrates in the presence of 10 mol% of these (*R*)-**DPLB**s in THF at room temperature (25 °C). The results are summarized in Scheme 2. As can be seen from Scheme 2, regardless of the benzyl group or long carbon chain in the polyether dendritic catalysts the asymmetric aza-MBH reaction proceeded smoothly to give the adducts in excellent results (up to 99% yield and 94% *ee*). Notably, the second generation of dendritic chiral phosphine Lewis base (*R*)-**DPLB3** provided the best result in the catalytic activity (99% yield, 93% *ee*) under identical conditions. Although the third generation of dendritic chiral phosphine Lewis base (*R*)-**DPLB4** showed slightly higher enantioselectivity (94% *ee*), a huge drop in reactivity was also observed (67% yield) under the standard conditions. Therefore, the second generation of polyether dendritic chiral phosphine Lewis base (*R*)-**DPLB3** was selected for the subsequent studies.

Since the catalytic performance, i.e., the activity, selectivity, and recyclability of these focal point-functionalized (active sites on a dendritic wedge) dendritic catalysts could depend considerably on the microen-



(*R*)-**DPLB**	Time [h]	Yield [%][a] of **2e**	*ee* [%][b] of **2e**
(*R*)-**DPLB1**, n = 0, R = Bn	24	90	93
(*R*)-**DPLB2**, n = 1, R = Bn	24	99	89
(*R*)-**DPLB3**, n = 2, R = Bn	24	99	93
(*R*)-**DPLB4**, n = 3, R = Bn	48	67	94
(*R*)-**DPLB5**, n = 1, R = C_6H_{13}	24	93	93
(*R*)-**DPLB6**, n = 2, R = C_6H_{13}	24	99	53
(*R*)-**DPLB7**, n = 2, R = $C_{13}H_{27}$	24	99	92

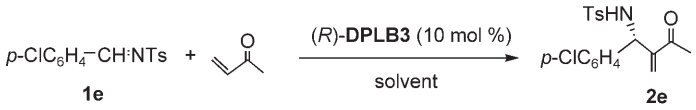
[a] Isolated yields.
[b] Determined by chiral HPLC.

Scheme 2. Asymmetric aza-Morita–Baylis–Hillman reactions of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide **1e** (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of polyether dendrimer-supported chiral phosphine Lewis base (*R*)-**DPLB** (10 mol %).

vironment of solvents, we carefully examined the influence of the employed solvents on this reaction.[5d] Next, using (*R*)-**DPLB3** as a chiral Lewis base promoter, *p*-chlorobenzylidene-4-methylbenzenesulfonamide **1e** and methyl vinyl ketone (MVK) as the substrates, the solvent effect was examined to clarify such microenvironment effect in dendrimer supported organocatalysts. The results are summarized in Table 1. Dendritic organocatalyst (*R*)-**DPLB3** with the benzyl group-tethered dendrimer showed the best solubility and activity in THF and no reaction occurred in *tert*-pentanol (Table 1, entries 1 and 7). In 1,2-dichloroethane (DCE), toluene, acetonitrile (MeCN), ether or DMF, **2e** was formed in 85–99% yields and 75–91% *ee*s under identical conditions (Table 1, entries 2–6). We also found that the corresponding aza-MBH reaction adduct **3e** was obtained in higher *ee* (up to 97%) along with 98% yield at the lower reaction temperature (−20 °C) (Table 1, entries 8 and 9).

To examine the scope and limitations of the aza-MBH reaction of *N*-sulfonated aldimines **1** with MVK by means of the dendritic oganocatalyst (*R*)-**DPLB3**, a series of *N*-sulfonated aldimines **1** was evaluated under the optimized reactions, and the results are summarized in Table 2. In general, regardless of the electronic nature of the *N*-sulfonated aldimines, excellent *ee*s of **2** were attained (Table 2, entries 1–10), because even for *N*-sulfonated aldimines **1b** and **1c** bearing an electron-donating group on the aromatic ring, the reaction also proceeded smoothly to

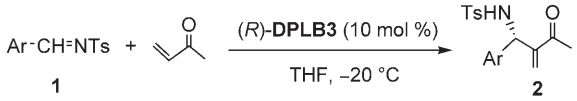
Table 1. Aza-Morita–Baylis–Hillman reactions of *N*-(arylmethylidene)arylsulfonamide **1e** (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of polyether dendrimer-supported chiral Lewis base (*R*)-**DPLB3** (10 mol %).



Entry	Solvent	Temp. [°C]	Time [h]	Yield [%][a]	*ee* [%][b]	Absolute configuration[c]
1	THF	25	24	99	93	*S*
2	$ClCH_2CH_2Cl$	25	24	99	87	*S*
3	toluene	25	36	72	90	*S*
4	MeCN	25	24	99	87	*S*
5	Et_2O	25	24	95	91	*S*
6	DMF	25	24	85	75	*S*
7	*t*-pentanol	25	24	-	-	-
8	THF	0	48	98	95	*S*
9	THF	–20	48	98	97	*S*

[a] Yields of isolated products.
[b] Determined by chiral HPLC.
[c] Determined by the sign of specific rotation.

Table 2. Aza-Morita–Baylis–Hillman reactions of *N*-(arylmethylidene)arylsulfonamide (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of polyether dendrimer-supported chiral Lewis base (*R*)-**DPLB3** (10 mol %).

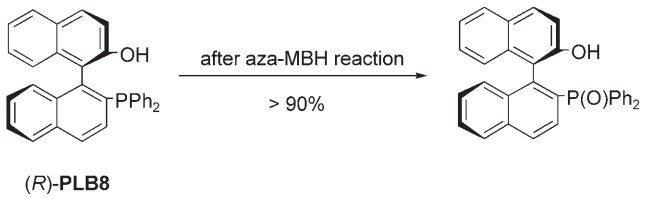


Entry	Ar	No.	Time [h]	Yield [%][a] of **2**	*ee* [%][b]	Absolute configuration[c]
1	C_6H_5	**1a**	36	**2a**, 95	91	*S*
2	*p*-MeC_6H_4	**1b**	48	**2b**, 90	90	*S*
3	*p*-$MeOC_6H_4$	**1c**	48	**2c**, 90	95	*S*
4	*p*-FC_6H_4	**1d**	36	**2d**, 84	93	*S*
5	*p*-ClC_6H_4	**1e**	24	**2e**, 99	97	*S*
6	*p*-BrC_6H_4	**1f**	36	**2f**, 85	89	*S*
7	*m*-FC_6H_4	**1g**	36	**2g**, 80	94	*S*
8	*p*-$NO_2C_6H_4$	**1h**	12	**2h**, 99	97	*S*
9	*m*-$NO_2C_6H_4$	**1i**	12	**2i**, 99	92	*S*
10	*trans*-C_6H_5CH=CH	**1j**	48	**2j**, 94	90	*S*
11[d]	*p*-$NO_2C_6H_4$	**1h**	24	**2h**, 91	90	*S*

[a] Yields of isolated products.
[b] Determined by chiral HPLC.
[c] Determined by the sign of specific rotation.
[d] The recovered chiral Lewis base was reused.

afford the aza-MBH reaction products **2b** and **2c** in good yields along with high *ee*s (Table 2, entries 2 and 3). Moreover, in several cases, 97 % *ee*s were realized (Table 2, entries 5 and 8). It should be pointed out that the dendritic oganocatalyst (*R*)-**DPLB3** can be recovered by filtration after the reaction was complete and the product was separated from the reaction mixtures by washing with the solvent mixture hexane/ether (8/1) and can be reused in the same reaction to give the adduct in similar results (Table 2, entry 11).

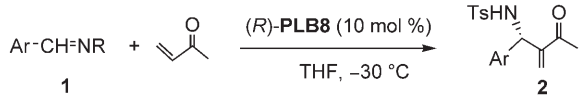
To compare with our original chiral phosphine Lewis base [(*R*)-2′-diphenylphosphanyl-[1,1′]binaphthalenyl-2-ol] (*R*)-**PLB8**, we examined the final product of the recovered (*R*)-**PLB8** by a similar manner after aza-MBH reaction was complete, and found that most of (*R*)-**PLB8** (>90 %) has been oxidized to the corresponding phosphine oxide, which has been confirmed by X-ray crystal structure diffraction (see Supporting Information),[7] and the catalytic activity disappeared completely with these recovered (*R*)-**PLB8** (Scheme 3). The results using original (*R*)-**PLB8** as a catalyst in aza-MBH reaction under similar conditions are shown in Table 3.[2b,h] As can be seen from Table 3 clearly, (*R*)-**DPLB3** is more effective than the original chiral phosphine Lewis base (*R*)-**PLB8** under the standard conditions. Therefore, we believe that the large branched polyether carbon chain in dendrimer supported organocatalyst (*R*)-**DPLB3** retarded the oxidation of phosphorus atom during the reaction and therefore, the recovered organocatalyst (*R*)-**DPLB3** can be reused to give the product in similar result.



Scheme 3. Final product of original chiral phosphine Lewis base (*R*)-**PLB8**.

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 reaction. The results are summarized in Table 4. As can be seen from Table 4, the corresponding aza-MBH adducts **3a–3f** were obtained in 73–99 % yields along with >94 % *ee* (Table 4, entries 1–6), and in several cases, 97 % *ee*s were attained (Table 4, entries 1, 2, and 5). Moreover, the aza-MBH reaction of *N*-tosylated aldimines **1** with acrolein in the presence of (*R*)-**DPLB3** was also examined under the standard conditions. We were pleased to found that the corresponding aza-MBH adducts **3g–i** were similarly ob-

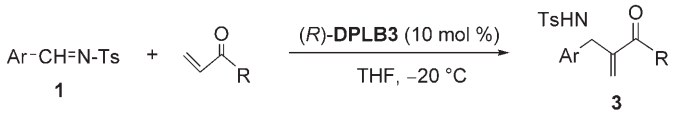
Table 3. Aza-Baylis–Hillman reactions of *N*-(arylmethylidene)arylsulfonamide **1** (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of chiral phosphine Lewis base (*R*)-**PLB8** (10 mol%).



Entry	Ar	R	No.	Time [h]	Yield [%][a] of **2**	*ee* [%][b]	Absolute configuration
1	C_6H_5	Ts	**1a**	24	**2a**, 49	83	*S*
2	*p*-MeC_6H_4	Ts	**1b**	24	**2b**, 53	80	*S*
3	*p*-FC_6H_4	Ts	**1d**	18	**2d**, 84	81	*S*
4	*p*-ClC_6H_4	Ts	**1e**	24	**2e**, 72	94	*S*
5	*p*-BrC_6H_4	Ts	**1f**	18	**2f**, 85	83	*S*
6	*m*-FC_6H_4	Ts	**1g**	36	**2g**, 26	91	*S*
7	*p*-$NO_2C_6H_4$	Ts	**1h**	12	**2h**, 60	94	*S*
8	*m*-$NO_2C_6H_4$	Ts	**1i**	12	**2i**, 54	90	*S*
9	*p*-EtC_6H_4	Ts	**1k**	36	**2k**, 62	76	*S*
10	*m*-ClC_6H_4	Ts	**1l**	18	**2l**, 62	88	*S*

[a] Yields of isolated products.
[b] Determined by chiral HPLC.

Table 4. Asymmetric aza-Morita–Baylis–Hillman reaction of *N*-tosyl aldimines with EVK and acrolein in the presence of polyether dendrimer-supported chiral Lewis base (*R*)-**DPLB3** (10 mol%).



Entry	Ar	R	Time [h]	Yield [%][a]	*ee* [%][b]	Absolute configuration[c]
1	*p*-ClC_6H_4, **1e**	Et	84	**3a**, 77	97	*S*
2	*p*-BrC_6H_4, **1f**	Et	84	**3b**, 73	97	*S*
3	*p*-$NO_2C_6H_4$, **1i**	Et	96	**3c**, 97	95	*S*
4	*m*-ClC_6H_4, **1j**	Et	96	**3d**, 99	94	*S*
5	*m*-FC_6H_4, **1g**	Et	96	**3e**, 85	97	*S*
6	*p*-FC_6H_4, **1d**	Et	96	**3f**, 90	95	*S*
7	*p*-ClC_6H_4, **1e**	H	12	**3g**, 86	89	*S*
8	*p*-FC_6H_4, **1d**	H	12	**3h**, 83	94	*S*
9	*p*-BrC_6H_4, **1f**	H	12	**3i**, 90	90	*S*

[a] Yields of isolated products.
[b] Determined by chiral HPLC.
[c] Determined by the sign of specific rotation.

tained in good yields along with 89–94% ee*s* (Table 4, entries 7–9).

Conclusions

In conclusion, we have synthesized a series of polyether dendritic chiral phosphine Lewis bases and in-

vestigated their application in asymmetric aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines with methyl vinyl ketone (MVK), ethyl vinyl ketone (EVK), and acrolein under mild conditions. The corresponding aza-MBH adducts can be obtained in good to excellent yields (up to 99%) and excellent enantioselectivities (up to 97%). In addition, the dendrimer-supported chiral phosphine Lewis bases can be easily recovered and reused after reaction. Efforts are underway to examine the effect of other types of dendrimer supporters in chiral organocatalysts and to elucidate the key factors of dendrimer-supported chiral Lewis bases in aza-MBH or MBH reactions.

Experimental Section

General Remarks

All solvents were purified by distillation. Unless otherwise stated, all reactions were carried out under argon atmosphere. ^{1}H 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 was measured by a Finnigan MA+ mass spectrometer. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. Melting points were obtained with a Yanagimoto micromelting point apparatus and are uncorrected. *N*-Sulfonated imines **1** were prepared according to the literature. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF_{254} 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) and the absolute configuration of the major enantiomer was assigned according to the sign of the specific rotation.

Typical Reaction Procedure for (*R*)-DPLB-Catalyzed aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imines with MVK.

A 10-mL of Schlenk tube containing *p*-chlorobenzylidene-4-methylbenzenesulfonamide **1e** (0.2 mmol) and 3-({3,5-Bis-[3,5-bis(benzyloxy)phenoxy]benzyloxy}methyl)-1-[2-(diphenylphosphino)naphthalen-1-yl]naphthalen-2-ol, (*R*)-**DPLB3**, (0.02 mmol) was degassed and the reaction vessel was protected under an argon atmosphere. Then, THF (1.0 mL) was added. After the reaction mixture had been cooled to −20 °C, methyl vinyl ketone (MVK) (0.6 mmol) was added into the Schlenk tube. The reaction mixture was stirred at −20 °C for 12–48 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (SiO_2, eluent: EtOAc/petroleum ether = 1/4) to yield the corresponding aza-Baylis–Hillman adduct as a colorless solid, which was immediately subjected to chiral HPLC for the analysis of the achieved enantiomeric excess.

Typical Reaction Procedure for the Recovery and Reuse of the Catalyst

After reaction, the solvent was removed under reduced pressure and the residue was washed with the solvent mixture hexane/ether (8/1) (20 mL). The product and the remaining MVK were extracted from the reaction mixtures and the dendritic oganocatalyst (*R*)-**DPLB3** can be partially recovered by filtration in 75% yield, which can be reused in the same reaction to give the adduct in similar results (Table 2, entry 11). However, the second recycling would lower the catalytic activity of the recovered catalyst to give the product in 50% yield and 89% *ee* since only about half of the initial amounts of the catalyst were recovered in the second recycling (the catalyst was recovered in 48% yield based on the initial amounts of catalyst during the second recycling).

Supporting Information

^{1}H NMR spectroscopic and analytical data for dendritic chiral phosphine Lewis bases (*R*)-**DPLB1--7**, aza-Morita-Baylis–Hillman reaction products, experimental details, and chiral HPLC traces of the compounds shown in Tables 1, 2, and 3 and Scheme 2 as well as the X-ray crystal data for Scheme 3 are presented in the Supporting Information.

Acknowledgements

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[7] The crystal data of this oxidation product have been deposited in CCDC with number 280606. Empirical formula: $C_{32}H_{23}O_2P$; formula weight: 470.47; crystal color, habit: colorless, prismatic; crystal dimensions: $0.492 \times 0.403 \times 0.357$ mm; crystal system: orthorhombic; lattice type: primitive; lattice parameters: $a = 9.6013(7)$ Å, $b = 14.3110(10)$ Å, $c = 17.4804(12)$ Å, $\alpha = 90°$, $\beta = 90°$, $\gamma = 90°$, $V = 2401.9$ (3) Å^3; space group: P2(1)2(1)2(1); $Z = 4$; $D_{calc} = 1.301$ g cm^{-3}; $F_{000} = 984$; diffractometer: Rigaku AFC7R; residuals: R.; Rw: 0.0454, 0.0499.

