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Asymmetric Aza-Morita–Baylis–Hillman Reaction of *N*-Sulfonated Imines with Methyl Vinyl Ketone Catalyzed by Chiral Phosphine Lewis Bases Bearing Perfluoroalkanes as "Pony Tails"

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Abstract: In the aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines (*N*-arylmethylidene-4-methylbenzenesulfonamides and others) with methyl vinyl ketone (MVK), we found that in the presence of a catalytic amount of the chiral phosphine Lewis bases (*R*)-(−)-6,6′-bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]-2′-(diphenylphosphanyl)-[1,1′]-binaphthalenyl-2-ol **LB2** and (*R*)-(−)-6,6′-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl) -2′-(diphenylphosphanyl)-[1,1′]binaphthalenyl-2-ol **LB3** bearing two perfluoroalkane chains at 6,6′-positions of the naphthalene framework, the corresponding adducts could be obtained in good yields with good to high ee (52–95% ee) at room temperature (15 °C) or low temperature (−20 °C) in THF, respectively. **LB3** is more effective in this reaction than the previously reported original chiral phosphine Lewis base (*R*)-(−)-2′-diphenylphosphanyl-[1,1′]binaphthalenyl-2-ol **LB1**.

Keywords: asymmetric organic catalysis; aza-Morita–Baylis–Hillman reaction; chiral phosphine Lewis base; methyl vinyl ketone; perfluoroalkane chain; *N*-sulfonated imines

Introduction

Great progress has been made in the execution of Morita–Baylis–Hillman reaction[1] since the seminal report in 1972[2] described the reaction of acetaldehyde with ethyl acrylate and acrylonitrile in the presence of catalytic amounts of 1,4-diazabicyclo[2.2.2]octane (DABCO). Recent advances include catalytic asymmetric versions of the reaction,[3,4] but limited to specialized α,β-unsaturated ketones or acrylates such as ethyl vinyl ketone (71% ee),[3a] 2-cyclohexen-1-one (96% ee)[3b] or 1,1,1,3,3,3-hexafluoroisopropyl acrylate (99% ee).[3c] Morita–Baylis–Hillman reactions involving simple Michael acceptors such as methyl vinyl ketone (MVK) or methyl acrylate have hitherto been characterized by poor enantioselectivity, thus offering a challenging and potentially fruitful area of investigation to broaden the scope of this general class of reactions. During our ongoing investigations on the Morita–Baylis–Hillman reaction,[5] we disclosed that the aza-Morita–Baylis–Hillman reactions of *N*-sulfonated imines (ArCH=NTs)[6] with MVK were promoted in the presence of catalytic amounts of Lewis bases such as triphenylphosphine (PPh_3) or DABCO to exclusively give the normal adducts in good yields for many substrates under mild conditions. On the basis of these results, we attempted a catalytic, asymmetric version of this reaction with a suitable chiral Lewis base. Previously, we reported an unprecedented catalytic, asymmetric aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines **1** with MVK utilizing a chiral nitrogen Lewis base [4-(3-ethyl-4-oxa-1-azatricyclo[4.4.0.0^{3,8}]dec-5-yl)-quinolin-6-ol: **β-ICD**[3c,7]] to achieve >90% ee in good yield.[6d, h] This is the first case in which high ee (>90%) can be realized using the simple Michael acceptor MVK. The structure of this nitrogen Lewis base is such that the phenolic hydroxy group plays a significant role in the reaction for achieving high ee.[3c,6d,6 h] Moreover, after screening several chiral phosphine Lewis base catalysts, we also found that (*R*)-2′-diphenylphosphanyl-[1,1′]binaphthalenyl-2-ol **LB1** having a phenolic hydroxy group, is also an effective chiral phosphine Lewis base for the catalytic, asym-

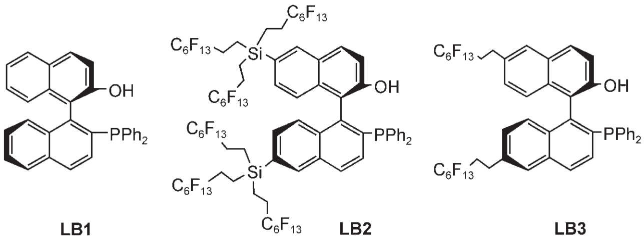


Figure 1. The structures of chiral phosphine Lewis bases bearing long perfluoroalkane chains "pony tails".

metric aza-Morita–Baylis–Hillman reaction in which high enantioselectivities (94% or 95% ee) can also be realized (Figure 1).[8,9] The significant advantage in this chiral phosphine Lewis base system is that it is a "structure tunable" catalyst as has been described before.[8b] In some cases, the previous results on asymmetric catalysis have indicated that long perfluoroalkane chains, so-called "pony tails", in a variety of chiral ligands can improve the enantioselectivities under identical conditions.[10] Therefore, we report in this paper the synthesis of chiral phosphine Lewis bases **LB2** and **LB3** bearing long perfluoroalkane chains "pony tails" (Figure 1) and their applications in catalytic, asymmetric aza-Morita–Baylis–Hillman reaction because, currently, the exploration of a novel and highly efficient chiral Lewis base for catalytic, asymmetric Morita–Baylis–Hillman reaction is a very attractive and competitive field.

Results and Discussion

Synthesis of Chiral Phosphine Lewis Bases LB2 and LB3 Bearing Perfluoroalkane "Pony Tails"

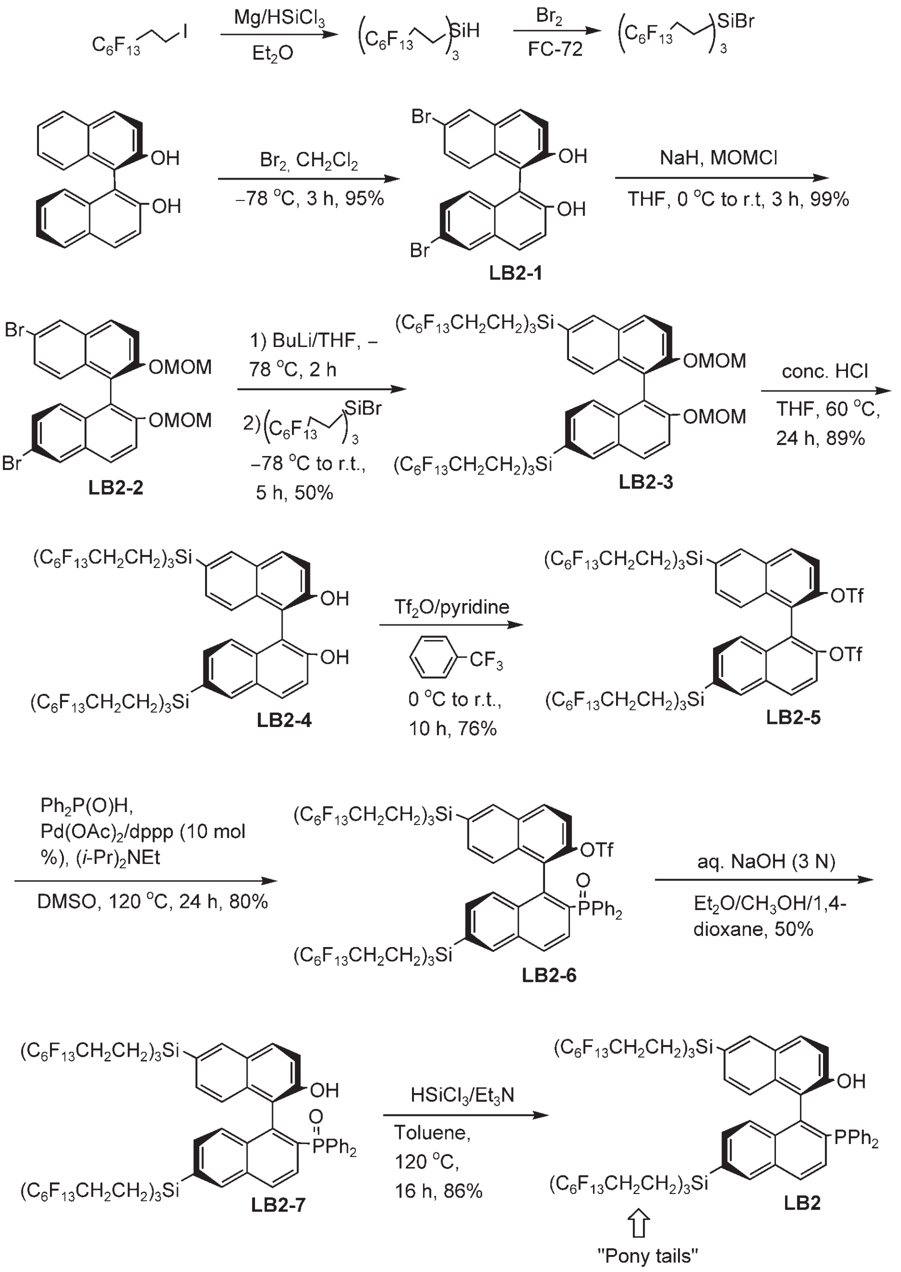
In Schemes 1 and 2, we present the synthesis of chiral Lewis bases **LB2** and **LB3** with two long perfluoroalkane chains ("pony tails") on the 6,6′-positions of the axially chiral binaphthalene skeleton. The preparations of **LB2-1**, **LB2-2**, **LB2-3**, **LB2-4** and **LB2-5** in Scheme 1 and **LB3-1**, **LB3-2** and **LB3-3** in Scheme 2 are according to the previous literature.[11,12,13]

For the synthesis of chiral phosphine Lewis base **LB2**, dibromination of (*R*)-binol at $-78\,^{\circ}$C gave **LB2-1** in 92% yield in dichloromethane. Two phenolic hydroxy groups were protected by MOMCl in THF at 0 °C to afford **LB2-2** in quantitative yield, as previously described.[11] The compound **LB2-2** was lithiated with BuLi in THF at $-78\,^{\circ\circ}$C and then the resultant solution was treated with 2.4 equivs. of [$(C_6F_{13}C_2H_4)_3SiBr$] which was prepared according to the previous literature as shown in Scheme 1 (top),[12a, b] to give the compound **LB2-3** at $-78\,^{\circ}$C in 50% yield. Deprotection of MOM group with HCl in THF produced **LB2-4** in 89% yield. The compound **LB2-5** was obtained in 76% yield by the reaction of **LB2-4** with Tf_2O in trifluoromethylbenzene in the presence of pyridine at 0 °C to room temperature for 10 h.[12c, d] The coupling reaction of **LB2-4** with diphenyl phosphite with $Pd(OAc)_2$ and dppp in DMSO at 120 °C afforded the compound **LB2-6** in 80% yield. Then, the hydrolysis of **LB2-6** with aqueous sodium hydroxide solution in diethyl ether/MeOH/dioxane mixed solvent produced the compound **LB2-7** in 50% yield. The reduction of phosphate **LB2-7** by $HSiCl_3$ and Et_3N in toluene at 120 °C produced **LB2** in 86% yield (Scheme 1).

For the synthesis of chiral phosphine Lewis base **LB3**, bromination and protection by benzyl group gave the product **LB3-1** in good yield[11] which was subjected to a Heck-type coupling reaction with 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluoro-1-octene in the presence of $Pd(OAc)_2$ and (*o*-Tol)$_3$P ligand in DMF at 125 °C to furnish product **LB3-2** in 81% yield. Catalytic hydrogenation over $Pd(OH)_2$/C in methanol afforded the product **LB3-3** in high yield.[12] After the same transformations as those mentioned above, the corresponding compounds **LB3-4** and **LB3-5** were obtained in good yields. Hydrolysis of **LB3-5** with aqueous sodium hydroxide solution in MeOH/dioxane mixing solvent produced the compound **LB3-6** in 98% yield. Reduction of the phosphate **LB3-6** by $HSiCl_3$ and Et_3N in toluene at 120 °C afforded **LB2** in 60% yield (Scheme 2).

Chiral Phosphine Lewis Bases LB2 and LB3 bearing Perfluoroalkane "Pony Tails" in Catalytic, Asymmetric Aza-Morita–Baylis–Hillman Reactions

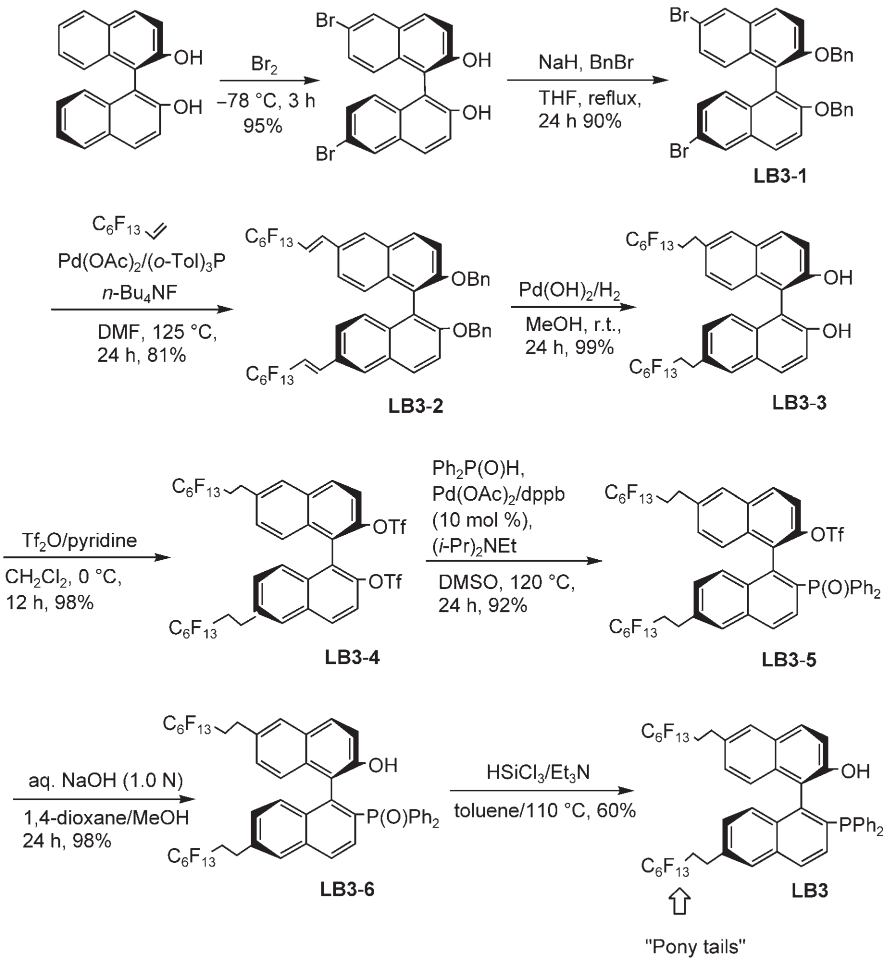
The chiral phosphine Lewis bases **LB2** and **LB3** having perfluoroalkyl groups, so-called "pony tails", were used as chiral promoters in the aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines **1** with MVK. Since chiral phosphine Lewis bases **LB2** and **LB3** are easily soluble in tetrahydrofuran (THF) and diethyl ether (Et_2O), and also on the basis of the previous results we reported,[8a, b] we utilized THF as solvent for this reaction. We found that using **LB2** as a chiral phosphine Lewis base promoter in the aza-Morita–Baylis–Hillman reaction of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**1c**) or *N*-(4-bromobenzylidene)-4-methylbenzenesulfonamide (**1d**) with MVK at low temperature (-20 to 0 °C), no reaction occurred. However, we were delighted to find that with **LB2** as a chiral promoter at 15 °C in THF, this catalytic, asymmetric aza-Morita–Baylis–Hillman reaction proceeded smoothly to give the corresponding adducts **2c** and **2d** in good yields with 71% and 70% ee, respectively. The results are summarized in Table 1. As can be seen from Table 1, for a variety of *N*-sulfonated imines **1**, moderate to good enantiomeric excesses (52% to 82% ee) of the corresponding adducts **2a**–**h** with the *S* configuration[8] can be achieved in 58–88% yields in tetrahydrofuran (THF) at 15 °C



Scheme 1. Synthesis of the chiral phosphine Lewis base **LB2**.

(Table 1, entries 1–8). For the *ortho*-substituted *N*-sulfonated imine **1f**, *N*-sulfonated cinnamoyl imine **1g**, and *N*-mesylated imine **1h** (ArCH=N-Ms), this catalytic, asymmetric aza-Morita–Baylis–Hillman reaction also proceeded smoothly at 15 °C to give the corresponding adducts in good yields with similarly moderate to good enantioselectivities (Table 1, entries 6–8).

Similarly, we found that using **LB3** as a chiral Lewis base promoter in aza-Morita–Baylis–Hillman reactions of *N*-sulfonated imines **1** with MVK, they proceed smoothly at various reaction temperatures in THF. The results are summarized in entries 1–3 of Table 2. At −20 °C, the adduct **2c** was obtained in 70% yield with 94% ee in the reaction of *N*-(4-chlorobenzylidene)-4-methylbenzenesulfonamide (**1c**) with MVK (Table 2, entry 3). In addition, at 0 °C or 25 °C, **2c** was also obtained in 93% yield with 91% ee and in 84% yield with 89% ee, respectively (Table 2, entries 1 and 2). Therefore, the achieved enantioselectivities slightly decreased at higher reaction temperature. At any rate, the best reaction temperature for this novel chiral phosphine Lewis base is −20 °C. At −20 °C in THF for a variety of *N*-sulfonated imines **1**, the corresponding adducts **2** were obtained in good yields with good to high ee (up to 95% ee) (Table 2, entries 4–11). For *ortho*-substituted *N*-sulfonated imine **1f**, the corresponding adduct **2f** was obtained in 90% yield with 89% ee at −20 °C in THF (Table 2, entry 9). For *N*-sulfonated cin-



Scheme 2. Synthesis of chiral phosphine Lewis base **LB3**.

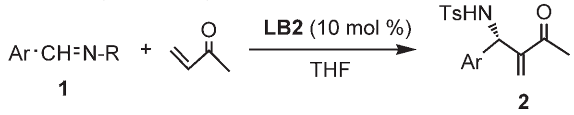
namoyl imine **1g**, the achieved ee of the corresponding adduct **2g** reached 78% ee in 98% yield (Table 2, entry 10). For *N*-mesylated imine **1h** (ArCH=N-Ms), this catalytic, asymmetric aza-Morita–Baylis–Hillman reaction also proceeded smoothly at $-20\,^{\circ}C$ in the presence of chiral phosphine promoter **LB3** in THF to give the corresponding adduct **2h** in 75% yields with 86% ee (Table 2, entry 11).

Therefore, chiral phosphine Lewis base **LB3** is more effective than **LB2** in catalytic, asymmetric aza-Morita–Baylis–Hillman reactions. In addition, the achieved enantioselectivities in these reactions are better than the original chiral phosphine Lewis base **LB1** under the similar conditions.[8a, b] At the present stage, we do not understand why chiral phosphine Lewis base **LB3** is more effective than **LB2** in this reaction. We believe that the steric bulkiness in **LB2** impairs its catalytic ability in the Morita–Baylis–Hillman reaction.

The mechanistic details of this chiral phosphine Lewis base in these reactions have been discussed in our previous papers.[8a, b] The key enolate intermediate in the Morita–Baylis–Hillman reaction, which has been stabilized by intramolecular hydrogen bonding, has been observed by ^{31}P and ^{1}H NMR spectroscopy before. Therefore, the chiral phosphine Lewis base catalyst **LB2** or **LB3** is also a bifunctional organocatalyst (**LBBA**: Lewis base and Brønsted acid cocatalyzed system) in Morita–Baylis–Hillman reactions.[9,14]

On the other hand, it is well known that this kind of Lewis base catalyst bearing perfluoroalkane "pony tails" can be used in supercritical carbon dioxide ($scCO_2$) according to previous reports.[15] Thus, we attempted this catalytic, asymmetric aza-Baylis–Hillman reaction in $scCO_2$ phase using **LB3** as a Lewis base catalyst. However, we found that the reaction became sluggish and the corresponding adduct was obtained in low yield under $scCO_2$ conditions (65 °C, 10 MPa), presumably due to the fact that the starting *N*-sulfonated imine cannot be dissolved very well in $scCO_2$. In addition, it is also well known that this kind of Lewis base catalysts bearing perfluoroalkane "pony tails" can be recovered by using fluorous solvents, but in our reaction system, the catalysts were completely oxidized to the corresponding phosphine oxides after the reaction was completed. Therefore, we can only recover the precursors of **LB2** and **LB3** by a flash column chromatography in 60–70% yield. The reduction of the recovered precursors affords the corresponding Lewis base promoters

Table 1. Aza-Baylis–Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of chiral phosphine Lewis base **LB2** (10 mol %).



Entry	Ar	R	No.	Temp. [°C]	Time [h]	Yield [%][a] 2	ee [%][b]	Absolute configuration
1	C_6H_5	Ts	**1a**	15	24	**2a**, 60	82	*S*
2	*p*-FC_6H_4	Ts	**1b**	15	24	**2b**, 58	76	*S*
3	*p*-ClC_6H_4	Ts	**1c**	15	24	**2c**, 73	71	*S*
4	*p*-BrC_6H_4	Ts	**1d**	15	24	**2d**, 88	70	*S*
5	*p*-$NO_2C_6H_4$	Ts	**1e**	15	24	**2e**, 53	78	*S*
6	*o*-ClC_6H_4	Ts	**1f**	15	48	**2f**, 82	76	*S*
7	*trans*-$C_6H_4CH{=}CH$	Ts	**1g**	15	48	**2g**, 77	52	*S*
8	*p*-ClC_6H_4	Ms	**1h**	15	48	**2h**, 78	80	*S*

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

LB2 and **LB3** in similar yields as those described in Schemes 1 and 2, respectively.

In conclusion, we found that in the aza-Morita–Baylis–Hillman reaction of *N*-sulfonated imines **1** with MVK using **LB3** bearing two perfluoroalkane long chains at the 6,6′-positions of the naphthalene framework as a chiral phosphine Lewis base, 78–95% ee can be achieved at −20 °C in THF in good to high yields. This chiral phosphine Lewis base is more effective than the original chiral phosphine Lewis base **LB1** under similar conditions, although it is not successful in the $scCO_2$ phase. Therefore, divergent structures of chiral phosphine Lewis bases can be designed and synthesized on the basis of the structure of the original **LB1** catalyst. We believe that the chiral Lewis bases of **LB2** and **LB3** acted as a bifunctional chiral catalyst (LBBA) in this reaction as well.[8,9] The phosphine atom acted as a Lewis base (**LB**) and the phenolic OH acted as a Lewis acid (**BA**) through hydrogen bonding. Efforts are underway to elucidate the mechanistic details of this reaction and the key factors of chiral Lewis bases in Morita–Baylis–Hillman reactions and to disclose the scope and limitations of this reaction. Work along this line is currently in progress.

Experimental Section

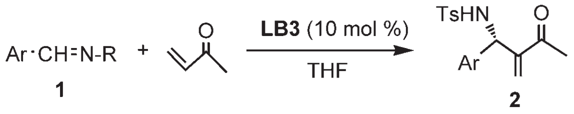
General Remarks

Melting points were obtained with a Yanagimoto micromelting point apparatus and are uncorrected. Unless otherwise stated, all reactions were carried out under an air atmosphere. All solvents were purified by distillation. Infrared spectra were measured on a Perkin-Elmer 983 spectrometer. ^1H NMR spectra was recorded on a Bruker AM-300 spectrometer as $CDCl_3$ solutions with tetramethylsilane (TMS), *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. *N*-Sulfonated imines **1** were prepared according to the literature.[16] 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 enantiomeric 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. Compounds **LB2–1**, **LB2–2**, **LB2–3**, **LB2–4**, and **LB2–5** in Scheme 1 and **LB3–1**, **LB3–2** and **LB3–3** in Scheme 2 are known compounds. The corresponding aza-Baylis–Hillman adducts **2a–j** are known compounds as well.[8a, b]

Synthesis of (*R*)-(−)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]-2′-(diphenylphosphinoyl)-2-trifluoromethansulfonyloxy-1,1′-binaphthalenyl, LB2–6

A three-necked round-bottom flask charged with a mixture of **LB2–5** (1.18 mmol), 3.0 mmol of diphenylphosphine oxide, 1,3-bis(diphenylphosphino)propane (dppp) (0.2 mmol), $Pd(OAc)_2$ (0.2 mmol) and diisopropylethylamine (6 mmol) in

Table 2. Aza-Baylis–Hillman reactions of *N*-sulfonated imines **1** (1.0 equiv.) with methyl vinyl ketone (3.0 equivs.) in the presence of chiral phosphine Lewis base **LB3** (10 mol %).



Entry	Ar	R	No.	Temp. [°C]	Time [h]	Yield [%][a] 2	ee [%][b]	Absolute configuration
1	*p*-ClC$_6$H$_4$	Ts	**1c**	25	12	**2c**, 84	89	*S*
2	*p*-ClC$_6$H$_4$	Ts	**1c**	0	12	**2c**, 93	91	*S*
3	*p*-ClC$_6$H$_4$	Ts	**1c**	–20	24	**2c**, 70	94	*S*
4	*p*-BrC$_6$H$_4$	Ts	**1d**	–20	24	**2d**, 83	93	*S*
5	*p*-NO$_2$C$_6$H$_4$	Ts	**1e**	–20	12	**2e**, 83	86	*S*
6	*m*-FC$_6$H$_4$	Ts	**1i**	–20	24	**2i**, 69	92	*S*
7	*m*-NO$_2$C$_6$H$_4$	Ts	**1j**	–20	24	**2j**, 84	95	*S*
8	C$_6$H$_5$	Ts	**1a**	–20	48	**2a**, 91	71	*S*
9	*o*-ClC$_6$H$_4$	Ts	**1f**	–20	48	**2f**, 90	89	*S*
10	*trans*-C$_6$H$_5$CH=CH	Ts	**1g**	–20	48	**2g**, 98	78	*S*
11	*p*-ClC$_6$H$_4$	Ms	**1h**	–20	48	**2h**, 75	86	*S*

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

10 mL of DMSO was heated to 120 °C for 24 h under an argon atmosphere. The solvent was removed under reduced pressure. To the residue were added water (50 mL) and Et$_2$O (200 mL), and the organic phase was washed with 10% of aqueous HCl (1 × 50 mL), brine, and water and finally dried over anhydrous Na$_2$SO$_4$. Evaporation to dryness yielded a crude material which was purified by flash column chromatography (SiO$_2$, eluent: Et$_2$O/petroleum ether = 1/7) to give the pure product as a yellow syrup; yield: 2.566 g (0.94 mmol, 80%); $[\alpha]_D^{20}$: −1.5 (*c* 1.10, THF); IR (KBr): ν = 2918, 2850, 1440, 1420, 1364, 1243, 1144, 1119, 1071, 965, 906, 812, 707 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.10–1.24 (12H, m), 1.80–2.03 (12H, m), 7.07–7.59 (16H, m), 7.87–7.96 (4H, m); ^{31}P NMR (121.45 MHz, CDCl$_3$, 85% H$_3$PO$_4$): δ = +29.11; ^{19}F NMR (282 MHz, CDCl$_3$, CFCl$_3$): δ = −126.81 to −126.77 (12F, m), −123.94 to −123.48 (24F, m), −122.56 to −122.55 (12F, m), −116.57 to −116.44 (12F, m), −81.43 (18F, s, br), −75.74 (3F, s); MS (MALDI): *m/e* = 2739.3 (M$^+$ + 1); HR-MS (MALDI): *m/e* = 2739.1063; calcd. for C$_{81}$H$_{45}$O$_4$F$_{81}$Si$_2$PS^{+1}: 2739.1016.

Synthesis of (*R*)-(−)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]-2′-(diphenylphosphinoyl)-1,1′-binaphthalenyl-2-ol, LB2–7

To a solution of the phosphine oxide triflate (0.72 mmol) **LB2–6** in a 1/1/1 mixture of Et$_2$O, 1,4-dioxane and MeOH (30 mL) was added 3 N aqueous NaOH solution at room temperature. The reaction mixture was stirred for 48 h at room temperature, acidified to pH = 7 by addition of concentrated HCl, and then extracted twice with Et$_2$O. The combined organic phases were dried over anhydrous MgSO$_4$, concentrated under reduced pressure, and chromatographed on a silica gel column (Et$_2$O/petroleum ether, 1/5) to give the product as a colorless solid; yield: 930 mg (0.36 mmol, 50%); $[\alpha]_D^{20}$: −22.7 (*c* 1.09, THF); mp 44–46 °C; IR (KBr): ν = 3205, 2950, 1620, 1474, 1441, 1354, 1310, 1184, 1144, 1119, 1070, 1018, 949, 907, 707 cm^{-1}; ^{1}H NMR (300 MHz, CDCl$_3$, TMS): δ = 1.12–1.20 (12H, m), 1.92–2.07 (12H, m), 6.50 (1H, d, *J* = 8.7 Hz), 6.71–6.72 (3H, m), 6.91 (1H, d, *J* = 8.7 Hz), 7.10 (1H, d, *J* = 9.0 Hz), 7.20–7.30 (3H, m), 7.44–7.72 (7H, m), 7.87–8.01 (4H, m), 9.30 (1H, s); ^{31}P NMR (121.45 MHz, CDCl$_3$, 85% H$_3$PO$_4$): δ = +31.93; ^{19}F NMR (282 MHz, CDCl$_3$, CFCl$_3$): δ = −126.80 to −126.68 (12F, m), −123.69 to −123.45 (24F, m), −122.54 to −122.52 (12F, m), −116.54 to −116.35 (12F, m), −81.37 to −81.32 (18F, m); MS (ESI): *m/e* = 2608.2 (M$^+$ + 1); HR-MS (MALDI): *m/e* = 2607.1503; calcd. for C$_{80}$H$_{46}$O$_2$F$_{78}$Si$_2$P^{+1}: 2607.1523.

Synthesis of (*R*)-(−)-6,6′-Bis[tris(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)silyl]-2′-(diphenylphosphanyl)-1,1′-binaphthalenyl-2-ol, LB2

At 0 °C, HSiCl$_3$ (5 mmol, 0.5 mL) was carefully added to a mixture of **LB2–7** (0.32 mmol) and triethylamine (10 mmol, 1.4 mL) in toluene (30 mL) in a three-necked round-bottom flask under an argon atmosphere. The mixture was heated to reflux for 36 h. To the cooled mixture were added ether (distilled) and sodium bicarbonate. Solids were removed by filtration and the solvent was removed under reduced pressure. The residue was purified by a flash column chromatography (SiO$_2$, EtOAc/petroleum ether = 1/20) to give the product as a colorless oil; yield: 710 mg (0.27 mmol, 86%); $[\alpha]_D^{20}$: −4.5 (*c* 1.18, THF); IR (KBr): ν = 3530, 2962, 2927, 2855, 1615, 1469, 1440, 1363, 1240, 1144, 1120, 1071, 905, 811, 745, 707 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 1.12–1.20 (12H, m), 1.95–2.12 (12H, m), 4.78 (1H, s), 6.74 (1H, d, *J* = 8.1 Hz), 6.93 (1H, d, *J* = 8.1 Hz), 7.0–7.15 (5H, m), 7.21–7.37 (8H, m), 7.53 (1H, dd, J_1 = 8.4 Hz, J_2 = 2.1 Hz), 7.88 (1H, s), 7.97 (1H, d, $J_{P\text{-}H}$ = 16.8 Hz), 8.0 (2H, d, $J_{P\text{-}H}$ = 16.2 Hz); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ = −12.20; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = −126.80 to −126.69 (12F, m), −123.78 to −123.39 (24F, m), −122.54 to −122.53 (12F, m), −116.50 to −116.33 (12F, m), −81.39 to −81.33 (18F, m); MS (MALDI): *m/e* = 2591.2 ($M^+ + 1$); HR-MS (MALDI): *m/e* = 2591.1565; calcd. for $C_{80}H_{46}OF_{78}Si_2P^{+1}$: 2591.1574.

Synthesis of (*R*)-(−)-6,6′-Bis-(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′,2-bis(trifluoromethansulfonyloxy)-[1,1′]binaphthalenyl, LB3–4

To a solution of the perfluoroalkanes substituted (*R*)-1,1′-bi-2-naphthol **LB3–3** (3.7 mmol) and pyridine (1.2 mL, 15.0 mmol) in CH_2Cl_2 was added trifluoromethanesulfonic anhydride (3.38 g, 2.0 mL, 12.0 mmol) at 0 °C, and the mixture was stirred for 6 h at room temperature. After removal of the solvent, the residue was diluted with 150 mL of EtOAc and then washed with 5% HCl, saturated $NaHCO_3$, and brine (once each). The organic phase was dried over Na_2SO_4, concentrated under reduced pressure, and chromatographed on silica gel (EtOAc/petroleum ether, 1/20) to give the product **LB3–4** as a white solid; yield: 4.620 g (3.63 mmol, 98%); $[\alpha]_D^{20}$: −69.1 (*c* 2.18, $CHCl_3$); mp 64–66 °C; IR (KBr): ν = 2961, 1630, 1597, 1509, 1425, 1221, 1142, 949, 818 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.41–2.58 (4H, m), 3.04–3.09 (4H, m), 7.15–7.24 (4H, m), 7.57 (2H, d, *J* = 9.0 Hz), 7.78 (2H, s), 8.06 (2H, d, *J* = 9.3 Hz); ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = −126.58 (4F, dd, J_1 = 9.0 Hz, J_2 = 14.1 Hz), −123.87 (4F, s, br), −123.29 (4F, s, br), −122.31 (4F, s, br), −115.08 to −114.90 (4F, m), −81.20 (6F, t, *J* = 9.6 Hz), −75.01 to −74.86 (6F, m); MS (MALDI): *m/e* = 1265 ($M^+ + 23$, 18.0), 1241 ($M^+ - 1$, 17.5), 1132 ($M^+ + 23 - 133$, 87.0), 999 ($M^+ + 23 - 266$, 14.0), 977 ($M^+ - 266 + 1$, 100); anal. calcd. for $C_{38}H_{18}F_{32}O_6S_2$: C 36.73, H 1.46%; found: C 37.03, H 1.57%.

(*R*)-(−)-6,6′-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′-(diphenylphosphinoyl)-2-trifluoromethansulfonyloxy-[1,1′]binaphthalenyl, LB3–5

This compound was prepared in the same manner as **LB2–6**; yield: 92%; $[\alpha]_D^{20}$: −1.0 (*c* 1.05, $CHCl_3$); mp 71–74 °C; IR (KBr): ν = 1438, 1419, 1207, 1143, 946, 814 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.34–2.51 (4H, m), 3.00–3.10 (4H, m), 6.93–7.03 (2H, m), 7.12–7.20 (2H, m), 7.26–7.62 (12H, m), 7.69 (1H, s), 7.70 (1H, s), 7.89 (1H, d, *J* = 9.0 Hz), 7.93–7.97 (1H, m); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ = +29.19; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): = δ −126.66 to −126.53 (4F, m), −123.90 (4F, s, br), −123.31 (4F, s, br), −122.34 (2F, s, br), −122.30 (2F, s, br), −115.14 to −114.94 (4F, m), −81.25 to −81.16 (6F, m), −75.41 (3F, d, *J* = 9.3 Hz); MS (MALDI): *m/e* = 1317.8 ($M^+ + 23$, 15.0), 1295.8 ($M^+ + 1$, 100), 1185.8 ($M^+ + 1 + 23 - 133$, 17.0), 1163.8 ($M^+ + 1 - 133$, 70.0), 1145.8 ($M^+ - 149$, 38); anal. calcd. for $C_{49}H_{28}F_{29}O_4PS$: C 45.46, H 2.18%; found: C 45.74, H 2.27%.

(*R*)-(−)-6,6′-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′-(diphenylphosphinoyl)-[1,1′]binaphthalenyl-2-ol, LB3–6

This compound was prepared in the same manner as **LB2–7**; yield: 98%; $[\alpha]_D^{20}$: −39.1 (*c* 1.05, $CHCl_3$); mp 97–99 °C; IR (KBr): ν = 3058, 2934, 1596, 1439, 1335, 1240, 1144, 983, 812 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.36–2.44 (4H, m), 2.90–3.07 (4H, m), 6.39 (1H, d, *J* = 8.4 Hz), 6.67–6.78 (4H, m), 7.08 (2H, s), 7.19–7.43 (5H, m), 7.55–7.63 (4H, m), 7.74 (1H, s), 7.85–7.94 (3H, m), 8.99 (1H, s); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ = +31.73; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = −126.60 to −126.53 (4F, m), −123.92 (4F, s, br), −123.44 (2F, s, br), −123.31 (2F, s, br), −122.34 (4F, s, br), −115.05 to −114.88 (4F, m), −81.24 to −81.10 (6F, m); MS (MALDI): *m/e* = 1185.8 ($M^+ + 23$, 66.0), 1163.8 ($M^+ + 1$, 100); anal. calcd. for $C_{48}H_{29}F_{26}O_2P$: C 49.59, H 2.51%; found: C 49.97, H 2.66%.

(*R*)-(−)-6,6′-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′-(diphenylphosphanyl)-[1,1′]binaphthalenyl-2-ol, LB3

This compound was prepared in the same manner as **LB2**; yield: 60%; $[\alpha]_D^{20}$: −15.7 (*c* 0.98, $CHCl_3$); mp 67–69 °C; IR (KBr): ν = 3055, 1683, 1601, 1480, 1436, 1364, 1239, 1144, 812, 696 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$, TMS): δ = 2.33–2.47 (4H, m), 2.93–3.08 (4H, m), 4.54 (1H, s), 6.67 (1H, d, *J* = 8.5 Hz), 6.82 (1H, d, *J* = 8.5 Hz), 7.01–7.32 (13H, m), 7.45 (1H, dd, J_1 = 8.5 Hz, J_2 = 2.0 Hz), 7.62 (1H, s), 7.74 (1H, s), 7.87 (2H, dd, J_1 = 8.7 Hz, J_2 = 9.9 Hz); ^{31}P NMR (121.45 MHz, $CDCl_3$, 85% H_3PO_4): δ −12.68; ^{19}F NMR (282 MHz, $CDCl_3$, $CFCl_3$): δ = −126.59 (4F, s, br), −123.95 (4F, s, br), −123.31 (4F, s, br), −122.33 (4F, s, br), −115.22 to −114.89 (4F, m), −81.24 (3F, s, br), −81.21 (3F, s, br); MS (MALDI): *m/e* = 1145.7 ($M^+ - 1$, 100), 1163.8 ($M^+ + 1$, 100); anal. calcd. for $C_{48}H_{29}F_{26}OP$: C 50.28, H 2.55%; found: C 50.74, H 2.69%.

Typical Procedure for the Reaction of (*R*)-(−)-6,6′-Bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′-(diphenylphosphanyl)-[1,1′]binaphthalenyl-2-ol (LB3)-Catalyzed Aza-Morita–Baylis–Hillman Reaction of *N*-(Benzylidene)-4-methylbenzenesulfonamide (1a) with MVK in THF

A 10-mL Schlenk tube containing *N*-(benzylidene)-4-methylbenzenesulfonamide (1a; 0.5 mmol) and (*R*)-(−)-6,6′-bis(3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl)-2′-(diphenylphosphanyl)-[1,1′]binaphthalenyl-2-ol (LB3; 57 mg, 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 −20 °C, methyl vinyl ketone (MVK) (125 μL, 1.5 mmol) was added into the Schlenk tube. The reaction mixture was stirred at −20 °C for 12–36 h.

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-Morita–Baylis–Hillman adduct as a colorless solid which was immediately subjected to the chiral HPLC for the analysis of the achieved enantiomeric excess.

Supporting Information Available

The chiral HPLC traces of the aza-Morita–Baylis–Hillman adducts shown in Tables 1 and 2. This material is available free of charge on the WWW under http://asc.wiley-vch.de/

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