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Chiral phosphine oxide BINAPO as a Lewis base catalyst for asymmetric allylation and aldol reaction of trichlorosilyl compounds

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Abstract—Chiral phosphine oxide BINAPO, which was readily prepared from chiral phosphine BINAP, exhibited good catalytic activities in the reaction of trichlorosilyl compounds via hypervalent silicate intermediates. The allylation of aldehydes with allyltrichlorosilanes in the presence of a catalytic amount of BINAPO gave the allylated adducts in good enantioselectivities (up to 79% ee) wherein a combination of diisopropylethylamine and tetrabutylammonium iodide as additives was crucial to accelerate the catalytic cycle. ^{31}P NMR analysis of the phosphine oxide suggested that the amine promoted the dissociation of phosphine oxide from silicon atom. BINAPO also promoted the enantioselective aldol reaction of aldehydes with trichlorosilyl enol ethers in the presence of diisopropylethylamine as an additive to afford the corresponding aldol adducts in high diastereo- and enantioselectivities (up to *syn*/*anti*=1/25, 96% ee (*anti*)).

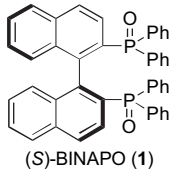
1. Introduction

Numerous chiral *base*-catalyzed reactions have been developed, but most base catalysts are Brønsted bases, such as amines or metal alkoxides.[1] Recently Lewis base-catalyzed reactions, utilizing the nucleophilicity toward a silicon atom have attracted considerable attention.[2,3] Lewis base catalysts such as phosphoramides,[4–6] pyridine *N*-oxides,[7,8] sulfoxides,[9] and formamides[10] attack an electron-deficient silicon atom to form a hypervalent silicate, which undergoes a reaction to release the product and the catalyst for further turnover.

Phosphine oxides possess a high nucleophilicity derived from the polarization between P–O bond.[11] This nucleophilicity allows phosphine oxides to act like other Lewis bases and produces hypervalent silicates[12] with trichlorosilyl compounds. In addition, chiral phosphine oxides are readily prepared from commercially available chiral phosphines. However, little attention has been paid to phosphine oxides as chiral Lewis base catalysts until recently when Kobayashi[13] reported the enantioselective allylation of benzoylhydrazones with allyltrichlorosilanes promoted by phosphine oxide, though more than a stoichiometric amount of phosphine oxide was required.

Enantioselective allylation of carbonyl compounds[14] and aldol reaction[15,16] are powerful and important processes, which are based on the nucleophilic addition to carbonyl derivatives and yield optically active homoallylic alcohols and β-hydroxy carbonyl compounds, respectively. The majority of their asymmetric versions have been achieved utilizing a chiral Lewis acid as a catalyst to activate the carbonyl groups via an acyclic transition state to provide predominantly *syn*-adducts without reflecting the *E*/*Z* ratio of allyl reagents or silyl enol ethers.

Kobayashi has reported that dimethylformamide activated allyltrichlorosilanes to promote the allylation of aldehydes.[17] The reaction proceeds via a six-membered transition state, which involves hypervalent silicate. Therefore, the stereochemistry of the products can be controlled. (*E*)- and (*Z*)-silane provide the *anti*- and *syn*-product, respectively. Thereafter, various chiral Lewis base catalysts for asymmetric allylation such as phosphoramides,[4,5] formamides[10] and pyridine *N*-oxides[7a] have been developed. Denmark has reported the first asymmetric aldol reaction



(*S*)-BINAPO (**1**)

Figure 1. Chiral phosphine oxide.

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of trichlorosilyl enol ethers promoted by a phosphoramide catalyst.[6] Similar to the allylation described above, this aldol reaction proceeds via a chair-like transition state involving a hypervalent silicate and yields products reflecting the *E*/*Z* ratio of enol ethers.

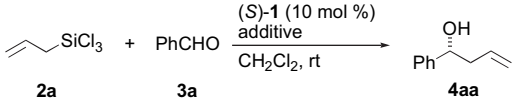
Herein we report the first example that employs chiral phosphine oxide BINAPO (**1**)[18] as an organocatalyst[19] in the enantioselective allylation and aldol reaction of trichlorosilyl compounds (Fig. 1).

2. Results and discussion

2.1. Phosphine oxide-catalyzed allylation[20]

We initially examined (*S*)-**1**-catalyzed allylation of allyltrichlorosilane (**2a**) with benzaldehyde (**3a**) in dichloromethane at rt. The reaction proceeded to give corresponding homoallylic alcohol (**4**), but the catalytic activity was quite low compared to other Lewis bases[4,7a] (Table 1, entry 1). To acquire a sufficient reactivity, we searched for an additive. We have previously investigated allylation catalyzed by pyridine *N*-oxide,[7a] in which the addition of diisopropylethylamine dramatically increased the activity of the catalyst (entry 2). As another activator, Berrisford has shown that tetrabutylammonium salts accelerate the allylation of aldehydes with allyltrichlorosilanes.[21] Although using either diisopropylethylamine or tetrabutylammonium salts alone did accelerate the reaction, the yields remained moderate (entries 3 and 4). After considerable screening, we found that the combination of diisopropylethylamine and tetrabutylammonium iodide remarkably increased the catalytic activity without decreasing the selectivity (entry 5).

Table 1. Effects of additives on chemical yield and enantioselectivity



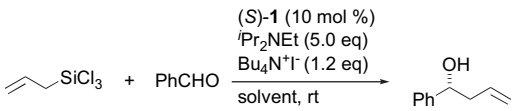
2a **3a** **4aa**

Entry	Additive[a]	Time, h	Yield,[b] %	ee,[c] %
1	None	24	32	36
2	$^{i}Pr_2NEt$	24	79	37
3	$Bu_4N^+I^-$	12	54	46
4	$Bu_4N^+OTf^-$	6	32	42
5	$^{i}Pr_2NEt$, $Bu_4N^+I^-$	4	92	43

[a] $^{i}Pr_2NEt$: 5.0 equiv, ammonium salt: 1.2 equiv.
[b] Isolated yield.
[c] Determined by HPLC (Daicel Chiralcel OD-H).

Next we screened solvents using diisopropylethylamine and tetrabutylammonium iodide as additives (Table 2). Benzene and tetrahydrofuran were not suitable as both gave low yields and enantioselectivities (entries 2 and 3). Acetonitrile gave a slightly higher yield, but the conversion took 24 h. Thus, dichloromethane was the solvent of choice in terms of both reactivity and enantioselectivity. Triphenylphosphine oxide, which is a typical monodentate phosphine oxide, gave a lower chemical yield, suggesting that the bidentate structure of the catalyst significantly influences the reaction (entries 1 vs 5).

Table 2. Screening of solvents



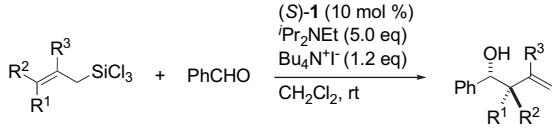
2a **3a** **4aa**

Entry	Solvent	Time, h	Yield,[a] %	ee,[b] %
1	CH_2Cl_2	4	92	43
2	Benzene	24	11	10
3	THF	48	8	16
4	CH_3CN	24	96	44
5[c]	CH_2Cl_2	24	7	—

[a] Isolated yield.
[b] Determined by HPLC (Daicel Chiralcel OD-H).
[c] Triphenylphosphine oxide (0.2 equiv) was used as a catalyst.

Table 3 shows the results obtained in the present allylation with various types of allyltrichlorosilanes. All the allyltrichlorosilanes smoothly react with aldehyde **3a** to give the corresponding homoallylic alcohols (**4**) in good yields with γ-selectivities. The *syn*-isomers were obtained from (*Z*)-crotyltrichlorosilane, while the *anti*-isomers were produced from (*E*)-crotyltrichlorosilane with complete selectivities (entries 2 and 3). These results suggest that the reaction proceeds via a six-membered chair-like transition state, which involves hypervalent silicate (Fig. 2). (*E*)-Crotyltrichlorosilane gave a good enantioselectivity similar to allyltrichlorosilane (entry 3), while (*Z*)-crotyltrichlorosilane

Table 3. Asymmetric allylation of **3a** with allyltrichlorosilanes (**2**) catalyzed by (*S*)-**1**



2 **3a** **4**

Entry	Allyltrichlorosilane				Time, h	Allylic alcohol		
		R^1	R^2	R^3			Yield,[a] %	ee,[b] %
1	**2a**	H	H	H	4	**4aa**	92	43
2[c]	**2b**	Me	H	H	4	**4ba**	92[d]	4
3[e]	**2c**	H	Me	H	2	**4ca**	87[f]	46
4	**2d**	Me	Me	H	4	**4da**	63	4
5	**2e**	H	H	Me	1	**4ea**	73	66
6	**2f**	H	H	Ph	1	**4fa**	80	59
7	**2g**	H	–$(CH_2)_4$–		3	**4ga**	81	64

[a] Isolated yield.
[b] Determined by HPLC.
[c] *E*/*Z*=1/99.
[d] *syn*/*anti*=99/1.
[e] *E*/*Z*=77/23.
[f] *syn*/*anti*=23/77.

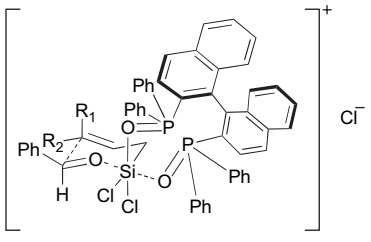
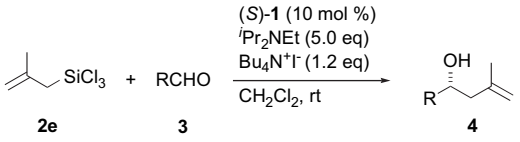


Figure 2. Plausible transition state.

and prenyltrichlorosilane, which have steric hindrance in the R^1 position in Table 2, decreased the enantioselectivities (entries 2 and 4). However, the most striking feature is that good enantioselectivities were obtained in the reaction of β-substituted allyltrichlorosilanes such as methallyltrichlorosilane and β-phenylallyltrichlorosilane (entries 5–7), which gave low enantioselectivities with other Lewis bases.[4,7a]

Table 4 summarizes the results obtained in the methallylation of various aldehydes catalyzed by BINAPO (**1**). Aromatic and unsaturated aldehydes underwent methallylation in good yields (entries 1 and 2), although aliphatic aldehyde decreased both the reactivity and enantioselectivity (entry 3). Aldehydes with electron-deficient substituents gave selectivities similar to that of **3a** (entry 4), while the introduction of electron-donating substituents into the *p*-position slightly decreased the enantioselectivities (entry 5). Steric hindrance in the *o*-position of benzaldehyde dramatically decreased the enantioselectivities (entry 9). The best result was obtained in the reaction of 3,5-dimethylbenzaldehyde (**3j**) at −23 °C (entry 11).

Table 4. Asymmetric allylation of aldehydes (**3**) with **2e** catalyzed by (*S*)-**1**



2e **3** **4**

Entry		Aldehyde, R	Time, h	Yield,[a] %	ee,[b] %
1	**3a**	Ph	1	73	66
2	**3b**	PhCH=CH	1	67	32
3	**3c**	$PhCH_2CH_2$	24	59	29
4	**3d**	4-Cl-C_6H_4	2	77	65
5	**3e**	4-MeO-C_6H_4	1	75	55
6	**3f**	2-Furyl	1	53	63
7	**3g**	1-Naphthyl	4	57	53
8	**3h**	2-Naphthyl	4	75	62
9	**3i**	2,4,6-Me_3-C_6H_2	2	63	5
10	**3j**	3,5-$Me_2C_6H_3$	2	67	71
11[c]	**3j**	3,5-$Me_2C_6H_3$	72	71	79
12	**3k**	3,5-$(CF_3)_2C_6H_3$	4	65	56
13	**3l**	3,4,5-$(MeO)_3C_6H_2$	4	61	57

[a] Isolated yield.
[b] Determined by HPLC.
[c] The reaction was conducted at −23 °C.

2.2. ^{31}P NMR analysis

Figure 3 shows a plausible reaction mechanism for Lewis base-catalyzed allylation with allyltrichlorosilanes.[17b] The binding of bidentate Lewis base to allyltrichlorosilane affords a pentacoordinate silicon complex. Then aldehyde attacks the enhanced electrophilic silicon to form a ternary complex, which provides the silylated allylic alcohol via a chair-like transition state and subsequently releases the Lewis base for further turnover. In this process, the addition of diisopropylethylamine increases the catalytic activity, although the details are unclear. To clarify the role of amine, we examined ^{31}P NMR analysis of phosphine oxide **1** in various steps of the reaction (Table 5). The ^{31}P NMR peak of pure **1** was observed at 28.6 ppm (entry 1), while signals for the presence of allyltrichlorosilane were at 43.3 ppm (entry 2), which suggest that phosphine oxide **1** coordinates to allylsilane **2a**. The addition of benzaldehyde (**3a**) gave

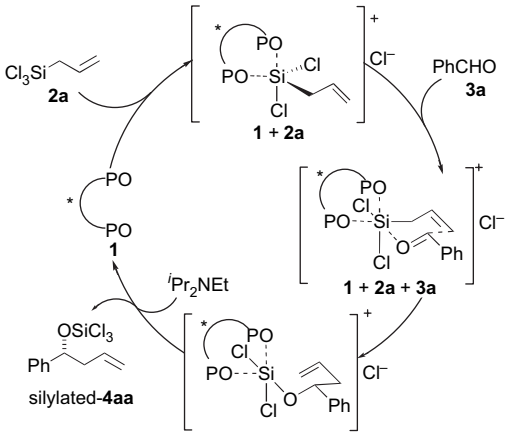


Figure 3. Plausible reaction mechanism.

Table 5. ^{31}P NMR analysis

Entry	Condition[a]	^{31}P NMR, ppm
1	**1**	28.6
2	**1**+**2a**	43.3
3	**1**+**2a**+**3a**	40.9, 43.3
4	**1**+**2a**+**3a**+ $^{i}Pr_2NEt$	28.6
5	**1**+**2a**+$^{i}Pr_2NEt$	28.6
6	**1**+**4aa**+$SiCl_4$+$^{i}Pr_2NEt$[b]	40.7

[a] **1**: 0.1 equiv, **2a**: 1.1 equiv, **3a**: 1.0 equiv, **4aa**: 1.1 equiv, $^{i}Pr_2NEt$: 5.0 equiv, $SiCl_4$: 1.1 equiv.
[b] $^{i}Pr_2NEt$: 1.1 equiv.

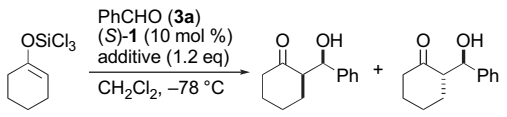
a new peak derived from the allylated product at 40.9 ppm along with the previous peak at 43.3 ppm (entry 3). In the control experiment, a mixture of **1**, **4aa**, $SiCl_4$, and amine gave a peak at 40.7 ppm (entry 6), which was derived from the allylated product. Under the presence of diisopropylethylamine, ^{31}P NMR peak in **1** appeared only at 28.6 ppm (entry 4). These results suggest that the amine dissociates **1** from the silicon atom to reproduce free **1**, which consequently increases the catalytic efficiency.

2.3. Phosphine oxide-catalyzed aldol reaction[22]

We then investigated the asymmetric aldol reaction of trichlorosilyl enol ethers catalyzed by phosphine oxide BINAPO.

We initially examined the aldol reaction of **5a** with **3a** in the presence of 10 mol % of **1** (Table 6, entry 1). The aldol adduct was obtained in moderate yield and diastereoselectivity, but a high enantioselectivity was observed in the *anti*-adduct. To improve the yield and selectivity, we searched for additives. The addition of 2-methyl-2-butene[9b] increased both the reactivities and selectivities (entry 2), probably due to its acid scavenging property, which neutralizes hydrogen chloride produced by adventitious hydrolysis of trichlorosilyl enol ethers. The addition of diisopropylethylamine further accelerated the reaction rate, which suggests that the amine works not only as an acid scavenger, but also increases the catalytic activity as well as the allylation described in Section 2.1 (entry 3). The addition of ammonium salts promoted the formation of the dehydrated adduct, which decreased the chemical yield of the aldol adduct (entry 5).

Table 6. Effects of additives on chemical yield and enantioselectivity



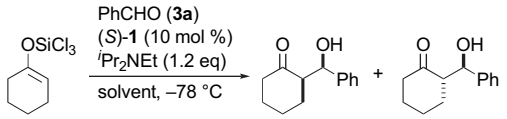
5a *syn*-**6aa** *anti*-**6aa**

Entry	Additive	Time, h	Yield,[a] %	*syn*/*anti*[b]	ee,[c] % (*anti*)
1	None	2	58	1/2	86
2	2-Methyl-2-butene	1	96	1/13	84
3	$^{i}Pr_2NEt$	0.25	94	1/14	87
4	2-Methyl-2-butene, $^{i}Pr_2NEt$	0.25	94	1/16	87
5	$^{i}Pr_2NEt$, $Bu_4N^{+}I^{-}$	0.25	75	1/8	82

[a] Isolated yield.
[b] Determined by ^{1}H NMR and HPLC.
[c] Determined by HPLC (Daicel Chiralcel OD-H).

To further optimize the aldol reaction, we next screened solvents in the same transformation using **1** (Table 7). Changing to either a more polar or less polar solvent dramatically decreased the chemical yields and stereoselectivities (entries 2–4). The reaction rate was also attenuated in a less polar solvent (toluene), while employing polar solvents (tetrahydrofuran and propionitrile) still provided moderate yields of the corresponding aldol adducts.

Table 7. Screening of solvents



5a *syn*-**6aa** *anti*-**6aa**

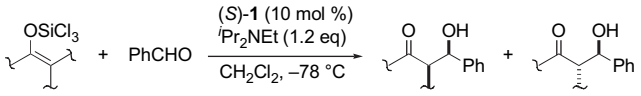
Entry	Solvent	Time, h	Yield,[a] %	*syn*/*anti*[b]	ee,[c] % (*anti*)
1	CH_2Cl_2	0.25	94	1/14	87
2	Toluene	1	11	1/1	29
3	THF	1	62	1/5	83
4	EtCN	2	49	1/2	43

[a] Isolated yield.
[b] Determined by ^{1}H NMR and HPLC.
[c] Determined by HPLC (Daicel Chiralcel OD-H).

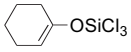
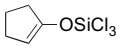
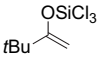
With the optimized conditions in hand, we then investigated the aldol reaction of various trichlorosilyl enol ethers with **3a** (Table 8). The trichlorosilyl enol ether derived from cyclopentanone (**5b**) gave the *anti*-adduct as the major product with a moderate enantioselectivity (entry 2). Although the reactivities of enol ethers derived from acyclic ketones were slightly lower (entries 3–5), the best enantioselectivity of 95% ee was observed in the reaction of enol ether **5e**, which was derived from pinacolone (entry 5). It is noteworthy that the *anti*-adducts were predominantly obtained from the (*E*)-enol ethers, while the corresponding *syn*-adducts were predominantly produced from the (*Z*)-enol ethers.

To establish a mechanistic profile of the phosphine oxide catalyzed process, we examined the aldol reactions of aldehyde **3a** with (*E*)- and (*Z*)-trichlorosilyl enol ethers (**7**) derived from heptanal (Table 9). These results indicate that the diastereoselectivity of the aldol adducts is reflected in the *E*/*Z* ratio of the enol ethers. These results suggest that the reaction proceeds via a six-membered transition state as proposed by Denmark.[23]

Table 8. Asymmetric aldol reactions of **3a** with trichlorosilyl enol ethers (**5**) catalyzed by (*S*)-**1**

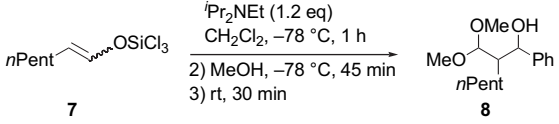


5 **3a** *syn*-**6** *anti*-**6**

Entry	Trichlorosilyl enol ether		Time, h	Yield,[a] %	*syn*/*anti*[b]	ee,[c] % (*syn*, *anti*)
1	**5a**		0.25	94	1/14	71, 87
2	**5b**		0.25	94	1/17	74, 69
3[d]	**5c**		8	62	1/6	59, 74
4[e]	**5d**		12	51	5/1	75, 14
5	**5e**		6	51	—	95

[a] Isolated yield.
[b] Determined by ^{1}H NMR and HPLC.
[c] Determined by HPLC.
[d] *E*/*Z*=6.5/1.
[e] *E*/*Z*=1/>10.

Table 9. Asymmetric aldol reaction of **3a** with **7** catalyzed by (*S*)-**1**



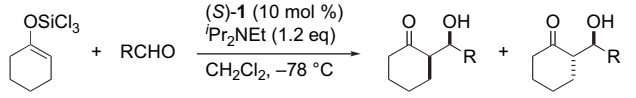
7 **8**

E/*Z*	Yield,[a] %	*syn*/*anti*[b]	ee,[c] % (*syn*, *anti*)
>10/1	96	1/25	28, 12
1/4	92	4/1	31, 13

[a] Isolated yield.
[b] Determined by ^{1}H NMR and HPLC.
[c] Determined by HPLC (Daicel Chiralcel OD-H).

Table 10 summarizes the results obtained in the reactions of aliphatic, α,β-unsaturated, and aromatic aldehydes with trichlorosilyl enol ether **5a** catalyzed by **1**. All the reactions resulted in high *anti*- and enantioselectivities, although the reaction of aliphatic aldehyde proceeded rather slow (entry 3). All the α,β-unsaturated and aromatic aldehydes reacted smoothly to produce the corresponding aldol adducts. In the reaction of sterically congested aldehydes, high diastereoselectivities were observed, but the enantioselectivities somewhat decreased (entries 4 and 5). Aldehydes with electron-donating substituents gave slightly lower enantioselectivities (entry 6), while aldehydes with electron-deficient substituents gave high stereoselectivities (entries 8–10). The best result was obtained in the reaction of *p*-nitrobenzaldehyde (**3p**) (entry 10).

Table 10. Asymmetric aldol reaction of aldehydes (**3**) with **5a** catalyzed by (*S*)-**1**



5a **3** *syn*-**6** *anti*-**6**

Entry		Aldehyde, R	Time, h	Yield,[a] %	*syn*/*anti*[b]	ee,[c] % (*anti*)
1	**3a**	Ph	0.25	94	1/14	87
2	**3b**	PhCH=CH	0.5	83	1/7	81
3	**3c**	$PhCH_2CH_2$	12	55	1/6	90
4	**3g**	1-Naphthyl	0.25	97	1/34	55
5	**3i**	2,4,6-$Me_3C_6H_2$	0.25	90	1/48	74
6	**3e**	4-MeO-C_6H_4	0.25	96	1/6	78
7	**3m**	4-Me-C_6H_4	0.25	92	1/7	83
8	**3n**	4-Br-C_6H_4	0.25	98	1/16	89
9	**3o**	4-CF_3-C_6H_4	0.25	87	1/21	93
10	**3p**	4-NO_2-C_6H_4	0.25	90	1/25	96

[a] Isolated yield.
[b] Determined by ^{1}H NMR and HPLC.
[c] Determined by HPLC.

3. Conclusion

We have demonstrated catalytic, enantioselective methods for the allylation and aldol reactions of trichlorosilyl compounds using a phosphine oxide as an organocatalyst. In these processes, phosphine oxide BINAPO gave *anti*-adducts from (*E*)-silanes and *syn*-adducts from (*Z*)-silanes. The employment of the appropriate additives dramatically increased the catalytic activity. ^{31}P NMR analysis of phosphine oxide revealed that the amine promotes the dissociation of phosphine oxide from the silicon atom, which increases the catalytic activity. The present reactions provide the first examples that use a chiral phosphine oxide as a catalyst for the enantioselective allylation and aldol reactions of aldehydes. Further work on a more detailed mechanism is currently in progress.

4. Experimental

4.1. General

Melting points were measured using a Büchi 535 melting point apparatus and were not corrected. Optical rotations were obtained on a JASCO DIP-370 digital polarimeter. Infrared spectra were recorded on a JASCO FT/IR-5300. ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL EX-270 (^{1}H, 270 MHz; ^{13}C, 68 MHz) and AL-300 (^{1}H, 300 MHz; ^{13}C, 75 MHz) spectrometer. Chemical shift values are expressed in parts per million relative to internal tetramethylsilane. Coupling constants (*J*) are reported in hertz (Hz). Abbreviations are as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad. Mass spectra were obtained by electron impact with ionization voltage of 70 eV on JEOL JMS-DX303. HPLC was performed on a JASCO PU-1580 with a JASCO UV-1575 (λ=254 nm) and chiral separations were performed using Daicel Chiralpak or Chiralcel columns (ϕ 0.46×25 cm). Allyltrichlorosilane (**2a**) was purchased from TCI and was used without further purification.

4.1.1. Synthesis of (*S*)-BINAPO (1).[24] H_2O_2 (30% aq, 1.74 mL, 1.61 mmol, 5.0 equiv) was added to a suspension of (*S*)-BINAP (2.0 g, 0.32 mmol, 1.0 equiv) in acetone (120 mL). After being stirred for 5 h, the reaction was quenched with MnO_2. Filtration through Celite and evaporation of the solvent furnished the crude product, which was purified by recrystallization (toluene/hex=3/1, 20 mL) to give (*S*)-BINAPO (**1**) (1.7 g, 81%) as pale yellowish prisms. TLC: R_f 0.38 (EtOAc, UV). Mp: 260.5–261.5 °C. $[\alpha]_D^{25}$ –391.2 (*c* 0.5, benzene). ^{1}H NMR ($CDCl_3$): δ 6.79 (d, 4H, *J*=3.9 Hz), 7.22–7.44 (m, 20H), 7.66–7.71 (m, 4H), 7.79–7.85 (m, 4H).

4.1.2. Synthesis of (*Z*)-crotyltrichlorosilane (2b).[25] To a suspension of trichlorosilane (6.9 mL, 51.1 mmol, 1.03 equiv) and $Pd(PPh_3)_4$ (150 mg, 0.13 mmol, 0.26 mol %) in an argon purged autoclave was added 1,3-butadiene (2.7 g, 50 mmol, 1.0 equiv) at −78 °C. After being stirred for 30 min, the mixture was allowed to warm to 100 °C, then stirred for 1 h at the same temperature. Distillation of the reaction mixture gave (*Z*)-crotyltrichlorosilane (**2b**) (4.48 g, 47%) as a colorless oil. Bp: 140.0–141.0 °C/760 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.71 (m, 3H), 2.25 (m, 2H), 5.38 (m, 1H), 5.59 (m, 1H).

4.1.3. Synthesis of (*E*)-crotyltrichlorosilane (2c).[26] To a solution of CuCl (215 mg, 2.18 mmol, 5 mol %) and triethylamine (7.2 mL, 52.2 mmol, 1.2 equiv) in dry ether (25 mL) was added a mixture of trichlorosilane (5.3 mL, 52.2 mmol, 1.2 equiv) and (*E*)-crotyl chloride (4.0 g, 43.5 mmol, 1.0 equiv, *E*/*Z*=77/23) at 0 °C and the mixture was stirred for 2 h at rt. Filtration through Celite and the distillation of the filtrate afforded (*E*)-crotyltrichlorosilane (**2c**) (5.5 g, 66%, *E*/*Z*=77/23) as a colorless oil. Bp: 80.0–81.0 °C/50 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.67 (dd, 3H, *J*=0.7, 6.7 Hz), 2.35 (dd, 2H, *J*=0.8, 8.9 Hz), 5.43 (m, 1H), 5.72 (m, 1H).

4.1.4. Prenyltrichlorosilane (2d).[17b] Bp: 113.0–114.0 °C/40 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.62 (s, 3H), 1.77 (s, 3H), 2.28 (d, 2H, *J*=7.8 Hz), 5.13 (t, 1H, *J*=7.8 Hz).

4.1.5. Methallyltrichlorosilane (2e).[26] Bp: 73.5–75.0 °C/95 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.87 (s, 3H), 2.37 (d, 2H, *J*=1.5 Hz), 4.84 (d, 1H, *J*=0.8 Hz), 4.94 (dt, 1H, *J*=1.5, 0.8 Hz).

4.1.6. β-Phenylallyltrichlorosilane (2f). Trichlorosilane **2f** was prepared as described for **2c**. Bp: 106.0–108.0 °C/20 mmHg. IR (neat): 1622, 899 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 2.85 (s, 2H), 5.25 (s, 1H), 5.47 (s, 1H), 7.33–7.50 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 32.0, 116.1, 126.6, 128.2, 128.6, 139.8, 140.6. MS (EI): *m*/*z* 250 (M^+), 252. HRMS: calcd for $C_9H_9Cl_3Si$ 249.9539, found 249.9533.

4.1.7. 1-(Trichlorosilylmethyl)cyclohexene (2g). Trichlorosilane **2g** was prepared as described for **2c**. Bp: 106.5–108.0 °C/15 mmHg. IR (neat): 1662 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.55–1.65 (m, 4H), 2.03–2.06 (m, 4H), 2.23 (s, 2H), 5.56 (s, 1H). ^{13}C NMR ($CDCl_3$): δ 22.1, 23.1, 25.7, 30.6, 34.3, 126.1, 128.5. MS (EI): *m*/*z* 228 (M^+), 230. HRMS: calcd for $C_7H_{11}Cl_3Si$ 227.9696, found 227.9700.

4.1.8. Representative procedure of asymmetric allylation catalyzed by (*S*)-1. 1-Phenyl-3-buten-1-ol (4aa).[27] To a stirred solution of (*S*)-**1** (30.8 mg, 0.047 mmol, 10 mol %), tetrabutylammonium iodide (207 mg, 0.56 mmol, 1.2 equiv), **2a** (50 mg, 0.47 mmol, 1.0 equiv), and diisopropylethylamine (0.41 mL, 2.35 mmol, 5.0 equiv) in CH_2Cl_2 (0.5 mL) was added allyltrichlorosilane in CH_2Cl_2 (1.12 M, 0.5 mL 0.56 mmol, 1.2 equiv) at rt, and the mixture was stirred at the same temperature for 4 h. The reaction was quenched with 10% NaOH (1 mL) and extracted with EtOAc (50 mL). The organic layer was washed with 5% HCl (15 mL), satd $NaHCO_3$ (15 mL) and brine (15 mL), dried over Na_2SO_4, and concentrated. The crude material was purified by column chromatography (hex/EtOAc=15/1, SiO_2, 7 g) to give corresponding homoallyl alcohol **4aa** as an oil (92%). (*S*)-**1** (24.1 mg, 97%) was quantitatively recovered by further elution with 3% EtOH in CH_2Cl_2 without any loss of optical purity. TLC: R_f 0.29 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{23}$ +21.8 (*c* 0.88, benzene) for 43% ee (lit.[27]; $[\alpha]_D^{18}$ −48.7 (*c* 6.92, benzene) for (*S*)-isomer). ^{1}H NMR ($CDCl_3$): δ 2.02 (d, 1H, *J*=3.2 Hz), 2.49–2.55 (m, 2H), 4.74 (m, 1H), 5.13–5.21 (m, 2H), 5.81 (m, 1H), 7.28–7.37 (m, 5H). HPLC: t_R 17.7 min (major, (*R*)-isomer), 20.5 min (minor, (*S*)-isomer) (Daicel Chiralcel OD, flow rate: 1.0 mL/min, hex/IPA=40/1).

4.1.9. *syn*-2-Methyl-1-phenyl-3-buten-1-ol (4ba).[28] TLC: R_f 0.34 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{23}$ −2.3 (*c* 0.56, $CHCl_3$) for 4% ee (lit.[28]; $[\alpha]_D^{25}$ −15.0 (*c* 0.93, $CHCl_3$) for (1*S*,2*R*)-isomer of 55% ee). ^{1}H NMR ($CDCl_3$): δ 1.02 (d, 3H, *J*=3.8 Hz), 1.93 (s, 1H), 2.61 (m, 1H), 4.62 (m, 1H), 5.04 (dd, 1H, *J*=2.2, 3.3 Hz), 5.09 (dd, 1H, *J*=2.2, 4.0 Hz), 5.77 (m, 1H), 7.24–7.38 (m, 5H). HPLC: t_R 16.3 min (minor, (1*R*,2*S*)-isomer), 18.9 min (major, (1*S*,2*R*)-isomer) (Daicel Chiralcel OD, flow rate: 0.5 mL/min, hex/IPA=19/1).

4.1.10. *anti*-2-Methyl-1-phenyl-3-buten-1-ol (4ca).[28] TLC: R_f 0.31 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{25}$ +44.7 (*c* 0.75, $CHCl_3$) for 46% ee (lit.[28]; $[\alpha]_D^{25}$ −73.4 (*c* 2.00, $CHCl_3$) for (1*S*,2*S*)-isomer of 66% ee). ^{1}H NMR ($CDCl_3$): δ 0.87 (d, 3H, *J*=6.5 Hz), 2.12 (d, 1H, *J*=2.1 Hz), 2.49 (m, 1H), 4.37 (dd, 1H, *J*=2.1, 7.8 Hz), 5.17–5.23 (m, 2H), 5.78–5.88 (m, 1H), 7.28–7.35 (m, 5H). HPLC: t_R 34.3 min (minor, (1*S*,2*S*)-isomer), 41.3 min (major, (1*R*,2*R*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=100/1).

4.1.11. 2,2-Dimethyl-1-phenyl-3-buten-1-ol (4da).[29] TLC: R_f 0.41 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +2.3 (*c* 0.95, $CHCl_3$) for 4% ee (lit.[29]; $[\alpha]_D^{24}$ +22 (*c* 0.84, $CHCl_3$) for (*R*)-isomer of 78% ee). ^{1}H NMR ($CDCl_3$): δ 0.97 (s, 3H), 1.02 (s, 3H), 1.99 (d, 1H, *J*=3.5 Hz), 4.44 (d, 1H, *J*=3.5 Hz), 5.08 (dd, 1H, *J*=3.3, 17.8 Hz), 5.15 (dd, 1H, *J*=3.3, 11.3 Hz), 5.92 (dd, 1H, *J*=11.3, 17.8 Hz), 7.28–7.30 (m, 5H). HPLC: t_R 6.7 min (major, (*R*)-isomer), 9.4 min (minor, (*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=9/1).

4.1.12. 3-Methyl-1-phenyl-3-buten-1-ol (4ea).[27] TLC: R_f 0.27 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +51.8 (*c* 0.58, benzene) for 66% ee (lit.[27]; $[\alpha]_D^{21}$ −46.6 (*c* 1.97, benzene) for (*S*)-isomer of 87% ee). ^{1}H NMR ($CDCl_3$): δ 1.81 (s, 3H), 2.11 (d, 1H, *J*=1.8 Hz), 2.43 (d, 2H, *J*=6.5 Hz), 4.83 (dt, 1H, *J*=1.8, 6.5 Hz), 4.87 (d, 1H, *J*=1.9 Hz), 4.93 (d, 1H, *J*=1.9 Hz), 7.28–7.38 (m, 5H). HPLC: t_R 30.8 min (minor, (*S*)-isomer), 35.2 min (major, (*R*)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=50/1).

4.1.13. 1,3-Diphenyl-3-buten-1-ol (4fa).[30] TLC: R_f 0.34 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{24}$ −16.7 (*c* 1.72, $CHCl_3$) for 59% ee. ^{1}H NMR ($CDCl_3$): δ 2.03 (d, 1H, *J*=2.7 Hz), 2.88 (dd, 1H, *J*=9.4, 14.1 Hz), 3.02 (dd, 1H, *J*=4.0, 14.0 Hz), 4.73 (m, 1H), 5.18 (s, 1H), 5.43 (s, 1H), 7.29–7.47 (m, 10H). HPLC: t_R 8.0 min (major, (*R*)-isomer), 8.9 min (minor, (*S*)-isomer) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=9/1) (lit.[30]: t_R 34.1 min (*R*)-isomer, 38.2 min (*S*)-isomer) (Daicel Chiralpak AD, flow rate: 0.5 mL/min, hex/IPA=30/1).

4.1.14. (2-Methylenecyclohexyl)(phenyl)methanol (4ga). TLC: R_f 0.36 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +40.2 (*c* 1.17, $CHCl_3$) for 64% ee. IR (neat): 3380, 1645, 1449 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21–1.61 (m, 5H), 1.76–1.85 (m, 1H), 2.26–2.33 (m, 3H), 2.41 (dt, 1H, *J*=10.4, 4.6 Hz), 4.74 (d, 1H, *J*=10.4 Hz), 4.98 (s, 2H), 7.28–7.40 (m, 5H). ^{13}C NMR ($CDCl_3$): δ 22.2, 28.3, 29.0, 32.7, 52.0, 72.9, 111.0, 127.1, 127.8, 128.3, 142.4, 149.6. HPLC: t_R 11.0 min (minor, (−)-isomer), 13.2 min (major, (+)-isomer) (Daicel Chiralpak AD, flow rate: 0.5 mL/min, hex/IPA=3/1). MS (EI): *m*/*z* 96, 107, 202 (M^+). HRMS: calcd for $C_{14}H_{18}O$ 202.1358, found 202.1364.

4.1.15. 5-Methyl-1-phenyl-1,5-hexadien-3-ol (4eb).[31] TLC: R_f 0.24 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +6.8 (*c* 0.39, benzene) for 32% ee (lit.[31]; $[\alpha]_D^{22}$ −19.4 (*c* 0.26, benzene) for (*S*)-isomer of 99% ee). ^{1}H NMR ($CDCl_3$): δ 1.82 (s, 3H), 1.86 (d, 1H, *J*=3.2 Hz), 2.33 (d, 1H, *J*=4.0 Hz), 2.36 (s, 1H), 4.43 (m, 1H), 4.87 (s, 1H), 4.93 (s, 1H), 6.24 (dd, 1H, *J*=6.7, 15.9 Hz), 6.68 (d, 1H, *J*=15.9 Hz), 7.24–7.40 (m, 5H). HPLC: t_R 13.2 min (major, (*R*)-isomer), 15.6 min (minor, (*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=19/1).

4.1.16. 1-Phenyl-5-methyl-5-hexen-3-ol (4ec).[31] TLC: R_f 0.27 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ −5.7 (*c* 0.99, $CHCl_3$) for 29% ee (lit.[31]; $[\alpha]_D^{22}$ +15.8 (*c* 0.85, $CHCl_3$) for (*R*)-isomer of 91% ee). ^{1}H NMR ($CDCl_3$): δ 1.71–1.83 (m, 6H), 2.15 (dd, 1H, *J*=9.0, 13.2 Hz), 2.24 (dd, 1H, *J*=3.3, 13.9 Hz), 2.64–2.89 (m, 2H), 3.76 (m, 1H), 4.81 (d, 1H, *J*=2.0 Hz), 4.89 (d, 1H, *J*=2.0 Hz), 7.18–7.31 (m, 5H). HPLC: t_R 14.6 min (major, (*S*)-isomer), 21.1 min (minor, (*R*)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=19/1).

4.1.17. 1-(4-Chlorophenyl)-3-methyl-3-buten-1-ol (4ed).[31] TLC: R_f 0.26 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +34.7 (*c* 0.55, benzene) for 65% ee (lit.[31]; $[\alpha]_D^{22}$ −44.5 (*c* 0.77, benzene) for (*S*)-isomer of 90% ee). ^{1}H NMR ($CDCl_3$): δ 1.80 (s, 3H), 2.13 (d, 1H, *J*=1.9 Hz), 2.39 (d, 2H, *J*=6.5 Hz), 4.79 (m, 1H), 4.86 (d, 1H, *J*=1.4 Hz), 4.94 (d, 1H, *J*=1.4 Hz), 7.32 (m, 4H). HPLC: t_R 27.2 min (minor, (*S*)-isomer), 31.1 min (major, (*R*)-isomer) (Daicel Chiralcel OJ-H, flow rate: 0.5 mL/min, hex/IPA=50/1).

4.1.18. 1-(4-Methoxyphenyl)-3-methyl-3-buten-1-ol (4ee).[31] TLC: R_f 0.14 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +42.4 (*c* 0.45, $CHCl_3$) for 55% ee (lit.[31]; $[\alpha]_D^{23}$ −67.9 (*c* 0.99, $CHCl_3$) for (*S*)-isomer of 94% ee). ^{1}H NMR ($CDCl_3$): δ 1.79 (s, 3H), 2.04 (s, 1H), 2.42 (d, 2H, *J*=3.2 Hz), 3.81 (s, 3H), 4.78 (m, 1H), 4.85 (d, 1H, *J*=1.3 Hz), 4.91 (d, 1H, *J*=1.3 Hz), 6.89 (d, 2H, *J*=11.9 Hz), 7.30 (d, 2H, *J*=11.9 Hz). HPLC: t_R 14.4 min (major, (*R*)-isomer), 15.6 min (minor, (*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=9/1).

4.1.19. 1-(2-Furyl)-3-methyl-3-buten-1-ol (4ef).[31] TLC: R_f 0.24 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +31.7 (*c* 0.49, $CHCl_3$) for 63% ee (lit.[31]; $[\alpha]_D^{21}$ −49.2 (*c* 0.61, $CHCl_3$) for (*S*)-isomer of 92% ee). ^{1}H NMR ($CDCl_3$): δ 1.76 (s, 3H), 2.05 (d, 1H, *J*=4.0 Hz), 2.58 (d, 2H, *J*=7.9 Hz), 4.82–4.89 (m, 1H), 4.86 (d, 1H, *J*=1.3 Hz), 4.91 (d, 1H, *J*=1.3 Hz), 6.27 (d, 1H, *J*=2.0 Hz), 6.34 (dd, 1H, *J*=1.3, 2.0 Hz), 7.39 (d, 1H, *J*=2.0 Hz). HPLC: t_R 21.4 min (minor, (*S*)-isomer), 23.0 min (major, (*R*)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=40/1).

4.1.20. 1-(1-Naphthyl)-3-methyl-3-buten-1-ol (4eg). TLC: R_f 0.41 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{23}$ +59.8 (*c* 0.54, $CHCl_3$) for 53% ee. IR (KBr): 3240, 1647 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.92 (s, 3H), 2.27 (d, 1H, *J*=1.9 Hz), 2.51 (dd, 1H, *J*=9.7, 14.6 Hz), 2.69 (dd, 1H, *J*=2.7, 14.6 Hz), 4.97 (s, 1H), 5.00 (s, 1H), 5.63 (dd, 1H, *J*=2.7, 9.7 Hz), 7.47–7.56 (m, 3H), 7.73 (d, 1H, *J*=6.5 Hz), 7.79 (d, 1H, *J*=7.8 Hz), 7.89 (dd, 1H, *J*=2.4, 7.0 Hz), 8.08 (d, 1H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 22.4, 47.4, 68.2, 114.0, 122.7, 122.8, 125.4, 125.6, 126.0, 127.9, 129.0, 130.2, 133.8, 139.6, 142.8. HPLC: t_R 7.3 min (minor, (−)-isomer), 13.6 min (major, (+)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=9/1). MS (EI): *m*/*z* 129, 157, 212 (M^+). HRMS: calcd for $C_{15}H_{16}O$ 212.1201, found 212.1208.

4.1.21. 1-(2-Naphthyl)-3-methyl-3-buten-1-ol (4eh). TLC: R_f 0.34 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +56.7 (*c* 0.51, $CHCl_3$) for 62% ee. IR (KBr): 3416, 1649 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H), 2.22 (d, 1H, *J*=1.8 Hz), 2.52 (d, 2H, *J*=7.3 Hz), 4.90 (s, 1H), 4.96 (s, 1H), 5.00 (dt, 1H, *J*=1.8, 7.3 Hz), 7.46–7.53 (m, 3H), 7.83–7.85 (m, 4H). ^{13}C NMR ($CDCl_3$): δ 22.3, 48.2, 71.5, 114.1, 124.0, 124.3, 125.7, 126.0, 127.6, 127.9, 128.1, 132.9, 133.3, 141.4, 142.3. HPLC: t_R 28.7 min (minor, (−)-isomer), 31.5 min (major, (+)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=19/1). MS (EI): m/*z* 129, 157, 212 (M^+). HRMS: calcd for $C_{15}H_{16}O$ 212.1201, found 212.1194.

4.1.22. 1-(2,4,6-Trimethylphenyl)-3-methyl-3-buten-1-ol (4ei). TLC: R_f 0.38 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ −1.7 (*c* 0.81, $CHCl_3$) for 5% ee. ^{1}H NMR ($CDCl_3$): δ 1.84 (s, 3H), 1.87 (d, 1H, *J*=2.1 Hz), 2.24 (s, 3H), 2.28 (m,1H), 2.42 (s, 6H), 2.71 (dd, 1H, *J*=10.5, 13.8 Hz), 4.92 (m, 2H), 5.26 (m, 1H), 6.82 (s, 2H), HPLC: t_R 11.8 min (minor, (+)-isomer), 13.3 min (major, (−)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=19/1).

4.1.23. 1-(3,5-Dimethylphenyl)-3-methyl-3-buten-1-ol (4ej). TLC: R_f 0.34 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{23}$ +46.2 (*c* 1.19, $CHCl_3$) for 79% ee. IR (neat): 3412, 1647, 1607, 1454 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.81 (s, 3H), 2.06 (d, 1H, *J*=2.2 Hz), 2.32 (s, 6H), 2.41 (d, 2H, *J*=6.3 Hz), 4.75 (dt, 1H, *J*=2.2, 6.3 Hz), 4.88 (d, 1H, *J*=1.3 Hz), 4.93 (d, 1H, *J*=1.3 Hz), 6.91 (s, 1H), 7.00 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 21.3, 22.3, 48.3, 71.4, 113.8, 123.5, 129.1, 137.9, 142.7, 144.0. HPLC: t_R 11.8 min (minor, (−)-isomer), 13.7 min (major, (+)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=19/1). MS (EI): *m*/*z* 107, 135, 190 (M^+). HRMS: calcd for $C_{13}H_{18}O$ 190.1358, found 190.1366.

4.1.24. 1-[3,5-Bis(trifluoromethyl)phenyl]-3-methyl-3-buten-1-ol (4ek). TLC: R_f 0.66 (CH_2Cl_2, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +26.4 (*c* 0.89, $CHCl_3$) for 56% ee. IR (neat): 3414, 1649, 1624, 1464 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.85 (s, 3H), 2.32–2.40 (m, 2H), 2.47 (dd, 1H, *J*=4.0, 14.0 Hz), 4.90 (s, 1H), 4.95 (m, 1H), 5.02 (s, 1H), 7.79 (s, 1H), 7.85 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 22.1, 48.6, 70.0, 115.4, 121.3, 125.4, 126.0, 131.6 (t, *J*=33 Hz), 141.2, 146.5. HPLC: t_R 15.5 min (minor, (−)-isomer), 16.9 min (major, (+)-isomer) (Daicel Chiralpak AD-H, flow rate: 0.5 mL/min, hex/IPA=100/1). MS (EI): *m*/*z* 195, 243, 298 (M^+). HRMS: calcd for $C_{13}H_{12}F_6O$ 298.0792, found 298.0790.

4.1.25. 1-(3,4,5-Trimethoxyphenyl)-3-methyl-3-buten-1-ol (4el). TLC: R_f 0.16 (hexane/EtOAc=2/1, stained purple with anisaldehyde). $[\alpha]_D^{22}$ +27.0 (*c* 1.15, $CHCl_3$) for 57% ee. IR (neat): 3478, 1647, 1593 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.83 (s, 3H), 2.14 (d, 1H, *J*=2.6 Hz), 2.42 (d, 2H, *J*=6.6 Hz), 3.84 (s, 3H), 3.88 (s, 6H), 4.75 (dt, 1H, *J*=2.0, 6.6 Hz), 4.90 (s, 1H), 4.96 (d, 1H, *J*=2.0 Hz), 6.62 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 22.3, 48.4, 56.1, 60.8, 71.5, 102.7, 114.1, 137.2, 139.8, 142.4, 153.2. HPLC: t_R 13.5 min (minor, (−)-isomer), 18.3 min (major, (+)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=19/1). MS (EI): *m*/*z* 169, 197, 252 (M^+). HRMS: calcd for $C1_4H_{20}O_4$ 252.1362, found 252.1356.

4.1.26. Synthesis of 1-cyclohexenyloxytrichlorosilane (5a).[6b] Silicon tetrachloride (22.5 mL, 196 mmol, 2.0 equiv) was added quickly to a suspension of $Hg(OAc)_2$ (312 mg, 0.98 mmol, 1 mol %) in CH_2Cl_2 (100 mL). 1-Cyclohexeneyltrimethylsilane (16.7 g, 98 mmol, 1.0 equiv) was then added to the solution dropwise over 15 min and the resulting solution was stirred at rt for 12 h. The mixture was concentrated under reduced pressure (70 mmHg) and the resulting oil was distilled to give the trichlorosilyl enol ether **5a** (11.9 g, 54%) as a colorless oil. Bp: 80.0–81.0 °C/20 mmHg. ^{1}H NMR (C_6D_6): δ 1.96–1.21 (m, 2H), 1.26–1.35 (m, 2H), 1.70–1.73 (m, 2H), 1.90–1.97 (m, 2H), 5.21 (t, 1H, *J*=3.9 Hz).

4.1.27. 1-Cyclopentenyloxytrichlorosilane (5b).[6c] Bp: 60.0–61.0 °C/8 mmHg. ^{1}H NMR (C_6D_6): δ 1.51 (m, 2H), 1.97 (m, 2H), 2.15 (m, 2H), 4.95 (t, 1H, *J*=2.4 Hz).

4.1.28. [(1-(1,1-Dimethylethyl)ethenyl)oxy]trichlorosilane (5e).[6d] Bp: 63.0–65.0 °C/40 mmHg. ^{1}H NMR (C_6D_6):

δ 0.95 (s, 9H), 4.24 (d, 1H, J=2.7 Hz), 4.46 (d, 1H, J=2.7 Hz).

4.1.29. Synthesis of (*E*)-1-trichlorosilyloxy-1-heptene ((*E*)-7).[23] A solution of the (*E*)-1-trimethylsilyloxy-1-heptene (5.5 g, 29.7 mmol, 1.0 equiv) in dry ether (75 mL) was added to a cold solution of methyllithium in ether (1.14 M, 39.7 mL, 44.6 mmol, 1.5 equiv) under argon atmosphere. After being stirred for 0.5 h at 0 °C, the reaction mixture was allowed to reach rt and was stirred for 3 h. The resulting solution was slowly added via cannula to a cold (−78 °C) solution of silicon tetrachloride (34.2 mL, 297 mmol, 10 equiv) in ether (70 mL). The reaction mixture was slowly warmed to rt. Solvent and volatile materials were removed under vacuum. The residue was distilled to give trichlorosilyl enol ether (*E*)-**7** (3.6 g, 49%, *E*/*Z*⩾10/1) as a clear, colorless oil. Bp: 71.5–75.0 °C/8 mmHg. ^{1}H NMR (C_6D_6): δ 0.83 (t, 3H, J=7.1 Hz), 1.08–1.20 (m, 6H), 1.56–1.64 (m, 2H), 5.25 (m, 1H), 5.98 (d, 1H, J=1.3 Hz).

4.1.30. (*E*)-1-Ethyl-1-propenyloxytrichlorosilane (5c).[32] Bp: 67.5–70.5 °C/50 mmHg. ^{1}H NMR ($CDCl_3$): δ 1.08 (t, 3H, J=7.3 Hz), 1.59 (d, 3H, J=6.8 Hz), 2.21 (q, 2H, J=7.3 Hz), 5.05 (q, 1H, J=6.8 Hz).

4.1.31. (*Z*)-1-Phenyl-1-propenyloxytrichlorosilane (5d).[6b] Bp: 103.0–105.5 °C/7 mmHg. ^{1}H NMR (C_6D_6): δ 1.06 (d, 3H, J=6.8 Hz), 5.23 (q, 1H, J=6.8 Hz), 7.19–7.40 (m, 5H).

4.1.32. (*Z*)-1-Trichlorosilyloxy-1-heptene ((*Z*)-7).[23] Bp: 74.0–77.0 °C/8 mmHg. ^{1}H NMR (C_6D_6): δ 0.85 (t, 3H, J=7.1 Hz), 1.12–1.42 (m, 6H), 2.09–2.18 (m, 2H), 4.86 (dt, 1H, J=4.8, 7.4 Hz), 6.25 (m, 1H).

4.1.33. Representative procedure of asymmetric aldol reaction catalyzed by (*S*)-1. 2-(Hydroxyphenylmethyl)-cyclohexanone (6aa).[16h] A solution of benzaldehyde (**3a**) in CH_2Cl_2 (0.378 M, 1.0 mL, 0.378 mmol, 1.0 equiv) and a solution of diisopropylethylamine in CH_2Cl_2 (0.904 M, 0.5 mL, 0.452 mmol, 1.2 equiv) were added to a solution of the (*S*)-**1** (24.6 mg, 0.038 mmol, 10 mol %) in CH_2Cl_2 (2 mL) at −78 °C. A solution of 1-cyclohexenyloxytrichlorosilane (**5a**) in CH_2Cl_2 (0.904 M, 0.5 mL, 0.452 mmol, 1.2 equiv) was slowly added to the mixture. After being stirred for 0.25 h, the reaction mixture was quickly poured into cold (0 °C) satd $NaHCO_3$ (10 mL) and the slurry was stirred for 1 h. The mixture was filtered through Celite, and the filtrate was extracted with CH_2Cl_2 (50 mL). The combined organic layers were washed with brine (2×30 mL), dried over Na_2SO_4, filtered, and concentrated. The crude product was purified by column chromatography (hex/EtOAc=6/1, SiO_2, 10 g) to give the product as a diastereomeric mixture (72.5 mg, 94%, *syn*/*anti*=1/14, 71% ee (*syn*), 87% ee (*anti*)). (*S*)-**1** (24.1 mg, 97%) was quantitatively recovered by further elution with 3% EtOH in CH_2Cl_2 without any loss of optical purity. *anti*-Isomer—TLC: R_f 0.28 (hex/EtOAc=3/1, stained red with anisaldehyde). $[\alpha]_D^{24}$ +22.1 (*c* 1.00, $CHCl_3$) for 87% ee (lit.[16h]: $[\alpha]_D^{29}$ +20.1 (*c* 1.0, $CHCl_3$) for (2*S*,1′*R*)-isomer of 93% ee). ^{1}H NMR ($CDCl_3$): δ 1.26–1.37 (m, 1H), 1.52–1.71 (m, 4H), 2.05–2.12 (m, 1H), 2.35–2.72 (m, 3H), 3.95 (br s, 1H), 4.78 (d, 1H, J=8.6 Hz), 7.29–7.35 (m, 5H). *syn*-Isomer—TLC: R_f 0.38 (hex/EtOAc=3/1, stained red with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.29–1.87 (m, 5H), 2.01–2.08 (m, 1H), 2.32–2.63 (m, 2H), 2.60 (m, 1H), 3.00 (br s, 1H), 5.39 (s, 1H), 7.29–7.37 (m, 5H). HPLC: t_R 8.5 min (*syn*-minor, (2*S*,1′*S*)-isomer), 9.7 min (*syn*-major, (2*R*,1′*R*)-isomer), 10.9 min (*anti*-major, (2*S*,1′*R*)-isomer), 15.9 min (*anti*-minor, (2*R*,1′*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=19/1).

4.1.34. 2-(Hydroxyphenylmethyl)cyclopentanone (6ba).[33] *anti*-Isomer—TLC: R_f 0.33 (hex/EtOAc=3/1, stained red with anisaldehyde). $[\alpha]_D^{23}$ −86.7 (*c* 1.15, $CHCl_3$) for 68% ee. ^{1}H NMR ($CDCl_3$): δ 1.43–1.57 (m, 1H), 1.64–1.81 (m, 2H), 1.92–2.01 (m, 1H), 2.17–2.31 (m, 1H), 2.39–2.49 (m, 2H), 4.56 (br s, 1H), 4.70 (d, 1H, J=9.2 Hz), 7.26–7.35 (m, 5H). *syn*-Isomer—TLC: R_f 0.36 (hex/EtOAc=3/1, stained red with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.63–1.86 (m, 2H), 1.95–2.06 (m, 2H), 2.09–2.19 (m, 1H), 2.32–2.37 (m, 1H), 2.45–2.49 (m, 1H), 3.19 (s, 1H), 5.29 (br s, 1H), 7.24–7.29 (m, 5H). HPLC: t_R 14.6 min (*syn*-minor, (2*S*,1′*S*)-isomer), 17.2 min (*syn*-major, (2*R*,1′*R*)-isomer), 20.4 min (*anti*-major, (2*S*,1′*R*)-isomer), 23.1 min (*anti*-minor, (2*R*,1′*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=9/1) (lit.[33]: t_R 8.8 min (*syn*-minor, (2*S*,1′*S*)-isomer), 10.6 min (*syn*-major, (2*R*,1′*R*)-isomer), 12.9 min (*anti*-major, (2*S*,1′*R*)-isomer), 15.3 min (*anti*-minor, (2*R*,1′*S*)-isomer) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=9/1).

4.1.35. 1-Hydroxy-2-methyl-1-phenyl-3-pentanone (6ca).[33] Diastereomeric mixture (*syn*/*anti*=15/85)—TLC: R_f 0.37 (hex/EtOAc=3/1, stained gray with phosphomolybdic acid/EtOH). ^{1}H NMR ($CDCl_3$): δ 0.89 (d, 2.55H, J=7.2 Hz), 0.96 (t, 0.45H, J=7.2 Hz), 1.03 (t, 2.55H, J=7.1 Hz), 1.08 (d, 0.45H, J=7.2 Hz), 2.26–2.61 (m, 2H), 2.74–2.85 (m, 1H), 2.93 (m, 0.85H), 3.11 (d, 0.15H, J=2.4 Hz), 4.76 (d, 0.85H, J=8.1 Hz), 5.07 (d, 0.15H, J=3.9 Hz), 7.27–7.39 (m, 5H). HPLC: t_R 15.7 min (*syn*-major), 18.4 min (*anti*-major), 20.9 min (*syn*-minor), 32.3 min (*anti*-minor) (Daicel Chiralpak AS-H, flow rate: 1.0 mL/min, hex/IPA=30/1).

4.1.36. 1,3-Diphenyl-3-hydroxy-2-methylpropan-1-one (6da).[6b] Diastereomeric mixture (*syn*/*anti*=81/19)—TLC: R_f 0.47 (hex/EtOAc=3/1, stained purple with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.07 (d, 0.6H, J=7.2 Hz), 1.20 (d, 2.4H, J=7.2 Hz), 2.99 (m, 0.2H), 3.66–3.74 (m, 1.6H), 3.84 (m, 0.2H), 5.00 (m, 0.2H), 5.25 (m, 0.8H). 7.25–7.61 (m, 8H), 7.92–7.99 (m, 2H). HPLC: t_R 9.5 min (*syn*-major), 11.1 min (*syn*-minor), 13.0 min (*anti*-minor), 15.2 min (*anti*-major) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=19/1).

4.1.37. 1-Hydroxy-4,4-dimethyl-1-phenyl-3-pentanone (6ea).[6d] TLC: R_f 0.44 (hex/EtOAc=3/1, stained blue with anisaldehyde). $[\alpha]_D^{22}$ +56.2 (*c* 1.02, $CHCl_3$) for 96% ee (lit.[6d]: $[\alpha]_D^{24}$ −33.9 (*c* 2.27, $CHCl_3$) for (*S*)-isomer of 52% ee). ^{1}H NMR ($CDCl_3$): δ 1.13 (s, 9H), 2.88 (d, 2H, J=6.0 Hz), 3.56 (br s, 1H), 5.14 (t, 1H, J=6.0 Hz), 7.25–7.38 (m, 5H). HPLC: t_R 10.7 min (major, (*R*)-isomer), 12.6 min (minor, (*S*)-isomer) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=19/1).

4.1.38. 2-[(*E*)-1-Hydroxy-3-phenyl-2-propenyl]cyclohexanone (6ab).[16h] *anti*-Isomer—TLC: R_f 0.19 (hex/EtOAc=3/1, stained violet with anisaldehyde). $[\alpha]_D^{23}$ −17.6 (*c* 0.72, $CHCl_3$) for 78% ee (lit.[16h]: $[\alpha]_D^{29}$ −18.3 (*c* 1.0, $CHCl_3$) for (2*S*,1′*R*)-isomer of 89% ee). ^{1}H NMR ($CDCl_3$): δ 1.28–1.91 (m, 4H), 2.08–2.14 (m, 2H), 2.34–2.52 (m, 3H), 3.67 (br s, 1H), 4.43 (t, 1H, *J*=7.5 Hz), 6.19 (dd, 1H, *J*=7.5, 15.9 Hz), 6.61 (d, 1H, *J*=15.9 Hz), 7.23–7.40, (m, 5H). *syn*-Isomer—TLC: R_f 0.24 (hex/EtOAc=3/1, stained violet with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.25–1.93 (m, 5H), 2.06–2.10 (m, 1H), 2.35–2.59 (m, 3H), 2.94 (br s, 1H), 4.77 (m, 1H), 6.21 (dd, 1H, *J*=5.7, 15.6 Hz), 6.63 (dd, 1H, *J*=1.1, 15.6 Hz), 7.20–7.39 (m, 5H). HPLC: t_R 36.8 min (*syn*-major), 45.0 min (*syn*-minor), 49.9 min (*anti*-major, (2*S*,1′*R*)-isomer), 59.6 min (*anti*-minor, (2*R*,1′*S*)-isomer) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=40/1).

4.1.39. 2-(1-Hydroxy-3-phenylpropyl)cyclohexanone (6ac).[16h] Diastereomeric mixture (*syn*/*anti*=15/85)—TLC: R_f 0.33 (hex/EtOAc=3/1, stained purple with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.49–1.92 (m, 6H), 2.06–2.12 (m, 2H), 2.25–2.42 (m, 3H), 2.64–2.93 (m, 2.15H), 3.55 (br s, 0.85H), 3.72–3.78 (0.85H), 4.05–4.13 (m, 0.15H), 7.14–7.34 (m, 5H). HPLC: t_R 59.9 min (*anti*-major), 64.5 min (*syn*-major), 71.0 min (*anti*-minor), 81.7 min (*syn*-minor) (Daicel Chiralcel OD-H and Chiralpak AD, flow rate: 0.5 mL/min, hex/IPA=30/1).

4.1.40. 2-[(1-Naphthyl)hydroxymethyl]cyclohexanone (6ag).[16h] *anti*-Isomer—TLC: R_f 0.25 (hex/EtOAc=3/1, stained red with anisaldehyde). $[\alpha]_D^{23}$ +5.7 (*c* 1.02, $CHCl_3$) for 51% ee (lit.[16h]: $[\alpha]_D^{28}$ +7.1 (*c* 1.0, $CHCl_3$) for (2*S*,1′*R*)-isomer of 90% ee). ^{1}H NMR ($CDCl_3$): δ 1.24–1.75 (m, 5H), 2.04–2.19 (m, 1H), 2.35–2.54 (m, 2H), 2.95–3.05 (m, 1H), 4.13 (br s, 1H), 5.58 (d, 1H, *J*=8.7 Hz), 7.45–7.58 (m, 4H), 7.78–7.89 (m, 2H), 8.25 (d, 1H, *J*=6.6 Hz). *syn*-Isomer—TLC: R_f 0.34 (hex/EtOAc=3/1, stained red with anisaldehyde). ^{1}H NMR ($CDCl_3$): δ 1.26–1.89 (m, 5H), 2.03–2.09 (m, 1H), 2.35–2.55 (m, 2H), 2.74–2.80 (m, 1H), 3.10 (br s, 1H), 6.25 (br s, 1H), 7.47–7.53 (m, 3H), 7.70 (d, 1H, *J*=7.2 Hz), 7.77–7.87 (m, 2H), 7.87–7.91 (m, 1H). HPLC: t_R 29.7 min (*syn*-minor), 41.3 min (*syn*-major), 71.9 min (*anti*-minor, (2*R*,1′*S*)-isomer), 85.6 min (*anti*-major, (2*S*,1′*R*)-isomer) (Daicel Chiralcel OD-H, flow rate: 0.5 mL/min, hex/IPA=40/1).

4.1.41. 2-[Hydroxy(mesityl)methyl]cyclohexanone (6ai). *anti*-Isomer—TLC: R_f 0.41 (hex/EtOAc=2/1, stained violet with anisaldehyde). $[\alpha]_D^{28}$ −40.8 (*c* 1.21, EtOH) for 74% ee. IR ($CHCl_3$): 1690 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20–1.25 (m, 1H), 1.53–1.76 (m, 4H), 2.04–2.11 (m, 1H), 2.24 (s, 3H), 2.40 (s, 6H), 2.33–2.52 (m, 2H), 3.02–3.07 (m, 1H), 3.55 (br s, 1H), 5.42 (d, 1H, *J*=9.7 Hz), 6.81 (s, 2H). ^{13}C NMR ($CDCl_3$): δ 20.7, 21.0, 25.1, 27.8, 30.4, 42.6, 55.1, 69.8, 130.1, 132.9, 136.8, 136.9, 215.6. MS (EI): *m*/*z* 98, 149, 228, 246 (M^+). HRMS: calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1608. HPLC: t_R 12.9 min (*syn*-major), 15.0 min (*syn*-minor), 17.5 min (*anti*-major), 20.9 min (*anti*-minor) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=49/1).

4.1.42. 2-[Hydroxy(4-methoxyphenyl)methyl]cyclohexanone (6ae).[16h] *anti*-Isomer—TLC: R_f 0.19 (hex/EtOAc=3/1, stained purple with anisaldehyde). $[\alpha]_D^{26}$ +15.2 (*c* 1.23, $CHCl_3$) for 77% ee. ^{1}H NMR ($CDCl_3$): δ 1.26–1.81 (m, 5H), 2.05–2.11 (m, 1H), 2.34–2.64 (m, 3H), 3.80 (s, 3H), 3.92 (br s, 1H), 4.74 (d, 1H, *J*=8.8 Hz), 6.86 (d, 2H, *J*=8.7 Hz), 7.24 (d, 2H, *J*=8.7 Hz). *syn*-Isomer—TLC: R_f 0.32 (hex/EtOAc=3/1, stained purple with anisaldehyde). $[\alpha]_D^{26}$ +90.1 (*c* 0.52, $CHCl_3$) for 87% ee. ^{1}H NMR ($CDCl_3$): δ 1.49–1.88 (m, 5H), 2.10 (m, 1H), 2.35–2.44 (m, 2H), 2.53–2.60 (m, 1H), 2.98 (br s, 1H), 3.80 (s, 3H), 5.32 (s, 1H), 6.87 (d, 2H, *J*=8.8 Hz), 7.22 (d, 2H, *J*=8.8 Hz). HPLC: t_R 41.6 min (*syn*-major), 48.6 min (*syn*-minor), 77.0 min (*anti*-minor), 79.8 (*anti*-major) (Daicel Chiralpak AD-H, flow rate: 0.5 mL/min, hex/IPA=19/1).

4.1.43. 2-[Hydroxy(*p*-tolyl)methyl]cyclohexanone (6am). *anti*-Isomer—TLC: R_f 0.35 (hex/EtOAc=2/1, stained violet with anisaldehyde). $[\alpha]_D^{23}$ +17.0 (*c* 0.41, $CHCl_3$) for 83% ee. Mp: 62.5–64.0 °C. IR ($CHCl_3$): 1694 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.28–1.37 (m, 1H), 1.54–1.82 (m, 4H), 2.07–2.13 (m, 1H), 2.32–2.52 (m, 2H), 2.36 (s, 3H), 2.59–2.67 (m, 1H), 3.91 (br s, 1H), 4.78 (dd, 1H, *J*=2.0, 8.6 Hz), 7.17 (d, 2H, *J*=7.9 Hz), 7.23 (d, 2H, *J*=7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 21.2, 24.7, 27.8, 30.9, 42.7, 57.4, 74.5, 126.9, 129.0, 137.5, 138.0, 215.6. MS (EI): *m*/*z* 98, 119, 121, 232 (M^+). HRMS: calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1306. *syn*-Isomer—TLC: R_f 0.46 (hex/EtOAc=2/1, stained violet with anisaldehyde). $[\alpha]_D^{25}$ +47.8 (*c* 0.11, $CHCl_3$) for 70% ee. Mp: 99.0–100.5 °C. IR ($CHCl_3$): 1691 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.21–1.38 (m, 1H), 1.41–1.80 (m, 4H), 1.98–2.04 (m, 1H), 2.31 (s, 3H), 2.24–2.54 (m, 3H), 2.89 (br s, 1H), 5.28 (s, 1H), 7.06 (d, 2H, *J*=7.8 Hz), 7.11 (d, 2H, *J*=7.8 Hz). ^{13}C NMR ($CDCl_3$): δ 21.1, 24.9, 26.1, 28.0, 42.6, 57.2, 70.6, 125.7, 128.8, 136.5, 138.5, 214.8. MS (EI): *m*/*z* 98, 121, 232 (M^+). HRMS: calcd for $C_{14}H_{18}O_2$ 218.1307, found 218.1313. HPLC: t_R 21.6 min (*syn*-minor), 24.0 min (*syn*-major), 25.4 min (*anti*-major), 31.5 min (*anti*-minor) (Daicel Chiralpak AS-H, flow rate: 0.5 mL/min, hex/IPA=9/1).

4.1.44. 2-[4-Bromophenyl(hydroxy)methyl]cyclohexanone (6an).[16h] *anti*-Isomer—TLC: R_f 0.30 (hex/EtOAc=2/1, stained red with anisaldehyde). $[\alpha]_D^{29}$ +21.0 (*c* 1.02, $CHCl_3$) for 89% ee (lit.[16h]: $[\alpha]_D$ +20.5 (*c* 1.7, $CHCl_3$) for (2*S*,1′*R*)-isomer of >99% ee.). ^{1}H NMR ($CDCl_3$): δ 1.25–1.36 (m, 1H), 1.51–1.82 (m. 4H), 2.04–2.12 (m 1H), 2.29–2.59 (m, 3H), 3.97 (d, 1H, *J*=2.6 Hz), 4.74 (dd, 1H, *J*=1.8, 8.6 Hz), 7.18 (d, 2H, *J*=8.3 Hz), 7.47 (d, 2H, *J*=8.3 Hz). *syn*-Isomer: TLC: R_f 0.35 (hex/EtOAc=2/1, stained red with anisaldehyde). $[\alpha]_D^{29}$ +46.5 (*c* 0.27, $CHCl_3$) for 60% ee. ^{1}H NMR ($CDCl_3$): δ 1.26–2.58 (m, 9H), 3.04 (br s, 1H), 5.34 (s, 1H), 7.17 (d, 2H, *J*=8.3 Hz), 7.49 (d, 2H, *J*=8.3 Hz). HPLC: t_R 10.6 min (*syn*-major), 12.6 min (*syn*-minor), 17.0 min (*anti*-minor), 19.9 min (*anti*-major) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=9/1).

4.1.45. 2-{Hydroxy[(4-trifluoromethyl)phenyl]methyl}cyclohexanone (6ao).[34] *anti*-Isomer—TLC: R_f 0.33 (hex/EtOAc=2/1, stained red with anisaldehyde). $[\alpha]_D^{25}$ +21.7 (*c* 0.84, $CHCl_3$) for 93% ee. IR ($CHCl_3$): 1691 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.25–1.83 (m, 5H), 2.07–2.12 (m, 1H), 2.30–2.64 (m, 3H), 4.05 (d, 1H, *J*=2.6 Hz), 4.85 (dd, 1H, *J*=2.6, 8.4 Hz), 7.44 (d, 2H, *J*=7.9 Hz), 7.60 (d, 2H, *J*=7.9 Hz). ^{13}C NMR ($CDCl_3$): δ 24.7, 27.7, 30.7, 42.6, 57.2, 74.2, 124.1 (q, *J*=272 Hz), 125.2 (q, *J*=4 Hz), 127.3,

129.9 (q, J=32.0 Hz), 145.0, 215.0. MS (EI): m/z 98, 127, 145, 254, 272 (M^+). HRMS: calcd for $C_{14}H_{15}O_2F_3$ 272.1024, found 272.1003. *syn*-Isomer—TLC: R_f 0.40 (hex/EtOAc=2/1, stained red with anisaldehyde). $[\alpha]_D^{23}$ +44.0 (c 0.26, $CHCl_3$) for 62% ee. IR ($CHCl_3$): 1694 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.49–1.84 (m, 5H), 2.01–2.11 (m, 1H), 2.38–2.58 (m, 3H), 3.10 (d, 1H, J=3.1 Hz), 5.44 (s, 1H), 7.42 (d, 2H, J=8.5 Hz), 7.60 (d, 2H, J=8.5 Hz). ^{13}C NMR ($CDCl_3$): δ 24.8, 24.9, 27.9, 42.7, 57.0, 70.2, 124.1 (q, J=271 Hz), 125.2 (q, J=4 Hz), 126.0, 129.2 (q, J=32 Hz), 145.0, 214.2. MS (EI): m/z 98, 145, 254, 272 (M^+). HRMS: calcd for $C_{14}H_{15}O_2F_3$ 272.1024, found 272.1018. HPLC: t_R 8.7 min (*syn*-major), 10.0 min (*syn*-major), 12.8 min (*anti*-minor), 15.7 min (*anti*-major) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=9/1).

4.1.46. 2-[Hydroxy(4-nitrophenyl)methyl]cyclohexanone (6ap).[35] *anti*-Isomer—TLC: R_f 0.13 (hex/EtOAc=3/1, stained red with anisaldehyde). $[\alpha]_D^{26}$ +10.6 (c 0.90, $CHCl_3$) for 96% ee (lit.[35]: $[\alpha]_D$ +12.8 (c 1.1, $CHCl_3$) for (2*S*,1′*R*)-isomer of 99% ee). ^1H NMR ($CDCl_3$): δ 1.34–1.84 (m, 5H), 2.07–2.13 (m, 1H), 2.24–2.68 (m, 3H), 4.08 (br s, 1H), 4.89 (dd, 1H, J=2.2, 8.3 Hz), 7.49 (d, 2H, J=8.6 Hz), 8.20 (d, 2H, J=8.6 Hz). *syn*-Isomer—TLC: R_f 0.18 (hex/EtOAc=3/1, stained red with anisaldehyde). ^1H NMR ($CDCl_3$): δ 1.28–1.89 (m, 5H), 2.08–2.16 (m, 1H), 2.43–2.69 (m, 3H), 3.17 (m, 1H), 5.49 (d, 1H, J=0.4 Hz), 7.48 (d, 2H, J=8.8 Hz), 8.21 (d, 2H, J=8.8 Hz). HPLC: t_R 11.8 min (*syn*-major), 12.3 min (*syn*-minor), 13.0 min (*anti*-minor), 17.0 min (*anti*-major) (Daicel Chiralpak AD-H, flow rate: 1.0 mL/min, hex/IPA=4/1).

4.1.47. Synthesis of 3,3-dimethoxy-2-pentyl-1-phenyl-1-propanol (8).[23] A solution of benzaldehyde (**3a**) in CH_2Cl_2 (0.378 M, 1.0 mL, 0.378 mmol, 1.0 equiv) and a solution of diisopropylethylamine in CH_2Cl_2 (0.904 M, 0.5 mL, 0.452 mmol, 1.2 equiv) were added to a solution of the (*S*)-**1** (24.6 mg, 0.038 mmol, 10 mol %) in CH_2Cl_2 (2 mL) at −78 °C. A solution of (*E*)-1-trichlorosilyloxy-1-heptene in CH_2Cl_2 (0.904 M, 0.5 mL, 0.452 mmol, 1.2 equiv) was slowly added to the mixture. After being stirred for 1 h, MeOH (5 mL) was added and the reaction mixture was stirred for 45 min. The reaction mixture was allowed to warm to rt, then poured into cold (0 °C) satd $NaHCO_3$ (5 mL) and was stirred for 2 h. The precipitate was filtered through Celite and washed with CH_2Cl_2. The organic phase was separated and the aqueous phase was extracted with CH_2Cl_2 (3×10 mL). The combined organic phases were washed with brine, dried over Na_2SO_4, and concentrated. The crude material was purified by column chromatography (SiO_2, 8 g, hex/EtOAc=8/1) to give the acetal as a diastereomeric mixture. TLC: R_f 0.47 (hex/EtOAc=3/1, stained red with anisaldehyde). ^1H NMR ($CDCl_3$): δ 5.16 (*syn*-isomer, t, 1H, J=2.6 Hz), 4.78 (*anti*-isomer, m, 1H). HPLC: t_R 11.4 min (*syn*-minor), 13.7 min (*anti*-minor), 17.4 min (*anti*-major), 23.3 min (*syn*-major) (Daicel Chiralcel OD-H, flow rate: 1.0 mL/min, hex/IPA=100/1).

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References and notes

1. (a) List, B. *Synlett* **2001**, 1675; (b) O'Brien, P. *J. Chem. Soc., Perkin Trans. 1* **1998**, 1439; (c) Berrisford, D. J.; Horkan, C.; Isherwood, M. L. *Organic Synthetic Highlights III*; Mulzer, H., Waldmann, H., Eds.; Wiley-VCH: Weinheim, 1998; pp 3–7; (d) Eames, J. *Eur. J. Org. Chem.* **2002**, 393.
2. (a) Denmark, S. E.; Fu, J. *Chem. Rev.* **2003**, *103*, 2763; (b) Rendler, S.; Oestreich, M. *Synthesis* **2005**, 1727; (c) Orito, Y.; Nakajima, M. *Synthesis* **2006**, 1391.
3. Other types of Lewis base-catalyzed reactions: France, S.; Guerin, D. J.; Miller, S. J.; Lectka, T. *Chem. Rev.* **2003**, *103*, 2985.
4. (a) Denmark, S. E.; Coe, D. M.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **1994**, *59*, 6161; (b) Denmark, S. E.; Fu, J.; Lawler, M. J. *J. Org. Chem.* **2006**, *71*, 1513; (c) Denmark, S. E.; Fu, J.; Coe, D. M.; Su, X.; Pratt, N. E.; Griedel, B. D. *J. Org. Chem.* **2006**, *71*, 1523.
5. (a) Iseki, K.; Kuroki, Y.; Takahashi, M.; Kobayashi, Y. *Tetrahedron Lett.* **1996**, *37*, 5149; (b) Iseki, K.; Kuroki, Y.; Takahashi, M.; Kishimoto, S.; Kobayashi, Y. *Tetrahedron* **1997**, *53*, 3513.
6. (a) Denmark, S. E.; Winter, S. B. D.; Su, X.; Wong, K.-T. *J. Am. Chem. Soc.* **1996**, *118*, 7404; (b) Denmark, S. E.; Wong, K.-T.; Stavenger, R. A. *J. Am. Chem. Soc.* **1997**, *119*, 2333; (c) Denmark, S. E.; Stavenger, R. A.; Wong, K.-T. *Tetrahedron* **1998**, *54*, 10389; (d) Denmark, S. E.; Stavenger, R. A.; Wong, K.-T. *J. Org. Chem.* **1998**, *63*, 918; (e) Denmark, S. E.; Stavenger, R. A.; Winter, S. B. D.; Wong, K.-T.; Barsanti, P. A. *J. Org. Chem.* **1998**, *63*, 9517; (f) Denmark, S. E.; Su, X.; Nishigaichi, Y. *J. Am. Chem. Soc.* **1998**, *120*, 12990; (g) Denmark, S. E.; Stavenger, R. A.; Wong, K.-T.; Su, X. *J. Am. Chem. Soc.* **1999**, *121*, 4982; (h) Denmark, S. E.; Stavenger, R. A. *J. Am. Chem. Soc.* **2000**, *122*, 8837.
7. (a) Nakajima, M.; Saito, M.; Shiro, M.; Hashimoto, S. *J. Am. Chem. Soc.* **1998**, *120*, 6419; (b) Nakajima, M.; Saito, M.; Hashimoto, S. *Tetrahedron: Asymmetry* **2002**, *13*, 2449; (c) Nakajima, M.; Yokota, T.; Saito, M.; Hashimoto, S. *Tetrahedron Lett.* **2004**, *45*, 61.
8. (a) Liu, B.; Feng, X.; Chen, F.; Zhang, G.; Cui, X.; Jiang, Y. *Synlett* **2001**, 1551; (b) Denmark, S. E.; Fan, Y. *J. Am. Chem. Soc.* **2002**, *124*, 4233; (c) Malkov, A. V.; Orsini, M.; Pernazza, D.; Muir, K. W.; Langer, V.; Maghani, P.; Kočovský, P. *Org. Lett.* **2002**, *4*, 1047; (d) Shimada, T.; Kina, A.; Ikeda, S.; Hayashi, T. *Org. Lett.* **2002**, *4*, 2799; (e) Malkov, A. V.; Dufkova, L.; Farrugia, L.; Kočovský, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 3674; (f) Traverse, J. F.; Zhao, Y.; Hoveyda, A. H.; Snapper, M. L. *Org. Lett.* **2005**, *7*, 3151.
9. (a) Massa, A.; Malkov, A. V.; Kočovský, P.; Scettri, A. *Tetrahedron Lett.* **2003**, *44*, 7179; (b) Kobayashi, S.; Ogawa, C.; Konishi, H.; Sugiura, M. *J. Am. Chem. Soc.* **2003**, *125*, 6610.
10. (a) Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron Lett.* **1998**, *39*, 2767; (b) Iseki, K.; Mizuno, S.; Kuroki, Y.; Kobayashi, Y. *Tetrahedron* **1999**, *55*, 977.
11. Dipole moment of triphenylphosphine oxide is 4.31 D and pK_a of its conjugate acid is −2.1. (a) Smyth, C. P. *J. Am. Chem. Soc.*

1938, *60*, 183; (b) Hadzi, D.; Klofutar, C.; Oblak, S. *J. Chem. Soc. A* **1968**, *48*, 905.
12. (a) Sakurai, H. *Synlett* **1989**, 1; (b) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.
13. Sugiura, M.; Kobayashi, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 6491.
14. Reviews for catalytic asymmetric allylations: (a) Roush, W. R. *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Heathcock, C. H., Eds.; Pergamon: Oxford, UK, 1991; Vol. 2, p 1; (b) Yamamoto, Y.; Asao, N. *Chem. Rev.* **1993**, *93*, 2207; (c) Marshall, J. A. *Chem. Rev.* **1996**, *96*, 31; (d) Cozzi, P. G.; Tagliavini, E.; Umani-Ronchi, A. *Gazz. Chim. Ital.* **1997**, *127*, 247.
15. Reviews for catalytic asymmetric aldol reactions with silyl enol ethers or ketene silyl acetals: (a) Nelson, S. G. *Tetrahedron: Asymmetry* **1998**, *9*, 357; (b) Gröger, H.; Vogl, E. M.; Shibasaki, M. *Chem.—Eur. J.* **1998**, *4*, 1137; (c) Mahrwald, R. *Chem. Rev.* **1999**, *99*, 1095; (d) Carreira, E. M. *Comprehensive Asymmetric Catalysis*; Jacobsen, E. N., Pfaltz, A., Yamamoto, H., Eds.; Springer: Heidelberg, Germany, 1999; Vol. 3, p 997; (e) Arya, P.; Qin, H. *Tetrahedron* **2000**, *56*, 917; (f) Machajewski, T. D.; Wong, C.-H. *Angew. Chem., Int. Ed.* **2000**, *39*, 1352.
16. Other recent examples of enantioselective aldol reactions: (a) Sasai, H.; Suzuki, T.; Arai, S.; Arai, T.; Shibasaki, M. *J. Am. Chem. Soc.* **1992**, *114*, 4418; (b) Sodeoka, M.; Ohrai, K.; Shibasaki, M. *J. Org. Chem.* **1995**, *60*, 2648; (c) Yanagisawa, A.; Matsumoto, Y.; Nakashima, H.; Asakawa, K.; Yamamoto, H. *J. Am. Chem. Soc.* **1997**, *119*, 9319; (d) Yamada, Y. M. A.; Yoshikawa, N.; Sasai, H.; Shibasaki, M. *Angew. Chem., Int. Ed.* **1997**, *36*, 1871; (e) Kuwano, R.; Miyazaki, H.; Ito, Y. *Chem. Commun.* **1998**, 71; (f) List, B.; Lerner, R. A.; Barbas, C. F., III. *J. Am. Chem. Soc.* **2000**, *122*, 2395; (g) Trost, B. M.; Ito, H. *J. Am. Chem. Soc.* **2000**, *122*, 12003; (h) Wadamoto, M.; Ozasa, N.; Yanagisawa, A.; Yamamoto, H. *J. Org. Chem.* **2003**, *68*, 5593; (i) Northrup, A. B.; MacMillan, D. W. C. *J. Am. Chem. Soc.* **2002**, *124*, 6798; (j) Evans, D. A.; Downey, C. W.; Hubbs, J. L. *J. Am. Chem. Soc.* **2003**, *125*, 8706; (k) Nakajima, M.; Orito, Y.; Ishizuka, T.; Hashimoto, S. *Org. Lett.* **2004**, *6*, 3763.
17. (a) Kobayashi, S.; Nishio, K. *Tetrahedron Lett.* **1993**, *34*, 3453; (b) Kobayashi, S.; Nishio, K. *J. Org. Chem.* **1994**, *59*, 6620.
18. Another example of BINAPO-catalyzed asymmetric reaction: Tokuoka, E.; Kotani, S.; Matsunaga, H.; Ishizuka, T.; Hashimoto, S.; Nakajima, M. *Tetrahedron: Asymmetry* **2005**, *16*, 2391.
19. Reviews for organocatalyst: (a) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2001**, *40*, 3726; (b) Benaglia, M.; Puglisi, A.; Cozzi, F. *Chem. Rev.* **2003**, *103*, 3401; (c) Dalko, P. I.; Moisan, L. *Angew. Chem., Int. Ed.* **2004**, *43*, 5138; (d) Special Issue: Asymmetric Organocatalysis, *Acc. Chem. Res.* **2004**, *37*, 487.
20. As a communication: Nakajima, M.; Kotani, S.; Ishizuka, T.; Hashimoto, S. *Tetrahedron Lett.* **2005**, *46*, 157.
21. Short, J. D.; Attenoux, S.; Berrisford, D. J. *Tetrahedron Lett.* **1997**, *38*, 2351.
22. As a communication: Kotani, S.; Hashimoto, S.; Nakajima, M. *Synlett* **2006**, 1116.
23. Denmark, S. E.; Ghosh, S. K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4759.
24. Shimada, T.; Kurushima, H.; Cho, Y.-H.; Hayashi, T. *J. Org. Chem.* **2001**, *66*, 8854.
25. Kira, M.; Hino, T.; Sakurai, H. *Tetrahedron Lett.* **1989**, *30*, 1099.
26. Furuya, N.; Sukawa, T. *J. Organomet. Chem.* **1975**, *96*, C1.
27. Minowa, N.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 3697.
28. Roush, W. R.; Ando, K.; Powers, D. B.; Palkowiz, A. D.; Halterman, R. L. *J. Am. Chem. Soc.* **1990**, *112*, 6339.
29. Manabe, S. *Chem. Commun.* **1997**, 737.
30. Kumagai, T.; Itsuno, S. *Tetrahedron: Asymmetry* **2001**, *12*, 2509.
31. Motoyama, Y.; Nishiyama, H. *Synlett* **2003**, 1883.
32. Denmark, S. E.; Pham, S. M. *J. Org. Chem.* **2003**, *68*, 5045.
33. Ishihara, K.; Kondo, S.; Yamamoto, H. *J. Org. Chem.* **2000**, *65*, 9125.
34. Majewski, M.; Gleave, D. M. *Tetrahedron Lett.* **1989**, *30*, 5681.
35. Córdova, A.; Zou, W.; Ibrahem, I.; Reyes, E.; Engqvist, M.; Liao, W.-W. *Chem. Commun.* **2005**, 3586.