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Asymmetric β-boration of α,β-unsaturated carbonyl compounds with chiral Rh[bis(oxazolinyl)phenyl] catalysts

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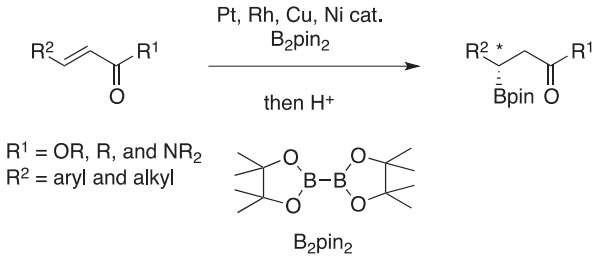
ABSTRACT

Chiral rhodium[bis(oxazolinyl)phenyl] complexes exhibited high catalytic activity for the β-boration of α,β-unsaturated esters, ketones, and amides with bis(pinacolato)diboron in the presence of sodium *tert*-butoxide to attain high enantioselectivity of up to 97%. The substrate scope and catalytic mechanism were discussed.

1. Introduction

Organoboronic acid derivatives have been examined as important precursors for organic transformation.[1] Especially, diborons can catalytically add to alkenes and alkynes via metal–boryl intermediates to provide a variety of useful functionalized compounds.[2] In 1993, Suzuki and Miyaura disclosed that addition of diborons to alkenes and alkynes can efficiently be promoted by Pt catalysts.[3] In the case of α,β-unsaturated carbonyl compounds, the conjugate boration can also be catalyzed by Pt,[4] Rh,[5] Cu,[6] Ni,[7a,b] and Pd[7b] catalysts to produce the corresponding β-boryl carbonyl derivatives (Scheme 1).



Scheme 1. Asymmetric catalytic β-boration of α,β-unsaturated carbonyl compounds.

In 2008, Yun et al. reported the asymmetric β-boration of α,β-unsaturated nitriles and esters using a copper-chiral ferrocenylphosphine catalyst and bis(pinacolato)diboron (B_2pin_2) to obtain 94% ee and 91% ee with cinnamonitriles and cinnamates, respectively.[8a] Yun et al. then extended the asymmetric boration to α,β-unsaturated ketones, amides, and cyclic carbonyl compounds as substrates including synthesis of functionalized chiral tertiary carbon skeletons.[8b–e] In 2009, Pérez and Fernández demonstrated that chiral Cu(*N*-hetereocarbene, NHC) catalysts showed activity for the boration of α,β-unsaturated esters and aldehydes, and Fernández and Guiry et al. reported the activity of copper catalysts with axially chiral P–N ligands.[9a,b] Hoveyda et al. also developed Cu–NHC catalyst for conjugate boration to attain construction of boron-substituted quaternary carbons in high enantioselectivity.[10] Mazet et al. also attained copper catalyzed β-boration of β,β-disubstituted cyclic enones with excellent ees.[11] Kanai and Shibasaki demonstrated enantioselective conjugate boration toward β,β-disubstituted enones with chiral secondary diamine–copper catalyst to attain 99% ee.[12] The copper catalyzed conjugate boration was applied to substrates of α,β-unsaturated sulfones.[13]

In 2009, Hoveyda et al. developed excellent non-asymmetric metal-free chiral NHC catalysis for conjugate boration of cyclic and acyclic enones.[14] Then they also attained asymmetric version of the metal-free catalysis.[15] In 2010, Gulyás and Fernández succeeded metal-free catalytic boration with chiral phosphines as organocatalysts to attain 90% ee,[16] and Bo, Gulyás, and Fernández found activation of the boration with Brønsted bases and alcohols.[17] Thus, attention has been focused on metal-free organocatalysts for the conjugate boration.

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In 2011, Whiting, Gulyás, and Fernández reported copper-catalyzed boration of α,β-unsaturated imines leading to synthesis of γ-aminoalcohols.[18] In 2011, Santos et al. reported sp^2–sp^3 diboron reagent applied to copper catalyzed conjugate boration.[19] In 2012, Zhao, Marder, and Lin reported DFT studies on platinum–diimine complex catalyzing conjugate boration.[20] Thus catalytic conjugate boration has been extensively studied as potent methods of growing interest for organic synthesis. It is also of importance that the corresponding borated compounds can readily be converted into optically active secondary alcohols by oxidation.

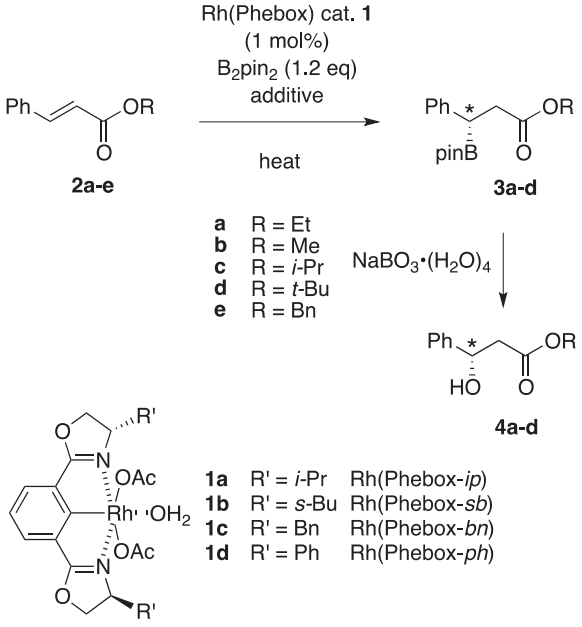
We have so far demonstrated highly enantioselective conjugate reductions using rhodium[bis(oxazolinyl)phenyl] catalysts, Rh(Phebox) in the presence of hydrosilanes.[21] Previously, we have preliminarily reported an asymmetric β-boration of α,β-unsaturated carbonyl compounds promoted by Rh(Phebox).[22] The reaction is the first example of chiral rhodium-catalyzed boration with high enantioselectivity. Comparing to the boration with copper or nickel catalysts,[7,8] which are accelerated by addition of protic solvent, such as methanol, the reaction with Rh(Phebox) directly produces rhodium enolate species giving β-boryl compounds after hydrolysis. Thus, Rh(Phebox) catalysts include important aspect from the view points of organic reaction. We here wish to report the efficient asymmetric β-boration of α,β-unsaturated compounds with our rhodium catalysts and to show scope and limitations.[22]

2. Results and discussion

2.1. Asymmetric boration of cinnamates

We examined the boration of ethyl (*E*)-cinnamate **2a** (0.5 mmol) with bis(pinacolato)diboron (B_2pin_2) (1.2 equiv) and Rh(Phebox) **1** (1.0 mol %) in a toluene solution (Table 1). The boration at 60 °C with the catalyst **1a** formed β-borated dihydrocinnamate **3a** in a low yield (entry 1). The boration at 80 °C gave **3a** in 64% with 94% ee (entry 2). Furthermore, addition of NaO*t*-Bu (5 mol %) accelerated the boration to improve the yield up to 92% with 93% ee even

Table 1
Asymmetric β-boration of cinnamates with chiral Rh(Phebox) catalysts[a]

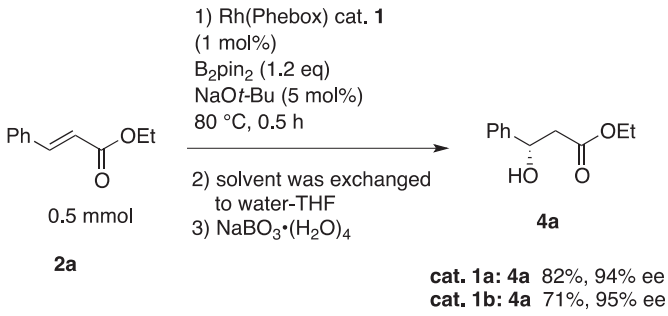


Entry	2	Cat.	Additive	Temp (°C)	Time (h)	Yield of 3 (%)		ee of 4 (%)	
1	**2a**	**1a**	—	60	12	**3a**	Trace	**4a**	—
2	**2a**	**1a**	—	80	12	**3a**	64	**4a**	94
3	**2a**	**1a**	NaO*t*-Bu	60	2.0	**3a**	92	**4a**	93
4	**2a**	**1a**	NaO*t*-Bu	80	0.5	**3a**	92 (84)[b]	**4a**	93 (95)[b]
5	**2a**	**1a**	KO*t*-Bu	80	0.5	**3a**	85	**4a**	95
6	**2a**	**1a**	NaOMe	80	1.0	**3a**	90	**4a**	93
7[c]	**2a**	**1a**	K_2CO_3	80	2.5	**3a**	83	**4a**	94
8[c]	**2a**	**1a**	Cs_2CO_3	80	1.5	**3a**	82	**4a**	95
9	**2a**	**1b**	NaO*t*-Bu	80	0.5	**3a**	86	**4a**	97
10[d]	**2a**	**1b**	NaO*t*-Bu	80	0.5	**3a**	86	**4a**	91
11	**2a**	**1c**	NaO*t*-Bu	80	0.5	**3a**	70	**4a**	58
12	**2a**	**1d**	NaO*t*-Bu	80	0.5	**3a**	58	**4a**	73
13	**2b**	**1a**	NaO*t*-Bu	80	1.0	**3b**	80	**4b**	92
14	**2b**	**1b**	NaO*t*-Bu	80	1.0	**3b**	87	**4b**	95
15	**2c**	**1a**	NaO*t*-Bu	80	0.5	**3c**	74	**4c**	92
16	**2c**	**1b**	NaO*t*-Bu	80	0.5	**3c**	78	**4c**	92
17	**2d**	**1a**	NaO*t*-Bu	80	0.5	**3d**	73	**4d**	88
18	**2d**	**1b**	NaO*t*-Bu	80	0.5	**3d**	82	**4d**	83
19	**2e**	**1a**	NaO*t*-Bu	80	0.5	**3e**	89	**4e**	91
20	**2e**	**1b**	NaO*t*-Bu	80	0.5	**3e**	83	**4e**	90

[a] The ester **2** (0.50 mmol), cat. **1** (0.005 mmol, 1.0 mol %), diboron (0.60 mmol), additive (0.025 mmol), toluene (1.0 mL).
[b] Ref. 22.
[c] Additive (0.05 mmol).
[d] The ester (1.0 mmol), cat. **1** (0.001 mmol, 0.10 mol %), NaO*t*-Bu (0.005 mmol), diboron (1.2 mmol), toluene (5.0 mL).

at 60 °C, and the reaction at 80 °C also gave 93% ee (entries 3 and 4). The enantioselectivity was measured after oxidative conversion of the product to the corresponding β-hydroxy dihydrocinnamate **4a**. Other bases as activating agents, such as KO*t*-Bu, NaOMe, K_2CO_3, and Cs_2CO_3 were examined at 80 °C to show almost similar results in yields and ees (entries 5–8). Thus, the reaction was not strongly affected by bases. Secondary butyl catalyst **1b** resulted in 97% ee (entry 9). It is noteworthy that the catalyst charge of 0.1 mol % could promote the reaction in 86% and the ee of 91% (entry 10). Benzyl catalyst **1c** and phenyl catalyst **1d** afforded the middle range of ees (entries 11 and 12). The reaction of methyl ester **2b** resulted 92–95% ees with the catalysts **1a** and **1b**, respectively (entries 13 and 14). The ees of **4b** were almost the same as those with the ethyl ester **4a**. Isopropyl and benzyl esters (**2c** and **2e**) gave high ees around 90%, respectively (entries 15, 16, 19, and 20). Bulky *tert*-butyl ester **2d** decreased ees to 83–88 % (entries 17 and 18).

We examined sequential method of the boration and oxidation in order to obtain the optically active β-hydroxy dihydrocinnamate **4a**. After the catalytic boration, the solvent was removed under reduced pressure. Then, water, THF and sodium peroxoborate were added into the mixture, which was stirred at room temperature to give **4a** in good total yields and ee up to 95% (Scheme 2).



Scheme 2. Sequential procedure to optically active β-hydroxy dihydrocinnamates.

2.2. Substrate scope and limitations

Other substrates of α,β-unsaturated esters were next examined with the catalyst **1a** and **1b** under the conditions similar to those of entries 4 and 9 in Table 1 (Table 2). Substituted ethyl cinnamates **2f**–**l** were subjected to the boration giving higher ees in the range of 92 up to 97% with **1b**. The substrate with an electron-withdrawing group **2h** (*p*-CF_3) decreased the yield to 75%.[23] 1- and 2-Naphthyl acrylates **2m** and **2n** were also borated in 69% and 62% yields, respectively, with good to excellent ees. (*Z*)-Cinnamate *Z*-**2a** was also readily borated to give adduct with the same absolute configuration *S* in 93% ee. It was thought that quick isomerization from *Z*-ester to *E*-ester occurred. On the basis of ^{1}H NMR experiment, the isomerization was confirmed in 50% within ca. 1 min at 80 °C; *Z*-**2a** (0.25 mmol), toluene-d_8 (0.5 mL), **1b** (1 mol %), B_2pin_2 (0.3 mmol), NaO*t*-Bu (5 mol %), in an NMR tube; without NaO*t*-Bu, the isomerization took place in ca. 30% for 5 min at 80 °C. Alkyl substituted acrylate **2o** was smoothly borated to give the adduct **3o** in 90% yield and 86–90% ee. It is interesting in that the *Z*-isomer of **2o** gave the reverse absolute configuration in 62% ee. The isomerization of *Z* to *E* of **2o** may be slow. Benzyl crotonate **2p** was also converted to the boryl ester **3p** in 82–84% ee.

The catalytic boration of several α,β-unsaturated ketones was examined (Table 3). Comparing to the boration of the esters, the unsaturated ketones **5a**–**f** were borated in moderate yields (64–89%) at 80 °C for 2 h with 1 mol % of the catalyst. The enantioselectivity were up to 85%. The reaction of phenyl propenyl ketone **5f** resulted in a low ee, 12%.

Table 2
Asymmetric β-boration of α,β-unsaturated esters with chiral Rh(Phebox) catalysts[a]

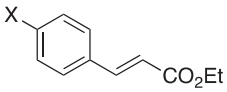
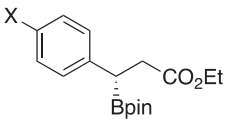
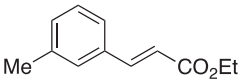
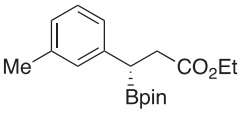
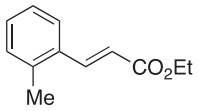
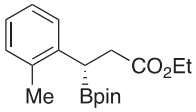
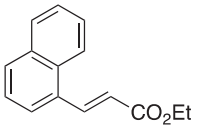
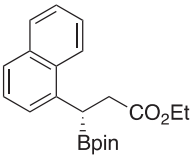
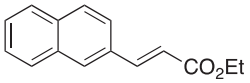
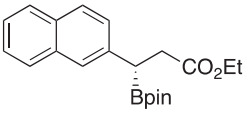
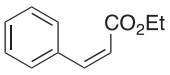
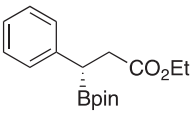
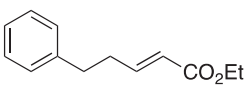
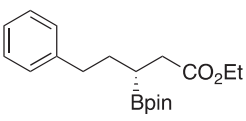
Substrate	Product	
		
2f X = MeO	**3f** X = MeO	**1a**: 91%, 83% ee **1b**: 89%, 94% ee
2g X = Me	**3g** X = Me	**1b**: 89%, 96% ee
2h X = CF_3	**3h** X = CF_3	**1b**: 75%, 92% ee
2i X = Cl	**3i** X = Cl	**1b**: 86%, 93% ee
2j X = *t*-Bu	**3j** X = *t*-Bu	**1b**: 95%, 97% ee
		
2k	**3k**	**1b**: 72%, 97% ee
		
2l	**3l**	**1b**: 75%, 92% ee
		
2m	**3m**	**1b**: 69%, 86% ee
		
2n	**3n**	**1b**: 62%, 84% ee
		
***Z*-2a**	**3a**	**1a**: 77%, 93% ee
		
2o	**3o**	**1a**: 90%, 86% ee **1b**: 90%, 90% ee

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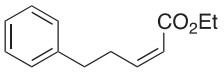
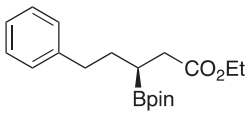
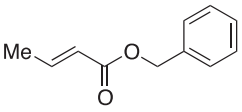
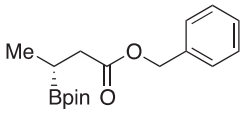
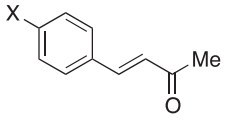
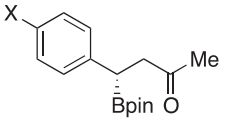
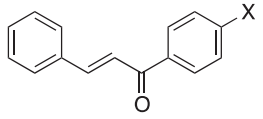
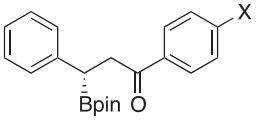
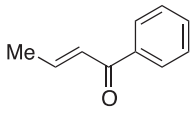
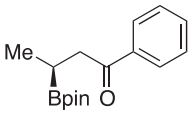
Table 2 (*continued*)

	
***Z*-2o**	**3o** **1b**: 91%, 62% ee
	
2p	**3p** **1a**: 88%, 82% ee **1b**: 87%, 84% ee

[a] The ester **2** (0.50 mmol), cat. **1** (0.005 mmol, 1.0 mol%), diboron (0.60 mmol), NaO*t*-Bu (0.025 mmol), toluene (1.0 mL). 80 °C, 0.5 h. Ees were determined by HPLC with chiral column of the corresponding β-hydroxy esters after oxidation of the borated product with $NaBO_3•(H_2O)_4$ in THF-H_2O. For **2g**, 3.0 mol% of **1b** was used.

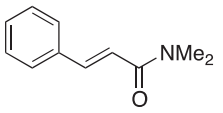
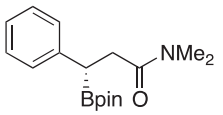
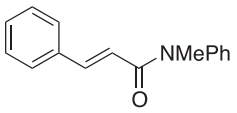
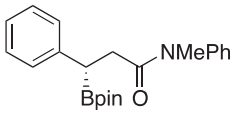
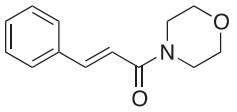
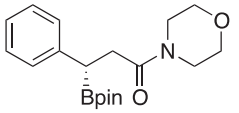
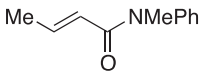
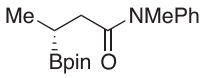
Table 3
Asymmetric β-boration of α,β-unsaturated ketones with chiral Rh(Phebox) catalysts[a]

Substrate	Product	
		
5a X = H	**6a** X = H	**1a**: 82%, 56% ee **1b**: 75%, 56% ee
5b X = MeO	**6b** X = MeO	**1a**: 89%, 70% ee **1b**: 84%, 57% ee
		
5c	**6c** X = H **6d** X = MeO **6e** X = CF_3	**1b**: 82%, 76% ee **1b**: 87%, 61% ee **1b**: 64%, 85% ee
		
5f	**6f**	**1b**: 73%, 12% ee

[a] The ketone **5** (0.50 mmol), cat. **1** (0.005 mmol, 1.0 mol%), diboron (0.60 mmol), NaO*t*-Bu (0.025 mmol), toluene (1.0 mL). 80 °C, 2.0 h. Ees were determined by HPLC with chiral column of the corresponding β-hydroxy ketones after oxidation of the borated product with $NaBO_3•(H_2O)_4$ in THF- H_2O.

Next, the catalytic boration of *N*,*N*-disubstituted α,β-unsaturated amides **7** were examined (Table 4). The boration of the cinnamoyl amides **7a**–**c** took place smoothly at 80 °C to give the borated products **8a**–**c** in good yields with high ees up to 97%. Crotonoyl amide **7d** was also resulted in a good ee of 93%, which was better than that of the corresponding ester **2p**. In terms of the catalytic asymmetric

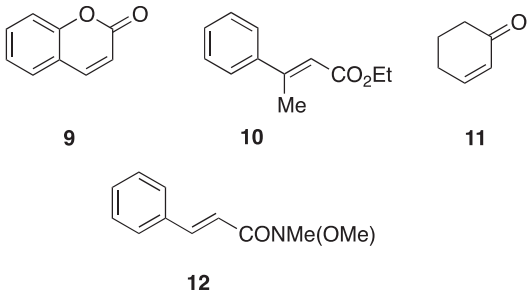
Table 4
Asymmetric β-boration of α,β-unsaturated amides with chiral Rh(Phebox) catalysts[a]

Substrate	Product
	
7a	**8a** **1a**: 70%, 97% ee **8a** **1b**: 74%, 93% ee
	
7b	**8b** **1b**: 79%, 95% ee
	
7c	**8c** **1b**: 91%, 91% ee
	
7d	**8d** **1b**: 91%, 93% ee

[a] The amide **7** (0.50 mmol), cat. **1** (0.005 mmol, 1.0 mol%), diboron (0.60 mmol), NaO*t*-Bu (0.025 mmol), toluene (1.0 mL). 80 °C, 0.5 h. Ees were determined by HPLC with chiral column of the corresponding β-hydroxy amides after oxidation of the borated product with $NaBO_3•(H_2O)_4$ in THF–H_2O.

boration of *N*-substituted or *N*,*N*-disubstituted amides, only Yun et al. reported one example for **7a** with copper/chiral phosphine catalyst to give 97% ee.[8c] As for the *N*-methoxy amide substrates, Hoveyda et al. reported ees up to 90% with NHC organocatalyst.[15]

In order to expand scope of substrates, we examined several functionalized compounds. However, the following a cyclic lactone, β,β-disubstituted acrylate, cyclic enone, and *N*-methoxy cinnamate did not react under the standard condition to be recovered.



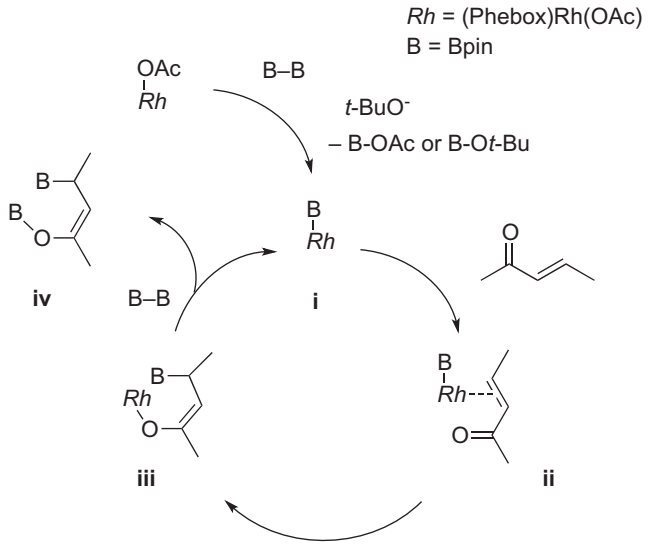
9 **10** **11**

12

2.3. Hypothetical catalytic cycle and stereoselection

In order to investigate the boration mechanism, a reaction of Rh(Phebox-*ip*) **1a** and B_2pin_2 (1.2 equiv) in a NMR tube in a toluene-d_8 solution was carried at 80 °C, in the presence and the absence of NaO*t*-Bu, respectively. However, the corresponding boryl Rh(Phebox-*ip*) species was not clearly confirmed. We think that the σ-metathesis of B–B bond and Rh–OAc bond occurs at the initial stage to form Rh–B bond. The addition of *tert*-butoxide anion can accelerate the exchange reaction. Although the evidence is still

lacked, we propose a possible catalytic cycle (Scheme 3). The Rh–boryl species (i) coordinates unsaturated carbonyl forming (ii), followed by boryl-insertion forming a Rh–enolate (iii), then the σ-metathesis to regenerate the active Rh–boryl species (i) producing the β-boryl-boryl-*O*-enolate (iv).



Scheme 3. Plausible catalytic cycle.

We also propose hypothetical transition-state structures (Fig. 1). Considering the absolute configuration of the borylated product E, the boryl group should attack the *si*-face of the cinnamate substrate. The structure A with *si*-face attack is most likely to form the major enantiomer E rather than *re*-face attack on the structure B. In the case of equatorial boryl structures C and D, although C can produce the major isomer E, both C and D cause steric repulsion between the substituent on the oxazoline skeleton and substrate.

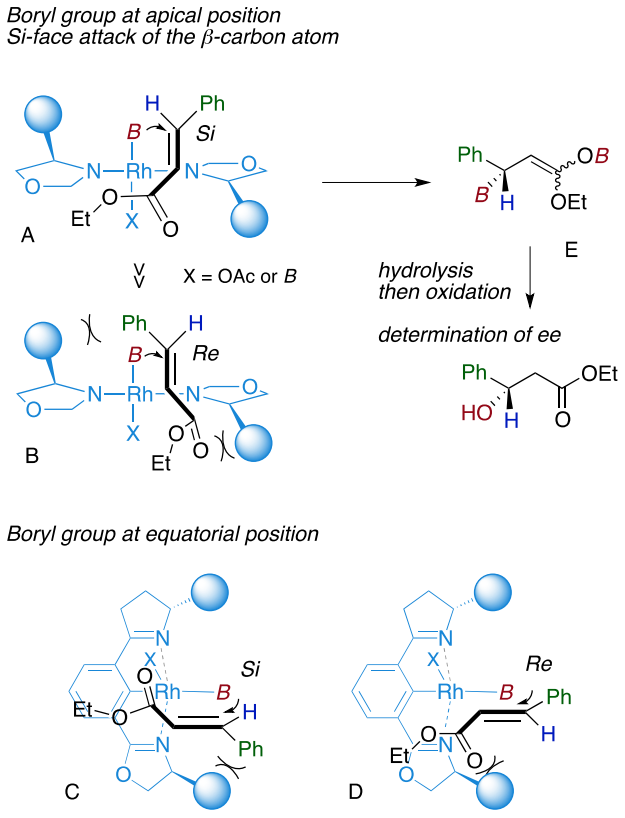


Fig. 1. Proposed transition-state model for asymmetric boration.

3. Conclusions

We have found that Rh(Phebox) complexes exhibit catalytic activity for asymmetric boration of α,β-unsaturated esters, ketones, and amides to attain high enantioselectivities up to 97%. As one-pot procedure, the boration mixture was subjected into oxidation with peroxoborate to produce the corresponding optically active β-hydroxy dihydrocinnamates in high yields and high enantioselectivity. Steric course of the boration providing the corresponding absolute configuration was also proposed.

4. Experimental section

4.1. General information

^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded on a Varian Mercury 300 spectrometer. ^{1}H and ^{13}C chemical shifts were reported in δ units, in parts per million relative to the singlet at 7.26 ppm and the triplet at 77.0 for $CDCl_3$, respectively. Infrared spectra were recorded on a JASCO FR/IR-230 spectrometer. Optical rotation was measured on a JASCO P-1020NS polarimeter. HRMS (FAB) was measured on double-focusing magnetic sector mass spectrometer, JEOL JMS-700 at Chemical Instrumentation Facility of Nagoya University. Rh(Phebox-*R*) complexes **1** were prepared by our method.[21] B_2pin_2 was purchased from Allychem Co. Ltd. (China) and was purified by crystallization from pentane according to the reported procedure.[24]

4.2. Typical procedure for asymmetric boration of (*E*)-ethyl cinnamate 2a and oxidation (Table 1, entry 9)

Rh(Phebox-*sb*) **1b** (2.8 mg, 0.0050 mmol), bis(pinacolato)-diboron (140 mg, 0.55 mmol), and NaO*t*-Bu (2.4 mg, 0.025 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, (*E*)-ethyl cinnamate **2a** (88.1 mg, 0.50 mmol) and toluene (1.0 mL) were added. The mixture was stirred at 80 °C for 0.5 h. At room temperature, the mixture was directly charged to a silica-gel column with an eluant of hexane/ethyl acetate to give the borylated product **3a** in 86% yield (131 mg, 0.43 mmol). A part of the product (ca. 0.2 mmol) was subjected to the oxidation with sodium peroxoborate (5 equiv) in THF (1 mL) and H_2O (1 mL) at room temperature for ca. 3 h to give the corresponding alcohol **4a**. The enantioselectivity was determined by chiral chromatography to give 97% ee.

For the one-pot reaction, bis(pinacolato)diboron (152 mg, 0.60 mmol) was used, and after the boration the solvent was removed under the reduced pressure. To the residue, water (1.0 mL), THF (1.0 mL), and $NaBO_3 \cdot (H_2O)_4$ (384 mg, 2.5 mmol) were added. The mixture was stirred at room temperature for 1 h, and was extracted with ethyl acetate. The crude product was purified by silica-gel column chromatography to give the corresponding alcohol **4a** in 71% yield (69.2 mg, 0.357 mmol) with 95% ee.

4.2.1. (S)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-phenylpropanoate ***3a***. Colorless oil. IR (film): ν 2978, 1731, 1371, 1323, 1141, 847, 701 cm^{-1}; ^{1}H NMR: δ_H 1.18 (s, 6H), 1.23 (s, 6H), 1.23 (t, *J* 7.2 Hz, 3H), 2.62–2.77 (m, 2H), 2.89 (dd, *J* 15.3, 9.6 Hz, 1H), 4.11 (m, 2H), 7.11–7.31 (m, 5H) ppm; ^{13}C NMR: δ_C 14.4, 24.6, 24.7, 28.2 (CB, broad), 37.4, 60.4, 83.5, 125.4, 128.0, 128.2, 141.1, 173.0; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 304.1840; calcd ($C_{17}H_{25}O_4B$): 304.1849; $[\alpha]_D^{27}$ +20.7 (*c* 1.07, $CHCl_3$), corresponding to 93% ee of **4a** from (*Z*)-cinnamate.

4.2.2. (S)-Ethyl 3-hydroxy-3-phenylpropanoate ***4a***. Colorless oil. IR (film): ν 3471 (broad), 2982, 1730, 1195, 1037, 760 cm^{-1}; ^{1}H NMR: δ_H

1.27 (t, *J* 7.2 Hz, 3H), 2.88 (m, 2H), 3.30 (d, *J* 3.3 Hz, 1H), 4.19 (q, *J* 7.2 Hz, 2H), 5.14 (m, 1H), 7.22–7.42 (m, 5H) ppm; ^{13}C NMR: δ_C 14.3, 43.4, 60.9, 70.3, 125.5, 127.6, 128.3, 142.2, 172.1. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 15.2 min (major), 18.3 min (minor), 97% ee (*S*); HRMS (FAB): [M+H$^+$] *m*/*z*, found: 195.1029; calcd ($C_{11}H_{15}O_3$): 195.1021; $[\alpha]_D^{26}$ −46.5 (*c* 1.04, $CHCl_3$), 97% ee determined by chiral LC; from (*Z*)-cinnamate: $[\alpha]_D^{25}$ −43.6 (*c* 1.0, $CHCl_3$), 93% ee determined by chiral LC; lit.,[8a] $[\alpha]_D^{28}$ −45.8 (*c* 0.25, $CHCl_3$), 90% ee (*S*); lit.,[25] $[\alpha]_D$ −52 (*c* 1, $CHCl_3$).

4.2.3. (S)-Methyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3b***. Colorless oil. IR (film): *ν* 2978, 1737, 1371, 1323, 1141, 846, 701 cm^{-1}; ^{1}H NMR: δ_H 1.18 (s, 6H), 1.23 (s, 6H), 2.63–2.80 (m, 2H), 2.90 (m, 1H), 3.66 (s, 3H), 7.13–7.30 (m, 5H) ppm; ^{13}C NMR: δ_C 24.6, 24.7, 25.2, 37.2, 51.6, 83.5, 125.5, 127.9, 128.3, 141.0, 173.4; *C*[B] was not detected; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 290.1701; calcd ($C_{16}H_{23}O_4B$): 290.1689; $[\alpha]_D^{16}$ +18.2 (*c* 1.25, $CHCl_3$), 95% ee of the corresponding alcohol.

4.2.4. (S)-Methyl 3-hydroxy-3-phenylpropanoate ***4b***. Colorless oil. IR (film): *ν* 3456, 1730, 1438, 1200, 762, 701 cm^{-1}; ^{1}H NMR: δ_H 2.67–2.81 (m, 2H), 3.21 (br, 1H), 3.73 (s, 3H), 5.15 (m, 1H), 7.26–7.40 (m, 5H) ppm; ^{13}C NMR: δ_C 43.2, 52.0, 70.3, 125.5, 127.7, 128.4, 142.2, 172.4. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 23.0 min (major), 36.4 min (minor), 95% ee (*S*); HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 203.0681; calcd ($C_{10}H_{12}O_3Na$): 203.0684; $[\alpha]_D^{16}$ −52.9 (*c* 1.00, $CHCl_3$), 95% ee determined by chiral LC; lit.,[26] $[\alpha]_D^{rt}$ −51.3 (*c* 1.3, $CHCl_3$), 93% ee for *S*.

4.2.5. (S)-Isopropyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3c***. Colorless oil. IR (film): *ν* 2979, 1725, 1371, 1139, 970, 768, 706 cm^{-1}; ^{1}H NMR: δ_H 1.18 (s, 6H), 1.19 (d, *J* 6.3 Hz, 6H), 1.28 (s, 6H), 2.62 (dd, *J* 5.7, 15.3 Hz, 1H), 2.73 (dd, *J* 5.7, 9.6 Hz, 1H), 2.85 (dd, *J* 9.6, 15.3 Hz, 1H), 4.98 (m, 1H), 7.15–7.30 (m, 5H) ppm; ^{13}C NMR: δ_C 22.2, 24.8, 24.9, 67.8, 83.6, 125.5, 128.2, 128.4, 141.3, 172.8; *C*[B] was not detected; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 319.2085; calcd ($C_{18}H_{28}O_4B$): 319.2084; $[\alpha]_D^{24}$ +18.2 (*c* 1.04, $CHCl_3$), 92% ee of the corresponding alcohol.

4.2.6. (S)-Isopropyl 3-hydroxy-3-phenylpropanoate ***4c***. Colorless oil. IR (film): *ν* 3060 (broad), 1729, 1107 cm^{-1}; ^{1}H NMR: δ_H 1.24 (d, *J* 6.0 Hz, 3H), 1.25 (d, *J* 6.3 Hz, 3H), 2.62-2.80 (m, 2H), 3.40 (br, 1H), 5.06 (m, 1H, C*H*(CH_3)$_2$), 5.12 (m, 1H, *CH*OH), 7.23–7.43 (m, 5H) ppm; ^{13}C NMR: δ_C 22.3, 44.0, 68.8, 70.1, 125.9, 127.9, 128.7, 142.6, 172.0. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (97:3, 0.5 mL/min), retention time: 23.1 min (minor), 24.8 min (major), 92% ee; absolute configuration was tentatively assigned to *S*, as analogy of the ethyl ester; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 209.1179; calcd ($C_{12}H_{17}O_3$): 209.1178; $[\alpha]_D^{24}$ −39.6 (*c* 0.94, $CHCl_3$), 93% ee determined by chiral LC; lit.,[27] $[\alpha]_D^{20}$ +39.4 (*c* 1.1, $CHCl_3$) for *R*.

4.2.7. (S)-tert-Butyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3d***. Colorless oil. IR (film): *ν* 2977, 1728, 1369, 1140, 846, 701 cm^{-1}; ^{1}H NMR: δ_H 1.17 (s, 6H), 1.23 (s, 6H), 1.41 (s, 9H), 2.60 (dd, *J* 5.5, 15.0 Hz, 1H), 2.68 (dd, *J* 5.5, 9.9 Hz, 1H), 2.80 (dd, *J* 9.9, 15.0 Hz, 1H), 7.05–7.30 (m, 5H) ppm; ^{13}C NMR: δ_C 24.8, 24.9, 28.4, 38.6, 80.2, 83.5, 125.4, 128.2, 128.3, 141.3, 172.6; *C*[B] was not detected; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 333.2244; calcd ($C_{19}H_{30}O_4B$): 333.2241; $[\alpha]_D^{24}$ +13.2 (*c* 1.59, $CHCl_3$), 74% ee of the corresponding alcohol.

4.2.8. (S)-tert-Butyl 3-hydroxy-3-phenylpropanoate ***4d***. Colorless oil. IR (film): *ν* 3443 (broad), 1730, 1368, 1149 cm^{-1}; ^{1}H NMR: δ_H 1.46 (s, 9H), 2.60–2.74 (m, 2H), 3.45 (d, *J* 3.3 Hz, 1H), 5.09 (ddd, *J* 3.3, 4.5, 7.8 Hz, 1H, O*H*), 7.26–7.42 (m, 5H) ppm; ^{13}C NMR: δ_C 28.4, 44.5, 70.5, 81.7, 125.7, 127.6, 128.4, 142.5, 171.7. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (99:1, 0.5 mL/min), retention time: 20.3 min (minor), 21.1 min (major), 88% ee. HRMS (FAB): [M+H$^+$] *m*/*z*, found: 223.1337; calcd ($C_{13}H_{19}O_3$): 223.1334; $[\alpha]_D^{24}$ −37.7 (*c* 1.2, $CHCl_3$), 85% ee in Scheme 3, determined by chiral LC; lit.,[28] $[\alpha]_D^{23}$ −10.5 (*c* 2.4, $CHCl_3$) for *S*, 42% ee.

4.2.9. (S)-Benzyl 3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3e***. Colorless oil. IR (film): *ν* 1734 cm^{-1}; ^{1}H NMR: δ_H 1.15 (s, 6H), 1.20 (s, 6H), 2.70–3.03 (m, 3H), 5.05 (d, *J* 12.3 Hz, 1H), 5.13 (d, *J* 12.3 Hz, 1H), 7.10–7.40 (m, 10H) ppm; ^{13}C NMR: δ_C 25.0, 25.1, 25.7, 37.8, 66.5, 83.9, 125.9, 128.2, 128.3, 128.4, 128.6, 128.7, 136.2, 142.3, 173.2; *C*[B] was not detected; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 367.2072; calcd ($C_{22}H_{27}O_4B$): 367.2081. $[\alpha]_D^{26}$ +19.7 (*c* 1.01, $CHCl_3$), corresponding to 91% ee.

4.2.10. (S)-Benzyl 3-hydroxy-3-phenylpropanoate ***4e***. Colorless oil. IR (film): *ν* 3464, 1732, 1158 cm^{-1}; ^{1}H NMR: δ_H 2.70–2.90 (m, 2H), 3.19 (s, 1H), 5.18 (m, 2H), 7.20–7.50 (m, 10H) ppm; ^{13}C NMR: δ_C 43.4, 66.7, 70.3, 125.5, 127.6, 128.2, 128.4, 131.1, 135.2, 142.1, 154.9, 171.8. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 21.6 min (major), 26.5 min (minor), 91% ee; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 279.0991; calcd ($C_{16}H_{16}O_3Na$): 279.0997; $[\alpha]_D^{26}$ −34.82 (*c* 1.12, $CHCl_3$), 91% ee; lit.,[29] $[\alpha]_D^{25}$ +28.6 (*c* 1.8, CH_2Cl_2) for *R*, 99% ee.

4.2.11. (S)-Ethyl 3-(4-methoxyphenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3f***. Colorless oil. IR (film): *ν* 2981, 1731, 1369, 1249, 1033, 840 cm^{-1}; ^{1}H NMR: δ_H 1.18 (s, 6H), 1.23 (s, 6H), 1.23 (t, *J* 7.2 Hz, 3H), 2,58–2.73 (m, 2H), 2.80–2.90 (m, 1H), 3.77 (s, 3H), 4.10 (m, 2H), 6.81 (m, 2H), 7.14 (m, 2H) ppm; ^{13}C NMR: δ_C 14.5, 24.7, 24.8, 37.8, 55.2, 60.4, 83.4, 113.7, 128.9, 133.1, 157.3, 173.1; *C*[B] was not observed; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 334.1943; calcd ($C_{18}H_{27}O_5B$): 334.1955; $[\alpha]_D^{26}$ +31.5 (*c* 1.0, $CHCl_3$), 94% ee of the corresponding alcohol. *(S)-Ethyl 3-hydroxy-3-(4-methoxyphenyl)propanoate*: colorless oil. IR (film): *ν* 3475 (broad), 2980, 1728, 1610, 1511, 1248, 1173, 1032, 838 cm^{-1}; ^{1}H NMR: δ_H 1.26 (t, *J* 7.2 Hz, 3H), 2.60–2.80 (m, 2H), 3.80 (s, 3H), 4.17 (q, *J* 7.2 Hz, 2H), 5.08 (m, 1H), 6.87 (m, 2H), 7.28 (m, 2H); ^{13}C NMR: δ_C 14.3, 42.4, 55.3, 60.8, 69.9, 113.7, 126.7, 134.5, 158.8, 172.0. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 14.7 min (minor), 18.4 min (major), 94% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 247.0944; calcd ($C_{12}H_{16}O_4Na$): 247.0946; $[\alpha]_D^{26}$ −28.6 (*c* 1.0, $CHCl_3$), 94% ee by chiral LC; lit.,[30] $[\alpha]_D$ +34 (*c* 2.0, $CHCl_3$), 86% ee for *R*.

4.2.12. (S)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(p-tolyl)propanoate ***3g***. Colorless oil. IR (film): *ν* 1732 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.28 (m, 15H), 2.30 (s, 3H), 2.61–2.72 (m, 2H), 2.82–2.90 (m, 1H), 4.08–4.13 (m, 2H), 7.06 (d, *J* 8.4 Hz, 2H), 7.11 (d, *J* 7.8 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.5, 21.2, 24.7, 24.8, 25.2, 37.6, 60.4, 83.4, 127.9, 129.0, 134.8, 138.0, 173.1; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 318.2008; calcd ($C_{18}H_{27}O_4B$): 318.2066; $[\alpha]_D^{30}$ +24.6 (*c* 1.20, $CHCl_3$), 96% ee of the corresponding alcohol. *(S)-Ethyl 3-hydroxy-3-(p-tolyl)propanoate*: colorless oil. IR (film): *ν* 3466, 1728 cm^{-1}; ^{1}H NMR: δ_H 1.28 (t, *J* 7.2 Hz, 3H), 2.35 (s, 3H), 2.71–2.75 (m, 2H), 4.19 (q, *J* 7.2 Hz, 2H), 5.11 (dd, *J* 8.7, 3.9 Hz, 1H), 7.16 (d, *J* 8.4 Hz, 2H), 7.27 (d, *J* 8.4 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.4, 21.3, 43.4, 60.9, 70.2, 125.4, 129.0, 137.3, 139.3, 172.1; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 231.1002; calcd ($C_{12}H_{16}O_3Na$): 231.0997. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 10.7 min (minor), 11.3 min (major), 96% ee; $[\alpha]_D^{29}$ −47.3 (*c* 1.00, $CHCl_3$), 96% ee, determined by chiral LC; lit.,[31] $[\alpha]_D^{25}$ −44.6 (*c* 1.2, $CHCl_3$), 98% ee for *S*.

4.2.13. (S)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(4-(trifluoromethyl)phenyl)propanoate ***3h***. White solids, mp 41–43 °C. IR (film): *ν* 1731 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.27 (m, 15H),

2.63–2.91 (m, 3H), 4.08–4.14 (m, 2H), 7.32 (d, *J* 8.4 Hz, 2H), 7.51 (d, *J* 8.7 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.4, 24.7, 24.7, 25.2, 37.0, 60.6, 83.5, 83.8, 125.1, 125.1, 125.2, 125.2, 126.0, 128.2, 145.4, 173.6; HRMS (FAB): [M+H$^+$] *m/z*, found: 373.1799; calcd ($C_{18}H_{24}O_4BF_3$): 373.1798; $[\alpha]_D^{28}$ +10.8 (*c* 1.07, $CHCl_3$), 92% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-*hydroxy*-3-(4-(*trifluoromethyl*)*phenyl*)*propanoate*: colorless oil. IR (film): ν 3430, 1729 cm^{-1}; ^{1}H NMR: δ_H 1.28 (t, *J* 7.2 Hz, 3H), 2.73 (d, *J* 6.9 Hz, 2H), 4.20 (q, *J* 7.2 Hz, 2H), 5.19 (br, 1H), 7.51 (d, *J* 8.1 Hz, 2H), 7.62 (d, *J* 8.1 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.3, 43.2, 61.2, 69.7, 125.2, 125.3, 125.3, 125.4, 125.8, 146.1, 171.8; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 285.0714; calcd ($C_{12}H_{13}O_3F_3$): 285.0714. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (98:2, 1.0 mL/min), retention time: 14.5 min (minor), 15.1 min (major), 92% ee; $[\alpha]_D^{20}$ −37.8 (*c* 1.20, $CHCl_3$), 92% ee; absolute configuration was tentatively assigned to *S*, as analogy of **4a**.

4.2.14. (S)-Ethyl 3-(4-chlorophenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3i***. Colorless oil. IR (film): ν 1724 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.28 (m, 15H), 2.59–2.74 (m, 2H), 2.80–2.88 (m, 1H), 4.06–4.15 (m, 2H), 7.14 (dt, *J* 9.0, 2.1 Hz, 2H), 7.22 (dt, *J* 9.0, 2.1 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.4, 24.7, 24.7, 25.2, 37.3, 60.5, 83.6, 128.3, 129.3, 139.7, 172.8; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 338.1465; calcd ($C_{17}H_{24}O_4BCl$): 338.1456; $[\alpha]_D^{30}$ +19.5 (*c* 1.12, $CHCl_3$), 93% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-(4-*chlorophenyl*)-3-*hydroxypropanoate*: colorless oil. IR (film): ν 3460, 1728 cm^{-1}; ^{1}H NMR: δ_H 1.27 (t, *J* 7.2 Hz, 3H), 2.70 (dd, *J* 7.8, 2.7 Hz, 2H), 4.19 (q, *J* 6.9 Hz, 2H), 5.11 (dd, *J* 7.5, 5.4 Hz, 1H), 7.32 (s, 4H) ppm; ^{13}C NMR: δ_C 14.4, 43.3, 61.1, 69.6, 85.4, 126.9, 128.5, 140.7, 171.9; HRMS (FAB): [M+Na$^+$] *m/z*, found: 251.0449; calcd ($C_{11}H_{13}O_3ClNa$): 251.0451. Chromatography: DAICEL CHIRALPAK AD-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 17.2 min (major), 18.9 min (minor), 93% ee; $[\alpha]_D^{32}$ −35.5 (*c* 1.18, $CHCl_3$), 93% ee; lit.,[31] $[\alpha]_D^{25}$ −43.7 (*c* 1.38, $CHCl_3$), 99% ee for *S*.

4.2.15. (S)-Ethyl 3-(4-(tert-butyl)phenyl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3j***. Colorless oil. IR (film): ν 1732 cm^{-1}; ^{1}H NMR: δ_H 1.19–1.29 (m, 24H), 2.61–2.73 (m, 2H), 2.82–2.90 (m, 1H), 4.08–4.14 (m, 2H), 7.13 (d, *J* 8.4 Hz, 2H), 7.26 (d, *J* 8.4 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.5, 24.7, 24.8, 25.2, 31.5, 34.4, 37.7, 60.4, 83.4, 125.2, 127.6, 137.8, 148.0, 173.2; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 360.2462; calcd ($C_{21}H_{33}O_4B$): 360.2472; $[\alpha]_D^{20}$ +23.4 (*c* 0.85, $CHCl_3$), 97% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-(4-(*tert-butyl*)*phenyl*)-3-*hydroxypropanoate*: colorless oil. IR (film): ν 3471, 1729 cm^{-1}; ^{1}H NMR: δ_H 1.25–1.33 (m, 12H), 2.67–2.83 (m, 2H), 3.17 (d, *J* 2.7 Hz, 1H), 4.19 (q, *J* 7.2 Hz, 2H), 5.12 (dd, *J* 8.1, 5.4 Hz, 1H), 7.28 (d, *J* 9.6 Hz, 2H), 7.39 (d, *J* 9.6 Hz, 2H) ppm; ^{13}C NMR: δ_C 14.4, 31.5, 34.7, 43.3, 60.9, 70.1, 125.2, 125.3, 139.2, 150.5, 172.2; HRMS (FAB): [M+Na$^+$] *m/z*, found: 273.1464; calcd ($C_{15}H_{23}O_3Na$): 273.1467. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (98:2, 1.0 mL/min), retention time: 17.2 min (minor), 19.4 min (major), 97% ee; $[\alpha]_D^{18}$ −34.3 (*c* 1.25, $CHCl_3$), 97% ee.

4.2.16. (S)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(m-tolyl)propanoate ***3k***. Colorless oil. IR (film): ν 1732 cm^{-1}; ^{1}H NMR: δ_H 1.26–1.19 (m, 15 H), 2.31 (s, 1H), 2.60–2.73 (m, 2H), 2.84–2.92 (m, 1H), 4.06–4.20 (m, 2H), 6.95–7.03 (m, 3H), 7.15 (t, *J* 7.5 Hz, 1H) ppm; ^{13}C NMR: δ_C 14.5, 21.6, 24.68, 24.74, 37.5, 60.4, 83.5, 124.9, 126.2, 128.1, 128.9, 137.7, 141.0, 173.1; *C*[B] was not observed; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 319.2095; calcd ($C_{18}H_{27}O_4B$): 319.2081; $[\alpha]_D^{26}$ +26.7 (*c* 0.96, $CHCl_3$), 97% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-*hydroxy*-3-(*m-tolyl*)*propanoate*: colorless oil. IR (film): ν 3457, 1726, 1391 cm^{-1}; ^{1}H NMR: δ_H 1.28 (t, *J* 7.2 Hz, 3H), 2.36 (s, 3H), 2.67–2.81 (m, 2H), 4.19 (q, *J* 7.2 Hz, 2H), 5.10 (m, 1H), 7.09–7.27 (m, 4H), ppm; ^{13}C NMR: δ_C 14.4, 21.6, 43.4, 60.9, 70.3, 122.5, 126.2, 128.2, 128.3, 138.0, 142.2, 172.1. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 14.2 min (major), 18.0 min (minor), 97% ee; HRMS (FAB): [M+H$^+$] *m/z*, found: 209.1183; calcd ($C_{12}H_{17}O_3$): 209.1178; $[\alpha]_D^{28}$ −44.3 (*c* 1.08, $CHCl_3$); lit.,[32] $[\alpha]_D^{20}$ −51 (*c* 1.00, $CHCl_3$), 98% ee for *S*.

4.2.17. (S)-Ethyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-3-(o-tolyl)propanoate ***3l***. Colorless oil. IR (film): ν 1732 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.25 (m, 15 H), 2.37 (s, 3H), 2.60 (m, 1H), 2.82–2.98 (m, 2H), 4.05–4.17 (m, 2H), 7.02–7.17 (m, 4H) ppm; ^{13}C NMR: δ_C 14.5, 20.2, 24.7, 24.8, 36.9, 60.4, 83.4, 125.3, 125.8, 127.4, 130.1, 135.9, 139.6, 173.2; *C*[B] was not observed; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 319.2071; calcd ($C_{18}H_{27}O_4B$): 319.2081; $[\alpha]_D^{27}$ +20.3 (*c* 1.09, $CHCl_3$), 92% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-*hydroxy*-3-(*o-tolyl*)*propanoate*: colorless oil. IR (film): ν 1726 cm^{-1}; ^{1}H NMR: δ_H 1.30 (t, *J* 7.2 Hz, 3H), 2.36 (s, 3H), 2.63–2.76 (m, 2H), 3.19 (s, 1H), 4.21 (q, *J* 7.2 Hz, 2H), 5.36 (m, 1H), 7.13–7.27 (m, 3H), 7.50 (d, *J* 7.2 Hz, 1H) ppm; ^{13}C NMR: δ_C 14.4, 19.2, 42.2, 61.0, 67.0, 125.0, 126.2, 127.4, 130.2, 134.1, 140.2, 172.3. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 15.0 min (major), 22.0 min (minor), 92% ee; HRMS (FAB): [M+H$^+$] *m/z*, found: 209.1183; calcd ($C_{12}H_{17}O_3$): 209.1178; $[\alpha]_D^{27}$ −58.6 (*c* 1.09, $CHCl_3$); lit.,[32] $[\alpha]_D^{20}$ −87.9 (*c* 1.00, $CHCl_3$), 92% ee for *S*.

4.2.18. (S)-Ethyl 3-(naphthalen-1-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3m***. White solids, mp 79–81 °C. IR (film): ν 1727 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.25 (m, 15H), 2.78 (m, 1H), 3.04 (m, 1H), 3.51 (dd, *J* 6.0, 9.6 Hz, 1H), 4.04–4.20 (m, 2H), 7.38–7.50 (m, 4H), 7.68 (d, *J* 6.6 Hz, 1H), 7.83 (d, *J* 7.5 Hz, 1H), 8.17 (d, *J* 8.4 Hz, 1H) ppm; ^{13}C NMR: δ_C 14.4, 24.7, 24.9, 37.3, 60.4, 83.7, 123.9, 125.2, 125.4, 125.5, 126.3, 128.6, 131.7, 133.9, 137.8, 173.1; *C*[B] was not observed; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 354.2006; calcd ($C_{21}H_{27}O_4B$): 354.2002; $[\alpha]_D^{26}$ +49.8 (*c* 1.0, $CHCl_3$), 86% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-*hydroxy*-3-(*naphthalen*-1-*yl*)*propanoate*: colorless oil. IR (film): ν 3488, 1726 cm^{-1}; ^{1}H NMR: δ_H 1.31 (t, *J* 7.2 Hz, 3H), 2.90 (m, 2H), 3.41 (br, 1H), 4.24 (q, *J* 7.2 Hz, 2H), 5.93 (dd, *J* 3.0, 9.0 Hz, 1H), 7.47–7.57 (m, 3H), 7.71 (d, *J* 6.0 Hz, 1H), 7.80 (d, *J* 7.8 Hz, 1H), 7.88 (d, *J* 7.2 Hz, 1H), 8.06 (d, *J* 8.1 Hz, 1H) ppm; ^{13}C NMR: δ_C 14.4, 42.3, 61.0, 67.3, 122.6, 122.8, 125.3, 125.4, 126.1, 128.1, 128.8, 129.7, 133.5, 137.7, 172.4. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 27.5 min (major), 33.6 min (minor), 86% ee; HRMS (FAB): [M+Na$^+$] *m/z*, found: 244.1087; calcd ($C_{15}H_{16}O_3$): 244.1099; $[\alpha]_D^{25}$ −64.8 (*c* 1.08, $CHCl_3$); absolute configuration was tentatively assigned to *S*, as analogy of **4a**; see Ref. 33 for the corresponding methyl ester.

4.2.19. (S)-Ethyl 3-(naphthalen-2-yl)-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanoate ***3n***. White solids, mp 48–50 °C. IR (film): ν 1725 cm^{-1}; ^{1}H NMR: δ_H 1.18–1.28 (m, 15 H), 2.80 (m, 1H), 2.90–3.05 (m, 2H), 4.08–4.17 (m, 2H), 7.42–7.46 (m, 3H), 7.65 (s, 1H), 7.3–7.80 (m, 3H) ppm; ^{13}C NMR: δ_C 14.5, 24.7, 24.8, 37.3, 60.5, 83.6, 124.9, 125.6, 125.9, 126.9, 127.3, 127.7, 131.7, 133.3, 138.7, 173.0; *C*[B] was not observed; HRMS (FAB): [M$^{\bullet+}$] *m/z*, found: 354.2018; calcd ($C_{21}H_{27}O_4B$): 354.2002; $[\alpha]_D^{27}$ +23.4 (*c* 1.12, $CHCl_3$), 84% ee of the corresponding alcohol. (*S*)-*Ethyl* 3-*hydroxy*-3-(*naphthalen*-2-*yl*)*propanoate*: colorless oil. IR (film): ν 1728 cm^{-1}; ^{1}H NMR: δ_H 1.28 (t, *J* 7.2 Hz, 3H), 2.78–2.90 (m, 2H), 3.40 (s, 1H), 4.21 (q, *J* 7.2 Hz, 2H), 5.31 (m, 1H), 7.46–7.51 (m, 3H), 7.83–7.86 (m, 4H) ppm; ^{13}C NMR: δ_C 14.4, 43.4, 61.0, 70.4, 123.5, 124.3, 125.8, 126.0, 127.5, 127.8, 128.2, 132.8, 133.0, 139.6, 172.1. Chromatography: DAICEL CHIRALPAC AS-H, hexane/2-propanol (99:1, 0.5 mL/min), retention time: 76.6 min (minor), 83.3 min (major), 84% ee; HRMS (FAB): [M+Na$^+$] *m/z*, found: 267.1001; calcd ($C_{15}H_{16}O_3$): 267.0997; $[\alpha]_D^{25}$ −16.3 (*c* 1.01, $CHCl_3$); lit.,[30] $[\alpha]_D$ +32 (*c* 1.8, $CHCl_3$), 80% ee.

4.2.20. (R)-Ethyl 5-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pentanoate ***3o***. Colorless oil. IR (film): ν 2981, 2930, 1731, 1378, 1320, 1146 cm^{-1}; ^{1}H NMR: δ_H 1.25 (t, *J* 7.2 Hz, 3H), 1.26 (s, 6H), 1.27 (s,

6H), 1.40 (m, 1H), 1.67 (m, 1H), 1.79 (m, 1H), 2.45 (m, 2H), 2.65 (m, 2H), 4.12 (q, *J* 7.2 Hz, 2H), 7.12–7.20 (m, 3H), 7.22–7.30 (m, 2H) ppm; ^{13}C NMR: δ_C 14.5, 20.0 (*C*-B), 24.9, 25.0, 32.8, 35.2, 35.9, 60.3, 83.2, 125.5, 128.1, 128.2, 142.3, 173.5; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 333.2244; calcd ($C_{19}H_{30}O_4B$): 333.2241; $[\alpha]_D^{26}$ +3.18 (*c* 1.03, $CHCl_3$), 86% ee of the corresponding alcohol. (*R*)-*Ethyl* 3-*hydroxy*-5-*phenylpentanoate*: colorless oil. IR (film): *ν* 1726, 1186, 1034 cm^{-1}; ^{1}H NMR: δ_H 1.28 (t, *J* 6.9 Hz, 3H), 1.72–1.92 (m, 2H), 2.40–2.56 (m, 2H), 2.70 (m, 1H), 2.80 (m, 1H), 3.12 (d, *J* 4.2 Hz, 1H), 4.02 (m, 1H), 4.17 (q, *J* 6.9 Hz, 2H), 7.16–7.21 (m, 3H), 7.24–7.29 (m, 2H) ppm; ^{13}C NMR: δ_C 14.3, 31.9, 38.2, 41.4, 60.7, 67.2, 125.6, 128.1, 128.2, 141.5, 172.6. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (90:10, 1.0 mL/min), retention time: 24.7 min (minor), 29.3 min (major), 86% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 245.1148; calcd ($C_{13}H_{18}O_3Na$): 245.1154; $[\alpha]_D^{26}$ +0.58 (*c* 1.0, $CHCl_3$), 86% ee determined by chiral LC; lit.,[34] $[\alpha]_D^{25}$ +1.0 (*c* 1.0, $CHCl_3$), 99% ee for *R*. (*S*)-Alcohol from *Z*-**2o**: colorless oil; $[\alpha]_D^{18}$ −0.64 (*c* 1.03, $CHCl_3$), 62% ee.

4.2.21. (R)-Benzyl 3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanoate ***3p***. Colorless oil. IR (film): *ν* 2975, 1735, 1380, 1148 cm^{-1}; ^{1}H NMR: δ_H 1.02 (d, *J* 7.5 Hz, 3H), 1.22 (s, 6H), 1.23 (s, 6H), 1.42 (m, 1H), 2.42 (dd, *J* 6.6, 16.5 Hz, 1H), 2.51 (dd, *J* 7.8, 16.5 Hz, 1H), 5.08 (d, *J* 14.4 Hz, 1H), 5.13 (d, *J* 14.4 Hz, 1H), 7.25–7.40 (m, 5H) ppm; ^{13}C NMR: δ_C 15.3, 24.8, 24.9, 33.8 (*C*-B), 37.8, 66.0, 83.1, 127.8, 127.9, 128.2, 136.0, 173.3; FAB-HRMS: [M+H$^+$] *m*/*z*, found: 305.1938; calcd ($C_{17}H_{26}O_4B$): 305.1927; $[\alpha]_D^{27}$ −2.38 (*c* 0.99, $CHCl_3$), 82% ee of the corresponding alcohol. (*R*)-*Benzyl* 3-*hydroxybutanoate*: colorless oil. IR (film): *ν* 1729, 1382, 1290, 1172 cm^{-1}; ^{1}H NMR: δ_H 1.24 (d, *J* 6.3 Hz, 3H), 2.44–2.59 (m, 2H), 2.98 (br, 1H), 4.22 (m, 1H), 5.16 (s, 2H), 7.33–7.40 (m, 5H) ppm; ^{13}C NMR: δ_C 22.6, 42.9, 64.3, 66.5, 128.0, 128.2, 128.4, 135.3, 172.3. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (98:2, 0.5 mL/min), retention time: 39.5 min (major), 56.1 min (minor), 82% ee; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 195.1017; calcd ($C_{11}H_{15}O_3$): 195.1021; $[\alpha]_D^{27}$ −26.0 (*c* 1.0, $CHCl_3$), 82% ee; lit.,[35] $[\alpha]_D$ +29.0 (*c* 1.0, $CHCl_3$), 94% ee for *S*.

4.2.22. (S)-4-Phenyl-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butan-2-one ***6a***. Colorless oil. IR (film): *ν* 2981, 1711, 1365, 1321, 1145, 699 cm^{-1}; ^{1}H NMR: δ_H 1.17 (S, 6H), 1.23 (s, 6H), 2.15 (s, 3H), 2.64 (m, 1H), 2.84 (dd, *J* 5.1, 18.3 Hz, 1H), 3.05 (dd, *J* 11.0, 18.3 Hz, 1H), 7.10–7.30 (m, 5H) ppm; ^{13}C NMR: δ_C 24.67, 24.69, 29.8, 47.6, 83.4, 125.3, 128.0, 128.3, 141.4, 207.9; *C*[B] was not observed; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 275.1818; calcd ($C_{16}H_{24}O_3B$): 275.1822; $[\alpha]_D^{26}$ +21.1 (*c* 1.0, $CHCl_3$), 58% ee of the corresponding alcohol. (*S*)-4-*Hydroxy*-4-*phenylbutan*-2-*one*: colorless oil. IR (film): *ν* 3452 (broad), 1707, 1362, 1059, 754, 697 cm^{-1}; ^{1}H NMR: δ_H 2.21 (s, 3H), 2.80–2.90 (m, 2H), 3.29 (br s, 1H), 5.16 (m, 1H), 7.20–7.40 (m, 5H) ppm; ^{13}C NMR: δ_C 30.9, 52.0, 69.8, 125.4, 127.5, 128.3, 142.4, 208.7. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.5 mL/min), retention time: 10.8 min (minor), 12.6 min (major), 58% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 187.0742; calcd ($C_{10}H_{12}O_2Na$): 187.0735; $[\alpha]_D^{26}$ −35.6 (*c* 1.0, $CHCl_3$), 58% ee; lit.,[36] $[\alpha]_D^{20}$ −51.3 (*c* 1.0, $CHCl_3$), 79% ee for *S*.

4.2.23. (S)-4-(4-Methoxyphenyl)-4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butan-2-one ***6b***. Colorless oil. IR (film): *ν* 2981, 1710, 1364, 1249, 1145, 833 cm^{-1}; ^{1}H NMR: δ_H 1.29 (s, 6H), 1.35 (s, 6H), 2.25 (s, 3H), 2.70 (dd, *J* 5.4, 10.5 Hz, 1H), 2.92 (dd, *J* 5.4, 18.0 Hz, 1H), 3.11 (dd, *J* 10.5, 18.0 Hz, 1H), 3.89 (s, 3H), 6.92 (m, 2H), 7.24 (m, 2H) ppm; ^{13}C NMR: δ_C 24.61, 24.63, 25.8 (broad, *C*[B]), 29.7, 47.6, 55.1, 83.2, 113.7, 128.8, 133.2, 157.2, 208.0; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 304.1844; calcd ($C_{17}H_{25}O_4B$): 304.1849; $[\alpha]_D^{26}$ +23.3 (*c* 1.0, $CHCl_3$), 70% ee of the corresponding alcohol. (*S*)-4-*Hydroxy*-4-(4-*methoxyphenyl*)*butan*-2-*one*: colorless oil. IR (film): *ν* 3500 (broad), 2929, 1707, 1513, 1249, 1173, 832 cm^{-1}; ^{1}H NMR: δ_H 2.20 (s, 3H), 2.78 (dd, *J* 3.6, 17.7 Hz, 1H), 2.89 (dd, *J* 9.0, 17.7 Hz, 1H), 3.80 (s, 3H), 5.10 (m, 1H), 6.87 (m, 2H), 7.27 (m, 2H) ppm; ^{13}C NMR: δ_C 30.9, 52.0, 55.3, 69.5, 113.7, 126.7, 134.6, 158.8, 208.7. Chromatography: DAICEL CHIRALPAK AD-H, hexane/2-propanol (95:5, 1.5 mL/min), retention time: 29.4 min (minor), 31.5 min (major), 70% ee; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 194.0940; calcd ($C_{11}H_{14}O_3$): 194.0943; $[\alpha]_D^{26}$ −33.9 (*c* 1.0, $CHCl_3$), 70% ee; lit.,[37] $[\alpha]_D^{16}$ −46.3 (*c* 0.4, $CHCl_3$), 67% ee for *R*.

4.2.24. (S)-1,3-Diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one ***6c***. Yellow oil. IR (film): *ν* 1683 cm^{-1}; ^{1}H NMR: δ_H 1.18 (s, 6H), 1.27 (s, 6H), 2.81 (m, 1H), 3.43 (m, 1H), 3.58 (m, 1H), 7.18 (m, 1H), 7.25–7.35 (m, 4H), 7.40–7.50 (m, 2H), 7.54–7.60 (m, 1H), 7.98 (m, 1H) ppm; ^{13}C NMR: δ_C 24.6, 24.7, 25.1, 43.4, 83.3, 125.4, 127.8, 128.2, 128.3, 128.3, 132.7, 136.5, 141.7, 199.2, *C*[B] was not detected; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 337.1973; calcd ($C_{21}H_{25}O_3B$): 337.1979; $[\alpha]_D^{28}$ +15.7 (*c* 1.01, $CHCl_3$), 72% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-1,3-*diphenylpropan*-1-*one*: colorless oil. IR (film): *ν* 3479, 1679 cm^{-1}; ^{1}H NMR: δ_H 3.39 (d, *J* 6.0 Hz, 2H), 3.66 (d, *J* 3.0 Hz, 1H, O*H*), 5.36 (dt, *J* 6.0, 3.0 Hz, 1H), 7.28–7.50 (m, 7H), 7.59 (tt, *J* 7.5, 1.2 Hz, 1H), 7.96 (dt, *J* 8.7, 1.5 Hz, 2H) ppm; ^{13}C NMR: δ_C 47.5, 70.0, 125.5, 127.4, 127.9, 128.3, 128.5, 133.4, 136.2, 142.6, 199.7; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 249.0891; calcd ($C_{15}H_{14}O_2Na$): 249.0883. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 17.2 min (major), 21.7 min (minor), 72% ee; $[\alpha]_D^{28}$ −58.1 (*c* 1.03, $CHCl_3$), 72% ee; lit.,[8b] $[\alpha]_D^{23}$ −107.3 (*c* 0.49, $CHCl_3$), 80% ee for *S*.

4.2.25. (S)-1-(4-Methoxyphenyl)-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one ***6d***. Colorless oil. IR (film): *ν* 1671 cm^{-1}; ^{1}H NMR: δ_H 1.17 (s, 6H), 1.24 (s, 6H), 2.78 (dd, *J* 10.7, 5.4 Hz, 1H), 3.35–3.55 (m, 2H), 3.86 (s, 3H), 6.91 (dd, *J* 12.0, 3.0 Hz, 2H), 7.14–7.19 (m, 1H), 7.25–7.32 (m, 4H), 7.94 (dt, *J* 12.0, 2.1 Hz, 2H); ^{13}C NMR: δ_C 14.3, 22.8, 24.7, 25.2, 43.1, 55.5, 83.2, 113.4, 125.3, 128.2, 128.3, 129.6, 130.1. 141.8, 163.0, 197.7; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 367.2096; calcd ($C_{22}H_{28}O_4B$): 367.2081; $[\alpha]_D^{15}$ +10.3 (*c* 0.96, $CHCl_3$), 62% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-1-(4-*methoxyphenyl*)-3-*phenylpropan*-1-*one*: colorless oil. IR (film): *ν* 3518, 1658 cm^{-1}; ^{1}H NMR: δ_H 3.31–3.38 (m, 2H), 3.82 (d, *J* 2.7 Hz, 1H), 3.88 (s, 3H), 5.31–5.35 (m, 1H), 6.93 (tt, *J* 8.7, 1.8 Hz, 2H), 7.28–7.46 (m, 5H) 7.93 (tt, *J* 9.0, 2.4 Hz, 2H) ppm; ^{13}C NMR: δ_C 47.0, 55.6, 70.1, 113.7, 125.5, 127.4, 128.3, 129.3, 130.3, 142.7, 163.6, 198.3. Chromatography: DAICEL CHIRALCEL OJ, hexane/2-propanol (90:10, 1.0 mL/min), retention time: 53.8 min (minor), 60.7 min (major), 62% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 279.0992; calcd ($C_{16}H_{16}O_3Na$): 27.0997; $[\alpha]_D^{18}$ −41.78 (*c* 0.99, $CHCl_3$), 62% ee; absolute configuration was tentatively assigned to *S*, as analogy of the corresponding alcohol derived from **6c**.

4.2.26. (S)-3-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-1-(4-(trifluoromethyl)phenyl)propan-1-one ***6e***. Colorless oil. IR (film): *ν* 1683 cm^{-1}; ^{1}H NMR: δ_H 1.17 (s, 6H), 1.27 (s, 6H), 2.80 (m, 1H), 3.35–3.45 (m, 1H), 3.53–3.63 (m, 1H), 7.17 (m, 1H), 7.20–7.30 (m, 4H), 7.70 (d, *J* 8.0 Hz, 2H), 8.06 (d, *J* 8.0 Hz, 2H); ^{13}C NMR: δ_C 24.6, 24.7, 25.1, 43.6, 83.4, 125.3, 125.4, 127.5, 128.1, 128.1, 128.4, 139.0, 141.2, 198.3, *C*[F] was not observed; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 405.1849; calcd ($C_{22}H_{25}O_3BF_3$): 405.1849; $[\alpha]_D^{18}$ +17.3 (*c* 1.05, $CHCl_3$), 85% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-3-*phenyl*-1-(4-(*trifluoromethyl*)*phenyl*)*propan*-1-*one*: colorless oil. IR (film): *ν* 3500, 1707 cm^{-1}; ^{1}H NMR: δ_H 3.31–3.50 (m, 3H), 5.38 (dd, *J* 9.0, 3.0 Hz, 1H), 7.29–7.46 (m, 5H), 7.73 (d, *J* 8.7 Hz, 2H), 8.06 (d, *J* 8.1 Hz, 2H) ppm; ^{13}C NMR: δ_C 47.9, 69.9, 125.5, 125.5, 125.6, 127.7, 128.3, 128.4, 138.9, 142.4, 198.5; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 317.0765; calcd ($C_{16}H_{13}OF_3Na$): 317.0765. Chromatography: DAICEL CHIRALCEL OJ-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 35.2 min (minor), 37.0 min (major), 85% ee; $[\alpha]_D^{21}$ −48.10 (*c* 1.04, $CHCl_3$), 85%

ee; absolute configuration was tentatively assigned to *S*, as analogy of the corresponding alcohol derived from **6c**.

4.2.27. (S)-1-Phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) butan-1-one ***6f***. Colorless oil. IR (film): ν 1683 cm^{-1}; ^1H NMR: δ_H 1.17 (s, 6H) 1.23 (s, 6H), 2.15 (s, 3H), 2.62 (m, 1H), 2.82 (dd, *J* 10.8, 5.4 Hz, 1H), 3.03 (m, 1H), 7.11–7.28 (m, 5H); ^{13}C NMR: δ_C 24.67, 24.69, 24.7, 29.7, 47.6, 83.4, 125.3, 128.0, 128.3, 141.4, 207.9; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 275.1819; calcd ($C_{16}H_{23}O_3B$): 275.1810. $[\alpha]_D^{20}$ +1.42 (*c* 1.0, $CHCl_3$), 12% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-1-*phenylbutan*-1-*one*: colorless oil. IR (film): ν 3500, 1707 cm^{-1}; ^1H NMR: δ_H 1.31 (d, *J* 6.3 Hz, 3H), 2.99 (br, 1H), 3.00–3.21 (m, 2H), 4.41 (m, 1H), 7.47 (tt, *J* 7.2, 2.1 Hz, 2H) 7.58 (tt, *J* 7.5, 1.5 Hz, 1H) 7.95 (dt, *J* 8.4, 1.5 Hz, 2H) ppm; ^{13}C NMR: δ_C 22.6, 46.6, 64.0, 127.8, 128.5, 133.3, 136.4, 200.4; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 187.0740; calcd ($C_{10}H_{12}O_2$): 187.0735. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (95:5, 1.0 mL/min), retention time: 12.6 min (minor), 13.7 min (major), 12% ee; $[\alpha]_D^{20}$ +7.63 (*c* 1.03, $CHCl_3$), 12% ee.

4.3. Typical procedure for asymmetric boration of cinnamamide 7b

Rh(Phebox-*sb*) **1b** (2.8 mg, 0.0050 mmol), bis(pinacolato) diboron (152 mg, 0.60 mmol, 1.2 equiv), NaO*t*-Bu (2.4 mg, 0.025 mmol) were placed in a flask with a stirring bar. Under an argon atmosphere, the cinnamamide **7b** (113 mg, 0.50 mmol) and toluene (1.0 mL) were added. The mixture was stirred at 80 °C for 0.5 h. At room temperature, the mixture was directly charged to a silica-gel column with eluant of hexane/ethyl acetate to give the borylated product **8b** in 79% (144.3 mg, 0.395 mmol). The solution of **8b** (48.5 mg, 0.130 mmol) and $NaBO_3 \cdot (H_2O)_4$ (100 mg, 0.65 mmol) in THF (1.0 mL) and H_2O (1.0 mL) was stirred at room temperature for 3 h. The mixture was extracted with ethyl acetate (15 mL×3). After concentration of the extract, the residue was purified by silica-gel column chromatography with hexane/ethyl acetate as eluant to give the corresponding β-hydroxyamide (31.6 mg, 0.124 mmol) in 93% yield; 95% ee by chiral LC.

4.3.1. (S)-N,N-Dimethyl-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide ***8a***. White solids, mp 108–109 °C. IR (KBr): ν 2978, 1642, 1361, 1139, cm^{-1}; ^1H NMR: δ_H 1.14 (s, 12H), 2.60 (m, 1H), 2.83 (m, 1H), 2.95 (m, 1H), 2.99 (s, 3H), 3.01 (s, 3H), 7.05–7.16 (m, 5H) ppm; ^{13}C NMR: δ_C 24.8, 24.9, 30.8 (*C*-B), 36.1, 37.3, 38.2, 82.0, 124.8, 127.9, 128.1, 142.8, 174.4; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 303.2011; calcd ($C_{17}H_{26}O_3NB$): 303.2009; $[\alpha]_D^{27}$ +38.4 (*c* 1.0, $CHCl_3$), 97% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-*N*,*N*-*dimethyl*-3-*phenylpropanamide*: colorless oil. IR (film): ν 3413 (broad), 1623, 1406 cm^{-1}; ^1H NMR: δ_H 2.80–2.88 (m, 2H), 2.95 (s, 3H), 2.99 (s, 3H), 4.80 (s, 1H, O*H*), 5.14 (m, 1H, *CH*OH), 7.24–7.46 (m, 5H) ppm; ^{13}C NMR: δ_C 35.3, 37.2, 42.0, 70.4, 125.5, 127.3, 128.2, 142.7, 171.9. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (95:5, 0.5 mL/min), retention time: 44.0 min (major), 51.6 min (minor), 97% ee; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 194.1175; calcd ($C_{11}H_{16}NO_2$): 194.1181; $[\alpha]_D^{26}$ −90.5 (*c* 1.07, $CHCl_3$), 97% ee; lit.,[8c] $[\alpha]_D^{24}$ −87.9 (*c* 0.40, $CHCl_3$), 96% ee for *S*.

4.3.2. (S)-N-Methyl-N,3-diphenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propanamide ***8b***. Colorless oil. IR (KBr): ν 1651, cm^{-1}; ^1H NMR: δ_H 1.20 (s, 6H), 1.22 (s, 6H), 2.45 (m, 1H), 2.60–2.66 (m, 2H), 3.27 (s, 3H), 7.08–7.37 (m, 10H) ppm; ^{13}C NMR: δ_C 24.75, 24.80, 37.6, 38.6, 82.8, 125.0, 127.0, 127.5, 128.0, 128.1, 129.4, 142.0, 143.5, 173.0; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 365.2171; calcd ($C_{22}H_{28}O_3NB$): 365.2162; $[\alpha]_D^{26}$ +34.8 (*c* 1.02, $CHCl_3$), 95% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-*N*-*methyl*-*N*,3-*diphenylpropanamide*: white solids, mp 88–90 °C. IR (film): ν 3414, 1637 cm^{-1}; ^1H NMR: δ_H 2.44 (m, 2H), 3.28 (s, 3H), 5.06 (m, 1H), 7.04–7.07 (m, 2H), 7.20–7.40 (m, 8H) ppm; ^{13}C NMR: δ_C 37.3, 42.2, 70.7, 125.5, 126.9, 127.2, 128.0, 128.1, 129.7, 142.7, 142.9, 172.0. Chromatography: DAICEL CHIRALCEL OD-H, hexane/2-propanol (95:5, 0.5 mL/min), retention time: 48.1 min (minor), 51.9 min (major), 95% ee; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 256.1334; calcd ($C_{16}H_{18}NO_2$): 256.1338; $[\alpha]_D^{26}$ −20.0 (*c* 1.08, $CHCl_3$); absolute configuration was tentatively assigned to *S*, as analogy of the corresponding alcohol derived from **8a**.

4.3.3. (S)-1-Morpholino-3-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)propan-1-one ***8c***. White solids, mp 146–148 °C. IR (KBr): ν 2976, 1634, 1437, 1358, 1231, 776, 705 cm^{-1}; ^1H NMR: δ_H 1.17 (s, 6H), 1.20 (s, 6H), 2.67 (m, 1H), 2.75–2.90 (m, 2H), 3.40 (m, 2H), 3.50–3.70 (m, 6H), 7.17 (m, 2H), 7.20–7.30 (m, 3H) ppm; ^{13}C NMR: δ_C 24.77, 24.79, 37.5, 42.4, 45.9, 66.5, 66.8, 82.8, 125.2, 128.1, 128.2, 142.0, 171.8; HRMS (FAB): [M$^{\bullet+}$] *m*/*z*, found: 345.2115; calcd ($C_{19}H_{28}O_4NB$): 345.2111; $[\alpha]_D^{18}$ +27.5 (*c* 1.01, $CHCl_3$), 91% ee of the corresponding alcohol. (*S*)-3-*Hydroxy*-1-*morpholino*-3-*phenylpropan*-1-*one*: colorless oil. IR (film): ν 3417, 2857, 1633, 1454, 1114, 702 cm^{-1}; ^1H NMR: δ_H 2.64 (d, *J* 6.3 Hz, 2H), 3.35 (m, 2H), 3.48–3.73 (m, 6H), 4.51 (d, *J* 2.7 Hz, 1H), 5.17 (m, 1H), 7.20–7.42 (m, 5H) ppm; ^{13}C NMR: δ_C 41.7, 41.8, 45.7, 66.3, 66.6, 70.3, 125.4, 127.3, 128.2, 142.6, 170.1. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (90:10, 1.0 mL/min), retention time: 46.3 min (major), 65.9 min (minor), 91% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 258.1113; calcd ($C_{13}H_{17}NO_3Na$): 258.1106; $[\alpha]_D^{20}$ −71.3 (*c* 1.10, $CHCl_3$); absolute configuration was tentatively assigned to *S*, as analogy of the corresponding alcohol derived from **8a**.

4.3.4. (R)-N-Methyl-N-phenyl-3-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)butanamide ***8d***. Colorless oil. IR (KBr): ν 2974, 1650, 1386, 1311, 1146, 861, 701 cm^{-1}; ^1H NMR: δ_H 0.88 (d, *J* 7.2 Hz, 3H), 1.24 (br, 1H), 1.257 (s, 6H), 1.260 (s, 6H), 2.17 (br, 2H), 3.25 (s, 3H), 7.17 (m, 2H), 7.30–7.45 (m, 3H) ppm; ^{13}C NMR: δ_C 15.3, 24.9, 25.2, 37.5, 38.5, 82.6, 127.1, 127.3, 129.4, 143.9, 173.2; HRMS (FAB): [M+H$^+$] *m*/*z*, found: 304.2085; calcd ($C_{17}H_{27}O_3NB$): 304.2084; $[\alpha]_D^{21}$ +28.7 (*c* 1.2, $CHCl_3$), 93% ee of the corresponding alcohol. (*R*)-3-*Hydroxy*-*N*-*methyl*-*N*-*phenylbutanamide*: Colorless oil. IR (film): ν 3435, 2969, 1644, 1496, 1391, 1124, 701 cm^{-1}; ^1H NMR: δ_H 1.07 (d, *J* 6.3 Hz, 3H), 2.09 (dd, *J* 9.0, 16.5 Hz, 1H), 2.22 (dd, *J* 3.0, 16.5 Hz, 1H), 3.28 (s, 3H), 4.11 (m, 1H), 4.38 (m, 1H, O*H*), 7.18 (m, 2H), 7.30–7.50 (m, 3H) ppm; ^{13}C NMR: δ_C 22.4, 37.2, 41.9, 64.5, 127.0, 127.9, 129.7, 143.1, 172.5. Chromatography: DAICEL CHIRALPAK AS-H, hexane/2-propanol (90:10, 0.5 mL/min), retention time: 34.7 min (major), 42.7 min (minor), 93% ee; HRMS (FAB): [M+Na$^+$] *m*/*z*, found: 216.0996; calcd ($C_{11}H_{15}NO_2Na$): 216.1000; $[\alpha]_D^{18}$ −4.6 (*c* 1.0, $CHCl_3$); absolute configuration was tentatively assigned to *R*.

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Supplementary data

^1H and ^{13}CNMR spectra of selected products and the corresponding alcohols and HPLC of the alcohols. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.02.086.

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