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Generation of Chiral Boron Enolates by Rhodium-Catalyzed Asymmetric 1,4-Addition of 9-Aryl-9-borabicyclo[3.3.1]nonanes (*B*-Ar-9BBN) to α,β-Unsaturated Ketones

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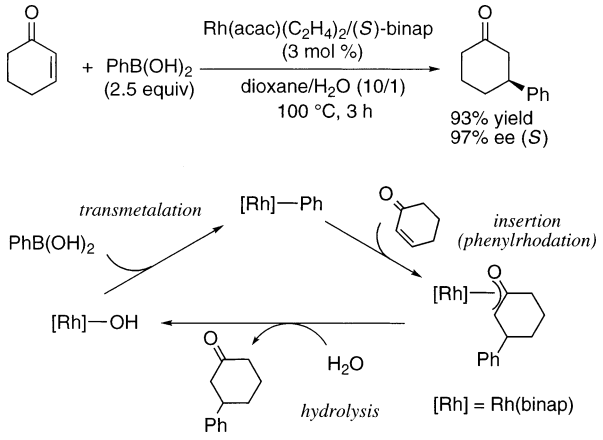
Asymmetric 1,4-addition of 9-phenyl-9-borabicyclo[3.3.1]nonane (**2m**) to 2-cyclohexenone (**1a**) proceeded with high enantioselectivity in toluene at 80 °C in the presence of 3 mol % of a rhodium catalyst generated from $[Rh(OMe)(cod)]_2$ and (*S*)-binap to give a high yield of boron enolate (*S*)-**3am**, which is 98% enantiomerically pure. Reaction of the boron enolate **3am** with electrophiles, methanol-*d*, propanal, and allyl bromide, gave the corresponding 2-substituted (3*S*)-3-phenylcyclohexanones with perfect regio- and diastereoselectivity.

Introduction

One of the recent topics in the field of asymmetric synthesis is the catalytic asymmetric 1,4-addition of organometallic reagents that creates a new stereogenic carbon center during the carbon−carbon bond formation.[1,2] The rhodium-catalyzed asymmetric 1,4-addition of organoboronic acids, which we have developed recently, has unique advantages over others.[3−5] Thus, in addition to its high enantioselectivity and high catalytic activity, the reaction is carried out in an aqueous solvent at a high temperature and some sp^2 carbons (aryl and alkenyl groups) can be introduced onto various types of electron-deficient olefins. A typical example is the reaction of 2-cyclohexenone with phenylboronic acid in the presence of a Rh/binap catalyst in dioxane/H_2O (10/1) at 100 °C, which gives the phenylation product of 97% ee (Scheme 1).[3a] The mechanistic studies revealed that the reaction involves transmetalation of an aryl group from boron to rhodium, 1,4-carborhodation of α,β-unsaturated ketone forming (oxa-π-allyl)rhodium and its hydrolysis giving the 1,4-addition product and the hydroxo-rhodium species.[6] One major drawback of this rhodium-catalyzed reaction is that the 1,4-addition product is hydrolyzed under the reaction conditions and hence the boron enolate cannot be obtained. Another is the competing hydrolysis of the organoboronic acid, which causes one to use an excess of the boronic acid for a reasonable yield of the 1,4-addition. Considering the great utility of boron enolates in organic synthesis,[7] it is important to develop a new reaction

SCHEME 1



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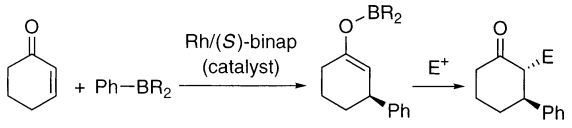
SCHEME 2



system that would allow us to obtain chiral boron enolates as the rhodium-catalyzed asymmetric 1,4-addition products and to use them for further transformations[8] (Scheme 2). Here we report that the use of 9-aryl-9-borabicyclo[3.3.1]nonanes (*B*-Ar-9BBN) realizes the formation of boron enolates with high enantioselectivity in the rhodium-catalyzed 1,4-addition. Very recently, we also found that enantiomerically enriched titanium enolates are generated by the rhodium-catalyzed addition of aryltitanium triisopropoxide ($ArTi(OPr\text{-}i)_3$) to α,β-unsaturated ketones.[9]

Results and Discussion

We examined several phenylboron reagents and rhodium−phosphine complexes for the rhodium-catalyzed addition to 2-cyclohexenone (**1a**) in an aprotic solvent and found that the 1,4-addition giving a boron enolate takes place with 9-phenyl-9-borabicyclo[3.3.1]nonane[10] (*B*-Ph-9BBN, **2m**) in toluene at 80 °C in the presence of [Rh(OMe)((*S*)-binap)]$_2$, generated from [Rh(OMe)(cod)]$_2$[11] and (*S*)-binap[12] (Scheme 3). Thus, a toluene-d_8 solution of **1a**, 3 mol % (Rh) of [Rh(OMe)(cod)]$_2$, and (*S*)-binap was heated at 80 °C for 2 min in an NMR sample tube. This heating before addition of **2m** is important for high enantioselectivity, because the replacement of cod in [Rh(OMe)(cod)]$_2$ by binap is slow at room temperature, and the phosphine-free rhodium complex, [Rh(OMe)(cod)]$_2$, is catalytically active for the present 1,4-addition. The generation of [Rh(OMe)((*S*)-binap)]$_2$ can be confirmed by its ^{31}P NMR where a doublet at δ 53.6 (d, J = 198 Hz) is observed in toluene-d_8. On addition of *B*-Ph-9BBN (**2m**) (1.0 equiv to **1a**) to the solution containing [Rh(OMe)((*S*)-binap)]$_2$, the ^{1}H resonances of 2-cyclohexenone (**1a**) were smoothly replaced by those of the 1,4-addition product, namely, boron enolate **3am**, and all the enone **1a** was converted into **3am** in 30 min. Under the same reaction conditions, no 1,4-addition was observed with *B*-phenylcatecholborane, *B*-phenylpinacolborane, or triphenylcyclotriboroxane ($(PhBO)_3$). It is as expected from their lower reactivity. The boron enolate **3am** was fully characterized by ^{1}H NMR, ^{11}B NMR, and ^{13}C NMR (see the Experimental Section). The formation of boron enolate **3am** is much slower with Rh(acac)$(C_2H_4)_2$ as a catalyst precursor. It takes longer than 12 h for the 1,4-addition to be completed. It is as expected from our previous studies on the mechanism of the rhodium-catalyzed 1,4-addition of organoboronic acids, where the rate of the transmetalation step is observed to be significantly influenced by anionic ligand on the rhodium catalyst.[6] Addition of methanol (2.5 equiv) to the boron enolate solution at 0 °C immediately caused protonolysis of **3am** to give a high yield of 3-phenylcyclohexanone (**4am**) together with *B*-MeO-9BBN. The phenylation product **4am** was determined to be an (*S*) isomer of 98% enantiomeric purity by HPLC analysis with a chiral stationary phase column (Chiralcel OD-H, hexane/2-propanol 98/2). It follows that the rhodium-catalyzed asymmetric 1,4-addition of *B*-Ph-9BBN (**2m**) to 2-cyclohexenone (**1a**) giving boron enolate **3am** proceeded with high enantioselectivity (98% ee), as high as the reaction of phenylboronic acid.[3a]

The boron enolate (*S*)-**3am** of 98% ee, which is generated by the rhodium-catalyzed asymmetric 1,4-addition,

SCHEME 3

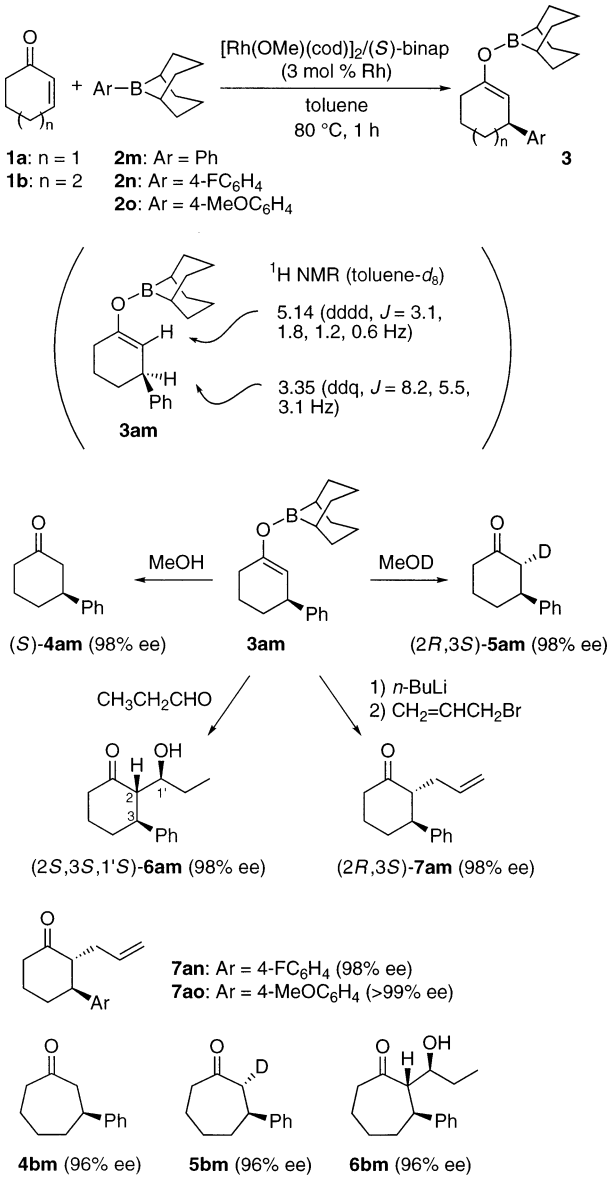


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TABLE 1. Rhodium-Catalyzed Asymmetric 1,4-Addition of *B*-Ar-9BBN 2 to Enones 1 and Reaction of the Resulting Boron Enolates 3 with Electrophiles[a]

entry	enone **1**	*B*-Ar-9BBN **2**	electrophile	product (yield, %)[c]	% ee[b] (config)
1[d]	**1a**	**2m**	MeOH	**4am** (81)	98 (*S*)
2[e]	**1a**	**2m**	MeOD	**5am** (81)	98 (2*R*,3*S*)
3[f]	**1a**	**2m**	C_2H_5CHO	**6am** (46)[g]	98 (2*S*,3*S*,1′*S*)
4[h]	**1a**	**2m**	*n*-BuLi, allyl bromide	**7am** (71)[i]	98 (2*R*,3*S*)
5[h]	**1a**	**2n**	*n*-BuLi, allyl bromide	**7an** (71)	98 (2*R*,3*S*)
6[h]	**1a**	**2o**	*n*-BuLi, allyl bromide	**7ao** (65)	>99 (2*R*,3*S*)
7[d]	**1b**	**2m**	MeOH	**4bm** (83)	96 (*S*)
8[e]	**1b**	**2m**	MeOD	**5bm** (82)	96 (2*R*,3*S*)
9[f]	**1b**	**2m**	C_2H_5CHO	**6bm** (47)[j]	96 (2*S*,3*S*,1′*S*)

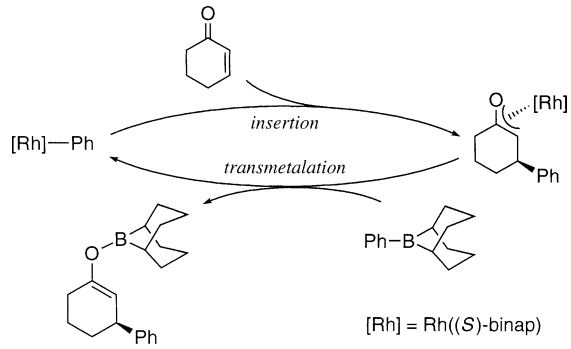
[a] The rhodium-catalyzed 1,4-addition was carried out with enone **1** (0.40 mmol) and *B*-Ar-9BBN **2** (0.44 mmol) in 1.0 mL of toluene in the presence of 3 mol % of the catalyst generated from $[Rh(OMe)(cod)]_2$ and (*S*)-binap (Rh/P = 1/2.2) at 80 °C for 1 h. [b] Determined by HPLC analysis with chiral stationary phase columns (Daicel Chiralcel OD-H (**4am**, **5am**, **4bm**, **5bm**), AD (**6am**, **6bm**), OJ (**7am**, **7ao**), and OB−H (**7an**)). [c] Isolated yield by silica gel chromatography. [d] MeOH (1.00 mmol) was added at 0 °C. [e] MeOD (1.00 mmol) was added at −78 °C. [f] The aldehyde (0.60 mmol) was added at −78 °C. [g] 31% of **4am** was also formed. [h] At −78 °C, *n*-BuLi (0.44 mmol) was added, and after 15 min allyl bromide (0.60 mmol) was added. [i] 11% of **4am** was also formed. [j] 21% of **4bm** was also formed.

was allowed to react with several electrophiles (entries 1−4 in Table 1). The reaction with methanol-*d* at −78 °C gave (2*R*,3*S*)-3-phenyl-2-deuteriocyclohexanone (**5am**) with perfect trans-selectivity. The exclusive incorporation of deuterium at the 2 position of 3-phenylcyclohexanone with trans-selectivity indicates that the double bond of the boron enolate is kept at the original position and it is attacked by the electrophile on the other face of the phenyl. One of the most useful reactions of boron enolates is the aldol reaction with aldehydes, which is known to proceed through a tight and well-organized transition state.[7] As expected from the transition state, the reaction with propanal at −78 °C gave the anti aldol product (2*S*,3*S*,1′*S*)-**6am** as a single diastereoisomer. This aldol reaction of the boron enolate has advantages over the reaction of the corresponding chiral titanium enolate, which gives the dehydration product of β-hydroxy ketone.[9] An alkylation of boron enolate was attained by way of an enolate of trialkylborate. Thus, treatment of the boron enolate **3am** with *n*-butyllithium (1.1 equiv) at −78 °C followed by addition of allyl bromide to the resulting borate gave a 71% yield of allylated cyclohexanone (2*R*,3*S*)-**7am** where phenyl and allyl groups are located trans to each other.

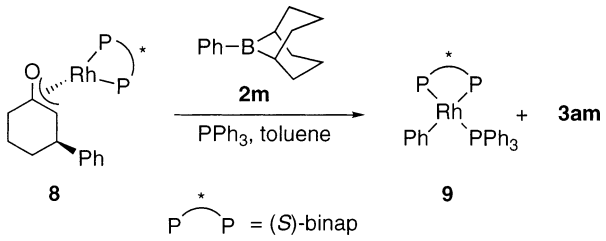
The rhodium-catalyzed asymmetric 1,4-addition forming a chiral boron enolate was also successful with the boron reagents containing substituted phenyl (*B*-Ar-9BBN, **2n,o**) (Scheme 3, entries 5−6 in Table 1). In the 1,4-addition to 2-cyclohexenone (**1a**), they gave the corresponding boron enolates **3an** and **3ao** in high yields, which were subjected to the allylation reaction by the *n*-butyllithium/allyl bromide treatment to give the allylation products **7an** and **7ao** of 98% and >99% ee, respectively. The catalytic asymmetric boron enolate formation also proceeded with high enantioselectivity for 2-cycloheptenone (**1b**) to give a high yield of the boron enolate **3bm**. Similarly to the reactions of **3am**, those of **3bm** with methanol-*d* and propanal gave the deuterated ketone **5bm** and the aldol product **6bm**, respectively, both of which are 96% enantiomerically pure (entries 7−9).

We have established that the catalytic cycle of the rhodium-catalyzed 1,4-addition in water involves a hydroxo-rhodium species as a key intermediate, which is generated by hydrolysis of an (oxa-π-allyl)rhodium intermediate and undergoes transmetalation giving a

SCHEME 4



SCHEME 5



phenyl-rhodium species (Scheme 1).[6] ^{31}P NMR studies revealed that a direct transmetalation of the phenyl group from boron to rhodium of the (oxa-π-allyl)rhodium complex is involved in the present reaction (Scheme 4). Thus, as a stoichiometric reaction, addition of *B*-Ph-9BBN (**2m**) to the (oxa-π-allyl)rhodium **8**[6] in the presence of triphenylphosphine in toluene gave the phenylrhodium complex **9**[6] coodinated with (*S*)-binap and triphenylphosphine (Scheme 5). No direct transmetalation to the (oxa-π-allyl)rhodium intermediate was observed on addition of *B*-phenylcatecholborane, *B*-phenylpinacolborane, or triphenylcyclotriboroxane ($(PhBO)_3$) in place of *B*-Ph-9BBN (**2m**). The addition of phenylrhodium complex **9** to 2-cyclohexenone forming **8** has been previously reported.[6]

In conclusion, catalytic asymmetric 1,4-addition forming chiral boron enolates was realized for the first time by use of a new reaction system consisting of 9-aryl-9-borabicyclo[3.3.1]nonane and $[Rh(OMe)((S)\text{-binap})]_2$. The chiral boron enolates whose enantiomeric excesses are higher than 96% were successfully subjected to further transformations such as aldol reaction. Unfortunately,

the boron enolate formation was not observed for 2-cyclopentenone or acyclic enones under the conditions shown here. We are currently working on improving the generality of this type of catalytic asymmetric 1,4-addition.

Experimental Section

General. Chemical shifts in NMR spectra are reported in δ ppm referenced to an internal $SiMe_4$ standard for ^1H NMR, chloroform-*d* (δ 7.26) for ^2H NMR, $BF_3{\cdot}Et_2O$ for ^{11}B NMR, and chloroform-*d* (δ 77.05) for ^{13}C NMR.

Materials. Toluene was distilled from sodium benzophenone-ketyl under nitrogen and stored in a glass flask with a Teflon stopcock under nitrogen. MeOH was dried over magnesium methoxide, distilled under nitrogen, and stored in a glass flask with a Teflon stopcock under nitrogen. MeOD and ^{n}BuLi in hexane were used as received. Rhodium complexes $Rh(acac)(C_2H_4)_2$[13] and $[Rh(OMe)(cod)]_2$[11] were prepared according to the reported procedures. 2-Cyclohexenone (**1a**), 2-cycloheptenone (**1b**), propanal, and allyl bromide were distilled before use. 9-Phenyl-9-borabicyclo[3.3.1]nonane (*B*-Ph-9BBN) (**2m**) was prepared according to the reported procedures.[10] 9-(*p*-Fluorophenyl)-9-borabicyclo[3.3.1]nonane (**2n**) and 9-(*p*-methoxyphenyl)-9-borabicyclo[3.3.1]nonane (**2o**) were prepared in a manner similar to **2m**. **2n**: ^1H NMR ($CDCl_3$) δ 1.26−1.35 (m, 2H), 1.76−1.83 (m, 4H), 1.93−2.04 (m, 6H), 2.22−2.29 (br m, 2H), 7.13 (t, J = 8.7 Hz, 2H), 7.98 (dd, J = 8.7, 6.4 Hz, 2H). **2o**: ^1H NMR ($CDCl_3$) δ 1.29−1.35 (m, 2H), 1.76−1.82 (m, 4H), 1.93−2.02 (m, 6H), 2.23−2.28 (br m, 2H), 3.87 (s, 3H), 6.99 (d, J = 8.6 Hz, 2H), 7.96 (d, J = 8.6 Hz, 2H).

NMR Studies on the Reaction of 2-Cyclohexenone (1a) with 9-Phenyl-9-borabicyclo[3.3.1]nonane (*B*-Ph-9BBN) (2m) in the Presence of a Rhodium Catalyst Generated from $[Rh(OMe)(cod)]_2$ and (*S*)-binap. A solution of $[Rh(OMe)(cod)]_2$ (1.5 mg, 3.0 μmol), (*S*)-binap (4.1 mg, 6.6 μmol), and 2-cyclohexenone (19.2 mg, 0.200 mmol) in toluene-d_8 (0.5 mL) was heated at 80 °C for 2 min in an NMR sample tube, and then *B*-Ph-9BBN (39.6 mg, 0.200 mmol) was added to the solution at the same temperature. The temperature of the mixture was maintained at 80 °C for 30 min. After cooling to room temperature, ^1H NMR measurement of the sample indicated clear formation of boron enolate **3am**. ^1H NMR (toluene-d_8) δ 1.32−1.40 (m, 3H), 1.45−1.53 (m, 3H), 1.59−1.66 (m, 1H), 1.76−1.94 (m, 11H), 2.00−2.06 (m, 1H), 2.07−2.15 (m, 1H), 3.35 (ddq, J = 8.2, 5.5, 3.1 Hz, 1H), 5.14 (dddd, J = 3.1, 1.8, 1.2, 0.6 Hz, 1H), 7.06 (tt, J = 6.9, 1.8 Hz, 1H), 7.13−7.19 (m, 4H). ^{11}B NMR (toluene-d_8) δ 57.2. ^{13}C NMR (toluene-d_8) δ 21.65, 23.61, 24.93 (br), 29.74, 32.84, 33.77, 33.84, 41.63, 111.42, 126.40, 127.88, 128.60, 146.72, 152.97.

Rhodium-Catalyzed Asymmetric Addition of *B*-Ph-9BBN (2m) to 2-Cyclohexenone (1a) and Reaction of the Resulting Boron Enolate 3am with Electrophiles. A solution of $[Rh(OMe)(cod)]_2$ (2.9 mg, 6.0 μmol), (*S*)-binap (8.2 mg, 13.2 μmol), and 2-cyclohexenone (38.5 mg, 0.400 mmol) in toluene (1.0 mL) was heated at 80 °C for 2 min. Then, *B*-Ph-9BBN (87.2 mg, 0.440 mmol) was added to the solution at the same temperature. The mixture was stirred for 1 h at 80 °C. This solution, which contains the boron enolate **3am**, was used for the reaction with electrophiles. **(a) Reaction with Methanol.** The solution was cooled to 0 °C, and MeOH (41 μL, 1.0 mmol) was added. The mixture was stirred at room temperature for a few minutes and concentrated in vacuo with gentle heating to remove solvent and *B*-MeO-9BBN, which was formed by the reaction of **3am** with MeOH. The residue was chromatographed on silica gel (hexane/AcOEt 3/1) to give (*S*)-3-phenylcyclohexanone (**4am**)[3a] (56.5 mg, 81% yield) as colorless oil. **(b) Reaction with Methanol-d_1.** In a similar manner, MeOD (41 μL, 1.0 mmol) was added at −78 °C and the chromatography on silica gel (hexane/AcOEt 3/1) gave (2*R*,3*S*)-*trans*-3-phenyl-2-deuteriocyclohexanone (**5am**) (56.8 mg, 81% yield). ^2H NMR ($CHCl_3$) δ 2.60. **(c) Reaction with Propanal.** The solution containing the boron enolate **3am** was cooled to −78 °C and propanal (43 μL, 0.60 mmol) was added. The mixture was stirred at the same temperature for 1 h. After removal of the dry ice bath from the reaction vessel, the mixture was stirred for 1 h. The resulting mixture was cooled to 0 °C and treated with 3 N NaOH (ca. 0.4 mL) and 30% H_2O_2 (ca. 0.4 mL). For complete oxidation of organoboranes, the mixture was heated at 50 °C for 1 h. The organic layer was diluted with AcOEt, washed with saturated K_2CO_3, and dried over $MgSO_4$. The residue was chromatographed on silica gel (hexane/AcOEt 3/1) to give aldol product (2*S*,3*S*,1′*S*)-*trans*-3-phenyl-2-(1-hydroxypropyl)cyclohexanone (**6am**) (42.7 mg, 46% yield) as white solid. Mp 49−51 °C. ^1H NMR ($CDCl_3$) δ 0.78 (t, J = 7.4 Hz, 3H), 1.40 (d quint, J = 15.3, 7.4 Hz, 1H), 1.72 (d quint, J = 15.3, 7.4 Hz, 1H), 1.80 (qt, J = 13.1, 4.3 Hz, 1H), 1.96 (qd, J = 12.8, 3.8 Hz, 1H), 2.05 (dq, J = 13.7, 3.1 Hz, 1H), 2.17 (d quint, J = 13.5, 2.9 Hz, 1H), 2.45 (br d, J = 12.5 Hz, 1H), 2.52 (td, J = 13.3, 6.2 Hz, 1H), 2.64 (d, J = 12.0 Hz, 1H), 2.91 (br d, J = 11.3 Hz, 1H), 2.96−3.03 (br m, 1H), 3.23 (td, J = 12.1, 3.9 Hz, 1H), 7.22−7.26 (m, 3H), 7.33 (t, J = 7.6 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 10.89, 27.11, 29.13, 34.45, 43.67, 49.31, 58.96, 71.95, 126.85, 127.35, 128.82, 143.14, 214.94. $[\alpha]^{20}_D$ −57.7 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{15}H_{20}O_2$: C, 77.55; H, 8.68. Found: C, 77.35; H, 8.84. **(d) Reaction with Allyl Bromide.** The solution containing the boron enolate **3am** was cooled to −78 °C and a solution of *n*-BuLi in hexane (1.55 mol/L, 284 μL, 0.44 mmol) was added. After 15 min, allyl bromide (52 μL, 0.60 mmol) was added and the mixture was stirred for 1 h at the same temperature. After removal of the dry ice bath from the reaction vessel, the mixture was stirred for 1 h to give an orange suspension that was treated with MeOH (41 μL, 1.0 mmol) and concentrated in vacuo. The residue was chromatographed on silica gel (hexane/AcOEt 3/1) to give (2*R*,3*S*)-*trans*-3-phenyl-2-(2-propenyl)cyclohexanone[9] (**7am**) (60.9 mg, 71% yield) as a colorless oil.

Rhodium-Catalyzed Asymmetric Addition of *B*-Ar-9BBN (2) to Enones 1 and Reaction of the Resulting Boron Enolate 3 with Electrophiles. The rhodium-catalyzed asymmetric 1,4-addition and the subsequent reaction with electrophiles were carried out in essentially the same manner as those described for **3am**. The results are summarized in Table 1. NMR data for the products are shown below. (2*R*,3*S*)-*trans*-3-(*p*-Fluorophenyl)-2-(2-propenyl)cyclohexanone (**7an**): ^1H NMR ($CDCl_3$) δ 1.70−1.79 (m, 1H), 1.84−1.92 (m, 1H), 1.96−2.05 (m, 2H), 2.08−2.15 (m, 2H), 2.42−2.53 (m, 2H), 2.61−2.66 (m, 1H), 2.74 (td, J = 11.7, 3.7 Hz, 1H), 4.76 (dq, J = 17.0, 1.5 Hz, 1H), 4.87 (ddt, J = 10.2, 2.1, 1.3 Hz, 1H), 5.71 (ddt, J = 17.0, 10.2, 6.8 Hz, 1H), 7.02 (t, J = 8.7 Hz, 2H), 7.16 (dd, J = 8.7, 5.4 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 26.20, 30.84, 34.91 (d, J = 1.0 Hz), 42.11, 49.80, 55.50, 115.45 (d, J = 21.2 Hz), 116.08, 128.71 (d, J = 7.8 Hz), 136.31, 139.21 (d, J = 3.1 Hz), 161.54 (d, J = 244.7 Hz), 210.93. $[\alpha]^{20}_D$ −29.1 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{15}H_{17}OF$: C, 77.56; H, 7.38. Found: C, 77.30; H, 7.42. (2*R*,3*S*)-*trans*-3-(*p*-Methoxyphenyl)-2-(2-propenyl)cyclohexanone (**7ao**): ^1H NMR ($CDCl_3$) δ 1.69−1.78 (m, 1H), 1.84−1.92 (m, 1H), 1.95−2.04 (m, 2H), 2.07−2.17 (m, 2H), 2.41−2.51 (m, 2H), 2.61−2.71 (m, 2H), 3.80 (s, 3H), 4.78 (dq, J = 17.2, 2.0 Hz, 1H), 4.87 (ddt, J = 10.2, 1.9, 0.9 Hz, 1H), 5.72 (ddt, J = 17.2, 10.2, 6.9 Hz, 1H), 6.87 (d, J = 8.8 Hz, 2H), 7.11 (d, J = 8.8 Hz, 2H). ^{13}C NMR ($CDCl_3$) δ 26.31, 30.88, 35.00, 42.22, 49.92, 55.27, 55.79, 114.01, 115.88, 128.23, 135.71, 136.63, 158.28, 211.41. $[\alpha]^{20}_D$ −28.9 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{16}H_{20}O_2$: C, 78.65; H, 8.25. Found: C, 78.46; H, 8.42. (2*R*,3*S*)-*trans*-3-Phenyl-2-deuteriocycloheptanone (**5bm**): ^2H NMR ($CHCl_3$) δ 2.65. (2*S*,3*S*,1′*R*)-*trans*-3-Phenyl-2-(1-hydroxypropyl)cycloheptanone (**6bm**): ^1H NMR

(13) Cramer, R. *Inorg. Synth.* **1974**, *15*, 16.

($CDCl_3$) δ 0.78 (t, J = 7.5 Hz, 3H), 1.30−1.43 (m, 2H), 1.46−1.55 (m, 1H), 1.67−1.76 (m, 2H), 1.88−1.99 (m, 3H), 2.46 (br s, 1H), 2.57 (dt, J = 11.5, 5.2 Hz, 1H), 2.74 (td, J = 11.8, 5.1 Hz, 1H), 2.81 (dd, J = 11.1, 2.4 Hz, 1H), 3.14 (ddd, J = 10.9, 9.6, 2.8 Hz, 1H), 3.19 (ddd, J = 8.2, 5.6, 2.6 Hz, 1H), 7.19−7.24 (m, 3H), 7.29−7.33 (m, 2H). ^{13}C NMR ($CDCl_3$) δ 10.49, 25.22, 27.63, 28.95, 37.27, 44.35, 44.96, 61.23, 73.37, 126.47, 127.59, 128.68, 145.33, 218.05. $[\alpha]^{20}_D$ −63.7 (*c* 1.00, $CHCl_3$). Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.97; H, 9.27.

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